

Supporting Information

Merging Iron Catalysis and Biocatalysis—Iron Carbonyl Complexes as Efficient Hydrogen Autotransfer Catalysts in Dynamic Kinetic Resolutions

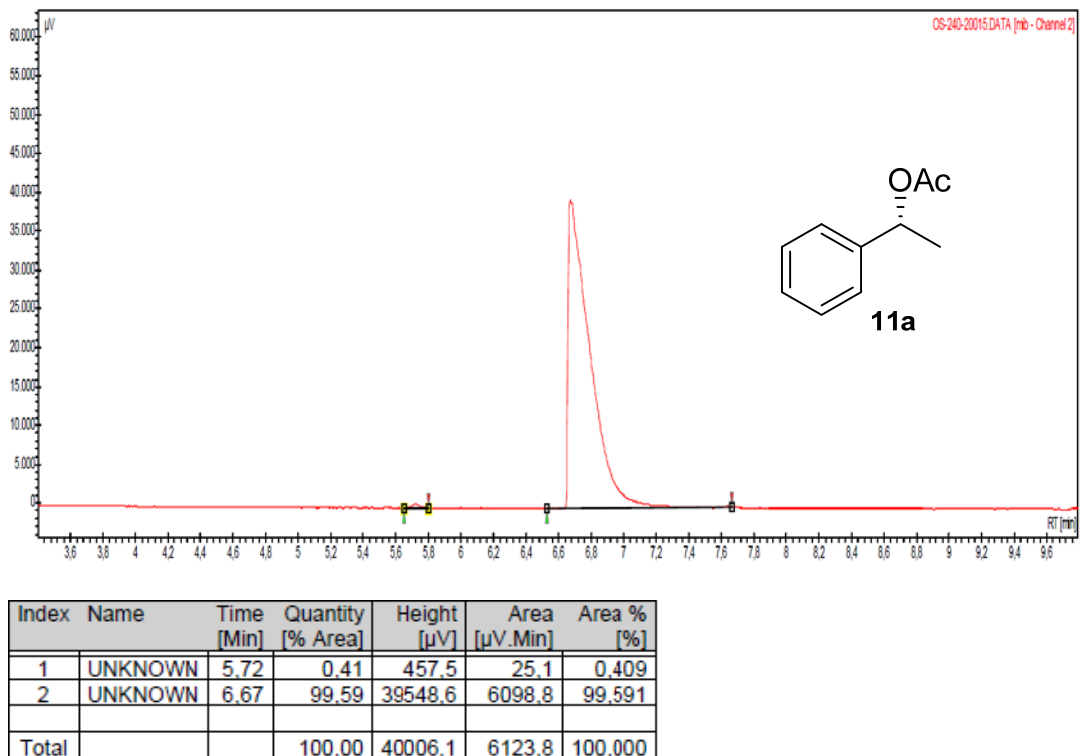
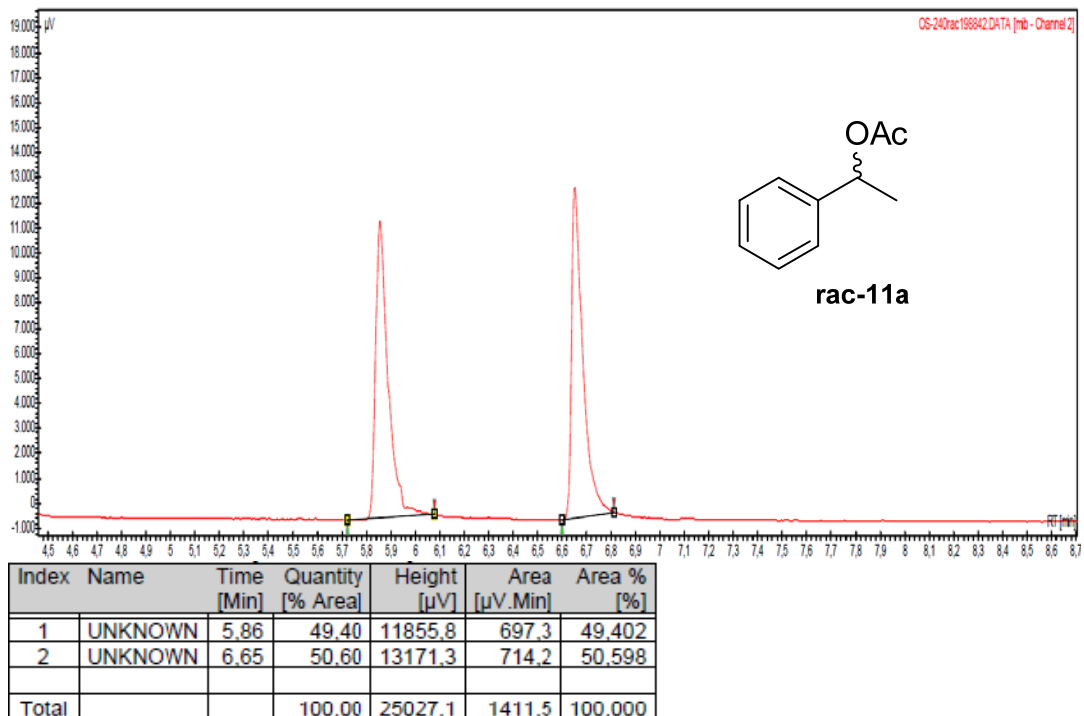
*Osama El-Sepelgy, Nurtalya Alandini, and Magnus Rueping**

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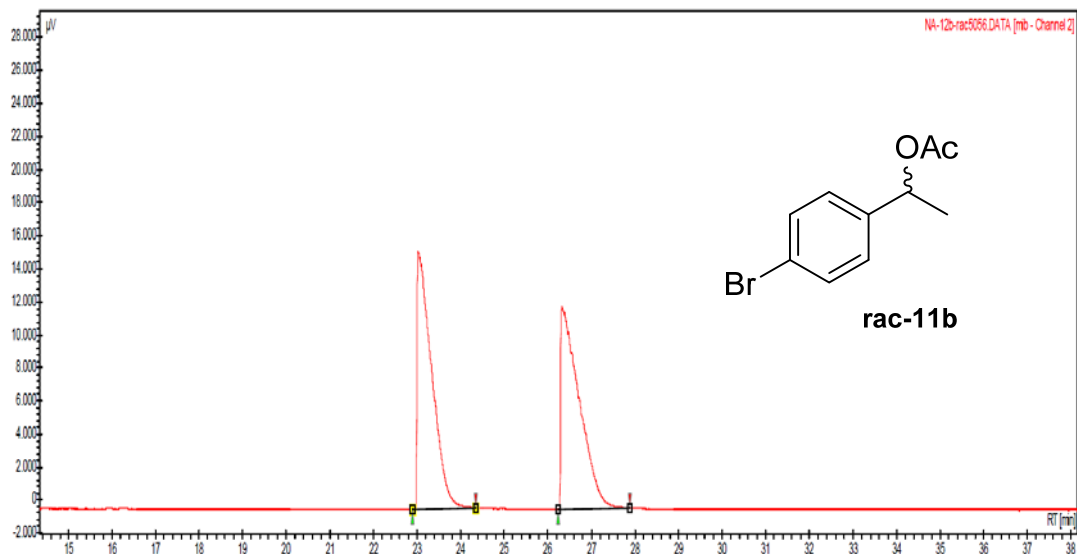
General: Unless otherwise noted, all reactions were carried out under inert atmosphere in oven-dried glassware. All commercially available compounds were used as provided without further purification. Solvents were purified and degassed by standard procedures. Acyl donor *p*-chlorophenyl acetate (PCPA)^[1], 1-ethoxyvinyl acetate^[2], or acetyl isopropyl carbonate^[3] were prepared according to literature procedure. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 pre-coated aluminium plates (Macherey-Nagel 0.20 mm thickness) with a fluorescent indicator UV₂₅₄. Visualization was performed with standard phosphomolybdic acid stain (10g in 100 mL EtOH) or UV light. Column chromatography was performed using silica gel (Macherey Nagel, particle size 0.040-0.063 mm). The enantiomeric excess was determined by analytical GC employing CP-Chirasil-Dex CB 25 m x 0.25 mm DF = 0.25 column. GC-program for the compounds **11h**, **11m** and **11n** 100 °C / 5 min / 180 °C / 10 °C min⁻¹, 20 min. For other compounds: 100 °C / 5 min / 120 °C / 1 °C min⁻¹, 20 min / 180 °C / 10 °C min⁻¹, 20 min.

