SUPPLEMENTARY INFORMATION

REDUCTION OF HEXAVALENT CHROMIUM USING NATURALLY-DERIVED FLAVONOIDS

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This supplementary information section provides additional information of interest to readers. Synthesis of both QSA and QPP: including the structural characterization of QCR, QSA and QPP; LC-MS of reaction products and UV-visible spectrum, reaction kinetics and time dependence analyses data.

Synthesis of QSA

Briefly, 10 ml of concentrated sulfuric acid was added to 2.5 g of anhydrous quercetin in a 50 ml round bottomed flask. The reaction mixture was vigorously stirred for 3 hrs at 80^{o}C in a sand bath under reflux conditions. This was followed by the addition of 12.5 mL of water to the cold reaction mixture with continuous stirring. An orange red precipitate was formed that was then separated through centrifugation and the product was recrystallized 3 times from saturated water solution. QSA was extracted using hexane to remove any present organics. This was followed by vacuum filtration while the resulting QSA was characterized using UV-visible spectroscopy, ESI-MS, H^{1}-NMR and C-13 NMR spectroscopy.

Synthesis of QPP

Briefly, 302.24 mg of QCR and 15 mL of acetonitrile anhydrous were transferred into a three necked round bottomed flask. The flask was placed in a styrofoam box filled with NaCl and ice. The styrofoam box was placed on top of a stirrer with a needle inserted with a source of nitrogen. The temperature was maintained at -10ºC or below. 2.00 mL of CCl_4, 1.5 mL of diisopropyl ethyl and 50.00 mg of 4-dimehtyl aminopyridine were added to the flask, followed by drop wise addition of 3.00 mL of dibenzyl phosphate. The setup was stirred for 45 minutes after which the reaction was quenched using 16 mL of KH_2PO_4 and 50 mL of acetonitrile. Then it was continuously stirred for about 2 hours to allow the solution to revert back to room temperature. Ethyl acetate was used for extraction purposes. The resultant organic extracts were washed with water and saturated NaCl before drying over anhydrous sodium sulfate powder and concentrated in vacuo. Preparative separation was achieved by passing the crude extract product through silica column using Telydyne/5 CO combiflash companion flash chromatography system capable of monitoring fractions at two different wavelengths. Debenzylation was achieved through catalytic hydrogenation at ambient room temperature under atmospheric pressure of hydrogen gas.

Captions for Supplementary Figures

Supplementary Figure 1: Negative ion ESI-MS of (A) MS/MS fragmentation of organic phase extract after treatment with Cr(VI), m/z 950.92 (B) QCR organic phase in acidic media without Cr(VI), inset QCR in pentanol only, (C) aqueous phase extract after treatment with Cr(VI),

