SUPPORTING INFORMATION

Acridine Orange as a Highly Sensitive Probe to Study the Stability of Onium Salts

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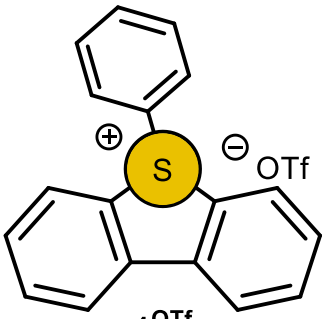
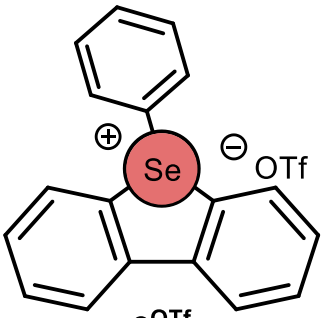
Characterization of the SHDs



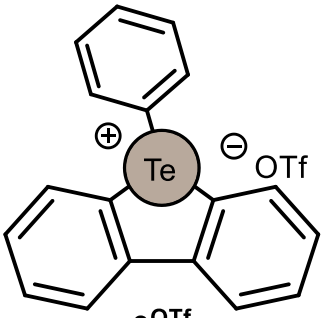
1^{OTf}

1^{OTf}. White crystalline solid. Yield: 84% (156 mg). M.p.: 192–193 °C. ^{1}H NMR (400.13 MHz, $(CD_3)_2CO$): δ = 8.56 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H), 8.42 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ =1.2 Hz, 2H), 8.03 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2H), 7.84 – 7.77 (m, 5H), 7.70–7.68 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $(CD_3)_2CO$): δ = 139.6, 134.9, 134.5, 132.5, 131.7, 131.6, 130.5, 128.4, 127.8, 124.7 (Ar), 121.6 (q, $^{1}J_{CF}$ = 321.9 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = −79.30 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* $[M]^+$ calcd for $C_{18}H_{13}S$: 261.0733; found: 261.0735.



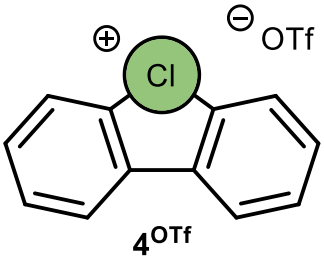
2^{OTf}

2^{OTf}. White crystalline solid. Yield: 80% (166 mg). M.p.: 200–202 °C. ^{1}H NMR (400.13 MHz, $(CD_3)_2CO$): δ = 8.47–8.44 (m, 4H, Ar), 7.93 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar), 7.74 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar), 7.69–7.67 (m, 2H, Ar), 7.64–7.60 (m, 1H, Ar), 7.56–7.52 (m, 2H, Ar). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $(CD_3)_2CO$): δ = 141.7, 135.7, 133.5, 132.9, 131.6, 131.3, 131.1, 130.0, 129.7, 125.2 (Ar), 121.4 (q, $^{1}J_{CF}$ = 321.9 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = −79.33 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* $[M]^+$ calcd for $C_{18}H_{13}Se$: 309.0177; found: 309.0180.



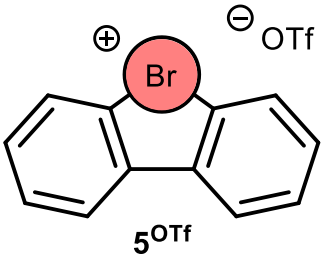
3^{OTf}

3^{OTf}. White crystalline solid. Yield: 93% (470 mg). M.p.: 219–222 °C (dec.). ^{1}H NMR (400.13 MHz, CD_3OD): δ = 8.27 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, Ar), 8.08 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, Ar), 7.80 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, Ar), 7.61 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, Ar), 7.49–7.44 (m, 3H, Ar), 7.39–7.35 (m, 2H, Ar). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3OD): δ = 147.2, 133.1, 133.0, 132.7, 132.3, 131.4, 130.0, 127.1, 125.2, 122.0 (Ar), 118.9 (q, $^{1}J_{CF}$ = 318.5 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = −79.28 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* [M]$^{+}$ calcd for $C_{18}H_{13}Te$: 359.0074; found: 359.0079.



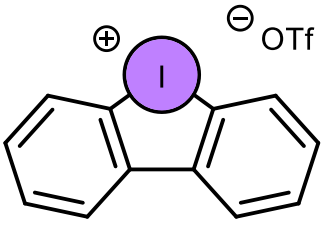
4^{OTf}

4^{OTf}. White crystalline solid. Yield: 58% (966 mg). M.p.: 158–160 °C. ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$) δ = 8.48 – 8.89 (m, 4H, Ar), 7.78 – 8.23 (m, 4H, Ar).^{13}C{^{1}H} NMR (100.61 MHz, $(CD_3)_2SO$) δ = 140.5, 132.5, 132.2, 126.0, 123.4 (Ar), 121.2 (d, $^{1}J_{CF}$ = 322.3 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = –79.28 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* [M]$^{+}$ calcd for $C_{12}H_8Cl$: 187.0309; found: 187.0310.



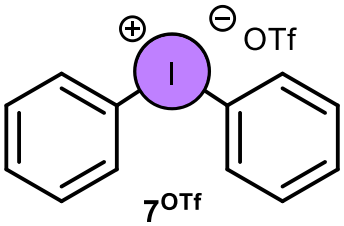
5^{OTf}

5^{OTf}. White crystalline solid. Yield: 60% (1136 mg). M.p.: 200–203 °C. ^{1}H NMR (400.13 MHz, CD_3CN) δ = 8.41 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.7, 2H, Ar), 8.32 (dd, $^{3}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2H, Ar), 7.96 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2H, Ar), 7.84 (ddd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.7 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN): δ = 136.7, 135.5, 132.3, 131.7, 126.6 and 125.1 (Ar); 121.1 (d, $^{1}J_{CF}$ = 320.7 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = −79.25 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* $[M]^+$ calcd for $C_{12}H_8Br$: 230.9804; found: 230.9807.



6^{OTf}

6^{OTf}. White crystalline solid. Yield: 90% (760 mg). M.p.: 240–242 °C. ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$): δ = 8.37 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, Ar), 8.15 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, Ar), 7.79 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, Ar), 7.67 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (100.61 MHz, $(CD_3)_2SO$): δ = 142.1, 131.5, 131.1, 131.0, 127.4, 121.9 (Ar), 121.2 (q, $^{1}J_{CF}$ = 322.3 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = −79.25 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* $[M]^+$ calcd for $C_{12}H_8I$: 278.9665; found: 278.9670.



7^{OTf}

7^{OTf}. White crystalline solid. Yield: 82% (1.41 g). M.p.: 168–170 °C. δ = 8.28 – 8.26 (m, 4H), 7.67 – 7.63 (m, 2H), 7.55 – 7.51 (m, 4H). ^{13}C{^{1}H} NMR (100.61 MHz, $(CD_3)_2SO$): δ = 135.66, 132.50, 132.21, 116.93 (Ar), 121.23 (q, $^{1}J_{CF}$ = 322.3 Hz, *C*F_3). ^{19}F NMR (376.49 MHz, CD_3CN): δ = –79.26 (s, C*F*$_3$). HRMS (ESI-TOF): *m/z* $[M]^+$ calcd for $C_{12}H_{10}I$: 280.9822; found: 280.9819.

