

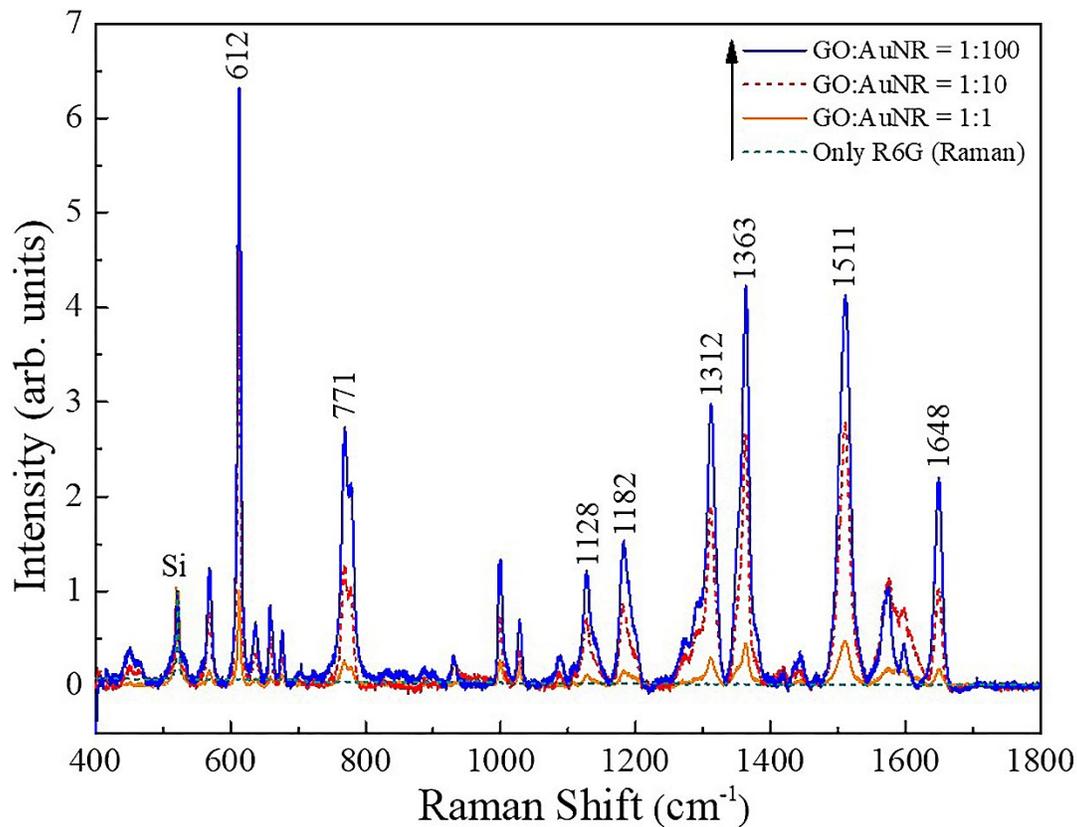
## Electronic Supporting Information (ESI)

Detection of Fipronil residue in egg on layered gold nanorod-Graphene  
oxide based 3D SERS substrate

