Supporting Information

Preorganization: A Powerful Tool in Intermolecular Halogen Bonding in Solution

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1. Experimental Section

1.1. Experimental Conditions

All experiments were carried out in flame dried Schlenk flasks under argon atmosphere and with dry solvents. Solvents used for chromatography were previously distilled. All used chemicals are commercially available and were used without further purification. Thin-layer chromatography was performed by using Merck TLC aluminium sheets (silica gel 60, F254). Column chromatography was performed with silica gel (grain size 0.04-0.063 cm, Merck Si60) at atmosphere pressure (1-1.5 atm using in some cases a hand pump). The corresponding solvents that were used as eluents as well as the $R_f$ values are listed at the corresponding experiment. Detection of the substances was obtained by fluorescence detection under UV light (wavelength $\lambda = 254$ nm).

1.2. Solvents

Dry DCM, ether and THF were received from a MBRAUN MB SPS-800. At first solvents were distilled, dried over 4 Å molecular sieve and finally dried on an Alox column. Further dry solvents were dried over flame dried 4Å molecular sieve. The moisture content was determined with a Karl Fischer Titroline®7500KF trace.

1.3. Chemicals

Chemicals were obtained from ABCR, Alfa Aesar, Carbolution, Merck, ChemPur, Sigma Aldrich or VWR. Commercially available reagents and starting materials were used without further purification (unless mentioned otherwise).

1.4. Analysis Methods

1.4.1. NMR Spectroscopy

$^1$H NMR spectra and $^{13}$C NMR spectra were recorded with an Avii 300 and a Bruker DRX 400 spectrometer at 298.5 K. $^{19}$F NMR spectra were recorded with a Bruker DPX-250 NMR spectrometer at 298.5 K. Peaks were referenced to residual $^1$H signals and $^{13}$C signals from the deuterated solvents and are reported in parts per million (ppm). For $^1$H NMR spectroscopically data, $^{13}$C NMR spectroscopically data and $^{19}$F NMR spectroscopically data, multiplicity, the relative integral and the coupling constant ($J$ in Hz) are indicated if possible.
1.4.2. **ATR-IR Measurements**

IR spectra were recorded with a *Shimadzu IR Affinity - 1S* spectrometer and are reported in $\nu = \text{cm}^{-1}$ and are indicated with w (weak), m (middle), s (strong) or vs (very strong).

1.4.3. **EI, ESI and MALDI-TOF Measurements**

Mass spectra were recorded with either a Bruker Daltonics Esquire 6000 instrument (ESI), a VG Instruments Autospec / EBEE-Geometrie (EI) or a *Ultraflex III* mass spectrometer from Bruker (MALDI-TOF).

1.4.4. **Elemental Analysis**

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

1.4.5. **Balance for Stock Solutions**

Starting materials for stock solutions were weight in on a *Mettler Toledo XSR 105 Dual Range* balance.

1.4.6. **ITC Measurements**

Extra dry acetonitrile was purchased from *Acros Organics* (< 10 ppm H$_2$O). Chloroform was dried over 3 Å molecular sieves and filtered over activated, basic aluminium oxide 90 (63–200 µm) to remove adventitious traces of hydrogen chloride. Methylene chloride was distilled, stored over 3 Å molecular sieves and finally dried on an alox column using a *MBRAUN MB SPS-800* solvent purification system. Commercially available tetraalkyl-ammonium halides were used without further purification. Synthesized compounds used in measurements were dried under high vacuum prior to use, weighed out and then solved in the respective amount of solvent to prepare stock solutions.
1.5. **Synthesis Procedures of known compounds**

1.5.1. **Compound TMABArF₄**

![Compound TMABArF₄](image1)

Compound TMABArF₄ was synthesized according to literature procedures.[1]

1.5.2. **Compound 9Im-OTf**

![Compound 9Im-OTf](image2)

Compound 9Im-OTf was synthesized according to literature procedures.[2]

1.5.3. **Compound 9ImBArF₄**

![Compound 9ImBArF₄](image3)

Compound 9ImBArF₄ was synthesized according to literature procedures.[3]
1.5.4. **Compound 9^{Blm-OTf}**

