SUPPORTING INFORMATION

Halogen Bonded Associates of Iodonium Salts with 18-Crown-6: Does Structural Flexibility or Structural Rigidity of the σ-Hole Donor Provide Efficient Substrate Ligation?

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Titration data

Table S1. Titration data of dibenziodolium triflate in CD_3CN.

Equivalents of dibenziodolium triflate	δ, ppm	Δδ, ppm
0	3.539	0.000
0.25	3.540	0.001
1	3.546	0.006
3	3.553	0.014
5	3.561	0.022
10	3.582	0.043
20	3.608	0.069

Table S2. Titration data of diphenyliodonium triflate in CD_3CN.

Equivalents of diphenyliodonium triflate	δ, ppm	Δδ, ppm
0	3.539	0.000
0.25	3.539	0.000
0.5	3.539	0.000
1	3.538	-0.002
2	3.538	-0.001
2.5	3.536	-0.004
2.75	3.539	-0.001
3	3.535	-0.004
3.25	3.538	-0.002
3.5	3.537	-0.002
4	3.539	-0.001
5	3.537	-0.002
10	3.541	0.001
15	3.549	0.010
20	3.556	0.017

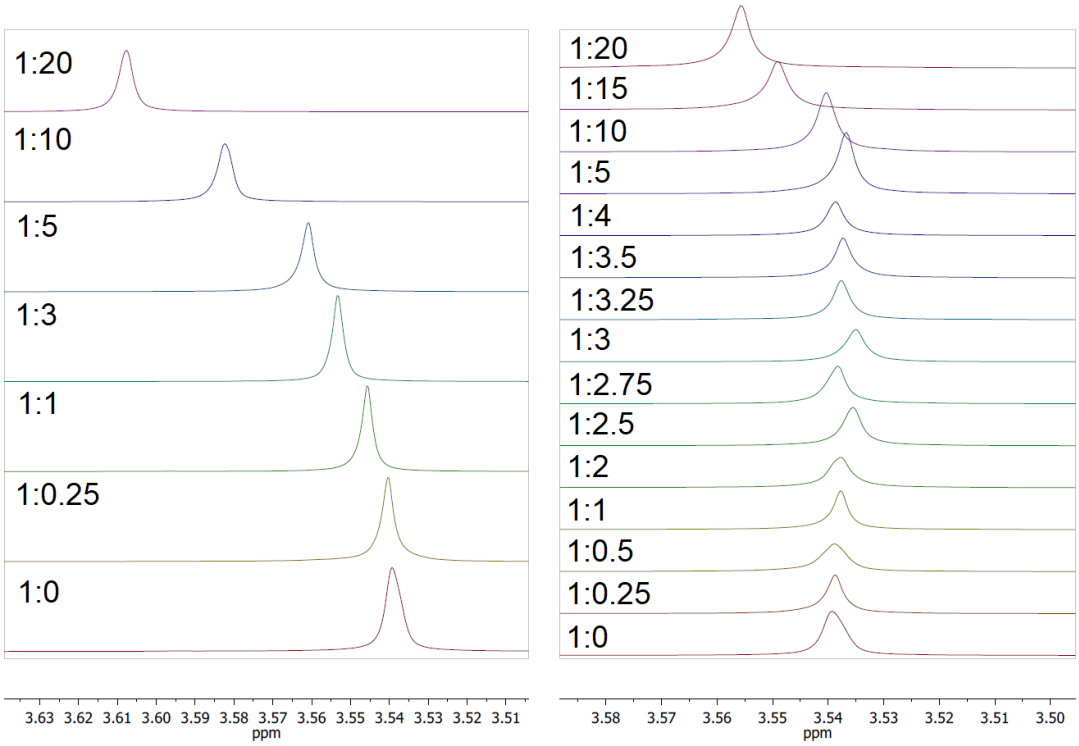

Figure S1. Stacked ^1H NMR spectra for the titration of 18-crown-6 with dibenziodolium triflate (left) or diphenyliodonium triflate (right) in CD_3CN.

Table S3. Titration data of dibenziodolium triflate in CD_3OD.

Equivalents of dibenziodolium triflate	δ, ppm	Δδ, ppm
0	3.660	0.000
1	3.656	-0.004
5	3.655	-0.005
10	3.653	-0.007
15	3.651	-0.009
20	3.649	-0.011
25	3.647	-0.013
50	3.639	-0.020

Table S4. Titration data of diphenyliodonium triflate in CD_3OD.

