Supplementary Information (SI) for ChemComm.

The Lewis basicity of amines on the Legault iodonium Lewis acidity scale

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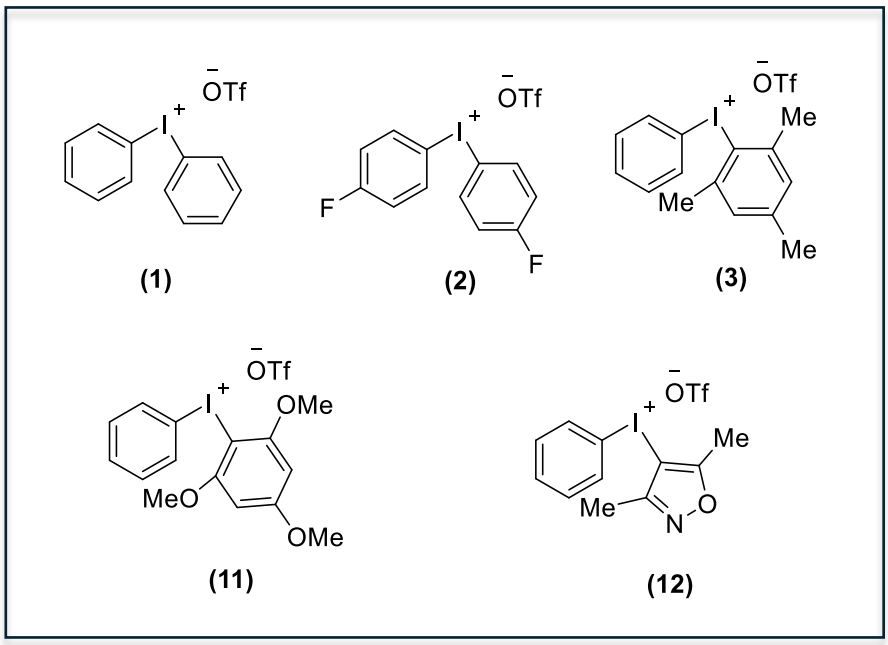
General considerations

Materials: Commercially available reagents and solvents were used without further purification unless otherwise stated. The percentage of active oxidant for *m*-CPBA was determined by iodometric titration.[1,2] Compound **2** was synthesized by a known method.[3] The tetrafluoroborate salt of diphenyliodonium and 3,5-dimethyl-4-isoxazolyl(phenyl)iodonium were synthesized by known methods.[4,5] Phenyl(2,4,6-trimethoxy iodonium)tosylate and phenyl(2,4,6-trimethyliodonium)tosylate were also synthesized using known methods.[6,7]

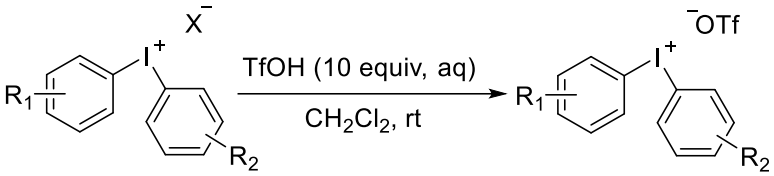
Methods: Reactions performed above ambient room temperature were done in an oil bath or aluminum block heated externally by a Heidolph MR Hei-Standard heating/stirring mantel equipped with a Heidolph EKT HeiCON temperature control. Reactions performed below ambient room temperature were done so in an aluminum block cooled in an ice bath. ^{1}H, $^{13}C\{1H\}$, and $^{19}F\{^{1}H\}$ spectra of synthesized compounds were recorded in DMSO-d_6 and ^{1}H NMR titrations were recorded in MeCN-d_6 or DCM-d_2 (with tetramethylsilane as an internal standard) on a Bruker Avance II 400 MHz spectrometer; the following notation issued: s – singlet, d – doublet, t – triplet, q – quartet.

Synthesis and characterization of Diaryliodonium salts

<u>Salts used in this study (Compound number)</u>:



Anion exchange of OTs or BF_4 for OTf

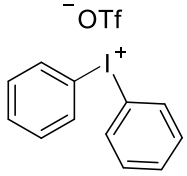


X = BF_4, OTs

General Procedure:

Diaryliodonium triflate (OTf) salts were synthesized by exchanging the counter anion of diaryliodonium tosylate (OTs) or tetrafluoroborate (BF_4) salts by the following method. An aqueous solution of triflic acid (10 mmol, 10 equiv) was prepared in water (45 ml). Diaryliodonium tosylate or tetrafluoroborate (1 mmol, 1 equiv) was dissolved in 15 mL of dichloromethane and repeatedly washed with the aqueous solution of triflic acid. The dichloromethane layer was evaporated under reduced pressure and triturated with diethyl ether. The precipitate was isolated by vacuum filtration and washed with excess diethyl ether (3 × 20 mL). After drying under air for 15 minutes the diaryliodonium salt was obtained in analytically pure form.

Diphenyliodonium triflate (1):



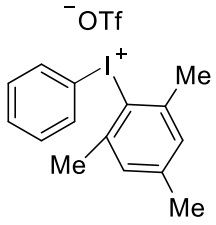
Prepared from the corresponding tetrafluoroborate salt using general procedure and obtained in an isolated yield of 81% (1.74 g) as white solid. Spectral data is consistent with that of previously reported.[8]

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.26 (d, J = 7.1 Hz, 4H), 7.67 (t, J = 7.5 Hz, 2H), 7.54 (t, J = 7.7 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ (ppm) 135.6, 132.5, 132.2, 121.1 (q, J = 323.2 Hz, OSO_2CF_3), 117.0.

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6 δ (ppm) -77.7.

Phenyl(2,4,6-trimethylphenyl)iodonium triflate (11):



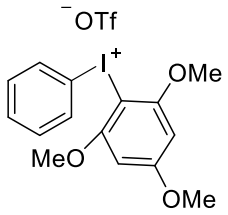
Prepared from the corresponding tosylate salt using general procedure and obtained in an isolated yield of 75% (1.77g) as a white solid. Spectral data is consistent with that of previously reported.[9]

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.98 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.22 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ (ppm) 143.0, 141.4, 134.4, 131.8, 131.7, 129.7, 122.4, 120.6 (q, *J* = 323.2 Hz, OSO_2CF_3), 114.4, 26.2, 20.4.

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6 δ (ppm) -77.8.

Phenyl(2,4,6-trimethylphenyl)iodonium triflate (11):



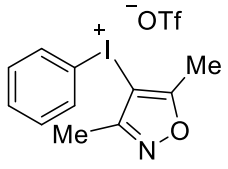
Prepared from the corresponding tosylate salt using general procedure and obtained in an isolated yield of 90% (2.34 g) as white solid. Spectral data is consistent with that of previously reported.[10]

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.92 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.47 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ (ppm) 166.1, 159.2, 134.2, 131.5, 120.6 (q, *J* = 323.2 Hz, OSO2CF3),116.0, 91.9, 86.8, 57.2, 56.0.

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6 δ (ppm) -77.8.

3,5-dimethyl-4-isoxazolyl(phenyl)iodonium triflate (12):



Prepared from the corresponding tetrafluoroborate salt using general procedure and obtained in an isolated yield of 82% (0.184 g) as white solid. Spectral data is consistent with that of previously reported.[11]

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.23 (d, *J* = 7.9 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 2.73 (s, 3H), 2.35 (s,3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ (ppm) 175.8, 160.4, 134.9, 132.3, 131.9,120.7 (q, *J* = 323.3 Hz, OSO2CF3),117.3, 86.1, 12.3, 10.9.

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6 δ (ppm) -77.9.

^{1}H NMR binding study:

NMR titration of diaryliodonium salts with amines were performed in the following manner. The concentration of diaryliodonium salt was held constant at 0.001 M in MeCN-d_6 and the concentration of amines was changed from 0 to 20 equivalence (0.02 M). The chemical shift of an aromatic proton on the diaryliodonium salt was measured (δ_{obs}) from the ^{1}H NMR spectrum for each experiment. The NMR chemical shift values were obtained to four decimal places.

