Electronic Supplementary Information

[¹⁸F]-Fluoride Capture and Release: azeotropic drying free nucleophilic aromatic radiofluorination assisted by a Phosphonium Borane.

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A. General Experimental Procedures, Materials and Instrumentation.

Instrumentation. Automated flash chromatography was performed with an Interchim Puriflash medium-pressure liquid chromatograph with prepacked C₁₈ (15 μ m) or silica gel (47-60 μ m) columns. ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer, and a Bruker Avance 400 (400 MHz) spectrometer. All spectra were recorded at ambient temperature (298 K) unless otherwise stated. Chemical shifts (δ) are reported in ppm according to the IUPAC recommendations (*i.e.* TMS for ¹H and ¹³C, H₃PO₄ for ³¹P, CFCl₃ for ¹⁹F and BF₃.Et₂O for ¹¹B),¹ and coupling constants are reported in Hz. The multiplicity of signals is indicated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, bs = broad singlet, bd = broad doublet, m = multiplet. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum One FT–IR spectrometer as thin films deposited in CH₃CN. Vibration frequencies are expressed in cm⁻¹. High-resolution mass spectrometry (HRMS) were measured at the Mass Spectrometry Service at the University Paul Sabatier. X-ray crystallography was performed on single crystal diffractometers: Agilent Gemini, Bruker Nonius and Bruker Kappa Apex II.

Materials. Tetrahydrofuran (THF), toluene, pentane, Et₂O, CH₃CN and CH₂Cl₂ were dried and distilled using standard methods.² TBACN (tetrabutylammonium cyanide) and other chemicals were purchased at the highest commercial quality and used without further purification unless noted otherwise. All reactions were monitored by TLC and/or multinuclear NMR spectra taken from reaction samples. Reactions were carried out under Ar atmosphere unless otherwise stated.

General Experimental Procedures. Reactions were performed in oven-dried borosilicate round bottom flasks fitted with a glass stopper, or in flame-dried borosilicate modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper under a positive pressure of Ar, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe. Double microfiber filters were prepared to carry out filtrations under rigorous inert conditions (no H₂O, no O₂) as follows: The filter consists of a glass microfiber filter (GF/A, $\emptyset = 25$ mm) adjusted to an extreme of a PTFE plastic tube ($\emptyset = 2$ mm) with a Teflon strip. A second glass microfiber filter (GF/A, $\emptyset = 25$ mm) is then mounted on top of the former. The other extreme of the PTFE plastic tube is placed through two threaded septa. Facile filtration can be carried out

¹ R.K. Harris, E.D. Becker, S.M. Cabral de Menezes, R. Goodfellow, P. Granger *Pure Appl. Chem.* 2001, *73*, 1795-1818.

by placing the double microfilter in the Schlenk flask containing the suspension of study and the other end is placed in another dried Schlenk flask under Ar. The transfert is driven by a positive pressure of Ar applied to the flask containing the suspension. Organic solutions were concentrated by rotary evaporation below 30 °C. Analytical thin layer chromatography (TLC) was performed using pre-coated Merck glass backed silica gel plates (Silicagel 60 F254). Visualization was achieved using ultraviolet light (254 nm) and chemical staining with silica gel impregnated with iodine, or a ceric ammonium molybdate solution as appropriate. Reversed phase analytical HPLC was performed on an Agilent Technologies separation module 1200 series equipped with an Agilent 1260 Infinity PDA detector and using a Waters Xbridge C_{18} column (100 x 3 mm, 3.5 µm).

² D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, Oxford, **1997**.

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B. Synthesis of Compounds 3⁺, 3-F and 3-CN.



(4-Bromophenyl)diphenylphosphine.³



^{*n*}BuLi (10 mL, 2.5 M in hexane, 25.05 mmol) was added to a solution of 1,4-dibromobenzene (5.91 g, 25.07 mmol) in 100 mL of Et₂O at -63 °C (CHCl₃ bath in liquid N₂). The reaction mixture is then allowed to warm up to rt and stirred for 2.5 h. The mixture was again cooled to -63 °C, and ClPPh₂ (4.50 mL, 25.05 mmol) was added dropwise. The reaction mixture was stirred and allowed to warm to rt overnight. The solvent is removed under reduced pressure and the residue is triturated with heptane - CHCl₃ (95:5). The resulting suspension was filtered through a 0.20 µm PTFE filter, leading to crystallization from the mother liquor at rt. The product was obtained as a white solid (8.42 g, 98% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.41 (m, 2H), 7.39 – 7.27 (m, 10H), 7.17 (dd, *J* = 8.5, 7.0 Hz, 2H). ³¹P NMR (121 MHz, CDCl₃) δ -6.44 (s). Characterization data matches previous literature reports.²

(4-(dimesitylboryl)phenyl)(methyl)diphenylphosphonium iodide (3⁺).⁴



(4-Bromophenyl)diphenylphosphine (1.020 g, 2.99 mmol) was dissolved in an anhydrous pentane-PhMe mixture (1:1, Et₂O 30 mL) in a Schlenk flask. The resulting solution was degassed (3 freeze-pump thaw cycles) and ^{*n*}BuLi (1.20 mL, 2.5 M in hexane, 2.99 mmol) was then added under Ar. The reaction mixture was stirred at r.t. for 24 h.

