Balancing Donor-Acceptor and Dispersion Effects in Heavy Main Group Element $\pi$ Interactions: Effect of Substituents on the Pnictogen-$\pi$ Arene Interaction

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Figure S2. Potential energy curves (in kJ mol\(^{-1}\)) for the interaction potentials of Bi(CH\(_3\))\(_3\) adduct with selected benzene derivatives calculated at the PBE-D3/def2-QZVP level of theory.
| Molecule | Polarizability (a.u.) |
|----------|----------------------|
| CF$_3$   | 84.3                 |
| OCHO     | 90.3                 |
| NO$_2$   | 88.7                 |
| OH       | 75.4                 |
| CHO      | 88.1                 |
| F        | 69.6                 |
| NH$_2$   | 82.0                 |
| benzene  | 69.0                 |

Table S4. NBO partial charges (a.u.) for idealized BiCl$_3$ adducts with substituted benzenes computed at the PBE-D3/def2-QZVP level of theory.

| BiCl$_3$ adduct with | Σq(BiCl$_3$)(adduct) | q(Bi)(adduct) | Δq(Bi) | Δq(Cl$_3$) |
|----------------------|----------------------|---------------|--------|------------|
| NO$_2$               | -0.039               | 1.273         | -0.001 | -0.039     |
| CF$_3$               | -0.045               | 1.286         | 0.012  | -0.057     |
| OCHO                 | -0.059               | 1.287         | 0.013  | -0.072     |
| benzene              | -0.059               | 1.289         | 0.015  | -0.074     |
| OH                   | -0.072               | 1.290         | 0.016  | -0.088     |
| NH$_2$               | -0.089               | 1.292         | 0.018  | -0.107     |
| 3NO$_2$              | -0.009               | 1.231         | -0.043 | 0.034      |
| 3CF$_3$              | -0.019               | 1.263         | -0.011 | -0.009     |
| 3OCHO                | -0.041               | 1.279         | 0.005  | -0.046     |
| 3OH                  | -0.080               | 1.283         | 0.009  | -0.089     |
| 3NH$_2$              | -0.132               | 1.284         | 0.011  | -0.143     |

Δq=q(adduct)-q(free). q – partial charge on a specific atom(s), Δq – difference between partial charge of an atom in BiCl$_3$ adduct and in an unbound BiCl$_3$ molecule.
Table S5. NBO partial charges (a.u.) for idealized MCl$_3$ adducts with selected substituted benzenes computed at the PBE-D3/def2-QZVP level of theory.

| Adduct | $\Sigma q$(MCl$_3$(adduct)) | q(M)(adduct) | $\Delta q$(M) | $\Delta q$(Cl$_3$) |
|--------|-----------------------------|--------------|---------------|------------------|
| AsCl$_3$···NO$_2$C$_6$H$_5$ | -0.020 | 0.862 | 0.007 | -0.027 |
| SbCl$_3$···NO$_2$C$_6$H$_5$ | -0.023 | 1.177 | -0.002 | -0.021 |
| BiCl$_3$···NO$_2$C$_6$H$_5$ | -0.039 | 1.273 | -0.001 | -0.038 |
| AsCl$_3$···C$_6$H$_6$ | -0.032 | 0.877 | 0.022 | -0.054 |
| SbCl$_3$···C$_6$H$_6$ | -0.038 | 1.195 | 0.016 | -0.055 |
| BiCl$_3$···C$_6$H$_6$ | -0.059 | 1.289 | 0.015 | -0.074 |
| AsCl$_3$···NH$_2$C$_6$H$_5$ | -0.055 | 0.888 | 0.033 | -0.088 |
| SbCl$_3$···NH$_2$C$_6$H$_5$ | -0.063 | 1.196 | 0.018 | -0.081 |
| BiCl$_3$···NH$_2$C$_6$H$_5$ | -0.089 | 1.292 | 0.018 | -0.107 |

$\Delta q = q$(adduct)−q(free)
Figure S6. Dispersion energy plots for equilibrium structures of Bi···π arene adducts computed at the DLPNO-CCSD(T)/cc-pVQZ (cc-pwCVQZ-PP for bismuth) level of theory with tightPNO settings.
Table S7. NBO partial charges (a.u.) for relaxed Bi···π arene adducts computed at the PBE-D3/def2-QZVP level of theory.

| BiCl₃ adduct with | Σq(BiCl₃)(adduct) | q(Bi) (adduct) | Δq(Bi) | Δq(Cl) |
|------------------|-------------------|---------------|--------|--------|
| NO₂              | -0.032            | 1.283         | 0.009  | -0.041 |
| CN               | -0.032            | 1.287         | 0.013  | -0.045 |
| CF₃              | -0.037            | 1.296         | 0.022  | -0.059 |
| CHO              | -0.039            | 1.292         | 0.019  | -0.057 |
| F                | -0.058            | 1.287         | 0.013  | -0.071 |
| Cl               | -0.050            | 1.292         | 0.018  | -0.068 |
| OCHO             | -0.056            | 1.290         | 0.016  | -0.072 |
| C₂H₃             | -0.061            | 1.301         | 0.028  | -0.089 |
| OH               | -0.076            | 1.297         | 0.023  | -0.099 |
| NH₂              | -0.088            | 1.303         | 0.029  | -0.117 |

Δq=q(adduct)-q(free)

Table S8. Energies of the frontier molecular orbitals (eV) computed at the PBE-D3/def2-QZVP level of theory.

