Supporting Information

The Aryne Phosphate Reaction**

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**Abbreviations**

d4T  1-[(2R,5S)-5-(Hydroxymethyl)-2,5-dihydrofurane-2-yl]-5-methylpyrimidine-2,4-dion
DBU  1,8-Diazabicyclo[5.4.0]undec-7-ene
DEACM  7-(diethylamino)-4-(hydroxymethyl)-coumarine
DCM  Dichloromethane
DMF  Dimethylformamide
DMSO  Dimethyl sulfoxide
Et₂O  Diethyl ether
ETT  5-(Ethylthio)-1H-tetrazole
Fm  Fluorenymethyl
mCPBA  *meta*-Chloroperoxybenzoic acid
MeCN  Acetonitrile
HPLC  Reverse phase high-performance liquid chromatography
HRMS  High resolution mass spectrometry
Pi  Inorganic phosphate
PPi  Inorganic pyrophosphate
qNMR  Quantitative NMR
RP-MPLC  Reverse phase medium pressure liquid chromatography
SAX  Strong anion exchange
TBA  Tetrabutylammonium
TBAF  Tetrabutylammoniumfluoride
TEA  Triethylammonium
TEAA  Triethylammonium acetate
TMS  Trimethylsilyl
1. General remarks

**Reactions** were carried out using glassware magnetically stirred, unless noted otherwise. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel canula.

**Reagents** were purchased from commercial suppliers (Acros, Aldrich, Fluka, TCI) and used without further purification, unless noted otherwise.

**Solvents** were obtained in analytical grade and used as received for extractions, precipitation and solid washing.

**Dry solvents** for reactions were purchased in a dry form from Sigma and stored over molecular sieves as well as under the atmosphere of dry N₂.

**Deuterated solvents** for NMR and reactions were obtained from Armar Chemicals, Switzerland and euriso-top, Germany, in the indicated purity grade and used as received for NMR spectroscopy.

**Strong ion-exchange chromatography** was performed using an automated Äkta® – system. Q-Sepharose was purchased from Aldrich. Buffer solutions were produced manually using milliQ H₂O.

**TBA-salt preparations** were performed by either using DowexH⁺ followed by TBA(OH) addition or Chelex®100 (preloaded with TBA). In both cases, the TBA salts were obtained after lyophilization.

**Commercially available phosphates** (e.g. phenylphosphate, phenylphosphonate) were transformed into their corresponding TBA-salts as described above.

**Commercially available aryne precursors** (2-(trimethylsilyl)phenyl triflate, 2-Bromo-6-(trimethylsilyl)phenyl triflate, Garg 4,5,-indolyne precursor) were purchased from Sigma and used without further purification.
Preparative RP-MPLC was performed using an automated Interchim®-system. The C18AQ-solid phase was purchased from Interchim.

Lyophilizations were done with Christ Freeze Dryer Alpha 1-4 LDplus and Christ Freeze Dryer Alpha 1-2 LDplus.

$^1$H-NMR spectra were recorded on Bruker 300 MHz spectrometers, Bruker 400 MHz (with cryoprobe) and Bruker 500 MHz spectrometers in the indicated deuterated solvent. Data are reported as follows: chemical shift ($\delta$, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br. s, broad signal), coupling constant(s) ($J$, Hz), integration. All signals were referenced to the internal solvent signal as standard ($D_2O$, $\delta$ 4.79; MeCN-$d_3$, $\delta$ 1.94, DMSO-$d_6$, $\delta$ 2.50, CDCl$_3$, $\delta$ 7.26).

In some phosphate products there is still acetate (mostly as TBA-salt) present after RP-MPLC followed by lyophilization. These buffer residues were considered for yield determination. After NaClO$_4$ – purification acetone residues were present in the products. These were also considered for yield determination.

$^{13}$C$\{^1$H$\}$-NMR spectra were recorded with $^1$H-decoupling on Bruker 126 MHz, Bruker 101 MHz (with cryoprobe) spectrometers at 298K in the indicated deuterated solvent. If possible, signals were referred to the internal solvent signal as standard (MeCN-$d_3$, $\delta$ 1.32, DMSO-$d_6$, $\delta$ 39.52, CDCl$_3$, $\delta$ 77.16).

$^{31}$P$\{^1$H$\}$-NMR spectra and $^{31}$P-NMR spectra were recorded with $^1$H-decoupling or $^1$H coupling, respectively, on Bruker 202 MHz, 162 MHz (with cryoprobe) and Bruker 122 MHz spectrometers in the indicated deuterated solvent. All signals were referenced to an internal standard (PPP).

Mass spectra were recorded by C. Warth (Mass spectrometry service of the University of Freiburg) on a Thermo LCQ Advantage [spray voltage: 2.5 – 4.0 kV, spray current: 5 $\mu$A, ion transfer tube: 250 (150) °C, evaporation temperature: 50 – 400°C.]
2. Screening overview

The TBA-salt of pyrophosphate and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate were used as a starting point for optimization of the aryne phosphate coupling (see supporting figure 1). The ratios between starting material and the arylated products was used as “reactivity” parameter: the higher the arylation rate, the better the reaction conditions. The turnover was determined by $^{31}$P-NMR analysis (see supporting figure 2). In summary, TBAF was the superior fluoride source. MeCN proved the most efficient solvent. A slow addition of the fluoride source was crucial for high turnover. A PP$_i$ concentration of 80 mM was suitable and TBAF excess was not necessary. The optimized conditions are presented in table entry 12.

Supporting figure 1: model reaction used for optimizing F-source, solvent, temperature, addition time and concentration.

Supporting table 1: selected reaction conditions and corresponding turnover results: SM = starting material, PP$_i$, 1 = monoarylation product, 2 = bisarylation product, 3 = trisarylation product.

| varied Parameters | Nr. | solvent (conc.) | F-Source (eq.) | Temp.[°C] | Addition time (F-source) | SM:1:2:3 [%] |
|-------------------|-----|-----------------|----------------|----------|--------------------------|--------------|
| F-sources         | 1   | MeCN (80 mM)    | CsF (3 eq.)    | 25       | -                        | 54:42:4:0    |
|                   | 2   | MeCN (80 mM)    | KF (3 eq.)     | 25       | -                        | 50:50:0:0    |
|                   | 3   | MeCN (80 mM)    | TBAF (3 eq.)   | 25       | 1 min                    | 36:54:10:0   |
| solvents          | 4   | Acetone (80 mM) | TBAF (3 eq.)   | 25       | 1 min                    | 41:53:6:0    |
|                   | 5   | DCM (80 mM)     | TBAF (3 eq.)   | 25       | 1 min                    | 76:23:1:0    |
|                   | 6   | THF (80 mM)     | TBAF (3 eq.)   | 25       | 1 min                    | 61:29:10:0   |
|                   | 7   | DME (80 mM)     | TBAF (3 eq.)   | 25       | 1 min                    | 93:4:3:0     |
| addition speed    | 8   | MeCN (80 mM)    | TBAF (3 eq.)   | 25       | 60 min                   | 21:43:29:7   |
| temperature       | 9   | MeCN (80 mM)    | TBAF (3 eq.)   | 0        | 60 min                   | 39:47:17:0   |
| concentration     | 10  | MeCN (110 mM)   | TBAF (3 eq.)   | 25       | 60 min                   | 44:48:8:0    |
|                   | 11  | MeCN (40 mM)    | TBAF (3.0 eq.) | 25       | 60 min                   | 23:42:28:7   |
| F-source (eq.)    | 12  | MeCN (80 mM)    | TBAF (1.7 eq.) | 25       | 60 min                   | 21:43:30:6   |
Supporting figure 2: exemplified $^{31}$P-NMR determination of starting material to product ratios during reaction optimization.
3. Syntheses adapted from literature

**Synthesis of 5′-Deoxy-5′-aminoadenosine (SI-1)**

Compound SI-1 was synthesized according to Ugarkar et al. The analytical data are in accordance with literature.\(^1\)

**Synthesis of 5′-Deoxy-5′-aminoguanosine (SI-2)**

Compound SI-2 was synthesized according to Dean. The analytical data are in accordance with literature.\(^2\)

**Synthesis of Pent-4-yn-1-ylphosphate (SI-3)**

Compound SI-3 was synthesized according to Singh et al. The analytical data are in accordance with literature.\(^3\) Cations were changed to TBA as described above.
Synthesis of (FmO)$_2$P-N(iPr)$_2$ (SI-4)

Compound SI-4 was synthesized according to BIALY et al. The analytical data are in accordance with literature.\(^4\)

d4T-monophosphate (SI-5)

d4T (500 mg, 2.32 mmol) and ETT (725 mg, 5.58 mmol, 2.5 eq.) were dissolved in DMF. (FmO)$_2$P-N(iPr)$_2$ (1.51 g, 2.90 mmol, 1.3 eq.) was added as solution in DMF (10 mL) and the resulting mixture was stirred for 1 h at rt. The solution was cooled to 0 °C and mCPBA (77%, 1.07 g, 4.35 mmol, 1.5 eq.) was added. The solution was stirred for 15 min at 0 °C and piperidine (10 vol%) was added. The solution was stirred for 40 min at rt. The solvent was removed under reduced pressure. The crude product was purified by RP-MPLC [C18-AQ, dryload on celite, elution with H$_2$O/MeCN/ TEAA (10 mM)]. The product (SI-5, 407 mg, 804 µmol, 36%) was isolated as white solid. NMR and HRMS data were in accordance with literature.\(^5\)

\(^1\)H-NMR (400 MHz, D$_2$O, $\delta$/ppm): 7.63 (q, $J = 1.2$ Hz, 1H), 6.96 (ddd, $J = 3.3, 1.9, 1.5$ Hz, 1H), 6.49 (dt, $J = 6.1, 1.7$ Hz, 1H), 5.95 (ddd, $J = 6.2, 2.4, 1.4$ Hz, 1H), 5.13 – 5.07 (m, 1H), 4.05 (dd, $J = 5.7, 3.2$ Hz, 2H), 1.89 (d, $J = 1.2$ Hz, 3H).* \(^3\)P\(^{1\text{H}}\)-NMR (162 MHz, D$_2$O, $\delta$/ppm): 0.41. HRMS (ESI) m/z for C$_{10}$H$_{12}$O$_2$N$_2$P [M-H]: calcd. 303.0388, found 303.0388.

*piperidinium and TBA-signals are not reported.
Synthesis of 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-6)

![SI-6](image)

Compound SI-6 was synthesized according to Ueta et al. The analytical data matched the previously published values.\(^6\)

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Synthesis of 3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-7)

![SI-7](image)

Compound SI-7 was synthesized according to Wang et al. The analytical data matched the previously published values.\(^7\)

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Synthesis of 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-8)

![SI-8](image)

Compound SI-8 was synthesized according to Xu et al. The analytical data matched the previously published values.\(^8\)

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Synthesis of 6-(trimethylsilyl)benzo[\(d\)][1,3]dioxol-5-yl trifluoromethanesulfonate (SI-9)

![SI-9](image)

Compound SI-9 was synthesized according to Ueta et al. The analytical data matched the previously published values.\(^6\)
Synthesis of 5-chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-10)

Compound SI-10 was synthesized according to PEÑA et al. The analytical data matched the previously published values.9

Synthesis of 4-(trifluoromethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-11)

Compound SI-11 was synthesized according to GHOTEKAR et al. The analytical data matched the previously published values.10

Synthesis of 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (SI-12)

Compound SI-12 was synthesized according to UETA et al. The analytical data matched the previously published values.6
4. Cluster 1: Synthesis of (Pyro-)phosphomonoesters

Preliminary experiments

When cluster I reactions were performed with comparable molarity in P$_i$ (17) and aryne precursor 15 (supporting figure 3), substantial overreaction towards diphenylphosphate 52 was observed. This is underlined by the $^{31}$P{^1}H-NMR spectrum of the corresponding crude product mixture shown in supporting figure 4. The reason is a similar reactivity of P$_i$ (17) and phosphomonoester 27 towards arynes. To suppress this overreaction and enable a coherent product formation, cluster I reactions were performed with an excess of P$_i$ or PP$_i$.

**Supporting figure 3:** reaction between P$_i$ (17) and a slight excess of aryne precursor 15.

**Supporting figure 4:** $^{31}$P-NMR spectrum of crude product mixture from reaction conditions according to supporting figure 3. Substantial overreaction towards diester 52 is observed.
General procedure A for the synthesis of phosphomonoesters:

The phosphate x TBA salt (900 µmol, 3.0 eq) was dissolved in dry MeCN (67 mM) before the aryne-precursor (300 µmol) was added. Subsequently the mixture was heated to 60 °C and TBAF (1 M in THF, 1.1 eq.) was added dropwise via syringe pump (1 h, 60°C, needle tip is below solvent surface). After removing the oil bath, the reaction mixture was cooled to rt and was then directly applied to a silica column (h = 6 cm, d = 2 cm, preconditioned with acetone). The column was washed with acetone (200 mL) and the product was eluted with acetone / AcOH (9/1, 50 mL). The solvent was removed, and the crude product was further purified by RP-MPLC [C18AQ, H2O/MeCN/TEAA (10 mM)]. The product containing fractions were identified by LC-MS and the products were isolated after lyophilization.

Synthesis of phenyl phosphate (27)

The compound was synthesized according to the general procedure A from phosphate x 1.05 TBA (17, 316 mg, 900 µmol, 3.0 eq) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 90 mg, 300 µmol). The product (27, 241 mg, 265 µmol, 88%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.48 – 7.32 (m, 2H), 7.26 – 7.11 (m, 3H), 3.22 – 3.14 (m, 21H), 1.63 (ddd, J = 12.0, 10.0, 6.2 Hz, 21H), 1.35 (h, J = 7.4 Hz, 21H), 0.94 (t, J = 7.4 Hz, 32H). $^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O, δ/ppm): 152.22 (d, J = 6.6 Hz), 129.64, 123.91, 120.45 (d, J = 4.3 Hz), 58.13 – 58.01 (m), 23.10, 19.12, 12.80. $^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O, δ/ppm): -3.53. HRMS (ESI) m/z for C$_6$H$_6$O$_4$P [M- H]: calcd. 173.0009, found 173.0010.

Synthesis of 2-naphthalen-2-yl phosphate (28)

The compound was synthesized according to the general procedure A from phosphate x 1.05 TBA (17, 316 mg, 900 µmol, 3.0 eq) and 3-(trimethylsilyl)naphthalen-2-yl
trifluoromethanesulfonate (SI-12, 105 mg, 300 µmol). The product (28, 173 mg, 195 µmol, 65%) was isolated as a colorless oil.

\[ ^1H-NMR \ (400 \text{ MHz}, \ D_2O, \ \delta/ppm): \ 7.95 - 7.73 (m, 3H), \ 7.67 (t, \ J = 2.1 \text{ Hz}, \ 1H), \ 7.60 - 7.33 (m, \ 3H), \ 3.12 - 2.89 (m, \ 19H), \ 2.09 - 1.55 (m, \ 29H), \ 0.91 (t, \ J = 7.4 \text{ Hz}, \ 1H) \]

\[ ^1H-NMR \ (400 \text{ MHz}, \ D_2O, \ \delta/ppm): \ 7.95 - 7.73 (m, 3H), \ 7.67 (t, \ J = 2.1 \text{ Hz}, \ 1H), \ 7.60 - 7.33 (m, \ 3H), \ 3.12 - 2.89 (m, \ 19H), \ 2.09 - 1.55 (m, \ 29H), \ 0.91 (t, \ J = 7.4 \text{ Hz}, \ 1H) \]

\[ 13C\{^1H\}-NMR \ (101 \text{ MHz}, \ D_2O, \ \delta/ppm): \ 150.43 (d, \ J = 6.8 \text{ Hz}), \ 133.88, \ 129.97 (d, \ J = 4.6 \text{ Hz}), \ 127.71, \ 127.32, \ 129.45, \ 127.45, \ 125.09, \ 121.45 (d, \ J = 4.6 \text{ Hz}), \ 62.59, \ 45.12 \ (m), \ 23.02, \ 19.08, \ 12.82 \]

\[ ^31P\{^1H\}-NMR \ (162 \text{ MHz}, \ D_2O, \ \delta/ppm): \ -3.43 \]

HRMS (APCI) m/z for C_{10}H_{18}O_4P [M-H]: calcd. 223.0166, found 223.0166.

Synthesis of 3,4-dimethylphenyl phosphate (29)

The compound was synthesized according to the general procedure A from phosphate x 1.05 TBA (17, 316 mg, 900 µmol, 3.0 eq) and 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-6, 98 mg, 300 µmol). The product (29, 204 mg, 277 µmol, 92%) was isolated as a colorless oil.

\[ ^1H-NMR \ (400 \text{ MHz}, \ D_2O, \ \delta/ppm): \ 7.17 - 7.10 (m, \ 1H), \ 7.01 (ddd, \ J = 2.4, \ 1.1, \ 0.5 \text{ Hz}, \ 1H), \ 6.93 (ddddd, \ J = 8.3, \ 2.6, \ 1.3, \ 0.6 \text{ Hz}, \ 1H), \ 3.19 - 3.07 (m, \ 16H), \ 2.23 (s, \ 3H), \ 2.20 (s, \ 3H), \ 1.74 - 1.47 (m, \ 16H), \ 1.34 (h, \ J = 7.4 \text{ Hz}, \ 16H), \ 1.07 - 0.78 (m, \ 24H) \]

\[ ^13C\{^1H\}-NMR \ (101 \text{ MHz}, \ D_2O, \ \delta/ppm): \ 150.19 (d, \ J = 6.8 \text{ Hz}), \ 138.26, \ 132.23 (d, \ J = 1.3 \text{ Hz}), \ 130.25, \ 121.45 (d, \ J = 4.3 \text{ Hz}), \ 117.54 (d, \ J = 4.2 \text{ Hz}), \ 64.51 - 53.21 (m), \ 23.08, \ 19.17 - 19.07 (m), \ 19.01, \ 18.13, \ 12.83 \]

\[ ^31P\{^1H\}-NMR \ (162 \text{ MHz}, \ D_2O, \ \delta/ppm): \ -3.68 \]

HRMS (APCI) m/z for C_{8}H_{10}O_4P [M-H]: calcd. 201.0322, found 201.0323.

Synthesis of 1H-indol-5-yl phosphate (30)

The compound was synthesized according to the general procedure A from phosphate x 1.05 TBA (17, 316 mg, 900 µmol, 3.0 eq) and 4-(trimethylsilyl)-1H-indol-5-yl
trifluoromethanesulfonate (101 mg, 300 µmol). The crude product was obtained as a 81:19 mixture (5-30:4-30). The product (30, 190 mg, 122 µmol, 41%) was isolated as a 96:4 mixture (5-30:4-30) as a light green solid. The NMR data are given for the major isomer.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.48 – 7.43 (m, 3H), 7.40 (s, 1H), 7.09 – 7.04 (m, 1H), 3.28 – 2.98 (m, 37H), 1.80 – 1.51 (m, 37H), 1.34 (h, $J = 7.4$ Hz, 37H), 0.94 (t, $J = 7.4$ Hz, 55H).

$^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O, δ/ppm): 145.54 (d, $J = 7.0$ Hz), 132.73, 127.62, 126.69, 115.62 (d, $J = 3.8$ Hz), 111.97, 110.97 (d, $J = 4.1$ Hz), 100.98, 60.10 – 56.30 (m), 23.07, 19.10, 12.80.

$^{31}$P{$^1$H}-NMR (122 MHz, D$_2$O, δ/ppm): -3.28, -3.59.

HRMS (ESI) m/z for C$_8$H$_7$O$_4$NP [M-H]$^{-}$: calcd. 212.0118, found 212.0118.

Synthesis of pyren-2-yl phosphate (31)

The compound was synthesized according to the general procedure A from phosphate x 1.05 TBA (17, 316 mg, 900 µmol, 3.0 eq) and 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate (SI-19, 127 mg, 300 µmol). The crude product was obtained as a 76:24 mixture (2-31:1-31). The product (31, 334 mg, 214 µmol, 71%) was isolated as a 62:38 mixture (2-31:1-31) as a light green oil. The $^1$H NMR and $^{31}$P NMR data are given for the mixture and the $^{13}$C NMR data are given for the major isomer.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 8.53 (d, $J = 9.2$ Hz, 0.6H), 8.29 (dd, $J = 8.5$, 1.0 Hz, 0.6H), 8.20 – 8.13 (m, 4H), 8.13 (dd, $J = 7.6$, 1.2 Hz, 0.6H), 8.10 – 8.03 (m, 1.3H), 8.00 (s, 4H), 7.99 – 7.90 (m, 3.6H), 3.17 – 2.82 (m, 38H), 1.66 – 1.48 (m, 38H), 1.38 – 1.17 (m, 38H), 0.93 (t, $J = 7.3$ Hz, 57H).

$^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 153.51 (d, $J = 7.1$ Hz), 133.12, 131.35, 128.57, 127.97, 126.29, 126.03, 117.74 (d, $J = 5.1$ Hz), 62.39 – 57.17 (m), 24.16, 22.20 – 18.70 (m), 13.70. $^{31}$P{$^1$H}-NMR (122 MHz, CD$_3$CN, δ/ppm): -3.31, -3.75. HRMS (ESI) m/z for C$_{16}$H$_{10}$O$_4$P [M-H]$^{-}$: calcd. 297.0322, found 297.0320.
Deuteration experiment using deuterated P$_1$ (17-D)

P$_1$ x 1.05 TBA (500 mg) was dissolved in D$_2$O (3.0 ml) and the resulting solution was incubated for 30 min at room temperature. Subsequently the solution was lyophilized to dryness. The resulting solid was applied as starting material in general procedure A. In this case, the TBAF-solution was stored over molecular sieves (3 Å) for 5 h before the reaction to reduce the water content. The deuteration ratio of the product was determined by HRMS.

**HRMS (ESI) m/z for C$_6$H$_5$H$_2$O$_4$P [M-H]$^-$:** calcd. 174.0072, found 174.0072.
General procedure B for the synthesis of pyrophosphomonoesters:

The pyrophosphate x TBA salt (1.50 mmol, 5.0 eq) was dissolved in dry MeCN (67 mM) before the aryne-precursor (300 µmol) was added. Subsequently TBAF (1 M in THF, 1.1 eq.) was added dropwise via syringe pump (1 h, rt, needle tip is below solvent surface). The reaction mixture was stirred 15 min at rt and was then diluted with Et₂O (15 mL) and H₂O (15 mL) and transferred to a separation funnel. The layers were separated, and the aqueous layer was washed with Et₂O (2 × 10 mL). Then, the combined organic layers were back-extracted with H₂O (5 × 10 mL) and the combined aqueous layers were lyophilized. The residue was further purified by RP-MPLC [C18AQ, H₂O/MeCN/TEAA (10 mM)]. The product containing fractions were identified by LC-MS and the products were isolated after lyophilization.

Synthesis of phenyl diphosphate (32)

The compound was synthesized according to the general procedure B from pyrophosphate x 2.39 TBA (18, 1.13 g, 1.50 mmol, 5.0 eq) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 90 mg, 300 µmol). The product (32, 358 mg, 272 µmol, 91%) was isolated as a colorless oil.

\(^1\text{H-NMR}\) (400 MHz, D₂O, δ/ppm): 7.50 – 7.36 (m, 2H), 7.32 – 7.15 (m, 3H), 3.51 – 2.96 (m, 27H), 1.98 (s, 5H), 1.81 – 1.57 (m, 31H), 1.37 (h, J = 7.7 Hz, 31H), 1.30 – 1.25 (m, 1H), 0.96 (t, J = 7.3 Hz, 46H). \(^{13}\text{C\{^1\text{H}\}-NMR}\) (101 MHz, D₂O, δ/ppm): 151.84 (d, J = 7.2 Hz), 129.64, 124.25 (d, J = 1.3 Hz), 120.60 (d, J = 4.4 Hz), 59.88 – 54.25 (m), 46.61, 23.10, 20.81 – 17.49 (m), 12.80, 8.20. \(^{31}\text{P\{^1\text{H}\}-NMR}\) (122 MHz, D₂O, δ/ppm): -10.90 (d, J = 20.6 Hz), -15.80 (d, J = 20.7 Hz). \(\text{HRMS (ESI)}\) m/z for C₉H₁₀O₇P₂ [M-H]: calcd. 252.9672, found 252.9675.
Synthesis of 2-naphthalen-2-yl diphosphate (33)

The compound was synthesized according to the general procedure B from pyrophosphate x 2.30 TBA (18, 1.10 g, 1.50 mmol, 5.0 eq) and 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (SI-12, 105 mg, 300 µmol). The product (33, 239 mg, 186 µmol, 62%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 8.03 – 7.90 (m, 3H), 7.75 (t, $J = 2.1$ Hz, 1H), 7.66 – 7.39 (m, 3H), 3.34 – 2.82 (m, 29H), 1.73 – 1.45 (m, 29H), 1.32 (h, $J = 7.4$ Hz, 29H), 0.92 (t, $J = 7.4$ Hz, 44H). $^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O, δ/ppm): 149.86 (d, $J = 7.3$ Hz), 133.81, 130.21, 129.52, 127.73, 127.49, 126.76, 125.31, 121.47 (d, $J = 4.7$ Hz), 116.54 (d, $J = 4.7$ Hz), 59.80 – 53.72 (m), 23.05, 19.10 (t, $J = 1.6$ Hz), 12.82. $^{31}$P{$^1$H}-NMR (122 MHz, D$_2$O, δ/ppm): -10.84 (d, $J = 20.7$ Hz), -15.94 (d, $J = 20.7$ Hz). HRMS (ESI) m/z for C$_{10}$H$_{18}$O$_7$P$_2$ [M-H]: calcd. 302.9829, found 302.9830.

