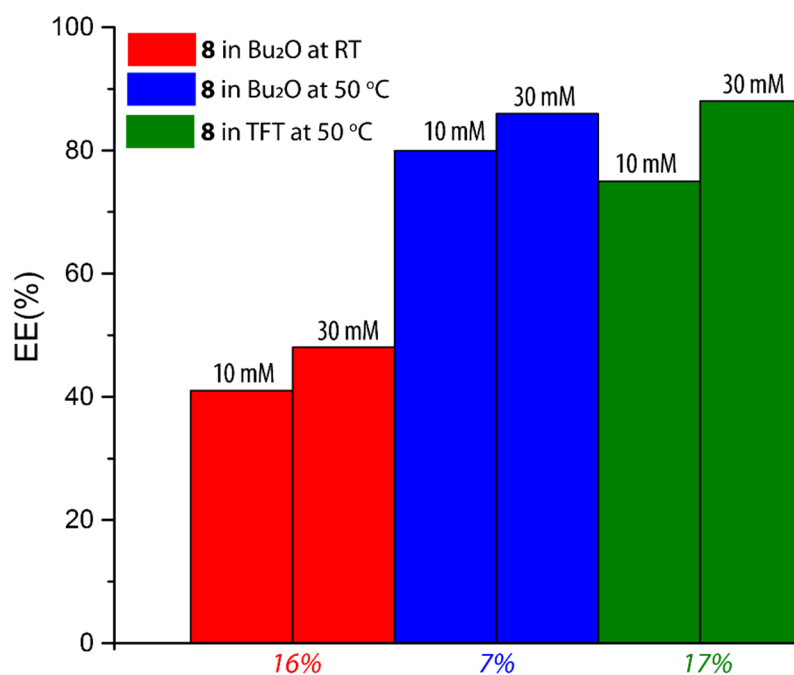


# Supplementary Materials: Recovery of Gallium-68 and Zinc from HNO<sub>3</sub>-Based Solution by Liquid–Liquid Extraction with Arylamino Phosphonates

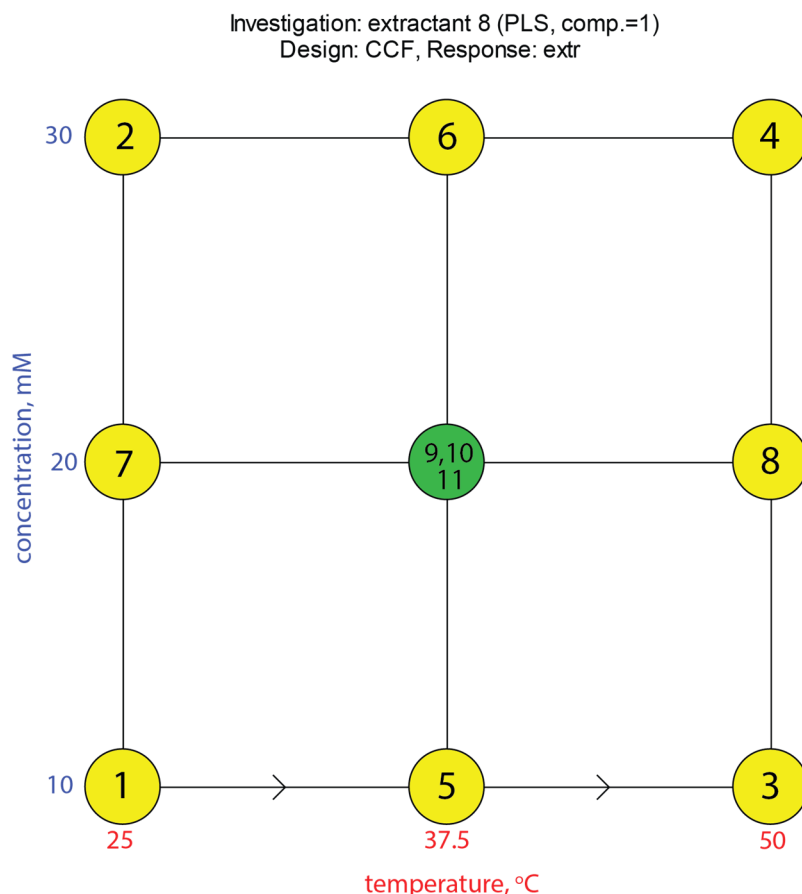
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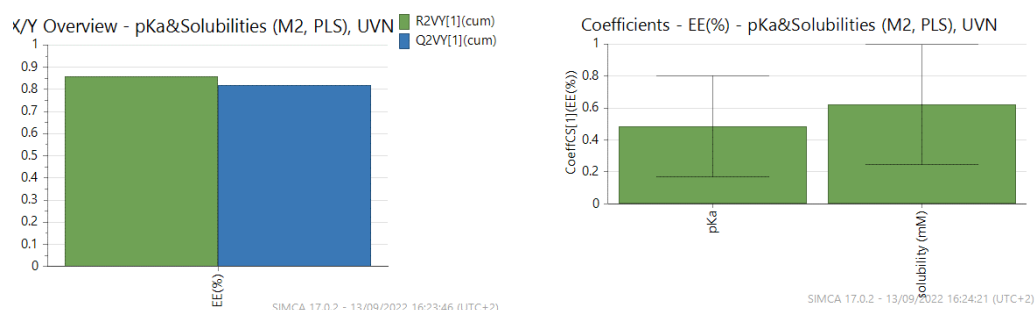
**Figure S1.** The extraction efficiencies for compound 8, performed at 10 mM and 30 mM in various solvents at RT and 50 °C. The relative increase in EE upon the increase in concentration of 8 from 10 to 30 mM is shown on the X axis.