³ B. Beele, J. Guenther, M. Perera, M. Stach, T. Oeser and J. Blumel, *New J. Chem.*, 2010, **34**, 2729-2731.

⁴ M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. P. Gabbaï, *Chem. Commun.*, 2007, 1133–1135.

In parallel, fluorodimesitylborane (801 mg, 2.99 mmol) was azeotroped to dryness with dry PhMe (3×3 mL), and then dissolved in dry PhMe (7.5 mL) in a separate Schlenk flask, and degassed (3 freeze-pump thaw cycles) under Ar. The fluorodimesitylborane solution was cannulated dropwise to the Schlenk flask containing the organolithium derivative, and the resulting mixture was stirred at r.t. overnight. The supernatant solution was transferred to a Schlenk flask using a double microfiber filter and solvents were then removed under vacuum to yield (4-(dimesitylboryl)phenyl)diphenylphosphine, which was used without further purification. Thus, the residue was then dissolved in dry and degassed Et₂O (3 freeze-pump thaw cycles, 50 mL) prior to the addition of MeI (560 µL, 8.97 mmol) under Ar. The resulting reaction mixture was then stirred at r.t. overnight. The supernatant solution was discarded using a double microfiber filter and the resulting yellow powder was dried under reduced pressure. The residue was purified by reverse-phase chromatography. Elution with H₂O/MeCN (90:10 to 80:20) gave 3^+ as a yellow solid (563 mg, 36%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.56 (m, 14H), 6.74 (s, 4H), 3.14 (d, J = 13.2 Hz, 3H), 2.20 (s, 6H), 1.90 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 153.6, 140.8, 140.0, 136.5 (d, J_{C-P} = 12.6 Hz), 135.3 (d, J_{C-P} = 3.0 Hz), 133.4 (d, J_{C-P} = 10.7 Hz), 132.6 (d, $J_{C-P} = 10.3$ Hz), 130.6 (d, $J_{C-P} = 12.9$ Hz), 128.6, 121.3 (d, $J_{C-P} = 90.2$ Hz), 118.8 (d, $J_{C-P} = 88.7$ Hz), 23.6, 21.3, 11.7 (d, $J_{C-P} = 56.6$ Hz). ¹¹B NMR (128 MHz, acetone- d_6) δ 76.2. ³¹P NMR (162 MHz, CDCl₃) δ 21.6. Characterization data matches previous literature reports.³

Fluorodimesityl(4-(methyldiphenylphosphonio)phenyl)borate (3-F).³



A solution of CsF (169 mg, 1.11 mmol) in H₂O (2 mL) was added to a solution of 3^+ (240 mg, 0.37 mmol) in acetone (20 mL). The resulting mixture was sonicated for 5 min and then stirred for 1 h at r.t. Solvents were then removed to dryness under reduced pressure. The residue was triturated with MeCN and solids were filtered off using a PTFE filter (0.20 µm). Solvent was then removed under reduced pressure to give **3-F** as a white solid (160 mg, 79%). ¹H NMR (300 MHz, acetone- d_6) δ 8.26 – 8.07 (m, 1H), 7.92 – 7.70 (m, 10H), 7.52 – 7.17 (m, 3H), 6.46 (s, 4H), 3.04 (d, *J* = 13.9 Hz, 3H), 2.10 (s, 6H), 1.93 (s, 6H), 1.92 (s, 6H). ¹³C NMR (75 MHz, acetone- d_6) δ 142.0 (d, J_{C-P} = 2.3 Hz), 135.4 (d, J_{C-P} = 3.0 Hz), 134.0 (d, J_{C-P} = 10.5 Hz), 132.0, 130.9 (d, J_{C-P} = 12.7 Hz), 130.6 (d, J_{C-P} = 10.5 Hz), 129.0, 123.0, 25.6 (d, J_{C-F} = 4.7 Hz), 21.0,

8.9 (d, J_{C-P} = 58.6 Hz). ¹¹B NMR (96 MHz, CD₃CN) δ 5.1 – 4.2 (m). ³¹P NMR (121 MHz, acetone- d_6) δ 20.4. ¹⁹F NMR (282 MHz, acetone- d_6) δ -174.9 – -182.4 (m). Characterization data matches previous literature reports.³

Cyanodimesityl(4-(methyldiphenylphosphonio)phenyl)borate (3-CN).



