

Supplementary Materials

# Catalyst Loading Controls Chemoselectivity: Unusual Effect in Rhodium(II) Carbene Insertion Reactions with Tetrahydrofuran

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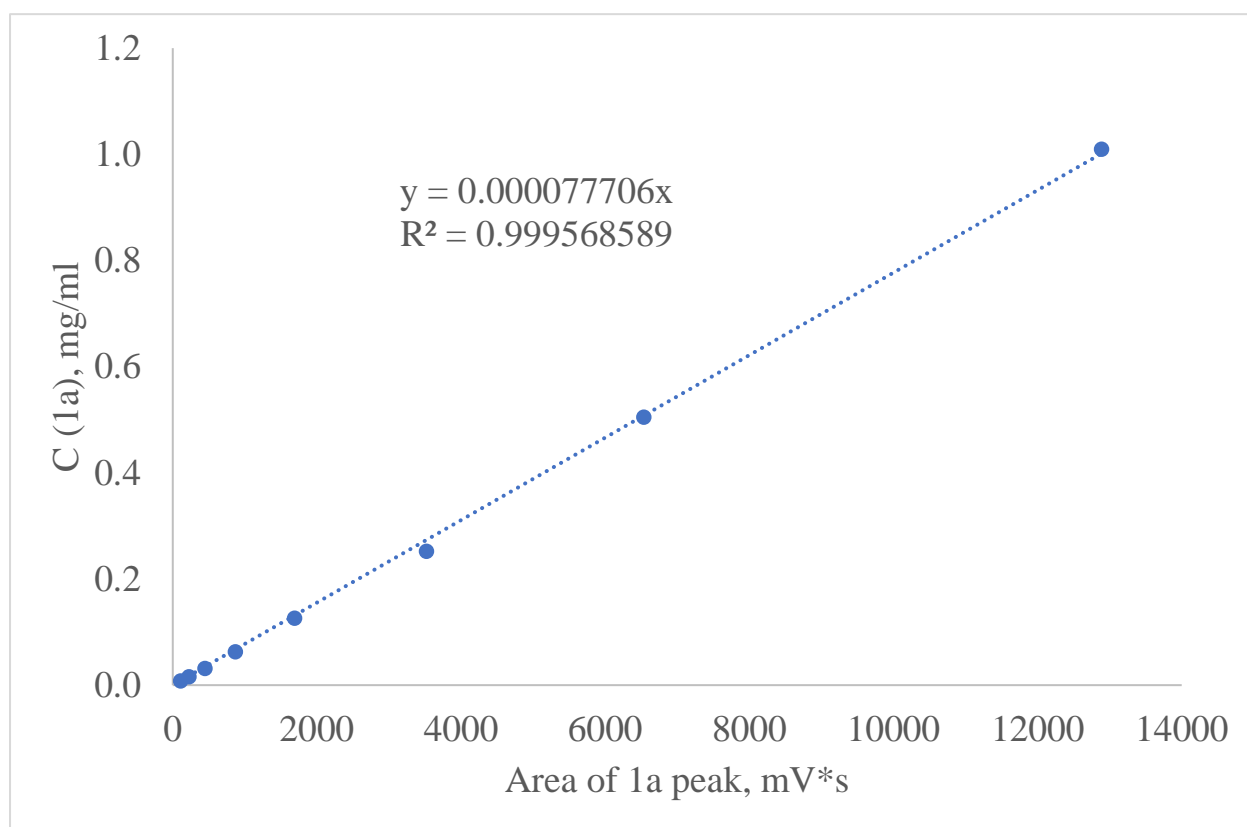
## 1. Calibration

For the possibility of quantitative analysis of the studied systems, calibration was carried out for the model substrate and the resulting products. Three measurements were made for each concentration value (*Table S1*).

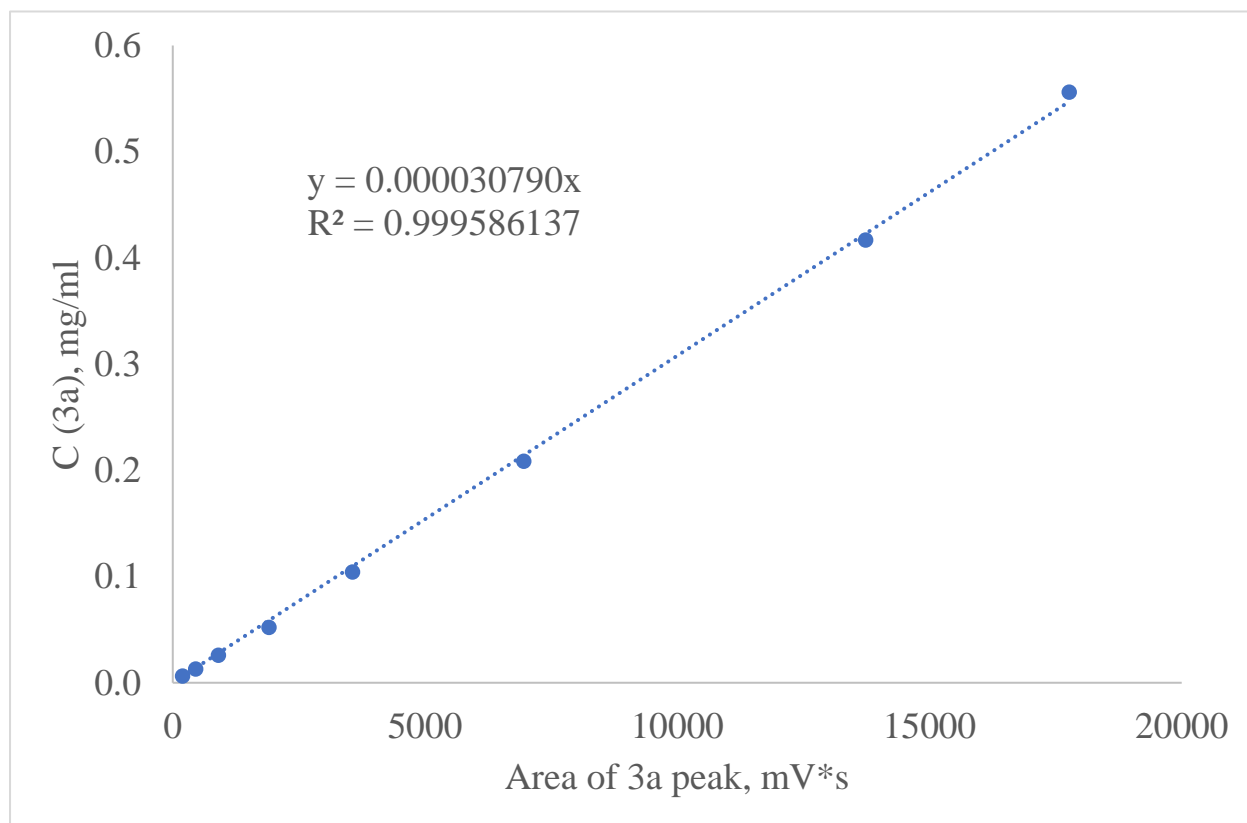
**Table S1:** Results of calibration measurements.

Entry	C (3a), mg/ml	C (1a), mg/ml	C (2a), mg/ml	Area of 3a peak, mV*s	Area of 1a peak, mV*s	Area of 2a peak, mV*s
1	0.556	1.01	0.483	17772.483	12889.307	13495.131
2				17303.525	12850.033	12965.550
3				17246.016	12618.125	12909.957
4	0.417	0.505	0.362	13737.729	6537.763	10379.871
5				12868.914	6458.718	9584.786
6				13169.631	6696.736	9856.617
7	0.2085	0.2525	0.181	6960.202	3521.901	5234.800
8				6972.000	3521.958	5259.620
9				7019.211	3353.182	5232.704
10	0.10425	0.12625	0.0905	3560.954	1690.826	2682.348
11				3610.960	1655.043	2713.874
12				3317.525	1674.094	2491.969
13	0.052125	0.063125	0.04525	1907.088	866.689	1433.015
14				1791.501	869.632	1341.662
15				1814.327	868.752	1359.543
16	0.0260625	0.0315625	0.022625	907.231	447.779	681.854
17				907.367	437.772	684.545
18				900.564	441.185	676.066
19	0.01303125	0.01578125	0.0113125	451.775	225.974	330.682
20				452.159	227.439	346.675
21				451.135	222.638	339.933
22	0.006515625	0.007890625	0.00565625	191.860	111.110	144.818
23				230.924	112.641	163.949
24				227.832	108.330	166.072

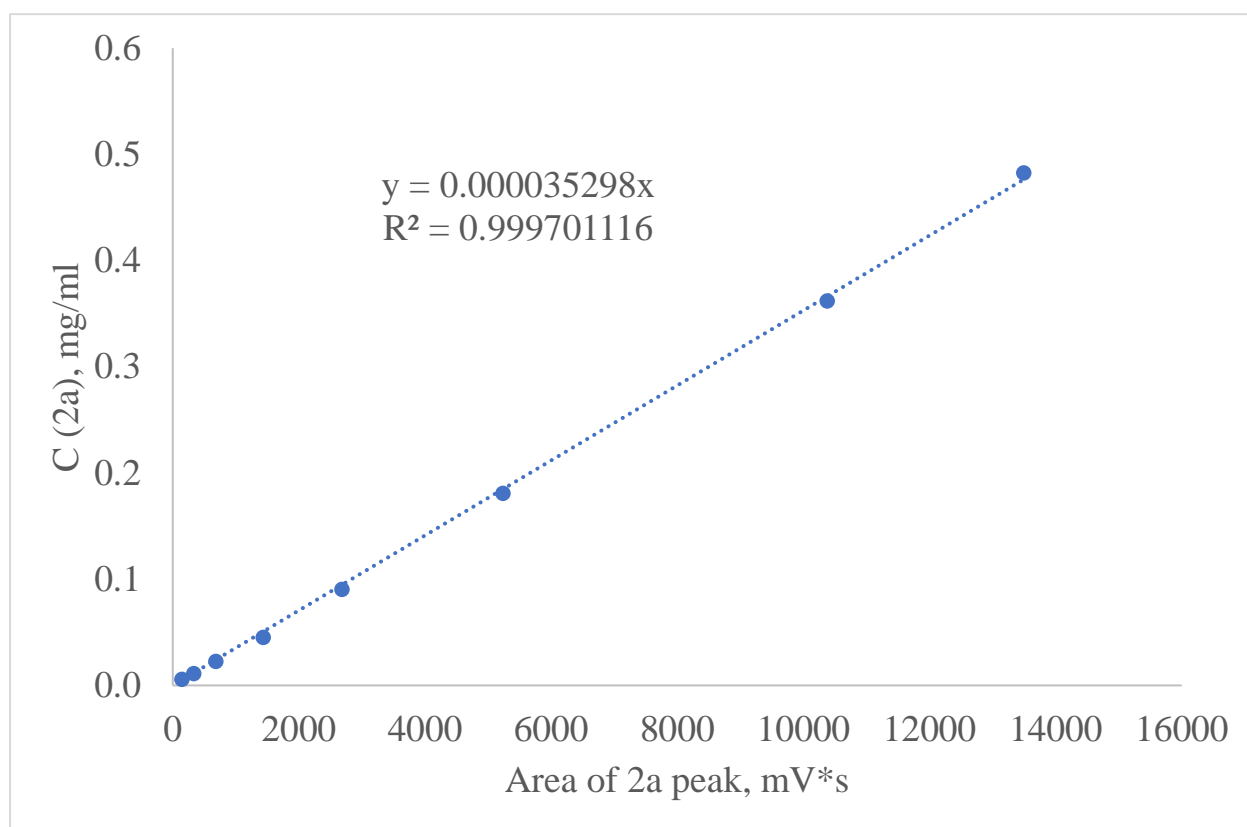
The obtained data can be presented in the form of calibration curves (*Figure S1 – S3*).



**Figure S1:** Calibration curve for **1a**.



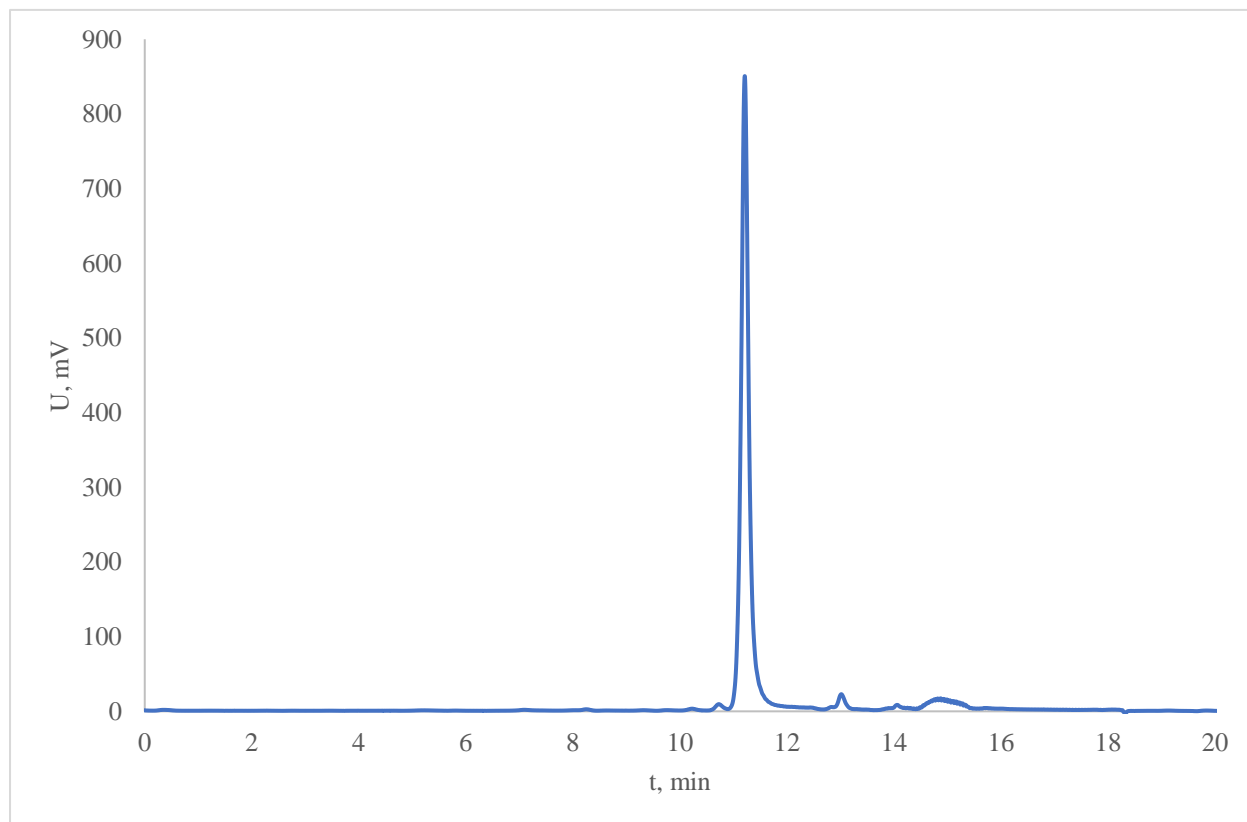
**Figure S2:** Calibration curve for **3a**.



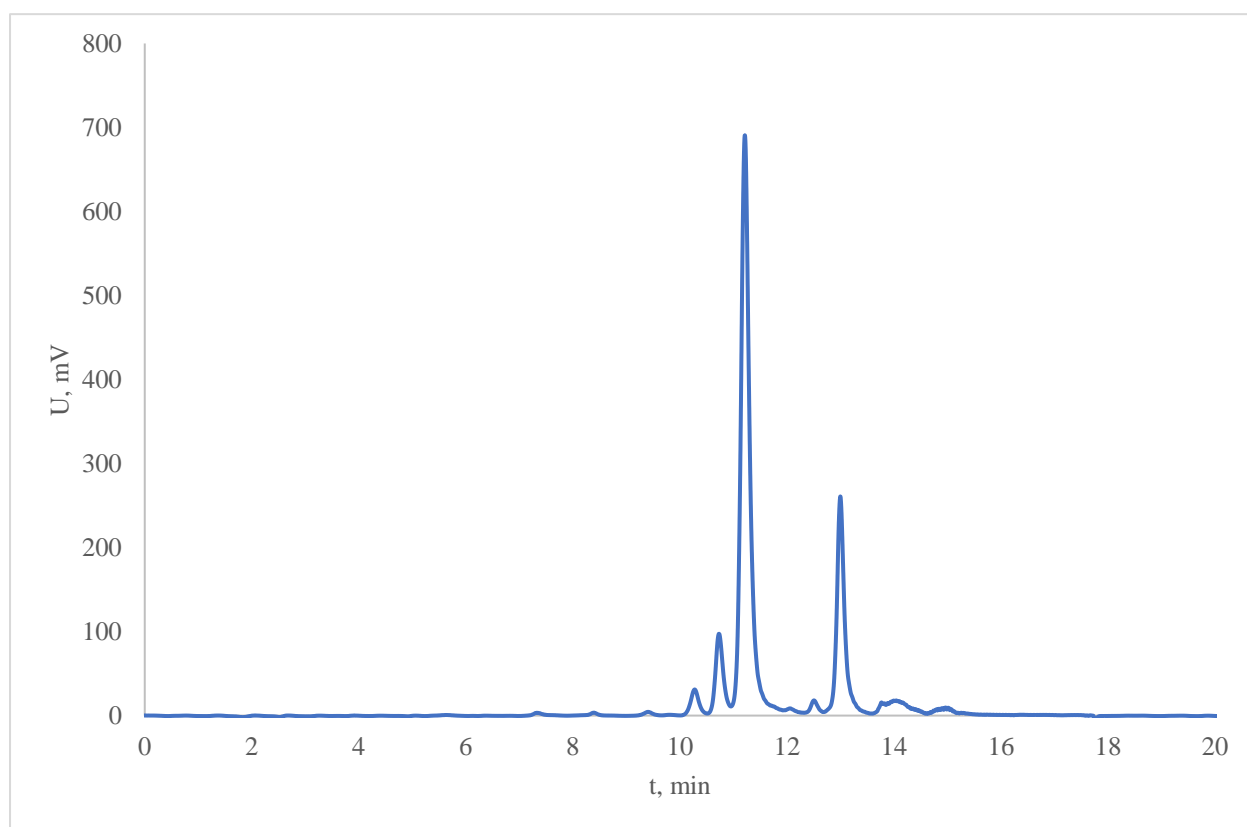
**Figure S3:** Calibration curve for **2a**.

## 2. HPLC Chromatograms

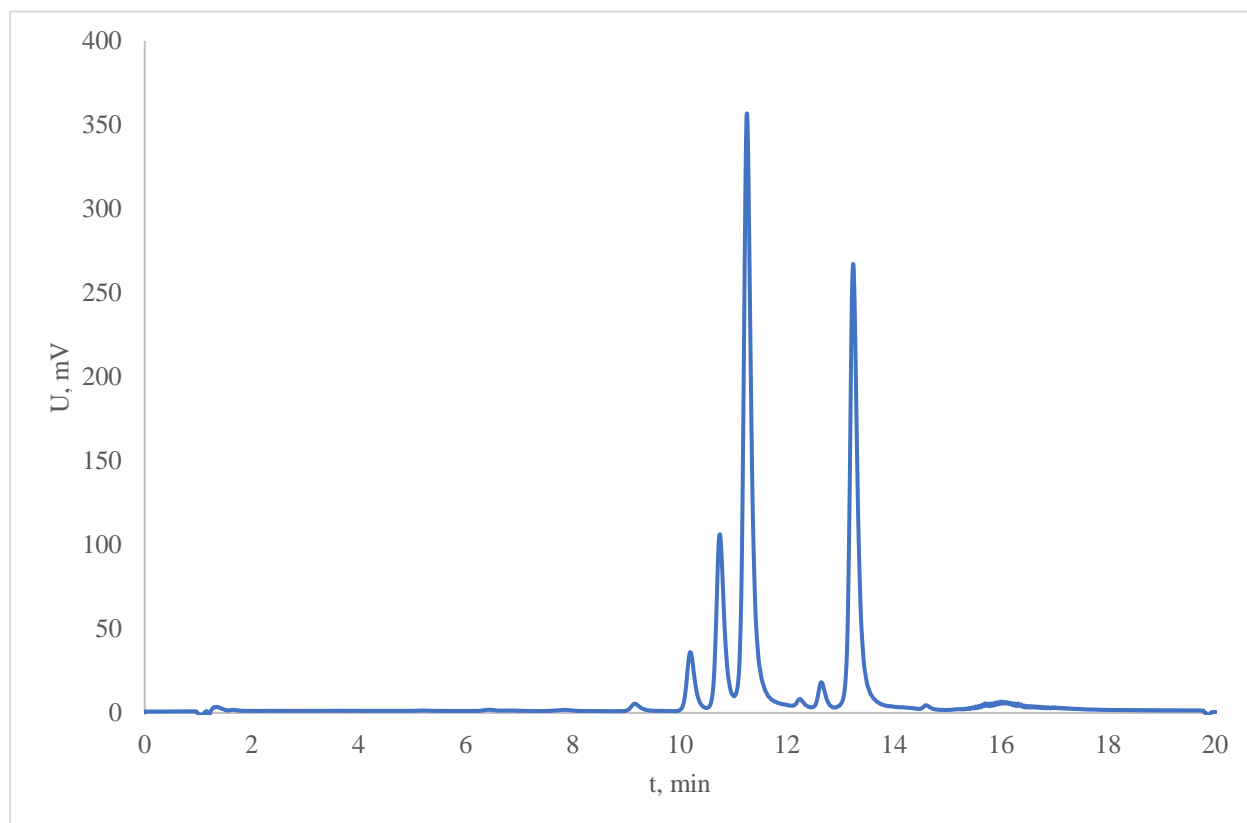
HPLC chromatograms of **1a**  $\rightarrow$  **2a** + **3a** reaction performed at different conversion (*Figure S4 – S15*). Reactions were run in 1 mL THF with model substrate **1a** (0.1 mmol) and  $\text{Rh}_2(\text{esp})_2$  as a catalyst (0.1 mol%) at 30 °C.



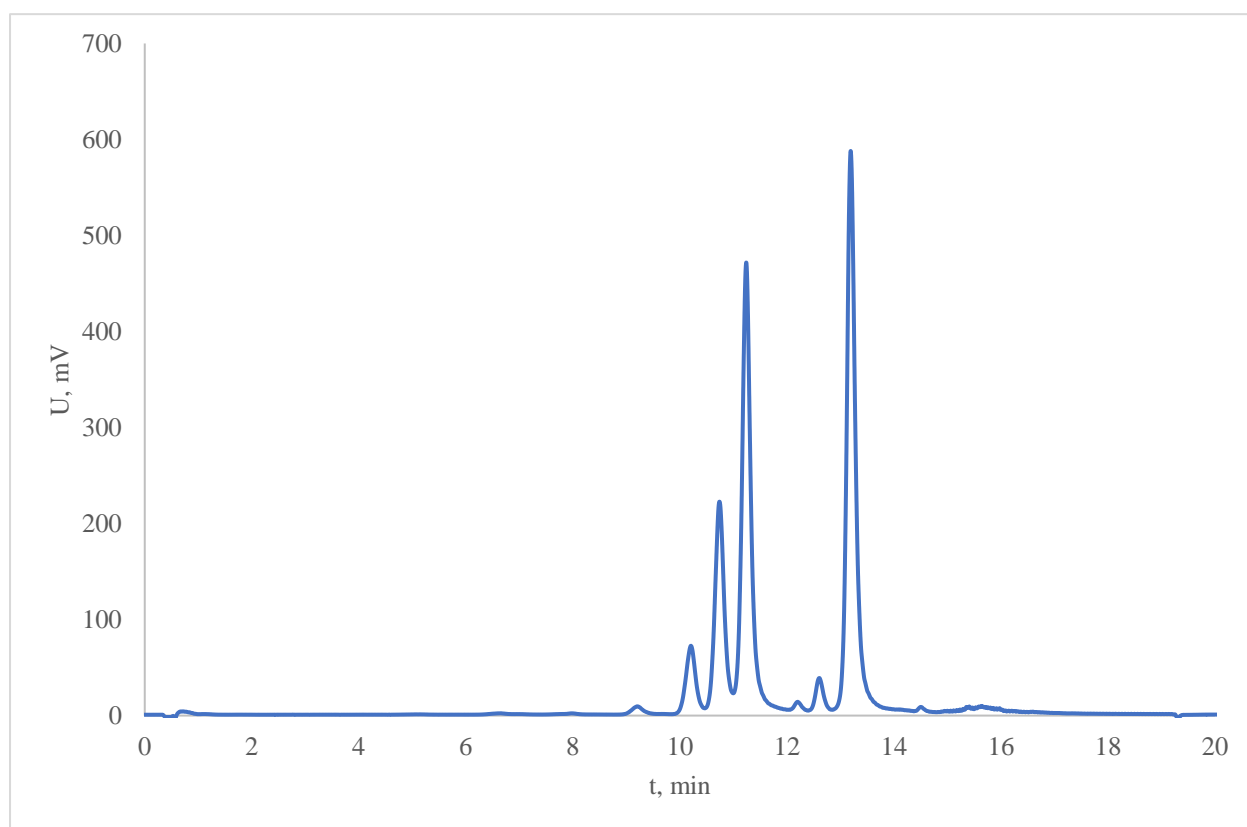
**Figure S4:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 2 min.