| Molecule | HOMO/π orbital / eV | LUMO / eV | Δε (π→σ*) |
|----------|---------------------|-----------|-----------|
| 3NO₂     | -7.73 / -8.78       | -4.64     | -5.55     |
| 3CF₃     | -7.82               | -2.98     | -4.58     |
| NO₂      | -6.81 / -7.12       | -3.53     | -3.89     |
| CN       | -6.83               | -2.56     | -3.59     |
| CF₃      | -6.87               | -2.00     | -3.63     |
| CHO      | -5.93 / -6.81       | -2.92     | -3.57     |
| 3OCHO    | -6.54               | -2.25     | -3.30     |
| F        | -6.21               | -1.52     | -2.97     |
| Cl       | -6.15               | -1.57     | -2.92     |
| OCHO     | -6.30               | -1.80     | -3.06     |
| C₆H₆     | -6.33               | -1.22     | -3.53     |
| C₂H₃     | -5.69               | -2.06     | -2.45     |
| OH       | -5.54               | -1.26     | -2.30     |
| 3OH      | -5.37               | -0.70     | -2.13     |
| NH₂      | -4.97               | -1.05     | -1.73     |
| 3NH₂     | -4.47               | -0.28     | -1.23     |
| BiCl₃    | -7.66               | -3.24     |           |
Figure S9. Correlation between energies of the LUMO and the DLPNO-CCSD(T) interaction energies of the Bi···π arene adducts.

Table S10. Sum of experimentally determined van der Waals radii\textsuperscript{a} (in Å) of bismuth ($r_{\text{vdW}} = 2.54$ Å) and donor atoms (O, N, F, and Cl) of substituents.

| Donor atom | $r_{\text{vdW}}$ | $\Sigma r_{\text{vdW}}$\textsuperscript{b} |
|------------|-----------------|----------------------------------|
| O          | 1.50            | 4.04                             |
| N          | 1.66            | 4.20                             |
| Cl         | 1.82            | 4.36                             |
| F          | 1.46            | 4.00                             |

\textsuperscript{a} S. Alvarez, *Dalton Trans.* 2013, 42, 8617.

\textsuperscript{b} $\Sigma r_{\text{vdW}}$ – sum of van der Waals radii of bismuth and appropriate donor atom (O, N, F, or Cl).

Table S11. NBO partial charges (a.u.) for relaxed Bi···R adducts computed at the PBE-D3/def2-QZVP level of theory.

| BiCl\textsubscript{3} adduct with | $\Sigma q_{\text{BiCl}3}$ (adduct) | $q_{\text{Bi}}$ (adduct) | $\Delta q_{\text{Bi}}$ | $\Delta q_{\text{Cl}3}$ |
|--------------------------------|----------------------------------|--------------------------|------------------------|------------------------|
| NO\textsubscript{2}            | -0.070                           | 1.303                    | 0.029                  | -0.099                 |
| CN                               | -0.045                           | 1.332                    | 0.058                  | -0.103                 |
| CHO                              | -0.075                           | 1.316                    | 0.043                  | -0.118                 |
| F                                | -0.019                           | 1.300                    | 0.027                  | -0.046                 |
| Cl                               | -0.050                           | 1.273                    | 0.000                  | -0.051                 |
| OH                               | -0.042                           | 1.303                    | 0.029                  | -0.071                 |
| NH\textsubscript{2}            | -0.110                           | 1.286                    | 0.012                  | -0.122                 |
Figure S12. Dispersion energy plots for equilibrium structures of Cl···π arene adducts computed at the DLPNO-CCSD(T)/cc-pVQZ (cc-pwCVQZ-PP for bismuth) level of theory with tightPNO settings.

Scheme S13. Numbering of the atoms in NMR calculations.
Table S14. $\Delta \delta$ (ppm) values (gas phase) for selected benzene derivatives with one substituent computed using various density functionals with the pcsSeg-3 basis set.

| $\text{Bi} \cdots \pi$ | $\Delta \delta$ ipso | $\Delta \delta$ ortho | $\Delta \delta$ meta | $\Delta \delta$ para | $\Delta \delta X1$ |
|-------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
|                         | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 |
| CHO                    | -1.25 | -1.41 | -1.40 | -2.58 | -2.67 | -2.57 | -3.82 | -3.83 | -3.82 | -2.52 | -3.10 | -2.55 | 0.47 | 0.45 | 0.55 |
| Cl                     | -7.01 | -6.81 | -6.51 | -5.01 | -5.08 | -4.61 | -2.89 | -2.89 | -3.09 | 0.15 | -0.18 | -0.36 | -4.54 | -5.16 | -4.34 |
| NO$_2$                 | -3.40 | -3.41 | -2.70 | -4.28 | -4.22 | -3.77 | -1.59 | -1.19 | -1.42 | -1.30 | -1.70 | -0.82 | -4.74 | -7.54 | -4.00 |
| OH                     | -2.88 | -2.67 | -2.85 | -4.75 | -4.43 | -4.80 | -5.03 | -4.80 | -4.81 | -5.78 | -5.52 | -4.91 | -4.74 | -7.54 | -4.00 |
|                         | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 |
| CHO                    | 2.43 | 3.43 | 2.37 | -2.89 | -3.19 | -2.98 | -0.90 | -0.91 | -0.88 | -4.54 | -5.16 | -4.34 | -4.74 | -7.54 | -4.00 |
| Cl                     | 5.29 | 5.77 | 4.88 | -1.73 | -2.00 | -1.75 | -0.53 | -0.37 | -0.64 | -2.39 | -2.76 | -2.31 | -4.74 | -7.54 | -4.00 |
| NO$_2$                 | 6.81 | 3.87 | 6.97 | 0.15 | -0.51 | 0.39 | -1.16 | -0.89 | -0.87 | -1.57 | -3.14 | -0.74 | -4.74 | -7.54 | -4.00 |
| OH                     | 5.64 | 6.25 | 5.45 | -2.87 | -2.54 | -2.73 | -0.92 | -0.61 | -0.78 | -5.08 | -4.92 | -4.34 | -4.74 | -7.54 | -4.00 |
|                         | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 | TPSS | B3LYP | KT2 |
| CHO                    | -0.25 | -0.02 | -0.71 | -1.25 | -1.33 | -1.24 | 0.26 | 0.12 | 0.26 | -0.67 | -1.16 | -0.71 | -1.58 | -1.81 | -1.81 |
| Cl                     | -0.04 | -0.18 | -0.09 | -0.96 | -1.03 | -1.12 | -1.35 | -1.45 | -1.49 | 0.40 | 0.31 | 0.47 | -1.58 | -1.81 | -1.81 |
| NO$_2$                 | 0.59 | 0.52 | 0.82 | -1.50 | -1.40 | -1.52 | -1.05 | -1.04 | -0.89 | -2.05 | -2.26 | -1.53 | -1.58 | -1.81 | -1.81 |
| OH                     | -0.05 | -0.06 | 0.25 | -1.84 | -1.66 | -2.01 | -0.12 | 0.06 | 0.09 | -0.19 | -0.10 | 0.18 | -1.58 | -1.81 | -1.81 |

