Supporting Information

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Materials and Methods

General: ^{1}H-NMR spectra: Bruker Avance II 300 (300 MHz) and Bruker Avance II+ 600 (600 MHz). ^{1}H chemical shifts are reported in ppm relative to residual peaks of deuterated solvents. Higher-order NMR spectra were approximately interpreted as first-order spectra, where possible. The observed signal multiplicities are characterized as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, and br = broad. Coupling constants (*J*) were reported in Hertz (Hz). ^{13}C-NMR spectra [additional APT (Attached Proton Test)]: Bruker Avance II 300 (75.5 MHz) and Bruker Avance II+ 600 (125.9 MHz). ^{13}C chemical shifts are reported relative to residual peaks of deuterated solvents. Low resolution ESI-MS: Finnigan LCQ. High resolution ESI-MS: Bruker APEX IV 7T FTICR MS. TLC: Merck precoated sheets, 0.25 mm Sil G/UV$_{254}$. The chromatograms were viewed under UV light and/or by treatment with phosphomolybdic acid (10% in ethanol). Column chromatography: Merck silica gel, grade 60, 230–400 mesh. Solvent proportions are indicated in a volume:volume ratio. All reactions were carried out with magnetic

stirring unless otherwise stated and, in the case of air- or moisture-sensitive substrates and/or reagents, were handled in flame-dried glassware under argon or nitrogen. Organic extracts were dried with anhydrous $MgSO_4$. 2-Formyl-*N*,*N*,*N*-trimethylanilinium triflate,[1] 4-formyl-*N*,*N*,*N*-trimethylanilinium triflate,[1] 4-formyl-*N*,*N*,*N*-trimethylanilinium iodide,[2] 3-formyl-*N*,*N*,*N*-trimethylanilinium iodide,[2] HCl·H-βAla-Phe-OMe,[3] TFA·H-βAla-Phe-OMe,[3] (4-carboxyphenyl)(4-methoxyphenyl)iodonium tosylate,[4] 1-*O*-methyl-2,3-*O*-isopropylidene-D-ribofuranoside (**9**),[5] and 1-*O*-methyl-2,3-*O*-isopropylidene-5-*O*-toluenesulfonyl-D-ribofuranoside (**12**)[6] and $Ag(PPh_3)_2HCO_3$[7] were prepared according to the literature.

HPLC analyses and purifications were carried out on Dionex Ultimate 3000 System with Ultimate 3000 Diode Array Detector coupled in series with Berthold NaI detector. Unless otherwise stated, a Chromolith® SpeedROD RP-18e column (Merck, Darmstadt Germany), 50×4.6 mm, was used for analyses and purifications of radiofluorinated products. Aqueous MeCN solutions were used as a mobile phase. StrataX (RP polymeric phase) cartridges were obtained from Phenomenex (Aschaffenburg, Germany),* Sep-Pak Accell Plus QMA carbonate plus light cartridges,** 40 mg sorbent per cartridge from Waters GmbH (Eschborn, Germany) and Chromafix® 30-PS-HCO_3 cartridges from Macherey-Nagel (Düren, Germany).** ^{18}F-labeled compounds were identified by spiking of the reaction mixture with ^{19}F-reference substances.

[^{18}F]Fluoride was produced via the $^{18}O(p,n)^{18}F$ reaction by bombardment of enriched [^{18}O]water with 16.5 MeV protons using a MC16 cyclotron (Scanditronix, Uppsala, Sweden). All isolated radiochemical yields are not decay-corrected. Unless otherwise indicated, all radiochemical experiments were carried out at least in triplicates.

* Preconditioned with 1 mL EtOH followed by 10 mL H_2O.
** Preconditioned with 1 mL H_2O

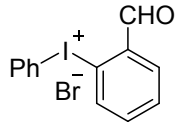
Chemistry

Preparation of (formylphenyl)(phenyl)iodonium bromides. General procedure 1 – (GP1): $BF_3 \cdot Et_2O$ (4.5 mmol) was added dropwise to an ice-cold solution of the appropriate formylphenylboronic acid (3.0 mmol) in anhydrous CH_2Cl_2 (15 mL) under Ar and the resulting mixture was stirred for 10 min. Thereafter, bis(acetoxy)iodobenzene (3.0 mmol) was added, the cooling bath was removed and the mixture was stirred for a further hour. The solvent was removed under reduced pressure. The rest was taken in CH_2Cl_2 (25 mL) and stirred vigorously with saturated NaBr (15 mL) for 15 min. Thereafter, CH_2Cl_2-insoluble (3- and 4-formylphenyl)(phenyl)iodonium bromides were filtered off, washed with H_2O (20 mL), MeCN (2×50 mL), Et_2O (2×50 mL) and dried. In the case of the more soluble (2-formylphenyl)(phenyl)iodonium bromide, the organic layer was repeatedly treated with saturated NaBr (4×15 mL), dried, filtered and concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2/Et_2O to give the desired iodonium salt.

Preparation of diaryliodonium and *N*,*N*,*N*-trimethylanilinium triflates, perchlorates and hydrogen carbonates using reaction of the corresponding bromides or iodides with the appropriate silver salts. General procedure 2 – (GP2): To prepare the corresponding triflate the appropriate bromide or iodide (0.5 mmol) was dissolved in MeOH (12 mL) and treated with AgOTf, $AgClO_4$ or $Ag(PPh_3)_2HCO_3$ (0.5 mmol). After vigorous shaking of the mixture for 2 min [or 1 h in the case of $Ag(PPh_3)_2HCO_3$] while shielded from light, the precipitate of silver halide was centrifuged off (4000 rpm, 10 min). The supernatant was concentrated under reduced pressure and the residue was recrystallized from CH_2Cl_2/Et_2O or acetone/Et_2O to give the desired salt. Diaryliodonium bicarbonate salts could not be prepared. In the case of *N*,*N*,*N*-trimethylanilinium bicarbonate salts incomplete anionic exchange was observed owing to the low solubility of

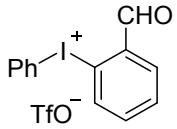
$Ag(PPh_3)_2HCO_3$ in MeOH. In this case the supernatant was used or radiochemical experiments. Solutions of 3- and 4-substituted *N*,*N*,*N*-trimethylanilinium bicarbonates could be stored at –80 °C for at least 4 weeks. 2-Formyl-*N*,*N*,*N*-trimethylanilinium bicarbonate was prepared directly before each experiment.

(2-Formylphenyl)(phenyl)iodonium bromide: The title compound (0.53 g, 54%) was obtained as



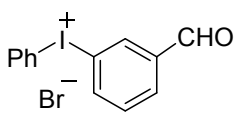
an off-white solid according to GP1 from 2-formylphenyl boronic acid (0.38 g, 2.53 mmol), $BF_3{\cdot}Et_2O$ (0.46 mL, 0.52 g, 3.66 mmol) and bis(acetoxy)iodobenzene (0.86 g, 2.53 mmol). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.58 (t, *J* = 7.6 Hz, 3 H), 7.55–7.75 (m, 2 H), 7.80–7.88 (m, 1 H), 8.20–8.32 (m, 3 H), 10.25 (s, 1 H); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 115.9, 118.8, 131.5, 131.8, 132.2, 132.6, 133.6, 136.2, 136.4, 137.5, 194.4. MS (ESI): positive mode *m/z* = 341.0 ($[M + MeOH]^+$), 309.0 ($[M + H]^+$); ESI HRMS: calcd for $C_{13}H_{10}OI^+$: 308.9771; found: 308.9779.

(2-Formylphenyl)(phenyl)iodonium triflate: The title compound (0.26 g, 74%) was obtained as a



colorless solid according to GP2 from (2-formylphenyl)(phenyl)iodonium bromide (0.3 g, 0.77 mmol) and AgOTf (198 mg, 0.77 mmol). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.39 (d, *J* = 7.9 Hz, 1 H), 7.55–7.75 (m, 2 H), 7.75–7.96 (m, 3 H), 8.31 (d, *J* = 7.5 Hz, 2 H), 8.38 (dd, *J* = 7.5, 1.6 Hz, 1 H), 10.29 (s, 1 H); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 111.1, 111.9, 113.0, 128.7 (q, *J* = 128.1 Hz), 131.9, 132.28, 132.30, 133.2, 137.1, 137.6, 138.1, 194.8. MS (ESI): positive mode *m/z* = 341.0 ($[M + MeOH]^+$), 309.0 ($[M + H]^+$); MS (ESI): negative mode *m/z* = 149.0 ($[CF_3SO_2]^-$); ESI HRMS: calcd for $C_{14}H_{14}O_2I^+$: 341.0033; found: 341.0024; calcd for $C_{13}H_{10}OI^+$: 308.9771; found: 308.9772

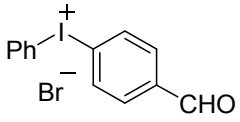
(3-Formylphenyl)(phenyl)iodonium bromide:[8] The title compound (1.23 g, 63%) was obtained as



a colorless solid according to GP1 from 3-formylphenyl boronic acid (0.75 g, 5 mmol), $BF_3{\cdot}Et_2O$ (1 mL, 1.07 g, 7.55 mmol) and bis(acetoxy)iodobenzene

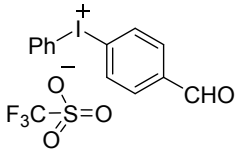
(1.61 g, 5 mmol). ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 7.42–7.50 (m, 2 H), 7.55–7.62 (m, 1 H), 7.69 (t, *J* = 7.8 Hz, 1 H), 8.10 (dt, *J* = 7.7, 1.2 Hz, 2 H), 8.23 (dd, *J* = 8.3, 1.1 Hz, 1 H), 8.46–8.50 (m, 1 H), 8.67 (t, *J* = 1.4 Hz, 1 H), 9.98 (s, 1 H).

(4-Formylphenyl)(phenyl)iodonium bromide: The title compound (0.89 g, 71%) was obtained as



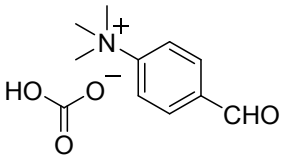
an off-white solid according to GP1 from 4-formylphenyl boronic acid (0.48 g, 3.2 mmol), $BF_3{\cdot}Et_2O$ (0.8 mL, 0.89 g, 6.32 mmol) and bis(acetoxy)iodobenzene (1.03 g, 3.2 mmol). ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 7.35–7.52 (m, 2 H), 7.55–7.65 (m, 1 H), 7.93 (d, *J* = 8.3 Hz, 2 H), 8.21 (d, *J* = 7.4 Hz, 2 H), 8.39 (d, *J* = 8.3 Hz, 2 H), 10.00 (s, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 120.77, 126.88, 131.99 (×2), 132.0, 135.5, 136.0, 137.9, 193.0. MS (ESI): positive mode *m/z* = 341.0 ([M + MeOH]$^+$), 309.0 ([M + H]$^+$); ESI HRMS: calcd for $C_{14}H_{14}O_2I^+$: 341.0033; found: 341.0035; calcd for $C_{13}H_{10}OI^+$: 308.9771; found: 308.9773.

(4-Formylphenyl)(phenyl)iodonium triflate: The title compound (0.58 g, 74%) was obtained as a



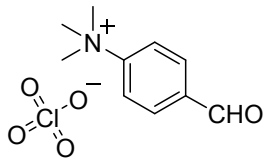
beige solid according to GP2 from (4-formylphenyl)(phenyl)iodonium bromide (0.814 g, 2.09 mmol) and AgOTf (0.538 g, 2.09 mmol). ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 7.49–7.60 (m, 2 H), 7.63–7.75 (m, 1 H), 8.00 (d, *J* = 8.3 Hz, 2 H), 8.29 (d, *J* = 7.4 Hz, 2 H), 8.45 (d, *J* = 8.3 Hz, 2 H), 10.02 (s, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 116.6, 122.2, 131.9 (×2), 132.5, 135.5, 135.8, 137.9, 192.5. MS (ESI): positive mode *m/z* = 341.0 ([M + MeOH]$^+$), 309.0 ([M + H]$^+$); MS (ESI): negative mode *m/z* = 149.0 ([CF_3SO_3]$^-$); ESI HRMS: calcd for $C_{14}H_{14}O_2I^+$: 341.0033; found: 341.0041; calcd for $C_{13}H_{10}OI^+$: 308.9771; found: 308.9777.

4-Formyl-*N*,*N*,*N*-anilinium bicarbonate: The title compound was prepared according to GP2 from



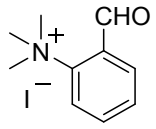
4-formyl-*N*,*N*,*N*-anilinium iodide (0.24 g, 0.82 mmol) and $Ag(PPh_3)_2HCO_3$ (0.572 g, 0.82 mmol) in MeOH (12 mL). The supernatant was used directly for radiolabeling experiments.

4-Formyl-*N*,*N*,*N*-anilinium perchlorate: The title compound was prepared according to GP2 from



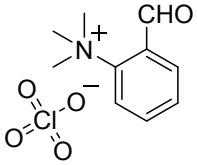
4-formyl-*N*,*N*,*N*-anilinium iodide (0.24 g, 0.82 mmol) and $AgClO_4$ (0.170 g, 0.82 mmol) in MeOH (12 mL). The supernatant was directly used for radiolabeling experiments.

2-Formyl-*N*,*N*,*N*-anilinium iodide:[2] NaI (0.23 g, 1.53 mol) was added to a stirred solution of 2-



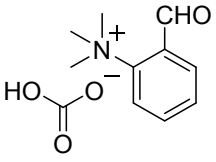
formyl-*N*,*N*,*N*-anilinium triflate[1] (0.48 g, 1.53 mmol) in acetone (10 mL). After 10 min stirring the precipitate was filtered off, washed with acetone and dried to give the title compound (0.35 g, 78%) as a colorless solid. The spectral data were in accordance with those reported in the literature.[2]

2-Formyl-*N*,*N*,*N*-anilinium perchlorate: $LiClO_4$ (0.13 g, 1.22 mmol) was added to a stirred



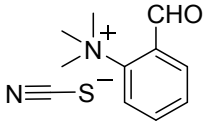
solution of 2-formyl-*N*,*N*,*N*-anilinium triflate[1] (0.38 g, 1.22 mmol) in acetone (20 mL). After 15 min stirring Et_2O (5 mL) was added and the precipitate was filtered off, washed with acetone/Et_2O and dried to give the title compound (0.23 g, 72%) as a colorless solid. ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 3.76 (s, 9 H), 7.87–8.03 (m, 2 H), 8.05–8.12 (m, 1 H), 8.27–8.40 (m, 1 H), 10.2 (s, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 56.7, 122.4, 129.5, 131.2, 135.8, 140.1, 144.2, 193.1. MS (ESI): positive mode *m/z* = 196.1 ([M + MeOH]$^+$), 164.1 ([M + H]$^+$); MS (ESI): negative mode *m/z* = 98.9 ([ClO_4]$^-$); ESI HRMS: calcd for $C_{11}H_{18}O_2N^+$: 196.1332.

2-Formyl-*N*,*N*,*N*-anilinium bicarbonate: The title compound was prepared according to GP2 from



2-formyl-*N*,*N*,*N*-anilinium iodide (0.12 g, 0.41 mmol) and $Ag(PPh_3)_2HCO_3$ (0.29 g, 0.42 mmol) in MeOH (6 mL). The supernatant was used directly for radiolabeling experiments.

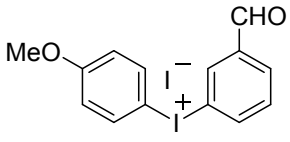
2-Formyl-*N*,*N*,*N*-anilinium thiocyanate: NaCNS (52 mg, 0.64 mmol) was added to a stirred



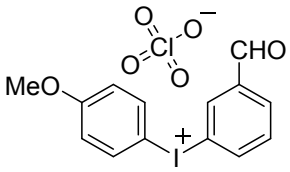
solution of 2-formyl-*N*,*N*,*N*-anilinium triflate[1] (0.2 g, 0.64 mmol) in acetone (10 mL). After 15 min stirring the reaction mixture was concentrated under

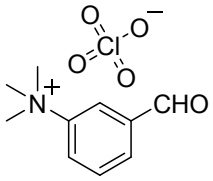
reduced pressure. The residue was recrystallized from acetone/Et_2O to give the title compound (0.23 g, 72%) as a colorless solid. ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 3.77 (s, 9 H), 7.81–7.95 (m, 2 H), 8.05–8.17 (m, 1 H), 8.32 (dd, *J* = 6.8, 1.5 Hz, 1 H), 10.2 (s, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 56.7, 122.5, 129.5, 131.2, 135.8, 140.2, 144.2, 193.1 (the signal of the thiocyanate carbon could not be observed). MS (ESI): positive mode *m/z* = 196.1 ([M + MeOH]$^+$), 164.1 ([M + H]$^+$); ESI HRMS: calcd for $C_{11}H_{18}O_2N^+$: 196.1332; found: 196.1335; calcd for $C_{13}H_{10}OI^+$: 164.1070; found: 164.1076.

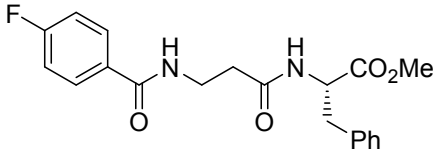
(3-Formylphenyl)(4-methoxyphenyl)iodonium iodide: Tos·H_2O (1.43 g, 7.50 mmol) was added



to a solution of 3-iodobenzaldehyde (1.16 g, 5.0 mmol), 3-chloroperoxybenzoic acid (1.29 g, 7.5 mmol, 89% purity) and anisol (0.85 g, 0.86 mL, 7.91 mmol) in CH_2Cl_2/2,2,2-trifluoroethanol 1:1 (25 mL) and the mixture was stirred for 3 days. The resulting suspension was concentrated under reduced pressure and the residue was triturated with Et_2O. The crude product was recrystallized from CH_2Cl_2/Et_2O to give known (3-formylphenyl)(4-methoxyphenyl)iodonium tosylate[9] (1.75 g, 69%) as a colorless solid. The latter was taken up in CH_2Cl_2 (40 mL) and the resulting solution was stirred vigorously with saturated NaI (4×20 mL). The precipitate was filtered off, washed with CH_2Cl_2 (30 mL), water (15 mL), acetone (15 mL), acetone/Et2O 1:1 (100 mL) and dried to give the title compound as a yellow solid. The CH_2Cl_2 washings were dried and concentrated under reduced pressure. The residue was recrystallized from acetone/Et_2O to give a second crop of product (total yield 1.07 g, 46% in two steps). ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 3.79 (s, 3 H), 7.02–7.08 (m, 2 H), 7.71 (t, *J* = 7.9 Hz, 1 H), 8.10–8.21 (m, 3 H), 8.44 (dt, *J* = 7.9, 1.2 Hz, 1 H), 8.65 (t, *J* = 1.2 Hz, 1 H), 9.99 (s, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 55.6, 106.6, 117.3, 118.8, 132.0, 132.5, 134.4, 137.1, 138.1, 139.7, 161.8, 191.4. MS (ESI): positive mode *m/z* = 371.0 ([M + MeOH]$^+$), 339.0 ([M + H]$^+$); MS (ESI): negative mode *m/z* = 126.9 ([I]$^-$); ESI HRMS: calcd for $C_{14}H_{12}O_2N^+$: 338.9876; found: 338.9878.

(3-Formylphenyl)(4-methoxyphenyl)iodonium perchlorate: The title compound was prepared  according to GP2 from (3-formylphenyl)(4-methoxyphenyl)iodonium iodide (0.12 g, 0.257 mmol) and $AgClO_4$ (50 mg, 0.245 mmol) in MeOH (12 mL). The supernatant was used directly for radiolabeling experiments.

3-Formyl-*N*,*N*,*N*-anilinium perchlorate: The title compound was prepared according to GP2 from  3-formyl-*N*,*N*,*N*-anilinium iodide[2] (0.11 g, 0.38 mmol) and $AgClO_4$ (74 mg, 0.36 mmol) in MeOH (9 mL). The supernatant was used directly for radiolabeling experiments.

4-Fluorobenzoyl-βAla-Phe-OMe (1): DIEA (0.27 mL, 0.198 g, 1.53 mmol) was added to a stirred  solution of HCl·H-βAla-Phe-OMe (0.22 g, 0.77 mmol) and 4-fluorobenzoyl chloride (90 µL, 0.12 g, 0.77 mmol) in CH_2Cl_2 (10 mL) and stirring was continued for 1 h. The mixture was concentrated under reduced pressure, the residue was taken up in EtOAc/H_2O (50 mL each), the organic layer was separated and washed with 1 N HCl (3×15 mL), H_2O (2×15 mL), 5% $NaHCO_3$ (3×15 mL), brine (2×15 mL), dried and concentrated under reduced pressure. The residue was recrystallized from EtOAc/hexane to give the title compound (0.26 g, 91%) as a colorless solid. R_f = 0.55, acetone:hexane = 1:1. ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 2.49 (t, *J* = 5.6 Hz, 2 H), 3.05 (dd, *J* = 13.9, 6.6 Hz, 1 H), 3.15 (dd, *J* = 13.9, 5.6 Hz, 1 H) 3.59–3.67 (m, 1 H), 3.69–3.76 (m, 1 H), 3.72 (s, 3 H), 4.83–4.88 (m, 1 H), 6.29 (d, *J* = 7.7 Hz, 1 H), 7.06–7.11 (m, 4 H), 7.16–7.25 (m, 4 H), 7.75–7.80 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): δ = 35.3, 36.0, 37.7, 52.5, 53.3, 115.5 (d, *J* = 22.6 Hz), 127.3, 128.7, 129.1, 129.4 (d, *J* = 7.5 Hz), 130.5 (d, *J* = 3.0 Hz), 135.7, 165.1 (d, *J* = 365.2 Hz), 165.6, 171.7, 172.0. MS (ESI): positive mode *m/z* = 1057.4 ([2 M + Na]$^+$), 1035.4 ([2 M + H]$^+$), 540.2 ([M + Na]$^+$), 518.2 ([M + H]$^+$); MS (ESI): negative mode *m/z* = 630.2 ([M + 2 HCOOH – H]$^-$), 516.2 ([M – H]$^-$); ESI HRMS: calcd for

$C_{29}H_{28}FN_3O_5Na^+$: 540.1905; found: 540.1907; calcd for $C_{29}H_{29}FN_3O_5^+$: 518.2086; found: 518.2085; calcd for $C_{29}H_{27}FN_3O_5^-$: 516.1940; found: 516.1933.

4-*N*,*N*-Dimethylaminobenzoyl-βAla-Phe-OMe: 4-*N*,*N*-Dimethylaminobenzoyl chloride (0.44 g, 2.42 mmol) was added to a stirred solution of HCl·H-βAla-Phe-OMe (0.69 g, 2.42 mmol) and DIEA (0.843 mL, 0.63 g, 4.84 mmol) in CH_2Cl_2 (10 mL) and stirring was continued for a further hour. Thereafter, 4-*N*,*N*-dimethylaminobenzoyl chloride (0.15 g, 2.42 mmol) was added and the reaction mixture was stirred for a further 1 h. The mixture was concentrated under reduced pressure, the residue was taken up in EtOAc/5% $NaHCO_3$ (50 mL each), the organic layer was separated and washed with H_2O (2×15 mL), 5% $NaHCO_3$ (3×15 mL), brine (2×15 mL), dried and concentrated under reduced pressure. The residue was recrystallized from Et_2O/hexane to give the title compound (0.64 g, 67%) as a colorless solid. R_f = 0.33, acetone:hexane = 1:1. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.48 (t, *J* = 5.8 Hz, 2 H), 3.03 (s, 6 H), 3.05 (dd, *J* = 14.0, 6.7 Hz, 1 H), 3.15 (dd, *J* = 14.0, 5.8 Hz, 1 H), 3.62–3.73 (m, 2 H), 3.71 (s, 3 H), 4.86 (q, *J* = 7.3 Hz, 1 H), 6.30 (d, *J* = 7.7 Hz, 1 H), 6.67 (d, *J* = 8.9 Hz, 2 H), 6.86–6.91 (br, 1 H), 7.05–7.10 (m, 2 H), 7.16–7.23 (m, 3 H), 7.66–7.70 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 35.7, 36.8, 37.7 40.1, 52.3, 53.2, 111.1, 121.8, 127.1, 128.5, 128.6, 129.1; 135.7, 152.4, 167.4, 171.7, 171.9. MS (ESI): positive mode *m/z* = 817.4 ([2 M + Na]$^+$), 795.4 ([2 M + H]$^+$), 420.2 ([M + Na]$^+$), 398.2 ([M + H]$^+$); MS (ESI): negative mode *m/z* = 396.2 ([M – H]$^-$); ESI HRMS: calcd for $C_{22}H_{27}N_3O_4Na^+$: 420.1894; found: 420.1887; calcd for $C_{22}H_{28}N_3O_4^+$: 398.2074; found: 398.2072; calcd for $C_{22}H_{26}N_3O_4^-$: 396.1929; found: 396.1919.

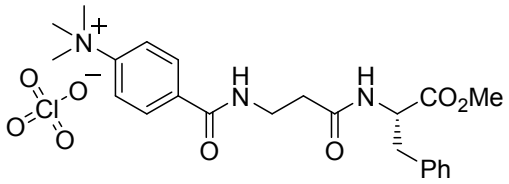
4-*N*,*N*,*N*-Trimethylammoniumbenzoyl-βAla-Phe-OMe iodide: Methyl iodide (0.28 mL, 0.64 g, 4.53 mmol) was added to a solution of 4-*N*,*N*-dimethylaminobenzoyl-βAla-Phe-OMe (0.6 g, 1.51 mmol) in acetone (10 mL) and the mixture was stirred under reflux for 16 h. Thereafter, the precipitate was

filtered off, washed with acetone (30 mL) and dried to give the title compound (0.63 g, 81%) as a colorless solid. ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ = 2.35–2.47 (m, 2 H), 2.88 (dd, *J* = 13.6, 9.1 Hz, 1 H), 3.01 (dd, *J* = 8.3, 5.5 Hz, 1 H), 3.41 (q, *J* = 6.7 Hz, 2 H), 3.58 (s, 3 H), 3.64 (s, 9 H), 4.42–4.54 (m, 1 H), 7.12–7.27 (m, 5 H), 8.05 (q, *J* = 10.2 Hz, 4 H), 8.43 (d, *J* = 7.9 Hz, 1 H), 8.67 (d, *J* = 5.5 Hz, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 34.7, 35.9, 36.6, 51.8, 53.5, 56.4, 120.7, 126.5, 128.2, 128.7, 128.9, 135.6, 137.2, 148.9, 164.4, 170.4, 172.0. MS (ESI): positive mode *m/z* = 412.2 ($[M]^+$); MS (ESI): negative mode *m/z* = 538.1 ($[M + I–H]^-$), 126.9 ($[I]^-$); ESI HRMS: calcd for $C_{23}H_{30}N_3O_4^+$: 412.2231; found: 412.2234; calcd for $C_{23}H_{30}N_3O_4I^-$: 538.1208; found: 538.1215.

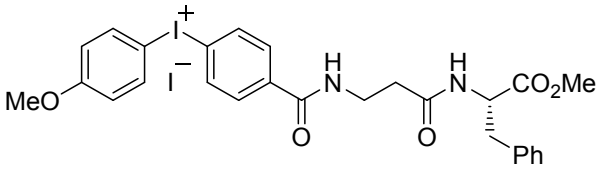
4-*N*,*N*,*N*-Trimethylammoniumbenzoyl-βAla-Phe-OMe triflate: The title compound (0.19 g, 95%) was obtained as a colorless solid according to GP2 from 4-*N*,*N*,*N*-trimethylammoniumbenzoyl-βAla-Phe-OMe iodide (0.2 g, 0.37 mmol) and AgOTf (95 mg, 0.37 mmol). ^{1}H-NMR [$(CD_3)_2SO$, 300 MHz]: δ= 2.31–2.47 (m, 2 H), 2.82–2.94 (m, 1 H), 3.01–3.08 (m, 1 H), 3.35–3.47 (m, 2 H), 3.58 (s, 3 H), 3.63 (s, 9 H), 4.47–4.53 (m, 1 H), 7.16–7.27 (m, 5 H), 7.99–8.10 (m, 4 H), 8.43 (d, *J* = 7.7 Hz, 1 H), 8.67 (t, *J* = 5.2 Hz, 1 H); ^{19}F-NMR [$(CD_3)_2SO$, 282.4 MHz]: δ= –77.74; ^{13}C-NMR [$(CD_3)_2SO$, 75.5 MHz]: δ = 34.7, 36.0, 36.7, 51.8, 53.5, 56.4, 120.6, 126.5, 128.2, 128.7, 129.0, 135.7, 137.2, 149.0, 164.4, 170.4, 172.0.

4-*N*,*N*,*N*-Trimethylammoniumbenzoyl-βAla-Phe-OMe bicarbonate: The title compound was prepared according to GP2 from 4-*N*,*N*,*N*-trimethylammoniumbenzoyl-βAla-Phe-OMe iodide (0.12 g, 0.22 mmol) and $Ag(PPh_3)_2HCO_3$ (0.154 g, 0.22 mmol) in MeOH (10 mL). The supernatant was used directly for radiolabeling experiments.

4-*N*,*N*,*N*-Trimethylammoniumbenzoyl-βAla-Phe-OMe perchlorate: The title compound was prepared according to GP2 from 4-*N*,*N*,*N*-trimethyl-ammoniumbenzoyl-βAla-Phe-OMe iodide (0.105 g, 0.19 mmol) and $AgClO_4$ (40 mg, 0.22 mmol) in MeOH (8.8 mL). The supernatant was used directly for radiolabeling experiments.

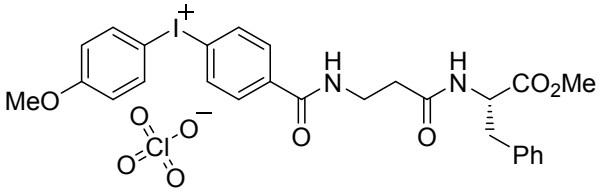


4-(4-Methoxyphenyliodonium)benzoyl-βAla-Phe-OMe iodide: TFA·H-βAla-Phe-OMe[3] prepared from Boc-βAla-Phe-OMe (0.3 g, 0.86 mmol) was taken up in toluene (25 mL) and the mixture was concentrated under reduced pressure to remove the traces of TFA (×3). The residue was dissolved in DMF (10 mL) under Ar, HOBt (12 mg, 0.089 mmol) and (4-carboxyphenyl)(4-methoxyphenyl)-iodonium tosylate (0.45 g, 0.85 mmol) were added and the heterogeneous mixture was cooled in an ice-water bath. DCC (0.176 g, 0.86 mmol) and thereafter 2,4,6-trimethylpyridine (0.23 mL, 0.21 g, 1.74 mmol) were added to the stirred reaction mixture. The cooling bath was removed and the mixture was stirred for a further 6 h. Afterwards, the reaction mixture was incubated at 4 °C for 16 h, DCU was filtered off and DMF was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and filtered. CH_2Cl_2 (20 mL) followed by saturated NaI (10 mL) were added and the mixture was stirred vigorously for 10 min. The resulting gel was centrifuged (4000 rpm, 15 min, 10 °C), the aqueous fraction was discarded, the pellet was resuspended in CH_2Cl_2 fraction, saturated NaI (10 mL) was added and the mixture was shaken vigorously for 10 min. The reaction mixture was centrifuged (4000 rpm, 15 min, 10 °C), the pellet was washed with CH_2Cl_2 (4×10 mL), H_2O (3×10 mL) and Et_2O (3×10 mL) (each time the pellet was suspended in the corresponding solvent, the suspension was centrifuged, the supernatant was discarded and the pellet was resuspended). Thereafter, the precipitate was triturated with acetone, filtered off and washed with acetone (30 mL) to give the title compound (0.31 g, 51%) as a colorless solid. ^{1}H-NMR [$(CD_3)_2SO$, 600 MHz]: δ=

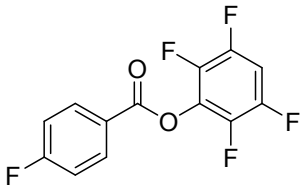


2.36 (dq, *J* = 18.0, 7.4 Hz, 2 H), 2.87 (dd, *J* = 13.8, 9.3 Hz, 1 H), 3.00 (dd, *J* = 13.8, 5.6 Hz, 1 H), 3.36–3.47 (m, 2 H), 3.55 (s, 3 H), 3.78 (s, 3 H), 4.47 (td, *J* = 8.4, 5.6 Hz, 1 H), 7.04 (d, *J* = 9.1 Hz, 2 H), 7.08–7.13 (m, 1 H), 7.15–7.20 (m, 4 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 8.15 (d, *J* = 9.2 Hz, 2 H), 8.26 (d, *J* = 8.4 Hz, 2 H), 8.38 (d, *J* = 7.7 Hz, 1 H), 8.56 (t, *J* = 5.4 Hz, 1 H); ^{13}C-NMR [$(CD_3)_2SO$, 150.9 MHz]: δ = 34.6, 35.9, 36.6, 51.8, 53.4, 55.7, 117.3, 121.0, 126.4, 128.1, 128.9, 129.8, 134.6, 137.1, 137.2, 150.9, 161.8, 164.9, 169.7, 170.3, 172.0. MS (ESI): positive mode *m/z* = 587.1 ($[M]^+$); MS (ESI): negative mode *m/z* = 126.9 ($[I]^-$); ESI HRMS: calcd for $C_{27}H_{28}N_2O_5I^+$: 587.1037; found: 587.1038.

