

MATERIAL SUPLEMENTAR

**MÉTODOS AMBIENTALMENTE AMIGÁVEIS PARA A IODAÇÃO
REGIOSSELETIVA DA 3,7,3',4'-TETRAMETOXI-QUERCETINA**

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6-Iodo-3,7,3',4'-tetrametoxi-quercetina (**2**) CONSTANTES FÍSICAS: sólido amarelo; R_f 0,55 [Hex (64 %): DCM (21 %): AcOEt (15 %): MeOH (4 gotas): HOAc (3 gotas)]; Ponto de fusão: 183 – 184 °C; IV ν_{\max} (KBr): 3086, 2924, 1643, 496; RMN ^1H (300 MHz, CDCl_3) δ 13,58 (s, 1H); 7,67 (dd, 1H, $J=9,0; 3,0$ Hz); 7,62 (d, 1H, $J=3,0$ Hz); 6,93 (d, 1H, $J=9,0$ Hz); 6,43 (s, 1H); 3,93 (s, 3H); 3,92 (s, 3H); 3,91 (s, 3H); 3,80 (s, 3H); RMN ^{13}C (75 MHz, CDCl_3) δ 177,8; 163,2; 160,9; 157,0; 156,5; 151,5; 148,8; 138,9; 122,6; 122,2; 111,3; 110,8; 106,1; 90,2; 69,4; 60,2; 56,9; 56,1; 56,0.

8-Iodo-3,7,3',4'-tetrametoxi-quercetina (**3**) CONSTANTES FÍSICAS: sólido amarelo; R_f 0,63 [Hex (64 %): DCM (21 %): AcOEt (15 %): MeOH (4 gotas): HOAc (3 gotas)]; Ponto de fusão: 193 – 194 °C; IV ν_{\max} (KBr): 3085, 2996, 1646, 466; RMN ^1H (300 MHz, CDCl_3) δ 12,90 (s, 1H); 8,05 (dd, 1H, $J=9,0; 3,0$ Hz); 7,96 (d, 1H, $J=3,0$ Hz); 7,01 (d, 1H, $J=9,0$ Hz); 6,40 (s, 1H); 4,00 (s, 3H); 3,98 (s, 3H); 3,96 (s, 3H); 3,91 (s, 3H); RMN ^{13}C (75 MHz, CDCl_3) δ 178,4; 163,7; 163,1; 155,9; 154,8; 151,5; 148,8; 138,7; 123,0; 122,7; 111,4; 110,9; 106,3; 95,2; 60,7; 60,0; 56,9; 56,1; 56,0.

6,8-Di-iodo-3,7,3',4'-tetrametoxi-quercetina (**4**) CONSTANTES FÍSICAS: sólido amarelo; R_f 0,74 [Hex (64 %): DCM (21 %): AcOEt (15 %): MeOH (4 gotas): HOAc (3 gotas)]; Ponto de fusão: 212-213 °C; IV ν_{\max} (filme): 3091; 2994; 1630; 463; RMN ^1H (300 MHz, CDCl_3) δ 13,85 (s, 1H); 8,05 (dd, 1H, $J=9,0; 3,0$ Hz); 7,94 (d, 1H, $J=3,0$ Hz); 7,01 (d, 1H, $J=9,0$ Hz); 4,00 (s, 3H); 3,99 (1s, 3H); 3,96 (s, 3H); 3,91 (s, 3H); RMN ^{13}C (75 MHz, CDCl_3) δ 177,8; 164,4; 161,9; 156,7; 154,9; 151,9; 148,9; 138,8; 123,2; 122,2; 111,4; 111,0; 108,3; 74,9; 67,2; 61,2; 60,0; 56,1; 56,0.

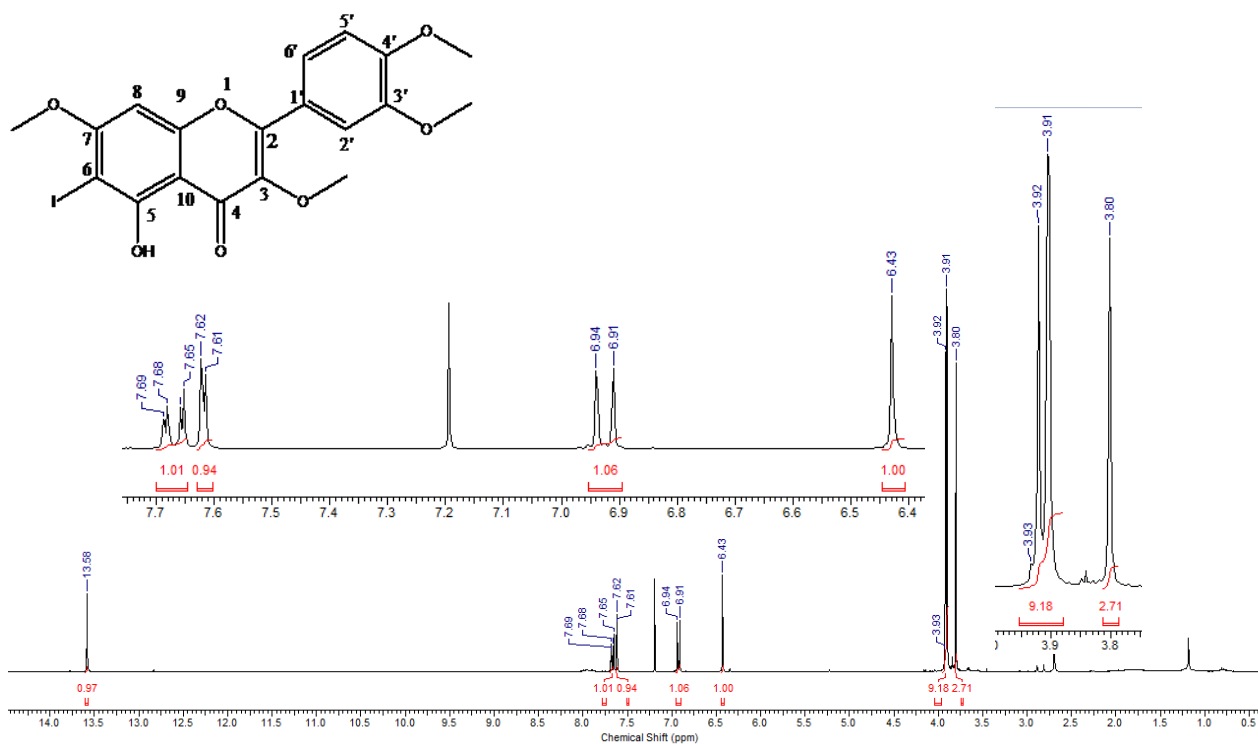


Figura 1S. Espectro de RMN ^1H do composto 2 (CDCl₃, 300 MHz)

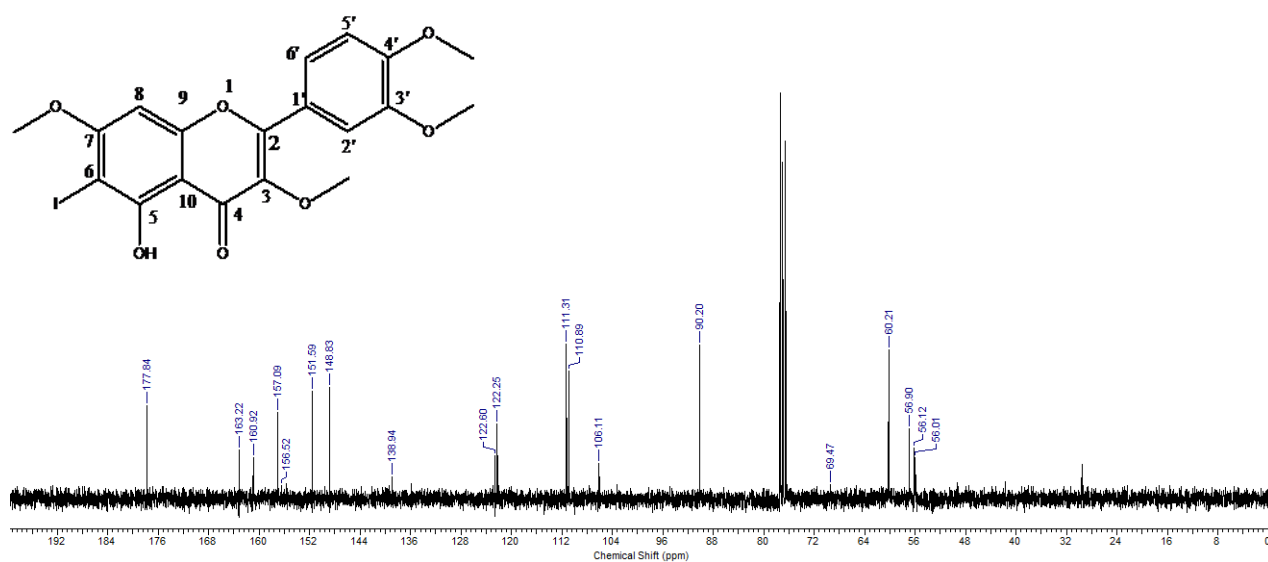


Figura 2S. Espectro de RMN ^{13}C do composto 2 (CDCl₃, 75 MHz)

