Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

An organocatalytic ionic liquid

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Supplementary Information

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1. Details of DFT calculations

Quantum chemical calculations have been performed by the Gaussian 03 program package[1] at the B3LYP/6-31+G* level. The nature of the stationary point obtained by geometry optimization has been verified by a subsequent analysis of the second derivatives, which have been found all positive in case of minima, and exhibited a single negative value in case of transition states.

The suggested reaction mechanism (see Figure S1 below) is analogous to that suggested by Breslow in the 50s for thiazole-2-ylidene (see ref. 5), and that obtained computationally for triazole-2-ylidenes (see ref. 10). The first step of the reaction is the addition of the carbene to the carbonyl group of the benzaldehyde, followed by a 1,2-H-shift (or rather a protonation and a subsequent deprotonation, see the high gap for the intramolecular process below), which results in the so-called Breslow-intermediate. To this fulvene-like compound the second aldehyde can be attached, and after a 1,4-H-shift the benzoin-carbene adduct can be formed. As expected, the formation of **4** is exothermic, though all structures involved in the reaction exhibit similar energy. The similar energy of these structures indicate that entropy and the variation in the concentration of the reactants have significant effect on the equilibrium.

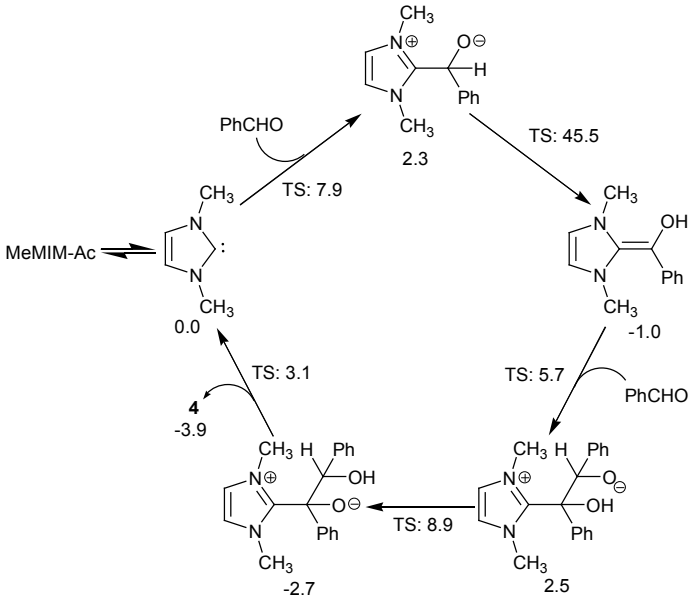


Figure S1. catalytic cycle of the formation of benzoin from benzaldehyde with B3LYP/6-31+G* level energies of the starting molecules, intermediates, products, and the corresponding transition states.

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.

XYZ coordinates and energies of the structures involved in the reaction at the B3LYP/6-31+G* level.

Benzaldehyde
E(B3LYP/6-31+G*) = -345.588808

C	-0.020934	0.000000	-0.020811
C	-0.025164	0.000000	1.459355
C	1.195778	0.000000	2.150185
C	1.213865	0.000000	3.546023
C	0.008141	0.000000	4.253851
C	-1.214670	0.000000	3.568348
C	-1.233892	0.000000	2.175904
H	2.129075	0.000000	1.590081
H	2.160449	0.000000	4.079753
H	0.018989	0.000000	5.340905
H	-2.148355	0.000000	4.124616
H	-2.169492	0.000000	1.624150
O	-1.016749	0.000000	-0.723239
H	0.989508	0.000000	-0.484619

1,3-dimethylimidazole-2-ylidene
E(B3LYP/6-31+G*) = -304.809081

C	-0.005205	0.000000	-0.003680
N	0.082877	0.022321	1.362796
N	1.312482	-0.022321	-0.376128
C	1.744700	-0.051433	-1.765053
C	-1.082542	0.051433	2.233269
C	1.397225	0.014202	1.820071
C	2.181721	-0.014202	0.710626
H	2.352470	0.829756	-2.000570
H	2.329902	-0.955205	-1.970216
H	0.850049	-0.050743	-2.388981
H	-1.101999	-0.829756	2.884786
H	-1.080904	0.955205	2.853391
H	-1.969003	0.050743	1.597761
H	3.257584	-0.029083	0.608462
H	1.659525	0.029083	2.868459

Transition state of the addition of the carbene to the carbonyl group of benzaldehyde

E(B3LYP/6-31+G*) = -650.385352

C	-0.077034	0.325888	0.306851
C	0.045884	0.976708	1.493514
N	1.373192	0.831734	1.882570
C	2.072427	0.099394	0.974974
N	1.173428	-0.196089	0.006778
C	1.919938	1.351679	3.131358
C	4.024327	-0.092265	0.672976
O	4.236196	0.038791	-0.562480
C	1.479338	-0.979323	-1.193734
H	2.537460	-0.834029	-1.425596
H	1.268614	-2.038401	-1.015011
H	0.858638	-0.617458	-2.017509
H	2.980884	1.565975	2.996824
H	1.400994	2.277269	3.393458
H	1.797770	0.625041	3.941124
H	-0.927539	0.199523	-0.346507
H	-0.675148	1.528682	2.078037
H	4.270931	0.755427	1.351507
C	4.301105	-1.427555	1.357648
C	4.445173	-1.515067	2.747893
C	4.726749	-2.736927	3.363709
C	4.876177	-3.891253	2.587692
C	4.755560	-3.807765	1.196561
C	4.476813	-2.582010	0.586434
H	4.347231	-0.616076	3.355405
H	4.840628	-2.788148	4.444348
H	5.099435	-4.843772	3.062293
H	4.891309	-4.697882	0.586053
H	4.415590	-2.494240	-0.494708

adduct of benzaldehyde and carbene

E(B3LYP/6-31+G*) = -650.394289

C	-0.121865	0.029281	0.557996
N	0.273784	-0.732253	1.607735
N	0.999498	0.586704	0.042235
C	1.043882	1.357954	-1.201596
C	-0.604465	-1.594550	2.397025
C	1.655383	-0.673247	1.734570
C	2.105250	0.152515	0.753305
H	2.090338	1.479792	-1.488312
H	0.499344	0.795127	-1.964061
H	0.581081	2.336837	-1.061656
H	0.014921	-2.165382	3.091402
H	-1.324492	-1.000393	2.964616
H	-1.134625	-2.282111	1.733050
H	3.104977	0.472144	0.502576
H	2.183863	-1.211493	2.505986
C	-1.489507	-0.056599	-0.137841
O	-1.268115	-0.882483	-1.168001
C	-2.055836	1.345452	-0.470291
C	-2.497629	1.592101	-1.772113
C	-3.059540	2.828783	-2.107428
C	-3.182032	3.832490	-1.141335
C	-2.747135	3.589184	0.166918
C	-2.193464	2.349051	0.497940
H	-2.387070	0.791401	-2.499037
H	-3.403956	3.009454	-3.123579
H	-3.617167	4.794632	-1.401482
H	-2.844100	4.362057	0.926549
H	-1.867609	2.163262	1.522250
H	-2.184678	-0.457031	0.646282

Transition state between the carbene – benzaldehyde adduct and the Breslow-intermediate.
E(B3LYP/6-31+G*) = -650.325303

C	-0.045530	0.441757	-0.234650
C	-0.242330	0.371575	1.105712
N	0.982208	0.075097	1.691762
C	1.942147	-0.036080	0.709561
N	1.297413	0.185008	-0.476712
C	1.265844	0.132050	3.117498
C	3.360739	-0.177753	0.912244
O	4.202971	0.389875	-0.153669
C	1.881883	-0.023759	-1.800341
H	2.945383	0.230350	-1.733823
H	1.770687	-1.070843	-2.102537
H	1.362668	0.619705	-2.516085
H	1.344689	-0.867857	3.553579
H	2.221568	0.647111	3.262185
H	0.466466	0.688074	3.612824
H	-0.736916	0.641198	-1.039055
H	-1.134267	0.513900	1.696350
H	3.924489	0.893677	0.998994
C	3.917372	-1.340405	1.645370
C	5.313461	-1.419827	1.831579
C	5.888402	-2.492997	2.509170
C	5.091461	-3.525565	3.019357
C	3.709840	-3.476070	2.819527
C	3.132128	-2.404585	2.132759
H	5.935670	-0.632444	1.417905
H	6.968057	-2.527020	2.637696
H	5.542582	-4.361493	3.547904
H	3.077257	-4.285139	3.178804
H	2.060802	-2.419458	1.945015