Table S1. The distribution ratio  $D_s = [^{68}\text{Ga}_{\text{tot}}]_{\text{org}} / [^{68}\text{Ga}_{\text{tot}}]_{\text{aq}}$  for batch LLE of  $^{68}\text{Ga}$  from 1 M zinc nitrate in 0.01 M nitric acid with 10 mM of extractant dissolved in various solvents and performed at RT or 50 °C.

Entry	Extractant	Solvent	T, °C	Ds
1	1	Heptane	RT	10.2
2	2	Anisole	RT	2.8
3	2	Anisole	50 °C	11.0
4	3	CHCl <sub>3</sub> /Heptane, 3/1 (v/v)	RT	7.0
5	4	Bu <sub>2</sub> O	RT	2.7
6	5	Bu <sub>2</sub> O	RT	11.4
7	6	Heptane/TFT1:1(V/V)	RT	16.6
8	6	Bu <sub>2</sub> O	RT	8.3
9	7	Heptane	RT	5.5
10	7	Heptane	50 °C	12.6
11	8	Bu <sub>2</sub> O	RT	13.8
12	8	Bu <sub>2</sub> O	50 °C	26.7
13	8	TFT	RT	20.2
14	8	TFT	50 °C	29.4
15	9	Bu <sub>2</sub> O	RT	23.0
16	9	Bu <sub>2</sub> O	50 °C	29.9



**Figure S2.** The design region for the central composite face-centered design shown in Table S1. The numbers in the circles correspond to the experiment numbers in Table S1. The center point was run in triplicate (experiments 9,10,11).



**Figure S3.** A PLS model correlating the  $^{68}\text{Ga}$  extraction efficiency with pKa and aqueous solubility of compounds 1-9

## Spectroscopic data for arylaminophosphonic acids 1-9

**1** was obtained using the general procedure in 45% yield

NMR (dmso- $d_6$ ,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 7.52–7.45 (apparent d, 2H), 7.32–7.23 (apparent t, 2H), 7.22–7.15 (apparent t, 1H), 7.01–6.94 (apparent t, 2H), 6.72–6.66 (apparent d, 2H), 6.52–6.46 (apparent t, 1H), 4.77 (d,  $J$  = 24.5 Hz, 1H), 3.89–3.68 (m, 2H), 1.49–1.37 (m, 2H), 1.31–1.11 (m, 10H), 0.85 (t,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 147.48 (d,  $J$  = 14.1 Hz), 138.23, 128.57, 128.20 (d,  $J$  = 5.3 Hz), 127.73 (d,  $J$  = 2.7 Hz), 126.77 (d,  $J$  = 3.1 Hz), 116.4, 113.25, 65.39 (d,  $J$  = 6.9 Hz), 54.82 (d,  $J$  = 147.6 Hz), 31.18, 30.10 (d,  $J$  = 5.6 Hz), 28.59, 28.55, 25.01, 22.06, 13.94.  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 19.19.