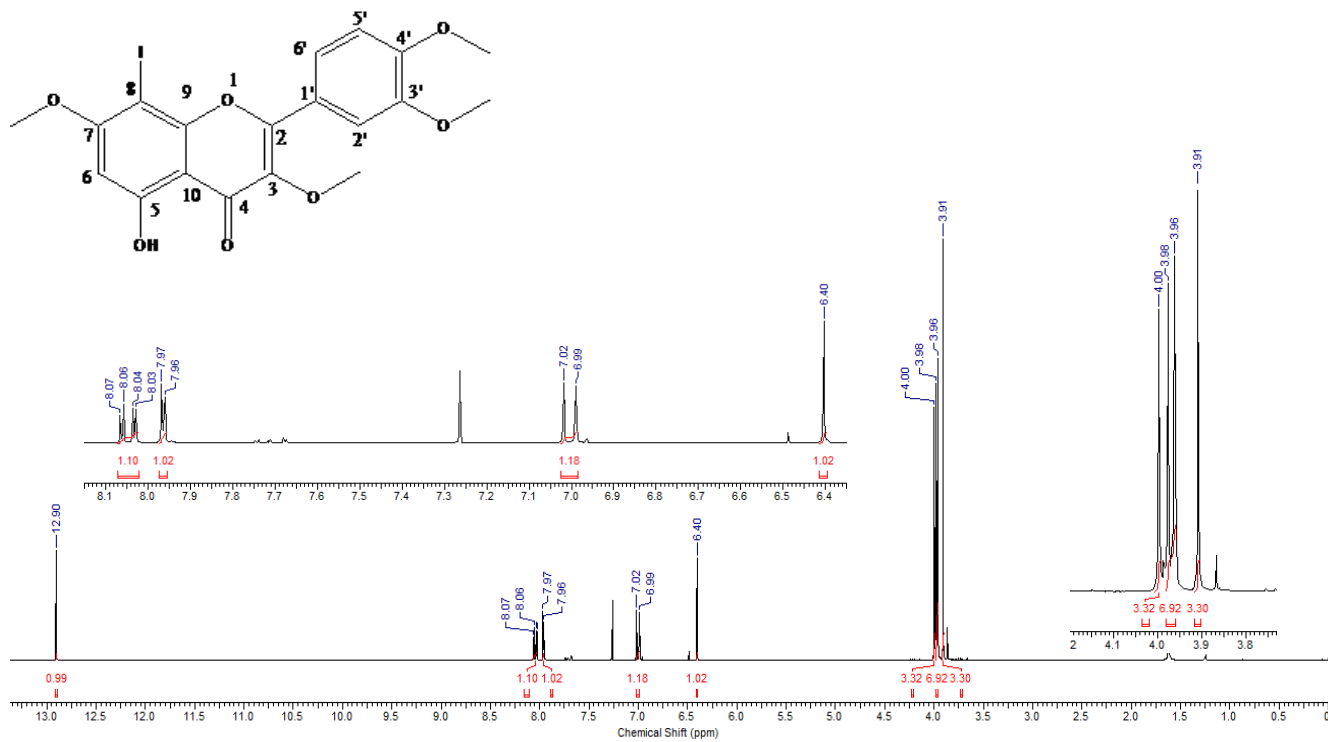


Figura 3S. Espectro de RMN ^1H do composto 3 (CDCl_3 , 300 MHz)

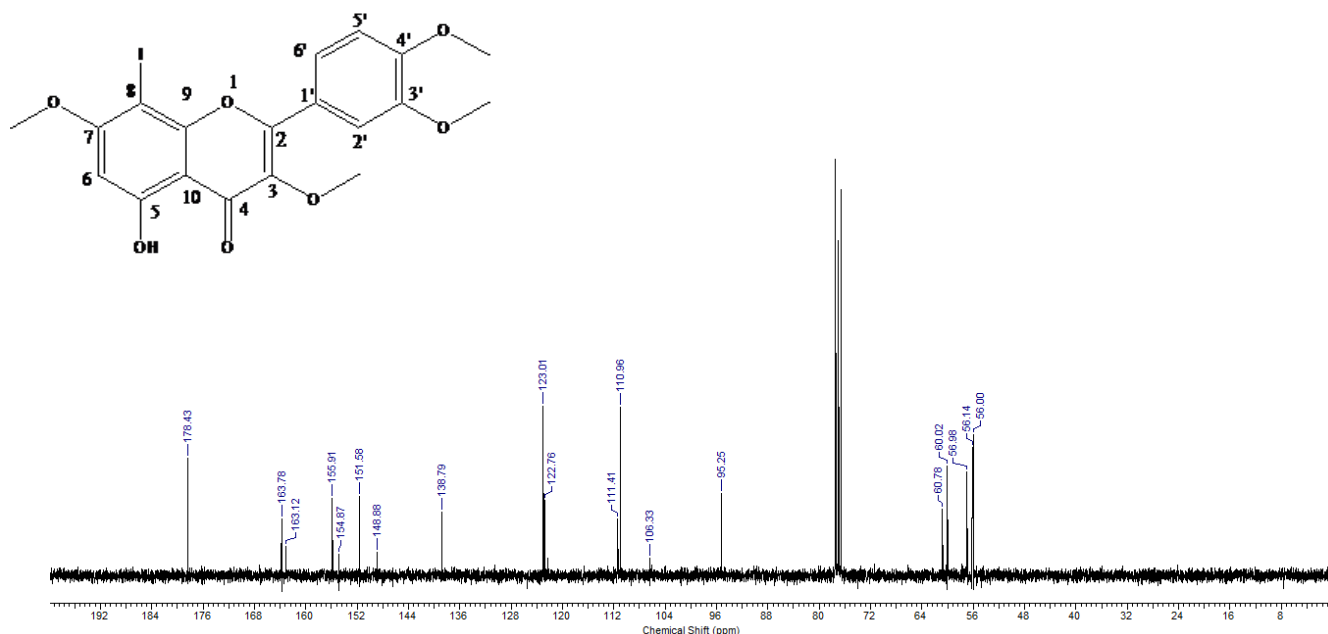


Figura 4S. Espectro de RMN ^{13}C do composto 3 (CDCl_3 , 75 MHz)

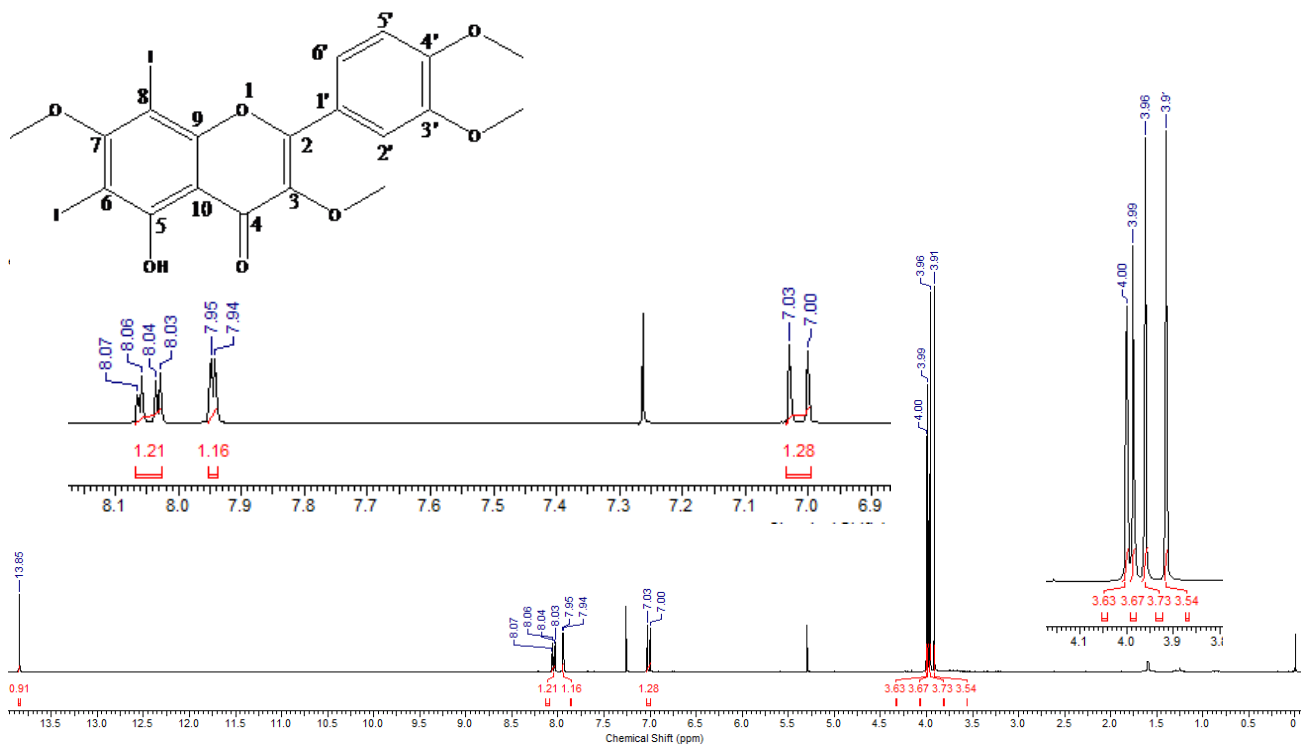


Figura 5S. Espectro de RMN ^1H do composto 4 (CDCl₃, 300 MHz)

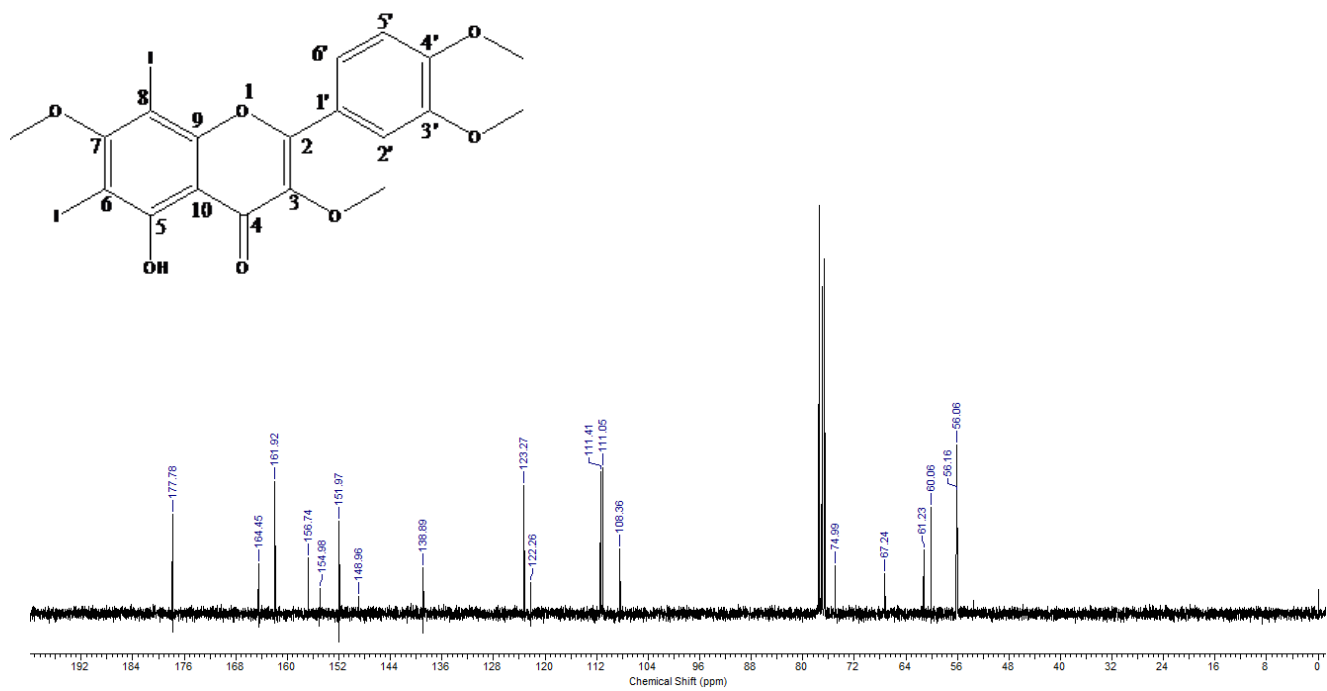


Figura 6S. Espectro de RMN ^{13}C do composto 4 (CDCl₃, 75 MHz)

