Electronic Supplementary Material (ESI) for Chemical Communications

2-(Pyridinium-1-yl)-1,1-bis(triflyl)ethanides: Structural Behaviour and Availability as Bis(triflyl)ethylating Reagents

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Electronic Supplementary Information

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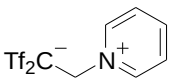
1. General and materials

All reactions were carried out under Ar atmosphere. Melting points were uncorrected. NMR spectra were recorded on a Bruker Avance II Nanobay 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F) in [D_6]acetone, [D_3]acetonitrile, and $CDCl_3$. Chemical shifts (in ppm) were referenced to the solvent signal ([D_6]acetone, 1.93 ppm for ^{1}H NMR and 29.3 ppm for ^{13}C NMR; [D_3]acetonitrile, 2.00 ppm for ^{1}H NMR and 118.2 ppm for ^{13}C NMR; $CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). Chemical shifts (in ppm) of ^{19}F NMR spectra were referenced to the signal of trifluoromethylbenzene (0 ppm) as a standard. Coupling constants (*J*) are given in Hz. Mass spectra were measured on a MICROMASS LCT mass spectrometer using electrospray ionization-time of flight (ESI-TOF). Column chromatography was performed on neutral silica gel (75-150 μm). Tf_2CH_2 **3** was kindly provided by Central Glass Co., Ltd. and this compound can be also prepared by the Waller's procedure in the laboratory.[1]

2. Synthesis of 2-(pyridinium-1-yl)-1,1-bis(triflyl)ethanides

2-(Pyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2a)

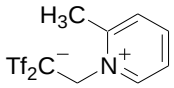


2a

To a solution of Tf_2CH_2 **3** (279 mg, 0.996 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90%

purity, 69.8 mg, 2.09 mmol) and pyridine (165 μL, 2.05 mmol) were added at room temperature. After being stirred for 4 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2a** in 99.6% yield (368 mg, 0.991 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 172-174 °C; IR (ATR) ν 3081, 1344, 1177, 1097, 1047, 856, 791, 597 cm^{-1}; ^1H NMR (400 MHz) δ in [D_3]acetonitrile 5.53 (2H, s), 8.01-8.21 (2H, m), 8.55 (1H, t, J = 7.8 Hz), 8.97 (2H, t, J = 5.8 Hz), δ in [D_6]acetone 5.58 (2H, s), 8.21-8.28 (2H, m), 8.70 (1H, t, J = 7.8 Hz), 9.09 (2H, t, J = 5.7 Hz); ^{13}C NMR (100 MHz) δ in [D_3]acetonitrile 62.5, 68.9, 121.6 (q, J_{CF} = 325 Hz), 129.0, 144.7, 147.0, in [D_6]acetone 63.5, 70.1, 122.4 (q, J_{CF} = 325 Hz), 129.7, 145.6, 147.7; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.7 (6F, s); MS (ESI-TOF) m/z 372 $[M+H]^+$; HRMS calcd for $C_9H_7F_6NO_4S_2$ $[M+H]^+$, 371.9799; found, 371.9789; Anal. Calcd for $C_9H_7F_6NO_4S_2$: C, 29.11; H, 1.90; N, 3.77. Found: C, 29.05; H, 2.13; N, 3.89.

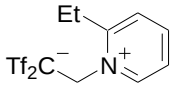
2-(2-Methylpyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2b)



2b

To a solution of Tf_2CH_2 **3** (281 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 69.5 mg, 2.09 mmol) and 2-methylpyridine (200 μL, 2.04 mmol) were added at room temperature. After being stirred for 4 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2b** in 97% yield (374 mg, 0.971 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 185-187 °C; IR (ATR) ν 3081, 1344, 1176, 1097, 1047, 856, 791, 597 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 2.94 (3H, s), 5.47 (2H, brs), 7.85 (1H, d, J = 7.9 Hz), 7.92-7.97 (1H, m), 8.33-8.39 (1H, m), 9.22 (1H, d, J = 6.2 Hz); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 20.8, 57.6, 67.6, 121.6 (q, J_{CF} = 326 Hz), 126.6, 130.6, 144.0, 146.1, 156.3; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.6 (6F, s); MS (ESI-TOF) m/z 386 $[M+H]^+$; HRMS calcd for $C_{10}H_{10}F_6NO_4S_2$ $[M+H]^+$, 385.9955; found, 385.9946; Anal. Calcd for $C_{10}H_9F_6NO_4S_2$: C, 31.17; H, 2.35; N, 3.64. Found: C, 31.41; H, 2.65; N, 3.65.

2-(2-Ethylpyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2c)

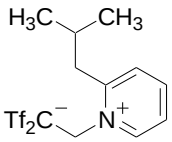


2c

To a solution of Tf_2CH_2 **3** (281 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 71.3 mg, 2.14 mmol) and 2-ethylpyridine (180 μL, 1.57 mmol) were added at room temperature. After being stirred for 8 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ to give zwitterion **2c** in 97% yield (387 mg, 0.969 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 157-158 °C; IR (ATR) ν 1345, 1178, 1098, 1049, 856, 600 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 1.42 (3H, t, J = 7.5 Hz), 3.30 (2H, q, J = 7.5 Hz), 5.51 (2H, brs), 7.89 (1H, d, J = 8.0 Hz), 7.92-7.97 (1H, m),

8.38-8.44 (1H, m), 9.24 (1H, d, J = 6.4 Hz); ^{13}C NMR (100 MHz, [D$_3$]acetonitrile) δ 12.6, 26.7, 57.1, 67.6, 121.6 (q, J_{CF} = 326 Hz), 126.4, 128.7, 144.0, 146.3, 160.8; ^{19}F NMR (376 Hz, [D$_3$]acetonitrile) δ –17.6 (6F, s); MS (ESI-TOF) m/z 422 $[M+Na]^+$; HRMS calcd for $C_{11}H_{11}F_6NNaO_4S_2$ $[M+Na]^+$, 421.9331; found, 421.9920; Anal. Calcd for $C_{11}H_{11}F_6NO_4S_2$: C, 33.08; H, 2.78; N, 3.51. Found: C, 32.82; H, 2.94; N, 3.58.

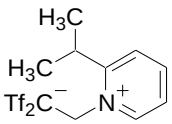
2-(2-Isobutylpyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2d)



2d

To a solution of Tf_2CH_2 **3** (280 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 70.2 mg, 2.11 mmol) and 2-isobutylpyridine (301 μL, 2.03 mmol) were added at room temperature. After being stirred for 6 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ to give zwitterion **2d** in 96% yield (412 mg, 0.964 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 175-176 °C; IR (ATR) ν 3071, 1347, 1193, 1167, 1055, 885, 598 cm^{-1}; ^{1}H NMR (400 MHz, [D$_3$]acetonitrile) δ 1.04 (6H, d, J = 6.6 Hz), 2.17 (1H, sep, J = 6.6 Hz), 3.18 (2H, brs), 5.53 (2H, brs), 7.83 (1dH, d, J = 7.6 Hz), 7.90-7.98 (1H, m), 8.35-8.41 (1H, m), 9.27 (1H, d, J = 6.4 Hz); ^{13}C NMR (100 MHz, [D$_3$]acetonitrile) δ 22.2, 29.1, 41.8, 57.5, 68.1, 121.6 (q, J_{CF} = 326 Hz), 126.7, 130.7, 144.5, 145.8, 158.6; ^{19}F NMR (376 Hz, [D$_3$]acetonitrile) δ –17.6 (6F, s); MS (ESI-TOF) m/z 450 $[M+Na]^+$, 136 $[M–C_4H_2F_6O_4S_2+H]^+$; HRMS calcd for $C_{13}H_{15}F_6NNaO_4S_2$ $[M+Na]^+$, 450.0244; found, 450.0257; Anal. Calcd for $C_{13}H_{15}F_6NO_4S_2$: C, 36.53; H, 3.54; N, 3.28. Found: C, 36.40; H, 3.48; N, 3.20.

2-(2-Isopropylpyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2e)

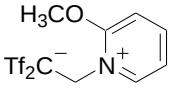


2e

A mixture of Tf_2CH_2 **3** (55.6 mg, 0.198 mmol), paraformaldehyde (90% purity, 13.8 mg, 0.414 mmol), and water (36 μL, 0.20 mmol) in chloroform (1.5 mL) was stirred for 6 h at room temperature. After the resulting mixture was treated with 2-isopropylpyridine (33 μL, 0.40 mmol) for 2 h at room temperature, this mixture was concentrated under reduced pressure. The residue was purified by washing with hexane (1.0 mL x 3) followed by Et_2O (1.5 mL) to give zwitterion **2e** in 53% yield (43.8 mg, 0.106 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 184-186 °C; IR (ATR) ν 1334, 1189, 1167, 1056, 860, 599 cm^{-1}; ^{1}H NMR (400 MHz, [D$_3$]acetonitrile) δ 1.43 (6H, d, J = 6.8 Hz), 3.94 (1H, sep, J = 6.8 Hz), 5.59 (2H, brs), 7.85-7.96 (1H, m), 7.98 (1H, d, J = 8.2 Hz), 8.40-8.48 (1H, m), 9.23 (1H, d, J = 5.8 Hz); ^{13}C NMR (100 MHz, [D$_3$]acetonitrile) δ 22.0, 30.6, 57.1, 67.9, 121.6 (q, J_{CF} = 326 Hz), 126.2, 126.4, 144.1, 146.5, 165.1; ^{19}F NMR (376 Hz, [D$_3$]acetonitrile) δ –17.6 (6F, s); MS (ESI-TOF) m/z 436 $[M+Na]^+$, 122 $[M–C_4H_2F_6O_4S_2+H]^+$; HRMS calcd for $C_{12}H_{14}F_6NNaO_4S_2$

$[M+Na]^+$, 436.0088; found, 436.0091. Anal. Calcd for $C_{12}H_{13}F_6NO_4S_2$: C, 34.87; H, 3.17; N, 3.39. Found: C, 34.69; H, 3.33; N, 3.39.

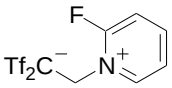
2-(2-Methoxylpyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2f)



2f

To a solution of Tf_2CH_2 **3** (289 mg, 1.03 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 72.0 mg, 2.16 mmol) and 2-methoxypyridine (216 μL, 2.00 mmol) were added at room temperature. After being stirred for 5 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (2.0 mL x 3) to give zwitterion **2f** in 99% yield (408 mg, 1.02 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 180-182 °C; IR (ATR) ν 1700, 1584, 1323, 1166, 1104, 1039, 859, 587 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 4.27 (3H, s), 5.40 (2H, brs), 7.50 (1H, d, J = 8.8 Hz), 7.52-7.59 (1H, m), 8.40-8.45 (1H, m), 8.81 (1H, d, J = 6.0 Hz); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 54.2, 59.9, 65.8, 111.6, 119.3, 121.7 (q, J_{CF} = 326 Hz), 148.7, 161.3; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.2 (6F, s); MS (ESI-TOF) m/z 402 $[M+H]^+$; HRMS calcd for $C_{10}H_{10}F_6NO_5S_2$ $[M+H]^+$, 401.9905; found, 401.9916; Anal. Calcd for $C_{10}H_9F_6NO_5S_2$: C, 29.93; H, 2.26; N, 3.49. Found: C, 30.20; H, 2.41; N, 3.55.

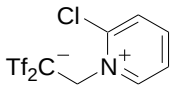
2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2g)



2g

To a solution of Tf_2CH_2 **3** (281 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 73.0 mg, 2.19 mmol) and 2-fluoropyridine (172 μL, 2.00 mmol) were added at room temperature. After being stirred for 8 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2g** in 91% yield (356 mg, 0.915 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Due to its low stability in solution phase, we could not detect suitable peaks in the MS spectra. Colorless crystals (CH_3CN/hexane); Mp. 151-153 °C; IR (ATR) ν 1351, 1183, 1106, 861, 776, 579 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 5.73 (2H, brs), 7.73-7.78 (1H, dd, J_{HH} = 8.4 Hz, J_{HF} = 4.0 Hz), 7.93 (1H, t, J = 6.8 Hz), 8.57-8.65 (1H, m), 8.92-9.01 (1H, m); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 60.2, 64.5, 115.1 (d, J_{CF} = 21.7 Hz), 121.5 (q, J_{CF} = 326 Hz), 125.3 (d, J_{CF} = 3.7 Hz), 142.9 (d, J_{CF} = 6.1 Hz), 147.4 (d, J_{CF} = 11.5 Hz), 159.6 (q, J_{CF} = 279 Hz); ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.1 (6F, s), –16.0 (1F, brs). Anal. Calcd for $C_9H_6F_7NO_4S_2$: C, 27.77; H, 1.55; N, 3.60. Found: C, 27.49; H, 1.49; N, 3.69.

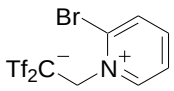
2-(2-Chloropyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2h)



2h

To a solution of Tf_2CH_2 **3** (282 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 64.5 mg, 2.08 mmol) and 2-chloropyridine (200 μL, 2.13 mmol) were added at room temperature. After being stirred for 5 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2h** in 99% yield (403 mg, 0.994 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 164-166 °C; IR (ATR) ν 3126, 1370, 1161, 1095, 863, 767, 577 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 5.78 (2H, brs), 8.03-8.08 (1H, m), 8.09 (1H, d, J = 7.3 Hz), 8.46 (1H, td, J = 7.3, 1.4 Hz), 9.28 (1H, dd, J = 6.3, 1.4 Hz); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 63.1, 68.5, 121.6 (q, J_{CF} = 326 Hz), 127.3 (2C), 130.8, 145.8, 147.9; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.1 (6F, s); MS (ESI-TOF) m/z 114 $[M–C_4H_2F_6O_4S_2+H]^{+\cdot}$ 116 $[M+2–C_4H_2F_6O_4S_2+H]^+$; Anal. Calcd for $C_9H_6ClF_6NO_4S_2$: C, 26.64; H, 1.49; N, 3.45. Found: C, 26.68; H, 1.75; N, 3.43.

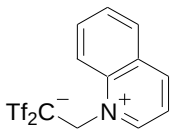
2-(2-Bromopyridin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2i)



2i

To a solution of Tf_2CH_2 **3** (280 mg, 0.998 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 71.4 mg, 2.14 mmol) and 2-bromopyridine (190 μL, 1.99 mmol) were added at room temperature. After being stirred for 4 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2i** in 98% yield (440 mg, 0.977 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 164-166 °C; IR (ATR) ν 3122, 1368, 1162, 1109, 1092, 864, 776, 576 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 5.77 (2H, brs), 8.07-8.20 (1H, m), 8.26 (1H, dd, J = 8.1, 1.3 Hz), 8.33 (1H, td, J = 8.1, 1.3 Hz), 9.36 (1H, dd, J = 6.3, 1.3 Hz); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 66.2, 69.2, 121.5 (q, J_{CF} = 326 Hz), 127.9, 135.0, 138.7, 146.2, 147.2; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.2 (6F, s); MS (ESI-TOF) m/z 158 $[M–C_4H_2F_6O_4S_2+H]^+$, 160 $[M+2–C_4H_2F_6O_4S_2+H]^+$; Anal. Calcd for $C_9H_6BrF_6NO_4S_2$: C, 23.01; H, 1.34; N, 3.11. Found: C, 23.39; H, 1.59; N, 3.25.

2-(Quinolin-1-ium-1-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2j)

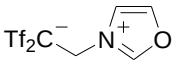


2j

To a solution of Tf_2CH_2 **3** (282 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 64.6 mg, 2.09 mmol) and quinoline (230 μL, 1.95 mmol) were added at room temperature. After being stirred

for 7 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2j** in 99% yield (418 mg, 0.993 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 195-198 °C; IR (ATR) ν 1353, 1185, 1174, 1111, 772, 578 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 5.96 (2H, brs), 8.00-8.07 (1H, m), 8.13 (1H, dd, J = 8.3, 5.8 Hz), 8.25-8.31 (1H, m), 8.40 (1H, d, J = 8.2 Hz), 8.82 (1H, d, J = 9.1 Hz), 9.12 (1H, d, J = 8.3 Hz), 9.62 (1H, d, J = 5.8 Hz); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 58.3, 66.2, 119.4, 121.6 (q, J_{CF} = 326 Hz), 122.3, 130.85, 130.91, 131.6, 136.5, 139.3, 147.9, 148.9; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.3 (6F, s); MS (ESI-TOF) m/z 444 $[M+Na]^+$, 130 $[M–C_4H_2F_6O_4S_2+H]^+$; HRMS calcd for $C_{13}H_9F_6NNaO_4S_2$ $[M+H]^+$, 443.9775; found, 443.9787; Anal. Calcd for $C_{13}H_9F_6NO_4S_2$: C, 37.06; H, 2.15; N, 3.32. Found: C, 37.06; H, 2.31; N, 3.37.

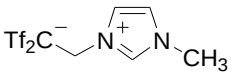
2-(2-Oxazol-3-ium-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2k)



2k

To a solution of Tf_2CH_2 **3** (282 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 70.1 mg, 2.10 mmol) and oxazole (130 μL, 1.96 mmol) were added at room temperature. After being stirred for 4 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ to give zwitterion **2k** (1.0 mL x 3) in 99% yield (358 mg, 0.991 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Due to its low stability in solution phase, we could not detect suitable peaks in the MS spectra. Colorless crystals (CH_3CN/hexane); Mp. 146-148 °C; IR (ATR) ν 3201, 1354, 1168, 1093, 1034, 896, 573 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 5.32 (2H, br), 8.00 (1H, s), 8.32 (1H, s), 9.53 (1H, s); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 51.2, 66.6, 121.6 (q, J_{CF} = 325 Hz), 122.3, 145.3, 154.5; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.6 (6F, s). Anal. Calcd for $C_7H_5F_6NO_5S_2$: C, 23.27; H, 1.40; N, 3.88. Found: C, 23.33; H, 1.63; N, 3.87.

2-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2m)

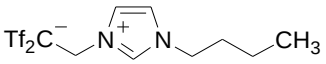


2m

To a solution of Tf_2CH_2 **3** (281 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 70.4 mg, 2.11 mmol) and 1-mehtyl-1*H*-imidazole (160 μL, 2.01 mmol) were added at room temperature. After being stirred for 6 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2m** in 99% yield (371 mg, 0.991 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 193-194 °C; IR (ATR) ν 3160, 1363, 1176, 1149, 1062, 851, 772, 749, 594 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 3.87 (3H, s), 5.12 (2H, brs), 7.35 (1H, t, J = 1.6 Hz), 7.55 (1H, t, J = 1.6 Hz), 8.59 (1H, brs); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 36.8, 50.2, 67.7, 121.8 (q, J_{CF} = 326 Hz), 122.9, 124.3, 136.4; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.7 (6F, s); MS (ESI-TOF) m/z 397 $[M+Na]^+$;

HRMS calcd for $C_8H_8F_6N_2NaO_4S_2$ $[M+Na]^+$, 396.9727; found, 396.9727; Anal. Calcd for $C_8H_8F_6N_2O_4S_2$: C, 25.67; H, 2.15; N, 7.48. Found: C, 25.67; H, 2.36; N, 7.44.

