Supporting information

S1. General Considerations

Thin-layer chromatography (TLC) was carried out with SilIcycle silica gel UV254 precoated plates (0.25 mm), and visualized with UV lamps or KMnO4 staining. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz or 500 MHz and are reported relative to residual solvent $CDCl_3$ (^{1}H, 7.26 ppm, ^{13}C, 77.0ppm). High resolution mass spectral analysis was performed with a Water Autospec at the mass spectrometry facility at the University of Wisconsin-Madison. Chromatography was carried out with an automated Isco Combiflash Rf® system with reusable high performance silica gel 60 (Silicycle) and eluted with hexane/ethyl acetate.

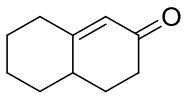
S1.1. X-ray Fluorescence measurement

The crystals were analyzed with the S8 Tiger, a commercial WD-XRF instrument from Bruker AXS. The S8 uses a Rh tube and has a maximum power of 4kW. The data were analysed with the semi-quantitative program Quant Express of Bruker's SpectraPlus software, which uses three standard crystals: XS-55 (multilayer), PET (pentaerythrite), LiF200 (lithium fluoride). A flow proportional counter is used to detect the fluorescence below ca. 5 keV, for higher fluorescent energies, a scintillation counter is used. The semi-quantitative program allows for detection of a wide range of elements (Na-U), with a suitable combination of tube current and tube voltage, crystals, collimators, etc. The fluorescence data indicate that the crystals do not contain a significant amount of phosphorous, silicon, calcium, or sulfur.

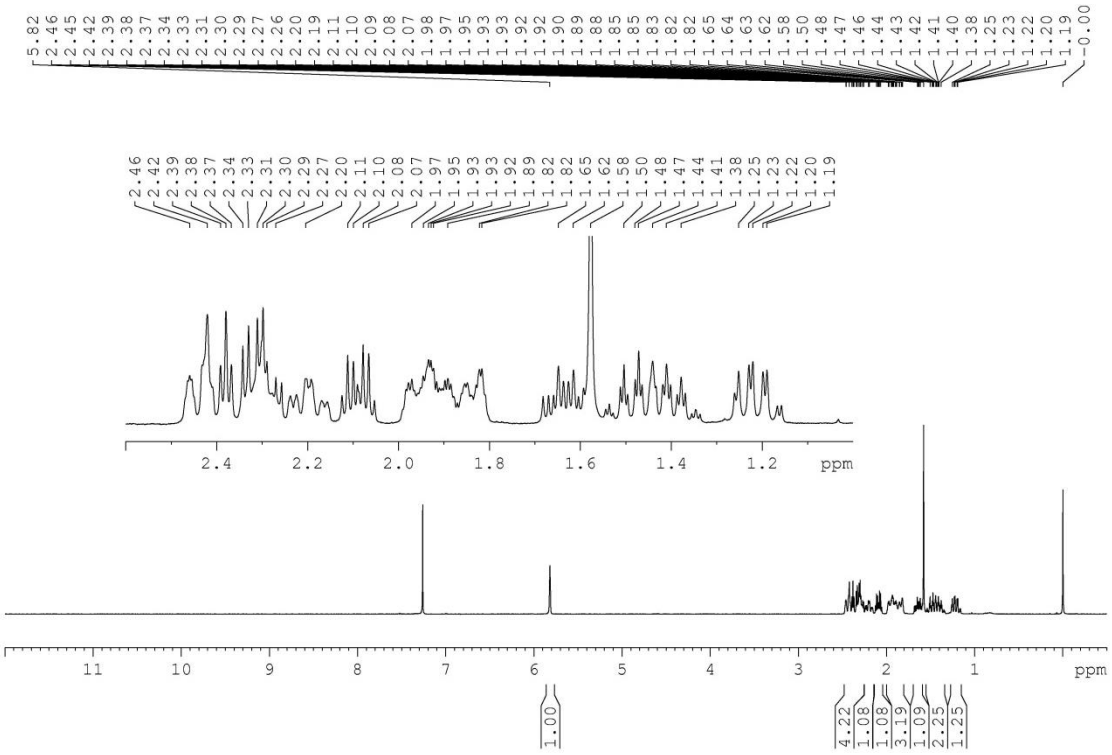
Formula	Z	Conc.	Status	Line 1	Net int.	Calc. conc.	Stat. error	LLD	Analysed layer	Total CSE
$C_{41}H_{43}O_5$	6	99.900%	Matrix							
P	15	0.024%	XRF 1	P KA1-HR-Tr	0.5974	0.024	4.49%	8.4 PPM	23.9 um	10.779 PPM
Si	14	0.011%	XRF 1	Si KA1-HR-Tr	0.1684	0.011	8.70%	9.1 PPM	15.6 um	9.892 PPM
Ca	20	86.139 PPM	XRF 1	Ca KA1-HR-Tr	0.435	0.0086	5.51%	5.1 PPM	145 um	4.738 PPM
S	16	30.339 PPM	XRF 1	S KA1-HR-Tr	0.1502	0.003	12.80%	6.8 PPM	36 um	3.874 PPM

