Fries rearrangement of aryl formates: a mechanistic study by means of ^{1}H, ^{2}H and ^{11}B NMR spectroscopy and DFT calculations

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Contents

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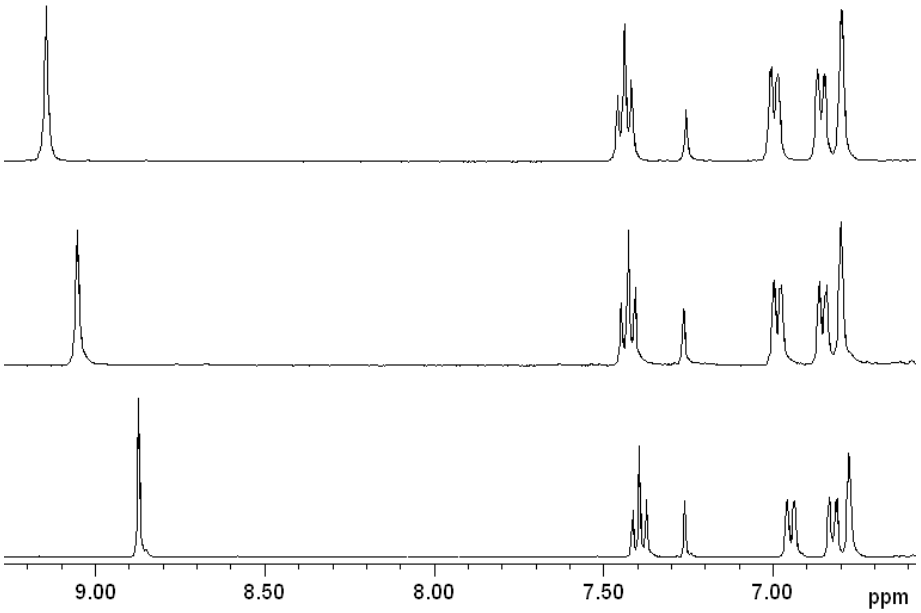


Figure S1. ^{1}H NMR spectra (400 MHz) of 3-methoxyphenyl formate just after the addition of BCl_3. Top to bottom: –5 °C, +7 °C, +25 °C. The resonance at 7.26 ppm is due to chloroform.

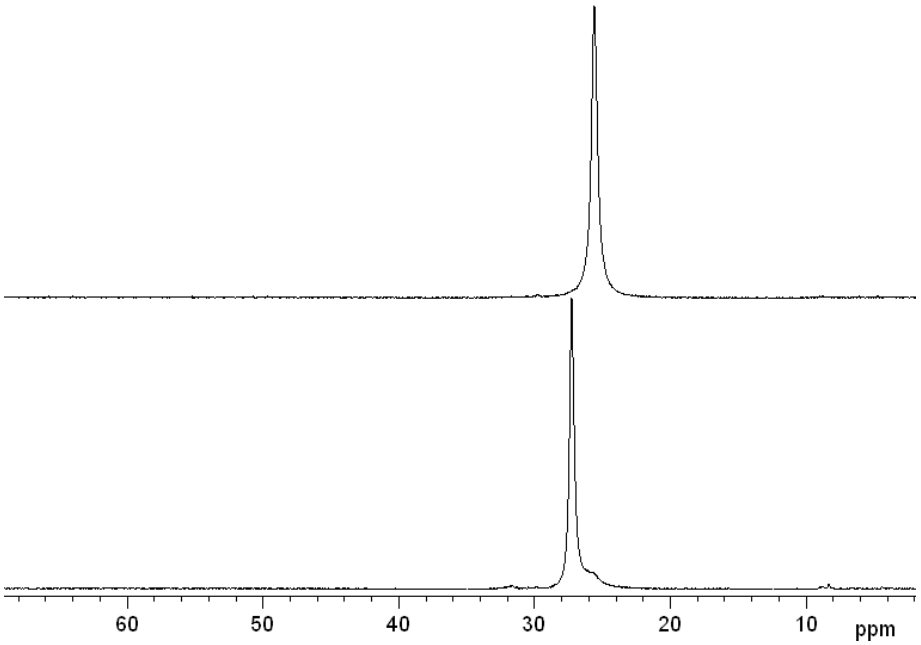


Figure S2. ^{11}B NMR spectra (96 MHz) of 3-methyoxyphenyl formate just after the addition of BCl_3. Top: –5 °C; bottom: +13 °C.

