Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

ELECTRONIC SUPPLEMENTARY INFORMATION

Solvent-modulated Binding Selectivity of Reaction Substrates to Onium-based σ-Hole Donors

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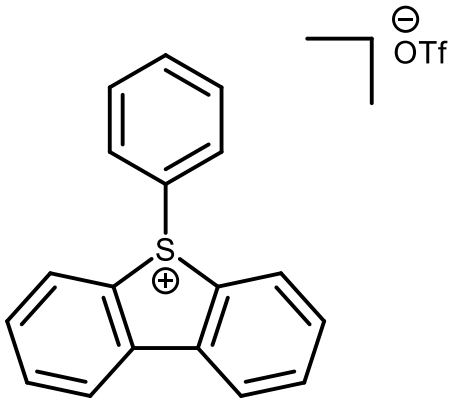
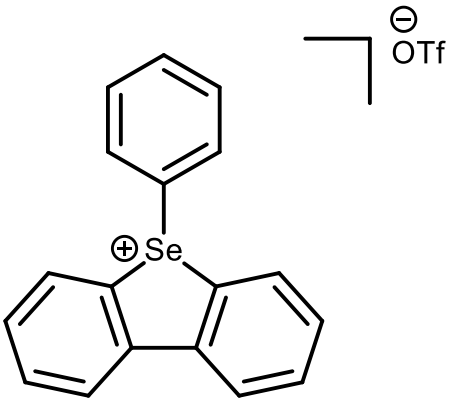
Synthesis of the sulfonium salt Cat1^{OTf}



To the mixture of dibenzothiophene (500 mg, 2.75 mmol) and diphenyliodonium triflate (775 mg, 1.81 mmol) in 1,2-dichloroethane (5 mL) was added $Cu(OTf)_2$ (66 mg, 0.18 mmol). and stirred for 30 min at 130 °C. Then the solvent was evaporated *in vacuo* at 50 °C and product were isolated via column chromatography (eluent: $CHCl_3$/MeOH, gradient from 5 to 10 %). After that the solvent was evaporated *in vacuo* at 50 °C, the residue was crystallized under Et_2O and dried at 50 °C in air.

Yield: 84 % (623 mg). M.p.: 192–193 °C. ^{1}H NMR (400.13 MHz, $(CD_3)_2CO$): δ = 8.56 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ar), 8.42 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar), 8.03 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, Ar), 7.84 – 7.79 (m, 5H, Ar), 7.70 – 7.66 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR (101.61 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, $^1J_{CF}$ = 321.9 Hz, CF_3). HRMS (ESI-TOF): m/z calcd for $C_{18}H_{13}S^+$: 261.0733; found: 261.0734.

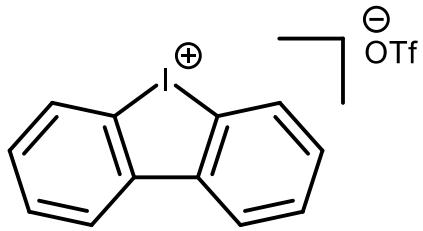
Synthesis of the sulfonium salt Cat2^{OTf}



$Cu(OTf)_2$ (33 mg, 0.09 mmol) was added to the mixture of dibenzoselenophene (253 mg, 1.10 mmol) and diphenyliodonium triflate (393 mg, 0.91 mmol) in 1,2-dichloroethane (5 mL) and the resulting mixture was stirred for 30 min at 130 °C. Then the solvent was evaporated *in vacuo* at 50 °C and product was isolated via column chromatography (eluent: $CHCl_3$/MeOH, 95:5). After that the solvent was evaporated in vacuo at 50 °C, the residue was crystallized using Et_2O and dried at 50 °C in air.

Yield: 80 % (335 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, $^3J_{HH}$ = 7.6 Hz, 2H, Ar), 7.74 (t, $^3J_{HH}$ = 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 (101.61 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, $^1J_{CF}$ = 321.9 Hz, CF_3). HRMS (ESI-TOF): m/z calcd for $C_{18}H_{13}Se^+$: 309.0177; found: 309.0183.

Synthesis of dibenziodolium triflate Cat3^{OTf}



This salt was synthesized according to published procedure (DOI: 10.1021/acs.joc.1c02885). *m*-CPBA (77%, 665 mg, 2.96 mmol) and TfOH (0.521 mL, 5.89 mmol) were added to a stirred solution of 2-iodo-1,1'-biphenyl (550 mg, 0.346 mL, 1.97 mmol) in dry CH_2Cl_2 (5 mL) and then stirred for 1 h at RT. After that the solvent was evaporated *in vacuo* at RT, and the product was crystallized under Et_2O (10 mL). The precipitate formed was stirred for 20 min at RT and filtered off, washed with Et_2O (10 mL), and dried at 50 °C in air.

Yield: 90 % (760 mg). M.p.: 240–242 °C. ^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 8.37 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar), 8.15 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar), 7.79 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.67 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, Ar). ^{13}C{1H} NMR (101.61 MHz, DMSO-d_6): δ = 142.1, 131.5, 131.1, 131.0, 127.4 and 121.9 (Ar); 121.2 (q, $^1J_{CF}$ = 322.3 Hz, CF_3). HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{12}H_8I$ 278.9665; Found 278.9667.

Spectra of Cat1^{OTf}–Cat3^{OTf}

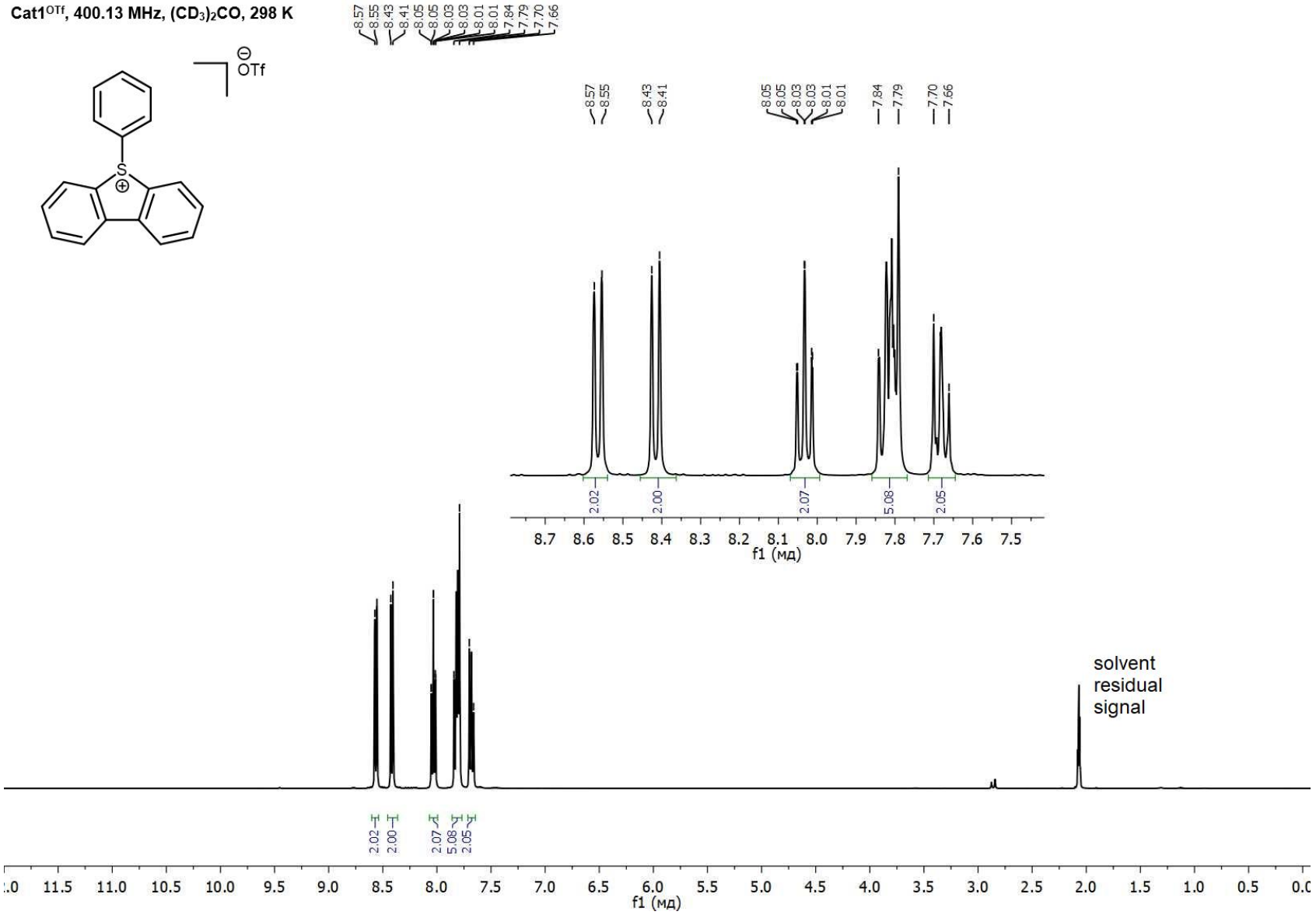


Figure S1. ^{1}H NMR spectrum of **Cat1^{OTf}**.