$\Delta \delta = \delta(\text{adduct}) - \delta(\text{free})$
Table S15. $^{13}$C NMR chemical shifts of the free monosubstituted arenes (C$_6$H$_5$R) and mixtures with BiCl$_3$ in a 1:1 and 1:7 molar ratio, measured in CD$_3$NO$_2$ solution at ambient temperature.

| R         | $^{13}$C-NMR (CD$_3$NO$_2$) | $\delta$-C$_{iso}$ | $\delta$-C$_{ortho}$ | $\delta$-C$_{meta}$ | $\delta$-C$_{para}$ | $\delta$-R |
|-----------|-----------------------------|---------------------|----------------------|---------------------|---------------------|-----------|
| C$_6$H$_5$F |                             | 164.25              | 116.37               | 131.61              | 125.70              | -         |
| C$_6$H$_5$F / BiCl$_3$ (1:1) |                   | 164.18              | 116.32               | 131.56              | 125.65              | -         |
| C$_6$H$_5$F / BiCl$_3$ (1:7) |                   | 163.79              | 116.07               | 131.31              | 125.40              | -         |
| C$_6$H$_5$Cl |                             | 135.13              | 129.77               | 131.41              | 128.17              | -         |
| C$_6$H$_5$Cl / BiCl$_3$ (1:1) |                   | 135.07              | 129.72               | 131.37              | 128.13              | -         |
| C$_6$H$_5$Cl / BiCl$_3$ (1:7) |                   | 134.71              | 129.44               | 131.12              | 128.87              | -         |
| C$_6$H$_5$CF$_3$ |                          | 131.26              | 126.41               | 130.40              | 133.66              | 125.98 |
| C$_6$H$_5$CF$_3$ / BiCl$_3$ (1:1) |               | 131.19              | 126.35               | 130.35              | 133.61              | 125.91 |
| C$_6$H$_5$CF$_3$ / BiCl$_3$ (1:7) |              | 130.82              | 126.08               | 130.11              | 133.38              | 125.59 |
| C$_6$H$_5$OH |                             | 157.74              | 116.48               | 130.98              | 121.53              | -         |
| C$_6$H$_5$OH / BiCl$_3$ (1:1) |                   | 157.61              | 116.47               | 130.96              | 121.56              | -         |
| C$_6$H$_5$OH / BiCl$_3$ (1:7) |                   | 156.93              | 116.46               | 130.82              | 121.62              | -         |
| C$_6$H$_5$CN |                             | 113.41              | 133.51               | 130.60              | 134.44              | 120.38 |
| C$_6$H$_5$CN / BiCl$_3$ (1:1) |                   | 113.23              | 133.50               | 130.57              | 134.47              | 120.42 |
| C$_6$H$_5$CN / BiCl$_3$ (1:7) |                   | 112.27              | 133.39               | 130.38              | 134.63              | 120.79 |
| C$_6$H$_5$NO$_2$ |                           | 149.61              | 124.61               | 130.86              | 136.33              | -         |
| C$_6$H$_5$NO$_2$ / BiCl$_3$ (1:1) |              | 149.51              | 124.57               | 130.82              | 136.32              | -         |
| C$_6$H$_5$NO$_2$ / BiCl$_3$ (1:7) |              | 148.99              | 124.38               | 130.63              | 136.30              | -         |
| C$_6$H$_5$CH=CH$_2$ |                         | 139.05              | 127.47               | 129.97              | 129.26              | 114.64 (CH$_2$) 138.24 (CH) |
| C$_6$H$_5$CH=CH$_2$ / BiCl$_3$ (1:1) |                | 138.99              | 127.44               | 129.94              | 129.22              | 114.63 (CH$_2$) 138.19 (CH) |
| C$_6$H$_5$CH=CH$_2$ / BiCl$_3$ (1:7) |               | 138.63              | 127.20               | 129.73              | 129.00              | 114.61 (CH$_2$) 137.82 (CH) |
| C$_6$H$_5$CH=O |                             | 138.05              | 130.81               | 130.43              | 135.87              | 194.53 |
| C$_6$H$_5$CH=O / BiCl$_3$ (1:1) |                   | 137.81              | 131.00               | 130.44              | 136.13              | 195.32 |
| C$_6$H$_5$CH=O / BiCl$_3$ (1:7) |                   | 136.85              | 131.57               | 130.36              | 136.96              | 197.91 |
Table S16. The difference between the chemical shift of the arene in the mixture with BiCl₃ and the chemical shift of the free monosubstituted arene.