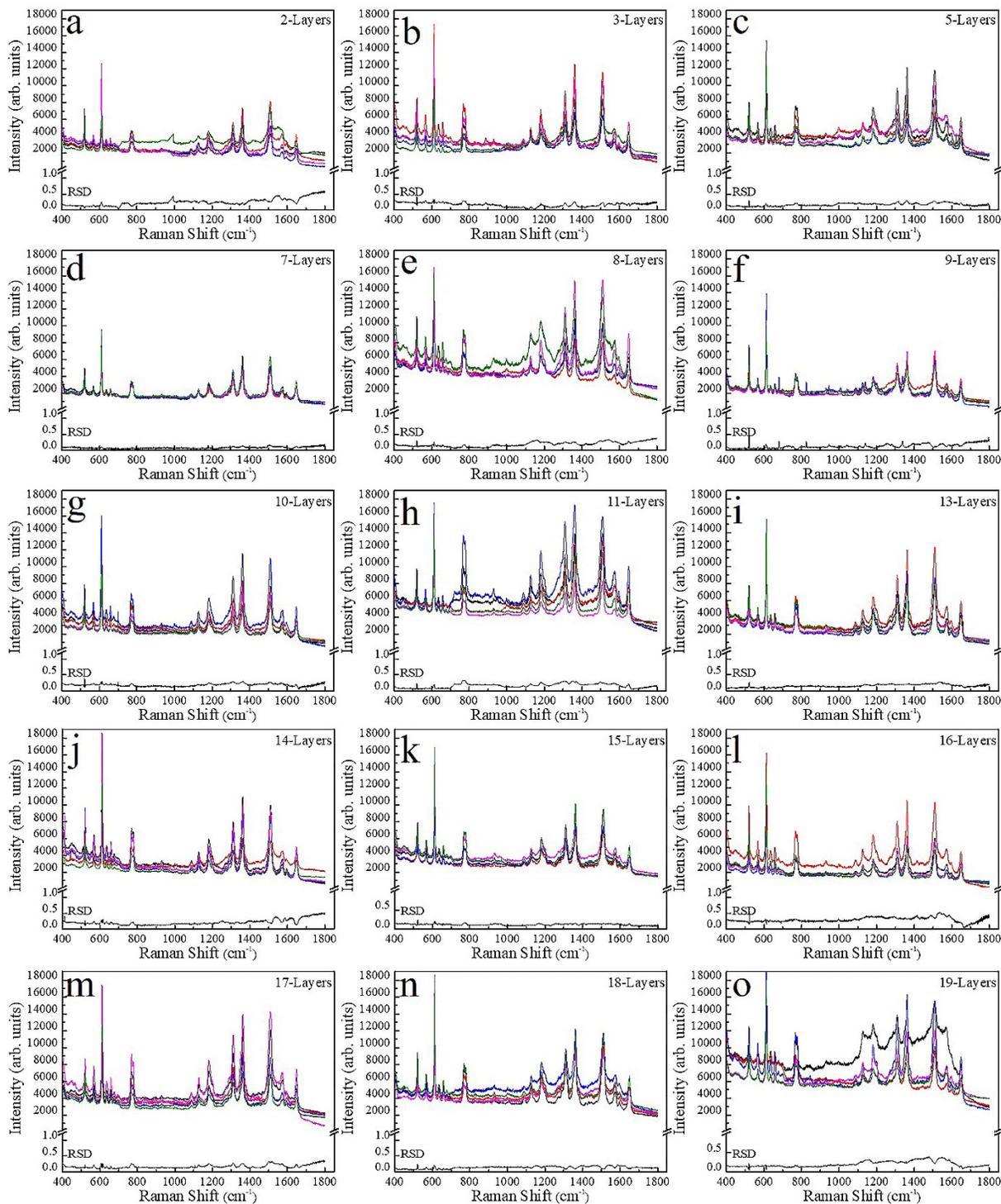
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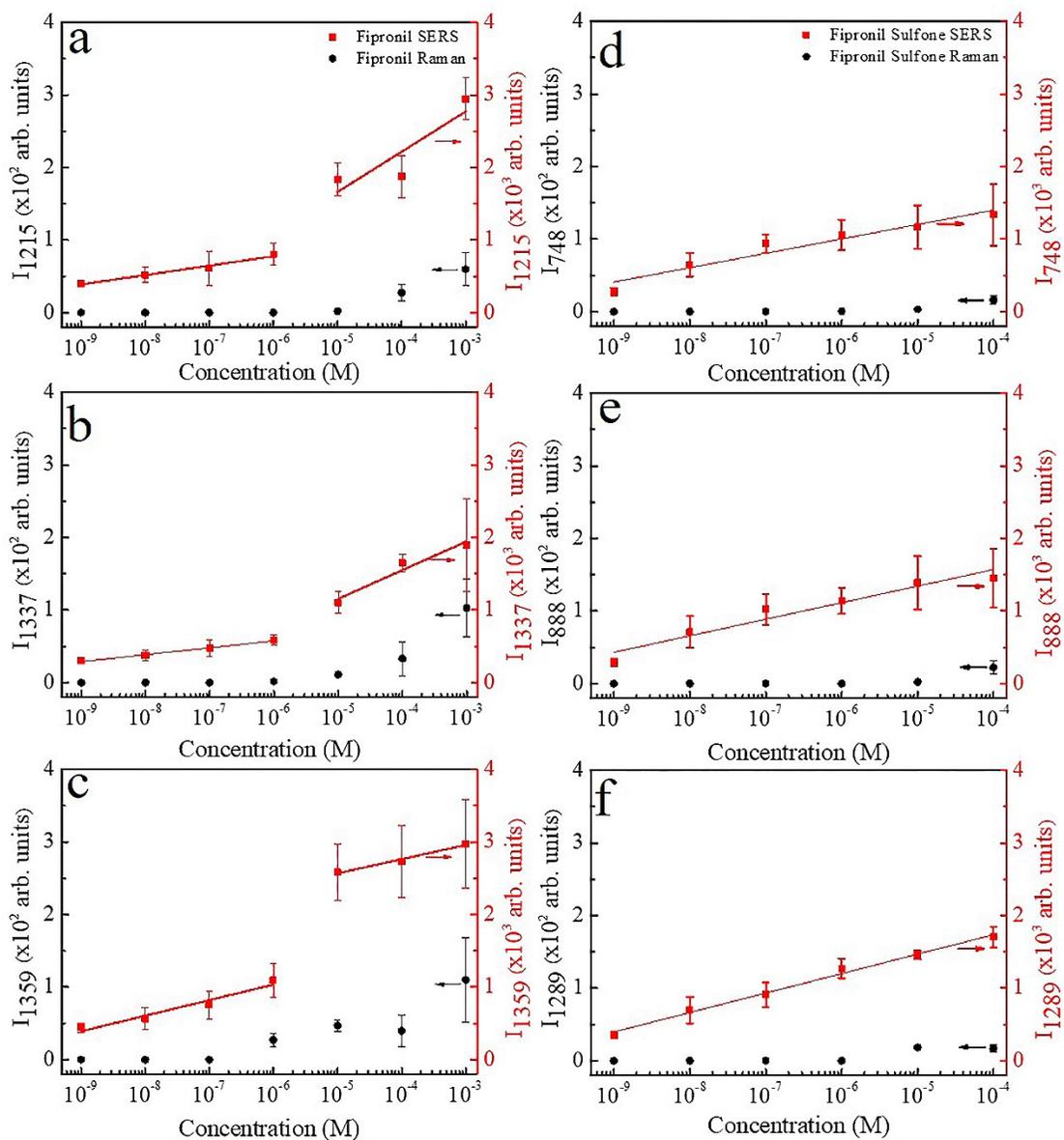
<sup>2</sup>Institute of Biophotonics, National Yang-Ming University, 155, sec-2 Li Nong  
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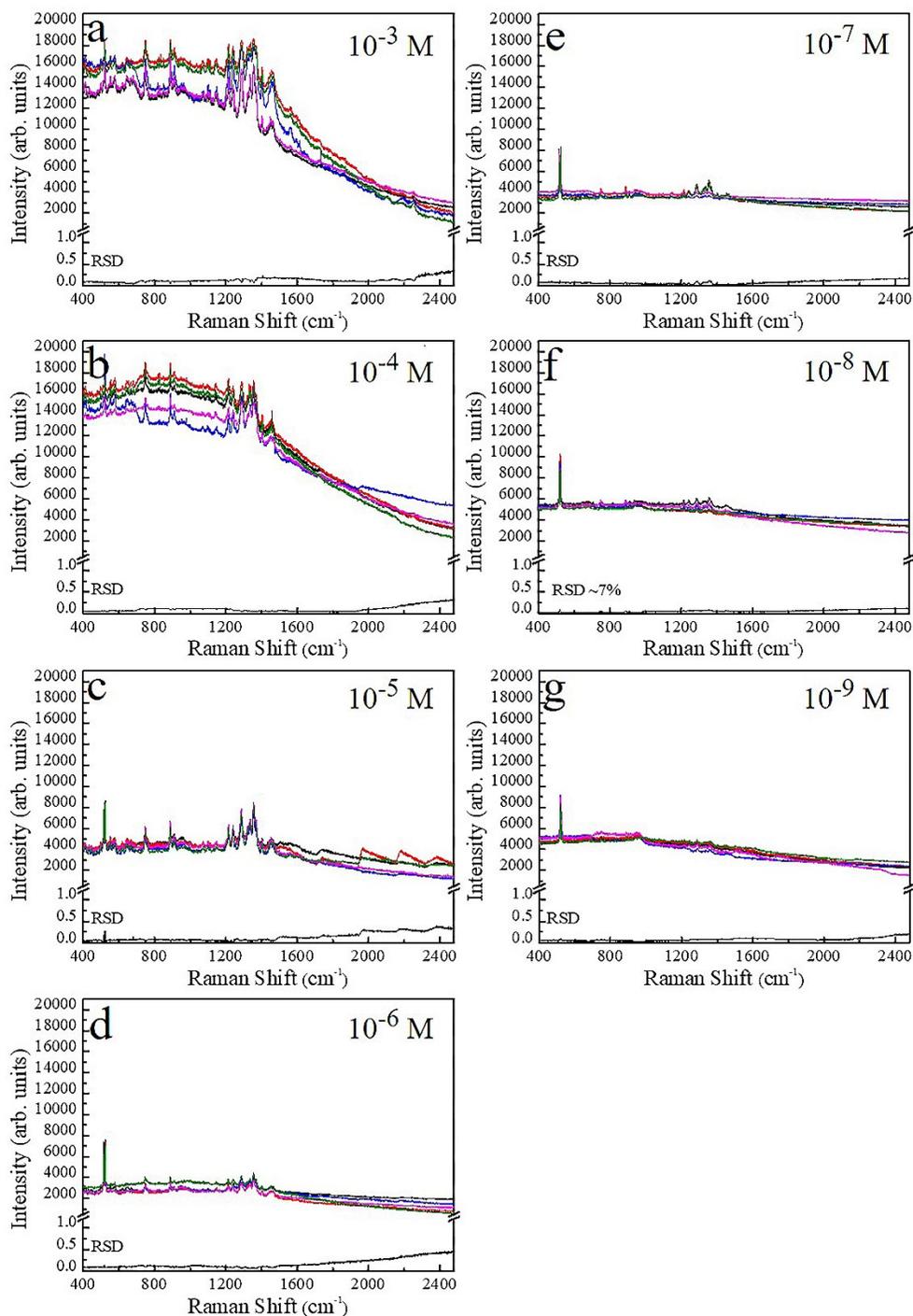
**Figure S1:** Optimization of GO:AuNR ratio for maximization of Raman signal enhancement. Surface enhanced Raman spectra (SERS) of Rhodamine 6G (R6G,  $10^{-6}$  M) loaded on bare silicon (Si), and on layers of AuNR-GO nanocomposites (dispersed of Si) having different volume ratios of AuNR and GO. R6G peaks are labelled with numbers, and silicon peak is marked with Si (at  $520\text{ cm}^{-1}$ ).



