Supporting Information

Benzotriazolium Salts: Emergent Readily Accessible Bench-stable Lewis Acid Catalysts

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1. General Information

$^1$H, $^{13}$C, $^{19}$F, $^{11}$B and $^{31}$P-NMR spectra were recorded in CDCl$_3$ (reference signals: $^1$H = 7.26 ppm; $^{13}$C = 77.16 ppm) or acetone-$d_6$ (reference signals: $^1$H = 2.05 ppm; $^{13}$C = 29.84 ppm) on a Bruker Avance II 300 or Bruker Avance II 400. NMR chemical shifts are referenced to the corresponding solvent signals, chemical shifts ($\delta$) are given in ppm and spin-spin coupling constants ($J$) are given in Hz. Analytical thin layer chromatography was performed using silica gel 60 F254 and column chromatography was performed on silica gel 60 (0.040-0.063 mm). ESI high resolution masses were measured on an Orbitrap LTQ XL (Thermo-Fisher Scientific, Bremen) with nano spray (alternatively loop injection). Electron ionization (EI) high resolution masses were measured on an Exact GC Orbitrap (Thermo-Fisher Scientific, Bremen). EI low resolution masses were measured on an ISQ 7000 GC/MS (Thermo-Fisher Scientific, Bremen). Solvents and commercially available reagents were used without further purification. Compounds 4,$^1$ 6,$^2$ Me$_2$-BZT$I$ salt,$^3$ NaB(C$_6$F$_5$)$_4$,$^4$ and [H(OEt)$_2$]$_2$[B(C$_6$F$_5$)$_4$]$^5$ were synthesized according to literature known procedures.

2. Synthesis of the Nitrenium Catalysts 1-3

General Procedure A:
The reaction between the corresponding triazole (1.0 eq.) and MeOTf or Me$_3$OBF$_4$ (3.0 eq. for double methylation or 1.5 eq. for one side methylation) in DCM (0.1 M) was set up inside the Glovebox. After stirring for 2-3 days, the reaction was purified under ambient atmosphere by quenching with MeOH and precipitation in Et$_2$O. The precipitate was washed multiple times with Et$_2$O until the washing solution was pH neutral and the obtained triazolium salt was dried under high vacuum.
1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium trifluoromethanesulfonate (1a)

According to general procedure A, benzotriazole (238.3 mg, 2.0 mmol, 1.0 eq.) and methyl trifluoromethanesulfonate (0.91 mL, 6.0 mmol, 3.0 eq.) were dissolved in DCM (20 mL) and stirred at room temperature for 3 days to yield the desired product 1a (302.0 mg, 1.09 mmol, 51%). \(^{1}H\) NMR (400 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 8.40 – 8.34 (m, 2H), 8.05 – 8.00 (m, 2H), 4.75 (s, 6H); \(^{13}C\) NMR (100 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 136.4, 131.9, 122.1 (q, J = 321.8 Hz), 114.6, 38.4; \(^{19}F\) NMR (376 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -78.92.\)

1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (1b)

According to general procedure A, benzotriazole (238.3 mg, 2.0 mmol, 1.0 eq.) and trimethylxonium tetrafluoroborate (887.4 mg, 6.0 mmol, 3.0 eq.) were dissolved in DCM (20 mL) and stirred at room temperature for 3 days to yield the desired product 1b (388.4 mg, 1.65 mmol, 83%). \(^{1}H\) NMR (400 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 8.43 – 8.37 (m, 1H), 8.11 – 8.05 (m, 1H), 4.82 (s, 2H); \(^{13}C\) NMR (100 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 136.4, 131.9, 114.6, 38.3; \(^{19}F\) NMR (376 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -150.51.\) \(^{19}B\) NMR (128 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -0.87.\)

Alternative synthetic route:

According to a modified literature known procedure, the previously freshly synthesized 1,3-dimethyl-1H-benzo[d][1,2,3]triazol-3-ium iodide (Me₂BZT⁺I⁻)\(^{19}\) (550.2 mg, 2.0 mmol, 1.0 eq., pale-yellow solid) and silver tetrafluoroborate (389.3 mg, 2.0 mmol, 1.0 eq.) were dissolved in DCM (20 mL) and stirred at room temperature for 18 hours under argon and in the dark. The mixture was filtered through celite to remove insoluble silver salts (intense yellow solid of AgI) and concentrated under reduced pressure to yield the desired product 1b (429.0 mg, 1.82 mmol, 91%) as a white solid.

* Note: The I⁻/BF₄⁻ anion exchange with NaBF₄ did not take place under similar reaction conditions.

1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1c)

According to general procedure B, 1,3-dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (47.0 mg, 0.2 mmol, 1.0 eq.) and sodium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (212.7 mg, 0.24 mmol, 1.2 eq.) were dissolved in DCM (4 mL) and stirred at room temperature for 18 h to yield the desired product 1c (189.7 mg, 0.19 mmol, 94%). \(^{1}H\) NMR (400 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 8.43 – 8.37 (m, 2H), 8.12 – 8.06 (m, 2H), 7.81 – 7.77 (m, 8H), 7.68 (t, J = 2.0 Hz, 4H), 4.82 (s, 6H); \(^{13}C\) NMR (100 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 163.7 – 161.6 (m), 136.5, 135.6, 132.2, 130.6 – 129.5 (m), 125.4 (q, J = 271.8 Hz), 118.7 – 116.3 (m), 114.6, 38.4; \(^{19}F\) NMR (376 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -63.24; \(^{19}B\) NMR (128 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -6.48.\)

* Note: Alternatively, 1c can also be obtained in 99% by anion exchange from Me₂-BZT⁺I⁻ with NaBAr₅⁻ in CH₂Cl₂ at room temperature.

1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis(pentafluorophenyl)borate (1d)

According to general procedure B, 1,3-dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (47.0 mg, 0.2 mmol, 1.0 eq.) and potassium tetrais(pentafluorophenyl)borate (172.4 mg, 0.24 mmol, 1.2 eq.) were dissolved in DCM (4 mL) and stirred at room temperature for 18 h to yield the desired product 1d (144.8 mg, 0.18 mmol, 88%). \(^{1}H\) NMR (400 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 8.43 – 8.38 (m, 2H), 8.07 (dd, J = 6.6, 3.1 Hz, 2H), 4.82 (s, 6H); \(^{13}C\) NMR (100 MHz, acetone-\(d_{6}\)) \(\delta/ppm = 150.6 – 150.1 (m), 148.3 – 147.6 (m), 140.6 – 140.1 (m), 138.6 – 138.1 (m), 138.1 – 137.7 (m), 136.2 – 135.6 (m), 132.2, 114.6, 38.4; \(^{19}F\) NMR (376 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -131.70 – 134.84 (m), -164.31 (t, J = 19.9 Hz), -168.26 (t, J = 19.1 Hz). \(^{19}B\) NMR (128 MHz, acetone-\(d_{6}\)) \(\delta/ppm = -16.60.\)

* Note: Alternatively, 1d can also be obtained in 98% by anion exchange from Me₂-BZT⁺I⁻ with NaB(CF₃)₅⁻ in CH₂Cl₂ at room temperature.
1-(2,2,2-Trifluoroethyl)-1H-benzo[d][1,2,3]triazole (8)

According to a modified procedure published before, benzotriazole (95.3 mg, 0.8 mmol, 1.0 eq.) and potassium tert-butoxide (89.8 mg, 0.8 mmol, 1.0 eq.) were dissolved in a mixture of THF (4 mL) and MeCN (4 mL). Inside a glovebox, a mixture of trifluoroethyl trifluoromethanesulfonate (230.7 μL, 1.6 mmol, 2.0 eq.) was added and the mixture was stirred for 2 days at room temperature. The solvent was removed and the residue purified by column chromatography (pentane/EtOAc 8:2) yielding the desired product 8 (95.7 mg, 0.48 mmol, 59%).

$^1$H NMR (400 MHz, CDCl$_3$) δ/ppm = 8.12 (dt, J = 8.4, 1.0 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.47 – 7.41 (m, 1H), 5.24 (q, J = 8.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ/ppm = 146.1, 133.4, 128.7, 124.7, 123.0 (q, J = 280.1 Hz), 120.5, 109.2 (d, J = 1.3 Hz), 49.3 (q, J = 36.3 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ/ppm = -70.34; HRMS (ESI): m/z calculated for C$_6$H$_4$F$_3$N$_3$Na$^+$ [M + Na$^+$] = 224.0406; found: 224.0403.

3-Methyl-1-(2,2,2-trifluoroethyl)-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (1e)

According to general procedure A, 1-(2,2,2-trifluoroethyl)-1H-benzo[d][1,2,3]triazole (95.7 mg, 0.48 mmol, 1.0 eq.) and trimethylsilyl tetrafluoroborate (105.6 mg, 0.71 mmol, 1.5 eq.) were dissolved in DCM (5 mL) and stirred at room temperature for 3 days to yield the desired product 1e (132.3 mg, 0.43 mmol, 91%). $^1$H NMR (400 MHz, acetone-d$_6$) δ/ppm = 8.50 (d, J = 8.6 Hz, 2H), 8.20 – 8.10 (m, 2H), 6.26 (q, J = 8.4 Hz, 2H), 4.90 (s, 3H); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ/ppm = 136.9, 133.5, 132.5, 123.5 (q, J = 279.2 Hz), 115.4, 114.2, 51.8 (q, J = 36.4 Hz), 39.3; $^{19}$F NMR (376 MHz, acetone-d$_6$) δ/ppm = -70.51, -151.75; $^1$B NMR (128 MHz, acetone-d$_6$) δ/ppm = -1.02; HRMS (ESI): m/z calculated for C$_6$H$_4$F$_3$N$_3$B$^+$ [M – BF$_4$]$^+$ = 216.0743; found: 216.0739.

3-Methyl-1-(2,2,2-trifluoroethyl)-1H-benzo[d][1,2,3]triazol-3-ium tetrais(pentafluorophenyl)borate (1f)

According to general procedure B, 3-methyl-1-(2,2,2-trifluoroethyl)-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (168.5 mg, 0.24 mmol, 1.2 eq.) were dissolved in DCM (4 mL) and stirred at room temperature for 18 h to yield the desired product 1f (174.8 mg, 0.19 mmol, 98%). $^1$H NMR (400 MHz, acetone-d$_6$) δ/ppm = 8.57 – 8.51 (m, 2H), 8.24 – 8.14 (m, 2H), 6.34 (q, J = 8.3 Hz, 2H), 4.96 (s, 3H); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ/ppm = 150.5 – 150.0 (m), 148.1 – 147.6 (m), 140.6 – 140.1 (m), 138.6 – 138.1 (m), 131.8 – 137.7 (m), 137.0, 136.2 – 135.6 (m), 133.7, 132.7, 123.5 (q, J = 279.2 Hz), 115.4, 114.2, 51.9 (q, J = 36.4 Hz), 39.4; $^{19}$F NMR (376 MHz, acetone-d$_6$) δ/ppm = -70.54, -132.89 – 133.16 (m), -164.40 (t, J = 20.0 Hz), -168.36 (t, J = 18.6 Hz); $^1$B NMR (128 MHz, acetone-d$_6$) δ/ppm = -16.61.