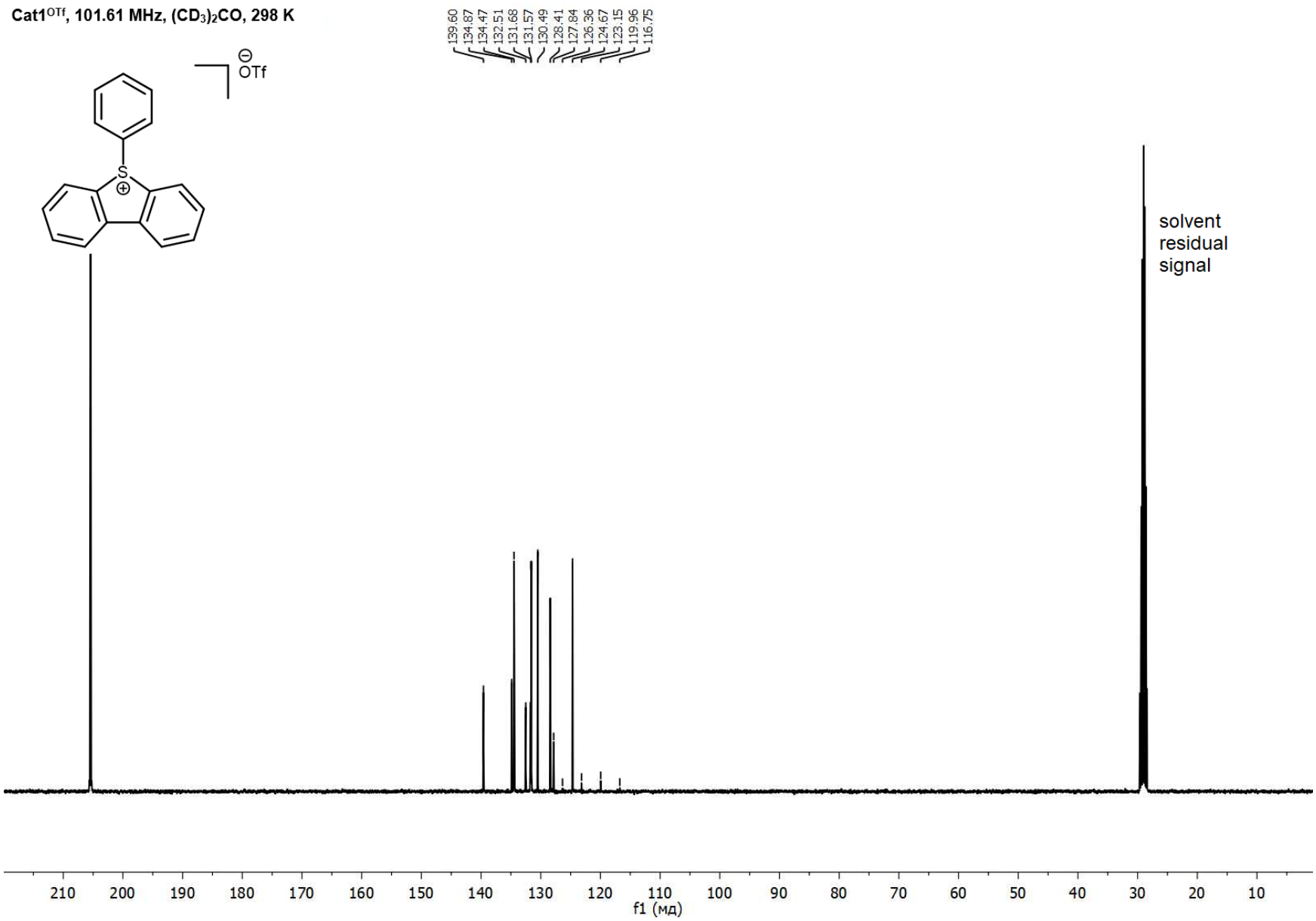


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **Cat1^{OTf}**.

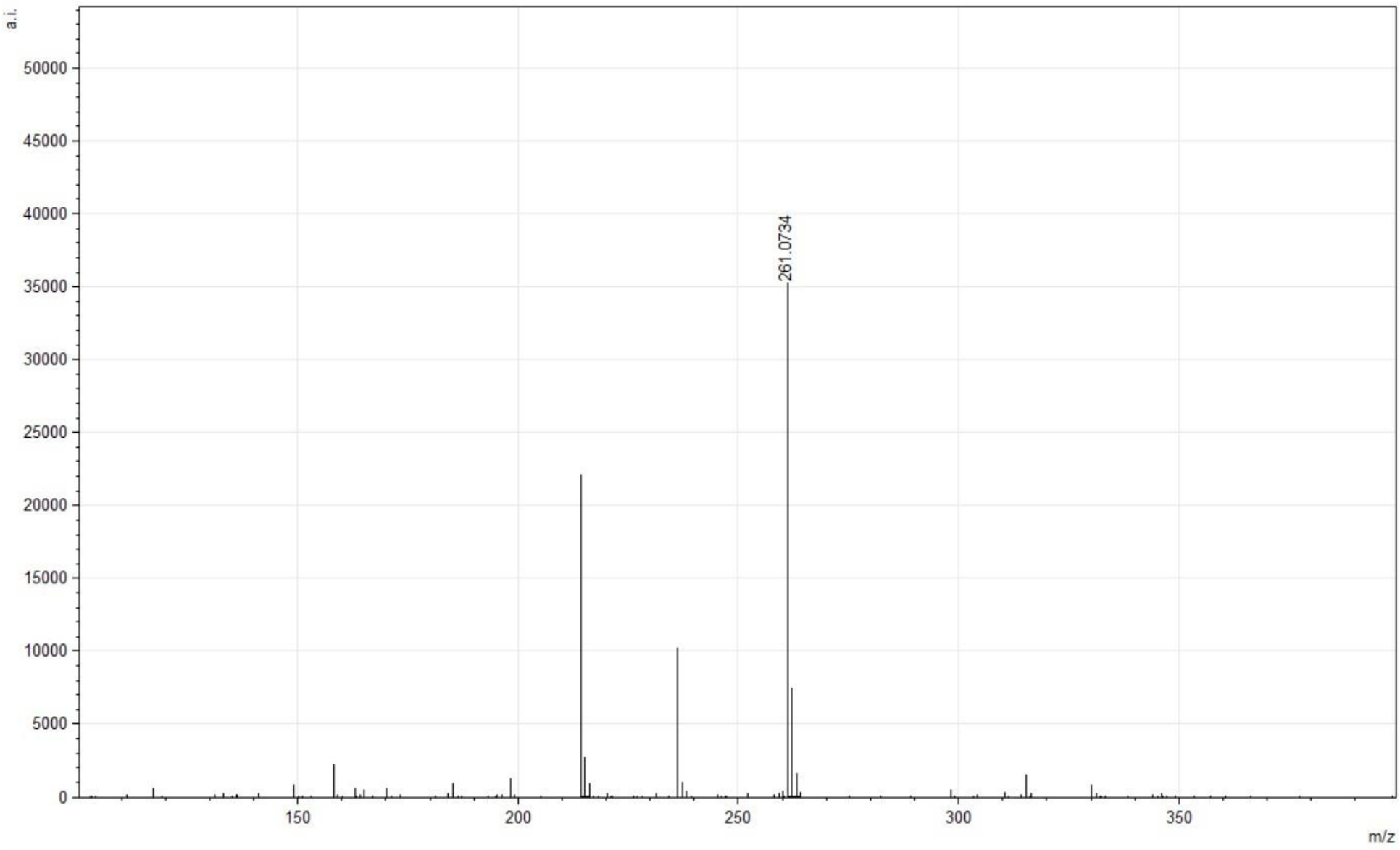


Figure S3. HRESI^{+}-MS of **Cat1^{OTf}**.

