Supporting Information

A halogen-bonding-catalyzed Michael addition reaction

Jan-Philipp Gliese, Stefan M. Huber*

1. General Information

Chemicals were purchased from *ABCR, Alfa Aesar, Fluorochem, Merck, Sigma-Aldrich* or *VWR*. Commercially available reagents were used without further purification. Dry DCM, ether and THF were received from a *MBRAUN MB SPS-800*. At first solvents were distilled, dried over 3 Å molecular sieve and finally dried on an alox column. Further dry solvents were dried over flame dried 4Å molecular sieve and stored under an argon atmosphere. The moisture content was determined with a *Karl Fischer Titroline®7500KF* trace. Dry DCM-d_2 for NMR-catalysis experiments were stored over molecular sieve 4Å. Other solvents were used after single distillation. *Merck TLC aluminium plates* (silica gel 60, F254) were used for thin layer chromatography (TLC). Detection of the substances was obtained by fluorescence detection under UV light (wavelength λ = 254 nm). Column chromatography was performed with silica gel (grain size 0.04-0.063 cm, *Merck* Si60).

^{1}H Nuclear magnetic resonance spectra (NMR-spectra) and ^{13}C NMR spectra were recorded with a *Bruker DPX-400* NMR or a *Aviii 300* spectrometer at 300 K. ^{19}F NMR spectra were recorded with a *Bruker DPX-250* NMR spectrometer at 300 K. Chemical shifts (δ) are given as parts per million (ppm) and refer to the shift of the hydrogen or carbon atoms in the used solvent. The following abbreviations were used for the assignment of the signals and their multiplicities: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), p (pentett), m (multiplet), dd (doublet of doublet), dddd (doublet of doublet of doublet of doublet).

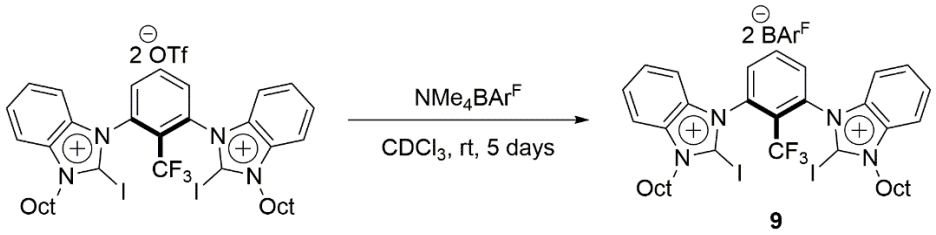
Mass spectra were recorded with either a *Bruker Daltonics Esquire 6000* instrument by using electron spray ionization (ESI) or a *VG Instruments Autospec / EBEE-Geometrie* by using Electron ionization (EI).

CHNS Elemental Analysis was performed with a *vario Micro cube* from *Elementar Analysentechnik*.

2. Synthesis Procedures

Tetramethylammoniumtetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TMA–BArF)[1] and the halogen bond donors **1**,[2] **2**,[1] **3**,[1] **4**,[1] **5**,[1] **6**,[1] **7**,[2] and **8** were synthesized according to literature-known procedures.

Synthesis of syn-1,3 -II-2-CF_3-BIm-Oct-$BArF_4$ (XB-Donor 9)



9

The reaction was performed in a flame dried flask and under an argon atmosphere. 500 mg (433 mmol, 1 eq.) of the triflate salt starting material was dissolved in 43.3 ml dry $CHCl_3$ to obtain a 10 mM solution. Subsequently, 1.22 g (1.3 mmol, 3 eq.) of $TMABAr^F{}_4$ were added. The suspension was stirred at r.t for 120 h. Following, the solvent was removed under reduced pressure and the residue was suspended in 20 ml diethyl ether and was sonicated for 6 min. The suspension was filtered off and the filter residue was washed with 10 ml cold diethyl ether. The solvent of the filtrate was removed and the residual was suspended in 10 ml chloroform. It was cooled to – 78 °C and the suspension was decanted. It was repeated four times. The solvent was removed and the residual was suspended in 5 ml pentane. The removal of the solvent yielded 0.30 g (0.13 mmol, 30 %) of **9** as a brown foam.

Chemical Formula: $C_{101}H_{69}B_2F_{51}I_2N_4$

Exact Mass: 582,30 g/mol

^{1}H NMR (300 MHz, Acetonitrile-d_3):

δ [ppm]= 8.75 (dd, ^3J = 9.2, 6.8 Hz, 1H, C$H_{arom.}$), 8.63 (d, ^3J = 7.7 Hz, 2H, C$H_{arom.}$), 8.37 (d, ^3J = 7.6 Hz, 2H, C$H_{arom.}$), 7.97 (d, ^3J = 7.7 Hz, 3H, C$H_{arom.}$), 7.80 (s, 19H, C$H_{arom.}$), 7.68 (s, 8H, C$H_{arom.}$), 4.98 (t, ^3J = 7.5 Hz, 4H, NCH_2), 1.41 (m, 24H, CH_2), 0.87 (d, ^3J = 6.4 Hz, 6H, CH_3).

