molecules

MDPI

Supporting information

Development of an Atmospheric Pressure Chemical Ionization Interface for GC-MS

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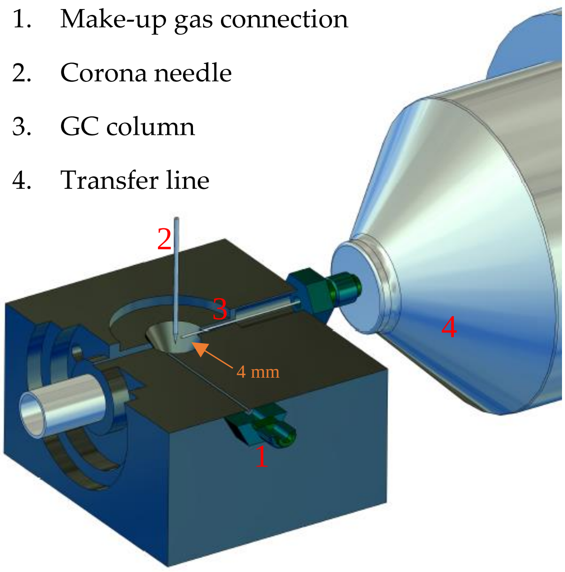
Academic Editor: Tomasz Tuzimski

1. GC-APCI-QqQ-coupling

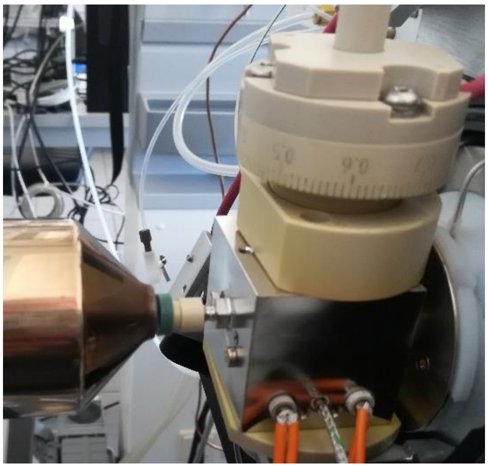
The model of the prototype GC-APCI-MS is shown in **Figure S1**A and S1B.

A. Schematically drawing of the GC-APCI ion source with:

1. Make-up gas connection
2. Corona needle
3. GC column
4. Transfer line



B. Realized coupling of the GC-APCI ion source with the 6495B QqQ form Agilent



Thermo couple

Figure S1. Developed prototype GC-APCI ion source. In S1A the optimum column position at 2 mm and the position of the GC column and corona needle in relation to each other. S1B shows the coupled system and the addition of the thermo couple.

2. Pesticide Residues

2.1. Humidity

The dependence of the detector response as a function of the make-up gas humidity is plotted in Figure S2A-F and shows that for almost all pesticides the detector response (Intensity in a.u.) are increased with the humidity. For all experiments 3 (n=3) replicates were measured.