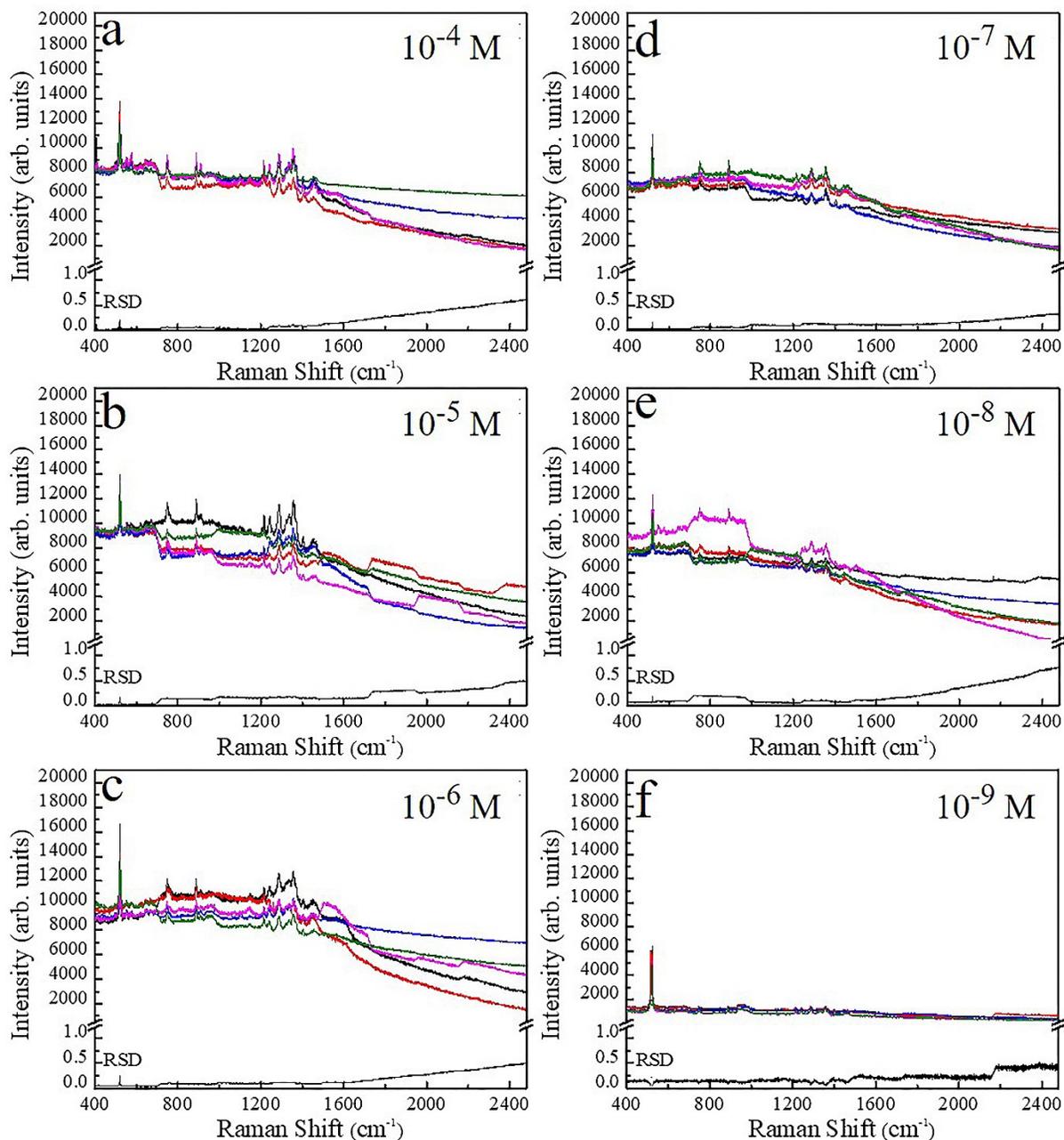
**Figure S2:** Reproducibility of the AuNR-GO based SERS substrates. (a-o) SERS spectra of R6G ( $10^{-6}$  M) measured on 5 different positions of the SERS substrate containing 2-19 layers of AuNR-GO nanocomposites. The layer numbers are mentioned on each panel. The relative standard deviation (RSD) of the signal is calculated from 5 independent measurements and presented at the bottom of each panel in a scale of 0-1.



