Benzylic fluorination induced by a charge-transfer complex with a solvent-dependent selectivity switch

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1. **General remarks**

Substrates, reagents, and solvents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded using a Varian 400 MHz (400, 100 and 376 MHz respectively for $^1$H-, $^{13}$C- and $^{19}$F-NMR) or a Bruker NEO 500 MHz spectrometer equipped with a H/F/C/N-TCI-Prodigy probe and are reported in ppm relative to the residual solvent peaks. Peaks are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, with coupling constants in Hz. Reaction monitoring via FTIR analysis was performed with a ReactIR™ 15 (Mettler-Toledo) console, with a DST 9.5mm SiComp™ probe attached. Analytical thin layer chromatography (TLC) was carried out using pre-coated TLC-sheets, ALUGRAM Xtra SIL G/UV254 sheets (Macherey-Nagel) and visualized with 254 nm light. Purification of synthesized compounds was carried out by flash chromatography on a Reveleris X2 Flash Chromatography System from GRACE. A prepacked column with 12 g, 40 μm silica gel was used at a 30 mL/min elution flow rate. Silica 60 M (0.04-0.063 mm) silica gel (Macherey-Nagel) was used for dry loading of the crude compounds. High resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF spectrometer using positive electrospray ionization (ESI).

2. **Initial experiments**

| Entry | Solvent            | Conversion [%]$^b$ | A [%]$^c$ | B [%]$^c$ |
|-------|--------------------|-------------------|-----------|-----------|
| 1     | MeCN               | 66                | 66        | n.d.      |
| 2     | MeCN:H$_2$O (1:1)  | 73                | 7         | 33        |

$^a$Reaction conditions: 4-fluorophenylacetic acid (0.3 mmol), Selectfluor (0.9 mmol), DMAP (0.6 mmol), solvent (1.5 mL, degassed) under nitrogen atmosphere at r.t for 3 h. $^b$Conversion of 4-biphenylacetic acid determined by $^1$H-NMR using dimethyl maleate as an internal standard. $^c$NMR yield determined by $^1$H-NMR using dimethyl maleate as an internal standard. n.d. = not detected.

### Table S2. Control studies in MeCN$^a$

| Entry | Variation         | Conversion [%]$^b$ | A [%]$^c$ | B [%]$^c$ |
|-------|-------------------|-------------------|-----------|-----------|
| 1     | No degassing      | 80                | 80        | n.d.      |
| 2     | No Selectfluor    | n.d.              | n.d.      | n.d.      |
| 3     | No DMAP           | n.d.              | n.d.      | n.d.      |

$^a$Reaction conditions: 4-fluorophenylacetic acid (0.3 mmol), Selectfluor (0.9 mmol), DMAP (0.6 mmol) in acetonitrile (anhydrous, 1.5 mL) at r.t for 3 h. $^b$Conversion of 4-biphenylacetic acid determined by $^1$H-NMR using dimethyl maleate as an internal standard. $^c$NMR yield determined by n.d. = not detected.
### Table S3. Control studies in MeCN:H₂O

| Entry | Variation         | Conversion [%] | A [%] | B [%] |
|-------|-------------------|----------------|-------|-------|
| 1     | No degassing      | 17             | 6     | 11    |
| 2     | No Selectfluor    | n.d            | n.d   | n.d   |
| 3     | No DMAP           | n.d            | n.d   | n.d   |

*a Reaction conditions: 4-fluorophenylacetic acid (0.3 mmol), Selectfluor (0.9 mmol), DMAP (0.6 mmol) in solvent (anhydrous, 1.5 mL) at r.t for 3 h. b Conversion of 4-biphenylacetic acid determined by ¹H-NMR using dimethyl maleate as an internal standard. c NMR yield determined by n.d = not detected.

### 3. Decarboxylative fluorination

**General experimental procedure for optimization experiments.** An oven dried crimp top vial (19 x 100 mm) equipped with a stir bar was charged with with 4-biphenylacetic acid and Selectfluor®. The solvent mixture was added and the mixture was stirred and sonicated for 5 min. Subsequently, 4-dimethylaminopyridine (and, if indicated, the additive) was added. The vial was sealed and the reaction mixture was stirred and sonicated for 5 min. The mixture was degassed by bubbling Argon for 10 min. The reaction mixture was stirred in an oil bath at 70 °C for the respective time. Afterwards, dimethyl maleate (1 equiv.) was added. The reaction mixture was quenched with HCl (1 M, 1 mL) and extracted with CDCl₃ (1 mL). An aliquot (~200 μL) of the organic phase was subsequently subjected to ¹H NMR analysis.
**Figure S1.** Example of a $^1$H-NMR spectrum for determining NMR yields.

### 3.1 Solvent screening

**Table S4.** Initial solvent screening$^a$

| Entry | Solvent          | Conversion [%]$^b$ | Yield [%]$^c$ |
|-------|------------------|--------------------|--------------|
| 1     | MeCN/H$_2$O 1:1  | 33                 | 28           |
| 2     | Acetone/ H$_2$O 1:1 | 41                | 40           |
| 3     | EtOH/ H$_2$O 1:1 | n.d.$^d$          | 18           |
| 4     | THF/ H$_2$O 1:1  | 14                 | 8            |
| 5     | DMF/ H$_2$O 1:1  | 44                 | 36           |
| 6     | H$_2$O           | 39                 | 26           |

$^a$Reaction conditions: 4-biphenylacetic acid (0.1 mmol), Selectfluor (0.3 mmol), DMAP (0.2 mmol), solvent (1 mL), r.t, 4 h. $^b$Conversion of 4-biphenylacetic acid determined by $^1$H-NMR using dimethyl maleate as an internal standard. $^c$NMR yield determined by $^1$H-NMR using dimethyl maleate as an internal standard $^d$Not determined due to overlapping signals.