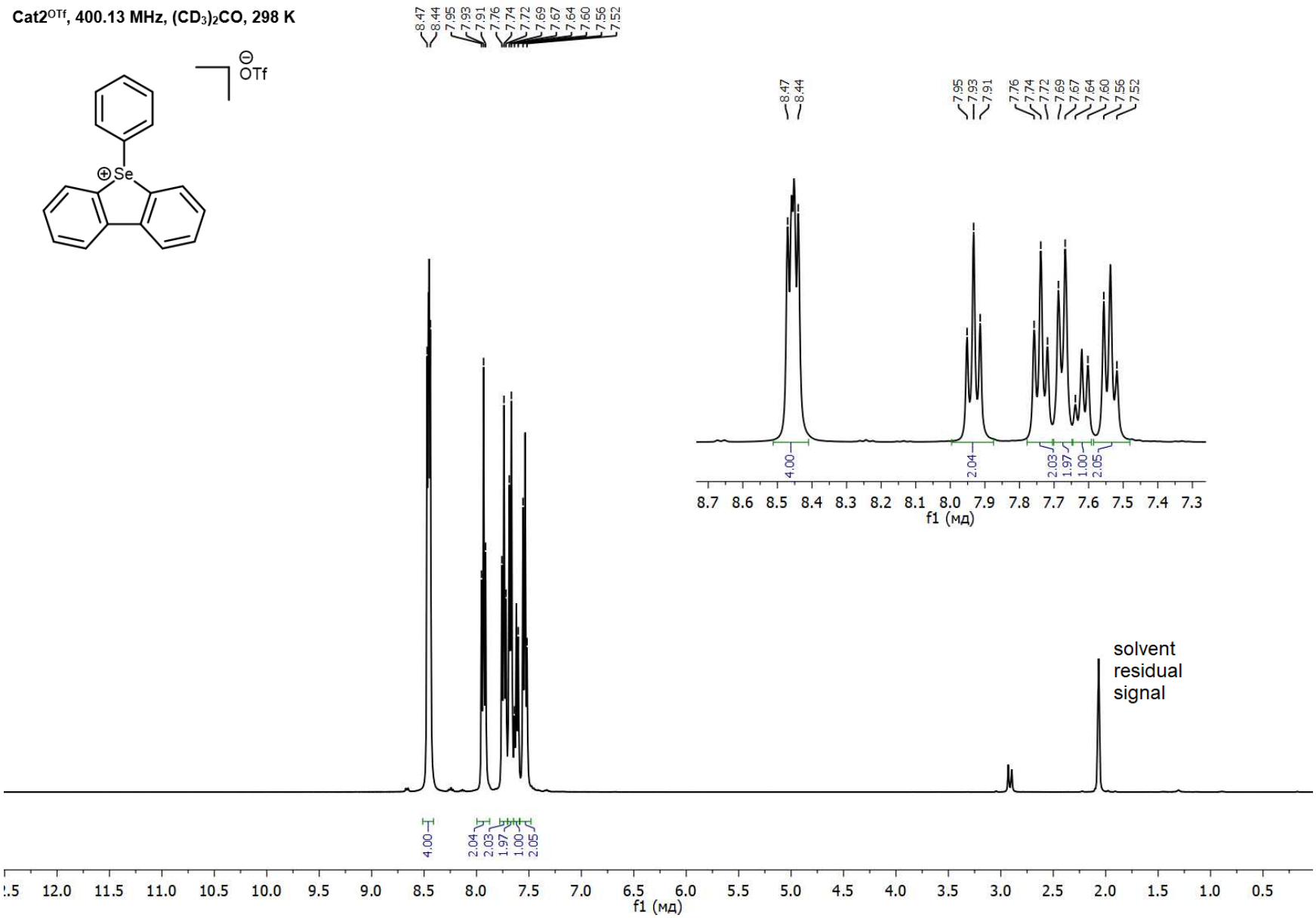


Figure S4. ^{1}H NMR spectrum of **Cat2^{OTf}**.

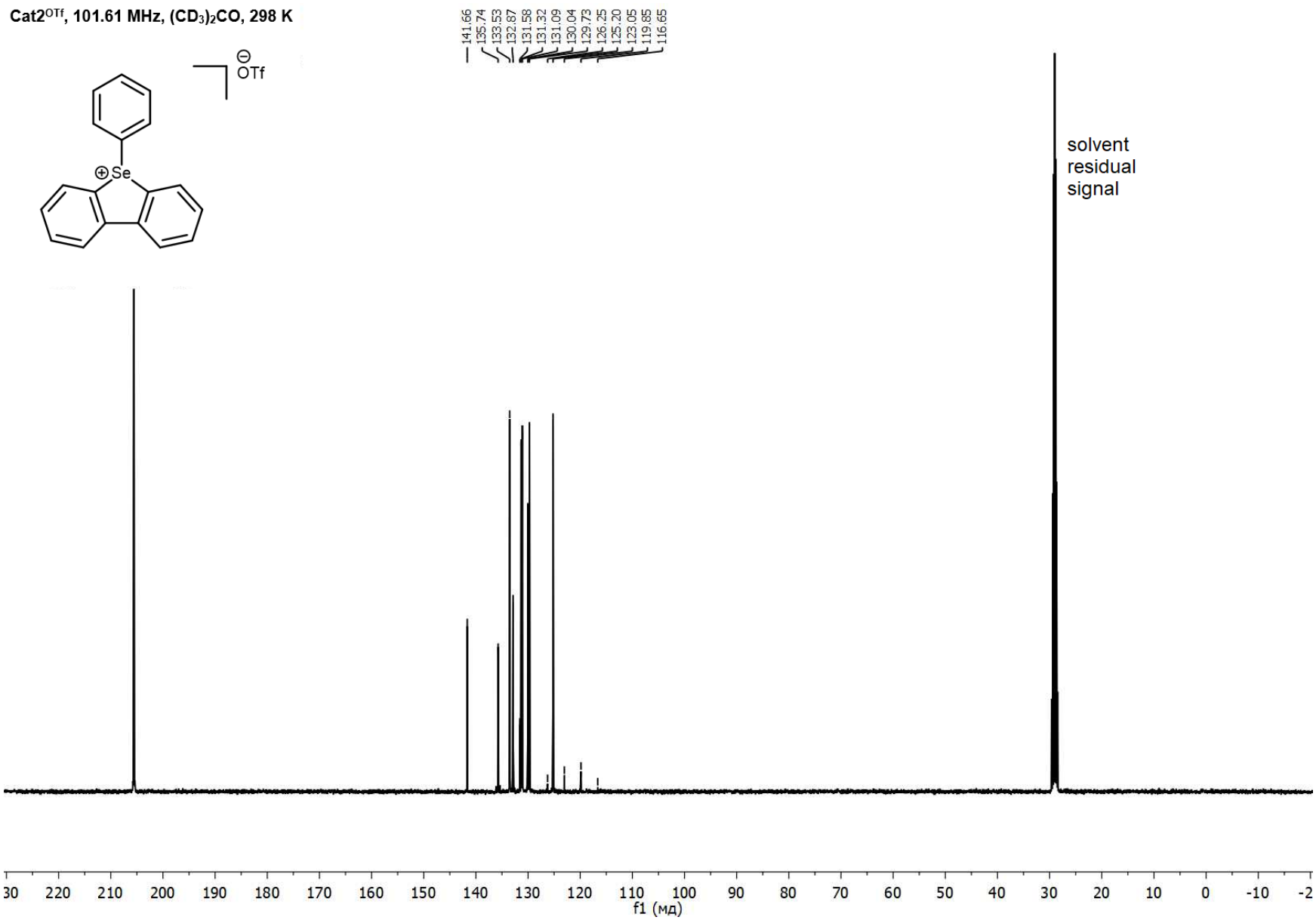


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **Cat2^{OTf}**.