N-(2-Nitrophenyl)-3,5-bis(trifluoromethyl)aniline (9)

N-(2-Nitrophenyl)-3,5-bis(trifluoromethyl)aniline (0.78 mL, 5.0 mmol, 1.0 eq.) and potassium tert-butoxide (673.3 mg, 6.0 mmol, 1.2 eq.) were dissolved in DMF (20 mL). The reaction was heated within an aluminum block to 90 °C and stirred for 2 h. The mixture was cooled to room temperature and 1-fluoro-2-nitrobenzene (0.63 mL, 6.0 mmol, 1.2 eq.) was added. It was heated again within an aluminum block to 90 °C and stirred for 2 days. After cooling to room temperature, the mixture was diluted with DCM, washed with water, dried over MgSO$_4$ and the solvent was removed. The residue was purified by column chromatography (pentane/EtOAc 98:2) to yield the desired product 9 (369.4 mg, 1.05 mmol, 21%) as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ/ppm = 9.48 (s, 1H), 8.24 (dd, J = 8.5, 1.6 Hz, 1H), 7.72 (s, 2H), 7.65 (s, 1H), 7.53 (ddd, J = 8.6, 7.0, 1.6 Hz, 1H), 7.33 (ddd, J = 8.5, 1.3 Hz, 1H), 6.99 (ddd, J = 8.4, 7.1, 1.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ/ppm = 141.3, 140.3, 138.2, 135.3, 133.4 (q, J = 33.6 Hz), 127.1, 123.1 (q, J = 272.9 Hz), 122.4 – 122.1 (m), 120.1, 118.0 (hept, J = 3.6 Hz), 116.3; $^{19}$F NMR (376 MHz, CDCl$_3$) δ/ppm = -63.14; HRMS (ESI): m/z calculated for C$_{15}$H$_{19}$N$_3$O$_4$F$_2$ [M – H$^+$] = 349.0406; found: 349.0411.

N’-[3,5-Bis(trifluoromethyl)phenyl]benzene-1,2-diamine (10)

N’-(2-Nitrophenyl)-3,5-bis(trifluoromethyl)aniline (483.2 mg, 1.38 mmol, 1.0 eq.) was dissolved in DCM (15 mL) and palladium on carbon (10 w%, 73.4 mg, 0.07 mmol, 0.05 eq.) was added. The mixture was stirred at room temperature and under hydrogen atmosphere for 18 h. The mixture was filtered and purified by column filtration (DCM) to yield the desired product 10 (288.4 mg, 0.9 mmol, 65%). $^1$H NMR (400 MHz, CDCl$_3$) δ/ppm = 7.26 (s, 1H), 7.16 – 7.09 (m, 2H), 7.05 (s, 2H), 6.88 – 6.78 (m, 2H), 5.57 (s, 1H), 3.70 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ/ppm = 147.0, 142.8, 132.7 (q, J = 32.9 Hz), 127.8, 126.5, 125.6, 123.6 (q, J = 272.7 Hz), 119.5, 116.7, 114.0 – 113.8 (m), 112.1 (hept, J = 3.9 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ/ppm = -63.14; HRMS (ESI): m/z calculated for C$_{15}$H$_{19}$N$_3$O$_4$F$_2$ [M + H$^+$] = 321.0821; found: 321.0821.
1-(3,5-Bis(trifluoromethyl)phenyl)-1H-benzo[d][1,2,3]triazole (11)

According to general procedure A, 1-(3,5-bis(trifluoromethyl)phenyl)-1H-benzo[d][1,2,3]triazole (244.6 mg, 0.74 mmol, 1.0 eq.) and sodium tetrakis[methyl(trifluoromethyl)borate] (106.3 mg, 0.12 mmol, 1.2 eq.) were dissolved in DCM (2 mL) and stirred at room temperature for 18 h to yield the desired product 11 (76.0 mg, 0.07 mmol, 74%). 1H NMR (400 MHz, acetone-d6) δ/ppm = 8.81 (s, 2H), 8.65 (s, 1H), 8.64 – 8.58 (m, 1H), 8.54 – 8.48 (m, 1H), 8.25 – 8.19 (m, 2H), 7.80 (s, 8H), 7.68 (s, 4H), 5.06 (s, 3H). 13C NMR (100 MHz, acetone-d6) δ/ppm = 163.5 – 161.8 (m), 137.0, 136.7, 136.3, 135.7 – 135.5 (m), 134.6 (q, J = 34.8 Hz), 134.0, 132.9, 130.6 – 129.5 (m), 127.5 – 127.3 (m), 127.3 – 127.1 (m), 125.4 (q, J = 271.8 Hz), 123.6 (q, J = 272.5 Hz), 118.6 – 118.3 (m), 115.2, 115.0, 39.4; 19F NMR (376 MHz, acetone-d6) δ/ppm = -63.45, -132.94 – -133.16 (m), -164.43 (t, J = 19.9 Hz), -168.38 (t, J = 19.1 Hz). 1B NMR (128 MHz, acetone-d6) δ/ppm = -16.61.

1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium trifluoromethanesulfonate (2a)

According to general procedure A, 1H-benzo[d][1,2,3]triazol-1-ol (270.3 mg, 2.0 mmol, 1.0 eq.) and methyl trifluoromethanesulfonate (0.91 mL, 6.0 mmol, 3.0 eq.) were dissolved in DCM (20 mL) and stirred at room temperature for 2 days to yield the desired product 2a (150.1 mg, 0.48 mmol, 24%). 1H NMR (400 MHz, acetone-d6) δ/ppm = 8.47 – 8.40 (m, 1H), 8.38 – 8.31 (m, 1H), 8.14 – 8.07 (m, 2H), 7.48 – 4.75 (m, 6H). 13C NMR (100 MHz, acetone-d6) δ/ppm = 136.6, 133.0, 132.9, 130.0, 122.0 (q, J = 321.5 Hz), 115.1, 112.9, 71.2, 38.9; 19F NMR (376 MHz, acetone-d6) δ/ppm = -78.97; HRMS (ESI): m/z calculated for C20H16NO2+ [M + OTf] = 304.0818; found: 304.0816.

1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (2b)

According to general procedure A, 1-hydroxybenzotriazole (270.3 mg, 2.0 mmol, 1.0 eq.) and trimethylsilylchloride (0.91 mL, 6.0 mmol, 3.0 eq.) were dissolved in DCM (20 mL) and stirred at room temperature for 3 days to yield the desired product 2b (229.7 mg, 0.92 mmol, 46%). 1H NMR (400 MHz, acetone-d6) δ/ppm = 8.45 – 8.39 (m, 1H), 8.37 – 8.31 (m, 1H), 8.14 – 8.08 (m, 2H), 7.99 – 7.68 (m, 2H). 13C NMR (100 MHz, acetone-d6) δ/ppm = 138.7, 133.1, 133.0, 115.1, 113.0, 71.3, 38.9; 19F NMR (376 MHz, acetone-d6) δ/ppm = -152.12; 1B NMR (128 MHz, acetone-d6) δ/ppm = -11.11; HRMS (ESI): m/z calculated for C20H16NO2+ [M – BF4] = 164.0818; found: 164.0816.
1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (2c)

According to general procedure B, 1-methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (25.1 mg, 0.1 mmol, 1.0 eq.) and sodium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (106.3 mg, 0.12 mmol, 1.2 eq.) were dissolved in DCM (2 mL) and stirred at room temperature for 18 h to yield the desired product 2c (94.5 mg, 0.09 mmol, 92%).

H NMR (400 MHz, acetone-d6) δ/ppm = 5.80 – 5.93 (m, 1H), 3.91 – 4.00 (m, 1H), 1.38 – 1.46 (m, 1H), 0.78 – 0.96 (m, 1H), 0.65 (s, 1H), 0.58 (s, 1H), 0.18 (d, J = 7.4 Hz, 1H), 0.10 (d, J = 7.4 Hz, 1H).

13C NMR (100 MHz, acetone-d6) δ/ppm = 135.5 (m), 133.3, 133.1, 130.1 (qdd, J = 31.5, 5.7, 2.8 Hz), 125.4 (q, J = 271.8 Hz), 118.6 – 118.3 (m), 115.0, 113.1, 71.3, 39.0; 19F NMR (376 MHz, acetone-d6) δ/ppm = -63.24; 11B NMR (128 MHz, acetone-d6) δ/ppm = -6.54.

1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetraakis(pentafluorophenyl)borate (2d)

According to general procedure B, 1-methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (25.1 mg, 0.1 mmol, 1.0 eq.) and potassium tetraakis(pentafluorophenyl)borate (86.2 mg, 0.12 mmol, 1.2 eq.) were dissolved in DCM (2 mL) and stirred for 18 h at room temperature to yield the desired product 2d (73.8 mg, 0.09 mmol, 88%).

H NMR (400 MHz, acetone-d6) δ/ppm = 8.50 – 8.43 (m, 1H), 8.41 – 8.35 (m, 1H), 8.19 – 8.12 (m, 2H), 4.83 (s, 3H), 4.78 (s, 3H); 13C NMR (100 MHz, acetone-d6) δ/ppm = 150.5 – 150.1 (m), 148.1 – 147.7 (m), 140.7 – 140.1 (m), 138.6 – 138.1 (m), 138.1 – 137.6 (m), 136.8, 136.2 – 135.6 (m), 133.3, 133.1, 130.1, 115.0, 113.1, 71.3, 39.0; 19F NMR (376 MHz, acetone-d6) δ/ppm = -132.90 – -132.24 (m), -164.39 (t, J = 20.0 Hz), -168.35 (t, J = 18.8 Hz); 11B NMR (128 MHz, acetone-d6) δ/ppm = -16.63.

1H-Naphtho[1,8-de][1,2,3]triazine (12)

According to a previously reported procedure, naphthalene-1,8-diamine (7.9 g, 50.0 mmol, 1.0 eq.) was dissolved in water (21 mL) and AcOH (90 mL). The mixture was cooled to 0 °C and a second solution of sodium nitrite (3.6 g, 52.5 mmol, 1.05 eq.) in water (21 mL) was added. After stirring for 1 h at 0 °C, the brown precipitate was filtered off, washed with water and dried under high vacuum at 50 °C in an aluminum block, yielding the desired product 12 (8.0 g, 47.6 mmol, 95%).

H NMR (400 MHz, DMSO-d6) δ/ppm = 13.28 (s, 1H), 7.26 (s, 2H), 7.14 (s, 1H), 7.04 (s, 1H), 6.89 (s, 1H), 6.14 (s, 1H). The analytical data is in accordance with the one in the literature.

