Supporting Information for:

N-Heterocycle Ligated Borocations as Highly Tunable Carbon Lewis Acids

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1 General Considerations

Unless otherwise indicated all manipulations were conducted under inert conditions either using standard Schlenk techniques or in a MBraun UniLab glovebox (< 0.1 ppm H_2O / O_2). Unless otherwise indicated, dichloromethane-d_2 and *protio*-dichloromethane were dried over CaH_2 and distilled prior to storage over 3 Å molecular sieves. Unless otherwise stated all compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker AvanceIII-400 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are frequency referenced relative to residual *protio*- impurities in the NMR solvents for ^{1}H and $^{13}C\{^{1}H\}$ respectively, while $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ shifts are referenced relative to external BF_3-Et_2O and hexafluorobenzene, respectively. Coupling constants *J* are given in Hertz (Hz) as positive values regardless of their real individual signs. The multiplicity of the signals are indicated as "s", "d", "t" "q" "pent", "sept" or "m" for singlet, doublet, triplet, quartet, pentet, septet or multiplet, respectively.

2 Synthesis of Borocations and Relevant Precursors

2.1 F_5-Acridine

A modified version of a literature preparation was used to prepare the title compound.[1] The relevant starting materials were dissolved in chlorobenzene and the mixture set to reflux for 72 hours. The solvent was removed under vacuum before the residue was purified by washing through a short (~5 cm) silica plug (50:50 DCM/pet. ether) and crystallisation from hot acetone. The identity and purity of the product was confirmed by ^{1}H and $^{19}F\{^{1}H\}$ NMR spectroscopic analysis which were consistent with that previously reported.

2.2 [Acr-BCl_3]

Made according to the standard literature procedure.[2]

2.3 [Acr-BCl_2][$AlCl_4$] ([1][$AlCl_4$])

Made according to the standard literature procedure.[2]

2.4 [Acr-BCat][$AlCl_4$] ([3][$AlCl_4$])

An oven dried Schlenk tube was loaded with acridine (500 mg, 2.79 mmol) which was dried under vacuum for 1 h prior to the addition of chlorocatecholborane (430 mg, 2.79 mmol) in a glovebox. Anhydrous dichloromethane (10 mL) was added to the combined solids which led to an immediate bright orange precipitate and stirring was continued for 1 h at ambient temperature. After this time, all volatiles were removed to afford a bright orange free-flowing solid tentatively assigned as [Acr-BCatCl]. Due to the poor solubility of [Acr-BCatCl] in common solvents it was not possible to obtain NMR spectroscopic data. A Schlenk flask was charged with [Acr-BCatCl] (150 mg, 0.45 mmol) and $AlCl_3$ (60 mg, 0.45 mmol) before DCM (5 mL) was added. The resulting mixture was left to stir overnight, after which time a clear orange solution formed. The solution was concentrated under vacuum and subsequently layered with pentane. After standing for 24 hours a crop of brown crystalline needles had grown, which were isolated, washed with pentane and dried under vacuum (168 mg, 80% yield). The title compound was characterised by NMR spectroscopy and the purity

verified by elemental analysis. Elemental analysis calc.: $C_{19}H_{13}AlBCl_4NO_2$: C, 48.88; H, 2.81; N, 3.00. Found: C, 48.69; H, 2.77; N, 3.15.

^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 10.01 (s, 1H, Acr-C^9*H*), 8.63 (d, *J* = 8 Hz, 2H, Acr-C*H*), 8.40 (t, *J* = 8 Hz, 2H, Acr-C*H*), 8.30 (d, *J* = 9 Hz, 2H, Acr-C*H*), 8.07 (t, *J* = 8 Hz, 2H, Acr-C*H*), 7.66 (dd, *J* = 8, 4 Hz, 2H, Cat-C*H*), 7.49 (dd, *J* = 6, 4 Hz, 2H, Cat-C*H*).

^{13}C{^{1}H} NMR (126 MHz, Methylene Chloride-d_2) δ 154.8 (Acr-*C*^{9}), 147.8 (Cat-*C*-O), 142.7 (Acr-*C*), 141.2 (Acr-*C*H), 132.6 (Acr-*C*H), 129.7 (Acr-*C*H), 126.9 (Acr-*C*), 126.1 (Cat-*C*H), 120.2 (Acr-*C*H), 114.8 (Cat-*C*H).

^{11}B{^{1}H} NMR (160 MHz, Methylene Chloride-d_2) δ 28.2.

^{27}Al{^{1}H} NMR (104 MHz, Methylene Chloride-d_2) δ 104.0.

2.5 [F_5Acr-BCat][$AlCl_4$] ([**5**][$AlCl_4$])

An oven dried J. Young's NMR tube was loaded with F_5-acridine (26.9 mg, 0.1 mmol), CatBCl (15.4 mg, 0.1 mmol) and d_2-dichloromethane (0.5 mL). $AlCl_3$ (13.3 mg, 0.1 mmol) was added to the reaction mixture followed by agitation at ambient temperature for 5 minutes to afford a bright yellow homogeneous solution which was confirmed as the desired borocation by ^{1}H, ^{11}B{^{1}H}, ^{27}Al and ^{19}F{^{1}H} NMR spectroscopy. The solvent was removed from the sample under vacuum, before the brown residue was washed with pentane (2 x 2 mL). The purity of the title compound was verified by satisfactory elemental analysis. Elemental analysis calc.: $C_{19}H_8AlBCl_4F_5NO_2$: C, 40.98; H, 1.45; N, 2.52. Found: C, 40.84; H, 1.50; N, 2.60.

In order to determine the isolated yield of the reaction the procedure was repeated identically, using F_5-acridine (25.9 mg, 0.96 mmol), CatBCl (14.9 mg, 0.96 mmol) and $AlCl_3$ (12.8 mg, 0.96 mmol) in 1 mL DCM. The product was isolated after washing with pentane and drying under vacuum, to yield [F_5Acr-BCat][$AlCl_4$] ([**5**][$AlCl_4$]) (35 mg, 0.63 mmol, 65 % yield). The identity of the product was confirmed by multinuclear NMR spectroscopic analysis.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 10.20 (s, 1H, Acr-C9*H*), 8.37 – 8.30 (m, 1H, Acr-C*H*), 8.29 – 8.23 (m, 1H, Acr-C*H*), 8.06 (dd, *J* = 10, 4 Hz, 1H, Acr-C*H*), 7.62 (dd, *J* = 6, 3 Hz, 2H, Cat-C*H*), 7.47 (dd, *J* = 6, 3 Hz, 2H, Cat-C*H*).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) δ 162.9 (Acr-*C*), 160.9 (Acr-*C*), 148.9 (Acr-*C9*H), 147.7 (Cat-*C*-O), 141.52 (Acr-*C*), 134.3 (d, J = 28 Hz, Acr-*C*H), 129.2 (Acr-*C*), 128.2 (d, *J* = 11 Hz, Acr-*C*), 126.2 (Cat-*C*H), 122.4 (d, *J* = 9 Hz, Acr-*C*H), 116.2 (Acr-*C*), 116.1 (d, *J* = 23 Hz, Acr-*C*H), 114.9 (Cat-*C*H).

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, 298 K) δ -102.84 (s), -129.52 (tdd, *J* = 19, 9, 3 Hz), -136.84 (td, *J* = 16, 10 Hz), -147.14 (dd, *J* = 18, 15 Hz), -148.81 (t, *J* = 18 Hz).

^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 298 K) δ 27.9.

^{27}Al NMR (104 MHz, Methylene Chloride-d_2) δ 103.4.

2.6 F_5Acr-$AlCl_3$ (6)

An oven dried J. Young's NMR tube was loaded with F_5-acridine (20.2 mg, 0.075 mmol) before d_2-dichloromethane (0.5 mL) was added. The sample was agitated before $AlCl_3$ (10.0 mg, 0.075 mmol) was added, causing an instantaneous colour change to yellow. The sample was sonicated for 15 minutes before submitting for analysis by NMR spectroscopy, which showed the formation of F_5-acridine-$AlCl_3$ and another minor F_5-acridine related product (*see Figure S61*). The identity of the title product was confirmed by ^{1}H, $^{13}C\{^{1}H\}$, ^{27}Al and $^{19}F\{^{1}H\}$ NMR spectroscopy. Crystals of F_5-acridine-$AlCl_3$ suitable for X-ray crystallography were grown from a concentrated DCM solution of the product layered with hexanes.

Only ^{1}H NMR signals pertaining to F_5-acridine-$AlCl_3$ reported (see Figure S61 for full spectra)
^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.63 (s, 1H, Acr-C9-*H*), 8.87 (dd, *J* = 10, 4 Hz, 1H, Acr-C*H*), 8.06 – 7.99 (m, 1H, Acr-C*H*), 7.94 (dd, *J* = 7, 3 Hz, 1H, Acr-C*H*).

Only ^{13}C NMR signals pertaining to F_5-acridine-$AlCl_3$ reported (see Figure S62 for full spectra)
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 162.6, 160.5, 146.9, 142.9, 142.0 (Acr-*C9*H), 140.8, 134.9, 129.9 (d, *J* = 9 Hz, Acr-*C*H), 128.8 (d, *J* = 11 Hz), 128.4 (d, *J* = 28 Hz, Acr-*C*H), 112.3 (d, *J* = 23 Hz, Acr-*C*H).

Only ^{19}F NMR signals pertaining to F_5-acridine-$AlCl_3$ reported (see Figure S63 for full spectra)
$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) δ -106.0, -129.6 (t, *J* = 16 Hz), -139.3 (t, *J* = 18 Hz), -143.8 – -145.3 (m), -152.5 (t, *J* = 18 Hz).

^{27}Al NMR (104 MHz, CD_2Cl_2) δ 104.1 ($AlCl_3$), 102.3 (br, F_5Acr-$AlCl_3$).

3 Hydride Abstraction Experiments

3.1 Hydride abstraction from Me-acridane with [Acr-BCat][$AlCl_4$] ([3][$AlCl_4$])

An ampule was loaded with Acr-CatBCl (16.7 mg, 0.05 mmol) and $AlCl_3$ (6.67 mg, 0.05 mmol) before DCM (0.5 mL) was added. The reaction mixture was stirred for 5 minutes, yielding a clear orange solution. Separately, a J. Young's NMR tube was equipped with a benzene-d_6 capillary and loaded with N-methyl-acridane (9.7 mg, 0.05 mmol). The [Acr-BCat][$AlCl_4$] solution was transferred into the NMR tube and the resulting sample mixed. Analysis of the mixture by multinuclear NMR spectroscopic experiments revealed complete consumption of the starting materials, along with formation of N-methyl-acridinium and Acridane=BCat.

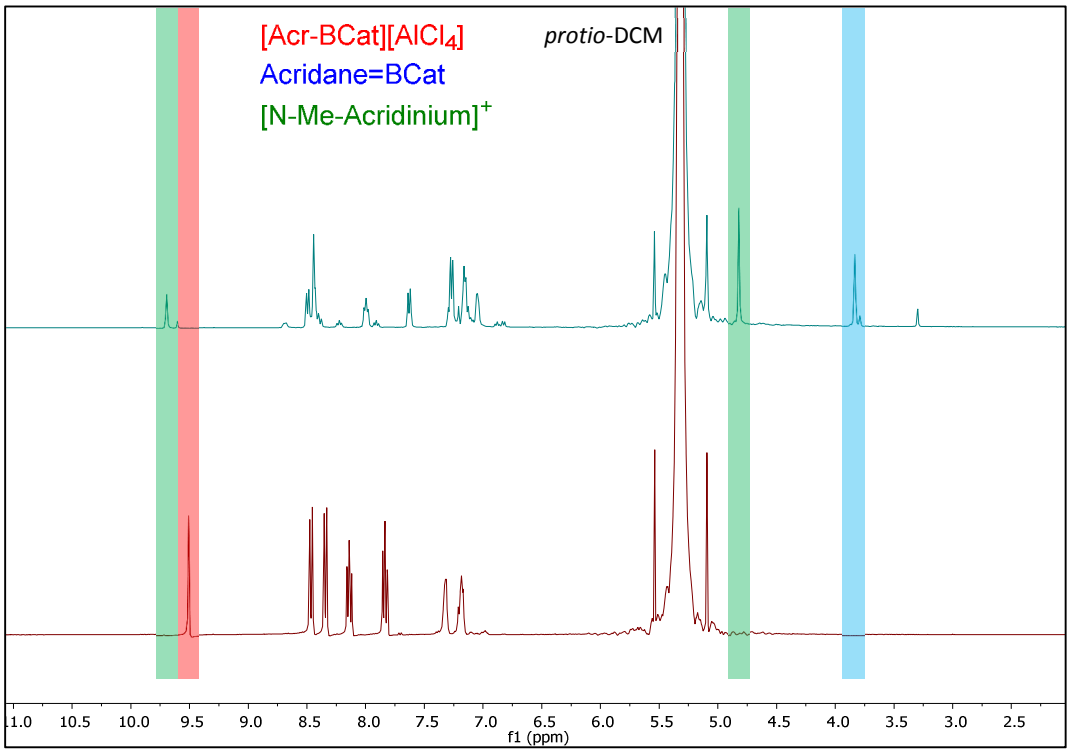

Figure S1: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert containing d_6-benzene) of: *in-situ* generated [Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 5 minutes after the addition of N-Me-acridane (top).

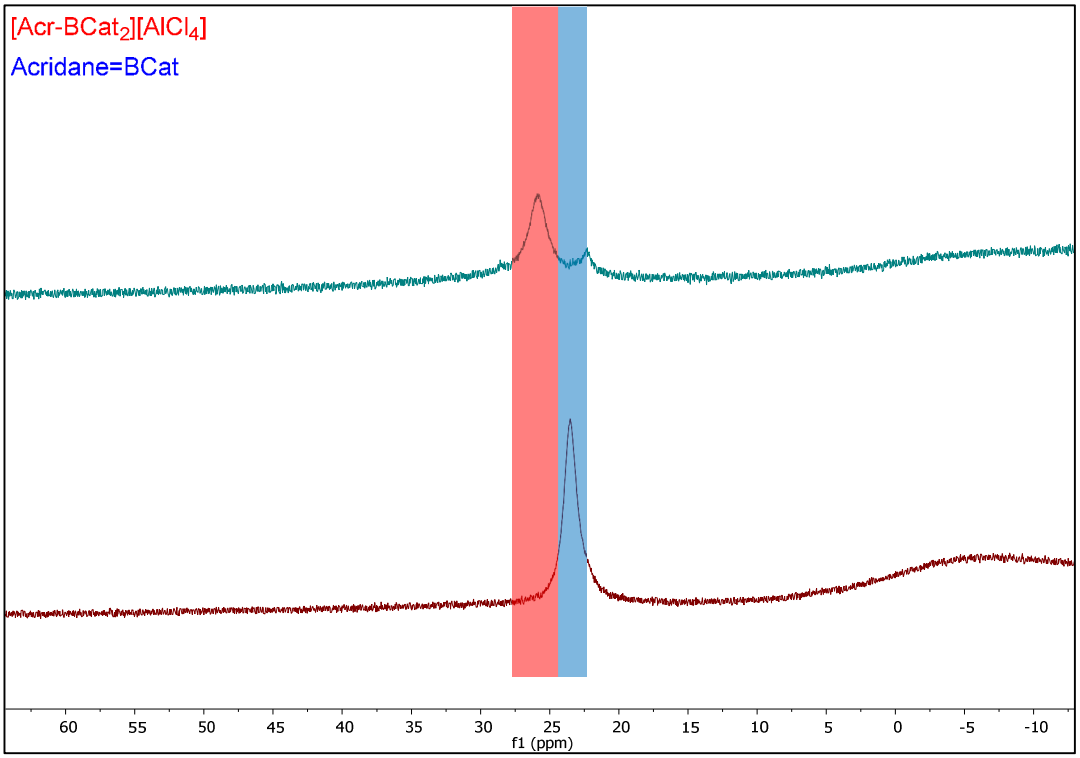

Figure S2: Collected $^{11}B\{^{1}H\}$ spectra (*protio*-DCM, 128.4 MHz, 298K) of: *in-situ* generated [Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 5 minutes after the addition of N-Me-acridane (top).

3.2 Hydride abstraction from C_7H_8 with [Acr-BCat][$AlCl_4$] ([3][$AlCl_4$])

In a glovebox an oven dried J. Young's NMR tube equipped with a d_6-DMSO capillary insert was loaded with [Acr-BCatCl] (33.3 mg, 0.1 mmol) and $AlCl_3$ (13.3 mg, 0.1 mmol) followed by *protio*-DCM (0.8 mL). The reaction mixture was agitated for 5 minutes at ambient temperature leading to a bright yellow, homogeneous solution which was confirmed as the desired borocation, [Acr-BCat][$AlCl_4$] by ^{1}H, $^{11}B\{^{1}H\}$ and ^{27}Al NMR spectroscopy, respectively. Cycloheptatriene (10.4 µL, 0.1 mmol) was added to the *in-situ* generated [Acr-BCat][$AlCl_4$] under an inert atmosphere followed by analysis by ^{1}H and $^{11}B\{^{1}H\}$ NMR spectroscopy after 5 minutes at ambient temperature which revealed the incomplete consumption of the [Acr-BCat][$AlCl_4$] C9 resonance (δ_H = 10.03 ppm) and the cycloheptatriene (δ_H CH_2 = 2.22 ppm) along with the generation of the expected tropylium cation (δ_H = 9.26 ppm) and [Acridane-BCat] (δ_H = 3.83 ppm) (*see Figure S3 – 2nd from top*). Heating the reaction mixture to 60°C for 16 h led to the complete consumption of the [Acr-BCat][$AlCl_4$] C9 resonance (δ_H = 10.03 ppm). The reduction in intensity of the tropylium cation is due to the poor solubility of the $AlCl_4$ salt in DCM (*see Figure S3 – top*). The $^{11}B\{^{1}H\}$ NMR spectra demonstrates the consumption of [Acr-BCat][$AlCl_4$] (δ_B = 28.2 ppm) and the generation of [Acridane-BCat] (δ_B = 25.4 ppm) (*see Figure S4 – top*).

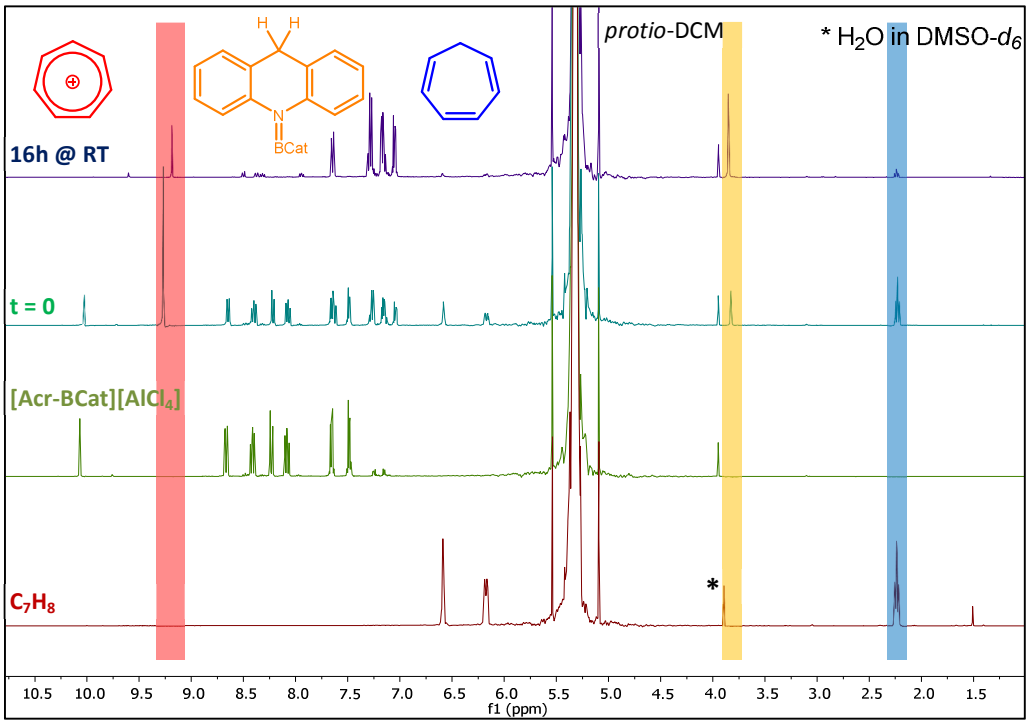

Figure S3: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert containing wet DMSO-d_6) of: cycloheptatriene (bottom); [Acr-BCat][$AlCl_4$] (2nd from bottom); the reaction mixture after 5 minutes at ambient temperature (2nd from top); and the reaction mixture after 16 h at ambient temperature (top).

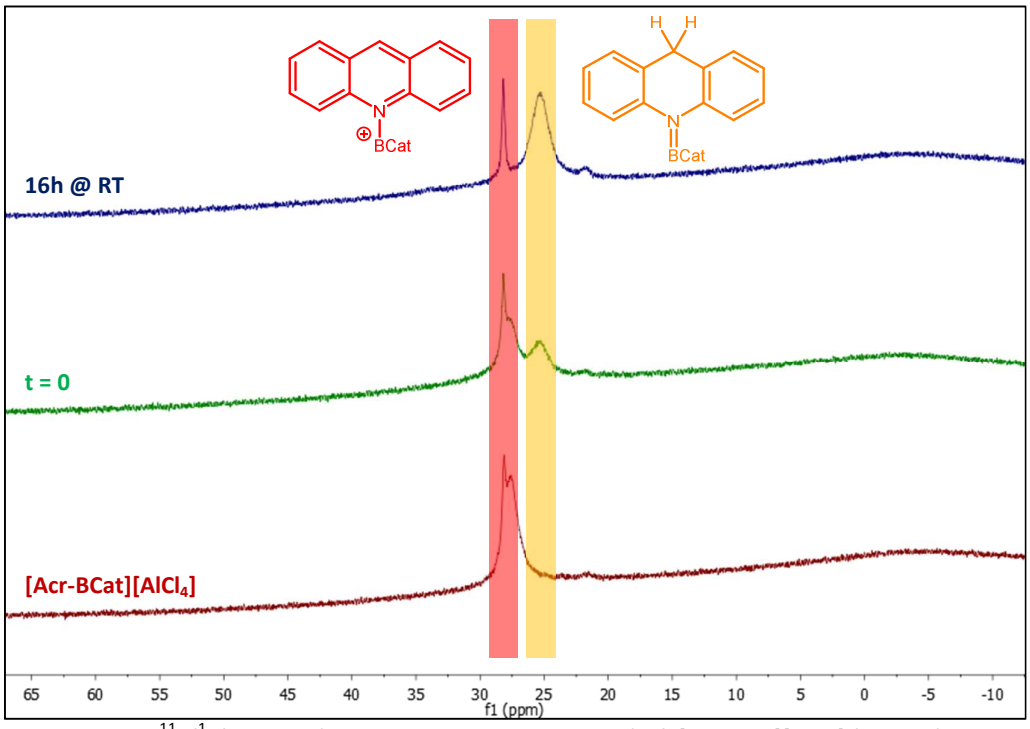

Figure S4: Collected ^{11}B{^{1}H} spectra (*protio*-DCM, 128.4 MHz, 298K) of: [Acr-BCat][$AlCl_4$] (bottom); the reaction mixture after 5 minutes at ambient temperature (middle); and the reaction mixture after 16 h at ambient temperature (top). A minor quantity of CatBCl is present throughout (sharp resonance, δ_B = 28 ppm)

3.3 Attempted hydride abstraction from dibenzosuberene with [Acr-BCat][$AlCl_4$] ([3][$AlCl_4$])

A J. Young's NMR tube was equipped with a d_6-benzene filled capillary and loaded with acridine (13.4 mg, 0.075 mmol) before drying under vacuum. DCM (0.5 mL) was added, followed by BCatCl (11.6 mg, 0.075 mmol) and $AlCl_3$ (10.0 mg, 0.075 mmol). The resulting mixture was agitated for 10 minutes, after which time it became a clear orange solution. The clean formation of [Acr-BCat][$AlCl_4$] was confirmed by NMR spectroscopic analysis. Dibenzosuberene (14.4 mg, 0.075 mmol) was added to the solution and mixed prior to analysis by ^{1}H, $^{27}Al\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectroscopy. No reaction was observed, and so the sample was mixed at RT for 16 hours before further NMR spectroscopic analysis confirmed no reaction had occurred. The reaction mixture was subjected to 20 hours heating at 60 °C, which still afforded no change in the ^{1}H or $^{11}B\{^{1}H\}$ NMR spectra (Figure S5).

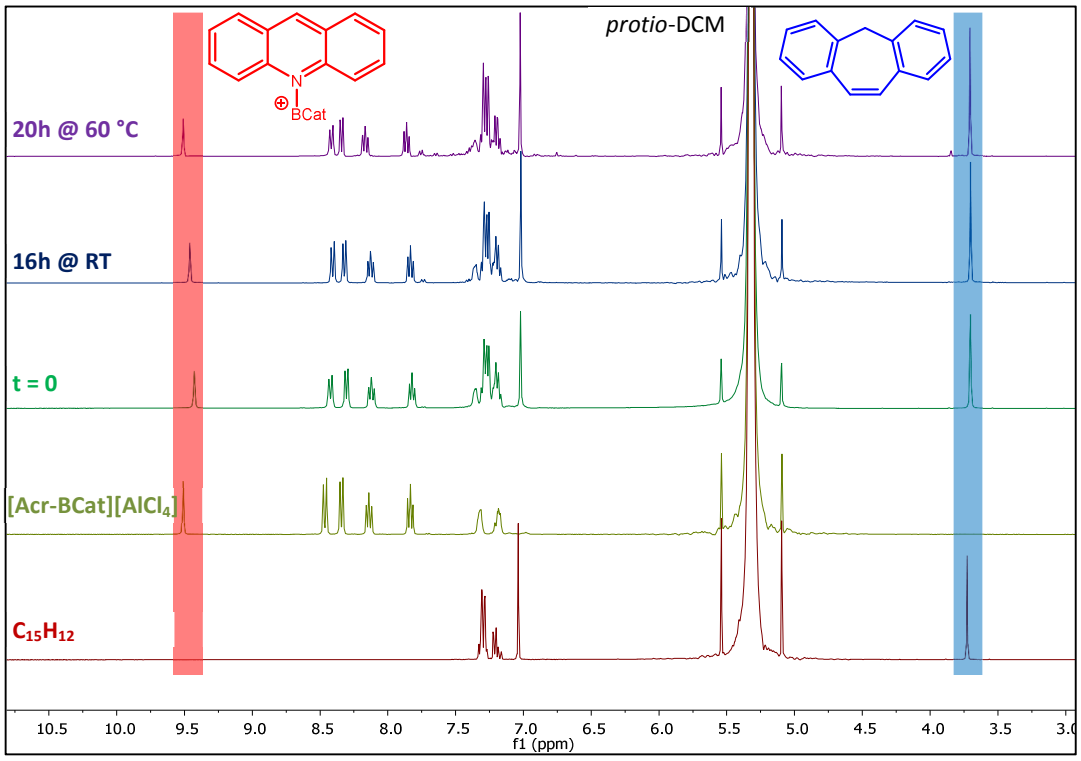

Figure S5: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with capillary insert of d_6-benzene) of: dibenzosuberene (bottom); *in-situ* generated [Acr-BCat][$AlCl_4$] (2nd from bottom); the reaction mixture after 5 minutes at ambient temperature (middle); the reaction mixture after 16 hours at room temperature (2nd from top); the reaction mixture after 20 hours at 60 °C (top).