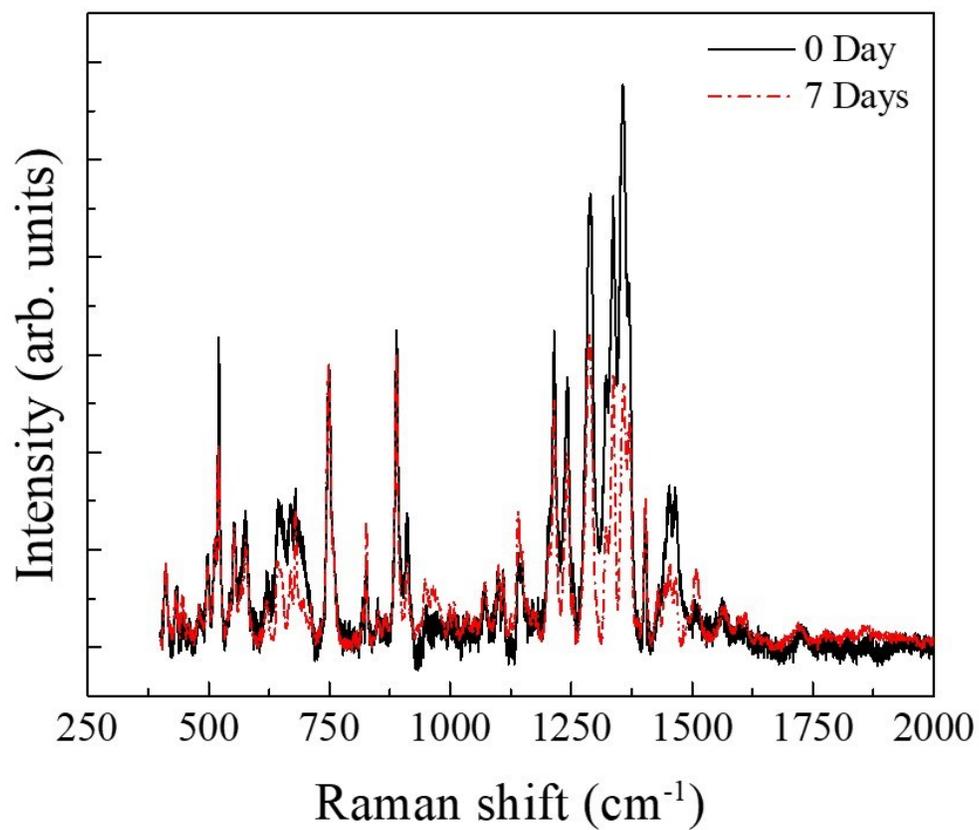
**Figure S3:** Variation of concentration dependent Raman and SERS signal intensities of Fipronil and Fipronil Sulfone. Variation of Fipronil band intensities at (a) 1215, (b) 1337, and (c) 1359  $\text{cm}^{-1}$  by Raman ( $\bullet$ ), and SERS ( $\blacksquare$ ) as a function of Fipronil concentration ( $10^{-3}$  to  $10^{-9}$  M). Variation of Fipronil Sulfone band intensities at (d) 748, (e) 888, and (f) 1289  $\text{cm}^{-1}$  by Raman ( $\bullet$ ), and SERS ( $\blacksquare$ ) as a function of Fipronil Sulfone concentration ( $10^{-4}$  to  $10^{-9}$  M). 4-layered GO-AuNR substrate used for SERS, and bare Si for Raman measurements. Raman signals of the analytes were assumed to be 0 where not detected. The line joining the SERS data points is a linear fit over the shown range of concentrations. The Raman data is not fitted due to negligible variation in signal.