KCN (2.9 mg, 43.8 μmol) was added in one solid portion to a solution of **3-F** (14.3 mg, 26.3 μmol) in a MeCN-MeOH mixture (1:1, 4.4 mL). The resulting mixture was sonicated for 5 min and then stirred for 1 h at r.t. Solvents were then removed to dryness under reduced pressure. The residue was triturated with MeCN and solids were filtered off using a PTFE filter (0.20 μm). Solvent was then removed under reduced pressure to give **3-CN** as a white solid (8.1 mg, 79%). IR v_{max}/cm⁻¹ (neat film): 3059, 2970, 2915, 2856, 2165, 1671, 1602, 1576, 1439, 1392, 1139, 1115, 898, 842, 782, 745710, 690. ¹H NMR (400 MHz, CD₃CN) δ 8.41 – 8.31 (m, 1H), 7.86 – 7.77 (m, 2H), 7.72 – 7.56 (m, 7H), 7.53 – 7.13 (m, 4H), 6.57 (s, 4H), 2.70 (d, *J* = 13.8 Hz, 3H), 2.15 (s, 6H), 1.88 (s, 12H). ¹³C NMR (101 MHz, CD₃CN) δ 142.5, 135.63 (d, *J*_{C-P} = 3.0 Hz), 134.01 (d, *J*_{C-P} = 10.6 Hz), 133.60, 131.0 (d, *J*_{C-P} = 12.8 Hz), 130.8 (d, *J*_{C-P} = 4.7 Hz), 129.8, 129.6, 121.7 (d, *J*_{C-P} = 88.9 Hz), 112.8 (d, *J*_{C-P} = 91.5 Hz), 25.8, 20.8, 9.4 (d, *J* = 59.2 Hz). B-C carbon peaks were not observed. ¹¹B NMR (128 MHz, CD₃CN) δ -13.4. ³¹P NMR (162 MHz, CD₃CN) δ 20.2. HRMS-ESI (m/z): found [M+H]⁺ 551.3029, calc'd ¹⁰BC₃₈H₄₀NP requires 551.3028.







70 60 f1 (ppm) 170 160 150 110 100 90 80 50 20 -10 -20 -30 -40 140 130 120 40 30 10 Ó









dcpK0188_1003/1003



D. Fluoride release ¹⁹F NMR timecourse from 3-F (13.0 mmol) with TBACN in CD₃CN at 333 K.





E. Fluoride release ¹¹B NMR timecourse from 3-F (13.0 mmol) with TBACN in CD₃CN at 333 K.



Fluoride release ¹⁹F NMR timecourse from 3-F (38.0 mmol) with TBACN in F. CD₃CN at 333 K.



-150 f1 (ppm)

G. X-Ray Crystal Data Tables of compound 3-CN.

CCDC 1472439 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif



Table 1. Crystal data and structure refinement for DP-II-206.

Identification code

DP-II-206

Empirical formula C38 H39 B N P, C2 H3 N

Formula weight 592.54					
Temperature 100(2) K					
Wavelength 0.71073 A					
Crystal system, space group triclinic, P -1					
Unit cell dimensions $a = 11.4284(12) \text{ A}$ alpha = 87.976(4) deg. b = 12.1152(13) A beta = 67.853(4) deg. c = 13.5551(14) A gamma = 72.668(4) deg.					
Volume 1653.1(3) A^3					
Z, Calculated density 2, 1.190 Mg/m ³					
Absorption coefficient 0.114 mm^-1					
F(000) 632					
Crystal size 0.26 x 0.08 x 0.04 mm					
Theta range for data collection 2.24 to 28.28 deg.					
Limiting indices -15<=h<=15, -16<=k<=16, -18<=l<=18					
Reflections collected / unique $47748 / 8213 [R(int) = 0.0648]$					
Completeness to theta = $28.28 99.9 \%$					
Max. and min. transmission 0.7461 and 0.7216					
Refinement method Full-matrix least-squares on F ²					
Data / restraints / parameters 8213 / 0 / 405					
Goodness-of-fit on F^2 1.034					
Final R indices $[I>2sigma(I)]$ R1 = 0.0516, wR2 = 0.1129					
R indices (all data) $R1 = 0.0776$, wR2 = 0.1262					
Largest diff. peak and hole 0.481 and -0.386 e.A^-3					

