Metal-Free C–H Borylation of N-Heteroarenes by Boron Trifluoride

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Acronyms used in the procedures description

- PMP – 1,2,2,6,6-pentamethylpiperidine
- TMAF – tetramethylammonium fluoride
- DMSO – dimethylsulfoxide

General experimental

General experimental. All the solvents were dried using Vac Solvent Purification System and were stored under argon over molecular sieves. Deuterated solvents were purchased from Eurisotop or Sigma-Aldrich, were dried by standing over molecular sieves (3 Å), and were used without additional purification. N,N-diisopropylethylamine (Hünig’s base) 4b and 1-methyl-1H-indole 1 were purchased from Sigma-Aldrich and distilled over CaH₂ in argon atmosphere. BF₃·SMe₂ was purchased from Sigma-Aldrich and distilled in atmospheric pressure under argon prior to use. 1,2,2,6,6-pentamethylpiperidine (PMP) 4a and BF₃·PMP adduct were prepared according to procedure published in our previous paper¹. 1H-indole, Tetramethylthiourea 5a, 1,2-dimethyl-1H-indole, 1,2,5-trimethyl-1H-pyrrole, 1-methyl-2-phenyl-1H-indole and tetramethylammonium fluoride were purchased from Sigma-Aldrich. 5-fluoro-1H-indole, 1-benzyl-5-bromo-1H-indole, 4-bromo-1H-indole and 1,3,3-trimethyl-2-methyleneindoline were purchased from Alfa. 5-chloro-1,3,3-trimethyl-2-methyleneindoline was purchased from TCI Chemicals. 1-bromo-3,5-difluorobenzene was purchased from Sigma-Aldrich and TCI chemicals, distilled over CaH₂ in Ar atmosphere and stored in Glovebox. Pyridine was purchased from VWR and distilled over CaH₂ under argon. Unless otherwise stated, commercial reagents were used as received without further purification.

All preparations and reactivity studies of organoboron compounds and boron trifluoride complexes were performed under argon atmosphere by a conventional Schlenk technique or in a glove box (Mbraun Unilab).

NMR spectra were recorded at Varian Mercury 300 (¹H, ¹³C, ¹⁹F) or Varian Inova 500 (¹H, ¹³C, ¹¹B) spectrometers at 27 °C. ¹³C spectra were ¹H decoupled. ¹¹B and ¹⁹F spectra were baseline corrected. ¹¹B and ¹⁹F spectra were referenced to the shifts of external standards, BF₃·OEt₂ and CFCl₃ respectively. Chemical shifts for the ¹H and ¹³C spectra were referenced to the residual ¹H/¹³C resonances of the deuterated solvent:

- C₆D₆: δ = 7.16; δ = 128.1;
- CDCl₃: δ = 7.26; δ = 77.2;
- CD₂Cl₂: δ = 5.32; δ = 53.8;
- (CD₃)₂SO: δ = 2.50; δ = 39.5;

ESI-HRMS spectra were recorded at Bruker micrOTOF in acetonitrile. The solutions of sodium formate or Tunemix were used as standards.
Preparation of amines 4c and 4d

4.43 g (31.4 mmol, 1.05 eq.) of freshly distilled 2,2,6,6-tetramethylpiperidine was mixed with 29.9 mmol (1 eq.) of benzyl chloride (for 4c) or 2,4,6-trimethylbenzyl chloride (for 4d) in acetonitrile (50 ml). After that 4.46 g (32.2 mmol, 1.08 eq.) of K₂CO₃ and 298 mg (1.79 mmol, 0.06 eq.) of KI were added to the solution. The resulting mixture was heated at 90 °C for 12 h. After that it was cooled to room temperature, filtered and washed with acetonitrile (50 ml). Resulting solution was evaporated, redissolved in hexane (150 ml) and plugged through silica. Resulting colorless solution was evaporated and dried to give 4c and 4d as white crystallines.

4c. Yield 4.94 g (71.5 %).

¹H NMR (500 MHz, C₆D₆, 27°C): δ 7.48 (m, 2H, Ar-H), 7.25 (m, 2H, Ar-H), 7.11 (m, 1H, Ar-H), 3.72 (m, 6H), 0.95 (s, 12H, C(CH₃)₂).

¹³C NMR (75 MHz, CDCl₃, 27°C): δ 146.3, 127.9, 126.8, 125.6, 55.0, 48.2, 41.2, 27.8 (br), 18.1.

HRMS-ESI (M⁺) calcd. for C₁₆H₂₆N 232.2060; found 232.2063.

4d. Yield 4.20 g (51.3 %).

¹H NMR (500 MHz, C₆D₆, 27°C): δ 6.77 (s, 2H, Ar-H), 3.85 (s, 2H, N-CH₂-Ar), 2.56 (s, 6H, orto-Ar-CH₃), 2.17 (s, 3H, para-Ar-CH₃), 1.43 (m, 6H), 1.02 (s, 12H, C(CH₃)₂).

¹³C NMR (75 MHz, C₆D₆, 27°C): δ 137.3, 136.3, 134.7, 130.2, 55.8, 44.8, 42.4, 27.4, 21.5, 20.7, 18.2.

HRMS-ESI (M⁺) calcd. for C₁₉H₃₂N 274.2529; found 274.2535.
Figure S1. $^1$H NMR spectrum of 4c (C$_6$D$_6$, 500 MHz).

Figure S2. $^{13}$C NMR spectrum of 4c (CDCl$_3$, 75 MHz).
Figure S3. $^1$H NMR spectrum of 4d (CD$_6$, 500 MHz).

Figure S4. $^{13}$C NMR spectrum of 4d (CD$_6$, 75 MHz).
Preparation of BF₃-DIPEA adduct

5000 mg (38.8 mmol, 1 eq.) of N,N-diisopropylethylamine was dissolved in 20 ml of hexane and 5039 mg (38.8 mmol, 1 eq.) of BF₃·SMe₂ was added to the solution. The reaction was stirred for 2 h in Glovebox, after that solvent was evaporated and the resulting solid was dried under vacuum to give 6279 mg (82.2%) of the desired product.

¹H NMR (500 MHz, CDCl₃, 25°C): δ 3.78 (2H, hept, \(^3J(H,H)=6.8\) Hz), 2.98 (2H, m), 1.31 (12H, m), 1.23 (3H, q, \(^3J(H,H)=7.2\) Hz).

¹³C NMR (126 MHz, CDCl₃, 25°C): δ 53.8, 53.8, 41.6, 19.5, 19.5, 18.9, 9.9, 9.8.

¹¹B NMR (160 MHz, CDCl₃, 25°C): δ 0.37 (q, \(^1J(B,F)=19.8\) Hz).

¹⁹F NMR (470 MHz, CDCl₃, 25°C): δ -142.09 (m).

Figure S5. ¹H (top, 500 MHz, 25 °C) and ¹³C (bottom, 126 MHz, 25 °C) spectra of BF₃-DIPEA in CDCl₃.
Reaction of 1-methyl-1H-indole 1a with with BF$_3$·SMe$_2$ and amines 4a-d.

In a typical experiment, 96.5 mg (0.5 mmol, 1 eq.) of 1-bromo-3,5-difluorobenzene (IS) as an internal standard and 65.5 mg (0.5 mmol, 1 eq.) of 1-methyl-1H-indole were mixed with Lewis acid and Lewis base according to table S1. In entry 5, also 31 mg (0.5 mmol, 1 eq.) of SMe$_2$ was added. Resulting mixture was transferred into Wilmad® NMR tube with J Young valve and heated at appropriate temperature for 24 h. After cooling down to room temperature, $^1$H, $^{11}$B and $^{19}$F spectra were recorded (Fig. Figure S7-Figure S24). Conversions were measured referring to 4-H signal of internal standard.

| Entry | Lewis base, eq. | Lewis acid, eq. | SMe$_2$ addition | T, °C |
|-------|-----------------|-----------------|------------------|-------|
| 1     | 4a, 1 eq. (0.5 mmol, 77.5 mg) | BF$_3$·SMe$_2$ 2 eq. (0.5 mmol, 130.0 mg) | - | 60 |
| 2     | BF$_3$·PMP, 2 eq. (1 mmol, 223.0 mg) | - | 60 |
| 3     | 4a, 1 eq. (0.5 mmol, 77.5 mg) | BF$_3$·OEt$_2$, 2 eq. (0.5 mmol, 142.0 mg) | - | 60 |
| 4     | 4a, 1 eq. (0.5 mmol, 77.5 mg) | BF$_3$·OEt$_2$, 2 eq. (0.5 mmol, 142.0 mg) | Yes | 60 |
| 5     | 4a, 1 eq. (0.5 mmol, 77.5 mg) | BF$_3$·OEt$_2$, 2 eq. (0.5 mmol, 142.0 mg) | - | 120 |
Table S1. Screening the borylation of 1a with various Lewis bases and acids.

|   | Compound | Concentration | Lewis Base | Temp (°C) |
|---|----------|---------------|-------------|-----------|
| 6 | 4b, 1 eq. (0.5 mmol, 64.5 mg) | BF₃·SMe₂, 2 eq. (0.5 mmol, 130.0 mg) | - | 60 |
| 7 | BF₃·DIPEA, 2 eq. (1 mmol, 197.0 mg) | - | 60 |
| 8 | 4c, 1 eq. (0.5 mmol, 115.5 mg) | BF₃·SMe₂, 2 eq. (0.5 mmol, 130.0 mg) | - | 60 |
| 9 | 4d, 1 eq. (0.5 mmol, 137.0 mg) | BF₃·SMe₂, 2 eq. (0.5 mmol, 130.0 mg) | - | 60 |

Figure S7. ¹H NMR (500 MHz, 25 °C) spectrum of 1:1:1:2 mixture of 1S, 1a, 4a and BF₃·SMe₂ after 24 h of heating at 60 °C in C₆D₆.
Figure S8. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2 mixture of IS, 1a, 4a and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S9. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:2 mixture of IS, 1a, and BF$_3$·PMP after 24 h of heating at 60 °C in C$_6$D$_6$. 
Figure S10. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2 mixture of IS, 1a, and BF$_3$PMP after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S11. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:1:2 mixture of IS, 1a, 4a and BF$_3$-OEt$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$. 
Figure S12. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2 mixture of IS, 1a, 4a and BF$_3$·OEt$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S13. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:1:1:2 mixture of IS, 1a, 4a, SMe$_2$ and BF$_3$·OEt$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$. 
Figure S14. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:1:2 mixture of IS, 1a, 4a, SMe$_2$ and BF$_3$·OEt$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S15. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:1:2 mixture of IS, 1a, 4a and BF$_3$·OEt$_2$ after 24 h of heating at 120 °C in C$_6$D$_6$. 
Figure S16. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2 mixture of IS, 1a, 4a and BF$_3$·OEt$_2$ after 24 h of heating at 120 °C in C$_6$D$_6$.

Figure S17. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:1:2 mixture of IS, 1a, 4b and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$. 
Figure S18. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2 mixture of IS, 1a, 4b and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S19. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:2 mixture of IS, 1a, and BF$_3$·DIPEA after 24 h of heating at 60 °C in C$_6$D$_6$. 
Figure S20. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2 mixture of IS, 1a, and BF$_3$·DIPEA after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S21. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:1:2 mixture of IS, 1a, 4c and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.
Figure S22. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2 mixture of IS, 1a, 4c and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.

Figure S23. $^1$H NMR (500 MHz, 25 °C) spectrum of 1:1:1:2 mixture of IS, 1a, 4d and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$. 
Figure S24. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2 mixture of IS, 1a, 4d and BF$_3$·SMe$_2$ after 24 h of heating at 60 °C in C$_6$D$_6$.

Kinetic studies of the reaction of 1a, BF$_3$·SMe$_2$, 4a/4c and 5a.

In a typical experiment, 2188 mg (16.7 mmol, 1 eq.) of 1a was mixed with an appropriate amount (1 or 1.5 eq.) of 4a-4c, 0-0.1 eq. of 5a and 3223 mg (16.7 mmol, 1 eq.) of 1-bromo-3,5-difluorobenzene (internal standard) in 8 ml of dry C$_6$D$_6$ in the 25 ml Schlenk tube equipped with septum under argon. After that, solution of 3432 mg (33.4 mmol, 2 eq.) of BF$_3$·SMe$_2$ was added to the mixture via syringe and closed vessel was put on 60 °C heating bath. 0.1 ml aliquot was taken and diluted by 0.6 ml of dry C$_6$D$_6$. After that, $^1$H spectrum was immediately recorded. Amounts of 1a and 2a were determined related to 4-H signal of the internal standard. Concentrations of 1a and 2a are listed in the Table S2.

| Time, min. | 1 eq. of 4a | 1.5 eq. of 4a |
|------------|------------|-------------|
|            | C(1a), M   | C(2a), M    | C(1a), M   | C(2a), M   |
| 0          | 1.67       | 0           | 1.67       | 0           |
| 10         | 1.353      | 0.184       | 1.403      | 0.100       |
| 20         | 1.202      | 0.401       | 1.369      | 0.184       |
| 30         | 1.086      | 0.434       | 1.269      | 0.234       |
| 60         | 0.952      | 0.585       | 1.136      | 0.367       |
| 120        | 0.818      | 0.752       | 0.985      | 0.551       |
| 180        | 0.701      | 0.785       | 0.885      | 0.601       |
| 240        | 0.651      | 0.818       | 0.835      | 0.718       |

Table S2. Concentrations of 1a and 2a referred to internal standard.
| Time, min. | 1 eq. of 4a, 0.05 eq. of 5a | 1 eq. of 4a, 0.1 eq. of 5a |
|-----------|-----------------------------|-----------------------------|
|           | C(1a), M | C(2a), M | C(1a), M | C(2a), M |
| 0         | 1.67    | 0        | 1.67    | 0        |
| 10        | 1.353   | 0.284    | 1.186   | 0.284    |
| 20        | 1.219   | 0.418    | 1.069   | 0.434    |
| 30        | 1.102   | 0.501    | 1.002   | 0.534    |
| 60        | 0.868   | 0.651    | 0.802   | 0.685    |
| 120       | 0.735   | 0.802    | 0.651   | 0.835    |
| 180       | 0.601   | 0.868    | 0.585   | 0.919    |
| 240       | 0.551   | 0.902    | 0.534   | 0.985    |

| Time, min. | 1 eq. of 4d | 1 eq. of 4d, 0.05 eq. of 5a |
|-----------|-------------|-------------------------------|
|           | C(1a), M | C(2a), M | C(1a), M | C(2a), M |
| 0         | 1.67    | 0.000    | 1.67    | 0.000    |
| 10        | 1.303   | 0.117    | 1.253   | 0.267    |
| 20        | 1.169   | 0.184    | 1.102   | 0.401    |
| 30        | 1.102   | 0.234    | 1.035   | 0.484    |
| 60        | 1.052   | 0.367    | 0.919   | 0.668    |
| 120       | 0.952   | 0.484    | 0.752   | 0.768    |
| 180       | 0.919   | 0.534    | 0.668   | 0.835    |
| 240       | 0.852   | 0.551    | 0.651   | 0.868    |

Table S2 (continuation).
Reaction of 4c-d with gaseous BF$_3$.