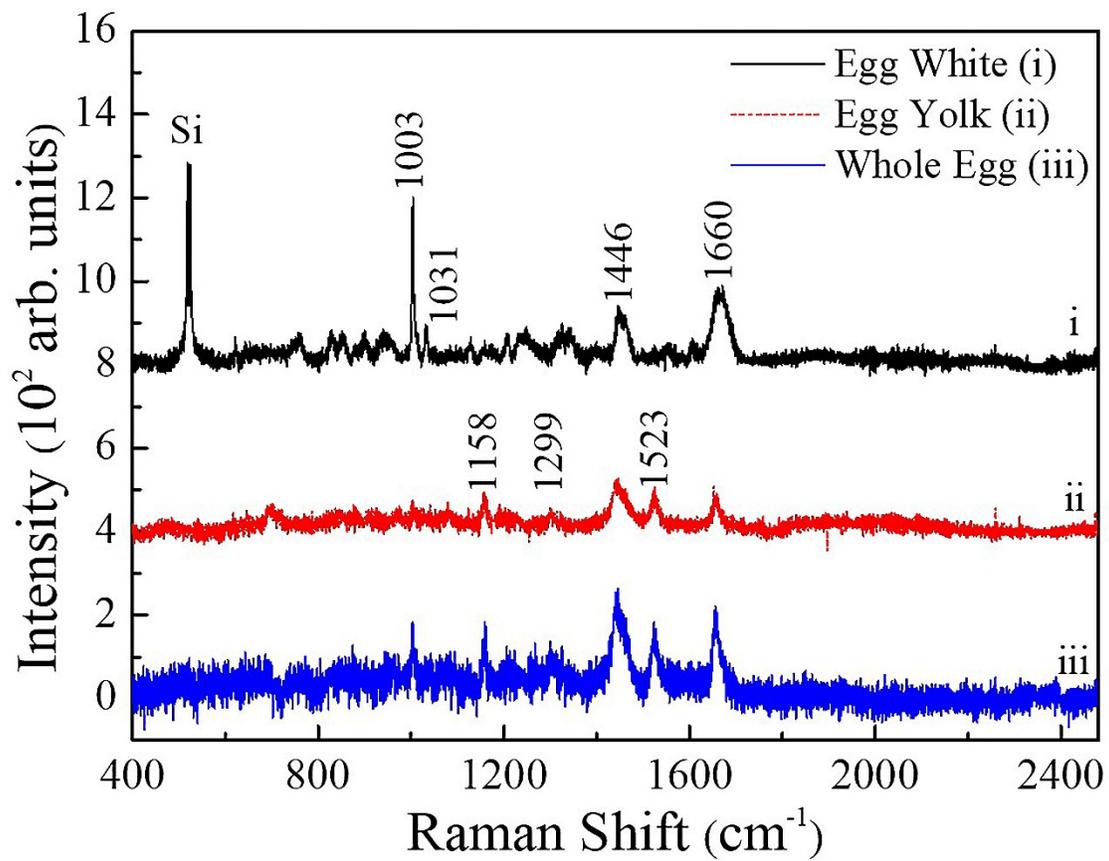
**Figure S4:** Reproducibility of the 3D GO-AuNR based SERS substrates. (a-g) Concentration dependent SERS spectra of Fipronil ( $10^{-3}$  to  $10^{-9}$  M) measured on 5 different positions of the SERS substrate containing 4 layers of AuNR-GO nanocomposites. The relative standard deviation (RSD) of the signal is calculated from 5 independent measurements and presented at the bottom of each panel in a scale of 0-1.