Table 2. Atomic coordinates ($x \ 10^{4}$) and equivalent isotropic displacement parameters (A² x 10³) for dpii206_a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x y	Z	U(eq)		
C(1)	2929(2)	8247(2)	6568(1)	14(1)	
C(2)	3779(2)	8653(1)	7932(1)	12(1)	
C(3)	4497(2)	9396(2)	7998(1)	14(1)	
C(4)	4087(2)	10120(2)	8927(1)	17(1)	
C(5)	2950(2)	10165(2)	9815(1)	19(1)	
C(6)	2212(2)	9469(2)	9745(1)	18(1)	
C(7)	2593(2)	8730(2)	8837(1)	15(1)	
C(8)	5779(2)	9432(2)	7112(1)	18(1)	
C(9)	2528(2)	10924(2)	10826(2)	28(1)	
C(10)	1683(2)	8022(2)	8894(2)	21(1)	
C(11)	4357(2)	6362(2)	7275(1)	13(1)	
C(12)	4015(2)	5546(2)	6803(1)	16(1)	
C(13)	4156(2)	4424(2)	7132(2)	20(1)	
C(14)	4615(2)	4055(2)	7935(2)	21(1)	
C(15)	5017(2)	4825(2)	8363(1)	20(1)	
C(16)	4923(2)	5946(2)	8040(1)	16(1)	
C(17)	3501(2)	5828(2)	5919(2)	21(1)	
C(18)	4714(2)	2851(2)	8306(2)	33(1)	
C(19)	5495(2)	6648(2)	8533(2)	23(1)	
C(20)	5485(2)	7656(1)	5804(1)	12(1)	
C(21)	5416(2)	8390(2)	4991(1)	14(1)	
C(22)	6513(2)	8367(2)	4071(1)	15(1)	
C(23)	7751(2)	7565(2)	3920(1)	13(1)	
C(24)	7845(2)	6794(2)	4696(1)	15(1)	
C(25)	6734(2)	6835(2)	5606(1)	15(1)	
C(26)	8832(2)	8/41(2)	2036(1)	18(1)	
C(27)	10470(2)	7677(2)	3238(1)	16(1)	
C(28)	1053/(2)	8//2(2)	3465(2)	24(1)	
C(29)	11495(2)	8836(2)	3839(2)	31(1)	
C(30)	12365(2)	(754(2))	3995(2)	25(1)	
C(31)	12289(2)	6/54(2)	$\frac{3}{83(1)}$	22(1)	
C(32)	1134/(2)	6670(2)	3402(1)	18(1)	
C(33)	9884(2)	6227(2)	1958(1)	14(1)	
C(34)	11120(2)	6022(2)	1110(1)	19(1)	
C(35)	1105/(2) 10075(2)	5011(2)	440(2)	25(1) 27(1)	
C(30)	109/5(2)	4206(2)	014(2)	$\frac{2}{(1)}$	
C(37)	9/38(2)	4403(2)	1440(2)	$\frac{2}{(1)}$	
$C(3\delta)$	9209(2) 406(2)	3419(2) 3261(2)	2121(2) 2604(2)	22(1)	
C(39)	470(<i>2</i>)	3201(2)	2711(2)	30(1)	
$\mathbf{D}(40)$	309(2) A180(2)	2009(2) 7609(2)	5/11(2) 6010(2)	39(1) 12(1)	
D(1) N(1)	4107(2)	1098(2) 8777(1)	6246(1)	12(1) 20(1)	
N(1)	2037(2) 505(2)	0///(1) /202(2)	0340(1) 3607(2)	20(1) 66(1)	
D(1)	303(3) 0214(1)	4202(2) 7555(1)	307/(2)	12(1)	
F(1)	7414(1)	1555(1)	∠ouu(1)	13(1)	

O(1) $N(1)$	1 152(2)
C(1)-N(1)	1.155(2)
C(1)-B(1)	1.625(3)
C(2) C(2)	1 411(2)
C(2)-C(3)	1.411(2)
C(2)-C(7)	1.425(2)
$C(2) \mathbf{P}(1)$	1 666(2)
C(2)- $D(1)$	1.000(5)
C(3)-C(4)	1.400(2)
C(3) - C(8)	1.516(2)
C(3)-C(0)	1.310(2)
C(4)-C(5)	1.387(3)
C(4)-H(4)	0 9500
C(5) C(6)	1.205(2)
C(3) - C(0)	1.383(3)
C(5)-C(9)	1.511(3)
C(6) - C(7)	1 396(2)
C(0) C(1)	1.570(2)
C(6)-H(6)	0.9500
C(7)-C(10)	1.513(2)
C(8)-H(8Å)	0.9800
	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(0) H(0A)	0.000
$C(9)$ - $\Pi(9A)$	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0 9800
C(10) U(10A)	0.0800
C(10)-11(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11) C(12)	1 415(2)
C(11)-C(12)	1.413(2)
C(11)-C(16)	1.422(2)
C(11)-B(1)	1 653(3)
C(12) C(12)	1.000(0)
C(12)-C(13)	1.398(3)
C(12)-C(17)	1.511(3)
C(13)-C(14)	1 385(3)
C(12) U(12)	0.0500
С(13)-П(13)	0.9300
C(14)-C(15)	1.383(3)
C(14)-C(18)	1.512(3)
C(15) C(16)	1.012(3)
C(13)-C(10)	1.398(2)
C(15)-H(15)	0.9500
C(16)-C(19)	1 516(3)
C(17) U(17A)	0.0200
$C(17)-\Pi(17A)$	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0 9800
C(19) II(19A)	0.0000
$C(18) - \Pi(18A)$	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0 9800
C(10) II(104)	0.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0 9800
C(20) C(21)	1 402(2)
U(20)-U(21)	1.403(2)
C(20)-C(25)	1.408(2)
C(20)-B(1)	1.652(2)
C(21) C(22)	1.002(2)
U(21)-U(22)	1.390(2)

Table 3. Bond lengths [A] and angles [deg] for dpii206_a.

