Supporting information

A Convenient Access to Fluorophosphonium Triflate Salts by Electrophilic Fluorination and Anion Exchange

Chun-Xiang Guo,[a] Sivatmeehan Yogendra,[a] Rosa M. Gomila,[b] Antonio Frontera,[b] Felix Hennersdorf,[a] Johannes Steup,[a] Kai Schwedtmann,[a] Jan J. Weigand*[a]

[a] Faculty of Chemistry and Food Chemistry, TU Dresden, Chair of Inorganic Molecular Chemistry, 01062 Dresden, Germany. E-mail: jan.weigand@tu-dresden.de

[b.] Department of Chemistry, Universitat de Illes Balears, 07122 Palma de Mallorca, Spain

Content

S1 Materials and methods

General Remarks: All manipulations are performed in a Glovebox (MB Unilab or Pure lab HE GP-1SR) or using Schlenk techniques under an atmosphere of purified Nitrogen. Dry, oxygen-free solvents (CH_2Cl_2, CH_3CN, C_6H_5F (distilled from CaH_2), Et_2O (distilled from potassium/benzophenone)) are employed. Deuterated benzene (C_6D_6) is purchased from Sigma-Aldrich and distilled from potassium. Anhydrous deuterated acetonitrile (CD_3CN), Nitromethane (CD_3NO_2), dichloromethane (CD_2Cl_2), and chloroform ($CDCl_3$) are purchased from Sigma-Aldrich. All distilled and deuterated solvents are stored over molecular sieves (4Å: CH_2Cl_2, Et_2O, *n*-pentane, C_6H_5F, C_6D_6, CD_2Cl_2, $CDCl_3$; 3Å: CH_3CN, CD_3CN, CD_3NO_2). All glassware is oven-dried at 160 °C prior to use. $(C_6F_5)_3P$,[1] $(C_6F_5)_2PhP$,[2] $(C_6F_5)Ph_2P$,[2] and tris(3,5-bis(trifluoromethyl)phenyl)phosphane[3] are prepared according to reported procedures. $[Lc^RPh_2P][OTf]$ **5^{R}a**[OTf], $[Lc^R(C_6F_5)_2P][OTf]$ **5^{R}b**[OTf] and $[Lc^R{}_2PhP][OTf]_2$ **7^R**$[OTf]_2$ (R = Me or *i*Pr) are prepared from $[Lc^RTMS][OTf]$[4] with Ph_2PCl, $PhPCl_2$ or $(C_6F_5)_2PBr$[5] according to literature.[6] All other chemicals are purchased from Sigma Aldrich, ABCR Chemicals, TCI, Manchester Organics or Acros Organics. *t*BuONa is purchased from TCI or Sigma Aldrich and further recrystallized from THF.

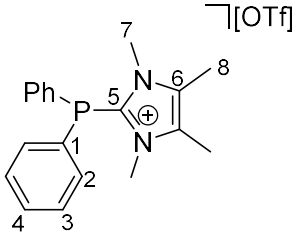
NMR spectra are measured on a Bruker AVANCE III HD Nanobay 400 MHz UltraShield (^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{31}P (161.98 MHz), ^{19}F (376.50 MHz)), or on a Bruker AVANCE III HDX, 500 MHz Ascend (^1H (500.13 MHz), ^{13}C (125.75 MHz), ^{31}P (202.45 MHz) ^{19}F (470.59 MHz)). All ^{13}C NMR spectra are exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the ^{13}C spectra are indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts are referenced to $\delta(Me_4Si)$ = 0.00 ppm (^1H, ^{13}C, externally), $\delta(CFCl_3)$ = 0.00 ppm (^{19}F, externally) and $\delta(H_3PO_4, 85\%)$ = 0.00 ppm (^{31}P, externally). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz.. Melting points are recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point *M*-560) in sealed capillaries under Nitrogen atmosphere and are uncorrected. Infrared (IR) and Raman spectra are recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) is used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Elemental analyses are performed on a Vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme 2 GmbH in CHNS modus.

S2 Preparation of imidazoliumyl-substituted phosphanes

General procedure for the preparation of imidazoliumyl-substituted phosphanes: $Cl_nPPh_{(3-n)}$ (n = 1 or 2) or $(C_6F_5)_2PBr$ is added to a suspension of [Lc^{R}TMS][OTf] (R = Me or *i*Pr) in C_6H_5F, and the reaction mixture was stirred for 16 h at 85 °C. After the addition of *n*-pentane, the resulting suspension was cooled at –30 °C for 12 h, followed by filtration. The residue is recrystallized from CH_2Cl_2/Et_2O and dried *in vacuo* to give the titled compounds as analytically pure, air-stable colorless solids.

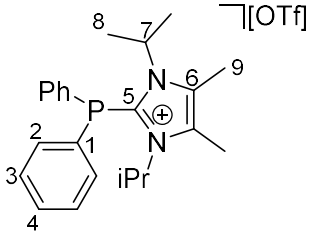
S2.1. Preparation of **5^{Me}a**[OTf]



Following the general procedure, Ph_2PCl (3.34 g, 15.0 mmol) and [Lc^{Me}TMS][OTf] (5.20 g, 15.0 mmol) are used as educts.

Yield: 6.56 g, 95%; **m.p.**: 105 – 108°C; **Raman** (35 mW, 450 scans, 298 K, in cm^{-1}): 3066 (15), 2962 (4), 2932 (10), 1635 (5), 1586 (32), 1573 (4), 1475 (9), 1406 (18), 1385 (8), 1342 (12), 1162 (5), 1101 (17), 1030 (24), 999 (54), 770 (2), 755 (7), 706 (2), 686 (4), 618 (5), 599 (7), 586 (2), 570 (5), 488 (2), 349 (5), 314 (7), 263 (4), 227 (11), 190 (4), 84 (100); **IR** (298 K, ATR, in cm^{-1}): 1634 (w), 1483 (w), 1435 (w), 1402 (w), 1258 (vs), 1224(w), 1141(m), 1096(vw), 1027(s), 999(vw), 919(vw), 857(w), 769(vw), 746(m), 701(m), 635(s); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 7.58 – 7.50 (6H, m, C3 and C4-H), 7.44 – 7.37 (4H, m, C2-H), 3.54 (6H, s, C7-H), 2.25 (6H, s, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 141.2 (d, $^1J_{CP}$ = 47 Hz, C5), 133.3 (d, $^2J_{CP}$ = 20 Hz, C2), 132.4 (s, C6), 131.4 (s, C4), 130.7 (d, $^3J_{CP}$ = 7 Hz, C3), 129.6 (d, $^1J_{CP}$ = 7 Hz, C1), 122.2 (q, $^1J_{CF}$ = 321 Hz, OTf), 35.2 (d, $^3J_{CP}$ = 11 Hz, C7), 9.4 (s, C8); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.3 (s, OTf); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -29.0 (s); **Elemental analysis:** calculated for $C_{20}H_{22}F_3N_2O_3PS$: C: 52.4, H: 4.8, N: 6.1, S: 7.0, found: C: 52.2, H: 4.8, N: 6.1, S: 7.4.

S2.2. Preparation of **5^{iPr}a**[OTf]

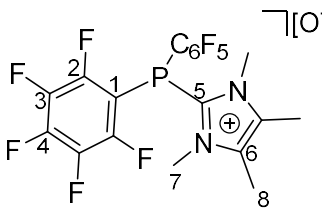


Following the general procedure, Ph_2PCl (4.41 g, 20.0 mmol) and [Lc^{iPr}TMS][OTf] (8.05 g, 20.0 mmol) are used as educts.

Yield: 9.33 g, 91%; **m.p.**: 133 – 136 ºC; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3058 (56), 2988 (30), 2945 (52), 1612 (25), 1584 (90), 1572 (28), 1452 (30), 1411 (26), 1361 (29), 1279 (58), 1097 (32), 1033 (55), 1027 (65), 998 (100), 887 (17), 756 (22), 617 (20), 350 (18), 317 (24);

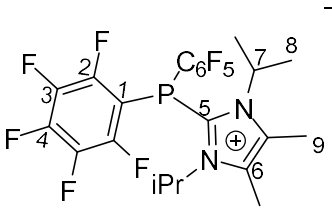
IR (298 K, ATR, in cm^{-1}): 3054 (vw), 2993 (vw), 2942 (vw), 1611 (vw), 1478 (vw), 1453 (w), 1436 (w), 1399 (w), 1379 (w), 1261 (vs), 1223 (s), 1144 (vs), 1115 (m), 1088 (w), 1073 (w), 1028 (vs), 998 (w), 905 (w), 853 (vw), 789 (w), 747 (vs), 713 (w), 699 (s), 657 (vw), 633 (vs), 572 (m), 546 (w), 517 (m), 505 (m), 486 (m), 477 (m), 437 (m); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 7.49 – 7.40 (10H, m, Ph), 5.02 (2H, br, C7-H), 2.37 (6H, s, C9-H), 1.30 (12H, br, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 140.3 (d, $^{1}J_{CP}$ = 54 Hz, C5), 132.9 (d, $^{3}J_{CP}$ = 19 Hz, C3), 131.2 (s, C4), 130.6 (d, $^{2}J_{CP}$ = 6 Hz, C2), 130.0 (d, $^{1}J_{CP}$ = 9 Hz, C1), 127.6 (s, C6), 122.2 (q, $^{1}J_{CF}$ = 324 Hz, OTf), 54.0 (d, $^{3}J_{CP}$ = 10 Hz, C7), 21.1 (s, br, C8), 11.0 (s, C9); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.3 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -27.9 (s); **Elemental analysis**: calculated for $C_{24}H_{30}F_3N_2O_3PS$: C 56.0, H 5.9, N 5.4, S 6.2, found C 55.7, H 5.9, N 5.2, S 6.0.

S2.3. Preparation of **5^{Me}b**[OTf]



Following the general procedure, $(C_6F_5)_2PBr$ (3.09 g, 6.93 mmol) and [Lc^{Me}TMS][OTf] (2.40 g, 6.93 mmol) are used as educts. **Yield**: 4.0 g, 90%; **m.p.**: decomposition at approx. 211°C; **Raman** (35 mW, 450 scans, 298 K, in cm^{-1}): 2968(5), 2940(29), 1648 (54), 1630 (11), 1453 (15), 1410 (39), 1388 (22), 1339 (47), 1276 (7), 1225(5), 1101(20), 1032 (36), 978 (5), 835 (13), 774 (5), 753 (15), 629 (5), 598 (16), 587 (36), 570 (14), 517 (5), 504 (30), 455 (15), 445 (6), 421 (10), 394 (22), 378 (6), 350 (5), 322 (15), 234 (5), 172 (9), 151 (12), 76 (100); **IR** (298 K, ATR, in cm^{-1}): 1647 (w), 1629 (vw), 1522 (m), 1473 (s), 1446 (vw), 1409 (w), 1382(w), 1338 (vw), 1263 (s), 1223 (w), 1151 (s), 1089 (m), 1031 (m), 972 (s), 855 (w), 773 (w), 753 (vw), 722 (vw), 636 (vs); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 3.75 (6H, s, C7-H), 2.30 (6H, s, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 147.4 (dm, $^{1}J_{CF}$ = 247 Hz, C3), 143.8 (dm, $^{1}J_{CF}$ = 258 Hz, C4), 138.3 (dm, $^{1}J_{CF}$ = 253 Hz, C2), 133.1 (s, C6), 133.1 (dm, $^{1}J_{CF}$ = 38 Hz, C5), 121.1 (q, $^{1}J_{CF}$ = 321 Hz, OTf), 101.4 (m, C1), 34.4 (d, $^{3}J_{CP}$ = 11 Hz, C7), 8.6 (s, C8); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.4 (s, OTf), -131.8 (m, C2-F), -148.8 (m, C4-F), -160.6 (m, C3-F); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -78.1 (quint, $^{3}J_{PF}$ = 33 Hz); **Elemental analysis:** calculated for $C_{20}H_{12}F_{13}N_2PS$: C: 37.6, H: 1.9, N: 4.4, found: C: 37.6, H: 2.0, N: 4.3.

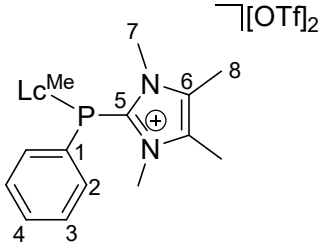
S2.4. Preparation of **5^{iPr}b**[OTf]



Following the general procedure, $(C_6F_5)_2PBr$ (4.45 g, 10.0 mmol) and [Lc^{iPr}TMS][OTf] (4.03 g, 10.0 mmol) are used as educts.

Yield: 4.34 g, 76%; **m.p.**: 180 – 182 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 2976 (40), 2945 (62), 1643 (71), 1612 (51), 1448 (51), 1419 (48), 1391 (56), 1371 (55), 1283 (100), 1225 (31), 1155 (32), 1033 (82), 887 (36), 849 (33), 831 (34), 754 (41), 629 (32), 586 (81), 573 (37), 547 (31), 518 (37), 506 (66), 463 (44), 447 (56); **IR** (298 K, ATR, in cm^{-1}): 2987 (vw), 1640 (vw), 1611 (vw), 1518 (s), 1471 (vs), 1419 (w), 1380 (w), 1263 (vs), 1223 (m), 1141 (s), 1119 (w), 1086 (vs), 1031 (vs), 974 (vs), 906 (vw), 848 (w), 830 (vw), 793 (w), 754 (w), 725 (vw), 664 (vw), 636 (vs), 586 (vw), 572 (w), 547 (vw), 516 (s), 458 (w), 448 (w), 433 (m); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 5.14 (2H, br, C7-H), 2.43 (6H, s, C9-H), 1.48 (12H, br, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 148.1 (dm, $^{1}J_{CF}$ = 247 Hz, C2), 144.7 (dm, $^{1}J_{CF}$ = 258 Hz, C4), 139.4 (dm, $^{1}J_{CF}$ = 255 Hz, C3), 135.12 (s, C6), 133.6 (d, $^{1}J_{CP}$ = 44 Hz, C5), 122.2 (q, $^{1}J_{CF}$ = 323 Hz, OTf), 102.7 (m, C1), 55.0 (d, $^{3}J_{CP}$ = 13 Hz, C7), 21.1 (s, C8), 11.3 (s, C9); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.2 (s, OTf), -131.2 (m, C2-F), -148.2 (m, C4-F), -160.3 (m, C3-F); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -74.0 (s, br). **Elemental analysis**: calculated for $C_{24}H_{20}F_{13}N_2O_3PS$: C 41.5, H 2.9, N 4.0, found: C 41.8, H 2.9, N 4.0.

S2.5. Preparation of **7^{Me}**[OTf]$_2$

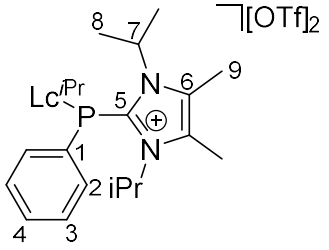


Following the general procedure, $PhPCl_2$ (358 mg, 2.0 mmol) and [Lc^{Me}TMS][OTf] (1.39 g, 4.0 mmol) are used as educts.

Yield: 706 mg, 54%; **m.p.**: 171 – 173°C; **Raman** (55 mW, 600 scans, 298 K, in cm^{-1}): 3065 (23), 3002 (6), 2967 (29), 2933 (100), 1638 (48), 1588 (42), 1574 (6), 1472 (10), 1451 (35), 1404 (65), 1383 (29), 1341 (58), 1275 (6), 1223 (13), 1099 (48), 1030 (74), 1000 (52), 753 (26), 602 (23), 570 (16), 347 (16), 313 (13), 240 (6), 205 (13); **IR** (298 K, ATR, in cm^{-1}): 1637 (w), 1480 (vw), 1437 (w), 1401 (vw), 1379 (w), 1258 (vs), 1222 (w), 1145 (m), 1028 (s), 8598 (w), 766 (w), 749 (m), 705 (w), 635 (vs), 572 (w), 516 (m), 489 (vw), 461 (w), 448 (m); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 7.70 (1H, m, C4-H), 7.65 – 7.60 (2H, m, C2-H), 7.60 – 7.54 (2H, m, C3-H), 3.52 (12H, s, C7-H), 2.30 (12H, s, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 134.7 (d, $^{2}J_{CP}$ = 23 Hz, C2), 134.2 (s, C4), 134.1 (d, $^{1}J_{CP}$ = 35 Hz, C5), 133.8 (s, C6), 131.8 (d,

$^3J_{CP}$ = 8.4 Hz, C3), 130.9 (d, $^1J_{CP}$ = 14 Hz, C1), 122.1 (q, $^1J_{CF}$ = 321 Hz, OTf), 35.3 (d, $^3J_{CP}$ = 10 Hz, C7), 9.7 (s, C8), C1 is not observed; **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.3 (s, OTf); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -51.1 (s); **Elemental analysis**: calculated for $C_{22}H_{29}F_6N_6O_6PS_2$: C: 40.4, H: 4.5, N: 8.6, S: 9.8; found: C: 40.3, H: 4.4, N: 8.5, S: 9.7.

S2.6. Preparation of **7^{iPr}**[OTf]$_2$

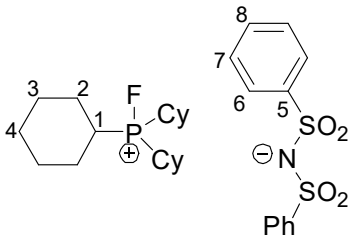


Following the general procedure, $PhPCl_2$ (1.79, 10.0 mmol) and [Lc^{iPr}TMS][OTf] (8.05 g, 20.0 mmol) are used as educts.

Yield: 6.14 g, 80%; **m.p.**: 196 – 198 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3063 (23), 2989 (37), 2942 (62), 1614 (47), 1585 (50), 1572 (12), 1462 (28), 1448 (28), 1415 (50), 1404 (38), 1360 (48), 1284 (100), 1223 (13), 1154 (20), 1089 (22), 1031 (83), 998 (50), 886 (18), 791 (14), 754 (26), 573 (16), 459 (11), 348 (32), 311 (29); **IR** (298 K, ATR, in cm^{-1}): 2986 (vw), 2942 (vw), 1613 (w), 1462 (vw), 1438 (vw), 1398 (w), 1380 (w), 1256 (vs), 1221 (s), 1140 (s), 1119 (m), 1090 (w), 1028 (vs), 983 (w), 907 (vw), 791 (vw), 751 (m), 710 (w), 700 (w), 635 (vs), 571 (m), 547 (w), 516 (s), 485 (m), 448 (w); **^{1}H NMR** (CD_3CN, 300 K, in ppm): *δ* = 7.77 – 7.63 (5H, m, Ph); 4.75 (2H, oct, $^3J_{HH}$ = 6.9 Hz, C7-H), 2.46 (12H, s, C9-H), 1.43 (12H, d, $^3J_{HH}$ = 6.9 Hz, C8-H), 1.38 (12H, d, $^3J_{HH}$ = 6.9 Hz, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): *δ* = 135.1 (s, C6), 135.1 (d, $^1J_{CP}$ = 25 Hz, C5), 134.4 (s, C4), 134.3 (d, $^3J_{CP}$ = 43 Hz, C3), 132.0 (d, $^2J_{CP}$ = 8 Hz, C2), 122.7 (d, $^1J_{CP}$ = 14 Hz, C1), 122.1 (q, $^1J_{CF}$ = 320 Hz, OTf), 54.9 (d, $^3J_{CP}$ = 13 Hz, C7), 21.4 (s, C8), 21.0 (s, C8), 11.6 (s, C9); **^{19}F NMR** (CD_3CN, 300 K, in ppm): *δ* = -79.2 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): *δ* = -46.6 (s); **Elemental analysis**: calculated for $C_{30}H_{45}F_6N_4O_6PS_2$: C 47.0, H 5.9, N 7.3, S 8.4, found C 47.1, H 6.0, N 7.0, S 8.1.

S3 Preparation of fluorophosphonium bis(phenylsulfonyl)amide salts

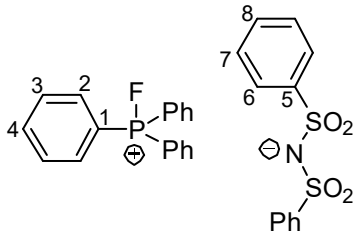
S3.1. Preparation of **2a**[NSI]



A solution of NFSI (315 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) is added dropwise to a solution of Cy_3P (280 mg, 1.0 mmol) in CH_2Cl_2 (2 mL). The colorless mixture is allowed to stir for 2 h at ambient temperature. After that the reaction mixture is concentrated to ca. 25% of its volume. The addition of Et_2O (2 mL) gives a colorless precipitate, which is filtered off, washed with Et_2O (3 x 1 mL), and dried *in vacuo* yielding the titled compound as a colorless solid.

Yield: 548 mg, 92%; **m.p.**: 115 – 117 °C; **Raman** (50 mW, 100 scans, 298 K, in cm^{-1}): 3065 (67), 2950 (100), 2930 (73), 2905 (40), 2871 (93), 1586 (40), 1444 (20), 1299 (17), 1282 (13), 1263 (10), 1183 (10), 1150 (40), 1032 (27), 1000 (63), 845 (7), 814 (17), 708 (20), 695 (23), 614 (10), 343 (7), 315 (10), 293 (7), 247 (10), 226 (10), 162 (13); **IR** (298 K, ATR, in cm^{-1})**:** 2930 (vw), 2856 (vw), 1446 (w), 1278 (s), 1262 (m), 1129 (m), 1087 (s), 1068 (w), 1052 (s), 1023 (w), 997 (w), 923 (vw), 889 (w), 861 (w), 850 (vw), 828 (vw), 791 (vw), 764 (w), 754 (m), 719 (s), 695 (m), 615 (w), 588 (vs), 554 (vs), 544 (s), 530 (m), 505 (vw), 481 (w), 459 (vw), 438 (vw), 414 (vw)**;** ^{1}**H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 7.76 – 7.73 (4H, m, C7-H), 7.37 – 7.34 (2H, m, C8-H), 7.31 – 7.27 (4H, m, C6-H), 2.98 – 2.96 (3H, m, C1-H), 2.06 – 2.03 (6H, m, C3-H), 1.88 – 1.84 (6H, m, C2-H), 1.77 – 1.74 (3H, m, C4-H), 1.58 – 1.47 (6H, m, C3-H), 1.47 – 1.37 (6H, m, C2-H), 1.32 – 1.21 (3H, m, C4-H); ^{13}**C{**^{1}**H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 146.8 (s, C5), 130.4 (s, C8), 128.4(s, C6), 127.1(s, C7), 33.8 (dd, $^{1}J_{CP}$ = 42 Hz, $^{2}J_{CF}$ = 8 Hz, C1), 26.3 (d, $^{2}J_{CP}$ = 14 Hz, C2) 25.6 (s, br, C3 and C4); ^{19}**F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -171.7 (d, $^{1}J_{FP}$ = 985 Hz); ^{31}**P{**^{1}**H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 134.3 (d, $^{1}J_{PF}$ = 985 Hz); **Elemental analysis**: calculated for $C_{30}H_{43}FNO_4PS_2$: C 60.5, H 7.3, N 2.4, found: C 60.2, H 7.1, N 2.3; Crystallographic data and details of the structure refinements are depicted in table S10.2.1.

S3.2. Preparation of **2b**[NSI]

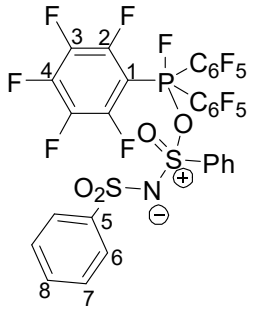


2b[NSI] is prepared in the same manner as **2a**[NSI] but with Ph_3P (262 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) as educts, yielding the titled compound as a colorless solid.

Yield: 949 mg, 95%; **m.p.**: 83 – 84 °C; **Raman** (40 mW, 512 scans, 298 K, in cm^{-1}): 3068 (84), 1586 (58), 1165 (11), 1149 (18), 1112 (15), 1028 (18), 999 (100), 795 (5), 696 (16), 614 (15), 348 (5), 275 (5), 245 (11), 159 (15); **IR** (298 K, ATR, in cm^{-1})**:** 3060 (vw), 1587 (vw), 1478 (vw), 1439 (m), 1367 (w), 1277 (m), 1262 (m), 1190 (vw), 1165 (w), 1127 (s), 1083 (s), 1048 (m), 1023 (m), 994 (m), 907 (w), 886 (w), 794 (vw), 734 (s), 719 (s), 680 (s), 614 (vw), 586 (s), 549 (vs), 529 (vs), 487 (m), 433 (vw); ^{1}**H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 8.05 – 8.02 (3H, m, C4-H), 7.85 – 7.81 (12H, m, C2-H, C3-H), 7.73 – 7.70 (4H, m, C6-H), 7.33 – 7.29 (2H, m, C8-H) 7.28 – 7.23 (4H, m, C7-H); ^{13}**C{**^{1}**H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 146.6 (s, C5), 138.9 (dd, $^{4}J_{CP}$ = 3 Hz, $^{5}J_{CF}$ = 2 Hz, C4), 134.6 (dd, $^{3}J_{CP}$ = 13 Hz, $^{4}J_{CF}$ = 2 Hz, C2), 131.2 (d, $^{2}J_{CP}$ = 11 Hz, C3), 130.5 (s, C8), 128.3 (s, C7), 127.2 (s, C6), 116.8 (dd, $^{1}J_{CP}$ = 108 Hz, $^{2}J_{CF}$ = 14 Hz, C1); ^{19}**F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -128.8 (d, $^{1}J_{FP}$ = 995 Hz); ^{31}**P{**^{1}**H} NMR** (CD_2Cl_2, 300 K, in

ppm): δ = 94.6 (d, $^1J_{FP}$ = 995 Hz); **Elemental analysis**: calculated for $C_{30}H_{25}FNO_4PS_2$: C 62.4, H 4.4, N 2.3, found: C 62.4, H 4.6, N 2.3; Crystallographic data and details of the structure refinements are depicted in table S10.2.1.

S3.3. Preparation of [**2c**(NSI)]



In a 100 mL Schlenk flask $(C_6F_5)_3P$ (5.32 g, 10.0 mmol) and NFSI (3.15 g, 10.0 mmol) are dissolved in 30 mL PhF and stirred for 2 days at ambient temperature resulting in a colorless suspension. The precipitate is filtered off and washed with PhF (3 x 5 mL), yielding [**2c**(NSI)] as colorless solid after evaporation of all volatiles *in vacuo*.

Yield: 7.20 g, 85%; **m.p.**: 159 – 160 °C; **Raman** (40 mW, 500 scans, 298 K, in cm^{-1}): 3080 (66), 1647 (34), 1586 (52), 1403 (10), 1156 (21), 1105 (21), 1027 (21), 1001 (100), 807 (17), 695 (24), 614 (17), 586 (31), 494 (34), 468 (14), 443 (21), 386 (17), 319 (10), 266 (10), 246 (14), 225 (10), 154 (24); **IR** (298 K, ATR, in cm^{-1}): 3074 (vw), 1647 (w), 1596 (vw), 1523 (m), 1487 (vs), 1449 (w), 1400 (w), 1363 (w), 1307 (m), 1259 (w), 1217 (vw), 1153 (m), 1105 (s), 1064 (s), 1026 (w), 984 (vs), 935 (m), 877 (w), 806 (w), 794 (w), 770 (w), 757 (s), 719 (s), 687 (s), 642 (w), 635 (w), 618 (w), 587 (vs), 542 (vs), 502 (w), 463 (s), 443 (w), 429 (w), 411 (s), **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 7.58 – 7.56 (4H, m, C7-H), 7.50 – 7.46 (2H, m, C8-H), 7.38 – 7.33 (4H, m, C6-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 146.9 (dm, $^1J_{CF}$ = 254 Hz, C2), 146.1 (dm, $^1J_{CF}$ = 265 Hz, C4), 142.9 (s, C5), 138.6 (dm, $^1J_{CF}$ = 257 Hz, C3), 133.0 (s, C8), 129.1 (s, C6), 126.7 (s, C7), 107.6 (dm, $^1J_{CP}$ = 194 Hz, C1); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -29.3 (d, $^1J_{FP}$ = 723 Hz, P-F), -129.5 (m, br, C2-F), -142.0 (m, C4-F), -157.9 (m, C3-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = -30.5 (d, $^1J_{PF}$ = 723 Hz, F-P); **Elemental analysis**: calculated for $C_{30}H_{43}FNO_4PS_2$: C 42.5, H 1.2, N 1.7, found: C 42.4, H 1.2, N 1.7; Crystallographic data and details of the structure refinements are depicted in table S10.2.1.

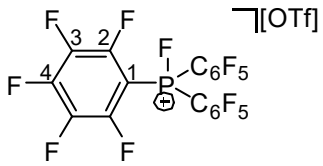
S4 Preparation of fluorophosphonium triflate salts

Unless stated otherwise, the fluorophosphonium triflate salts are prepared by the following general procedure:

A mixture of the corresponding phosphane and an equimolar amount of NFSI is stirred in the specified solvent at ambient temperature for the stated amount of time. After that, one equivalent of MeOTf is added to the reaction mixture followed by further stirring at ambient

temperature for 4 h. If the corresponding fluorophosphonium triflate salt is not precipitating from the reaction mixture, Et_2O is added until precipitation. The obtained solid is then filtered off, washed with three portions of Et_2O, and dried *in vacuo* to yield the titled fluorophosphonium triflate salt as analytically pure, air-sensitive, and colorless solid.

S4.1. Preparation of **2c**[OTf]



Following the general procedure, $(C_6F_5)_3P$ (5.32 g, 10.0 mmol) and NFSI (3.15g, 10.0 mmol) are used as educts and reacted in PhF (30 mL) for 48 h before the addition of MeOTf (1.64 g, 10.0 mmol).

Yield: 6.58 g, 94%; **m.p.**: 151 – 153 °C; **Raman** (40 mW, 500 scans, 298 K, in cm^{-1}): 1651 (100), 1411 (29), 1394 (43), 1036 (57), 967 (29), 587 (57), 499 (86), 441 (43), 392 (43), 157 (29); **IR** (298 K, ATR, in cm^{-1}): 1650 (w), 1522 (m), 1488 (vs), 1393 (m), 1315 (m), 1278 (m), 1259 (s), 1227 (w), 1151 (m), 1113 (vs), 1035 (s), 988 (vs), 965 (s), 900 (vw), 846 (vw), 772 (w), 763 (w), 728 (w), 635 (s), 593 (m), 574 (w), 538 (s), 519 (m), 455 (s), 441 (m), 421 (w);

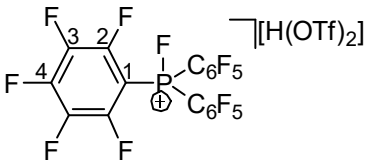
NMR in CD_2Cl_2: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 K, in ppm): δ = 147.2 (dm, $^1J_{CF}$ = 258 Hz, C4), 146.8 (dm, $^1J_{CF}$ = 267 Hz, C3), 138.7 (dm, $^1J_{CF}$ = 258 Hz, C2), 119.2 (q, $^1J_{CF}$ = 319 Hz, OTf), 105.3 (dm, $^1J_{CP}$ = 187.3 Hz, C1); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -42.2 (d, $^1J_{FP}$ = 761 Hz, P-F), -78.8 (s, OTf), -129.3 (m, br, C2-F), -139.5 (m, C4-F), -157.0 (m, C3-F); **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 300 K, in ppm): δ = -15.5 (d, $^1J_{PF}$ = 761 Hz);

NMR In MeCN: ^{19}F NMR (C_6D_6capillary, 300 K, in ppm): -78.6 (s, OTf), -108.3 (d, $^1J_{FP}$ = 1000 Hz, P-F), -125 (m, C2-F), -130.8 (m, C4-F), -155.2 (m, C3-F); **$^{31}P\{^1H\}$ NMR** (C_6D_6capillary, 300 K, in ppm): δ = 57.9 (d, $^1J_{PF}$ = 1000 Hz);

NMR in PhCN: ^{19}F NMR (C_6D_6capillary, 300 K, in ppm): δ = -72.5 (d, $^1J_{FP}$ = 870 Hz, P-F), -78.1 (s, OTf), -127.1 (m, br, C2-F), -135.1 (m, C4-F), -155.8 (m, C3-F); **$^{31}P\{^1H\}$ NMR** (C_6D_6capillary, 300 K, in ppm): δ = 19.4 (d, $^1J_{PF}$ = 870 Hz).

Elemental analysis: calculated for $C_{19}F_{19}O_3PS$: C 32.6, S 4.6, found: C 32.4, S 5.4; Sulfur determination was not accurately possible due to the high F-content.

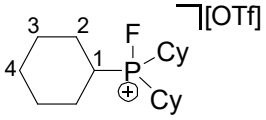
S4.2. Preparation of **2c**[H(OTf)$_2$]



In a 10 mL Schlenk tube, [(C$_6$F$_5$)$_3$PF][OTf] (350 mg, 0.5 mmol) is suspended in CH_2Cl_2 (2 mL). HOTf (75.0 mg, 44 uL, 0.5 mmol) is added through a syringe. After stirring for 2 h, all volatiles are removed *in vacuo*. The resulting yellow oil is recrystallized from CH_2Cl_2/*n*-pentane to give **2c**[H(OTf)$_2$] as a colorless solid.

Yield: 388 mg, 89%; **m.p.**: decomposition at approx. 111 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 1652 (1987), 1413 (7), 1396 (12), 1036 (8), 588 (7), 501 (541), 459 (8), 443 (8), 405 (7), 392 (10), 350 (21), 317 (10)**; IR** (298 K, ATR, in cm^{-1}): 1650 (w), 1522 (m), 1490 (vs), 1392 (m), 1316 (m), 1279 (m), 1260 (m), 1226 (w), 1202 (m), 1150 (m), 1115 (vs), 1035 (m), 989 (vs), 967 (m), 961 (m), 921 (w), 900 (w), 846 (vw), 772 (w), 764 (w), 728 (w), 637 (s), 592 (m), 558 (vw), 539 (s), 518 (w), 501 (w), 477 (w), 455 (vs), 441 (w), 420 (w), 404 (vw); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 15.03 (1H, s, br, [HOTf$_2$]), **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 147.8 (dm, $^1J_{CF}$ = 258 Hz, C4 and C3), 138.8 (dm, $^1J_{CF}$ = 260 Hz, C2), 119.4 (q, $^1J_{CF}$ = 318 Hz, OTf), 103.1 (dm, $^1J_{CP}$ = 177 Hz, C1); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -57.8 (d, br, $^1J_{FP}$ = 820 Hz, P-F), -78.8 (s, OTf), -128.0 (s, br, C2-F), -136.6 (s, br, C4-F), -156.1 (m, C3-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 3.6 (d, br, $^1J_{FP}$ = 820 Hz); Crystallographic data and details of the structure refinements are depicted in table S10.2.2, Elemental analysis not determined.

S4.3. Preparation of **2a**[OTf]

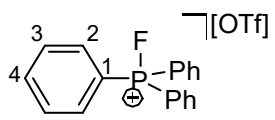


Following the general procedure, Cy_3P (280 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and react in CH_2Cl_2 (3 mL) for 1 h before the addition of MeOTf (164 mg, 1.0 mmol)

Yield: 435 mg, 97%; **m.p.**: 160 – 162 °C; **Raman** (40 mW, 500 scans, 298 K, in cm^{-1}): 2949 (100), 2863 (59), 1446 (35), 1360 (6), 1301 (12), 1289 (18), 1221 (12), 1030 (53), 846 (12), 817 (18), 751 (18), 718 (12), 571 (6), 439 (6), 346 (12), 309 (12), 226 (18); **IR** (298 K, ATR, in cm^{-1}): 2945 (w), 2859 (w), 1447 (w), 1262 (vs), 1220 (m), 1143 (s), 1027 (s), 1007 (w), 926 (vw), 902 (m), 887 (m), 856 (w), 825 (vw), 751 (vw), 632 (vs), 563 (m), 547 (w), 528 (w), 516 (m), 491 (w), 464 (vw), 432 (w), 419 (w); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 2.90 – 2.82 (3H, m, C1-H), 2.10 – 2.07 (6H, m, C3-H), 1.98 – 1.94 (6H, m, C2-H), 1.84 – 1.81 (3H, m, C4-H), 1.59 (6H, m, C3-H), 1.48 (6H, m, C2-H), 1.33 (3H, m, C4-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300

K, in ppm): δ = 121.5 (q, $^{1}J_{CF}$ = 321 Hz, OTf), 33.6 (dd, $^{1}J_{CP}$ = 8 Hz, $^{2}J_{CF}$ = 42 Hz, C1), 26.1 (d, $^{2}J_{CP}$ = 13 Hz, C2), 25.5 (m, C3 and C4); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -78.9 (s, OTf), -171.7 (d, $^{1}J_{FP}$ = 988 Hz, P-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 134.0 (d, $^{1}J_{PF}$ = 988 Hz). **Elemental analysis**: calculated for $C_{19}H_{33}F_4O_3PS$: C 50.9, H 7.4, S 7.2, found: C 50.7, H 6.5, S 7.4; Crystallographic data and details of the structure refinements are depicted in table S10.2.3.

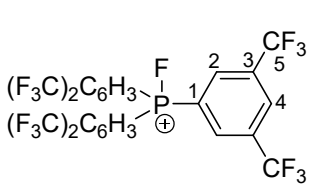
S4.4. Preparation of **2b**[OTf]



Following the general procedure, Ph_3P (262 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 1 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 366 mg, 92%; **m.p.**: 167 – 169 °C; **Raman** (40 mW, 500 scans, 298 K, in cm^{-1}): 3149 (6), 3066 (88), 2381 (6), 2202 (79), 1583 (76), 1187 (6), 1170 (6), 1113 (6), 1096 (12), 1029 (9), 1023 (29), 998 (100), 755 (12), 702 (6), 648 (9), 613 (12), 572 (6), 348 (9), 313 (6), 277 (6), 254 (9), 203 (9); **IR** (298 K, ATR, in cm^{-1}): 3091 (vw), 3032 (vw), 1587 (w), 1440 (m), 1258 (vs), 1223 (m), 1157 (s), 1124 (vs), 1029 (s), 996 (m), 896 (s), 833 (vw), 760 (m), 738 (vs), 685 (s), 636 (vs), 573 (w), 554 (w), 529 (vs), 515 (vs), 488 (m), 449 (w); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 8.08 – 8.05 (3H, m, C4-H), 7.87-7.85 (12H, m, C2-H and C3-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 138.9 (d, $^{4}J_{CP}$ = 2 Hz, C4), 134.5 (d, $^{3}J_{CP}$ = 13 Hz, C3), 131.4 (d, $^{2}J_{CP}$ = 15 Hz, C2), 121.5 (q, $^{1}J_{CF}$ = 321 Hz, OTf), 116.7 (dd, $^{1}J_{CP}$ = 108 Hz, $^{2}J_{CF}$ = 14 Hz, C1); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -78.9 (s, OTf), -128.7 (d, $^{1}J_{PF}$ = 996 Hz, P-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 94.6 (d, $^{1}J_{FP}$ = 996 Hz). **Elemental analysis**: calculated for $C_{19}H_{15}F_4O_3PS$: C 53.0, H 3.5, S 7.5, found: C 52.9, H 3.4, S 7.8; Crystallographic data and details of the structure refinements are depicted in table S10.2.2.

S4.5. Preparation of **2d**[OTf].

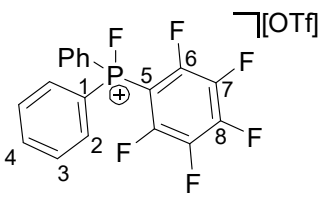


Following the general procedure, $((CF_3)_2C_6H_3)_3P$ (6.70 g, 10.0 mmol) and NFSI (3.15g, 10.0 mmol) are used as educts and react in PhF (30 mL) for 48 h before the addition of MeOTf (1.64 g, 10.0 mmol).

Yield: 8.05 g, 96%; **m.p.**: 154 – 155 ºC; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3094 (17), 3045 (7), 1623 (17), 1611 (45), 1365 (30), 1141 (6), 1117 (12), 1101 (16), 1030 (31), 1020

(14), 1001 (100), 865 (9), 812 (6), 760 (13), 712 (49), 575 (7), 348 (13), 317 (12), 285 (24), 267 (16), 251 (20), 193 (50), 185 (56), 165 (72), 129 (67); **IR** (298 K, ATR, in cm^{-1}): 1609 (vw), 1362 (w), 1278 (s), 1243 (w), 1183 (m), 1129 (vs), 1114 (s), 1101 (s), 1028 (w), 1020 (w), 936 (vw), 899 (w), 864 (vw), 843 (w), 694 (w), 682 (m), 636 (m), 614 (m), 574 (vw), 536 (s), 519 (w), 495 (w), 405 (vw); **^{1}H NMR** (CD_2Cl_2, 300K, in ppm): δ = 8.49 (3H, br, C2-H), 8.47 (6H, br, C2-H and C4-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): δ = 134.4 (qd, $^{2}J_{CF}$ = 35 Hz, $^{3}J_{CP}$ = 17 Hz, C3), 134.4 (dm, $^{2}J_{CP}$ = 15 Hz, C2), 131.1 (m, C4), 126.1 (dd, $^{1}J_{CP}$ = 138 Hz, $^{2}J_{CF}$ = 17 Hz, C1), 122.7 (q, $^{1}J_{CF}$ = 319 Hz, OTf), 119.7(dq, $^{1}J_{CF}$ = 274 Hz, $^{4}J_{CP}$ = 3 Hz, C5); **^{19}F NMR** (CD_2Cl_2, 300K, in ppm): δ = -63.6 (s, C5-F), -79.6 (s, OTf), -86.3 (d, $^{1}J_{FP}$ = 835 Hz, P-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): δ = 56.3 (d, $^{1}J_{PF}$ = 835 Hz, P); **Elemental analysis**: calculated for $C_{25}H_9F_{22}O_3PS$: C 35.8, H 1.1, S 3.8, found: C 35.7, H 1.2, S 4.2. Crystallographic data and details of the structure refinements are depicted in table S10.2.3.

S4.6. Preparation of **4a**[OTf].

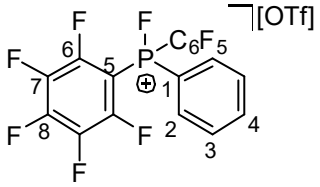


Following the general procedure, $(C_6F_5)Ph_2P$ (352 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 2 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 500 mg, 96%; **m.p.**: 69 – 70 ºC; **Raman** (100 mW, 250 scans, 298 K, in cm^{-1}): 3077 (100), 1653 (26), 1590 (95), 1399 (17), 1198 (9), 1175 (10), 1119 (21), 1032 (63), 1000 (99), 906 (23), 877 (10), 760 (15), 706 (26), 615 (16), 550 (15), 486 (16), 443 (14), 398 (11), 353 (13), 317 (12), 291 (17), 266 (8), 230 (12), 210 (28), 168 (6), 150 (11); **IR** (298 K, ATR, in cm^{-1}): 3053 (vw), 1638 (w), 1517 (m), 1464 (vs), 1432 (s), 1381 (m), 1312 (vw), 1288 (w), 1088 (s), 1026 (w), 1001 (vw), 968 (vs), 922 (w), 912 (w), 865 (vw), 846 (vw), 832 (w), 739 (vs), 726 (w), 693 (vs), 630 (w), 618 (w), 586 (w), 511 (m), 496 (s), 486 (s), 443 (s), 416 (m); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 8.01-8.03 (6H, m, C3-H and C4-H) 7.90-7.86 (4H, m, C2-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): 149.7 (dm, $^{1}J_{CF}$ = 272 Hz, C8), 149.5 (dm, $^{1}J_{CF}$ = 262 Hz, C7), 139.8(d, $^{4}J_{CP}$ = 3 Hz, C4), 139.7 (dm, $^{1}J_{CF}$ = 258 Hz, C6), 134.7 (d, $^{3}J_{CP}$ = 15 Hz, C3), 131.6 (d, $^{2}J_{CP}$ = 16 Hz, C2), 121.3 (q, $^{1}J_{CF}$ = 321 Hz, OTf), 116.0 (dd, $^{1}J_{CP}$ = 114 Hz, $^{2}J_{CF}$ = 14 Hz, C1), 94.2 (dm, $^{1}J_{CP}$ = 116 Hz, C5); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -79.2 (s, OTf), -123.2 (dm, $^{1}J_{FP}$ = 1014 Hz, P-F), -124.8 (m, C6-F), -132.8 (m, C7-F), -155.3 (m, C8-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 87.1 (d, $^{1}J_{PF}$ = 1014 Hz);

Elemental analysis: calculated for $C_{19}H_{10}F_9O_3PS$: C 43.9, H 1.9, S 6.2, found: C 43.8, H 2.0, S 6.5.

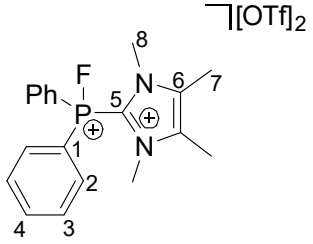
S4.7. Preparation of **4b**[OTf]



Following the general procedure, $(C_6F_5)_2PhP$ (442 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 16 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 530 mg, 87%; **m.p.**: 141 – 142 ºC; **Raman** (100 mW, 1000 scans, 298 K, in cm^{-1}): 3105 (18), 3077 (45), 3061 (27), 1652 (91), 1586 (91), 1528 (18), 1401 (55), 1392 (45), 1312 (27), 1175 (18), 1114 (27), 1029 (100), 997 (100), 930 (64), 898 (18), 866 (27), 756 (36), 722 (27), 613 (27), 589 (45), 574 (18), 531 (36), 485 (36), **IR** (298 K, ATR, in cm^{-1}): 3064 (vw), 1651 (w), 1587 (vw), 1528 (m), 1490 (vs), 1442 (w), 1389 (w), 1353 (vw), 1312 (m), 1276 (s), 1259 (vs), 1225 (w), 1199 (vw), 1162 (m), 1147 (m), 1119 (vs), 1030 (s), 987 (vs), 935 (m), 897 (vw), 866 (vw), 832 (vw), 773 (w), 750 (m), 728 (w), 720 (w), 684 (m), 637 (s), 612 (vw), 593 (w), 574 (w), 549 (s), 527 (s), 518 (s), 483 (w), 472 (s), 451 (m), 440 (w), 410 (w); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 8.30 – 8.26 (2H, m, C2-H), 8.13 – 8.20 (1H, m, C4-H), 7.96 – 7.91 (2H, m, C3-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm):δ = 150.9 (dm, $^1J_{CF}$ = 269 Hz, C8), 150.5 (dm, $^1J_{CF}$ = 262 Hz, C7), 142.2 (s, C4), 135.7 (d, $^3J_{CP}$ = 16 Hz, C3), 132.5 (d, $^2J_{CP}$ = 17 Hz, C2), 122.6 (q, $^1J_{CF}$ = 331 Hz, OTf), 115.4 (dd, $^1J_{CP}$ = 120 Hz, $^2J_{CF}$ = 13 Hz, C1), 94.2 (dm, $^1J_{CP}$ = 126 Hz, C5); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.4 (s, OTf), -120.6 (dm, $^1J_{FP}$ = 1034 Hz, P-F), -125.2 (m, C6-F), -133.2 (m, C7-F), -156.5 (m, C8-F); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 78.8 (d, $^1J_{PF}$ = 1034 Hz), **Elemental analysis**: calculated for $C_{19}H_5F_{14}O_3PS$: C 37.4, H 0.8, S 5.3, found: C 37.1, H 1.0, S 5.6; Crystallographic data and details of the structure refinements are depicted in table S10.2.3.

S4.8. Preparation of **6^{Me}a**$[OTf]_2$

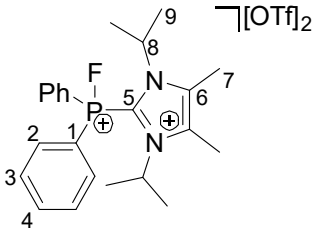


Following the general procedure, $[Lc^{Me}Ph_2P][OTf]$ (430 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in PhF (3 mL) for 16 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 589 mg, 94%; **m.p.**: decomposition at approx. 144 °C; **Raman** (30 mW, 512 scans, 298 K, in cm^{-1}): 3074 (53), 3012 (8), 2986 (14), 2939 (36), 1613

(17), 1587 (100), 1486 (6), 1456 (8), 1408 (31), 1330 (36), 1277 (11), 1227 (11), 1197 (6), 1173 (6), 1115 (14), 1100 (14), 1031 (97), 999 (64), 908 (17), 791 (11), 757 (25), 705 (25), 615 (14), 596(25), 572 (22), 537(6), 518(6), 350(28), 316(19), 284(11), 233(8); **IR** (298 K, ATR, in cm^{-1}): 3064 (vw), 1615 (vw), 1586 (w), 1490 (vw), 1441 (w), 1402 (w), 1374 (vw), 1331 (w), 1259 (vs), 1224 (w), 1150 (m), 1123 (w), 1112 (w), 1030 (s), 995 (w), 908 (m), 855 (w), 787 (w), 754 (w), 743 (m), 704 (w), 684 (m), 635 (s), 614 (w); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 8.32 – 8.26 (4H, m, C2-H), 8.17 – 8.14 (2H, m, C4-H), 7.96 – 7.91 (4H, m, C3-H), 3.58 (6H, s, C7-H), 2.48 (6H, d, $^{4}J_{HP}$ = 1.3 Hz, C8-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 140.9 (dd, $^{3}J_{CP}$ = 7 Hz, $^{4}J_{CF}$ = 1 Hz, C4), 140.8 (dd, $^{4}J_{CP}$ = 3 Hz, $^{5}J_{CF}$ = 2 Hz, C6), 136.0 (d, $^{2}J_{CP}$ = 15 Hz, C2), 132.2 (d, $^{3}J_{CP}$ = 16 Hz, C3), 121.2 (q, $^{1}J_{CF}$ = 321 Hz, OTf), 120.8 (dd, $^{1}J_{CP}$ = 160 Hz, $^{2}J_{CF}$ = 21 Hz, C5), 114.5 (dd, $^{1}J_{CP}$ = 117 Hz, $^{2}J_{CF}$ = 15 Hz, C1), 36.8 (s, C7), 10.7 (s, C8); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -79.0 (s, OTf), -114.4 (d, $^{1}J_{FP}$ = 1026 Hz, P-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 71.6 (d, $^{1}J_{PF}$ = 1026 Hz, P-F); **Elemental analysis**: calculated for $C_{21}H_{22}F_7N_2O_6PS_2$: C 40.3, H 3.5, N 4.5, S 10.2, found: C 39.8, H 3.5, N 4.4, S 10.6; Crystallographic data and details of the structure refinements are depicted in table S10.2.4.

S4.9. Preparation of **6$^{i\mathrm{Pr}}$a**$[OTf]_2$

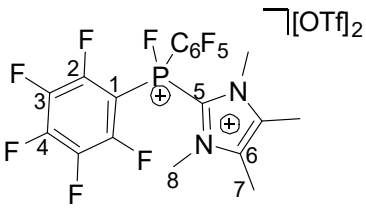


Following the general procedure, [Lc$^{i\mathrm{Pr}}$Ph$_2$P][OTf] (683 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in PhF (3 mL) for 16 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 601 mg, 88%; **m.p.**: decomposition at approx. 160 °C; **Raman** (60 mW, 512 scans, 298 K, in cm^{-1}): 3085 (31), 3064 (54), 2999 (31), 2953 (54), 1587 (100), 1397 (38), 1269 (46), 1109 (23), 1034 (100), 998 (77), 756 (38), 706 (31), 614 (23), 349 (23), 315 (23), 296 (23), 147 (31); **IR** (298 K, ATR, in cm^{-1}): 3062 (vw), 1587 (vw), 1441 (w), 1397 (vw), 1376 (vw), 1260 (vs), 1223 (m), 1156 (s), 1125 (s), 1110 (m), 1028 (vs), 996 (vw), 907 (m), 854 (vw), 807 (w), 743 (m), 706 (vw), 685 (m), 633 (vs), 573 (w), 538 (s), 515 (vs), 475 (w), 455 (vw), 429 (vw), 413 (vw); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 8.36 – 8.31 (4H, m, C2-H), 8.19 – 8.16 (2H, m, C4-H), 7.99 – 7.95 (4H, m, C3-H), 4.33 (2H, sept, $^{1}J_{HH}$ = 6.9 Hz, C8-H), 2.60 (6H, d, $^{5}J_{PH}$ = 1.4 Hz, C7-H), 1.52 (12H, d, $^{1}J_{HH}$ = 6.9 Hz, C8-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 142.0 (d, $^{3}J_{CP}$ = 7 Hz, C6), 141.0 (dd, $^{4}J_{CP}$ = 2 Hz, $^{5}J_{CF}$ = 2 Hz, C4), 136.1 (d, $^{2}J_{CP}$ = 15 Hz, C2), 132.3 (d, $^{3}J_{CP}$ = 16 Hz, C3), 121.3 (q,

$^1J_{CF}$ = 320 Hz, OTf), 118.8 (dd, $^1J_{CP}$ = 162 Hz, $^2J_{CF}$ = 20 Hz, C5), 116.0 (dd, $^1J_{CP}$ = 16 Hz, $^2J_{CF}$ = 15 Hz, C1), 57.2 (s, C8), 20.8 (s, C9), 12.7 (s, C7); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -78.9 (s, OTf), -108.4 (d, $^1J_{FP}$ = 1025 Hz, P-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 76.1 (d, $^1J_{PF}$ = 1025 Hz, P-F); **Elemental analysis**: calculated for $C_{25}H_{30}F_7N_2O_6PS_2$: C 44.0, H 4.4, N 4.1, S 9.4, found: C 43.7, H 4.0, N 4.2, S 9.5.