**Table S5.** Initial solvent screening$^a$

| Entry | Acetone:H$_2$O | Conversion [%]$^b$ | Yield [%]$^c$ |
|-------|----------------|--------------------|--------------|
| 1     | 1:2            | 34                 | 33           |
| 2     | 1:1            | 41                 | 40           |
| 3     | 2:1            | 20                 | 20           |
| 4     | 5:1            | 12                 | 10           |

$^a$Reaction conditions: 4-biphenylacetic acid (0.1 mmol), Selectfluor (0.3 mmol), DMAP (0.2 mmol), solvent (1 mL), r.t, 4 h. $^b$Conversion of 4-biphenylacetic acid determined by $^1$H-NMR using dimethyl maleate as an internal standard. $^c$NMR yield determined by $^1$H-NMR using dimethyl maleate as an internal standard.
3.2 Temperature & Additive screening

Table S6. Temperature screening

| Entry | Temperature [°C] | Conversion [%] | Yield [%] |
|-------|------------------|---------------|-----------|
| 1     | r.t.             | 41            | 40        |
| 2     | 50               | 47            | 44        |
| 3     | 70               | **62**        | 50        |
| 4     | 90               | 43            | 16        |

*Reaction conditions: 4-biphenylacetic acid (0.1 mmol), Selectfluor (0.3 mmol), DMAP (0.2 mmol), acetone/H₂O (1:1, 1 mL), 4 h. Conversion of 4-biphenylacetic acid determined by ¹H-NMR using dimethyl maleate as an internal standard. NMR yield determined by ¹H-NMR using dimethyl maleate as an internal standard.

Table S7. Additive screening

| Entry | Additive | Conversion [%] | Yield [%] |
|-------|----------|---------------|-----------|
| 1     | --       | 62            | 50        |
| 2     | NaHCO₃   | 33            | 22        |
| 3     | Cs₂CO₃   | 13            | traces    |
| 4     | Li₂CO₃   | 23            | traces    |
| 5     | K₂CO₃    | 17            | traces    |
| 6     | KF       | 84            | 56        |
| 7     | CsF      | 84            | 62        |
| 8     | K₃PO₄    | 21            | traces    |
| 9     | K₃HPO₄   | 42            | 34        |
| 10    | LiF      | 70            | 56        |
| 11    | MgF₂     | 64            | 54        |
| 12    | CaF₂     | 61            | 52        |
| 13    | (tBu)₄NF | 31            | 30        |
| 14    | **NaF**  | **75**        | **66**    |
| 15    | NH₄F     | 76            | 60        |

*Reaction conditions: 4-biphenylacetic acid (0.1 mmol), Selectfluor (0.3 mmol), DMAP (0.2 mmol), acetone/H₂O (1:1, 1 mL), 70°C, 4 h. Conversion of 4-biphenylacetic acid determined by ¹H-NMR using dimethyl maleate as an internal standard. NMR yield determined by ¹H-NMR using dimethyl maleate as an internal standard.
3.3 Reaction time and concentration

Table S8. Optimization of reaction time and concentration

| Entry | Additive | Concentration [M] | Time | T [ºC] | Conversion [%]\textsuperscript{b} | Yield [%]\textsuperscript{c} |
|-------|----------|-------------------|------|--------|---------------------------------|-----------------------------|
| 1     | -        | 0.1               | 4 h  | r.t.   | 41                              | 40                          |
| 2     | -        | 0.2               | 4 h  | r.t.   | 48                              | 48                          |
| 3     | -        | 0.2               | 4 h  | 70 ℃   | 80                              | 70                          |
| 4     | NaF      | 0.2               | 4 h  | 70 ℃   | 88                              | 86                          |
| 5     | NaF      | 0.2               | 1 h  | 70 ℃   | 90                              | 86                          |
| 6     | NaF      | 0.2               | 30 min | 70 ℃  | 86                              | 85                          |
| 7     | NaF      | 0.2               | 10 min | 70 ℃  | 85                              | 82                          |

\textsuperscript{a}Reaction conditions: 4-biphenylacetic acid (0.1 mmol), Selectfluor (0.3 mmol), DMAP (0.2 mmol), acetone/H\textsubscript{2}O (1:1). \textsuperscript{b}Conversion of 4-biphenylacetic acid determined by \textsuperscript{1}H-NMR using dimethyl maleate as an internal standard. \textsuperscript{c}NMR yield determined by \textsuperscript{1}H-NMR using dimethyl maleate as an internal standard.

3.4 Control studies

Table S9. Control studies

| Entry | Variation    | Conversion [%]\textsuperscript{b} | Yield [%]\textsuperscript{c} |
|-------|--------------|-----------------------------------|-----------------------------|
| 1     | none         | 88                                | 86                          |
| 2     | Selectfluor (2 equiv) | 64                                | 42                          |
| 3     | DMAP (1 equiv) | 95                                | 86\textsuperscript{c}       |
| 4     | DMAP (10 mol%) | 48                                | 30                          |
| 5     | NaF (1 equiv) | 67                                | 56                          |
| 6     | Temperature (r.t.) | 40                                | 32                          |

\textsuperscript{a}Reaction conditions: 4-biphenylacetic acid (0.1 mmol), Selectfluor, DMAP and NaF in acetone/water under N\textsubscript{2} atmosphere for 4 h. \textsuperscript{b}Determined by \textsuperscript{1}H-NMR using dimethyl maleate as an internal standard. \textsuperscript{c}The use of 1 equiv. of DMAP generated an unidentified side product.
Scheme S1. Decarboxylative fluorination reaction of 2-(4-(tert-butyl)phenyl)-2-fluoroacetic acid

