

Supporting Information:

Alkylammoniotrifluoroborate functionalized polystyrenes: polymeric pre-catalysts for the metal-free borylation of heteroarenes

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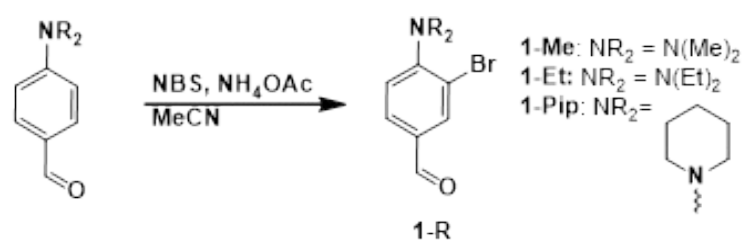
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Submitted to *Dalton Transactions*

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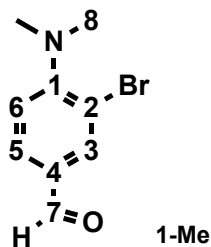
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1.1 Synthesis of compounds 1-R



Scheme S1 : General synthesis of compounds **1-R** as reported by Reddy et al.

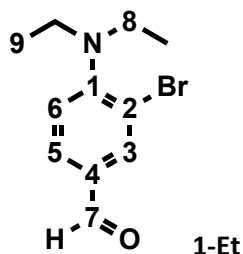
Following reported literature procedures¹, compound **1-R** could be synthesized and purified using column chromatography with methylene chloride as the eluant. Their structures were confirmed by ¹H and ¹³C NMR. NMR spectra were in accordance with data from the literature¹.



Isolated yield: 90 %, pale yellow oil

¹H-NMR (CDCl₃, 500 MHz): δ 9.81 (s, 1H, H7); 8.03 (d, 1H, ³J_{H-H}=2Hz, H3); 7.73 (dd, 1H, J_{H-H}=2Hz, 8 Hz), H5); 7.07(d, 1H, J_{H-H} = 8Hz, H6); 2.96 (s, 6H, H8).

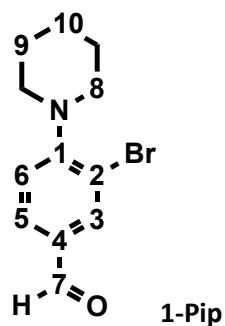
¹³C {¹H} (CDCl₃, 126 MHz): δ 189.6 (s, 1C, C7); 156.6 (s, 1C, C4), 136.1, 131.0, 126.9, 119.4, 116.6 (s, 5C, C1, C2, C3, C5 and C6); 44.1(s, 2C, C8).



Isolated Yield: 55 %, brown oil

¹H NMR (CDCl₃, 400 MHz): δ 9.82 (s, 1H, H7); 8.06 (d, 1H, J_{H-H}=2Hz, H3); 7.73 (dd, 1H, J_{H-H}=2Hz, 8 Hz), H5); 7.09 (d, 1H, J_{H-H} = 8Hz, H6)); 3.28 (q, J_{H-H} = 7Hz, 4H, H8); 1.11(t, J_{H-H} = 7Hz, 6H, H9).

¹³C {¹H} NMR (CDCl₃, 126 MHz): δ 189.6 (s, 1C, C7); 156.1 (s, 1C, C4), 136.1, 131.2 129.2, 122.2, 119.3 (s, 5C, C1, C2, C3, C5 and C6); 46.0 (s, 2C, C8), 12.4 (s, 2C, C9).

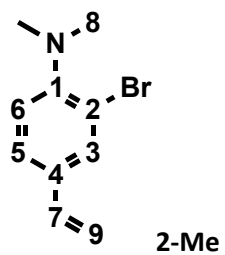


Isolated yield: 45 %, red oil

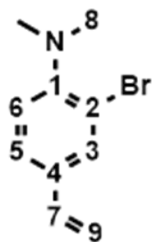
¹H NMR (CDCl₃, 400 MHz): δ 9.82 (s, 1H, H7); 8.04 (d, 1H, J_{H-H}=2Hz, H3); 7.74 (dd, 1H, J_{H-H}=2Hz, 8 Hz, H5); 7.09 (d, 1H, J_{H-H} = 8Hz, H6); 3.10 (t, J_{H-H} = 7Hz, 4H, H8); 1.79-1.74(m, 4H, H9); 1.65-1.61(m, 2H, H10).

¹³C {¹H} NMR (CDCl₃, 126 MHz): δ 190.3 (s, 1C, C7); 157.8 (s, 1C, C4), 135.5, 131.3, 130.6, 120.0, 119.3 (s, 5C, C1, C2, C3, C5 and C6); 52.3 (s, 2C, C8), 26.2 (s, 2C, C9), 24.0 (s, 1C, C10).

1.2 Synthesis of compounds 2-R (2-Me, 2-Et and 2-Pip).



Isolated Yield: 89 % (60 % after distillation) of a clear oil.



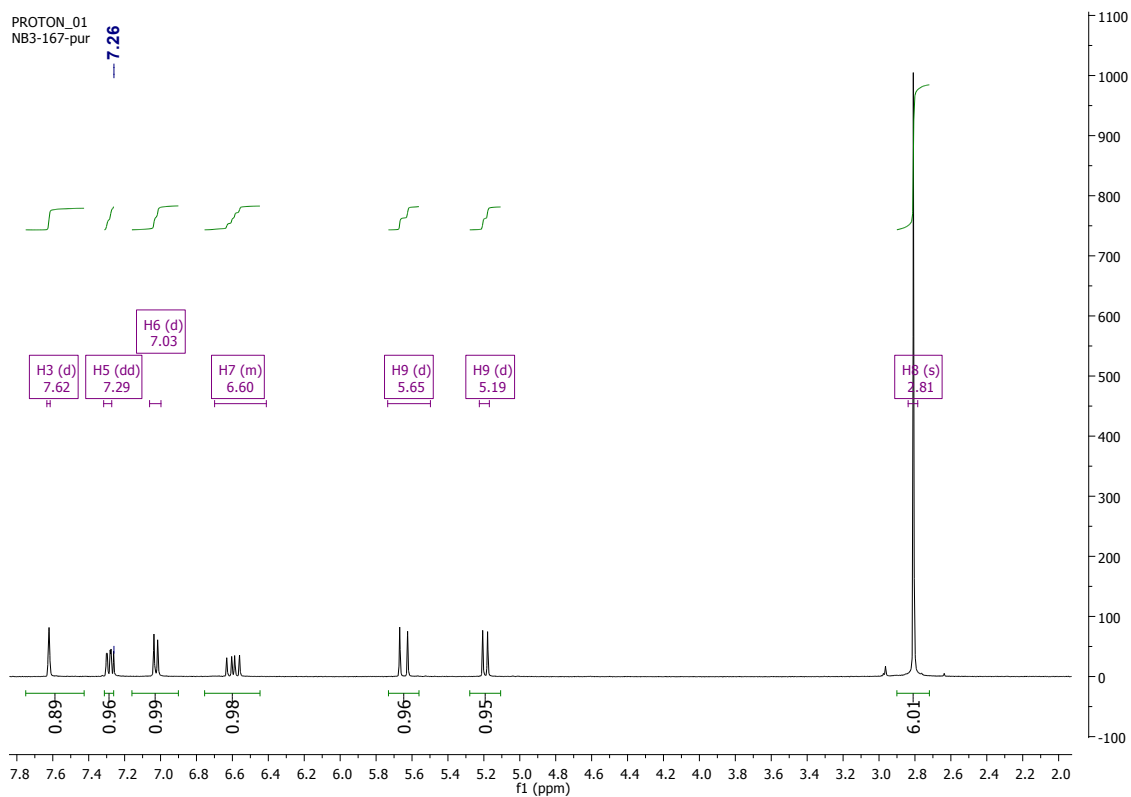


Figure S1. ^1H NMR of compound **2-Me** (CDCl_3 , 500 MHz).



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2-Me_13C

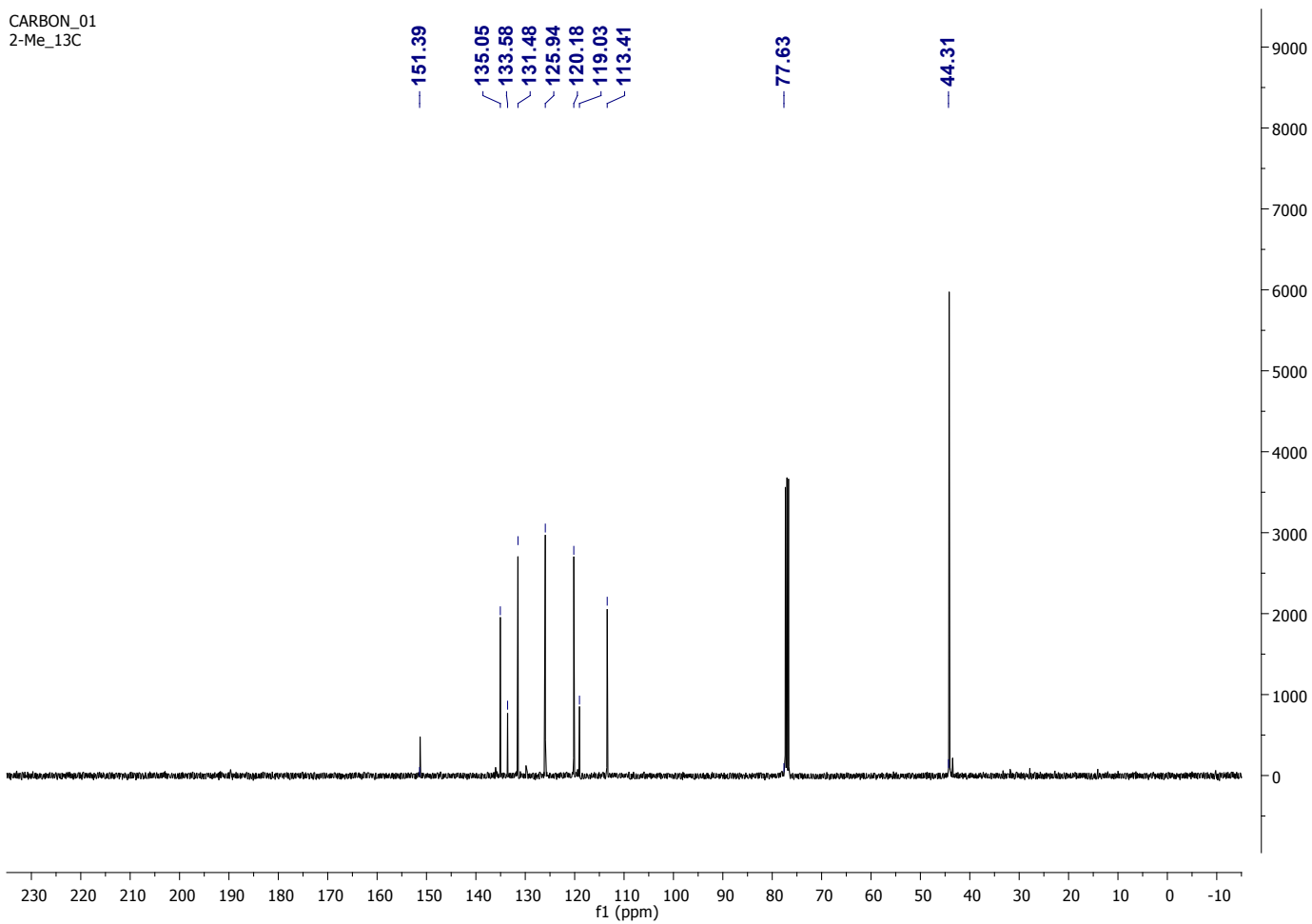
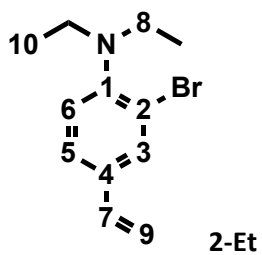


Figure S2. ^{13}C $\{^1\text{H}\}$ NMR of 2-Me (126 MHz, CDCl_3)



Isolated yield: 83% (55 % by vacuum distillation) of a clear oil.

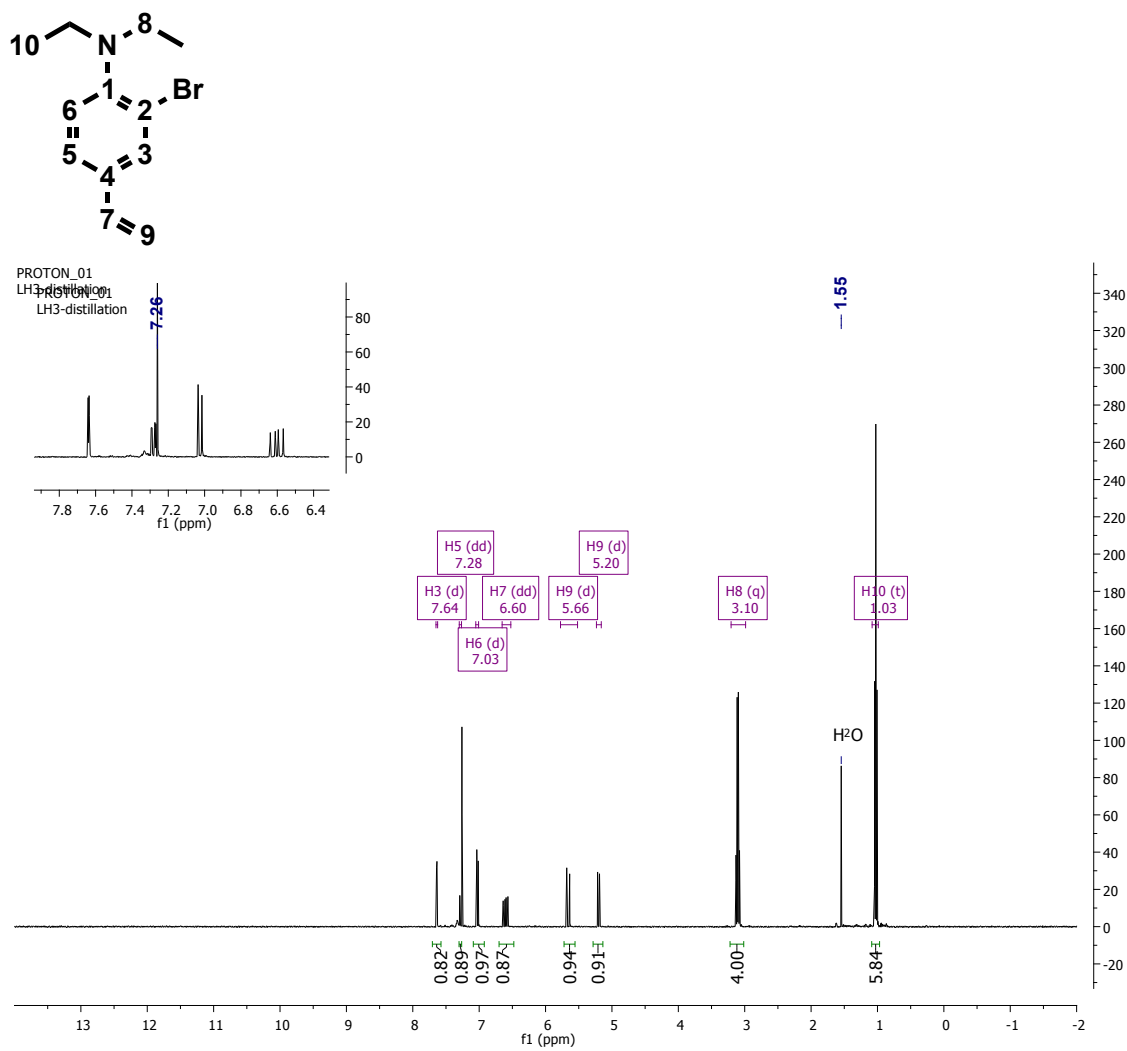


Figure S3 : ¹H NMR of 2-Et (400 MHz, CDCl₃).

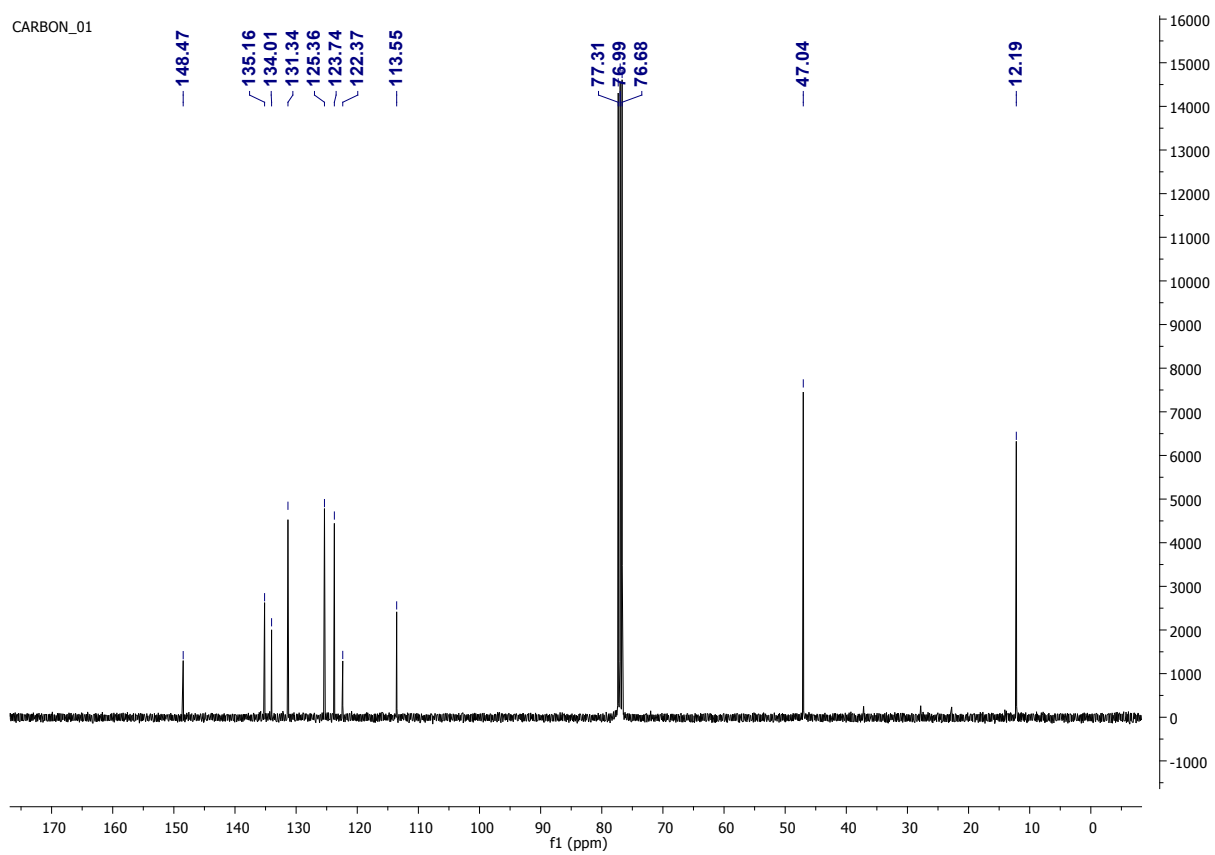
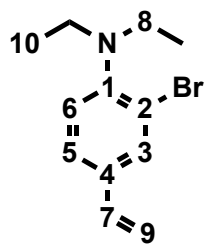
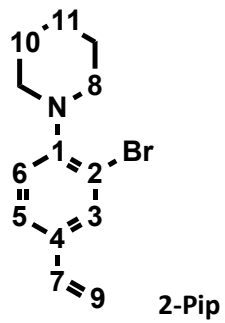


Figure S4. ^{13}C [^1H] NMR of 2-Et (126 MHz, CDCl_3).