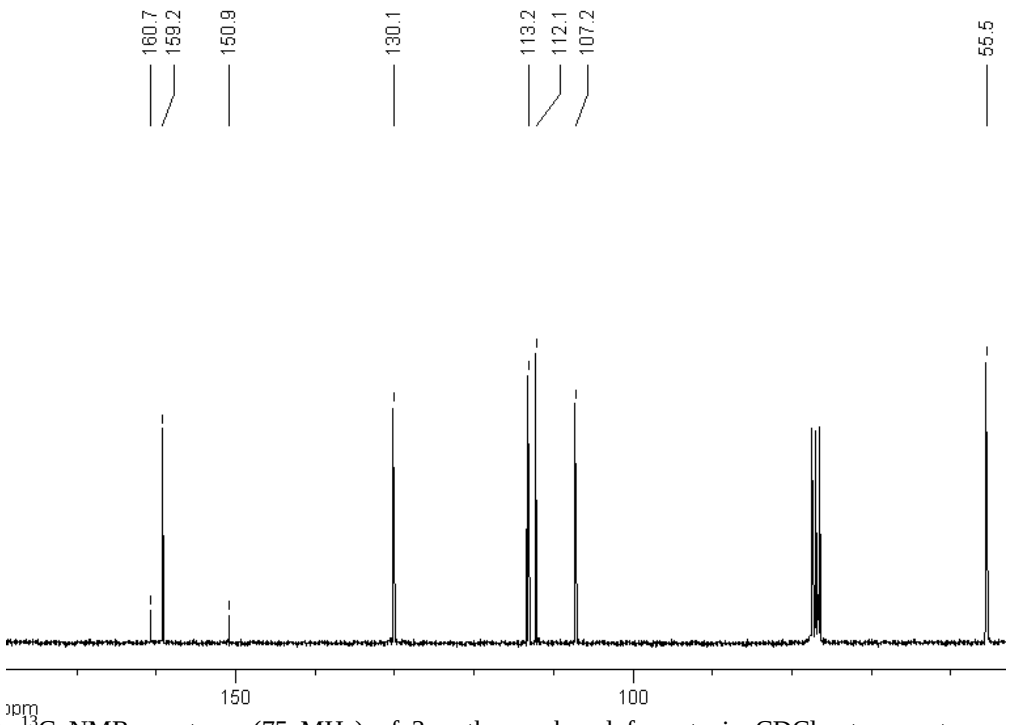


Figure S3. ^{13}C NMR spectrum (75 MHz) of 3-methyoxyphenyl formate in $CDCl_3$ at room temperature. The resonance at 77 ppm is the solvent.

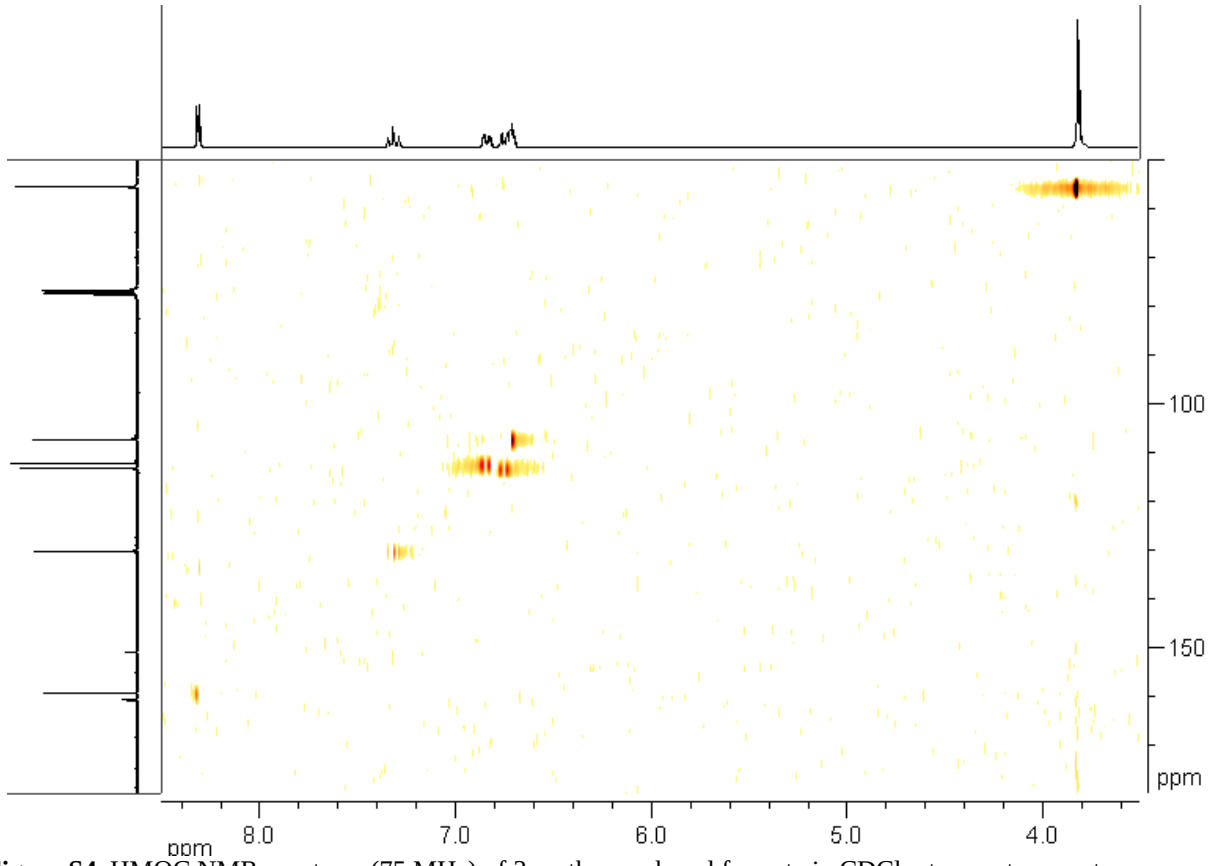


Figure S4. HMQC NMR spectrum (75 MHz) of 3-methyoxyphenyl formate in $CDCl_3$ at room temperature.