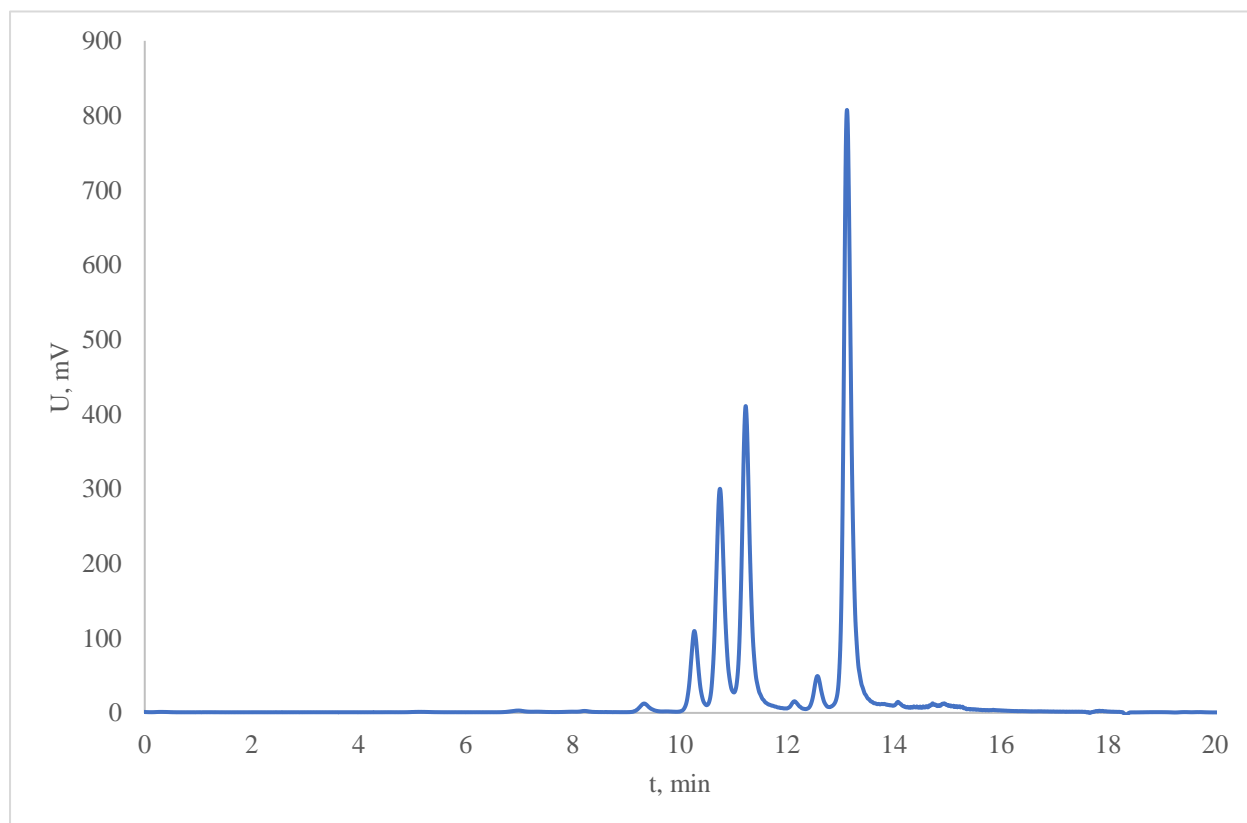
**Figure S5:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 15 min.



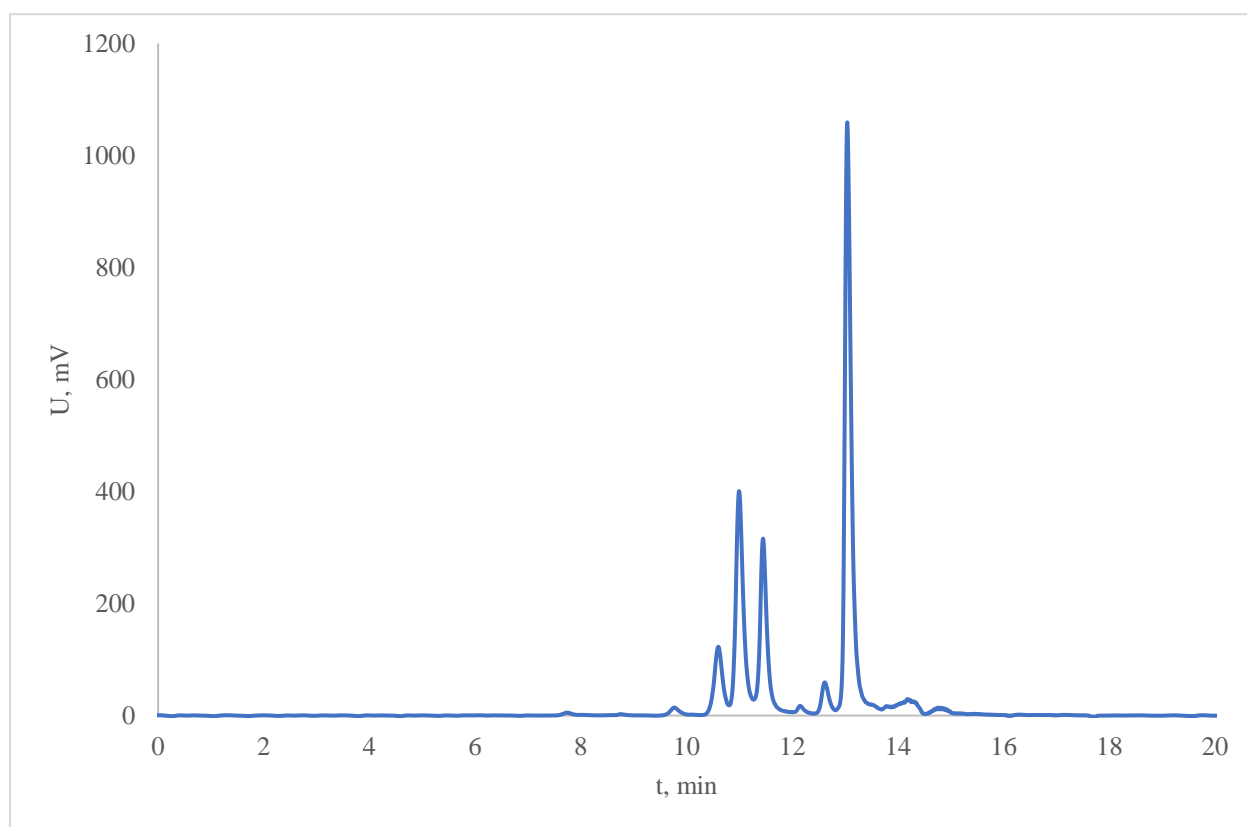
**Figure S6:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 30 min.



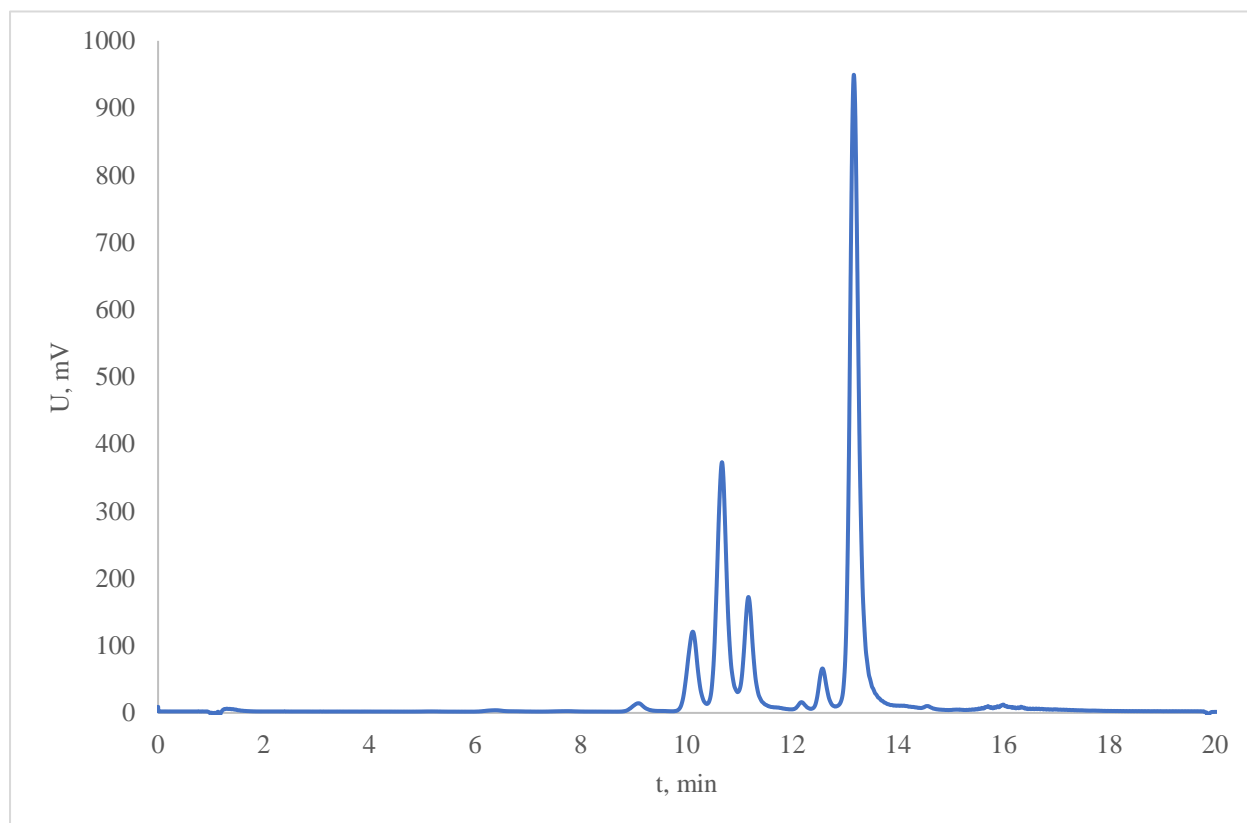
**Figure S7:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 45 min.



**Figure S8:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 60 min.

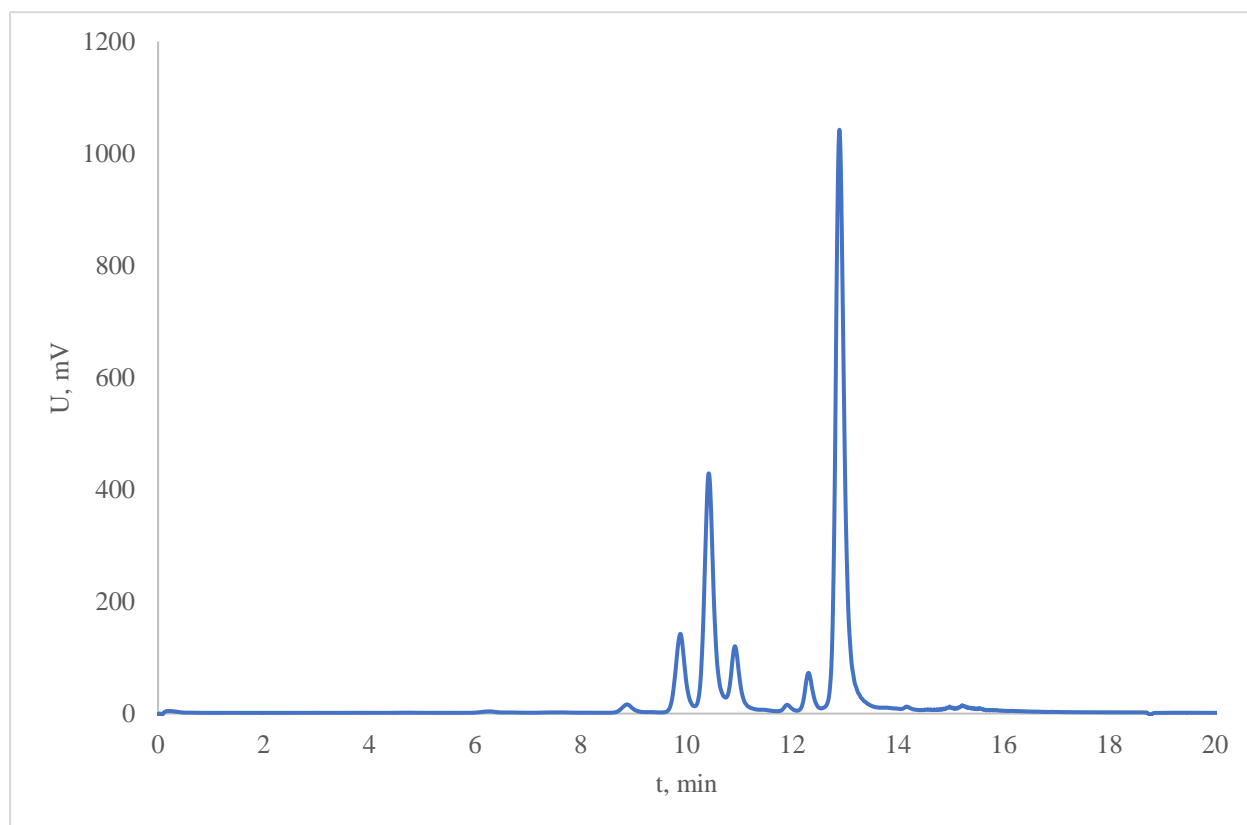


**Figure S9:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 90 min.

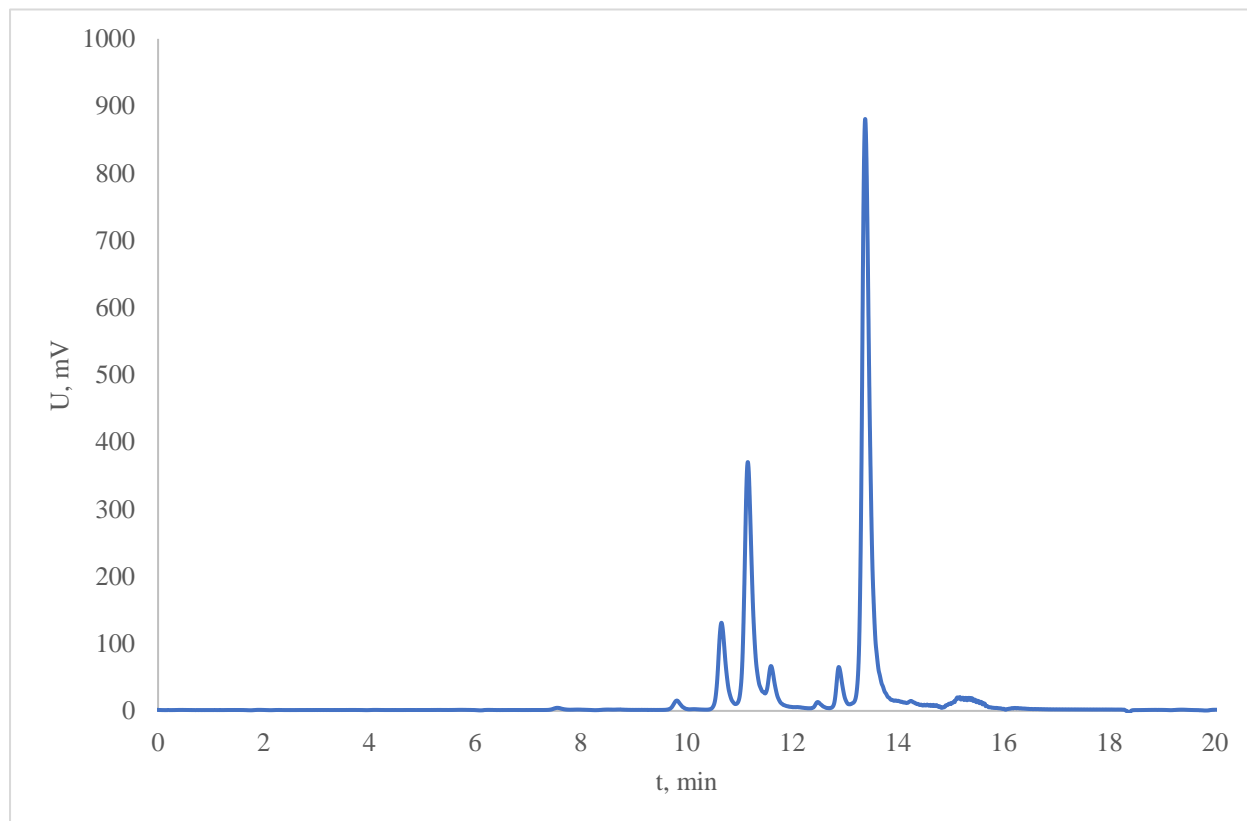


**Figure S10:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 120 min.

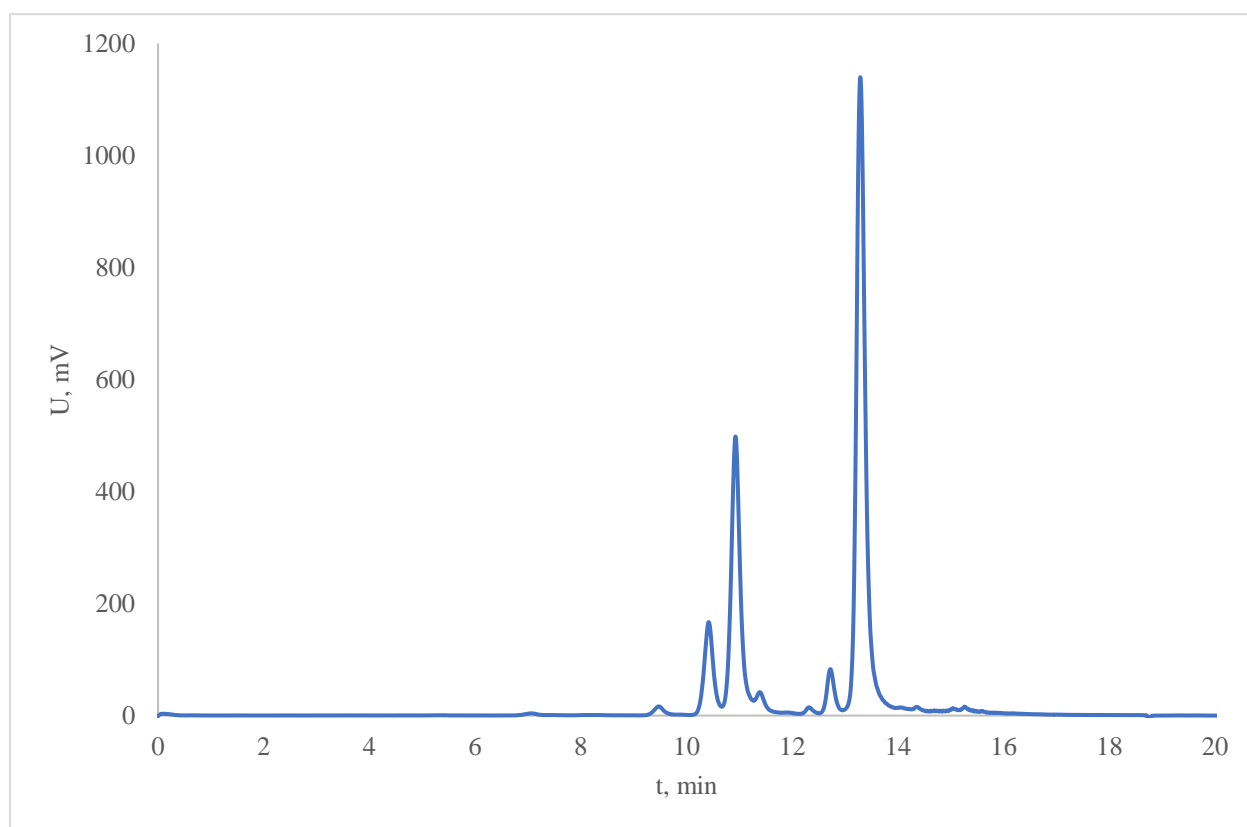




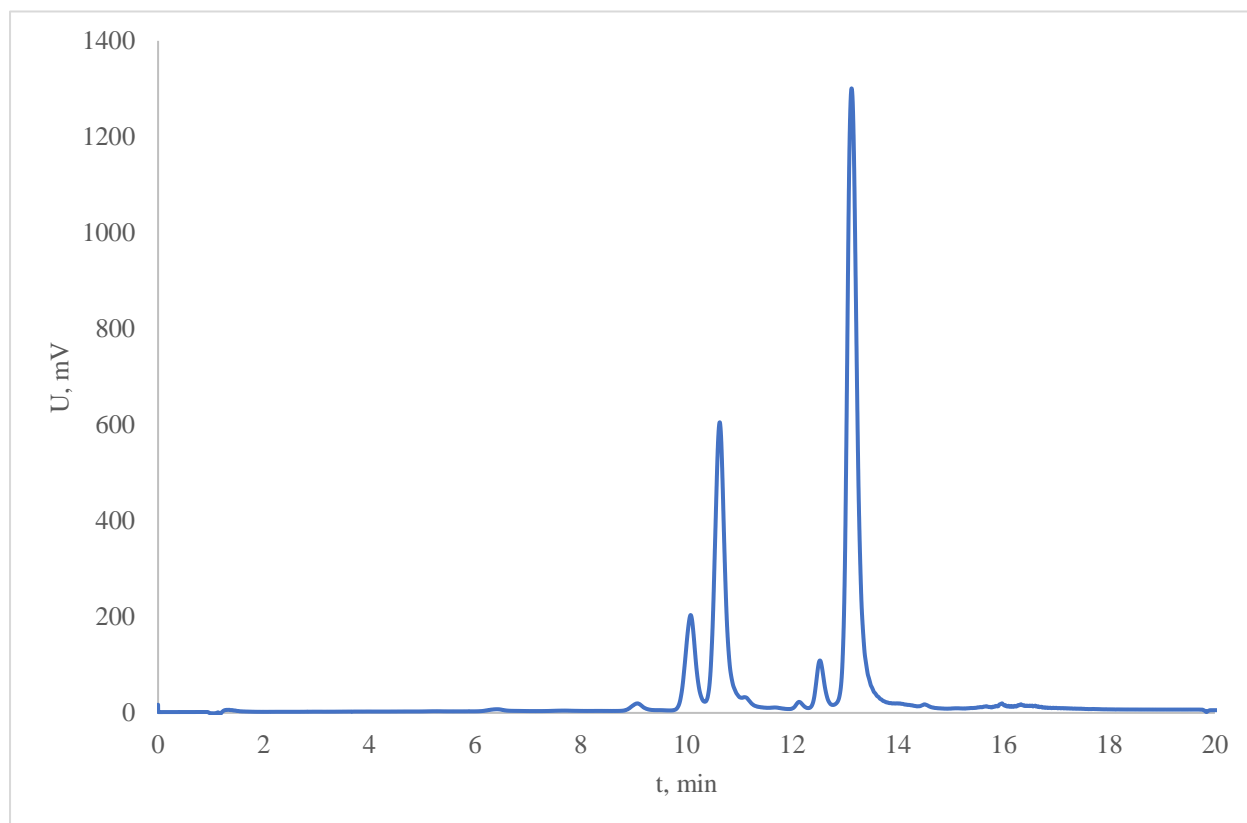
**Figure S11:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 150 min.



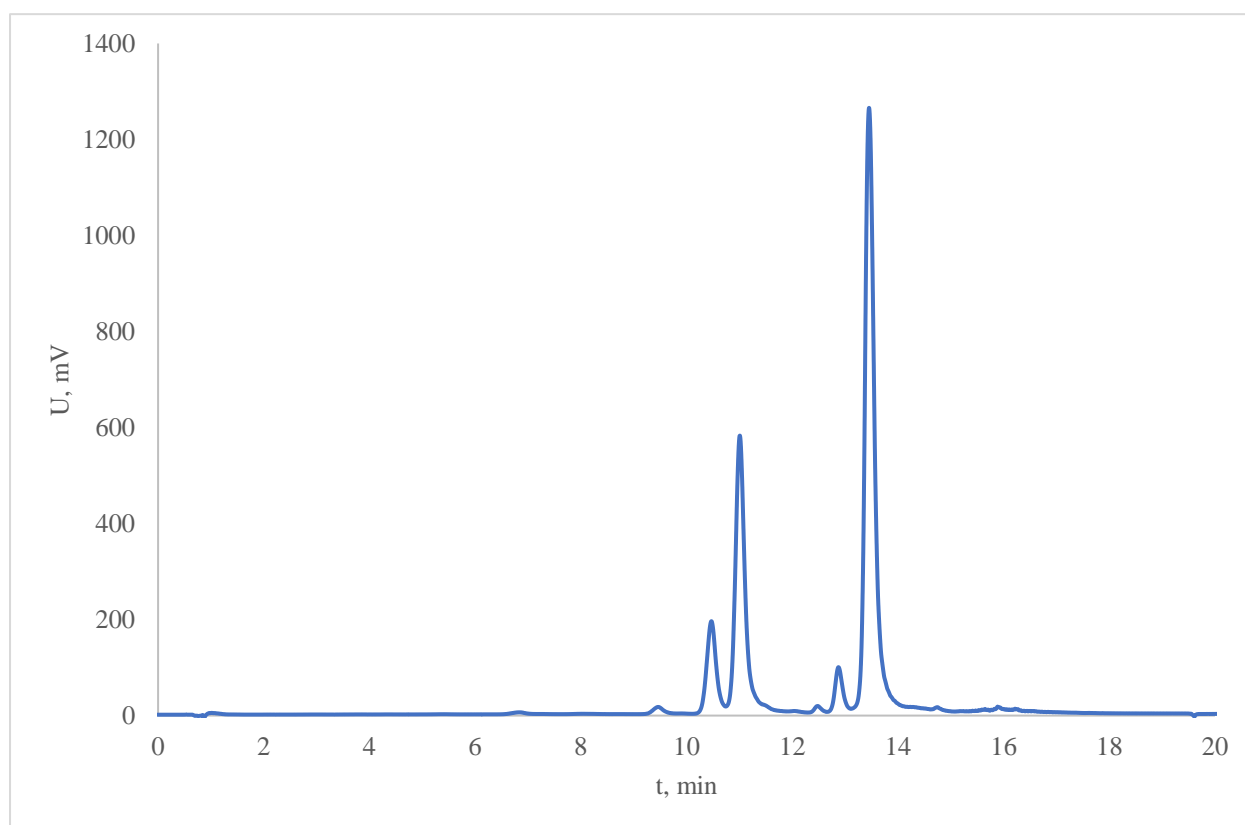
**Figure S12:** HPLC chromatogram of reaction **1a**  $\rightarrow$  **2a** + **3a** after 180 min.



