Safer aromatic process diluents for solvent extraction of critical metals from spent batteries

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General procedure of liquid-liquid extraction experiments

All Liquid-liquid experiments described were performed according to the following procedure. Glass Specimen Vials with a capacity of 3.5 ml were charged with equal volumes (700 ml) of the aqueous and organic phase. Unless otherwise noted the concentration for the metals in the aqueous phase was prepared to be 400 ppm. Each vial was weighted empty, after addition of the aqueous phase and after addition of the organic phase. The Vials were sealed with polyethylene push-in caps. To prevent accidental leakages during the shaking procedure each vial was further sealed with parafilm to cover the joints between glass vial and plastic cap. Prepared vials were transferred to a shaker (IKA VXR basic Vibrax®) equipped with a temperature-controlled vial holder. Unless stated otherwise, all liquid-liquid experiments were performed at a set temperature (25 °C) for a shaking time of 1 hour to reach equilibrium and a constant shaking speed of 1500 shakes per minute. After one hour of Shaking the vials were transferred to a centrifuge (Thermo Scientific Heraeus Labofuge 200) and were centrifuged at 4000 rpm for a set time of 5 minutes to achieve a quick phase separation. After very careful removal of the push-in caps a sample (400 ml) from the lower layer (in all the experiments mentioned in this work the lower layer is the aqueous phase) was transferred into a preweighed polythene ICP vial (15 ml). It is important to avoid taking any droplets of organic phase. To prevent this issue the following steps should be followed to ensure a correct transfer of the lower phase. Typically, a 1000 ml air displacement pipette was fitted with a 1000 ml tip and set to a volume of 400 ml. The control button on the pipette was pushed down with the thumb to the first stop, the tip was inserted through the top layer into the bottom layer. The force delivered by the thumb was increased slightly to push out a bubble of air from the tip. Then the force on the control button was slowly relaxed allowing liquid to rise into the tip. When no force was pressing down on the button the pipette was raised thus taking the tip out of the vial. The outside of the tip was wiped with a fresh bit of paper towel. The weight of the so loaded sample was noted, and the sample was diluted by the addition of hydrochloric acid (1M acid containing *circa* 1 ppm of either ruthenium or rhodium). If samples containing refractory metals in high oxidation states (such as Zr(IV), Nb(V) or Ta(V)) were present in the samples then 1 % oxalic acid was present in the hydrochloric acid, and the internal standard was always rhodium. In an early experiment it was found that oxalic acid causes ruthenium to disappear from the aqueous solutions, rhodium was chosen as a replacement as it has a lower rate of ligand substitution.

Analysis was performed either by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) or by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) depending on the concentration of the samples. ICP-OES was used for concentrations within the ppm-range, while ICP-MS was mainly used for concentrations in the ppt-range.

General Procedure for calculation of the distribution ratios

The ICP raw data was measured as intensity. As mentioned in the main article, the distribution ratio (*D*) is defined as the ratio of the total analytical concentration of an element in one phase (the organic phase, $\overline{[c]}$) to its total analytical concentration in the other phase (the aqueous phase,$[c]$)

$$D = \frac{\overline{[c]}}{[c]} \qquad (1)$$

Since the measured intensity is proportional to the concentration of the analyte equation 2 can be used and the calculation can be done by using the Intensities.

$$I = [c] \cdot f$$

(2)

To correct matrix effects and fluctuations during the measurement as well as differences during the sample preparation an internal standard was used (either ruthenium or rhodium). External calibration was used to verify and check the linearity of the instrument during the measurement, since intensities are only reliable within the range of linearity. First the intensities for the internal standard (IS) were corrected using equation 3

$$I_{cor.}^{Std} = \frac{I_{ini.}^{Std}}{AF} \qquad (3)$$

With $I_{cor.}^{Std}$ being the corrected internal standard intensity, $I_{ini.}^{Std}$ being the raw measured intensity of the internal standard and AF the acid fraction after dilution of the sample. The acid fraction can be calculated using equation 4.

$$AF = 1 - \left(\frac{1}{DF}\right) \qquad (4)$$

Here DF is the dilution factor. The dilution factor can be calculated by using the volumes of the used dilution acid (V_{HA}) and the used volume of the aqueous sample (V_{aq}).

$$DF = \frac{(V_{HA} + V_{aq})}{V_{aq}} \qquad (5)$$

After the raw intensities of the IS are corrected using equation 3, the sample intensities can now be corrected for matrix effects and fluctuations. Since the dilution acid contains the internal standard, any variation of the measured intensity due to instrument errors or other factors will influence the measured sample intensity in the same manner. Similar to equation 3, the correction of the sample intensities can be done using equation 6.

$$I_{cor.}^{Sample} = \frac{I_{ini.}^{Sample}}{I_{cor.}^{Std}} \qquad (6)$$

Multiplication of $I_{cor.}^{Sample}$ with the dilution factor DF gives the original Intensity that should be present in the original shaking vial in the aqueous phase. To calculate the amount of metal in the organic phase after extraction equation 7 can be used.

$$I_{cor.}^{Sample} = \frac{I_{cor.start}^{Sample} - I_{cor.}^{Sample}}{\theta} \qquad (7)$$

Here $I_{cor.start}^{Sample}$ is the intensity of the starting reference that is the sample without extraction and would be the value if no extraction would occur. $I_{cor.}^{Sample}$ is the sample after extraction and Θ is the phase ratio of organic to aqueous. The phase ratio is defined by the ration of the used volume of the organic divided by the used volume of the aqueous phase equation 8.

$$\theta = \frac{\overline{V}}{V} \qquad (8)$$

General Experimental Methods and parameters

Analytical Methods

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

Samples in the ppm-range were evaluated with a Thermo Scientific iCap Pro ICP-OES equipped with a Teledyne CETAC ASX-560 Autosampler. System setup ware recorded with Nebulizer gas flow: 0.45 l/min, Aux gas flow: 0.50 l/min, RF power: 1.150 W and a peristaltic pump speed of 45 rpm.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Samples in the ppt-range were evaluated with a Thermo Scientific iCap Q ICP-MS equipped with a CETAC ASX-520 Autosampler. All measurements were performed with KED-Mode.