General procedure: A 50 mL Schlenk flask equipped with a stir bar was charged with the iron catalyst **8** (39.2 mg; 10 mol%), Novozyme-435 (15 mg) and degassed toluene (5 mL) under argon. The racemic alcohol (**10**, 1 mmol) was added and the reaction mixture was stirred for 5 minutes. Then 4-chlorophenyl acetate (512 mg, 3 mmol) was introduced and reaction mixture was stirred for 24 h at 60°C and monitored by GC. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was treated with a 4:1 mixture of methanol and saturated NaHCO₃ (8 mL) for 2.5 h at room temperature. Methanol was removed and the aqueous phase was extracted with Et₂O (3 x 15 mL). The combined organic phases were washed with 2M NaOH and brine, dried over Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel using pentane/ether mixtures as eluent to give pure acetates **11**.

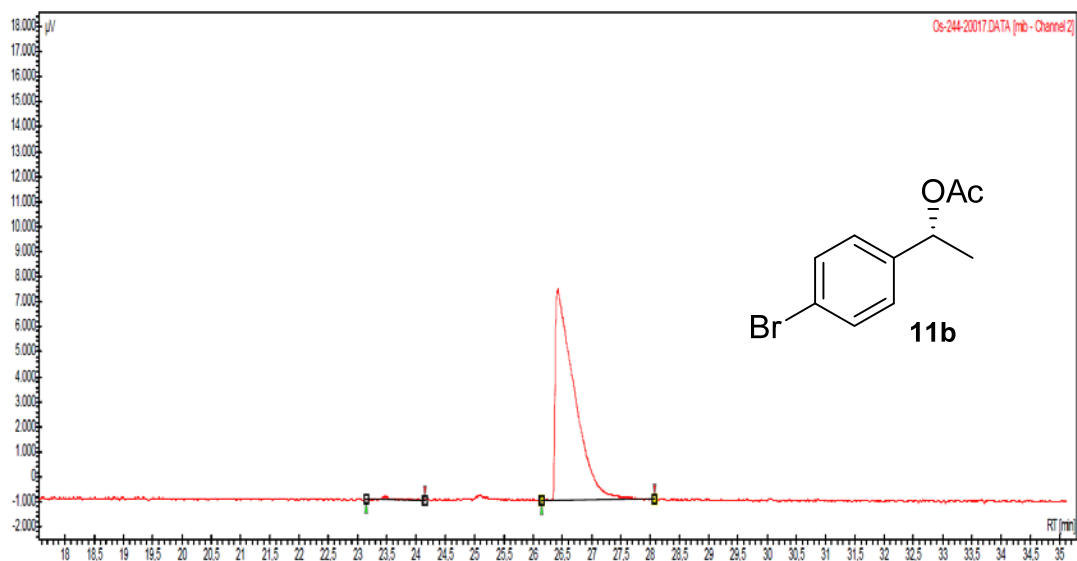
(R)-1-Phenethyl acetate (11a)



(R)-1-(4-Bromophenyl)ethyl acetate (11b)

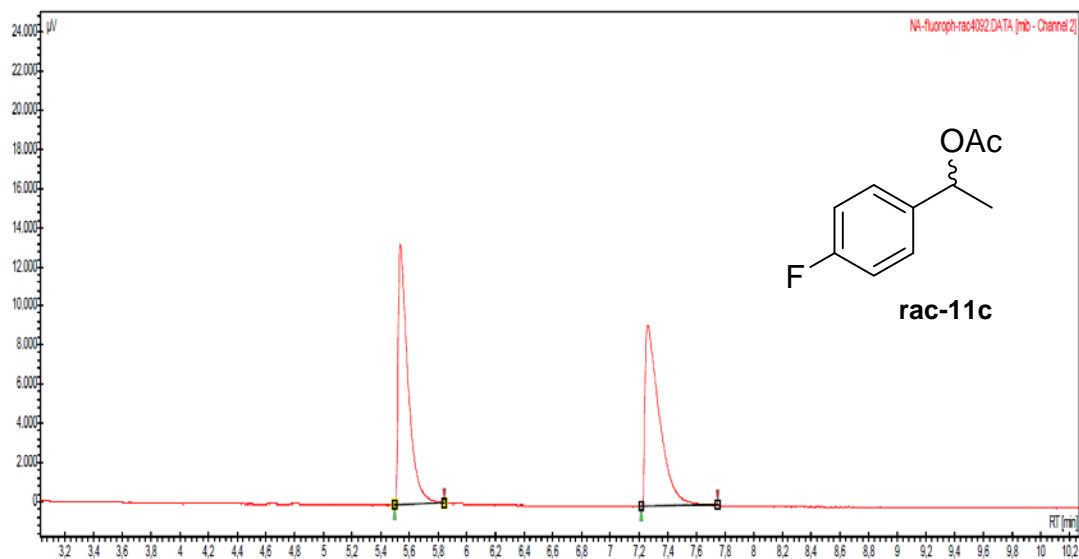


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	23.03	49.88	15600.6	6022.5	49.878
2	UNKNOWN	26.32	50.12	12299.4	6052.0	50.122
Total			100.00	27900.0	12074.5	100.000

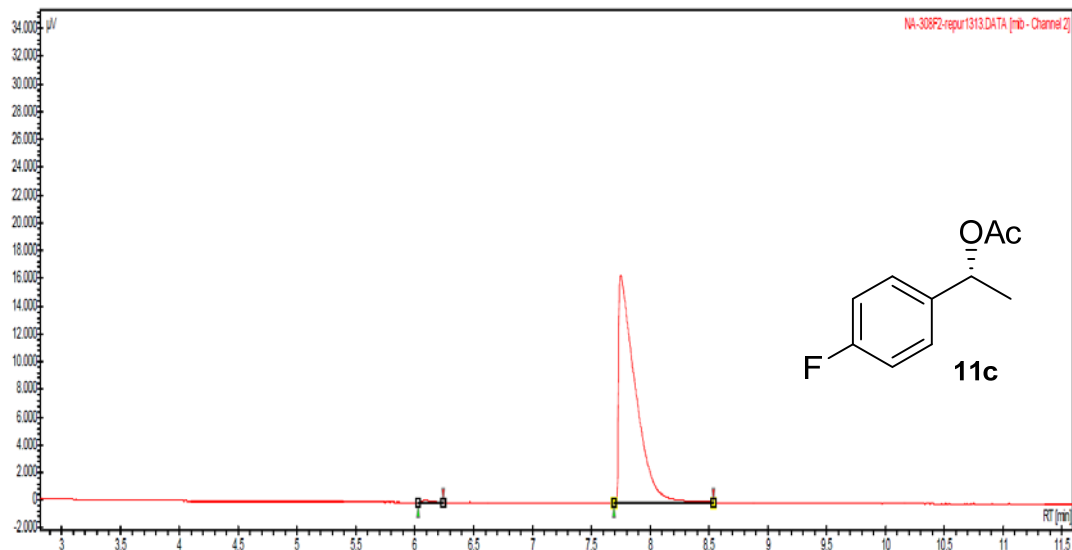


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
2	UNKNOWN	23.46	0.56	126.2	17.9	0.561
1	UNKNOWN	26.43	99.44	8451.8	3177.7	99.439
Total			100.00	8577.9	3195.7	100.000

(R)-1-(4-Fluorophenyl)ethyl acetate (11c)