Isolated yield: 61 %, deep red oil.

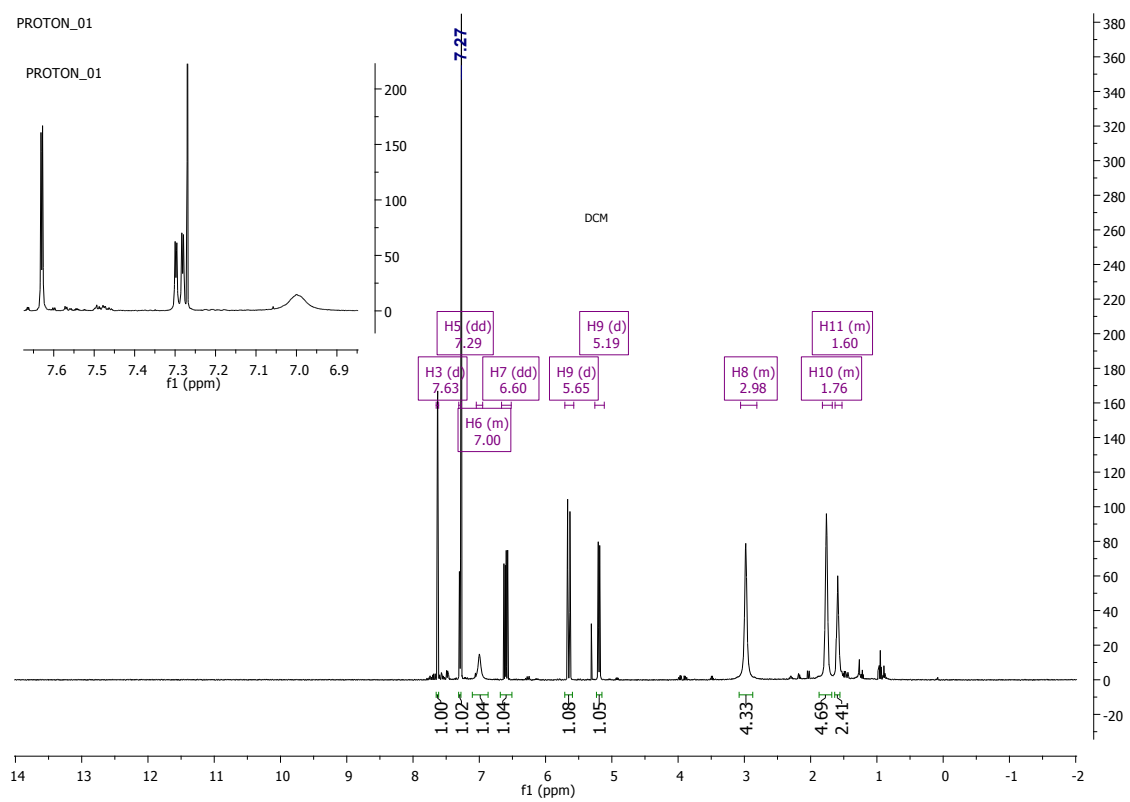
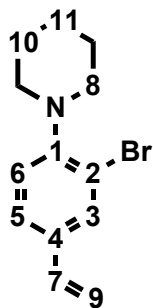
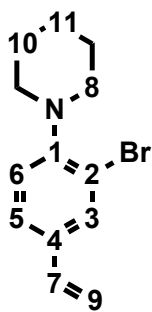


Figure S5. ^1H NMR of compound 2-Pip (CDCl_3 , 400 MHz).



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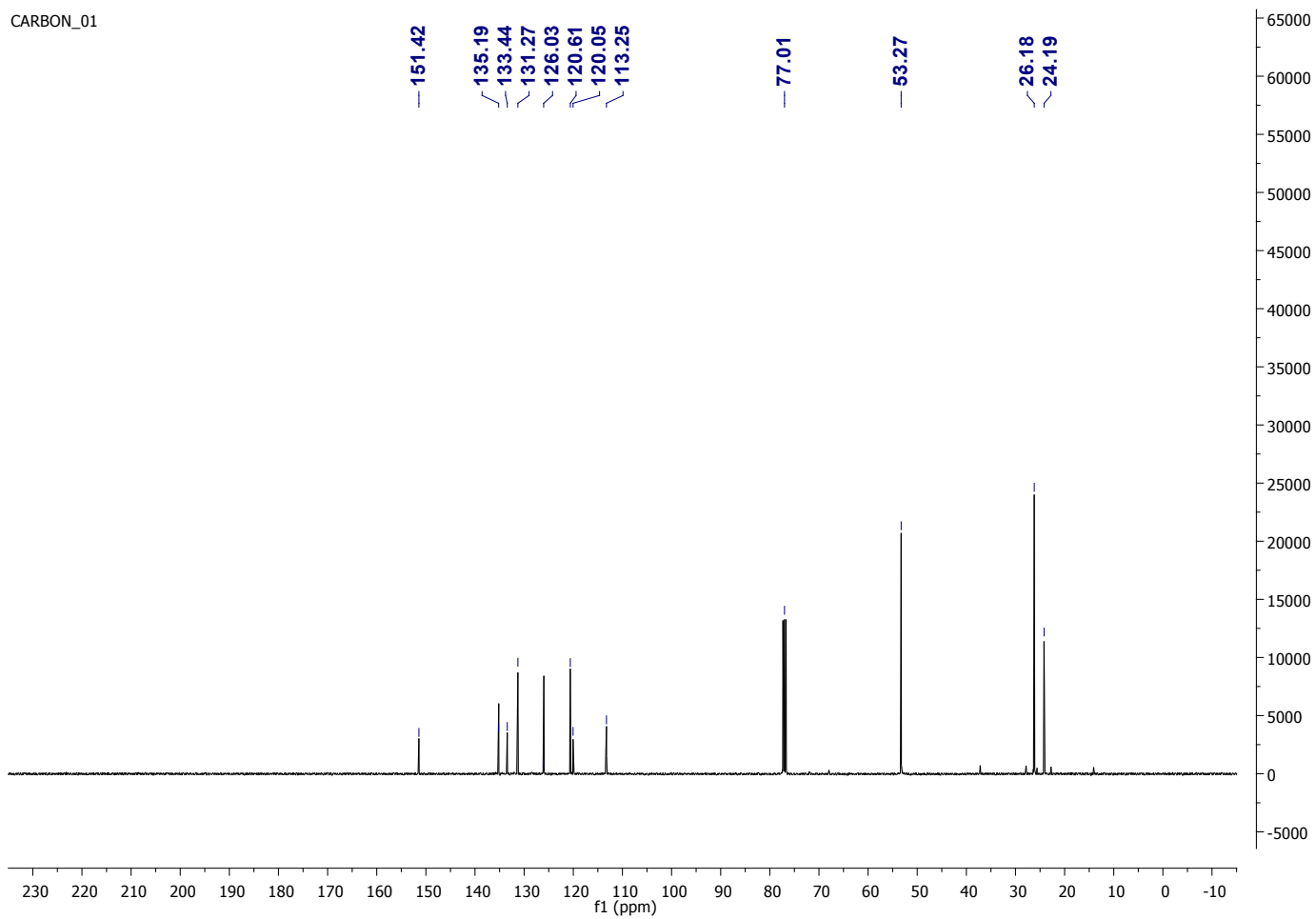
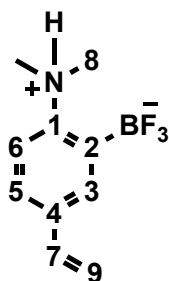


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2-Pip** (CDCl_3 , 126 MHz).

1.3 Synthesis of compounds 3-R (3-Me, 3-Et and 3-Pip).



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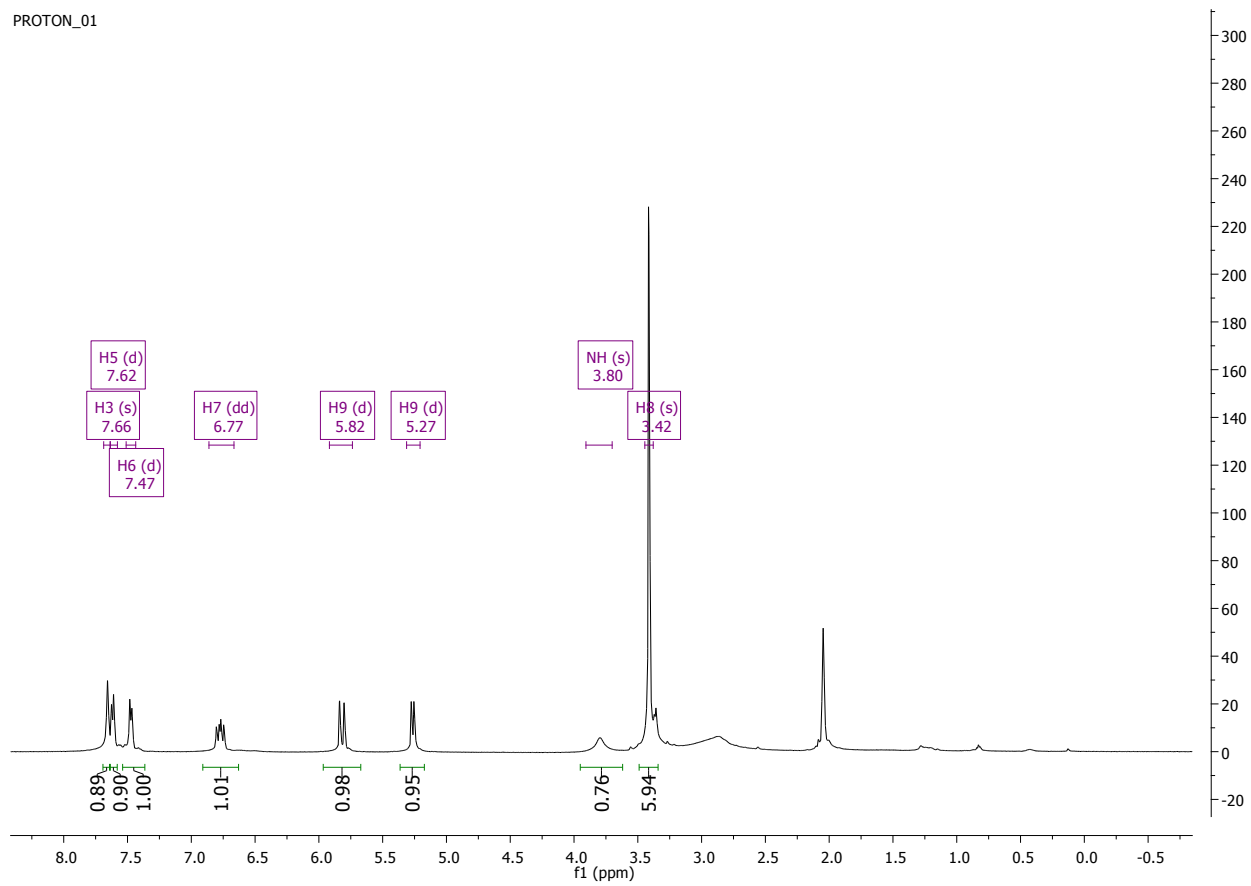
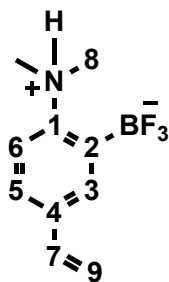


Figure S7. ^1H NMR of 3-Me (acetone- d_6 , 500 MHz).



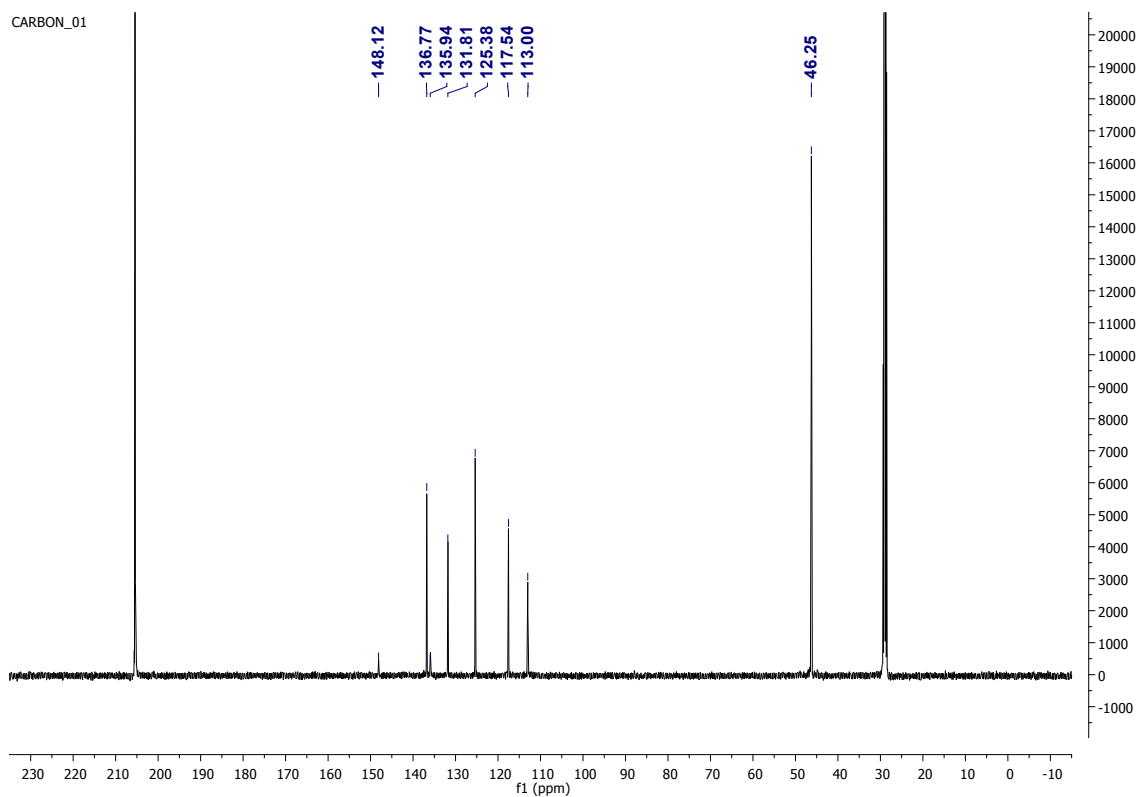
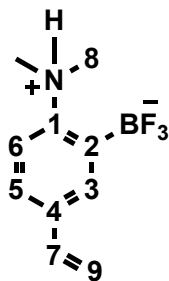


Figure S8. ^{13}C $\{^1\text{H}\}$ NMR of **3-Me** (acetone- d_6 , 126 MHz).



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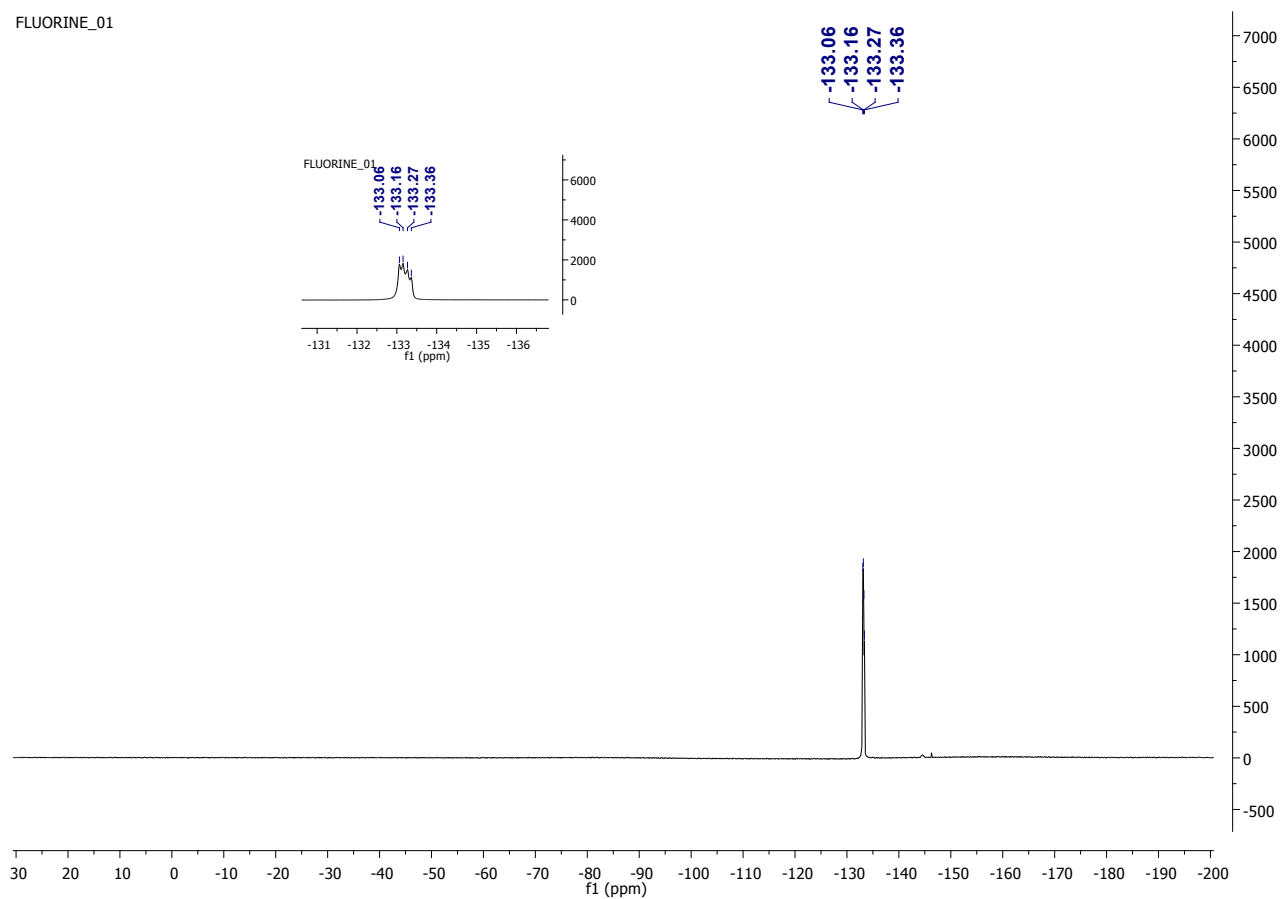
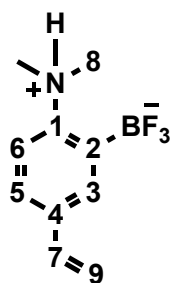


Figure S9. ^{19}F NMR of compound **3-Me** ($\text{acetone-}d_6$, 470 MHz).