3.4 Hydride abstraction from C_7H_8 with [Acr-BCat][$AlCl_4$] ([3][$AlCl_4$]), followed by hydride abstraction from (Acridane=BCat) with dibenzotropylium

A Young's NMR tube was equipped with a d_6-benzene capillary before adding DCM (0.5 mL). Solid Acr-BCatCl (25 mg, 0.075 mmol) and $AlCl_3$ (10 mg, 0.075 mmol) were added, yielding a clear orange solution after mixing, which was confirmed to be [Acr-BCat][$AlCl_4$] by ^{1}H, $^{11}B\{^{1}H\}$ and ^{27}Al NMR spectroscopy. Cycloheptatriene (7.8 µL, 0.075 mmol) was subsequently added, and further NMR spectroscopic experiments confirmed the formation of Acridane=BCat and [C_7H_7][$AlCl_4$].

In a second Young's NMR tube [Ph_3C][$AlCl_4$] (30 mg, 0.075 mmol) and dibenzosuberene (15 mg, 0.079 mmol) were combined in DCM (0.2 mL) yielding a dark brown solution. This mixture, now containing [Dibenzotropylium][$AlCl_4$] was transferred to the first NMR tube, and the resulting combined solutions were mixed. NMR spectroscopic experiments revealed the regeneration of the borenium salt [Acr-BCat][$AlCl_4$], caused by hydride abstraction by the dibenzotropylium salt.

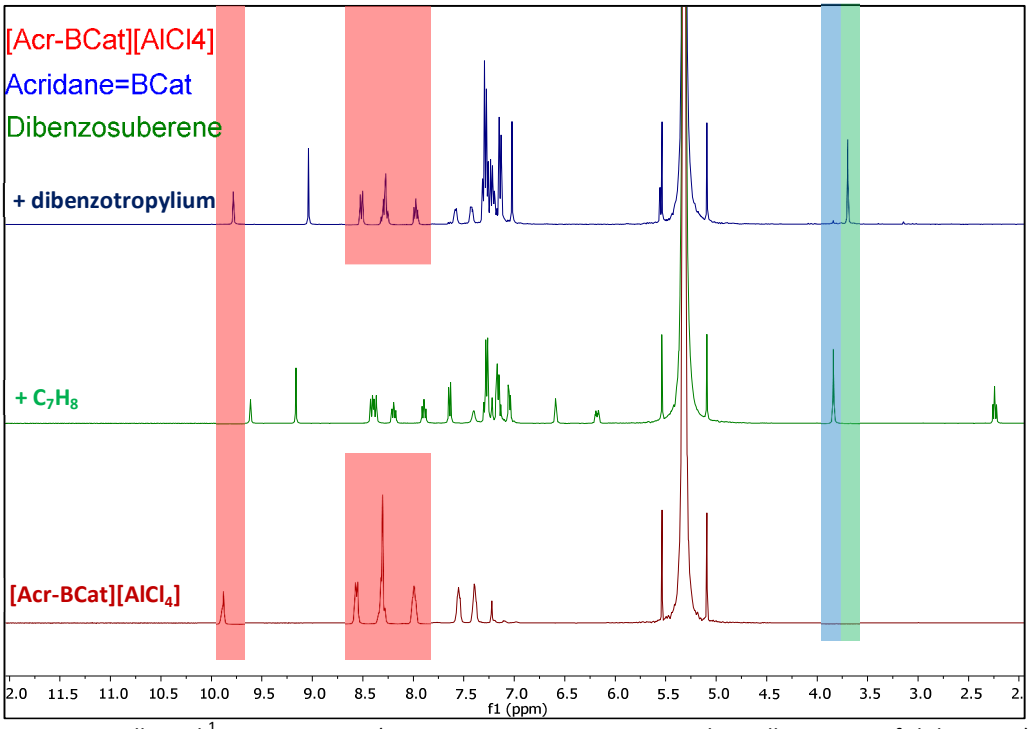

Figure S6: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with capillary insert of d_6-benzene) of: *in-situ* generated [Acr-BCat][$AlCl_4$] (bottom), the reaction after the addition of cycloheptatriene (middle) and the reaction after the addition of dibenzotropylium (top).

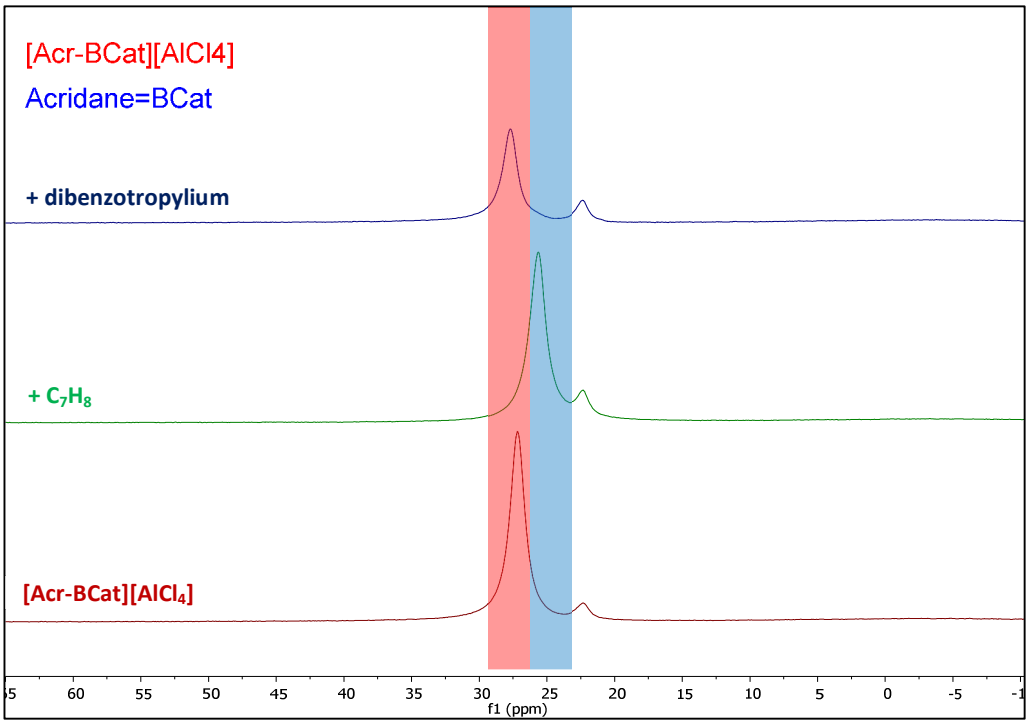

Figure S7: Collected $^{11}B\{^1H\}$ spectra (*protio*-DCM, 128.4 MHz, 298K) of: : *in-situ* generated [Acr-BCat][$AlCl_4$] (bottom), the reaction after the addition of cycloheptatriene (middle) and the reaction after the addition of dibenzotropylium (top)

3.5 Hydride abstraction from C_7H_8 with [Acr-BCat][$AlCl_4$] ([3][$AlCl_4$]), followed by hydride abstraction from (Acridane=BCat) with [Ph_3C][$BArF_{20}$]

In a glovebox an oven dried J. Youngs NMR tube equipped with a d_6-DMSO capillary insert was loaded with [Acr-BCatCl] (33.3 mg, 0.1 mmol) and $AlCl_3$ (13.3 mg, 0.1 mmol) followed by *protio*-DCM (0.8 mL). The reaction mixture was agitated for 5 minutes at ambient temperature leading to a bright yellow, homogeneous solution which was confirmed as the desired borocation, [Acr-BCat][$AlCl_4$] by ^1H, $^{11}B\{^1H\}$ and ^{27}Al NMR spectroscopy, respectively. Cycloheptatriene (10.4 µL, 0.1 mmol) was added to the *in-situ* generated [Acr-BCat][$AlCl_4$] under an inert atmosphere and the reaction mixture was agitated at ambient temperature for 30 minutes followed by analysis by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy, confirming hydride abstraction (*see Figure S8 – 2nd from top*). The addition of [Ph_3C][$BArF_{20}$] (33.0 mg, 0.1 mmol) in a glovebox led to the complete consumption of the acridane resonance (δ_H = 3.83 ppm) and the re-generation of the [Acr-BCat][X] species (δ_H C9 = 10.03 ppm, X = $AlCl_4$ or $BArF_{20}$) (*see Figure S8 – top*).

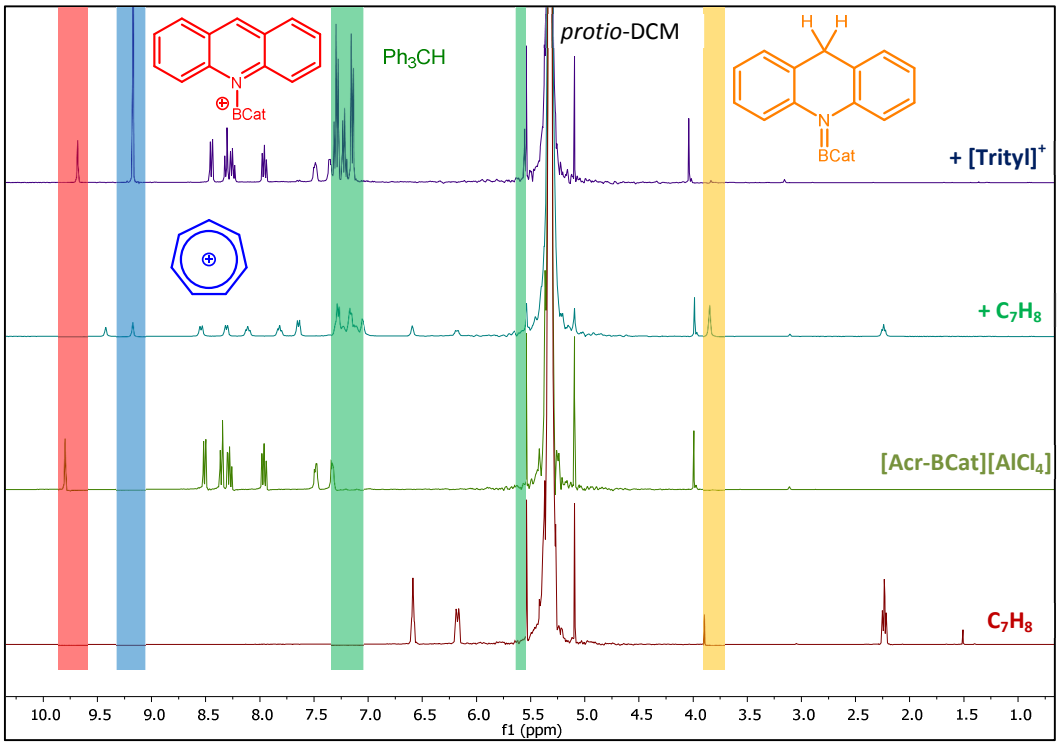

Figure S8: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with capillary insert of d_6-benzene) of: cycloheptatriene (bottom); [Acr-BCat][$AlCl_4$] (2nd from bottom); reaction mixture 30 minutes after the addition of cycloheptatriene at ambient temperature (2nd from top); reaction mixture 5 minutes after the addition of [Ph_3C][$BArF_{20}$] at ambient temperature (top).

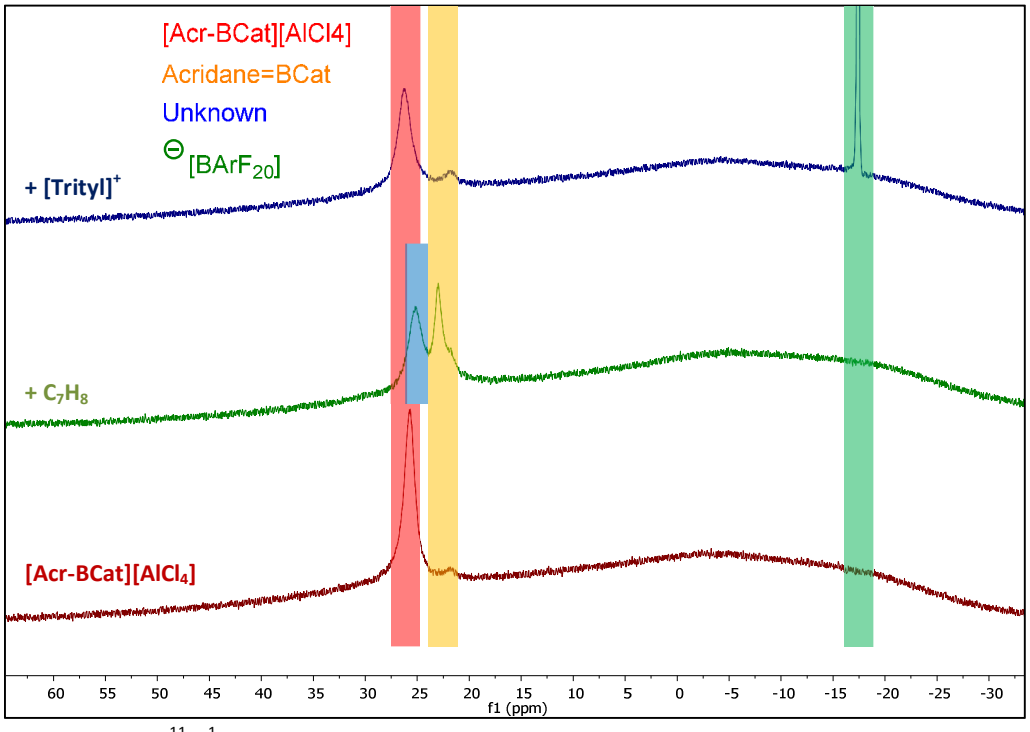

Figure S9: Collected $^{11}B\{^{1}H\}$ spectra (*protio*-DCM, 128.4 MHz, 298K) of: [Acr-BCat][$AlCl_4$] (bottom); reaction mixture 30 minutes after the addition of cycloheptatriene at ambient temperature (middle); reaction mixture 5 minutes after the addition of [Ph_3C][$BArF_{20}$] at ambient temperature (top).

3.6 Hydride abstraction from C_7H_8 with [Acr-BCl_2][$AlCl_4$] ([1][$AlCl_4$])

In a glovebox an oven dried J. Youngs NMR tube equipped with a wet d_6-DMSO capillary insert was loaded with [Acr-BCl_3] (29.6 mg, 0.1 mmol) and $AlCl_3$ (13.3 mg, 0.1 mmol) followed by *protio*-DCM (0.8 mL). The reaction mixture was agitated for 5 minutes at ambient temperature leading to a bright yellow, homogeneous solution. Cycloheptatriene (10.4 µL, 0.1 mmol) was added to the *in-situ* generated [Acr-BCl_2][$AlCl_4$] under an inert atmosphere followed by analysis by ^{1}H and ^{11}B{^{1}H} NMR spectroscopy which revealed the complete consumption of the [Acr-BCl_2][$AlCl_4$] C9 resonance (δ_H = 10.03 ppm) and the presence of the expected tropylium cation (δ_H = 9.27 ppm) in the ^{1}H NMR spectra (*see Figure S10)* Continued agitation of the reaction mixture for 16 h at ambient temperature afforded no further change. The ^{11}B{^{1}H} NMR spectra demonstrated the complete consumption of [Acr-BCl_2][$AlCl_4$] (δ_B = 48.5 ppm) with the generation of the scrambling products [Acr-BCl(Acridane)][$AlCl_4$] (δ_B = 32.1 ppm) and BCl_3 (δ_B = 45.8 ppm) (*Figure S11*).

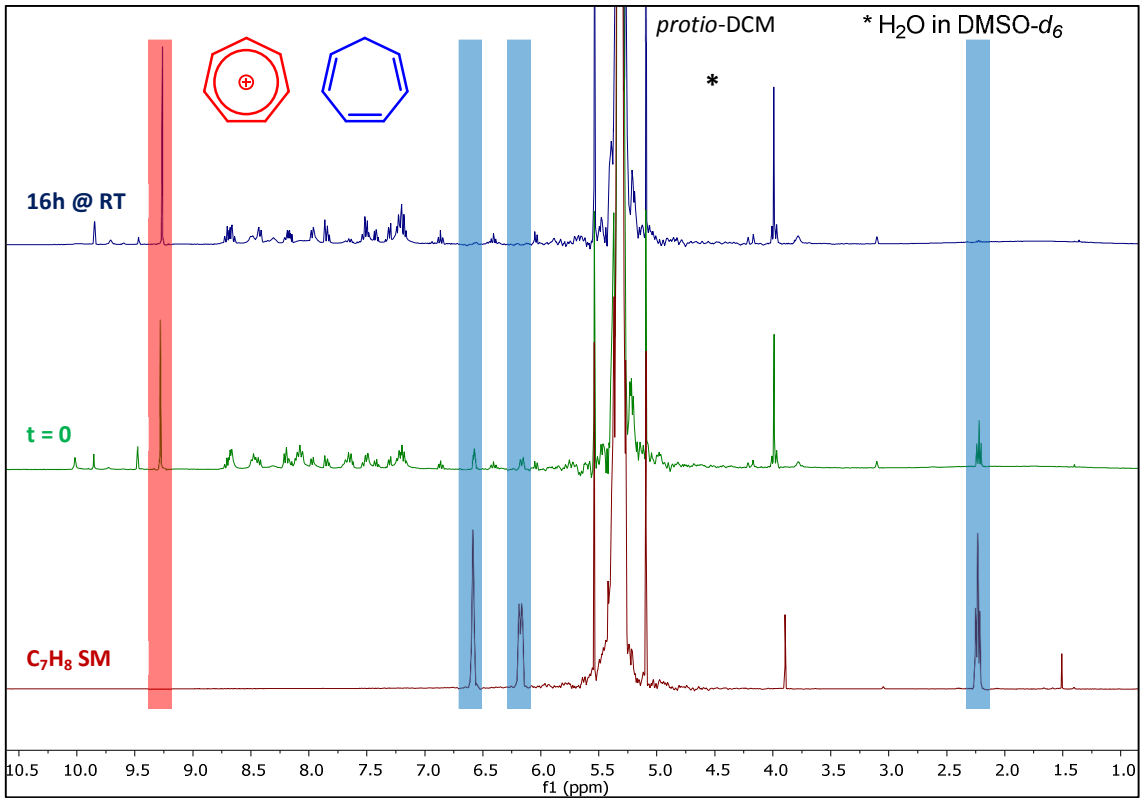

Figure S10: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert of wet DMSO-d_6) of cycloheptatriene (bottom); the reaction mixture after 5 minutes at ambient temperature (middle); and the reaction mixture after 16 h at ambient temperature (top).

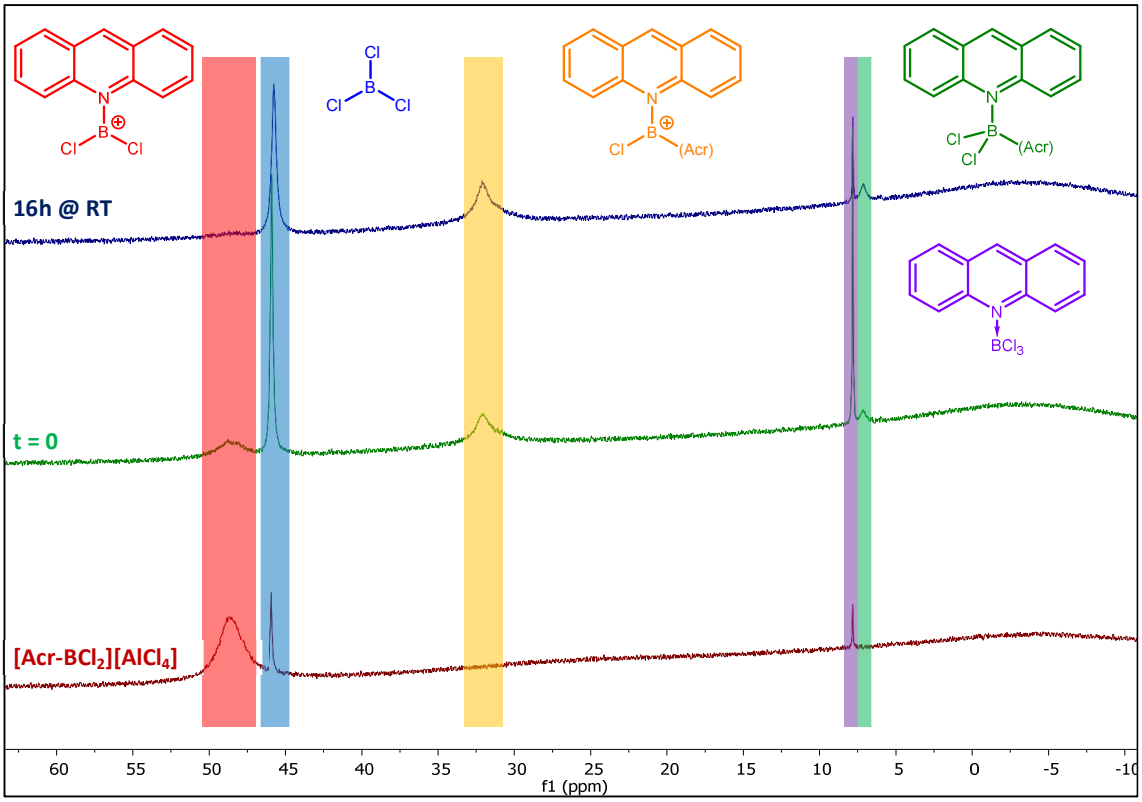

Figure S11: Collected $^{11}B\{^{1}H\}$ spectra (*protio*-DCM, 128.4 MHz, 298K) of: *in-situ* generated [Acr-BCl_2][$AlCl_4$] (bottom); the reaction mixture after 5 minutes at ambient temperature (middle); and the reaction mixture after 16 h at ambient temperature (top). The broad resonance at 7.1 ppm is tentatively assigned as the boronium cation [Acr_2BCl_2][$AlCl_4$], and the sharper resonance at 7.8 ppm is $AcrBCl_3$.

3.7 Hydride abstraction from dibenzosuberene with [Acr-BCl_2][$AlCl_4$] ([1][$AlCl_4$])

In a glovebox a J. Young's NMR tube equipped with a d6-benzene capillary was loaded with acridine-BCl_3 (22 mg, 0.075 mmol) and $AlCl_3$ (10 mg, 0.075 mmol), followed by the addition of *protio*-DCM (0.7 mL). After 5 minutes of sonication the mixture yielded a clear yellow solution. Dibenzosuberene was added to the tube, and upon mixing the solution turned red. Analysis of the mixture by multinuclear NMR spectroscopic experiments revealed that no major reaction had occurred. The sample was set to mix at room temperature for 17 hours, after which time further NMR spectroscopic analysis showed that no hydride abstraction from dibenzosuberene had occurred, but degradation of the starting borocation had started. The reaction was subsequently heated at 60 °C for 5 hours, after which time the formation of acridane signals was observed by 1H NMR spectroscopy in conjunction with decomposition products.

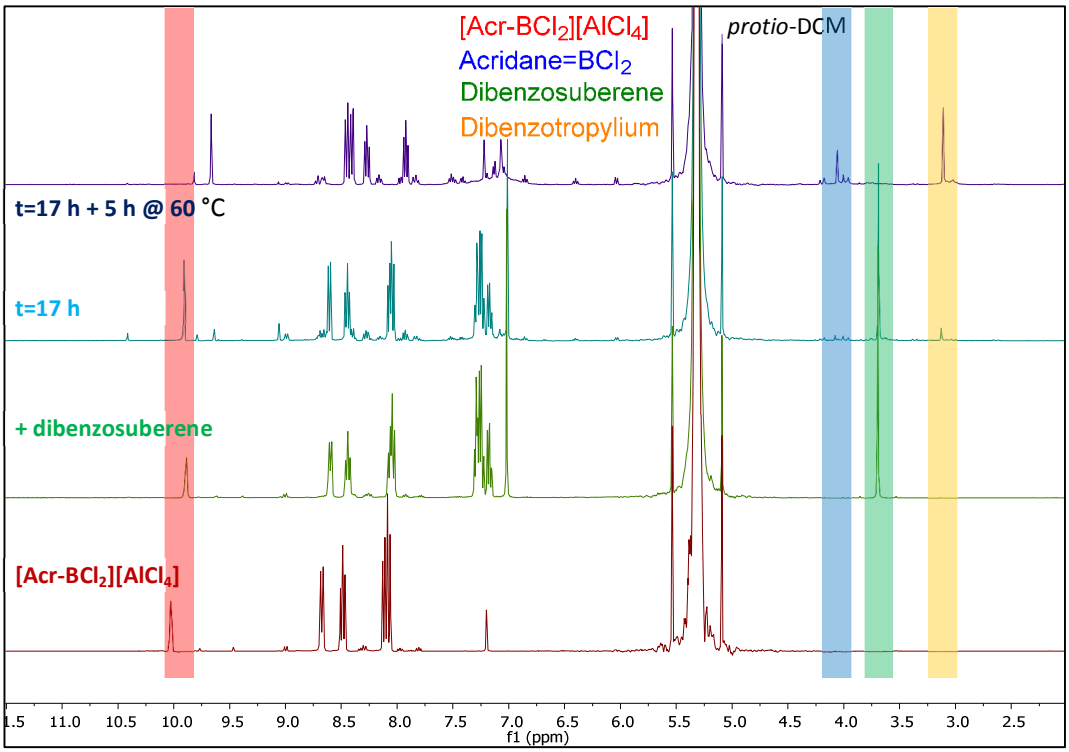

Figure S12: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert containing d_6-benzene) of: *in-situ* generated [Acr-BCl_2][$AlCl_4$] (bottom); reaction mixture after 5 minutes at ambient temperature (2nd from bottom); the reaction mixture after 17 h at room temperature (2nd from top); and the reaction after heating at 60 °C for 5 hours.