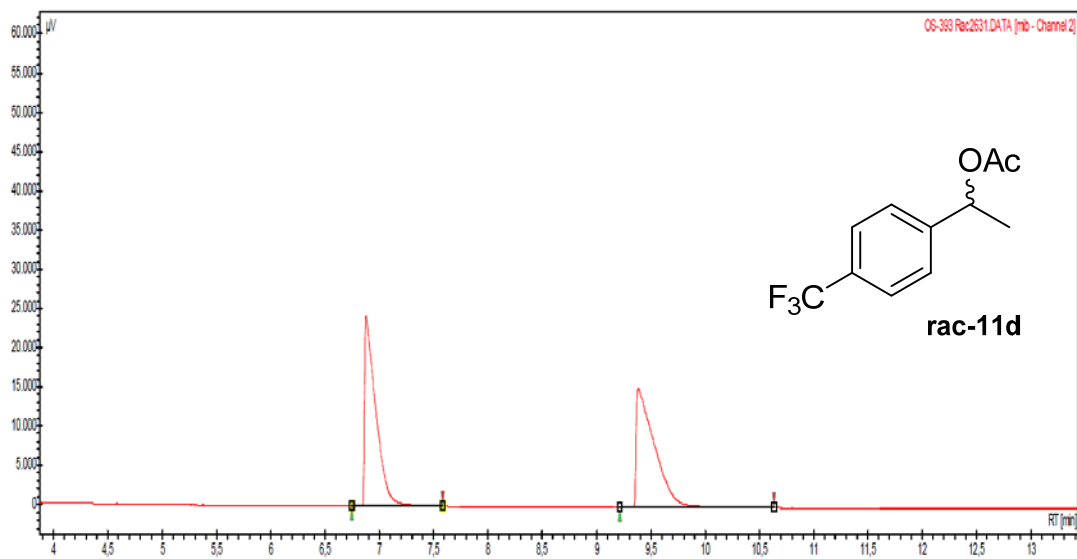


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	5.54	49.56	13315.1	1052.6	49.565
2	UNKNOWN	7.26	50.44	9246.3	1071.0	50.435
Total			100.00	22561.5	2123.6	100.000

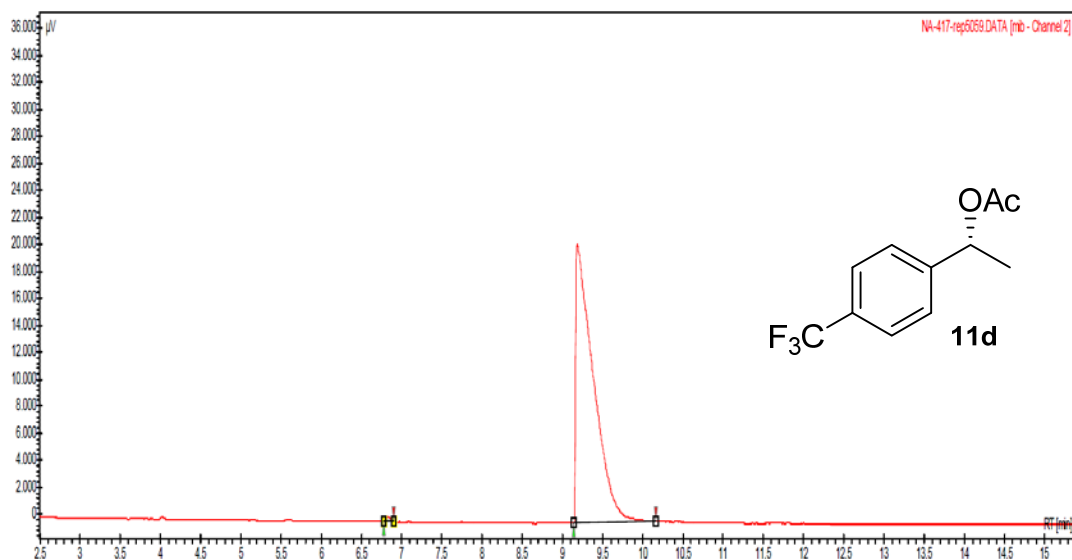


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
2	UNKNOWN	6.09	0.37	158.9	10.1	0.374
1	UNKNOWN	7.75	99.63	16458.5	2593.9	99.626
Total			100.00	16617.4	2704.0	100.000

(R)-1-(4-(Trifluoromethyl)phenyl)ethyl acetate (11d)

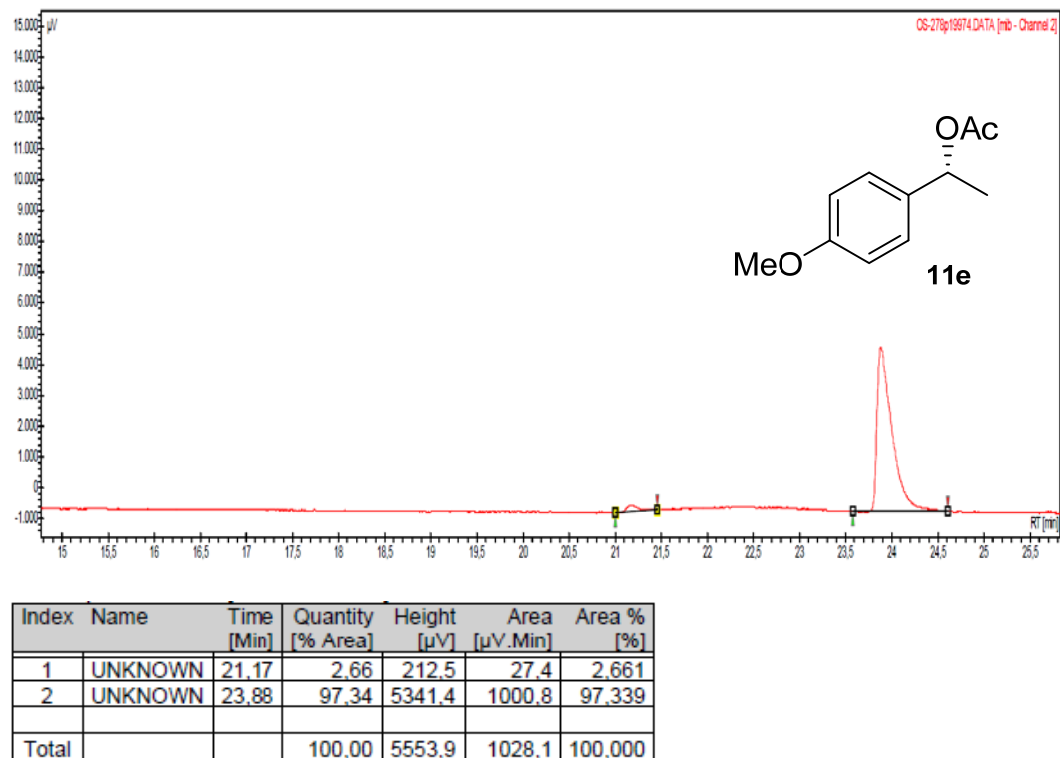
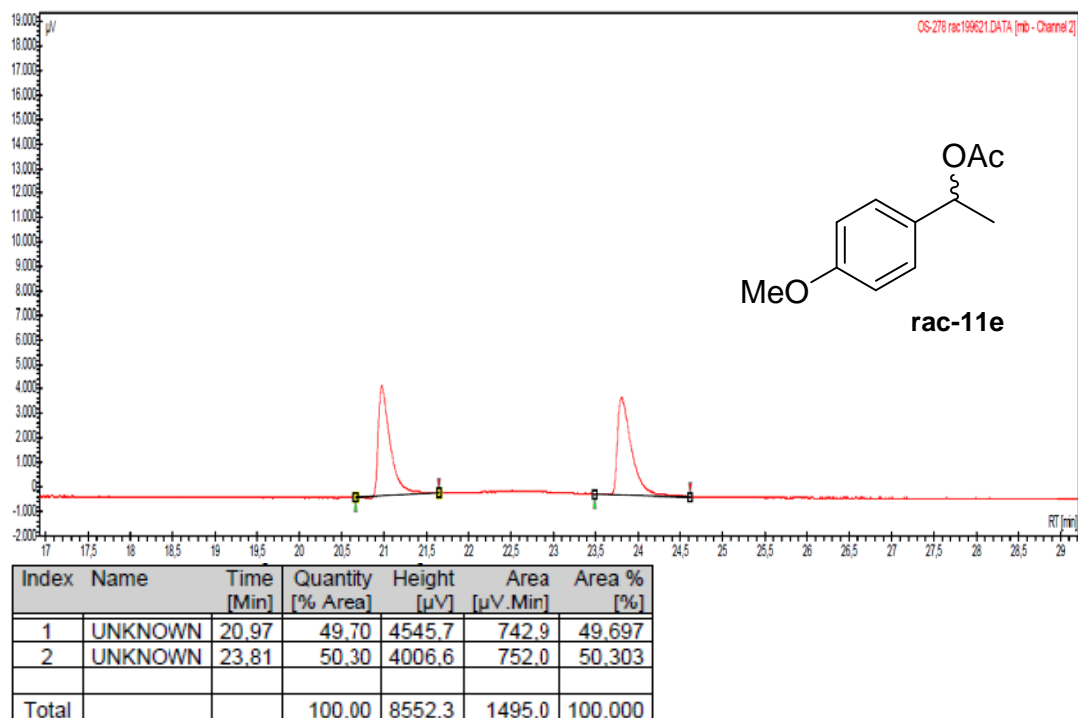