¹¹B NMR of compound 3-Me.

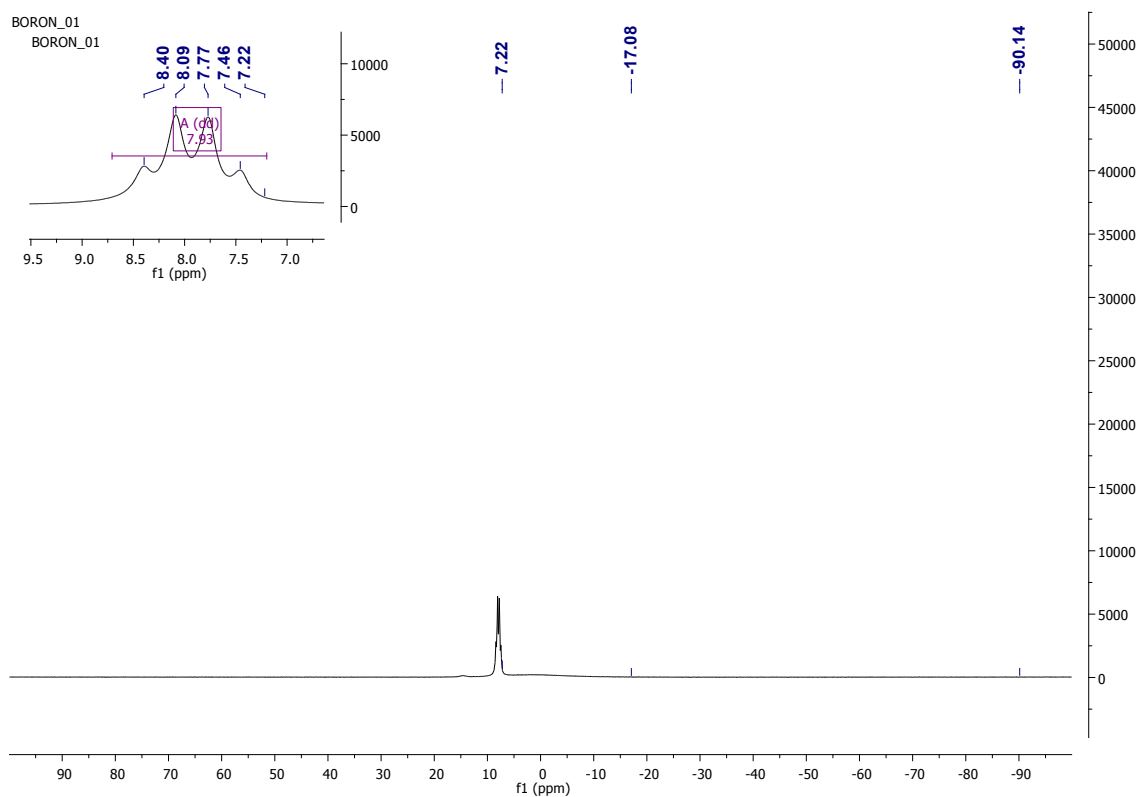
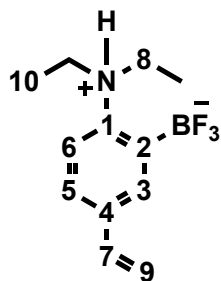


Figure S10. ¹¹B {¹H} NMR of 3-Me (acetone-d₆, 160 MHz).



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NB4-2-CDCL3HSQCC

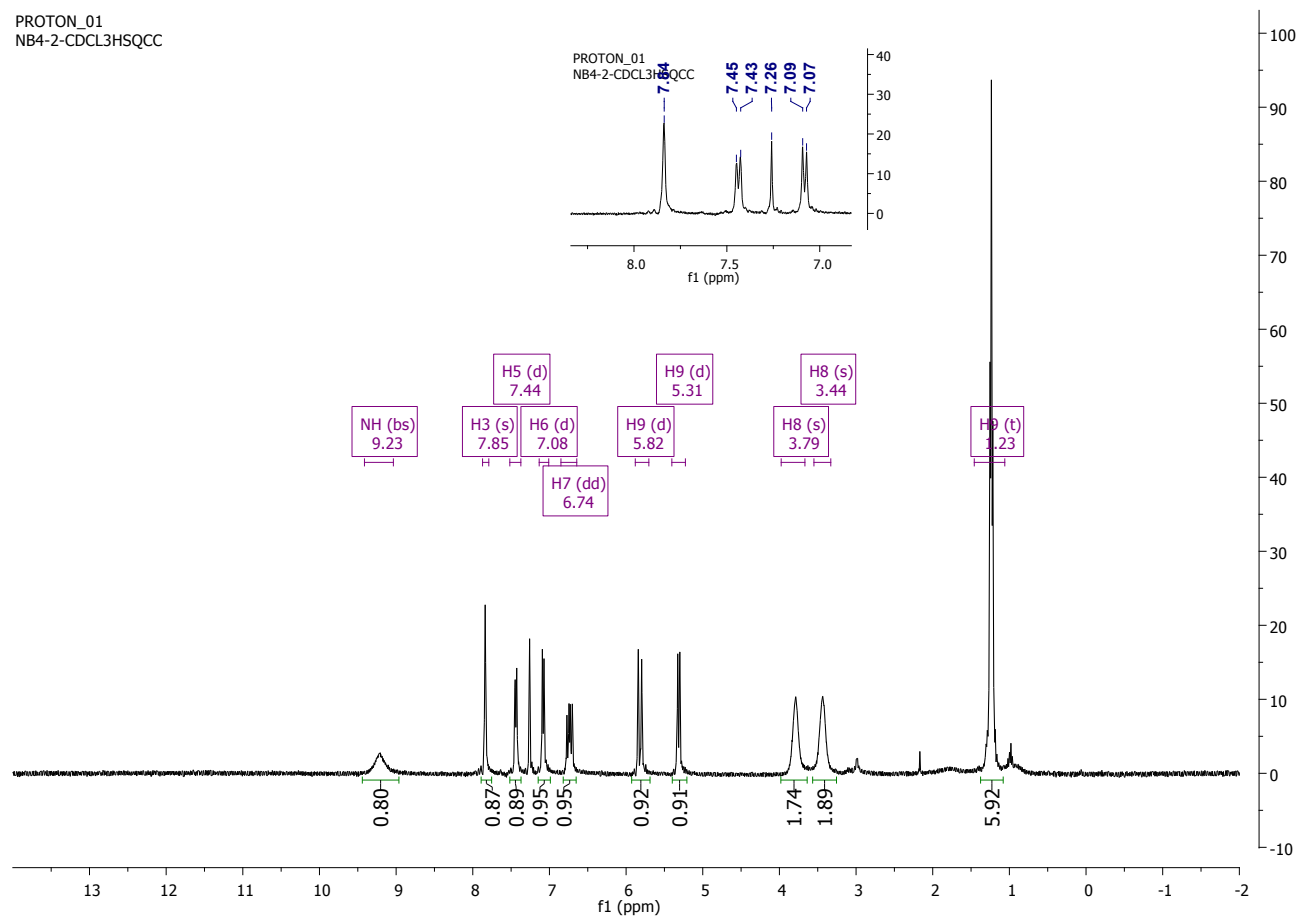
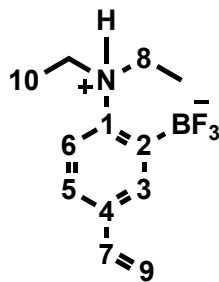


Figure S11. ^1H NMR of compound **3-Et** (CDCl_3 , 500MHz).



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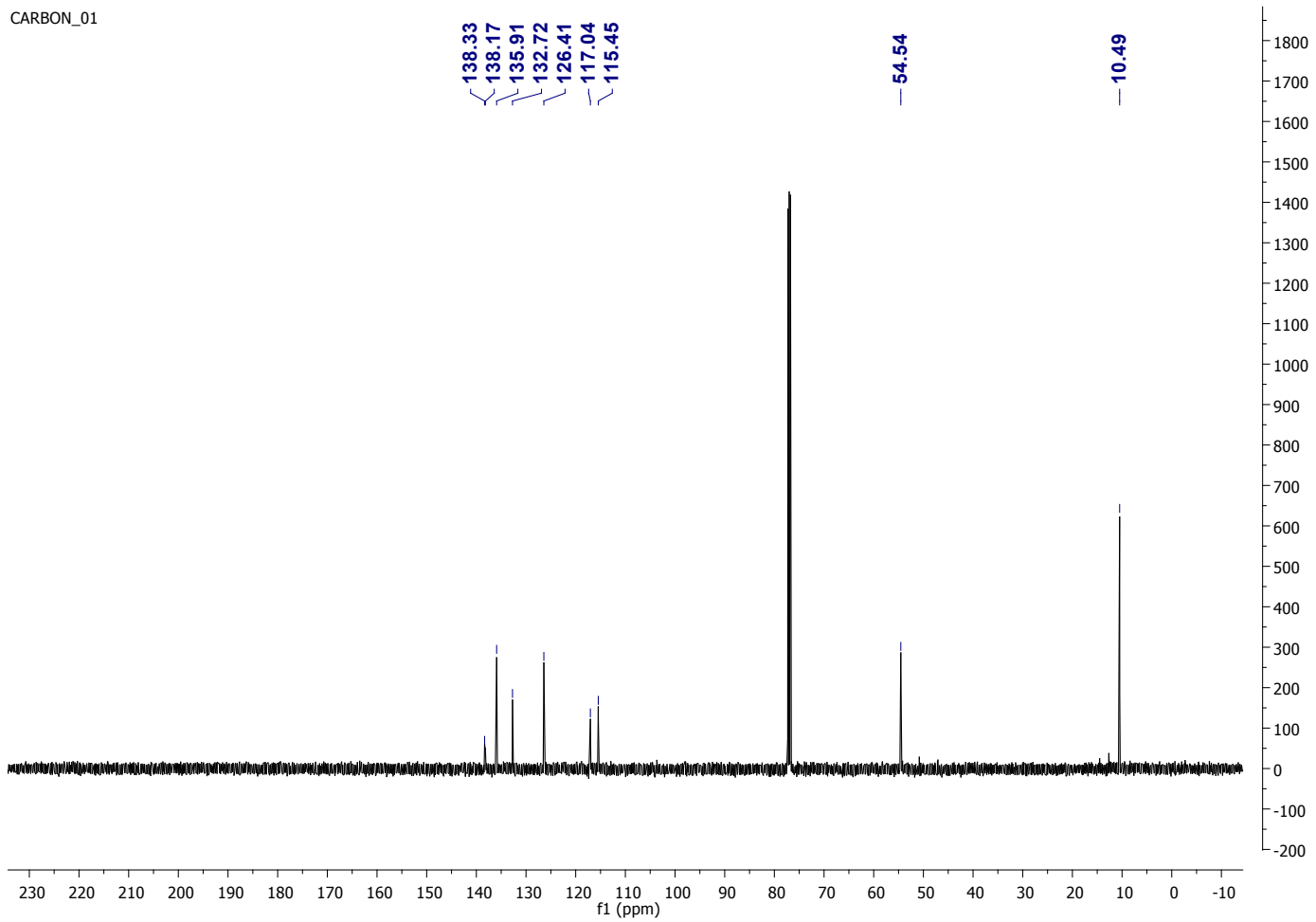


Figure S12. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz) of 3-Et.

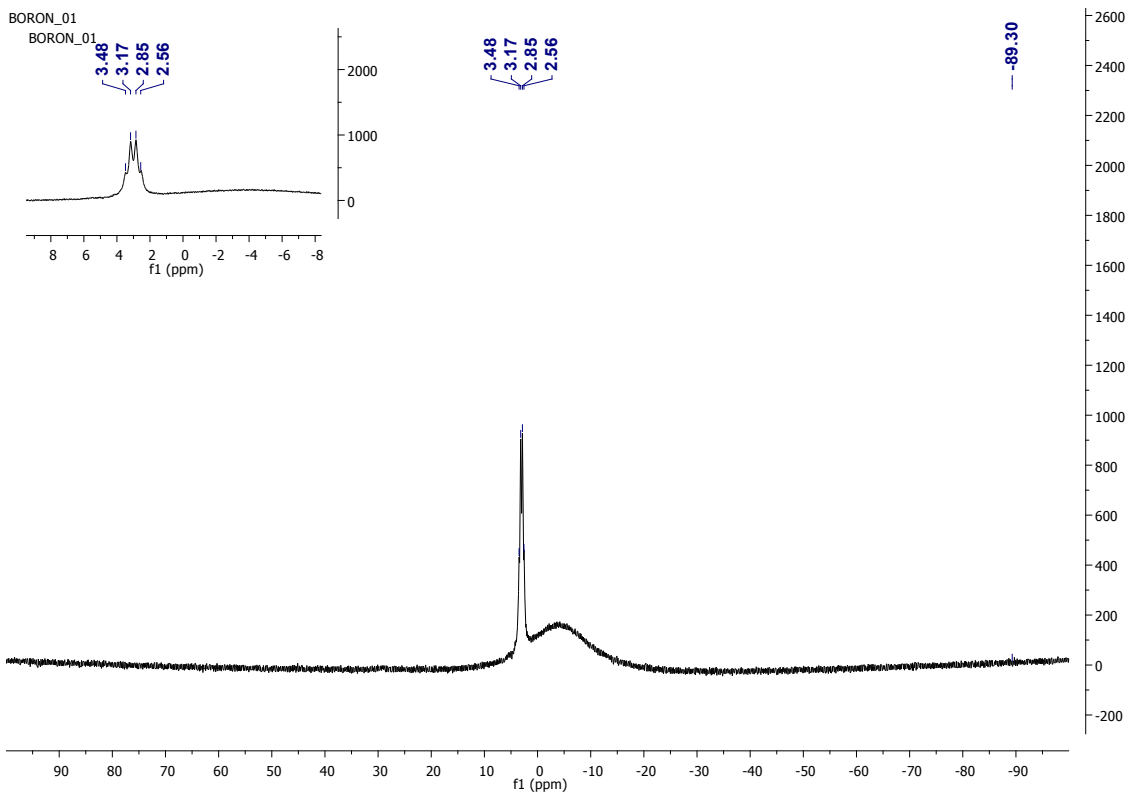
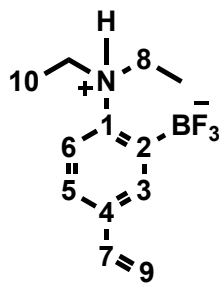


Figure S13. ^{11}B $\{^1\text{H}\}$ NMR of compound 3-Et (CDCl_3 , 160 MHz)

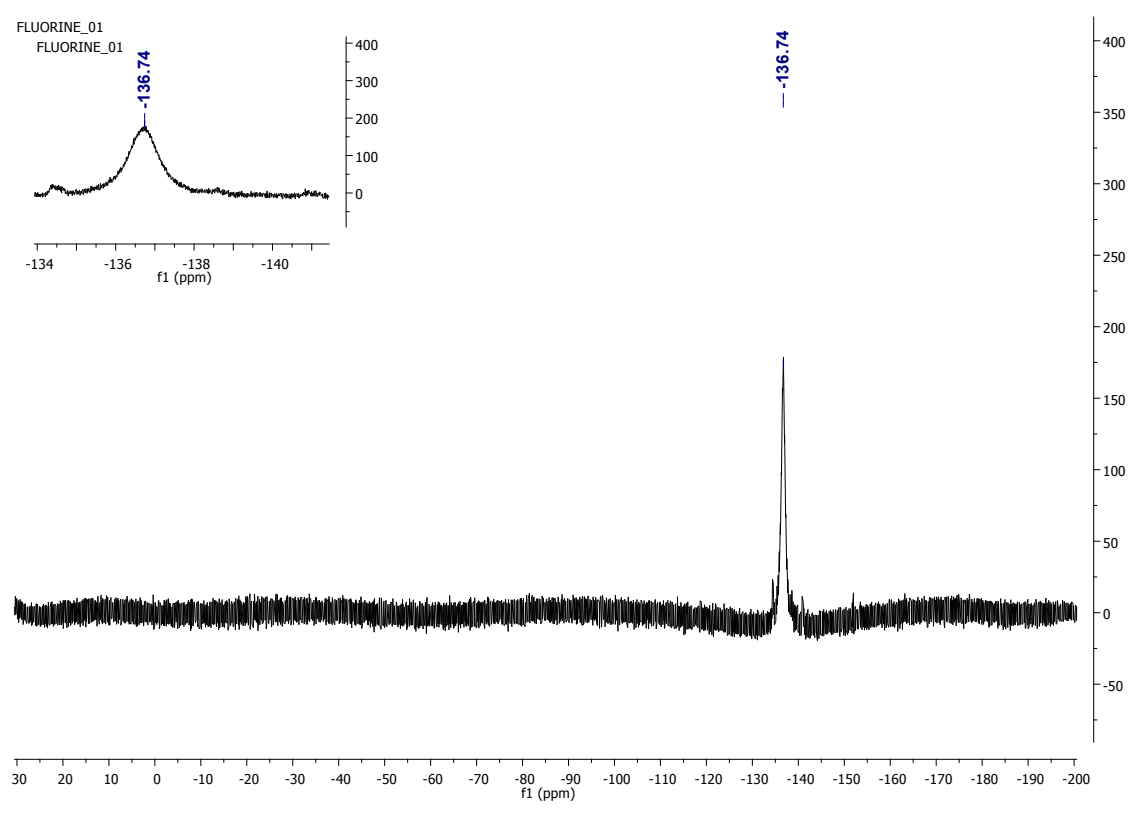
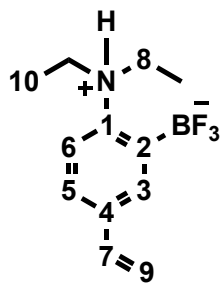


Figure S14. ¹⁹F NMR of 3-Et (CDCl₃, 470 MHz).