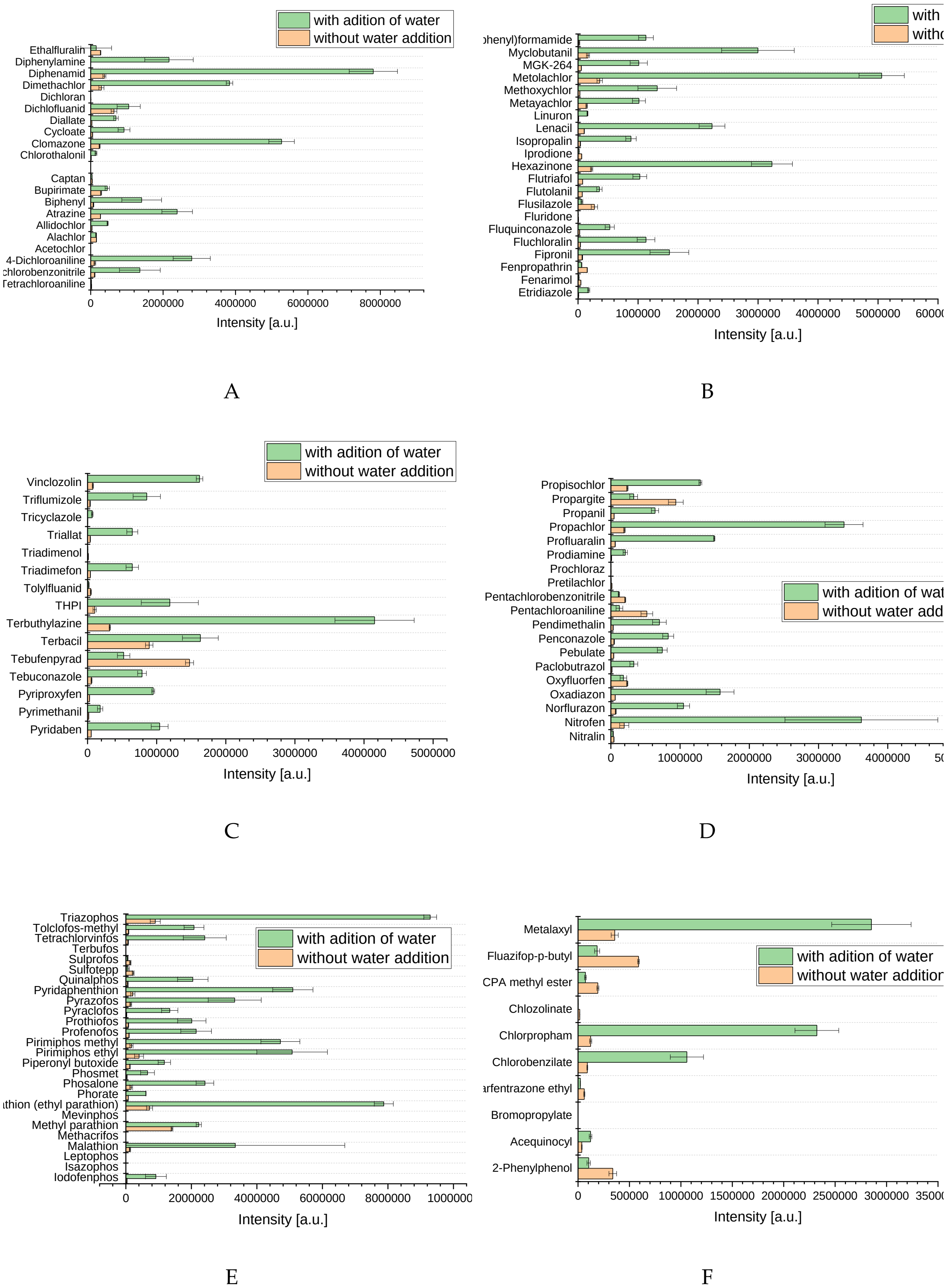


Figure S2A–D. Comparison of the detector response (a.u.) for pesticides with and without water addition to the make-up gas.

2.2. dMRM-Method

The dMRM-method are summarized in Table S 1, Table S2 and Table S3. The retention time, transient, collision energy, recovery rates and LOD of the compounds are shown. The corona needle was set to 1 µA and the transfer capillary to 250 V. The ion source was operated at 200 °C without humidified make-up gas (Nitrogen). Substances with (–) showing LODs higher than 500 g L^{-1}. For all substances 2 µL were injected in splitless mode at 250 °C.

Table S1. dMRM-Method Information for OPP.