3-Methyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium trifluoromethanesulfonate (3a)

According to a previously reported procedure, 1H-naphtho[1,8-de][1,2,3]triazine (338.4 mg, 2.0 mmol, 1.0 eq.) was dissolved in DCM (20 mL), methyl trifluoromethanesulfonate (679 µL, 6.0 mmol, 3.0 eq.) was added and the mixture was stirred for 3 days at room temperature. The reaction was quenched with Methanol and the solvent was removed. The residue was purified by a short column chromatography (DCM → DCM/MeOH 10:1), yielding the desired product 3a (354.3 mg, 1.02 mmol, 51%).

H NMR (400 MHz, acetone-d6) δ/ppm = 7.74 (d, J = 8.5 Hz, 1H), 7.58 (t, J = 8.1 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 4.07 (s, 2H); 13C NMR (100 MHz, acetone-d6) δ/ppm = 134.6, 132.3, 130.0, 127.1, 123.2, 122.1 (q, J = 321.3 Hz), 109.0, 44.8; 19F NMR (376 MHz, acetone-d6) δ = -78.95. The analytical data is in accordance with the one in the literature.

3-Methyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium tetrafluoroborate (3b)

According to a slightly modified procedure, 1H-naphtho[1,8-de][1,2,3]triazine (338.4 mg, 2.0 mmol, 1.0 eq.) was dissolved in DCM (20 mL), trimethylsilyltrimethylsilylborate (887.4 mg, 6.0 mmol, 3.0 eq.) was added and the mixture was stirred for 3 days at room temperature. The reaction was quenched with Methanol and the solvent was removed. The residue was purified by a short column chromatography (DCM → DCM/MeOH 10:1), yielding the desired product 3b (150.8 mg, 0.53 mmol, 26%).

H NMR (400 MHz, acetone-d6) δ/ppm = 7.75 (d, J = 8.6 Hz, 1H), 7.59 (t, J = 8.1 Hz, 7H), 7.23 (d, J = 7.7 Hz, 8H), 4.08 (s, 2H); 13C NMR (100 MHz, acetone-d6) δ/ppm = 134.5, 132.3, 130.0, 127.0, 123.2, 109.0, 44.7; 19F NMR (376 MHz, acetone-d6) δ/ppm = -152.67; 11B NMR (128 MHz, acetone-d6) δ/ppm = -0.97.

3-Methyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium tetraakis(pentafluorophenyl)borate (3c)

According to a previously reported procedure, 1,3-dimethyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium trifluoromethanesulfonate (20.2 mg, 0.06 mmol, 1.0 eq.) was dissolved in DCM and K[BCF3][3] (50.0 mg, 0.07 mmol, 1.2 eq.) was added. After stirring for 18 h, the precipitate was filtered off, the solvent of the filtrate reduced and the desired product 3c (27.0 mg, 0.03 mmol, 51%) was precipitated in pentane. H NMR (400 MHz, acetone-d6) δ/ppm = 7.77 (d, J = 8.6 Hz, 2H), 7.61 (t, J = 8.1 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 4.13 (s, 6H); 13C NMR (100 MHz, acetone-d6) δ/ppm = 150.5 – 150.1 (m), 148.1 – 147.7 (m), 140.5 – 140.0 (m), 138.8 – 137.7 (m), 136.3 – 135.5 (m), 134.6, 132.3, 130.0, 127.2, 123.2, 109.0, 44.7; 19F NMR (376 MHz, acetone-d6) δ/ppm = -132.92 – -133.18 (m), -164.35 (t, J = 20.0 Hz), -168.32 (t, J = 18.4 Hz); 11B NMR (128 MHz, acetone-d6) δ/ppm = -16.62. The analytical data is in accordance with the one in the literature.
Bench/moisture stability:

\[
\text{BF}_3^- + \text{H}_2\text{O} \rightarrow \text{THF (air, 5d)} \quad \text{traces}
\]

Catalyst 1b (11.7 mg, 0.05 mmol, 1.0 eq.) was dissolved in THF (0.5 mL), water (0.9 µL, 0.05 mmol, 1.0 eq.) was added and the mixture was stirred under air and at room temperature. After 5 days the solvent was removed, the residue dried in vacuum and analyzed by NMR showing traces of decomposition compounds, which could be identified as mono and di-demethylation products by ESI-MS.

\[
\text{B(C}_6\text{F}_5)_4^- + \text{H}_2\text{O} \rightarrow \text{DCM (air, 5d)} \quad \text{no decomposition}
\]

Catalyst 1d (41.4 mg, 0.05 mmol, 1.0 eq.) was dissolved in DCM (0.5 mL), water (0.9 µL, 0.05 mmol, 1.0 eq.) was added and the mixture was stirred under air and at room temperature. After 5 days the solvent was removed, the residue dried in vacuum and analyzed by NMR, showing no change compared to the freshly synthetized catalyst.

3. Gutmann-Beckett Test

In order to benchmark the catalyst for a better comparison the Gutmann-Beckett test was performed and the Acceptor Number (AN) calculated. Every compound was reacted with OPEt in a 1:1 ratio in acetone-\text{d}_6 and investigated by \textsuperscript{31}P-NMR spectroscopy. The AN was calculated with the resulting shift and the following equation.

\[
\text{AN} = 2.21(\delta - 41)
\]

Table S1. Summary of \textsuperscript{31}P NMR chemical shifts and Acceptor Numbers (AN) for the nitrenium cations series 1-3.

| Nitrenium cation | Counteranion | \textsuperscript{31}P Shift [ppm] | AN  |
|------------------|--------------|----------------------------------|-----|
| -----            | OTf (1a)     | 47.58                            | 14.5|
| N=N               | BF\textsubscript{3}^- (1b) | 48.37                           | 16.3|
| N=N               | BAr\textsubscript{4}^- (1c)  | 48.06                           | 15.6|
| N=N               | B(C\textsubf{6}F\textsub{5})\textsubscript{4}^- (1d) | 47.65                          | 14.7|
| F\textsubscript{3}C \quad N=N \quad F\textsubscript{3}C | BF\textsubscript{3}^- (1e) | 47.68                          | 14.8|
| F\textsubscript{3}C \quad N=N \quad F\textsubscript{3}C | B(C\textsubf{6}F\textsub{5})\textsubscript{4}^- (1f) | 48.56                          | 16.7|
| F\textsubscript{3}C \quad N=N \quad F\textsubscript{3}C | BF\textsubscript{3}^- (1g) | 47.68                          | 14.8|
| F\textsubscript{3}C \quad N=N \quad F\textsubscript{3}C | BAr\textsubscript{4}^- (1h)  | 48.31                           | 16.2|
| F\textsubscript{3}C \quad N=N \quad F\textsubscript{3}C | B(C\textsubf{6}F\textsub{5})\textsubscript{4}^- (1i) | 48.56                          | 16.7|
| -----            | OTf (2a)     | 49.65                            | 19.1|
| N=N               | BF\textsubscript{3}^- (2b) | 48.11                           | 15.7|
| N=N               | BAr\textsubscript{4}^- (2c)  | 49.07                           | 17.8|
| N=N               | B(C\textsubf{6}F\textsub{5})\textsubscript{4}^- (2d) | 51.52                          | 23.2|
| -----            | OTf (3a)     | 53.02                            | 26.6|
| N=N               | BF\textsubscript{3}^- (3b) | 48.47                           | 16.5|
| N=N               | B(C\textsubf{6}F\textsub{5})\textsubscript{4}^- (3c) | 48.09                          | 15.7|
For a better understanding of the obtained Acceptor Numbers and comparison of the relative Lewis acidity of these systems presenting low AN difference, titration experiments with the catalyst series 1a-1d were performed in acetone-d$_6$. For every catalyst a 12.5 µM stock solution (A) and for OPEt$_3$ a 10.0 µM stock solution (B) was prepared. 100 µL from solution A was transferred to every NMR-Tube and different equivalents (0.2 – 3.0) of solution B were added to the single tubes. Finally, pure solvent was added to reach an overall volume of 0.55 mL of acetone-d$_6$ and the $^{31}$P-NMR was measured. With the obtained shifts from the NMR the association constants $K_A$ were calculated by using bindfit.

Table S2. Summary of the association constants ($K_A$) and Acceptor Numbers (AN) for the benzotriazolium series 1a-1d.

| Catalyst | $K_A$ [M$^{-1}$] | AN  | Catalyst | $K_A$ [M$^{-1}$] | AN  |
|----------|-----------------|-----|----------|-----------------|-----|
| 1a       | 1549            | 16.9| 1c       | 106             | 15.6|
| 1b       | 1016            | 16.3| 1d       | 20              | 14.7|
4. DFT Calculations

Methods

All calculations were performed with TURBOMOLE 7.5.1. The structures were optimized without any geometry constraints using the TPSS meta-GGA functional and an atom-pairwise dispersion correction (D3). A flexible triple zeta basis set (def2-TZVP) was used in all calculations. Harmonic force constants and vibrational frequencies were calculated and had only positive values, proving that the optimized structures are energetic minima. Single point energy DFT calculations to obtain orbital energies were performed with Turbomole using the hybrid functional PW6B95-D3. Free energies of solvation $G_{\text{solv}}$ were obtained with the COSMO-RS model for 298 K using acetone as solvent. Calculation of isotropic NMR chemical shielding (DFT-GIAO) was performed with B3LYP using the def2-TZVP basis set and the COSMO solvation model for acetone ($\varepsilon = 21.3$).

Results

Table S3: Electronic energies, enthalpy and free energy contributions of translation, rotation and harmonic vibration ($H_{298}$, $G_{298}$) after optimization (TPSS-D3/def2-TZVP) of all structures discussed in the supporting information. Electronic single point energies of these structures with PW6B95-D3/def2-TZVP. Solvation free energies $G_{\text{solv}}$ as obtained with COSMO-RS (solvent: acetone).

| Structure | $E_{\text{el}}$ (TPSS-D3) | $H_{298}$ (TPSS-D3) | $G_{298}$ (TPSS-D3) | $E_{\text{el}}$ (PW6B95-D3) | $G_{\text{solv}}$ COSMO-RS |
|-----------|--------------------------|---------------------|---------------------|-----------------------------|---------------------------|
| [BZT']    | -475.166857              | 114.87              | 86.55               | -475.661140                 | -44.82                    |
| [BZT'][OTf] | -1437.229256            | 137.72              | 96.89               | -1438.574971                | -21.05                    |
| [BZT'][BF$_4$] | -900.048724            | 128.09              | 91.23               | -900.978245                 | -21.36                    |
| [BZT'][B(C$_6$F$_5$)$_4$] | -3413.115222         | 265.31              | 185.63              | -3416.607306                | -30.02                    |
| [F][BZT'] | -575.228433              | 116.01              | 85.14               | -575.813052                 | -12.53                    |
| [F][BZT'][BF$_4$] | -1000.005257            | 129.21              | 89.16               | -1001.024677                | -55.63                    |
| [F][BZT'][OTf] | -1537.186384            | 138.84              | 94.65               | -1538.622301                | -53.91                    |
| [F][BZT'][B(C$_6$F$_5$)$_4$] | -3513.095078         | 266.44              | 183.18              | -3516.677988                | -49.17                    |
| O-CF$_3$  | -413.160767              | 12.52               | -7.99               | -413.566786                 | -52.76                    |
| O=CF$_2$  | -313.188582              | 11.16               | -7.34               | -313.497210                 | 2.53                      |
| Trityl$^+$ | -733.271544              | 183.08              | 147.81              | -734.069128                 | -40.37                    |
| TritylF    | -833.399663              | 184.63              | 147.31              | -834.302089                 | -10.79                    |
Figure S3: Optimized structures of benzotriazolium cation (BZT⁺) and ion pair complexes with OTf⁻, BF₄⁻ and B(C₆F₅)₄⁻ (TPSS-D3/def2-TZVP).