**Figure S13:** HPLC chromatogram of reaction **1a** → **2a** + **3a** after 240 min.



**Figure S14:** HPLC chromatogram of reaction **1a** → **2a** + **3a** after 300 min.



**Figure S15:** HPLC chromatogram of reaction **1a** → **2a** + **3a** after 360 min.

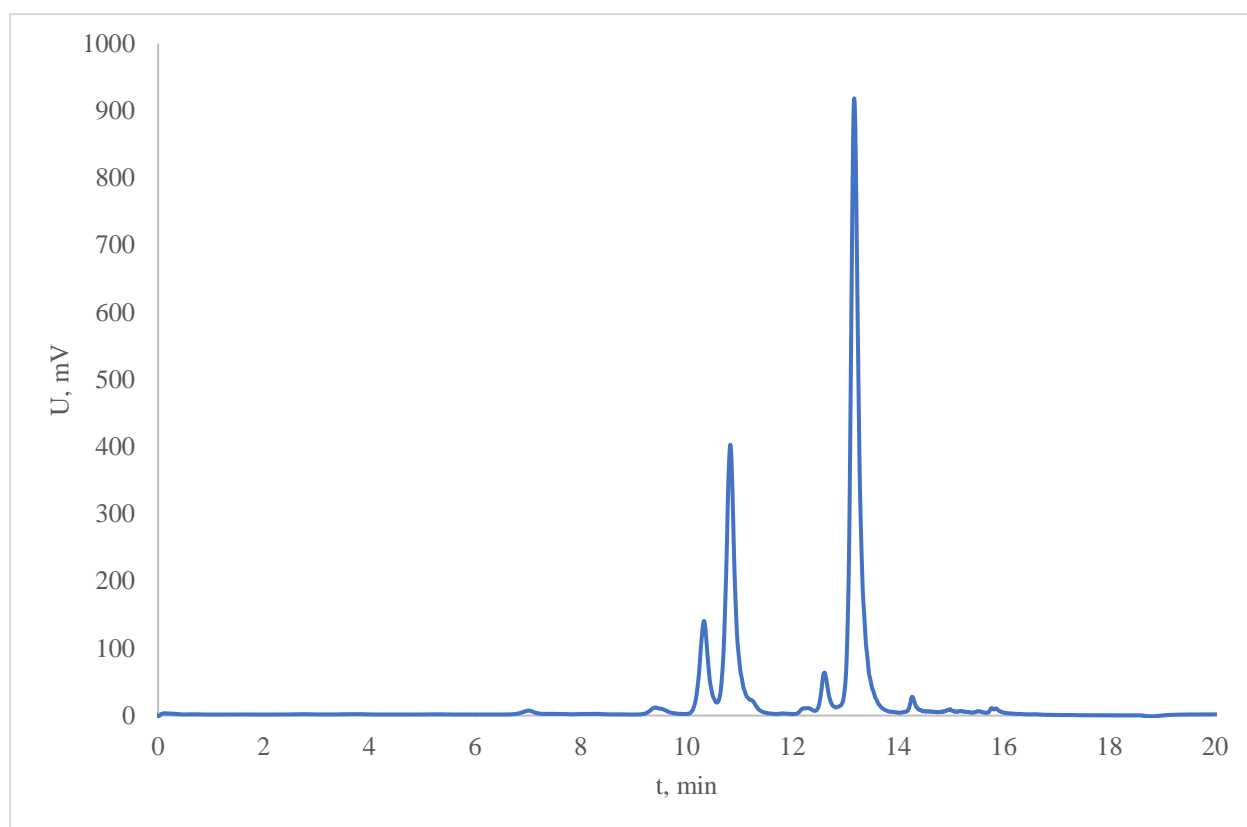
**Table S2:** Outcome of **1a** → **2a** + **3a** reactions performed with different catalysts and catalyst loadings.

Catalyst	[Rh] mol%	Yield <b>3a</b> , %	Yield <b>2a</b> , %	Fraction of <b>3a</b> , %	Conversion, %
Rh <sub>2</sub> (AdmCOO) <sub>4</sub>	10	78	7	92	100
	5	77	12	86	100
	2	68	28	71	100
	1	42	28	60	100
	0.1	27	53	33	100
	0.01	17	37	31	81
	0.01*	20	43	32	100
Rh <sub>2</sub> (PivO) <sub>4</sub>	10	81	10	89	100
	5	76	18	80	100
	2	67	38	64	100
	1	45	42	52	100
	0.1	23	54	30	100
	0.01	12	34	26	62
	0.01*	18	48	28	100
Rh <sub>2</sub> (esp) <sub>2</sub>	10	81	7	92	100

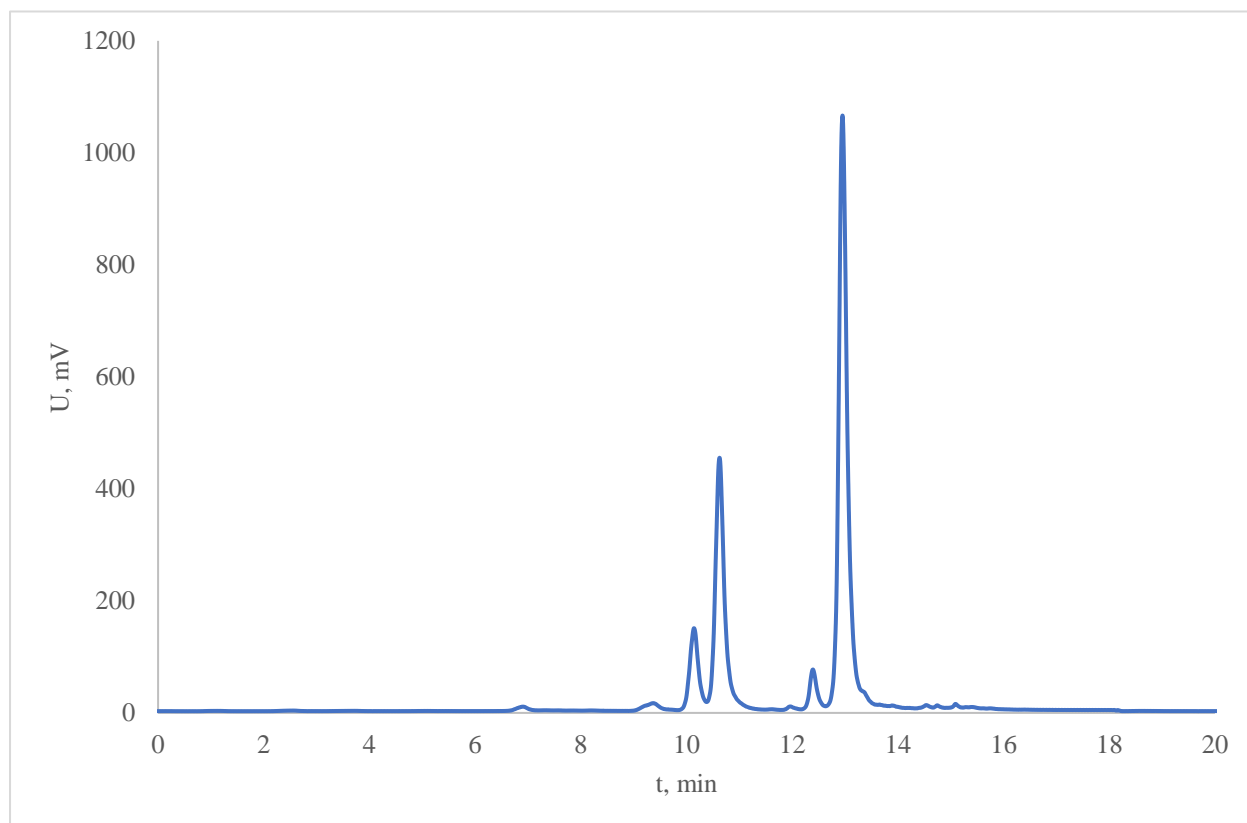
	5	80	12	87	100
	2	71	24	75	100
	1	53	34	61	100
	0.1	26	52	34	100
	0.01	18	46	28	72
	0.01*	19	52	27	100
Rh <sub>2</sub> (AcO) <sub>4</sub>	10	63	27	70	100
	5	39	29	57	100
	2	22	35	38	100
	1	22	66	25	100
	0.1	4	47	8	100
	0.01	3	32	8	47
	0.01*	3	51	5	100
Rh <sub>2</sub> (n-C <sub>4</sub> H <sub>9</sub> COO) <sub>4</sub>	10	81	16	84	100
	5	72	27	73	100
	2	54	39	59	100
	1	33	48	41	100
	0.1	14	55	20	100
	0.01	5	28	16	83
	0.01*	8	47	15	100
Rh <sub>2</sub> (n-C <sub>7</sub> H <sub>15</sub> COO) <sub>4</sub>	10	61	13	82	100
	5	55	26	68	100
	2	28	30	48	100
	1	31	54	36	100
	0.1	24	82	23	100
	0.01	5	27	16	54
	0.01*	7	42	14	100

\* Reactions were run at 50 °C

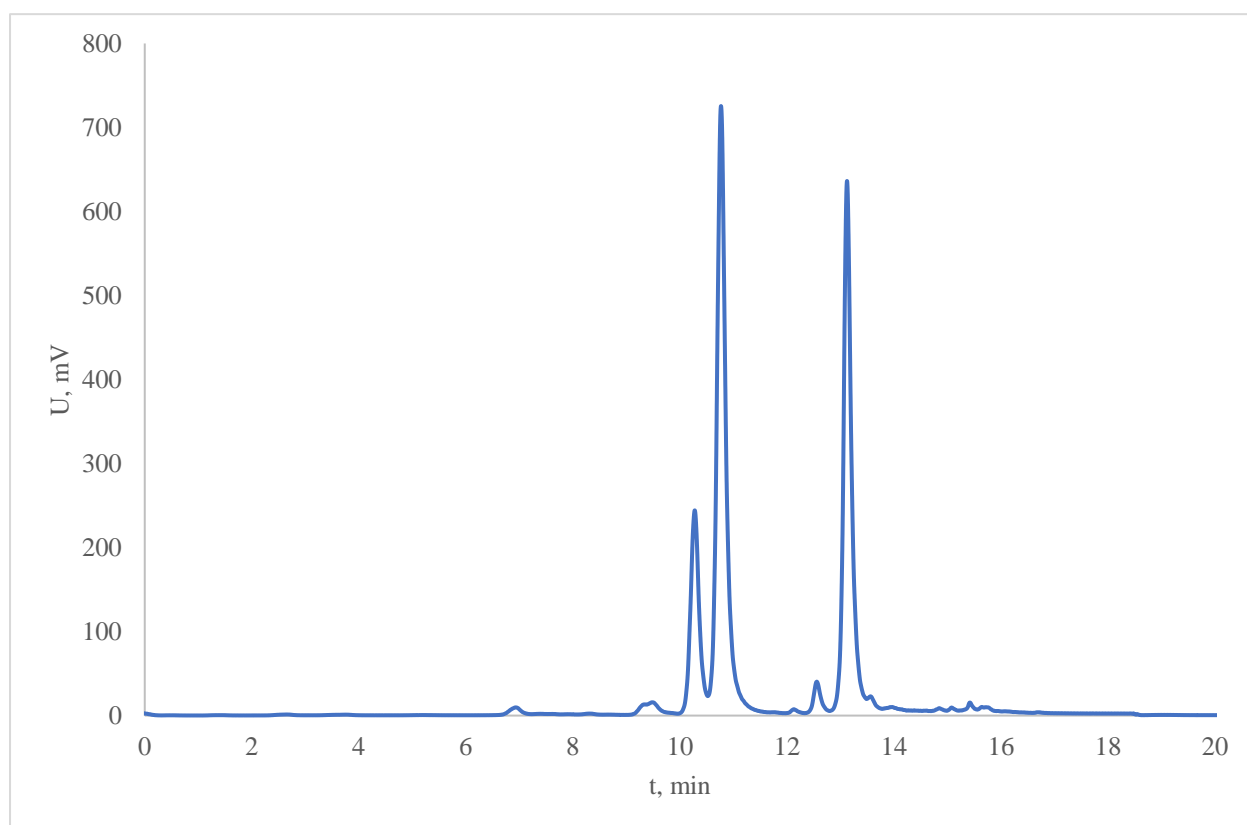
HPLC chromatograms of **1a** → **2a** + **3a** reaction performed with different catalysts and catalyst loadings (Figure S16 – S51). Reactions were run in 1 ml THF with model substrate **1a** (0.1 mmol) at 30 °C for 72 h (except for the reactions catalyzed by 0.01 mol% of the Rh(II) catalyst for which the temperature was raised to 50 °C in order to achieve full conversion over the same period of time).



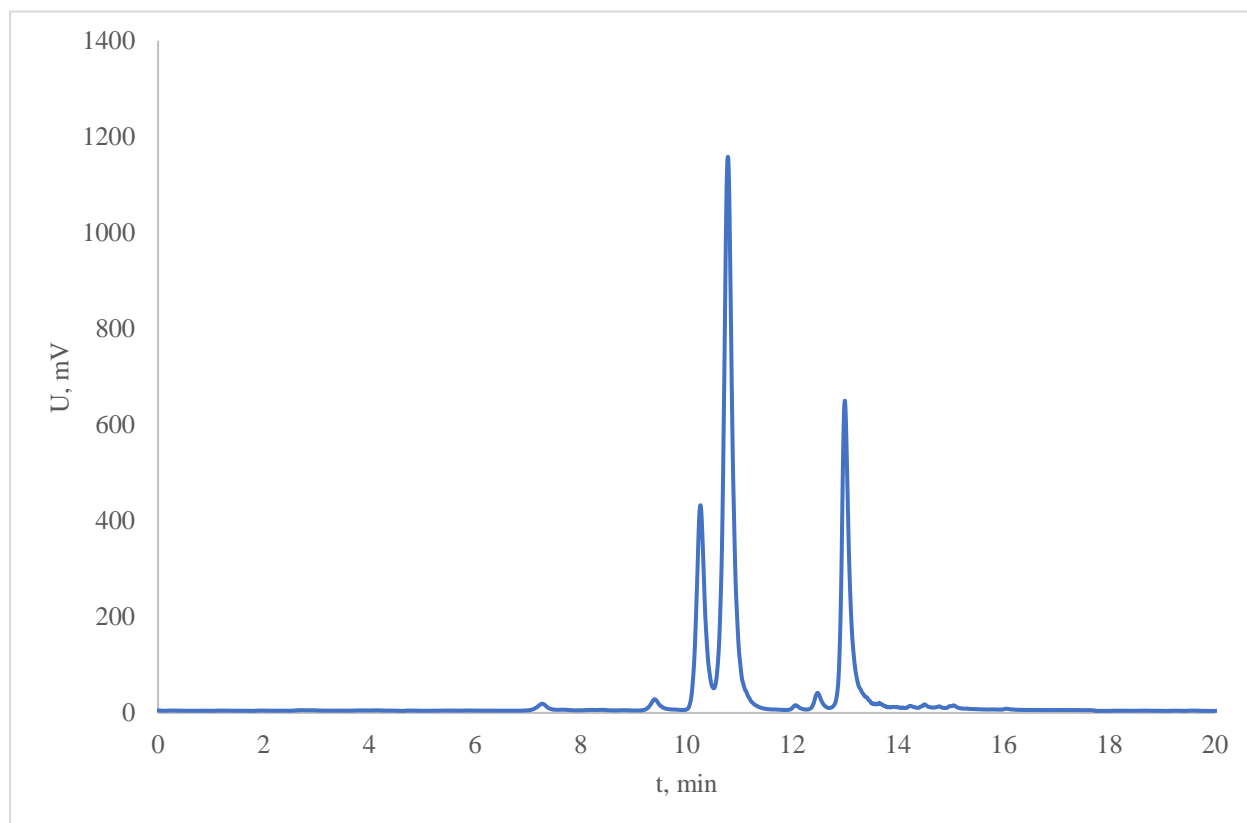
**Figure S16:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AdmCOO})_4$  (0.01 mol%).



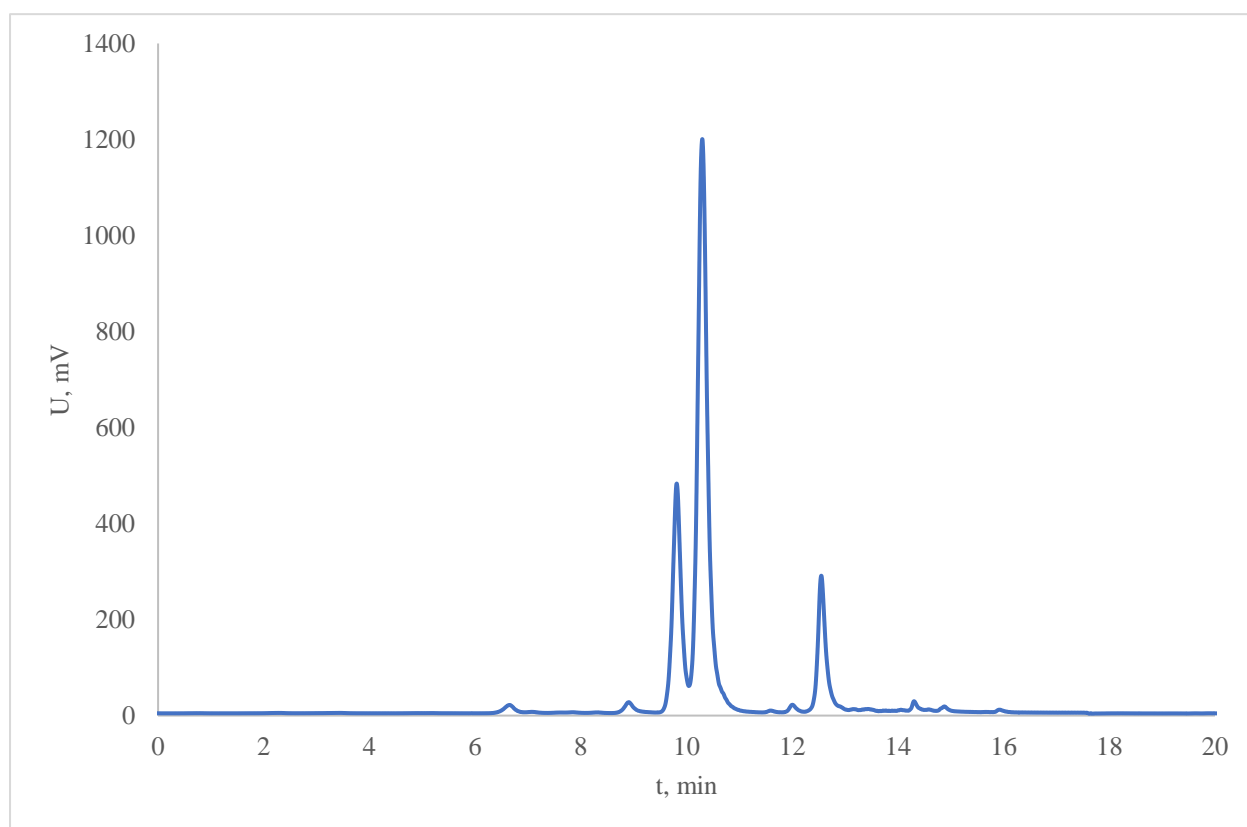
**Figure S17:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AdmCOO})_4$  (0.1 mol%).



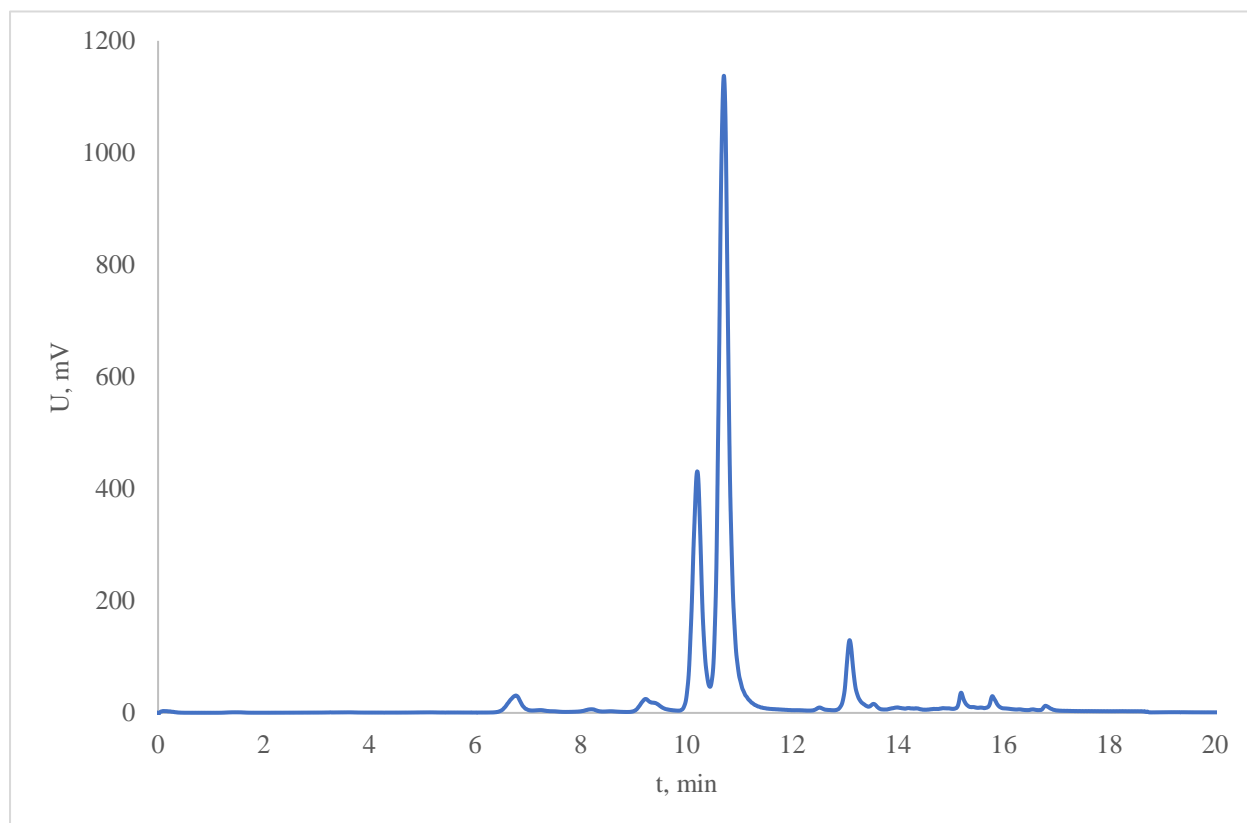
**Figure S18:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AdmCOO})_4$  (1.0 mol%).



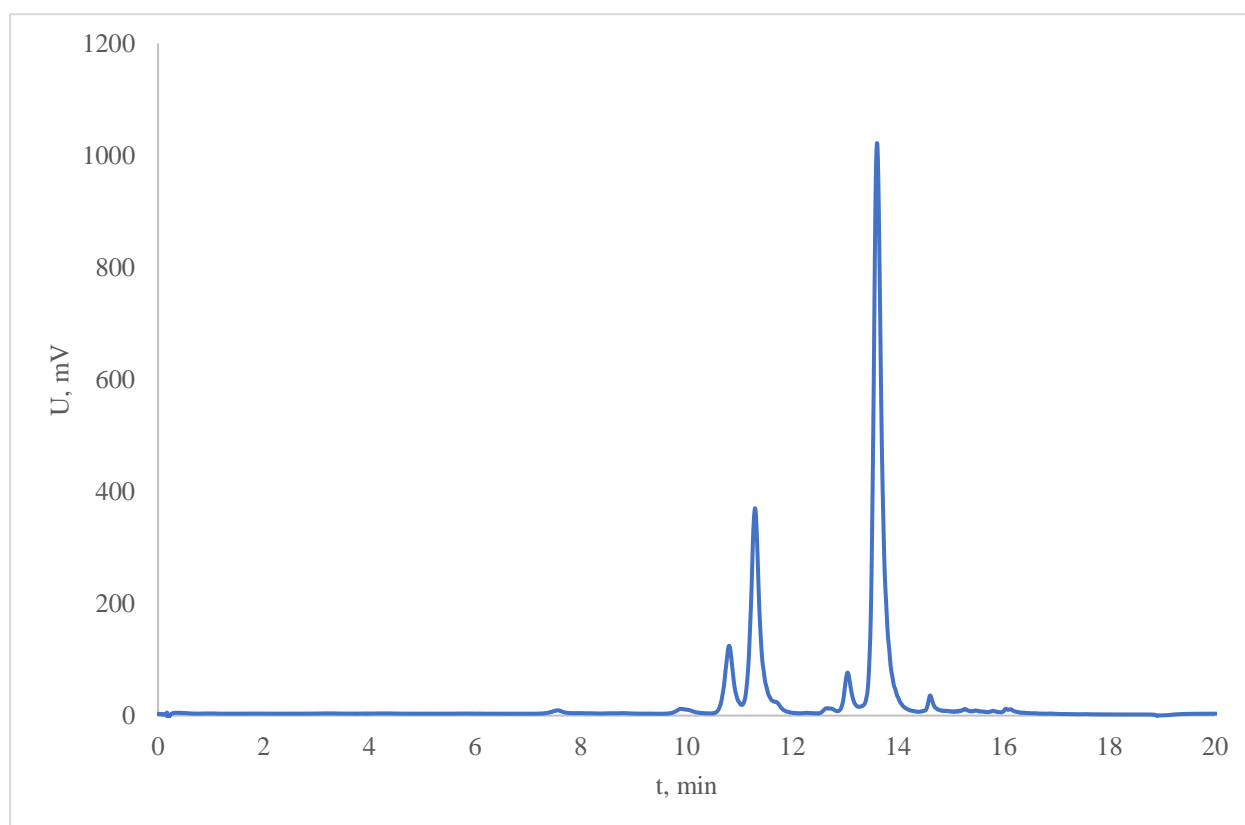
**Figure S19:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AdmCOO})_4$  (2.0 mol%).



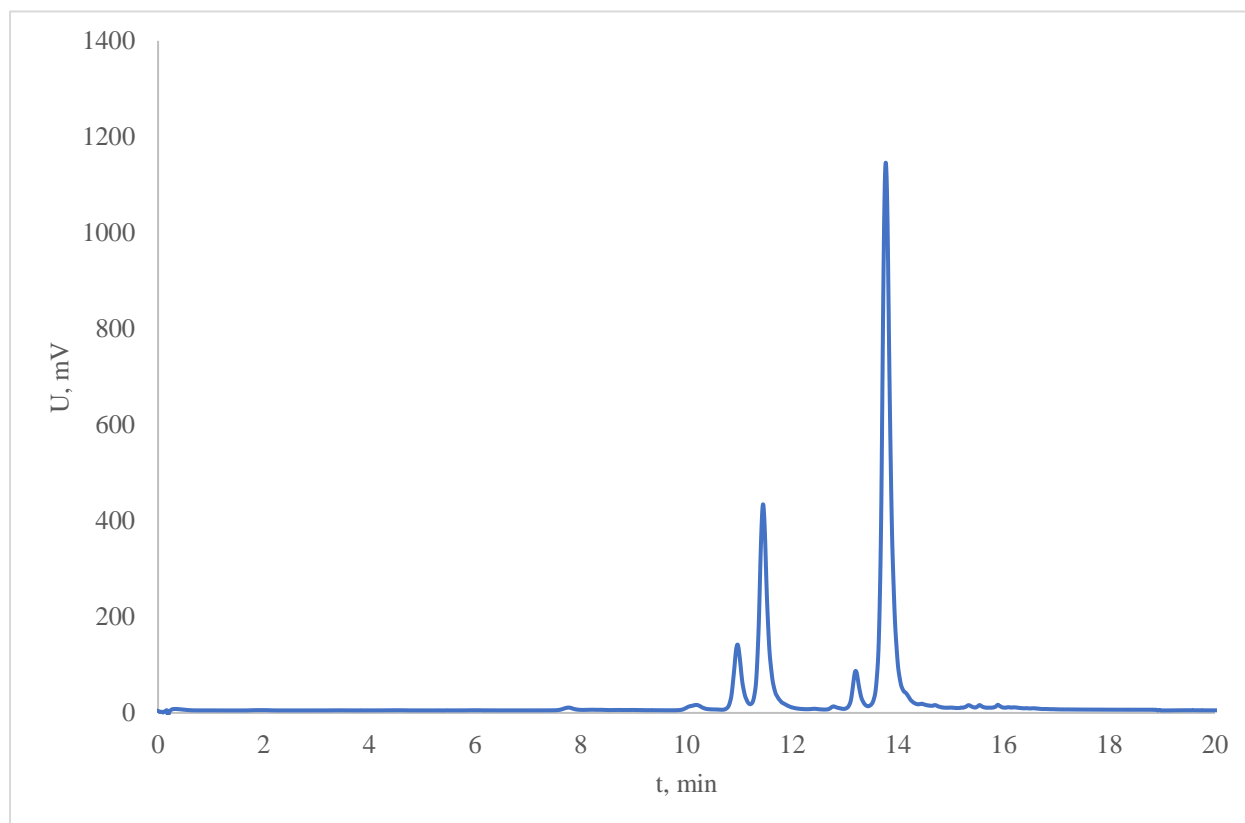
**Figure S20:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AdmCOO})_4$  (5.0 mol%).