Gas Chromatography with Mass Spectrometry (GC-MS)

GC-MS experiments were performed on an Agilent Technologies 7890A GC System coupled to an Agilent Technologies 5977A MSD mass detector (EI, 70 eV). The System was equipped with an HP-5MS column (30 m x 250 µm x 0.25 µm) and Helium was used as carrier gas. The injection volume was 1 µl with a viscosity delay of 2 seconds and a split ratio of 20:1 (split flow 24 ml/min). The initial temperature (setpoint) was set to 60 °C and then increased with a rate of 20 °C/min to 300 °C and held for 2 min The MS-transfer line was set to 280 °C. The complete runtime lasts 15 min in total.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H, and ^{13}C NMR spectra were recorded at room temperature on a Bruker AvanceNeo 600 device. All chemical shifts (δ) are givin relative to tetramethylsilane (TMS) and are referenced to used residual solvent signals as tabulated by Gottlieb et al.[1] or Fulmer et al.[2] Chemical shift are given with two decimals for (^{1}H) and two decimals for (^{13}C). The recorded data is reported in the following order Chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = septet, m = multiplet, br = broad signal], coupling constant (J [Hz]) and number of H-atoms).

Liquid Scintillation Counting

Radioactivity was measured with a Perkin Elmer Guardian 1414 liquid scintillation counter. All samples were tested for potential quenching effects, and the measurements were corrected according to the quenching.

Preparation of the Aqueous Phase

All Aqueous solutions that were used in the experiments were prepared in one of the following methods or by combining several prepared aqueous stock-solutions to generate the final aqueous phase that was used for the experiments.

Sodium chloride stock solution

Several experiments were performed with a different sodium chloride (NaCl) concentration. For this purpose, a strong NaCl stock solution was made by dissolving 77.3014 g od NaCl in a 250 ml volumetric flask and filled up to 250 ml final volume. The concentration of the sodium chloride solution was 5.6 M and was determined by titration with silver nitrate ($AgNO_3$). The density (ρ) was measured at room temperature (22 °C) and was 1.20 g/ml.

Potassium hexacyanocobalt(III) stock solution

An aqueous potassium hexacyanocobalat(III) solution was prepared according to a procedure described by P. S. Poskozim[3].
Cobalt(II) chloride was first dissolved in water before potassium cyanide (NaCN, 2. equiv.) were carefully added. The resulting solid was obtained by filtration and was washed several times with water. The solid was then treated with a small excess of potassium cyanide. The mixture was heated up and filtered hot, before evaporation to dryness to give a yellow solid. To further purify the complex, it was recrystallized from a small volume of hot water.

Oxoniobium oxalate stock solution

A porcelain crucible was loaded with niobium(V) oxide (3.85 grams. 28.95 mmol of niobium) and heated in a mixture of potassium sulfate (20 grams) and concentrated sulfuric acid (6.25 ml) at 400 °C overnight. The reaction mixture was cooled to room temperature before it was dissolved in a hot solution of oxalic acid (32.6 g oxalic acid in 300 ml water). The resulting mixture was filtered and concentrated ammonia was added dropwise to the filtrate until no further white solid was formed (pH = 9). The resulting niobium oxide was separated from the supernatant by centrifugation. After washing with water, the solid was dissolved in hot aqueous oxalic acid (15 g in 100 ml water), the resulting niobium solution was diluted by the addition of water until its volume was 300 ml. Concentrated ammonia was added until the pH was equal to nine. The resulting solid was washed with water before it was dissolved using oxalic acid dihydrate (14.1 g, 112 mmol) in the smallest amount of water that was possible. The resulting mixture was filtered and then diluted to a final volume of 100 ml. This forms a solution of niobium with a concentration of *circa* 27 grams per liter.

Aqueous phase with niobium and cobalt with variable sodium chloride concentration

The aqueous phase containing Nb and Co with variable sodium chloride concentration that was used for the solvent extraction experiments was made by combining the individual prepared Potassium hexacyanocobalt(III) stock solution and the Oxoniobium oxalate stock solution together with the sodium chloride (NaCl) stock solution and water to a series of preweigthed polyethylene vials (15 ml). The exact composition based on the weight of each compound is summarized in Tab. S1.

Tab. S1: preparation of the Nb, Co stock with variable NaCl concentration.

Label	Gross mass / g					
	Empty	NaCl stock	cobalt stock	niobium stock	with water	NaCl concentration mol/l
100 % NaCl	6.6643	18.5415	18.6791	18.8153	18.8165	5,6
90 % NaCl	6.6680	17.3333	17.4697	17.6058	18.6241	5,0
80 % NaCl	6.6993	16.1526	16.2894	16.4256	18.4443	4,5
70 % NaCl	6.6958	14.9856	15.1219	15.2587	18.2633	3,9
60 % NaCl	6.2059	13.8095	13.9459	14.0821	18.0715	3,4
50 % NaCl	6.7049	12.6391	12.7750	12.9109	17.9081	2,8
40 % NaCl	6.2089	11.4569	11.5930	11.7310	17.7257	2,2
30 % NaCl	6.7219	10.3232	10.4589	10.9954	17.5828	1,7
20 % NaCl	6.7181	9.1099	9.2450	9.3819	17.3785	1,1
10 % NaCl	6.6857	7.9621	8.0965	8.2309	17.2317	0,6

Aqueous phase aluminum (Al), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn) with 95 % sodium chloride concentration

A Stock solution was prepared by dissolving $MnCl_2 \cdot 4H_2O$ (5.444 g), $CoCl_2 \cdot 6H_2O$ (6.371 g), $NiCl_2 \cdot 6H_2O$ (6.255 g), $CuCl_2$ (3.326 g), $AlCl_3 \cdot 6H_2O$ (13.595 g), $CdNO_3 \cdot 4H_2O$ (3.825 g) and $ZnCl_2$ (3.11 g) in 100 ml of deionized water. The pH was measured to be 3. Then 1 ml of 3 M hydrochloric acid (HCl) was added, and the resulting solution was filled up with water to a final volume of 200 ml. The aqueous phase that was used for the solvent extraction experiment was made in a 50 ml Polyethylene vial by combining 2 ml of the metal stock solution and 38 ml of the NaCl stock solution, that was described previously. The exact composition is based on the weight and the preparations summarized in Tab. S2

Tab. S2: preparation of the stock solution containing Al, Cd, Co, Cu, Mn, Ni, Zn with constant NaCl concentration

Label	gross mass / g			
	Empty	Metal stock solution	NaCl stock solution	NaCl concentration mol/l
95 % NaCl	14.9519	17.2096	62.6847	5.3

Aqueous phase containing aluminum (Al), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn) with variable acid concentration