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot \text{Min}$]	Area % [%]
1	UNKNOWN	6.88	49.83	24370.3	2946.8	49.832
2	UNKNOWN	9.38	50.17	15114.7	2966.7	50.168
Total			100.00	39485.0	5913.5	100.000

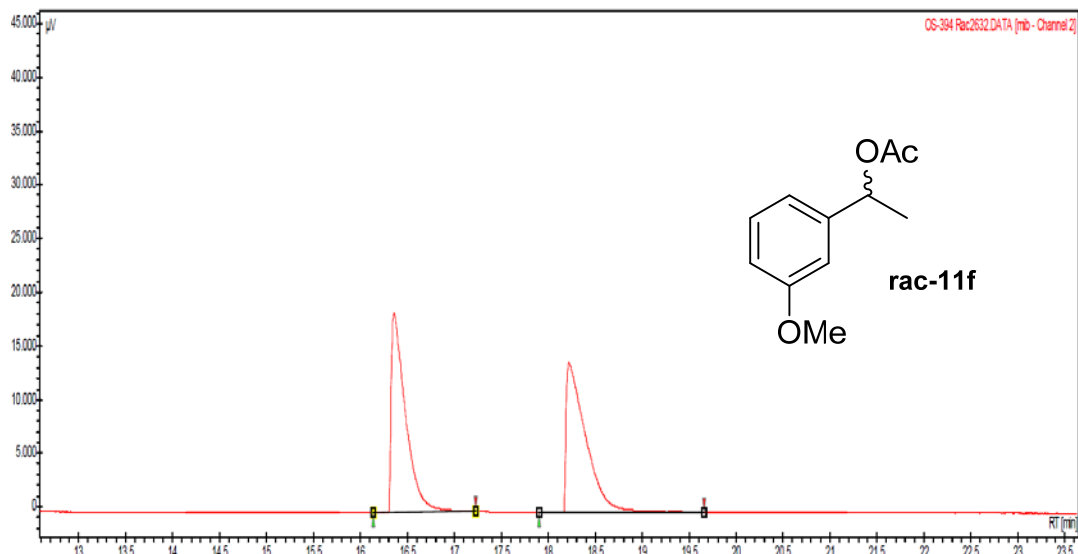


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot \text{Min}$]	Area % [%]
1	UNKNOWN	6.83	0.43	362.3	22.7	0.430
2	UNKNOWN	9.19	99.57	20660.3	5247.7	99.570
Total			100.00	21022.6	5270.3	100.000

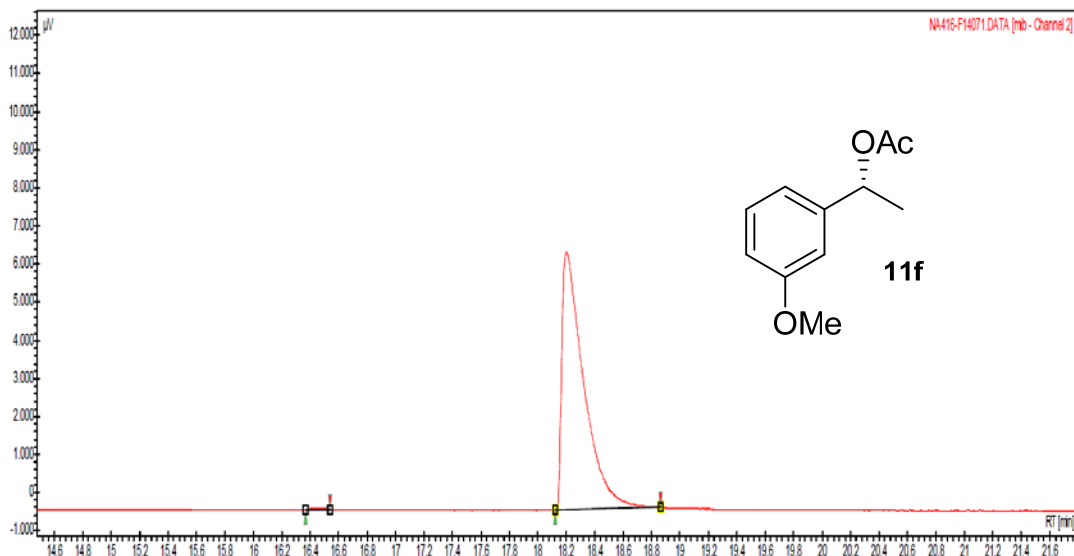
(R)-1-(4-Methoxyphenyl)ethyl acetate (11e)



(R)-1-(3-(Methoxyphenyl)ethyl acetate (11f)

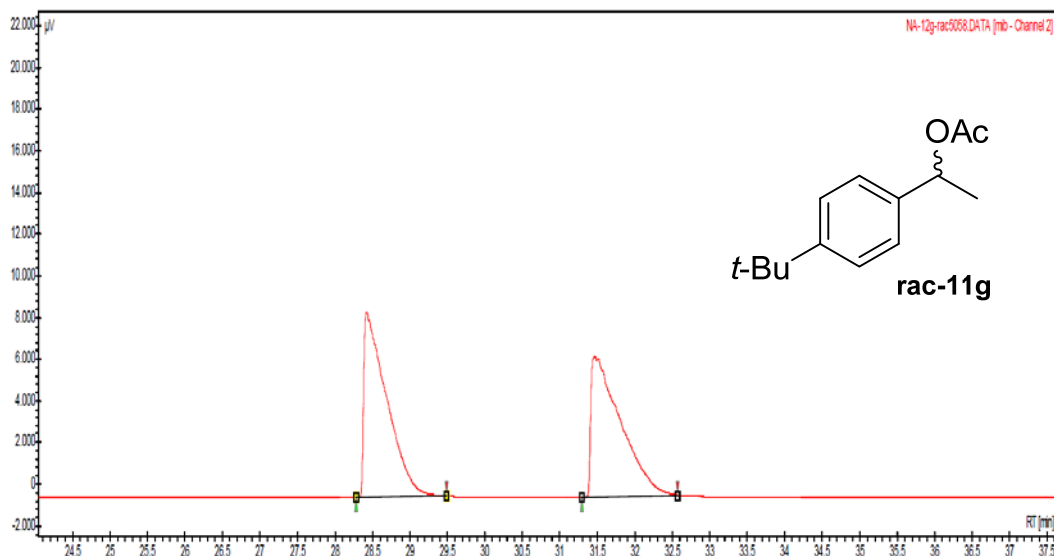


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	16.36	49.39	18585.4	3280.9	49.389
2	UNKNOWN	18.22	50.61	13945.7	3362.1	50.611
Total			100.00	32531.2	6643.0	100.000