2-(1-Butyl-1*H*-imidazol-3-ium-3-yl)-1,1-bis((trifluoromethyl)sulfonyl)ethan-1-ide (2n)

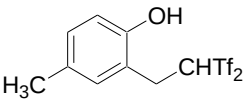


2n

To a solution of Tf_2CH_2 **3** (282 mg, 1.00 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 70.0 mg, 2.10 mmol) and 1-butyl-1*H*-imidazole (263 μL, 2.00 mmol) were added at room temperature. After being stirred for 4 h at 60 °C, the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$ (1.0 mL x 3) to give zwitterion **2n** in 98% yield (410 mg, 0.986 mmol). The structure of this compound was also confirmed by an X-ray crystallographic analysis. Colorless crystals (CH_3CN/hexane); Mp. 142-143 °C; IR (ATR) ν 3142, 3088, 1169, 1058, 854, 769, 599 cm^{-1}; ^1H NMR (400 MHz, [D_3]acetonitrile) δ 0.99 (3H, t, J = 7.4 Hz), 1.35 (2H, sex, J = 7.4 Hz), 1.79-1.89 (2H, m), 4.19 (2H, t, J = 7.2 Hz), 5.12 (2H, brs), 7.39-7.43 (1H, m), 7.55-7.59 (1H, m), 8.62 (1H, s); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ 13.4, 19.7, 32.5, 50.2, 67.7, 121.8 (q, J_{CF} = 326 Hz), 123.0, 123.1, 135.8; ^{19}F NMR (376 Hz, [D_3]acetonitrile) δ –17.7 (6F, s); MS (ESI-TOF) m/z 417 $[M+H]^+$; HRMS calcd for $C_{11}H_{15}F_6N_2O_4S_2$ $[M+H]^+$, 417.0377; found, 417.0382; Anal. Calcd for $C_{11}H_{14}F_6N_2O_4S_2$: C, 31.73; H, 3.39; N, 6.73. Found: C, 32.01; H, 3.53; N, 6.65.

3. Bis(triflyl)ethylation reaction

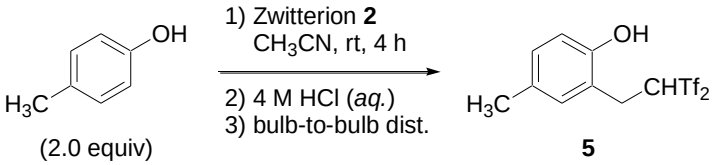
2-(2,2-Bis(trifluoromethylsulfonyl)ethyl)-4-methylphenol (5)



5

To a solution of *p*-cresole (21.0 μL, 0.20 mmol) in CH_3CN (0.5 mL), zwitterion **2** (0.10 mmol) was added at room temperature. After being stirred at the same temperature for 4 h, the reaction mixture was evaporated. This residue was dissolved in hydrochloric acid (7.0 mL), then it was extracted with Et_2O (15 mL x 3). After concentration of the combined organic layer, the resultant mixture was purified by bulb-to-bulb distillation (195-210 °C, 5 mmHg) using a kugelrohr oven to give carbon acid **5**. Yields are summarized in Table S1. The structure was confirmed by comparison of ^1H and ^{13}C NMR data reported in the literature.[2] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (3H, s), 3.73 (2H, d, J = 6.8 Hz), 5.36-5.52 (1H, br, OH), 5.91-5.97 (1H, m), 6.66 (1H, m), 7.03 (1H, d, J = 8.1 Hz), 7.05 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 28.0, 76.0, 115.0, 117.6, 119.2 (q, $J_{C\text{-}F}$ = 330.0 Hz), 130.5, 130.9, 133.0, 151.2; ^{19}F NMR (282 Hz, $CDCl_3$) δ –10.6 (6F, s). Anal. Calcd for $C_{11}H_{10}F_6O_5S_2$: C, 33.00; H, 2.52. Found: C, 32.90; H, 2.71.

Table S1. Bis(trifluoromethanesulfonyl)ethylation reaction of *p*-cresol using zwitterions

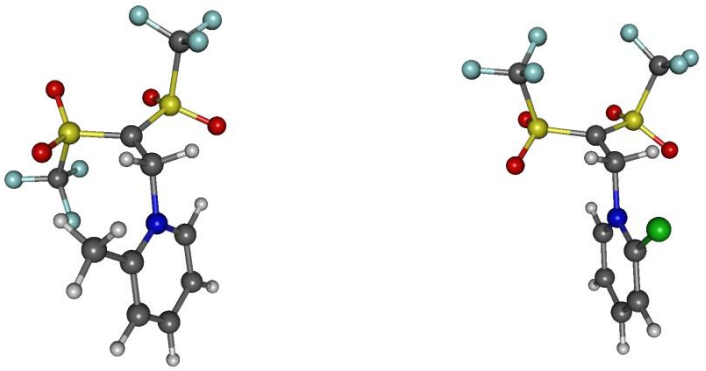


Entry	2	pK_{aH}[a]	Yield[b] (%)
1	**2a** (pyridinium)	5.17	8 (<5)
2	**2b** (2-methylpyridinium)	5.00	0
3	**2g** (2-fluoropyridinium)	-0.44	92 (91)
4	**2h** (2-chloropyridinium)	0.72	84 (81)
5	**2j** (quinolinium)	4.85	32
6	**2k** (oxazolium)	0.80	76 (74)
7	**2m** (3-methylimidazolium)	7.40	14

[a] A. R. Katritzky, C. A. Ramsden, J. A. Joule, V. V. Zhdankin, Reactivity of Six-membered Rings, in: *Handbook of Heterocyclic Chemistry (3rd Ed.)*, Elsevier, **2010**, pp. 242-382; (b) R. Linnell, *J. Org. Chem.* **1960**, *25*, 290.
[b] Yield on the basis of ^{19}F NMR of crude mixture. Isolated yield is shown in parenthesis.

4. Computational methods

All theoretical calculations were carried out by using the GAMESS 11 program.[3] Restricted Hartree-Fock (RHF) wave functions were calculated by this program. 6-311++G(2d,p) basis sets were used. Geometries were fully optimized at the RHF/6-311++G(2d,p) levels of theory. The orbital interaction energies were calculated by using the natural bond orbital (NBO) method[4] at the RHF/6-311++G(2d,p) level.

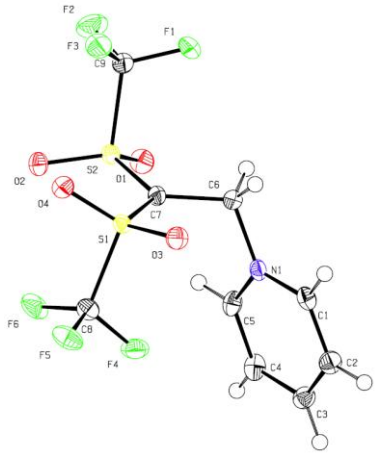


(A) (B)

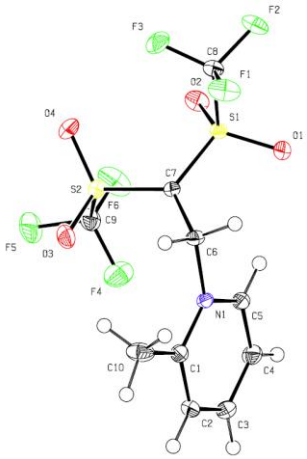
RHF/6-311++G(2d,p) optimized structures. (A) *anti*-**2b**, C^-–C = 148.9 pm, C–N^+ = 152.2 pm. (B) *syn*-**2h**, C^-–C = 147.6 pm, C–N^+ = 155.3 pm.

5. X-ray crystallographic data

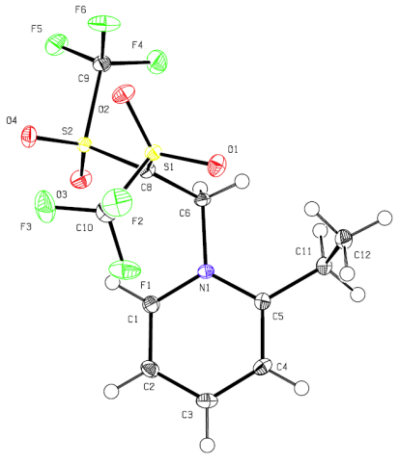
Crystallographic data for the X-ray crystal structure analysis of **2a-2n** have been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication Nos. CCDC 948820 (**2a**), 948821 (**2b**), 948822 (**2c**), 948823 (**2d**), 948824 (**2e**), 948825 (**2f**), 948826 (**2g**), 948827 (**2h**), 948828 (**2i**), 948829 (**2j**), 948830 (**2k**), 948831 (**2m**), and 948832 (**2n**). These data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.



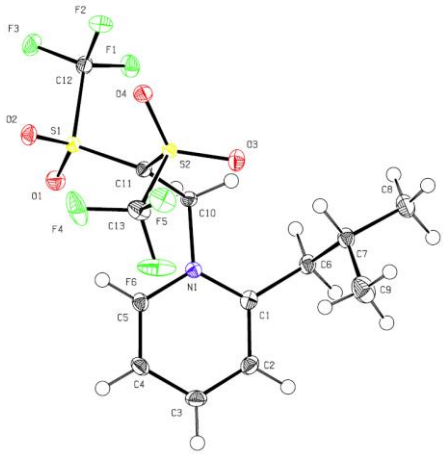
X-ray structure of **2a**



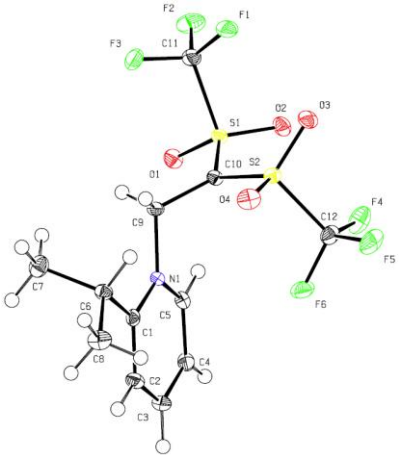
X-ray structure of **2b**



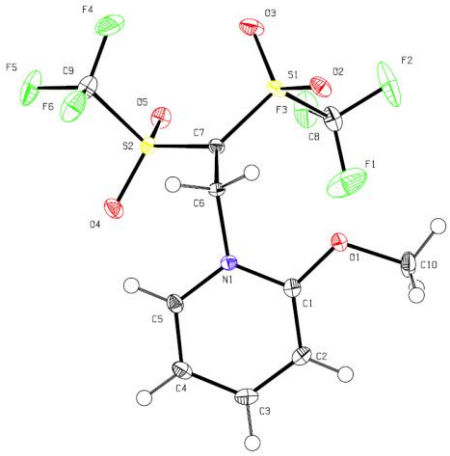
X-ray structure of **2c**



X-ray structure of **2d**



X-ray structure of **2e**



X-ray structure of **2f**

Table S2. Crystal data and structure refinement for **2a**.

Empirical formula	$C_9H_7F_6NO_4S_2$	
Formula weight	371.28	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.8808(6) Å	α = 90°.

	b = 10.4392(5) Å	β = 91.5270(10)°.
	c = 42.5523(18) Å	γ = 90°.
Volume	6607.9(5) $Å^3$	
Z	20	
Density (calculated)	1.866 g/cm^3	
Absorption coefficient	0.493 mm^{-1}	
F(000)	3720	
Crystal size	0.24 x 0.15 x 0.12 mm^3	
Theta range for data collection	2.17 to 25.03°.	
Index ranges	-17<=h<=13, -7<=k<=12, -42<=l<=50	
Reflections collected	30937	
Independent reflections	11691 [R(int) = 0.0249]	
Completeness to theta = 25.03°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.9432 and 0.8907	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11691 / 0 / 991	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0733	
R indices (all data)	R1 = 0.0368, wR2 = 0.0767	
Largest diff. peak and hole	0.417 and -0.421 $eÅ^{-3}$	

Table S3. Crystal data and structure refinement for **2b**.

Empirical formula	$C_{10}H_9F_6NO_4S_2$	
Formula weight	385.30	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.9290(14) Å	α = 90°.
	b = 10.0352(11) Å	β = 115.3760(10)°.
	c = 12.0294(13) Å	γ = 90°.
Volume	1410.2(3) $Å^3$	
Z	4	
Density (calculated)	1.815 g/cm^3	
Absorption coefficient	0.466 mm^{-1}	
F(000)	776	
Crystal size	0.20 x 0.09 x 0.09 mm^3	

Theta range for data collection	2.68 to 25.03°.
Index ranges	-15<=h<=14, -11<=k<=11, -10<=l<=14
Reflections collected	6577
Independent reflections	2484 [R(int) = 0.0215]
Completeness to theta = 25.03°	99.8 %
Absorption correction	Analytical
Max. and min. transmission	0.9593 and 0.9125
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2484 / 0 / 209
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0701
R indices (all data)	R1 = 0.0312, wR2 = 0.0725
Largest diff. peak and hole	0.401 and -0.358 $eÅ^{-3}$

Table S4. Crystal data and structure refinement for **2c**.

Empirical formula	$C_{11}H_{11}F_6NO_4S_2$	
Formula weight	399.33	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.8277(11) Å	α = 90°.
	b = 10.1124(8) Å	β = 91.5270(10)°.
	c = 12.5805(10) Å	γ = 90°.
Volume	1461.8(2) $Å^3$	
Z	4	
Density (calculated)	1.814 g/cm^3	
Absorption coefficient	0.453 mm^{-1}	
F(000)	808	
Crystal size	0.24 x 0.25 x 0.29 mm^3	
Theta range for data collection	2.68 to 27.64°.	
Index ranges	-16<=h<=16, -13<=k<=13, -16<=l<=9	
Reflections collected	8329	
Independent reflections	3381 [R(int) = 0.0150]	
Completeness to theta = 25.03°	99.4 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8990 and 0.8798	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3381 / 0 / 218
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0709
R indices (all data)	R1 = 0.0278, wR2 = 0.0723
Largest diff. peak and hole	0.526 and -0.344 eÅ^{-3}

Table S5. Crystal data and structure refinement for **2d**.

Chemical formula	$C_{13}H_{15}F_6NO_4S_2$	
Formula weight	427.38	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.230 x 0.360 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.7218(8) Å	α = 90°
	b = 11.6643(11) Å	β = 91.9270(10)°
	c = 16.8924(15) Å	γ = 90°
Volume	1717.6(3) Å^3	
Z	4	
Density (calculated)	1.653 g/cm^3	
Absorption coefficient	0.392 mm^{-1}	
F(000)	872	
Theta range for data collection	2.12 to 25.03°	
Index ranges	-10<=h<=6, -13<=k<=12, -20<=l<=19	
Reflections collected	8174	
Independent reflections	3033 [R(int) = 0.0172]	
Coverage of independent reflections	99.8%	
Absorption correction	numerical	
Max. and min. transmission	0.9258 and 0.8719	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3033 / 0 / 238	

Goodness-of-fit on F^2	1.049	
Final R indices	2847 data; $I>2\sigma(I)$	R1 = 0.0260, wR2 = 0.0667
	all data	R1 = 0.0275, wR2 = 0.0678
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0320P)^2+1.2705P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.333 and -0.384 eÅ^{-3}	
R.M.S. deviation from mean	0.051 eÅ^{-3}	

Table S6. Crystal data and structure refinement for **2e**.

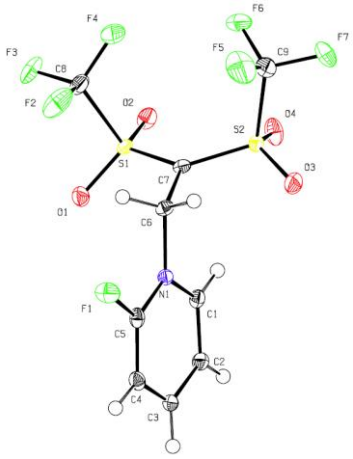
Chemical formula	$C_{12}H_{13}F_6NO_4S_2$	
Formula weight	413.35	
Wavelength	0.71073 Å	
Crystal size	0.130 x 0.140 x 0.210 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.5646(8) Å	α = 90°
	b = 12.1042(11) Å	β = 101.8640(10)°
	c = 16.0084(14) Å	γ = 90°
Volume	1624.1(3) Å^3	
Z	4	
Density (calculated)	1.691 g/cm^3	
Absorption coefficient	0.411 mm^{-1}	
F(000)	840	
Theta range for data collection	2.13 to 25.03°	
Index ranges	-10<=h<=5, -14<=k<=13, -15<=l<=19	
Reflections collected	7745	
Independent reflections	2865 [R(int) = 0.0219]	
Coverage of independent reflections	99.9%	
Absorption correction	numerical	
Max. and min. transmission	0.9485 and 0.9187	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	

Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2865 / 0 / 228	
Goodness-of-fit on F^2	1.046	
Δ/σ_{max}	0.001	
Final R indices	2610 data; I>2σ(I)	R1 = 0.0263, wR2 = 0.0673
	all data	R1 = 0.0293, wR2 = 0.0698
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0341P)^2+0.8839P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.350 and -0.377 eÅ^{-3}	
R.M.S. deviation from mean	0.050 eÅ^{-3}	

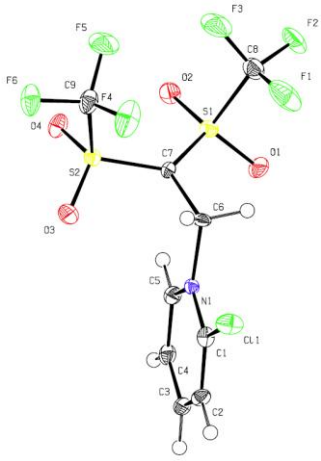
Table S7. Crystal data and structure refinement for **2f**.

Chemical formula	$C_{10}H_9F_6NO_5S_2$	
Formula weight	401.30	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.140 x 0.160 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.6307(12) Å	α = 90°
	b = 10.0920(13) Å	β = 96.144(2)°
	c = 14.9590(19) Å	γ = 90°
Volume	1445.6(3) Å^3	
Z	4	
Density (calculated)	1.844 g/cm^3	
Absorption coefficient	0.464 mm^{-1}	
F(000)	808	
Theta range for data collection	2.40 to 27.55°	
Index ranges	-12<=h<=12, -13<=k<=10, -16<=l<=19	
Reflections collected	8230	
Independent reflections	3323 [R(int) = 0.0229]	
Coverage of independent reflections	99.6%	
Absorption correction	numerical	

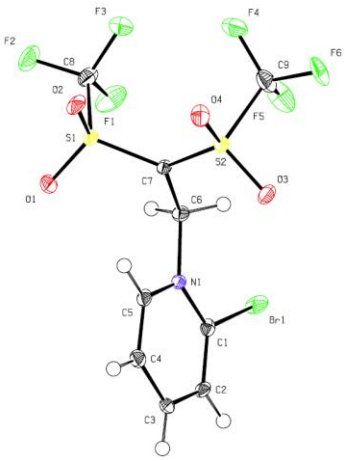
Max. and min. transmission	0.9683 and 0.9295	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3323 / 0 / 218	
Goodness-of-fit on F^2	1.018	
Δ/σ_{max}	0.001	
Final R indices	2900 data; $I>2\sigma(I)$	R1 = 0.0309, wR2 = 0.0775
	all data	R1 = 0.0371, wR2 = 0.0816
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0404P)^2+0.9149P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.521 and -0.392 eÅ^{-3}	
R.M.S. deviation from mean	0.062 eÅ^{-3}	



X-ray structure of **2g**



X-ray structure of **2h**



X-ray structure of **2i**

Table S8. Crystal data and structure refinement for **2g**.