Compound 9^{Blm-OTf} was synthesized according to literature procedures.[4]

1.5.5. **Synthesis of 9^{BlmBarF4}**

Compound 9^{BlmBarF4} was synthesized according to literature procedures.[4]

1.5.6. **Compound 9^{Blm-CF3-OTf}**

Compound 9^{Blm-CF3-OTf} was synthesized according to literature procedures.[1]
1.5.7. **Compound $9^{\text{BlmBArF4}}$**

![Compound $9^{\text{Blm-CF3-BArF4}}$](image)

Compound $9^{\text{Blm-CF3-BArF4}}$ was synthesized according to literature procedures.[5]

1.6. **Synthesis of New Compounds**

1.6.1. **Synthesis of compound 7**

![Compound 7](image)

In a dry flamed 250 ml Schlenk flask 2,6-difluoro-1-trifluoromethanebenzene (6) (2.90 g, 15.9 mmol) was dissolved in 90 ml DMF and after 15 min. imidazole (2.71 g, 39.8 mmol, 2.5 eq.) and K$_3$PO$_4$ (33.8 g, 159 mmol, 10.0 eq.) were added. The white suspension was stirred for 30 min. at r.t. and for further 3 days at reflux temperature. The solvent was removed in high vacuum and the black residue was washed several times with aceton (8 $\times$ 100 ml). The combined organic filtrates were dried with Na$_2$SO$_4$ and the solvent was removed. Final purification by column chromatography (4 $\times$ 40 cm, DCM:MeOH 20:1, $R_f$: 0.48) yielded 7 as a red coloured solid (1.76 g, 6.34 mmol, 39.8%).

$R_f$ = 0.48 (DCM : MeOH)

$^1$H NMR (250 MHz, CDCl$_3$):

$\delta$ [ppm] = 7.77 (t, $^3$J = 8.3 Hz, 1H, $CH_{arom}$), 7.67 (s, 1H, NCH$_N$), 7.54 (d, $^3$J = 8.2 Hz, 2H, $CH_{arom}$), 7.22 (d, $^3$J = 14.1 Hz, 4H, NCH).

$^{13}$C NMR (63.9 MHz, CDCl$_3$):

$\delta$ [ppm] = 137.9 (s), 137.1 (s), 133.3 (s), 129.9-129.7 (d), 121.14 (s).
\(^{19}\text{F NMR (250 MHz, CDCl}_3\):} \\
\(\delta \text{ [ppm]} = -54.9 \text{ (s, 3F, CF}_3\).}

**ATR-IR:** 
\(\tilde{\nu} \text{ [cm}^{-1}] = 3143 \text{ (w), 3120 (w), 3103 (w), 1602 (m), 1589 (m), 1490 (s), 1465 (m), 1384 (m), 1309 (w), 1290 (s), 1273 (s), 1242 (s), 1205 (m), 1165 (m), 1128 (s), 1116 (s), 1107 (s), 1060 (m), 1039 (m), 1014 (m), 908 (s), 839 (m), 813 (m), 758 (s), 746 (s), 686 (w), 663 (s), 632 (m), 597 (w), 499 (w), 451 (w), 441 (w).}

**EI-MS (70 Ev):**  
\(m/z \text{ (%) } = 278.1 \text{ (100) [M]^+}, 211 \text{ (8) [(M – C}_3\text{H}_5\text{N}_2]^+}, 144 \text{ (8) [(M – C}_6\text{H}_6\text{N}_4]^+}, 75 \text{ (5) [(M – C}_7\text{H}_6\text{N}_4\text{F}_3]^+}.\)

**CHNS:**  
Calc. C = 56.12, H = 3.26, N = 20.14, found C = 55.55, H = 2.77, N = 19.64.

### 1.6.2. Synthesis of compound 8

![Chemical structure of compound 8](image)