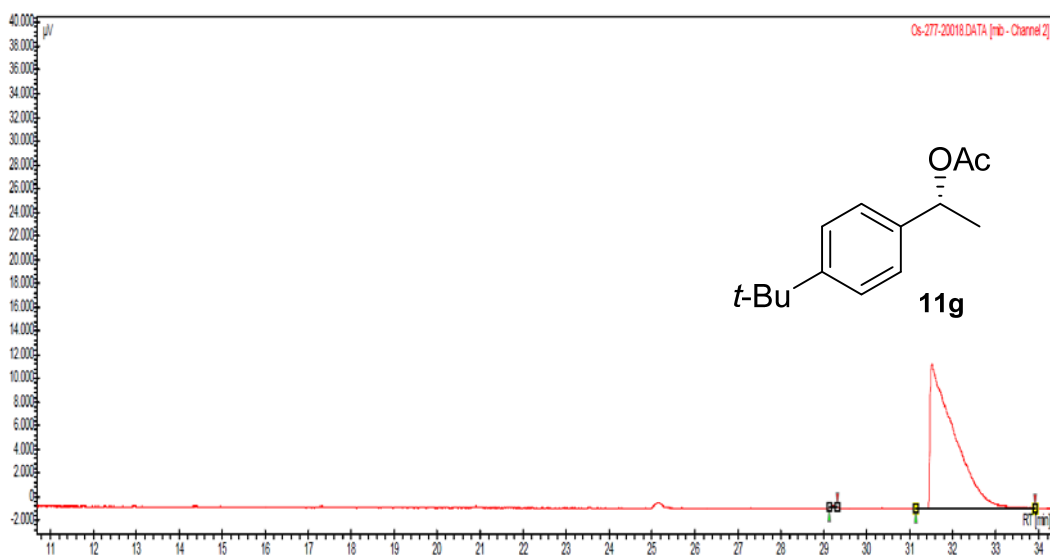


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
2	UNKNOWN	16.44	0.21	24.7	2.5	0.209
1	UNKNOWN	18.20	99.79	6765.4	1209.7	99.791
Total			100.00	6790.1	1212.2	100.000

(R)-1-(4-(*tert*-Butyl)phenyl)ethyl acetate (11g)

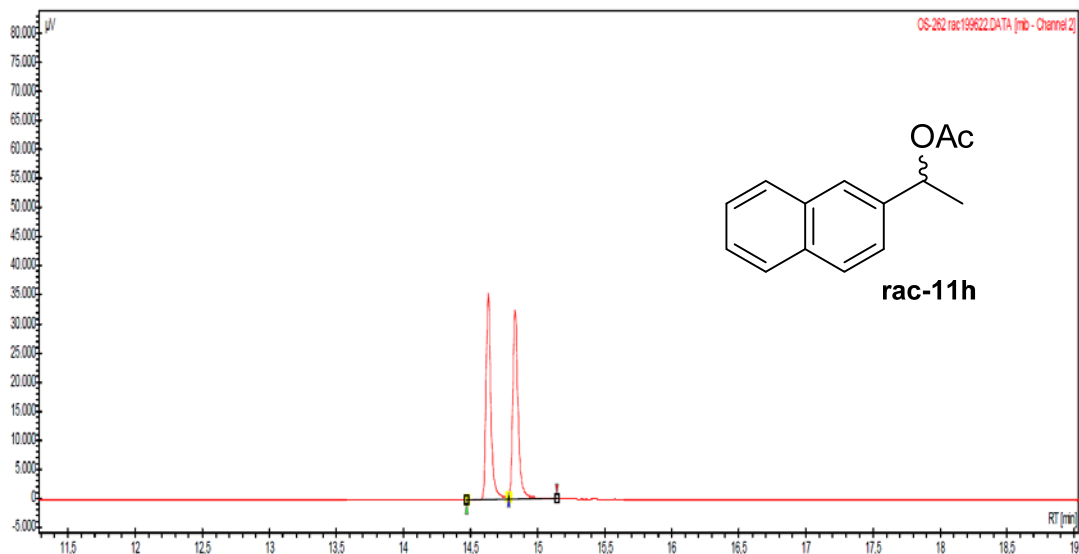


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot \text{Min}$]	Area % [%]
1	UNKNOWN	28.43	50.34	8905.0	3127.6	50.341
2	UNKNOWN	31.46	49.66	6728.1	3085.3	49.659
Total			100.00	15633.2	6212.0	100.000

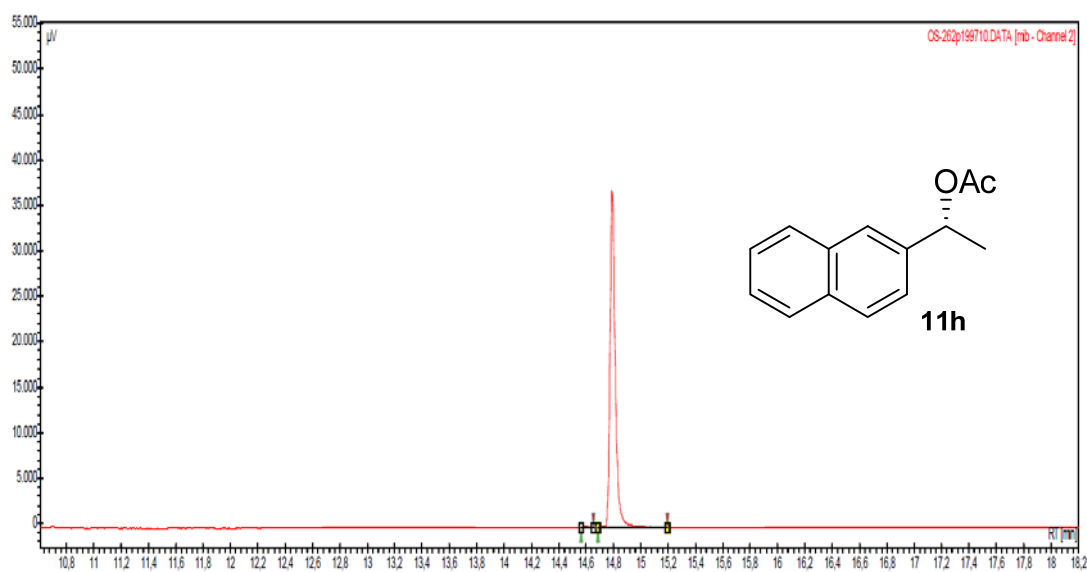


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot \text{Min}$]	Area % [%]
2	UNKNOWN	29.21	0.12	101.2	9.2	0.113
1	UNKNOWN	31.53	99.88	12140.6	7847.1	99.882
Total			100.00	12241.8	7856.3	100.000

(R)-1-(2-Naphthyl)ethyl acetate (11h)

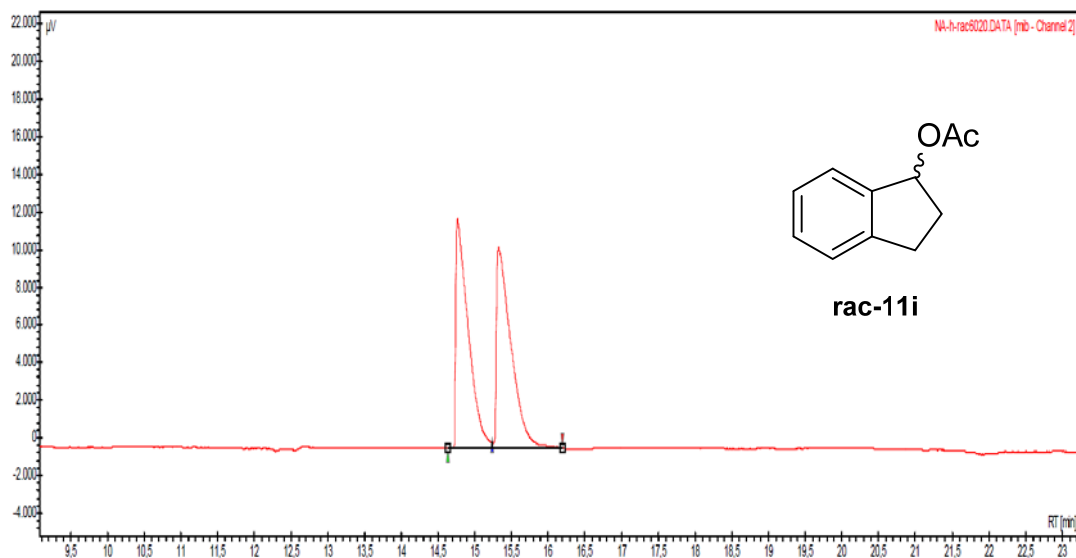


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot \text{Min}$]	Area %
1	UNKNOWN	14.63	49.61	35165.0	1193.9	49.611
2	UNKNOWN	14.83	50.36	32658.0	1515.5	50.359
Total			100.00	68122.9	3009.4	100.000