^{13}C NMR (75 MHz, CD_2Cl_2)

δ [ppm]= 163.31, 162.65, 161.99, 161.34, 136.14, 135.37, 133.20, 130.17, 129.69, 129.65, 129.61, 129.56, 129.31, 129.27, 129.23, 129.19, 126.96, 123.35, 119.74, 118.12, 118.07, 118.02, 114.06, 113.46, 52.39, 32.12, 29.71, 29.46, 29.45, 27.08, 23.08, 14.29.

^{19}F NMR (250 MHz, Acetonitrile-d_3):

δ [ppm]= -56.20 (s, 3F, CF_3), -63.25 (s, 48F, CF_3) ppm.

ESI-MS:

m/z (+): calc. 428.08 $[M]^{2+}$, found 428.263 $[M]^{2+}$

m/z (-): calc. 863.07 $[M]^-$, found 862.68 $[M]^-$

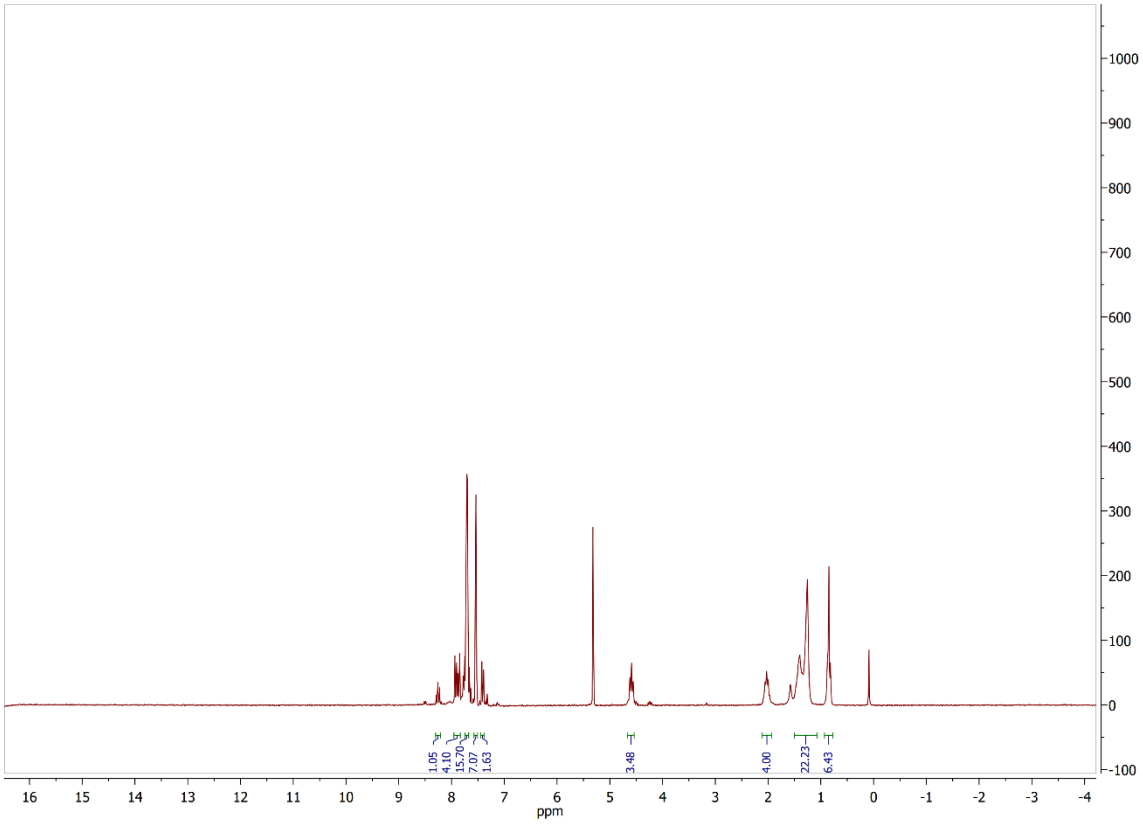


Figure S1: ^{1}H-NMR spectrum of XB-catalyst **9**

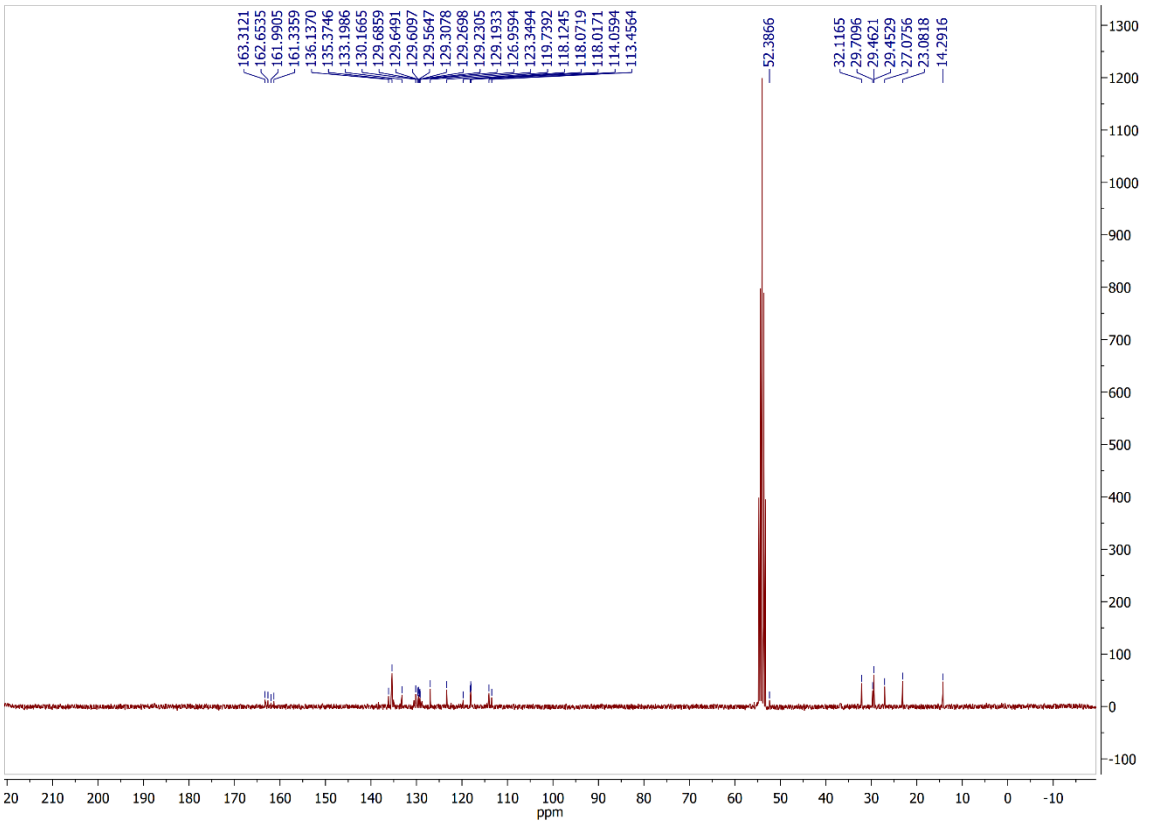


Figure S2: ^{13}C-NMR spectrum of XB-catalyst **9**

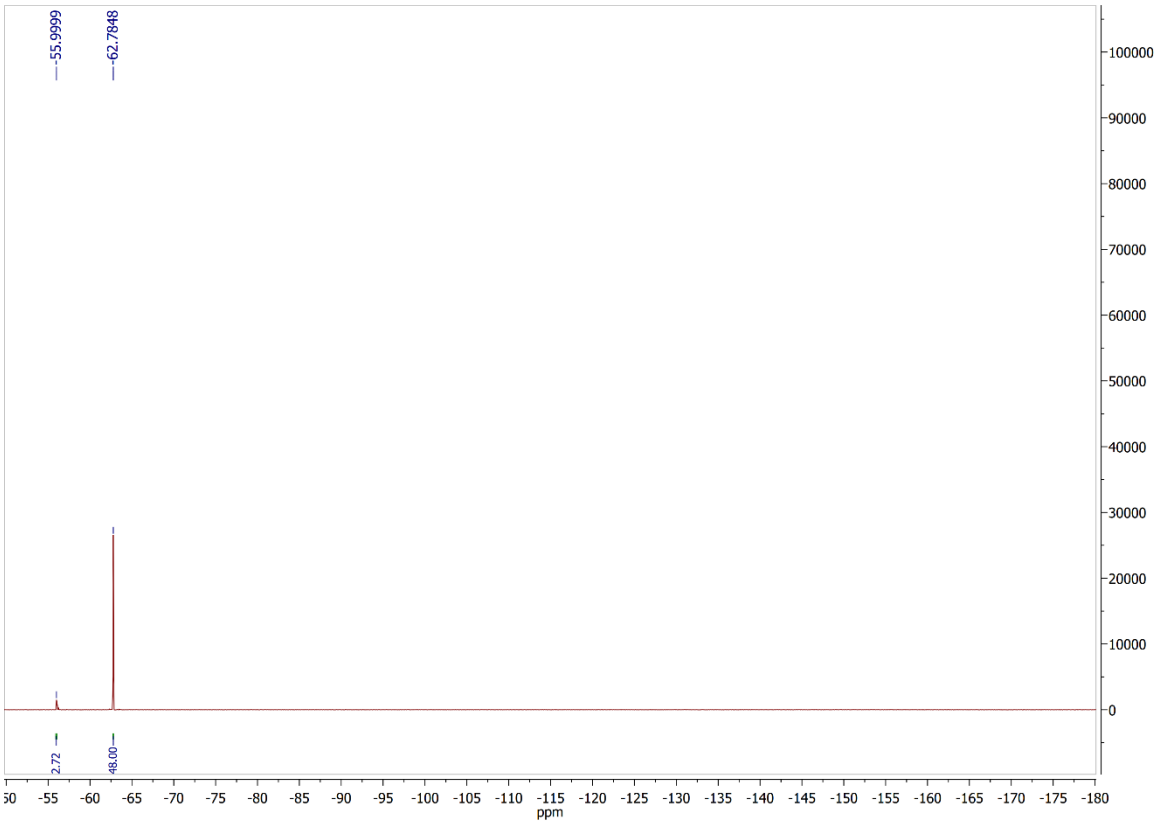


Figure S3: ^{19}F-NMR spectrum of XB-catalyst **9**

3. NMR-Experiments

All NMR-Experiments were recorded on the *AVII-300* spectrometer of *Bruker*. CD_2Cl_2 was dried over 3 Å molecular sieves and stored under argon-atmosphere. Water content was measured via Karl-Fischer-Titration and kept below 10 ppm in all measurements. All measurements were performed in Young-NMR-tubes which were dried overnight in a drying closet. 7.03 mg of indole **A** (60 µmol) and 12 µmol of the used XB catalyst were dissolved in 0.4 mL of dry CD_2Cl_2 and transferred into the Young-NMR-tube. Then, 0.2 mL of a 300 mM - solution of the Michael acceptor **B** in dry CD_2Cl_2 were added into the Young-NMR-tube. The offset time was determined by the difference of the injection time of the Michael acceptor solution and the acquisition time given in the .fid data set.