Chemical formula	$C_9H_6F_7NO_4S_2$
Formula weight	389.27
Wavelength	0.71073 Å
Crystal size	0.060 x 0.160 x 0.220 mm
Crystal system	monoclinic
Space group	P 1 21/n 1

Unit cell dimensions	a = 9.6880(10) Å	α = 90°
	b = 21.565(2) Å	β = 101.4530(10)°
	c = 13.5597(13) Å	γ = 90°
Volume	2776.5(5) $Å^3$	
Z	8	
Density (calculated)	1.862 g/cm^3	
Absorption coefficient	0.484 mm^{-1}	
F(000)	1552	
Theta range for data collection	2.34 to 25.02°	
Index ranges	-9<=h<=11, -25<=k<=20, -15<=l<=16	
Reflections collected	13387	
Independent reflections	4901 [R(int) = 0.0244]	
Coverage of independent reflections	99.9%	
Absorption correction	numerical	
Max. and min. transmission	0.9697 and 0.9030	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4901 / 0 / 415	
Goodness-of-fit on F^2	1.051	
Final R indices	4075 data; I>2σ(I)	R1 = 0.0375, wR2 = 0.1003
	all data	R1 = 0.0456, wR2 = 0.1067
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0585P)^2+2.0617P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.939 and -0.383 $eÅ^{-3}$	
R.M.S. deviation from mean	0.072 $eÅ^{-3}$	

Table S9. Crystal data and structure refinement for **2h**.

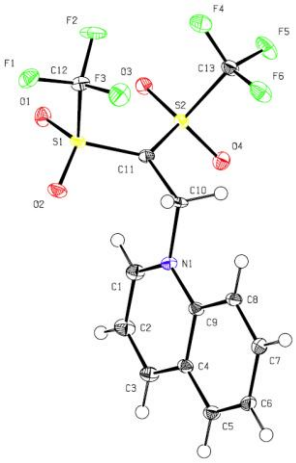
Empirical formula	$C_9H_6ClF_6NO_4S_2$
Formula weight	405.72
Temperature	90 K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 9.8403(17) Å	α = 90°.
	b = 21.718(4) Å	β = 103.359(2)°.
	c = 13.666(2) Å	γ = 90°.
Volume	2841.4(9) $Å^3$	
Z	8	
Density (calculated)	1.897 g/cm^3	
Absorption coefficient	0.650 mm^{-1}	
F(000)	1616	
Crystal size	0.50 x 0.40 x 0.25 mm^3	
Theta range for data collection	2.32 to 25.03°.	
Index ranges	-11<=h<=11, -25<=k<=17, -16<=l<=15	
Reflections collected	6772	
Independent reflections	2510 [R(int) = 0.0467]	
Completeness to theta = 25.03°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8544 and 0.7371	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2510 / 0 / 208	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0733	
R indices (all data)	R1 = 0.0617, wR2 = 0.0807	
Largest diff. peak and hole	0.367 and -0.346 e.$Å^{-3}$	

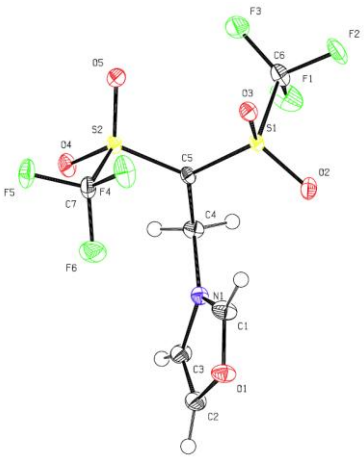
Table S10. Crystal data and structure refinement for **2i**.

Chemical formula	$C_9H_6BrF_6NO_4S_2$	
Formula weight	450.18	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.210 x 0.230 mm	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 9.926(2) Å	α = 90°
	b = 21.888(5) Å	β = 103.046(3)°
	c = 13.659(3) Å	γ = 90°
Volume	2891.0(12) $Å^3$	
Z	8	

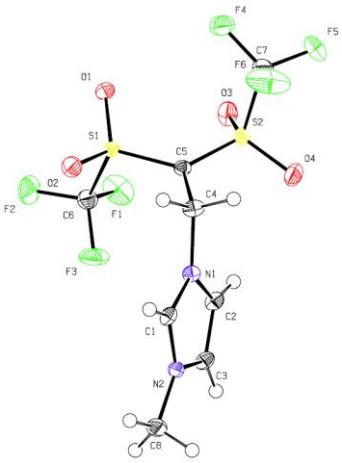
Density (calculated)	2.069 g/cm^3	
Absorption coefficient	3.218 mm^{-1}	
F(000)	1760	
Theta range for data collection	2.30 to 25.02°	
Index ranges	-11<=h<=9, -19<=k<=26, -16<=l<=15	
Reflections collected	6803	
Independent reflections	2551 [R(int) = 0.1148]	
Coverage of independent reflections	99.6%	
Max. and min. transmission	0.8304 and 0.5248	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2551 / 120 / 208	
Goodness-of-fit on F^2	0.987	
Δ/σ_{max}	0.002	
Final R indices	2227 data; I>2σ(I)	R1 = 0.0331, wR2 = 0.0687
	all data	R1 = 0.0373, wR2 = 0.0702
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0303P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.999 and -0.591 eÅ^{-3}	
R.M.S. deviation from mean	0.112 eÅ^{-3}	



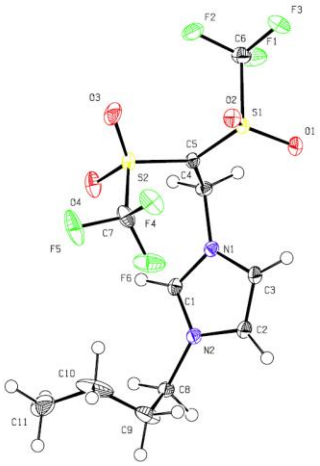
X-ray structure of **2j**



X-ray structure of **2k**



X-ray structure of **2m**



X-ray structure of **2n**

Table S11. Crystal data and structure refinement for **2j**.

Chemical formula	$C_{13}H_9F_6NO_4S_2$	
Formula weight	421.33	
Wavelength	0.71073 Å	
Crystal size	0.210 x 0.260 x 0.360 mm	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 18.3052(16) Å	α = 90°
	b = 11.2926(10) Å	β = 106.7430(10)°
	c = 15.9199(14) Å	γ = 90°
Volume	3151.3(5) $Å^3$	
Z	8	
Density (calculated)	1.776 g/cm^3	
Absorption coefficient	0.426 mm^{-1}	
F(000)	1696	
Theta range for data collection	2.15 to 25.03°	
Reflections collected	2771	
Coverage of independent reflections	99.5%	
Max. and min. transmission	0.9159 and 0.8618	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	

Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2771 / 0 / 236	
Goodness-of-fit on F^2	1.053	
Final R indices	2615 data; I>2σ(I)	R1 = 0.0527, wR2 = 0.1493
	all data	R1 = 0.0539, wR2 = 0.1508
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1190P)^2+3.8675P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.594 and -0.837 eÅ^{-3}	
R.M.S. deviation from mean	0.130 eÅ^{-3}	

Table S12. Crystal data and structure refinement for **2k**.

Chemical formula	$C_7H_5F_6NO_5S_2$	
Formula weight	361.24	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.120 x 0.200 mm	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 33.764(3) Å	α = 90°
	b = 8.8317(7) Å	β = 126.4270(10)°
	c = 20.2876(15) Å	γ = 90°
Volume	4867.6(6) Å^3	
Z	16	
Density (calculated)	1.972 g/cm^3	
Absorption coefficient	0.539 mm^{-1}	
F(000)	2880	
Theta range for data collection	2.42 to 25.03°	
Index ranges	-40<=h<=37, -10<=k<=10, -24<=l<=22	
Reflections collected	11425	
Independent reflections	4293 [R(int) = 0.0206]	
Coverage of independent reflections	99.8%	
Absorption correction	numerical	
Max. and min. transmission	0.9382 and 0.8999	
Structure solution technique	direct methods	

Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4293 / 0 / 379	
Goodness-of-fit on F^2	1.035	
Δ/σ_{max}	0.001	
Final R indices	3909 data; I>2σ(I)	R1 = 0.0266, wR2 = 0.0652
	all data	R1 = 0.0298, wR2 = 0.0673
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0287P)^2+9.6428P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.567 and -0.351 eÅ^{-3}	
R.M.S. deviation from mean	0.057 eÅ^{-3}	

Table S13. Crystal data and structure refinement for **2m**.

Chemical formula	$C_8H_8F_6N_2O_4S_2$	
Formula weight	374.28	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.150 x 0.190 mm	
Crystal system	monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 14.813(3) Å	α = 90°
	b = 10.590(2) Å	β = 120.578(3)°
	c = 10.069(2) Å	γ = 90°
Volume	1359.9(5) Å^3	
Z	4	
Density (calculated)	1.828 g/cm^3	
Absorption coefficient	0.482 mm^{-1}	
F(000)	752	
Theta range for data collection	2.50 to 25.01°	
Index ranges	-17<=h<=11, -12<=k<=12, -11<=l<=11	
Reflections collected	3133	
Independent reflections	1717 [R(int) = 0.0146]	

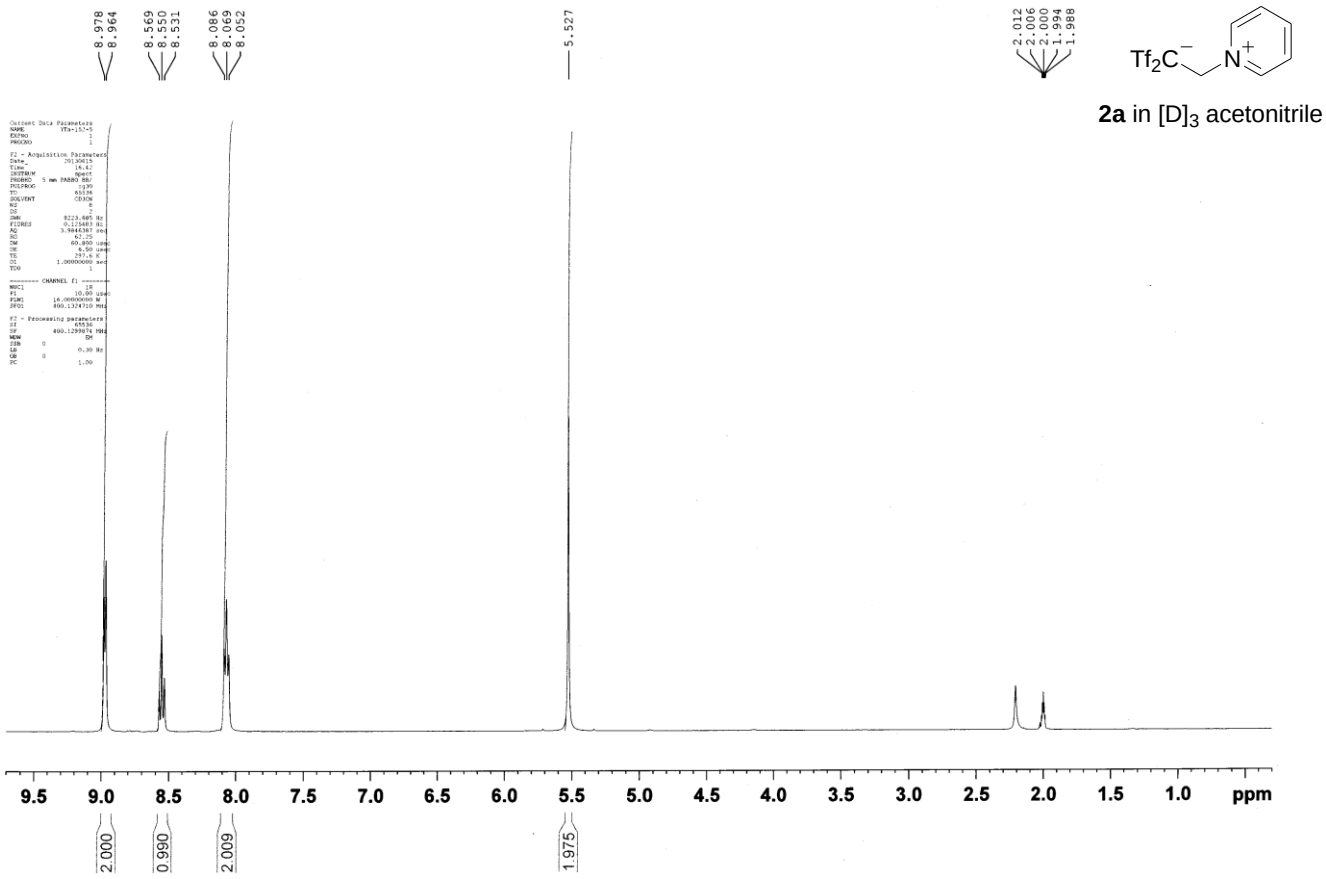
Coverage of independent reflections	99.8%	
Absorption correction	numerical	
Max. and min. transmission	0.9444 and 0.9140	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1717 / 2 / 200	
Goodness-of-fit on F^2	1.051	
Final R indices	1690 data; $I>2\sigma(I)$	R1 = 0.0207, wR2 = 0.0513
	all data	R1 = 0.0213, wR2 = 0.0517
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0252P)^2+1.1742P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.2(1)	
Largest diff. peak and hole	0.297 and -0.245 eÅ^{-3}	
R.M.S. deviation from mean	0.040 eÅ^{-3}	

Table S14. Crystal data and structure refinement for **2n**.

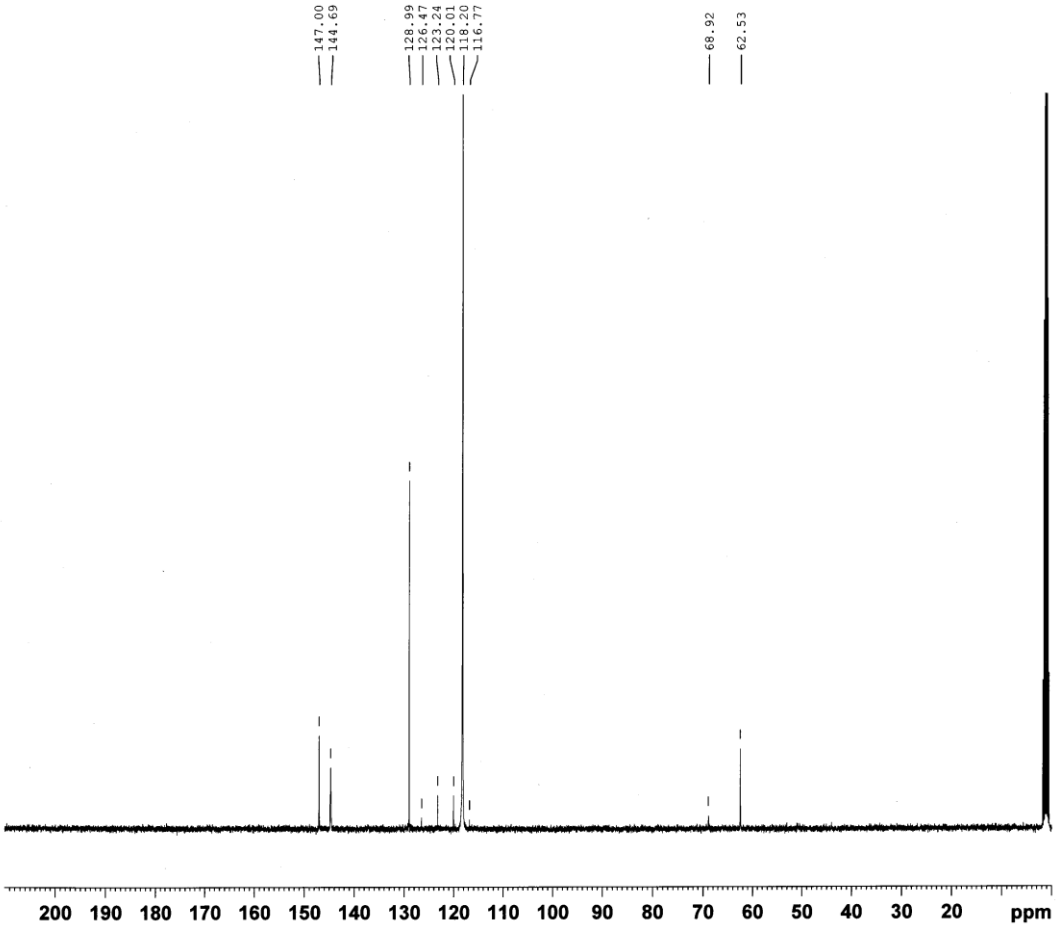
Chemical formula	$C_{11}H_{14}F_6N_2O_4S_2$	
Formula weight	416.36	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.230 x 0.310 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.1898(14) Å	α = 90°
	b = 12.4495(15) Å	β = 107.577(2)°
	c = 12.4571(15) Å	γ = 90°
Volume	1654.3(3) Å^3	
Z	4	
Density (calculated)	1.672 g/cm^3	
Absorption coefficient	0.406 mm^{-1}	
F(000)	848	

Theta range for data collection	2.37 to 25.02°	
Index ranges	-10<=h<=13, -13<=k<=14, -14<=l<=14	
Reflections collected	7856	
Independent reflections	2921 [R(int) = 0.0165]	
Coverage of independent reflections	99.8%	
Absorption correction	numerical	
Max. and min. transmission	0.9454 and 0.8846	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1997)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2921 / 3 / 227	
Goodness-of-fit on F^2	1.006	
Final R indices	2716 data; I>2σ(I)	R1 = 0.0288, wR2 = 0.0738
	all data	R1 = 0.0310, wR2 = 0.0754
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0389P)^2+1.4223P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.506 and -0.339 eÅ^{-3}	
R.M.S. deviation from mean	0.050 eÅ^{-3}	

6. ^{1}H and ^{13}C NMR spectra of all products



2a in $[D]_3$ acetonitrile

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DE                 6.50 usec
TE                297.8 K
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D11            0.03000000 sec
TD0                    1