**2** was obtained using the general procedure in 44% yield.

NMR (dmso- $d_6$ ,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 7.44–7.36 (m, 2H), 7.34–7.27 (m, 2H), 7.05–6.97 (apparent d, 2H), 6.69–6.61 (apparent d, 2H), 4.76 (d,  $J$  = 24.9 Hz, 1H), 3.53 (d,  $J$  = 10.6 Hz, 3H), 1.25 (s, 9H), 1.16 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 149.18 (d,  $J$  = 3.1 Hz), 144.93 (d,  $J$  = 14.9 Hz),

138.75, 134.85 (d, J = 1.1 Hz), 127.86 (d, J = 5.3 Hz), 125.27, 124.67 (d, J = 2.5 Hz), 112.94, 54.03 (d, J = 149.7 Hz), 52.49 (d, J = 6.3 Hz), 34.15 (d, J = 1.1 Hz), 33.41, 31.38, 31.16.  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 23.48.

**3** was obtained using the general procedure in 51% yield.

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 7.37–7.31 (apparent d, 1H), 7.16–7.10 (m, 1H), 6.96–6.91 (m, 1H), 6.75–6.69 (m, 2H), 6.67–6.61 (m, 2H), 5.00 (d, J = 24.1 Hz, 1H), 3.94–3.76 (m, 2H), 3.60 (s, 3H) 1.52–1.41 (m, 2H), 1.30–1.10 (m, 10H), 0.84 (t, J = 6.9, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 151.49, 141.99, 141.16 (d, J = 13.9 Hz), 126.44 (d, J = 2.3 Hz), 126.02 (d, J = 7.0 Hz), 124.83 (d, J = 3.2 Hz), 114.58, 114.23, 65.70, 65.63, 51.72 (d, J = 155.1 Hz), 31.19, 30.08 (d, J = 6.1 Hz), 28.59, 28.54, 24.98, 22.05, 13.9.  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 18.37.

**4** was obtained using the general procedure in 41% yield.

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 7.47–7.39 (m, 2H), 7.36–7.26 (apparent t, 4H), 7.03–6.93 (m, 1H), 6.90–6.84 (apparent d, 2H), 4.95–4.80 (apparent dd, 1H), 3.92–3.72 (m, 2H), 1.53–1.36 (m, 2H), 1.35–1.03 (m, 19H), 0.83 (t, J = 7.0 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 150.80 (d, J = 13.5 Hz), 149.39 (d, J = 3.1 Hz), 141.61 (d, J = 13.9 Hz), 134.21, 127.91 (d, J = 5.3 Hz), 125.9 (d, J = 4.1 Hz), 125.7 (q, J = 270.8 Hz), 124.7 (d, J = 2.2 Hz), 116.09 (q, J = 32.1 Hz), 115.91, 112.55, 65.50 (d, J = 6.3 Hz), 53.70 (d, J = 149.9), 34.16, 31.14, 30.04 (d, J = 6.3 Hz), 28.57 (d, J = 4.4 Hz), 25.00, 22.03, 13.89.  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 19.28.  $^{19}\text{F}$  (377 MHz) -59.11.

**5** was obtained using the general procedure in 53% yield.

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 7.73–7.61 (m, 4H), 6.71–6.58 (m, 4H), 4.91 (d, J = 25.0, 1H), 3.94–3.75 (m, 2H), 3.57 (s, 3H), 1.51–1.38 (m, 2H), 1.29–1.12 (m, 10H), 0.84 (t, J = 6.9 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 151.33, 143.45, 141.02 (d, J = 15.3 Hz), 128.98 (d, J = 4.5 Hz), 127.48 (q, J = 31.2 Hz), 125.02 (d, J = 6.5 Hz), 124.57, 124.39 (q, J = 275.0 Hz), 114.51, 144.26, 65.52 (d, J = 6.4 Hz), 55.22 (d, J = 148.0 Hz), 55.12, 31.17, 30.03 (d, J = 5.6 Hz), 28.56 (d, J = 5.8 Hz), 24.97, 22.04, 13.89.  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 19.10.  $^{19}\text{F}$  (377 MHz) -60.83.