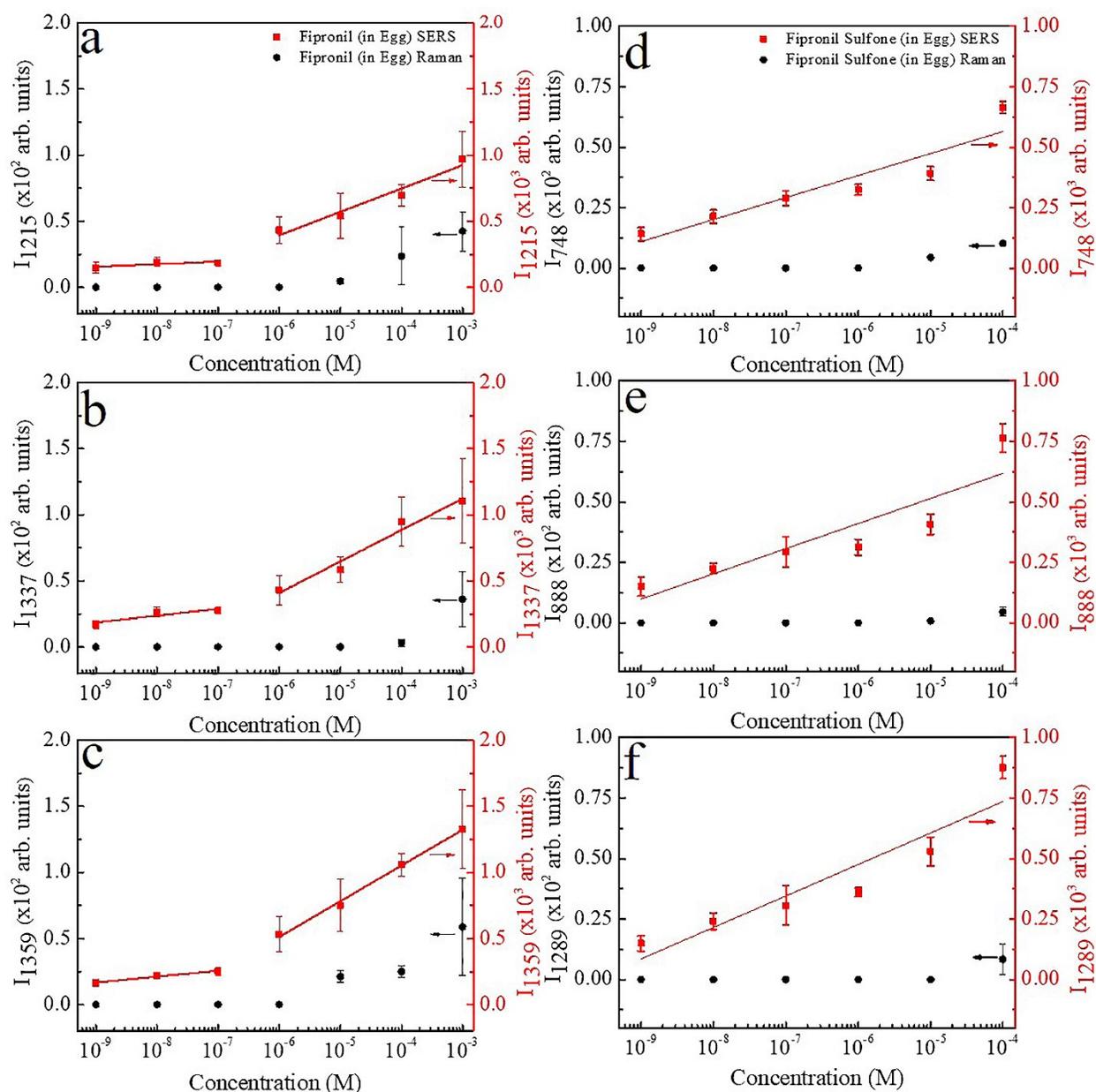
**Figure S5:** Reproducibility of the 3D GO-AuNR based SERS substrates. (a-g) Concentration dependent SERS spectra of Fipronil Sulfone ( $10^{-4}$  to  $10^{-9}$  M) measured on 5 different positions of the SERS substrate containing 4 layers of AuNR-GO nanocomposites. The relative standard deviation (RSD) of the signal is calculated from 5 independent measurements and presented at the bottom of each panel in a scale of 0-1.