4-(4-Methoxyphenyliodonium)benzoyl-βAla-Phe-OMe perchlorate: The title compound was prepared according to GP2 from 4-(4-methoxyphenyliodonium)benzoyl-βAla-Phe-OMe iodide (0.126 g, 0.18 mmol) and $AgClO_4$ (36.6 mg, 0.18 mmol) in MeOH (10.5 mL). The supernatant was used directly for radiolabeling experiments.

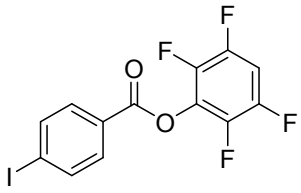


2,3,5,6-Tetraphenyl 4-fluorobenzoate (2): Et_3N (0.54 mL, 0.39 g, 3.87 mmol) was added dropwise to a vigorously stirred solution of 4-fluorobenzoyl chloride (0.46 mL, 0.61 g, 3.87 mmol) and 2,3,5,6-tetrafluorophenol (0.64 g, 3.87 mmol) in Et_2O (30 mL) and the stirring was continued for a further 10 min. The reaction mixture was filtered, washed with H_2O (15 mL) and brine (2×10 mL), dried and concentrated under reduced pressure. The residue was recrystallized from hexane to give **4** (0.41 g) as a colorless solid. The mother liquor was concentrated under reduced pressure and the residue was recrystallized from hexane to give a second crop of **4** (0.45 g, total 77%). R_f = 0.62, EtOAc:hexane = 1:10. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.07 (tt, J = 9.9, 7.1 Hz, 1 H), 7.21–7.30 (m, 2 H), 8.21–8.37 (m, 2 H); ^{19}F-NMR ($CDCl_3$, 282.4 MHz): δ = –152.75, –138.93, –102.24; ^{13}C-NMR($CDCl_3$, 75.5 MHz): δ = 103.4 (t, *J* = 21.9 Hz), 116.2 (d, *J* = 21.9 Hz), 123.5 (d, *J* = 1.5 Hz),



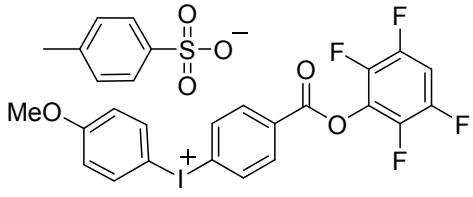
133.5 (d, J = 2.3 Hz), 139.0–142.7 (m), 144.5–145.1 (m), 147.3–148.2 (m), 163.3 (d, J = 259.7 Hz), 168.5. MS (ESI): positive mode *m/z* = 288.3 ($[M]^+$). MS (EI, 70 eV): m/z (%): 165.0 [$C_6HF_4O^+$] (10), 123.0 [$C_6H_4FO^+$] (100), 95.0 [$C_6H_4F^+$] (10).

2,3,5,6-Tetraphenyl 4-iodobenzoate: Et_3N (1.504 mL, 0.76 g, 7.51 mmol) was added dropwise to



a vigorously stirred solution of 4-iodobenzoyl chloride (2 g, 7.51 mmol) and 2,3,5,6-tetrafluorophenol (1.25 g, 7.51 mmol) in Et_2O (60 mL) and the stirring was continued for a further 10 min. The reaction mixture was filtered, the filter cake was washed with Et_2O (30 mL) and the filtrate was concentrated under reduced pressure. The residue was dissolved Et_2O (10 mL) and filtered. The filtrate was concentrated under reduced pressure. The residue was recrystallized from Et_2O/hexane to give the title compound (1.38 g, 48%) as a colorless solid. R_f = 0.46, EtOAc:hexane = 1:10. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.07 (tt, J = 9.9, 7.1 Hz, 1 H), 7.82–7.98 (m, 4 H); ^{19}F-NMR ($CDCl_3$, 282.4 MHz): δ= –152.70, –138.80; ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 103.0, 103.4 (t, J = 23.0 Hz), 126.6, 131.9, 138.3, 138.9–142.7 (m), 144.4 (dt, J = 3.8, 12.1 Hz), 147.7 (dt, J = 4.5, 12.1 Hz), 162.2. MS (ESI): positive mode *m/z* = 397.3 ($[M + H]^+$). MS (EI, 70 eV): m/z (%): 395.9 [M^+] (3), 230.9 [$C_7H_4OI^+$] (100), 202.9 [$C_6H_3I^+$] (100), 104.0 [$C_7H_4O^+$] (10).

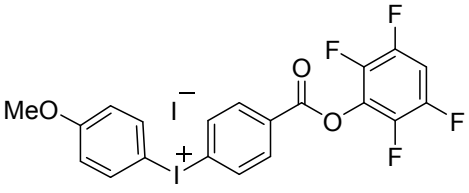
(4‑Methoxyphenyl)[4‑(2,3,5,6‑tetrafluorophenoxycarbonyl)phenyl]iodonium tosylate:



Tos·H_2O (0.72 g, 3.79 mmol) was added to a solution of 2,3,5,6-tetraphenyl 4-iodobenzoate (1 g, 2.52 mmol), mCPBA [1.44 g, 85% purity, 7.09 mmol; commercially available 77% mCPBA (Aldrich) was dried at 2 mbar and 40 °C for 3 h before use] and anisole (0.51 mL, 0.51 g, 4.72 mmol) in 50% CF_3CH_2OH in CH_2Cl_2 (20 mL) and the mixture was stirred for 3 days. The reaction mixture was added to vigorously stirred Et_2O (450 mL) and stirring was continued for a further 45 min. The precipitate was filtered off and washed with Et_2O (100 mL),

redissolved in CH_2Cl_2 (20 mL) and filtered through Celite®. The filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2/Et_2O to give the title compound (1.53 g, 90%) as a colorless solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.28 (s, 3 H), 3.77 (s, 3 H), 6.80 (d, *J* = 9.0 Hz, 2 H), 6.97 (d, *J* = 6.0 Hz, 2 H), 7.01–7.14 (m, 1 H), 7.36 (d, *J* = 9.0 Hz, 2 H), 7.98–8.03 (m, 4 H), 8.18 (d, *J* = 9.0 Hz, 2 H); ^{19}F-NMR ($CDCl_3$, 282.4 MHz): δ= –152.70, –138.55; ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 21.2, 55.5, 103.7 (t, *J* = 23.0 Hz), 104.7, 117.4, 123.0, 125.9, 128.5, 129.3, 132.7, 135.3, 137.9, 138.8–142.3 (m), 139.6, 142.2, 144.4 (dt, *J* = 3.8, 15.9 Hz), 147.7 (dt, *J* = 4.5, 16.6 Hz), 161.3, 162.4. MS (ESI): positive mode *m/z* = 503.0 ($[M]^+$); MS (ESI): negative mode *m/z* = 171.0 ($[C_7H_7SO_3]^-$); ESI HRMS: calcd for $C_{20}H_{12}F_4O_3I^+$: 502.9762; found: 502.9769.

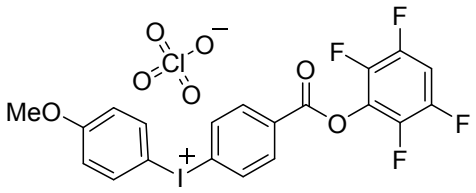
(4‐Methoxyphenyl)[4‐(2,3,5,6‐tetrafluorophenoxycarbonyl)phenyl]iodonium iodide:



(4‐Methoxyphenyl)[4‐(2,3,5,6‐tetrafluorophenoxy-carbonyl)phenyl]iodonium tosylate (1.19 g, 1.76 mmol) was dissolved in CH_2Cl_2 (20 mL). After addition of saturated NaI (10 mL), the mixture was vigorously stirred for 15 min and centrifuged (4000 rpm, 15 °C, 10 min). The aqueous solution and precipitate were separated off, saturated NaI (10 mL) was added and the mixture was vigorously stirred for 15 min and centrifuged (×3). The organic fraction was filtered, dried and concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2/Et_2O, the precipitate was filtered off, washed with acetone (10 mL) and Et_2O (80 mL) to give the title compound (0.29 g, 26%) as an off-white solid. The substance could be stored at 4 °C under Ar at least for 4 months. However, it was unstable in solution especially at elevated temperatures (dissolved in DMF or DMSO it was unstable already at ambient temperature). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 3.79 (s, 3 H), 6.65–6.73 (m, 2 H), 6.95–7.10 (m, 1 H), 7.56 (d, *J* = 8.9 Hz, 2 H), 7.81–8.05 (m, 3 H), 8.21–8.35 (m, 1 H); ^{19}F-NMR ($CDCl_3$, 282.4 MHz): δ= –152.63, –138.72; ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 55.5, 82.3, 103.0, 103.5 (t, *J* = 22.6 Hz), 116.4, 126.6, 128.8, 131.9,

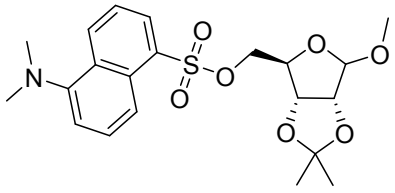
138.3, 138.6–142.5 (m), 144.2–144.7 (m), 144.5–144.9 (m), 159.5, 162.2. MS (ESI): positive mode *m/z* = 502.9 ([M]$^+$); MS (ESI): negative mode *m/z* = 126.9 ([I]$^-$); ESI HRMS: calcd for $C_{20}H_{12}F_4O_3I^+$: 502.9762; found: 502.9741.

(4‑Methoxyphenyl)[4‑(2,3,5,6‑tetrafluorophenoxycarbonyl)phenyl]iodonium perchlorate:



The title compound (168 mg, 88%) was obtained as a colorless solid according to GP2 from (4-methoxyphenyl)[4-(2,3,5,6-tetrafluorophenoxycarbonyl)phenyl]iodonium iodide (0.2 g, 0.32 mmol) and $AgClO_4$ (66 mg, 0.32 mmol) in acetone (10 mL). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 3.80 (s, 3 H), 6.88–6.98 (m, 2 H), 7.06 (tt, *J* = 9.9, 7.1 Hz, 1 H), 8.04–8.13 (m, 2 H), 8.14–8.18 (m, 2 H), 8.21–8.26 (m, 2 H); ^{19}F-NMR ($CDCl_3$, 282.4 MHz): δ= –152.52, –138.48; ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 55.5, 101.1, 103.8 (t, *J* = 21.1 Hz), 118.4, 120.1, 130.6, 133.5, 135.1, 138.3, 138.7–139.3 (m), 142.1–144.4 (m), 147.5–147.7 (m), 161.0, 163.4. MS (ESI): positive mode *m/z* = 503.0 ([M]$^+$); ESI HRMS: calcd for $C_{20}H_{12}F_4O_3I^+$: 502.9762; found: 502.9769. MS (ESI): positive mode *m/z* = 503.0 ([M]$^+$); MS (ESI): negative mode *m/z* = 171.0 ([$C_7H_7SO_3$]$^-$); ESI HRMS: calcd for $C_{20}H_{12}F_4O_3I^+$: 502.9762; found: 502.9749.

1-*O*-Methyl-2,3-*O*-isopropylidene-5-*O*-[5-(*N*,*N*-dimethylamino)naphthalene-1-sulfonyl]-D-ribofuranoside (8):



Dansyl chloride (2.9 g, 10.75 mmol) was added to a stirred ice-cold solution of 1-*O*-methyl-2,3-*O*-isopropylidene-D-ribofuranoside (**9**) (1.7 g, 8.32 mmol) and Et_3N (1.6 g, 15.81 mmol) in CH_2Cl_2 (25 mL), the cooling bath was removed and the reaction mixture was stirred for further 16 h. The mixture was concentrated under reduced pressure. Et_2O and H_2O (100 mL each) were added to the residue, the organic fraction was separated and washed with H_2O (3×20 mL), 5% $NaHCO_3$ (3×20 mL) and brine (2×20 mL), then dried and concentrated under reduced pressure. The residue was purified by column chromatography [EtOAc/hexane = 1:4, silica gel (0.1% CaO)] and

recrystallization from Et_2O/pentane gave **10** (2.85 g, 78%) as a yellow solid. R_f = 0.11, EtOAc:hexane = 1:8. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.24 (s, 3 H), 1.42 (s, 3 H), 2.90 (s, 6 H), 3.14 (s, 3 H), 3.93–4.0 (m, 2 H), 4.32 (t, *J* = 7.2 Hz, 1 H), 4.43–4.56 (m, 2 H), 4.88 (s, 1 H), 7.18–7.27 (m, 1 H), 7.53–7.65 (m, 2 H), 8.25–8.33 (m, 2 H), 8.63 (d, *J* = 8.5 Hz, 1 H); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 24.8, 26.3, 45.4, 54.9, 69.5, 81.4, 83.5, 84.8, 109.4, 112.6, 115.7, 119.4, 123.0, 128.8, 129.8, 129.9, 130.6, 130.9, 131.7. MS (ESI): positive mode *m/z* = 897.3 ([2 M + Na]$^+$), 875.3 ([2 M + H]$^+$), 460.2 ([M + Na]$^+$), 438.2 ([M + H]$^+$); ESI HRMS: calcd for $C_{22}H_{27}N_3O_4Na^+$: 420.1894; found: 420.1887; calcd for $C_{21}H_{27}NO_7Na^+$: 460.1400; found: 460.1394; calcd for $C_{21}H_{26}NO_7^+$: 438.1581; found: 438.1579.

1-*O*-Methyl-2,3-*O*-isopropylidene-5-*O*-[5-(*N*,*N*,*N*-trimethylammonium)naphthalene-1- sulfon-yl]-D-ribofuranoside triflate (9): MeOTf (0.251 mL, 0.376 g, 2.29 mmol) was added to a solution **10** (1 g, 2.29 mmol) in CH_2Cl_2 (5 mL) in a dry box under Ar. The reaction flask was then removed from the dry box and the reaction mixture was incubated at ambient temperature for 3 days. Thereafter, Et_2O (50 mL) was added and the precipitated oil was separated, recrystallized twice from CH_2Cl_2/Et_2O, sonicated with Et_2O (3×20 mL) and thoroughly dried under reduced pressure to give **11** (1.05 g, 69%) as a colorless foam. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.26 (s, 3 H), 1.41 (s, 3 H), 3.17 (s, 3 H), 3.95–4.15 (m, 2 H), 4.08 (s, 9 H), 4.30 (dt, *J* = 0.6, 14.1 Hz, 1 H), 4.50–4.54 (m, 1 H), 4.58–4.62 (m, 1 H), 4.90 (s, 1 H), 7.83 (t, *J* = 8.3 Hz, 1 H), 8.0 (dd, *J* = 8.9, 7.6 Hz, 1 H), 8.21 (d, *J* = 8.3 Hz, 1 H), 8.47 (d, *J* = 8.9 Hz, 1 H), 8.89–8.97 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 24.8, 26.3, 55.1, 58.7, 70.5, 81.2, 83.5, 84.7, 109.5, 112.8, 120.6 (q, *J* = 320.1 Hz), 122.7, 125.2, 127.2, 127.6, 129.4, 131.16, 131.22, 133.9, 142.1. MS (ESI): positive mode *m/z* = 452.3 ([M]$^+$); MS (ESI): negative mode *m/z* = 149.0 ([CF_3SO_3]$^-$); ESI HRMS: calcd for $C_{22}H_{30}NO_7S^+$: 452.1737; found: 452.1739.

Radiochemistry

Synthesis of [^{18}F]fluorobenzaldehydes from iodonium precursors alone without any evaporation steps. General procedure 3 – (GP3): [^{18}F]Fluoride (100–330 MBq) was fixed on a QMA cartridge. The cartridge was washed with the appropriate solvent (1 mL) and the radiofluoride was eluted with a solution of the corresponding iodonium salt (5 mg, unless not otherwise stated) in the appropriate solvent (0.5 mL). The elution yield was determined by comparing the radioactivity eluted into the reaction vial with the total radioactivity trapped on the anion exchange resin. The reaction mixture was stirred at the temperature and for the indicated time in Table S1. Subsequently the mixture was cooled down to room temperature, water (4 mL) was added and the reaction mixture was shaken vigorously for 30 s. Thereafter, RCC was determined by radio-HPLC.

Unless stated, HPLC conditions: Eluent: 30% MeCN, flow rate: 1.5 mL/min.

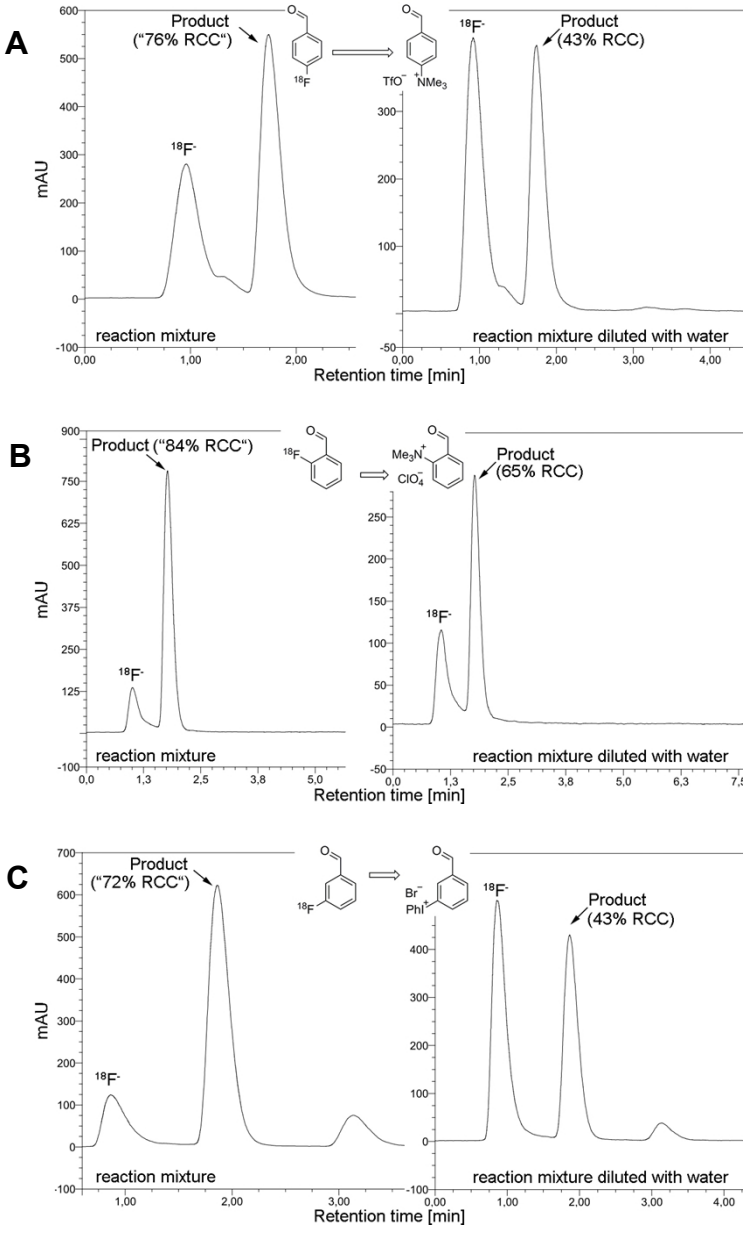
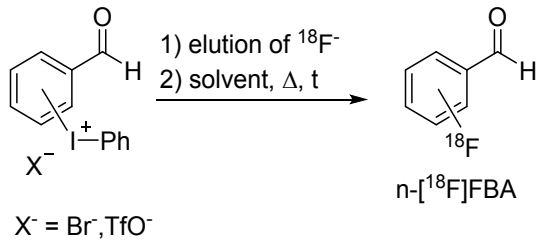


Figure S1. False high *vs.* correct radiochemical conversions obtained by the direct HPLC analysis of reaction mixtures and the HPLC analysis of reaction mixtures diluted with an excess of water: A – 4-[^{18}F]FBA (from 4-formyl-*N*,*N*,*N*-trimethylanilinium triflate, K2.2.2/K_2CO_3 protocol, GP5), B – 2-[^{18}F]FBA (from only 2-formyl-*N*,*N*,*N*-trimethylanilinium perchlorate, GP4), C – 3-[^{18}F]FBA (from (3-formylphenyl)(phenyl)iodonium bromide, $CsHCO_3$/TEMPO protocol, GP6).

Table S1. Synthesis of [^{18}F]fluorobenzaldehydes from iodonium precursors alone without any evaporation steps[a]

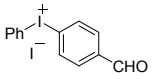
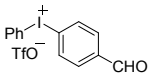
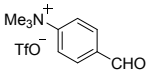


entry	LG^+X	n	solvent	temperature [°C], time [min]	elution yield [%]	RCC [%]
1	TfO^-	2	95% DMF	130, 10	30	2
2[b]	TfO^-	3	DMSO	130, 10	30	22
3	Br^-	3	DMF	160, 10	6	34
4	Br^-	3	95% DMF	160, 15	30	4
5	Br^-	4	DMSO	90, 10	20	51
6	TfO^-	4	90% DMSO	160, 15	30	35
7	TfO^-	4	90% DMF	160, 15	55	51

[a] All experiments were carried out as described in GP3; [b] with 20 mg precursor

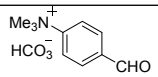
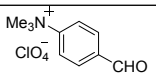
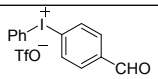
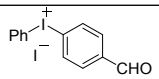
Elution of $^{18}F^-$ from a QMA cartridge with onium salts in anhydrous alcohols (Table S2): [^{18}F]Fluoride (50–200 MBq) was fixed on a QMA cartridge. The cartridge was washed with the appropriate alcohol (1 mL), and the radiofluoride was eluted with a solution of the corresponding onium salt (5 mg) in the appropriate alcohol (0.5 mL). The elution yield was determined by comparing the radioactivity eluted into the reaction vial with the total radioactivity trapped on the anion exchange resin.

Table S2. Recovery yield for the elution of $^{18}F^-$ from a QMA cartridge with onium salts in anhydrous alcohols.

entry	**solvent**	 **recovery [%]**	 **recovery [%]**	 **recovery [%]**
1	MeOH	99	99	98
2	EtOH	95	92	95
3	1-PrOH	88	88	84
4	*i*-BuOH	61	82	80
5	*i*-PrOH	59	73	78
6	*n*-BuOH	43	64	69
7	2-BuOH	7	37	23
8	*t*-BuOH	2	27	23

Elution of $^{18}F^-$ from a QMA cartridge with different amounts of onium salts (Table S3): [^{18}F]Fluoride (50–500 MBq) was fixed on a QMA cartridge. The cartridge was washed with the appropriate alcohol (1 mL) and the radiofluoride was eluted with a solution of the corresponding onium salt (see Table S3) in MeOH (0.5 mL). The elution yield was determined by comparing the radioactivity eluted into the reaction vial with the total radioactivity trapped on the anion exchange resin.

Table S3. Elution of $^{18}F^-$ from a QMA cartridge with different amounts of onium salts.

entry	precursor amount [mg]	 recovery [%]	 recovery [%]	 recovery [%]	 recovery [%]
1	10	99	-	-	-
2	8	-	98	-	-
3	5	99	-	99	98
4	2.5	99	-	97	92
5	1	-	96	-	-
6	0.7	-	89	-	-
7	0.5	97	78	80	84
8	0.3	-	-	68	82
9	0.1	85	44	65	76

Synthesis of ^{18}F-labeled compounds from only onium precursors. General procedure 4 – (GP4): Aqueous [^{18}F]fluoride (0.05–50 GBq) was trapped on a anion-exchange resin (QMA or Chromafix® 30-PS-HCO_3 cartridge). It should be noted, that in the case of QMA cartridges, the aqueous [^{18}F]fluoride was loaded onto the cartridge from the male side, whereas MeOH flushing and $^{18}F^-$ elution were done from the female side of the cartridge. If the QMA has been loaded, flushed and eluted from the female side only, sometimes a significant amount of [^{18}F]fluoride remained on the resin (this is probably because QMA-light (46 mg) cartridges have a single frit on the male side but four on the female side).

Unless otherwise stated the cartridge was washed with MeOH (1 mL) and [^{18}F]fluoride was eluted into a reaction vial with a solution of the appropriate precursor (5 mg; unless otherwise stated) in MeOH (0.5 mL). Methanol was evaporated under reduced pressure at 70 °C within 2–3 min. After cooling to room temperature the appropriate solvent (500 µL) was added. The reaction mixture was

stirred under the conditions given in Tables S4–S10. Subsequently the mixture was cooled down to room temperature, water (4 mL) was added and the reaction mixture was shaken vigorously for 30 s. Thereafter, RCC was determined by radio-HPLC.

Unless stated, HPLC conditions: Eluent: 30% MeCN, flow rate: 1.5 mL/min.

Preparation of ^{18}F-labeled compounds using K2.2.2/K_2CO_3 protocol. General procedure 5 – (GP5): [^{18}F]Fluoride (0.05–50 GBq) was fixed on a QMA cartridge and eluted with 0.066 M K_2CO_3 (360 µL) into a solution of K2.2.2 (20 mg, 53.1 µmol) in MeCN (700 µL). After evaporation, the corresponding onium precursor (5 mg) dissolved in DMSO (500 µL) was added to the dry cryptate ([K⊂2.2.2]$^+$/^{18}F$^-$) and the reaction mixture was stirred at the temperature and for the indicated time (Tables S4–5, 8). The mixture was cooled down to room temperature, water (4 mL) was added and the reaction mixture was shaken vigorously for 30 s. Thereafter, RCC was determined by radio-HPLC.

Unless otherwise stated, HPLC conditions: Eluent: 30% MeCN, flow rate: 1.5 mL/min.

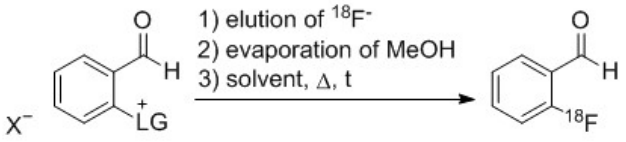
Synthesis of ^{18}F-labeled compounds using $CsHCO_3$/TEMPO protocol. General procedure 6 – (GP6): [^{18}F]Fluoride (0,05–50 GBq) was fixed on an anion-exchange resin and eluted with an aqueous solution of $CsHCO_3$ (400 µL; 2.5 mg/mL) into the reaction vial containing MeCN (1 mL). After azeotropic drying under helium at 110 °C (×3), a solution of the appropriate iodonium salt (1–2 mg) and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) (0.5–1 mg) in DMF (1 mL) was added and the reaction mixture was stirred at the temperature and for the indicated time (Tables S6). The mixture was cooled down to room temperature, water (4 mL) was added and the reaction mixture was shaken vigorously for 30 s. Thereafter, RCC was determined by radio-HPLC.

Unless otherwise stated, HPLC conditions: Eluent: 30% MeCN, flow rate: 1.5 mL/min.

Preparative synthesis of 2-/4-[^{18}F]fluorobenzaldehydes (2-/4-[^{18}F]FBA): The ^{18}F-labeled compounds were prepared according to GP4. After cooling to ambient temperature, the reaction

mixture was diluted with water (9 mL) and loaded onto a Strata X cartridge. The cartridge was washed with 0.1 M HCl (10 mL) and H_2O (5 mL) and the corresponding [^{18}F]fluorobenzaldehyde (up to 35 GBq, 65–75% EOB; not decay corrected) was eluted with EtOH (0.3 mL). The radiochemical and chemical purities after solid phase extraction (SPE) purification were > 99%.

Table S4. Synthesis of 2-[^{18}F]FBA.[a]



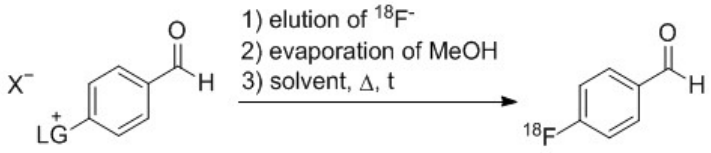
$LG^+ = Me_3N^+, PhI^+$

$X^- = I^-, Br^-, ClO_4^-, TfO^-, SCN^-, HCO_3^-$

entry	LG^+X^-	solvent	temperature [°C], time [min]	RCC [%]
1	$Me_3N^+HCO_3^-$	DMF	80, 10	58
2	$Me_3N^+HCO_3^-$	MeCN	80, 10	68
3	$Me_3N^+I^-$	DMSO	80, 10	62(*62*)[c]
4	$Me_3N^+I^-$	DMSO	130, 10	63
5	$Me_3N^+I^-$	MeCN	130, 10	24
6	$Me_3N^+SCN^-$	DMSO	80, 10	26
7	$Me_3N^+SCN^-$	DMSO	130, 10	56
8	$Me_3N^+SCN^-$	MeCN	130, 10	46
9	PhI^+TfO^-	DMF	160, 15	35
10	$Me_3N^+TfO^-$	DMSO	130, 15	64(*46*)[c]
11	PhI^+Br^-	DMSO	80, 2	10
12	PhI^+Br^-	DMSO	160, 15	61
13	PhI^+Br^-	DMF	160, 10	5
14	$Me_3N^+ClO_4^-$	DMSO	80, 15	63
15	$Me_3N^+ClO_4^-$	DMSO	150, 10	80(*30*)[c]
16	$Me_3N^+ClO_4^-$	DMSO	200, 10	65
17	$Me_3N^+ClO_4^-$	MeCN	80, 10	37
18[b]	$Me_3N^+TfO^-$	DMSO	80, 2	46

[a] Unless otherwise stated, all experiments were carried out as described in GP4; [b] carried out according to the K2.2.2/K_2CO_3 protocol (GP5); [c] RCC with 2 mg precursor in 100 µL solvent.