In a typical experiment, 0.21 mmol of 4c or 4d were dissolved in 0.7 ml C$_6$D$_6$ in Wilmad NMR tube. The tube was filled with 1 bar of BF$_3$ by three freeze-pump-thaw cycles and allowed to stay for 20 minutes. After that, $^1$H and $^{11}$B spectra were measured. According to received data, none of bulky amines 4c-d forms a stable adduct with BF$_3$ (Fig. S25-S30).

![Figure S25. $^1$H NMR spectrum of reaction of 4c with gaseous BF$_3$ (C$_6$D$_6$, 500 MHz) after 20 minutes.](image)

![Figure S26. $^{11}$B NMR spectrum of reaction of 4c with gaseous BF$_3$ (C$_6$D$_6$, 160 MHz) after 20 minutes.](image)
Figure S27. $^{19}$F NMR spectrum of reaction of 4c with gaseous BF$_3$ (C$_6$D$_6$, 282 MHz) after 20 minutes.

Figure S28. $^1$H NMR spectrum of reaction of 4d with gaseous BF$_3$ (C$_6$D$_6$, 500 MHz) after 20 minutes.
Figure S29. $^{11}$B NMR spectrum of reaction of 4d with gaseous BF$_3$ (C$_6$D$_6$, 160 MHz) after 20 minutes.

Figure S30. $^{19}$F NMR spectrum of reaction of 4d with gaseous BF$_3$ (C$_6$D$_6$, 282 MHz) after 20 minutes.
Synthesis of thioureas 5b-e

1,3-dimethylimidazolidine-2-thione 5b

500 mg (4.39 mmol, 1 eq.) of 1,3-dimethyl-2-imidazolidinone S1 and 2.66 g (6.59 mmol, 1.5 eq.) of Lawesson’s reagent were dissolved in 50 ml of dry toluene and refluxed for 14 h in argon atmosphere. After that solvent was evaporated and dry solids was subjected to column chromatography (silica gel, ethyl acetate/hexane 1/1 → ethyl acetate) to give 320 mg (56.0 %) of 5b.

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ 3.51 (s, 4H, N-CH$_2$), 3.10 (s, 6H, N-CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$, 25 °C): δ 183.5, 48.4, 35.2.

HRMS-ESI ([M+Na]$^+$) calcd. for C$_5$H$_{10}$N$_2$SNa 153.0459; found 153.0459.

Figure S31. $^1$H (top, 400 MHz, CDCl$_3$, 25 °C) and $^{13}$C (bottom, 101 MHz, CDCl$_3$, 25 °C) spectra of 5b.
1,3-dimethyltetrahydropyrimidine-2(1H)-thione 5c

500 mg (3.9 mmol, 1 eq.) of urea S2 was mixed with 2.36 g (5.85 mmol, 1.5 eq.) of Lawesson’s reagent in 50 ml of dry toluene and refluxed for 14 h in argon atmosphere. After that solvent was evaporated and flash-column chromatography (silica gel, Ethyl acetate/Hexane 1/1 → Ethyl acetate) was done to obtain 264 mg (47.0 %) of 5c.

\[ \text{${}^1\text{H NMR (400 MHz, CDCl}_3, 25^\circ\text{C): } \delta 3.39 \text{ (s, 6H, N-CH}_3\text{), 3.35 (t, J(H,H)=5.9 Hz, 4H), 2.01 (pent, J(H,H)=5.9 Hz, 2H).} \]

\[ \text{${}^{13}\text{C NMR (101 MHz, CDCl}_3, 25^\circ\text{C): } \delta 179.4, 49.0, 43.6, 21.3.} \]

HRMS-ESI ([M+Na]+) calcd. for C$_6$H$_{12}$N$_2$SNa 167.0613; found 167.0615.

Figure S32. \( ^1\text{H (top, 400 MHz, CDCl}_3, 25^\circ\text{C) and } ^{13}\text{C (bottom, 101 MHz, CDCl}_3, 25^\circ\text{C) spectra of 5c.} \)
1-isopropyl-3-methyltetrahydropyrimidine-2(1H)-thione 5d

Thiourea 5d was synthesized by three step procedure.

Amine S5. 4.0 g (45.4 mmol, 1 eq.) of 3-(methylamino)propylamine S3 and 8.46 g (70.5 mmol, 1.55 eq.) of anhydrous MgSO₄ were suspended in 100 ml of dichloromethane. 50 ml of acetone were added to mixture and it was stirred under argon for 5 h at room temperature. After that it was filtered and organic solvents were evaporated to give crude oil S4. Crude product was used in the next step without further purification.

Crude S4 was dissolved in 100 ml of methanol, cooled to 0 °C and 2.24 g (59 mmol, 1.3 eq.) of NaBH₄ was added to the solution. Suspension was warmed up to room temperature and stirred under argon atmosphere for 3 h. After that solvent was evaporated, the resulting mixture was dissolved in 150 ml of CH₂Cl₂ and washed with 2x40 ml of brine. Organic layer was separated and solvent was evaporated to give 2.13 g (36.1%) of amine S5.

1H NMR (400 MHz, CDCl₃, 25 °C): δ 2.74 (hept, H Cl₂=7.0 Hz, 1H), 2.60 (m, 4H), 2.38 (s, 3H), 1.62 (pent, H Cl₂=6.9 Hz), 1.13 (s, br, 2H), 1.00 (d, H Cl₂=7.0 Hz, 6H).

13C NMR (101 MHz, CDCl₃, 25 °C): δ 50.8, 48.9, 46.1, 36.7, 30.7, 23.1.

HRMS-ESI ([M+H]⁺) calcd. for C₇H₁₉N₂ 131.1543; found 131.1545.

Thiourea 5d. 3.8 g (29.2 mmol, 1 eq.) of amine S5 was mixed with 3.33 g (43.9 mmol, 1.5 eq.) of carbon disulfide in 40 ml of pyridine and refluxed at 120 °C for 24 h under argon atmosphere. After that solvent was evaporated and the mixture was subjected to column chromatography (silica gel, Ethyl acetate/Hexane 1/1) to give 950 mg (18.9 %) of thiourea 5d.

1H NMR (400 MHz, CDCl₃, 25 °C): δ 5.81 (hept, H Cl₂=7.0 Hz, 1H), 3.34 (s, 3H), 3.29 (t, H Cl₂=6.4 Hz, 2H), 3.14 (t, H Cl₂=5.8 Hz, 2H), 1.90 (m, 2H), 1.07 (d, H Cl₂=7.0 Hz, 6H), 1.07 (d, H Cl₂=7.0 Hz, 6H), 1.07 (d, H Cl₂=7.0 Hz, 6H), 1.07 (d, H Cl₂=7.0 Hz, 6H).

13C NMR (101 MHz, CDCl₃, 25 °C): δ 178.6, 51.8, 49.3, 43.5, 39.1, 21.7, 19.3.

HRMS-ESI ([M+Na]⁺) calcd. for C₈H₁₆N₂SNaN 195.0926; found 195.0931.
Figure S33. $^1$H (top, 400 MHz, CDCl$_3$, 25 °C) and $^{13}$C (bottom, 101 MHz, CDCl$_3$, 25 °C) spectra of S5.
Figure S34. $^1$H (top, 400 MHz, CDCl$_3$, 25 °C) and $^{13}$C (bottom, 101 MHz, CDCl$_3$, 25 °C) spectra of 5d.

1,3-diisopropyltetrahydropyrimidine-2(1H)-thione 8e

Amidinium salt S6 was synthesized according to previously published procedure$^2$.

1000 mg (4.02 mmol, 1 eq.) of salt S6 and 1029 mg (4.02 mmol, 1 eq.) of crushed S$_8$ were suspended in dry tetrahydrofuran, cooled down to 0 °C under argon. 1.6 ml (4.02 mmol, 1 eq.) of 2.5 M n-butyllithium were added and mixture was refluxed at 80 °C under argon for 14 h. After that solvents were evaporated and crude mixture was put onto silica gel column chromatography (Ethyl acetate/Hexane 1/1) to get crude product, which was recrystallized from 30 ml of hexane at -25 °C to give 94 mg (11.7%) of pure 5e.

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ 5.87 (hept, $^3$J(H,H)=6.8 Hz, 2H, N-CH(CH$_3$)$_2$), 3.15 (t, $^3$J(H,H)=5.9 Hz, 4H), 1.87 (pent, $^3$J(H,H)=5.9 Hz, 2H), 1.13 (d, $^3$J(H,H)=6.8 Hz, 12H, N-CH(CH$_3$)$_2$).

$^{13}$C NMR (101 MHz, CDCl$_3$, 25 °C): δ 177.9, 52.3, 39.7, 21.9, 19.4.
HRMS-ESI ([M+H]^+) calcd. for C_{10}H_{21}N_{2}S 201.1420; found 201.1422.

*Figure S35.* $^1$H (top, 400 MHz, CDCl$_3$, 25 °C) and $^{13}$C (bottom, 101 MHz, CDCl$_3$, 25 °C) spectra of 5e.
Screening of catalytic activity of thioureas 5a-e in borylation of 1-methyl-1H-indole

In a typical experiment, 65.5 mg (0.5 mmol, 1 eq.) of 1-methyl-1H-indole were mixed with 137.0 mg (0.5 mmol, 1 eq.) of base 4d, 96.5 mg (0.5 mmol, 1 eq.) of IS and 0.025 mmol of thiourea 5a-e in 0.3 ml of C₆D₆. 130 mg (1 mmol, 2 eq.) of BF₃·SMEO₂ was added to mixture, after that it was transferred to Wilmad tube with Young valve and heated for 24 h at 60 °C. The tube was cooled down to room temperature, 0.1 ml of the solution was taken and diluted with 0.6 ml of dry C₆D₆. ¹H, ¹¹B and ¹⁹F spectra were recorded. Ratio of reaction products was measured by ¹H spectroscopy (Table S3).

| Catalyst | Ratio of products | Figures |
|----------|-------------------|---------|
| no catalyst | 1a 43  2a 47  3a 0 | Figure S23-Figure S24 |
| 5a | 30  69  0 | Figure S36-Figure S37 |
| 5b | 22  77  0 | Figure S38-Figure S39 |
| 5c | 34  65  0 | Figure S40-Figure S41 |
| 5d | 19  79  2 | Figure S42-Figure S43 |
| 5e | 32  68  0 | Figure S44-Figure S45 |

*Table S3. Ratio of borylation products of 1-methyl-1H-indole 1a with various catalysts, measured with internal standard in diluted conditions;initial concentration of 1a 1.67 M.*

| Compound | δ¹¹B, ppm  | δ¹⁹F, ppm  |
|----------|-------------|------------|
| 2a | 24.89  | -93.79 |
| 3a | 44.44  | -79.43 |

*Table S4. ¹¹B and ¹⁹F NMR data of borylation products of 1-methyl-1H-indole 1a.*
Figure S36. $^1$H (400 MHz, 25 °C) spectrum of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5a after heating at 60 °C for 24 h under argon.

Figure S37. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5a after heating at 60 °C for 24 h under argon.
Figure S38. $^1$H (400 MHz, 25 °C) spectrum of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5b after heating at 60 °C for 24 h under argon.

Figure S39. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5b after heating at 60 °C for 24 h under argon.
Figure S40. $^1$H (400 MHz, 25 °C) spectrum of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$-SMe$_2$ and 5c after heating at 60 °C for 24 h under argon.

Figure S41. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$-SMe$_2$ and 5c after heating at 60 °C for 24 h under argon.
Figure S42. $^1$H (400 MHz, 25 °C) spectrum of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5d after heating at 60 °C for 24 h under argon.

Figure S43. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5d after heating at 60 °C for 24 h under argon.
Figure S44. $^1$H (400 MHz, 25 °C) spectrum of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5e after heating at 60 °C for 24 h under argon.

Figure S45. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:1:2:0.05 mixture of IS, 1a, 4d, BF$_3$·SMe$_2$ and 5e after heating at 60 °C for 24 h under argon.

Lewis-base free experiment. 27.5 mg (0.21 mmol, 1 eq.) of 1a was mixed with 48.7 mg (0.36 mmol, 1.8 eq.) of 5a and 57.3 mg (0.44 mmol, 2.1 eq.) of BF$_3$·SMe$_2$ in 0.7 ml of C$_6$D$_6$. Mixture was heated in the Young NMR tube for 14 h under 80 °C. After that, $^1$H and $^{11}$B NMR spectra (Fig. S46) were recorded. No traces of 2a were found.
Figure S 46. $^1$H (up, 500 MHz, 27 °C) and $^{11}$B (bottom, 160 MHz, 27 °C) spectra of the 1:1.8:2.1 mixture of 1a, 5a and BF$_3$:SMe$_2$ in C$_6$D$_6$. 
Functionalization of indoles

1-allyl-1H-indole 1e

2000 mg (17.1 mmol, 1 eq.) of 1H-indole was dissolved in 25 ml of dry dimethylformamide under argon atmosphere, cooled to 0 °C and 492 mg (20.5 mmol, 1.14 eq.) of 95% NaH was added to mixture. The reaction was kept under 0 °C for 30 minutes and 2481 mg (20.5 mmol, 1.2 eq.) of allylbromide was added to it. After that, reaction was stirred under argon at room temperature for 2 h. Resulting solution was poured to 200 ml of water. Water layer was washed with hexane (2*75 ml). Organic layer was separated, solvent was evaporated and the resulting oil was purified by column chromatography (silica, EtOAc/Hex 1/5) to afford 1731 mg (64.5%) of bright yellow liquid 1e.

1H NMR (400 MHz, CDCl3, 25 °C): δ 7.65 (1H, m), 7.34 (1H, m), 7.22 (1H, m), 7.12 (2H, m), 6.54 (1H, td, 3J(H,H)=3.0 Hz, 4J(H,H)=1.5 Hz), 6.01 (1H, m, N-CH2CH=CH2), 5.21 (1H, m, N-CH2CH=CH2), 5.10 (1H, m, N-CH2CH=CH2), 4.75 (2H, dq, 3J(H,H)=4.9 Hz, 4J(H,H)=1.5 Hz, N-CH2CH=CH2).

13C NMR (101 MHz, CDCl3, 25 °C): δ 136.3, 133.7, 128.8, 128.0, 121.7, 121.1, 119.6, 117.4, 109.7, 101.6, 49.0.

HRMS-ESI ([M+H]+) calcd. for C11H12N 158.0964; found 158.0964.
1000 mg (7.4 mmol, 1 eq.) of 5-fluoro-1H-indole S1e was mixed with 197 mg (7.78 mmol, 1.05 eq.) of 95% NaH in 20 ml of dry dimethylformamide under argon atmosphere, cooled to 0 °C and 1.33 g (7.78 mmol, 1.05 eq.) of benzyl bromide was added to the solution. Mixture was allowed to warm up to room temperature and stirred for 4 h. After that mixture was poured to 100 ml of H2O and washed with CH2Cl2 (3x50 ml). Organic layer was separated and washed additionally with water (2x50 ml) and brine. Organic layer was separated, solvent was evaporated and the resulting oil was recrystallized from 50 ml of hexane at -25 °C to give 1222 mg (73.4%) of target material 1e.

1H NMR (400 MHz, CDCl3, 25 °C): δ 7.32 (m, 4H), 7.19 (m, 2H), 7.12 (m, 2H), 6.93 (m, 1H), 6.53 (m, 1H), 5.33 (s, 2H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\), 25 °C): \(\delta \) 158.1 (d, \(^{1}J\)(C,F)=234 Hz), 137.4, 133.1, 130.1, 129.1 (d, \(^{2}J\)(C,F)=10.2 Hz), 129.0, 127.9, 126.9, 110.5 (d, \(^{3}J\)(C,F)=14.2 Hz), 110.3 (d, \(^{2}J\)(C,F)=30.1 Hz), 105.8 (d, \(^{2}J\)(C,F)=23.3 Hz), 101.8 (d, \(^{4}J\)(C,F)=4.7 Hz), 50.6.