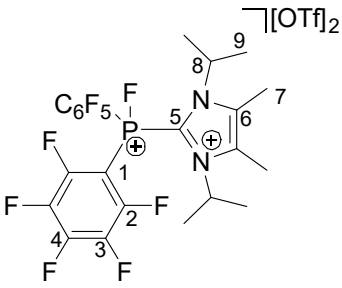
S4.10. Preparation of **6^{Me}b**[OTf]$_2$



Following the general procedure, [Lc^{Me}(C_6F_5)$_2$P][OTf] (638 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 48 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 758 mg, 94%; **m.p.**: decomposition at approx. 198 °C; **Raman** (35 mW, 450 scans, 298 K, in cm^{-1}): 2968 (5), 2940 (29), 1648 (54), 1630 (11), 1453 (15), 1410 (39), 1388 (22), 1339 (47), 1276 (7), 1225 (5), 1101 (20), 1032 (36), 978 (5), 835 (13), 774 (5), 753 (15), 629 (5), 598 (16), 587 (36), 570 (14), 517 (5), 504 (30), 455 (15), 445 (6), 421 (10), 394 (22), 378 (6), 350 (5), 322 (15), 234 (5), 172 (9), 151 (12), 76 (100); **IR** (298 K, ATR, in cm^{-1}): 1647 (w), 1629 (vw), 1522 (m), 1473 (s), 1446 (vw), 1409 (w), 1382 (w), 1338 (vw), 1263 (s), 1223 (w), 1151 (s), 1089 (m), 1031 (m), 972 (s), 855 (w), 773 (w), 753 (vw), 722 (vw), 636 (vs); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 3.90 (6H, s, C8-H), 2.46 (6H, d, $^5J_{PH}$ = 1.4 Hz, C7-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 149.5 (dm, $^1J_{CF}$ = 24 Hz, C1), 148.0 (dm, $^1J_{CF}$ = 262 Hz, C3), 139.7 (d, $^3J_{CP}$ = 8 Hz, C6), 139.3 (dm, $^1J_{CF}$ = 241 Hz, C2), 121.2 (dd, $^1J_{CP}$ = 230 Hz, ^2J_C = 27 Hz, C5), 120.5 (q, $^1J_{CF}$ = 320 Hz), 97.3 (dm, $^1J_{CP}$ = 187 Hz, C1), 36.7 (d, $^3J_{CP}$ = 2 Hz, C8); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -73.4 (d, $^1J_{FP}$ = 891 Hz, P-F), -79.1 (s, OTf), -26.3 (m, C2-F), -133.2 (m, C4-F), -155.7 (m, C3-F); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 9.1 (d, $^1J_{PF}$ = 891 Hz, P-F); **Elemental analysis**: calculated for $C_{21}H_{12}F_{17}N_2O_6PS$: C 31.3, H 1.5, N 3.4, S 8.0, found: C 31.3, H 1.4, N 3.5, S 7.8; Crystallographic data and details of the structure refinements are depicted in table S10.2.4.

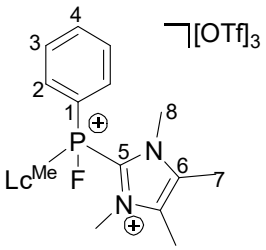
S4.11. Preparation of **6^{iPr}b**[OTf]$_2$



Following the general procedure, [Lc^{iPr}(C$_6$F$_5$)$_2$P][OTf] (695 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 48 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 877 mg, 91%; **m.p.**: decomposition at approx. 100 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3012 (13), 2995 (91), 2970 (16), 2951 (100), 1652 (38), 1577 (49), 1402 (16), 1389 (83), 1358 (31), 1249 (55), 1226 (14), 1034 (23), 918 (50), 755 (28), 534 (36), 482 (26), 147 (39), 128 (15); **IR** (298 K, ATR, in cm^{-1}): 2988 (vw), 1650 (w), 1579 (vw), 1524 (m), 1494 (vs), 1400 (w), 1382 (w), 1358 (vw), 1314 (w), 1277 (s), 1263 (vs), 1248 (vs), 1224 (m), 1151 (s), 1113 (vs), 1031 (s), 989 (s), 917 (w), 863 (vw), 804 (w), 773 (vw), 741 (w), 633 (s), 594 (w), 573 (w), 553 (w), 534 (w), 517 (w), 481 (w), 462 (w), 437 (vw); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 4.70 (2H, sept, $^1J_{HH}$ = 6.8 Hz, C8-H), 2.62 (6H, d, $^5J_{PH}$ = 1.5 Hz, C7-H), 1.62 (12H, d, $^1J_{HH}$ = 2.8Hz, C9-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 152.7 (dm, $^1J_{CF}$ = 273 Hz, C4), 150.6 (dm, $^1J_{CF}$ = 272 Hz, C3), 145.1 (d, $^1J_{CF}$ = 8 Hz, C), 141.3 (dm, $^1J_{CF}$ = 259 Hz, C2), 122.4 (q, $^1J_{CF}$ = 330 Hz, OTf), 117.7 (dd, $^1J_{CP}$ = 211 Hz, $^2J_{CF}$ = 21 Hz, C5), 95.2 (dm, $^1J_{CP}$ = 153 Hz, C1), 59.5 (dd, $^3J_{CP}$ = 2 Hz, C8), 21.7 (s, C9), 13.8 (s, C7); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.3 (s, OTf), -94.6 (d, $^1J_{FP}$ = 995 Hz, P-F), -123.5 (m, C2-F), -127.9 (m, C4-F), -154.2 (m, C3-F); ^{31}**P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 36.7 (d, $^1J_{PF}$ = 995 Hz). **Elemental analysis**: calculated for $C_{20}H_{20}F_{17}N_2O_6PS2$: C 34.8, H 2.3, N 3.3, found: C 35.2, H 2.6, N 3.4.

S4.12. Preparation of **8^{Me}**[OTf]$_3$

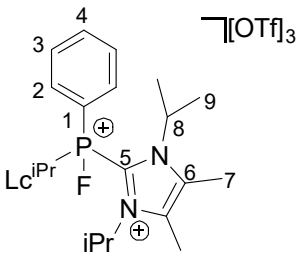


Following the general procedure, [Lc$^{Me}_2$PhP][OTf]$_2$ (655 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 24 h before the addition of MeOTf (164 mg, 1.0 mmol).

Yield: 674 mg, 82%; **m.p.**: decomposition at approx. 130 °C; **Raman** (40 mW, 500 scans, 298 K, in cm^{-1}): 3074 (20), 3061 (20), 3006 (20), 2997 (20), 2980 (40), 2939 (80), 2587 (20), 1600 (60), 1580 (40), 1502 (20), 1481 (20), 1452 (20), 1405 (60), 1376 (20), 1323 (60), 1227 (20), 1097 (60), 1034 (100), 996 (60), 911 (40), 757 (60), 728 (20), 589 (40), 568 (40), 508 (20), 373 (20), 349 (40), 314 (40), 256 (20), 174 (40); **IR** (298 K, ATR, in cm^{-1}): 1599 (vw), 1581 (vw), 1440 (w), 1405 (vw), 1377 (vw), 1319

(w), 1252 (vs), 1224 (s), 1157 (s), 1113 (m), 1098 (m), 1028 (vs), 996 (vw), 910 (w), 854 (w), 794 (w), 756 (m), 727 (w), 686 (vw), 634 (vs), 603 (m), 572 (m), 530 (s), 516 (s), 506 (s), 444 (w); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 8.53 (2H, m, C2-H), 8.39 (1H, m, C4-H), 8.07 (2H, m, C3-H), 3.76 (12H, s, C7-H), 2.56 (12H, d, C8-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 145.0 (dd, $^{3}J_{CP}$ = 7 Hz, $^{4}J_{CF}$ = 1 Hz, C4), 144.2 (dd, $^{4}J_{CP}$ = 3 Hz, $^{5}J_{CF}$ = 2 Hz, C6), 138.0 (d, $^{2}J_{CP}$ = 17 Hz, C2), 133.6 (d, $^{3}J_{CP}$ = 18 Hz, C3), 122.1 (q, $^{1}J_{CF}$ = 307 Hz, OTf), 116.9 (dd, $^{1}J_{CF}$ = 25 Hz, $^{2}J_{CP}$ = 186 Hz, C5), 111.2 (dd, $^{1}J_{CF}$ = 16 Hz, $^{2}J_{CP}$ = 127 Hz, C1), 38.2 (s, C7), 11.2 (s, C8); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -79.3 (s, OTf), -98.1 (d, $^{1}J_{PF}$ = 1043 Hz, P-F); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 43.8 (d, $^{1}J_{FP}$ = 1043 Hz, P-F); **Elemental analysis:** calculated for $C_{23}H_{29}F_{10}N_4O_9PS_3$: C 33.6, H 3.6, N 6.8, S 11.7, found: C 33.2, H 3.6, N 6.8, S 11.5; Crystallographic data and details of the structure refinements are depicted in table S10.2.4.

S4.13. Preparation of **8$^{i\mathrm{Pr}}$**[OTf]$_3$



Following the general procedure, [Lc$^{i\mathrm{Pr}}_2$PhP][OTf]$_2$ (762 mg, 1.0 mmol) and NFSI (315 mg, 1.0 mmol) are used as educts and reacted in CH_2Cl_2 (3 mL) for 24 h before the addition of MeOTf (164 mg, 1.0 mmol).

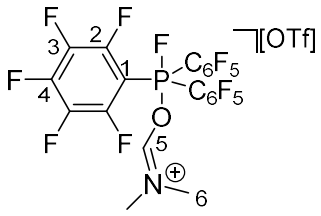
Yield: 860 mg, 92%; **m.p.**: decomposition at approx. 159 °C; **Raman** (100 mW, 512 scans, 298 K, in cm^{-1}): 2988 (38), 2954 (85), 1582 (62), 1470 (15), 1446 (23), 1387 (38), 1360 (15), 1244 (62), 1226 (23), 1144 (23), 1111 (23), 1033 (100), 997 (23), 911 (46), 882 (23), 755 (31), 573 (23), 349 (31), 314 (23), 184 (23), 142 (31); **IR** (298 K, ATR, in cm^{-1}): 3001 (vw), 1579 (vw), 1444 (vw), 1385 (vw), 1358 (vw), 1277 (m), 1256 (vs), 1225 (m), 1210 (w), 1141 (s), 1111 (m), 1031 (vs), 911 (w), 816 (w), 804 (w), 747 (w), 725 (vw), 684 (w), 665 (vw), 635 (vs), 586 (w), 572 (w), 552 (m), 540 (m), 517 (s), 505 (m), 462 (vw), 445 (w), 416 (vw); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 8.55 (2H, br, C2-H), 8.32 – 8.30 (1H, m, C4-H), 8.06 – 8.02 (2H, m, C3-H), 4.55 (4H, br, C8-H), 2.68 (12H, d, C7-H), 1.60 – 1.49 (24H, d, br, C9-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 146.9 (br, C6), 143.5 (s, C4), 137.9 (d, $^{2}J_{CP}$ = 17 Hz, C2), 113.4 (d, $^{2}J_{CP}$ = 17 Hz, C3), 122.1 (q, $^{1}J_{CF}$ = 310 Hz, OTf), 116.1 (dd, $^{1}J_{CP}$ = 184 Hz, $^{2}J_{CF}$ = 22 Hz, C5), 115.1 (dd, $^{1}J_{CP}$ = 124 Hz, $^{2}J_{CF}$ = 14 Hz, C1), 59.0 (s, C8), 21.2 (br, C9), 20.9 (br, C7), 13.5 (s, C8); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -78.2 (s, OTf), -95.1 (d, $^{1}J_{PF}$ = 1044 Hz, P-F), **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 47.3 (d,

$^1J_{PF}$ = 1044 Hz, P-F); **Elemental analysis:** calculated for $C_{31}H_{45}F_{10}N_4O_9PS_3$: C 39.1, H 4.7, N 6.1, S 10.4, found: C 39.0, H 4.7, N 5.7, S 10.6.

S5 Reaction of fluorophosphonium triflate salts with nucleophiles

General procedure for the preparation of fluorophosphonium-formamide adducts: A mixture of the corresponding fluorophosphonium salt and a stoichiometric amount of formamide is stirred in CH_2Cl_2 at ambient temperature for 2 h. After that *n*-pentane is added until precipitation. The obtained solid is then filtered off, washed with three portions of *n*-pentane and dried *in vacuo* to yield the titled compounds as analytically pure, air-sensitive and colorless solid. Elemental analysis is not determined because these formamide adducts are highly air-sensitive.

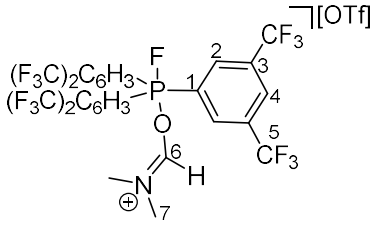
S5.1. Preparation of **9a**[OTf]



Following the general procedure, **2c**[OTf] (140 mg, 0.2 mmol) and DMF (15 mg, 0.2 mmol) are used as educts.

Yield: 145 mg, 94%; **m.p.**: decomposition at approx. 137 °C; **Raman** (40 mW, 500 scans, 298 K, in cm^{-1})**:** 3006 (40), 2967 (60), 2959 (60), 2266 (40), 2117 (40), 1684 (40), 1649 (100), 1432 (40), 1418 (40), 1410 (20), 1399 (20), 1032 (80), 756 (40), 585 (60), 493 (60), 471 (20), 443 (40), 389 (20), 349 (40), 166 (20), 152 (40), 128 (20); **IR** (298 K, ATR, in cm^{-1}): 3005 (vw), 1685 (m), 1648 (w), 1524 (m), 1486 (vs), 1429 (vw), 1400 (w), 1301 (s), 1277 (m), 1253 (s), 1226 (m), 1160 (m), 1105 (vs), 1031 (s), 981 (vs), 771 (w), 756 (w), 716 (m), 675 (m), 636 (vs), 594 (s), 574 (w), 552 (vs), 517 (m), 472 (s), 421 (s); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 7.97 (1H, s, C5-H), 3.25 (3H, s, CH_3, C6-H), 2.95 (3H, s, CH_3, C6-H) **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 160.9 (s, C5), 147.3 (dm, $^1J_{CF}$ = 261 Hz, C2 and C3), 140.2 (dm, $^1J_{CF}$ = 253 Hz, C3), 122.5 (q, $^1J_{CF}$ = 317 Hz, OTf), 106.9 (dm, $^1J_{CP}$ = 197 Hz, C1), 42.5 (s, CH_3, C6), 37.8 (s, CH_3, C6); **^{19}F NMR** (CD_3CN, 300 K, in ppm): δ = -5.6 (d, $^1J_{FP}$ = 704 Hz, P-F), -79.5 (s, OTf), -132.2 (br, C2-F), -144.1 (m, C4-F), -158.5 (m, C3-F); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -45.4 (d, $^1J_{PF}$ = 704 Hz); Crystallographic data and details of the structure refinements are depicted in table S10.2.5.

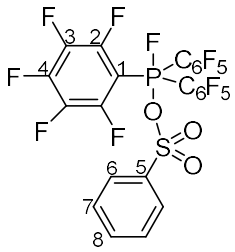
S5.2. Preparation of **9b**[OTf]



Following the general procedure, **2d**[OTf] (419 mg, 0.5 mmol) and DMF (37 mg, 0.5 mmol) are used as educts.

Yield: 81%; **m.p.**: 153 – 154 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3099 (8), 3025 (7), 2966 (8), 1673 (8), 1626 (15), 1610 (22), 1433 (17), 1411 (6), 1366 (19), 1227 (6), 1135 (11), 1114 (14), 1031 (39), 1001 (100), 858 (6), 806 (13), 756 (15), 710 (35), 574 (8), 349 (14), 314 (15), 287 (24), 259 (13), 242 (14), 222 (16), 199 (26), 177 (44); **IR** (298 K, ATR, in cm^{-1}): 3023 (vw), 1672 (w), 1625 (vw), 1431 (vw), 1364 (w), 1331 (vw), 1281 (vs), 1253 (m), 1226 (vw), 1176 (w), 1128 (vs), 1112 (s), 1102 (s), 1030 (m), 925 (vw), 902 (w), 844 (vw), 756 (vw), 699 (w), 683 (w), 657 (w), 638 (s), 620 (m), 600 (vw), 573 (vw), 546 (m), 516 (w), 452 (vw), 412 (w); **^{1}H NMR** (CD_3NO_2, 300K, in ppm): δ = 8.67 (6H, d, $^{3}J_{PH}$ = 15.7 Hz, C2-H), 8.55 (3H, s, C4-H), 7.78 (1H, s, C6-H), 3.05 (6H, s, C7); **^{13}C{^{1}H} NMR** (CD_3NO_2, 300K, in ppm): δ = 163.9 (s, C6) 135.6 (dm, $^{2}J_{CP}$ = 15 Hz, C2), 134.6 (qd, $^{2}J_{CF}$ = 34 Hz, $^{3}J_{CP}$ = 18 Hz, C3), 131.5 (dm, $^{4}J_{CP}$ = 3 Hz, C4), 127.8 (dd, br, $^{1}J_{CP}$ = 150 Hz, $^{2}J_{CF}$ = 21 Hz, C1), 124.0 (qd, $^{1}J_{CF}$ = 273 Hz, $^{4}J_{CP}$ = 2 Hz, C5), 122.3 (q, $^{1}J_{CF}$ = 322 Hz, OTf), 39.7(s, C7), 34.7 (s, C7); **^{19}F NMR** (CD_3NO_2, 300K, in ppm): δ = -64.3 (s, CF_3), -72.3 (d, br, $^{1}J_{FP}$ = 837 Hz, P-F), -79.8 (s, OTf); **^{31}P{^{1}H} NMR** (CD_3NO_2, 300K, in ppm): δ = 20.8 (d, br, $^{1}J_{PF}$ = 837 Hz, P-F); Crystallographic data and details of the structure refinements are depicted in table S10.2.5.

S5.3. Preparation of **10**

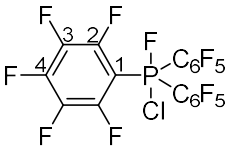


Following the general procedure, DMF (18 mg, 0.25 mmol) and [**2c**(NSI)] (222 mg, 0.25 mmol) are used as educts. After stirring for 48 h *n*-pentane (2 mL) is added to the clear reaction mixture. Upon cooling to -30 °C colorless crystals of **10** are obtained in X-ray quality.

Yield: 60 mg, 34%; **m.p.**: 159 – 161 °C; **Raman** (100 mW, 512 scans, 298 K, in cm^{-1}): 3099 (17), 3082 (54), 3071 (50), 1646 (50), 1584 (54), 1405 (21), 1359 (13), 1190 (38), 1172 (29), 1160 (17), 1094 (13), 1020 (17), 1001 (96), 833 (17), 731 (17), 615 (21), 585 (100), 493 (83), 479 (13), 467 (29), 444 (54), 422 (21), 385 (75), 346 (17), 321 (17), 272 (25), 232 (17), 195 (17), 185 (17), 159 (46), 149 (38); **IR** (298 K, ATR, in cm^{-1}): 1646 (w), 1521 (m), 1485 (vs), 1447 (w), 1404 (w), 1383 (vw), 1355 (m), 1301 (w), 1188 (m), 1152 (vw), 1103 (vs), 1030 (vw), 982 (vs), 940 (vw), 854 (s), 765 (m), 757 (m), 729 (w), 686 (s), 644 (m), 634

(m), 592 (vs), 549 (vs), 514 (w), 466 (m), 444 (w), 420 (vs); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 7.67 – 7.65 (2H, m, C6-H), 7.55 – 7.52 (1H, m, C8-H), 7.43 – 7.40 (2H, m, C7-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 146.4 (dm, $^{1}J_{CF}$ = 255 Hz, C2), 145.1 (dm, $^{1}J_{CF}$ = 262 Hz, C4), 140.8 (s, C5), 138.5 (dm, $^{1}J_{CF}$ = 255 Hz, C3), 133.6 (s, C8), 129.4 (s, C7), 126.7 (s, C6), 110.3 (dm, $^{1}J_{CP}$ = 202 Hz); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = -3.9 (dm, $^{1}J_{FP}$ = 673 Hz, P-F), -132.0 (br, C5-F), -145.1 (m, C4-F), -159.0 (m, C5-F); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = -55.7 (d, $^{1}J_{FP}$ = 673 Hz); Crystallographic data and details of the structure refinements are depicted in table S10.2.5.

S5.4. Preparation of **12**



[**2c**(NSI)] (222 mg, 0.25 mmol) and DMF (18.3 mg, 0.25 mmol) are stirred in CH_2Cl_2 (2 mL) at ambient temperature for 48 h. To the clear solution, NaCl (29 mg, 0.5 mmol) is added. After stirring for further 16 h, the suspension is filtered. Addition of *n*-pentane (2 mL) to the filtrate and cooling to -30 ºC yields colorless crystals of **12** in X-ray quality.

Yield: 41 mg, 28%; **m.p.**: 155 – 158 °C; **Raman** (100 mW, 250 scans, 298 K, in cm^{-1}): 1645 (65), 1404 (28), 832 (29), 587 (85), 494 (100), 467 (41), 445 (67), 407 (20), 385 (67), 356 (22), 314 (54), 266 (21), 165 (30), 150 (80); **IR** (298 K, ATR, in cm^{-1}): 1645 (w), 1521 (m), 1490 (vs), 1481 (vs), 1401 (w), 1379 (vw), 1367 (vw), 1303 (w), 1277 (vw), 1150 (vw), 1106 (s), 1059 (vw), 1024 (vw), 980 (vs), 876 (vw), 768 (w), 761 (vw), 727 (vw), 692 (m), 639 (m), 593 (m), 543 (vs), 464 (vs), 444 (w), 421 (w), 405 (w); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 145.6 (dm, $^{1}J_{CF}$ = 255 Hz, C2), 145.4 (dm, $^{1}J_{CF}$ = 253 Hz, C2), 144.8 (dm, $^{1}J_{CF}$ = 266 Hz, C4), 139.0 (dm, $^{1}J_{CF}$ = 255 Hz, C3), 138.2 (dm, $^{1}J_{CF}$ = 255 Hz, C3), 115.2 (dm, $^{1}J_{CF}$ = 190 Hz, C1); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = 12.2 (dq, $^{1}J_{FP}$ = 673 Hz, P-F), -137.8 (m, C_6F_5), -133.3 (m, C_6F_5), -146.5 (m, C_6F_5), -158.6 (m, C_6F_5), -159.6 (m, C_6F_5); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = -73.5 (d, $^{1}J_{FP}$ = 673 Hz, P-F); Crystallographic data and details of the structure refinements are depicted in table S10.2.6.

S6 Synthesis of $HN(SO_2R)(SO_2Ph)$ and corresponding $Na[N(SO_2R)(SO_2Ph)]$

S6.1. General procedure for the formation of *N*-sulfonyl-sulfonamides

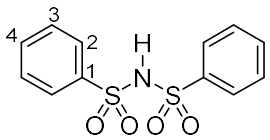
A modified method based on the procedure from Yin *et al.*[7] is used for the synthesis of $HN(SO_2R)(SO_2Ph)$ **24a-h**:

At 55 °C, $PhSO_2NH_2$ (20 mmol, 3.14 g) is dissolved in a aqueous solution of NaOH (1 M, 20 mL). RSO_2Cl (10 mmol) is added to the solution and the reaction mixture is stirred at 55 °C for 6 h. The pH value of the mixture is monitored and adjusted to 8-9 with a NaOH solution (1 M) every 30 min. After cooling down to ambient temperature, the pH of the reaction mixture is adjusted to 6-7 with HCl (1 M) solution. The resulting slurry is stirred for 1 h and the surplus $PhSO_2NH_2$ is removed by filtration. The filtrate is poured into HCl solution (1 M, 20 mL) and the obtained colorless precipitate is filtered off and recrystallized from warm water. After all volatiles are removed *in vacuo* all *N*-sulfonyl-sulfonamides are obtained as colorless, crystalline solids.

S6.2. General procedure for the formation of sodium bis(sulfonyl)amides

A solution of $HN(SO_2R)(SO_2Ph)$ **24a-h** (5 mmol) in THF (10 mL) is added to a solution of *t*BuONa (5 mmol) in THF and stirred at room temperature for 4 h. The resulting precipitate is filtered off, washed with THF (3 x 1 mL), and dried *in vacuo* to afford all $Na[N(SO_2R)(SO_2Ph)]$ **23a-h** as colorless solids.

S6.3. Preparation of $HN(SO_2Ph)_2$, $Na[N(SO_2Ph)_2]$ and $[nBu_4N][N(SO_2Ph)_2]$



$HN(SO_2Ph)_2$ is prepared from $PhSO_2NH_2$ (15.72 g, 100 mmol) and $PhSO_2Cl$ (6.8 mL, 50 mmol) following the general procedure in 6.1.

Yield: 7.65 g, 52%; **m.p.**: 156 – 158 °C; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.95 – 7.94 (4H, m, C2-H), 7.64 – 7.61 (2H, m, C4-H), 7.52 – 7.49 (4H, m, C3-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 139.7 (s, C1), 134.3 (s, C4), 129.4 (s, C2), 128.0 (s, C3).

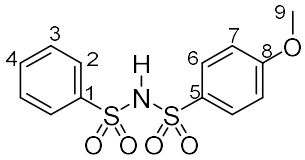
$Na[N(SO_2Ph)_2]$ is prepared by the deprotonation of $HN(SO_2Ph)_2$ (595 mg, 2 mmol), following the general procedure in 6.2.

Yield: 562 mg, 88%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.62 – 7.61 (4H, m, C2-H), 7.53 – 7.50 (2H, m, C4-H), 7.40 – 7.37 (4H, m, C3-H); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 140.9 (s, C1), 132.3 (s, C4), 128.9 (s, C2), 126.1 (s, C3).

[*n*Bu$_4$N][N(SO$_2$Ph)$_2$] is prepared with the following procedure: HN(SO$_2$Ph)$_2$ (2.97 g, 10 mmol) and NaOH (0.4 g, 10 mmol) are stirred in MeOH (50 mL) for 2 h. [*n*Bu$_4$N]Cl (2.78 g, 10 mmol) is added to the suspension. After stirring for 16 h the formed NaCl is removed by filtration and all volatiles are removed in *vacuo*. The resulting yellowish oil is redissolved in CH_2Cl_2 (10 mL) and filtered to remove residual NaCl. Upon the addition of E_2O (30 mL) to the filtrate, the title compound is precipitating as colorless solid.

Yield: 4.20 g, 78%; **m.p.**: 79 – 80 °C; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.76 – 7.65 (4H, m, C2-H), 7.21 – 7.17 (2H, m, C4-H), 7.13 – 7.09 (4H, m, C3-H), 3.14 – 3.09 (8H, m, *n*Bu), 1.52 – 1.45 (8H, hept, $^3J_{HH}$ = 7.4 Hz, *n*Bu), 0.87 (12H, t, $^3J_{HH}$ = 7.4 Hz, *n*Bu); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 145.4 (s, C1), 130.1 (s, C4), 127.8 (s, C2), 126.9 (s, C3), 58.8 (s, *n*Bu), 24.1 (s, *n*Bu), 19.8 (s, *n*Bu), 13.8 (s, *n*Bu).

S6.4. Preparation of **24a** and **22a**



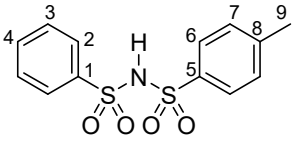
HN(SO$_2$Ph)(SO$_2$(*p*-MeO-C$_6$H$_4$)) (**24a**) is prepared from PhSO$_2$NH$_2$ (7.86 g, 50 mmol) and (*p*-MeO-C$_6$H$_4$)SO$_2$Cl (6.89 g, 33.3 mmol) following the general procedure in 6.1.

Yield: 15.06 g, 92%; **m.p.**: 151 – 152 °C; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.97 – 7.95 (2H, m, C2-H), 7.90 – 7.88 (2H, m, C6-H), 7.68 (br, 1H, NH), 7.65 – 7.61(1H, m, C4-H), 7.54 – 7.50 (2H, m, C3-H), 6.97 – 6.96 (2H, m, C7-H), 3.87 (3H, s, C9-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 164.3 (s, C8), 139.8 (s, C1), 134.2 (s, C4), 131.1 (s, C5), 130.5 (s, C6), 129.4 (s, C2), 128.0 (s, C3), 114.6 (s, C7), 56.0 (s, C9); Crystallographic data and details of the structure refinements are depicted in table S10.2.6.

Na[N(SO$_2$Ph)(SO$_2$(*p*-MeO-C$_6$H$_4$))] (**22a**) is prepared by the deprotonation of HN(SO$_2$Ph)(SO$_2$(*p*-MeO-C$_6$H$_4$)) (655 mg, 2 mmol), following the general procedure in 6.2**.**

Yield: 377 mg, 54%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.56 – 7.49 (5H, m, C2, C6 and C4-H), 7.40 – 7.37 (2H, m, C3-H), 6.88 – 6.86 (2H, m, C7-H); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 161.8 (s, C8), 140.6 (s, C1), 132.6 (s, C5), 132.1 (s, C4), 128.8 (s, C6), 128.4 (s, C2), 126.2 (s, C3), 114.0 (s, C7), 55.6(s, C9).

S6.5. Preparation of **24b** and **22b**.



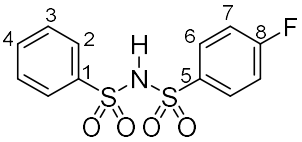
HN(SO_2Ph)(SO_2(*p*-Me-C_6H_4)) (**24b**) is prepared from $PhSO_2NH_2$ (3.14 g, 20 mmol) and (*p*-Me-C_6H_4)SO_2Cl (1.91 g, 10 mmol) following the general procedure in 6.1.

Yield: 3.00 g, 96%; **m.p.**: 164 – 166 ºC; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.95 – 7.93 (2H, m, C2-H), 7.83 – 7.81 (2H, m, C6-H), 7.63 – 7.60 (1H, m, C4-H), 7.51 – 7.48 (2H, m, C3-H), 7.30 – 2.24 (2H, m, C7-H), 2.42 (3H, s, C9-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 145.5 (s, C8), 139.8 (s, C1), 136.8 (s, C5), 134.2 (s, C4), 130.0 (s, C6), 129.4 (s, C2), 128.1 (s, C7), 128.0 (s, C3), 21.9 (s, C9). Spectral data are in accordance with those reported in the literature.[8]

Na[N(SO_2Ph)(SO_2(*p*-Me-C_6H_4))] (**22b**) is prepared by the deprotonation of HN(SO_2Ph)(SO_2(*p*-Me-C_6H_4)) (1.25 g, 4 mmol), following the general procedure in 6.2**.**

Yield: 1.01 g, 76%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.58 – 7.56 (2H, m, C2-H), 7.56 – 7.51 (1H, m, C4-H), 7.46 – 7.45 (2H, m, C6-H) 7.39 – 7.36 (2H, m, C3-H), 7.18 – 7.16 (2H, m, C7-H); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 143.5 (s, C8), 140.8 (s, C1), 137.6 (s, C5), 132.1 (s, C4), 129.3 (s, C6), 128.8 (s, C2), 126.2 (s, C7), 126.2 (s, C3), 20.5 (s, C9).

S6.6. Preparation of **24c** and **22c**



HN(SO_2Ph)(SO_2(*p*-F-C_6H_4)) (**24c**) is prepared from $PhSO_2NH_2$ (2.36 g, 15 mmol) and (*p*-F-C_6H_4)SO_2Cl (1.95 g, 10 mmol) following the general procedure in 6.1.

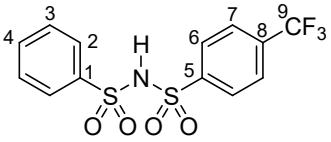
Yield: 3.01 g, 96%; **m.p.**:145 – 146 ºC; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.00 – 7.95 (4H, m, C2 and C6-H), 7.67 – 7.64 (1H, m, C4-H), 7.5 – 7.51 (2H, m, C3-H), 7.19 – 7.16 (2H, m, C7-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 166.1 (d, $^1J_{CF}$ = 258 Hz, C8), 139.5 (s, C1), 135.6 (d, $^4J_{CF}$ = 4 Hz, C5), 134.4 (s, C4), 131.1 (d, $^3J_{CF}$ = 10 Hz, C6), 129.4 (s, C2), 128.0 (s, C3), 116.7 (d, $^2J_{CF}$ = 22 Hz, C7); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = -102.3 (m). Crystallographic data and details of the structure refinements are depicted in table S10.2.6.

Na[N(SO_2Ph)(SO_2(*p*-F-C_6H_4))] (**22c**) is prepared by the deprotonation of HN(SO_2Ph)(SO_2(*p*-F-C_6H_4)) (0.80 g, 2.5 mmol), following the general procedure in 6.2**.**

Yield: 0.48 g, 56%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.65 – 7.61 (4H, m, C2 and C6-H), 7.58 – 7.55 (1H, m, C4-H), 7.45 – 7.42 (2H, m, C3-H), 7.13 – 7.10 (2H, m, C7-H); **^{13}C{^{1}H}**

NMR (D_2O, 300 K, in ppm): δ = 164.5 (d, $^1J_{CF}$ = 252 Hz, C8), 140.7 (s, C1), 137.0 (d, $^4J_{CF}$ = 2 Hz, C5), 132.4 (s, C4), 129.0 (d, $^3J_{CF}$ = 10 Hz, C6), 128.9 (s, C2), 126.2 (s, C3), 115.8 (d, $^2J_{CF}$ = 23 Hz, C7); **^{19}F NMR** (D_2O, 300 K, in ppm): δ = -107.5 (m).

S6.7. Preparation of **24d** and **22d**



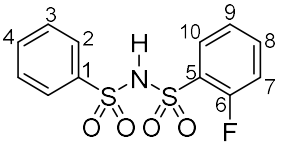
$HN(SO_2Ph)(SO_2(p\text{-}CF_3\text{-}C_6H_4))$ (**24d**) is prepared from $PhSO_2NH_2$ (0.69 g, 4.42 mmol) and $(p\text{-}CF_3\text{-}C_6H_4)SO_2Cl$ (0.9 g, 3.68 mmol) following the general procedure in 6.1.

Yield: 0.57 g, 40%; **m.p.**: 131 – 134 °C; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.15 – 8.16 (2H, m, C6-H), 8.02 – 8.01 (2H, m, C2-H), 7.84 – 7.83 (2H, m, C7-H), 7.72 – 7.69 (1H, m, C4-H), 7.60 – 7.57 (2H, m, C3-H), N-H not observed; **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 143.1 (s, C5), 139.4 (s, C1), 135.9 (q, $^2J_{CF}$ = 33 Hz, C8), 135.5 (s, C4), 130.0 (s, C2), 128.7 (s, C3), 128.1 (s, C6), 126.6 (q, $^3J_{CF}$ = 4 Hz, C7), 123.2 (q, $^1J_{CF}$ = 272 Hz, C9); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = 63.3 (s).

$Na[N(SO_2Ph)(SO_2(p\text{-}CF_3\text{-}C_6H_4))]$ (**22d**) is prepared by the deprotonation of $HN(SO_2Ph)(SO_2(p\text{-}CF_3\text{-}C_6H_4))$ (365 mg, 1 mmol) following the general procedure in 6.2**.**

Yield: 0.23 g, 59%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.70 – 7.64 (4H, m, C2 and C6-H), 7.54 – 7.52 (2H, m, C7-H), 7.51 – 7.49 (1H, m, C4-H), 7.36 – 7.33 (2H, m, C3-H); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 143.9 (s, C5), 140.1 (s, C1), 132.9 (q, $^2J_{CF}$ = 33 Hz, C8), 132.4 (s, C4), 128.8 (s, C2), 126.9 (s, C3), 126.2 (s, C6), 125.9 (q, $^1J_{CF}$ = 4 Hz, C7), 123.4 (q, $^1J_{CF}$ = 272 Hz, C9); **^{19}F NMR** (D_2O, 300 K, in ppm): δ = 63.0 (s); Crystallographic data and details of the structure refinements are depicted in table S10.2.7.

S6.8. Preparation of **24e** and **22e**



$HN(SO_2Ph)(SO_2(m\text{-}F\text{-}C_6H_4))$ (**24e**) is prepared from $PhSO_2NH_2$ (5.89 g, 37 mmol) and $(m\text{-}F\text{-}C_6H_4)SO_2Cl$ (4.87 g, 3.2 ml 25 mmol) following the general procedure in 6.1.

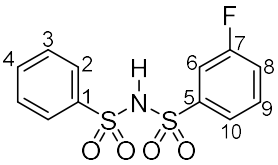
Yield: 3.00 g, 38%; **m.p.**: 179 – 182 °C; **^{1}H NMR** (CD_3OD, 300 K, in ppm): δ = 7.86 – 7.48 (5H, m, C3, C4, C8 and C9-H), 7.49 – 7.45 (2H, m, C2-H), 7.32 – 7.28 (1H, m, C10-H), 7.19 – 7.14 (1H, m, C7-H); **^{13}C{^{1}H} NMR** (CD_3OD, 300 K, in ppm): δ = 160.0 (d, $^1J_{CF}$ = 256 Hz, C6), 141.4 (s, C1), 137.3 (d, $^3J_{CF}$ = 9 Hz, C8), 134.6 (s, C4), 131.6 (s, C9), 130.1 (s, C2), 129.3 (d, $^2J_{CF}$ = 13 Hz, C5), 128.3 (s, C3), 125.6 (d, $^3J_{CF}$ = 4 Hz, C10), 118.1 (d, $^2J_{CF}$ = 21 Hz, C7);

^{19}F NMR (CH_3OD, 300 K, in ppm): δ = -110.8 (m); Crystallographic data and details of the structure refinements are depicted in table S10.2.7.

Na[N(SO_2Ph)(SO_2(*o*-F-C_6H_4))] (**22e**) is prepared by the deprotonation of HN(SO_2Ph)(SO_2(*o*-F-C_6H_4)) (1.58 g, 5 mmol), following the general procedure in 6.2**.**

Yield: 1.20 g, 71%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.62 – 7.49 (5H, m, C3, C4, C8 and C9-H), 7.42 – 7.34 (2H, m, C2-H), 7.19 – 7.15 (1H, m, C10-H), 7.07 – 7.02 (1H, m, C7-H); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 158.1 (d, $^1J_{CF}$ = 253 Hz, C6), 140.2 (s, C1), 135.1 (d, $^3J_{CF}$ = 9 Hz, C8), 132.4 (s, C4), 129.1 (s, C9), 128.8 (s, C2), 127.9 (d, $^2J_{CF}$ = 14 Hz, C5), 126.0 (s, C3), 124.3 (d, $^3J_{CF}$ = 4 Hz, C10), 116.8 (d, $^2J_{CF}$ = 22 Hz, C7); **^{19}F NMR** (D_2O, 300 K, in ppm): δ = -110.86 (m).

S6.9. Preparation of **24f** and **22f**



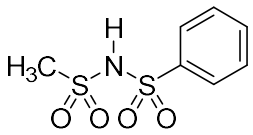
HN(SO_2Ph)(SO_2(*m*-F-C_6H_4)) (**24f**) is prepared from $PhSO_2NH_2$ (5.89 g, 37 mmol) and (*m*-F-C_6H_4)SO_2Cl (4.87 g, 3.4 ml 25 mmol) following the general procedure in 6.1.

Yield: 2.90 g, 37%**; m.p.**: 119 – 120 ºC; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.93 – 7.91 (2H, m, C2-H), 7.73 – 7.71 (1H, m, C10-H), 7.62 – 7.58 (2H, m, C4 and C6-H), 7.49 – 7.43 (3H, m, C3 and C9-H), 7.30 – 7.24 (1H, m, C8-H), N-H not observed; **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 162.3 (d, $^1J_{CF}$ = 252 Hz, C7), 141.3 (d, $^3J_{CF}$ = 7 Hz, C5), 139.2 (s, C1), 134.4 (s, C4), 131.2 (d, $^3J_{CF}$ = 8 Hz, C9), 129.4 (s, C2), 128.0 (s, C3), 123.8 (d, $^4J_{CF}$ = 4 Hz, C10), 121.5 (d, $^2J_{CF}$ = 21 Hz, C8), 115.4 (d, $^2J_{CF}$ = 26 Hz, C6); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = -108.9 (m); Crystallographic data and details of the structure refinements are depicted in table S10.2.7.

Na[N(SO_2Ph)(SO_2(*m*-F-C_6H_4))] (**22f**) is prepared by the deprotonation of HN(SO_2Ph)(SO_2(*m*-F-C_6H_4)) (1.58 g, 5 mmol), following the general procedure in 6.2**.**

Yield: 1.40 g, 83%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.63 – 7.62 (2H, m, C2-H), 7.56 – 7.53 (1H, m, C4-H), 7.44 – 7.38 (4H, m, C3, C6, C10-H), 7.31 – 7.24 (2H, m, C8 and C9-H); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 161.8 (d, $^1J_{CF}$ = 248 Hz, C7), 142.7 (d, $^3J_{CF}$ = 7 Hz, C5), 140.6 (s, C1), 132.5 (s, C4), 130.9 (d, $^3J_{CF}$ = 8 Hz, C9), 128.9 (s, C2), 126.2 (s, C3), 122.2 (d, $^4J_{CF}$ = 4 Hz, C10), 119.3 (d, $^2J_{CF}$ = 22 Hz, C8), 113.5 (d, $^2J_{CF}$ = 25 Hz, C6); **^{19}F NMR** (D_2O, 300 K, in ppm): δ = -111.9 (m).

S6.10. Preparation of **24g** and **22g**



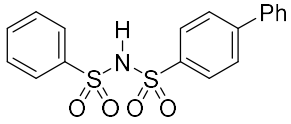
$HN(SO_2Ph)(SO_2Me)$ (**24g**) is prepared from $MeSO_2NH_2$ (1.90 g, 20 mmol) and $PhSO_2Cl$ (1.9 ml, 13.3 mmol) following the general procedure in 6.1.

Yield: 4.32 g, 92%; **m.p.**: 135 – 137 °C; **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.98 – 7.97 (2H, m, C2-H), 7.66 – 7.63 (1H, m, C4-H), 7.55 – 7.52 (1H, m, C3-H), 3.35 (3H, s, C5-H), N-H not observed; **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 139.3 (s, C1), 134.5 (s, C4), 129.4 (s, C2), 128.2 (s, C3), 44.2 (s, C5).

$Na[N(SO_2Ph)(SO_2Me)]$ (**22g**) is prepared by the deprotonation of $HN(SO_2Ph)(SO_2Me)$ (706 mg, 3 mmol), following the general procedure in 6.2**.**

Yield: 617 mg, 80%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.93 – 7.91 (2H, m, C2-H), 7.68 – 7.67 (1H, m, C4-H), 7.63 – 7.62 (2H, m, C3-H), 3.06 (3H, s, C5-H) **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 124.4 (s, C1), 132.5 (s, C4), 129.1 (s, C2), 126.1 (s, C3), 42.3 (s, C5).

S6.11. Preparation of **24h** and **22h**



$HN(SO_2Ph)(SO_2(p\text{-}Ph\text{-}C_6H_4))$ (**24h**) is prepared from $PhSO_2NH_2$ (3.14 g, 20 mmol) and $(p\text{-}Ph\text{-}C_6H_4)SO_2Cl$ (2.53 g, 10 mmol) following the general procedure in 6.1.

Yield: 3.70 g, 91%; **m.p.**: 163 – 165 °C; **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 9.76 (1H, s, br, NH), 7.87 – 7.82 (4H, m, Ar), 7.71 – 7.69 (2H, m, Ar), 7.65 – 7.63 (2H, m, Ar), 7.62 – 7.60 (1H, m, Ar), 7.52 – 7.43 (5H, m, Ar); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 147.4 (s, Ar), 140.3 (s, Ar), 139.8 (s, Ar), 138.9 (s, Ar), 135.0 (s, Ar), 130.3 (s, Ar), 130.2 (s, Ar), 129.8 (s, Ar), 129.0 (s, Ar), 128.7 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar). Spectral data are in accordance with those reported in the literature.[9, 10]

$Na[N(SO_2Ph)(SO_2(p\text{-}Ph\text{-}C_6H_4))]$ (**22h**) is prepared by the deprotonation of $HN(SO_2Ph)(SO_2(p\text{-}Ph\text{-}C_6H_4))$ (1.49 g, 4 mmol), following the general procedure in 6.2**.**

Yield: 1.09 g, 69%; **^{1}H NMR** (D_2O, 300 K, in ppm): δ = 7.41 – 7.36 (4H, m, Ar), 7.27 – 7.17 (5H, m, Ar), 7.08 – 7.05 (2H, m, Ar), 6.93 – 6.86 (3H, m, Ar); **^{13}C{^{1}H} NMR** (D_2O, 300 K, in ppm): δ = 143.7 (s, Ar), 140.4 (s, Ar), 139.1 (s, Ar), 139.0 (s, Ar), 131.4 (s, Ar), 128.9 (s, Ar), 128.4 (s, Ar), 128.2 (s, Ar), 127.0 (s, Ar), 127.0 (s, Ar), 126.7 (s, Ar), 126.3 (s, Ar).

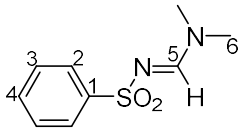
S7 Synthesis of *N*-sulfonyl amidines

S7.1. General procedure for the catalytic formation of *N*-sulfonyl amidines

Anhydrous formamide (1.0 mmol) is added to a suspension of $Na[N(SO_2Ph)(SO_2R)]$ (1.0 mmol) and fluorophosphonium triflate salt in MeCN (2 mL/mmol). The reaction mixture is stirred for 1 h at ambient temperature. The formed $NaSO_3Ph$ is removed by filtration and the filtrate is concentrated *in vacuo*. The *N*-sulfonyl amidines are purified by flash column chromatography on silica gel (40-63µm).

S7.2. Preparation of **11**

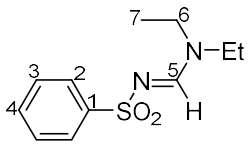
According to the general procedure in 7.1, **11** is synthesized from Me_2CHO (73 mg, 1.0 mmol) and $Na[N(SO_2Ph)_2]$ (319 mg, 1.0 mmol), with $\mathbf{8^{iPr}}[OTf]_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/cyclohexane = 1:8) affords **11** as a colorless solid.



Yield: 197 mg, 93%; **m.p.**: 131 – 133 °C; **Raman** (100 mW, 1024 scans, 298 K, in cm^{-1}): 3090 (23), 3071 (77), 3056 (37), 3010 (21), 2972 (28), 2931 (58), 2821 (21), 2793 (7), 1586 (56), 1441 (12), 1423 (49), 1406 (9), 1337 (7), 1280 (12), 1184 (7), 1165 (16), 1146 (63), 1128 (7), 1026 (12), 1000 (100), 902 (21), 846 (7), 722 (23), 613 (14), 599 (14), 577 (9), 560 (7), 488 (9), 394 (9), 338 (21), 318 (14), 265 (19); **IR** (298 K, ATR, in cm^{-1}): 3071 (vw), 2928 (vw), 1807 (vw), 1614 (vs), 1492 (vw), 1448 (w), 1429 (m), 1406 (vw), 1338 (s), 1280 (vs), 1245 (w), 1145 (s), 1129 (m), 1086 (vs), 1027 (w), 998 (w), 906 (s), 846 (vs), 752 (m), 723 (s), 685 (vs), 601 (s), 575 (vs), 558 (vs), 491 (w), 459 (vw); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.10 (1H, s, C5-H), 7.85 – 7.83 (2H, m, C2-H), 7.48 – 7.44 (1H, m, C4-H), 7.42 – 7.39 (2H, m, C3-H), 3.08 (3H, s, C6-H), 2.97 (3H, s, C6-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 159.4 (s, C5), 142.6 (s, C1), 132.0 (s, C4), 128.8 (s, C3), 126.5 (s, C2), 41.6 (s, C6), 35.6 (s, C6); **Elemental analysis:** calculated for $C_9H_{12}N_2O_2S$: C 50.9, H 5.7, N 13.2, S 15.1, found: C 51.3, H 5.6, N 13.0, S 14.7; Crystallographic data and details of the structure refinements are depicted in table S10.2.8; Spectral data are in accordance with those reported in the literature.[11]

S7.3. Preparation of **13**

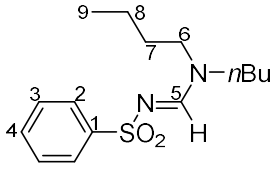
According to the general procedure in 7.1, **13** is synthesized from Et_2NCHO (101 mg, 1.0 mmol) and $Na[N(SO_2Ph)_2]$ (319 mg, 1.0 mmol), with $\mathbf{8^{iPr}}[OTf]_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/cyclohexane = 1:5) affords **13** as a colorless solid.



Yield: 220 mg, 92%; **m.p.**: 73 – 74 °C; **Raman** (400 mW, 2000 scans, 298 K, in cm^{-1}): 3082 (30), 3067 (55), 2974 (50), 2938 (35), 2922 (30), 2878 (25), 1588 (75), 1455 (70), 1296 (25), 1274 (25), 1148 (75), 1001 (100); **IR** (298 K, ATR, in cm^{-1}): 3066 (vw), 2973 (w), 2939 (w), 1607 (vs), 1449 (m), 1384 (w), 1350 (s), 1281 (s), 1270 (vs), 1210 (w), 1165 (vw), 1143 (vs), 1089 (s), 1079 (vs), 1020 (w), 1000 (w), 991 (w), 952 (s), 875 (vs), 847 (w), 823 (m), 795 (m), 773 (m), 758 (s), 724 (s), 689 (s), 605 (vs), 588 (vs), 552 (vs), 536 (m), 498 (m), 460 (m), 413 (vw); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.13 (1H, s, C5-H), 7.86 – 7.84 (2H, m, C2-H), 7.47 – 7.45 (3H, m, C3 and C4-H), 3.45 (2H, q, $^{3}J_{HH}$ = 7.2 Hz, C6-H), 3.35 (2H, q, $^{3}J_{HH}$ = 7.2 Hz, C6-H), 1.23 (3H, t, $^{3}J_{HH}$ = 7.2 Hz, C7-H), 1.11 (3H, t, $^{3}J_{HH}$ = 7.2 Hz, C7-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 158.4 (s, C5), 142.8 (s, C1), 131.9 (s, C4), 128.9 (s, C3), 126.5 (s, C2), 47.3 (s, C6), 41.2 (s, C6), 14.7 (s, C7), 12.3 (s, C7); **Elemental analysis:** calculated for $C_9H_{12}N_2O_2S$: C 55.0, H 6.7, N 11.7, found: C 55.1, H 6.3, N 11.3; Spectral data are in accordance with those reported in the literature.[12]

S7.4. Preparation of **14**

According to the general procedure in 7.1, **14** is synthesized from nBu$_2$NCHO (157 mg, 1.0 mmol) and Na[N(SO$_2$Ph)$_2$] (319 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/cyclohexane = 1:10) affords **14** as a colorless solid.