Supplementary Figure 2: Suggested QCr- Cr(III) complexes

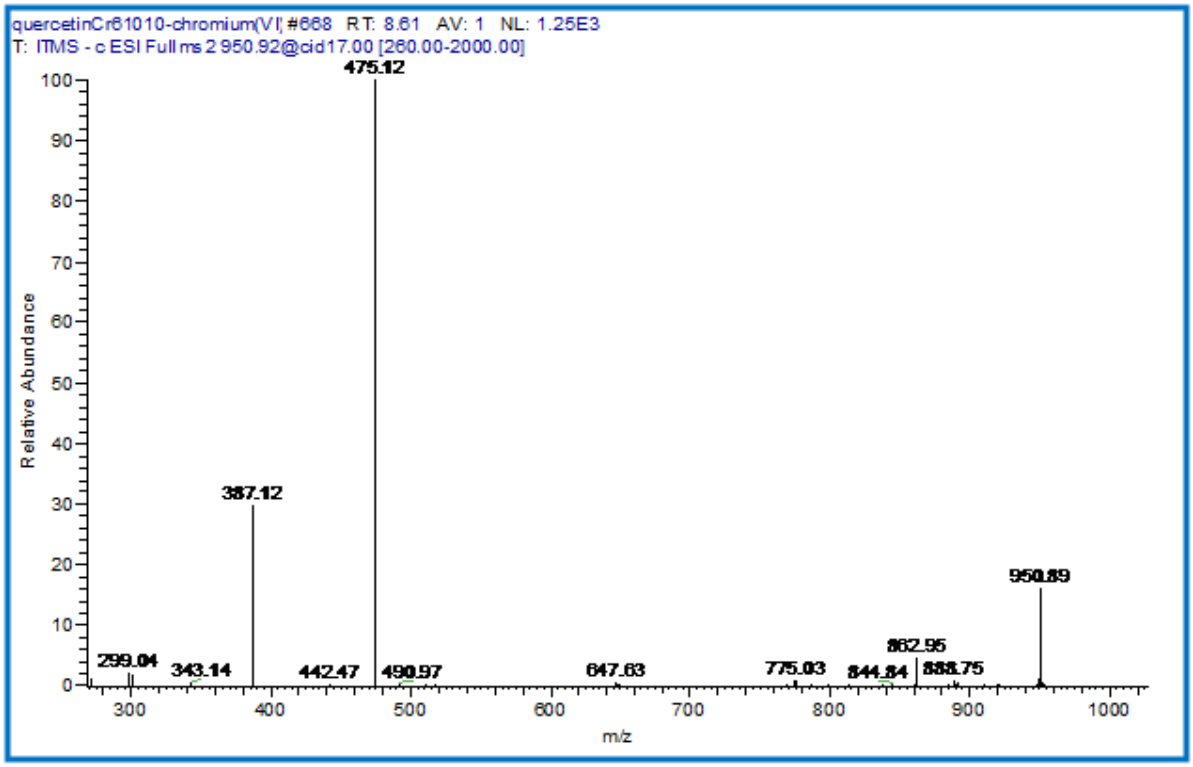
Supplementary Figure 3: Absorption spectra of the [A] aqueous and [B] organic phase extract containing a reaction mixture of 1:2 and 1:3 QCR:Cr(VI) respectively. [QCR] $1.5x10^{-3}$M, [HCl] 0.5 M at 25^{o}C under vacuum conditions

Supplementary Figure 4: Job's method of continuous variation for the reaction of Cr(VI) and QSA, [Inset; QPP]; equimolar concentration of $1.33x\ 10^{-5}$ mol/L used , pH 2.0.

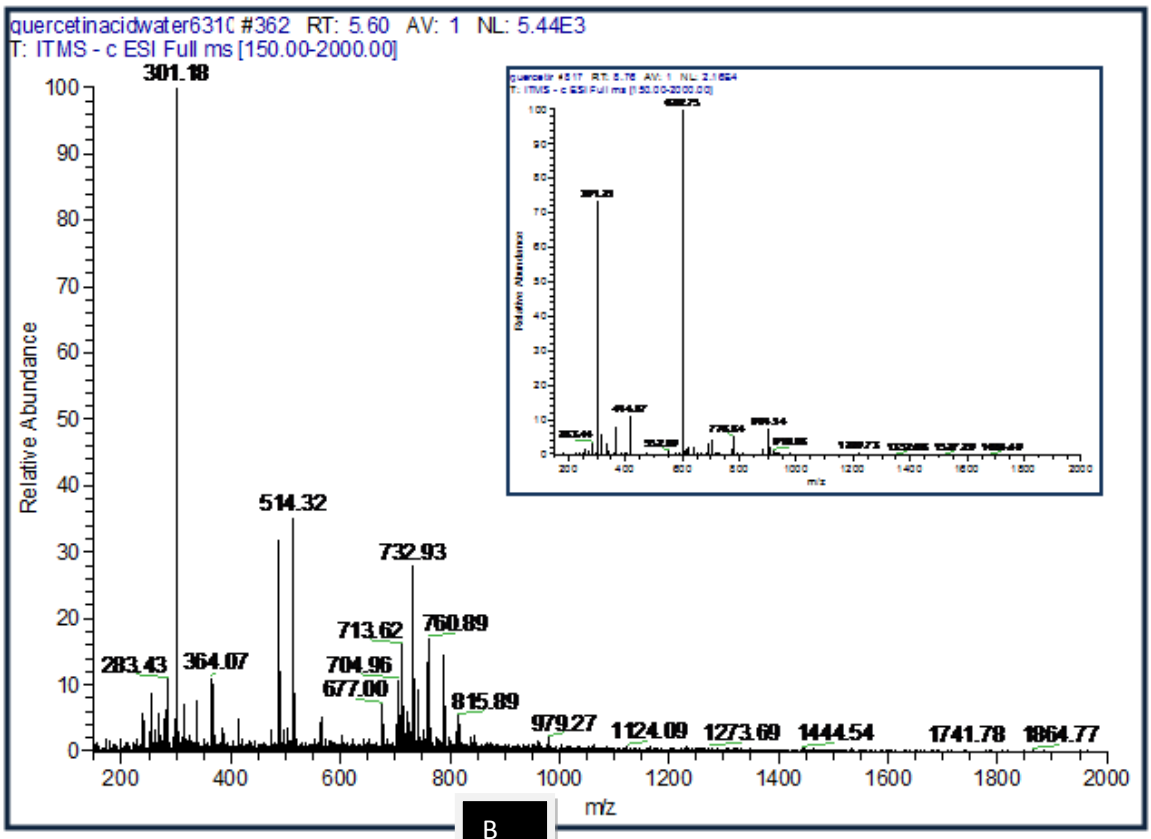
Supplementary Figure 5: Time dependence analysis for flavonoid reaction with Cr(VI); [QSA] 1.33X10^{-4} M, [Cr(VI)] 3.3X10^{-5} M, 1.0 mg PdNPs, [HCl] 0.5 M, [QPP] 4.09 X10^{-4}M.