The equilibrium constant was determined for a 1:1 binding interaction between host (H, diaryliodonium) and guest (G, amine) based on equation (1). In our experiments, diphenyliodonium salts were treated as host and amines were treated as guests.

$$H + G \rightleftharpoons HG \tag{1}$$

where [H] is the concentration of Host, [G] is the concentration of Guest and [HG] is the concentration of the Host-Guest adduct. If K_a is the binding constant between the host and the guest.

$$K_a = \frac{[HG]}{[H][G]} \tag{2}$$

From mass balance, the following equations can be written (considering 1:1 binding):

$$[H]_0 = [H] + [HG] \qquad or, [H] = [H]_0 - [HG] \tag{3}$$

$$[G]_0 = [G] + [HG] \qquad or, [G] = [G]_0 - [HG] \tag{4}$$

Substituting $[H]_o$ and $[G]_o$ in eq 2:

$$K_a = \frac{[HG]}{([H]_0 - [HG])([G]_0 - [HG])}$$

$$or, \qquad [HG]^2 - [HG]\left([H]_0 + [G]_0 + \frac{1}{K_a}\right) - [H]_0[G]_0 = 0 \tag{5}$$

Solving the quadratic eq 5:

$$[HG] = \frac{1}{2}\left[\left([G]_0 + [H]_0 + \frac{1}{K_a}\right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right)^2 - 4[H]_0[G]_0}\right] \tag{6}$$

In the case of NMR spectroscopy, the chemical shift observed (δ_{obs}) for the host is described by the sum of the individual components as a function of mole fraction (X_H or X_{HG}) (eq 7):

$$\delta_{obs} = \delta_H X_H + \delta_{HG} X_{HG} \tag{7}$$

$$where, X_H = \frac{[H]}{[H]_0} \; ; \; X_{HG} = \frac{[HG]}{[H]_0} \; and \; (X_H + X_{HG}) = 1$$

Eq 7 can be rearranged and rewritten as:

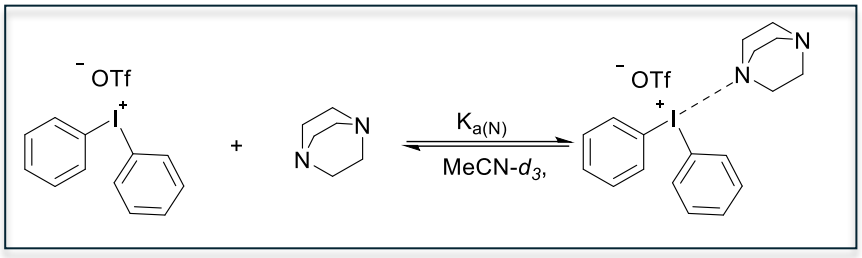
$$\delta_{obs} = \delta_H(1 - X_{HG}) + \delta_{HG} X_{HG}$$

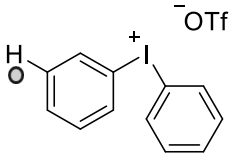
$$or, \qquad (\delta_{obs} - \delta_H) = (\delta_{HG} - \delta_H) X_{HG}$$

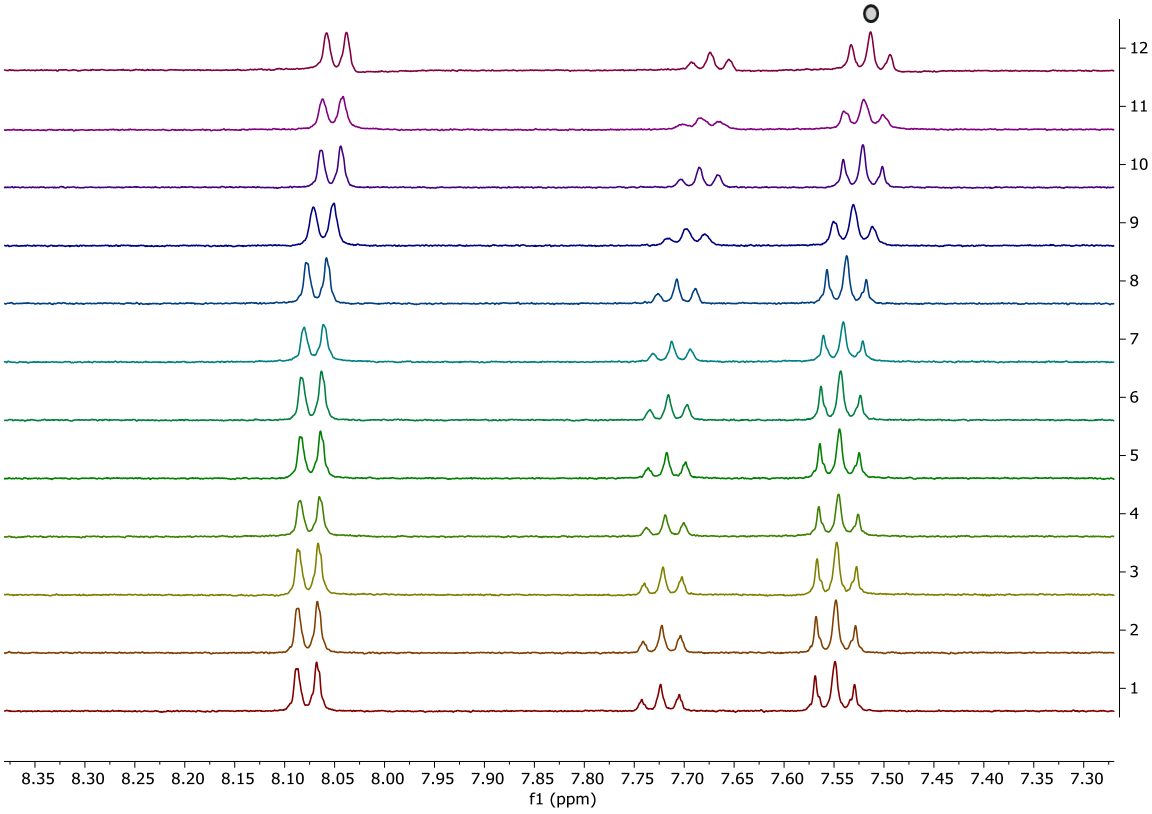
$$or, \qquad \Delta\delta_{obs} = \delta_{max}\left(\frac{[HG]}{[H]_0}\right) \qquad \text{where, } \Delta\delta_{obs} = \delta_{obs} - \delta_H \text{ and } \delta_{max} = \delta_{HG} - \delta_H$$

$$or, \qquad \Delta\delta_{obs} = \frac{\delta_{max}}{2\,[H]_0}\left[\left([G]_0 + [H]_0 + \frac{1}{K_a}\right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right)^2 - 4[H]_0[G]_0}\right] \qquad (8)$$

The binding constant between diphenyliodonium salt and amines were then quantified by fitting the raw data $\Delta\delta_{obs}$ into eq (8).





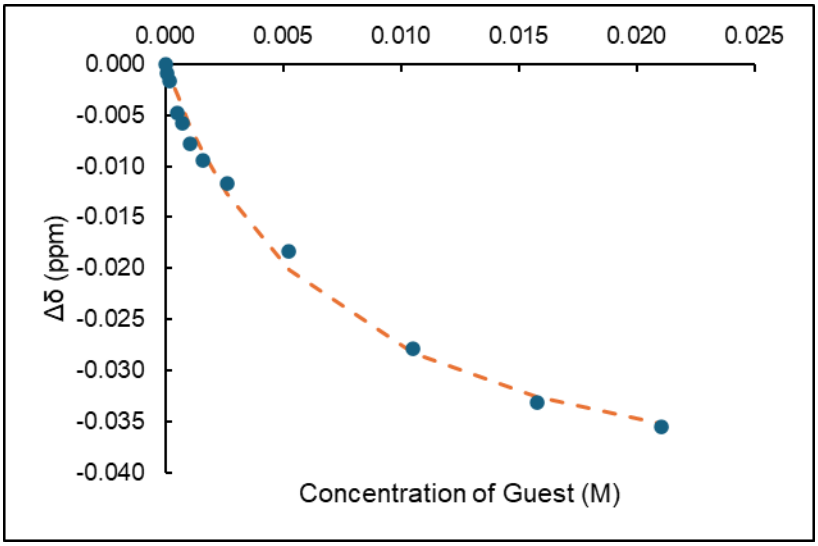


K_a = 1.64 x 10^2 M^{-1}

Fig S1: Representative NMR titration stacked spectra of Ph_2IOTf (0.001 M) titrating with DABCO in MeCN-d_3

