Electronic Supplementary Information

Spacer-Tuned Diphosphine Dioxides as Preorganised Co-Ligands for Synergistic Lithium Extraction with β-Diketonates

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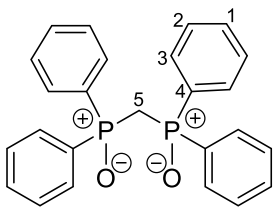
1 General remarks

All manipulations were performed with HPLC grade, analytical grade or technical grade reagents and solvents, which were used without further purification. The starting materials used were purchased from SIGMA-ALDRICH, FLUKA, MERCK, VWR, TCI, ABCR CHEMICALS, ACROS, CARL ROTH or WAKO. Manipulations under dry and oxygen-free conditions were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified nitrogen. Dry, oxygen-free solvents (CH_2Cl_2, CH_3CN (distilled from CaH_2), n-pentane, Et_2O (distilled from potassium)) were employed. Anhydrous deuterated acetonitrile (CD_3CN), dichloromethane (CD_2Cl_2), chloroform ($CDCl_3$) and methanol (CD_3OD) were purchased from Sigma-Aldrich, Deutero or Eurisotop. All distilled and deuterated solvents were stored over molecular sieves (4 Å: CH_2Cl_2, CD_2Cl_2, C_6D_6, n-hexane, Et_2O; 3 Å: CH_3CN, CD_3CN). All glassware was oven-dried at 160 °C prior to use. NMR spectra were measured on a Bruker AVANCE III HD Nanobay, 400 MHz UltraShield (^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{31}P (161.98 MHz), ^7Li (155.51 MHz)) or on a Bruker AVANCE III HDX, 500 MHz Ascend (^1H (500.13 MHz), ^{13}C (125.75 MHz), ^{31}P (202.45 MHz), ^7Li (194.37 MHz)). All ^{13}C NMR spectra were exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the ^{13}C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to the respective solvent to $\delta = 7.26$ ppm (^1H), 77.16 ppm (^{13}C) for $CDCl_3$, $\delta = 5.32$ ppm (^1H), 53.84 ppm (^{13}C) for CD_2Cl_2, $\delta = 1.94$ ppm (^1H), and δH_3PO_4 (85%) = 0.00 ppm (^{31}P, externally). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries (under nitrogen atmosphere for air or moisture sensitive compounds) and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on a Vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS modus. For the mass spectrometry experiments a Waters ACQUITY UPLC H-Class system in combination with an ACQUITY TQ Detector V4.1 SCN849 SCN896 was used. MassLynx V4.1 SCN849 SCN896 served as the evaluation software. The required ionization was provided by the electrospray method (ESI). The diluent for the samples was an acetonitrile–water mixture containing both solvents in a 70:30 (acetonitrile:water) ratio and additionally 0.1% of formic acid.

2 Synthesis of biphosphine oxides

To prepare the diphosphine oxide, reported methods were adapeted.[1,2] The respective diphosphines were dissolved in dichloromethane (CH_2Cl_2), treated with H_2O_2 in a separation funnel and the reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the organic phase was separated, washed with water, dried over anhydrous Na_2SO_4, concentrated and dried under reduced pressure. The crude product was recrystallized from a mixture of toluene and CH_2Cl_2 to give white solids.

2.1 Preparation of Methylenebis(diphenylphosphine oxide) (1)



1,2-Bis(diphenylphosphino)methane (5.00 g, 13.01 mmol) was dissolved in dichloromethane (CH_2Cl_2, 500 mL). The resulting solution was transferred to a separatory funnel and carefully shaken with hydrogen peroxide (51.5 mL, 30 wt% aqueous solution), which was added dropwise. The progress of the reaction (approx. 5 min) was monitored by thin-layer chromatography (TLC) using 100% CH_2Cl_2 as the eluent. Upon completion, the organic phase was separated, washed with water (5 × 50 mL), dried over anhydrous Na_2SO_4 overnight, and concentrated under reduced pressure using rotary evaporation. The resulting residue was further dried under vacuum on a Schlenk line for 3 hours, affording a white powder. This crude product was recrystallized from a mixture of toluene and CH_2Cl_2. Filtration of the recrystallized solid afforded **1** as a white solid (5.36 g).

Yield: 5.36 g (98.9%); mp: 185.1 °C; **IR** (ATR, 300 K, [cm^{-1}]): 3949 (vw), 3932 (vw), 3903 (vw), 3882 (vw), 3871 (vw), 3853 (vw), 3839 (vw), 3820 (vw), 3801 (vw), 3780 (vw), 3769 (vw), 3750 (vw), 3735 (vw), 3724 (vw), 3711 (vw), 3690 (vw), 3676 (vw), 3649 (vw), 3629 (vw), 3618 (vw), 3587 (vw), 3567 (vw), 3546 (vw), 3526 (vw), 350334472360 (vw), 2342 (vw), 2017199219671943 (vw), 192118901869 (vw), 1845 (vw), 1829 (vw), 18111792 (vw), 1772 (vw), 1749 (vw), 1734 (vw), 1717 (vw), 1699 (vw), 1684 (vw), 1670 (vw); **^{1}H NMR** (500 MHz, CD_2Cl_2, 300 K, [ppm]): $\delta = 14.04$ (2H, t, $^{2}J_{HP} = 3.5$ Hz, H5), 7.46 (8H, td, $^{3}J_{HH} = 2.2$ Hz, $^{4}J_{HP} = 7.3$ Hz, H2), 7.46 (4H, t, $^{3}J_{HH} = 6.9$ Hz, H1), 7.70-7.73 (8H, m, H3). **^{13}C{^{1}H} NMR** (500 MHz, CD_2Cl_2, 300 K, [ppm]): $\delta = 34.49$ (1C, t, $^{1}J_{CP} = 58.76$ Hz, C5), 128.82 (8C, dd, $^{3}J_{CP} = 6.16$ Hz, $^{5}J_{CP} = 6.16$ Hz, C2), 131.29 (8C, dd, $^{2}J_{CP} = 5.06$ Hz, $^{4}J_{CP} = 5.06$ Hz, C3), 132.11 (4C, dd, $^{1}J_{CP} = 1.32$ Hz, $^{3}J_{CP} = 1.32$ Hz, C4), 133.86 (4C, d, $^{4}J_{CP} = 105.5$ Hz, C1). **^{31}P{1H} NMR** (CD_2Cl_2, 300K, in ppm): $\delta = 23.5$ (s, P). **ESI-MS (m/z, [Da/e]):** 417.1 [M+H]$^{+}$ (ESI^{+}).

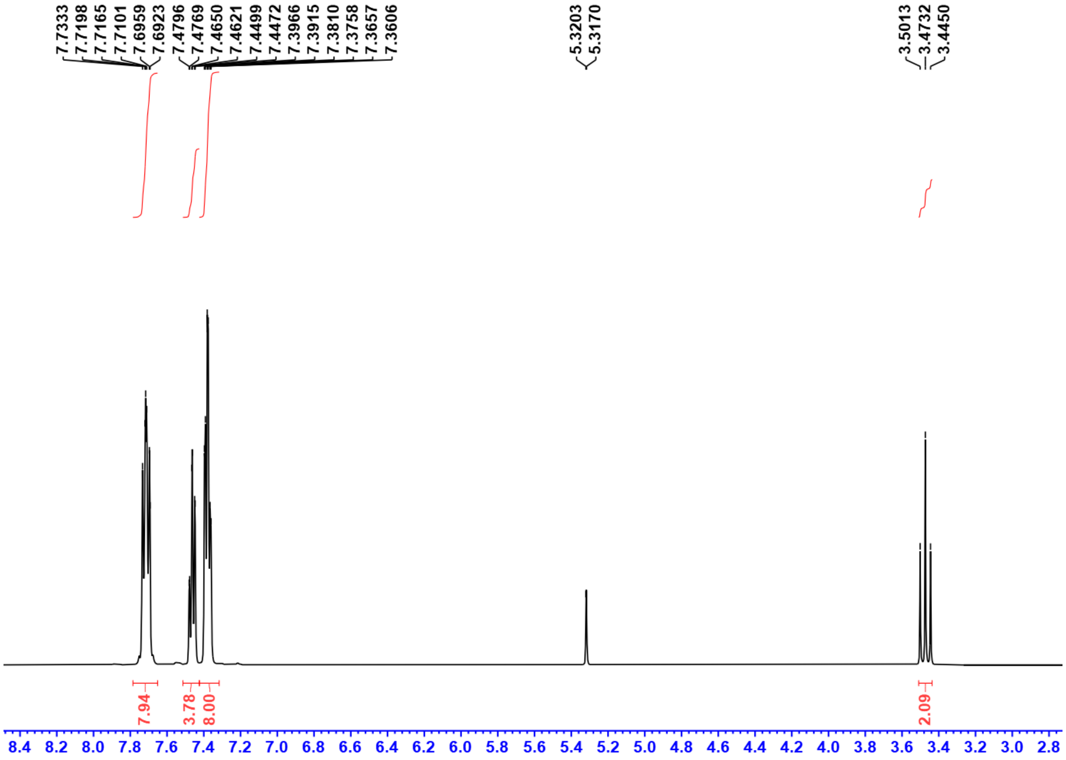


Figure S1. ^{1}H NMR of **1** (CD_2Cl_2, 300 K).

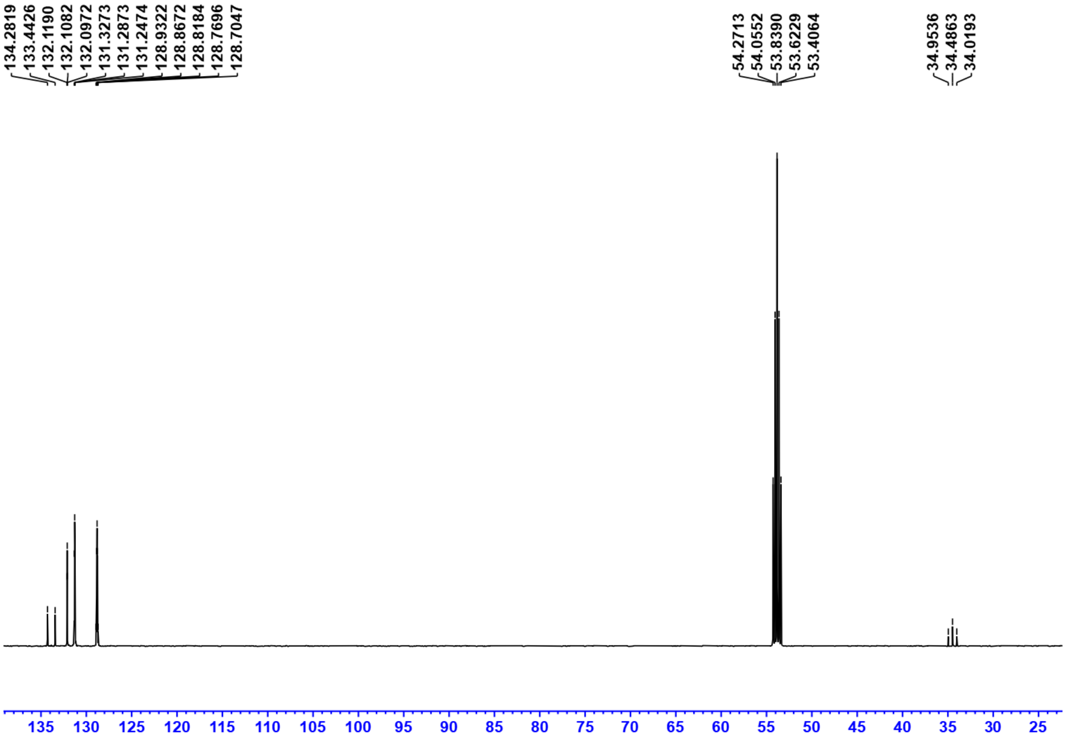


Figure S2. ^{13}C{^{1}H} NMR of **1** (CD_2Cl_2, 300 K).