The conversions were determined by the integration of the terminal methyl group of the Michael acceptor **B** against the same methyl group in product **C**.

For the exclusion of bromine activation, a control experiment was performed with cyclohexene as bromine scavenger. Therefore, 1.2 µL (12 µmol) cyclohexene were added to the solution of indole **A** and bromine containing catalyst **3**. The results of this experiment are shown in Table S*4*.

Tabulated results of the Michael addition reaction

Table S1: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **1**

time [min]	Conversion [%]
00	0,0
09	0,1
72	0,1
231	0,1
311	0,1
450	0,1
560	0,1
671	0,1
1031	0,1
1392	0,1
1751	0,1
2112	0,1
2472	0,1
2830	0,1
3191	0,1
3550	0,1
3913	0,1
4272	0,1
5601	0,1
6379	0,1
6812	0,2

Table S2: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **2**

time [min]	Conversion [%]
00	0,0
08	0,7
73	1,0
253	1,7
435	2,2
614	2,9
797	3,4
973	3,9
1153	4,3
1336	4,7
2053	6,0
2782	7,1
3493	7,8
4225	8,4
4933	8,6
5654	9,1
6373	9,4
7094	9,6
7813	9,6
8534	9,8
9253	9,8
9973	9,8
10682	9,9
11403	10,0

Table S3: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **3**

time [min]	Conversion [%]
00	0,0
11	0,5
140	1,3
252	2,0
372	2,5
493	3,2
612	3,7
733	4,2
1032	5,4
1400	6,7
1752	8,0
2113	9,0
2473	10,1
2835	11,3
3193	12,1
3553	13,1
3913	14,1
4282	15,0
4635	14,9
4993	16,6
5594	18,1
6072	19,1
6554	20,3
7042	21,4
7512	22,4
7992	23,3
8472	24,1
8953	25,1

Table S4: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **3** and 20 mol-% of cyclohexene

time [min]	Conversion [%]
00	0,0
09	0,3
84	1,3
262	2,5
441	3,1
621	3,7
906	4,8
1567	6,3
2287	7,3
3012	8,2
3727	9,8
4446	11,3

Table S5: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **4**

time [min]	Conversion [%]
00	0,0
230	1,5
405	2,0
585	2,6
765	3,3
944	4,1
1124	4,9
1304	5,3
1902	8,1
2499	10,3
3103	13,1
3702	16,0
4306	17,0
4919	19,0
5504	20,5
6116	22,2
6716	24,3
7312	25,7
7913	27,1
8514	28,6
9162	30,2
9706	31,7
10305	32,0
11525	33,8
11540	33,9
12110	35,6

Table S6: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **5**

time [min]	Conversion [%]
00	0,0
08	0,3
130	2,3
249	3,8
369	5,0
502	6,2
609	6,8
799	7,9
848	8,6
969	8,9
1089	9,6
1228	9,7
1330	10,7
1449	10,9
2182	13,8
2889	15,1
3613	18,1
4329	18,9
5049	21,3
5769	23,3
6489	26,0
7209	26,9
7929	30,4
8649	32,0

Table S7: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **6**

time [min]	Conversion [%]
00	0,0
17	0,8
317	6,8
497	10,2
677	12,3
857	15,3
1037	18,9
1457	22,8
1842	27,2
2177	31,6
2537	33,6
2897	37,4
3257	40,2
3631	42,0
3977	45,8
4337	47,9
4697	50,2
5057	53,5
5417	53,7
5777	56,7
6137	57,8
6497	59,6
6857	60,4
7226	63,1
10005	69,1

Table S8: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **7**

time [min]	Conversion [%]
00	0,0
232	10,0
406	16,7
464	20,3
587	24,7
766	30,8
946	36,7
1063	38,7
1126	41,0
1306	46,5
1665	53,1
2264	62,8
2864	63,5
3464	68,8
4064	69,8
4673	70,5
5267	71,2
5877	72,0
6476	72,4
7065	72,5
7671	72,5
8264	73,7
8873	73,9
9464	74,2
10064	74,0
10663	75,0

Table S9: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **8**

time [min]	Conversion [%]
00	0,0
09	0,3
45	2,2
231	15,0
405	26,9
585	32,1
765	41,9
945	46,2
1125	49,1
1305	51,5
1910	57,0
2505	57,3
3111	61,1
3710	62,7
4314	61,9
4920	64,0
5505	63,6
6107	63,3
6708	65,0
7305	64,3
7905	64,0
8505	63,4
9154	66,5
9705	65,9
10304	61,0

Table S10: Conversion vs. time table of the Michael addition benchmark reaction with catalyst **9**

time [min]	Conversion [%]
00	0,0
08	21,7
188	58,0
374	63,0
555	64,9
728	65,8
908	66,4
1088	66,9
1819	67,9
2548	68,6
3269	69,3
3979	69,5
4699	69,9
5419	70,3
6139	70,6
6859	70,9
7579	71,2
8300	71,5

4. Determination of k_{rel} values

The k_{rel} values were determined by a linear fit from the kinetic plot (Figure S*4*). Therefore, the gradient between zero hours and the second or third measuring point of the corresponding conversion of **C** was determined for selected curves. For the linear fit a straight line was pasted.

