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# Fluoromethyl-2,4,6-trinitrophenylsulfonate: A New Electrophilic Monofluoromethylating Reagent

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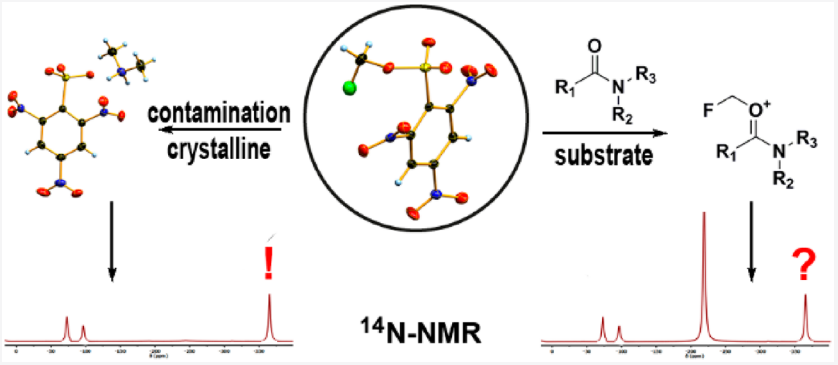


**ABSTRACT:** Fluoromethyl-2,4,6-trinitrophenylsulfonate has been prepared for the first time and qualified as a simple to use monofluoromethylating reagent. Its molecular structure in the solid state has been determined by single-crystal X-ray diffraction studies. This reagent proves to be effective for the electrophilic introduction of a $CH_2F$ group into selected chalcogen and nitrogen nucleophiles. Monofluoromethyl derivatives of various bifunctional N,O-nucleophiles have been synthesized using fluoromethyl-2,4,6-trinitrophenylsulfonate. Due to the good crystallizing properties of the anion, the fluoromethylated products as well as side products that are difficult to identify by nuclear magnetic resonance spectroscopy can readily be characterized by X-ray crystallographic techniques.

## INTRODUCTION

Monofluoromethyl-containing organic compounds are greatly important in the pharmaceutical industry. The bioisosterism of the -$CH_2F$ group to essential functional groups occurring in living systems, combined with the enhanced metabolic stability, lipophilicity, and membrane permeability induced by the fluorine substituent, allows an efficient drug design.[1] The most prominent representative is Fluticasone, a drug widely used against inflammatory diseases and as analgesics for the treatment of certain types of cancer.[2] Although a large number of biologically active monofluoromethyl-containing substances have been described in the literature, their synthesis by introduction of the $CH_2F$ group as such remains a challenge and a series of new electrophilic fluoromethylation reagents such as $CH_2FI$ have been developed in the past decade.[3] In most cases, however, either ozone-depleting fluoromethyl halides like $CH_2FCl$ or $CH_2FBr$ or reagents made by tedious multistep syntheses were used. Among the $CH_2F$ transferring reagents, fluoromethyl sulfonates, e.g., fluoromethyl triflate, are mainly used today, usually for $^{18}F$ labeling.[3a,4] However, their synthesis requires generally quite harsh conditions.

Pharmaceuticals often require Good Manufacturing Practices (GMP) certification, which certifies the high purity of the drug and the identification of all byproducts occurring during its synthesis.[5] The identification of byproducts often represents a difficult task, particularly when identification via multinuclear NMR spectroscopy is not unambiguous. X-ray crystallography is a method of determining byproducts and identifying their structures without doubt. In the case of salts, the formation of suitable single crystals strongly depends on the anion and in some cases the salts are hard to crystallize.[6] A fluoromethylation reagent, which is similar in strength to fluoromethyl triflate in terms of its alkylation power and at the same time provides an anion with good crystallization properties, would be particularly important for GMP processes with regard to the identification and structural characterization of ionic impurities. Because protonation is generally similar to methylation, the $pK_a$ values can be used to roughly estimate the alkylating power

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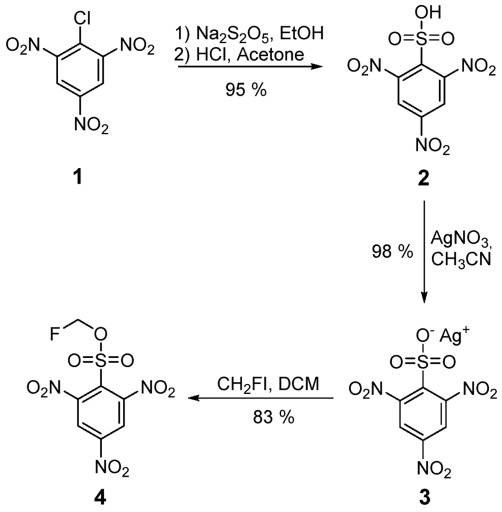
of a reagent. This is the case for triflic acid ($pK_a$ = 11.4) and trinitrobenzenesulfonic acid ($pK_a$ = 11.3).

In fact, 2,4,6-trinitrobenzenesulfonic acid methyl ester is reported to be a stronger methylating agent than methyl triflate, whereby selected weak nucleophiles like dimethyl ether can be methylated.[7] At the same time, good crystallization properties can be anticipated for the trinitrobenzenesulfonate anion.[8] Here, we present the synthesis and first applications of fluoromethyl-2,4,6-trinitrobenzenesulfonate **4**, a new electrophilic fluoromethylating reagent (Scheme 1).

**Scheme 1. Preparation of Fluoromethyl-2,4,6-trinitrobenzenesulfonate (4)**




## RESULTS AND DISCUSSION

Picryl chloride (**1**), from which traces of picric acid were carefully removed by washing with acetone, was used as the starting material. Reaction with sodium metabisulfite followed by hydrolysis with aqueous HCl yields sulfonic acid **2**, which was converted to the corresponding silver salt **3** by reaction with $AgNO_3$ (Scheme 1). These reactions were carried out following a slightly modified literature procedure.[9] It is greatly important to completely remove traces of picric acid before starting the synthesis to prevent formation of explosive silver picrate. In contrast, silver trinitrosulfonate does not have a critical impact and frictional sensitivity and can be handled safely. In the final step, the reaction of **3** with $CH_2FI$ in DCM yields fluoromethyl sulfonate **4** (83%). This final step worked only using dry DCM as the solvent. Traces of moisture or solvents with lone pairs of electrons like acetonitrile, diethyl ether, or THF will cause decomposition of **4** via formation of a brownish solid.

Fluoromethyl sulfonate **4** was obtained as a colorless microcrystalline solid. All intermediates in its synthesis were isolated and characterized by single-crystal X-ray diffraction and further analyses (see the Supporting Information). Reagent **4** is stable at ambient temperature and was stored for one year under dry argon without decomposition. Due to its alkylating properties, **4** should be handled under dry protective gas in dry non-nucleophilic solvents. It exhibits a melting point of 136.5 °C and a decomposition point of 138 °C. Single crystals of **4** were obtained by slow evaporation of a solution in DCM. The molecular structure of **4** in the crystal together with selected bond distances and bond angles is shown in Figure 1.

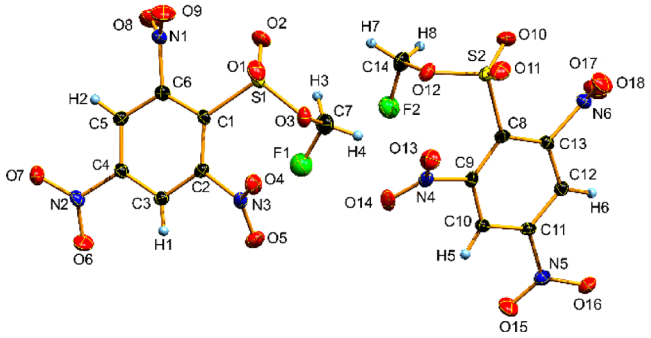



**Figure 1.** Molecular structure of **4** in the crystal; view of the asymmetric unit. DIAMOND representation, thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): F1−C7, 1.355(5); F2−C14, 1.359(5); O3−C7, 1.438(6); O12−C14, 1.436(6); O3−S1, 1.571(3); O12−S2, 1.572(3); F1−C7−O3, 107.8(3); F2−O12−C14, 107.3(3); C7−O3−S1, 120.5(3); C14−O12−S2, 120.3(3); F1−C7−O3−S1, −92.9(4); F2−C14−O12−S2, 95.6(4).