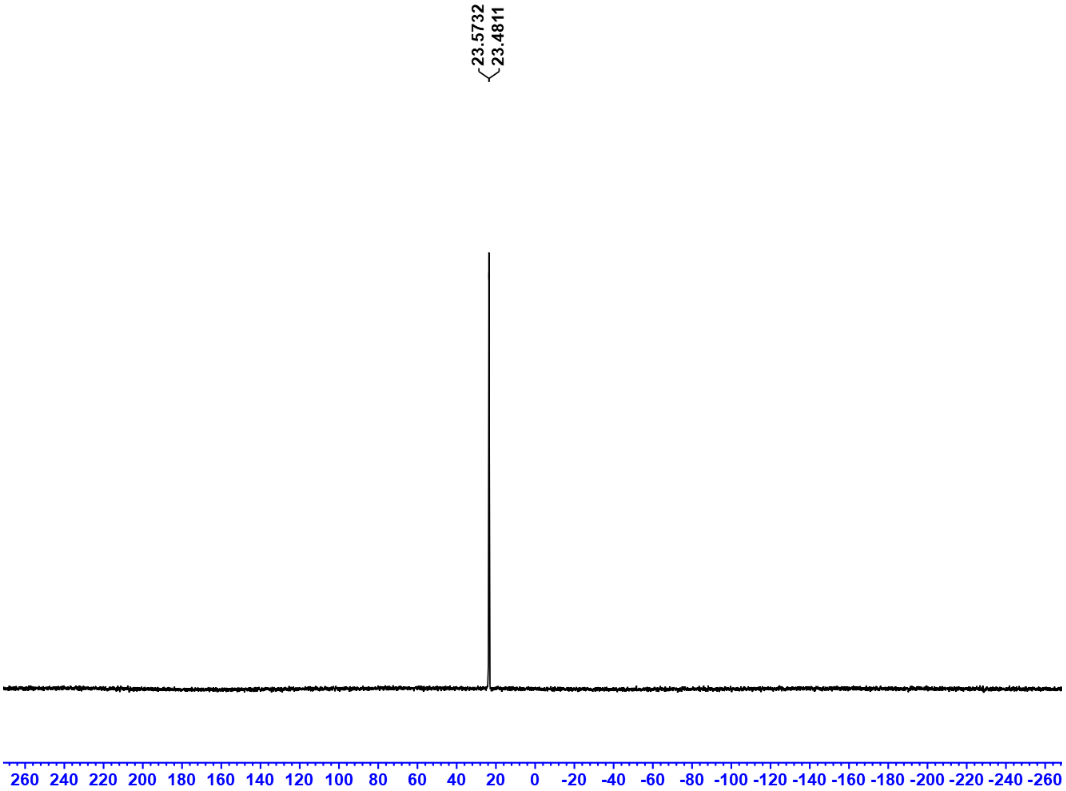
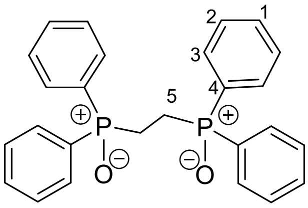


Figure S3. $^{31}P\{1H\}$ NMR of **1** (CD_2Cl_2, 300 K).

2.1 Preparation of Ethane-1,2-diylbis(diphenylphosphine oxide) (2)



1,2-Bis(diphenylphosphino)ethane (5.00 g, 12.54 mmol) was dissolved in dichloromethane (CH_2Cl_2, 500 mL). The resulting solution was transferred to a separatory funnel and carefully shaken with hydrogen peroxide (50 mL, 30 wt% aqueous solution), which was added dropwise. The progress of the reaction (approx. 5 min) was monitored by thin-layer chromatography (TLC) using CH_2Cl_2 as the eluent. Upon completion, the organic phase was separated, washed with water (5 × 50 mL), dried over anhydrous Na_2SO_4 overnight, and concentrated under reduced pressure using rotary evaporation. The resulting residue was further dried under vacuum on a Schlenk line for 3 hours, affording a white powder. This crude product was recrystallized from a mixture of toluene and CH_2Cl_2. Filtration of the recrystallized solid afforded **2** as a white solid (5.17 g).

Yield: 5.17 g (95.7%); mp: 270.4 °C; **IR** (ATR, 300 K, [cm^{-1}]): 3853 (vw), 3750 (vw), 3735 (vw), 3675 (vw), 3649 (vw), 2360 (vw), 2342 (vw), 1717 (vw), 1653 (vw), 1636 (vw), 1617 (vw), 1576 (vw), 1558 (vw), 1541 (vw), 1521 (vw), 1508 (vw), 1487 (vw), 1474 (vw), 1457 (vw), 1438 (vw), 1421 (vw), 1397 (vw), 1340 (vw), 1320 (vw), 1186 (m), 1174 (m), 1122 (w), 1103 (vw), 1087 (vw), 1071 (vw), 1028 (vw), 995 (vw), 927 (vw), 763 (w), 754 (w), 741 (m), 730 (vs), 715 (vw), 694 (s), 617 (vw), 533 (vs), 512 (vs), 456 (vw), 409 (vw); **^{1}H NMR** (500 MHz, CD_2Cl_2, 300 K, [ppm]): δ = 2.45 (4H, d, $^3J_{HH}$ = 2.6 Hz, H5), 7.46 (8H, t, $^3J_{HH}$ = 7.4 Hz, H2), 7.53 (4H, t, $^3J_{HH}$ = 7.3 Hz, H1), 7.66-7.70 (8H, m, H3). **$^{13}C\{^1H\}$ NMR** (500 MHz, CD_2Cl_2, 300 K, [ppm]): δ =21.6-22.6 (2C, m, C5), 129.1 (8C, dd, $^3J_{CP}$ =5.9 Hz, $^6J_{CP}$ = 5.9 Hz, C2), 131.1

(8C, dd, $^{2}J_{CP}$ =4.7 Hz, $^{5}J_{CP}$ = 4.7 Hz, C3), 132.4-133.5 (4C, m, C4), 132.4 (4C, m, C1). **^{31}P{1H} NMR** (CD_2Cl_2, 300K, [ppm]): $\delta = 31.0$ (s, P); **ESI-MS (m/z, [Da/e]):** 431.7 $[M+H]^+$ (ESI^+).

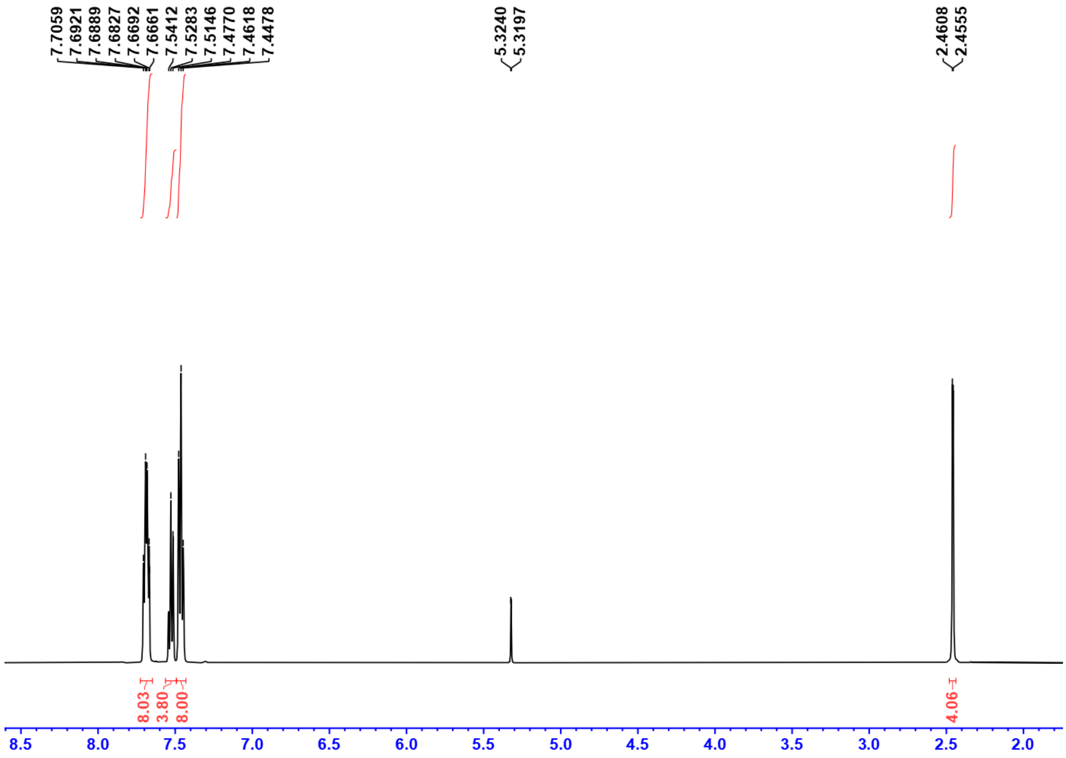


Figure S4. ^{1}H NMR of **2** (CD_2Cl_2, 300 K).

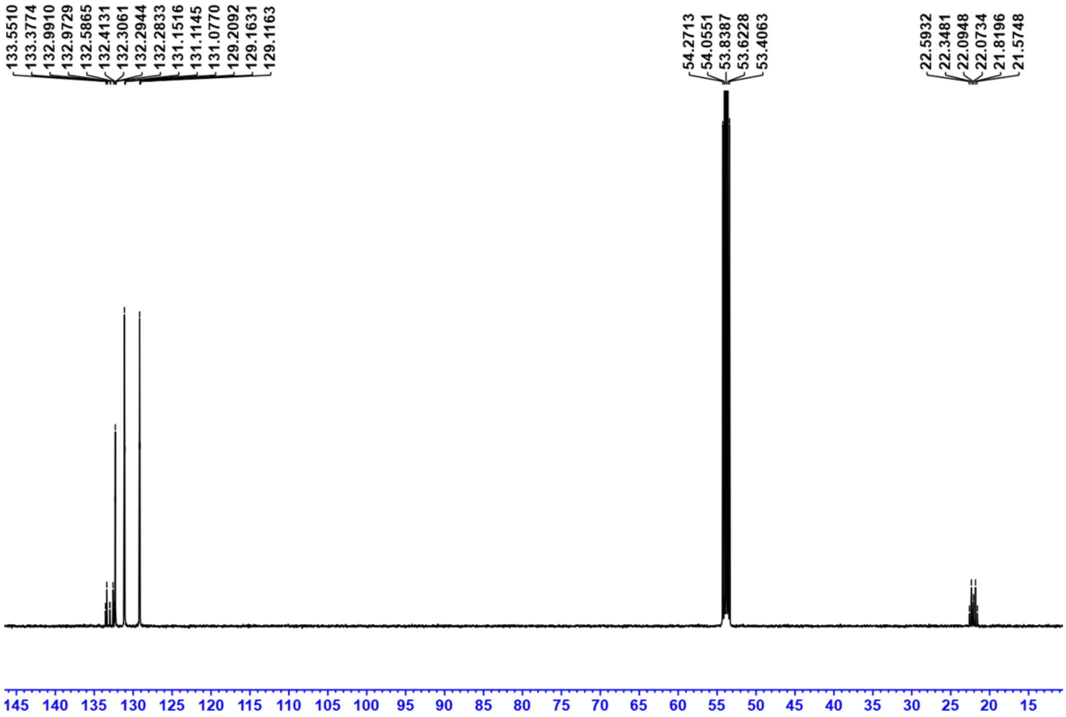


Figure S5. ^{13}C{^{1}H} NMR of **2** (CD_2Cl_2, 300 K).