3.5 Scope

General experimental procedure for the synthesis of 4-(fluoromethyl)-1,1'-biphenyl (1). An oven dried vessel equipped with a stir bar was charged with substrate (424.5 mg, 2 mmol, 0.2 mM) and Selectfluor® (2.13 g, 6 mmol, 3 equiv.). Aceton: H2O (10 mL, 1:1) was added and the mixture was stirred and sonicated for 5 min. Subsequently, 4-dimethylaminopyridine (488.7 mg, 4 mmol, 2 equiv.) and NaF (167.9 mg, 4 mmol, 2 equiv.) were added. The vial was sealed and the reaction mixture was stirred and sonicated for 5 min. The mixture was degassed by bubbling Argon for 10 min. The reaction mixture was stirred in an oil bath at 70 °C for the respective time. The reaction mixture was quenched with HCl (1 M, 10 mL) and extracted with CHCl3 (3 x 10 mL). The combined organic phases were washed with brine (10 mL), dried over MgSO4 under concentrated under reduced pressure. Purification was performed by column chromatography using hexane. The title compound was isolated as a colorless solid (267.9 mg, 1.44 mmol, 72%). 1H NMR (400 MHz, CDCl3) δ. 7.71 – 7.66 (m, 4H), 7.54 – 7.50 (m, 4H), 7.47 – 7.41 (m, 1H), 7.47 – 7.41 (m, 1H), 5.48 (d, J = 47.8 Hz, 1H). 13C NMR (400 MHz, CDCl3) δ ppm 141.9, 140.7, 135.3 (d, J = 17.2 Hz), 129.0, 128.3 (d, J = 5.9 Hz), 127.7, 127.5, 127.3, 84.6 (d, J = 166.2 Hz). 19F NMR (400 MHz, CDCl3) δ ppm -206.2 (t, J = 47.9 Hz). These data are in full agreement with those previously published in the literature.1

General experimental procedure products that were not isolated due to their low boiling point. An oven dried crimp top vial (19 x 100 mm) equipped with a stir bar was charged with substrate (0.1 mmol, 0.2 mM) and Selectfluor® (0.3 mmol, 3 equiv.). Aceton:H2O (2 mL, 1:1) was added and the mixture was stirred and sonicated for 5 min. Subsequently, 4-dimethylaminopyridine (0.2 mmol, 2 equiv.) and NaF (0.2 mmol, 2 equiv.) were added. The vial was sealed and the reaction mixture was stirred and sonicated for 5 min. The mixture was degassed by bubbling Argon for 10 min. The reaction mixture was stirred in an oil bath at 70 °C for the respective time. Upon completion, dimethyl maleate (12.4 μL, 0.1 mmol, 1 equiv.) was added. The reaction mixture was quenched with HCl (1 M, 1 mL) and extracted with CDCl3 (1 mL). An aliquote (~200 μL) of the organic phase was subsequently subjected to 1H NMR analysis.
1-(tert-butyl)-4-(fluoromethyl)benzene (2). The compound was synthesized following the general procedure. An NMR yield of 84% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.

1-(fluoromethyl)-2-methylbenzene (3). The compound was synthesized following the general procedure. An NMR yield of 80% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.
2-(2-methoxyphenyl)acetic acid (4). The compound was synthesized following the general procedure. An NMR yield of 56% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.

(Fluoromethyl)benzene (5). The compound was synthesized following the general procedure. An NMR yield of 60% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.
1-(fluoromethyl)-4-methylbenzene (6). The compound was synthesized following the general procedure. An NMR yield of 66% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.

1-bromo-4-(fluoromethyl)benzene (7). The compound was synthesized following the general procedure. An NMR yield of 50% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.
1-chloro-4-(fluoromethyl)benzene (8). The compound was synthesized following the general procedure. An NMR yield of 60% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.

1-(fluoromethyl)-4-(trifluoromethyl)benzene (9). The compound was synthesized following the general procedure. An NMR yield of 20% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.
1-(1-fluoroethyl)-4-isobutylbenzene (10). The compound was synthesized following the general procedure. An NMR yield of 44% was determined using dimethyl maleate as an internal standard. The product was not isolated due to its low boiling point.
4. α-fluorination

**General experimental procedure for optimization experiments.** An oven-dried vessel (19 x 100 mm) equipped with a stir bar was charged with 4-fluorophenylacetic acid (or, if indicated another phenylacetic acid derivative), 4-dimethylaminopyridine and Selectfluor®. Solvent was added, the vessel was sealed with a septum and sonicated for 5 minutes. The mixture was stirred at room temperature for the respective reaction time. Upon completion, dimethyl maleate (1 equiv.) was added. The reaction mixture was quenched with HCl (1 M, 1 mL) and extracted with CDCl₃ (1 mL). An aliquote (~200 μL) of the organic phase was subsequently subjected to ¹H NMR analysis. NMR spectra were taken in CDCl₃ or MeOD-d₃. A representative ¹H NMR spectrum for determining the yield is shown in Figure S2.

![Figure S2. Example of a ¹H-NMR spectrum (400 MHz) for determining NMR yields.](image)
4.1 N–F Reagents

Table S10. Tests using different fluorinating agents

| Entry | Additive | Conversion [%] b | Yield [%] c |
|-------|----------|-----------------|-------------|
| 1     | Selectfluor | 80              | 80          |
| 2     | NFSI      | 40              | 40          |
| 3     | NFpy      | -               | -           |

*Reaction conditions: 4-fluorophenylacetic acid (0.3 mmol), N-F reagent (0.9 mmol), DMAP (0.6 mmol) in MeCN (anhydrous, 1.5 mL), r.t for 1 h. bConversion of 4-biphenylacetic acid determined by 1H-NMR using dimethyl maleate as an internal standard. cNMR yield determined by 1H-NMR using dimethyl maleate as an internal standard.

4.2 Solvent screening

Table S11. Solvent screening

| Entry | Additive | Conversion [%] b | Yield [%] c |
|-------|----------|-----------------|-------------|
| 1     | MeCN     | 80              | 80          |
| 2     | Acetone  | 56              | 56          |
| 3     | DMF      | 73              | 73          |
| 4     | MeOH     | 75              | n.d         |
| 5     | THF      | 0               | n.d         |
| 6     | CHCl3    | 0               | n.d         |
| 7     | DCM      | 0               | n.d         |

*Reaction conditions: 4-fluorophenylacetic acid (0.3 mmol), Selectfluor (0.9 mmol), DMAP (0.6 mmol) in solvent (anhydrous, 1.5 mL), r.t for 1 h. bConversion of 4-biphenylacetic acid determined by 1H-NMR using dimethyl maleate as an internal standard. cNMR yield determined by 1H-NMR using dimethyl maleate as an internal standard.
4.3 Optimization of the equivalents of Selectfluor and DMAP

Table S12. Optimization experiments of the equivalents of Selectfluor and DMAP

| Entry | Selectfluor (equiv) | DMAP (equiv) | Conversion [%] | Yield [%] |
|-------|---------------------|--------------|----------------|-----------|
| 1     | 3                   | 2            | 80             | 80        |
| 2     | 3                   | 1            | 38             | 38        |
| 3     | 3                   | 0.5          | 3              | 3         |
| 4     | 3                   | 0.1          | 2              | 2         |
| 5     | 3                   | 2            | 80             | 80        |
| 6     | 2                   | 2            | 89             | 89        |
| 7     | 1.2                 | 2            | 97             | 97        |

*aReaction conditions: 4-fluorophenylacetic acid (0.3 mmol), Selectfluor and DMAP in MeCN (anhydrous, 1.5 mL), r.t for 1 h.  
*bConversion of 4-biphenylacetic acid determined by 1H-NMR using dimethyl maleate as an internal standard.  
*cNMR yield determined by 1H-NMR using dimethyl maleate as an internal standard.