Fluoromethyl sulfonate **4** crystallizes in orthorhombic space group $Pca2_1$ with two crystallographically independent molecules in the unit cell. The C−O distances to the $CH_2F$ group are 1.438(6) and 1.436(6) Å, in the same range as reported for fluoromethyl nitrate and significantly longer than that observed in structurally characterized compounds with O- and N-bonded $CH_2F$ groups (1.302−1.397 Å).[10] The C−F distances within the $CH_2F$ group are 1.355(5) and 1.359(5) Å, slightly shorter than that reported for the same compounds (1.372−1.399 Å).[10] Both anticipate a fluoromethylation activity for new reagent **4**.

In fact, fluoromethyl sulfonate **4** qualified as a suitable reagent for the fluoromethylation of selected chalcogen and nitrogen nucleophiles. Its applicability seems to be limited, however. It showed no reaction with the potassium salts of carboxylic acids like benzoic acid and substituted benzoic acids. With the potassium salts of phenols, only decomposition of **4** was observed. In the case of nucleophiles, like potassium isopropanolate, DBU, thiourea, *N,N,N′,N′*-tetramethyl guanidine, pyridine, 4-DMAP, diverse imidazoles, dimethylamine, and benzoxazole, an intensely red-colored solution was formed immediately after the addition of the reagent, in which no fluoromethylated product could be observed by NMR spectroscopy. In the case of dimethylamine, 2,4,6-trinitroaniline was isolated and identified by single-crystal X-ray diffraction (see the Supporting Information). Most likely, the change in color to red derives from the formation of a Janovsky product,[11] whereby the nucleophile attacks the ipso position of the reagent, rendering it inoperable (Scheme 2).[12] A similar behavior is reported for the corresponding 2,4,6-trinitrophenylsulfonic acid methyl ester, which was used as a color reagent for the detection of creatin. Furthermore, the decomposition of the methyl ester was also observed with selected substrates like dimethyl sulfite, sulfolane, or methylsulfonyl chloride.[1a−c]

The fluoromethylation ability of new reagent **4** was tested using a series of amides of carbonic acids (Table 1). The amides were selected on the basis of the experience from the methylation using methyl triflate. In these cases, the resulting



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**Scheme 2. Proposed Mechanism for the Reaction of 4 with Dimethylamine, Resulting in the Formation of 2,4,6-Trinitroaniline**

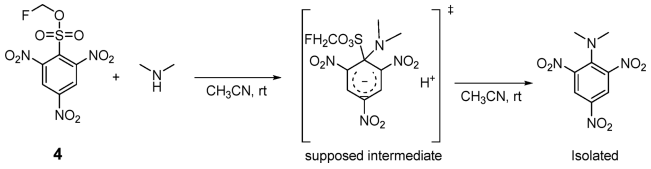
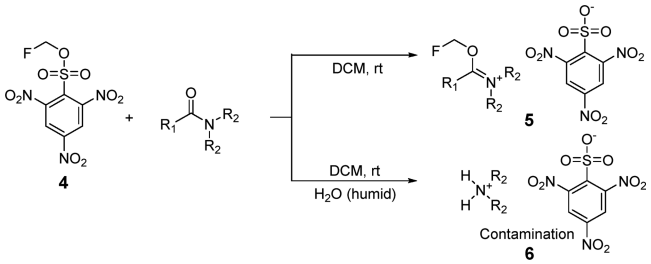
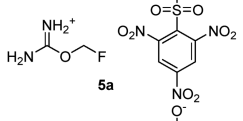
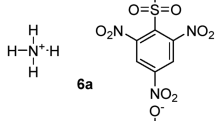
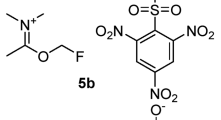
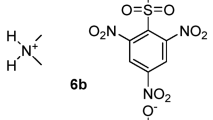
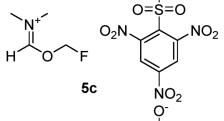
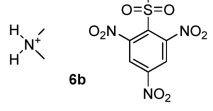



**Table 1. Fluoromethylation of Amides with 4 to Yield Salts 5**[a]




| entry | starting material | decomposition/product | yield (%) |
|---|---|---|---|
| 1 |  |  5a | 80 |
| 2 |  |  6a | 3 |
| 3 |  |  5b | 78 |
| 4 |  |  6b | 4 |
| 5 |  |  5c | 82 |
| 6 |  |  6b | 3 |

[a]The main byproducts are ammonium salts **6**.

triflate salts form ionic liquids,[6] and also traces of byproducts were present in the reaction mixture. Mostly amides disubstituted at the nitrogen atom yielded isolatable and stable monofluoromethyl products. The products resulting from the fluoromethylation of *N*-methylacetamide or acetamide were too unstable and could not be isolated. All other fluoromethylated amides were obtained as crystalline 2,4,6-trinitrophenyl sulfonium salts and were characterized by multinuclear ($^{1}$H, $^{13}$C, and $^{14}$N) NMR spectroscopy and single-crystal X-ray diffraction (Figures 2−4).

As a main byproduct (3−4%), ammonium salts **6** were identified by NMR spectroscopy and single-crystal X-ray

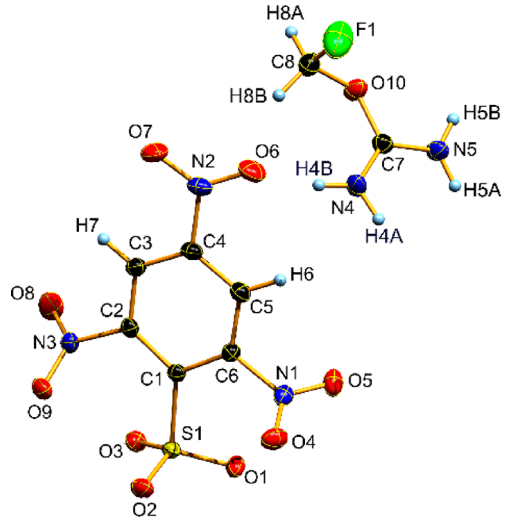



**Figure 2.** Molecular structure of **5a** in the crystal; view of the asymmetric unit. DIAMOND representation, thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): F1−C8, 1.353(2); O10−C8, 1.411(2); O10−C7, 1.330(2); F1−C8−O10, 108.1(2); F1−C8−O10−C7, 75.9(2).

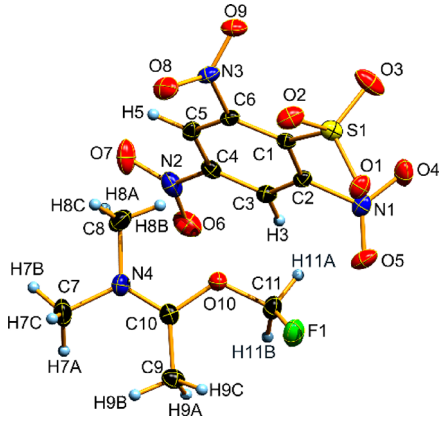



**Figure 3.** Molecular structure of **5b** in the crystal; view of the asymmetric unit. DIAMOND representation, thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): F1−C11, 1.367(2); C11−O10, 1.412(2); F1−C11−O10, 109.2(2); F1−C11−O10−C10, −80.5(2).

diffraction (Table 1 and the Supporting Information). The formation of **6** indicates the possible presence of traces of water. To further investigate the formation of **6**, pure monofluoromethylated dimethylacetamide **5b** was allowed to react with $D_2O$. The $^{1}$H NMR spectrum of the reaction solution indicated the formation of $Me_2ND_2^+$ (Scheme 3), identified by the $^{1}$H NMR signal of the methyl protons. Unfortunately, the fate of the fluoromethyl substituent could not be determined with certainty.