Synthesis of 3,4-dimethylphenyl diphosphate (34)

The compound was synthesized according to the general procedure B from pyrophosphate x 2.39 TBA (18, 1.13 g, 1.50 mmol, 5.0 eq) and 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-6, 98 mg, 300 µmol). The product (34, 281 mg, 281 µmol, 94%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.19 – 7.13 (m, 1H), 7.07 (ddd, $J = 2.5$, 1.5, 0.9 Hz, 1H), 6.99 (dddd, $J = 8.3$, 2.7, 1.2, 0.6 Hz, 1H), 3.31 – 3.04 (m, 22H), 2.25 (s, 3H), 2.22 (s, 3H), 1.75 – 1.51 (m, 22H), 1.35 (h, $J = 7.4$ Hz, 22H), 1.08 – 0.72 (m, 33H). $^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O, δ/ppm): 149.84 (d, $J = 7.2$ Hz), 138.31, 132.59 (d, $J = 1.4$ Hz), 130.24, 121.56 (d, $J = 4.5$ Hz), 117.66 (d, $J = 4.3$ Hz), 59.22 – 56.56 (m), 23.09, 19.12 (t, $J = 1.6$ Hz), 18.99, 18.15, 12.83. $^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O, δ/ppm): -10.90 (d, $J = 20.5$ Hz), -15.72 (d, $J = 21.1$ Hz). HRMS (ESI) m/z for C$_8$H$_{11}$O$_7$P$_2$ [M-H]: calcd. 280.9985, found 280.9987.
Synthesis of $1H$-indol-5-yl diphosphate (35)

The compound was synthesized according to the general procedure B from pyrophosphate x 2.30 TBA (18, 1.10 g, 1.50 mmol, 5.0 eq) and 4-(trimethylsilyl)-$1H$-indol-5-yl trifluoromethanesulfonate (101 mg, 300 µmol). The crude product was obtained as a 88:12 mixture (5-35:4-35). The product (35, 216 mg, 126 µmol, 42%) was isolated as a 96:4 mixture (5-35:4-35) as a light green oil. The NMR data are given for the major isomer.

$^1H$-NMR (300 MHz, D$_2$O, δ/ppm): 7.51 (ddd, J = 2.3, 1.6, 0.6 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.45 – 7.39 (m, 1H), 7.14 (dddd, J = 8.8, 2.4, 1.2, 0.4 Hz, 1H), 6.58 (dd, J = 3.1, 0.9 Hz, 1H), 3.30 – 2.89 (m, 4H), 1.63 (dq, J = 11.7, 7.7 Hz, 40H), 1.36 (h, J = 7.4 Hz, 40H), 1.26 (t, J = 7.3 Hz, 60H), 0.95 (t, J = 7.3 Hz, 60H). $^{13}$C{$^1H$}-NMR (101 MHz, D$_2$O, δ/ppm): 145.44 (d, J = 7.4 Hz), 132.80, 127.58, 126.62, 115.72 (d, J = 3.9 Hz), 111.92, 111.18 (d, J = 4.3 Hz), 101.30, 59.29 – 55.57 (m), 23.07, 19.11 (t, J = 1.5 Hz), 12.82. $^{31}$P{$^1H$}-NMR (162 MHz, D$_2$O, δ/ppm): -10.74 (d, J = 20.5 Hz), -15.01 (d, J = 20.4 Hz). HRMS (ESI) m/z for C$_8$H$_7$HO$_7$P$_2$ [M-H]: calcd. 292.9844, found 292.9845.

Synthesis of pyren-2-yl diphosphate (36)

The compound was synthesized according to the general procedure B from pyrophosphate x 2.39 TBA (18, 1.13 g, 1.50 mmol, 5.0 eq) and 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate (SI-19, 127 mg, 300 µmol). The crude product was obtained as a 86:14 mixture (2-36:1-36). The product (36, 379 mg, 278 µmol, 93%) was isolated as an 82:18 mixture (2-36:1-36) as a light green oil. The NMR data are given for the major isomer.

$^1H$-NMR (400 MHz, D$_2$O, δ/ppm): 8.17 – 8.13 (m, 2H), 8.07 (d, J = 9.1 Hz, 2H), 7.91 (t, J = 8.8 Hz, 4H), 7.71 (t, J = 7.6 Hz, 1H), 2.81 – 2.58 (m, 30H), 1.52 – 1.22 (m, 30H), 1.14 (h, J = 7.3 Hz, 30H), 0.81 (t, J = 7.3 Hz, 45H). $^{13}$C{$^1H$}-NMR (101 MHz, D$_2$O, δ/ppm): 150.68 (d, J = 6.8 Hz), 132.08, 130.20, 127.85, 127.46, 125.76, 125.27, 123.82, 120.80, 117.11 (d, J = 4.9 Hz),
57.68 (t, J = 2.8 Hz), 22.83, 18.96, 12.80. $^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O, δ/ppm): -10.63 (d, J = 19.4 Hz), -16.18 (d, J = 19.9 Hz). HRMS (ESI) m/z for C$_{16}$H$_{11}$O$_2$P$_2$ [M-H]: calcd. 376.9985, found 376.9987.

5. Cluster 2A: Synthesis of (Pyro-)phosphodiesters (aryne-Scope)

**General procedure C for the synthesis of phosphodiesters:**

The phosphate x TBA salt (150 - 500 µmol) was dissolved in dry MeCN (200 mM) before the aryne-precursor (2.5 eq.) was added. Subsequently TBAF (1 M in THF, 2.5 eq.) was added dropwise via syringe pump (1 h, rt, needle tip is below solvent surface). Subsequently the reaction mixture is stirred for 15 min at rt and directly applied to a silica column (h = 6 cm, d = 2 cm, preconditioned with acetone). The column was washed with acetone (200 mL) and the product was eluted with acetone / AcOH (9/1, 50 mL). The solvent was removed, and the crude product was further purified by RP-MPLC [C18AQ, H$_2$O/MeCN/TEAA (10 mM)]. The product containing fractions were identified by LC-MS and the products were isolated after lyophilization.

**5,5,5-Trifluoropentyl-phenylphosphate (40)**

![Diagram of 5,5,5-Trifluoropentyl-phenylphosphate (40)](image)

The compound was synthesized according to the general procedure C from 5,5,5,-trifluoropentylphosphate x 1.5 TBA (38, 173 mg, 300 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 182 µl, 223 mg, 750 µmol, 2.5 eq.). The product (40, 66.0 mg, 152 µmol, 51%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.32 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 7.08 – 7.01 (m, 1H), 3.91 (dt, J = 6.8, 6.0 Hz, 2H), 3.13 – 3.04 (m, 3H), 2.95 (q, J = 7.3 Hz, 2H), 2.21 – 2.07 (m, 2H), 1.69 – 1.52 (m, 7H), 1.40 – 1.29 (m, 3H), 1.19 (t, J = 7.3 Hz, 4H), 0.96 (t, J = 7.4 Hz, 4H). $^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 154.36 (d, J = 6.5 Hz), 130.12, 123.82, 121.14 (d, J = 5.0 Hz), 65.94 (d, J = 6.1 Hz), 59.31, 46.53, 33.58 (q, J = 28.0 Hz), 30.25 (d, J = 7.5
Hz), 24.31, 20.34, 19.24 (q, $J = 3.3$ Hz), 13.79, 8.88. $^{19}$F NMR (377 MHz, CD$_3$CN, δ/ppm): -66.98 (t, $J = 11.4$ Hz). $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -6.72. HRMS (ESI) m/z for C$_{11}$H$_{13}$F$_3$O$_4$P [M-H]: calcd. 297.0509, found 297.0507.

**Synthesis of 3,4-dimethylphenyl (5,5,5-trifluoropentyl) phosphate (41)**

![Chemical Structure](image)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-6, 245 mg, 750 µmol, 2.5 eq). The product (41, 142 mg, 201 µmol, 67%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.00 – 6.94 (m, 2H), 6.93 – 6.85 (m, 1H), 3.93 – 3.72 (m, 2H), 3.23 – 2.93 (m, 11H), 2.19 (s, 3H), 2.16 (s, 3H), 2.16 – 2.06 (m, 2H), 1.69 – 1.49 (m, 15H), 1.34 (h, $J = 7.4$ Hz, 11H), 0.96 (t, $J = 7.3$ Hz, 17H). $^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 153.58 (d, $J = 6.6$ Hz), 137.71, 130.47, 130.35, 128.74 (q, $J = 275.5$ Hz), 122.10 (d, $J = 4.7$ Hz), 118.16, 64.85 (d, $J = 6.1$ Hz), 60.82 – 54.61 (m), 33.58 (q, $J = 27.9$ Hz), 30.47 (d, $J = 7.3$ Hz), 24.26, 21.63 – 19.39 (m), 19.90, 19.36 (q, $J = 3.1$ Hz), 18.90, 13.74. $^{19}$F NMR (377 MHz, CD$_3$CN, δ/ppm): -66.97 (t, $J = 11.1$ Hz). $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -5.40. HRMS (ESI) m/z for C$_{13}$H$_{17}$F$_3$O$_4$P [M-H]: calcd. 325.0822, found 325.0820.

**Synthesis of 2,5-dimethylphenyl (5,5,5-trifluoropentyl) phosphate (42)**

![Chemical Structure](image)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.47 TBA (38, 173 mg, 300 µmol) and 3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-7, 245 mg, 750 µmol, 2.5 eq). The product (42, 124 mg, 180 µmol, 60%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.22 (s, 1H), 6.96 (d, $J = 7.5$ Hz, 1H), 6.70 – 6.59 (m, 1H), 4.03 – 3.56 (m, 2H), 3.15 – 3.04 (m, 11H), 2.23 (d, $J = 0.7$ Hz, 3H), 2.22 – 2.07 (m, 5H),
1.71 – 1.48 (m, 15H), 1.44 – 1.16 (m, 11H), 0.96 (t, J = 7.3 Hz, 17H). $^{13}$C($^1$H)-NMR (101 MHz, CD$_3$CN, δ/ppm): 153.71 (d, J = 6.7 Hz), 136.61, 130.74, 130.13 (q), 126.44 (d, J = 6.4 Hz), 123.03, 121.45 (d, J = 2.5 Hz), 64.93 (d, J = 6.3 Hz), 60.62 – 54.40 (m), 33.62 (q, J = 27.9 Hz), 30.53 (d, J = 7.3 Hz), 24.25, 21.15, 20.64 – 19.62 (m), 19.41 (q, J = 3.2 Hz), 16.51, 13.74.

$^{19}$F NMR (377 MHz, CD$_3$CN, δ/ppm): -66.95 (t, J = 11.4 Hz).

$^{31}$P($^1$H)-NMR (162 MHz, CD$_3$CN, δ/ppm): -5.36. HRMS (ESI) m/z for C$_{13}$H$_{17}$F$_3$O$_4$P [M-H]: calcd. 357.0720, found 357.0721.

Synthesis of 3,4-dimethoxyphenyl (5,5,5-trifluoropentyl) phosphate (43)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-8, 269 mg, 750 µmol, 2.5 eq). The product (43, 121 mg, 172 µmol, 57%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 6.87 (dd, J = 2.6, 0.9 Hz, 1H), 6.77 (d, J = 8.7 Hz, 1H), 6.70 (ddd, J = 8.7, 2.6, 1.1 Hz, 1H), 3.84 – 3.76 (m, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.13 – 3.01 (m, 11H), 2.26 – 2.05 (m, 2H), 1.68 – 1.48 (m, 15H), 1.44 – 1.24 (m, 11H), 0.96 (t, J = 7.4 Hz, 15H), 0.89 (t, J = 7.2 Hz, 0.5H). $^{13}$C($^1$H)-NMR (101 MHz, CD$_3$CN, δ/ppm): 150.26, 149.80 (d, J = 4.9 Hz), 145.07, 128.74 (q, J = 275.6 Hz), 113.15, 111.93 (d, J = 4.7 Hz), 106.22 (d, J = 6.5 Hz), 145.07, 128.74 (q, J = 275.6 Hz), 113.15, 111.93 (d, J = 4.7 Hz), 106.22 (d, J = 4.9 Hz), 64.95 (d, J = 6.3 Hz), 61.17 – 57.30 (m), 56.80, 56.16, 33.59 (q, J = 27.9 Hz), 30.48 (d, J = 7.3 Hz), 24.25, 21.75 – 19.05 (m), 19.36 (q, J = 3.2 Hz), 13.73. $^{19}$F NMR (377 MHz, CD$_3$CN, δ/ppm): -66.95 (t, J = 11.4 Hz). $^{31}$P($^1$H)-NMR (162 MHz, CD$_3$CN, δ/ppm): -5.36. HRMS (ESI) m/z for C$_{13}$H$_{17}$F$_3$O$_4$P [M-H]: calcd. 357.0720, found 357.0721.
Synthesis of 4-(trifluoromethyl)phenyl (5,5,5-trifluoropentyl) phosphate (44)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 5-(trifluoromethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-11, 275 mg, 750 µmol, 2.5 eq). The crude product was obtained as a 68:32 mixture (para:meta). The product (44, 116 mg, 149 µmol, 50%) was isolated as a 85:15 mixture (para:meta) as a colorless oil. The NMR data are given for the major isomer.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.60 – 7.52 (m, 2H), 7.48 – 7.33 (m, 2H), 3.92 – 3.77 (m, 2H), 3.17 – 3.03 (m, 14H), 2.24 – 2.04 (m, 2H), 1.70 – 1.47 (m, 18H), 1.46 – 1.23 (m, 14H), 0.96 (t, $J = 7.3$ Hz, 20H). $^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 158.46 (d, $J = 6.1$ Hz), 128.68 (q, $J = 275.5$ Hz), 127.27 – 127.10 (m), 125.74 (q, $J = 270.4$ Hz), 123.98 (q, $J = 32.2$ Hz), 121.10 (d, $J = 5.0$ Hz), 65.40 (d, $J = 6.3$ Hz), 59.79 – 54.70 (m), 35.90 – 32.26 (m), 30.29 (d, $J = 7.4$ Hz), 24.25, 21.09 – 19.13 (m), 19.26 (q, $J = 3.3$ Hz), 13.73. $^{19}$F-NMR (377 MHz, CD$_3$CN, δ/ppm): -61.94 (para), -62.98 (meta), -66.94 – -67.13 (m, both). $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -1.32. HRMS (ESI) m/z for C$_{12}$H$_{12}$F$_6$O$_4$P [M-H]: calcd. 365.0383, found 365.0381.

Synthesis of benzo[d][1,3]dioxol-5-yl (5,5,5-trifluoropentyl) phosphate (45)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (SI-9, 257 mg, 750 µmol, 2.5 eq). The product (45, 89 mg, 184 µmol, 61%) was isolated as a colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 6.79 (dd, $J = 2.2$, 0.8 Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.64 (ddd, $J = 8.4$, 2.3, 1.1 Hz, 1H), 5.91 (s, 2H), 4.22 – 3.79 (m, 2H), 3.25 – 2.89 (m, 5H), 2.26 – 2.03 (m, 2H), 1.71 – 1.49 (m, 9H), 1.46 – 1.27 (m, 5H), 0.96 (t, $J = 7.3$ Hz, 7H). $^{13}$C{$^1$H}-
NMR (101 MHz, CD$_3$CN, δ/ppm): 148.76 (d, $J = 6.7$ Hz), 148.64, 144.11, 128.69 (q, $J = 275.6$ Hz), 113.20 (d, $J = 4.9$ Hz), 108.38, 103.50 (d, $J = 4.5$ Hz), 102.47, 66.01 (d, $J = 6.0$ Hz), 63.00 – 54.55 (m), 33.52 (q, $J = 275.6$ Hz), 30.17 (d, $J = 7.4$ Hz), 24.24, 21.30 – 19.63 (m), 19.14 (q, $J = 3.3$ Hz), 13.72. $^{19}$F NMR (377 MHz, CD$_3$CN, δ/ppm): -66.98 (t, $J = 11.4$ Hz). $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -6.49.

HRMS (ESI) m/z for C$_{12}$H$_{13}$F$_3$O$_6$P [M-H]: calcd. 341.0407, found 341.0403.

**Synthesis of 4-ethynylphenyl (5,5,5-trifluoropentyl) phosphate (46)**

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate (SI-23, 253 mg, 750 µmol, 2.5 eq). The crude product was obtained as a 84:16 mixture (para:meta). The product (46, 127 mg, 193 µmol, 64%) was isolated as a 63:37 mixture (para:meta) as a colorless oil. The NMR data are given for the mixture, an assignment to the isomers was made if possible.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.39 – 7.31 (m, 1.5H, both), 7.22 – 7.16 (m, 1.9H, both), 7.11 – 7.04 (m, 0.4H, meta), 3.85 – 3.76 (m, 2H, both), 3.33 (s, 0.4H, meta), 3.26 (s, 0.6H, para), 3.16 – 3.03 (m, 10H, both), 2.23 – 2.02 (m, 2H, both), 1.68 – 1.46 (m, 14H, both), 1.44 – 1.24 (m, 10H, both), 1.05 – 0.90 (m, 15H, both). $^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 156.48 (d, $J = 6.4$ Hz, para), 155.69 (d, $J = 6.4$ Hz, meta), 133.70 (para), 130.00 (meta), 128.73 (q, $J = 275.6$ Hz, both), 126.02 (para), 123.18 (meta), 122.02 (d, $J = 5.1$ Hz, meta), 120.94 (d, $J = 5.2$ Hz, para), 115.59, 84.50 (para), 84.23 (meta), 78.24 (meta), 77.21 (para), 65.06 (d, $J = 6.3$ Hz, both), 62.17 – 57.65 (m, both), 33.58 (qd, $J = 28.0$, 2.3 Hz, both), 30.42 (dd, $J = 7.3$, 3.1 Hz, both), 24.25 (both), 21.89 – 19.93 (m, both), 19.99 – 18.48 (m, both), 13.73 (both). $^{19}$F NMR (377 MHz, CD$_3$CN, δ/ppm): -66.84 – -67.09 (m, both). $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -5.61 (meta), -5.77 (para). HRMS (ESI) m/z for C$_{13}$H$_{13}$F$_3$O$_6$P [M-H]: calcd. 321.0509, found 321.0507.
Synthesis of 3-bromophenyl (5,5,5-trifluoropentyl) phosphate (47)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 2-bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (283 mg, 750 µmol, 2.5 eq). The crude product was obtained as an 88:12 mixture (meta:ortho). The product (47, 121 mg, 172 µmol, 57%) was isolated as a colorless oil in a similar regioisomeric ratio. Redundant TBA counterions are assumed to be hydroxide.

\[ \text{HRMS (ESI) m/z for C}_{11}H_{12}BrF_{3}O_{4}P [M-H]}: \text{calcd. 374.9614, found 374.9613.} \]

Synthesis of 4-chlorophenyl (5,5,5-trifluoropentyl) phosphate (48)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 5-chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (SI-10, 250 mg, 750 µmol, 2.5 eq). The crude product was obtained as a 78:22 mixture (para:meta). The product (48, 123 mg, 171 µmol, 57%) was isolated as a colorless oil. The NMR data are given for the major isomer. Redundant TBA-counterions are assumed to be hydroxide.

\[ \text{HRMS (ESI) m/z for C}_{11}H_{12}BrF_{3}O_{4}P [M-H]}: \text{calcd. 374.9614, found 374.9613.} \]
Hz), 122.37 (d, $J = 5.0$ Hz), 122.23, 65.03 (d, $J = 6.3$ Hz), 61.89 – 53.86 (m), 33.57 (q, $J = 28.0$ Hz), 30.41 (d, $J = 7.3$ Hz), 24.25, 21.72 – 19.36 (m), 19.31 (q, $J = 3.2$ Hz), 13.73. ¹⁹F NMR (377 MHz, CD₃CN, δ/ppm): -66.99 (t, $J = 11.4$ Hz). ³¹P{¹H}-NMR (162 MHz, CD₃CN, δ/ppm): -5.53. HRMS (ESI) m/z for C₁₁H₁₂ClF₃O₄P [M-H]: calcd. 331.0119, found 331.0119.

**Synthesis of naphthalen-2-yl (5,5,5-trifluoropentyl) phosphate (49)**

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (SI-12, 261 mg, 750 µmol, 2.5 eq). The product (49), 95 mg, 129 µmol, 43%) was isolated as a colorless oil.

¹H-NMR (400 MHz, CD₃CN, δ/ppm): 7.84 – 7.71 (m, 3H), 7.68 – 7.62 (m, 1H), 7.48 – 7.38 (m, 2H), 7.34 (ddd, $J = 8.1$, 6.8, 1.3 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.13 – 3.03 (m, 1H), 2.20 – 2.02 (m, 2H), 1.71 – 1.47 (m, 16H), 1.48 – 1.24 (m, 12H), 0.95 (t, $J = 7.3$ Hz, 18H). ¹³C{¹H}-NMR (101 MHz, CD₃CN, δ/ppm): 153.45 (d, $J = 6.4$ Hz), 135.30, 130.36, 129.34, 128.70 (q, $J = 275.5$ Hz), 128.34, 127.79, 126.81, 124.70, 124.71 (d, $J = 5.4$ Hz), 115.88 (d, $J = 5.0$ Hz), 65.07 (d, $J = 6.3$ Hz), 61.18 – 55.22 (m), 33.56 (q, $J = 27.8$ Hz), 30.45 (d, $J = 7.5$ Hz), 24.23, 21.85 – 19.03 (m), 19.34 (q, $J = 3.3$ Hz), 13.73. ¹⁹F NMR (377 MHz, CD₃CN, δ/ppm): -66.98 (t, $J = 11.4$ Hz). ³¹P{¹H}-NMR (162 MHz, CD₃CN, δ/ppm): -5.44. HRMS (ESI) m/z for C₁₅H₁₅F₃O₄P [M-H]: calcd. 347.0666, found 347.0666.

**Synthesis of 1H-indol-5-yl (5,5,5-trifluoropentyl) phosphate (50)**

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 4-(trimethylsilyl)-1H-indol-5-yl trifluoromethanesulfonate (253 mg, 750 µmol, 2.5 eq). The crude product was obtained as a 85:15 mixture (5-50:4-50). The product (50), 107 mg, 114 µmol, 38%) was isolated as a 92:8 mixture (5-50:4-50) as a light green solid. The NMR data are given for the major isomer.
Synthesis of pyren-2-yl (5,5,5-trifluoropentyl) phosphate (51)

The compound was synthesized according to the general procedure C from 5,5,5-trifluoropentyl phosphate x 1.22 TBA (38, 155 mg, 300 µmol) and 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate (SI-19, 317 mg, 750 µmol, 2.5 eq). The crude product was obtained as a 78:22 mixture (2-51:1-51). The product (51, 125 mg, 174 µmol, 58%) was isolated as a 78:22 mixture (2-51:1-51) as a light-yellow oil. The NMR data are given for the major isomer. Redundant TBA counterions are assumed to be hydroxide.

\[ ^{1}H\text{-NMR (400 MHz, CD}_{3}\text{CN, }\delta/\text{ppm): 9.78 (s, 1H), 7.35 (td, } J = 1.4, 0.6 \text{ Hz, 1H), 7.25 (dd, } J = 8.7, 0.8 \text{ Hz, 1H), 7.18 (ddd, } J = 3.0, 2.4, 0.4 \text{ Hz, 1H), 6.97 (dddd, } J = 8.8, 2.3, 1.0, 0.4 \text{ Hz, 1H), 6.33 (ddd, } J = 3.0, 2.0, 0.9 \text{ Hz, 1H), 3.89 – 3.77 (m, 2H), 3.17 – 2.96 (m, 17H), 2.24 – 2.05 (m, 2H), 1.66 – 1.49 (m, 21H), 1.42 – 1.24 (m, 17H), 0.96 (t, } J = 7.3 \text{ Hz, 26H).} \]
\[ ^{13}C\{^{1}H\}\text{-NMR (101 MHz, CD}_{3}\text{CN, }\delta/\text{ppm): 149.00 (d, } J = 6.8 \text{ Hz), 133.03, 129.08, 128.78 (q, } J = 275.5 \text{ Hz), 126.20, 116.55 (d, } J = 4.9 \text{ Hz), 111.79, 110.93 (d, } J = 4.3 \text{ Hz), 101.92, 64.81 (d, } J = 6.1 \text{ Hz), 33.62 (q, } J = 27.9 \text{ Hz), 30.58 (d, } J = 7.3 \text{ Hz), 24.25, 21.45 – 18.68 (m), 19.38 (q, } J = 3.3 \text{ Hz), 13.73.} \]
\[ ^{19}F\text{-NMR (377 MHz, CD}_{3}\text{CN, }\delta/\text{ppm): -66.96 (t, } J = 11.3 \text{ Hz).} \]
\[ ^{31}P\{^{1}H\}\text{-NMR (162 MHz, CD}_{3}\text{CN, }\delta/\text{ppm): -4.70.} \]

\[ \text{HRMS (ESI) m/z for C}_{13}\text{H}_{14}\text{F}_{3}\text{NO}_{4}\text{P [M-H]: calcd. 336.0618, found 336.0617.} \]
6. Cluster 2B: Synthesis of (Pyro-)phosphodiester (phosphate-Scope)

**Diphenylphosphate (52)**

![Diphenylphosphate](52)

The compound was synthesized according to the general procedure C from phenylphosphate x 1.0 TBA (200 mg, 467 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 2.5 eq.). The product (52, 102 mg, 254 µmol, 55%) was isolated as colorless oil.

**¹H-NMR** (400 MHz, D₂O, δ/ppm): δ 7.45 – 7.38 (m, 4H), 7.27 – 7.20 (m, 6H), 3.27 – 3.12 (m, 6H), 1.71 – 1.59 (m, 4H), 1.48 – 1.32 (m, 3H), 1.28 (t, J = 7.4 Hz, 4H), 0.95 (t, J = 7.4 Hz, 5H).