Breslow-intermediate

E(B3LYP/6-31+G*) = -650.399459

C	0.112725	-0.011308	0.224839
N	0.405052	-0.235567	1.574406
N	1.349370	0.134474	-0.409181
C	1.556821	0.013276	-1.842542
C	-0.511204	0.049451	2.664431
C	1.795236	-0.276086	1.734314
C	2.363900	-0.059691	0.529955
H	2.631898	0.046108	-2.036915
H	1.158252	-0.941902	-2.213139
H	1.063116	0.827701	-2.374126
H	0.071072	0.317162	3.550158
H	-1.156339	0.891061	2.387476
H	-1.155206	-0.804525	2.901325
H	3.404541	-0.021263	0.245476
H	2.243873	-0.437100	2.702598
C	-1.137126	0.113319	-0.353592
O	-1.182120	0.905565	-1.520447
H	-1.707334	0.435892	-2.191109
C	-2.395130	-0.441783	0.116411
C	-3.623506	0.172854	-0.237117
C	-4.845948	-0.380920	0.141181
C	-4.896929	-1.565598	0.884035
C	-3.695129	-2.197158	1.228513
C	-2.469900	-1.656843	0.844657
H	-3.604315	1.108918	-0.788505
H	-5.768173	0.123924	-0.139104
H	-5.851108	-1.994842	1.177826
H	-3.713915	-3.134612	1.780737
H	-1.554311	-2.198555	1.068775

TS of the addition of the second benzaldehyde to the Breslow-intermediate

E(B3LYP/6-31+G*) = -995.977617

C	-0.022332	0.217846	0.062483
C	0.006436	-0.086681	1.436376
C	1.263225	-0.236937	2.044529
C	2.446268	-0.054531	1.321301
C	2.399308	0.271878	-0.035447
C	1.155725	0.402607	-0.662822
C	-1.316345	-0.299115	2.153683
C	-1.884523	0.831589	2.906900
N	-1.299609	1.982990	3.360176
C	-2.225117	2.719525	4.088045
C	-3.388422	2.027724	4.073636
N	-3.175833	0.869246	3.351003
C	0.054410	2.483963	3.115461
C	-4.249817	-0.108763	3.110637
O	-2.287443	-0.783048	1.279849
C	-1.182593	-1.870611	3.337728
O	-2.059216	-2.668433	2.807899
C	-1.377095	-1.481744	4.795170
C	-0.447030	-0.695362	5.494460
C	-0.622442	-0.395348	6.847213
C	-1.737611	-0.885376	7.535157
C	-2.661115	-1.686896	6.857185
C	-2.478122	-1.984892	5.503981
H	0.796757	1.884405	3.644741
H	0.282399	2.475435	2.050149
H	0.091664	3.510388	3.485497
H	-1.964502	3.660416	4.546316
H	-4.345663	2.247080	4.519832
H	-5.012922	0.062274	3.873702
H	-3.865035	-1.121831	3.197563
H	-4.670678	0.036967	2.114114
H	-2.390865	-1.755286	1.596618
H	1.333988	-0.507660	3.092811
H	3.404417	-0.184278	1.819320
H	3.318375	0.407015	-0.600220
H	1.102623	0.642350	-1.722314
H	-0.985805	0.292405	-0.431111
H	-0.120740	-2.090809	3.128813
H	-3.167672	-2.637405	4.976279
H	-3.517873	-2.096111	7.388606
H	-1.874293	-0.659180	8.589923
H	0.115816	0.211121	7.367811
H	0.436253	-0.320174	4.981781

Adduct of the Breslow-intermediate and the second benzaldehyde

E(B3LYP/6-31+G*) = -995.982753

C	-0.556220	-0.440839	-0.445456
C	-0.092356	-0.292936	0.870950
C	1.256086	-0.563062	1.143275
C	2.116175	-0.973292	0.122742
C	1.646049	-1.122014	-1.186144
C	0.303987	-0.851868	-1.467281
C	-1.010103	0.217069	1.964597
O	-0.534168	-0.102824	3.257424
C	-2.381245	-0.485540	1.871532
N	-2.485995	-1.838299	1.957724
C	-3.812099	-2.211654	1.903166
C	-4.537965	-1.069960	1.787455
N	-3.648761	-0.009497	1.775041
C	-1.382360	-2.789790	2.139901
C	-4.121124	1.388691	1.768288
H	-3.492613	1.954963	2.475961
H	-4.061505	1.799088	0.757314
H	-5.162840	1.375447	2.094332
H	-0.879938	-2.974653	1.188137
H	-0.677780	-2.374836	2.859236
H	-1.807401	-3.719245	2.524120
H	-5.603199	-0.911144	1.729106
H	-4.117283	-3.244969	1.960241
H	1.619778	-0.441669	2.157984
H	3.160332	-1.173187	0.351026
H	2.318258	-1.441768	-1.978341
H	-0.075234	-0.958490	-2.480906
H	-1.597614	-0.227934	-0.682679
C	-1.181467	1.832851	2.004619
O	-1.730078	2.090283	3.213781
C	0.150579	2.555319	1.752921
H	-1.823403	2.078750	1.127974
C	0.559726	2.913066	0.461486
C	1.756729	3.603028	0.248574
C	2.565763	3.949652	1.334514
C	2.158918	3.611357	2.629469
C	0.957724	2.927996	2.835197
H	-0.065937	2.653796	-0.390851
H	2.053459	3.874383	-0.762402
H	3.496525	4.489321	1.174539
H	2.773178	3.892447	3.482483
H	0.613366	2.698534	3.838663
H	-0.929906	0.690320	3.758784

TS of the 1,4-H-shift yielding the carbene-benzoin adduct

E(B3LYP/6-31+G*) = -995.972451

C	0.062709	0.151412	-0.004779
C	0.026186	0.011781	1.391951
C	1.250783	-0.060317	2.076907
C	2.467002	0.045314	1.397748
C	2.488791	0.220223	0.010480
C	1.278926	0.266582	-0.687018
C	-1.256366	-0.212944	2.195111
O	-1.097901	-0.126355	3.553626
C	-2.643652	0.636852	1.915012
O	-3.353210	0.312091	3.082075
C	-2.613684	2.174483	1.971825
N	-3.752876	2.908845	1.832918
C	-3.485877	4.239213	2.084486
C	-2.168330	4.327138	2.396067
N	-1.644005	3.047169	2.334172
C	-5.114609	2.390432	1.640240
C	-0.263253	2.757330	2.751423
C	-3.336309	0.154910	0.643262
C	-3.247664	0.830946	-0.583233
C	-3.866711	0.326221	-1.730702
C	-4.586464	-0.870159	-1.671009
C	-4.682167	-1.550966	-0.453046
C	-4.067152	-1.041482	0.692702
H	-5.308070	2.190841	0.584962
H	-5.219663	1.475344	2.223405
H	-5.808542	3.148212	2.010039
H	-4.254597	4.994440	2.030758
H	-1.557013	5.173845	2.665674
H	0.066884	3.592976	3.372157
H	0.385305	2.663043	1.879896
H	-0.266954	1.830526	3.333049
H	-2.400146	0.052015	3.685993
H	-2.689000	1.762602	-0.653030
H	-3.783743	0.868599	-2.669742
H	-5.068408	-1.265383	-2.561617
H	-5.242076	-2.481203	-0.392602
H	-4.159576	-1.553470	1.645384
H	-1.610492	-1.222468	1.895166
H	1.223955	-0.204669	3.152361
H	3.400318	-0.016700	1.953520
H	3.433992	0.302264	-0.520943
H	1.277105	0.380034	-1.769071
H	-0.858086	0.152729	-0.576537

Adduct of 1,3-dimethylimidazole-2-ylidene and benzoin

E(B3LYP/6-31+G*) = -995.991045

C	-0.541125	-0.306487	-0.459610
C	-0.083845	-0.251370	0.864056
C	1.235441	-0.625885	1.137464
C	2.084185	-1.039975	0.107562
C	1.621600	-1.092473	-1.211426
C	0.302370	-0.725028	-1.493248
C	-0.975807	0.241552	2.028548
O	-0.545106	-0.056291	3.269987
C	-2.363893	-0.495686	1.885427
N	-2.440711	-1.837721	2.079254
C	-3.756986	-2.248116	2.060869
C	-4.515895	-1.142713	1.853581
N	-3.647598	-0.064947	1.746351
C	-1.310207	-2.733670	2.354542
C	-4.147565	1.299690	1.525549
H	-3.687457	1.973932	2.249528
H	-3.935741	1.623422	0.503052
H	-5.229001	1.277615	1.671419
H	-0.787174	-2.975543	1.426398
H	-0.640080	-2.208742	3.039361
H	-1.708771	-3.644230	2.807049
H	-5.585205	-1.018784	1.783592
H	-4.033466	-3.280891	2.206445
H	1.572563	-0.583825	2.168963
H	3.110067	-1.321494	0.334518
H	2.281700	-1.416909	-2.012263
H	-0.069766	-0.764322	-2.514678
H	-1.566904	-0.022699	-0.695296
C	-1.146110	1.825280	1.935138
O	-1.773390	2.193777	3.155996
C	0.168313	2.560201	1.730796
H	-1.805011	2.102207	1.104654
C	0.459738	3.153442	0.495821
C	1.657728	3.844376	0.291911
C	2.584034	3.954343	1.331515
C	2.299826	3.371196	2.571112
C	1.101813	2.682642	2.770615
H	-0.257784	3.075015	-0.319194
H	1.862604	4.299294	-0.674526
H	3.515739	4.494540	1.180518
H	3.013815	3.455511	3.387399
H	0.886693	2.229444	3.732476
H	-1.427882	1.485665	3.766014