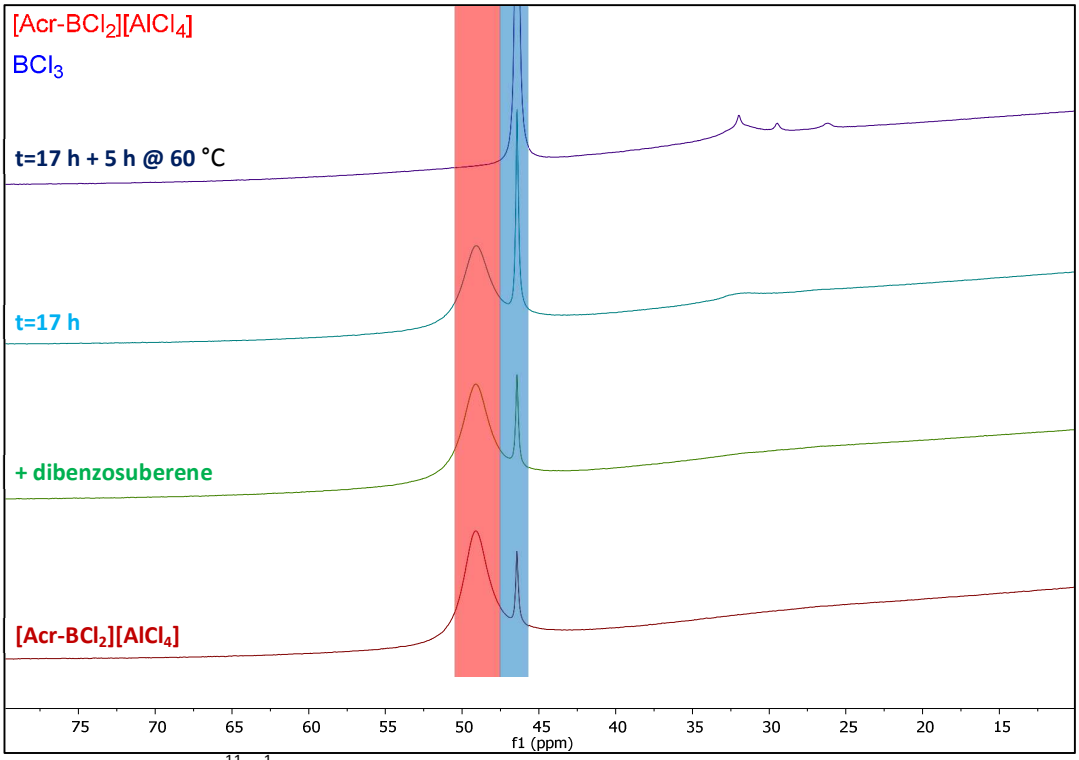

Figure S13: Collected ^{11}B{^{1}H} NMR spectra (*protio*-DCM, 128 MHz, 298K) of: *in-situ* generated [Acr-BCl_2][$AlCl_4$] (bottom); reaction mixture after 5 minutes at ambient temperature (2nd from bottom); the reaction mixture after 17 h at room temperature (2nd from top); and the reaction after heating at 60 °C for 5 hours

3.8 Attempted hydride abstraction from triphenylmethane with [Acr-BCl_2][$AlCl_4$] ([1][$AlCl_4$])

In a glovebox an oven dried J. Youngs NMR tube equipped with a wet d_6-DMSO capillary insert was loaded with [Acr-BCl_3] (29.6 mg, 0.1 mmol) and $AlCl_3$ (13.3 mg, 0.1 mmol) followed by *protio*-DCM (0.8 mL). The reaction mixture was agitated for 5 minutes at ambient temperature leading to a bright yellow, homogeneous solution. Triphenylmethane (24.4 mg, 0.1 mmol) was added to the *in-situ* generated [Acr-BCl_2][$AlCl_4$] under an inert atmosphere and analysis of the reaction mixture after 5 minutes at ambient temperature by ^{1}H and $^{11}B\{^{1}H\}$ NMR spectroscopy (*see Figure S14 and Figure S15, respectively*) demonstrated the persistence of the [Acr-BCl_2][$AlCl_4$] C9 resonance (δ_H = 10.03 ppm) and the [Acr-BCl_2][$AlCl_4$] resonance in the $^{11}B\{^{1}H\}$ NMR (δ_B = 48.5 ppm), indicative of no hydride abstraction. Heating the reaction mixture to 60 °C for a further 16 h led to no observable hydride abstraction (*see Figure S14 - top*). The $^{11}B\{^{1}H\}$ NMR demonstrates the persistence of [Acr-BCl_2][$AlCl_4$] (δ_B = 48.5 ppm) (*see Figure S15 - top*), as well as a degree of redistribution occurring between [Acr-BCl_2]$^+$, Acr-BCl_3, and BCl_3.

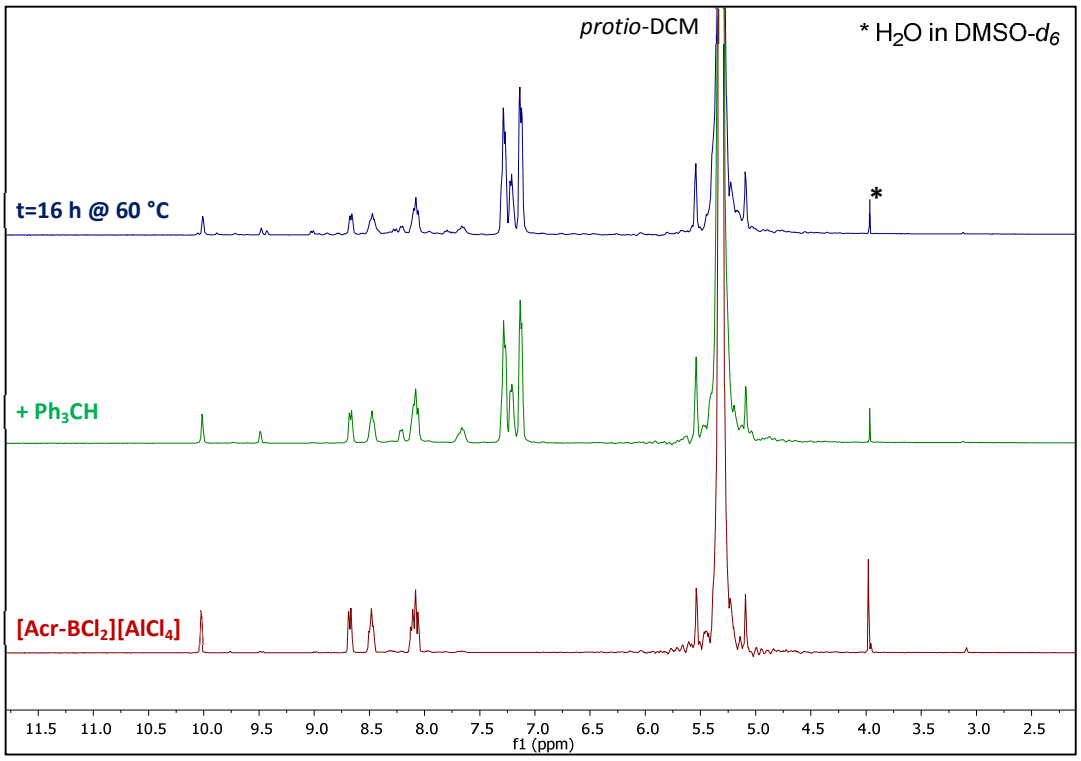

Figure S14: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert containing wet DMSO-d_6) of: *in-situ* generated [Acr-BCl_2][$AlCl_4$] (bottom); reaction mixture after 5 minutes at ambient temperature (middle); and the reaction mixture after 16 h at 60°C (top).

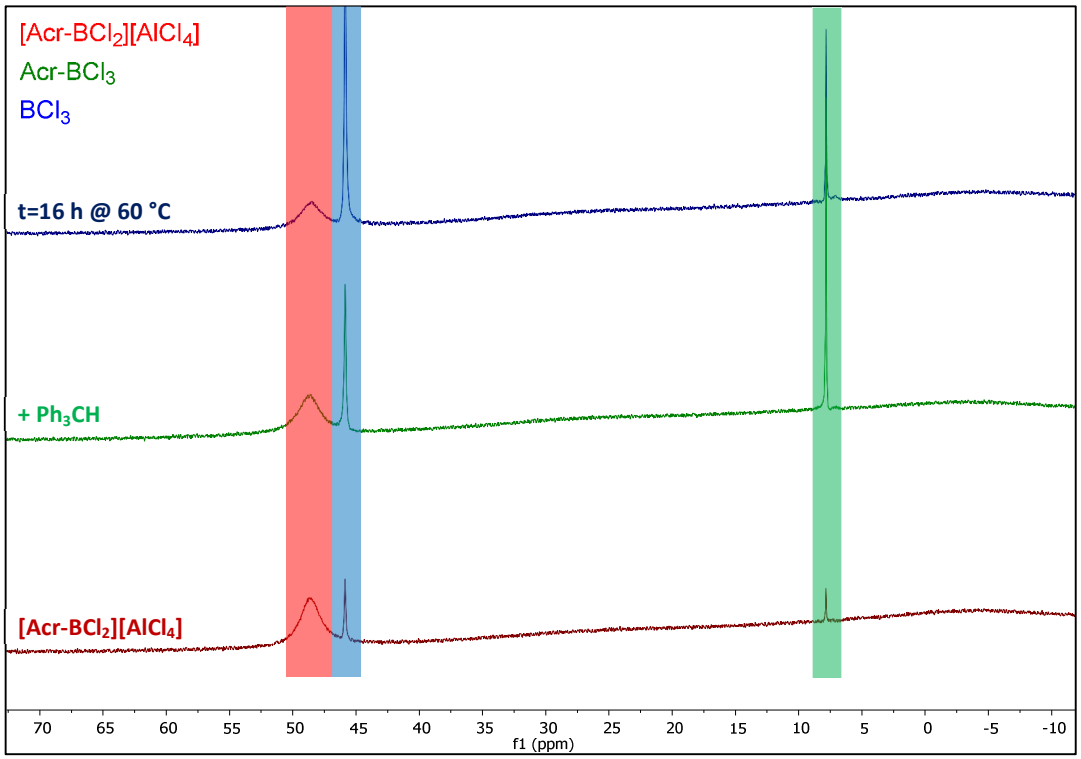

Figure S15: Collected $^{11}B\{^{1}H\}$ NMR spectra (*protio*-DCM, 128 MHz, 298K) of: *in-situ* generated [Acr-BCl_2][$AlCl_4$] (bottom); reaction mixture after 5 minutes at ambient temperature (middle); and the reaction mixture after 16 h at 60°C (top).

3.9 Hydride abstraction from C_7H_8 with [F_5Acr-BCat][$AlCl_4$] ([**5**][$AlCl_4$])

In a glovebox an oven dried J. Youngs NMR tube equipped with a d_6-DMSO capillary insert was loaded with F_5-Acridine (26.9 mg, 0.1 mmol), CatBCl (15.4 mg, 0.1 mmol) and *protio*-DCM (0.8 mL). The reaction mixture was agitated at ambient temperature for 5 minutes to afford a homogeneous yellow solution (no sign of Lewis adduct formation by $^{11}B\{^{1}H\}$ NMR spectroscopy). $AlCl_3$ (13.3 mg, 0.1 mmol) was subsequently added to the reaction mixture and sample agitated for a further 5 minutes at ambient temperature. Generation of the desired borocation, [F_5-Acr-BCat][$AlCl_4$] ([**5**][$AlCl_4$]) was confirmed by ^{1}H, $^{11}B\{^{1}H\}$ and ^{27}Al NMR spectroscopy, respectively. Cycloheptatriene (10.4 µL, 0.1 mmol) was added to the *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] under an inert atmosphere and the reaction mixture was agitated at ambient temperature for 10 minutes followed by analysis by ^{1}H and $^{11}B\{^{1}H\}$ NMR spectroscopy (*see Figure S16 - bottom*). The ^{1}H NMR spectra demonstrated the complete consumption of the [F_5-Acr-BCat][$AlCl_4$] C9 resonance (δ_H = 10.18 ppm) and cycloheptatriene (δ_H CH_2 = 2.22 ppm) with the corresponding generation of the acridane species [F_5-Acridane=BCat] (δ_H C9 = 3.09 ppm) and the tropylium cation (X = $AlCl_4$) (δ_H = 9.26 ppm) (*see Figure S16– top*). The $^{11}B\{^{1}H\}$ NMR spectra clearly demonstrates the consumption of the [F_5-Acr-BCat][$AlCl_4$] resonance (δ_B = 28.1 ppm) and the generation of the corresponding acridane=BCat species (δ_B = 24.7 ppm) (*see Figure S17 – top*).

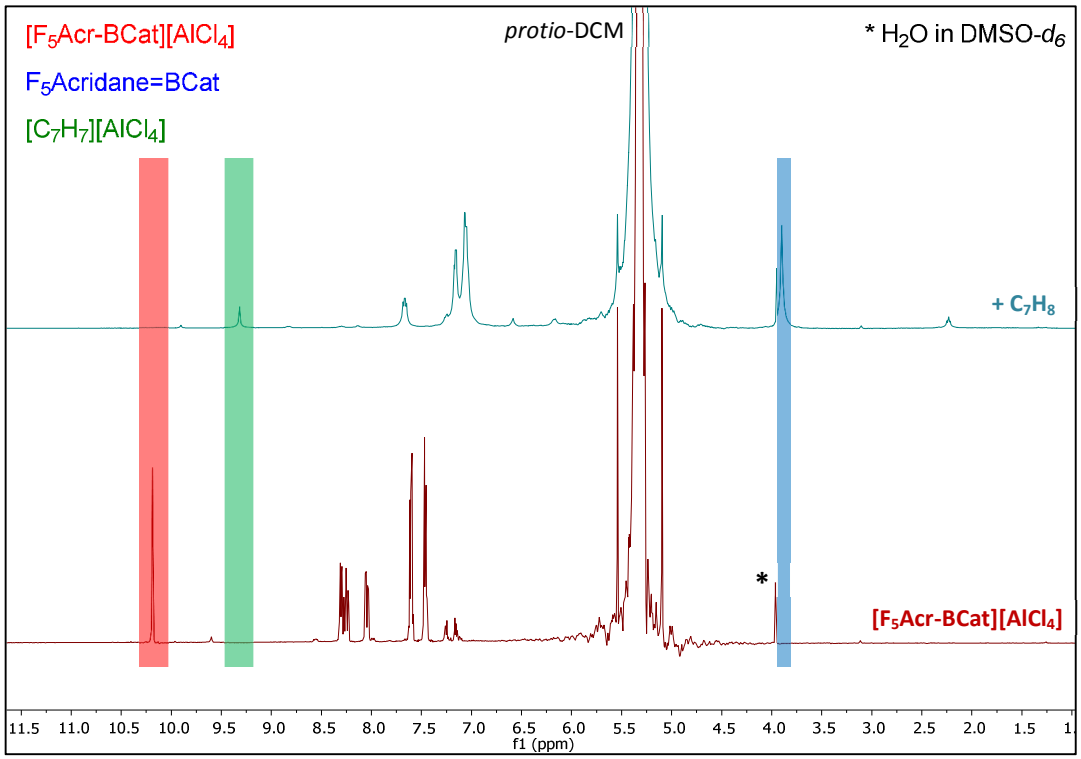

Figure S16: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert of d_6-DMSO) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 10 minutes after the addition of cycloheptatriene at room temperature (top).

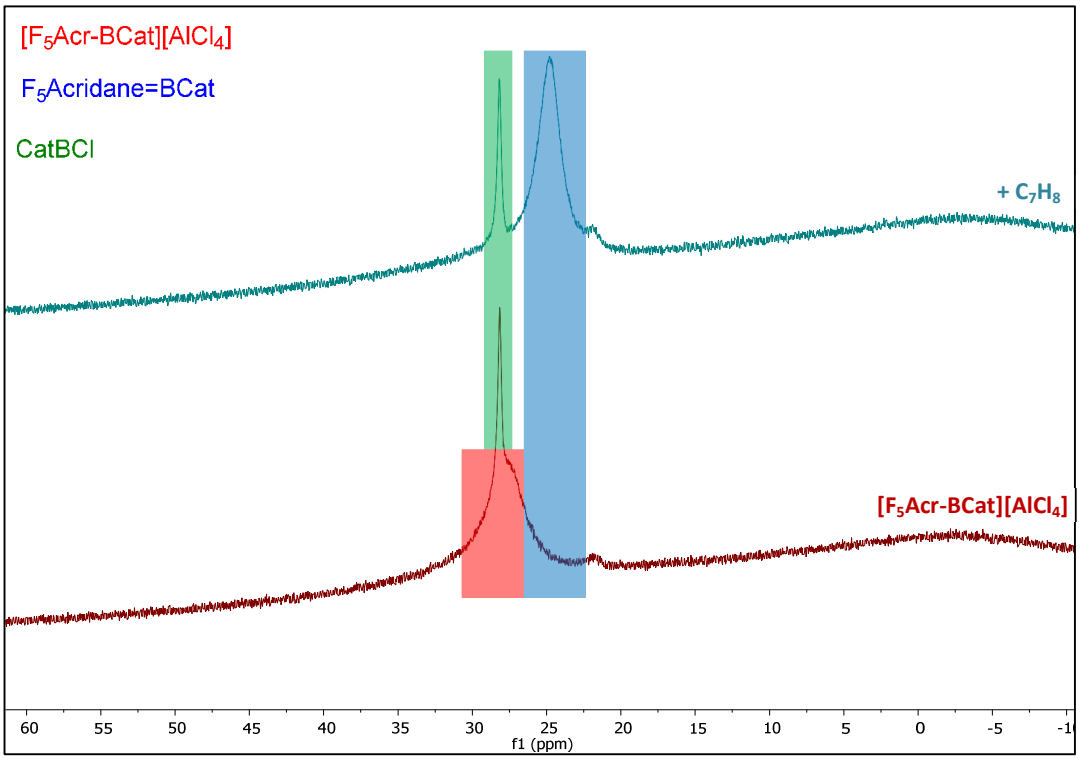

Figure S17: Collected $^{11}B\{^{1}H\}$ spectra (*protio*-DCM, 128.4 MHz, 298K) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 10 minutes after the addition of cycloheptatriene at room temperature (top). A minor impurity of CatBCl is present throughout.

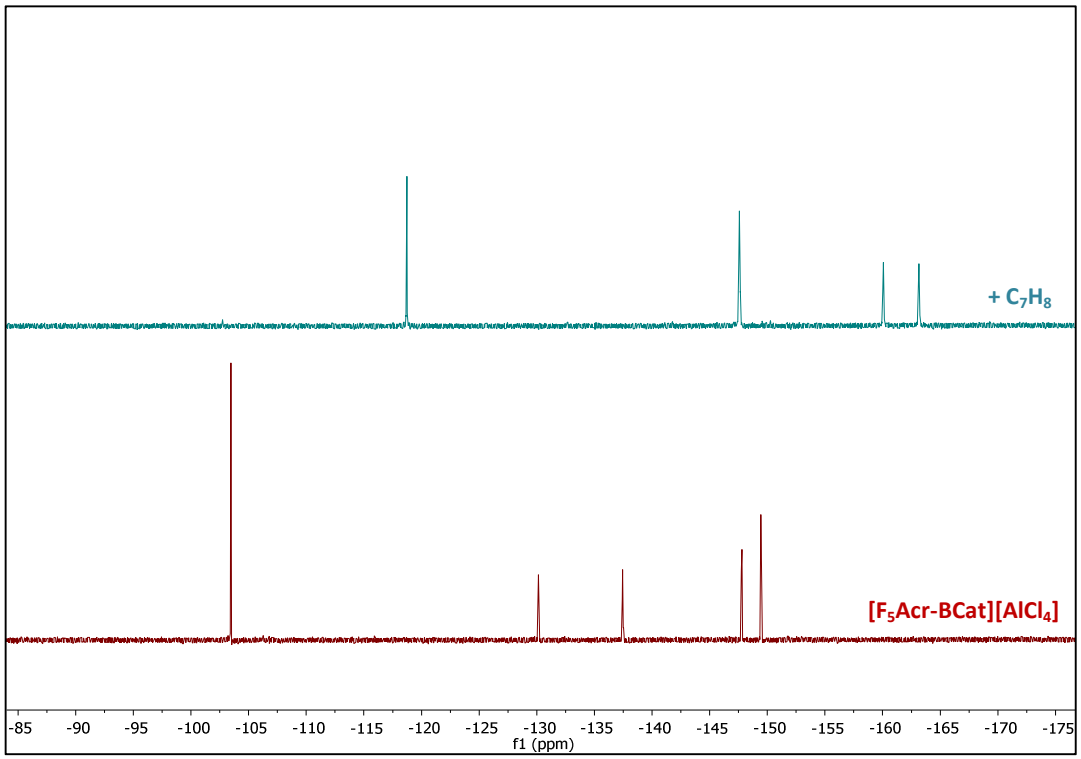

Figure S18: Collected $^{19}F\{^{1}H\}$ spectra (*protio*-DCM, 376 MHz, 298K) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 10 minutes after the addition of cycloheptatriene at ambient temperature (top).

3.10 Hydride abstraction from dibenzosuberene with [F_5Acr-BCat][$AlCl_4$] ([5][$AlCl_4$])

A J. Young's NMR tube was equipped with a benzene-d_6 filled capillary, and charged with F_5-acridine (20.2 mg, 0.075 mmol) before drying under vacuum. The F_5-acridine was dissolved in DCM (0.5 mL), before CatBCl (11.6 mg, 0.075 mmol) and $AlCl_3$ (10.0 mg, 0.075 mmol) were added. The sample was agitated for 5 minutes before the generation of the desired borocation was confirmed by NMR spectroscopic analysis. Dibenzosuberene (14.4 mg, 0.075 mmol) was subsequently added which caused and instant colour change to red. ^{1}H NMR spectroscopy confirmed partial conversion of dibenzosuberene to dibenzotropylium had occurred (*see Figure S19, middle*). The sample was set to mix at room temperature for 16 hours, after which time NMR spectroscopic analysis demonstrated further dibenzosuberene conversion, but still the presence of the borocation and dibenzosuberene starting materials (*see Figure S19 – 2nd from top*). As a result, the sample was left to mix at room temperature for a further 72 hours. Final analysis by ^{1}H, $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$, NMR spectroscopy confirmed the complete consumption of dibenzosuberene (*see Figure S19 – top*), but also the partial decomposition of the F_5Acridane=BCat product. One of these decomposition products is assumed to be [F_5-Acridinium]$^+$, based upon the presence of a resonance in the ^{1}H NMR spectrum at δ_H = 13.47 ppm, indicative of a highly acidic proton, N^+-*H*.

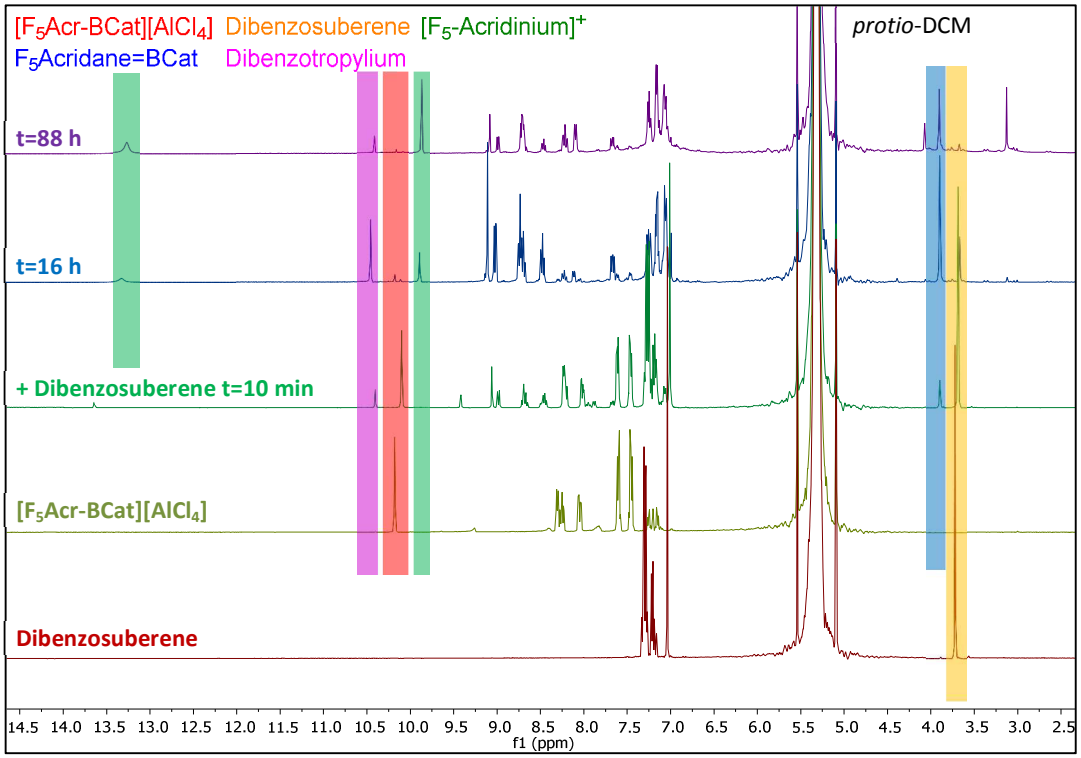

Figure S19: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K with a capillary insert of d_6-benzene) of: dibenzosuberene (bottom); *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (2nd from bottom); the reaction mixture 10 minutes after the addition of dibenzosuberene at room temperature (middle); the reaction mixture after 16 h (2nd from top); the reaction mixture after 88h (top).

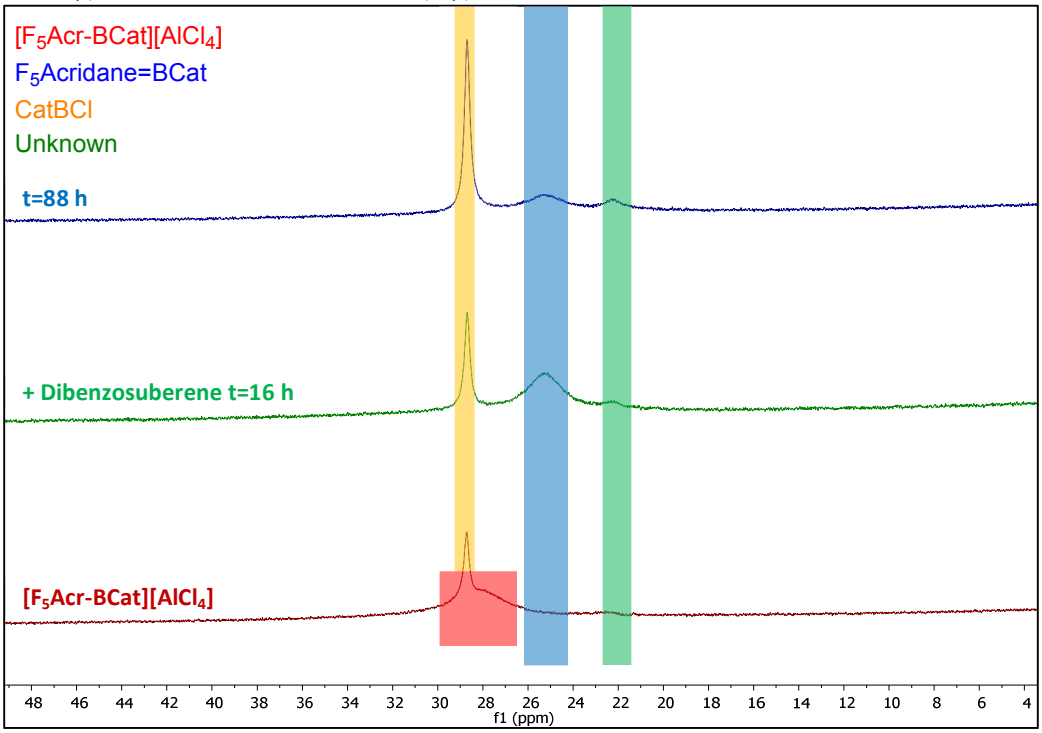

Figure S20: Collected ^{11}B{^{1}H} NMR spectra (*protio*-DCM, 128 MHz, 298K) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 16 hours after the addition of dibenzosuberene at room temperature (middle); the reaction mixture after 88h (top). The unknowns in this case are attributed to formation of CatBOR and protonated F_5-acridinium.

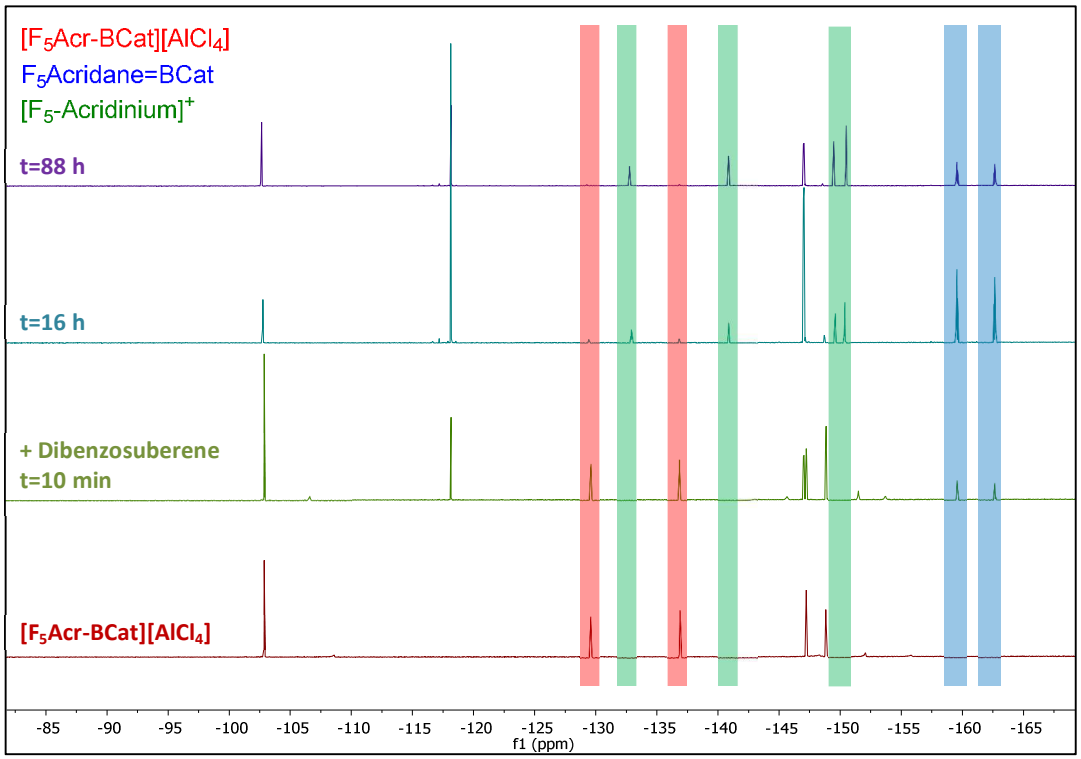

Figure S21: Collected $^{19}F\{^{1}H\}$ NMR spectra (*protio*-DCM, 376 MHz, 298K) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 10 minutes after addition of dibenzosuberene (2nd from bottom) the reaction mixture 16 hours (2nd from top); the reaction mixture after 88 hours (top).