Figure S4: Frontier orbitals of [BZT⁺] and ion pair complexes with OTf⁻, BF₄⁻ and B(C₆F₅)₄⁻. If the HOMO does not contain atomic contributions of the BZT cation, the highest occupied MO with BZT contribution is shown in addition.
Table S4: Energies of frontier orbitals shown in Figure S4.\textsuperscript{[l]} Ionization potential (IP), electron affinity (EA) and derived values ($\eta$, $\mu$ and global electrophilicity index $\omega$)\textsuperscript{[ll]} for [BZT$^+$] and ion pairs (Figure S3).

|                | $\epsilon$(LUMO) [eV] | $\epsilon$(HOMO) [eV] | IP = $\epsilon$(HOMO) [eV] | EA = $\epsilon$(LUMO) [eV] | $\eta$ [eV] | $\mu$ [eV] | $\omega$ [eV] |
|----------------|------------------------|-----------------------|-----------------------------|-----------------------------|--------------|------------|------------|
| 1a, [BZT$^+$][OTf]$^-$ | -2.753                 | -6.862                | 6.862                       | 2.753                       | 4.109        | -4.807     | 2.81       |
| (HOMO-2)$^{[cd]}$ | -2.753                 | -8.029                | 8.029                       | 2.753                       | 5.276        | -5.391     | 2.75       |
| 1b, [BZT$^+$][BF$_4^-$]$^-$ | -2.694                 | -8.122                | 8.122                       | 2.694                       | 5.428        | -5.408     | 2.69       |
| 1d, [BZT$^+$][B(C$_6$F$_5$)$_4^-$]$^-$ | -3.580                 | -6.750                | 6.750                       | 3.580                       | 3.170        | -5.165     | 4.21       |
| (HOMO-8)$^{[cd]}$ | -3.580                 | -8.943                | 8.943                       | 3.580                       | 5.363        | -6.262     | 3.66       |
| [BZT$^+$]       | -6.228                 | -11.588               | 11.588                      | 6.228                       | 5.360        | -8.908     | 7.40       |

[a] PW6B95/def2-TZVP // TPSS-D3/def2-TZVP. [b] $\eta$ = IP - EA, $\mu$ = ($\eta$ + EA)/2, $\omega$ = $\mu^2/(2\eta)$. [c] Occupied orbital with highest orbital energy with AO contributions of the BZT$^+$ unit.

Figure S5: Donor-acceptor complexes of fluoride anion with BZT cation and ion pairs of BZT$^+$ with OTf$^-$, BF$_4^-$ and B(C$_6$F$_5$)$_4^-$ for the determination of the fluoride ion affinity (FIA).

The fluoride ion affinity has been calculated from the enthalpy of reaction (1) as $-\Delta$H$_{\text{FIA}}$ = $- (\Delta$H$_1$ - $\Delta$H$_2$).

\begin{align*}
(1) \quad & [\text{F}_2\text{CO}]^- + \text{LA} \rightarrow \text{F}_2\text{CO} + [\text{LA-F}]^- \\
(2) \quad & \text{F}_2\text{CO} + \text{F} \rightarrow [\text{F}_3\text{CO}]^- \\
(3) \quad & \text{LA} + \text{F} \rightarrow [\text{LA-F}]^{-} \\
\end{align*}

$\Delta$H$_1$ = 209 kJ/mol

Table S5: Fluoride ion affinity (FIA) of trityl cation, BZT cation and BzF/anion ion pairs.

|                | $\Delta$E (1) [kJ/mol] | $\Delta$H$_{\text{FIA}}$(1) [kJ/mol] | $\Delta$H (1) [kJ/mol] | FIA [kJ/mol] |
|----------------|------------------------|--------------------------------------|------------------------|--------------|
| Trityl$^+$     | -428.97                | 0.81                                 | -428.16                | 637.2        |
| [BZT$^+$]      | -216.17                | -0.92                                | -217.09                | 426.1        |
| 1a, [BZT$^+$][OTf]$^-$ | 58.40                  | -1.00                                | 57.40                  | 151.6        |
| 1b, [BZT$^+$][BF$_4^-$]$^-$ | 60.76                  | -0.98                                | 59.79                  | 149.2        |
| 1d, [BZT$^+$][B(C$_6$F$_5$)$_4^-$]$^-$ | -2.91                  | -0.95                                | -3.85                  | 212.9        |
5. Allylic Cyclization

5.1. Optimization Screening

Table S6. Reaction conditions screening for the allylic cyclization of 4a.

![Chemical Structure]

| Entry | Catalyst | Solvent | T        | 4a NMR-Yield [%] | 5a NMR-Yield [%] |
|-------|----------|---------|----------|------------------|------------------|
| 1     | 1a       | THF     | r.t.     | 4                | 1                |
| 2     | 1b       | THF     | r.t.     | 0                | 2                |
| 3     | 1d       | THF     | r.t.     | 0                | 0                |
| 4     | 3a       | THF     | r.t.     | 90               | 1                |
| 5     | 3b       | THF     | r.t.     | >99              | 0                |
| 6     | 1b       | DCM     | r.t.     | 0                | 0                |
| 7     | 1b       | ACN     | r.t.     | 48               | 3                |
| 8     | 1b       | ACN     | 70 °C    | 58               | 15               |
| 9     | 1b       | THF     | 70 °C    | 0                | 77               |
| 10    | 1b       | DCE     | 70 °C    | 0                | 6                |
| 11    | 1b       | EtOH    | 70 °C    | 0                | 6                |
| 12    | 1b       | MeOH    | 70 °C    | >99              | 0                |
| 13    | 1b       | THF     | 30 °C    | 0                | 9                |
| 14    | 1b       | THF     | 40 °C    | 0                | 21               |
| 15    | 1b       | THF     | 50 °C    | 0                | 37               |
| 16    | 1b       | THF     | 60 °C    | 0                | 62               |
| 17    | 1b       | THF     | 80 °C    | 0                | 72               |
| 18    | ---      | THF     | 70 °C    | >99              | 0                |
| 19    | 1a       | THF     | 70 °C    | 82               | 4                |
| 20    | 1c       | THF     | 70 °C    | 0                | 16               |
| 21    | 1d       | THF     | 70 °C    | 0                | 4                |
| 22    | 1e       | THF     | 70 °C    | 17               | 2                |
| 23    | 1f       | THF     | 70 °C    | 0                | 6                |
| 24    | 1g       | THF     | 70 °C    | 78               | 2                |
| 25    | 1h       | THF     | 70 °C    | 0                | 4                |
| 26    | 1i       | THF     | 70 °C    | 0                | 14               |
| 27    | 2a       | THF     | 70 °C    | 0                | 4                |
| 28    | 2b       | THF     | 70 °C    | 0                | 74               |
| 29    | 2c       | THF     | 70 °C    | 0                | 20               |
| 30    | 2d       | THF     | 70 °C    | 0                | 4                |
| 31    | 3a       | THF     | 70 °C    | 0                | 6                |
| 32    | 3b       | THF     | 70 °C    | 84               | 2                |
| 33    | 3c       | THF     | 70 °C    | 0                | 60               |
| 34    | 1b (5 mol%) | THF     | 70 °C    | 0                | 38               |
| 35    | 1b (20 mol%) | THF     | 70 °C    | 0                | 63               |
| 36    | 1b      | THF     | 70 °C    | 0                | 33               |

* Conditions: 4a (0.2 mmol), LA (10 mol%) in the corresponding solvent (0.1 M) and temperature (heated within an aluminium block if needed) for 18 h under Ar. * Yield determined by 1H-NMR using CHBr3 as internal standard. * Reaction performed under air.
5.2. Control Experiments

Table S7. Control experiments for the allylic cyclization of 4a.a

| Entry | Catalyst   | Solvent | T     | 4a NMR-Yield [%] | 5a NMR-Yield [%] |
|-------|------------|---------|-------|-----------------|-----------------|
| 1     | FeCl3      | THF     | 70 °C | 0               | 57              |
| 2     | BF3·OEt2   | THF     | 70 °C | 0d              | 0               |
| 3     | HOTf       | THF     | 70 °C | 0d              | 0               |
| 4     | [H(OEt2)]+·[B(C6F5)4]b | THF | 70 °C | 0d              | 0               |
| 5     | [H(OEt2)]+·[B(C6F5)4]b | THF | r.t. | 0d              | 0               |
| 6     | NaBF4      | THF     | 70 °C | >99             | 0               |
| 7     | Me3OBF6    | THF     | 70 °C | 0d              | 6               |

a Conditions: 4a (0.2 mmol), LA (10 mol%) in THF (0.1 M) at 70 °C (aluminum block) for 18 h under Ar. b Conditions: 4a (0.2 mmol), LA (1 mol%) in the THF (0.1 M) and corresponding temperature for 18 h. Yield determined by 1H-NMR using CH3Br2 as internal standard. Complete (or partial) decomposition of the substrate was observed.

5.3. General Procedure and Analytical Data of 5

General Procedure for the LA-Catalyzed Allylic Cyclization: In a pre-dried Schlenk tube, the corresponding 2-(1-hydroxyallyl)phenol 4 (0.20 mmol, 1.0 eq.) was dissolved in THF (2 mL, 0.1M) under Ar. Catalyst 1b (10 mol%) was added and the mixture was stirred for 18 h heated to 70 °C within an aluminum block. The reaction was cooled to room temperature, the solvent removed. Due to the instability of the chromene products 5, the corresponding NMR yield first was recorded using CH3Br2 as internal standard and, subsequently, the residue purified by column chromatography with an appropriate mixture of pentane and diethylether as eluent.