Benzoin

E(B3LYP/6-31+G*) = -691.183773

C	0.207747	-0.268819	-0.009530
C	0.284106	-0.018226	1.513972
C	1.546537	0.000709	-0.692377
H	-0.065686	-1.319010	-0.179030
O	-0.816808	0.539542	-0.556387
O	-0.324079	0.953275	1.954620
C	1.061533	-0.915692	2.412386
C	1.715934	-2.071091	1.952705
C	2.414223	-2.886824	2.843884
C	2.467412	-2.557439	4.201081
C	1.818250	-1.408524	4.668186
C	1.119198	-0.594358	3.780796
H	1.692285	-2.336161	0.901587
H	2.917863	-3.777442	2.478007
H	3.012762	-3.193840	4.893381
H	1.858258	-1.150792	5.723178
H	0.607848	0.298131	4.127067
H	-1.065964	1.173075	0.147177
C	2.075896	-0.928427	-1.595431
C	3.279451	-0.673409	-2.259347
C	3.966104	0.520167	-2.025200
C	3.440365	1.457473	-1.129663
C	2.238406	1.199717	-0.468701
H	1.537140	-1.853610	-1.792382
H	3.674525	-1.402629	-2.962257
H	4.901891	0.722227	-2.540013
H	3.967141	2.390556	-0.946264
H	1.832287	1.939179	0.217612

2. Experimental details

Materials and methods:

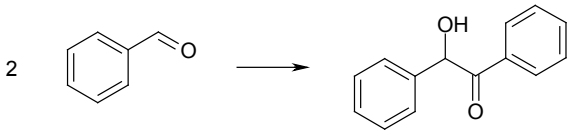
1-Ethyl-3-methylimidazolium acetate (EMIM-Ac), and 1-butyl-3-methylimidazolium acetate (BMIM-Ac) were products of BASF. Benzaldehyde, 4-bromobenzaldehyde, 4-isopropylbenzaldehyde and benzoin were purchased from Aldrich, while toluene, dichloromethane, ethyl acetate, hexane from Romil. Silica gel 60 (35-70 μm) for flash chromatography was produced by Merck. Solvents were evaporated by rotary evaporator under vacuum (10 Hgmm) at 40-60 ºC. TLC was executed on Silica gel 60 F_{254} aluminium sheets purchased from Merck. The IR spectra were recorded in KBr pellets on a Bruker ALPHA FT-IR spectrometer. The NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-300 spectrometer operating at 300 and 75 MHz and are reported in ppm on the δ scale. The GC-MS spectra were recorded on a Shimadzu QP2000 GC-MS Spectrometer.

Pre-cleaning of ionic liquids, and other chemicals:

EMIM-Ac and BMIM-Ac were heated under vacuum (0.4–0.8 Hgmm) at 80 ºC for one hour, and they were stored under argon till use. Toluene was stored on sodium wire; dichloromethane was distilled from phosphorus pentoxide before use. Benzaldehyde and 4-isopropylbenzaldehyde was distilled under vacuum, and then was stored under argon at 5 ºC. Carbon-dioxid generated from solid state was dried with molecular sieves 0.3 nm, product of Merck.

Reactions of benzaldehyde in presence of ILs under inert atmosphere:

Mixture of benzaldehyde (3 mL, 3.135 g, 29.5 mmol), IL (2 mL) and solvent (20 mL, if applied) was heated at 60 ºC for 6 h under argon atmosphere. The solvent (if applied) was removed by evaporation; the residue was treated with 20 mL of 0.1 M HCl solution and extracted by 3×20 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give benzoin. The product was identical with the commercial sample (TLC, and mp).

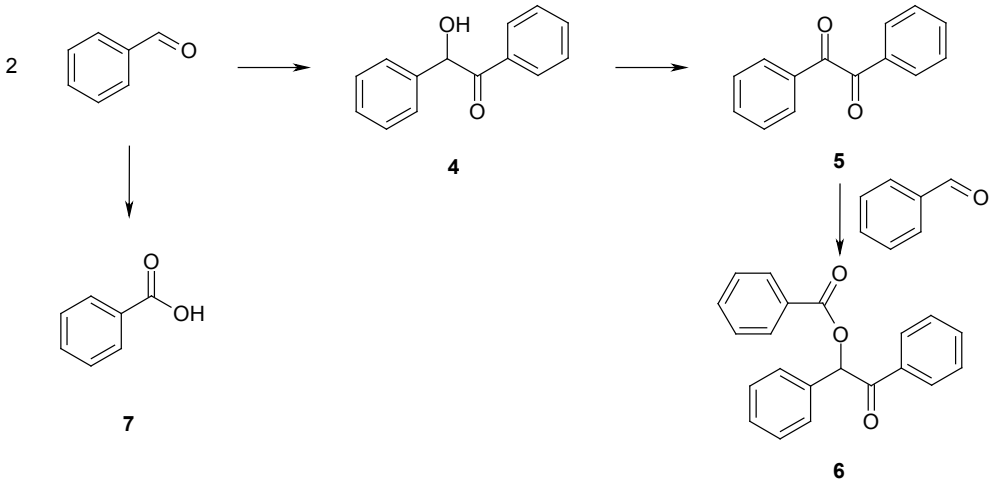


4

Entry	IL	Solvent	Product: benzoin (**4**)		
			g	mmol	%
1	EMIM-Ac	toluene	1.96 g	9.2	62.6
2	EMIM-Ac	dichloromethane	no product formation was observed		
3	EMIM-Ac	neat	2.11 g	9.9	67.4
4	BMIM-Ac	toluene	1.80 g	8.5	57.5
5	BMIM-Ac	dichloromethane	no product formation was observed		
6	BMIM-Ac	neat	2.07 g	9.8	66.1

Reactions of benzaldehyde in presence of IL under air:

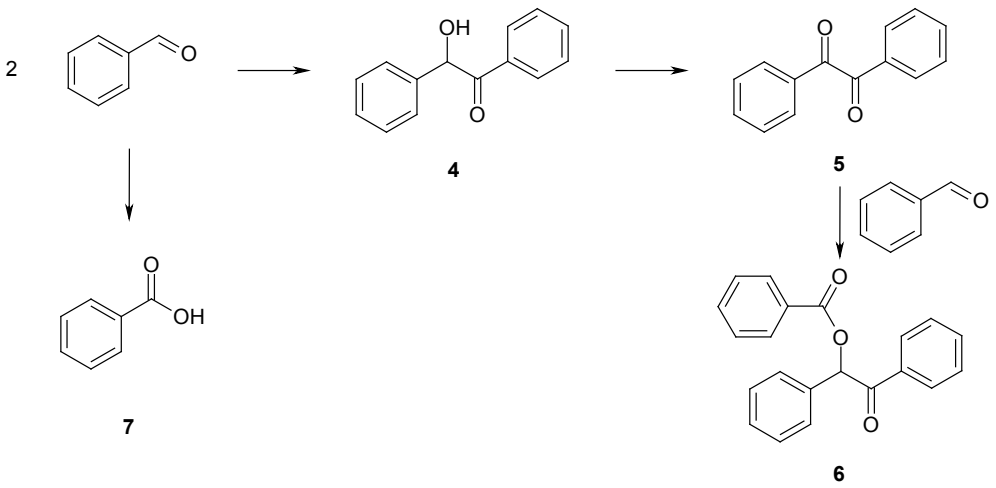
Mixture of benzaldehyde (2 mL, 2.090 g, 19.7 mmol), IL (EMIM-Ac, 2 mL, 2.054 g, 12 mmol) and solvent (20 mL, if applied) was heated at 60 ºC for 6 h under air. The solvent (if applied) was removed by evaporation; the residue was treated with 20 mL of 0.1 M HCl solution and extracted by 3×20 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give the products. The isolated benzil (**5**) and benzoic acid (**7**) were identical with the commercial samples (TLC, and mp). The structure of the 2-oxo-1,2-diphenylethyl benzoate (**6**) was supported by NMR analysis. In the course of the reaction benzoin (**4**) could be detected by TLC, but it has been used up at the end of reactions. At the very start of the reaction benzoin (**4**) and benzil (**5**) could be detected by TLC as the main intermediate products.