A Stock solution was prepared by dissolving $MnCl_2 \cdot 4H_2O$ (5.444 g), $CoCl_2 \cdot 6H_2O$ (6.371 g), $NiCl_2 \cdot 6H_2O$ (6.255 g), $CuCl_2$ (3.326 g), $AlCl_3 \cdot 6H_2O$ (13.595 g), $CdNO_3 \cdot 4H_2O$ (3.825 g) and $ZnCl_2$ (3.11 g) in 100 ml of deionized water. The pH was measured to be 3. Then 1 ml of 3 M hydrochloric acid (HCl) was added, and the resulting solution was filled up with

water to a final volume of 200 ml. The aqueous phase that was used for the solvent extraction experiment was made in a series of 15 ml Polyethylene vials by combining the metal stock solution (Aqueous phase containing aluminum (Al), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn)) together with sulfuric acid (H_2SO_4) and water to dilute to the appropriate concentration. The exact composition is based on the weight and the preparations summarized in Tab. S3.

Tab. S3: preparation of the stock solution containing Al, Cd, Co, Cu, Mn, Ni, Zn with variable sulfuric acid concentration.

Label Nominal acid %	Gross mass / g Empty	Metal stock	Acid (H_2SO_4)	Water
0.2	6.9179	7.2126	7.6427	16.9428
0.1	6.8967	7.186	7.4057	16.9332
0.05	6.9051	7.1944	8.2027	16.8836
0.02	6.9029	7.1929	7.6021	16.8787
0.01	6.935	7.2263	7.4356	16.9229
0.005	6.9364	7.2247	7.3351	16.9295
0	6.8306	7.1214	7.1214	16.7925

Aqueous phase containing cobalt (Co), copper (Cu), zinc (Zn) and magnesium (Mg) with variable sodium chloride concentration

A stock solution was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (1.56 g, 9.77 mmol), $MgCl_2$ (1.58 g, 1.5 mmol), $ZnSO_4 \cdot 2H_2O$ (1.77 g, 6.16 mmol), $CoCl_2 \cdot 6H_2O$ (1.61 g, 5.53 mmol) in water. The aqueous phase that was used for the solvent extraction experiment was made in a series of 15 ml Polyethylene vials by combining the metal stock solution (Aqueous phase containing aluminum (Al), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn)) together with the sodium chloride stock solution and water to dilute to the appropriate concentration. The exact composition is based on the weight and the preparations summarized in Tab. S4.

Tab. S4: preparation of the stock solution containing Al, Cd, Co, Cu, Mn, Ni, Zn with variable sodium chloride concentration.

Label	Gross mass /g Empty	water	NaCl stock solution	Metal stock	NaCl concentration mol/l
100 % NaCl	13.9803	13.9803	49.4872	51.1069	5,6
90 % NaCl	13.9348	16.9982	48.9050	50.5263	5,0
80 % NaCl	13.9763	20.0561	48.5555	50.1770	4,5
70 % NaCl	13.9695	23.0255	47.9873	49.6112	3,9
60 % NaCl	13.9843	26.0362	47.4010	49.0360	3,4
50 % NaCl	13.9411	29.0360	46.8541	48.4841	2,8
40 % NaCl	13.9406	32.0441	46.4108	48.0308	2,2
30 % NaCl	14.1169	35.0876	45.7422	41.3633	1,7
20 % NaCl	13.9339	31.8591	45.0318	48.6536	1,1
10 % NaCl	14.0229	40.9079	44.5151	46.1279	0,6

Preparation of the organic Phase

The solvents (organic phase containing the diluent and the extractant) that were used for the solvent extraction experiments were prepared according to the following procedure. A glass vial was weighed, and the mass was noted. Then an appropriate volume of the used extractant was transferred to the glass vial via pipetting and the

mass was noted. Then the appropriate volume of the diluent was pipetted into the glass vial, and the solvent was shaken until both phases mixed and the solvent was completely homogenized. Again, the end weight was noted. By knowing the density of each compound added and the weight. The end concentration was calculated. An overview of all prepared organic phases and the concentration is summarized in Tab. S5.

Tab. S5: Summary of the solvent compositions that were used as the organic phase for the solvent extraction experiments.

Solvent composition Concentration Extractant (v/v) / %	Extractant	Diluent
30	Aliquat 336	Eucalyptol
30	Aliquat 336	Ethylbenzene
30	Aliquat 336	1,4-di-tert-pentylbenzene
30	Aliquat 336	1-methyl-4-(tert-pentyl) benzene
30	Aliquat 336	Solvesso™ 150ND
30	Aliquat 336	Solvesso™ 200
30	Aliquat 336	tert-butylbenzene (TBB)
30	Aliquat 336	1,3-Diisopropylbenzene
30	Aliquat 336	(3-butoxypropyl) benzene
10	Aliquat 336	Ethylbenzene
10	Aliquat 336	1,4-di-tert-pentylbenzene
10	Aliquat 336	1-methyl-4-(tert-pentyl)benzene
10	Aliquat 336	Solvesso 150 ND
30	Cyanex 272	Solvesso 150 ND
30	Cyanex 272	HVO100
30	Cyanex 272	1,4-di-tert-pentylbenzene
30	Cyanex 272	tert-butylbenzene (TBB)
30	Cyanex 272	1-methyl-4-(tert-pentyl) benzene
30	DEHPA	HVO100
30	DEHPA	1,4-di-tert-pentylbenzene
30	DEHPA	1-methyl-4-(tert-pentyl) benzene

Oxidation of diluents to the corresponding esters

The oxidation of the diluents with potassium permanganate ($KMnO_4$) was performed according to the chemistry by Morrison and Boyd[4] and the methanol (MeOH) derivatisation of the acids were performed following a procedure reported by Xiao[5]. Analysis of the ester derivates were performed using a modified GC-MS method reported by Xiao[5]. The injection volume was 1 µl with a viscosity delay of 2 seconds and a split ratio of 20:1 (split flow 24 ml/min). The initial temperature (setpoint) was set to 60 °C and then increased with a rate of 10 °C/min to 280 °C and held for 2 min. The MS transfer line was heated to 280 °C. For mass spectrometry the ionization energy was 70 eV. The complete runtime lasts 26 min in total. Compounds were identified by comparison of the mass spectra with those in the NIST Mass Spectral Library (NIST 20).