Spectra of the SHDs

1^{OTf}, 400.13 MHz, $(CD_3)_2CO$, 298 K

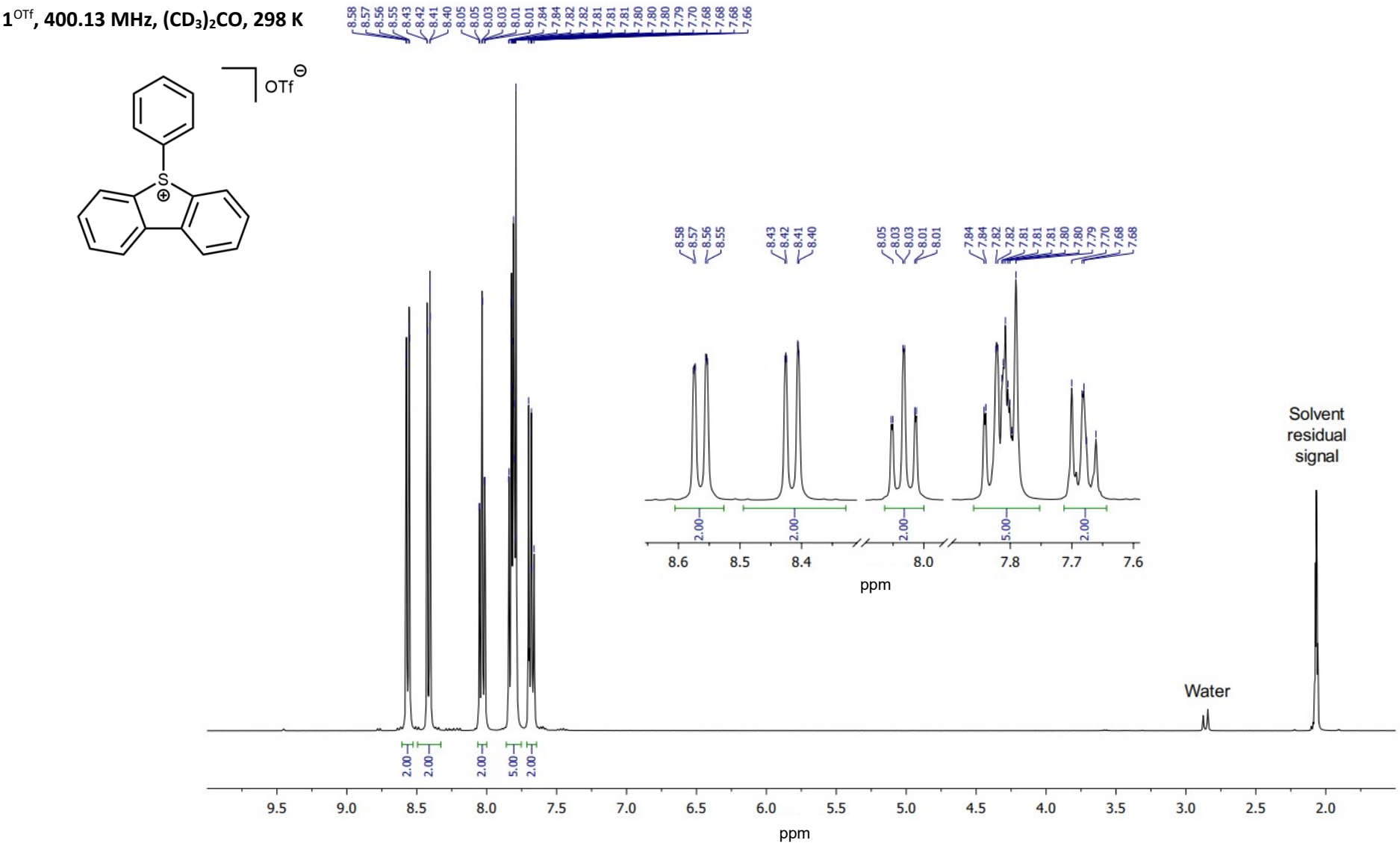


Figure S1. ^{1}H NMR spectrum of the **1^{OTf}**

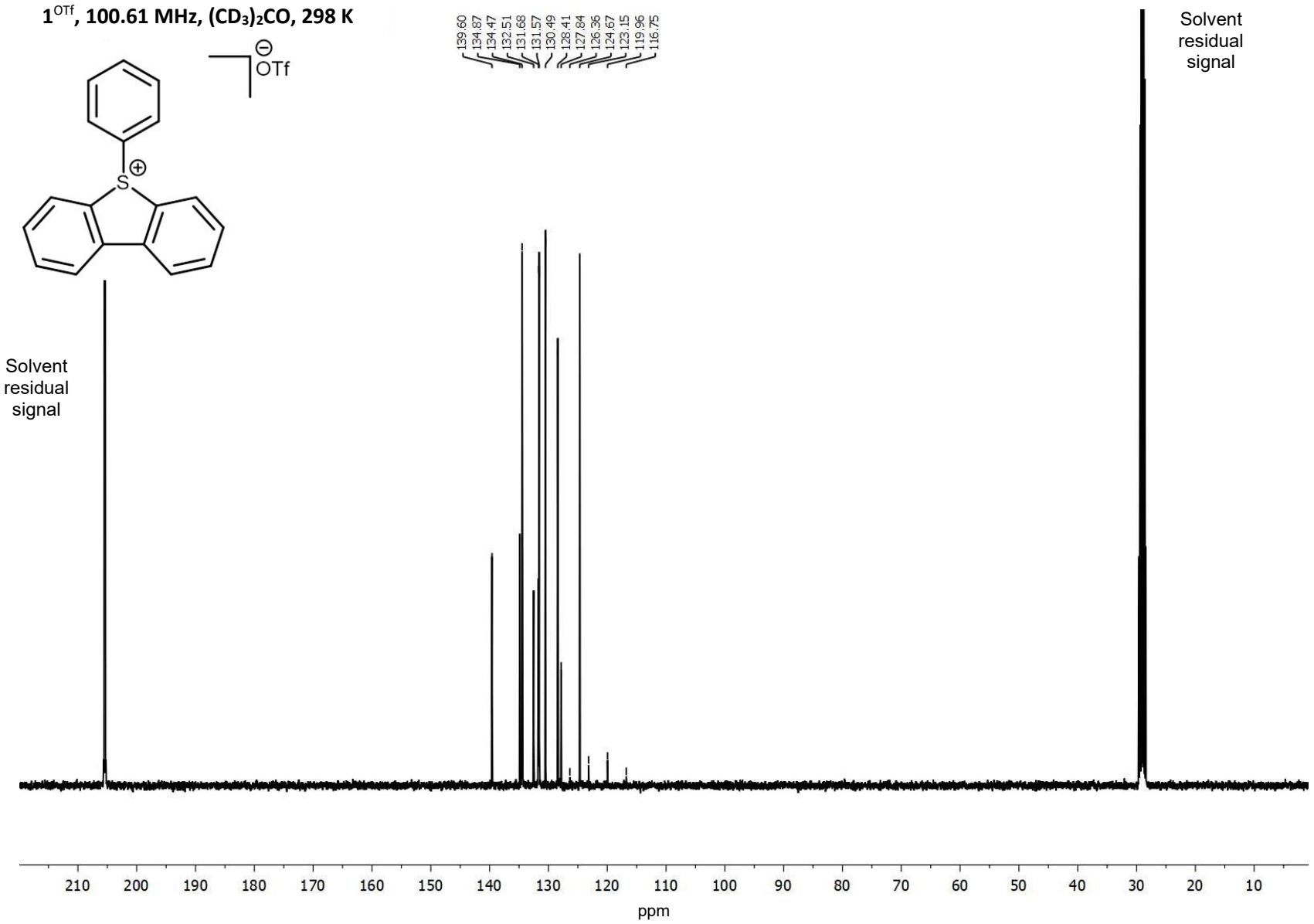


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of the **1**^{OTf}

1^{OTf}, 376.49 MHz, CD_3CN, 298 K

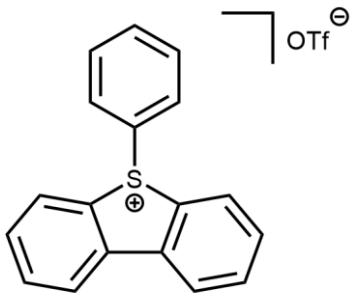


Figure S3. ^{19}F NMR spectrum of the **1^{OTf}**

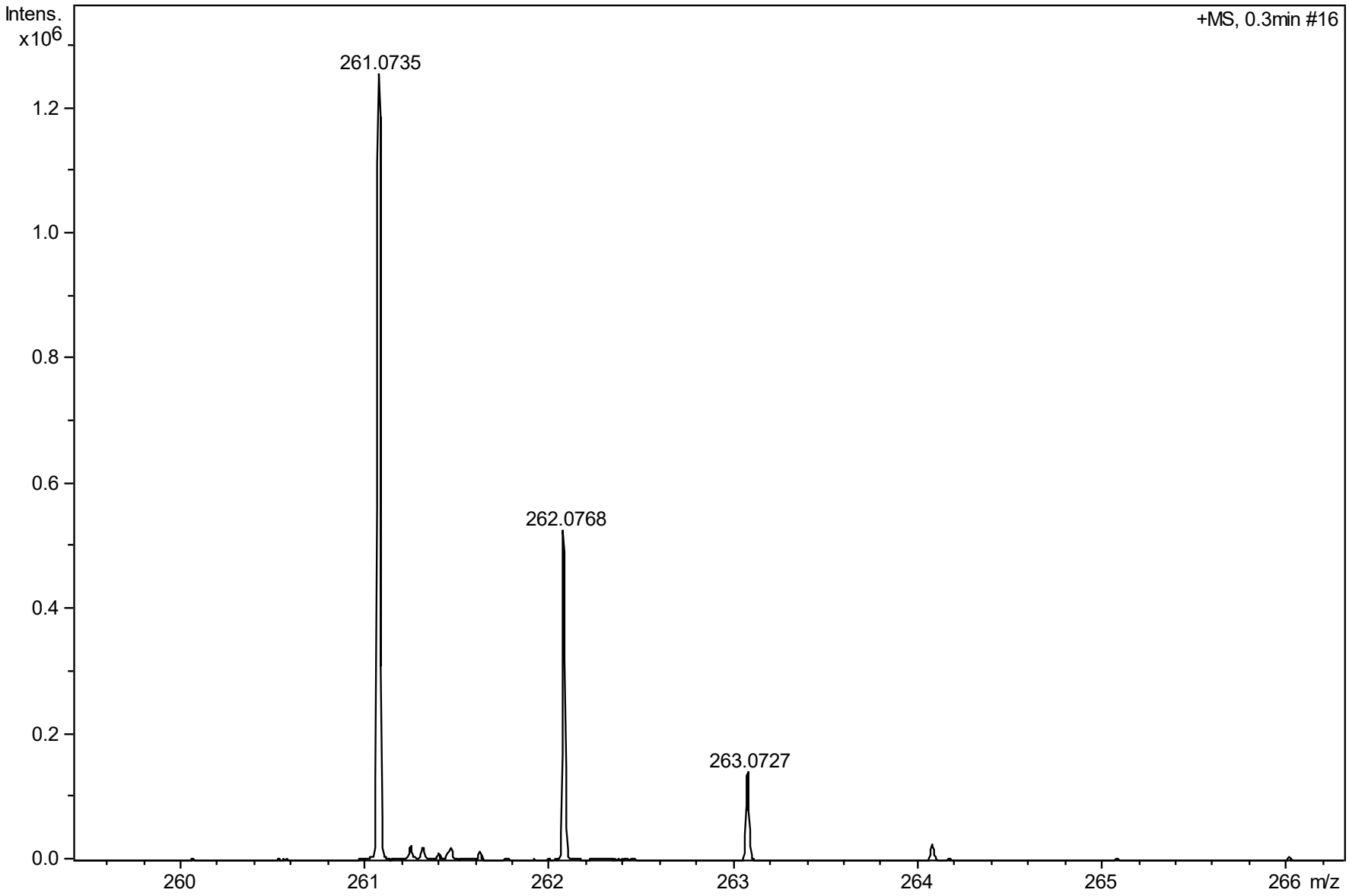


Figure S4. HRESI^{+}-MS of the **1**^{OTf}

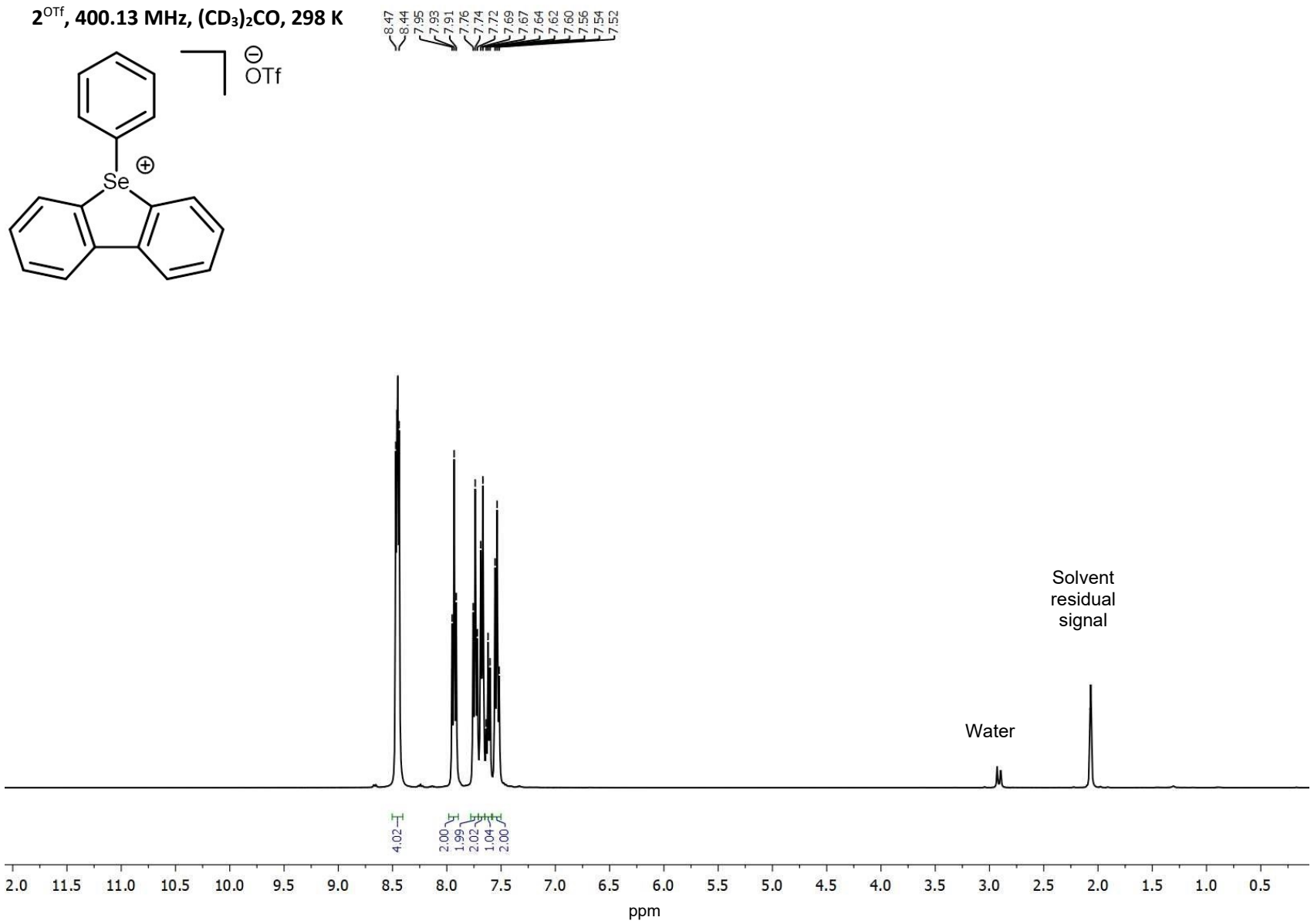