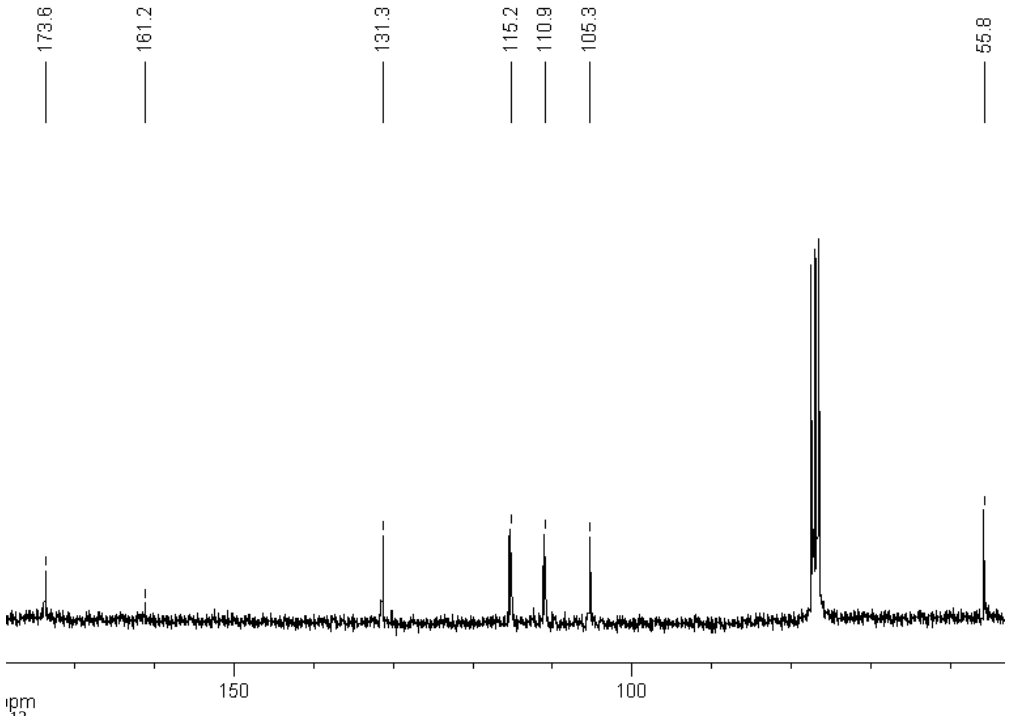


Figure S5. ^{13}C NMR spectrum (75 MHz) of 3-methyoxyphenyl formate in $CDCl_3$, just after the addition of BCl_3, at –10 °C. The resonance at 77 ppm is the solvent.

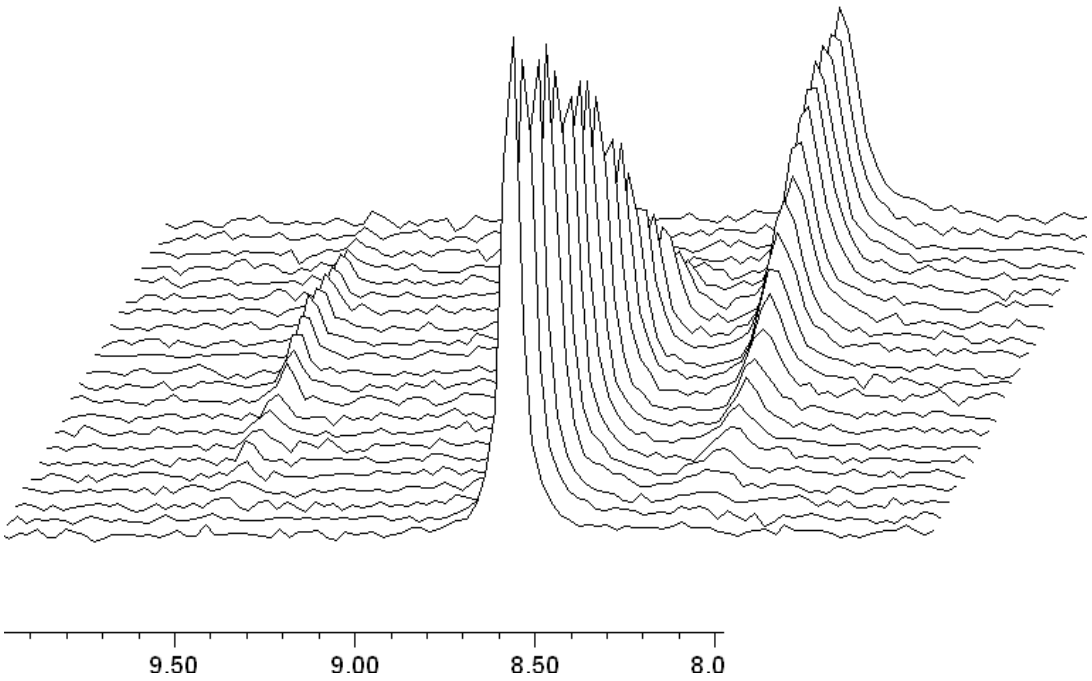


Figure S6. Time evolution over 17 hours of the ^{2}H NMR spectra (61 MHz) of the **1-d**-BCl_3 reacting system at +7 °C, aldehydic region.

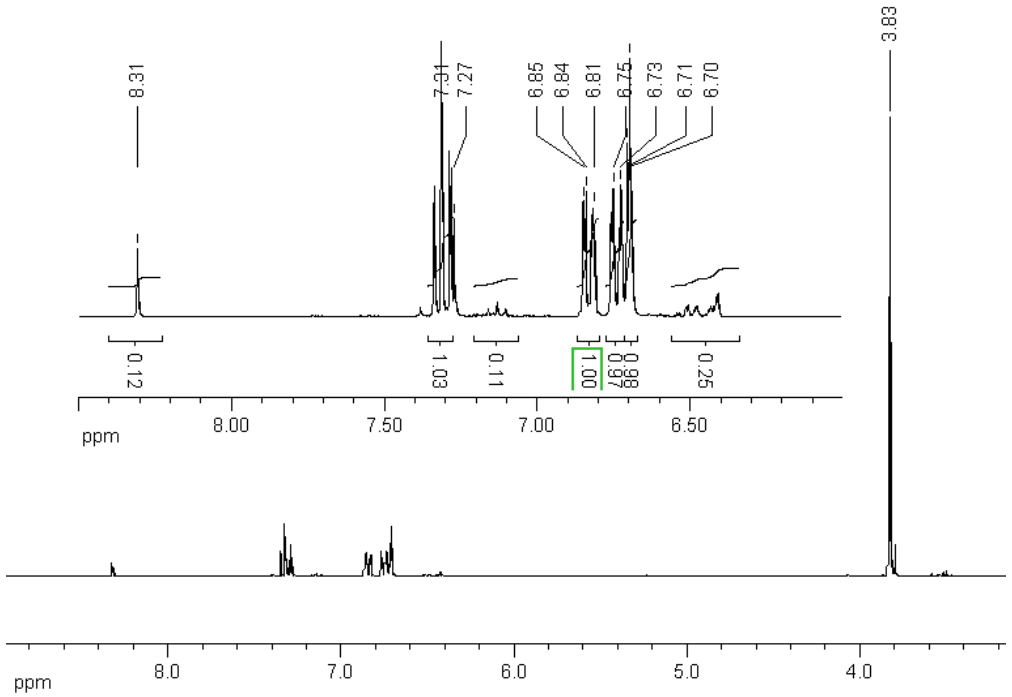


Figure S7. ^{1}H NMR spectra (300 MHz) of **1-d** at room temperature. Residual signal of non-deuterated sample (12%) is visible at 8.31 ppm.