**Figure S21:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AdmCOO})_4$  (10.0 mol%).

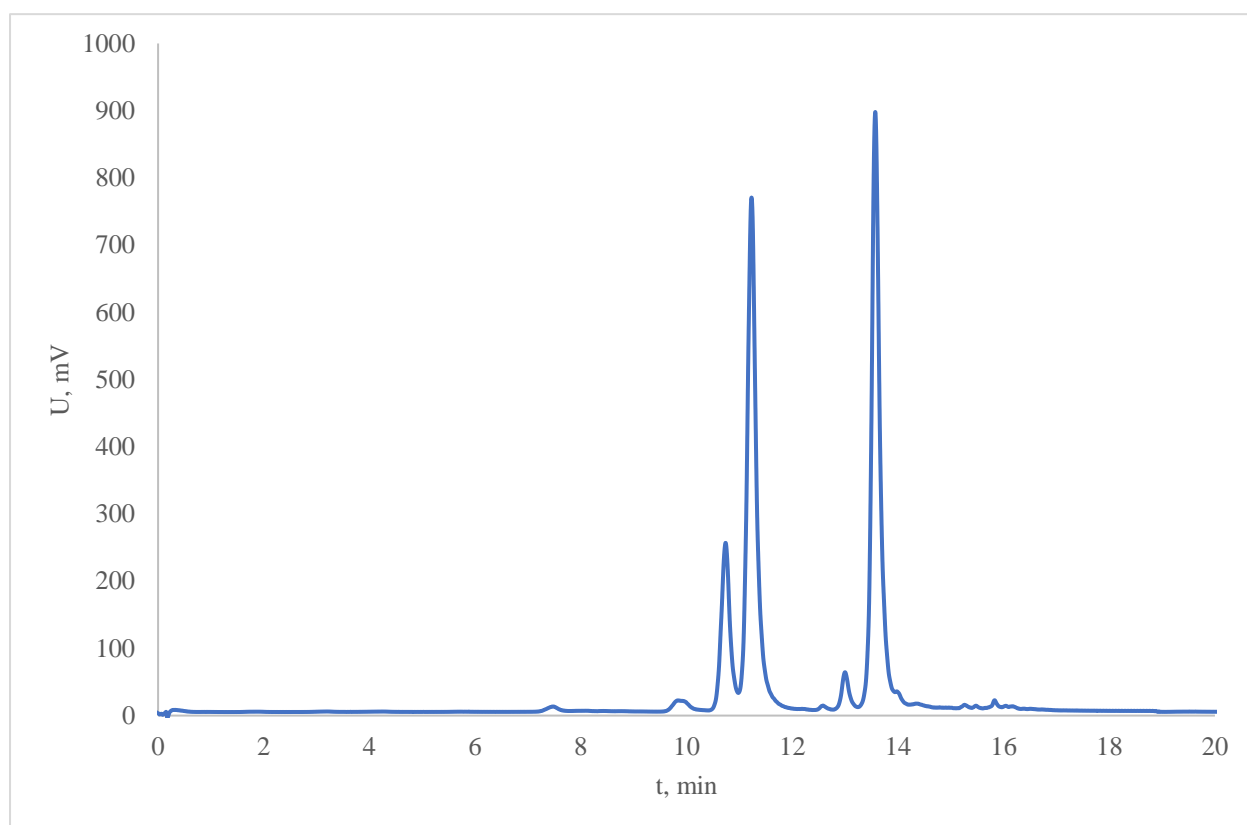


**Figure S22:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{PivO})_4$  (0.01 mol%).

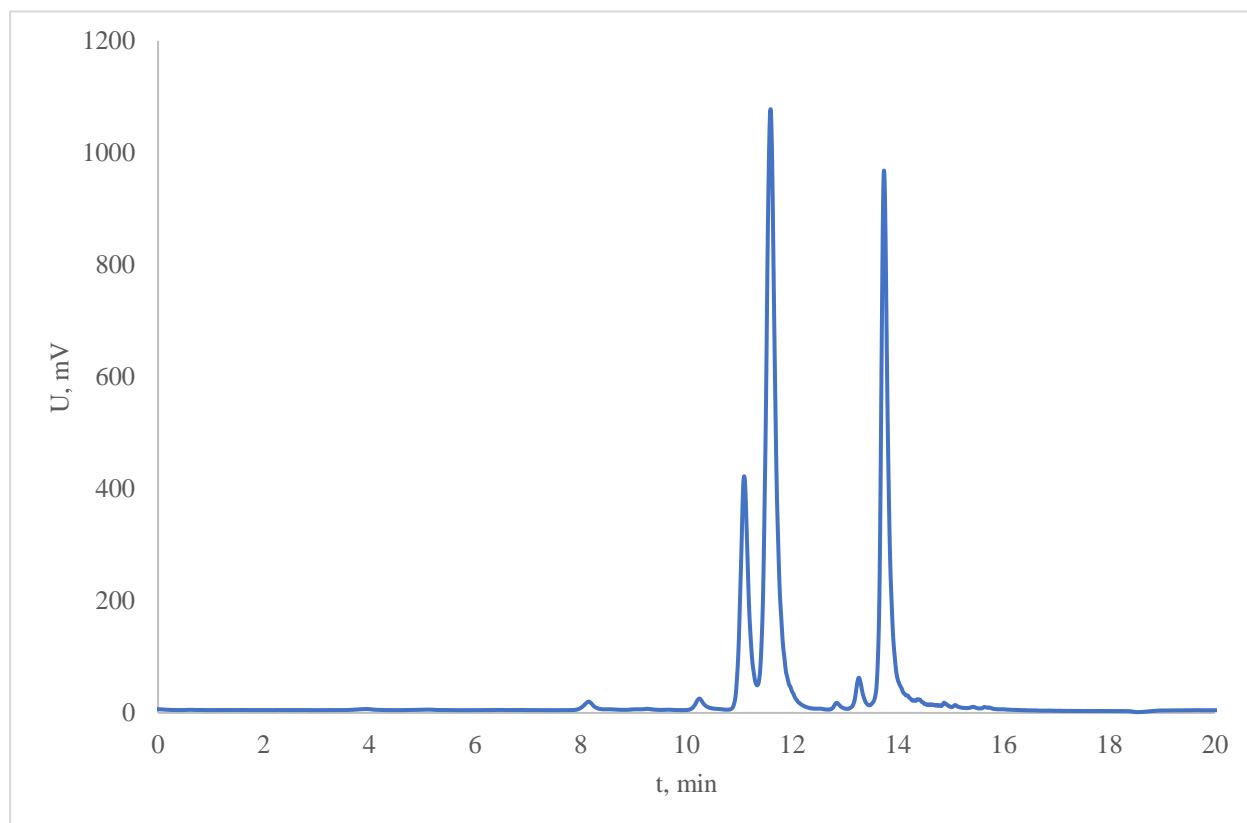


**Figure S23:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{PivO})_4$  (0.1 mol%).

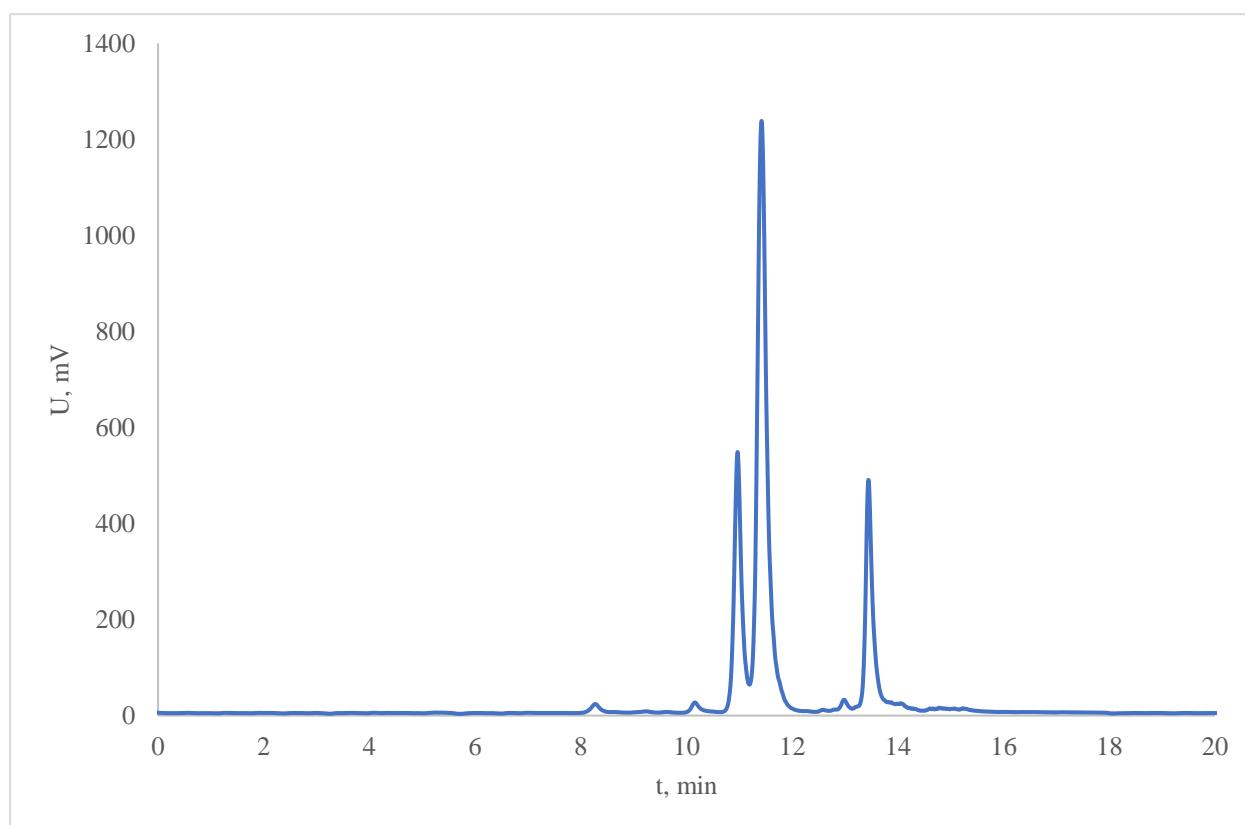




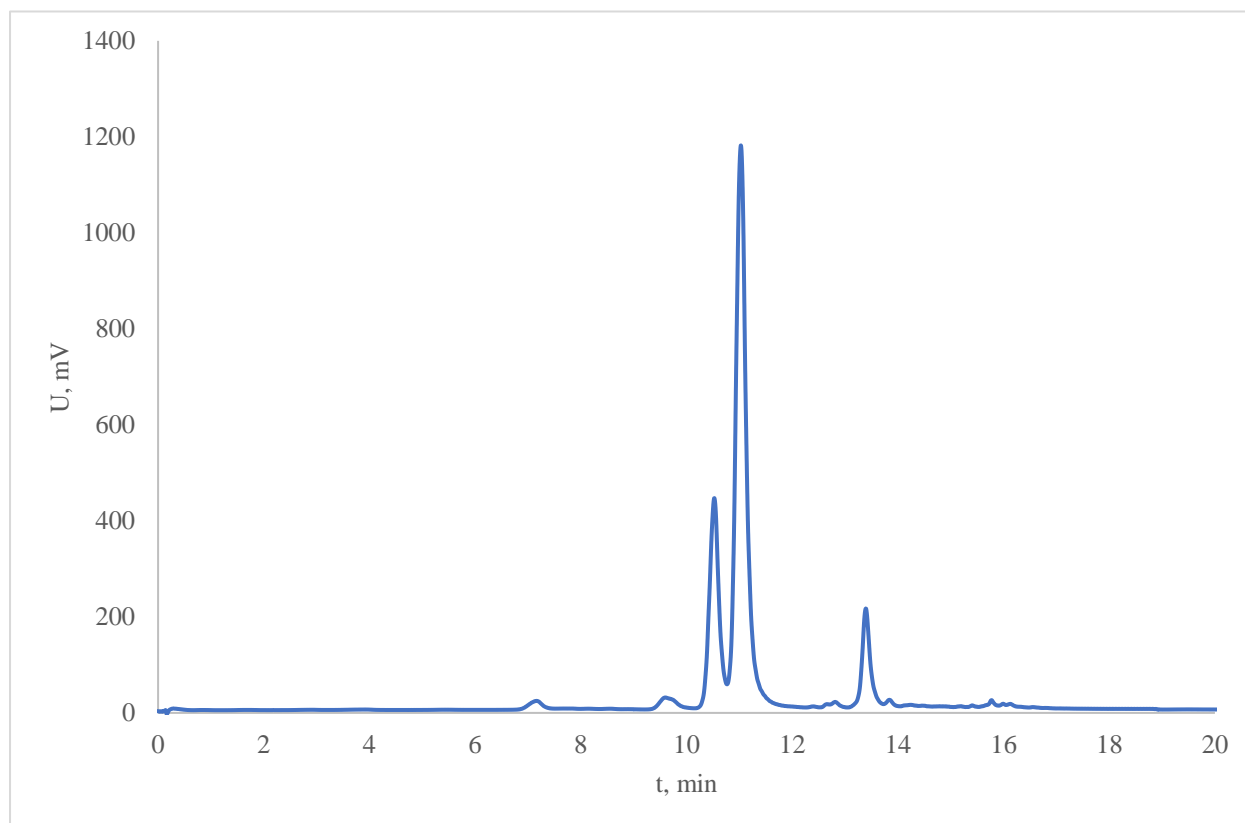
**Figure S24:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{PivO})_4$  (1.0 mol%).



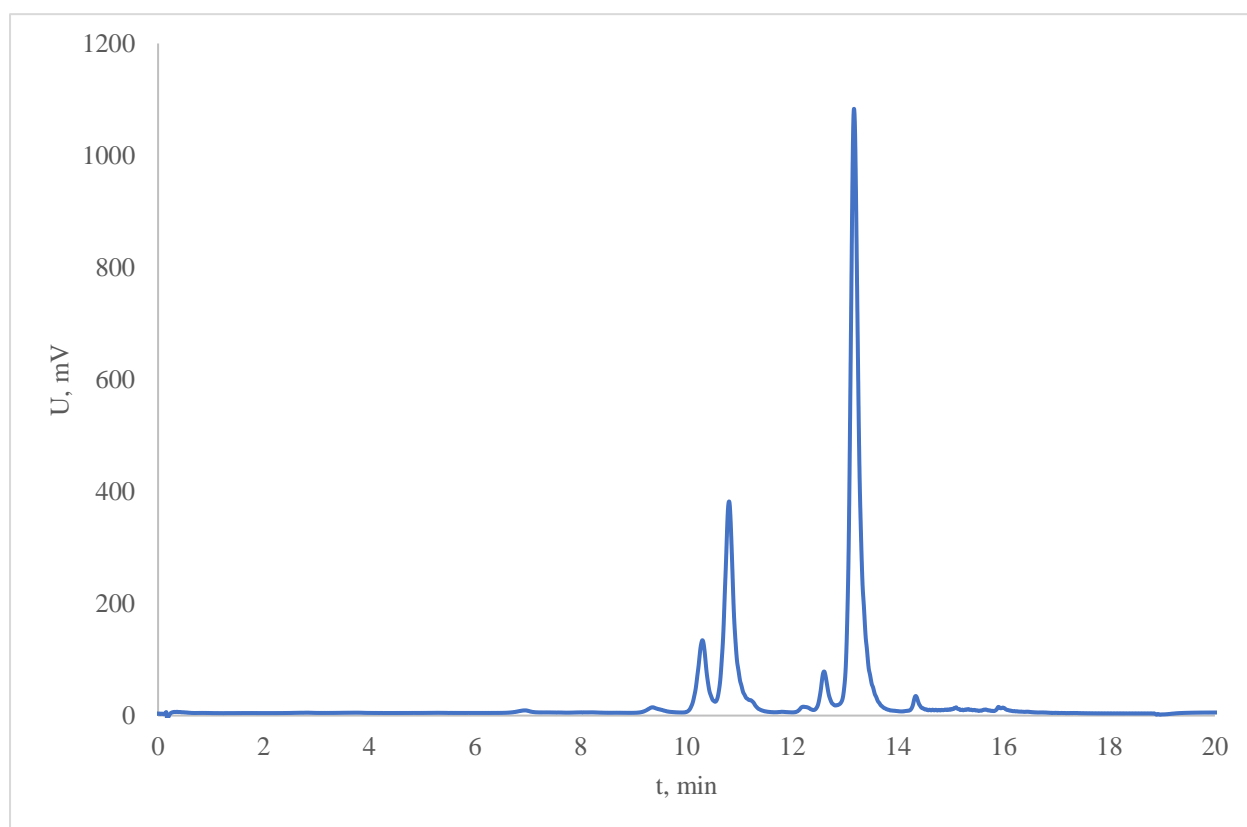
**Figure S25:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{PivO})_4$  (2.0 mol%).



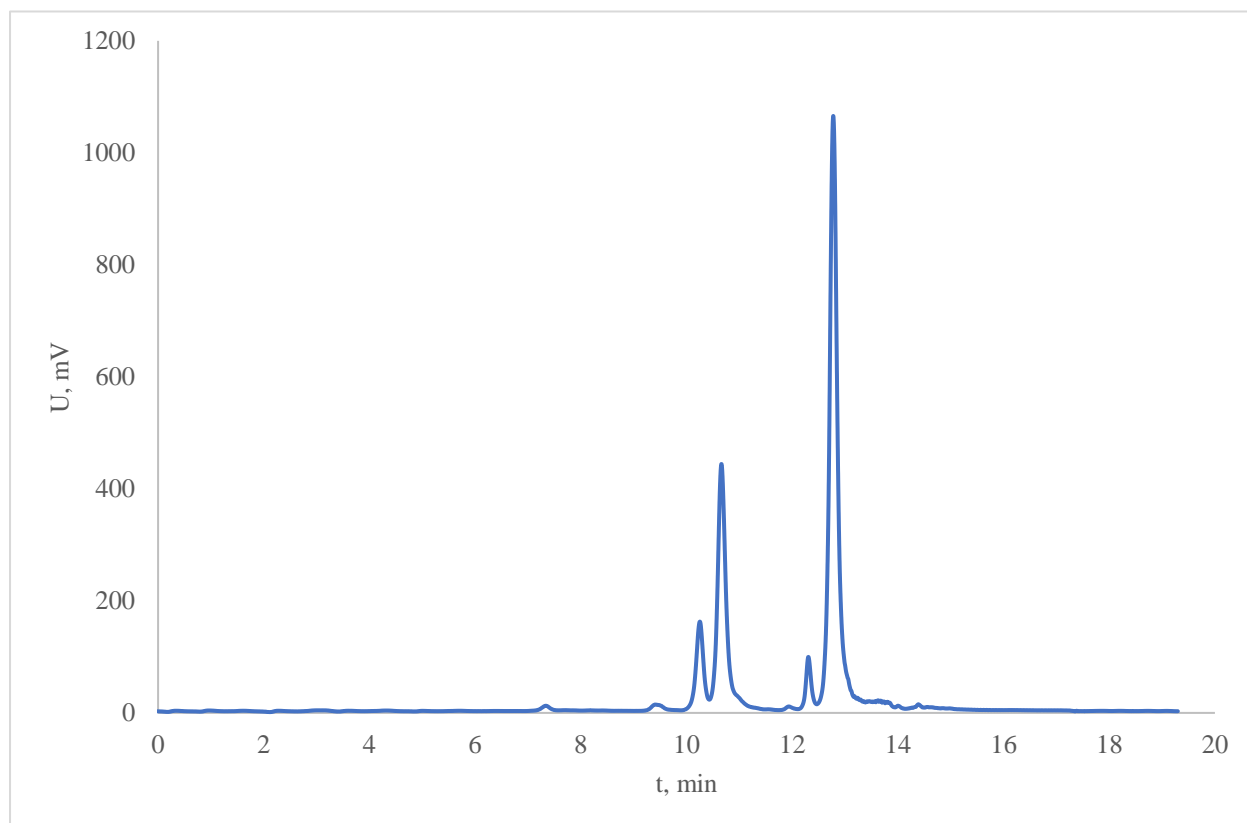
**Figure S26:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{PivO})_4$  (5.0 mol%).



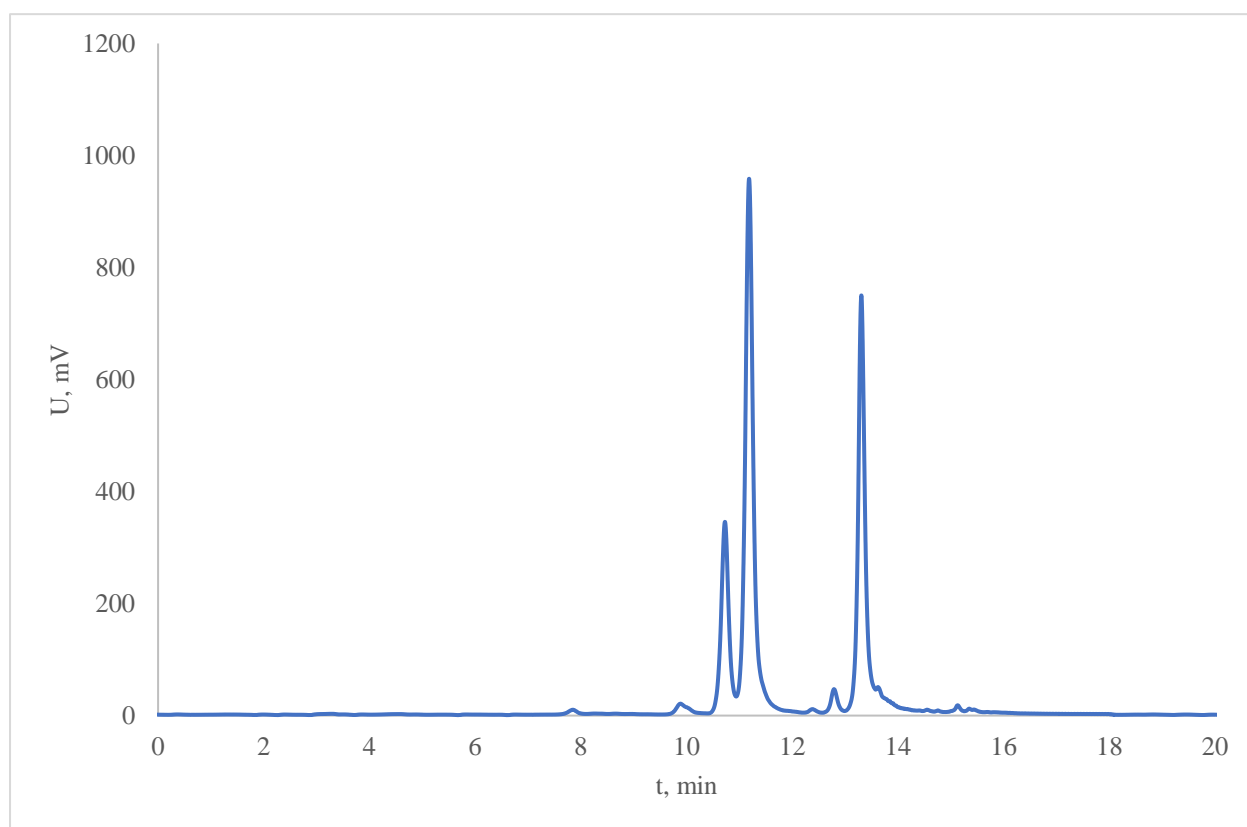
**Figure S27:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{PivO})_4$  (10.0 mol%).



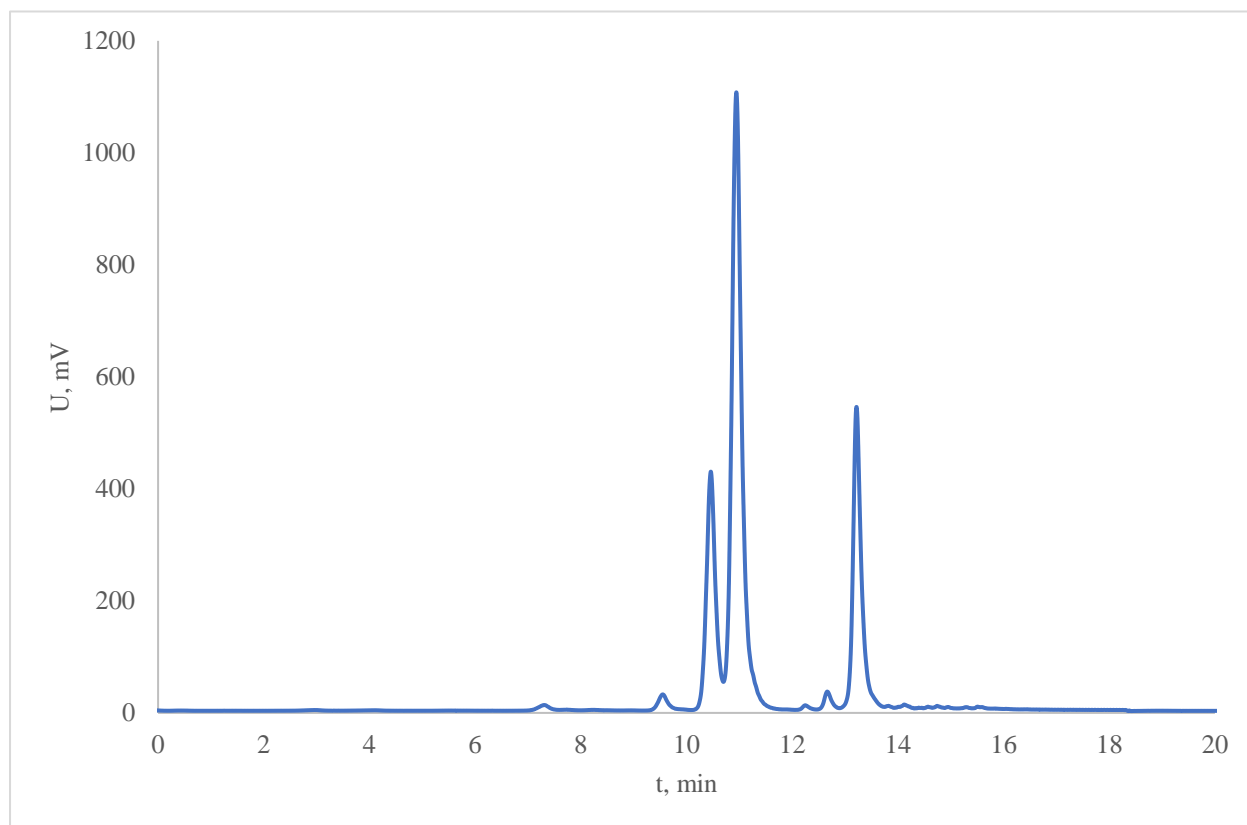
**Figure S28:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with Rh<sub>2</sub>(esp)<sub>2</sub> (0.01 mol%).