\[
\Delta \delta = \delta(\text{adduct with BiCl}_3) - \delta(\text{free})
\]

| 13C-NMR (CD₃NO₂) | Δδ-C_{ipso} | Δδ-C_{ortho} | Δδ-C_{meta} | Δδ-C_{para} | Δδ-R |
|------------------|-------------|--------------|-------------|-------------|------|
| C₆H₅F / BiCl₃ (1:1) | -0.07 | -0.05 | -0.05 | -0.05 | - |
| C₆H₅F / BiCl₃ (1:7) | -0.46 | -0.33 | -0.30 | -0.30 | - |
| C₆H₅Cl / BiCl₃ (1:1) | -0.06 | -0.05 | -0.04 | -0.04 | - |
| C₆H₅Cl / BiCl₃ (1:7) | -0.42 | -0.33 | -0.29 | 0.70 | - |
| C₆H₂CF₃ / BiCl₃ (1:1) | -0.07 | -0.06 | -0.05 | -0.05 | -0.07 |
| C₆H₂CF₃ / BiCl₃ (1:7) | -0.44 | -0.33 | -0.29 | -0.28 | -0.39 |
| C₆H₅OH / BiCl₃ (1:1) | -0.13 | -0.01 | -0.02 | 0.03 | - |
| C₆H₅OH / BiCl₃ (1:7) | -0.81 | -0.02 | -0.16 | 0.09 | - |
| C₆H₅CN / BiCl₃ (1:1) | -0.18 | -0.01 | -0.03 | 0.03 | 0.04 |
| C₆H₅CN / BiCl₃ (1:7) | -0.62 | -0.23 | -0.23 | -0.03 | - |
| C₆H₅CH=CH₂ / BiCl₃ (1:1) | -0.06 | -0.03 | -0.03 | -0.04 | -0.01 (CH₂) -0.05 (CH) |
| C₆H₅CH=CH₂ / BiCl₃ (1:7) | -0.42 | -0.27 | -0.24 | -0.26 | -0.03 (CH₂) -0.42 (CH) |
| C₆H₅CH=O / BiCl₃ (1:1) | -0.24 | 0.19 | 0.01 | 0.26 | 0.79 |
| C₆H₅CH=O / BiCl₃ (1:7) | -1.20 | 0.76 | -0.07 | 1.09 | 3.38 |

13C NMR studies in solution were carried out in order to investigated the interaction between dispersion energy donors i.e. BiCl₃ and a series of monosubstituted arene ligands in a 1:1 and 7:1 molar ratio, in CD₃NO₂ solution. The experimental results of the solution 13C NMR spectroscopy show changes for all analyzed systems and in almost all cases a high-field shift is observed for the chemical shifts of the arene in the mixture with BiCl₃ compared to the respective free monosubstituted arene. Larger chemical shifts are observed as the content of BiCl₃ is increased. In contrast to the ipso, ortho and meta carbons the para carbon shows only minor changes of the chemical shift and for about half of the analyzed systems a low-field shift is observed. In the case of the assumed benzaldehyde-BiCl₃ adduct larger shifts were observed for the C atoms, but this most likely is due to the fact that the benzaldehyde preferentially coordinates over the O atom and not to the π system, implying that oxygen is a better donor than the π system. This is in accordance with the theoretical calculations as discussed and given in Table 6. The chemical shifts observed from the experiment are significantly smaller than those obtained from the theoretical calculations and a trend with regard to the substituents as found in the theoretical part, does not become obvious. Most likely, this is because we have to consider certain equilibria and interference with the polar solvent nitromethane (see Figure S4).
Table S17. $^{13}$C NMR chemical shifts of the free trisubstituted arenes ($C_6H_3R_3-1,3,5$) and mixtures with BiCl$_3$ and in a 1:1 and 1:7 molar ratio, measured in CD$_3$NO$_2$ solution at ambient temperature. The difference between the chemical shift of the BiCl$_3$ adduct and the chemical shift of the free trisubstituted arene.