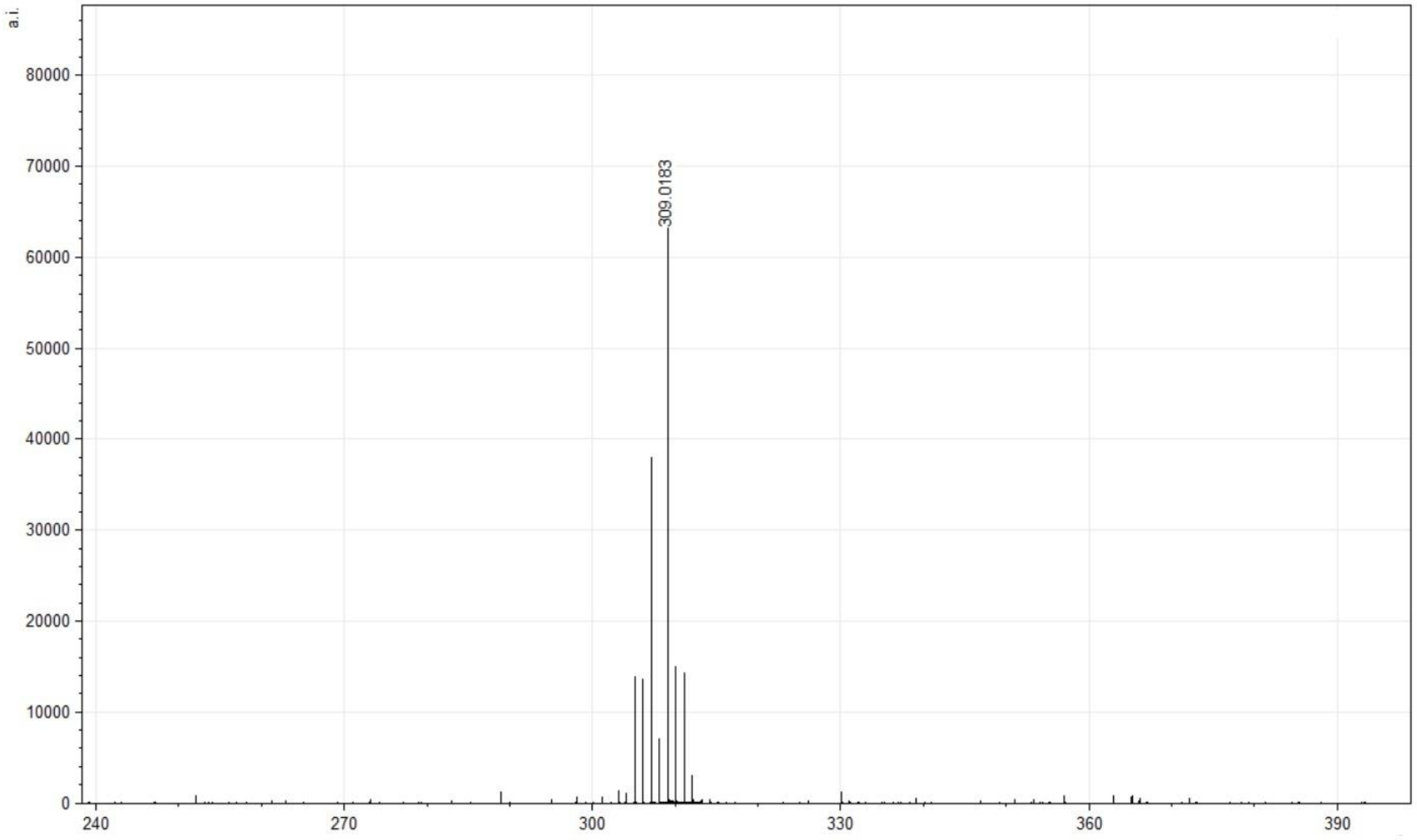


Figure S6. HRESI^{+}-MS of **Cat2^{OTf}**.

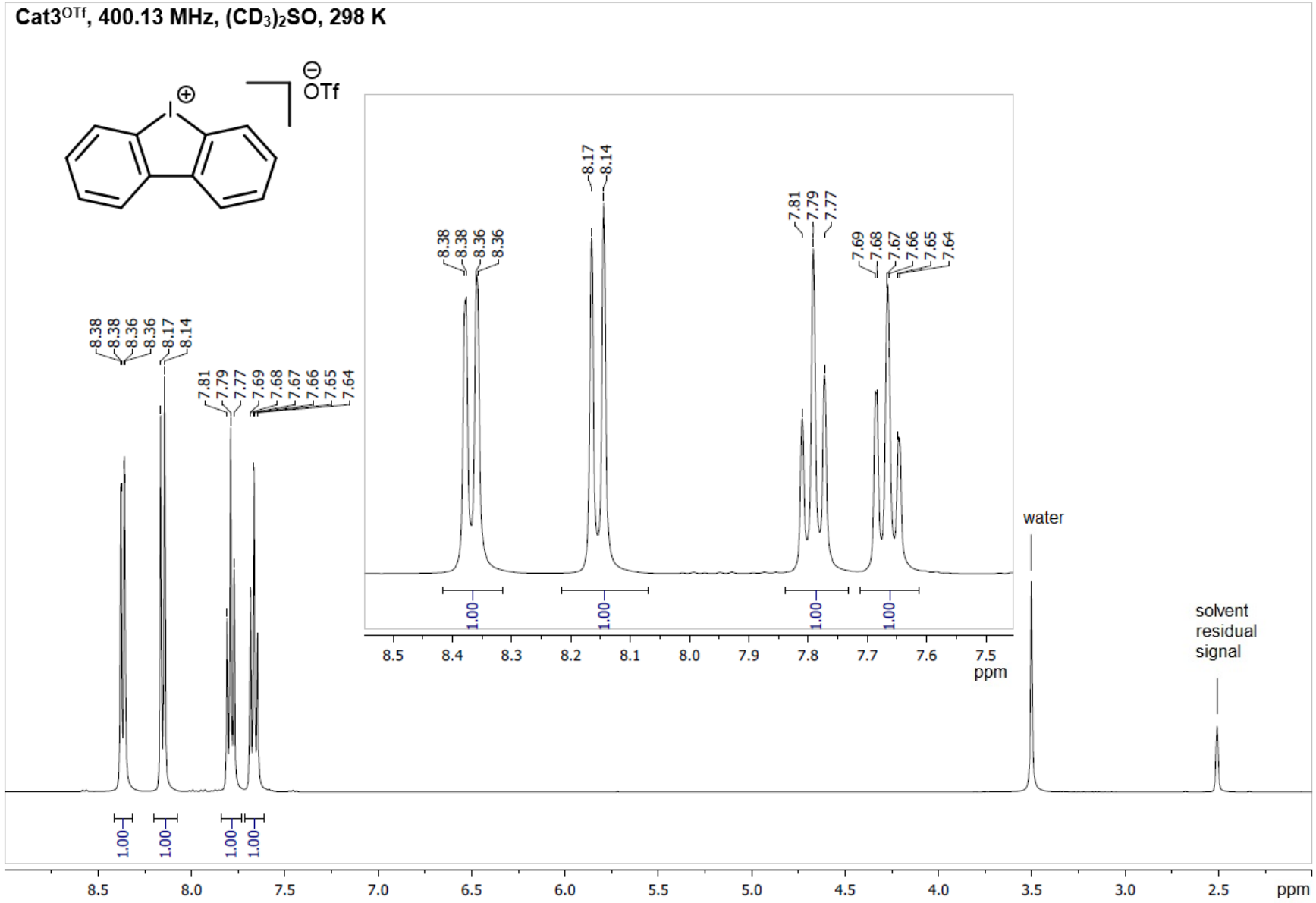


Figure S7. ^{1}H NMR spectrum of **Cat3^{OTf}**.