To further explore the fluoromethylation ability of sulfonate **4**, the transfer of the $CH_2F$ group to the chalcogen atom of the triphenylphosphine chalcogenides $Ph_3PX$ (X = O, S, or Se) was investigated (Table 2). As one can see from Table 2, the reaction of **4** with triphenylphosphine sulfide and selenide proceeds in a straightforward manner, producing fluoromethylated derivatives **7b** and **7c** in good yields. Fluoromethylated selenide **7c**, on one hand, is highly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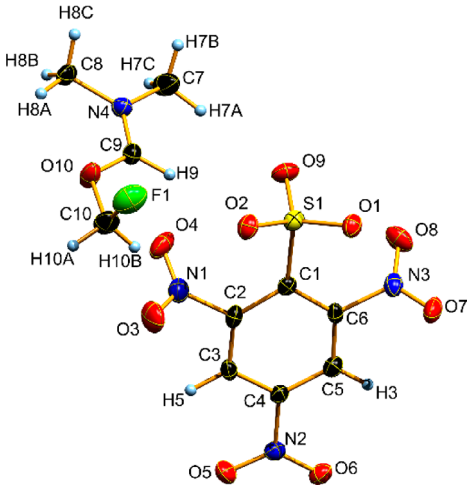



**Figure 4.** Molecular structure of **5c** in the crystal; view of the asymmetric unit. DIAMOND representation, thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): F1−C10, 1.349(4); C10−O10, 1.4243(3); O10−C9, 1.317(3); F1−C10−O10, 107.2(3); C10−O10−C9, 116.3(2); F1−C10−O10−C9, 84.7(4).

**Scheme 3. Reaction of 5b with $D_2O$**

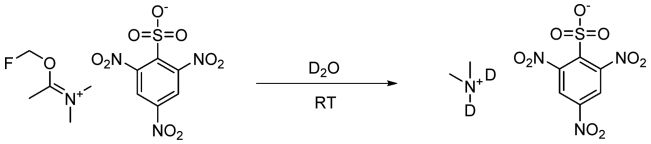
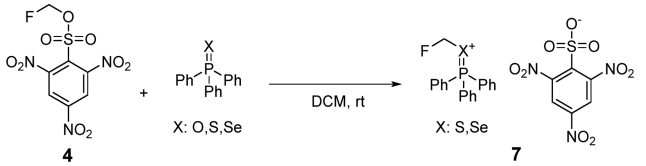
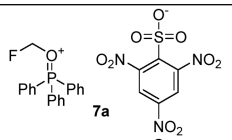
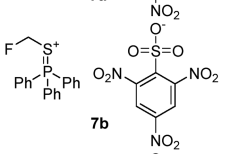
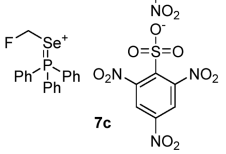



**Table 2. Fluoromethylation of $Ph_3PX$ (X = O, S, or Se) with 4**




| entry | starting material | decomposition/product | yield (%) |
|---|---|---|---|
| 1 |  |  **7a** | 0 |
| 2 |  |  **7b** | 78 |
| 3 |  |  **7c** | 66 |

sensitive to air, while sulfide **7b**, on the other, is sufficiently stable and could be characterized by single-crystal X-ray diffraction (Figure 5). No reaction was observed with triphenylphosphine oxide. Fluoromethylation of diphenyl sulfide, butyrolactone, and benzaldehyde was also not possible with this reagent.

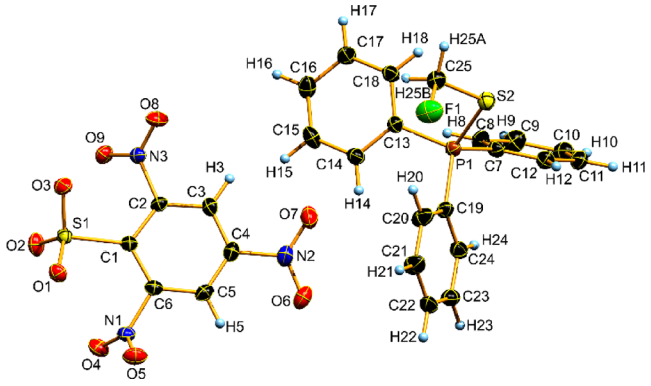
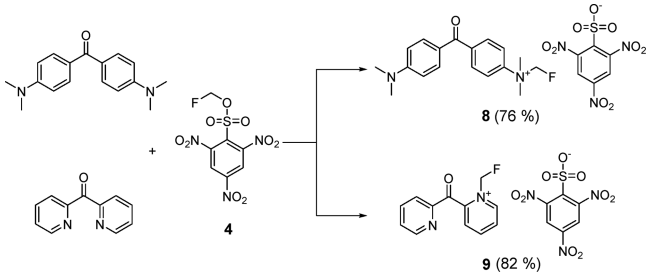



**Figure 5.** Molecular structure of **7b** in the crystal; view of the asymmetric unit. DIAMOND representation, thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): F1−C25, 1.378(2); C25−S2, 1.813(2); S2−P1, 2.076(1); F1−C25−S2, 111.3(2); C25−S2−P1, 104.5(1); F1−C25−S2−P1, 88.5(2).

Fluoromethylation of Michler's ketone and dipyridyl ketone with sulfonate **4** occurs in both cases at the nitrogen (Scheme 4). Salt **9** was isolated as a colorless microcrystalline

**Scheme 4. Fluoromethylation of Michler's Ketone and Dipyridyl Ketone with Sulfonate 4**




solid. Single crystals of **9** were obtained from a dichloromethane solution by slow evaporation of the solvent. The molecular structure of **9** in the crystal was determined by single-crystal X-ray diffraction and is shown in Figure 6 together with selected bond lengths and angles.

## CONCLUSION

In conclusion, we have prepared the new sulfonic acid fluoromethyl ester (**4**) that acts as an electrophilic monofluoromethylating reagent. With the new reagent, the fluoromethyl group was successfully transferred to carbonic acid amides, phosphorus chalcogenides, and aromatic ketones. Reaction with several other organic substrates showed, however, that the fluoromethylation ability of **4** seems to be limited. The 2,4,6-trinitrophenylsulfonyl anion qualified as strongly crystallization-supporting. Byproducts, which are formed during fluoromethylation, could readily be isolated and identified via single-crystal X-ray diffraction.