3.11 Attempted hydride abstraction from triphenylmethane with [F_5Acr-BCat][$AlCl_4$] ([5][$AlCl_4$])

A J. Young's NMR tube was equipped with a benzene-d_6 filled capillary and loaded with F_5-acridine (20.2 mg, 0.075 mmol) which was dried under vacuum. The sample was dissolved in *o*-DCB (0.5 mL) followed by the addition of CatBCl (11.6 mg, 0.075 mmol) and $AlCl_3$ (10.0 mg, 0.075 mmol). The reaction resulted in a homogenous orange solution, and the formation of the desired borocation was confirmed by NMR spectroscopic analysis. Triphenylmethane (18.33 mg, 0.075 mmol) was subsequently added and analysis by NMR spectroscopy showed no reaction had occurred. The solution was then heated at 100 °C for 16 hours, after which time further NMR spectroscopic analysis revealed the formation of 10 % F_5Acridane=BCat (δ_H 3.88 ppm), and a degree of borocation decomposition. The reaction was heated for a further 72 hours at 100 °C before NMR spectroscopic experiments showed that no further hydride abstraction had occurred, and any remaining borocation had decomposed (*see Figure S22 – top*). The reaction was repeated, yielding the same degree of hydride abstraction, confirming that an equilibrium between [F_5Acr-BCat]$^+$/triphenylmethane had been reached. The decomposition on prolonged heating appears to be forming protonated F_5-acridinium and a CatBOR species, presumably from scavenging trace protic species.

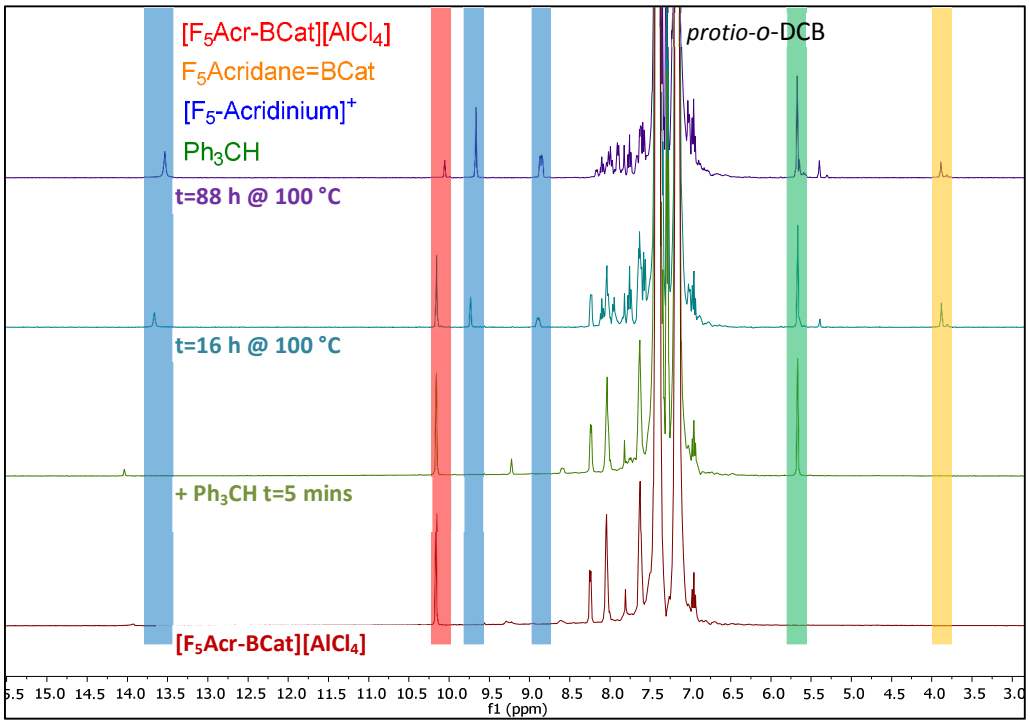

Figure S22: Collected ^{1}H NMR spectra (*protio-o*-DCB, 400 MHz, 298K with a capillary insert of benzene-d_6) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 5 minutes after addition of triphenylmethane (2nd from bottom); the reaction mixture after heating at 100 °C for 16 hours (2nd from top); the reaction mixture after heating at 100 °C for 88 hours (top).

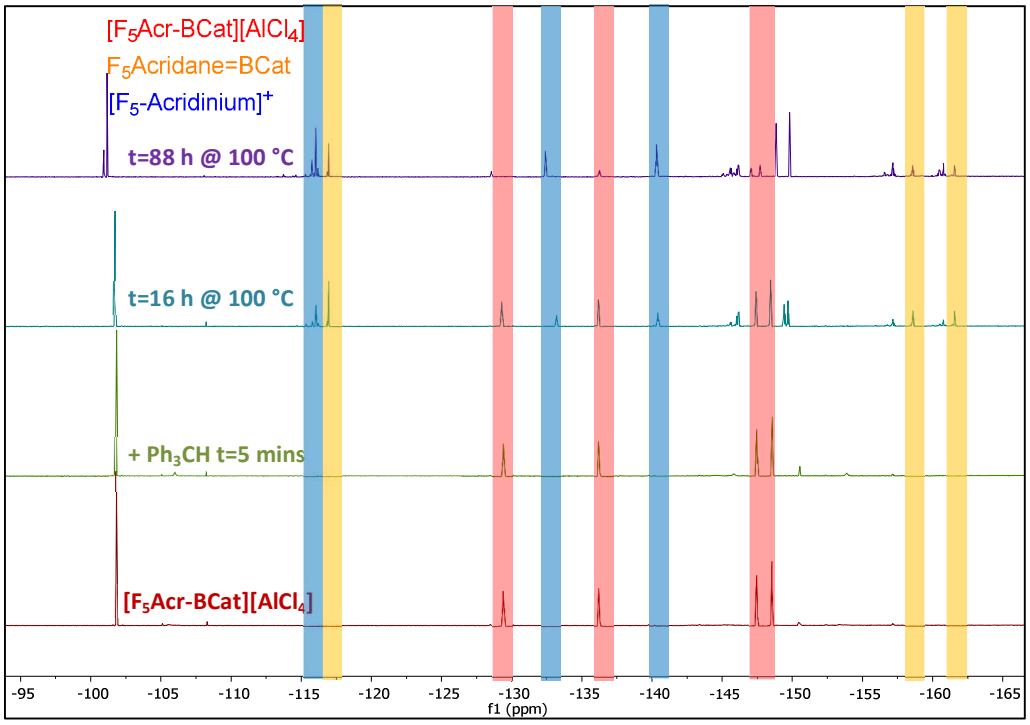

Figure S23: Collected $^{19}F\{^{1}H\}$ NMR spectra (*protio-o*-DCB, 376 MHz, 298K) of: *in-situ* generated [F_5-Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 5 minutes after addition of triphenylmethane (2nd from bottom); the reaction mixture after heating at 100 °C for 16 hours (2nd from top); the reaction mixture after heating at 100 °C for 88 hours (top).

3.12 Hydride abstraction from F_5Acridane=BCat with [Trityl][$BArF_{20}$]

A J. Young's NMR tube was equipped with a benzene-d_6 filled capillary and loaded with F_5-acridine (20.2 mg, 0.075 mmol) which was dried under vacuum. The sample was dissolved in *o*-DCB (0.5 mL) followed by the addition of CatBCl (11.6 mg, 0.075 mmol) and K[$BArF_{20}$] (10.0 mg, 0.075 mmol) at which point a solid precipitated out, assumed to be KCl. The formation of the desired borocation was confirmed by NMR spectroscopic analysis. Cycloheptatriene (7.8 µL, 0.075 mmol) was added to the tube, and the tube was set to mix. After 5 hours ^{1}H NMR spectroscopic analysis exhibited signals corresponding to unreacted cycloheptatriene. The reaction was mixed for a further 16 hours, and further NMR spectroscopic analysis demonstrated the complete consumption of cycloheptatriene, and formation of F_5Acridane=BCat (*see Figure S24 – 3rd from bottom*). Subsequently, [Trityl][$BArF_{20}$] was added causing an instant colour change of the solution from orange to red. NMR spectroscopy demonstrated a small amount of triphenylmethane formation after 10 minutes of agitating the reaction tube. The reaction mixture was mixed for a further 4 hours at room temperature, after which time no further triphenylmethane formation was seen, and so the reaction was set to heat at 100 °C for 16 hours. After this heating, analysis by NMR spectroscopy revealed the formation of predominantly triphenylmethane, significant consumption of F_5Acridane=BCat (86 % hydride abstraction, 14 % unreacted F_5Acridane=BCat), reformation of [F_5Acr-BCat][$BArF_{20}$] and a small amount of borocation decomposition. In an attempt to achieve complete conversion of F_5Acridane=BCat to [F_5Acr-BCat][$BArF_{20}$], the reaction was heated at 100 °C for a further 24 hours. Surprisingly no further reaction was observed by NMR spectroscopic analysis, suggesting that the reaction had reached an equilibrium point.

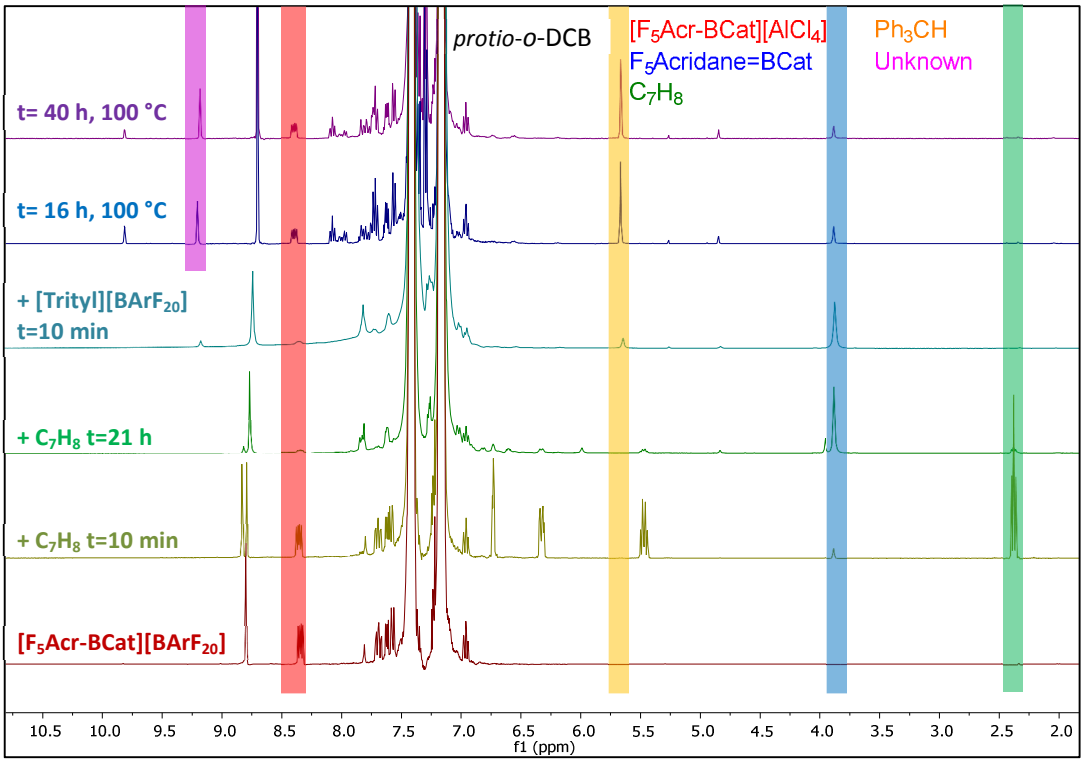

Figure S24: Collected ^{1}H NMR spectra (*protio-o*-DCB, 400 MHz, 298K with a capillary insert containing benzene-d_6) of: *in situ* generated [F_5Acr-BCat][$BArF_{20}$] (bottom); the reaction mixture 10 minutes after addition of C_7H_8 (2nd from bottom); the reaction mixture 21 hours after addition of C_7H_8 (3rd from bottom); the reaction mixture 10 minutes after the addition of [Trityl][$BArF_{20}$] (3rd from top); the reaction mixture after heating at 100 °C for 16 hours (2nd from top); the reaction mixture after heating at 100 °C for 40 hours (top).

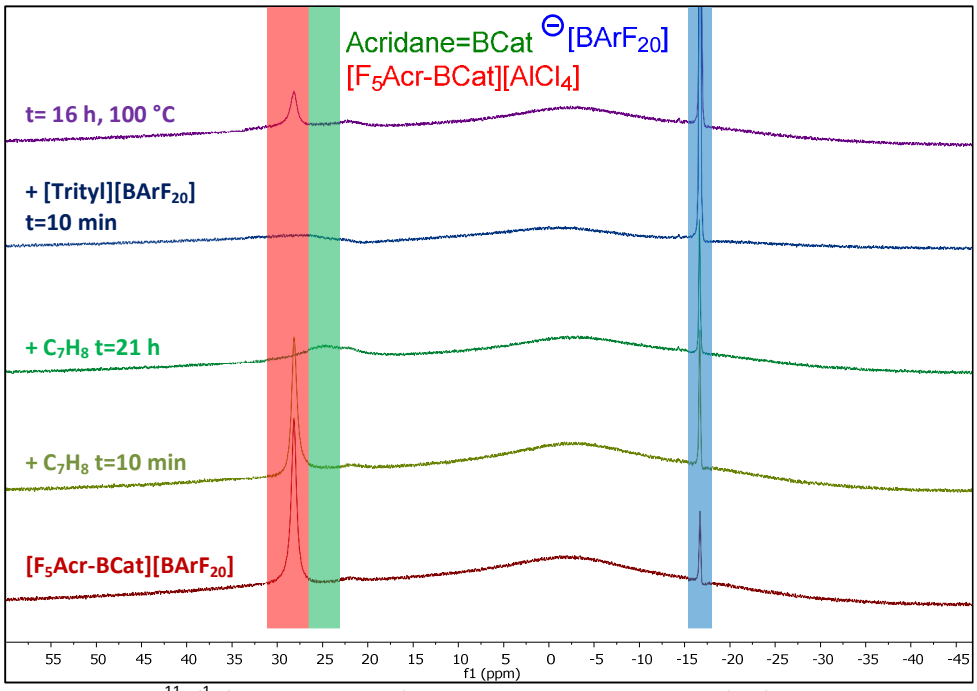

Figure S25: Collected $^{11}B\{^1H\}$ NMR spectra (*protio-o*-DCB, 128 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$BArF_{20}$] (bottom); the reaction mixture 10 minutes after addition of C_7H_8 (2nd from bottom); the reaction mixture 21 hours after addition of C_7H_8 (middle); the reaction mixture 10 minutes after the addition of [Trityl][$BArF_{20}$] (2nd from top); the reaction mixture after heating at 100 °C for 16 hours (top).

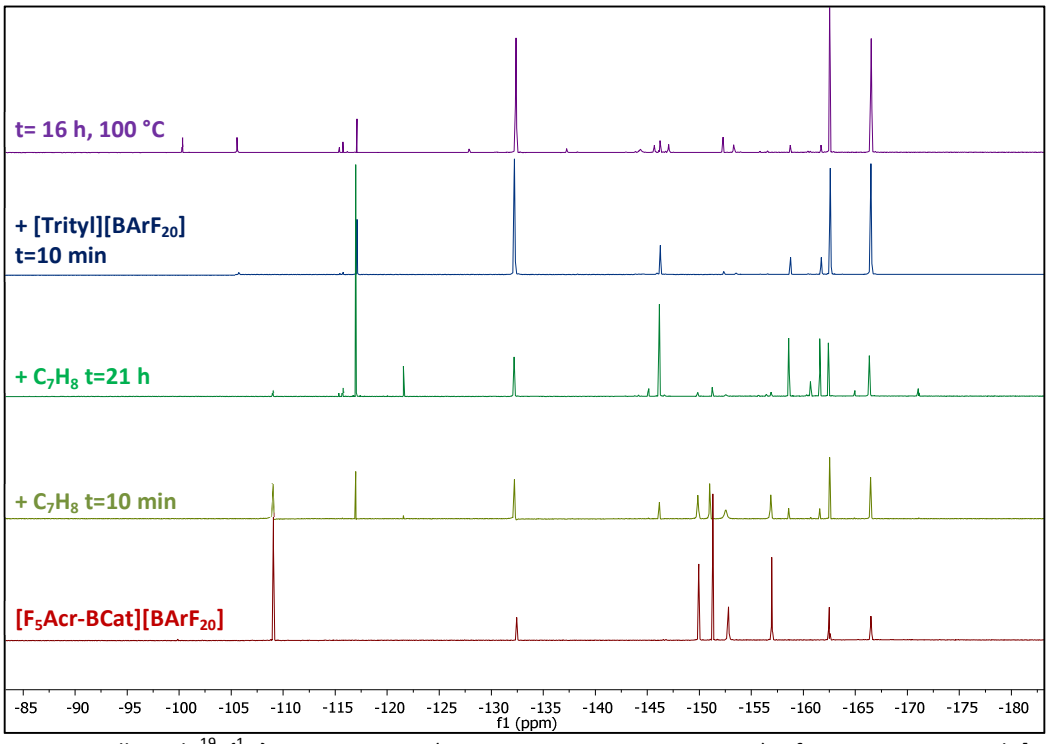

Figure S26: Collected $^{19}F\{^1H\}$ NMR spectra (*protio-o*-DCB, 376 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$BArF_{20}$] (bottom); the reaction mixture 10 minutes after addition of C_7H_8 (2nd from bottom); the reaction mixture 21 hours after addition of C_7H_8 (middle); the reaction mixture 10 minutes after the addition of [Trityl][$BArF_{20}$] (2nd from top); the reaction mixture after heating at 100 °C for 16 hours (top).

3.13 Hydride abstraction from triphenylmethane with $[F_5Acr\text{-}BCl_2][AlCl_4]$ ($[4][AlCl_4]$)

A J Young's NMR tube was loaded with F_5-acridine (20.2 mg, 0.075 mmol) and dried under vacuum. DCM-d_2 (0.5 mL) was added, followed by BCl_3 (75 µL 1M solution in DCM, 0.075 mmol) which caused an instant colour change to yellow. The sample was taken into a glovebox and $AlCl_3$ (10.0 mg, 0.075 mmol) was added to the mixture, before analysis by NMR spectroscopy confirmed formation of the desired borocation had occurred (as judged by the formation of a broad resonance at δ_B 47.2 ppm), along with the presence of $F_5Acr\text{-}AlCl_3$. The reaction mixture was then loaded with triphenylmethane (18.3 mg, 0.075 mmol), and subsequent NMR spectroscopic analysis revealed that no instantaneous reaction had occurred. The reaction mixture was then set to mix for 20 hours, after which time the yellow reaction mixture had turned brown. Further NMR spectroscopic experiments demonstrated the complete loss of $[F_5Acr\text{-}BCl_2][AlCl_4]$, along with the formation of $[F_5AcridiniumH]^+$ and a trace of F_5-acridane=BCl_2. The reaction was set to mix for a further 20 hours, after which time acridane formation was observed by ^1H NMR spectroscopy (δ_H 3.97 ppm), indicative of successful hydride abstraction from triphenylmethane. After mixing for another 24 hours no change in the NMR spectra measured was seen.

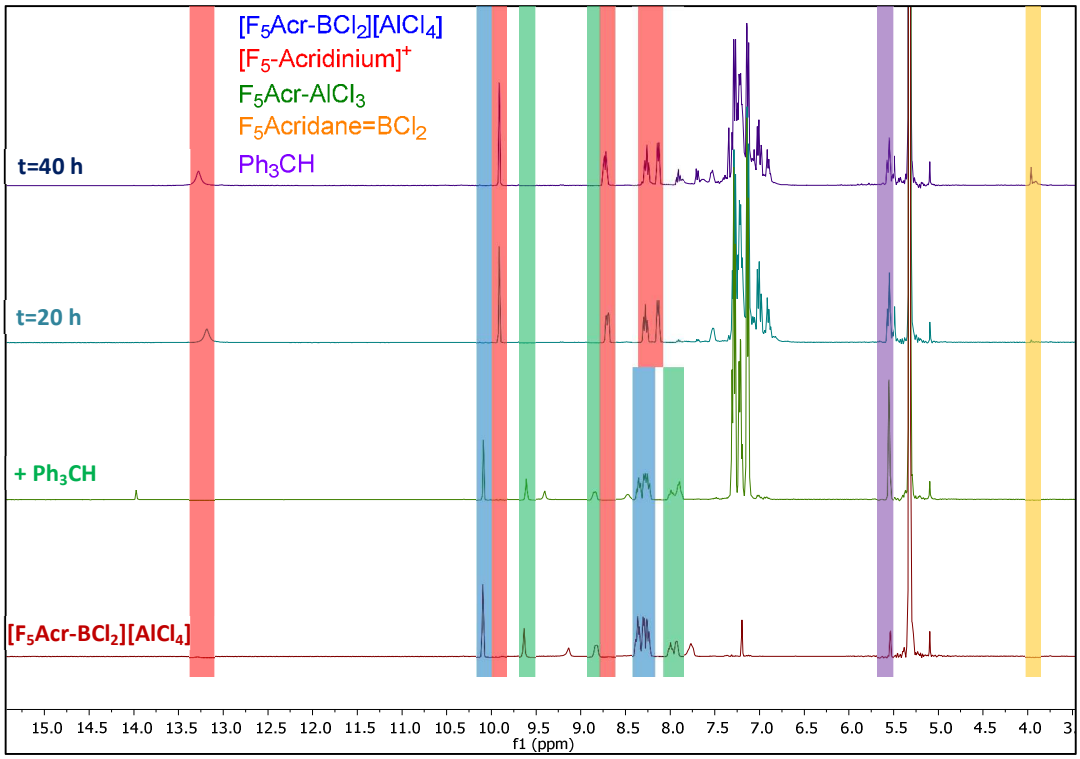

Figure S27: Collected ^1H NMR spectra (DCM-d_2, 400 MHz, 298K) of: a mixture of *in situ* generated $[F_5Acr\text{-}BCl_2][AlCl_4]$ and F_5-acridine-$AlCl_3$ (bottom); the reaction mixture 5 minutes after the addition of triphenylmethane (2nd from bottom); the reaction mixture after mixing for 20 hours (2nd from top); the reaction mixture after mixing for 40 hours (top).

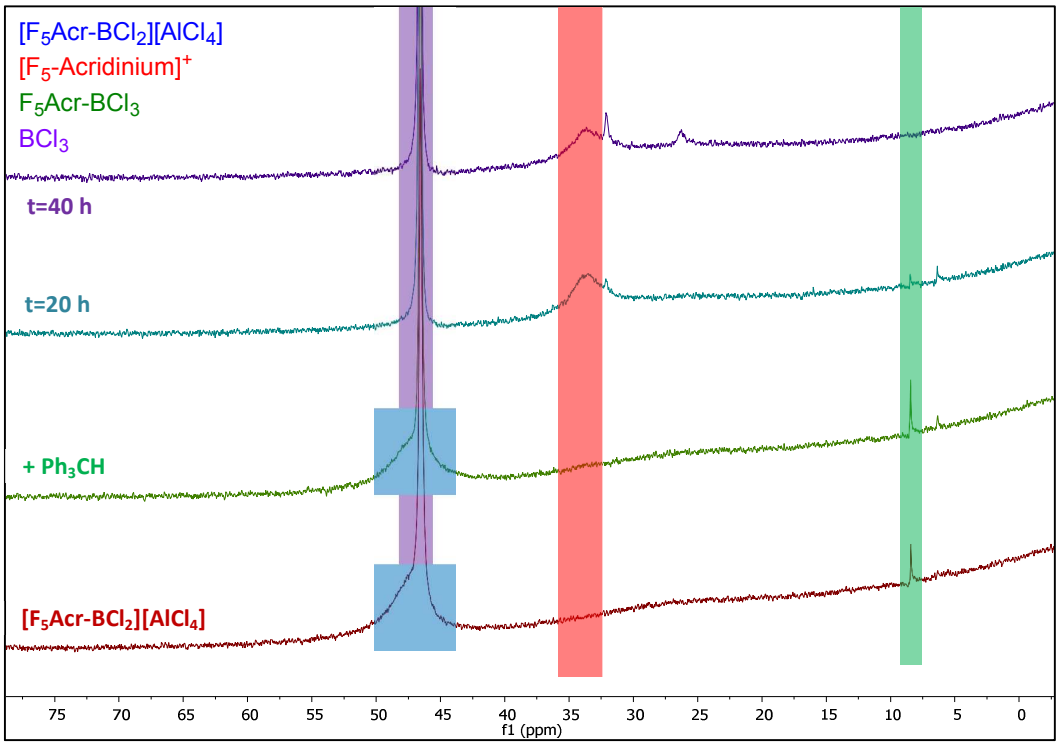

Figure S28: Collected $^{11}B\{^{1}H\}$ NMR spectra (DCM-d_2, 128 MHz, 298K) of: a mixture of *in situ* generated [F_5Acr-BCl_2][$AlCl_4$] and F_5-acridine-$AlCl_3$ (bottom); the reaction mixture 5 minutes after the addition of triphenylmethane (2nd from bottom); the reaction mixture after mixing for 20 hours (2nd from top); the reaction mixture after mixing for 40 hours (top).