Oxidation of Solvesso 150

A round bottom flask (1 L) was charged with 400 ml of an aqueous potassium permanganate solution (24 g, 0.152 mol $KMnO_4$ in 400 ml distilled water) and 4 ml of Solvesso 150. The Flask was equipped with a condenser and was heated until reflux for 12 hours. The reaction was allowed to cool down to room temperature before the brownish-coloured suspension was filtered using a glass fibre disk in a Büchner funnel using suction. The aqueous filtrate was acidified with concentrated H_2SO_4 until slightly acidic and then extracted with dichloromethane (DCM) (3 x 40 ml) to recover unreacted starting material. The aqueous phase was evaporated under reduced pressure. The crude product was obtained as a white solid (17.9 g) and was used without further purification. A 250 ml round bottom flask was charged with the crude acid material and 100 ml of methanol (MeOH) and 5 ml of concentrated sulfuric acid (H_2SO_4) were added. The flask was equipped with a condenser, and the reaction mixture was stirred and heated to 65 °C for 24 hours. After completion the reaction mixture was allowed to cool down to room temperature before the present sulfuric acid was neutralized with sodium bicarbonate until the solution was neutral. The mixture was extracted with cyclohexane (5 x 40 ml) and the organic phases were combined, dried over sodium sulfate (Na_2SO_4), filtered and concentrated under reduced pressure. The esters were obtained as an amberlike coloured liquid (0.7508 g).

Oxidation of 1-methyl-4-(tert-pentyl)benzene

A round bottom flask (1 L) was charged with 400 ml of an aqueous potassium permanganate solution (24 g, 0.152 mol $KMnO_4$ in 400 ml distilled water) and 7 ml of **1-methyl-4-(tert-pentyl)benzene**. The Flask was equipped with a condenser and was heated until reflux for 12 hours. The reaction was allowed to cool down to room temperature. The purple-coloured mixture was treated with ethanol to reduce the remaining $KMnO_4$ into manganese dioxide. The manganese dioxide (MnO_2) was removed The filtrate was extracted several times with dichlormethane (DCM) (3 x 40 ml) to recover unreacted staring material. The aqueous phase was evaporated under reduced pressure, and the crude acid (3 g) was obtained as a white solid and was used without further purification. A 250 ml round bottom flask was charged with the crude acid material and 100 ml of methanol (MeOH) and 5 ml of concentrated sulfuric acid (H_2SO_4) were added. The flask was equipped with a condenser, and the reaction mixture was stirred and heated to 65 °C for 24 hours. After completion the reaction mixture was allowed to cool down to room temperature before the present sulfuric acid was neutralized with sodium bicarbonate until the solution was neutral. The mixture was extracted with cyclohexane (5 x 40 ml), dried over sodium sulfate (Na_2SO_4), filtered and concentrated under reduced pressure. The esters were obtained as a colourless/slightly yellowish liquid (0.9755 g).

Oxidation of 1,4-di-tert-pentylbenzene

A round bottom flask (1 L) was charged with 400 ml of an aqueous potassium permanganate solution (24 g, 0.152 mol $KMnO_4$ in 400 ml distilled water) and 7 ml of **1,4-di-tert-pentylbenzene**. The flask was equipped with a condenser and heated until reflux for 12 hours. The reaction mixture was allowed to cool down to room temperature before the purple-coloured suspension was filtered before being shaken with dichloromethane (5 x 50 ml). The dichloromethane extracts were combined and were allowed to stand over anhydrous sodium sulfate before being filtered. After filtration the dichloromethane was removed using a rotary evaporator furnishing a heavy oil (*circa* 5 ml, 4.5 g, 72 % recovered starting material)

Bibliography

(1) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem.* **1997**, *62* (21), 7512–7515. https://doi.org/10.1021/jo971176v.

(2) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179. https://doi.org/10.1021/om100106e.

(3) Poskozim, P. S. The Preparation of Potassium Hexacyanocobaltate(III). *J. Chem. Educ.* **1969**, *46* (6), 384. https://doi.org/10.1021/ed046p384.

(4) Robert Thornton Morrison; Robert Neilson Boyd. *Organic Chemistry*, Fifth Edition.; Allzn and Bacon, Inc.: Newton, Massachusetts, 1987.

(5) Xiao, J. B. Identification of Organic Acids and Quantification of Dicarboxylic Acids in Bayer Process Liquors by GC–MS. *Chromatographia* **2007**, *65* (3), 185–190. https://doi.org/10.1365/s10337-006-0135-0.

Physicochemical Properties

Viscosity

Viscosity was measured was calculated according to equation 9

$$\eta_{compound} = \eta_{reference} \frac{\rho_{compound} t_{compound}}{\rho_{reference} t_{reference}} \quad (9)$$

1,4-di-tert-pentylbenzene		**1-methyl-4-(tert-pentyl) benzene**		**Water reference**	
Temperature / °C	25 ± 1	**Temperature / °C**	25 ± 1	**Temperature / °C**	25 ± 1
Measurements	recorded time / s	Measurements	recorded time / s	Measurements	recorded time / s
t1	19,84	t1	4,83	t1	3,86
t2	20	t2	4,96	t2	3,8
t3	19,14	t3	4,92	t3	3,92
t4	19,48	t4	4,91	t4	3,97
t5	19,35	t5	5,04	t5	3,98
t6	19,34	t6	4,89	t6	4,18

Solubility via Liquid Scintillation Counting (LSC)

Measurement data from LSC is listed below. Sample name 16 refers to 1-methyl-4-(tert-pentyl) benzene and samplename 15 refers to 1,4-di-tert-pentylbenzene.