**6** was obtained using the general procedure in 50% yield.

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 8.25 (apparent s, 2H), 8.00 (apparent s, 1H), 7.37–7.24 (m, 3H), 7.0–6.91 (apparent d, 2H) 5.53–5.39 (apparent dd, 1H), 3.59 (d, J = 10.5 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 150.30 (d, J = 12.3 Hz), 141.59, 129.85 (q, J = 32.8), 128.9 (br s), 126.56 (d, J = 4.0 Hz), 125.07 (q, J = 269.8 Hz), 123.40 (q, J = 273.2 Hz), 121.07 (br s), 116.84 (q, J = 31.9 Hz), 112.75, 52.81 (d, J = 147.1 Hz), 53.06 (d, J = 6.5 Hz).  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 18.64.  $^{19}\text{F}$  (377 MHz) -59.25 (s, 3F), -61.21 (s, 6F).

**7** was obtained using the general procedure in 48% yield

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz) 7.49–7.44 (m, 2H), 7.41 (br s, 2H), 7.37–7.30 (apparent d, 3H), 7.02 (br s, 1H), 5.19–5.07 (apparent dd, 1H), 3.94–3.75 (m, 2H), 1.41–1.36 (m, 2H), 1.34–1.05 (m, 19H), 0.88–0.78 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 149.56 (d, J = 3.0 Hz), 149.19 (d, J = 12.0 Hz), 133.7 (J = 0.8 Hz), 130.68 (q, J = 31.9 Hz), 127.97 (d, J = 5.3 Hz), 124.7 (d, J = 2.1 Hz), 123.7 (q, J = 272.9 Hz), 113.05, 108.37, 65.46 (d, J = 6.6 Hz), 53.32 (d, J = 149.9 Hz), 34.18, 31.14, 31.10, 30.05, 29.99, 28.55 (d, J = 2.1 Hz), 25.03, 22.00, 13.84.  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 19.34.  $^{19}\text{F}$  (377 MHz) -61.78.

**8** was obtained using the general procedure in 46% yield

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz), 8.25 (br s, 2H), 7.99 (br s, 1H), 7.39–7.32 (apparent d, 2H), 7.29–7.19 (m, 1H), 6.99–6.91 (apparent d, 2H), 5.50–5.36 (apparent dd, 1H), 4.11–3.96 (m, 2H), 3.54–3.40 (m, 4H), 3.39–3.32 (m, 2H), 3.19 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 150.33 (d, J = 13.3 Hz), 147.7, 129.89 (q, J = 32.15 Hz), 128.94 (br s), 126.15 (q, J = 269.8), 126.11 (d, J = 3.1 Hz), 123.44 (q, J = 273.62 Hz), 121.10, 116.87 (q, J = 31.9 Hz), 112.79, 71.16, 69.71 (d, J = 5.1 Hz), 69.52, 65.18 (d, J = 6.3 Hz), 58.01, 53.21 (d, J = 147.9 Hz).  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 17.75.  $^{19}\text{F}$  (377 MHz) -59.26 (s, 3F), -61.20 (s, 6F).

**9** was obtained using the general procedure in 41% yield

NMR (dmso-*d*<sub>6</sub>,  $\delta$  in ppm):  $^1\text{H}$  (400.25 MHz), 8.20 (br s, 2H), 7.88 (br s, 1H), 7.28 (br s, 2H), 6.97 (br s, 1H), 5.28–4.99 (apparent d, 1H), 4.04–3.80 (m, 2H), 3.54–3.31 (m, 8H), 3.17 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz)  $\delta$ , 149.26 (d, J = 13.1 Hz), 143.81, 130.60 (q, J = 32.1 Hz), 129.43 (q, J = 32.4 Hz), 128.70 (br s), 123.58 (q, J = 272.5 Hz), 123.51 (q, J = 273.5 Hz), 120.00 (br s), 112.24, 107.61, 71.14, 70.23 (d, J = 4.7 Hz), 69.39, 64.00 (d, J = 5.6 Hz), 57.90, 54.52 (d, J = 138 Hz).  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz) 13.46.  $^{19}\text{F}$  (377 MHz) -59.26 (s, 3F), -61.96 (s, 6F), -61.31 (s, 6F).