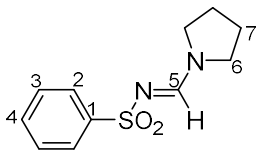


Yield: 276 mg, 93%; **m.p.**: 54 – 55 °C; **Raman** (400 mW, 2000 scans, 298 K, in cm^{-1}): 3069 (72), 3053 (45), 2968 (39), 2934 (70), 2914 (100), 2886 (48), 2871 (67), 2851 (29), 1585 (39), 1450 (36), 1137 (26), 999 (38); **IR** (298 K, ATR, in cm^{-1}): 2954 (w), 2932 (w), 2872 (w), 1609 (vs), 1443 (m), 1364 (m), 1345 (s), 1282 (vs), 1252 (w), 1226 (w), 1185 (w), 1147 (vs), 1137 (s), 1115 (w), 1085 (vs), 1070 (m), 1022 (w), 991 (w), 956 (w), 941 (w), 908 (w), 892 (vs), 856 (s), 827 (w), 786 (s), 761 (s), 738 (s), 721 (m), 689 (s), 607 (vs), 585 (vs), 534 (vs), 448 (w), 421 (w); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.02 (1H, s, C5-H), 7.73 – 7.70 (2H, m, C2-H), 7.35 – 7.27 (3H, m, C3 and C4-H), 3.24 (2H, t, $^{3}J_{HH}$ = 7.2 Hz, C6-H), 3.15 (2H, t, $^{3}J_{HH}$ = 7.2 Hz, C6-H), 1.43 – 1.32 (4H, m, C7 and C8-H), 1.16 – 1.04 (4H, m, C7 and C8-H), 0.75 (3H, t, $^{3}J_{HH}$ = 7.2 Hz, C9-H), 0.67 (3H, t, $^{3}J_{HH}$ = 7.2 Hz, C9-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 158.8 (s, C5), 142.6 (s, C1), 131.4 (s, C4), 128.4 (s, C3), 127.0 (s, C2), 52.1 (s, C6), 45.7 (s, C6), 30.4 (s, C7), 28.4 (s, C7), 19.6 (s, C8), 19.3 (s, C8), 13.4 (s, C9), 13.3 (s, C9); **Elemental analysis**: calculated for $C_{15}H_{24}N_2O_2S$: C 60.8, H 8.2, N 9.5, S 10.8, found: C 61.0,

H 7.8, N 9.2, S 10.7; Crystallographic data and details of the structure refinements are depicted in table S10.2.8. Spectral data are in accordance with those reported in the literature.[12]

S7.5. Preparation of **15**

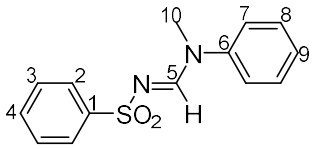
According to the general procedure in 7.1, **15** is synthesized from *N*-formylpyrrolidine (99 mg, 1.0 mmol) and Na[N(SO_2Ph)$_2$] (319 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/cyclohexane = 1:5) affords **15** as a colorless solid.



Yield: 208 mg, 87%; **m.p.**: 133 – 135 °C; **Raman** (400 mW, 2000 scans, 298 K, in cm^{-1}): 3067 (100), 3029 (18), 2984 (71), 2934 (43), 2886 (39), 1587 (29), 1454 (11), 1442 (14), 1144 (25), 1003 (21), 318 (11), 227 (14), 164 (11), 155 (11); **IR** (298 K, ATR, in cm^{-1}): 2973 (vw), 2878 (vw), 1609 (vs), 1480 (vw), 1447 (w), 1347 (w), 1335 (w), 1308 (m), 1294 (m), 1279 (vs), 1225 (vw), 1188 (vw), 1143 (vs), 1088 (vs), 1027 (vw), 998 (vw), 977 (w), 933 (w), 893 (s), 852 (s), 809 (w), 759 (m), 722 (s), 691 (s), 666 (s), 588 (vs), 558 (vs); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.29 (1H, s, C5-H), 7.86 – 7.85 (2H, m, C2-H), 7.48 – 7.40 (3H, m, C3 and C4-H), 3.55 (2H, t, $^3J_{HH}$ = 6.5 Hz, C6-H), 3.42 (2H, t, $^3J_{HH}$ = 6.5 Hz, C6-H), 1.92 – 1.90 (4H, m, C7-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 156.1 (s, C5), 142.7 (s, C1), 131.9 (s, C4), 128.8 (s, C3), 126.6 (s, C2), 50.2 (s, C6), 46.6 (s, C6), 25.1 (s, C7), 24.5 (s, C7); **Elemental analysis**: calculated for $C_{11}H_{14}N_2O_2S$: C 55.4, H 5.9, N 11.8, found: C 55.4, H 5.6, N 11.5. Spectral data are in accordance with those reported in the literature.[11]

S7.6. Preparation of **16**

According to the general procedure in 7.1, **16** is synthesized from PhMeNCHO (135 mg, 1.0 mmol) and Na[N(SO_2Ph)$_2$] (319 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/cyclohexane = 1:5) affords **16** as a colorless solid.

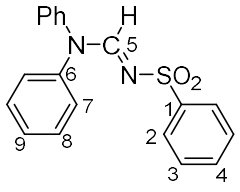


Yield: 213 mg, 78%; **m.p.**: 98 – 101 °C; **Raman** (400 mW, 2000 scans, 298 K, in cm^{-1}): 3073 (79), 1602 (66), 1585 (72), 1571 (41), 1498 (41), 1396 (100), 1292 (48), 1274 (34), 1162 (38), 1150 (100), 1030 (52), 994 (97), 167 (52); **IR** (298 K, ATR, in cm^{-1}): 3059 (vw), 3044 (vw), 3021 (vw), 2932 (vw), 1608 (s), 1578 (vs), 1498 (m), 1464 (vw), 1450 (vw), 1418 (w), 1397 (vw), 1348 (m), 1286 (s), 1205 (s), 1118 (vs), 1032 (w), 1007 (w), 995 (w), 961 (s), 889 (s), 788 (vs), 764 (s), 749 (m), 696 (s), 639 (w), 622 (s), 592 (w), 562 (m), 555 (m), 519 (vs), 501 (vs), 448 (m), 413 (w); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.55 (1H, s, C5-H), 7.93 – 7.91 (2H, m, C2-H),

7.54 – 7.48 (1H, m, C4-H), 7.48 – 7.45 (2H, m, C3-H), 7.43 – 7.39 (2H, m, C8-H), 7.32 – 7.28 (1H, m, C9-H), 7.18 – 7.16 (2H, m, C7-H), 3.42 (3H, s, C10-H); **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 300 K, in ppm): δ = 158.7 (s, C5), 143.3 (s, C1), 142.0 (s, C6), 132.3 (s, C4), 130.1 (s, C8), 129.0 (s, C3), 127.6 (s, C9), 127.0 (s, C2), 122.3 (s, C7), 36.3 (s, C10); **Elemental analysis**: calculated for $C_{14}H_{14}N_2O_2S$: C 61.3, H 5.1, N 10.2, S 11.7, found: C 61.2, H 5.1, N 9.8, S 11.3; Crystallographic data and details of the structure refinements are depicted in table S10.2.8. Spectral data are in accordance with those reported in the literature.[13]

S7.7. Preparation of **17**

According to the general procedure in 7.1, **17** is synthesized from Ph_2NCHO (197 mg, 1.0 mmol) and $Na[N(SO_2Ph)_2]$ (319 mg, 1.0 mmol) with **8^{iPr}**$[OTf]_3$ (23 mg, 2.5 mol%) as catalyst and reacted for 16 h and 80 °C. Column chromatography (EtOAc/cyclohexane = 1:10) affords **17** as a colorless solid.

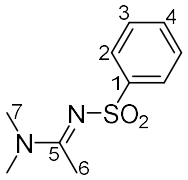


Yield: 315 mg, 94%; **m.p.**: 187 – 188 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3070 (94), 1607 (23), 1590 (82), 1494 (16), 1459 (17), 1389 (67), 1351 (24), 1312 (6), 1288 (10), 1272 (19), 1181 (9), 1153 (60), 1085 (7), 1028 (13), 1000 (100); **IR** (298 K, ATR, in cm^{-1}): 3070 (vw), 1606 (w), 1586 (w), 1561 (s), 1493 (s), 1445 (w), 1388 (w), 1348 (m), 1311 (w), 1280 (s), 1177 (w), 1151 (m), 1142 (s), 1083 (s), 1029 (w), 1000 (w), 975 (m), 916 (w), 862 (vw), 839 (w), 818 (s), 795 (s), 760 (m), 751 (m), 743 (m), 722 (m), 695 (s), 681 (s), 643 (m), 625 (w), 612 (m), 586 (s), 551 (vs), 534 (s), 510 (m), 469 (s), 456 (m), 424 (w); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.78 (1H, s, C5-H), 7.78 – 7.75 (2H, m, C2-H), 7.52 – 7.49 (1H, m, C4-H), 7.47 – 7.42 (2H, m, C3-H), 7.39 – 7.24 (6H, m, C7 and C8-H), 7.21 – 7.19 (2H, m, C6-H), 7.13 – 7.11 (2H, m, C6-H); **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 300 K, in ppm): δ = 158.3 (s, C5), 143.5 (s, C6), 141.6 (s, C1), 139.9 (s, C6), 132.4 (s, C4), 130.0 (s, C8), 129.5 (s, C8), 129.0 (C3), 128.1 (s, C9), 127.7 (s, C9), 126.8 (s, C2), 126.7 (s, C7), 124.2 (s, C7); **Elemental analysis:** calculated for $C_{19}H_{16}N_2O_2S$: C 67.8, H 4.7; N 8.3, S 9.5, found: C 67.7, H 4.8, N 8.3, S 9.5; Crystallographic data and details of the structure refinements are depicted in table S10.2.9.

S7.8. Preparation of **18**

According to the general procedure in 7.1, **18** is synthesized from Me_2NCOMe (44 mg, 0.5 mmol) and $Na[N(SO_2Ph)_2]$ (160 mg, 0.5 mmol) with **6^{Me}b**$[OTf]_2$ (40 mg, 5 mol%) as

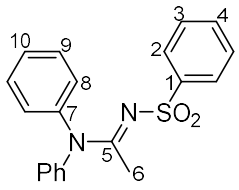
catalyst and reacted for 16 h and 80 °C. Column chromatography (MeOH/Et_2O = 1:5) affords **18** as a colorless oil, which solidifies upon standing for a few days.



Yield: 107 mg, 94%; **m.p.**: 60 – 61 °C; **Raman** (100 mW, 600 scans, 298 K, in cm^{-1}): 3082 (16), 3068 (78), 2969 (5), 2932 (53), 1585 (100), 1495 (7), 1448 (7), 1421 (12), 1371 (8), 1251 (28), 1170 (13), 1155 (19), 1129 (91), 1090 (9), 1021 (13), 1007 (9), 999 (80), 739 (37), 724 (6), 615 (28), 566 (15), 307 (8), 260 (16), **IR** (298 K, ATR, in cm^{-1}): 3533 (vw), 3059 (vw), 2923 (w), 2853 (w), 1586 (m), 1571 (s), 1493 (m), 1476 (m), 1442 (m), 1424 (m), 1400 (m), 1370 (w), 1269 (m), 1246 (vs), 1160 (m), 1137 (vs), 1085 (vs), 1069 (s), 1033 (s), 1010 (s), 994 (s), 935 (w), 847 (s), 801 (m), 767 (s), 738 (m), 723 (vs), 696 (s), 642 (w), 618 (vs), 611 (vs), 579 (s), 565 (vs), 529 (vs), 506 (s), 483 (s); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 7.87 – 7.85 (2H, m, C2-H), 7.42 – 7.36 (3H, m, C3 and C4-H), 3.00 (3H, s, C7-H), 3.00 (3H, s, C7-H), 2.40 (3H, s, C6-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 166.0 (s, C5), 144.0 (s, C1), 131.4 (s, C4), 128.6 (s, C3), 126.2 (s, C2), 39.0 (s, C7), 38.9 (s, C7), 18.0 (s, C6). Elemental analysis is not determined. Spectral data are in accordance with those reported in the literature.[14]

S7.9. Preparation of **19**

According to the general procedure in 7.1, **19** is synthesized from Ph_2NCOCH_3 (106 mg, 0.5 mmol) and $Na[N(SO_2Ph)_2]$ (160 mg, 0.5 mmol) with **8^{Me}**$[OTf]_3$ (41 mg, 10 mol%) as catalyst and reacted for 16 h and 80 °C. Column chromatography (acetone/cyclohexane = 1:5) affords **19** as a colorless solid.

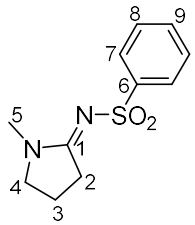


Yield: 60 mg, 34%; **m.p.**: 180 – 181 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3068 (74), 2939 (11), 1602 (9), 1587 (52), 1540 (8), 1461 (6), 1405 (11), 1273 (16), 1197 (29), 1169 (9), 1139 (34), 1090 (5), 1024 (16), 999 (100), 736 (17), 713 (8), 614 (13), 563 (5), 548 (6), 304 (7), 269 (9), 216 (14); **IR** (298 K, ATR, in cm^{-1}): 3414 (vw), 3059 (w), 2924 (w), 2854 (vw), 1601 (vw), 1586 (w), 1535 (s), 1488 (s), 1463 (m), 1446 (m), 1398 (s), 1370 (m), 1294 (w), 1269 (s), 1259 (s), 1197 (w), 1178 (w), 1138 (s), 1089 (vs), 1049 (s), 1035 (m), 1020 (m), 997 (m), 928 (w), 918 (w), 911 (w), 899 (w), 809 (vs), 758 (vs), 732 (s), 700 (vs), 689 (vs), 642 (s), 627 (s), 588 (w), 564 (vs), 545 (vs), 525 (vs), 500 (m), 484 (m), 470 (m), 437 (m), 411 (w); **^{1}H NMR** ($CDCl_3$, 250K, in ppm) : δ = 7.76 – 7.74 (2H, m, C2-H), 7.50 – 7.44 (3H, m, C3 and C4-H), 7.42 – 7.37 (3H, m, C8 and C10-H), 7.35 – 7.33 (2H, m, C8-H), 7.29 – 7.24 (5H, m, C8, C9 and C10-H), 2.56 (3H, s); **^{13}C{^{1}H} NMR** ($CDCl_3$, 250K, in ppm): δ = 166.7 (s, C5), 142.8 (s, C7), 142.6 (s, C7), 141.9 (s, C1), 131.8 (s, C4), 130.2 (s, C3), 129.2 (s, C8), 128.7 (s, C9), 128.6

(s, C10), 128.0 (s, C9), 127.4 (s, C10), 127.2 (s, C8), 126.1 (s, C2), 20.9 (s, C6); Crystallographic data and details of the structure refinements are depicted in table S10.2.9. Elemental analysis is not determined; Spectral data are in accordance with those reported in the literature.[14]

S7.10. Preparation of **20**

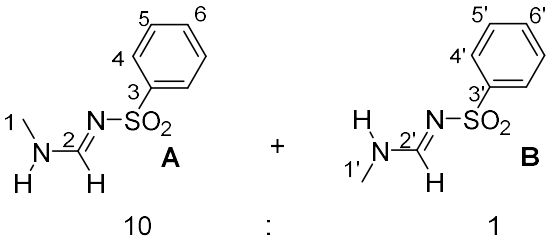
According to the general procedure in 7.1, **20** is synthesized from 1-Methyl-2-pyrrolidinone (50 mg, 0.5 mmol) and $Na[N(SO_2Ph)_2]$ (160 mg, 0.5 mmol) with $\mathbf{8^{Me}}[OTf]_3$ (41 mg, 10 mol%) as catalyst and reacted for 16 h and 80 °C. Column chromatography ($MeOH/Et_2O$ = 1:10) affords **20** as a colorless solid.



Yield: 40 mg, 40%; **m.p.**: 99 – 100 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3060 (85), 2999 (10), 2971 (13), 2936 (69), 2893 (10), 1582 (65), 1480 (16), 1453 (29), 1421 (7), 1287 (12), 1163 (10), 1142 (63), 1091 (5), 1023 (10), 998 (100), 944 (10), 718 (31), 615 (16), 577 (15), 442 (7), 332 (16), 310 (22), 253 (11); **IR** (ATR, 298 K, in cm^{-1}): 3419 (vw), 3060 (vw), 2923 (w), 2854 (vw), 1593 (s), 1475 (m), 1444 (m), 1410 (w), 1399 (w), 1297 (m), 1285 (s), 1259 (m), 1142 (s), 1113 (w), 1089 (s), 1074 (m), 998 (w), 901 (m), 881 (m), 838 (w), 759 (s), 736 (m), 717 (m), 691 (s), 606 (vs), 574 (vs), 482 (m), 439 (m), 413 (w); **^{1}H NMR** ($CDCl_3$, 300K, in ppm): δ = 7.93 – 7.90 (2H, m, C7-H), 7,49 – 7.40 (3H, m, C8 and C9-H), 3.44 (2H, t, $^3J_{HH}$ = 7.5 Hz, C4-H), 3.04 (2H, t, $^3J_{HH}$ = 8.1 Hz, C2-H), 2.95 (3H, s, C5-H), 2.03 (2H, quint, $^3J_{HH}$ = 7.1 Hz, C3-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300K, in ppm) : δ = 170.2 (s, C1), 143.6 (s, C6), 131.7 (s, C9), 128.7 (s, C8), 126.7 (s, C7), 51.9 (s, C4), 32.3 (s, C5), 31.0 (s, C2), 19.2 (s, C3); Crystallographic data and details of the structure refinements are depicted in table S10.2.9. Elemental analysis is not determined; Spectral data are in accordance with those reported in the literature.[12]

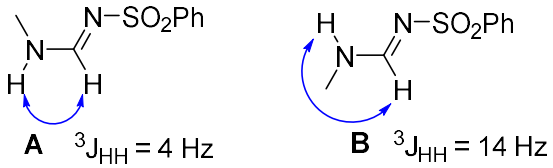
S7.11. Preparation of **21a**,**b**

According to the general procedure in 7.1, **21a**,**b** are synthesized from MeHNCHO (59 mg, 1 mmol) and $Na[N(SO_2Ph)_2]$ (319 mg, 1 mmol) with $\mathbf{6^{Me}b}[OTf]_2$ (81 mg, 10 mol%) as catalyst and reacted for 16 h and 80 °C. Column chromatography ($MeOH/Et_2O$ = 1:10) affords **21a**,**b** as a colorless solid.



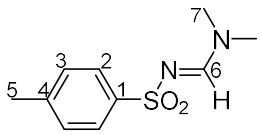
Yield: 102 mg, 51% in total; **m.p.**: 123 – 123 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3080 (8), 3067 (100), 3010 (8), 2937 (16), 2805 (5), 1583 (85), 1547 (9), 1330 (5), 1287 (54), 1175 (17), 1167 (7), 1146 (91), 1089 (9), 1025 (22), 998 (96), 972 (5), 898 (15), 729 (22), 637 (19), 616 (15), 549 (5), 502 (12), 393 (12), 360 (15), 322 (32), 294 (9), 271 (21); **IR** (298 K, ATR, in cm^{-1}): 3380 (w), 3062 (vw), 2935 (vw), 1614 (s), 1545 (w), 1476 (vw), 1450 (w), 1408 (w), 1329 (m), 1276 (s), 1144 (vs), 1085 (s), 1016 (w), 998 (w), 973 (w), 933 (vw), 897 (s), 853 (w), 758 (w), 729 (vs), 690 (s), 659 (m), 637 (vs), 590 (vs), 547 (vs), 500 (m), 467 (w); for the isomer **A**: **^{1}H NMR** ($CDCl_3$, 300K, in ppm): δ = 8.27 (1H, d, $^{3}J_{HH}$ = 3.9 Hz, C2-H),7.83 – 7.81 (2H, m, C4-H), 7.51 – 7.47 (1H, m, C6-H), 7.45 – 7.41 (2H, m, C5-H), 6.98 (br, N-H), 2.88 (1H, d, $^{3}J_{HH}$ = 4.4 Hz, C1-H); **^{13}C{^{1}H}NMR** ($CDCl_3$, 300K, in ppm): δ = 159.0 (s, C2), 142.2 (s, C3), 132.3 (s, C6), 129.0 (s, C5), 126.5 (s, C4), 28.6 (s, C1); for the isomer **B**: **^{1}H NMR** ($CDCl_3$, 300K, in ppm) : δ = 8.07 (1H, d, $^{3}J_{HH}$ = 13.0 Hz, C2'-H), 7.80 (m, 2H, C4'-H), 7.51 – 7.41 (3H, m, C6'-H and C5'-H, merged in C5-H and C6-H), 7.44 (br, N-H), 3.03 (3H, d, $^{3}J_{HH}$ = 4.4 Hz, C1'-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300K, in ppm): δ = 161.5 (s, C2'), 141.7 (s, C3'), 132.6 (s, C6'), 129.2 (s, C5'), 126.8 (s, C4'), 32.8 (s, C1'); Elemental analysis is not determined; Crystallographic data and details of the structure refinements of isomer **21a** is depicted in table 10.2.10.

VT NMR and 2D NMR experiments of a mixture of **21a**/**b** suggest a hindered rotation around the (H,Me)N-C bond which is also indicated by the partial double bond character derived from the x-ray structure of **21a**. The assignment follows the trend that for vicinal proton couplings in ethylene/imine derivatives, the trans-coupling (**21b**: ^{3}J = 14 Hz) is larger compared to the cis-coupling (**21a**: ^{3}J = 4 Hz).



S7.12. Preparation of **23b**

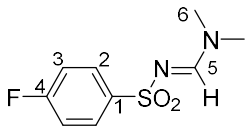
According to the general procedure in 7.1, **23b** is synthesized from Me_2CHO (73 mg, 1.0 mmol) and $Na[N(SO_2Ph)(SO_2(p\text{-}Me\text{-}C_6H_4))]$ (**22b**) (333 mg, 1.0 mmol), with **8^{iPr}**$[OTf]_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/*n*-Hexane = 1:7) affords **23b** as a colorless solid.



Yield: 37 mg, 16%; **m.p.**: 129 – 131 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3065 (50), 3051 (21), 3004 (20), 2972 (28), 2936 (51), 2926 (52), 2817 (19), 1598 (56), 1448 (27), 1432 (75), 1425 (64), 1378 (20), 1342 (22), 1287 (20), 1142 (100), 1081 (23), 914 (30), 812 (24), 798 (35), 677 (22), 636 (36), 588 (25), 368 (26), 359 (20), 313 (19), 290 (54), 177 (21); **IR** (298 K, ATR, in cm^{-1}): 2924 (vw), 2853 (vw), 1621 (m), 1429 (w), 1343 (w), 1294 (w), 1280 (m), 1250 (w), 1135 (m), 1081 (m), 905 (s), 852 (s), 838 (m), 809 (m), 705 (w), 672 (vs), 589 (vs), 567 (m), 549 (vs), 500 (w), 462 (w); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.15 (1H, s, C6-H), 7.80 – 7.78 (2H, m, C2-H), 7.28 – 7.27 (1H, m, C3-H), 3.14 (3H, s, C-7-H), 3.03 (3H, s, C7-H), 2.42 (3H, s, C5-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 159.3 (s, C6), 142.6 (s, C1), 139.8 (s, C4), 129.5 (s, C3), 126.7 (s, C2), 41.6 (s, C7), 25.7 (s, C7), 21.7 (s, C5); Crystallographic data and details of the structure refinements are depicted in table S10.2.10. Elemental analysis is not determined; Spectral data are in accordance with those reported in the literature.[11]

S7.15. Preparation of **23c**

According to the general procedure in 7.1, **23c** is synthesized from Me_2CHO (73 mg, 1.0 mmol) and $Na[N(SO_2Ph)(SO_2(p\text{-}F\text{-}C_6H_4))]$ (**22c**) (337 mg, 1.0 mmol), with **8^{iPr}**$[OTf]_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (EtOH/isohexane = 1:7) affords **23c** as a colorless solid.

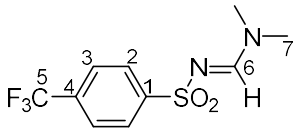


Yield: 112 mg, 60%; **m.p.**: 145 – 145 °C; **Raman** (500 mW, 2000 scans, 298 K, in cm^{-1}): 3081 (100), 3056 (10), 3014 (20), 3004 (13), 2980 (37), 2939 (53), 2903 (20), 2892 (17), 2877 (13), 2870 (10), 2855 (10), 2820 (23), 1435 (13), 1426 (20), 1157 (13), 1145 (30), 912 (10), 826 (10), 818 (13), 633 (13), 588 (13), 330 (10), 289 (27), 132 (13); **IR** (298 K, ATR, in cm^{-1}): 3103 (vw), 3075 (vw), 2926 (vw), 2870 (vw), 2854 (vw), 2820 (vw), 1901 (vw), 1818 (vw), 1624 (vs), 1601 (m), 1590 (s), 1491 (m), 1449 (w), 1429 (m), 1412 (w), 1382 (vw), 1332 (s), 1302 (s), 1291 (m), 1281 (vs), 1248 (w), 1231 (m), 1217 (s), 1159 (m), 1141 (vs), 1094 (w), 1081 (vs), 1023 (vw), 1011 (w), 986 (vw), 958 (vw), 942 (vw), 905 (vs), 848 (vs), 830 (vs), 814 (s), 749 (vw), 725 (vw), 707 (w), 675 (vs), 629 (vw), 606 (vw), 564 (s), 509 (m), 470 (w); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.09 (1H, s, CHO), 7.86 – 7.84 (2H, m, C3-H), 7.24 – 7.07 (2H, m, C2-H), 3.10 (3H, s, C6-H), 2.98 (3H, s, C6-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 164.7 (d, $^{1}J_{CF}$ = 253 Hz, C4), 159.3 (s, C5), 138.8 (d, $^{4}J_{CF}$ = 3 Hz, C1), 129.2 (d, $^{3}J_{CF}$ = 9 Hz, C2), 115.9 (d, $^{2}J_{CF}$ = 23 Hz, C3), 41.7 (s, C6), 35.7 (s, C6); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = -107.1 (m); **Elemental analysis**: calculated for $C_9H_{11}FN_2O_2S$: C 47.0, H 4.8, N 12.2, S 13.9, found: C 46.9,

H 4.6, N 12.1, S 13.7; Crystallographic data and details of the structure refinements are depicted in table S10.2.11. Spectral data are in accordance with those reported in the literature.[11]

S7.16. Preparation of **23d**

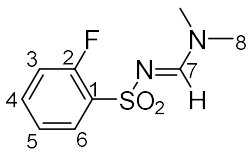
According to the general procedure in 7.1, **23d** is synthesized from Me_2CHO (37 mg, 0.5 mmol) and Na[N(SO_2Ph)(SO_2(*p*-CF_3-C_6H_4))] (**22d**) (194 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (12 mg, 2.5 mol%) as catalyst. Column chromatography (acetone/*n*-hexane = 1:10) affords **23d** as a colorless solid.



Yield: 120 mg, 86%; **m.p.**: 167 – 158.0 °C; **Raman** (200 mW, 500 scans, 298 K, in cm^{-1}): 3082 (80), 3026 (23), 2991 (41), 2948 (68), 2833 (25), 1607 (100), 1456 (21), 1432 (84), 1415 (29), 1319 (42), 1309 (22), 1293 (20), 1151 (64), 1134 (44), 1060 (35), 916 (31), 785 (57), 634 (38), 627 (31), 341 (30), 271 (22), 216 (30); **IR** (298 K, ATR, in cm^{-1}): 2923 (w), 2853 (vw), 1630 (s), 1607 (m), 1487 (vw), 1435 (w), 1425 (w), 1401 (w), 1322 (vs), 1306 (s), 1284 (vs), 1249 (m), 1183 (w), 1153 (vs), 1141 (s), 1124 (vs), 1103 (vs), 1085 (vs), 1061 (vs), 1012 (m), 966 (w), 911 (vs), 849 (s), 834 (vs), 783 (w), 736 (vw), 713 (vs), 617 (vs), 601 (vs), 584 (vs), 559 (s), 502 (w), 471 (w), 428 (s); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.12 (1H, s, C6), 7.99 (2H, m, C2-H), 7.69 (2H, m, C3-H), 3.13 (3H, s, C7-H), 3.00 (3H, s, C7-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 159.6 (s, C6), 146.2 (q, $^5J_{CF}$ = 1 Hz, C1), 133.7 (q, $^2J_{CF}$ = 33 Hz, C4), 127.2 (s, C2), 126.0 (q, $^3J_{CF}$ = 4 Hz, C3), 123.6 (q, $^1J_{CF}$ = 272 Hz), 41.8 (s, C7), 35.8 (s, C7); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = -63.0 (s); Crystallographic data and details of the structure refinements are depicted in table S10.2.11. Elemental analysis is not determined; Spectral data are in accordance with those reported in the literature.[11]

S7.17. Preparation of **23e**

According to the general procedure in 7.1, **23e** is synthesized from Me_2CHO (73 mg, 1.0 mmol) and Na[N(SO_2Ph)(SO_2(*o*-F-C_6H_4))] (**22e**) (337 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (Et_2O) affords **23e** as a colorless solid.

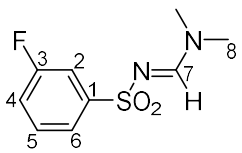


Yield: 210 mg, 91%; **m.p.**: 118 – 119 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3086 (40), 3021 (19), 2997 (13), 2980 (21), 2942 (46), 2830 (16), 1603 (57), 1449 (15), 1427 (100), 1222 (30), 1165 (19), 1148 (69), 1118 (15), 1031 (52), 911 (31), 824 (23), 698 (29), 534 (32), 388 (16), 335 (13), 294 (33), 277 (35), 223 (19), 138 (44); **IR** (298 K, ATR, in cm^{-1}): 2939 (vw), 1620 (vs), 1601 (m), 1579 (w), 1492 (vw), 1472 (m), 1452 (w), 1432 (m), 1411 (vw), 1335 (s),

1286 (s), 1262 (m), 1245 (m), 1220 (w), 1148 (s), 1118 (s), 1071 (s), 1030 (w), 1006 (vw), 949 (vw), 909 (vs), 848 (vs), 823 (m), 760 (s), 714 (w), 696 (vs), 601 (vs), 586 (vs), 566 (s), 531 (s), 482 (m), 469 (m), 446 (w), 406 (s); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.19 (1H, d, $^{6}J_{FH}$ = 2.3 Hz, C7-H), 7.96 – 7.93 (1H, m, C5-H), 7.49 – 7.45 (1H, m, C4-H), 7.21 – 7.18 (1H, m, C6-H), 7.10 – 7.06 (1H, m, C3-H), 3.14 (3H, s, C8-H), 3.00 (3H, s, C8-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 160.7 (d, $^{5}J_{CF}$ = 3.3 Hz, C7-H), 159.0 (d, $^{1}J_{CF}$ = 254 Hz, C2), 134.4 (d, $^{3}J_{CF}$ = 9 Hz, C4), 130.1 (d, $^{2}J_{CF}$ = 14 Hz, C1), 129.6 (s, C5), 124.3 (d, $^{3}J_{CF}$ = 5 Hz, C6), 116.8 (d, $^{2}J_{CF}$ = 21 Hz, C3), 41.8 (s, C8), 25.8 (s, C8); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = -111.0 (m); **Elemental analysis**: calculated for $C_9H_{11}FN_2O_2S$: C 47.0, H 4.8, N 12.2, S 13.9, found: C 47.0, H 4.5, N 12.2, S 13.9; Crystallographic data and details of the structure refinements are depicted in table S10.2.11.

S7.18. Preparation of **23f**

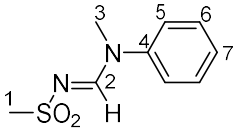
According to the general procedure in 7.1, **23f** is synthesized from Me_2CHO (73 mg, 1.0 mmol) and $Na[N(SO_2Ph)(SO_2(o\text{-}F\text{-}C_6H_4))]$ (**22f**) (337 mg, 1.0 mmol), with **8^{iPr}**$[OTf]_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (Et_2O) affords **23f** as a colorless solid.



Yield: 180 mg, 78%; **m.p.**: 107 – 109 ºC; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3078 (43), 3024 (17), 2982 (30), 2942 (56), 2906 (16), 2828 (16), 1631 (15), 1601 (31), 1588 (17), 1452 (17), 1428 (96), 1410 (19), 1288 (14), 1274 (12), 1216 (23), 1163 (15), 1140 (47), 1125 (25), 1087 (15), 1002 (100), 923 (33), 700 (29), 623 (25), 541 (18), 382 (13), 327 (32), 318 (23), 306 (23), 299 (23), 253 (56), 149 (31), 139 (31); **IR** (298 K, ATR, in cm^{-1}): 3076 (vw), 2937 (vw), 1626 (vs), 1597 (w), 1490 (vw), 1475 (w), 1447 (vw), 1431 (m), 1331 (s), 1308 (w), 1286 (vs), 1278 (s), 1245 (w), 1224 (m), 1139 (s), 1124 (vs), 1084 (s), 1069 (m), 1028 (vw), 1002 (vw), 916 (vs), 882 (w), 846 (vs), 797 (m), 787 (m), 752 (vw), 724 (vw), 696 (s), 675 (vs), 613 (vs), 604 (vs), 590 (vs), 569 (s), 557 (s), 537 (s), 522 (m), 473 (w), 449 (vw); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.11 (1H, s, C7-H), 7.66 – 7.65 (1H, m, C6-H), 7.57 – 7.54 (1H, m, C2-H), 7.42 – 7.39 (1H, m, C5-H), 7.19 – 7.15 (1H, m, C4-H), 3.12 (3H, s, C8-H), 3.01 (3H, s, C8-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 163.4 (d, $^{1}J_{CF}$ = 250 Hz, C3), 159.6 (s, C7), 144.7 (d, $^{3}J_{CF}$ = 7 Hz, C1), 130.7 (d, $^{3}J_{CF}$ = 8 Hz, C5), 122.4 (d, $^{4}J_{CF}$ = 3 Hz, C6), 119.1 (d, $^{2}J_{CF}$ = 21 Hz, C4), 114.1 (d, $^{2}J_{CF}$ = 25 Hz, C2), 41.8 (s, C8), 35.8 (s, C8); **^{19}F NMR** ($CDCl_3$, 300 K, in ppm): δ = -110.7 (m); **Elemental analysis:** calculated for $C_9H_{11}FN_2O_2S$: C 47.0, H 4.8, N 12.2, S 13.9, found: C 47.3, H 4.7, N 12.0, S 14.4.

S7.19. Preparation of **23g**

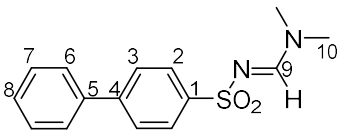
According to the general procedure in 7.1, **23g** is synthesized from MePhNCHO (135 mg, 1.0 mmol) and Na[N(SO_2Ph)(SO_2Me)] (**22g**) (257 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (23 mg, 2.5 mol%) as catalyst and reacted for 16 h at room temperature. Column chromatography (acetone/cyclohexane = 1:7) affords **23g** as a colorless oil.



Yield: 43 mg, 16%; **Raman** (100 mW, 250 scans, 298 K, in cm^{-1}): 3069 (63), 3014 (35), 2933 (100), 1606 (48), 1589 (73), 1500 (39), 1416 (42), 1397 (95), 1349 (23), 1293 (50), 1280 (30), 1134 (73), 1033 (34), 997 (100), 794 (33), 617 (23), 256 (43), 186 (31); **IR** (298 K, ATR, in cm^{-1}): 3059 (vw), 3044 (vw), 3021 (vw), 2932 (vw), 1608 (s), 1578 (vs), 1498 (m), 1464 (vw), 1450 (vw), 1418 (w), 1397 (vw), 1348 (m), 1286 (s), 1205 (s), 1118 (vs), 1032 (w), 1007 (w), 995 (w), 961 (s), 889 (s), 788 (vs), 764 (s), 749 (m), 696 (s), 639 (w), 622 (s), 592 (w), 562 (m), 555 (m), 519 (vs), 501 (vs), 448 (m), 413 (w); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.46 (1H, s, C2-H), 7.43 – 7.38 (2H, m, C6-H), 7.32 – 7.37 (1H, m, C7-H), 7.20 – 7.16 (2H, m, C5-H), 3.44 (3H, s, C3-H), 3.00 (3H, s, C1-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 158.8 (s, C2-H), 143.4 (s, C4-H), 130.1 (s, C6-H), 127.6 (s, C7-H), 122.3 (s, C5-H), 42.1 (s, C1-H), 36.2 (s, C3-H); Elemental analysis is not determined; Spectral data are in accordance with those reported in the literature.[15]

S7.20. Preparation of **23h**

According to the general procedure in 7.1, **23h** is synthesized from Me_2CHO (73 mg, 1.0 mmol) and Na[N(SO_2Ph)(SO_2(*p*-C_6H_5-C_6H_4))] (**22h**) (395 mg, 1.0 mmol), with **8^{iPr}**[OTf]$_3$ (23 mg, 2.5 mol%) as catalyst. Column chromatography (EtOAc/$CHCl_3$ = 1:1) affords **23h** as a colorless solid.



Yield: 91 mg, 32%; **m.p.**: 188 – 189 °C; **Raman** (100 mW, 500 scans, 298 K, in cm^{-1}): 3079 (7), 3062 (48), 2978 (12), 2942 (21), 1599 (100), 1445 (9), 1428 (39), 1408 (8), 1286 (52), 1184 (10), 1144 (65), 1128 (7), 1038 (15), 1008 (12), 998 (30), 913 (11), 852 (7), 769 (39), 613 (13), 420 (11), 354 (7), 317 (9), 283 (11), 254 (12), 207 (19), 183 (14), 162 (26); **IR** (298 K, ATR, in cm^{-1}): 3047 (vw), 3023 (vw), 2926 (vw), 1818 (vw), 1618 (vs), 1561 (vw), 1491 (vw), 1479 (w), 1454 (vw), 1444 (vw), 1436 (w), 1423 (w), 1407 (vw), 1390 (vw), 1333 (s), 1301 (vw), 1278 (s), 1244 (w), 1181 (vw), 1141 (s), 1127 (m), 1104 (vw), 1088 (vs), 1059 (w), 1019 (vw), 1006 (w), 973 (vw), 949 (vw), 912 (vs), 848 (vs), 833 (m), 827 (m), 769 (w), 759 (s), 722 (w), 694 (s), 675 (vs), 633 (vw), 608 (vs), 583 (vs), 564 (m), 557 (s), 539 (w), 512 (w), 475 (vw),

416 (vw), 404 (vw); **^{1}H NMR** ($CDCl_3$, 300 K, in ppm): δ = 8.15 (1H, s, C9-H), 7.95 – 7.92 (2H, m, C3-H), 7.66 – 7.64 (2H, m, C6-H), 7.58 – 7.55 (2H, m, C2-H), 7.46 – 7.44 (2H, m, C7-H), 7.39 – 7.35 (1H, m, C8-H), 3.12 (3H, s, C10-H), 3.02 (3H, s, C10-H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K, in ppm): δ = 159.4 (s, C9), 145.0 (s, C1), 141.3 (s, C4), 139.9 (C5), 129.4 (s, C7), 128.4 (s, C8), 127.6 (s, C6), 127.5 (s, C2), 127.2 (s, C3), 41.7 (s, C10), 35.8 (s, C10); Elemental analysis is not determined; Crystallographic data and details of the structure refinements are depicted in table S10.2.10.

S8 NMR spectra of the fluorophosphonium salts

Note: the highly water-sensitive fluorophosphonium salts react with the trace amounts water in dried (only CH_3CN, CD_3CN after drying with CaH_2 according to the described procedure) solvents and the decomposed products are marked in the ^{31}P NMR with an asterisk.

S8.1 NMR spectra of **2a**[NSI]

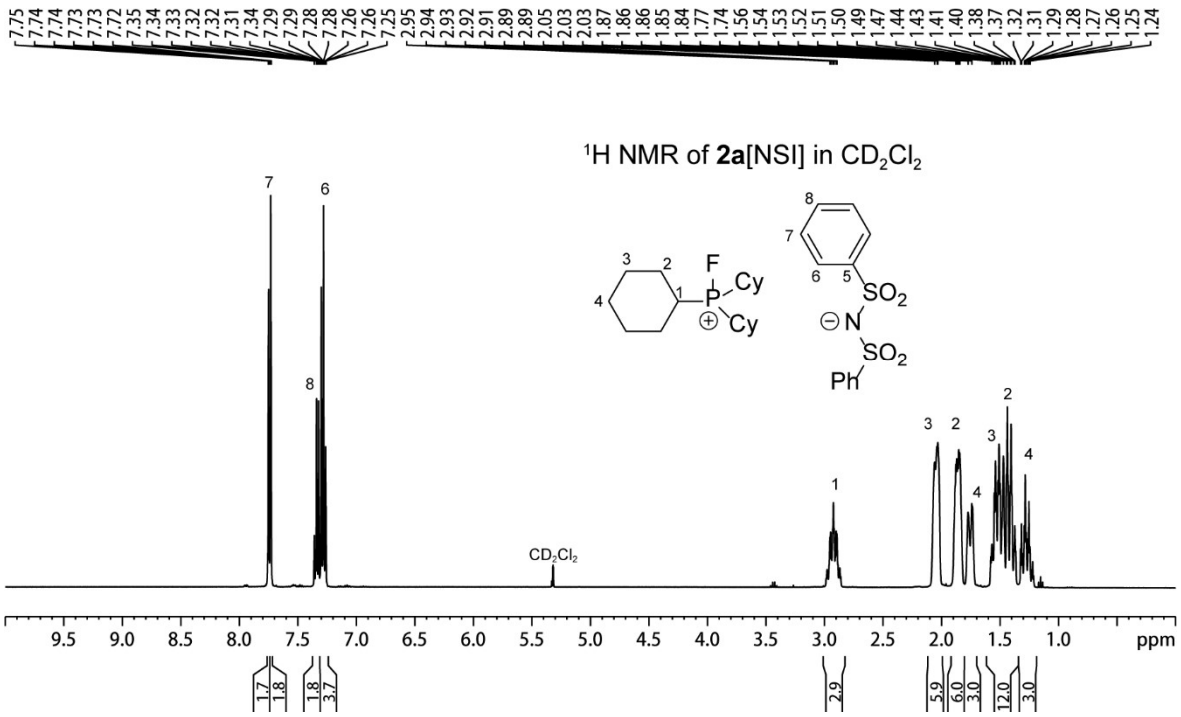


Figure S8.1. ^{1}H NMR spectrum of **2a**[NSI] (500MHz, CD_2Cl_2, 300 K), details are listed in section S3.1.

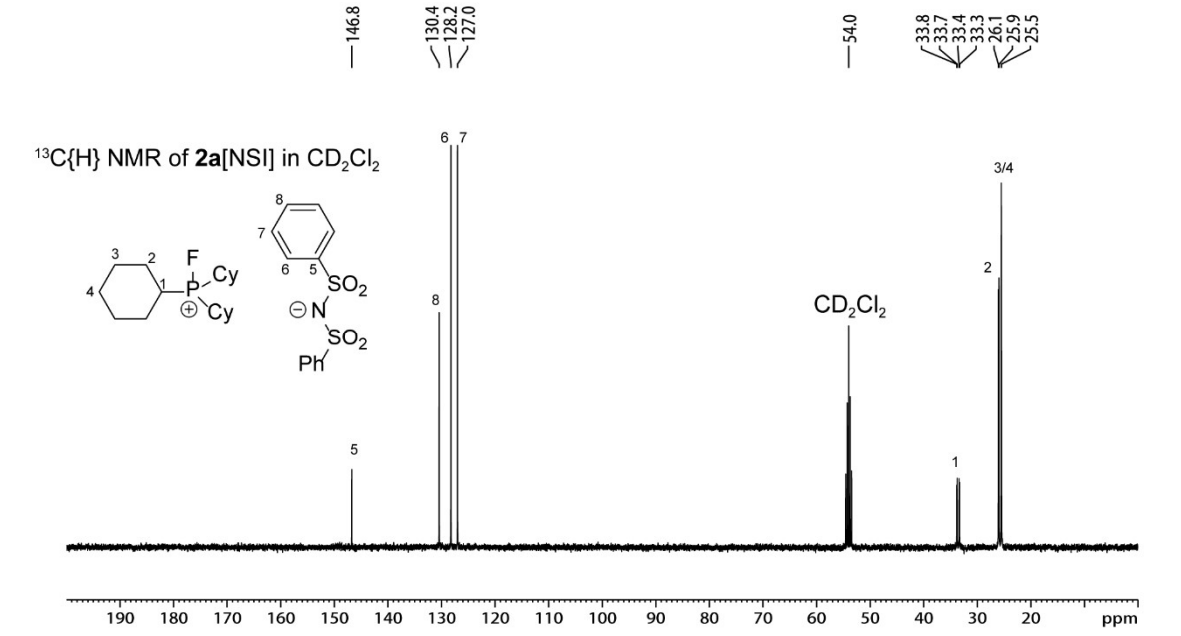


Figure S8.2. ^{13}C{H} NMR spectrum of **2a**[NSI] (126MHz, CD_2Cl_2, 300 K), details are listed in section S3.1.

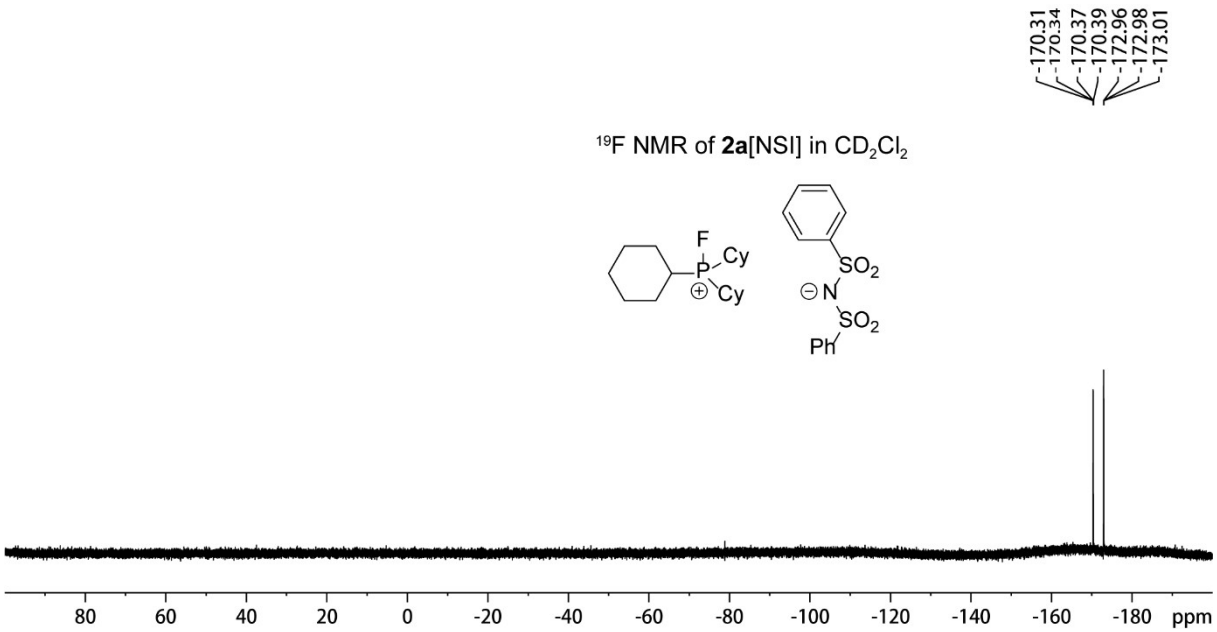


Figure S8.3. ^{19}F NMR spectrum of **2a**[NSI] (471MHz, CD_2Cl_2, 300 K), details are listed in section S3.1.

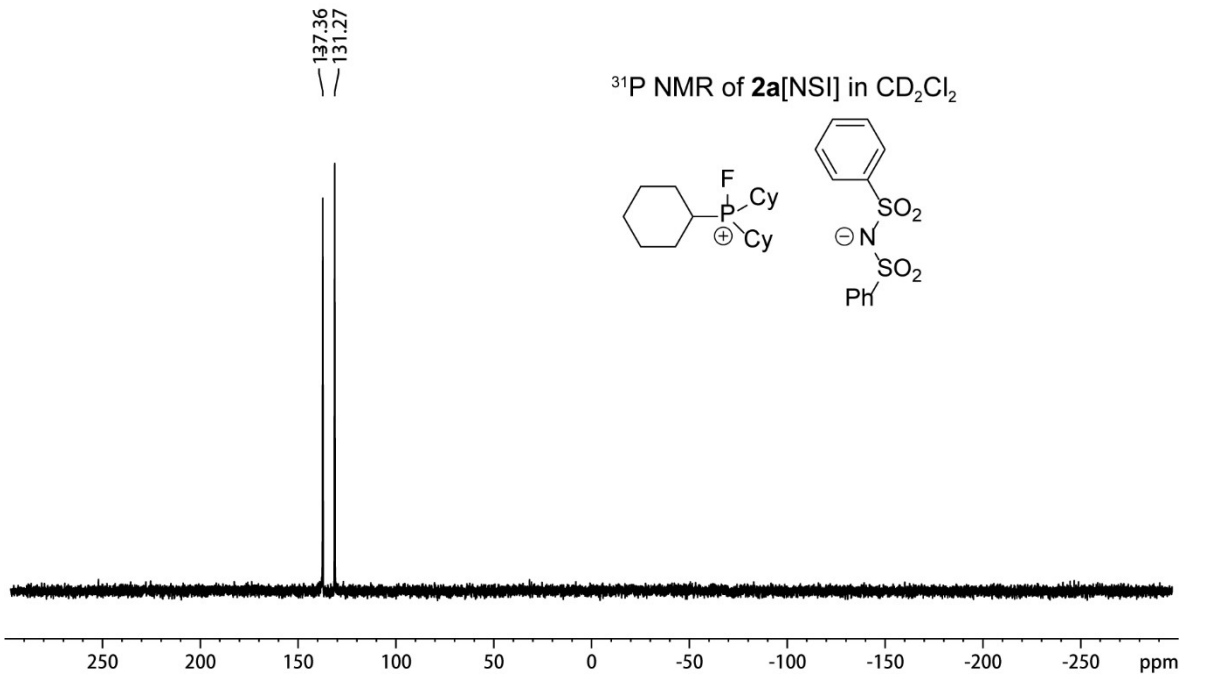


Figure S8.4. ^{31}P NMR spectrum of **2a**[NSI] (202MHz, CD_2Cl_2, 300 K), details are listed in section S3.1.

S8.2 NMR spectra of **2b**[NSI]

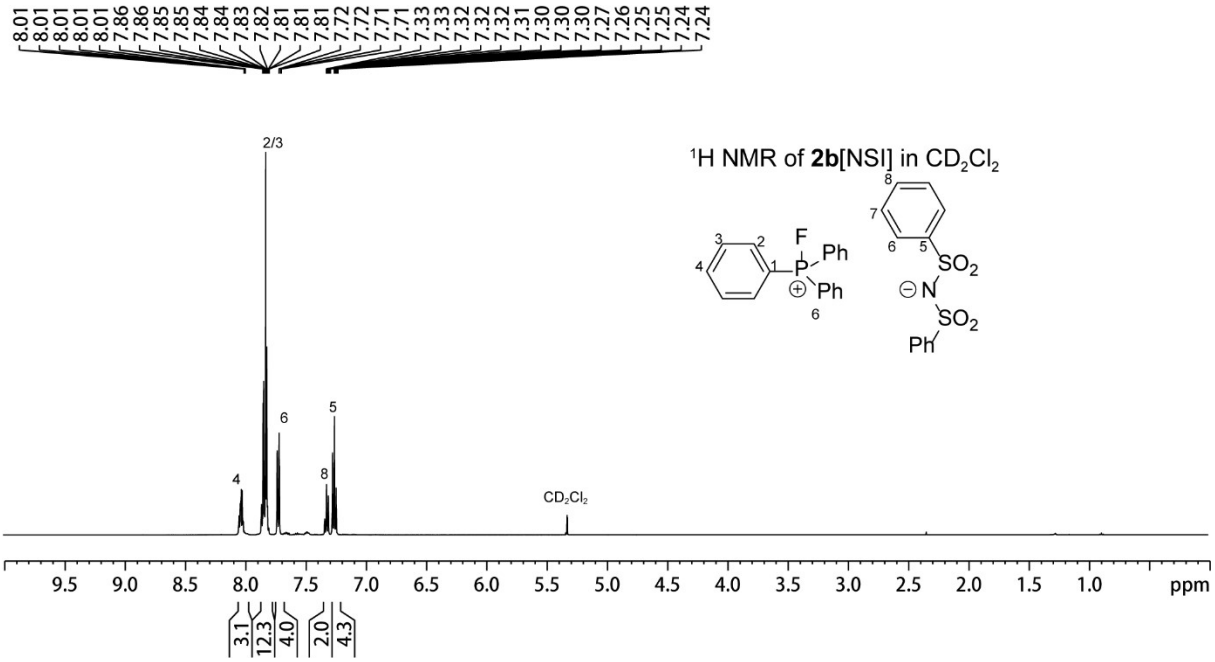


Figure S8.5. ^{1}H NMR spectrum of **2b**[NSI] (500MHz, CD_2Cl_2, 300 K), details are listed in section S3.2.