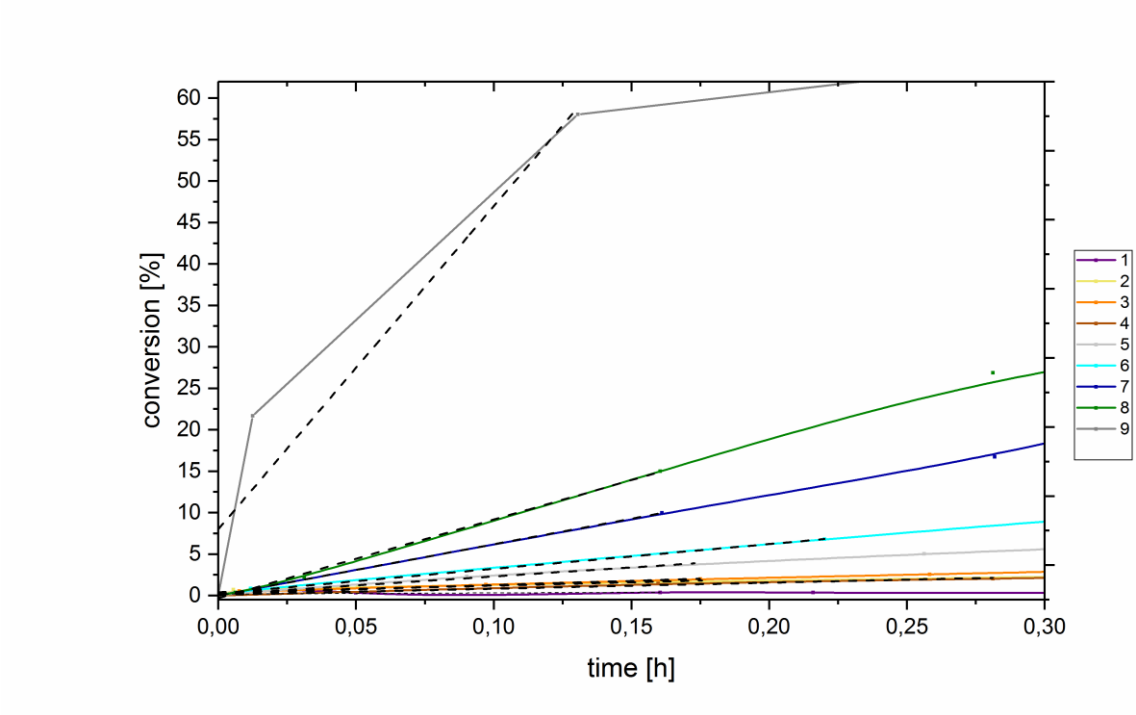


Figure S4: Linear fit of the conversion-time-curves for the determination of K_{rel}

5. DFT Calculations

DFT calculations were performed using the M06-2X functional with Grimme D3 dispersion corrections and the triple-zeta def2-TZVPP basis set (including the corresponding pseudpotential for iodine). For all corresponding literature references, see the research article. All geometries were fully optimized and the nature of the respective species was confirmed by frequency calculations (N_{imag} = 0 for minima, N_{imag} = 1 for transition states). The reaction paths of the transition states were further elucidated by slight distortion along the negative frequency and subsequent reoptimization, leading to starting materials and products. Subsequently, single point calculations using the SMD intrinsic solvation model with parameters for dichloromethane were performed with the optimized gas-phase energies. All energies mentioned in the paper refer to Gibbs free energies.

Coordinates and Gibbs free energies of all relevant minima and transition states are provided below.

Supporting Information

Uncatalyzed reaction: starting materials

G = -825.8544461 ht

C	-1.54691300	-2.01029400	-1.24593300
C	-0.44973500	-1.25962700	-1.20053300
H	-0.43654300	-0.28572800	-1.67407400
C	0.71808500	-1.68144600	-0.39364400
O	0.72455000	-2.70827400	0.25345000
H	-1.52857000	-2.96055500	-0.72074800
C	-2.80297100	-1.62276900	-1.94414000
H	-3.06450600	-2.35784000	-2.70804100
H	-3.63062000	-1.59648000	-1.23198400
H	-2.71465400	-0.64159400	-2.40782500
C	1.89804400	-0.75494400	-0.33113000
C	2.74191200	-0.84657200	0.77446100
C	2.16733800	0.18915900	-1.31776700
C	3.81896700	0.01371700	0.90948600
H	2.53665900	-1.60895700	1.51545000
C	3.26110800	1.03474200	-1.19602700
H	1.53161300	0.26518700	-2.18865900
C	4.07910500	0.95772900	-0.07778600
H	4.46101500	-0.05350600	1.77739100
H	3.46978100	1.75929900	-1.97140600
H	4.92231500	1.62785000	0.02300600
C	-2.27889800	0.78492800	0.69746400
C	-0.90967100	0.89043700	1.02828700
C	-0.08693300	1.88687900	0.50587500
C	-0.65634500	2.77599700	-0.38241200
C	-2.01415100	2.68492700	-0.73699800
C	-2.82719400	1.70654800	-0.20292700
C	-2.78491600	-0.36302300	1.38848000
C	-1.73929700	-0.90473400	2.07507200
H	0.96124600	1.94592600	0.77153900