Table S5. Preparation of 4-[^{18}F]FBA.[a]

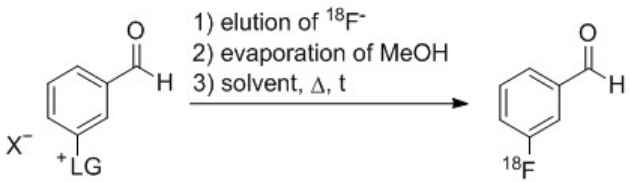


$LG^+ = Me_3N^+$, PhI^+
$X^- = I^-$, Br^-, ClO_4^-, TfO^-, HCO_3^-

entry	LG^+X^-	solvent	temperature [°C], time [min]	RCC [%]
1	$Me_3N^+HCO_3^-$	DMF	80, 10	28
2	$Me_3N^+HCO_3^-$	MeCN	130, 10	45
3	$Me_3N^+HCO_3^-$	DMSO	80, 10	87(*40*)[c]
4	$Me_3N^+HCO_3^-$	sulfolane	200, 10	80
5	$Me_3N^+I^-$	DMSO	80, 10	75(*65*)[c]
6	PhI^+TfO^-	DMF	160, 15	50
7	PhI^+Br^-	DMF	115, 5	61
8	$Me_3N^+ClO_4^-$	DMSO	150, 10	90(*33*)[c]
9	$Me_3N^+ClO_4^-$	sulfolane	200, 10	89
10	$Me_3N^+TfO^-$	DMF	115, 10	63
11[b]	$Me_3N^+TfO^-$	DMSO	80, 10	65

[a] Unless otherwise stated, all experiments were carried out as described in GP4; [b] carried out according to the K2.2.2/K_2CO_3 protocol (GP5); [c] RCC with 2 mg precursor in 100 µL solvent.

Table S6. Preparation of 3-[^{18}F]FBA.[a]

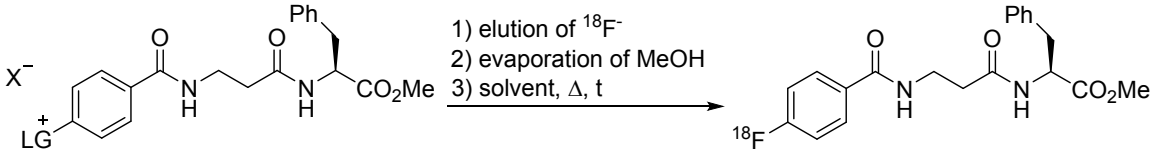


$LG^+ = Me_3N^+, PhI^+, (4\text{-}OMePh)I^+$
$X^- = I^-, Br^-, ClO_4^-, TfO^-, HCO_3^-$

entry	LG^+X^-	solvent	temperature [°C], time [min]	RCC [%]
1	PhI^+I^-	95% DMSO	130, 10	14
2	PhI^+I^-	95% DMF	130, 10	12
3	PhI^+I^-	95% MeCN	130, 10	5
4	$(4\text{-}OMePh)I^+I^-$	DMSO	80, 10	12
5	$(4\text{-}OMePh)I^+I^-$	DMSO	130, 10	31
6	PhI^+Br^-	DMSO	80, 10	0
7	$Me_3N^+HCO_3^-$	DMSO	80, 10	0
8	$Me_3N^+I^-$	DMSO	130, 10	0
9	$Me_3N^+I^-$	sulfolane	200, 10	6
10	PhI^+TfO^-	DMF	160, 15	10
11	$(4\text{-}OMePh)I^+ClO_4^-$	DMSO	80, 10	22
12	$(4\text{-}OMePh)I^+ClO_4^-$	DMSO	150, 10	40
13	$(4\text{-}OMePh)I^+ClO_4^-$	95% MeCN	80, 10	2
14	$(4\text{-}OMePh)I^+ClO_4^-$	95% DMSO	80, 10	6
15[b]	PhI^+Br^-	DMF	130, 10	45

[a] Unless otherwise stated, all experiments were carried out as described in GP4; [b] carried out according to the TEMPO/$CsHCO_3$ protocol (GP6).

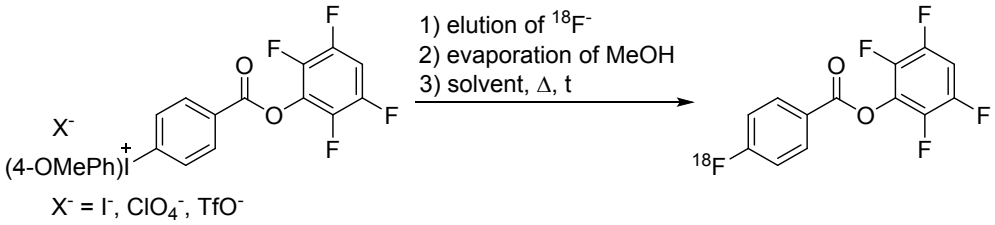
Table S7. Synthesis of dipeptide [^{18}F]**1**.[a]



entry	LG^+X^-	solvent	temperature [°C], time [min]	RCC [%]
1	$Me_3N^+HCO_3^-$	sulfolane	130, 15	30
2	$Me_3N^+HCO_3^-$	sulfolane	200, 20	31
3	$Me_3N^+HCO_3^-$	diglyme	200, 15	4
4	$Me_3N^+HCO_3^-$	DMSO	130, 15	29
5	$Me_3N^+ClO_4^-$	DMSO	140, 15	12
6	$(4\text{-OMePh})I^+I^-$	DMSO	130, 10	56
7	$(4\text{-OMePh})I^+ClO_4^-$	DMSO	140, 15	12
8[b]	$(4\text{-OMePh})I^+I^-$	DMF	120, 10	56
9[b]	$(4\text{-OMePh})I^+I^-$	diglyme	120, 10	16
10[c]	$Me_3N^+I^-$	DMSO	90, 10	0
11[c]	$Me_3N^+I^-$	sulfolane	150, 10	0
12[c]	$Me_3N^+TfO^-$	DMSO	150, 10	0
13[c]	$Me_3N^+TfO^-$	sulfolane	150, 10	0

[a] Unless otherwise stated, all experiments were carried out as described in GP4; [b] carried out according to the K2.2.2/K_2CO_3 protocol (GP5); [c] carried out according to the TEMPO/$CsHCO_3$ protocol (GP6).

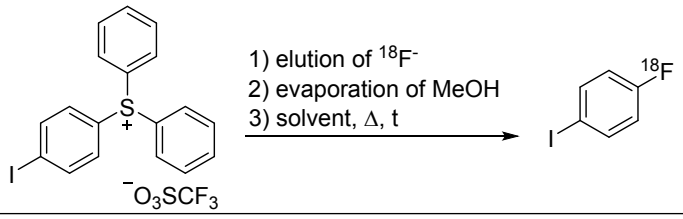
Table S8. Synthesis of 2,3,4,6-tetrafluoro 4-[^{18}F]fluorobenzoate (4-[^{18}F]TFP, [^{18}F]**2**).[a]



entry	X^-	solvent	temperature [°C], time [min]	RCC [%]
1[b]	I^-	DMSO	130, 10	10–25
2	ClO_4^-	DMSO	130, 10	23–25
3	$TosO^-$	DMSO	130, 10	11

[a] All experiments were carried out as described in GP4; [b] large fluctuations of RCCs were observed. HPLC conditions: Eluent: 50% MeCN, flow rate: 3 mL/min

Table S10. Synthesis of 1-[^{18}F]fluoro-4-iodobenzene ([^{18}F]FIB, [^{18}F]**4**).[a]

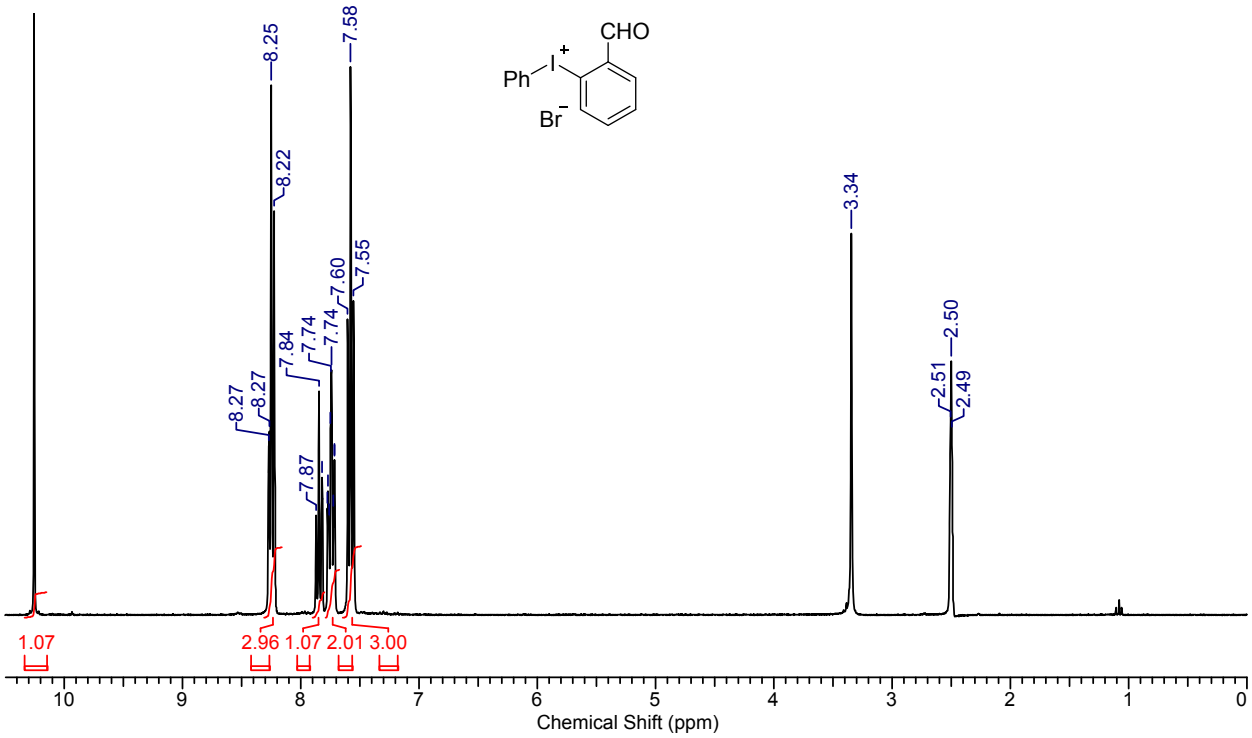


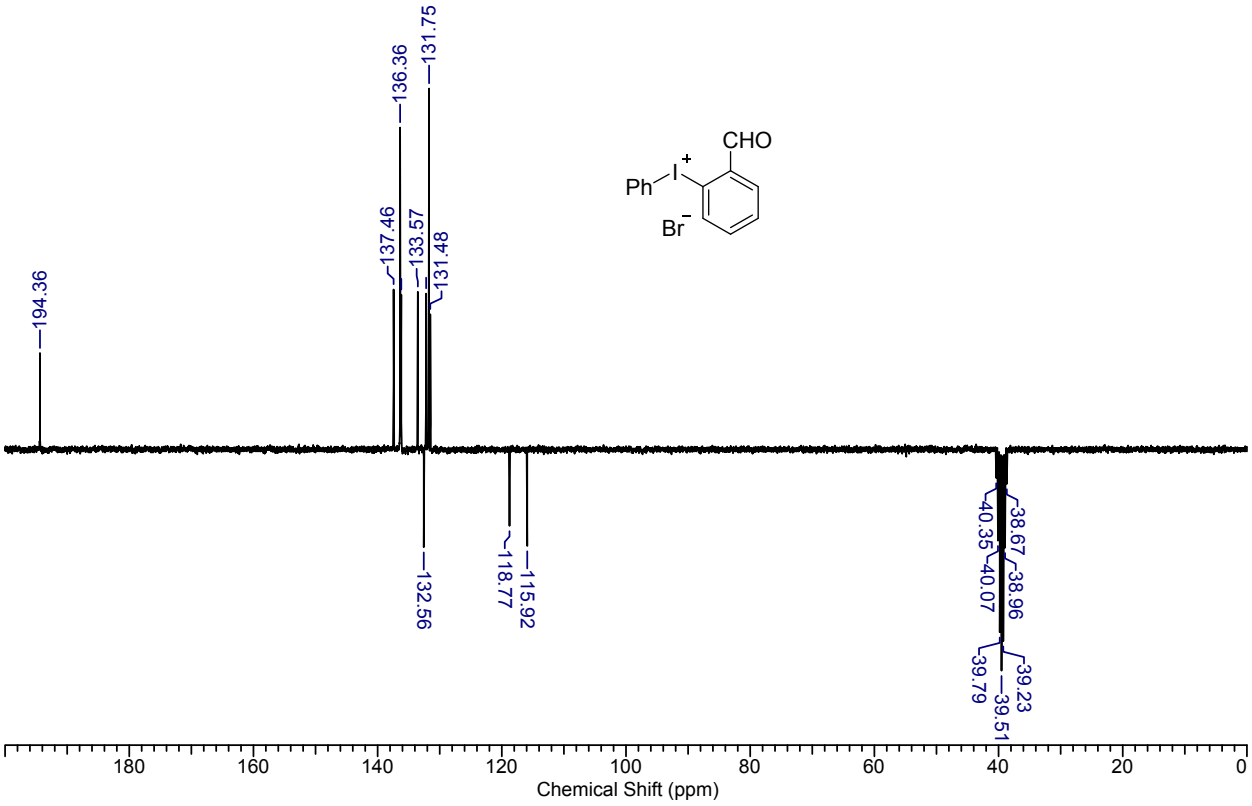
entry	solvent	temperature [°C], time [min]	RCC [%]
1	diglyme	85, 15	66
2	MeCN	85, 15	41
3	DMSO	85, 15	16
4	sulfolane	85, 15	41
5	DMF	85, 15	29
6[b]	MeCN	85, 15	50
7[b]	diglyme	85, 15	42

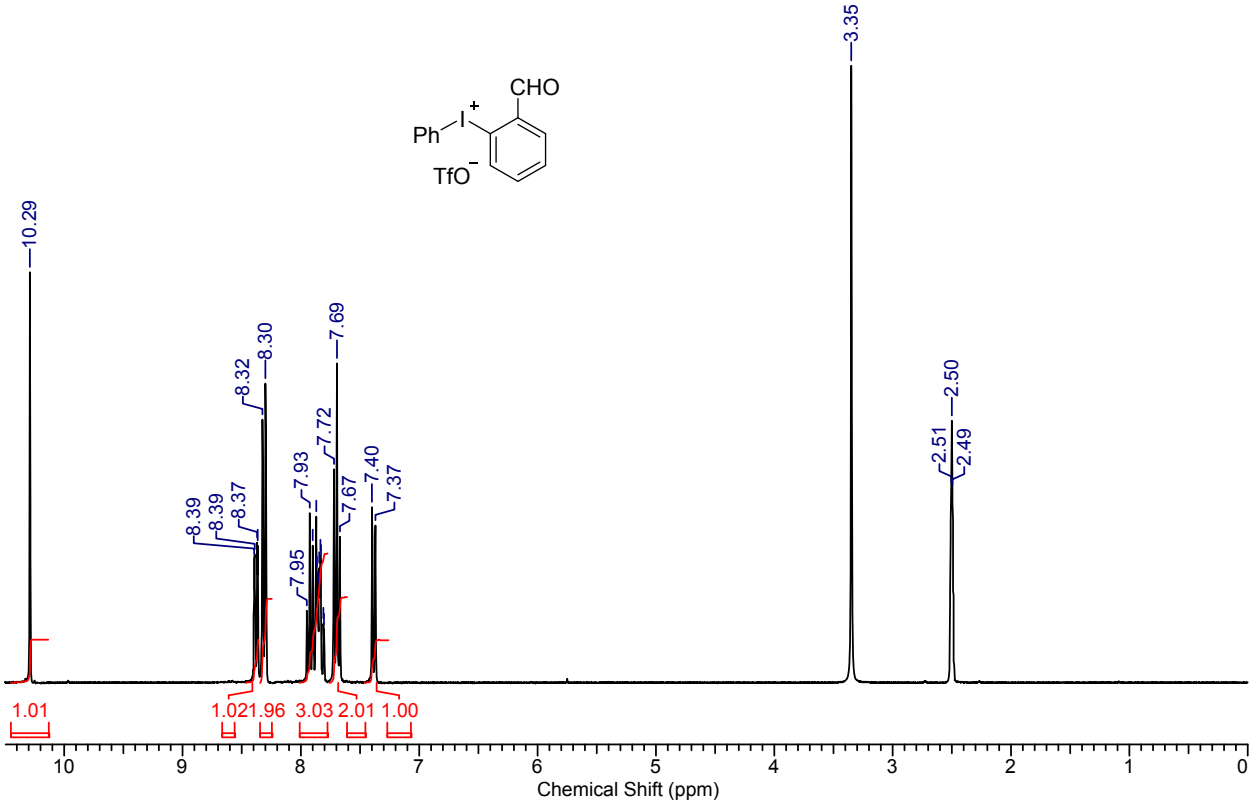
[a] All experiments were carried out as described in GP4. [b] carried out according to the K2.2.2/K_2CO_3 protocol (GP5). HPLC conditions: Eluent: 50% MeCN, flow rate: 1.5 mL/min.

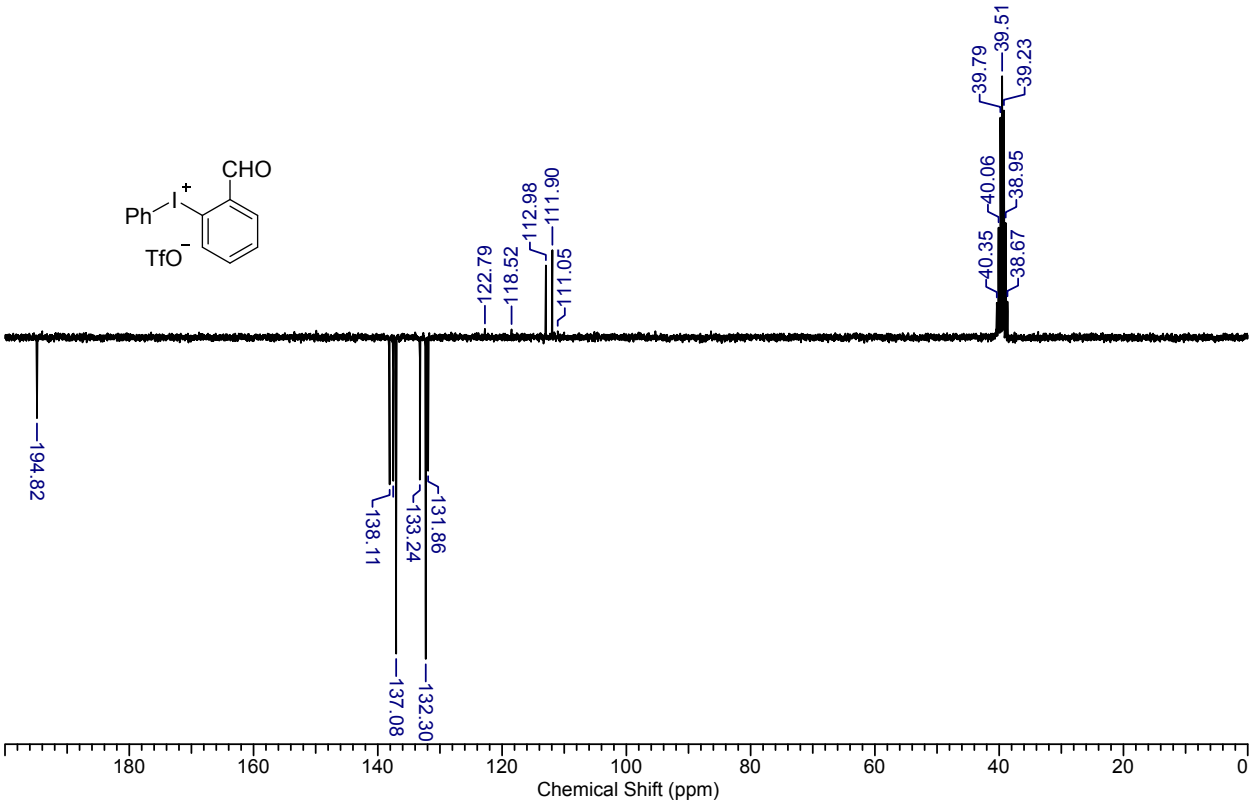
Preparation of 5-[^{18}F]fluoro-D-ribose ([^{18}F]FDR, [^{18}F]4): The protected intermediate of [^{18}F]FDR was obtained from precursor **11** according to GP4 using MeCN as solvent. The reaction was carried out at 80 °C for 10 min. Removal of the protective groups was performed by incubation of the crude reaction mixture with 1 M HCl (400 µL) for 5 min at 105 °C. Thereafter, the reaction mixture was neutralized with 1 M NaOH (400 µL) to give [^{18}F]**8** in 74% RCC (determined by radio-HPLC). [^{18}F]**8** was also prepared using the conventional K2.2.2/K_2CO_3 protocol according to GP5. The subsequent deprotection of the radiolabeled intermediate gave [^{18}F]**8** in 58% RCC (determined by radio-HPLC). HPLC conditions: Column: Luna C-18 (2) 5µm (250×4.6 mm, Phenomenex), eluent: 55% MeCN, flow rate: 1.5 mL/min.

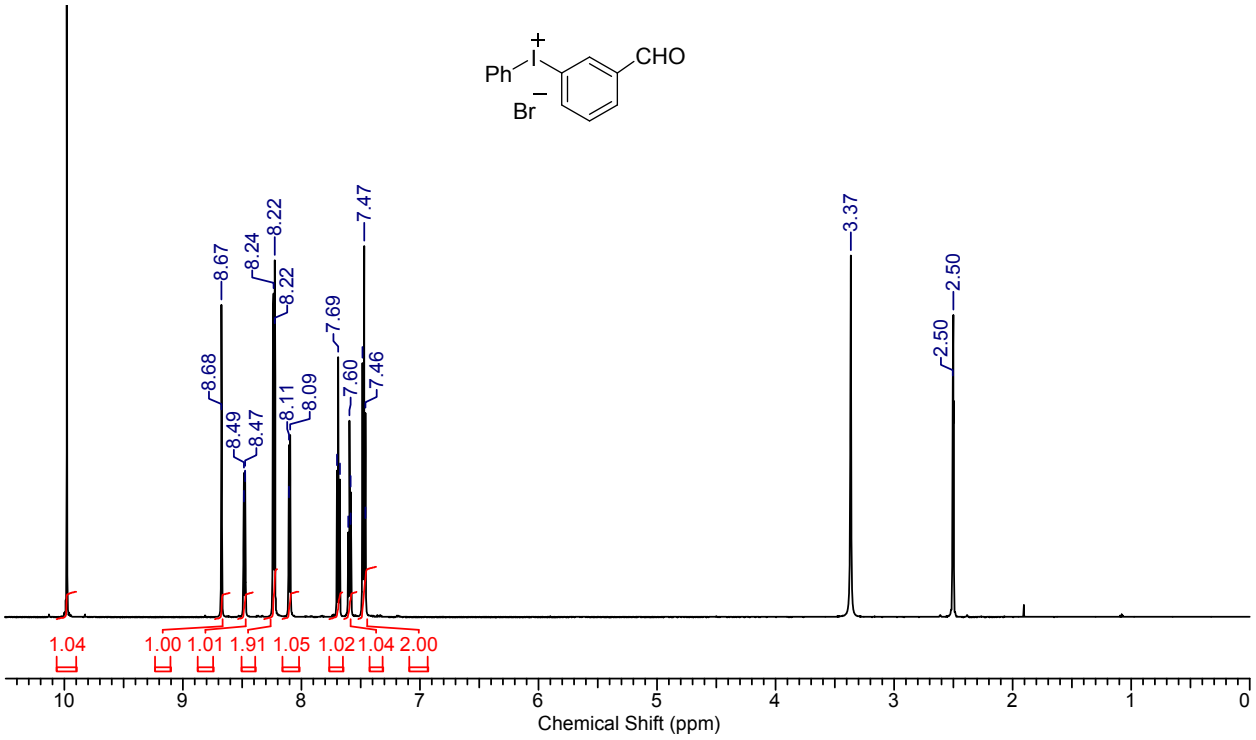
[1]H- and APT-NMR Spectra

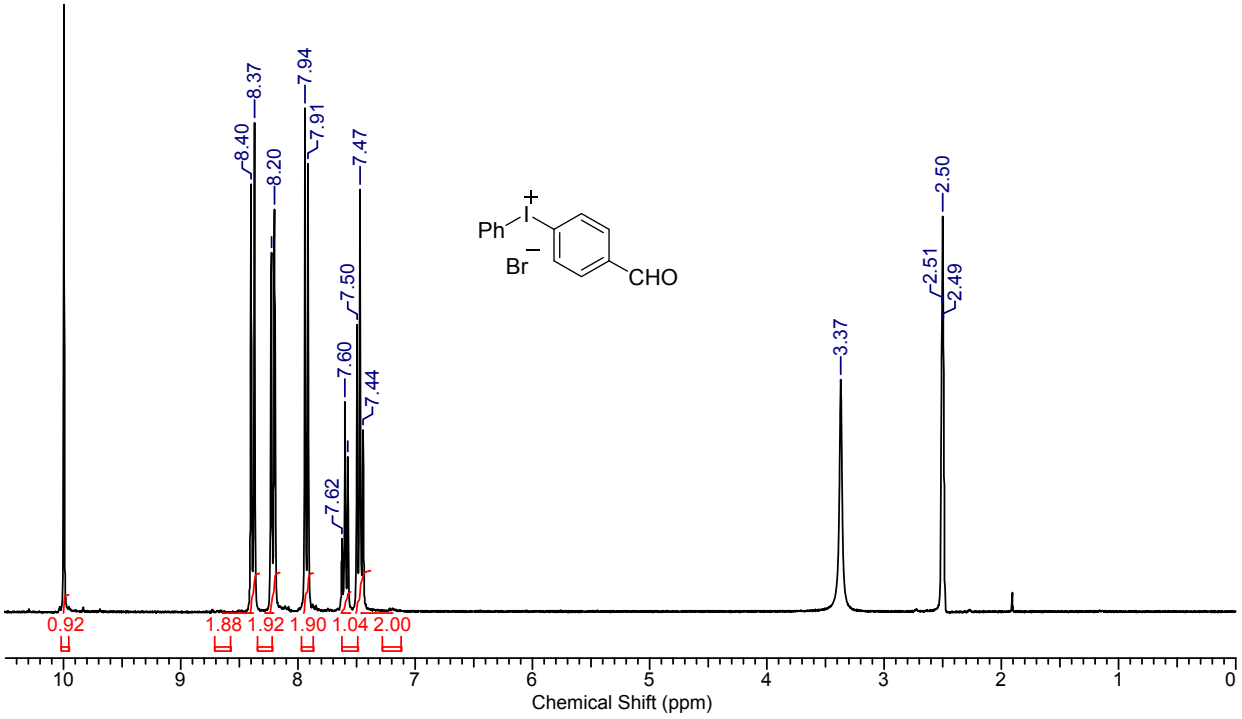


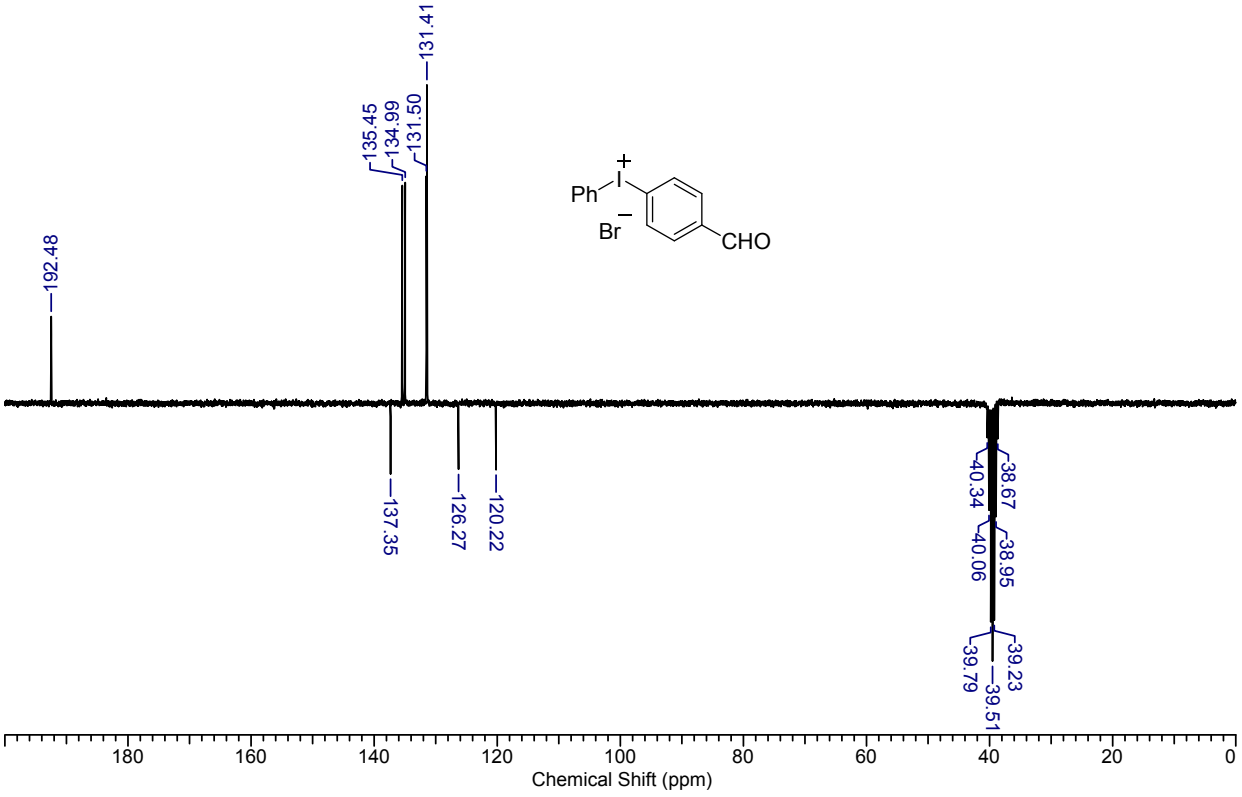


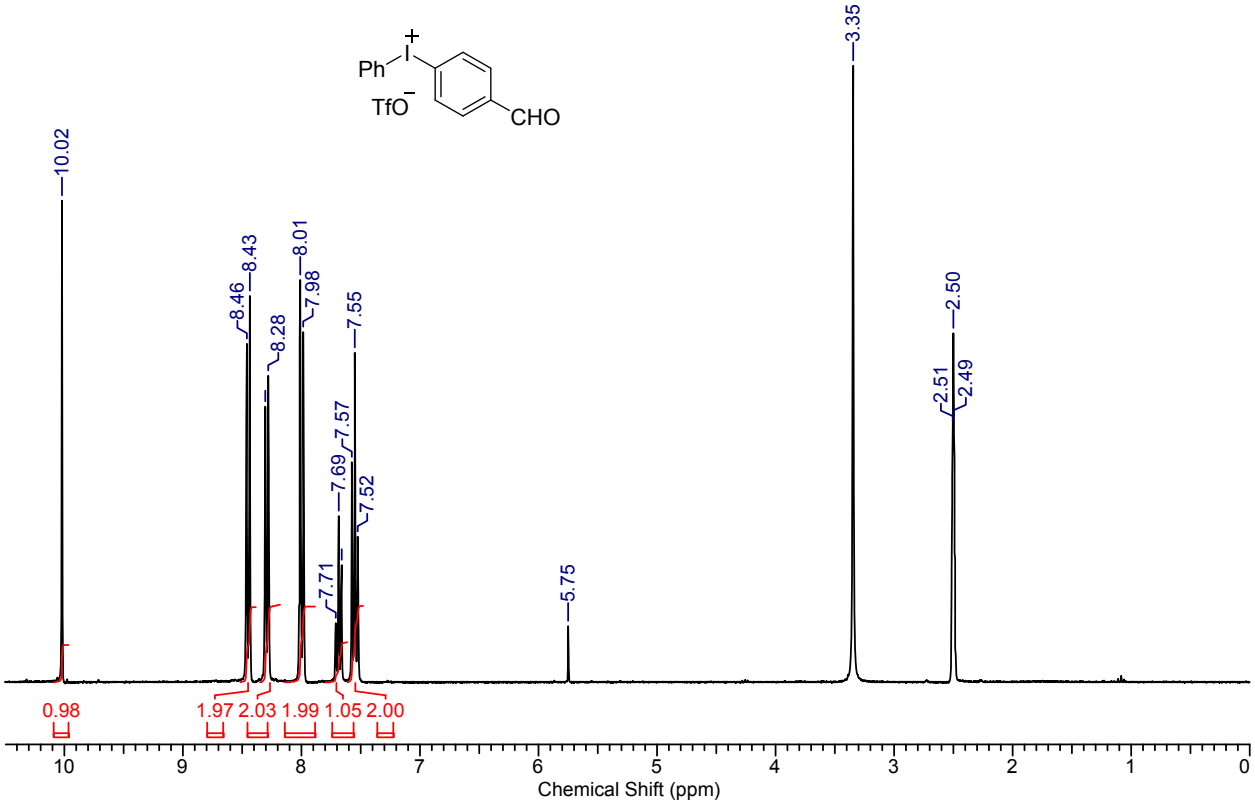

CHO
Ph
I
+
TfO
−
10.29
8.39
8.39
8.37
8.32
8.30
7.95
7.93
7.72
7.69
7.67
7.40
7.37
3.35
2.51
2.50
2.49
1.01
1.02
1.96
3.03
2.01
1.00
Chemical Shift (ppm)