C(21) U(21)	0.0500
$C(21)-\Pi(21)$	0.9300
C(22)-C(23)	1.401(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.396(2)
C(23)-P(1)	1.7821(17)
C(24) C(25)	1.7021(17) 1.286(2)
C(24) - C(23)	1.360(2)
C(24)-H(24)	0.9500
C(25)-H(25)	0.9500
C(26)-P(1)	1.7853(18)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26) II(26D)	0.0000
$C(20)-\Pi(20C)$	0.9800
C(27)-C(32)	1.401(3)
C(27)-C(28)	1.403(3)
C(27)-P(1)	1.7911(18)
C(28)-C(29)	1.390(3)
C(28) - H(28)	0.9500
$C(20) - \Pi(20)$	0.9300
C(29)-C(30)	1.38/(3)
C(29)-H(29)	0.9500
C(30)-C(31)	1.388(3)
C(30)-H(30)	0.9500
C(31) - C(32)	1.387(3)
C(31) - H(31)	0.9500
$C(31)$ - $\Pi(31)$	0.9500
$C(32) - \Pi(32)$	0.9300
C(33)-C(38)	1.381(3)
C(33)-C(34)	1.402(2)
C(33)-P(1)	1.7926(18)
C(34)-C(35)	1.382(3)
C(34)-H(34)	0.9500
C(35)-C(36)	1 383(3)
C(35) = U(35)	0.9500
$C(33)$ - $\Pi(33)$	0.3300 1.270(2)
C(30)-C(37)	1.379(3)
C(36)-H(36)	0.9500
C(37)-C(38)	1.388(3)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(39)-N(2)	1.144(3)
C(39) - C(40)	1 440(3)
$C(40) \amalg (40A)$	0.0900
$C(40) - \Pi(40A)$	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
N(1)-C(1)-B(1)	1/0.91(18)
C(3)-C(2)-C(7)	116.11(15)
C(3)-C(2)-B(1)	126.48(15)
C(7)-C(2)-B(1)	117.41(15)
C(4)-C(3)-C(2)	121 18(16)
C(4)-C(3)-C(8)	
	$115 \pm 40(16)$
C(2) $C(2)$ $C(2)$	115.40(16) 122.26(15)
C(2)-C(3)-C(8)	$115.40(16) \\123.36(15) \\122.21(17)$
C(2)-C(3)-C(8) C(5)-C(4)-C(3)	$115.40(16) \\123.36(15) \\122.21(17) \\112.21(17)$

C(3)-C(4)-H(4)	118.9
C(6)-C(5)-C(4)	117.12(16)
C(6)-C(5)-C(9)	120 79(17)
C(4)-C(5)-C(9)	122 09(18)
C(5)-C(6)-C(7)	122.35(17)
C(5)- $C(6)$ - $H(6)$	118.8
C(7)- $C(6)$ - $H(6)$	118.8
C(6)-C(7)-C(2)	120.97(16)
C(6)-C(7)-C(10)	115 69(16)
C(2)- $C(7)$ - $C(10)$	123 33(16)
C(3)-C(8)-H(8A)	109 5
C(3)-C(8)-H(8R)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A) - C(8) - H(8C)	109.5
H(8R) C(8) H(8C)	109.5
$\Gamma(0D) - C(0) - \Gamma(0C)$ $\Gamma(5) \Gamma(0) + \Gamma(0A)$	109.5
$C(5) - C(9) - \Pi(9R)$	109.5
U(0A) C(0) U(0B)	109.5
$\Gamma(3A) = C(3) = \Pi(3D)$ $C(5) = C(0) = \Pi(0C)$	109.5
U(0A) C(0) U(0C)	109.5
$\Pi(9A) - C(9) - \Pi(9C)$	109.5
$\Gamma(9D) - C(9) - \Pi(9C)$ C(7) C(10) H(10A)	109.5
$C(7) - C(10) - \Pi(10A)$ $C(7) - C(10) - \Pi(10A)$	109.5
U(10A) C(10) H(10D)	109.5
$\Pi(10A)-C(10)-\Pi(10D)$ C(7) C(10) U(10C)	109.5
U(10A) C(10) H(10C)	109.5
$\Pi(10A) - C(10) - \Pi(10C)$ $\Pi(10D) C(10) \Pi(10C)$	109.5
$\Pi(10D)-C(10)-\Pi(10C)$	109.3
C(12)- $C(11)$ - $C(10)C(12)$ $C(11)$ $D(1)$	110.07(10) 122.07(15)
C(12)- $C(11)$ - $D(1)C(16)$ $C(11)$ $D(1)$	122.07(13) 121.77(15)
C(10)-C(11)-D(1) C(12)-C(12)-C(11)	121.77(13) 120.07(17)
C(13)-C(12)-C(11) C(12)-C(17)	120.9/(17)
C(13)-C(12)-C(17) C(11) C(12) C(17)	110.03(10) 122.27(16)
C(11)- $C(12)$ - $C(17)$	122.37(10) 122.41(19)
C(14)- $C(13)$ - $C(12)C(14)$ $C(13)$ $H(13)$	122.41(10)
$C(14)$ - $C(13)$ - $\Pi(13)$ $C(12)$ $C(13)$ $\Pi(13)$	110.0
$C(12)$ - $C(13)$ - $\Pi(13)$ C(15) $C(14)$ $C(12)$	110.0 117.05(17)
C(15)-C(14)-C(15) C(15)-C(14)-C(19)	117.03(17) 121.22(10)
C(13)-C(14)-C(18) C(12)-C(14)-C(18)	121.52(19) 121.60(10)
C(13)-C(14)-C(16)	121.00(19) 122.27(17)
C(14)- $C(15)$ - $C(16)$	122.3/(1/)
$C(14)$ - $C(15)$ - $\Pi(15)$ $C(16)$ $C(15)$ $\Pi(15)$	110.0
$C(10)$ - $C(15)$ - $\Pi(15)$ C(15) $C(16)$ $C(11)$	110.0 120.96(17)
C(15)- $C(10)$ - $C(11)C(15)$ $C(16)$ $C(10)$	120.80(17) 115.52(16)
C(13)-C(16)-C(19) C(11)-C(16)-C(19)	113.33(10) 123.58(16)
C(11)- $C(10)$ - $C(19)C(12)$ $C(17)$ $U(17A)$	125.56(10)
$C(12) - C(17) - \Pi(1/A)$ $C(12) - C(17) - \Pi(17B)$	109.3
$U(12) - U(17) - \Pi(17)$ U(17A) C(17) U(17D)	109.5
$\Gamma(1/A) = C(1/) = \Pi(1/D)$ C(12) = C(17) = U(17C)	109.5
$U(12)-U(17)-\Pi(17U)$ U(17A) C(17) U(17C)	109.3
$\Pi(1/A) - U(1/) - \Pi(1/U)$	109.3