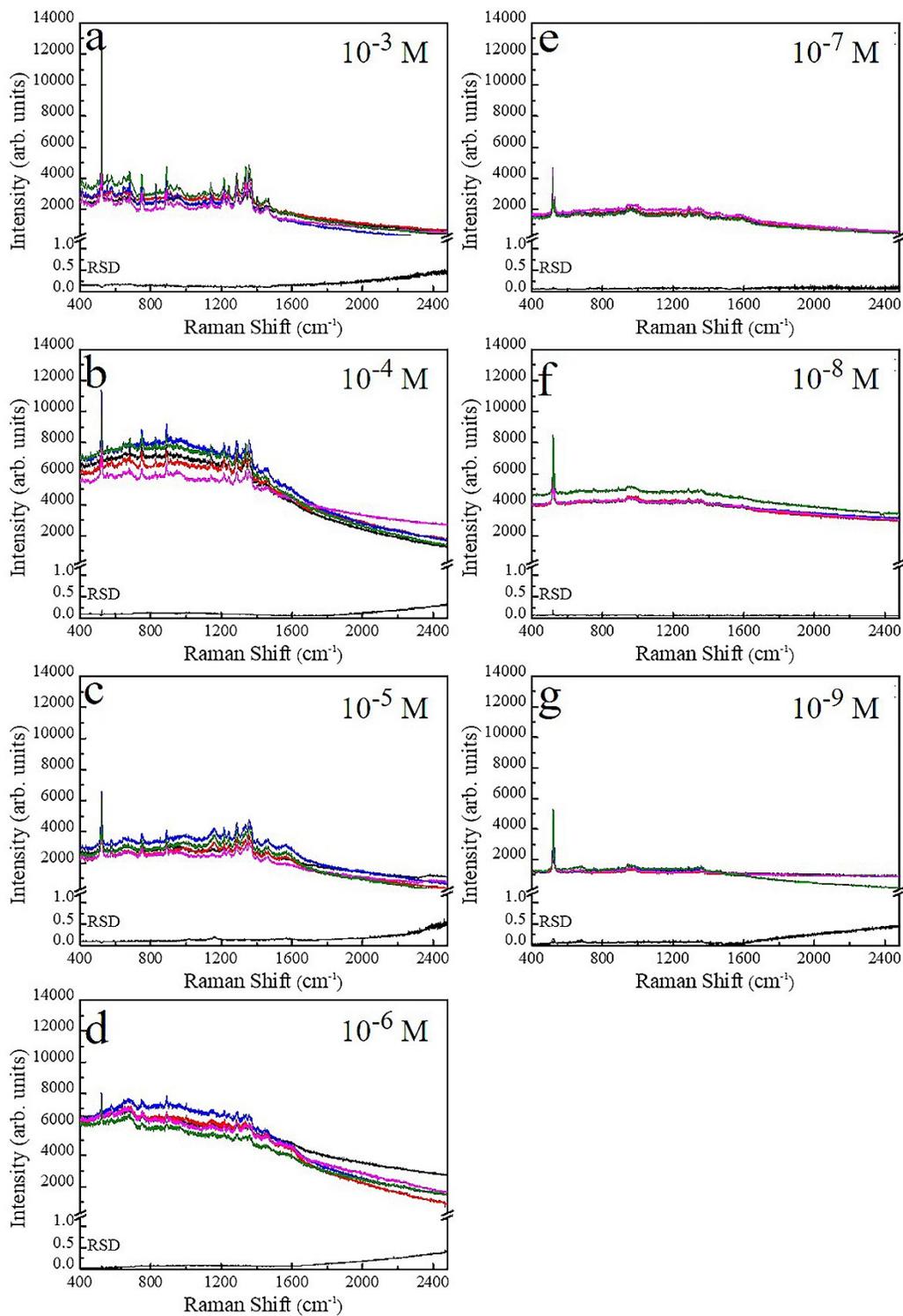
**Figure S6:** SERS spectrum of Fipronil ( $10^{-3}$  M) on the optimized 3D SERS substrate on (black) day 0, and (red) day 7, measured under identical conditions.