In a dry flamed 250 ml Schlenk flask diisopropylamine (1.97 ml, 1.42 g, 14.0 mmol, 2.6 eq.) was suspended in 100 ml dry THF and cooled to 0 ℃. n-BuLi (8.09 ml, 828 mg, 1.6 M in hexane, 2.4 eq.) was slowly added and the solution was stirred for further 15 min. at 0 ℃ and was finally cooled to –78 ℃. Then a solution of \(7\) (1.50 g, 5.39 mmol, 1 eq.) in 20 ml dry THF was added over the course of 1 h and the mixture was stirred for 1 h –78 ℃. At –78 ℃ a 0.65M THF solution of iodine (3.28 g, 12.9 mmol) was added over the course of 30 min. and the mixture was stirred over night while warming up to r.t.. The solvent was removed, and the residue was taken up in 300 ml DCM. The organic phase was washed with saturated Na\(_2\)S\(_2\)O\(_3\) solution and dried over Na\(_2\)SO\(_4\). Purification by column chromatography (4 × 40 cm, DCM:MeOH 40:1.5, \(R_f\) 0.33) yielded \(8\) as yellow foam (700 mg, 1.32 mmol, 25%).  

\(R_f = 0.33 \text{ (DCM:MeOH).}\)
$^1$H NMR (250 MHz, CDCl$_3$):
$\delta$ [ppm] =  7.86 (t, $^2$J = 8.49 Hz, 1H, $CH_{arom}$), 7.57 (d, $^2$J = 8.49 Hz, 2H, $CH_{arom}$),
7.26-7.24 (m, 4H, NCH$_3$).

$^{13}$C NMR (100 MHz, CD$_3$CN):
$\delta$ [ppm] =  138.7 (s), 134.9 (s), 134.6-134.5 (d, $^2$J = 8.4 Hz), 133.3-133.2 (d, $^2$J = 5.29 Hz),
127.6 (s), 127.1 (s), 93.7 (s).

$^{19}$F NMR (250 MHz, CDCl$_3$):
$\delta$ [ppm] =  55.33 (s, 3F, $CF_3$).

ATR-IR:
$\tilde{\nu}$ [cm$^{-1}$] =  3076 (w), 1732 (w), 1598 (s), 1585 (s), 1506 (w), 1477 (vs), 1419 (vs), 1373 (w),
1352 (w), 1286 (vs), 1211 (m), 1170 (m), 1130 (vs), 1089 (s), 1041 (s), 966 (m),
904 (m), 848 (w), 813 (m), 765 (m), 736 (vs), 688 (w), 655 (s), 640 (w), 599 (m),
501 (m), 470 (w), 451 (m).

EI-MS (70 Ev):
$\text{m/z} (%) = 530.0 (100) \ [\text{M}^+]$, 404 (15) \ [(\text{M} - \text{I})^+]$.

GC / MS:
$t_R$: 33.5 min, $\text{m/z} = 530$.

CHNS:
Calc. C = 29.46, H = 1.33, N = 10.57, found C = 29.54, H = 2.01, N = 10.12.

1.6.3. $\textit{Synthesis of compound 9}^{Im-CF_3-OTf}$

In a dry flamed 25 ml Schlenk flask 8 (200 mg, 0.38 mmol) was dissolved in 7.5 ml DCM
($\approx$0.05 M) and subsequently octyltriflate (348 $\mu$L, 417 mg, 1.51 mmol, 4eq.) was added. The
mixture was stirred for 3 days at r.t. while a solid precipitated.
The solvent was removed and the crude, solid residue was suspended in MeOH. Addition of ether precipitated $\text{9}^\text{Im-CF3-OTf}$ as white solid (207 mg, 191 $\mu$mol, 51%).

$^1$H NMR (250 MHz, CDCl$_3$):
$\delta$ [ppm] = 8.25 (m, 1H, $CH$$_\text{arom.}$), 7.95 (m, 4H, NCH), 7.87 (br. d, 2H, $CH$$_\text{arom.}$), 4.25 (t, $J$ = 7.72 Hz, 4H, $CH_2$), 2.2 (br. s, 4H, $CH_2$), 1.30 (m, 20H, $CH_2$), 0.89 (t, $J$ = 6.51 Hz, 6H, $CH_3$).