## EXPERIMENTAL SECTION

**General Aspects.** All compounds were handled using Schlenk techniques under dry Ar. Fluoroiodomethane (donated by F-Select GmbH) was distilled under inert conditions before use. For purification, picryl chloride (internal stockpile) was suspended in acetone and the solution was poured onto ice. The remaining solid was filtered off, and the procedure was repeated until the solid was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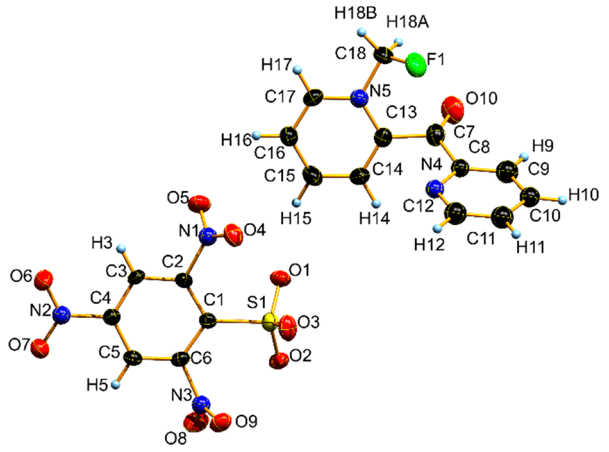


**Figure 6.** Molecular structure of **9** in the crystal; view of the asymmetric unit. DIAMOND representation, thermal ellipsoids are drawn at the 50% probability level. The nonfluoromethylated pyridine ring is disordered over two positions. Only the more populated (55%) position is shown. Selected bond lengths (angstroms) and angles (degrees): F1−C18, 1.357(4); C18−N5, 1.480(4); F1−C18−N5, 107.8(3).

colorless. All other chemicals were purchased from VWR and Sigma-Aldrich and used without further purification. Melting and/or decomposition points were determined with a Linseis DSC-PT10 instrument or with an OZM DTA 552-Ex instrument under an inert atmosphere and ambient conditions. The samples for infrared spectroscopy were placed under ambient conditions without further preparation onto a Smith DuraSampLIR II ATR device using a PerkinElmer BX II FR-IR System spectrometer. Samples for Raman spectroscopy were sealed in glass tubes. The measurement was carried out with a Bruker MultiRam FT Raman device using a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser ($\lambda$ = 1064 nm) with 1074 mW. The samples for NMR spectroscopy were prepared under an inert atmosphere using Ar as the protective gas. The solvents were dried using 3 Å molecular sieves and stored under an Ar atmosphere. Spectra were recorded with a Bruker Avance III spectrometer operating at 400.1 MHz ($^{1}$H), 376.4 MHz ($^{19}$F), 100.6 MHz ($^{13}$C), 161.9 MHz ($^{31}$P), 76.3 MHz ($^{77}$Se), and 28.9 MHz ($^{14/15}$N). Chemical shifts are referred to TMS ($^{1}$H/$^{13}$C), $CFCl_3$ ($^{19}$F), 85% $H_3PO_4$ ($^{31}$P), $Me_2Se$ ($^{77}$Se), and $MeNO_2$ ($^{14}$N). All spectra were recorded at 299.15 K (26 °C). For compound **5a**, $^{15}$N NMR was measured directly, and for **8** and **9**, $^{1}$H−$^{15}$N HMBC spectra were recorded. Elemental analyses were performed with an Elemental Vario EL Analyzer. The samples were prepared under a $N_2$ atmosphere. High-resolution mass spectral data (HRMS) were acquired using a Jeol MStation Sectorfield in ESI-TOF/DEI-TOF mode. Single crystals, suitable for X-ray diffraction, were obtained by slow evaporation of a solution in acetonitrile or DCM. The crystals were introduced into perfluorinated oil, and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data were collected with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Data collection and data reduction were performed with the CrysAlisPro software.[13] Absorption correction using the multiscan method[14] was applied. The structures were determined with SHELXS-97,[15] refined with SHELXL-97,[15] and finally checked using PLATON.[16] Details for data collection and structure refinement are summarized in the Supporting Information.

**Caution!** *Picryl chloride is an energetic material and is sensitive to impact and friction. It must be washed free from picric acid residues before use to prevent the formation of highly shock and friction sensitive picrates such as silver picrate! Even if no accident occurs during the synthesis, Kevlar gloves and plastic spatulas should be used when synthesizing the silver sulfonate or working with the picryl chloride.*

**2,4,6-Trinitrobenzenesulfonic Acid (2).** The preparation of **2** was performed according to a modified literature-known synthesis.[5] Picric acid-free picryl chloride (6.54 g, 26.4 mmol) was dissolved in ethanol (70 mL). To the vigorously stirred solution was added sodium metabisulfite (6.54 g, 34.4 mmol) in small portions over 30 min. The reaction mixture was heated in an oil bath under reflux for 4 h. The mixture was cooled to room temperature, and the solid was filtered off and washed with cold ethanol (3 × 150 mL), until the filtrate was colorless. After the solid was dried at room temperature, it was suspended in acetone (20 mL) and concentrated (32%) hydrochloric acid (6.5 mL) was added dropwise to the reaction mixture over 15 min. The precipitated sodium chloride was filtered off, and the solvent was removed under vacuum, yielding 7.33 g of colorless solid **2**. Yield: 95%. $T_{mp}$: 194 °C. $T_{dec}$: 260 °C. $^{1}$H NMR ($CD_3CN$, 400 MHz): $\delta$ 8.59 (s, 1H), 6.64 (bs, 1H). $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 101 MHz): $\delta$ 150.6, 149.3, 137.1, 122.2. $^{14}$N NMR ($CD_3CN$, 29 MHz): $\delta$ −14.7 (s, 2N), −21.4 (s, 1N). IR (ATR): $\tilde{\nu}$ 3530 (m), 3447 (m), 3084 (m), 1724 (w), 1605 (w), 1539 (s), 1349 (s), 1268 (m), 1199 (m), 1128 (m), 1072 (s), 1032 (s), 924 (s), 733 (m), 718 (s), 626 (s), 552 (m), 445 (m). Raman: $\tilde{\nu}$ 3085 (m), 1604 (s), 1552 (m), 1552 (m), 1374 (s), 1351 (s), 1272 (w), 1190 (w), 1077 (s), 1040 (w), 937 (w), 826 (w), 772 (s), 752 (w), 721 (w), 554 (w), 353 (m), 324 (m), 170 (s). HRMS (DEI) $m/z$: $M^+$ calcd for $C_6H_3N_3O_9S$, 292.9590; found, 292.9590.

**Silver 2,4,6-Trinitrobenzenesulfonate (3).** The preparation of **2** was performed according to a modified literature-known synthesis.[5] Picrylsulfonic acid (6.62 g, 22.6 mmol) dissolved in water (10 mL) and silver nitrate (5.10 g, 30.1 mmol) dissolved in water (10 mL) were poured together in one portion while being stirred, and the reaction mixture was heated in an oil bath to 50 °C for 30 min in the dark. Stirring was continued while the reaction mixture was cooled to room temperature and then further cooled in an ice bath. The formed colorless solid was filtered off and washed with ethanol (2 × 25 mL) and diethyl ether (1 × 25 mL). The product was recrystallized from a dry diethyl ether/acetonitrile mixture (1:1, 60 mL), filtered off, and dried *in vacuo*, yielding 8.85 g of white solid **3**. Yield: 98%. $T_{mp}$: 119 °C. $T_{dec}$: 295 °C. $^{1}$H NMR ($CD_3CN$, 400 MHz): $\delta$ 8.52 (s, 1H). $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 101 MHz): $\delta$ 150.6, 149.0, 137.6, 122.1. $^{14}$N{$^{1}$H} NMR ($CD_3CN$, 29 MHz): $\delta$ −11.4 (s, 2N), −18.4 (s, 1N). IR (ATR): $\tilde{\nu}$ 2963 (m), 2917 (m), 2853 (w), 1576 (w), 1543 (w), 1260 (s), 1093 (s), 1020 (s), 863 (w), 798 (s). Raman: $\tilde{\nu}$ 3088 (w), 1605 (m), 1557 (w), 1541 (w), 1370 (m), 1656 (s), 1188 (w), 1072 (m), 937 (w), 387 (m), 359 (w), 342 (w), 327 (m), 238 (w), 216 (w), 182 (w). Anal. Calcd for $C_6H_2AgN_3O_9S{\cdot}2H_2O$: C, 16.53; H, 1.39; N, 9.64; S, 7.35. Found: C, 16.56; H, 1.40; N, 9.43; S, 7.44. FS: >360N. IS: >40 J.