Equivalents of diphenyliodonium triflate	δ, ppm	Δδ, ppm
0	3.660	0.000
1	3.655	-0.004
5	3.652	-0.008
10	3.648	-0.012
15	3.644	-0.016
20	3.642	-0.018
25	3.640	-0.019
50	3.634	-0.026

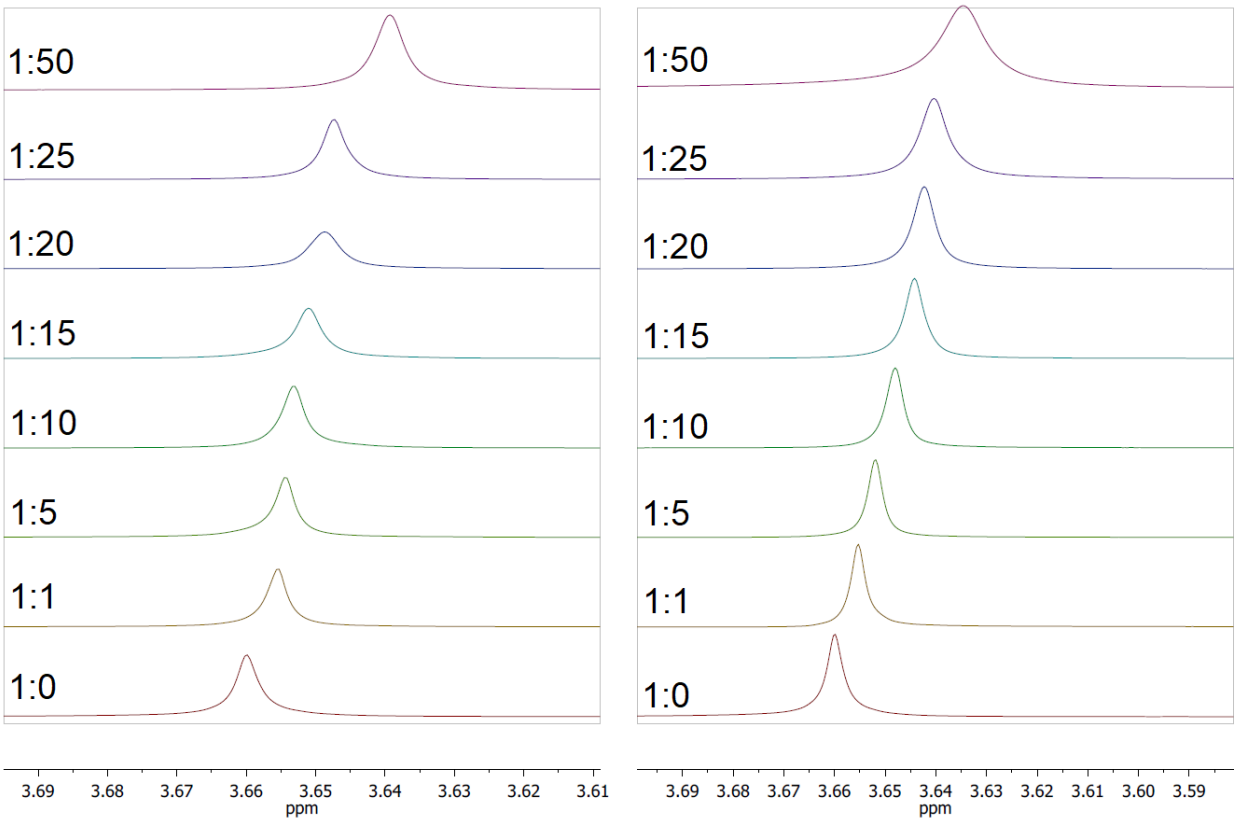

Figure S2. Stacked ^1H NMR spectra titration of dibenziodolium triflate (left) and diphenyliodonium triflate (right) in CD_3OD.