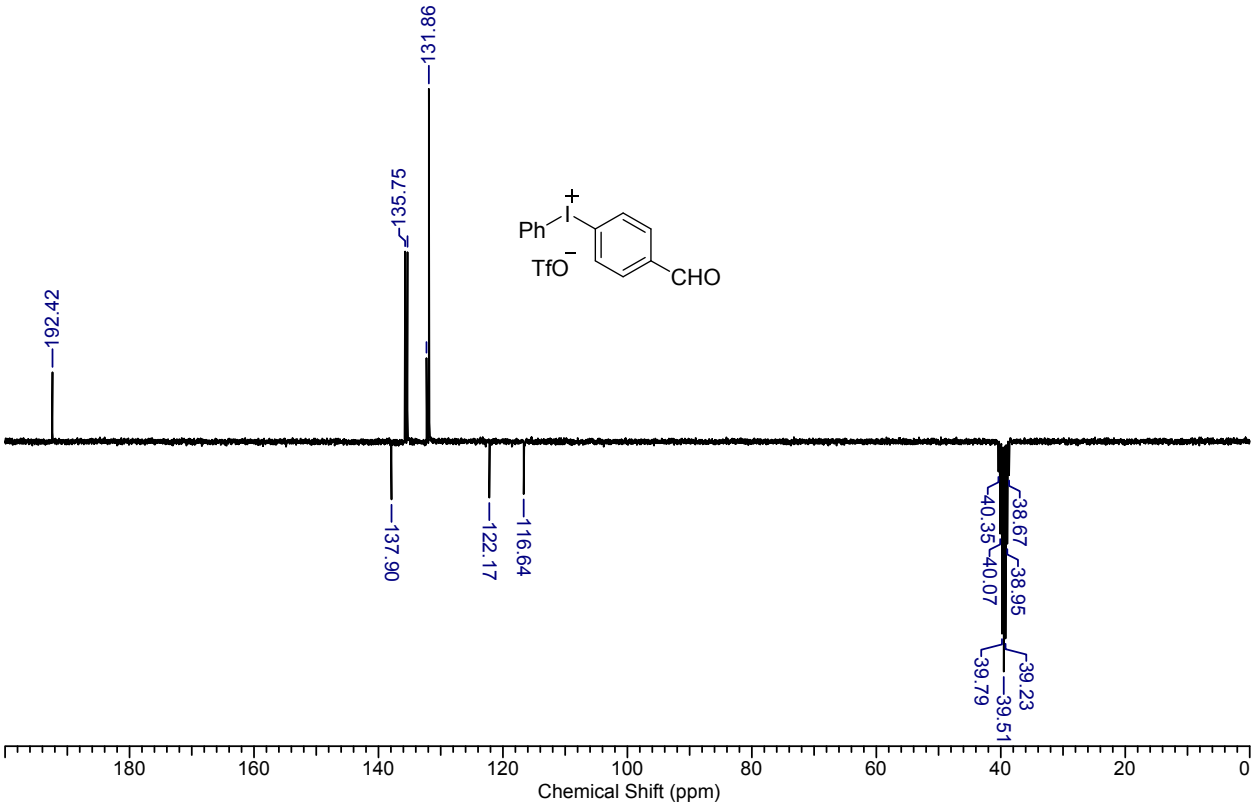

CHO
Ph
I
+
TfO
−
194.82
138.11
137.08
133.24
132.30
131.86
122.79
118.52
112.98
111.90
111.05
39.79
39.51
39.23
40.06
38.95
40.35
38.67
Chemical Shift (ppm)

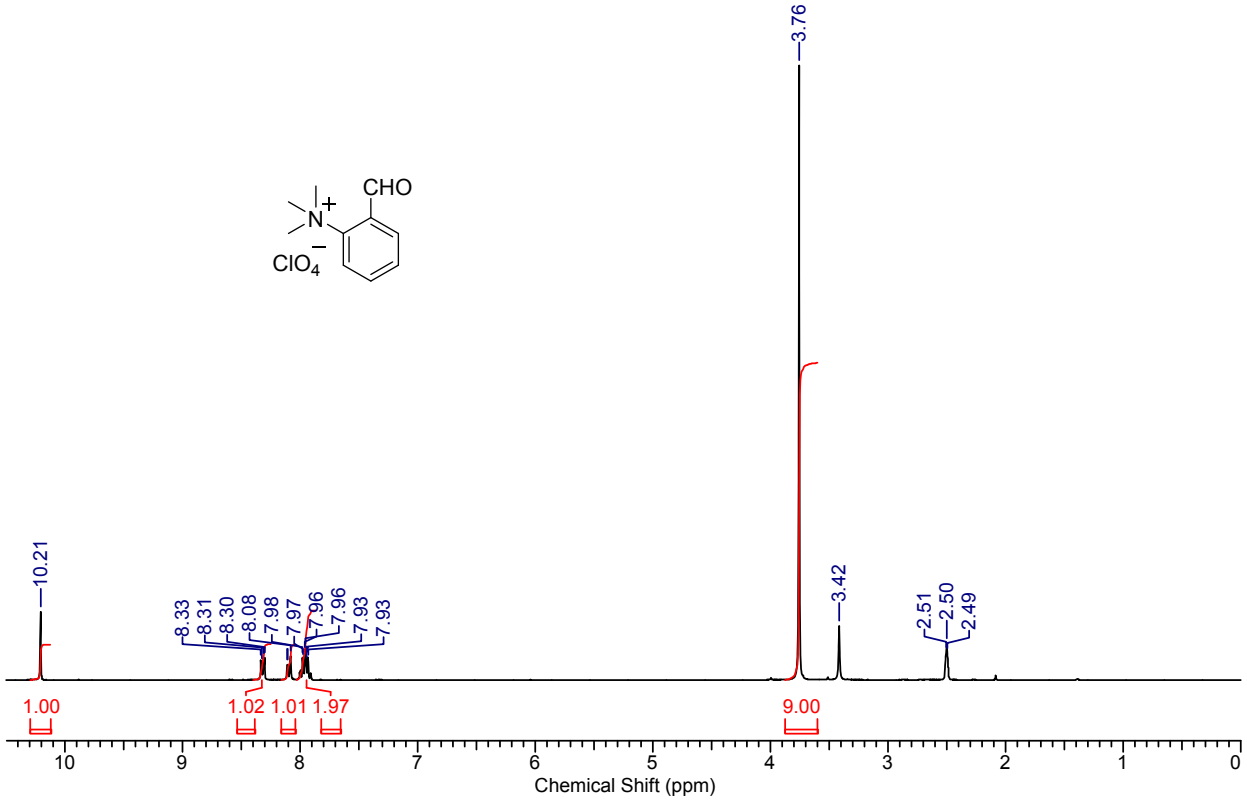

Ph
I
+
Br
−
CHO
8.67
8.68
8.49
8.47
8.24
8.22
8.22
8.11
8.09
7.69
7.60
7.47
7.46
3.37
2.50
2.50
1.04
1.00
1.01
1.91
1.05
1.02
1.04
2.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

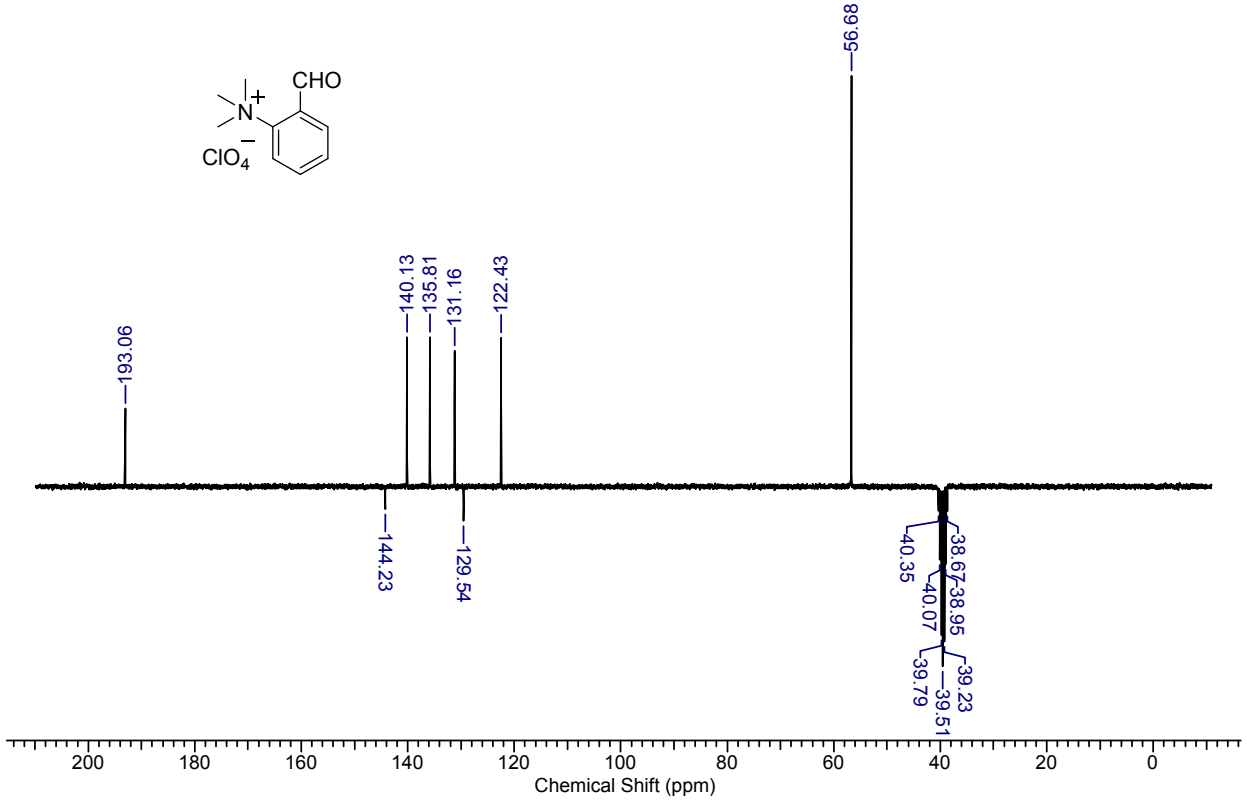

8.40
8.37
8.20
7.94
7.91
7.62
7.60
7.50
7.47
7.44
3.37
2.51
2.50
2.49
Ph
I
Br
CHO
0.92
1.88
1.92
1.90
1.04
2.00
Chemical Shift (ppm)

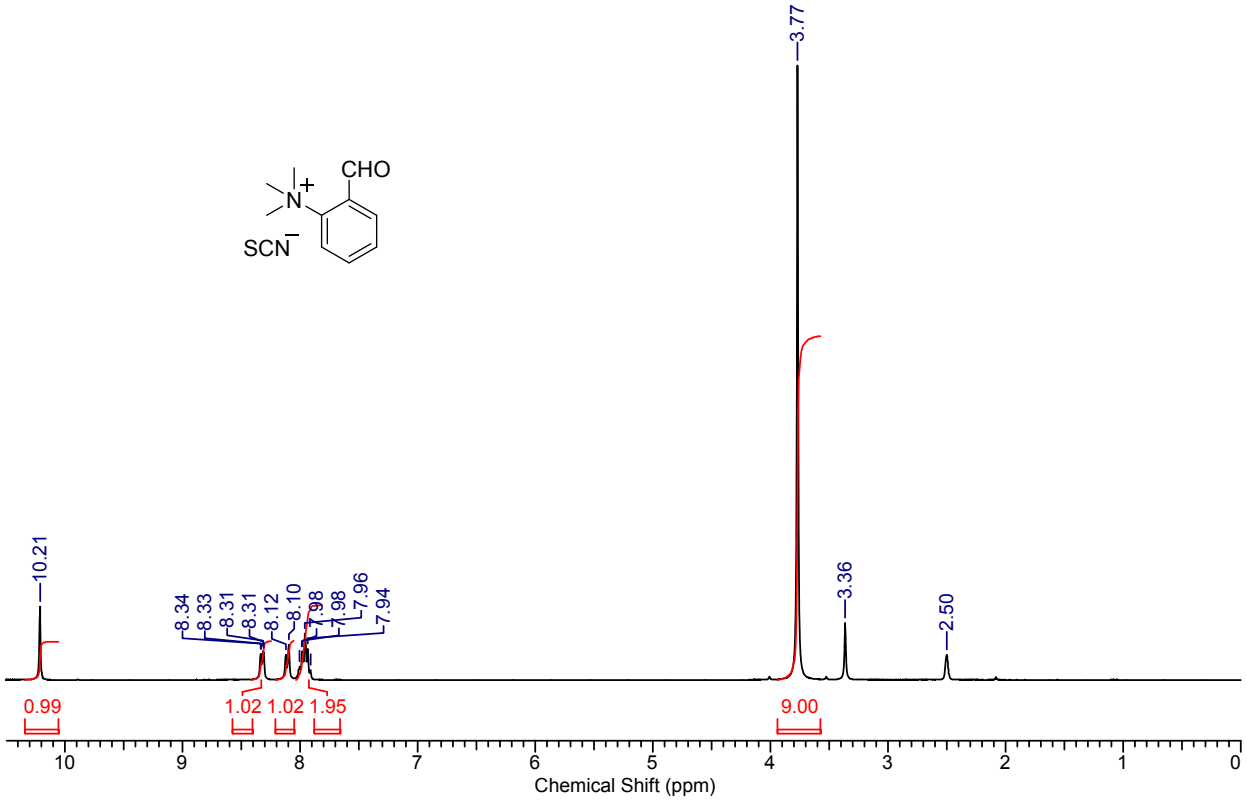

192.48
135.45
134.99
131.50
131.41
137.35
126.27
120.22
40.34
40.06
39.79
39.51
39.23
38.95
38.67
Ph
I
Br
CHO
Chemical Shift (ppm)

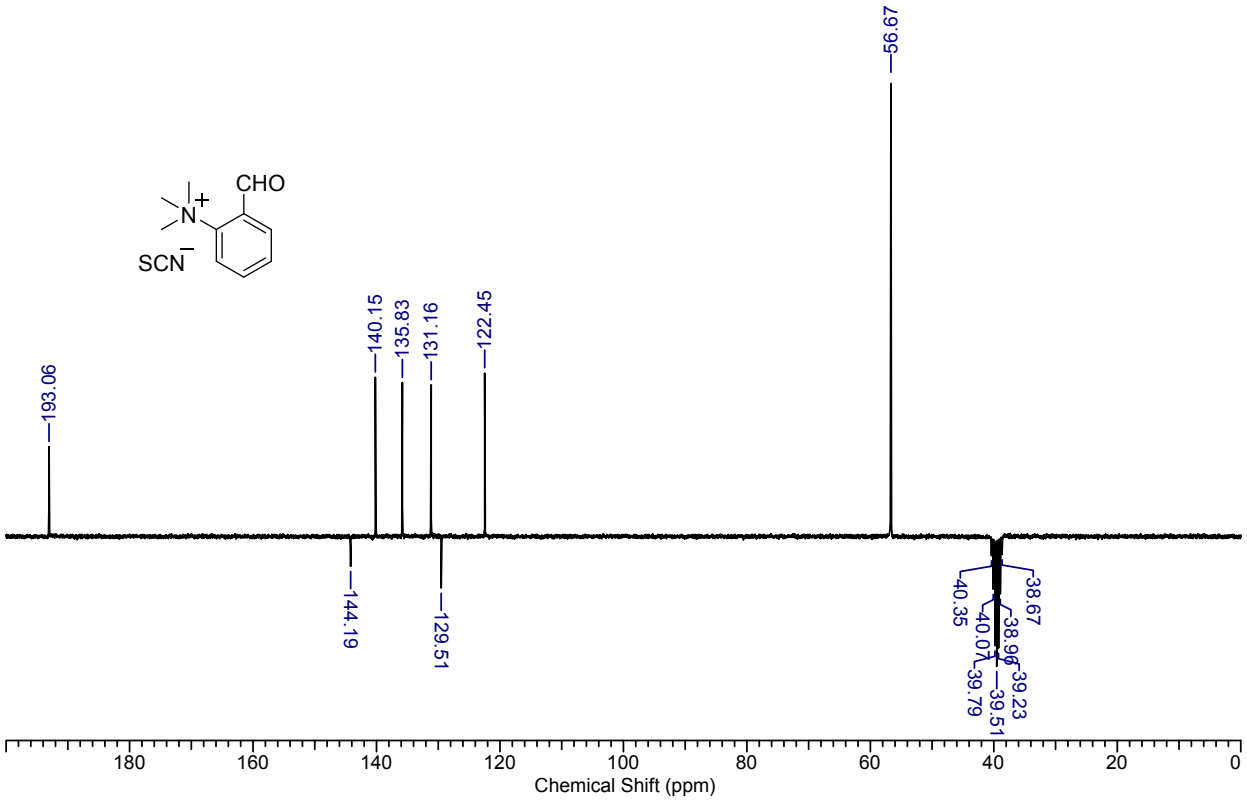

Ph
I
TfO
CHO
10.02
8.46
8.43
8.28
8.01
7.98
7.71
7.69
7.57
7.55
7.52
5.75
3.35
2.51
2.50
2.49
0.98
1.97
2.03
1.99
1.05
2.00
Chemical Shift (ppm)

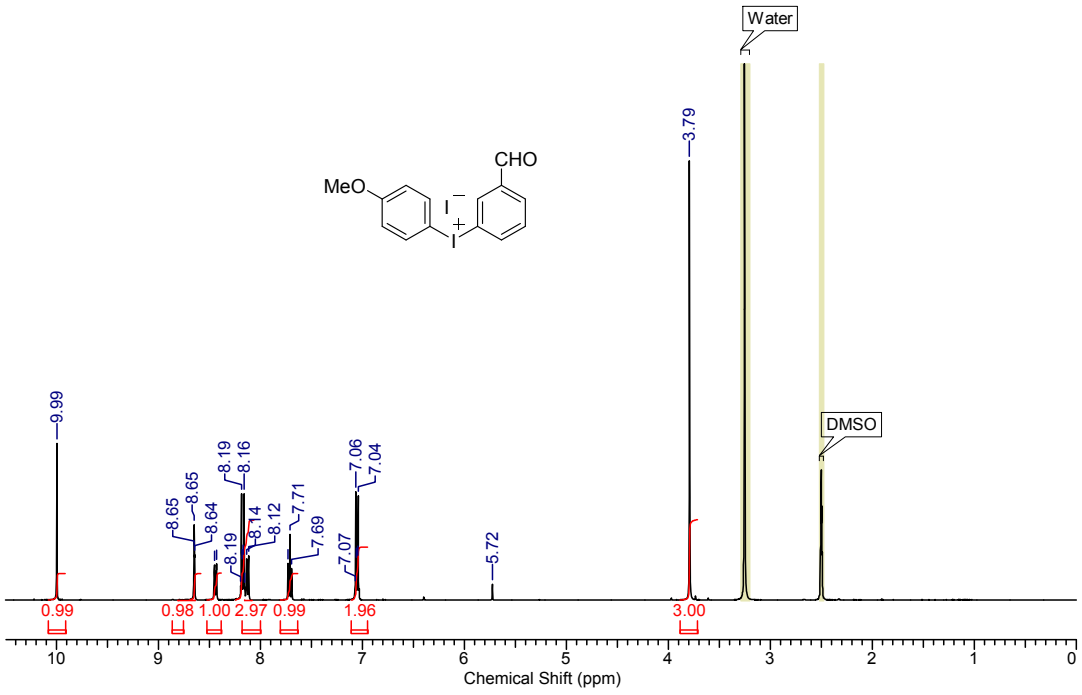

Ph
I
TfO
CHO
192.42
137.90
135.75
131.86
122.17
116.64
40.35
40.07
39.79
38.67
38.95
39.23
39.51
Chemical Shift (ppm)

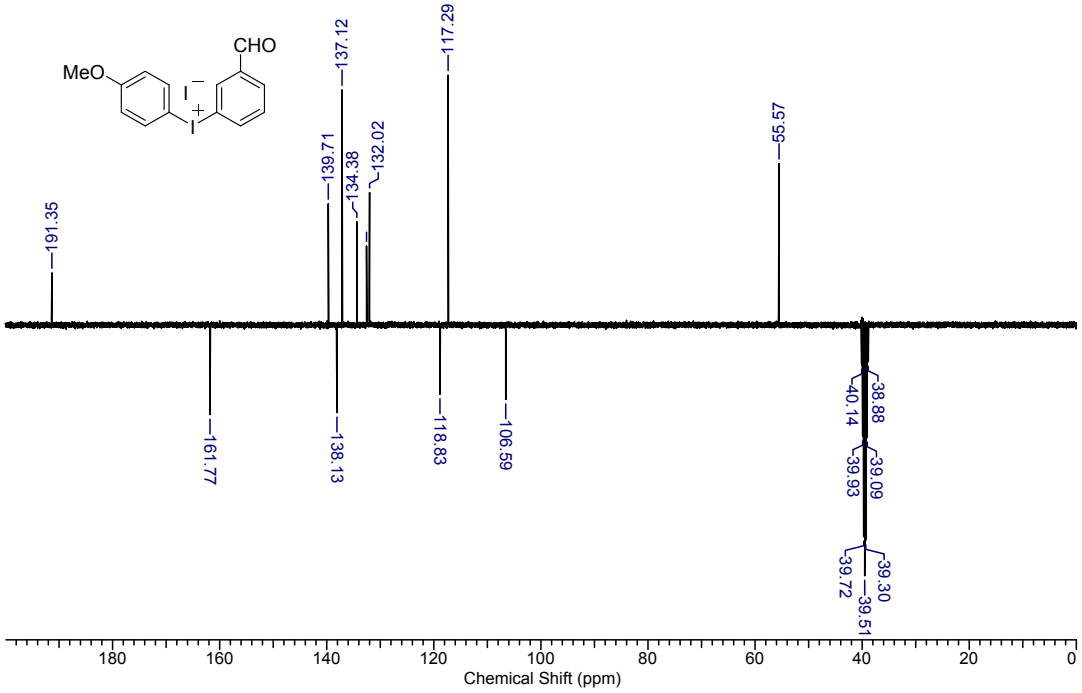

CHO
N+
ClO4−
10.21
8.33
8.31
8.30
8.08
7.98
7.97
7.96
7.96
7.93
7.93
3.76
3.42
2.51
2.50
2.49
1.00
1.02
1.01
1.97
9.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

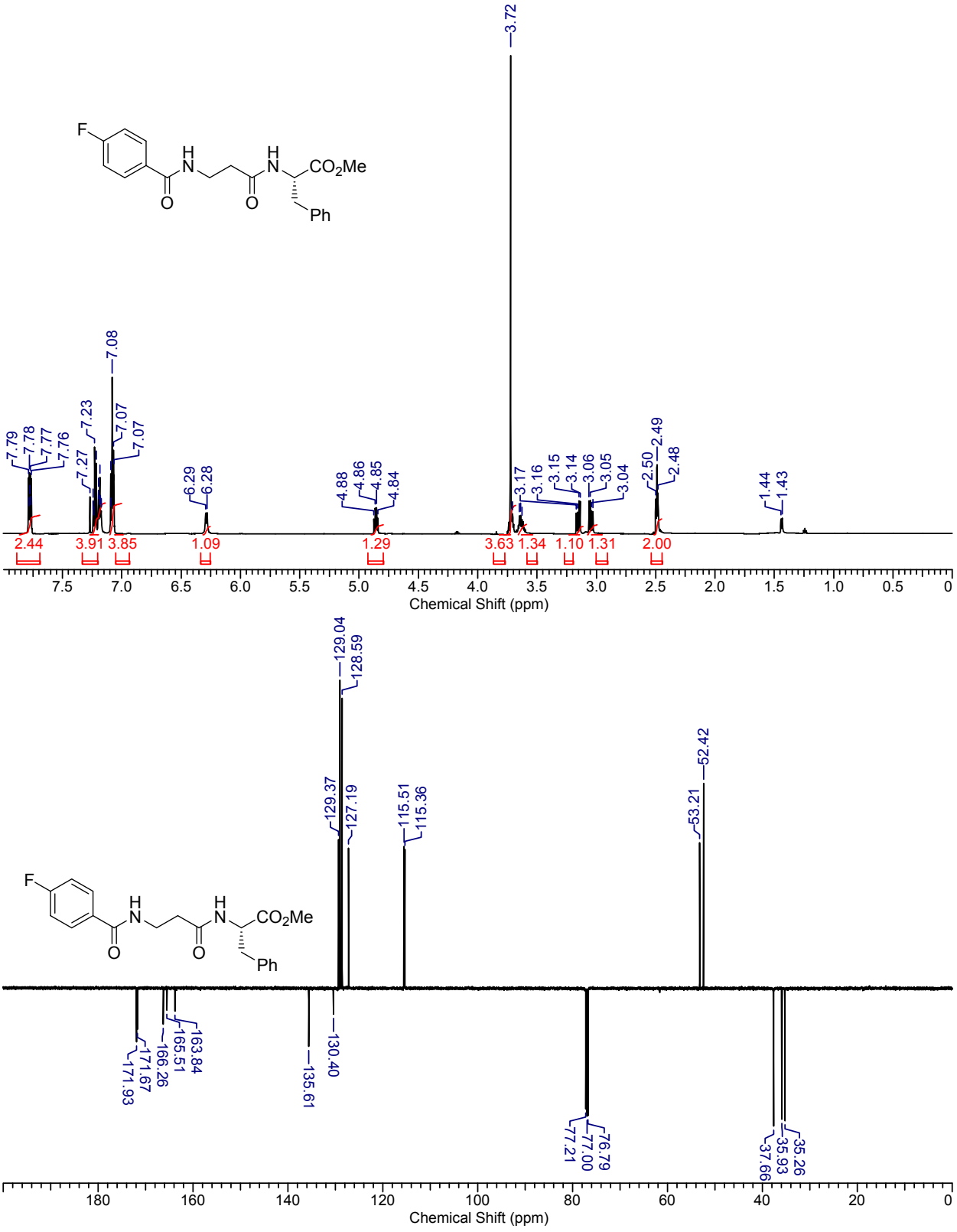

CHO
N+
ClO4−
193.06
140.13
135.81
131.16
122.43
56.68
144.23
129.54
40.35
40.07
39.79
39.51
39.23
38.95
38.67
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

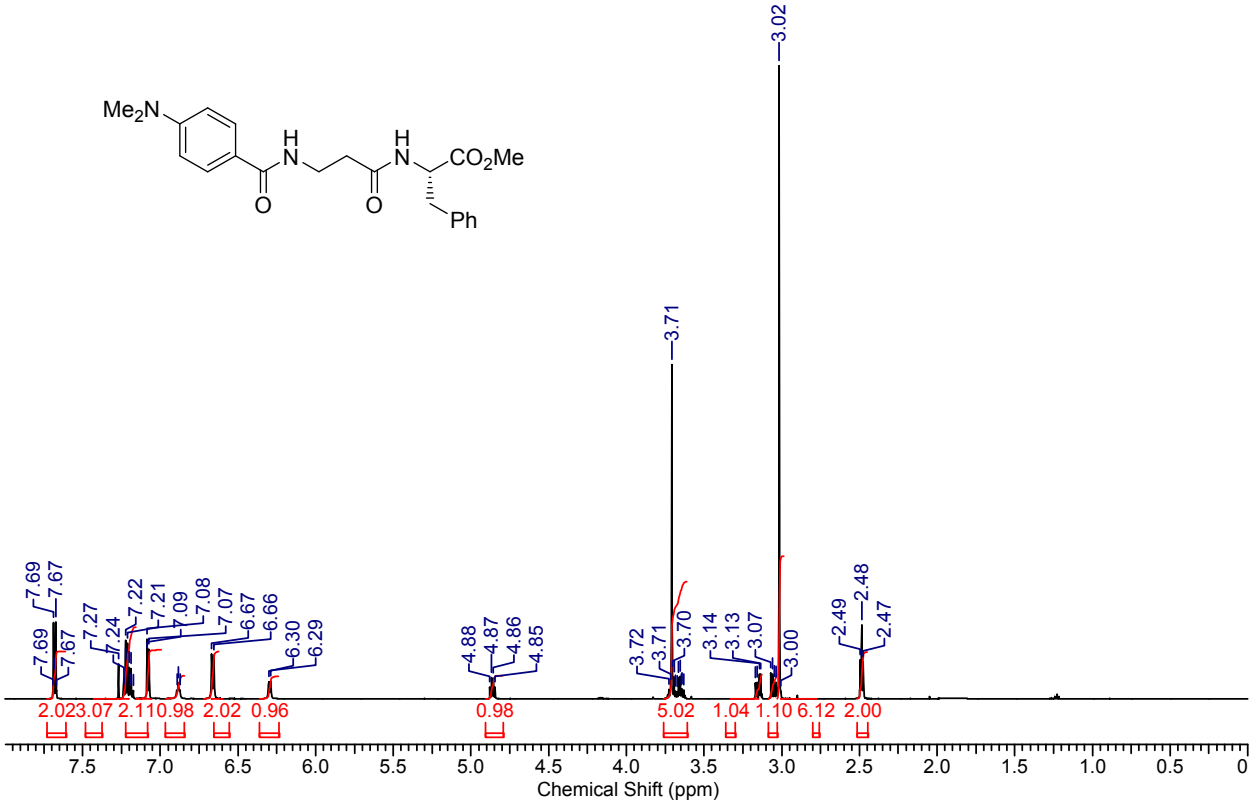

CHO
N+
SCN−
10.21
8.34
8.33
8.31
8.31
8.12
8.10
7.98
7.98
7.96
7.94
3.77
3.36
2.50
0.99
1.02
1.02
1.95
9.00
Chemical Shift (ppm)