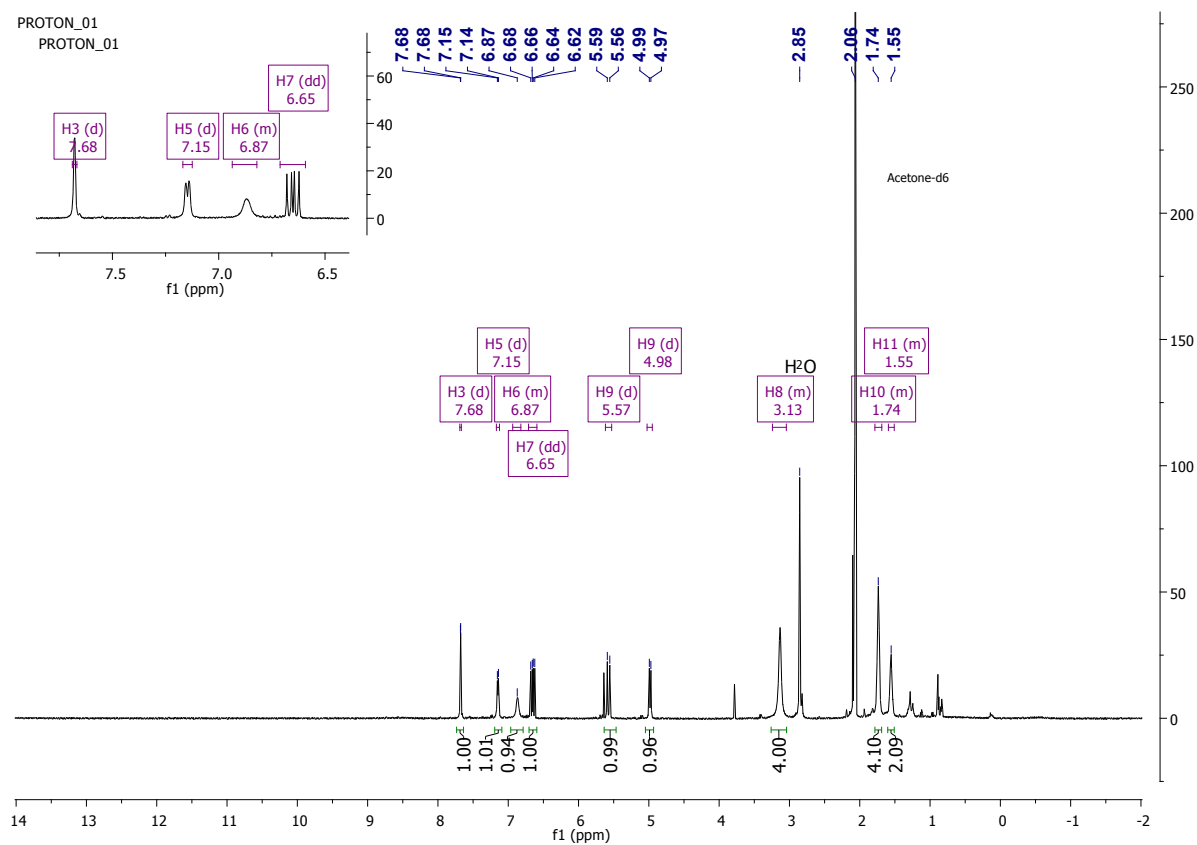
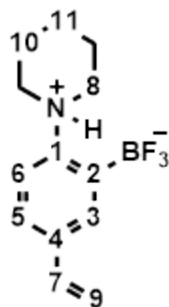


Figure S15. ^1H NMR of 3-Pip (acetone- d_6 , 500 MHz).

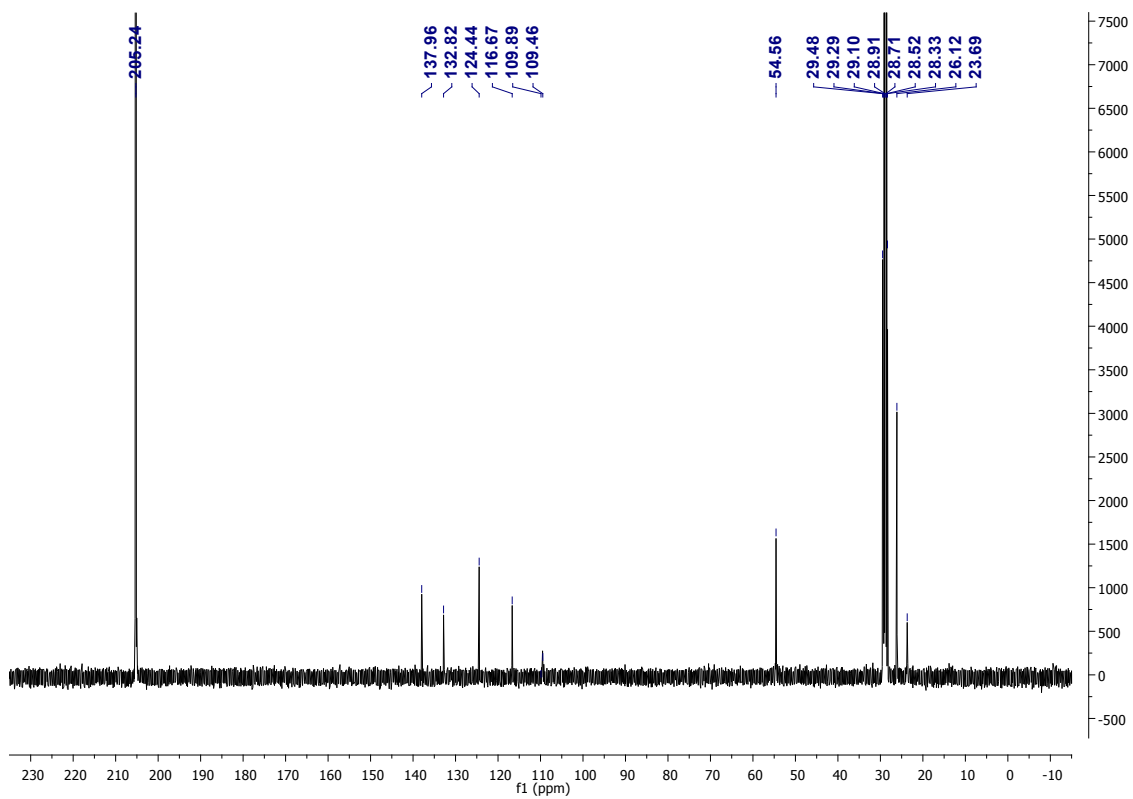
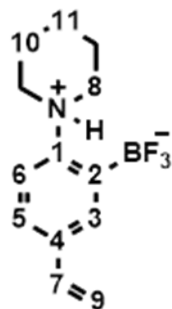


Figure S16. ^{13}C [^1H] NMR of **3-Pip** (acetone- d_6 , 126 MHz).

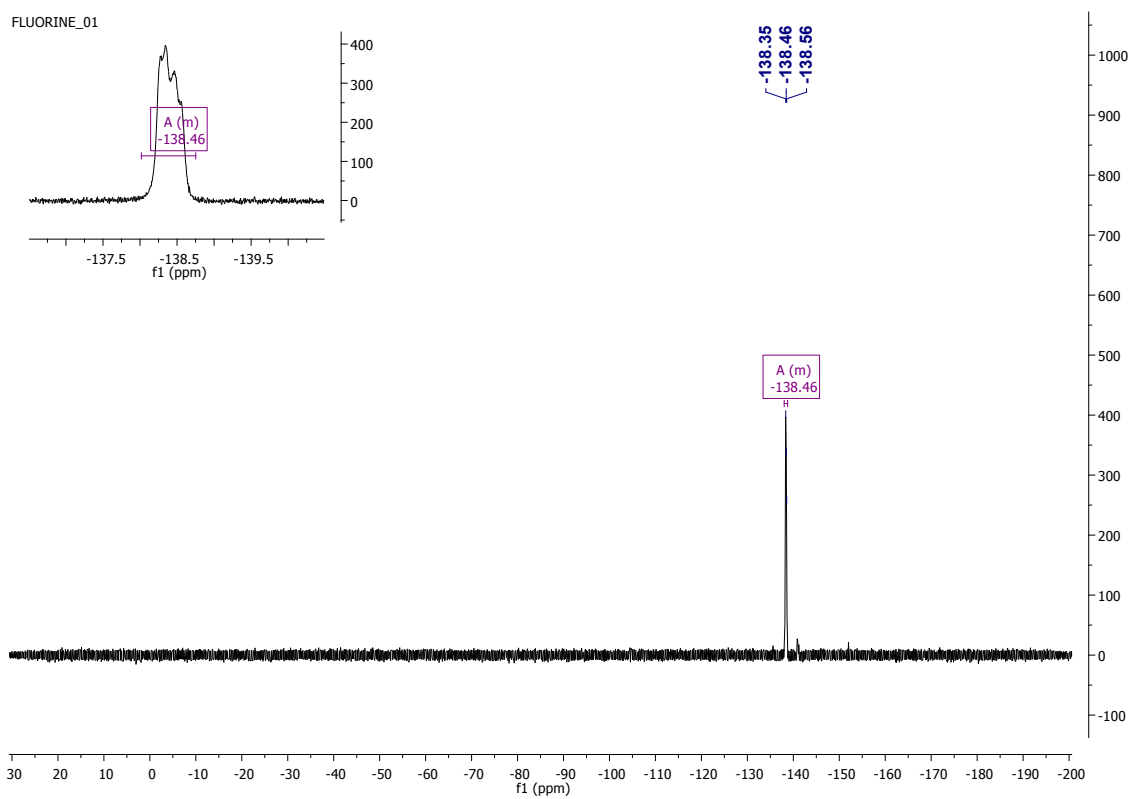


Figure S17. ¹⁹F NMR of 3-Pip (acetone-d₆, 470 MHz).

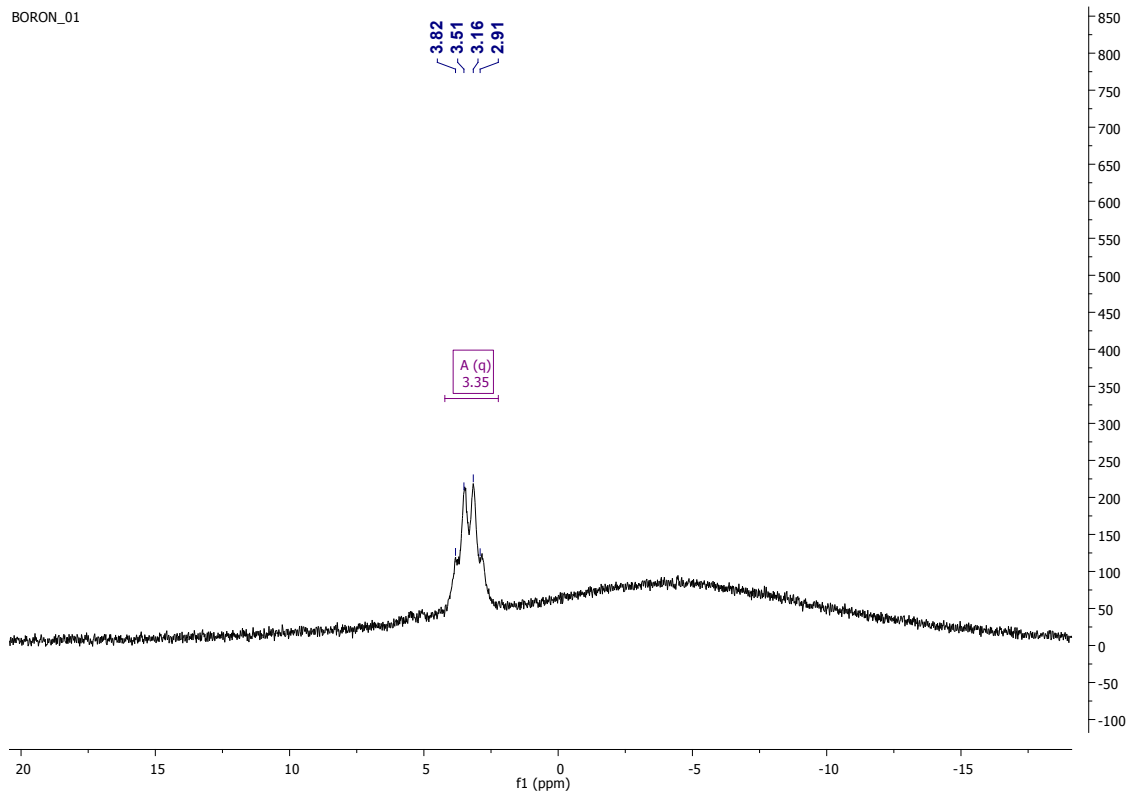
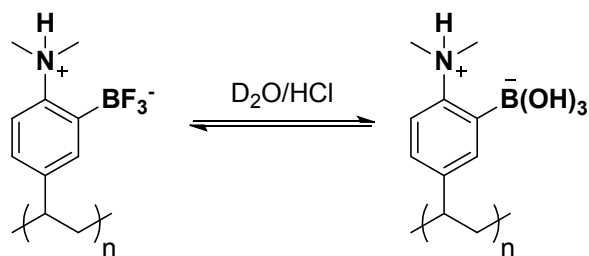


Figure S18. ¹¹B NMR of 3-Pip (acetone-d₆, 160 MHz).

1.4 Synthesis of polymers P-R.

Synthesis of P-Me.



Scheme S2. In situ hydrolysis of P-Me in $\text{D}_2\text{O}/\text{HCl}$ NMR solvent.

Isolated yield (based on monomer) : 73 %

^1H NMR (D_2O , H^+) 500 MHz): δ 7.47- 6.36 (m, 3H, Ar-H), 3.03 (bs, 6H, N- CH_3), 1.69-1.09 (m, 3H, CH_2CH).

^{11}B NMR (D_2O , H^+ , 160 MHz): δ 0.0 (q, $J_{\text{B-F}} = 50$ Hz, 1B, BF_3), -1.5 (s, 1B, Ar- $\text{B}(\text{OH})_3^-$)

^{19}F NMR (D_2O , H^+ , 470 MHz): δ -129,7 (m, 3F), -150.1 (s, 2F, HF_2^-)²

(See next section for SEC-GPC datas).

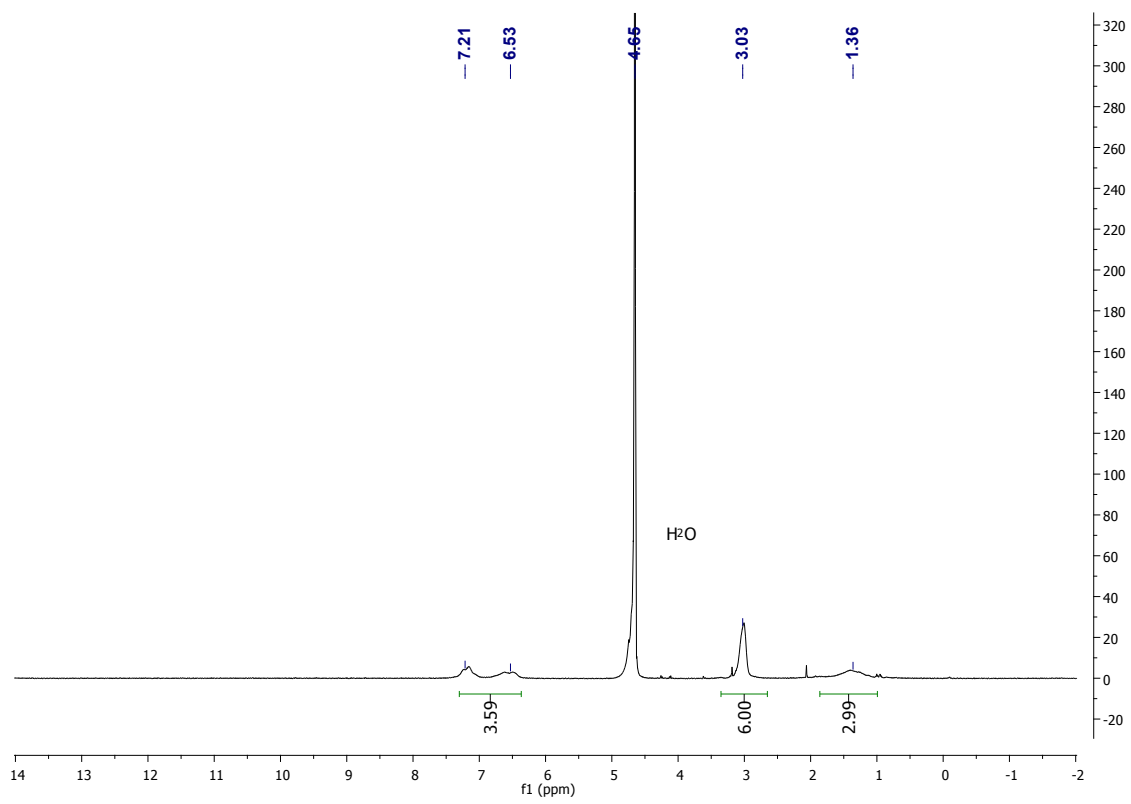


Figure S19. ¹H NMR of compound **P-Me** (D₂O/HCl), 500 MHz).