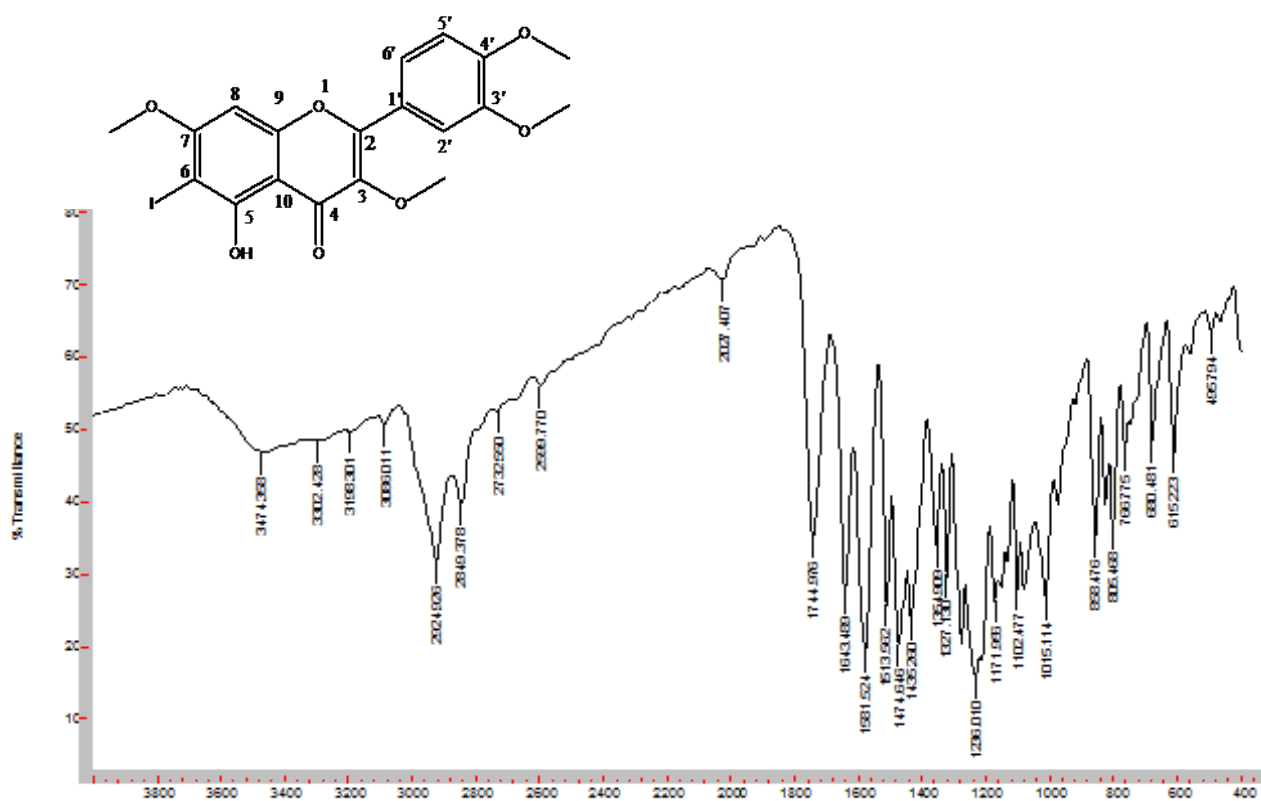


Figura 7S. Espectro de IV (KBr) do composto 2

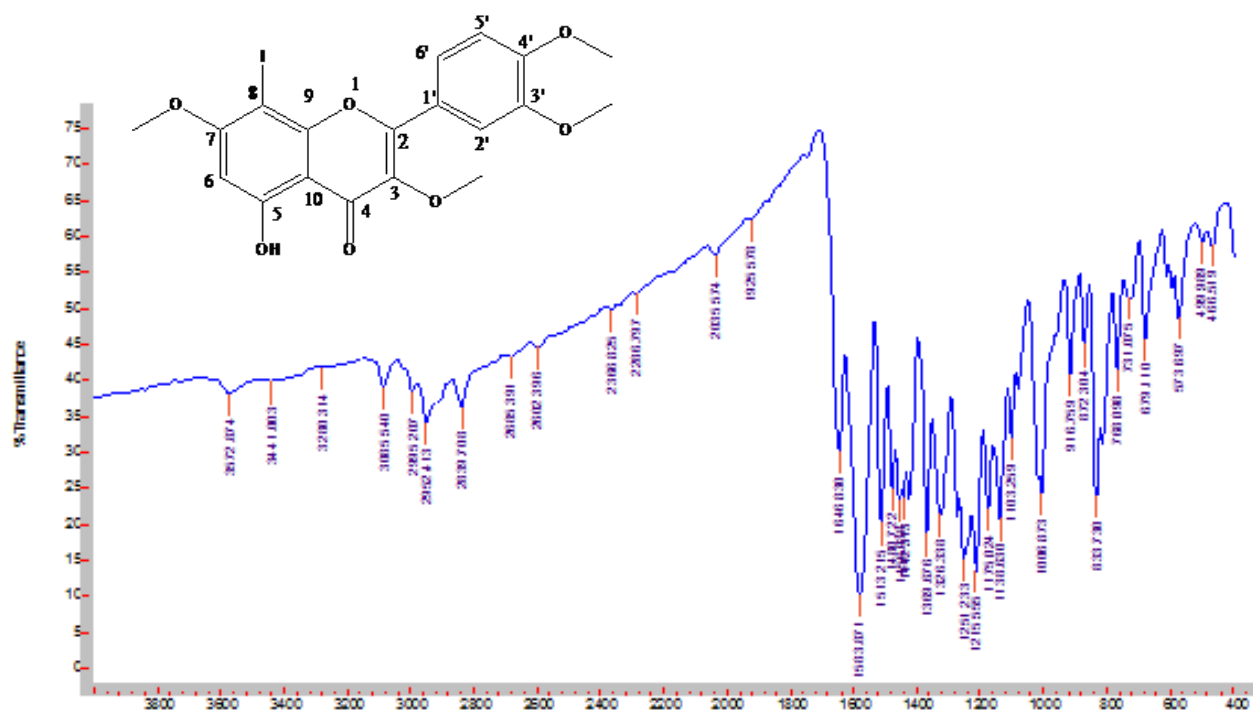


Figura 8S. Espectro de IV (KBr) do composto 3

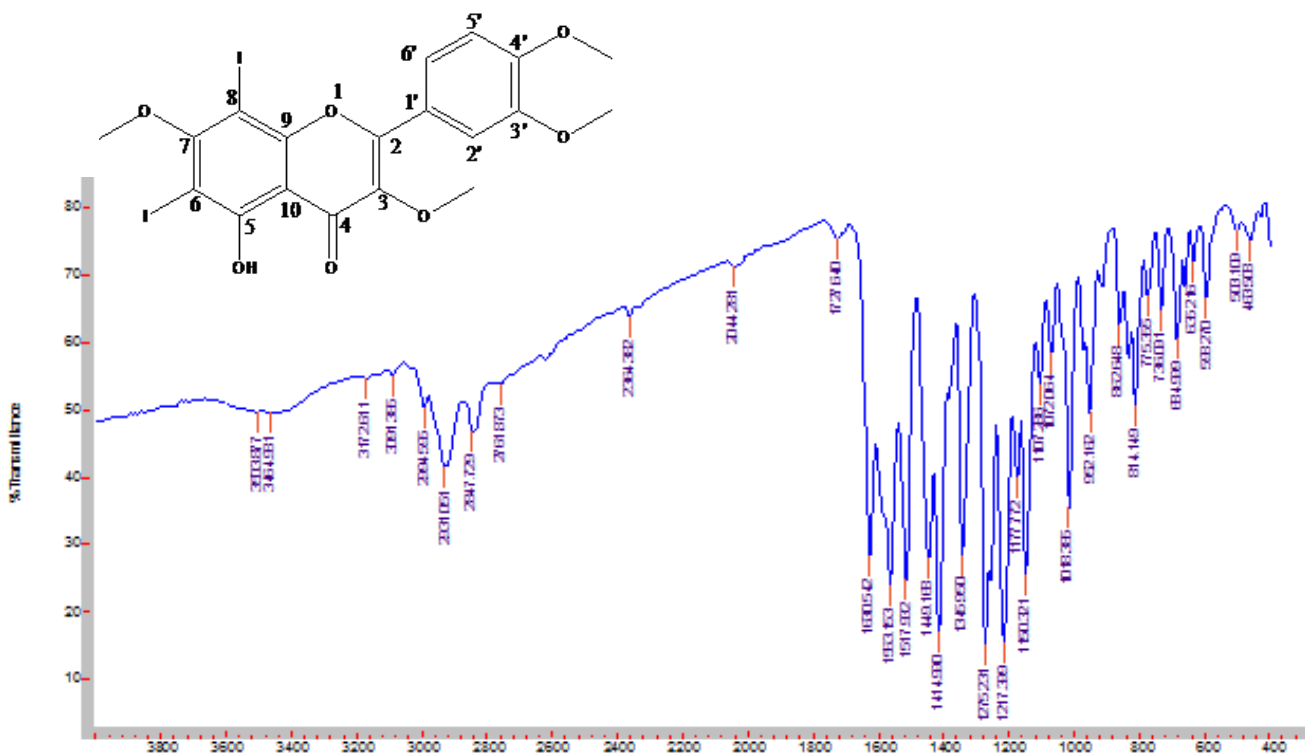


Figura 9S. Espectro de IV (KBr) do composto 4

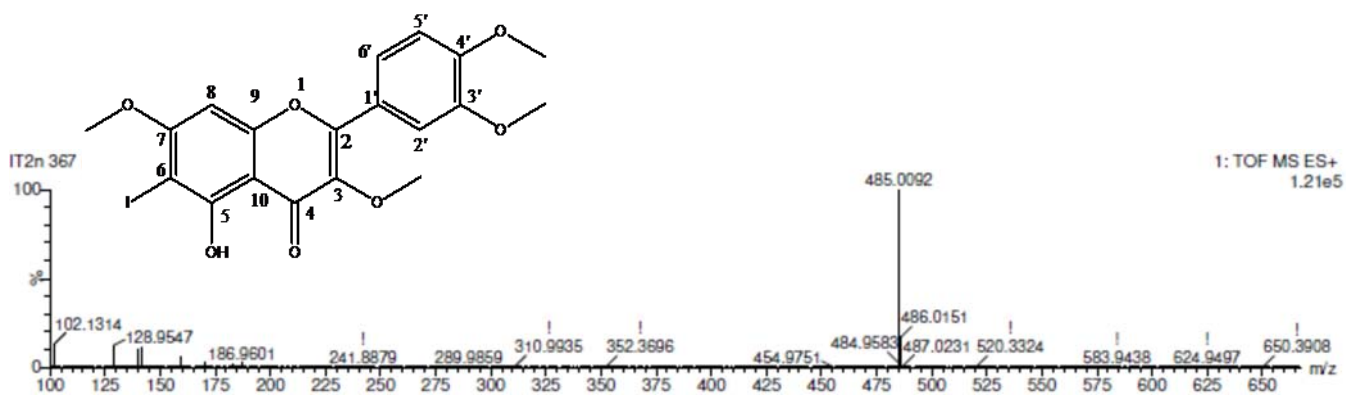


Figura 10S. Espectros de EM-ES do composto 2

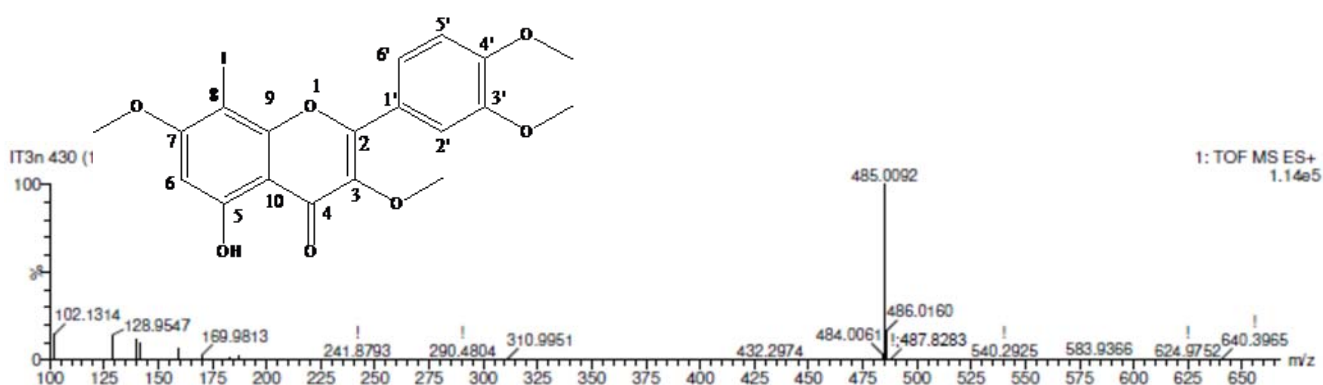


Figura 11S. Espectros de EM-ES do composto 3

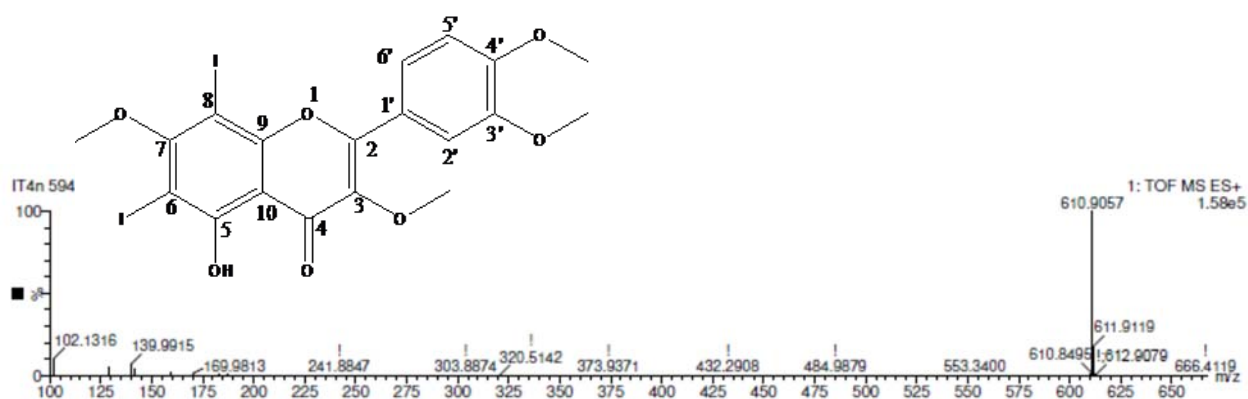


Figura 12S. Espectros de EM-ES do composto 4

Tabela 1S. Dados da curva de calibração

| Padrões dos compostos | T.R. (min) | UV (nm) | LD | LQ | Equação da reta | r ² |
|-----------------------|------------|-------------|-------|-------|-----------------------|----------------|
| 1 | 2,882 | 254/351 | 0,076 | 0,255 | y= 60769,7x + 64242,5 | 0,9996 |
| 2 | 3,412 | 259/349 | 0,143 | 0,478 | y= 41360,4x - 1733,5 | 0,9999 |
| 3 | 3,823 | 258/272/364 | 0,252 | 0,840 | y= 27191,9x - 11035,5 | 0,9999 |
| 4 | 5,475 | 265/278/362 | 0,495 | 1,649 | y= 45751,2x - 700,2 | 0,9999 |

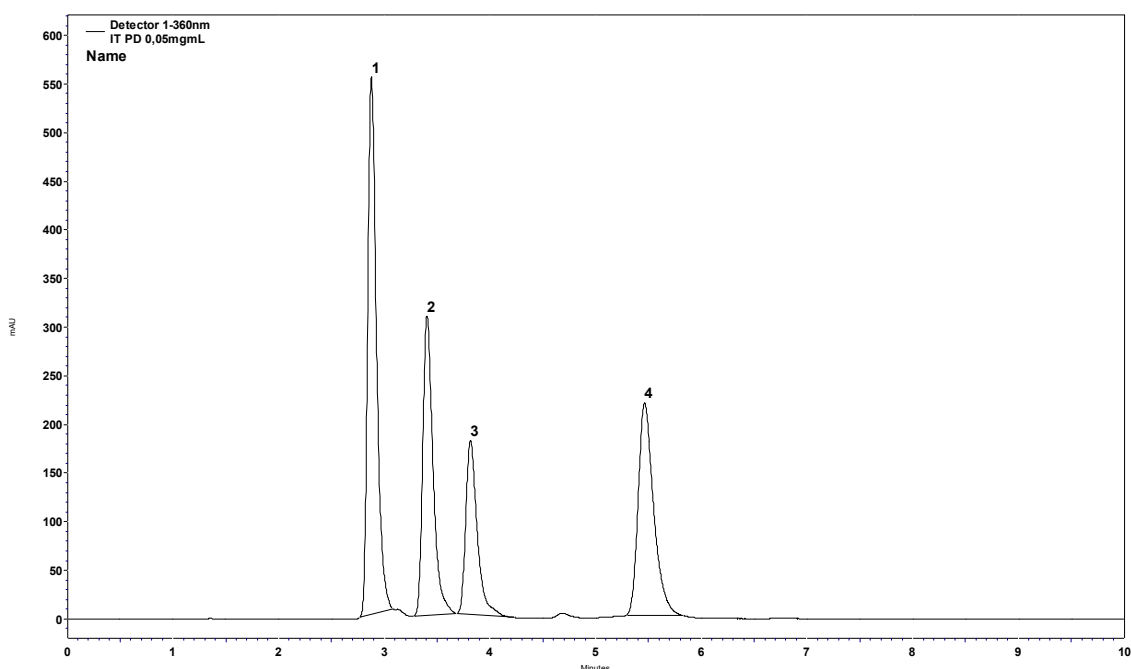


Figura 13S. Cromatogramas dos padrões retusin (1), 6-iodo-retusin (2), 8-iodo-retusin (3) e 6,8-di-iodo-retusin (4) (360 mn)

Das reações, que foram codificadas em entradas 1-7; 9-10; 13-17; 19-21 foram injetadas 5µL nas concentrações de 50µg/mL cada e em triplicata.

Os valores da área percentual (%) estão nas tabelas 2S. Os cromatogramas seguem abaixo nas Figuras 14S a 30S.

Tabela 2S. Área percentual

| Entrada | Condições | Retusin (1) | 6-iodo-retusin (2) | 8-iodo-retusin (3) | 6,8-di-iodo-retusin (4) |