Spectra of the iodonium salts

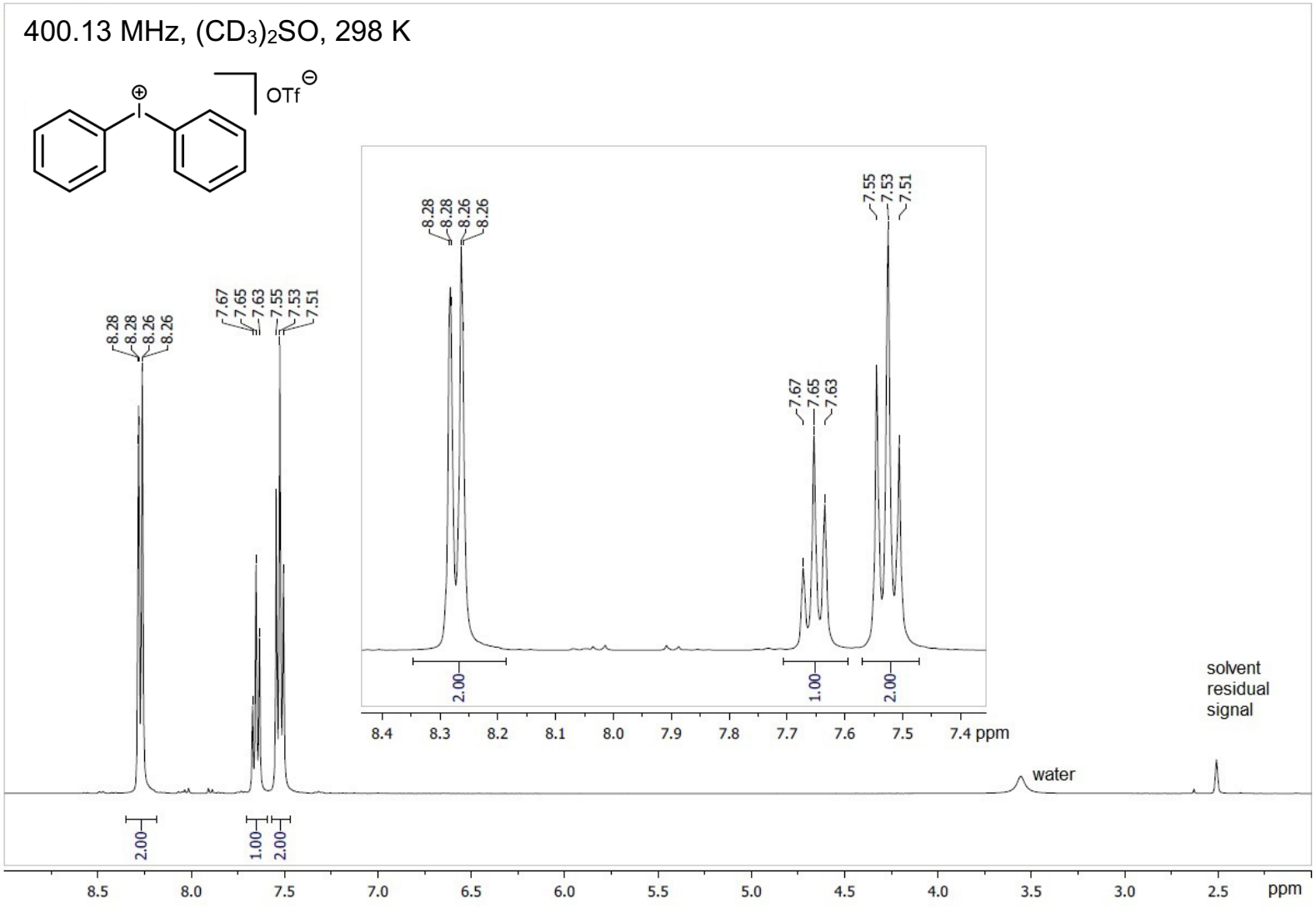

Figure S3. ^{1}H NMR spectrum of the **1**^{OTf}.