$^{13}$C NMR (100 MHz, CD$_3$CN):
$\delta$ [ppm] = 137.4 (s), 136.6 (s), 135.4 (s), 128.7 (s), 127.3 (s), 118.3 (s), 103.86 (s), 54.54 (s), 32.4 (s), 30.3 (s), 29.9 (s), 29.6 (s), 26.7 (s), 23.3 (s), 14.7 (s).

$^{19}$F NMR (250 MHz, CD$_3$CN):
$\delta$ [ppm] = $-55.52$ (p), $-79.27$ (s).

ATR-IR:
$\tilde{\nu}$ [cm$^{-1}$] = 3128 (w), 3105 (w), 2927 (m), 2858 (m), 1602 (w), 1587 (w), 1564 (w), 1490 (w), 1444 (w), 1413 (w), 1280 (s), 1251 (vs), 1222 (vs), 1157 (s), 1139 (s), 1095 (m), 1041 (w), 912 (w), 817 (w), 754 (m), 723 (w), 661 (w), 632 (s), 597 (w), 572 (m), 514 (m), 451 (m).

ESI-MS:
$m / z$ (+) = calc. 754.92[M$^+$], found 642.7 [M$^+$ – Oct], 377 [M$^{2+}$], 265 (8) [(M$^{2+}$ – C$_{16}$H$_{34}$)], 192 [M$^{4+}$ + Li].

$m / z$ (-) = calc. 149.08 [M$^-$], found 148.73 [M$^-$].

CHNS:
Calc. C = 34.39, H = 3.45, N = 5.18, S = 5.92; found C = 33.38, H = 4.01, N = 5.24, S = 6.54.

1.6.4. **Synthesis of compound $\text{9}^\text{Im-CF3-BArF4}$**
In a dry flamed 25 ml Schlenk flask 9\(^{\text{In}-\text{CF}_3}\)-OTf, (120 mg, 0.11 mmol) was dissolved in 20 ml dry chloroform and subsequently TMABAr\(^F_4\) was added in one portion. The mixture was stirred at rt for three days. Next the solvent was removed, and the crude residue was taken up in 15 ml ether, cooled to 0 °C and the precipitating TMAOTf was filtered of. The solution was evaporated, and the crude was dissolved in 10 ml chloroform and cooled to -10 °C. The precipitating TMABAR\(^F_4\) was filtered of and the solution was evaporated to yield 9\(^{\text{In}-\text{CF}_3}\)-BAr\(^F_4\) as slightly reddish solid (216 mg, 0.09 mmol, 77%).

\(^1\)H NMR (300 MHz, Methylene Chloride-d2):
\[\delta \ [ppm] = 8.11 \ (m, 1H, CH\text{arom.}), 7.81 \ (d, J = 8.2 \ Hz, 2H, CH\text{arom.}), 7.72 \ (d, J = 2.30 \ Hz, 19H, CH\text{arom.}), 7.65 \ (d, J = 2.3 \ Hz, 1H, CH\text{arom.}), 7.57 \ (s, 8H, CH\text{arom.}), 4.32 \ (m, 4H, CH\text{2}), 1.94 \ (t, J = 7.6 \ Hz, 4H, CH\text{2}), 1.28 \ (m, 20H, CH\text{2}), 0.86 \ (t, J = 6.63 \ Hz, 6H, CH\text{3}).\]

\(^{13}\)C NMR (75 MHz, Methylene Chloride-d2):
\[\delta \ [ppm] = 161.71 \ (q, J = 99.6, 49.8 \ Hz), 134.85 \ (d, J = 11.2 \ Hz), 128.91 \ (m), 126.54 \ (d, J = 26.1 \ Hz), 122.76 \ (s), 119.15 \ (s), 117.51 \ (p, J = 4.0 \ Hz), 54.98 \ (s), 31.49 \ (s), 29.57 \ (s), 28.75 \ (d, J = 9.6 \ Hz), 25.99 \ (s), 22.48 \ (s), 13.67 \ (s).\]

\(^{19}\)F NMR (250 MHz, CD\text{3}CN):
\[\delta \ [ppm] = \]