|---------|--|--------------|--------------------|--------------------|-------------------------|
| 1 | I ₂ , KOH, MeOH | 1,437±0,009 | 6,844±0,003 | 69,680±0,068 | 22,039±0,061 |
| 2 | I ₂ , KOH, DMF | 14,470±0,110 | 58,467±1,885 | 13,758±0,179 | 12,328±0,394 |
| 3 | I ₂ , K ₂ CO ₃ [#] | 10,406±0,074 | 66,697±0,150 | 21,109±0,029 | 1,789±0,072 |
| 4 | I ₂ , KOH [#] | 16,711±0,051 | 56,884±0,034 | 19,083±0,023 | 7,325±0,005 |
| 5 | I ₂ , LiOH, MeOH | ND | 4,250±0,118 | 78,903±0,217 | 16,847±0,164 |
| 6 | I ₂ , Cs ₂ CO ₃ , MeOH | 2,035±0,050 | 4,087±0,218 | 57,870±0,464 | 36,008±0,695 |
| 7 | I ₂ , triton B, MeOH | 0,747±0,044 | 1,455±0,279 | 63,076±0,356 | 34,471±0,754 |
| 9 | NIS, DMF | ND | 69,376±0,020 | 18,831±0,013 | 11,793±0,014 |
| 10 | NIS [#] | 0,121±0,002 | 71,839±0,041 | 26,058±0,030 | 1,982±0,012 |
| 13 | KICl ₂ , HCl, MeOH/DCM | ND | 33,754±0,256 | 66,179±0,242 | ND |
| 14 | DCIBTMA, MeOH/DCM | 32,505±0,045 | 11,289±0,040 | 56,206±0,080 | ND |
| 15 | DCIBTMA, DMF | 59,288±0,025 | 20,238±0,070 | 16,784±0,046 | 3,690±0,002 |
| 16 | DCIBTMA ^{#,¥} | 2,887±0,017 | 64,106±0,181 | 33,007±0,165 | ND |

| | | | | | |
|----|--|-------------|--------------|--------------|--------------|
| 17 | KICl ₂ , Triton B, MeOH | 0,275±0,012 | 0,731±0,070 | 76,095±0,126 | 22,900±0,058 |
| 19 | DIH, H ₂ SO ₄ , EtOH | 1,373±0,006 | 28,819±0,046 | 51,350±0,042 | 17,844±0,020 |
| 20 | DIH [#] | 0,340±0,039 | 75,696±0,046 | 13,737±0,060 | 10,227±0,032 |
| 21 | DIH (1,2 eq.) [#] | ND | ND | 12,090±0,057 | 87,910±0,057 |