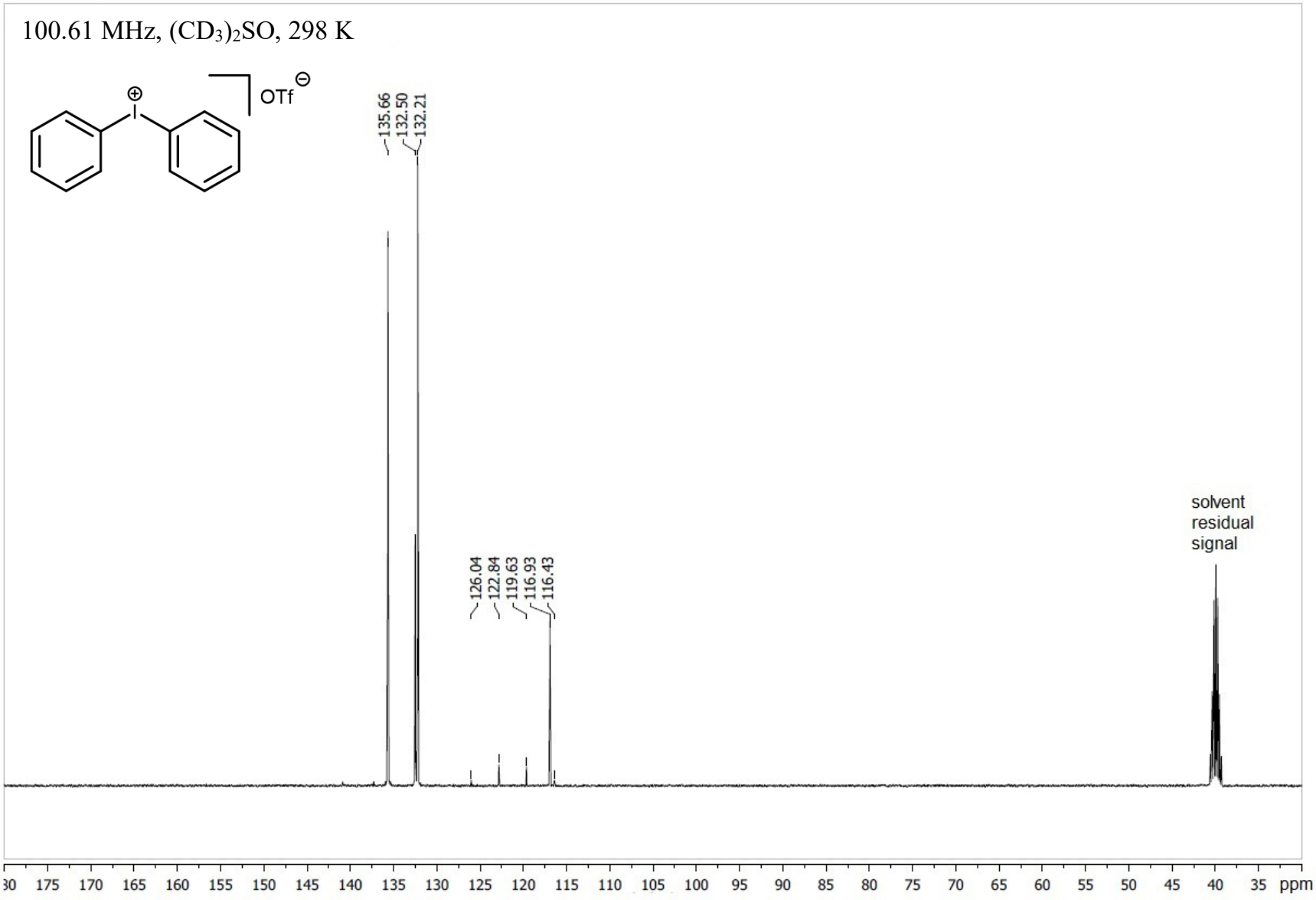

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of the **1**^{OTf}.

100.61 MHz, $(CD_3)_2SO$, 298 K

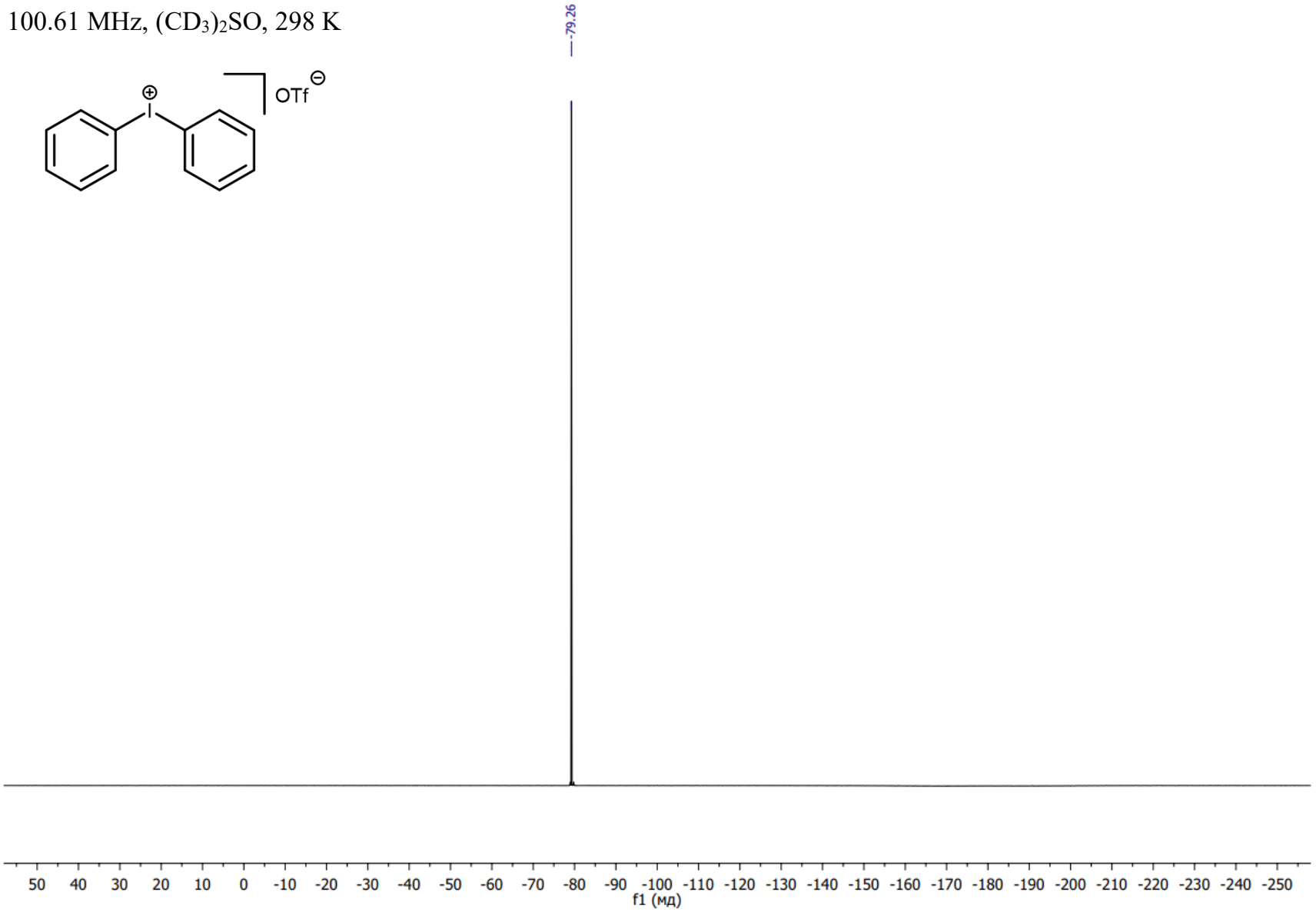

Figure S5. ^{19}F NMR spectrum of the $\mathbf{1}^{OTf}$.