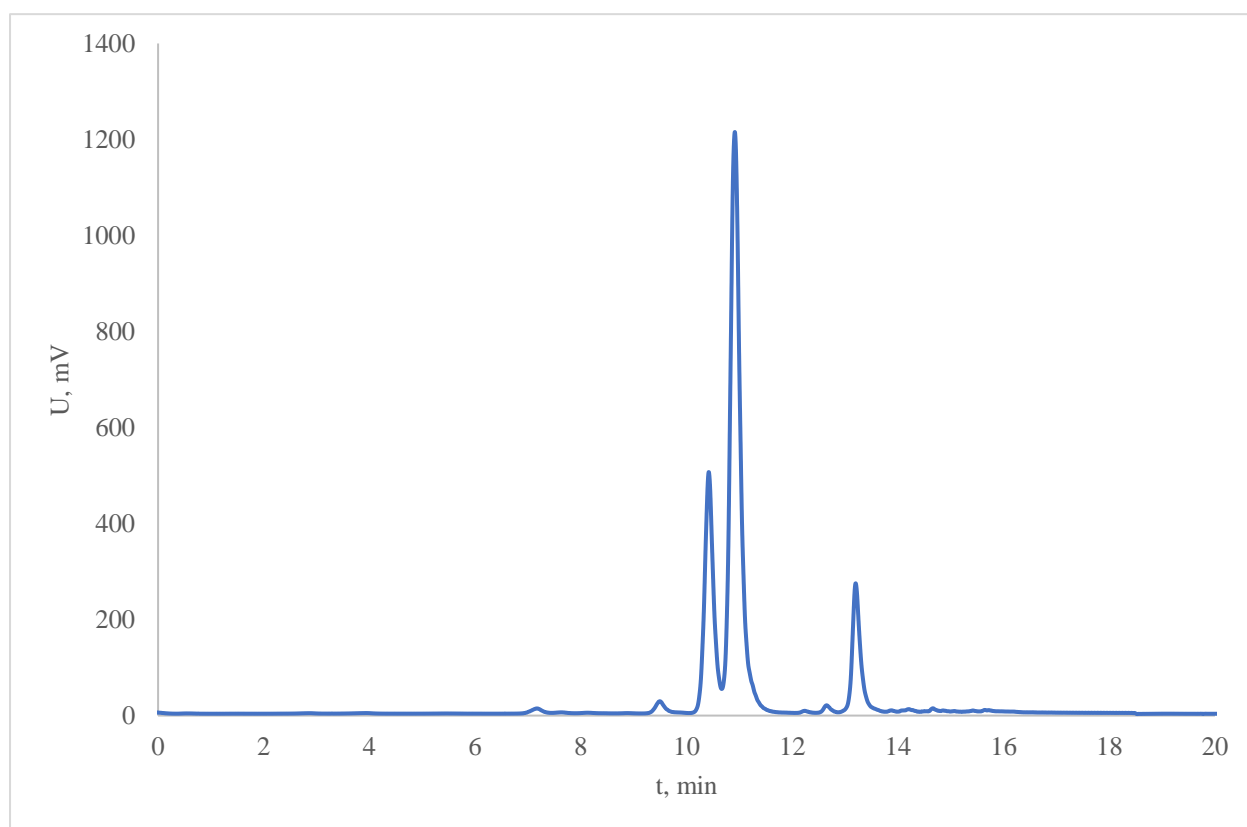
**Figure S29:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with Rh<sub>2</sub>(esp)<sub>2</sub> (0.1 mol%).



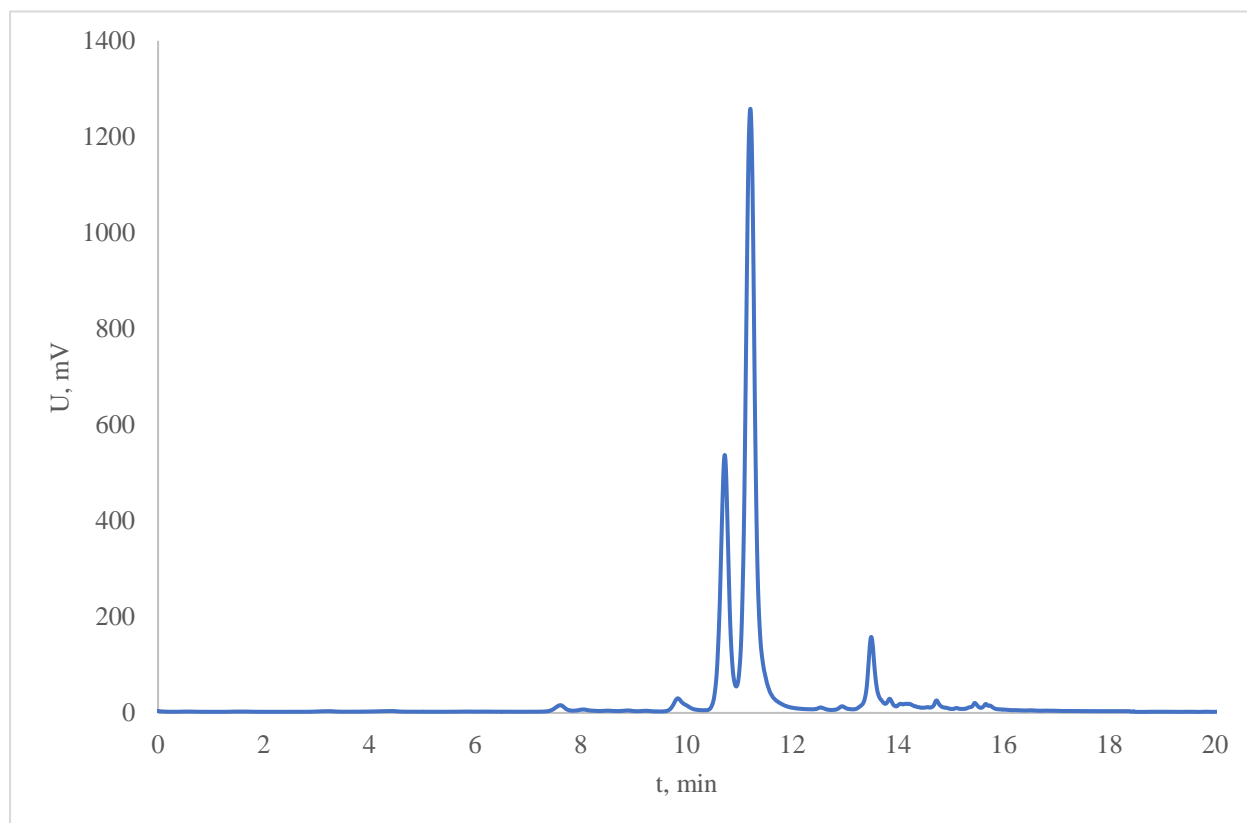
**Figure S30:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{esp})_2$  (1.0 mol%).



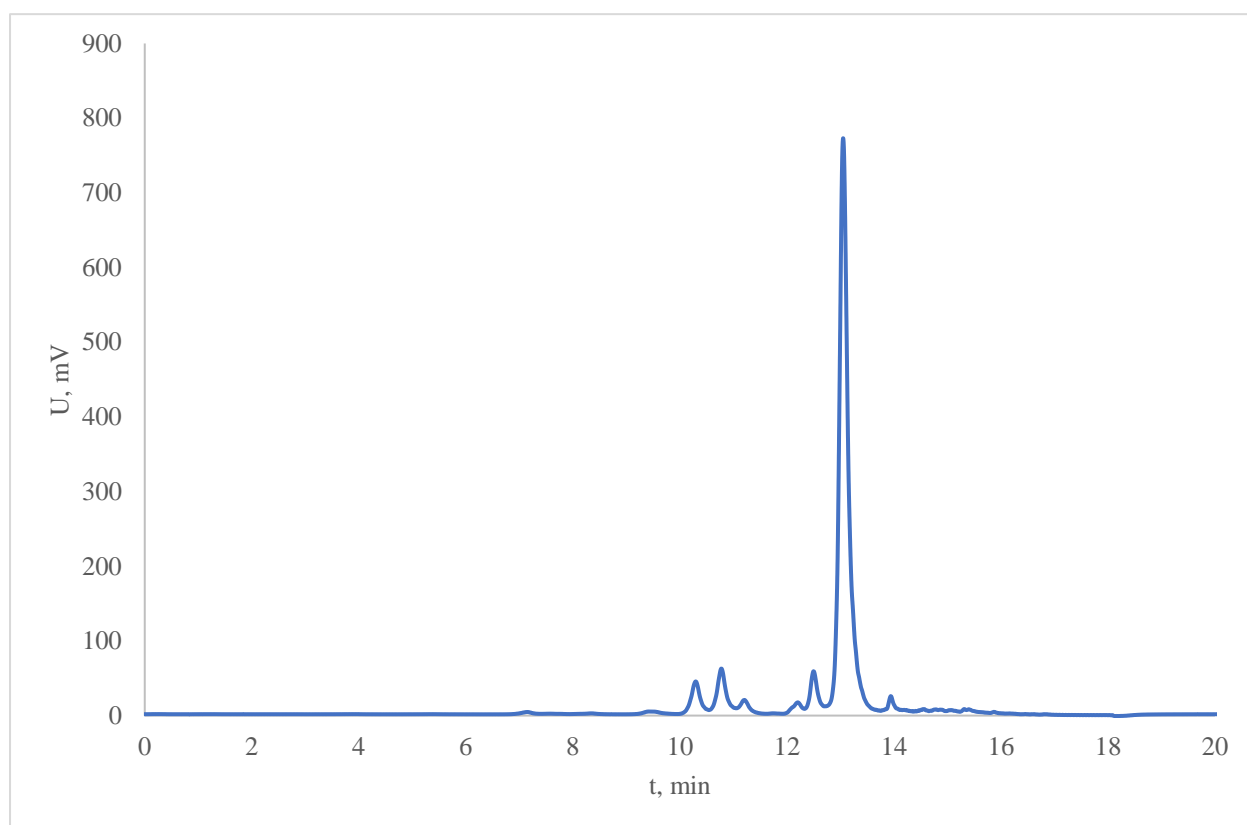
**Figure S31:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{esp})_2$  (2.0 mol%).



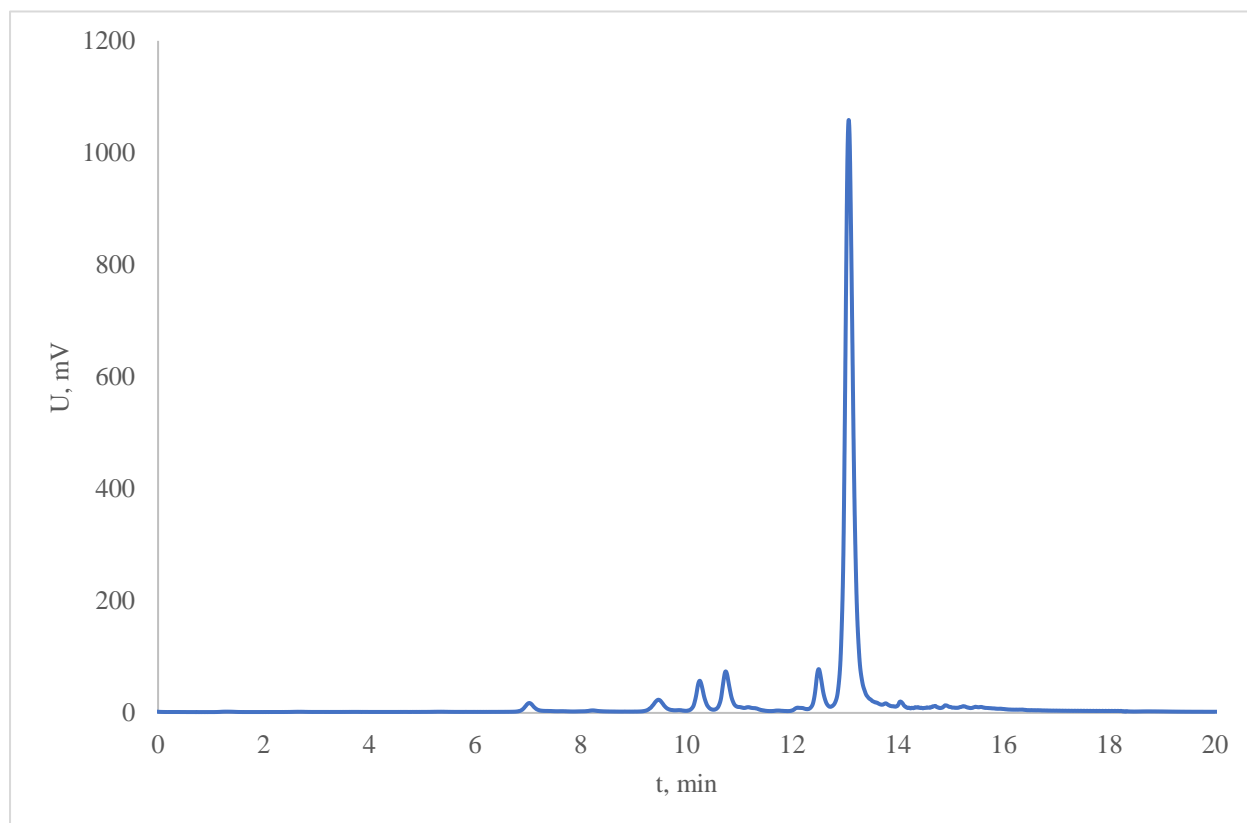
**Figure S32:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{esp})_2$  (5.0 mol%).



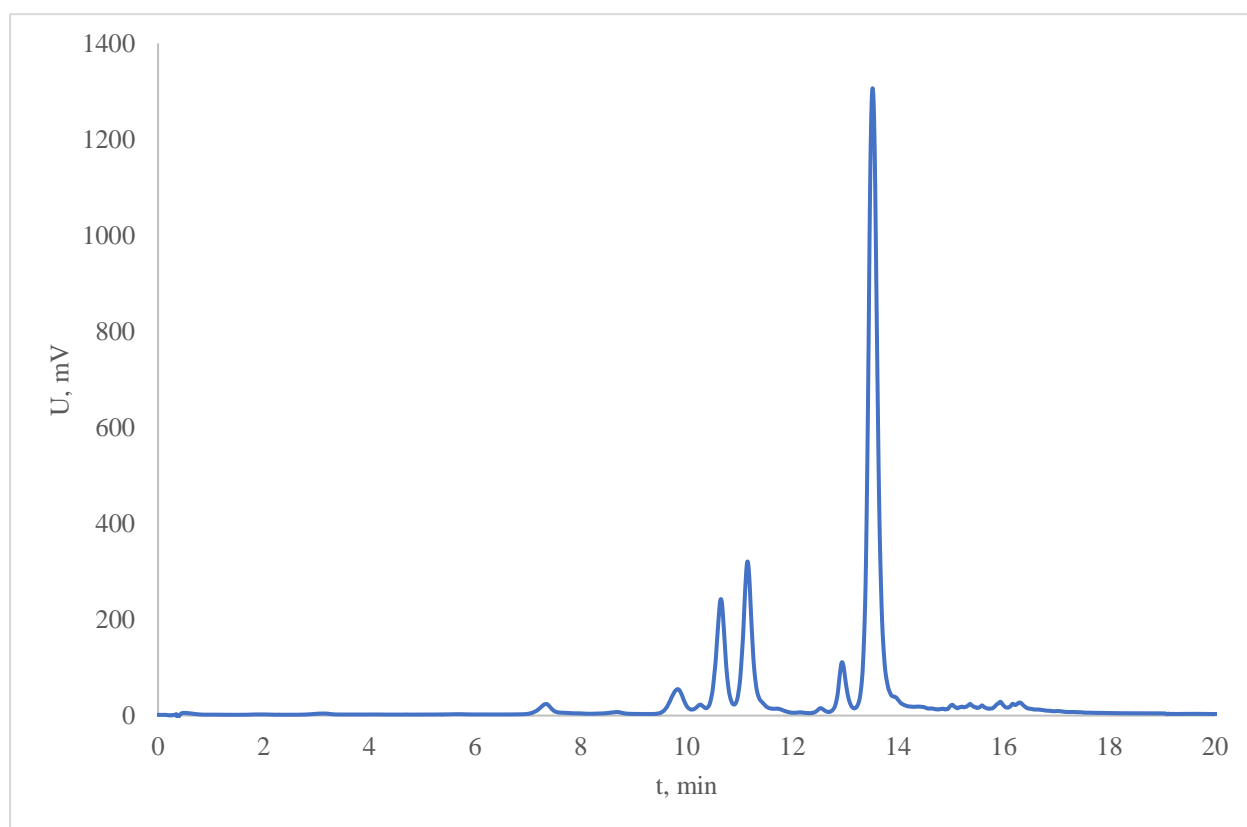
**Figure S33:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{esp})_2$  (10.0 mol%).



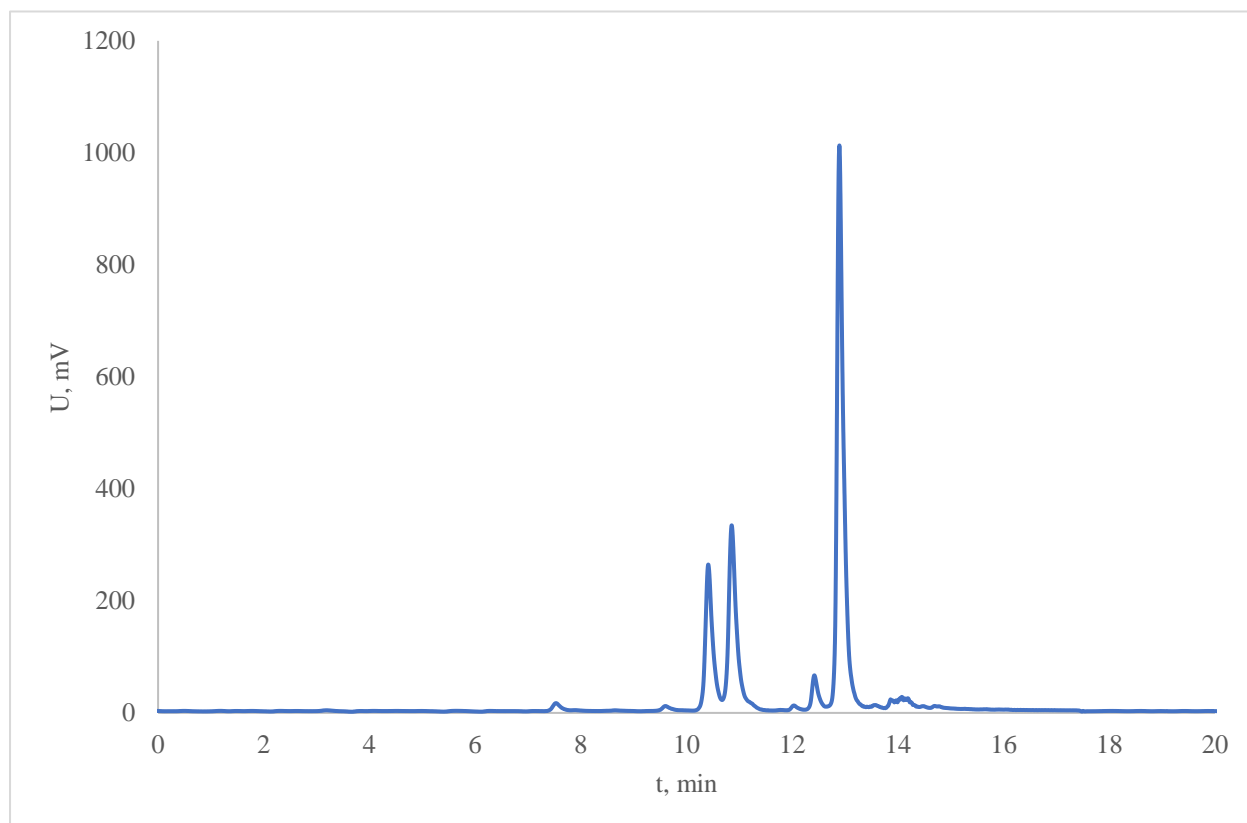
**Figure S34:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AcO})_4$  (0.01 mol%).



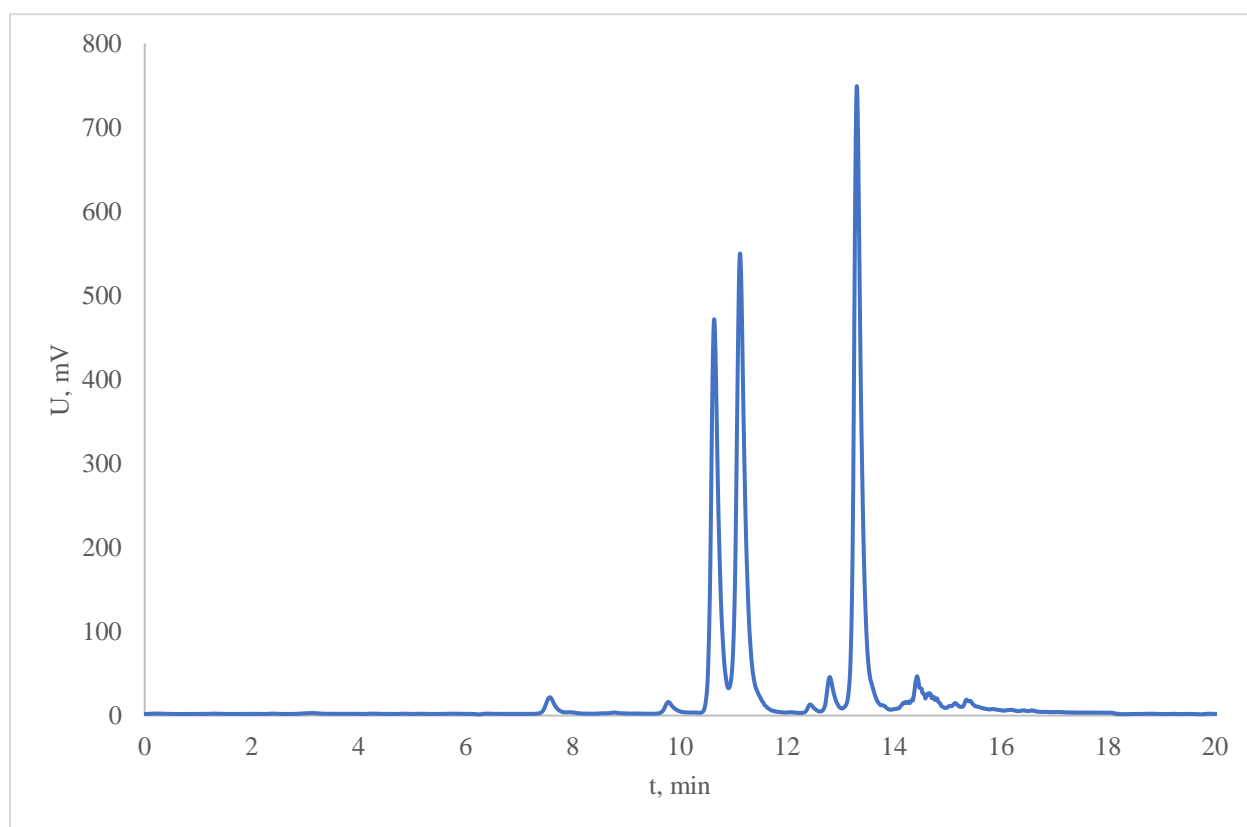
**Figure S35:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AcO})_4$  (0.1 mol%).



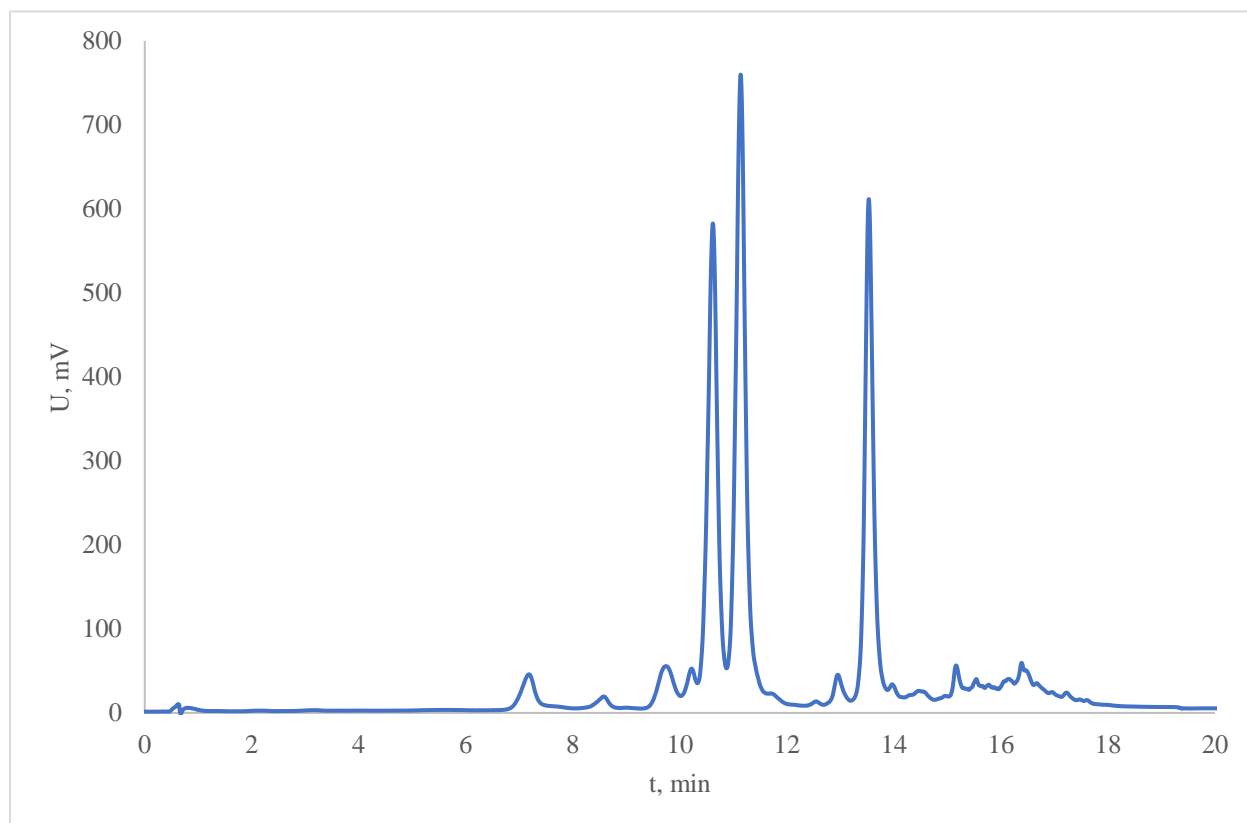
**Figure S36:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AcO})_4$  (1.0 mol%).