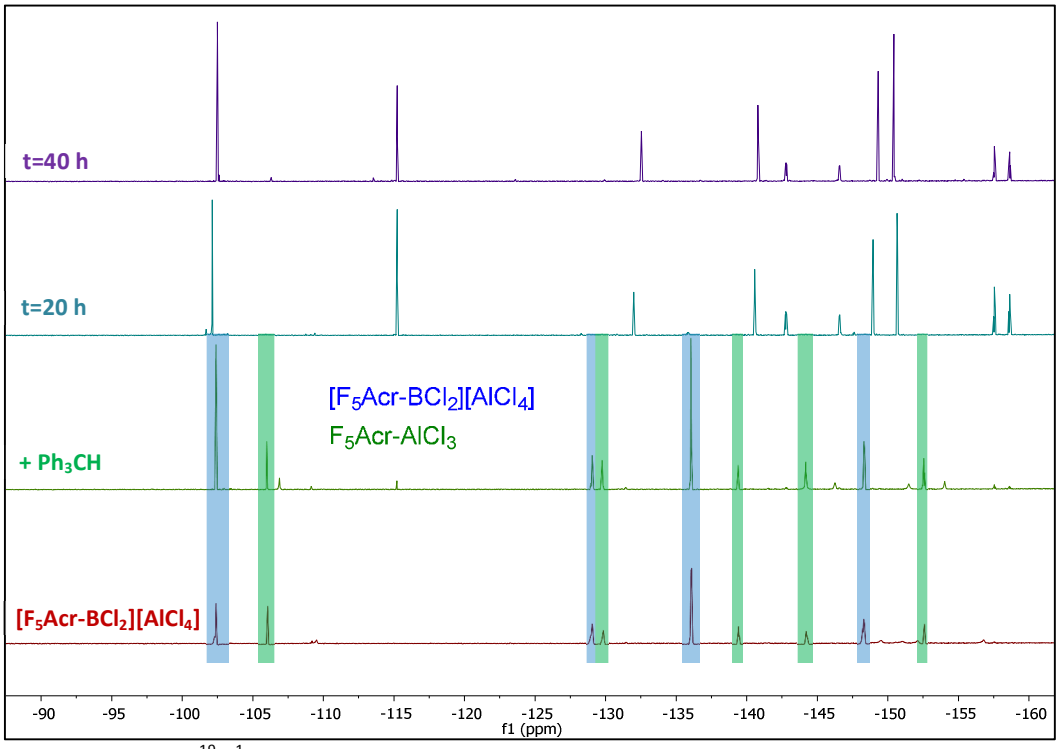

Figure S29: Collected $^{19}F\{^{1}H\}$ spectra (DCM-d_2, 376 MHz, 298K) of: a mixture of *in situ* generated [F_5Acr-BCl_2][$AlCl_4$] and F_5-acridine-$AlCl_3$ (bottom); the reaction mixture 5 minutes after the addition of triphenylmethane (2nd from bottom); the reaction mixture after mixing for 20 hours (2nd from top); the reaction mixture after mixing for 40 hours (top).

4 FLP tests

4.1 Activation of H_2 with [F_5Acr-BCat][$AlCl_4$] ([5][$AlCl_4$]) and 2,6-ditertbutylpyridine

A J. Young's NMR tube was equipped with a benzene-d_6 filled capillary, and charged with F_5-acridine (20.2 mg, 0.075 mmol) before drying under vacuum. The F_5-acridine was dissolved in *o*-DCB (0.5 mL), before CatBCl (11.6 mg, 0.075 mmol) and $AlCl_3$ (10.0 mg, 0.075 mmol) were added. The sample was agitated for 5 minutes before the generation of the desired borocation was confirmed by NMR spectroscopic analysis. 2,6-ditertbutylpyridine (16.8 µL, 0.075 mmol) was added to the reaction mixture, and further NMR spectroscopic analysis showed a small amount of F_5-acridine was generated (*Figure S32, 2nd from bottom*). The reaction was subsequently degassed and placed under 4 atmospheres of H_2 (3 x freeze-pump-thaw cycles, followed by cooling the J. Young's NMR tube to 77 K and backfilling with H_2). After warming to room temperature, NMR spectroscopic experiments revealed that no instantaneous H_2 activation had occurred. The reaction was set to heat at 100 °C for 24 hours, after which time ^{1}H and ^{19}F{^{1}H} NMR spectroscopy revealed the formation of new signals corresponding to F_5Acridane=BCat CH_2 (δ_H 3.87 ppm) (*see Figure S30 – 3rd from top*), indicative of H_2 activation . The reaction mixture was heated at 100 °C for a further 72 hours, after which time a small increase in the F_5Acridane=BCat CH_2 signal was observed by ^{1}H NMR spectroscopy (*see Figure S30 – 2nd from top*). After another 24 hours of heating at 100 °C no further change in the ^{1}H or ^{19}F{^{1}H} NMR spectra were seen.

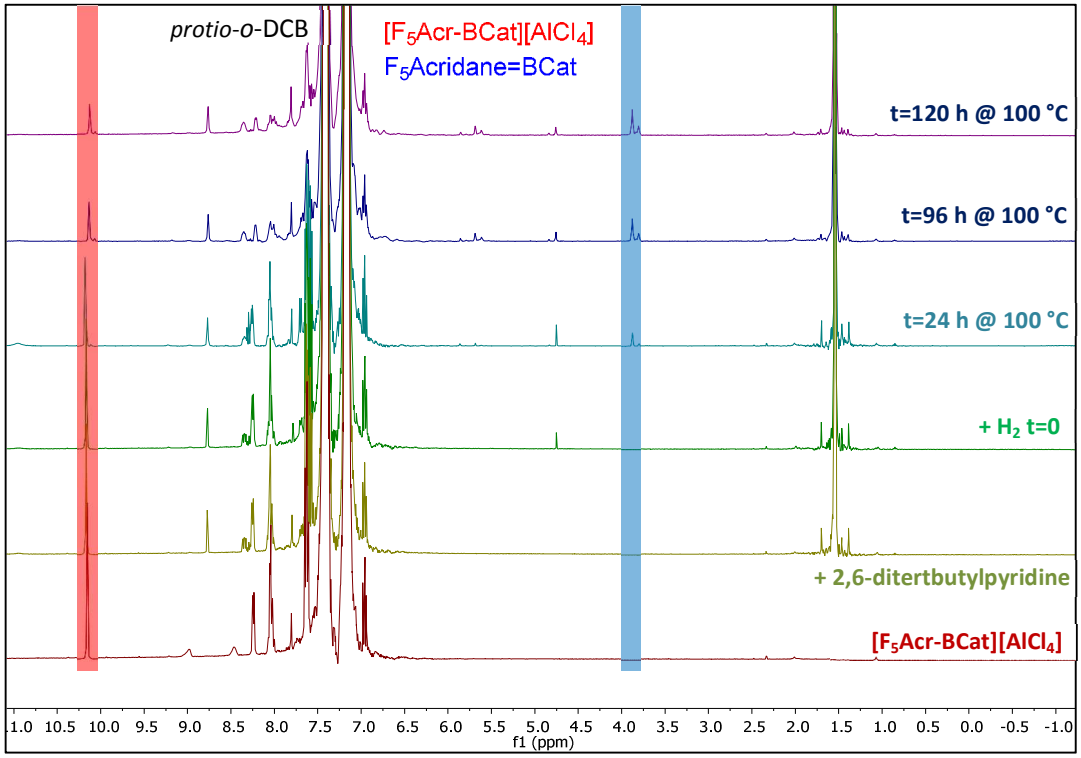

Figure S30: Collected ^{1}H NMR spectra (*protio-o*-DCB, 400 MHz, 298K with a capillary insert of benzene-d_6) of: *in situ* generated [F_5Acr-BCat][$AlCl_4$] (bottom); the reaction mixture after the addition of 2,6-ditertbutylpyridine (2nd from bottom); the reaction mixture 5 minutes after placing under 4 bar H_2 (3rd from bottom); the reaction mixture after heating at 100 °C for 24 hours (3rd from top); the reaction mixture after heating at 100 °C for 96 hours (2nd from top); the reaction mixture after heating at 100 °C for 96 hours (top).

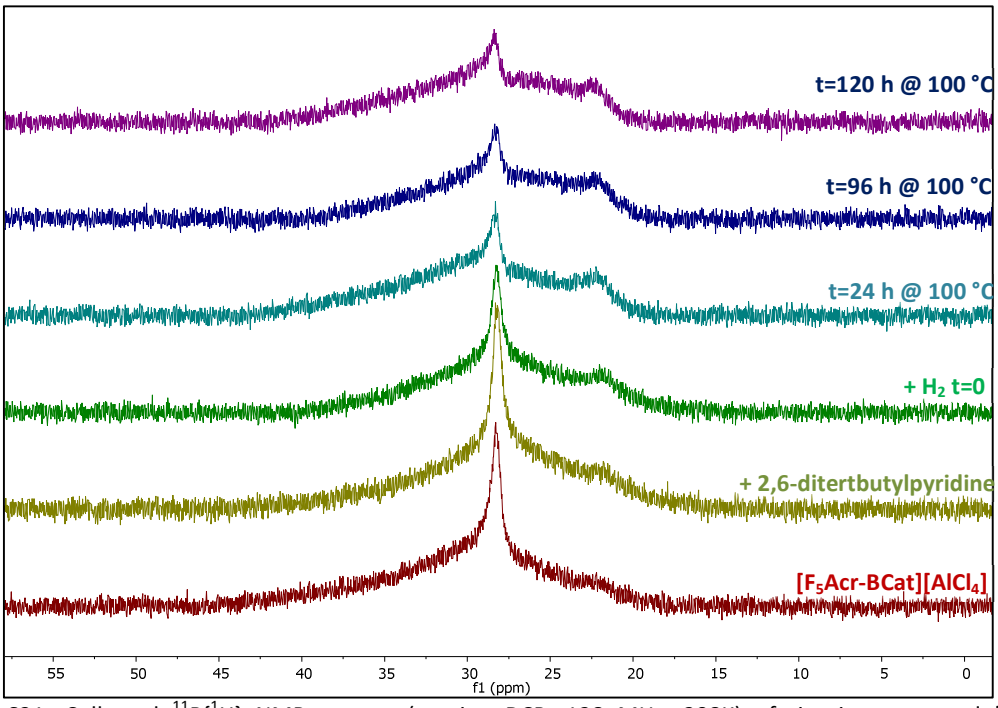

Figure S31: Collected $^{11}B\{^1H\}$ NMR spectra (*protio-o*-DCB, 128 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$AlCl_4$] (bottom); the reaction mixture after the addition of 2,6-ditertbutylpyridine (2nd from bottom); the reaction mixture 5 minutes after placing under 4 bar H_2 (3rd from bottom); the reaction mixture after heating at 100 °C for 24 hours (3rd from top); the reaction mixture after heating at 100 °C for 96 hours (2nd from top); the reaction mixture after heating at 100 °C for 96 hours (top).

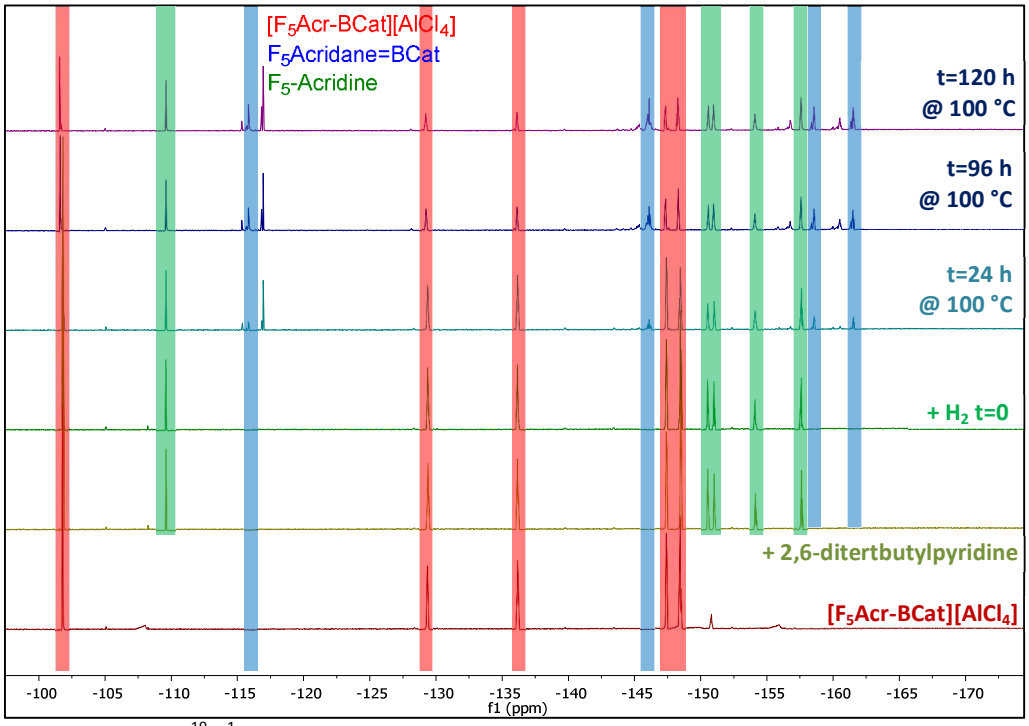

Figure S32: Collected $^{19}F\{^1H\}$ NMR spectra (*protio-o*-DCB, 376 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$AlCl_4$] (bottom); the reaction mixture after the addition of 2,6-ditertbutylpyridine (2nd from bottom); the reaction mixture 5 minutes after placing under 4 bar H_2 (3rd from bottom); the reaction mixture after heating at 100 °C for 24 hours (3rd from top); the reaction mixture after heating at 100 °C for 96 hours (2nd from top); the reaction mixture after heating at 100 °C for 96 hours (top).

5 Friedel-Crafts Chemistry

5.1 Reaction of [F_5Acr-BCat][$AlCl_4$] ([5][$AlCl_4$]) and 2,6-ditertbutylpyridine with 1,1-diphenylethylene

A J. Young's NMR tube was equipped with a benzene-d_6 filled capillary, and charged with F_5-acridine (20.2 mg, 0.15 mmol) before drying under vacuum. The F_5-acridine was dissolved in DCM-d_2 (0.5 mL), before CatBCl (11.6 mg, 0.075 mmol) and $AlCl_3$ (10.0 mg, 0.075 mmol) were added. The sample was agitated for 5 minutes before the generation of the desired borocation was confirmed by NMR spectroscopic analysis. 2,6-Ditertbutylpyridine (16.8 µL, 0.075 mmol) was added and the sample mixed, before 1,1-diphenylethylene (13.2 µL, 0.075 mmol) was also placed in the tube. Upon mixing the sample instantly became a dark green colour. ^{1}H NMR spectroscopic analysis showed the formation of an AB doublet system (δ_H 6.01 (d, *J* = 10 Hz) and 5.00 (d, *J* = 10 Hz) ppm) indicative of the formation of **7**, but with the retention of a small amount of starting material (*see Figure S33 – middle*). The reaction mixture was set to mix for 16 hours, in which time the sample turned a turquoise colour and colourless crystals formed (assumed to be [2,6-ditertbutylpyridinium][$AlCl_4$]). Further analysis by ^{1}H NMR spectroscopy demonstrated the complete consumption of [F_5acridine-BCat][$AlCl_4$]. The sample was then left to stand for one week, over which time the sample turned from turquoise to colourless. The reaction mixture was then hydrolysed by washing with water (3 x 2 mL), the organic fraction dried over $MgSO_4$ and filtered to give a pale yellow solution. The solvent was removed under vacuum, leaving a yellow oily residue. The non-polar reaction products were extracted by washing with pentane, before the pentane was removed in vacuo to leave a yellow oil containing a mixture of **7**, 2,6-ditertbutylpyridine and traces of F_5-acridine. The identity of **7** was confirmed by ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectroscopy as well as accurate mass spectrometry.

Only ^{1}H signals pertaining to **7** *reported (see Figure S36 for full spectra)*
^{1}H NMR (500 MHz, Methylene Chloride-d_2): δ 7.58 – 7.52 (m, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.39 (m, 2H), 7.33 (s, 2H), 7.21 – 7.18 (m, 2H), 7.16 – 7.14 (m, 1H), 6.92 – 6.86 (m, 1H), 6.84 – 6.80 (m, 1H), 6.76 (d, *J* = 9 Hz, 1H), 6.37 (s, 1H), 6.13 (d, *J* = 10 Hz, 1H), 5.03 (d, *J* = 10 Hz, 1H).

Only ^{13}C{^{1}H} signals pertaining to **7** *reported, assigned through the use of COSY, HMBC and HSQC NMR experiments (see Figure S37 for full spectra)*
^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 160.0, 158.1, 141.9, 140.5, 139.6, 134.1, 130.5 (d, *J* = 2 Hz), 129.2, 128.7, 128.3 (d, *J* = 5 Hz), 128.1 (d, *J* = 11 Hz), 127.6, 125.7, 123.0 (d, *J* = 7 Hz), 116.2 (d, *J* = 8 Hz), 115.6 (d, *J* = 23 Hz), 115.3 (d, *J* = 23 Hz), 106.9 (d, *J* = 20 Hz), 36.47.

Only ^{19}F{^{1}H} signals pertaining to **7** *reported (see Figure S38 for full spectra)*
^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -122.0, -143.7 (dd, *J* = 22, 10 Hz), -160.5 (t, *J* = 21 Hz), -164.9 (ddd, *J* = 21, 10, 5 Hz), -170.7 (td, *J* = 22, 5 Hz).

MS (Accurate mass, ESI$^+$) *m/z* Calc: $[C_{27}H_{16}F_5N]^+$, 449.1197. Found: 449.1195

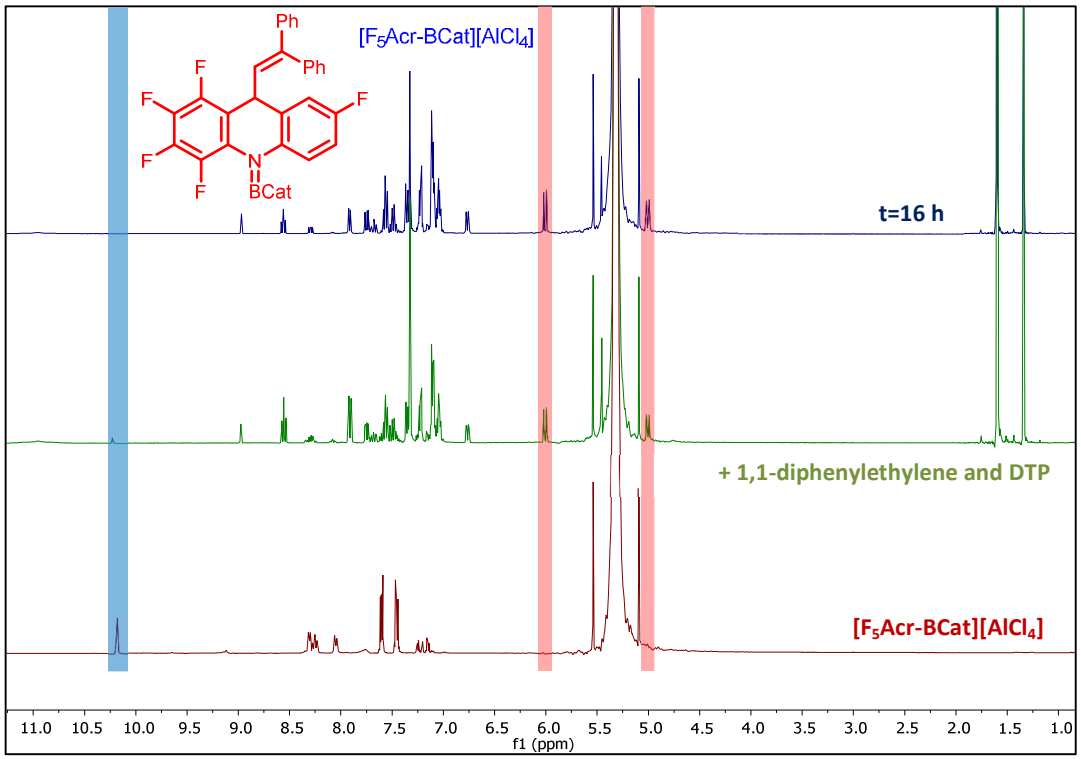

Figure S33: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$AlCl_4$] (bottom); the sample 5 minutes after the addition of 2,6-ditertbutylpyridine and 1,1-diphenylethylene (middle); the sample after mixing for 16 hours (top).

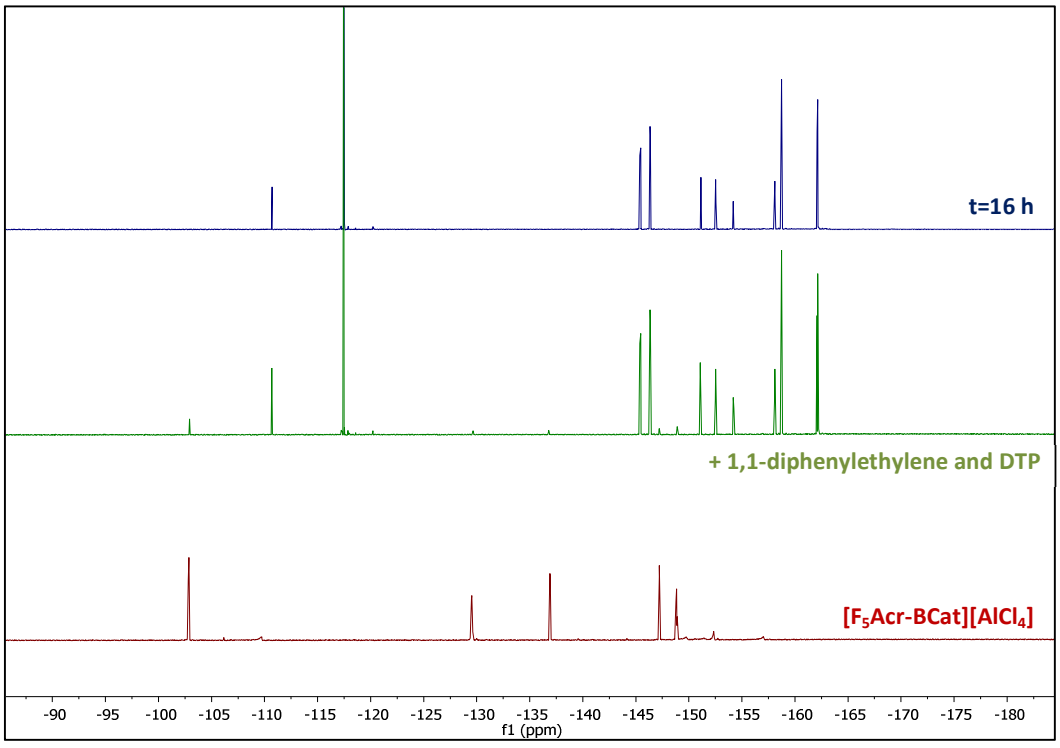

Figure S34: Collected ^{19}F{^{1}H} NMR spectra (DCM-d_2, 376 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$AlCl_4$] (bottom); the sample 5 minutes after the addition of 2,6-ditertbutylpyridine and 1,1-diphenylethylene (middle); the sample after mixing for 16 hours (top).

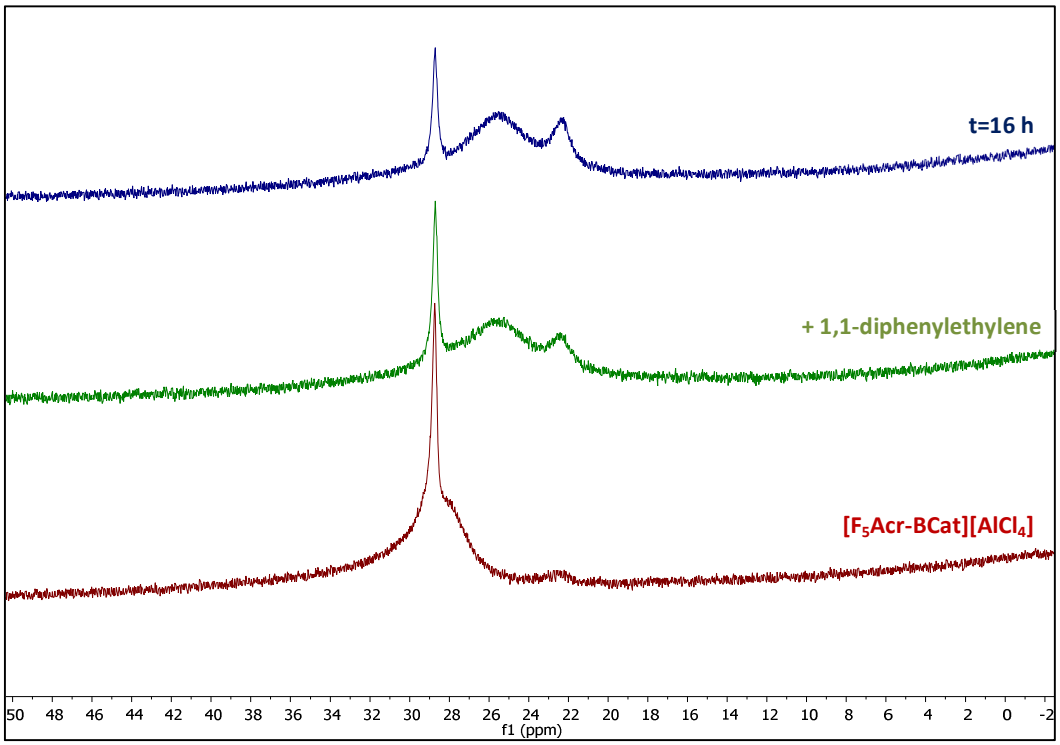

Figure S35: Collected $^{11}B\{^{1}H\}$ NMR spectra (DCM-d_2, 128 MHz, 298K) of: *in situ* generated [F_5Acr-BCat][$AlCl_4$] (bottom); the sample 5 minutes after the addition of 2,6-ditertbutylpyridine and 1,1-diphenylethylene (middle); the sample after mixing for 16 hours (top).

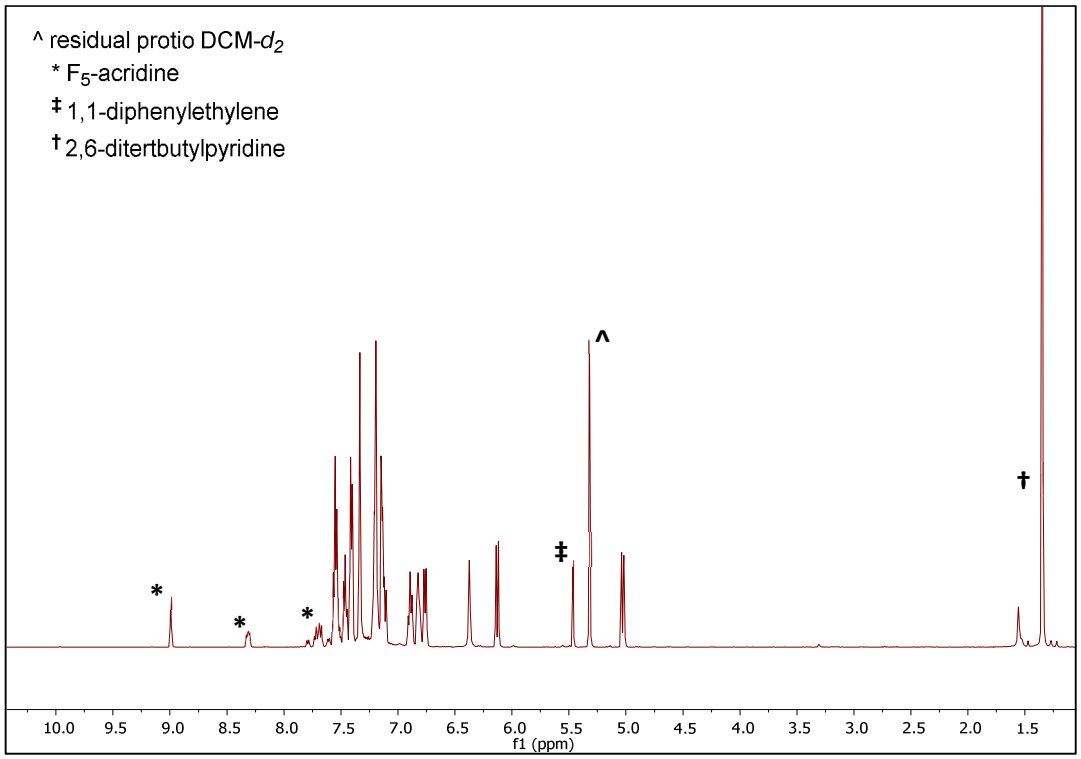

Figure S36: ^{1}H NMR spectrum (DCM-d_2, 500 MHz, 298 K) of **7**, including traces of F_5-acridine, 2,6-ditertbutylpyridine and 1,1-diphenylethylene.