§Reação com o composto 2; *Reação com o composto 3; †Dicloriodato de benziltrimetilamônio; # sem solvente;
 ND = não detectado

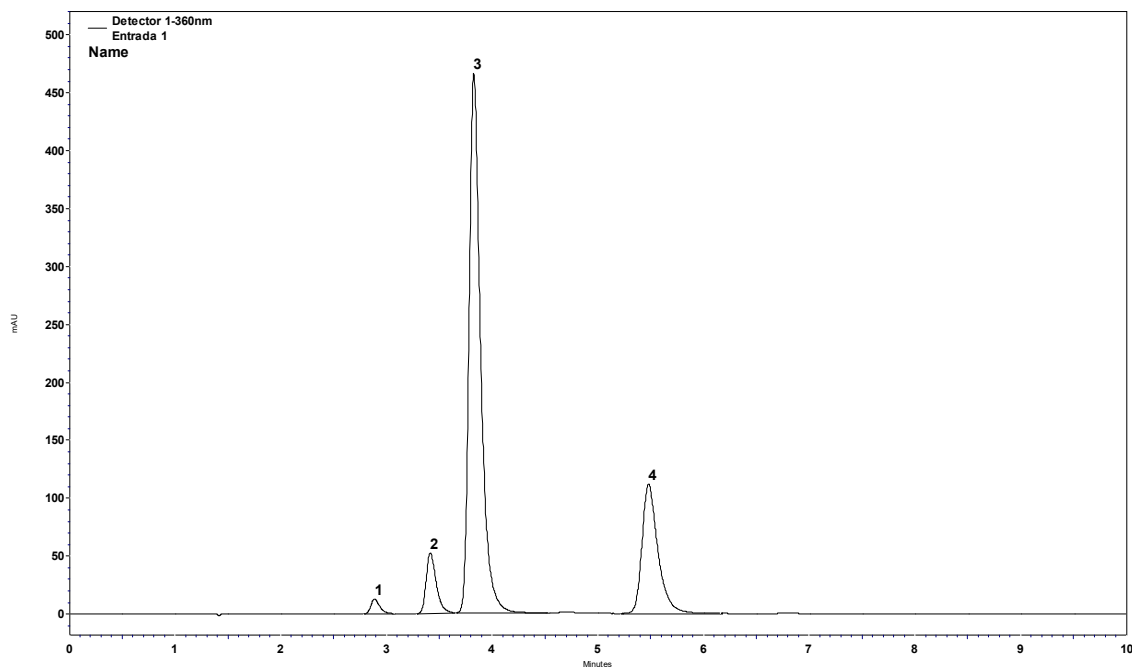


Figura 14S. Cromatograma da entrada 1 (360 mn)

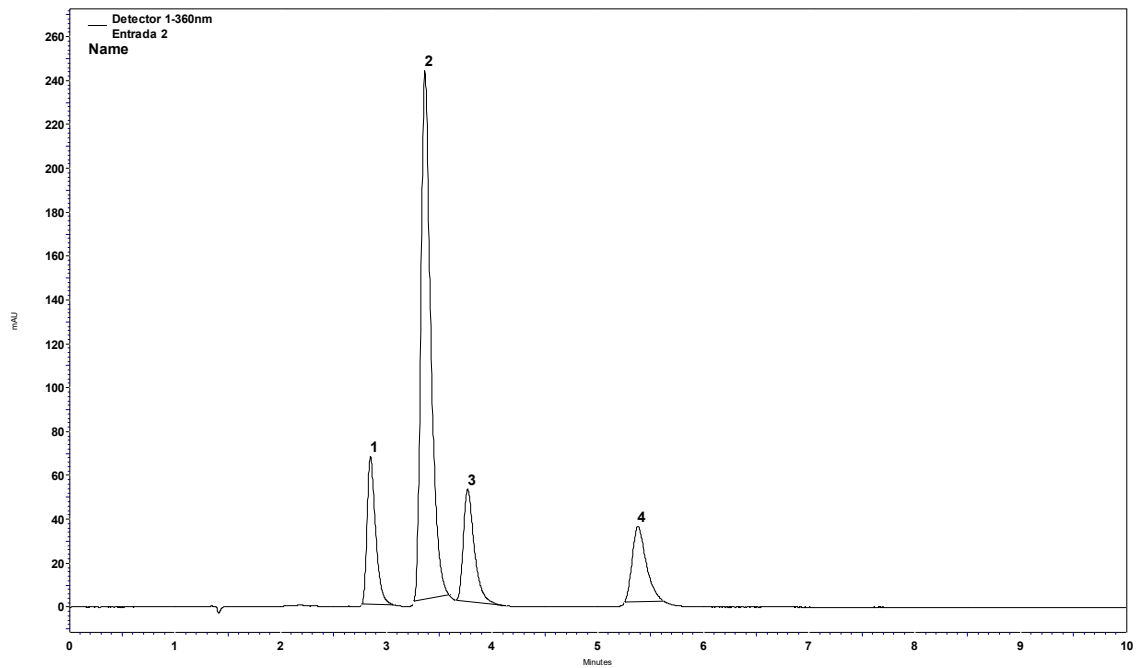


Figura 15S. Cromatograma da entrada 2 (360 mn)

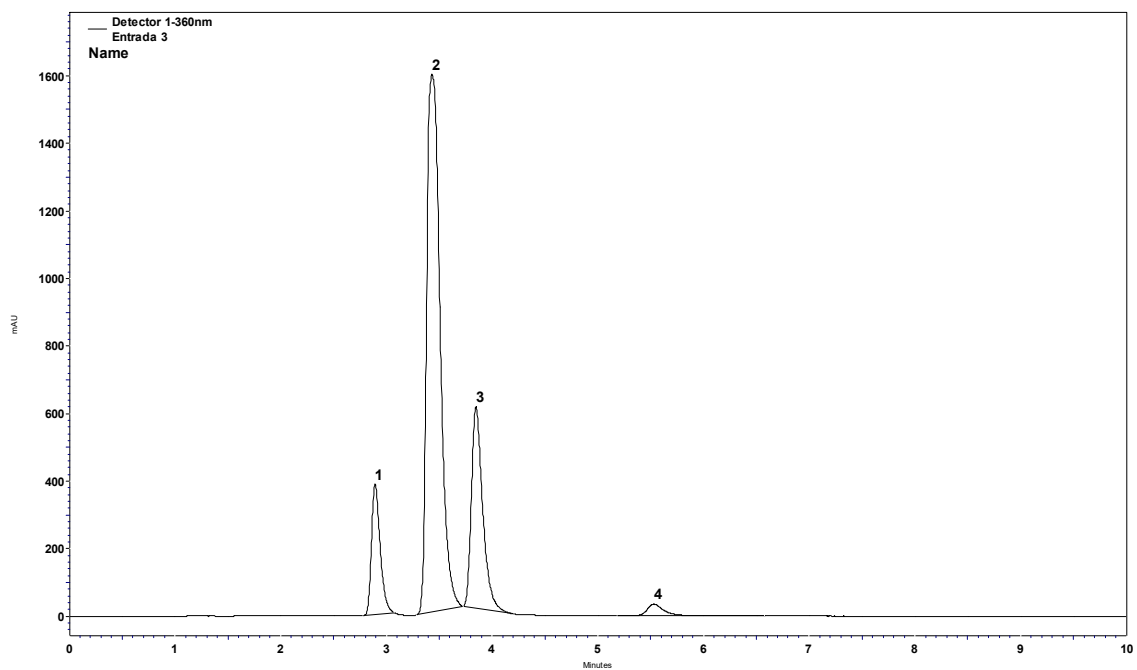


Figura 16S. Cromatograma da entrada 3 (360 mn)

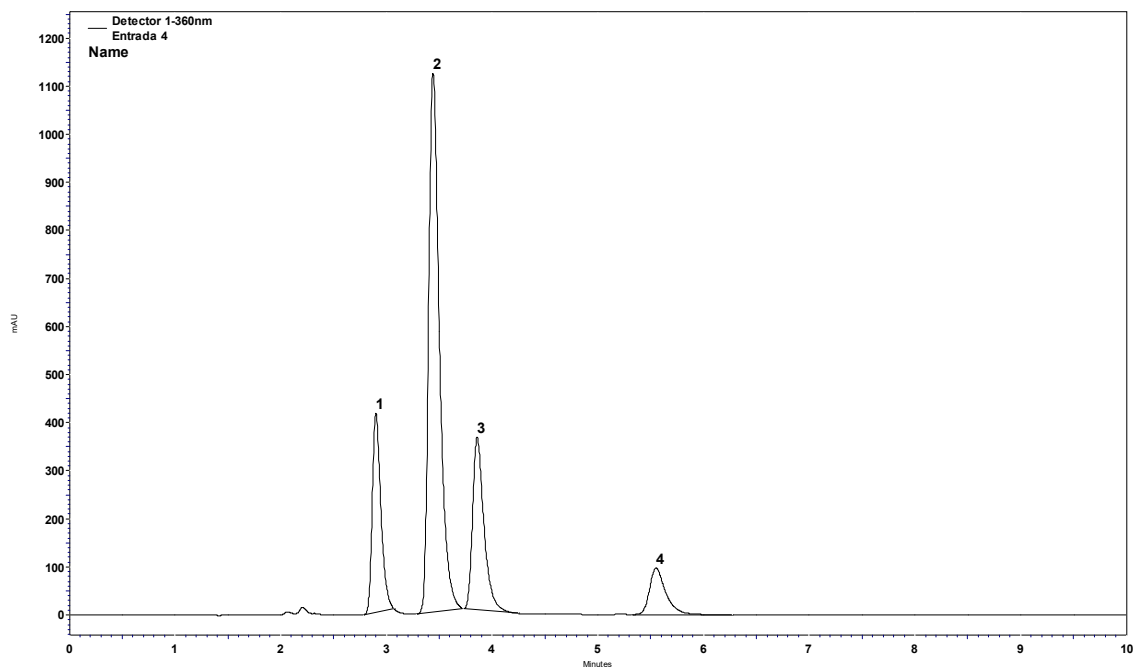


Figura 17S. Cromatograma da entrada 4 (360 mn)