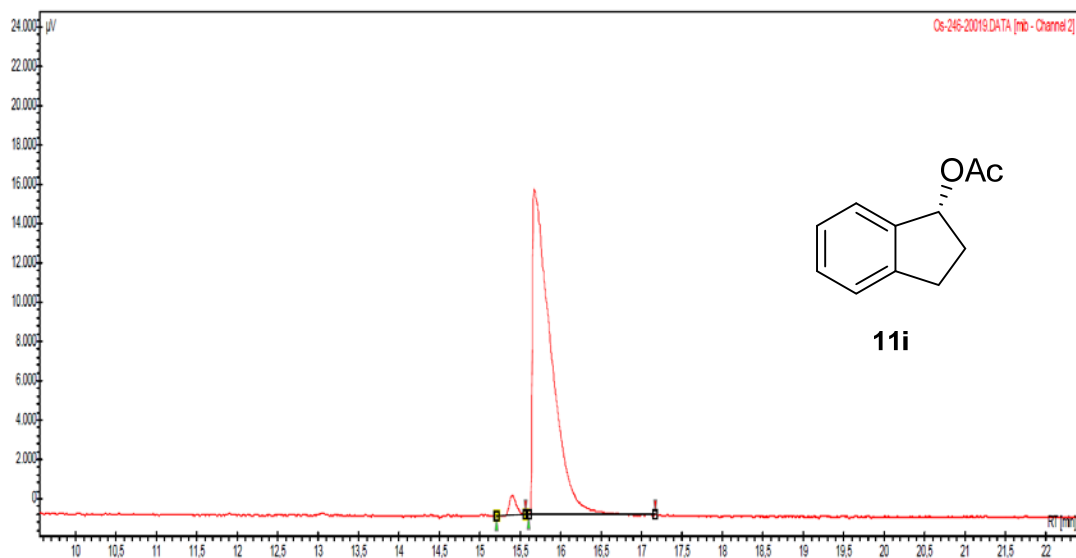


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot \text{Min}$]	Area %
2	UNKNOWN	14.60	0.43	198.4	7.0	0.429
1	UNKNOWN	14.79	99.57	37084.8	1632.7	99.571
Total			100.00	37283.2	1639.3	100.000

(R)-1-Indanyl acetate (11i)

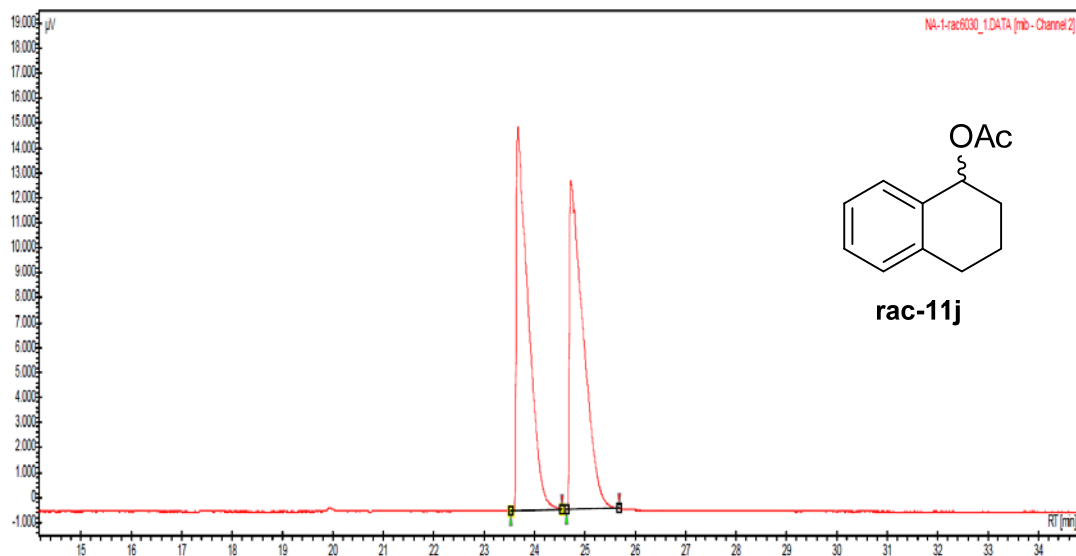


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	14.77	49.23	12184.1	2381.3	49.235
2	UNKNOWN	15.32	50.77	10691.4	2455.4	50.765
Total			100.00	22875.5	4836.7	100.000

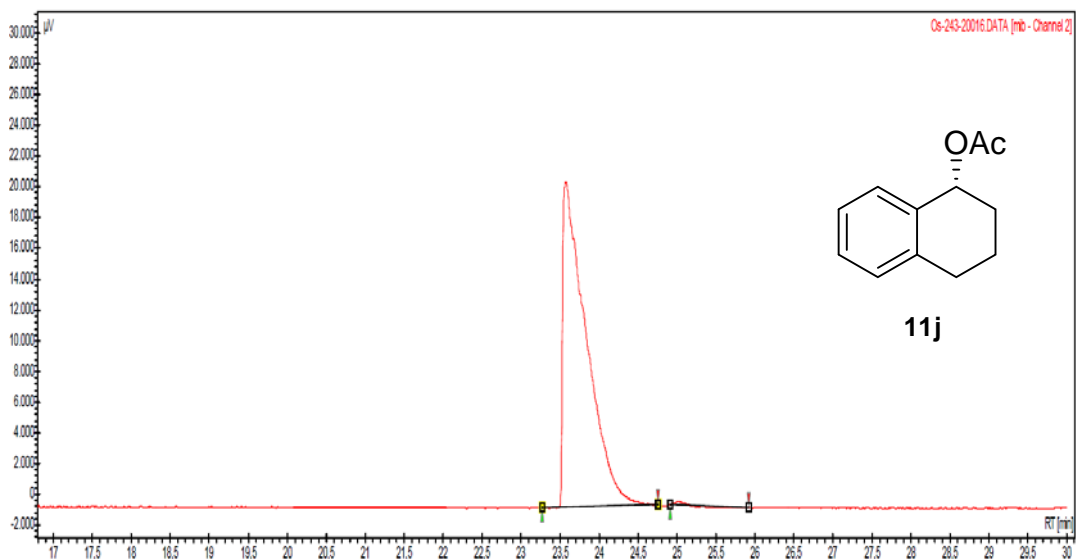


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	15.40	2.20	1000.2	97.8	2.202
2	UNKNOWN	15.67	97.80	16582.6	4345.8	97.798
Total			100.00	17582.8	4443.7	100.000

(R)-1,2,3,4-Tetrahydro-1-naphthyl acetate (11j)