**Figure S37:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AcO})_4$  (2.0 mol%).

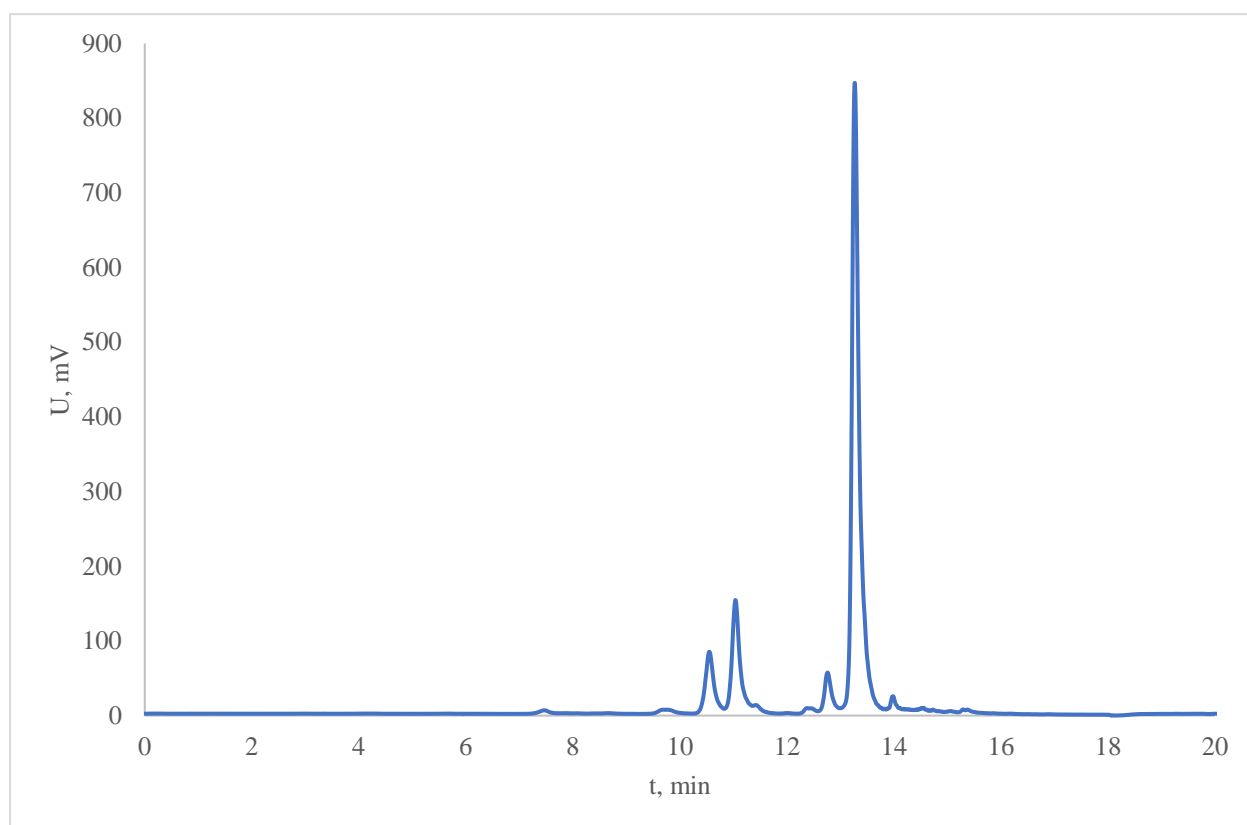


**Figure S38:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AcO})_4$  (5.0 mol%).

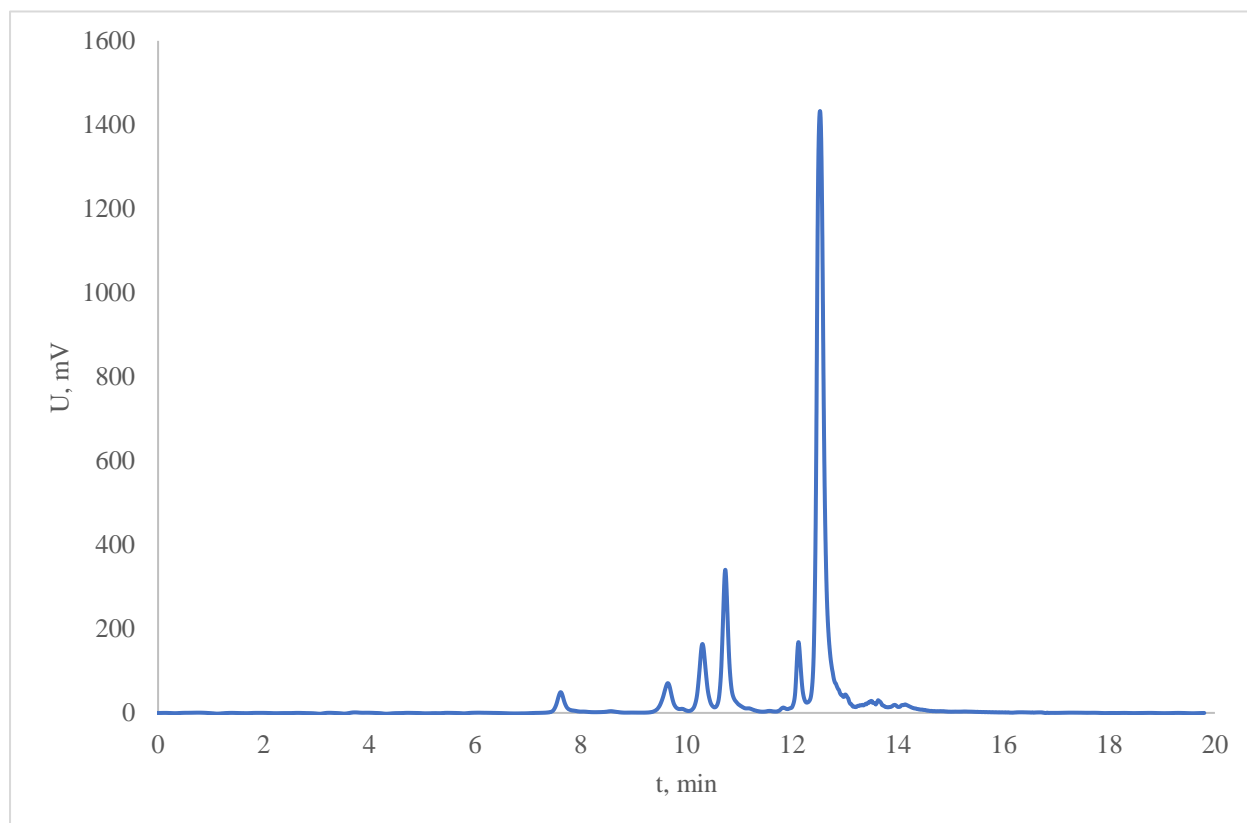


**Figure S39:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(\text{AcO})_4$  (10.0 mol%).

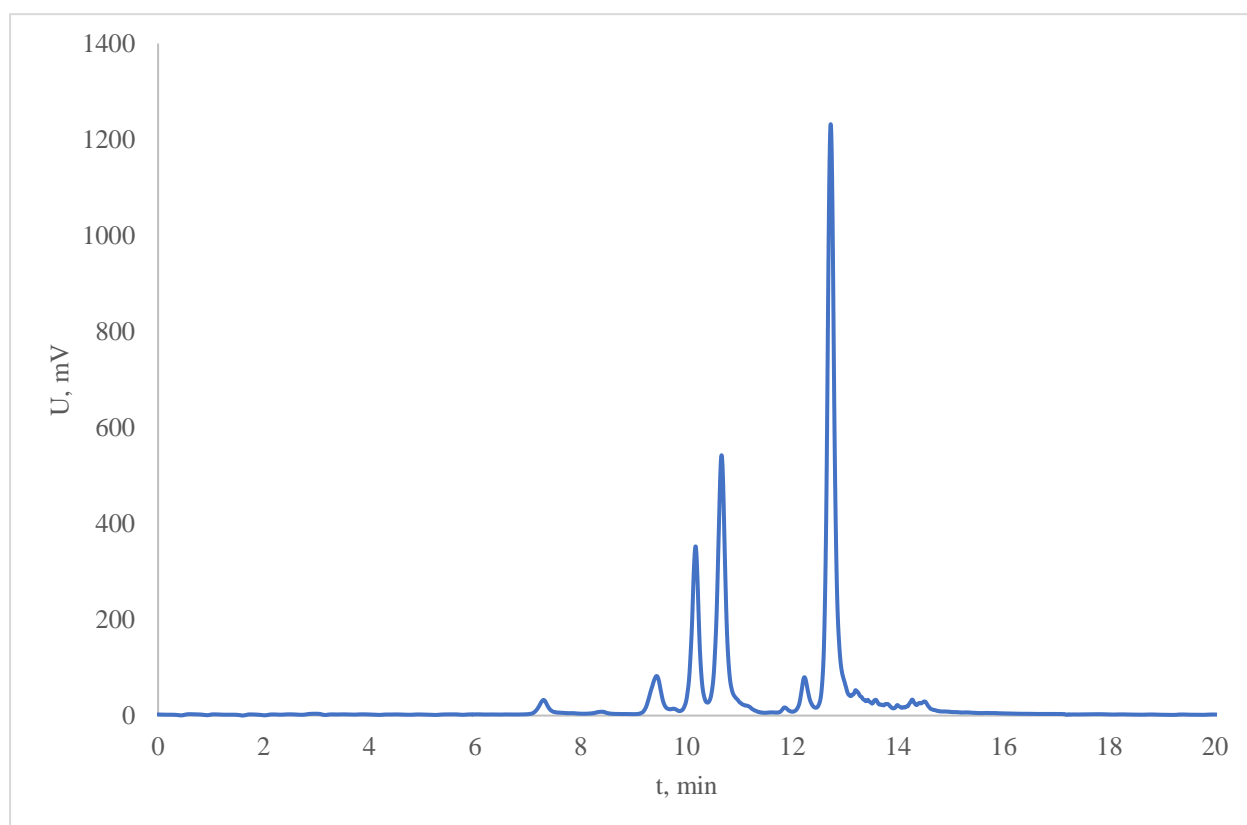




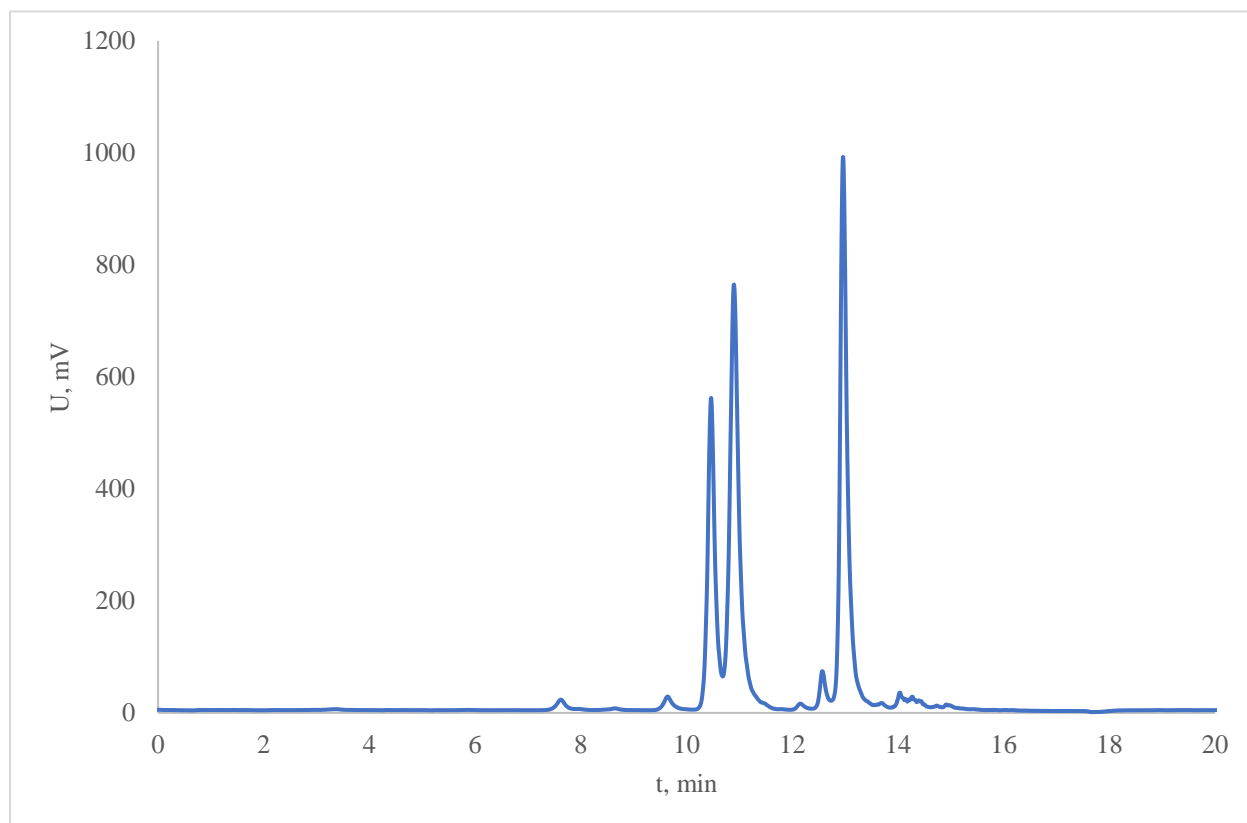
**Figure S40:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_4\text{H}_9\text{COO})_4$  (0.01 mol%).



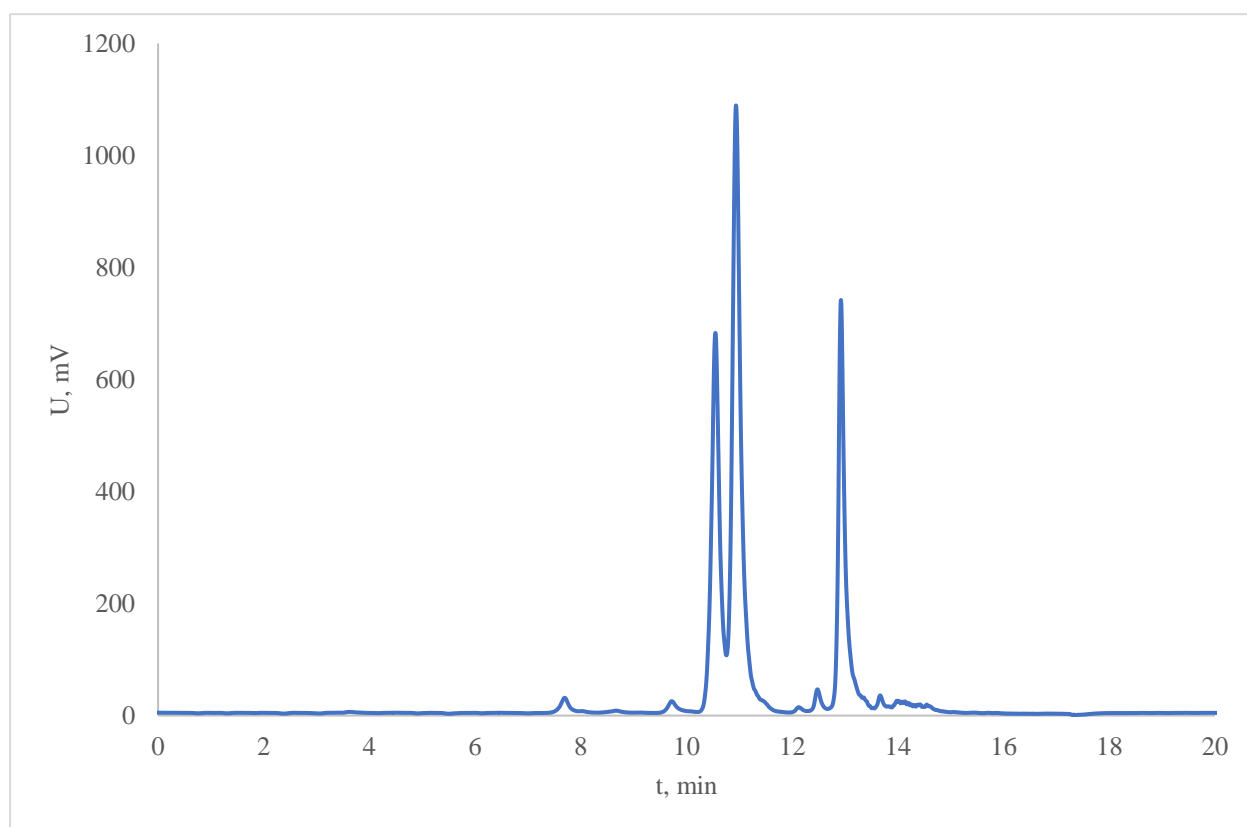
**Figure S41:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_4\text{H}_9\text{COO})_4$  (0.1 mol%).



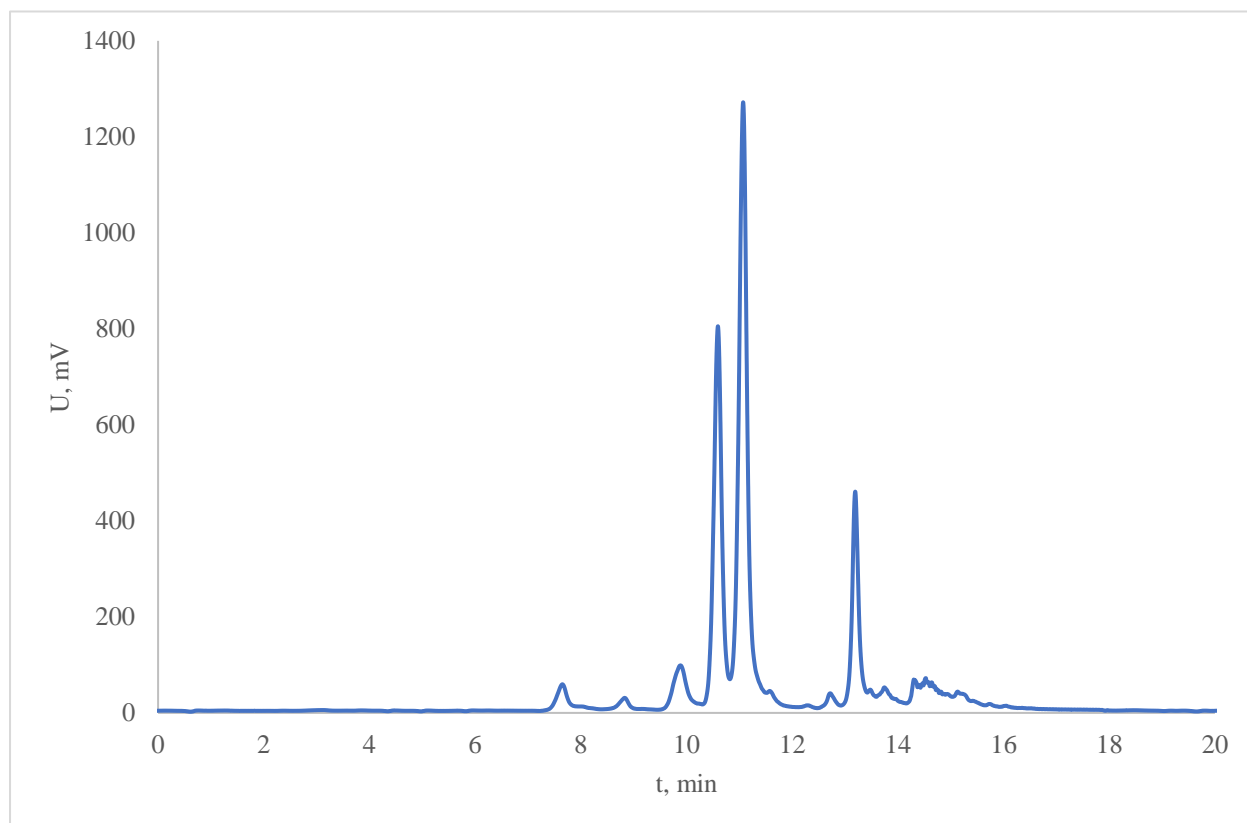
**Figure S42:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_4\text{H}_9\text{COO})_4$  (1.0 mol%).



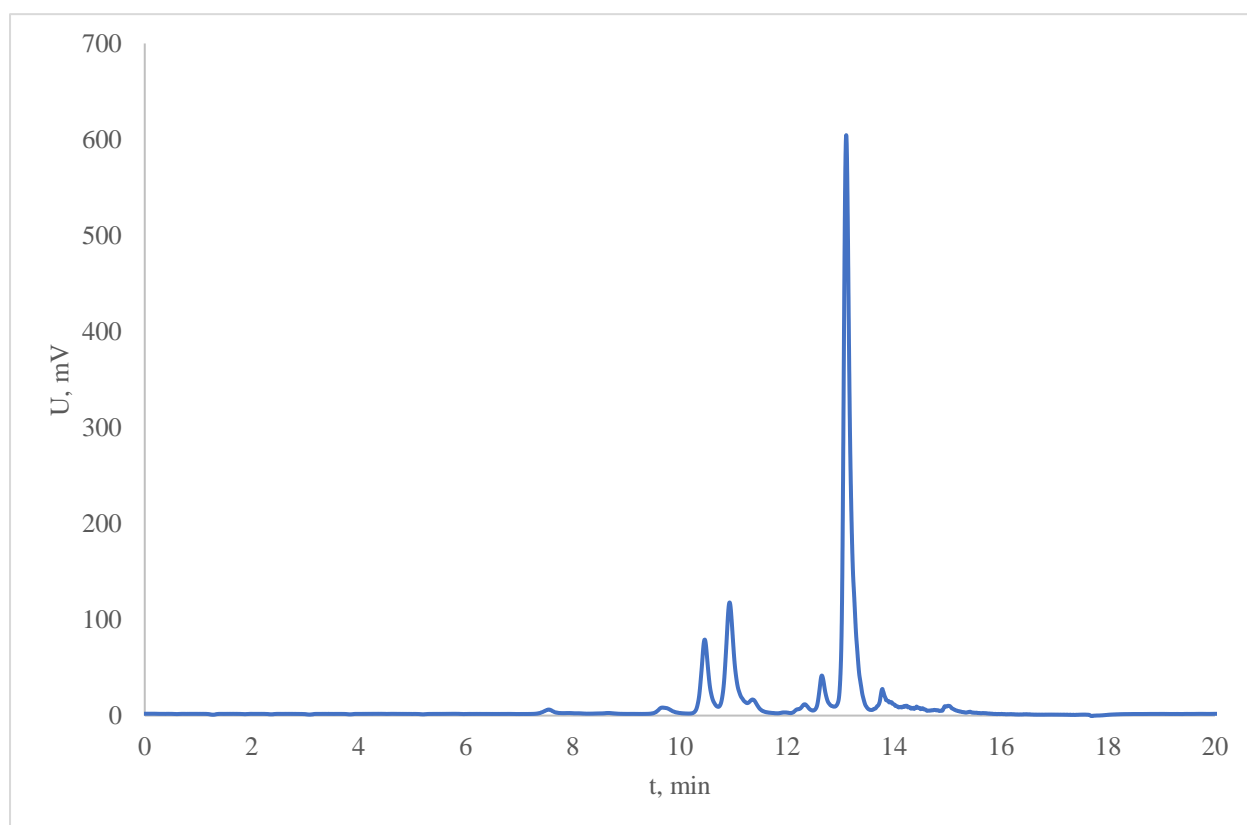
**Figure S43:** HPLC chromatogram of **1a** → **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_4\text{H}_9\text{COO})_4$  (2.0 mol%).



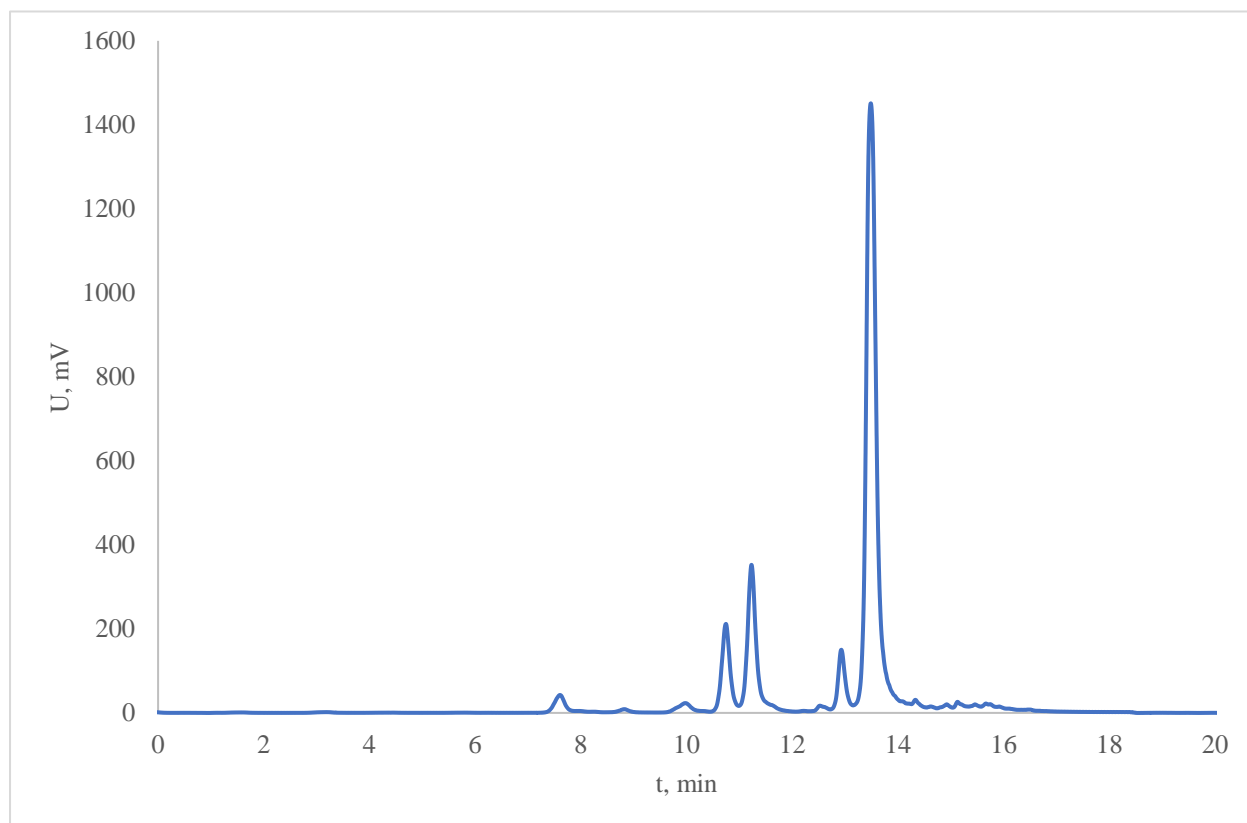
**Figure S44:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_4\text{H}_9\text{COO})_4$  (5.0 mol%).