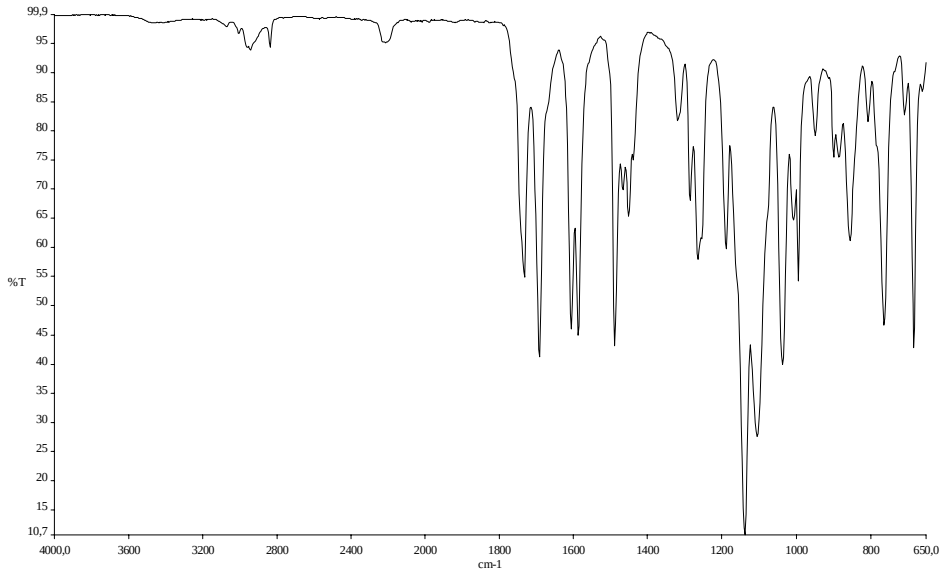
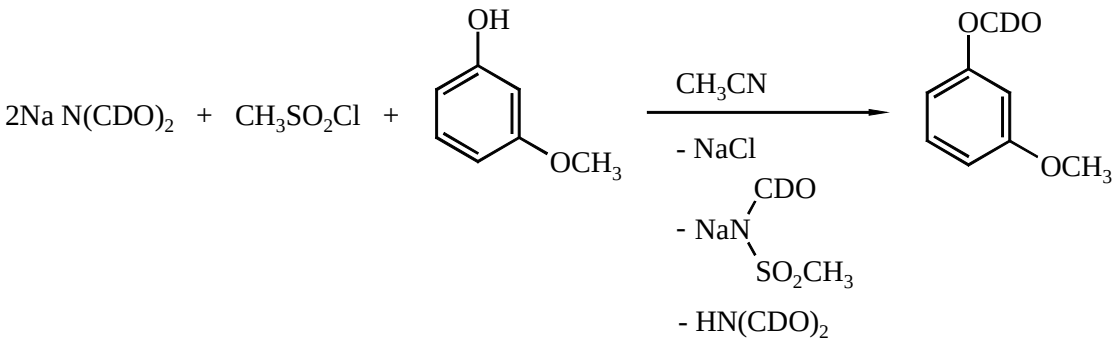


Figure S8. IR spectrum of 3-methyoxyphenyl formate-1-d.

Table S1. Main IR absorption bands of **1-d**.

ν, cm^{-1}	%T	ν, cm^{-1}	%T
2945	94	1490	43
2835	95	1138	12
1734	55	1106	28
1694	41	1038	40
1606	46	764	47
1589	45	683	43



Scheme S1. Final step of the synthesis of deuterated 3-methoxyphenyl formate-1-d, **1-d**.

Table S2. Thermochemical data for the formation of complexes **1a-c**.[a]

Species	E DFT a.u.	H DFT a.u.	G DFT a.u.	E MP2 a.u.	ΔE DFT kcal/mol	ΔH DFT kcal/mol	ΔG DFT kcal/mol	ΔE MP2 kcal/mol	ΔG MP2 kcal/mol
1	-535.288344	-535.126389	-535.173179	-534.006191					
BCl_3	-1405.668158	-1405.654972	-1405.689380	-1403.840466					
1+BCl_3	-1940.956502	-1940.781361	-1940.862559	-1937.846657	7.09	5.62	-6.74	9.10	-4.74
Δ**1a**	-0.011306	-0.008963	0.010742	-0.014498	-7.09	-5.62	6.74	-9.10	4.74
Δ**1b**	-0.002773	0.008007	-0.000392	-0.014794	-1.74	-0.60	6.49	-9.28	-1.05
Δ**1c**	-0.001461	0.000298	0.020814	-0.021196	-0.92	0.19	13.06	-13.30	0.68
Δ**1a** BSSE	-0.054676				-34.31				
Δ**1b** BSSE	0.001093				0.69				
Δ**1c** BSSE	-0.041956				-26.33				

[a] Electronic energy, enthalpy with ZPE and thermal corrections at 298 K, 1 atm, and Gibbs free energy with ZPE thermal corrections at 298 K, 1 atm (hartrees). DFT: MPW1K/6-311+G**//MPW1K/6-311+G**; MP2: MP2/6-311+G**//MPW1K/6-311+G**. For bimolecular states the energies are calculated by adding those of the isolated molecules. No BSSE correction has been applied except where indicated.