1. Binding constant between Ph_2IOTf and DABCO in MeCN-d_3

[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.5490	0.0000
0.0011	0.0001	7.5481	-0.0009
0.0011	0.0002	7.5474	-0.0016
0.0011	0.0005	7.5442	-0.0048
0.0011	0.0007	7.5432	-0.0058
0.0011	0.0011	7.5412	-0.0078
0.0011	0.0016	7.5396	-0.0094
0.0011	0.0026	7.5373	-0.0117
0.0011	0.0053	7.5306	-0.0184
0.0011	0.0105	7.5211	-0.0279
0.0011	0.0158	7.5159	-0.0331
0.0011	0.0210	7.5134	-0.0356

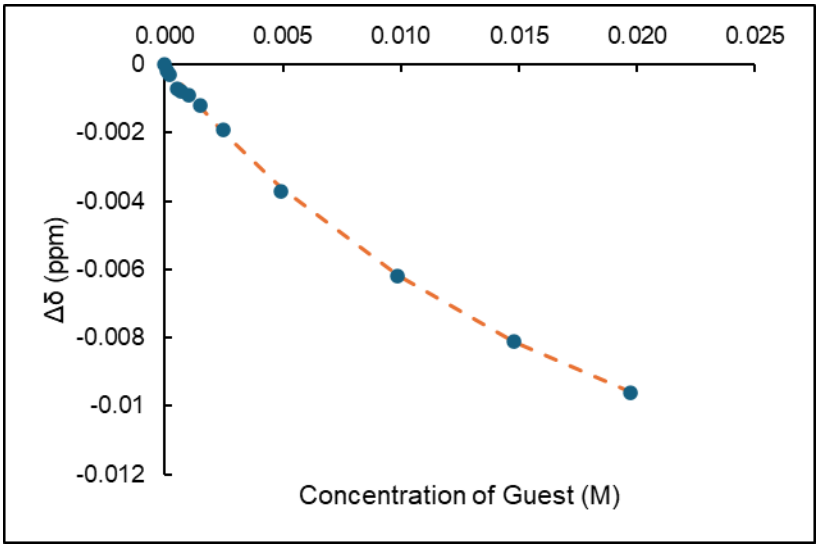


The association constant K_a = 1.64 x 10^2 M^{-1}

The association constant (K_a) calculated as the average of triplicate run = (1.64 ± 0.005) x 10^2 M^{-1}

2. Binding constant between Ph_2IOTf and morpholine in MeCN-d_3

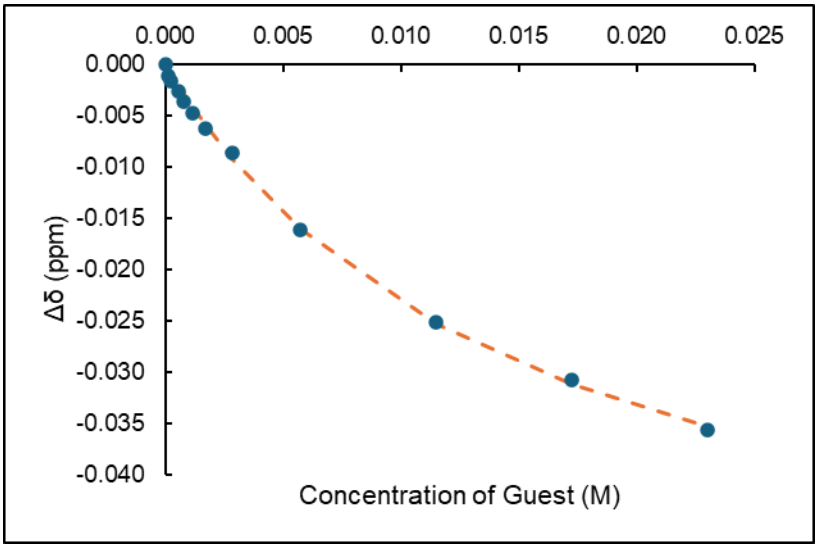
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5490	0.0000
0.0010	0.0001	7.5488	-0.0002
0.0010	0.0002	7.5487	-0.0003
0.0010	0.0005	7.5483	-0.0007
0.0010	0.0007	7.5482	-0.0008
0.0010	0.0010	7.5481	-0.0009
0.0010	0.0015	7.5478	-0.0012
0.0010	0.0025	7.5471	-0.0019
0.0010	0.0049	7.5453	-0.0037
0.0010	0.0099	7.5428	-0.0062
0.0010	0.0148	7.5409	-0.0081
0.0010	0.0197	7.5394	-0.0096



The association constant $K_a = 4.38 \times 10^1\ M^{-1}$

3. Binding constant between Ph_2IOTf and piperidine in MeCN-d_3

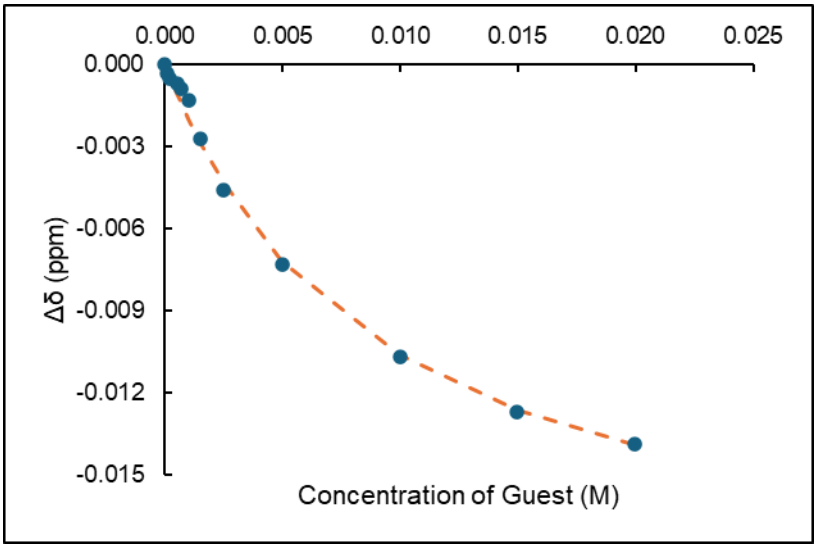
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5490	0.0000
0.0010	0.0001	7.5479	-0.0011
0.0010	0.0002	7.5474	-0.0016
0.0010	0.0006	7.5464	-0.0026
0.0010	0.0008	7.5454	-0.0036
0.0010	0.0012	7.5442	-0.0048
0.0010	0.0017	7.5427	-0.0063
0.0010	0.0029	7.5404	-0.0086
0.0010	0.0058	7.5329	-0.0161
0.0010	0.0115	7.5239	-0.0251
0.0010	0.0173	7.5182	-0.0308
0.0010	0.0230	7.5133	-0.0357



The association constant $K_a = 7.16 \times 10^1\ M^{-1}$

4. Binding constant between Ph_2IOTf and dibutyl amine in MeCN-d_3

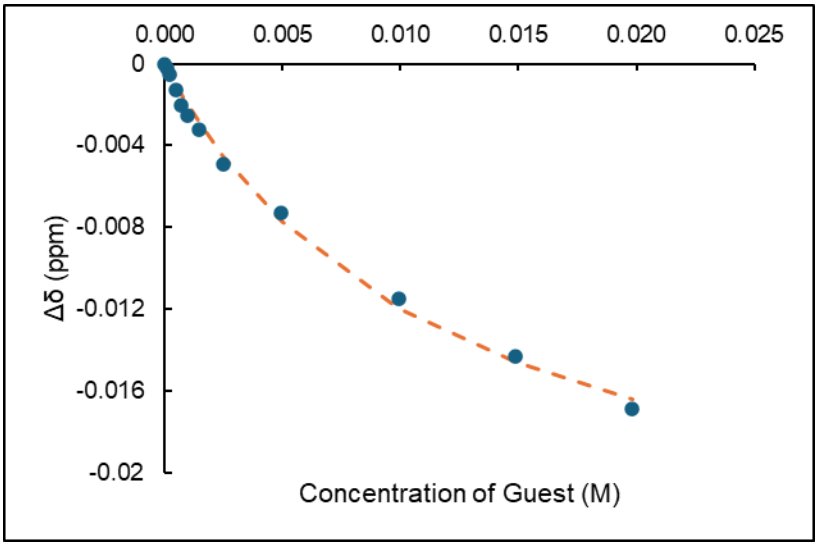
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.5491	0.0000
0.0011	0.0001	7.5488	-0.0003
0.0011	0.0002	7.5486	-0.0005
0.0011	0.0005	7.5484	-0.0007
0.0011	0.0007	7.5482	-0.0009
0.0011	0.0010	7.5478	-0.0013
0.0011	0.0015	7.5464	-0.0027
0.0011	0.0025	7.5445	-0.0046
0.0011	0.0050	7.5418	-0.0073
0.0011	0.0100	7.5384	-0.0107
0.0011	0.0150	7.5364	-0.0127
0.0011	0.0199	7.5352	-0.0139