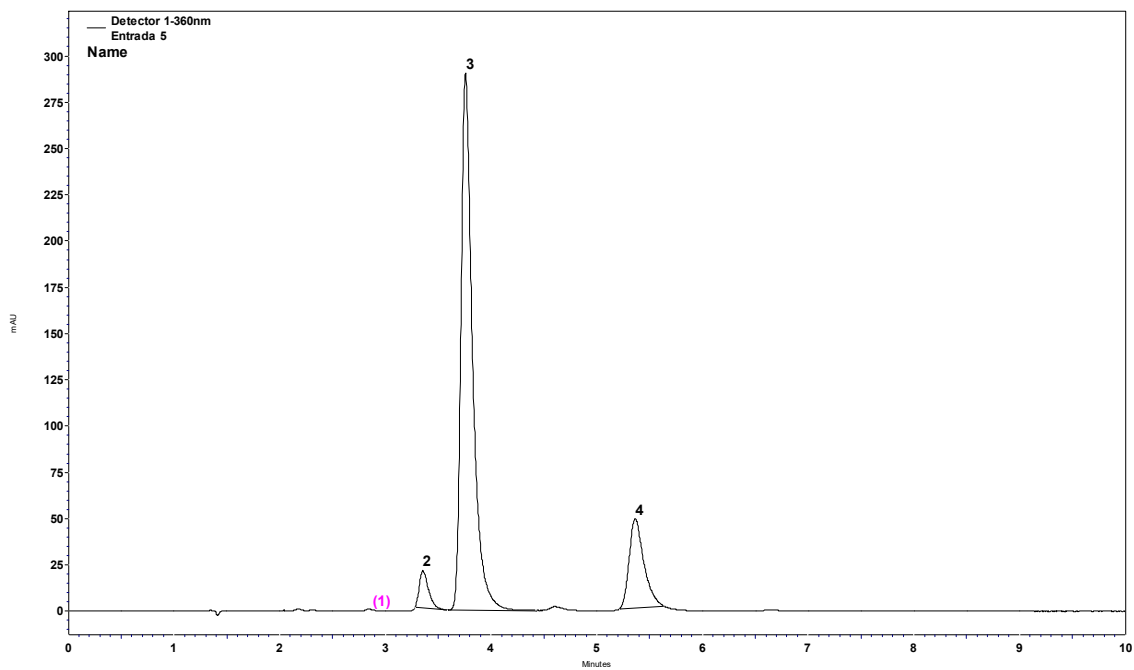


Figura 18S. Cromatograma da entrada 5 (360 mn)

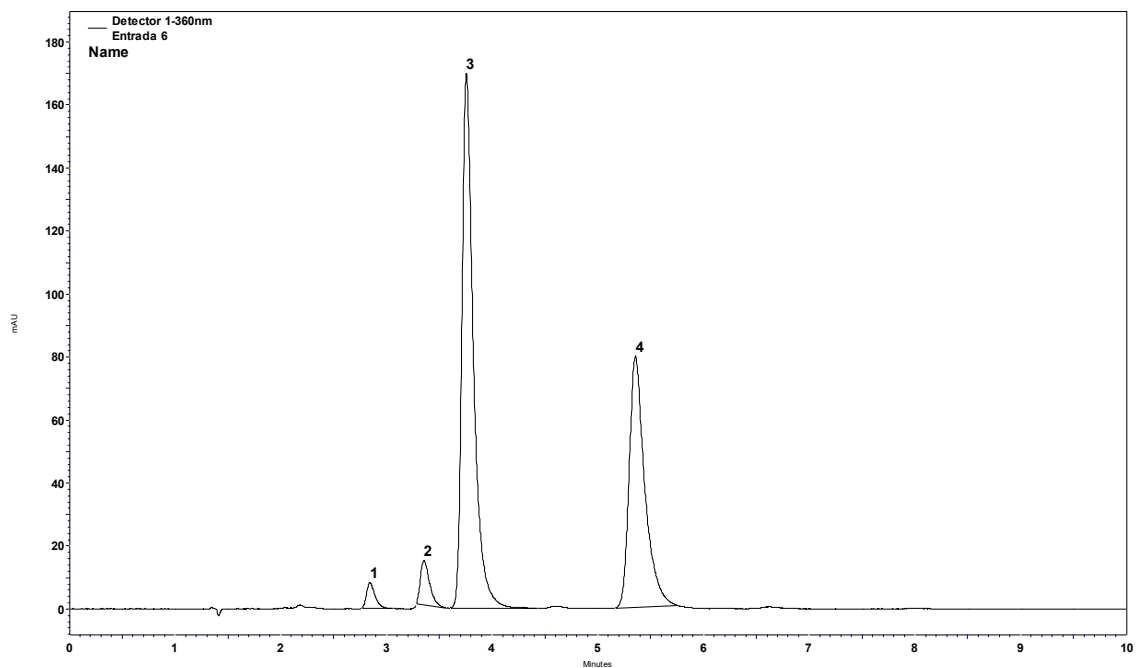


Figura 19S. Cromatograma da entrada 6 (360 mn)

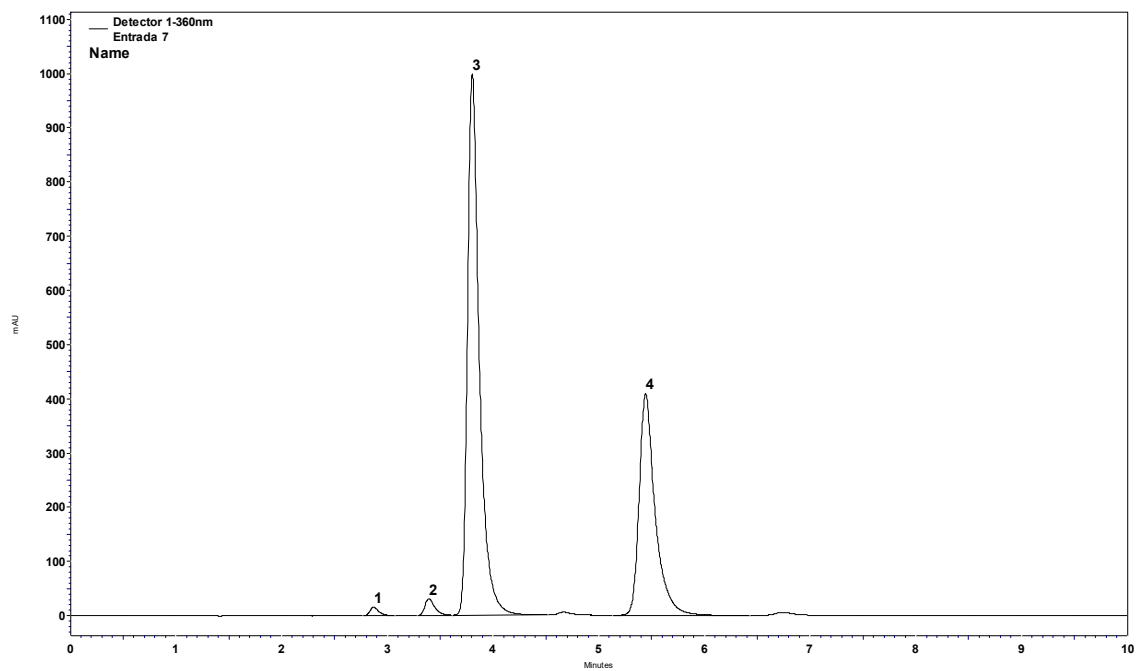


Figura 20S. Cromatograma da entrada 7 (360 mn)

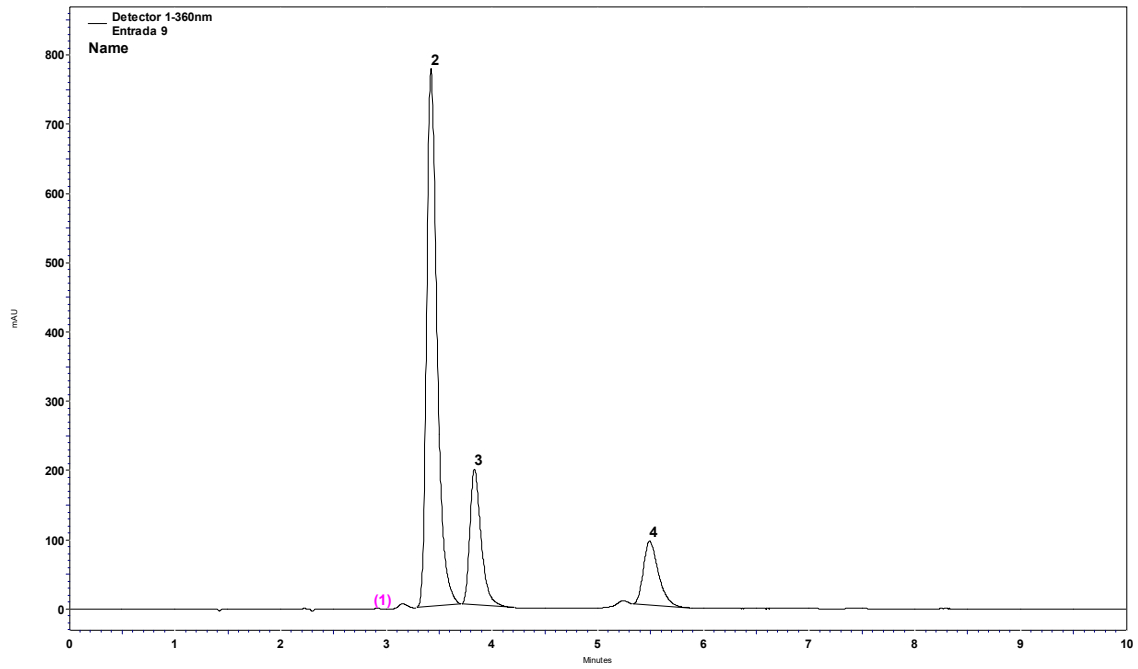


Figura 21S. Cromatograma da entrada 9 (360 mn)