4.4 Screening of different activators

Table S13. Activator screening

| Entry | Activator            | Conversion [%] | Yield [%] |
|-------|----------------------|----------------|-----------|
| 1     | DMAP                 | 97             | 97        |
| 2     | N,N-Dimethylanilin   | 0              | n.d       |
| 3     | Pyridine             | 9              | 9         |
| 4     | 4-Methoxypyridine    | 66             | 66        |
| 5     | 4-Aminopyridine      | 82             | 82        |
| 6     | 2-Phenylpyridine     | 0              | n.d       |
| 7     | Quinoline            | 0              | n.d       |
| 8     | 3-Hydroxypyridine    | 0              | n.d       |
| 9     | 6-Cyanopyridine      | 0              | n.d       |
| 10    | 2-Chloropyridine     | 0              | n.d       |
| 11    | 2,6-Lutidine         | 52             | n.d       |
| 12    | DABCO                | 0              | n.d       |

*aReaction conditions: 4-fluorophenylacetic acid (0.3 mmol), Activator (0.36 mmol), DMAP (0.6 mmol) in solvent (anhydrous, 1.5 mL), r.t for 1 h.  
*bConversion of 4-biphenylacetic acid determined by 1H-NMR using dimethyl maleate as an internal standard.  
*cNMR yield determined by 1H-NMR using dimethyl maleate as an internal standard.
4.5 Concentration and reaction time studies

Table S14. Concentration/time studies\(^a\)

| Entry | Concentration [mM] | Conversion [%]\(^b\) | Yield [%]\(^c\) |
|-------|--------------------|----------------------|-----------------|
| 1     | 0.2                | 92                   | 92              |
| 2     | 0.1                | 85                   | 85              |
| 3     | 0.05               | 58                   | 58              |
| 4     | 0.2\(^d\)          | 79                   | -               |

\(^a\)Reaction conditions: 4-tert-Butylphenylacetic acid (0.3 mmol), Selectfluor (0.36 mmol), DMAP (0.6 mmol) in MeCN (anhydrous), r.t for 1 min.
\(^b\)Conversion of 4-biphenylacetic acid determined by \(^1\)H-NMR using dimethyl maleate as an internal standard.
\(^c\)NMR yield determined by \(^1\)H-NMR using dimethyl maleate as an internal standard.
\(^d\)0°C

Table S15. One minute experiments using different substrates\(^a\)

| Entry | Substrate | Conversion [%]\(^b\) | Yield [%]\(^c\) |
|-------|-----------|----------------------|-----------------|
| 1     | \[\text{PhOH}\] | 96                   | 96              |
| 2     | \[\text{AcOH}\] | 89                   | 89              |
| 3     | \[\text{PhOH}\] | 93                   | 93              |
| 4     | \[\text{AcOH}\] | 92                   | 92              |
| 5     | \[\text{AcOH}\] | 99                   | 99              |

\(^a\)Reaction conditions: Phenylacetic acid derivative (0.3 mmol), Selectfluor (0.36 mmol), DMAP (0.6 mmol) in MeCN (anhydrous, 1.5 mL), r.t for 1 min. min.
\(^b\)Conversion of 4-biphenylacetic acid determined by \(^1\)H-NMR using dimethyl maleate as an internal standard.
\(^c\)NMR yield determined by \(^1\)H-NMR using dimethyl maleate as an internal standard.
4.6 Mechanistic investigations

Figure S3. $^1$H spectrum (400 MHz) of phenylacetic acid (bottom), and a mixture of phenylacetic acid and DMAP (2 equiv.) in CD$_3$CN.
Scheme S2. Radical clock experiment. The substrate was synthesized according to literature.²

Scheme S3. Experiment in presence of TEMPO.

Scheme S4. Competition experiment between phenylacetic acid and deuterium-labelled phenylacetic acid. The labelled compound was synthesized according to a literature procedure.³

Scheme S5. Competitive experiments between phenylacetic acids derivatives.
4.7 Delayed addition experiments

Table S16. Delayed addition experiments\(^a\)

![Chemical structure](image)

| Entry | Compound added after 30 min | Conversion [%]\(^b\) | Yield [%]\(^c\) |
|-------|-----------------------------|----------------------|----------------|
| 1     | Substrate                  | n.d                  | n.d            |
| 2     | Selectfluor                | 100                  | 100            |
| 3     | DMAP                        | 88                   | 88             |

\(^a\)Reaction conditions: 4-\text{tert-}Butylphenylacetic acid (0.3 mmol), Selectfluor (0.36 mmol), DMAP (0.6 mmol) in MeCN (anhydrous, 1.5 mL), r.t. for 1 h. \(^b\)Conversion of 4-biphenylacetic acid determined by \(^1\)H-NMR using dimethyl maleate as an internal standard. \(^c\)NMR yield determined by \(^1\)H-NMR using dimethyl maleate as an internal standard.

4.8 Reaction monitoring using a ReactIR

To maintain a constant operating temperature, the ReactIR console was filled with liquid nitrogen every 12 hours. Prior to each experiment, a background spectrum was recorded before attaching the reaction vessel. The raw ReactIR data was treated with a negative second derivative function, to aid in separation of peaks. The reference spectrum of the solvent was subtracted. The product peak appeared at ~1648 cm\(^{-1}\) (C-H bending, aromatic), Selectfluor was detected at 1005 cm\(^{-1}\) (N-F bond) and the consumption of DMAP was observed at 1608 cm\(^{-1}\) (C=C semicircle stretch). Data obtained from the iCiR was processed using OriginPro2021.