Figure S5. ^{1}H NMR spectrum of the **2**^{OTf}

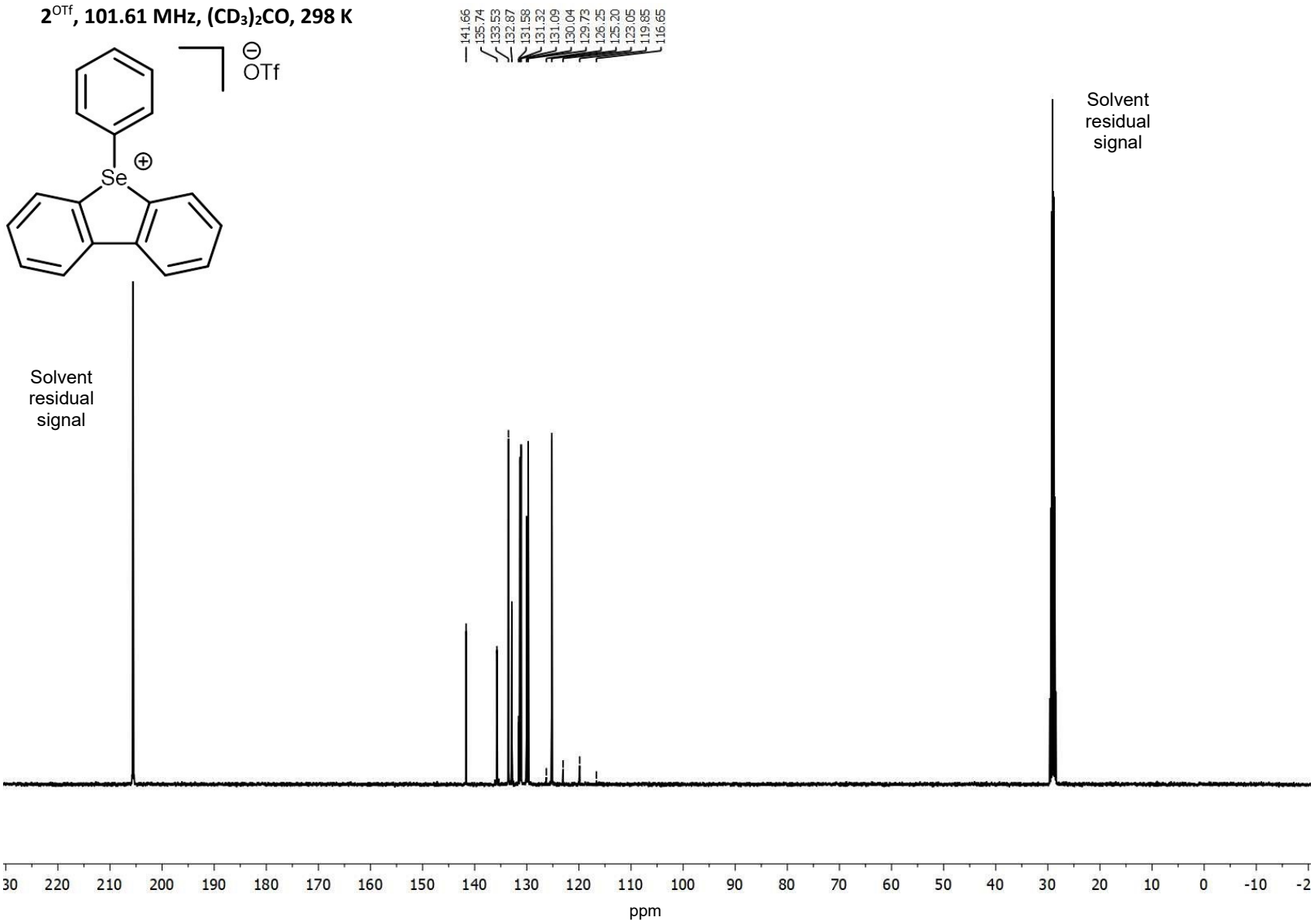


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of the **2**^{OTf}

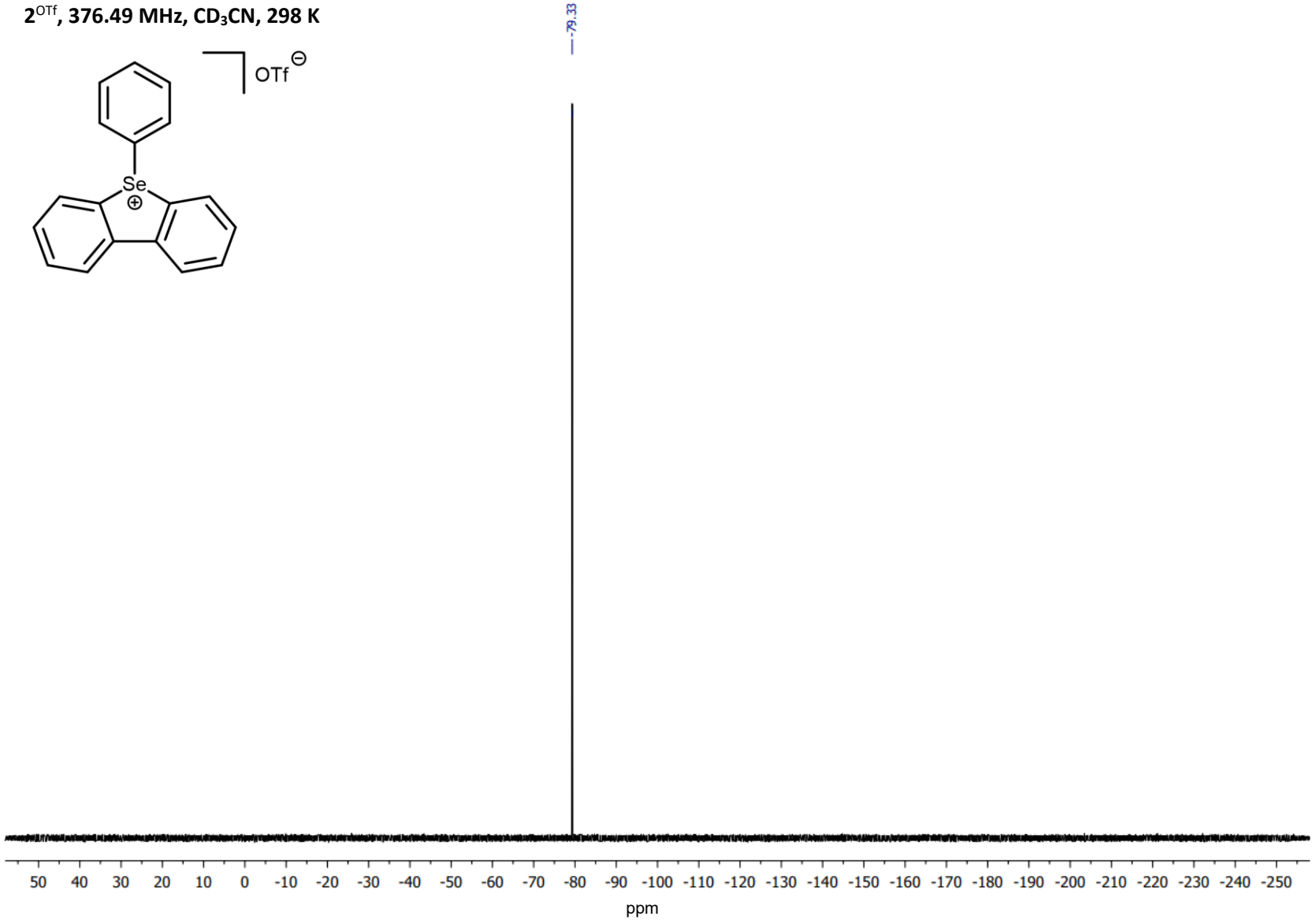


Figure S7. ^{19}F NMR spectrum of the **2**^{OTf}

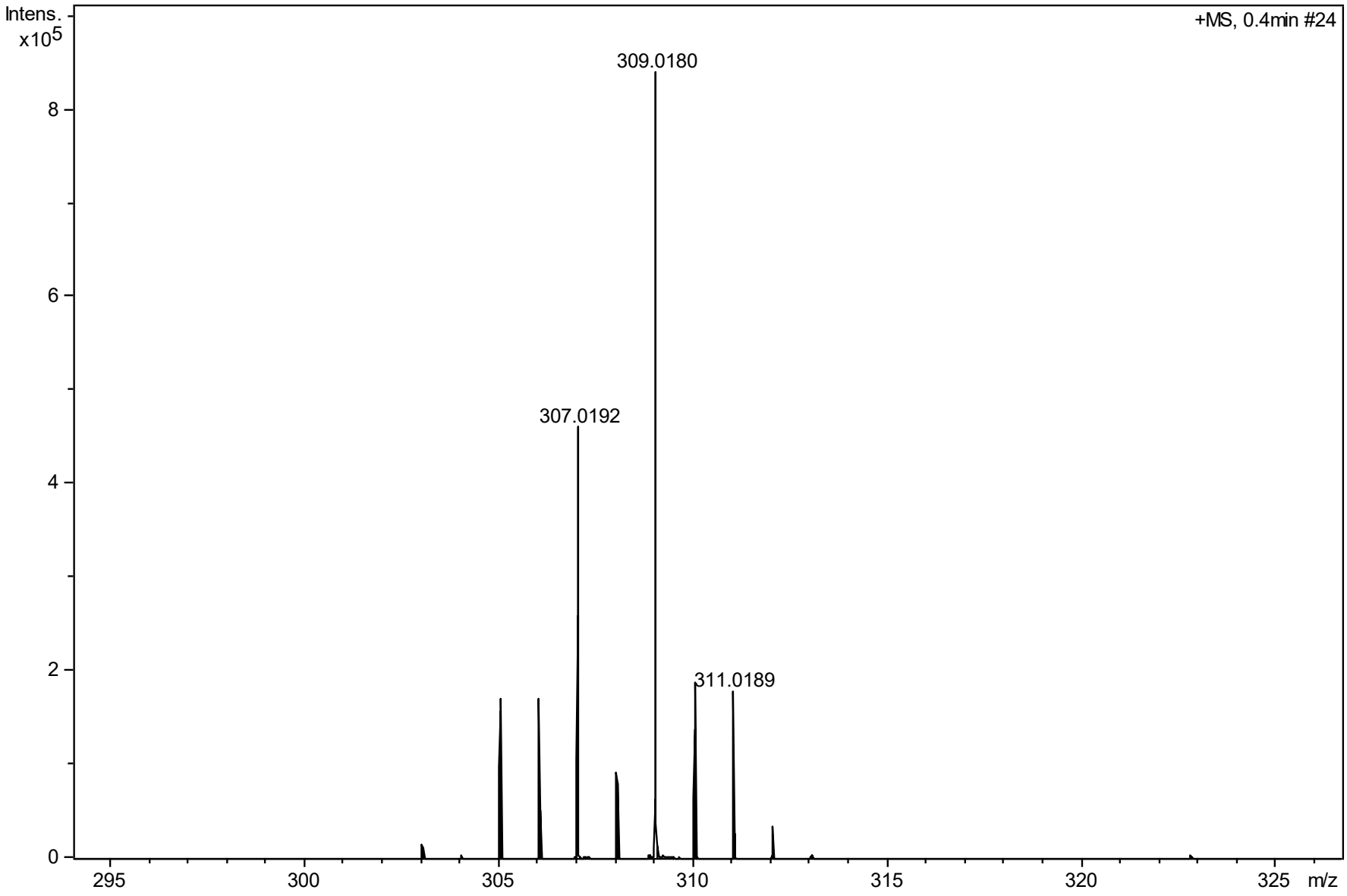


Figure S8. HRESI^{+}-MS of the **2**^{OTf}

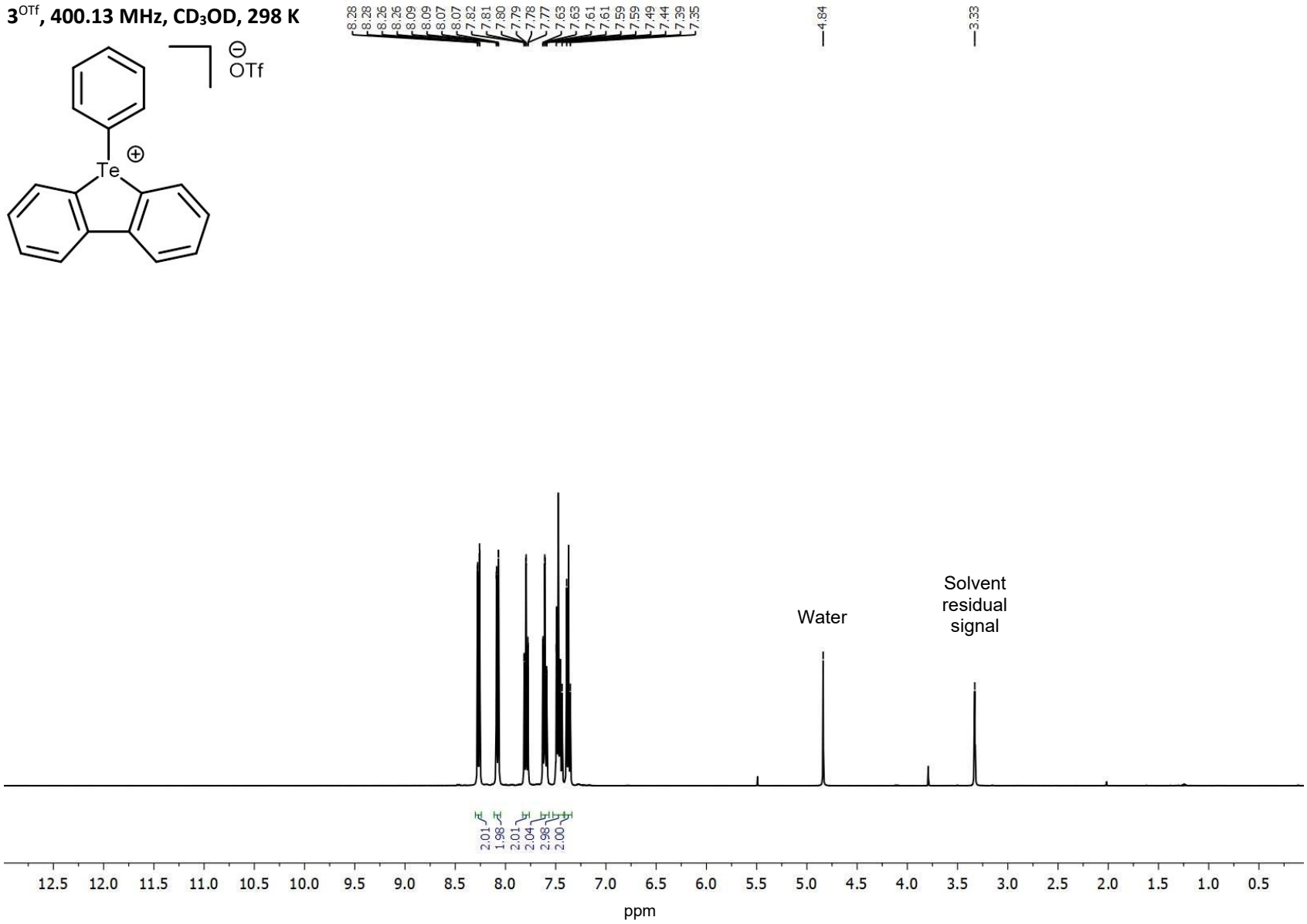


Figure S9. ^{1}H NMR spectrum of the **3**^{OTf}

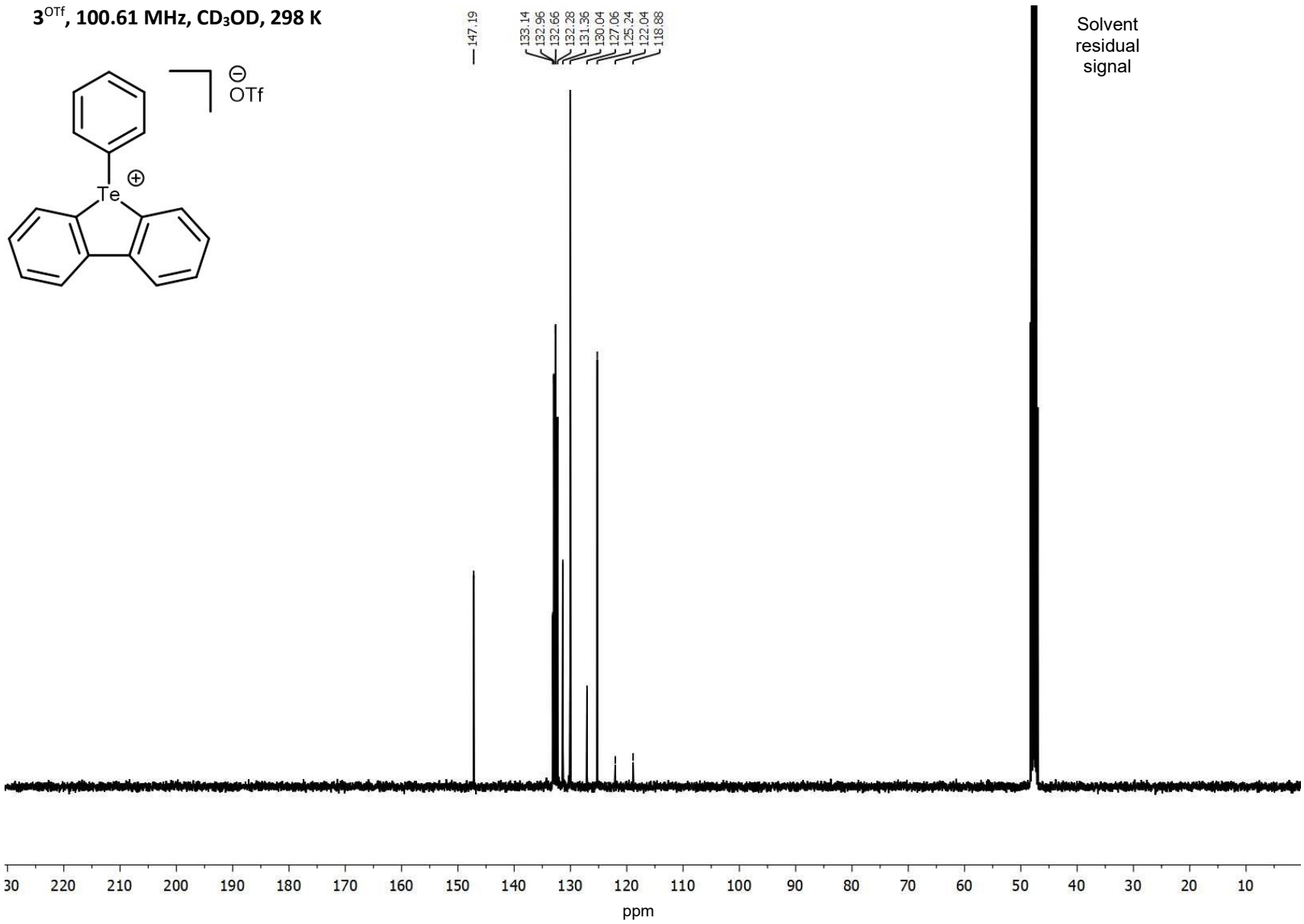


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of the **3**^{OTf}