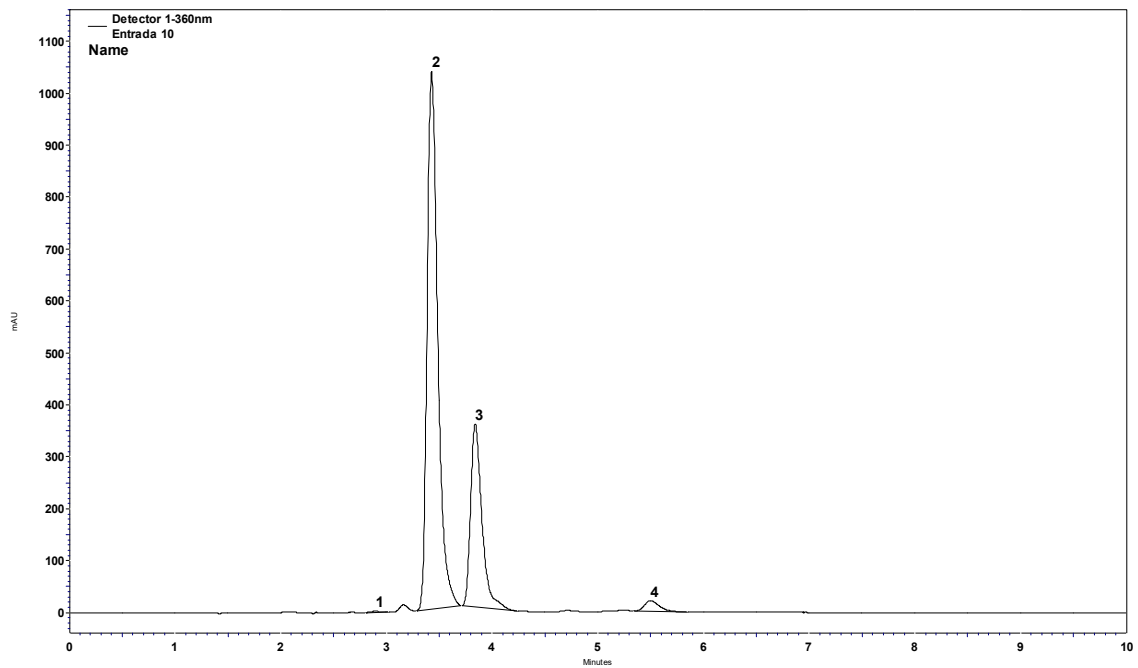


Figura 22S. Cromatograma da entrada 10 (360 mn)

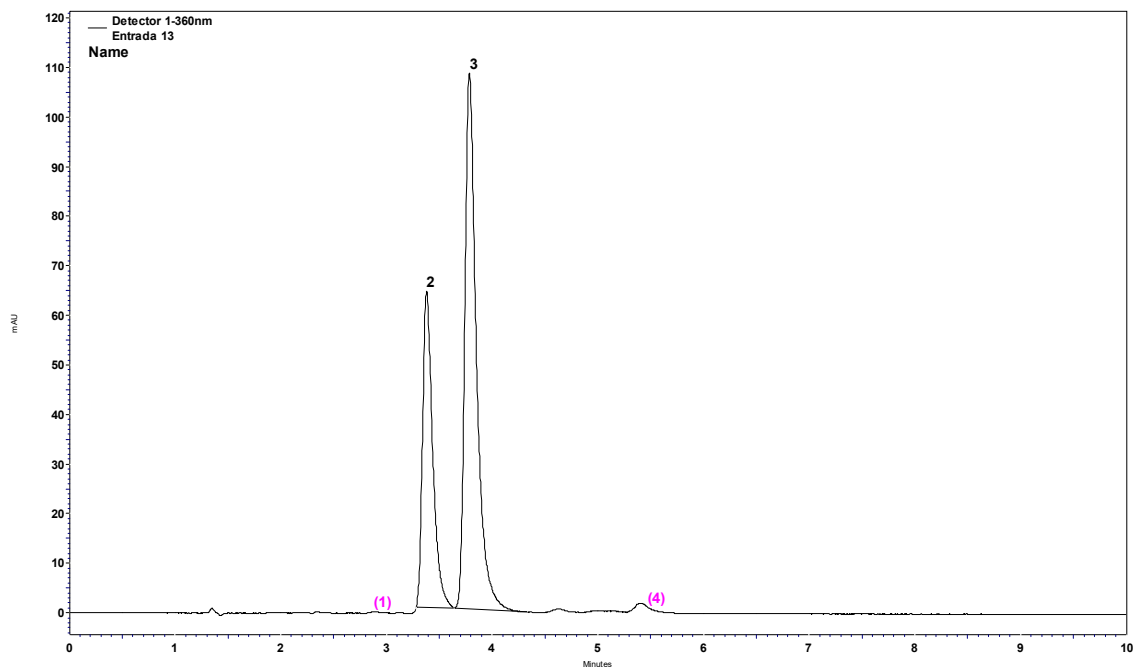


Figura 23S. Cromatograma da entrada 13 (360 nm)

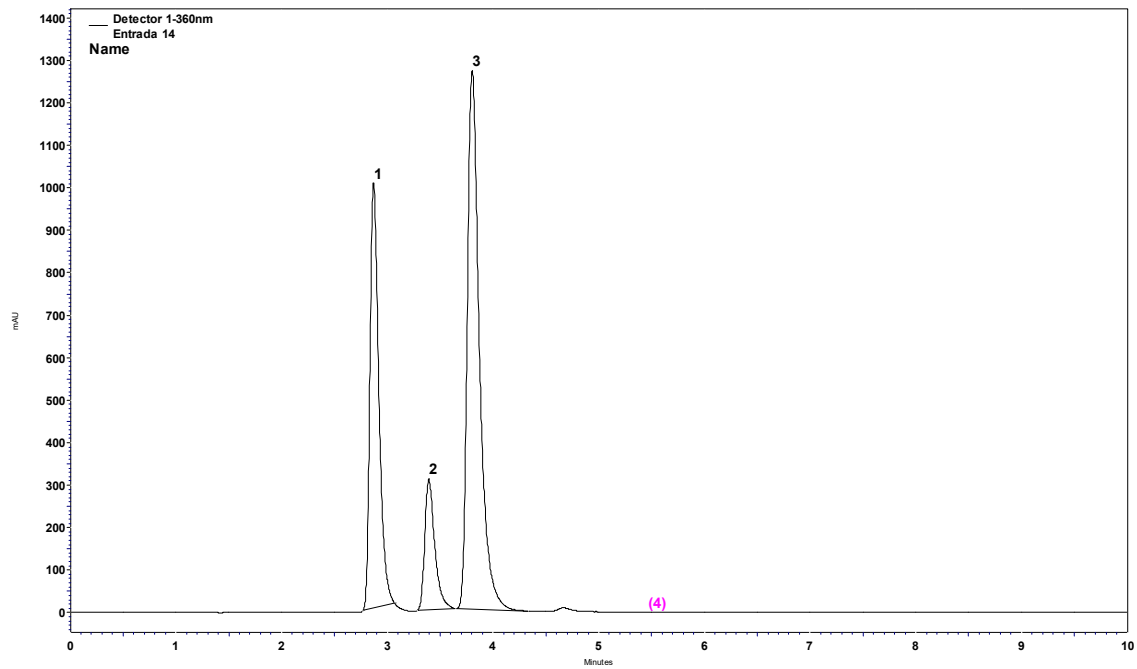


Figura 24S. Cromatograma da entrada 14 (360 nm)

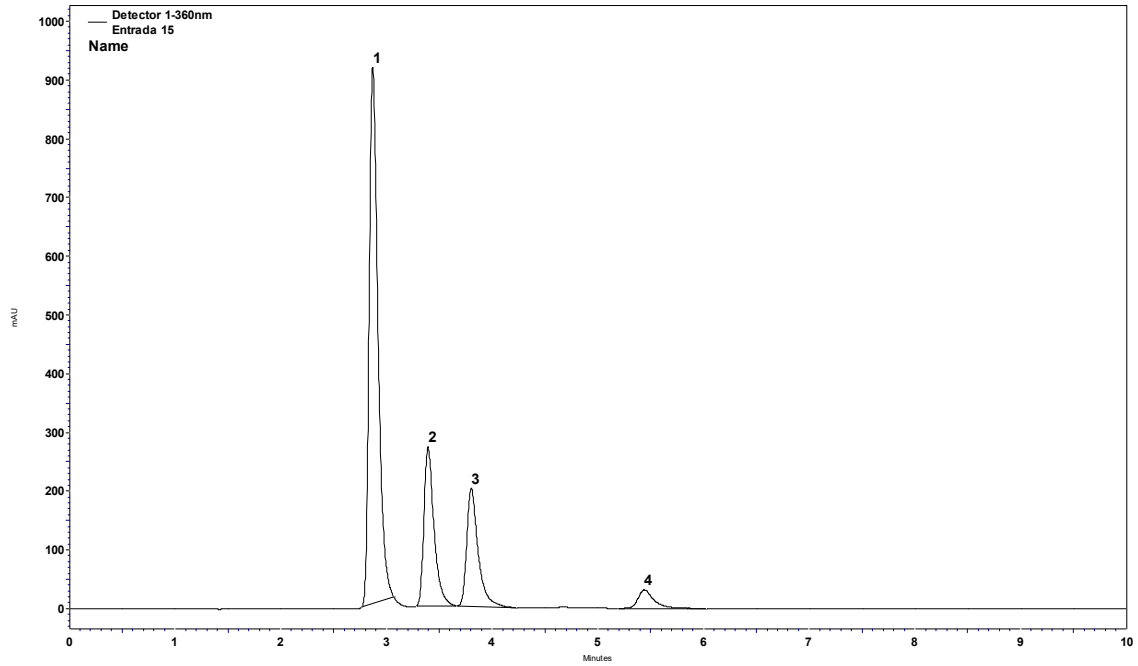


Figura 25S. Cromatograma da entrada 15 (360 mn)

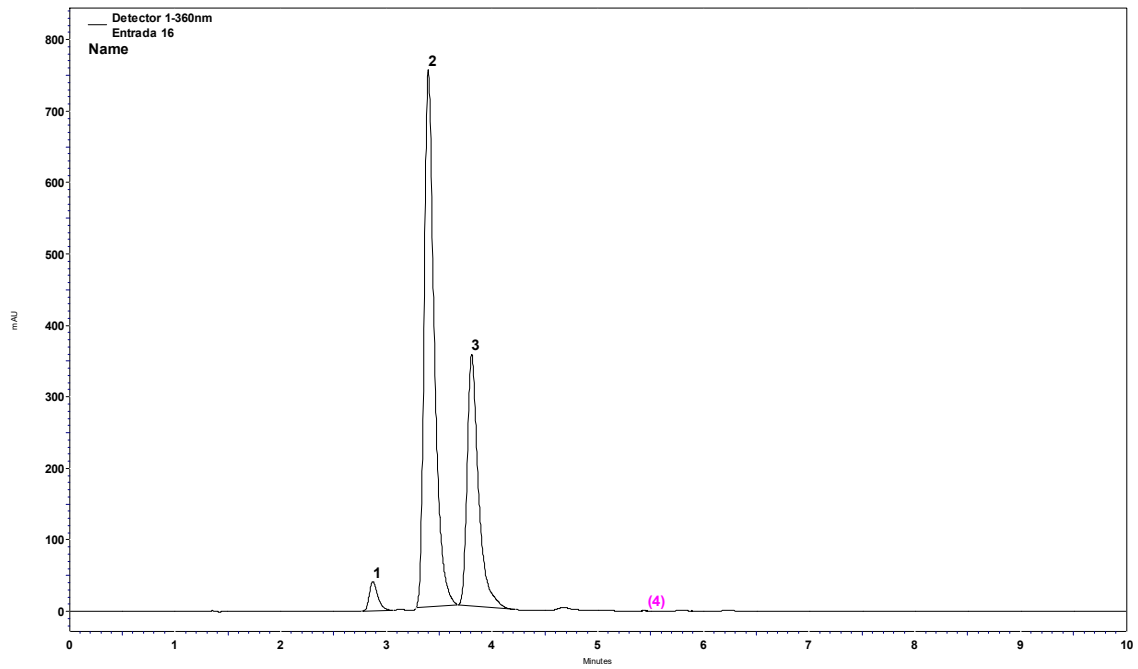


Figura 26S. Cromatograma da entrada 16 (360 mn)