![ReactIR setup](image)

**Figure S4.** ReactIR setup shown with reaction vessel attached to the probe. The custom-made sidearm allows the delayed addition of reagents, degassing or sampling.
Experimental procedure for reaction monitoring. A custom-made reaction vessel (19 x 100 mm) with a sidearm (Figure S4) was equipped with a stir bar and charged with 4-tert-butylphenylacetic acid (115.35 mg, 0.2 mM, 0.6 mmol) and 4-dimethylaminopyridine (146.6 mg, 1.2 mmol, 2 equiv.). MeCN (3 mL) was added, the vessel was sealed and sonicated for 5 minutes. The reaction vessel was attached to a PTFE adapter affixed to the ReactIRs probe (Figure S3). The reaction mixture was stirred for 30 min while collecting data (Figure S4). After this period, Selectfluor (255.06 mg, 0.72 mmol, 1.2 equiv.) was added and the mixture was stirred for 1 h at r.t.

Figure S5. Reaction monitoring of the fluorination of 2-(4-(tert-butyl)phenyl)acetic acid using ReactIR. Raw data output (left) and processed reaction profile ((right).

Figure S6. Monitoring of the reaction of DMAP and Selectfluor in absence of starting material using ReactIR. Raw data output (left) and processed reaction profile ((right).
4.9 NMR experiments

Initial NMR experiments with SelectFluor and DMAP in absence of starting material indicated that HF (signs of glass etching of the NMR tubes). To prevent glass etching and consumption of HF by this process, we used poly propylene micro reaction caps and Teflon NMR inserts for further measurements. DMAP forms an adduct with HF (Figure S7 and S8). The triplet signal at 11.42 ppm shows a long-range coupling to the pyridinium nitrogen in the $^1$H-$^{15}$N-HMBC spectrum (Figure S8). Similar pyridinium polyhydrogen fluorides are known, such as Olahs reagent.⁶

**Figure S7.** $^1$H NMR spectrum (500 MHz) of DMAP in presence of HF in CD$_3$CN. HF (48%, 0.038 mL, 1.06 mmol) was added to DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL). DMAP forms an adduct with HF. The triplet at 11.4 ppm originates from (F-H-F)$^-$ coordinated to the pyridine nitrogen of DMAP. The two $^{19}$F coupling partners lead to a triplet splitting of the $^1$H signal.

**Figure S8.** $^{15}$N-$^1$H-HMBC spectrum of DMAP in presence of HF in CDCN$_3$. HF (48%, 0.038 mL, 1.06 mmol) was added to DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL).
In the $^1$H NMR spectrum of a mixture of SelectFluor with DMAP, we observed the same triplet signal indicative of a pyridinium HF adduct (Figure S9 and S10).

The superposition of the $^1$H-$^{15}$N-HMBC spectra of the DMAP/HF mixture with the reaction mixture of SelectFluor/DMAP shows that, also when using SelectFluor, the pyridinium nitrogen resonance shifts to ca. 160 ppm indicative of the formation of the (F-H-F)-adduct. In this case, however, the (F-H-F)-Triplet is too broad such that the long-range correlation signal could not be detected.

**Figure S9.** $^1$H NMR spectrum (500 MHz) of a reaction mixture of Selectfluor (17.7 mg, 0.05 mmol) and DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL) after a reaction time of three days.

**Figure S10.** Superposition of $^1$H-$^{15}$N-HMBC spectra. Red: HF (48%, 0.038 mL, 1.06 mmol) was added to DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL). Blue: Selectfluor (17.7 mg, 0.05 mmol) and DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL) after a reaction time of 3 days.
$^{19}$F NMR measurements show that HF is liberated very early after mixing the reactants ($\delta_{19F} = -166$ ppm, see Figure S10). Right after mixing, additional, transient signals ($\delta_{19F} = -19$ and -14 ppm, respectively) are observed in the $^{19}$F NMR spectrum. These might originate from N-fluorinated species. However, we have not been able to prove this beyond doubt. After a reaction time of (here) several days, these transient signals have disappeared, and the $^{19}$F signal of HF has shifted slightly to ($\delta_{19F} = -177$ ppm, Figure S11). In this regard, it has to be noted that the $^{19}$F chemical shift of HF depends strongly on its concentration, the presence of H$^+$ and other coordinating agents.

**Figure S11.** $^{19}$F NMR (471 MHz) spectrum directly after mixing Selectfluor (17.7 mg, 0.05 mmol) and DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL). The large signal at ca. -150 ppm originates from BF$_4^-$.

**Figure S12.** $^{19}$F NMR spectrum (471 MHz) of a reaction mixture of Selectfluor (17.7 mg, 0.05 mmol) and DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL) after three days. Transient $^{19}$F signals, observed right after mixing, have disappeared. Only the large signals of BF$_4^-$ at ca. -150 ppm and HF at -177 ppm are visible.
Neutralization with NaOH converts HF into $F^-$. Applied to the sample shown in Figure S11, still only two $^{19}F$ signals are observed, confirming the presence of BF$_4^-$ and $F^-$ (Figure S12). The amount of HF and $F^-$, resp., increases with time. Calibrating the integral of the BF$_4^-$ signal to 100%, the integrals of the HF signals change from 20% (after mixing), 26% (after 4h) to 28% and reach 25% for the quenched $F^-$ signal.

**Figure S13:** $^{19}F$ NMR spectrum (471 MHz) of a reaction mixture of Selectfluor (17.7 mg, 0.05 mmol) and DMAP (6.1 mg, 0.05 mmol) in CD$_3$CN (0.35 mL) after 4 days after adding 0.2 ml 1M NaOH (0.2 mmol) for neutralization. The large signal at -150 ppm originates from of BF$_4^-$ and the signal at -120 ppm originates from $F^-$. 
5 Scope

General experimental procedure. An oven-dried vessel (19 x 100 mm) equipped with a stir bar was charged with substrate (1.8 mmol, 1 equiv, 0.2 mM), 4-dimethylaminopyridine (3.6 mmol, 2 equiv.) and Selectfluor. MeCN (9 mL) was added, the vessel was sealed stirred at room temperature for one hour. HCl (10 mL, 1 M) was added and the mixture was extracted with diethylether (3 x 10 mL). The combined organic phases were dried over Na$_2$SO$_4$, filtered and concentrated. The product was purified by column chromatography (SiO$_2$, Hexane/EtOAc or Hexane/MeOH) on a Grace™ Reveleris™ system.

