Supporting Information

Uncatalyzed Direct Transfer of Sulfonylimino Group of Imino-λ^3-Bromane to *N*-Heterocycles and Trialkylamines: Synthesis of *N*-Iminoammonium Ylides under Metal-Free Conditions

Masahito Ochiai,* Yufuko Kawano, Takao Kaneaki, Norihiro Tada, and Kazunori Miyamoto

Graduate School of Pharmaceutical Sciences, University of Tokushima, 1-78 Shomachi, Tokushima 770-8505, Japan
E-mail: mochiai@ph.tokushima-u.ac.jp

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General Information. IR spectra were recorded on Perkin Elmer 1720 FT-IR spectrometers. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 or JNM-AL400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on either a JEOL JMX-SX 102A, Waters LCT Premier, or SHIMADZU Model GCMS-QP 505 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254). Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected. Dichloromethane and acetonitrile were dried over CaH_2 and distilled.

Substrates. [*p*-(Trifluoromethyl)phenyl][*N*-(trifluoromethanesulfonyl)imino]-λ^3-bromane **1** was prepared according to a literature method.[1]

General Procedure for the Synthesis of *N*-Triflyliminoammonium Ylides. A Typical Example (Table 1, entry 1): Pyridinium (Trifluoromethanesulfonyl)imide (2a).[2] To a stirred solution of sulfonylimino-λ^3-bromane **1** (29 mg, 0.08 mmol) in acetonitrile (2.5 mL) was added pyridine (6.2 mg, 0.08 mmol) at room temperature under argon and the mixture was stirred for 10 min. The reaction mixture was evaporated under an aspirator vacuum to give a pale yellow solid, which was washed with hexane by decantation at room temperature. Silica gel column chromatography using dichloromethane and ethyl acetate gave the *N*-triflyliminopyridinium ylide **2a**[2] (17.8 mg, 100%): colorless needles (recrystallized from dichloromethane-hexane); mp 113-115 °C; IR (neat) 3120, 1620, 1475, 1335, 1200-1130, 964, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 6.1 Hz, 2H), 8.19 (t, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 7.7, 6.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 140.7, 127.1, 121.6 (q, $^1J_{CF}$ = 325.5 Hz); MS (ESI, positive) *m/z* 249 [(M+Na)$^+$]. Anal. Calcd for $C_6H_5F_3N_2O_2S$: C, 31.86; H, 2.21; N, 12.39. Found: C, 31.60; H, 1.81; N, 12.72.

2-Methylpyridinium (Trifluoromethanesulfonyl)imide (2b): colorless prisms (recrystallized from dichloromethane-hexane); mp 113-115 °C; IR (neat) 3141, 1622, 1496, 1336, 1200-1110, 1039, 953, 810, 789, 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 6.5, 1.3 Hz, 1H), 8.03 (m, 1H), 7.67 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.62 (m, 1H), 2.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 146.4, 139.6, 128.3, 124.3, 121.4 (q, $^1J_{CF}$ = 325.3 Hz), 20.2; HRMS (ESI, positive) calcd for $C_7H_7F_3N_2NaO_2S$ [(M+Na)$^+$] 263.0078, found 263.0070. Anal. Calcd for $C_7H_7F_3N_2O_2S{\cdot}1/6H_2O$: C, 34.57; H, 3.04; N, 11.52. Found: C, 34.32; H, 3.33; N, 11.82.

3-Methylpyridinium (Trifluoromethanesulfonyl)imide (2c):[3] colorless prisms (recrystallized from dichloromethane-hexane); mp 113-115 °C; IR (neat) 3130, 1618, 1489, 1336, 1267, 1230-1110, 1026, 980, 860, 804, 746, 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.46 (1H), 8.47 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 142.6, 141.5, 138.6, 126.4, 121.5 (q, $^1J_{CF}$ = 325.9 Hz), 18.6; HRMS (ESI, positive) calcd for $C_7H_7F_3N_2NaO_2S$ [(M+Na)$^+$] 263.0078, found 263.0076. Anal. Calcd for $C_7H_7F_3N_2O_2S$: C, 35.00; H, 2.94; N, 11.66. Found: C, 34.76; H, 3.13; N, 11.75.

4-Methylpyridinium (Trifluoromethanesulfonyl)imide (2d): colorless prisms (recrystallized from dichloromethane-hexane); mp 152-154 °C; IR (neat) 3126, 1631, 1498, 1392, 1336, 1240-1110, 949, 839, 623, 590 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.3 Hz, 2H), 7.58 (d, *J* = 6.3Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 144.6, 127.7, 121.5 (q, $^1J_{CF}$ = 325.7 Hz), 21.8; HRMS (ESI, positive) calcd for $C_7H_7F_3N_2NaO_2S$ [(M+Na)$^+$] 263.0078, found 263.0079. Anal. Calcd for $C_7H_7F_3N_2O_2S$: C, 35.00; H, 2.94; N, 11.66. Found: C, 34.76; H, 3.00; N, 11.70.

3,5-Dimethylpyridinium (Trifluoromethanesulfonyl)imide (2e): colorless plates (recrystallized from ethyl acetate-hexane); mp 163-165 °C; IR (neat) 3101, 1599, 1479, 1338, 1300, 1174, 1138, 1055, 879, 660, 607cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 2H), 7.76 (s, 1H), 2.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 142.2, 137.6, 121.6 (q, $^{1}J_{CF}$ = 325.3 Hz), 18.5; HRMS (ESI, positive) calcd for $C_8H_9F_3N_2NaO_2S$ [(M+Na)$^+$] 277.0235, found 277.0250. Anal. Calcd for $C_8H_9F_3N_2O_2S$: C, 37.79; H, 3.57; N, 11.02. Found: C, 37.72; H, 3.54; N, 11.04.