The association constant K_a = 1.24 x 10^2 M^{-1}

5. Binding constant between Ph_2IOTf and butyl amine in MeCN-d_3

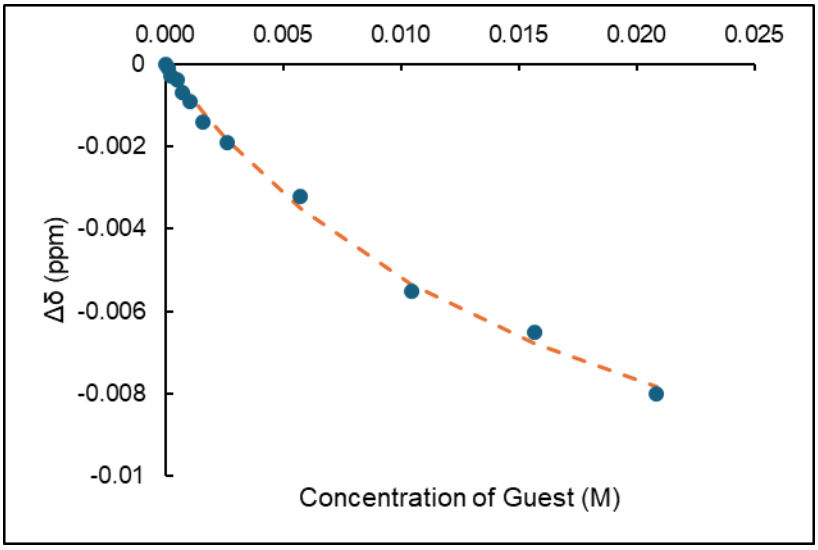
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5488	0.0000
0.0010	0.0001	7.5486	-0.0002
0.0010	0.0002	7.5483	-0.0005
0.0010	0.0005	7.5475	-0.0013
0.0010	0.0007	7.5468	-0.0020
0.0010	0.0010	7.5463	-0.0025
0.0010	0.0015	7.5456	-0.0032
0.0010	0.0025	7.5439	-0.0049
0.0010	0.0050	7.5415	-0.0073
0.0010	0.0099	7.5373	-0.0115
0.0010	0.0149	7.5345	-0.0143
0.0010	0.0198	7.5319	-0.0169



The association constant $K_a = 9.16 \times 10^1\ M^{-1}$

6. Binding constant between Ph_2IOTf and aniline in MeCN-d_3

[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.5420	0.0000
0.0011	0.0001	7.5419	-0.0001
0.0011	0.0002	7.5417	-0.0003
0.0011	0.0005	7.5416	-0.0004
0.0011	0.0007	7.5413	-0.0007
0.0011	0.0010	7.5411	-0.0009
0.0011	0.0016	7.5406	-0.0014
0.0011	0.0026	7.5401	-0.0019
0.0011	0.0057	7.5388	-0.0032
0.0011	0.0104	7.5365	-0.0055
0.0011	0.0156	7.5355	-0.0065
0.0011	0.0209	7.5340	-0.0080

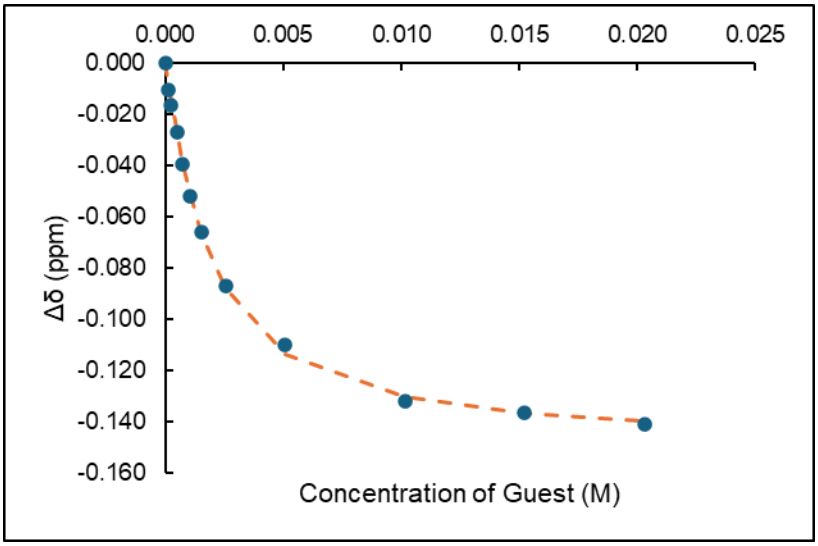


The association constant K_a = 5.81 x 10^1 M^{-1}

The association constant (K_a) calculated as the average of triplicate run = (6.26 ± 0.40) x 10^1 M^{-1}

7. Binding constant between $(Ph\text{-}F)_2$ IOTf and DABCO in MeCN-d_3

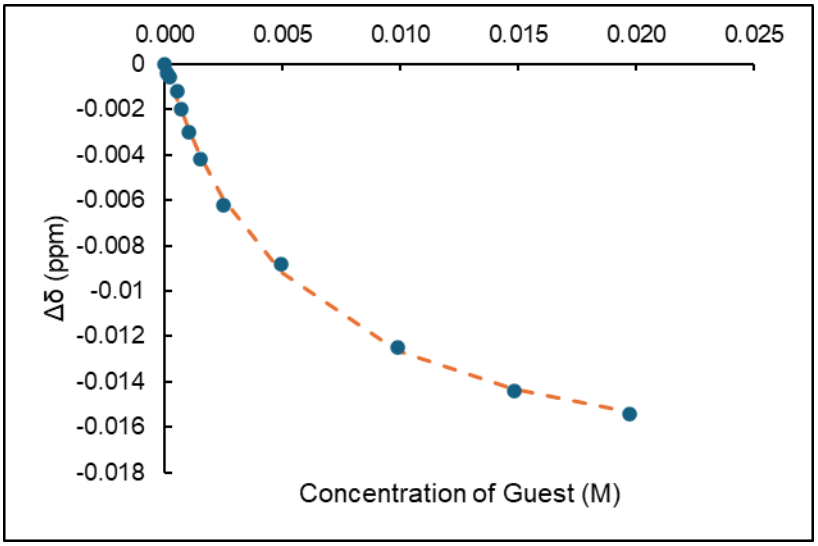
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.3082	0.0000
0.0010	0.0001	7.2979	-0.0103
0.0010	0.0002	7.2921	-0.0161
0.0010	0.0005	7.2815	-0.0267
0.0010	0.0007	7.2688	-0.0394
0.0010	0.0010	7.2564	-0.0518
0.0010	0.0015	7.2423	-0.0659
0.0010	0.0025	7.2212	-0.0870
0.0010	0.0051	7.1984	-0.1098
0.0010	0.0102	7.1764	-0.1318
0.0010	0.0152	7.1717	-0.1365
0.0010	0.0203	7.1674	-0.1408