Supplementary Figure 6:[Cr(VI)] 3.3e-5M, [QSA] 1.33e-4M, 1.0 mg PdNPs, [HCl] 0.5 M. Reaction carried out 45^{o}C

Supplementary Figure 7: Cr(VI)] 3.3x10^{-5}M, [QSA] 1.33x10^{-4}M – 1.33x10^{-1}M, 1.0 mg PdNPs, [HCl] 0.5 M. Reaction carried out 45^{o}C.



A



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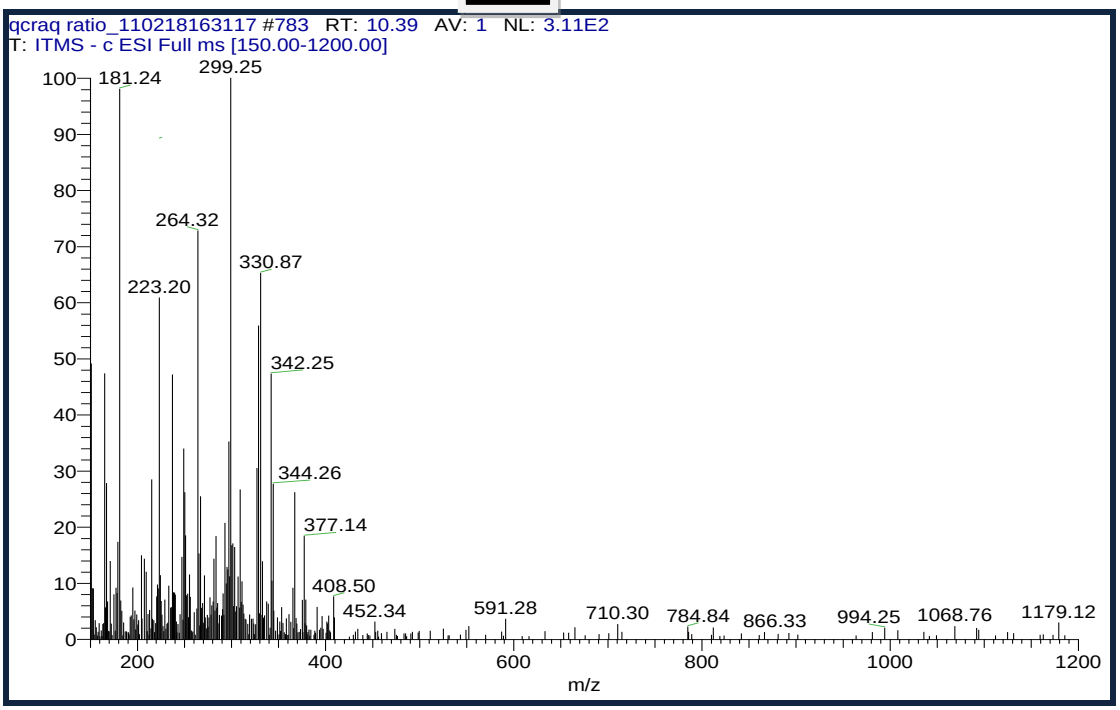