2,4,6-Trimethylpyridinium (Trifluoromethanesulfonyl)imide (2f): a white powder (recrystallized from acetone-hexane); mp 89-91 °C; IR (neat) 2918, 1633, 1566, 1477, 1333, 1210-1120, 1036, 970, 935, 631cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.28 (s, 2H), 2.80 (s, 6H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 152.0, 126.8, 120.8 (q, $^{1}J_{CF}$ = 326.0 Hz), 21.2, 21.1; HRMS (ESI, positive) calcd for $C_9H_{11}F_3N_2NaO_2S$ [(M+Na)$^+$] 291.0391, found 291.0388.

4-Chloropyridinium (Trifluoromethanesulfonyl)imide (2g): colorless prisms (recrystallized from ethyl acetate-hexane); mp 156-158 °C; IR (neat) 3120, 1614, 1471, 1446, 1344, 1230-1090, 953, 843, 793, 725, 687, 656, 615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 6.7 Hz, 2H), 7.75 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 150.0, 147.6, 128.9, 122.7 (q, $^{1}J_{CF}$ = 325.9 Hz); HRMS (ESI, positive) calcd for $C_6H_4ClF_3N_2NaO_2S$ [(M+Na)$^+$] 282.9532, found 282.9529. Anal. Calcd for $C_6H_4ClF_3N_2O_2S$: C, 27.65; H, 1.55; N, 10.75. Found: C, 27.65; H, 2.04; N, 11.07.

4-Bromopyridinium (Trifluoromethanesulfonyl)imide (2h): colorless plates (recrystallized from acetone-hexane); mp 174-176 °C; IR (neat) 3111, 1604, 1475, 1437, 1335, 1220-1120, 951, 858, 613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.0 Hz, 2H), 7.92 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 147.2, 139.0, 132.0, 122.7 (q, $^{1}J_{CF}$ = 326.1 Hz); HRMS (ESI, positive) calcd for $C_6H_4BrF_3N_2NaO_2S$ [(M+Na)$^+$] 326.9027, found 326.9056. Anal. Calcd for $C_6H_4BrF_3N_2O_2S$: C, 23,62; H, 1.32; N, 9.18. Found: C, 23.63; H, 1.62; N, 9.24.

4-Cyanopyridinium (Trifluoromethanesulfonyl)imide (2i): white plates (recrystallized from ethyl acetate-dichloromethane-hexane); mp 170-172 °C; IR (neat) 3126, 2247, 1624, 1489, 1441, 1344, 1235-1105, 947, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 6.6 Hz, 2H), 8.03 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 147.5, 131.6, 125.0, 122.6 (q, $^{1}J_{CF}$ = 325.3 Hz), 115.4; HRMS (ESI, positive) calcd for $C_7H_4F_3N_3NaO_2S$ [(M+Na)$^+$] 273.9874, found 273.9860.

Quinolinium (Trifluoromethanesulfonyl)imide (2j): colorless prisms (recrystallized from ethyl acetate-hexane); mp 190-192 °C; IR (neat) 3074, 3028, 1622, 1520, 1335, 1215, 1180, 1159, 943, 831, 602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, *J* = 6.1, 1.2 Hz, 1H), 8.96 (d, *J* = 9.2 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.16-8.05 (m, 2H), 7.91 (t, *J* = 7.6 Hz, 1H), 7.77 (dd, *J* = 8.4, 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 141.5, 140.5, 134.8, 130.3, 130.0, 128.8, 121.3 (q, $^{1}J_{CF}$ = 325.3 Hz), 120.7, 120.5; HRMS (ESI, positive) calcd for $C_{10}H_7F_3N_2NaO_2S$ [(M+Na)$^+$] 299.0078, found 299.0087. Anal. Calcd for $C_{10}H_7F_3N_2O_2S \cdot 1/4\ H_2O$: C, 42.78; H, 2.69; N, 9.98. Found: C, 43.13; H, 3.09; N, 10.20.

Isoquinolinium (Trifluoromethanesulfonyl)imide (2k):[3] colorless prisms (recrystallized from ethyl acetate-hexane); mp 179-181 °C; IR (neat) 3084, 1633, 1504, 1335, 1230-1100, 989, 953, 833, 760, 606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, *J* = 1.5 Hz, 1H), 8.39 (dd, *J* = 6.9, 1.5 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.11-8.04 (m, 3H), 7.94 (ddd, *J* = 8.3, 5.8, 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 137.5, 135.6, 135.5, 131.1, 129.3, 127.8, 127.1, 125.1, 121.6 (q, $^{1}J_{CF}$ = 325.5 Hz); HRMS (ESI, positive) calcd for $C_{10}H_7F_3N_2NaO_2S$ [(M+Na)$^+$] 299.0078, found 299.0092. Anal. Calcd for $C_{10}H_7F_3N_2O_2S$: C, 43.48; H, 2.55; N, 10.14. Found: C, 43.06; H, 2.48; N, 10.06.