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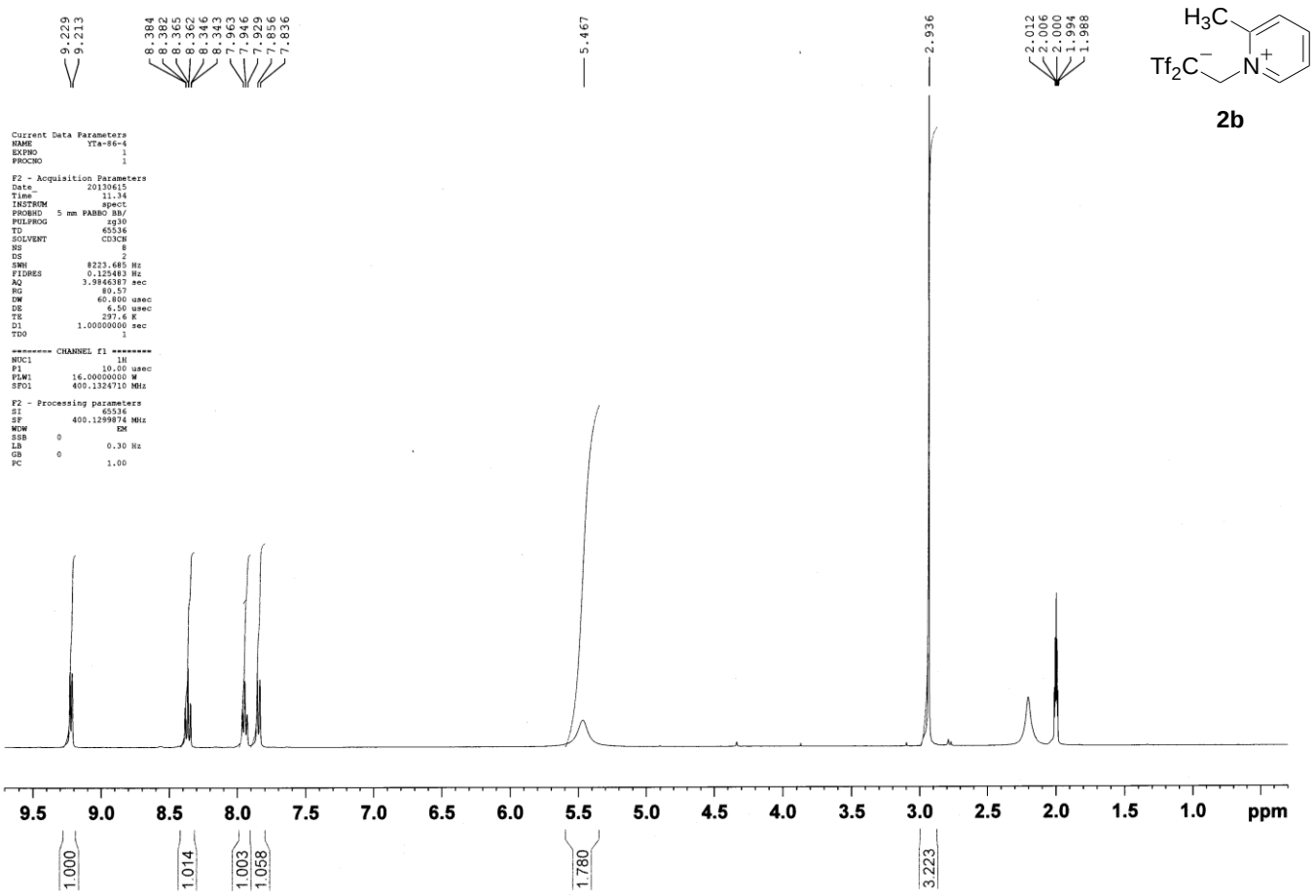
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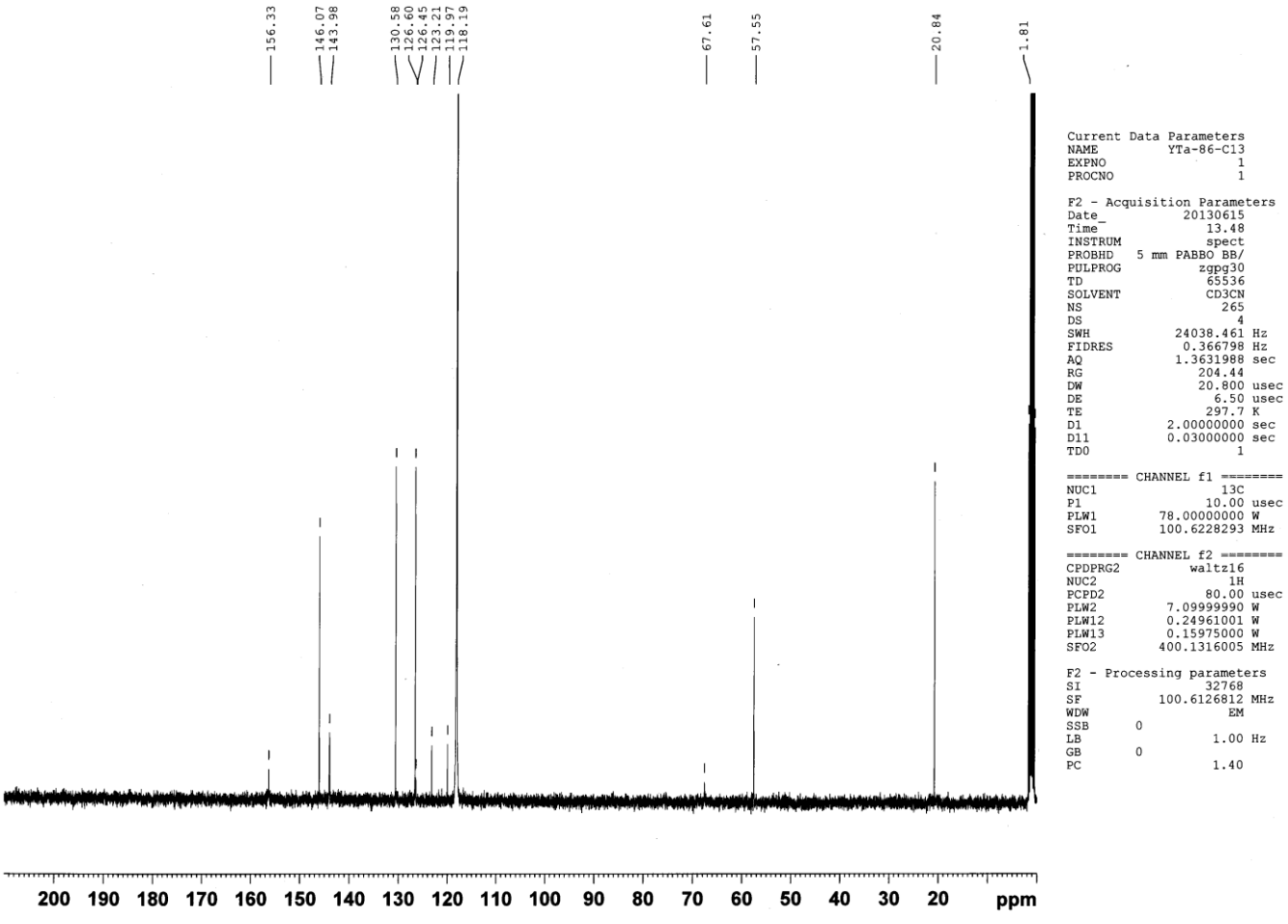
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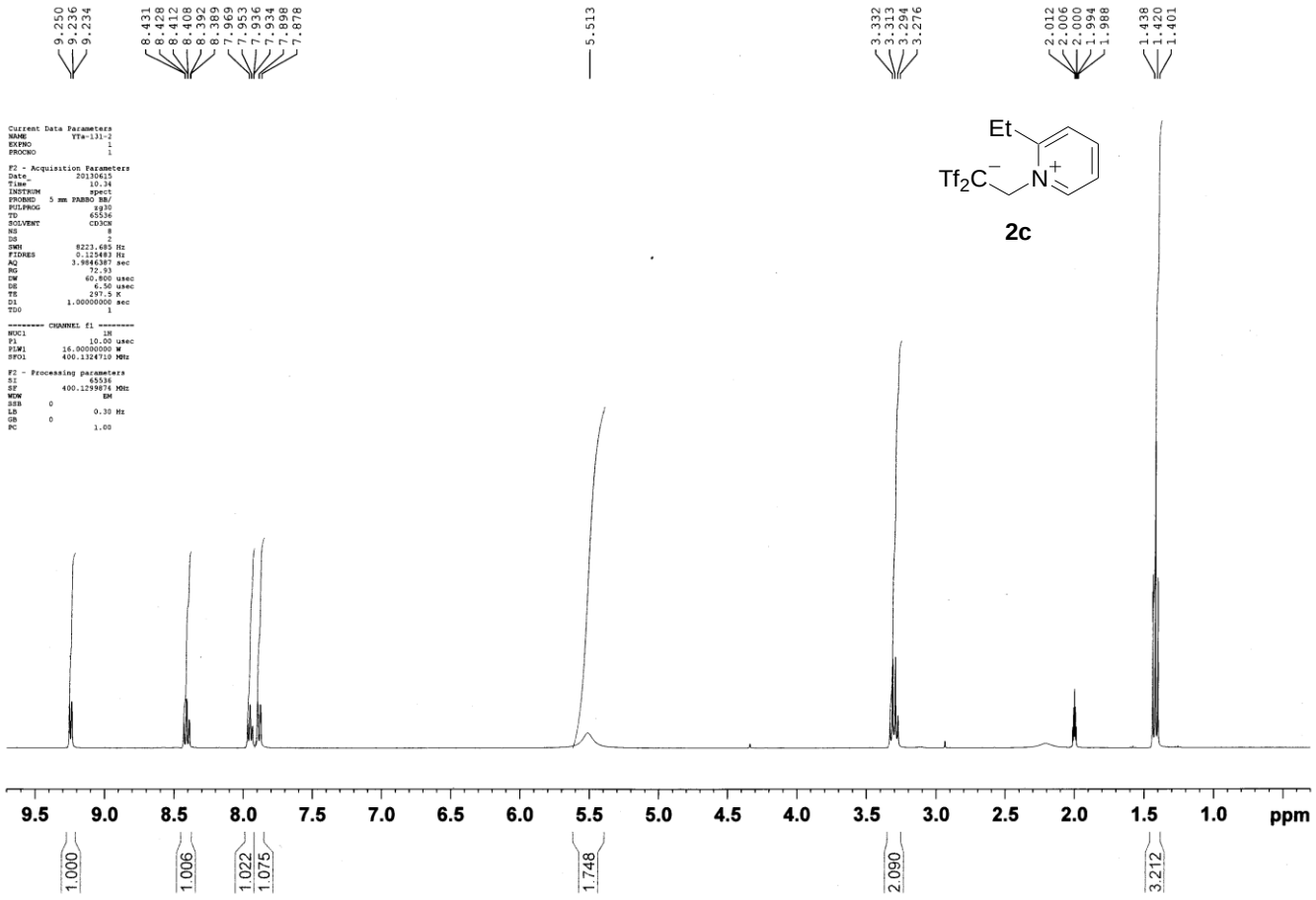

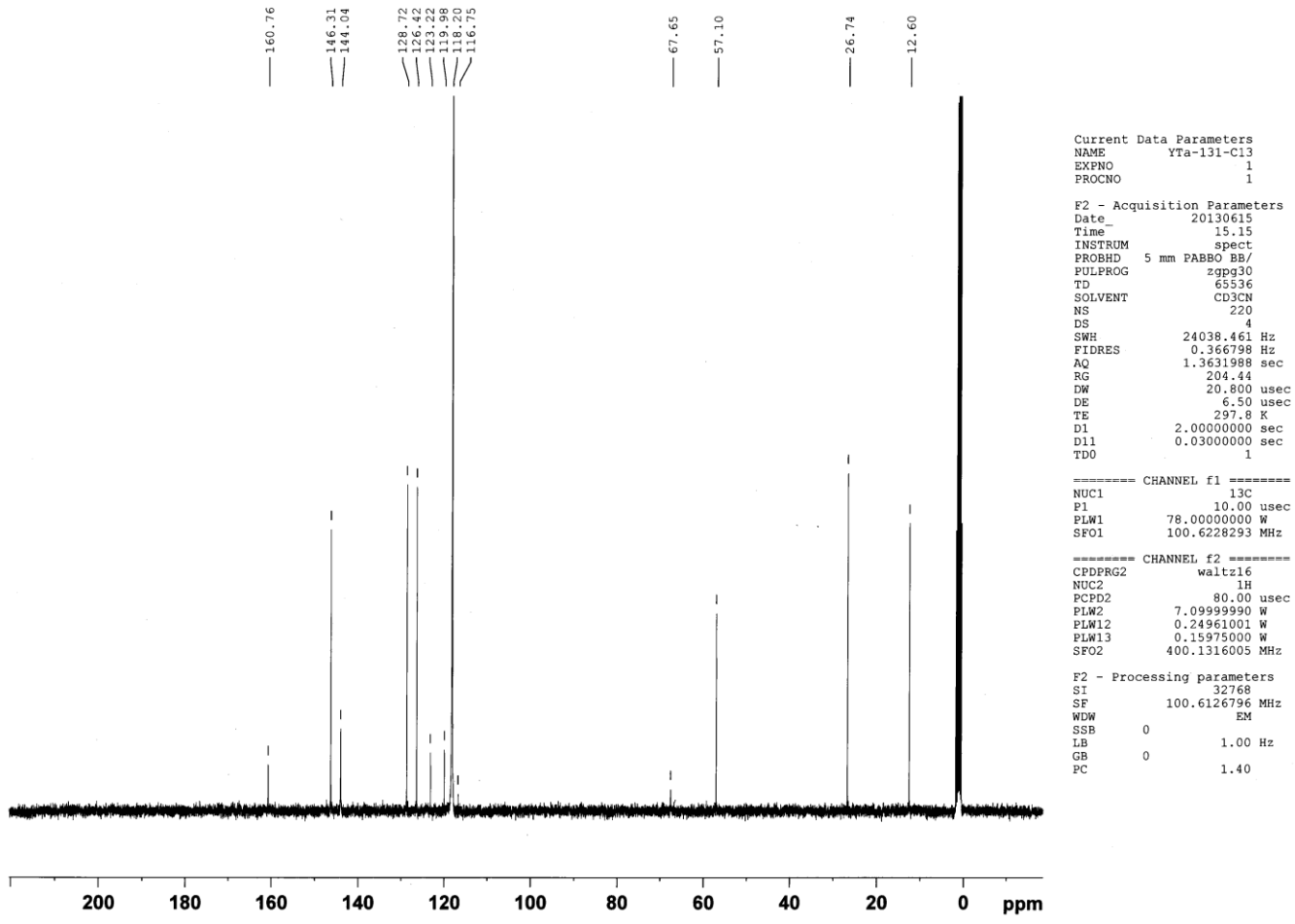


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PLW13         0.15975000 W
SFO2         400.1316005 MHz