C

Supplementary Figure 1

Table S1: Major NMR Chemical Shifts and Solubility of QCR, QSA and QPP Derivatives

	H^1-NMR δ ppm	C-13NMR δ ppm	P-NMR δ ppm	Solubility	Reference
QCR	9.2-12.5 (s, 5 OH), 7.7(d, 1H), 7.6(dd, 1H), 6.9(d, 1H), 6.4(d, 1H), 6.2(d, 1H)	-	-	<10 µg/mL	[29]
QSA	6.2 (d, 1H), 6.4 (d, 1H), 7.6 (d, 1H), 7.9 (d,1H), 5.0(broad OH)	175.9, 164.0, 160.7, 156.2, 146.1, 145.5, 144.2, 136.1, 131.0, 120.9, 117.8, 115.5, 103.0, 98.3, 93.4	-	27.32 mg/mL [30]	
QPP	8.25 (broad *s,* -OH) (phosphate)), 6.56-7.47 (m, 5H, aromatic)	-	0.516 (*s*, 1P), δ (negative ppm) 4.62 (s, 1P), 4.96 (s, 1P), 5.17 (s, 1P), 5.77 (s, 1P)	848 mg/ml	[29]

Table S2: Experimental set up for the interaction of QCR with Cr(VI)

EXPT #	[Cr(VI)]M 2000µL	[QCR] M 2000µL	[HCl] M 200µL	Rate
1	**$1.5x10^{-3}$**	**$5x10^{-6}$**	**0.5**	**$1.09 x10^{-5}$**
2	**$1.5x10^{-3}$**	**$1 x 10^{-5}$**	**0.5**	**$1.08 x10^{-5}$**
3	**$3 x 10^{-3}$**	**$5x10^{-6}$**	**0.5**	**$2.38 x10^{-5}$**
4	**$1.5x10^{-3}$**	**$5x10^{-6}$**	**1.0**	**$1.24 x10^{-5}$**

Table S3: Experimental set up for the interaction of QPP with Cr(VI)

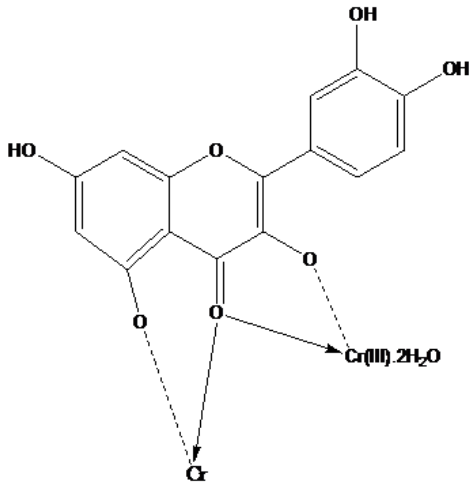
EXP #	[Cr(VI)] M	[QPP] M	[HCl] M	Rate (M/min)
1	3.3×10^{-5}	4.09×10^{-5}	0.1	1.24×10^{-3}
2	3.3×10^{-5}	4.09×10^{-5}	0.2	1.52×10^{-3}
3	6.60×10^{-5}	4.09×10^{-5}	0.1	3.14×10^{-3}
4	6.60×10^{-5}	8.18×10^{-5}	0.1	1.25×10^{-3}