**¹³C{¹H}-NMR** (101 MHz, D₂O, δ/ppm): 151.62 (d, J = 7.2 Hz), 129.80, 124.52 (d, J = 1.2 Hz), 120.22 (d, J = 4.6 Hz), 58.72 – 57.16 (m), 46.64, 23.10, 20.47 – 18.36 (m), 12.79, 8.19. **³¹P{¹H}-NMR** (162 MHz, D₂O, δ/ppm): -8.85. **HRMS** (ESI) m/z for C₁₂H₁₀O₄P [M-H]: calcd. 249.0322, found 249.0322.

**Pentyl-phenylphosphate (53)**

![Pentyl-phenylphosphate](53)

The compound was synthesized according to the general procedure C from pentylphosphate x 1.0 TBA (67, 123 mg, 300 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 2.5 eq.). The product (53, 0.65 TBA, 67.0 mg, 167 µmol, 56%) was isolated as colorless oil.

**Alternative procedure (avoiding THF-side reaction):**

TBAF (1 M in THF, 750 µL, 750 µmol, 2.5 eq.) was dried under high vacuum and dissolved in dry MeCN (750 µL). This was repeated twice and the resulting solution was then added to a solution of Pentylphosphate x 1.1 TBA (67, 130 mg, 300 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 182 µL, 750 µmol, 2.5 eq.) in MeCN (1.5 mL) with a syringe pump (1 h, needle tip is below solvent surface). Purification was done according to the general
procedure C. The product (53, 0.65 TEA, 67.2 mg, 216 µmol, 72%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.29 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 7.06 – 6.99 (m, 1H), 3.87 (q, $J$ = 6.6 Hz, 2H), 3.15 – 3.04 (m, 5H), 1.65 – 1.50 (m, 2H), 1.41 – 1.22 (m, 9H), 0.96 (t, $J$ = 7.3 Hz, 7H), 0.89 – 0.84 (m, 3H). $^{13}$C$^{[1]$H$}$-NMR (101 MHz, CD$_3$CN, δ/ppm): 154.47 (d, $J$ = 6.5 Hz), 130.02, 123.61, 121.15 (d, $J$ = 5.0 Hz), 66.66 (d, $J$ = 6.3 Hz), 59.74 – 58.85 (m), 31.15 (d, $J$ = 7.3 Hz), 28.74, 24.32, 23.09, 21.39 – 19.80 (m), 14.34, 13.82. $^{31}$P$^{[1]$H$}$-NMR (162 MHz, CD$_3$CN, δ/ppm): -6.80. HRMS (ESI) m/z for C$_{11}$H$_{16}$O$_3$P [M-H]: calcd. 243.0792, found 243.0791.

Phenyl-phenylphosphonate (54)

The compound was synthesized according to the general procedure C from phenylphosphonate x 1.0 TBA (201 mg, 500 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (I, 2.5 eq.). The product (54, 127 mg, 229 µmol, 46%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.81 – 7.73 (m, 2H), 7.61 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 7.34 – 7.27 (m, 2H), 7.18 – 7.12 (m, 1H), 7.04 – 6.99 (m, 2H), 3.25 – 3.11 (m, 9H), 1.70 – 1.57 (m, 9H), 1.36 (h, $J$ = 7.4 Hz, 9H), 0.95 (t, $J$ = 7.3 Hz, 14H). $^{13}$C$^{[1]$H$}$-NMR (101 MHz, D$_2$O, δ/ppm): 151.51 (d, $J$ = 7.1 Hz), 132.66 (d, $J$ = 181.1 Hz), 131.39 (d, $J$ = 3.0 Hz), 131.18 (d, $J$ = 9.5 Hz), 129.58, 128.38 (d, $J$ = 14.1 Hz), 124.19 (d, $J$ = 1.3 Hz), 121.02 (d, $J$ = 3.8 Hz), 58.69 – 57.62 (m), 23.09, 19.51 – 17.77 (m), 12.79. $^{31}$P$^{[1]$H$}$-NMR (162 MHz, D$_2$O, δ/ppm): 12.99. HRMS (ESI) m/z for C$_{12}$H$_{16}$O$_3$P [M-H]: calcd. 233.0373, found 233.0373.
Pent-4-yn-1-yl-phenylphosphate (55)

The compound was synthesized according to the general procedure C from pent-4-yn-1-ylphosphate x 1.0 TBA (SI-3, 203 mg, 500 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (I, 2.5 eq.). The product (55, 136 mg, 242 µmol, 48%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, D$_2$O/MeCN-d$_3$, δ/ppm): 7.66 – 7.58 (m, 2H), 7.46 – 7.38 (m, 3H), 4.24 (q, J = 6.3 Hz, 2H), 3.46 – 3.33 (m, 10H), 2.58 (t, J = 2.7 Hz, 1H), 2.50 (td, J = 7.1, 2.7 Hz, 2H), 2.04 (td, J = 7.1, 6.1, 0.9 Hz, 2H), 1.85 (ddd, J = 11.8, 10.0, 6.3 Hz, 10H), 1.59 (h, J = 7.4 Hz, 10H), 1.19 (t, J = 7.4 Hz, 14H).

$^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O/MeCN-d$_3$, δ/ppm): 152.43 (d, J = 6.8 Hz), 129.85, 124.09, 120.40 (d, J = 4.6 Hz), 84.85, 69.82, 65.00 (d, J = 5.9 Hz), 58.94 – 57.12 (m), 29.12 (d, J = 7.6 Hz), 23.36, 20.48 – 18.45 (m), 14.43, 13.09.

$^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O/MeCN-d$_3$, δ/ppm): -4.34. HRMS (ESI) m/z for C$_{11}$H_{12}O$_4$P [M-H]: calcd. 239.0479, found 239.0480.

Isoprenyl-phenylphosphate (56)

The compound was synthesized according to the general procedure C from isoprenylphosphate x 1.25 TBA (SI-15, 134 mg, 288 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (I, 2.5 eq.). The product (56, 33.3 mg, 112 µmol, 39%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.33 – 7.27 (m, 2H), 7.22 – 7.17 (m, 2H), 7.12 – 7.06 (m, 1H), 4.77 (dqt, J = 2.2, 1.5, 0.7 Hz, 1H), 4.72 (dq, J = 2.2, 1.2 Hz, 1H), 4.04 (q, J = 6.8 Hz, 2H), 2.96 (qd, J = 7.3, 4.7 Hz, 3H), 2.32 (tdd, J = 6.8, 1.2, 0.6 Hz, 2H), 1.71 (td, J = 1.0, 0.5 Hz, 3H), 1.18 (t, J = 7.3 Hz, 5H). $^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 153.75 (d, J = 6.7 Hz), 143.49, 130.28, 124.40, 121.22 (d, J = 4.7 Hz), 112.50, 65.39 (d, J = 6.2 Hz), 46.75, 39.20 (d, J = 7.7 Hz), 22.56, 8.94. $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -6.95. HRMS (ESI) m/z for C$_{11}$H$_{14}$O$_4$P [M-H]: calcd. 241.0635, found 241.0636.
Geranyl-phenylphosphate (57)

The compound was synthesized according to the general procedure C from geranylphosphate x 1.4 TBA (SI-14, 158 mg, 275 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 2.5 eq.). In this case the purification procedure required modification. After the reaction, the solvent was removed, and the residue was dissolved in TEAA-buffer (10 mM). Insolubles were removed and the solution was directly applied to RP-MPLC (see general procedure C). The product (57, 25.1 mg, 74.7 µmol, 27%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, CD$_3$CN, δ/ppm): 7.30 – 7.24 (m, 2H), 7.21 – 7.16 (m, 2H), 7.07 – 7.01 (m, 1H), 5.32 (tq, J = 6.7, 1.3 Hz, 1H), 5.08 (tdt, J = 5.7, 2.9, 1.4 Hz, 1H), 4.41 (m, 2H), 2.96 (q, J = 7.3 Hz, 2H), 1.66 – 1.64 (m, 3H), 1.61 (d, J = 1.3 Hz, 3H), 1.59 – 1.57 (m, 3H), 1.19 (t, J = 7.3 Hz, 3H). $^{13}$C{$^1$H}-NMR (101 MHz, CD$_3$CN, δ/ppm): 154.32 (d, J = 5.3 Hz), 140.90, 132.47, 130.21, 124.94, 123.93, 121.87 (d, J = 6.7 Hz), 121.16 (d, J = 3.2 Hz), 63.48 (d, J = 3.6 Hz), 46.65, 40.14, 27.12, 25.82, 17.79, 16.53, 8.92. $^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -5.83. HRMS (ESI) m/z for C$_{16}$H$_{22}$O$_4$P [M-H]: calcd. 309.1261, found 309.1266.

6-Hydroxyhexyl-phenylphosphate (58)

The compound was synthesized according to the general procedure C from 6-hydroxyhexylphosphate x 1.20 TBA (SI-13, 183 mg, 377 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 2.5 eq.). The product (58, 28.0 mg, 55.8 µmol, 15%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, D$_2$O/MeCN-d3, δ/ppm): 7.58 – 7.51 (m, 2H), 7.38 – 7.31 (m, 3H), 4.09 (q, J = 6.5 Hz, 2H), 3.69 (t, J = 6.8 Hz, 2H), 3.34 – 3.26 (m, 7H), 1.83 – 1.71 (m, 9H), 1.65 (p, J = 6.8 Hz, 2H), 1.57 – 1.44 (m, 11H), 1.41 (t, J = 7.3 Hz, 1H), 1.11 (t, J = 7.4 Hz, 10H).
$^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O/MeCN-d3, δ/ppm): 152.97 (d, $J = 6.8$ Hz), 130.54, 124.84, 120.99 (d, $J = 4.6$ Hz), 67.43 (d, $J = 6.3$ Hz), 62.52, 59.63 – 57.79 (m), 47.46, 32.23, 30.63 (d, $J = 7.2$ Hz), 25.63 (d, $J = 8.8$ Hz), 23.99, 21.10 – 19.15 (m), 13.74. $^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O/MeCN-d3, δ/ppm): -4.22. HRMS (ESI) m/z for C$_{12}$H$_{18}$O$_5$P [M-H]: calcd. 273.0897, found 273.0899.

D4T-phenylphosphate (59)

The compound was synthesized according to the general procedure C from d4T-monophosphate x 1.44 TBA (SI-5, 120 mg, 184 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (I, 2.5 eq.). The product (59, 45.4 mg, 74.5 µmol, 41%) was isolated as colorless oil.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.33 (q, $J = 1.2$ Hz, 1H), 7.25 (dd, $J = 8.4$, 7.3 Hz, 2H), 7.12 – 7.02 (m, 3H), 6.90 (dt, $J = 3.2$, 1.7 Hz, 1H), 6.49 (dt, $J = 6.2$, 1.8 Hz, 1H), 5.90 (dt, $J = 6.2$, 2.0 Hz, 1H), 5.21 – 5.12 (m, 1H), 4.25 (dt, $J = 11.6$, 2.8 Hz, 1H), 4.09 (dt, $J = 11.6$, 3.6 Hz, 1H), 3.21 (q, $J = 7.3$ Hz, 1H), 1.60 (d, $J = 1.1$ Hz, 3H), 1.29 (t, $J = 7.3$ Hz, 16H). $^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O, δ/ppm): δ 166.43, 152.19, 151.42 (d, $J = 7.2$ Hz), 138.22, 134.22, 129.09, 125.04, 124.38, 120.21 (d, $J = 4.4$ Hz), 110.72, 89.95, 85.65 (d, $J = 10.4$ Hz), 66.19 (d, $J = 5.5$ Hz), 46.63, 11.28, 8.20. $^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O, δ/ppm): -4.85. HRMS (ESI) m/z for C$_{16}$H$_{16}$N$_2$O$_7$P [M-H]: calcd. 379.0701, found 379.0706.
D4T-phenylpyrophosphate (60)

The compound was synthesized according to the general procedure C from d4T-monophosphate x 2.37 TBA (SI-17, 150 mg, 157 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 2.5 eq.). In this case the purification procedure required modification. After the reaction, the crude product was precipitated by the addition of Et₂O/pentene (1/1, 40 mL). The precipitate was separated by centrifugation, washed with Et₂O/pentane (1/1, 2 x 30 mL) and dried over high vac. The resulting crude product was dissolved in TEAA-buffer (10 mM) and the solution was directly applied to RP-MPLC (see general procedure C). The product (60, 38.8 mg, 52.1 µmol, 33%) was isolated as colorless oil.

\(^1\)H-NMR (400 MHz, D₂O, δ/ppm): 7.52 (q, J = 1.2 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.18 – 7.09 (m, 3H), 6.97 – 6.91 (m, 1H), 6.45 (dt, J = 6.1, 1.8 Hz, 1H), 5.88 (dd, J = 6.2, 2.4, 1.4 Hz, 1H), 5.13 – 5.05 (m, 1H), 4.22 – 4.10 (m, 2H), 3.19 (q, J = 7.3 Hz, 15H), 1.78 (dd, J = 1.2, 0.4 Hz, 3H), 1.27 (t, J = 7.3 Hz, 21H). \(^{13}\)C\(^{(1)}\)H\)-NMR (101 MHz, D₂O, δ/ppm): 166.42, 152.09, 151.71 (d, J = 7.2 Hz), 138.24, 134.06, 129.39, 125.34, 124.09 (d, J = 1.2 Hz), 120.19 (d, J = 4.8 Hz), 111.31, 89.71, 85.89 (d, J = 9.7 Hz), 66.53 (d, J = 5.9 Hz), 46.61, 11.41, 8.20. \(^{31}\)P\(^{(1)}\)H\)-NMR (162 MHz, D₂O, δ/ppm): -11.95 (d, J = 22.0 Hz), -16.41 (d, J = 22.0 Hz). HRMS (ESI) m/z for C\(_{16}\)H\(_{17}\)N\(_2\)O\(_{10}\)P\(_2\) [M-H]: calcd. 459.0364, found 459.0365.
Diphenylpyrophosphate (61)

The compound was synthesized according to the general procedure C from Phenylpyrophosphate x 2.4 TBA (SI-16, 215 mg, 260 µmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1, 2.5 eq.). In this case the purification procedure required modification. After the reaction, the solvent was removed and the residue was dissolved in TEAA-buffer (10 mM). Insolubles were removed and the solution was directly applied to RP-MPLC (see general procedure C). The product (61, 89.4 mg, 123 µmol, 47%) was isolated as colorless oil.

\(^1H\)-NMR (400 MHz, D\textsubscript{2}O, δ/ppm): 7.42 – 7.34 (m, 4H), 7.24 – 7.17 (m, 6H), 3.25 – 3.14 (m, 14H), 1.72 – 1.59 (m, 12H), 1.36 (h, J = 7.4 Hz, 12H), 1.28 (t, J = 7.3 Hz, 3H), 0.95 (t, J = 7.4 Hz, 18H). \(^1^3C\{^1H\}\)-NMR (101 MHz, D\textsubscript{2}O, δ/ppm): 151.68 (t, J = 3.7 Hz), 129.63, 124.35, 120.55 (t, J = 2.2 Hz), 58.09, 46.63, 23.10, 19.12, 12.79, 8.19. \(^31P\{^1H\}\)-NMR (162 MHz, D\textsubscript{2}O, δ/ppm): -16.13. HRMS (ESI) m/z for C\textsubscript{6}H\textsubscript{14}O\textsubscript{5}P [M-H]: calcd. 197.0584, found 197.0584.
7. Cluster 3: Synthesis of Arylpolyphosphates (cyclophosphate reactions)

7.1. Preparation of cyclic metaphosphate \( (n = 4, 5, 7, 8) \times \text{TBA} \) – salts:

Trimetaphosphate was commercially available. Tetrametaphosphate was synthesized as Na-salt on gram-scale according to Bell et al.\(^\text{11}\). A mixture of higher cyclic metaphosphates \( (n = 3 \text{–} 8) \) was prepared on multi-gram scale according to Glonek et al.\(^\text{12}\) from crystalline orthophosphoric acid and DCC in TMU. Preparative separation was possible by automated SAX (Äkta-system, Q-Sepharose). Tri- to heptametaphosphate were eluted with Triethylammoniumbicarbonate-buffer (0.1 - 1M, pH 7.5). Octametaphosphate was eluted with \( \text{NH}_4\text{HCO}_3 \) – buffer. The sample qualities were polished during a second run of automated SAX (Äkta-system, Q-Sepharose, \( \text{NH}_4\text{HCO}_3 \) – buffer). The procedure delivered pentametaphosphate, heptametaphosphate and octametaphosphate as \( \text{NH}_4 \) – salts. Hexametaphosphate could not be isolated sufficient purity. The different ring-sizes were assigned by HRMS.

**HRMS – data:**

**HRMS (ESI) m/z for \( \text{H}_3\text{O}_{15}\text{P}_5 \) [M-H]**: calcd. 398.8244, found 398.8255.

**HRMS (ESI) m/z for \( \text{H}_6\text{O}_{21}\text{P}_7 \) [M-H]**: calcd. 558.7570, found 558.7587.

**HRMS (ESI) m/z for \( \text{H}_7\text{O}_{24}\text{P}_8 \) [M-H]**: calcd. 638.7234, found 638.7238.

For solubility reasons the cations had to be changed to TBA before subsequent reactions. This was achieved by using either DowexH\(^+\) or Chelex\(^\text{®}\)TBA\(^+\) as described above. After lyophilization, the TBA-salts were dissolved in MeCN, passed through a syringe filter and evaporated to dryness. The isolated metaphosphate TBA – salts were isolated as white solids and could be stored for months in the fridge.

The metaphosphate / TBA – ratios were determined by the addition of tetramethylphosphonium bromide and qNMR measurements. The TBA-amounts were usually higher than expected according to phosphate units present. We hypothesize the surplus TBA-ions are part of hydroxide salts. Consequently, the following molecular weights were determined:

**Trimetaphosphate** (68, DowexH\(^+\)): 3MP x 3.9 TBA (MW = 1194 g/mol)

**Tetrametaphosphate** (69, Chelex\(^\text{®}\)TBA\(^+\)): 4MP x 6.0 TBA (MW = 1803 g/mol)
Pentametaphosphate (70, Chelex®TBA⁺): 5MP x 5.3 TBA (MW = 1683 g/mol)

Heptametaphosphate (71, Chelex®TBA⁺): 7MP x 8.2 TBA (MW = 2559 g/mol)

Octametaphosphate (72, Chelex®TBA⁺): 8MP x 11.3 TBA. (MW = 3424 g/mol)

7.2. Synthesis of arylpolyphosphates

General procedure D for the synthesis of arylpolyphosphates:

The cyclophosphate x TBA salt (100 µmol) was dissolved in dry MeCN (ca. 70 mM) and the corresponding aryne-precursor (4.0 – 5.0 eq.) was added. Subsequently, TBAF (1 M in THF, 5.0 eq.) was added dropwise via syringe pump (1 h, rt, needle tip is below solvent surface). The reaction mixture was stirred for additional 15 min at rt before the amine-nucleophile (2.5 – 20 eq.) was added. The resulting solution was stirred 24 - 48 h, and the crude product was precipitated by pipetting the reaction mixture into a NaClO₄-solution (0.5 M in acetone, -20°C, 35 mL). The suspension was incubated for 20 min at -20°C and the precipitate was separated by centrifugation. The resulting pellet was washed with acetone (30 mL) and dried over high vacuum.

Purification method D1:

The crude product was purified by automated SAX (Äkta system, Q-Sepharose, NaClO₄-buffer). Product containing fractions (80 – 150 mM) were combined and lyophilized. The resulting solid was washed with acetone (3 x 30 mL), separated by centrifugation and dried over high vacuum. The products were isolated as Na – salts.

Purification method D2:

The crude product was purified by automated RP-MPLC (Interchim system, C18-AQ, H₂O/MeCN/TEAA [10 mM]). The product containing fractions were combined and lyophilized. The products were isolated as TEA – salts.
PhenylP₃-propargylamidate (78)

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoro-methanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Propargylamine (16.0 µL, 13.8 mg, 250 µmol, 2.5 eq.) was applied for nucleophilic ring-opening (24 h). The crude product was purified according to purification method D2. The product (78, 32.6 mg, 68.7 µmol, 69%) was isolated as colorless oil.

1H-NMR (400 MHz, D₂O, δ/ppm): 7.45 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 3.66 (dd, J = 9.9, 2.5 Hz, 2H), 3.21 (q, J = 7.3 Hz, 2H), 2.55 (t, J = 2.5 Hz, 1H), 1.29 (t, J = 7.4 Hz, 3H). 13C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 151.75 (d, J = 7.2 Hz), 129.68, 124.33 (d, J = 1.4 Hz), 120.59 (d, J = 4.6 Hz), 82.96 (d, J = 11.7 Hz), 71.35, 46.64, 30.96, 8.20. 31P{¹H}-NMR (162 MHz, D₂O, δ/ppm): -2.83 (d, J = 20.6 Hz), -15.91 (d, J = 19.8 Hz), -23.02 (t, J = 20.1 Hz). HRMS (ESI) m/z for C₉H₁₁NO₄P₃ [M-H]−: calcd. 369.9652, found 369.9652.

PhenylP₃-amidate (79)

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoro-methanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Aqu. NH₃ (25%, 17.0 µL, 250 µmol, 2.5 eq.) was applied for nucleophilic ring-opening (24 h). The crude product was purified according to purification method D1. The product (79, 26.7 mg, 66.9 µmol, 67%) was isolated as white solid.

1H-NMR (400 MHz, D₂O, δ/ppm): 7.47 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H). 13C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 151.70 (d, J = 7.2 Hz), 129.72, 124.44 (d, J = 1.5 Hz), 120.61 (d, J = 4.5 Hz). 31P{¹H}-NMR (162 MHz, D₂O, δ/ppm): -1.03 (d, J = 19.1 Hz), -
15.76 (d, J = 19.9 Hz), -22.68 (t, J = 19.4 Hz). HRMS (ESI) m/z for C_{6}H_{9}NO_{3}NP_{3} [M-H]⁻: calcd. 331.9496, found 331.9493.

**PhenylP₃-anthracen-9-ylmethanamidate (80)**

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Anthracen-9-ylmethanamine (51.3 mg, 250 µmol, 2.5 eq.) was applied for nucleophilic ring-opening (24 h). The crude product was purified according to purification method D1. The product (80, 27.1 mg, 46.0 µmol, 46%) was isolated as white solid.

$^1$H-NMR (400 MHz, D₂O, δ/ppm): 8.56 (s, 1H), 8.51 (dd, J = 8.9, 1.0 Hz, 2H), 8.11 (ddd, J = 8.4, 1.6, 0.8 Hz, 2H), 7.63 (ddd, J = 8.9, 6.5, 1.5 Hz, 2H), 7.57 (ddd, J = 7.8, 6.6, 1.1 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.13 (m, 2H), 6.96 – 6.89 (m, 1H), 4.98 (s, 2H). $^{13}$C{$^1$H}-NMR (101 MHz, D₂O, δ/ppm): 151.76 (d, J = 7.2 Hz), 131.27 (d, J = 12.7 Hz), 131.27, 129.61, 129.49, 128.80, 127.28, 126.57, 125.41, 124.47, 123.99, 120.35 (d, J = 4.7 Hz), 37.82. $^{31}$P{$^1$H}-NMR (162 MHz, D₂O, δ/ppm): -2.15 (d, J = 21.2 Hz), -15.91 (d, J = 19.4 Hz), -22.67 (t, J = 21.2 Hz). HRMS (ESI) m/z for C_{21}H_{18}NO_{3}P_{3} [M-H₃]²⁻: calcd. 260.5102, found 260.5102.

**PhenylP₃-5'-deoxyadenosyl-5’-amidate (81)**

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Nucleophilic ring-opening was induced by dropping the reaction mixture into a solution of 5'-Deoxy-5’-aminoadenosine (SI-1, 66.5 mg, 250 µmol, 2.5 eq.) and DBU (74.5 µL, 76.0 mg, 500 µmol, 5.0 eq.) in DMF
(1.5 mL). The resulting solution was stirred for 48 h. The crude product was purified according to purification method D1. The product (81, 34.5 mg, 53.2 µmol, 53%) was isolated as white solid.

\[ ^1H-\text{NMR} \ (400 \text{ MHz, D}_2\text{O, }\delta/\text{ppm}) : 8.33 \text{ (s, 1H)}, 8.23 \text{ (d, } J = 0.5 \text{ Hz, 1H)}, 7.24 – 7.17 \text{ (m, 2H)}, 7.12 \text{ (dddd, } J = 7.9, 1.9, 1.3, 0.5 \text{ Hz, 2H)}, 7.00 \text{ (dp, } J = 7.0, 0.8 \text{ Hz, 1H)}, 5.98 \text{ (d, } J = 6.4 \text{ Hz, 1H)}, 4.78 – 4.75 \text{ (m, 1H)}, 4.41 \text{ (dd, } J = 5.4, 3.3 \text{ Hz, 1H)}, 4.22 \text{ (q, } J = 3.4 \text{ Hz, 1H)}, 3.34 – 3.17 \text{ (m, 2H)}. \]

\[ ^13C\{^1H\}-\text{NMR} \ (101 \text{ MHz, D}_2\text{O, }\delta/\text{ppm}) : 155.51, 152.79, 151.51 \text{ (d, } J = 7.1 \text{ Hz)}, 148.87, 140.21, 129.32, 123.98, 120.27 \text{ (d, } J = 4.6 \text{ Hz)}, 118.90, 87.11, 85.44 \text{ (d, } J = 8.9 \text{ Hz)}, 73.27, 70.79, 43.14. \]

\[ ^31P\{^1H\}-\text{NMR} \ (162 \text{ MHz, D}_2\text{O, }\delta/\text{ppm}) : -1.58 \text{ (d, } J = 21.0 \text{ Hz)}, -15.79 \text{ (d, } J = 19.0 \text{ Hz)}, -22.78 \text{ (t, } J = 19.2 \text{ Hz}). \]

HRMS (ESI) m/z for C\(_{16}\)H\(_{20}\)N\(_6\)O\(_{12}\)P\(_3\) [M-H]: calcd. 581.0358, found 581.0361.