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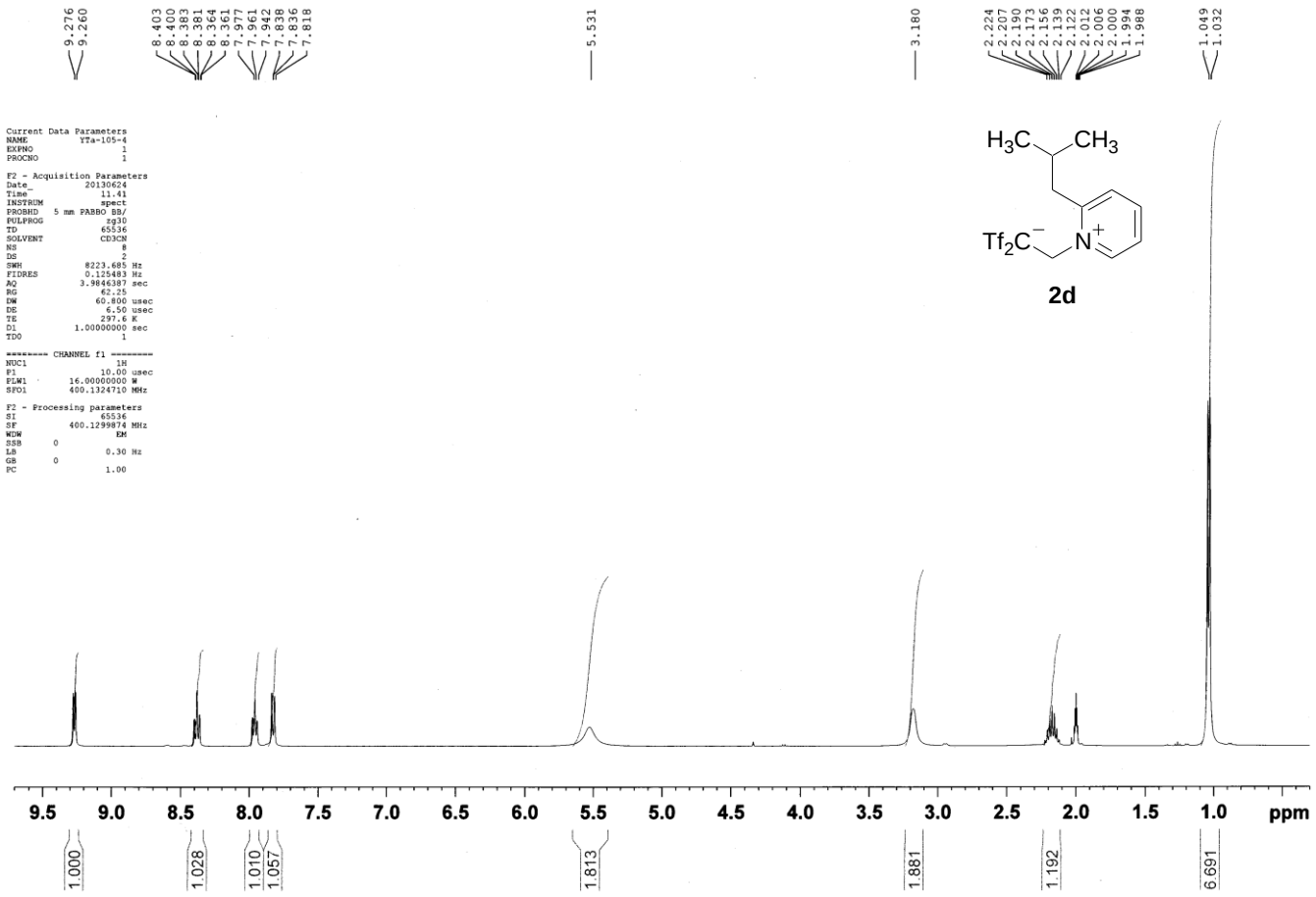
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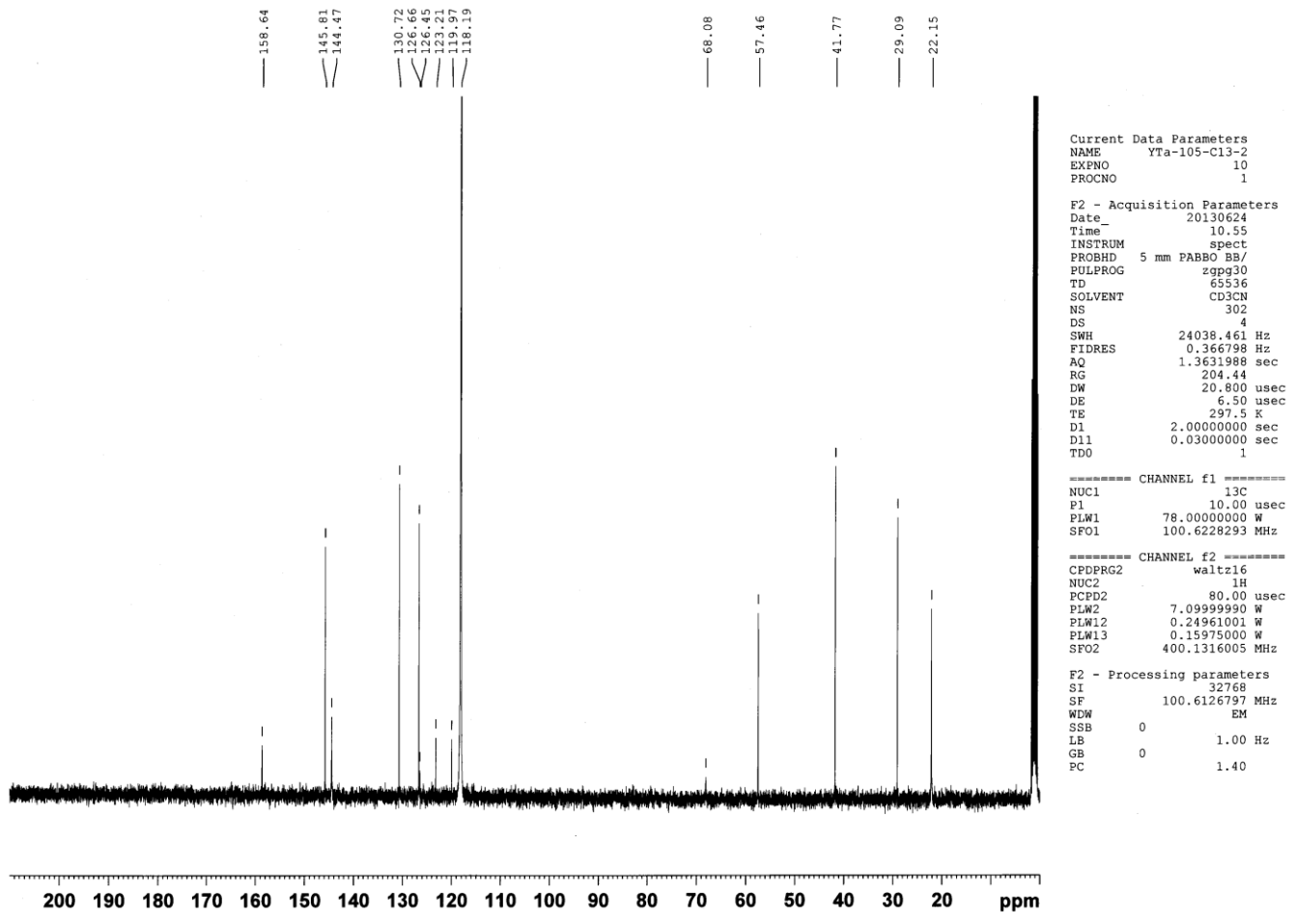
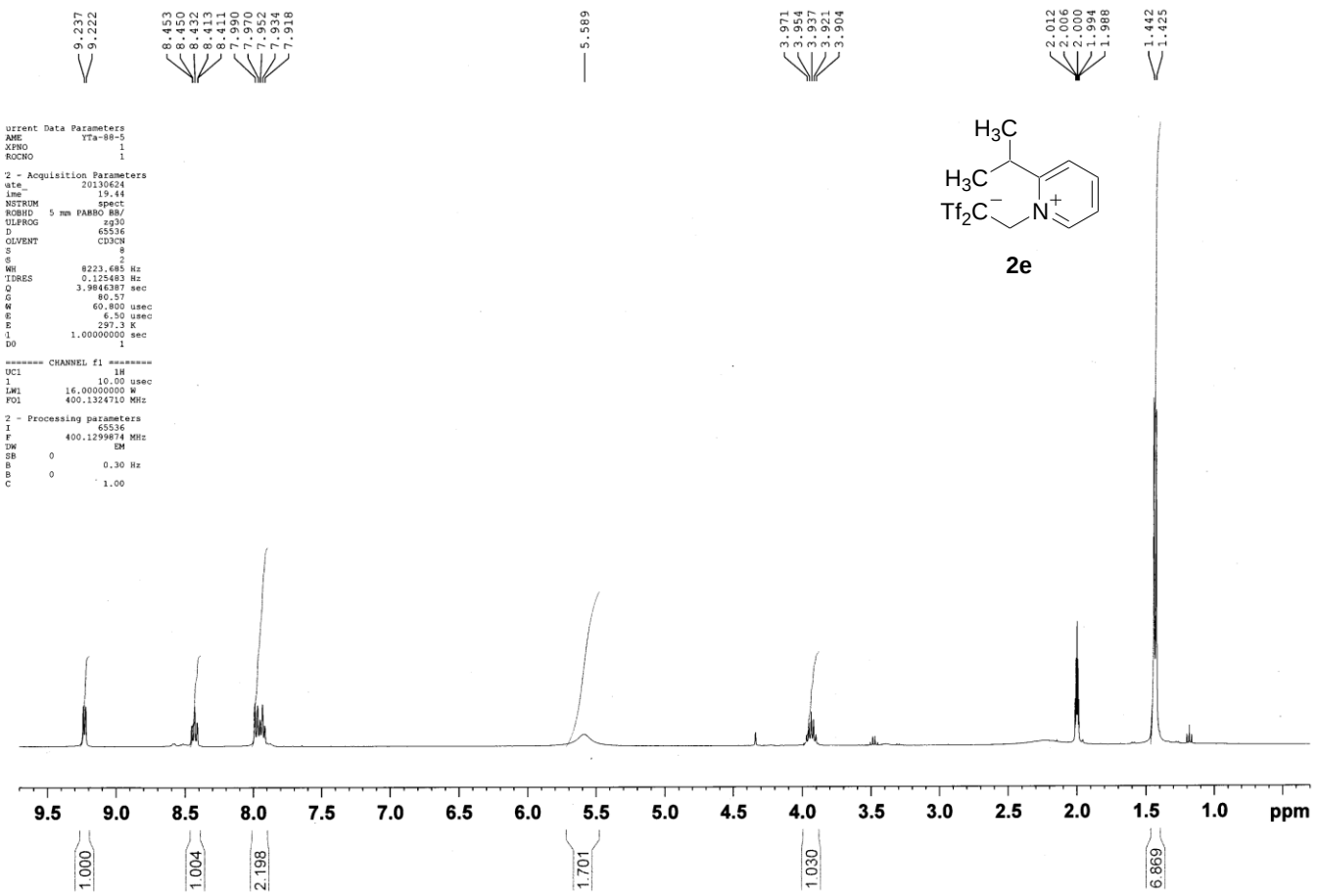
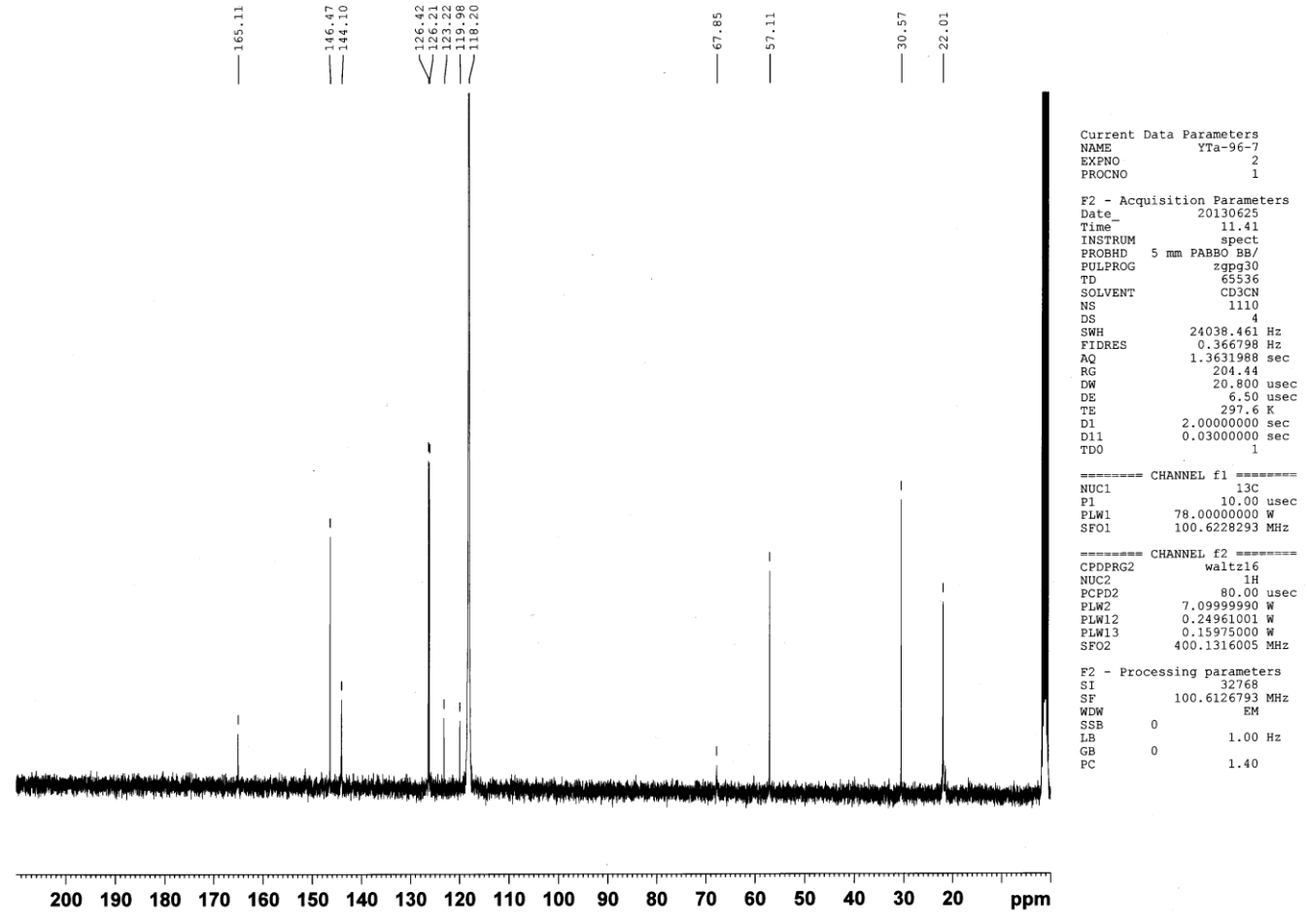
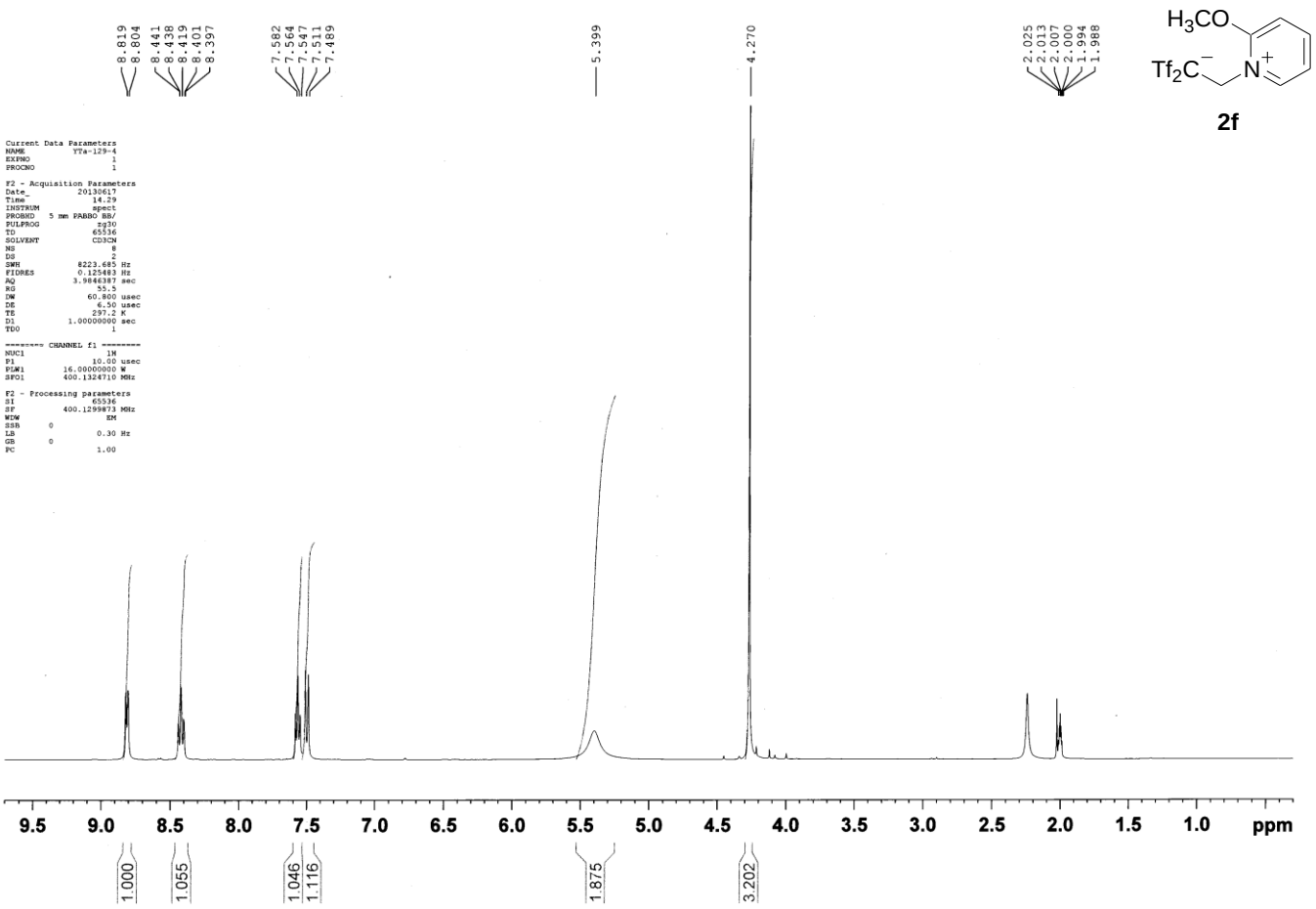
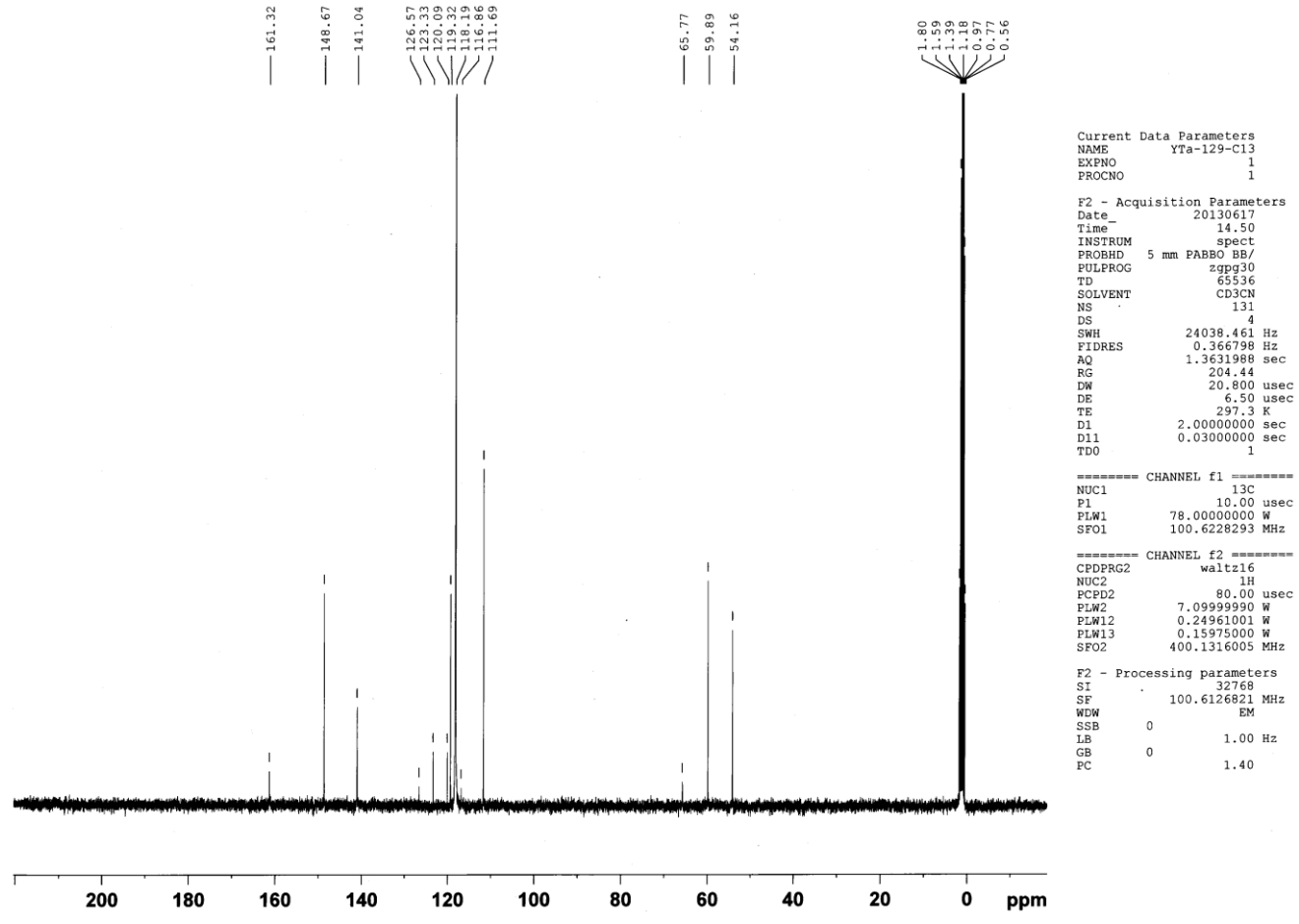
F2 - Acquisition Parameters
Date_ 20130624
Time_ 11.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 62.25
DW 60.800 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1299874 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H3C
CH3
Tf2C
N+
2d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000
1.028
1.010
1.057
1.813
1.881
1.192
6.691


158.64
145.81
144.47
130.72
126.66
126.45
123.21
119.97
118.19
68.08
57.46
41.77
29.09
22.15
Current Data Parameters
NAME YTa-105-C13-2
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130624
Time_ 10.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 302
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126797 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


9.237
9.222
8.453
8.450
8.432
8.413
8.411
7.990
7.970
7.952
7.934
7.918
5.589
3.971
3.954
3.937
3.921
3.904
2.012
2.006
2.000
1.994
1.988
1.442
1.425
urrent Data Parameters
AME YTa-88-5
XPNO 1
ROCNO 1
2 - Acquisition Parameters
ate_ 20130624
ime_ 19.44
NSTRUM spect
ROBHD 5 mm PABBO BB/
ULPROG zg30
D 65536
OLVENT CD3CN
S 8
G 2
WH 8223.685 Hz
IDRES 0.125483 Hz
Q 3.9846387 sec
G 80.57
W 60.800 usec
E 6.50 usec
E 297.3 K
1 1.00000000 sec
D0 1
====== CHANNEL f1 ======
UC1 1H
1 10.00 usec
LW1 16.00000000 W
FO1 400.1324710 MHz
2 - Processing parameters
I 65536
F 400.1299874 MHz
DW EM
SB 0
B 0.30 Hz
B 0
C 1.00
H3C
H3C
Tf2C
N+
2e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000
1.004
2.198
1.701
1.030
6.869