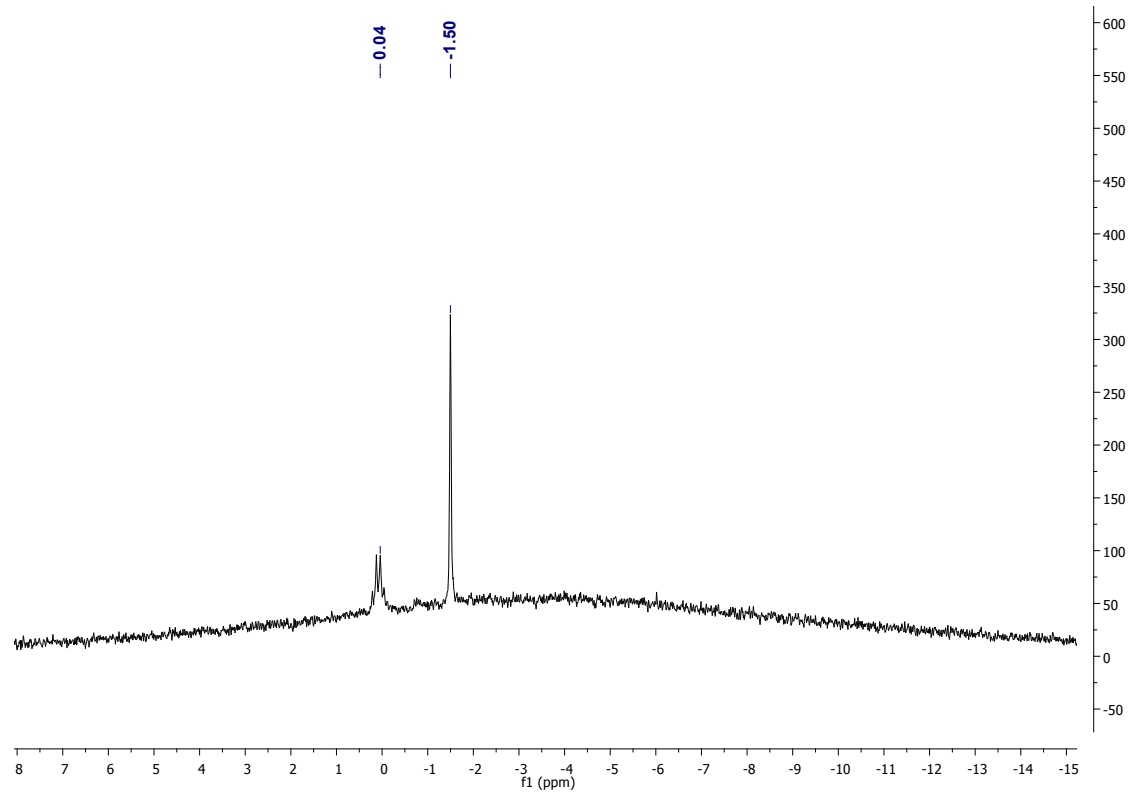


Figure S20. ^{11}B NMR of *P-Me* ($\text{D}_2\text{O}/\text{HCl}$, 160 MHz).

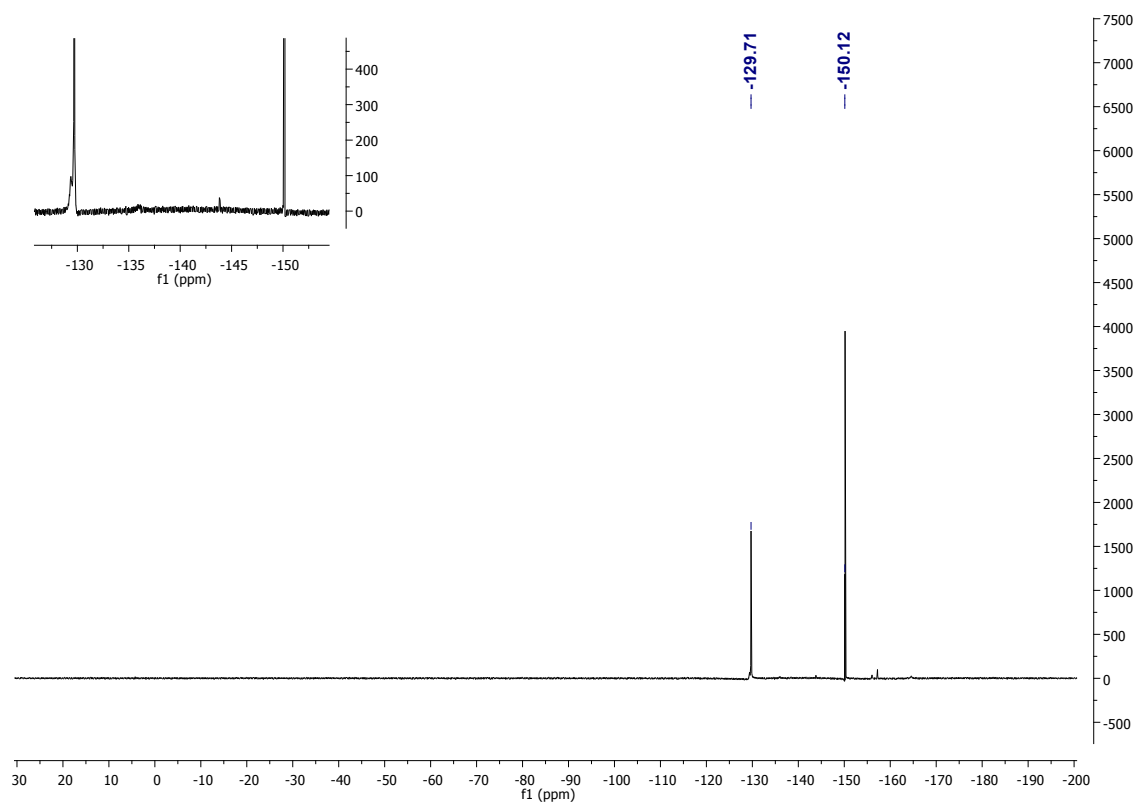


Figure S21. ^{19}F NMR of compound *P-Me* (D_2O , H^+ , 470 MHz).

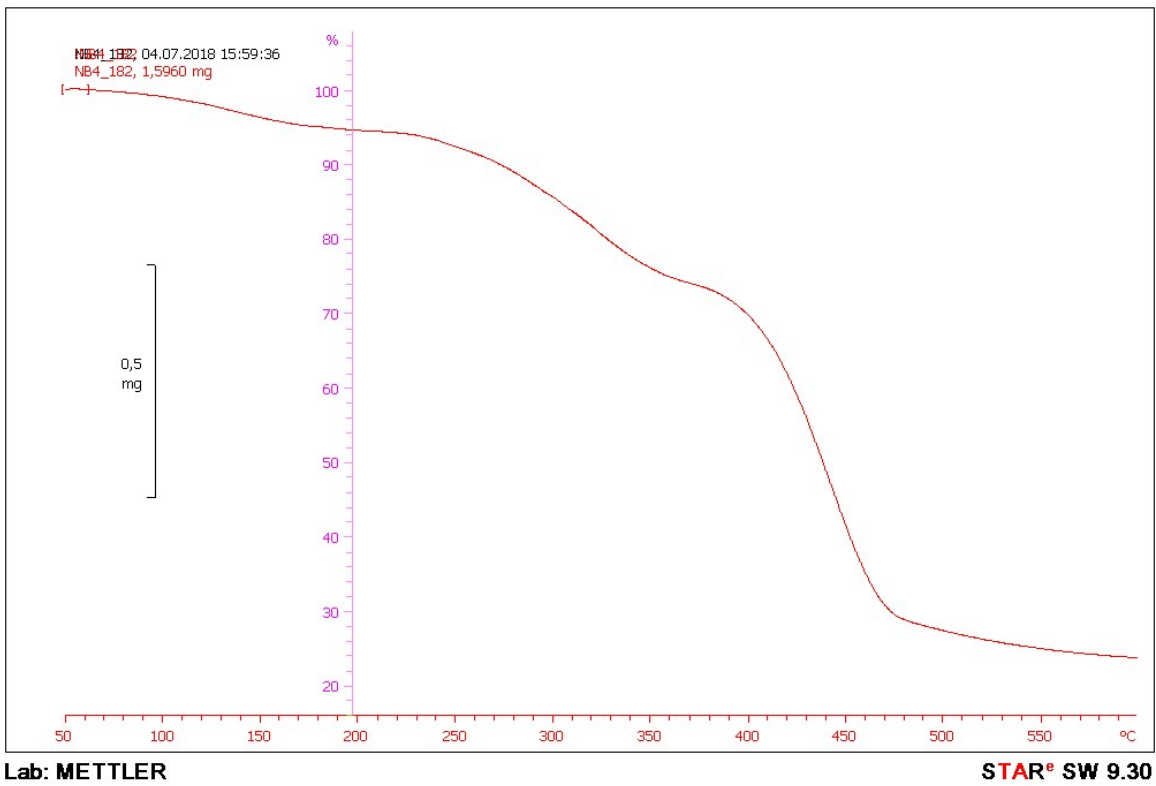


Figure S22. TGA curve of polymer P-Me.

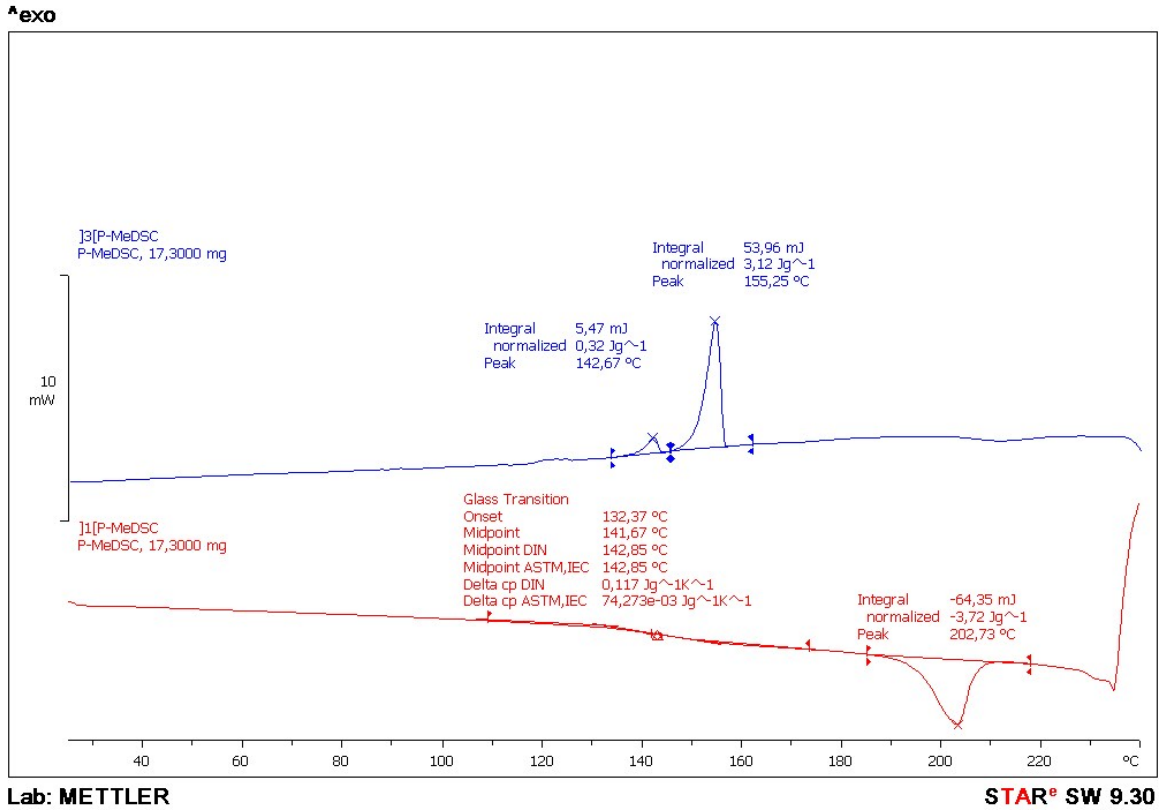
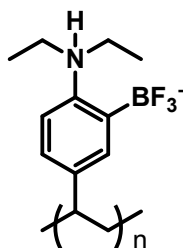


Figure S23. DSC heating (red) and cooling (blue) curves for P-Me.

Synthesis of P-Et



P-Et

Isolated Yield: 72 %

¹H NMR (DMSO-*d*₆, 500 MHz): δ 8.54 (bs, 1H, N-H), 7.60- 6.01 (m, 3H, Ar-H), 3.79-3.47 (m, 4H, N-CH₂-CH₃, incorporated in solvent peaks), 1.06-0.7 (bs, 6H, CH₃-CH₂-N) 2.18-1.25 (Aliphatic chain protons) ppm.

¹¹B NMR (DMSO-*d*₆, 160 MHz): δ 1.6 (m, 1B, BF₃)

¹⁹F NMR (DMSO-*d*₆, 470 MHz): δ -132.1 (m, 3F), -148.1 (s, 2F, HF₂⁻)²

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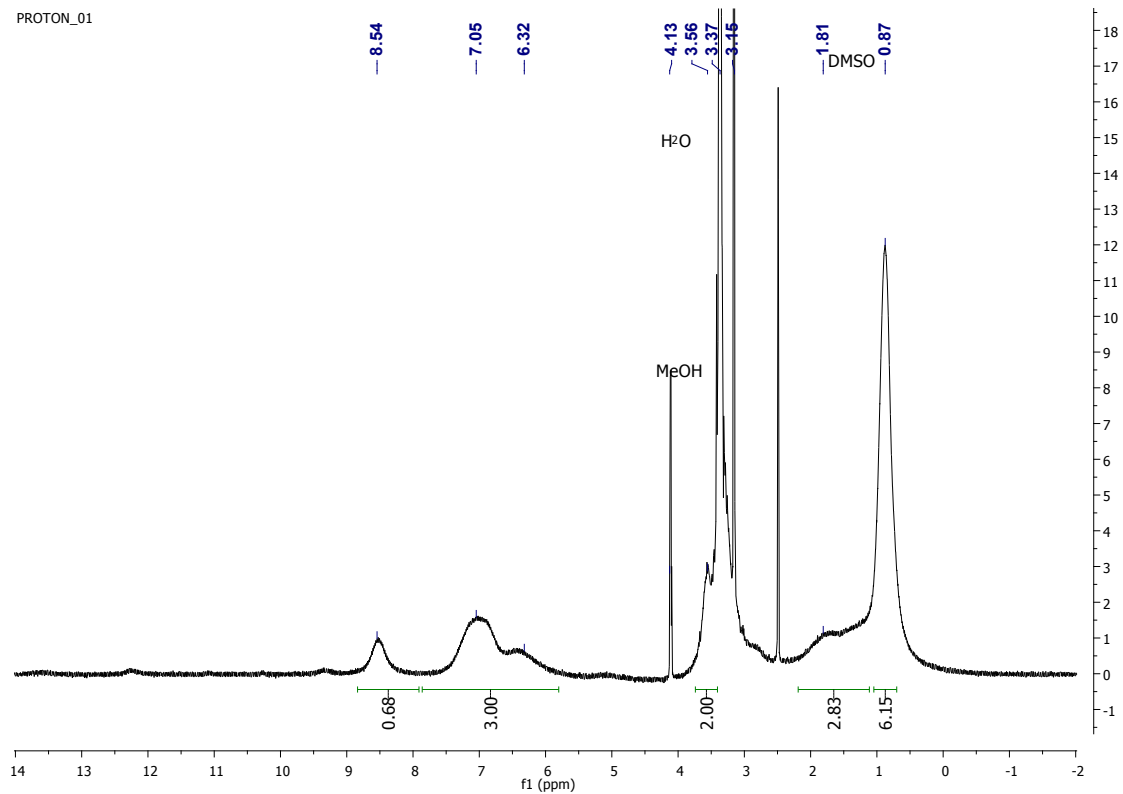


Figure S24. ^1H NMR of compound P-Et ($\text{DMSO-}d_6$, 500 MHz).

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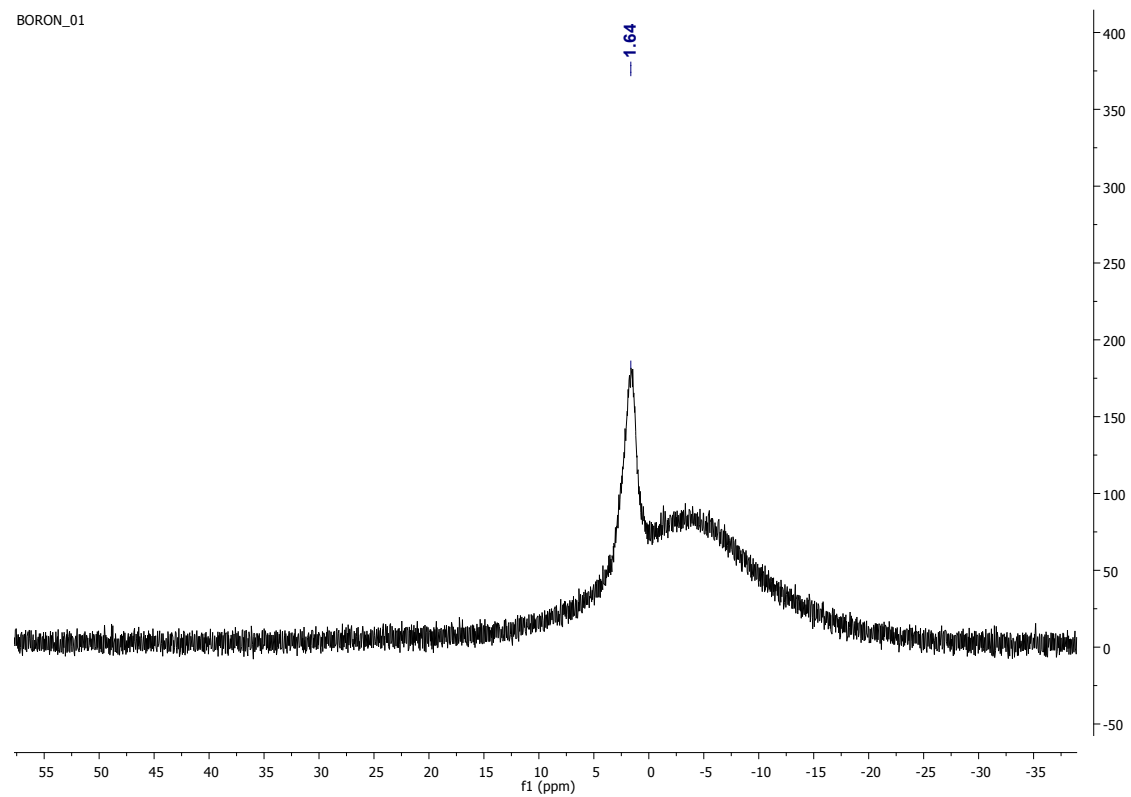


Figure S25. ^{11}B NMR of *P-Et* (DMSO-d_6 , 160 MHz).