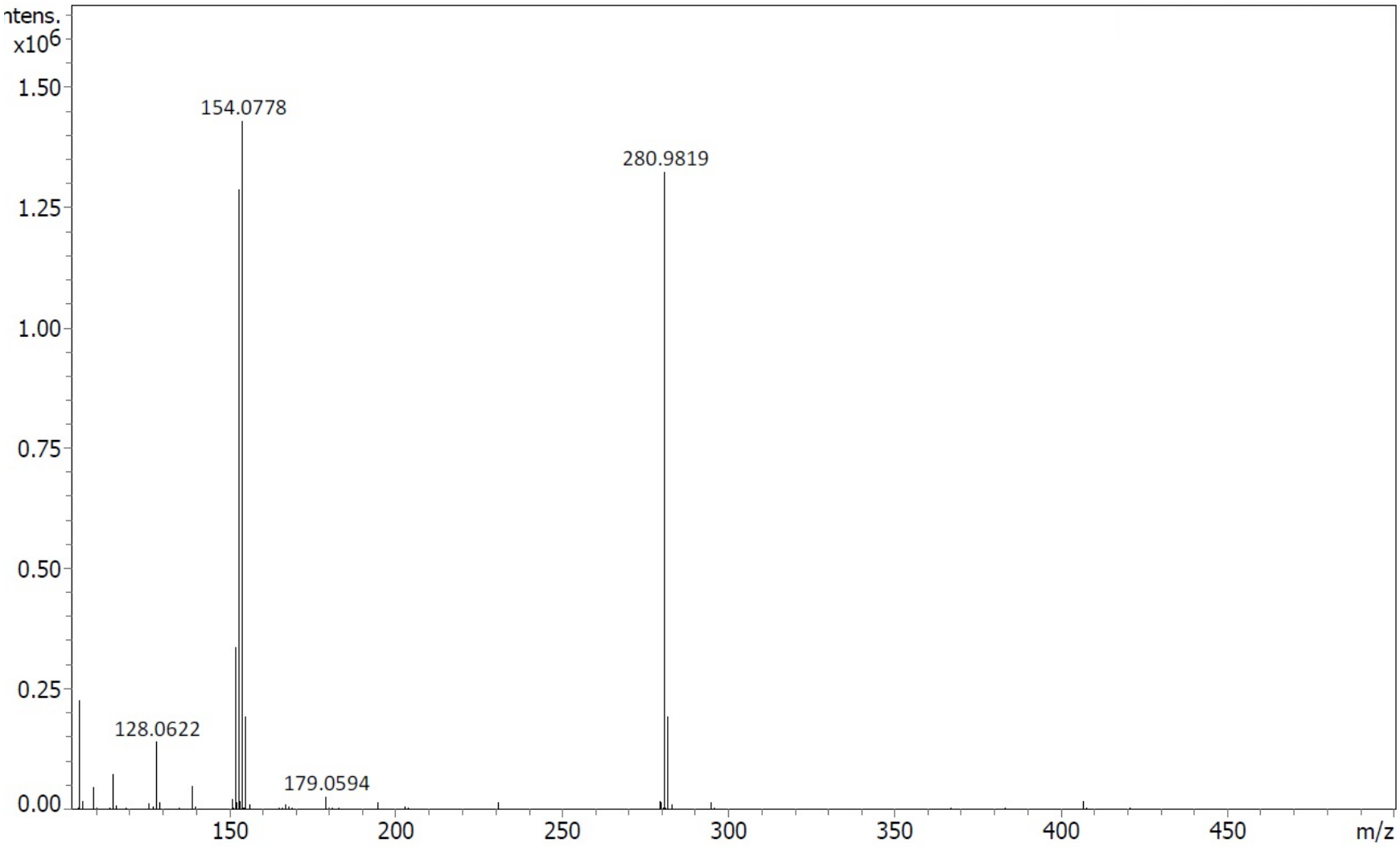

Figure S6. HRES^{+}-MS spectrum of the **1**^{OTf}.