3^{OTf}, 376.49 MHz, CD_3CN, 298 K

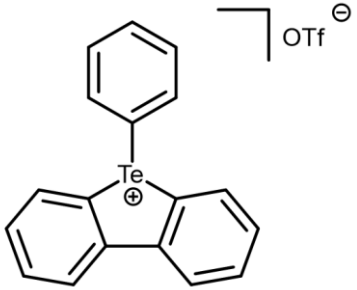


Figure S11. ^{19}F NMR spectrum of the **3^{OTf}**

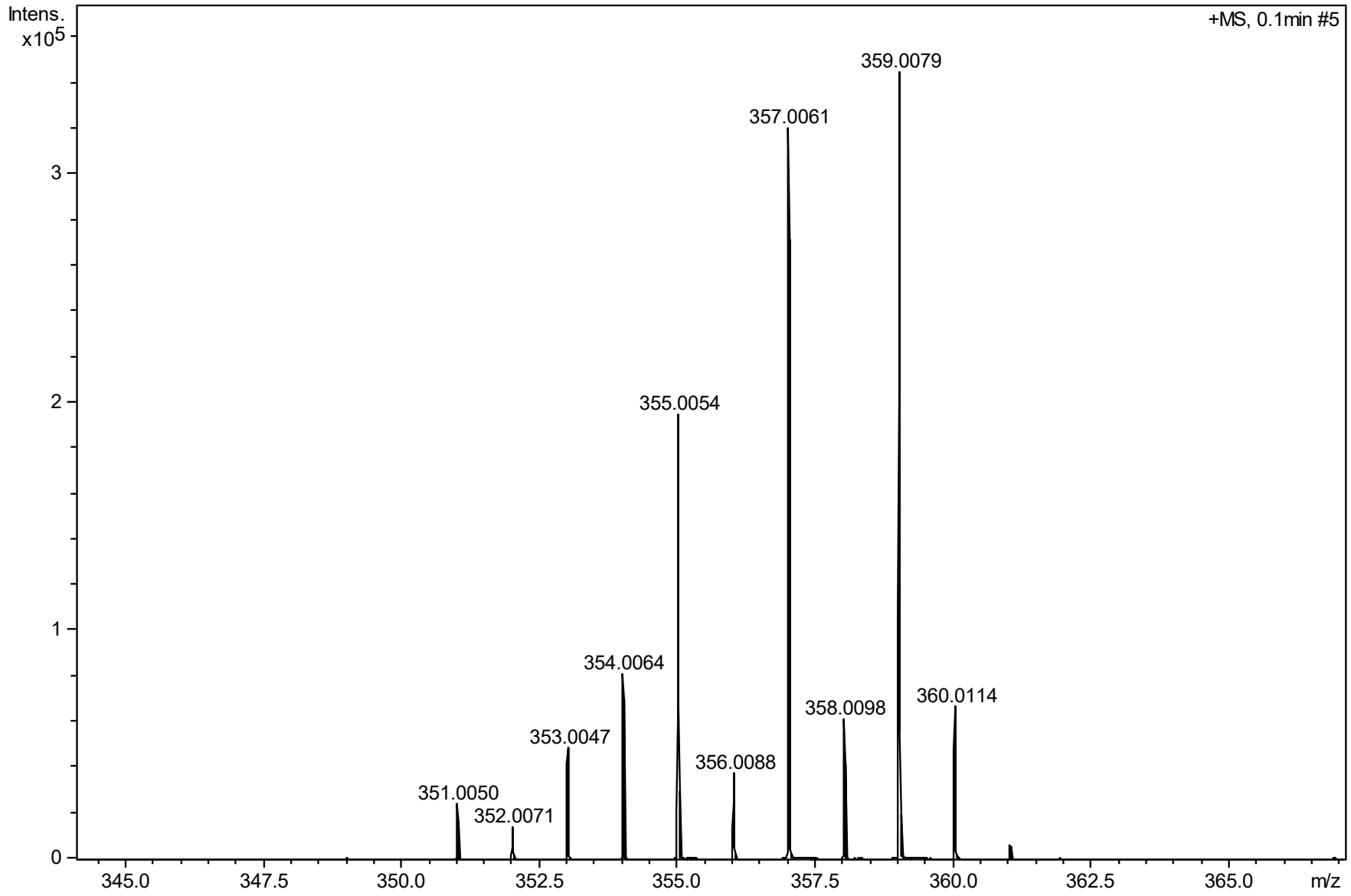


Figure S12. HRES^{+}-MS spectrum of the **3**^{OTf}

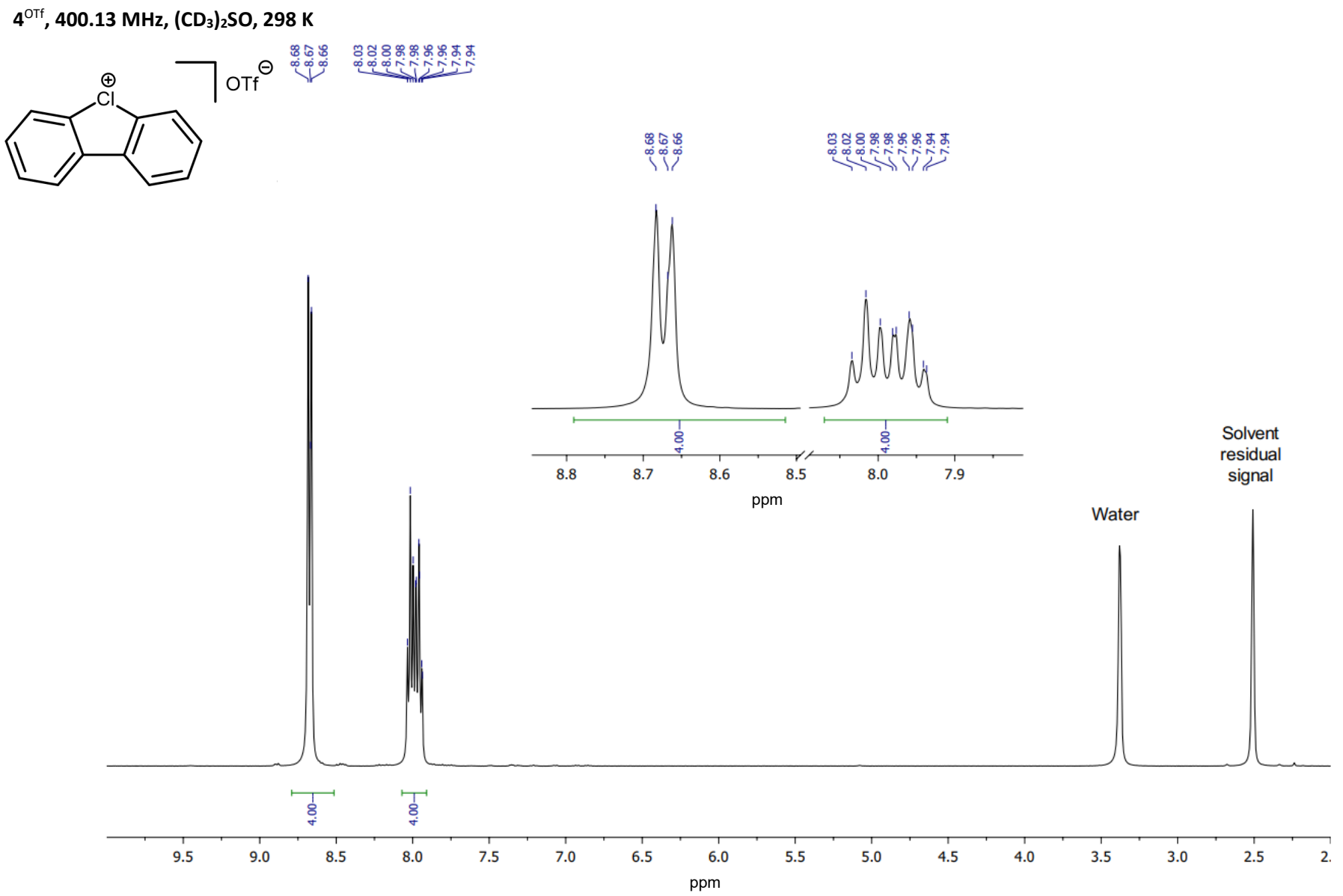


Figure S13. ^{1}H NMR spectrum of the **4**^{OTf}

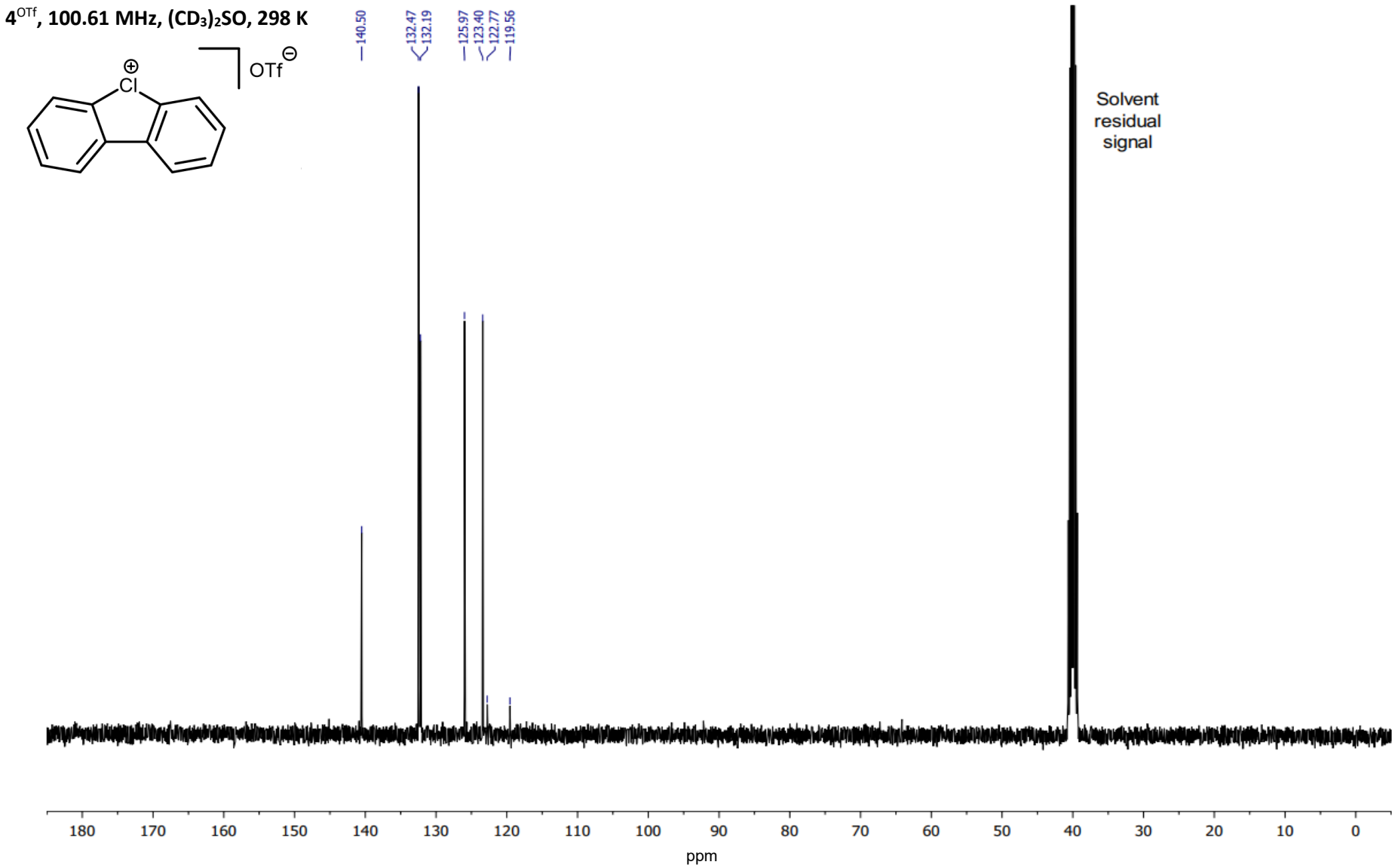


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of the **4**^{OTf}

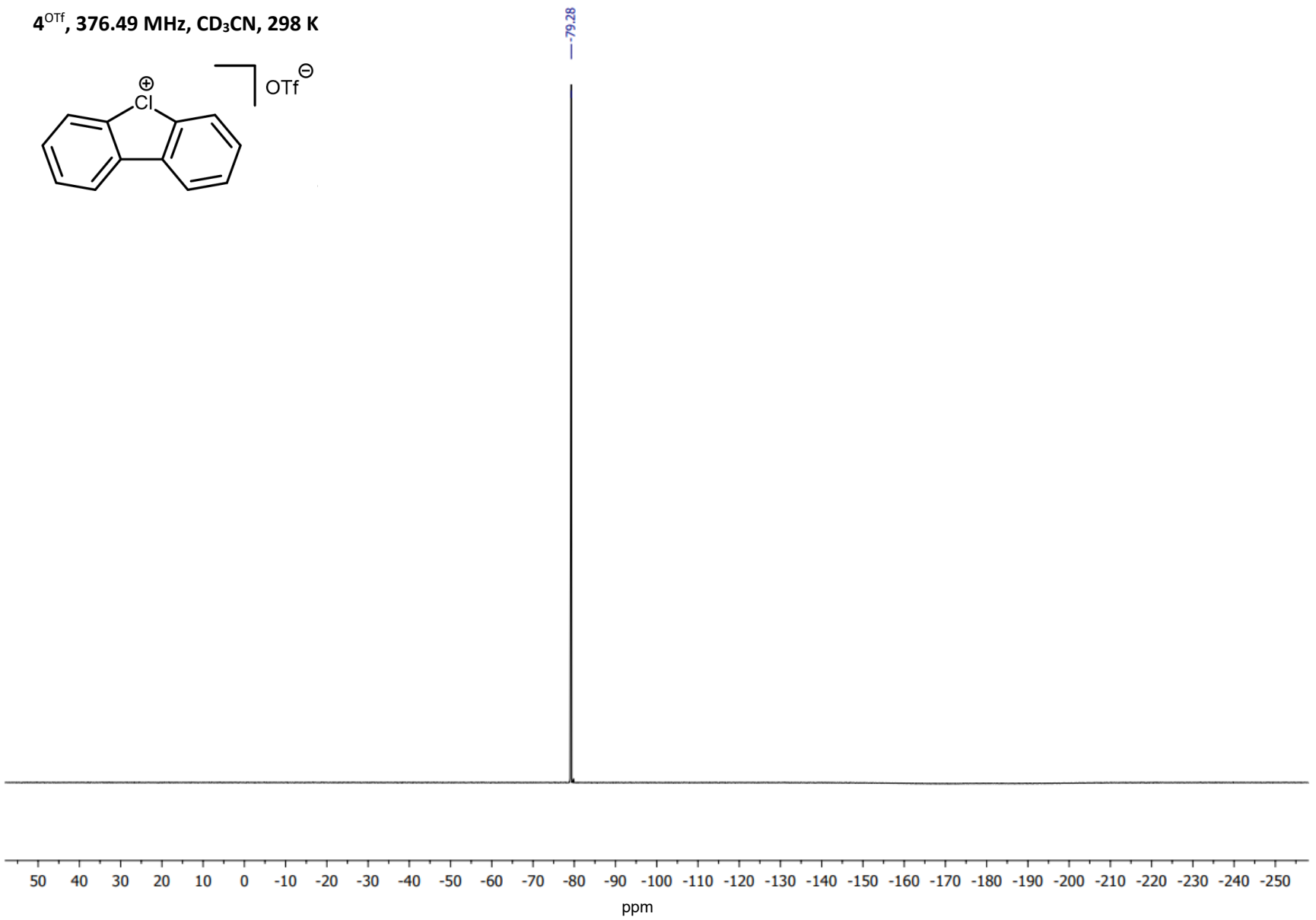


Figure S15. ^{19}F NMR spectrum of the **4**^{OTf}