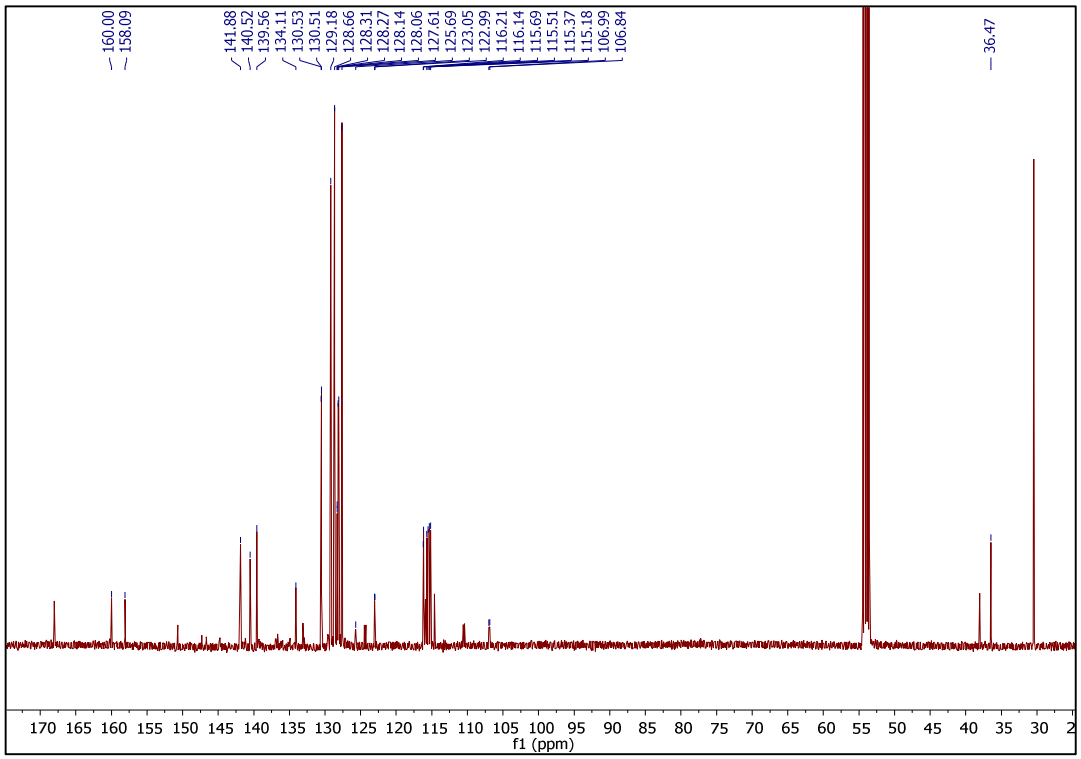

Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum (DCM-d_2, 126 MHz, 298 K) of **7**, including traces of F_5-acridine, 2,6-ditertbutylpyridine and 1,1-diphenylethylene.

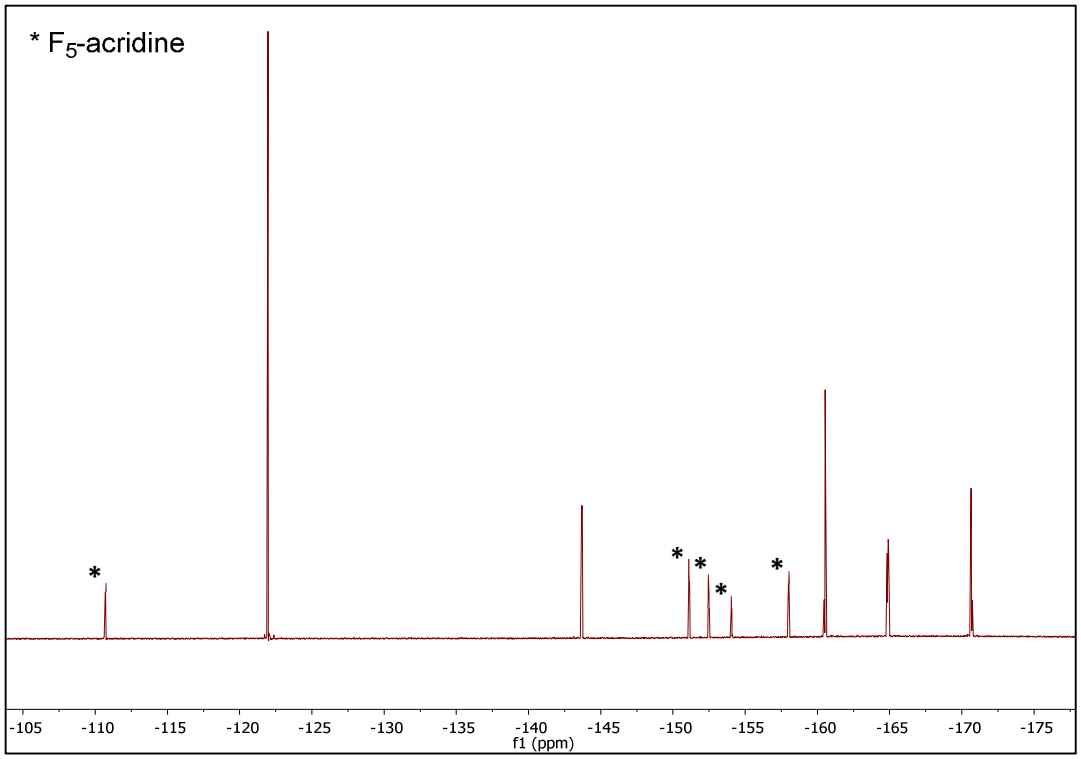

Figure S38: $^{19}F\{^{1}H\}$ NMR spectrum (DCM-d_2, 376 MHz, 298 K) of **7**, including traces of F_5-acridine.

5.2 Attempted reaction of [Acr-BCat][$AlCl_4$] and 2,6-ditertbutylpyridine with 1,1-diphenylethylene

A J. Young's NMR tube was equipped with a benzene-d_6 filled capillary, and charged with Acridine-BCatCl (25 mg, 0.075 mmol) before drying under vacuum. DCM (0.5 mL) was added to the tube, along with $AlCl_3$ (10.0 mg, 0.075 mmol) and the mixture was agitated for 10 minutes to yield a clear orange solution. NMR spectroscopic analysis confirmed the clean formation of the desired borocation. Next, 2,6-ditertbutylpyridine (16.8 µL, 0.075 mmol) and 1,1-diphenylethylene (13.2 µL, 0.075 mmol) were added and the sample was mixed. Subsequent analysis of the mixture by NMR spectroscopy revealed that no reaction had occurred. The reaction was set to mix for 24 hours, after which time NMR spectroscopic analysis showed a trace of an AB doublet system (6.33 (d, J = 10 Hz) and 4.60 (d, J = 10 Hz)) indicative of 9-(2,2-diphenylethylidene)-9,10-dihydroacridine. The mixture was then left to heat at 60 °C for 72 hours, after which time analysis by NMR spectroscopy showed decomposition of the [Acr-BCat]$^+$, but no further consumption of 1,1-diphenylethylene.

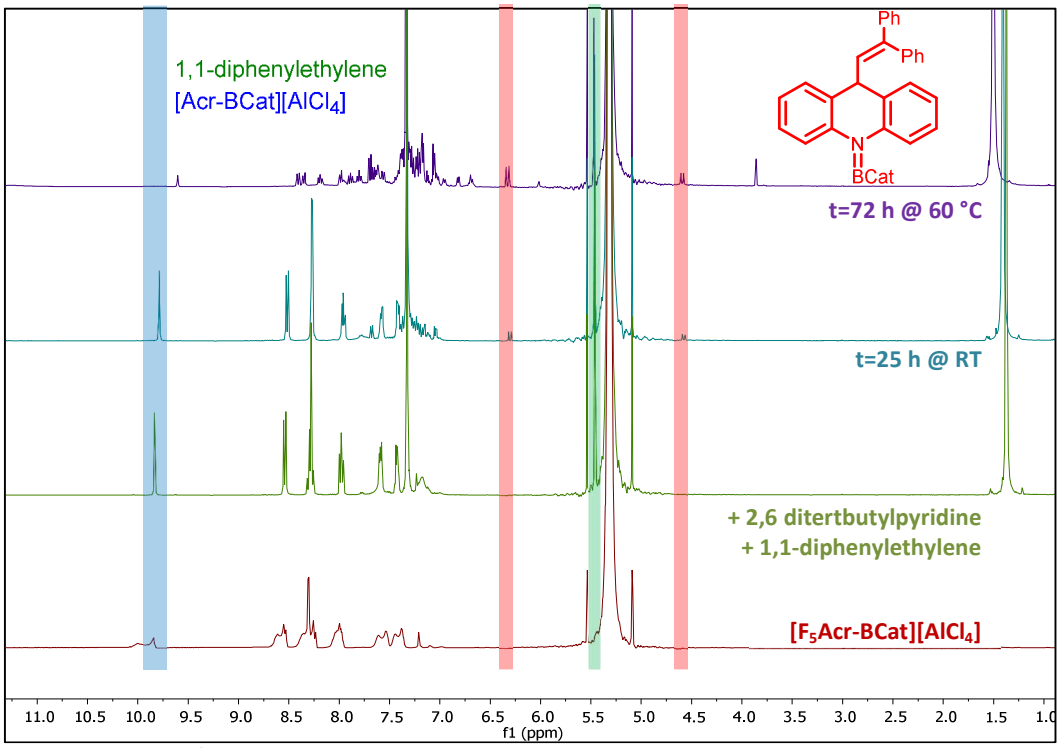

Figure S39: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K) of: *in situ* generated [Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 5 minutes after the addition of 2,6-ditertbutylpyridine and 1,1-diphenylethylene (2nd from bottom); the reaction mixture after mixing at room temperature for 25 hours (2nd from top); the reaction mixture after heating at 60 °C for 72 hours (top).

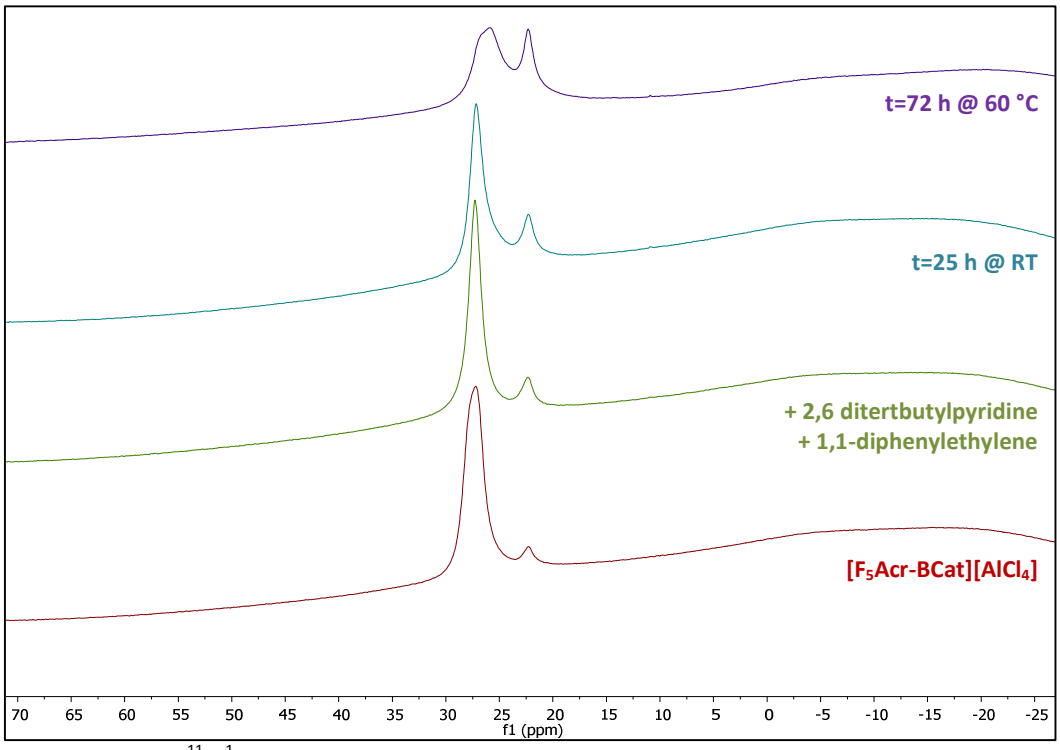

Figure S40: Collected $^{11}B\{^{1}H\}$ NMR spectra (*protio*-DCM, 400 MHz, 298K) of: *in situ* generated [Acr-BCat][$AlCl_4$] (bottom); the reaction mixture 5 minutes after the addition of 2,6-ditertbutylpyridine and 1,1-diphenylethylene (2nd from bottom); the reaction mixture after mixing at room temperature for 25 hours (2nd from top); the reaction mixture after heating at 60 °C for 72 hours (top).

6 Quinoline and Pyridine Reduction Chemistry

6.1 Reduction of Quinoline with HBPin and catalytic benzimidazolium salt

A Young's NMR tube equipped with a benzene-d_6 capillary was placed under and atmosphere of N_2 before being charged with quinoline (11.8 µL, 01 mmol), DCM (0.5 mL) and HBPin (18.6 µL, 0.12 mmol). Analysis of the mixture by ^{1}H and ^{11}B NMR spectroscopy revealed no reaction occurs. Solid [*N,N*-dimethyl-2-phenylbenzimidazolium][B(3,5-$C_6H_4Cl_2)_4$] (4.1 mg, 0.05 mmol) was added to the mixture, and further NMR spectroscopic experiments demonstrated no instantaneous reactivity. The reaction sample was set to mix at room temperature for 19 hours, after which time NMR spectroscopy revealed that complete consumption of quinoline had occurred, and the formation of a mixture of *N*-pinacolborane-4-dihydroquinoline and N-pinacolborane-2-dihydroquinoline (2:1 ratio, respectively). The results match those reported by Wright et al., and so no further analysis was undertaken.[3]

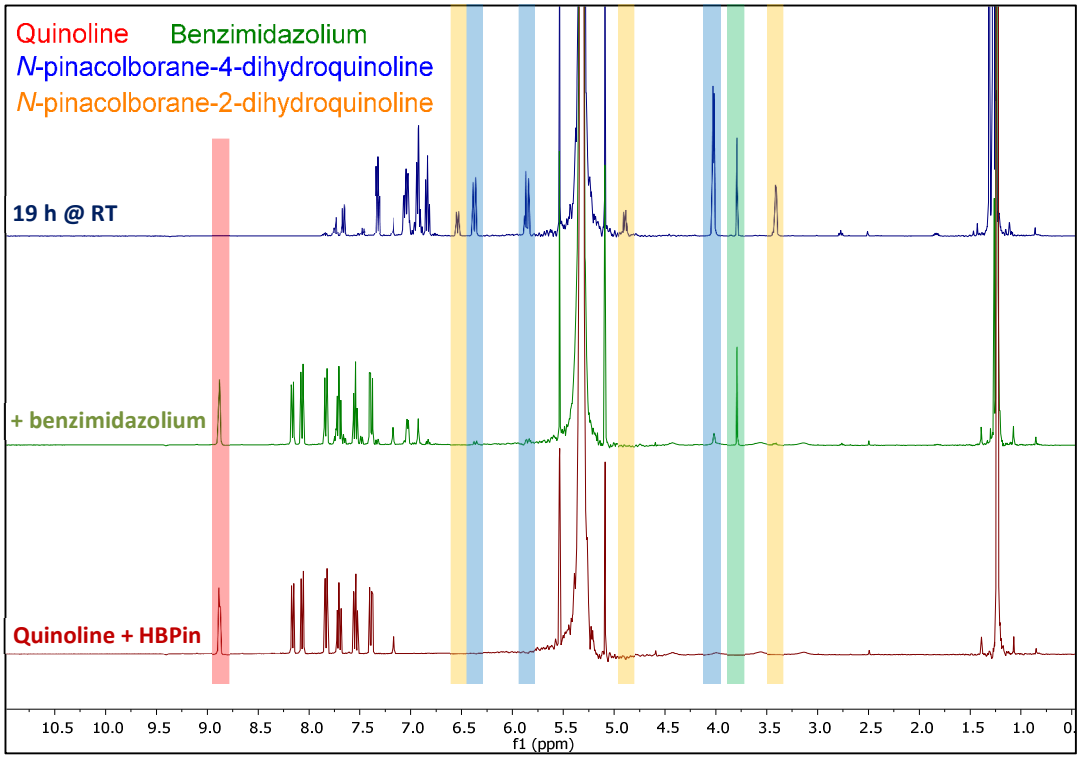

Figure S41: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K, benzene-d_6 capillary) of: A mixture of quinoline and HBPin (bottom), the reaction after the addition of [*N,N*-dimethyl-2-phenylbenzimidazolium][B(3,5-$C_6H_4Cl_2)_4$] (middle), the reaction mixture after 19 hours at room temperature (top).

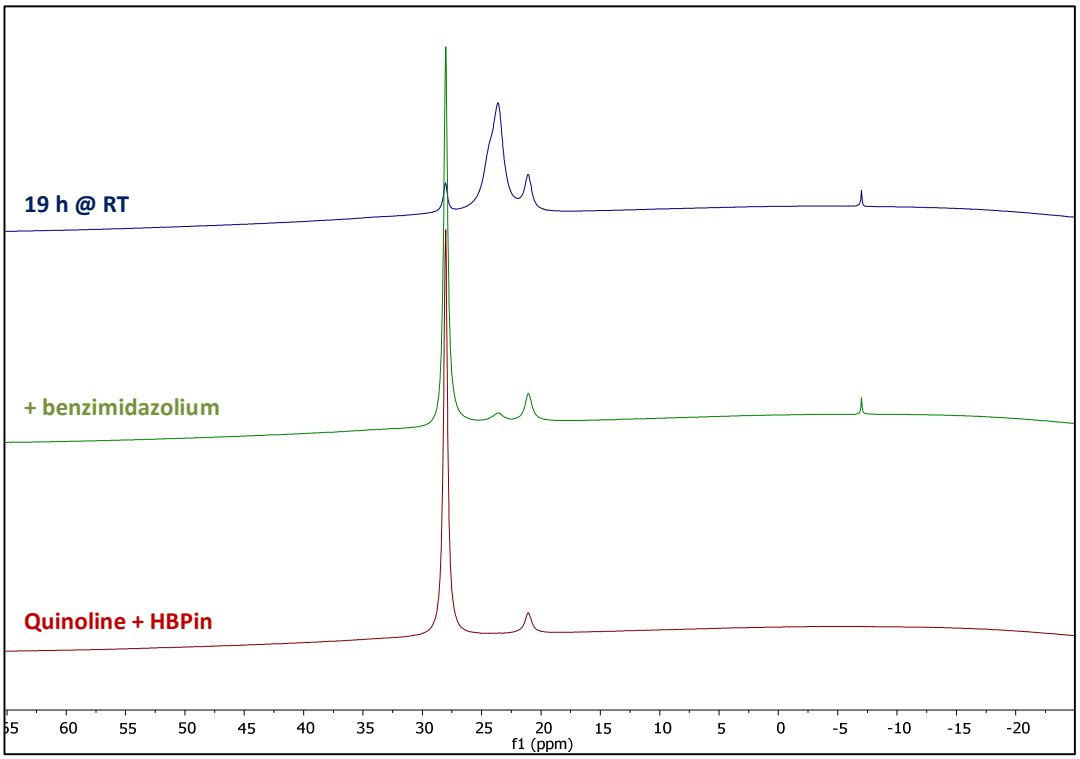

Figure S42: Collected $^{11}B\{^{1}H\}$ NMR spectra (*protio*-DCM, 400 MHz, 298K) of: A mixture of quinoline and HBPin (bottom), the reaction after the addition of [*N,N*-dimethyl-2-phenylbenzimidazolium][B(3,5-$C_6H_4Cl_2)_4$] (middle), the reaction mixture after 19 hours at room temperature (top).

6.2 Reduction of Pyridine with HBPin and catalytic benzimidazolium salt

A Young's NMR tube equipped with a benzene-d_6 capillary was placed under and atmosphere of N_2 before being charged with quinoline (11.8 µL, 01 mmol), DCM (0.5 mL) and HBPin (12.7 µL, 0.10 mmol). Solid [*N,N*-dimethyl-2-phenylbenzimidazolium][B(3,5-$C_6H_4Cl_2)_4$] (4.1 mg, 0.05 mmol) was added to the mixture, and further NMR spectroscopic experiments demonstrated no instantaneous reactivity. The NMR tube was set to mix at room temperature for 18 hours, after which time NMR spectroscopic experiments revealed the formation of a small amount of *N*-pinacolborane-4-dihydropyridine. The reaction was set to heat at 60 °C for 24 hours, after which time further NMR spectroscopic analysis demonstrated the formation of more *N*-pinacolborane-4-dihydropyridine. By integration of the ^{1}H NMR signals pertaining to the starting materials and products it was found that the reaction had gone to 75 % conversion. The NMR spectroscopic data measured for *N*-pinacolborane-4-dihydropyridine matched that reported by Wright et al., and so no further analysis was undertaken.[3]

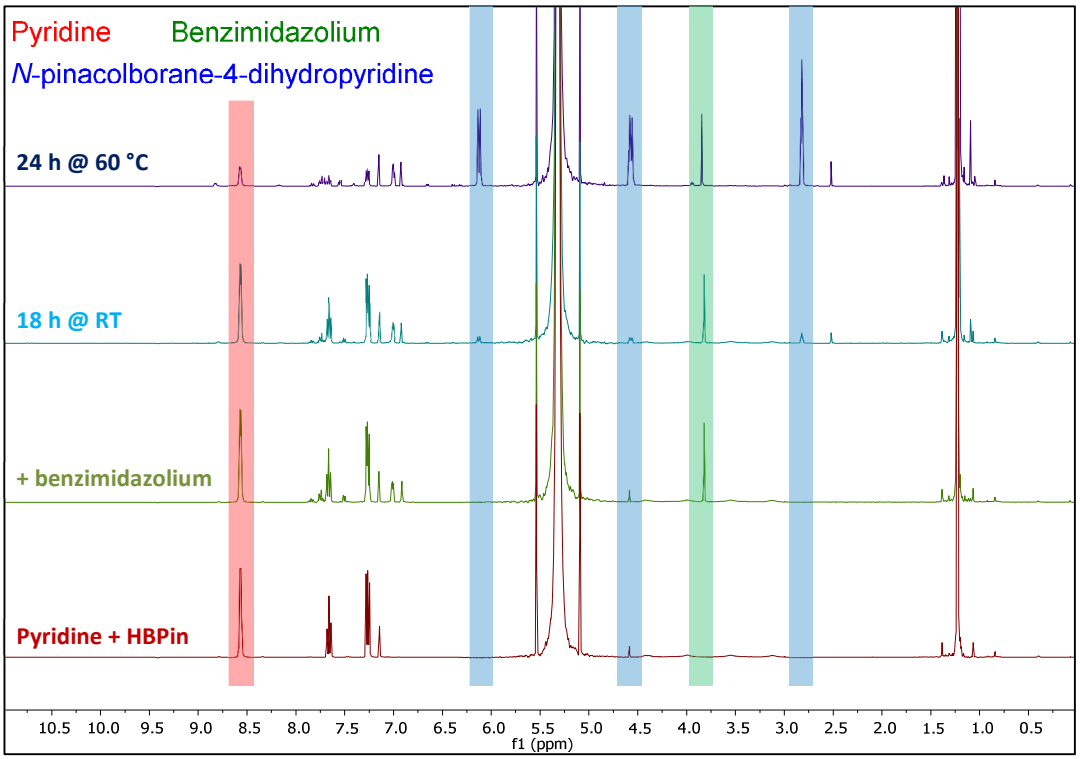

Figure S43: Collected ^{1}H NMR spectra (*protio*-DCM, 400 MHz, 298K, benzene-d_6 capillary) of: A mixture of pyridine and HBPin (bottom), the reaction after the addition of [*N*,*N*-dimethyl-2-phenylbenzimidazolium][B(3,5-$C_6H_4Cl_2)_4$] (2nd from bottom), the reaction mixture after 18 hours at room temperature (2nd from top), the reaction mixture after heating at 60 °C for 24 hours (top).

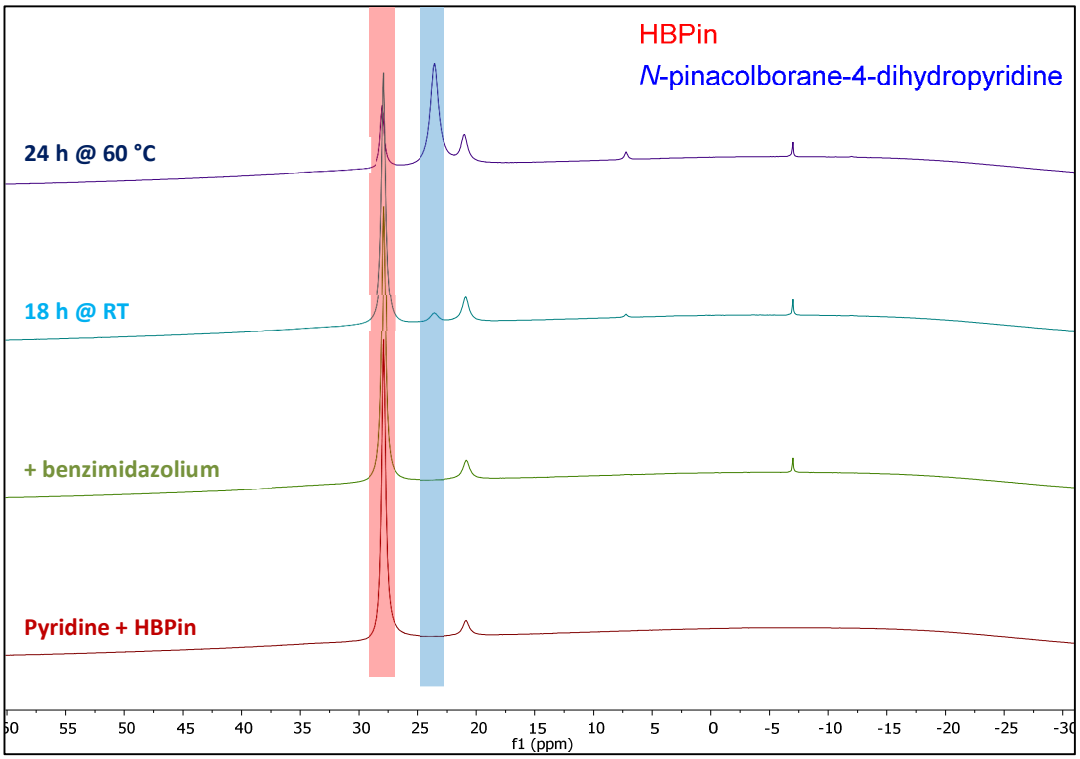

Figure S44: Collected $^{11}B\{^{1}H\}$ NMR spectra (*protio*-DCM, 400 MHz, 298K) of: A mixture of pyridine and HBPin (bottom), the reaction after the addition of [*N,N*-dimethyl-2-phenylbenzimidazolium][$B(3,5\text{-}C_6H_4Cl_2)_4$] (2nd from bottom), the reaction mixture after 18 hours at room temperature (2nd from top), the reaction mixture after heating at 60 °C for 24 hours (top).