The association constant $K_a = 7.28 \times 10^2\ M^{-1}$

8. Binding constant between $(Ph\text{-}F)_2IOTf$ and morpholine in MeCN-d_3

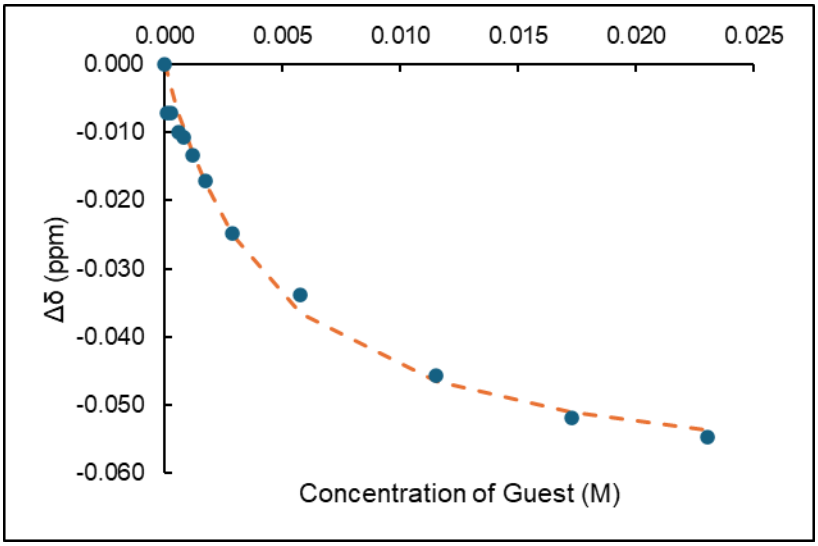
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.3042	0.0000
0.0010	0.0001	7.3038	-0.0004
0.0010	0.0002	7.3036	-0.0006
0.0010	0.0005	7.3030	-0.0012
0.0010	0.0007	7.3022	-0.0020
0.0010	0.0010	7.3012	-0.0030
0.0010	0.0015	7.3000	-0.0042
0.0010	0.0025	7.2980	-0.0062
0.0010	0.0049	7.2954	-0.0088
0.0010	0.0099	7.2917	-0.0125
0.0010	0.0148	7.2898	-0.0144
0.0010	0.0197	7.2888	-0.0154



The association constant $K_a = 2.04 \times 10^2\ M^{-1}$

9. Binding constant between $(Ph\text{-}F)_2IOTf$ and piperidine in MeCN-d_3

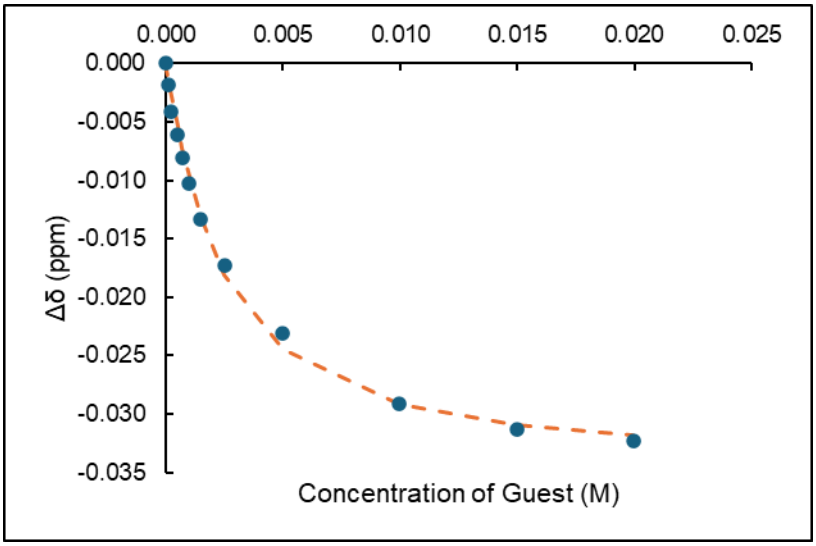
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.3042	0.0000
0.0010	0.0001	7.2971	-0.0071
0.0010	0.0002	7.2970	-0.0072
0.0010	0.0006	7.2943	-0.0099
0.0010	0.0008	7.2934	-0.0108
0.0010	0.0012	7.2909	-0.0133
0.0010	0.0017	7.2871	-0.0171
0.0010	0.0029	7.2794	-0.0248
0.0010	0.0058	7.2704	-0.0338
0.0010	0.0115	7.2585	-0.0457
0.0010	0.0173	7.2524	-0.0518
0.0010	0.0230	7.2495	-0.0547



The association constant $K_a = 2.74 \times 10^2\ M^{-1}$

10. Binding constant between $(Ph\text{-}F)_2IOTf$ and dibutyl amine in MeCN-d_3

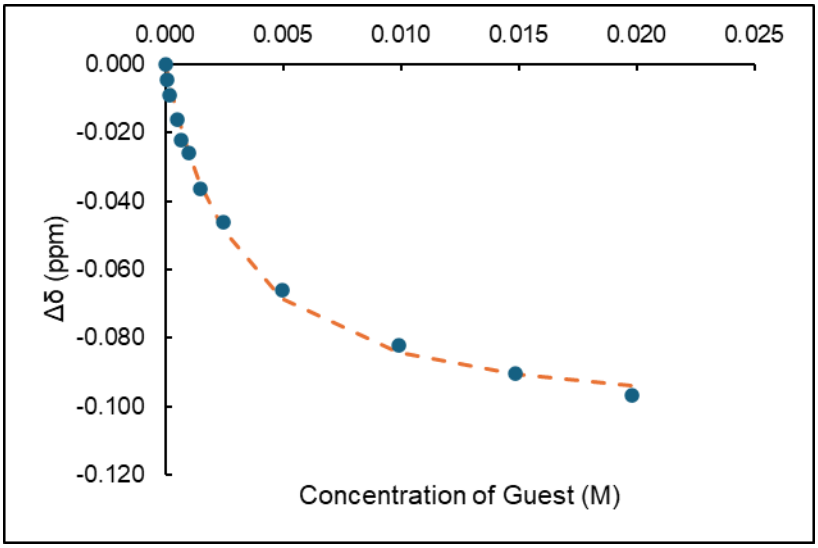
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.3045	0.0000
0.0011	0.0001	7.3027	-0.0018
0.0011	0.0002	7.3004	-0.0041
0.0011	0.0005	7.2984	-0.0061
0.0011	0.0007	7.2964	-0.0081
0.0011	0.0010	7.2942	-0.0103
0.0011	0.0015	7.2912	-0.0133
0.0011	0.0025	7.2872	-0.0173
0.0011	0.0050	7.2814	-0.0231
0.0011	0.0100	7.2754	-0.0291
0.0011	0.0150	7.2732	-0.0313
0.0011	0.0199	7.2722	-0.0323



The association constant $K_a = 5.64 \times 10^2\ M^{-1}$

11. Binding constant between $(Ph\text{-}F)_2IOTf$ and butyl amine in MeCN-d_3

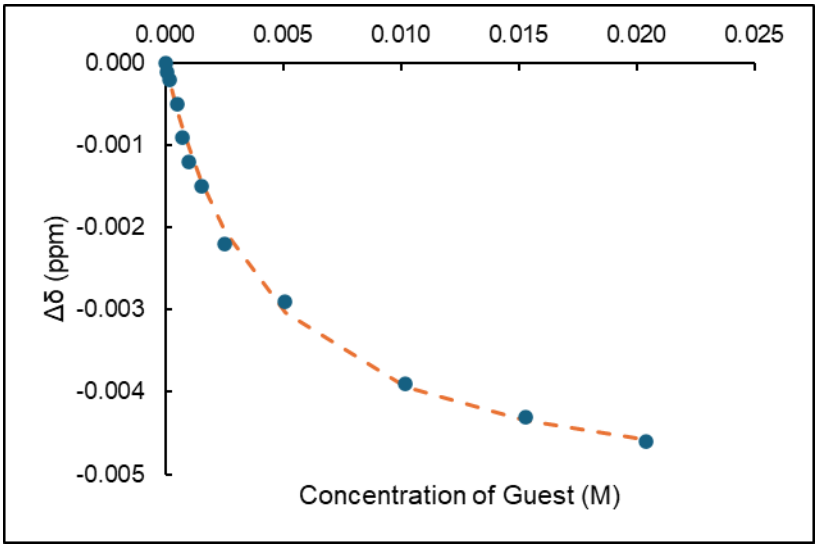
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.3047	0.0000
0.0010	0.0001	7.3002	-0.0045
0.0010	0.0002	7.2957	-0.0090
0.0010	0.0005	7.2885	-0.0162
0.0010	0.0007	7.2824	-0.0223
0.0010	0.0010	7.2786	-0.0261
0.0010	0.0015	7.2682	-0.0365
0.0010	0.0025	7.2587	-0.0460
0.0010	0.0050	7.2386	-0.0661
0.0010	0.0099	7.2225	-0.0822
0.0010	0.0149	7.2142	-0.0905
0.0010	0.0198	7.2081	-0.0966