Table S4. Comparative study with other reductants

Reductant	Initial Cr(VI) mM	Rate constant (k) mol-1.L.S-1	Reaction order	Reaction time (mins)	Reference
Formic acid/PdNPs	7.14	1.0878	Pseudo-first	5	21
Sulfur/PdNPs	0.40	0.1078	Pseudo-first	60	19
1-Butanol	11.8	Not reported	Pseudo-first	15	35
Hydrogen sulfide	0.02	31.9	Pseudo-first	70	34
Lactic acid	0.25	4.74	Pseudo-first	2.5	36
PAA/PdNPs	0.0005	0.2885	Pseudo-first	14	20
QCR	1.5	0.0931	Pseudo-first	30	This work
QSA	0.033	0.7073	Pseudo-first	60	This work
QPP	0.033	0.0259	Pseudo-first	60	This work

Table S5. Negative ESI-MS/MS fragmentation patterns

475.12	**343.20**	**299.08**	**271.21**	**179.06**
776.92	688.74	475.05	387.1	299.01
688.92	387.10	299.12	271.22	179.01



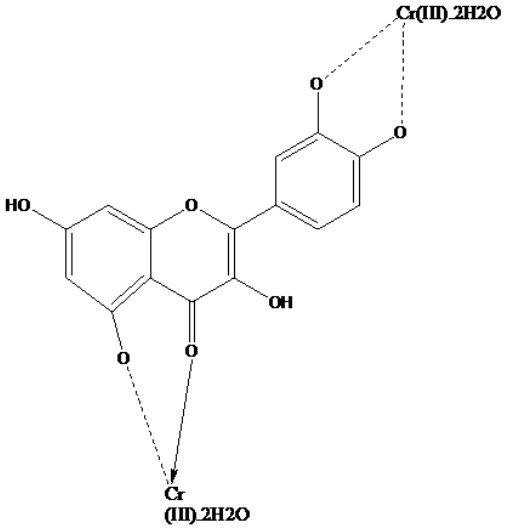
Cr
(III).2H2O

$C_{15}H_{16}Cr_2O_{11}$

Exact Mass: 475.95

Mol. Wt.: 476.27

m/e: 475.95 (100.0%), 476.95 (39.2%), 477.95 (12.9%), 473.96 (10.3%), 474.96 (2.9%), 478.95 (2.3%), 477.96 (1.4%)



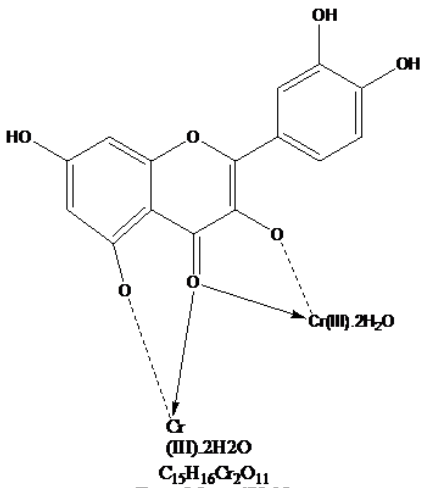
Cr
(III).2H2O

$C_{15}H_{15}Cr_2O_{11}$

Exact Mass: 474.94

Mol. Wt.: 475.27

m/e: 474.94 (100.0%), 475.94 (22.7%), 475.95 (16.9%), 472.95 (10.4%), 476.95 (7.4%), 476.94 (6.9%), 473.95 (2.9%), 477.94 (1.6%), 477.95 (1.5%)