Name	POS	DPM1	Rack	CPM1	Rackpos	Ctime	SQPI	SQPE	CPM
blank + tritium	1	2202292,8	59	709473,2	1	4	106,84	749,27	769303,8
16C	2	1292,9	59	449,1	2	5327	116,25	759,66	467,6
16B	3	1316,4	59	452,2	3	5290	116,02	758,18	470,9
16A	4	1267,9	59	436,8	4	5468	116,3	758,6	455,5
15C	5	1690,6	59	597	5	4014	116,2	761,57	620,88
15B	6	1586,1	59	557,6	6	4301	116,44	762,29	579,2
15A	7	1471,9	59	515,8	7	4633	116,84	760,85	537,7

blank_1	8	15,2	59	5,3	8	7200	347,77	759,86	16
blank_2	9	16,5	59	4,9	9	7200	334,54	737,9	16,2

Solubility via UV/Vis

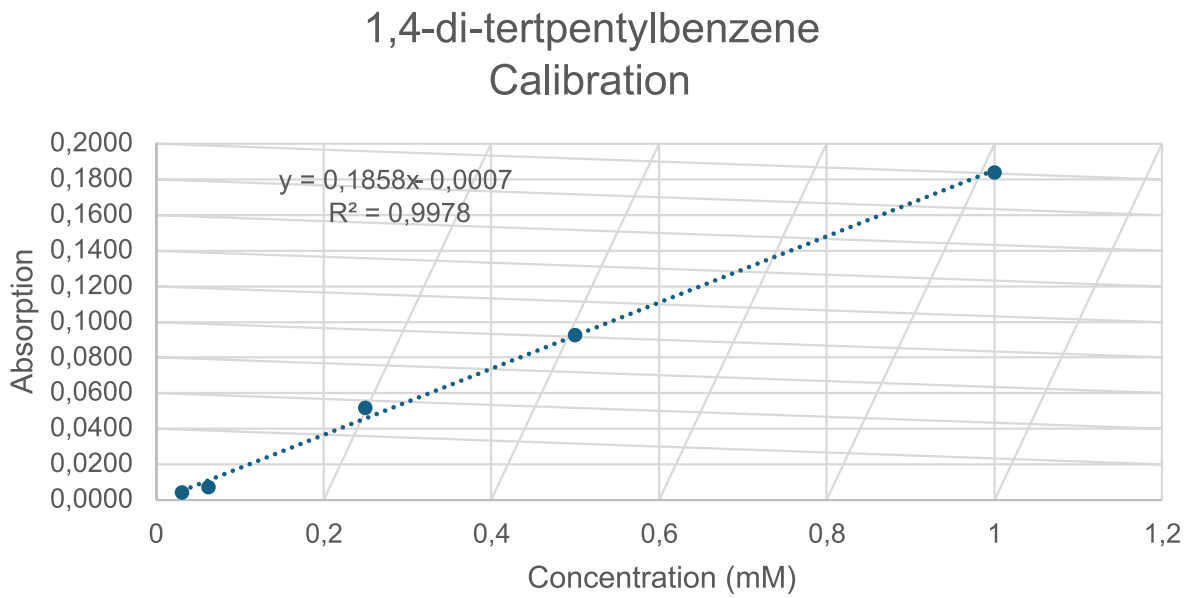

Figure S1: Calibration curve for 1,4-di-tertpentylbenzene.

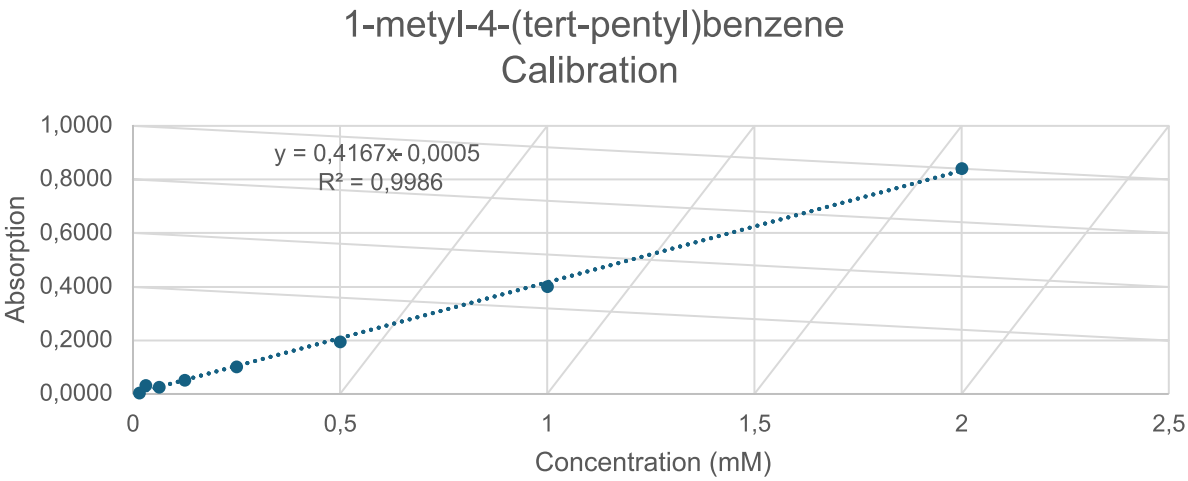

Figure S2: Calibration curve for 1,4-di-tertpentylbenzene.

Flash point

Experiment	Temperature / °C	Experiment	Temperature / °C
1,4-di-tert-pentylbenzene	133	1-metyl-4-(tert-pentyl)benzene	93
1,4-di-tert-pentylbenzene	137	1-metyl-4-(tert-pentyl)benzene	89
1,4-di-tert-pentylbenzene	131	1-metyl-4-(tert-pentyl)benzene	87