400.13 MHz, $(CD_3)_2SO$, 298 K

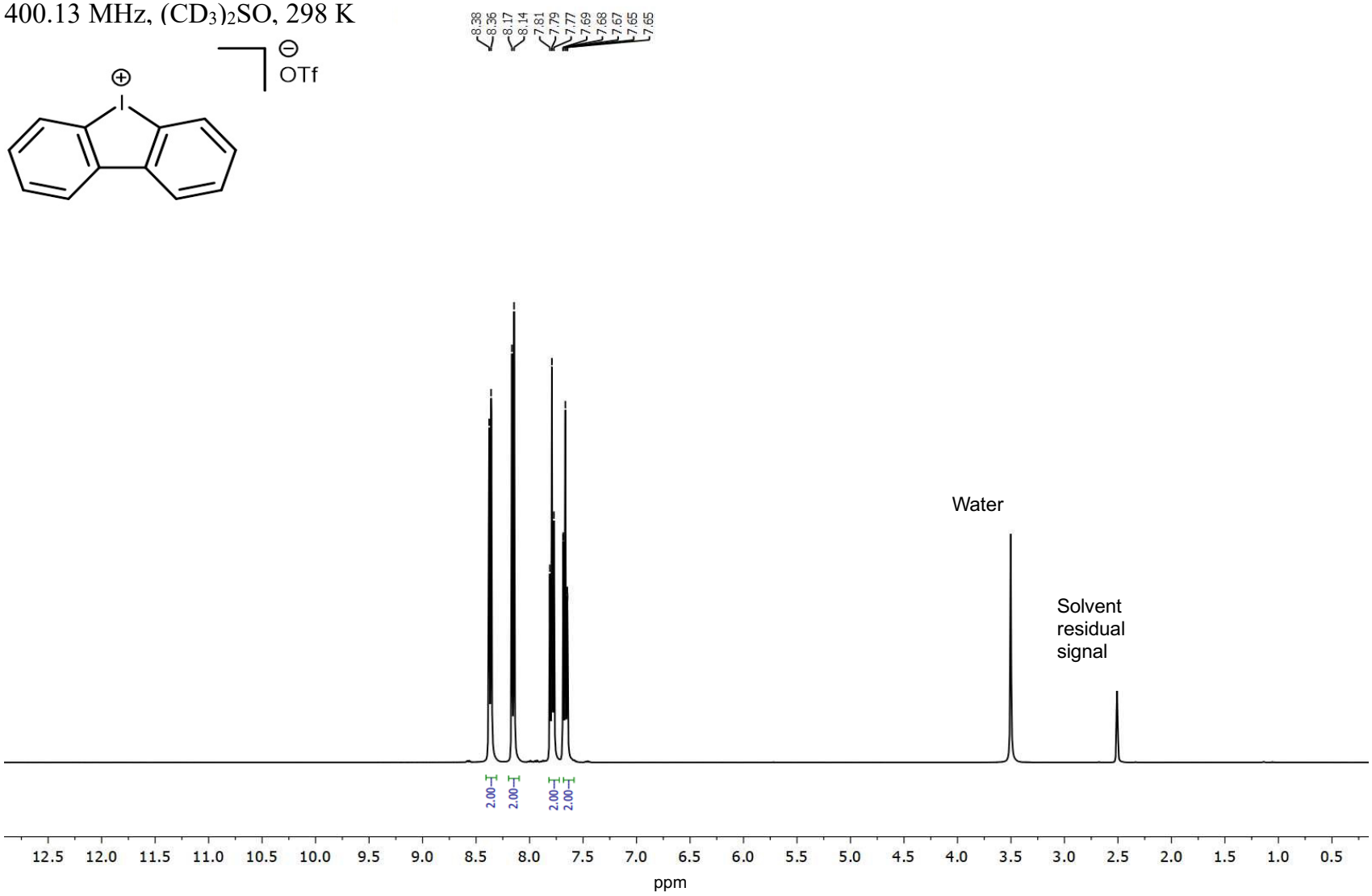

Figure S7. ^{1}H NMR spectrum of **2**^{OTf}.