Entry	Solvent	Products	product		
			g	mmol	%
7	toluene	(**5**)	trace		
		(**6**)	0.36 g	1.1	17.3
		(**7**)	0.46 g	3.8	19.1
		benzaldehyde	0.31 g	2.9	14.8
8	dichloromethane		no product formation was observed		
9	neat	(**5**)	trace		
		(**6**)	0.44	1.4	21.2
		(**7**)	0.54	4.4	22.4
		benzaldehyde	0.35	3.3	16.7

Reactions of benzaldehyde in presence of IL under carbon-dioxide atmosphere:

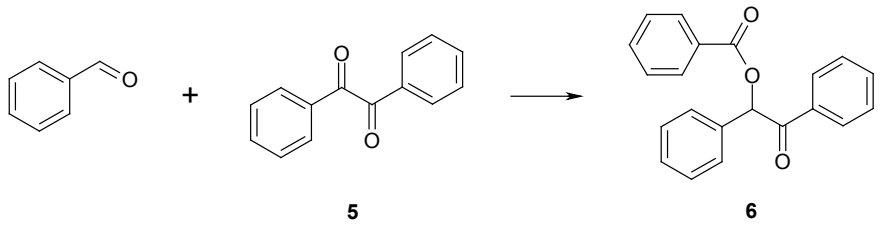
Mixture of benzaldehyde (0.37 g, 3.5 mmol), IL (EMIM-Ac, 0.60 g, 3.5 mmol) and solvent (10 mL toluene) was heated at 60 ºC for 4 h under dried carbon-dioxide atmosphere. The solvent was removed by evaporation; the residue was treated with 10 mL of 0.1 M HCl solution and extracted by 3×10 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give the products.



Entry	Solvent	Products	product		
			g	mmol	%
10	toluene	(**5**)	trace		
		(**6**)	0.09 g	0.28	24.4
		(**7**)	0.08 g	3.8	18.7

Reactions of benzaldehyde with benzil in presence of IL under inert atmosphere:

Mixture of benzaldehyde (0.37 g, 3.5 mmol), benzil (0.74 g, 3.5 mmol), IL (EMIM-Ac, 0.60 g, 3.5 mmol) and solvent (20 mL toluene) was stirred at room temperature for 1 h under argon atmosphere. The solvent was removed by evaporation; the residue was treated with 10 mL of 0.1 M HCl solution and extracted by 3×10 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give the product.



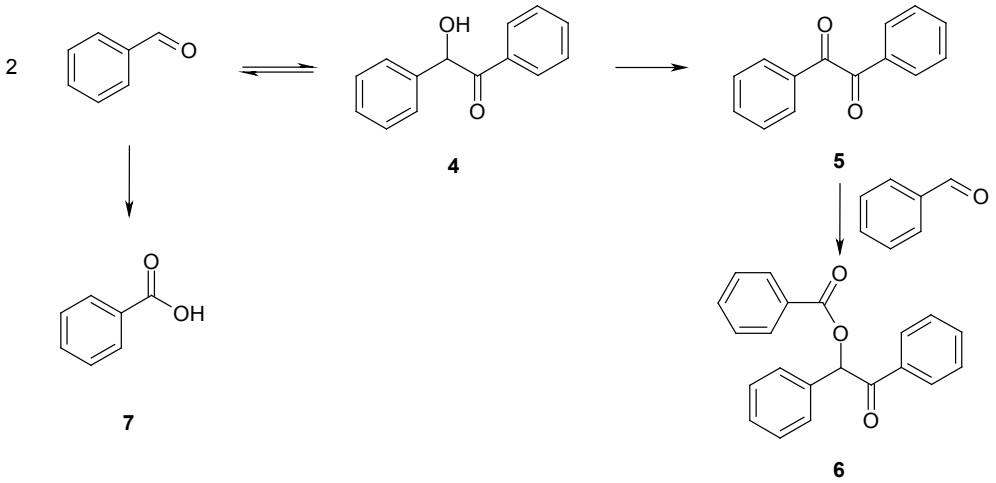
5 6

Entry	Solvent	Products	product		
			g	mmol	%
11	toluene	(**6**)	0.96 g	3.03	86.7

Reactions of benzoin in presence of IL under air:

Mixture of benzoin (1.00 g, 4.7 mmol), IL (EMIM-Ac, 2 mL, 2.054 g, 12 mmol) and solvent (20 mL, if applied) was stirred at room temperature for 8 h under air. The solvent (if applied)

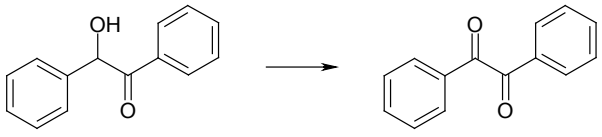
was removed by evaporation; the residue was treated with 20 mL of 0.1 M HCl solution and extracted by 3×20 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give the products. At the very start of the reaction benzil (**5**) could be detected by TLC as the main intermediate products.



Run	Solvent	Products	product		
			g	mmol	%
12	toluene	(**5**)	trace		
		(**6**)	0.35 g	1.1	35.3
		(**7**)	0.5 g	4.1	43.6
13	dichloromethane		no product formation was observed		
14	neat	(**5**)	trace		
		(**6**)	0.40	1.3	40.4
		(**7**)	0.31	2.5	27.0

Reactions of benzoin in presence of IL at 10 ºC under carbon-dioxide atmosphere:

Mixture of benzoin (1.00 g, 4.7 mmol), IL (EMIM-Ac, 2 mL, 2.054 g, 12 mmol) and toluene (20 mL), was stirred at 10 ºC for 4 h under carbon-dioxide atmosphere. The solvent was removed by evaporation; the residue was treated with 20 mL of 0.1 M HCl solution and extracted by 3×20 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give the products.

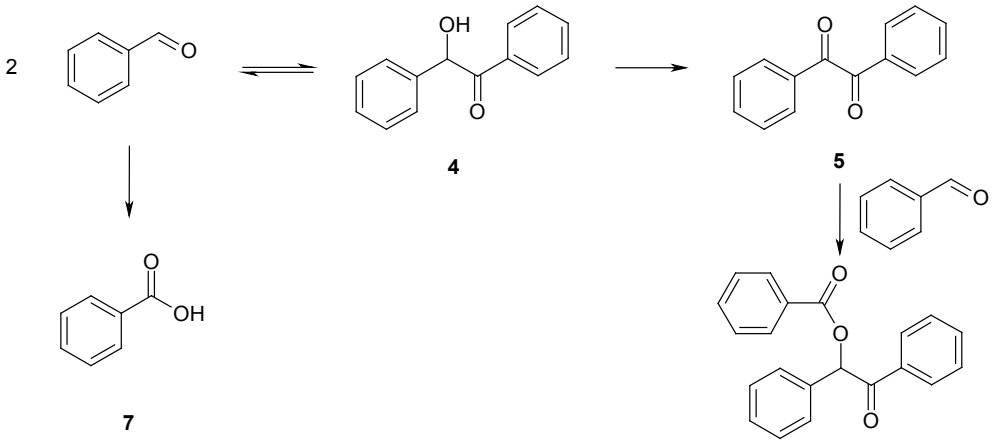


4 5

Entry	Solvent	Products	product		
			g	mmol	%
15	toluene	(**5**)	0,13	0,62	13
		(**6**)	trace		

Reactions of benzoin in presence of IL at 60 ºC under carbon-dioxide atmosphere:

Mixture of benzoin (1.00 g, 4.7 mmol), IL (EMIM-Ac, 2 mL, 2.054 g, 12 mmol) and toluene (20 mL), was stirred at 60 ºC for 4 h under carbon-dioxide atmosphere. The solvent was removed by evaporation; the residue was treated with 20 mL of 0.1 M HCl solution and extracted by 3×20 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give the products.

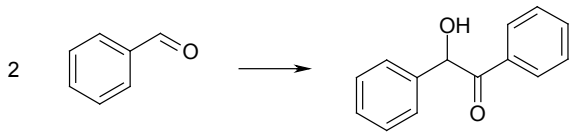


4 5 7 6

Entry	Solvent	Products	product		
			g	mmol	%
16	toluene	(**5**)	trace		
		(**6**)	0,47	1,5	47,7
		(**7**)	0,11	0,9	9,7

Reactions of benzaldehyde in presence of catalytic IL under inert atmosphere:

Benzaldehyde was stirred over sodium carbonate and anhydrous magnesium sulphate for 1 h under argon atmosphere. Before use it was filtered. Mixture of benzoic acid free benzaldehyde (3.71 g, 35.0 mmol), IL (EMIM-Ac, 0.60 g, 3.5 mmol) and solvent (20 mL toluene) was heated at 60 ºC for 6 h under argon atmosphere. The solvent was removed by evaporation; the residue was treated with 20 mL of 0.1 M HCl solution and extracted by 3×20 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give benzoin.