GC-Chromatograms

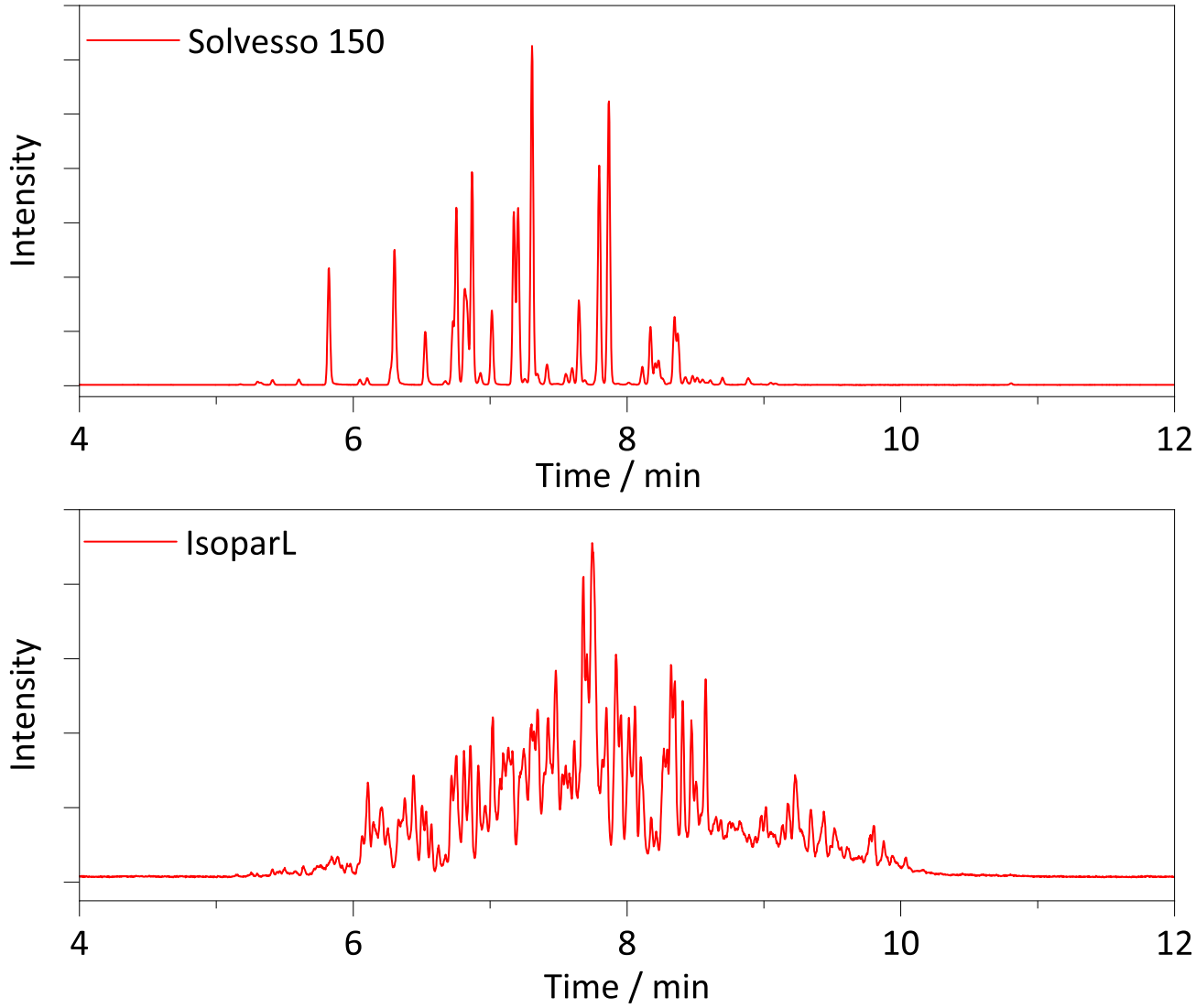

Figure S3*:* GC-Chromatograms of unmodified samples of Solvesso150ND (top) and IsoparL (bottom). Both diluents are common process chemicals in solvent extraction application.

Spectra

1,4-di-tert-pentylbenzene

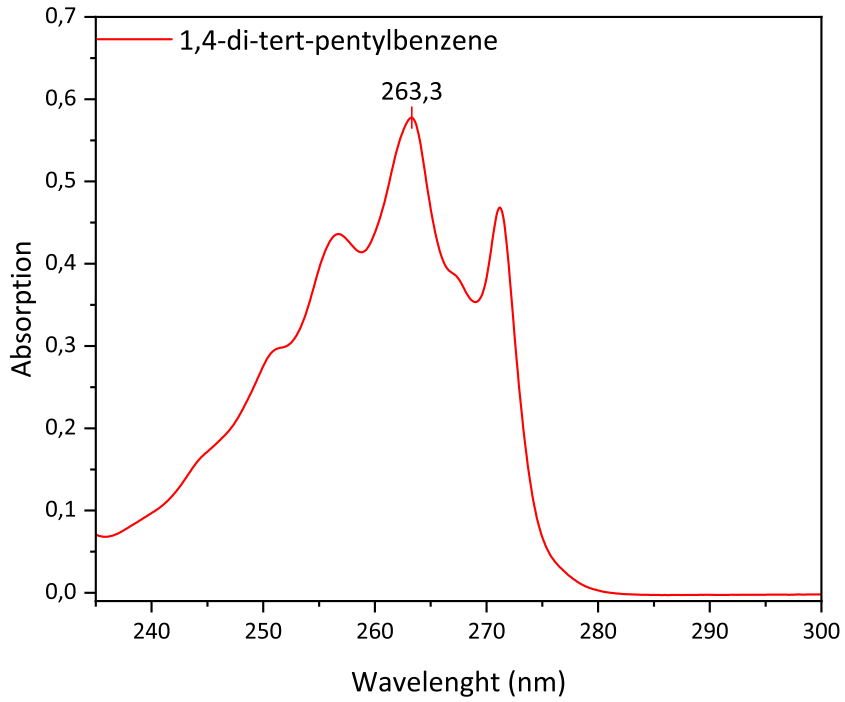

Figure S4: UV-Vis spectra of 1,4-di-tert-pentybenzene.

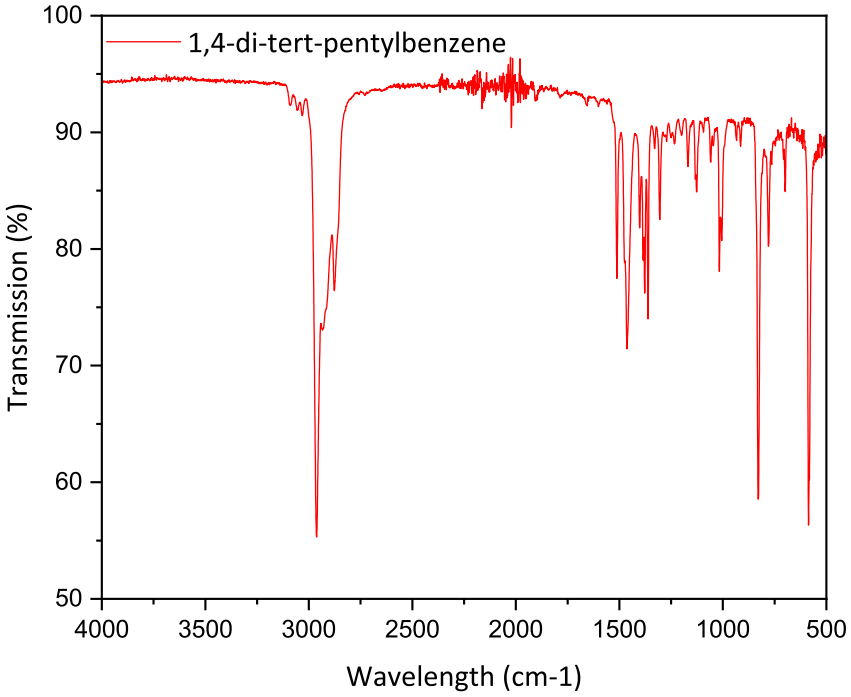

Figure S5*:* FTIR spectra of 1,4-di-tert-pentybenzene.