**Fluoromethyl-2,4,6-trinitrobenzenesulfonate (4).** Silver salt **3** (3.60 g, 9.00 mmol) was suspended in dry dichloromethane (40 mL) under an argon atmosphere. To the cooled suspension (ice bath) was added dropwise fluoroiodomethane (0.7 mL, 10.0 mmol) over a period of 15 min. The mixture was stirred for 1 h, and the precipitated silver iodide was filtered off and washed with dry dichloromethane (100 mL). The solvent was removed *in vacuo*, yielding 2.44 g of colorless solid **4**. Yield: 83%. $T_{mp}$: 136 °C. $T_{dec}$: 138 °C. $^{1}$H NMR (acetone-$d_6$, 400 MHz): $\delta$ 9.21 (s, 2H), 6.11 (d, 2H, $J$ = 49.1 Hz). $^{13}$C{$^{1}$H} NMR (acetone-$d_6$, 101 MHz): $\delta$ 152.7, 151.0, 128.6, 124.0, 102.2 (C−F, $^{1}J_{C-F}$ = 236.9 Hz). $^{19}$F{$^{1}$H} NMR (acetone-$d_6$, 376 MHz): $\delta$ −151.1 (s). $^{19}$F NMR (acetone-$d_6$, 376 MHz): $\delta$ −151.1 ($CH_2F$, $^{2}J_{F-H}$ = 49.1 Hz). $^{14}$N{$^{1}$H} NMR (acetone-$d_6$, 29 MHz): $\delta$ −19.7 (s, 2N), −23.4 (s, 1N). IR (ATR): $\tilde{\nu}$ 3086 (m), 2959 (w), 2927 (w), 1727 (w), 1608 (m), 1547 (s), 1453 (w), 1417 (w), 1393 (m), 1348 (s), 1300 (w), 1204 (w), 1189 (s), 1150 (m), 1120 (m), 1074 (s), 944 (s), 920 (s), 826 (w), 794 (m), 746 (s), 735 (s), 717 (s), 662 (w), 619 (s), 582 (w), 542 (m), 511 (m). Raman: $\tilde{\nu}$ 3086 (m), 3019 (w), 2905 (w), 1603 (m), 1550 (m), 1369 (s), 1354 (s), 1191 (m), 1055 (m), 826 (m), 807 (m), 437 (m), 395 (m), 365 (m), 340 (m), 323 (m), 285 (m), 253 (m). HRMS (DEI) $m/z$: $M^+$ calcd for $C_7H_4FN_3O_9S$, 324.9652; found, 324.9647. Anal. Calcd for $C_7H_4FN_3O_9S$: C, 25.86; H, 1.24; N, 12.92; S, 9.86. Found: C, 26.01; H, 1.41; N, 12.82; S, 10.28.


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**2-(Fluoromethyl)isouronium-2,4,6-trinitrobenzenesulfonate (5a).** Reagent **4** (100 mg, 309 μmol) was dissolved in acetonitrile (1.5 mL) and added dropwise to a solution of urea (18.6 mg, 309 μmol) in acetonitrile (5 mL). The resulting solution was stirred overnight, and the solvent was removed *in vacuo*. The crude product was recrystallized from a dichloromethane/acetonitrile mixture (5 mL/0.3 mL). The mixture was centrifuged, and the solvent was decanted. The remaining solid was dried *in vacuo*, yielding 95 mg of a white solid. Yield: 80%. $T_{mp}$: 180 °C. $T_{dec}$: 200 °C. $^1$H NMR ($CD_3CN$, 400 MHz): δ 8.57 (s, 2H), 7.49 (d, 4H, $J$ = 136.0 Hz), 5.80 (d, 2H, $J$ = 50.2 Hz). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 101 MHz): δ 162.2, 150.8, 149.3, 137.8, 122.1, 99.9 (C−F, $^1J_{C-F}$ = 229.0 Hz). $^{19}F\{^1H\}$ NMR ($CD_3CN$, 376 MHz): δ −156.5 (s). $^{19}F$ NMR ($CD_3CN$, 376 MHz): δ −156.5 ($CH_2F$, $^2J_{F-H}$ = 50.2 Hz). $^{15}N\{^1H\}$ NMR (acetone-$d_6$, 29 MHz): δ −15.6 (s, 2N), −22.6 (s, 1N), −298.3 (s, 1N). IR (ATR): $\tilde{\nu}$ 3419 (m), 3393 (m), 3352 (m), 3247 (m), 3183 (m), 3162 (m), 3113 (m), 3085 (m), 1703 (s), 1643 (w), 1603 (w), 1556 (s), 1544 (s), 1531 (s), 1414 (w), 1349 (s), 1282 (w), 1235 (s), 1188 (w), 1168 (m), 1121 (m), 1095 (w), 1072 (m), 1026 (s), 934 (w), 926 (w), 912 (w), 892 (m), 826 (w), 749 (m), 731 (m), 719 (s), 637 (s), 564 (m), 547 (s), 526 (m), 483 (m), 451 (m), 441 (s). Raman: $\tilde{\nu}$ 3084 (w), 1602 (m), 1567 (m), 1547 (m), 1377 (m), 1351 (s), 1187 (w), 1075 (m), 1030 (w), 893 (m), 826 (m), 529 (w), 454 (w), 442 (m), 352 (m), 318 (w), 276 (w), 238 (w), 207 (s), 172 (s). HRMS (ESI) $m/z$: $M^+$ calcd for $C_2H_6FN_2O^+$, 93.0459; found, 93.0459. Anal. Calcd for $C_8H_8FN_5O_{10}S$: C, 24.94; H, 2.09; N, 18.18; S, 8.32. Found: C, 24.94; H, 2.38; N, 18.34; S, 8.03.

**Fluoromethyl-dimethylacetamidinium-2,4,6-trinitrobenzenesulfonate (5b).** Reagent **4** (126 mg, 387 μmol) was dissolved in acetonitrile (1.0 mL) and added dropwise to a solution of dimethylacetamide (33.7 mg, 387 μmol) in acetonitrile (5 mL). The yellowish solution was stirred for 18 h at room temperature. After the solvent was removed *in vacuo*, the crude product was recrystallized from a dichloromethane/acetonitrile mixture (10 mL/0.3 mL). The mixture was centrifuged, and the solvent was decanted. The remaining solid was dried *in vacuo*, yielding 143 mg of **5b** as a colorless solid. Yield: 78%. $T_{mp}$: 175 °C. $T_{dec}$: 185 °C. $^1$H NMR ($CD_3CN$, 400 MHz): δ 8.53 (s, 2H), 5.95 (d, 2H, $J$ = 49.7 Hz), 3.39 (s, 3H), 3.30 (s, 3H), 2.55 (s, 3H). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 101 MHz): δ 175.9, 150.6, 148.9, 139.4, 121.7, 100.8 (C−F, $^1J_{C-F}$ = 231.3 Hz), 42.8, 40.8, 16.1. $^{19}F\{^1H\}$ NMR ($CD_3CN$, 376 MHz): δ −154.7 (s). $^{19}F$ NMR ($CD_3CN$, 376 MHz): δ −154.7 ($CH_2F$, $^2J_{F-H}$ = 49.7 Hz). $^{14}N\{^1H\}$ NMR ($CD_3CN$, 29 MHz): δ −15.2 (s, 2N), −22.4 (s, 1N), −232.9 (s, 1N). IR (ATR): $\tilde{\nu}$ 3090 (m), 1686 (m), 1606 (m), 1535 (s), 1448 (w), 1395 (w), 1352 (s), 1263 (s), 1247 (s), 1190 (m), 1151 (w), 1122 (m), 1068 (m), 1050 (m), 1035 (s), 1005 (s), 936 (w), 917 (w), 902 (m), 826 (w), 766 (w), 749 (s), 733 (s), 718 (s), 631 (s), 586 (m), 559 (s), 528 (w), 513 (w), 482 (m), 455 (m), 440 (s). Raman: $\tilde{\nu}$ 3097 (m), 3029 (w), 2962 (m), 1601 (w), 1558 (m), 1544 (m), 1381 (m), 1353 (s), 1265 (w), 1188 (w), 1070 (m), 827 (m), 725 (w), 352 (w), 322 (m), 234 (w), 212 (w), 173 (m), 116 (m). HRMS (ESI) $m/z$: $M^+$ calcd for $C_5H_{11}FNO^+$, 120.0819; found, 120.0820. Anal. Calcd for $C_{11}H_{13}FN_4O_{10}S$: C, 32.04; H, 3.18; N, 13.59; S, 7.78. Found: C, 31.83; H, 3.03; N, 13.40; S, 7.71.