**PhenylP\(_3\)-5'-deoxyguanosyl-5'-amidate (82)**

![PhenylP\(_3\)-5'-deoxyguanosyl-5'-amidate (82)](image)

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Nucleophilic ring-opening was induced by dropping the reaction mixture into a solution of 5'-Deoxy-5'-aminoguanosine (SI-2, 56.4 mg, 200 µmol, 2.0 eq.) in DMSO/DMF (1/1, 1.5 mL) and stirring the resulting solution for 48 h. The crude product was purified according to purification method D1. The product (82, 43.9 mg, 66.1 µmol, 66%) was isolated as white solid.

\[ ^1H-\text{NMR} \ (400 \text{ MHz, D}_2\text{O, }\delta/\text{ppm}) : 7.83 \text{ (s, 1H)}, 7.17 – 7.02 \text{ (m, 4H)}, 6.91 \text{ (ddt, } J = 7.3, 6.3, 1.3 \text{ Hz, 1H)}, 5.73 \text{ (d, } J = 8.1 \text{ Hz, 1H)}, 5.17 \text{ (dd, } J = 8.0, 5.5 \text{ Hz, 1H)}, 4.45 \text{ (dd, } J = 5.5, 1.4 \text{ Hz, 1H)}, 4.33 – 4.28 \text{ (m, 1H)}, 3.38 \text{ (dddd, } J = 14.1, 5.0, 3.0 \text{ Hz, 1H)}, 3.25 \text{ (dddd, } J = 14.1, 9.3, 2.5 \text{ Hz, 1H}). \]

\[ ^13C\{^1H\}-\text{NMR} \ (101 \text{ MHz, D}_2\text{O, }\delta/\text{ppm}) : 159.37, 153.76, 151.50 \text{ (d, } J = 7.0 \text{ Hz)}, 151.26, 139.68, 129.07, 123.68, 120.16 \text{ (d, } J = 4.5 \text{ Hz)}, 117.25, 88.70, 86.60 \text{ (d, } J = 9.8 \text{ Hz)}, 71.47, 71.07, 43.36. \]

\[ ^31P\{^1H\}-\text{NMR} \ (162 \text{ MHz, D}_2\text{O, }\delta/\text{ppm}) : -1.59 \text{ (d, } J = 22.9 \text{ Hz)}, -15.76 \text{ (d, } J = 19.2 \text{ Hz)}, -22.87 \text{ (dd, } J = 22.6, 19.5 \text{ Hz}). \]

HRMS (ESI) m/z for C\(_{16}\)H\(_{20}\)N\(_6\)O\(_{12}\)P\(_3\) [M-H]: calcd. 597.0307, found 597.0309.
Napht-2-ylP₃-5'-deoxyguanosyl-5'-amidate (83)

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 3-(Trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (SI-12, 174 mg, 500 µmol, 5.0 eq.). Nucleophilic ring-opening was induced by dropping the reaction mixture into a solution of 5’-Deoxy-5’-aminoguanosine (SI-2, 56.4 mg, 200 µmol, 2.0 eq.) in DMSO/DMF (1/1, 1.5 mL) and stirring the resulting solution for 48 h. The crude product was purified according to purification method D2 and D1 subsequently. The product (83, 34.9 mg, 48.9 µmol, 49%) was isolated as white solid.

$^1$H-NMR (400 MHz, D$_2$O, $\delta$/ppm): 7.69 (d, $J = 9.1$ Hz, 1H), 7.67 (s, 1H), 7.65 – 7.57 (m, 2H), 7.55 (d, $J = 2.1$ Hz, 1H), 7.34 – 7.30 (m, 1H), 7.29 – 7.22 (m, 2H), 5.64 (d, $J = 8.0$ Hz, 1H), 5.02 (dd, $J = 7.9$, 5.5 Hz, 1H), 4.40 (dd, $J = 5.5$, 1.5 Hz, 1H), 4.33 (t, $J = 2.3$ Hz, 1H), 3.48 (ddd, $J = 14.0$, 4.1, 2.9 Hz, 1H), 3.29 (ddd, $J = 14.0$, 9.1, 2.4 Hz, 1H). $^{13}$C{$^1$H}-NMR (101 MHz, D$_2$O, $\delta$/ppm): 158.22, 152.77, 150.69, 149.24 (d, $J = 7.6$ Hz), 139.30, 133.25, 129.81, 129.03, 127.10 (d, $J = 3.3$ Hz), 125.95, 124.87, 120.85, 120.81, 116.71, 116.37 (d, $J = 4.8$ Hz), 88.80, 86.52 (d, $J = 10.5$ Hz), 71.43, 71.07, 43.43. $^{31}$P{$^1$H}-NMR (162 MHz, D$_2$O, $\delta$/ppm): -1.35 (d, $J = 23.0$ Hz), -15.81 (d, $J = 20.1$ Hz), -22.43 (dd, $J = 23.0$, 20.0 Hz). HRMS (ESI) m/z for C$_{20}$H$_{21}$N$_6$NaO$_{13}$P$_3$ [M-H]: calcd. 669.0283, found 669.0285.
Pyren-2-ylP₃-5'-deoxyadenosyl-5'-amidate (84)

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 1-(Trimethylsilyl)pyren-2-yl trifluoromethanesulfonate (SI-19, 212 mg, 500 µmol, 5.0 eq.). Nucleophilic ring-opening was induced by dropping the reaction mixture into a solution of 5’-Deoxy-5’-aminoadenosine (SI-1, 66.5 mg, 250 µmol, 2.5 eq.) and DBU (74.5 µL, 76.0 mg, 500 µmol, 5.0 eq.) in DMF (1.5 mL). The resulting solution was stirred for 48 h. The crude product was purified according to purification method D1. The product (84, 31.9 mg, 41.1 µmol, 41%) was isolated as white solid.

The product is formed in an 88:12 (2-84:1-84) regioisomeric ratio. ¹H- and ¹³C{¹H}-NMR signals from the major product are given.

¹H-NMR (400 MHz, D₂O, δ/ppm): 8.10 (d, J = 7.7 Hz, 2H), 7.98 – 7.89 (m, 7H), 7.51 (s, 1H), 7.42 (s, 1H), 5.33 (d, J = 5.0 Hz, 1H), 4.16 – 4.05 (m, 3H), 3.32 (ddd, J = 14.0, 7.0, 4.0 z, 1H), 3.23 (ddd, J = 14.1, 9.5, 4.5 Hz, 1H). ¹³C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 153.85, 151.27, 149.50 (d, J = 6.8 Hz), 146.99, 138.55, 131.74, 129.95, 127.74, 126.72, 125.65, 125.21, 123.16, 120.48, 117.41, 116.28 (d, J = 4.9 Hz), 87.03, 84.38 (d, J = 9.7 Hz), 73.90, 70.36, 43.29.

³¹P{¹H}-NMR (162 MHz, D₂O, δ/ppm): -1.62 (d, J = 22.0 Hz), -15.82 (d, J = 19.9 Hz), -22.75 (dd, J = 22.0, 19.2 Hz). HRMS (ESI) m/z for C₂₆H₃₂N₆O₁₂P₃ [M-H]: calcd. 705.0671, found 705.0677.
Benzo[1,3]dioxol-5-ylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate (85)

The compound was synthesized according to the general procedure D from trimetaphosphate x 3.9 TBA (68, 119 mg, 100 µmol) and 6-(Trimethylsilyl)benzo[1,3]dioxol-5-yl trifluoromethanesulfonate (SI-9, 171 mg, 500 µmol, 5.0 eq.). Amino-DEACM (SI-26, 61.3 mg, 250 µmol, 2.5 eq.) was applied for nucleophilic ring-opening (24 h). The crude product was purified according to purification method D1. The product (85, 39.7 mg, 59.1 µmol, 59%) was isolated as white solid.

$^1$H-NMR (400 MHz, D₂O, δ/ppm): 7.35 (d, J = 9.1 Hz, 1H), 6.69 (dd, J = 9.2, 2.5 Hz, 1H), 6.67 (ddd, J = 2.4, 1.0, 0.5 Hz, 1H), 6.64 – 6.60 (m, 1H), 6.58 – 6.54 (m, 2H), 6.26 – 6.23 (m, 1H), 5.75 (s, 2H), 4.18 (dd, J = 8.6, 1.5 Hz, 2H), 3.44 (q, J = 7.1 Hz, 4H), 1.19 (t, J = 7.1 Hz, 6H). $^{13}$C($^1$H)-NMR (101 MHz, D₂O, δ/ppm): 166.19, 158.12 (d, J = 9.7 Hz), 155.16, 151.02, 146.98, 146.27 (d, J = 7.6 Hz), 143.09, 125.03, 112.67 (d, J = 4.9 Hz), 109.95, 107.82, 106.89, 103.25, 102.57 (d, J = 4.7 Hz), 101.36, 96.95, 44.43, 41.71, 11.55. $^{31}$P($^1$H)-NMR (162 MHz, D₂O, δ/ppm): -2.28 (d, J = 21.2 Hz), -15.87 (d, J = 20.0 Hz), -22.92 (t, J = 20.6 Hz). HRMS (ESI) m/z for C₂₁H₂₄N₂O₁₃P₃ [M-H]⁻: calcd. 605.0497, found 605.0500.

Synthesis of PhenylP₄-propargylamide (86)

The compound was synthesized according to the general procedure D from tetrametaphosphate x 6.0 TBA (69, 180 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Propargylamine (16.0 µL, 13.8 mg, 250 µmol, 2.5 eq.) was applied for nucleophilic ring-opening (24 h). The crude product was purified according to purification method D2. The product (86, 35.1 mg, 40.9 µmol, 41%) was isolated as colorless oil.
\(^1\)H-NMR (400 MHz, D\(_2\)O, \(\delta/\text{ppm}\)): 7.48 – 7.38 (m, 2H), 7.30 (dq, \(J = 7.7, 1.2\) Hz, 2H), 7.26 – 7.19 (m, 1H), 3.70 (dd, \(J = 10.2, 2.5\) Hz, 2H), 3.21 (q, \(J = 7.3\) Hz, 11H), 2.56 (t, \(J = 2.5\) Hz, 1H), 1.29 (t, \(J = 7.3\) Hz, 16H). \(^{13}\)C\[^1\)H\]-NMR (101 MHz, D\(_2\)O, \(\delta/\text{ppm}\)): 151.73 (d, \(J = 7.1\) Hz), 129.71, 124.36, 120.65 (d, \(J = 4.6\) Hz), 83.11 (d, \(J = 11.4\) Hz), 71.32, 46.64, 30.99, 8.21. \(^{31}\)P\[^1\)H\]-NMR (162 MHz, D\(_2\)O, \(\delta/\text{ppm}\)): -2.52 (d, \(J = 19.4\) Hz, 1P), -15.70 (d, \(J = 18.0\) Hz, 1P), -22.45 – -23.22 (m, 2P). HRMS (ESI) m/z for C\(_{9}\)H\(_{11}\)NO\(_{12}\)P\(_{4}\) [M-H\(_2\)]\(^2\): calcd. 224.4621, found 224.4623.

Pyren-2-ylP-5'-deoxyguanosyl-5'-amidate (87)

The compound was synthesized according to the general procedure D from tetrametaphosphate x 6.0 TBA (69, 180 mg, 100 µmol) and 1-(Trimethylsilyl)pyren-2-yl trifluoromethanesulfonate (SI-19, 212 mg, 500 µmol, 5.0 eq.). Nucleophilic ring-opening was induced by dropping the reaction mixture into a solution of 5'-Deoxy-5'-aminoguanosine (SI-2, 56.4 mg, 200 µmol, 2.0 eq.) in DMSO/DMF (1/1, 1.5 mL) and stirring the resulting solution for 48 h. The crude product was purified according to purification method D1. The product (87, 40.5 mg, 45.1 µmol, 45%) was isolated white solid.

The product is formed in an 88:12 (2-87:1:87) regioisomeric ratio. \(^1\)H- and \(^{13}\)C\[^1\)H\]-NMR signals from the major product are given.

\(^1\)H-NMR (400 MHz, D\(_2\)O, \(\delta/\text{ppm}\)): 8.10 – 7.92 (m, 8H), 7.90 – 7.83 (m, 1H), 7.20 (s, 1H), 5.21 (d, \(J = 7.6\) Hz, 1H), 4.55 (dd, \(J = 7.7, 5.4\) Hz, 1H), 4.17 (dd, \(J = 5.5, 1.7\) Hz, 1H), 4.12 (q, \(J = 2.5\) Hz, 1H), 3.33 (dt, \(J = 14.0, 3.7\) Hz, 1H), 3.15 (ddd, \(J = 14.0, 9.3, 2.5\) Hz, 1H). \(^{13}\)C\[^1\)H\]-NMR (101 MHz, D\(_2\)O, \(\delta/\text{ppm}\)): 157.23, 151.96, 149.79, 149.67 (d, \(J = 7.4\) Hz), 138.26, 131.98, 130.02, 127.95, 126.88, 125.63, 125.13, 123.25, 120.75, 116.61 (d, \(J = 4.6\) Hz), 115.70, 88.34, 85.98 (d, \(J = 10.4\) Hz), 71.49, 71.23, 43.01. \(^{31}\)P\[^1\)H\]-NMR (162 MHz, D\(_2\)O, \(\delta/\text{ppm}\)): -1.08 (d, \(J = 22.3\) Hz), -15.45 (d, \(J = 18.0\) Hz), -21.99 (dd, \(J = 22.2, 13.9\) Hz), -22.59 (dd, \(J = 17.8, 13.8\) Hz). HRMS (ESI) m/z for C\(_{26}\)H\(_{23}\)N\(_{6}\)O\(_{16}\)P\(_{4}\) [M-H\(_3\)]\(^3\): calcd. 266.3379, found 266.3379.
Synthesis of PhenylP₄-5′-deoxyguanosyl-5′-amidate (88)

The compound was synthesized according to the general procedure D from tetrametaphosphate x 6.0 TBA (69, 180 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Nucleophilic ring-opening was induced by dropping the reaction mixture into a solution of 5′-Deoxy-5′-aminoguanosine (SI-2, 56.4 mg, 200 µmol, 2.0 eq.) in DMSO/DMF (1/1, 1.5 mL) and stirring the resulting solution for 48 h. The crude product was purified according to purification method D2 and D1 subsequently. The product (88, 32.6 mg, 42.5 µmol, 43%) was isolated as white solid.

1H-NMR (400 MHz, D₂O, δ/ppm): 7.67 (s, 1H), 7.10 – 6.94 (m, 4H), 6.80 – 6.69 (m, 1H), 5.57 (d, J = 8.0 Hz, 1H), 4.97 (dd, J = 7.9, 5.5 Hz, 1H), 4.32 (dd, J = 5.5, 1.5 Hz, 1H), 4.17 – 4.09 (m, 1H), 3.23 – 3.04 (m, 2H).

13C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 158.96, 153.47, 151.51 (d, J = 7.2 Hz), 151.27, 139.68, 129.29, 123.83, 120.36 (d, J = 4.3 Hz), 117.15, 88.68, 86.60 (d, J = 9.7 Hz), 71.40, 71.23, 43.17.

3¹P{¹H}-NMR (162 MHz, D₂O, δ/ppm): -1.22 (d, J = 21.1 Hz), -15.50 (d, J = 17.5 Hz), -22.29 (dd, J = 21.4, 15.2 Hz), -22.90 (dd, J = 17.9, 15.1 Hz).

HRMS (ESI) m/z for C₁₆H₁₉N₆O₁₆P₄ [M-H₃]⁺: calcd. 224.9941, found 224.9942.

3,4-DimethylphenylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate (89)

The compound was synthesized according to the general procedure D from tetrametaphosphate x 6.0 TBA (69, 180 mg, 100 µmol) and 4,5-Dimethyl-2-(trimethylsilyl)phenyl-trifluoromethanesulfonate (SI-6, 163 mg, 500 µmol, 5.0 eq.). Amino-DEACM (SI-26, 61.3 mg, 250 µmol, 2.5 eq.) was applied for nucleophilic ring-opening (24 h). The crude product was purified according to purification method D1. The product (89, 16.6 mg, 22.0 µmol, 22%) was isolated as white solid.
Synthesis of PhenylP₅-propargylamidate (90)

The compound was synthesized according to the general procedure D from pentametaphosphate x 5.3 TBA (70, 168 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.). Propargylamine (64.0 µL, 55.0 mg, 1.00 mmol, 10 eq.) was applied for nucleophilic ring-opening (48 h). The crude product was purified according to purification method D1. The product (90, 15.2 mg, 23.1 µmol, 23%) was isolated as white solid.

\(^1\text{H-NMR}\) (400 MHz, D₂O, δ/ppm): 7.47 – 7.39 (m, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 3.73 (dd, J = 10.7, 2.4 Hz, 2H), 2.57 (td, J = 2.5, 0.5 Hz, 1H). \(^{13}\text{C}\{^1\text{H}\}-\text{NMR}\) (101 MHz, D₂O, δ/ppm): 151.70 (d, J = 7.2 Hz), 129.71, 124.39 (d, J = 1.4 Hz), 120.68 (d, J = 4.4 Hz), 68.14, 30.95. \(^{31}\text{P}\{^1\text{H}\}-\text{NMR}\) (162 MHz, D₂O, δ/ppm): -2.34 (d, J = 19.7 Hz, 1P), -15.55 (d, J = 16.9 Hz, 1P), -21.84 – -23.03 (m, 3P). \textbf{HRMS} (ESI) m/z for C₂₂H₂₉N₂O₁₃P₅ [M-H]: calcd. 529.8979, found 529.8980.
Synthesis of PhenylP$_7$-propargylamidate (91)

The compound was synthesized according to the general procedure D from heptametaphosphate x 8.2 TBA (71, 255 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 96.9 µL, 119 mg, 400 µmol, 4.0 eq.). Propargylamine (64.0 µL, 55.0 mg, 1.0 mmol, 10 eq.) was applied for nucleophilic ring-opening (48 h). The crude product was purified according to purification method D1. The product (91, 30.9 mg, 36.6 µmol, 37%) was isolated as white solid.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.51 – 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 3.76 (dd, $J = 10.8, 2.5$ Hz, 2H), 2.64 (t, $J = 2.5$ Hz, 1H). $^{13}$C($^1$H)-NMR (101 MHz, D$_2$O, δ/ppm): 151.66 (d, $J = 7.3$ Hz), 129.80, 124.56, 120.67 (d, $J = 4.5$ Hz), 83.09 (d, $J = 10.6$ Hz), 71.49, 30.30. $^{31}$P($^1$H)-NMR (162 MHz, D$_2$O, δ/ppm): -1.83 – -2.25 (m, 1P), -15.33 (d, $J = 17.7$ Hz, 1P), -21.62 – -22.03 (m, 4P), -22.20 (dd, $J = 17.7, 13.7$ Hz, 1P). HRMS (ESI) m/z for C$_9$H$_{15}$NO$_2$P$_7$ [M-H]: calcd. 689.8305, found 689.8306.

Synthesis of PhenylP$_8$-propargylamidate (92)

The compound was synthesized according to the general procedure D from octametaphosphate x 11.3 TBA (72, 342 mg, 100 µmol) and 2-(Trimethylsilyl)phenyl-trifluoromethanesulfonate (1, 96.9 µL, 119 mg, 400 µmol, 4.0 eq.). Propargylamine (64.0 µL, 55.0 mg, 1.0 mmol, 10 eq.) was applied for nucleophilic ring-opening (48 h). The crude product was purified according to purification method D1. The product (92, 21.2 mg, 22.4 µmol, 22%) was isolated as white solid.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 7.47 – 7.39 (m, 2H), 7.30 (dq, $J = 7.8, 1.2$ Hz, 2H), 7.26 – 7.20 (m, 1H), 3.73 (dd, $J = 10.7, 2.5$ Hz, 2H), 2.60 (t, $J = 2.5$ Hz, 1H). $^{13}$C($^1$H)-NMR (101 MHz, D$_2$O, δ/ppm): 151.65 (d, $J = 7.3$ Hz), 129.73, 124.45, 120.65 (d, $J = 4.6$ Hz), 71.38, 30.93. $^{31}$P($^1$H)-NMR (162 MHz, D$_2$O, δ/ppm): -2.24 (d, $J = 20.1$ Hz, 1P), -15.49 (d, $J = 17.8$ Hz, 1P), -21.71 – -22.25 (m, 5P), -22.33 – -22.62 (m, 1P). HRMS (ESI) m/z for C$_9$H$_{15}$NO$_2$P$_8$ [M-H$_2$]$^2$: calcd. 384.3948, found 384.3946.
Phenyl-cyclotriphosphate as storable triphosphorylation reagent (73)

The cyclophosphate x TBA salt (68, 100 µmol) was dissolved in dry MeCN (ca. 70 mM) and 2-(Trimethylsilyl)phenyl-trifluoro-methanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.) (4.0 – 5.0 eq.) was added. Subsequently TBAF (1 M in THF, 5.0 eq.) was added dropwise via syringe pump (1 h, rt, needle tip is below solvent surface). Then, the reaction mixture is stirred for 15 min at rt. The product is precipitated with Et₂O (40 mL) and the resulting oil is washed with Et₂O (2 x 30 mL). The phenyl-cyclotriphosphate 73 is dried over high vacuum and can be stored as triphosphorylation reagent in the fridge for weeks without substantial decomposition. Furthermore, storage as solution in MeCN at rt is possible for weeks.

$^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -23.61 (d, $J = 25.1$ Hz), -26.19 (t, $J = 24.4$ Hz).

HRMS (ESI) m/z for C$_6$H$_5$O$_9$P$_3$ [M-H$_2$]$^2$-: calcd. 156.9578, found 156.9579.

Phenyl-cyclostetraphosphate as storable tetraphosphorylation reagent (74)

The cyclophosphate x TBA salt (69, 100 µmol) was dissolved in dry MeCN (ca. 70 mM) and 2-(Trimethylsilyl)phenyl-trifluoro-methanesulfonate (1, 121 µL, 149 mg, 500 µmol, 5.0 eq.) was added. Subsequently TBAF (1 M in THF, 5.0 eq.) was added dropwise via syringe pump (1 h, rt, needle tip is below solvent surface). Then, the reaction mixture is stirred for 15 min at rt. The product is precipitated with Et₂O (40 mL) and the resulting oil is washed with Et₂O (2 x 30 mL). The phenyl-cyclostetraphosphate 74 is dried over high vacuum and can be stored as tetraphosphorylation reagent in the fridge for weeks without substantial decomposition. Furthermore, storage as solution in MeCN at rt is possible for weeks.

$^{31}$P{$^1$H}-NMR (162 MHz, CD$_3$CN, δ/ppm): -25.03 – -25.65 (m, 3P), -29.37 – -29.89 (m, 1P).

HRMS (ESI) m/z for C$_6$H$_7$O$_{12}$P$_4$ [M-H]: calcd. 394.8893, found 394.8892.
8. Synthesis of phosphate starting materials without literature precedence

**General procedure E for the synthesis of mono- and diphosphates**

Alcohol (or Monophosphate TBA-salt) and ETT were dissolved in DMF. \((\text{FmO})_2\text{P-NiPr}_2\text{ (SI-4)}\) was added as solution in DMF and the resulting mixture was stirred for 1 h at rt. The solution was cooled to 0 °C and \(m\text{CPBA (77%, 1.2 eq.)}\) was added. The solution was stirred for 15 min at 0 °C and piperidine (10 vol%) was added. The solution was stirred for 40 min at rt.

**Purification method E1:**
The crude product was either precipitated with ether (40 mL), washed with ether (40 mL) and dried over high vac. Purification was performed by automated SAX (Äkta-system, Q-Sepharose, \(\text{NH}_4\text{HCO}_3\) – buffer). The product containing fractions were identified by NMR and the product was isolated after lyophilization.

**Purification method E2:**
The solvent was removed under reduced pressure. The crude product was purified by RP-MPLC [C18-AQ, dryload on celite, elution with H\(_2\)O/MeCN/ TEAA (10 mM)]. The product containing fractions were identified by NMR or HPLC and the product was isolated after lyophilization.

Afterwards cations were exchanged to TBA by Dowex or Chelex before application in subsequent reactions.
6-Hydroxyhexylphosphate (SI-13)

The compound was synthesized according to the general procedure E with 1,6-hexanediol (849 mg, 7.19 mmol, 5.0 eq.), (FmO)₂P-NiPr₂ (SI-14, 750 mg, 1.44 mmol, 1.0 eq.), ETT (340 mg, 2.88 mmol, 2.0 eq.) and mCPBA (77%, 386 mg, 1.72 mmol, 1.2 eq.) in DMF (4.0 mL). Purification was performed by purification method E1 and the product (SI-13, 225 mg, 970 µmol, 67%) was isolated as white solid.

¹H-NMR (400 MHz, D₂O, δ/ppm): 3.82 (dt, J = 6.6 Hz, 2H), 3.59 (t, J = 6.6 Hz, 2H), 1.68 – 1.50 (m, 4H), 1.44 – 1.30 (m, 4H).

³¹P{¹H}-NMR (162 MHz, D₂O, δ/ppm): 1.34. ¹³C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 65.48 (d, J = 5.4 Hz), 61.72, 31.15, 29.83 (d, J = 6.8 Hz), 24.68, 24.66. HRMS (ESI) m/z for C₆H₁₄O₅P [M-H]: calcd. 197.0584, found 197.0584.