Pyrazinium (Trifluoromethanesulfonyl)imide (2l): a white powder (recrystallized from ethyl acetate-hexane); mp 65-67 °C; IR (neat) 3116, 1599, 1471, 1429, 1350, 1240-1100, 1014, 953, 837,

779, 727, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.17-9.11 (m, 2H), 8.74-8.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 135.5, 121.2 (q, $^1J_{CF}$ = 324.5 Hz); HRMS (ESI, positive) calcd for $C_5H_4F_3N_3NaO_2S$ [$(M+Na)^+$] 249.9874, found 249.9878.

4,4'-Bipyridinium (Trifluoromethanesulfonyl)imide (3a): colorless prisms (recrystallized from ethyl acetate-hexane); mp 189-191 °C; IR (neat) 3111, 1626, 1597, 1537, 1479, 1444, 1410, 1342, 1230-1110, 950, 870, 816, 602 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 8.91 (d, J = 6.5 Hz, 2H), 8.87-8.84 (m, 2H), 8.46 (d, J = 6.5 Hz, 2H), 8.0-7.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 150.2, 145.8, 141.3, 124.6, 121.6 (q, $^1J_{CF}$ = 325.5 Hz), 121.2; HRMS (ESI, positive) calcd for $C_{11}H_8F_3N_3NaO_2S$ [$(M+Na)^+$] 326.0187, found 326.0201. Anal. Calcd for $C_{11}H_8F_3N_3O_2S \cdot 1/6H_2O$: C, 43.14; H, 2.74; N, 13.72. Found: C, 43.24; H, 3.05; N, 14.06.

4,4'-Bipyridinium Bis[(trifluoromethanesulfonyl)imide] (3b): colorless plates (recrystallized from ethyl acetate-acetone-hexane); mp 296-298 °C; IR (neat) 3124, 1626, 1481, 1336, 1204-1163, 1126, 941, 835, 777, 600 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 9.03 (d, J = 6.2 Hz, 4H), 8.65 (d, J = 6.2 Hz, 4H); ^{13}C NMR (75 MHz, acetone-d_6) δ 147.5, 147.1, 127.3, 122.7 (q, $^1J_{CF}$ = 325.9 Hz); HRMS (ESI, positive) calcd for $C_{12}H_8F_6N_4NaO_4S_2$ [$(M+Na)^+$] 472.9789, found 472.9802. Anal. Calcd for $C_{12}H_8F_6N_4O_4S_2$: C, 32.00; H, 1.79; N, 12.44. Found: C, 32.11; H, 2.10; N, 12.80.

Dimethyl(benzyl)ammonium (Trifluoromethanesulfonyl)imide (4a): colorless plates (recrystallized from dichloromethane-hexane); mp 115-117 °C; IR (neat) 3030, 2970, 1481, 1456, 1313, 1220-1100, 1030, 966, 829, 760, 744, 609, 582 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.43 (m, 5H), 4.68 (s, 2H), 3.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.9, 130.9, 129.1, 128.2, 120.5 (q, $^1J_{CF}$ = 325.7 Hz), 75.9, 55.5; HRMS (ESI, positive) calcd for $C_{10}H_{13}F_3N_2NaO_2S$ [$(M+Na)^+$] 305.0548, found 305.0569. Anal. Calcd for $C_{10}H_{13}F_3N_2O_2S$: C, 42.55; H, 4.64; N, 9.92. Found: C, 42.37; H, 4.57; N, 9.88.

***N*-Methylpiperidinium (Trifluoromethanesulfonyl)imide (4b):** colorless needles (recrystallized from dichloromethane-hexane); mp 99-100 °C; IR (neat) 2954, 2870, 1475, 1456, 1309, 1205, 1171, 1076, 1026, 953, 787, 700, 633, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.94-3.83 (m, 2H), 3.43 (s, 3H), 3.26-3.15 (m, 2H), 2.45-2.30 (m, 2H), 1.87-1.67 (m, 3H), 1.56-1.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.6 (q, $^1J_{CF}$ = 326.1 Hz), 68.4, 55.9, 21.4, 21.0. Anal. Calcd for $C_7H_{13}F_3N_2O_2S$: C, 34.14; H, 5.32; N, 11.37. Found: C, 34.27; H, 5.21; N, 11.38.

Quinuclidinium (Trifluoromethanesulfonyl)imide (4c): colorless plates (recrystallized from dichloromethane-ethyl acetate-hexane); mp 209-211 °C; IR (neat) 2962, 2887, 1466, 1329, 1315, 1220-1120, 1068, 987, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.86-3.79 (m, 6H), 2.17 (sept, J = 3.2 Hz, 1H), 2.08-2.02 (m, 6H); ^{13}C NMR (75 MHz, acetone-d_6) δ 121.9 (q, $^1J_{CF}$ = 327.2 Hz), 62.2, 26.3, 20.4; HRMS (ESI, positive) calcd for $C_8H_{13}F_3N_2NaO_2S$ [$(M+Na)^+$] 281.0548, found 281.0549.

4-Aza-1-azoniabicyclo[2.2.2]octane (Trifluoromethanesulfonyl)imide (4d): colorless needles (recrystallized from ethyl acetate-hexane); mp 192-194 °C; IR (neat) 2964, 1624, 1464, 1306, 1210-1120, 1070, 1055, 999, 970, 829, 634 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (t, J = 7.8 Hz, 6H), 3.23 (t, J = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, acetone-d_6) δ 121.8 (q, $^1J_{CF}$ = 326.6 Hz), 60.0, 47.6; HRMS (ESI, positive) calcd for $C_7H_{12}F_3N_3NaO_2S$ [$(M+Na)^+$] 282.0500, found 282.0497.