ATR-IR:
\[\tilde{\nu} \ [\text{cm}^{-1}] = 2933 \ (w), 2864 \ (w). 1610 \ (m), 1489 \ (m), 1469 \ (m), 1354 \ (vs), 1271 \ (vs), 1109 \ (vs), 945 \ (w), 933 \ (w), 887 \ (s), 839 \ (s), 817 \ (w), 779 \ (w), 744 \ (w), 709 \ (vs), 680 \ (vs), 669 \ (vs), 580 \ (w), 503 \ (w), 449 \ (m).\]

ESI-MS:
\[m/z \ (+) = \text{calc.} 754.92 \ [\text{M}^+], \text{found} 762.94 \ [\text{M}^+\text{+Li}]\]

\[m/z \ (-) = \text{calc.} 863.06 \ [\text{M}^+], \text{found} 862.74 \ [\text{M}].\]

CHNS:
Calc. C = 44.99, H = 2.64, N = 2.26, S = /; found C = 44.29, H = 2.42, N = 1.49, S = /.
2. **Determination of $k_{rel}$ values**

$k_{rel}$ was determined by a linear fit from the kinetic plot each reaction. Therefore, the gradient between zero hours and $x$ h (see below) and the corresponding yield of the product was determined for selected experiments. All used values for the slope determination are rounded to $x$ h and the next highest number.

2.1. **Activation of benzhydryl bromide (10).**

![Figure 1](image-url)  
*Figure 1. Conversion vs. time profile for the activation of benzhydryl bromide (10) in presence of different halogen bond activators. The conversion was determined by integration of selected signals of the $^1H$ NMR spectrum after defined periods.*

| Compound          | Time / h | ~Yield / % | ~Slope = $\frac{\Delta y}{\Delta x}$ | $k_{rel}$ |
|-------------------|----------|------------|---------------------------------------|-----------|
| Blank             | 0.6      | 0.042      | 0.07                                  | 1         |
| 9Blm-CF$_3$-OTf   | 0.5      | 5.2        | 10.4                                  | 150       |
| 9Blm-OTf          | 0.6      | 9.5        | 14.2                                  | 225       |
| 9Im-OTf           | 0.6      | 24.7       | 37.8                                  | 540       |
| 9Im-CF$_3$-OTf    | 0.42     | 29.4       | 72                                    | 1000      |

| 9Blm-CF$_3$-OTf | Blank | 0.6 | 0.042 | 0.07 | 1 |
|-----------------|-------|-----|-------|------|---|
| 9Blm-OTf        | 0.5   | 5.2 | 10.4  | 150  |  |
| 9Im-OTf         | 0.6   | 9.5 | 14.2  | 225  |  |
| 9Blm-OTf        | 0.65  | 24.7| 37.8  | 540  |  |
| 9Im-CF$_3$-OTf  | 0.42  | 29.4| 72    | 1000 |  |
2.2. *Friedel-Crafts reaction of benzhydryl bromide (10) and 1,3,5.trimethoxy benzene (12).*

![Conversion vs. time profile for the acylation of trimethoxy benzene (12) with benzhydryl bromide (10) in presence of different halogen bond activators. The conversion was determined by integration of selected signals of the $^1$H NMR spectrum after defined periods. $9\text{Im-CF}_3\text{-OTf}$ could not be tested in the reaction due to solubility issues.](image)

**Table 2:** Determination of $k_{rel}$ values.

| Compound          | Time / h | ~Yield / % | ~Slope $= \frac{\Delta y}{\Delta x}$ | $k_{rel}$ |
|-------------------|----------|------------|---------------------------------------|-----------|
| Blank             | 0.6      | 0.14       | 0.23                                  | 1         |
| $9\text{Im-OTf}$ | 0.5      | 24.3       | 48.6                                  | 210       |
| $9\text{BIm-OTf}$| 0.55     | 32.2       | 58.5                                  | 250       |
| $9\text{BIm-CF}_3\text{-OTf}$ | 0.6 | 39.3       | 65.5                                  | 290       |
2.3. **Diels Alder reaction of Cp (17) and MVK (18).**

![Graph showing conversion vs. time profile](image)

**Figure 3.** Conversion vs. time profile for the Diels Alder reaction of cyclopentadiene (17) and methyl vinyl ketone (18) in presence of different halogen bond activators. The conversion was determined by integration of selected signals of the $^1$H NMR spectrum after defined periods.