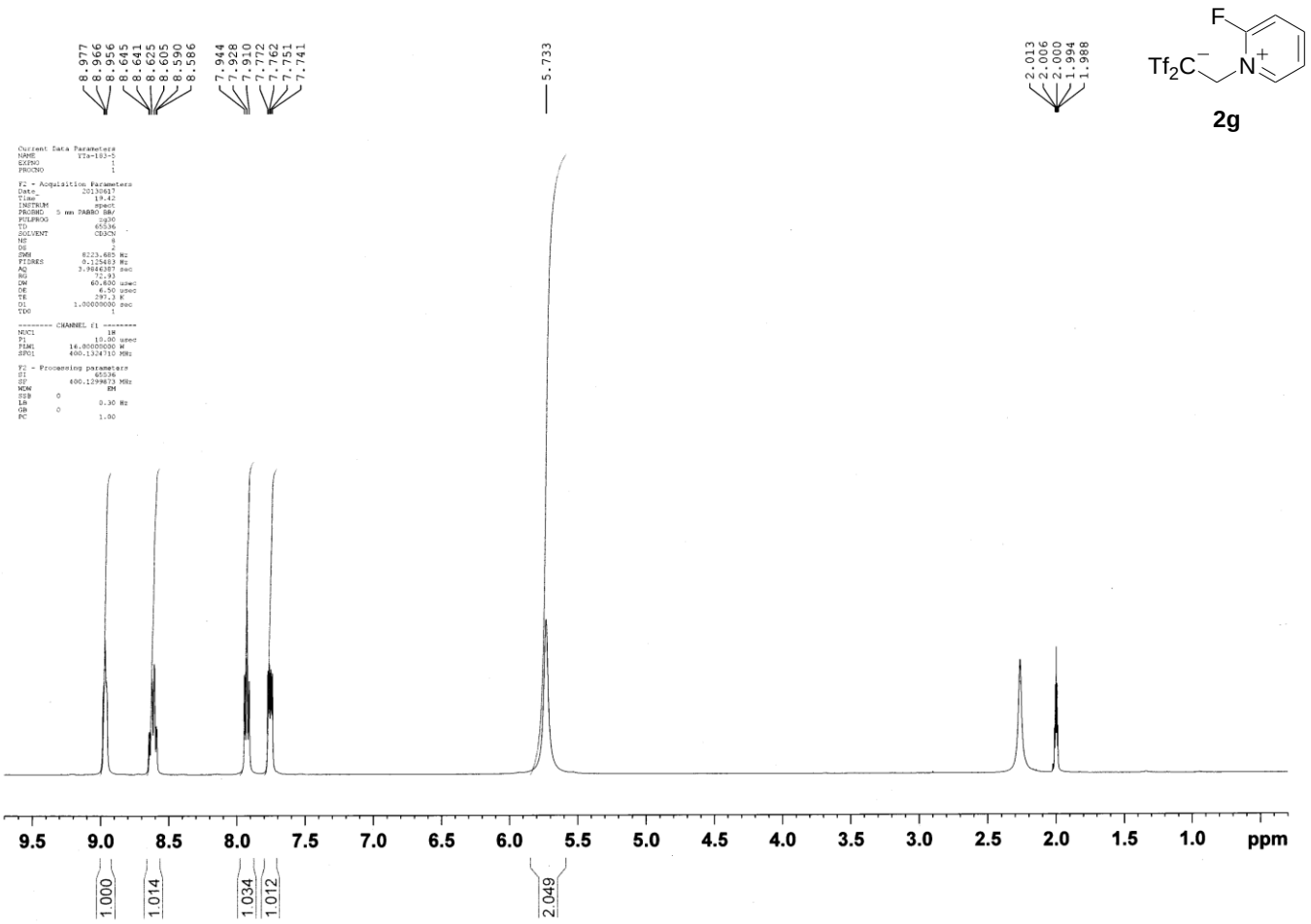

165.11
146.47
144.10
126.42
126.21
123.22
119.98
118.20
67.85
57.11
30.57
22.01
Current Data Parameters
NAME YTa-96-7
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130625
Time 11.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 1110
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126793 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

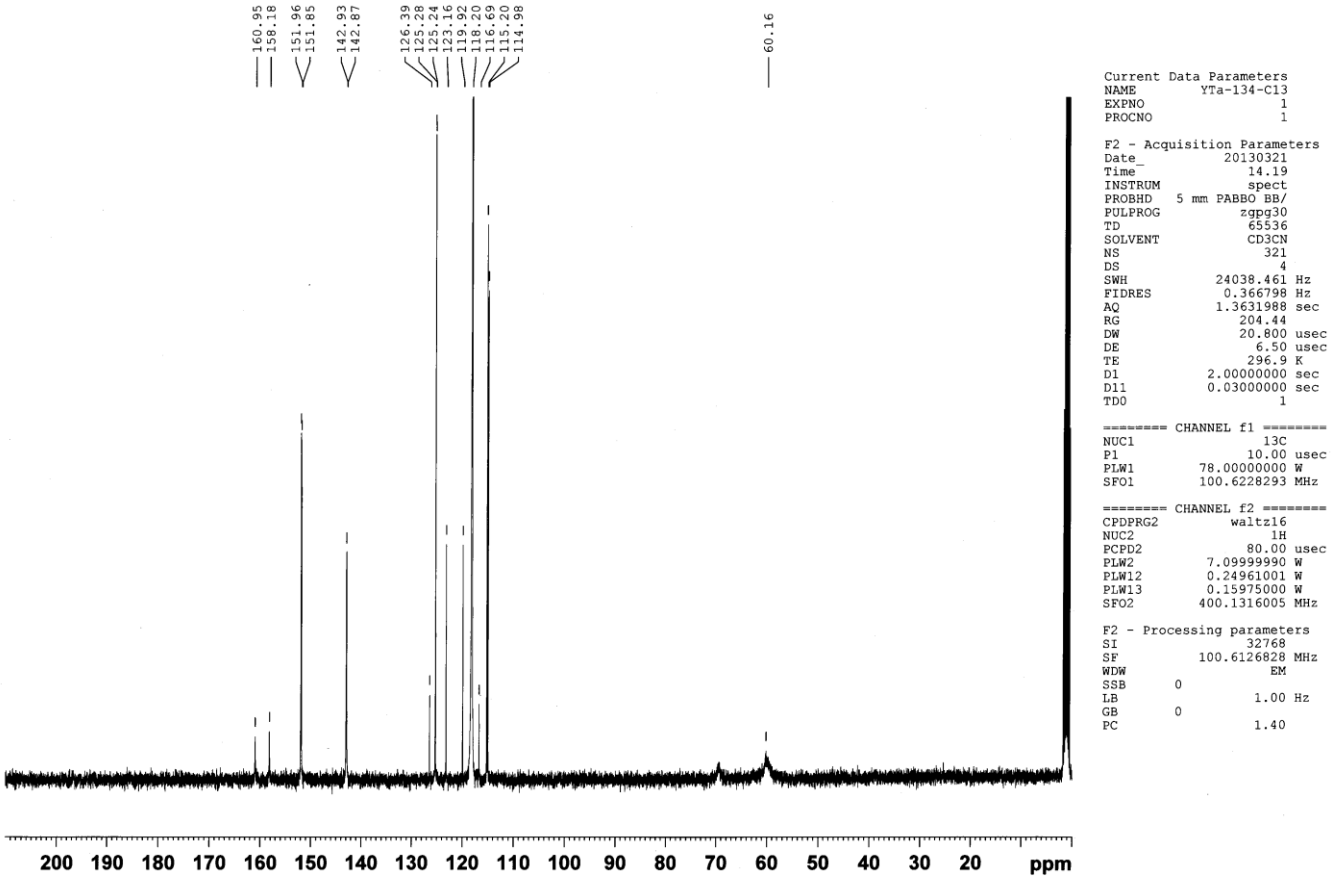

8.819
8.804
8.441
8.438
8.419
8.401
8.397
7.582
7.564
7.547
7.511
7.489
5.399
4.270
2.025
2.013
2.007
2.000
1.994
1.988
Current Data Parameters
NAME YTa-129-4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130617
Time 14.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1299873 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000
1.055
1.046
1.116
1.875
3.202


161.32
148.67
141.04
126.57
123.33
120.09
119.32
118.19
116.86
111.69
65.77
59.89
54.16
1.80
1.59
1.39
1.18
0.97
0.77
0.56
Current Data Parameters
NAME YTa-129-C13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130617
Time 14.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 131
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126821 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

H3CO
Tf2C−
N+

2f





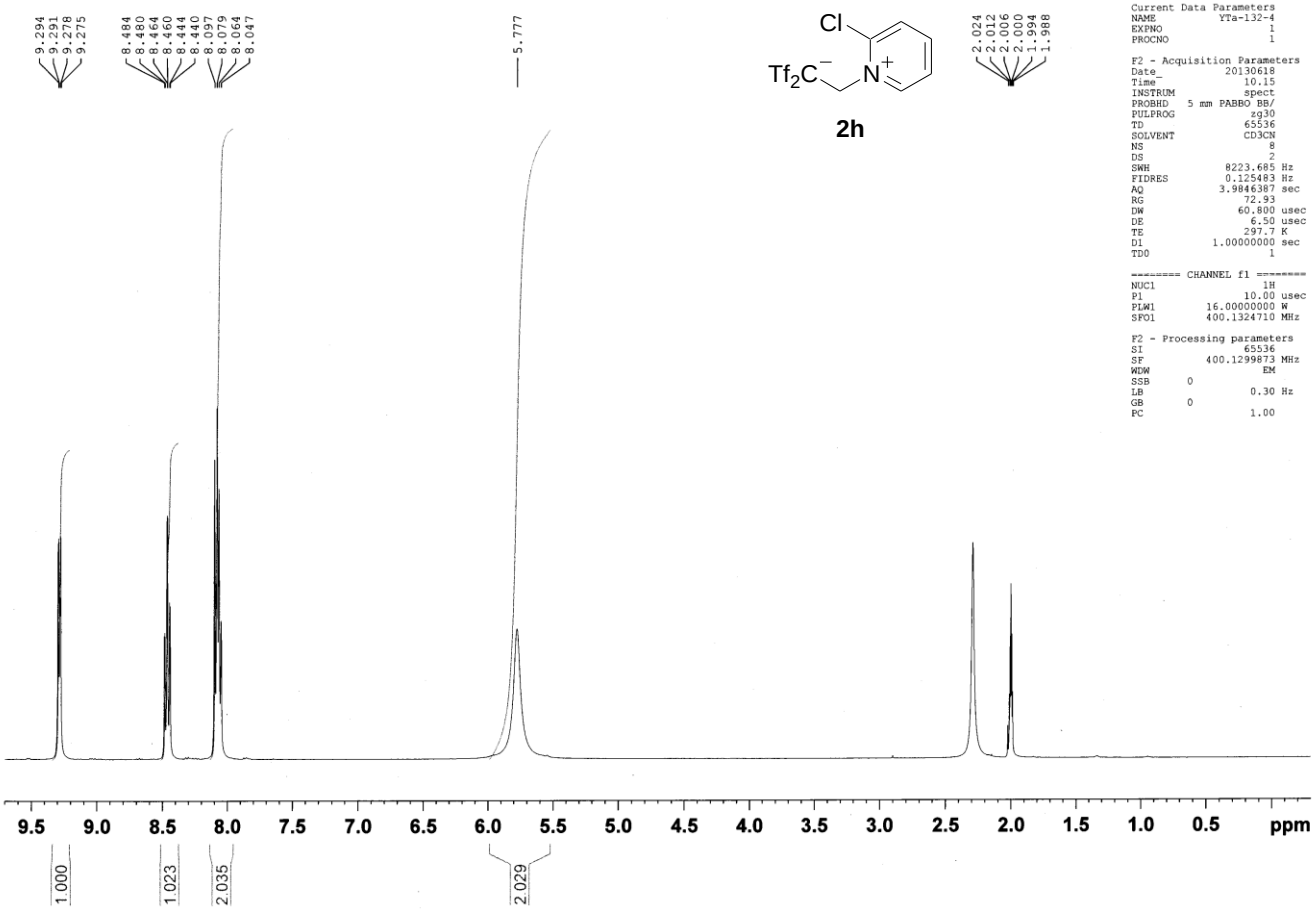
Current Data Parameters
NAME YTa-134-C13
EXPNO 1
PROCNO 1

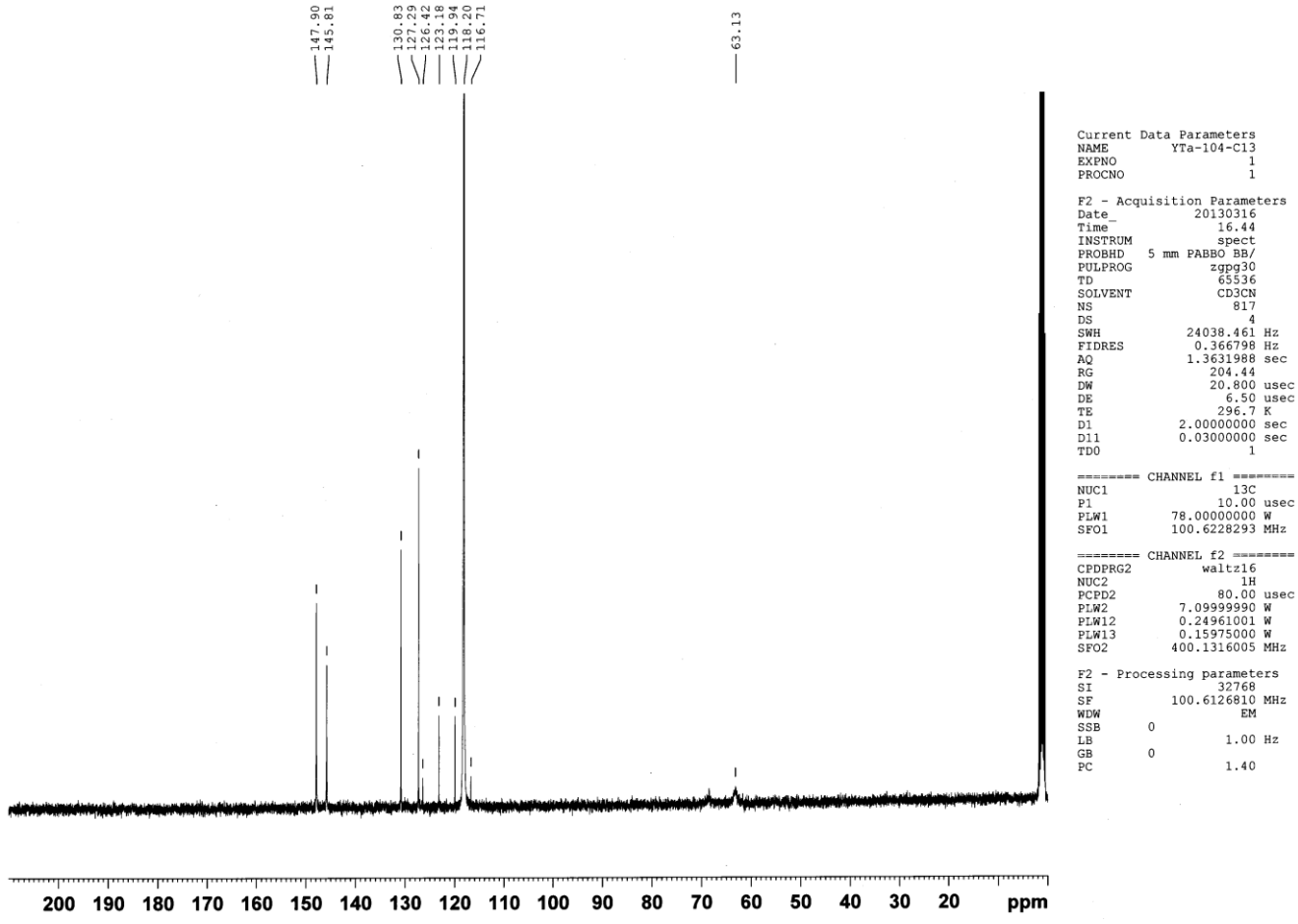
F2 - Acquisition Parameters
Date_ 20130321
Time 14.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 321
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

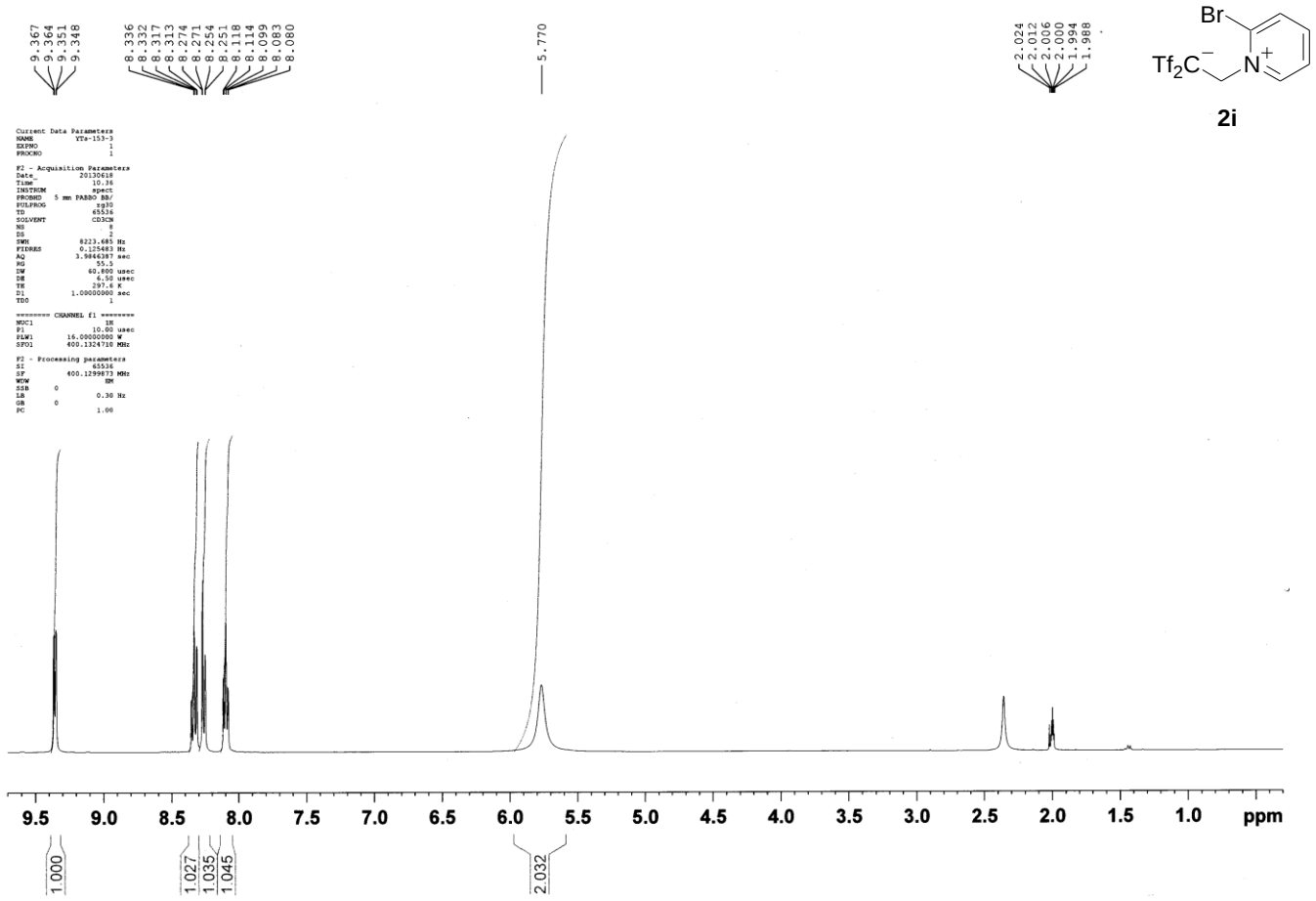
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