The association constant $K_a = 4.23 \times 10^2\ M^{-1}$

12. Binding constant between $(Ph\text{-}F)_2IOTf$ and aniline in MeCN-d_3

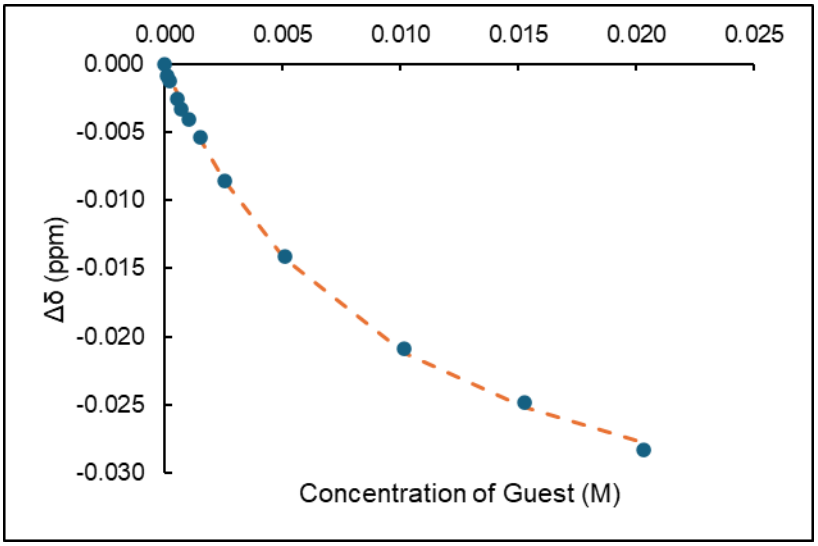
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.2972	0.0000
0.0010	0.0001	7.2971	-0.0001
0.0010	0.0002	7.2970	-0.0002
0.0010	0.0005	7.2967	-0.0005
0.0010	0.0007	7.2963	-0.0009
0.0010	0.0010	7.2960	-0.0012
0.0010	0.0015	7.2957	-0.0015
0.0010	0.0025	7.2950	-0.0022
0.0010	0.0051	7.2943	-0.0029
0.0010	0.0102	7.2933	-0.0039
0.0010	0.0153	7.2929	-0.0043
0.0010	0.0204	7.2926	-0.0046



The association constant $K_a = 2.84 \times 10^2\ M^{-1}$

13. Binding constant between Ph(Mes)IOTf and DABCO in MeCN-d_3

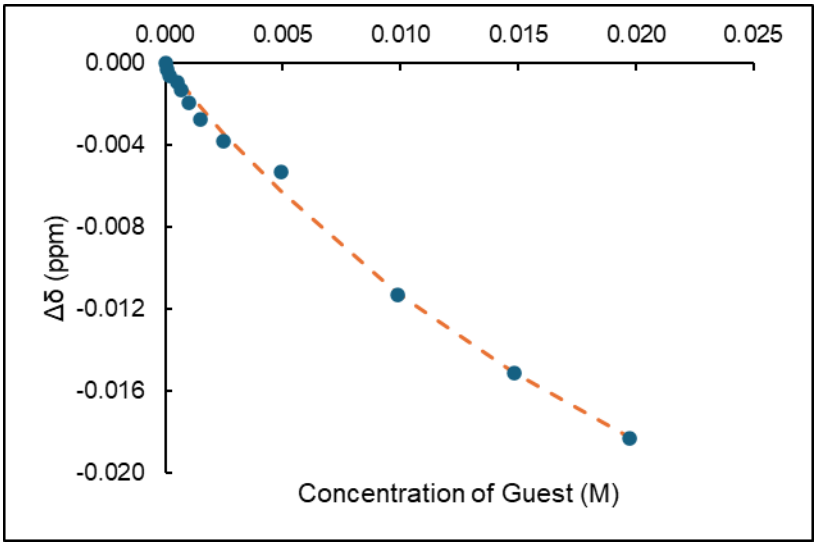
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5030	0.0000
0.0010	0.0001	7.5021	-0.0009
0.0010	0.0002	7.5017	-0.0013
0.0010	0.0005	7.5004	-0.0026
0.0010	0.0007	7.4997	-0.0033
0.0010	0.0010	7.4989	-0.0041
0.0010	0.0015	7.4976	-0.0054
0.0010	0.0025	7.4944	-0.0086
0.0010	0.0051	7.4889	-0.0141
0.0010	0.0102	7.4821	-0.0209
0.0010	0.0152	7.4782	-0.0248
0.0010	0.0203	7.4747	-0.0283



The association constant K_a = 1.18 x 10^2 M^{-1}

14. Binding constant between Ph(Mes)IOTf and morpholine in MeCN-d_3

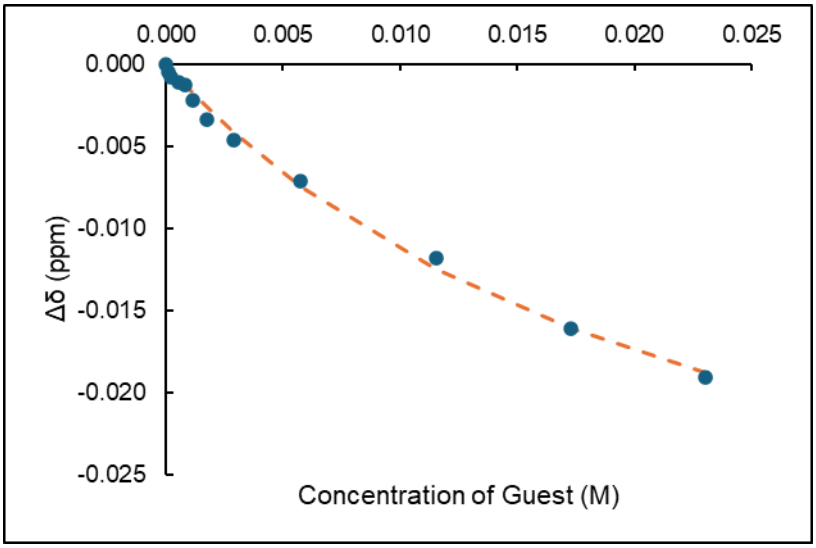
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5027	0.0000
0.0010	0.0001	7.5024	-0.0003
0.0010	0.0002	7.5021	-0.0006
0.0010	0.0005	7.5018	-0.0009
0.0010	0.0007	7.5014	-0.0013
0.0010	0.0010	7.5008	-0.0019
0.0010	0.0015	7.5000	-0.0027
0.0010	0.0025	7.4989	-0.0038
0.0010	0.0049	7.4974	-0.0053
0.0010	0.0099	7.4914	-0.0113
0.0010	0.0148	7.4876	-0.0151
0.0010	0.0197	7.4844	-0.0183



The association constant K_a = 3.03 x 10^1 M^{-1}

15. Binding constant between Ph(Mes)IOTf and piperidine in MeCN-d_3

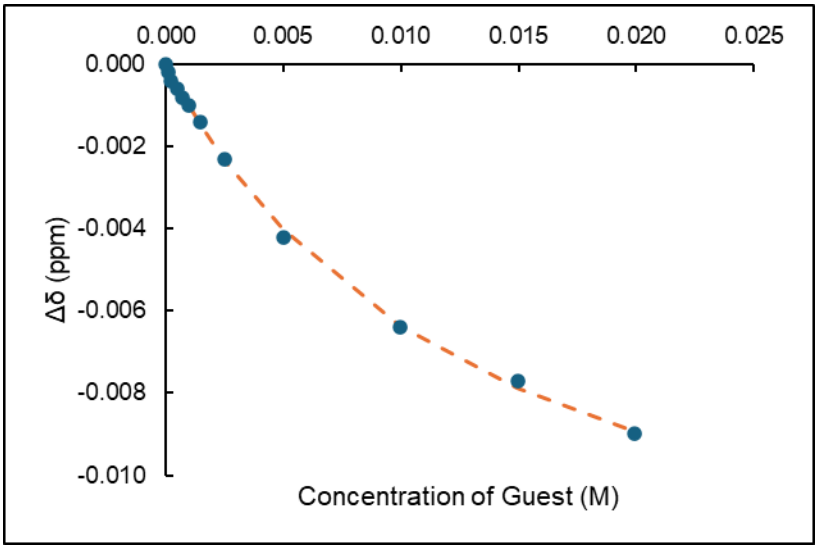
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.5032	0.0000
0.0011	0.0001	7.5027	-0.0005
0.0011	0.0002	7.5024	-0.0008
0.0011	0.0006	7.5021	-0.0011
0.0011	0.0008	7.5019	-0.0013
0.0011	0.0012	7.5010	-0.0022
0.0011	0.0017	7.4998	-0.0034
0.0011	0.0029	7.4986	-0.0046
0.0011	0.0058	7.4961	-0.0071
0.0011	0.0115	7.4914	-0.0118
0.0011	0.0173	7.4871	-0.0161
0.0011	0.0230	7.4841	-0.0191