7 Hydride Ion Affinity Calculations

7.1 General Comments:

All calculations were conducted at the M06-2X/6-311G(d,p) level with a solvation model (PCM, CH_2Cl_2) using the Gaussian software package.[4] All calculations (except $[Acr\text{-}BCl_2]^+$ and $[Ph_3C]^+$)[2,5] were performed by Dr Jessica Cid. The optimised energies were confirmed as true minima by frequency analysis and the absence of any imaginary frequencies. The HIAs of all compounds were calculated using the methodology reported by Ingleson et al.[6]

7.2 Full table of calculated HIA values

Compound	HIA @ Boron (kcal mol^{-1})	HIA @ Carbon (kcal mol^{-1})
Tropylium	n/a	-58.1
Dibenzosuberene	n/a	-63.5
N-TMS-Pyridinium	n/a	-28.3
N-Me-Pyridinium	n/a	-27.2
N-Me-Quinolinium @ C2	n/a	-35.4
N-Me-Quinolinium @ C4	n/a	-37.2
Quin-BF_3 @ C2	n/a	-12.4
Quin-BF_3 @ C4	n/a	-17.6
F_5Acr-$AlCl_3$ (**6**)	n/a	-57.4
Acr-BBr_2	-62.6	-73.8
Br_2Acr-BCl_2	-62.9	-80.0
Br_2Acr-BCat	-37.3	-72.3
Acr-BBN	-30.1	-65.4
F_5Acr-BBN	-35.1	-78.5
Acr-BCat **[3]**$^+$	-32.7	-65.7
F_5Acr-BCat **[5]**$^+$	-36.1	-76.7
F_5Acr-BCl_2 **[4]**$^+$	-60.6	-84.9
Acr_2-BCl_2	n/a	-58.8
Py-BPin @ C2 **[9]**$^+$	-26.5	-35.1
Py-BPin @ C4 **[9]**$^+$	-26.5	-38.5
Quin-BPin @ C4 **[8]**$^+$	-27.4	-46.0
Quin-BPin @ C4 **[8]**$^+$	-27.4	-46.9
$[Quin\text{-}BCat]^+$ @ C2	-40.4	-51.8
$[Quin\text{-}BCat]^+$ @ C4	-40.4	-52.2
$[Py_2\text{-}BPin]^+$ @ C2	n/a	-15.4
$[Py_2\text{-}BPin]^+$ @ C4	n/a	-18.5
$[Quin_2\text{-}BPin]^+$ @ C2	n/a	-27.0
$[Quin_2\text{-}BPin]^+$ @ C4	n/a	-30.3

Table S1: A table of collected HIA calculated HIA values, relative to BEt_3 (BEt_3 HIA = 0 kcal mol^{-1}). All calculated at M06-2X/6-311G(d,p) level with a solvation model (PCM, CH_2Cl_2).

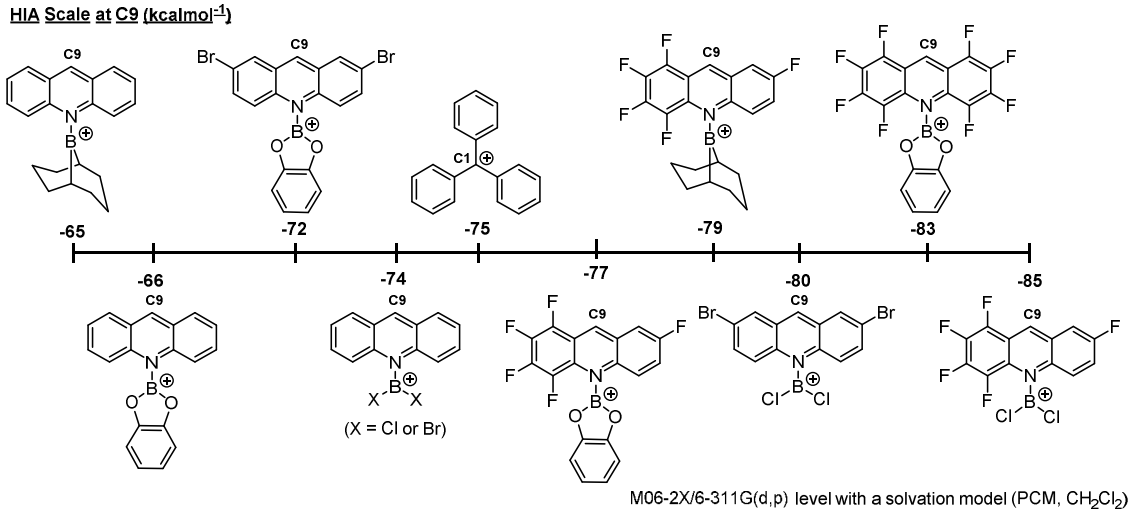

Figure S45: Calculated hydride ion affinity (HIA) at the C9 position of various acridine derived borocations and the trityl cation.

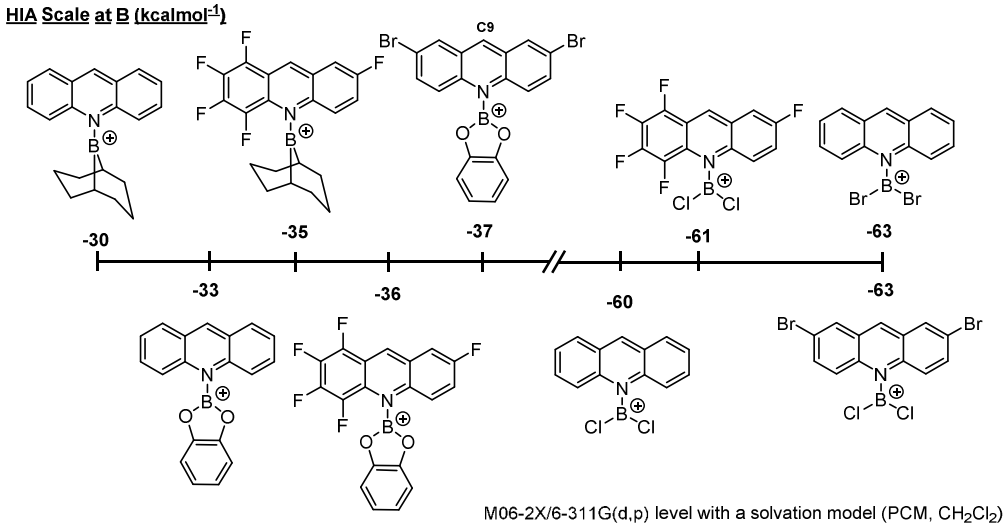

Figure S46: Calculated hydride ion affinity (HIA) at boron of various acridine derived borocations.

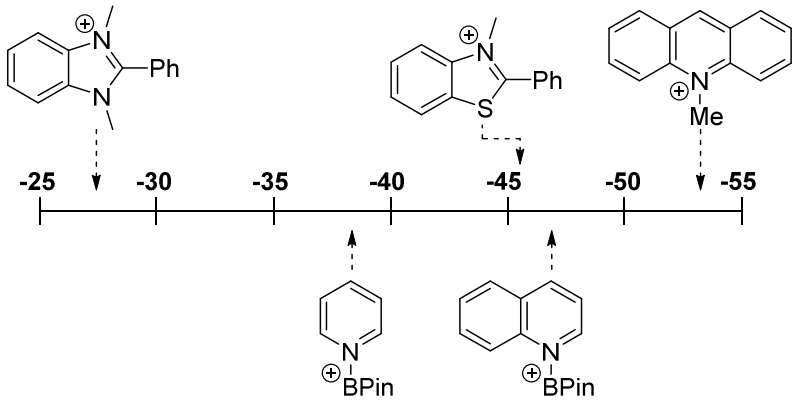

Figure S47: HIAs of Py-BPin and Quin-BPin derivatives at C4 (values in kcal mol^{-1}, relative to BEt_3), along with other known carbon Lewis acidic species for comparison.

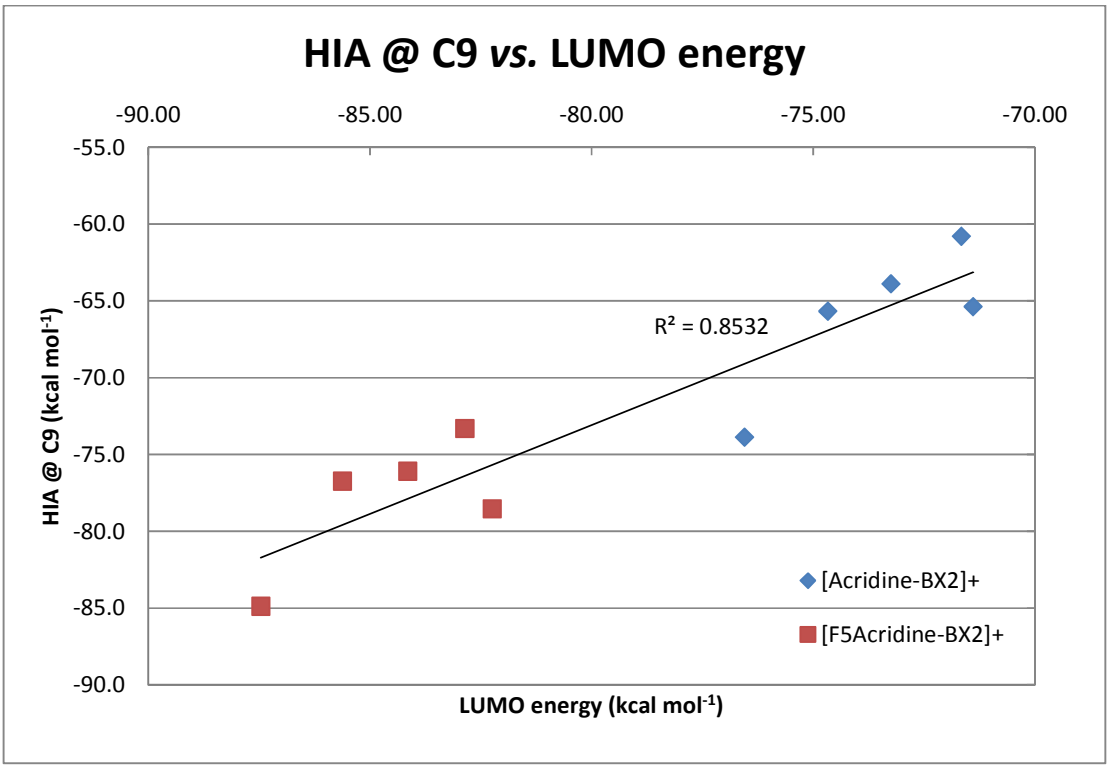

Figure S48: Graph plotting calculated HIAs at C9 against calculated LUMO energies for a series of [acridine-BX_2]$^+$ and [F_5acridine-BX_2]$^+$ borenium salts.

8 X-Ray Structures

Crystallographic data for compounds **3** **5** and **6** were recorded on an Agilent Supernova diffractometer, at 150 K with Mo Kα radiation (mirror monochromator, λ=0.7107). The CrysAlisPro[7] software package was used for data collection, cell refinement and data reduction. For all data sets the CrysAlisPro software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All further data processing was undertaken within the Olex2 software package.[8] The molecular structures of all compounds were solved with the ShelXT[9] structure solution program using Intrinsic Phasing and refined with the ShelXL[10] refinement package using Least Squares minimisation. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically.

8.1 [Acr-BCat][$AlCl_4$], [3][$AlCl_4$] (CCDC No.: 1580954)

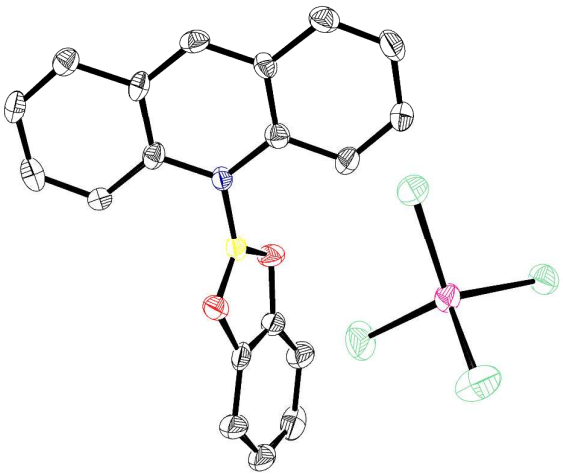

Figure S49: ORTEP plot for the molecular structure of [Acr-BCat][$AlCl_4$] with thermal ellipsoids set at 50 % level and hydrogens omitted for clarity.

Empirical formula	$C_{19}H_{13}AlBCl_4NO_2$
Formula weight	466.89
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.1701(3)
b/Å	15.3795(7)
c/Å	19.2113(8)
α/°	90
β/°	100.090(4)
γ/°	90
Volume/$Å^3$	2085.73(16)
Z	4
$\rho_{calc}g/cm^3$	1.487
μ/mm^{-1}	0.625
F(000)	944.0
Crystal size/mm^3	0.4 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.83 to 49.426
Index ranges	-8 ≤ h ≤ 5, -12 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	7779
Independent reflections	3436 [R_{int} = 0.0420, R_{sigma} = 0.0401]
Data/restraints/parameters	3436/0/253
Goodness-of-fit on F^2	1.121
Final R indexes [I>=2σ (I)]	R_1 = 0.0975, wR_2 = 0.2279
Final R indexes [all data]	R_1 = 0.1005, wR_2 = 0.2290
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.48

Table S2: Table of crystallographic information for compound [**3**][$AlCl_4$]

8.2 [F_5-Acr-BCat][$AlCl_4$], [5][$AlCl_4$] (CCDC No.: 1580955)

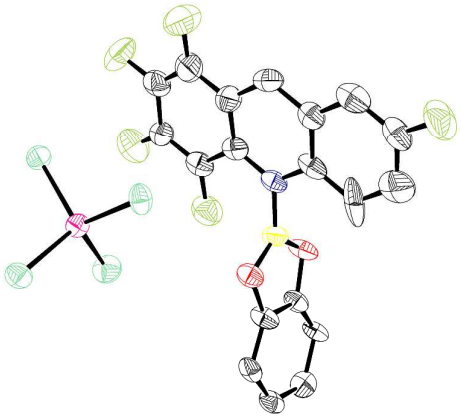

Figure S50: ORTEP plot for the molecular structure of [F_5-Acr-BCat][$AlCl_4$] with thermal ellipsoids set at 50 % level and hydrogens omitted for clarity.

Empirical formula	$C_{19}H_8AlBCl_4F_5NO_2$
Formula weight	556.85
Temperature/K	150.03(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.2070(9)
b/Å	9.7926(6)
c/Å	16.0678(11)
α/°	90
β/°	94.847(6)
γ/°	90
Volume/$Å^3$	2227.4(3)
Z	4
$\rho_{calc}g/cm^3$	1.661
μ/mm^{-1}	0.631
F(000)	1104.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.002 to 49.426
Index ranges	-16 ≤ h ≤ 16, -11 ≤ k ≤ 11, -18 ≤ l ≤ 10
Reflections collected	6319
Independent reflections	6321 [R_{int} = 0.0430, R_{sigma} = 0.0705]
Data/restraints/parameters	6319/79/631
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0710, wR_2 = 0.1986
Final R indexes [all data]	R_1 = 0.0760, wR_2 = 0.2049
Largest diff. peak/hole / e $Å^{-3}$	1.06/-0.35
Flack parameter	0.14(6)

Table S3: Table of crystallographic information for compound [**5**][$AlCl_4$]

Due to low quality of the data collected for [**5**][$AlCl_4$] the C-C bond lengths measured have low precision (0.017 Å). Therefore highly detailed discussion of these metrics cannot be undertaken.

One $[AlCl_4]^-$ counteranion was found to be disordered in the structure in a ratio of 69 % to 31 %. SIMU restraints were used on all atoms in the disordered units in order to aid the modelling.

8.3 [F_5Acr-$AlCl_3$], 6 (CCDC No.: 1580956)

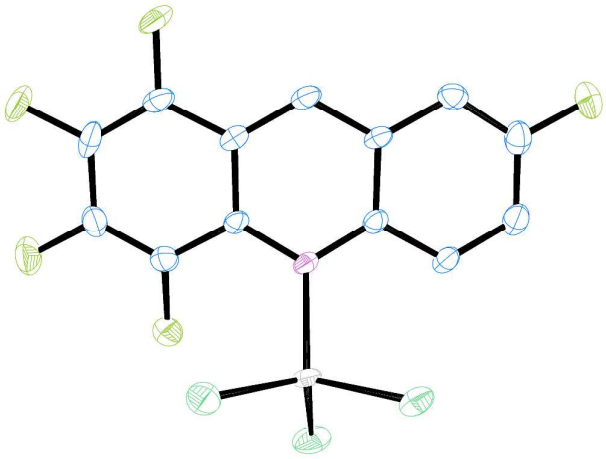

Figure S51: ORTEP plot for the molecular structure of [F_5Acr-$AlCl_3$] with thermal ellipsoids set at 50 % level, and hydrogens omitted for clarity.

Empirical formula	$C_{13}H_4AlCl_3F_5N$
Formula weight	402.50
Temperature/K	150.03(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.6382(19)
b/Å	9.327(3)
c/Å	12.269(2)
α/°	86.788(19)
β/°	86.97(2)
γ/°	72.91(3)
Volume/$Å^3$	724.4(3)
Z	2
$\rho_{calc}g/cm^3$	1.830
μ/mm^{-1}	0.737
F(000)	396.0
Crystal size/mm^3	0.1 × 0.1 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.658 to 58.188
Index ranges	-9 ≤ h ≤ 8, -12 ≤ k ≤ 8, -16 ≤ l ≤ 15
Reflections collected	6848
Independent reflections	6848 [R_{int} = 0.1281, R_{sigma} = 0.0331]
Data/restraints/parameters	6848/0/209
Goodness-of-fit on F^2	1.142
Final R indexes [I>=2σ (I)]	R_1 = 0.1094, wR_2 = 0.2688
Final R indexes [all data]	R_1 =0.1199, wR_2 = 0.2764
Largest diff. peak/hole / e $Å^{-3}$	1.14/-1.09

Table S4: Table of crystallographic information for compound **6**

9 NMR Spectra of Novel Compounds

9.1 [Acr-BCat][$AlCl_4$]

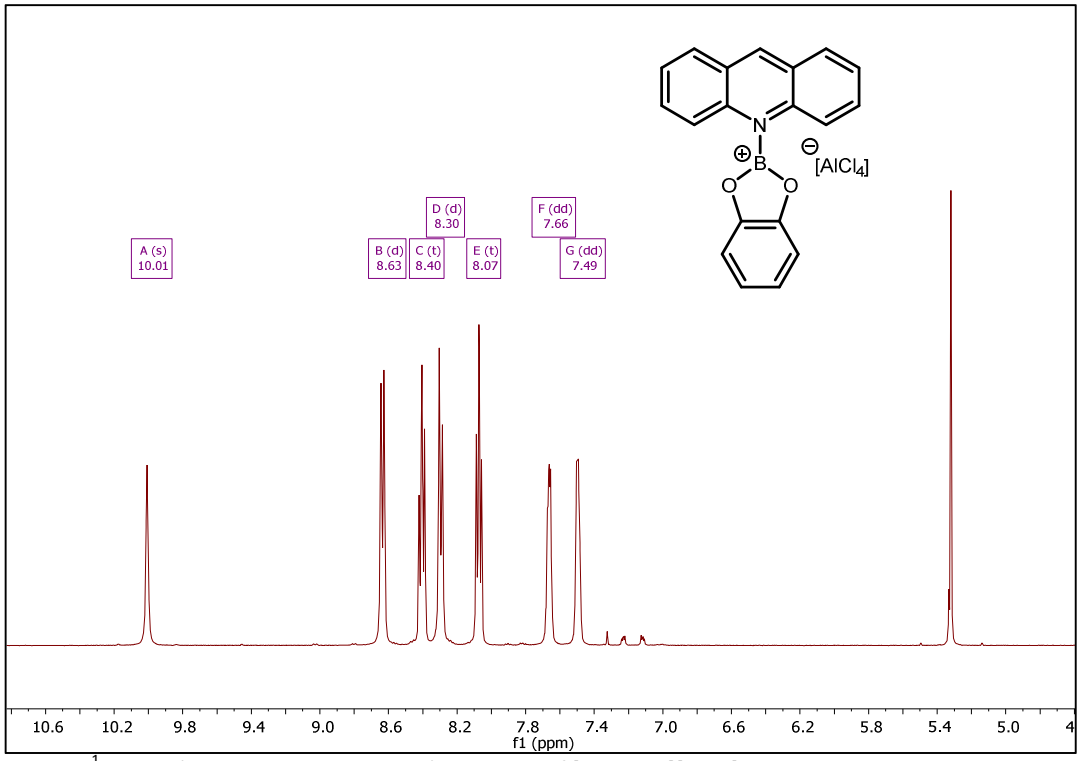

Figure S52: ^{1}H NMR (500 MHz, DCM-d_2, 298K) spectrum of [Acr-BCat][$AlCl_4$]

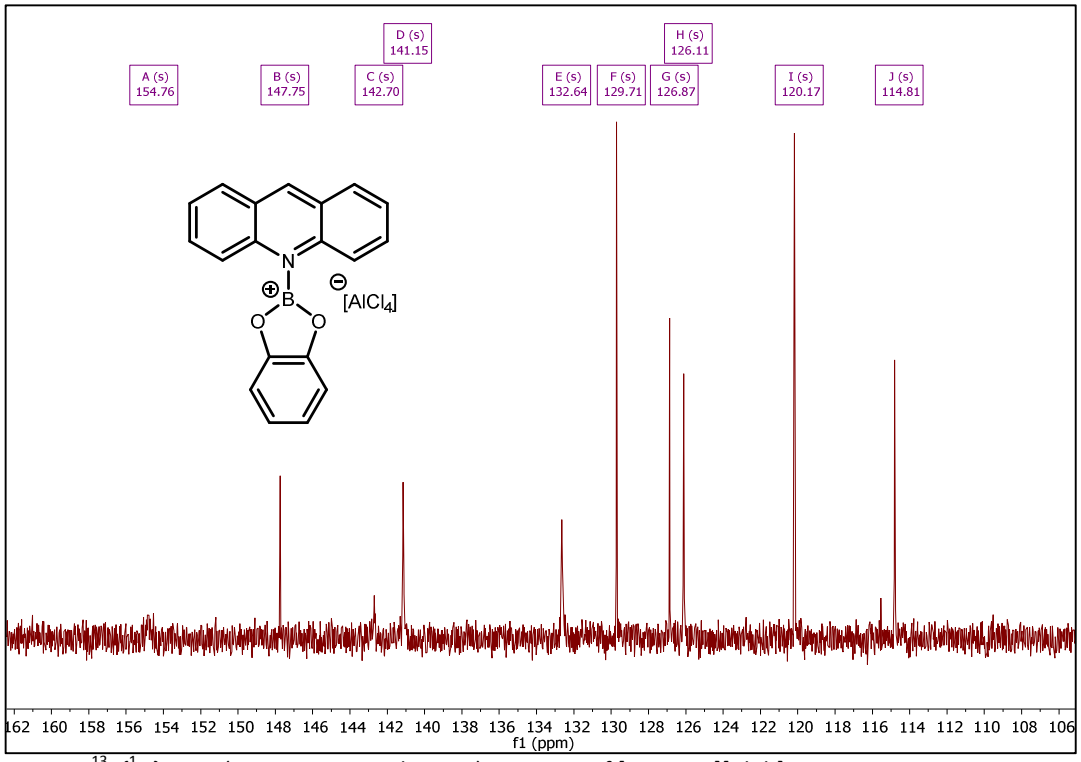

Figure S53: $^{13}C\{^{1}H\}$ NMR (126 MHz, DCM-d_2, 298K) spectrum of [Acr-BCat][$AlCl_4$]

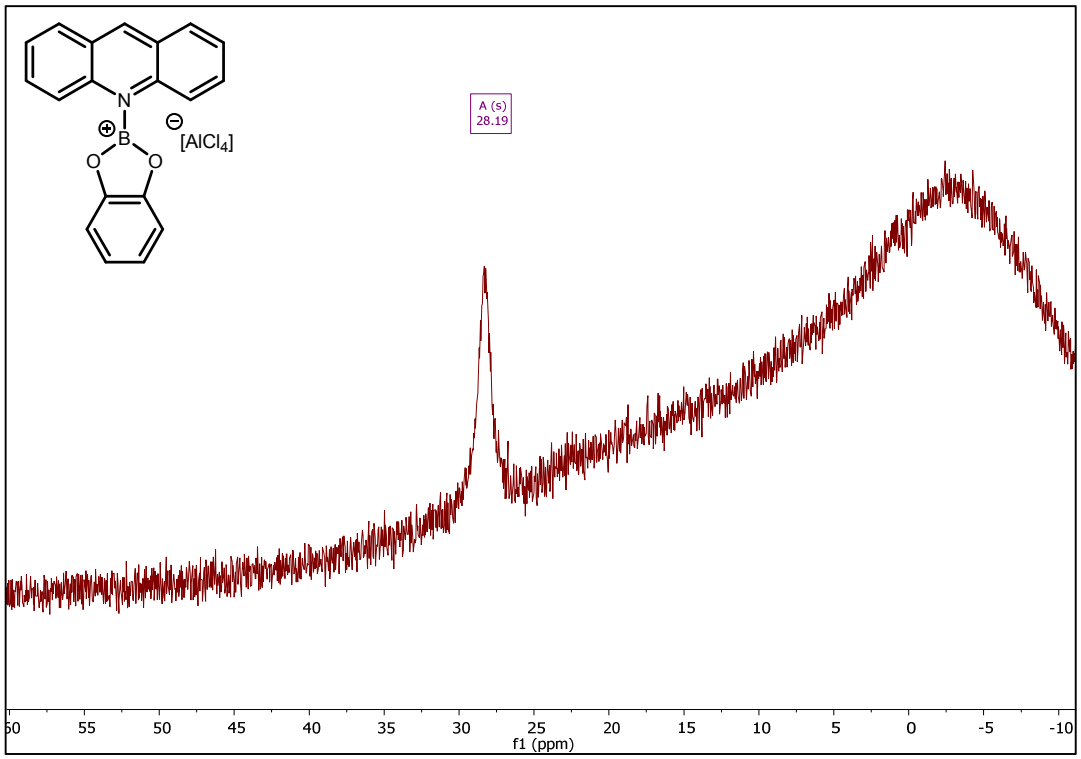

Figure S54: $^{11}B\{^{1}H\}$ NMR (160 MHz, DCM-d_2, 298K) spectrum of [Acr-BCat][$AlCl_4$]

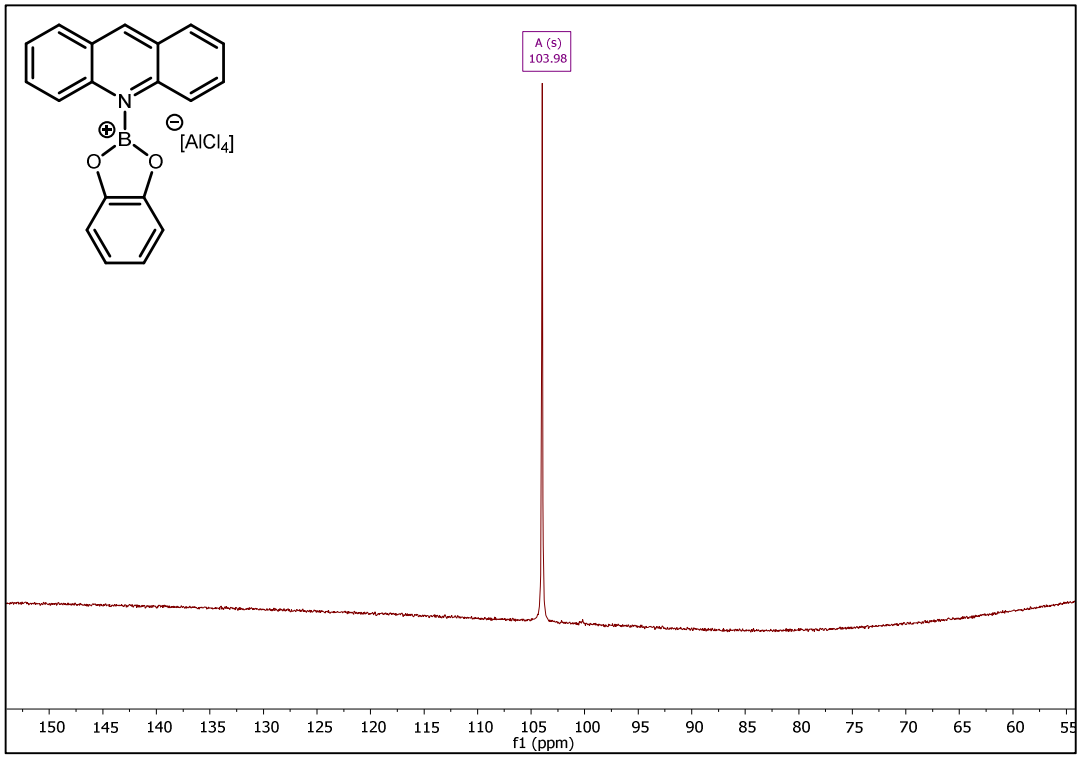

Figure S55: ^{27}Al NMR (104 MHz, DCM-d_2, 298K) spectrum of [Acr-BCat][$AlCl_4$]