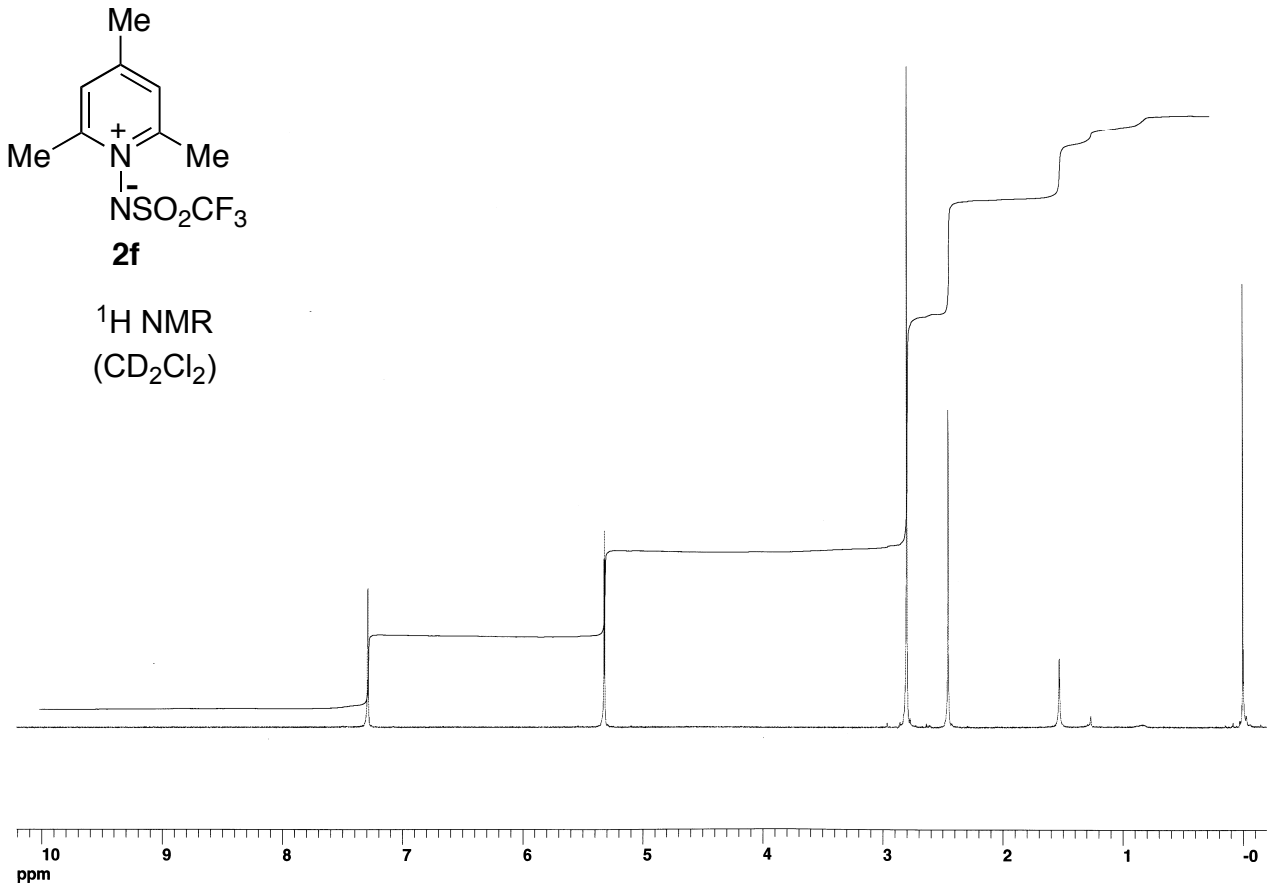
1,4-Diazoniabicyclo[2.2.2]octane Bis[(trifluoromethanesulfonyl)imide] (4e): white plates (recrystallized from ethyl acetate-hexane); mp >300 °C; IR (neat) 3068, 1714, 1635, 1462, 1365, 1323, 1220-1130, 1082, 984, 843, 820 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 4.48 (s, 12H); ^{13}C NMR (75 MHz, acetone-d_6) δ 121.5 (q, $^1J_{CF}$ = 325.5 Hz), 59.8; HRMS (ESI, positive) calcd for $C_8H_{12}F_6N_4NaO_4S_2$ [$(M+Na)^+$] 429.0102, found 429.0116.

References

(1) Ochiai, M.; Kaneaki, T.; Tada, N.; Miyamoto, K.; Chuman, H.; Shiro, M.; Hayashi, S.; Nakanishi, W. *J. Am. Chem. Soc.* **2007**, *129*, 12939.

(2) Xu, Y.; Zhu, S. *Tetrahedron* **1999**, *55*, 13725.