2H-Chromene (5a)

According to the general procedure, the cyclization of 2-(1-hydroxyallyl)phenol (30.0 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/ Et2O, 95:5) the desired product 5a (13.3 mg, 0.1 mmol, 50%; 77% NMR yield) as a yellowish oil. The scaling up reaction of 4a (150.2 mg, 1.0 mmol, 1.0 eq.) with catalyst 1d (23.5 mg, 0.1 mmol, 10 mol%) provided the product in 65% NMR yield and 46% isolated yield (61.1 mg, 0.46 mmol).

1H NMR (400 MHz, CDCl3) δ/ppm = 7.10 (dd, J = 7.8, 1.7 Hz, 1H), 6.96 (dd, J = 7.4, 1.8 Hz, 1H), 6.86 (dd, J = 7.4, 1.1 Hz, 1H), 6.77 (dt, J = 8.1, 1.0 Hz, 1H), 6.42 (dt, J = 9.8, 1.9, 0.7 Hz, 1H), 5.77 (dt, J = 9.8, 3.6 Hz, 1H), 4.83 (dd, J = 3.6, 1.9 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ/ppm = 155.7, 138.1, 129.6, 127.7, 125.5, 120.1, 117.4, 116.6, 76.5; LRMS (EI): m/z (relative intensity) 132.11 (M+-, 44), 131.09 ([M-H]+, 100). The analytical data is in accordance with the literature.1

6-Methyl-2H-chromene (5b)

According to the general procedure, the cyclization of 2-(1-hydroxyallyl)-4-methylphenol (32.8 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/ Et2O, 95:5) the desired product 5b (15.4 mg, 0.11 mmol, 53%; 76% NMR yield) as a yellowish oil. 1H NMR (400 MHz, CDCl3) δ/ppm = 6.90 (dd, J = 8.2, 2.2 Hz, 1H), 6.78 (d, J = 2.2 Hz, 1H), 6.68 (d, J = 8.1 Hz, 1H), 6.39 (dt, J = 9.8, 2.0 Hz, 1H), 5.77 (dt, J = 9.8, 3.6 Hz, 1H), 4.78 (dd, J = 3.6, 1.9 Hz, 2H), 2.25 (s, 3H); 13C NMR (100 MHz, CDCl3) δ/ppm = 152.0, 130.7, 129.6, 127.2, 124.8, 122.3, 115.5, 65.6, 20.7; HRMS (EI): m/z calculated for C13H13O+ [M+] = 146.0726; found: 146.0719. The analytical data is in accordance with the literature.1

8-Methyl-2H-chromene (5c)

According to the general procedure, the cyclization of 2-(1-hydroxyallyl)-6-methylphenol (32.8 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/ Et2O, 95:5) the desired product 5c (12.3 mg, 0.08 mmol, 42%; 68% NMR yield) as a yellowish oil. 1H NMR (400 MHz, CDCl3) δ/ppm = 6.97 (dd, J = 7.3, 2.0, 0.9 Hz, 1H), 6.83 − 6.74 (m, 2H), 6.42 (dt, J = 9.8, 1.9 Hz, 1H), 5.76 (dt, J = 9.8, 3.6 Hz, 1H), 4.84 (dd, J = 3.6, 1.9 Hz, 2H), 2.18 (s, 3H); 13C NMR (100 MHz, CDCl3) δ/ppm = 152.2, 130.9, 125.2, 125.1, 124.4, 122.0, 121.8, 120.8, 65.6, 15.6; HRMS (ESI): m/z calculated for C13H13O+Na+ [M + Na+] = 169.0624; found: 169.0621. The analytical data is in accordance with the literature.1

4-Methyl-2H-chromene (5d)

According to the general procedure, the cyclization of 2-(2-hydroxybut-3-en-2-yl)phenol (32.8 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/ Et2O, 95:5) the desired product 5d (14.8 mg, 0.1 mmol, 51%; 53% NMR yield) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ/ppm = 7.18 − 7.10 (m, 2H), 6.91 (td, J = 7.5, 1.2 Hz, 1H), 6.81 (ddd, J = 7.9, 1.2 Hz, 1H), 5.58 (tt, J = 3.6, 1.7 Hz, 1H), 4.75 (dq, J = 3.6,
3H-Benzof[chromene (5e)]:

According to the general procedure, the cyclization of 1-(1-hydroxyallyl)napthalen-2-ol (40.0 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/Et₂O, 95:5) the desired product 5e (31.9 mg, 0.18 mmol, 88%) as a white solid. ¹³C NMR (400 MHz, CDCl₃) δ/ppm = 154.2, 130.1, 129.0, 124.3, 123.5, 121.1, 118.4, 115.7, 65.4, 18.0. The analytical data is in accordance with the literature.¹

6-Methoxy-2H-chromene (5f):

According to the general procedure, the cyclization of 2-(1-hydroxyallyl)-4-methoxyphenol (36.0 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/Et₂O, 95:5) the desired product 5f (14.8 mg, 0.09 mmol, 46%; 83% NMR yield) as a yellowish oil. Ratio of rotomers: 8:1.

6-Bromo-2H-chromene (5h):

According to the general procedure, the cyclization of 4-bromo-2-(1-hydroxyallyl)phenol (45.8 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/Et₂O, 95:5) the desired product 5h (9.8 mg, 0.05 mmol, 23%; 44% NMR yield) as a yellowish oil. ¹³C NMR (400 MHz, CDCl₃) δ/ppm = 7.17 (dd, J = 8.6, 2.4 Hz, 1H), 7.06 (dd, J = 2.4 Hz, 1H), 6.64 (dd, J = 8.5, 0.8 Hz, 1H), 6.34 (dd, J = 9.9, 1.9, 0.7 Hz, 1H), 5.80 (dd, J = 9.9, 3.5 Hz, 1H), 4.82 (dd, J = 3.6, 1.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm = 153.2, 131.7, 129.2, 124.3, 123.7, 117.6, 113.4, 65.8; HRMS (ESI): m/z calculated for C₁₉H₁₅OBr⁺ [M + Na⁺] = 305.0854; found: 305.0865. The analytical data is in accordance with the literature.¹⁰

6-Nitro-2H-chromene (5i):

According to the general procedure, the cyclization of 2-(1-hydroxyallyl)-4-nitrophenol (39.0 mg, 0.2 mmol, 1.0 eq.) in the presence of catalyst 1b (4.7 mg, 0.02 mmol, 10 mol%), yielded after column chromatography (pentane/Et₂O, 90:10) the desired product 5i (9.9 mg, 0.05 mmol, 28%; 30% NMR yield) as a yellow solid. ¹³C NMR (400 MHz, CDCl₃) δ/ppm = 8.00 (dd, J = 8.9, 2.7 Hz, 1H), 7.84 (dd, J = 2.8 Hz, 1H), 6.79 (dd, J = 8.9, 0.8 Hz, 1H), 6.44 (dt, J = 10.1, 2.0 Hz, 1H), 5.87 (dt, J = 10.1, 3.4 Hz, 1H), 5.00 (dd, J = 3.4, 2.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm = 159.6, 141.9, 125.5, 123.8, 123.0, 122.3, 121.8, 116.1, 66.8; LRMS (ESI): m/z (relative intensity) 177.09 (M⁺ 76, 76.07 (M-[H⁺])²⁺, 100. The analytical data is in accordance with the literature.¹
6. Nazarov Cyclization

6.1. Optimization Screening

Table S8. Reaction conditions screening for the Nazarov cyclization of 6a.*

| Entry | Catalyst | Comment | 1 mol% cat. | 5 mol% cat. |
|-------|----------|---------|-------------|-------------|
| 1 | --- | -- | 0 | -- |
| 2 | 1a | -- | 0 | -- |
| 3 | 1b | 20 h | 47 | 65 |
| 4 | 1c | 20 h | 30 | 98 |
| 5 | 1d | 20 h | 99 (86)\(^{[e]}\) | >99\(^{[d]}\) |
| 6 | 1e | -- | 0 | -- |
| 7 | 1f | -- | 0 | -- |
| 8 | 1g | -- | 0 | -- |
| 9 | 1h | -- | 0 | -- |
| 10 | 1i | -- | 0 | -- |
| 11 | 2a | -- | 0 | -- |
| 12 | 2b | -- | 0 | -- |
| 13 | 2c | -- | 0 | -- |
| 14 | 2d | 20 h | 15 | 35 |
| 15 | 3a | 20 h | 7 | 27 |
| 16 | 3b | -- | 0 | -- |
| 17 | 3c | -- | 0 | -- |

* Conditions: 6a (0.2 mmol) and LA catalyst in CH\(_2\)Cl\(_2\) (0.1 M) at r.t. for 20-24 h under Ar. \(^{[b]}\) Yield determined by \(^1\)H-NMR using CH\(_2\)Br\(_2\) as internal standard. \(^{[c]}\) >20:1 d.r. determined by \(^1\)H-NMR for all catalytic reactions. \(^{[d]}\) Isolated yield in brackets.

6.2. Kinetic Study

The kinetic studies were carried out in a single NMR-tube with the model substrate 6a (0.1 mmol, 1.0 eq.) and the corresponding Lewis acid catalysts 1a, 1b, 1d, 2d and 3a (5 mol%) at rt using CD\(_2\)Cl\(_2\) (0.1M) as solvent (generally lower yields were obtained as in the reaction with normal stirring in CH\(_2\)Cl\(_2\)). The kinetic profile was followed by \(^1\)H-NMR in a 60 MHz benchtop-NMR at rt each 15 min until 1 h and then each hour until 15 h (10 scans each). The yield was determined by \(^1\)H-NMR analysis using CH\(_2\)Br\(_2\) (0.05 mmol, 0.5 eq.) as internal standard.
6.3. General Procedure and Analytical Data of 7

General Procedure for the LA-Catalyzed Nazarov Cyclization: In a pre-dried schlenk tube, the corresponding divinyl ketone 6 (0.20 mmol, 1.0 eq.) and catalyst 1c (1 or 5 mol%) were dissolved in DCM (1 mL, 0.2 M) and stirred at room temperature for 24 h under Ar. Then, the solvent was evaporated under reduced pressure and the residue purified by column chromatography with an appropriate mixture of pentane and EtOAc to yield the desired product 7.