$$
\Delta \delta = \delta(\text{adduct with BiCl}_3) - \delta(\text{free})
$$

| $^{13}$C-NMR (CD$_3$NO$_2$) | $\delta$-C$_6$H$_3$R$_3$-1,3,5 | $\Delta \delta$ | $\Delta \delta$-R |
|---------------------------|-------------------------------|----------------|-------------------|
|                           | $\delta$ _C$_1$, C$_3$, C$_5$ | $\delta$ _C$_2$, C$_4$, C$_6$ | $\Delta \delta$ _C$_1$, C$_3$, C$_5$ | $\Delta \delta$ _C$_2$, C$_4$, C$_6$ | $\Delta \delta$-R |
| 1,3,5-C$_6$H$_3$F$_3$      | 164.71                         | 101.46         | -                 | -                 | -                 |
| 1,3,5-C$_6$H$_3$F$_3$/BiCl$_3$ (1:1) | 164.64                         | 101.41         | -0.07             | -0.05             | -                 |
| 1,3,5-C$_6$H$_3$F$_3$/BiCl$_3$ (1:7) | 164.27                         | 101.17         | -0.44             | -0.29             | -                 |
| 1,3,5-C$_6$H$_3$Cl$_3$     | 136.70                         | 128.51         | -                 | -                 | -                 |
| 1,3,5-C$_6$H$_3$Cl$_3$/BiCl$_3$ (1:1) | 136.64                         | 128.45         | -0.06             | -0.06             | -                 |
| 1,3,5-C$_6$H$_3$Cl$_3$/BiCl$_3$ (1:7) | 136.29                         | 128.16         | -0.41             | -0.35             | -                 |
| 1,3,5-C$_6$H$_3$(CF$_3$)$_3$ | 133.56                         | 127.72         | 124.34            | -                 | -                 |
| 1,3,5-C$_6$H$_3$(CF$_3$)$_3$/BiCl$_3$ (1:1) | 133.50                         | 127.66         | 124.28            | -0.06             | -0.06             | -0.06             |
| 1,3,5-C$_6$H$_3$(CF$_3$)$_3$/BiCl$_3$ (1:7) | 133.15                         | 127.34         | 123.93            | -0.41             | -0.38             | -0.41             |
| 1,3,5-C$_6$H$_3$(CN)$_3$   | 116.26                         | 140.92         | 116.96            | -                 | -                 |
| 1,3,5-C$_6$H$_3$(CN)$_3$/BiCl$_3$ (1:1) | 116.19                         | 140.91         | 116.93            | -0.07             | -0.01             | -0.03             |
| 1,3,5-C$_6$H$_3$(CN)$_3$/BiCl$_3$ (1:7) | 115.89                         | 140.88         | 116.84            | -0.37             | -0.04             | -0.12             |

Low-field $\rightarrow$ High-field
Table S18. Δδ values for nitrobenzene computed at the M06L/pcSseg-3 level of theory in the gas phase, with CPCM solvation model and with explicit solvent molecules.

| Position | Gas phase | CPCM \(^a\) | Explicit solvent \(^b\) |
|----------|-----------|--------------|------------------------|
| ipso     | -3.86     | -3.69        | 0.21                   |
| ortho    | -3.98     | -3.73        | -3.55                  |
| meta     | -0.61     | -1.32        | -2.98                  |
| para     | -0.77     | 0.76         | 6.22                   |

\(^a\) Δδ\(^{\text{CPCM}}\) = δ(adduct\(^{\text{CPCM}}\)) - δ(free\(^{\text{CPCM}}\))

\(^b\) Δδ\(^{\text{explicit}}\) = δ(nitrobenzene\(^{\text{explicit solvent}}\)) - δ(nitrobenzene\(^{\text{gas phase}}\))

Figure S19. Nitrobenzene molecule surrounded by explicit nitromethane molecules optimized at the PBE-D3/def2-SVP level of theory.

Figure S20. Possible motifs of interaction between solvent and BiCl\(_3\) molecule as calculated at the PBE-D3/def2-QZVP level of theory. The interaction energy for structure A amounts to -41 kJ mol\(^{-1}\) while the interaction energy for structure B is -46 kJ mol\(^{-1}\).
In order to assess the influence of the solvation on the computed NMR spectra we have chosen nitrobenzene and nitrobenzene adduct with the BiCl₃ molecule and used the CPCM solvation model with acetonitrile as a solvent due to the fact that its dielectric constant (ε=36.6) is similar to the one of nitromethane. Additionally, we examined the influence of explicit solvation on the $^{13}$C $\Delta\delta$ values for free nitrobenzene. Therefore, we optimized nitrobenzene surrounded by eleven nitromethane molecules as a first solvation shell at the PBE-D3/def2-SVP level of theory. The obtained $^{13}$C $\delta$ values were compared to the $^{13}$C NMR chemical shifts computed for nitrobenzene in gas phase. The structure of the system is shown in Figure S5 and the results both for CPCM as well as for explicit solvation are shown in Table S12. The results were compared to the $^{13}$C $\Delta\delta$ values from the gas phase calculations. The CPCM model gives similar trend as the gas phase calculations for predicting the carbon chemical shifts. An estimate of the solvent effects using explicit molecules yields similar trends but also shows that for a quantitative agreement long MD simulations with snapshot NMR calculations would be necessary, which goes beyond the scope of the current investigation.

**Experimental details of NMR measurements**

$^1$H and $^{13}$C{$^1$H} NMR spectra were recorded at ambient temperature in CD$_3$NO$_2$ with an Avance III 500 spectrometer (Bruker) at 500.30 and 125.81 MHz, respectively, and are referenced internally to the deuterated solvent relative to Si(CH$_3$)$_4$ ($\delta = 0.00$ ppm). The NMR spectra were processed using the software MestReNova (version 11.0.0-17609 / version 11.0.4-18998).

References:

1. *MestReNova*, (version 11.0.0-17609), Mestrelab Research S. L., Santiago de Compostela, 2016.
2. *MestReNova*, (version 11.0.4-18998), Mestrelab Research S. L., Santiago de Compostela, 2017.
### Cartesian coordinates