(3) Crystal data for **2c**: $C_7H_7F_3N_2O_2S$, colorless prism, dimensions 0.50 x 0.40 x 0.40 mm^3, monoclinic, $P2_1/n$ (No. 14), a = 10.483(5), b = 7.230(4), c = 13.081(6) Å, β = 107.27(4)°, V = 946.7(8) $Å^3$, Z = 4, ρ_{calcd} = 1.685 g cm^{-3}. Data collected on a Rigaku RAXIS RAPID imaging plate diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71075 Å) at T = 93 K, $2\theta_{max}$ = 50.7°, 6747 reflections measured, of which 1731 unique (R_{int} = 0.031), μ = 3.697 cm^{-1}. R = 0.0451, R_w = 0.1522. For **2k**: $C_{10}H_7F_3N_2O_2S$, colorless prism of dimensions 0.20 x 0.20 x 0.20 mm^3, triclinic, P-1 (No. 2), a = 6.808(3), b = 9.009(3), c = 10.357(4) Å, α = 65.29(3)°, β = 81.76(3)°, γ = 66.58(3)°, V = 529.4(4) $Å^3$, Z = 2, ρ_{calcd} = 1.733 g cm^{-3}. Data collected on a Rigaku RAXIS RAPID imaging plate diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71075 Å) at T = 93 K, $2\theta_{max}$ = 55.0°, 5254 reflections measured, of which 2407 unique (R_{int} = 0.022), μ = 3.436 cm^{-1}. R = 0.0415, R_w = 0.088. CCDC-705152 (**2c**) and CCDC-705153 (**2k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.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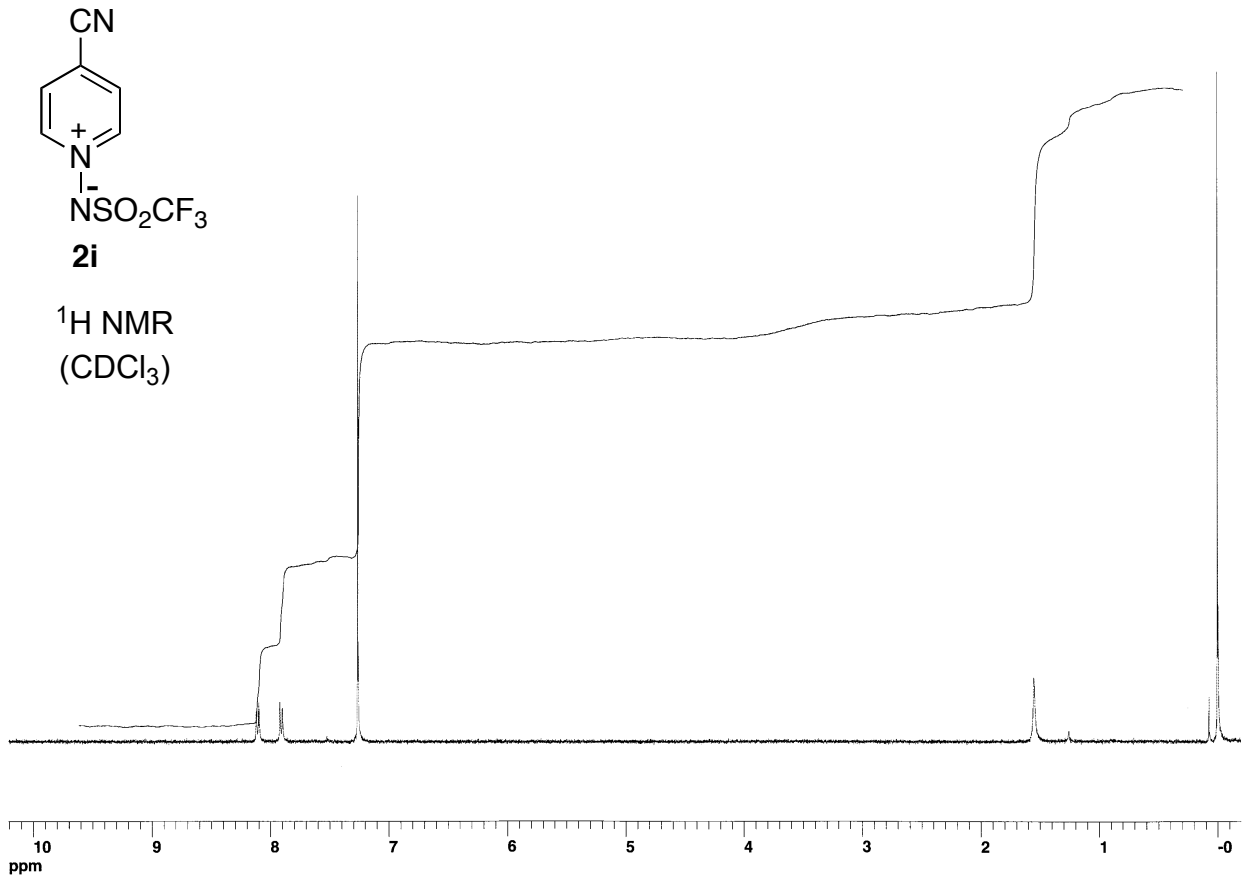
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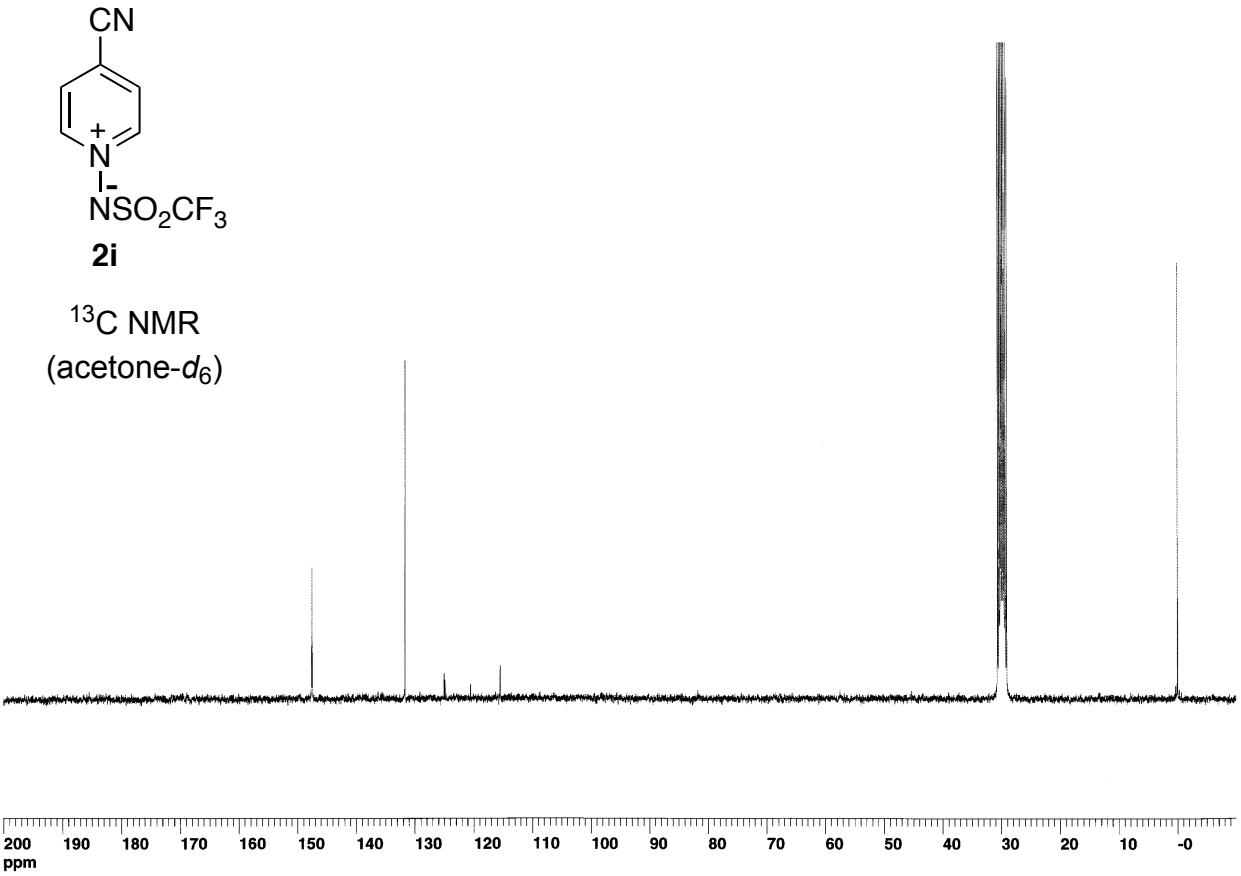
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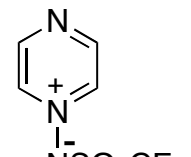