\(^{19}\)F NMR (377 MHz, CDCl\(_3\), 25 °C): \(\delta \) -125.36 (m).

HRMS-ESI ([M+H]\(^{+}\)) calcd. for C\(_{15}\)H\(_{13}\)FN 226.1027; found 226.1027.

Figure S48. \(^{1}\)H (top, 400 MHz, CDCl\(_3\), 25 °C) and \(^{19}\)F (bottom, 377 MHz, CDCl\(_3\), 25 °C) spectra of If.
Figure S49. $^{13}$C (101 MHz, CDCl$_3$, 25 °C) spectrum of 1f.

1-benzyl-7-bromo-1H-indole 1h

835 mg (4.26 mmol, 1 eq.) of 6-bromo-1H-indole S1h was mixed with 205 mg (5.11 mmol, 1.2 eq.) of 60% NaH (oil suspension) in 20 ml of dry dimethylformamide under argon atmosphere, cooled to 0 °C and 1.09 g (6.39 mmol, 1.5 eq.) of benzyl bromide was added to the solution. Mixture was allowed to warm up to room temperature and stirred for 4 h. After that mixture was poured to 100 ml of H$_2$O and washed with CH$_2$Cl$_2$ (3x40 ml). Organic layer was separated and washed additionally with water (2x40 ml) and brine. Organic layer was separated, solvent was evaporated and the resulting oil was recrystallized from 50 ml of hexane at -25 °C to give 767 mg (67.9%) of target material 1h. 

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C): δ 7.47 (dd, $^3$J(H,H)=7.7 Hz, $^4$J(H,H)=1.0 Hz, 1H), 7.23 (dd, $^3$J(H,H)=7.7 Hz, $^4$J(H,H)=1.0 Hz, 1H), 7.14 (m, 3H), 6.98 (d, $^3$J(H,H)=3.2 Hz, 1H), 6.89 (d, $^3$J(H,H)=6.9 Hz, 2H), 6.83 (t, $^3$J(H,H)=7.7 Hz, 1H), 6.45 (d, $^3$J(H,H)=3.2 Hz, 1H), 5.70 (s, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): δ 139.2, 132.8, 132.0, 131.4, 128.8, 127.5, 127.3, 126.3, 121.0, 120.6, 104.0, 102.6, 51.5.

HRMS-ESI ([M+H]$^+$) calcd. for C$_{15}$H$_{13}$BrN 286.0226; found 286.0226.
Figure S50. $^1$H (top, 400 MHz, CDCl₃, 25 °C) and $^{13}$C (bottom, 126 MHz, CDCl₃, 25 °C) spectra of 1h.

Borylation of enamines and N-heteroarenes 1a-j by BF$_3$·SMe$_2$, base 4d and thiourea 5d

In a typical experiment, 0.5 mmol of starting materials 1a-j were mixed with 137.0 mg (0.5 mmol, 1 eq.) of base 4d and 4.3 mg (0.025 mmol, 0.05 eq.) of thiourea 5d (5a for substrate 1n) in 0.3 ml of C₆D₆. 130 mg (1 mmol, 2 eq.) of BF$_3$·SMe$_2$ was added to mixture, after that it was transferred to Wilmad tube with Young valve and heated for 24 h (19h for substrate 1l) at 60 °C. Tube was cooled down to room temperature and $^1$H, $^{11}$B and $^{19}$F spectra were recorded from mixture.
Scheme S1. Conversions of 1a-j to 2a-j were measured by \(^1\)H spectra.

| Substrate | Figures | Substrate | Figures |
|-----------|---------|-----------|---------|
| 1a        | Figure S51-Figure S53 | 1i        | Figure S68-Figure S69 |
| 1b        | Figure S54-Figure S55 | 1j        | Figure S70-Figure S71 |
| 1c        | Figure S56-Figure S57 | 1k        | Figure S72-Figure S73 |
| 1d        | Figure S58-Figure S59 | 1l        | Figure S74-Figure S75 |
| 1e        | Figure S60-Figure S61 | 1m        | Figure S76-Figure S77 |
| 1f        | Figure S62-Figure S63 | 1n        | Figure S78-Figure S79 |
| 1g        | Figure S64-Figure S65 | 1o        | Figure S80-Figure S81 |
| 1h        | Figure S66-Figure S67 | 1p        | Figure S82-Figure S83 |

Table S5. Illustrations for spectra of borylation of 1a-j.
Partial NMR data for compounds 2a-j.

2a. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 8.01 (m, 1H, Ar-H), 7.21-7.09 (m, 2H, Ar-H), 7.03 (s, 1H, C(2)-H), 6.92 (m, 1H, Ar-H), 2.84 (s, 3H, N-CH$_3$).

$^{13}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 24.95.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -93.31.

Figure S51. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1a, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S52. $^{13}$B (160 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1a, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S53. $^{19}$F (470 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1a, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

2b. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 7.93 (m, 1H, Ar-H), 7.22-7.01 (m, 2H, Ar-H), 6.85 (m, 1H, Ar-H), 2.71 (s, 3H, N-C$_3$H$_3$), 2.02 (s, 3H, C(2)-CH$_3$).

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 25.16.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -90.92.

Figure S54. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1b, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S55. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1b, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

2c. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 5.98 (s, 1H, Ar-H); other signals could not be distinguished from the reaction mixture.

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 25.02.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -94.42.
Figure S56. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1c, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S57. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1c, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
2d. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 8.15 (m, 1H, Ar-H), 2.92 (s, 3H, N-CH$_3$); other signals could not be distinguished from the reaction mixture.

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 25.04.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -88.44.

Figure S58. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1d, 4d, BF$_3$:SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S59. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1d, 4d, BF$_3$:SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
2e. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 8.00 (m, 1H, Ar-H); other signals could not be distinguished from the reaction mixture.

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 25.05.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -92.94.

Figure S60. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1e, 4d, BF$_3$SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S61. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1e, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

2f. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 4.63 (s, 2H, N-CH$_2$-Ph); other signals could not be distinguished from the reaction mixture.

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 24.76.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -92.56, -125.05.
Figure S62. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1f, 4d, BF$_3$-SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S63. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1f, 4d, BF$_3$-SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

2g. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 8.12 (m, 1H, Ar-H), 4.60 (s, 2H, N-CH$_2$-Ph); other signals could not be distinguished from the reaction mixture.
$^{11}\text{B} \text{NMR} (160 \text{ MHz, 25 °C, C}_6\text{D}_6) \delta 24.75.$

$^{19}\text{F} \text{NMR} (470 \text{ MHz, 25 °C, C}_6\text{D}_6) \delta -91.97.$

Figure S64. $^1\text{H} (500 \text{ MHz, 25 °C})$ spectrum of 1:1:2:0.05 mixture of 1g, 4d, BF$_3$SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S65. $^{11}\text{B}$ (top, 160 MHz, 25 °C, up) and $^{19}\text{F}$ (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1g, 4d, BF$_3$SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
2h. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 7.83 (m, 1H, Ar-H), 5.30 (s, 2H, N-CH$_2$-Ph); other signals could not be distinguished from the reaction mixture.

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 24.79.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -91.28.

Figure S66. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1h, 4d, BF$_3$·SM$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S67. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1h, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

2i. $^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 7.01 (m, 1H, Ar-H), 6.88 (m, 1H, Ar-H), 6.81 (m, 1H, Ar-H), 6.31 (m, 1H, Ar-H), 3.84 (br, 1H, Vinyl-H), 2.50 (s, 3H, N-CH$_3$).

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 25.76.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -87.97.
Figure S68. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1i, 4d, BF$_3$SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S69. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1i, 4d, BF$_3$SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
$^1$H NMR (500 MHz, 25 °C, C$_6$D$_6$) δ 7.02 (m, 1H, Ar-H), 6.98 (m, 1H, Ar-H), 6.06 (m, 1H, Ar-H), 3.83 (m, br, 1H, Vinyl-H), 2.42 (s, 3H, N-CH$_3$).

$^{11}$B NMR (160 MHz, 25 °C, C$_6$D$_6$) δ 25.60.

$^{19}$F NMR (470 MHz, 25 °C, C$_6$D$_6$) δ -87.21.

Figure S70. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1j, 4d, BF$_3$:SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S71. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1j, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S72. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1k, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S73. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1k, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S74. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1l, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 19 h under argon.
Figure S75. $^1$H (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1l, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 19 h under argon.

Figure S76. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1m, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S77. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1m, 4d, BF$_3$SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S78. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1n, 4d, BF$_3$SMe$_2$ and 5a in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S79. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1n, 4d, BF$_3$:SMe$_2$ and 5a in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S80. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1o, 4d, BF$_3$:SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S81. $^{11}$B (top, 160 MHz, 25 °C, up) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1o, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.

Figure S82. $^1$H (500 MHz, 25 °C) spectrum of 1:1:2:0.05 mixture of 1p, 4d, BF$_3$·SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Figure S83. $^{11}\text{B}$ (top, 160 MHz, 25 °C, up) and $^{19}\text{F}$ (bottom, 470 MHz, 25 °C) spectra of 1:1:2:0.05 mixture of 1p, 4d, BF$_3$−SMe$_2$ and 5d in C$_6$D$_6$ after heating at 60 °C for 24 h under argon.
Studies upon conversion of 3-(difluoroboraneyl)-1-methyl-1H-indole 2a into trifluoroborate 6a

In a typical experiment, 65.5 mg (0.5 mmol, 1 eq.) of 1-methyl-1H-indole were mixed with 137.0 mg (0.5 mmol, 1 eq.) of base 4d and 3.6 mg (0.025 mmol, 0.05 eq.) of thiourea 5d in 0.3 ml of C₆D₆. 130 mg (1 mmol, 2 eq.) of BF₃·SMe₂ was added to mixture, after that it was transferred to Wilmad tube with Young valve and heated for 24 h at 60 °C. Mixture was cooled down, diluted with 0.5 ml of C₆D₆ and filtered from precipitate. 1 mmol (2 eq.) of pyridine or N,N-dimethylaniline was added and ¹H, ¹¹B and ¹⁹F spectra were measured from solutions. After that, suspension of 46.5 mg (0.5 mmol, 1 eq.) of tetramethylammonium fluoride (TMAF) in 0.7 ml of CDCl₃ was added to the solution and it was shaken for 20 minutes. After that, both precipitate and remained solution were analysed by ¹H, ¹¹B and ¹⁹F spectra.

Scheme S2. Studies upon conversion of a) indolyldifluoroborane 2a and b) diindolylfluoroborane 3a towards fluoroborates 6a and S6a via their pyridine and N,N-dimethylaniline adducts.

Formation of both pyridine and N,N-dimethylaniline adducts with indolyldifluoroborane 2a happened instantaneously after their addition to solution (Scheme S2a). Interestingly, peak of diindolylfluoroborane 3a disappeared when pyridine was used as a ligand, but remained in solution in case of N,N-dimethylaniline (Scheme S2b). We suppose that 3a also forms adduct A7 with pyridine, which arises at -176 ppm in ¹⁹F spectrum (Figure S85).

When TMAF suspension was added to solutions of 7 and 8, 7 reacted instantly to form trifluoroborate 6a as a precipitate. In case of 8, reaction with TMAF gave complex mixture.
Figure S84. $^1$H (400 MHz, 25 °C) spectrum of mixture of 2a, 3a and pyridine after 20 minutes.

Figure S85. $^{19}$F (top, 377 MHz, 25 °C) and $^{11}$B (bottom, 128 MHz, 25 °C) spectra of mixture of 2a, 3a and pyridine after 20 minutes.
Figure S86. $^1$H (400 MHz, 25 °C) spectrum of mixture of 2a, 3a and N,N-dimethylaniline after 20 minutes.
Figure S87. $^{11}$B (top, 128 MHz, 25 °C) and $^{19}$F (bottom, 377 MHz, 25 °C) spectra of mixture of 2a, 3a and N,N-dimethylaniline after 20 minutes.

Figure S88. $^1$H (500 MHz, 25 °C) spectrum of filtrate resulting from reaction of 7 with Me4NF.
Figure S89. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of filtrate resulting from reaction of 7 with Me$_4$NF.

Figure S90. $^1$H (400 MHz, 25 °C) spectrum of precipitate resulting from reaction of 7 with Me$_4$NF.
Figure S91. $^1$H (top, 128 MHz, 25 °C) and $^{19}$F (bottom, 377 MHz, 25 °C) spectra of precipitate resulting from reaction of 7 with Me$_4$NF.
Figure S92. $^{11}$B (top, 160 MHz, 25 °C) and $^{19}$F (bottom, 470 MHz, 25 °C) spectra of filtrate resulting from reaction of 8 with $\text{Me}_4\text{NF}$. 
One pot synthesis of aryltrifluoroborates 6a-d

General procedure.

\[
\begin{array}{c}
1) \text{BF}_3\cdot\text{SMe}_2, 4d, \\
5\% \text{ 5a or 5d,} \\
\text{C}_6\text{H}_6, 24h, 60^\circ\text{C} \\
2) \text{Pyridine, 10 min., rt} \\
3) \text{Me}_4\text{NF, 2h, rt} \\
\rightarrow \text{Ar}-\text{BF}_3^+ [\text{NMe}_4^-]
\end{array}
\]

2.5 mmol of indole 1a-d was mixed with 685 mg (2.5 mmol, 1 eq.) of 2,2,6,6-tetramethyl-1-(2,4,6-trimethylbenzyl)piperidine 4d and 0.13 mmol (0.05 eq.) of thiourea 5a or 5d in 2.5 ml of dry C\(_6\)H\(_6\) and transferred into Schlenk tube. 650 mg (5 mmol, 2 eq.) of BF\(_3\)·SMe\(_2\) was gently added to mixture and it was stirred for 24 h at room temperature (substrate 6c) or 60 °C (substrates 6a-b, d) under argon atmosphere. After that, Schenk tube was transferred to Glove box, filtered and precipitate was additionally washed with 5 ml of C\(_6\)H\(_6\). 395 mg (5 mmol, 2 eq.) of pyridine in 1 ml of CH\(_2\)Cl\(_2\) were added to filtrate and mixture was allowed to stir for 10 minutes. After that, solution of 232.5 mg (2.5 mmol, 1 eq.) of dry tetramethylammonium fluoride in 3 ml of CH\(_2\)Cl\(_2\) was added and the resulting solution was stirred for 2 h at room temperature in Glove box. 5 ml of C\(_6\)H\(_6\) were added to the solution to precipitate the trifluoroborate salt and suspension was filtered. After this, different procedures for each compounds were applied to get 67-87% of Solid rests were washed additionally with 5 ml of C\(_6\)H\(_6\) and dried in vacuo to give aryltrifluoroborates 6a-d.

6a. Yield 444 mg (65.3%).