Name	Retention time min	Precursor m/z	Product Ion m/z	Energy V	Recovery %	Lod µg/L
Azinphos ethyl	41.63	346.1	132	10	55.3	25.0
Azinphos methyl	31.4	318	131.9	10	40.1	125
Bromfenvinfos-methyl	32.46	377	126.9	5	52.2	12,5
Bromfenvinphos	34.01	405	127	20	37.1	12,5
Bromophos ethyl	33.17	395	338.7	20	56.0	12,5
Bromophos methyl	31.49	367	124.8	20	73.5	12,5
Carbophenothion	36.88	343.1	157.8	20	34.8	125
Chlorfenvinphos	32.54	359.1	155	10	54.3	25.0
Chlorpyrifos	30.92	350	197.8	20	49.9	5.00
Chlorpyrifos methyl	28.96	324	124.9	20	81.8	1,25
Chlorthiophos	36.3	361	326	10	169.5	-
Coumaphos	43.1	363.1	108.9	20	87.5	-
Diazinon	27.3	305.2	153.1	20	56.7	1.25
Edifenphos	36.9	311.1	109	30	-	25.0
EPN	39.16	324.1	296	10	35.0	1.25
Fenchlorphos	29.52	321	124.9	30	80.2	50.0
Fenitrothion	30.13	278.1	124.9	20	71.0	0.50
Fenthion	30.86	279.1	108.9	20	63.3	25.0
Fonofos	25.85	247.1	109.1	20	-	1.25
Iodofenphos	33.97	413	124.7	30	64.9	50.0
Leptophos	33.94	413	170.9	20	65.6	-
Malathion	30.64	331.1	127	10	23.4	0.50
Methyl parathion	29.29	264.1	109.1	20	50.2	1.25
Phosalone	40.42	368.1	181.9	10	39.8	5.00
Phosmet	39.00	318	159.9	5	64.8	12.5
Pirimiphos ethyl	31.91	334.2	198	20	75.1	1.25
Pirimiphos methyl	30.26	306.2	164	20	41.6	2.50
Profenofos	34.26	375.0	304.8	20	58.3	1.25
Prothiofos	34.1	345.0	240.8	20	42.4	12.5

Pyraclofos	42.02	361.1	256.9	20	31.5	50.0
Pyrazofos	41.77	374.2	222.2	20	43.1	5.00
Pyridaphenthion	39.03	341.1	189	20	37.7	25.0
Quinalphos	32.61	299.2	147	20	49.3	-
Sulfotepp	24.81	323.2	145.9	30	39.8	100
Sulprofos	36.55	323.1	96.6	30	-	125
Tetrachlorvinfos	33.53	367	126.9	20	60.3	-
Tolclofos-methyl	29.10	301	124.9	20	71.6	0.5
Triazophos	26.80	314.2	162	20	-	25

Table S2. dMRM-Method Information for ONP.

	Retention time	Precursor	Product Ion	Energy	Recovery	Lod
Name	min	m/z	m/z	V	%	μg/L
2. 3. 5. 6-Tetrachloroaniline	23.45	231.4	195.7	20	200.0	25.0
2. 6-Dichlorobenzonitrile	16.83	172	136	30	312.5	2.50
3. 4-Dichloroaniline	19.16	162	127	20	7.8	50.0
Atrazine	26.26	216.1	174	20	106.1	2.50
Biphenyl	17.7	155.1	77.1	30	117.8	50.0
Bupirimate	35.05	317.2	209.1	20	71.9	2.50
Dichlofluanid	30.27	223.9	122.9	20	119.1	5.00
Dimethachlor	28.61	256.1	224.1	20	120.0	0.50
Diphenamid	31.61	240.2	134	30	145.5	2.50
Diphenylamine	23.66	170.1	92.1	20	105.8	5.00
Ethalfluralin	24.34	334.2	317.2	5	64.5	12.5
Etridiazole	19.38	248.9	220.8	5	135.7	0.50
Fenarimol	41.3	331.1	139	5	110.0	50.0
Fipronil	32.82	437.1	367.8	20	96.9	2.50
Fluchloralin	27.53	356.2	314	10	75.0	0.50
Flutriafol	33.72	302.1	70	20	91.7	12.5
Hexazinone	37.76	253.2	171	10	75.0	2.50
Lenacil	37.23	235.1	153	20	71.2	12.5
MGK-264	31.48	276.1	210.1	10	58.7	2.50
Myclobutanil	34.79	289.2	70.1	20	124.3	2.50
Oxadiazon	34.71	345.1	219.9	20	77.4	0.50
Paclobutrazol	33.25	294.2	276.1	10	-	25.0
Pebulate	19.55	204.1	128.1	10	90.0	2.50
Penconazole	32.25	284.1	70	30	32.0	100
Pendimethalin	32.13	282.1	211.9	5	15.3	0.5
Prodiamine	30.4	351.2	246.9	20	7.0	2.50
Profluralin	27	348.2	232	10	4.2	0.5
Propargite	38.08	350.2	201	10	70.7	5.0
Pyrimethanil	27.27	200.1	82.2	20	177.6	12.5
Pyriproxyfen	40.81	322.2	95.9	30	68.4	100