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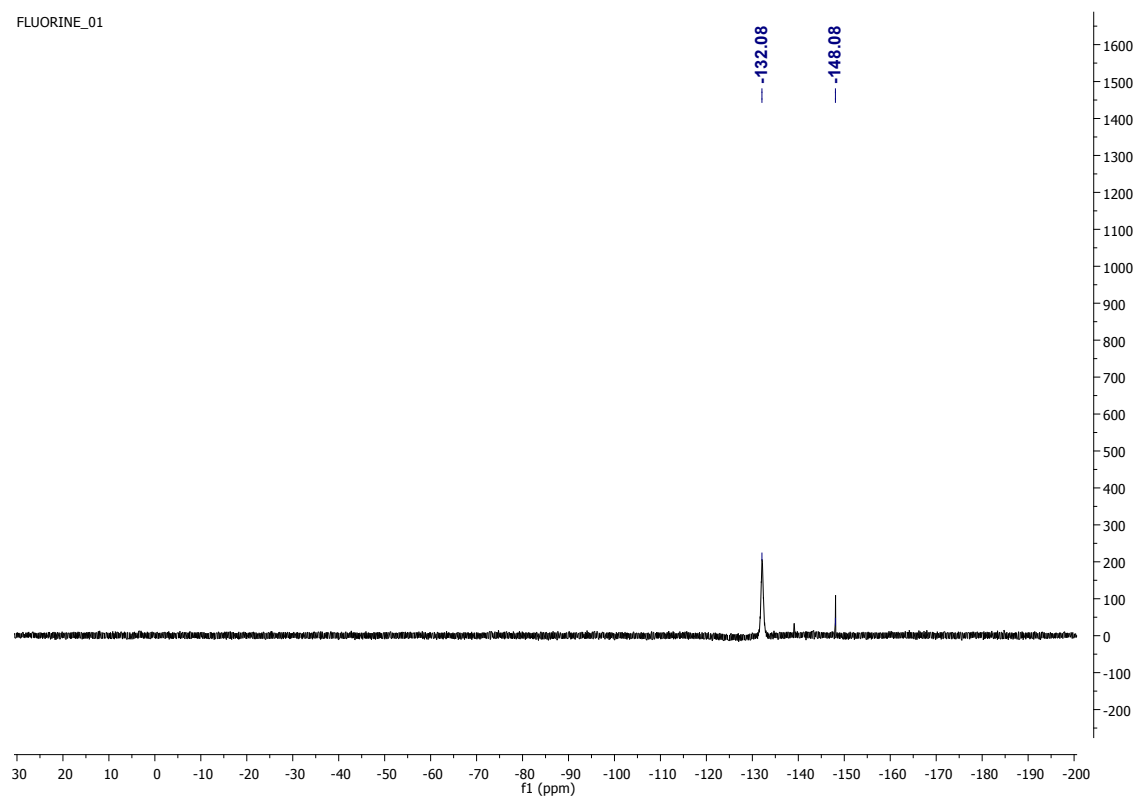
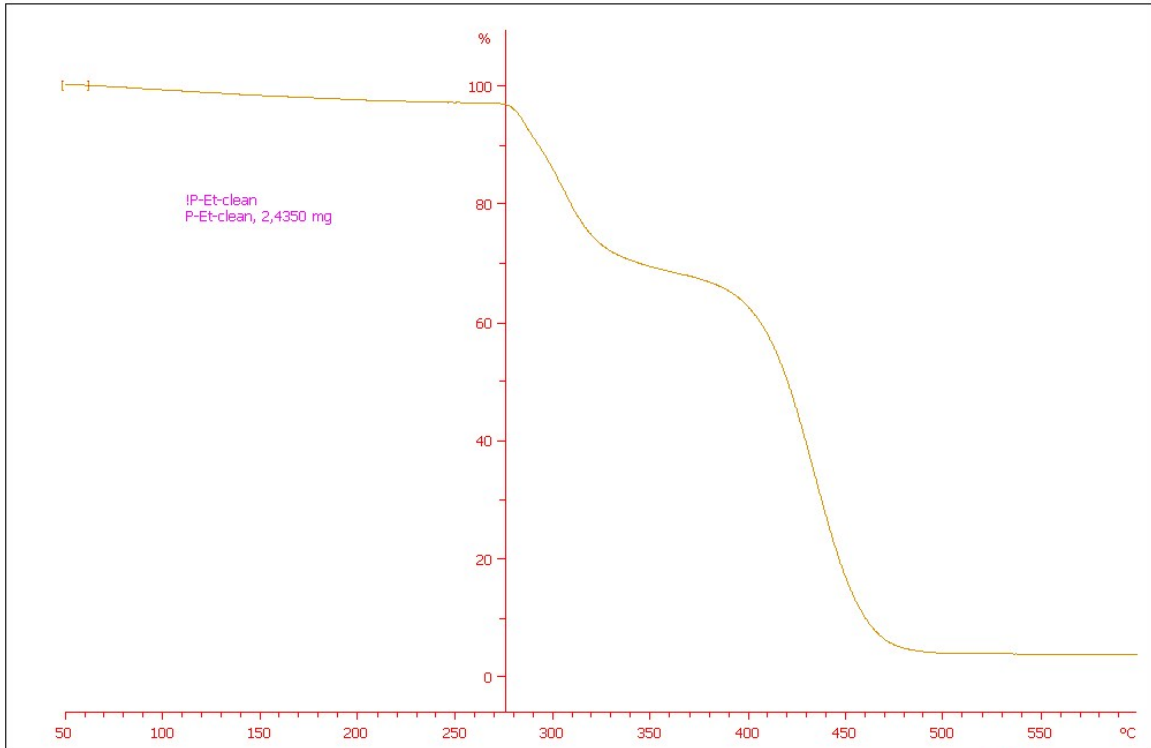


Figure S26. ^{19}F NMR of P-Et (DMSO- d_6 , 470 MHz).

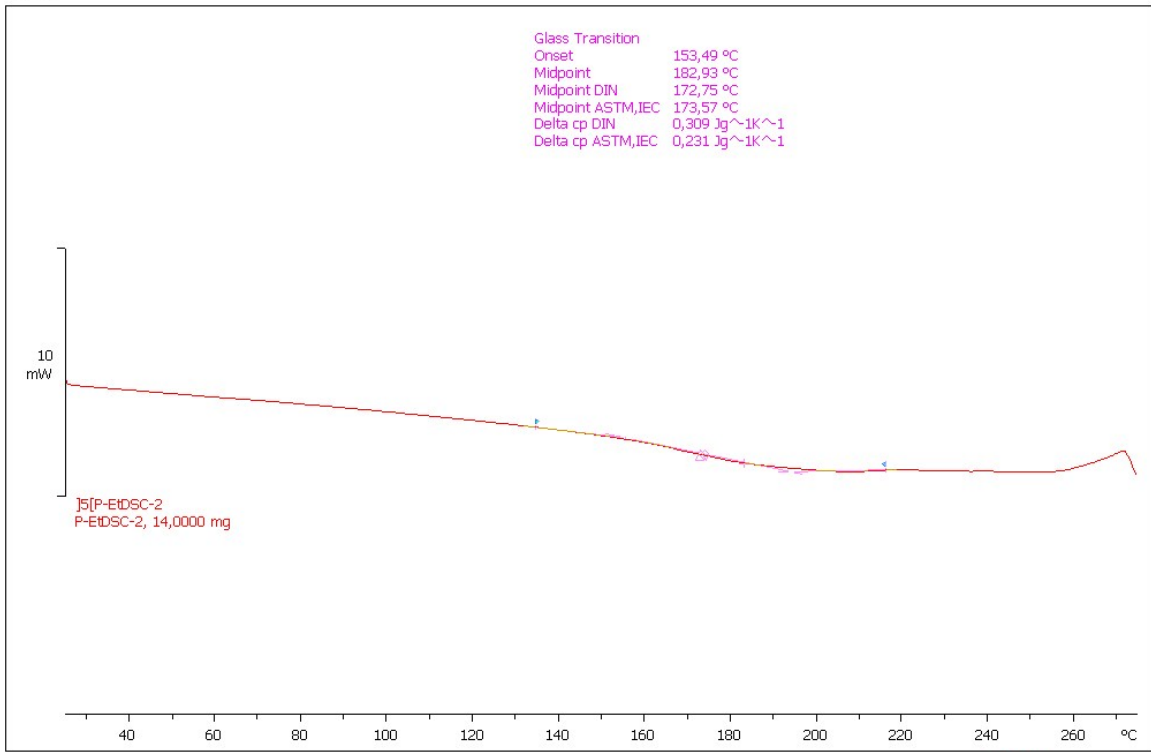


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Figure S27. TGA curve of P-Et.

^exo

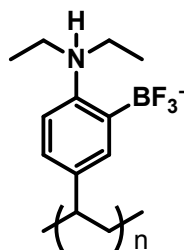


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Figure S28. DSC heating curve of P-Et.

Synthesis of P-Et*



P-Et

Isolated Yield: 70 %

¹H NMR (DMSO-d₆, 500 MHz): δ 8.54 (bs, 1H, N-H), 7.60- 6.01 (m, 3H, Ar-H), 3.79-3.47 (m, 4H, N-CH₂-CH₃, incorporated in solvent peaks), 1.06-0.7 (bs, 6H, CH₃-CH₂-N) 2.18-1.25 (Aliphatic chain protons) 2.02-1.63 (Residual cyclohexanol) ppm.

¹¹B {¹H} NMR (DMSO-d₆, 160 MHz): δ 1.6 (m, 1B, BF₃) (same as **P-Et**).

¹⁹F {¹H} NMR (DMSO-d₆, 470 MHz): δ -132.1 (m, 3F), -148.1 (s, 2F, HF₂⁻)² (same as P-Et).

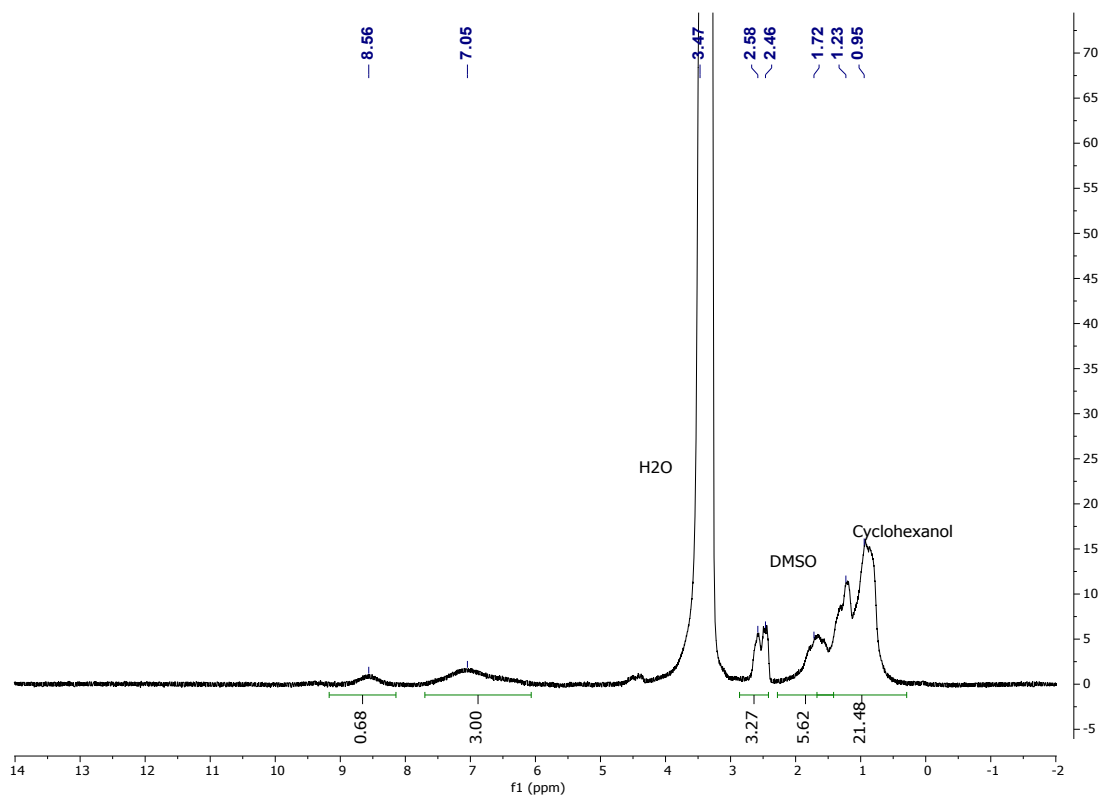
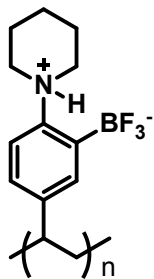


Figure S29. ^1H NMR of compound *P-Et** in DMSO-d_6 (500 MHz).



P-Pip

Isolated Yield: 83 %

^1H NMR (DMSO- d_6 , 500 MHz): δ 8.44 (bs, 1H, N-H), 7.70- 6.01 (m, 3H, Ar-H), c.a 3.6-3.24 (m, 4H, N-CH₂), 2.02-0.70 (m, 6H, **CH-CH₂-CH₂-N**, aliphatic (9H) + residual cyclohexanol)

^{11}B { ^1H } NMR (DMSO- d_6 , 160 MHz): δ 2.0 (m, 1B, BF₃), 0.6 (m, 1B, BF₃)

^{19}F { ^1H } NMR (DMSO- d_6 , 470 MHz): δ -137.6 (m, 3F)

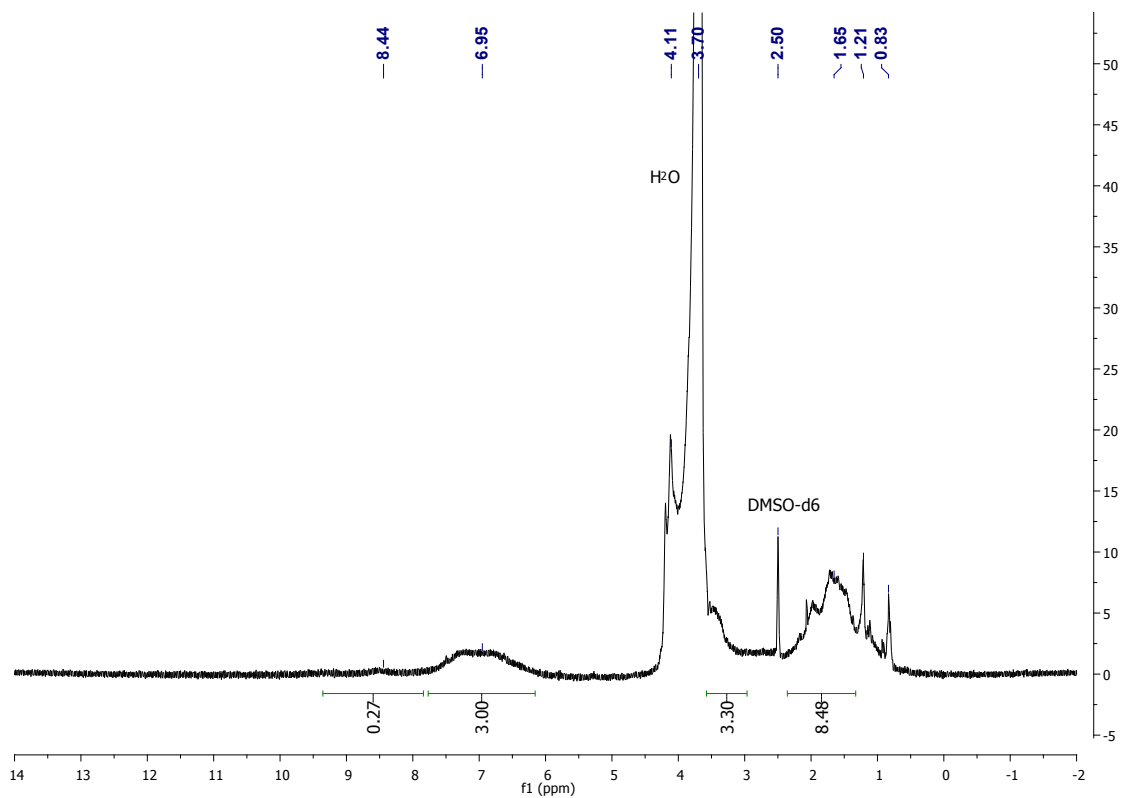


Figure S30. ^1H NMR of **P-Pip** (DMSO-d_6 , 500 MHz).

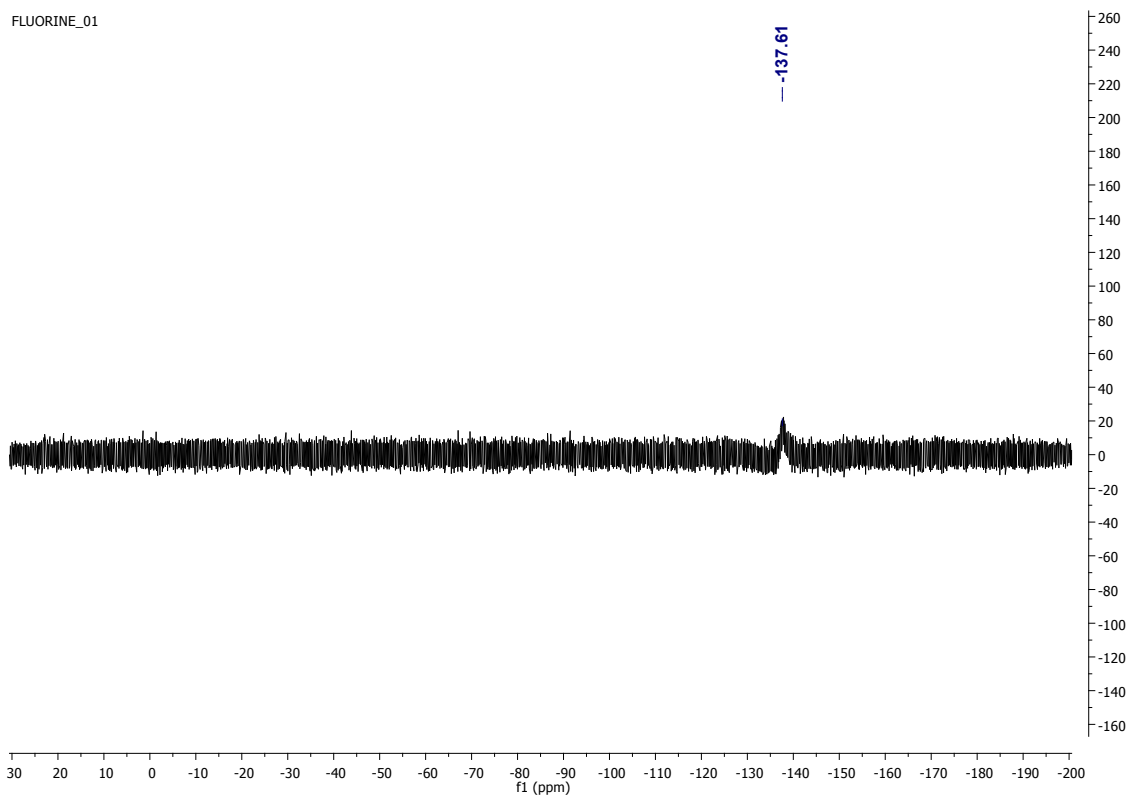


Figure S31. ^{19}F NMR of *P-Pip* ($\text{DMSO-}d_6$, 470 MHz).