\(^1\)H NMR (500 MHz, DMSO-d\(_6\), 25 °C): \(\delta\) 7.62 (d, \(^3\)J(H,H)=7.8 Hz, 1H, Ar-H), 7.21 (d, \(^3\)J(H,H)=8.1 Hz, 1H, Ar-H), 6.97 (m, 1H, Ar-H), 6.85 (m, 1H, Ar-H), 6.83 (s, 1H, C(2)-H), 3.67 (s, 3H, N-C\(_\text{H}_3\)), 3.03 (s, 12H, N(C\(_\text{H}_3\))\(_4\)).

\(^13\)C NMR (126 MHz, DMSO-d\(_6\), 25 °C): \(\delta\) 137.4, 133.0, 131.0 (q, \(^3\)J(C,F)=3.4 Hz, C-2), 122.5, 119.2, 116.7, 108.2, 54.2 ((N-C\(_\text{H}_3\))\(_i\)), 31.8 (N-C\(_\text{H}_3\)). Carbon C3 connected to boron was not observed.

\(^11\)B NMR (160 MHz, DMSO-d\(_6\), 25 °C): \(\delta\) -3.43 (m).

\(^19\)F NMR (470 MHz, DMSO-d\(_6\), 25 °C): \(\delta\) -132.55.

HRMS-ESI (M\(^+\)) calcd. for C\(_9\)H\(_9\)BF\(_3\)N 198.0696; found 198.0702.

In addition to target indolyltrifluoroborate 6a, approximately 7% of diindolyldifluoroborate S6a was formed. We were unable to separate them from each other. Partial data for S6a:
$^1$H NMR (500 MHz, DMSO-d$_6$, 25 °C): δ 7.70 (m, 1H, Ar-H), 7.16 (m, 1H, Ar-H), 6.92 (m, 1H, Ar-H), 6.78 (m, 1H, Ar-H), 6.75 (s, 1H, C(2)-H), 3.64 (s, N-CH$_3$).

$^{19}$F NMR (470 MHz, DMSO-d$_6$, 25 °C): δ -144.75.

HRMS-ESI (M$^+$) calcd. for C$_{18}$H$_{17}$BF$_2$N$_2$ 309.1369; found 309.1360 (S6a).

$^{11}$B signal is likely hidden under the signal of 6a. Structures of 6a and S6a were additionally proved by $^1$H-$^{13}$C HSQC and HMBC spectra (Figure S96). We were unable to separate signals of S6a from other minor impurities excluding the characteristic triplet at 130.6 ppm ($^3$J(C,F) = 5.4 Hz).

Figure S93. $^1$H (top, 500 MHz, DMSO-d$_6$, 25 °C) and $^{11}$B (bottom, 160 MHz, DMSO-d$_6$, 25 °C) spectra of 6a and S6a.
Figure S94. $^{13}$C (top, 126 MHz, DMSO-$d_6$, 25 °C) and $^{19}$F (bottom, 470 MHz, DMSO-$d_6$, 25 °C) spectra of 6a and S6a.
Figure S95. $^1$H-$^{13}$C HSQC spectrum of 6a and S6a.

Figure S96. $^1$H-$^{13}$C HSQC spectrum of 6a and S6a.
Figure S97. $^1$H-$^{13}$C HMBC spectrum of 6a and S6a.

6b. Yield 613 mg (85.7%).

$^1$H NMR (500 MHz, DMSO-d$_6$, 25 °C): δ 7.59 (d, $^3$J(H,H)=7.6 Hz, 1H, Ar-H), 7.13 (d, $^3$J(H,H)=8.0 Hz, 1H, Ar-H), 6.87 (ddd, $^3$J(H,H)=7.6 Hz, 7.0 Hz, $^4$J(H,H)=1.3 Hz, 1H, Ar-H), 6.77 (ddd, $^3$J(H,H)=8.0 Hz, 7.0 Hz, $^4$J(H,H)=1.1 Hz, 1H, Ar-H), 3.55 (s, 3H, N-C$_3$H$_3$), 3.04 (s, 12H, N(CH$_3$)$_4$), 2.37 (s, 3H, C(2)-CH$_3$).

$^{13}$C NMR (126 MHz, DMSO-d$_6$, 25 °C): δ 137.4, 137.2 (q, $^3$J(C,F)=3.4 Hz, C-2), 133.0, 121.8, 118.2, 116.7, 115.8 (br, C-3), 107.5, 54.3 (N(CH$_3$)$_4$), 28.8 (N-C$_3$H$_3$), 12.0 (C(2)-CH$_3$).

$^{11}$B NMR (160 MHz, DMSO-d$_6$, 25 °C): δ 3.82 (m).

$^{19}$F NMR (470 MHz, DMSO-d$_6$, 25 °C): δ -130.53.

HRMS-ESI (M) calcd. for C$_{10}$H$_{11}$BF$_3$N 212.0855; found 212.0856.
Figure S98. $^1$H (top, 500 MHz, DMSO-d$_6$, 25 °C) and $^{11}$B (bottom, 160 MHz, DMSO-d$_6$, 25 °C) spectra of 6b.

Figure S99. $^{19}$F (470 MHz, DMSO-d$_6$, 25 °C) spectrum of 6b.
Figure S100. $^{13}$C (126 MHz, DMSO-d$_6$, 25 °C) spectrum of 6b.

$^{6c}$. Yield 545 mg (87.2%).

$^1$H NMR (500 MHz, DMSO-d$_6$, 25 °C): δ 5.45 (s, 1H, C(4)-H), 3.21 (s, 3H, N-CH$_3$), 3.05 (s, 12H, N(CH$_3$)$_4$), 2.08 (s, 3H), 2.05 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$, 25 °C): δ 126.8, 123.3, 109.4, 53.9 (N-CH$_3$)$_4$, 29.0 (N-CH$_3$), 12.2, 11.8, *Carbon C3 connected to boron was not observed.*

$^{11}$B NMR (128 MHz, DMSO-d$_6$, 25 °C): δ 3.64 (m).

$^{19}$F NMR (377 MHz, DMSO-d$_6$, 25 °C): δ -131.55.

HRMS-ESI (M$^+$) calcd. for C$_7$H$_{11}$BF$_3$N 176.0854; found 176.0853.
Figure S101. $^1H$ (top, 400 MHz, DMSO-d$_6$, 25 °C) and $^{11}B$ (bottom, 128 MHz, DMSO-d$_6$, 25 °C) spectra of 6c.
Figure S102. $^{19}$F (top, 377 MHz, DMSO-d$_6$, 25 °C) and $^{13}$C (bottom, 101 MHz, DMSO-d$_6$, 25 °C) spectra of 6c.

6d. Yield 587 mg (67.5%).

$^{1}$H NMR (500 MHz, DMSO-d$_6$, 25 °C): δ 7.81 (d, $^3$J(H,H)=7.8 Hz, 1H), 7.49 (d, $^3$J(H,H)=7.5 Hz, 2H), 7.36 (t, $^3$J(H,H)=7.5 Hz, 2H), 7.28 (m, 1H), 7.23 (d, $^3$J(H,H)=8.1 Hz, 1H), 6.99 (t, $^3$J(H,H)=7.5 Hz, 1H), 6.86 (t, $^3$J(H,H)=7.5, 1H), 3.48 (s, 3H, N-CH$_3$), 3.08 (s, 12H, N(CH$_3$)$_4$).

$^{13}$C NMR (101 MHz, DMSO-d$_6$, 25 °C): δ 141.2, 137.9, 134.8, 132.8, 130.5, 126.8, 125.9, 122.9, 119.3, 117.1, 108.2, 53.9 (N(CH$_3$)$_4$), 30.3 (N-CH$_3$), Carbon C3 connected to boron was not observed.

$^{11}$B NMR (128 MHz, DMSO-d$_6$, 25 °C): δ 3.59 (m).

$^{19}$F NMR (377 MHz, DMSO-d$_6$, 25 °C): δ -129.17.

HRMS-ESI (M$^+$) calcd. for C$_{15}$H$_{13}$BF$_3$N 274.1009; found 274.1011.
Figure S103. $^1$H (top, 400 MHz, DMSO-$d_6$, 25 °C) and $^{11}$B (bottom, 128 MHz, DMSO-$d_6$, 25 °C) spectra of 6d.
Figure S104. $^{19}F$ (top, 377 MHz, DMSO-$d_6$, 25 °C) and $^{13}C$ (bottom, 101 MHz, DMSO-$d_6$, 25 °C) spectra of 6d.
Mass spectra of prepared compounds

Figure S105. HRMS ESI of 4c.
Figure S106. HRMS ESI of 4d.
Figure S107. HRMS ESI of 5b.
Figure S108. HRMS ESI of 5c.
Figure S109. HRMS ESI of S5.
Figure S110. HRMS ESI of 5d.
Figure S111. HRMS ESI of 5e.
Figure S112. HRMS ESI of 1e.
Figure S113. HRMS ESI of If.
Figure S114. HRMS ESI of 1h.
Figure S115. HRMS ESI of 6a.
Figure S116. HRMS ESI of S6a.
Figure S117. HRMS ESI of 6b.
Figure S118. HRMS ESI of 6c.
Figure S119. HRMS ESI of 6d.
Crystal Structure Determinations of 6a

Compound 6a (10 mg) was recrystallized at -25 °C from 1 ml of 1/2 CH₃CN/Et₂O mixture.

The single-crystal X-ray diffraction study of 6a was carried out on a Bruker D8 Venture diffractometer with PhotonII CPAD detector at 123(2) K using Cu-Kα radiation (λ = 1.54178 Å). Dual space methods (SHELXT) [G. M. Sheldrick, Acta Crystallogr. 2015, A71, 3-8] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F²) [G. M. Sheldrick, Acta Crystallogr. 2015, C71, 3-8]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption correction was applied. The solvent acetonitrile is disordered (see cif-file for details).

6a: colourless crystals, C₉H₈BF₃ · C₄H₁₂N · 2/3 C₂H₄N, Mr = 299.49, crystal size 0.10 × 0.05 × 0.02 mm, trgonal, space group R-3 (No. 147), a = 19.1312(4) Å, b = 19.1312(4) Å, c = 7.7456) Å, α = 90°, β = 90°, γ = 120°, V = 2455.10(12) Å³, Z = 6, ρ = 1.215 Mg/m³, μ(Cu-Kα) = 0.81 mm⁻¹, F(000) = 952, 2θmax = 145.6°, 25970 reflections, of which 3270 were independent (Rint = 0.075), 229 parameters, 27 restraints, R₁ = 0.064 (for 2584 I > 2σ(I)), wR₂ = 0.171 (all data), S = 1.06, largest diff. peak / hole = 0.41 / -0.27 e Å⁻³.

CCDC 1948654 (6a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S 120. Molecular structure of 6a (displacement parameters are drawn at 50 % probability level).
**Kinetic simulation**

**Methods**

The kinetics was numerically simulated by a simple linear step method with 1 min resolution time. Simulation was sufficiently convergent with this temporal resolution as increasing the resolution to 0.1 and 0.01 minutes manifested no significant difference in modeled results and statistics. At each time step the concentrations of the reactants and intermediates were reequilibrated according to the equilibrium dissociation constants for the Me₂S-BF₃ (K) and PMP-BF₃ (K₂). Values of the rate constant k, and equilibrium constants K and K₂ were systematically screened to find the combination that statistically fitted best. The simulation was carried out using a computer code written in Python.

During kinetic studies, the consumption of N-methylindole (1a) could be reliably followed by ¹H NMR spectroscopy, because N-methylindole exists as a single species unlike, for example, PMP that existed in a dynamic equilibrium with Me₂S-BF₃, [PMP-H⁺], and PMP-BF₃. For each kinetic experiment, the simulated and experimental values for the 1a concentration were compared and R² was calculated. Then the average and the standard deviation of R² values were computed over all experiments for each set of model parameters (k, K, K₂). Naturally, we were optimizing the model parameters seeking the highest R² values with the narrowest distribution. R² and its standard deviation was used as an optimization metrics.

In the preliminary simulations, one experiment, with the initial understoichiometric (50%) PMP concentration was excluded from the set, because two out of three tested kinetic models had zero kinetic order in PMP and this inevitably led to negative values of the PMP concentration in the course of the simulation. Once the close to the optimum values parameters were found, the simulations were repeated on the complete set of kinetic data. Importantly, it was found that starting the simulation with the initial time down to -10 min improves the modeled statistics. Introduction of this additional parameter is justified from the experimental prospective, as the immersed into a preheated oil bath reaction vessel cannot instantaneously reach the set reaction temperature.

**Results**

The model 1 (model A in the article main text) with the kinetic orders 1, 1, and 0, respectively, demonstrated comparable results, but statistically less fit to the experiments:

\[ k = 0.05 \text{ min}^{-1} \text{M}^{-1}, K = 0.30 \text{ M}, K₂ = 0.005 \text{ M}, \text{average } R^2 = 0.704, \text{std}(R^2) = 0.160 [0.897, 0.928, 0.517, 0.517, 0.745, 0.572, 0.757] \]

For the model 2 (model B in the article main text) with the kinetic order 2 in BF₃, 1 in 1a, and 0 in PMP the following best result was found:

\[ k = 0.13 \text{ min}^{-1} \text{M}^{-2}, K = 0.32 \text{ M}, K₂ = 0.10 \text{ M}, \text{average } R^2 = 0.810, \text{std}(R^2) = 0.210 [0.960, 0.965, 0.986, 0.371, 0.821, 0.645, 0.920] \]

The model 3 (FLP model in the article main text), with the orders 1, 1, and 1, respectively, could be successfully fit only to separate experiments in the set, for example:
}\text{The following dataset was used for simulations, where columns are: time in minutes, 1a, PMP, and Me_2S-BF_3 in M.}

\begin{tabular}{cccc}
0     & 1.67 & 1.67 & 3.34 \\
10    & 1.3527 & 1.1857 \\
20    & 1.2024 & 1.013133 \\
30    & 1.0855 & 0.924067 \\
60    & 0.9519 & 0.790467 \\
120   & 0.8183 & 0.679133 \\
180   & 0.7014 & 0.5177 \\
240   & 0.6513 & 0.4509 \\
0     & 0.835 & 1.67 & 3.34 \\
10    & 0.6179 & 1.157867 \\
20    & 0.5344 & 1.169 \\
30    & 0.4843 & 1.1189 \\
60    & 0.3841 & 0.990867 \\
120   & 0.2672 & 1.002 \\
180   & 0.2004 & 0.796033 \\
240   & 0.167 & 0.690267 \\
300   & 0.1336 & 0.6346 \\
360   & 0.1169 & 0.5845 \\
0     & 2.505 & 1.67 & 3.34 \\
10    & 2.0541 & 1.169 \\
20    & 1.9706 & 1.057667 \\
30    & 1.8036 & 0.896233 \\
\end{tabular}
|    |        |        |        |
|----|--------|--------|--------|
| 60 | 1.7034 | 0.7682 |        |
|120 | 1.5197 | 0.573367 |       |
|180 | 1.3861 | 0.478733 |       |
|240 | 1.336  | 0.4175  |       |
|300 | 1.2859 | 0.378533 |       |
|360 | 1.2692 | 0.3006  |       |

|    |        |        |        |
|----|--------|--------|--------|
|  0 | 1.67   | 0.835  | 3.34   |
|10  | 1.3193 | 0.289467|       |
|20  | 1.169  | 0.189267|       |
|30  | 1.0187 | 0.1336  |       |
|60  | 0.9686 | 0.027833|       |
|120 | 0.8183 | 0.005567|       |
|180 | 0.7515 |        |       |
|240 | 0.6346 |        |       |

|    |        |        |        |
|----|--------|--------|--------|
|  0 | 1.67   | 2.505  | 3.34   |
|10  | 1.4028 | 2.015133|       |
|20  | 1.3694 | 2.0541  |       |
|30  | 1.2692 | 1.875967|       |
|60  | 1.1356 | 1.6867  |       |
|120 | 0.9853 | 1.697833|       |
|180 | 0.8851 | 1.4362  |       |
|240 | 0.835  | 1.4195  |       |

|    |        |        |        |
|----|--------|--------|--------|
|  0 | 1.67   | 1.67   | 1.67   |
|10  | 1.503  | 1.336  |       |
|20  | 1.5197 | 1.3026 |       |
|30  | 1.4696 | 1.363833|       |
|60  | 1.4696 | 1.391667|       |
120  1.3861  1.2859
180  1.336   1.22467
240  1.3026  1.169
300  1.2859  1.14733
360  1.2692  1.157867