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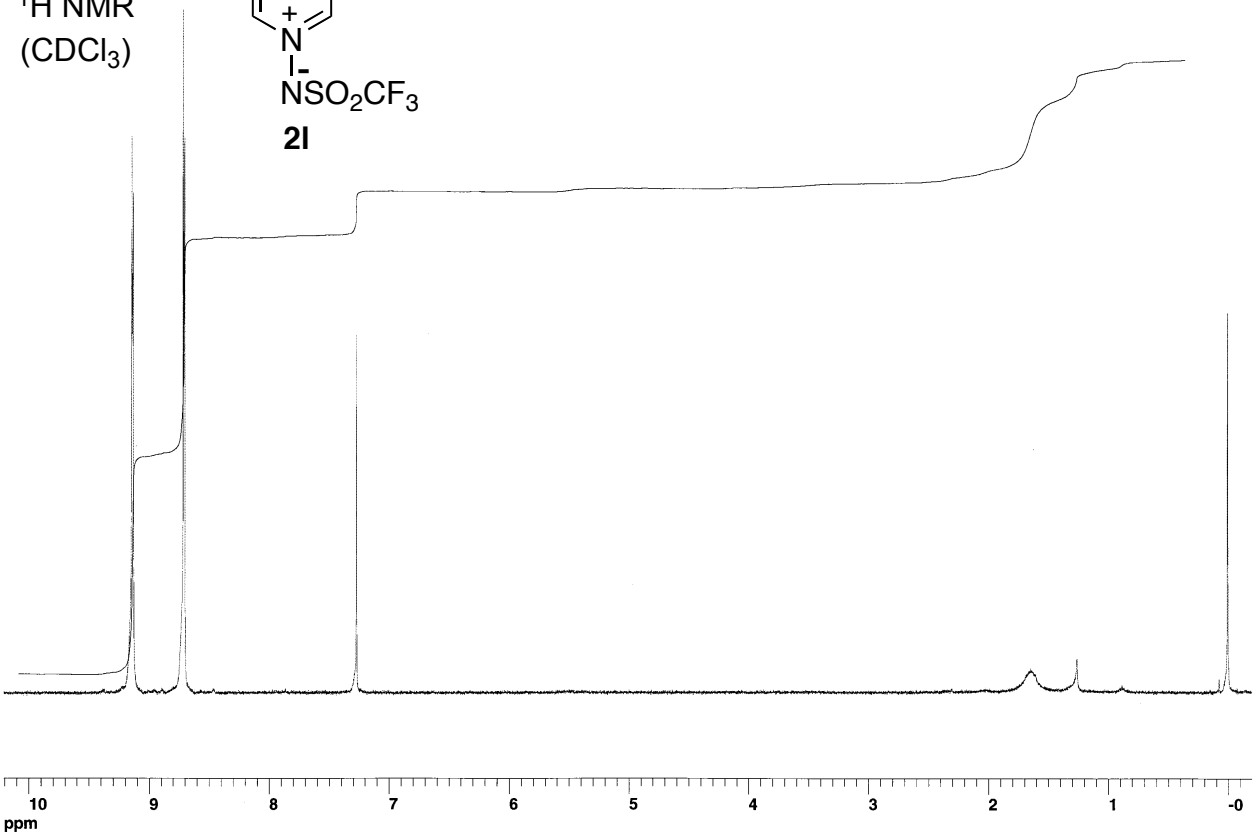
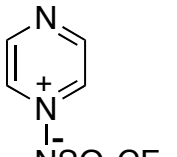
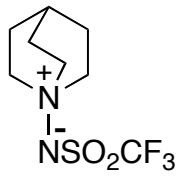