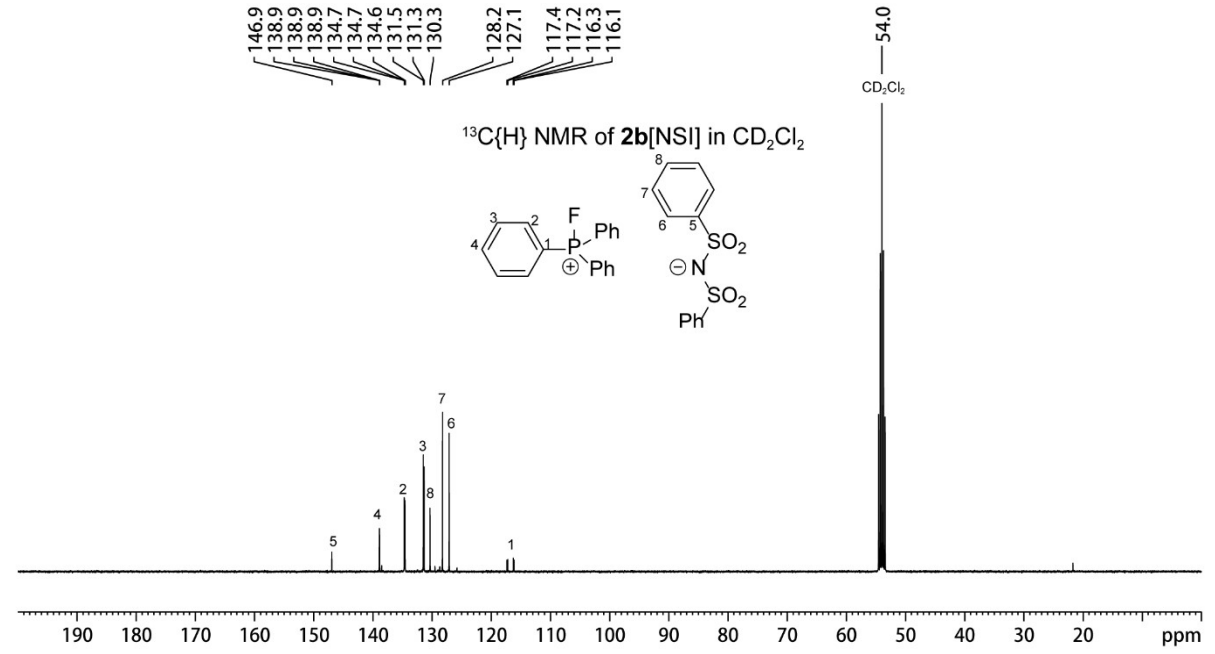


Figure S8.6. ^{13}C{H} NMR spectrum of **2b**[NSI] (126MHz, CD_2Cl_2, 300 K), details are listed in section S3.2.

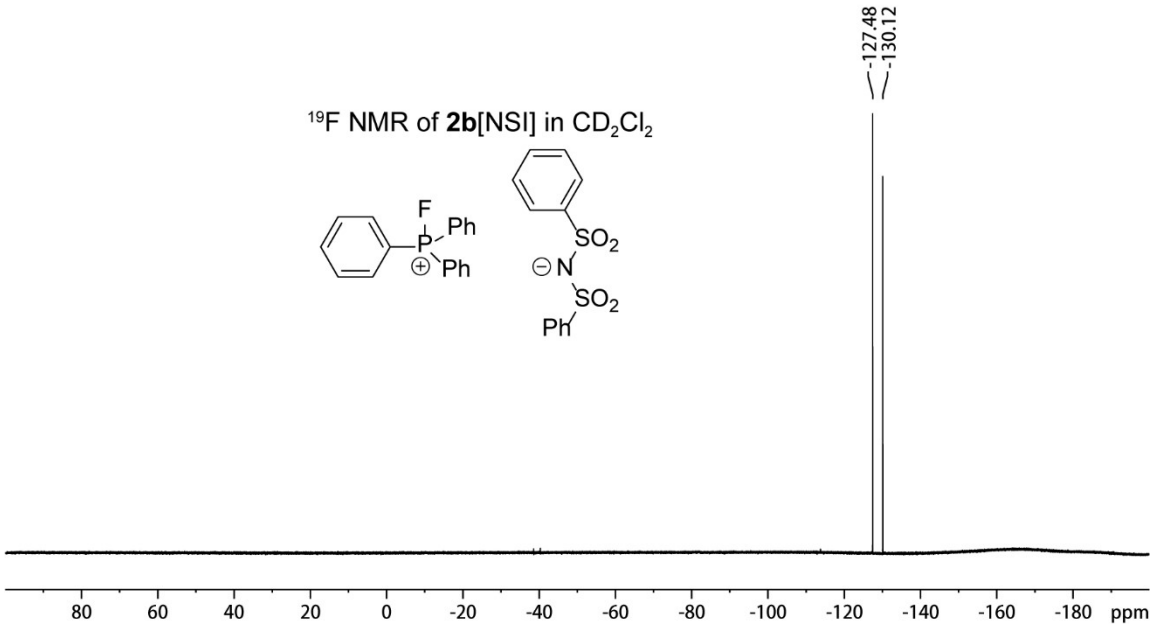


Figure S8.7. ^{19}F NMR spectrum of **2b**[NSI] (471MHz, CD_2Cl_2, 300 K), details are listed in section S3.2.

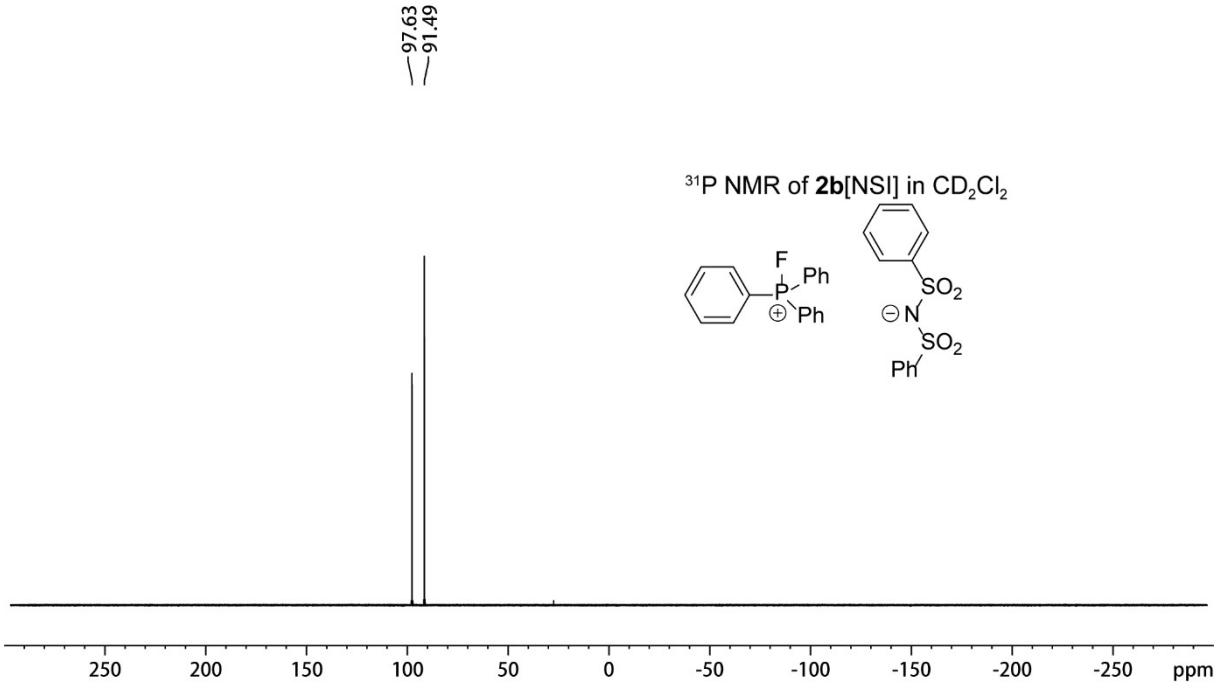


Figure S8.8. $^{31}P\{H\}$ NMR spectrum of **2b**[NSI] (202MHz, CD_2Cl_2, 300 K), details are listed in section S3.2.

S8.3 NMR spectra of (**2c**[NSI])

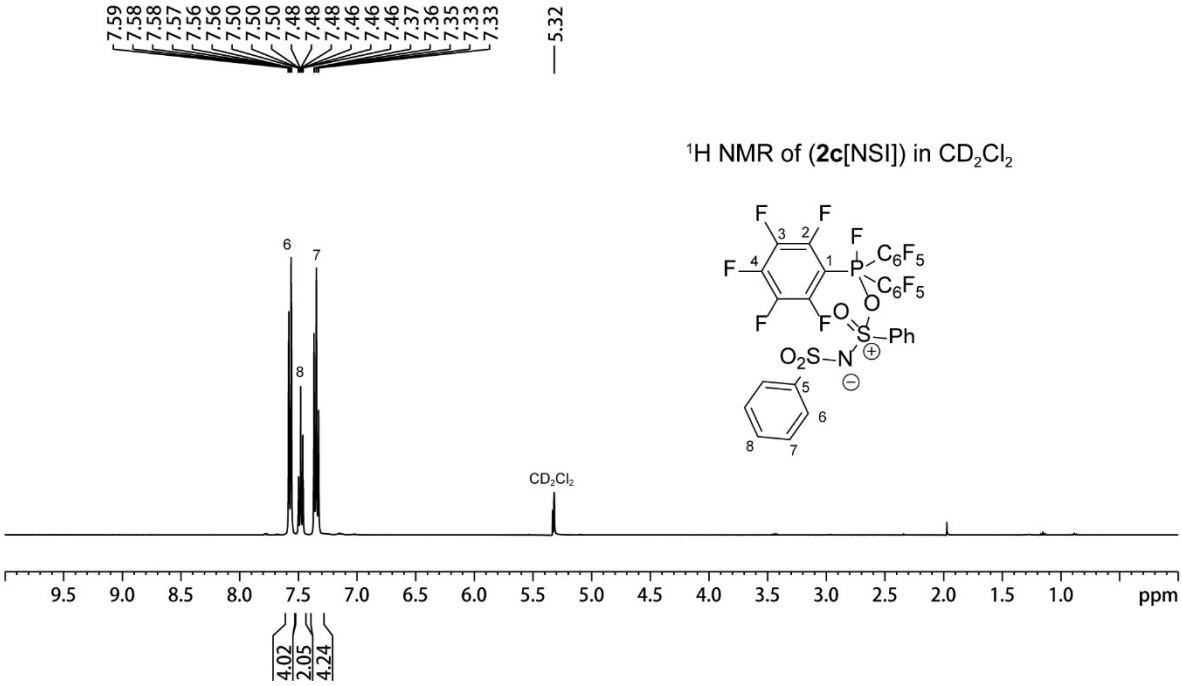


Figure S8.9. ^{1}H NMR spectrum of (**2c**[NSI]) (500MHz, CD_2Cl_2, 300 K), details are listed in section S3.3.

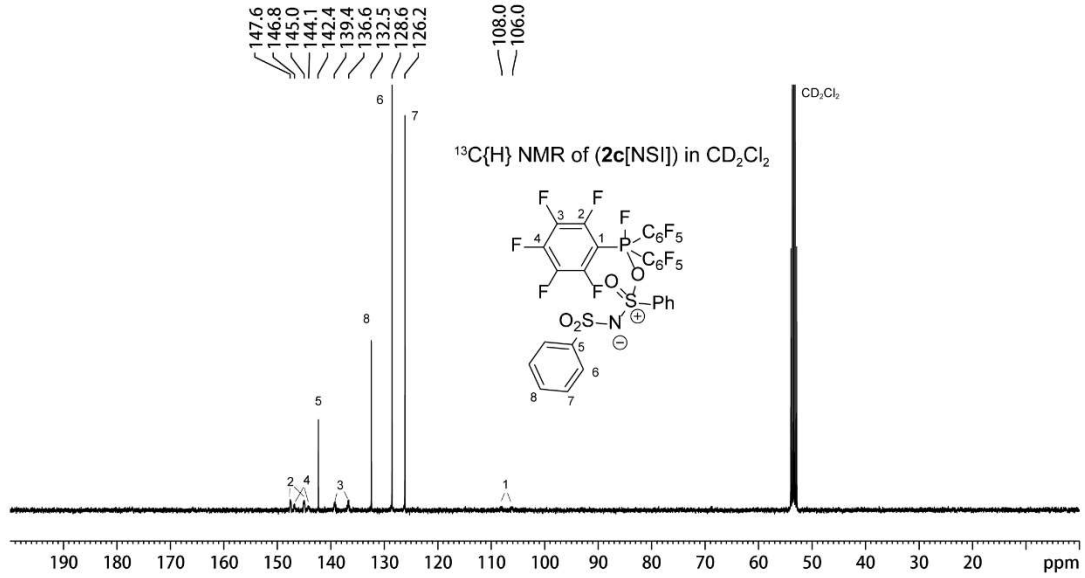


Figure S8.10. ^{13}C{H} NMR spectrum of (**2c**[NSI]) (126MHz, CD_2Cl_2, 300 K), details are listed in section S3.3.

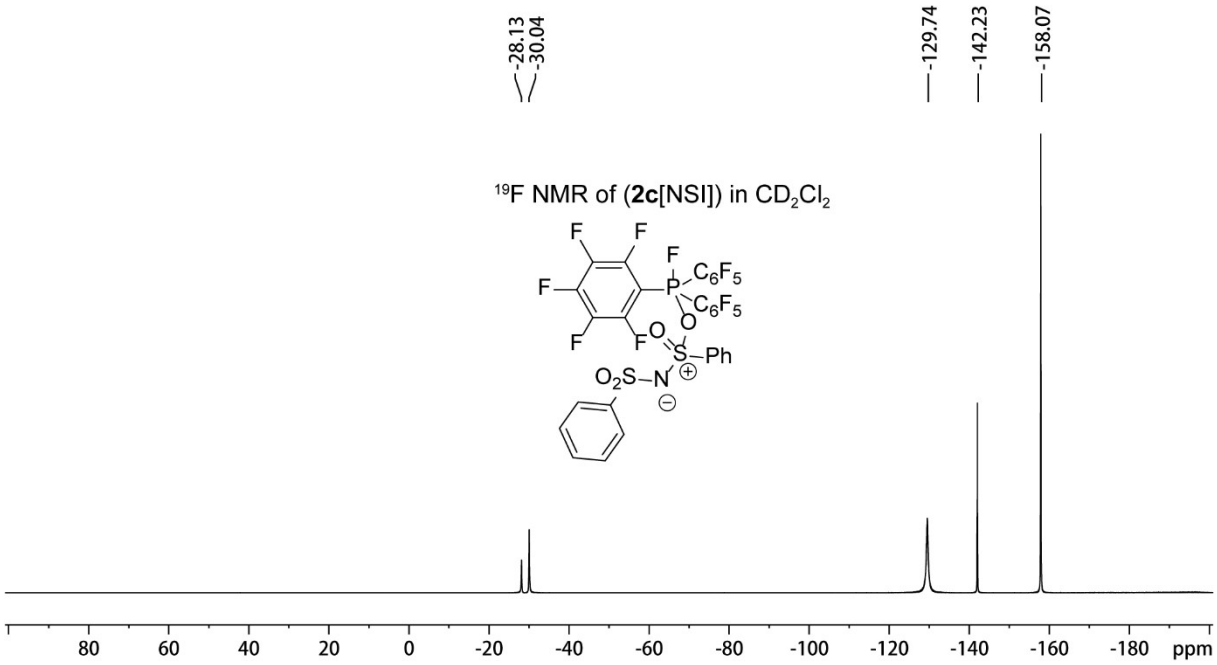


Figure S8.11. $^{19}F\{H\}$ NMR spectrum of (**2c**[NSI]) (471MHz, CD_2Cl_2, 300 K), details are listed in section S3.3.

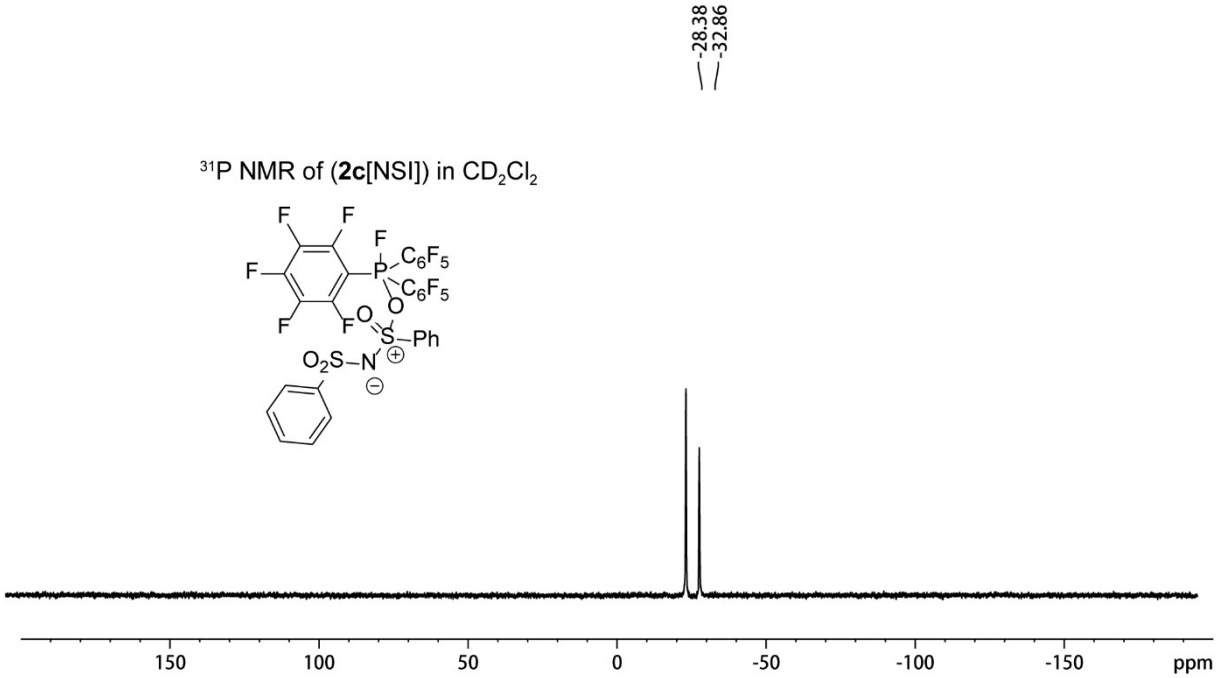


Figure S8.12. $^{31}P\{H\}$ NMR spectrum of (**2c**[NSI]) (202MHz, CD_2Cl_2, 300 K), details are listed in section S3.3.

S8.4 NMR spectra of **2a**[OTf]

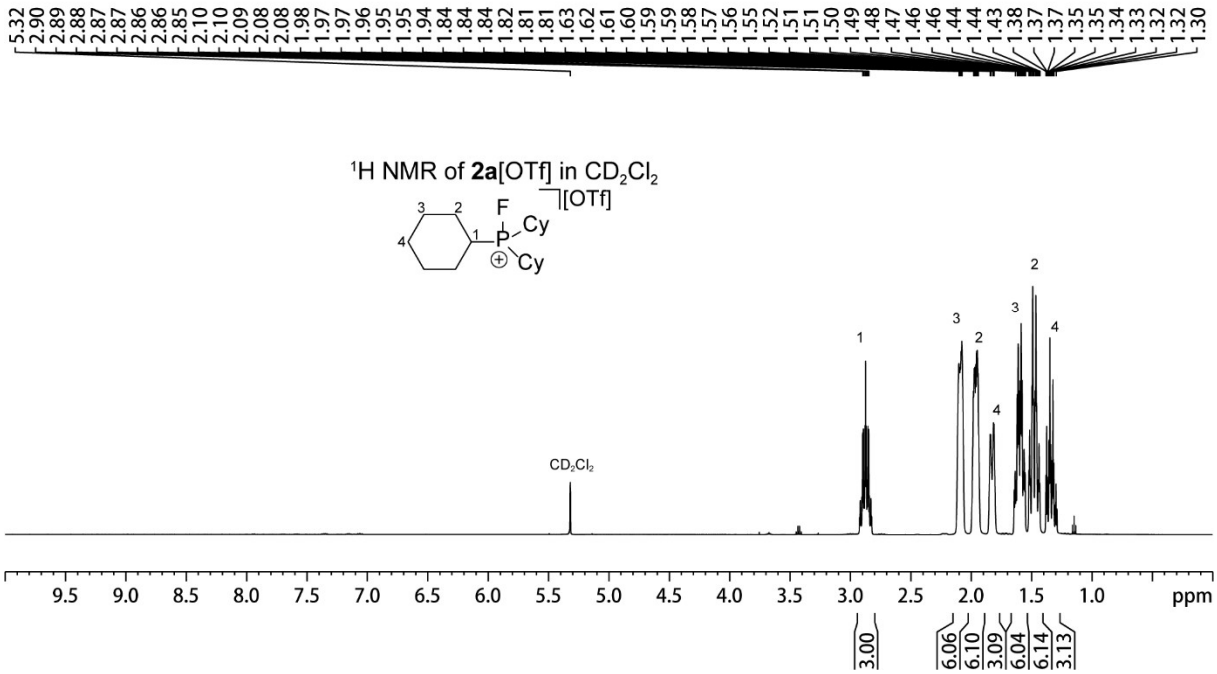


Figure S8.13. ^{1}H NMR spectrum of **2a**[OTf] (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.3.

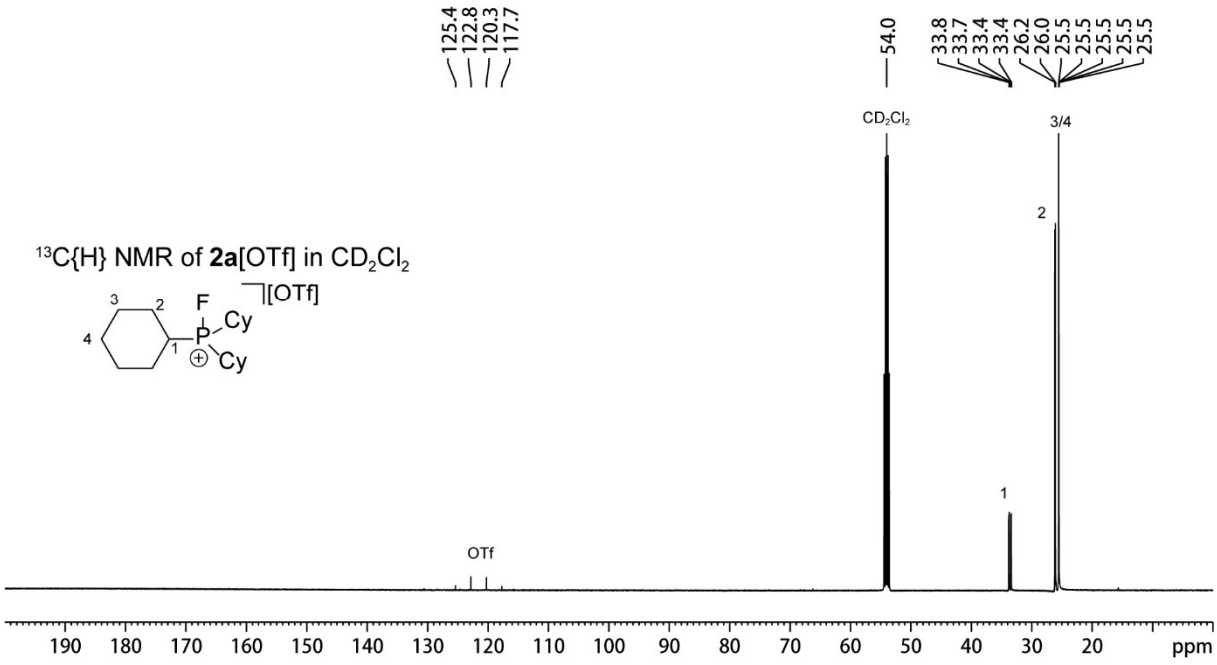


Figure S8.14. ^{13}C{H} NMR spectrum of **2a**[OTf] (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.3.

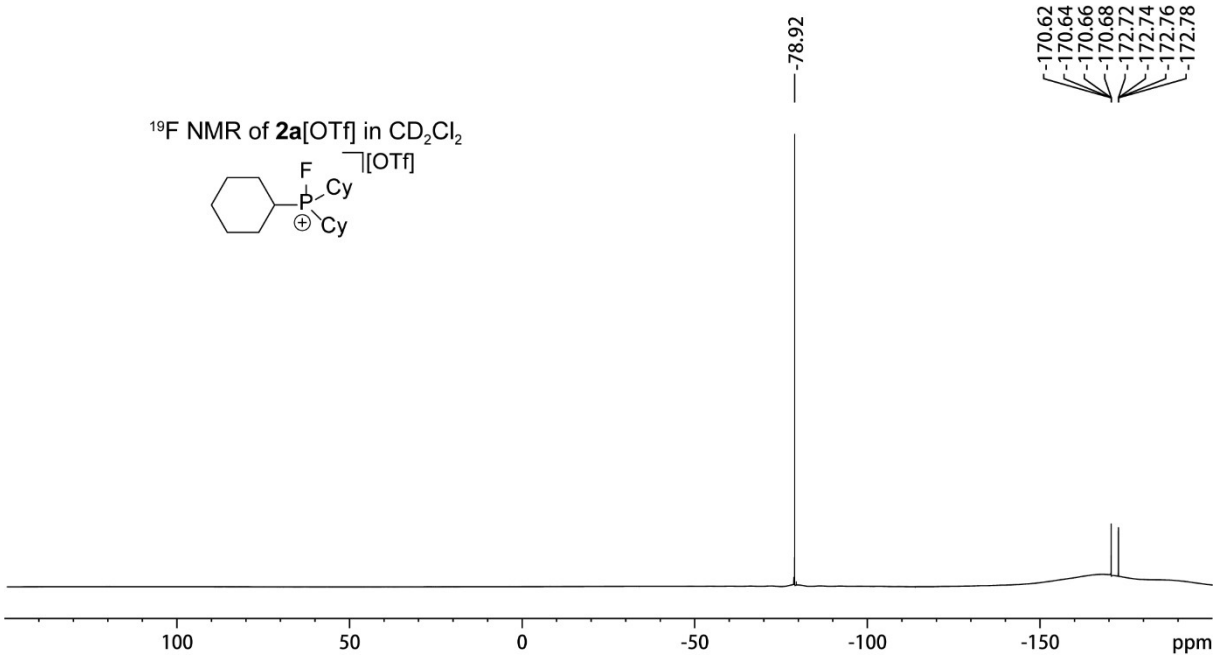


Figure S8.15. ^{19}F NMR spectrum of **2a**[OTf] (471MHz, CD_2Cl_2, 300 K), details are listed in section S4.3.

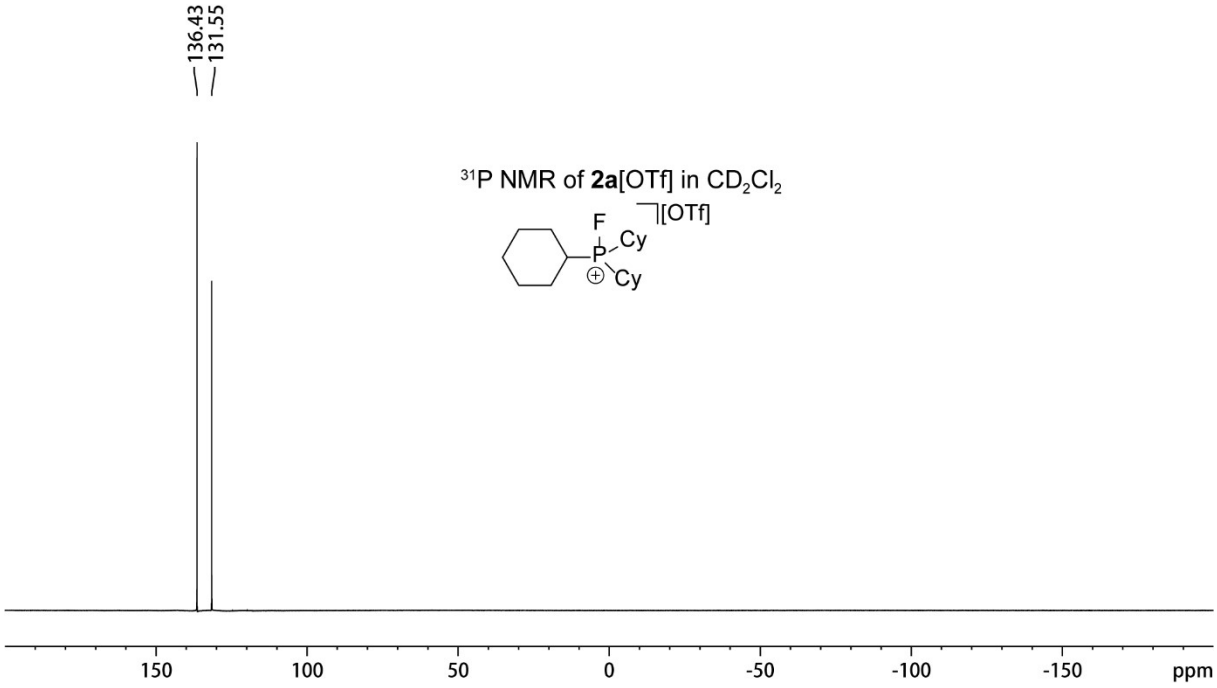


Figure S8.16. $^{31}P\{H\}$ NMR spectrum of **2a**[OTf] (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.3.

S8.5 NMR spectra of **2b**[OTf]

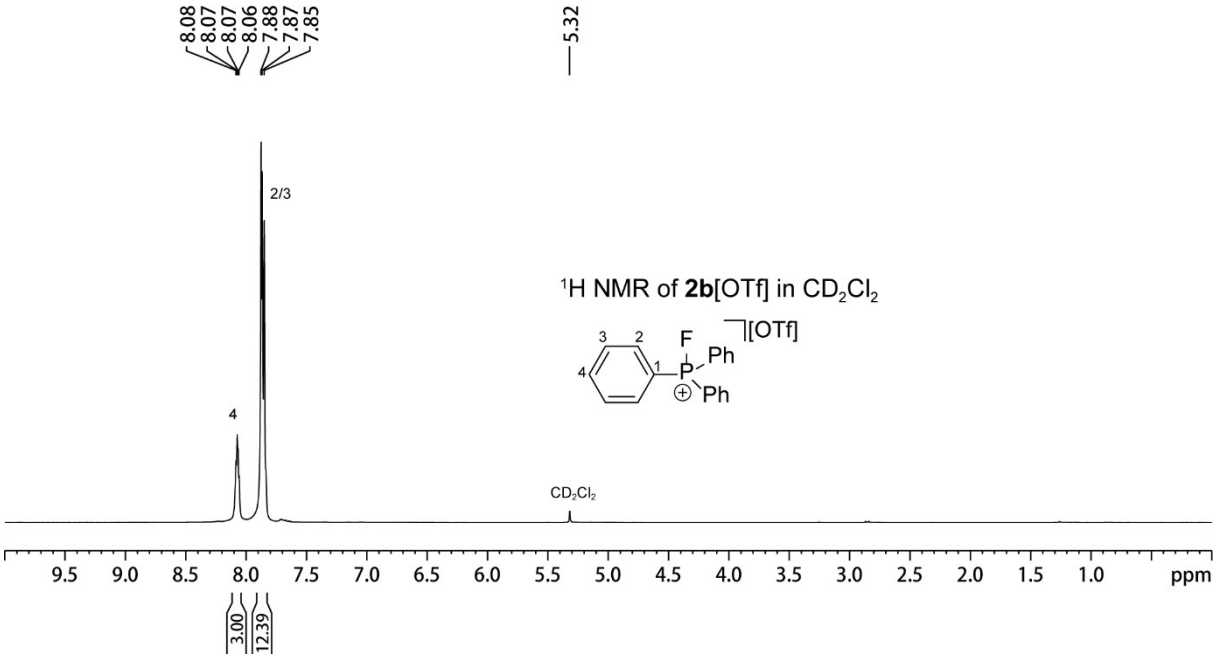


Figure S8.17. ^{1}H NMR spectrum of **2b**[OTf] (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.4.

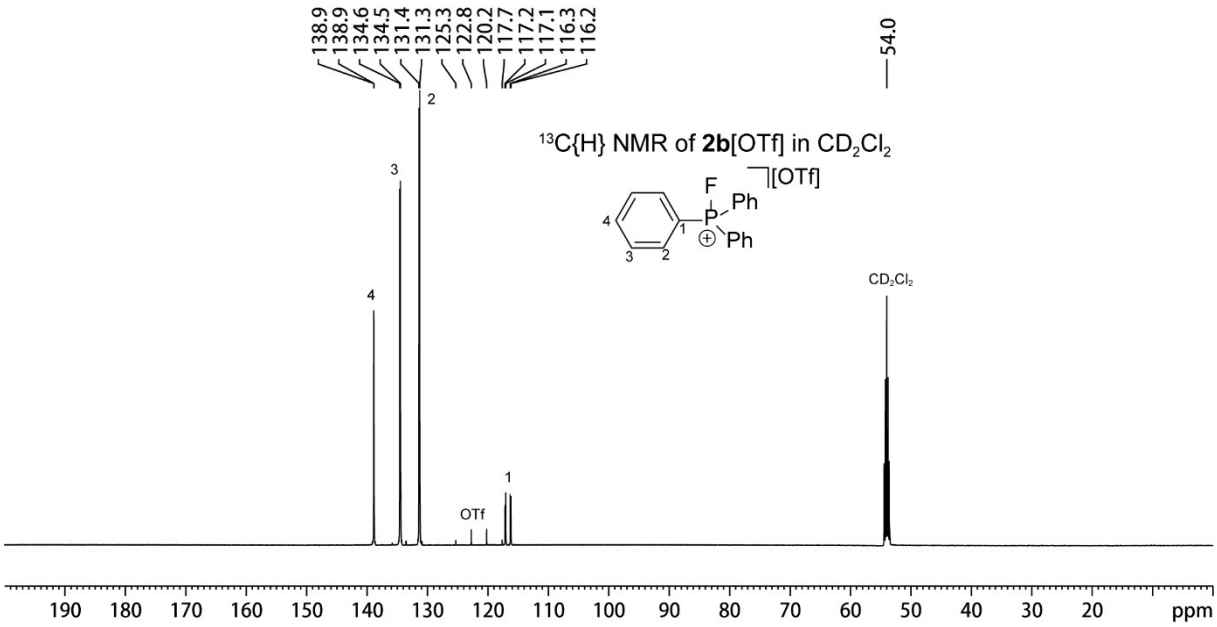


Figure S8.18. ^{13}C{H} NMR spectrum of **2b**[OTf] (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.4.

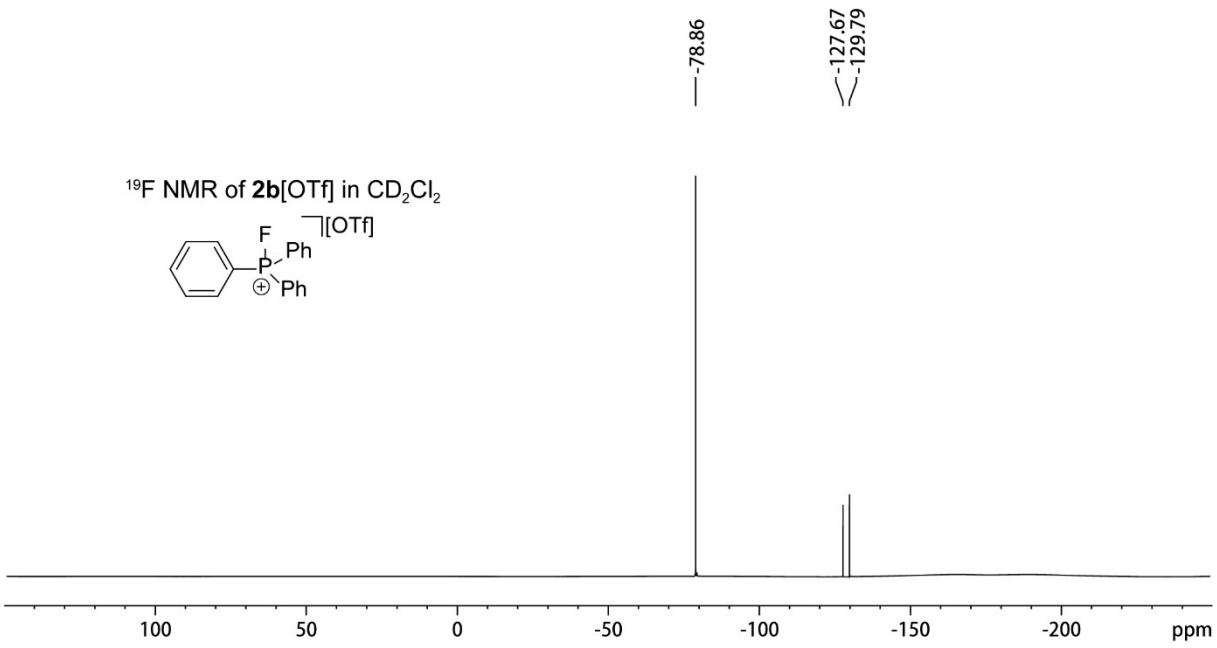


Figure S8.19. ^{19}F NMR spectrum of **2b**[OTf] (471MHz, CD_2Cl_2, 300 K), details are listed in section S4.4.

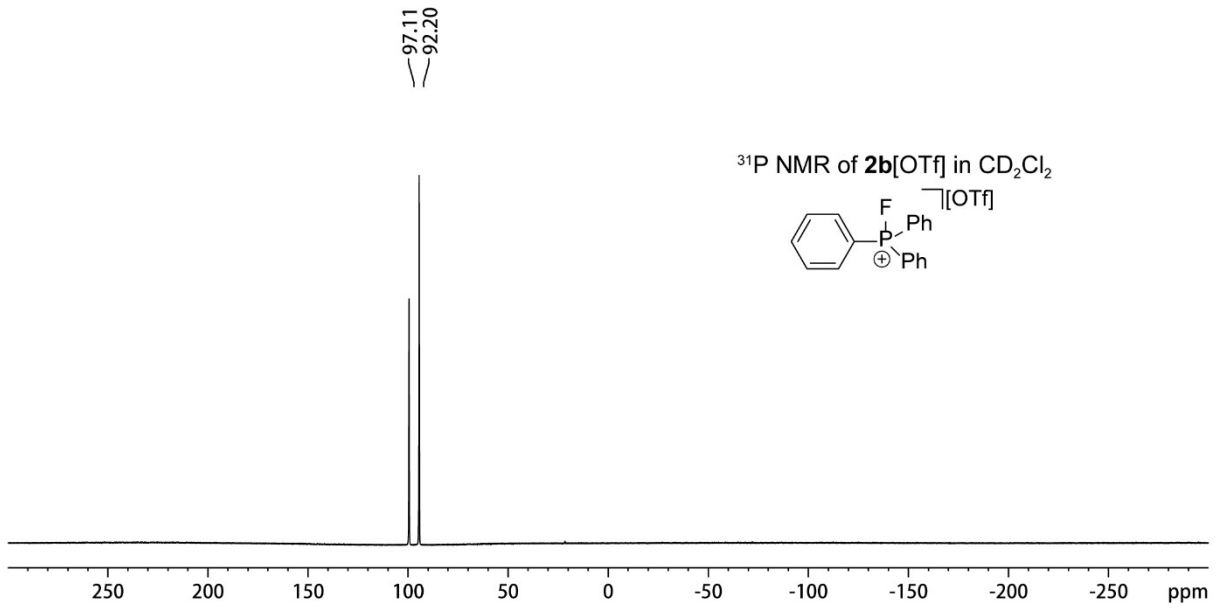


Figure S8.20. $^{31}P\{H\}$ NMR spectrum of **2b**[OTf] (202MHz,CD_2Cl_2, 300 K), details are listed in section S4.4.

S8.6 NMR spectra of **2c**[OTf]

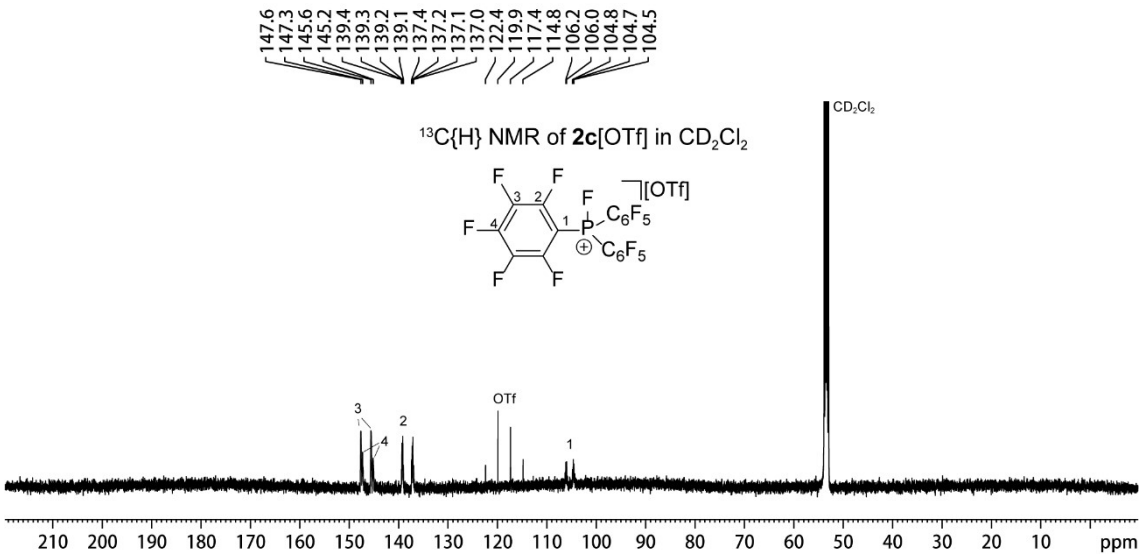


Figure S8.21. $^{13}C\{H\}$ NMR spectrum of **2c**[OTf] (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.1.

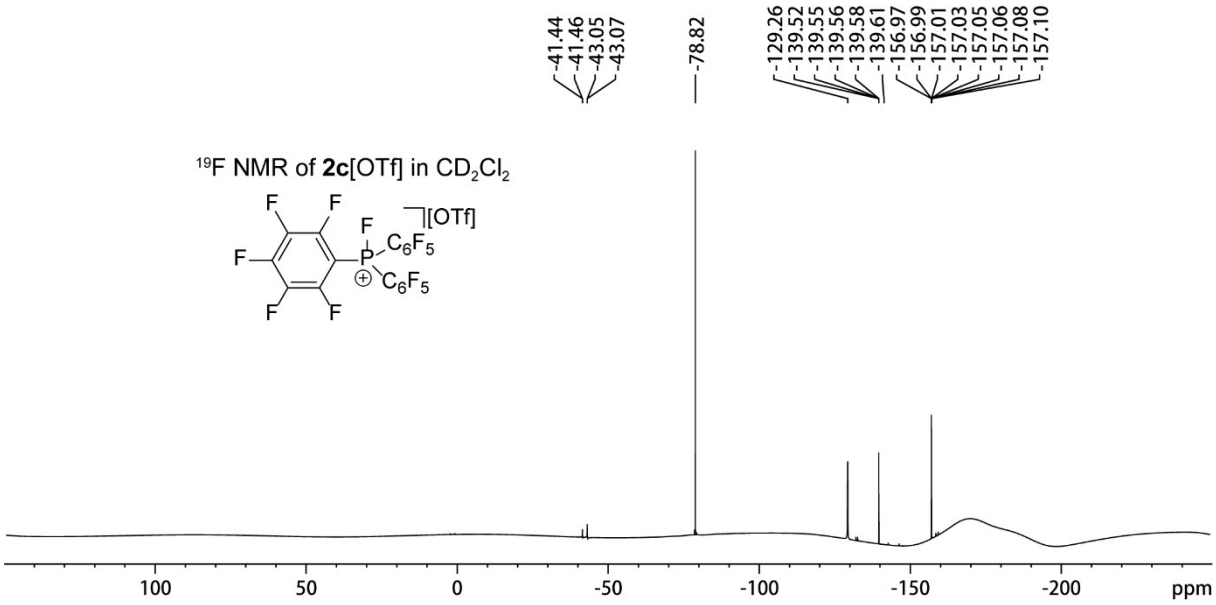


Figure S8.22. ^{19}F NMR spectrum of **2c**[OTf] (471MHz,CD_2Cl_2, 300 K), details are listed in section S4.1.

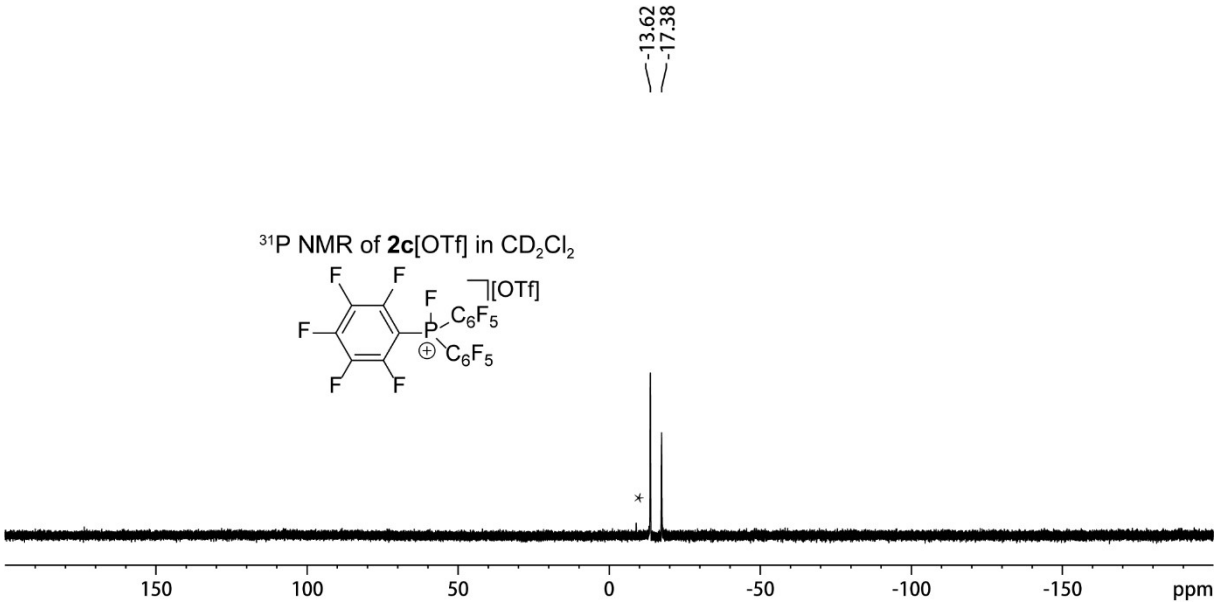


Figure S8.23. $^{31}P\{H\}$ NMR spectrum of **2c**[OTf] (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.1; Asterisks indicate small amounts of unidentified side products.

S8.7 NMR spectra of **2c**[H(OTf)2]

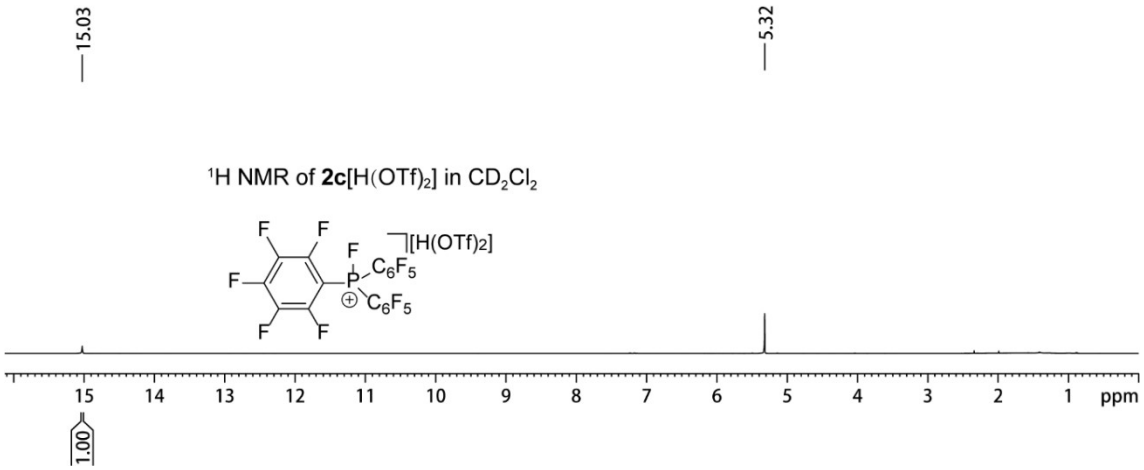


Figure S8.24. ^{1}H NMR spectrum of **2c**[HOTf2] (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.2;

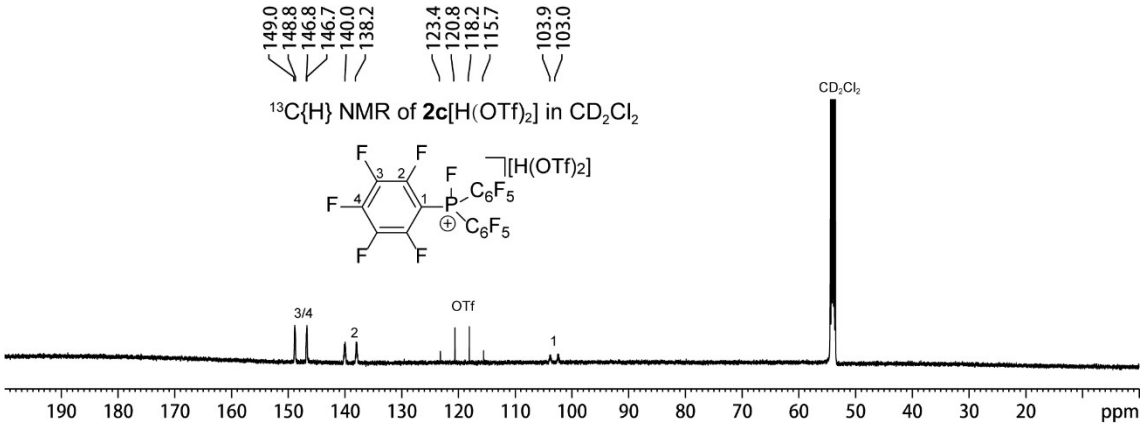


Figure S8.25. $^{13}C\{H\}$ NMR spectrum of **2c**[HOTf2] (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.2;

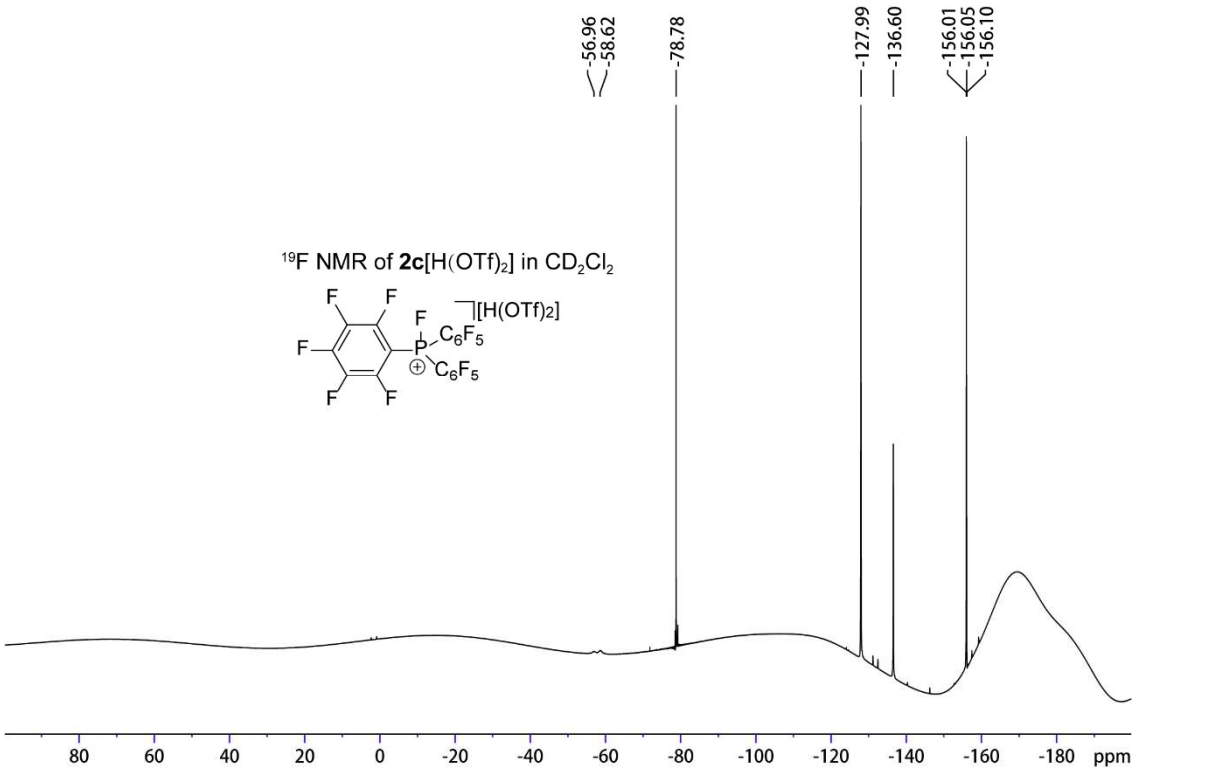


Figure S8.26. ^{19}F NMR spectrum of **2c**[$HOTf_2$] (471MHz, CD_2Cl_2, 300 K), details are listed in section S4.2;

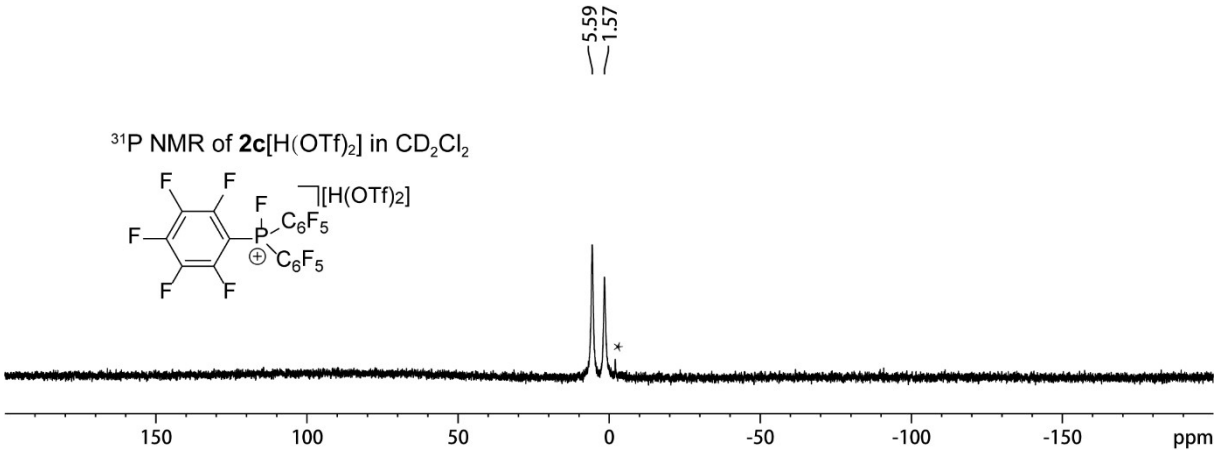


Figure S8.27. $^{31}P\{H\}$ NMR spectrum of **2c**[$HOTf_2$] (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.2; Asterisks indicate small amounts of unidentified side products.