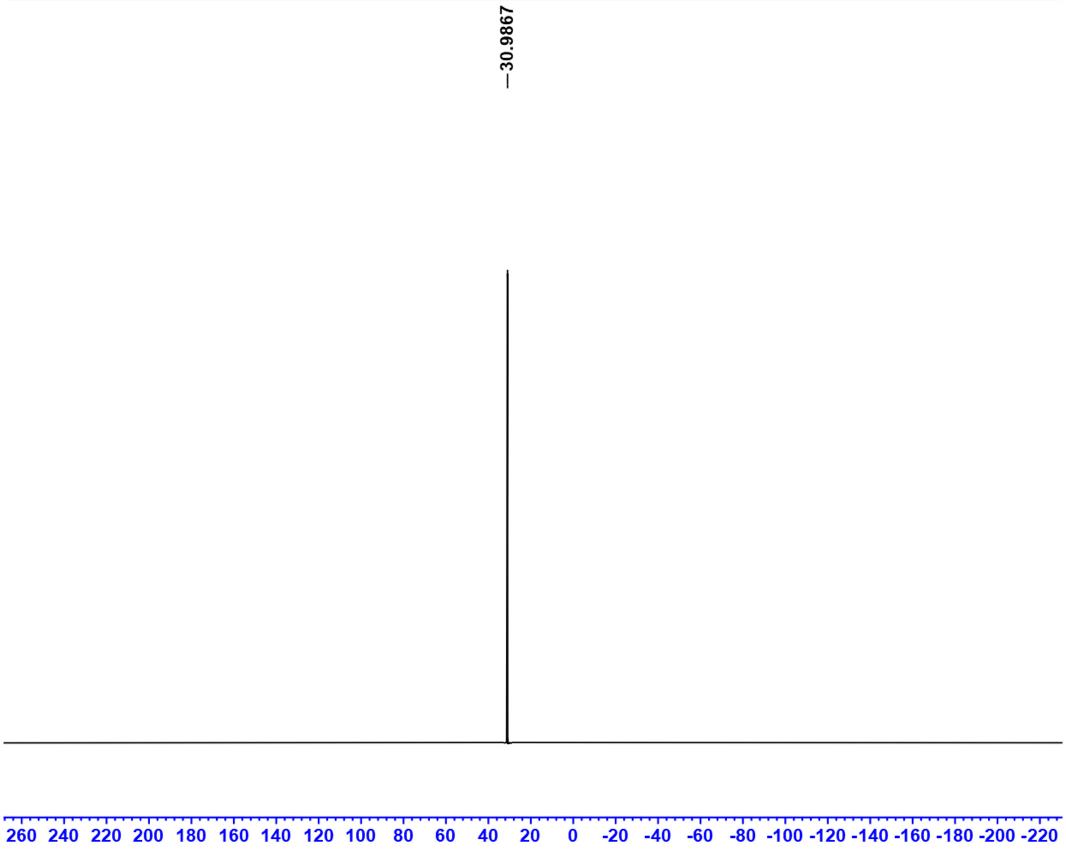


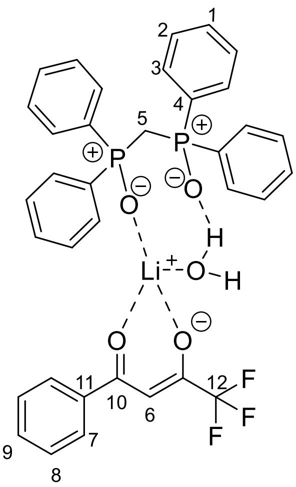
Figure S6. $^{31}P\{1H\}$ NMR of **2** (CD_2Cl_2, 300 K).

3 Synthesis of lithium complexes

3.1 General procedure for the synthesis of the lithium complexes

To prepare the Li(I)-complexes, equimolar amounts of diphosphine oxide and HBTA (1.0 equiv. each) were dissolved in CH_2Cl_2, followed by the addition of $LiOH\cdot H_2O$. The reaction mixture was stirred at 25 °C overnight, filtered, and the solvent was removed under reduced pressure. The crude product was dried in the absence of air and moisture for 2 h. Suitable single crystals for X-ray diffraction analysis were obtained either by slow diffusion of pentane into a CH_2Cl_2 solution of the complex at 25 °C, or by slow evaporation of a toluene/DCM solution containing the crude product.

3.2 Preparation of [Li(BTA)(1)·H_2O]



[Li(BTA)(**1**)·H_2O] was prepared according to the general procedure. HBTA (270.2 mg, 1.25 mmol, 1.0 equiv.) and **1** (520.5 mg, 1.25 mmol, 1.0 equiv.) were dissolved in 25 mL CH_2Cl_2, and $LiOH\cdot H_2O$ (105 mg, 2.5 mmol, 2.0 equiv.) was added. Suitable single crystals for X-ray diffraction analysis were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex at 25 °C.

Yield: 229.0 mg (27.9%); **mp:** 85.0 °C; **IR** (ATR, 300 K, [cm^{-1}]): 3057 (vw), 28872360 (vw), 2342 (vw), 1684 (vw), 1628 (w), 1597 (vw), 1579 (vw), 1528 (vw), 1496 (w), 1484 (w), 1438 (vw), 1358 (vw), 1313 (vw), 1281 (w), 1234 (vw), 1176 (w), 1120 (w), 1073 (vw), 1025 (vw), 997 (vw), 974 (vw), 942 (vw), 927 (vw), 848 (vw), 806 (vw), 779 (w), 761 (w), 739 (w), 715 (vw), 690 (w), 633 (vw), 617 (vw), 571 (vw), 553 (vw), 505 (w), 431 (vw), 405 (vw); **^{1}H NMR** (400 MHz, CD_2Cl_2, 300 K, [ppm]): δ = 3.56 (2H, t, $^{3}J_{HP}$ = 12.59 Hz, H5), 6.27 (1H, s, H9), 7.37 (8H, td, $^{3}J_{HH}$ = 8.56 Hz, $^{4}J_{HP}$ = 2.69 Hz, H2), 7.39-7.48 (7H, m, H1, H8, and H9), 7.64-7.69 (8H, m, H3), 7.97 (2H, d, $^{3}J_{HH}$ = 7.09 Hz, H7). **^{13}C{^{1}H} NMR** (500 MHz, CD_2Cl_2, 300 K, [ppm]): δ = 31.70 (1C, t, $^{1}J_{CP}$ =58.63 Hz, C5), 89.99 (1C, s, C10), 127.68 (2C, s, C7), 128.40 (2C, s, C8), 129.13 (8C, dd, $^{3}J_{CP}$ =6.38 Hz, $^{5}J_{CP}$ =6.38 Hz, C2), 130.86 (1C, s, C9), 131.04 (8C, dd, $^{2}J_{CP}$ =5.30 Hz, $^{4}J_{CP}$ =4.95 Hz, C3), 131.93 (1C, s, C12), 132.84 (4C, s, C4), 141.23 (1C, s, C11), 171.84 (4C, d, $^{4}J_{CP}$ =30.38 Hz, C1) 188.71 (1C, s, C6). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300K, [ppm]): δ = 29.12 (s, P). **^{7}Li NMR** (CD_2Cl_2, 300K, [ppm]): δ = 1.81 (s, Li). **^{19}F{} NMR** (CD_2Cl_2, 300K, [ppm]): δ = -75.81(s, F). **Elemental analysis** for $C_{35}H_{30}F_3LiO_5P_2\cdot 0.1CH_2Cl_2$ ((Li(BTA)(**1**)·H_2O)·0.1CH_2Cl_2): calculated: C: 63.40, H: 4.58; N: 0.00 found: C: 63.09, H: 4.43 N:0.00; **ESI-MS (m/z, [Da/e]):** 423.1 [M-(BTA)-H_2O]$^{+}$ (ESI^{+}), 644.3 [M-H_2O+Li]$^{+}$ (ESI^{+}), 839.4 [Li($\mathbf{1}$)$_2$]$^{+}$ (ESI^{+}).

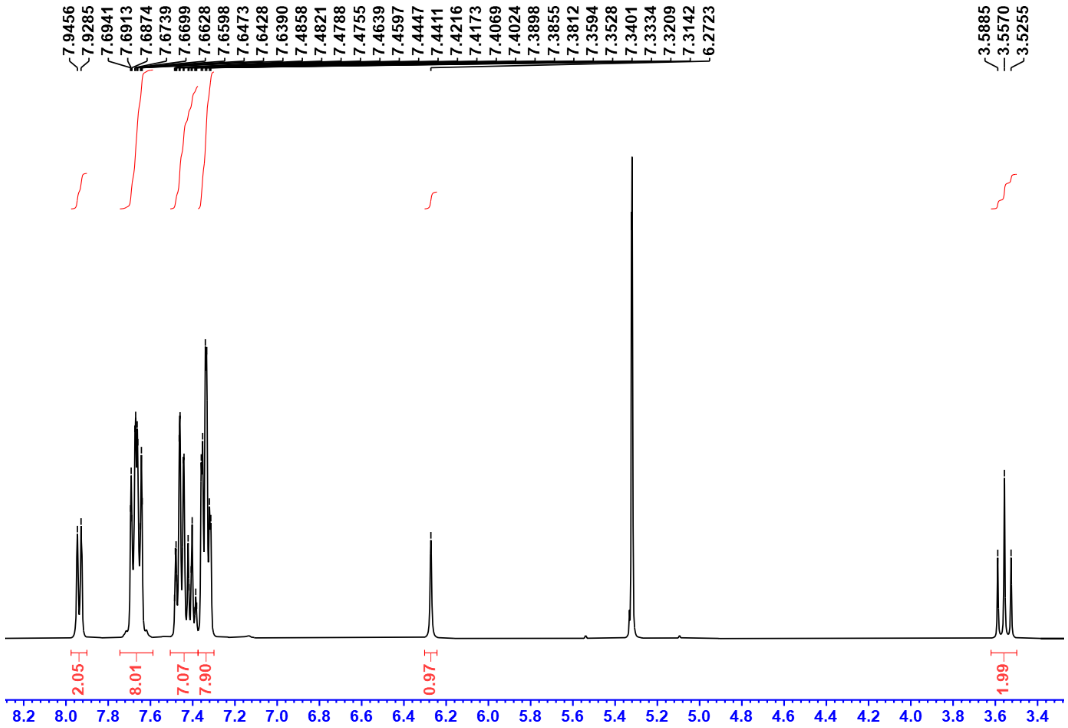


Figure S7. ^{1}H NMR of [Li(BTA)(**1**)·H_2O] (CD_2Cl_2, 300 K).