0    1.67    1.67    2.505
10   1.4529  1.3527
20   1.336   1.230233
30   1.3193  1.213533
60   1.2525  1.1189
120  1.1189  0.979733
180  1.0354  0.896233
240  0.9853  0.8851

**Computer code**

The following python code was used for simulations:

```python
import numpy as np
import csv
import re as re
import random

def reeq3(BFS0,B,P,K,K2,acc): #reequilibration of reaction components and each kinetic step
    x=False
    while x==False:
        Me2S=random.random()*BFS0 #starting concentration of Me2S is chosen between 0 and the initial concentration of BFS
        BFS=BFS0-Me2S  #current concentration of BFS
        BF3=K*BFS/Me2S  # current concentration of BF3
        PMPB=B-BFS-BF3  # current concentration of PMP-BF3
```

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PMP=P−PMPB # current concentration of PMP
Keff=Me2S*BF3/BFS # calculate effective equilibrium constant for BFS dissociation
Keff2=PMP*BF3/PMPB # calculate effective equilibrium constant for PMP−BF3 dissociation
rss=(Keff−K)**2+(Keff2−K2)**2 # Residual sum of squares between effective and real eq. constants

while rss>acc:
    if Me2S<−10 or Me2S>10: # convergence failure correction
        Me2S=random.random()*BFS0
        Me2S=Me2S*1.005 # new Me2S concentration, all other concentrations recalculated
        BFS=BFS0−Me2S
        BF3=K*BF3/Me2S
        PMPB=B−BFS−BF3
        PMP=P−PMPB
        Keff=Me2S*BF3/BFS # new effective equilibrium constants
        Keff2=PMP*BF3/PMPB
    if rss>(Keff−K)**2+(Keff2−K2)**2: # check whether new eff. eq. constants are closer to the real ones
        rss=(Keff−K)**2+(Keff2−K2)**2
    else:
        Me2S=Me2S/1.003 # new Me2S concentration, all other concentrations recalculated
        BFS=BFS0−Me2S
        BF3=K*BF3/Me2S
        PMPB=B−BFS−BF3
        PMP=P−PMPB
        Keff=Me2S*BF3/BFS
        Keff2=PMP*BF3/PMPB
    if rss>(Keff−K)**2+(Keff2−K2)**2:
        rss=(Keff−K)**2+(Keff2−K2)**2
    if PMP>=0 and Me2S>=0 and BF3>=0 and BFS>=0 and PMPB>=0: # check whether the found equation roots are all positive
        x=True
        # print(PMP, Me2S, BF3, BFS, PMPB)
        return(PMP, Me2S, BF3, BFS, PMPB)
def mod1(k, BF3, PMP, NMI, dt): # kinetic model 1
    return k*BF3*NMI*dt
def mod2(k, BF3, PMP, NMI, dt): # kinetic model 2
    return k*BF3**2*NMI*dt
def mod3(k, BF3, PMP, NMI, dt): # kinetic model 3
return \( k \cdot BF3 \cdot NMI \cdot PMP \cdot dt \)

def simu(k,K,K2,NMI,PMP,BFS0,dt):
    time=-10 #starting time adjusted to -10 min to account for the vessel thermal inertia
    acc=0.00001 #accuracy of the reequilibration
    P=PMP #P is a variable for the changing concentration of PMP + PMP-BF3
    ti=[]
    b=[]
    bs=[]
    nmi=[]
    pmp=[]
    m=[]
    B=BFS0 #total active boron
    while time<=360: #cycle over 6 hours
        if P>0.001 and B>0.001 and NMI>0.001: #cancel reequilibration if the limiting reagent consumed
            (PMP, Me2S, BF3, BFS, PMPB)=reeq3(BFS0,B,P,K,K2,acc) #get reequilibrated concentrations
        delta=abs(mod1(k,BF3,PMP,NMI,dt)) #change in the reaction step
        if (P-delta)>0 :
            P=P-delta
            NMI=NMI-delta
            B=B-2*delta
            Me2S=Me2S+2*delta
        time=time+dt
        ti.append(time) # record found values
        b.append(BF3)
        bs.append(BFS)
        nmi.append(NMI)
        pmp.append(PMP)
        m.append(Me2S)
    return (ti,nmi,pmp) #return timestamp, and the concentrations of N-methylindole and PMP

def extract(ti,nmi,pmp):
    #extract simulated data points relevant to the experimental ones
    timepoints=[10,20,30,60,120,180,240,300,360]
simudata=[]
for point in timepoints:
    for timestamp in ti:
        if abs(point-timestamp)<0.000001:
            ind=ti.index(float(timestamp))
            simudata.append([point,nmi[ind],pmp[ind]])
return(simudata)

def dataimport(): #import experimental data from file

    exps=[]
    points=[]
    exp=[]
    point=[]
    d = open("kinetic_data")
    exps = d.read().split('n')
    for i in range(0,len(exps)):
        exp=exps[i].split('n') #split the data into separate experiments
        points=[]
        for j in range(0,len(exp)):
            if not { exp[j] == '' or re.search("^#", exp[j]): #remove empty or missing data lines
                point=[]
                for value in exp[j].split():
                    point.append(float(value))
                points.append(point)

        exps[i]=points
    return(exps)
exps=dataimport()

def stat_treatment(real,simulated): #calculate R2 for each experiment, its mean and std over the set of experiments
    r=np.asarray(real)
    s=np.asarray(simulated)
    rss=np.sum(np.square(r-s))
    sstot=np.sum(np.square(r-np.mean(r)))
r2=1-rss/sstot
return(rss,r2)

init_cond=[]
for exp in exps:
    init_cond.append(exp[0][1:4]) # extract starting concentrations

dt=1 # set the time resolution

for k in np.arange(0.1,0.2,0.01): # loop over k, K, K2
    res=open("model1.res", "a+") # results output file
    writer = csv.writer(res)
    writer.writerow(["rate constant, K, K2, average R2, std(R2), [R2 values]"]) for K in np.arange(0.05,0.4,0.01):
        r2=np.array([]) # array of R2 for each experiment
        for exp in exps:
            real=[]
            simulated=[]
            ti,nmi,pmp=simu(k,K,K2,exp[0][1],exp[0][2],exp[0][3],dt) # simulate using experiment starting conditions
            s_data=extract(ti,nmi,pmp)
            mylist=exp[1]
            for point in exp[1:-1]:
                if len(point)>1:
                    # print (point, s_data[exp.index(point)-1]) # print experimental and simulated values
                    real.append(point[1])
                    simulated.append(s_data[exp.index(point)-1][1])
            r2=np.append(r2,stat_treatment(real,simulated)[1])
        print(k,K,K2,np.mean(r2),np.std(r2),r2) # print to stdout
        writer.writerow([k,K,K2,np.mean(r2),np.std(r2),r2]) # print to file
    res.close()
Computational Details

In the computational analysis, the DFT calculations were performed using the ωB97X-D range separated hybrid functional [1]. The Pople basis set of 6-311G** was employed for geometry optimizations, vibrational analysis and solvent correction calculations, while the electronic energies were always recalculated using the more extended 6-311++G(3df,3pd) set [2–4]. Thermal corrections were calculated (at T=333 K, p=27.34 atm) employing the rigid-rotor – harmonic oscillator (RRHO) approximation. Solvent effects (for benzene as a solvent) were obtained from the implicit PCM solvation model, using the SMD parametrization [5,6]. The ultrafine grid was used for calculating numerical integrals, all as implemented in Gaussian16 (Revision A.03) [7].

The reported relative stabilities are obtained from Gibbs free energies defined as

$$G = E_0' + (G_0 - E_0) + (G_{\text{sol}} - E_0)$$

where $E_0'$ and $E_0$ are electronic energies computed with the 6-311++G(3df,3pd) and the 6-311G** basis sets, $G_0$ and $G_{\text{sol}}$ denote gas-phase and solution-phase Gibbs free energies obtained from ωB97X-D/6-311G** calculations.

References:

1. a) Chai J-D, Head-Gordon M: Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. Phys Chem Chem Phys 2008, 10:6615–6620; b) Chai J-D, Head-Gordon M: Systematic optimization of long-range corrected hybrid density functionals. J Chem Phys 2008, 128: 084106.
2. Ditchfield R, Hehre WJ, Pople JA: Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. J Chem Phys 1971, 54:724–728.
3. Hariharan PC, Pople JA: The influence of polarization functions on molecular orbital hydrogenation energies. Theor Chim Acta 1973, 28:213–222.
4. Hehre WJ, Ditchfield R, Pople JA: Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J Chem Phys 1972, 56:2257–2261.
5. Marenich AV, Cramer CJ, Truhlar DG: Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. J Phys Chem B 2009, 113:6378–6396.
6. Ribeiro RF, Marenich AV, Cramer CJ, Truhlar DG: Use of Solution-Phase Vibrational Frequencies in Continuum Models for the Free Energy of Solvation. J Phys Chem B 2011, 115:14556–14562.
7. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, et al.: Gaussian16 Revision A.03 2016,
PMP mediated borenium pathway

The species identified computationally on the PMP mediated borenium pathway are depicted in Figure S121. They involve the PMP-borenium ion pair (4a-BF$_2^+$/BF$_4^-$), the transition state corresponding to the BF$_2^+$ transfer to Me-indole (TS$_{bor}$), and the formed intermediate (1a-BF$_2^+$(4a)/BF$_4^-$). This process is not favored neither kinetically (the barrier is 34.7 kcal/mol), nor thermodynamically (the formation of the 1a-BF$_2^+$(4a)/BF$_4^-$ intermediate is highly endergonic).

Figure S121. Species identified computationally on the PMP mediated borenium pathway. Relative stabilities are shown in parentheses (in kcal/mol; with respect to the 1a + 4a + 2 BF$_3$ reactant state).

TMTU mediated borenium pathway

The species identified computationally on the TMTU mediated borenium pathway are depicted in Figure S122. The BF$_2^+$ transfer to 1a takes place from ion pair 5a-BF$_2^+/$/BF$_4^-$ via transition state TS$_{bor}^{TMTU}$ and yields the 1a-BF$_2^+$(5a)/BF$_4^-$ intermediate.

Figure S122. Species identified computationally on the TMTU mediated borenium pathway. Relative stabilities are shown in parentheses (in kcal/mol; with respect to the 1a + 5a + 2 BF$_3$ reactant state).

In this case, we examined the deprotonation process as well. Two pathways corresponding to deprotonation via the S and N basic centers of TMTU were explored (see Figure S123), of which the former is predicted to be clearly more favored. The predicted barriers are 29.9 and 36.6 kcal/mol, respectively.
Figure S123. Deprotonation of borenium 1a-BF$_2^+$ acting TMTU as an S- and N-centered base. Relative stabilities are shown in parentheses (in kcal/mol; with respect to the 1a + 5a + 2 BF$_3$ reactant state).

**TMTU mediated FLP pathway**

The transition state identified computationally on the pathway corresponding to the FLP mechanism with TMTU as a Lewis base and BF$_3$ as a Lewis acid is depicted in Figure S124. The predicted barrier (31.7 kcal/mol) is slightly higher than that obtained with PMP (29.6 kcal/mol), but still comparable.

Figure S124. Transition state of the FLP pathway with TMTU as a base. Relative stabilities are shown in parentheses (in kcal/mol; with respect to the 1a + 5a + BF$_3$ reactant state).

**Total Energies**

Table S6. Calculated total energy components of species discussed in the main text. All values are in hartree. The energy components are defined in the Computational Details.
|    | Cartesian Coordinates                                                                 |
|----|---------------------------------------------------------------------------------------|
|    | Cartesian coordinates of the optimized geometries are given below in standard XYZ     |
|    | format (units are in Å). The first line shows the total number of atoms, the second  |
|    | line is the molecule name (as defined above in Table S6).                             |
| 4  | BF₃                                                                                   |
|    | B -0.382224 -0.425401 0.000000                                                       |
|    | F -1.039307 -1.563413 0.000000                                                       |
|    | F 0.931861 -0.425401 0.000000                                                        |
|    | F -1.039307 0.712612 0.000000                                                         |
| 13 | BF₃-SMe₂                                                                              |
|    | S -0.265344 -0.868005 0.295888                                                        |
|    | C 1.312404 -1.048889 -0.566861                                                        |
|    | H 1.954905 -0.195660 -0.353423                                                        |
|    | H 1.773000 -1.961325 -0.190372                                                        |
|    | H 1.130723 -1.150367 -1.636321                                                        |
|    | C -0.961995 0.560674 -0.564313                                                        |
|    | H -1.975078 0.691185 -0.186173                                                        |
|    | H -0.370673 1.450148 -0.350818                                                        |
|    | H -0.998832 0.356716 -1.633935                                                        |
|    | B -1.382576 -2.445140 -0.682098                                                       |
|    | F -0.750369 -3.554539 -0.226438                                                       |
|    | F -1.180552 -2.157586 -2.001382                                                       |
|    | F -2.638403 -2.218381 -0.224323                                                       |
SMe₂
S  -0.386004 -1.038164  0.082310
C  1.292956 -1.049998  0.595656
H  1.871218  -0.200464  0.226862
H  1.770767  -1.971255  0.261063
H  1.275574  -1.039816  1.292956
H  0.828579  -0.603425  0.541995
H  1.770767  -1.971255  0.261063
H  1.275574  -1.039816  1.292956
H  0.828579  -0.603425  0.541995

4a
C  -1.028253  -0.089824  2.449995
C  -1.349435   0.637459  1.133699
C  -1.354989  -1.643437  -0.033949
C  -1.033846  -2.287392  1.325089
C  -1.578128  -1.505000  2.508375
H  0.062170   -0.133264  2.556041
H  -1.409699   0.513507  3.279984
H  -1.419660  -3.311857  1.321645
H  0.056483  -2.352726  1.420293
H  -2.673332  -1.497496  2.499154
H  -1.282559  -1.985506  3.445648
C  -2.838420  -1.883882  -0.389836
C  -3.118379  -1.351133  -1.302035
H  -3.007293  -2.949992  -0.568058
H  -3.518696  -1.571915  0.402790
C  -0.499424  -2.385360  -1.076848
H  -0.569706  -3.462701  -0.904393
H  -0.829653  -2.203044  -2.101937
H  0.547082   -2.085137  -0.983763
C  -0.489000  1.914019  1.124039
H  -0.818050  2.640317  0.377498
H  -0.555338  2.404256  2.099031
H  0.556148  1.659030  0.932656
C  -2.831190  1.072397  1.123637
H  -2.995658  1.840907  1.884697
H  -3.111340  1.502104  0.158646
H  -3.514266  0.249603  1.335216
C  -1.071819  0.442525  -1.298571
H  -0.570706  1.409224  -1.276717
H  -0.574133  -0.142221  -2.070903
H  -2.109624  0.614281  -1.629607
N  -0.947558  -0.217022  -0.010722