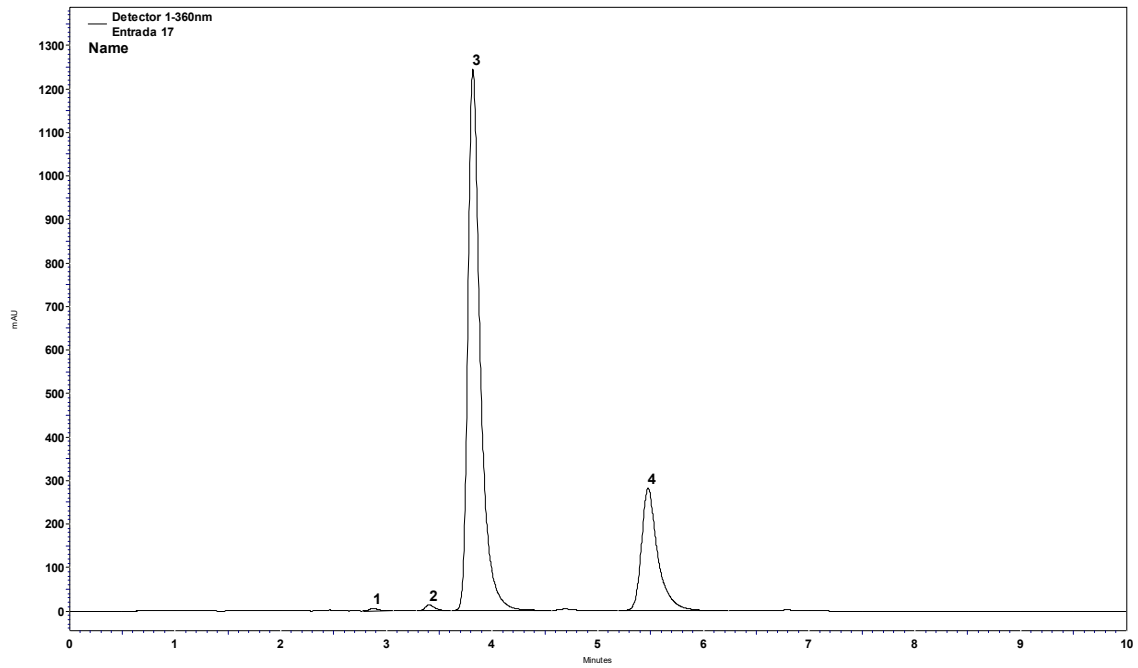


Figura 27S. Cromatograma da entrada 17 (360 mn)

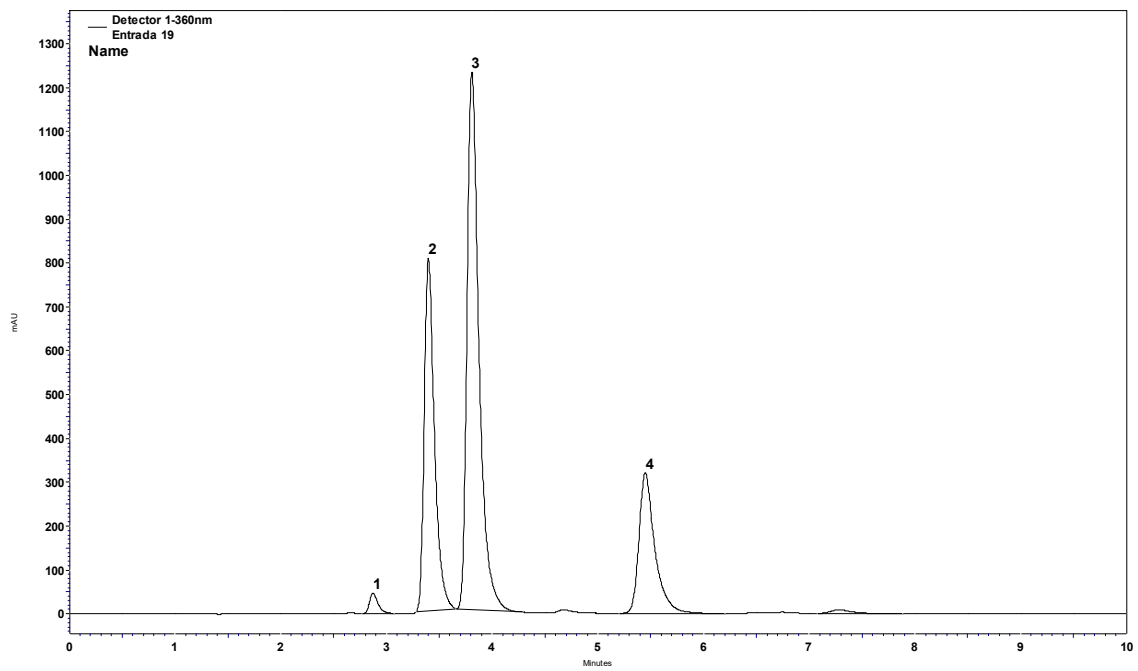


Figura 28S. Cromatograma da entrada 19 (360 mn)

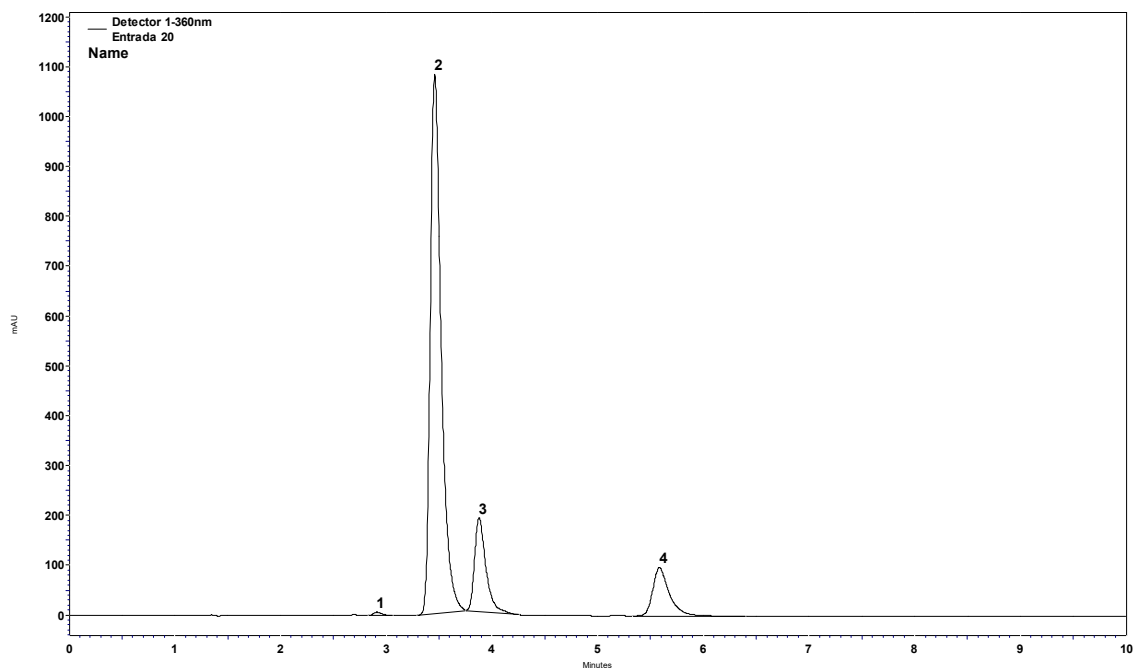


Figura 29S. Cromatograma da entrada 20 (360 mn)

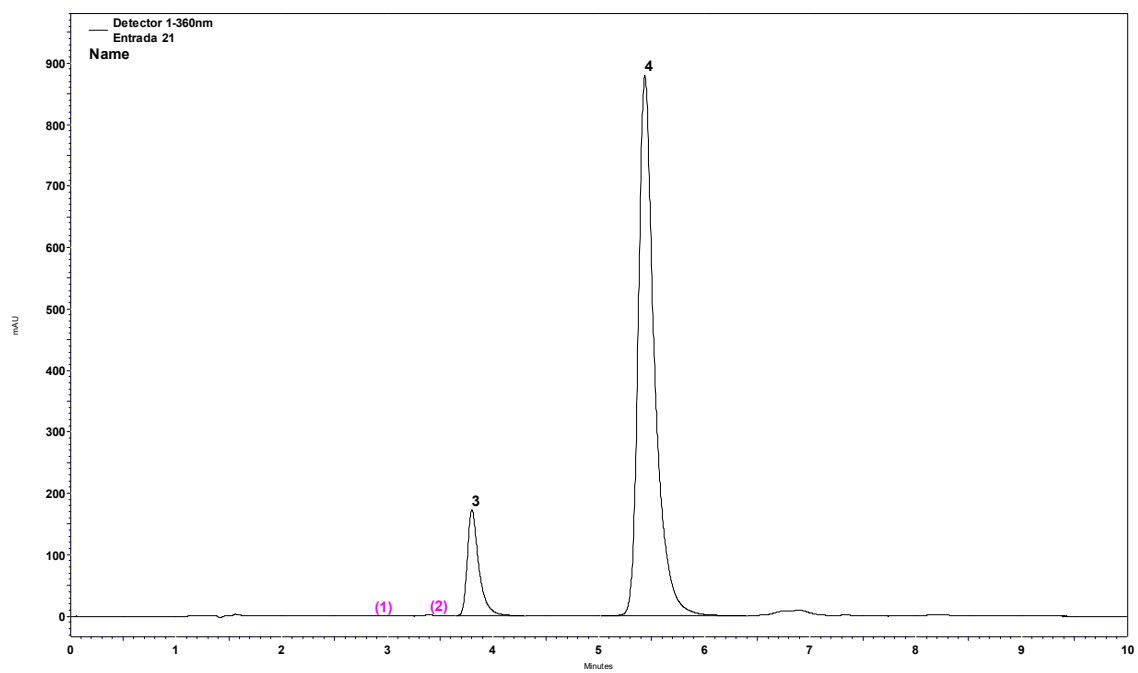


Figura 30S. Cromatograma da entrada 21 (360 mn)