H	-0.04694400	3.55866800	-0.81396300
H	-2.42510500	3.40068600	-1.43601600
H	-3.87225600	1.64715200	-0.47910000
H	-3.79290100	-0.74116400	1.37295100
H	-1.70008300	-1.78312000	2.69630900
H	0.30523200	-0.37210300	2.21449400
N	-0.61389800	-0.14677800	1.87630100

Uncatalyzed reaction: transition state

G = -825.8045571 ht

C	1.14478900	-1.94130200	0.79656400
C	-0.00095100	-1.12741900	1.06912300
H	0.02036200	-0.41538700	1.88060200
C	-1.04159000	-1.19708000	0.15358700
O	-0.94174400	-1.96666300	-0.84958800
H	0.86984000	-2.90413800	0.37319200
C	2.18182200	-2.04521100	1.89139500
H	1.77510100	-2.64988400	2.70245700
H	3.10246600	-2.51886300	1.54847800
H	2.42509200	-1.06437100	2.29876300
C	-2.25387500	-0.32058100	0.25588600
C	-3.36151500	-0.63027100	-0.53072300
C	-2.31247600	0.79915100	1.08516800
C	-4.50581800	0.15221200	-0.48245100
H	-3.30182600	-1.49691800	-1.17484400
C	-3.45399100	1.58520500	1.13060900
H	-1.45644600	1.07126000	1.68744700
C	-4.55608100	1.26297700	0.34888900
H	-5.36143100	-0.10550000	-1.09286700
H	-3.48261900	2.45414700	1.77483300
H	-5.44688900	1.87580300	0.38663400
C	2.44359200	0.04379000	-0.37219200

C	1.51341200	0.88979100	-0.98098700
C	1.50931500	2.26095300	-0.80249800
C	2.50161900	2.79110700	0.01127900
C	3.45434500	1.97142900	0.61270300
C	3.42749900	0.59240700	0.43301700
C	2.02926400	-1.34284300	-0.67582100
C	1.02552500	-1.19369400	-1.70035900
H	0.76914100	2.89252500	-1.27428600
H	2.53899800	3.85960800	0.17276300
H	4.22570200	2.41486300	1.22682700
H	4.16830600	-0.03639700	0.90857100
H	2.76774700	-2.12409700	-0.79811800
H	0.66348600	-1.92211500	-2.39973700
H	-0.08662400	0.43353200	-2.32890700
N	0.69631800	0.09507300	-1.79346000

Iodine-catalyzed reaction: starting materials

G = -1421.154314 ht

C	0.90692200	-1.19248200	1.98597000
C	1.86264900	-0.35615400	1.58530800
H	2.90156400	-0.65831500	1.63021300
C	1.53430500	0.93764700	0.96139100
I	-2.26318700	0.56438300	0.27190800
O	0.38817900	1.30158300	0.75194400
H	-0.12703500	-0.87478100	1.89548500
C	1.15943100	-2.55288800	2.53129300
H	0.66552800	-3.29749200	1.90301300
H	2.22381100	-2.77826100	2.56693400
H	0.73518200	-2.65181900	3.53233800
C	2.66438800	1.81123100	0.51547300
C	2.41999000	2.72724200	-0.50669500
C	3.93806500	1.72969900	1.07173500

C	3.44204800	3.52755800	-0.98896500
H	1.41689600	2.79852900	-0.90733000
C	4.95567800	2.54998600	0.60638300
H	4.14035800	1.03428000	1.87408800
C	4.71293000	3.43848600	-0.43163400
H	3.25028800	4.22585100	-1.79228600
H	5.94032500	2.48950300	1.04943600
H	5.51151900	4.06628200	-0.80354400
C	2.45633300	-2.51651000	-0.81410200
C	2.81978000	-1.22383500	-1.25314500
C	4.12235500	-0.73821700	-1.15643300
C	5.06570100	-1.56635900	-0.58327800
C	4.72633000	-2.85217000	-0.12605300
C	3.43860400	-3.33413200	-0.24215800
C	1.04852200	-2.65071400	-1.03915400
C	0.61789100	-1.47295800	-1.57388000
H	4.37743800	0.25766100	-1.49702000
H	6.08597500	-1.22057900	-0.48494400
H	5.49341700	-3.47333800	0.31611300
H	3.18829600	-4.32751600	0.10788200
H	0.43296900	-3.50896300	-0.83012800
H	-0.37130100	-1.16949200	-1.87127400
H	1.62288800	0.33030600	-2.05083300
N	1.67911400	-0.61403200	-1.71223000
I	-4.78773600	-0.09172000	-0.30814300