| Compound                  | Time / h | ~Yield / % | ~Slope $= \frac{\Delta y}{\Delta x}$ | $k_{rel}$ |
|---------------------------|----------|------------|----------------------------------------|-----------|
| Blank                     | 0.27     | 4.8        | 18                                     | 1         |
| $9_{\text{Im-CF}_3-\text{BArF}_4}$ | 0.25     | 8          | 40                                     | 2         |
| $9_{\text{Im-BArF}_4}$     | 0.23     | 7.1        | 31                                     | 2         |
| $9_{\text{BIm-BArF}_4}$    | 0.1      | 10.9       | 109                                    | 6         |
| $9_{\text{BIm-CF}_3-\text{BArF}_4}$ | 0.05     | 21         | 420                                    | 23        |

**Table 3:** Determination of $k_{rel}$ values.
2.4. *Michael addition reaction between indole (20) and trans-β-crotonophenone (21).*

Figure 4. Conversion vs. time profile for the Michael addition reaction of indole (20) and trans-β-crotonophenone (21) in presence of different halogen bond activators. The conversion was determined by integration of selected signals of the $^1$H NMR spectrum after defined periods.

Table 4: Determination of $k_{rel}$ values.

| Compound          | Time / h | ~Yield / % | ~Slope = $\frac{\Delta y}{\Delta x}$ | $k_{rel}$ |
|-------------------|----------|------------|--------------------------------------|-----------|
| Blank             | 1        | 0.037      | 0.037                                | 1         |
| $g_{\text{Im-CF3-BAr4}}$ | 1.02      | 12.4       | 12.0                                 | 325       |
| $g_{\text{Im-BAr4}}$     | 1.01      | 5.52       | 5.52                                 | 150       |
| $g_{\text{Im-BAr4}}$      | 0.8       | 7          | 8.8                                  | 240       |
| $g_{\text{Blm-CF3-BAr4}}$ | 0.8       | 36         | 45                                   | 1200      |
2.5. *Nitro-Michael addition reaction between 5-methoxyindole (23) and trans-β-nitrostyrene (24).*

![Graph depicting conversion vs. time profile for nitro Michael addition reaction](image)

*Figure 5.* Conversion vs. time profile for the nitro Michael addition reaction of 5-methoxyindole (23) and trans-β-nitrostyrene (24) in presence of different halogen bond activators. The conversion was determined by integration of selected signals of the $^1H$ NMR spectrum after defined periods.

**Table 5: Determination of $k_{rel}$ values.**

| Compound          | Time / h | Yield / % | Slope = ($\Delta Y$/$\Delta X$) | $k_{rel}$ |
|-------------------|----------|-----------|----------------------------------|-----------|
| Blank             | 6        | 0.075     | 0.0125                           | 1         |
| 9Im-CF3-BArF4     | 6        | 1.6       | 0.27                             | 20        |
| 9Im-BArF4         | 6        | 0.900     | 0.15                             | 12        |
| 9BIm-BArF4        | 6.2      | 3.6       | 0.6                              | 55        |
| 9BIm-CF3-BArF4    | 6.6      | 7.72      | 1.2                              | 100       |
3. **ITC Titration Experiments**

3.1. **Experimental Setup and ITC Measurements**

ITC measurements were performed on a MicroCal VP-ITC system from GE Healthcare using a reference power of 34.7 µcal/s, a filter period of 2 s, a stirrer speed of 329 rpm, an injection volume of 8.0 µL of the guest solution (ammonium salt) and a time spacing of 160 s between injections. All titrations were performed at a jacket temperature of either 30 °C (303.15 K) when using acetonitrile or chloroform as solvent or 20 °C (293.15 K) when using methylene chloride as solvent. Evaluation of the data sets was performed using Origin 7 with manual integral correction and, if necessary, a subtraction of straight lines. In the following Table 5, the host and guest used, their respective stock solution concentration and the experimental setup is shown.