| Substrates          | BiCl₃          | Bi(CH₃)₃        |
|---------------------|---------------|-----------------|
| Cl                  | 2.151045000   | -0.953513000    |
| Cl                  | -1.076060000  | -0.953512000    |
| Cl                  | -1.076060000  | 1.907159000     |
| Cl                  | -0.469763000  | -0.469763000    |
| Cl                  | -2.021208000  | -0.818903000    |
| Cl                  | 1.976193000   | 1.976193000     |
| Cl                  | 1.085976000   | 1.085976000     |
| F                   | -0.528586000  | 0.083725000     |
| C                   | -0.834879000  | -0.834879000    |
| C                   | 0.655063000   | 0.655063000     |
| C                   | -1.423843000  | -1.423843000    |
| C                   | 1.238460000   | 1.238460000     |
| C                   | -0.083100000  | -0.083100000    |
| C                   | -0.083545000  | -0.083545000    |
| C                   | 0.055160000   | 0.055160000     |
| C                   | 0.563050000   | 0.563050000     |
| C                   | -1.302370000  | -1.302370000    |
| C                   | -0.585352000  | -0.585352000    |
| C                   | -0.083493000  | -0.083493000    |
| C                   | -0.083493000  | -0.083493000    |
| C                   | -0.083493000  | -0.083493000    |
| C                   | -0.083493000  | -0.083493000    |
| C                   | 1.030111182   | 1.030111182     |
| C                   | 1.081409000   | 1.081409000     |

| AsCl₃               | SbCl₃          |
|---------------------|---------------|
| As                  | -0.003313867  | -0.00000000565 |
| Cl                  | -0.968839221  | 0.430445273    |
| Cl                  | 0.973993261   | -0.103111209   |
| Cl                  | 1.030111182   | 1.030111182    |

| Ethylenbenzene (C₃H₃-C₆H₆) | Trifluoromethylbenzene (CF₃-C₆H₅) |
|-----------------------------|----------------------------------|
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |
| C                            | C                                |

| Benzaldehyde (CHO-C₆H₅) | Chlorobenzene (Cl-C₆H₅) |
|-------------------------|------------------------|
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |
| C                        | C                      |

| Benzonitrile (CN-C₆H₅) | Fluorobenzene (F-C₆H₅) |
|------------------------|------------------------|
| C                       | C                      |
| C                       | C                      |
| C                       | C                      |
| C                       | C                      |
| C                       | C                      |
| C                       | C                      |

### Substrates

| Substrates          | Cartesian coordinates |
|---------------------|-----------------------|
| Benzaldehyde (CHO)  | C: 0.001074000 Cl: 2.151045000 |
| Chlorobenzene (Cl)  | C: 0.000000000 Cl: -0.953513000 |
| Fluorobenzene (F)   | C: 0.000000000 Cl: -0.953513000 |
| H       | -2.144254000 | -0.632198000 | -2.957015000 |
|---------|--------------|--------------|--------------|
| H       | 1.977269000  | 0.632198000  | -2.957015000 |
| C       | -0.083493000 | 0.000000000 | -2.807745000 |
| H       | -0.083493000 | 0.000000000 | -6.689367000 |
| C       | -0.083492000 | 0.000000000 | -1.379140000 |
| N       | -0.083492000 | 0.000000000 | -0.214079000 |
| Aniline (NH₂-C₆H₅) | Nitrobenzene (NO₂-C₆H₅) |
| C       | -0.089667000 | -0.008614000 | -5.619061000 |
| C       | -1.072803000 | 0.682023000  | -4.906382000 |
| C       | 0.908634000  | -0.682840000 | -4.911759000 |
| H       | -1.859691000 | 1.216059000  | -5.439841000 |
| C       | 1.686064000  | -1.226319000 | -5.449357000 |
| C       | 0.106274000  | 0.700693000  | -3.513616000 |
| C       | 0.927732000  | -0.670446000 | -3.518985000 |
| H       | -1.839166000 | 1.240368000  | -2.968062000 |
| C       | 1.711025000  | -1.204800000 | -2.978090000 |
| C       | -0.095856000 | 0.023390000  | -2.797754000 |
| H       | -0.100425000 | -0.019908000 | -6.707952000 |
| N       | -0.081129000 | 0.001219000  | -1.402978000 |
| C       | 0.757586000  | 0.752930000  | -0.957921000 |
| H       | 0.811467000  | -0.199220000 | -0.959406000 |
| Oxophenoxyethyl (OCHO-C₆H₅) | Phenol (OH-C₆H₅) |
| C       | -0.036150000 | -0.084670000 | -5.595787000 |
| C       | 1.004419000  | -0.682840000 | -4.955415000 |
| C       | 0.160756000  | 0.771606000  | -4.842568000 |
| H       | -1.668467000 | -1.465651000 | -5.350938000 |
| H       | -1.561379000 | 1.382683000  | -5.320035000 |
| C       | -1.138473000 | -0.709120000 | -3.566692000 |
| C       | 0.686014000  | 0.814300000  | -3.453071000 |
| H       | -1.888716000 | -1.394354000 | -0.624400000 |
| C       | 1.328684000  | 1.448141000  | -2.845111000 |
| C       | -0.284930000 | 0.030998000  | -2.833037000 |
| O       | 0.067039000  | -0.082090000 | -6.608385000 |
| O       | -0.411365000 | 0.173999000  | -1.404370000 |
| O       | 0.416375000  | -0.937958000 | -0.647866000 |
| O       | -0.302589000 | -0.208167000 | -1.002460000 |
| H       | -0.538511000 | -0.596285000 | 0.396868000 |
| 1,3,5-triethenylbenzene | 1,3,5-tri(trifluoromethyl)benzene |
| C       | -0.045620000 | 0.017693000  | -0.630720000 |
| C       | -0.821937000 | -0.954131000 | -4.944428000 |
| C       | -0.708342000 | 0.958217000  | -4.894058000 |
| C       | -0.824854000 | -0.967055000 | -3.545229000 |
| C       | 0.688244000  | 0.912652000  | -3.487527000 |
| H       | -1.425144000 | -1.718590000 | -0.329440000 |
| C       | 1.268577000  | 1.629845000  | -2.911016000 |
| C       | -0.075683000 | -0.038620000 | -2.797852000 |
| H       | -0.025345000 | 0.049227000  | -6.693412000 |
| C       | -0.056396000 | 0.030169000  | -1.330472000 |
| C       | 0.572839000  | 0.748713000  | -0.889672000 |
| C       | -0.713286000 | -0.856303000 | -0.503400000 |
| H       | -1.359999000 | -1.656803000 | -0.862632000 |
| H       | -0.621680000 | -0.792549000 | 0.576435000  |
| C       | -1.624403000 | -1.952095000 | -5.613712000 |
| C       | -2.169404000 | -2.645484000 | -5.013883000 |
| H       | -1.751037000 | -2.092959000 | -6.988673000 |
| C       | -1.242143000 | -1.442183000 | -7.699899000 |
| C       | -2.378681000 | -2.876606000 | -7.409372000 |
| C       | 1.490474000  | 1.948695000  | -5.643119000 |
| H       | 1.453943000  | 1.828147000  | -6.729912000 |
| C       | 2.216336000  | 2.958410000  | -5.141924000 |
| H       | 2.296022000  | 3.150075000  | -4.071630000 |
| H       | 2.758306000  | 3.636278000  | -5.799067000 |