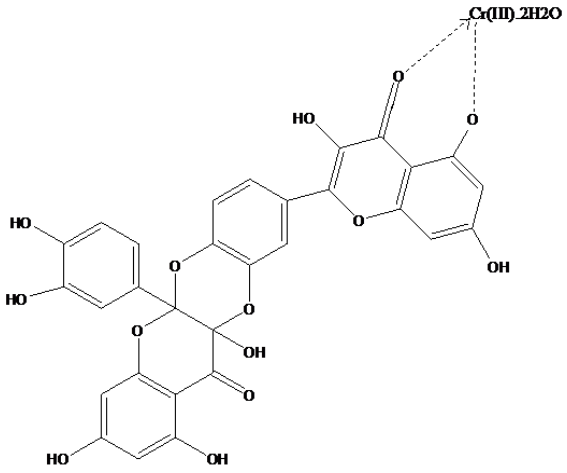
Cr
(III).2H2O

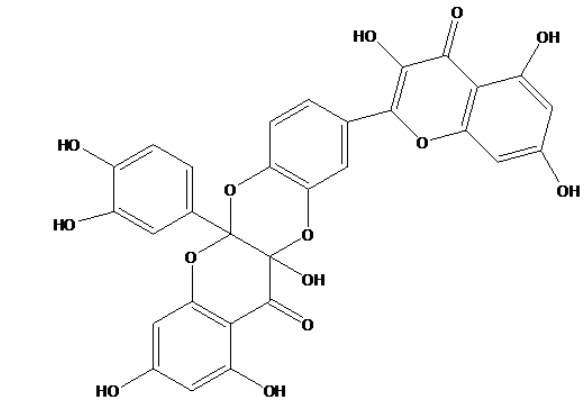
$C_{15}H_{16}Cr_2O_{11}$

Exact Mass: 475.95

Mol. Wt.: 476.27

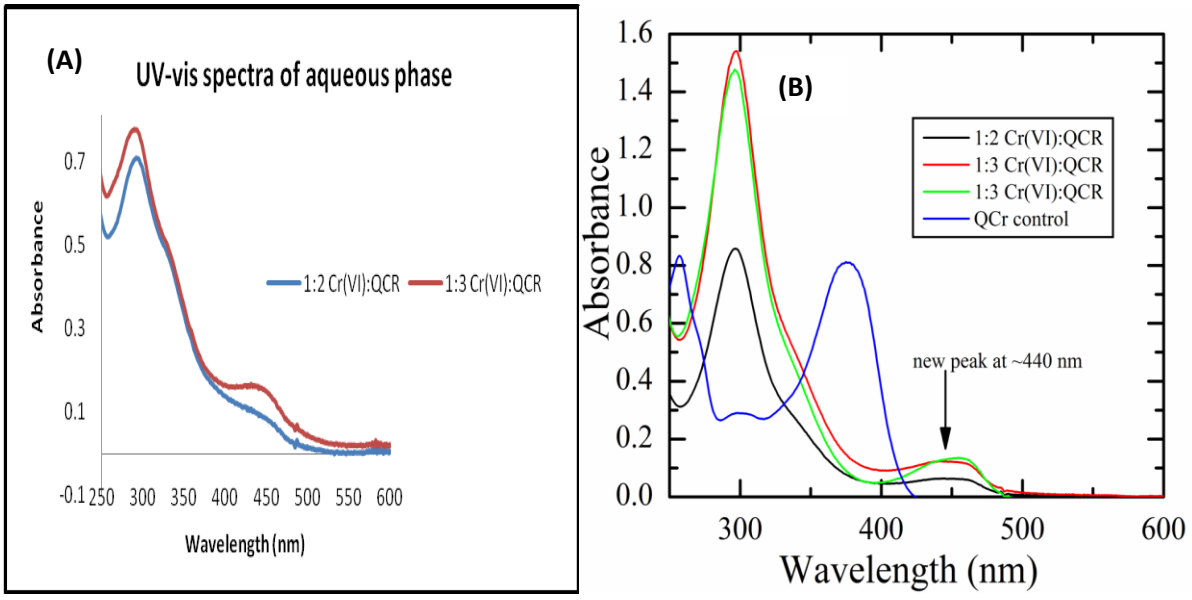
m/e: 475.95 (100.0%), 476.95 (39.2%), 477.95 (12.9%), 473.96 (10.3%), 474.96 (2.9%), 478.95 (2.3%), 477.96 (1.4%)