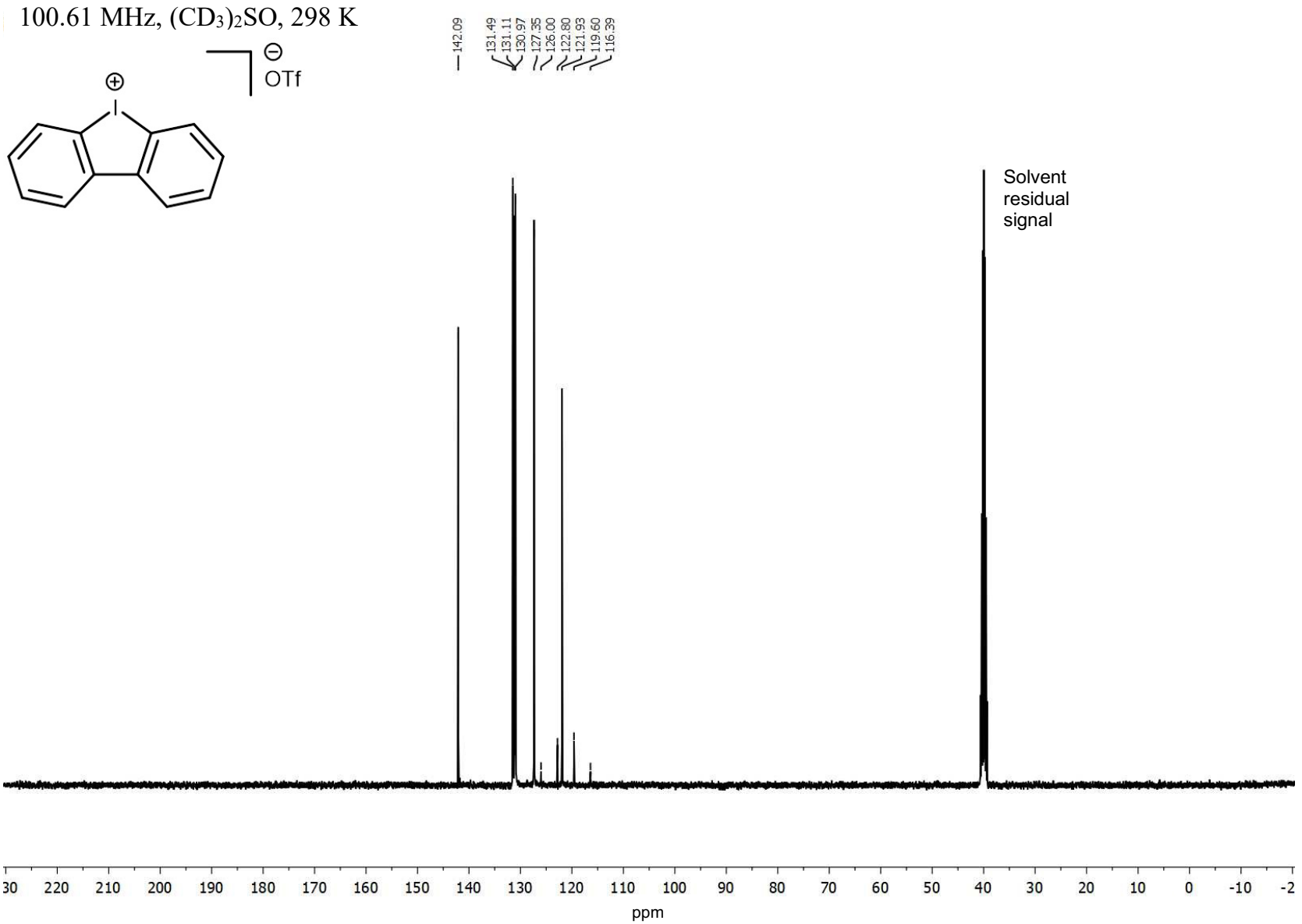

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of the **2**^{OTf}.

376.49 MHz, CD_3CN, 298 K

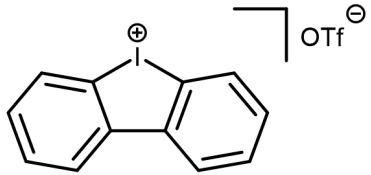

Figure S9. ^{19}F NMR spectrum of the **2**^{OTf}.