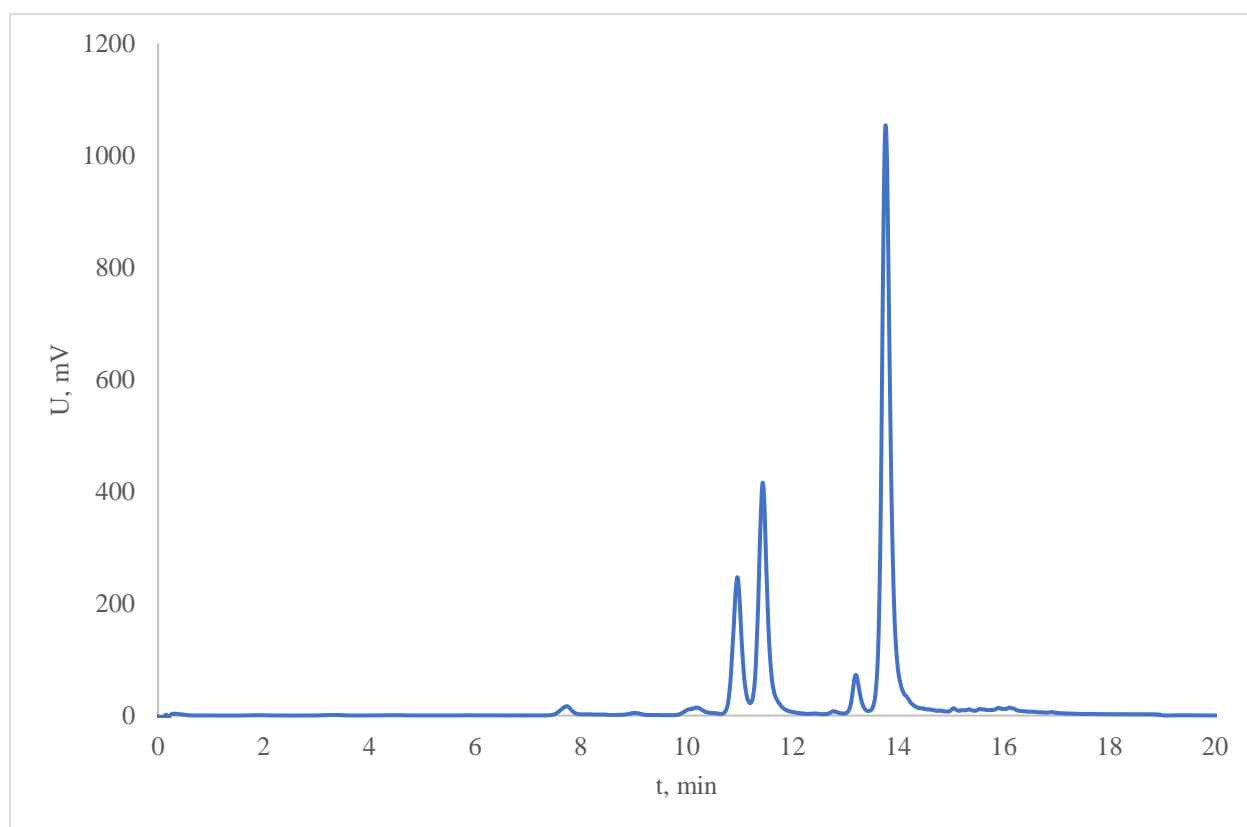
**Figure S45:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_4\text{H}_9\text{COO})_4$  (10.0 mol%).



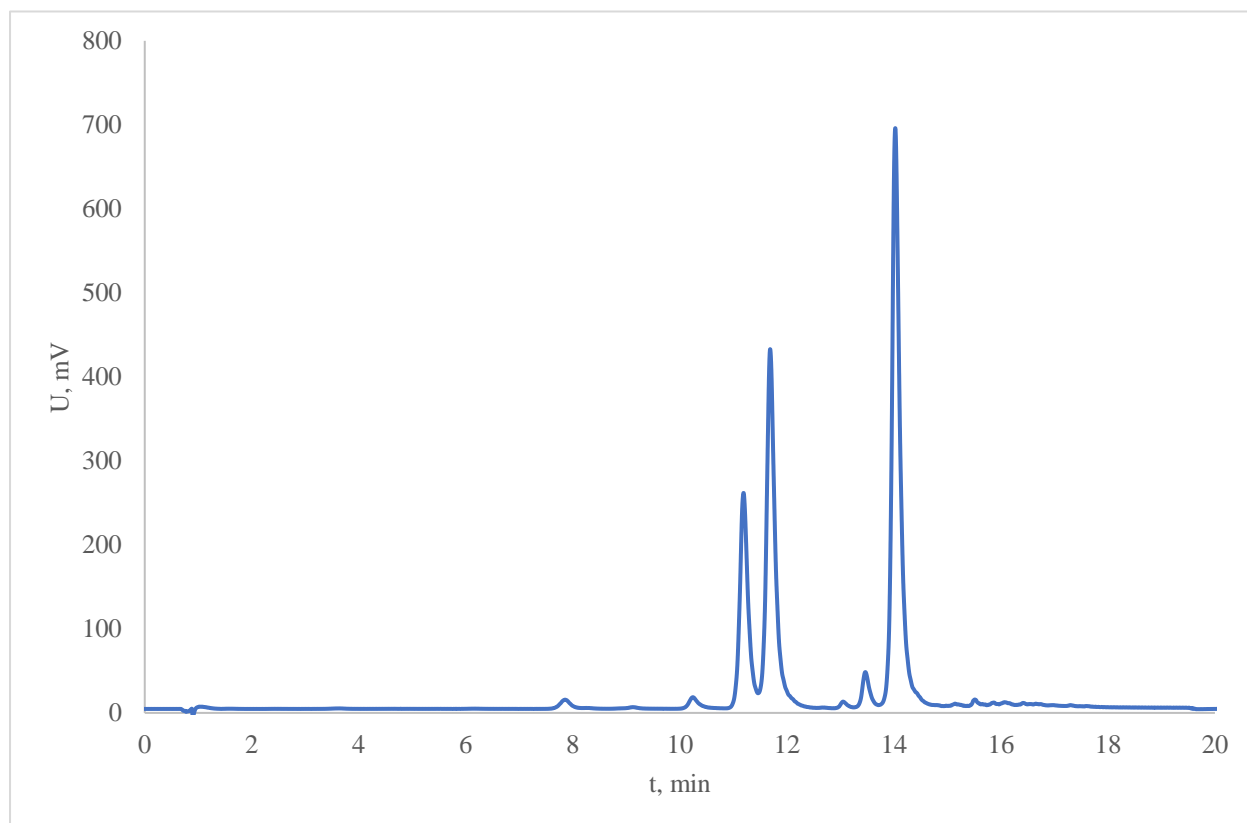
**Figure S46:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_7\text{H}_{15}\text{COO})_4$  (0.01 mol%).



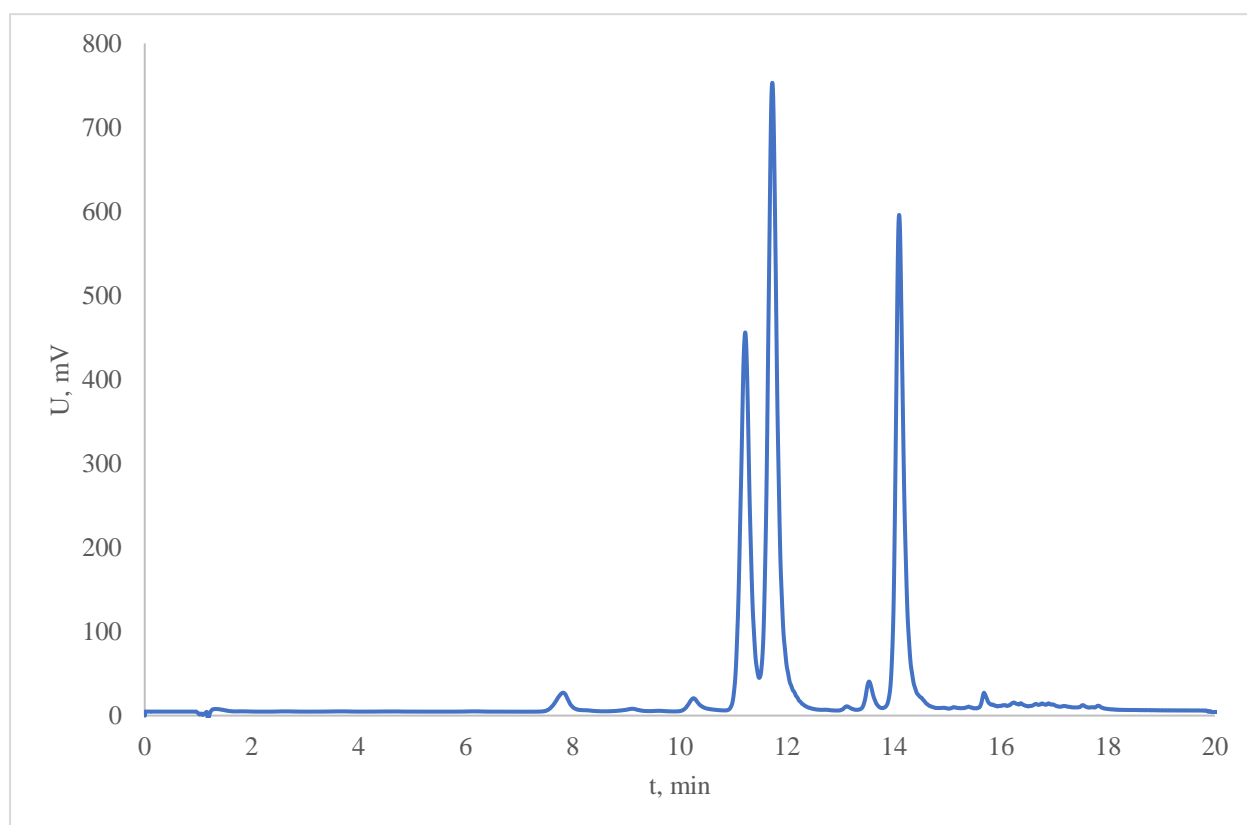
**Figure S47:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_7\text{H}_{15}\text{COO})_4$  (0.1 mol%).



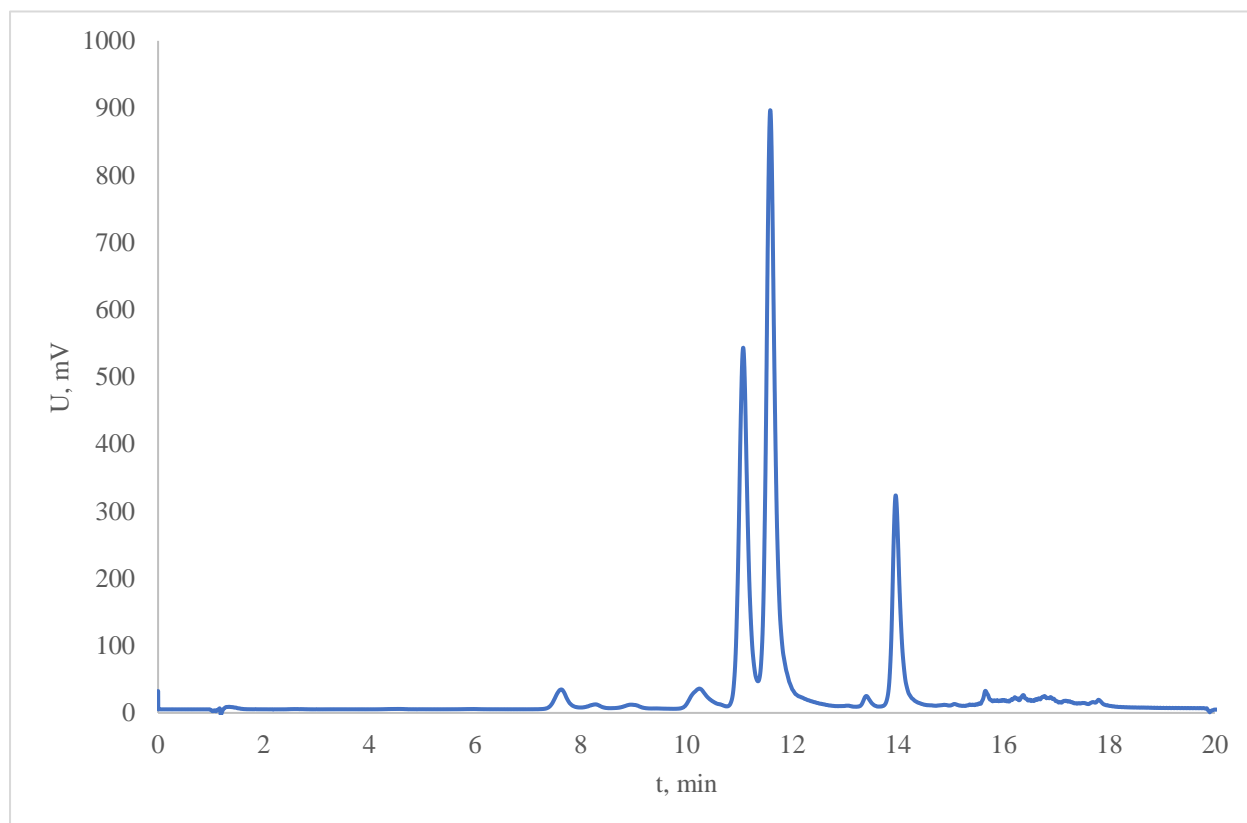
**Figure S48:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_7\text{H}_{15}\text{COO})_4$  (1.0 mol%).



**Figure S49:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_7\text{H}_{15}\text{COO})_4$  (2.0 mol%).

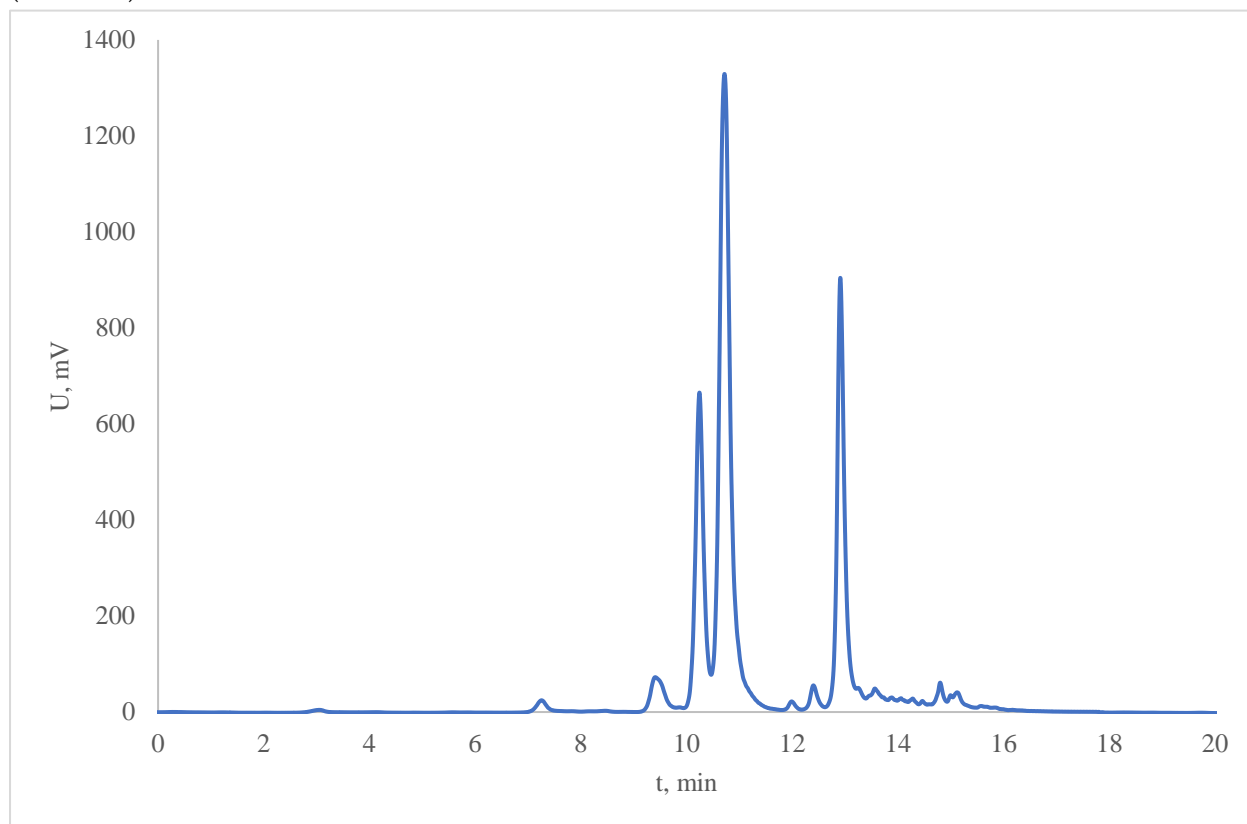


**Figure S50:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_7\text{H}_{15}\text{COO})_4$  (5.0 mol%).

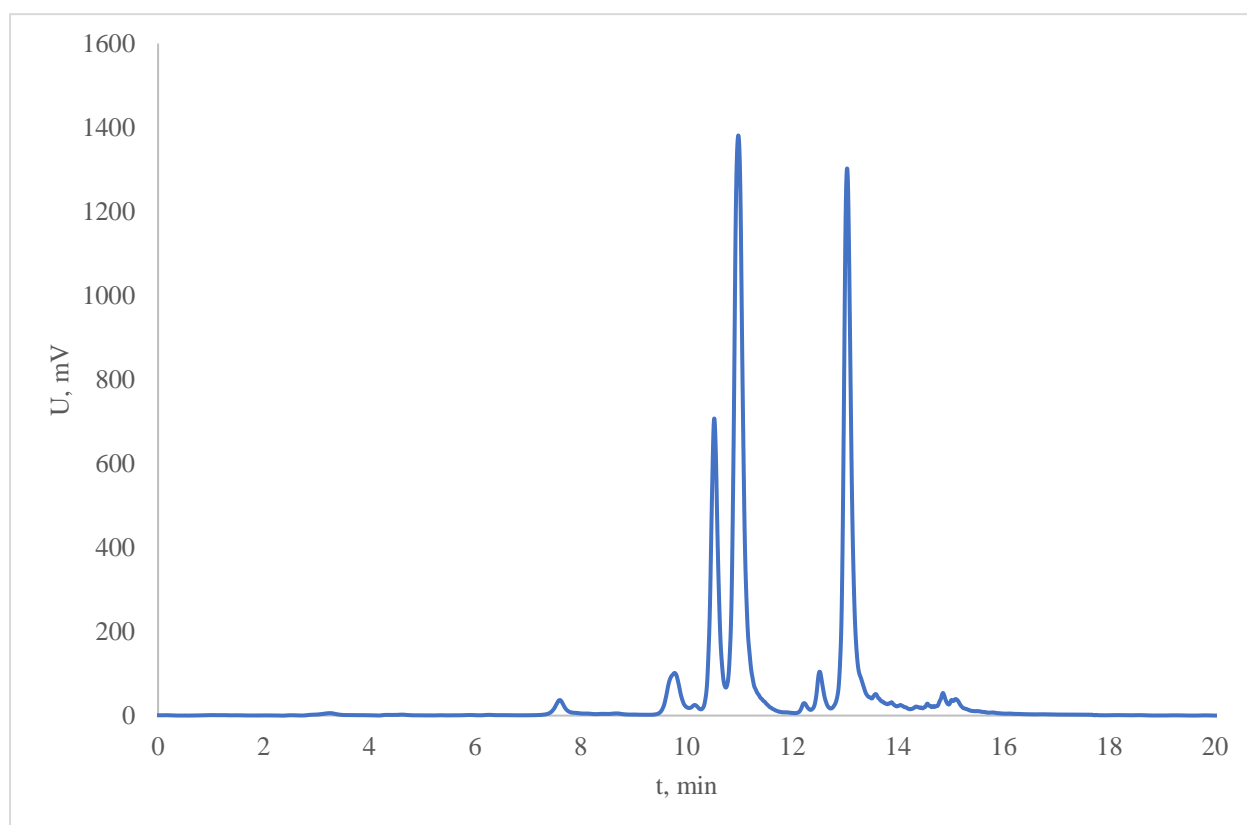


**Figure S51:** HPLC chromatogram of **1a**  $\rightarrow$  **2a** + **3a** reaction performed with  $\text{Rh}_2(n\text{-C}_7\text{H}_{15}\text{COO})_4$  (10.0 mol%).

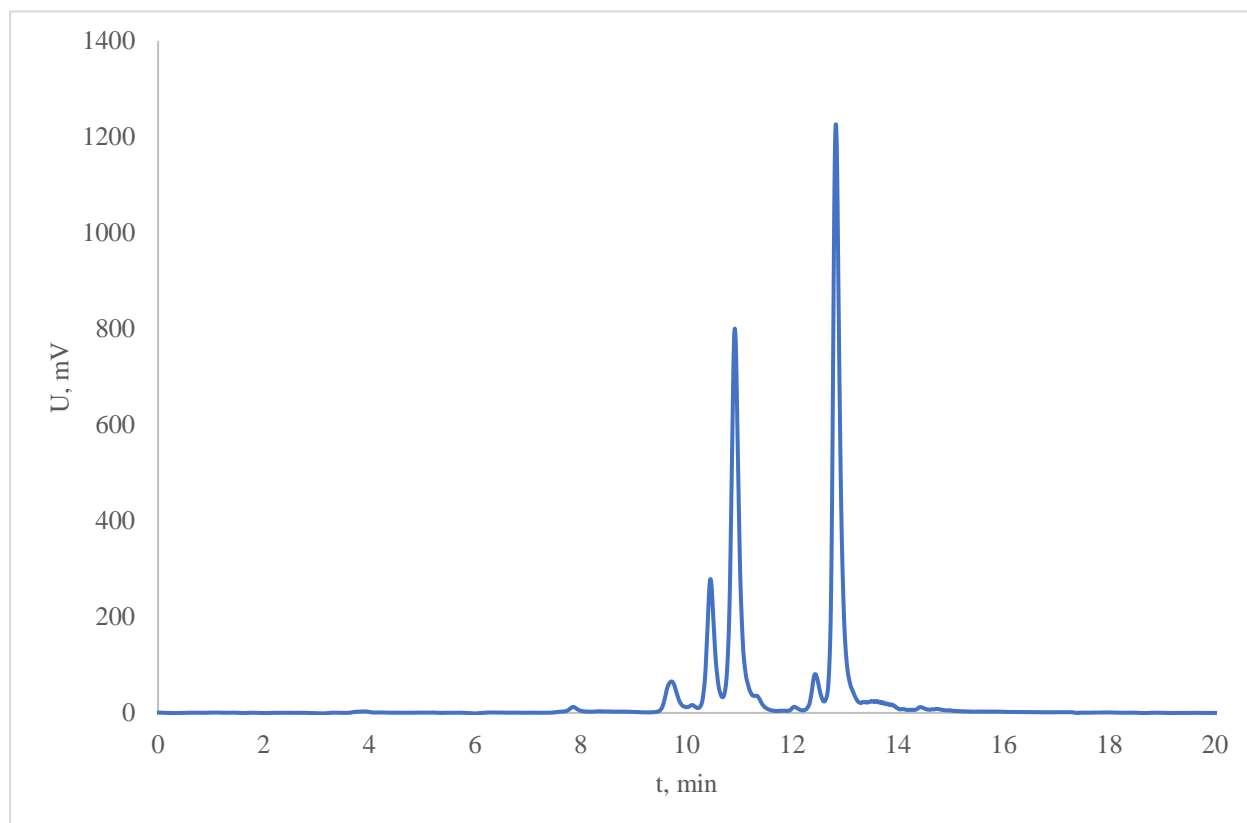
HPLC chromatograms of **1a**  $\rightarrow$  **2a** + **3a** reactions performed at different dilutions (Figure S52 – S56). For all reactions varying volumes THF with constant temperature (30 °C), amount of Rh<sub>2</sub>(esp)<sub>2</sub> catalyst (1 mol%) and diazo reagent **1a** (0.1 mmol).