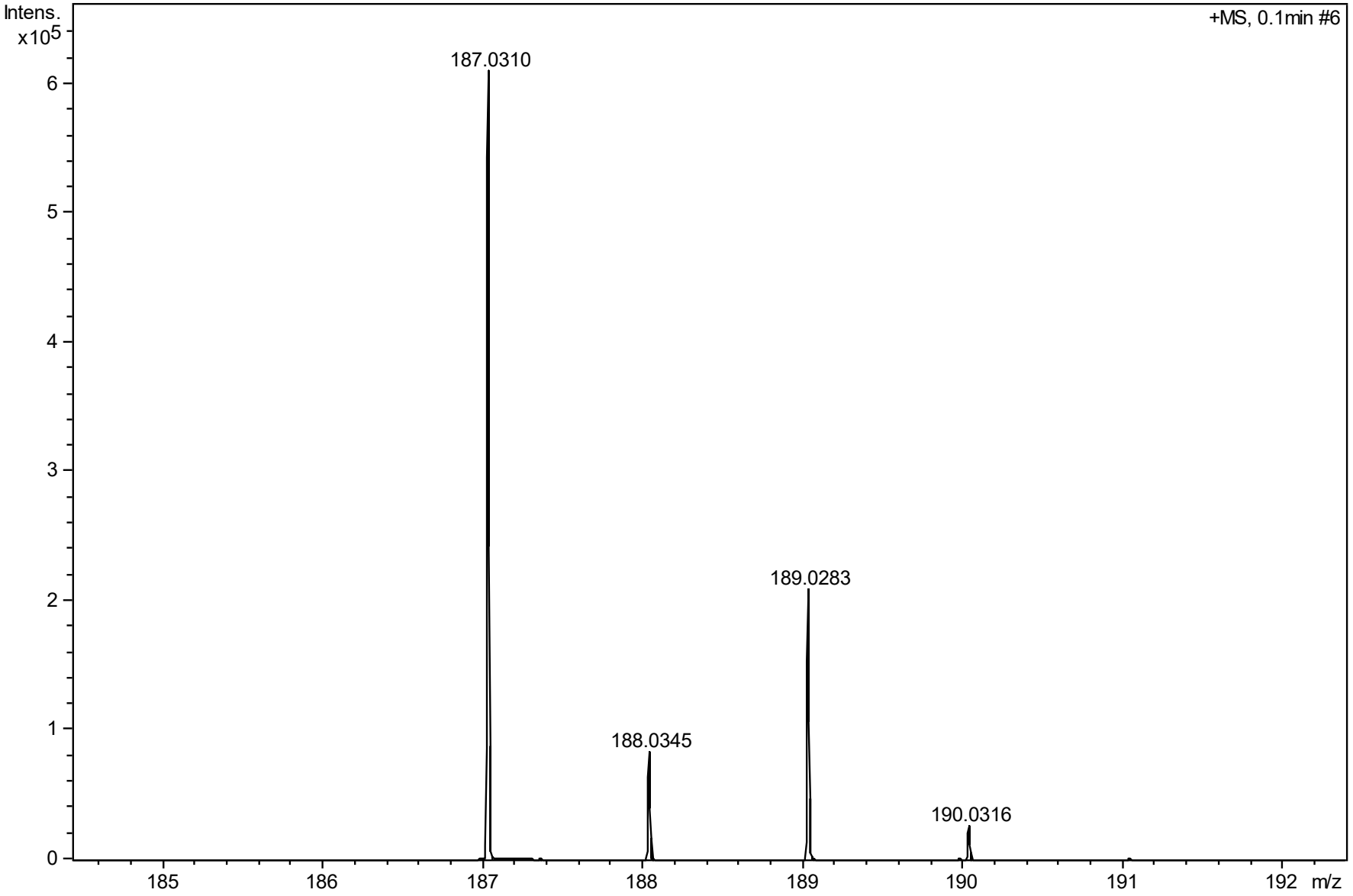


Figure S16. HRES^{+}-MS spectrum of the **4**^{OTf}

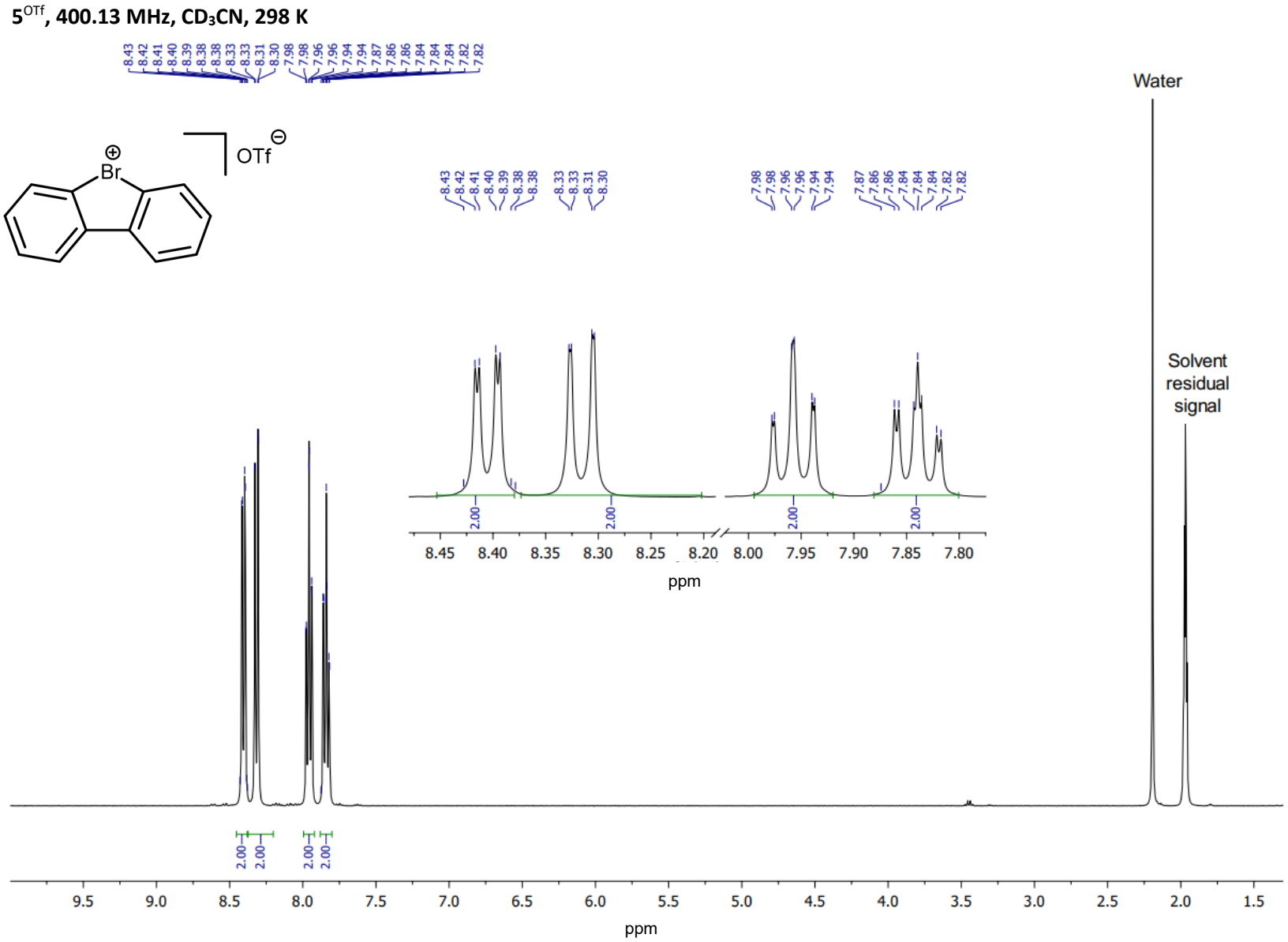


Figure S17. ^{1}H NMR spectrum of the **5**^{OTf}

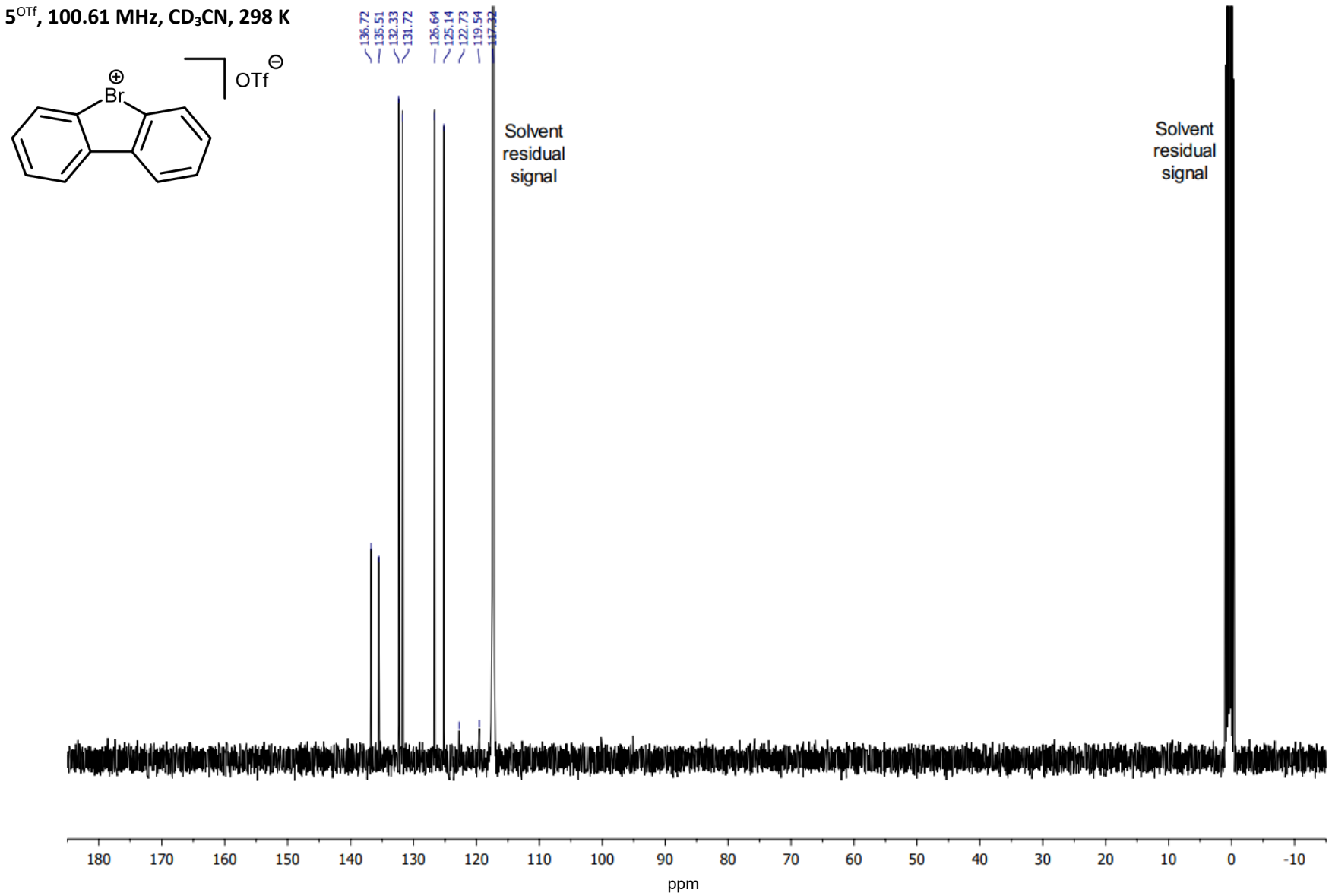


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of the **5**^{OTf}

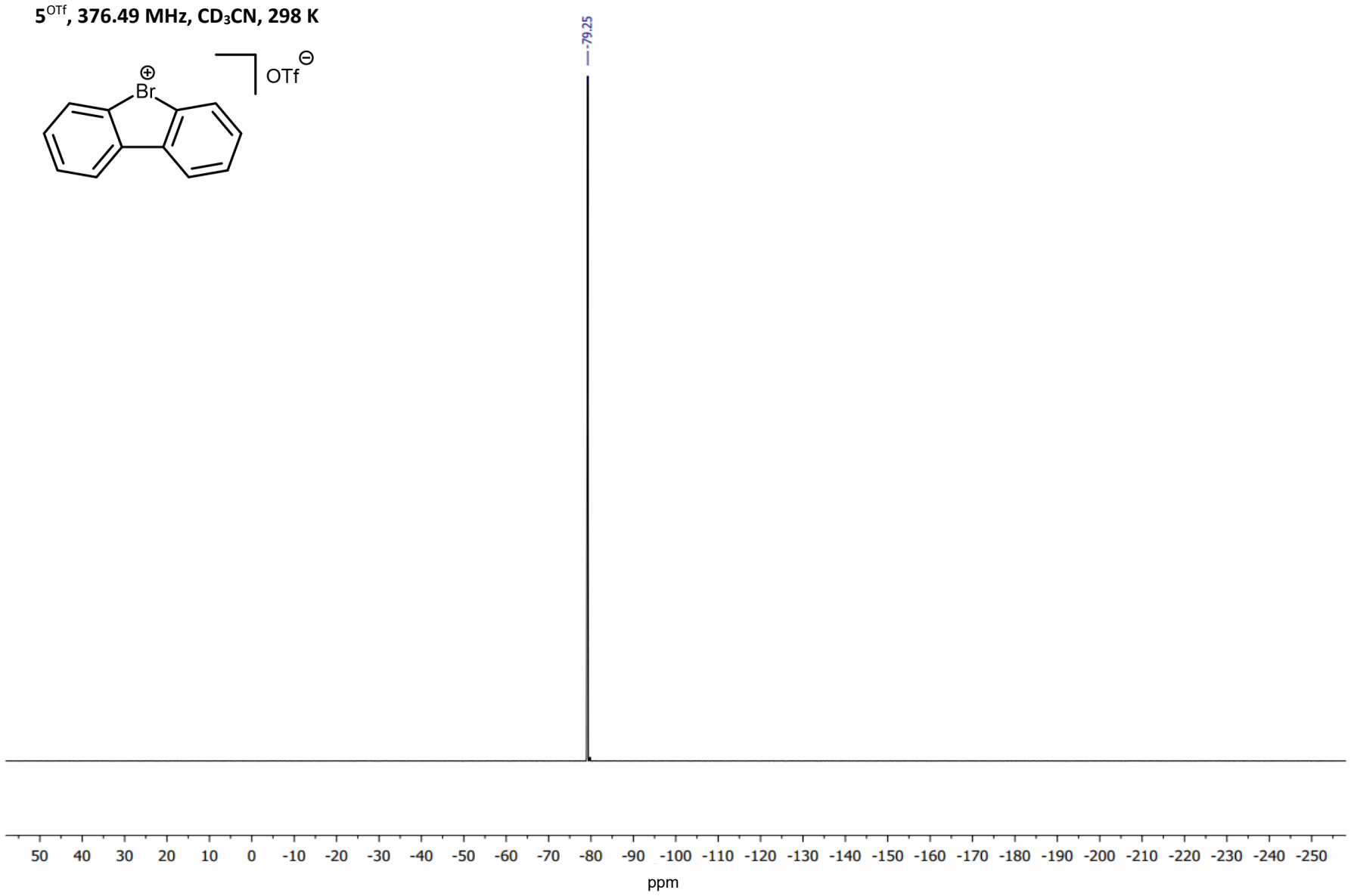


Figure S19. ^{19}F NMR spectrum of the **5**^{OTf}

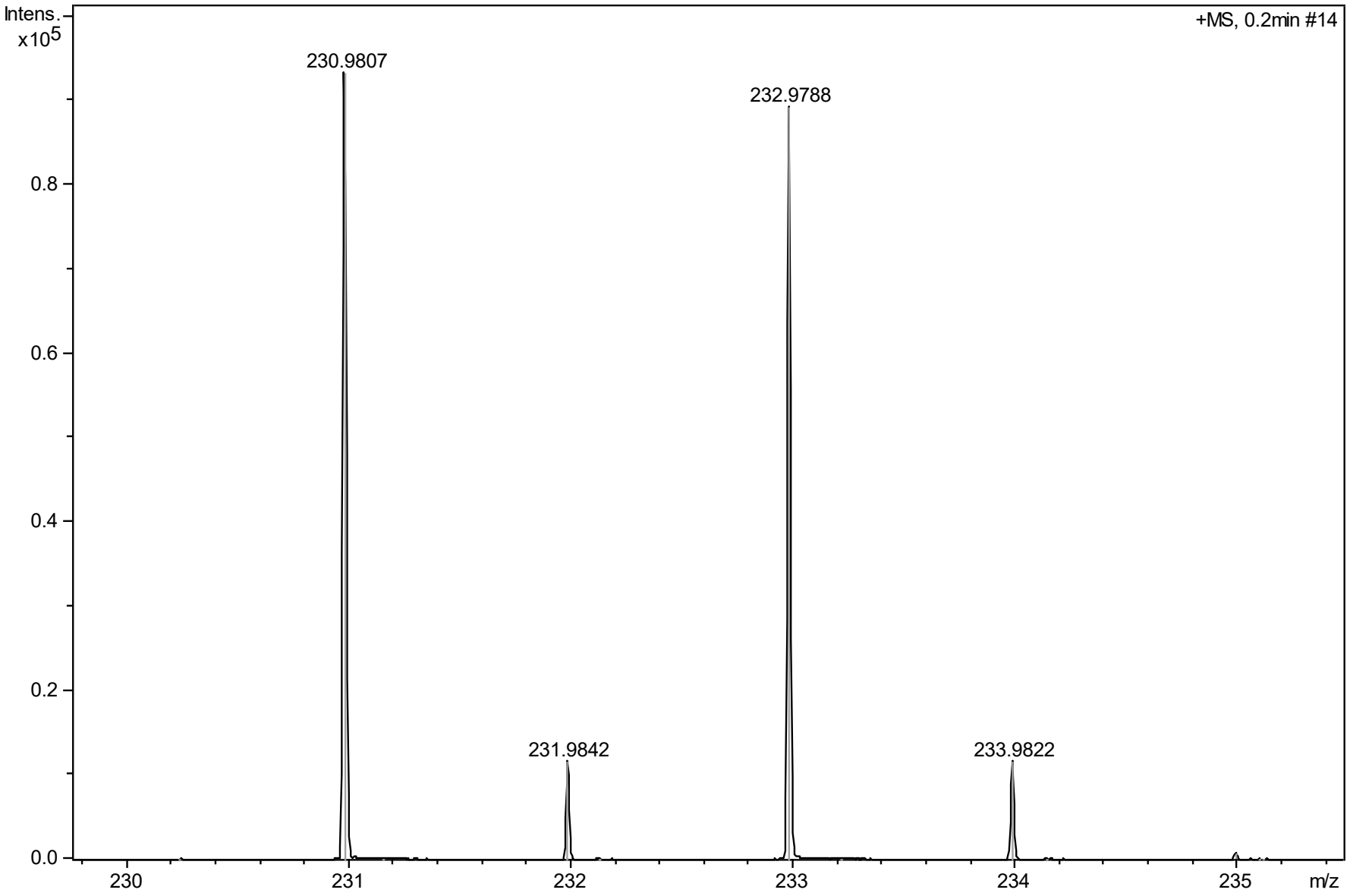


Figure S20. HRES^{+}-MS spectrum of the **5**^{OTf}