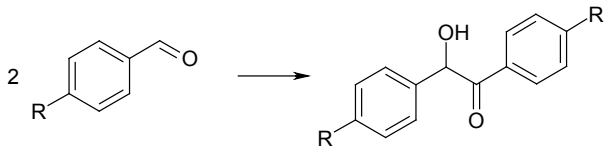


4

Entry	Solvent	Products	product		
			g	mmol	%
17	toluene	**4**	2.82 g	13.3	75.9

Reactions of 4-substituted-benzaldehydes in IL under inert atmosphere:

Mixture of 4-bromobenzaldehyde (0.65 g, 3.5 mmol), or 4-isopropylbenzaldehyde (0.52 g, 3.5 mmol), and IL (EMIM-Ac, 0.6 g, 3.5 mmol) in solvent (10 mL toluene) was heated at 60 ºC for 6 h under argon atmosphere. The solvent was removed by evaporation; the residue was treated with 10 mL of 0.1 M HCl solution and extracted by 3×10 mL of ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed by evaporation. The residue was purified by flash chromatograpy (hexane:ethyl acetate 4:1) to give 4,4'-disubstituted-benzoins (**8**, m.p.: 94ºC, or **9**, m.p.: 100ºC), structures of them were supported by NMR analysis.

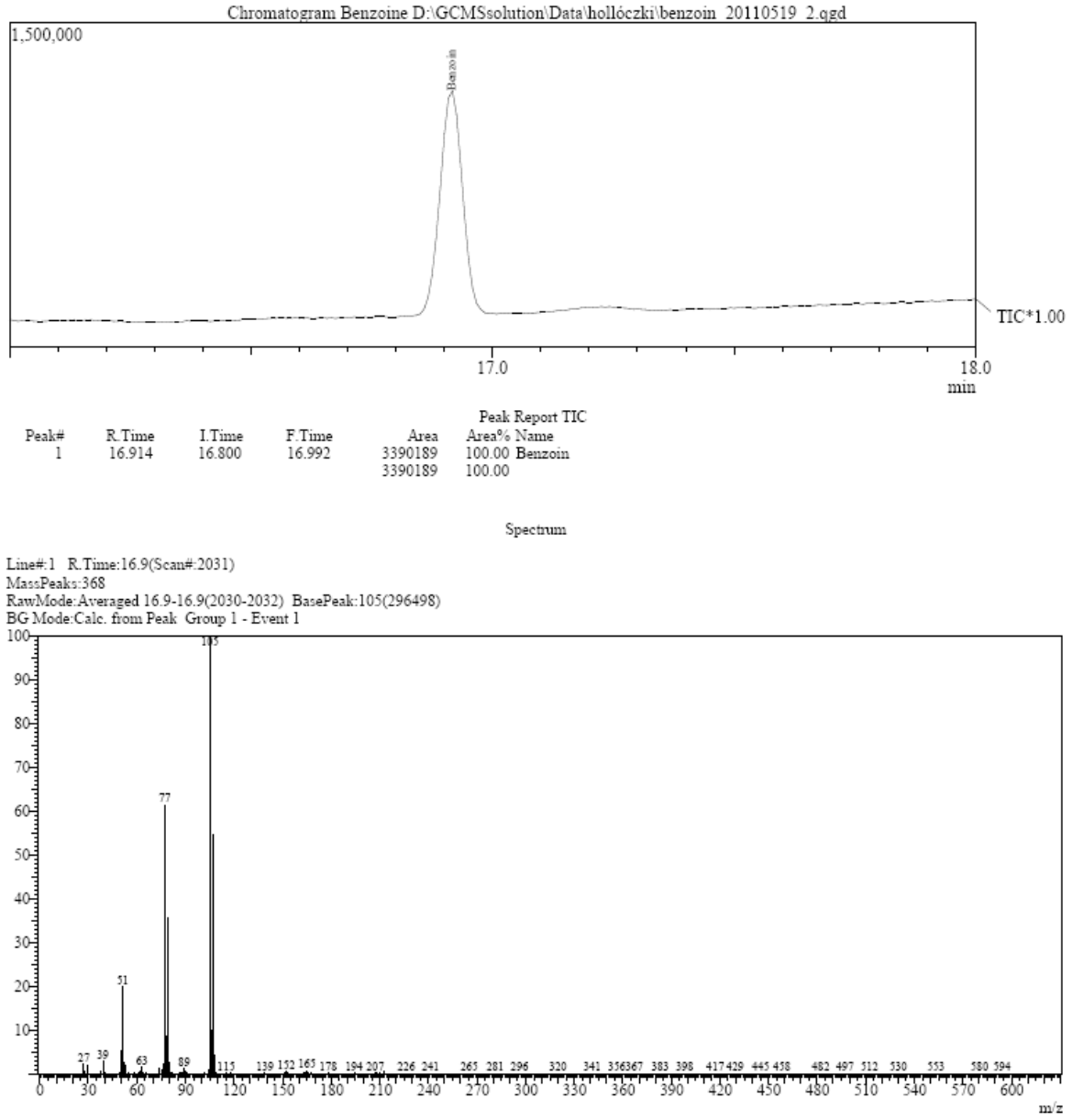


8 R = Br; **9** R = iPr

Entry	Substituent	Product	product		
			g	mmol	%
18	4-Br	**8**	0.35 g	0.95	54.0
19	4-iPr	**9**	0.36 g	1.21	69.4

Analytical data of products:

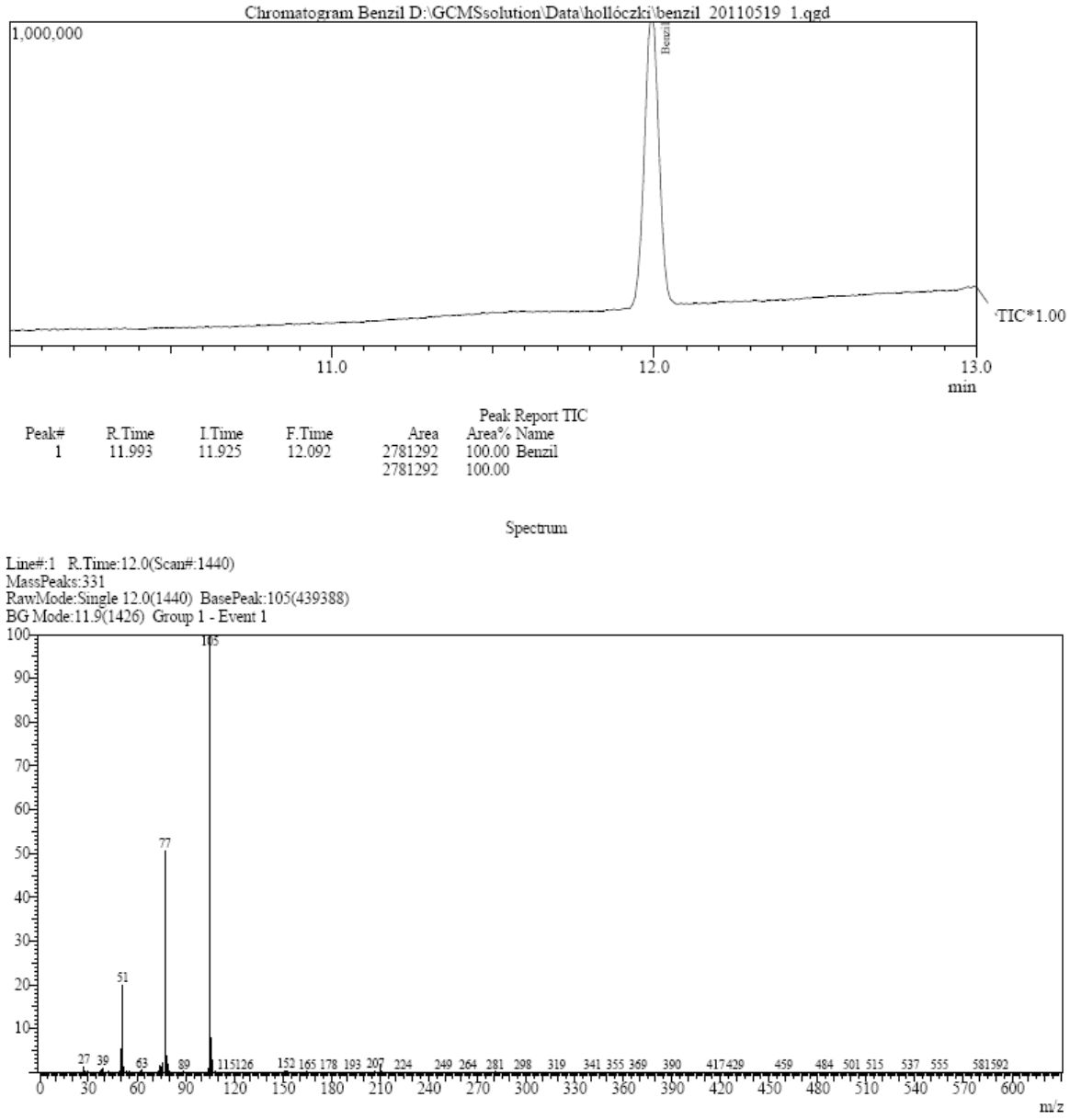
Benzoin (**4**): Mp.: 136ºC; IR (KBr): ν 3380, 1680, 1595, 1578, 1491, 1449, 1389, 1338, 1307, 1263, 1206, 1179, 1092, 1068, 1028, 1004, 978, 929, 856, 832, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.5 (br s, 1H, OH), 5.97 (s, 1H, CH), 7.29–7.56 (m, 8H, ArH), 7.91–7.94 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 76.44, 127.99, 128.79, 128.90, 129.34, 129.36, 133.72, 134.11, 139.22, 199.16 ppm; MS: *m/z* 107, 105, 79, 77, 51.