1,3,5-trichlorobenzene | 1,3,5-Benzenetricarboxaldehyde
|         | x         | y         | z         |
|---------|-----------|-----------|-----------|
| C       | -0.083492000 | 0.000000000 | -5.630421000 |
| C       | -1.226950000 | -0.350856000 | -4.912467000 |
| C       | 1.059966000 | 0.350856000 | -4.912467000 |
| C       | -1.249677000 | -0.357919000 | -3.517680000 |
| C       | 1.082692000 | 0.357919000 | -3.517680000 |
| H       | -2.149290000 | -0.634034000 | -2.974130000 |
| H       | 1.982306000 | 0.634034000 | -2.974130000 |
| C       | -0.083492000 | 0.000000000 | -1.804932000 |
| Cl      | -0.083493000 | 0.000000000 | -6.717152000 |
| Cl      | -2.665029000 | -0.791780000 | -5.781313400 |
| Cl      | 2.498044000 | 0.791780000 | -5.781313400 |
|         |           |           |           |
| 1,3,5-Benzene-tricarbonitrile | 1,3,5-trifluorobenzene |
| C       | -0.083493000 | 0.000000000 | -5.623585000 |
| C       | -1.241922000 | -0.355452000 | -4.917963000 |
| C       | 1.074937000 | 0.355452000 | -4.917963000 |
| C       | -1.246960000 | -0.357015000 | -3.515754000 |
| C       | 1.079975000 | 0.357014000 | -3.515754000 |
| H       | -2.147619000 | -0.633312000 | -2.971733000 |
| H       | 1.980634000 | 0.633311000 | -2.971733000 |
| C       | -0.083493000 | 0.000000000 | -2.819234000 |
| H       | -0.083493000 | 0.000000000 | -6.714760000 |
| C       | -0.083493000 | 0.000000000 | -1.389740000 |
| N       | -0.083492000 | 0.000000000 | -0.225831000 |
| N       | -2.425499000 | -0.785212000 | -5.632621000 |
| N       | -3.389325000 | -1.014970000 | -6.214227000 |
| N       | 2.258514000 | 0.718252000 | -5.632621000 |
| N       | 3.222340000 | 0.101497000 | -6.214228000 |
| 1,3,5-Benzene-triamine | 1,3,5-trinitrobenzene |
| C       | -0.063100000 | 0.030696000 | -5.617842000 |
| C       | -1.062081000 | 0.717595000 | -4.913832000 |
| C       | 0.937839000 | -0.659370000 | -4.915610000 |
| C       | -1.057017000 | 0.719327000 | -3.511880000 |
| C       | 0.943217000 | -0.657838000 | -3.517660000 |
| H       | -1.843242000 | 1.242105000 | -2.969340000 |
| H       | 1.714305000 | -1.206911000 | -2.974415000 |
| C       | -0.056058000 | 0.290307000 | -2.813920000 |
| H       | -0.075372000 | 0.017318000 | -6.709313000 |
| N       | -0.088217000 | -0.022940000 | -1.416649000 |
| H       | -0.576176000 | 0.748108000 | -0.973562000 |
| H       | 0.807717000 | -0.202772000 | -0.976348000 |
| C       | -2.096689000 | 1.352151000 | -5.609086000 |
| H       | -1.865378000 | 1.627358000 | -6.557640000 |
| N       | 1.869613000 | -1.397949000 | -5.621216000 |
| H       | 2.762705000 | -1.156913000 | -5.177660000 |
| H       | 2.067012000 | -0.108010000 | -6.569483000 |
| 1,3,5-trifluoro-1,3,5-Benzenetriol | 1,3,5-Benzenetriol |
| C       | 0.101385000 | -0.093843000 | -5.557016000 |
| C       | -0.734025000 | -1.015703000 | -4.930868000 |
| C       | 0.955674000 | 0.659425000 | -4.755760000 |
| C       | -0.748338000 | -1.198105000 | -3.549700000 |
| C       | 0.977829000 | 0.513257000 | -3.371723000 |
| H       | -1.408623000 | -1.920828000 | -3.083341000 |
| C       | 1.648244000 | 1.110720000 | -2.758318000 |
| C       | 0.118574000 | -0.414996000 | -2.791737000 |
| H       | 0.078150000 | 0.015658000 | -6.637628000 |
| H       | 1.632117000 | -1.268201000 | -2.944833000 |
O  0.230902000  -0.573962000  -1.405663000  C  -0.094102000  0.008058000  -2.817948000
C  -0.897818000  -0.577234000  -0.629694000  H  -0.080845000  -0.002182000  -6.706189000
O  -2.029846000  -0.425978000  -1.002797000  O  -0.051746000  -0.023253000  -1.447447000
H  -0.574870000  -0.737815000  0.414972000  H  -0.781454000  0.515239000  -1.102392000
O  -1.619583000  -1.697076000  -5.772870000  C  -1.775833000  -3.052204000  -5.649212000
O  -1.207805000  -3.777278000  -4.877791000  H  -2.523136000  -3.363299000  -6.401597000
O  1.783592000  1.660407000  0.527516500  C  2.531273000  1.424717000  -6.398100000
O  2.586144000  0.404348000  -7.030114000  H  3.088410000  2.353769000  -6.617607000