![Structure of 2-fluoro-2-(4-fluorophenyl)acetic acid (11)](image)

2-Fluoro-2-(4-fluorophenyl)acetic acid (11). From 2-(4-fluorophenyl)acetic acid (277.45 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)-pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 5-20% EA in hexane to afford the title compound as a white powder (221.8 mg, 1.3 mmol, 72%).

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 8.84 (s, 1H), 7.49–7.46 (m, 2H), 7.15–7.07 (m, 2H), 5.81 (d, $J = 47.2$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.8 (d, $J = 28.2$ Hz), 163.7 (dd, $J = 249.5, 2.2$ Hz), 129.4 (dd, $J = 21.1, 3.4$ Hz), 129.0–128.8 (m), 116.2 (d, $J = 22.1$ Hz), 88.3 (d, $J = 187.3$ Hz) $^{19}$F NMR (376 MHz, CDCl$_3$) δ -110.59–-110.67 (m). These data are in full agreement with those previously published in the literature.

![Structure of 2-fluoro-2-(3-fluorophenyl)acetic acid (12)](image)

2-fluoro-2-(3-fluorophenyl)acetic acid (12). From 2-(3-fluorophenyl)acetic acid (277.45 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)-pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0–10% EA in hexane to afford the title compound as a yellowish powder (160.0 mg, 0.93 mmol, 52%).

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 11.56 (s, 1H), 7.40–7.35 (m, 2H), 7.26–7.24 (m, 1H), 7.19 (d, $J = 9.2$ Hz, 1H), 7.12–7.07 (m, 1H), 5.80 (d, $J = 47.1$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.3 (d, $J = 27.5$ Hz), 162.9 (d, $J = 247.9$ Hz), 135.6 (dd, $J = 27.9, 8.9$ Hz), 130.8 (d, $J = 8.2$ Hz), 122.3 (dd, $J = 6.6, 3.1$ Hz), 117.1 (dd, $J = 21.0, 1.8$ Hz), 113.8 (dd, $J = 23.2, 6.9$ Hz), 88.1 (dd, $J = 188.6, 2.2$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.37, -183.17 (d, $J = 47.3$ Hz) ppm. HRMS (ESI) m/z calculated [M+2Na-H] 217.0011, found, 217.0012.
2-Fluoro-2-(2-fluorophenyl)acetic acid (13). From 2-(2-fluorophenyl)acetic acid (277.45 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0–10% EA in hexane to afford the title compound as a yellowish powder (163.1 mg, 0.95 mmol, 53%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.87 (s, 1H), 7.55 – 7.40 (m, 2H), 7.27 – 7.09 (m, 2H), 6.13 (d, $J$ = 48.5 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.3 (dd, $J$ = 28.1, 1.3 Hz), 160.4 (dd, $J$ = 250.7, 4.4 Hz), 132.1 (dd, $J$ = 8.3, 2.6 Hz), 128.9 (dd, $J$ = 5.1, 2.6 Hz), 124.7 (dd, $J$ = 4.1, 1.2 Hz), 121.2 (dd, $J$ = 20.9, 13.9 Hz), 116.0 (d, $J$ = 20.9 Hz), 83.2 (dd, $J$ = 185.6, 3.9 Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.09 (m), -181.17 (d, $J$ = 46.7 Hz) ppm. These data are in full agreement with those previously published in the literature.

2-(3,4-difluorophenyl)-2-fluoroacetic acid (14). From 2-(3,4-difluorophenyl)acetic acid (309.8 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0-10% EA in hexane to afford the title compound as white crystals (161.6 mg, 0.85 mmol, 47%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.34 (m, 1H), 7.28 – 7.20 (m, 2H), 5.82 (d, $J$ = 47.0 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.2 (d, $J$ = 27.8 Hz), 151.4 (ddd, $J$ = 249.8, 10.5, 2.1 Hz), 150.6 (dd, $J$ = 249.7, 12.1 Hz), 130.2 (ddd, $J$ = 21.6, 5.8, 3.9 Hz), 123.2 (td, $J$ = 6.7, 3.8 Hz), 118.1 (d, $J$ = 17.8 Hz), 116.0 (dd, $J$ = 18.9, 6.6 Hz), 87.6 (dd, $J$ = 188.8, 1.5 Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -135.10 – -135.16 (m), -135.54 – -135.63 (m), -181.48 (d, $J$ = 47.2 Hz) ppm. HRMS (ESI) m/z calculated [M+2Na-H] 234.9911, found, 234.9918.

2-(4-chlorophenyl)-2-fluoroacetic acid (15). From 2-(4-chlorophenyl)acetic acid (307.8 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0–10% EA in hexane to afford the title compound as a white solid (286.7 mg, 1.5 mmol, 84%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.98 – 10.64 (m, 1H), 7.49 – 7.38 (m, 4H), 5.83 (d, $J$ = 47.5 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.1 (d, $J$ = 32.3 Hz), 136.1 (d, $J$ = 2.5 Hz), 131.8 (d, $J$ = 21.1 Hz), 129.2, 127.9 (d, $J$ = 6.2 Hz), 88.0 (d, $J$ = 188.2 Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -181.97 (d, $J$ = 47.2 Hz) ppm. These data are in full agreement with those previously published in the literature.
2-(3-chlorophenyl)-2-fluoroacetic acid (16). From 2-(3-chlorophenyl)acetic acid (307.8 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (30% EA in hexane) to afford the title compound as a yellow oil (164.5 mg, 0.87 mmol, 48%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (s, 1H), 7.39 – 7.34 (m, 3H), 5.77 (d, $J = 47.3$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.6 (d, $J = 27.3$ Hz), 136.1 (d, $J = 21.0$ Hz), 134.9, 130.2, 126.8 (d, $J = 6.8$ Hz), 124.8 (d, $J = 6.3$ Hz), 88.6 (d, $J = 187.2$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -182.24 (d, $J = 47.4$ Hz) ppm. These data are in full agreement with those previously published in the literature.