Tebuconazole	37.81	308.1	70	20	94.3	12.5
Terbacil	27.71	161	144	20	81.3	12.5
Terbuthylazine	26.75	230.1	174	20	85.0	2.5
Tetrahydrophthalimide	20.15	152.2	81.1	10	78.0	5.0
Triadimefon	31.09	294.2	224.9	10	64.6	2.50
Tricyclazole	35.13	190.1	163	20	88.9	-
Triflumizole	33.12	346.1	278	5	66.2	12.5
Vinclozolin	29.06	286	241.9	10	108.4	0.50

Table S3. dMRM-Method Information for HME.

Name	Retention time min	Precursor m/z	Product Ion m/z	Energy V	Recovery %	Lod µg/L
2-Phenylphenol	6.98	171	142	30	164.7	-
Chlorpropham	7.7	172	154	10	86.5	0.50
Metalaxyl	9.8	280	220	10	-	0.50
DCPA methyl ester	9.52	333	301.9	20	64.8	125.0
Chlozolinate	9.82	332.1	186.9	20	84.7	25.0
Chlorobenzilate	10.5	307.2	250.9	20	64.7	2.50
Acequinocyl	12.85	343.3	188.9	20	176.5	12.5

Table S4. dMRM-Method Information for SPP.

Name	Retention time min	Precursor m/z	Product Ion m/z	Energy V	Recovery %	Lod µg/L
Allethrin	10.4	303.2	135.0	10	64	20
Bifenthrin	13.8	181.0	165.0	30	62	2
Cypermethrin	16.5	416.1	191.0	10	69	10
Deltamethrin	17.9	504.0	278.8	10	69	100
Tetramerthrin	13.8	332.2	164.0	30	129	20
Transfluthrin	8.8	371.0	163.0	20	69.9	20
Phenothrin	14.2	351.2	183.0	20	64	100

Overlaid EICs of the analyzed pesticides standards (1 mg L^{-1} in toluene) from Restek are shown in Figure S 3 OPP, Figure S 4 ONP, Figure S5 SPP and Figure S6 HME.