The association constant K_a = 4.47 x 10^1 M^{-1}

16. Binding constant between Ph(Mes)IOTf and dibutyl amine in MeCN-d_3

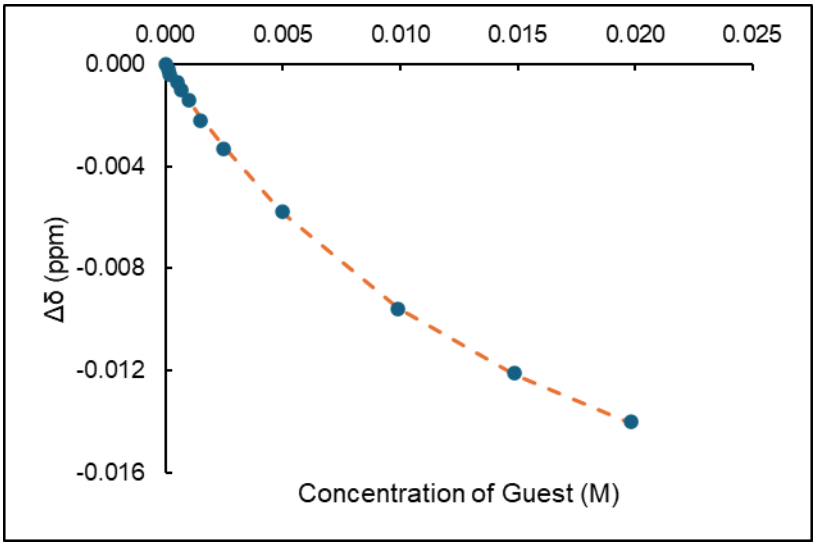
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5029	0.0000
0.0010	0.0001	7.5027	-0.0002
0.0010	0.0002	7.5025	-0.0004
0.0010	0.0005	7.5023	-0.0006
0.0010	0.0007	7.5021	-0.0008
0.0010	0.0010	7.5019	-0.0010
0.0010	0.0015	7.5015	-0.0014
0.0010	0.0025	7.5006	-0.0023
0.0010	0.0050	7.4987	-0.0042
0.0010	0.0100	7.4965	-0.0064
0.0010	0.0150	7.4952	-0.0077
0.0010	0.0199	7.4939	-0.0090



The association constant K_a = 7.96 x 10^1 M^{-1}

17. Binding constant between Ph(Mes)IOTf and butyl amine in MeCN-d_3

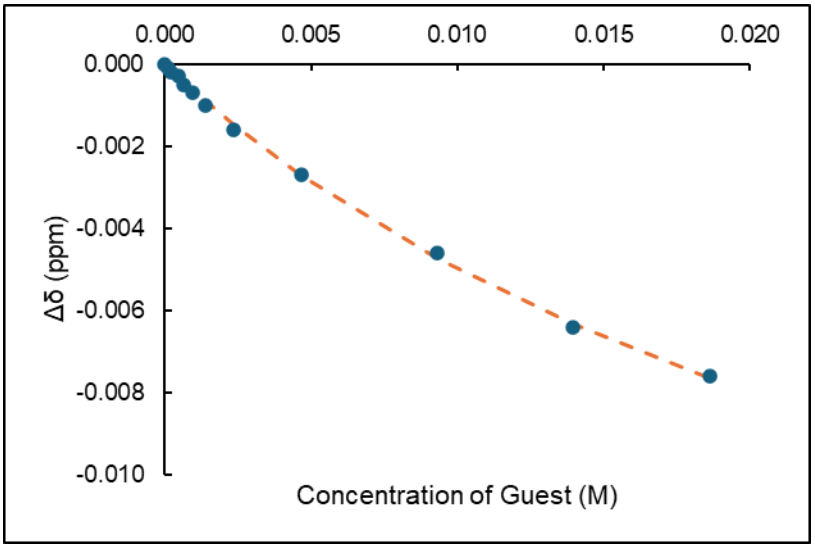
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.4999	0.0000
0.0010	0.0001	7.4997	-0.0002
0.0010	0.0002	7.4995	-0.0004
0.0010	0.0005	7.4992	-0.0007
0.0010	0.0007	7.4989	-0.0010
0.0010	0.0010	7.4985	-0.0014
0.0010	0.0015	7.4977	-0.0022
0.0010	0.0025	7.4966	-0.0033
0.0010	0.0050	7.4941	-0.0058
0.0010	0.0099	7.4903	-0.0096
0.0010	0.0149	7.4878	-0.0121
0.0010	0.0198	7.4859	-0.0140



The association constant K_a = 6.07 x 10^1 M^{-1}

18. Binding constant between Ph(Mes)IOTf and aniline in MeCN-d_3

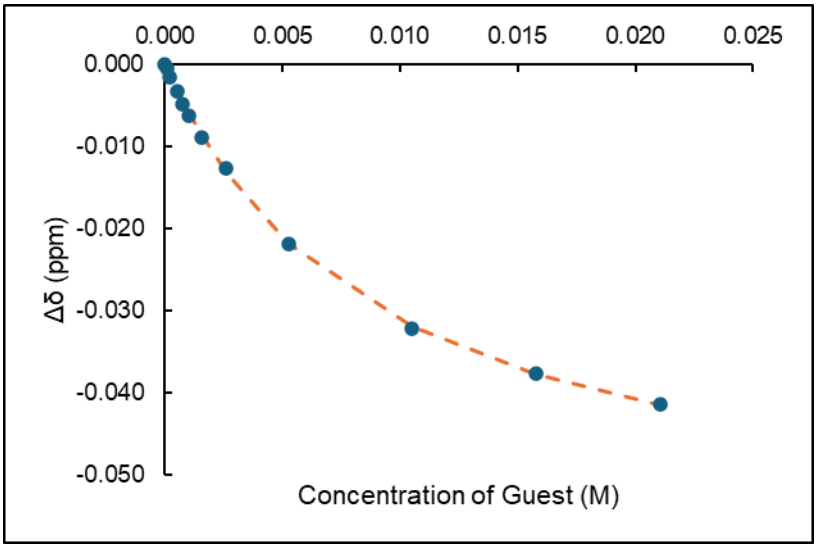
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0009	0.0000	7.4909	0.0000
0.0009	0.0001	7.4908	-0.0001
0.0009	0.0002	7.4907	-0.0002
0.0009	0.0005	7.4906	-0.0003
0.0009	0.0007	7.4904	-0.0005
0.0009	0.0009	7.4902	-0.0007
0.0009	0.0014	7.4899	-0.0010
0.0009	0.0023	7.4893	-0.0016
0.0009	0.0047	7.4882	-0.0027
0.0009	0.0093	7.4863	-0.0046
0.0009	0.0140	7.4845	-0.0064
0.0009	0.0186	7.4833	-0.0076