Geranylphosphate (SI-14)

The compound was synthesized according to the general procedure E with Geraniol (210 mg, 236 µL, 1.36 mmol), (FmO)₂P-NiPr₂ (SI-4, 782 mg, 1.50 mmol, 1.1 eq.), ETT (355 mg, 2.73 mmol, 2.0 eq.) and mCPBA (77%, 402 mg, 1.63 mmol, 1.2 eq.) in DMF (10 mL). Purification was performed by method E2 and the product (SI-14, 268 mg, 615 µmol, 45%) was isolated as 2.0 TEAA salt.

As the TEAA-salt was not stable in solution (decomposition by phosphate elimination) the cations were immediately changed to TBA by chelex.

¹H-NMR (400 MHz, D₂O, δ/ppm): 5.50 – 5.39 (m, 1H), 5.22 (tdd, J = 5.5, 2.9, 1.4 Hz, 1H), 4.37 (ddd, J = 7.2, 6.2, 0.8 Hz, 2H), 3.25 – 3.16 (m, 11H), 2.23 – 2.08 (m, 4H), 1.74 – 1.59 (m, 20H), 1.37 (h, J = 7.4 Hz, 11H), 0.95 (t, J = 7.4 Hz, 17H). ³¹P{¹H}-NMR (162 MHz, D₂O, δ/ppm): 1.61. ¹³C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 142.18, 133.69, 124.13, 120.13 (d, J = 7.8 Hz), 61.74 (d, J = 4.9 Hz), 59.15 – 56.63 (m), 38.75, 25.56, 24.79, 23.11, 19.87 – 18.66 (m), 16.93, 15.46, 12.80. HRMS (ESI) m/z for C₁₀H₁₈O₄P [M-H]: calcd. 233.0948, found 233.0946.
Isoprenylphosphate (SI-15)

The compound was synthesized according to the general procedure E with Isoprenol (130 mg, 151 µL, 1.51 mmol), (FmO)$_2$P-NiPr$_2$ (SI-4, 1.02 g, 1.97 mmol, 1.3 eq.), ETT (491 mg, 3.78 mmol, 2.5 eq.) and mCPBA (77%, 724 mg, 2.95 mmol, 1.5 eq.) in DMF (5.0 mL). Purification was performed by purification method E2. The product (SI-15, 175 mg, 573 µmol, 38%) was isolated as white solid.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 4.89 – 4.86 (m, 1H), 4.84 – 4.82 (m, 1H), 3.99 (td, $J = 6.7$, 6.6 Hz, 2H), 3.19 – 3.13 (m, 7H), 3.12 – 3.04 (m, 1H), 2.38 (d, $J = 2549.5$ Hz, 1H), 1.85 – 1.71 (m, 10H), 1.70 – 1.63 (m, 3H), 1.27 (t, $J = 7.3$ Hz, 1H). $^{13}$C($^1$H)-NMR (101 MHz, D$_2$O, δ/ppm): 143.62, 111.52, 63.71 (d, $J = 5.2$ Hz), 44.51, 37.92 (d, $J = 7.2$ Hz), 27.12, 22.18, 21.55, 21.45, 14.47. $^{31}$P($^1$H)-NMR (162 MHz, D$_2$O, δ/ppm): 0.49. HRMS (ESI) m/z for C$_5$H$_{10}$O$_4$P [M-H]: calcd. 165.0322, found 165.0323.

Pentylphosphate (67)

The compound was synthesized according to the general procedure E with pentan-1-ol (309 mg, 380 µL, 3.52 mmol), (FmO)$_2$P-NiPr$_2$ (SI-4, 2.02 g, 3.87 mmol, 1.1 eq.), ETT (916 mg, 7.04 mmol, 2.0 eq.) and mCPBA (77%, 1.13 g, 5.06 mmol, 1.4 eq.) in MeCN (15 mL). Purification was performed by purification method E2. Cations were directly changed to TBA. The product (67, 2.65 g, 3.52 mmol, quant) was isolated colorless oil. Redundant anions are assumed to be hydroxide.

$^1$H-NMR (400 MHz, D$_2$O, δ/ppm): 3.85 (q, $J = 6.7$ Hz, 2H), 3.23 – 3.04 (m, 21H), 1.69 – 1.53 (m, 19H), 1.42 – 1.25 (m, 26H), 0.92 (t, $J = 7.4$ Hz, 25H), 0.89 – 0.84 (m, 3H). $^{13}$C($^1$H)-NMR (101 MHz, D$_2$O, δ/ppm): 65.97 (d, $J = 5.5$ Hz), 58.58 – 56.88 (m), 46.49, 29.55 (d, $J = 6.8$ Hz), 27.15, 26.98, 23.07, 21.67, 19.24 – 18.75 (m), 14.36, 13.29, 12.80. $^{31}$P($^1$H)-NMR (162 MHz, D$_2$O, δ/ppm): 0.46. HRMS (ESI) m/z for C$_5$H$_{12}$O$_4$P [M-H]: calcd. 167.0479, found 167.0480.
5,5,5-Trifluorpentylphosphate (38)

The compound was synthesized according to the general procedure E with 5,5,5-trifluoropentan-1-ol (500 mg, 370 µL, 3.52 mmol), (FmO)₂P-NiPr₂ (SI-4, 2.02 g, 3.87 mmol, 1.1 eq.), ETT (916 mg, 7.04 mmol, 2.0 eq.) and mCPBA (77%, 1.13 g, 5.06 mmol, 1.4 eq.) in MeCN (15 mL). Purification was performed by purification method E2. Cations were directly changed to TBA. The product (38, 2.28 g, 2.97 mmol, 84%) was isolated colorless oil.

1H-NMR (400 MHz, D₂O, δ/ppm): 3.88 (q, J = 6.3 Hz, 2H), 3.19 – 3.10 (m, 19H), 2.31 – 2.13 (m, 2H), 1.77 – 1.53 (m, 20H), 1.41 – 1.27 (m, 21H), 0.93 (t, J = 7.6 Hz, 24H).

13C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 127.62 (q, J = 275.8 Hz), 65.11 (d, J = 5.4 Hz), 59.59 – 57.42 (m), 46.48, 32.32 (q, J = 27.9 Hz), 28.86 (d, J = 7.1 Hz), 26.99, 23.08, 17.82 (q, J = 3.3 Hz), 14.32, 12.79.

19F-NMR (377 MHz, D₂O, δ/ppm): -66.06 (t, J = 11.4 Hz).

31P{¹H}-NMR (162 MHz, D₂O, δ/ppm): 0.41.

HRMS (ESI) m/z for C₅H₉F₃O₄P [M-H]: calcd. 221.0196, found 221.0196.

Phenylpyrophosphat (SI-16)

The compound was synthesized according to the general procedure E with phenylphosphate x 1.0 TBA (800 mg, 1.93 mmol), (FmO)₂P-NiPr₂ (SI-4, 1.11 g, 2.13 mmol, 1.1 eq.), ETT (570 mg, 4.83 mmol, 2.5 eq.) and mCPBA (77%, 691 mg, 3.09 mmol, 1.6 eq.) in DMF (10 mL). The compound was purified according to the general procedure E2. The product (SI-16, 445 mg, 989 µmol, 51%) was isolated as white solid.

1H-NMR (400 MHz, D₂O, δ/ppm): 7.45 – 7.38 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.20 (m, 1H), 3.21 – 3.11 (m, 10H), 1.83 – 1.73 (m, 10H), 1.73 – 1.59 (m, 5H).

13C{¹H}-NMR (101 MHz, D₂O, δ/ppm): 151.79 (d, J = 7.2 Hz), 129.65, 124.30 (d, J = 1.4 Hz), 120.55 (d, J = 4.3 Hz), 44.50, 22.18, 21.45.

31P{¹H}-NMR (162 MHz, D₂O, δ/ppm): -10.80 (d, J = 21.0 Hz), -15.71 (d, J = 20.9 Hz). HRMS (ESI) m/z for C₆H₇O₂P₂ [M-H]: calcd. 252.9672, found 252.9674.
D4T-diphosphate (SI-17)

The compound was synthesized according to the general procedure E with d4T-monophosphate x 1.4 TBA (SI-5, 275 mg, 426 µmol), (FmO)₂P-NiPr₂ (SI-4, 288 mg, 554 µmol, 1.3 eq.), ETT (139 mg, 1.07 mmol, 2.5 eq.) and mCPBA (77%, 204 mg, 913 µmol, 2.1 eq.) in DMF (10 mL). The crude product was precipitated with ether and subsequently purified according to the general procedure E2. The product (SI-17, 177 mg, 263 µmol, 62%) was isolated as white solid.

\(^1\text{H-NMR}\) (400 MHz, D₂O, δ/ppm): 7.62 (q, J = 1.4 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.53 (dt, J = 6.2, 1.8 Hz, 1H), 5.94 (ddd, J = 6.5, 2.6, 1.6 Hz, 1H), 5.15 – 5.09 (m, 1H), 4.14 (ddd, J = 6.2, 3.4, 1.9 Hz, 2H), 3.19 (q, J = 7.4 Hz, 18H), 1.90 (d, J = 1.3 Hz, 18H), 1.28 (t, J = 7.3 Hz, 27H).

\(^{13}\text{C}\{^1\text{H}\}-\text{NMR}\) (101 MHz, D₂O, δ/ppm): 166.77, 152.26, 138.18, 134.33, 125.10, 111.52, 89.95, 85.97 (d, J = 8.5 Hz), 66.27 (d, J = 5.7 Hz), 46.63, 11.43, 8.19. \(^{31}\text{P}\{^1\text{H}\}-\text{NMR}\) (162 MHz, D₂O, δ/ppm): -10.20 (d, J = 20.9 Hz), -11.42 (d, J = 20.7 Hz). \(\text{HRMS (ESI) m/z for C}_{10}\text{H}_{13}\text{N}_{2}\text{O}_{10}\text{P}_{2} [\text{M-H}]:}\) calcd. 383.0051, found 383.0042.
9. Synthesis of aryne precursors without literature precedence

**2-bromopyrene-1-ol (SI-18)**

![SI-18](image)

Compound SI-18 was synthesized according to Ghotekar et al. The analytical data matched the previously published values.\(^1\)

**2-(trimethylsilyl)pyren-1-yl trifluromethanesulfonate (SI-19)**

![SI-19](image)

A flame-dried, argon-filled 50 mL three-necked flask equipped with a magnetic stir bar and a reflux condenser was charged with a solution of 2-bromopyrene-1-ol (SI-18, 1.52 g, 5.12 mmol) in THF (17 mL). Then HMDS (1.16 mL, 5.63 mmol, 1.1 eq) was added and the mixture was heated to reflux for 5 h. After cooling to rt, the solvent was removed under reduced pressure. The crude product was used in the next step without further purification.

A flame-dried, argon-filled 100 mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of the crude product [(2-bromopyrene-1-yl)oxy]trimethylsilane in THF (23 mL). The solution was cooled to –78°C and \(\text{n-BuLi}\) was added dropwise. After stirring for 1 h at –78°C, \(\text{TF}_2\text{O}\) was added dropwise and stirring was continued for 1 h at –78°C. An aqueous saturated NaHCO₃ solution (15 mL) was then added at –78°C and the mixture was allowed to warm to rt. The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 20 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The product was purified by column chromatography (cyclohexane/ethyl acetate, 100:1) and obtained as a yellowish solid (SI-19, 1.37 g, 3.23 mmol, 63%). Crystallization from hot chloroform (50°C) at room temperature gave single crystals suitable for a X-ray analysis (see below for the report).
$R_f$ (cyclohexane/ethyl acetate, 100:1) = 0.45. $^1$H-NMR (400 MHz, CDCl$_3$, $\delta$/ppm): 8.30 (s, 1H), 8.27 (d, $J$ = 9.3 Hz, 1H), 8.20 – 8.11 (m, 3H), 8.07 – 7.90 (m, 3H), 0.66 (s, 9H). $^{13}$C$\{^1$H$\}$-NMR (101 MHz, CDCl$_3$, $\delta$/ppm): 145.59, 132.20, 132.17, 131.16, 130.78, 130.52, 129.09, 128.55, 127.10, 126.89, 126.61, 125.97, 123.96, 123.91, 120.40 (q, $J$ = 1.7 Hz), 119.02 (q, $J$ = 320.2 Hz), 0.63.

$^{19}$F NMR (377 MHz, CDCl$_3$, $\delta$/ppm): -72.59.

HRMS (APCI) m/z for C$_{20}$H$_{16}$F$_3$O$_3$Si [M-H]: calcd. 421.0547, found 421.0550.

4-((trimethylsilyl)ethynyl)phenol (SI-20)

![SI-20](image)

Compound SI-20 was synthesized according to HUDSON et al. The analytical data matched the previously published values.$^{14}$

4-(trimethylsilyl)ethynyl)phenyl isopropylcarbamate (SI-21)

![SI-21](image)

A flame-dried, argon-filled 100 mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of 4-((trimethylsilyl)ethynyl)phenol (SI-20, 1.90 g, 10.0 mmol) in CH$_2$Cl$_2$ (33 mL). Subsequently $i$-PrNCO (1.28 g, 15.0 mmol, 1.5 eq) was added, followed by NEt$_3$ (274 µL, 2.00 mmol, 0.2 eq) and then the mixture was stirred for 2 h at rt. After that the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/ethyl acetate, 5:1) and the product (SI-21, 2.60 g, 9.45 mmol, 95%) was obtained as a colorless solid.

$R_f$ (cyclohexane/ethyl acetate, 5:1) = 0.35. $^1$H-NMR (400 MHz, CDCl$_3$, $\delta$/ppm): 7.49 – 7.40 (m, 2H), 7.16 – 7.04 (m, 2H), 4.83 (d, $J$ = 7.9 Hz, 1H), 4.01 – 3.79 (m, 1H), 1.23 (d, $J$ = 6.6 Hz, 6H), 0.24 (s, 9H). $^{13}$C$\{^1$H$\}$-NMR (101 MHz, CDCl$_3$, $\delta$/ppm): 153.28, 151.24, 133.16, 121.57, 120.13, 104.61, 94.04, 43.65, 23.05, 0.12. HRMS (ESI) m/z for C$_{15}$H$_{22}$NO$_2$Si [M+H]$^+$: calcd. 276.1414, found 276.1416.
2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl isopropylcarbamate (SI-22)

A flame-dried, argon-filled 250 mL Schlenk flask equipped with a magnetic stir bar was charged with 4-((trimethylsilyl)ethynyl)phenyl isopropylcarbamate (SI-21, 2.60 g, 9.45 mmol) and Et₂O (94.5 mL). After cooling to 0°C, TMEDA (1.56 mL, 10.4 mmol, 1.1 eq) was added, followed by a solution of TBSOTf in n-pentane (8 mL, 1.3 M, 10.4 mmol, 1.1 eq) and then the mixture was stirred for 5 min at 0°C and further 30 min at rt. Additional TMEDA (2.83 mL, 18.9 mmol, 2.0 eq) was added and the mixture was cooled to –78°C. Then n-BuLi (7.60 mL, 2.48 M in n-hexane, 18.9 mmol, 2.0 eq) was added dropwise over 60 min. After an additional hour at –78°C, TMSCl was added dropwise over 35 min and the mixture was stirred for a further 85 min at –78°C. An aqueous saturated NaHSO₄ solution (40 mL) was then added at –78°C and the mixture was allowed to warm to rt. The layers were separated, and the organic layer was washed with aqueous saturated NaHSO₄ solution (60 mL) and brine (60 mL). The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The product was purified by column chromatography (cyclohexane/ ethyl acetate, 50:1 to 20:1) and obtained as a colorless solid (SI-22, 1.91 g, 5.50 mmol, 58%).

R<sub>f</sub> (cyclohexane/ ethyl acetate, 10:1) = 0.20. ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 7.53 (d, J = 2.1 Hz, 1H), 7.46 (dd, J = 8.4, 2.1 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 4.86 (d, J = 8.0 Hz, 1H), 3.90 (dp, J = 8.0, 6.5 Hz, 1H), 1.22 (d, J = 6.6 Hz, 6H), 0.28 (s, 9H), 0.25 (s, 9H). ¹³C{¹H}-NMR (101 MHz, CDCl₃, δ/ppm): 155.66, 153.44, 138.64, 134.02, 132.08, 122.18, 119.97, 105.04, 93.82, 43.57, 23.01, 0.13, -0.87. HRMS (ESI) m/z for C₁₈H₃₀NO₂Si₂ [M+H]<sup>+</sup>: calcd. 348.1810, found 348.1808.
Synthesis of 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl trifluoromethane-sulfonate (SI-23)

A flame-dried, argon-filled 250 mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl isopropylcarbamate (SI-22, 1.51 g, 4.36 mmol) in MeCN (44 mL). Then DBU (980 µL, 6.54 mmol, 1.5 eq), and Et₂NH (540 µL, 5.23 mmol, 1.2 eq) were added, and the mixture was heated to 40°C and stirred for 45 min. The reaction mixture was cooled to rt and a solution of PhNTf₂ (2.34 g, 6.54 mmol, 1.5 eq) in MeCN (13 mL) was added dropwise and stirred for 2 h. After that a saturated aqueous NaHSO₄ solution (30 mL) was added and the mixture was diluted with ethyl acetate (30 mL). The layers were separated, and the organic layer was washed with saturated aqueous NaHSO₄ solution (30 mL) and aqueous NaOH (10%, 2 × 30 mL). The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (n-pentane) and the product (SI-23, 1.43 g, 3.62 mmol, 83%) was isolated as a colorless liquid.

¹H-NMR (400 MHz, CDCl₃, δ/ppm): 7.59 (dd, J = 2.2, 0.4 Hz, 1H), 7.51 (dd, J = 8.6, 2.2 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 0.37 (s, 9H), 0.26 (s, 9H). ¹³C{¹H}-NMR (101 MHz, CDCl₃, δ/ppm): 154.51, 139.87, 134.77, 133.08, 123.01, 119.51 (d, J = 1.7 Hz), 118.61 (q, J = 320 Hz), 103.46, 96.26, 0.00, -0.79. ¹⁹F NMR (377 MHz, CDCl₃, δ/ppm): -73.83. HRMS (APCI) m/z for C₁₅H₂₂F₃O₃SSi₂ [M+H]⁺: calcd. 395.0775, found 395.0775.
10. Synthesis of Amino-DEACM

The synthetic route towards amino-DEACM (SI-26) is shown in the supporting figure 5 below. Mesylate SI-24 was synthesized according to Wong et al. Analytical data were in accordance with literature.

**Supporting figure 5:** Synthesis of Amino-DEACM SI-26 from Mesylate SI-24.

**Step 1:** 2-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl)isoindoline-1,3-dione (SI-25)

Potassium phthalimide (990 mg, 5.30 mmol, 1.2 eq.) was added to a solution of (7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl methanesulfonate (SI-24, 1.50 g, 4.61 mmol, 1.0 eq.) in DMF (90 mL) and it was stirred for 2 h at 80 °C. Afterwards the reaction mixture was poured into ice water (450 mL). The yellow precipitate was collected via Büchner funnel and was dried in a desiccator, over CaCl₂ and under vacuum, for 3 days. The dry solid was purified by recrystallization (toluene, 45 mL) and the title compound (SI-25, 950 mg, 2.52 mmol, 57%) was obtained as dark yellow crystals.

**¹H-NMR** (400 MHz, CDCl₃, δ/ppm): 7.95 – 7.86 (m, 2H), 7.81 – 7.74 (m, 2H), 7.55 (d, J = 9.0 Hz, 1H), 6.62 (dd, J = 9.0, 2.6 Hz, 1H), 6.51 (d, J = 2.6 Hz, 1H), 5.86 (t, J = 1.2 Hz, 1H), 4.94 (d, J = 1.2 Hz, 2H), 3.42 (q, J = 7.1 Hz, 4H), 1.21 (t, J = 7.1 Hz, 6H). **¹³C{¹H}-NMR** (101 MHz, CDCl₃, δ/ppm): 167.61, 161.79, 156.34, 150.76, 149.14, 134.47, 131.83, 124.66, 123.74, 108.73, 106.80, 106.57, 97.88, 44.78, 37.61, 12.45. **HRMS** (APCI) m/z for [C₂₂H₂₁N₂O₄]⁺: calcd. 377.1496, found 377.1491. **Rt** = 0.54 (silica gel, CH:EA 1:1).
Step 2: 4-(aminomethyl)-7-(diethylamino)-2H-chromen-2-one (Amino-DEACM) (SI-26)

![Chemical Structure]

Ethylenediamine (220 µL, 198 mg, 3.3 mmol, 5.0 eq.) was added to a solution of 2-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl)isoindoline-1,3-dione (SI-25, 250 mg, 664 µmmol, 1.0 eq.) in DCM/EtOH (1:1, 25 mL). The solution was stirred for 5 h at 40 °C. Afterwards, the reaction mixture was directly dry loaded on deactivated silica (ca. 4 spatulas) and purified by flash chromatography (deactivated silica gel, DCM:MeOH 95:5). **Attention:** Solvent removal should be carried out below 35°C. The title compound (SI-26, 160 mg, 650 µmol, 98%) was obtained as a yellow oil.

**1H-NMR** (300 MHz, CDCl₃, δ/ppm): 7.37 (d, J = 9.0 Hz, 1H), 6.57 (dd, J = 9.0, 2.6 Hz, 1H), 6.50 (d, J = 2.6 Hz, 1H), 6.18 (t, J = 1.3 Hz, 1H), 3.98 (d, J = 1.3 Hz, 2H), 3.40 (q, J = 7.1 Hz, 4H), 1.53 (br. s, 2H), 1.19 (t, J = 7.1 Hz, 6H). **13C{1H}-NMR** (101 MHz, CDCl₃, δ/ppm): 162.51, 156.60, 156.24, 150.47, 124.39, 108.50, 107.10, 105.68, 97.87, 44.74, 42.27, 12.46. **HRMS** (ESI) m/z for [C₁₄H₁₉N₂O₂]⁺: calcd. 247.1441 found 247.1442. **Rₚ = 0.10** (deactivated silica gel, DCM:MeOH 95:5).
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12. NMR - spectra

(aligned according to molecule numbering)
Compound 27, phenyl phosphate, $^1$H - NMR (D$_2$O, 400 MHz)

TBA salt

acetate

**27**
Compound 27, phenyl phosphate, $^{31}\text{P} \{^1\text{H}\}$ - NMR ($D_2O$, 162 MHz)

TBA salt

27

A (s) -3.53
Compound 27, phenyl phosphate, $^{13}\text{C} - \text{NMR} (\text{D}_2\text{O}, 101 \text{ MHz})$

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{P} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{Ph} \\
\text{TBA salt}
\end{array}
\]

27

- A (d) 120.45
- B (s) 123.91
- C (s) 129.64
- D (d) 152.22
- E (s) 12.80
- F (s) 19.12
- G (s) 23.10
- H (m) 58.08

acetate

acetate
Compound 28, 2-napthalen-2-yl phosphate, $^1$H - NMR ($D_2O$, 400 MHz)

TBA salt

![Molecular structure of compound 28]

$^{13}$C NMR (acetate)

- A (m) 7.89
- B (t) 7.67
- C (m) 7.46
- D (m) 3.03
- E (m) 1.52
- F (h) 1.29
- G (t) 0.91

acetate
Compound 28, 2-napthalen-2-yl phosphate, $^{31}$P $^{1}$H - NMR (D$_2$O, 162 MHz)

TBA salt

28
Compound 28, 2-napthalen-2-yl phosphate, $^{13}$C - NMR ($D_2O$, 101 MHz)

TBA salt

28
Compound 29, 3,4-dimethylphenyl phosphate, $^1$H - NMR (D$_2$O, 400 MHz)

\[
\begin{align*}
\text{TBA salt} & \\
29
\end{align*}
\]
Compound 29, 3,4-dimethylphenyl phosphate, $^{31}P\{^1H\} - NMR (D_2O, 162 MHz)

TBA salt

A (s)
-3.68
Compound 29, 3,4-dimethylphenyl phosphate, $^{13}$C - NMR ($D_2O$, 101 MHz)

TBA salt

![Structural formula of 3,4-dimethylphenyl phosphate](image)

- A (s) 12.83
- B (s) 18.13
- C (s) 19.01
- D (m) 19.11
- E (s) 23.08
- F (m) 58.03
- G (d) 117.54
- H (d) 121.46
- I (s) 130.25
- J (d) 132.23
- K (s) 138.26
- L (d) 150.19
- TBA salt

acetate

acetate
Compound 30, 1H-indol-5-yl phosphate, $^1$H - NMR ($D_2$O, 400 MHz)

TBA salt

30
Compound 30, 1H-indol-5-yl phosphate, $^{31}P \{^1H\} - NMR (D_2O, 162 MHz)

TBA salt

30
Compound 30, 1H-indol-5-yl phosphate, $^{13}\text{C}$ - NMR ($D_2O$, 101 MHz)

TBA salt

30

 acetate

acetate
Compound 31, pyren-2-yl phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

TBA salt

$^{31}P$
Compound 31, pyren-2-yl phosphate, \(^{31}P\){'H} - NMR (CD\(_3CN\), 122 MHz)

\[ \text{TBA salt} \]

\[ 31 \]
Compound 31, pyren-2-yl phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)

TBA salt

- A (d) 153.51
- B (s) 133.12
- C (s) 131.35
- D (s) 128.57
- E (s) 127.97
- F (s) 126.29
- G (s) 126.03
- H (d) 117.74
- I (m) 59.10
- J (s) 24.16
- K (m) 20.20
- L (s) 13.70

SI - 72
Compound 32, phenyl diphosphate, $^1$H - NMR (D$_2$O, 400 MHz)

TBA/TEA salt

$^1$H NMR (D$_2$O, 400 MHz)
Compound 32, phenyl diphosphate, $^{31}$P $^1$H - NMR (D$_2$O, 122 MHz)

TBA/TEA salt

32
Compound 32, phenyl diphosphate, $^{13}$C - NMR (D$_2$O, 101 MHz)

TBA/TEA salt

32
Compound 33, 2-naphthalen-2-yl diphosphate, $^1$H - NMR (D$_2$O, 400 MHz)

TBA salt

33

\[
\text{\begin{tabular}{c c}
\text{B (t)} & 7.75 \\
\text{A (m)} & 7.94 \\
\text{C (m)} & 7.52 \\
\text{D (m)} & 3.10 \\
\text{E (m)} & 1.58 \\
\text{F (h)} & 1.32 \\
\text{G (t)} & 0.92 \\
\end{tabular}}
\]
Compound 33, 2-naphthalen-2-yl diphosphate, \textsuperscript{31}P \textsuperscript{1}H - NMR (D\textsubscript{2}O, 122 MHz)

\[
\begin{align*}
\text{OH} & \quad \text{O} \\
\text{P} & \quad \text{O} \\
\text{O} & \quad \text{P} \\
\text{O} & \quad \text{OH}
\end{align*}
\]

TBA salt

\textbf{33}

\begin{align*}
\text{B (d)} & \quad -15.94 \\
\text{A (d)} & \quad -10.84
\end{align*}
Compound 33, 2-naphthalen-2-yl diphosphate, $^{13}$C - NMR ($D_2O$, 101 MHz)

TBA salt

33

 acetate

acetate
Compound 34, 3,4-dimethylphenyl diphosphate, $^1$H - NMR (D$_2$O, 400 MHz)

$$\text{TBA salt}$$

34
Compound 34, 3,4-dimethylphenyl diphosphate, $^{31}$P $^1$H - NMR (D$_2$O, 162 MHz)
Compound 34, 3,4-dimethylphenyl diphosphate, $^{13}$C - NMR ($D_2O$, 101 MHz)

$\text{H}_3\text{C}$

$\text{H}_3\text{C}$

$\text{P}$

$\text{P}$

$\text{O}$

$\text{O}$

$\text{OH}$

$\text{OH}$

$\text{OH}$

$\text{OH}$

$\text{OH}$

$\text{TBA salt}$

34

acetate

acetate

$\text{A (d)}$ 149.84

$\text{B (s)}$ 138.31

$\text{C (d)}$ 132.59

$\text{D (s)}$ 130.24

$\text{E (d)}$ 121.56

$\text{F (d)}$ 117.66

$\text{G (m)}$ 58.05

$\text{H (s)}$ 23.09

$\text{I (t)}$ 19.12

$\text{J (s)}$ 18.99

$\text{K (s)}$ 18.15

$\text{L (s)}$ 12.83

acetate
Compound 35, 1H-indol-5-yl diphosphate, $^1$H - NMR (D$_2$O, 300 MHz)

TBA/TEA salt

35

acetate
Compound 35, 1H-indol-5-yl diphosphate, $^{31}$P {^1}H - NMR (D$_2$O, 162 MHz)

TBA/TEA salt

35

A (d) -10.74

B (d) -15.01
Compound 35, 1H-indol-5-yl diphosphate, $^{13}$C - NMR ($D_2O$, 101 MHz)

$^{13}$C NMR spectrum of Compound 35, showing the chemical shifts and peak assignments for various carbon atoms.