GC-MS spectrum of benzoin (**4**)

The product was identical with the commercial sample (TLC, and mp).

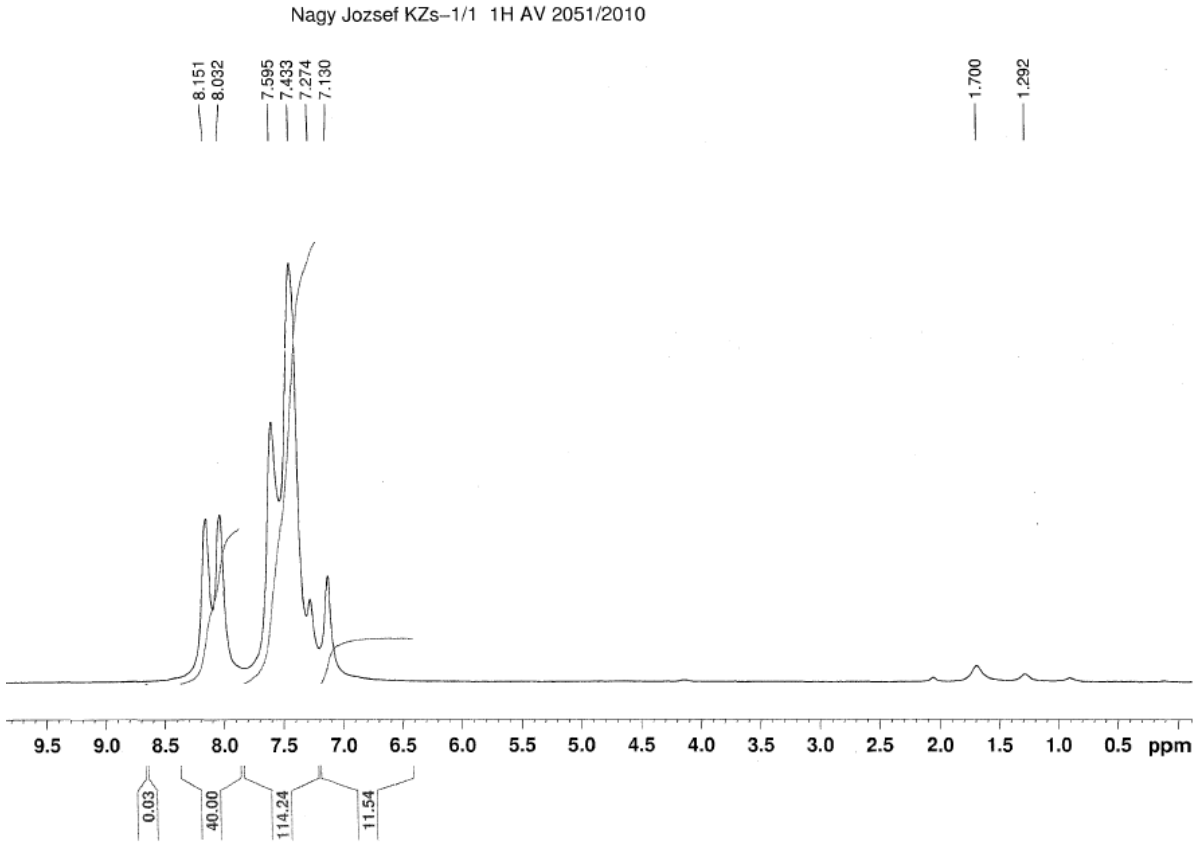
Benzil (**5**): Mp.: 95ºC; IR (KBr):ν 3064, 1659, 1593, 1579, 1450, 1325, 1315, 1211, 1174, 998, 876, 795 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.49–7.55 (m, 4H, ArH), 7.64-7.70 (m, 2H, ArH), 7.97–8.00 (m, 4H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 129.23, 130.12, 133.22, 135.09, 194,78 ppm; MS: *m/z* 105, 77, 51.



GC-MS spectrum of benzil (**5**)

The product was identical with the commercial sample (TLC, and mp).

2-Oxo-1,2-diphenylethyl benzoate (**6**): Mp.: 125ºC; IR (KBr): ν 3069, 1713, 1696, 1598, 1582, 1500, 1450, 1355, 1340, 1314, 1280, 1245, 1177, 1120, 1098, 1071, 957, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.13 (br s, 1H, CH), 7,31–7,53 (br s, 7H, ArH), 7,53–7,79 (br s, 4H, ArH), 7.92–8.09 (br s, 2H, ArH), 8.09–8.30 (br s, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 78.12, 128.59, 128.85, 129.03, 129.32, 129.50, 129.58, 130.17, 133.55, 133.68, 133.94, 134.90, 166.21, 193.88 ppm

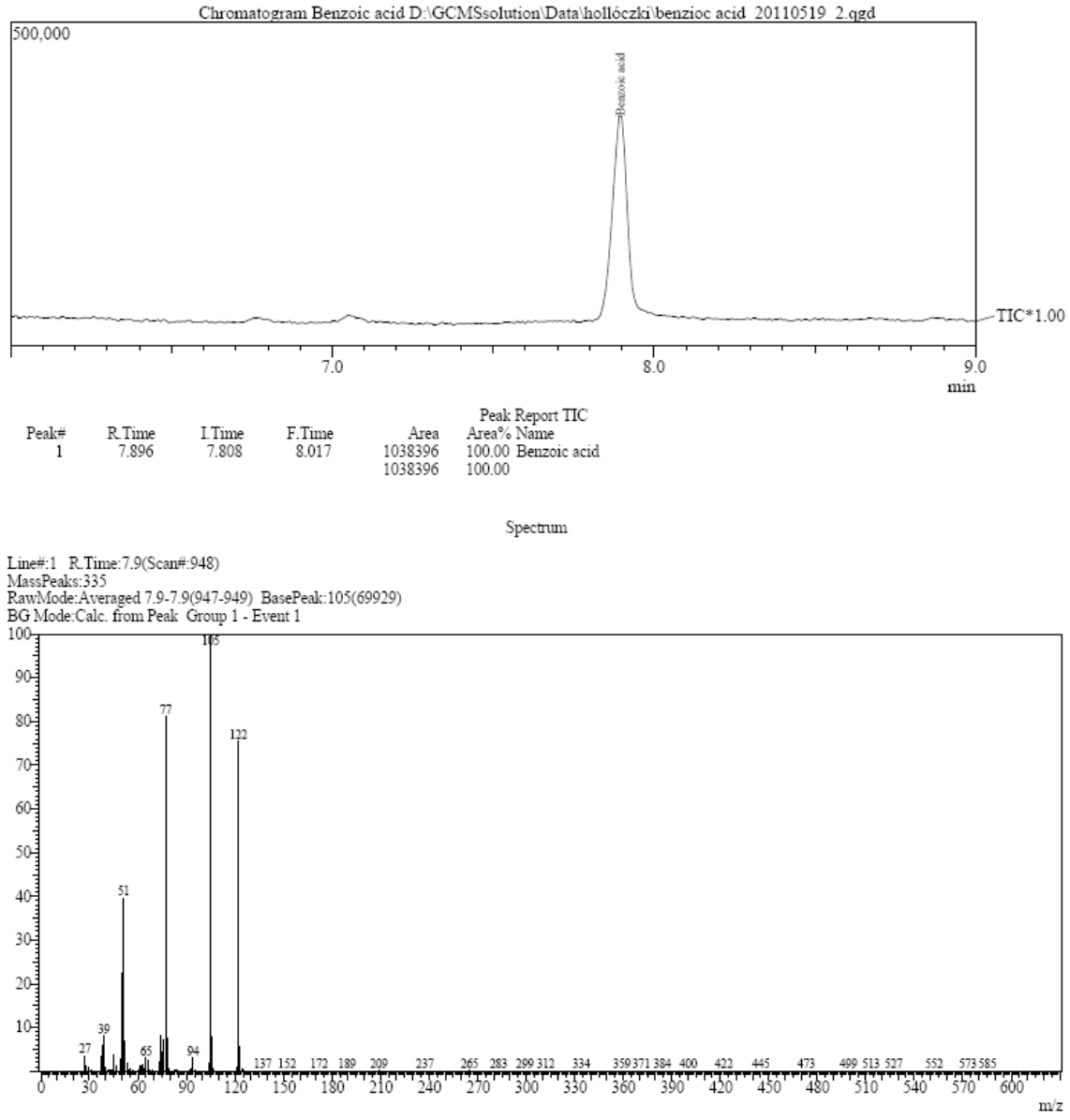


^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 2-oxo-1,2-diphenylethyl benzoate (**6**)

The sample was identical with one prepared by acylating of benzoin according to *Cutulic et al.* [2]

[2] *Sylvain P. Y. Cutulic, Neil J. Findlay, Sheng-Ze Zhou, Ewan J. T. Chrystal, and John A. Murphy*: Metal-Free Reductive Cleavage of C-O σ-bonds in Acyloin Derivatives by an Organic Neutral Super-Electron-Donor. *J. Org. Chem*. **2009**, *74*, 8713–8718.