**Ethyl 5-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7a)**

According to the general procedure, the cyclization of divinyl ketone 6a (63.3 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (1.7 mg, 0.002 mmol, 1 mol%) yielded after column chromatography (pentane/EtOAc 10:1 → 5:1) the desired product 7a (53.1 mg, 0.17 mmol, 84%) as a yellow oil. The reaction with 5 mol% of catalyst 1c provided the product in 99% yield (62.6 mg, 0.198 mmol). The scaling-up reaction of 6a (316.4 mg, 1.0 mmol, 1.0 eq.) with catalyst 1c (8.3 mg, 0.01 mmol, 1 mol%) yielded the product in 75% yield (237.3 mg, 0.75 mmol). The analytical data is in accordance with the literature.2a

**Methyl 5-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7b)**

According to the general procedure, the cyclization of divinyl ketone 6b (60.0 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (1.7 mg, 0.002 mmol, 1 mol%) yielded after column chromatography (pentane/EtOAc 8:1 → 5:1) the desired product 7a (37.5 mg, 0.124 mmol, 62%) as an orange oil. The analytical data is in accordance with the literature.2b

**t-Butyl 5-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7c)**

According to the general procedure, the cyclization of divinyl ketone 6c (68.8 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (1.7 mg, 0.002 mmol, 1 mol%) yielded after column chromatography (pentane/EtOAc 10:1 → 8:1) the desired product 7a (67.2 mg, 0.195 mmol, 98%) as a yellow solid. HRMS (ESI): m/z calculated for C_{18}H_{17}O_{3}Na⁺ [M + Na⁺] = 325.1047; found: 325.1054. The analytical data is in accordance with the literature.2b

**Figure 56. Monitoring of the model Nazarov cyclization reaction of 6a with various nitrenium Lewis acids 1-3.**
Ethyl 7-oxo-5-phenyl-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7d)

According to the general procedure, the cyclization of divinyl ketone 6d (57.3 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (8.3 mg, 0.01 mmol, 5 mol%) yielded after column chromatography (pentane/EtOAc 8:1) the desired product 7a (46.4 mg, 0.162 mmol, 81%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ/ppm = 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 7.17 – 7.11 (m, 2H), 4.26 – 4.10 (m, 5H), 3.30 (d, J = 2.2 Hz, 1H), 2.27 – 2.17 (m, 1H), 2.09 (dt, J = 19.8, 5.6 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm = 193.2, 168.4, 149.9, 147.4, 140.0, 129.2, 127.67, 127.4, 67.1, 61.9, 59.34, 47.7, 22.3, 21.3, 14.2; HRMS (ESI): m/z calculated for C₂₁H₂₂O₇Na⁺ [M + Na⁺] = 399.1098; found: 399.1093. The analytical data is in accordance with the literature.²a

Ethyl 5-(4-methylphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7e)

According to the general procedure, the cyclization of divinyl ketone 6e (60.1 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (1.7 mg, 0.002 mmol, 1 mol%) yielded after column chromatography (pentane/EtOAc 8:1) the desired product 7e (30.0 mg, 0.099 mmol, 50%) as a yellow oil. The reaction of 6e (48.1 mg, 0.16 mmol, 1.0 eq.) with 5 mol% of catalyst 1c provided the product in 62% yield (29.8 mg, 0.099 mmol). ¹H NMR (400 MHz, CDCl₃) δ/ppm = 7.15 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.18 – 4.11 (m, 3H), 3.28 (d, J = 2.4 Hz, 1H), 2.33 (s, 3H), 2.26 – 2.03 (m, 2H), 2.01 – 1.85 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm = 193.4, 168.6, 149.9, 147.8, 137.5, 137.0, 129.9, 127.4, 67.2, 62.0, 59.6, 47.5, 29.8, 22.35, 21.4, 14.3; HRMS (ESI): m/z calculated for C₁₅H₁₅O₂Na⁺ [M + Na⁺] = 323.1254; found: 323.1263.

Ethyl 5-(4-fluorophenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7f)

According to the general procedure, the cyclization of divinyl ketone 6f (60.9 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (8.3 mg, 0.01 mmol, 5 mol%) yielded after column chromatography (pentane/EtOAc 6:1) the desired product 7a (28.0 mg, 0.092 mmol, 46%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ/ppm = 7.10 (dd, J = 8.6, 5.4 Hz, 2H), 7.03 (t, J = 8.6 Hz, 2H), 4.28 – 4.09 (m, 5H), 3.24 (d, J = 2.4 Hz, 1H), 2.28 – 2.14 (m, 1H), 2.13 – 2.02 (m, 1H), 2.02 – 1.86 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm = 193.0, 168.4, 162.3 (d, J = 246.5 Hz), 150.1, 147.0, 135.8, 129.1 (d, J = 8.2 Hz), 116.2 (d, J = 21.5 Hz), 67.2, 62.1, 59.6, 47.1, 22.3, 21.4, 14.3; ¹⁹F NMR (376 MHz, CDCl₃) δ/ppm = -114.52; HRMS (ESI): m/z calculated for C₁₅H₁₄F₂O₇Na⁺ [M + Na⁺] = 327.1003; found: 327.1010.

Ethyl 7-oxo-5-(3,4,5-trimethoxyphenyl)-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7g)

According to the general procedure, the cyclization of divinyl ketone 6g (75.3 mg, 0.20 mmol, 1.0 eq.) in the presence of catalyst 1d (1.7 mg, 0.002 mmol, 1 mol%) yielded after column chromatography (pentane/EtOAc 6:1 → 4:1) the desired product 7a (75.0 mg, 0.199 mmol, 99%) as a yellow solid. ¹H NMR (400 MHz, 400 MHz, CDCl₃) δ/ppm = 6.30 (s, 2H), 5.4 2.22 (q, J = 7.1 Hz, 2H), 4.16 – 4.12 (m, 3H), 3.81 (s, 9H), 3.30 (d, J = 2.3 Hz, 1H), 2.29 – 2.04 (m, 2H), 2.03 – 1.82 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz CDCl₃) δ/ppm = 193.2, 168.4, 153.9, 149.8, 147.5, 135.7, 104.2, 67.2, 62.0, 60.9, 59.3, 56.3, 48.0, 29.8, 22.3, 21.4, 14.3; HRMS (ESI): m/z calculated for C₂₉H₃₅O₇Na⁺ [M + Na⁺] = 399.1414; found: 399.1423.
7. X-Ray Structure Analysis of 1a-d, 1f, 1i, and 2a-d

Data sets for compounds 1a, 1b, 1c, 1d, 1f, 1i, 2a, 2b, 2c and 2d were crystallized from DCM/pentane and collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., 2016);\textsuperscript{21} cell refinement: SAINT V8.37A (Bruker AXS Inc., 2015); data reduction: SAINT V8.37A (Bruker AXS Inc., 2015); absorption correction, SADABS V2014/7 (Bruker AXS Inc., 2014); structure solution SHELXT-2015 (G. M. Sheldrick, Acta Cryst. 2015, A71, 3-8);\textsuperscript{22} structure refinement SHELXL-2015 (G. M. Sheldrick, Acta Cryst. 2015, C71 (1), 3-8);\textsuperscript{23} and graphics, XP (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998).\textsuperscript{24} R-values are given for observed reflections, and wR2 values are given for all reflections.

Exceptions and special features: For compounds 1c and 2c five CF\textsubscript{3} groups and one dichloromethane molecule, for compound 1d one triazolium cation, for compound 2b two BF\textsubscript{4} anions and for compound 2d the triazolium cation were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

X-ray crystal structure analysis of 1a:\textsuperscript{25} CCDC Nr.: 2087003

A colorless plate-like specimen of Cs\textsubscript{6}H\textsubscript{8}F\textsubscript{3}N\textsubscript{2}O\textsubscript{3}S, approximate dimensions 0.066 mm x 0.170 mm x 0.282 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Im\textsubscript{s} (MoK\textsubscript{α}, λ = 0.71073 Å) and a MX mirror monochromator. A total of 408 frames were collected. The total exposure time was 1.81 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 18162 reflections to a maximum θ angle of 26.77° (0.79 Å resolution), of which 2608 were independent (average redundancy 6.964, completeness = 99.5%, R\textsubscript{int} = 3.98%, R\textsubscript{wp} = 2.23%) and 2301 (88.23%) were greater than 2σ(F\textsuperscript{2}). The final cell constants of a = 6.5145(3) Å, b = 11.3688(5) Å, c = 16.6105(7) Å, β = 93.233(2)°, volume = 1228.25(9) Å\textsuperscript{3}, are based upon the refinement of the XYZ-centroids of 7865 reflections above 2σ(I) with 4.912° < 2θ < 53.51°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.891. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9180 and 0.9800. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2\textsubscript{1}/c, with Z = 4 for the formula unit, Cs\textsubscript{6}H\textsubscript{8}F\textsubscript{3}N\textsubscript{2}O\textsubscript{3}S. The final anisotropic full-matrix least-squares refinement on F\textsuperscript{2} with 174 variables converged at R\textsubscript{1} = 3.14%, for the observed data and wR2 = 8.36% for all data. The goodness-of-fit was 1.074. The largest peak in the final difference electron density synthesis was 0.374 e/Å\textsuperscript{3} and the largest hole was -0.371 e/Å\textsuperscript{3} with an RMS deviation of 0.050 e/Å\textsuperscript{3}. On the basis of the final model, the calculated density was 1.608 g/cm\textsuperscript{3} and F(000), 608 e\textsuperscript{`.}

![Figure 57. Crystal structure of 1a. Ellipsoid contours given at the 50% probability level.](image-url)
X-ray crystal structure analysis of 1b: CCDC Nr.: 2087006
A colorless plate-like specimen of C_8H_10BF_4N_3, approximate dimensions 0.124 mm x 0.136 mm x 0.170 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 408 frames were collected. The total exposure time was 2.83 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 14295 reflections to a maximum θ angle of 25.37° (0.83 Å resolution), of which 1880 were independent (average redundancy 7.604, completeness = 99.3%, R_int = 5.72%, R_factor = 3.58%) and 1807 (96.12%) were greater than 2σ(F^2). The final cell constants of a = 7.3042(2) Å, b = 9.6885(3) Å, c = 14.5447(4) Å, volume = 1029.28(5) Å^3, are based upon the refinement of the XYZ-centroids of 6917 reflections above 2σ(I) with 5.051° < 2θ < 50.72°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.941. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9760 and 0.9820. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2_12_121, with Z = 4 for the formula unit, C_8H_10BF_4N_3. The final anisotropic full-matrix least-squares refinement on F^2 with 147 variables converged at R1 = 4.23%, for the observed data and wR2 = 11.28% for all data. The goodness-of-fit was 1.058. The largest peak in the final difference electron density synthesis was 0.626 e/Å^3 and the largest hole was -0.245 e/Å^3 with an RMS deviation of 0.064 e/Å^3. On the basis of the final model, the calculated density was 1.516 g/cm^3 and F(000), 480 e^-.

Figure S8. Crystal structure of 1b. Ellipsoid contours given at the 50% probability level.