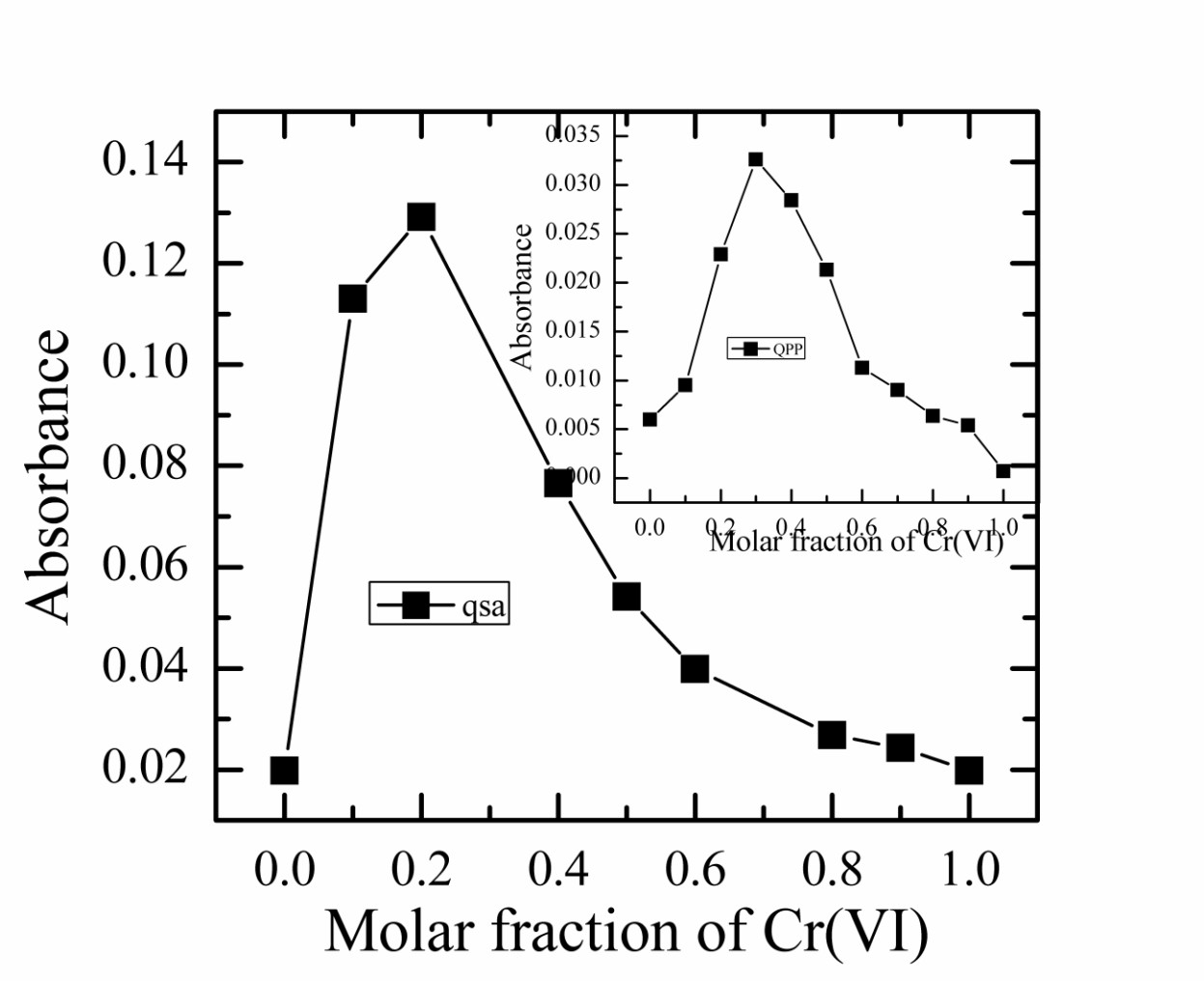


Chemical Formula: $C_{30}H_{18}O_{14}$
Exact Mass: 602.07
Molecular Weight: 602.46
m/z: 602.07 (100.0%), 603.07 (33.0%), 604.08 (5.3%), 604.07 (2.9%), 605.08 (1.5%)
Elemental Analysis: C, 59.81; H, 3.01; O, 37.18