S8.8 NMR spectra of **2d**[OTf]

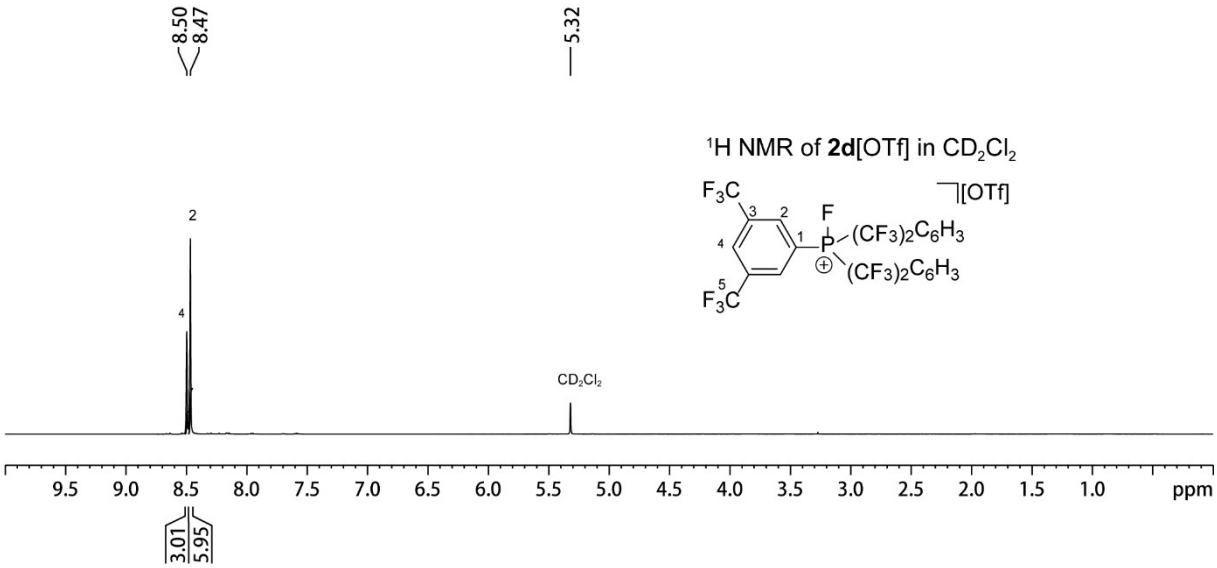


Figure S8.28. ^{1}H NMR spectrum of **2d**[OTf] (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.5.

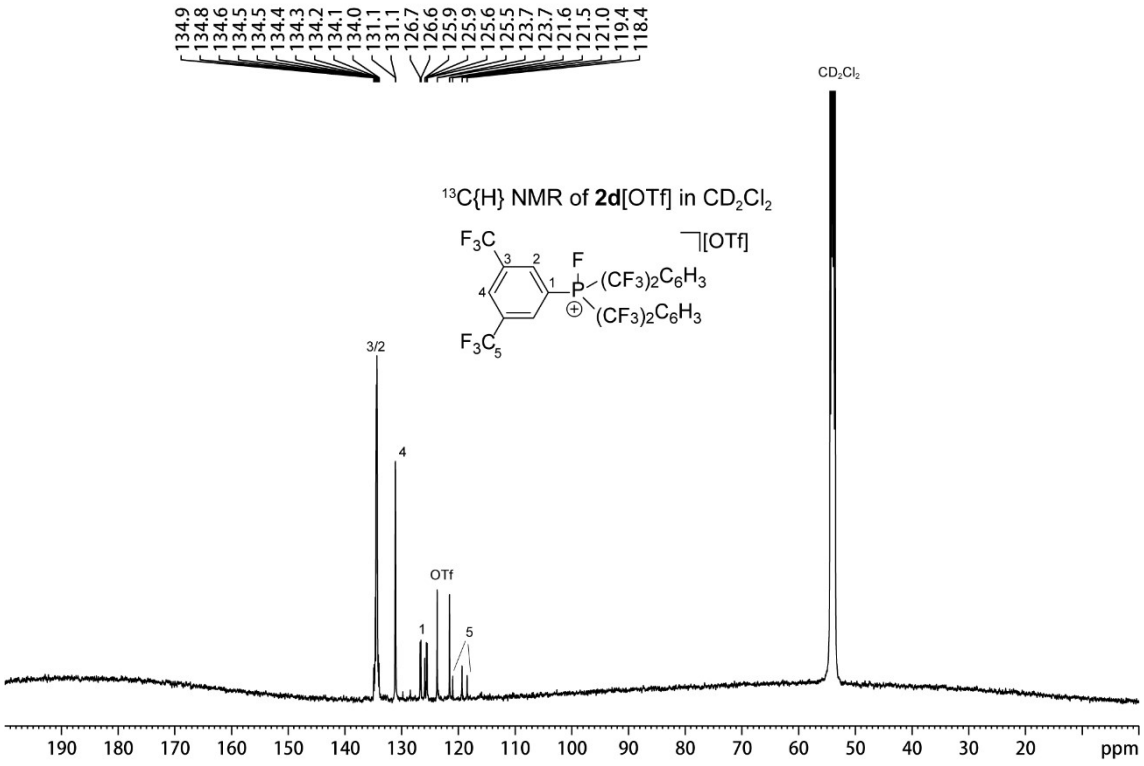


Figure S8.29. ^{13}C{H} NMR spectrum of **2d**[OTf] (126Mhz, CD_2Cl_2, 300 K), details are listed in section S4.5.

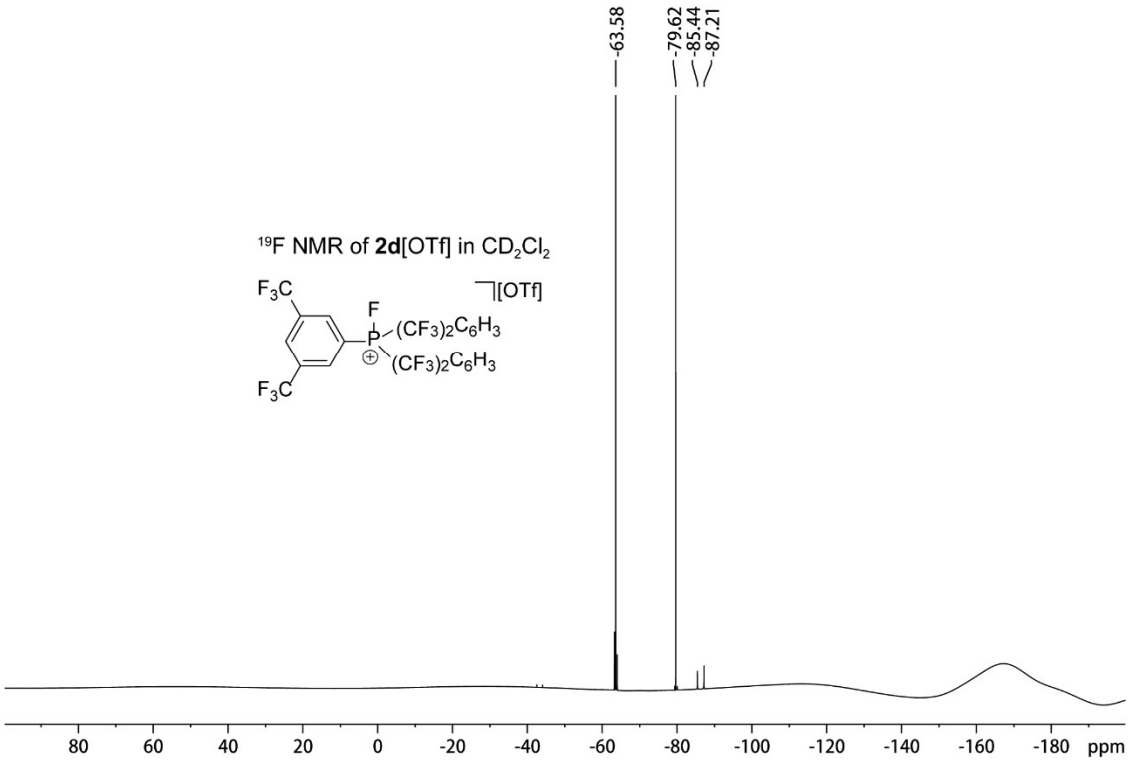


Figure S8.30. ^{19}F NMR spectrum of **2d**[OTf] (471MHz, CD_2Cl_2, 300 K), details are listed in section S4.5.

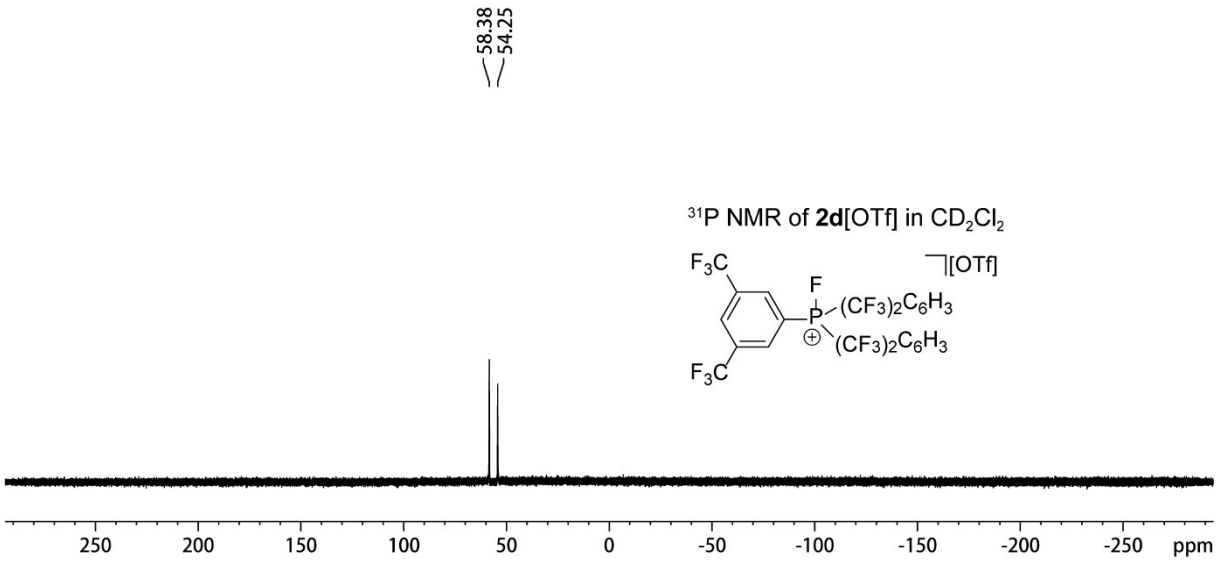


Figure S8.31. $^{31}P\{H\}$ NMR spectrum of **2d**[OTf] (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.5.

S8.9 NMR spectra of **4a**[OTf]

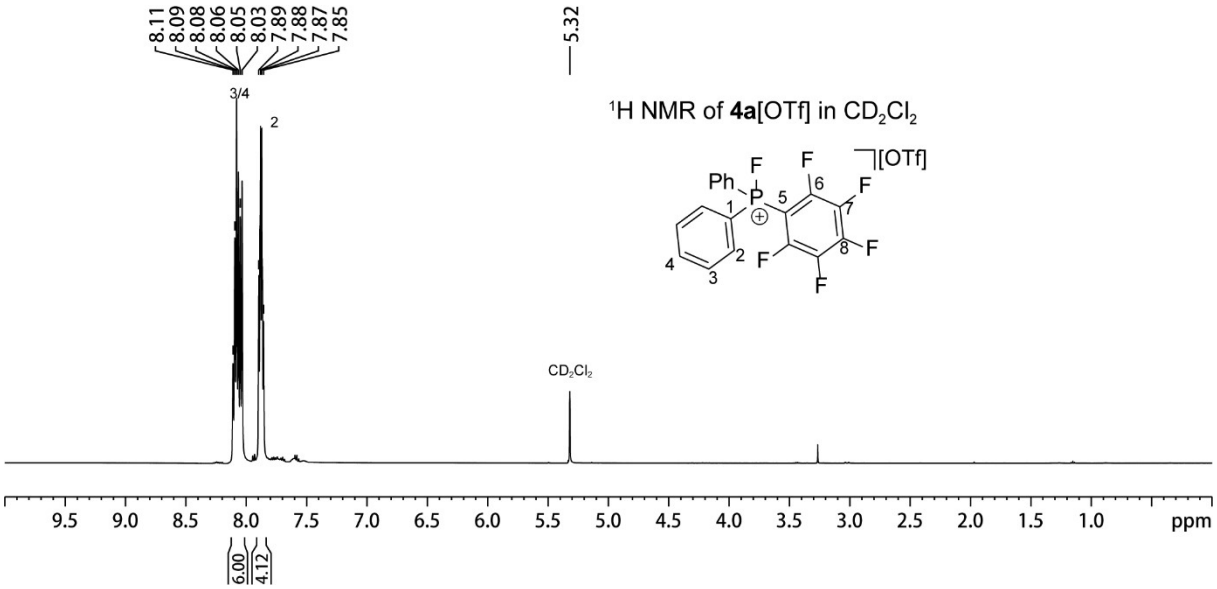


Figure S8.32. ^{1}H NMR spectrum of **4a**[OTf] (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.6.

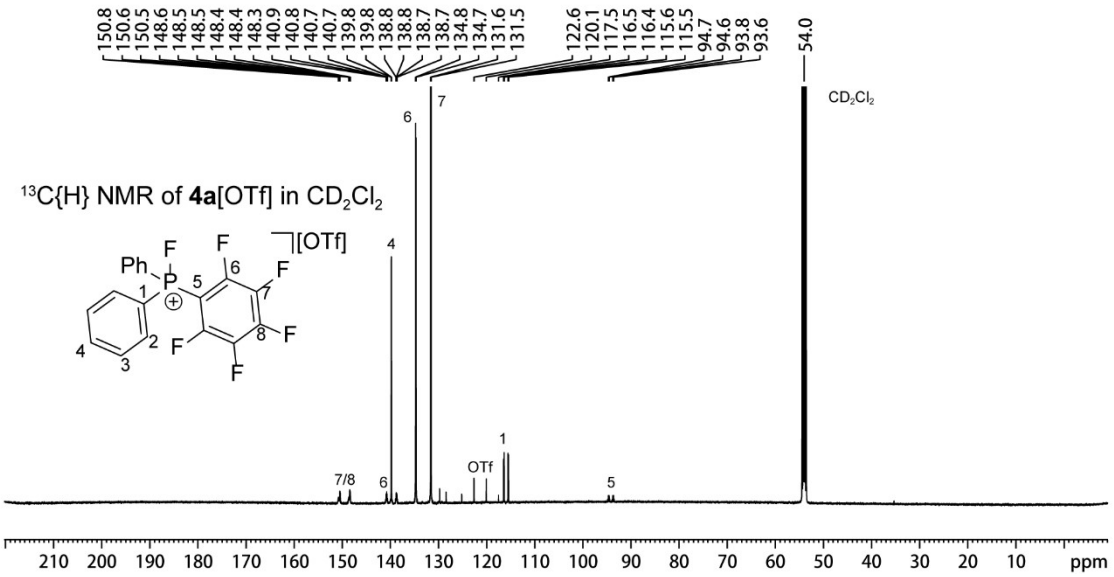


Figure S8.33. ^{13}C{H} NMR spectrum of **4a**[OTf] (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.6.

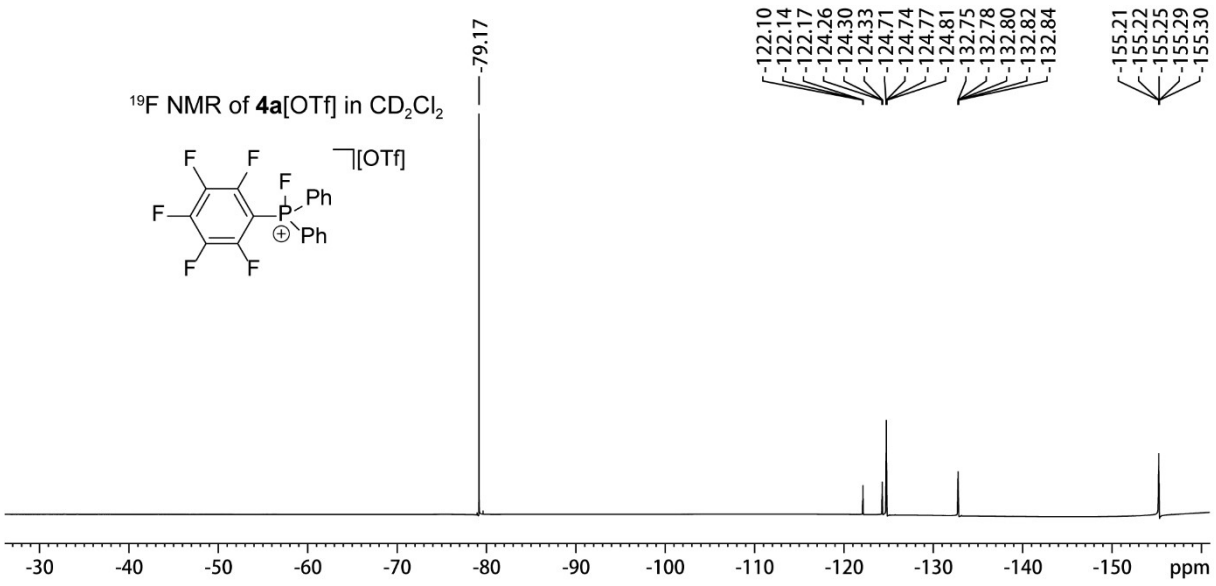


Figure S8.34. ^{19}F NMR spectrum of **4a**[OTf] (471MHz, CD_2Cl_2, 300 K), details are listed in section S4.6.

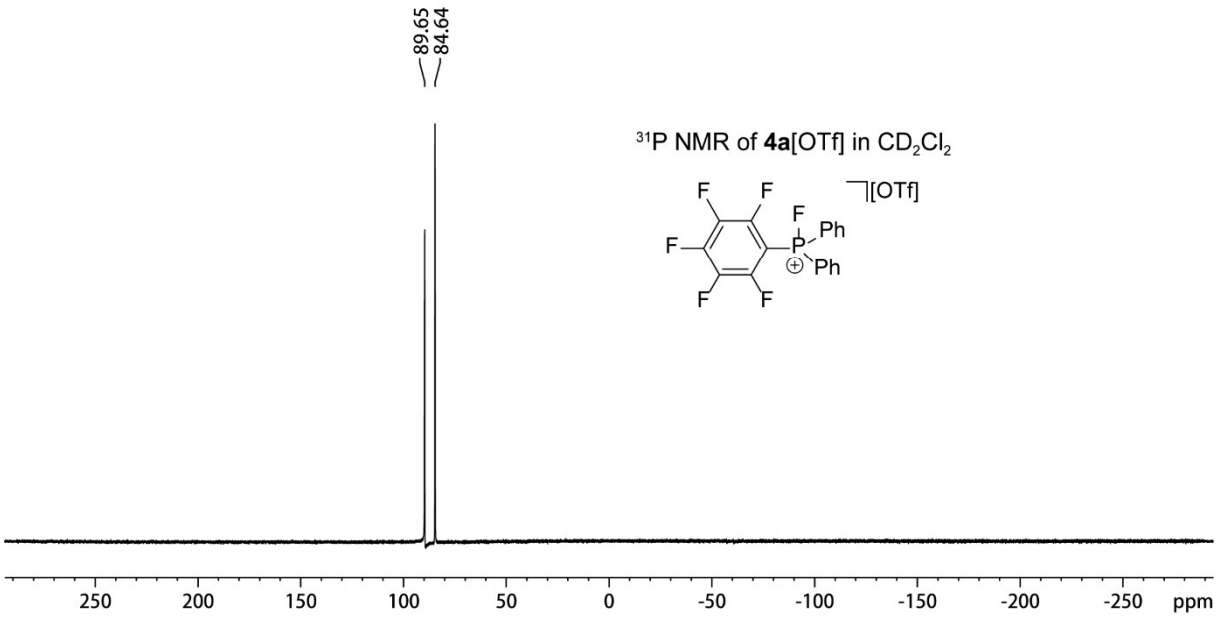


Figure S8.35. $^{31}P\{H\}$ NMR spectrum of **4a**[OTf] (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.6.

S8.10 NMR spectra of **4b**[OTf]

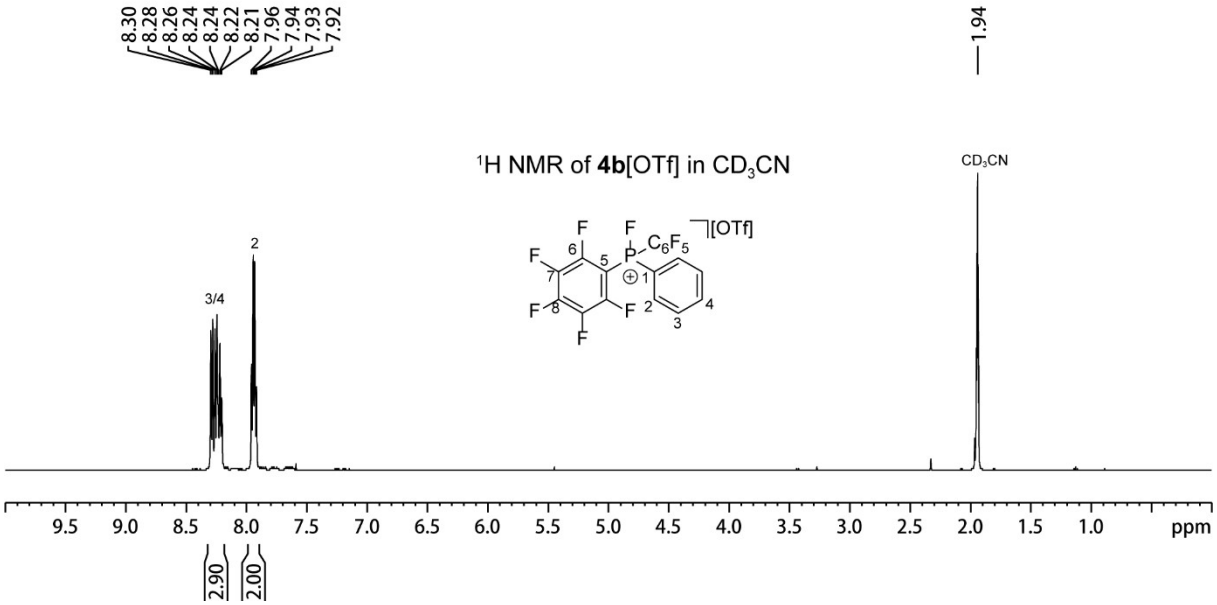


Figure S8.36. ^{1}H NMR spectrum of **4b**[OTf] (500MHz, CD_3CN, 300 K), details are listed in section S4.7.

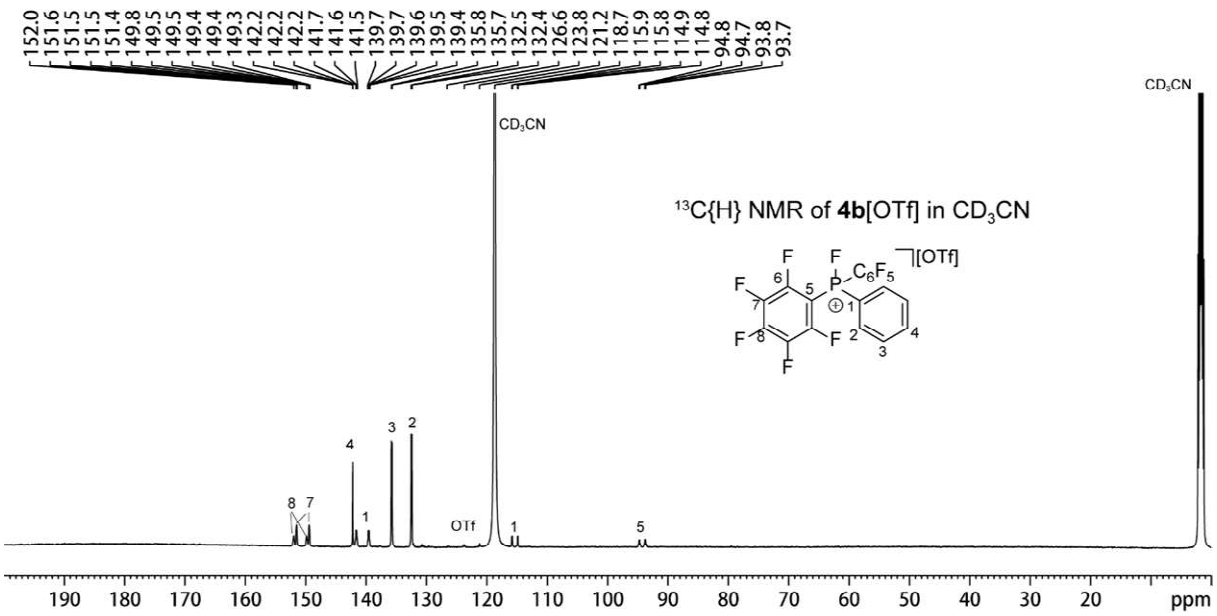


Figure S8.37. ^{13}C{H} NMR spectrum of **4b**[OTf] (126MHz, CD_3CN, 300 K), details are listed in section S4.7.

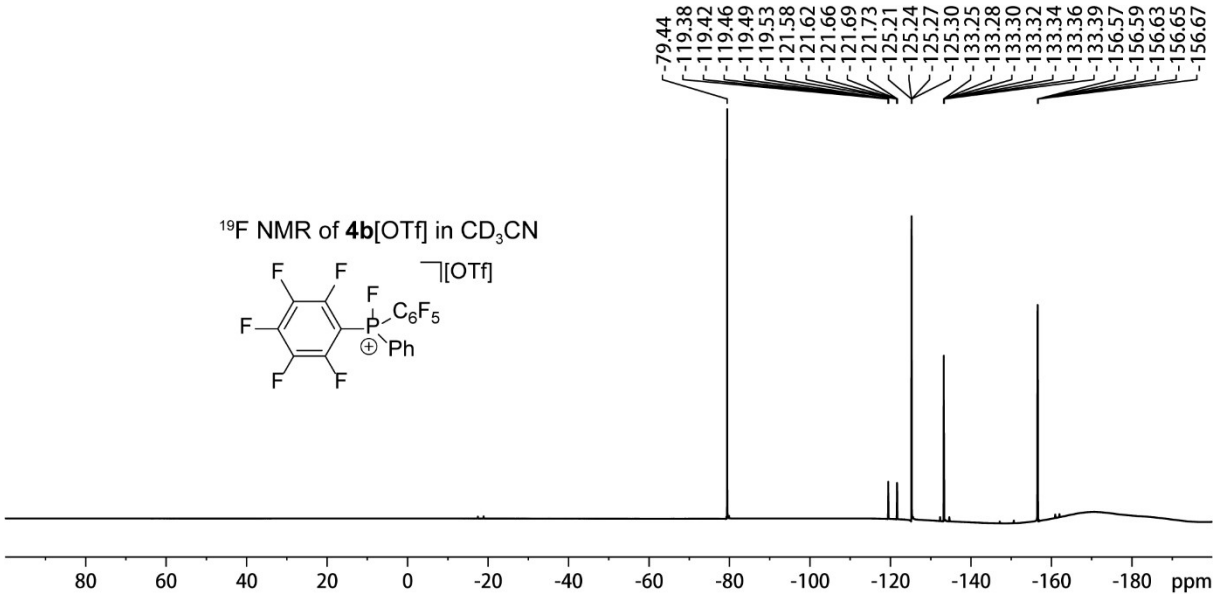


Figure S8.38. ^{19}F NMR spectrum of **4b**[OTf] (471MHz, CD_3CN, 300 K), details are listed in section S4.7.

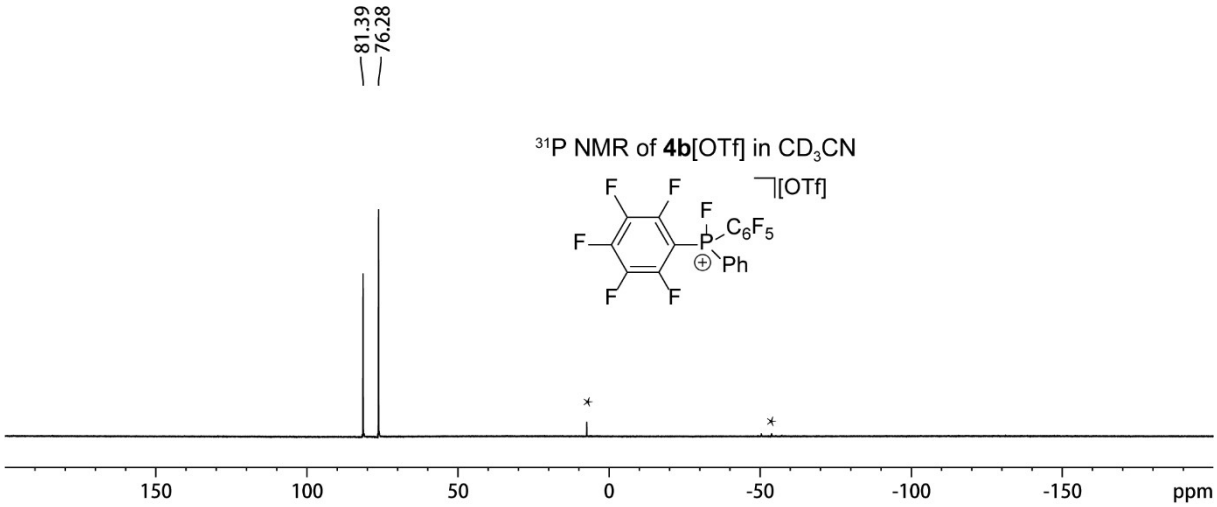


Figure S8.39. $^{31}P\{H\}$ NMR spectrum of **4b**[OTf] (202MHz, CD_3CN, 300 K), details are listed in section S4.7; Asterisks indicate small amounts of unidentified side products.

S8.11 NMR spectra of $\mathbf{6^{Me}a}[OTf]_2$

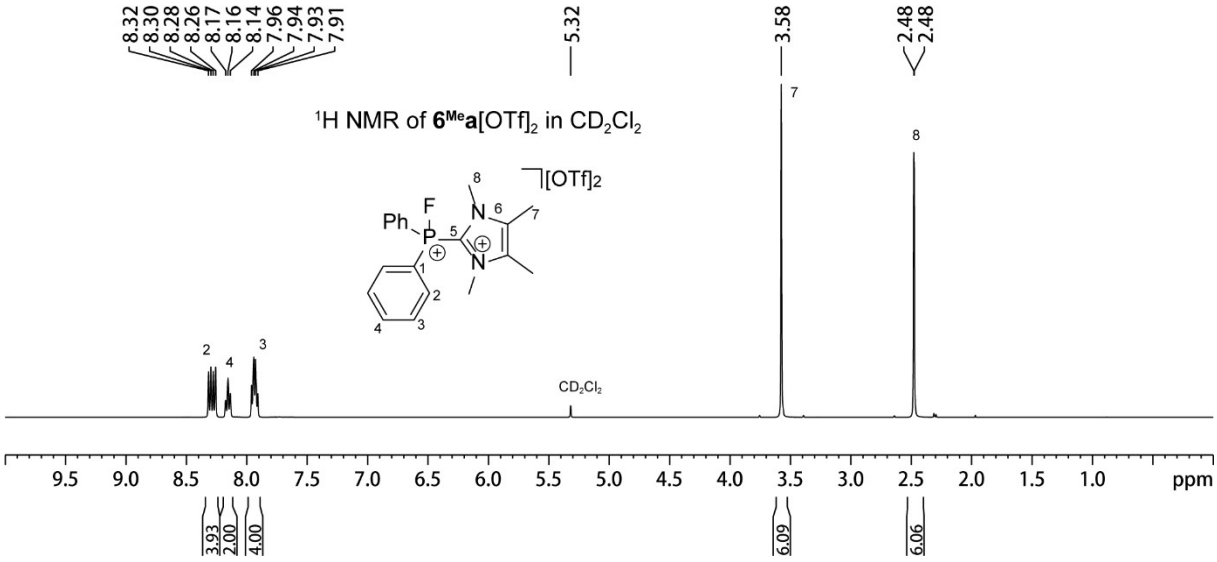


Figure S8.40. ^{1}H NMR spectrum of $\mathbf{6^{Me}a}[OTf]_2$ (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.8.

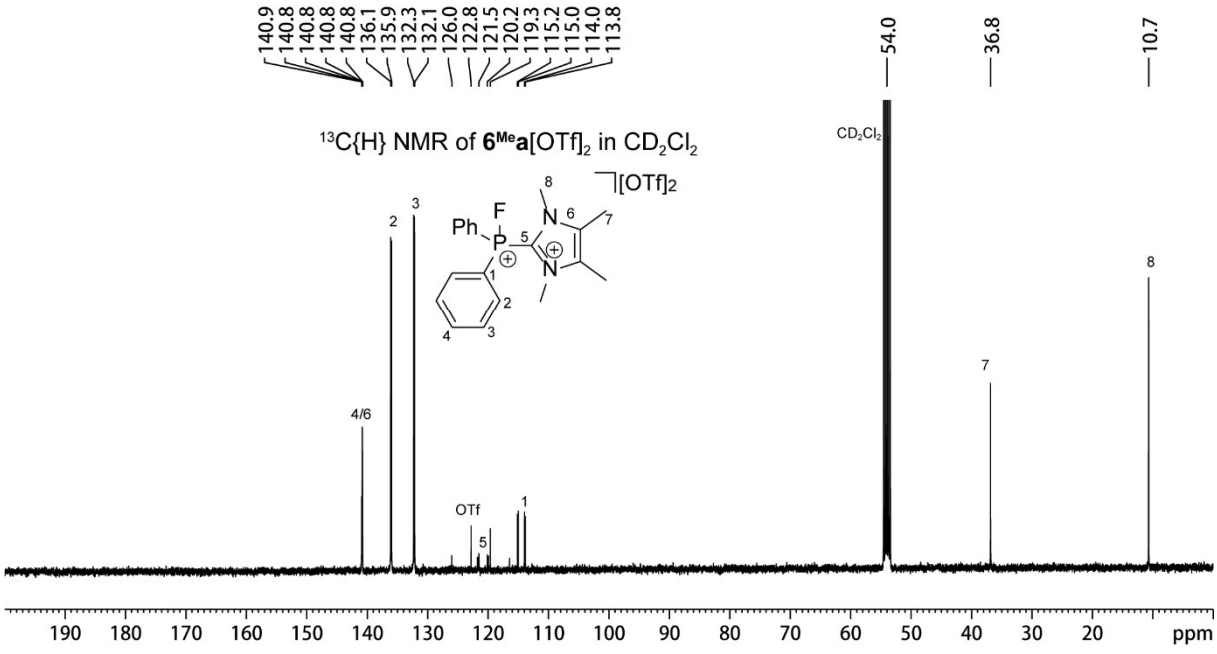


Figure S8.41. ^{13}C{H} NMR spectrum of $\mathbf{6^{Me}a}[OTf]_2$ (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.8.

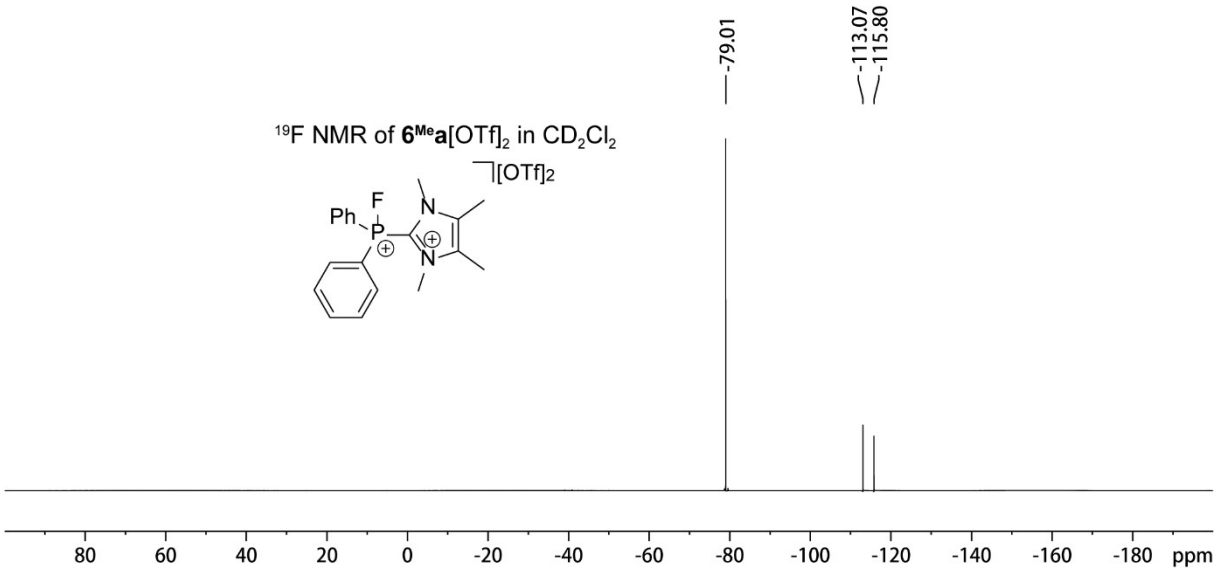


Figure S8.42. ^{19}F NMR spectrum of **6^{Me}a**[OTf]$_2$ (471MHz, CD_2Cl_2, 300 K), details are listed in section S4.8.

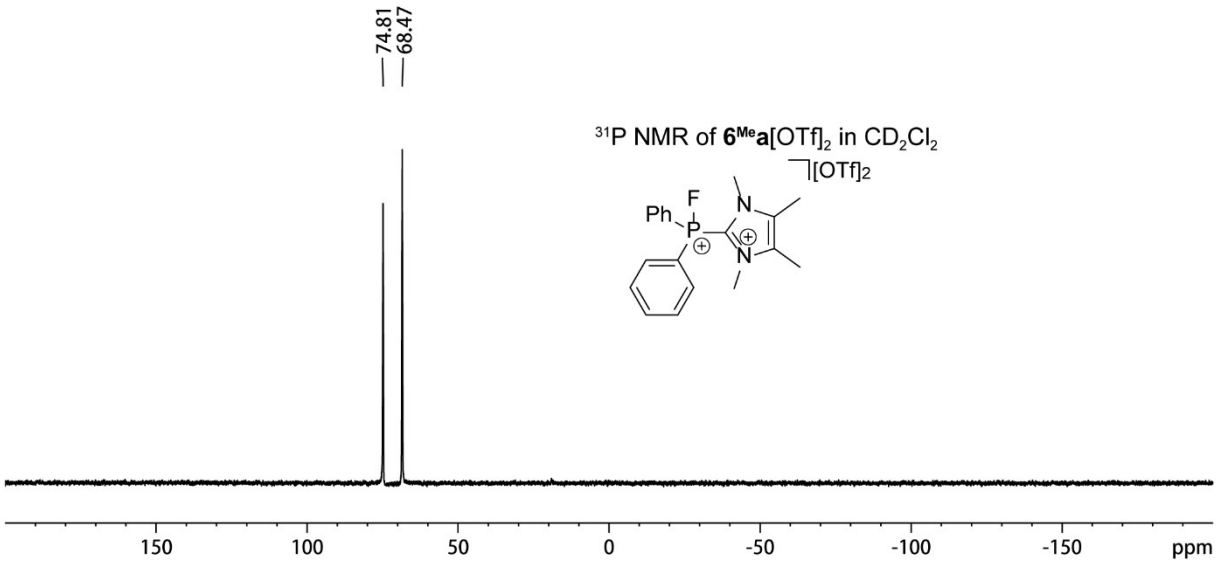


Figure S8.43. $^{31}P\{H\}$ NMR spectrum of **6^{Me}a**[OTf]$_2$ (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.8.

S8.12 NMR spectra of $\mathbf{6^{iPr}a}[OTf]_2$

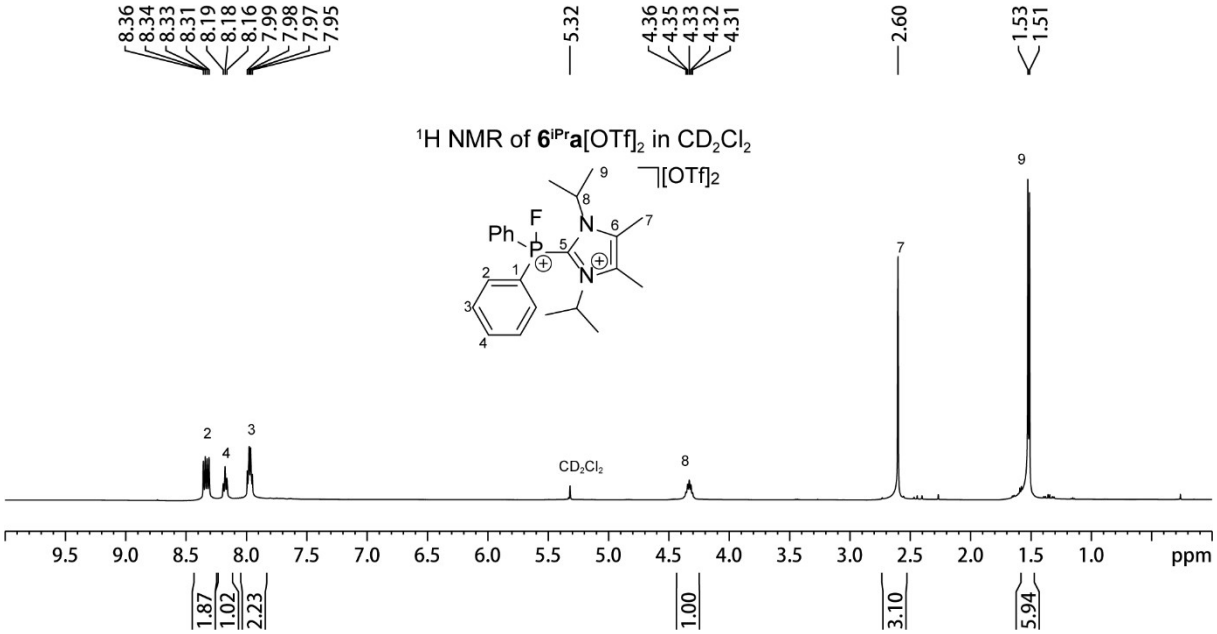


Figure S8.44. ^{1}H NMR spectrum of $\mathbf{6^{iPr}a}[OTf]_2$ (500MHz, CD_2Cl_2, 300 K), details are listed in section S4.9.

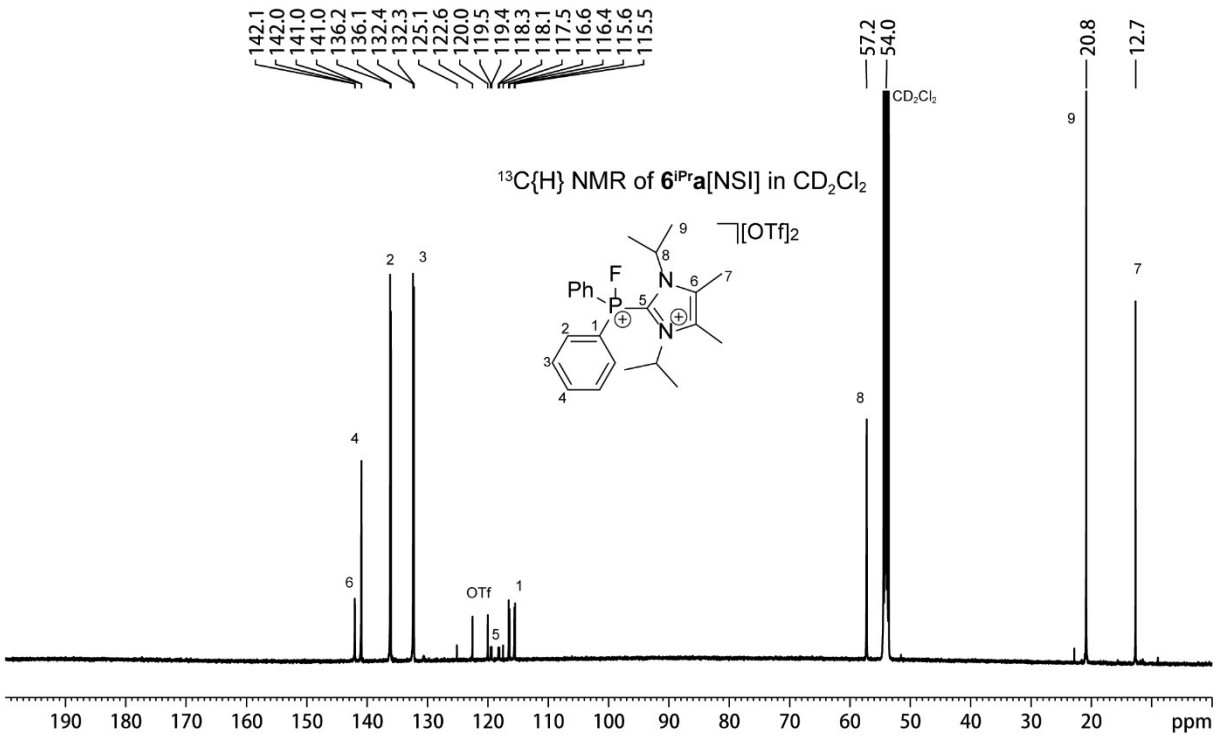


Figure S8.45. $^{13}C\{H\}$ NMR spectrum of $\mathbf{6^{iPr}a}[OTf]_2$ (126MHz, CD_2Cl_2, 300 K), details are listed in section S4.9.

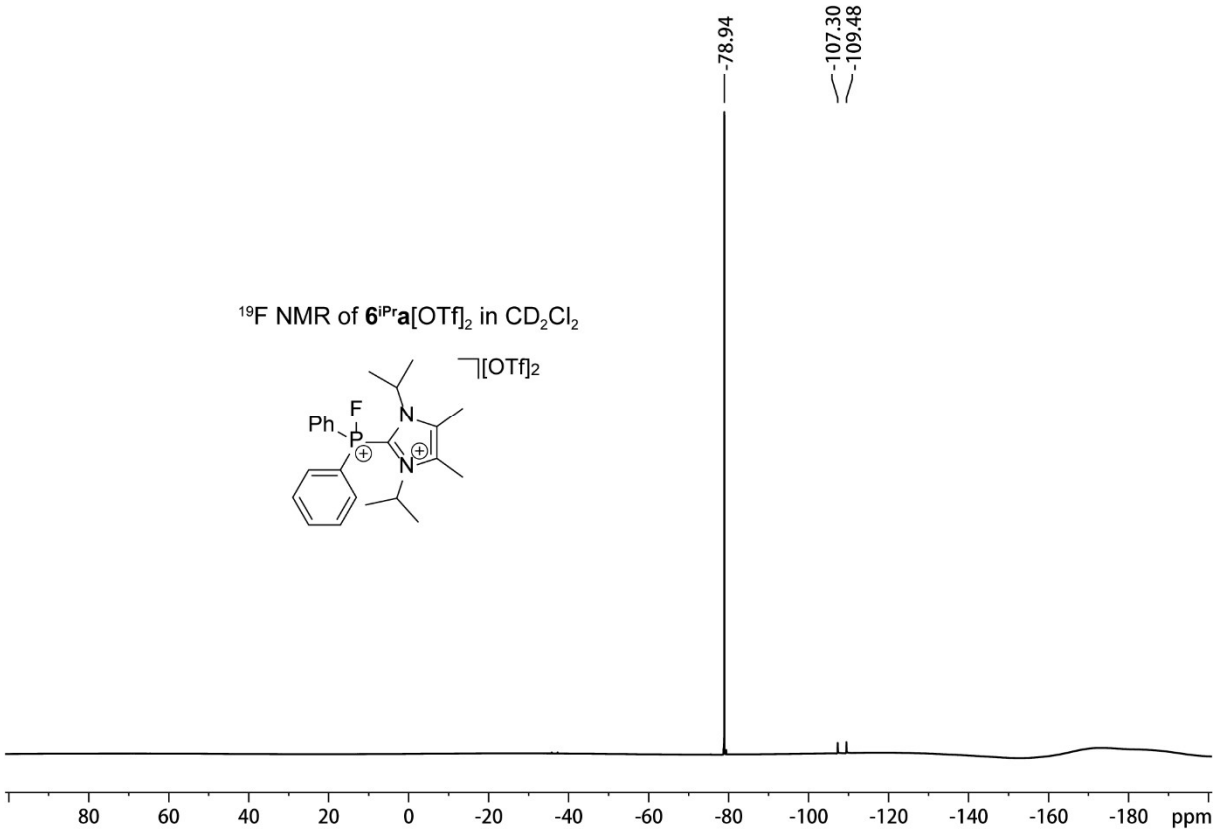


Figure S8.46. ^{19}F NMR spectrum of **6^{iPr}a**[OTf]$_2$ (471 MHz, CD_2Cl_2, 300 K), details are listed in section S4.9.