Iodine-catalyzed reaction: transition state

G = -1421.11424 ht

C	1.21380400	-1.55336900	0.93080000
C	1.63479300	-0.17771300	1.09067600
H	2.36901800	0.06160200	1.84619600
C	1.14894000	0.78288200	0.23307100

I	-2.13780800	0.03553900	-0.26665700
O	0.31574500	0.48476800	-0.70023600
H	0.18231800	-1.63464100	0.59674000
C	1.49810200	-2.45604700	2.11359900
H	1.28677700	-3.50333100	1.89762800
H	2.53412900	-2.36404700	2.43895500
H	0.86101700	-2.14638500	2.94199300
C	1.61135800	2.20270700	0.30350600
C	0.80232200	3.19190900	-0.25227600
C	2.82792600	2.57001600	0.87848000
C	1.18952400	4.52286000	-0.21411600
H	-0.13262100	2.89647200	-0.70910100
C	3.21912500	3.89998500	0.90882000
H	3.48219100	1.81079600	1.28672500
C	2.39877900	4.88096800	0.36657500
H	0.54663700	5.28273400	-0.63813500
H	4.16770400	4.17164300	1.35279900
H	2.70332200	5.91870300	0.39323400
C	3.46196500	-2.16841600	-0.27749900
C	3.83781400	-1.05319800	-1.02653700
C	5.10872800	-0.51118800	-1.00238700
C	6.03820500	-1.14453800	-0.18941000
C	5.69426100	-2.27076500	0.55700600
C	4.40402900	-2.78729800	0.52721600
C	2.00295900	-2.33596700	-0.45756200
C	1.68794800	-1.45126100	-1.55083900
H	5.36680400	0.36311900	-1.58372000
H	7.04757000	-0.76061700	-0.14029200
H	6.44558100	-2.74994800	1.16899700
H	4.14678600	-3.65826400	1.11465100
H	1.55083100	-3.31919800	-0.44970600
H	0.75961900	-1.34110400	-2.08228400
H	2.67038300	0.15508700	-2.36812400

N	2.71796400	-0.66698900	-1.78431100
I	-4.77206500	-0.47405400	0.14195500

Reaction catalyzed by simplified halogen bond donor 7: starting materials

G =-2181.479812 ht

C	2.48680800	-2.38450000	-0.37543000
C	2.98289500	-1.62419200	0.60651600
H	3.95163600	-1.84772900	1.03026300
C	2.25964900	-0.45440100	1.09458800
H	-3.52866200	0.47644700	0.60216100
C	-3.71140400	0.29635300	-0.44851300
C	-4.26778000	-0.15538700	-3.14893500
C	-4.04381800	-0.96895100	-0.90931000
C	-3.63809200	1.32516600	-1.37566600
C	-3.91392800	1.11396600	-2.71854800
C	-4.32588200	-1.20600900	-2.24605800
H	-3.84268200	1.93418400	-3.42028300
H	-4.57823600	-2.20481900	-2.57609200
C	-3.12735400	-2.58711200	0.74297000
N	-3.62211400	-3.62252700	1.42183800
C	-2.16565300	3.05982500	-0.36005300
N	-2.25206900	4.37939200	-0.18651800
I	-1.18496400	-1.89580000	0.78402200
I	-0.57833300	1.85066000	0.17369600
C	-2.86150000	-4.47574900	2.33671300
H	-3.54213200	-5.20700700	2.75991500
H	-2.43486100	-3.86763400	3.13018500
H	-2.07040200	-4.98226400	1.78957900
C	-1.21897000	5.22335700	0.41593900
H	-1.59730100	6.23924900	0.46032700
H	-0.32011200	5.19161500	-0.19464800
H	-0.99979700	4.86813200	1.41950400

O	1.06659200	-0.26420800	0.80195000
H	-4.48240400	-0.32977800	-4.19336400
H	-6.20951900	-2.56035400	-0.24601000
H	-5.08957500	3.66235800	-1.61220000
C	-5.27864300	-2.80543000	0.23285000
C	-4.95690200	-3.77447000	1.11702400
C	-4.11880600	3.75498200	-1.15956300
C	-3.45734700	4.82939000	-0.67811700
N	-4.13154500	-2.06679000	0.01202900
N	-3.30681600	2.65607000	-0.95081600
H	-5.55574200	-4.55086000	1.55857100
H	-3.73701000	5.86686400	-0.63575100
H	1.53056600	-2.10189800	-0.80506500
C	3.15502200	-3.58193100	-0.94243900
H	3.20253700	-3.50462600	-2.02913100
H	4.16391500	-3.70532500	-0.55528400
H	2.57232400	-4.47782600	-0.71282100
C	2.95372900	0.51335400	1.97525100
C	2.19382500	1.35306300	2.79276200
C	4.34657200	0.60455300	2.00431500
C	2.81490000	2.27077700	3.62149800
H	1.11679700	1.25064700	2.79827900
C	4.96539200	1.53831200	2.82018800
H	4.94868300	-0.03493300	1.37364400
C	4.20189000	2.36910200	3.63003400
H	2.22512100	2.90158300	4.27217300
H	6.04408500	1.61152600	2.83264300
H	4.68812800	3.08561100	4.27789300
C	4.46734200	-0.85432000	-2.52486600
C	4.86644900	0.09692600	-1.56456600
C	6.14802900	0.10869700	-1.01306500
C	7.02247400	-0.87663000	-1.42190900
C	6.64090900	-1.84537200	-2.36646000