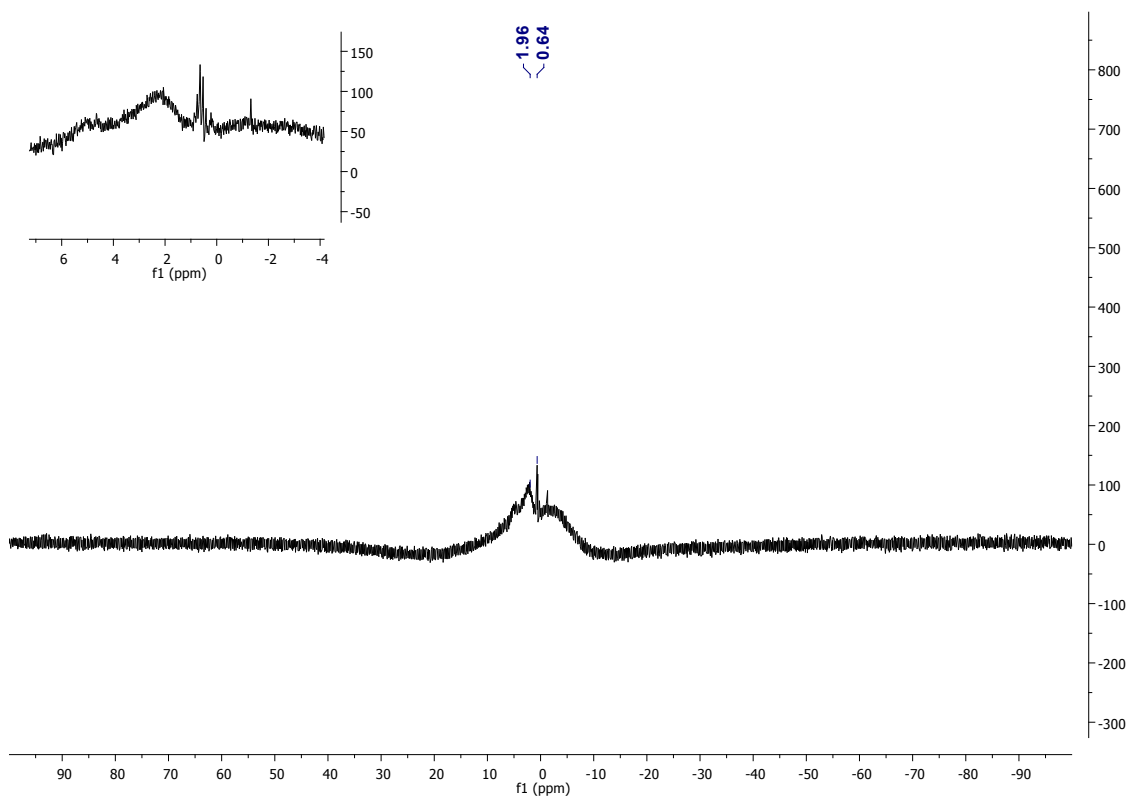
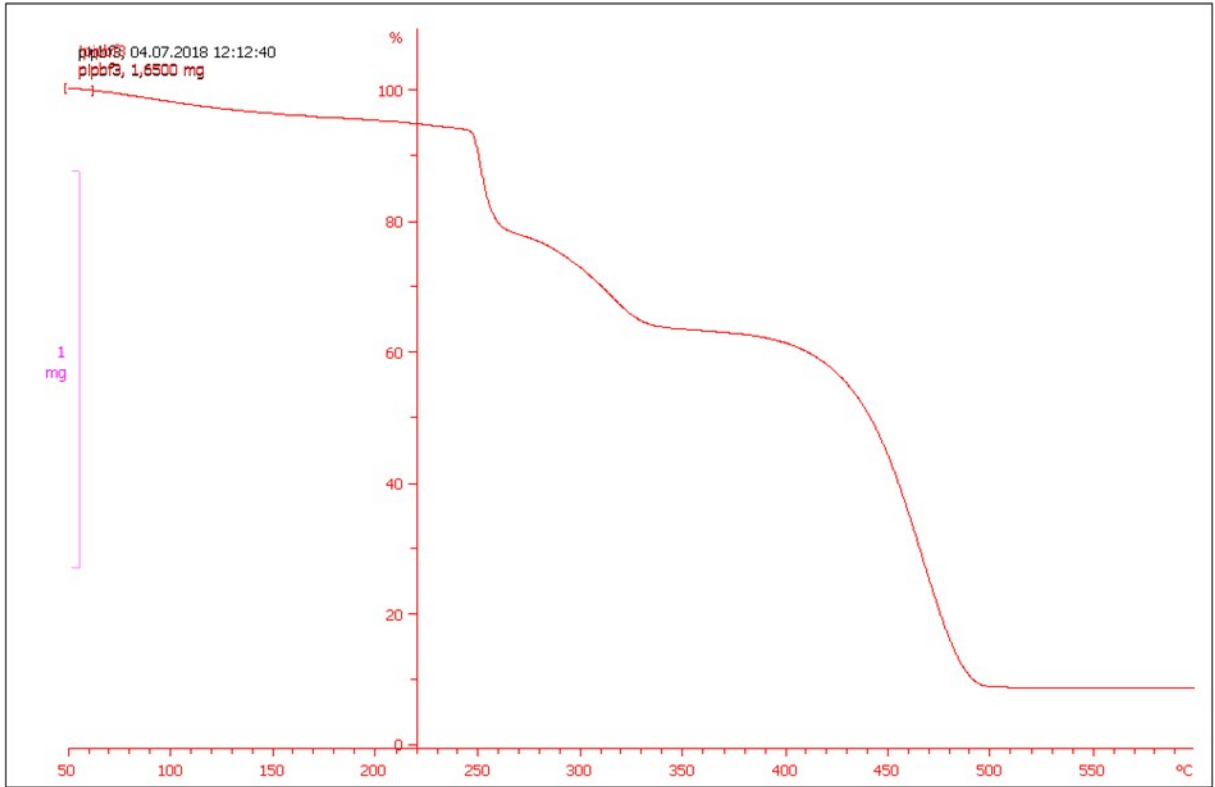


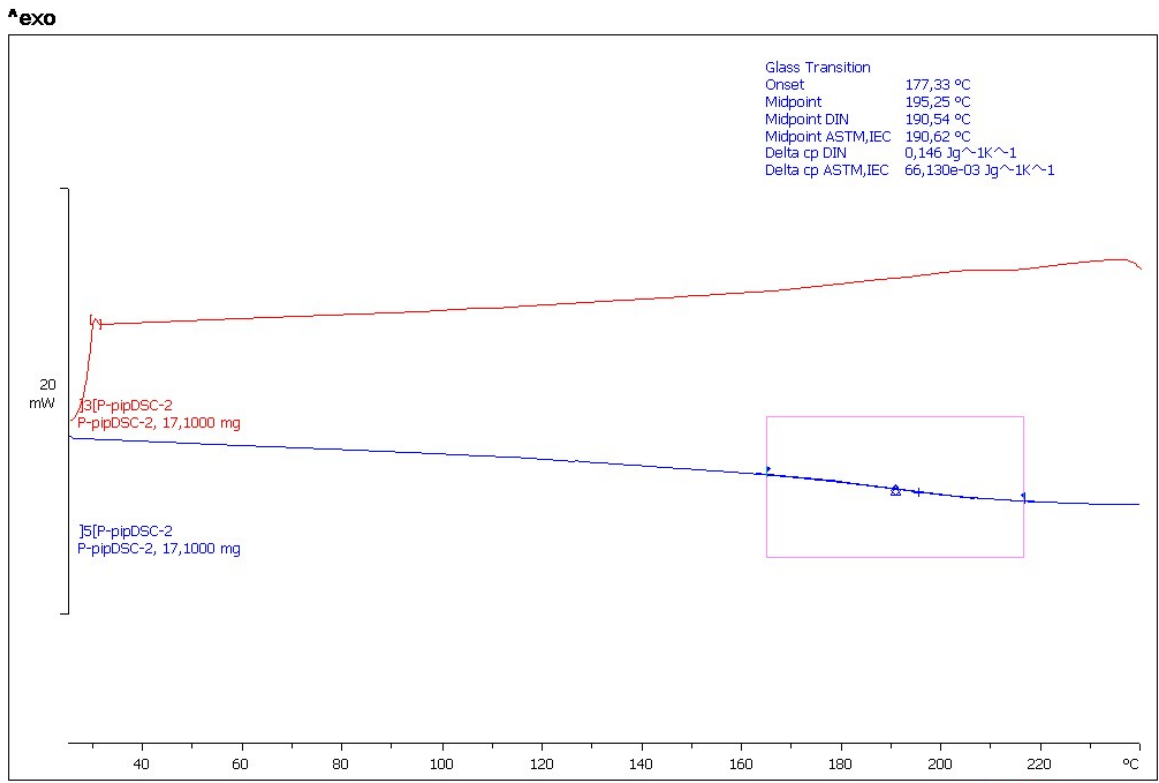
Figure S32. ^{11}B NMR of P-Pip ($\text{DMSO-}d_6$, 160 MHz).



Lab: METTLER

STAR^e SW 9.30

Figure S33. TGA curve of P-Pip.

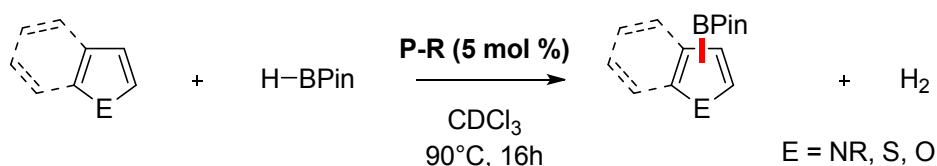


Lab: METTLER

STAR[®] SW 9.30

Figure S34. DSC heating (blue) and cooling (red) curves of P-Pip.

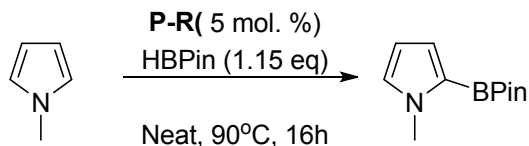
1.5 General procedure for the metal-free catalytic borylation of heteroarenes.



Scheme S3. General borylation conditions.

In a nitrogen-filled glovebox, HBpin and the heteroaromatic substrate were added to a J-Young NMR tube in the specified quantities. 0.023 mmol (5 mg for **P-Me**, 5.6 mg for **P-Et** and 5.9 mg for **P-pip**) of the pre-catalyst **P-R** were added to the J-young tube along with 400 μ L of CDCl₃ if specified. The tube was sealed and put to heat for a timed duration of 16h or 32h (see specified details). The tube was re-entered in the glovebox and filled with CDCl₃ to record the ¹H NMR conversion. The conversions were monitored based on the integration of new peaks on the spectrum that are attributed to the previously reported borylated substrates³⁻⁵.

Borylation of 1-methylpyrrole

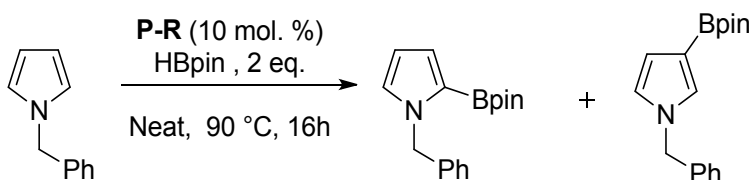


Scheme 54. Borylation of 1-methylpyrrole.

The general procedure was followed. 1-methylpyrrole (39.4 μL , 99.1 mg, 1.22 mmol) was reacted with HBPin (65.4 μL , 156 mg, 1.22 mmol). Conversion was measured by ^1H NMR, based on the apparition of the borylated compound³.

1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole (**3a**): ^1H NMR (400 MHz, CDCl_3) δ 6.81 (m, 2H), 6.15 (m, 1H), 3.84 (s, 3H), 1.31 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 128.3, 122.0, 108.6, 83.2, 36.7, 25.0. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3) : δ 28.1.

Borylation of 1-benzylpyrrole



Scheme 55. Borylation of 1-benzylpyrrole.

Quantity of 1-benzylpyrrole: 35.5 μL

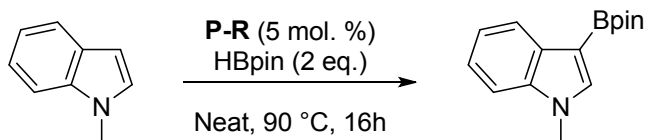
Quantity of HBpin : 76.75 μL

1-benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.17 (m, 3H), 7.12 – 7.06 (m, 2H), 6.89 (dd, J = 2.4, 1.6 Hz, 1H), 6.86 (dt, J = 3.6, 1.9 Hz, 1H), 6.23 – 6.19 (m, 1H), 5.39 (s, 2H), 1.24 – 1.21 (m, 13H).

1-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.26 (m, 3H), 7.17 – 7.12 (m, 3H), 6.73 – 6.68 (m, 1H), 6.51 (dd, $J = 2.6, 1.7$ Hz, 1H), 5.06 (s, 2H), 1.31 (s, 12H).

Mixture: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 139.8, 137.7, 130.4, 128.9, 128.5, 127.9, 127.7, 127.5, 127.2, 127.0, 122.4, 122.3, 114.6, 109.1, 83.3, 82.9, 53.5, 52.9, 25.0, 24.8. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3) δ 27.8.

Borylation of 1-methylindole



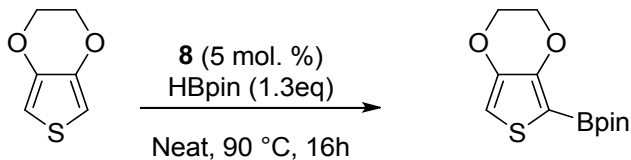
Scheme S6. Borylation of 1-methylindole.

Quantity of 1-methylindole: 57.4 μL

Quantity of HBpin : 153.5 μL

^1H NMR (400 MHz, CDCl_3) δ 8.04 (ddd, $J = 7.7, 1.4, 0.8$ Hz, 1H), 7.52 (s, 1H), 7.35 – 7.31 (m, 1H), 7.25 – 7.15 (m, 2H), 3.80 (s, 3H), 1.37 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.6, 138.0, 132.6, 122.8, 121.9, 120.3, 109.3, 82.9, 33.1, 25.0. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3) δ 29.7.

Borylation of 3,4-ethylenedioxythiophene



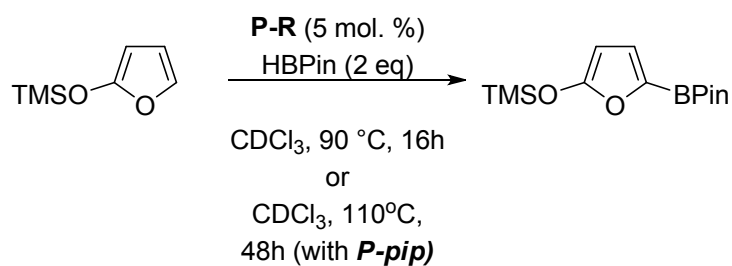
Scheme S7. Borylation of 3,4-ethylenedioxythiophene.

Quantity of 3,4-ethylenedioxythiophene: 49.6 μL

Quantity of HBpin : 76.75 μL

^1H NMR (500 MHz, CDCl_3) δ 6.63 (s, 1H), 4.31 – 4.28 (m, 2H), 4.19 – 4.17 (m, 2H), 1.34 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 149.2, 142.5, 107.6, 84.0, 65.2, 64.4, 24.9; $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3) δ 28.2.

Borylation of 2-silyloxyfuran



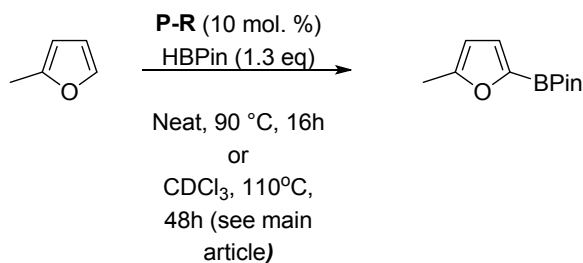
Scheme S8. Borylation of 2-silyloxyfuran.

Quantity of 2-silyloxyfuran : 76.9 μL

Quantity of HBpin : 153.5 μL

^1H NMR (400 MHz, CDCl_3) δ 6.96 (d, $J = 3.3$, 1H), 5.18 (d, $J = 3.3$, 1H), 1.31 (s, 12H), 0.30 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 126.4, 110.2, 85.5, 83.9, 24.9, -0.1. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3) δ 26.7.

Borylation of 2-methylfuran



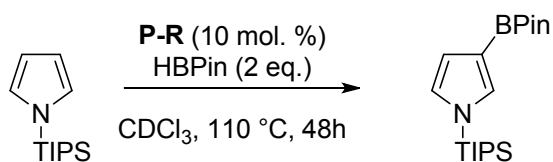
Scheme S9. Borylation of 2-methylfuran.

Quantity of 2-methylfuran : 20.8 μ L

Quantity of HBpin : 43.4 μ L

¹H NMR (400 MHz, CDCl₃) δ 6.99 (d, *J* = 3.3 Hz, 1H), 6.03 (dq, *J* = 3.3, 0.9 Hz, 1H), 2.36 (s, 3H), 1.34 (s, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 157.9, 125.0, 107.0, 84.2, 24.9, -14.1. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 27.1.

Borylation of 1-(triisopropylsilyl)pyrrole



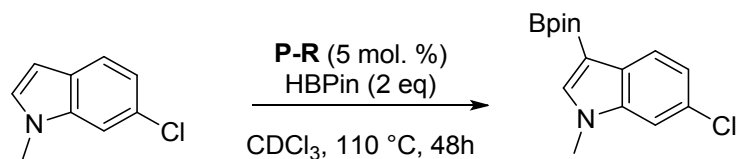
Scheme S10. Borylation of 1-(triisopropylsilyl)pyrrole.

Quantity of 1-(triisopropylsilyl)pyrrole : 56.9 μ L

Quantity of HBpin : 76.8 μ L

¹H NMR (400 MHz, CDCl₃) δ 7.23 (br. s, 1H), 6.81 (m, 1H), 6.62 (m, 1H), 1.46 (sept, *J* = 7.3 Hz, 3H), 1.32 (s, 12H), 1.09 (d, *J* = 7.3 Hz, 18H). ¹³C{¹H} NMR δ (126 MHz, CDCl₃) δ 133.8, 125.1, 115.7, 82.9, 25.0, 18.0, 11.8. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 30.0.