- A (d) 145.44
- B (s) 132.80
- C (s) 127.58
- D (s) 126.62
- E (d) 115.72
- F (s) 111.92
- G (d) 111.18
- H (s) 101.30
- I (m) 58.03
- J (s) 23.07
- K (t) 19.11
- L (s) 12.82

TBA/TEA salt

$^{13}$C NMR spectrum showing the chemical shifts for the acetate groups (acetate) at approximately 16.3 ppm and -17.3 ppm.

SI - 84
Compound 36, pyren-2-yl diphosphate, $^1$H - NMR ($D_2O$, 400 MHz)

TBA salt

36
Compound 36, pyren-2-yl diphosphate, $^{31}$P {$^1$H} - NMR (D$_2$O, 162 MHz)

TBA salt

36

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{OH} \\
\text{P} \\
\text{O} \\
\text{OH} \\
\end{array}
\]
Compound 36, pyren-2-yl diphosphate, $^{13}$C - NMR ($D_2O$, 101 MHz)

TBA salt

36

acetate
Compound 38, 5,5,5-Trifluoropentylphosphate, \(^1\)H - NMR (D\(_2\)O, 400 MHz)

TBA/TEA - salt

F
F

O
P
O

O

- O

F
F

38

A (q) 3.88
B (m) 3.15
C (m) 2.21
D (m) 1.62
E (m) 1.32
F (t) 0.93

acetate
Compound 38, 5,5,5-Trifluoropentylphosphate, $^{19}$F - NMR (D2O, 377 MHz)

\[\text{TBA/TEA - salt} \]

38
Compound 38, 5,5,5-Trifluoropentylphosphate, $^{31}$P($^1$H) - NMR (D2O, 162 MHz)

TBA/TEA - salt

38
Compound 38, 5,5,5-Trifluoropentylphosphate, $^{13}$C($^1$H) - NMR (D2O, 101 MHz)

acetate

TBA/TEA - salt
Compound 39, 5,5,5-Trifluoropentyl-phenylphosphate, \(^1\text{H}\) - NMR (MeCN-d3, 400 MHz)

TBA / TEA - salt 39
Compound 39, 5,5,5-Trifluoropentyl-phenylphosphate, $^{19}$F - NMR (MeCN-d3, 377 MHz)

TBA / TEA - salt

39

f$_1$ (ppm)

-66.7 -66.8 -66.9 -67.0 -67.1 -67.2 -67.3 -67.4
Compound 39, 5,5,5-Trifluoropentyl-phenylphosphate, $^{31}P\{^1H\}$ - NMR (MeCN-d3, 162 MHz)

TBA / TEA - salt

39
Compound 39, 5,5,5-Trifluoropentyl-phenylphosphate, $^{13}$C \(\{^1H\} - NMR (MeCN-d3, 101 MHz)

TBA / TEA - salt

39
Compound 41, 3,4-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

TBA salt

41

$^{1}$H - NMR (CD$_3$CN, 400 MHz)

- A (m) 6.96
- B (m) 6.90
- C (m) 3.78
- D (m) 3.10
- E (s) 2.19
- F (s) 2.16
- G (m) 2.12
- H (m) 1.59
- I (h) 1.34
- J (t) 0.96
Compound 41, 3,4-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)

TBA salt

$^{19}$F NMR spectrum of Compound 41, showing a peak at $-66.97$ ppm.
Compound 41, 3,4-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{31}P \{^1H\} - NMR (CD$_3$CN, 162 MHz)
Compound 41, 3,4-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)
Compound 42, 2,5-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

TBA salt

42
Compound 42, 2,5-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)
Compound 42, 2,5-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{31}P\left({}^1H\right)$ - NMR (CD$_3$CN, 162 MHz)
Compound 42, 2,5-dimethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)

TBA salt

$^{13}$C NMR spectrum of Compound 42.
Compound 43, 3,4-dimethoxyphenyl (5,5,5-trifluoropentyl) phosphate, \(^1\text{H} - \text{NMR} (\text{CD}_3\text{CN}, 400 \text{ MHz})\)

![Chemical structure of Compound 43](image-url)

- A (dd) 6.87
- B (d) 6.77
- C (ddd) 6.70
- D (m) 3.80
- E (s) 3.75
- F (s) 3.73
- G (m) 3.09
- H (m) 2.14
- I (m) 1.59
- J (m) 1.35
- K (t) 0.89
- L (t) 0.96

**TBA/TEA salt**
Compound 43, 3,4-dimethoxyphenyl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)

TBA/TEA salt

$^{19}$F NMR ($\text{CD}_3\text{CN}$, 377 MHz)

A (t) -66.95
Compound 43, 3,4-dimethoxyphenyl (5,5,5-trifluoropentyl) phosphate, $^{31}\text{P} \{^1\text{H}\}$ - NMR (CD$_3$CN, 162 MHz)

TBA/TEA salt

43
Compound 43, 3,4-dimethoxyphenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR ($\text{CD}_3\text{CN}$, 101 MHz)

TBA/TEA salt

acetate
Compound 44, 4-(trifluoromethyl)phenyl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

TBA salt

44
Compound 44, 4-(trifluoromethyl)phenyl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)
Compound 44, 4-(trifluoromethyl)phenyl (5,5,5-trifluoropentyl) phosphate, $^{31}$P ($^1$H) - NMR (CD$_3$CN, 162 MHz)
Compound 44, 4-(trifluoromethyl)phenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)
Compound 45, benzo[d][1,3]dioxol-5-yl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

TBA salt

45
Compound 45, benzo[d][1,3]dioxol-5-yl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)

![Chemical structure of Compound 45]

TBA salt

45

$^{19}$F NMR spectrum showing the resonance at -66.98 ppm.
Compound 45, benzo[d][1,3]dioxol-5-yl (5,5,5-trifluoropentyl) phosphate, $^{31}$P $\{^1H\}$ - NMR (CD$_3$CN, 162 MHz)

TBA salt

45
Compound 45, benzo[d][1,3]dioxol-5-yl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)
Compound 46, 4-ethynylphenyl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

![NMR spectrum](image)

TBA salt

$^1$H NMR (CD$_3$CN, 400 MHz)

- **A (m)**: 7.35
- **B (m)**: 7.20
- **C (m)**: 3.79
- **D (m)**: 7.08
- **E (s)**: 3.33
- **F (s)**: 3.26
- **G (m)**: 3.08
- **H (m)**: 2.13
- **I (m)**: 1.59
- **J (m)**: 1.35
- **K (m)**: 0.97
Compound 46, 4-ethylphenyl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)
Compound 46, 4-ethynylphenyl (5,5,5-trifluoropentyl) phosphate, $^{31}$P $\{^1$H$\}$ - NMR (CD$_3$CN, 162 MHz)

TBA salt

46
Compound 46, 4-ethynylphenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)

TBA salt

46
Compound 47, 3-bromophenyl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)

$\textbf{47}$

$\mathrm{Br}$

$\mathrm{O}$

$\mathrm{P}$

$\mathrm{O}$

$\mathrm{O}$

$\mathrm{F}$

$\mathrm{F}$

$\mathrm{F}$

$\mathrm{C} (\text{m})$

$3.81$

$\mathrm{D} (\text{m})$

$3.08$

$\mathrm{E} (\text{m})$

$2.13$

$\mathrm{F} (\text{m})$

$1.59$

$\mathrm{H} (\text{t})$

$0.96$

$\mathrm{SI} - 120$
Compound 47, 3-bromophenyl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)

$\text{TBA salt}$

47

$\text{f1 (ppm)}$

-66.8 -66.9 -67.0 -67.1 -67.2 -67.3

$\text{A (t)}$

-66.99
Compound 47, 3-bromophenyl (5,5,5-trifluoropentyl) phosphate, $^{31}\text{P}\{^1\text{H}\} -\text{NMR (CD}_3\text{CN, 162 MHz)}$

\[
\text{TBA salt}
\]

$\text{47}$
Compound 47, 3-bromophenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)

TBA salt

47
Compound 48, 4-chlorophenyl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)
Compound 48, 4-chlorophenyl (5,5,5-trifluoropentyl) phosphate, $^{19}\text{F} - \text{NMR (CD}_3\text{CN, 377 MHz)}$

$^{19}\text{F} - \text{NMR (CD}_3\text{CN, 377 MHz)}$

TBA salt

48
Compound 48, 4-chlorophenyl (5,5,5-trifluoropentyl) phosphate, $^{31}\text{P} \{^1\text{H}\} - \text{NMR (CD}_3\text{CN, 162 MHz)}$

![Molecular structure of Compound 48]

$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum showing a signal at -5.53 ppm for the TBA salt of Compound 48.
Compound 48, 4-chlorophenyl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)

TBA salt

48
Compound 49, naphthalen-2-yl (5,5,5-trifluoropentyl) phosphate, $^1$H - NMR (CD$_3$CN, 400 MHz)
Compound 49, naphthalen-2-yl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)

TBA salt

49
Compound 49, naphthalen-2-yl (5,5,5-trifluoropentyl) phosphate, $^{31}\text{P} \{^1\text{H}\}$ NMR (CD$_3$CN, 162 MHz)
Compound 49, naphthalen-2-yl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)

TBA salt

- A (d) 153.45
- B (s) 135.30
- C (q) 128.70
- D (s) 130.36
- E (s) 129.34
- F (s) 128.34
- G (s) 127.79
- H (s) 126.81
- I (s) 124.70
- J (d) 122.71
- K (d) 115.88
- L (d) 65.07
- M (m) 59.20
- N (q) 33.56
- O (d) 30.45
- P (s) 24.23
- Q (m) 20.25
- R (q) 19.34
- S (s) 13.73

SI - 131
Compound 50, 1H-indol-5-yl (5,5,5-trifluoropentyl) phosphate, \( ^1H \) - NMR (CD\(_3\)CN, 400 MHz)

\[
\begin{align*}
TBA \text{ salt} & \\
50
\end{align*}
\]
Compound 50, 1H-indol-5-yl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)

- $f_1$ (ppm)
- $A$ (t)
- $-66.96$

TBA salt

$^{19}$F NMR spectrum for compound 50.
Compound 50, 1H-indol-5-yl (5,5,5-trifluoropentyl) phosphate, $^{31}P\{^1H\}$ - NMR (CD$_3$CN, 162 MHz)
Compound 50, 1H-indol-5-yl (5,5,5-trifluoropentyl) phosphate, $^{13}$C NMR (CD$_3$CN, 101 MHz)

**TBA salt**

50
Compound 51, pyren-2-yl (5,5,5-trifluoropentyl) phosphate, \(^1\)H - NMR (CD\(_3\)CN, 400 MHz)
Compound 51, pyren-2-yl (5,5,5-trifluoropentyl) phosphate, $^{19}$F - NMR (CD$_3$CN, 377 MHz)
Compound 51, pyren-2-yl (5,5,5-trifluoropentyl) phosphate, $^{31}$P ($^1$H) - NMR (CD$_3$CN, 162 MHz)
Compound 51, pyren-2-yl (5,5,5-trifluoropentyl) phosphate, $^{13}$C - NMR (CD$_3$CN, 101 MHz)
Compound 52, Diphenylphosphate, $^1$H - NMR (D$_2$O, 400 MHz)

**Structure:**

![Structure of Compound 52, Diphenylphosphate](image)

**Experimental Details:**

- **Chemical Formula:** O=P=O
- **Salt:** TBA / TEA
- **Resonance Frequencies:**
  - A (m): 7.41 ppm
  - B (m): 7.23 ppm
  - C (m): 3.19 ppm
  - D (m): 1.64 ppm
  - E (m): 1.36 ppm
  - F (t): 1.28 ppm
  - G (t): 0.95 ppm

**Additional Information:**

- **Label:** acetate

---

*SI - 140*
Compound 52, Diphenylphosphate, $^{31}P\{'^1\text{H}\}$ - NMR (D2O, 162 MHz)

TBA / TEA - salt

52
Compound 52, Phenylphenylphosphonate, $^{13}$C - NMR (D2O, 101 MHz)

**TBA/TEA - salt**

52
Compound 53, Pentyll-phenylphosphate, $^1$H - NMR (MeCN-d3, 400 MHz)

TBA - salt

acetate
Compound 53, Pentyl-phenylphosphate, $^{31}P$ {\textit{I}H} - NMR (MeCN-d$_3$, 162 MHz)

TBA - salt

53

$\text{H}_3\text{C}$

\begin{center}
\begin{tabular}{c}
\includegraphics[width=0.5\textwidth]{compound_53}\end{tabular}
\end{center}

A (s)

-6.80
Compound 53, Pentyl-phenylphosphate, $^{13}$C ($^1$H) - NMR (MeCN-d$_3$, 101 MHz)

TBA - salt

$\text{H}_3\text{C} - \begin{array}{c} \text{O} \\ \text{P} \\ \text{O} \\ - \text{O} \end{array} \begin{array}{c} \text{C} \\ \text{H}_3 \end{array}$
Compound 54, Phenylphenylphosphonate, $^1$H - NMR (D$_2$O, 400 MHz)

TBA - salt

54

acetate
Compound 54, Phenylphenylphosphonate, $^{31}\text{P} \{^1\text{H}\} - \text{NMR (D}_2\text{O, 162 MHz)}}$

$^{31}\text{P} \{^1\text{H}\} - \text{NMR}$ spectrum for Compound 54.

**TBA - salt**

$54$

$A\ (s)\ 12.99$
Compound 54, Phenylphenylphosphonate, $^{13}$C - NMR (D2O, 101 MHz)

TBA - salt

54
Compound 55, Pent-4-yn-1-yl-phenyl phosphate, $^1$H - NMR (D$_2$O / MeCN-d3, 400 MHz)
Compound 55, Pent-4-yn-1-yl-phenylphosphate, $^{31}$P {$^1$H} - NMR (D2O/MeCN-d3, 162 MHz)
Compound 55, Pent-4-yn-1-yl-phenylphosphate, $^{13}$C \{\textsuperscript{1}H\} - NMR (D$_2$O / MeCN-d3, 101 MHz)

- A (d) 152.43
- B (s) 129.85
- C (s) 124.09
- D (d) 120.40
- E (s) 84.85
- F (s) 69.82
- G (d) 65.00
- H (m) 58.31
- I (d) 29.12
- J (s) 13.09
- K (s) 14.43
- L (m) 19.39

TBA - salt

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

55
Compound 56, Isoprenyl-phenylphosphate, $^1$H - NMR (MeCN-d$_3$, 400 MHz)

A (m) 7.30
B (m) 7.19
C (m) 7.09
D (dq) 4.72
E (dqt) 4.77
F (tdd) 2.32
G (qd) 2.96
H (t) 1.18
I (td) 1.71
J (q) 4.04

$^{13}$C-NMR (MeCN-d$_3$, 125 MHz)

$^1$H - NMR (MeCN-d$_3$, 400 MHz)

TEA- salt

56
Compound 56, Isoprenyl-phenylphosphate, $^{31}P\{^1H\} - NMR (MeCN-d3, 162 MHz)

A (s)  
-6.95

TEA- salt

56

![Chemical Structure](image-url)
Compound 56, Isoprenyl-phenylphosphate, $^{13}$C \{^1H\} - NMR (MeCN-d3, 101 MHz)

\[
\begin{align*}
\text{H}_{2}C & \quad \text{CH}_{3} \\
\text{C} & \quad \text{O} \\
\text{P} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

TEA- salt

56
Compound 57, Geranyl-phenylphosphate, $^1$H - NMR (MeCN-d3, 400 MHz)

![Chemical Structure of Compound 57]

- **A (m)** 7.26
- **B (m)** 7.18
- **C (m)** 7.04
- **D (m)** 4.41
- **E (tdt)** 5.08
- **F (tq)** 5.32
- **G (q)** 2.96
- **H (t)** 1.19
- **I (m)** 1.58
- **J (d)** 1.61
- **K (m)** 1.65

TEA - salt

57
Compound 57, Geranyl-phenylphosphate, $^{31}\text{P} \{^1\text{H}\} - \text{NMR (MeCN-d3, 162 MHz)}$

$$
\text{CH}_3
\text{CH}_3
\text{CH}_3
\text{CH}_3
\text{CH}_3
\text{CH}_3
\text{CH}_3
\text{CH}_3
\text{TEA - salt}
57
$$

A (s) -5.83
Compound 57, Geranyl-phenylphosphate, $^{31}P$ - NMR (MeCN-d3, 162 MHz)

![Chemical structure of Compound 57, Geranyl-phenylphosphate](image)

A (t)  
-5.83
Compound 57, Geranyl-phenylphosphate, $^{13}\text{C} \{^1\text{H}\} - NMR (\text{MeCN-d3, 101 MHz})$

![NMR spectrum with peaks labeled A to P]

- **A (d)** 63.48
- **B (d)** 154.32
- **C (s)** 140.90
- **D (s)** 132.47
- **E (s)** 130.21
- **F (s)** 124.94
- **G (s)** 123.93
- **H (d)** 121.87
- **I (d)** 121.16
- **J (s)** 46.65
- **K (s)** 40.14
- **L (s)** 27.12
- **M (s)** 25.82
- **N (s)** 17.79
- **O (s)** 16.53
- **P (s)** 8.92

[SI - 158]
Compound 58, 6-Hydroxyhexyl-phenylphosphate, $^1$H - NMR (D$_2$O / MeCN-d$_3$, 400 MHz)

**Chemical Structure:**

![Chemical Structure](SI - 159)

**NMR Spectra:**

- A (m) 7.54
- B (m) 7.35
- C (t) 3.69
- D (q) 4.09
- E (m) 3.29
- F (m) 1.77
- G (p) 1.65
- H (m) 1.49
- I (t) 1.41
- J (t) 1.11
Compound 58, 6-Hydroxyhexyl-phenylphosphate, $^{31}P \left\{ ^1H \right\} -$ NMR ($D_2O/MeCN-d3$, 162 MHz)

TBA - salt

58
Compound 58, 6-Hydroxyhexyl-phenylphosphate, $^1$H - $^{31}$P - HMBC (D$_2$O/MeCN-d3)
Compound 58, 6-Hydroxyhexyl-phenylphosphate, $^{13}$C $^{3}$$^{1}$H - NMR (D$_2$O/MeCN-d3, 101 MHz)

TBA - salt

58

A (d) 152.97
B (s) 130.54
C (s) 124.84
D (d) 120.99
E (d) 67.43
F (s) 62.52
G (m) 58.94
H (s) 47.46
I (s) 32.23
J (d) 30.63
K (d) 25.63
L (s) 23.99
M (m) 20.02
N (s) 13.74
Compound 59, D4T-phenylphosphate, $^1$H - NMR (D$_2$O, 400 MHz)

A (q) 7.33
B (dd) 7.25
C (m) 7.06
D (dt) 6.90
E (dt) 6.49
F (m) 5.15
G (dt) 5.90
H (dt) 4.09
I (dt) 4.25
J (q) 3.21
K (t) 1.29
L (d) 1.60

$^1$H-NMR spectrum of Compound 59, D4T-phenylphosphate in D$_2$O at 400 MHz. The spectrum shows signals for each proton in the molecule, with peak assignments indicated for each chemical shift. The TEA-salt form is also shown in the diagram. The compound is labeled as Compound 59.
Compound 59, D4T-phenylphosphate, $^{31}P$ {$^1H$} - NMR ($D_2O$, 162 MHz)

A (s) -4.85

TEA - salt

59
Compound 59, D4T-phenylphosphate, $^{13}$C {$^1$H} - NMR ($D_2O$, 101 MHz)

$^1$H NMR (D$_2$O, 101 MHz)

- A (s) 166.43
- B (s) 152.19
- C (d) 151.42
- D (s) 138.22
- E (s) 134.22
- F (s) 129.09
- G (s) 125.04
- H (s) 124.38
- I (d) 120.21
- J (d) 110.72
- K (s) 89.95
- L (d) 85.65
- M (d) 66.19
- N (s) 46.63
- O (s) 11.28
- P (s) 8.20

59

TEA - salt
Compound 60, D4T-phenylpyrophosphate, $^1$H - NMR (D$_2$O, 400 MHz)

A (q) 7.52
B (m) 7.30
C (m) 7.13
D (m) 6.94
E (dt) 6.45
F (ddd) 5.88
G (m) 5.08
H (m) 4.16
I (q) 3.19
J (t) 1.27
K (dd) 1.78

- Salt

60
Compound 60, D4T-phenylpyrophosphate, $^{31}P \{^1H\} - NMR (D_2O, 162 MHz)

TEA - salt

60
Compound 60, D4T-phenylpyrophosphate, $^{13}$C {$^1$H} - NMR ($D_2O$, 101 MHz)

Acetate

TEA - salt

60

acetate
Compound 61, Diphenylpyrophosphate, $^1H$ - NMR ($D_2O$, 400 MHz)

TBA / TEA - salt

61
Compound 61, Diphenylpyrophosphate, $^{31}P$ ($^1H$) - NMR (D2O, 162 MHz)

TBA / TEA - salt

61

A (s)
-16.13
Compound 61, Diphenylpyrophosphate, $^{13}$C - NMR (D2O, 101 MHz)

TBA / TEA - salt

61

acetate

f1 (ppm)
Compound 67, Pentylphosphate, $^1$H - NMR ($D_2$O, 400 MHz)

TBA/TEA - salt

67

A (q) 3.85  B (m) 3.12  C (m) 1.59  D (m) 1.31  E (t) 0.92  F (m) 0.87
Compound 67, Pentylphosphate, \(^{31}\text{P}\{^{1}\text{H}\} - \text{NMR (D}_2\text{O, 162 MHz)}

\[
\text{O} \quad \text{P} \quad \text{O}
\]

\[
\text{H}_3\text{C} - \text{O} - \text{PO}_3\text{O}^{-}
\]

TBA/TEA - salt

67
Compound 67, Pentylyphosphate, $^{13}C(\text{H})$ - NMR (D2O, 101 MHz)

H$_3$C

$\text{O}$

$\text{O}$

TBA/TEA - salt

67

acetate

acetate

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$

$\text{O}$
Compound 73, Phenylcyclotriphosphate, $^{31}$P {$^1$H} - NMR (MeCN-d$_3$, 162 MHz)
Compound 74, Phenylcycloctetraphosphate, $^{31}$P $^1$H NMR (MeCN-d3, 162 MHz)

Tetrametaphosphate (unreacted)

$\text{B (m)}$
-25.44

$\text{A (m)}$
-29.63

$\text{74}$
Compound 74, Phenylcyclotetr phosphate, $^{31}\text{P} \{^1\text{H}\}$ - NMR (MeCN-d3, 162 MHz)

Compound 74, Phenylcyclotetr phosphate, $^{31}\text{P} \{^1\text{H}\}$ - NMR (spinsimulator)
Compound 78, PhenylP$_3$-propargylamidate, $^1$H - NMR (D$_2$O, 400 MHz)

A (m) 7.29
B (m) 7.22
C (m) 7.43

$^1$H - NMR (D$_2$O, 400 MHz)
Compound 78, PhenyloP₃-propargylamidate, $^{31}$P {¹H} - NMR (D2O, 162 MHz)
Compound 78, PhenylP₃-propargylamidate, ¹H - ³¹P - HMBC (D₂O MHz)
Compound 78, PhenylP₃-propargylamidate, $^{13}$C{¹H} - NMR (D2O, 101 MHz)

```
O
P
O
O
P
O
O
P
O
O
H
P
O
O
H
N
H
C

A (d) 151.75
B (s) 129.68
C (d) 124.33
D (d) 120.59
E (d) 82.96
F (s) 71.35
G (s) 46.64
H (s) 30.96
I (s) 8.20

TEA - salt
78
```
Compound 79, PhenylP$_3$-amidate, $^1$H - NMR (D2O, 400 MHz)

Na - salt

$\text{f}_1$ (ppm)

- B (m) 7.30
- A (m) 7.43
- C (m) 7.24

O
O
O
- O
O
O
- N
H$_2$
Compound 79, Phenyl$P_3$-amidate, $^{31}P \quad ^1H$ - NMR (D2O, 162 MHz)
Compound 79, PhenylP₃-amidate, $^{13}$C($^1$H) - NMR (D2O, 101 MHz)

- A (d) 151.70
- C (d) 124.44
- D (d) 120.61
- B (s) 129.72

\[
\begin{align*}
\text{Na - salt} \\
\text{SI - 184}
\end{align*}
\]
Compound 80, PhenyIP₃-anthracen-9-ylmethanamide, ¹H - NMR (D₂O, 400 MHz)

Na - salt

acetone
Compound 80, PhenylP<sub>3</sub>-anthracen-9-ylmethanamide, $^{31}$P {$^1$H} - NMR (D2O, 162 MHz)

Na - salt

80
Compound 80, PhenylP$_3$-anthracen-9-ylmethanamidate, $^{13}$C($^1$H) - NMR (D2O, 101 MHz)

Na - salt

80
Compound 81, PhenylP$_3$-5'-deoxyadenosyl-5'-amidate, $^1$H - NMR (D$_2$O, 400 MHz)

A (s) 8.33
B (d) 8.23
C (d) 7.20
D (m) 5.98
E (dddd) 5.98
F (dp) 4.77
G (m) 4.22
H (dd) 4.22
I (q) 3.25
J (m) 3.25

Na - salt

81

acetone

SI - 188
**Compound 81, PhenylP$_3$-5'-deoxyadenosyl-5'-amidate, $^{31}$P {$^1$H} - NMR (D2O, 162 MHz)**

Na - salt

81
Compound 81, PhenylP₃-5'-deoxyadenosyl-5'-amidate, DQF-COSY (D2O)

Ar-H

1'-H

2'-H

3'-H

4'-H

5'-H

5'-H₂

1'-H

2'-H

3'-H

4'-H

5'-H

Ar-H
Compound 81, PhenylP₃-5'-deoxygenosyl-5'-amidate, HSQC (D2O)

- Ar-H
- 1'-H
- 2'-H, 3'-H, 4'-H
- 5'-H₂
- 5'-C
- 4'-C
- 3'-C
- 2'-C
- 1'-C
- Ar-C

Na - salt
Compound 81, PhenylP$_3$-5'-deoxyadenosyl-5'-amidate, $^1$H - $^{31}$P - HMBC (D2O)
Compound 81, PhenylP₃-5'-deoxyadenosyl-5'-amidate, $^{13}C\{^1H\}$ - NMR (D2O, 101 MHz)

The diagram shows the NMR spectrum of Compound 81, PhenylP₃-5'-deoxyadenosyl-5'-amidate, along with its chemical structure and the assignments of peaks in the spectrum.