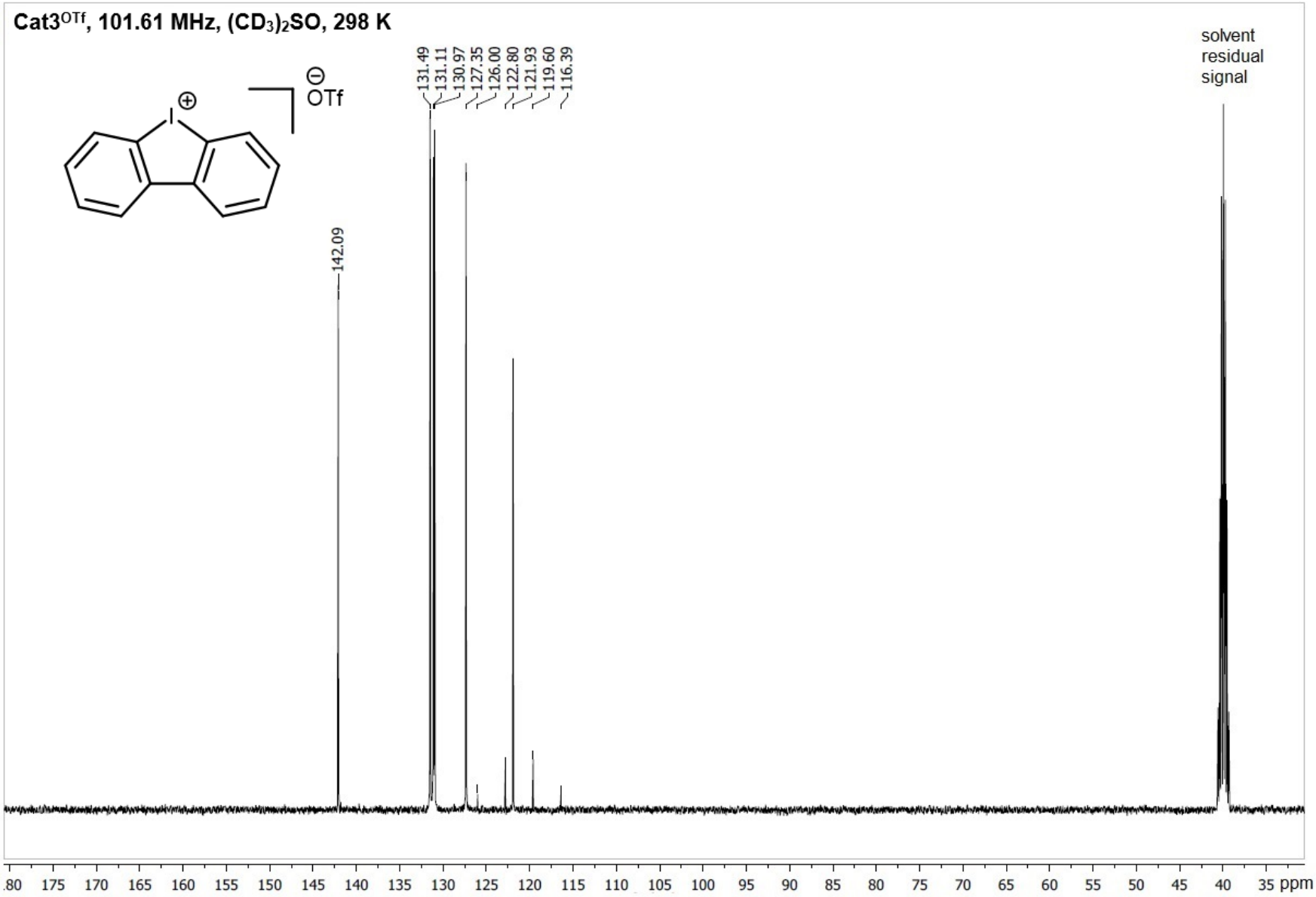


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **Cat3^{OTf}**.

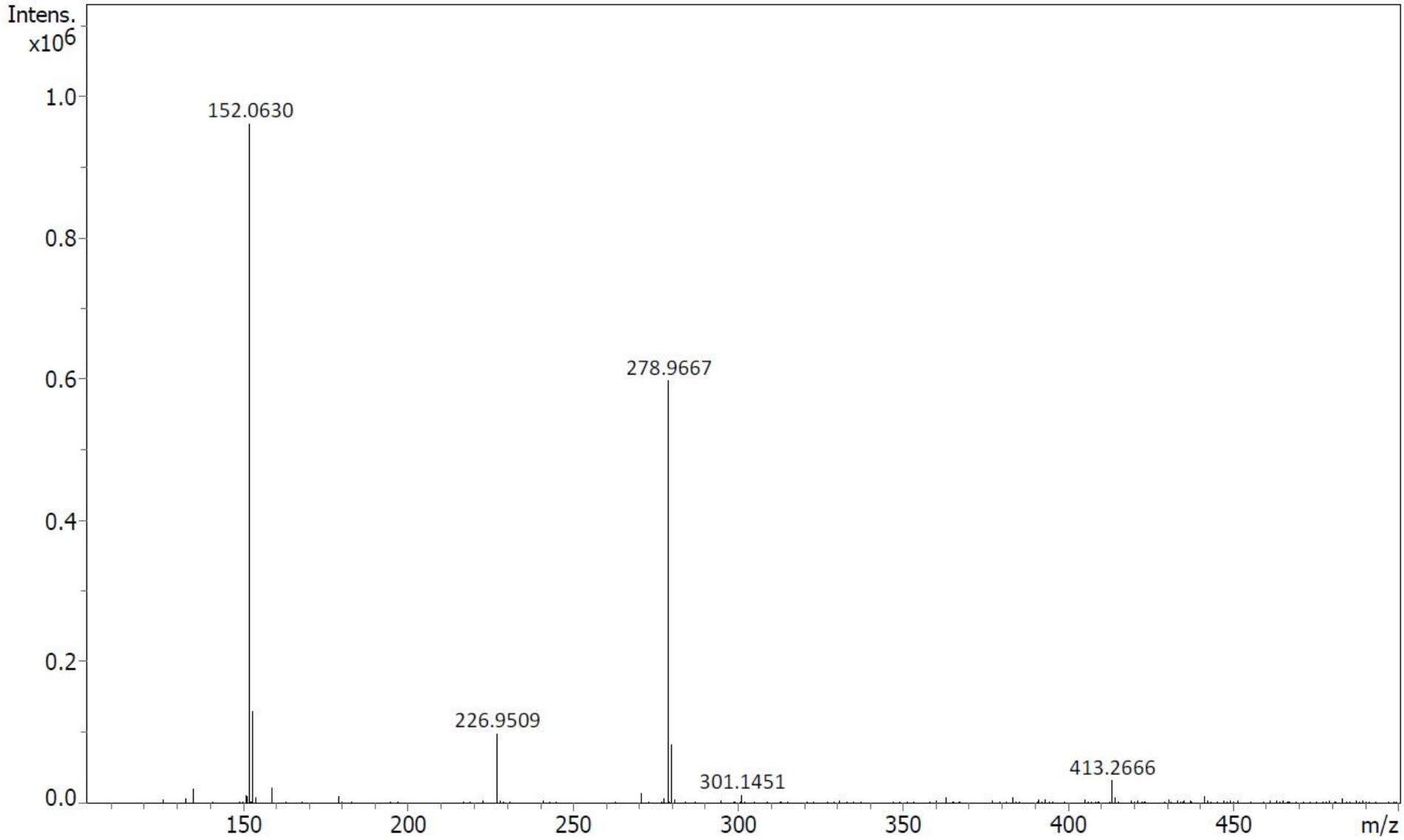


Figure S9. HRESI^{+}-MS of **Cat3^{OTf}**.