**Fluoromethyl-dimethylformamidinium-2,4,6-trinitrobenzenesulfonate (5c).** Reagent **4** (358 mg, 1.10 mmol) was dissolved in dichloromethane (5 mL), and dimethylformamide (80.5 mg, 1.10 mmol) was added. The yellowish solution was stirred for 24 h at room temperature. After the precipitate was centrifuged, the solvent was decanted and the crude product was washed with dichloromethane (3 × 5 mL). The remaining solid was dried *in vacuo*, yielding 359 mg of **5c** as a colorless solid. Yield: 82%. $T_{mp}$: 150 °C. $^1$H NMR ($CD_3CN$, 400 MHz): δ 8.58 (septet, 1H, $J$ = 0.9 Hz), 8.54 (s, 2H), 5.96 (d, 2H, $J$ = 49.2 Hz), 3.41 (s, 3H), 3.26 (s, 3H). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 101 MHz): δ 166.5, 150.8, 148.9, 138.9, 121.9, 104.6 (C−F, $^1J_{C-F}$ = 234.6 Hz), 43.1, 38.1. $^{19}F\{^1H\}$ NMR ($CD_3CN$, 376 MHz): δ −153.1 (s). $^{19}F$ NMR ($CD_3CN$, 376 MHz): δ −153.1 ($CH_2F$, $^2J_{F-H}$ = 49.2 Hz). $^{14}N\{^1H\}$ NMR ($CD_3CN$, 29 MHz): δ −14.9 (s, 2N), −22.7 (s, 1N), −230.9 (s, 1N). IR (ATR): $\tilde{\nu}$ 3095 (m), 3041 (w), 2997 (m), 2904 (w), 1723 (m), 1607 (m), 1542 (s), 1443 (w), 1403 (w), 1353 (s), 1314 (m), 1269 (s), 1236 (s), 1187 (w), 1164 (w), 1120 (m), 1056 (m), 1035 (m), 1004 (m), 991 (s), 937 (w), 924 (w), 912 (w), 902 (w), 844 (m), 825 (w), 749 (s), 732 (m), 718 (s), 632 (s). Raman: $\tilde{\nu}$ 3095 (w), 3039 (w), 3025 (w), 3972 (m), 1722 (w), 1602 (m), 1554 (w), 1431 (w), 1381 (m), 1358 (s), 1071 (m), 827 (m), 349 (w), 319 (w), 268 (m), 231 (m), 168 (w), 151 (m). Anal. Calcd for $C_{10}H_{11}FN_4O_{10}S$: C, 30.16; H, 2.78; N, 14.07; S, 8.05. Found: C, 30.01; H, 2.93; N, 14.23; S, 7.82.

**Ammonium-2,4,6-trinitrobenzenesulfonate (6a).** From the filtrate of the synthesis of **5a**, the solvent was slowly removed under reduced pressure, yielding 3.5 mg of colorless crystals. $T_{dec}$: 254.8 °C. $^1$H NMR ($CD_3CN$, 400 MHz): δ 8.54 (s, 2H), 5.96 (t, 4H, $J$ = 50.2 Hz). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 101 MHz): δ 121.8. $^{14}N\{^1H\}$ NMR ($CD_3CN$, 29 MHz): δ −15.2 (s, 2N), −22.4 (s, 1N), −360.1 (s, 1N). IR (ATR): $\tilde{\nu}$ 3462 (w), 3208 (s), 3072 (s), 2895 (w), 1842 (w), 1658 (w), 1600 (w), 1532 (s), 1415 (s), 1350 (s), 1249 (s), 1227 (s), 1120 (s), 1072 (s), 1032 (s), 983 (m), 936 (m), 918 (s), 827 (w), 749 (s), 733 (s), 714 (s), 663 (m), 633 (s), 559 (s), 520 (m), 479 (m), 454 (s), 435 (m). Raman: $\tilde{\nu}$ 3078 (w), 1602 (m), 1558 (m), 1544 (m), 1371 (s), 1353 (s), 1078 (s), 827 (s), 770 (s), 561 (w), 523 (w), 455 (w), 436 (m), 356 (m), 321 (w), 275 (w), 240 (w), 215 (w), 177 (m), 128 (m). HRMS (ESI) $m/z$: $M^+$ calcd for $C_6H_{10}N_5O_9S^+$, 328.0194; found, 328.0190.

**Dimethylammonium-2,4,6-trinitrobenzenesulfonate (6b).** From either of the filtrates obtained during the syntheses of **5b** or **5c**, the solvent was slowly removed under reduced pressure, yielding 2 or 13 mg, respectively, of colorless crystals. $T_{dec}$: 189 °C. $^1$H NMR ($CD_3CN$, 400 MHz): δ 8.57 (s, 2H), 6.62 (t, 2H, $J$ = 50.7 Hz), 2.65 (t, 6H, $J$ = 5.7 Hz). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 101 MHz): δ 150.8, 149.1, 138.6, 121.9, 36.1. $^{14}N\{^1H\}$ NMR ($CD_3CN$, 29 MHz): δ −15.5 (s, 2N), −22.9 (s, 1N), −358.9 (s, 1N). IR (ATR): $\tilde{\nu}$ 3159 (m), 3099 (m), 1665 (w), 1607 (m), 1541 (s), 1467 (m), 1354 (s), 1275 (m), 1223 (s), 1153 (m), 1122 (m), 1071 (m), 1034 (m), 984 (w), 926 (w), 911 (m), 901 (m), 883 (w), 823 (w), 749 (s), 732 (m), 719 (s). Raman: $\tilde{\nu}$ 3097 (w), 3051 (w), 2980 (m), 1604 (m), 1549 (m), 1533 (w), 1469 (w), 1370 (s), 1355 (s), 1189 (w), 1074 (s), 883 (w), 824 (m), 450 (w), 354 (m), 322 (m), 271 (m), 234 (s), 181 (s). HRMS (ESI) $m/z$: $M^+$ calcd for $C_{10}H_{18}N_5O_9S^+$, 384.0820; found, 384.0819.

**Dimethylammonium-$d_2$-2,4,6-trinitrobenzenesulfonate.** Dimethylacetamidinium-fluoromethyl-2,4,6-trinitrobenzenesulfonate (5 mg, 0.01 mmol) was introduced in an NMR tube under argon and dissolved in $D_2O$ (0.6 mL). The resulting solution was monitored by $^1$H NMR after 5 min. $^1$H NMR ($D_2O$, 400 MHz): δ 8.93 (s, 2H), 2.74 (quint, 6H, $J$ = 0.7 Hz).