Borylation of 6-chloro-1-methylindole



Scheme S11. Borylation of 6-chloro-1-methylindole.

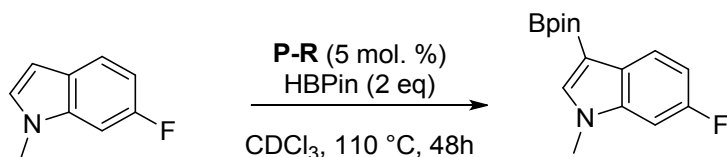
Quantity of 6-chloro-1-methylindole: 76.19 mg

Quantity of HBPin: 153.5 μ L

Apparition of the borylated product is conform with previous reports⁴:

¹H NMR (500 MHz, CDCl₃) δ 8.18 (dd, J = 1.9, 0.5 Hz, 1H), 7.50 (s, 1H), 7.32 (dd, J = 8.6, 2.0 Hz, 1H), 7.15 (dd, J = 8.6, 0.6 Hz, 1H), 3.74 (s, 3H), 1.39 (s, 12H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 139.37, 136.52, 134.22, 125.03, 124.61, 113.89, 110.72, 82.96, 33.14, 24.94. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 29.88.

Borylation of 6-fluoro-1-methylindole



Scheme S12. Borylation of 6-fluoro-1-methylindole.

Quantity of 6-chloro-1-methylindole: 68.62 mg

Quantity of HBPin: 153.5 μ L

Apparition of the borylated product is conform with previous reports⁴:

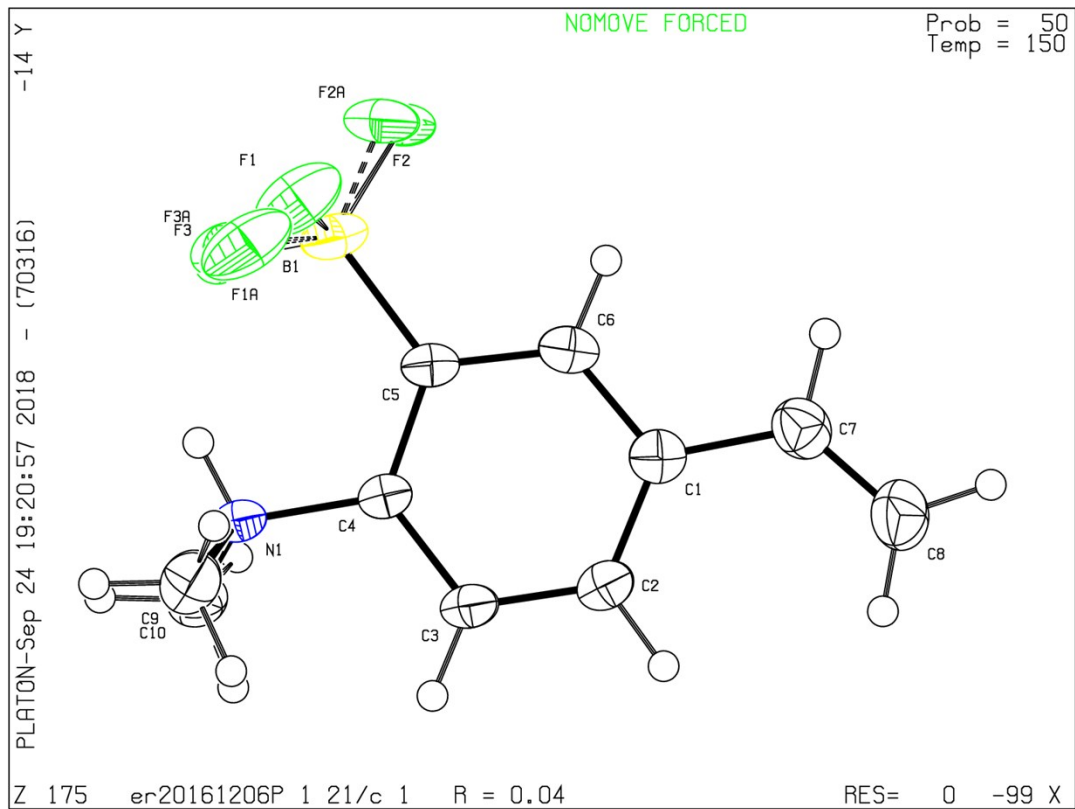
¹H NMR (500 MHz, CDCl₃) δ 7.97 (dd, J = 8.6, 5.5 Hz, 1H), 7.51 (s, 1H), 7.06 – 6.93 (m, 2H), 3.75 (s, 3H), 1.39 (s, 12H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 160.84, 158.95, 138.83, 138.80, 137.90, 137.80, 128.77, 123.45, 123.37, 108.83, 108.64, 95.80, 95.60, 82.86, 33.04, 24.93. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 30.21. ¹⁹F NMR (470 MHz, CDCl₃) δ -120.93

1.6 Crystallographic details

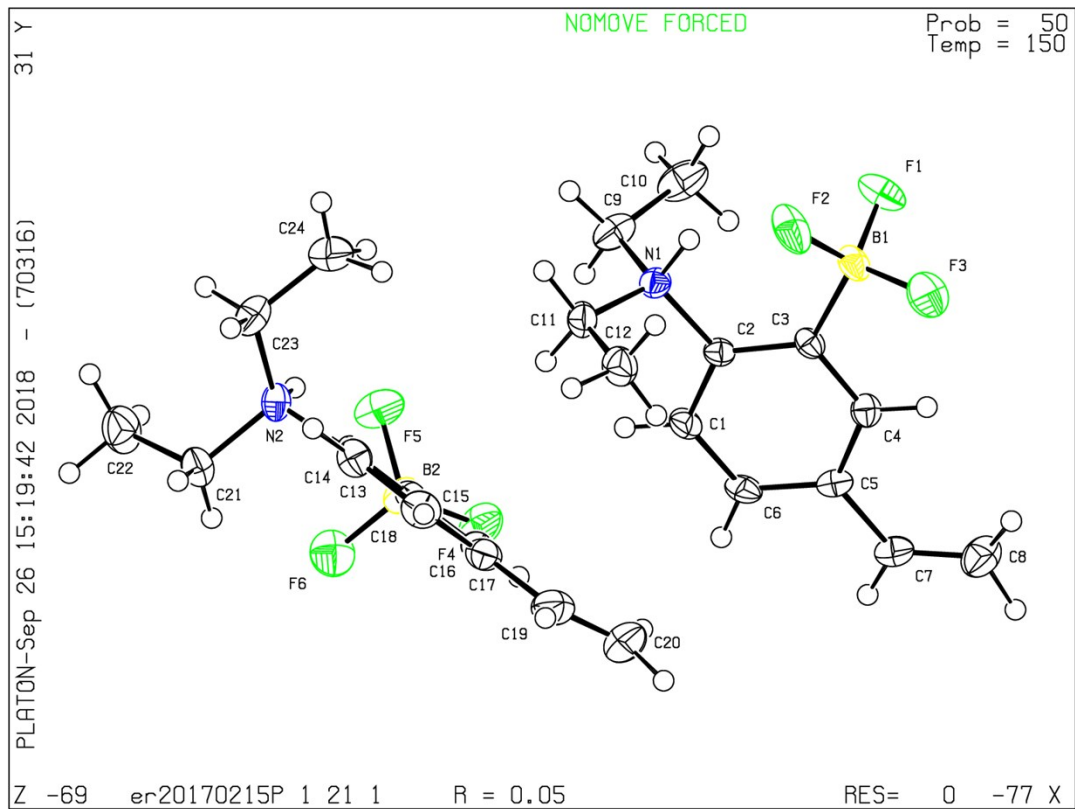
Table S1. Crystal data and structure refinements for compounds **3-Et** and **3-Me**.

Compound	3-Et	3-Me
Empirical formula	C ₁₂ H ₁₇ BF ₃ N	4 (C ₁₀ H ₁₃ BF ₃ N)
Formula weight	243.08	860.09
Temperature	150 K	150K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21	P1 21/C1
Unit cell dimensions	a=8.1685 (7) Å b=14.6515 (13) Å c=10.9025 (10) Å α= γ = 90°. β= 108.176(10)°	a=13.504 (3) Å b=10.4434 (19) Å c=7.9038 (15) Å α= γ = 90°. β= 104.354(3)°
Volume	1239.71(19) Å ³	1079.9(3) Å ³
Z	4	1
Density (calculated)	1.302 Mg/m ³	1.323 Mg/m ³
Absorption coefficient	0.106 mm ⁻¹	0.113
F(000)	512.0	448.0
Crystal size	0.30 x 0.26 x 0.15 mm ³	0.26 x 0.5 x 0.26mm ³
Reflections collected	17578	15534
Ind. reflections	7013 [R(int) = 0.0252]	15071 [R(int) = 0.0368]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.0460	1.0560
Final R indices [I>2σ(I)]	R1 = 0.0542	R1 = 0.0446
R indices (all data)	R1 = 0.0664, wR2 = 0.1480	R1 = 0.0757 , wR2 = 0.1288
Largest diff. peak and hole	0.6 and -0.2 e.Å ⁻³	0.3 and -0.3 e.Å ⁻³

Structure of compound **3-Me**



Structure of compound **3-Et**



1.7 SEC-GPC data.

All SEC-GPC data were performed with a KF-804 column using a RI detector. The system was purged overnight with DMF/LiBr 20mM as the mobile phase. The RI detector was left on to stabilize at sensibility level 10. Baseline of the polymer peaks were normalized and analyzed with the calibration curve made with Agilent technologies High Easy vials standards (logM in function of elution time) (see figure below). M_w and M_n were calculated using statistical treatments of raw data with Excel. The flow was set to 1mL/min at c.a. 1000 psi of pressure. All samples were filtered on a 0.45 μ M PTFE filter prior to injection.

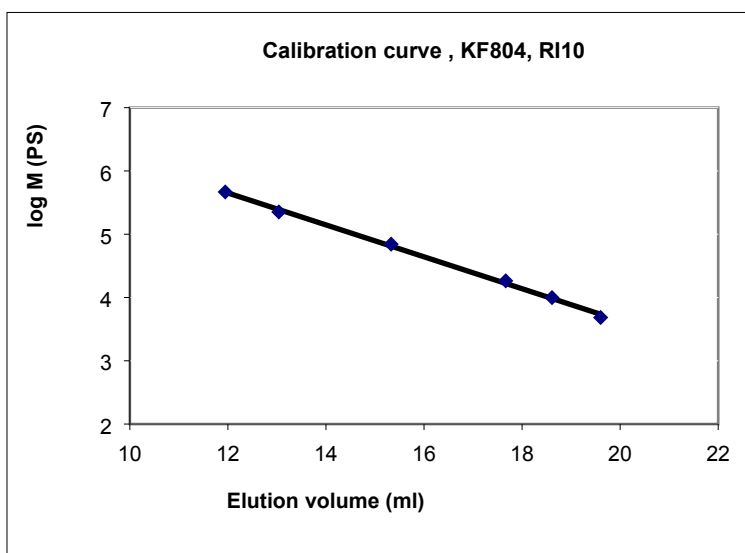


Figure S35. Calibration curve for SEC-GPC using polystyrene standards in DMF/LiBr (20 mM).

Table S2. Calibration curve raw data.

M (PS)	V (PS)	logM (PS)
465600	11.946	5.66801297
224900	13.039	5.35198946
69650	15.329	4.84292112
18340	17.666	4.26339933
9970	18.61	3.99869516
4830	19.602	3.68394713

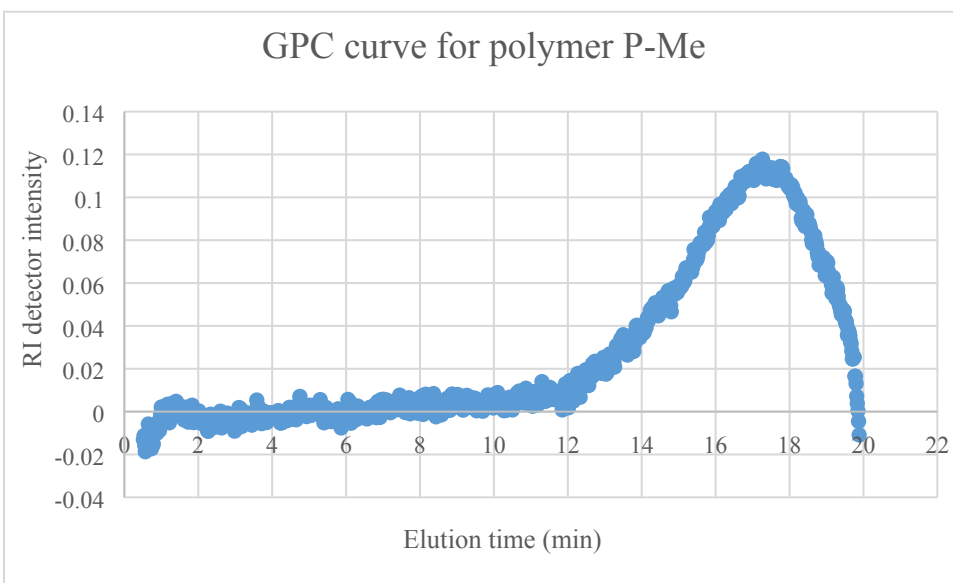


Figure S36. SEC-GPC chromatogram for polymer **P-Me** in DMF/Libr (20 mM).

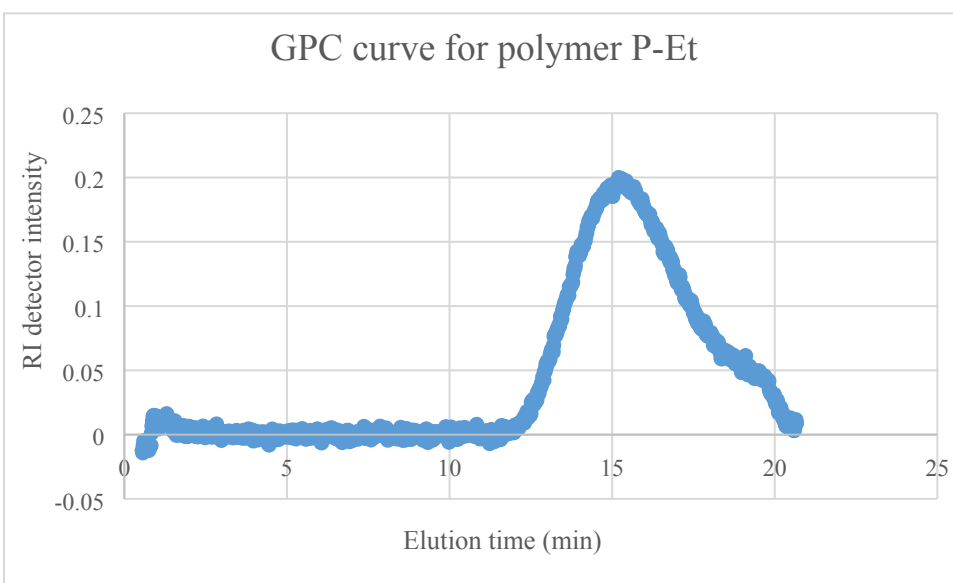


Figure S37. SEC-GPC chromatogram for polymer **P-Et** in DMF/Libr (20 mM).

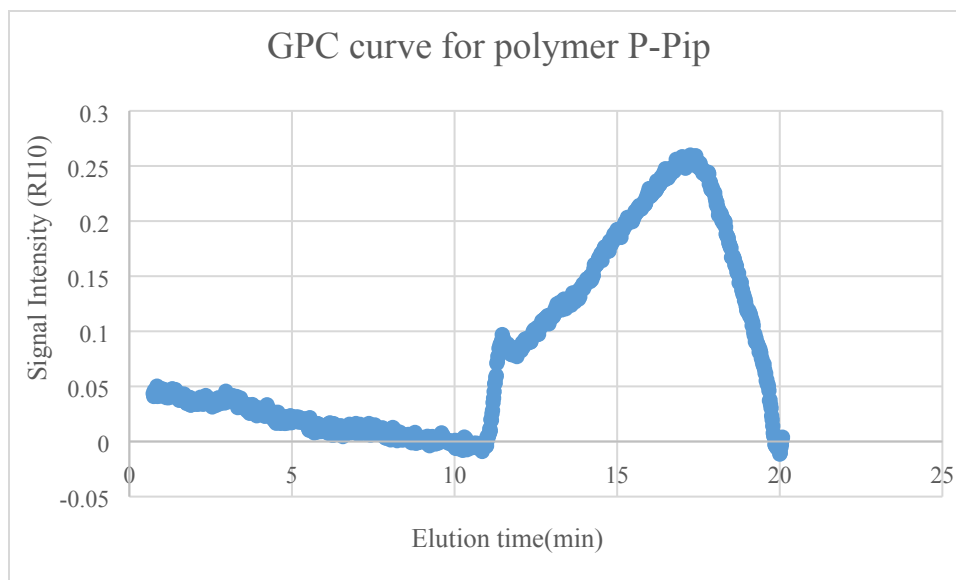


Figure S38. SEC-GPC chromatogram for polymer **P-Pip** in DMF/Libr (20 mM).

References:

- (1) Das, B.; Venkateswarlu, K.; Majhi, A.; Siddaiah, V.; Reddy, K. R. *J. Mol. Catal. A Chem.* **2007**, *267*, 30–33.
- (2) Hudlicky, M. *J. Fluor. Chem.* **1985**, *28* (4), 461–472.
- (3) (a) Légaré, M.-A.; Courtemanche, M.-A.; Rochette, É.; Fontaine, F.-G. *Science*, **2015**, *349* (6247), 513 LP – 516. (b) Légaré Lavergne, J.; Jayaraman, A.; Misal Castro, L. C.; Rochette, É.; Fontaine, F. G. *J. Am. Chem. Soc.* **2017**, *139* (41), 14714–14723. (c) Légaré, M.-A.; Rochette, É.; Légaré Lavergne, J.; Bouchard, N.; Fontaine, F.-G. *Chem. Commun.* **2016**, *52* (31), 5387–5390.
- (4) (a) E. Rochette and F.-G. Fontaine, *ChemRxiv*, 2018, DOI:10.26434/chemrxiv.7354331.v1. (b) A. Jayaraman, L. C. Misal Castro and F.-G. Fontaine, *Org. Process Res. Dev.*, 2018, **22**, 1489–1499.