NSO_2CF_3

2l

^{13}C NMR
($CDCl_3$)



4c

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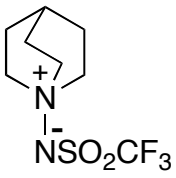
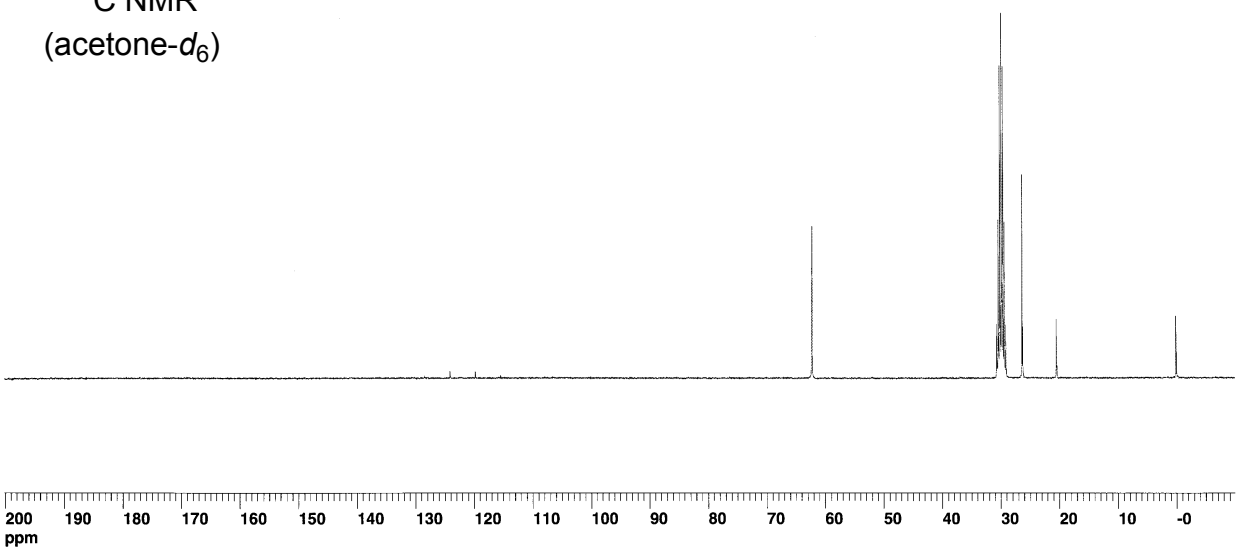
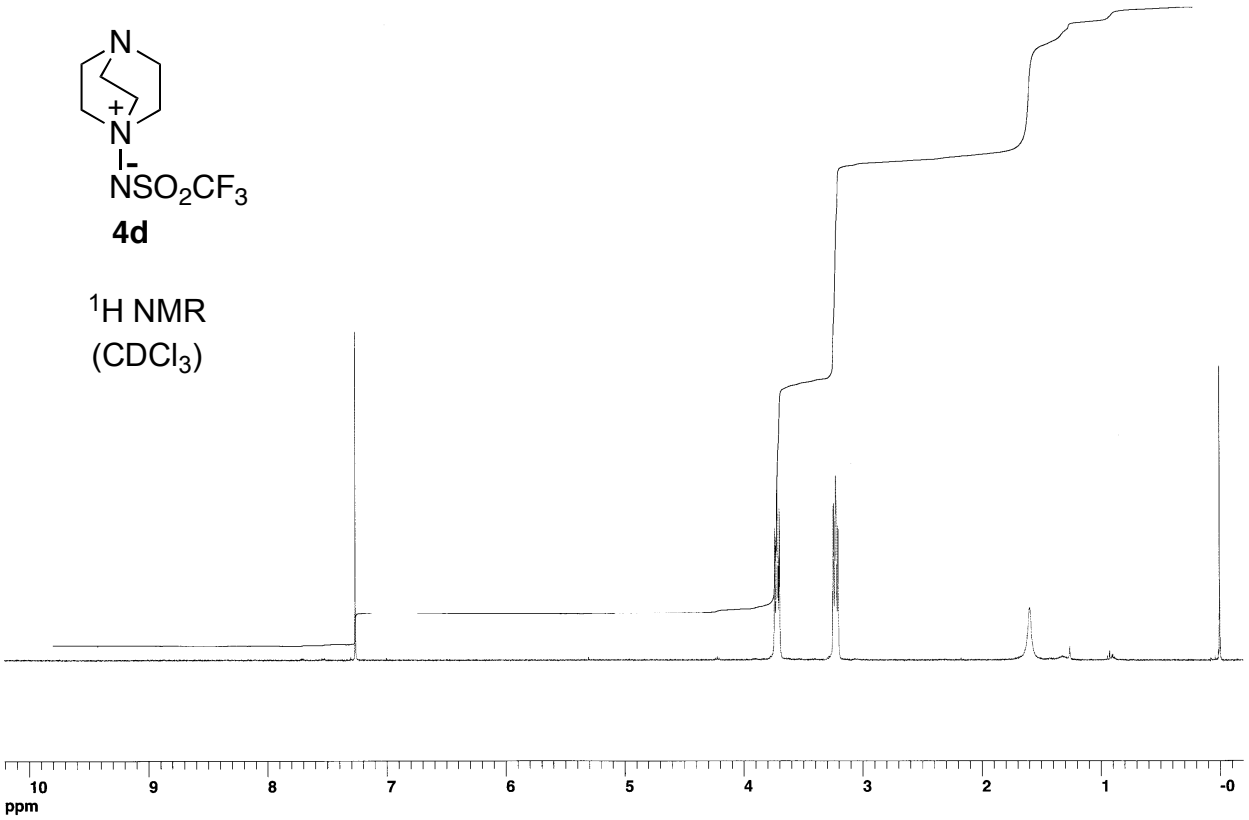
($CDCl_3$)