Table S3. Thermochemical data for the relevant intermediates and transition states of the Fries rearrangement.[a]

Species	E DFT a.u.	H DFT a.u.	G DFT a.u.	E MP2 a.u.	ΔE DFT kcal/mol	ΔH DFT kcal/mol	ΔG DFT kcal/mol	ΔE MP2 kcal/mol	ΔG MP2 kcal/mol
1	-535.288344	-535.126389	-535.173179	-534.006191					
BCl_3	-1405.668158	-1405.654972	-1405.689380	-1403.840466					
1+BCl_3	-1940.956502	-1940.781361	-1940.862559	-1937.846657	7.09	5.62	-6.74	9.10	-4.74
1a	-1940.967808	-1940.790324	-1940.851817	-1937.861155	0.00	0.00	0.00	0.00	0.00
1b	-1940.959275	-1940.782317	-1940.852209	-1937.861451	5.35	5.02	-0.25	-0.19	-5.79
1c	-1940.957963	-1940.781063	-1940.841745	-1937.867853	6.18	5.81	6.32	-4.20	-4.06
4	-1940.964359	-1940.785878	-1940.846204	-1937.856830	2.16	2.79	3.52	2.71	4.07
4+BCl_3	-3346.632517	-3346.440850	-3346.535584	-3341.697296					
TS42a	-1940.924669	-1940.749313	-1940.807597	-1937.826819	27.07	25.73	27.75	21.55	22.22
TS42b	-3346.611256	-3346.420633	-3346.490968	-3341.707473					
Δ**TS42b**	0.021261	0.020217	0.044616	-0.010177	13.34	12.69	28.00	-6.39	8.27
2	-1366.817015	-1366.666616	-1366.719250	-1364.536464					
HCOCl	-574.140723	-574.116679	-574.145972	-573.316569					
2+HCOCl	-1940.957738	-1940.783295	-1940.865222	-1937.853033	6.32	4.41	-8.41	5.10	-9.63
TS23	-1940.937633	-1940.761982	-1940.818942	-1937.838070	18.94	17.78	20.63	14.49	16.18
5	-1940.974533	-1940.796301	-1940.852512	-1937.866484	-4.22	-3.75	-0.44	-3.34	0.44
3	-1480.155285	-1479.992350	-1480.045020	-1477.635517					
HCl	-460.837255	-460.826400	-460.847575	-460.244701					
3+HCl	-1940.992540	-1940.818750	-1940.892595	-1937.880218	-15.52	-17.84	-25.59	-11.96	-22.03

[a] Electronic energy, enthalpy with ZPE and thermal corrections at 298 K, 1 atm, and Gibbs free energy with ZPE thermal corrections at 298 K, 1 atm (hartrees). DFT: MPW1K/6-311+G**//MPW1K/6-311+G**; MP2: MP2/6-311+G**//MPW1K/6-311+G**. For bimolecular states the energies are calculated by adding those of the isolated molecules. No BSSE correction has been applied except where indicated. Columns labeled ΔE, ΔH, ΔG report values relative to **1a**.

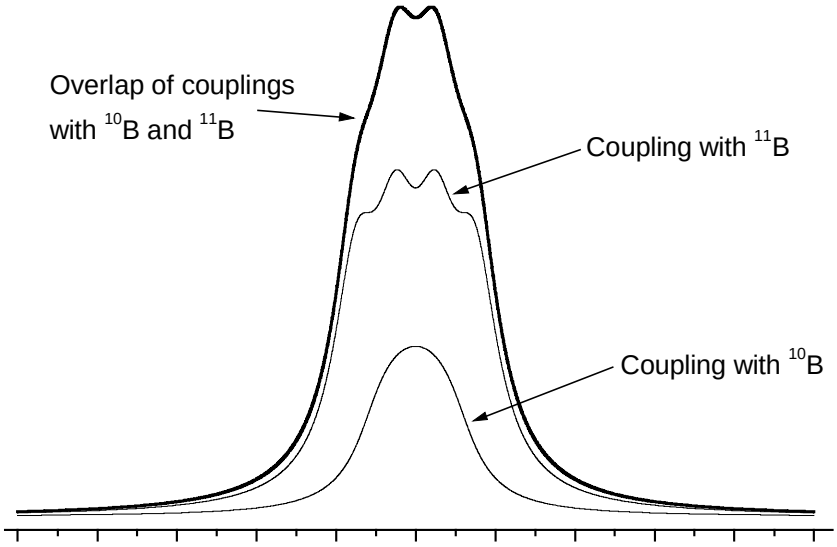


Figure S9. Calculated lineshape of the aldehyde resonance of the final product **3**. The experimental signal is shown in Figure 4. The trace labeled "Coupling with ^{11}B" (I = 3/2, nat. ab. 80%) is obtained by overlapping four 1:1:1:1 Lorentzian lineshapes separated by 6 Hz on the x (frequency) axis with a linewidth of 15 Hz and an amplitude of 0.8. The line labeled "Coupling with ^{10}B" (I = 3, nat. ab. 20%) is obtained by overlapping seven 1:1:1:1:1:1:1 Lorentzian lineshapes separated by 2 Hz on the frequency axis (since $\gamma(^{10}\mathrm{B})$ is about 1/3 of $\gamma(^{11}\mathrm{B})$) with a linewidth of 15 Hz and an amplitude of 0.2. The Lorentzian function used is $F(x) = 2Aw/\pi[(x\text{-}x_c)^2 + w^2]$ where A is the amplitude, w is the linewidth and x_c the center of the Lorentzian curve. The thick line is the superposition of the traces corresponding to coupling to ^{11}B and ^{10}B. Therefore a linewidth of 15 Hz is needed to reproduce the observed lineshape, which is consistent with the small but non-negligible quadrupole moment of ^{10}B and ^{11}B. Isotope shifts and the different linewidths of ^{1}H signals coupled to ^{10}B and ^{11}B have been neglected.