2-(2-chlorophenyl)-2-fluoroacetic acid (17). From 2-(2-chlorophenyl)acetic acid (307.8 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (30% EA in hexane) to afford the title compound as a yellowish powder (274.5 mg, 1.5 mmol, 81%).

$^1$H NMR (400 MHz, MeOD-d$_4$): δ 7.57–7.35 (m, 4H), 6.24 (d, $J = 46.8$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, MeOD-d$_4$): δ 170.1 (d, $J = 27.4$ Hz), 133.5 (d, $J = 4.1$ Hz), 132.9 (d, $J = 20.2$ Hz), 130.9 (d, $J = 2.6$ Hz), 129.7 (d, $J = 1.1$ Hz), 128.8 (d, $J = 5.5$ Hz), 127.2 (d, $J = 1.2$ Hz), 86.1 (d, $J = 182.1$ Hz) ppm. $^{19}$F NMR (376 MHz, MeOD-d$_4$): δ -180.44 (d, $J = 45.7$ Hz) ppm. HRMS (ESI) m/z calculated [M+2Na-H] 232.9711, found, 232.9720.

2-(2-chloro-6-fluorophenyl)-2-fluoroacetic acid (18). From 2-(2-chloro-6-fluorophenyl)acetic acid (339.44 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. A yield of 64% was determined by $^1$H NMR, using dimethyl maleate as an internal standard. The product could not be separated from the substrate by column chromatography.
2-(4-bromophenyl)-2-fluoroacetic acid (19). From 2-(4-bromophenyl)acetic acid (387.9 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (40% EA in hexane) to afford the title compound as white powder (254.5 mg, 1.2 mmol, 61%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.58 (d, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H) 5.81 (d, $J = 47.0$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.8 (d, $J = 27.8$ Hz), 133.1 (d, $J = 20.8$ Hz), 132.7 (d, $J = 21.0$ Hz), 132.2, 128.3 (d, $J = 5.8$ Hz), 124.3 (d, $J = 2.5$ Hz), 88.8 (d, $J = 186.4$ Hz), 88.3 (d, $J = 187.2$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -182.43 (d, $J = 49$ Hz) ppm. These data are in full agreement with those previously published in the literature.

2-(3-bromophenyl)-2-fluoroacetic acid (20). From 2-(3-bromophenyl)acetic acid (387.9 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (40% EA in hexane) to afford the title compound as white powder (157.6 mg, 0.68 mmol, 38%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.94 (s, 1H), 7.61 (s, 1H), 7.53–7.51 (m, 1H), 7.40–7.37 (m, 1H), 7.28–7.24 (m, 1H) 5.76 (d, $J = 47.1$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.0 (d, $J = 27.7$ Hz), 135.5 (d, $J = 20.8$ Hz), 133.2 (d, $J = 1.8$ Hz), 130.6, 129.6 (d, $J = 6.8$ Hz), 125.2 (d, $J = 6.3$ Hz), 123.0, 87.9 (d, $J = 188.8$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -183.16 (d, $J = 49$ Hz) ppm. These data are in full agreement with those previously published in the literature.

2-(2-bromophenyl)-2-fluoroacetic acid (21). From 2-(2-bromophenyl)acetic acid (387.9 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (40% EA in hexane) to afford the title compound as white powder (212.6 mg, 0.91 mmol, 51%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, $J = 8.1$ Hz, 1H), 7.54–7.51 (m, 1H), 7.42–7.37 (m, 1H), 7.32–7.28 (m, 1H), 6.28 (d, $J = 46.3$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.9 (d, $J = 28.1$ Hz), 133.4, 133.3 (d, $J = 20.7$ Hz), 131.5 (d, $J = 2.5$ Hz), 128.7 (d, $J = 6.2$ Hz), 128.0, 123.4 (d, $J = 4.7$ Hz), 87.9 (d, $J = 186.9$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -180.05 (d, $J = 46.2$ Hz) ppm. HRMS (ESI) m/z calculated [M+2Na-H] 276.9211, found, 278.9203.
2-Fluoro-2-(perfluorophenyl)acetic acid (22). From 2-(perfluorophenyl)acetic acid (406.9 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0–10% EA in hexane to afford the title compound as yellow oil (163.8 mg, 0.67 mmol, 38%).

$^1$H NMR (400 MHz, DMSO) δ 14.17 (s, 1H), 6.48 (d, $J = 44.7$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 167.5 (d, $J = 26.0$ Hz), 146.1, 143.6, 140.7, 138.5, 136.0 ppm. $^{19}$F NMR (376 MHz, DMSO) δ $-142.28$–$-142.42$ (m), $-149.81$–$-151.43$ (m), $-160.86$–$-161.85$ (m), $-180.97$ (d, $J = 44.5$ Hz) ppm. HRMS (ESI) $m/z$ calculated [M+2Na-H], 288.9711, found, 288.9639.

2-fluoro-2-(4-iodophenyl)acetic acid (23). From 2-(4-iodophenyl)acetic acid (225.8 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0–10% EA in hexane to afford the title compound as a white solid (86.2 mg, 0.31 mmol, 35%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J = 7.6$ Hz, 2H), 7.26 (d, $J = 8.7$ Hz, 2H), 5.81 (d, $J = 47.2$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.9 (d, $J = 26.0$ Hz), 138.2, 133.1 (d, $J = 20.9$ Hz), 128.4 (d, $J = 6.2$ Hz), 96.3 (d, $J = 2.7$ Hz), 88.3 (d, $J = 188.1$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ $-182.15$ (d, $J = 47.0$ Hz) ppm. HRMS (ESI) $m/z$ calculated [M+2Na-H], 324.9111, found, 324.9089.