Representative ^{1}H NMR monitoring spectra

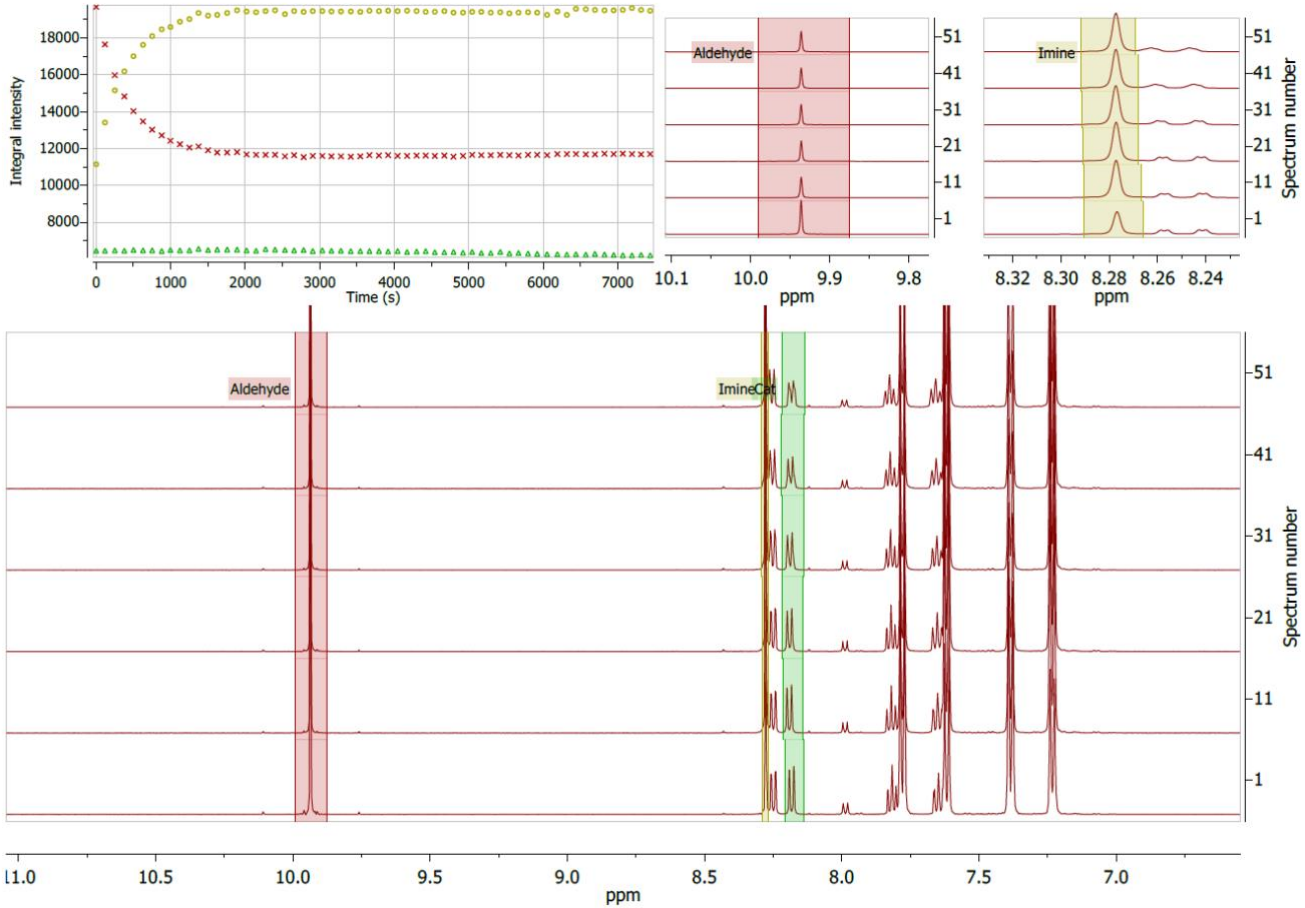
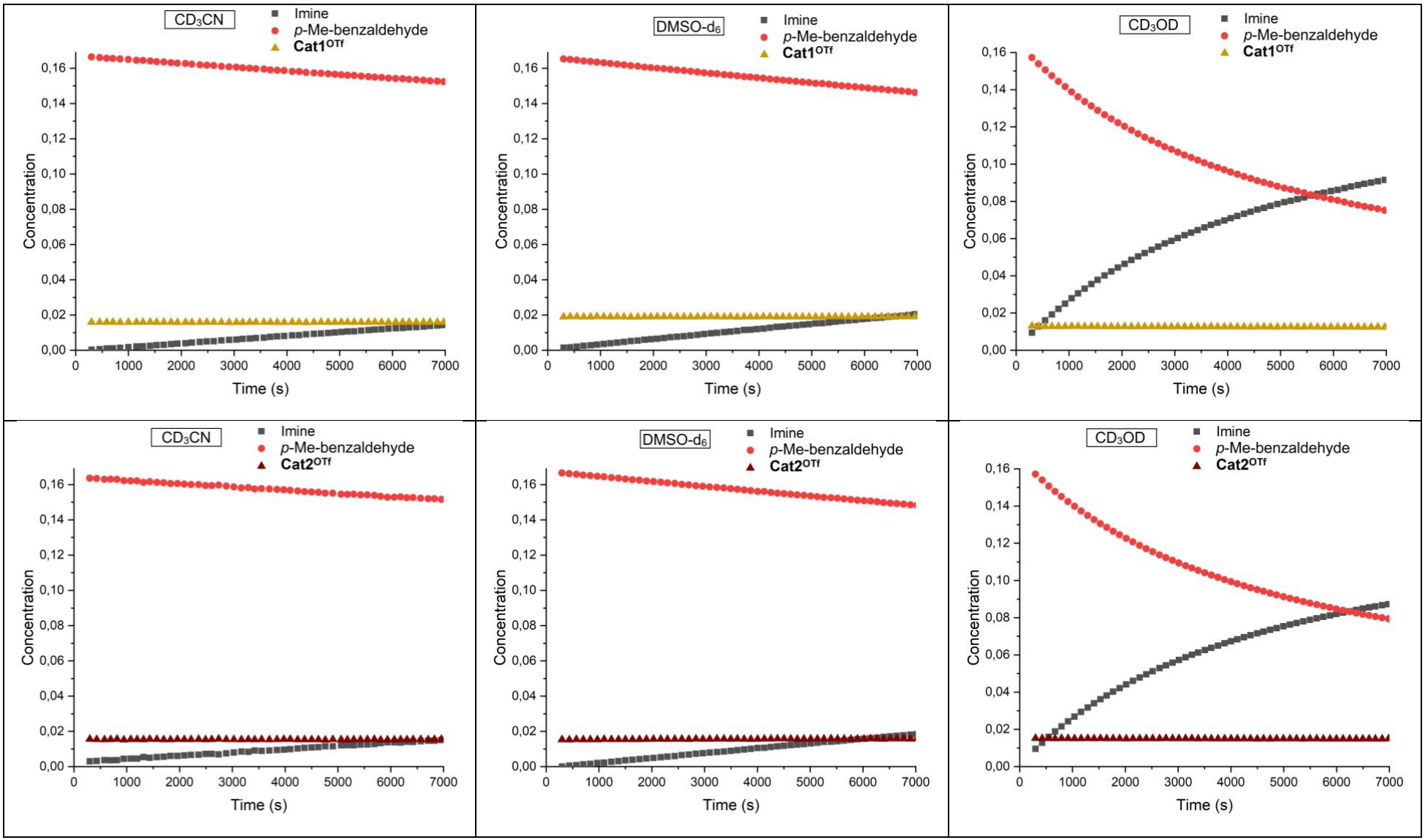
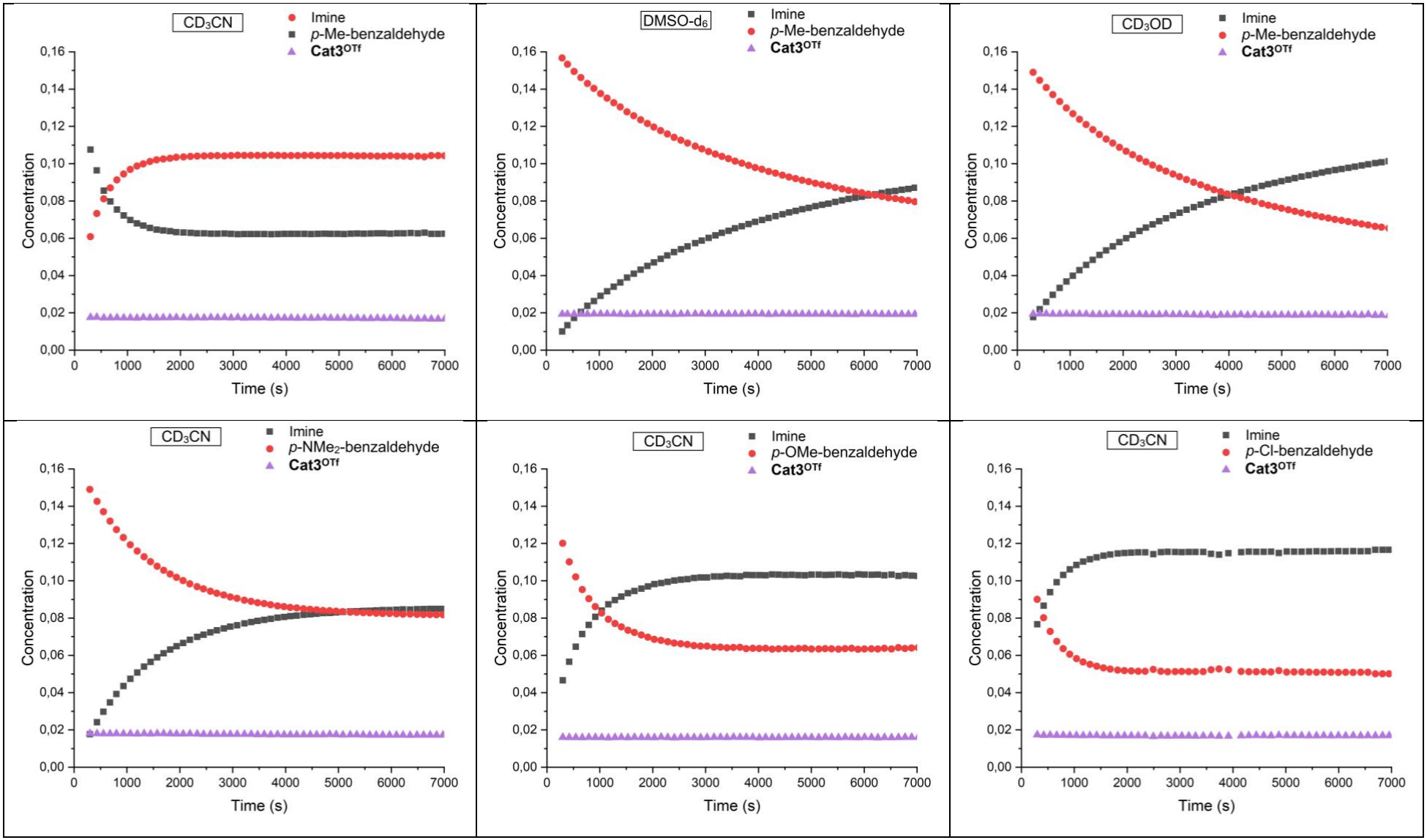
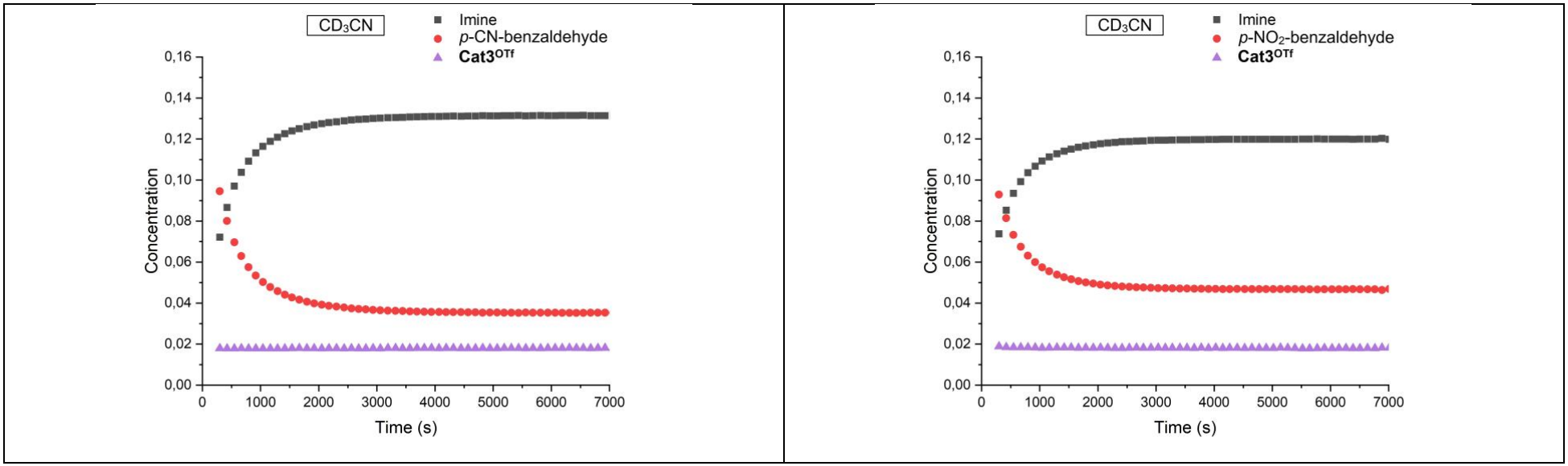