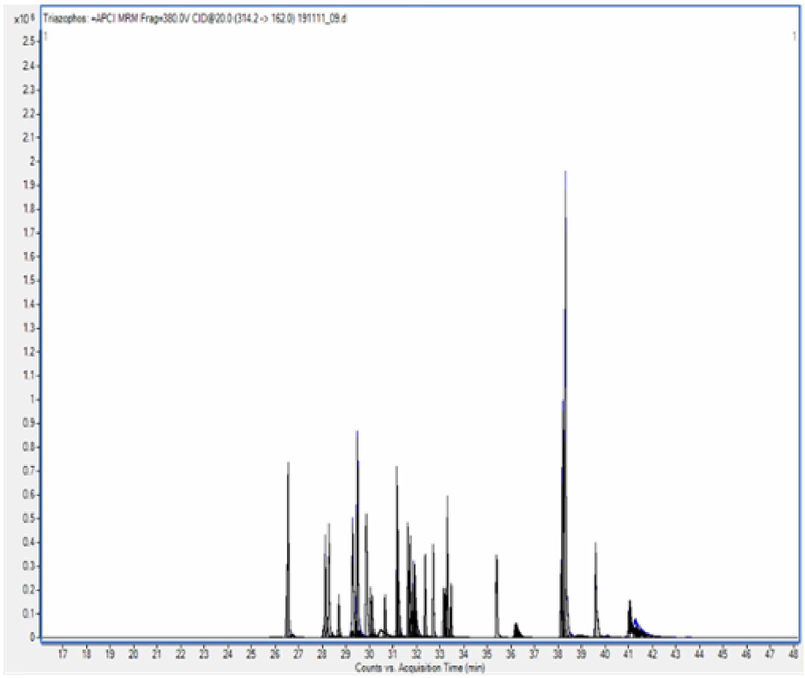


Figure S3. Overlaid EICs for OPP standards from Restek 32563; 32570 and 32571 at 1 mg L^{-1}. GC-Method: 50 (1min) to 330 °C (2 min), 5 °C/min; transfer line: 290 °C, injector: 250 °C; injection: 1 µL; constant flow: 1 mL/min He.

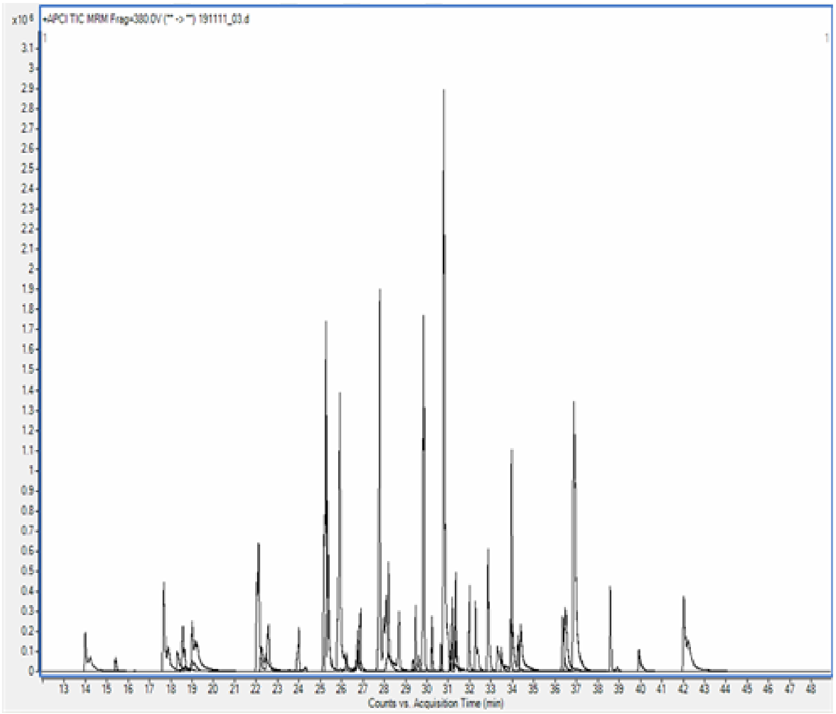


Figure S4. Overlaid EICs for ON standard from Restek 32565; 32566, 32567 at 1 mg L^{-1}. GC-Method: 50 (1 min) to 330 °C (2 min); 5 °C/min; transfer line: 290 °C; injector: 250 °C; injection: 1 µL; constant flow: 1 mL/min He.