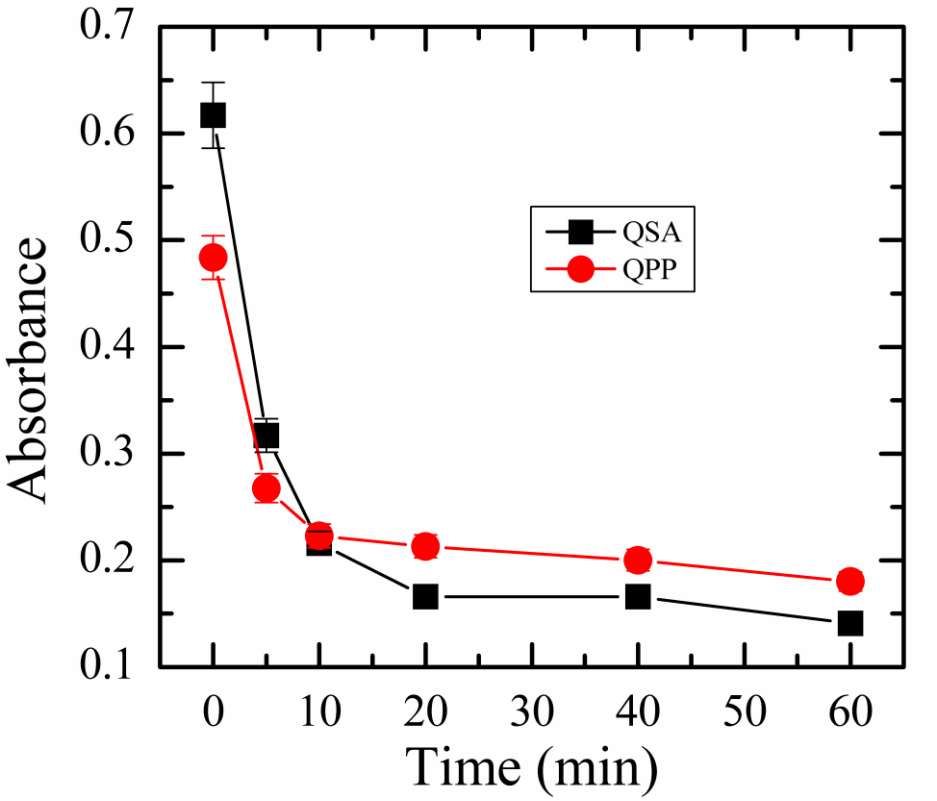
Supplementary Figure 2



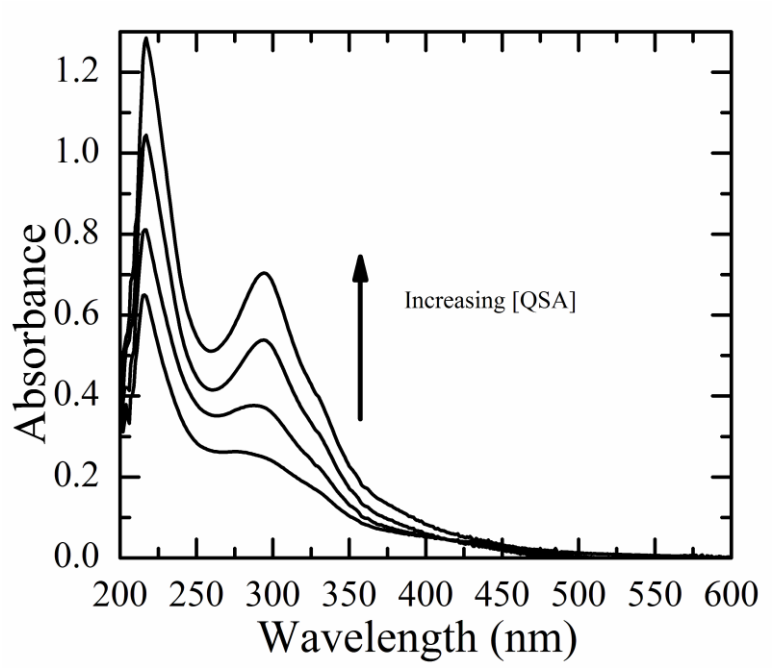
Supplementary Figure 3



Supplementary Figure 4



Supplementary Figure 5



Supplementary Figure 6