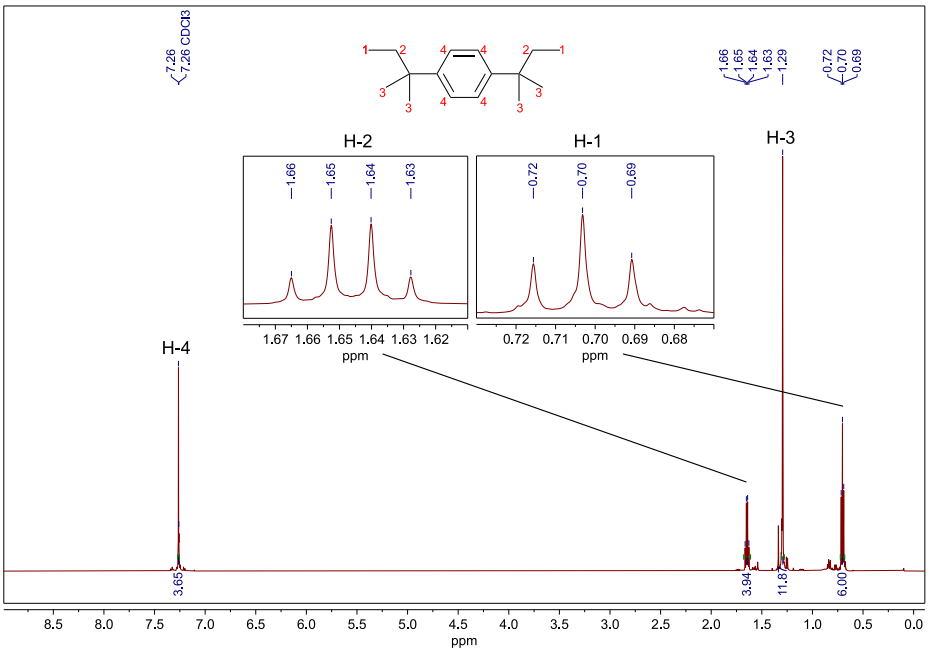

Figure S6*:* H-NMR spectra of 1,4-di-tert-pentybenzene.

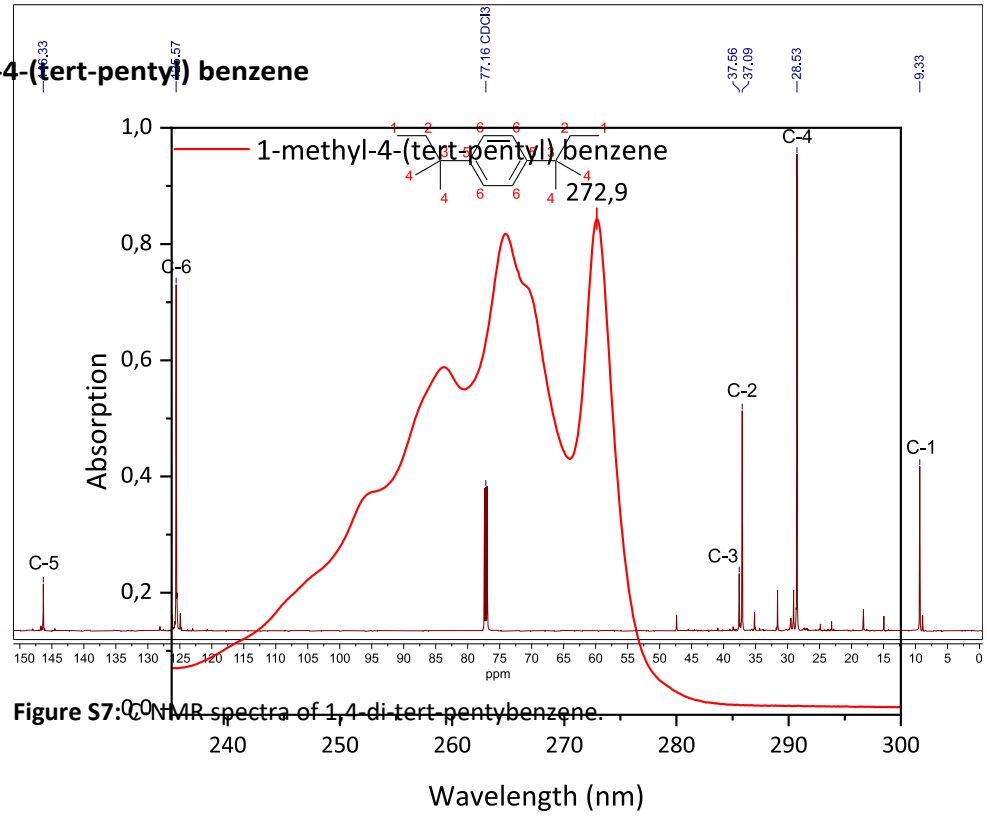

Figure S7: C-NMR spectra of 1,4-di-tert-pentybenzene.

Figure S8: UV-Vis spectra of 1-methyl-4-(tert-pentyl) benzene.