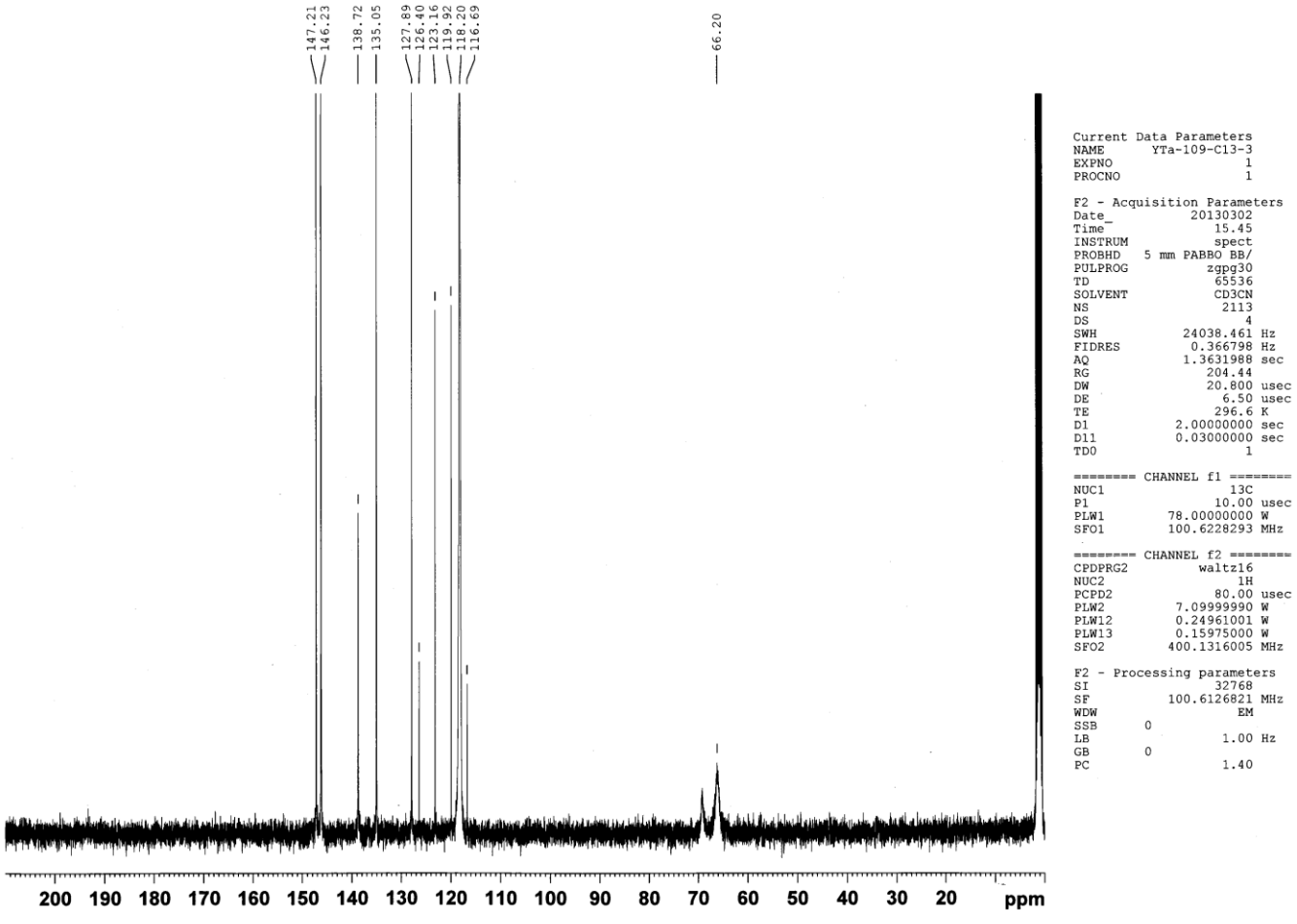
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

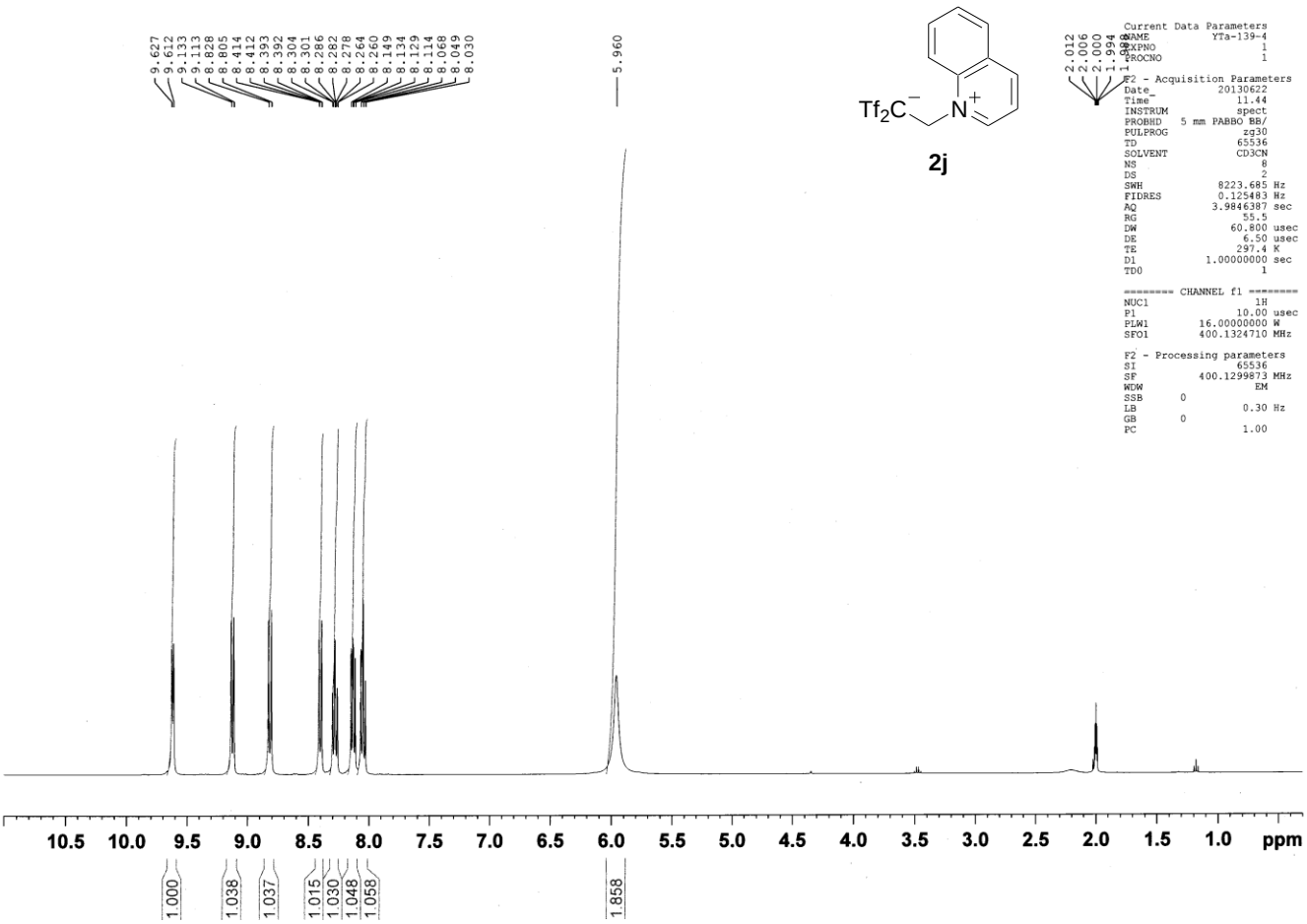
F2 - Processing parameters
SI 32768
SF 100.6126828 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

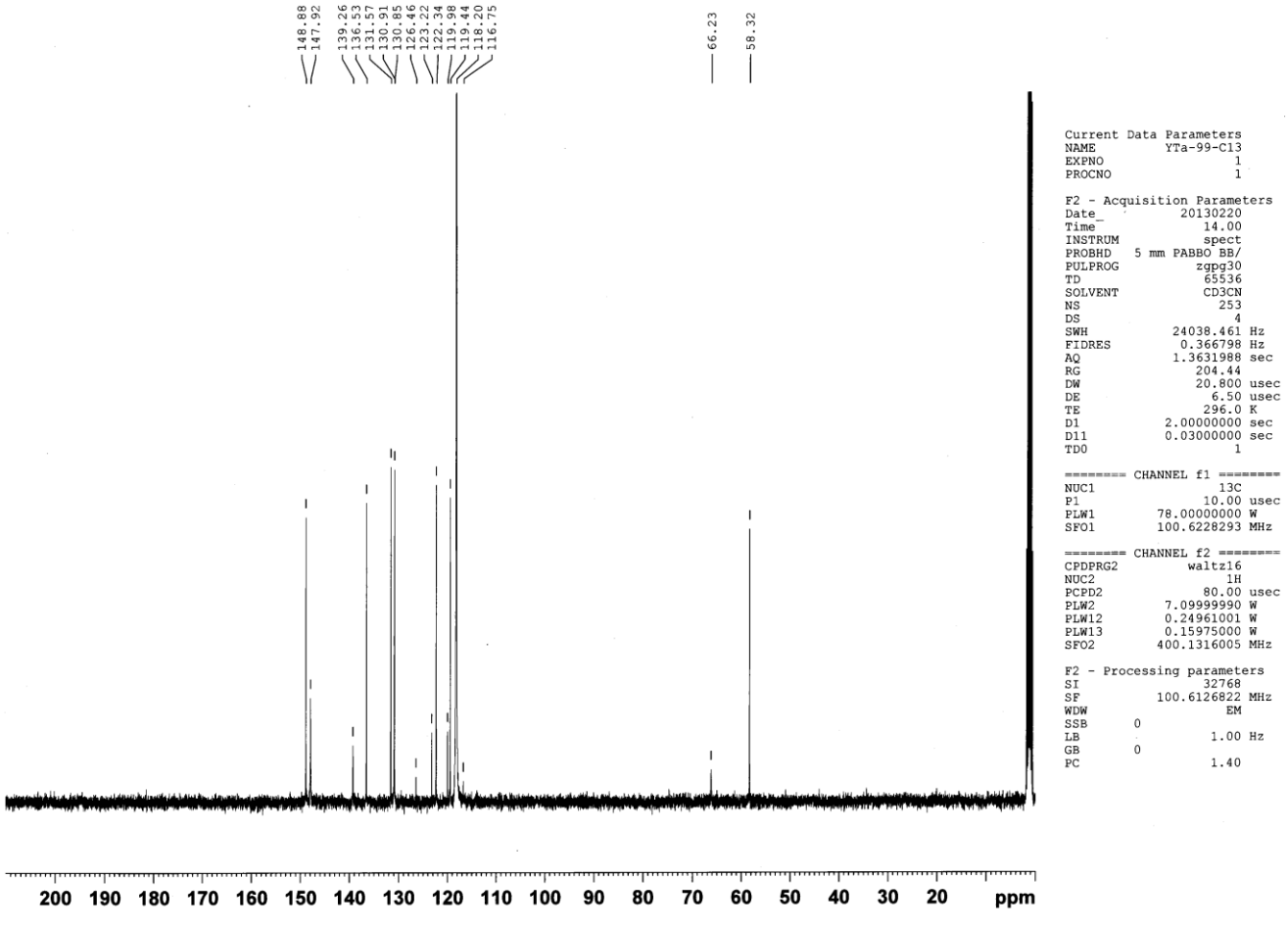

9.294
9.291
9.278
9.275
8.484
8.480
8.464
8.460
8.444
8.440
8.097
8.079
8.064
8.047
5.777
2.024
2.012
2.006
2.000
1.994
1.988
Cl
Tf2C−
N+
2h
Current Data Parameters
NAME YTa-132-4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130618
Time_ 10.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 72.93
DW 60.800 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1299873 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.023
2.035
2.029

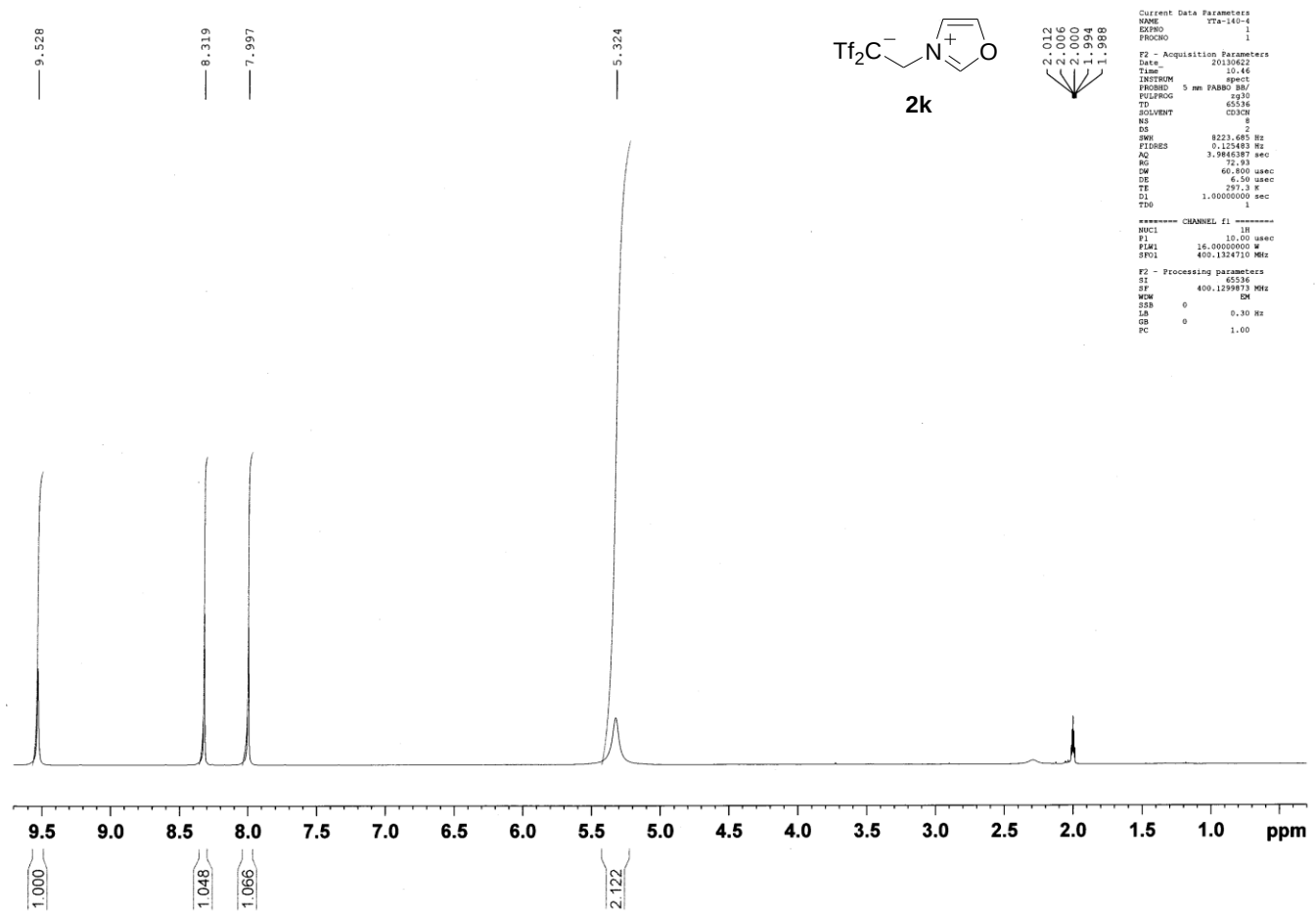

147.90
145.81
130.83
127.29
126.42
123.18
119.94
118.20
116.71
63.13
Current Data Parameters
NAME YTa-104-C13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130316
Time_ 16.44
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 817
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126810 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