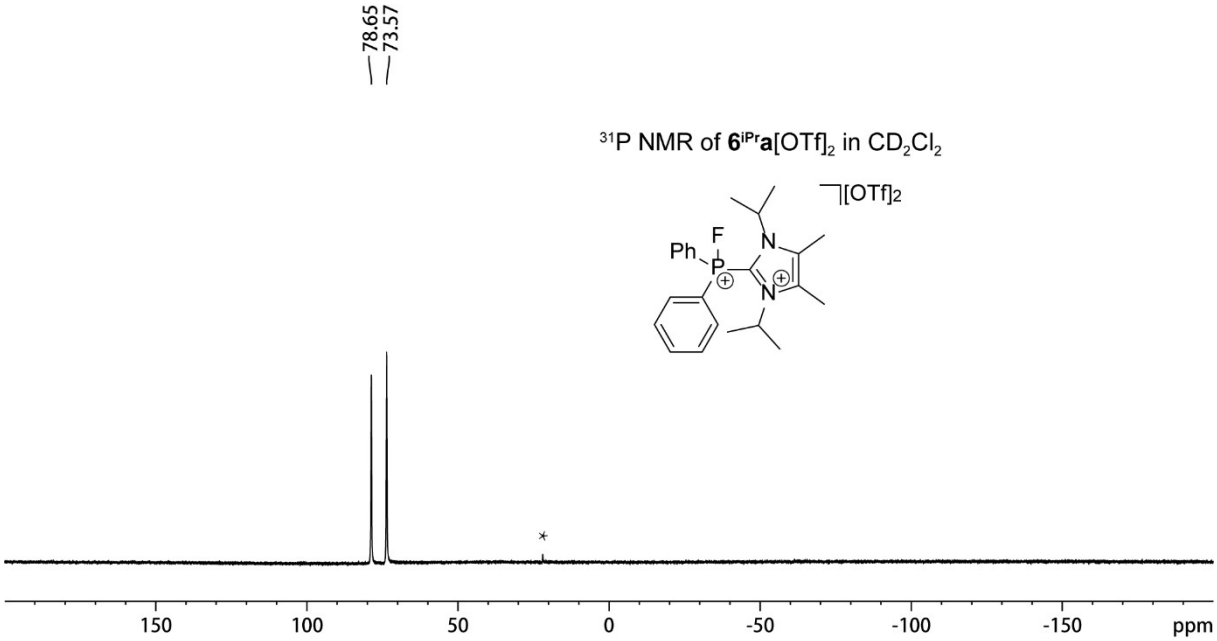


Figure S8.47. $^{31}P\{H\}$ NMR spectrum of **6^{iPr}a**[OTf]$_2$ (202MHz, CD_2Cl_2, 300 K), details are listed in section S4.9. Asterisks indicate small amounts of unidentified side products.

S8.13 NMR spectra of $\mathbf{6^{Me}b}[OTf]_2$

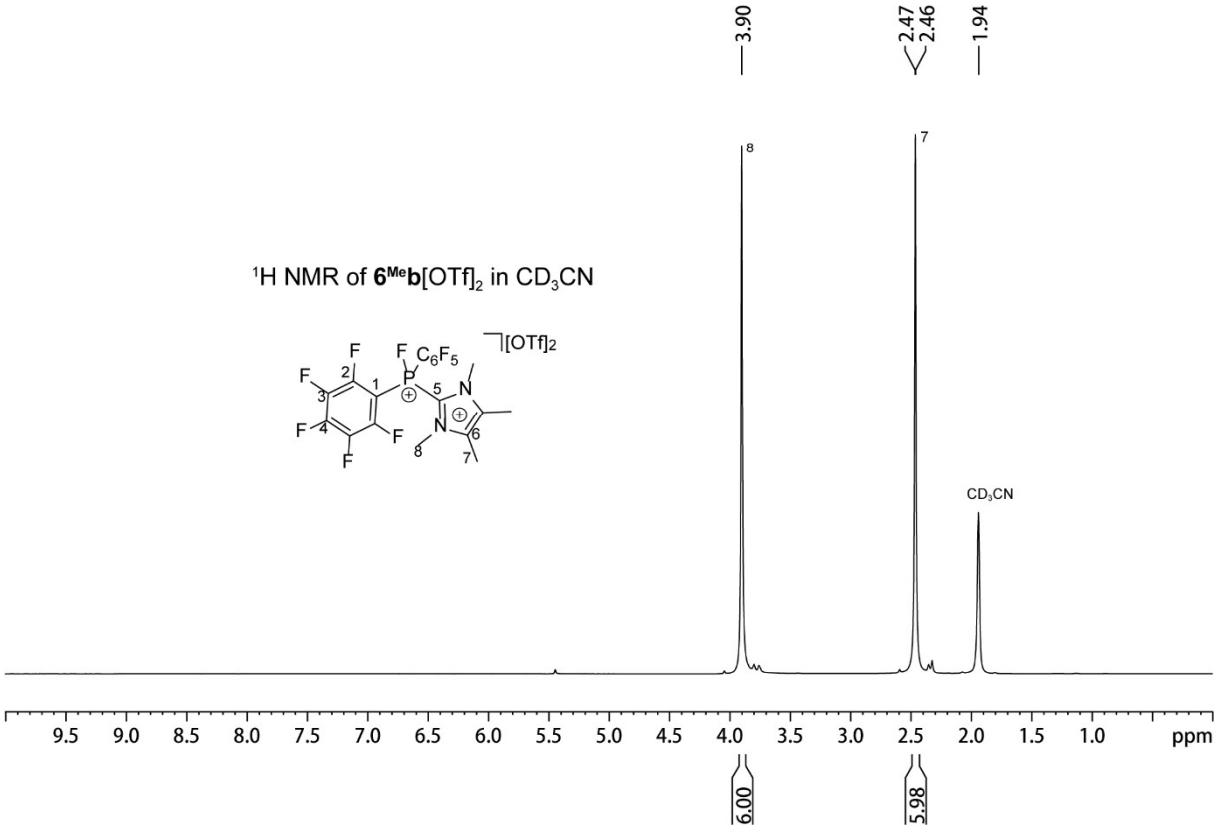


Figure S8.48. ^{1}H NMR spectrum of $\mathbf{6^{Me}b}[OTf]_2$ (500MHz, CD_3CN, 300 K), details are listed in section S4.10.

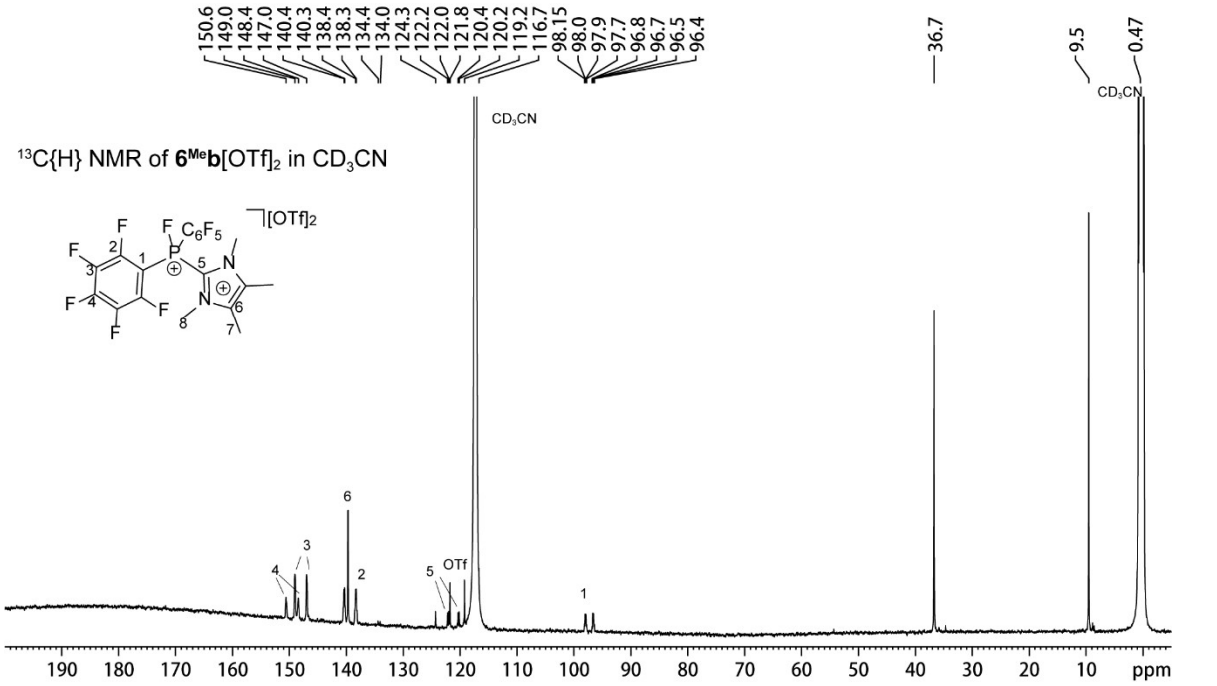


Figure S8.49. ^{13}C{H} NMR spectrum of $\mathbf{6^{Me}b}[OTf]_2$ (126MHz, CD_3CN, 300 K), details are listed in section S4.10.

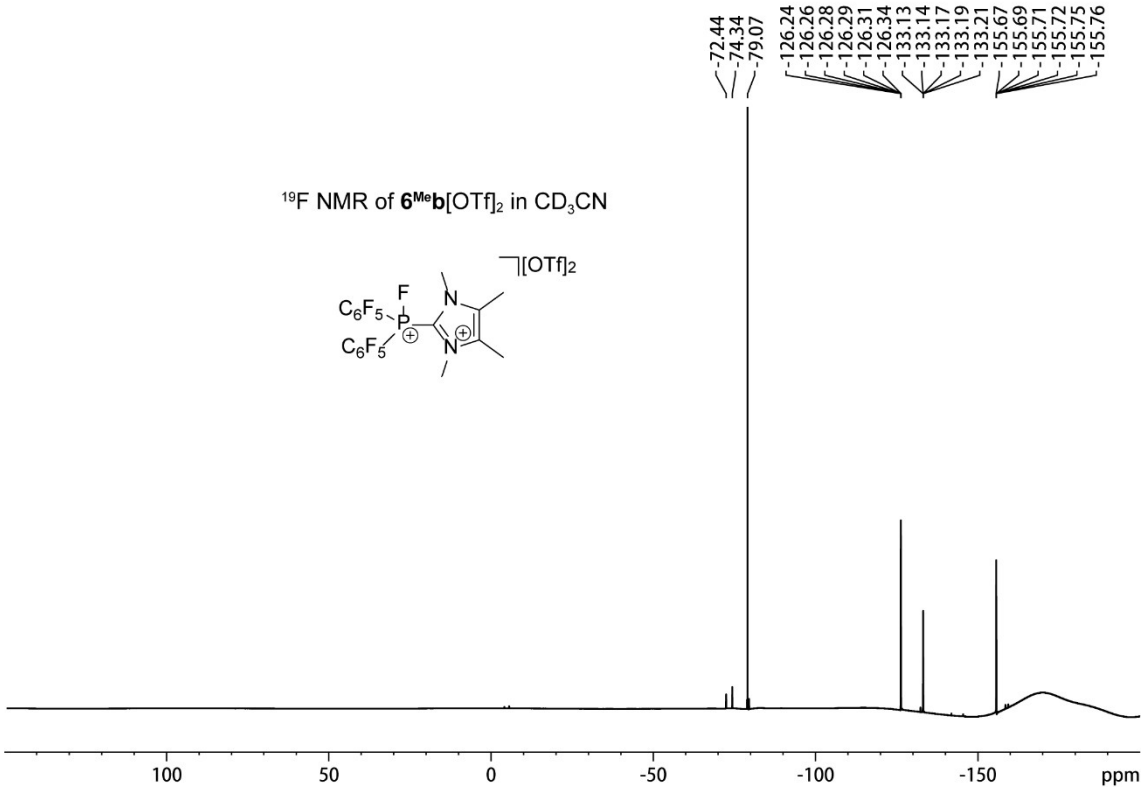


Figure S8.50. ^{19}F NMR spectrum of **6^{Me}b**$[OTf]_2$ (471 MHz, CD_3CN, 300 K), details are listed in section S4.10.

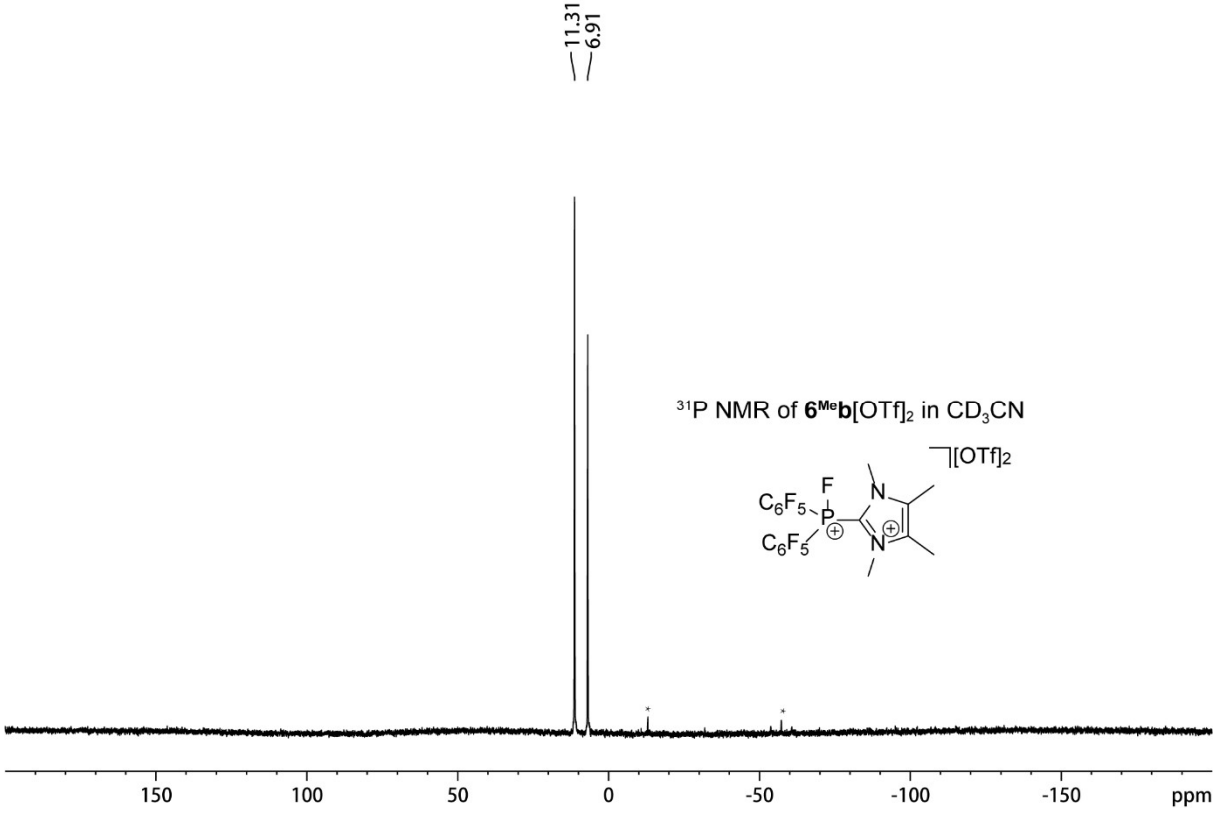


Figure S8.51. $^{31}P\{H\}$ NMR spectrum of **6^{Me}b**$[OTf]_2$ (202MHz, CD_3CN, 300 K), details are listed in section S4.10. Asterisks indicate small amounts of unidentified side products.

S8.14 NMR spectra of $\mathbf{6^{iPr}b}[OTf]_2$

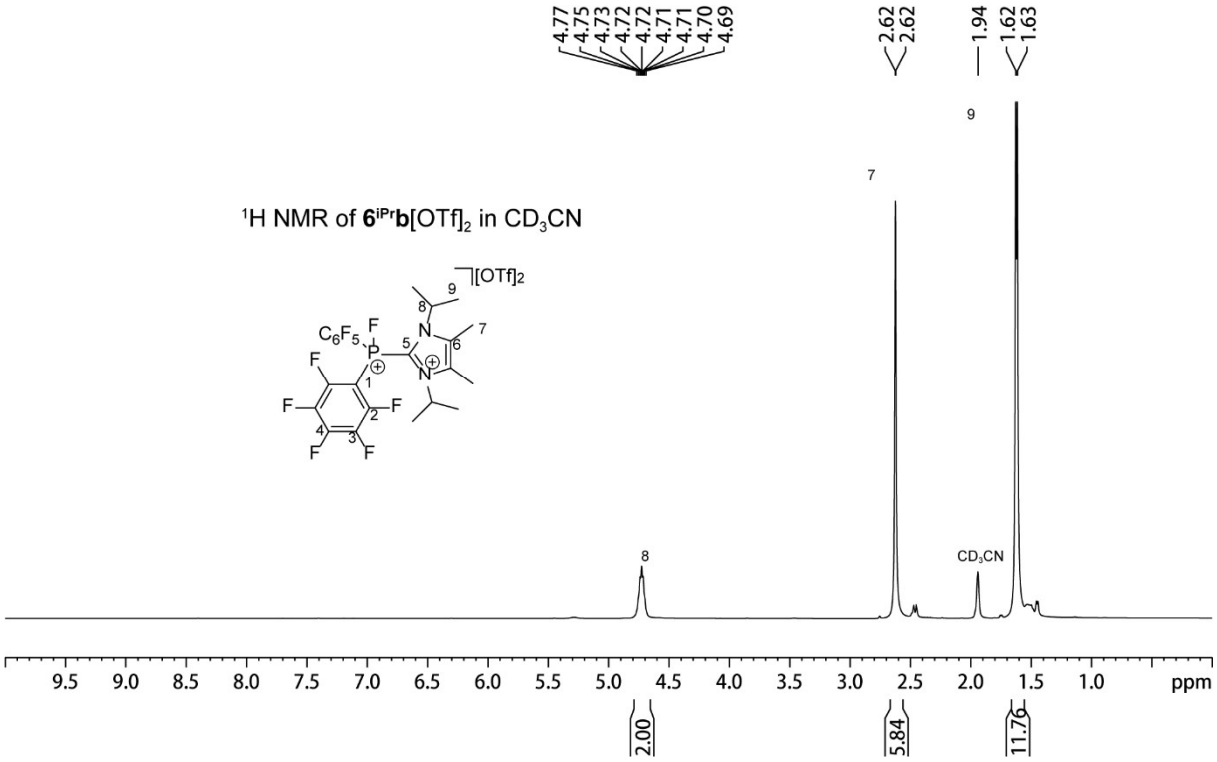


Figure S8.52. ^{1}H NMR spectrum of $\mathbf{6^{iPr}b}[OTf]_2$ (500MHz, CD_3CN, 300 K), details are listed in section S4.11.

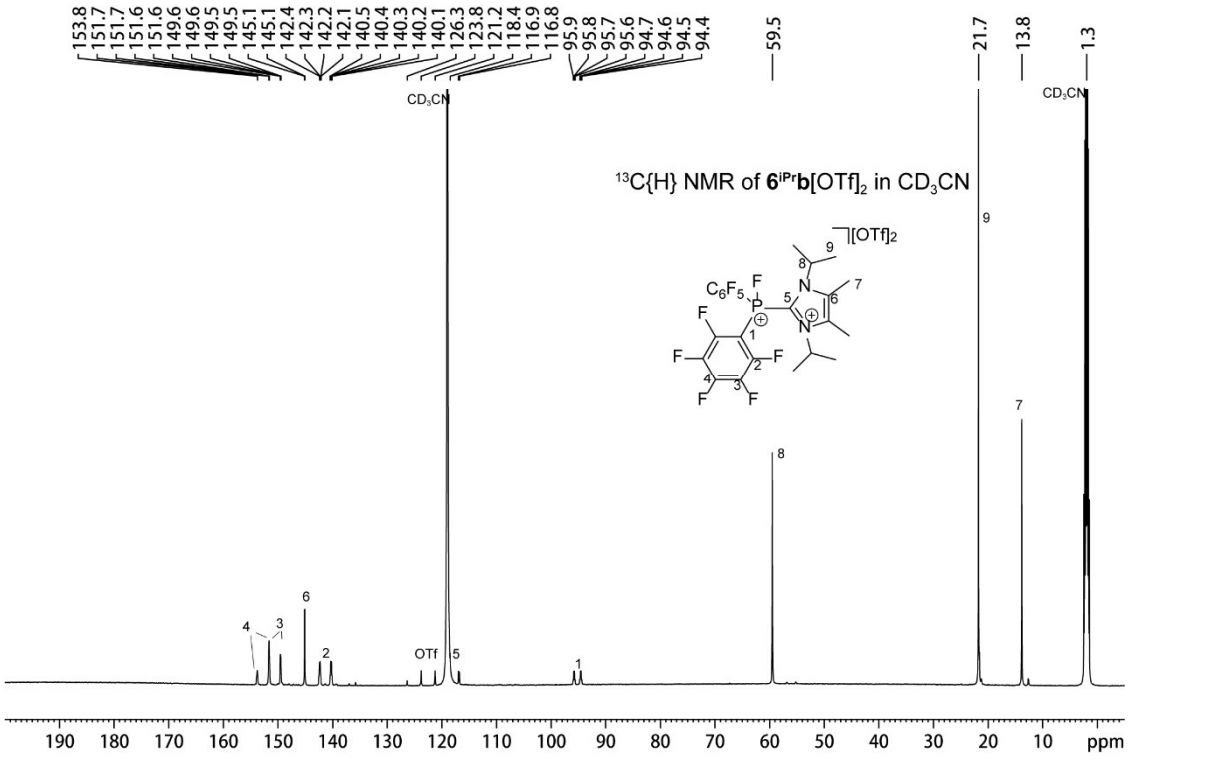


Figure S8.53. $^{13}C\{H\}$ NMR spectrum of $\mathbf{6^{iPr}b}[OTf]_2$ (126MHz, CD_3CN, 300 K), details are listed in section S4.11.

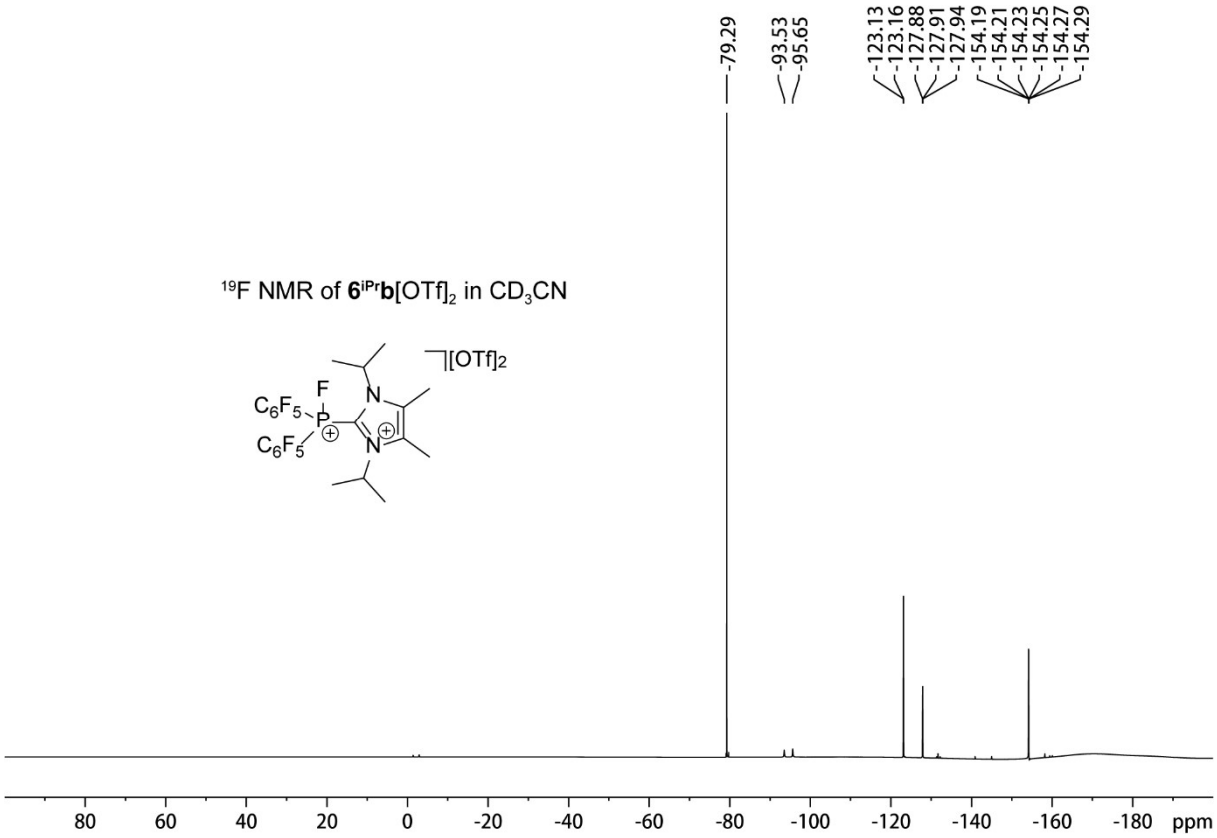


Figure S8.54. ^{19}F NMR spectrum of **6^{iPr}b**[OTf]$_2$ (471MHz, CD_3CN, 300 K), details are listed in section S4.11.

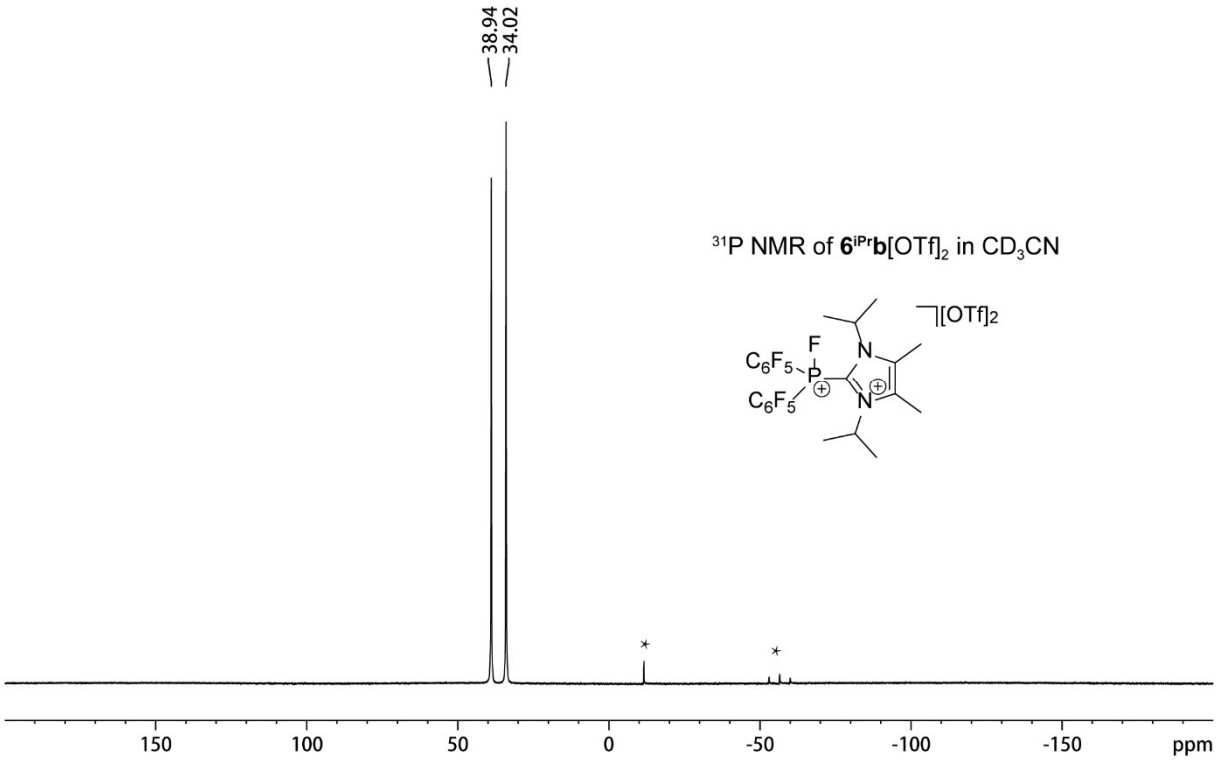


Figure S8.55. ^{31}P NMR spectrum of **6^{iPr}b**[OTf]$_2$ (202MHz, CD_3CN, 300 K), details are listed in section S4.11. Asterisks indicate small amounts of unidentified side products

S8.15 NMR spectra of $\mathbf{8^{Me}}[OTf]_3$

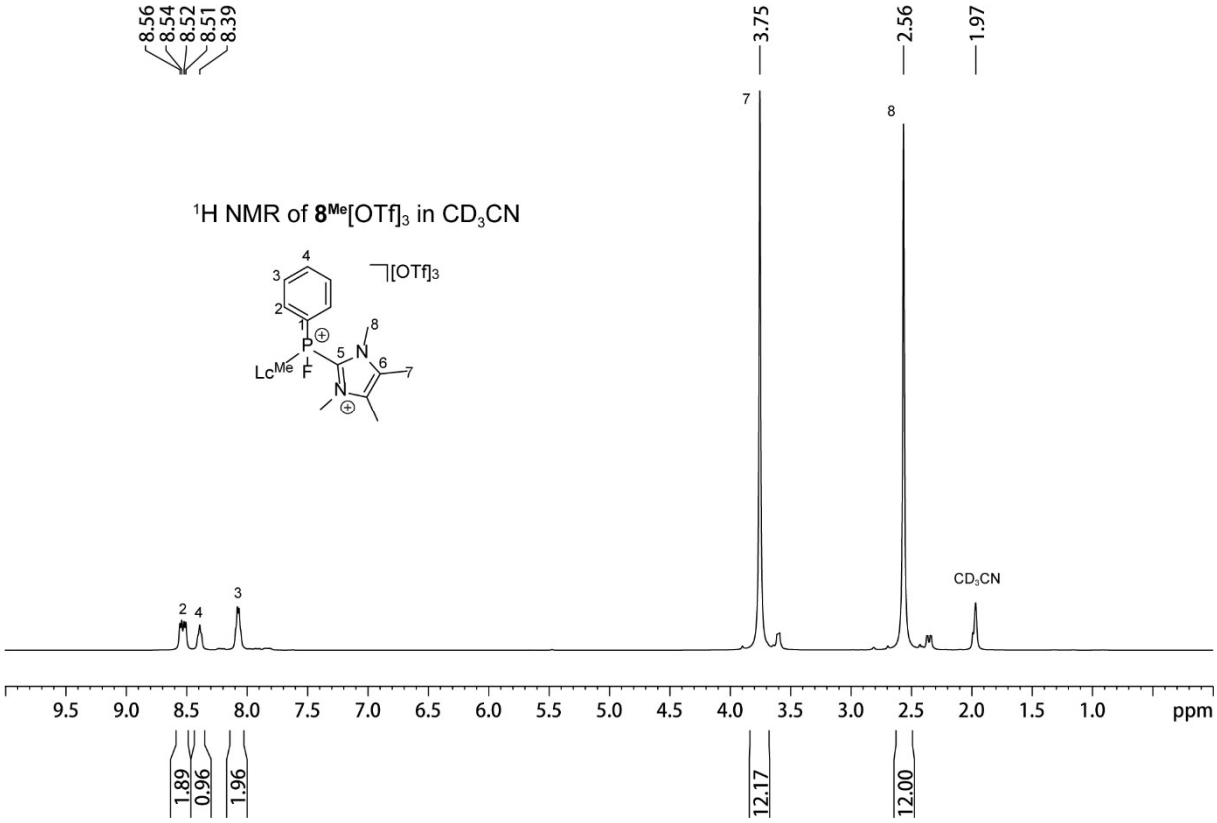


Figure S8.56. ^{1}H NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (500MHz, CD_3CN, 300 K), details are listed in section S4.12.

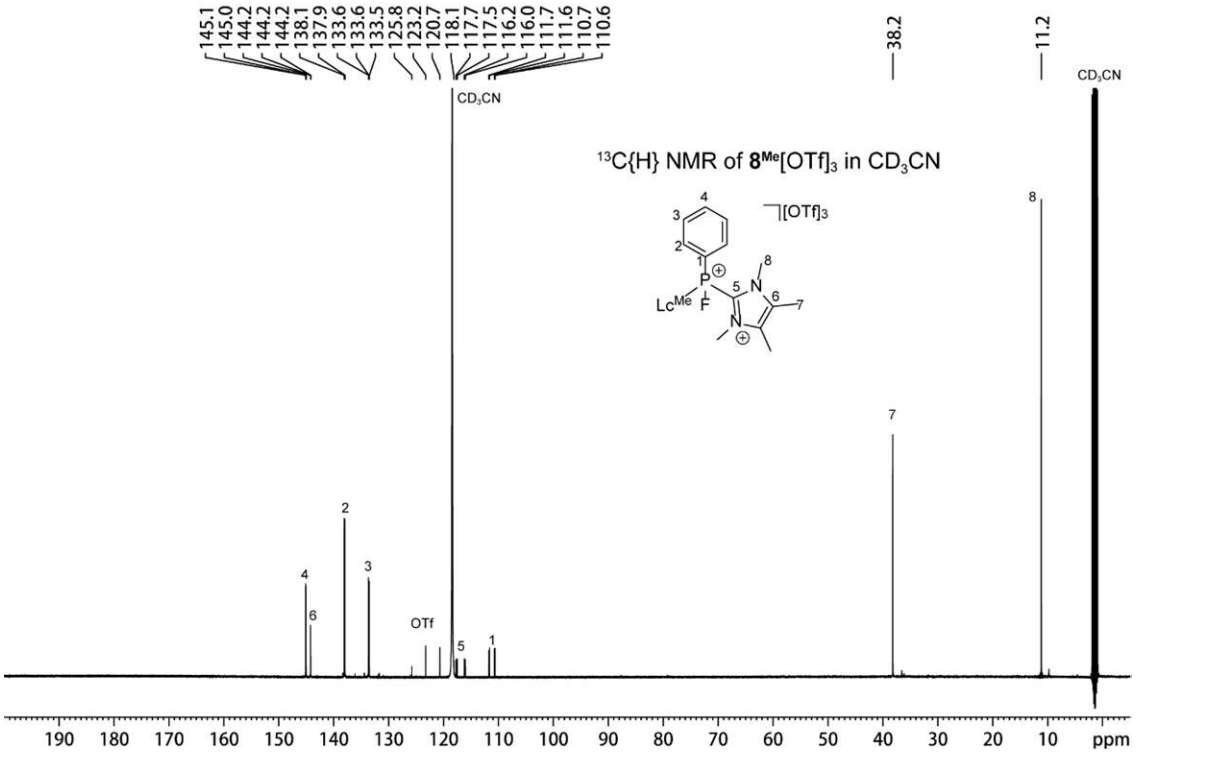


Figure S8.57. ^{13}C{H} NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (126MHz, CD_3CN, 300 K), details are listed in section S4.12.

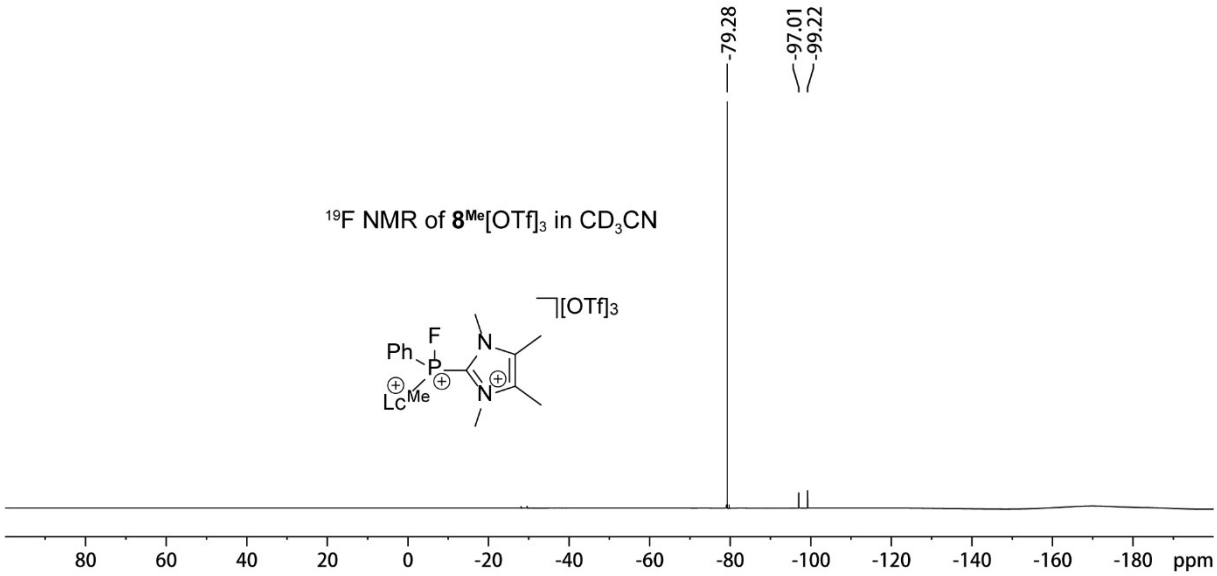


Figure S8.58. ^{19}F NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (471 MHz, CD_3CN, 300 K), details are listed in section S4.12.

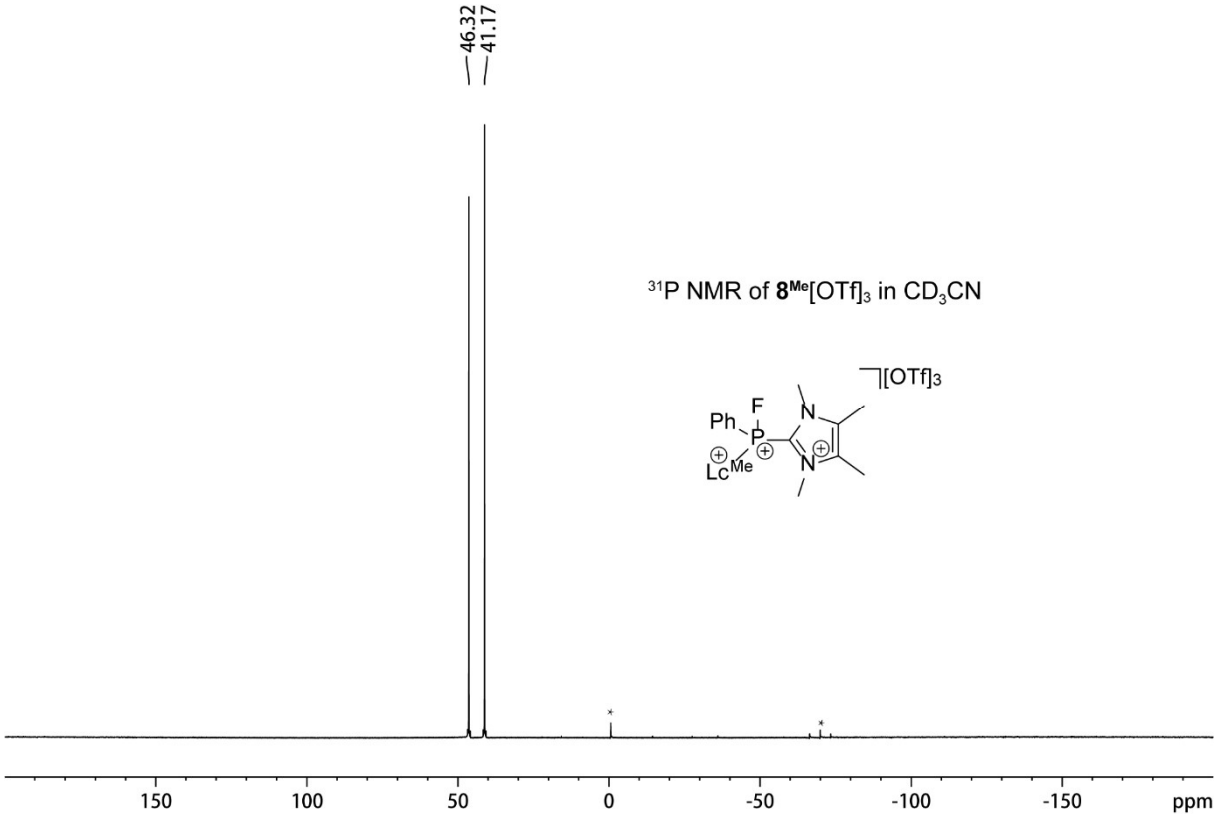


Figure S8.59. $^{31}P\{H\}$ NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (202MHz, CD_3CN, 300 K), details are listed in section S4.12. Asterisks indicate small amounts of unidentified side products.

S8.16 NMR spectra of $\mathbf{8^{iPr}}[OTf]_3$

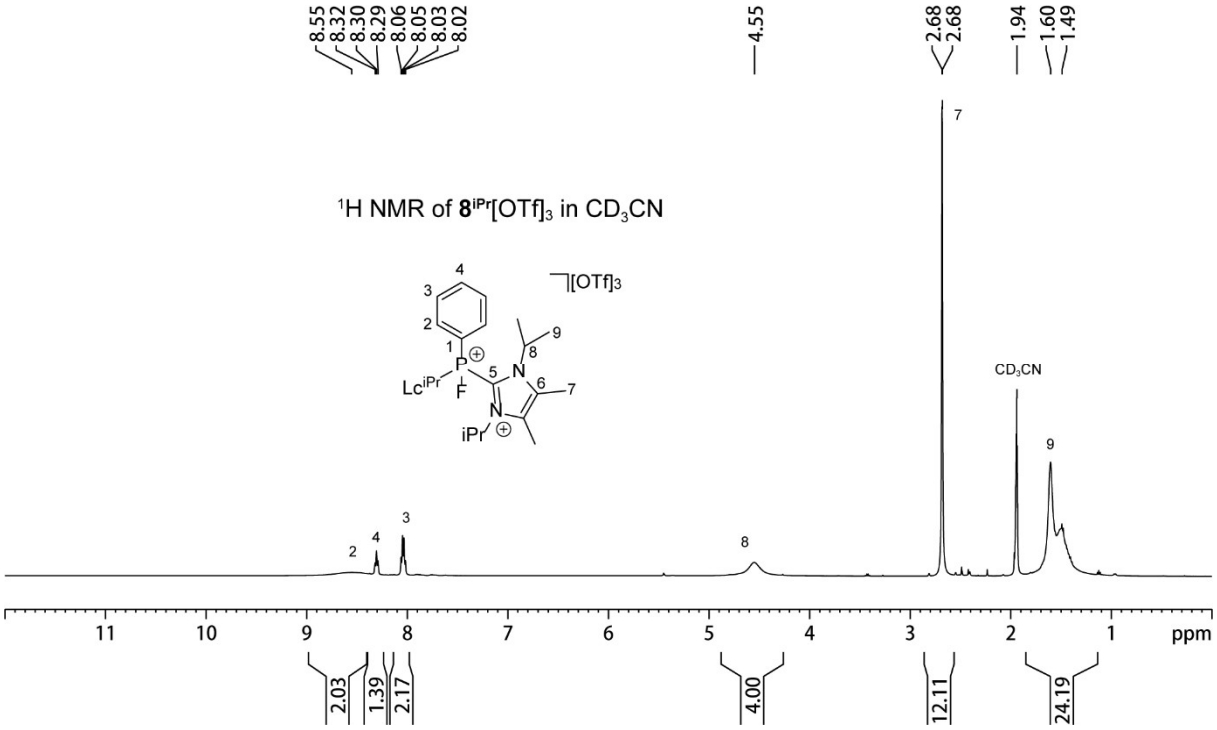


Figure S8.60. ^{1}H NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (500MHz, CD_3CN, 300 K), details are listed in section S4.13.

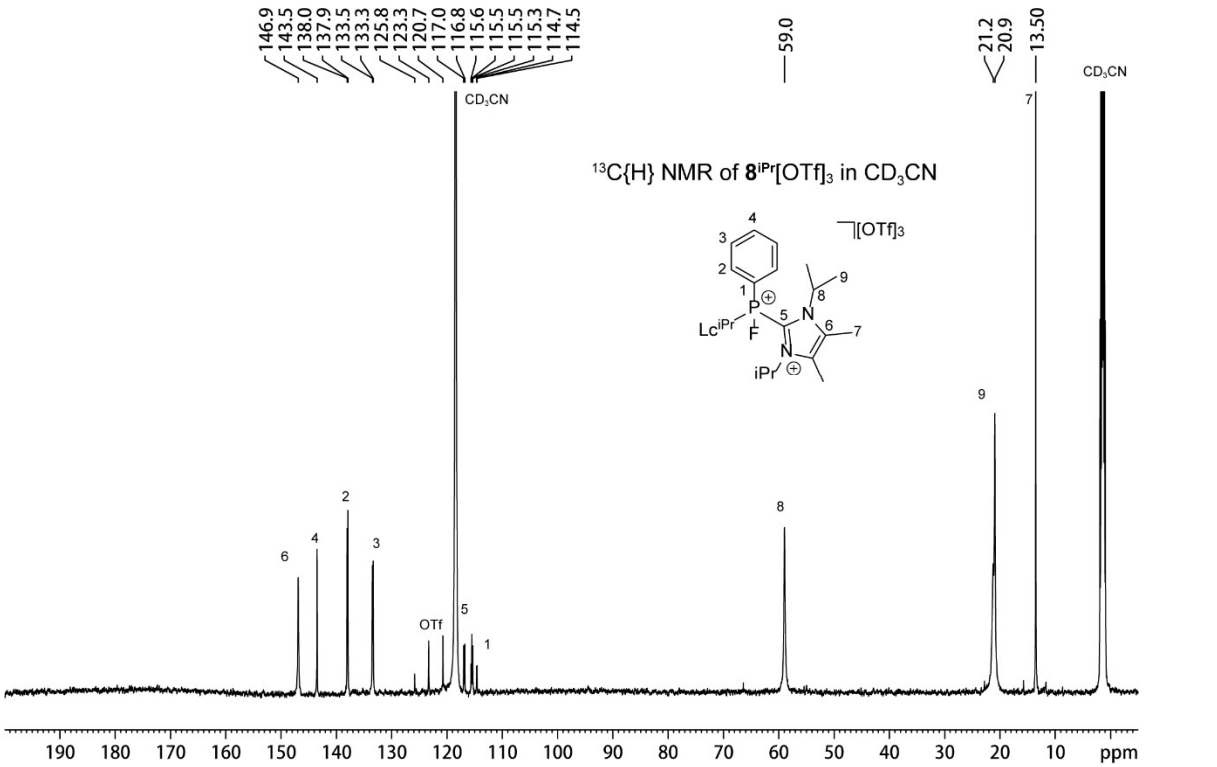


Figure S8.61. ^{13}C{H} NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (126MHz, CD_3CN, 300 K), details are listed in section S4.13.

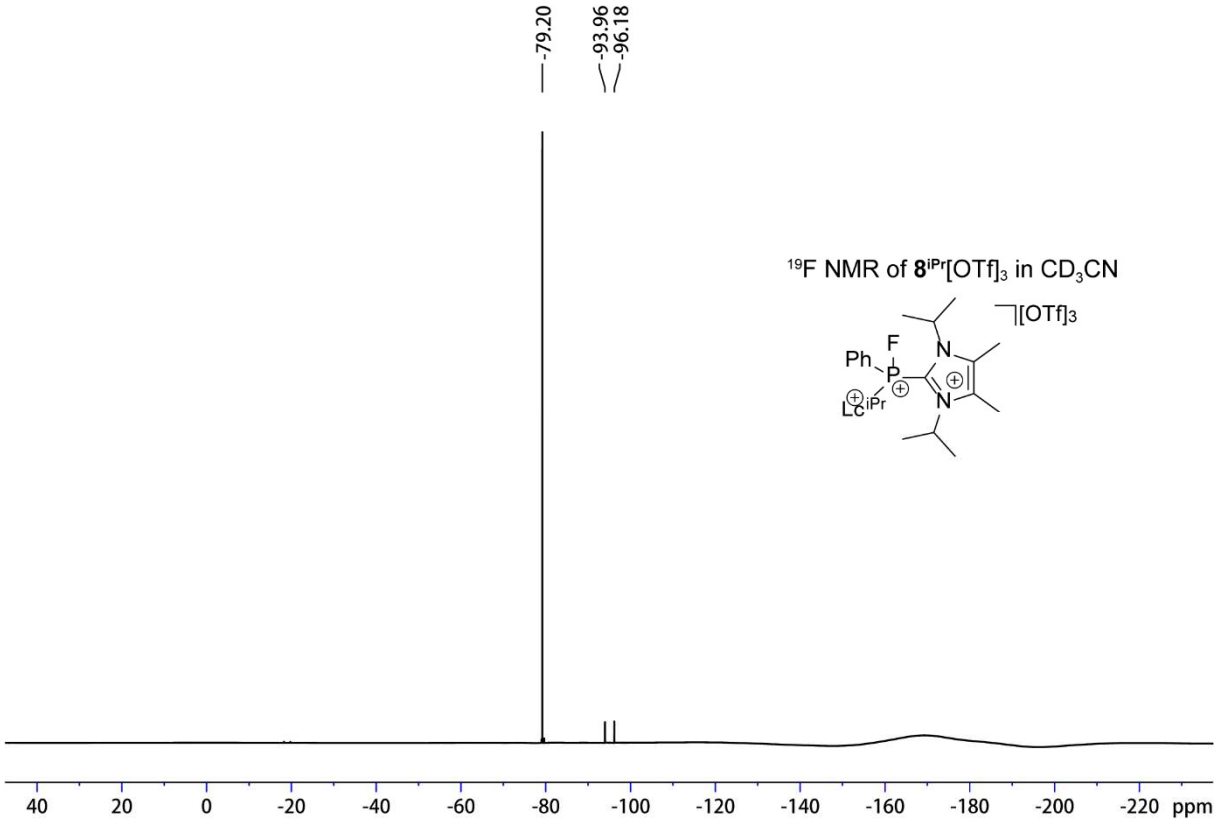


Figure S8.62. ^{19}F NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (471 MHz, CD_3CN, 300 K), details are listed in section S4.13.

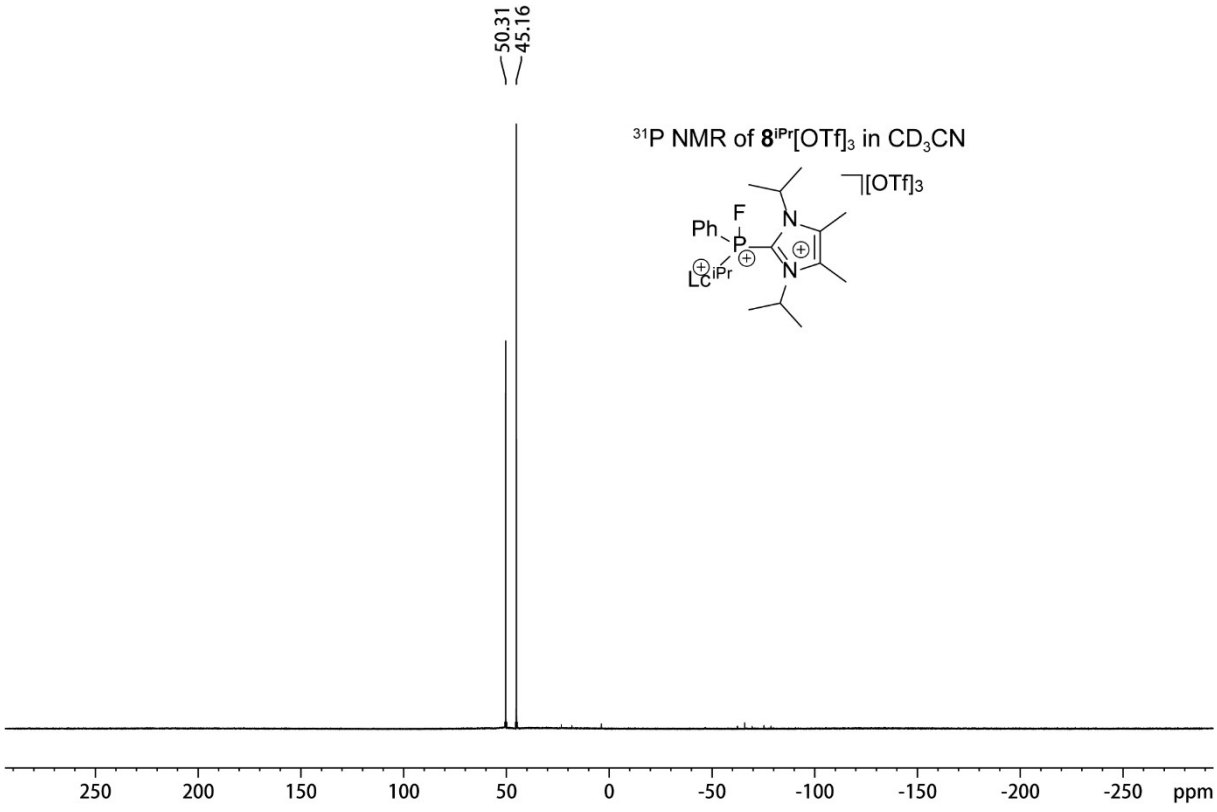


Figure S8.63. ^{31}P NMR spectrum of $\mathbf{8^{Me}}[OTf]_3$ (202MHz, CD_3CN, 300 K), details are listed in section S4.13.