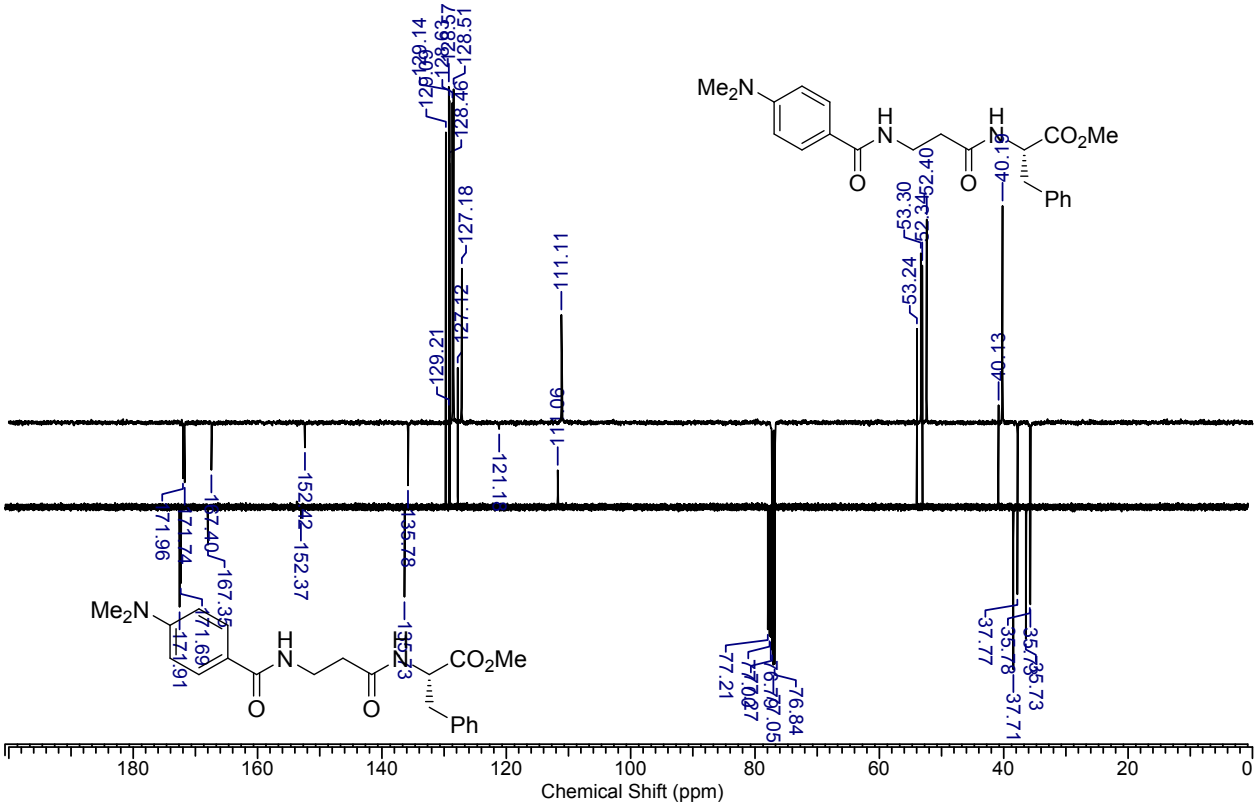

CHO
N+
SCN−
193.06
140.15
135.83
131.16
122.45
56.67
144.19
129.51
40.35
40.07
39.79
39.51
39.23
38.98
38.67
Chemical Shift (ppm)

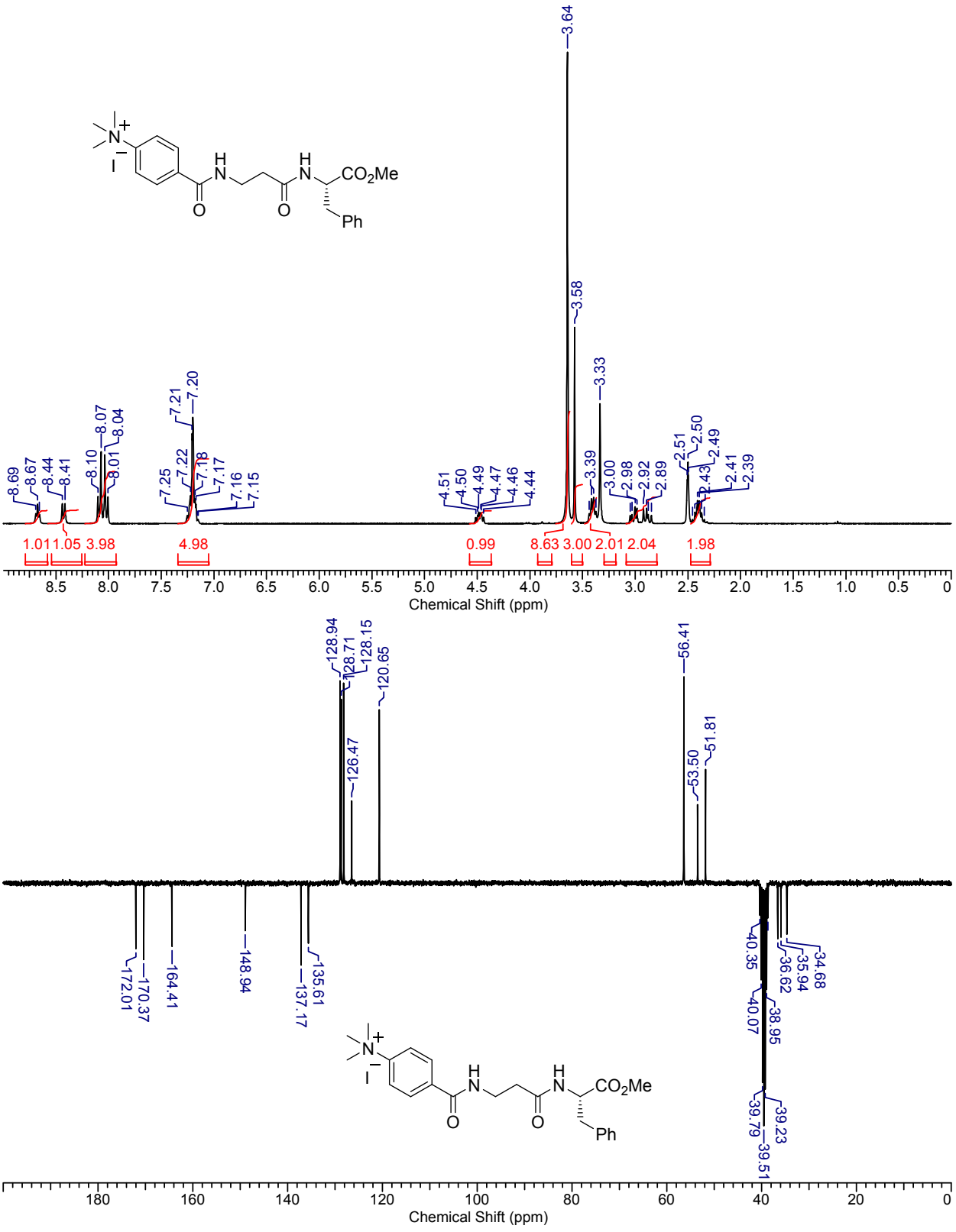

Water
DMSO
CHO
MeO
9.99
8.65
8.65
8.64
8.19
8.19
8.16
8.14
8.12
7.71
7.69
7.07
7.06
7.04
5.72
3.79
0.99
0.98
1.00
2.97
0.99
1.96
3.00
Chemical Shift (ppm)

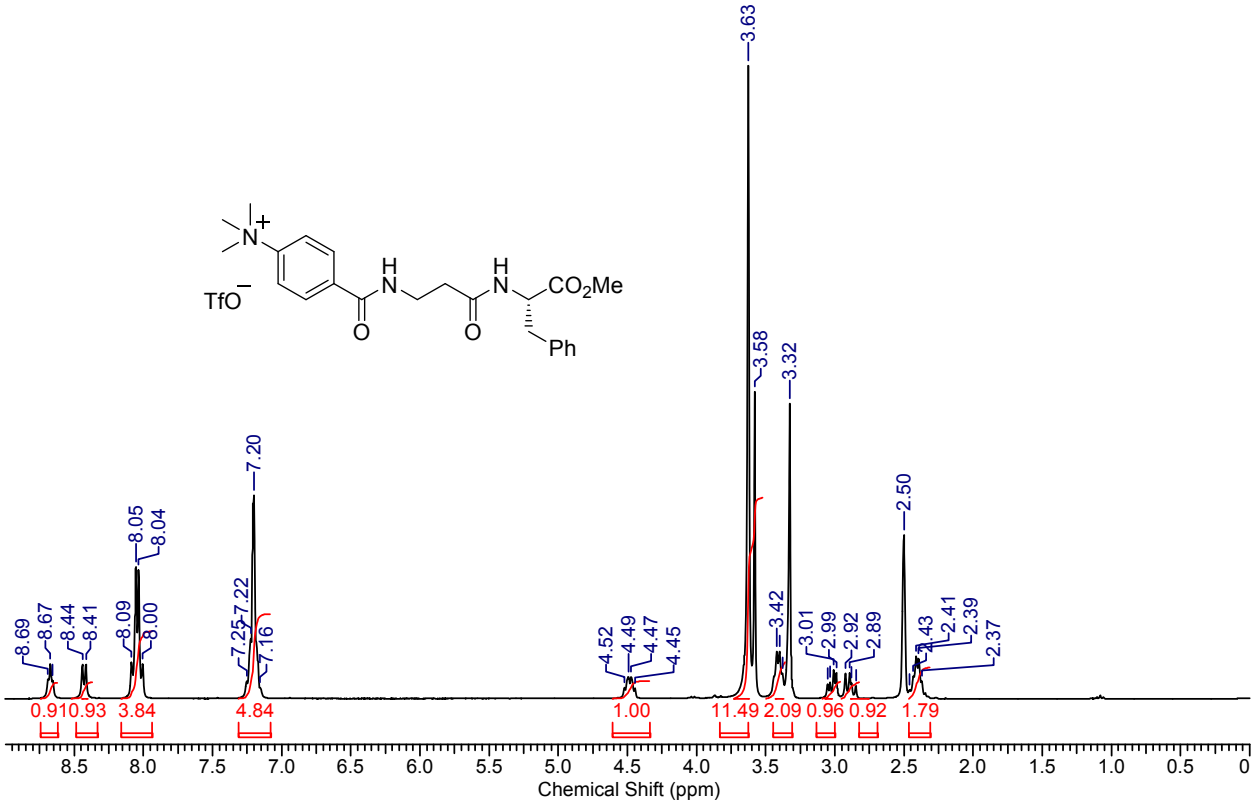

CHO
MeO
191.35
139.71
137.12
134.38
132.02
117.29
55.57
161.77
138.13
118.83
106.59
40.14
39.93
39.72
38.88
39.09
39.30
39.51
Chemical Shift (ppm)

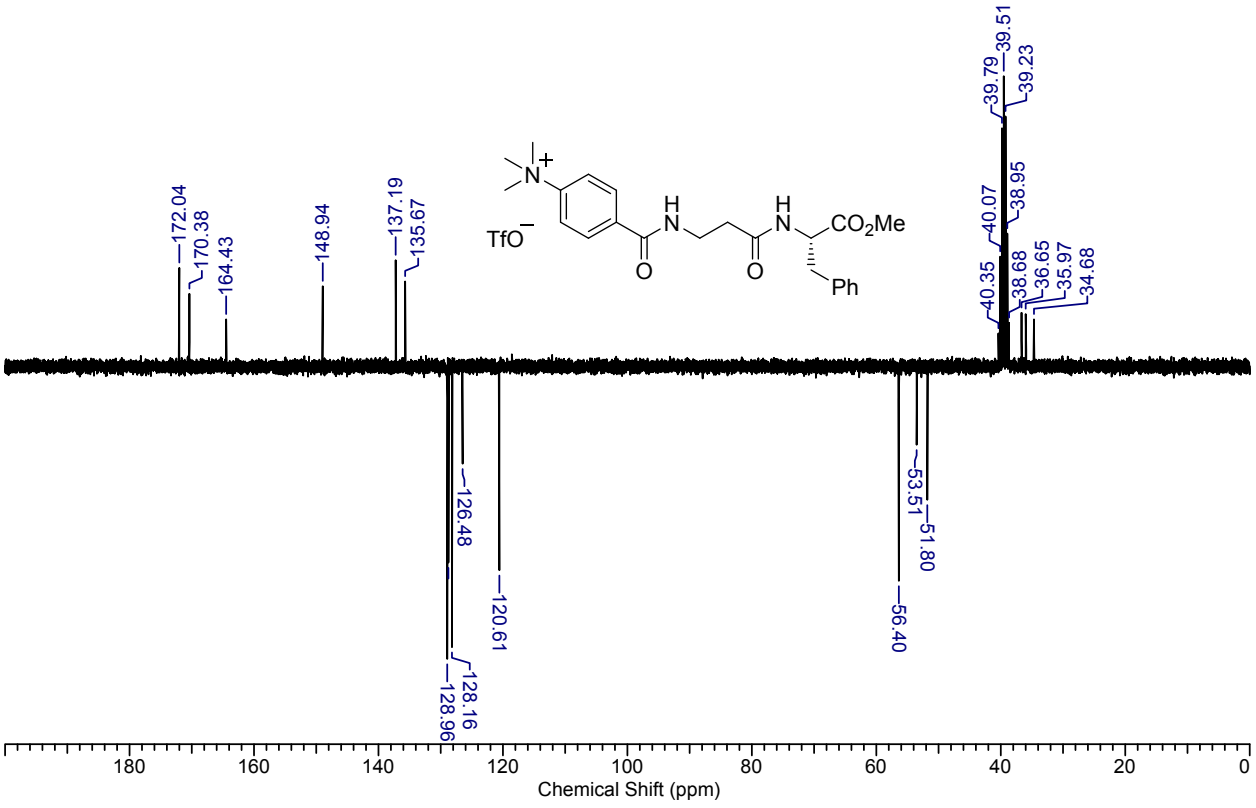

F
H
N
O
H
N
O
CO2Me
Ph
3.72
7.79
7.78
7.77
7.76
7.27
7.23
7.08
7.07
7.07
6.29
6.28
4.88
4.86
4.85
4.84
3.17
3.16
3.15
3.14
3.06
3.05
3.04
2.50
2.49
2.48
1.44
1.43
2.44
3.91
3.85
1.09
1.29
3.63
1.34
1.10
1.31
2.00
Chemical Shift (ppm)
129.04
128.59
129.37
127.19
115.51
115.36
52.42
53.21
171.93
171.67
166.26
165.51
163.84
135.61
130.40
77.21
77.00
76.79
37.66
35.93
35.26
Chemical Shift (ppm)

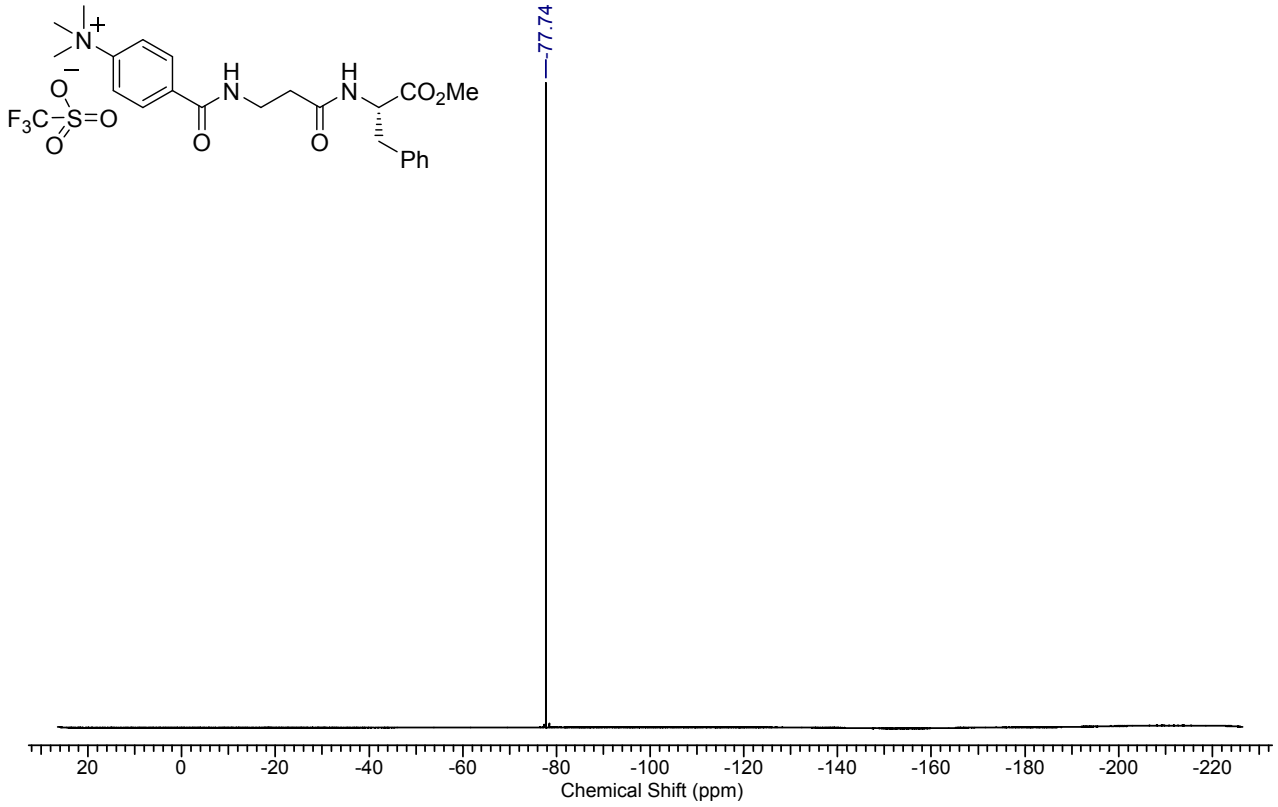

Me2N
H
N
O
H
N
O
CO2Me
Ph
3.02
3.71
7.69
7.67
7.27
7.24
7.22
7.21
7.09
7.08
7.07
6.67
6.66
6.30
6.29
4.88
4.87
4.86
4.85
3.72
3.71
3.70
3.14
3.13
3.07
3.00
2.49
2.48
2.47
2.02
3.07
2.11
0.98
2.02
0.96
0.98
5.02
1.04
1.10
6.12
2.00
Chemical Shift (ppm)

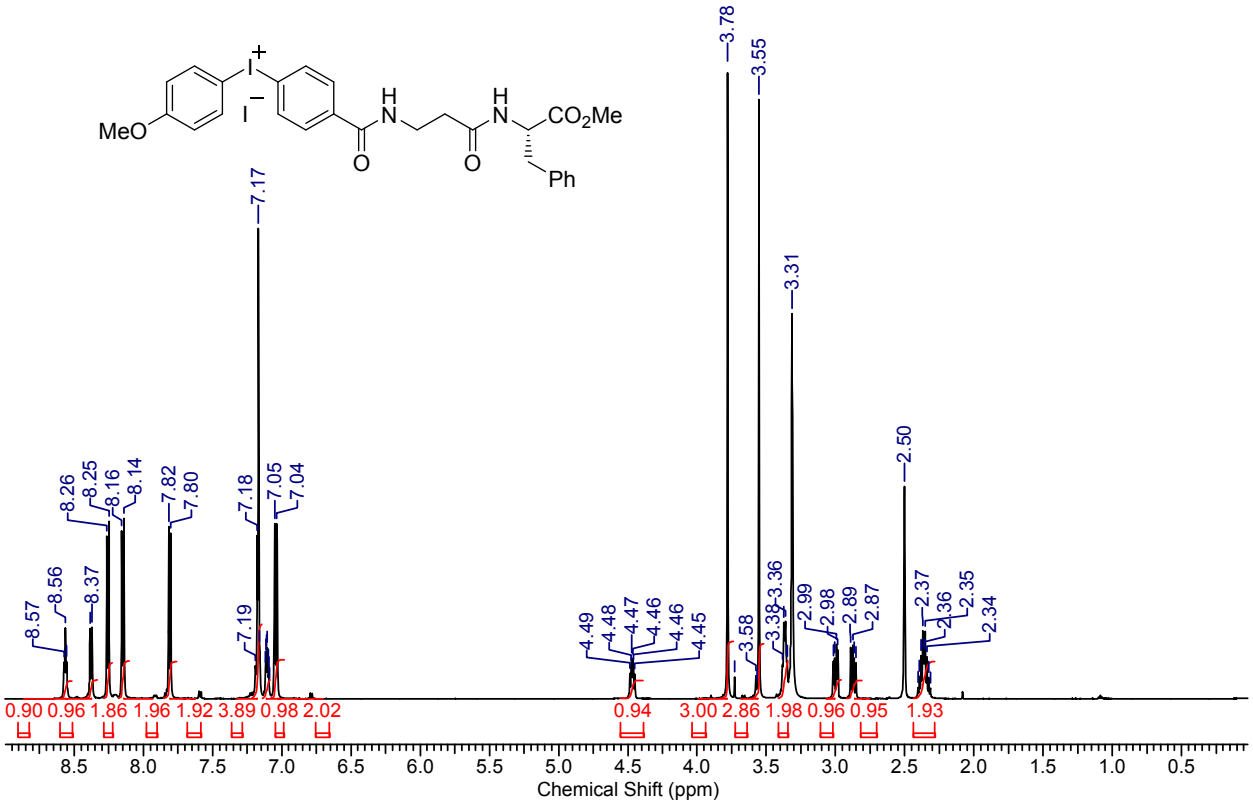

Me2N
H
N
O
H
N
O
CO2Me
Ph
129.21
127.18
127.12
111.11
53.30
52.40
53.24
40.13
152.42
152.37
135.78
77.21
76.84
37.77
35.78
37.71
Chemical Shift (ppm)

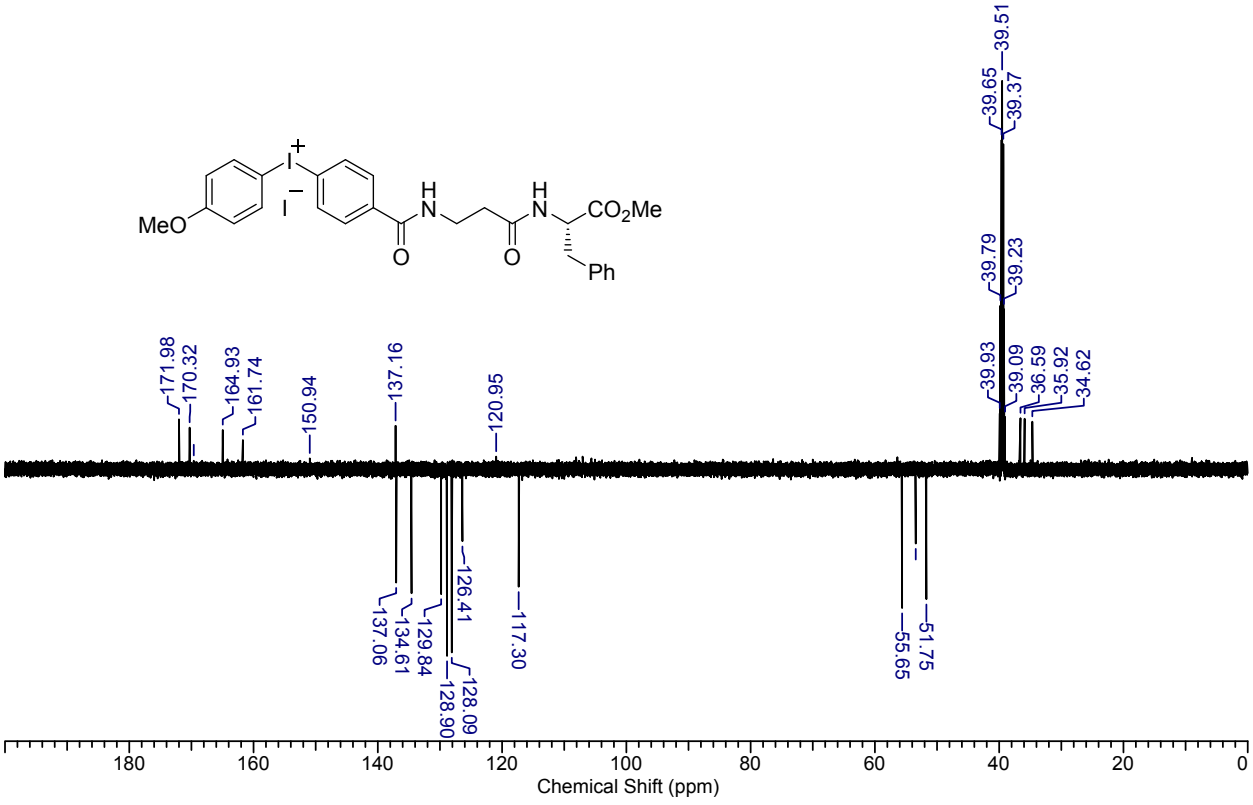

3.64
3.58
3.33
8.69
8.67
8.44
8.41
8.10
8.07
8.04
8.01
7.25
7.22
7.21
7.20
7.18
7.17
7.16
7.15
4.51
4.50
4.49
4.47
4.46
4.44
3.39
3.00
2.98
2.92
2.89
2.51
2.50
2.49
2.43
2.41
2.39
1.01 1.05 3.98
4.98
0.99
8.63 3.00 2.01 2.04
1.98
Chemical Shift (ppm)
128.94
128.71
128.15
120.65
126.47
56.41
53.50
51.81
172.01
170.37
164.41
148.94
137.17
135.61
40.35
40.07
39.79
39.51
39.23
38.95
36.62
35.94
34.68
Chemical Shift (ppm)

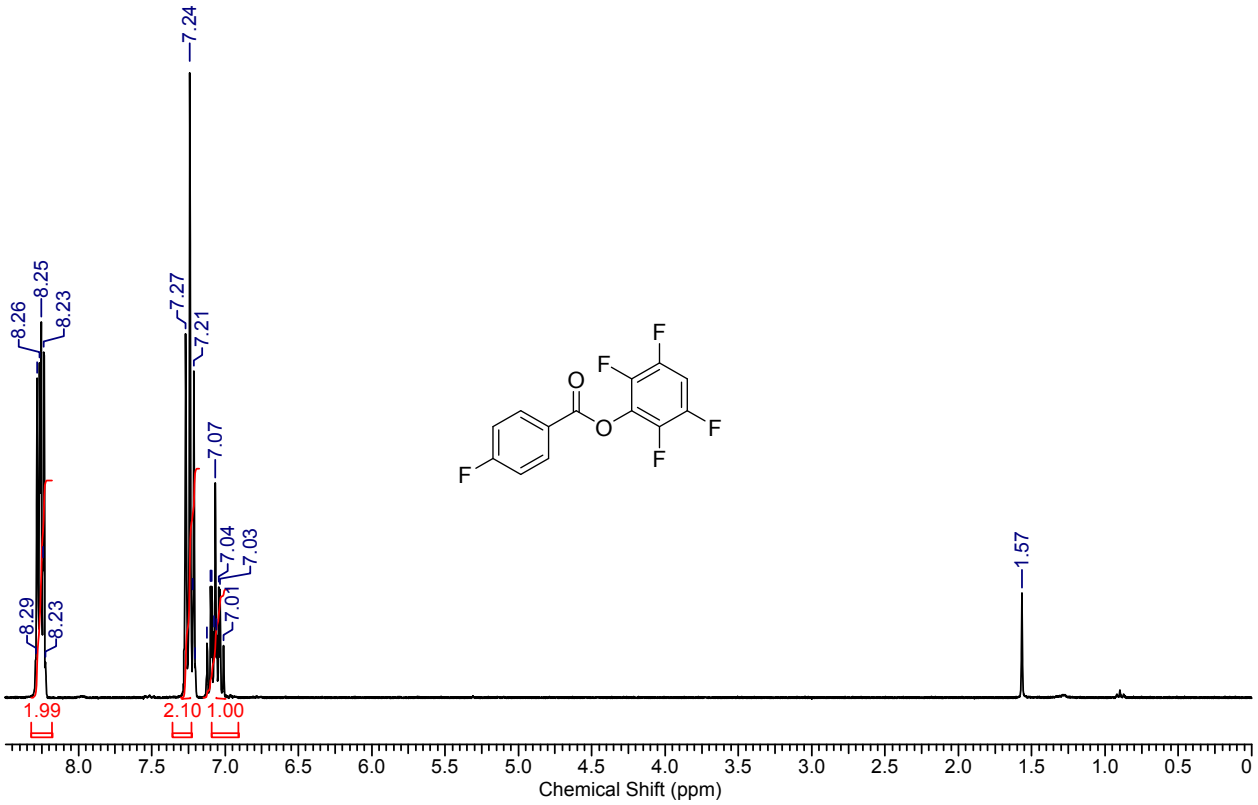

3.63
3.58
3.32
7.20
8.05
8.04
2.50
8.69
8.67
8.44
8.41
8.09
8.00
7.25
7.22
7.16
4.52
4.49
4.47
4.45
3.42
3.01
2.99
2.92
2.89
2.43
2.41
2.39
2.37
0.91 0.93 3.84 4.84 1.00 11.49 2.09 0.96 0.92 1.79
Chemical Shift (ppm)

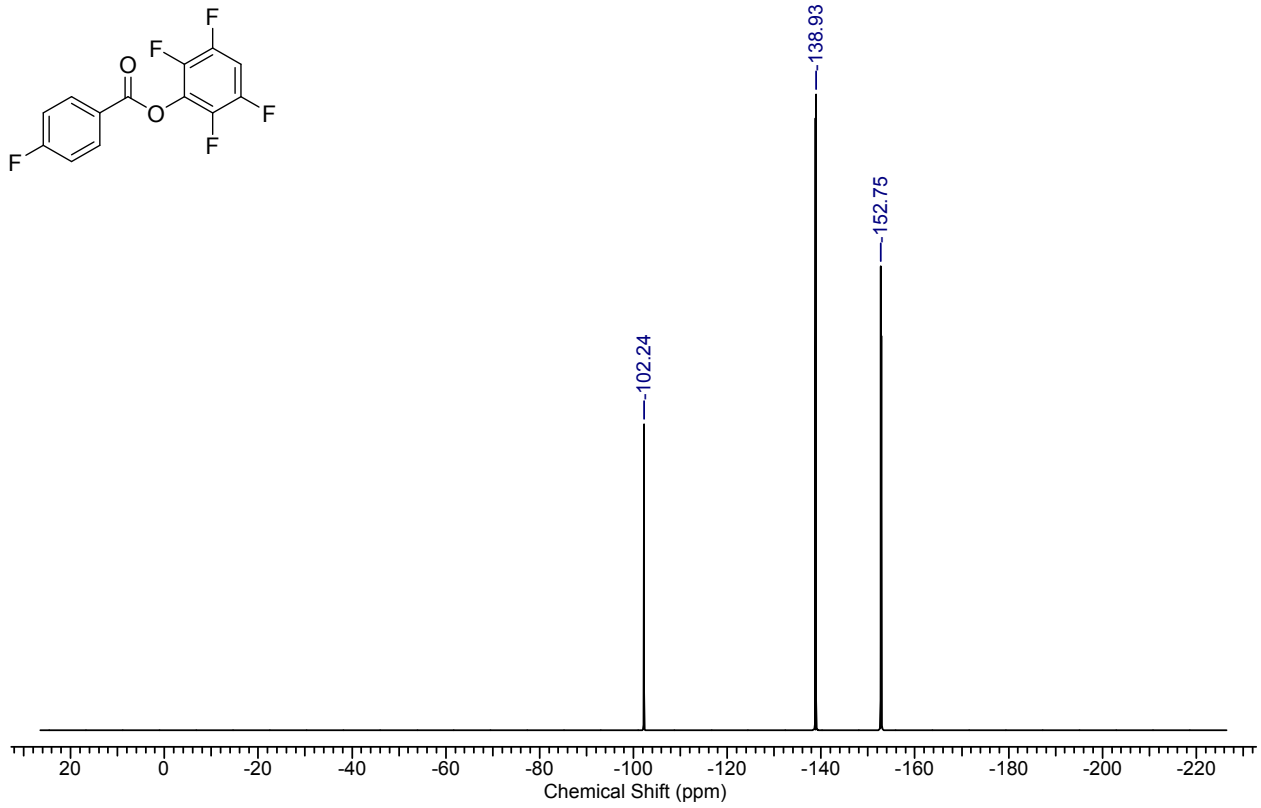

39.79
39.51
39.23
172.04
170.38
164.43
148.94
137.19
135.67
40.07
38.95
40.35
38.68
36.65
35.97
34.68
126.48
120.61
128.96
128.16
53.51
51.80
56.40
Chemical Shift (ppm)