**Dimethyl-2,4,6-trinitroaniline.** A solution of **4** (3.61 g, 11.1 mmol) in acetonitrile (10 mL) was added while stirring to a solution of dimethylamine (500 mg, 11.1 mmol) in acetonitrile (10 mL). The resulting deep red solution was stirred for 30 min at room temperature, and the formed solid was filtered off. The solvent was slowly removed from the filtrate *in vacuo*, yielding 2.10 g of yellowish crystals. Yield: 73%. $T_{mp}$: 138 °C (lit.[17] 138 °C). $T_{dec}$: 250 °C. $^1$H NMR ($CD_3CN$, 400 MHz): δ 8.69 (s, 2H), 2.90 (s, 6H). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 101 MHz): δ 144.1, 142.9, 137.4, 126.8, 43.1. $^{14}N\{^1H\}$ NMR ($CD_3CN$, 29 MHz): δ −14.2 (s, 2N), −20.1 (s, 1N). IR (ATR): $\tilde{\nu}$ 3062 (m), 2956 (w), 2924 (w), 2875 (w), 2819 (w), 1857 (w), 1603 (m), 1575 (s), 1530 (s), 1505 (s), 1473 (s), 1456 (s), 1428 (m), 1411 (m), 1376 (m), 1359 (m), 1325 (m), 1302 (s), 1235 (s), 1179 (m), 1170 (m), 1131 (w), 1086 (m), 1063 (m), 953 (m), 930 (s), 821 (m), 760 (m), 748 (s), 732 (s), 708 (m), 662 (w), 624 (w), 545 (m), 517 (m), 430 (w). Raman: $\tilde{\nu}$ 2956 (w), 1607 (w), 1542 (w), 1476 (w), 1447 (w), 1422 (w), 1343 (m), 1328 (s), 1180 (w), 1088 (w), 934 (w), 823 (w), 761 (w), 667 (w), 331 (w), 195 (w). HRMS (DEI) $m/z$: $M^+$ calcd for $C_8H_8N_4O_6$, 256.0444; found, 256.0444. Anal. Calcd for $C_8H_8N_4O_6$: C, 37.51; H, 3.15; N, 21.87. Found: C, 37.41; H, 3.26; N, 21.89.


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**Fluoromethylthio-triphenylphosphonium-2,4,6-trinitrobenzenesulfonate (7b).** Reagent **4** (54.0 mg, 166 μmol) was dissolved in dichloromethane (2 mL), and triphenylphosphine sulfide (49.0 mg, 166 μmol) was added in one portion. The mixture was stirred for 5 days at 40 °C (in an oil bath) in the dark. The solvent was removed *in vacuo*, and the resulting crude product was dissolved in dichloromethane (0.5 mL). Diethyl ether (5 mL) was added dropwise while the mixture was being stirred over a period of 15 min. The precipitate formed was centrifuged, and the solvent was decanted. This procedure was repeated three times to finally yield 80 mg of **7b** as a colorless solid. Yield: 78%. $T_{dec}$: 164 °C. $^{1}$H NMR ($CD_3CN$, 400 MHz): δ 8.52 (s, 2H), 7.92−7.97 (m, 3H), 7.83−7.87 (m, 4H), 7.75−7.81 (m, 8H), 5.72 (dd, 2H, $J$ = 49.0 Hz, $J$ = 20.3 Hz). $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 101 MHz): δ 150.9, 148.7, 137.8, 137.3 (C−P, $J_{C-P}$ = 3.3 Hz), 135.2 (C−P, $^{2}J_{C-P}$ = 11.6 Hz, C−F, $J_{C-F}$ = 0.8 Hz), 131.6 (C−P, $J_{C-P}$ = 13.9 Hz), 121.6, 118.9 (C−P, $^{1}J_{C-P}$ = 85.1 Hz, C−F, $^{4}J_{C-F}$ = 0.8 Hz), 84.5 (C−F, $^{1}J_{C-F}$ = 228.3 Hz, C−P, $^{2}J_{C-P}$ = 5.1 Hz). $^{19}$F{$^{1}$H} NMR ($CD_3CN$, 376 MHz): δ −186.5 (F−P, $^{3}J_{F-P}$ = 4.6 Hz). $^{19}$F NMR ($CD_3CN$, 376 MHz): δ −186.5 ($CH_2F$, $^{2}J_{F-H}$ = 49.0 Hz, F−P, $^{3}J_{F-P}$ = 4.6 Hz). $^{31}$P{$^{1}$H} NMR ($CD_3CN$, 162 MHz): δ 46.9 (P−F, $^{3}J_{C-P}$ = 4.6 Hz). $^{31}$P NMR ($CD_3CN$, 162 MHz): δ 46.9 (m). IR (ATR): $\tilde{\nu}$ 3109 (w), 3056 (w), 3015 (w), 2951 (w), 1607 (w), 1539 (s), 1485 (w), 1439 (m), 1398 (w), 1353 (m), 1244 (m), 1188 (w), 1107 (m), 1068 (m), 1024 (m), 996 (m), 926 (w), 899 (w), 825 (w), 747 (m), 721 (m), 686 (s), 630 (m), 569 (m), 507 (s), 449 (w). Anal. Calcd for $C_{25}H_{19}FN_3O_9PS_2$: C, 48.47; H, 3.09; N, 6.78; S, 10.35. Found: C, 47.17; H, 3.29; N, 6.54; S, 10.33 (formation of phosphorus carbide!).

**Fluoromethylseleno-triphenylphosphonium-2,4,6-trinitrobenzenesulfonate (7c).** Reagent **4** (125 mg, 0.384 mmol) and triphenylphosphine selenide (131 mg, 0.384 mmol) were dissolved in degassed dichloromethane (5 mL) and stirred for 1 day at 50 °C (in an oil bath). The solvent was slowly removed *in vacuo*, until a precipitate was formed. The remaining solvent was decanted, and the solid dried *in vacuo*. The crude brownish product was suspended in diethyl ether (4 mL) and centrifuged, and the solvent was decanted. This procedure was repeated three times. Finally, 169 mg of a beige solid was obtained. Yield: 66%. $T_{dec}$: 147 °C. $^{1}$H NMR ($CD_3CN$, 400 MHz): δ 8.52 (s, 2H), 7.86−7.95 (m, 3H), 7.65−7.83 (m, 12H), 5.94 (dd, 2H, $J$ = 48.7 Hz, $J$ = 17.1 Hz, $^{77}$Se-sats: $CH_2F$, $^{2}J_{H,Se}$ = 20.4 Hz). $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 101 MHz): δ 150.8, 148.8, 136.9 (C−P, $J_{C-P}$ = 3.3 Hz), 135.4 (C−P, $J_{C-P}$ = 11.7 Hz, C−F, $J_{C-F}$ = 0.8 Hz), 131.6 (C−P, $J_{C-P}$ = 13.8 Hz), 121.7, 119.3 (C−P, $^{1}J_{C-P}$ = 87.7 Hz, C−F, $^{4}J_{C-F}$ = 1.0 Hz), 83.2 (C−F, $^{1}J_{C-F}$ = 228.3 Hz, C−P, $^{2}J_{C-P}$ = 5.5 Hz). $^{19}$F{$^{1}$H} NMR ($CD_3CN$, 376 MHz): δ −190.2 (F−P, $^{3}J_{F-P}$ = 4.6 Hz, $^{77}$Se-sats: $CH_2F$, $^{2}J_{F-Se}$ = 100.9 Hz). $^{19}$F NMR ($CD_3CN$, 376 MHz): δ −190.2 ($CH_2F$, $^{2}J_{F-H}$ = 48.7 Hz, F−P, $^{3}J_{F-P}$ = 4.6 Hz, $^{77}$Se-sats: $CH_2F$, $^{2}J_{F-Se}$ = 100.9 Hz). $^{31}$P{$^{1}$H} NMR ($CD_3CN$, 162 MHz): δ 37.9 (P−F, $^{3}J_{P-F}$ = 4.6 Hz, $^{77}$Se-sats: $^{1}J_{P-Se}$ = 426.6 Hz). $^{31}$P NMR ($CD_3CN$, 162 MHz): δ 37.9 (m, $^{77}$Se-sats: $^{1}J_{P-Se}$ = 426.6 Hz). $^{77}$Se{$^{1}$H} NMR ($CD_3CN$, 76 MHz): δ 293.5 (Se−F, $^{2}J_{Se-F}$ = 100.9 Hz, Se−P, $^{1}J_{Se-P}$ = 426.6 Hz). IR (ATR): $\tilde{\nu}$ 3104 (w), 1604 (w), 1539 (w), 1439 (w), 1399 (w), 1399 (w), 1341 (w), 1241 (w), 1104 (w), 1068 (w), 1033 (w), 829 (w), 899 (w), 824 (w), 747 (w), 719 (w), 688 (w), 630 (w), 535 (w), 502 (w), 445 (w). Raman: $\tilde{\nu}$ 3059 (w), 1599 (w), 1548 (w), 1353 (m), 1185 (w), 1094 (w), 1068 (w), 1027 (w), 999 (w), 935 (w), 826 (w). Due to the high sensitivity to oxidation and hydrolysis, no HRMS and EA could be measured.