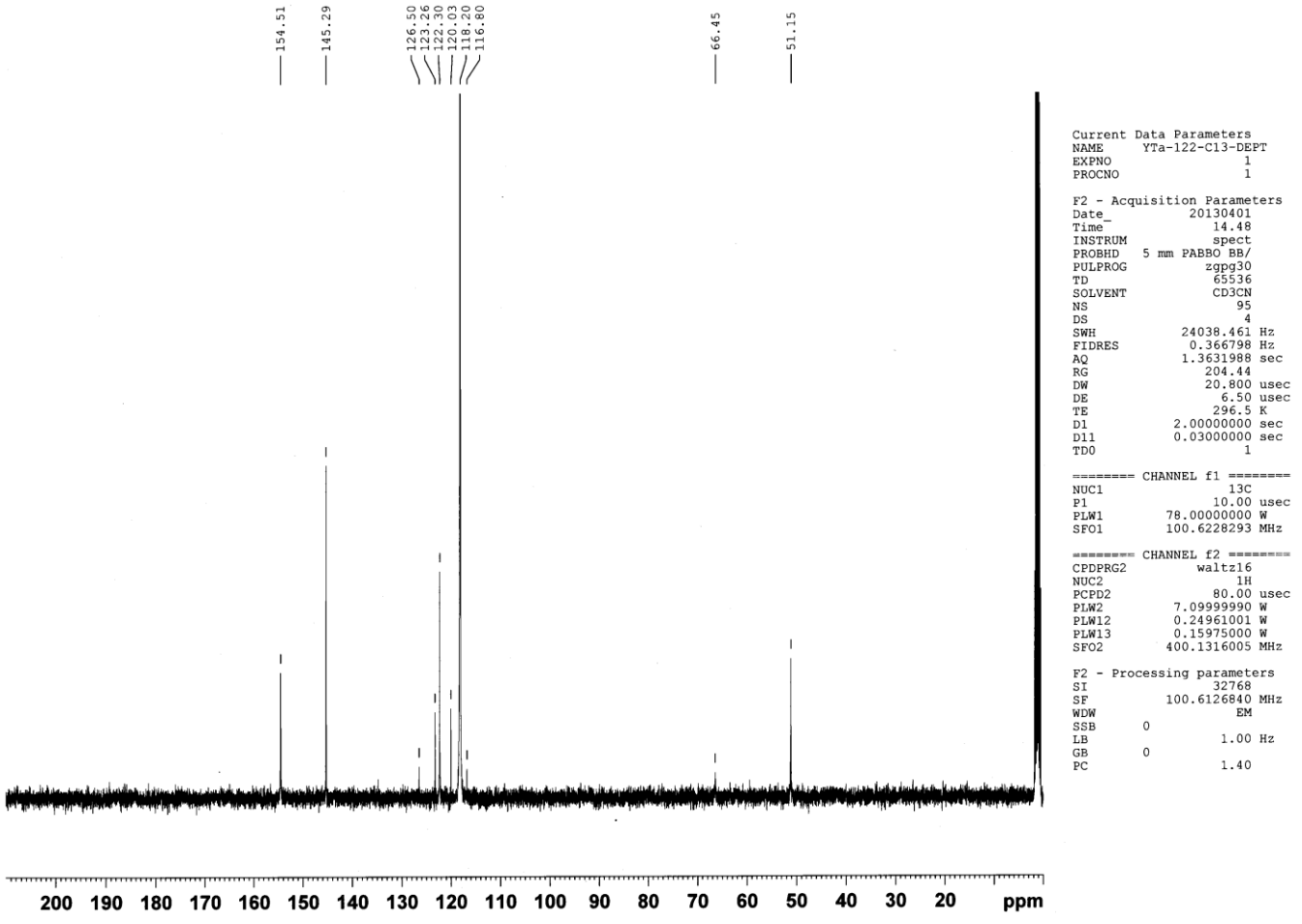

9.367
9.364
9.351
9.348
8.336
8.332
8.317
8.313
8.274
8.271
8.254
8.251
8.118
8.114
8.099
8.083
8.080
5.770
2.024
2.012
2.006
2.000
1.994
1.988
Br
Tf2C−
N+
2i
Current Data Parameters
NAME YTa-153-3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130618
Time 10.36
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1299873 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000
1.027
1.035
1.045
2.032

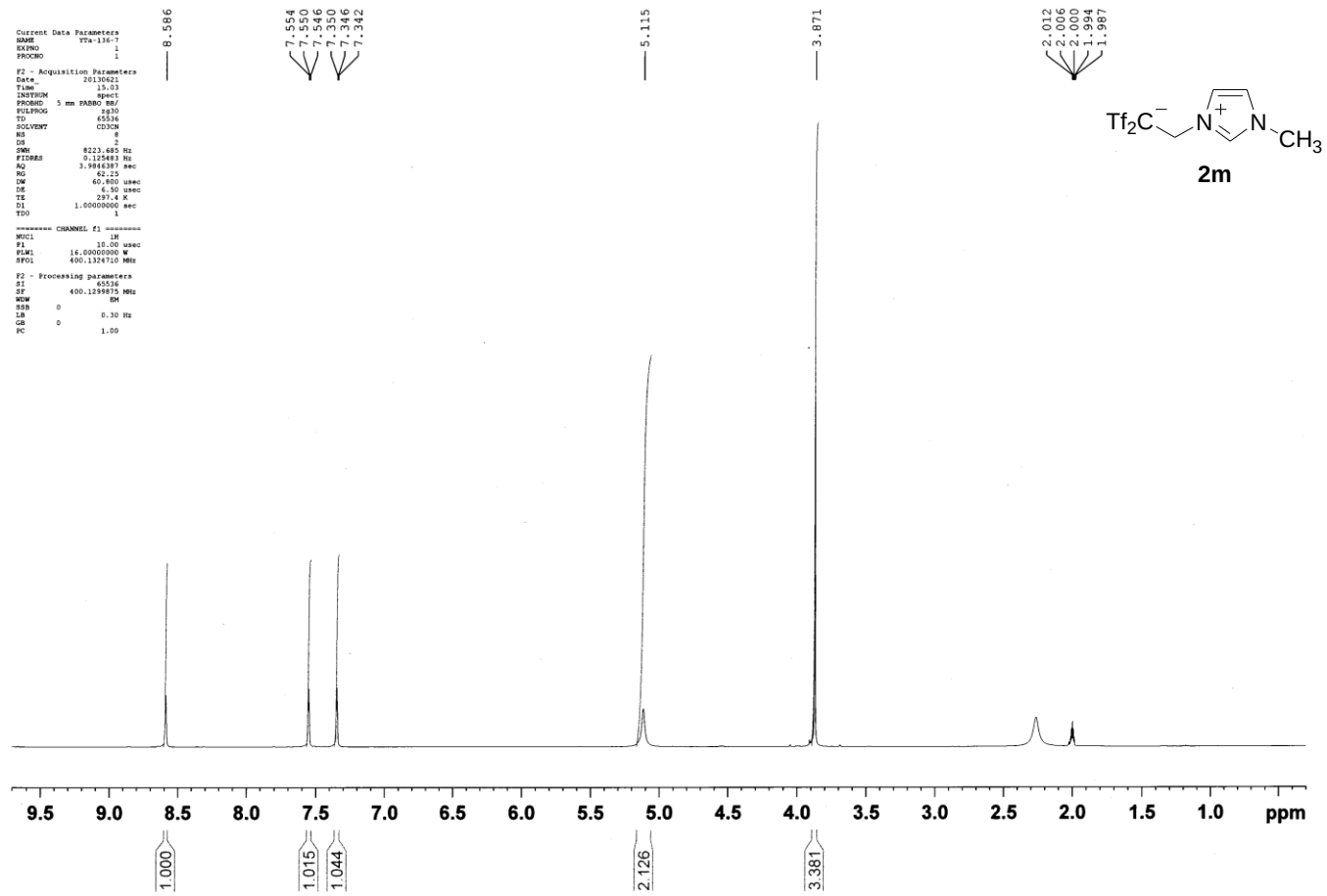

147.21
146.23
138.72
135.05
127.89
126.40
123.16
119.92
118.20
116.69
66.20
Current Data Parameters
NAME YTa-109-C13-3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130302
Time 15.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 2113
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126821 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


9.627
9.612
9.133
9.113
8.828
8.805
8.414
8.412
8.393
8.392
8.304
8.301
8.286
8.282
8.278
8.264
8.260
8.149
8.134
8.129
8.114
8.068
8.049
8.030
5.960
2.012
2.006
2.000
1.994
1.988
Tf2C
N
2j
Current Data Parameters
NAME YTa-139-4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130622
Time 11.44
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1299873 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000
1.038
1.037
1.015
1.030
1.048
1.058
1.858

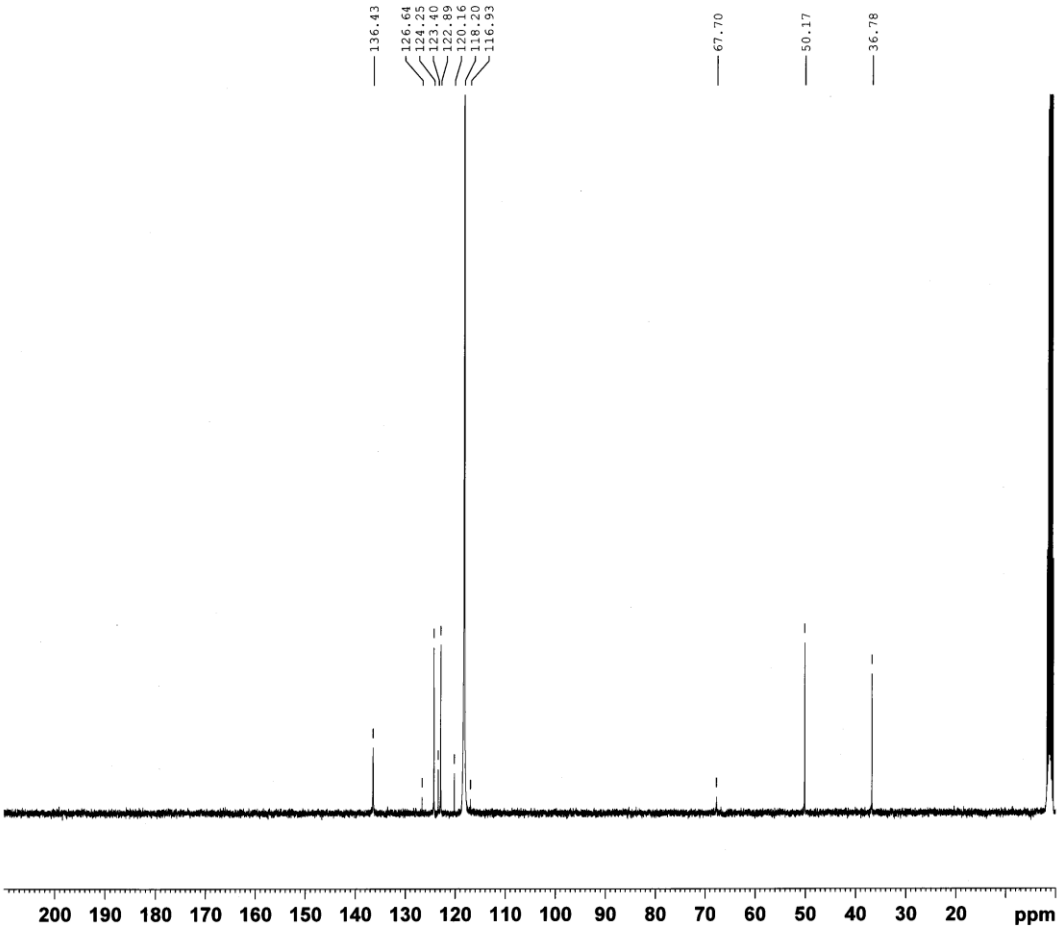

148.88
147.92
139.26
136.53
131.57
130.91
130.85
126.46
123.22
122.34
119.98
119.44
118.20
116.75
66.23
58.32
Current Data Parameters
NAME YTa-99-C13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130220
Time 14.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 253
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126822 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


9.528
8.319
7.997
5.324
2.012
2.006
2.000
1.994
1.988
2k
Current Data Parameters
NAME YTa-140-4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130622
Time 10.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 72.93
DW 60.800 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1299873 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000
1.048
1.066
2.122


154.51
145.29
126.50
123.26
122.30
120.03
118.20
116.80
66.45
51.15
Current Data Parameters
NAME YTa-122-C13-DEPT
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130401
Time 14.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 95
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6126840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



2m



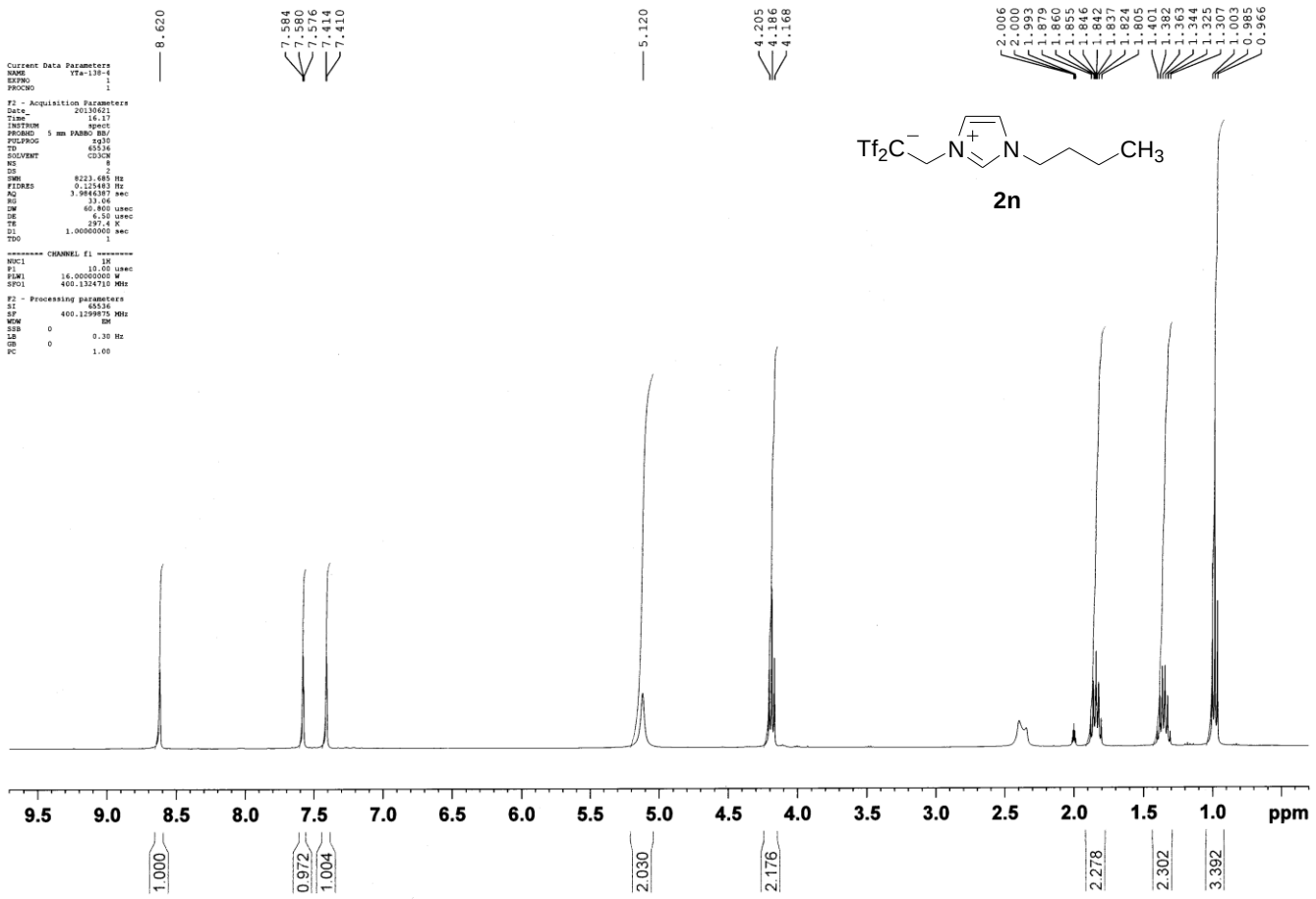

```
Current Data Parameters
NAME      YTa-120C-C13-3
EXPNO                 1
PROCNO                1

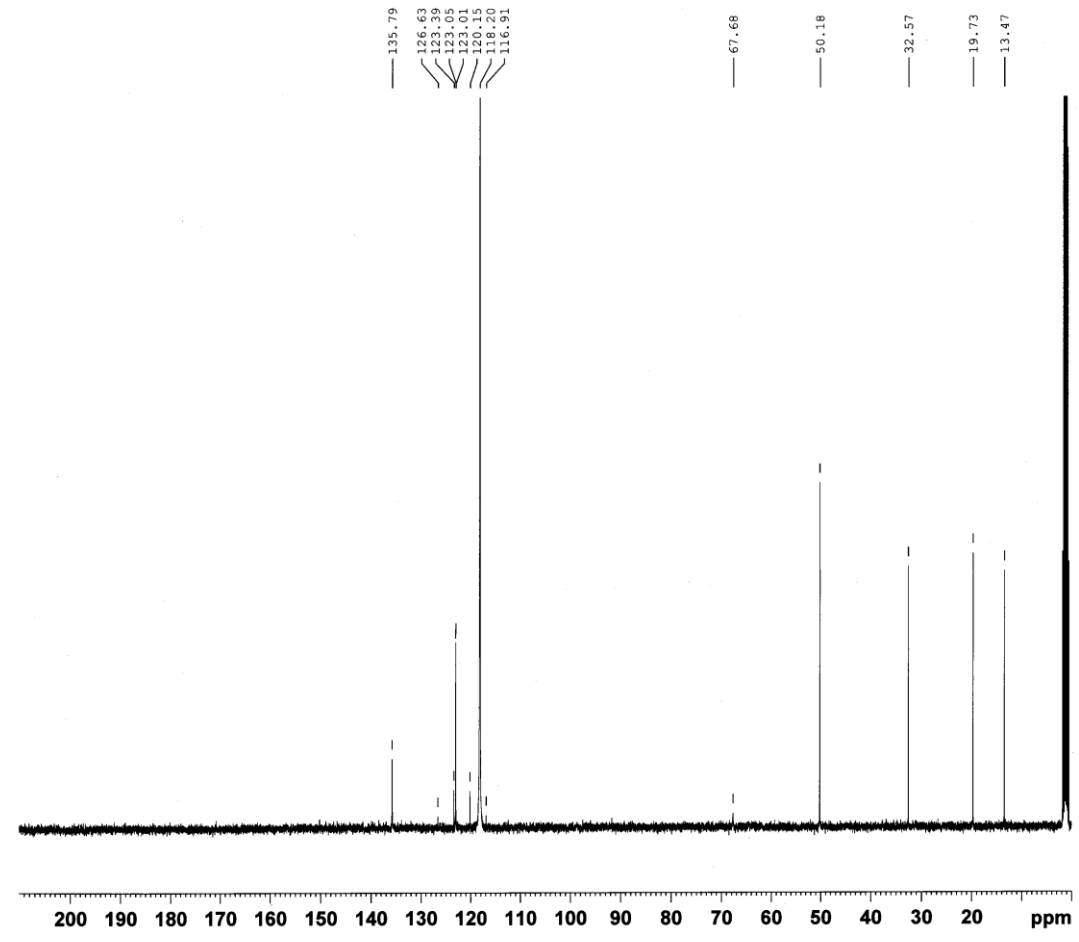
F2 - Acquisition Parameters
Date_          20130223
Time              12.02
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                 726
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG               204.44
DW               20.800 usec
DE                6.50 usec
TE               296.6 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PLW1        78.00000000 W
SFO1       100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2           80.00 usec
PLW2         7.09999990 W
PLW12        0.24961001 W
PLW13        0.15975000 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF         100.6126814 MHz
WDW                    EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```



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Current Data Parameters
NAME          YTa-118-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20130219
Time              18.57
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                 404
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG               204.44
DW               20.800 usec
DE                6.50 usec
TE               295.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PLW1         78.00000000 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PLW2          7.09999990 W
PLW12         0.24961001 W
PLW13         0.15975000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6126816 MHz
WDW                EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

7. References

1. (a) Waller, F. J.; Barrett, A. G. M., Braddock, D. C.; Ramprasad, D.; McKinnell, R. M.; White, A. J. P.; Williams, D. J.; Ducray, R. J. *J. Org. Chem.* **1999**, *64*, 2910. (b) Yanai, H.; Takahashi, A.; Taguchi, T. *Tetrahedron* **2007**, *63*, 12149.
2. Yanai, H.; Ogura, H.; Fukaya, H.; Kotani, A.; Kusu, F.; Taguchi, T. *Chem.–Eur. J.* **2011**, *17*, 11747.
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4. (a) NBO 5.G: E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2004; http://www.chem.wisc.edu/~nbo5. (b) Weinhold, F.; Clark, L., *Valence and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, UK, 2005.