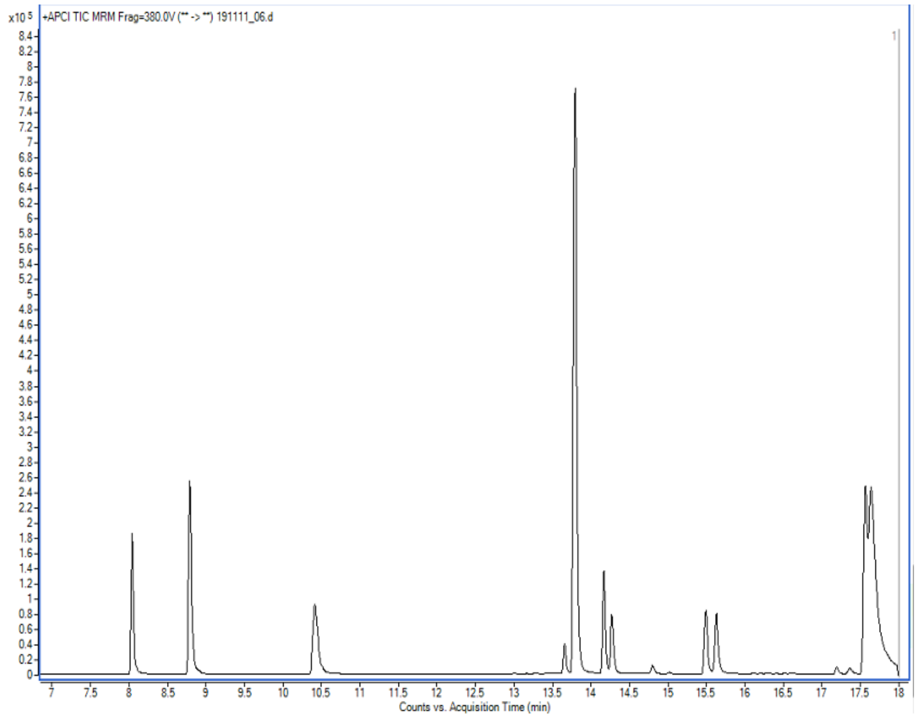


Figure S5. Overlaid EICs for SPP standard from Restek 32568 at 1 mg L⁻¹. GC-Method: 100 (1min) to 150 °C; 25 °C/min; 150 to 300 °C (3 min); 10°C/min; transfer line: 290 °C; injector: 250 °C; Injection: 1 µL; constant flow: 1 mL/min He.

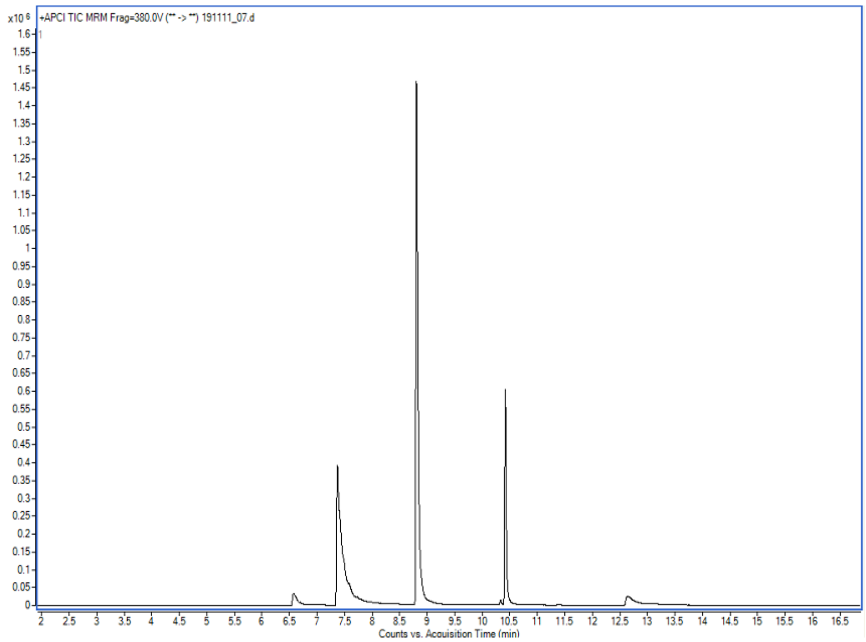


Figure S6. Overlaid EICs for HME standard from Restek 32569 at 1 mg L⁻¹. GC-Method: 100 (1 min) to 150 °C; 25 °C/min; 150 to 300 °C (3 min); 10 °C/min; transfer line: 290 °C; injector: 250 °C; Injection: 1 µL; constant flow: 1 mL/min He.