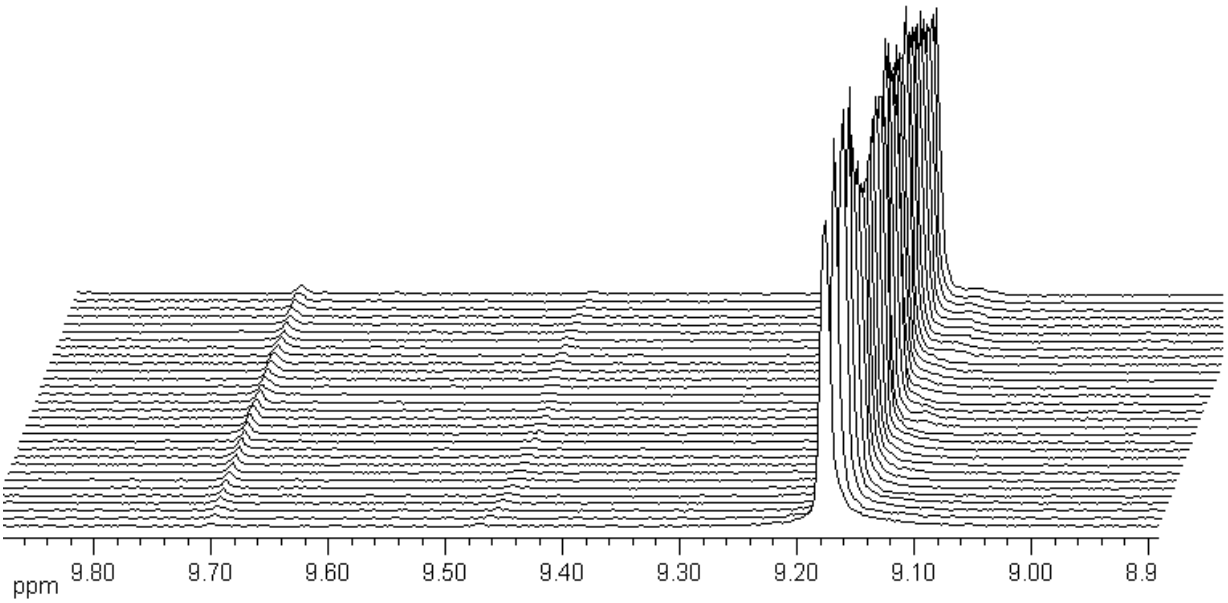
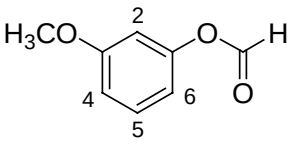


Figure S10. Time evolution, over 18 hours, of the ^{1}H NMR (400 MHz) spectra of a mixture of phenyl formate and BCl_3 in a ratio 1:1.2. T = 273 K. The signal at 9.70 ppm, attributed to formyl chloride, is clearly developing.

3-Methoxyphenyl formate **1**
E (hartree): -535.288344

C	1.101349	-0.027029	1.659388
C	0.654214	0.061604	2.968058
C	-0.475775	-0.641825	3.371190
C	-1.148053	-1.430963	2.466421
C	-0.714160	-1.539416	1.154074
C	0.406148	-0.836450	0.779085
O	1.255304	0.806218	3.911006
C	2.412725	1.515372	3.565273
O	0.763076	-0.914592	-0.555210
C	2.022743	-1.152188	-0.922340
O	2.955796	-1.300805	-0.207867
H	1.976333	0.498407	1.324365
H	-1.230616	-2.148691	0.431378
H	-2.025272	-1.973342	2.782648
H	-0.801041	-0.552955	4.394813
H	2.058055	-1.189475	-2.013137
H	2.737750	2.020189	4.466870
H	3.201995	0.846215	3.223899
H	2.208385	2.258532	2.794472



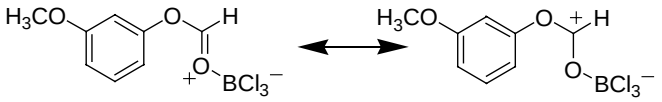
1

BCl_3
E (hartree): -1405.668158

B	0.000089	-0.000421	0.002499
Cl	-0.099053	1.731918	-0.000245
Cl	-1.450609	-0.951657	-0.000245
Cl	1.549637	-0.780137	-0.000245

3-Methoxyphenyl formate·BCl_3, O-acyl complex **1a**
E (hartree): -1940.967808

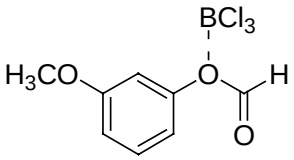
C	0.735856	-0.361595	-0.319272
C	-0.086241	-0.899424	0.651528
C	0.242339	-0.969487	1.978877
C	1.474140	-0.449975	2.352975
C	2.321741	0.109053	1.425116
C	1.959541	0.158160	0.081676
O	-1.310442	-1.454772	0.260111
C	-2.137590	-0.705575	-0.369583
O	-3.173347	-1.189874	-0.801205
O	2.844042	0.709261	-0.752795
C	2.526818	0.791265	-2.118604
H	-0.436439	-1.411133	2.688582
H	1.769404	-0.483205	3.389519
H	3.278706	0.513441	1.711474
H	0.434310	-0.377263	-1.353350
H	-1.889138	0.344964	-0.499837
H	3.369907	1.276453	-2.593391
H	2.392673	-0.198449	-2.553554
H	1.631313	1.389769	-2.281035
B	-4.174192	-0.269569	-1.627570
Cl	-5.540037	-1.346335	-2.062822
Cl	-4.623134	1.102475	-0.507773
Cl	-3.197026	0.317627	-3.064813



1a

3-Methoxyphenyl formate·BCl_3, O-aryl complex **1b**
E (hartree): -1940.959275

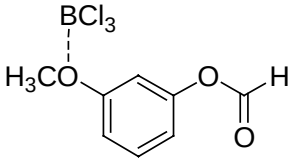
C	0.965023	-0.069082	1.534021
C	0.572065	-0.025330	2.861365
C	-0.476843	-0.826019	3.302508
C	-1.118932	-1.663183	2.420459
C	-0.735948	-1.726600	1.088055
C	0.301257	-0.927266	0.678145
O	1.146060	0.761368	3.786197
C	2.220581	1.572042	3.399137
O	0.643414	-0.935119	-0.667070
C	1.804423	-1.493270	-1.031241
O	2.598825	-1.985724	-0.306449
B	-1.023324	0.815159	-2.534721
Cl	-1.981020	1.329185	-1.185629
Cl	-1.500288	-0.570270	-3.468932
Cl	0.380244	1.730001	-3.006252
H	1.771093	0.534533	1.155514
H	-1.230934	-2.374312	0.383900
H	-1.932186	-2.280064	2.769192
H	-0.765038	-0.771060	4.339669
H	1.899740	-1.420429	-2.116388
H	2.533079	2.103316	4.289868
H	3.052869	0.975721	3.026221
H	1.920040	2.293545	2.639426