2-Fluoro-2-(4-(trifluoromethyl)phenyl)acetic acid (24). From 2-(4-(trifluoromethyl)phenyl)acetic acid (225.8 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (10% EA in hexane) to afford the title compound as yellow crystals (343.3 mg, 1.55 mmol, 86%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 11.54 (s, 1H), 7.83 – 7.50 (m, 4H), 5.90 (d, $J = 47.1$ Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.9 (d, $J = 27.2$ Hz), 137.2 (d, $J = 21.1$ Hz), 132.7–131.7 (m), 126.9 (d, $J = 6.7$ Hz), 126.0 (d, $J = 3.8$ Hz), 88.1 (d, $J = 189.0$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ $-62.95$, $-185.25$ (d, $J = 47.3$ Hz) ppm. These data are in full agreement with those previously published in the literature.\(^8\)
2-fluoro-2-(3-(trifluoromethyl)phenyl)acetic acid (25). From 2-(3-(trifluoromethyl)phenyl)acetic acid (367.47 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)-pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography using an eluent gradient of 0-20% EA in hexane to afford the title compound as a yellowish powder (126.6 mg, 0.57 mmol, 32%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.67 (s, 1H), 7.79 (s, 1H), 7.72 (d, $J$ = 7.9 Hz, 2H), 7.59 (t, $J$ = 7.8 Hz, 1H), 5.93 (d, $J$ = 47.2, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.2 (d, $J$ = 27.2 Hz), 134.3 (d, $J$ = 21.4 Hz), 131.3 (q, $J$ = 32.9 Hz), 129.7 (d, $J$ = 6.5 Hz), 129.5, 126.8–126.7 (m), 123.2–123.3 (m), 87.9 (d, $J$ = 188.9 Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.81, -184.25 (d, $J$ = 46.7 Hz) ppm. HRMS (ESI) $m/z$ calculated [M+2Na-H] 267.0011, found, 266.9985.

2-fluoro-2-(4-nitrophenyl)acetic acid (26). From 2-fluoro-2-(4-nitrophenyl)acetic acid (326.07 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. A yield of 87% was determined by $^1$H NMR, using dimethyl maleate as an internal standard. Isolation was not possible, because the title compound decomposed during column chromatography.

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.40 (s, 1H) 7.61–7.33 (m, 5H), 5.86 (d, $J$ = 47.4 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.6 (d, $J$ = 28.0 Hz), 133.5 (d, $J$ = 20.4 Hz), 130.1 (d, $J$ = 2.2 Hz), 129.0, 126.8 (d, $J$ = 6.1 Hz), 88.9 (d, $J$ = 186.6Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -180.82 (d, $J$ = 47.5 Hz) ppm. These data are in full agreement with those previously published in the literature.\(^8\)

2-fluoro-2-phenylacetic acid (27). From 2-phenylacetic acid (245.07 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography (5% EA in hexane) to afford the title compound as white crystals (136.8 mg, 0.89 mmol, 49%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.40 (s, 1H) 7.61–7.33 (m, 5H), 5.86 (d, $J$ = 47.4 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.6 (d, $J$ = 28.0 Hz), 133.5 (d, $J$ = 20.4 Hz), 130.1 (d, $J$ = 2.2 Hz), 129.0, 126.8 (d, $J$ = 6.1 Hz), 88.9 (d, $J$ = 186.6Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -180.82 (d, $J$ = 47.5 Hz) ppm. These data are in full agreement with those previously published in the literature.\(^8\)
2-[(1,1'-biphenyl)-4-yl]-2-fluoroacetic acid (28). From 2-[(1,1'-biphenyl)-4-yl]acetic acid (382.05 mg, 1.8 mmol, 0.2 mM) using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography using an eluent gradient of 5–10% EA in hexane to afford the title compound as a yellowish powder (308.7 mg, 1.34 mmol, 75%).

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1^1H\text{ NMR (400 MHz, MeOD)} \delta 7.68 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 6.6 Hz, 1H), 5.90 (d, J = 47.9 Hz, 1H)\text{ ppm.} 1^3C\text{ NMR (100 MHz, MeOD-d}_4): \delta 170.8 (d, J = 28.0 Hz), 141.2 (d, J = 214.3 Hz), 134.0 (d, J = 20.4 Hz), 128.6 – 126.6 (m), 88.9 (d, J = 182.1 Hz) ppm. 1^9F\text{ NMR (376 MHz, MeOD-d}_4): \delta -179.43 (d, J = 47.5 Hz) ppm. These data are in full agreement with those previously published in the literature.\]

2-(4-(tert-butyl)phenyl)-2-fluoroacetic acid (29). From 2-(4-(tert-butyl)phenyl)acetic acid (346.06 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The crude mixture was purified over silica with flash chromatography, using an eluent gradient of 0–10% EA in hexane to afford the title compound as white crystals (185.4 mg, 0.88 mmol, 49%).

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1^1H\text{ NMR (400 MHz, CDCl}_3) \delta 10.50 (s, 1H), 7.48 – 7.39 (m, 4H), 5.80 (d, J = 47.5 Hz, 1H) 1.33 (s, 9H) ppm. 1^3C\text{ NMR (101 MHz, CDCl}_3) \delta 174.7 (d, J = 28.3 Hz), 153.4 (d, J = 2.3 Hz), 130.5 (d, J = 20.6 Hz), 126.7 (d, J = 5.7 Hz), 126.0, 88.8 (d, J = 186.1 Hz), 34.9, 31.3 ppm. 1^9F\text{ NMR (376 MHz, CDCl}_3) \delta -179.39 (d, J = 47.5 Hz) ppm. These data are in full agreement with those previously published in the literature.\]

2-fluoro-2-(thiophen-2-yl)acetic acid (30). From 2-(thiophen-2-yl)acetic acid (255.02 mg, 1.8 mmol, 0.2 mM), using 4-(dimethylamino)pyridine (439.8 mg, 3.6 mmol, 2 equiv.) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(tetrafluoroborate) (765.2 mg, 2.16 mmol, 1.2 equiv.) in 9 mL MeCN. The yield of 83% was determined by \(^1H\text{ NMR},\) using dimethyl maleate as an internal standard. Isolation was not possible, because the title compound decomposed during column chromatography.
Scheme S6. Unsuccessful substrates

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Copies of NMR spectra of isolated compounds