S9 ^{31}P NMR spectra of fluoride exchange reactions

Unless stated otherwise, fluoride exchange reactions are conducted by the following general procedure: Fluorophosphonium triflate salt (0.05 mmol) reacted with conjugate difluorophosphorane compound of another fluorophosphonium triflate salt (0.05 mmol) in CD_3CN at r.t. overnight and submitted for NMR. The conjugate difluorophosphoranes of **6^{Me}b**[OTf]$_2$ and **8^{Me}**[OTf]$_3$ are in situ synthesized from the reaction of [(Lc^{iPr})Ph$_2$PF$_2$][OTf] (0.05 mmol) with the corresponding fluorophosphonium salts (0.05 mmol) in CD_3CN overnight. Selected ^{31}P NMR of the reaction NMR are listed below.

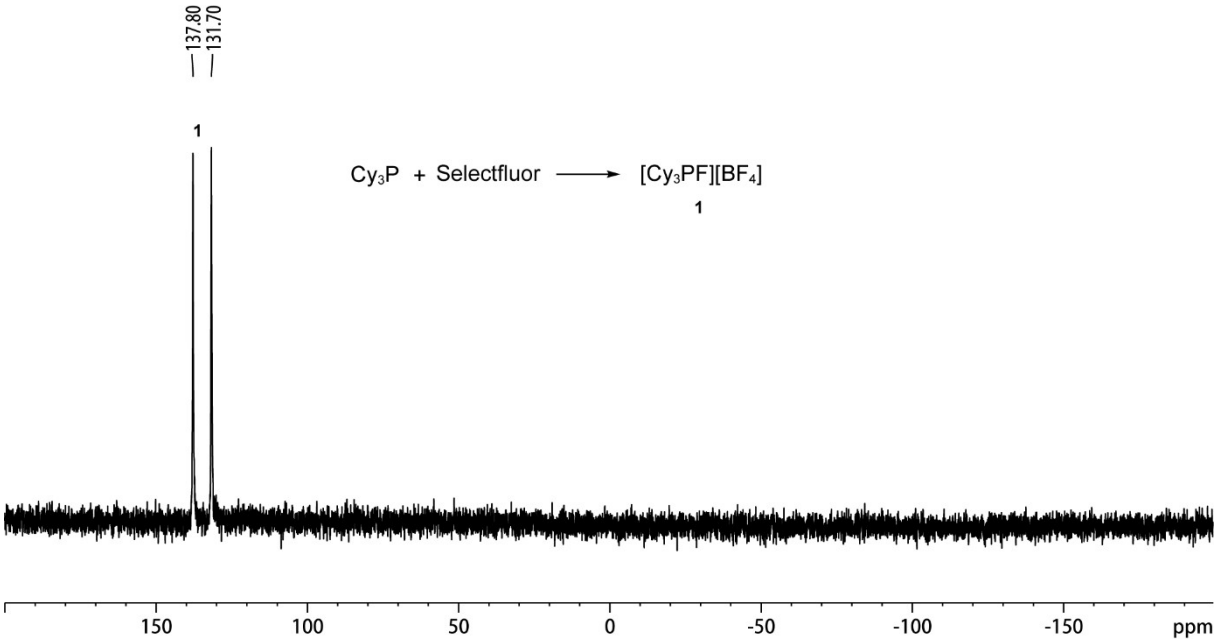


Figure S9.1. ^{31}P{H} NMR spectrum of reaction mixture Cy_3P and selectfluor in CD_3CN (202MHz, 300 K).

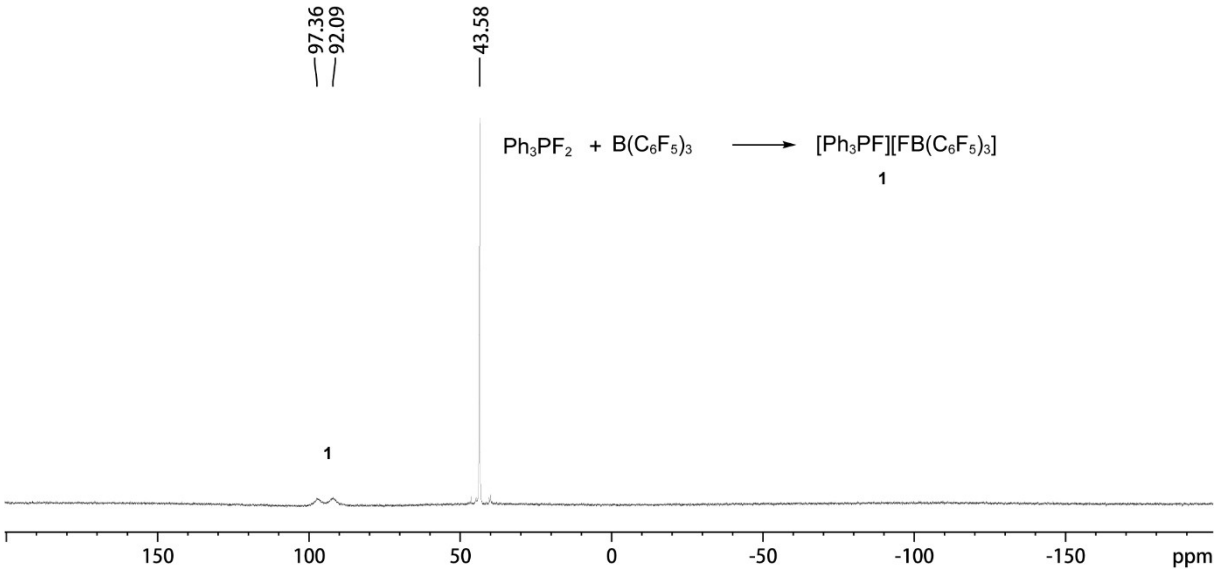


Figure S9.2. ^{31}P{H} NMR spectrum of reaction mixture Ph_3PF_2 and $B(C_6F_5)_3$ in CD_3CN (202MHz, 300 K).

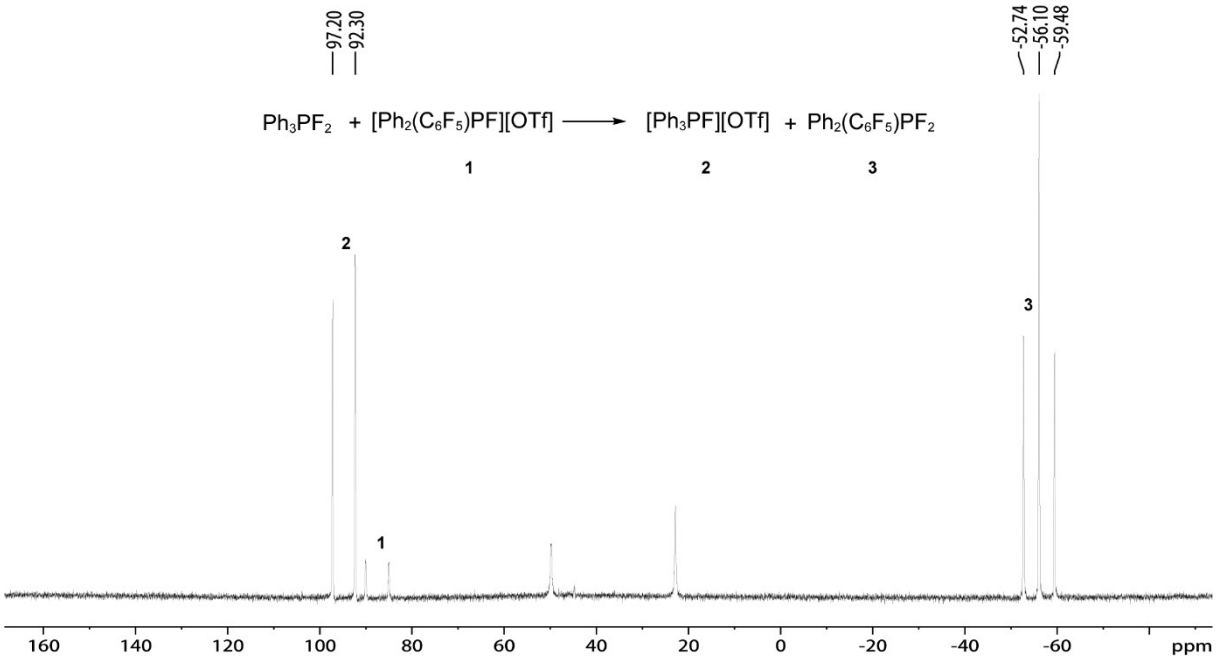


Figure S9.3. $^{31}P\{H\}$ NMR spectrum of reaction mixture Ph_3PF_2 and **4a**[OTf] in CD_3CN (202MHz, 300 K).

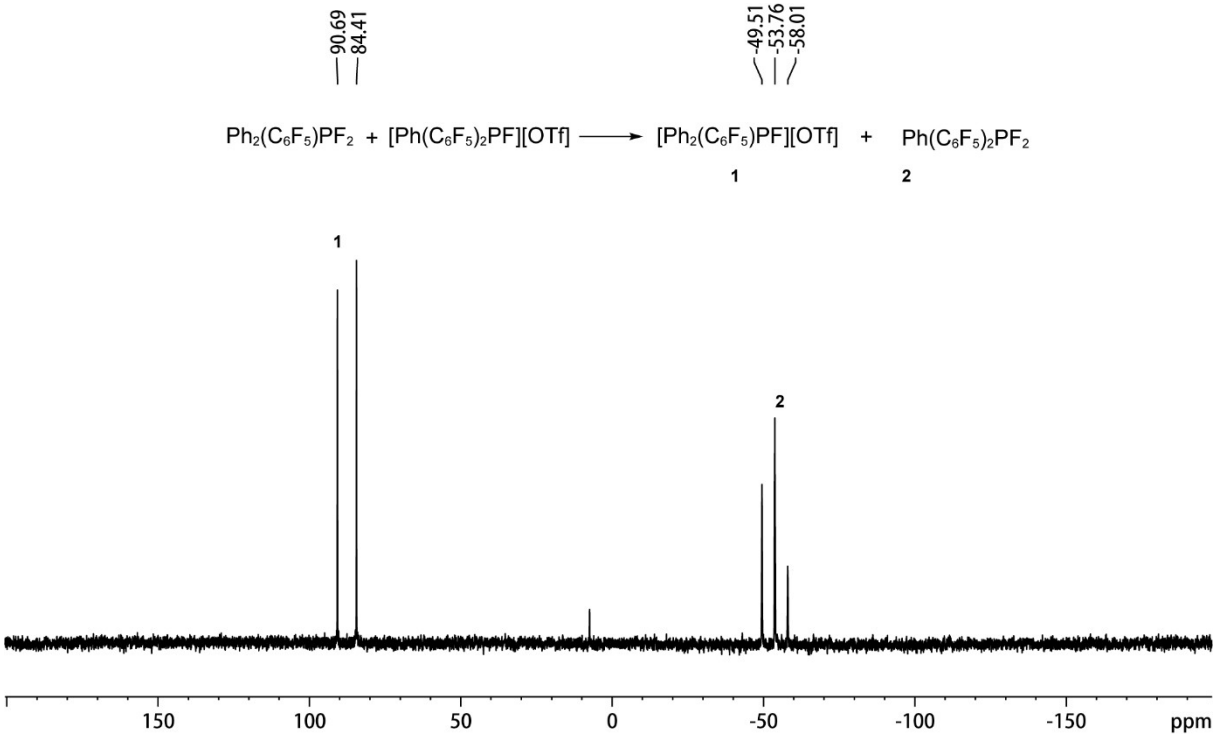


Figure S9.4. $^{31}P\{H\}$ NMR spectrum of reaction mixture $Ph_2(C_6F_5)PF_2$ and **4b**[OTf] in CD_3CN (202MHz, 300 K).

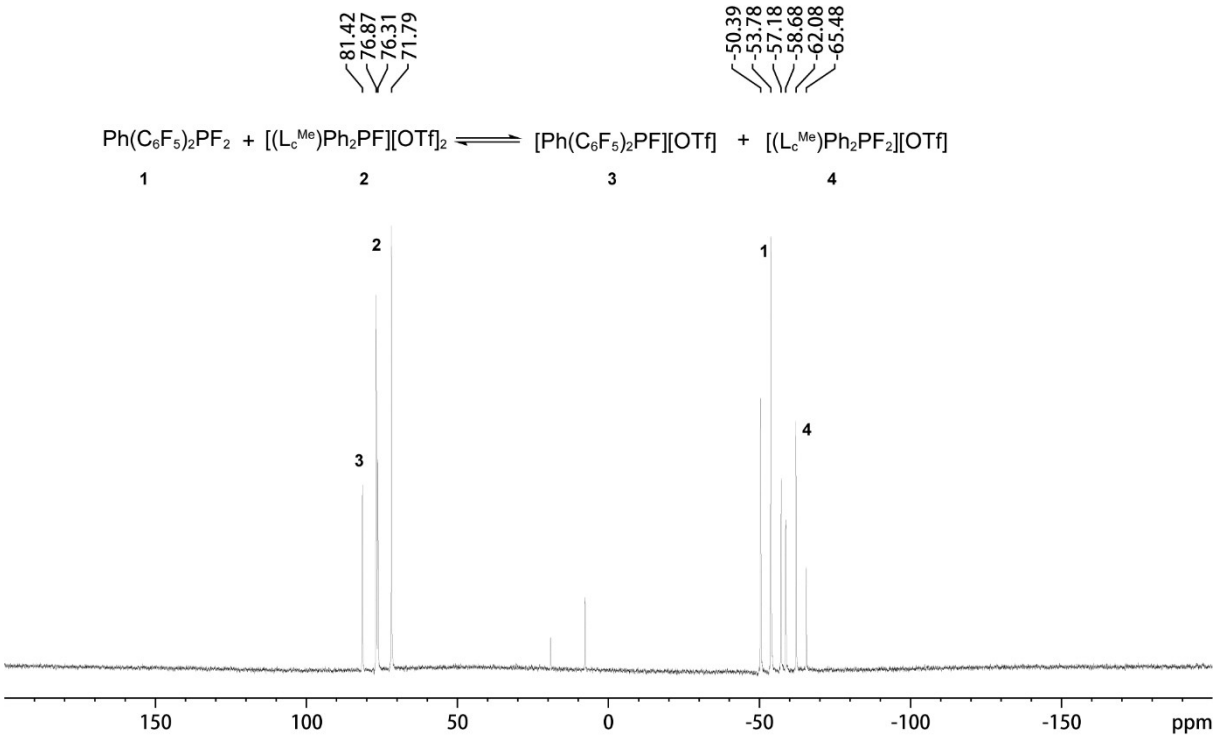


Figure S9.5. $^{31}P\{H\}$ NMR spectrum of reaction mixture $Ph(C_6F_5)PF_2$ and **6^{Me}a**$[OTf]_2$ in CD_3CN (202MHz, 300 K).

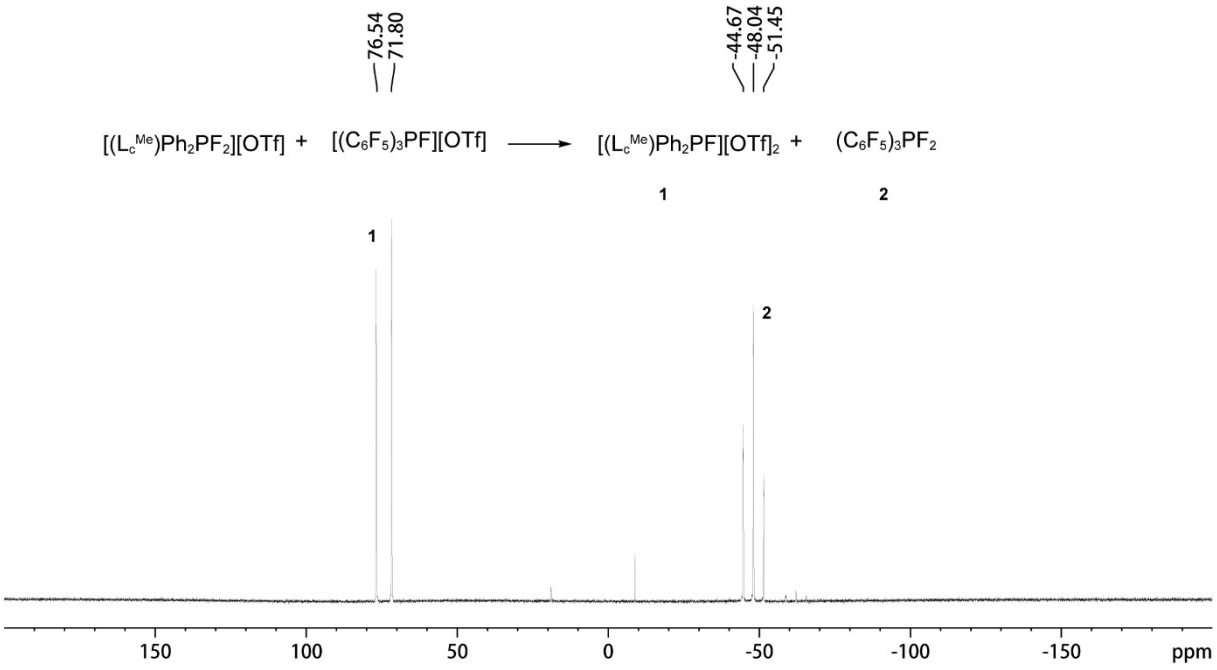


Figure S9.6. $^{31}P\{H\}$ NMR spectrum of reaction mixture $[L_c^{Me}Ph_2PF_2][OTf]$ and **2c**[OTf] in CD_3CN (202MHz, 300 K).

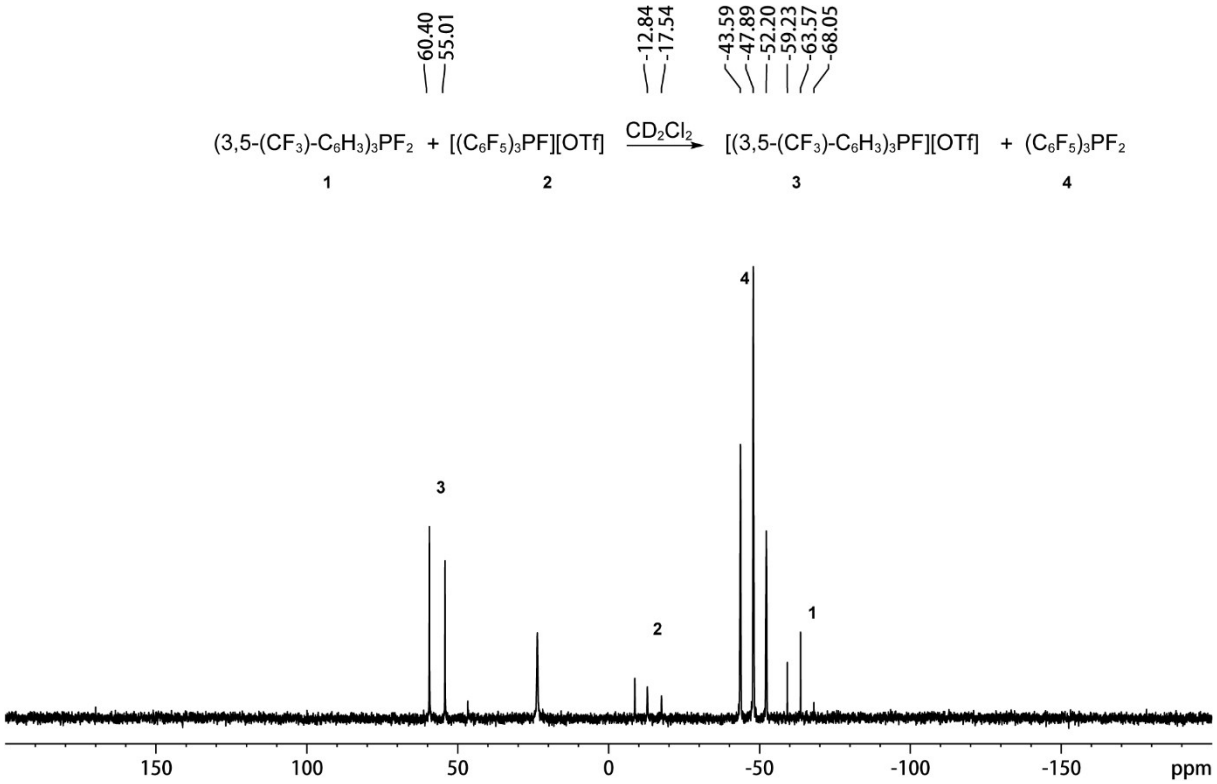


Figure S9.7. $^{31}P\{H\}$ NMR spectrum of reaction mixture **2d**[OTf] and $(C_6F_5)_3PF_2$ in CD_2Cl_2 (202MHz, 300 K).

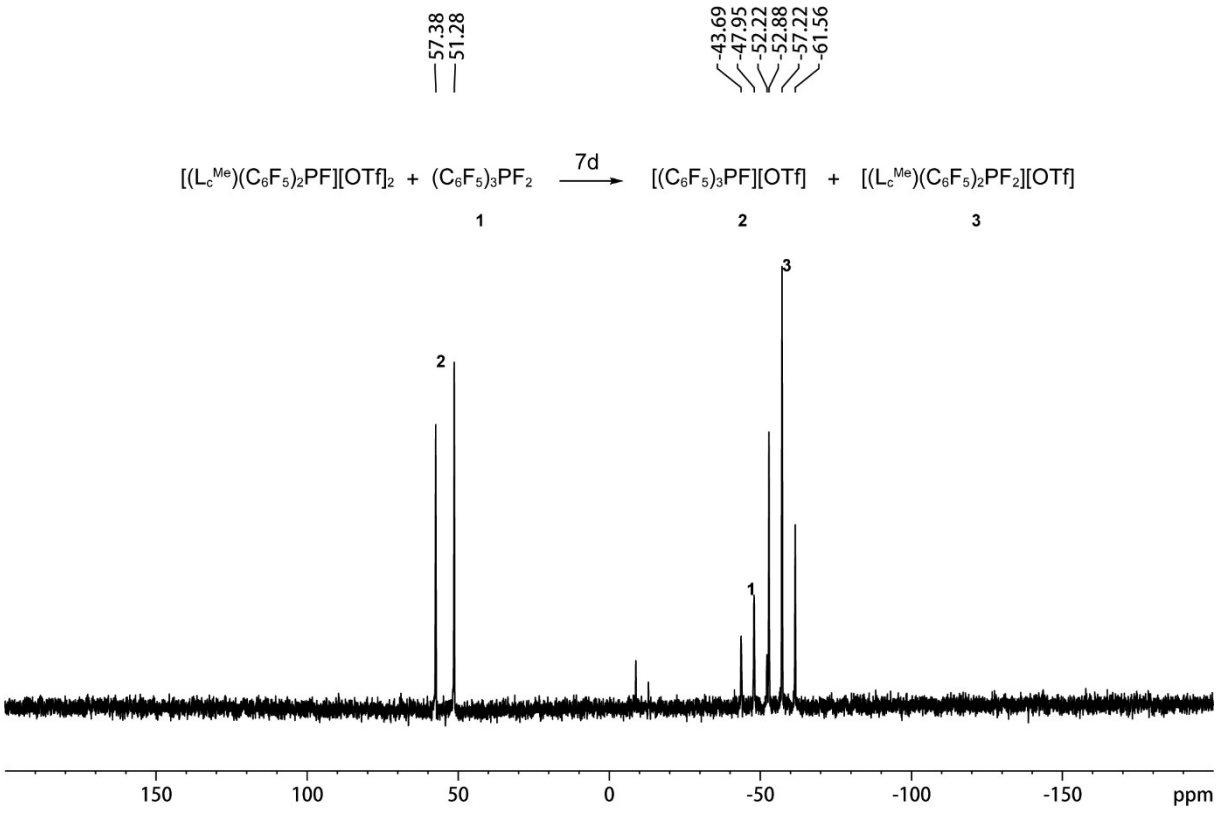


Figure S9.8. $^{31}P\{H\}$ NMR spectrum of reaction mixture $\mathbf{6^{Me}b}[OTf]_2$ and $(C_6F_5)_3PF_2$ in CD_3CN (202MHz, 300 K).

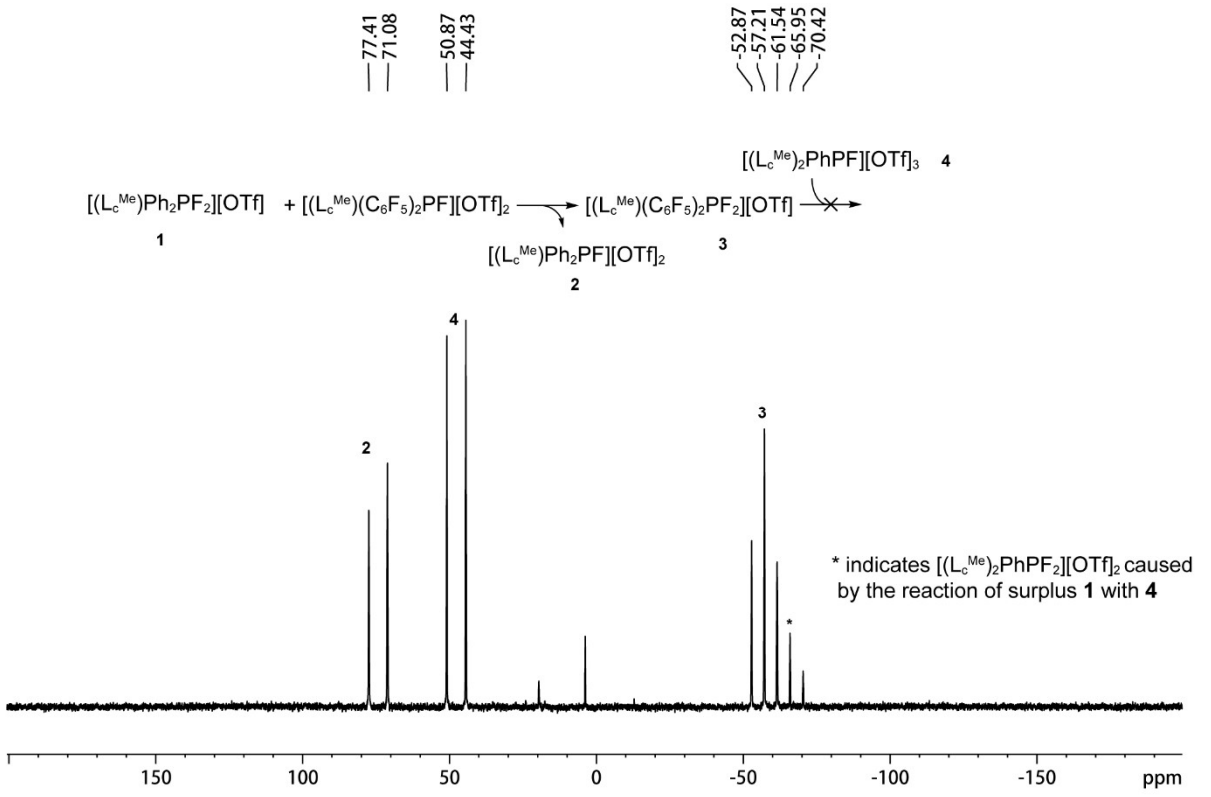


Figure S9.9. $^{31}P\{H\}$ NMR spectrum of reaction mixture $[L_c^{Me}(C_6F_5)_2PF_2][OTf]$ and $\mathbf{8^{Me}}[OTf]_3$ in CD_3CN (202MHz, 300 K).

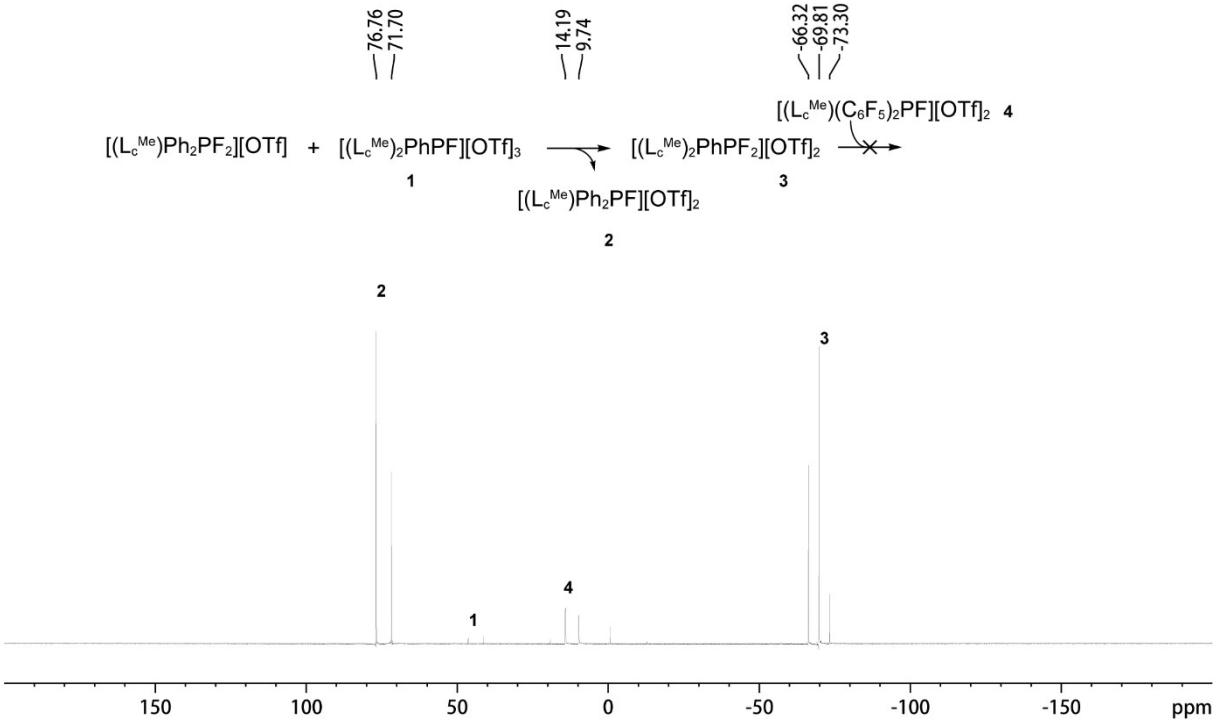


Figure S10. $^{31}P\{H\}$ NMR spectrum of reaction mixture $[(L_c^{Me})_2PhPF_2][OTf]_2$ and $\mathbf{6^{Me}b}[OTf]_2$ in CD_3CN (202MHz, 300 K).

S10 Crystallographic details

S10.1 X-ray Diffraction refinements

Single crystals suitable for X-ray analysis are obtained by vapor diffusion of a poor solvent into a saturated solution of the target compound, coated with Paratone-N oil or Fomblin Y25 PFPE oil, mounted using either glass fiber or nylon loop and frozen in the cold nitrogen stream. Crystals are measured at 100 K on an Oxford Diffraction Rigaku SuperNova diffractometer with Atlas S2 detector using Cu-K_α radiation generated by a Nova microfocus X-ray tube. Data reduction and absorption correction are performed with CrysaAlisPro software. Using Olex2[16], the structures are solved with SHELXS/T[17] by direct methods and refined with SHELXL[18] by least-square minimization against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms are added to the structure models on calculated positions using the riding model. All other hydrogen atoms are localized in the difference Fourier map. If necessary, disorders of solvent molecules, anions or both are treated with appropriate restraints (SADI, SIMU, DFIX, SUMP). Images of the structures are produced with Olex2 software.

Two structures were refined as twins. **9b**[OTf] was refined as inversion twin in space group *Cc* in the ratio 65:35. **22d** was refined as non-merohedral twin with two components in the ratio 75:25 related by 180° rotation around [001].

S10.2 Crystallographic details

S10.2.1. Crystallographic data and details of the structure refinements of compounds $[Cy_3PF][N(SO_2Ph)_2]$ **2a**[NSI], $[Ph_3PF][N(SO_2Ph)_2]$ **2b**[NSI], and [**2c**(NSI)].

	2a[NSI]	**2b**[NSI]·MeCN	[**2c**(NSI)]·PhF
Empirical formula	$C_{30}H_{43}FNO_4PS_2$	$C_{32}H_{28}FN_2O_4PS_2$	$C_{36}H_{15}F_{17}NO_4PS_2$
Formula weight	595.74	618.65	943.58
Temperature/K	100.00(10)	100.00(10)	100.00(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a/Å	17.3319(6)	10.36741(12)	10.38086(16)
b/Å	9.2282(3)	19.7011(2)	11.00296(13)
c/Å	19.4881(8)	15.3653(2)	17.74265(15)
α/°	90	90	98.0935(8)
β/°	109.282(4)	106.7433(13)	96.9660(10)
γ/°	90	90	115.6840(14)
Volume/Å^3	2942.13(19)	3005.31(7)	1770.00(4)
Z	4	4	2
ρ_{calc}g/cm^3	1.345	1.367	1.770
μ/mm^{-1}	2.506	2.499	3.042
F(000)	1272.0	1288.0	940.0
Crystal size/mm^3	0.52×0.272×0.063	0.414×0.081×0.06	0.295×0.21×0.112
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.402 to 152.836	7.498 to 153.454	5.14 to 153.19
Index ranges	-21≤h≤18, -8≤k≤11, -24≤l≤22	-12≤h≤12, -24≤k≤23, -18≤l≤19	-12≤h≤12, -13≤k≤9, -21≤l≤22
Reflections collected	15236	36790	17480
Independent reflections	6089 [R_{int} = 0.0273, R_{sigma} = 0.0266]	6264 [R_{int} = 0.0292, R_{sigma} = 0.0172]	7339 [R_{int} = 0.0135, R_{sigma} = 0.0152]
Data/restraints/parameters	6089/0/524	6264/0/480	7339/222/654
Goodness-of-fit on F^2	1.032	1.053	1.060
Final R indexes [I> = 2σ (I)]	R_1 = 0.0368, wR_2 = 0.1023	R_1 = 0.0308, wR_2 = 0.0828	R_1 = 0.0301, wR_2 = 0.0815
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.1033	R_1 = 0.0333, wR_2 = 0.0851	R_1 = 0.0306, wR_2 = 0.0820
Largest diff. peak/hole / e Å^{-3}	0.41/-0.55	0.35/-0.46	0.72/-0.50
CCDC	2051024	2051027	2051034

S10.2.2. Crystallographic data and details of the structure refinements of compounds, $MeN(SO_2Ph)_2$ (**25**) and $[(C_6F_5)_3PF][H(OTf)_2]$ **2c**$[H(OTf)_2]$ and $[Ph_3PF][OTf]$ **2b**[OTf].

	25	**2c**$[H(OTf)_2]$	**2b**[OTf]
Empirical formula	$C_{13}H_{13}NO_4S_2$	$C_{20}HF_{22}O_6PS_2$	$C_{19}H_{15}F_4O_3PS$
Formula weight	311.36	850.30	430.34
Temperature/K	99.97(10)	100.01(10)	100.0(2)
Crystal system	monoclinic	orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a/Å	10.92417(13)	8.05930(3)	11.08382(11)
b/Å	8.34450(8)	18.09719(7)	8.60083(9)
c/Å	15.03139(17)	18.21036(6)	19.8529(2)
α/°	90	90	90
β/°	103.0225(12)	90	93.8036(9)
γ/°	90	90	90
Volume/Å3	1334.97(3)	2655.992(17)	1888.41(3)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.549	2.126	1.514
μ/mm-^{1}	3.747	4.277	2.854
F(000)	648.0	1656.0	880.0
Crystal size/mm^3	0.427×0.147×0.097	0.36×0.25×0.025	0.383×0.248×0.066
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.104 to 153.016	6.886 to 153.29	8.896 to 152.982
Index ranges	-13≤h≤13, -10≤k≤6, -15≤l≤18	-10≤h≤10, -22≤k≤22, -18≤l≤22	-13≤h≤9, -10≤k≤10, -24≤l≤24
Reflections collected	6529	38601	9791
Independent reflections	2778 [R_{int} = 0.0185, R_{sigma} = 0.0205]	5549 [R_{int} = 0.0228, R_{sigma} = 0.0117]	3918 [R_{int} = 0.0176, R_{sigma} = 0.0192]
Data/restraints/parameters	2778/0/233	5549/0/461	3918/0/313
Goodness-of-fit on F^2	1.112	1.037	1.090
Final R indexes [I> = 2σ (I)]	R_1 = 0.0348, wR_2 = 0.0879	R_1 = 0.0184, wR_2 = 0.0495	R_1 = 0.0316, wR_2 = 0.0810
Final R indexes [all data]	R_1 = 0.0353, wR_2 = 0.0883	R_1 = 0.0185, wR_2 = 0.0495	R_1 = 0.0323, wR_2 = 0.0815
Largest diff. peak/hole/e $Å^{-3}$	0.48/-0.59	0.19/-0.24	0.43/-0.33
Flack parameter		-0.001(3)	
CCDC	2051049	2051032	2051026

S10.2.3. Crystallographic data and details of the structure refinements of compounds and [Cy_3PF][OTf] **2a**[OTf], [(3,5-$DiCF_3C_6H_3)_3PF$][OTf] **2d**[OTf] and [$(C_6F_5)_2PhPF$][OTf] **4b**[OTf].

	2a[OTf]	**2d**[OTf]·PhF	**4b**[OTf]
Empirical formula	$C_{19}H_{33}F_4O_3PS$	$C_{31}H_{14}F_{23}O_3PS$	$C_{76}H_{20}O_{12}F_{56}P_4S_4$
Formula weight	448.48	934.45	2441.04
Temperature/K	99.97(13)	101(1)	100.01(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	10.37115(14)	11.52196(12)	8.0000(2)
b/Å	18.9500(2)	19.20788(18)	15.2994(5)
c/Å	11.19583(15)	15.90714(14)	16.8567(8)
α/°	90	90	90
β/°	95.5133(12)	101.4808(9)	91.765(3)
γ/°	90	90	90
Volume/$Å^3$	2190.17(5)	3450.01(6)	2062.19(13)
Z	4	4	1
$\rho_{calc}g/cm^3$	1.360	1.799	1.966
μ/m*m*-^{1}	2.463	2.784	3.578
F(000)	952.0	1848.0	1200.0
Crystal size/mm^3	0.641×0.468×0.049	0.233×0.058×0.011	0.269×0.116×0.058
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.566 to 152.882	7.304 to 152.974	7.806 to 153.208
Index ranges	-12≤h≤12, -23≤k≤23, -11≤l≤13	-14≤h≤14, -22≤k≤24, -19≤l≤13	-10≤h≤8, -19≤k≤15, -20≤l≤21
Reflections collected	11001	19620	12741
Independent reflections	4513 [R_{int} = 0.0363, R_{sigma} = 0.0345]	7179 [R_{int} = 0.0307, R_{sigma} = 0.0350]	4245 [R_{int} = 0.0583, R_{sigma} = 0.0519]
Data/restraints/parameters	4513/0/385	7179/0/532	4245/0/343
Goodness-of-fit on F^2	1.032	1.017	1.078
Final R indexes [I> = 2σ (I)]	R_1 = 0.0469, wR_2 = 0.1238	R_1 = 0.0393, wR_2 = 0.0977	R_1 = 0.0875, wR_2 = 0.2328
Final R indexes [all data]	R_1 = 0.0497, wR_2 = 0.1278	R_1 = 0.0488, wR_2 = 0.1044	R_1 = 0.0953, wR_2 = 0.2392
Largest diff. peak/hole / e $Å^{-3}$	0.78/-0.59	0.68/-0.53	1.13/-0.74
CCDC	2051025	2051029	2051031

S10.2.4. Crystallographic data and details of the structure refinements of compounds $[Im^{Me}Ph_2PF][OTf]_2$ **6^{Me}a**$[OTf]_2$, $[Im^{Me}(C_6F_5)_2PF][OTf]_2$ **6^{Me}b**$[OTf]_2$, $[Im^{Me}{}_2PhPF][OTf]_3$ **8^{Me}**$[OTf]_3$.

	6^{Me}a$[OTf]_2$	**6^{Me}b**$[OTf]_2$	**8^{Me}**$[OTf]_3$
Empirical formula	$C_{42}H_{44}N_4O_{12}F_{14}P_2S_4$	$C_{21}H_{12}F_{17}N_2O_6PS_2$	$C_{23}H_{29}F_{10}N_4O_9PS_3$
Formula weight	1252.99	806.42	822.65
Temperature/K	100.0(2)	100.01(10)	100.00(10)
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	$P2_1/c$	*P*-1
a/Å	8.0319(2)	16.4153(3)	7.85245(9)
b/Å	11.7116(3)	12.2793(2)	20.1873(3)
c/Å	14.8524(4)	14.2726(2)	21.8327(4)
α/°	104.286(3)	90	72.7551(14)
β/°	94.065(2)	103.780(2)	85.1945(11)
γ/°	106.325(3)	90	82.5742(11)
Volume/Å^3	1284.46(7)	2794.10(8)	3273.83(9)
Z	1	4	4
ρ_{calc}g/cm^3	1.620	1.917	1.669
μ/m*m*-^{1}	3.329	3.772	3.578
F(000)	640.0	1600.0	1680.0
Crystal size/mm^3	0.163×0.092×0.063	0.264×0.177×0.114	0.276×0.077×0.066
Radiation	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.212 to 153.42	5.544 to 153.526	5.288 to 153.342
Index ranges	-9≤h≤10, -14≤k≤14, -18≤l≤14	-17 ≤ h ≤ 20, -14 ≤ k ≤ 15, -16 ≤ l ≤ 17	-9≤h≤6, -25≤k≤25, -27≤l≤27
Reflections collected	12175	18052	34017
Independent reflections	5341 [R_{int} = 0.0207, R_{sigma} = 0.0273]	5822 [R_{int} = 0.0468, R_{sigma} = 0.0448]	13606 [R_{int} = 0.0308, R_{sigma} = 0.0339]
Data/restraints/parameters	5341/0/356	5822/229/519	13606/66/997
Goodness-of-fit on F^2	1.044	1.037	1.033
Final R indexes [I> = 2σ (I)]	R_1 = 0.0312, wR_2 = 0.0825	R_1 = 0.0535, wR_2 = 0.1439	R_1 = 0.0464, wR_2 = 0.1184
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0840	R_1 = 0.0608, wR_2 = 0.1530	R_1 = 0.0500, wR_2 = 0.1220
Largest diff. peak/hole / e Å^{-3}	0.41/-0.41	0.81/-0.59	1.56/-0.88
CCDC	2051028	2051030	2051040

S10.2.5. Crystallographic data and details of the structure refinements of compounds $[(C_6F_5)_3PF(Me_2NCHO)][OTf]$ **9a**[OTf], $[((CF_3)_2C_6H_3)_3PF(Me_2NCHO)][OTf]$ **9b**[OTf] and $(C_6F_5)_3PFSO_3Ph$ **10**

	9a[OTf]	**9b**[OTf]	**10**
Empirical formula	$C_{22}H_7F_{19}NO_4PS$	$C_{28}H_{16}F_{22}NO_4PS$	$C_{24}H_5F_{16}O_3PS$
Formula weight	773.32	911.45	708.31
Temperature/K	100.00(19)	101(1)	100.0(2)
Crystal system	Monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	Cc	$P2_1/n$
a/Å	8.82043(6)	16.8642(2)	10.96730(9)
b/Å	15.38084(11)	20.8497(2)	14.03475(13)
c/Å	19.59298(12)	9.53500(13)	16.23076(14)
α/°	90	90	90
β/°	93.0239(6)	104.5237(15)	100.4112(8)
γ/°	90	90	90
Volume/Å^3	2654.39(3)	3245.50(8)	2457.16(4)
Z	4	4	4
ρ_{calc}g/cm^3	1.935	1.865	1.915
μ/m*m*$^{-1}$	3.268	2.924	3.238
F(000)	1520.0	1808.0	1392.0
Crystal size/mm^3	0.477×0.399×0.284	0.307×0.252×0.168	0.272 × 0.213 × 0.122
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.31 to 153.33	6.876 to 152.356	8.388 to 153.214
Index ranges	-11≤h≤10, -19≤k≤19, -24≤l≤16	-21≤h≤18, -26≤k≤25, -9≤l≤11	-11 ≤ h ≤ 13, -17 ≤ k ≤ 12, -20 ≤ l ≤ 18
Reflections collected	15070	15589	13517
Independent reflections	5520 [R_{int} = 0.0238, R_{sigma} = 0.0220]	4886 [R_{int} = 0.0220, R_{sigma} = 0.0220]	5111 [R_{int} = 0.0180, R_{sigma} = 0.0189]
Data/restraints/parameters	5520/0/439	4886/2/517	5111/0/426
Goodness-of-fit on F^2	1.108	1.019	1.043
Final R indexes [I> = 2σ (I)]	R_1 = 0.0351, wR_2 = 0.0901	R_1 = 0.0247, wR_2 = 0.0658	R_1 = 0.0292, wR_2 = 0.0762
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0908	R_1 = 0.0248, wR_2 = 0.0659	R_1 = 0.0303, wR_2 = 0.0772
Largest diff. peak/hole / e Å^{-3}	0.50/-0.49	0.23/-0.28	0.32/-0.54
Flack parameter		0.349(17)	
CCDC	2051046	2051033	2051036

S10.2.6. Crystallographic data and details of the structure refinements of compound$(C_6F_5)_3PFCl$ **11**, *p*-MeO-C_6H_4-SO_2NHSO_2Ph **24a,** and *p*-F-C_6H_4-SO_2NHSO_2Ph **24c**.

	12	**24a**	**24c**
Empirical formula	$C_{18}ClF_{16}P$	$C_{13}H_{13}NO_5S_2$	$C_{12}H_{10}FNO_4S_2$
Formula weight	586.60	327.36	315.33
Temperature/K	100.00(10)	100.00(10)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$	$I2/a$
a/Å	10.12255(19)	8.12358(8)	7.56523(13)
b/Å	17.5721(3)	7.45938(6)	13.96865(19)
c/Å	11.27435(17)	11.44023(10)	24.4631(3)
α/°	90	90	90
β/°	107.7948(18)	97.7219(8)	93.8142(13)
γ/°	90	90	90
Volume/Å^3	1909.48(6)	686.956(11)	2579.44(7)
Z	4	2	8
ρ_{calc}g/cm^3	2.041	1.583	1.624
μ/m*m*-^{1}	4.128	3.730	4.005
F(000)	1136.0	340.0	1296.0
Crystal size/mm^3	0.21 × 0.066 × 0.029	0.126×0.105×0.097	0.125×0.075×0.063
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.176 to 153.692	7.798 to 153.182	7.244 to 153.284
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 22, -13 ≤ l ≤ 14	-10≤h≤10, -9≤k≤9, -14≤l≤14	-9≤h≤8, -17≤k≤16, -30≤l≤23
Reflections collected	14156	6494	6394
Independent reflections	3979 [R_{int} = 0.0197, R_{sigma} = 0.0170]	2836 [R_{int} = 0.0148, R_{sigma} = 0.0197]	2677 [R_{int} = 0.0199, R_{sigma} = 0.0244]
Data/restraints/parameters	3979/0/344	2836/1/191	2677/0/191
Goodness-of-fit on F^2	1.050	1.092	1.026
Final R indexes [I> = 2σ (I)]	R_1 = 0.0322, wR_2 = 0.0770	R_1 = 0.0231, wR_2 = 0.0604	R_1 = 0.0341, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0778	R_1 = 0.0233, wR_2 = 0.0606	R_1 = 0.0351, wR_2 = 0.0934
Largest diff. peak/hole / e Å^{-3}	0.44/-0.32	0.18/-0.29	0.75/-0.69
Flack parameter		0.224(7)	
CCDC	2051038	2051053	2051054

S10.2.7. Crystallographic data and details of the structure refinements of compounds *p*-CF_3-C_6H_4-$SO_2N(Na)SO_2Ph$ **22d**, *o*-F-C_6H_4-SO_2NHSO_2Ph **24e,** and *m*-F-C_6H_4-SO_2NHSO_2Ph **24f**.

	22d·H_2O	**24e**	**24f**
Empirical formula	$C_{13}H_{11}F_3NNaO_5S_2$	$C_{12}H_{10}FNO_4S_2$	$C_{12}H_{12.01}FNO_5S_2$
Formula weight	405.34	315.33	333.21
Temperature/K	99.99(18)	100.0(4)	100.5(8)
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/n$
a/Å	5.9137(3)	15.93411(17)	13.2220(3)
b/Å	7.5914(3)	11.15685(12)	13.3607(3)
c/Å	17.6496(11)	14.40620(14)	16.1071(4)
α/°	101.675(4)	90	90
β/°	92.879(4)	99.6810(10)	103.931(2)
γ/°	97.709(4)	90	90
Volume/Å^3	766.49(7)	2524.58(5)	2761.72(11)
Z	2	8	8
ρ_{calc}g/cm^3	1.756	1.659	1.603
μ/m*m*-^{1}	4.029	4.092	3.828
F(000)	412.0	1296.0	1376.0
Crystal size/mm^3	0.12×0.04×0.02	0.21 × 0.114 × 0.027	0.219×0.171×0.061
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.13 to 154.222	5.626 to 153.38	7.79 to 153.304
Index ranges	-7≤h≤7, -9≤k≤9, -22≤l≤21	-19 ≤ h ≤ 20, -13 ≤ k ≤ 13, -18 ≤ l ≤ 17	-11≤h≤16 -16≤k≤16, -20≤l≤20
Reflections collected	4353	29126	16013
Independent reflections	4353 [R_{int} = ?, R_{sigma} = 0.0089]	5280 [R_{int} = 0.0277, R_{sigma} = 0.0230]	5763 [R_{int} = 0.0251, R_{sigma} = 0.0265]
Data/restraints/parameters	4353/0/234	5280/1/374	5763/2/427
Goodness-of-fit on F^2	1.087	1.128	1.136
Final R indexes [I> = 2σ (I)]	R_1 = 0.0433, wR_2 = 0.1306	R_1 = 0.0351, wR_2 = 0.0904	R_1 = 0.0629, wR_2 = 0.1669
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.1320	R_1 = 0.0362, wR_2 = 0.0911	R_1 = 0.0646, wR_2 = 0.1676
Largest diff. peak/hole / e Å^{-3}	0.67/-0.36	0.90/-0.56	0.81/-0.87
CCDC	2051037	2051056	2051055

S10.2.8. Crystallographic data and details of the structure refinements of compounds $PhSO_2N{=}CHNMe_2$ **11**, $PhSO_2N{=}CHN(nBu)_2$ **14,** and $PhSO_2N{=}CHNMePh$ **16**.

	11	**14**	**16**
Empirical formula	$C_9H_{12}N_2O_2S$	$C_{15}H_{24}N_2O_2S$	$C_{14}H_{14}N_2O_2S$
Formula weight	212.27	296.42	274.33
Temperature/K	100.01(10)	100.0(3)	99.99(10)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a/Å	5.82907(14)	9.91994(16)	10.77093(12)
b/Å	12.3343(2)	7.80758(13)	11.69446(14)
c/Å	13.5531(2)	20.4247(4)	10.46614(12)
α/°	90	90	90
β/°	90	100.3314(17)	91.3982(10)
γ/°	90	90	90
Volume/Å^3	974.43(3)	1556.26(5)	1317.92(3)
Z	4	4	4
ρ_{calc}g/cm^3	1.447	1.265	1.383
μ/m*m*-^{1}	2.767	1.873	2.183
F(000)	448.0	640.0	576.0
Crystal size/mm^3	0.268×0.052×0.037	0.315×0.055×0.027	0.211×0.117×0.078
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.696 to 153.154	8.802 to 152.76	8.212 to 153.074
Index ranges	-5≤h≤7, -15≤k≤14, -16≤l≤16	-12≤h≤12, -9≤k≤9, -24≤l≤25	-13≤h≤13, -13≤k≤14, -12≤l≤13
Reflections collected	4519	10157	6774
Independent reflections	2022 [R_{int} = 0.0244, R_{sigma} = 0.0313]	3210 [R_{int} = 0.0299, R_{sigma} = 0.0257]	2729 [R_{int} = 0.0170, R_{sigma} = 0.0202]
Data/restraints/parameters	2022/0/129	3210/0/183	2729/0/173
Goodness-of-fit on F^2	1.058	1.057	1.048
Final R indexes [I> = 2σ (I)]	R_1 = 0.0264, wR_2 = 0.0672	R_1 = 0.0439, wR_2 = 0.1178	R_1 = 0.0284, wR_2 = 0.0740
Final R indexes [all data]	R_1 = 0.0271, wR_2 = 0.0680	R_1 = 0.0463, wR_2 = 0.1211	R_1 = 0.0295, wR_2 = 0.0750
Largest diff. peak/hole / e Å^{-3}	0.17/-0.35	0.59/-0.81	0.34/-0.42
CCDC	2051035	2051047	2051048

S10.2.9. Crystallographic data and details of the structure refinements of compounds $Ph_2NCH{=}NSO_2Ph$ **17**, $Ph_2NC(Me){=}NSO_2Ph$ **19,** and (1-methylpyrrolidin-2-ylidene)benzenesulfonamide **20**.