1b

3-Methoxyphenyl formate·BCl_3, O-Methoxy complex **1c**
E (hartree): -1940.957963

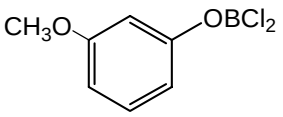
C	0.965023	-0.069082	1.534021
C	0.572065	-0.025330	2.861365
C	-0.476843	-0.826019	3.302508
C	-1.118932	-1.663183	2.420459
C	-0.735948	-1.726600	1.088055
C	0.301257	-0.927266	0.678145
O	1.146060	0.761368	3.786197
C	2.220581	1.572042	3.399137
O	0.643414	-0.935119	-0.667070
C	1.804423	-1.493270	-1.031241
O	2.598825	-1.985724	-0.306449
B	-1.023324	0.815159	-2.534721
Cl	-1.981020	1.329185	-1.185629
Cl	-1.500288	-0.570270	-3.468932
Cl	0.380244	1.730001	-3.006252
H	1.771093	0.534533	1.155514
H	-1.230934	-2.374312	0.383900
H	-1.932186	-2.280064	2.769192
H	-0.765038	-0.771060	4.339669
H	1.899740	-1.420429	-2.116388
H	2.533079	2.103316	4.289868
H	3.052869	0.975721	3.026221
H	1.920040	2.293545	2.639426



1c

3-Methoxyphenol dichloroborate ester **2**
E (hartree): -1366.817015

C	1.671303	2.204636	-0.344996
C	2.697569	1.333383	-0.061069
C	2.455215	-0.036146	-0.038954
C	1.182288	-0.518132	-0.300589
C	0.172910	0.386452	-0.574712
C	0.390128	1.743114	-0.609297
O	-1.070024	-0.116990	-0.879039
B	-2.114688	-0.168534	-0.053124
Cl	-2.036129	0.381167	1.606199
Cl	-3.608857	-0.827865	-0.674758
H	-0.417619	2.418001	-0.839183
H	1.866137	3.265483	-0.363887
H	3.695587	1.684392	0.144061
H	0.953174	-1.569574	-0.301791
H	4.281276	-2.637007	0.527554
H	2.594710	-2.488418	1.046007
H	2.992583	-2.591398	-0.685624
O	3.507954	-0.820131	0.242511
C	3.318159	-2.207186	0.280937



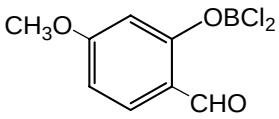
2

HCOCl
E (hartree): -574.140723

Cl	2.230987	4.864559	-0.167258
C	2.118299	3.112498	-0.151889
O	1.132993	2.529384	-0.388097
H	3.084441	2.674938	0.105154

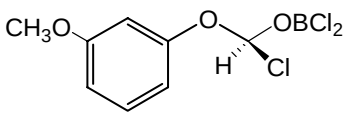
3-Methoxysalicylaldehyde dicloroborate ester **3**
E (hartree): -1480.155285

C	-0.608631	0.902800	0.092966
C	-1.678258	1.808306	0.287172
C	-3.010534	1.348305	0.202386
C	-3.270326	0.044417	-0.048236
C	-2.191671	-0.852437	-0.246305
C	-0.878340	-0.431152	-0.188198
C	-1.349679	3.148287	0.440443
O	-0.170742	3.571912	0.543682
B	0.983496	2.600935	0.710663
Cl	1.222970	2.412640	2.522481
O	-2.552811	-2.101999	-0.487276
C	-1.559166	-3.079227	-0.696405
O	0.621088	1.316908	0.125612
Cl	2.416400	3.287093	-0.151253
H	-3.818952	2.049485	0.345603
H	-4.272959	-0.343151	-0.109348
H	-0.046095	-1.095136	-0.339132
H	-2.122103	3.910791	0.451497
H	-2.088485	-4.007708	-0.865836
H	-0.955866	-2.839478	-1.569420
H	-0.921318	-3.178083	0.179265



3

3-Methoxyphenol chloroalkyl dichloroborate **4**
E (hartree): -1940.964359



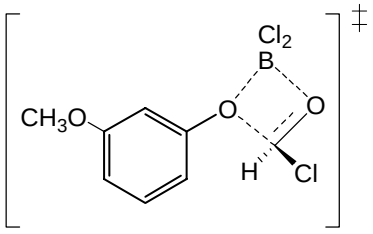
4

C	-2.843393	0.905138	2.196452
C	-3.842127	0.383970	1.412296
C	-3.513686	-0.248918	0.215357
C	-2.190755	-0.355980	-0.169833
C	-1.203438	0.174554	0.647402
C	-1.505345	0.816418	1.828500
O	0.066958	0.000233	0.168723
C	1.132369	0.244555	0.970137
O	2.197872	-0.502093	0.542163
B	2.743676	-0.568013	-0.686781
Cl	2.246801	0.396193	-2.047391
Cl	1.567953	1.993588	1.001475
Cl	4.049886	-1.710799	-0.877051
H	-0.747663	1.270468	2.443254
H	-3.099057	1.405698	3.117250
H	-4.879672	0.456049	1.693736
O	-4.541847	-0.729138	-0.500488
H	-1.890098	-0.841556	-1.081615
H	0.943499	-0.022376	2.002636
C	-4.269630	-1.362921	-1.719764
H	-5.228679	-1.659506	-2.126415
H	-3.778230	-0.686061	-2.418219
H	-3.651764	-2.249325	-1.577694