Figure S10. Example of used signals in ^{1}H NMR monitoring in case of system CD_3CN – **Cat3^{OTf}**

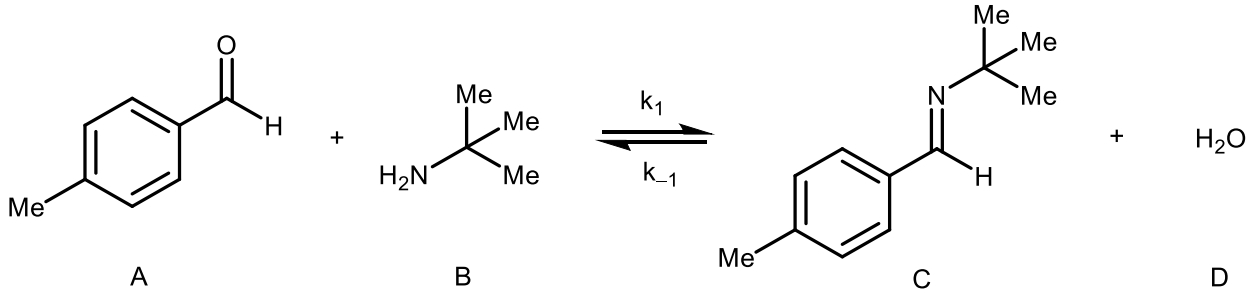
Plots representing the catalysts' stability in each ^{1}H NMR monitoring experiments.




CD3CN
Imine
p-Me-benzaldehyde
Cat3OTf
Concentration
Time (s)
DMSO-d6
Imine
p-Me-benzaldehyde
Cat3OTf
Concentration
Time (s)
CD3OD
Imine
p-Me-benzaldehyde
Cat3OTf
Concentration
Time (s)
CD3CN
Imine
p-NMe2-benzaldehyde
Cat3OTf
Concentration
Time (s)
CD3CN
Imine
p-OMe-benzaldehyde
Cat3OTf
Concentration
Time (s)
CD3CN
Imine
p-Cl-benzaldehyde
Cat3OTf
Concentration
Time (s)


CD3CN
Imine
p-CN-benzaldehyde
Cat3OTf
Concentration
Time (s)
0,00
0,02
0,04
0,06
0,08
0,10
0,12
0,14
0,16
0
1000
2000
3000
4000
5000
6000
7000
CD3CN
Imine
p-NO2-benzaldehyde
Cat3OTf
Concentration
Time (s)

Derivation of equations for calculating the reaction rate constants



The rate of the reversible reaction (ω) can be represented as the difference between the rates of the forward reaction (ω_1) and reverse reaction (ω_{-1}):

$$\omega = \omega_1 - \omega_{-1}.$$

The rate of the forward reaction is:

$$\omega_1 = k_1 ab,$$

where k_1 – the rate constant of the forward reaction (M^{-1} s^{-1}), a – concentration of aldehyde (M), b – concentration of amine (M).

The rate of the reverse reaction is:

$$\omega_{-1} = k_{-1} cd,$$

where k_{-1} – the rate constant of the reverse reaction (M^{-1} s^{-1}), c – concentration of imine (M), d – concentration of water (M).

Then,

$$\omega = k_1 ab - k_{-1} cd.$$

Since the experiments have always used equivalent amounts of aldehyde and amine, it is possible to replace the designation of amine concentration with aldehyde concentration:

$$a_0 = b_0 \Rightarrow a = b \; and \; a_{eq} = b_{eq},$$

where $a_{eq} \; and \; b_{eq}$ – equilibrium concentrations of aldehyde and amine,

$$\omega = k_1 a^2 - k_{-1} cd.$$

When equilibrium is reached, the rate of the reversible reaction becomes 0:

$$\omega_{eq} = k_1 {a_{eq}}^2 - k_{-1} c_{eq} d_{eq} = 0.$$

Now we can express the equilibrium constant as the ratio of the reaction rate constants or the ratio of the equilibrium concentrations:

$$k_1 {a_{eq}}^2 = k_{-1} c_{eq} d_{eq}$$

$$K = \frac{k_1}{k_{-1}} = \frac{c_{eq} d_{eq}}{{a_{eq}}^2},$$

where K – equilibrium constant.

We introduce x – the depth of the reversible reaction (M):

$$x = a_0 - a = b_0 - b = c - c_0 = d - d_0,$$

It means that

$$a = a_0 - x = b_0 - x,$$

$$c = x + c_0,$$

But due to the fact that we do not have an imine at the beginning of the reaction, i.e. $c_0 = 0$,

$$c = x$$

and

$$d = x + d_0,$$

because the solvent contains trace amounts of water, $d_0 \neq 0$. We determined the concentration d_0 for each experiment. The concentration x_{eq} has been determined as equilibrium concentration of imine ($x_{eq} = c_{eq}$). Also, we can use it for calculating of K:

$$K = \frac{x_{eq}(x_{eq} + d_0)}{\left(a_0 - x_{eq}\right)^2}$$

Let's write an expression for the reaction rate, where we express all concentrations in terms of x:

$$\omega = k_1 (a_0 - x)^2 - k_{-1} x (x + d_0)$$

This expression must be factorized. To do this, you need to find the roots of the quadratic equation at a reversible reaction rate of 0, i.e. at equilibrium concentrations (x_{eq}):

$$k_1 (a_0 - x_{eq})^2 - k_{-1} x_{eq} \left(x_{eq} + d_0\right) = 0$$

by Vieta's theorem:

$$x_{eq} + x_{eq}^* = \frac{2k_1a_0 + k_{-1}d_0}{k_1 - k_{-1}} \quad | \div k_{-1},$$

where x_{eq} – experimental depth of the reversible reaction, x_{eq}^* – an additional value that has no physical meaning

$$x_{eq} + x_{eq}^* = \frac{2Ka_0 + d_0}{K - 1}$$

$$x_{eq}^* = \frac{2Ka_0 + d_0}{K - 1} - x_{eq}$$

Represent the reaction rate function in the factorized form:

$$\omega = (k_1 - k_{-1})(x - x_{eq})(x - x_{eq}^*)$$

In differential form:

$$\omega = \frac{dx}{dt} = (k_1 - k_{-1})(x - x_{eq})(x - x_{eq}^*)$$

We can integrate it:

$$\int \frac{dx}{(x - x_{eq})(x - x_{eq}^*)} = \int (k_1 - k_{-1})\, dt$$

$$\ln \frac{x_{eq}^*(x - x_{eq})}{x_{eq}(x - x_{eq}^*)} = (k_1 - k_{-1})\left(x_{eq} - x_{eq}^*\right)t$$

We can represent this function as a straight line in linearized coordinates $(t; \ln \frac{x_{eq}^*(x - x_{eq})}{x_{eq}(x - x_{eq}^*)})$ with the slope $S = (k_1 - k_{-1})\left(x_{eq} - x_{eq}^*\right)$.