H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-H(18A)	109.5
C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-C(25)	115.65(15)
C(21)-C(20)-B(1)	123.16(14)
C(25)-C(20)-B(1)	$121\ 15(15)$
C(22)-C(21)-C(20)	123.00(15)
C(22)-C(21)-H(21)	118.5
C(20)- $C(21)$ - $H(21)$	118.5
C(21)-C(22)-C(23)	119 64(16)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	118.82(15)
C(24)-C(23)-P(1)	11940(13)
C(22) - C(23) - P(1)	121.71(13)
$C(22) C(23) \Gamma(1)$ C(25) - C(24) - C(23)	120.34(15)
C(25) - C(24) - H(24)	119.8
C(23) - C(24) - H(24)	119.8
C(24)-C(25)-C(20)	122 44(16)
C(24)-C(25)-H(25)	118.8
C(24) C(25) H(25) C(20) C(25) H(25)	118.8
P(1)-C(26)-H(26A)	109.5
P(1)-C(26)-H(26R)	109.5
H(26A)-C(26)-H(26B)	109.5
P(1)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26R) - C(26) - H(26C)	109.5
C(32)-C(27)-C(28)	120 08(17)
C(32) - C(27) - P(1)	120.00(17) 119 43(14)
C(28)-C(27)-P(1)	120.42(14)
C(29) - C(28) - C(27)	120.12(11) 118.93(19)
C(29)- $C(28)$ - $H(28)$	120.5
C(27)-C(28)-H(28)	120.5
C(20) - C(20) - C(28)	120.3 120.8(2)
C(30) - C(29) - H(29)	119.6
C(28)-C(29)-H(29)	119.6
$C(20) - C(20) - \Gamma(20)$ $C(20) - C(20) - \Gamma(20)$	120 20(18)
C(29) - C(30) - C(31) C(29) - C(30) - H(30)	110.0
C(2) = C(30) = H(30) C(31) = C(30) = H(30)	110.0
C(31) = C(30) = II(30) C(32) = C(31) = C(30)	110 88(18)
C(32) - C(31) - C(30) C(32) - C(21) - U(21)	120 1
С(32)-С(31)-П(31)	120.1

C(30)-C(31)-H(31)	120.1
C(31)-C(32)-C(27)	120.03(18)
C(31)-C(32)-H(32)	120.0
C(27)-C(32)-H(32)	120.0
C(38)-C(33)-C(34)	119.86(17)
C(38)-C(33)-P(1)	121.71(14)
C(34)-C(33)-P(1)	118.42(14)
C(35)-C(34)-C(33)	119.82(18)
C(35)-C(34)-H(34)	120.1
C(33)-C(34)-H(34)	120.1
C(34)-C(35)-C(36)	119.81(18)
C(34)-C(35)-H(35)	120.1
C(36)-C(35)-H(35)	120.1
C(37)-C(36)-C(35)	120.59(19)
C(37)-C(36)-H(36)	119.7
C(35)-C(36)-H(36)	119.7
C(36)-C(37)-C(38)	120.01(19)
C(36)-C(37)-H(37)	120.0
C(38)-C(37)-H(37)	120.0
C(33)-C(38)-C(37)	119.92(18)
C(33)-C(38)-H(38)	120.0
C(37)-C(38)-H(38)	120.0
N(2)-C(39)-C(40)	178.2(3)
C(39)-C(40)-H(40A)	109.5
C(39)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(1)-B(1)-C(20)	103.69(13)
C(1)-B(1)-C(11)	114.46(14)
C(20)-B(1)-C(11)	107.87(13)
C(1)-B(1)-C(2)	99.40(13)
C(20)-B(1)-C(2)	119.11(14)
C(11)-B(1)-C(2)	112.02(13)
C(23)-P(1)-C(26)	109.49(8)
C(23)-P(1)-C(27)	110.32(8)
C(26)-P(1)-C(27)	109.51(9)
C(23)-P(1)-C(33)	111.24(8)
C(26)-P(1)-C(33)	108.92(8)
C(27)-P(1)-C(33)	107.31(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A² x 10³) for dpii206_a. The anisotropic displacement factor exponent takes the form: -2 pi² [h² a^{*} U11 + ... + 2 h k a^{*} b^{*} U12]