	17	**19**	**20**
Empirical formula	$C_{19}H_{16}N_2O_2S$	$C_{20}H_{18}N_2O_2S$	$C_{11}H_{14}N_2O_2S$
Formula weight	336.40	350.42	238.30
Temperature/K	100.00(11)	100.01(10)	100.00(10)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a/Å	16.5728(2)	9.37570(10)	7.75339(8)
b/Å	5.43550(10)	10.2532(2)	11.53653(10)
c/Å	18.1303(2)	11.0768(2)	25.2615(2)
α/°	90	115.593(2)	90
β/°	101.7630(10)	91.0640(10)	97.2713(9)
γ/°	90	113.686(2)	90
Volume/Å^3	1598.91(4)	855.33(3)	2241.40(4)
Z	4	2	8
ρ_{calc}g/cm^3	1.397	1.361	1.412
μ/m*m*-^{1}	1.912	1.808	2.471
F(000)	704.0	368.0	1008.0
Crystal size/mm^3	0.39×0.196×0.088	0.262×0.219×0.147	0.438×0.424×0.134
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.446 to 153.314	9.102 to 153.492	7.056 to 152.94
Index ranges	-20≤h≤20, -5≤k≤6, -22≤l≤21	-10≤h≤11, -12≤k≤12, -13≤l≤13	-9≤h≤9, -14≤k≤10, -31≤l≤28
Reflections collected	13858	7531	11491
Independent reflections	3338 [R_{int} = 0.0237, R_{sigma} = 0.0185]	3540 [R_{int} = 0.0208, R_{sigma} = 0.0261]	4666 [R_{int} = 0.0191, R_{sigma} = 0.0214]
Data/restraints/parameters	3338/0/217	3540/0/227	4666/0/291
Goodness-of-fit on F^2	1.040	1.039	1.038
Final R indexes [I> = 2σ (I)]	R_1 = 0.0322, wR_2 = 0.0872	R_1 = 0.0355, wR_2 = 0.0904	R_1 = 0.0324, wR_2 = 0.0841
Final R indexes [all data]	R_1 = 0.0338, wR_2 = 0.0887	R_1 = 0.0380, wR_2 = 0.0927	R_1 = 0.0340, wR_2 = 0.0856
Largest diff. peak/hole / e Å^{-3}	0.32/-0.49	0.38/-0.56	0.32/-0.43
CCDC	2051041	2051051	2051039

S10.2.10. Crystallographic data and details of the structure refinements of compounds MeHNCH=NSO_2Ph **21a**, *p*-C_6H_5-$C_6H_4SO_2N$=$CHNMe_2$ **23h,** and *p*-Me-$C_6H_4SO_2N$=$CHNMe_2$ **23b**.

	21a	**23h**	**23b**
Empirical formula	$C_8H_{10}N_2O_2S$	$C_{15}H_{16}N_2O_2S$	$C_{10}H_{14}N_2O_2S$
Formula weight	198.24	288.36	226.29
Temperature/K	100.01(10)	99.97(15)	100.0(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P21/n$
a/Å	8.40980(10)	6.7867(3)	7.49968(10)
b/Å	7.39730(10)	8.5309(4)	25.7462(3)
c/Å	15.1632(2)	12.6966(6)	17.1284(3)
α/°	90	76.999(4)	90
β/°	95.8890(10)	77.348(4)	94.8660(13)
γ/°	90	83.351(4)	90
Volume/$Å^3$	938.32(2)	697.15(6)	3295.39(8)
Z	4	2	12
ρcalcg/cm^3	1.403	1.374	1.368
μ/m*m*-^{1}	2.835	2.089	2.488
F(000)	416.0	304.0	1440.0
Crystal size/mm^3	0.328×0.108×0.075	0.223×0.089×0.049	0.128×0.065×0.065
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.558 to 153.216	7.292 to 152.928	6.214 to 153.174
Index ranges	-10≤h≤9, -9≤k≤8, -18≤l≤19	-8≤h≤7, -10≤k≤9, -15≤l≤15	-9≤h≤9, -32≤k≤19, -21≤l≤19
Reflections collected	8201	5616	18870
Independent reflections	1957 [R_{int} = 0.0213, R_{sigma} = 0.0177]	2876 [R_{int} = 0.0108, R_{sigma} = 0.0141]	6884 [Rint = 0.0195, Rsigma = 0.0213]
Data/restraints/parameters	1957/0/123	2876/0/183	6884/0/415
Goodness-of-fit on F^2	1.056	1.077	1.148
Final R indexes [I> = 2σ (I)]	R_1 = 0.0308, wR_2 = 0.0792	R_1 = 0.0286, wR_2 = 0.0778	R1 = 0.0495, wR2 = 0.1341
Final R indexes [all data]	R_1 = 0.0314, wR_2 = 0.0797	R_1 = 0.0291, wR_2 = 0.0783	R1 = 0.0516, wR2 = 0.1353
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.41	0.29/-0.44	0.71/-0.45
CCDC	2051043	2051045	2051044

S10.2.11. Crystallographic data and details of the structure refinements of compounds *p*-F-$C_6H_4SO_2N$=$CHNMe_2$ **23c**, *p*-CF_3-$C_6H_4SO_2N$=$CHNMe_2$ **23d,** and *o*-F-$C_6H_4SO_2N$=$CHNMe_2$ **23e**.

	23c	**23d**	**23e**
Empirical formula	$C_9H_{11}FN_2O_2S$	$C_{10}H_{11}F_3N_2O_2S$	$C_9H_{11}FN_2O_2S$
Formula weight	230.26	280.27	230.26
Temperature/K	99.99(10)	100.00(10)	100.3(7)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$
a/Å	9.8618(4)	6.5646(3)	13.0075(5)
b/Å	13.77947(14)	8.3986(3)	13.3299(5)
c/Å	12.7595(6)	11.3918(6)	11.8029(4)
α/°	90	105.687(4)	90
β/°	144.027(10)	96.554(4)	91.320(3)
γ/°	90	98.490(4)	90
Volume/$Å^3$	1018.50(16)	590.16(5)	2045.96(12)
Z	4	2	8
ρcalcg/cm^3	1.502	1.577	1.495
μ/m*m*-^{1}	2.843	2.821	2.830
F(000)	480.0	288.0	960.0
Crystal size/mm^3	0.159×0.078×0.042	0.172×0.096×0.033	0.283×0.117×0.043
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.984 to 152.81	8.17 to 152.85	6.798 to 153.616
Index ranges	-12≤h≤11, -17≤k≤12, -16≤l≤15	-8≤h≤7, -10≤k≤10, -14≤l≤13	-16 ≤h≤15, -16 ≤k≤ 12, -9 ≤l≤14
Reflections collected	4910	4954	10625
Independent reflections	2108 [Rint = 0.0158, Rsigma = 0.0207]	2450 [Rint = 0.0188, Rsigma = 0.0283]	4243 [R_{int} = 0.0389, R_{sigma} = 0.0416]
Data/restraints/parameters	2108/0/138	2450/57/193	4243/0/275
Goodness-of-fit on F^2	1.071	1.036	1.122
Final R indexes [I> = 2σ (I)]	R_1 = 0.0267, wR_2 = 0.0701	R_1 = 0.0387, wR_2 = 0.1021	R_1 = 0.0569, wR_2 = 0.1536
Final R indexes [all data]	R_1 = 0.0287, wR_2 = 0.0721	R_1 = 0.0408, wR_2 = 0.1043	R_1 = 0.0610, wR_2 = 0.1561
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.35	0.48/-0.52	0.41/-0.48
CCDC	2051052	2051050	2051042

10.3 Molecular structures

Table S10.1. Selected geometrical parameters of crystallographically characterized fluorophosphonium salts.

Compound	P-F in Å	P-C [a] in Å	F-P-C [a] in °	C-P-C [a] in °
2a[OTf]	1.5582(10)	1.793	104.8	113.7
2a[NSI]	1.5589(10)	1.797	105.6	113.0
2b[OTf]	1.5533(9)	1.766	105.5	113.2
2b[NSI]	1.5475(9)	1.766	106.8	112.0
2c[H(OTf)$_2$]	1.5286(11)	1.767	106.0	112.7
[**2c**(NSI)]	1.6100(9)	1.805	92.6	119.8
2d[OTf]	1.5618(12)	1.772	103.5	114.7
4b[OTf]	1.540(3)	1.764	105.7	113.0
6^{Me}a[OTf]$_2$	1.5453(9)	1.767	105.8	112.8
6^{Me}b[OTf]$_2$	1.5392(16)	1.772	103.0	115.1
8^{Me}[OTf]$_3$	1.5431(13)	1.763	104.9	113.6

a) Average bond lengths and angles are given.

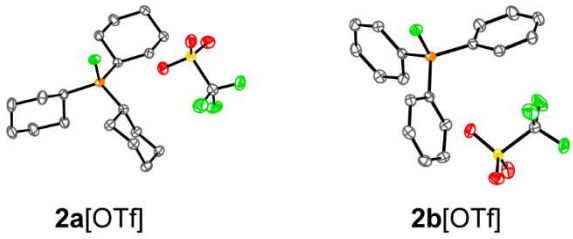


Figure S10.1. Molecular structure of **2a**,**b**[OTf] (hydrogen atoms and non-coordinating anions are omitted for clarity; ellipsoids are set at 50% probability).

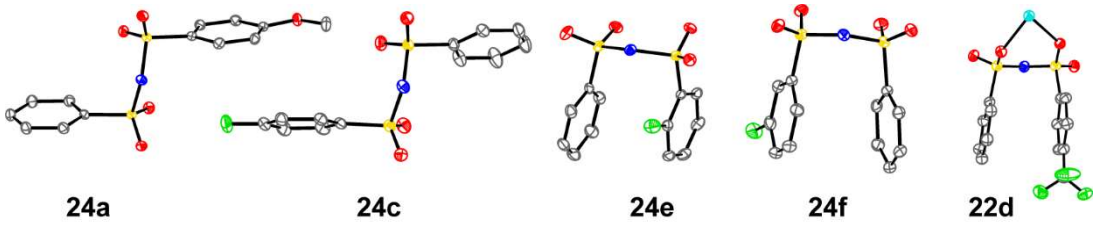


Figure S10.2. Molecular structure of **24a**,**c**,**e**,**f** and **22d** (hydrogen atoms and non-coordinating anions are omitted for clarity; ellipsoids are set at 50% probability).

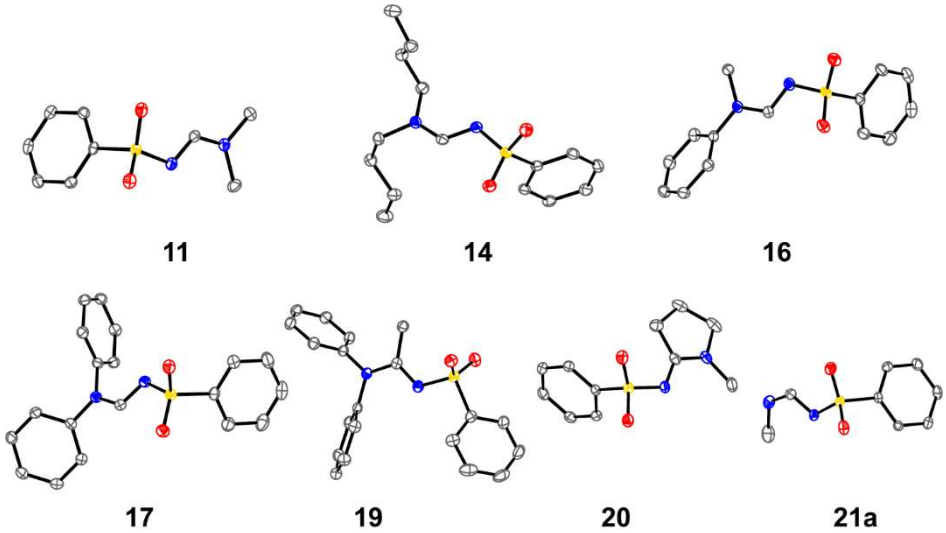


Figure S10.3. Molecular structure of **11**, **14**, **16**, **17**, **19**, **20** and **21a** (hydrogen atoms and non-coordinating anions are omitted for clarity; ellipsoids are set at 50% probability).

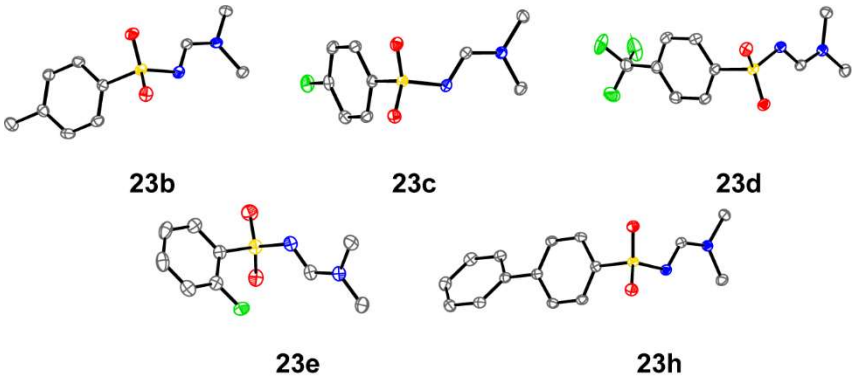


Figure S10.4. Molecular structure of **23b-e, h** (hydrogen atoms and non-coordinating anions are omitted for clarity; ellipsoids are set at 50% probability).

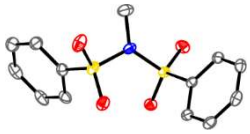


Figure S10.5. Molecular structure of **25** (hydrogen atoms and non-coordinating anions are omitted for clarity; ellipsoids are set at 50% probability).

S11 Computational methods

All calculations of GEI and FIA were computed using Gaussian 09[19] in the gas phase and in solution. The geometry optimization has been performed at the BP86/def2-TZVP level of theory[20-23]. Frequency calculations are carried out on all optimized structures, and the absence of any imaginary frequencies confirmed that each optimized structure is located at a minimum on its potential energy hypersurface. Energies are subsequently recalculated on the optimized structures at the MP2/def2-TZVP level of theory[24-26]. The Global Electrophilicity Index (GEI) and fluoride ion affinity (FIA) are calculated based on the literature reported.[27-30] We have also taken into consideration solvent effects by using COSMO[32] (solvent = acetonitrile). These calculations have been performed using the TURBOMOLE 7.2 program.[33]

The calculations of intermediates II_A and II_B shown in the main text (see Fig. 8) for substrates **22a** and **22d** were computed at the RI-PB86-D3/def2-QZVPD//RI-PB86-D3/def2-TZVP level of theory. This level of theory uses Grimme's D3[31] correction to account for dispersion effects. Moreover, it also includes diffuse functions in the basis set that is convenient when dealing with anionic substrates.

The GEI (ω/eV) values are calculated based on the chemical potential μ, and chemical hardness η, as depicted in Scheme S11.1 **I-III**.

GEI:

(I) $\omega = \mu^2/2\eta$

(II) $\mu = -(E_{HOMO} + E_{LUMO})/2$

(III) $\eta = (E_{LUMO} - E_{LUMO})$

FIA:

(IV) $R_3PF^+ + F^- \longrightarrow R_3PF_2 \quad \Delta H = -FIA$

(V) $F_2CO + F^- \longrightarrow F_3CO^- \quad \Delta H = -209\ KJ/mol$

Scheme **S11.1.** Method used to calculate GEI and FIA values.

The FIA value is defined as the negative energy change for reaction **IV**. Due to the difficulties of obtaining accurate energies for the F^- anion, the energy of the F^- anion (-261834.54 KJ/mol) is obtained by the combination of the experimentally obtained energy change for reaction **V** (-209 KJ/mol) with the calculation energies of F_2CO (-820803.50 KJ/mol) and F_3CO^- (-1082847.04 KJ/mol) (Scheme **S11.1**).

Calculation results are summarized in Table **S11.1**.

Table **S11.1.** HOMO LUMO energies and GEI .

	HOMO (eV)	**LUMO** (eV)	**GEI** (eV)
F_2CO			
2a$^+$	-14.779	0.058	1.826
2b$^+$	-12.808	-1.894	2.476
2c$^+$	-14.077	-3.368	3.552
2d$^+$	-14.357	-3.184	3.442
4a$^+$	-13.049	-2.204	2.682
4b$^+$	-13.398	-2.806	3.098
6^{Me}a^{2+}	-15.711	-5.578	5.591
6^{iPr}a^{2+}	-15.519	-5.251	5.252
6^{Me}b^{2+}	-16.444	-6.516	6.637
6^{iPr}b^{2+}	-16.088	-6.190	6.268
8^{Me}$^{3+}$	-18.516	-9.025	9.990
8^{iPr}$^{3+}$	-18.007	-8.294	8.903

Table **S11.2.** FIA values in the gas phase and in solution.

	Energy (KJ/mol)	**Energy of F$^-$ adduct** (KJ/mol)	**FIA** (Gas) (KJ/mol)	**Energy** (KJ/mol)	**Energy of F$^-$ adduct** (KJ/mol)	**FIA** (solution) (KJ/mol)
F2CO	-820803.50	-1082847.04		-817725.13	-1078992.69	
2a$^+$	-3005116.55	-3267595.01	643.9	-2993464.89	-3254800.75	277.3
2b$^+$	-2976920.74	-3239416.59	661.3	-2965905.29	-3227278.89	315.0
2c$^+$	-6880706.48	-7143330.97	790.0	-6856448.37	-7117923.03	416.1
2d$^+$	-8280099.89	-8542708.15	773.7	-8249979.32	-8511426.53	388.7
4a$^+$	-4278181.77	-4540724.36	708.1	-4262757.32	-4524166.36	350.5
4b$^+$	-5579443.87	-5842029.47	751.1	-5559607.05	-5821049.18	383.6
6^{Me}a^{2+}	-3373879.49	-3636716.76	1002.7	-3361191.95	-3622694.00	443.5
6^{iPr}a^{2+}	-3785787.33	-4048607.63	985.8	-3770847.95	-4032349.76	443.3
6^{Me}b^{2+}	-5976372.77	-6239279.50	1072.2	-5954859.05	-6216431.92	514.3
6^{iPr}b^{2+}	-6388286.56	-6651175.93	1054.8	-6364510.26	-6626076.33	507.5
8^{Me}$^{3+}$	-3770586.22	-4033749.10	1328.3	-3756397.58	-4018023.54	567.4
8^{iPr}$^{3+}$	-4594425.62	-4857541.57	1281.4	-4575699.40	-4837330.34	572.4

Figure S11.1 shows a detail of the interaction between the SO_2 group (compound **22a**) and the L_c^{iPr} ring of the catalyst (**8^{iPr}**). One O-atom of the SO_2 group basically interacts by means of an lp–π interaction and the other one by a bifurcated H-bond with two H-atoms of the isopropyl group.

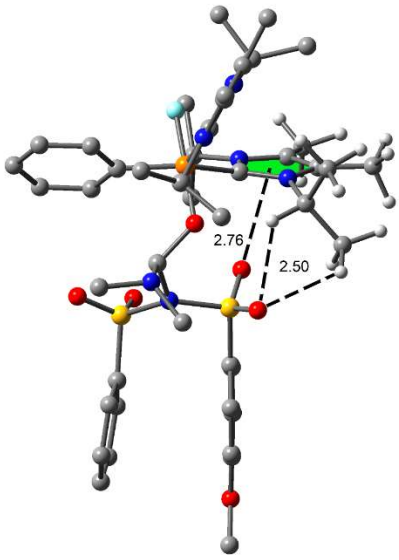


Figure S11.1. Optimized geometry of Intermediate **II_A** of **22a** +DMF + $\mathbf{8}^{i\mathbf{Pr3}+}$; Distances in Å.

Cartesian coordinates of the intermediates shown in Fig. 8 (main manuscript)

II_A (22a)

O	-0.9991177	0.3766052	-0.7485175
C	0.0645436	1.3850396	-0.9368536
N	0.1444655	1.8258881	-2.2788093
H	-0.1954345	2.2564314	-0.3351453
P	-2.2888690	0.4952489	0.3457050
F	-3.4262001	0.5725928	1.6327860
N	-4.8734019	-0.5360471	-0.4403167
N	-3.9033986	0.5742279	-2.0754151
N	-1.7613668	-1.4501226	2.3873938
N	-1.8888552	-2.3814240	0.3973574
C	-5.1454283	0.1766804	-2.5356921
C	-5.7141466	0.4574600	-3.8852033
H	-6.1178212	1.4775482	-3.9513960
H	-6.5324642	-0.2413012	-4.0901818
H	-4.9751016	0.3336334	-4.6834052
C	-5.7574632	-0.5100288	-1.5057941
C	-3.7256032	0.1430117	-0.7919808
C	-1.7647863	-2.8227214	2.5841899
C	-1.8539989	-1.1843662	1.0612402
C	-7.1240642	-1.1084642	-1.5383966
H	-7.0972565	-2.1713785	-1.8161809
H	-7.7305616	-0.5835156	-2.2848830
H	-7.6430297	-1.0184290	-0.5800565
C	-5.1567520	-1.2835089	0.8442924
H	-4.1977150	-1.3271933	1.3546911
C	-1.1873134	2.7474214	1.7106617
H	-0.4782034	2.0736029	2.1928690
C	-2.0861938	2.2883271	0.7393481
C	-1.8796565	-3.4060999	1.3396858
C	-2.9461255	3.1929665	0.0990122
H	-3.6804587	2.8505847	-0.6286814
C	-1.5216012	-0.4067633	3.4356164
H	-1.5216393	0.5325983	2.8763556
C	-2.8938828	1.3145486	-2.8960556
H	-2.1231838	1.6261754	-2.1924297
C	-1.6569216	-2.5883280	-1.0806232
H	-1.2775943	-1.6186706	-1.4134769
C	-1.5956009	-3.5167743	3.8911123
H	-2.1219968	-3.0160214	4.7091708
H	-0.5332794	-3.5922058	4.1636712
H	-1.9840364	-4.5393066	3.8185661
C	-2.8848769	4.5514766	0.4160679
H	-3.5542711	5.2498007	-0.0871228
C	-1.9843900	5.0103934	1.3800835
H	-1.9405640	6.0711521	1.6260089
C	-1.1405922	4.1060913	2.0254752
H	-0.4177817	4.4547491	2.7622374
C	-2.0001058	-4.8624554	1.0436614
H	-2.6311674	-5.0541568	0.1695111
H	-2.4627639	-5.3691437	1.8994573
H	-1.0229051	-5.3336909	0.8704943
C	-6.1273268	-0.4974111	1.7255545
H	-7.1375695	-0.4560100	1.3004369
H	-6.2038771	-1.0021174	2.6980802
H	-5.7702858	0.5237564	1.8943702
C	-5.5899841	-2.7336243	0.6090368
H	-5.4517697	-3.2707446	1.5567173
H	-6.6428854	-2.8389924	0.3317602
H	-4.9709983	-3.2292813	-0.1463967
C	-2.2378649	0.3498023	-3.8804927
H	-1.7098716	-0.4459839	-3.3421202
H	-2.9613572	-0.1059218	-4.5676384
H	-1.5045503	0.9005441	-4.4798751
C	-3.4588483	2.5808446	-3.5431905

H	-4.1119381	3.1371071	-2.8584541
H	-2.6108012	3.2318798	-3.7907269
H	-4.0053248	2.3886357	-4.4722910
C	-2.6623172	-0.3277477	4.4470140
H	-2.6599977	-1.1663970	5.1531891
H	-2.5413659	0.5905537	5.0360471
H	-3.6339527	-0.2810820	3.9419251
C	-0.1316345	-0.5628658	4.0518007
H	0.0761157	0.3277092	4.6595090
H	-0.0641168	-1.4347243	4.7124909
H	0.6344331	-0.6299463	3.2700178
C	-2.9132413	-2.9526648	-1.8680166
H	-2.6271828	-3.0697791	-2.9221441
H	-3.3408895	-3.9098614	-1.5433561
H	-3.6927449	-2.1868295	-1.8212402
C	-0.5514021	-3.6237629	-1.3253893
H	-0.9404511	-4.6475676	-1.3487132
H	-0.1019947	-3.4121459	-2.3021433
H	0.2476299	-3.5478451	-0.5813834
S	1.5937465	-0.8569482	-0.2284245
O	0.8982798	-1.3806426	0.9398847
N	1.3367888	0.8550838	-0.3352391
S	2.1274148	1.9126720	0.7956851
O	1.5017970	3.2044410	0.5674948
O	2.0900765	1.2984860	2.1115479
C	3.8079455	2.0354535	0.2348235
C	4.8384101	1.8053704	1.1472606
C	4.0587266	2.5003589	-1.0611811
C	6.1552092	2.0384155	0.7420456
H	4.6104502	1.4523304	2.1509897
C	5.3763862	2.7191274	-1.4531677
H	3.2349839	2.6949229	-1.7460048
C	6.4229838	2.4904281	-0.5511061
H	6.9701335	1.8631413	1.4440765
H	5.5884645	3.0829430	-2.4585676
C	3.3108082	-1.0289259	0.0156714
C	4.1732681	-0.8701811	-1.0773425
C	3.8043769	-1.3507265	1.2911741
C	5.5421268	-1.0053407	-0.8977147
H	3.7683030	-0.6401262	-2.0618872
C	5.1675740	-1.4962296	1.4684725
H	3.1157185	-1.4644197	2.1256094
C	6.0502108	-1.3045744	0.3836667
H	6.2081803	-0.8685667	-1.7459869
H	5.5883749	-1.7388943	2.4435599
O	1.2247494	-1.3393318	-1.5481210
C	0.2425509	3.2875521	-2.4077197
H	-0.4904073	3.7711998	-1.7480419
H	1.2407791	3.6830540	-2.1514198
H	0.0127779	3.5670639	-3.4441554
C	0.9912609	1.0968231	-3.2182312
H	0.7043980	0.0442759	-3.2604023
H	0.8735835	1.5408456	-4.2143956
H	2.0604826	1.1469238	-2.9419776
O	7.3580604	-1.4126191	0.6775986
C	8.3273682	-1.2282096	-0.3723742
H	8.2059724	-1.9895693	-1.1573780
H	8.2470382	-0.2195420	-0.8056072
H	9.3024117	-1.3479182	0.1085498
H	7.4520849	2.6787609	-0.8585589

II_B (22a)

O	-1.0020338	0.4165303	-0.7041606
C	0.0579819	1.4401391	-0.8714516
N	0.1251707	1.9292842	-2.1987865
H	-0.2058114	2.2867361	-0.2380053
P	-2.3099887	0.5198314	0.3627582

F	-3.4405912	0.5875191	1.6519192
N	-4.8705549	-0.5544401	-0.4413342
N	-3.8770788	0.5187764	-2.0875112
N	-1.7540871	-1.4101256	2.4160063
N	-1.8879287	-2.3592559	0.4359469
C	-5.1052381	0.0950893	-2.5615118
C	-5.6440544	0.3221485	-3.9331933
H	-6.0578511	1.3340871	-4.0457756
H	-6.4486625	-0.3937908	-4.1331808
H	-4.8833537	0.1795061	-4.7078127
C	-5.7335123	-0.5656492	-1.5243522
C	-3.7230393	0.1261340	-0.7884108
C	-1.7506226	-2.7811653	2.6257272
C	-1.8574296	-1.1562625	1.0888357
C	-7.0952384	-1.1744113	-1.5669380
H	-7.0567399	-2.2428177	-1.8214478
H	-7.6926631	-0.6695739	-2.3344630
H	-7.6305333	-1.0675683	-0.6194199
C	-5.1681038	-1.2745626	0.8556021
H	-4.2163755	-1.3003190	1.3806065
C	-1.3072537	2.8457585	1.6875511
H	-0.5970698	2.2061729	2.2126691
C	-2.1709084	2.3314229	0.7113246
C	-1.8669502	-3.3760650	1.3871815
C	-3.0362242	3.1940343	0.0223555
H	-3.7457238	2.8117391	-0.7099031
C	-1.5008672	-0.3556154	3.4495999
H	-1.4886477	0.5757400	2.8752437
C	-2.8600822	1.2529281	-2.9059062
H	-2.1160164	1.6074866	-2.1934625
C	-1.6517167	-2.5756317	-1.0392031
H	-1.2910435	-1.6018151	-1.3812954
C	-1.5776795	-3.4618461	3.9392028
H	-2.0958044	-2.9477836	4.7543930
H	-0.5144573	-3.5420097	4.2068025
H	-1.9744443	-4.4821688	3.8806829
C	-3.0147000	4.5638954	0.2943147
H	-3.6903304	5.2276765	-0.2459581
C	-2.1448633	5.0774907	1.2585251
H	-2.1300236	6.1469125	1.4676971
C	-1.2957741	4.2155004	1.9535956
H	-0.5980747	4.6058823	2.6936760
C	-1.9739558	-4.8358512	1.1033314
H	-2.6024548	-5.0411863	0.2304284
H	-2.4320212	-5.3399149	1.9631783
H	-0.9921128	-5.2990626	0.9345923
C	-6.1563839	-0.4739826	1.7031413
H	-7.1593188	-0.4460979	1.2599705
H	-6.2471031	-0.9565767	2.6855990
H	-5.8057402	0.5522667	1.8547260
C	-5.5864969	-2.7330108	0.6474087
H	-5.4666223	-3.2447625	1.6115503
H	-6.6317796	-2.8538222	0.3486438
H	-4.9459180	-3.2430018	-0.0802477
C	-2.1544613	0.2723701	-3.8393755
H	-1.6062896	-0.4806872	-3.2614841
H	-2.8499642	-0.2361242	-4.5187448
H	-1.4307522	0.8244077	-4.4494694
C	-3.4334086	2.4837853	-3.6112329
H	-4.1200532	3.0464175	-2.9656925
H	-2.5923407	3.1459621	-3.8527456
H	-3.9450945	2.2494593	-4.5504174
C	-2.6363738	-0.2503319	4.4642224
H	-2.6436939	-1.0852985	5.1750201
H	-2.4972937	0.6688458	5.0478816
H	-3.6095383	-0.1915409	3.9638072
C	-0.1117864	-0.5225582	4.0649331

H	0.1195296	0.3818760	4.6428767
H	-0.0623410	-1.3742279	4.7531124
H	0.6493670	-0.6300099	3.2834533
C	-2.8984770	-2.9739360	-1.8254526
H	-2.6077349	-3.0920209	-2.8782059
H	-3.3045021	-3.9382397	-1.4944796
H	-3.6958138	-2.2266900	-1.7859127
C	-0.5256713	-3.5916813	-1.2725694
H	-0.8954458	-4.6228762	-1.2844703
H	-0.0801150	-3.3825113	-2.2515736
H	0.2701171	-3.4926140	-0.5279424
S	1.5753457	-0.7957077	-0.2477268
O	0.9208138	-1.3656478	0.9223403
N	1.3331385	0.9030369	-0.2990597
S	2.1108170	1.9389070	0.8960777
O	1.4578466	3.2212572	0.6914808
O	2.0427958	1.2699114	2.1834660
C	3.7756914	2.0677104	0.3657527
C	4.8093369	1.6669787	1.2249319
C	4.0544021	2.6549996	-0.8732124
C	6.1228088	1.8401901	0.8266138
H	4.5733733	1.2237220	2.1903658
C	5.3729593	2.8211672	-1.2789323
H	3.2422932	2.9872444	-1.5182959
C	6.4202466	2.4081622	-0.4287650
H	6.9487009	1.5401444	1.4704727
H	5.5822531	3.2797630	-2.2429420
C	3.3187581	-1.0044997	-0.0648390
C	4.1456621	-0.7739620	-1.1713227
C	3.8174511	-1.4880384	1.1483626
C	5.5085041	-1.0305855	-1.0480740
H	3.7219876	-0.4103112	-2.1061539
C	5.1827437	-1.7584143	1.2473264
H	3.1434866	-1.6447042	1.9881811
C	6.0231538	-1.5290823	0.1548355
H	6.1710895	-0.8521649	-1.8943633
H	5.5905138	-2.1451256	2.1811660
O	1.1800209	-1.2553869	-1.5686668
C	0.1587419	3.3984332	-2.2719011
H	-0.6074510	3.8250760	-1.6105112
H	1.1351006	3.8244684	-1.9816649
H	-0.0641248	3.7068202	-3.3015564
C	1.0267249	1.2838761	-3.1491892
H	0.8207344	0.2136045	-3.2117442
H	0.8766059	1.7359584	-4.1375108
H	2.0881617	1.4152878	-2.8680480
H	7.0900018	-1.7370765	0.2395236
O	7.7307042	2.5104256	-0.7219032
C	8.1236154	3.1241072	-1.9637363
H	7.7759782	4.1670704	-2.0139266
H	9.2171877	3.1012911	-1.9657209
H	7.7406759	2.5548616	-2.8249431

II_B (22d)

O	-1.0931255	0.1719733	-0.9607234
C	0.0888690	0.9467918	-1.1619095
N	0.3295535	1.0705850	-2.5497539
H	-0.0445898	1.9643728	-0.7849397
P	-2.2463163	0.3201423	0.2845652
F	-3.1448205	0.3163561	1.6945416
N	-5.0659999	-0.1083474	-0.2248036
N	-4.0376377	0.6386690	-2.0261707
N	-1.3031091	-1.7788382	2.1018046
N	-1.6051080	-2.5165403	0.0537157
C	-5.3984687	0.7161831	-2.2656241
C	-6.0497666	1.2271882	-3.5066313
H	-5.9974952	2.3231466	-3.5660774

H	-7.1064735	0.9401623	-3.5089750
H	-5.6043688	0.8198842	-4.4195983
C	-6.0408223	0.2599124	-1.1342588
C	-3.8177313	0.1617428	-0.7534582
C	-0.9687063	-3.1246463	2.0967717
C	-1.6915818	-1.4033083	0.8489650
C	-7.5176485	0.1950838	-0.9279424
H	-7.9352575	-0.7733275	-1.2361954
H	-7.9990352	0.9726117	-1.5321538
H	-7.8009337	0.3763287	0.1121017
C	-5.3943763	-0.8610700	1.0501833
H	-4.4406119	-1.2908429	1.3608465
C	-1.8978566	2.6647075	1.8753664
H	-1.9322758	2.0216205	2.7498500
C	-1.9931546	2.1275177	0.5821868
C	-1.1716105	-3.5907412	0.8150000
C	-1.9508684	2.9992912	-0.5198959
H	-2.0013725	2.6147577	-1.5342267
C	-1.2256547	-0.8868236	3.3105562
H	-1.2535876	0.1217585	2.8978932
C	-3.0167179	0.8808942	-3.1032663
H	-2.0552824	0.8469176	-2.5932723
C	-2.1277404	-2.6212853	-1.3464733
H	-2.1376037	-1.5860490	-1.6936344
C	-0.4452395	-3.8930109	3.2598572
H	-0.9937109	-3.6802226	4.1841166
H	0.6180480	-3.6773095	3.4306152
H	-0.5399345	-4.9667636	3.0640413
C	-1.8231021	4.3739011	-0.3334835
H	-1.8022524	5.0342073	-1.2005941
C	-1.7042479	4.8967241	0.9560216
H	-1.5835131	5.9700842	1.1027021
C	-1.7378378	4.0376718	2.0554497
H	-1.6415246	4.4362084	3.0652686
C	-0.9451650	-4.9720235	0.3063109
H	-1.8148620	-5.3723030	-0.2284200
H	-0.7412604	-5.6433468	1.1468620
H	-0.0783179	-5.0115831	-0.3667450
C	-5.9091017	0.0741594	2.1457066
H	-6.9178230	0.4439044	1.9252436
H	-5.9716846	-0.4905155	3.0858568
H	-5.2465182	0.9301398	2.2995259
C	-6.3555863	-2.0341194	0.8012027
H	-6.2038709	-2.7634664	1.6075640
H	-7.4077535	-1.7356995	0.8328930
H	-6.1671249	-2.5465446	-0.1498652
C	-3.0447229	-0.2682746	-4.1138203
H	-2.8831684	-1.2372855	-3.6276657
H	-3.9859691	-0.3203402	-4.6733346
H	-2.2367377	-0.1140969	-4.8393372
C	-3.1490894	2.2586315	-3.7652281
H	-3.4721756	3.0302295	-3.0553332
H	-2.1584016	2.5442554	-4.1433391
H	-3.8376472	2.2607453	-4.6170664
C	-2.4410415	-1.1168518	4.2092577
H	-2.4409827	-2.1273628	4.6379634
H	-2.4049005	-0.4055839	5.0452052
H	-3.3803509	-0.9625701	3.6671357
C	0.0982674	-1.0024511	4.0715206
H	0.2436410	-0.0626227	4.6184440
H	0.0962535	-1.8153968	4.8050441
H	0.9383008	-1.1239363	3.3822488
C	-3.5543166	-3.1667808	-1.3216827
H	-3.9831809	-3.1215344	-2.3318873
H	-3.5805250	-4.2142994	-0.9957146
H	-4.1890978	-2.5840133	-0.6498558
C	-1.2443598	-3.4102200	-2.3171067

H	-1.4165199	-4.4896823	-2.2563437
H	-1.5170450	-3.1056676	-3.3371010
H	-0.1828596	-3.1985279	-2.1729925
S	1.7945650	-1.1222501	-0.1252093
O	1.6346351	-1.5770307	1.2460019
N	1.2554707	0.4901041	-0.2581792
S	1.5367961	1.6034168	1.0635477
O	1.3582837	2.9158727	0.4688263
O	0.7140181	1.2061785	2.1917555
C	3.2377595	1.3765299	1.4821546
C	3.5571561	0.7463333	2.6853834
C	4.2179391	1.8906189	0.6240526
C	4.9005255	0.6218528	3.0394432
H	2.7667217	0.3651689	3.3278809
C	5.5528483	1.7473663	0.9804831
H	3.9337503	2.3936072	-0.2987829
C	5.8883280	1.1135350	2.1850639
H	5.1796853	0.1396104	3.9747659
H	6.3390192	2.1272815	0.3291601
C	3.5287808	-1.0721215	-0.5030071
C	3.9522056	-0.5568838	-1.7330562
C	4.4331407	-1.6095194	0.4164192
C	5.3116046	-0.5653017	-2.0365475
H	3.2307740	-0.1530607	-2.4400539
C	5.7919759	-1.6140796	0.0971951
H	4.0760960	-2.0011720	1.3666474
C	6.2308963	-1.0900369	-1.1206400
H	5.6557238	-0.1650902	-2.9902438
H	6.5117098	-2.0162024	0.8092024
O	1.1009590	-1.8159136	-1.1938471
C	1.2867443	2.1314376	-2.8625379
H	1.0419372	3.0372010	-2.2927521
H	2.3279911	1.8511811	-2.6192295
H	1.2307988	2.3588540	-3.9345481
C	0.4242073	-0.1036142	-3.4137098
H	-0.3148502	-0.8489794	-3.1100013
H	0.2134069	0.2130518	-4.4447261
H	1.4118317	-0.5899970	-3.3960202
H	7.2948304	-1.0888429	-1.3571149
C	7.3578475	0.9738966	2.5335690
F	7.5529939	0.2723939	3.6724950
F	7.9371711	2.1880594	2.6820244
F	8.0218772	0.3266570	1.5327491

II_A (22d)

O	-0.9690479	0.3909261	-0.6825746
C	0.0926702	1.4058321	-0.8386891
N	0.1748450	1.9048041	-2.1590436
H	-0.1602594	2.2506451	-0.1981937
P	-2.2956244	0.5079432	0.3689498
F	-3.4283913	0.5861026	1.6510510
N	-4.8631413	-0.5284885	-0.4538773
N	-3.8441344	0.5306087	-2.0941553
N	-1.7714981	-1.4364245	2.4174698
N	-1.9029431	-2.3766595	0.4329642
C	-5.0778731	0.1300801	-2.5735109
C	-5.6082280	0.3704112	-3.9462211
H	-6.0024433	1.3902941	-4.0572135
H	-6.4257670	-0.3295807	-4.1502113
H	-4.8486204	0.2154039	-4.7194471
C	-5.7218588	-0.5217120	-1.5400246
C	-3.7023488	0.1329512	-0.7949056
C	-1.7823113	-2.8082263	2.6218893
C	-1.8652867	-1.1762446	1.0904605
C	-7.0940870	-1.1057910	-1.5894879
H	-7.0737624	-2.1736518	-1.8485360
H	-7.6798236	-0.5872884	-2.3569087

H	-7.6305700	-0.9934282	-0.6433570
C	-5.1778760	-1.2487983	0.8394230
H	-4.2285802	-1.2923414	1.3679114
C	-1.2890551	2.8256932	1.7045830
H	-0.5980883	2.1782423	2.2453737
C	-2.1407989	2.3195494	0.7135241
C	-1.8969448	-3.3973460	1.3801711
C	-2.9829372	3.1913040	0.0079692
H	-3.6843592	2.8167328	-0.7357084
C	-1.5172112	-0.3887256	3.4579607
H	-1.4930356	0.5451387	2.8879099
C	-2.8091880	1.2424939	-2.9096341
H	-2.0590797	1.5812345	-2.1956306
C	-1.6667399	-2.5901187	-1.0426145
H	-1.2962566	-1.6186063	-1.3808884
C	-1.6237546	-3.4958430	3.9336098
H	-2.1411830	-2.9799298	4.7480232
H	-0.5629506	-3.5885302	4.2068135
H	-2.0307827	-4.5117101	3.8688246
C	-2.9500347	4.5613833	0.2783903
H	-3.6085920	5.2320415	-0.2743126
C	-2.0910100	5.0665632	1.2564717
H	-2.0670613	6.1361025	1.4641458
C	-1.2649427	4.1956787	1.9682490
H	-0.5768561	4.5791749	2.7208752
C	-2.0149214	-4.8551326	1.0904093
H	-2.6412647	-5.0524147	0.2141834
H	-2.4808387	-5.3584256	1.9464393
H	-1.0361982	-5.3259933	0.9246926
C	-6.1571387	-0.4363551	1.6861982
H	-7.1578673	-0.3921115	1.2395244
H	-6.2590224	-0.9213585	2.6663895
H	-5.7925313	0.5841642	1.8431808
C	-5.6189320	-2.6994205	0.6233363
H	-5.5128751	-3.2165228	1.5861662
H	-6.6644401	-2.8018277	0.3186874
H	-4.9831734	-3.2173935	-0.1028943
C	-2.1246880	0.2460279	-3.8422788
H	-1.5935450	-0.5195493	-3.2648253
H	-2.8309918	-0.2480494	-4.5209635
H	-1.3901425	0.7812523	-4.4543707
C	-3.3528351	2.4853918	-3.6177396
H	-4.0308017	3.0627600	-2.9762194
H	-2.4968106	3.1297862	-3.8551636
H	-3.8643772	2.2618137	-4.5595608
C	-2.6594027	-0.2784793	4.4645968
H	-2.6787111	-1.1161281	5.1719226
H	-2.5176032	0.6371861	5.0530694
H	-3.6284013	-0.2101439	3.9573752
C	-0.1342933	-0.5698519	4.0831956
H	0.0990271	0.3289084	4.6692193
H	-0.0962061	-1.4260312	4.7663206
H	0.6326502	-0.6790548	3.3075178
C	-2.9165252	-2.9730016	-1.8316189
H	-2.6257808	-3.0928240	-2.8841666
H	-3.3335727	-3.9332237	-1.5027114
H	-3.7054299	-2.2169447	-1.7917584
C	-0.5512534	-3.6173776	-1.2788215
H	-0.9327623	-4.6440575	-1.2977559
H	-0.1007324	-3.4083769	-2.2556401
H	0.2434279	-3.5332736	-0.5312064
S	1.5863574	-0.8600710	-0.2209471
O	0.9257127	-1.4352372	0.9412486
N	1.3639684	0.8447192	-0.2600113
S	2.1548421	1.8515780	0.9373782
O	1.5057905	3.1415937	0.7843706
O	2.1286036	1.1507636	2.2081074

C	3.8257720	2.0159814	0.3704777
C	4.8667419	1.7035911	1.2469731
C	4.0626267	2.5655348	-0.8948793
C	6.1804821	1.9329900	0.8322174
H	4.6489951	1.2873285	2.2287861
C	5.3784080	2.7796076	-1.2964660
H	3.2315524	2.8254887	-1.5481890
C	6.4355939	2.4617355	-0.4346375
H	7.0049020	1.6868794	1.5010080
H	5.5817579	3.2053936	-2.2790160
C	3.3309828	-1.0548492	-0.0230670
C	4.1602968	-0.8159830	-1.1234816
C	3.8329034	-1.4784927	1.2107657
C	5.5340537	-0.9763939	-0.9718029
H	3.7349921	-0.5048283	-2.0759887
C	5.2076139	-1.6515970	1.3455346
H	3.1563189	-1.6459579	2.0459061
C	6.0512486	-1.3824266	0.2624903
H	6.2056462	-0.7741671	-1.8039198
H	5.6303550	-1.9682180	2.2984104
O	1.2052274	-1.3073290	-1.5486433
C	7.5488366	-1.5369876	0.4488497
F	8.2461124	-0.9112971	-0.5292785
F	7.9441702	-1.0058717	1.6384193
F	7.9059344	-2.8428673	0.4472930
H	7.4641071	2.6323567	-0.7526446
C	0.2455667	3.3731596	-2.2234266
H	-0.5097030	3.8137922	-1.5588322
H	1.2317937	3.7749144	-1.9332082
H	0.0286077	3.6927449	-3.2507598
C	1.0435879	1.2347213	-3.1227261
H	0.7985139	0.1731228	-3.1910228
H	0.9015334	1.6991105	-4.1063255
H	2.1117807	1.3242095	-2.8521598

S12 References

1. M. Reißmann, A. Schäfer, S. Jung and T. Müller, Silylium Ion/Phosphane Lewis Pairs, *Organometallics.*, 2013, **32**, 6736-6744.
2. A. M. Trzeciak, H. Bartosz-Bechowski, Z. Ciunik, K. Niesyty and J. J. Ziólkowski, Structural studies of $PdCl_2L_2$ complexes with fluorinated phosphines, phosphites, and phosphinites as precursors of benzyl bromide carbonylation catalysts, and and X-ray crystal structure of cis-$PdCl_2[PPh_2(OEt)]_2$, *Can J Chemistry*, 2001, **79**, 752-759.
3. A. Jakab, Z. Dalicsek, T. Holczbauer, A. Hamza, I. Pápai, Z. Finta, G. Timári and T. Soós, Superstable Palladium(0) Complex as an Air- and Thermostable Catalyst for Suzuki Coupling Reactions, *Eur. J. Org. Chem.*, 2015, **2015**, 60-66.
4. F. D. Henne, A. T. Dickschat, F. Hennersdorf, K. O. Feldmann and J. J. Weigand, Synthesis of Selected Cationic Pnictanes $[L_nPnX_{3-n}]^{n+}$ (L = Imidazolium-2-yl; Pn = P, As; n = 1–3) and Replacement Reactions with Pseudohalogens, *Inorg. Chem.*, 2015, **54**, 6849-6861.
5. Y. Brinkmann, R. J. Madhushaw, R. Jazzar, G. Bernardinelli and E. P. Kündig, Chiral ruthenium Lewis acid-catalyzed nitrile oxide cycloadditions, *Tetrahedron*, 2007, **63**, 8413-8419.
6. S. Yogendra, Dissertation, 2017.
7. C. Yin, Z. Liu and Q. Cai, Optimization of the synthesis process of dibenzenesulfonimide, *Chemical Engineer*, 2009, **23**, 59-60.
8. Y. Sakakibara, E. Ito, T. Kawakami, S. Yamada, K. Murakami and K. Itami, Direct Coupling of Naphthalene and Sulfonimides Promoted by DDQ and Blue Light, *Chem. Lett.*, 2017, **46**, 1014-1016.
9. V. Bocanegra-Garcia, J. C. Villalobos-Rocha, B. Nogueda-Torres, M. E. Lemus-Hernandez, A. Camargo-Ordonez, N. M. Rosas-Garcia and G. Rivera, Synthesis and Biological Evaluation of New Sulfonamide Derivatives as Potential Anti-Trypanosoma cruzi Agents, *Med Chem*, 2012, **8**, 1039-1044.
10. A. Camargo-Ordonez, C. Moreno-Reyes, F. Olazaran-Santibanez, S. Martinez-Hernandez, V. Bocanegra-Garcia and G. Rivera, Efficient Synthesis of Sulfonamide Derivatives on Solid Supports Catalyzed Using Solvent-Free and Microwave-Assisted Methods, *Quim. Nova.*, 2011, **34**, 787-791.
11. S. Chen, Y. Xu and X. Wan, Direct Condensation of Sulfonamide and Formamide: NaI-Catalyzed Synthesis of N-Sulfonyl Formamidine Using TBHP as Oxidant, *Org Lett*, 2011, **13**, 6152-6155.
12. W. Z. Bi, W. J. Zhang, Z. J. Li, X. Y. Xia, X. L. Chen, L. B. Qu and Y. F. Zhao, Air-Induced One-Pot Synthesis of N-Sulfonylformamidines from Sulfonyl Chlorides, NaN3, and Tertiary/Secondary Amines, *Eur. J. Org. Chem.*, 2019, **2019**, 6071-6076.
13. P. Jakobsen and S. Treppendahl, On the structure of n-sulphonylformamidines, *Tetrahedron*, 1981, **37**, 829-831.
14. M. Aswad, J. Chiba, T. Tomohiro and Y. Hatanaka, Coupling reaction of thioamides with sulfonyl azides: an efficient catalyst-free click-type ligation under mild conditions, *Chem Commun*, 2013, **49**, 10242-10244.
15. M. Gazvoda, M. Kocevar and S. Polanc, In Situ Formation of Vilsmeier Reagents Mediated by Oxalyl Chloride: a Tool for the Selective Synthesis of N-Sulfonylformamidines, *Eur. J. Org. Chem.*, 2013, **2013**, 5381-5386.
16. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
17. G. Sheldrick, A short history of SHELX, *Acta Crystallogr. A*, 2008, **64**, 112-122.
18. G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallogr. A*, 2015, **71**, 3-8.
19. Gaussian 09, Revision E.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, J. A., Jr.; 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.

20. A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys Rev A Gen Phys*, 1988, **38**, 3098-3100.
21. J. P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys Rev B Condens Matter*, 1986, **33**, 8822-8824.
22. F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
23. F. Weigend, Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
24. M. J. Frisch, M. Headgordon and J. A. Pople, A Direct Mp2 Gradient-Method, *Chem. Phys. Lett.*, 1990, **166**, 275-280.
25. S. Sæbø and J. Almlöf, Avoiding the integral storage bottleneck in LCAO calculations of electron correlation, *Chem. Phys. Lett.*, 1989, **154**, 83-89.
26. M. Head-Gordon, J. A. Pople and M. J. Frisch, MP2 energy evaluation by direct methods, *Chem. Phys. Lett.*, 1988, **153**, 503-506.
27. A. R. Jupp, T. C. Johnstone and D. W. Stephan, Improving the Global Electrophilicity Index (GEI) as a Measure of Lewis Acidity, *Inorg. Chem.*, 2018, **57**, 14764-14771.
28. R. G. Parr, L. Von Szentpaly and S. B. Liu, Electrophilicity index, *J. Am. Chem. Soc.*, 1999, **121**, 1922-1924.
29. A. R. Jupp, T. C. Johnstone and D. W. Stephan, The global electrophilicity index as a metric for Lewis acidity, *Dalton Trans.*, 2018, **47**, 7029-7035.
30. P. Pérez, L. R. Domingo, A. Aizman and R. Contreras, in *Theoretical Aspects of Chemical Reactivity*, ed. A. Toro-Labbé, Elsevier, 2007, vol. 19, pp. 139-201.