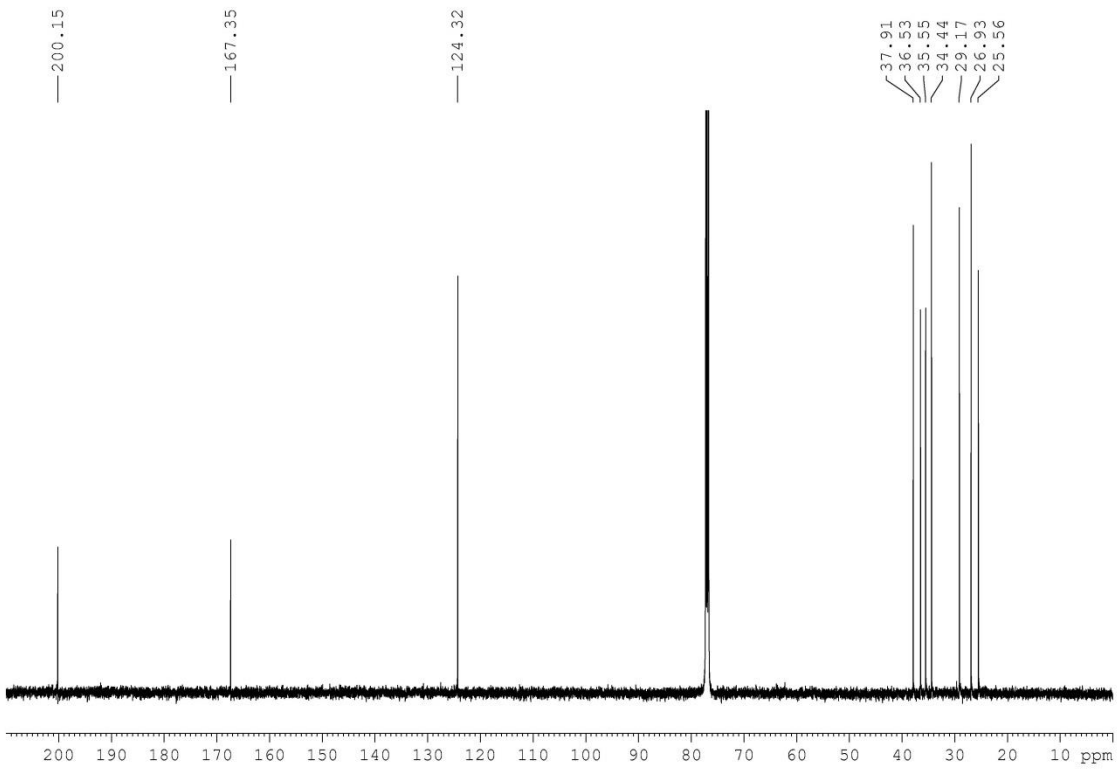
assumed diameter: 1.2 cm, mass: 0.250g, Compton ratio: 107.831%

S1.2. NMR and MS data for (II)

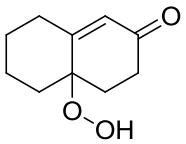


$C_{10}H_{14}O$ (II), TLC (Hex:EtOAc 8:2) R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): 5.82 (s, 1H), 2.46 – 2.25 (m, 4H), 2.19 (dt, *J* = 5.64 Hz, *J* = 13.6 Hz, 1H), 2.09 (qd, *J* = 5.0 Hz, *J* = 13.6 Hz, 1H), 1.80 – 2.00 (m, 3H), 1.64 (m, 1H), 1.44 (m, 2H), 1.22 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 200.15, 167.35, 125.32, 37.90, 36.53, 35.55, 34.44, 29.17, 26.93, 25.56. HRMS (ESI) calculated for $C_{10}H_{14}O$ $[M+H]^+$ requires *m/z* 151.1119, found 151.1118.