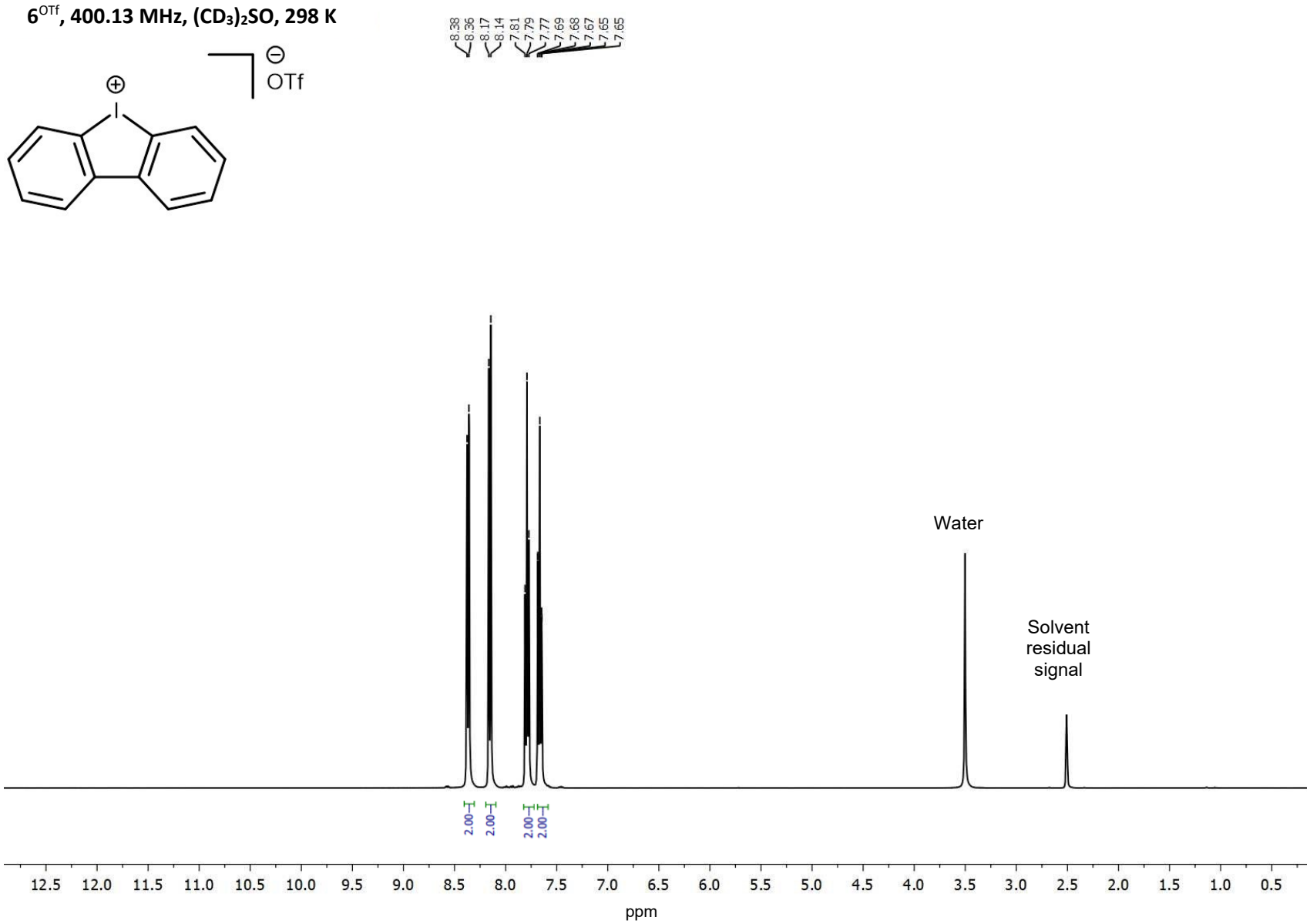


Figure S21. ^{1}H NMR spectrum of the **6**^{OTf}

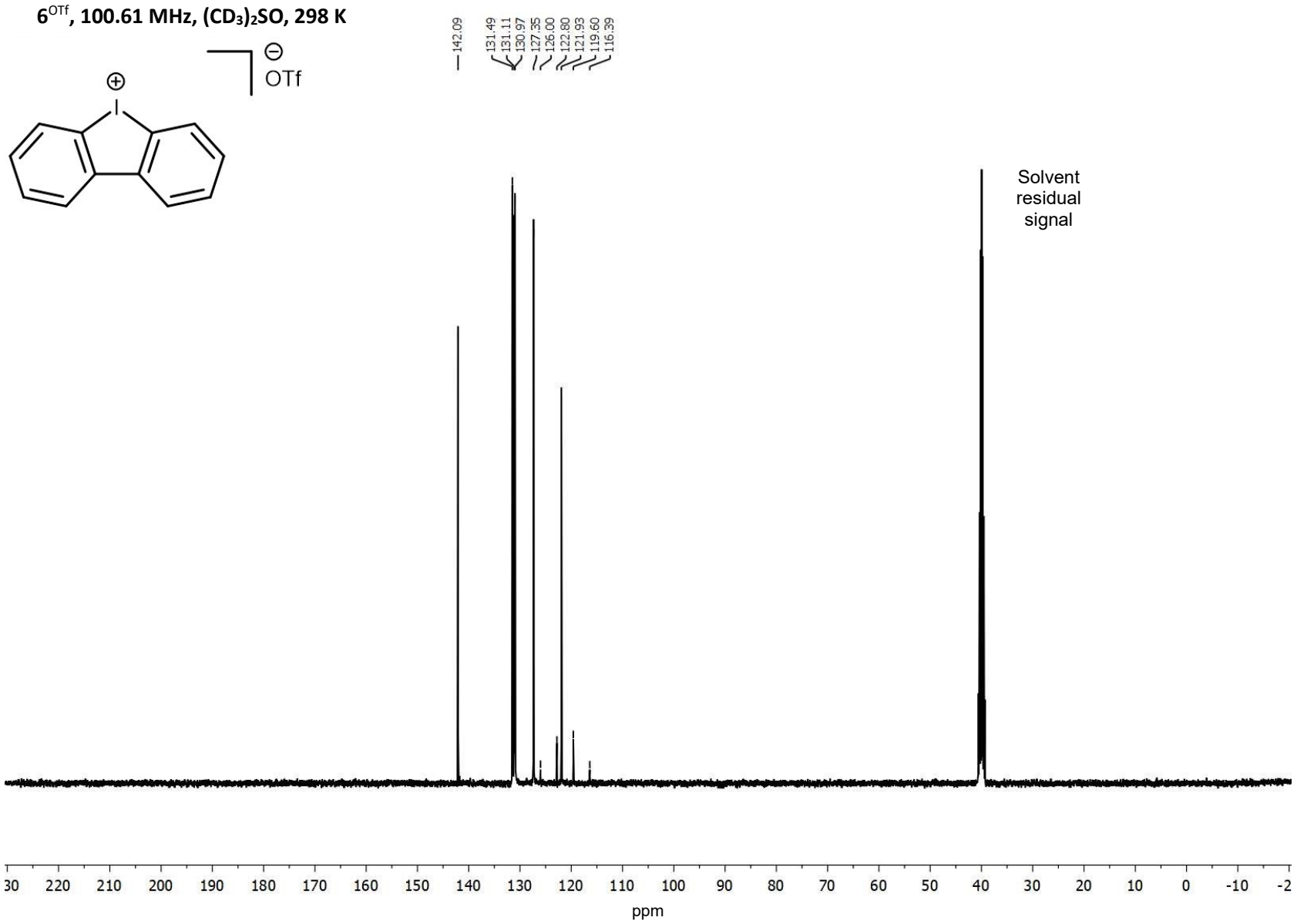


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of the **6**^{OTf}

6^{OTf}, 376.49 MHz, CD_3CN, 298 K

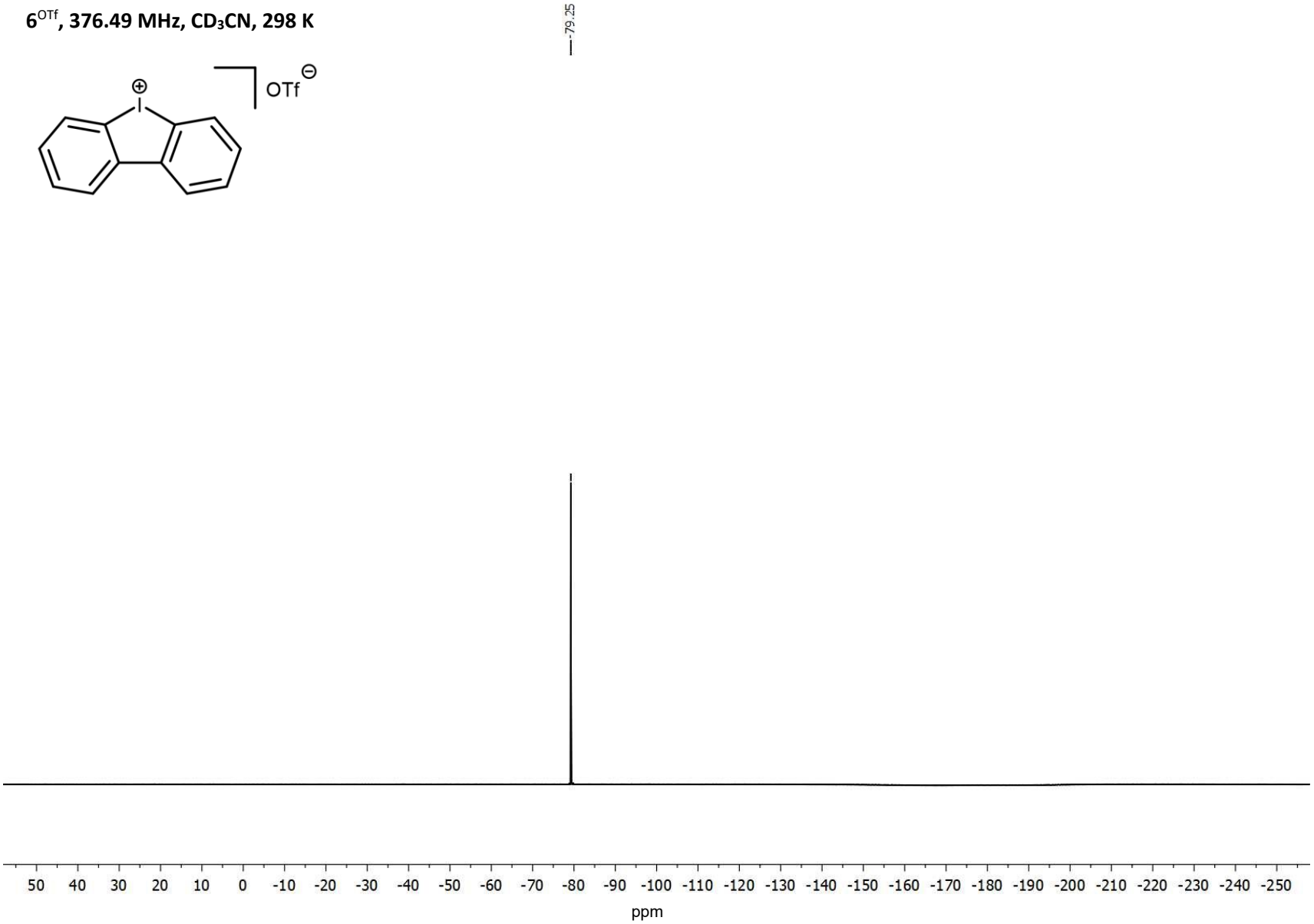


Figure S23. ^{19}F NMR spectrum of the **6^{OTf}**

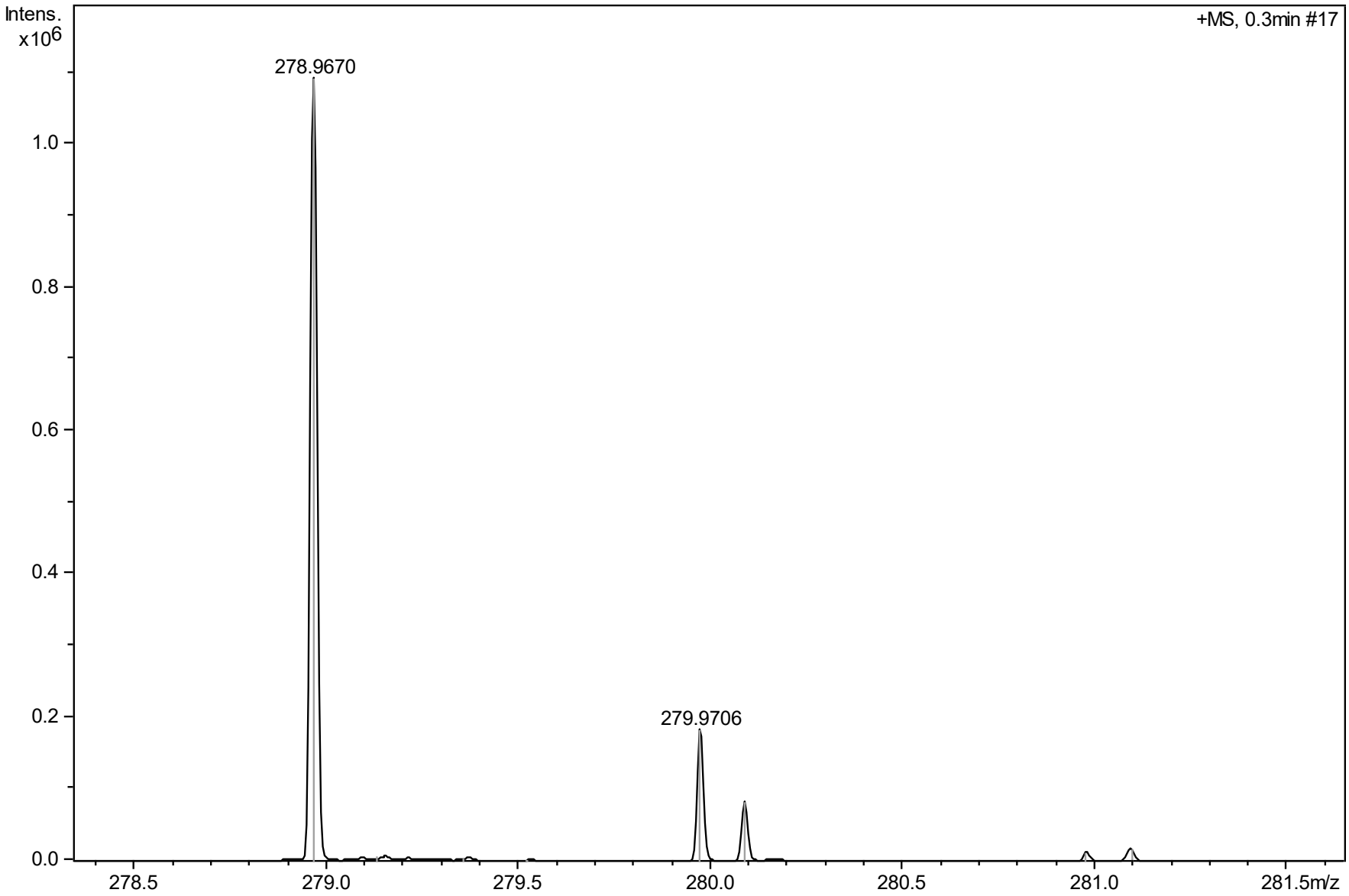


Figure S24. HRES^{+}-MS spectrum of the **6**^{OTf}

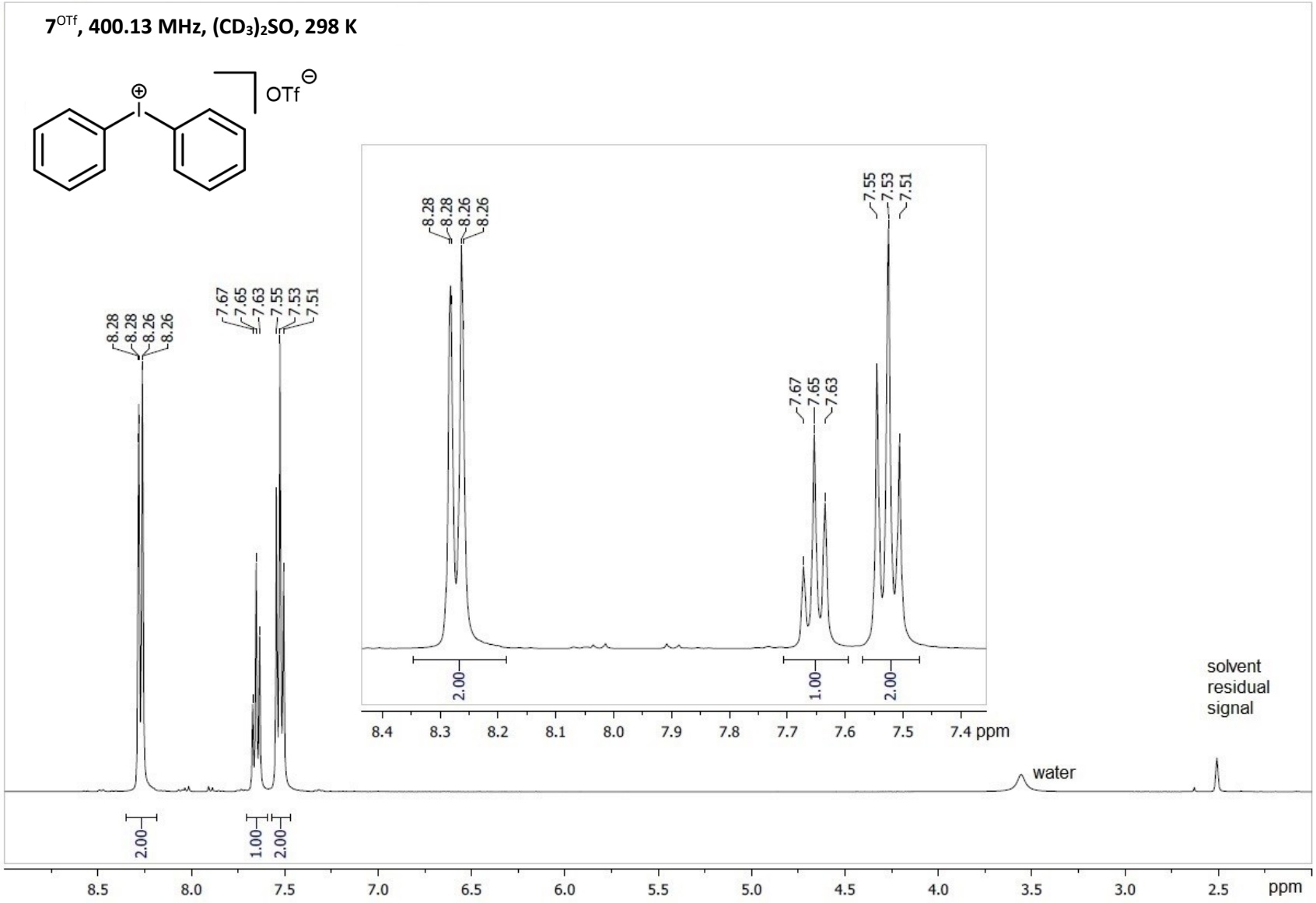


Figure S25. ^{1}H NMR spectrum of the **7**^{OTf}

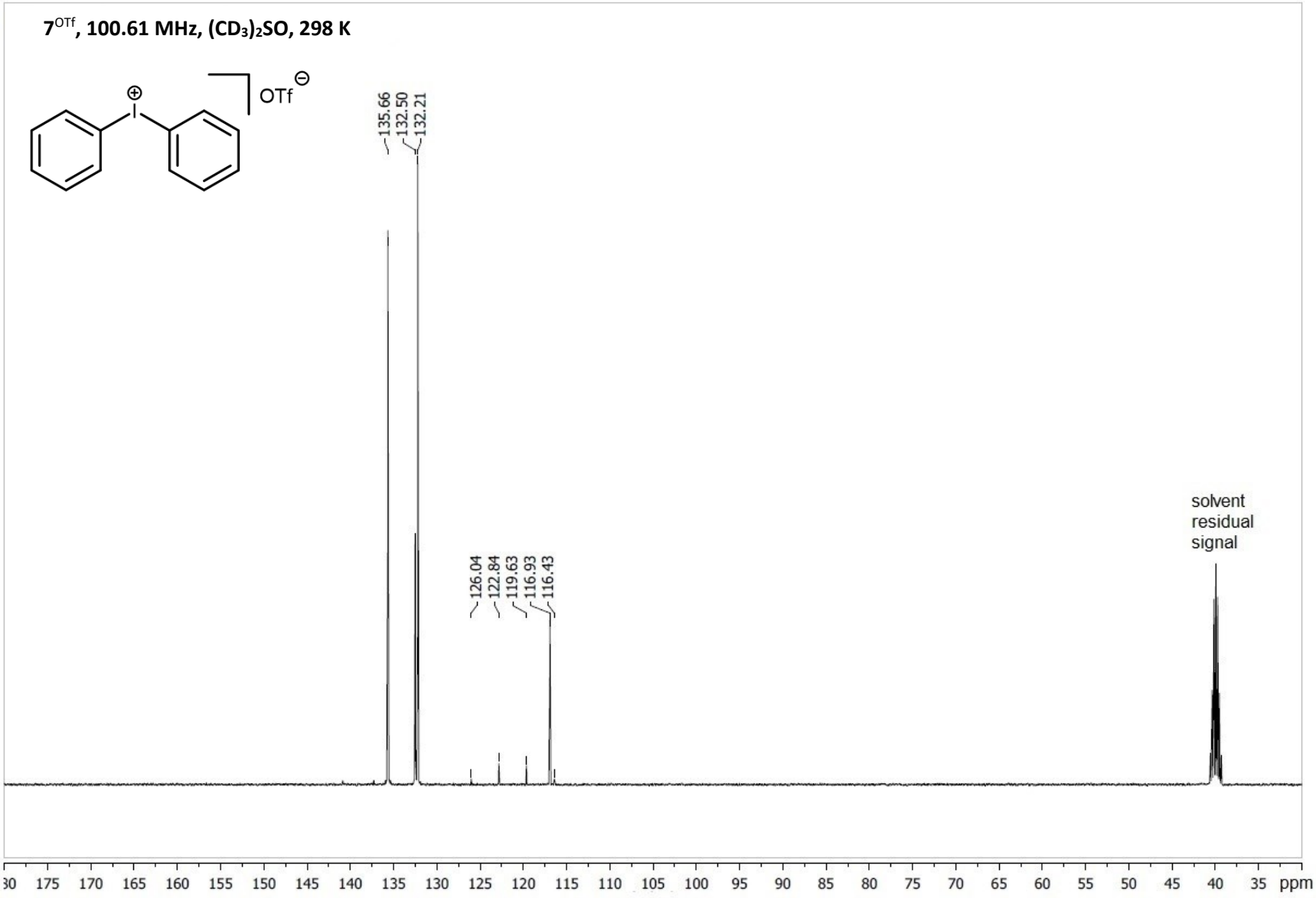