- **A (s):** 155.51 ppm
- **B (s):** 152.79 ppm
- **C (d):** 151.51 ppm
- **D (s):** 148.87 ppm
- **E (s):** 140.21 ppm
- **F (s):** 129.32 ppm
- **G (s):** 123.98 ppm
- **H (d):** 120.27 ppm
- **I (s):** 118.90 ppm
- **J (s):** 87.11 ppm
- **K (d):** 85.44 ppm
- **L (s):** 73.27 ppm
- **M (s):** 70.79 ppm
- **N (s):** 43.14 ppm

The compound is a salt, and the spectrum is recorded in D2O with acetone as the solvent.
Compound 82, PhenylP₃-5'-deoxyguanosyl-5'-amidate, ¹H - NMR (D₂O, 400 MHz)

A (s) 7.83
B (m) 7.08
C (ddt) 6.91
D (d) 5.73
E (dd) 5.17
F (dd) 4.45
G (m) 4.31
H (ddd) 3.38
I (ddd) 3.25

Acetone

Na - salt

82
Compound 82, PhenylP$_3$-5'-deoxyguanosyl-5'-amidate, $^{31}$P {$^1$H} - NMR (D2O, 162 MHz)

$^{31}$P NMR spectrum of Compound 82 shows the following chemical shifts:

- A (d) at -1.59 ppm
- B (d) at -15.76 ppm
- C (dd) at -22.87 ppm

The chemical structure of Compound 82 is shown on the left side of the image.
Compound 82, PhenylP3-5'-deoxyguanosyl-5'-amidate, DQF-COSY (D2O)
Compound 82, PhenylP₃-5'-deoxyguanosyl-5'-amidate, HSQC (D2O)
Compound 82, PhenylP$_3$-5'-deoxyguanosyl-5'-amidate, $^1$H - $^{31}$P - HMBC (D2O)

Na - salt

82
Compound 82, PhenylP₃-5'-deoxyguanosyl-5'-amidate, $^{13}$C($^1$H) - NMR (D₂O, 101 MHz)

***Sidechain***

Na - salt

82

![Compound 82, PhenylP₃-5'-deoxyguanosyl-5'-amidate, $^{13}$C($^1$H) - NMR (D₂O, 101 MHz)](image)
Compound 83, Napht-2-ylP3-5′-deoxyguanosyl-5′-amidate, $^1$H - NMR (D2O, 400 MHz)

decane

$83$

$\text{Na - salt}$

$f_1$ (ppm)

acetone
Compound 83, Napht-2-ylP₃-5’-deoxyguanosyl-5’-amidate, $^{31}P \{^1H\}$ - NMR (D2O, 162 MHz)

Na-salt 83

$\begin{align*}
\text{Na-salt} & \\
\text{83} & \\
\end{align*}$
Compound 83, Napht-2-ylP₃-5′-deoxyguanosyl-5′-amidate, DQF-COSY (D2O)
Compound 83, Napht-2-ylP3-5'-deoxyguanosyl-5'-amidate, HSQC (D2O)

Ar-H
1'-H
2'-H
3'-H
4'-H
5'-H
5'-C
3'-C
2'-C
4'-H
1'-C
Ar-C
acetone

f1 (ppm)
f2 (ppm)

Na - salt
83
Compound 83, Naph-2-y1P₃-5′-deoxyguanosyl-5′-amide, $^1$H - $^{31}$P - HMBC (D2O)
Compound 83, Napht-2-yLP_3-5'-deoxyguanosyl-5'-amidate, $^{13}$C{^1}H_{s}NMR (D2O, 101 MHz)

Acetone

Na - salt

83
Compound 84, PyrenylP₃-5'-deoxyadenosyl-5'-amidate, $^1$H - NMR (D2O, 400 MHz)

Na - salt

pyren-2-yl-product

(= main regioisomer)

84
Compound 84, PyrenylP₃-5'-deoxyadenosyl-5'-amidate, $^{31}$P {$^1$H} - NMR (D2O, 162 MHz)

Na - salt
pyren-2-yl-product
(= main regioisomer)

84
Compound 84, PyrenylP$_3$-5'-deoxyadenosyl-5'-amidate, DQF-COSY (D2O)

Ar-H

5'-H$_2$

2'-H, 3'-H, 4'-H

1'-H

Na - salt

pyren-2-yl-product

(= main regioisomer)

84
Compound 84, PyrenylP$_3$-5'-deoxyadenosyl-5'-amidate, HSQC (D2O)

- Ar-H
- 1'-H
- 3'-H
- 4'-H
- 5'-H
- 1'-C
- 3'-C
- 5'-C
- Ar-C
- acetone

**Structure**

- pyren-2-yl-product (main regioisomer)
- Na - salt

**Chemical Shifts**

- f2 (ppm)
  - 8.5 to 15.0
- f1 (ppm)
  - 2.0 to 150.0

**Legend**

- acetone
Compound 84, PyrenylP₃-5'-deoxyadenosyl-5'-amidate, $^1H - {^{31}P}$ - HMBC (D₂O)

- $Ar-H$
- $1'-H$
- $2'-H$
- $3'-H$
- $4'-H$
- $5'-H$

Na - salt
pyren-2-yl-product
(= main regioisomer)

SI - 210
Compound 84, PyrenylP$_3$-5'-deoxyadenosyl-5'-amidate, $^{13}$C($^1$H) - NMR (D2O, 101 MHz)

acetone

Na - salt

pyren-2-yl-product

(= main regioisomer)

84
Compound 85, Benzo[1,3]dioxol-5-ylP4((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, $^1$H - NMR (D2O, 400 MHz)
Compound 85, Benzo[1,3]dioxol-5-ylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, $^{31}P \{^1H\} - NMR (D2O, 162 MHz)
Compound 85, Benzo[1,3]dioxol-5-ylP$_4$-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, DQF-COSY (D2O)

ArH (7 H)

CH$_2$ (dioxol)

CH$_2$ (benzylic)

2 x CH$_2$

2 x CH$_3$

Na -salt

85
Compound 85, Benzo[1,3]dioxol-5-ylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, HSQC (D2O)

ArH (7 H)  CH₂ (dioxol)  CH₂ (benzylic)  2 x CH₂  2 x CH₃
Compound 85, Benzo[1,3]dioxol-5-ylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, ¹H - ³¹P - HMBC (D2O)

ArH (7 H)  
CH₂(dioxol)  
CH₂(benzylic)  
2 x CH₂  
2 x CH₃

P(b)  
P(c)  
P(a)

Na-salt

85
**Compound 85, Benzo[1,3]dioxol-5-ylP4-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, $^{13}$C{¹H} - NMR (D2O, 101 MHz)**

- **A (s)** 166.19
- **B (d)** 158.12
- **C (s)** 155.16
- **D (s)** 151.02
- **E (s)** 146.98
- **F (d)** 146.27
- **G (s)** 143.09
- **H (s)** 125.03
- **I (d)** 112.67
- **J (s)** 109.95
- **K (s)** 107.82
- **L (s)** 106.89
- **M (s)** 103.25
- **N (d)** 102.57
- **O (s)** 101.36
- **P (s)** 96.95
- **Q (s)** 44.43
- **R (s)** 41.71
- **S (s)** 11.55

**Na-salt 85**
Compound 86, PhenylP₄-propargylamidate, $^1$H - NMR (D2O, 400 MHz)

![NMR spectrum with peaks labeled]

- **A (m)** 7.43
- **B (dq)** 7.30
- **C (m)** 7.23
- **D (dd)** 3.70
- **E (t)** 2.56
- **F (q)** 3.21
- **G (t)** 1.29

**Acetate**

**86**

[Structure of Compound 86]
Compound 86, PhenylP₄-propargylamidate, $^{31}$P {$^1$H} - NMR (D2O, 162 MHz)

TEA - salt

86
Compound 86, PhenylP₄-propargylamidate, $^1H$ - $^{31}P$ - HMBC (D₂O)

**Diagram:**
- The diagram shows a 2D NMR spectrum with peaks at specific chemical shifts.
- The compound structure is depicted with phosphorus atoms and a propargyl group.
- The peaks are labeled with their respective chemical shifts in ppm.

**Annotation:**
- TEA - salt
- 86
Compound 86, PhenylP₄-proparglamidate, $^{13}\text{C}^\{1\text{H}\}$ - NMR (D2O, 101 MHz)

- A (d) 151.73
- B (s) 129.71
- C (s) 124.36
- D (d) 120.65
- E (d) 83.11
- F (s) 71.32
- G (s) 46.64
- H (s) 30.99
- I (s) 8.21

Diagram showing the structure of Compound 86 and the NMR spectrum with chemical shifts for various peaks.
Compound 87, PyrenylP₄-5'-deoxyguanosyl-5'-amidate, ^1^H - NMR (D₂O, 400 MHz)

Na - salt
pyren-2-yl-product
(= main regioisomer)
Compound 87, PyrenylP₄-5'-deoxyguanosyl-5'-amidate, $^{31}\text{P} \{'^1\text{H}'\}$ - NMR (D2O, 162 MHz)

$^{31}\text{P} \{'^1\text{H}'\}$ - NMR spectrum for Compound 87 shows the chemical shifts for different protons.

- $A$ (dd): -22.59 ppm
- $B$ (dd): -21.99 ppm
- $C$ (d): -1.08 ppm
- $D$ (d): -15.45 ppm

$Na$ - salt pyren-2-yl-product
(= main regioisomer)

Formula: 

```
\begin{align*}
\text{N} & - \text{N} \\
\text{O} & - \text{O} \\
\text{H} & - \text{O} \\
\text{N} & - \text{H} \\
\text{O} & - \text{P} \\
\text{O} & - \text{O} \\
\text{O} & - \text{P} \\
\text{O} & - \text{O} \\
\end{align*}
```
Compound 87, PyrenylP-5'-deoxyguanosyl-5'-amidate, DQF-COSY (D2O)

- **f1 (ppm)**: 9.0 to 3.0
- **f2 (ppm)**: 9.0 to 3.0

**Pyren-2-yl-product**
- *(= main regioisomer)*

**Na-salt**

**87**

- Ar-H
- 1'-H
- 2'-H
- 3'-H
- 4'-H
- 5'-H
- 5'-H2
- 4'-H
- 3'-H
- 2'-H
- 1'-H
- Ar-H

**Chemical Structure**

*Diagram showing the molecular structure of Compound 87, highlighting the pyrenyl group and the deoxyguanosyl moiety.*
Compound 87, PyrenylP₄-5'-deoxyguanosyl-5'-amidate, HSQC (D2O)
Compound 87, PyrenylP₄-5'-deoxyguanosyl-5'-amidate, H-MBC (D2O)
Compound 87, PyrenylP₄-5'-deoxyguanosyl-5'-amidate, $^{13}C\{^1H\}$ - NMR (D2O, 101 MHz)

Na - salt
pyren-2-yl-product
(= main regioisomer)

87
Compound 88, PhenylP-5'-deoxyguanosyl-5'-amidate, $^1$H - NMR (D2O, 400 MHz)

A (s) 7.67  B (m) 7.00  C (m) 6.76  D (d) 5.57  E (dd) 4.97  F (dd) 4.32  G (m) 4.13  H (m) 3.14

$^1$H - NMR spectra of Compound 88, PhenylP-5'-deoxyguanosyl-5'-amidate, in D2O at 400 MHz, showing the chemical shifts and coupling constants.
Compound 88, PhenylP₄-5'-deoxyguanosyl-5'-amidate, $^{31}P \{^1H\} - NMR (D2O, 162 MHz)
Compound 88, PhenylP$_4$-5'-deoxyguanosyl-5'-amidate, DQF-COSY (D2O)
Compound 88, PhenylP γ,5'-deoxyguanosyl-5'-amidate, HSQC (D2O)

Ar-H  1'-H  2'-H  3'-H  4'-H  5'-H  5'-H₂

5'-C  3'-C  2'-C  4'-H  1'-C

Ar-C  1'-C
Compound 88, PhenylP₄-5'-deoxyguanosyl-5'-amidate, $^1$H - $^{31}$P - HMBC (D2O)
Compound 88, PhenylP₄-5'-deoxyguanosyl-5'-amidate, $^{31}$P - $^{31}$P - COSY (D2O)
Compound 88, PhenylP<sub>4</sub>-5'-deoxyguanosyl-5'-amidate, $^{13}$C<sup>{1}H</sup> - NMR (D2O, 101 MHz)

Na - salt 88
Compound 89, 3,4-DimethylphenylP<sub>4</sub>-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, <sup>1</sup>H - NMR (D<sub>2</sub>O, 400 MHz)

Na - salt

89

acetone
Compound 89, 3,4-DimethylphenylP$_7$: (7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, $^{31}$P $^1$H - NMR (D$_2$O, 162 MHz)

Na - salt

89
Compound 89, 3,4-DimethylphenylP-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, $^1$H - $^{31}$P - HMBC (D2O)
Compound 89, 3,4-DimethylphenylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate, $^{13}$C{\textit{H}} - NMR (D2O, 101 MHz)

\[\text{acetone} \]

\[\text{Na - salt} \]
Compound 90, PhenylP$_5$-propargylamidate, $^1$H - NMR (D2O, 400 MHz)

$$\text{Na - salt}$$

90

B (m) 7.30
A (m) 7.43
C (m) 7.23
D (dd) 3.73
E (td) 2.57

acetone
Compound 90, PhenylP₅-propargylamide, $^{31}P\{^1H\}$ - NMR (D2O, 162 MHz)

Na-salt 90

$$\text{PhenylP}_5\text{-propargylamide}$$
Compound 90, PhenylP₅-propargylamidate, ¹H - ³¹P - HMBC (D₂O)

Na - salt

90
Compound 90, PhenylP$_5$-propargylamidate, $^{13}$C($^1$H) - NMR (D$_2$O, 101 MHz)

Na - salt

90

A (d) 151.70
B (s) 129.71
C (d) 124.39
D (d) 120.68
G (s) 68.14
F (s) 30.95
Compound 91, PhenylP\(_7\)-propargylamidate, \(^1\)H - NMR (D2O, 400 MHz)

![NMR Spectrum](image)

- **A (m)**: 7.47 ppm
- **B (m)**: 7.33 ppm
- **C (m)**: 7.28 ppm
- **D (dd)**: 3.76 ppm
- **E (t)**: 2.64 ppm

**Na-salt 91**

![Chemical Structure](chemical_structure)
Compound 91, PhenylP-propargylamidate, $^{31}P \{^1H\}$ - NMR (D2O, 162 MHz)

Na - salt

91
Compound 91, PhenylP₇-propargylamidate, ^1^H - ^3^1P - HMBC (D2O) 

- P(f)
- P(b-e)
- P(g)
- P(a)
Compound 91, PhenylP7-propargylamidate, PP-COSY (D2O)
Compound 91, PhenylP7-propargylamidate, $^{13}$C{H} - NMR (D2O, 101 MHz)

Na-salt

91

A (d) 151.66
B (s) 129.80
C (s) 124.56
D (d) 120.67
E (d) 83.09
F (s) 71.49
H (s) 30.30

acetone
Compound 92, PhenylP$_5$-propargylamidate, $^1$H - NMR (D2O, 400 MHz)

- **A (m)**: 7.43 ppm
- **B (dq)**: 7.30 ppm
- **C (m)**: 7.24 ppm
- **D (dd)**: 3.73 ppm
- **E (t)**: 2.60 ppm

Na - salt

92
Compound 92, PhenylP\textsubscript{8}-propargylamidate,\textsuperscript{31}P {\textsuperscript{1}H} - NMR (D2O, 162 MHz)

Na - salt

92
Compound 92, PhenylP₈-propargylamidate, "H - ³¹P - HMBC (D2O)
Compound 92, PhenylP$_8$-propargylamidate, PP-COSY (D2O)
Compound 92, Phenyl₆-propargylamide, ¹³C{¹H} - NMR (D₂O, 101 MHz)

Na - salt

acetone

acetone
Compound SI-5, D4T-monophosphate, $^1H$ - NMR ($D_2O$, 400 MHz)

Mixed piperidinium / TBA - salt

SI-5
Compound SI-5, D4T-monophosphate, $^{31}P\{^1H\}$ - NMR (D2O, 162 MHz)

mixed piperidinium / TBA - salt

SI-5
Compound SI-5, D4T-monophosphate, $^{31}$P - NMR (D2O, 162 MHz)

SI-5

mixed piperidinium / TBA - salt

$^{31}P$-NMR spectrum of Compound SI-5, D4T-monophosphate (D2O, 162 MHz). The peak at 0.41 ppm is labeled A(t).
Compound SI-5, D4T-monophosphate, $^{13}$C($^1$H) - NMR (D2O, 101 MHz)

mixed piperidinium / TBA - salt

SI-5

A (s) 166.75  B (s) 152.26  C (s) 138.26  D (s) 134.23  
E (s) 125.21  F (s) 111.36  G (s) 89.95  H (d) 86.00  
I (d) 65.46  J (s) 11.42
Compound SI-13, Hydroxyhexylphosphate, $^1$H - NMR (D$_2$O, 400 MHz)

SI-13

$2\text{NH}_4^+$
Compound SI-13, Hydroxyhexylphosphate, $^{31}$P (H) - NMR (D2O, 162 MHz)

SI-13
Compound SI-13, Hydroxyhexylphosphate, $^{31}\text{P} - \text{NMR (D2O, 162 MHz)}$

$\text{SI-13}$

\[
\text{HO-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \quad 2\text{NH}_4^+ \quad \text{P-O-P-O} \quad \text{A (t) 1.34}
\]
Compound SI-13, Hydroxyhexylphosphate, $^{13}\text{C} - \text{NMR (D}_2\text{O, 101 MHz)}$

SI-13

\[
\text{HO-} - \text{C-C-C-C-C-C-C-} \text{O-P-} \text{O}^- \text{O}^- 2 \text{NH}_4^+
\]

\[
\begin{align*}
\text{A (d)} & \quad 65.48 \\
\text{B (s)} & \quad 61.72 \\
\text{C (s)} & \quad 31.15 \\
\text{D (s)} & \quad 24.68 \\
\text{E (d)} & \quad 29.83 \\
\text{F (s)} & \quad 24.66
\end{align*}
\]
Compound SI-14, Geranylphosphate, $^1$H - NMR ($D_2$O, 400 MHz)

TBA - salt

SI-14
Compound SI-14, Geranylphosphate, $^{31}P{(^1H)}$ - NMR (D2O, 162 MHz)

TBA - salt

SI-14
Compound SI-14, Geranylphosphate, $^{13}C{^1H}$ - NMR (D2O, 101 MHz)

TBA - salt

SI-14
Compound SI-15, Isoprenylphosphate, $^1H$ - NMR ($D_2O$, 400 MHz)
Compound SI-15, Isoprenylphosphate, $^{31}\text{P}^{'\text{H}}$ - NMR (D2O, 162 MHz)

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_2\text{C} \quad \text{O} \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{O} & \quad \text{PO}_3^- \\
\end{align*}
\]

piperidinium/TEAA salt

SI-15

A (s) 0.49
Compound SI-15, Isoprenylphosphate, $^{31}$P - NMR (D2O, 162 MHz)

SI-15

$$\text{piperidinium/TEAA salt}$$
Compound SI-15, Isoprenylphosphate, $^{13}\text{C}[^1\text{H}]$ - NMR (D2O, 101 MHz)

$^{13}\text{C}[^1\text{H}]$ NMR spectrum of SI-15 in D2O at 101 MHz shows chemical shifts for various carbon nuclei.