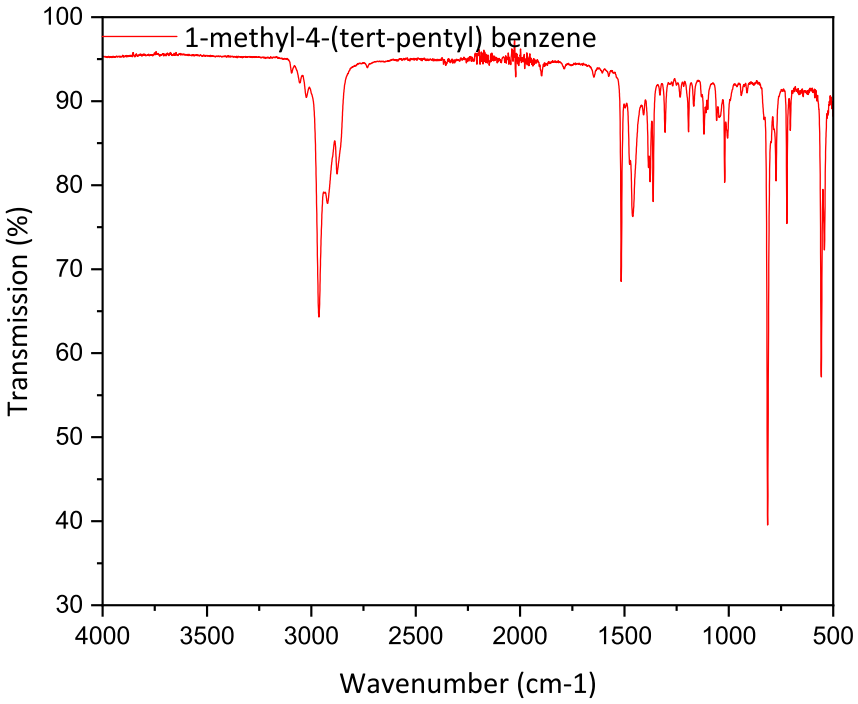

Figure S9*:* FTIR spectra of 1-methyl-4-(tert-pentyl) benzene.

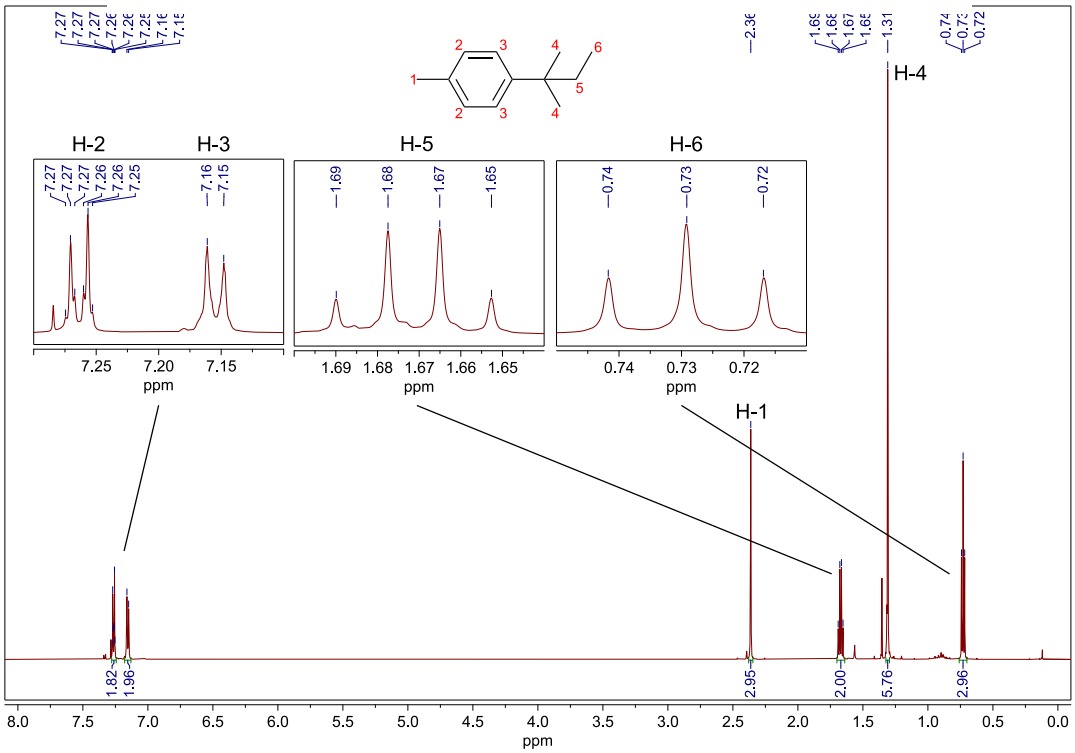

Figure S10*:* H-NMR spectra of 1-methyl-4-(tert-pentyl) benzene.

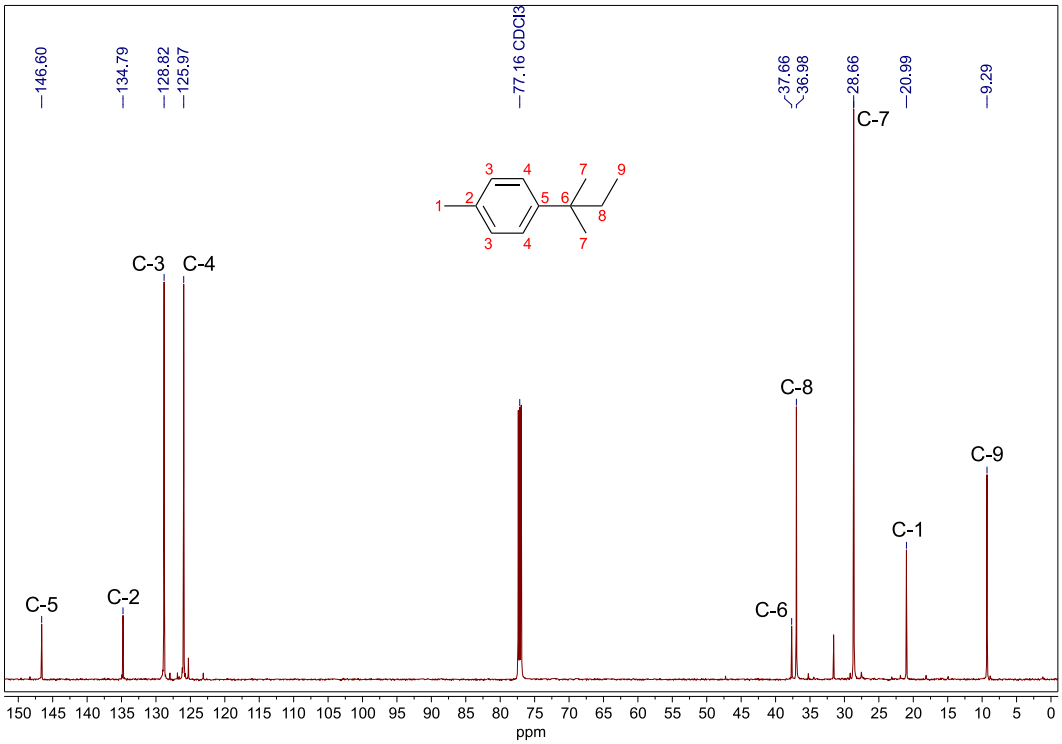

Figure S11: C-NMR Spectra of 1-methyl-4-(tert-pentyl) benzene.