HCl
E (hartree): -460.837255

Cl	2.435034	4.370252	-0.102823
H	2.890966	3.188718	0.043013

Transition state **TS42a**
E (hartree): -1940.924669, ν_i: -259.0 cm^{-1}



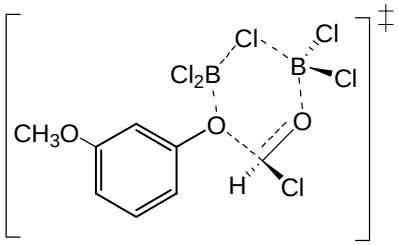
TS42a

C	-1.892089	2.710741	0.108440
C	-3.014040	1.915726	0.076618
C	-2.876501	0.540063	-0.076815
C	-1.617671	-0.029108	-0.189959
C	-0.509218	0.799534	-0.149474
C	-0.622676	2.165395	-0.006573
O	0.745384	0.271452	-0.294169
C	2.434252	0.616470	0.440828
O	2.677810	-0.585685	0.153225
B	1.234970	-1.102513	0.066867
Cl	1.059284	-2.329597	-1.224357
Cl	3.284217	1.845622	-0.355834
Cl	0.657570	-1.630943	1.707768
H	0.255582	2.789702	-0.000041
H	-2.000429	3.778112	0.221636
H	-4.004569	2.330626	0.164285
O	-4.014292	-0.169205	-0.105119
H	-1.486291	-1.088775	-0.314982
H	2.022159	0.921635	1.396421
C	-3.933186	-1.561817	-0.250425
H	-4.953607	-1.924653	-0.240268
H	-3.464990	-1.835476	-1.195379
H	-3.382333	-2.015398	0.572701

Transition state **TS42b**

E (hartree): -3346.611256, ν_i:-234.1 cm^{-1}

C	1.682389	-1.077566	-0.661639
C	0.367302	-1.372594	-0.374372
C	-0.154044	-0.899969	0.814604
C	0.577337	-0.146386	1.698110
C	1.903035	0.141787	1.390507
C	2.456663	-0.324845	0.207336
O	-1.490658	-1.178373	1.080709
C	-2.675445	0.273763	0.959249
Cl	-2.185720	1.006049	-0.489755
O	2.560367	0.872765	2.300802
C	3.906950	1.183456	2.066583
O	-2.465316	0.927498	2.014158
B	-3.067201	0.538291	3.318939
Cl	-2.160418	-1.152227	3.781812
Cl	-2.584906	1.736776	4.550421
Cl	-4.835270	0.235858	3.168975
H	0.159377	0.213734	2.622323
H	3.481571	-0.112625	-0.044602
H	2.120918	-1.438655	-1.578505
H	-0.245626	-1.961332	-1.035725
H	-3.521484	-0.393949	0.866580
H	4.234330	1.762154	2.921318
H	4.514245	0.282024	1.990256
H	4.025393	1.781058	1.163178
B	-1.906210	-2.206271	2.012391
Cl	-3.522886	-2.849941	1.565403
Cl	-0.669666	-3.424237	2.407506

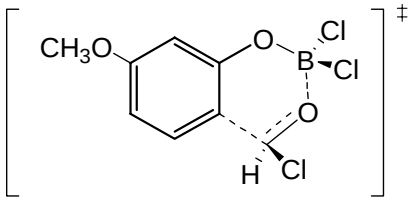


TS42b

Transition state **TS23**

E (hartree): -1940.937633, ν_i: -322.9 cm^{-1}

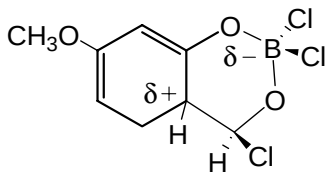
C	1.579537	1.578699	1.108785
C	2.804689	1.152673	0.710251
C	2.939211	-0.137627	0.152676
C	1.840092	-0.950132	-0.023152
C	0.580589	-0.500100	0.372245
C	0.425463	0.784609	0.931220
O	-0.441520	-1.265432	0.067390
C	-0.824902	1.250927	-0.807509
O	-1.850131	0.647350	-0.436064
B	-1.814368	-0.830058	0.041767
Cl	-2.567731	-0.789853	1.706488
Cl	-0.909173	2.959317	-0.884288
Cl	-2.736845	-1.814088	-1.164154
H	-0.461257	1.013080	1.499281
H	1.473374	2.545988	1.574474
H	3.690055	1.755024	0.827344
O	4.176152	-0.476075	-0.189814
H	1.902561	-1.924430	-0.474765
H	-0.109129	0.832344	-1.503196
C	4.409643	-1.755003	-0.728632
H	5.475991	-1.813847	-0.904349
H	4.112752	-2.533386	-0.028565
H	3.879513	-1.885227	-1.670360



TS23

Wheland intermediate **5**
E(hartree): -1940.974533

C	1.642090	-0.274704	-1.418016
C	0.473619	-0.161722	-0.661020
C	0.514663	-0.106740	0.821825
C	1.865706	-0.048408	1.407471
C	2.962184	-0.128526	0.658221
C	2.852320	-0.253657	-0.774810
O	-0.648844	-0.140562	-1.231079
B	-1.903792	0.131466	-0.390374
Cl	-3.163112	0.774010	-1.512382
Cl	-2.374207	-1.498935	0.362369
O	-1.541071	1.121776	0.575444
C	-0.444715	0.989196	1.336368
Cl	-0.840504	0.596291	3.064145
H	0.043726	-1.051884	1.130410
H	1.928699	0.041237	2.480938
H	3.955124	-0.106404	1.076004
O	4.010895	-0.334654	-1.378893
H	1.545311	-0.349526	-2.486388
H	0.069174	1.942422	1.407536
C	4.060067	-0.457590	-2.788071
H	5.110172	-0.512430	-3.040652
H	3.555010	-1.364778	-3.109357
H	3.611294	0.411229	-3.262461



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