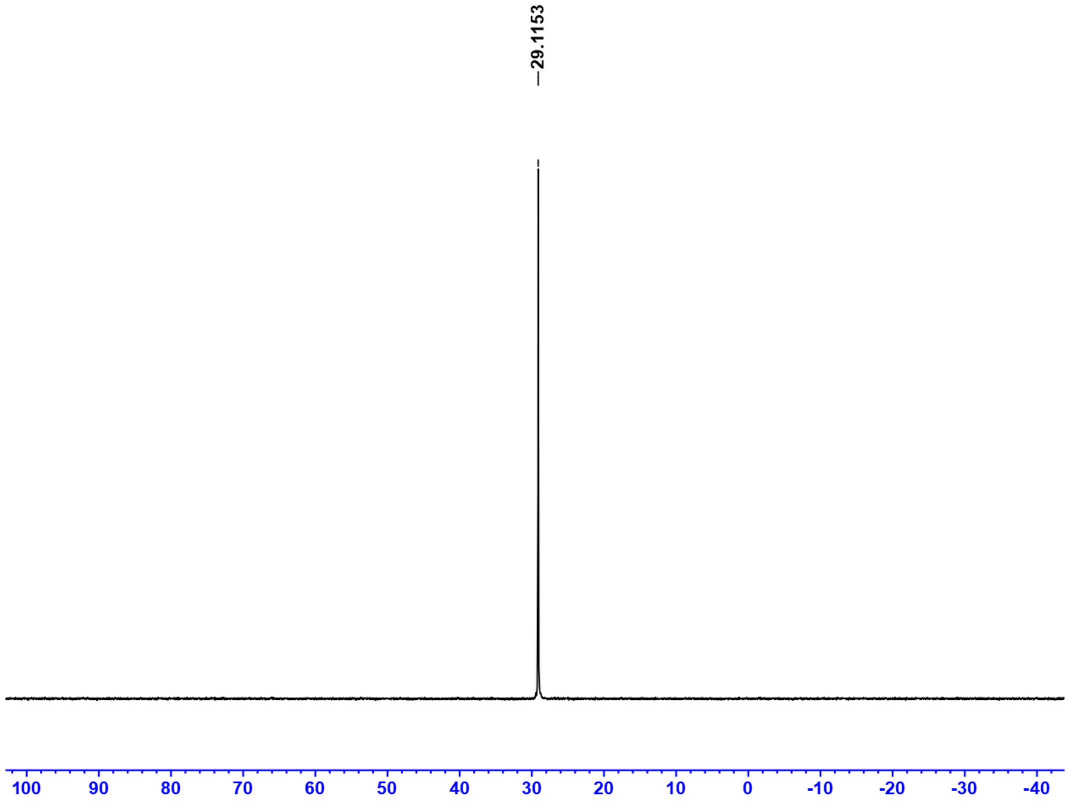


Figure S8. ^{31}P{1H} NMR of [Li(BTA)(**1**)·H_2O] (CD_2Cl_2, 300 K).

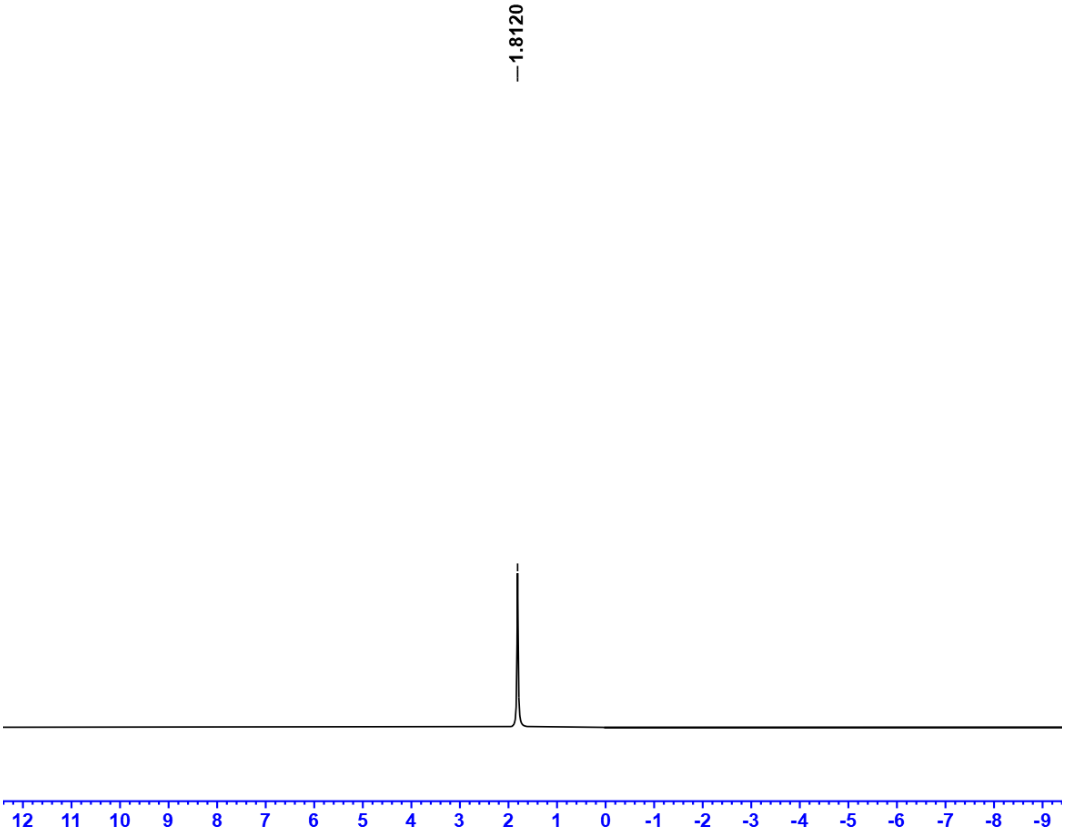


Figure S9. ^{7}Li NMR of [Li(BTA)(**1**)·H_2O] (CD_2Cl_2, 300 K).

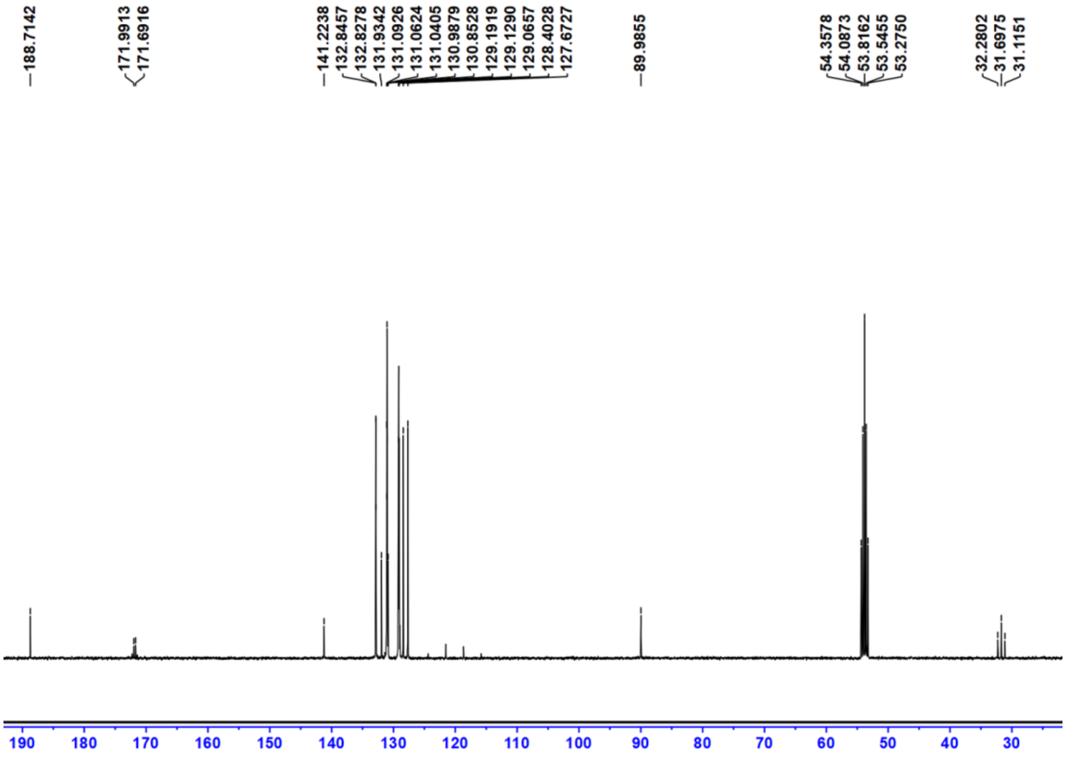


Figure S10. ^{13}C{H} NMR of [Li(BTA)(**1**)·H_2O] (CD_2Cl_2, 300 K).

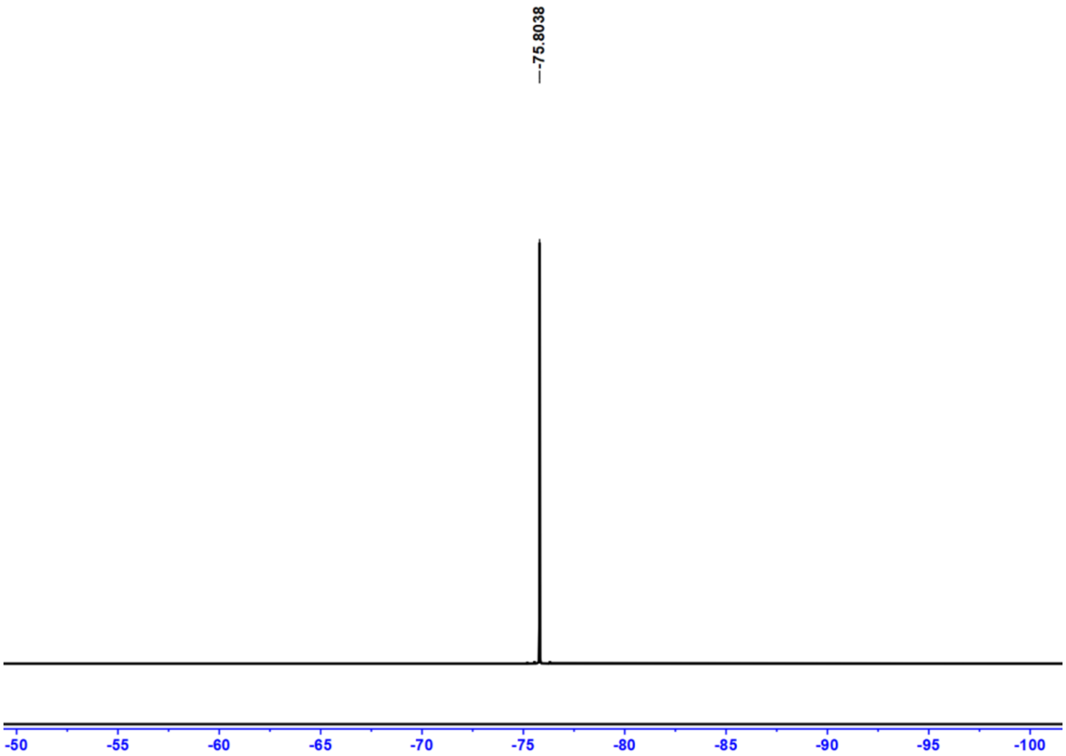
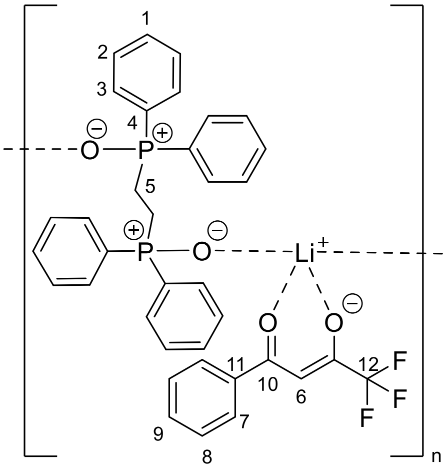


Figure S11. ^{19}F{} NMR of [Li(BTA)(**1**)·H$_2$O] (CD$_2$Cl$_2$, 300 K).