C	5.38103400	-1.83819800	-2.92492300
C	3.11355200	-0.54106700	-2.88396900
C	2.75235900	0.55200500	-2.15471700
H	6.45422600	0.87412200	-0.31149900
H	8.02678800	-0.89517000	-1.02208600
H	7.35883900	-2.59382500	-2.67117600
H	5.10699800	-2.57214100	-3.67186900
H	2.50148000	-1.04636700	-3.61225100
H	1.83014500	1.10835800	-2.15584100
H	3.81720900	1.75606800	-0.76910600
N	3.79404100	0.93174900	-1.34318700

Reaction catalyzed by simplified halogen bond donor 7: transition state

G = -2181.445952 ht

C	2.97782100	-2.09727200	-0.89387100
C	3.13171300	-1.34132700	0.30711700
H	4.02195700	-1.48600000	0.90298000
C	2.20141700	-0.40313000	0.69607100
H	-3.35039800	0.26629500	0.73671400
C	-3.73585100	0.13498400	-0.26493500
C	-4.81070500	-0.19546800	-2.82092800
C	-4.08988500	-1.12175300	-0.73431800
C	-3.90097800	1.21813300	-1.11568400
C	-4.43680200	1.06652100	-2.38614800
C	-4.62857600	-1.29777500	-1.99995800
H	-4.54993000	1.92793100	-3.03062200
H	-4.89153500	-2.28996100	-2.34137000
C	-2.76769800	-2.75330300	0.60067800
N	-3.05778200	-3.86605900	1.27597100
C	-2.32930800	2.97092900	-0.29730500
N	-2.44090100	4.27131200	-0.02111900
I	-0.90089200	-1.86784200	0.36095000

I	-0.62203000	1.79356700	-0.12709600
C	-2.08236100	-4.70311300	1.97496300
H	-2.61763500	-5.51114700	2.46257500
H	-1.55867600	-4.10724800	2.71803300
H	-1.37248000	-5.11057900	1.25964900
C	-1.34834300	5.13283900	0.43039300
H	-1.76218200	6.10716700	0.66857300
H	-0.60876600	5.23072100	-0.36037800
H	-0.88906700	4.70146000	1.31610900
O	1.10076100	-0.20616200	0.03414700
H	-5.22760200	-0.32310500	-3.80944200
H	-5.97684800	-2.92525700	0.18422100
H	-5.46917800	3.48132500	-0.91483800
C	-4.95859800	-3.12062200	0.46825000
C	-4.41178200	-4.11176300	1.20426800
C	-4.43318600	3.60213200	-0.65445400
C	-3.73775300	4.68218000	-0.23930300
N	-3.92645600	-2.27601700	0.10371700
N	-3.54809800	2.54019100	-0.68024500
H	-4.86235000	-4.96113700	1.68561200
H	-4.04869100	5.69805100	-0.07362100
H	1.95670400	-2.16491200	-1.25590800
C	3.75077300	-3.38831700	-0.99618800
H	3.70644500	-3.82883100	-1.99029000
H	4.79278100	-3.24392600	-0.71472100
H	3.31646500	-4.09978100	-0.29177800
C	2.43326600	0.42075300	1.91442600
C	1.35639800	0.76546400	2.73075100
C	3.71180900	0.85647400	2.26235400
C	1.55299800	1.52315400	3.87481500
H	0.36585000	0.40718700	2.47993600
C	3.90625700	1.62759700	3.39852700
H	4.55512600	0.59863200	1.63370800

C	2.82841200	1.96110500	4.20771000
H	0.71556500	1.76376600	4.51591100
H	4.90073600	1.96535200	3.65600700
H	2.98313500	2.55341800	5.09899900
C	5.02070100	-0.71737400	-2.00033900
C	4.90750000	0.54974500	-1.42472000
C	5.96697000	1.21786900	-0.83385300
C	7.18785900	0.56373900	-0.83674300
C	7.33063600	-0.70184500	-1.41367300
C	6.25531300	-1.35552000	-1.99479200
C	3.67381600	-1.11359600	-2.41686000
C	2.88632200	0.05461400	-2.26611300
H	5.85311600	2.20183900	-0.39961200
H	8.04904900	1.04579600	-0.39621200
H	8.30290300	-1.17391600	-1.41260000
H	6.38177800	-2.32983600	-2.44701500
H	3.47016200	-1.83514400	-3.19299900
H	1.84664800	0.20454700	-2.50384800
H	3.19956300	1.83313900	-1.25800200
N	3.57712200	0.96396000	-1.60318500

6. References

(1) Jungbauer, S. H.; Huber, S. M., *J. Am. Chem. Soc.* **2015,** 137, 12110-20.
(2) Jungbauer, S. H.; Walter, S. M.; Schindler, S.; Rout, L.; Kniep, F.; Huber, S. M., *Chem. Comm.* **2014,** 50, 6281-4.