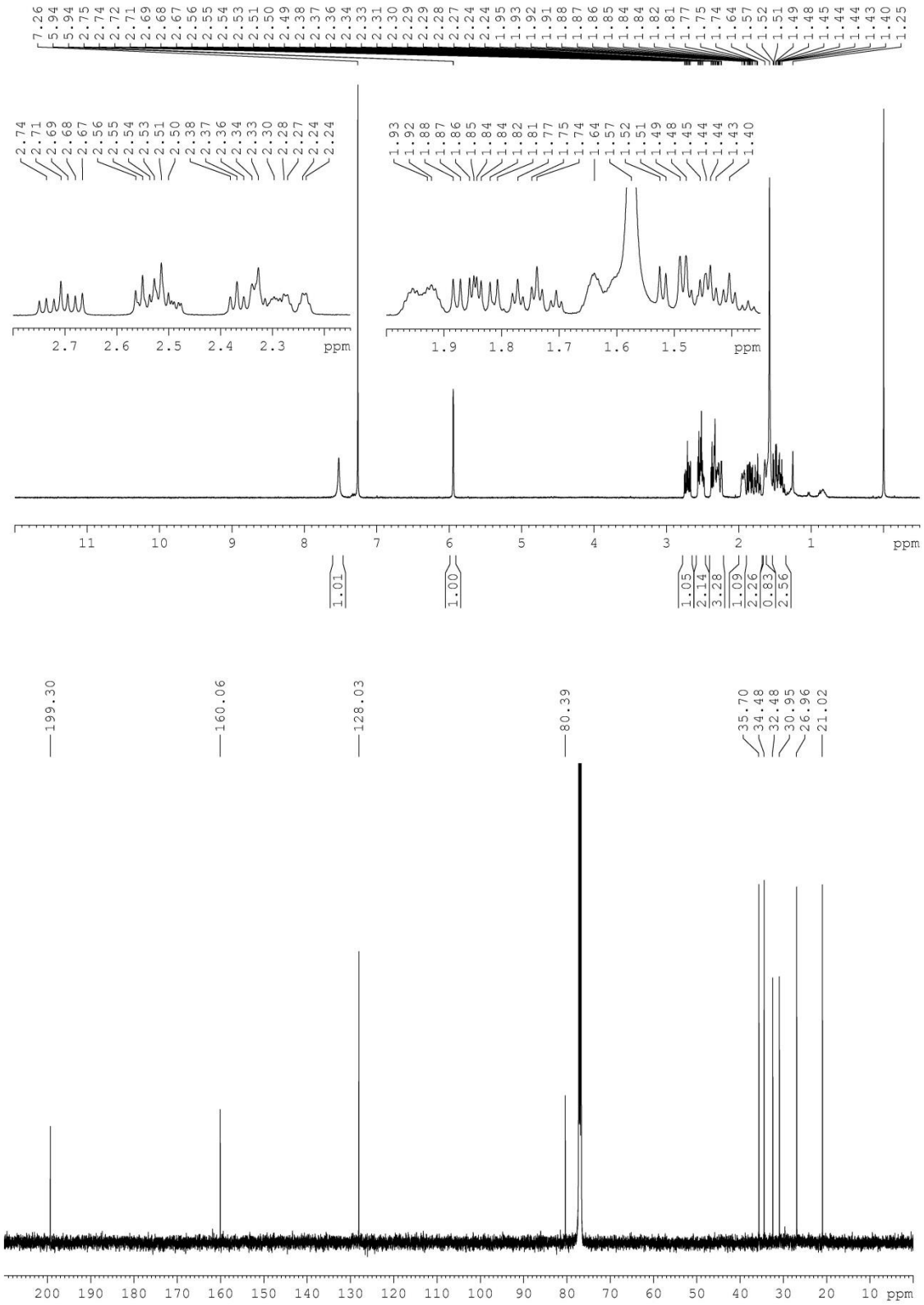




S1.3. NMR and MS data for (III)



C10H14O3, TLC (Hex:EtOAc 8:2) Rf = 0.1. 1H NMR (400 MHz, CDCl3): 7.52 (br s, 1H), 5.94 (d, J = 1.7 Hz, 1H), 2.70 (m, 1H), 2.52 (d, 2H), 2.39 – 2.22 (m, 3H), 1.93 (m, 1H), 1.85 (ddd, J = 5.0 Hz, J = 11.3 Hz, J = 14.3 Hz, 1H), 1.73 (tt, J = 3.8 Hz, J = 13.3 Hz), 1.64 (m, 1H), 1.39 – 1.53 (m, 2H). 13C NMR (125 MHz, CDCl3): 199.30, 160.06, 128.03, 80.39, 35.70, 34.48, 32.48, 30.95, 26.96, 21.02. HRMS (ESI) calculated for C10H14O3 $[M+H]^+$ requires m/z 183.1016, found 183.1010.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200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm