

Highly Efficient, Organocatalytic Aerobic Alcohol Oxidation

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General experimental procedures:

All reactions were carried out under an atmosphere of argon unless otherwise specified. Ethereal solvents and dichloromethane (anhydrous; KANTO CHEMICAL CO., INC.) were used as received. All other solvents were dried and distilled by standard procedures. Yields refer to chromatographically and spectroscopically ($^1\text{H-NMR}$) homogeneous materials unless otherwise stated. Reagents were purchased from commercial suppliers and used without further purification unless otherwise stated.

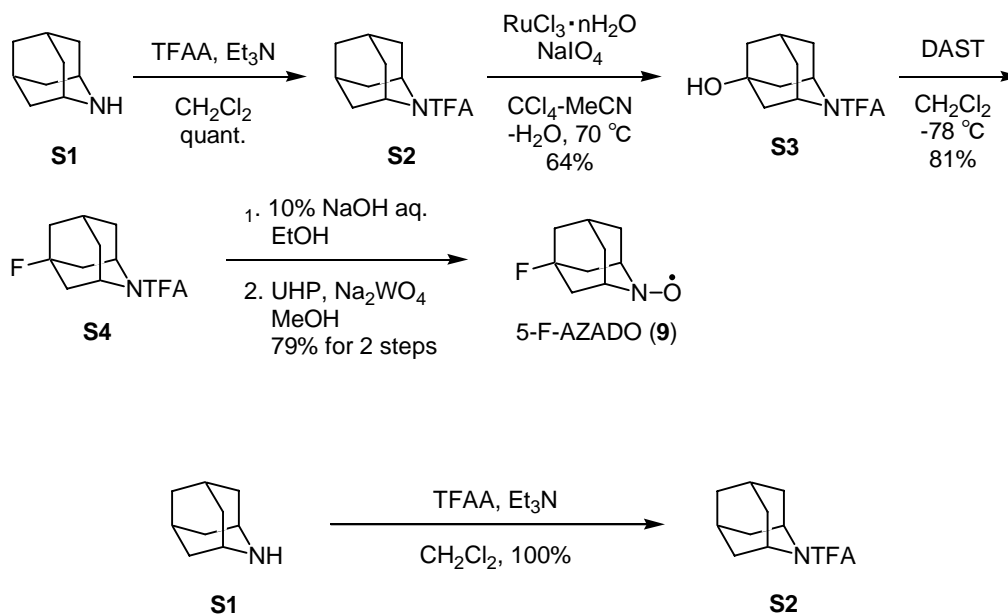
Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F₂₅₄) using UV light as visualizing agent and *p*-anisaldehyde in ethanol/aqueous $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$ for staining. Column chromatography was performed with Silica Gel 60N (spherical, particle size 0.063-0.210 mm, neutral, KANTO CHEMICAL CO., INC.) or Silica Gel 60N (spherical, particle size 0.040-0.050 mm, neutral, KANTO CHEMICAL CO., INC.). The eluents employed are reported as volume : volume percentages.

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded using a JEOL JNM-AL400 (400 MHz), and a JEOL ECA-600 (600 MHz) spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Carbon-13 nuclear magnetic resonance ($^{13}\text{C-NMR}$) spectra were recorded using a JEOL JNM-AL400 (100 MHz) and a JEOL ECA-600 (150 MHz) spectrometers. Chemical shift is reported in ppm relative to the center line of the triplet of CDCl_3 .

Melting points were determined using Yazawa BY-2 melting point apparatus and are reported uncorrected. In parentheses after melting point, the recrystallization solvents are shown. Infrared spectra were obtained on a JASCO FT-IR-410 at 4.0 cm^{-1} resolution and are reported in wavenumbers. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 using electron impact (EI). Low resolution mass spectra (MS) were recorded on a JEOL JMS-DX303. Elemental analyses were performed using Yanaco CHN CORDER MT-6.

Synthesis of 5-F-AZADO (9)

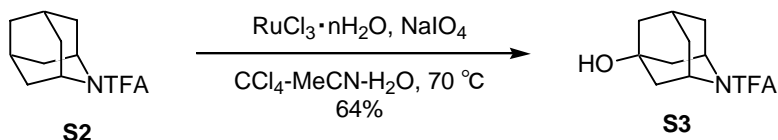
Scheme S1. Synthesis of 5-F-AZADO (9)



N-Trifluoroacetyl-2-azaadamantane (S2)

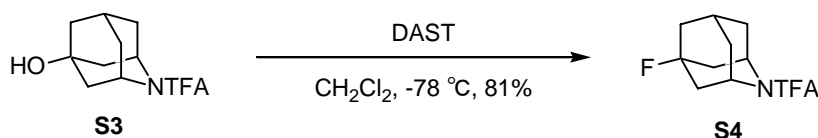
To a solution of 2-azaadamantane **S1**¹ (4.0 g, 29.1 mmol) in CH₂Cl₂ (0.2 M, 150 mL), Et₃N (6.1 mL, 43.7 mmol), TFAA (6.1 mL, 43.7 mmol) was added at 0 °C. After the mixture was stirred for 2 hr at ambient temperature, sat. NaHCO₃ was poured and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO₄ and evaporated. The crude amide was purified with column chromatography (AcOEt – Hexane = 1 : 8) to afford amide **S2** (6.8 g, 29.1 mmol, 100%) as a colorless oil.

¹H-NMR (400 MHz, CDCl₃): δ 4.76 (br s, 1H), 4.23 (br s, 1H), 2.14 (br s, 2H), 1.83-1.91 (m, 10H).
¹³C-NMR (100 MHz, CDCl₃): δ 154.1 (q, *J* = 35.3 Hz), 116.8 (q, *J* = 288.4 Hz), 49.7 (q, *J* = 3.3 Hz), 46.2, 36.1, 35.2, 35.1, 26.2. IR (neat, cm⁻¹): 1685. MS *m/z*: 233 (*M*⁺), 233 (100%). HRMS (EI): Calcd. for C₁₁H₁₄F₃NO: 233.1027, found: 233.1023.



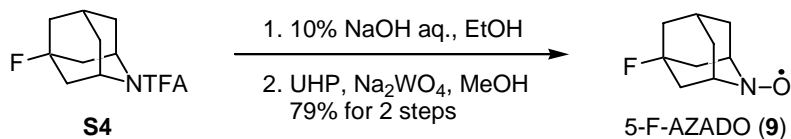
***N*-Trifluoroacetyl-5-hydroxy-2-azaadamantane (S4)**

To a solution of amide **S2** (500 mg, 2.14 mmol) in CCl_4 – MeCN – H_2O (1.65 M, 1.3 mL – 1.1 M, 1.9 mL – 1.1 M, 1.9 mL), NaIO_4 (1.05 g, 4.90 mmol), $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (44 mg, 0.214 mmol) was added at ambient temperature. After the reaction mixture was vigorously stirred for 20 hr at 70 °C, sat. NaHCO_3 and sat. $\text{Na}_2\text{S}_2\text{O}_3$ was poured and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO_4 and evaporated. The crude 5-hydroxy-amide was purified with column chromatography (AcOEt – Hexane = 1 : 2) to afford 5-hydroxy-amide **S3** (341 mg, 1.37 mmol, 64%, 80% brsm) as a white solid accompanied with recovered amide **S2** (100 mg). mp 95-96 °C (CHCl_3 - Et_2O). ^1H -NMR (400 MHz, CDCl_3): δ 4.97 (br s, 1H), 4.43 (br s, 1H), 2.40 (br s, 1H), 1.89-1.73 (m, 10H). ^{13}C -NMR (100 MHz, CDCl_3): δ 154.0 (q, J = 35.3 Hz), 116.5 (q, J = 288.3 Hz), 66.6, 51.5 (q, J = 3.6 Hz), 48.3, 43.6, 43.1, 42.9, 34.9, 34.0, 28.8. IR (neat, cm^{-1}): 3425, 1681. MS m/z : 249 (M^+), 249 (100%). HRMS (EI): Calcd. for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}_2$: 249.0977, found: 249.0956. Anal.: Calcd. for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}_2$: C, 53.01; H, 5.66; N, 5.62, found: C, 52.88; H, 5.66; N, 5.62.



5-Fluoro-*N*-trifluoroacetyl-2-azaadamantane (S4)

To a solution of 5-hydroxy-amide **S4** (2.77 g, 11.1 mmol) in CH_2Cl_2 (0.6 M, 18.5 mL), DAST (2.9 mL, 22.2 mmol) was added at -78 °C. After the reaction mixture was stirred for 1 hr at 0 °C, the mixture was diluted with Et_2O then quenched with H_2O . The mixture was extracted with AcOEt. The organic layer was washed with brine and dried over MgSO_4 and evaporated. The crude 5-fluoro-amide was purified with column chromatography (AcOEt – Hexane = 1 : 4) to afford 5-fluoro-amide **S4** (2.30 g, 8.98 mmol, 81%) as a white solid. mp 52 °C (Hexane). ^1H -NMR (600 MHz, CDCl_3): δ 5.02 (br s, 1H), 4.48 (br s, 1H), 2.47 (br d, J = 1.8 Hz, 2H), 2.06-1.94 (m, 6H), 1.81-1.77 (m, 2H), 1.73-1.67 (m, 2H). ^{13}C -NMR (150 MHz, CDCl_3): δ 154.1 (q, J = 35.6 Hz), 116.6 (q, J = 289.7 Hz), 89.9 (d, J = 187.9 Hz), 52.0 (m), 48.8 (d, J = 11.5 Hz), 41.4 (d, J = 20.1 Hz), 40.7 (d, J = 17.2 Hz), 40.7 (d, J = 18.6 Hz), 34.7, 33.8, 29.6 (d, J = 10.1 Hz). IR (neat, cm^{-1}): 1681, 1232, 1179, 1132, 1064. MS m/z : 251 (M^+), 251 (100%). HRMS (EI): Calcd. for $\text{C}_{11}\text{H}_{13}\text{F}_4\text{NO}$: 251.0933, found: 251.0919. Anal.: Calcd. for $\text{C}_{11}\text{H}_{13}\text{F}_4\text{NO}$: C, 52.43; H, 5.22; N, 5.58, found: C, 52.59; H, 5.22; N, 5.58.



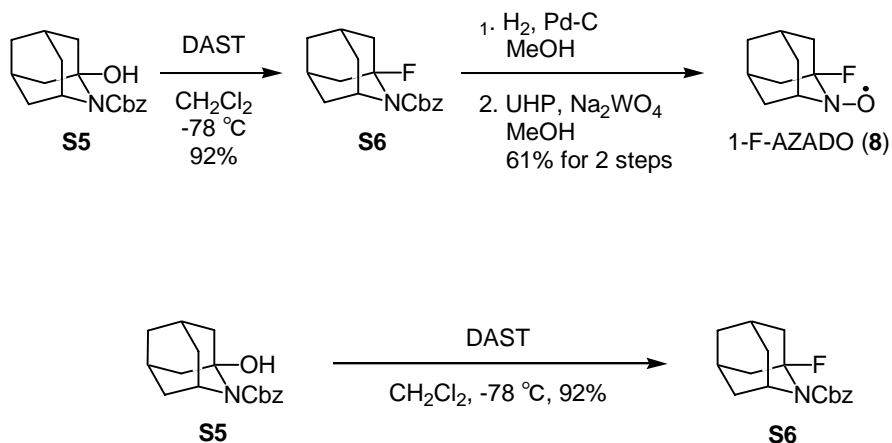
5-Fluoro-2-azaadamantane *N*-oxyl (**9**)

To a solution of 5-fluoro-amide **S4** (2.3 g, 8.98 mmol) in EtOH (54 mL), *aq.* NaOH (10%← 27 mL) was added at ambient temperature. After the reaction mixture was stirred for 2 hr, the mixture was diluted with H₂O and extracted with CHCl₃. The organic layer was dried over K₂CO₃ and evaporated. The crude amine was used without further purification. After a solution of the crude amine and Na₂WO₄·2H₂O (1.5 g, 4.5 mmol) in MeOH (0.5 M, 18 mL) was stirred at ambient temperature for 30 min, UHP (3.4 g, 35.9 mmol) was added. After 1 hr, additional UHP (0.84 g, 8.98 mmol) was added and the mixture was stirred for another 5 hr. The mixture was diluted with sat. NaHCO₃ and the solvent was removed under reduced pressure. H₂O was added to the residue and the mixture was extracted with CHCl₃. The organic layer was dried over K₂CO₃ and evaporated and purified with column chromatography (Et₂O – Hexane = 2 : 1) to afford 5-F-AZADO (**9**, 1.2 g, 7.05 mmol, 79% for 2 steps) as a yellow solid.

mp 115 °C (CHCl₃-Et₂O). IR (neat, cm⁻¹): 1442, 1347, 1282. MS *m/z*: 170 (M⁺), 170 (100%). HRMS (EI): Calcd. for C₉H₁₃FNO: 170.0981, found: 170.0965. Anal.: Calcd. for C₉H₁₅FNO: C, 63.51; H, 7.70; N, 8.23, found: C, 63.32; H, 7.62; N, 8.13.

Synthesis of 1-F-AZADO (**8**)

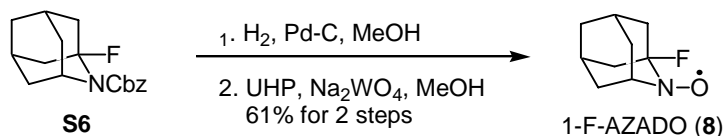
Scheme S2. Synthesis of 1-F-AZADO (**8**)



***N*-Benzyloxycarbonyl-1-fluoro-2-azaadamantane (**S6**)**

To a solution of carbamate **S5**² (227 mg, 0.79 mmol) in CH₂Cl₂ (1.43 mL), DAST (0.32 mL, 2.37 mmol) was added at -78 °C. After the reaction mixture was stirred for 1 hr at 0 °C, the mixture was diluted with Et₂O and quenched with H₂O. The mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO₄ and evaporated. The crude carbamate was purified with column chromatography (AcOEt – Hexane = 1 : 4) to afford carbamate **S6** (211 mg, 0.729 mmol, 92%) as a yellow oil.

¹H-NMR (600 MHz, CDCl₃): δ 7.37-7.36 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.26 (m, 1H), 5.19 (s, 2H), 4.62 (m, 1H), 2.32 (br d, *J* = 2.5 Hz, 2H), 2.13-2.10 (m, 2H), 1.92-1.88 (m, 2H), 1.79-1.69 (m, 4H), 1.61-1.58 (m, 2H). ¹³C-NMR (150 MHz, CDCl₃): δ 155.8 (d, *J* = 2.9 Hz), 136.8, 128.4, 127.7, 127.6, 100.0 (d, *J* = 218.0 Hz), 66.9, 53.7, 41.0 (d, *J* = 20.1 Hz), 34.2, 29.9 (d, *J* = 10.1 Hz). IR (neat, cm⁻¹): 1720, 1687, 1392. MS *m/z*: 289 (M⁺), 91 (100%). HRMS (EI): Calcd. for C₁₇H₂₀FNO₂: 289.1478, found: 289.1465.



1-Fluoro-2-azaadamantane *N*-oxyl (8**)**

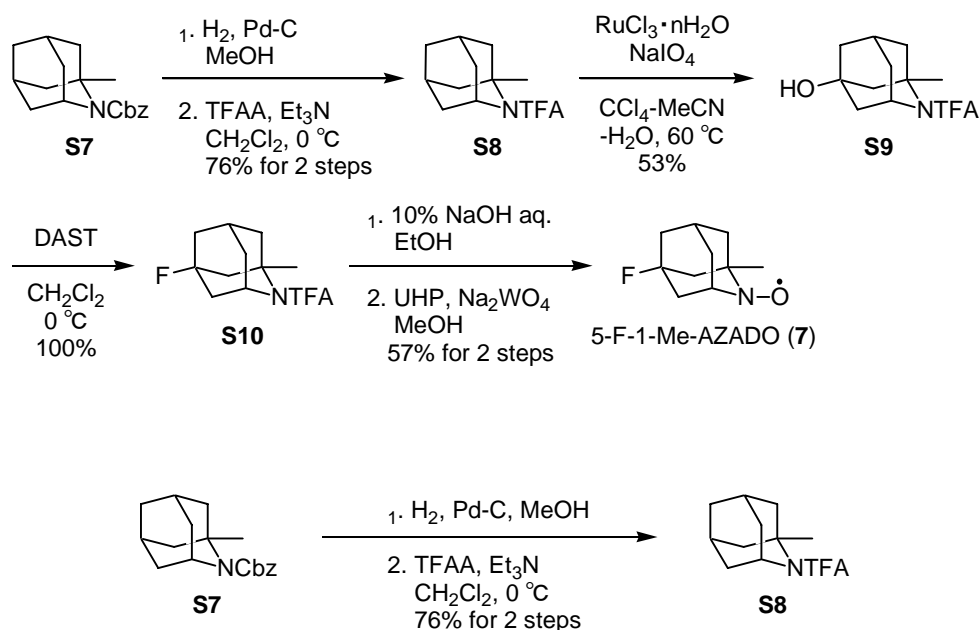
To a solution of carbamate **S6** (155 mg, 0.535 mmol) in MeOH (6 mL, 0.1 M), 10% Pd-C (16 mg) was added under Ar atmosphere. After the reaction flask was purged with H₂ three times, the reaction mixture was stirred at ambient temperature for 2 hr under hydrogen atmosphere. After the reaction flask was purged with Ar atmosphere, the reaction mixture was filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The residue was diluted with CHCl₃ and the solution was washed with sat. Na₂CO₃, dried over K₂CO₃ and evaporated. The crude product was used without further purified. A solution of the crude product and Na₂WO₄·2H₂O (74.3 mg, 0.225 mmol) in MeOH (0.5 M, 0.9 mL) was stirred at ambient temperature for 30 min. UHP (169 mg, 1.8 mmol) was added to the mixture at 0 °C. After the mixture was stirred at ambient temperature for 3 hr, it was diluted with sat. NaHCO₃ and the solvent was removed under reduced pressure. H₂O was added to the residue and the mixture was extracted with CHCl₃. The organic layer was dried over K₂CO₃ and evaporated. The crude 1-F-AZADO (**8**) was purified with column chromatography (Et₂O – Hexane = 2 : 1) to afford 1-F-AZADO (**8**; 56.0 mg, 0.329 mmol, 61% for 2 steps) as a yellow solid.

mp 148-150 °C (CHCl₃-Et₂O) (Color change: to red at 58-59 °C). IR (neat, cm⁻¹): 1449, 1323,

1257. MS m/z : 170 (M^+), 97 (100%). HRMS (EI): Calcd. for $C_9H_{13}FNO$: 170.0981, found: 170.0968. Anal.: Calcd. for $C_9H_{13}FNO$: C, 63.51; H, 7.70; N, 8.23, found: C, 63.44; H, 7.67; N, 8.23.

Synthesis of 5-F-1-Me-AZADO (7)

Scheme S3. Synthesis of 5-F-1-Me-AZADO (7)

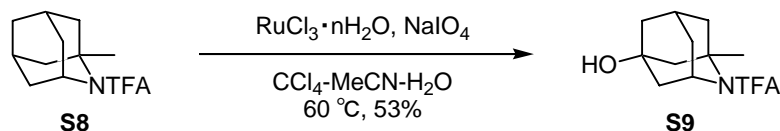


1-Methyl-N-trifluoroacetyl-2-azaadamantane (S8)

To a solution of carbamate **S7**² (1.89 g, 6.61 mmol) in MeOH (66 mL, 0.1 M), 10% Pd-C (189 mg) was added under Ar atmosphere. After the reaction flask was purged with H_2 three times, the reaction mixture was stirred at ambient temperature for 2 hr under atmosphere of hydrogen. After the reaction flask was purged with Ar atmosphere, the reaction mixture was filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The residue was diluted with $CHCl_3$ and washed with sat. $NaHCO_3$, dried over K_2CO_3 and evaporated. The crude product was not further purified. To a solution of the crude product in CH_2Cl_2 (33 mL, 0.2 M), Et_3N (1.4 mL, 9.91 mmol), TFAA (1.4 mL, 9.91 mmol) was added at $0\text{ }^\circ C$. After the mixture was stirred for 2 hr at ambient temperature, H_2O was poured and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The crude amide was purified with column chromatography (AcOEt – Hexane = 1 : 30) to afford amide **S8** (1.25 g, 5.04 mmol, 76%) as a white solid.

mp $42\text{ }^\circ C$ (Hexane). 1H -NMR (400 MHz, $CDCl_3$): δ 4.18 (br., 1H), 2.12 (br., 2H), 2.03 (br., d, J =

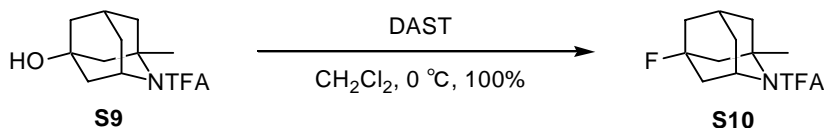
11 Hz, 2H), 1.89 (m, 3H), 1.85-1.70 (m, 3H), 1.63 (s, 3H), 1.58 (br., d, $J = 12.6$ Hz, 2H). ^{13}C -NMR (100 MHz, CDCl_3): δ 156.1 (q, $J = 33.7$ Hz), 116.9 (q, $J = 292.1$ Hz), 57.6, 50.6 (q, $J = 4.1$ Hz), 43.7, 35.9, 34.4, 29.4, 26.5. IR (neat, cm^{-1}): 1693. MS m/z : 247 (M^+), 190 (100%). HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{16}\text{F}_3\text{NO}$: 247.1184 (M^+), found: 247.1174.



5-Hydroxy-1-methyl-*N*-trifluoroacetyl-2-azaadamantane (S9)

To a solution of amide **S8** (2.27 g, 9.19 mmol) in $\text{CCl}_4 - \text{MeCN} - \text{H}_2\text{O}$ (1.65 M, 5.6 mL \rightarrow 1.1 M, 8.4 mL \rightarrow 1.1 M, 8.4 mL), NaIO_4 (4.52 g, 21.1 mmol) and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (95 mg, 0.460 mmol) was added at ambient temperature. After the reaction mixture was stirred vigorously for 9 hr at 60 $^\circ\text{C}$, sat. NaHCO_3 and sat. $\text{Na}_2\text{S}_2\text{O}_3$ was poured and the mixture was extracted with AcOEt . The organic layer was washed with brine, dried over MgSO_4 and evaporated. The crude 5-hydroxy-amide was purified with column chromatography ($\text{AcOEt} - \text{Hexane} = 1 : 2$) to afford 5-hydroxy-amide **S9** (1.29 g, 4.87 mmol, 53%) as a white solid.

mp 91 $^\circ\text{C}$ (Hexane). ^1H -NMR (400 MHz, CDCl_3): δ 4.37 (br., 1H), 2.38 (br., 1H), 1.95 (br., d, $J = 12.5$ Hz, 2H), 1.9-1.7 (m, 5H), 1.69 (s, 3H), 1.63 (br., d, $J = 13.0$ Hz, 1H), 1.57 (br., d, $J = 12.1$ Hz, 1H), 1.48 (br., d, $J = 13.0$ Hz, 1H). ^{13}C -NMR (100 MHz, CDCl_3): δ 156.1 (q, $J = 34.6$ Hz), 116.7 (q, $J = 291.3$ Hz), 66.71, 66.66, 52.3 (q, $J = 4.9$ Hz), 51.3, 43.3, 42.4, 34.6, 29.0, 28.8. IR (neat, cm^{-1}): 3428, 1692. MS m/z : 263 (M^+), 206 (100%). HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{16}\text{F}_3\text{NO}_2$: 263.1133 (M^+), found: 263.1118.

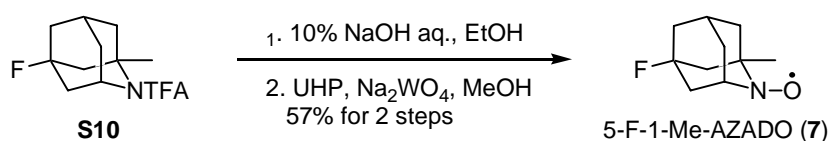


5-Fluoro-1-methyl-*N*-trifluoroacetyl-2-azaadamantane (S10)

To a solution of 5-hydroxy-amide **S9** (184 mg, 0.69 mmol) in CH_2Cl_2 (1.43 M, 0.5 mL), DAST (0.46 mL, 3.5 mmol) was added at -78 $^\circ\text{C}$. After the reaction mixture was stirred for 1 hr at 0 $^\circ\text{C}$, the mixture was diluted with Et_2O and quenched with H_2O . The mixture was extracted with AcOEt . The organic layer was washed with brine, dried over MgSO_4 and evaporated. The crude 5-fluoro-amide was purified with column chromatography ($\text{AcOEt} - \text{Hexane} = 1 : 30$) to afford

5-fluoro-amide **S10** (183 mg, 0.69 mmol, 100%) as a white solid.

mp 48 °C (Hexane). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 4.45 (br., 1H), 2.46 (br., 1H), 2.14-2.10 (m, 1H), 2.01-1.95 (m, 5H), 1.94-1.65 (m, 6H), 1.56-1.50 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 156.1 (q, $J = 34.4$ Hz), 116.6 (q, $J = 290.6$ Hz), 89.8 (d, $J = 186.8$ Hz), 61.3 (d, $J = 10.7$ Hz), 52.7 (m), 48.6 (d, $J = 18.0$ Hz), 42.1 (d, $J = 1.6$ Hz), 41.1 (d, $J = 18.8$ Hz), 39.9 (d, $J = 18.0$ Hz), 34.4 (d, $J = 1.6$ Hz), 29.6 (d, $J = 9.0$ Hz), 28.6. IR (neat cm^{-1}): 1698. MS m/z : 265 (M^+), 190 (100%). HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{15}\text{F}_4\text{NO}$: 265.1090 (M^+), found: 265.1068.



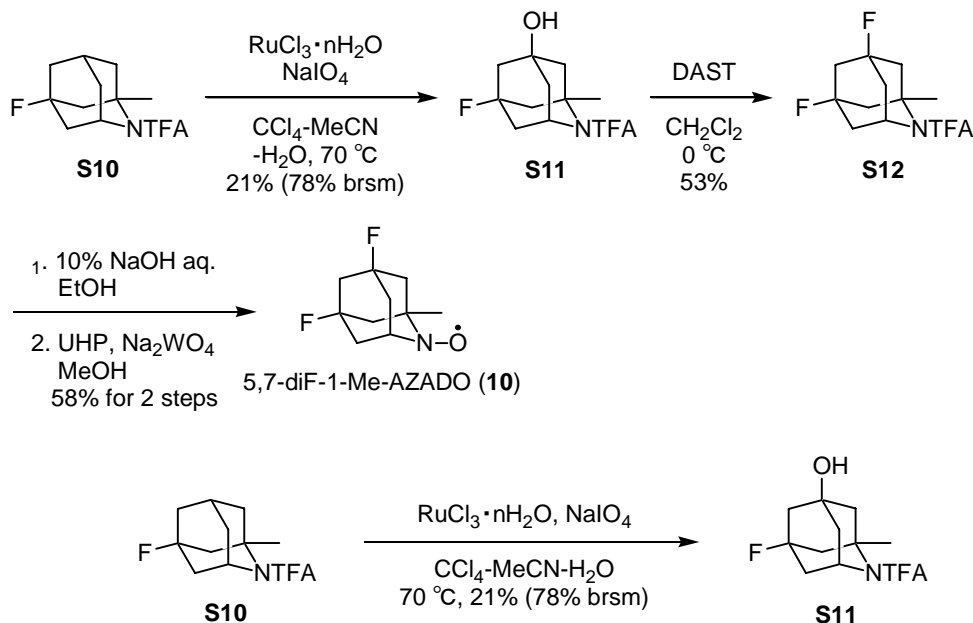
5-Fluoro-1-methyl-2-azaadamantane *N*-oxyl (**7**)

To a solution of 5-fluoro-amide **S10** (270 mg, 1.02 mmol) in EtOH (6 mL), *aq.* NaOH (10%, 3 mL) was added at ambient temperature. After the reaction mixture was stirred for 2 hr at ambient temperature, the mixture was diluted with H_2O and extracted with CHCl_3 . The organic layer was dried over K_2CO_3 and evaporated. The crude product was used without further purification. A solution of the crude product and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (160 mg, 0.485 mmol) in MeOH (0.5 M, 2 mL) was stirred at ambient temperature for 30 min. UHP (365 mg, 3.88 mmol) was added to the mixture at 0 °C. After the mixture was stirred at ambient temperature for 1.5 hr, it was diluted with H_2O and MeOH was removed under reduced pressure. H_2O was added to the residue and the mixture was extracted with CHCl_3 . The organic layer was dried over K_2CO_3 and evaporated. The crude 5-F-1-Me-AZADO (**7**) was purified with column chromatography (AcOEt – Hexane = 1 : 7) to afford 5-F-1-Me-AZADO (**7**; 106 mg, 0.579 mmol, 57% for 2 steps) as a yellow solid.

IR (neat, cm^{-1}): 1215. MS m/z : 184 (M^+), 111 (100%). HRMS (EI): Calcd. for $\text{C}_{10}\text{H}_{15}\text{FNO}$: 184.1138 (M^+), found: 184.1126. Anal.: Calcd. for $\text{C}_{11}\text{H}_{18}\text{NO}_2$: C, 65.19; H, 8.21; N, 7.60, found C, 65.27; H, 8.09; N, 7.33.

Synthesis of 5,7-diF-1-Me-AZADO (10)

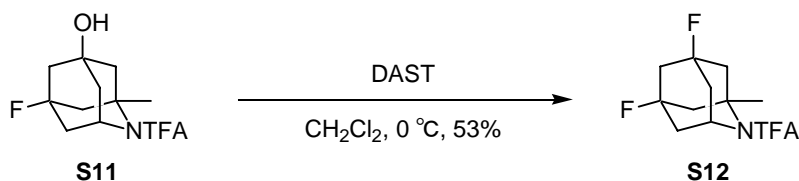
Scheme S4. Synthesis of 5,7-diF-1-Me-AZADO (10)



5-Fluoro-*N*-trifluoroacetyl-7-hydroxy-1-methyl-2-azaadamantane (43)

To a solution of amide **S10** (320 mg, 1.21 mmol) in $\text{CCl}_4 - \text{MeCN} - \text{H}_2\text{O}$ (1.65 M, 0.73 mL \rightarrow 1.1 M, 1.1 mL \rightarrow 1.1 M, 1.1 mL), NaIO_4 (595 mg \leftarrow 2.78 mmol) and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (50.0 mg \leftarrow 0.242 mmol) was added at ambient temperature. After the reaction mixture was stirred vigorously for 3.5 days at 70°C , sat. NaHCO_3 and sat. $\text{Na}_2\text{S}_2\text{O}_3$ was poured and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO_4 and evaporated. The crude 5-hydroxy-7-fluoro-amide was purified with column chromatography (AcOEt – Hexane = 1 : 4) to afford 5-hydroxy-7-fluoro-amide **S11** (71.6 mg, 0.254 mmol, 21%, 77% brsm) as a white solid accompanied with recovered amide **S10** (234 mg).

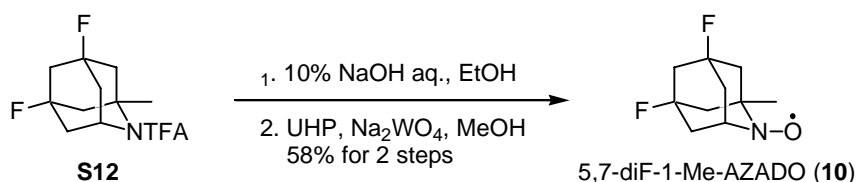
mp 97°C (Et₂O-Hexane). $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 4.46 (br., 1H), 2.01 (dt, $J = 12.2, 4.4, 2.2$ Hz, 1H), 1.97-1.81 (m, 5H), 1.74-1.65 (m, 3H), 1.70 (s, 3H), 1.52 (dd, $J = 12.6, 2.5$ Hz, 1H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 156.2 (q, $J = 34.4$ Hz), 116.4 (q, $J = 290.0$ Hz), 90.8 (d, $J = 189.2$ Hz), 69.4 (d, $J = 11.5$ Hz), 61.5 (d, $J = 11.5$ Hz), 52.17 (m), 50.1, 47.9 (d, $J = 17.2$ Hz), 47.4 (d, $J = 18.0$ Hz), 42.2 (d, $J = 1.7$ Hz), 40.0 (d, $J = 19.7$ Hz), 28.1. IR (neat, cm^{-1}): 3415, 1701. MS m/z : 281 (M^+), 206 (100%). HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{15}\text{F}_4\text{NO}_2$: 281.1039, found: 281.1034.



5,7-Difluoro-N-trifluoroacetyl-1-methyl-2-azaadamantane (S12)

To a solution of 5-hydroxy-7-fluoro-amide **S11** (26.0 mg, 0.092 mmol) in CH_2Cl_2 (1.43 mL), DAST (0.061 mL, 0.46 mmol) was added at $-78\text{ }^\circ\text{C}$. After the reaction mixture was stirred for 1 hr at $0\text{ }^\circ\text{C}$, the mixture was diluted with Et_2O and quenched with H_2O . The mixture was extracted with AcOEt . The organic layer was washed with brine, dried over MgSO_4 and evaporated. The crude 5,7-difluoro-amide was purified with column chromatography (AcOEt – Hexane = 1 : 15) to afford 5,7-difluoro-amide **S12** (14 mg, 0.049 mmol, 53%) as a white solid.

mp $99\text{ }^\circ\text{C}$ (Hexane). $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 4.52 (br s, 1H), 2.15-2.11 (m, 2H), 2.06-2.00 (m, 2H), 1.95-1.84 (m, 4H), 1.72 (s, 3H), 1.73-1.68 (m, 2H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 156.3 (q, $J = 34.9\text{ Hz}$), 116.3 (q, $J = 290.2\text{ Hz}$), 90.9 (dd, $J = 191.5, 13.6\text{ Hz}$), 61.6 (t, $J = 11.5\text{ Hz}$), 51.9 (m), 47.6 (m), 45.7 (m), 40.0 (t, $J = 19.4\text{ Hz}$), 28.0. IR (neat, cm^{-1}): 1698. MS m/z : 283 (M^+), 208 (100%). HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{14}\text{F}_5\text{NO}$: 283.0966, found.: 283.0993.



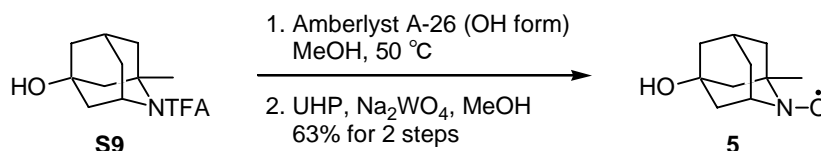
5,7-Difluoro-1-methyl-2-azaadamantane N-oxyl (10)

To a solution of 5,7-difluoro-amide **S12** (30 mg, 0.106 mmol) in EtOH (1 mL), *aq.* NaOH (10%, 0.32 mL) was added at ambient temperature. After the reaction mixture was stirred for 0.25 hr at ambient temperature, the mixture was diluted with H_2O and extracted with CHCl_3 . The organic layer was dried over K_2CO_3 and evaporated. The crude product was used without further purification. A solution of the crude product and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (16.5 mg, 0.053 mmol) in MeCN (0.5 M, 212 μL) was stirred at ambient temperature for 30 min. UHP (49.9 mg, 0.53 mmol) was added to the mixture at $0\text{ }^\circ\text{C}$. After the mixture was stirred at ambient temperature for 4 hr, it was diluted with H_2O and extracted with CHCl_3 . The organic layer was dried over K_2CO_3 and evaporated. The crude 5,7-diF-1-Me-AZADO (**10**) was purified with column chromatography (Et_2O – Hexane = 1 : 2) to afford 5,7-diF-1-Me-AZADO (**10**; 12.3 mg, 0.061 mmol, 58% for 2 steps) as a yellow solid.

mp $104\text{--}105\text{ }^\circ\text{C}$ ($\text{CHCl}_3\text{--Et}_2\text{O}$). IR (neat, cm^{-1}): 1443, 1143. MS m/z : 202 (M^+), 129 (100%). HRMS (EI): Calcd. for $\text{C}_{10}\text{H}_{14}\text{F}_2\text{NO}$: 202.1043, found.: 202.1043.

Synthesis of 5-OH-1-Me-AZADO (5)

Scheme S5. Synthesis of 5-OH-1-Me-AZADO (5)



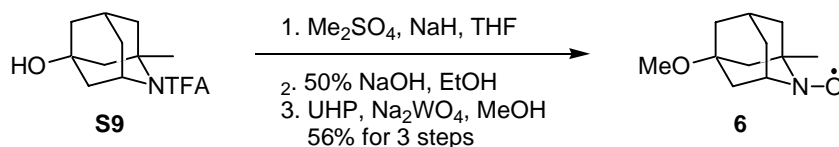
5-Hydroxy-1-methyl-2-azaadamantane *N*-oxyl (5)

To a solution of hydroxy-amide **S9** (500 mg, 1.90 mmol) in (0.5 M, 40 mL), Amberlyst[®] A-26 (OH form) (5.50 g) was added at ambient temperature. After the reaction mixture was stirred for 40 hr at 50 °C, the reaction mixture was filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The crude product was not further purified. A solution of the crude product and Na₂WO₄·2H₂O (314 mg, 0.95 mmol) in MeOH (0.5 M, 4 mL) was stirred at ambient temperature for 30 min. UHP (715 mg, 7.6 mmol) was added to the mixture at ambient temperature. After the mixture was stirred at ambient temperature for 2 hr, it was diluted with H₂O then MeOH was removed under reduced pressure. H₂O was added to the residue and the mixture was extracted with CHCl₃. The organic layer was dried over K₂CO₃ and evaporated. The crude 5-OH-AZADO (**5**) was purified with column chromatography (AcOEt – Hexane = 4 : 1) to afford 5-OH-AZADO (**5**; 217.5 mg, 1.19 mmol, 63% for 2 steps) as a orange solid.

IR (neat, cm⁻¹): 3396. MS *m/z*: 182 (M⁺), 182 (100%). HRMS (EI): Calcd. for C₁₀H₁₆NO₂ 182.1181 (M⁺), found: 182.1161. Anal.: Calcd. for C₁₁H₁₈NO₂: C, 65.91; H, 8.85; N, 7.69, found: C, 65.69; H, 8.83; N, 7.65.

Synthesis of 5-MeO-1-Me-AZADO (6)

Scheme S6. Synthesis of 5-MeO-1-Me-AZADO (6)



5-Methoxy-1-methyl-2-azaadamantane *N*-oxyl (6)

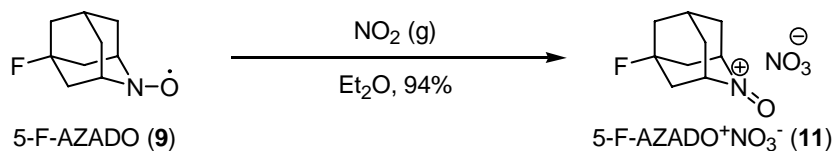
To a mixture of NaH (82 mg, 3.42 mmol) in THF (1.0 mL), a solution of hydroxy-amide **S9** (300 mg, 1.14 mmol) in THF (2.8 mL) was added at 0 °C. After the reaction mixture was stirred for 0.5 hr at 0 °C, Me_2SO_4 (0.32 mL, 3.42 mmol) was added dropwise. After the reaction mixture was stirred for 3 hr at ambient temperature, another NaH (82 mg, 3.42 mmol) and Me_2SO_4 (0.32 mL, 3.42 mmol) was added. After the reaction mixture was stirred for 1 hr at ambient temperature, H_2O was added and extracted with Et_2O . The organic layer was washed with brine, dried over MgSO_4 and evaporated. The crude product was purified with column chromatography (AcOEt – Hexane = 1 : 15) to afford mixture of the methylated product and Me_2SO_4 (403 mg). The mixture was not further purified. To a solution of the mixture (333 mg of 403 mg) in EtOH (4 mL), *aq.* NaOH (50%, 2 mL) was added at ambient temperature. After the reaction mixture was stirred for 1 hr at ambient temperature, the mixture was diluted with H_2O and extracted with CHCl_3 . The organic layer was dried over K_2CO_3 and evaporated. The crude product was not further purified. A solution of the crude product and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (122 mg, 0.37 mmol) in MeOH (0.5 M, 1.5 mL) was stirred at ambient temperature for 30 min. UHP (280 mg, 2.96 mmol) was added to the mixture at 0 °C. After the mixture was stirred at ambient temperature for 3 hr, it was diluted with H_2O and MeOH was removed under reduced pressure. H_2O was added to the residue and the mixture was extracted with CHCl_3 . The organic layer was dried over K_2CO_3 and evaporated. The crude 5-MeO-AZADO (**6**) was purified with column chromatography (AcOEt – Hexane = 1 : 4) to afford 5-MeO-AZADO (**6**; 105 mg, 0.534 mmol, 56% for 3 steps) as a orange solid.

IR (neat, cm^{-1}): 1215. MS m/z : 196 (M^+), 196 (100%). HRMS (EI): Calcd. for $\text{C}_{11}\text{H}_{18}\text{NO}_2$ 196.1338 (M^+), found: 196.1319. Anal.: Calcd. for $\text{C}_{11}\text{H}_{18}\text{NO}_2$: C, 67.32; H, 9.24; N, 7.14, found: C, 67.14; H, 9.16; N, 7.10.

Preparation of 5-F-AZADO⁺NO₃⁻ (**11**)

Method 1: using NO₂ gas

Scheme S7. Preparation of 5-F-AZADO⁺NO₃⁻ (**11**) using NO₂ gas³

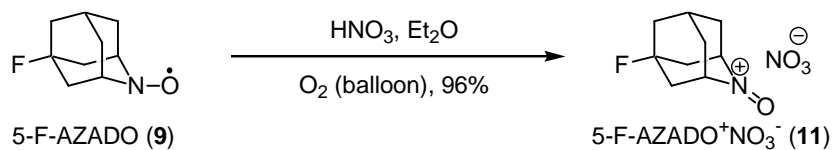


NO₂ gas was bubbled to the solution of 5-F-AZADO (**9**; 16 mg, 0.094 mmol) and Et₂O at ambient temperature. After the solution turned colorless, the yellow precipitate was filtered, washed with Et₂O, and dried *in vacuo* to yield 5-F-AZADO⁺NO₃⁻ (**11**; 20.5 mg, 0.088 mmol, 94%) as a yellow solid.

mp 135-140 °C (dec). IR (neat, cm⁻¹): 1628, 1372, 1333. MS *m/z*: 171 (M⁺ + H – NO₃), 153 (100%). HRMS (EI): Calcd. for C₉H₁₄FNO 171.1054, found: 171.1040. Anal.: Calcd. for C₉H₁₃FN₂O₄: C, 46.55; H, 5.64; N, 12.06, found: C, 46.26; H, 5.73; N, 11.86.

Method 2: using HNO₃

Scheme S8. Preparation of 5-F-AZADO⁺NO₃⁻ (**11**) using HNO₃



To a solution of 5-F-AZADO (**9**; 54.04 mg, 0.318 mmol) in Et₂O (0.1 M, 4.8 mL), conc. HNO₃ (70% aqueous solution; 21 μL, 0.477 mmol) was added at ambient temperature and the solution was stirred under O₂ atmosphere. After the solution turned colorless, the yellow precipitate was filtered, washed with Et₂O, and dried *in vacuo* to yield 5-F-AZADO⁺NO₃⁻ (**11**; 70.6 mg, 0.304 mmol, 96 %) as a yellow solid.

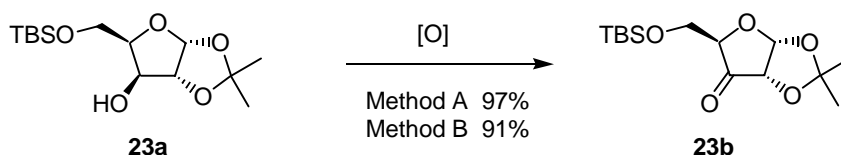
Representative Procedures of Aerobic Oxidation

Method A : To a solution of 4-methoxybenzyl alcohol (**13a**; 181 mg, 1.31 mmol) in AcOH (1.3 ml, 1 M), 5-F-AZADO (**9**; 2.21 mg, 0.013 mmol) and NaNO₂ (9.0 mg, 0.131 mmol) was added at ambient temperature and the solution was stirred under Air atmosphere (balloon) for 3 h. The reaction mixture was diluted with Et₂O and quenched with sat. Na₂SO₃ and sat. Na₂CO₃. The mixture was extracted with Et₂O and the organic layer was washed with brine, dried over MgSO₄ and evaporated. The crude aldehyde was purified with column chromatography.(Et₂O : hexane = 1 : 2) to afford 4-methoxybenzaldehyde (**13b**; 172 mg, 1.26 mmol, 96%) as a colorless oil.

Method B : To a solution of 4-methoxybenzyl alcohol (**13a**; 69.1 mg, 0.50 mmol) in AcOH (1.5 ml, 0.33 M), 5-F-AZADO⁺NO₃⁻ (**11**, 5.8 mg, 0.025 mmol) was added at ambient temperature and the solution was stirred under air atmosphere (balloon) for 45 min. The reaction mixture was diluted with Et₂O and quenched with sat. Na₂SO₃ and sat. Na₂CO₃. The mixture was extracted with Et₂O and the organic layer was washed with brine, dried over MgSO₄ and evaporated. The crude aldehyde was purified with column chromatography (Et₂O : hexane = 1 : 2) to afford 4-methoxybenzaldehyde (**13b**; 65.1 mg, 0.478 mmol, 96%) as a colorless oil.

Selected Examples of Aerobic Oxidation

Scheme S9. Aerobic oxidation of **23a**



Method A : To a solution of **23a** (296 mg, 0.97 mmol) in AcOH (0.97 ml), 5-F-AZADO (**9**; 1.65 mg, 0.0097 mmol) and NaNO₂ (6.7 mg, 0.097 mmol) was added at ambient temperature and the solution was stirred under Air atmosphere (balloon) for 2 h. The reaction mixture was diluted with AcOEt and quenched with sat. Na₂SO₃. The mixture was extracted with Et₂O and the organic layer was washed with brine, dried over MgSO₄ and evaporated. The crude aldehyde was purified with column chromatography.(Et₂O : hexane = 1 : 4) to afford 4-methoxybenzaldehyde (**23b**; 285 mg, 0.94 mmol, 97 %) as a colorless oil.

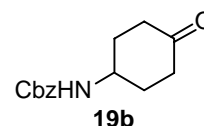
Method B : To a solution of **23a** (104 mg, 0.34 mmol) in AcOH (1.0 ml), 5-F-AZADO⁺NO₃⁻ (**11**, 3.98 mg, 0.0017 mmol) was added at ambient temperature and the solution was stirred under air

Figure 1. Chemical reactor of 0.1-scale oxidation



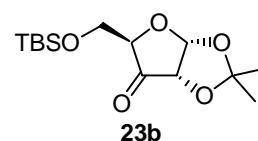
Characterization of 19b, 23b, 25b

Benzyl 4-oxocyclohexylcarbamate (19b)



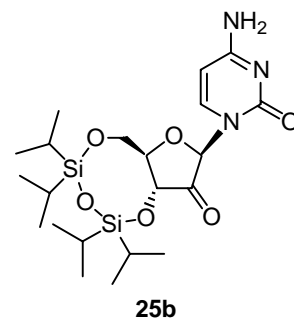
$^1\text{H-NMR}$ (400MHz, CDCl_3): δ 7.37-7.30 (m, 5H), 5.12 (s, 2H), 4.72 (br s, 1H), 3.99 (br s, 1H), 2.42-2.38 (m, 4H), 2.28-2.24 (m, 2H), 1.74-1.65 (m, 2H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ 209.5, 155.6, 136.3, 128.5, 128.2, 128.1, 66.8, 47.9, 38.8, 32.1. IR (neat, cm^{-1}): 1717, 1685, 1532. MS m/z : 247 (M^+), 91 (100%). HRMS (EI): Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_3$: 247.1208, found: 247.1172.

5-*O*-*tert*-Butyldimethylsilyl-1,2-*O*-isopropylidene- α -D-erythro-3-pentulofuranose (23b)



$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.13 (d, J = 4.6 Hz, 1H), 4.37-4.35 (m, 1H), 4.27 (dd, J = 4.6, 1.0 Hz, 1H), 3.88 (dd, J = 10.9, 1.7 Hz, 1H), 3.82 (dd, J = 10.9, 2.2 Hz, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 0.86 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 210.9, 114.1, 103.8, 81.7, 77.1, 63.9, 27.7, 27.1, 25.8, 18.1, -5.5, -5.7. IR (neat, cm^{-1}): 1776. MS m/z : 245 ($\text{M}^+ - t\text{Bu}$), 245 (100%). HRMS (EI): Calcd. for $\text{C}_{10}\text{H}_{17}\text{O}_5\text{Si}$: 245.0845, found: 245.0849.

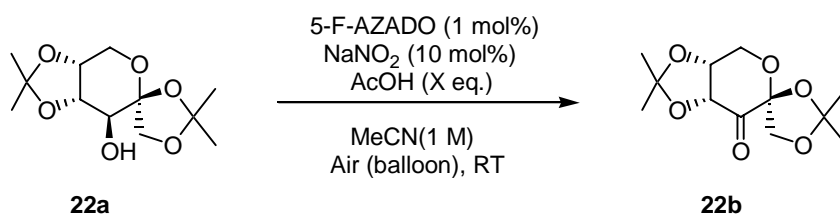
**1-(3',5'-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-
β-D-*erythro*-pentofuran-2-ulosyl)-cytosine (25b)**



$^1\text{H-NMR}$ (400 MHz, DMSO): δ 7.62 (d, $J = 7.2$ Hz, 1H), 7.46 (br s, 1H), 7.37 (br s, 1H), 5.73 (d, $J = 7.2$ Hz, 1H), 5.24 (s, 1H), 5.00 (d, $J = 8.2$ Hz, 1H), 4.04-3.86 (m, 3H), 1.07-0.96 (m, 28H). $^{13}\text{C-NMR}$ (100 MHz, DMSO): δ 205.3, 166.7, 154.4, 145.7, 94.9, 85.3, 78.8, 71.7, 63.1, 17.3, 17.1, 16.7, 16.7, 16.6, 12.8, 12.4, 12.0, 11.9. IR (neat, cm^{-1}): 1776. MS m/z : 483 (M^+), 440 (100%). HRMS (EI): Calcd. for $\text{C}_{21}\text{H}_{37}\text{N}_3\text{O}_6\text{Si}_2$: 483.2221, found: 483.2202.

The effect of AcOH

Table S1. The effect of AcOH under 5-F-AZADO/ NaNO_2 condition in MeCN

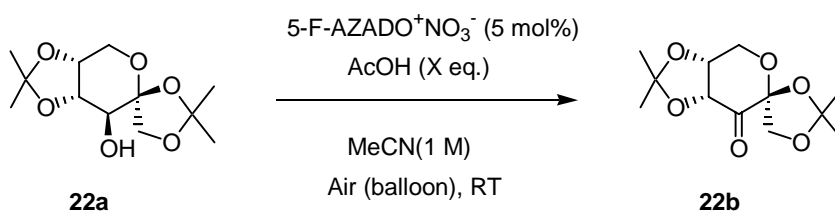


Entry	AcOH (X eq.)	Time (h)	Conv. (%) ^a	Yield (%) ^b
1	0	24	0	0
2	2	18	88	88
3	5	5	100	98
4	solvent	2	100	98

a) Calculated from NMR of crude products.

b) Isolated yield

Table S2 The effect of AcOH under $5\text{-F-AZADO}^+\text{NO}_3^-$ condition in MeCN



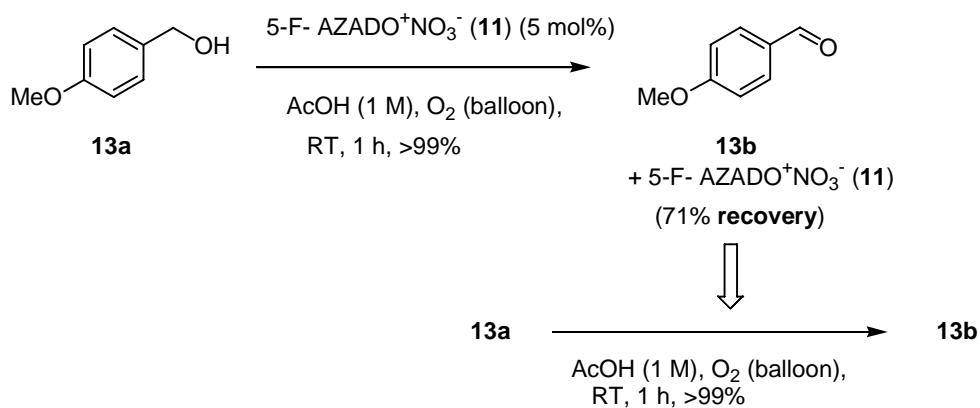
Entry	AcOH (X eq.)	Time (h)	Conv. (%) ^a	Yield (%) ^b
1	0	4.5	100	94
2	2	2.5	100	96
3	solvent	0.5	100	98

a) Calculated from NMR of crude products.

b) Isolated yield

Recycling of 5-F-AZADO⁺NO₃⁻ (**13b**)

Scheme S13 Recycling of 5-F-AZADO⁺NO₃⁻ (**13b**)

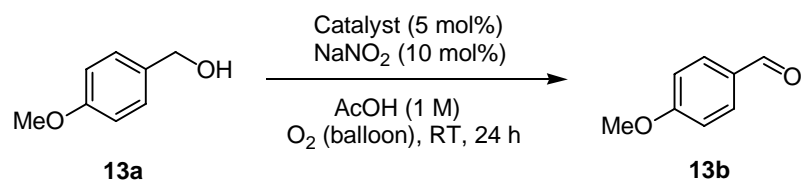


To a solution of 4-methoxybenzyl alcohol (**13a**; 69.1 mg, 0.50 mmol) in AcOH (0.5 ml, 1 M), 5-F-AZADO⁺NO₃⁻ (**11**, 5.8 mg, 0.025 mmol) was added at ambient temperature and the solution was stirred under O₂ atmosphere (balloon) for 1 h (Conv. >99%, select. >99% (determined by GC)). Hexane was added to the reaction mixture. After colorless solution was removed by pipet, excess amount of Et₂O was poured to the remaining yellow residue. The precipitated yellow 5-F-AZADO⁺NO₃⁻ (**11**) was filtered and washed with Et₂O. 5-F-AZADO⁺NO₃⁻ (**11**, 4.2 mg 0.018 mmol, 72 %) was recovered.

To a solution of 4-methoxybenzyl alcohol (**13a**; 47.0 mg, 0.34 mmol) in AcOH (0.34 ml, 1 M), 5-F-AZADO⁺NO₃⁻ (**11**, 5.8 mg, 0.025 mmol) was added at ambient temperature and the solution was stirred under O₂ atmosphere (balloon) for 1 h. Conv. >99%, select. >99% was conformed by GC.

Reactivity of Substituted TEMPO

Table S3. Evaluation of catalytic efficiency of 4-substituted TEMPO



Entry	Catalyst	yield (%) ^a	
		13b	13a
1	TEMPO	25	75
2	4-HO-TEMPO	34	66
3	4-MeO-TEMPO	42	58

a) Calculated from NMR of crude products.

Electrochemical Measurement⁴

The cyclic voltammograms were measured on a Cypress CS-2010 electrochemical analyzer with a conventional three-electrode configuration at room temperature (approximately 23 °C). MeCN solution of nitroxyl radicals (1 mM) were used throughout the cyclic voltammetric measurements. Glassy carbon (BAS, 3 mm diameter), platinum wire, and Ag/Ag⁺ (BAS type RE-5) were used as working, auxiliary, and reference electrodes, respectively. Electric potential values reported herein referred to this reference electrode. NaClO₄ (0.2 M) was used as supporting electrolyte.

The cyclic voltammograms of AZADO, 1-F-AZADO and 5-F-AZADO are shown in Fig. S1, and that of 1-Me-AZADO, 5-F-1-Me-AZADO and 5,7-diF-1-Me-AZADO are shown in Fig. S2. The cyclic voltammograms obtained various potential sweep rates (ν) are independently given in Fig. S3 (1-F-AZADO), Fig. S4 (5-F-AZADO), Fig. S5 (5-F-1-Me-AZADO), Fig. S6 (5,7-diF-1-Me-AZADO).

The $E^{\circ'}$ values of the nitroxyl radicals, which were calculated by $(E_{pa} + E_{pc}) / 2$, are summarized in Table S1 (E_{pa} and E_{pc} denote anodic and cathodic peak potentials, respectively).

Figure S2. Cyclic voltammograms of various AZADO derivatives at scan rate of 50 mVs⁻¹.

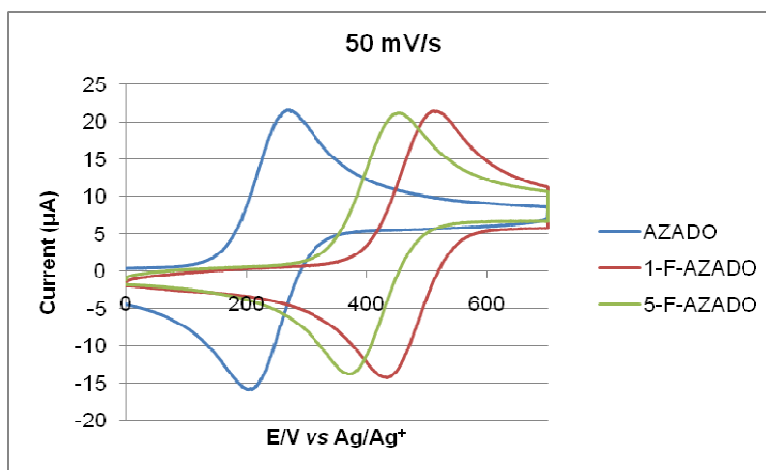


Figure S3. Cyclic voltammograms of various 1-Me-AZADO derivatives at scan rate of 50 mVs⁻¹.

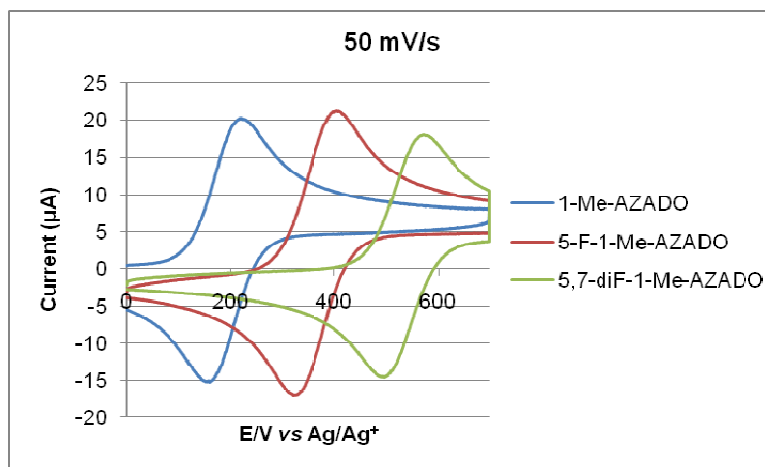


Figure S4. Cyclic voltammograms of 1-F-AZADO at varying scan rates.

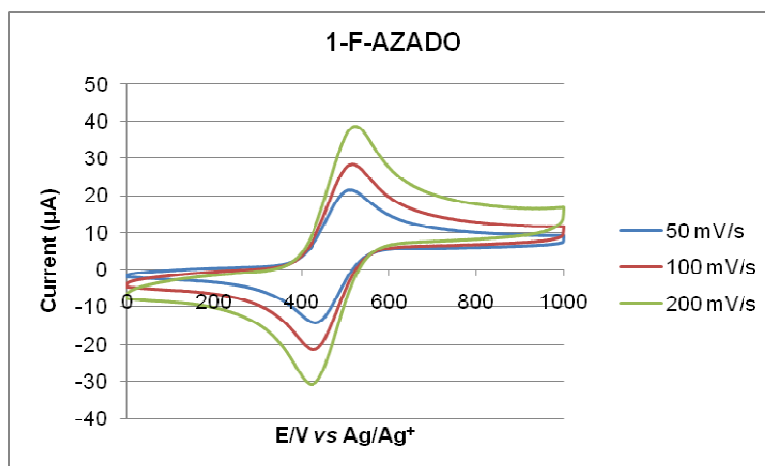


Figure S5. Cyclic voltammograms of 5-F-AZADO at varying scan rates.

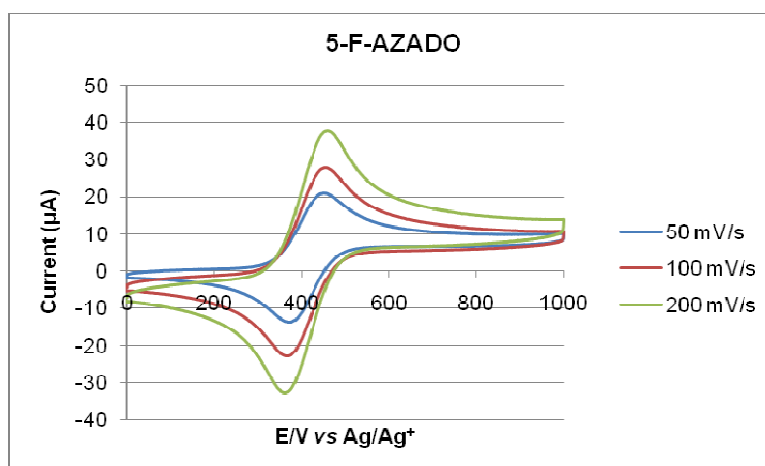


Figure S6. Cyclic voltammograms of 5-F-1-Me-AZADO at varying scan rates.

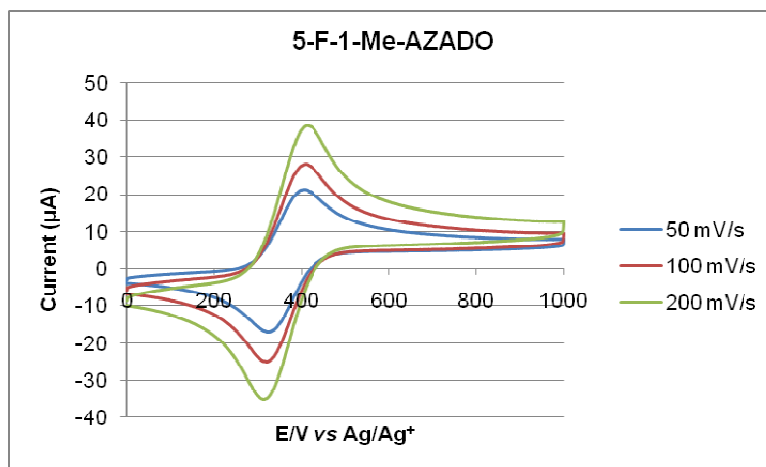


Figure S7. Cyclic voltammograms of 5,7-diF-1-Me-AZADO at varying scan rates.

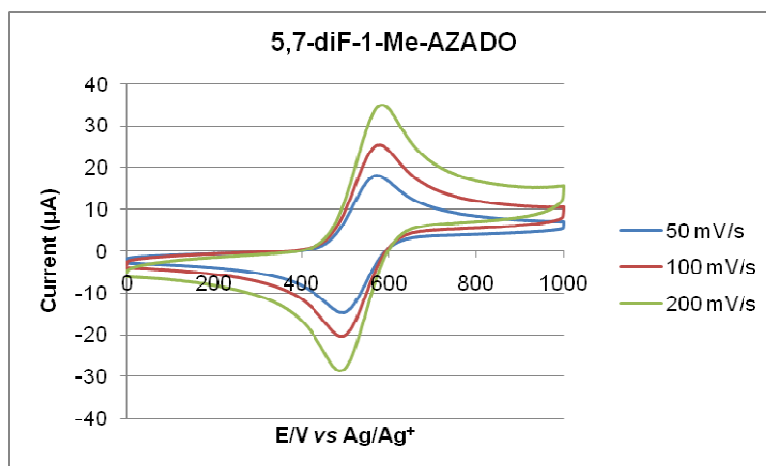
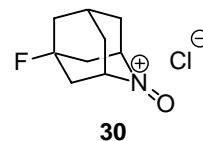


Table S4. The formal potential of various nitroxyl radicals

Nitroxyl radical	$E^{0'}$ vs Ag/Ag ⁺
AZADO	+ 236 mV
5-F-AZADO	+ 413 mV
1-F-AZADO	+ 471 mV
<hr/>	
1-Me-AZADO	+ 186 mV
5-F-1-Me-AZADO	+ 363 mV
5,7-diF-1-Me-AZADO	+ 534 mV

Preparation of oxoammonium chlorides⁵

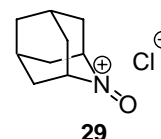
5-F-AZADO⁺Cl⁻ (**30**)



Cl₂ gas was bubbled to the mixture of 5-F-AZADO (**9**; 63.3 mg, 0.372 mmol) and CCl₄ (1.24 mL, 0.3 M) at ambient temperature. After stirring for 30 min, the orange precipitate was filtered and washed with Et₂O and dried *in vacuo* to yield 5-F-AZADO⁺Cl⁻ (**30**; 46.8 mg, 0.228 mmol, 61%).

mp 79-83 °C (dec). IR (neat, cm⁻¹): 1624, 1360. MS *m/z*: 171 (M⁺+H – Cl), 171 (100%). HRMS (EI): Calcd. for C₉H₁₄FNO 171.1054, found: 171.1054.

AZADO⁺Cl⁻ (**29**)



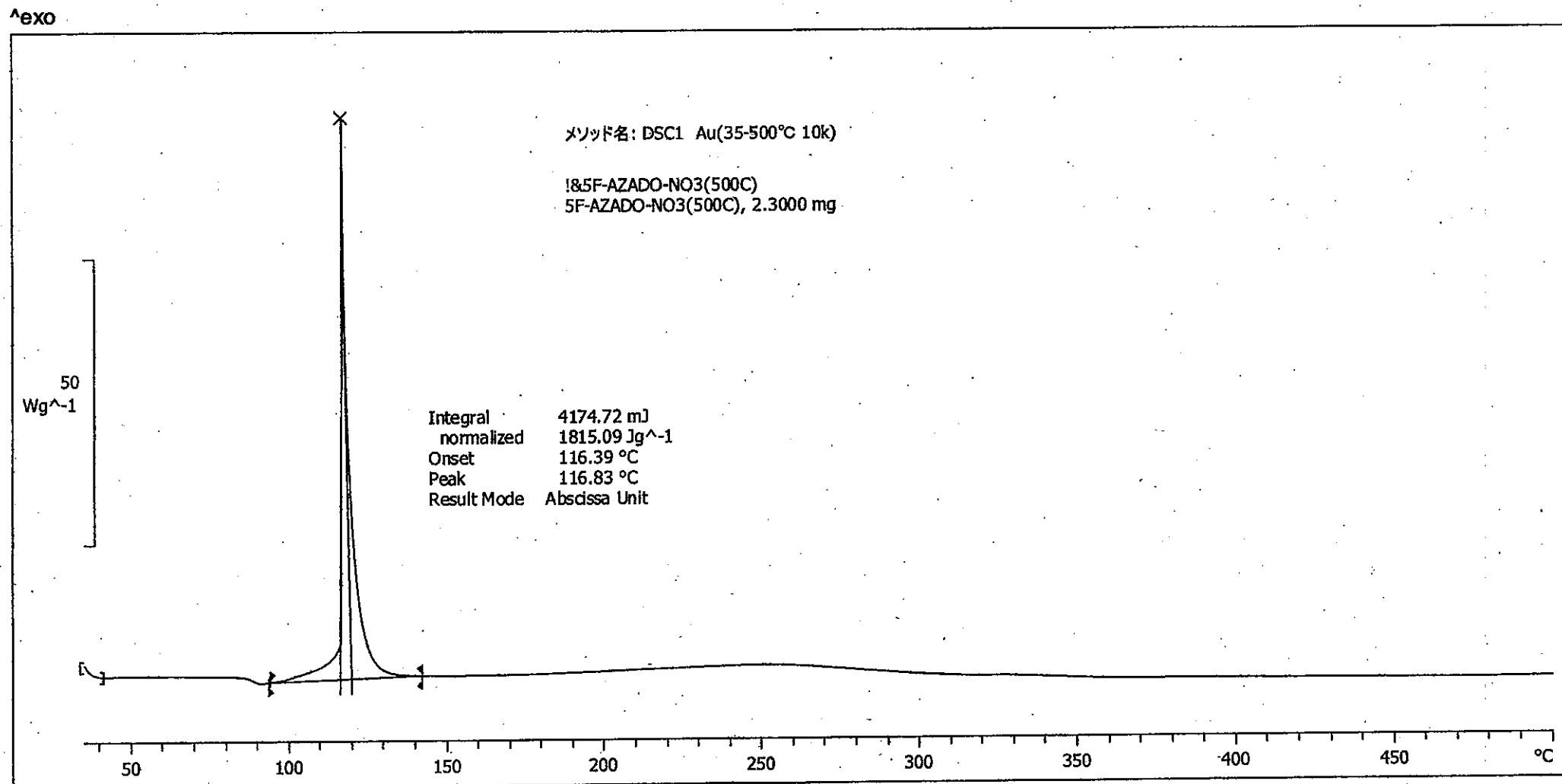
The same procedure with AZADO (**3**) instead of 5-F-AZADO (**9**) provided AZADO⁺Cl⁻ (**29**).

IR (neat, cm⁻¹): 1627. MS *m/z*: 187 (M⁺), 153 (100%). HRMS (EI): Calcd. for C₉H₁₄ClNO (M⁺), 187.0764, found: 187.0743. Anal.: Calcd. for C₉H₁₄ClNO C, 57.6; H, 7.52; N, 7.46, found: C, 57.1; H, 7.39; N, 7.06.

References and Notes

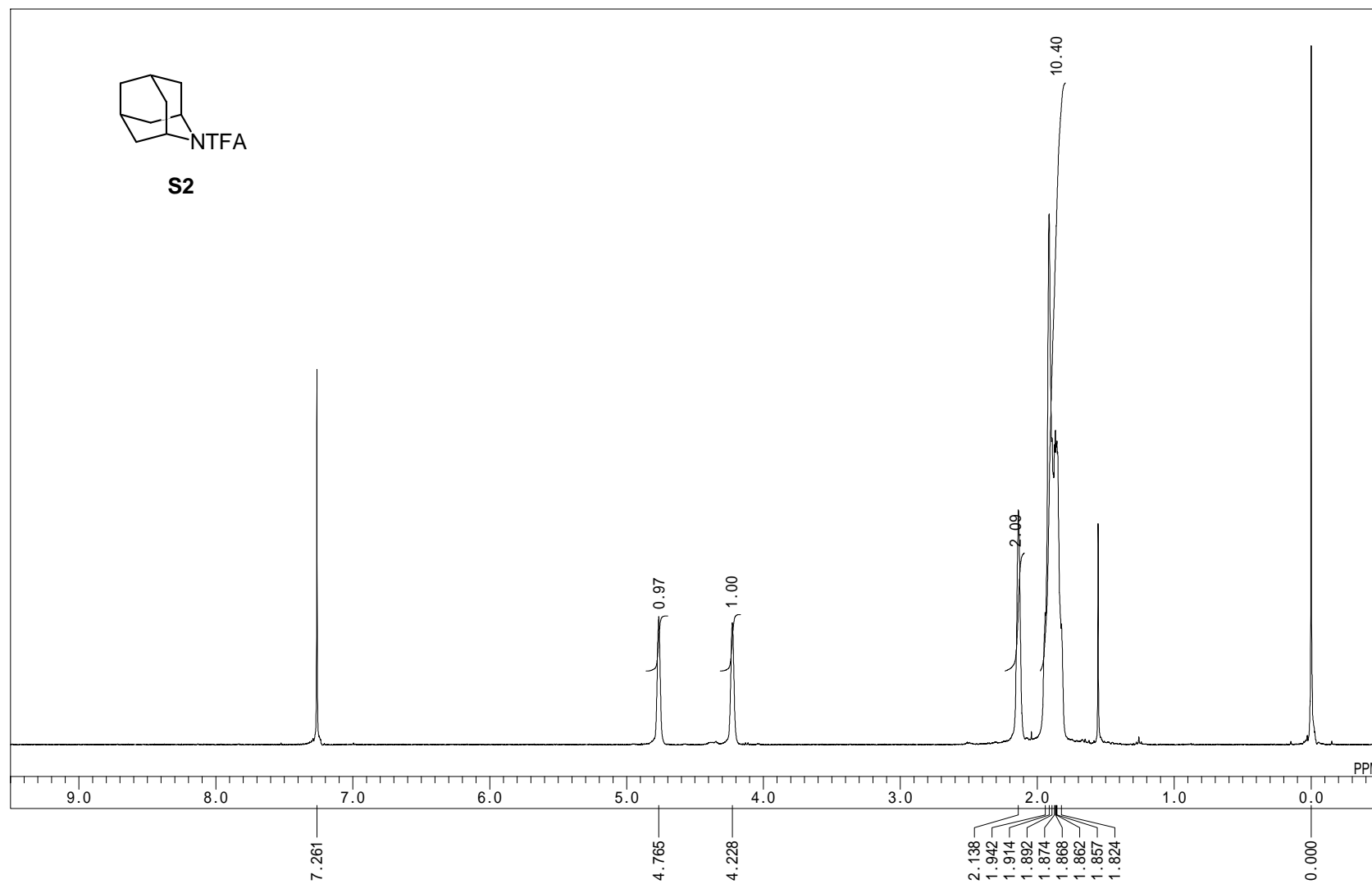
1. 2-Azaadamantane **S1** was prepared by scalable 3-step method from 2-adamantanone. (WO 2009066735)
2. Shibuya, M.; Tomizawa, M.; Suzuki, I.; Iwabuchi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 8412.
3. Chou, S.; Nelson, J. A.; Spencer, T. A. *J. Org. Chem.* **1974**, *39*, 2356.
4. The cyclic voltammograms of AZADO and 1-Me-AZADO were previously measured under same conditions; see Reference 2.
5. (a) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1965**, 1898. (b) Shibuya, M.; Sato, T.; Tomizawa, M.; Iwabuchi, Y. *Chem. Commun.* **2009**, 1739.

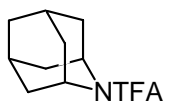
5F-AZADO-NO₃ 金ノキ密封セル
10℃/min 昇温
35-500℃



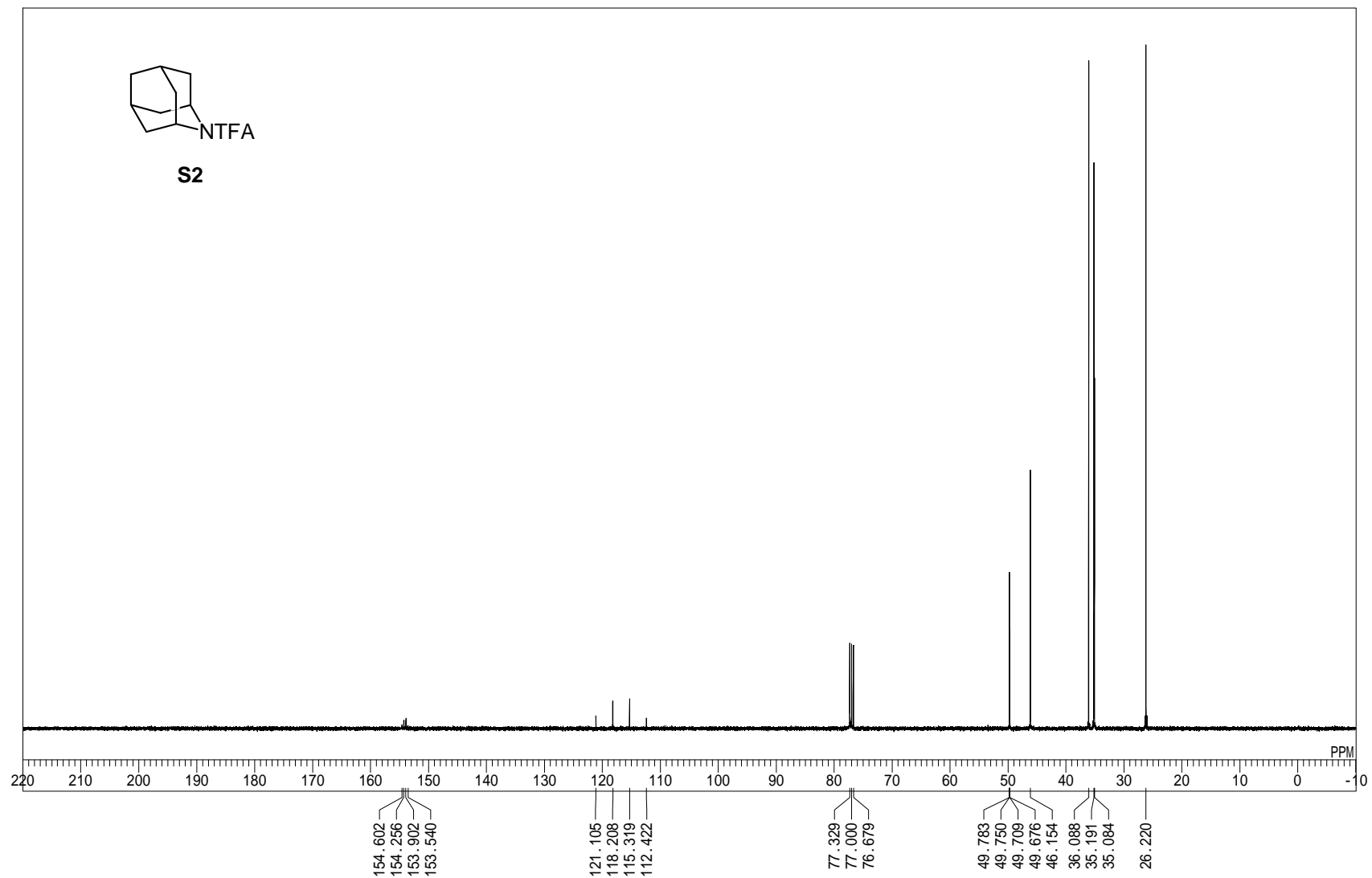
NISSAN CHEMICAL: METTLER

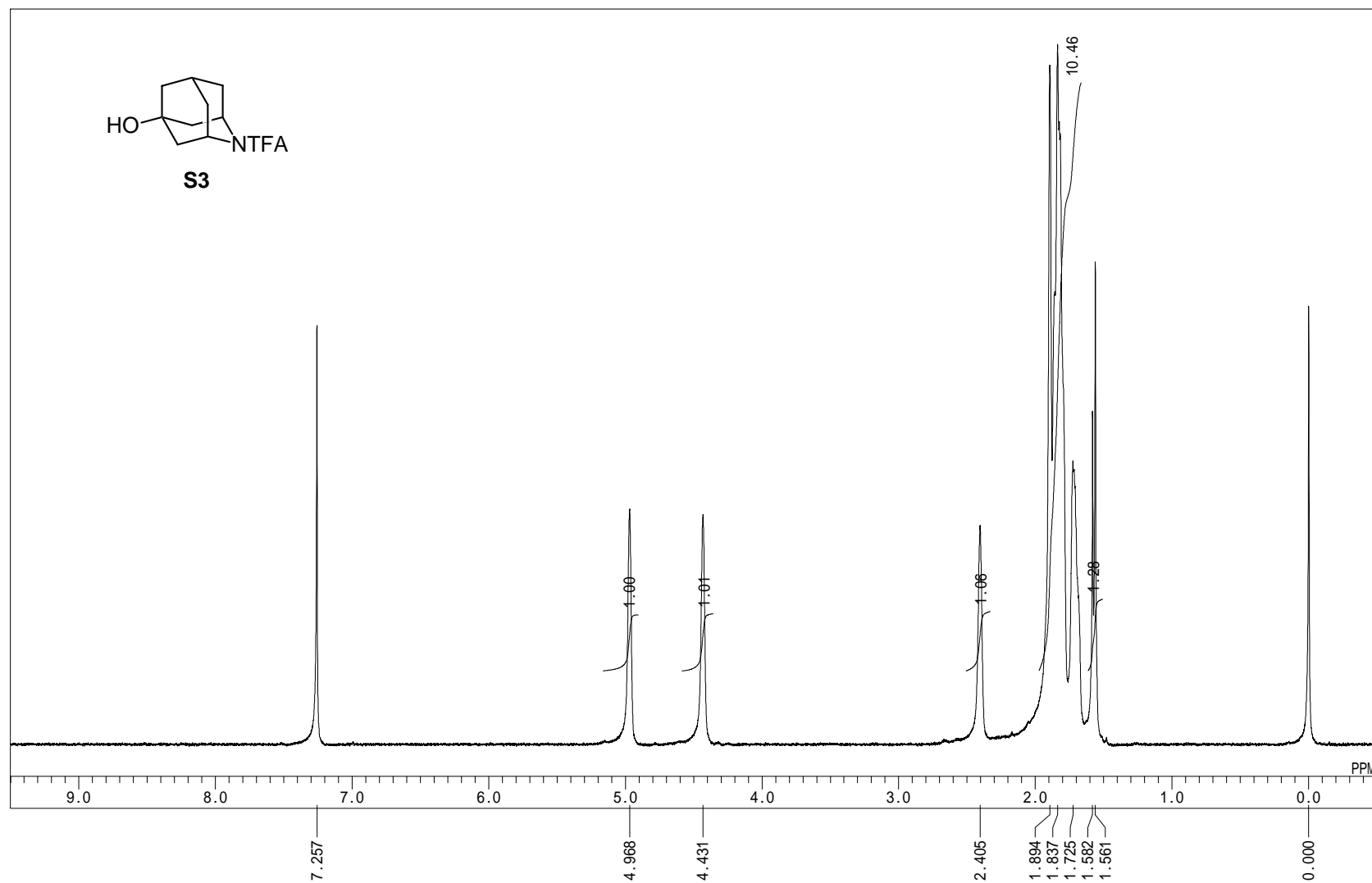
STAR® SW 9.20