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of the **7**^{OTf}

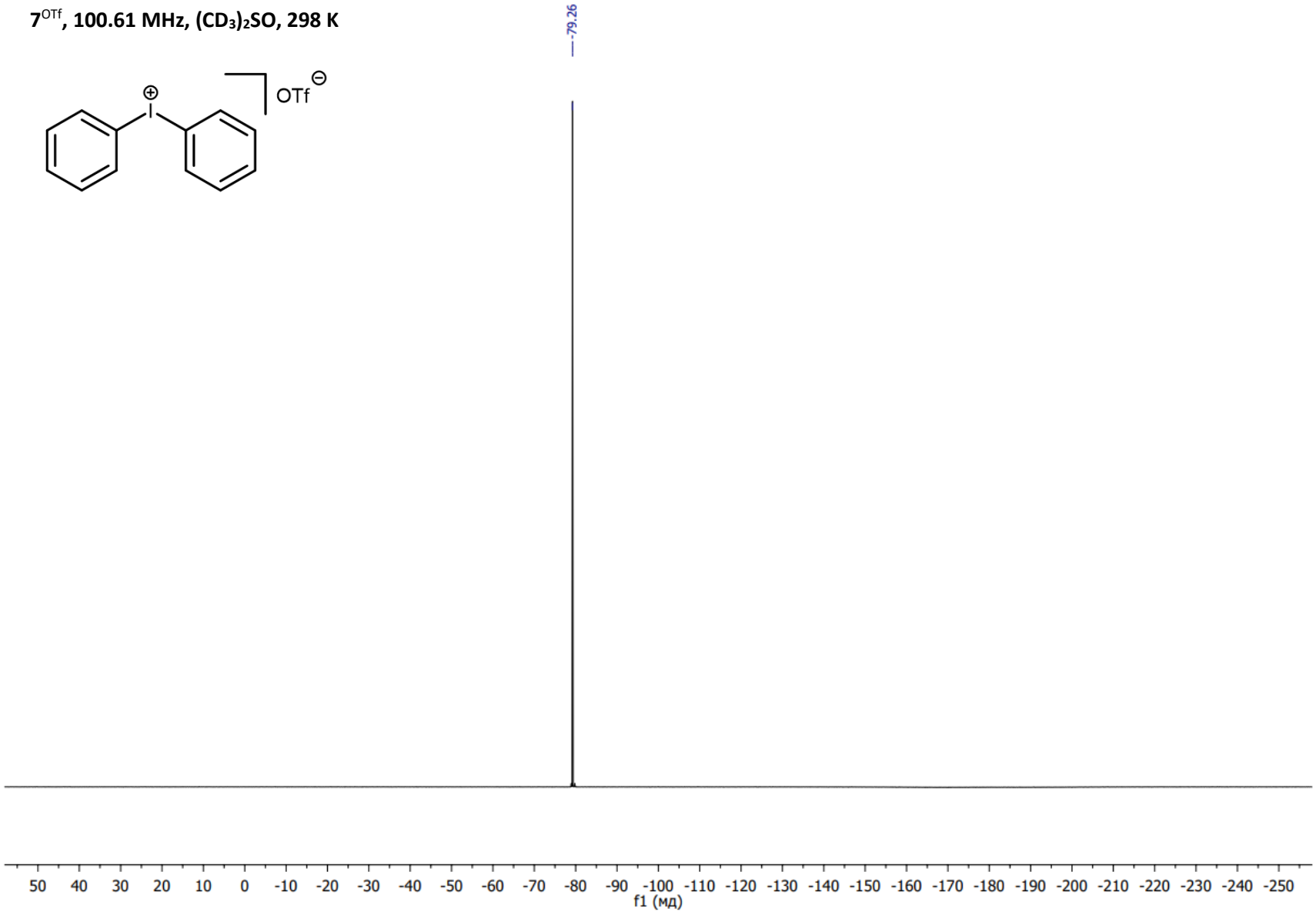


Figure S27. ^{19}F NMR spectrum of the **7**^{OTf}

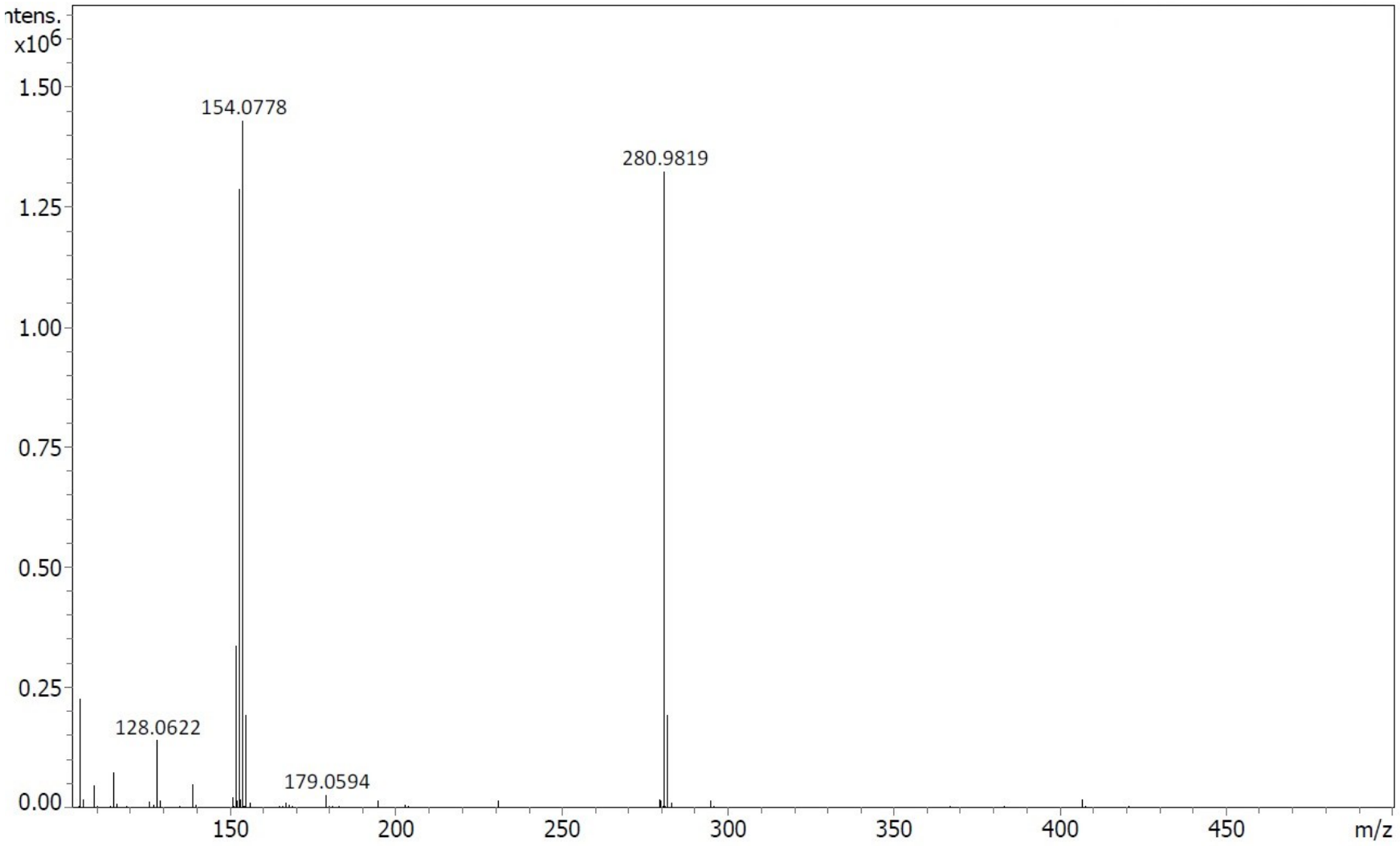
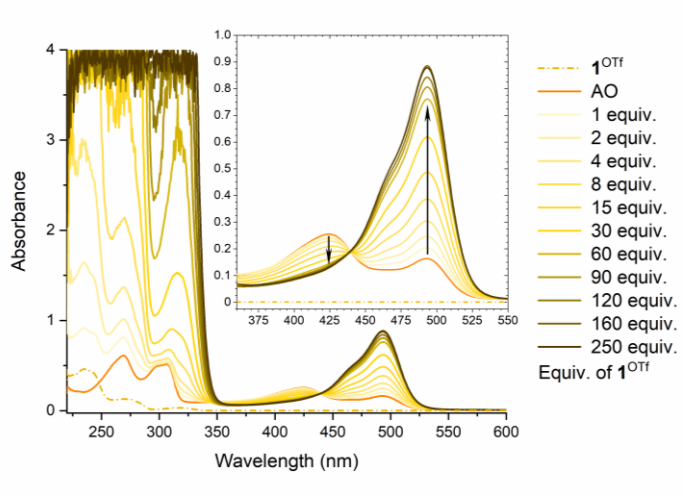
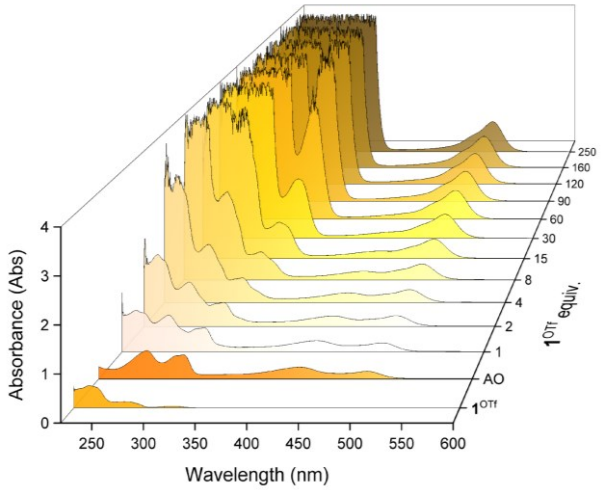
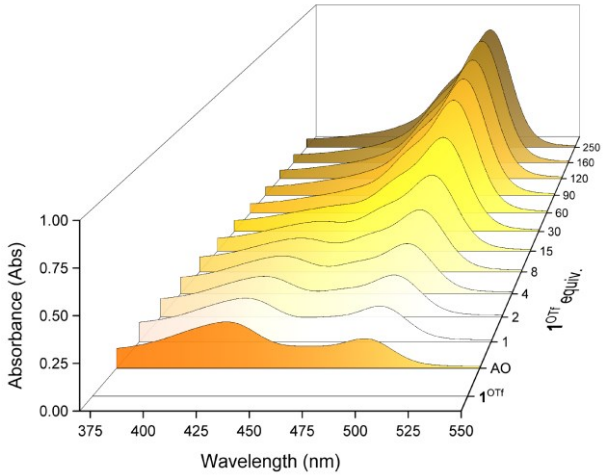


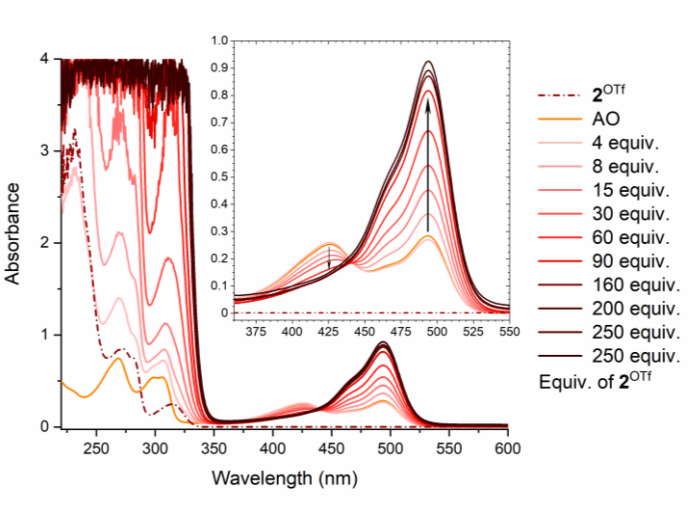
Figure S28. HRES^{+}-MS spectrum of the **7**^{OTf}

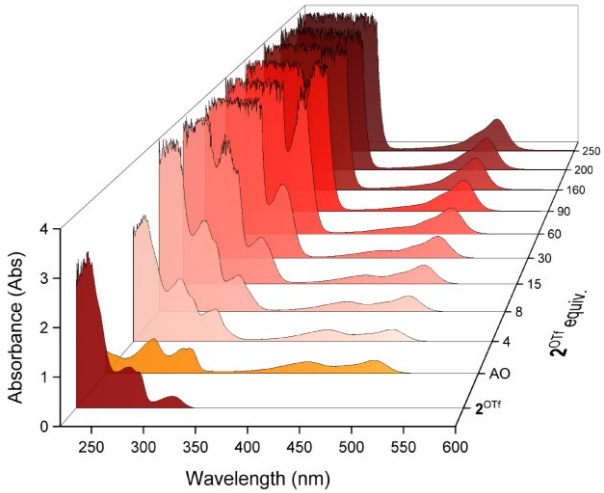
Absorbance Spectra of Photometric Titration