X-ray crystal structure analysis of 1c: CCDC Nr.: 2087004
A colorless plate-like specimen of C_41H_24BCl_2F_24N_3, approximate dimensions 0.100 mm x 0.226 mm x 0.277 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 648 frames were collected. The total exposure time was 3.60 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data
using a monoclinic unit cell yielded a total of 93990 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 8047 were independent (average redundancy 11.680, completeness = 99.9%, Rint = 7.55%, Rsigma = 2.82%) and 6148 (76.40%) were greater than 2σ(F^2). The final cell constants of ɑ = 12.9624(5) Å,  β = 19.2535(6) Å,  γ = 17.7444(7) Å,  α = 96.0580(10)°, volume = 4403.8(3) Å³, are based upon the refinement of the XYZ-centroids of 9933 reflections above 20σ(I) with 4.82° < 2θ < 52.74°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.901. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9250 and 0.9720. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P21/n, with Z = 4 for the formula unit, C41H24BCl2F24N3. The final anisotropic full-matrix least-squares refinement on F^2 with 810 variables converged at R1 = 4.14%, for the observed data and wR2 = 10.68% for all data. The goodness-of-fit was 1.042. The largest peak in the final difference electron density synthesis was 0.668 e/Å³ and the largest hole was -0.328 e/Å³ with an RMS deviation of 0.051 e/Å³. On the basis of the final model, the calculated density was 1.654 g/cm³ and F(000), 2184 e.

Figure S9. Crystal structure of 1c. Ellipsoid contours given at the 40% probability level.

X-ray crystal structure analysis of 1d: CCDC Nr.: 2087005
A colorless needle-like specimen of C32H10BF20N3, approximate dimensions 0.055 mm x 0.087 mm x 0.176 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 510 frames were collected. The total exposure time was 4.25 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 58911 reflections to a maximum θ angle of 26.02° (0.81 Å resolution), of which 23034 were independent (average redundancy 2.558, completeness = 99.9%, Rint = 5.17%, Rsigma = 5.89%) and 19689 (85.48%) were greater than 2σ(F^2). The final cell constants of ɑ = 10.5364(3) Å,  β = 16.9367(5) Å,  γ = 17.6386(5) Å,  α = 97.6290(10)°,  β = 91.4380(10)°,  γ =
= 93.799(10)°, volume = 3111.10(16) Å³, are based upon the refinement of the XYZ-centroids of 9936 reflections above 20σ(I) with 4.454° < 2θ < 52.87°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.913. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9680 and 0.9900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P1, with Z = 4 for the formula unit, C32H10BF23N3. The final anisotropic full-matrix least-squares refinement on F² with 2123 variables converged at R1 = 3.91%, for the observed data and wR2 = 8.22% for all data. The goodness-of-fit was 1.011. The largest peak in the final difference electron density synthesis was 0.279 e/Å³ and the largest hole was -0.338 e/Å³ with an RMS deviation of 0.043 e/Å³. On the basis of the final model, the calculated density was 1.766 g/cm³ and F(000), 1632 e.

Figure S10. Crystal structure of 1d. Ellipsoid contours given at the 40% probability level.

X-ray crystal structure analysis of 1f: CCDC Nr.: 2117634
A colorless prism-like specimen of C32H10BF23N3, approximate dimensions 0.250 mm x 0.320 mm x 0.340 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Kappa CCD Bruker APEXII Diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuKα, λ = 1.54178 Å) and a graphite monochromator. A total of 1442 frames were collected. The total exposure time was 19.49 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 46667 reflections to a maximum θ angle of 66.65° (0.84 Å resolution), of which 5803 were independent (average redundancy 8.042, completeness = 99.7%, Rint = 4.37%, Rmax = 2.64%) and 5325 (91.76%) were greater than 2σ(F²). The final cell constants of a = 13.3716(2) Å, b = 14.2756(2) Å, c = 17.2659(3) Å, β = 94.2990(10)°, volume = 3286.57(9) Å³, are
based upon the refinement of the XYZ-centroids of 9979 reflections above 20σ(I) with 10.18° < 2θ < 133.2°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.886. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5760 and 0.6580. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/c, with Z = 4 for the formula unit, C₃₉H₁₀BF₂₆N₃. The final anisotropic full-matrix least-squares refinement on F² with 542 variables converged at R1 = 2.96%, for the observed data and wR2 = 7.32% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.233 e/Å³ and the largest hole was -0.280 e/Å³ with an RMS deviation of 0.048 e/Å³. On the basis of the final model, the calculated density was 1.809 g/cm³ and F(000), 1760 e.

Figure S11. Crystal structure of 1f. Ellipsoid contours given at the 50% probability level.

X-ray crystal structure analysis of 1f: CCDC Nr.: 2087007
A colorless plate-like specimen of C₃₉H₁₀BF₂₆N₃, approximate dimensions 0.055 mm x 0.062 mm x 0.163 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoKα (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 1652 frames were collected. The total exposure time was 16.06 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 55307 reflections to a maximum 2θ angle of 25.75° (0.82 Å resolution), of which 7009 were independent (average redundancy 7.891, completeness = 99.6%, Rint = 5.22%, Rwp = 2.84%) and 5597 (79.85%) were greater than 2σ(F²). The final cell constants of a = 10.6465(6) Å, b = 37.338(2) Å, c = 10.4831(6) Å, β = 117.880(2)°, volume = 3683.5(4) Å³, are based upon the refinement of the XYZ-centroids of 9980 reflections above 20σ(I) with 4.529° < 2θ < 51.00°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.933. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9680 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/c, with Z = 4 for the formula unit, C₃₉H₁₀BF₂₆N₃. The final anisotropic full-matrix least-squares refinement on F² with 623 variables converged at R1 = 3.35%, for the observed data and wR2 = 7.89% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.337 e/Å³ and the largest hole was -0.304 e/Å³ with an RMS deviation of 0.050 e/Å³. On the basis of the final model, the calculated density was 1.849 g/cm³ and F(000), 2016 e.
Figure S12. Crystal structure of 1i. Ellipsoid contours given at the 50% probability level.

X-ray crystal structure analysis of 2a: CCDC Nr.: 2087009

A colorless plate-like specimen of $C_9H_{10}F_3N_3O_4S$, approximate dimensions 0.055 mm x 0.105 mm x 0.151 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoKα ($\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 536 frames were collected. The total exposure time was 4.47 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 26449 reflections to a maximum $\theta$ angle of 26.74° (0.79 Å resolution), of which 2723 were independent (average redundancy 9.713, completeness = 99.6%, $R_{int} = 4.32$%, $R_{sym} = 1.86$%) and 2430 (89.24%) were greater than 2σ($F^2$). The final cell constants of $a = 6.6911(2)$ Å, $b = 11.6613(3)$ Å, $c = 16.4927(4)$ Å, $\beta = 94.4270(10)^\circ$, volume = 1283.04(6) Å³, are based upon the refinement of the XYZ-centroids of 9271 reflections above 20σ(I) with 6.063° < $\theta$ < 53.48°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.941. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9550 and 0.9830. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $C_9H_{10}F_3N_3O_4S$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 183 variables converged at $R_1 = 2.78$%, for the observed data and $wR2 = 7.14$% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.433 e/Å³ and the largest hole was -0.350 e/Å³ with an RMS deviation of 0.045 e/Å³. On the basis of the final model, the calculated density was 1.622 g/cm³ and F(000), 640 e⁻.
X-ray crystal structure analysis of 2b: CCDC Nr.: 2087008
A colorless plate-like specimen of C₈H₁₀BF₄N₃O, approximate dimensions 0.075 mm x 0.128 mm x 0.184 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoKα (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 887 frames were collected. The total exposure time was 2.46 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 103632 reflections to a maximum θ angle of 26.75° (0.79 Å resolution), of which 6874 were independent (average redundancy 15.076, completeness = 99.5%, R_int = 8.80%, R_sig = 3.02%) and 5082 (73.93%) were greater than 2σ(F²). The final cell constants of ɑ = 12.1044(4) Å,  β = 12.5844(4) Å,  γ = 21.3556(8) Å,  β = 94.0010(10)°, volume = 3245.10(19) Å³, are based upon the refinement of the XYZ-centroids of 9236 reflections above 20σ(I) with 4.961° < 2θ < 53.34°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.934. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/c, with Z = 12 for the formula unit, C₈H₁₀BF₄N₃O. The final anisotropic full-matrix least-squares refinement on F² with 540 variables converged at R1 = 4.32%, for the observed data and wR2 = 12.24% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.374 e/Å³ and the largest hole was -0.273 e/Å³ with an RMS deviation of 0.047 e/Å³. On the basis of the final model, the calculated density was 1.541 g/cm³ and F(000), 1536 e⁻.
A colorless plate-like specimen of \( \text{C}_{41} \text{H}_{24} \text{BCl}_{2} \text{F}_{24} \text{N}_{3} \text{O} \), approximate dimensions 0.038 mm x 0.100 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoK\( \alpha \) (MoK\( \alpha \), \( \lambda = 0.71073 \) Å) and a MX mirror monochromator. A total of 768 frames were collected. The total exposure time was 4.27 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 64890 reflections to a maximum \( \theta \) angle of 26.79° (0.79 Å resolution), of which 9475 were independent (average redundancy 6.849, completeness = 99.7%, \( R_{int} = 8.54\)%) and 6004 (63.37%) were greater than 2\( \sigma (F^2) \). The final cell constants of \( a = 12.4318(8) \) Å, \( b = 13.0870(9) \) Å, \( c = 14.9723(11) \) Å, \( \alpha = 79.929(2)\)°, \( \beta = 81.885(2)\)°, \( \gamma = 68.583(2)\)°, volume = 2224.8(3) Å\(^3\), are based upon the refinement of the XYZ-centroids of 9206 reflections above 20 \( \sigma (I) \) with 4.671° < 2\( \theta \) < 50.75°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.919. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9400 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group \( \text{P}-1 \), with \( Z = 2 \) for the formula unit, \( \text{C}_{41} \text{H}_{24} \text{BCl}_{2} \text{F}_{24} \text{N}_{3} \text{O} \). The final anisotropic full-matrix least-squares refinement on \( F^2 \) with 849 variables converged at \( R1 = 6.46\)%, for the observed data and \( wR2 = 19.02\)% for all data. The goodness-of-fit was 1.020. The largest peak in the final difference electron density synthesis was 0.641 e/Å\(^3\) and the largest hole was -0.431 e/Å\(^3\) with an RMS deviation of 0.069 e/Å\(^3\). On the basis of the final model, the calculated density was 1.660 g/cm\(^3\) and \( F(000) = 1108 \) e\(^-\).
Crystal structure analysis of 2d: CCDC Nr.: 2087010
A colorless plate-like specimen of C_{32}H_{10}BF_{20}N_{3}O, approximate dimensions 0.058 mm x 0.086 mm x 0.136 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoKα (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 681 frames were collected. The total exposure time was 3.78 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 156031 reflections to a maximum θ angle of 26.77° (0.79 Å resolution), of which 6529 were independent (average redundancy 23.898, completeness = 99.9%, R_{int} = 12.12%, R_{sig} = 2.96%) and 4597 (70.41%) were greater than 2σ(F^2). The final cell constants of a = 20.0092(7) Å, b = 13.3894(5) Å, c = 22.8715(9) Å, volume = 6127.5(4) Å^3, are based upon the refinement of the XYZ-centroids of 9936 reflections above 20σ(I) with 5.082° < 2θ < 51.34°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.957. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9740 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pbcn, with Z = 8 for the formula unit, C_{32}H_{10}BF_{20}N_{3}O. The final anisotropic full-matrix least-squares refinement on F^2 with 628 variables converged at R1 = 3.98%, for the observed data and wR2 = 9.86% for all data. The goodness-of-fit was 1.056. The largest peak in the final difference electron density synthesis was 0.366 e/Å^3 and the largest hole was -0.260 e/Å^3 with an RMS deviation of 0.052 e/Å^3. On the basis of the final model, the calculated density was 1.828 g/cm^3 and F(000), 3328 e^−.
Figure S16. Crystal structure of 2d. Ellipsoid contours given at the 40% probability level.