	U11	U22	U33	U23	U13	U12	
C(1)	14(1)	13(1)	11(1)	-3(1)	0(1)	-6(1)	
C(2)	13(1)	11(1)	12(1)	2(1)	-5(1)	-3(1)	
C(3)	14(1)	12(1)	15(1)	3(1)	-7(1)	-3(1)	
C(4)	22(1)	12(1)	19(1)	1(1)	-10(1)	-6(1)	
C(5)	24(1)	15(1)	15(1)	-2(1)	-9(1)	-2(1)	
C(6)	16(1)	22(1)	11(1)	1(1)	-2(1)	-3(1)	
C(7)	16(1)	14(1)	14(1)	2(1)	-4(1)	-5(1)	
C(8)	16(1)	20(1)	19(1)	0(1)	-3(1)	-10(1)	
C(9)	33(1)	28(1) 26(1)	20(1) 16(1)	-/(1)	-10(1)	-3(1) 12(1)	
C(10) C(11)	19(1)	20(1) 13(1)	10(1) 12(1)	-1(1) 0(1)	0(1)	-12(1)	
C(11) C(12)	10(1)	13(1) 14(1)	12(1) 18(1)	-2(1)	0(1)	-3(1)	
C(12) C(13)	14(1)	14(1)	25(1)	-4(1)	1(1)	-6(1)	
C(14)	16(1)	14(1)	20(1)	2(1)	5(1)	-1(1)	
C(15)	20(1)	17(1)	14(1)	2(1)	-1(1)	0(1)	
C(16)	14(1)	16(1)	12(1)	-1(1)	0(1)	-2(1)	
C(17)	20(1)	17(1)	27(1)	-6(1)	-10(1)	-5(1)	
C(18)	35(1)	16(1)	33(1)	4(1)	1(1)	-6(1)	
C(19)	29(1)	20(1)	23(1)	3(1)	-17(1)	-4(1)	
C(20)	13(1)	12(1)	12(1)	-1(1)	-4(1)	-5(1)	
C(21)	11(1)	15(1)	14(1)	1(1)	-4(1)	-1(1)	
C(22)	14(1)	17(1)	12(1)	3(1)	-4(1)	-2(1)	
C(23)) $\Pi(1)$	15(1)	11(1)	-l(l)	-2(1)	-4(1)	
C(24)	11(1)	14(1)	1/(1)	1(1)	-4(1)	-1(1)	
C(25)	15(1)	15(1) 10(1)	14(1) 14(1)	3(1) 2(1)	-0(1)	-3(1)	
C(20)	10(1)	19(1) 21(1)	14(1) 12(1)	2(1) 2(1)	-3(1)	-3(1) 5(1)	
C(27)	11(1)	21(1) 21(1)	31(1)	-2(1)	-1(1) -8(1)	-3(1) -2(1)	
C(20)	25(1)	21(1) 28(1)	40(1)	-10(1)	-12(1)	-2(1) -8(1)	
$C(2^{2})$	16(1)	37(1)	23(1)	-6(1)	-7(1)	-7(1)	
C(31)	13(1)	32(1)	16(1)	2(1)	-4(1)	-3(1)	
C(32)	16(1)	21(1)	15(1)	0(1)	-4(1)	-5(1)	
C(33)	13(1)	16(1)	13(1)	-1(1)	-5(1)	-2(1)	
C(34)	14(1)	22(1)	16(1)	-1(1)	-3(1)	-4(1)	
C(35)	19(1)	29(1)	18(1)	-5(1)	-4(1)	1(1)	
C(36)	31(1)	22(1)	24(1)	-10(1)	-12(1)	1(1)	
C(37)	33(1)	23(1)	29(1)	-3(1)	-13(1)	-12(1)	
C(38)	18(1)	24(1)	21(1)	-2(1)	-4(1)	-7(1)	
C(39)	39(1)	40(1)	44(1)	7(1)	-28(1)	-11(1)	
C(40)	29(1)	40(1)	40(1)	-10(1)	-4(1)	-12(1)	
$\mathbf{B}(1)$	11(1) 14(1)	14(1) 20(1)	11(1) 20(1)	1(1) 5(1)	-3(1)	-4(1)	
N(1)	10(1) 01(2)	20(1) 44(2)	20(1) 07(2)	-3(1) 28(1)	-0(1)	-2(1) 27(1)	
P(1)	91(2) 10(1)	44(<i>2)</i> 17(1)	$\frac{9}{(2)}$	20(1)	-72(2)	-27(1)	
1(1)	10(1)	14(1)	11(1)	$\mathcal{O}(1)$	-2(1)	-3(1)	