Finally, the system of equations must be solved:

$$\begin{cases} S = (k_1 - k_{-1})\left(x_{eq} - x_{eq}^*\right) \\ K = \dfrac{k_1}{k_{-1}} \end{cases}$$

$$k_1 = \frac{SK}{(x_{eq} - x_{eq}^*)(K - 1)}$$

$$k_{-1} = \frac{k_1}{K} = \frac{S}{(x_{eq} - x_{eq}^*)(K - 1)}$$

Table S1. 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
H_2O	-76.3733780915	-76.348052	-76.369486	45.111
Me_2SO	-553.065637884	-552.978329	-553.012939	72.843
MeCN	-132.692388989	-132.641721	-132.670260	60.065
MeOH	-115.654766560	-115.598251	-115.625092	56.491
$CHCl_3$	-1419.16396168	-1419.138146	-1419.172634	72.587
DMF	-248.392497055	-248.281154	-248.317282	76.039
Pyridine	-248.171803951	-248.076658	-248.109232	68.558
THF	-232.336639049	-232.212121	-232.245959	71.218
$H_2O\cdots H_2O$	-152.759928707	-152.706132	-152.738057	67.192
$Me_2SO\cdots Me_2SO$	-1106.15823194	-1105.981024	-1106.032622	108.599
MeCN···MeCN	-265.390057597	-265.286684	-265.334079	99.751
MeOH···MeOH	-231.323554167	-231.207966	-231.248838	86.023
$CHCl_3\cdots CHCl_3$	-2838.33319760	-2838.279537	-2838.335211	117.176
DMF···DMF	-496.803514693	-496.578030	-496.629587	108.511
Pyridine···Pyridine	-496.351167709	-496.158989	-496.208832	104.905
THF···THF	-464.680697093	-464.429474	-464.481684	109.886
$Cat1^+$	-1091.36335792	-1091.092011	-1091.149702	121.422
$Cat2^+$	-3092.65033002	-3092.379265	-3092.437958	123.529
$Cat3^+$	-472.960288041	-472.788091	-472.834997	98.721
$Cat1^+\cdots H_2O$	-1167.75756654	-1167.458135	-1167.522213	134.863
$Cat1^+\cdots Me_2SO$	-1644.45985240	-1644.099410	-1644.172767	154.393
$Cat1^+\cdots$MeCN	-1224.07631922	-1223.751791	-1223.823670	151.283
$Cat1^+\cdots$MeOH	-1207.03926423	-1206.709695	-1206.777125	141.918
$Cat1^+\cdots CHCl_3$	-2510.53719308	-2510.237787	-2510.316798	166.292
$Cat1^+\cdots$DMF	-1339.78308928	-1339.397629	-1339.475774	164.470
$Cat1^+\cdots$Pyridine	-1339.55908935	-1339.189811	-1339.263685	155.481
$Cat1^+\cdots$THF	-1323.72409936	-1323.325185	-1323.398728	154.785
$Cat2^+\cdots H_2O$	-3169.05297747	-3168.753785	-3168.818663	136.547
$Cat2^+\cdots Me_2SO$	-3645.76055126	-3645.399655	-3645.474634	157.807
$Cat2^+\cdots$MeCN	-3225.37213906	-3225.047777	-3225.119496	150.946
$Cat2^+\cdots$MeOH	-3208.33584886	-3208.005666	-3208.074713	145.322
$Cat2^+\cdots CHCl_3$	-4511.83230102	-4511.533004	-4511.609431	160.854
$Cat2^+\cdots$DMF	-3341.08159936	-3340.696110	-3340.773480	162.839
$Cat2^+\cdots$Pyridine	-3340.85891056	-3340.489890	-3340.563515	154.958
$Cat2^+\cdots$THF	-3325.02178704	-3324.623101	-3324.697059	155.657
$Cat3^+\cdots H_2O$	-549.361722782	-549.161279	-549.215885	114.928
$Cat3^+\cdots Me_2SO$	-1026.06889066	-1025.807532	-1025.870812	133.184
$Cat3^+\cdots$MeCN	-605.681394758	-605.456105	-605.518922	132.208
$Cat3^+\cdots$MeOH	-588.643269351	-588.411677	-588.470182	123.134
$Cat3^+\cdots CHCl_3$	-1892.13640412	-1891.936201	-1892.004105	142.916
$Cat3^+\cdots$DMF	-721.390298114	-721.103678	-721.171538	142.822
$Cat3^+\cdots$Pyridine	-721.166518191	-720.896305	-720.960062	134.188
$Cat3^+\cdots$THF	-705.328407926	-705.028736	-705.093573	136.461
A	-384.717531131	-384.569220	-384.612192	90.443

Cat1^{+}···A	-1476.10413555	-1475.682017	-1475.766144	177.059
Cat2^{+}···A	-3477.40157908	-3476.979625	-3477.063335	176.183
Cat3^{+}···A	-857.709720608	-857.386549	-857.460651	155.961
H_2O···A	-461.105461234	-460.928754	-460.978219	104.108
Me_2SO···A	-937.797733385	-937.559962	-937.622910	132.485
MeCN···A	-517.418829065	-517.217644	-517.274872	120.447
MeOH···A	-500.388179329	-500.180660	-500.234318	112.934
$CHCl_3$···A	-1803.89174769	-1803.715634	-1803.778537	132.391
DMF···A	-633.119409418	-632.858380	-632.920617	130.989
Pyridine···A	-632.896848513	-632.651220	-632.712957	129.938
THF···A	-617.064590221	-616.789341	-616.849561	126.742
B	-213.685990129	-213.527504	-213.563836	76.468
Cat1^{+}···B	-1305.07030503	-1304.637993	-1304.714859	161.777
Cat2^{+}···B	-3306.37316144	-3305.940502	-3306.016805	160.592
Cat3^{+}···B	-686.680433630	-686.346826	-686.413226	139.751
H_2O···B	-290.078585633	-289.891661	-289.934314	89.771
Me_2SO···B	-766.768146356	-766.519913	-766.574831	115.586
MeCN···B	-346.388391530	-346.178258	-346.227059	102.711
MeOH···B	-329.361045750	-329.143581	-329.191133	100.083
$CHCl_3$···B	-1632.86500130	-1632.678440	-1632.734547	118.087
DMF···B	-462.088866185	-461.816542	-461.874375	121.721
Pyridine···B	-461.868720839	-461.612863	-461.667442	114.872
THF···B	-446.032847610	-445.747287	-445.800717	112.454
TS	-812.085680245	-811.621371	-811.694353	153.603
Cat1^{+}···TS	-1903.49670315	-1902.757157	-1902.870561	238.678
Cat2^{+}···TS	-3904.80357124	-3904.062362	-3904.172320	231.425
Cat3^{+}···TS	-1285.11961289	-1284.477134	-1284.579537	215.525
H_2O···TS	-888.492976092	-888.000243	-888.077846	163.328
Me_2SO···TS	-1365.17326486	-1364.618151	-1364.708493	190.140
MeCN···TS	-944.795846664	-944.277351	-944.364468	183.354
MeOH···TS	-927.774996811	-927.252184	-927.333441	171.018
Cat1^{+}···TS*	-1766.18964935	-1765.581834	-1765.678960	204.418
Cat2^{+}···TS*	-3767.48258353	-3766.876734	-3766.974469	205.700
Cat3^{+}···TS*	-1147.79563290	-1147.288462	-1147.378491	189.481
Me_2SO···TS*	-1227.86712966	-1227.445153	-1227.521709	161.127
MeCN···TS*	-807.490975634	-807.105230	-807.178382	153.962
MeOH···TS*	-790.461448830	-790.069790	-790.143832	155.835