3.3 Preparation of $\{[Li(BTA)(2)]\cdot(H_2O)_{0.75}\cdot(DCM)_{0.09}\}_n$



$\{[Li(BTA)(\mathbf{2})]\cdot(H_2O)_{0.75}\cdot(DCM)_{0.09}\}_n$ was prepared according to the general procedure. HBTA (270.2 mg, 1.25 mmol, 1.0 equiv.) and **2** (538.0 mg, 1.25 mmol, 1.0 equiv.) and were dissolved in 25 mL of CH_2Cl_2, and $LiOH\cdot H_2O$ (105 mg, 2.5 mmol, 2.0 equiv.) was added. Suitable single crystals for X-ray diffraction analysis were obtained by slow evaporation of a toluene/CH_2Cl_2 solution containing the crude product at 25 °C.

Yield: 205.4 mg (25.2%); **mp:** 220.1 °C; **IR** (ATR, 300 K, [cm^{-1}]): 3058 (vw), 2913236023431683 (vw), 1630 (vw), 1598 (vw), 1580 (vw), 1529 (vw), 1500 (vw), 1486 (vw), 1438 (vw), 1410 (vw), 136213351312 (vw), 1282 (vw), 1236 (vw), 1188 (vw), 1174 (w), 1160 (vw), 1124 (w), 1099 (vw), 1071 (vw), 1026 (vw), 998 (vw), 976941 (vw), 926 (vw), 856808 (vw), 790 (vw), 762 (vw), 743 (w), 728 (w), 714 (vw), 694 (w), 635 (vw), 618 (vw), 575 (vw), 535 (w), 527 (w), 511 (w), 458 (vw), 434 (vw); **^{1}H NMR** (400 MHz, CD_2Cl_2, 300 K, [ppm]): δ = 2.55 (4H, s, H5), 6.24 (1H, s, H6), 7.35-7.39 (10H, m, H2 and H8), 7.48 (4H, t, $^3J_{HH}$ = 7.3 Hz, H1), 7.65-7.70 (9H, m, H3 and H9), 7.87 (2H, d, $^3J_{HH}$ = 7.3 Hz, H7). **^{13}C{^{1}H} NMR** (500 MHz, CD_2Cl_2, 300 K, [ppm]): δ = 21.34-22.19 (2C, m, C5), 90.18 (1C, s, C10), 127.71 (2C, s, C7), 128.43

(2C, s, C8), 129.21 (8C, dd, $^3J_{CP}$ =5.94 Hz, $^6J_{CP}$ =5.94 Hz, C2), 131.28 (8C, dd, $^2J_{CP}$ =4.95 Hz, $^5J_{CP}$ =4.84 Hz, C3), 131.54 (1C, s, C9), 131.95 (1C, s, C12), 132.55 (4C, s, C4), 141.12 (1C, s, C11), 171.78 (4C, d, $^4J_{CP}$ =30.48 Hz, C1) 188.77 (1C, s, C6). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300K, [ppm]): δ = 34.58 (s, P). **^{7}Li NMR** (CD_2Cl_2, 300K, [ppm]): δ = 1.75 (s, Li). **^{19}F{} NMR** (CD_2Cl_2, 300K, [ppm]): δ = -75.90 (s, F). **Elemental analysis** for $C_{36}H_{30}F_3LiO_4P_2$ ([Li(BTA)(**2**)]): calculated: C: 66.27, H: 4.63, N: 0.0; found: C: 66.63, H: 4.29, N:0.0; **ESI-MS (m/z, [Da/e]):** 437.7 [M-(BTA)]$^+$ (ESI$^+$), 867.9 [Li(**2**)$_2$]$^+$ (ESI$^+$).

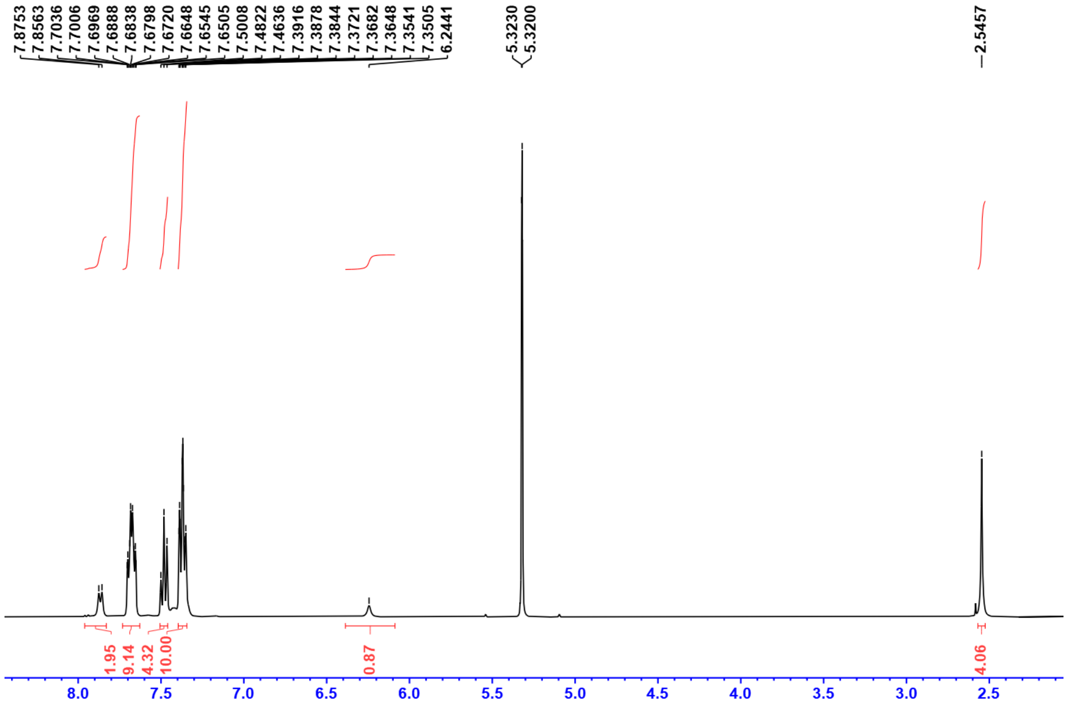


Figure S12. ^{1}H NMR of {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$ (CD_2Cl_2, 300 K).

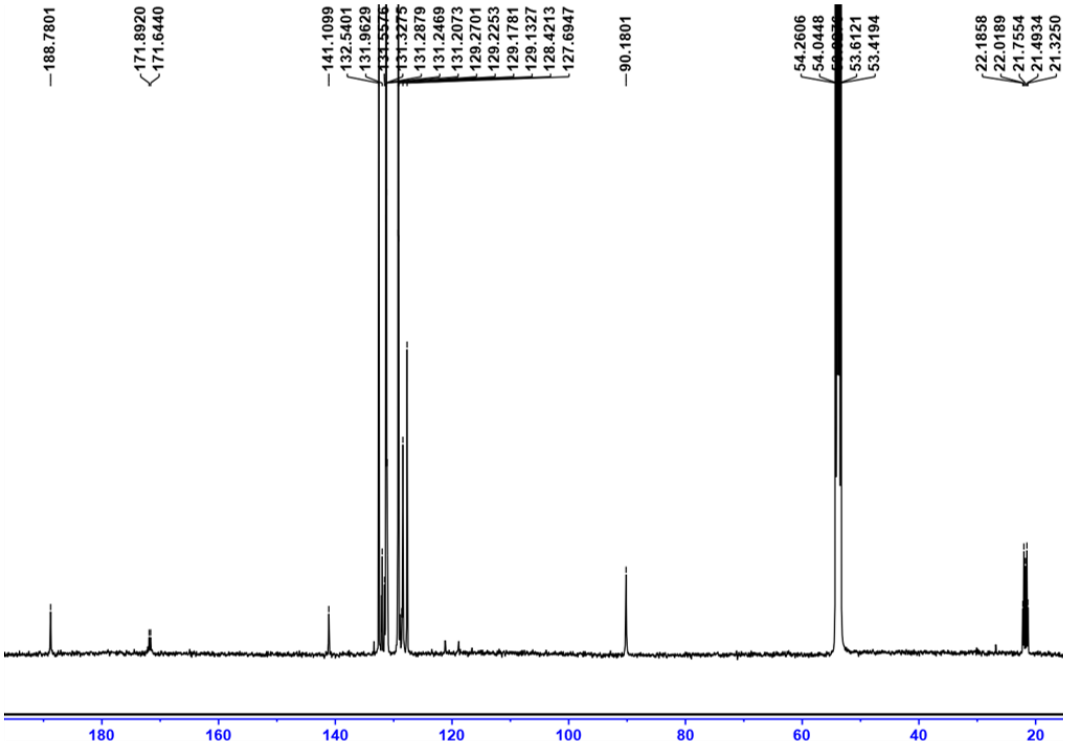


Figure S13. ^{13}C{^{1}H} NMR of {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$ (CD_2Cl_2, 300 K).