- A (s) 143.62 ppm
- B (s) 111.52 ppm
- C (d) 63.71 ppm
- D (d) 37.92 ppm
- E (s) 44.51 ppm
- F (s) 22.18 ppm
- G (s) 21.45 ppm
- H (s) 21.55 ppm
- I (s) 27.12 ppm
- J (s) 14.47 ppm

The compound is a piperidinium/TEA salt.
Compound SI-16, Phenyldiphosphate, $^1H$ - NMR ($D_2O$, 400 MHz)

SI-16
Compound SI-16, Phenyldiphosphate, $^{31}P{^1}H$ - NMR (D2O, 162 MHz)

\[ \text{SI-16, Phenyldiphosphate, } ^{31}P{^1}H \text{ - NMR (D2O, 162 MHz)} \]

- **B (d)**: -10.80 ppm
- **A (d)**: -15.71 ppm

**SI-16 (piperidinium salt)**

\[ \text{SI-16 (piperidinium salt)} \]
Compound SI-16, Phenylidiphosphosphate, $^{13}$C{H} - NMR (D2O, 101 MHz)

SI-16 piperidinium salt
Compound SI-17, D4T-diphosphate, $^1H$ - NMR ($D_2O$, 400 MHz)

$TEA$ - salt

SI-17
Compound SI-17, D4T-diphosphate, $^{31}\text{P}^{1\text{H}}$ - NMR (D2O, 162 MHz)

SI-17

$\text{TEA - salt}$

$f_1$ (ppm)
Compound SI-17, D4T-diphosphate, $^{31}$P - NMR (D2O, 162 MHz)

$\text{SI-17}$

$\text{TEA - salt}$

$\text{f1 (ppm)}$
Compound SI-17, D4T-diphosphate, $^{13}\text{C}^1(\text{H})$ - NMR (D2O, 101 MHz)

TEA - salt

SI-17

$\text{f}_1$ (ppm)

A (s) 166.77
B (s) 152.26
C (s) 138.18
D (s) 134.33
E (s) 125.10
F (s) 111.52
G (s) 89.95
H (d) 85.97
I (d) 66.27
J (s) 46.63
K (s) 8.19
L (s) 11.43

acetate

acetate
Compound SI-19, 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate, $^1$H - NMR (CDCl$_3$, 400 MHz)
Compound SI-19, 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate, $^{19}$F - NMR (CDCl$_3$, 377 MHz)
Compound SI-19, 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate, $^{13}$C - NMR (CDCl$_3$, 101 MHz)
Compound SI-21, 4-(trimethylsilyl)ethynyl)phenyl isopropylcarbamate, $^1$H - NMR (CDCl$_3$, 400 MHz)
Compound SI-21, 4-(trimethylsilyl)ethynyl)phenyl isopropylcarbamate, $^{13}$C - NMR (CDCl$_3$, 101 MHz)
Compound SI-22, 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl isopropylcarbamate, \(^1\)H - NMR (CDCl\(_3\), 400 MHz)
Compound SI-22, 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl isopropylcarbamate, $^{13}$C - NMR (CDCl$_3$, 101 MHz)
Compound SI-23, 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate, $^1$H - NMR (CDCl$_3$, 400 MHz)
Compound SI-23, 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate, $^{19}\text{F} - \text{NMR} (\text{CDCl}_3, 377 \text{ MHz})$

A (s)
-73.83
Compound SI-23, 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate, $^{13}$C - NMR (CDCl$_3$, 101 MHz)
Compound SI-25, 2-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl)isoindoline-1,3-dione, $^1$H - NMR (D$_2$O, 400 MHz)

SI-25
Compound SI-25, 2-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl)isoindoline-1,3-dione, $^{13}$C/$^1$H - NMR (D2O, 101 MHz)
Compound SI-26, 4-(aminomethyl)-7-(diethylamino)-2H-chromen-2-one, $^1$H - NMR (D$_2$O, 400 MHz)
Compound SI-26, 4-(aminomethyl)-7-(diethylamino)-2H-chromen-2-one, $^{13}$C{[$^1$H]} - NMR (D2O, 101 MHz)

SI-26

A (s) 162.64
B (s) 156.73
C (s) 156.37
D (s) 150.60
E (s) 124.52
F (s) 108.63
G (s) 107.23
H (s) 105.81
I (s) 98.00
J (s) 44.87
K (s) 42.40
L (s) 12.59
13. MS – spectra

(aligned according to molecule numbering)
HRMS (ESI) Analysis of compound 27: phenyl phosphate
HRMS (APCI) Analysis of compound 28: 2-naphthalen-2-yl phosphate
HRMS (APCI) Analysis of compound 29: 3,4-dimethylphenyl phosphate

Formula: C₉H₁₀O₄P
Mass: 201.0322
HRMS (ESI) Analysis of compound 30: 1H-indol-5-yl phosphate
HRMS (ESI) Analysis of compound 31: pyren-2-yl phosphate

**31**

Formula: C_{16}H_{10}O_4P^-

Mass: 297.0322

297.0320
C_{16}H_{10}O_4P = 297.0322
-0.7951 ppm

217.0659
C_{16}H_9O = 217.0659
-0.0038 ppm

360.3119
HRMS (ESI) Analysis of compound 32: phenyl diphosphate

252.9675
C₆H₇O₇P₂ = 252.9672
0.9278 ppm

263.9520

Structure:

32
Formula: C₆H₇O₇P₂⁻
Mass: 252.9672
HRMS (ESI) Analysis of compound 33: 2-naphthalen-2-yl diphosphate

Formula: C_{10}H_{9}O_{7}P_{2}^{2-}
Mass: 302.9829

m/z 302.9830
C_{10}H_{9}O_{7}P_{2} = 302.9829
0.4401 ppm

m/z 303.9863

33

Relative Abundance

m/z 302.9830

RT: 0.02
AV: 1
NL: 1.23E8
T: FTMS - p ESI Full ms [80.00-1000.00]
HRMS (ESI) Analysis of compound 34: 3,4-dimethylphenyl diphosphate

280.9987
C₈H₁₁O₇P₂ = 280.9985
0.6026 ppm

Formula: C₈H₁₁O₇P₂⁻
Mass: 280.9985
HRMS (ESI) Analysis of compound 35: 1H-indol-5-yl diphosphate
HRMS (ESI) Analysis of compound 36: pyren-2-yl diphosphate

Formula: C_{16}H_{11}O_7P_2^-
Mass: 376.9985
HRMS (ESI) Analysis of compound 37: deutero-phenylphosphate

\[
\text{Ratio (27 : 38) = 57\% : 43\%}
\]
HRMS (ESI) Analysis of compound 38: 5,5,5-trifluoropentyl phosphate
HRMS (ESI) Analysis of compound 40: phenyl (5,5,5-trifluoropentyl) phosphate
HRMS (ESI) Analysis of compound 41: 3,4-dimethylphenyl (5,5,5-trifluoropentyl) phosphate
HRMS (ESI) Analysis of compound 42: 2,5-dimethylphenyl (5,5,5-trifluoropentyl) phosphate

Formula: C₁₃H₁₇O₄F₃P
Mass: 325.08
HRMS (ESI) Analysis of compound 43: 3,4-dimethoxyphenyl (5,5,5-trifluoropentyl) phosphate

Formula: C₁₃H₁₇O₆F₃P
Mass: 357.0720
**HRMS (ESI) Analysis of compound 44: 4-(trifluoromethyl)phenyl (5,5,5-trifluoropentyl) phosphate**

- **RT:** 0.02
- **AV:** 1
- **NL:** 5.03E8

**Formula:** C_{12}H_{17}O_{4}F_{3}P = 365.0383

-0.6368 ppm

**Mass:** 365.0383

**Chart:**
- m/z values:
  - 365.0381
  - 277.0822
  - 731.0844
  - 972.3614

- Relative Abundance

- **SI - 306**
HRMS (ESI) Analysis of compound 45: benzo[d][1,3]dioxol-5-yl (5,5,5-trifluoropentyl) phosphate

[Diagram showing the molecular structure of compound 45 and its molecular formula: C_{12}H_{13}O_{6}F_{3}P = 341.0407, -1.4069 ppm.]

[Graph showing mass spectrum with m/z values and relative abundance.]
HRMS (ESI) Analysis of compound 46: 4-ethynylphenyl (5,5,5-trifluoropentyl) phosphate

Formula: C_{13}H_{13}O_{4}F_{3}P
Mass: 321.0509

C_{13}H_{13}O_{4}F_{3}P = 321.0509
-0.7603 ppm

C_{6}H_{4}O_{3}P = 154.9904
1.6906 ppm

C_{14}H_{14}O_{4}P = 277.0635
-0.2623 ppm

884.3865

154.9906
HRMS (ESI) Analysis of compound 47: 3-bromophenyl (5,5,5-trifluoropentyl) phosphate
HRMS (ESI) Analysis of compound 48:4-chlorophenyl (5,5,5-trifluoropentyl) phosphate

Formula: C_{11}H_{12}ClF_{3}O_{4}P
Mass: 331.0119

m/z 331.0119
C_{11}H_{12}O_{4}ClF_{3}P = 331.0119
0.0043 ppm

904.3088
HRMS (ESI) Analysis of compound 49, naphthalen-2-yl (5,5,5-trifluoropentyl) phosphate

Formula: C_{15}H_{15}O_{4}F_{3}P
Mass: 347.0666
**HRMS (ESI) Analysis of compound 50: 1H-indol-5-yl (5,5,5-trifluoropentyl) phosphate**

Formula: C_{13}H_{14}F_{3}NO_{4}P^-

Mass: 336.0618

m/z 336.0617
C_{13}H_{14}F_{3}O_{4}N P = 336.0618
-0.2850 ppm

m/z 212.0119
C_{8}H_{7}O_{4}N P = 212.0118
0.5418 ppm
HRMS (ESI) Analysis of compound 51: pyren-2-yl (5,5,5-trifluoropentyl) phosphate

Formula: C_{21}H_{17}O_{4}F_{3}P
Mass: 421.0822

421.0819
C_{21}H_{17}O_{4}F_{3}P = 421.0822
-0.6263 ppm

1084.4485
HRMS (ESI) Analysis of compound 52: Diphenylphosphate

Formula: C₁₂H₁₀O₄P
Mass: 249.0322
HRMS (ESI) Analysis of compound 53: Pentyl-phenylphosphate

Formula: C_{11}H_{16}O_4P
Mass: 243.0792
HRMS (ESI) Analysis of compound 54: Phenyl-phenylphosphonate

Formula: C₁₂H₁₀O₃P⁻
Mass: 233.0373

C₁₂H₁₀O₃P = 233.0373
0.0160 ppm
HRMS (ESI) Analysis of compound 55: Pent-4-yn-1-yl-phenylphosphate

Formula: C_{11}H_{12}O_{4}P
Mass: 239.0479
HRMS (ESI) Analysis of compound 56: Isoprenol-phenylphosphate

Formula: C_{11}H_{14}O_{4}P
Mass: 241.06
HRMS (ESI) Analysis of compound 57: Geranyl-phenylphosphate

Formula: C_{16}H_{22}O_{4}P^-
Mass: 309,1261

309.1266
C_{16}H_{22}O_{4}P = 309.1261
1.5138 ppm
HRMS (ESI) Analysis of compound 58: D4T-phenylpyrophosphate
HRMS (ESI) Analysis of compound 59: D4T-phenylphosphate

Formula: C_{16}H_{16}N_{2}O_{7}P
Mass: 379.07
HRMS (ESI) Analysis of compound 60: D4T-phenylpyrophosphate

Formula: C_{18}H_{17}N_{2}O_{5}P_{2}
Mass: 459.04
HRMS (ESI) Analysis of compound 61: Diphenylpyrophosphate

Formula: C_{12}H_{11}O_{7}P_{2}^-
Mass: 328.9985
HRMS (ESI) Analysis of compound 67: Pentylphosphate

Formula: C₁₅H₂₄O₄P
Mass: 167.05
HRMS (ESI) Analysis of compound 70: Pentametaphosphate
HRMS (ESI) Analysis of compound 71: Heptametaphosphate

Formula: $H_2O_7P_7^-$
Mass: 558.76
HRMS (ESI) Analysis of compound 72: Octametaphosphate
HRMS (ESI) Analysis of compound 73: Phenylcyclotriphosphate
HRMS (ESI) Analysis of compound 74: Phenylcyclotetraphosphate

Formula: $C_6H_7O_{12}P_4^-$
Mass: 394.89
HRMS (ESI) Analysis of compound 78: PhenylP₃-propargylamidate

Formula: C₉H₁₁NO₇P₃⁻
Mass: 369.9652
**HRMS (ESI) Analysis of compound 79: PhenylP₃-amidate**

Formula: C₂H₁₀O₇N₃P₃⁻
Mass: 331,9496
HRMS (ESI) Analysis of compound 80: PhenylP₃-anthracen-9-ylmethanamidate

Formula: C₂₁H₁₈NO₉P₃²⁻
Mass: 521.0205
m/z: 260.5102
HRMS (ESI) Analysis of compound 81: PhenylP₃-5’-deoxyadenosyl-5’-amidate

Formula: C₁₆H₂₀N₆O₁₂P₃⁻
Mass: 581,0358
HRMS (ESI) Analysis of compound 82: PhenylP$_3$-5'-deoxyguanosyl-5'-amidate

Formula: C$_{16}$H$_{20}$N$_6$O$_{13}$P$_3^-$
Mass: 597.0307
HRMS (ESI) Analysis of compound 83: Napht-2-ylP₃-5’-deoxyguanosyl-5’-amidate

**Formula:** C₂₀H₁₂N₁₃O₁₃P₃⁻

**Mass:** 669.0283
HRMS (ESI) Analysis of compound 84: Pyren-2-ylP3-5’-deoxyadenosyl-5’-amidate
**HRMS (ESI) Analysis of compound 85: Benzo[1,3]dioxol-5-ylP$_3$-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methylamidate**

**Formula:** C$_{21}$H$_{24}$N$_2$O$_{13}$P$_3^-$

**Mass:** 605.0497
HRMS (ESI) Analysis of compound 86: PhenylP₄-propargylamidate

Formula: C₉H₁₁NO₁₂P₄²⁻
Mass: 448.9243
m/z: 224.4621
**HRMS (ESI) Analysis of compound 87: Pyren-2-ylP$_4$-5’-deoxyguanosyl-5’-amidate**

- **Formula:** $C_{26}H_{23}O_{16}N_{6}P_{4}^z$
- **Mass:** 799.0137
- **m/z:** 266.3379

The diagram shows the mass spectrum with peaks at various m/z values, indicating the presence of different isotopes of the compound 87. The peaks are labeled with their corresponding masses and charge states (z). The compound is characterized by its molecular formula and mass, which are critical for identifying and analyzing its structure.
HRMS (ESI) Analysis of compound 88: PhenylP4-5’-deoxyguanosyl-5’-amidate

Formula: C16H19N6O16P4+^z=
Mass: 674.9824
m/z: 224.9941
HRMS (ESI) Analysis of compound 89: 3,4-DimethylphenylP₄-(7-(diethylamino)-2-oxo-2H-chromen-4-yl) methylamidate

**Formula:** C$_{22}$H$_{23}$N$_{2}$O$_{4}$P$_{4}$

**Mass:** 669.0575
HRMS (ESI) Analysis of compound 90: PhenylP₅-propargylamidate

The sample was stored in D₂O (for NMR) one day before HRMS-measurement. This led to a partial H/D-scrambling of the acetylenic proton.
HRMS (ESI) Analysis of compound 91: PhenylPγ-propargylamidate
HRMS (ESI) Analysis of compound 92: PhenylP₈-propargylamidate

Formula: C₉H₁₆NO₃P₈²⁻
Mass: 768.7896
m/z: 384.3948
HRMS (ESI) Analysis of compound SI-5: D4T - monophosphate
HRMS (ESI) Analysis of compound SI-13: 6-Hydroxyhexylphosphate
HRMS (ESI) Analysis of compound SI-14: Geranylmonophosphate

Formula: C_{10}H_{18}O_4P
Mass: 233.09
HRMS (ESI) Analysis of compound SI-15: Isoprenylmonophosphate

Formula: C_{10}H_{16}O_4P
Mass: 165.03
HRMS (ESI) Analysis of compound SI-16: phenyldiphosphate

SI-16
Formula: C6H7O7P2
Mass: 252.97
HRMS (ESI) Analysis of compound SI-17: D4T - diphosphate

Formula: C_{10}H_{12}N_{2}O_{7}P_{2}^-
Mass: 383.0051
HRMS (APCI) Analysis of compound SI-19: 2-(trimethylsilyl)pyren-1-yl trifluoromethanesulfonate
HRMS (ESI) Analysis of compound SI-21: 4-(trimethylsilyl)ethynyl)phenyl isopropylcarbamate

SI-21
Formula: C_{15}H_{22}NO_{3}Si
Mass: 275,1342

TMS\(\text{CH}_{3}\text{SiN}_2\)
HRMS (ESI) Analysis of compound SI-22: 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl isopropylcarbamate

SI-22

Formula: C_{18}H_{30}NO_{2}Si_{2}

Mass: 347.1737

m/z

Relative Abundance

348.1808
C_{18}H_{30}O_{2}N Si_{2} = 348.1810
-0.3203 ppm

263.1282
C_{14}H_{23}O Si_{2} = 263.1282
-0.0800 ppm

712.3809
466.2228

216.0838
C_{12}H_{14}O N Si = 216.0839
-0.4655 ppm

381.1699
623.3148
483.2492
623.3148
712.3809
HRMS (APCI) Analysis of compound SI-23: 2-(trimethylsilyl)-4-((trimethylsilyl)ethynyl)phenyl trifluoromethanesulfonate

Analysis Report

Sample Spectra

Spectrum Peaks

| m/z | Absent | % | m/z (Calc) | Diff (ppm) | Ion Species | Formula | Ion Type |
|-----|--------|---|------------|------------|-------------|---------|----------|
| 395.0775 | 1 | 100.00 | 395.0775 | 0.09 | (M+H)+ | C_{15}H_{21}F_{3}O_{3}S | C15H21F3O3SSi2 |
| 412.041 | 1 | 100.00 | 412.0409 | 0.07 | (M+H)+ | C_{15}H_{21}F_{3}O_{3}S | C15H21F3O3SSi2 |

Spectrum Identification Table

| No. | Name | Formula | Species | m/z | Diff (ppm) | CAS Score | Score (LIB) | Score (DB) | Score (MPG) | Lib/DB |
|-----|------|---------|---------|-----|------------|------------|-------------|-------------|-------------|--------|
| No. 104 | MFG | C_{15}H_{21}F_{3}O_{3}S | (M+H)+ | 395.0775 | 0.09 | 56.82 | 56.82 | 56.82 |
| No. 105 | MFG | C_{15}H_{21}F_{3}O_{3}S | (M+H)+ | 412.041 | 0.07 | 56.82 | 56.82 | 56.82 |

Macromaker Qual 13.0
(End of Report)
HRMS (ESI) Analysis of compound SI-25: 2-((7-(diethylamino)-2-oxo-2H-chromen-4-yl)methyl)isoindoline-1,3-dione
HRMS (ESI) Analysis of compound SI-26: 4-(aminomethyl)-7-(diethylamino)-2H-chromen-2-one (Amino-DEACM)
14. Structure Tables (X-ray data)

Crystals were obtained from a solvent mixture of dichloromethane and chloroform in which the compound was dissolved at 40 °C. The solution was first cooled down to room temperature, and slow evaporation of the solvent caused the formation of crystals. The data for Jessen_WS_47_a were collected from a shock-cooled single crystal at 100(2) K on a Bruker SMART APEX2 QUAZAR three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker APEXII detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoKα radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.[1,2] The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3.[3,4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[5] CCDC 2062089 contain 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/structures. This report and the CIF file were generated using FinalCif.[6]

Table 1. Crystal data and structure refinement for Jessen_WS_47_a

| Property                          | Value                   |
|----------------------------------|-------------------------|
| CCDC number                      | 2062089                 |
| Empirical formula                | CaH1.5F4Os5Si           |
| Formula weight                   | 422.48                  |
| Temperature [K]                  | 100(2)                  |
| Crystal system                   | monoclinic              |
| Space group (number)             | P2₁/n (14)              |
| a [Å]                            | 8.9023(7)               |
| b [Å]                            | 16.4839(12)             |
| c [Å]                            | 13.5475(10)             |
| α [°]                            | 90                      |
| β [°]                            | 107.9570(10)            |
| γ [°]                            | 90                      |
| Volume [Å³]                      | 1891.2(2)               |
| Z                                | 4                       |
| ρcalc [gcm⁻³]                    | 1.484                   |
| μ [mm⁻¹]                         | 0.282                   |
| F(000)                           | 872                     |
| Crystal size [mm³]               | 0.170×0.150×0.100       |
| Crystal colour                   | colourless              |
| Crystal shape                    | block                   |
| Radiation                        | MoKα (λ=0.71073 Å)      |
| 2θ range [°]                     | 4.01 to 55.11 (0.77 Å)  |
| Index ranges                     | -11 ≤ h ≤ 11            |
|                                | -21 ≤ k ≤ 21            |
|                                | -17 ≤ l ≤ 17            |
| Reflections collected            | 39111                   |
| Independent reflections          | 4368                    |
| Rint                             | 0.0298                  |
| Rwork                            | 0.0160                  |
| Completeness to θ = 25.242°     | 99.9 %                  |
| Data / Restraints / Parameters   | 4368/0/256              |
| Goodness-of-fit on F²            | 1.062                   |
| Final R indexes                  | R₁ = 0.0290             |
|                                | wR₂ = 0.0780            |
| Final R indexes [all data]       | R₁ = 0.0341             |
|                                | wR₂ = 0.0814            |
| Largest peak/hole [eÅ⁻³]         | 0.47/-0.37              |
Table 2. Atomic coordinates and $U_{eq}$ [Å$^2$] for Jessen_WS_47_a

| Atom | x     | y     | z     | $U_{eq}$ |
|------|-------|-------|-------|----------|
| S1   | 0.30474(4) | 0.35973(2) | 0.81748(2) | 0.01550(9) |
| S1   | 0.29667(4) | 0.17974(2) | 0.61769(3) | 0.01555(9) |
| F1   | 0.06123(11) | 0.30635(6) | 0.86700(7) | 0.0295(2) |
| F2   | 0.22234(11) | 0.38224(6) | 0.98151(7) | 0.0311(2) |
| F3   | 0.06171(11) | 0.43591(6) | 0.84399(7) | 0.0285(2) |
| O1   | 0.18751(11) | 0.34506(6) | 0.70625(7) | 0.01582(19) |
| O2   | 0.38573(12) | 0.43478(6) | 0.82526(8) | 0.0215(2) |
| O3   | 0.38844(12) | 0.28781(6) | 0.85899(8) | 0.0230(2) |
| C1   | 0.24254(15) | 0.35737(8) | 0.61689(10) | 0.0144(3) |
| C2   | 0.29429(15) | 0.28991(8) | 0.57493(10) | 0.0152(3) |
| C3   | 0.34438(15) | 0.30589(8) | 0.48816(10) | 0.0163(3) |
| C4   | 0.242691 | 0.481374 | 0.256218 | 0.023 |
| C5   | 0.32021(15) | 0.54065(8) | 0.35500(10) | 0.0169(3) |
| C6   | 0.26746(14) | 0.52759(8) | 0.44499(10) | 0.0150(3) |
| C7   | 0.27939(14) | 0.44887(8) | 0.57686(10) | 0.0178(3) |
| C8   | 0.39467(15) | 0.39853(9) | 0.328064 | 0.021 |
| C9   | 0.38552(15) | 0.47321(9) | 0.31410(11) | 0.0188(3) |
| C10  | 0.328620 | 0.216986 | 0.457278 | 0.020 |
| C11  | 0.34077(15) | 0.38317(8) | 0.44499(10) | 0.0150(3) |
| C12  | 0.39467(15) | 0.39853(9) | 0.328064 | 0.021 |
| C13  | 0.32021(15) | 0.54065(8) | 0.35500(10) | 0.0169(3) |
| C14  | 0.26746(14) | 0.52759(8) | 0.44499(10) | 0.0150(3) |
| C15  | 0.27939(14) | 0.44887(8) | 0.57686(10) | 0.0178(3) |
| C16  | 0.39467(15) | 0.39853(9) | 0.328064 | 0.021 |
| C17  | 0.38552(15) | 0.47321(9) | 0.31410(11) | 0.0188(3) |
| U eq is defined as 1/3 of the trace of the orthogonalized $U_{ij}$ tensor. |

Table 3. Bond lengths and angles for Jessen_WS_47_a

| Atom–Atom | Length [Å] | S1–O3 | S1–O1 |
|-----------|-----------|-------|-------|
| S1–O2     | 1.4206(10) |       |       |
| S1–O3     |           | 1.4208(10) |   |
| S1–O1     |           | 1.5648(10) |   |
| Atom–Atom–Atom–Atom | Torsion Angle [°] | C2–C1–C10–C9 | -3.7(2) |
|----------------------|-------------------|----------------|---------|
| O2–S1–O1–C1         | 48.43(11)         | O1–C1–C10–C9  | -179.13(10) |
| O3–S1–O1–C1         | -89.94(10)        | C2–C1–C10–C11 | 174.50(12) |
| C20–S1–O1–C1        | 160.08(10)        | O1–C1–C10–C11 | -0.95(18) |
| S1–O1–C1–C2         | 96.23(12)         | C4–C9–C10–C1  | 0.32(18)  |
| S1–O1–C1–C10        | -87.93(12)        | C8–C9–C10–C1  | 179.57(11) |
| C10–C1–C2–C3        | 4.0(2)            | C4–C9–C10–C11 | -177.97(11) |
| O1–C1–C2–C3         | 179.40(11)        | C8–C9–C10–C11 | 1.28(18)  |
| C10–C1–C2–Si1       | -173.22(10)       | C1–C10–C11–C12 | -178.78(12) |
| O1–C1–C2–Si1        | 2.16(18)          | C9–C10–C11–C12 | -0.64(19) |
| C1–C2–C3–C4         | -1.08(19)         | C10–C11–C12–C13 | -0.4(2)  |
| Si1–C2–C3–C4        | 176.47(10)        | C7–C8–C13–C14 | 0.53(19)  |
| C2–C3–C4–C9         | -1.9(2)           | C9–C8–C13–C14 | -179.30(12) |
| C2–C3–C4–C5         | 179.13(12)        | C7–C8–C13–C12 | 179.62(12) |
| C3–C4–C5–C6         | 177.83(13)        | C9–C8–C13–C12 | -0.21(18) |
| C9–C4–C5–C6         | -1.16(19)         | C11–C12–C13–C14 | 179.92(13) |
| C4–C5–C6–C7         | -0.4(2)           | C11–C12–C13–C8 | 0.9(2)   |
| C5–C6–C7–C16        | -178.84(13)       | C8–C13–C14–C15 | -0.4(2)  |
| C5–C6–C7–C8         | 1.0(2)            | C12–C13–C14–C15 | -179.46(13) |
| C16–C7–C8–C13       | -0.08(19)         | C13–C14–C15–C16 | -0.2(2)  |
| C6–C7–C8–C13        | -179.90(12)       | C14–C15–C16–C7 | 0.7(2)   |
| C16–C7–C8–C9        | 179.75(12)        | C8–C7–C16–C15 | -0.5(2)  |
| C6–C7–C8–C9         | -0.07(18)         | C6–C7–C16–C15 | 179.29(13) |
| C3–C4–C9–C10        | 2.25(19)          | O2–S1–C20–F3  | 52.21(12) |
| C5–C4–C9–C10        | -178.72(11)       | O3–S1–C20–F3  | -177.44(10) |
| C3–C4–C9–C8         | -176.99(12)       | O1–S1–C20–F3  | -63.24(11) |
| C5–C4–C9–C8         | 2.03(18)          | O2–S1–C20–F1  | 173.81(10) |
| C7–C8–C9–C4         | -1.44(18)         | O3–S1–C20–F1  | -55.84(11) |
| C13–C8–C9–C4        | 178.39(11)        | O1–S1–C20–F1  | 58.36(11) |
| C7–C8–C9–C10        | 179.32(12)        | O2–S1–C20–F2  | -67.20(11) |
| C13–C8–C9–C10       | -0.85(18)         | O3–S1–C20–F2  | 63.16(11) |
|                     |                   | O1–S1–C20–F2  | 177.35(10) |

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