4a-BF₃
C  -1.014126  -0.136566  2.505499
C  -1.251397  0.652619  1.205466
C  -1.256162 -1.708134 -0.007612
C  -1.017961 -2.306351  1.390404
C  -1.640023 -1.515764  2.522766
H   0.063045  -0.238035  2.681653
H  -1.395450  0.483152  3.321125
H  -1.401900  -3.329332  1.362038
H   0.059303   0.239320  1.573650
H   0.063045  -0.238035  2.681653
H   1.443948 -2.007596  3.479190
C  -2.726469 -1.899867 -0.407380
H  -2.892074 -1.640877  1.449804
H  -2.963047 -2.958315 -0.676280
H  -3.429661 -1.331338  0.192261
C  -0.436639  -2.576947 -0.981386
H  -0.876928  -3.576215 -0.958973
H  -0.480880  -2.209975  -2.002524
H   0.604960  -2.684638 -0.676280
C  -0.427120  1.947281  1.343964
H  -0.470773  2.564357  0.451415
H  -0.863973  2.512021  2.170468
H   0.614289  1.758207  1.607274
C  -2.720253  1.094422  1.130577
H  -2.953662  1.603824  2.068645
H  -2.884658  1.791389  0.313058
H  -3.426477  0.278255  1.018993
C   0.679104   -0.145862 -0.151713
H   0.992100   -0.664323 -1.049462
H   0.995082   0.884887  -0.254071
H   1.146488   -0.596455  0.724169
N  -0.812407  -0.190986  -0.058117
F  -0.768709  -0.196545  -2.541518
F  -0.765954  1.831829  -1.498794
F  -2.685318  0.595619  -1.583056
B  -1.310691  0.558718  -1.515023

4a-BF$_2^+/BF_4^-$
N  -0.726742  -0.269539  0.273250
C  -1.400235  0.627637  1.414018
C  -1.442733  -0.160672  2.730137
C  -2.099006  -1.525489  2.631492
C  -1.334672  -2.356584  1.620583
C  -1.279879  -1.775947  0.203665
C  -0.552678  1.883681  1.675358
C  -2.821424  1.056150  1.010107
C  -2.653007  -1.755454  -0.474706
C  -0.344573  -2.691107  -0.602171
C  0.784576  -0.282251  0.496837
B  -0.773161  0.399560  -1.075631
F  -0.976446  1.690880  -1.202343
F  -0.523397  -0.266237  -2.176778
F   3.278941  -2.817966   3.431109
B   2.467115  -2.160900   2.543955
F   3.157490  -1.198632   1.784299
F   1.831443  -3.068742   1.647249
F   1.404674  -1.474460   3.244938
H   -0.430595  -0.294405   3.118298
H   -1.975791   0.479374   3.439539
H   -1.777109  -3.351298   1.517387
H   -0.313924  -2.508539   1.977695
H   -3.162630  -1.453049   2.379843
H   -2.043627  -2.014282   3.605929
H   -2.607885  -1.357927  -1.492412
H   -2.991718  -2.788868  -0.561324
H   -3.412974  -1.214974   0.805010
H   -0.860923  -3.650379  -0.678810
H   -0.151998  -2.348608  -1.615887
H   0.588048  -2.884194  -0.072886
H   -0.442332  2.530573   0.807229
H   -1.077069  2.455544   2.442620
H   0.427655  1.642756   2.082966
H   -3.076573  1.941371   1.594351
H   -2.925331  1.335716  -0.037707
H   -3.567363  0.300813   1.243837
H   1.247578  -1.014926  -0.150987
H   1.191484  0.704240   0.277847
H   0.991109  -0.540473   1.530752

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1a
C  -2.882090  -0.625889  -0.009477
C  -1.468778  -0.630846  -0.009487
C  -0.718578  0.546745  -0.009382
C  -1.411163  1.742925  -0.009266
C  -2.816335  1.771154  -0.009255
C  -3.553870  0.603032  -0.009360
C  -3.298116  -1.997793  -0.009581
C  -2.162472  -2.750876  -0.009706
H  0.365533  0.528064  -0.009398
H  -0.860567  2.676798  -0.009183
H  -3.325969  2.727964  -0.009161
H  -4.637926  0.635296  -0.009344
H  -4.308966  -2.373473  -0.009587
H  -2.044354  -3.824334  -0.009824
N  -1.050228  -1.939609  -0.009628
C  0.326005  -2.370998  -0.009712
H  0.848591  -2.007236  -0.899234
H  0.848669  -2.007311  0.879795
H  0.358427  -3.460253  -0.009756
| Atom | x | y | z |
|------|---|---|---|
| C    | -2.184784 -0.197020 0.218182 |
| C    | -2.521337 1.251807 0.410982 |
| C    | -2.213993 -0.954554 1.467830 |
| B    | 1.544426 -1.473004 1.902975 |
| C    | 1.059362 -0.274005 -0.499132 |
| C    | 1.758840 -1.299531 -1.074260 |
| H    | -0.000085 -0.273016 -0.262873 |
| H    | -1.556966 -0.494095 2.198847 |
| H    | -1.811882 -1.950745 1.309824 |
| H    | -3.215793 -1.055015 1.919478 |
| H    | 1.423340 -2.288581 -1.349563 |
| F    | 1.015853 -0.431072 2.520056 |
| F    | 2.854278 -1.560556 1.764334 |
| C    | 1.990203 0.811046 -0.350667 |
| N    | 3.062731 -0.934430 -1.290009 |
| C    | 3.232387 0.355586 -0.841481 |
| C    | 1.900063 2.108830 0.167265 |
| H    | 0.957087 2.485117 0.550793 |
| C    | 4.380076 1.149415 -0.820293 |
| H    | 5.331059 0.782507 -1.189295 |
| C    | 4.259508 2.425562 -0.303975 |
| H    | 5.129892 3.070989 -0.271744 |
| C    | 3.030542 2.902070 0.183753 |
| H    | 2.974751 3.908465 0.582571 |
| C    | -2.914844 -0.888053 -0.893182 |
| F    | 0.789558 -2.530671 1.648284 |
| C    | 4.124837 -1.799631 -1.743826 |
| H    | 4.682714 -1.324831 -2.554597 |
| H    | 4.812364 -2.035713 -0.926377 |
| H    | 3.692679 -2.726889 -2.119099 |
| C    | -4.047906 1.464742 -0.490664 |
| H    | -4.258164 2.538242 0.547358 |
| H    | -4.413966 1.024439 1.426514 |
| H    | -4.436398 -0.648210 -0.796542 |
| C    | -1.894004 1.773529 1.715200 |
| H    | -0.823010 1.556455 1.753350 |
| H    | -2.024768 2.856866 1.760212 |
| H    | -2.363620 1.357138 2.607516 |
| C    | -1.916452 2.122824 -0.711488 |
| H    | -1.847865 3.158256 -0.368963 |
| H    | -0.912316 1.782699 -0.969461 |
| H    | -2.512035 2.138889 -1.621233 |
| C    | -2.382586 -0.445450 -2.271216 |
| H    | -2.726422 0.537121 -2.582008 |
| H    | -1.290589 -0.439705 -2.272412 |
| H    | -2.723826 -1.151995 -3.032216 |
| C    | -2.662953 -2.404367 -0.836607 |
|       |       |       |       |
|-------|-------|-------|-------|
| H     | -3.088297 | -2.864881 | -1.730948 |
| H     | -1.590918 | -2.622801 | -0.820567 |
| H     | -3.130773 | -2.882199 | 0.025128 |
| C     | -4.799220 | 0.829474  | -0.676371 |
| H     | -4.817852 | -1.177154 | 0.085781 |
| H     | -4.927719 | -1.097333 | -1.666389 |
| H     | -5.877555 | 0.936229  | -0.526029 |
| H     | -4.571182 | 1.354892  | -1.609678 |
|       |       |       |       |
| TSP   |       |       |       |
| N     | -1.667089 | 0.195429  | -0.225366 |
| C     | -1.814748 | -1.089814 | -1.031922 |
| C     | -2.234582 | 1.345653  | -0.970238 |
| B     | 0.923251  | 2.311551  | -0.824842 |
| C     | 1.024938  | 0.871797  | 0.033466 |
| C     | 1.296149  | 0.948610  | 1.404952 |
| H     | -0.270228 | 0.541964  | 0.093870 |
| H     | -1.743649 | 1.429782  | -1.930891 |
| H     | -1.996838 | 2.265069  | -0.450572 |
| H     | -3.315997 | 1.257119  | -1.106784 |
| H     | 0.886064  | 1.647494  | 2.121229 |
| F     | 0.449953  | 2.013120  | -2.122822 |
| F     | 2.177571  | 2.899756  | -0.892053 |
| C     | 1.914724  | -0.203227 | -0.414143 |
| N     | 2.162068  | 0.010758  | 1.814603 |
| C     | 2.565471  | -0.736670 | 0.706508 |
| C     | 2.213112  | -0.727935 | -1.672177 |
| H     | 1.772766  | -0.289847 | -2.558782 |
| C     | 3.451042  | -1.806982 | 0.640806 |
| H     | 3.936027  | -2.206547 | 1.524132 |
| C     | 3.698390  | -2.334924 | -0.615664 |
| H     | 4.383389  | -3.168490 | -0.718279 |
| C     | 3.095045  | -1.792104 | -1.758705 |
| H     | 3.336647  | -2.208335 | -2.730006 |
| C     | -2.240165 | 0.132012  | 1.183063 |
| F     | 0.017577  | 3.153782  | -0.134387 |
| C     | 2.625151  | -0.210375 | 3.167102 |
| H     | 2.344505  | -1.210751 | 3.505381 |
| H     | 3.711408  | -0.107683 | 3.214517 |
| C     | 2.169847  | 0.529012  | 3.824382 |
| C     | -3.285847 | -1.546229 | -1.029034 |
| C     | -3.346228 | -2.498485 | -1.564826 |
| H     | -3.886584 | -0.832827 | -1.603052 |
| C     | -3.695318  | -0.376554 | 1.148451 |
| C     | -1.367473  | -0.829328 | -2.479345 |
| H     | -0.438014 | -0.260049 | -2.509293 |
| H     | -1.204887 | -1.786046 | -2.978695 |
| H     | -2.117552 | -0.284627 | -3.054144 |
| C     | -0.920394 | -2.220530 | -0.494917 |
H -0.947750 -3.041521 -1.214404
H 0.116835 -1.902506 -0.402042
H -1.246313 -2.626050 0.458018
H -1.214404 -0.781866 2.101701
H -1.799419 -1.789651 2.174364
H -0.359904 -0.866053 1.770800
H -1.385958 -0.372611 3.113614
C -2.236900 1.542717 1.798989
H -2.444137 1.459918 2.867655
H -1.281051 2.049928 1.660523
H -3.010175 2.180671 1.370575
C -3.871211 -1.679574 0.373762
H -4.332072 0.392848 0.699308
H -4.035986 -0.491512 2.182613
H -4.934298 -1.926999 0.310323
H -3.399845 -2.512254 0.905189

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int
N -2.013970 0.307366 0.115213
C -2.626505 -0.532419 -1.034434
C -2.801313 1.541955 0.406652
B 0.711899 2.352853 -0.459817
C 1.718405 1.217385 0.048768
C 2.212425 1.052309 1.310827
H -1.136041 0.688288 -0.294835
H -2.954570 2.083686 -0.517596
H -2.204238 2.185028 1.041568
H -3.754683 1.287738 0.867419
H 2.077062 1.680545 2.180473
F -0.294634 1.674754 -1.337733
F 1.257740 3.382335 -1.196647
C 2.218672 0.084040 -0.690935
N 2.970786 -0.099996 1.418405
C 2.985587 -0.713212 0.190883
C 2.057160 -0.345303 -2.015059
H 1.481955 0.259297 -2.707074
C 3.586372 -1.908646 -0.209180
H 4.177661 -2.504857 0.477574
C 3.402574 -2.305515 -1.521703
H 3.857045 -3.227337 -1.867888
C 2.645136 -1.530959 -2.417160
H 2.531531 -1.867796 -3.441786
C -1.654823 -0.471688 1.408219
F -0.055898 2.869780 0.631743
C 3.673758 -0.559931 2.588177
H 3.376017 -1.581351 2.846010
H 4.757297 -0.541208 2.434036
H 3.432220 0.092859 3.427133
C -3.804803 -1.340228 -0.482014
|       |       |       |       |
|-------|-------|-------|-------|
| H     | -4.170650 -1.978764 -1.290832 |
| H     | -4.624390 -0.654644 -0.236567 |
| C     | -2.882263 -1.280987 1.844792  |
| C     | -3.111574 0.403674 -2.149630  |
| H     | -2.319099 1.090492 -2.453961  |
| H     | -3.378117 -0.212836 -3.009540  |
| H     | -4.002445 0.968622 -1.873021  |
| C     | -1.539269 -1.421589 -1.653079  |
| H     | -1.915740 -1.805578 -2.602551  |
| H     | -0.634896 -0.845820 -1.859972  |
| H     | -1.268621 -2.278683 -1.045489  |
| C     | -0.433925 -1.375836 1.171143  |
| H     | -0.693591 -2.359668 0.787679  |
| H     | 0.291254 -0.917131 0.499652   |
| H     | 0.070609 -1.528068 2.125883  |
| C     | -1.275030 0.530393 2.505217   |
| H     | -0.894757 -0.036885 3.356190  |
| H     | -0.493916 1.211415 2.162323   |
| H     | -2.128040 1.110218 2.859753   |
| C     | -3.460422 -2.170905 0.749274  |
| H     | -3.660754 -0.596437 2.200898  |
| H     | -2.581532 -1.878685 2.709755  |
| H     | -4.360879 -2.667351 1.119181  |
| H     | -2.758736 -2.967984 0.488537  |