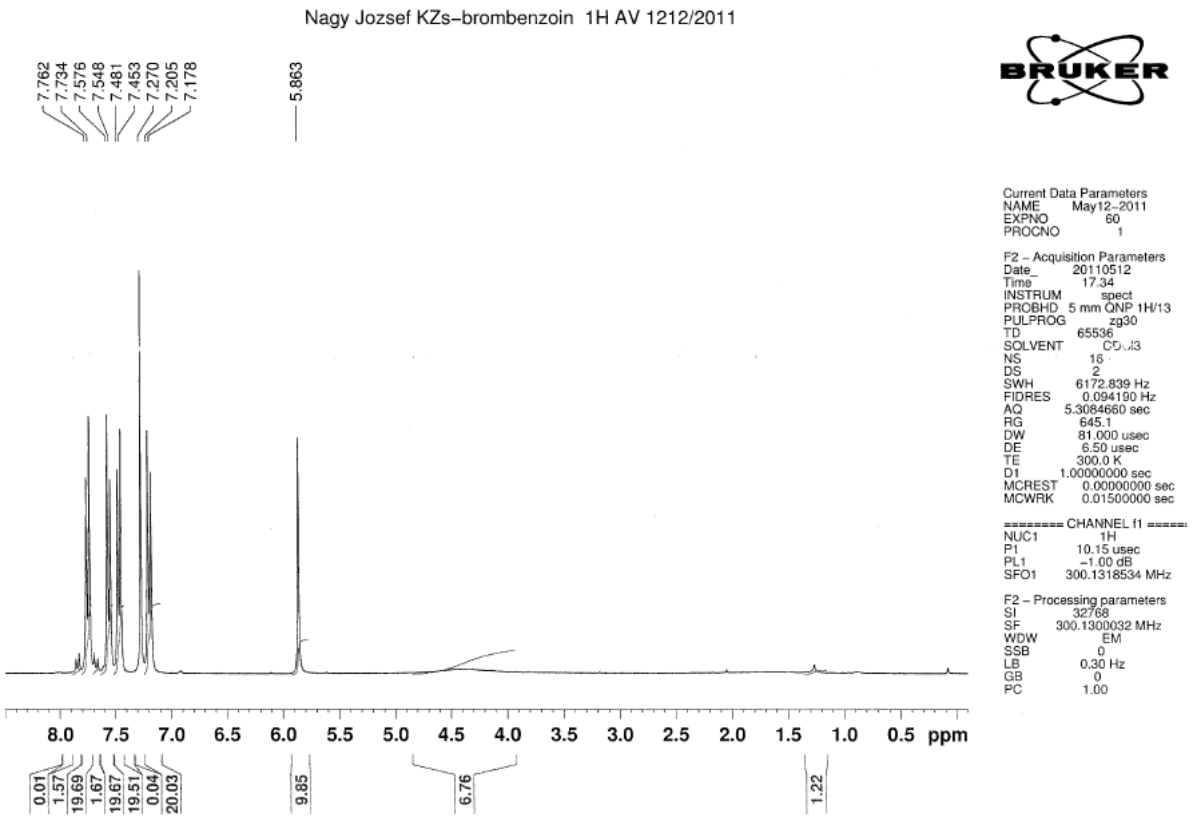
Benzoic acid (**7**): Mp.: 122ºC; IR (KBr): ν 3072–2562 br, 1685, 1602, 1583, 1454, 1424, 1326, 1292, 1180, 1128, 1073, 1027, 934, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.47–7.53 (m, 2H, ArH), 7.61-7.66 (m, 1H, ArH), 8.13–8.17 (m, 2H, ArH), 11.37 (br, 1H, OH) ppm; ^{13}C NMR ($CDCl_3$): δ 128.71, 129.55, 130.44, 134.04, 172.64 ppm; MS: *m/z* 122, 105, 77. 51.



GC-MS spectrum of benzoic acid (**7**)

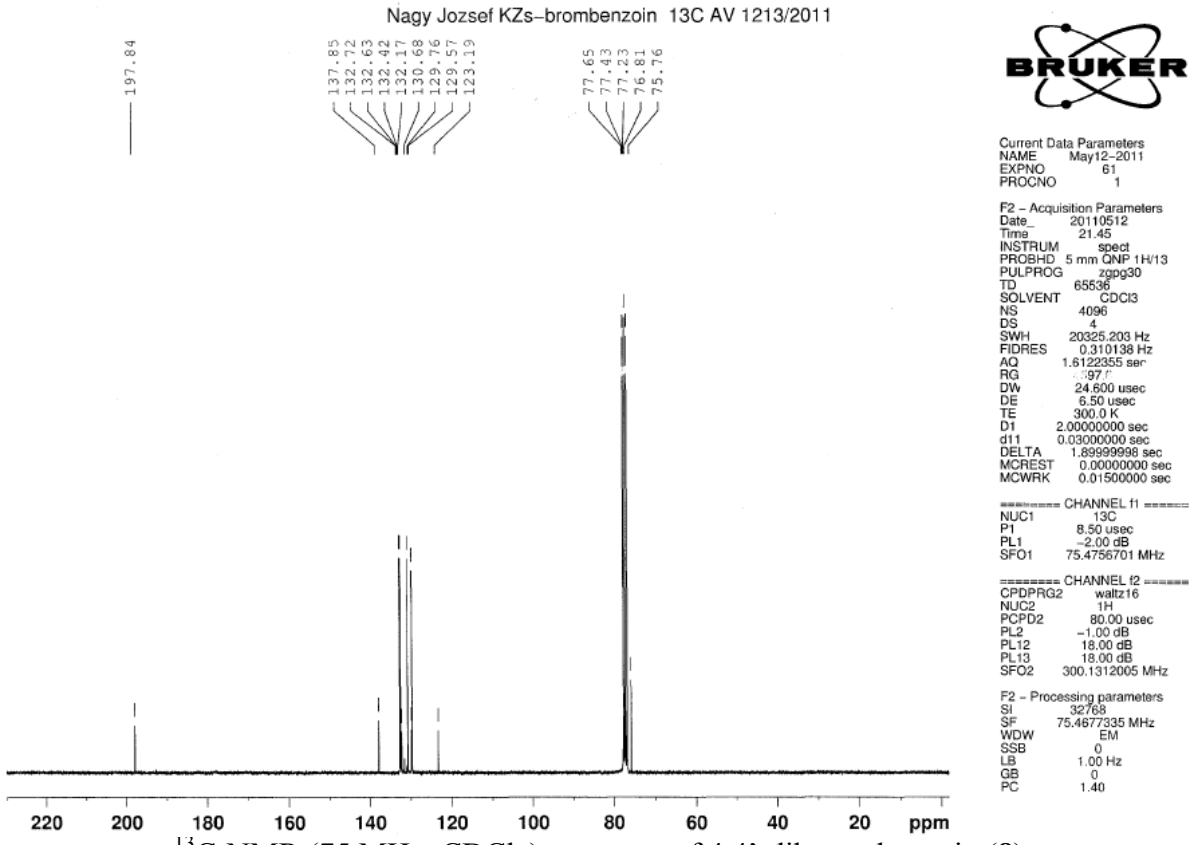
The product was identical with the commercial sample (TLC, and mp).

4,4'-Dibromobenzoin (**8**): Mp.: 94ºC[3]; IR (KBr): ν 3445, 3403, 1688, 1674, 1584, 1486, 1400, 1250, 1207, 1175, 1086, 1070, 1010, 974, 806 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.4 (br s, 1H, OH), 5.86 (s, 1H, CH), 7.18–7.20 (m, 2H, ArH), 7.45–7.48 (m, 2H, ArH), 7.55–7.58 (m, 2H, ArH), 7.73–7.76 (m, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 75.76, 123.19, 129.57, 129.76, 130.68, 132.17, 132.42, 132.63, 137.85, 197.84 ppm; MS: *m/z* 187, 185, 183, 159, 157, 155, 77, 76, 51, 50.