8. References

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9. NMR Collection

1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium trifluoromethanesulfonate (1a)

$^1$H-NMR spectrum (400 MHz, (CD$_3$)$_2$CO) of 1a

$^{13}$C-NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 1a
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 1a

1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (1b)

$^1$H-NMR spectrum (400 MHz, (CD$_3$)$_2$CO) of 1b
$^{13}$C-NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 1b

$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 1b
1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-i um tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1c)

\[ 1H-NMR \text{ spectrum (400 MHz, (CD}_3)_2CO \text{ of 1c) } \]
$^{13}$C-NMR spectrum (100 MHz, (CD$_2$)$_2$CO) of 1c

$^{19}$F-NMR spectrum (376 MHz, (CD$_2$)$_2$CO) of 1c
1,3-Dimethyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis(pentafluorophenyl)borate (1d)

$^1$H-NMR spectrum (400 MHz, (CD$_3$)$_2$CO) of 1d

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 1c
$^{13}$C-NMR spectrum (100 MHz, CD$_3$CO) of 1d

$^{19}$F-NMR spectrum (376 MHz, CD$_3$CO) of 1d
$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 1d

1-(2,2,2-Trifluoroethyl)-1H-benzo[d][1,2,3]triazole (8)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 8
$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 8

$^{19}$F-NMR spectrum (376 MHz, CDCl$_3$) of 8
3-Methyl-1-(2,2,2-trifluoroethyl)-1H-benzo[⊂][1,2,3]triazol-3-ium tetrafluoroborate (1e)

\[ \text{CF}_3N\equivN\equivNBF_4^- \]

\( ^1H \text{-NMR spectrum (400 MHz, (CD}_3)_2\text{CO) of 1e} \)

\( ^{13}C \text{-NMR spectrum (100 MHz, (CD}_3)_2\text{CO) of 1e} \)
$^{19}$F-NMR spectrum (376 MHz, (CD)$_3$CO) of \textbf{1e}

$^{11}$B-NMR spectrum (128 MHz, (CD)$_3$CO) of \textbf{1e}
3-Methyl-1-(2,2,2-trifluoroethyl)-1H-benzo[d][1,2,3]triazol-3-ium tetrakis(pentafluorophenyl)borate (1f)

$\text{CF}_3$®$\text{N}_2$®$\text{N}^+$

$^{13}$C-NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 1f
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 1f

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 1f
N-(2-Nitrophenyl)-3,5-bis(trifluoromethyl)aniline (9)

$^{1}H$-NMR spectrum (400 MHz, CDCl$_3$) of 9

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 9
$^{19}$F-NMR spectrum (376 MHz, CDCl$_3$) of 9

$N^1$-(3,5-Bis(trifluoromethyl)phenyl)benzene-1,2-diamine (10)

$^{1}$H-NMR spectrum (400 MHz, CDCl$_3$) of 10
$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 10

$^{19}$F-NMR spectrum (376 MHz, CDCl$_3$) of 10
1-(3,5-Bis(trifluoromethyl)phenyl)-1H-benzo[d][1,2,3]triazole (11)

$\text{\textsuperscript{1}}$H-NMR spectrum (400 MHz, CDCl$_3$) of 11

$\text{\textsuperscript{13}}$C-NMR spectrum (100 MHz, CDCl$_3$) of 11
$^{19}$F-NMR spectrum (376 MHz, CDCl$_3$) of 11
1-(3,5-Bis(trifluoromethyl)phenyl)-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (1g)

\[\text{Chemical Structure Image}\]

\[\text{1H-NMR Spectrum (400 MHz, (CD}_3\text{)CO) of 1g}\]

\[\text{13C-NMR Spectrum (100 MHz, (CD}_3\text{)CO) of 1g}\]
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 1g

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 1g
1-(3,5-Bis(trifluoromethyl)phenyl)-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (1h)

$\text{CF}_3$

$\text{CF}_3$

$\text{N}^+ \text{N}^+ \text{BARF}_2^-$

$\text{1H-NMR spectrum (400 MHz, (CD}_3\text{)}_2\text{CO) of 1h}$

$\text{13C-NMR spectrum (100 MHz, (CD}_3\text{)}_2\text{CO) of 1h}$
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 1h

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 1h
1-(3,5-Bis(trifluoromethyl)phenyl)-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis(pentafluorophenyl)borate (1i)

$\text{(CD}_3\text{CO)}$

$\text{B(C}_6\text{F}_5)_4^-$

$\text{CF}_3$

$\text{CF}_3$

$\text{N}^+\text{N}^-$

$\text{N}^+\text{N}^-$

$\text{H-NMR spectrum (400 MHz, (CD}_3\text{CO)}$ of 1i

$\text{C-NMR spectrum (100 MHz, (CD}_3\text{CO)}$ of 1i
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 1i

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 1i
1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-iium trifluoromethanesulfonate (2a)

\[ \text{O} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{OTf} \]

\( ^1H\)-NMR spectrum (400 MHz, (CD\(_3\))\(_2\)CO) of 2a

\( ^13C\)-NMR spectrum (100 MHz, (CD\(_3\))\(_2\)CO) of 2a
1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrafluoroborate (2b)
$^{13}$C-NMR spectrum (100 MHz, (CD)$_3$CO) of 2b

$^{19}$F-NMR spectrum (376 MHz, (CD)$_3$CO) of 2b
1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2c)
$^{13}$C-NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 2c

$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 2c
1-Methoxy-3-methyl-1H-benzo[d][1,2,3]triazol-3-ium tetrakis(pentafluorophenyl)borate (2d)
$^{13}$C-NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 2d

$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 2d
3-Methyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium trifluoromethanesulfonate (3a)

$\text{H-NMR spectrum (400 MHz, (CD$_3$)$_2$CO) of 3a}$
$^{13}$C-NMR spectrum (100 MHz, (CD)$_3$CO) of 3a

$^{19}$F-NMR spectrum (376 MHz, (CD)$_3$CO) of 3a
3-Methyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium tetrafluoroborate (3b)

$\text{N}^+\text{N}^+\text{BF}_4^-$

$^1$H-NMR spectrum (400 MHz, (CD$_3$)$_2$CO) of 3b

$^13$C-NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 3b
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 3b

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 3b
3-Methyl-1H-naphtho[1,8-de][1,2,3]triazin-3-ium tetrakis(pentafluorophenyl)borate (3c)

$\text{H}-\text{NMR spectrum (400 MHz, (CD$_3$)$_2$CO) of 3c}$

$\text{C}-\text{NMR spectrum (100 MHz, (CD$_3$)$_2$CO) of 3c}$
$^{19}$F-NMR spectrum (376 MHz, (CD$_3$)$_2$CO) of 3c

$^{11}$B-NMR spectrum (128 MHz, (CD$_3$)$_2$CO) of 3c
2H-Chromene (5a)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 5a

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 5a
6-Methyl-2H-chromene (5b)

$\text{H-NMR spectrum (400 MHz, CDCl}_3 \text{) of 5b}$

$\text{C-NMR spectrum (100 MHz, CDCl}_3 \text{) of 5b}$
8-Methyl-2H-chromene (5c)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 5c

$^1$C-NMR spectrum (100 MHz, CDCl$_3$) of 5c
4-Methyl-2H-chromene (5d)

$\text{H-NMR spectrum (400 MHz, CDCl}_3\text{) of 5d}$

$\text{C-NMR spectrum (100 MHz, CDCl}_3\text{) of 5d}$
3H-Benzo[f]chromene (5e)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 5e

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 5e
6-Methoxy-2H-chromene (5f)

$\text{MeO}$

$\text{H-NMR spectrum (400 MHz, CDCl}_3\text{) of 5f}$

$\text{C-NMR spectrum (100 MHz, CDCl}_3\text{) of 5f}$
S-Methoxy-2H-chromene (5g)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 5g

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 5g

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6-Bromo-2H-chromene (5h)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 5h

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 5h
6-Fluoro-2H-chromene (5i)

$\text{H-NMR spectrum (400 MHz, CDCl}_3\text{) of 5i}$

$\text{C-NMR spectrum (100 MHz, CDCl}_3\text{) of 5i}$
$^1$H-NMR spectrum (376 MHz, CDCl$_3$) of 5i
6-Nitro-2H-chromene (5j)

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 5j

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 5j
Ethyl 5-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7a)

$\text{H}-\text{NMR spectrum (400 MHz, CDCl}_3\text{) of 7a}$

$\text{C}-\text{NMR spectrum (100 MHz, CDCl}_3\text{) of 7a}$
Methyl 5-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7b)

$\text{H-NMR spectrum (400 MHz, CDCl}_3\text{) of 7b}$

$\text{C-NMR spectrum (100 MHz, CDCl}_3\text{) of 7b}$
tert-Butyl 5-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7c)

$\text{H-NMR spectrum (400 MHz, CDCl}_3$ of 7c

$\text{C-NMR spectrum (100 MHz, CDCl}_3$ of 7c
Ethyl 7-oxo-5-phenyl-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7d)

¹H-NMR spectrum (400 MHz, CDCl₃) of 7d

¹³C-NMR spectrum (100 MHz, CDCl₃) of 7d
Ethyl 5-(4-methylphenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7e)

$\text{H-NMR spectrum (400 MHz, CDCl}_3\text{) of 7e}$

$\text{C-NMR spectrum (100 MHz, CDCl}_3\text{) of 7e}$
Ethyl 5-(4-fluorophenyl)-7-oxo-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7f)
$^{19}$F-NMR spectrum (376 MHz, CDCl$_3$) of 7f
Ethyl 7-oxo-5-(3,4,5-trimethoxyphenyl)-2,3,4,5,6,7-hexahydrocyclopenta[b]pyran-6-carboxylate (7g)

$\begin{array}{c}
\text{O} & \text{CO}_2\text{Et} \\
\text{MeO} & \text{OMe}
\end{array}$

$^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 7g

$^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of 7g

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