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**int-BF₃**

|       |       |       |       |
|-------|-------|-------|-------|
| N     | -2.125997 -0.597147 -0.321170 |
| C     | -2.643843 -0.980301 1.091604 |
| C     | -2.357873 -1.675365 -1.327685 |
| B     | 1.241191 -0.881232 -1.062221 |
| C     | 1.569143 0.646514 -0.824319 |
| C     | 1.567707 1.657162 -1.743570 |
| H     | -1.096230 -0.601480 -0.211118 |
| H     | -1.941362 -2.600223 -0.949037 |
| H     | -1.803428 -1.436689 -2.226751 |
| H     | -3.421965 -1.783680 -1.532053 |
| H     | 1.454180 1.599894 -2.817282 |
| F     | 0.356586 -1.340323 -0.001246 |
| F     | 2.402105 -1.769119 -0.962913 |
| C     | 1.754682 1.298523 0.448985  |
| N     | 1.729971 2.887769 -1.141231 |
| C     | 1.844906 2.688242 0.214056 |
| C     | 1.827894 0.825428 1.766226 |
| H     | 1.789983 -0.240980 1.958618 |
| C     | 1.999375 3.613095 1.248757 |
| H     | 2.075523 4.677360 1.054158 |
| C     | 2.057617 3.117202 2.538787 |
| H     | 2.180316 3.805431 3.367781 |
| C     | 1.974404 1.737523 2.795197 |
H 2.041747 1.385603 3.818587
C -2.530949 0.803355 -0.846249
F 0.602128 -1.137326 -2.281901
C 1.827956 4.162916 -1.805759
H 1.081823 4.862491 -1.416648
H 2.821473 4.602027 -1.673749
H 1.649351 4.023005 -2.871851
C -4.155140 -0.738062 1.139711
H -4.484852 -0.935651 2.163281
H -4.656505 -1.479618 0.506733
C -4.049410 0.955309 -0.704559
C -2.338390 -2.459736 1.363358
H -1.281340 -2.684794 1.204103
H -2.571548 -2.658770 2.410433
H -2.950352 -3.136410 0.766122
C -1.881510 -0.173051 2.152132
H -2.053426 -0.643253 3.121396
H -0.806029 -0.189121 1.963270
H -2.201904 0.860226 2.237456
C -1.767306 1.897695 -0.083705
H -2.227639 2.172589 0.861157
H -0.729191 1.616711 0.101004
H -1.750974 2.795386 -0.703065
C -2.126327 0.920432 -2.321045
H -2.296086 1.952511 -2.631470
H -1.067109 0.692136 -2.459986
H -2.722349 0.284584 -2.976288
C -4.571345 0.661248 0.698493
H -4.546989 0.290868 -1.420596
H -4.302696 1.975571 -1.005572
H -5.661329 0.736688 0.704775
H -4.210619 1.410298 1.408776
F 3.724075 -3.682545 -0.338304
F 1.445665 -3.925561 -0.245751
F 2.527343 -2.651473 1.323941
B 2.545015 -3.234510 0.109760

TS_{trans}
N 2.192358 0.192484 -0.321569
C 2.792204 0.434169 1.089940
C 2.606599 1.237379 -1.304322
B -1.079587 1.088075 -0.974483
C -1.727765 -0.339637 -0.782215
C -1.959167 -1.292125 -1.733884
H 1.182858 0.383953 -0.190001
H 2.354796 2.210885 -0.901829
H 2.019549 1.119093 -2.206208
H 3.673467 1.165250 -1.510709
H -1.854625 -1.220480 -2.807626
| A   |   B        |   C        |   D    |
|-----|-----------|-----------|-------|
| 1.23 | 1.3458    | 0.12345   | 1.2345 |
| 4.56 | 7.89      | 0.98765   | 1.2345 |
| 7.89 | 0.9876    | 1.2345    | 1.2345 |
| 1.23 | 4.5689    | 0.12345   | 1.2345 |
| 7.89 | 0.9876    | 1.2345    | 1.2345 |
| 1.23 | 4.5689    | 0.12345   | 1.2345 |
2a-4aH+/BF₄⁻
N 2.194551 0.134675 0.544721
C 3.480726 0.208757 -0.318894
C 2.466449 -0.444166 1.893955
B -1.976222 0.455109 -2.747214
C -2.417333 0.034768 -1.363241
C -2.425045 -1.259291 -0.880494
H 1.589441 -0.553504 0.061029
H 2.872093 -1.440768 1.768425
H 1.530103 -0.558706 2.421500
H 3.153461 0.196726 2.444237
H -2.144540 -2.174370 -1.380212
F -1.643720 -0.416136 -3.699688
F -0.366230 -3.662391 -0.270126
C -2.799540 0.863238 -0.244052
N -2.790563 -1.290942 0.422546
C -3.019552 0.002525 0.849940
C -2.948081 2.241985 -0.059019
H -2.795387 2.921942 -0.889288
C -3.369703 0.470555 2.114618
C -3.531358 -0.208325 2.943914
C -3.497973 1.839647 2.272773
H -3.768740 2.241477 3.242482
C -3.291401 2.716228 1.195494
H -3.411411 3.782659 1.351004
C 1.336212 1.429295 0.616525
F -1.862232 1.746891 -3.088231
C -2.906652 -2.472937 1.251577
H -2.298583 -2.352268 2.148227
H -3.951392 -2.645022 1.523353
H -2.513981 -3.323908 0.700247
C 4.285365 1.441598 0.107198
H 5.137416 1.523833 -0.573280
H 4.706046 1.269691 1.104578
C 2.247328 2.594159 1.010429
C 4.305629 -1.066027 -0.097787
H 3.701670 -1.962254 -0.259585
H 5.121565 -1.066606 -0.822055
H 4.756209 -1.112372 0.893959
C 3.115096 0.238875 -1.810550
H 4.010975 -0.011815 -2.380353
H 2.352496 -0.506842 -2.040661
H 2.776375 1.208677 -2.160841
C 0.642638 1.662584 -0.731578
H 1.276129 2.122359 -1.483886
H 0.241418 0.726834 -1.122323
H -0.202550 2.330675 -0.568944
C 0.226008 1.232632 1.655281
H -0.490484 2.049118 1.555306
H -0.315078 0.300637 1.478917
H 0.598132 1.246967 2.680492
C 3.478746 2.737013 0.120535
H 2.564926 2.468271 2.052061
H 1.640525 3.503225 0.982099
H 4.105898 3.551096 0.491895
H 3.187004 3.017621 -0.895269
F 1.799229 -3.244744 0.449053
F 0.047468 -2.067453 1.345547
F 0.696859 -1.683987 -0.818528
B 0.531791 -2.720994 0.187932

21
2a
C -2.902597 -0.595808 -0.009461
C -1.494906 -0.617806 -0.009520
C -0.722804 0.542848 -0.009403
C -1.398542 1.749424 -0.009219
C -2.801971 1.796268 -0.009151
C -3.559280 0.639730 -0.009268
C -3.350229 -1.970674 -0.009634
C -2.201151 -2.730116 -0.009813
H 0.30675 0.506292 -0.009446
H -0.835388 2.675559 -0.009119
H -3.297478 2.760352 -0.009000
H -4.641775 0.681607 -0.009216
H -2.101290 -3.806238 -0.009976
N -1.093649 -1.942010 -0.009672
C 0.280695 -2.387945 -0.009729
H 0.801588 -2.025098 -0.899428
H 0.801604 -2.025293 0.880040
H 0.302262 -3.476999 -0.009847
B -4.762161 -2.528439 -0.009667
F -4.999352 -3.841915 -0.009468
F -5.839887 -1.743910 -0.009983

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4aH "/BF4-
N 2.202638 0.117826 0.546075
C 3.493573 0.199755 -0.311445
C 2.461264 -0.460343 1.898770
H 1.603304 -0.572753 0.052688
H 2.926358 -1.429650 1.777467
H 1.511729 -0.640945 2.384978
H 3.087612 0.214151 2.480999
F -0.286298 -3.656725 -0.323209
C 1.339984 1.406178 0.616135
C 4.288256 1.439624 0.110089
H 5.147461 1.518818 -0.561669
H 4.697411 1.279688 1.114307
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 2.243301 | 2.585300 | 0.990547 |
| C    | 4.329208  | -1.066393 | -0.807779 |
| H    | 3.730512  | -1.966789 | -0.238994 |
| H    | 5.145288  | -1.063221 | 0.908628  |
| C    | 3.129693  | 0.220314  | 0.990547  |
| H    | 4.027254  | -0.027382  | -2.372135 |
| C    | 2.370629  | -0.530737  | -2.028361 |
| H    | 2.786430  | 1.187239  | -2.159142 |
| C    | 0.619149  | 1.626555  | -0.722447 |
| H    | 1.251492  | 2.049200  | -1.497486 |
| H    | 0.184454  | 0.694573  | -1.087288 |
| H    | -0.193779 | 2.334216  | -0.553966 |
| C    | 0.246084  | 1.221102  | 1.675570  |
| H    | -0.439260 | 2.066668  | 1.599708  |
| H    | -0.316967 | 0.300904  | 1.503875  |
| C    | 0.639737  | 1.216503  | 2.692394  |
| H    | 3.473807  | 2.729098  | 0.100968  |
| H    | 2.563948  | 2.475280  | 2.032914  |
| H    | 1.629625  | 3.489590  | 0.952751  |
| H    | 4.091956  | 3.553933  | 0.463558  |
| H    | 3.182638  | 2.993487  | -0.919529 |
| F    | 1.317886  | 0.727888  | 0.470778  |
| F    | 0.809157  | 1.284474  | 0.893224  |
| C    | 1.846742  | 0.066709  | 1.548964  |
| N    | -0.976256 | -1.100025 | 0.108366  |
| C    | -1.001104 | 0.281681  | 0.712945  |
| H    | -0.194491 | 0.380408  | 1.429048  |
| H    | -1.954015 | 0.483733  | 1.184892  |
| C    | -1.494790 | -2.114636 | 1.262346  |
| C    | -1.900133 | -1.100377 | -1.197146 |
| C    | -3.011688 | -1.943241 | 1.454028  |
| C    | -1.162465 | -3.578801 | 0.944402  |
| H    | -1.797250 | -4.011986 | 0.177009  |

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BF₄⁻
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| B    | -0.382224 | -0.425401 | -0.000005 |
| F    | -1.048062 | -1.578589 | -0.470778 |
| F    | 0.949403  | -0.425401 | -0.470815 |
| F    | -1.048062 | 0.727788  | -0.470777 |
| F    | -0.382275 | -0.425401 | 1.412375 |

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TSbor
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| B    | 0.525179 | -1.448556 | -0.159821 |
| F    | 1.317886 | -1.284474 | 0.893224 |
| F    | 0.809157 | -2.432442 | -1.009092 |
| C    | 1.846742 | 0.066709  | -1.548964 |
| N    | -0.976256 | -1.100025 | 0.108366 |
| C    | -1.001104 | 0.281681  | 0.712945 |
| H    | -0.194491 | 0.380408  | 1.429048 |
| H    | -1.954015 | 0.483733  | 1.184892 |
| C    | -1.494790 | -2.114636 | 1.262346 |
| C    | -1.900133 | -1.100377 | -1.197146 |
| C    | -3.011688 | -1.943241 | 1.454028 |
| C    | -1.162465 | -3.578801 | 0.944402 |
| H    | -1.797250 | -4.011986 | 0.177009 |
H -0.121445  -3.736558  0.666067
H -1.337357  -4.149319  1.858172
C -3.359178  -0.914469  -0.762113
H -3.486658   0.078125  -0.321927
H -3.952435  -0.911509  -1.679737
C -1.554905   0.070846  -0.032192
H -1.811414  -1.046463  -2.037749
C -3.325076  -0.829055   0.062962
C -4.076373  -1.188270  -1.003170
C -4.362776  -0.867063   0.931114
C -5.167795  -1.150870  -0.154457
H -3.968135  -1.981582  -1.733908
C -5.307342  -0.136007   0.804663
H -4.470527   1.651834   1.670487
H -5.930246  -1.917823  -0.226800
H -6.173077  -1.136716   1.456995
C -1.379209   1.261662  -1.022585
H  0.515684   1.858269  -1.285863
N  2.191961   1.688727  -0.033710
C  1.942696   2.842707   0.813185
H  2.644979   3.645762   0.579284
H  0.918815   1.805047   0.658643
H  2.056711   2.557794   1.861082
C -1.744554  -2.377077  -2.037750
C -0.811818  -2.379388  -2.596838
H -1.805002  -3.306479  -1.484707
H -2.562895  -2.375757  -2.760629
C -0.845572  -1.791318   2.619863
H  0.225512  -1.973140   2.639264
H -1.044358  -0.776370   2.956850
H -1.310395  -2.461613   3.345613
F -1.287620   3.029204   1.309474
F -2.498950   4.560836   0.075435
F -3.030891   2.316040  -0.018466
F -1.077022   3.070917  -0.973847
B -2.002124   3.283817   0.112183
H -0.863961   1.015573  -0.060516
C -3.845913  -1.991173   0.187783
H -4.894042  -1.818380   0.442022
H -3.798645  -2.979738  -0.280609
H -3.312251  -2.735434   2.145641
H -3.207944  -1.000070   1.971313
H  1.515045  -0.376760  -2.474732

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1a-BF₂⁺(4a)/BF₄⁻
B  0.000000   0.000000   0.000000
| Atoms | X     | Y     | Z     |
|-------|-------|-------|-------|
| F     | -0.000000 | -0.000000 | 1.389848 |
| F     | -1.255631 | 0.298796 | -0.512222 |
| C     | 0.260940 | -1.627202 | -0.480521 |
| N     | 1.090899 | 1.176827 | -0.469357 |
| C     | 2.387001 | 0.805206 | 0.181360 |
| H     | 2.219716 | 0.593455 | 1.230066 |
| C     | 0.662906 | 2.592212 | -0.480521 |
| N     | 1.090899 | 1.176827 | -0.469357 |
| C     | 2.387001 | 0.805206 | 0.181360 |

-continued-
B  5.057631  -1.374412  -0.363465  
H  2.799069  -0.076913  -0.275340  
C  1.544580  3.783320  -1.941642  
H  2.161658  4.621313  -2.275340  
H  0.541590  3.950280  -2.346682  
H  1.138518  4.653399  -0.003061  
H  2.553404  3.632627  -0.068484  
H  0.112080  3.950280  -1.559020  

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5a

C  -1.086899  0.055678  -0.075267  
S  -1.802925  0.974561  -1.279514  
N  -1.500857  0.093872  1.229793  
N  -0.040448  -0.794529  -0.316284  
C  0.663932  -0.735882  -1.583789  
H  1.630116  -1.231059  -1.459279  
H  0.102077  -1.233828  -2.382980  
H  0.825134  0.299620  -1.876007  
C  0.036915  -2.090636  0.345743  
H  0.982457  -2.214965  0.883958  
H  -0.787751  -2.062331  1.045838  
H  -0.039808  -2.884175  -0.405271  
C  -2.754024  0.739842  1.573975  
H  -3.521362  0.481740  0.847180  
H  -3.058612  0.386610  2.562227  
H  -2.654871  1.831686  1.594214  
C  -0.535622  0.052753  2.321111  
H  0.472062  -0.066618  1.928807  
H  -0.576425  0.997228  2.874187  
H  -0.746785  -0.764946  3.018181  

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5a-BF₃

S  -2.570228  0.245145  -0.753449  
C  -0.906914  0.238541  -0.355652  
C  -1.031167  -2.118163  0.319158  
H  -0.404032  -2.711257  0.988357  
H  -1.947385  -1.840020  0.833722  
H  -1.288921  -2.719758  -0.558101  
C  1.118486  -1.146709  -0.364243  
H  1.494118  -0.343626  -0.995468  
H  1.729331  -1.207549  0.541565  
H  1.210422  -2.089763  -0.908917  
C  0.820246  1.581056  0.728538  
H  0.781366  0.770564  1.452882  
H  1.836244  1.672907  0.332542  
H  0.551342  2.505021  1.245382  
C  -0.541670  2.565219  -1.049023  
H  -1.160774  2.308115  -1.904809  

S121
H -1.102473 3.244165 -0.404619
H 0.372463 3.054993 -1.394043
N -0.157709 1.357649 -0.330006
N -0.288749 -0.923638 -0.059546
B -3.312188 1.815579 0.507331
F -2.316723 1.998936 1.443213
F -3.509445 2.902150 -0.297240
F -4.449620 1.249331 0.989783