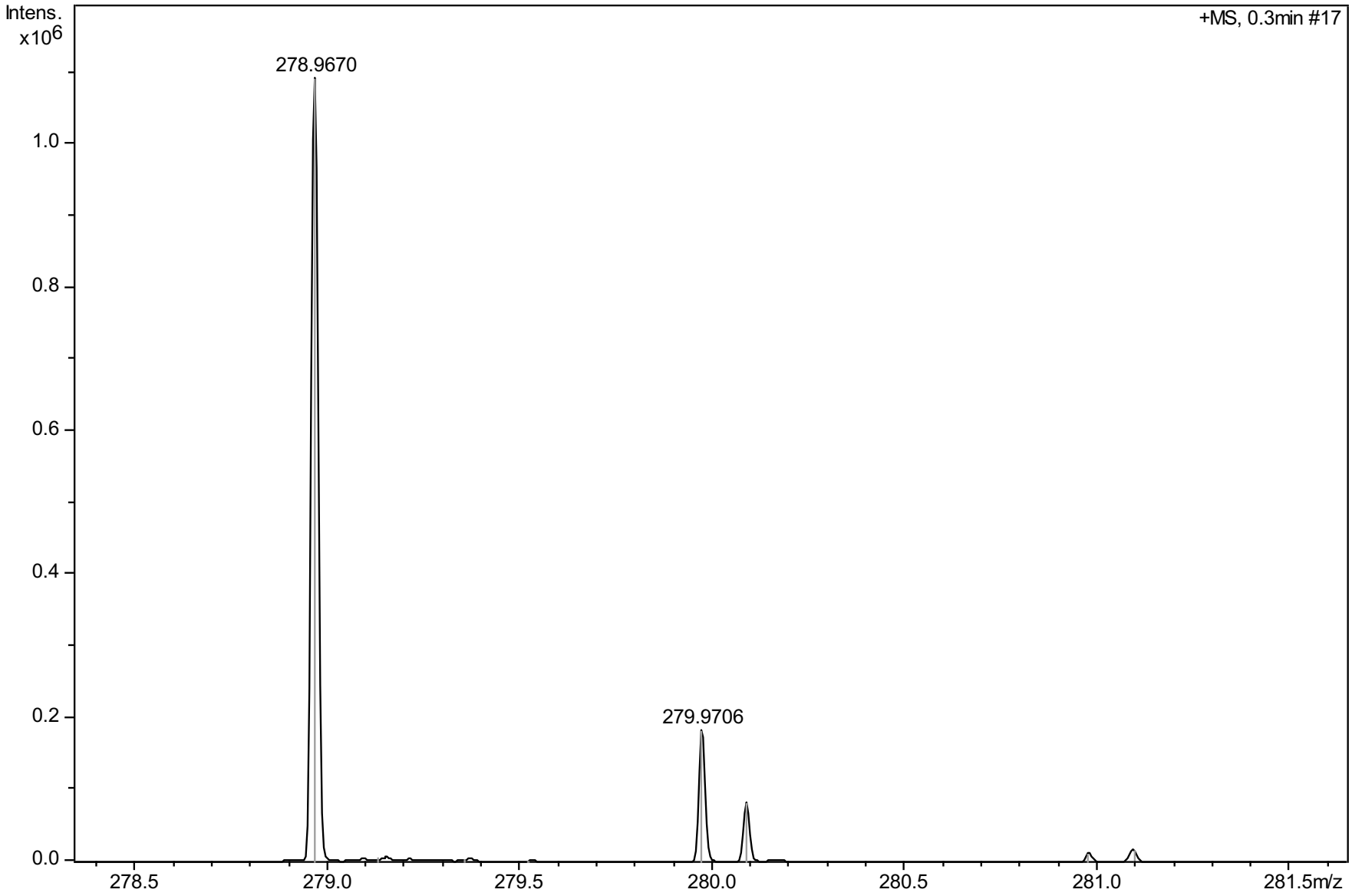

Figure S10. HRES^{+}-MS spectrum of the **2**^{OTf}.

Calculation data

Table S5. Calculated total electronic energies (E, in Hartree), enthalpies (H, in Hartree), Gibbs free energies (G, in Hartree), and entropies (S, cal/mol•K) for optimized equilibrium model structures.

Model structure	E	H	G	S
Methanol				
1^{+}	−473.144237450	−472.971681	−473.019871	101.425
2^{+}	−474.335753748	−474.139961	−474.192883	111.384
18C6	−922.741190214	−922.345039	−922.414328	145.830
1^{+}·18C6	−1395.91484689	−1395.343345	−1395.438290	199.828
1^{+}·18C6·**1**$^{+}$	−1869.08023905	−1868.332622	−1868.455242	258.076
2^{+}·18C6	−1397.10930217	−1396.514667	−1396.612652	206.225
2^{+}·18C6·**2**$^{+}$	−1871.47395117	−1870.680486	−1870.807811	267.979
Acetonitrile				
1^{+}	−473.147252794	−472.974707	−473.023674	103.061
2^{+}	−474.338820481	−474.143126	−474.195292	109.793
18C6	−922.728721993	−922.334731	−922.403613	144.974
1^{+}·18C6	−1395.90566093	−1395.334750	−1395.429152	198.684
1^{+}·18C6·**1**$^{+}$	−1869.07473186	−1868.326635	−1868.443322	245.588
2^{+}·18C6	−1397.10104862	−1396.507161	−1396.604943	205.799
2^{+}·18C6·**2**$^{+}$	−1871.46746102	−1870.674637	−1870.801292	266.567

Table S6. Crystal data for $\mathbf{1}^{OTf}$·18C6·$\mathbf{1}^{OTf}$.

Identification code	$\mathbf{1}^{OTf}$·18C6·$\mathbf{1}^{OTf}$
Empirical formula	$C_{38}H_{44}F_6I_2O_{12}S_2$
Formula weight	1124.65
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.5421(2)
b/Å	9.8378(2)
c/Å	12.7043(2)
α/°	89.682(2)
β/°	88.449(2)
γ/°	63.993(2)
Volume/Å^3	1071.41(4)
Z	1
ρ_{calc} g/cm^3	1.743
μ/mm^{-1}	13.199
F(000)	560
Crystal size/mm^3	0.07 × 0.05 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data	6.96 to 124.998
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -
Reflections collected	11991
Independent reflections	3403 [R_{int} = 0.0714, R_{sigma} =
Data/restraints/parameters	3403/0/265
Goodness-of-fit on F^2	1.083
Final R indexes [I⩾2σ (I)]	R_1 = 0.0533, wR_2 = 0.1390
Final R indexes [all data]	R_1 = 0.0548, wR_2 = 0.1404
Largest diff. peak/hole / e·Å^{-3}	3.15/-1.41
CSD code	2361448