9.2 [F_5Acr-BCat][$AlCl_4$]

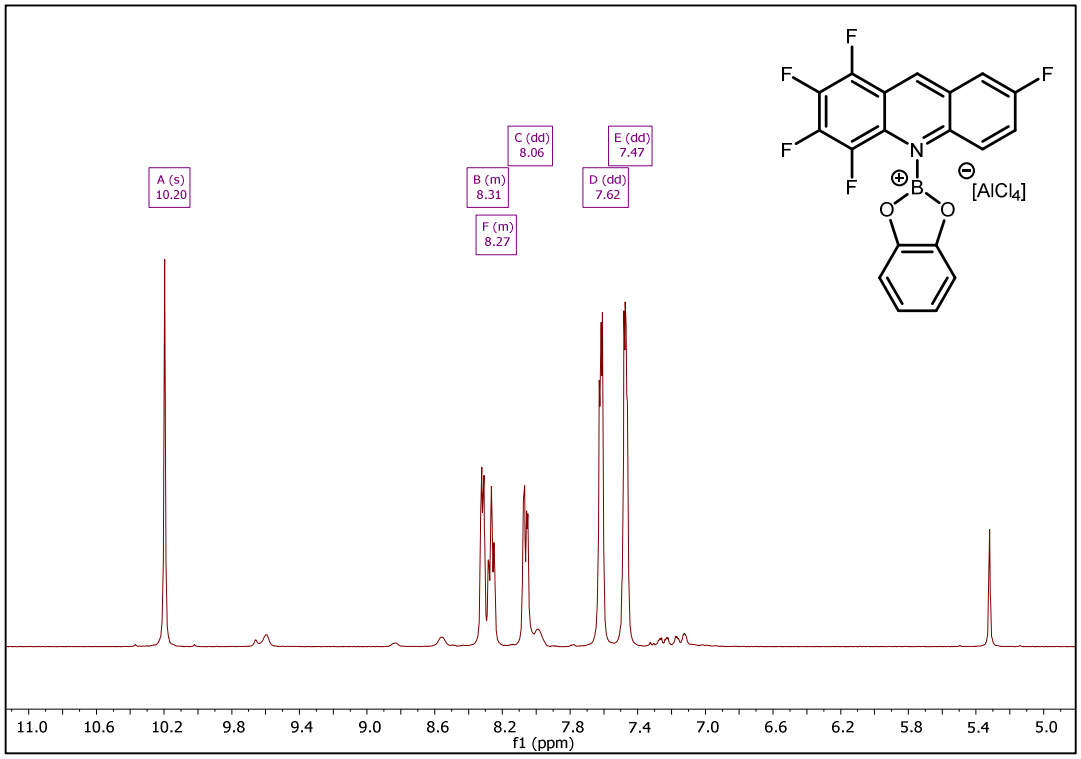

Figure S56: ^{1}H NMR (500 MHz, DCM-d_2, 298K) spectrum of [F_5Acr-BCat][$AlCl_4$]

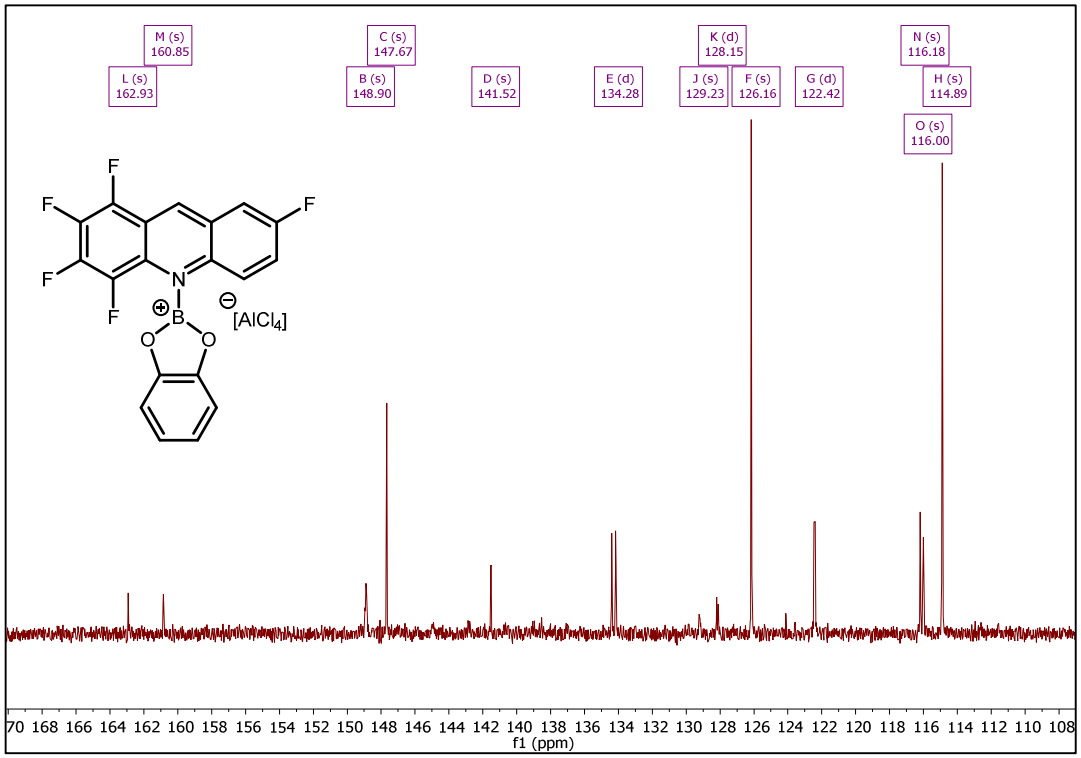

Figure S57: $^{13}C\{^{1}H\}$ NMR (126 MHz, DCM-d_2, 298K) spectrum of $[F_5Acr\text{-}BCat][AlCl_4]$

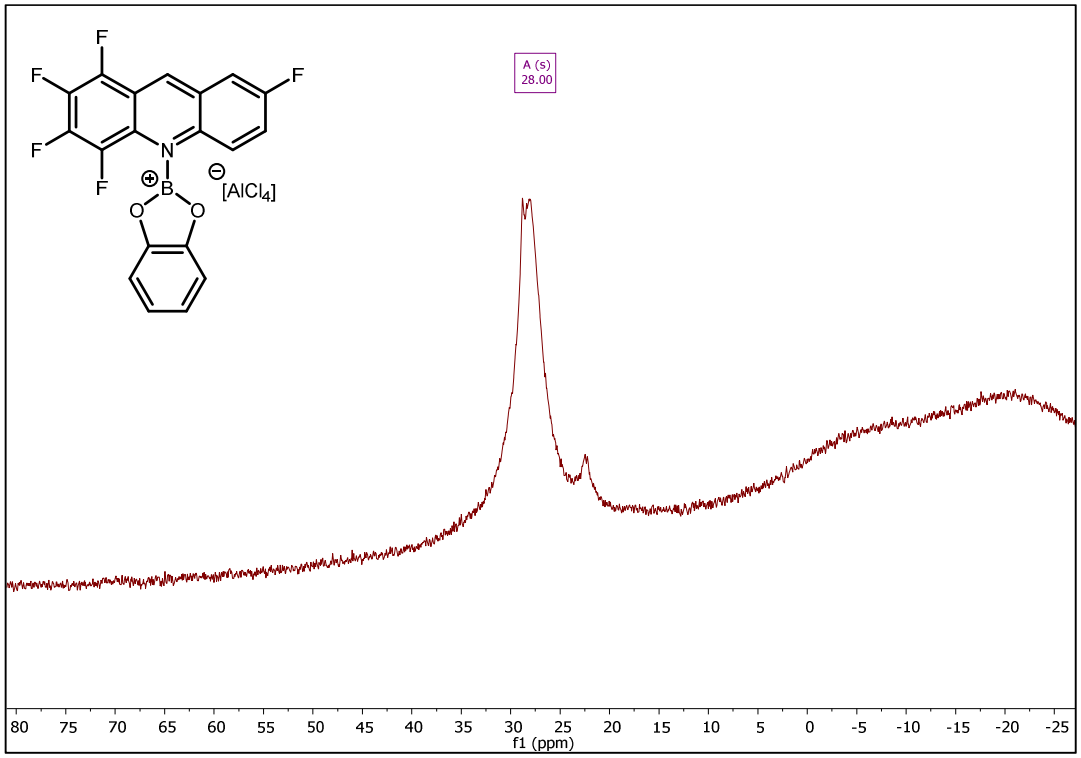

Figure S58: $^{11}B\{^{1}H\}$ NMR (160 MHz, DCM-d_2, 298K) spectrum of $[F_5Acr\text{-}BCat][AlCl_4]$

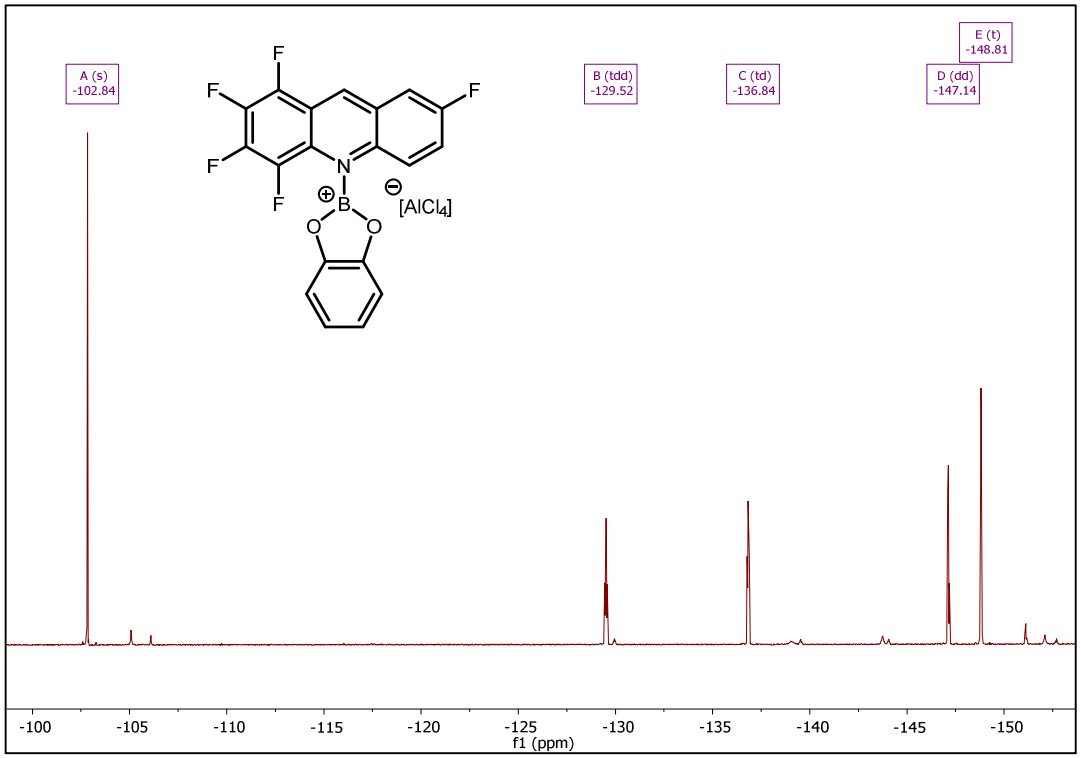

Figure S59: ^{19}F NMR (376 MHz, DCM-d_2, 298K) spectrum of [F_5Acr-BCat][$AlCl_4$]

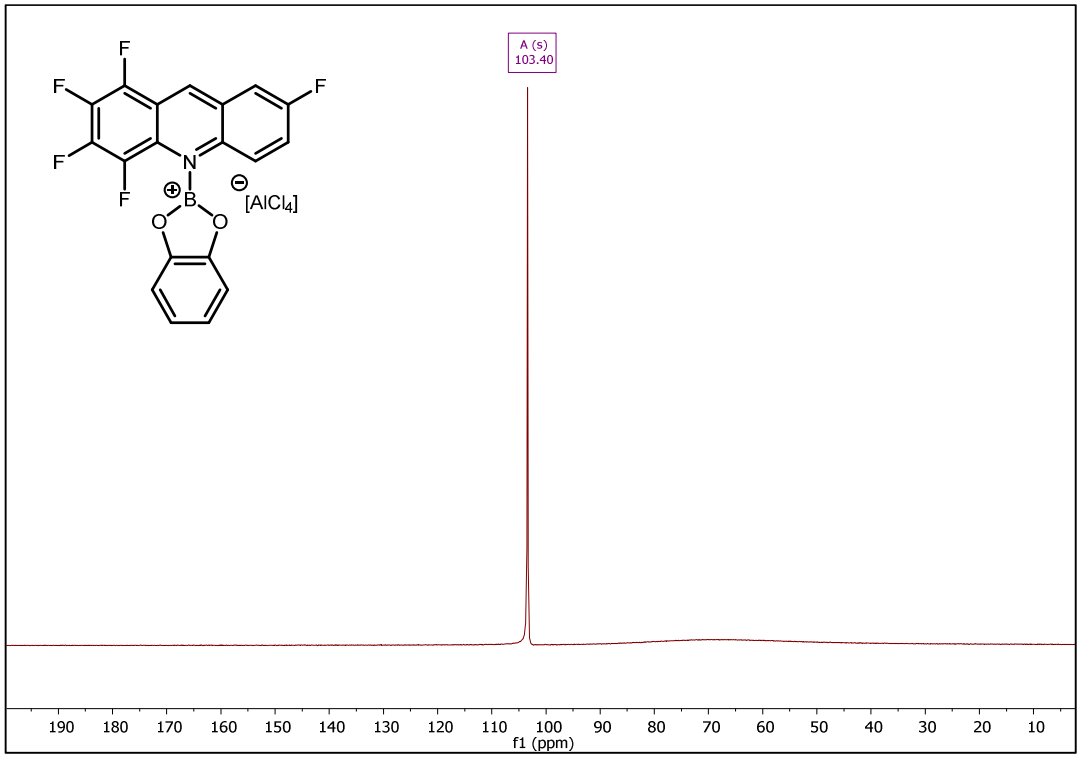

Figure S60: ^{27}Al NMR (104 MHz, DCM-d_2, 298K) spectrum of [F_5Acr-BCat][$AlCl_4$]

9.3 F_5Acr-$AlCl_3$

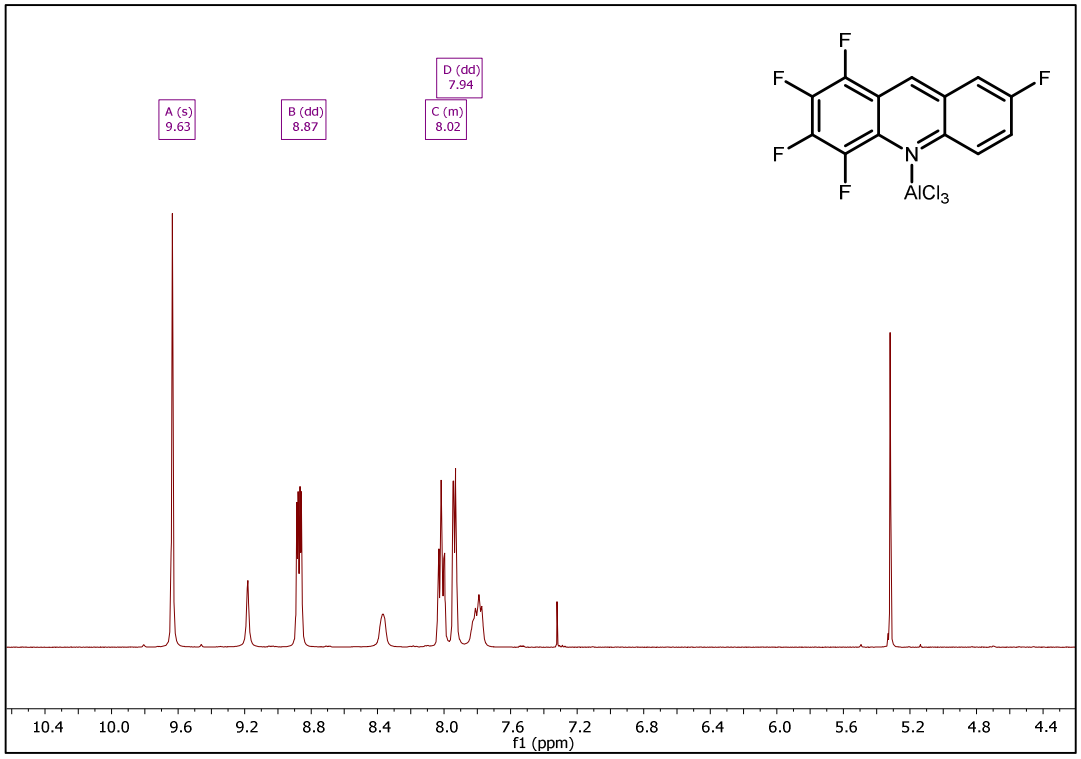

Figure S61: ^{1}H NMR (500 MHz, DCM-d_2, 298K) spectrum of F_5Acr-$AlCl_3$

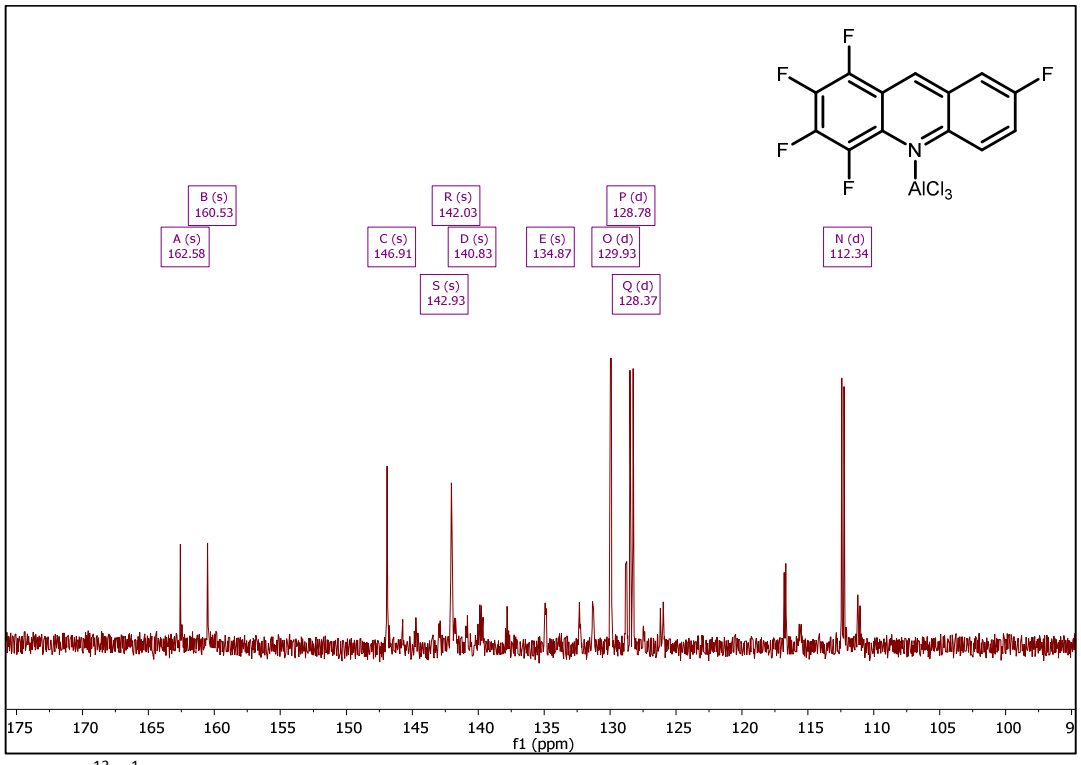

Figure S62: ^{13}C{^{1}H} NMR (126 MHz, DCM-d_2, 298K) spectrum of F_5Acr-$AlCl_3$

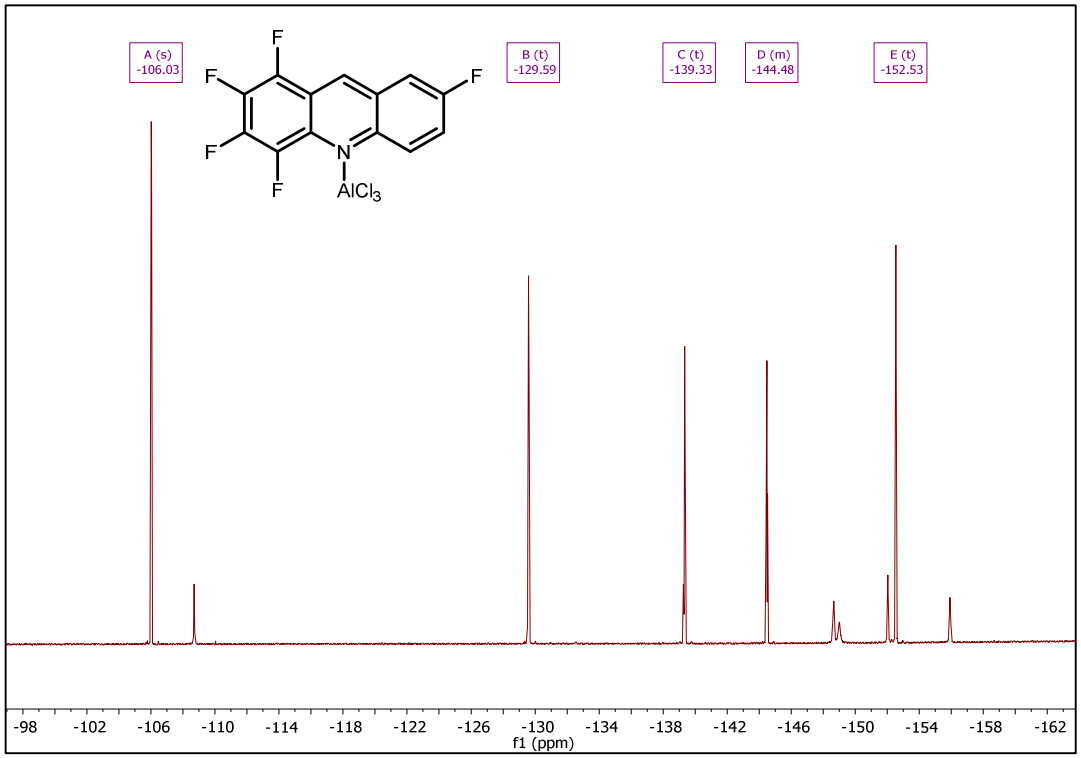

Figure S63: $^{19}F\{^{1}H\}$ NMR (376 MHz, DCM-d_2, 298K) spectrum of F_5Acr-$AlCl_3$

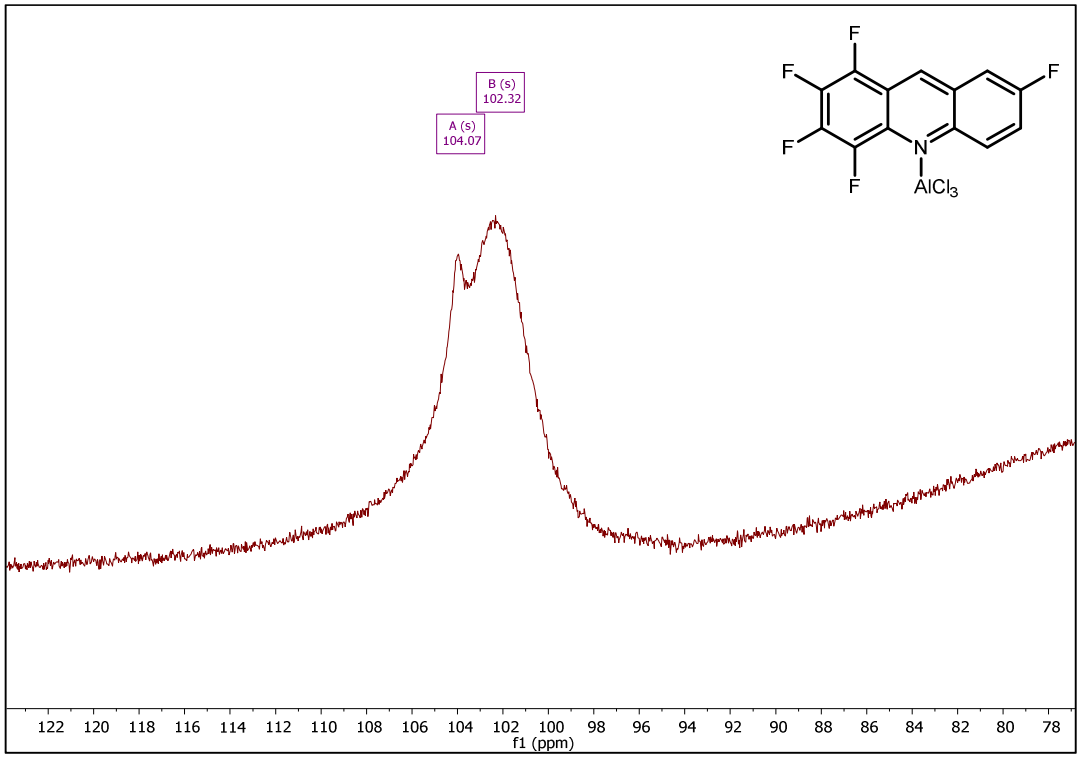

Figure S64: ^{27}Al NMR (104 MHz, DCM-d_2, 298K) spectrum of mixture of $AlCl_3$ and F_5Acr-$AlCl_3$

10 Reference

[1] Adamson, A. J.; Banks, R. E.; Tipping, A. E. *J. Fluorine Chem.* **1993**, *64*, 5-10.
[2] Clark, E. R.; Ingleson, M. J. *Organometallics* **2013**, *32*, 6712-6717.
[3] Keyzer, E. N., Kang, S. S., Hanf, S., Wright, D. S., *Chem. Commun*., **2017**, *53*, 9434-9437
[4] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**
[5] Clark, E. R., Ingleson, M. J., *Angew. Chem. Int. Ed*., **2014**, *53*, 11306-11309
[6] Clark, E. R., Del Grosso, A., Ingleson, M. J., *Chem. Eur. J*. **2013**, *19*, 2462-2466
[7] CrysAlisPro, Agil. Technol. Version 1.1 71.35.19 (release 27-10-2011 CrysAlis171.NET) (compiled Oct 27 2011,150211)
[8] Dolomanov, O. V., Bourhis, L. J., Gildea. R. J., Howard. J. A. K., and Puschmann, H. *J. Appl. Crystallogr*. **2009**, *42*, 339-341
[9] Sheldrick, G. M., *Acta Cryst*. **2015**, *A71*, 3-8.
[10] Sheldrick, G. M., *Acta Cryst*. **2015**, *C71*, 3-8.