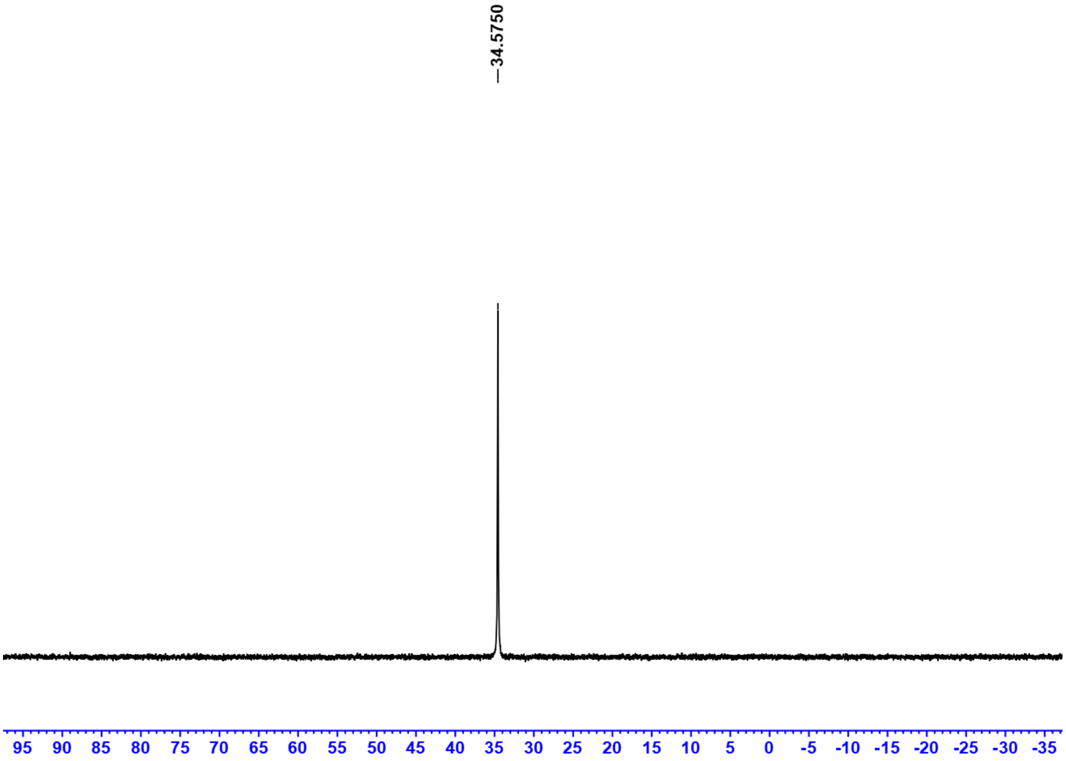


Figure S14. ^{31}P{1H} NMR of {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$ (CD_2Cl_2, 300 K).

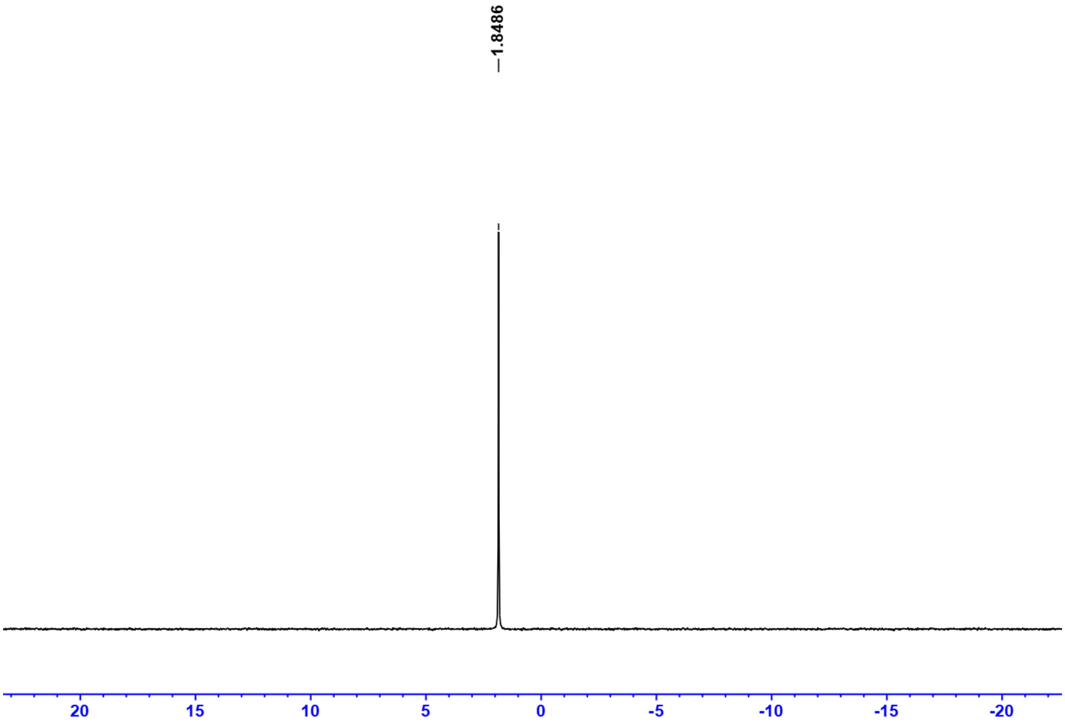


Figure S15. ^{7}Li NMR of {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$ (CD_2Cl_2, 300 K).

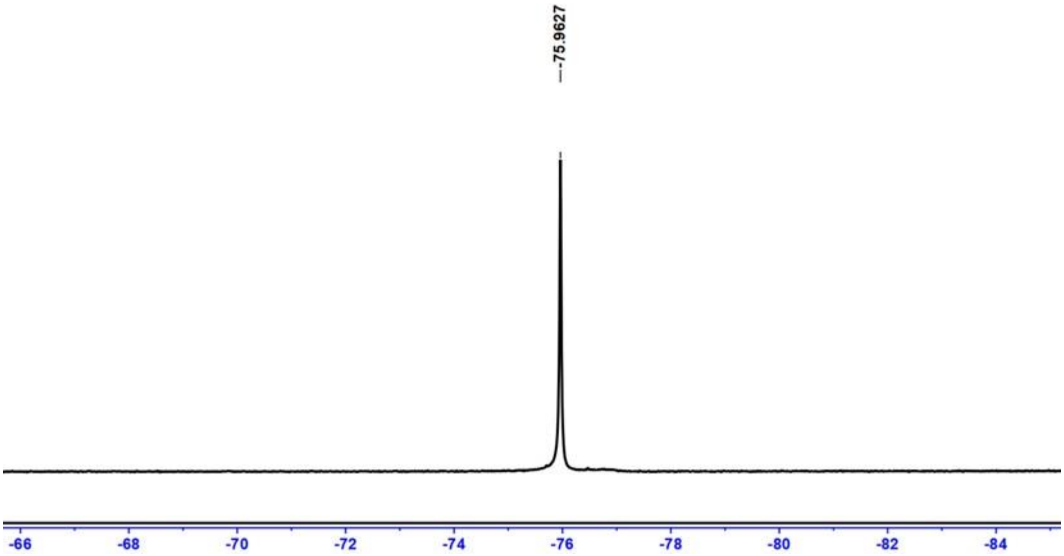


Figure S16. ^{19}F{} NMR of {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$ (CD_2Cl_2, 300 K).

4 Li(I) recognition

To probe interactions of **1** and **2** with Li(I) preliminary solid-liquid extraction experiments were performed. Defined quantities of solid $LiClO_4 \cdot 3H_2O$ (0.1 mmol, 160 mg) were contacted with 0.8 mL of a 0.1 mM CH_2Cl_2 solution of **1** and **2**, respectively, in the absence and presence of equimolar amounts of HTBA. The mixtures were stirred overnight at room temperature, filtered and the ^{31}P and ^{7}Li NMR spectra of the obtained solution were recorded. A C_6D_6 capillary was added to the solutions prior the NMR experiment. The ^{31}P NMR spectra for experiment involving **1** are displayed in Figure S17, whereas an excerpt of the stacked spectra is shown in Figure 1. The ^{7}Li NMR spectra of these experiments and control experiments in the absence of the diphosphine oxides and the ß-diketones are displayed in Figure S18. The recorded spectra for the comparable experiments with **2** and the ß-diketone HBTA are shown in Figure S19 to Figure S21.

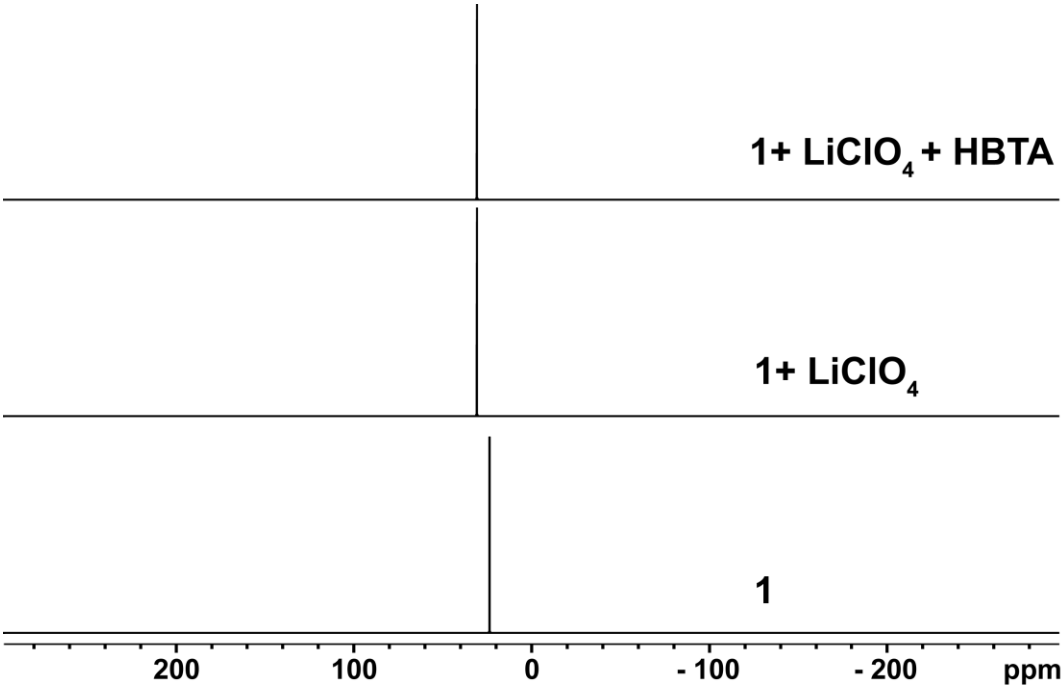


Figure S17. $^{31}P\{^{1}H\}$ spectra of **1** in CH_2Cl_2 before and after contact with $LiClO_4$, and for mixture of HBTA and **1** after contact with $LiClO_4$.

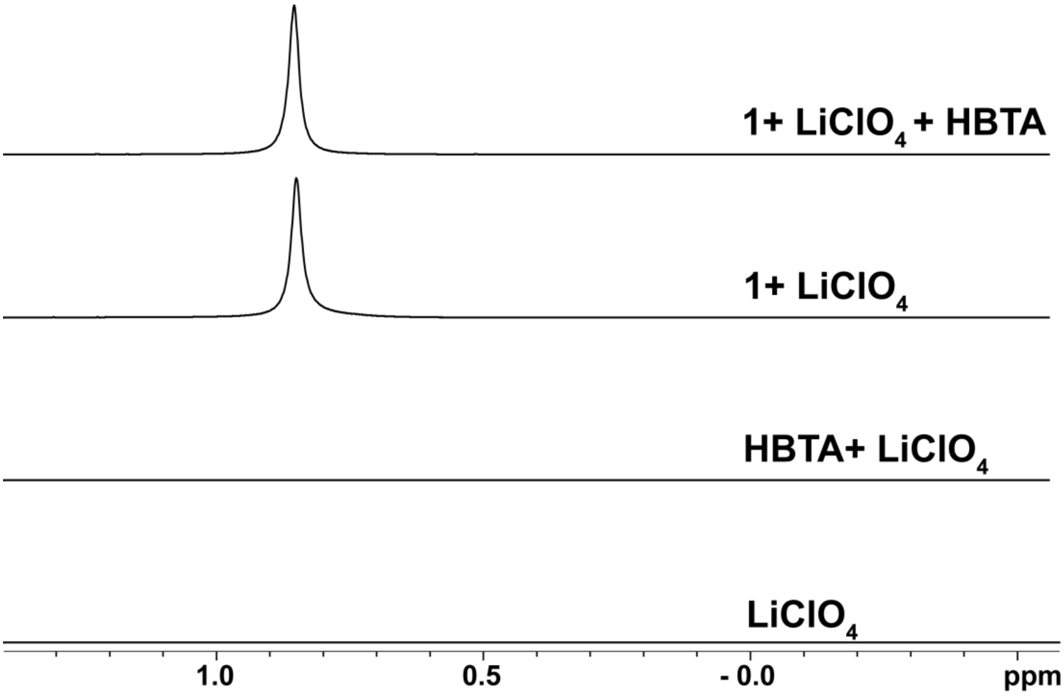


Figure S18. Stack of cutout of ^{7}Li spectra of the CH_2Cl_2 supernatant after contact with $LiClO_4$, HBTA in CH_2Cl_2 after contact with $LiClO_4$, **1** in CH_2Cl_2 after contact with $LiClO_4$ and a mixture of **1** and HBTA after contact with $LiClO_4$.