**Figure S52:** HPLC chromatogram of the reaction **1a**  $\rightarrow$  **2a** + **3a** in 0.5 ml of THF.

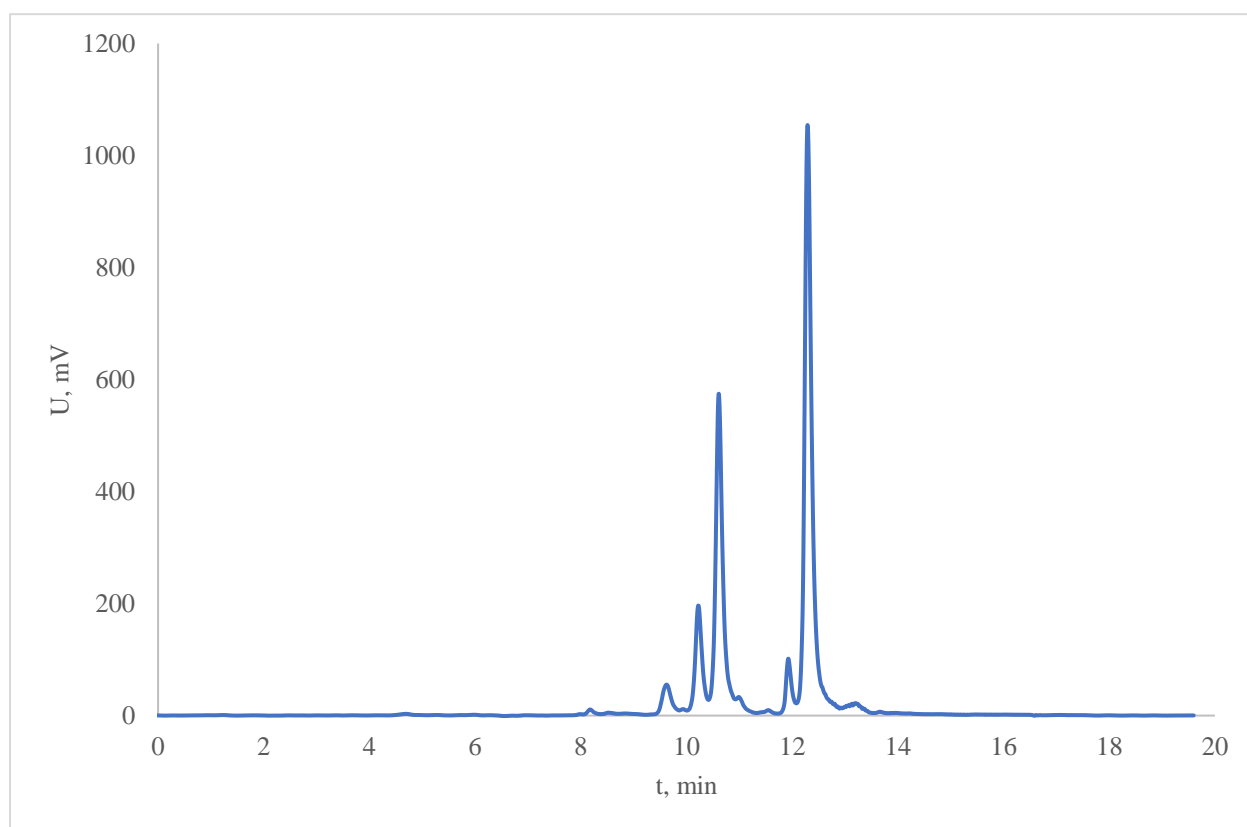


**Figure S53:** HPLC chromatogram of the reaction **1a**  $\rightarrow$  **2a** + **3a** in 1 ml of THF.

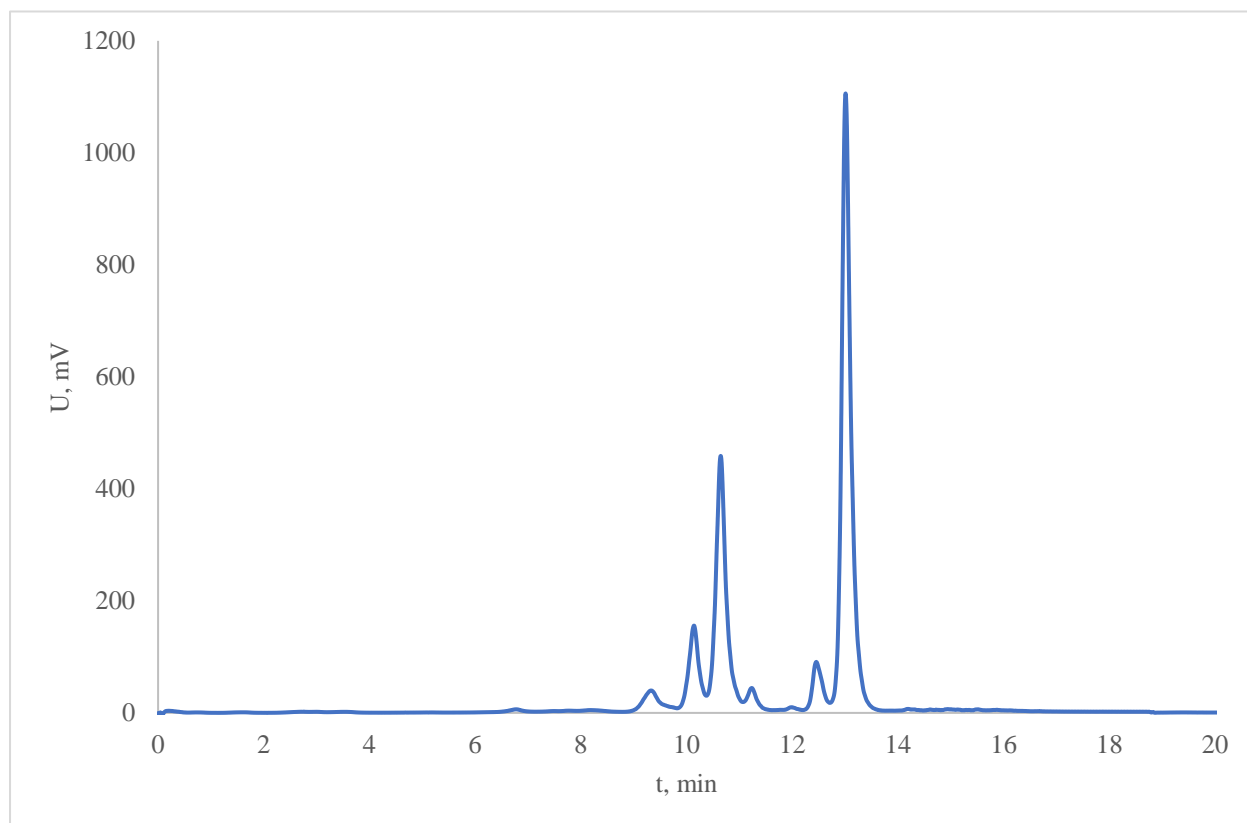


**Figure S54:** HPLC chromatogram of the reaction **1a**  $\rightarrow$  **2a** + **3a** in 3 ml of THF.





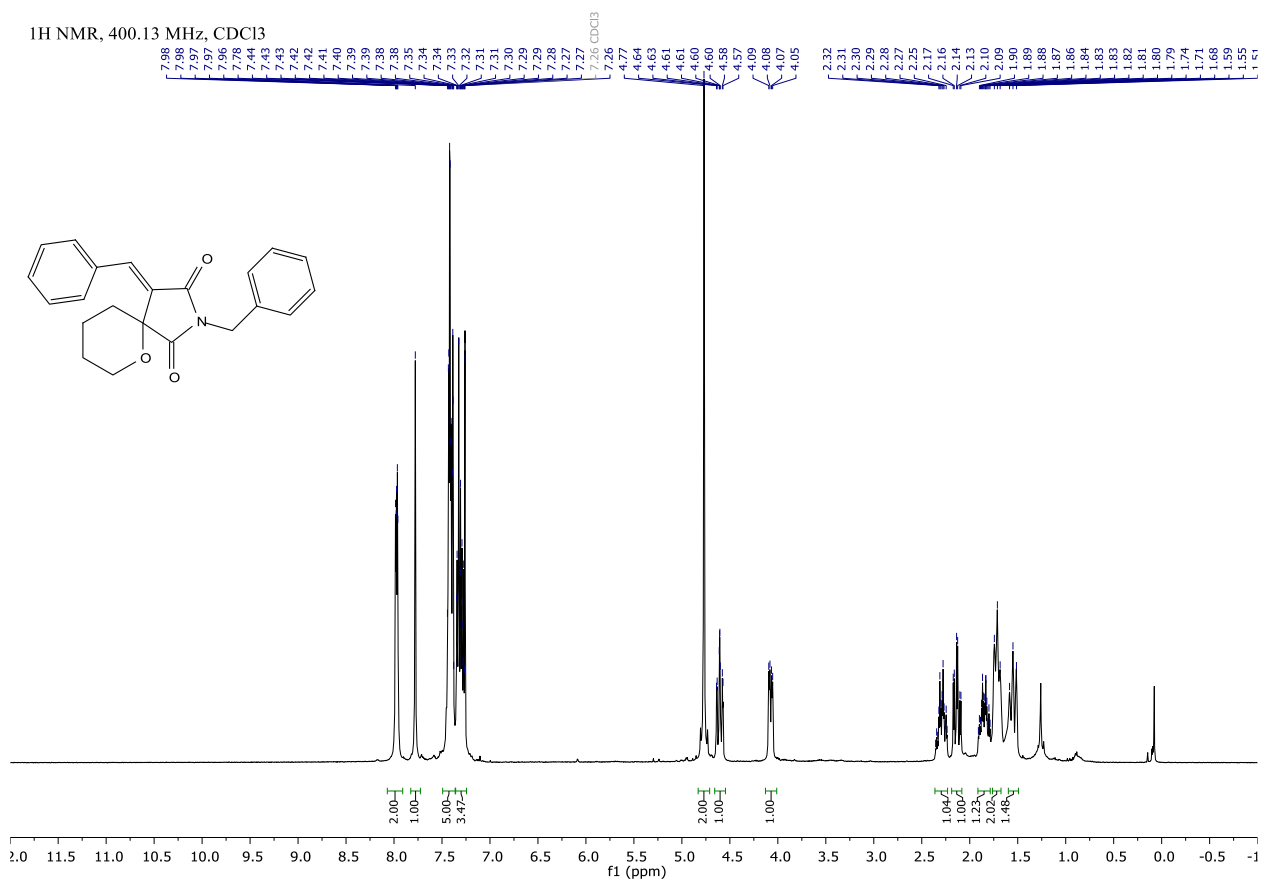
**Figure S55:** HPLC chromatogram of the reaction **1a**  $\rightarrow$  **2a** + **3a** in 5 ml of THF.



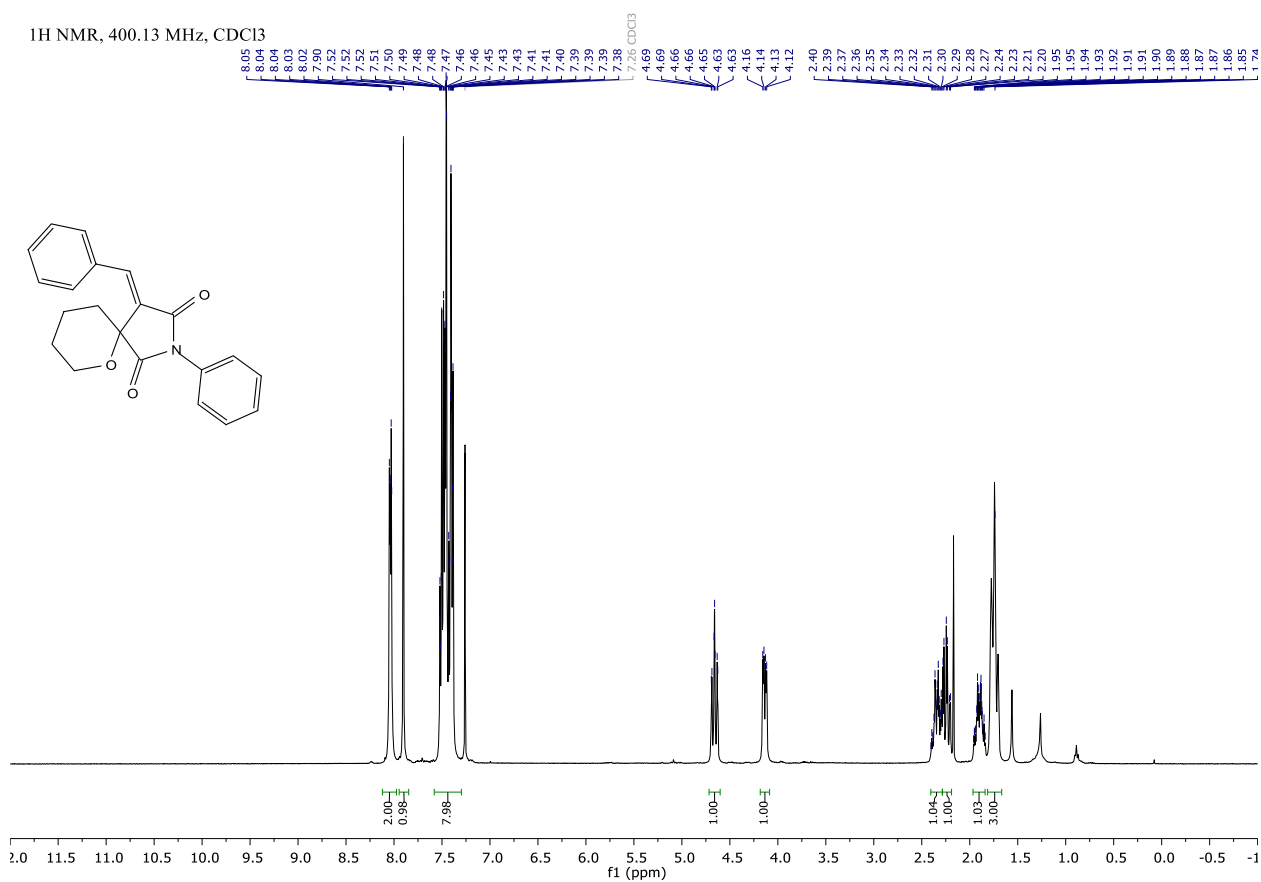
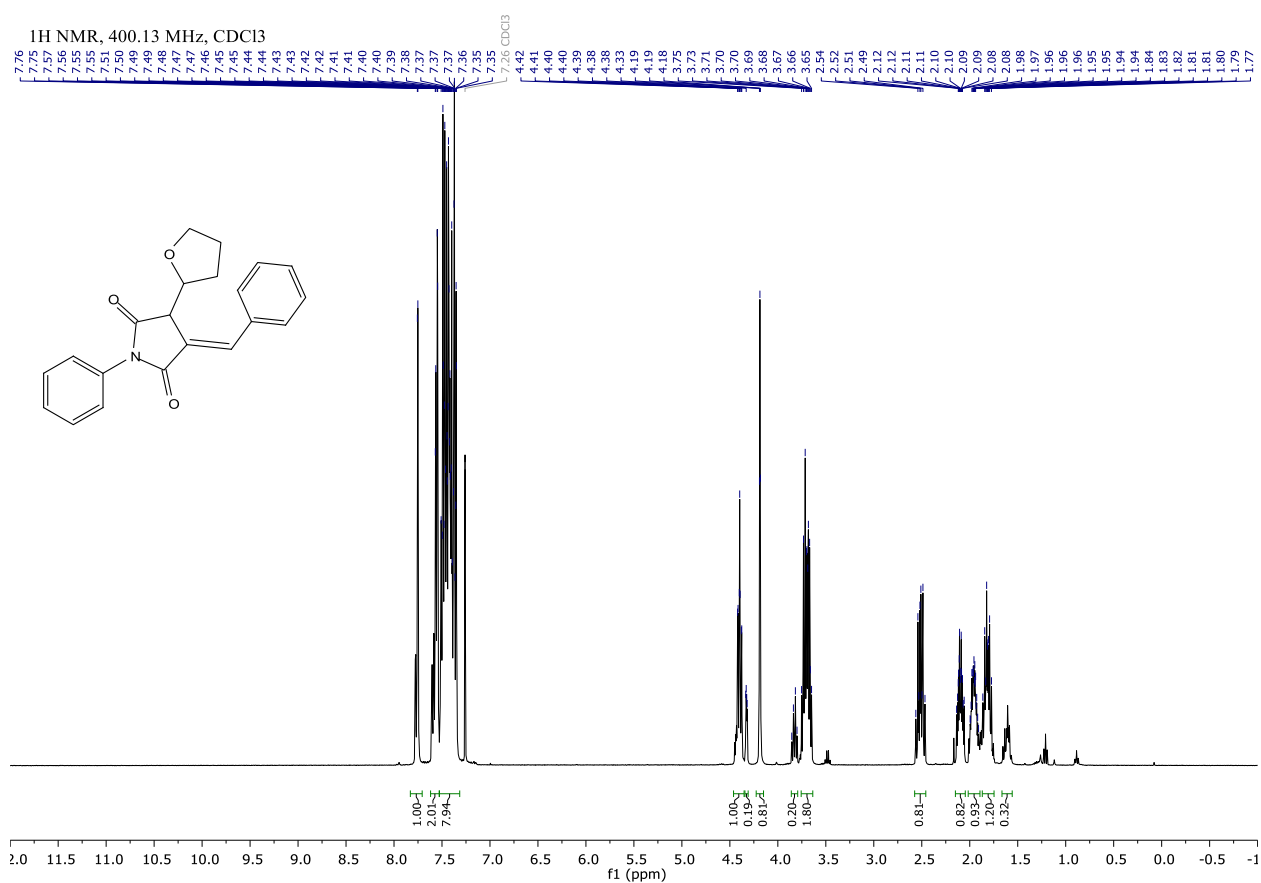
**Figure S56:** HPLC chromatogram of the reaction **1a**  $\rightarrow$  **2a** + **3a** in 10 ml of THF.

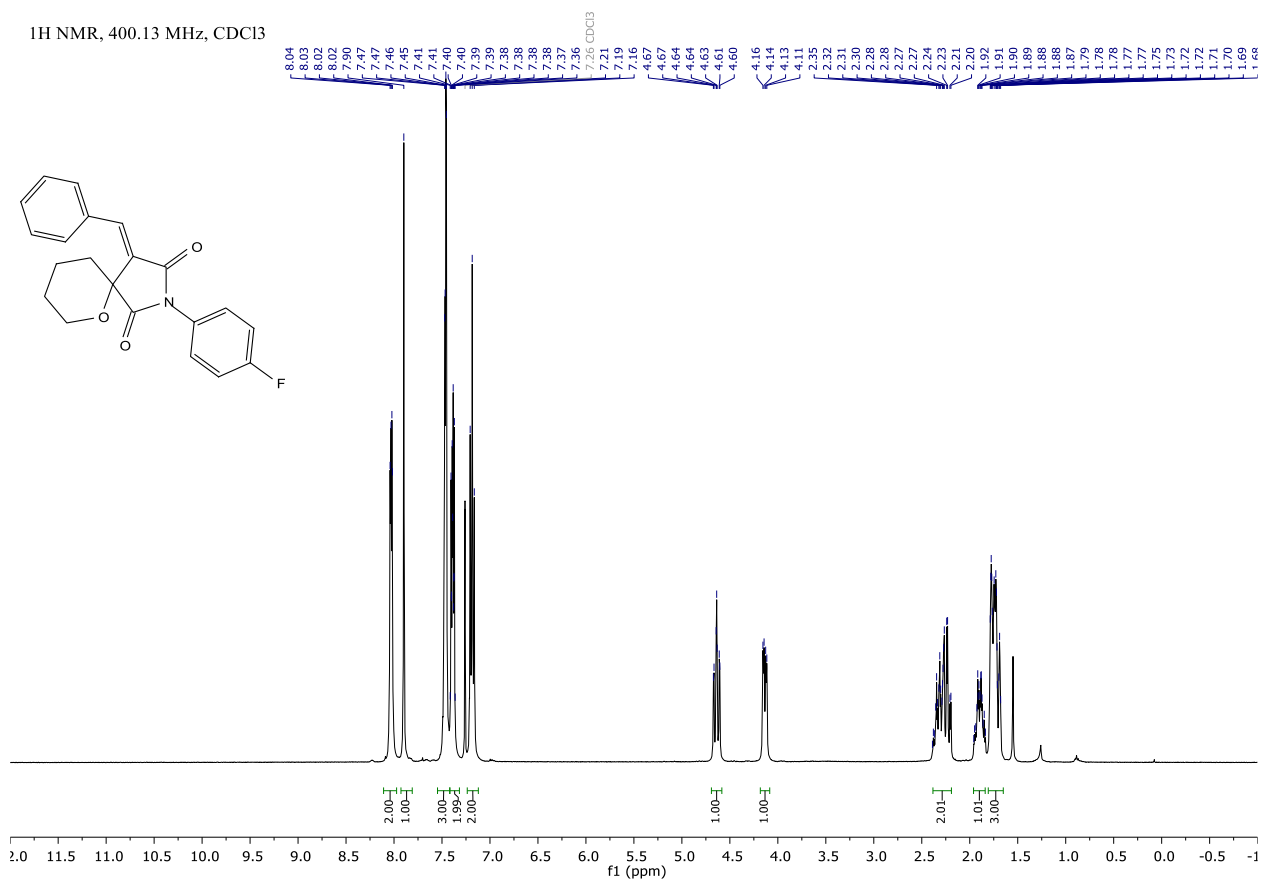
### 3. Spectra

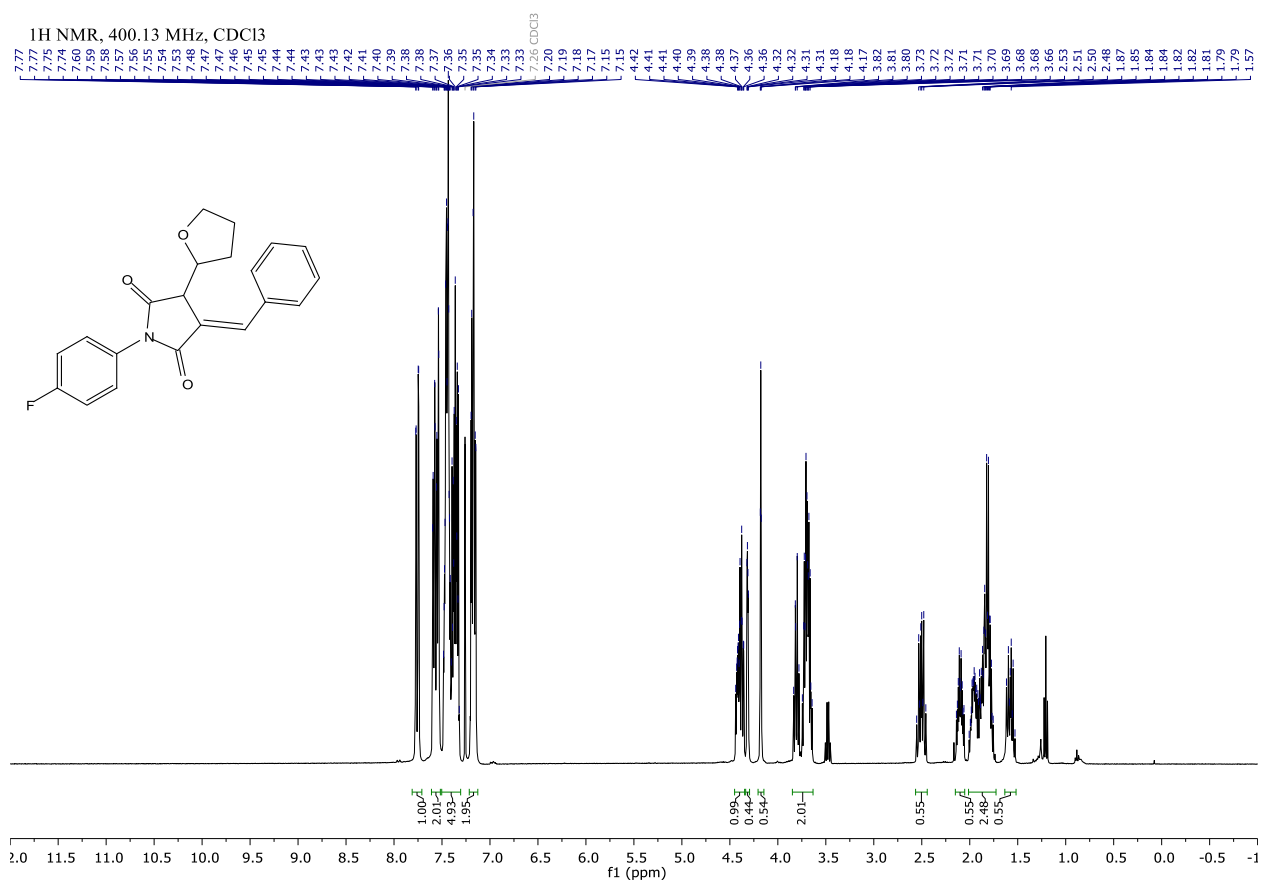
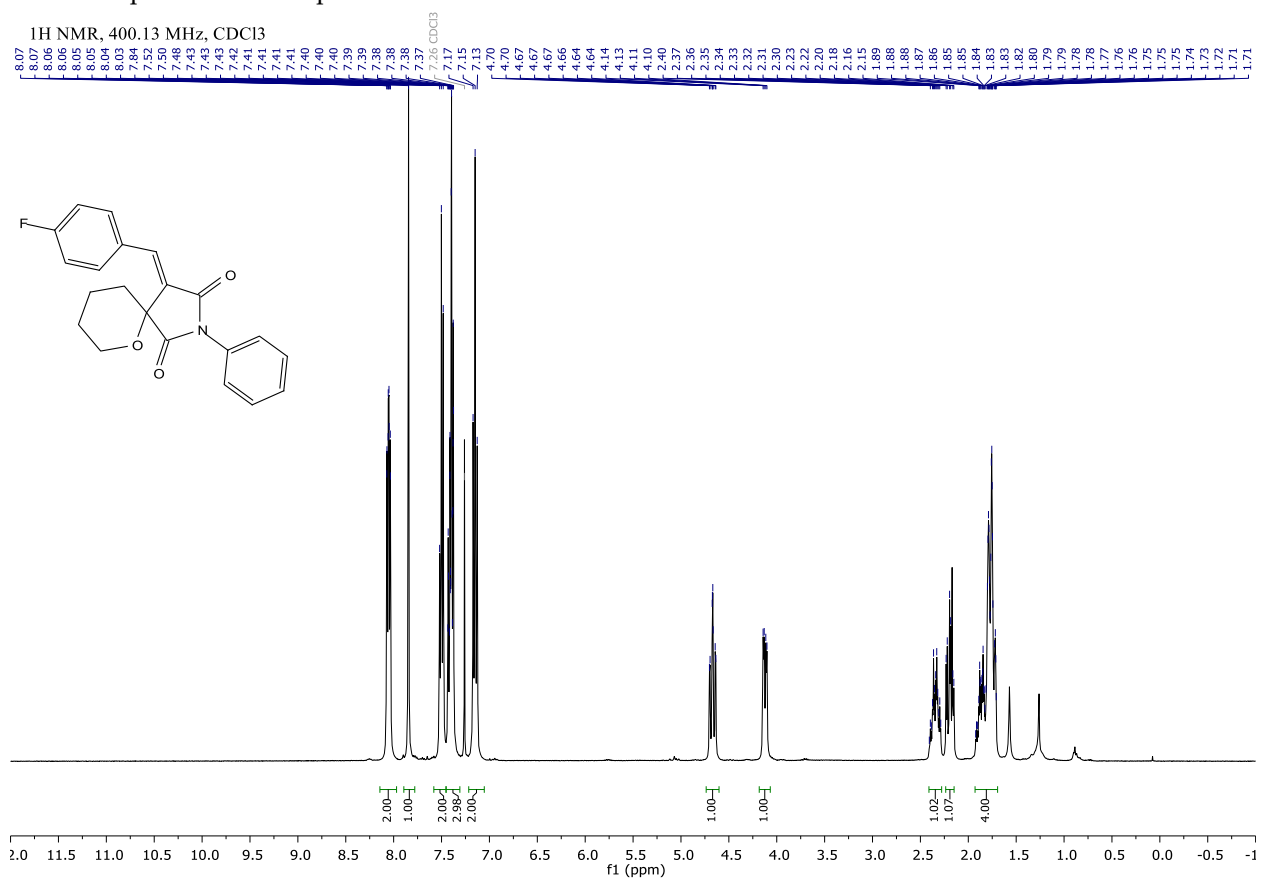
#### <sup>1</sup>H NMR spectrum of compound 2a



[illegible]<sup>1</sup>H NMR spectrum of compound **2b**

<sup>1</sup>H NMR spectrum of compound **3b**

<sup>1</sup>H NMR spectrum of compound 2c<sup>1</sup>H NMR spectrum of compound 3c

<sup>1</sup>H NMR spectrum of compound 2d

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra of compound **3d**