Equilibrium structures

Bi···π arene adducts

\[ \text{C}_2\text{H}_5\text{BiCl}_3 \]
\[ \text{CF}_3\text{C}_6\text{H}_5\text{BiCl}_3 \]

CHO-C\text{H}_5\text{···BiCl}_3

\[ \text{C}_6\text{H}_5\text{···BiCl}_3 \]

CN-C\text{H}_5\text{···BiCl}_3

\[ \text{F}_3\text{C}_6\text{H}_5\text{···BiCl}_3 \]

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BiCl₃ interaction with NO₂CH₃

| Motif A                  | Motif B                  |
|-------------------------|-------------------------|
| C 1.090330000          | 3.796431000             | 2.789565000 |
| H 0.096859000          | 3.548761000             | 3.167948000  |
| H 1.176507000          | 4.826287000             | 2.437689000  |
| H 1.389786000          | 3.095434000             | 1.999878000  |
| N 2.077206000          | 3.591900000             | 3.889076000  |
| O 1.816235000          | 2.751775000             | 4.748815000  |
| O 3.131833000          | 4.230285000             | 3.832017000  |
| Bi 4.929213000         | 1.918311000             | 4.681219000  |
| Cl 7.016782000         | 2.887627000             | 3.804429000  |
| Cl 5.817482000         | -0.259637000            | 5.441999000  |
| Cl 3.977346000         | 1.144837000             | 2.524095000  |

NO₂CH₃

| C 1.028604000          | 4.012105000             | 2.834891000  |
| H 0.321674000          | 4.389442000             | 3.579558000  |
| H 1.438666000          | 4.809885000             | 2.214124000  |
| H 0.545078000          | 3.234714000             | 2.235402000  |
| N 2.156588000          | 3.356478000             | 3.582528000  |
| O 1.847713000          | 2.455406000             | 4.358490000  |
| O 3.295859000          | 3.761339000             | 3.365218000  |

NO₂-C₆H₅ with explicit NO₂CH₃ molecules

| C -0.721354000         | 0.729646000             | -6.646500000 |
| C -1.222314000         | -0.536120000            | -6.294250000 |
| C -0.057184000         | 1.519705000             | -5.694051000 |
| H -1.756384000         | -1.152975000            | -7.026270000 |
| H 0.368989000          | 2.497641000             | -5.960421000 |
| C -1.051870000         | -1.035370000            | -4.997454000 |
| C 0.093698000          | 1.050715000             | -4.384942000 |
| H -1.453018000         | -2.011914000            | -4.697672000 |
| H 0.600843000          | 1.652069000             | -3.622537000 |
| C -0.393653000         | -0.223294000            | -4.066263000 |
| H -0.872111000         | 1.105463000             | -7.667177000 |
| N -0.172431000         | -0.713149000            | -2.701582000 |
| O -0.011207000         | -1.924949000            | -2.532576000 |
| O -0.129139000         | 0.131636000             | -1.809639000 |
| C 2.078235000          | -2.985655000            | -4.703086000 |
| H 2.972676000          | -2.451853000            | -4.342023000 |
| H 1.220652000          | -2.757832000            | -4.034311000 |
| H 2.220133000          | -4.077575000            | -4.770170000 |
| N 1.699980000          | -2.493853000            | -6.056267000 |
| O 2.122146000          | -1.394283000            | -6.418118000 |
| O 0.949753000          | -3.205133000            | -6.727426000 |
| C 2.802385000          | -0.888412000            | -0.440829000 |
| C 3.406564000          | -1.590229000            | 0.155596000  |
| C 3.025165000          | 0.172276000             | -0.206226000 |
| H 1.718934000          | -1.084017000            | -0.305103000 |
| Element | x         | y         | z         |
|---------|-----------|-----------|-----------|
| N       | 3.126274  | -1.118613 | -1.876816 |
| O       | 3.794803  | -2.106346 | -2.175270 |
| O       | 2.681996  | -0.311687 | -2.702771 |
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| H       | 1.425261  | -0.405907 | -9.967481 |
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| H       | 3.314171  | 0.627800  | -6.218640 |
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| H       | -4.846152 | -1.437140 | -3.540780 |
| N       | -0.740066 | -1.581632 | -2.378711 |
| O       | -4.726312 | -1.361922 | -1.358077 |
| O       | -2.900680 | -1.932452 | -2.409148 |
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| H       | 0.920725  | 2.289918  | -0.177333 |
| H       | 1.170755  | 3.486151  | -1.539339 |
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| O       | 3.607176  | 2.225201  | 0.136543  |
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| H       | 0.092188  | 1.912874  | -9.900584 |
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