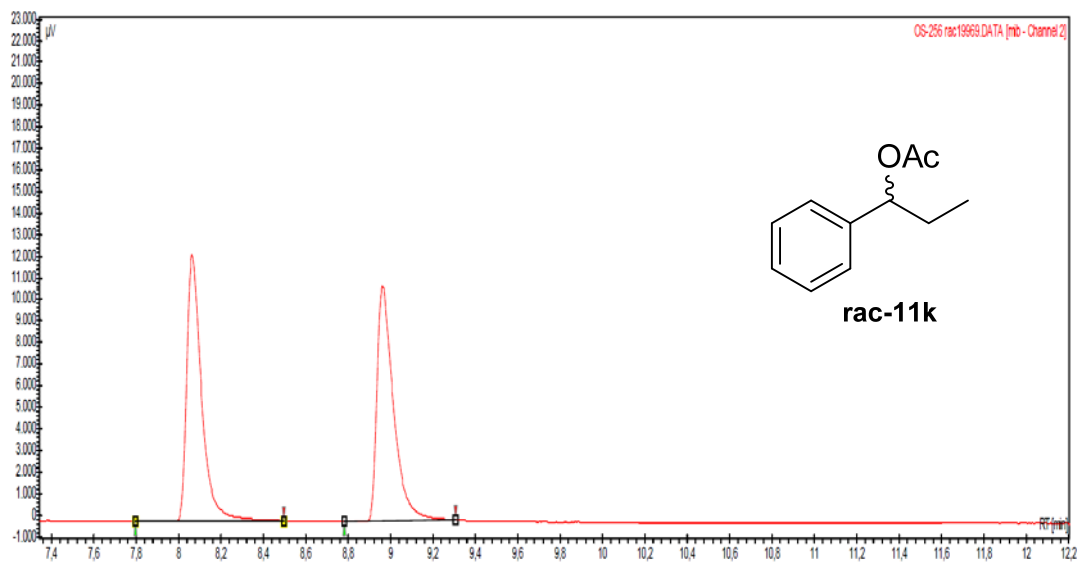


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot Min$]	Area % [%]
1	UNKNOWN	23.67	50.17	15351.6	4202.4	50.171
2	UNKNOWN	24.72	49.83	13160.7	4173.7	49.829
Total			100.00	28512.3	8376.1	100.000

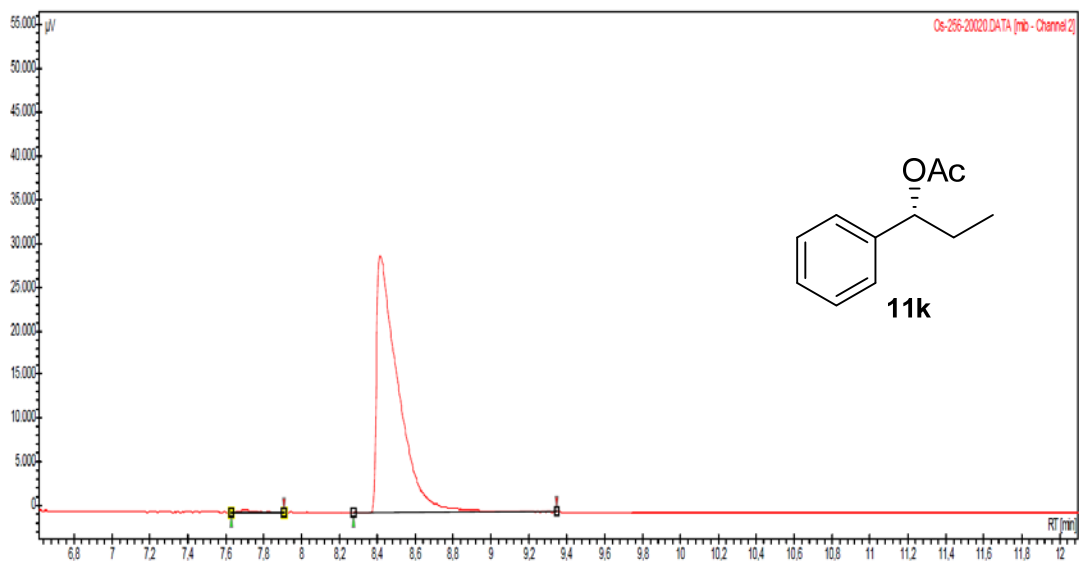


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu V \cdot Min$]	Area % [%]
1	UNKNOWN	23.58	99.94	21162.1	7445.5	99.944
2	UNKNOWN	25.02	0.06	208.1	4.2	0.056
Total			100.00	21370.2	7449.7	100.000

(R)-1-Phenylpropyl acetate (11k)

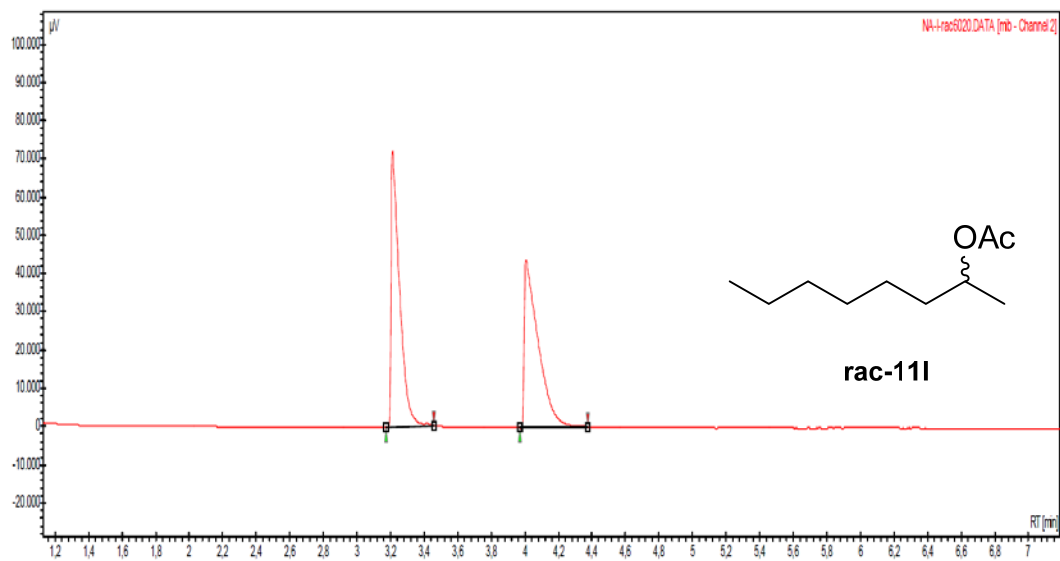


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	8.07	50.51	12350.0	1001.4	50.510
2	UNKNOWN	8.96	49.49	10872.5	981.2	49.490
Total			100.00	23222.5	1982.6	100.000

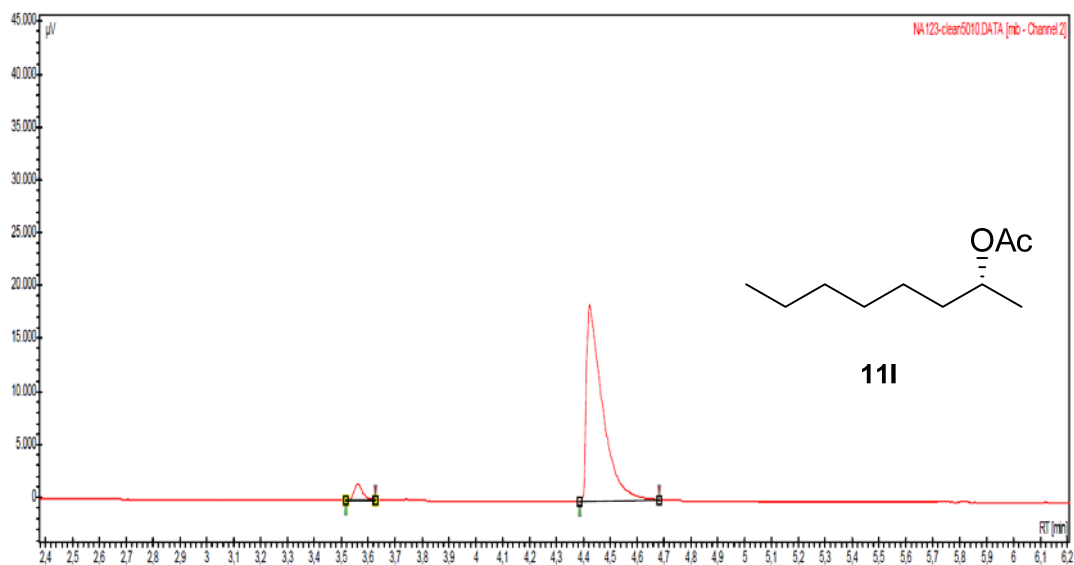


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	7.71	0.50	248.3	19.6	0.504
2	UNKNOWN	8.41	99.50	29342.2	3874.3	99.496
Total			100.00	29590.5	3893.9	100.000