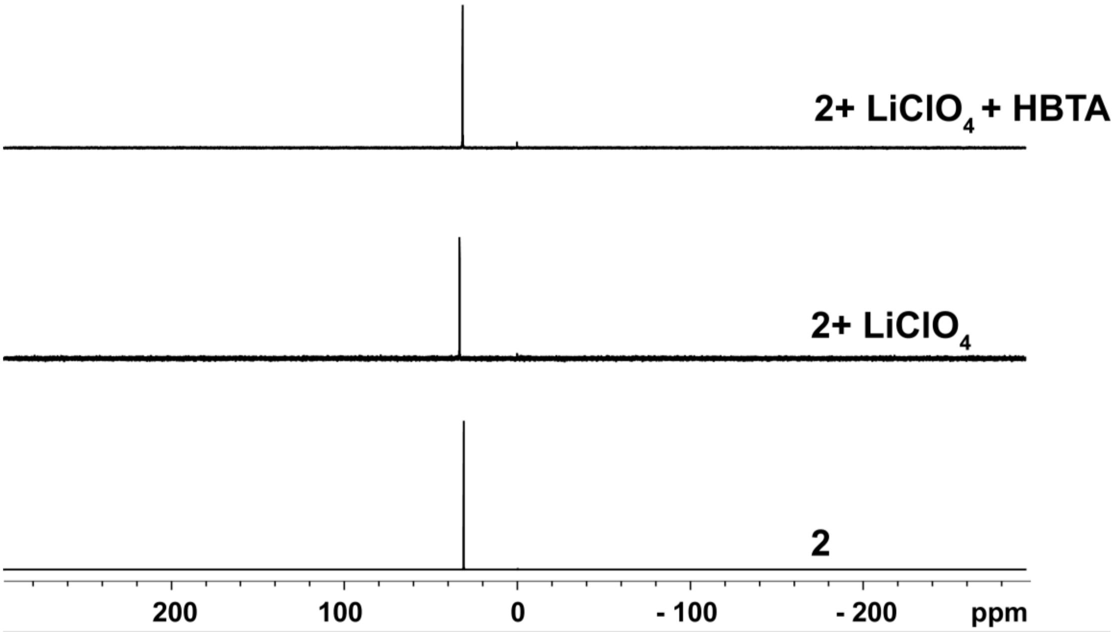


Figure S19. $^{31}P\{^{1}H\}$ spectra of **2** in CH_2Cl_2 before and after contact with $LiClO_4$, and for mixture of HBTA and **2** after contact with $LiClO_4$;

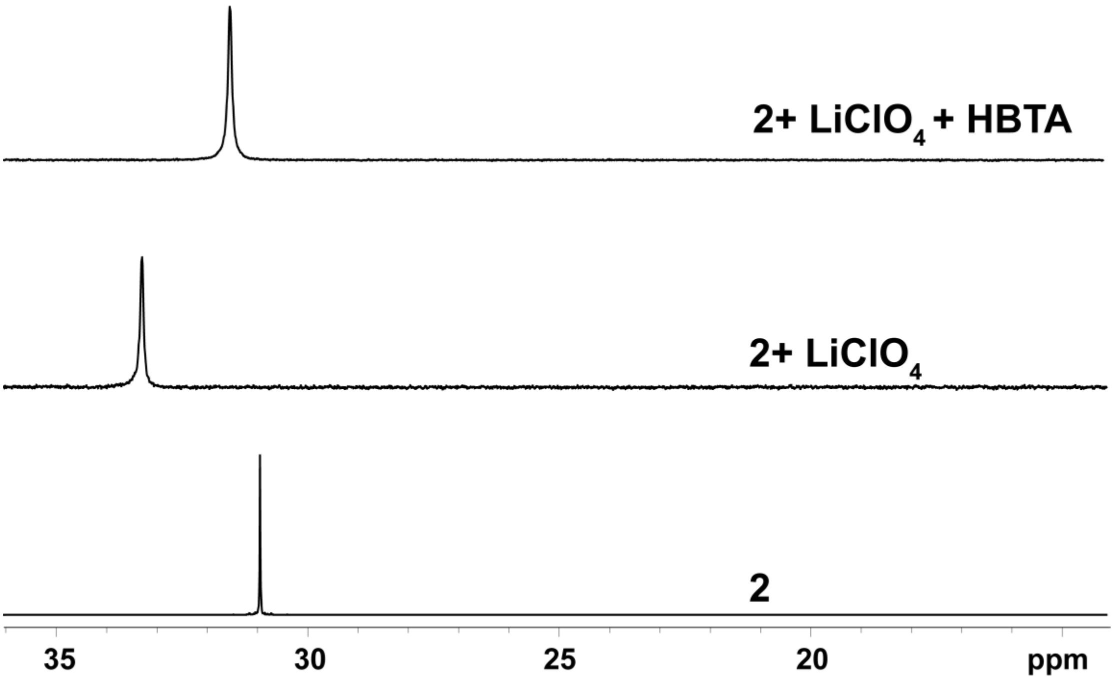


Figure S20. Cutout of the $^{31}P\{^1H\}$ spectra of **2** in CH_2Cl_2 before and after contact with $LiClO_4$, and for mixture of HBTA and **2** after contact with $LiClO_4$;

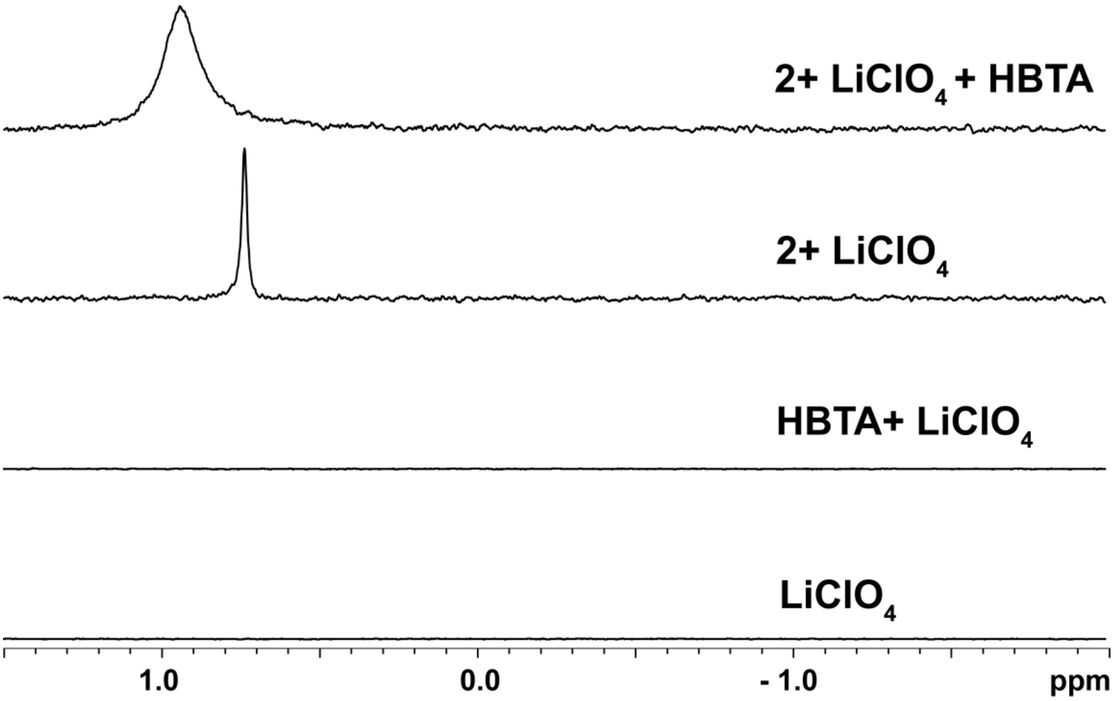


Figure S21. Stack of cutout of ^7Li spectra of the CH_2Cl_2 supernatant after contact with $LiClO_4$, HBTA in CH_2Cl_2 after contact with $LiClO_4$, **2** in CH_2Cl_2 after contact with $LiClO_4$ and a mixture of **2** and HBTA after contact with $LiClO_4$.

5 Liquid-Liquid Extraction

The concentration of metals in the organic phase (c_{org}) was determined by calculating the difference between the initial metal concentration in the aqueous phase (c_0) and the equilibrium concentration after extraction (c_{t}), based on a mass balance approach. The distribution ratio (D_M) was defined as the ratio of the metal concentration in the organic phase to that in the aqueous phase (Eq. S1). The extraction efficiency (E, %) was subsequently calculated from the distribution ratio using Eq. S2. The percent stripping (S, %) was calculated by Eq. S3:

$$D = \frac{(C_0 - C_{\mathrm{t}})}{C_t} \tag{S1}$$

$$E(\%) = \frac{D_M}{(D_M + \frac{V_{(aq)}}{V_{(org)}})} * 100 \tag{S2}$$

$$S(\%) = \frac{c_{\mathrm{S}}}{c_{\mathrm{org}}} * 100 \tag{S3}$$

where c_s (mg·L^{-1}) represent the concentration of metal in the stripping aqueous phase and V_{aq} and V_{org} (mL) refer to the volumes of the aqueous and organic phases. The phase ratio (V_{aq}: V_{org}) was maintained at 1:1 in all experiments. The Tris/HCl buffer was prepared by mixing 0.1 M tris(hydroxymethyl)aminomethane (Tris) with 0.1 M HCl. All liquid–liquid extraction experiments were carried out by mechanically shaking the two-phase system, followed by centrifugation to separate the organic and aqueous phases. Each extraction experiment was performed in duplicate, and both the average values and standard deviations are reported. Initial studies employing different shaking time show that a short contact time of 15 minutes is sufficient, after which variations within the margin of experimental error can be observed (Figure S22). To simplify the procedure, contact times of 12 hours or overnight were selected for this study.