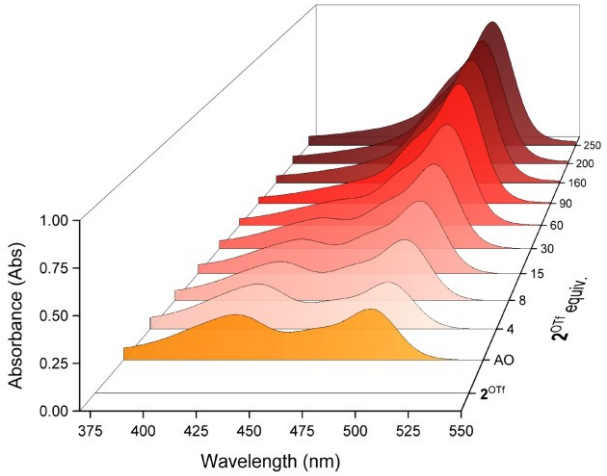


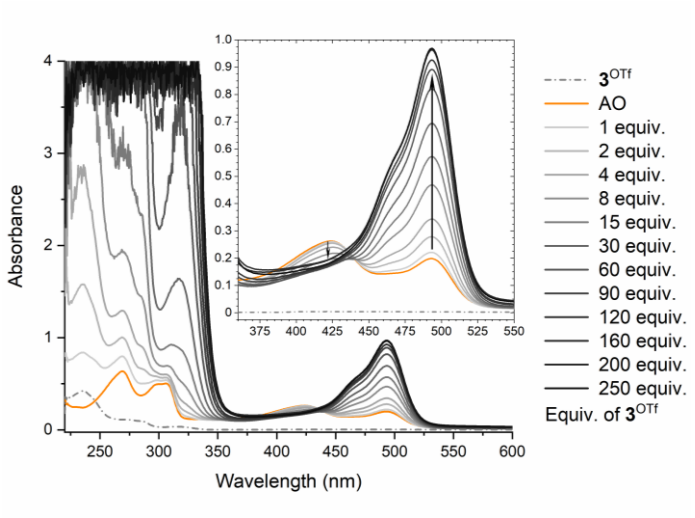


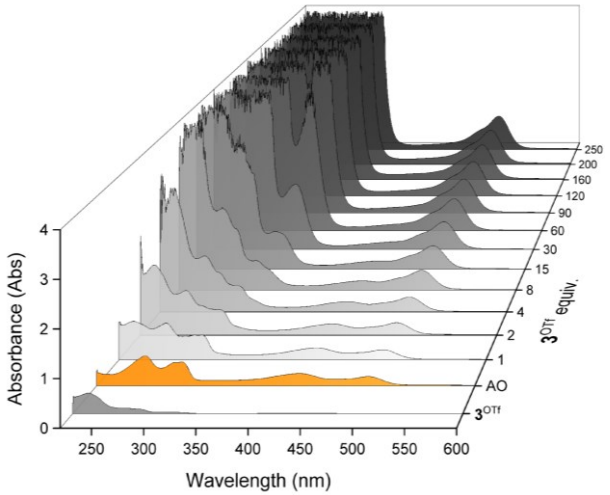


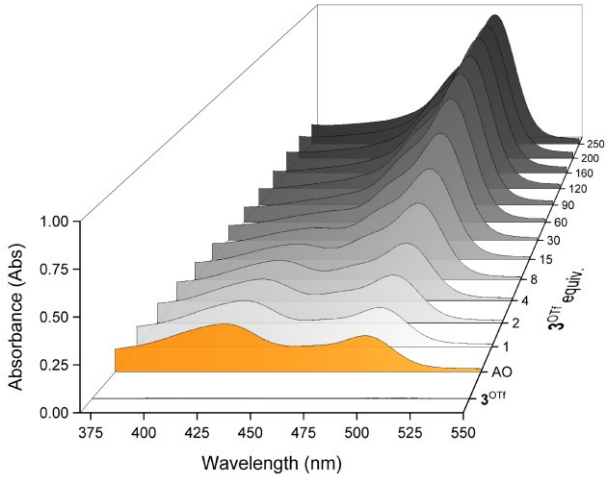


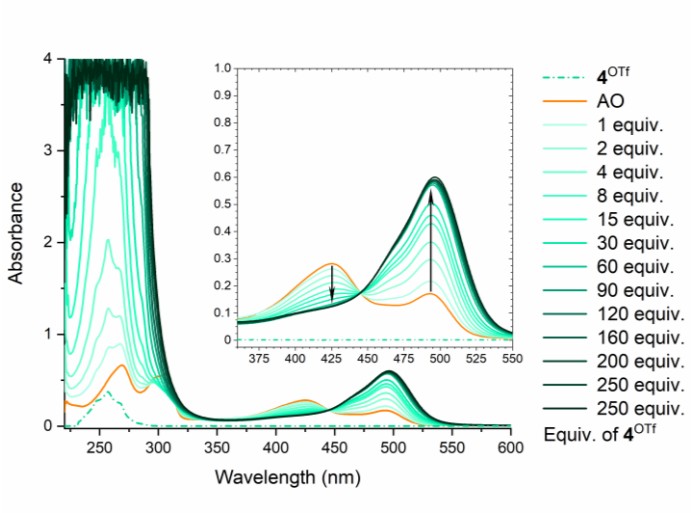


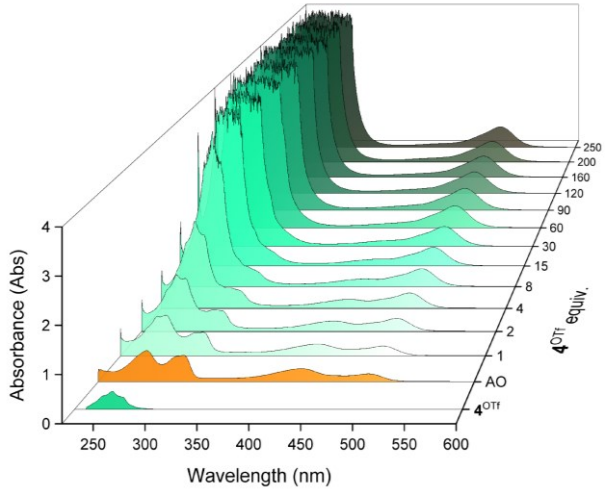


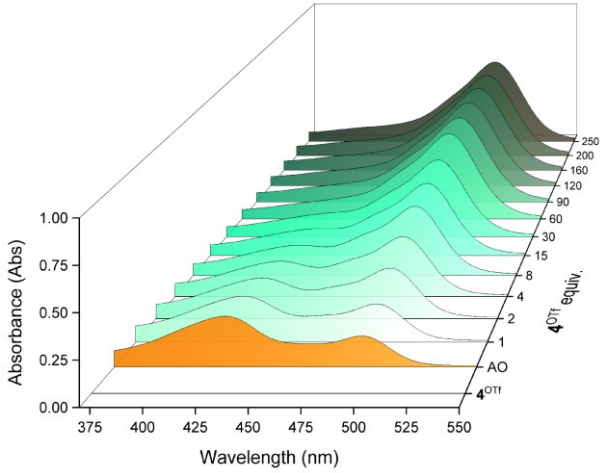

Absorbance
Wavelength (nm)
3OTf
AO
1 equiv.
2 equiv.
4 equiv.
8 equiv.
15 equiv.
30 equiv.
60 equiv.
90 equiv.
120 equiv.
160 equiv.
200 equiv.
250 equiv.
Equiv. of 3OTf

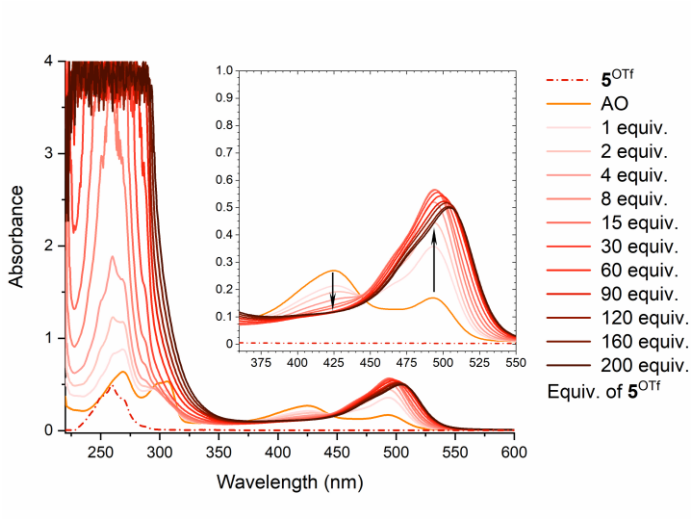

Absorbance (Abs)
Wavelength (nm)
3OTf equiv.
AO
3OTf

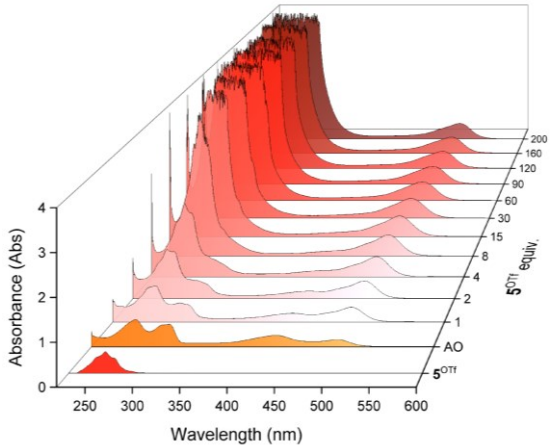

Absorbance (Abs)
Wavelength (nm)
3OTf equiv.
AO
3OTf

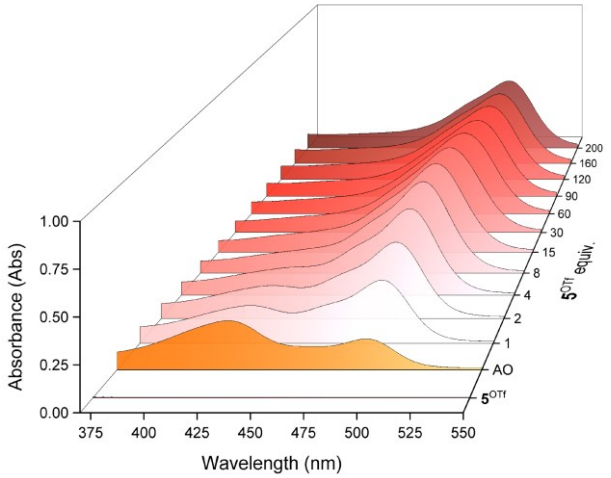

Absorbance
Wavelength (nm)
4OTf
AO
1 equiv.
2 equiv.
4 equiv.
8 equiv.
15 equiv.
30 equiv.
60 equiv.
90 equiv.
120 equiv.
160 equiv.
200 equiv.
250 equiv.
250 equiv.
Equiv. of 4OTf

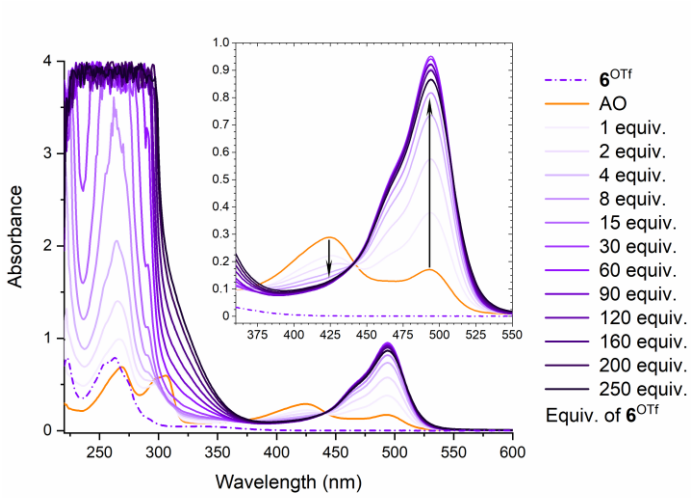

Absorbance (Abs)
Wavelength (nm)
4OTf equiv.
AO
4OTf

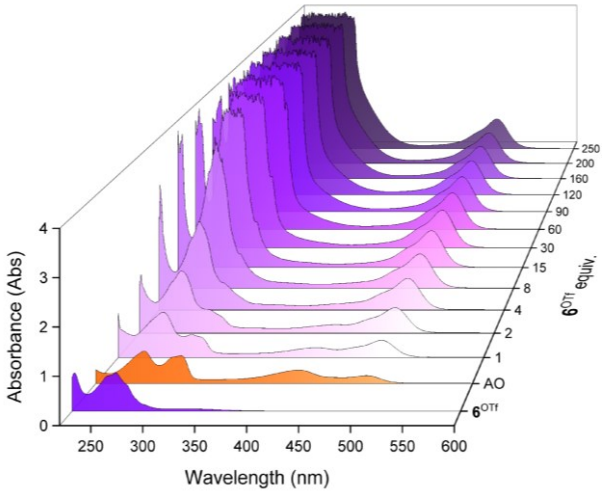

Absorbance (Abs)
Wavelength (nm)
4OTf equiv.
AO
4OTf

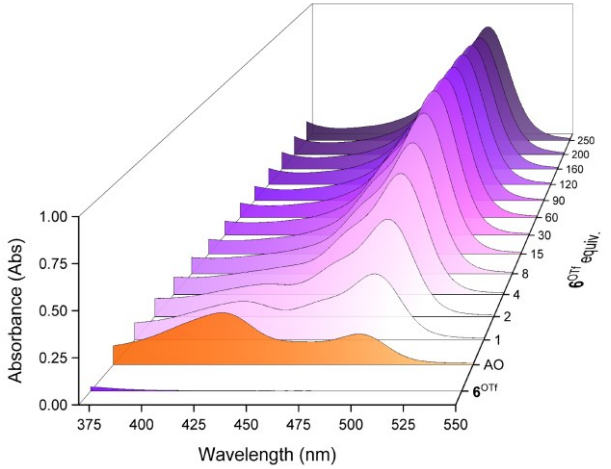

Absorbance
Wavelength (nm)
5OTf
AO
1 equiv.
2 equiv.
4 equiv.
8 equiv.
15 equiv.
30 equiv.
60 equiv.
90 equiv.
120 equiv.
160 equiv.
200 equiv.
Equiv. of 5OTf

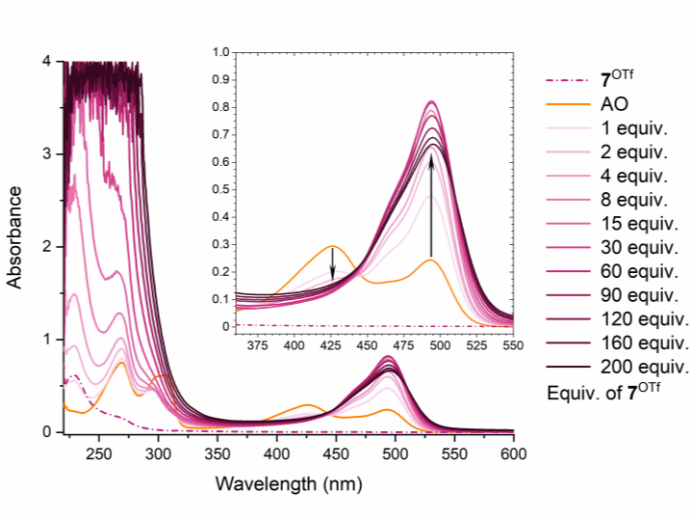

Absorbance (Abs)
Wavelength (nm)
5OTf equiv.
AO
5OTf

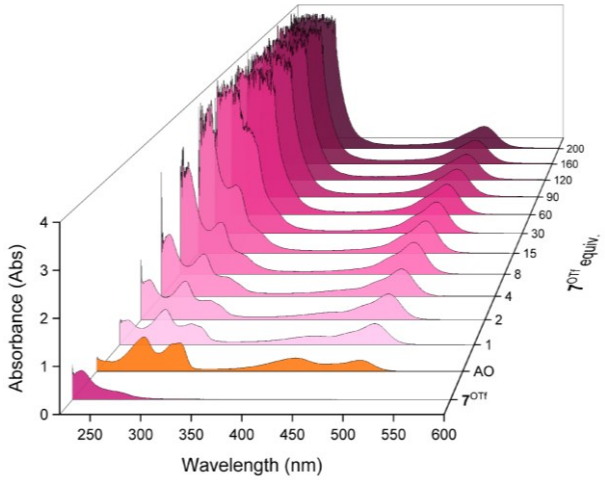

Absorbance (Abs)
Wavelength (nm)
5OTf equiv.
AO
5OTf

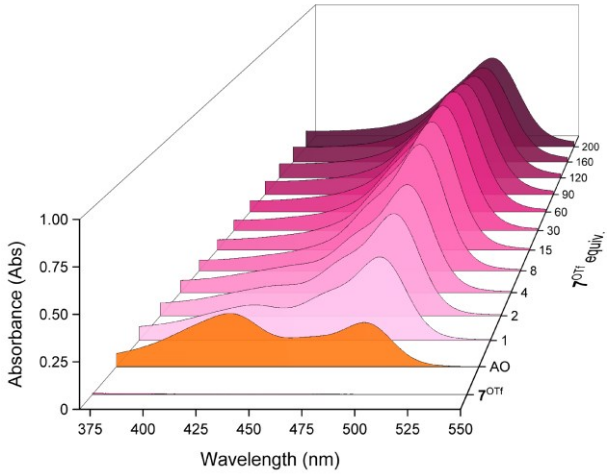

Absorbance
Wavelength (nm)
6OTf
AO
1 equiv.
2 equiv.
4 equiv.
8 equiv.
15 equiv.
30 equiv.
60 equiv.
90 equiv.
120 equiv.
160 equiv.
200 equiv.
250 equiv.
Equiv. of 6OTf


Absorbance (Abs)
Wavelength (nm)
6OTf equiv.
AO
6OTf


Absorbance (Abs)
Wavelength (nm)
6OTf equiv.
AO
6OTf


Absorbance
Wavelength (nm)
7OTf
AO
1 equiv.
2 equiv.
4 equiv.
8 equiv.
15 equiv.
30 equiv.
60 equiv.
90 equiv.
120 equiv.
160 equiv.
200 equiv.
Equiv. of 7OTf


Absorbance (Abs)
Wavelength (nm)
7OTf equiv.
200
160
120
90
60
30
15
8
4
2
1
AO
7OTf


Absorbance (Abs)
Wavelength (nm)
7OTf equiv.
200
160
120
90
60
30
15
8
4
2
1
AO
7OTf