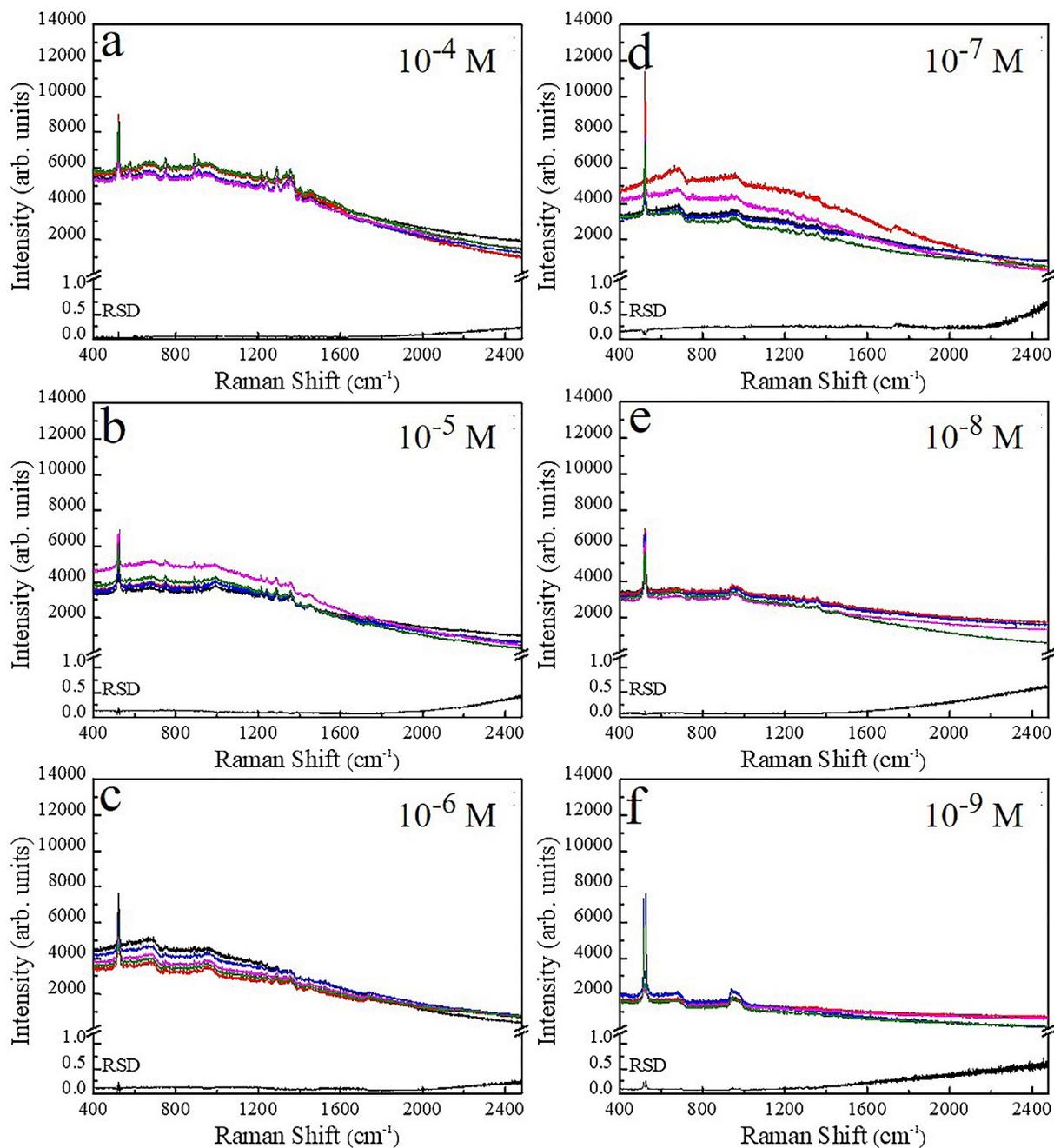
**Figure S7:** Raman spectra of beaten (i) egg white (ii) egg yolk, and (iii) whole egg dispersed on Si. The corresponding Raman bands are marked in the panel.



**Figure S8:** Variation of Raman and SERS signal intensities of Fipronil and Fipronil Sulfone in spiked real (whole) egg samples. Variation of Fipronil band intensities at (a) 1215, (b) 1337, and (c) 1359  $\text{cm}^{-1}$  by Raman (●), and SERS (■) as a function of Fipronil concentration ( $10^{-3}$  to  $10^{-9}$  M) in real egg. Variation of Fipronil Sulfone band intensities at (d) 748, (e) 888, and (f) 1289  $\text{cm}^{-1}$  by Raman (●), and SERS (■) as a function of Fipronil Sulfone concentration ( $10^{-4}$  to  $10^{-9}$  M) in real egg. 4-layered GO-AuNR substrate used for SERS, and bare Si for Raman measurements. Raman signals of the analytes were assumed to be 0 where not detected. The line joining the SERS data points is a linear fit over the shown range of concentrations. The Raman data is not fitted due to negligible variation in signal.



**Figure S9:** Reproducibility of 4 layered 3D GO-AuNR SERS substrates for real samples. (a-g) SERS spectra of real egg spiked with known concentrations of Fipronil ( $10^{-3}$  to  $10^{-9}$  M). The relative standard deviation (RSD) of the signals is calculated from 5 independent measurements and presented at the bottom of each panel in a scale of 0-1.



**Figure S10:** Reproducibility of 4 layered 3D GO-AuNR SERS substrates for real samples. (a-g) SERS spectra of real egg spiked with known concentrations of Fipronil Sulfone ( $10^{-4}$  to  $10^{-9}$  M). The relative standard deviation (RSD) of the signals is calculated from 5 independent measurements and presented at the bottom of each panel in a scale of 0-1.

**Table S1.** Measured SERS intensities of 1359, and 748  $\text{cm}^{-1}$  for Fipronil, and Fipronil Sulfone, respectively, under low (C1, C3), and high (C2, C4) spike condition.

<b>Analytes</b>	<b>Spike Conc.</b> (M)	<b>Measured Int.</b> (Mean $\pm$ SD)	<b>Expected Int.</b>	$\frac{\text{Measured}}{\text{Expected}}\%$
Fipronil	Low Spike ( $10^{-7}$ , C1)	242.2 $\pm$ 49.2	256 (I <sub>1359</sub> )	94.5
	High Spike ( $10^{-3}$ , C2)	1147.6 $\pm$ 160	1322 (I <sub>1359</sub> )	86.8
Fipronil	Low Spike ( $10^{-8}$ , C3)	193.2 $\pm$ 25	200.6 (I <sub>748</sub> )	96.3
Sulfone	High Spike ( $10^{-4}$ , C4)	552.5 $\pm$ 73	546.3 (I <sub>748</sub> )	97.9

Conc.-Concentration; Int.-Intensity; SD-Standard deviation.