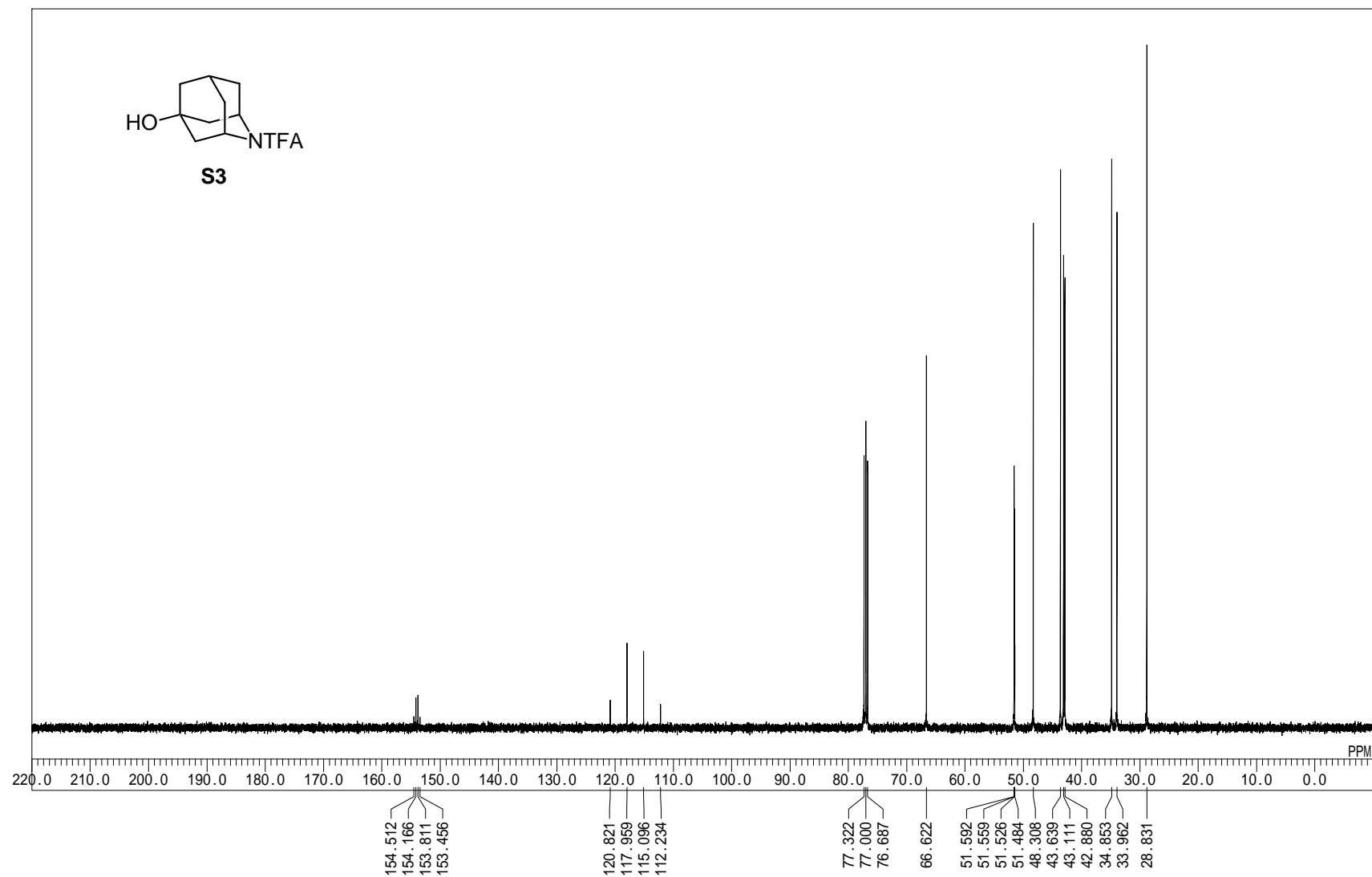


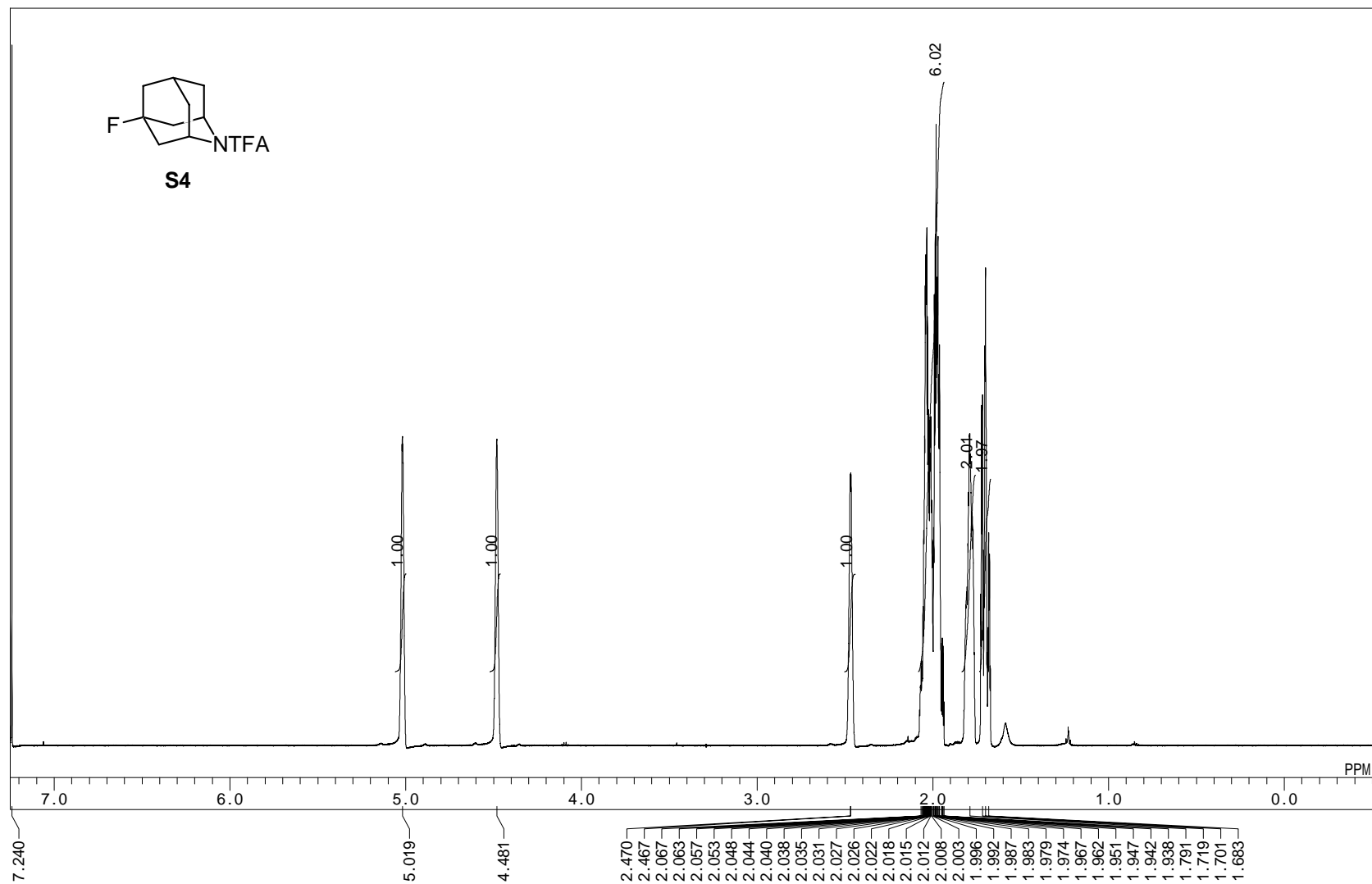


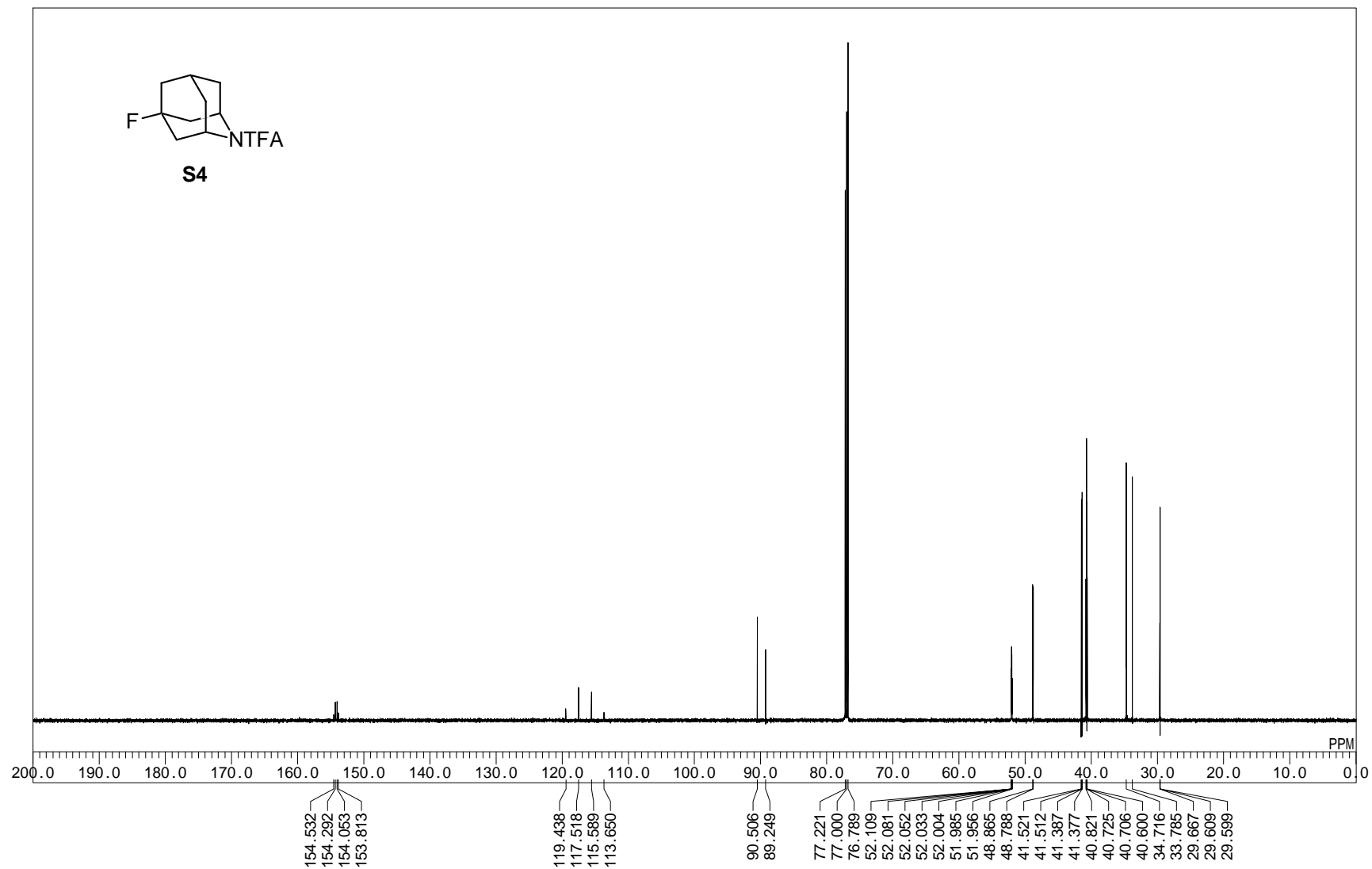
S2

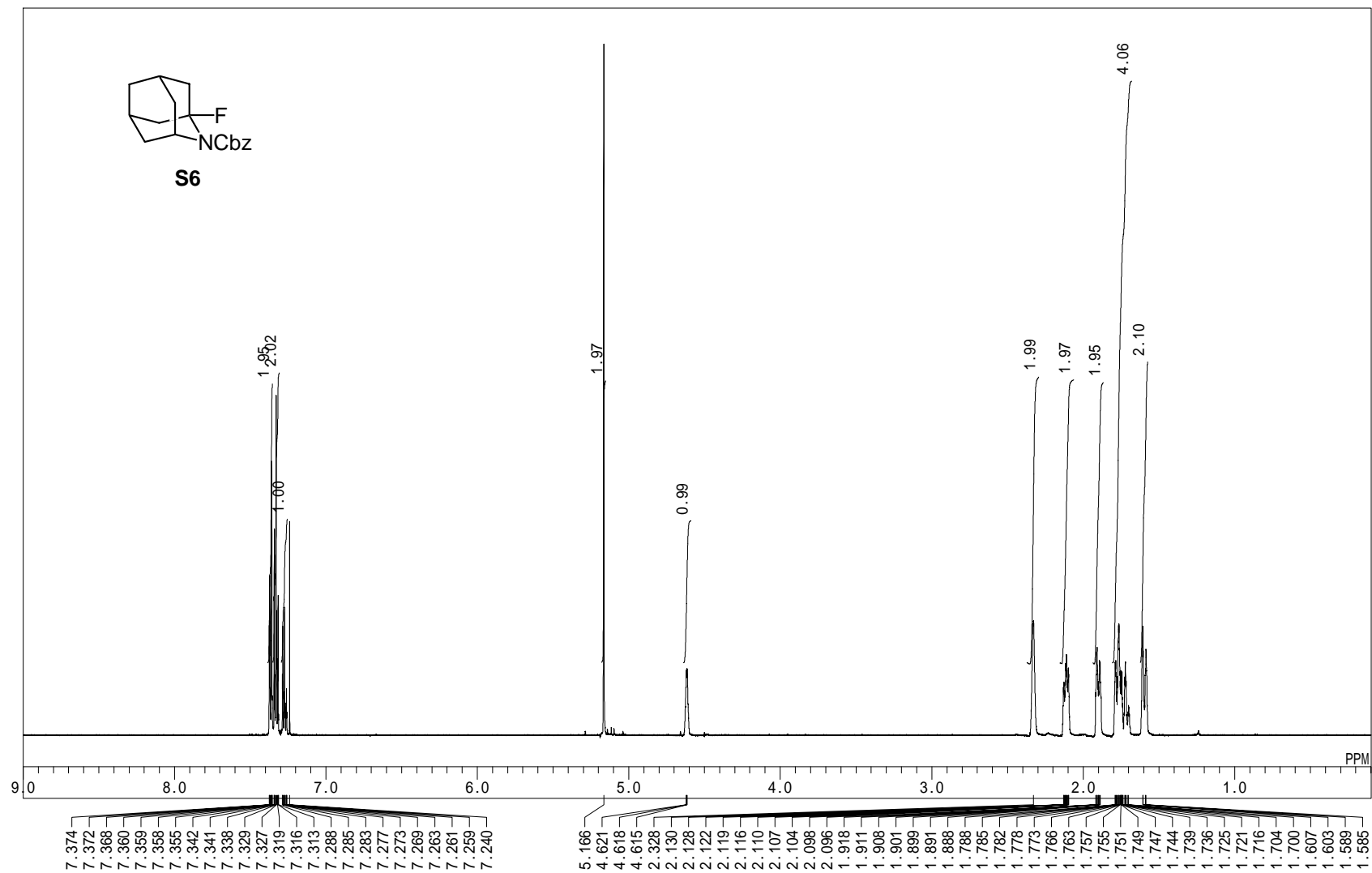


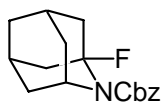












S6