H. Radiochemistry

General. No-carrier-added aqueous [¹⁸F]-fluoride was produced by ¹⁸O[p,n]¹⁸F nuclear reaction of a target consisting of ¹⁸O-enriched water (97%, Eurisotop, France) irradiated with a 18 MeV proton beam using Cyclone 18/9 (IBA) cyclotron at the Cyceron PET Center. [¹⁸F]Fluoride was separated from ¹⁸O-enriched water using ion exchange resin (QMA light, Water, ABX) eluted with a solution of potassium carbonate K₂CO₃ (2.1 mg) and Kryptofix 2.2.2 (K₂₂₂, 6.8 mg) in water (300 µL) and acetonitrile (300 µL). The [¹⁸F]-fluoride solution was collected into a conical Reactivial®. Between 37 MBq (1 mCi) and 180 MBq (5 mCi) of [¹⁸F]KF/K₂₂₂ solution were obtained. Radiofluorination reactions were performed in conical Reactivial®. Analyses were performed by radio-TLC and by radio-HPLC to establish the radiochemical yields. Identity of the radiofluorinated compounds was assessed by HPLC by comparison with nonradioactive reference ¹⁹F-compounds. RadioTLC was performed on silica plates using a mixture of dichloromethane/methanol (96:4, v,v) as eluent. HPLC system was equipped with a Waters 600 pump and controller, a Waters 717 plus autosampler and a Waters 996 photodiode arrays detector ($\lambda = 210$ -380 nm) coupled with a NaI probe radioactive detector (Novelec β +-flow detector). Radioactivity detector was placed in line after the UV detector generating a delay of 0.48 min between both UV and radioactive signals. Radioactivity measurements were carried out with a Capintec R15C.

General Procedure for Radiofluorination of Dinitrobenzene Under Conventiobnal Conditions as Reference Reaction: After recovery of the [18 F]KF/K₂₂₂ solution from ion exchange resin, [18 F]-fluoride was dried by three successive azeotropic evaporations with acetonitrile (3 × 1 mL) at 110 °C under nitrogen steam, then cooled down to RT. Dinitrobenzene (5 mg) in dimethylsulfoxide (500 µL) was added to the dried [18 F]KF/K₂₂₂ complex and the reaction mixture was heated at 50, 90 or 150 °C for 5, 10, 15, 20 or 30 min. Aliquots (10 µL) were taken off, diluted in acetonitrile (200 µL), and analyzed by radioTLC and HPLC.

General One-pot Procedure for Radiofluorination of Dinitrobenzene via the [¹⁸F]Fluoride Capture/Release Method: Phosphonium borane 3^+ (5 mg, 7.7 µmol) in acetonitrile (100 µL) was added to a solution of [K/K₂₂₂]⁺¹⁸F⁻ in water/ acetonitrile (750 µL). The mixture was stirred at rt for 5 min. The water was removed azeotropically with acetonitrile (3 × 1 mL) at 110 °C under a stream of nitrogen. To the dried residue was added a solution of tetra-*n*-butylammonium cyanide (0.21, 1.1, 2.1 or 4.2 mg; 0.77 or 3.9, 7.7 or 15.4 µmol) in dimethylsulfoxide (0.5 mL), then dinitrobenzene (5 mg, 30 µmol). The mixture was heated at 150 °C for 5, 10, 20 or 30 min. Aliquot (20 µL) were taken off, diluted in acetonitrile (150 µL) and analyzed by radioTLC and HPLC.

General procedure for Radiofluorination of Dinitrobenzene Using the [¹⁸F]Fluoride Cartridge-Based Trapping-Release Method: A solution of phosphonium borane 3^+ (20 mg, 30.8 µmol) in acetonitrile (200 µL) was adsorbed on an reversed phase C-18 cartridge (900 mg sorbent, 37-55 µm particle) preconditioned with water (1 mL). After drying by flushing air, the cartridge was washed with water (1 mL) and dried. A solution of $[K/K_{222}]^{+18}F^{-}$ in water (1 mL) was slowly passed through the borane-loaded cartridge. Cartridge was then dried under a stream of nitrogen for 2 min. The radioactivity trapped on cartridge was counted. A solution of tetra-*n*-butylammonium cyanide (8.4 mg; 30.8 µmol) in acetonitrile (1 mL) was passed through the cartridge. The radioactive fraction was collected and the radioactivity was counted. Dinitrobenzene (5 mg, 30 µmol) in dimethylsulfoxide (0.5 mL) was added to the radioactive fraction. The mixture was heated at 150 °C for 5, 10, 20 or 30 min. Aliquot (20 µL) were diluted in acetonitrile (150 µL) and analyzed by radioTLC and HPLC.

Examples of RadioTLC Chromatograms for [¹⁸F]Fluoronitrobenzene Radiosynthesis:

Eluent: dichloromethane/methanol (96:4, v,v)



Top) Reference reaction; Bottom) Cartridge-Based trapping-release method

Examples of HPLC Chromatograms for [¹⁸F]Fluoronitrobenzene Radiosynthesis:

XBridge BEH C18 Column, 4.6×75 mm, 2.5μ m, XP; Eluent: NH₄HCO₃ (10 mM) / acetonitrile, linear gradient 5% to 80% acetonitrile over 25 min with a flow rate of 1 mL/min.

A) Radioactive trace for reference reaction; B) Radioactive trace for cartridge-based trapping-release method; C) UV trace for reference fluoronitrobenzene; D) UV trace for cartridge-based trapping-release method.