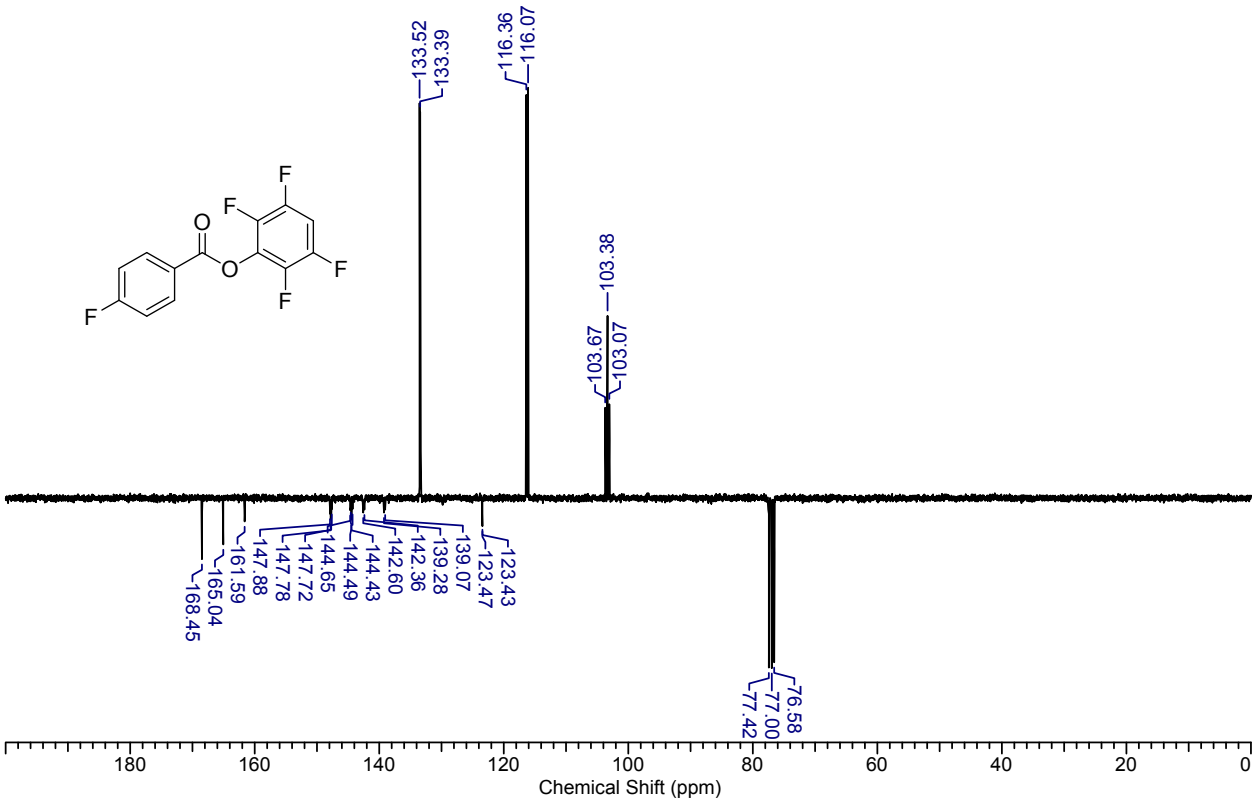

77.74
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)


MeO
I
I
H
N
O
H
N
O
CO2Me
Ph
3.78
3.55
7.17
3.31
2.50
8.26
8.25
8.16
8.14
7.82
7.80
7.18
7.05
7.04
8.57
8.56
8.37
7.19
4.49
4.48
4.47
4.46
4.45
3.58
3.39
3.36
2.99
2.98
2.89
2.87
2.37
2.36
2.35
2.34
0.90 0.96 1.86 1.96 1.92 3.89 0.98 2.02
0.94 3.00 2.86 1.98 0.96 0.95 1.93
Chemical Shift (ppm)


MeO
I
I
H
N
O
H
N
O
CO2Me
Ph
39.51
39.65
39.37
39.79
39.23
39.93
39.09
36.59
35.92
34.62
171.98
170.32
164.93
161.74
150.94
137.16
120.95
137.06
134.61
129.84
128.90
128.09
126.41
117.30
55.66
51.75
Chemical Shift (ppm)


7.24
8.26
8.25
8.23
7.27
7.21
7.07
7.04
7.03
7.01
8.29
8.23
1.57
1.99
2.10
1.00
F
F
O
O
F
F
F
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


F
F
O
O
F
F
F
138.93
152.75
102.24
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)


F
F
O
O
F
F
F
133.52
133.39
116.36
116.07
103.38
103.97
103.07
168.45
165.04
161.59
147.88
147.78
147.72
144.65
144.49
144.43
142.60
142.36
139.28
139.07
123.47
123.43
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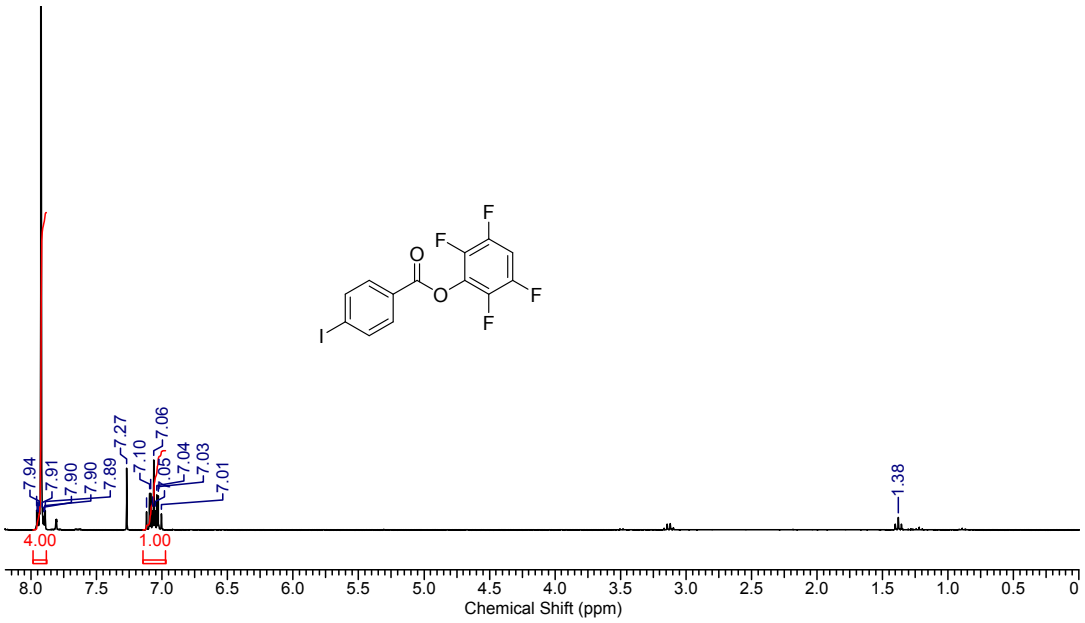
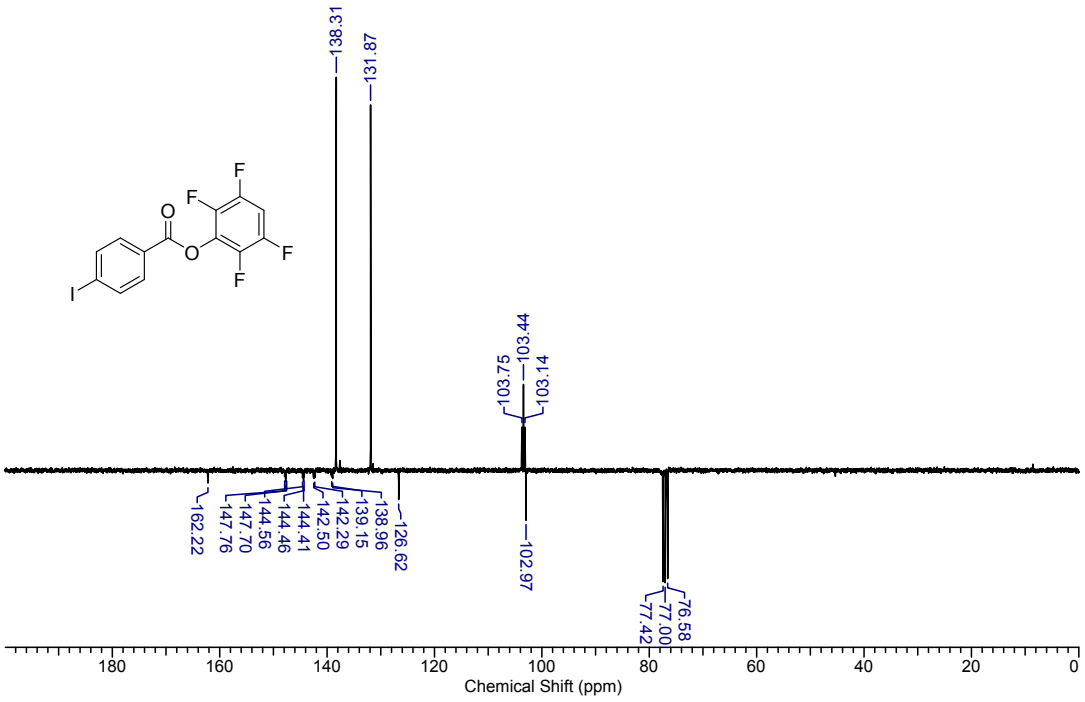
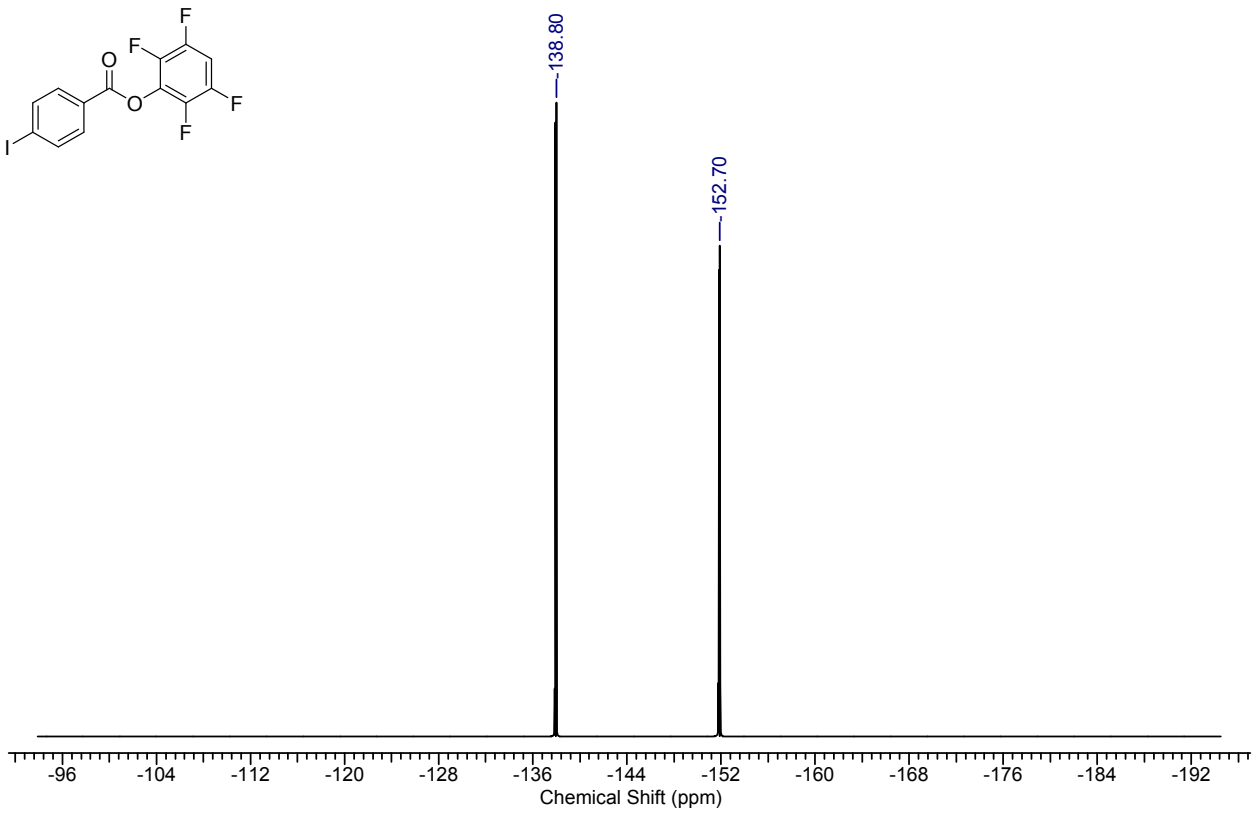
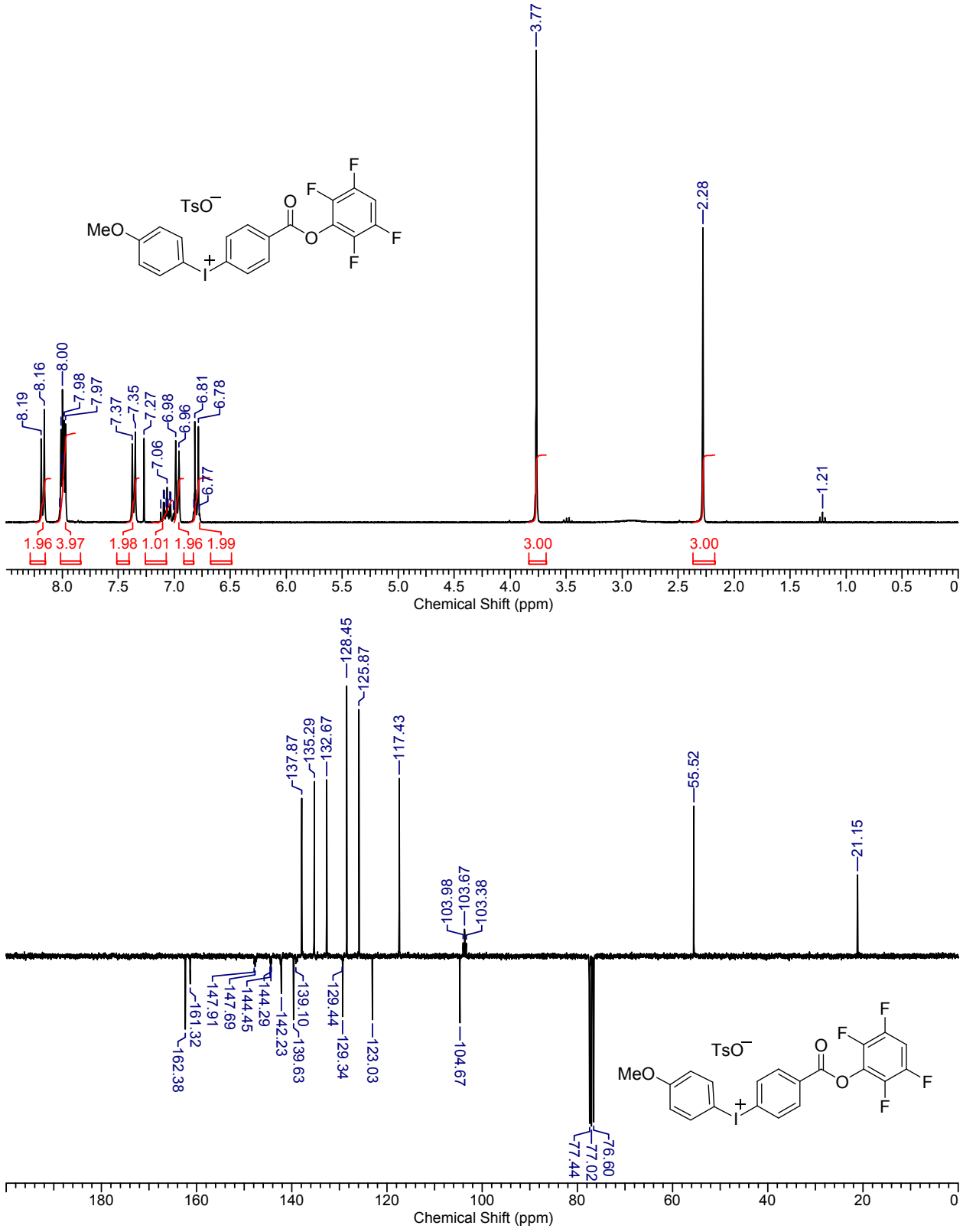
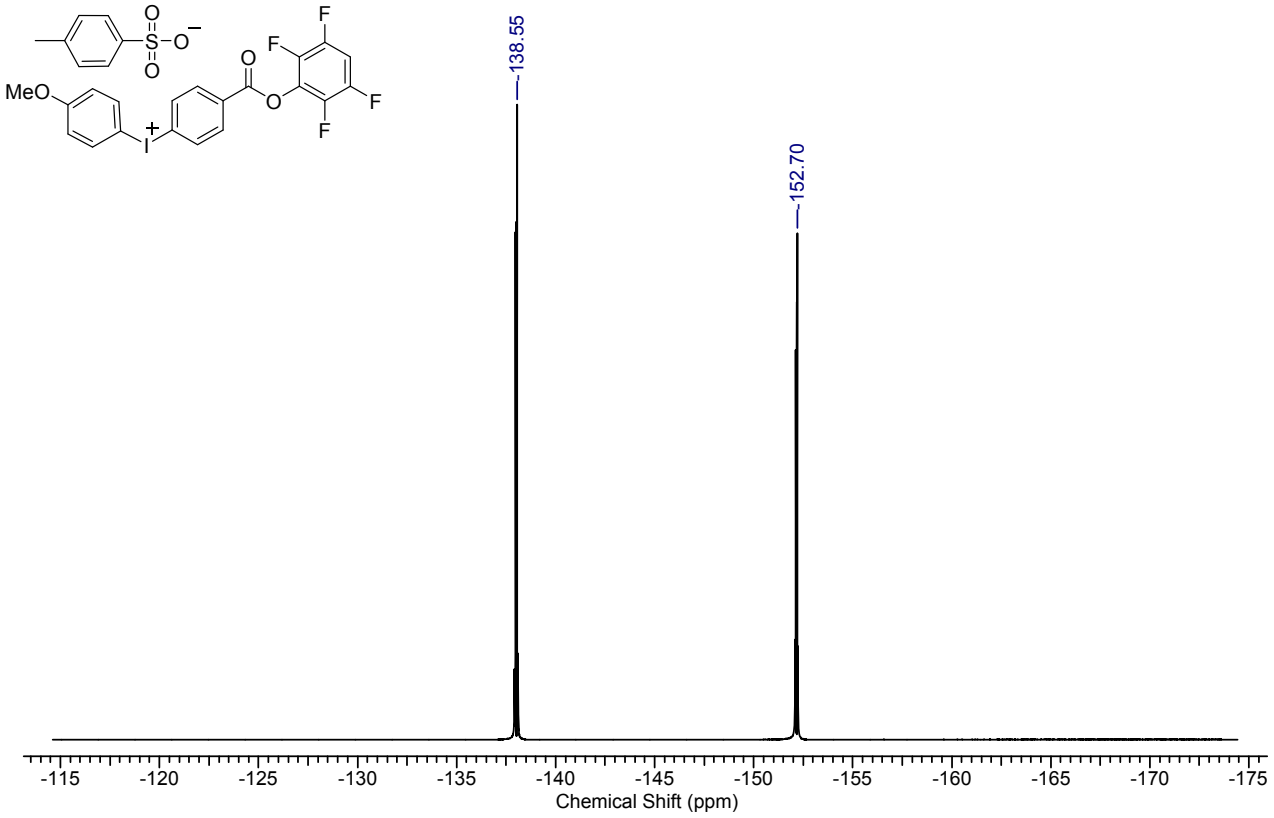
77.00
76.58
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

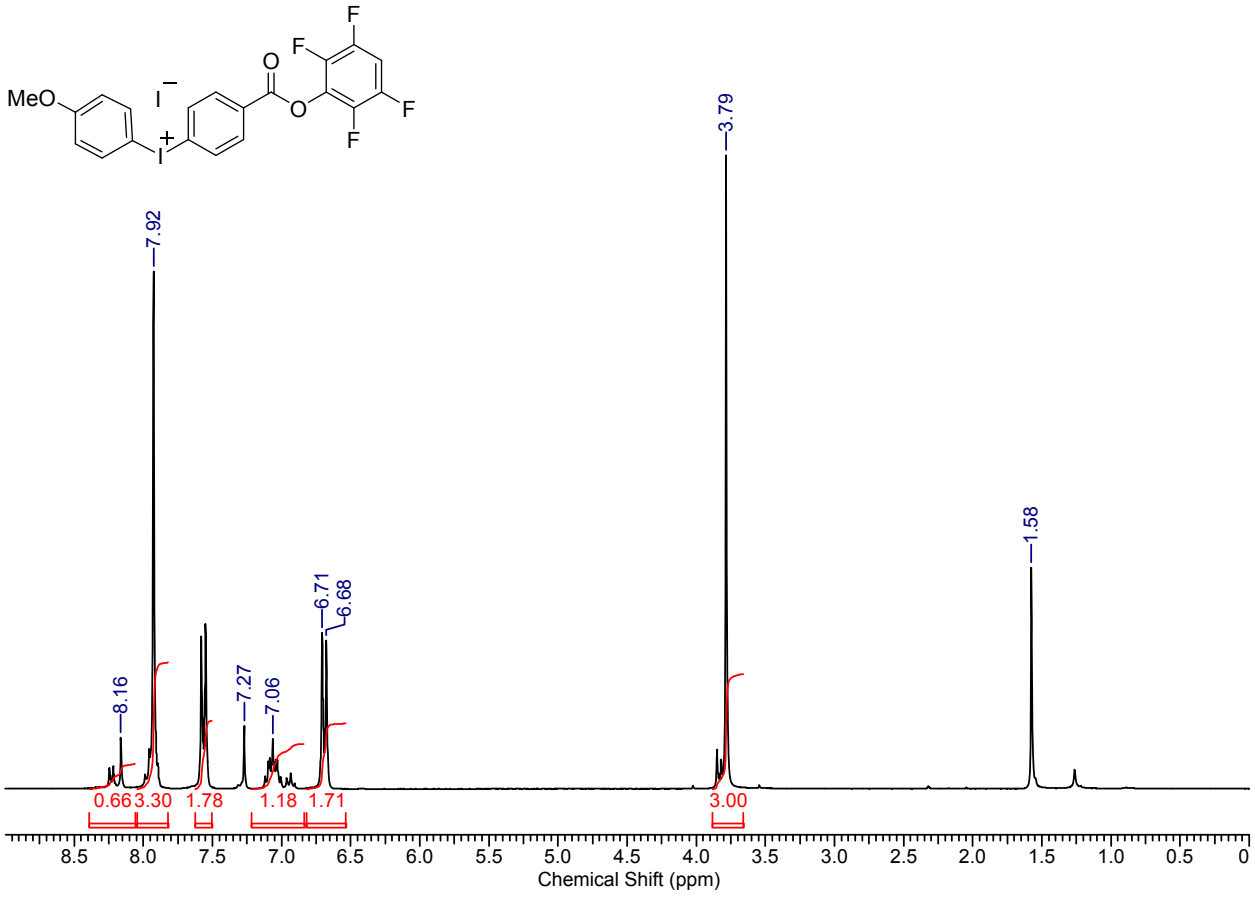

F
F
O
O
F
F
I
7.94
7.91
7.90
7.90
7.89
7.27
7.10
7.06
7.05
7.04
7.03
7.01
1.38
4.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

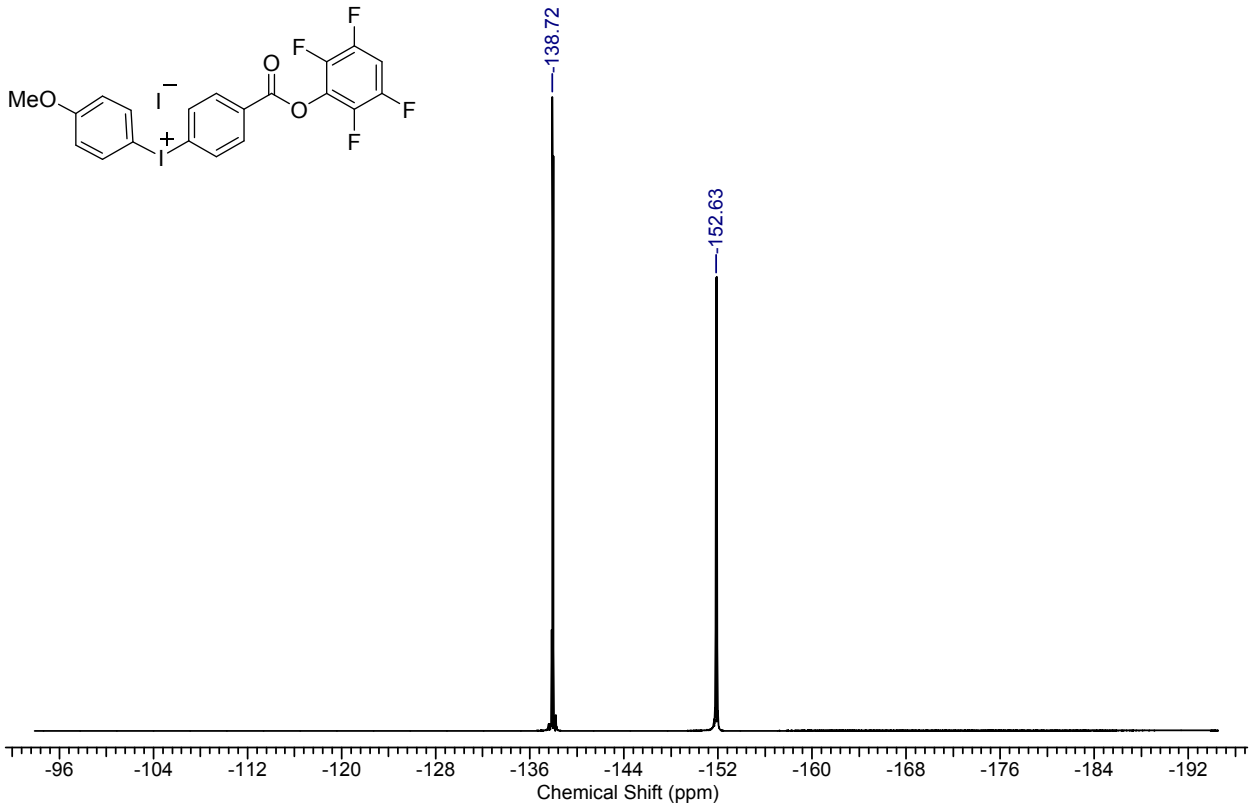

F
F
O
O
F
F
I
138.31
131.87
103.75
103.44
103.14
162.22
147.76
147.70
144.56
144.46
144.41
142.50
142.29
139.15
138.96
126.62
102.97
77.42
77.00
76.58
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

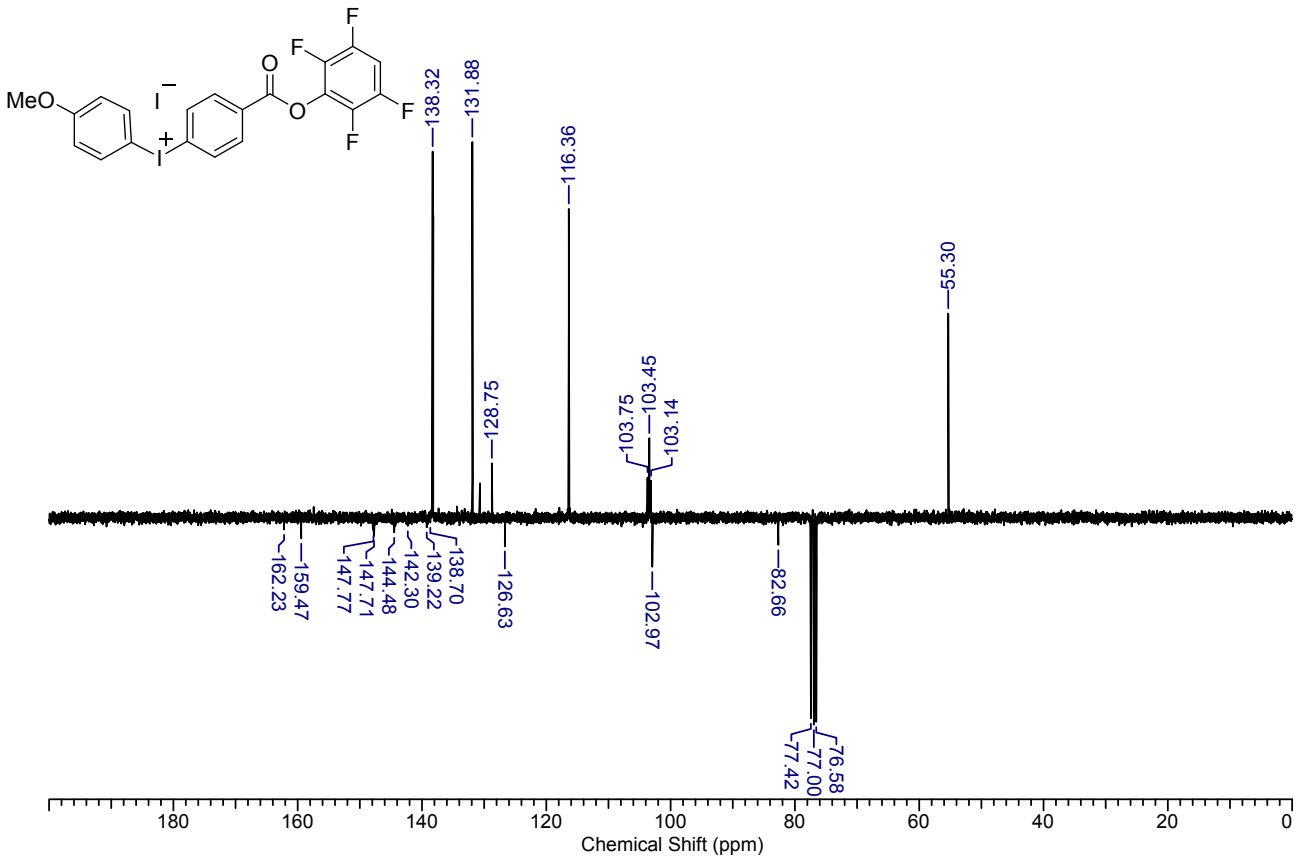

F
F
O
O
F
F
I
138.80
152.70
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