**Table 5**: Host and Guest, their respective concentration as well as the solvents used in ITC experiments.

| Entry | Host (XB Donor) | Guest | solvent | c[syringe / mM] | c[cell / mM] |
|-------|----------------|-------|---------|----------------|-------------|
| 1     | 9^{Hm}-CF3-OTf | (nBu)$_4$NCl | MeCN     | 10.0           | 1.00        |
| 2     | 9^{Hm}-CF3-OTf | (nBu)$_4$NCl* | MeCN     | 10.0           | 1.00        |
| 3     | 9^{Hm}-CF3-OTf | (nBu)$_4$NBr | MeCN     | 10.0           | 1.00        |
| 4     | 9^{Hm}-CF3-OTf | (nBu)$_4$NI | MeCN     | 10.0           | 1.00        |
| 5     | 9^{Hm}-OTf     | (nBu)$_4$NCl | MeCN     | 10.0           | 1.00        |
| 6     | 9^{Hm}-OTf     | (nBu)$_4$NBr | MeCN     | 10.0           | 1.03        |
| 7     | 9^{Hm}-OTf     | (nBu)$_4$NI | MeCN     | 10.0           | 1.00        |
| 8     | 9^{Im}-CF3-OTf | (nBu)$_4$NCl | MeCN     | 10.0           | 1.00        |
| 9     | 9^{Im}-CF3-OTf | (nBu)$_4$NBr | MeCN     | 10.0           | 1.00        |
| 10    | 9^{Im}-CF3-OTf | (nBu)$_4$NI | MeCN     | 10.0           | 1.00        |
| 11    | 9^{Im}-OTf     | (nBu)$_4$NCl | MeCN     | 10.0           | 1.00        |
| 12    | 9^{Im}-OTf     | (nBu)$_4$NBr | MeCN     | 10.0           | 1.00        |
| 13    | 9^{Im}-OTf     | (nBu)$_4$NI | MeCN     | 10.0           | 1.00        |
Table 5 (continuation): Host and Guest, their respective concentration as well as the solvents used in ITC experiments.

| Entry | Catalyst          | Guest          | solvent | c[syringe / mM] | c[cell / mM] |
|-------|-------------------|----------------|---------|-----------------|--------------|
| 14    | 9BIm-CF3-OTf      | (nOct)₄NCl    | CHCl₃   | 10.0            | 1.00         |
| 15    | 9BIm-CF3-OTf      | (nOct)₄NBr    | CHCl₃   | 10.0            | 1.00         |
| 16    | 9BIm-CF3-OTf      | (nBu)₄NI      | CHCl₃   | 10.0            | 1.00         |
| 17    | 9BIm-OTf          | (nOct)₄NCl    | CHCl₃   | 5.00            | 0.50         |
| 18    | 9BIm-OTf          | (nOct)₄NBr    | CHCl₃   | 5.00            | 0.50         |
| 19    | 9BIm-OTf          | (nBu)₄NI      | CHCl₃   | 10.0            | 1.00         |
| 20    | 9Im-OTf           | (nOct)₄NCl    | CHCl₃   | 10.0            | 1.00         |
| 21    | 9Im-OTf           | (nOct)₄NBr    | CHCl₃   | 10.0            | 1.00         |
| 22    | 9Im-OTf           | (nBu)₄NI      | CHCl₃   | 10.0            | 1.00         |
| 23    | 9BIm-CF3-OTf      | (nOct)₄NCl    | CH₂Cl₂  | 10.0            | 1.00         |
| 24    | 9BIm-CF3-OTf      | (nOct)₄NBr    | CH₂Cl₂  | 10.0            | 1.00         |
| 25    | 9BIm-CF3-OTf      | (nBu)₄NI      | CH₂Cl₂  | 10.0            | 1.00         |
| 26    | 9BIm-OTf          | (nOct)₄NCl    | CH₂Cl₂  | 10.0            | 1.00         |
| 27    | 9BIm-OTf          | (nOct)₄NBr    | CH₂Cl₂  | 10.0            | 1.00         |
| 28    | 9BIm-OTf          | (nBu)₄NI      | CH₂Cl₂  | 10.0            | 1.00         |
| 29    | 9Im-CF3-OTf       | (nOct)₄NCl    | CH₂Cl₂  | 5.56            | 0.51         |
| 30    | 9Im-CF3-OTf       | (nOct)₄NBr    | CH₂Cl₂  | 5.00            | 0.50         |
| 31    | 9Im-CF3-OTf       | (nBu)₄NI      | CH₂Cl₂  | 5.00            | 0.50         |
| 32    | 9Im-OTf           | (nOct)₄NCl    | CH₂Cl₂  | 10.0            | 1.00         |
| 33    | 9Im-OTf           | (nOct)₄NBr    | CH₂Cl₂  | 10.0            | 1.00         |
| 34    | 9Im-OTf           | (nBu)₄NI      | CH₂Cl₂  | 10.0            | 1.00         |