**4-[4-(Dimethylamino)benzoyl]-*N*-(fluoromethyl)-*N*,*N*-dimethylbenzeneaminium-2,4,6-trinitrobenzenesulfonate (8).** Michler's ketone was recrystallized (twice) from dichloromethane and purified by column chromatography (twice) before use. Reagent **4** (105 mg, 0.323 mmol) was dissolved in an acetonitrile/dichloromethane mixture (1:1, 5 mL), and the purified ketone (87.0 mg, 0.323 mmol), dissolved in an acetonitrile/dichloromethane mixture (1:1, 5 mL), was added in one portion. The reaction mixture was heated to reflux in an oil bath in the dark for 16 h. One-third of the solvent was removed *in vacuo*, until a green solid precipitated. The precipitate was filtered off and washed with chloroform (3 × 5 mL). The product was dried *in vacuo*, yielding 145 mg of **8** as a green solid. Yield: 76%. $T_{dec}$: 218 °C. $^{1}$H NMR ($CD_3CN$, 400 MHz): δ 8.52 (s, 2H), 7.87 (s, 4H), 7.71 (2H, X-part of AA′XX′, $N$ = 9.0 Hz, Ar−H), 6.82 (2H, A-part of AA′XX′, $N$ = 9.0 Hz), 5.65 (d, 2H, $J$ = 44.8 Hz), 3.65 (d, 6H, $J$ = 2.1 Hz), 3.08 (s, 6H). $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 101 MHz): δ 194.1, 155.2, 150.7, 149.1, 144.5, 142.8, 138.2, 133.7, 131.8, 123.8 (C−F, $J$ = 0.9 Hz), 122.3 (C−F, $J$ = 1.4 Hz), 122.1, 111.9, 99.8 (C−F, $^{1}J_{C-F}$ = 225.9 Hz), 51.9 (C−F, $^{3}J_{C-F}$ = 1.7 Hz), 40.4. $^{19}$F{$^{1}$H} NMR ($CD_3CN$, 376 MHz): δ −188.3 (s). $^{19}$F NMR ($CD_3CN$, 376 MHz): δ −188.3 ($CH_2F$, $^{2}J_{F-H}$ = 44.8 Hz). $^{1}$H−$^{15}$N HMBC. $^{15}$N NMR ($CD_3CN$, 29 MHz): δ −15.1 (s, 1N), −22.3 (s, 2N), −311.8 (s, 1N), −323.6 (s, 1N). IR (ATR): $\tilde{\nu}$ 3135 (w), 1643 (w), 1596 (s), 1550 (s), 1503 (s), 1475 (w), 1445 (w), 1351 (s), 1327 (s), 1290 (m), 1246 (s), 1192 (m), 1152 (m), 1117 (m), 1091 (m), 1067 (m), 1032 (m), 1001 (m), 978 (w), 930 (m), 907 (m), 849−813 (m), 769 (s), 748 (s), 721 (s), 688 (m), 631 (m), 593 (s), 559 (s), 513 (m). Raman: $\tilde{\nu}$ 3086 (w), 1641 (m), 1589 (s), 1555 (w), 1544 (w), 1371 (m), 1351 (m), 1154 (m), 1068 (m), 825 (m), 774 (w), 724 (w), 645 (w), 625 (w), 569 (w), 355 (w), 325 (w), 231 (w), 173 (w). HRMS (ESI) $m/z$: $M^+$ calcd for $C_{18}H_{22}FN_2O^+$, 301.1711; found, 301.1709. Anal. Calcd for $C_{24}H_{24}FN_5O_{10}S$: C, 48.57; H, 4.08; N, 11.80; S, 5.40. Found: C, 48.30; H, 4.36; N, 11.62; S, 5.49.

**1-(Fluoromethyl)-2-picolinoylpyridin-1-ium-2,4,6-trinitrobenzenesulfonate (9).** Reagent **4** (178 mg, 0.547 mmol) was dissolved in dichloromethane (12 mL), and bipyridyl ketone (101 mg, 0.547 mmol) dissolved in dichloromethane (3 mL) was added in one portion. The mixture was stirred for 24 h in the dark at room temperature. The precipitate was filtered off, washed with an acetonitrile/dichloromethane mixture (10:1, 5 × 3 mL), and dried *in vacuo*, yielding 217 mg of **9** as a colorless solid. Yield: 82%. $T_{mp}$: 184 °C. $T_{dec}$: 202 °C. $^{1}$H NMR ($CD_3CN$, 400 MHz): δ 9.10 (d, 1H, $J$ = 6.1 Hz), 8.83 (t, 1H, $J$ = 7.9 Hz,), 8.81−8.82 (m, 1H), 8.67 (m, 1H), 8.52 (s, 2H), 8.25−8.41 (m, 3H), 7.70−7.79 (m, 1H), 6.52 (d, 2H, $J$ = 46.0 Hz). $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 101 MHz): δ 187.4, 151.6 (C−F, $J_{C-F}$ = 0.8 Hz), 150.8, 150.1 (C−F, $J_{C-F}$ = 1.2 Hz), 147.2, 139.4, 130.9, 130.7, 130.5, 125.9, 121.7, 94.8 (C−F, $^{1}J_{C-F}$ = 215.0 Hz). $^{19}$F{$^{1}$H} NMR ($CD_3CN$, 376 MHz): δ −174.7 (s). $^{19}$F NMR ($CD_3CN$, 376 MHz): δ −174.7 ($CH_2F$, $^{2}J_{F-H}$ = 46.8 Hz). $^{1}$H−$^{15}$N HMBC. $^{15}$N NMR ($CD_3CN$, 29 MHz): δ −15.2 (s, 1N), −22.4 (s, 2N). IR (ATR): $\tilde{\nu}$ 3108 (m), 3086 (s), 1700 (s), 1622−1605 (w), 1557 (s), 1534 (s), 1480 (s), 1443 (m), 1354 (s), 1333−1289 (w), 1241 (s), 1179 (m), 1126 (m), 1095 (s), 1068 (s), 1034 (s), 995 (w), 946 (m), 834 (m), 814 (m), 785 (m), 752−702 (s), 656 (m), 633 (s), 614 (s), 559 (s), 527 (s), 479 (w), 442, 405 (w). Raman: $\tilde{\nu}$ 3106 (w), 3057 (w), 1700 (m), 1603 (m), 1584 (m), 1570 (m), 1387 (m), 1349 (s), 1197 (w), 1071 (m), 1046 (m), 995 (m), 826 (m), 350 (m), 319 (w), 266 (w), 228 (w), 170 (m), 152 (m). HRMS (DEI) $m/z$: $M^+$ calcd for $C_{12}H_{10}FN_2O^+$, 217.0772; found, 217.0781. Anal. Calcd for $C_{18}H_{12}FN_5O_{10}S$: C, 42.44; H, 2.37; N, 13.75; S, 6.29. Found: C, 42.11; H, 2.40; N, 13.75; S, 6.16.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02670.

NMR spectra, X-ray structures, and DSC data (PDF)

### Accession Codes

CCDC 2025108−2025112 and 2025114−2025117 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



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