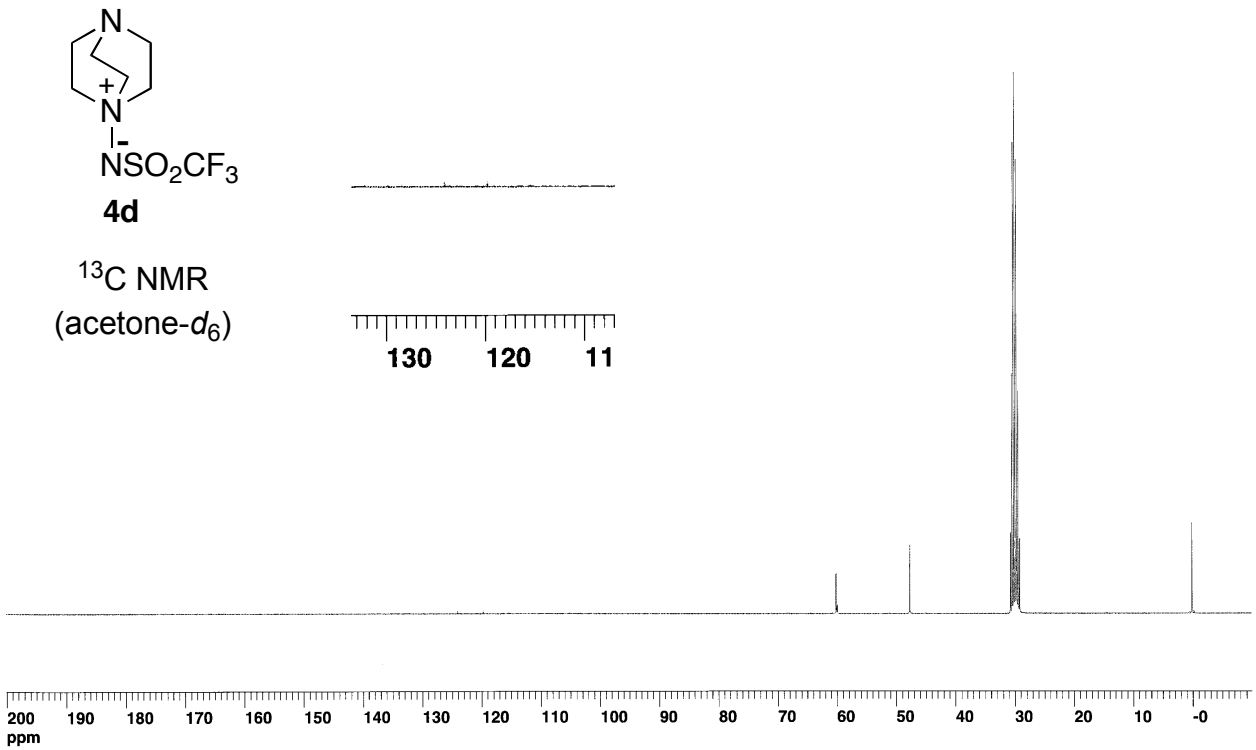


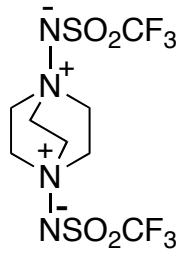
4c

^{13}C NMR
(acetone-d_6)



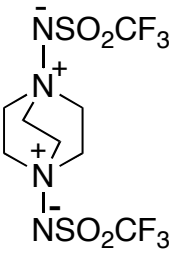

N
+
N
I-
NSO2CF3
4d
1H NMR
(CDCl3)
10
9
8
7
6
5
4
3
2
1
-0
ppm


N
+
N
I-
NSO2CF3
4d
13C NMR
(acetone-d6)
130
120
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-0
ppm



4e

^{1}H NMR
(acetone-d_6)



4e

^{13}C NMR
(acetone-d_6)