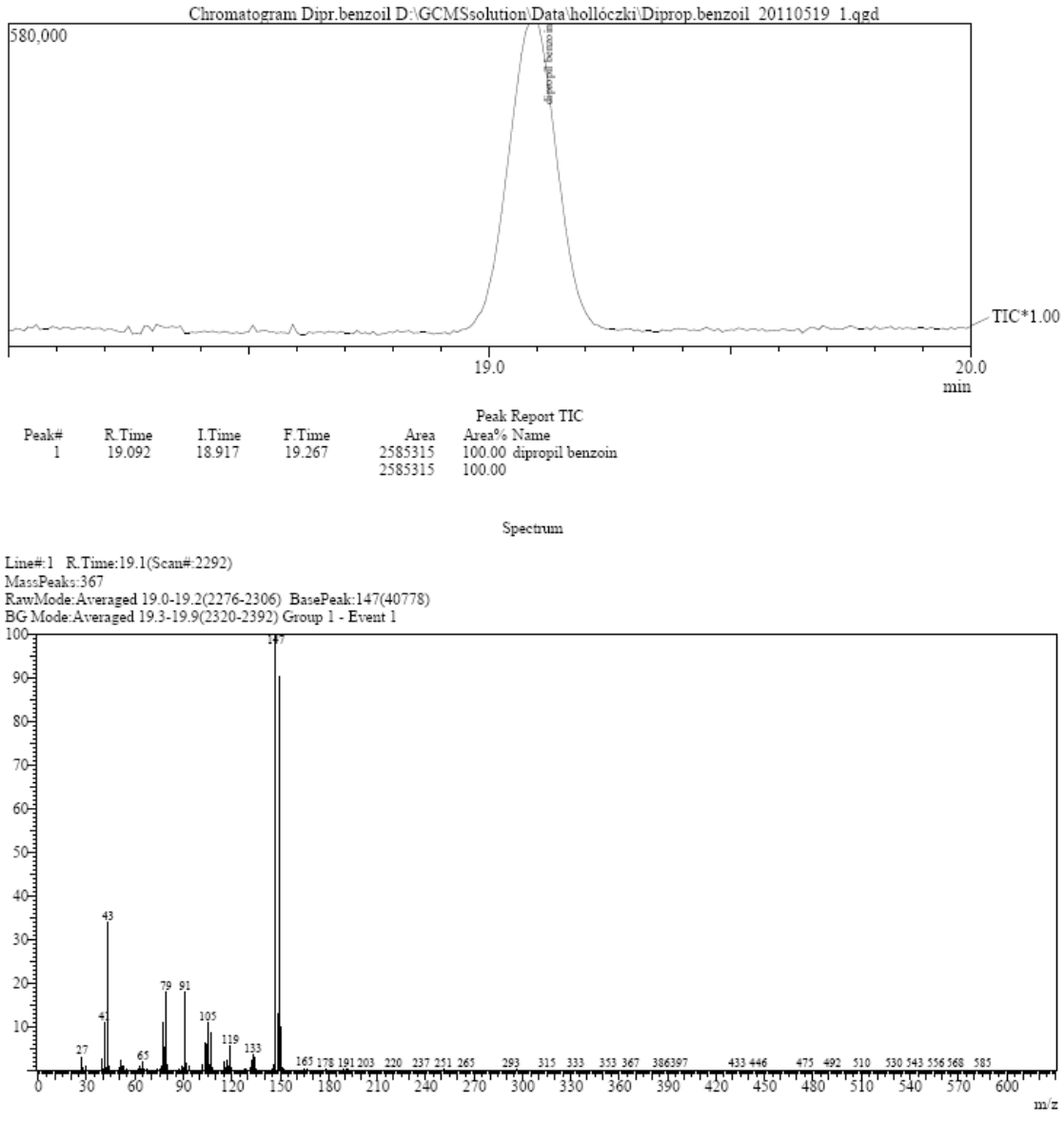
^1H-NMR (300 MHz, $CDCl_3$) spectrum of 4,4'-dibromobenzoin (**8**)

[3] *Yuuki Shimakawa, Takashi Morikawa and Satoshi Sakaguchi*: Facile route to benzils from aldehydes via NHC-catalyzed benzoin dimerization under metal-free conditions. *Tetrahedron Letters* **2010**, *51*, 1786–1789

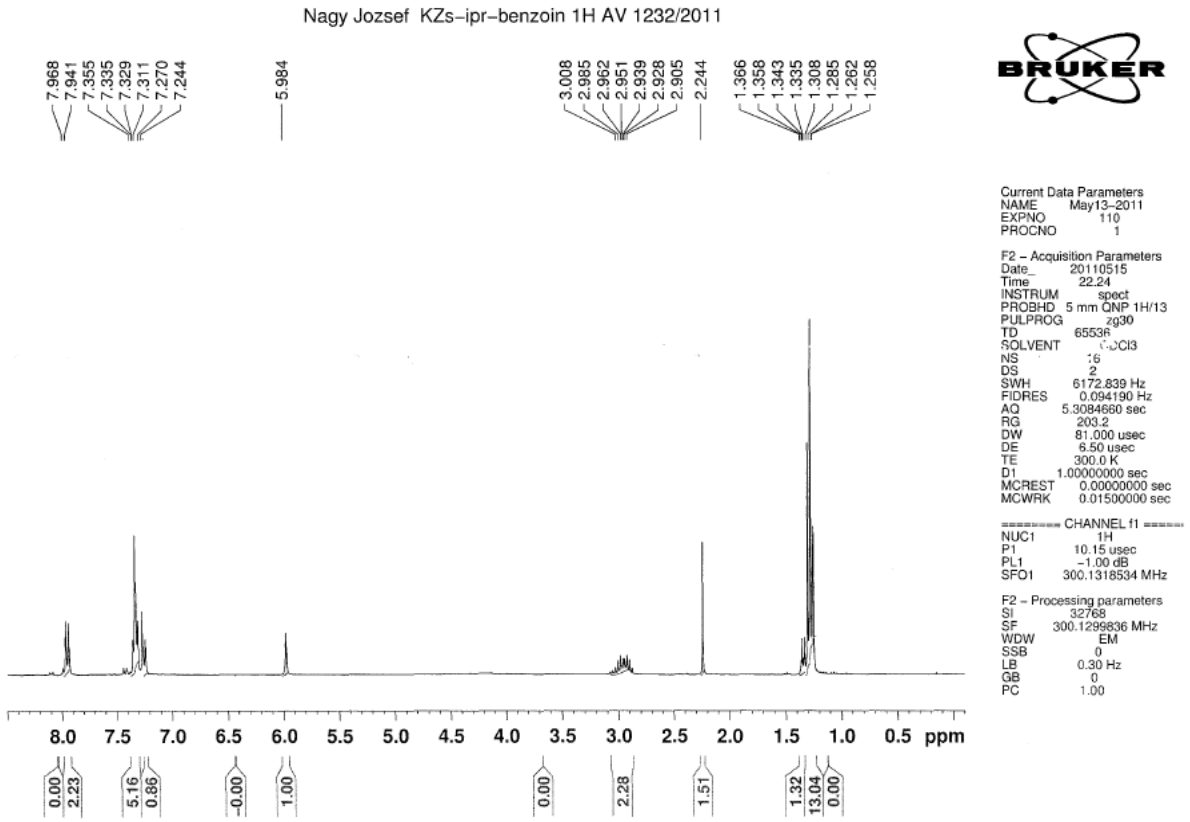


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of 4,4'-dibromobenzoin (**8**)

4,4'-Diizopropilbenzoin (**9**): Mp.: 100ºC; IR (KBr): ν 3422, 2960, 1676, 1606, 1569, 1510, 1462, 1417, 1387, 1257, 1224, 1181, 1088, 1054, 978, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.20–1.26 (m, 12H, 4×CH_3), 2.80–3.02 (m, 2H, 2×CH), 5.93 (s, 1H, CH), 7.10–7.31 (m, 6H, ArH), 7.88–7.91 (m, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 23.68, 23.72, 24.02, 24.03, 34.00, 34.48, 75.99, 127.01, 127.42, 127.90, 129.70, 131.53, 136.88, 149.40, 155.73, 198.66 ppm; MS: *m/z* 149, 147, 133, 119, 107, 105, 91, 79, 77, 43, 41.



GC-MS spectrum of 4,4'-diizopropilbenzoin (**9**)



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 4,4'-diizopropilbenzoin (**9**)[4]

^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of 4,4'-diizopropilbenzoin (**9**)[4]

[4] The sample contains some acetone.