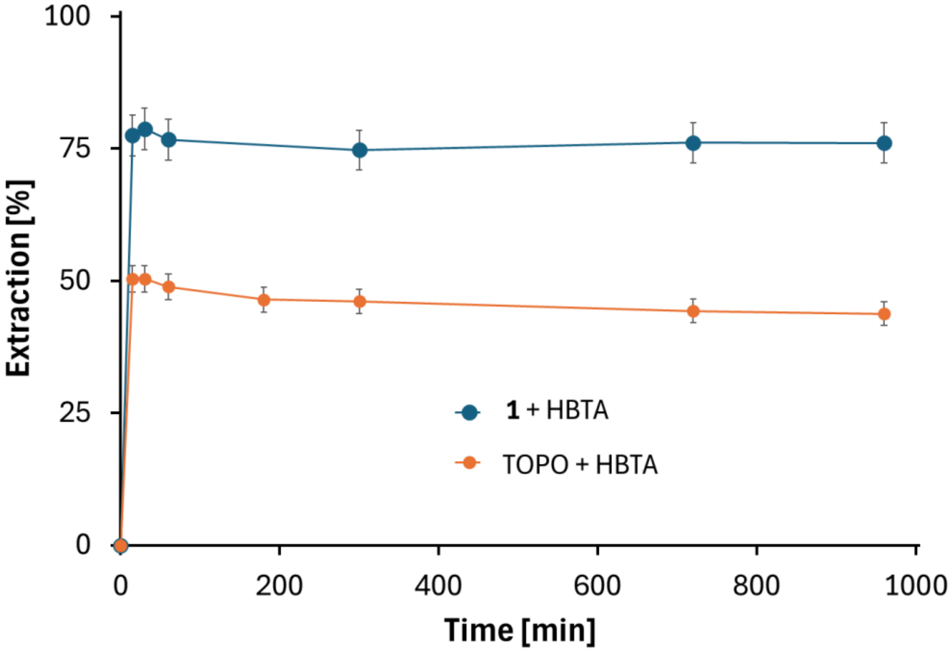


Figure S22. Percent extraction of Li(I) by **1** and TOPO in the presence of HBTA in dependence of the contact time. [LiCl] = 0.01 M, [NH_4Cl] = 0.1 M, (Tris buffer), [**1**] = 0.1 M, [TOPO] = 0.1 M, [HBTA] = 0.1 M in $CHCl_3$.

6 Slope analysis experiments

The reaction scheme for liquid-liquid extraction can be expressed by Eq. (S4):

$$M^{a+}{}_{(aq)} + mHL_{(org)} + nS_{(org)} = M \cdot (H_{m-a}L)_m \cdot S_{n(org)} + aH^+{}_{(aq)} \qquad \text{(S4)}$$

where M is the metal cation with $a+$ charge, H**L** is the ligand (HBTA) and S is the co-ligand with the stoichiometry coefficients being m and n. The index aq and org refer to the aqueous and organic phase.

The extraction constant K_{ex} is expressed by Eq. (S5):

$$K_{ex} = \frac{[M \cdot (H_{m-a}L)_m \cdot S_n]_{(org)} \cdot [H^+]^a{}_{(aq)}}{[M^{a+}]_{(aq)} \cdot [HL]^m{}_{(org)} \cdot [S]^n{}_{(org)}} \qquad \text{(S5)}$$

The distribution ratio (D_M) is defined as the ratio of the concentration of metal present in the organic phase to the concentration of metal present in the aqueous phase ($\frac{[M \cdot (H_{m-a}L)_m \cdot S_n]_{(org)}}{[M^{a+}]_{(aq)}}$). Hence, Eq. (S5) can be coverted to Eq. (S6):

$$LogD_M = LogK_{ex} + mlog[L] + nlog[S] + apH \qquad \text{(S6)}$$

According to Eq. (S6), for a simple reactive extraction system, the distribution ratio (D_M) depends on the pH, the ligand concentration, and the concentration of the co-ligand. When the pH and ligand concentration are held constant, the coefficient n can be determined from the slope of a log D_M versus $\log[S]_{(org)}$ plot. It is important to note that this method is valid only when the concentrations of the ligand and co-ligand are in large excess relative to the metal concentration, such that the formation of metal–ligand complexes does not significantly alter the calculated values of $\log[S]_{(org)}$. Additionally, a constant ionic strength must be maintained in the aqueous phase to minimize the influence of activity coefficient variations on the concentration-dependent extraction constant. To ensure this, the counterion is added in large excess.

7 Liquid-liquid extraction reusability test

The two co-ligands, **1** and **2**, were employed in the reusability tests. After each extraction cycle, a 0.5 M HCl aqueous solution was used to strip Li(I) from the loaded organic phase. The phase ratio (V_{aq}:V_{org}) in the stripping experiments was maintained at 1:1. The organic phase, containing HBTA and **1** or **2**, was reused for four consecutive extraction cycles, while a fresh Li(I)-containing aqueous solution was used in each cycle. The Li(I) concentration in the aqueous phase after each extraction was determined by ICP-OES analysis, and the extraction efficiency for each cycle is presented in Figure 3b. Additionally, the lithium content in the stripping phase was measured, and the stripping efficiency (S, %) was calculated using Eq. (S3). Under the applied conditions, quantitative stripping was achieved (Table S1).

Table S1. Comparison between extraction and stripping percentage for the completed cycles of the reuse assay.

		1st	2ed	3rd	4th
1+HBTA	E (%)	54.6	55.8	54.7	55.4
	S (%)	100	100	100	100
2+HBTA	E (%)	24.3	26.4	26.9	25.7
	S (%)	100	100	100	100

8 Influence of pH and earth alkali metal ions

The Li(I) extraction of **1** in the presence of HBTA in dependence of the pH was probed and the obtained data is displayed in Figure S23. Furthermore, preliminary competitive extraction experiments were conducted in the presence of Li(I), Na(I), K(I), Mg(II), and Ca(II) and the determined percentage extraction for each ion is shown in Table S2.

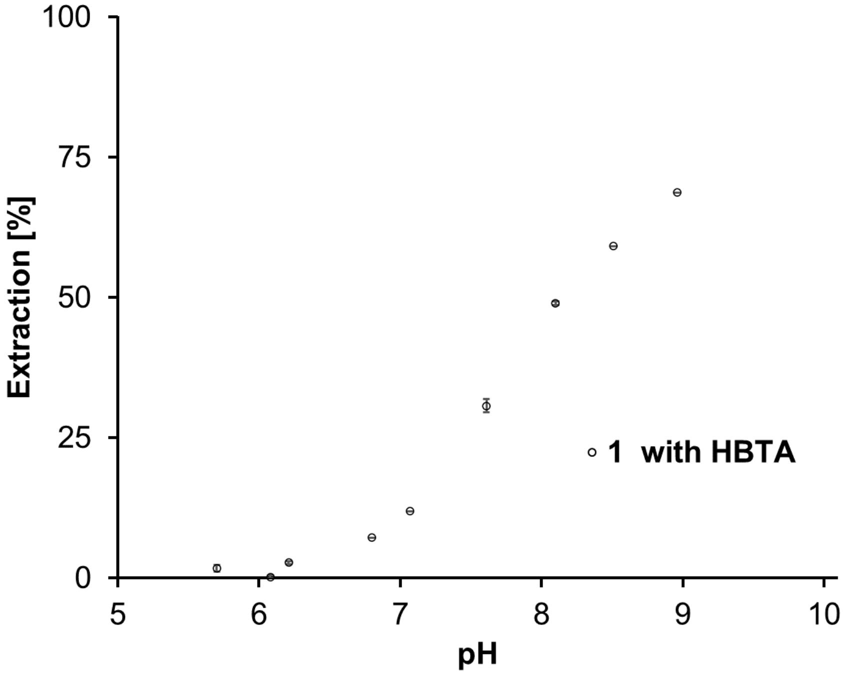


Figure S23. Percent extraction of Li(I) by **1** and HBTA in dependence of the pH of the aqueous phase. [LiCl] = 0.01 M, [NH_4Cl] = 0.1 M, (Tris/HCl / Tris/NaOH buffer), [**1**] = 0.1 M, [HBTA] = 0.1 M in $CHCl_3$, 300 K, overnight.

Table S2. Percentage extraction by **1** in the presence of HBTA in competitive extraction experiments containing Li(I), Na(I), K(I), Mg(II), and Ca(II). [LiCl] = 0.01 M, [NaCl] = 0.01 M, [KCl] = 0.01 M, [$MgCl_2$] = 0.01 M, [$CaCl_2$] = 0.01 M, [NH_4Cl] = 0.1 M, pH=8.5 (Tris/HCl buffer), [**1**] = 0.1 M, [HBTA] = 0.1 M in $CHCl_3$, 298 K, overnight.

		Li(I)	Na(I)	K(I)	Mg(II)	Ca(II)
1+HBTA	E (%)	5.2 ± 1.2	8.0 ± 1.4	5.4 ± 1.8	100	98 ± 0.1

9 Crystallographic details

Suitable single crystals were coated with Paratone-N or Fomblin Y25 PFPE oil, mounted on a glass fibre, and cooled under a stream of cold nitrogen. X-ray diffraction data for Li(BTA)·(**1**)·H_2O were collected at 170 K on a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer using Mo Kα radiation (λ = 0.71073 Å) or for {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}n at 100 K on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu Kα radiation (λ = 1.54184 Å) both generated from a micro-focus source. Data reduction and absorption correction were carried out using CrysAlisPro.[3] The structures were solved with Olex2[4] employing the SHELXT[5] package, and refined using SHELXL[6]. Hydrogen atoms bonded to carbon were positioned at calculated sites and refined using the riding model. Structural illustrations were generated using Olex2 software. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and are available free of charge under deposition numbers 2538695 and 2538696.

Table S3. Crystallographic data for [Li(BTA)(**1**)·H_2O] (b) and {[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$

	Li(BTA) (**1**)·H_2O	{[Li(BTA)(**2**)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$
Empirical formula	$C_{35}H_{30}F_3LiO_5P_2$	$C_{36.09}H_{31.68}Cl_{0.17}F_3LiO_{4.75}P_2$
Formula weight	656.47	673.39
Color, habit	colourless, plate	colourless, needle
Temperature/K	170.00(10)	100.00(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.1389(4)	12.5215(7)
b/Å	11.9692(4)	12.7280(6)
c/Å	14.6521(5)	13.3509(6)
α/°	94.060(3)	64.326(5)
β/°	102.209(3)	89.184(4)
γ/°	112.235(3)	65.971(5)
Volume/Å^3	1586.14(10)	1717.20(17)
Z	2	2
ρ_{calc}g/cm^3	1.375	1.304
μ/mm^{-1}	0.197	1.754
F(000)	680.0	698.0
Crystal size/mm^3	0.235 × 0.214 × 0.122	0.21 × 0.07 × 0.05
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.318 to 68.17	7.494 to 153.262
Index ranges	-14 ≤ h ≤ 15, -17 ≤ k ≤ 18, -22 ≤ l ≤ 22	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -16 ≤ l ≤ 12
Reflections collected	32586	17731
Independent reflections	11086 [R_{int} = 0.0550, R_{sigma} = 0.0626]	7105 [R_{int} = 0.0401, R_{sigma} = 0.0416]
Data/restraints/parameters	11086/0/423	7105/0/455
Goodness-of-fit on F^2	1.045	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1113	R_1 = 0.0498, wR_2 = 0.1317
Final R indexes [all data]	R_1 = 0.0707, wR_2 = 0.1219	R_1 = 0.0559, wR_2 = 0.1378
Largest diff. peak/hole / e Å^{-3}	0.50/-0.40	0.97/-0.36
CCDC	2538696	2538695

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