(R)-2-Octyl acetate (11I)

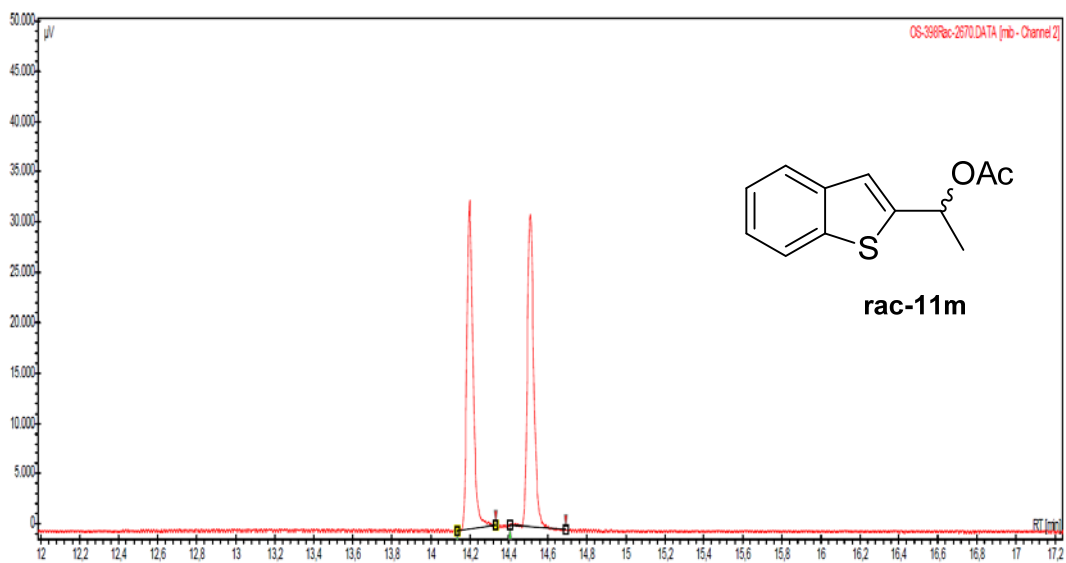


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	3.21	49.93	72201.7	4221.8	49.932
2	UNKNOWN	4.01	50.07	43896.9	4233.2	50.068
Total			100.00	116098.6	8455.0	100.000

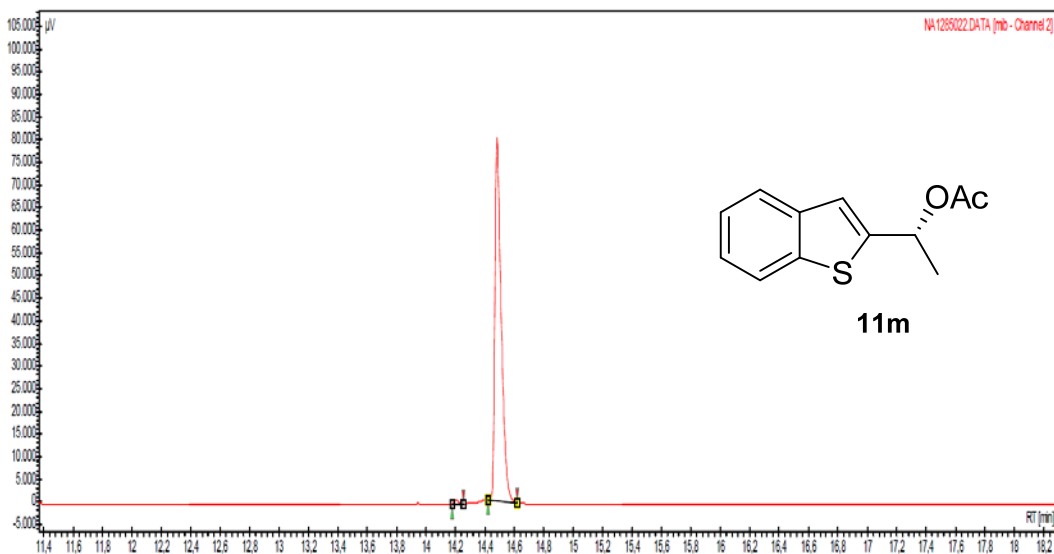


Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	3.56	4.28	1516.5	57.4	4.277
2	UNKNOWN	4.42	95.72	18587.0	1284.7	95.723
Total			100.00	20103.5	1342.1	100.000

(1*R*)-1-Acetoxy-1-(benzo[*b*]thiophen-2-yl)ethane (11m)

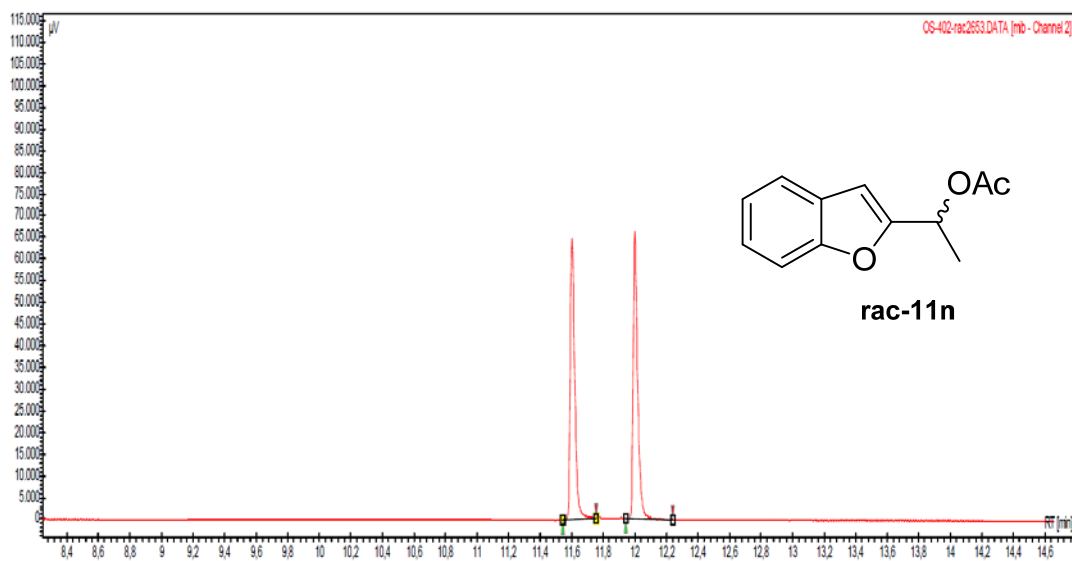


Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	14.20	50.87	32758.9	1209.7	50.866
2	UNKNOWN	14.51	49.13	31080.7	1168.5	49.134
Total			100.00	63839.6	2378.3	100.000



Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
2	UNKNOWN	14.20	0.68	909.3	27.6	0.679
1	UNKNOWN	14.48	99.32	80124.3	4033.8	99.321
Total			100.00	81033.6	4061.4	100.000

(1*R*)-1-Acetoxy-1-(benzofuran-2-yl)ethane (11n)



Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	11.60	50.30	65101.0	2195.7	50.303
2	UNKNOWN	12.00	49.70	66236.1	2169.3	49.697
Total			100.00	131337.1	4365.0	100.000



Index	Name	Time [Min]	Quantity [% Area]	Height [μV]	Area [$\mu\text{V}\cdot\text{Min}$]	Area % [%]
1	UNKNOWN	11.67	1.03	632.3	17.1	1.027
2	UNKNOWN	12.05	98.97	43170.9	1643.2	98.973
Total			100.00	43803.2	1660.3	100.000

References

- [1] B. A. Persson, A. L. E. Larsson, M. Le Ray, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1999**, *121*, 1645-1650.
- [2] P. Vongvilai, R. Larsson, O. Ramström, *Adv. Synth. Catal.* **2008**, *350*, 448-452.
- [3] S. Y. Lee, J. M. Murphy, A. Ukai, G. C. Fu, *J. Am. Chem. Soc.* **2012**, *134*, 15149-15153.