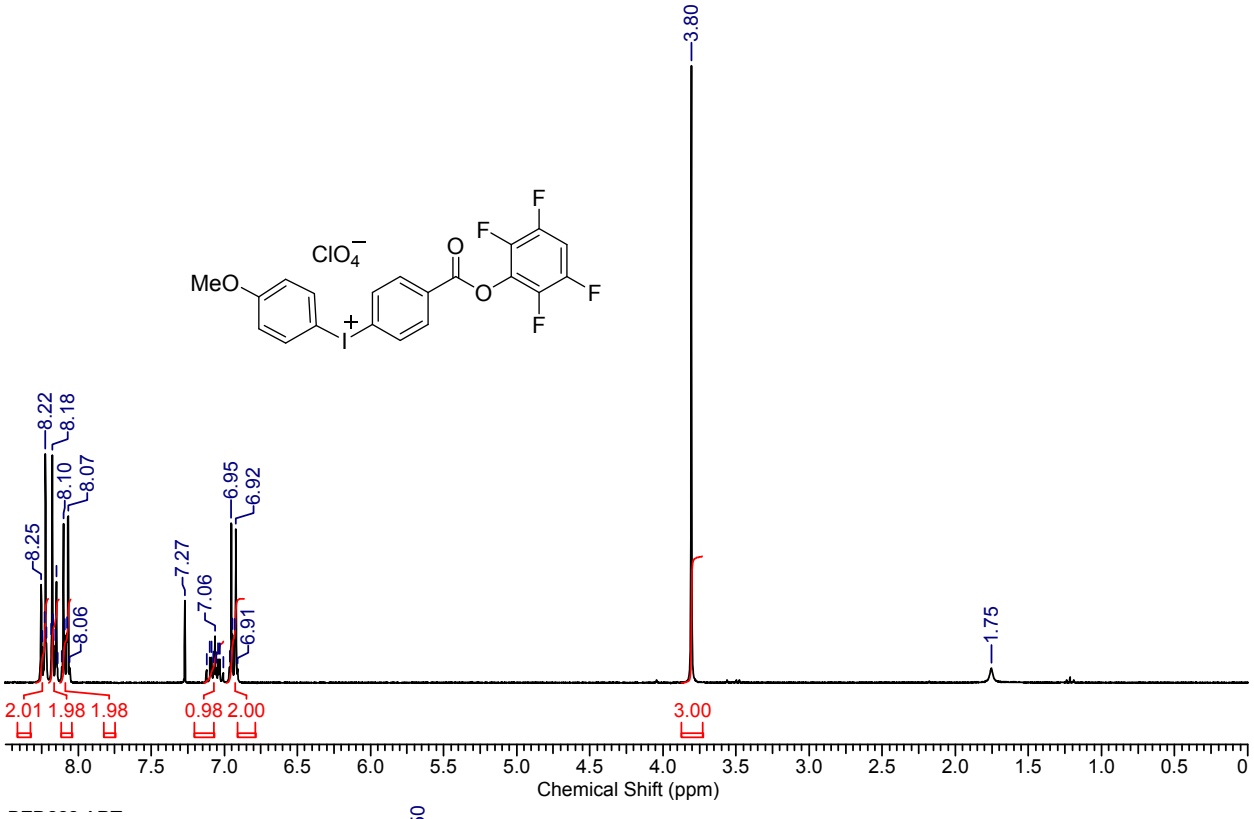

TsO⁻
MeO
I
O
O
F
F
F
F
8.19
8.16
8.00
7.98
7.97
7.37
7.35
7.27
7.06
6.98
6.96
6.81
6.78
6.77
3.77
2.28
1.21
1.96
3.97
1.98
1.01
1.96
1.99
3.00
3.00
Chemical Shift (ppm)
128.45
125.87
117.43
137.87
135.29
132.97
55.52
21.15
103.98
103.67
103.38
162.38
161.32
147.91
147.69
144.45
144.29
142.23
139.10
139.63
129.44
129.34
123.03
104.67
77.44
77.02
76.60
Chemical Shift (ppm)

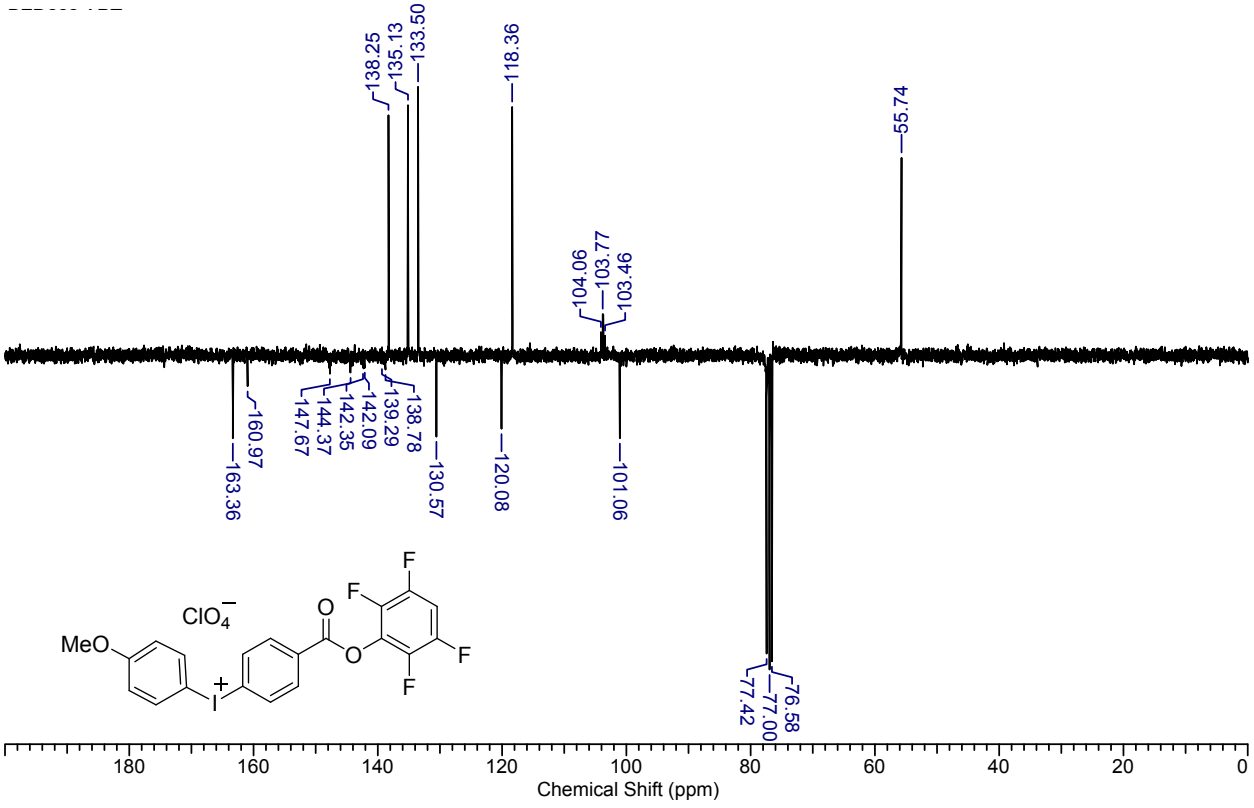

MeO
O
S
O
O
O
I
O
O
F
F
F
F
138.55
152.70
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
Chemical Shift (ppm)

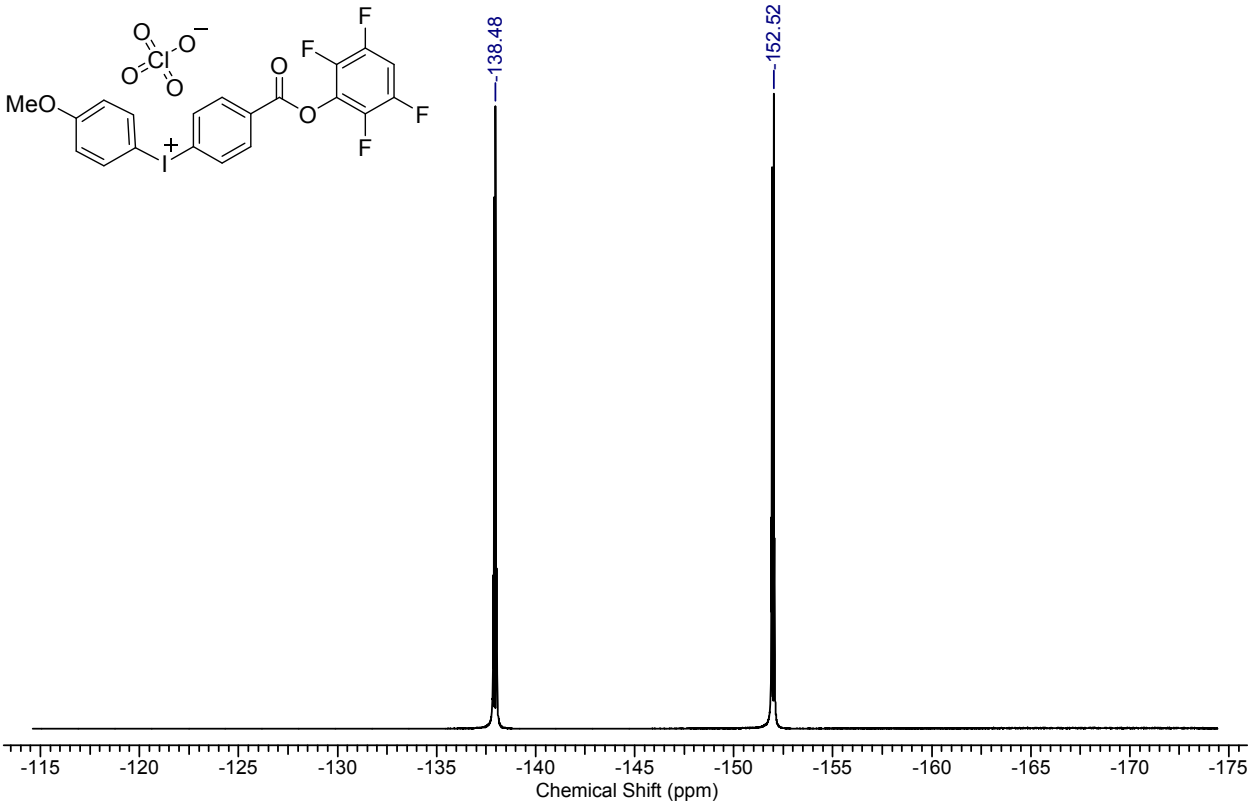

MeO
I
O
O
F
F
F
F
3.79
7.92
1.58
6.71
6.68
8.16
7.27
7.06
0.66
3.30
1.78
1.18
1.71
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

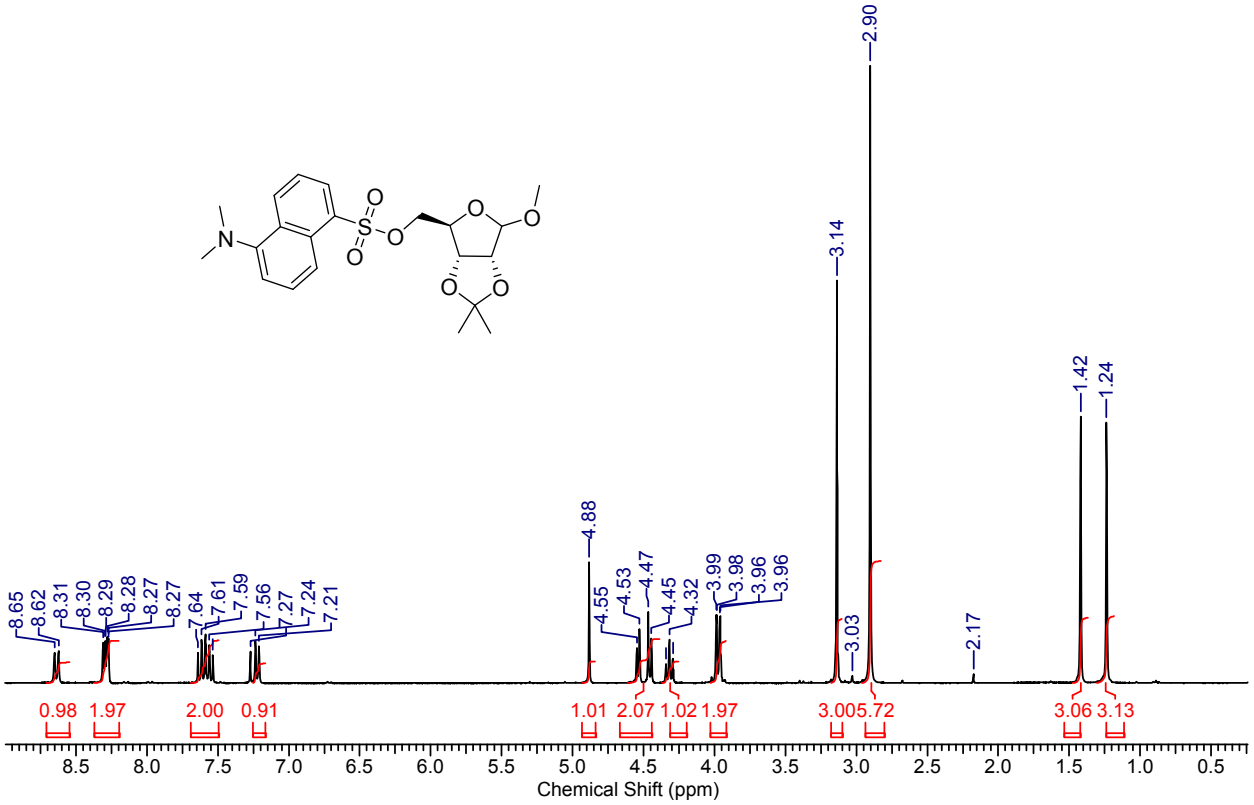

MeO
I
O
O
F
F
F
F
138.72
152.63
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

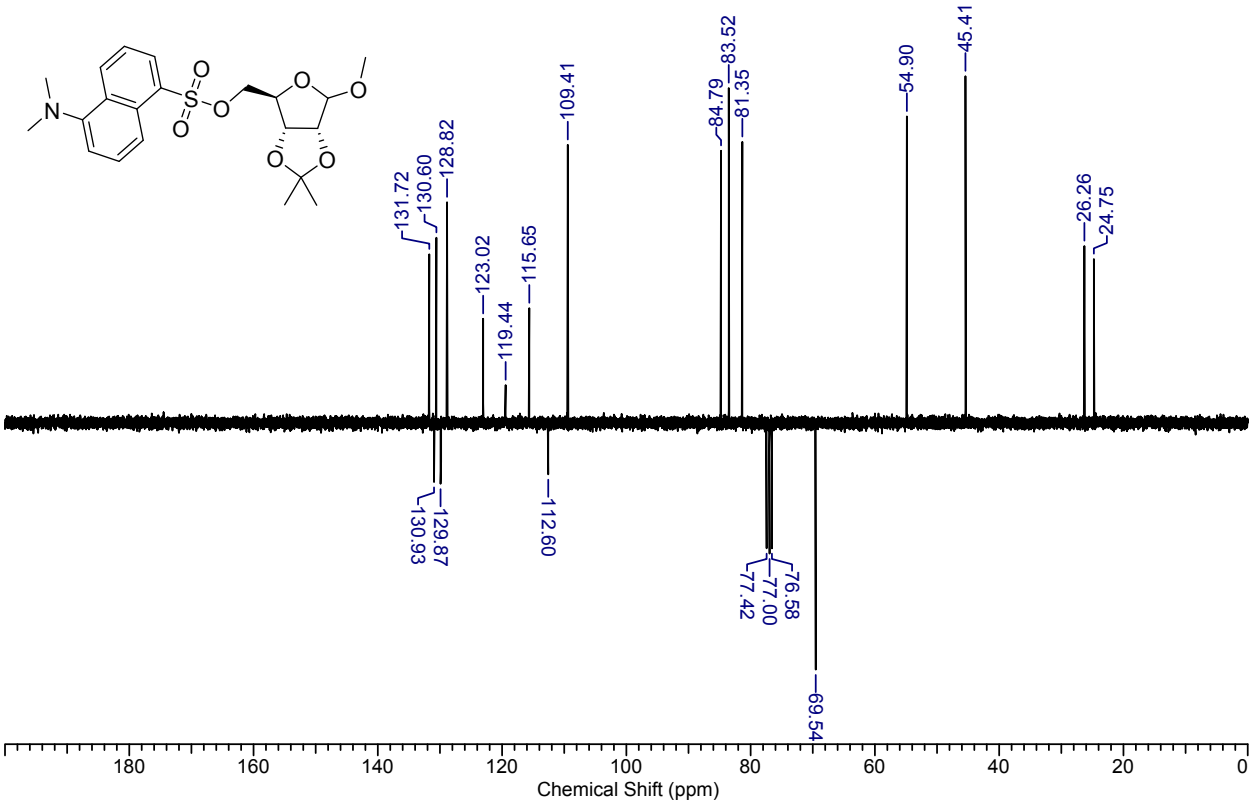

MeO
I
I
O
O
F
F
F
F
138.32
131.88
116.36
128.75
103.75
103.45
103.14
55.30
162.23
159.47
147.71
147.77
144.48
142.30
139.22
138.70
126.63
102.97
82.66
77.42
77.00
76.58
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

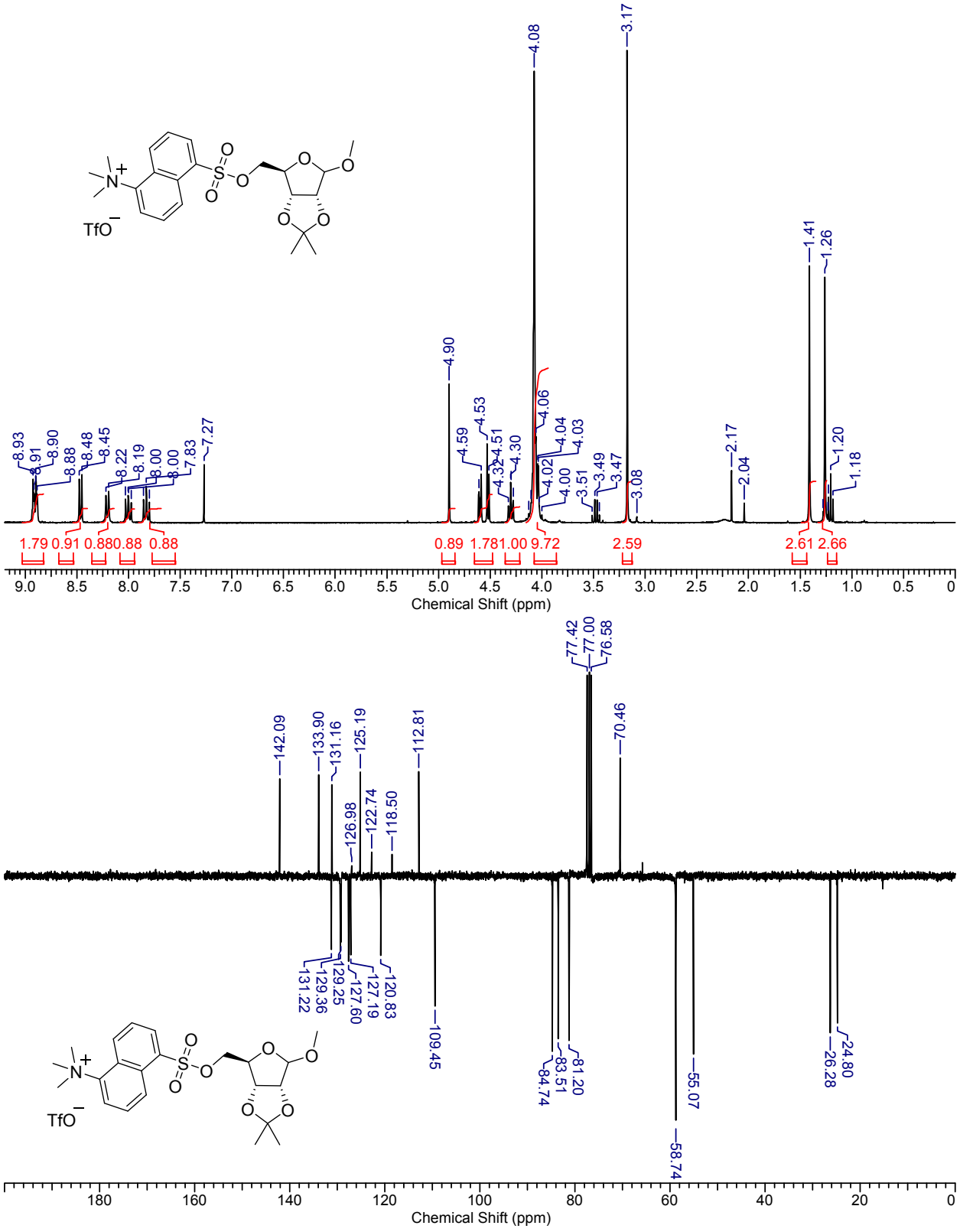

3.80
8.22
8.18
8.10
8.07
8.25
8.06
7.27
7.06
6.95
6.92
6.91
1.75
2.01 1.98 1.98 0.98 2.00 3.00
Chemical Shift (ppm)


138.25
135.13
133.50
118.36
55.74
104.06
103.77
103.46
160.97
163.36
147.67
144.37
142.35
142.09
139.29
138.78
130.57
120.08
101.06
77.42
77.00
76.58
Chemical Shift (ppm)

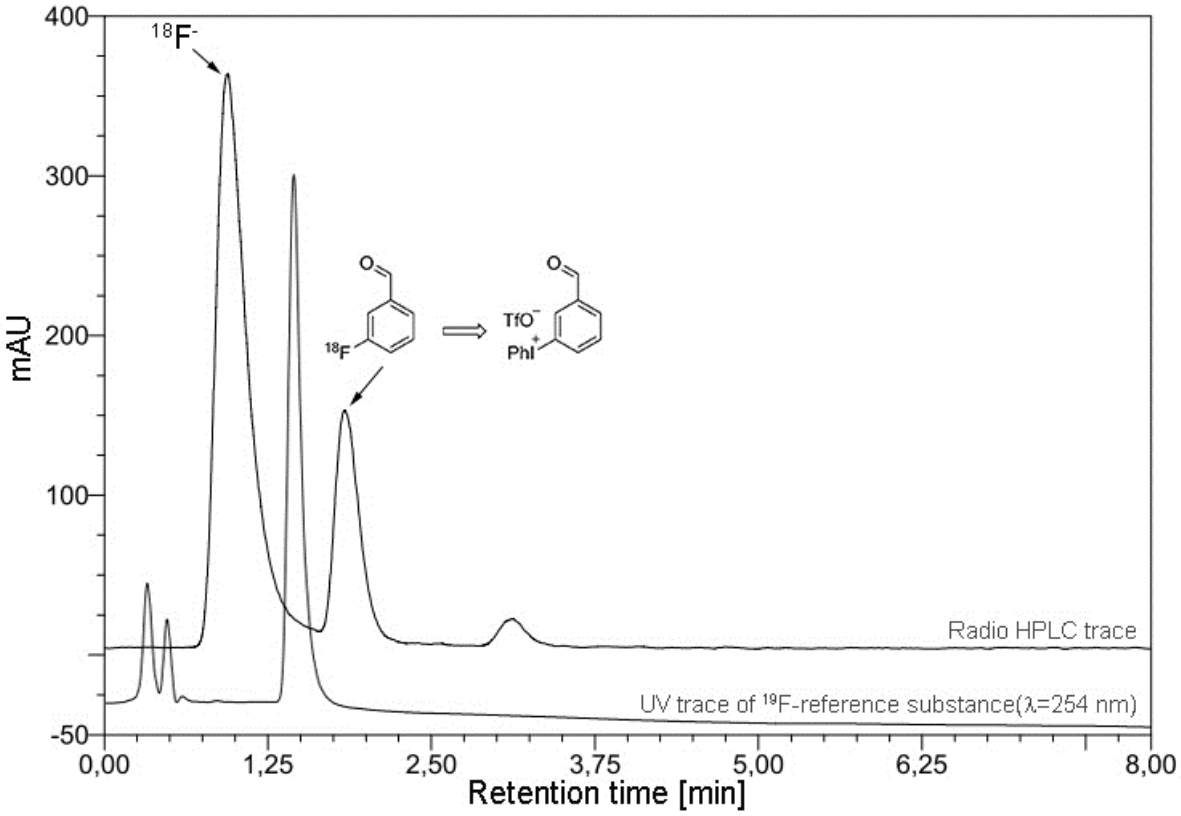

MeO
O
Cl
O
O
O
I
+
O
O
F
F
F
F
-138.48
-152.52
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
Chemical Shift (ppm)

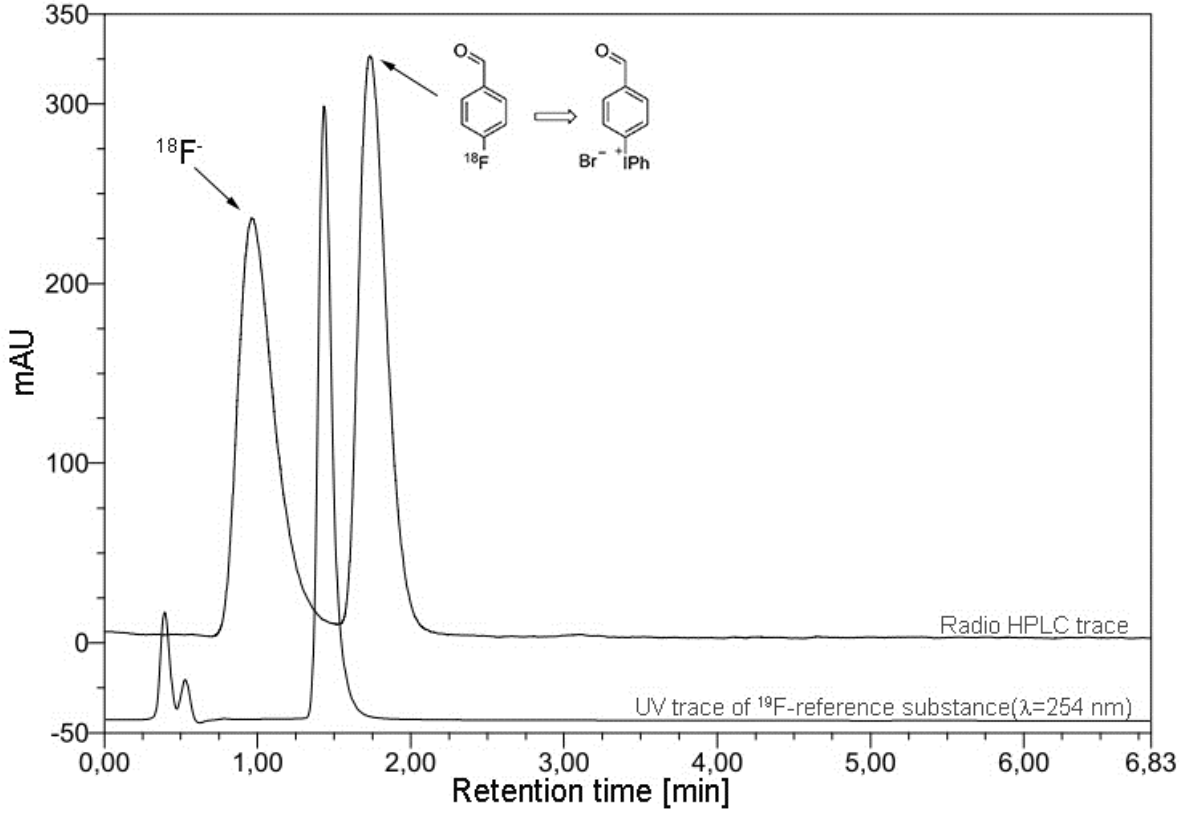

8.65
8.62
8.31
8.30
8.29
8.28
8.27
8.27
7.64
7.61
7.59
7.56
7.27
7.24
7.21
4.88
4.55
4.53
4.47
4.45
4.32
3.99
3.98
3.96
3.96
3.14
3.03
2.90
2.17
1.42
1.24
0.98
1.97
2.00
0.91
1.01
2.07
1.02
1.97
3.00
5.72
3.06
3.13
Chemical Shift (ppm)

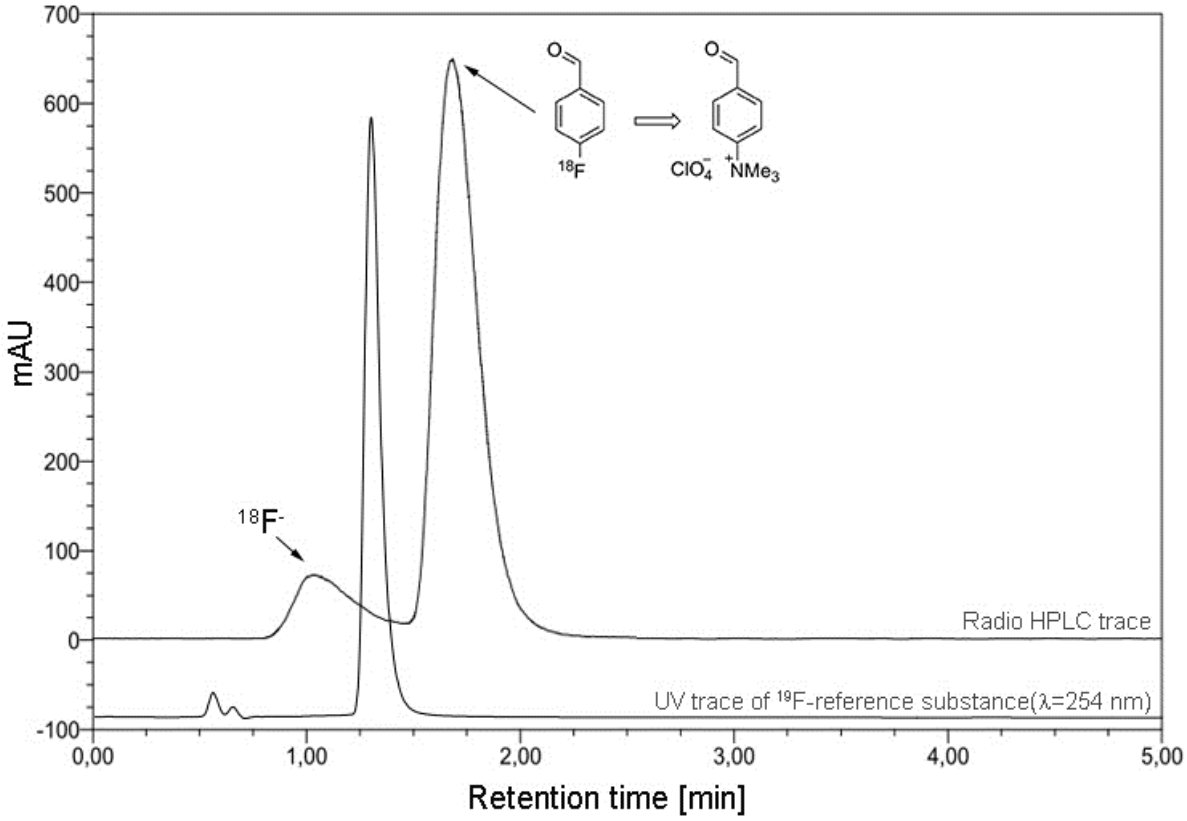

131.72
130.60
128.82
123.02
119.44
115.65
109.41
84.79
83.52
81.35
54.90
45.41
26.26
24.75
130.93
129.87
112.60
77.42
77.00
76.58
69.54
Chemical Shift (ppm)