*(nBu)₄Cl was dried in a desiccator using silica gel as a drying agent prior to use. The respective solution of (nBu)₄Cl was prepared under Argon using schlenk techniques.
The plots of the raw ITC data and the respective titration curves are shown on the following pages. Figure 7 exemplifies the legend that contains thermodynamic data of the measurements in every ITC curve. Figures 8–40 show the ITC curves and fittings to titrations mentioned in table 5.

**Figure 7:** Exemplary legend for the thermodynamic data of ITC experiments.

| Data: MV3E334Cl_NDH |
|---------------------|
| Model: OneSites |
| $\chi^2$ |
| Degrees of freedom |
| Chi^2/DoF = 1020 |
| Molarity ratio: |
| N | 1.08 $\pm 9.76E-4$ Sites |
| Binding Constant: |
| K | 1.23E6 $\pm 6.98E4$ M$^{-1}$ |
| Enthalpy: |
| $\Delta H$ | -4018 $\pm 8.589$ cal/mol |
| Entropy: |
| $\Delta S$ | 14.6 cal/mol/deg |
Figure 8: ITC curve related to titration entry 1, table 5.
Figure 9: ITC curve related to titration entry 2, table 5.
Figure 10: ITC curve related to titration entry 3, table 5.
Figure 11: ITC curve related to titration entry 4, table 5.
Figure 12: ITC curve related to titration entry 5, table 5.
Figure 13: ITC curve related to titration entry 6, table 5.
Figure 14: ITC curve related to titration entry 7, table 5.
Figure 15: ITC curve related to titration entry 8, table 5.
Figure 16: ITC curve related to titration entry 9, table 5.
Figure 17: ITC curve related to titration entry 10, table 5.
Figure 18: ITC curve related to titration entry 11, table 5.

Data: MV3E327CI_NDH
Model: OneSites
Chi²/DoF = 1683
N 1.10 ±0.00182 Sites
K 5.7E5 ±1.2E4 M⁻¹
ΔH -3317 ±11.03 cal/mol
ΔS 15.4 cal/mol/deg
Figure 19: ITC curve related to titration entry 12, table 5.
Figure 20: ITC curve related to titration entry 13, table 5.
Figure 21: ITC curve related to titration entry 14, table 5.
Figure 22: ITC curve related to titration entry 15, table 5.
Figure 23: ITC curve related to titration entry 16, table 5.
Figure 24: ITC curve related to titration entry 17, table 5.
Figure 25: ITC curve related to titration entry 18, table 5.
Figure 26: ITC curve related to titration entry 19, table 5.
Figure 27: ITC curve related to titration entry 20, table 5.
Figure 28: ITC curve related to titration entry 21, table 5.
Figure 29: ITC curve related to titration entry 22, table 5.
Figure 30: ITC curve related to titration entry 23, table 5.
Figure 31: ITC curve related to titration entry 24, table 5.
Figure 32: ITC curve related to titration entry 25, table 5.
Figure 33: ITC curve related to titration entry 26, table 5.
Figure 34: ITC curve related to titration entry 27, table 5.
Figure 35: ITC curve related to titration entry 28, table 5.
Figure 36: ITC curve related to titration entry 29, table 5.
Figure 37: ITC curve related to titration entry 30, table 5.
Figure 38: ITC curve related to titration entry 31, table 5.
Figure 39: ITC curve related to titration entry 32, table 5.
Figure 40: ITC curve related to titration entry 33, table 5.
Figure 41: ITC curve related to titration entry 34, table 5.
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