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5a-BF₂⁺/BF₄⁻
C -0.301999 -0.387905 -0.087512
S 1.359669 -1.056253 -0.144176
N -0.473587 0.887523 -0.403397
N -1.282753 -1.182302 0.297616
C -1.049199 -2.524577 0.831783
H -1.891717 -2.776824 1.475489
H -0.999850 -3.225291 -0.004741
H -0.134131 -2.566135 1.415106
C -2.681147 -0.960028 -0.101371
H -3.276311 -0.631569 0.753855
H -2.721575 -0.262728 -0.931120
H -3.052062 -1.909230 -0.481623
C 0.389531 1.578444 -1.361539
H 1.105636 2.220001 -0.839124
H 0.881173 0.853923 -2.003467
H -0.256748 2.185873 -1.995052
C -1.539783 1.707771 0.154524
H -1.098439 2.667052 0.432742
H -2.333965 1.876468 -0.575467
H -1.945423 1.244325 1.050848
B 2.120524 0.003209 1.116409
F 3.391335 -0.204485 1.393320
F 1.470570 0.956023 1.763109
F 0.283836 -1.054625 -2.842632
B -1.090160 -1.280401 -3.146612
F -1.543874 -2.326239 -2.300020
F -1.796557 -0.084349 -2.802734
F -1.267634 -1.588908 -4.470832

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TS_{bor}^{TMTU}
C 0.000000 0.000000 0.000000
S 0.000000 -0.000000 1.802633
N -0.538871 1.009070 -0.661274
N 0.399108 -1.132146 -0.577810
C 0.515678 -2.386993 0.168151
H 0.412476 -3.198386 -0.552709
H 1.491372 -2.461724 0.652318
H -0.265928 -2.484129 0.916119
|     |   X      |   Y      |   Z      |
|-----|---------|---------|---------|
| C   | 1.037666| -1.20824| -1.900477|
| H   | 2.029818| -1.638825| -1.757930|
| H   | 0.449093| -1.845661| -2.073600|
| H   | -1.140877| -0.095016| -2.348008|
| H   | -1.816772| 1.530568| -2.199654|
| H   | -0.114565| 1.333912| -2.700203|
| C   | -0.551053| 2.372994| -0.132884|
| H   | -0.685231| 2.361620| 0.944157|
| H   | 0.396656| 2.850916| -0.383007|
| H   | -1.382847| 2.906309| -0.590389|
| B   | 1.412978| 1.078224| 2.357943|
| F   | 1.760530| 0.846165| 3.611354|
| F   | 1.696749| 2.242584| 1.815982|
| C   | 3.496831| -0.497691| 1.368690|
| H   | 3.023439| -0.791847| 0.447344|
| C   | 3.756646| -1.268563| 2.551784|
| C   | 3.753582| -0.448888| 3.400755|
| C   | 4.942022| -0.860328| 4.668508|
| C   | 3.811072| -2.966056| 4.246547|
| H   | 2.819907| -3.211184| 2.363063|
| C   | 4.571541| -2.127962| 5.077714|
| H   | 5.528405| -0.213707| 5.311286|
| H   | 3.543711| -3.956691| 4.596260|
| H   | 4.874651| -2.482364| 6.056222|
| C   | 4.138706| 0.701661| 1.531238|
| H   | 4.194058| 1.531960| 0.843098|
| N   | 4.757787| 0.744279| 2.749854|
| C   | 5.441326| 1.884923| 3.312962|
| H   | 6.450807| 1.608806| 3.627421|
| H   | 4.893800| 2.280135| 4.173434|
| H   | 5.512649| 2.661776| 2.552944|
| B   | 3.007689| 1.447785| -1.818897|
| F   | 2.099283| 1.674042| -2.886380|
| F   | 3.688789| 0.244246| -2.020068|
| F   | 3.869746| 2.512002| -1.637905|
| F   | 2.201023| 1.300733| -0.633720|

1a-BF$_2$+(5a)/BF$_4^-$

|     |   X      |   Y      |   Z      |
|-----|---------|---------|---------|
| C   | 0.000000| 0.000000| 0.000000|
| S   | 0.000000| 0.000000| 1.738196|
| N   | -0.358298| 1.114265| -0.639317|
| N   | 0.298434| -1.100384| -0.717784|
| C   | 0.089490| -2.450479| -0.211830|
| H   | -0.406129| -3.033362| -0.992947|
| H   | 1.038231| -2.929246| 0.041426|
| H   | -0.530299| -2.431657| 0.679838|
| Atom | X  | Y  | Z   |
|------|----|----|-----|
| C    | 0.973841 | -1.035598 | -2.014195 |
| H    | 1.826576  | -1.718612  | -1.978062  |
| H    | 0.312392  | -1.349513  | -2.826927  |
| H    | 1.360597  | -0.037170  | -2.198882  |
| C    | -0.976325 | 1.097874   | -1.963383  |
| H    | -1.345498 | 0.100744   | -2.192924  |
| H    | 1.360597  | 0.037170   | -2.198882  |
| C    | -0.976325 | 1.097874   | -1.963383  |
| H    | -1.345498 | 0.100744   | -2.192924  |
| B    | 1.667102  | -1.006310  | 2.385688   |
| F    | 1.405544  | -2.362324  | 2.461063   |
| F    | 1.869211  | -0.430048  | 3.620470   |
| C    | 2.915379  | -0.736196  | 1.331653   |
| H    | 2.570652  | -1.099545  | 0.359019   |
| C    | 4.211567  | -1.341100  | 1.762919   |
| C    | 5.147566  | -0.317148  | 1.877044   |
| C    | 5.899740  | -2.866640  | 2.475184   |
| H    | 3.868207  | -3.445278  | 2.020213   |
| C    | 6.821009  | -1.823754  | 2.574607   |
| H    | 7.163212  | 0.300630   | 2.357715   |
| H    | 6.213106  | -3.874180  | 2.721961   |
| H    | 7.835247  | -2.033642  | 2.892066   |
| C    | 3.268420  | 0.670877   | 1.193874   |
| H    | 2.639075  | 1.485622   | 0.868154   |
| N    | 4.506706  | 0.896380   | 1.513524   |
| C    | 5.178396  | 2.183766   | 1.408487   |
| H    | 5.525018  | 2.498811   | 2.393458   |
| H    | 4.477128  | 2.902418   | 0.989211   |
| H    | 6.024214  | 2.078139   | 0.728340   |
| B    | 2.978283  | 2.263204   | -1.703066  |
| F    | 1.810376  | 2.256825   | -2.489065  |
| F    | 3.280669  | 0.912212   | -1.347113  |
| F    | 4.044934  | 2.840258   | -2.347357  |
| F    | 2.697754  | 2.966534   | -0.484435  |

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TS_{depS}

| Atom | X  | Y  | Z   |
|------|----|----|-----|
| C    | 0.000000  | 0.000000  | 0.000000  |
| S    | 0.000000  | -0.000000 | 1.732387  |
| N    | -0.705329 | 0.934586  | -0.645696 |
| N    | 0.618385  | -0.970634 | -0.697723 |
| C    | 1.129623  | -2.166765 | -0.045712 |
| H    | 1.129979  | -2.977151 | -0.778034 |
| H    | 2.153845  | -2.010788 | 0.310110  |
| H    | 0.501897  | -2.441768 | 0.797785  |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 1.177665 | -0.754167 | -2.032415 |
| H       | 2.227826 | -1.048159 | -2.004781 |
| H       | 0.655614 | -1.358029 | -2.781261 |
| H       | 1.152677 | 0.298537  | -2.292473 |
| H       | -1.312248 | -0.320841 | -2.218017 |
| H       | -2.328354 | 1.093306  | -1.918715 |
| H       | -0.758118 | 1.302283  | -2.724074 |
| C       | -1.296435 | 0.735826  | -1.960541 |
| H       | -2.054000 | 2.165383  | 0.412194  |
| H       | -0.319992 | 2.476278  | 0.721713  |
| B       | 2.294347  | 0.923041  | 4.070691  |
| F       | 1.831209  | 0.089731  | 4.991038  |
| F       | 2.210763  | 2.218444  | 4.318556  |
| C       | 2.868212  | 0.381868  | 2.743645  |
| H       | 1.694042  | 0.264160  | 2.142786  |
| C       | 3.471434  | -0.953340 | 2.581298  |
| C       | 4.497535  | -0.828666 | 1.641917  |
| C       | 3.156477  | -2.208275 | 3.088867  |
| C       | 5.230562  | -1.909890 | 1.175836  |
| C       | 3.882937  | -3.301487 | 2.636946  |
| H       | 2.358683  | -2.324940 | 3.811581  |
| C       | 4.903882  | -3.155956 | 1.692037  |
| H       | 6.017308  | -1.792190 | 0.440692  |
| H       | 3.654098  | -4.288911 | 3.020313  |
| H       | 5.449154  | -4.030085 | 1.356719  |
| C       | 3.665591  | 1.218231  | 1.902483  |
| H       | 3.526954  | 2.732724  | 1.712261  |
| N       | 4.591994  | 0.524510  | 1.278037  |
| C       | 5.480231  | 1.027716  | 0.242774  |
| H       | 6.516153  | 0.941045  | 0.575194  |
| H       | 5.218801  | 2.059616  | 0.021151  |
| H       | 5.321306  | 0.446327  | -0.664972 |
| B       | 2.410962  | 2.480478  | -0.838275 |
| F       | 1.465674  | 2.589837  | -1.863657 |
| F       | 2.677514  | 1.090855  | -0.610174 |
| F       | 3.613528  | 3.110348  | -1.167259 |
| F       | 1.909610  | 3.015855  | 0.368560  |

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**TS\_{depr}^N**

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 0.000000 | 0.000000 | 0.000000 |
| S       | 0.000000 | 0.000000 | 1.677895 |
| N       | -0.695087 | 0.848117 | -0.739668 |
| N       | 0.882685  | -0.950590 | -0.636674 |
| C       | 0.520101  | -2.367076 | -0.452347 |
| H       | -0.293055 | -2.645443 | -1.129553 |
| H       | 1.399155  | -2.972470 | -0.677590 |
| H       | 0.221901  | -2.533225 | 0.579599 |
|   |     |     |     |
|---|-----|-----|-----|
| C | 1.472097 | -0.684995 | -1.964325 |
| H | 2.418036 | -1.229165 | -2.001196 |
| H | 0.845802 | -1.045635 | -2.780028 |
| H | 1.675879 | 0.376706 | -2.084914 |
| C | -1.070303 | 0.648846 | -2.137976 |
| H | -1.064041 | -0.407280 | -2.394897 |
| H | -2.093200 | 1.010051 | -2.250867 |
| H | -0.421615 | 1.225959 | -2.798776 |
| C | -1.250605 | 2.058762 | -0.139595 |
| H | -1.289362 | 2.817670 | -0.918700 |
| H | -2.245069 | 1.859231 | 0.270170 |
| H | -0.591386 | 2.402887 | 0.651613 |
| B | 2.605415 | -1.104199 | 2.230338 |
| F | 2.299923 | -2.396731 | 2.376438 |
| F | 2.688040 | -0.367312 | 3.328324 |
| C | 3.139557 | -0.626998 | 0.845699 |
| H | 2.013432 | -0.762299 | 0.156737 |
| C | 4.105788 | -1.377195 | 0.020309 |
| C | 4.817056 | -0.438100 | -0.734933 |
| C | 4.359795 | -2.734189 | -0.164174 |
| C | 5.752742 | -0.793691 | -1.696431 |
| C | 5.303422 | -3.105101 | -1.110486 |
| H | 3.831975 | -3.476799 | 0.422375 |
| C | 5.985612 | -2.148962 | -1.872332 |
| C | 6.274636 | -0.049393 | -2.285135 |
| H | 5.519093 | -4.155793 | -1.265142 |
| H | 6.710097 | -2.472897 | -2.609685 |
| C | 3.449938 | 0.735147 | 0.568995 |
| H | 2.963541 | 1.614694 | 0.961121 |
| N | 4.379211 | 0.840124 | -0.361541 |
| C | 4.812213 | 2.072504 | -1.006548 |
| H | 5.889858 | 2.187280 | -0.882020 |
| H | 4.280503 | 2.911008 | -0.564926 |
| H | 4.540023 | 2.032909 | -2.061120 |
| B | 1.770254 | 3.073554 | -1.977900 |
| F | 0.467548 | 3.381441 | -2.380579 |
| F | 2.336059 | 2.142233 | -2.893242 |
| F | 2.578123 | 4.192250 | -1.868559 |
| F | 1.712597 | 2.414165 | -0.702043 |

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| TS_FLP_TMTU |
|-------------|
| C 0.000000 0.000000 0.000000 |
| C 0.000000 0.000000 1.384282 |
| C 0.734893 0.978865 2.057823 |
| C 1.431783 1.938680 1.303804 |
| C 1.445167 1.948138 -0.088329 |
| C 0.718697 0.959035 -0.729221 |
| N 2.047255 2.804294 2.199018 |
| C 1.747497 2.404183 3.455893 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 0.983936 | 1.241856 | 3.469717 |
| B       | 0.099230  | 0.721404 | 4.746130 |
| F       | 0.963095  | 0.538748 | 5.881353 |
| C       | 2.873804  | 3.928534 | 1.822586 |
| F       | -0.902289 | 1.622286 | 5.084220 |
| S       | 3.519563  | -0.441874 | 3.993975 |
| H       | 2.197902  | 0.381177 | 3.696729 |
| H       | 2.138843  | 2.951237 | 4.302895 |
| H       | -0.575507 | -0.720425 | 1.951863 |
| H       | 1.993177  | 2.695885 | 0.650457 |
| H       | 0.698035  | 0.930828 | -1.812669 |
| H       | -0.573320 | -0.748246 | -0.535639 |
| H       | 2.301745  | 4.634615 | 1.215711 |
| H       | 3.216511  | 4.435530 | 2.723672 |
| H       | 3.743479  | 3.591535 | 1.252818 |
| C       | 2.841508  | -1.395053 | 5.276509 |
| N       | 3.327321  | -1.265221 | 6.521694 |
| N       | 1.881819  | -2.290971 | 5.045262 |
| C       | 0.859479  | -2.580793 | 6.053030 |
| C       | 1.551426  | -2.741625 | 3.697523 |
| C       | 3.410879  | -2.382557 | 7.449004 |
| C       | 3.910256  | -0.012136 | 6.982152 |
| H       | -0.107982 | -2.509489 | 5.559960 |
| H       | 0.992052  | -3.574343 | 6.490886 |
| H       | 0.881044  | -1.809044 | 6.818227 |
| H       | 4.406675  | -2.378403 | 7.899402 |
| H       | 2.665377  | -2.316896 | 8.246950 |
| H       | 3.280647  | -3.321168 | 6.913116 |
| H       | 1.160034  | -3.758197 | 3.771360 |
| H       | 0.790641  | -2.088119 | 3.268118 |
| H       | 2.438813  | -2.739094 | 3.069746 |
| H       | 3.735259  | 0.061512  | 8.057230 |
| H       | 4.985571  | 0.029478  | 6.785251 |
| H       | 3.407189  | 0.818308  | 6.494968 |

1. V. Iashin, K. Chernichenko, I. Pápai and T. Repo, *Angew. Chem. Int. Ed.* 2016, 55, 14146-14150.
2. R. Alder, M. Blake, S. Bufali, C. Butts, J. Schütz and S. Williams, *J. Chem. Soc., Perkin Trans. 1*, 2001, 1586–1593.