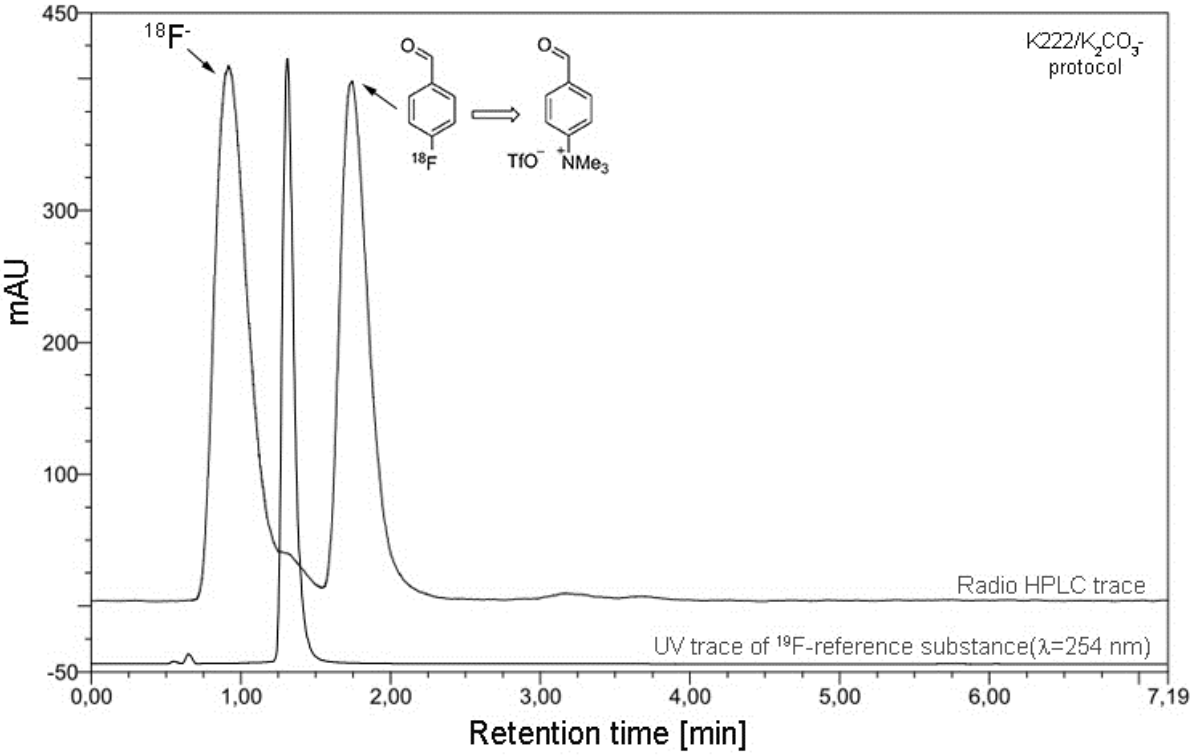

TfO−
8.93
8.91
8.90
8.88
8.48
8.45
8.22
8.19
8.00
8.00
7.83
7.27
4.90
4.59
4.53
4.51
4.32
4.30
4.08
4.06
4.04
4.03
4.02
4.00
3.51
3.49
3.47
3.17
3.08
2.17
2.04
1.41
1.26
1.20
1.18
1.79 0.91 0.88 0.88 0.88
0.89 1.78 1.00 9.72
2.59
2.61 2.66
Chemical Shift (ppm)
142.09
133.90
131.16
125.19
126.98
122.74
118.50
112.81
77.42
77.00
76.58
70.46
131.22
129.36
129.25
127.60
127.19
120.83
109.45
84.74
83.51
81.20
58.74
55.07
26.28
24.80
TfO−
Chemical Shift (ppm)

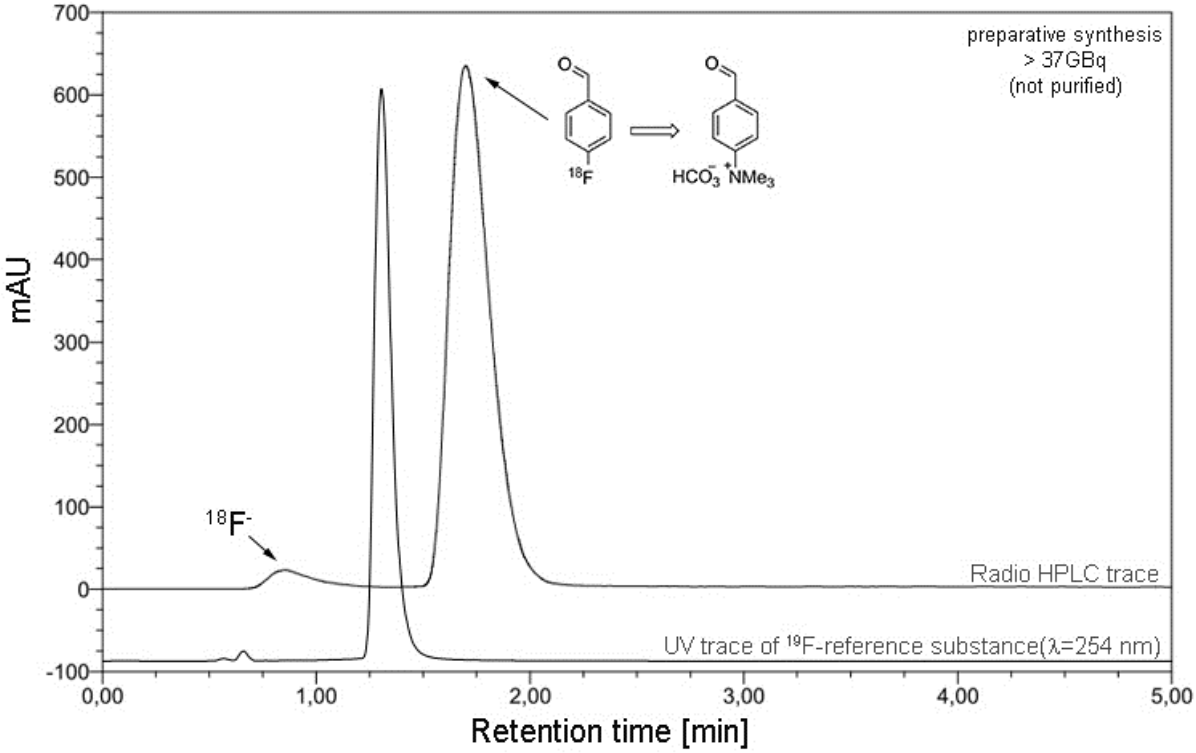
HPLC Traces

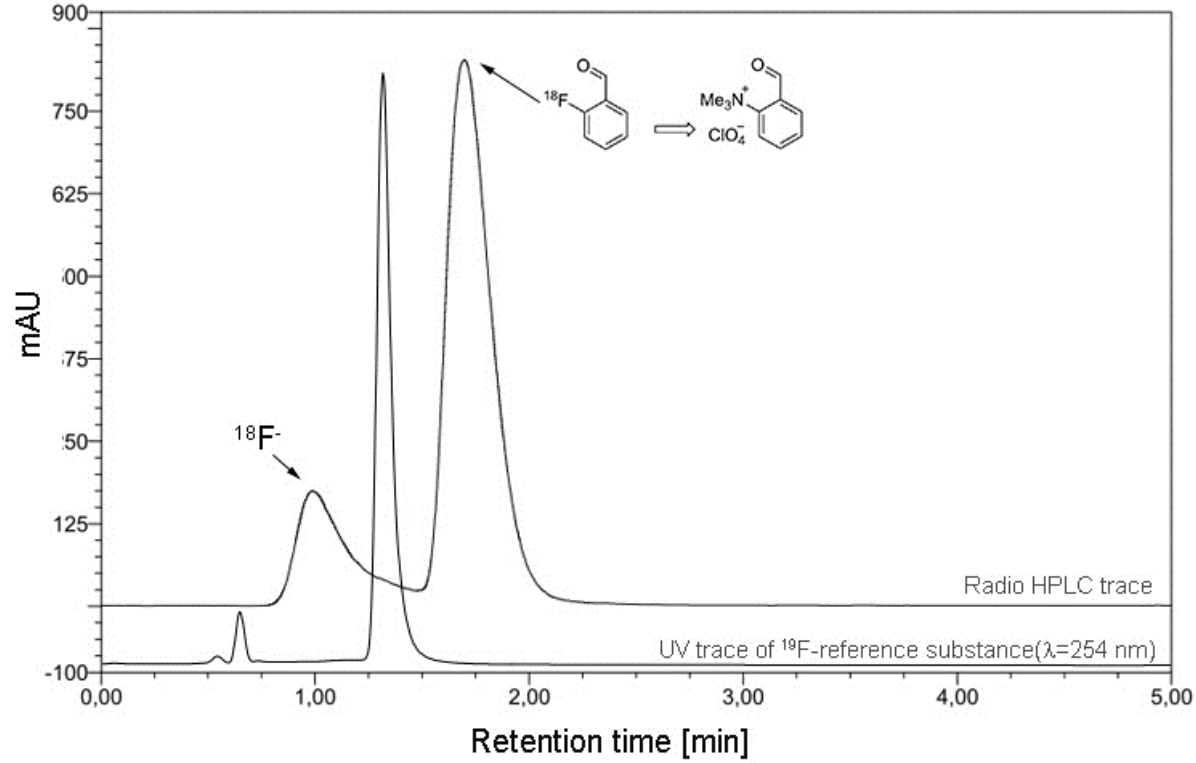

400
300
200
100
-50
mAU
$^{18}F^-$
^{18}F
TfO$^-$
PhI$^+$
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,00
1,25
2,50
3,75
5,00
6,25
8,00
Retention time [min]

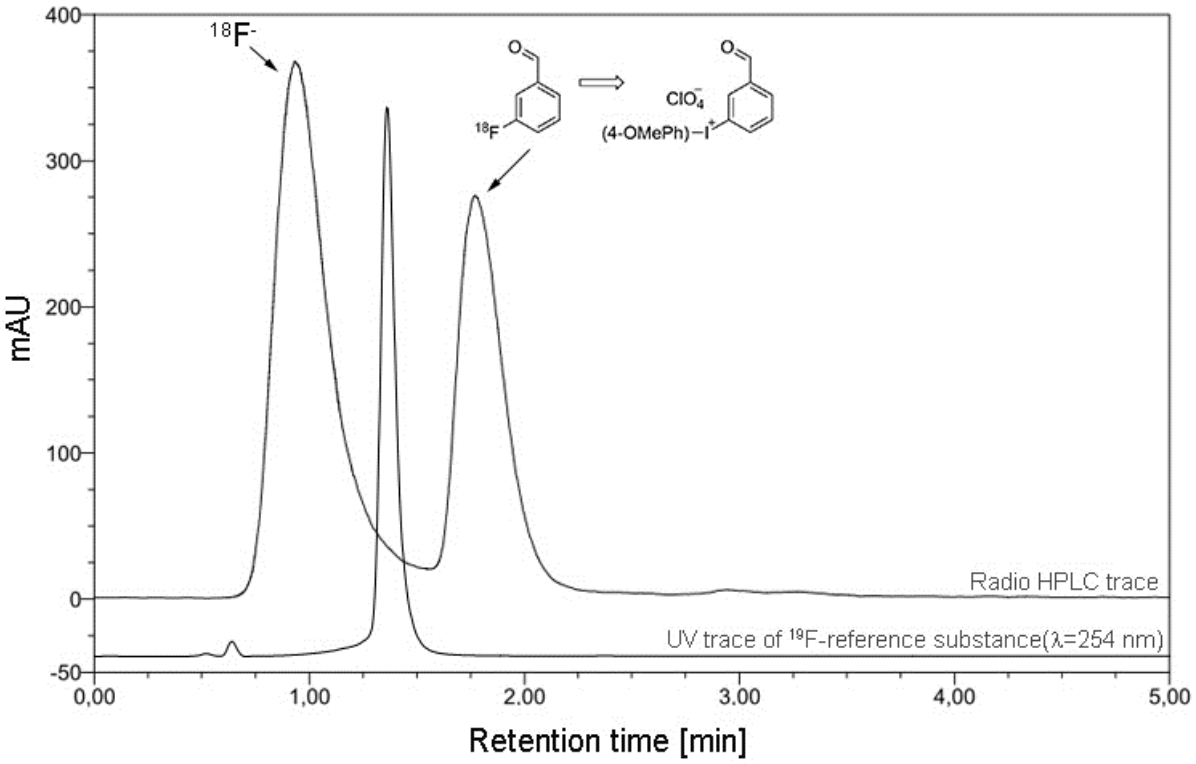

350
300
200
100
0
-50
mAU
$^{18}F^-$
^{18}F
Br$^-$
IPh
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,00
1,00
2,00
3,00
4,00
5,00
6,00
6,83
Retention time [min]

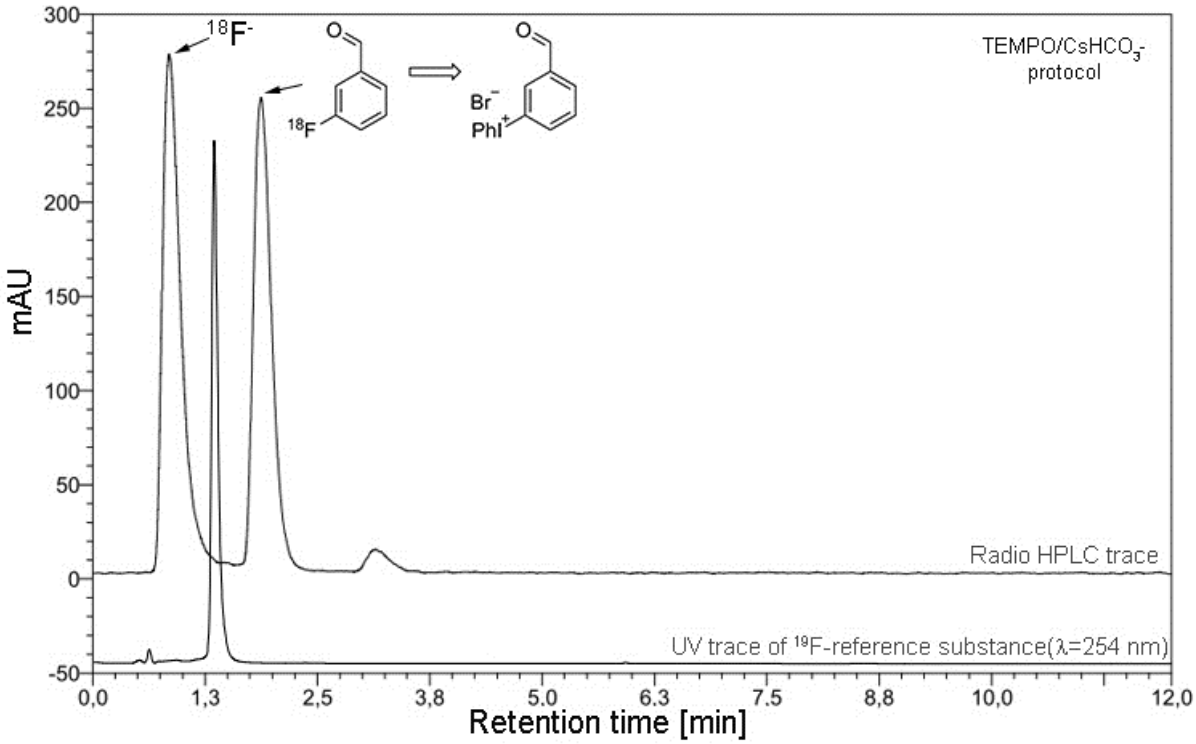

mAU
Retention time [min]
$^{18}F^-$
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
^{18}F
ClO_4^-
$^+NMe_3$

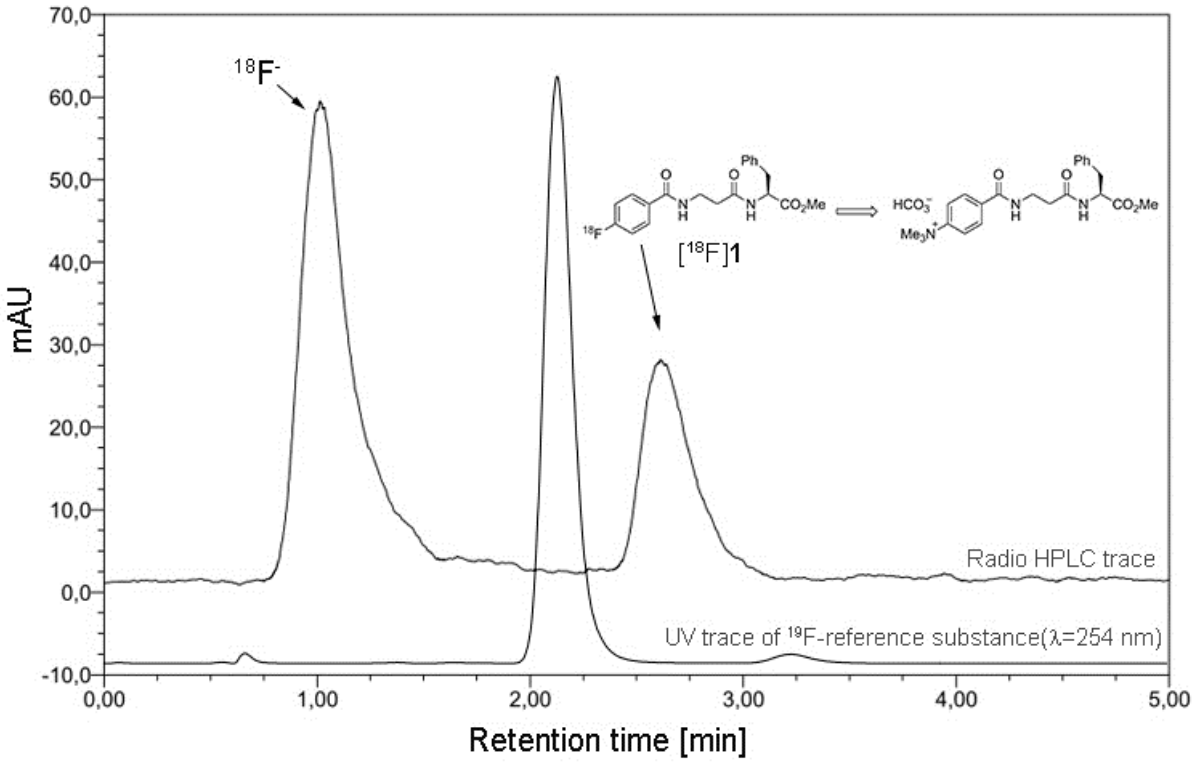

mAU
Retention time [min]
$^{18}F^-$
K222/K_2CO_3-protocol
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
^{18}F
TfO^-
$^+NMe_3$

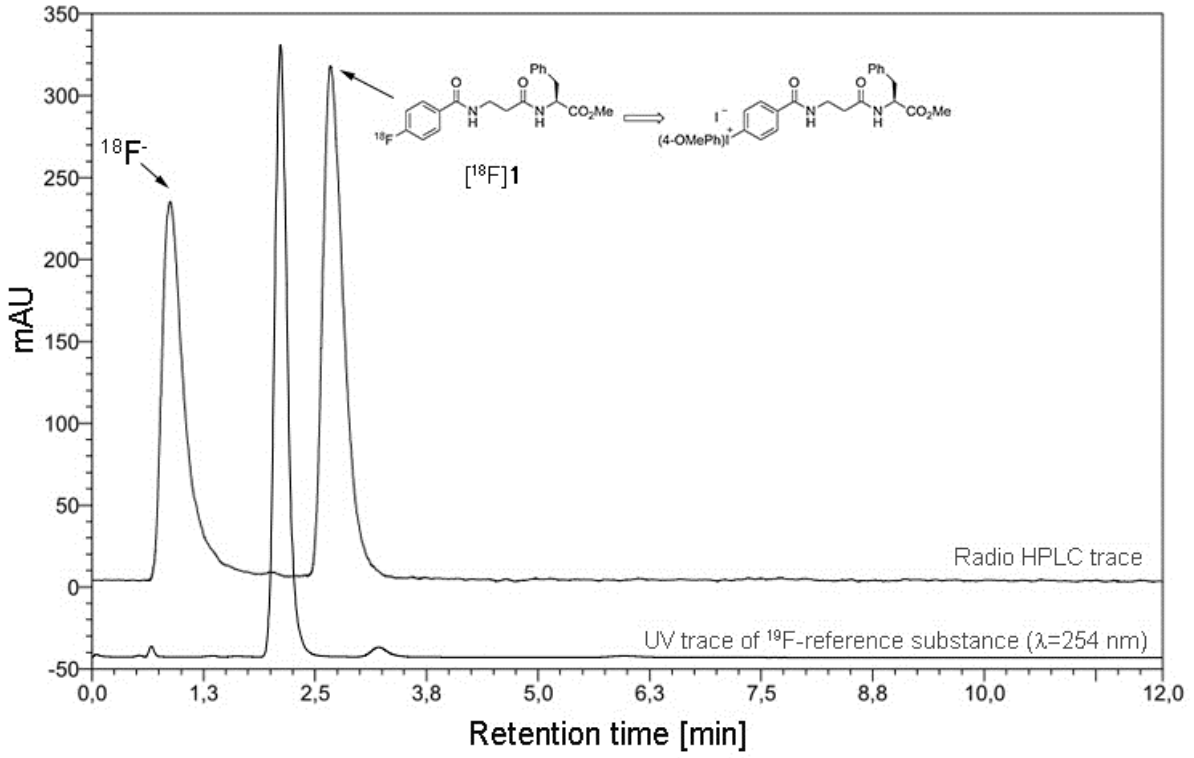

preparative synthesis
> 37GBq
(not purified)
mAU
700
600
500
400
300
200
100
0
-100
$^{18}F^-$
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,00
1,00
2,00
3,00
4,00
5,00
Retention time [min]

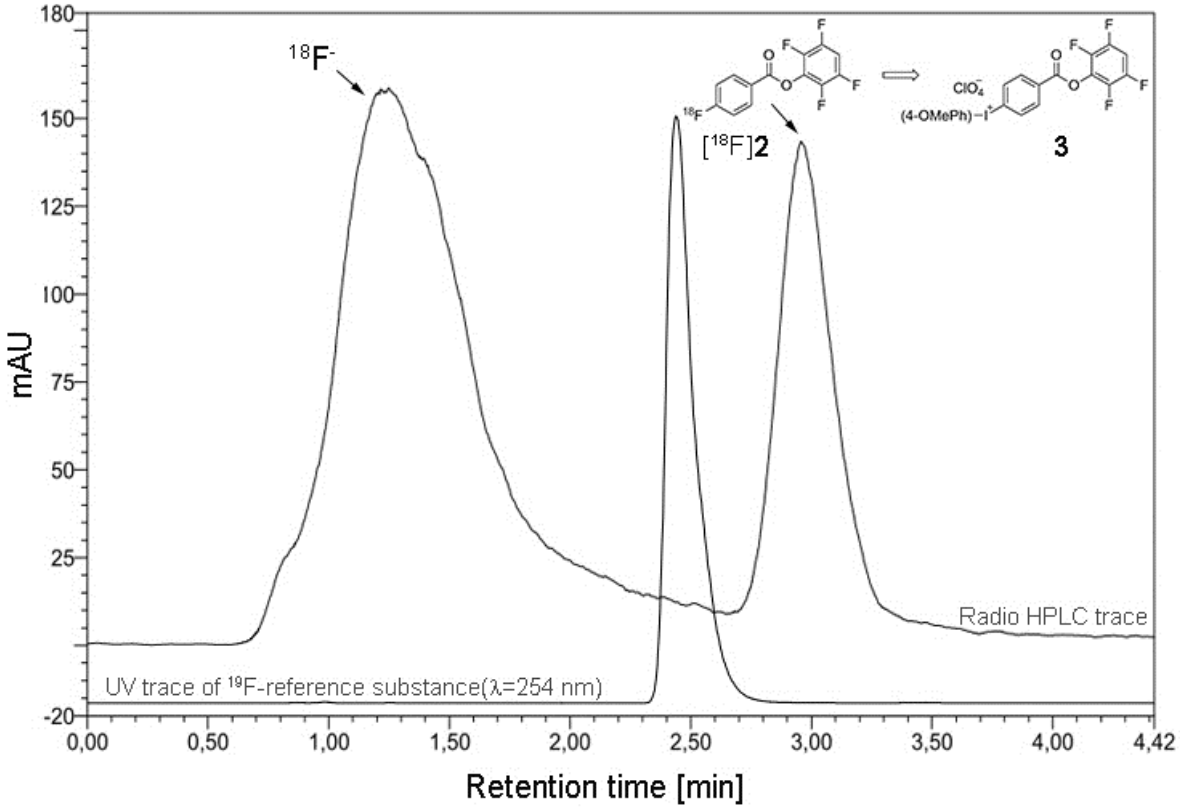

mAU
900
750
625
125
$^{18}F^-$
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
-100
0,00
1,00
2,00
3,00
4,00
5,00
Retention time [min]

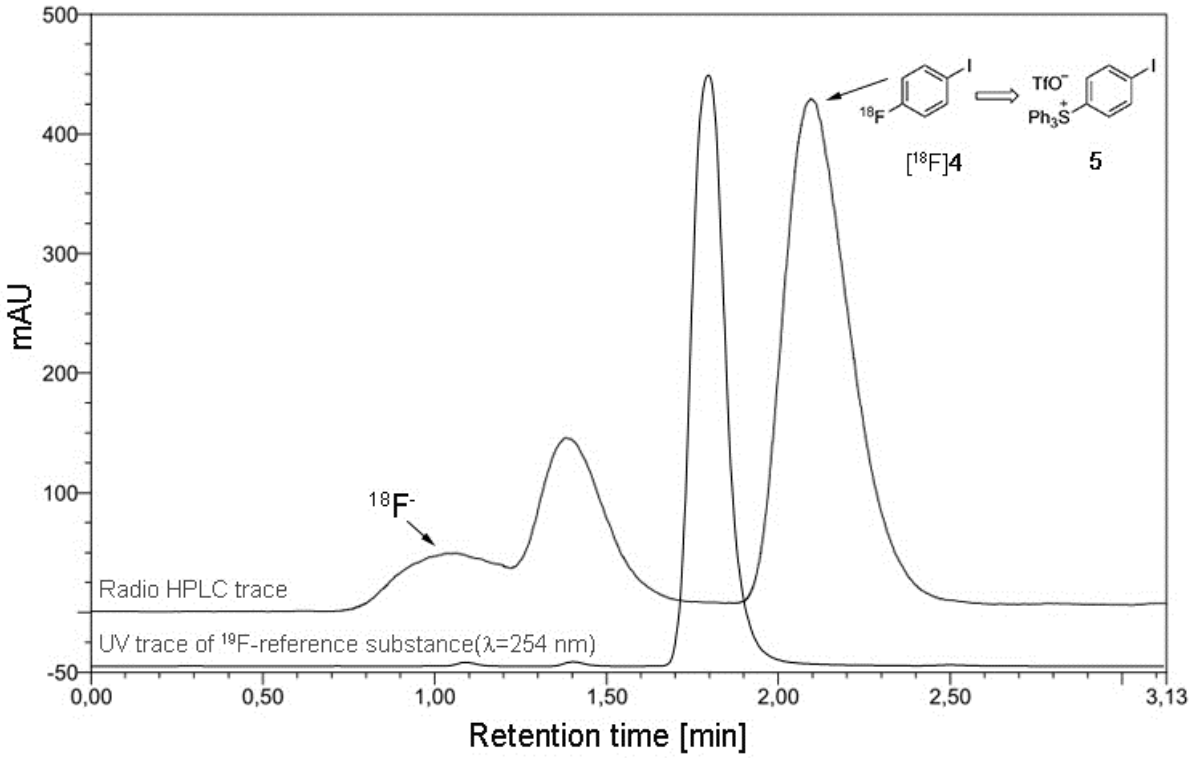

400
300
200
100
0
-50
mAU
$^{18}F^-$
ClO_4^-
(4-OMePh)–I$^+$
^{18}F
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,00
1,00
2,00
3,00
4,00
5,00
Retention time [min]

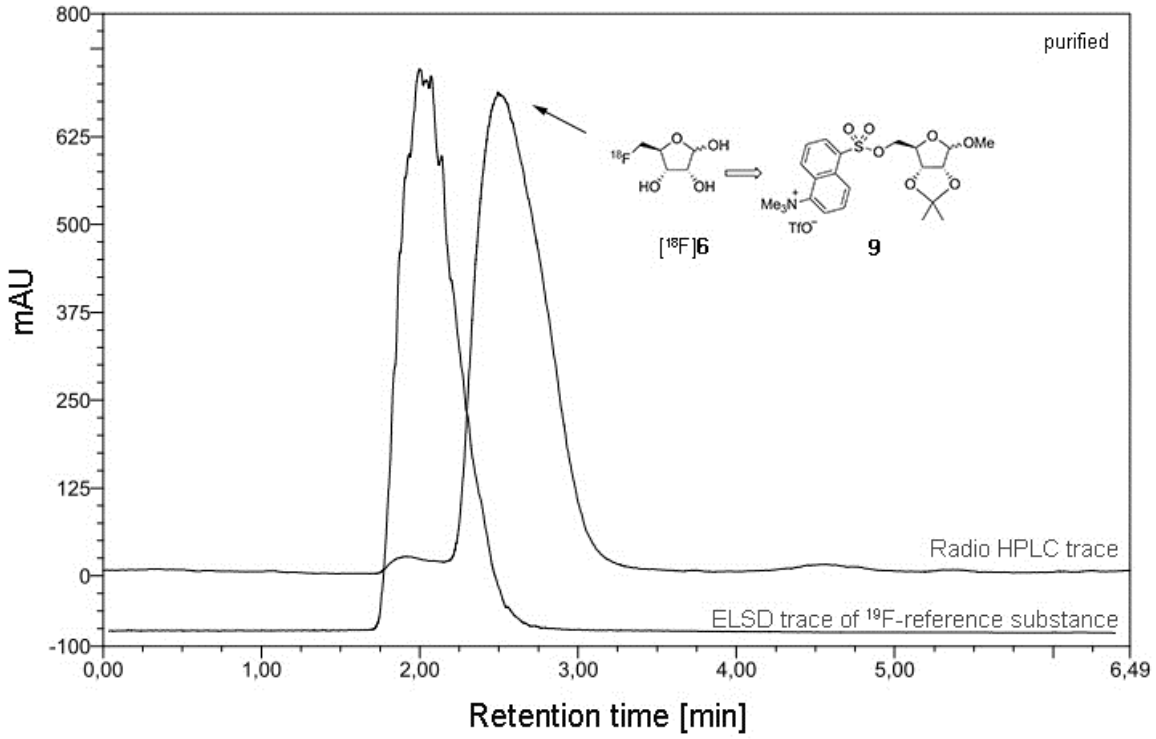

300
250
200
150
100
50
0
-50
mAU
$^{18}F^-$
^{18}F
Br^-
PhI$^+$
TEMPO/CsHCO$_3$-protocol
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,0
1,3
2,5
3,8
5,0
6,3
7,5
8,8
10,0
12,0
Retention time [min]


70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
-10,0
mAU
0,00
1,00
2,00
3,00
4,00
5,00
Retention time [min]
$^{18}F^-$
[^{18}F]**1**
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)


350
300
250
200
150
100
50
0
-50
mAU
0,0
1,3
2,5
3,8
5,0
6,3
7,5
8,8
10,0
12,0
Retention time [min]
$^{18}F^-$
[^{18}F]**1**
Radio HPLC trace
UV trace of ^{19}F-reference substance (λ=254 nm)


180
150
125
100
75
50
25
-20
mAU
$^{18}F^-$
[^{18}F]2
3
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,00
0,50
1,00
1,50
2,00
2,50
3,00
3,50
4,00
4,42
Retention time [min]


500
400
300
200
100
-50
mAU
$^{18}F^-$
[^{18}F]4
5
Radio HPLC trace
UV trace of ^{19}F-reference substance(λ=254 nm)
0,00
0,50
1,00
1,50
2,00
2,50
3,13
Retention time [min]



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