The association constant K_a = 3.61 x 10^1 M^{-1}

19. Binding constant between Ph(TMP)IOTf and DABCO in MeCN-d_3

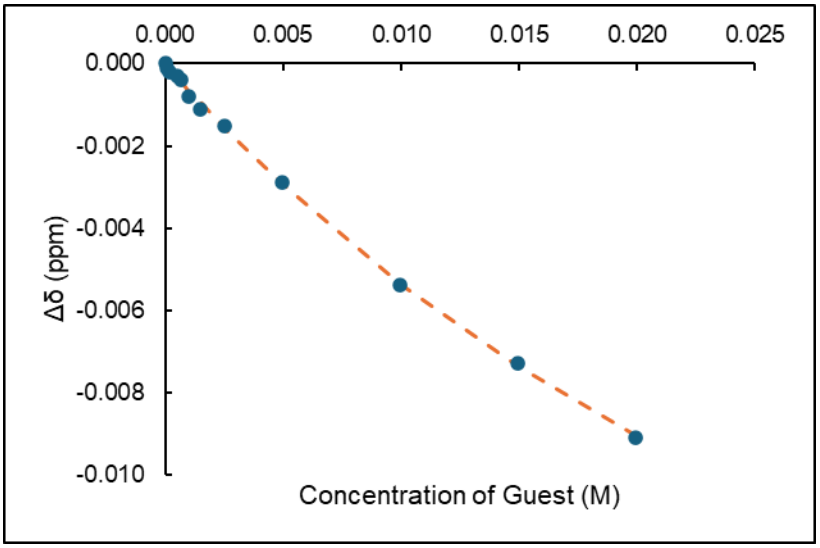
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.4771	0.0000
0.0011	0.0001	7.4767	-0.0004
0.0011	0.0002	7.4755	-0.0016
0.0011	0.0005	7.4739	-0.0032
0.0011	0.0007	7.4723	-0.0048
0.0011	0.0011	7.4709	-0.0062
0.0011	0.0016	7.4682	-0.0089
0.0011	0.0026	7.4645	-0.0126
0.0011	0.0053	7.4553	-0.0218
0.0011	0.0105	7.4449	-0.0322
0.0011	0.0158	7.4394	-0.0377
0.0011	0.0210	7.4356	-0.0415



The association constant K_a = 1.24 x 10^2 M^{-1}

20. Binding constant between Ph(TMP)IOTf and morpholine in MeCN-d_3

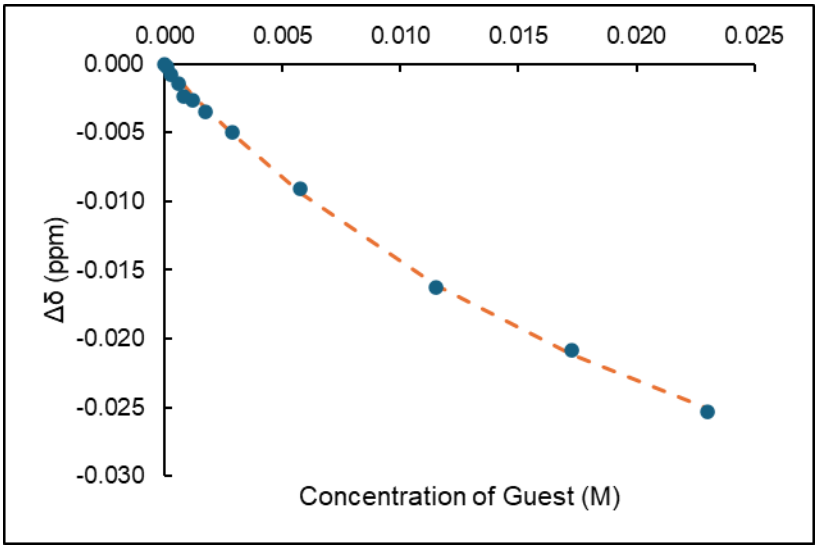
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.4667	0.0000
0.0011	0.0001	7.4666	-0.0001
0.0011	0.0002	7.4665	-0.0002
0.0011	0.0005	7.4664	-0.0003
0.0011	0.0007	7.4663	-0.0004
0.0011	0.0010	7.4659	-0.0008
0.0011	0.0015	7.4656	-0.0011
0.0011	0.0025	7.4652	-0.0015
0.0011	0.0050	7.4638	-0.0029
0.0011	0.0100	7.4613	-0.0054
0.0011	0.0150	7.4594	-0.0073
0.0011	0.0199	7.4576	-0.0091



The association constant K_a = 2.36 x 10^1 M^{-1}

21. Binding constant between Ph(TMP)IOTf and piperidine in MeCN-d_3

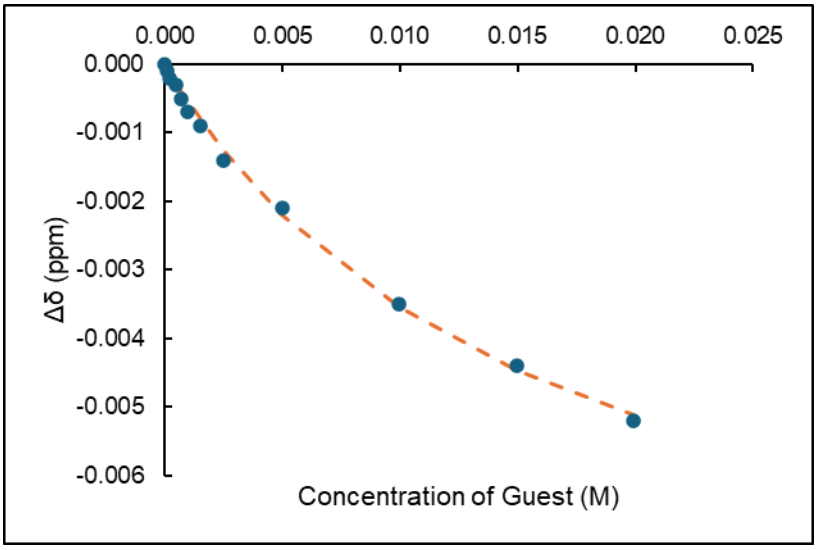
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.4667	0.0000
0.0010	0.0001	7.4665	-0.0002
0.0010	0.0002	7.4659	-0.0008
0.0010	0.0006	7.4653	-0.0014
0.0010	0.0008	7.4644	-0.0023
0.0010	0.0012	7.4641	-0.0026
0.0010	0.0017	7.4632	-0.0035
0.0010	0.0029	7.4617	-0.0050
0.0010	0.0058	7.4576	-0.0091
0.0010	0.0115	7.4504	-0.0163
0.0010	0.0173	7.4459	-0.0208
0.0010	0.0230	7.4414	-0.0253



The association constant K_a = 3.67 x 10^1 M^{-1}

22. Binding constant between Ph(TMP)IOTf and dibutyl amine in MeCN-d_3

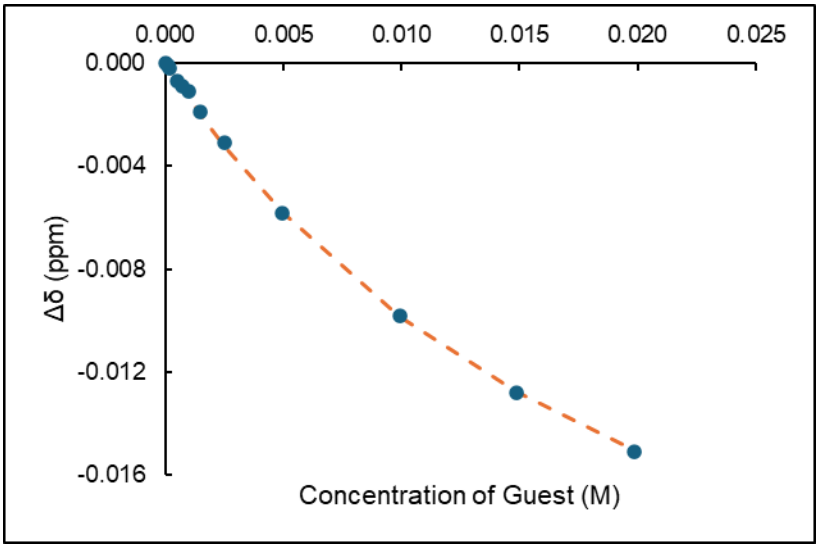
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.4766	0.0000
0.0011	0.0001	7.4765	-0.0001
0.0011	0.0002	7.4764	-0.0002
0.0011	0.0005	7.4763	-0.0003
0.0011	0.0007	7.4761	-0.0005
0.0011	0.0010	7.4759	-0.0007
0.0011	0.0015	7.4757	-0.0009
0.0011	0.0025	7.4752	-0.0014
0.0011	0.0050	7.4745	-0.0021
0.0011	0.0100	7.4731	-0.0035
0.0011	0.0150	7.4722	-0.0044
0.0011	0.0199	7.4714	-0.0052



The association constant K_a = 6.85 x 10^1 M^{-1}

23. Binding constant between Ph(TMP)IOTf and butyl amine in MeCN-d_3

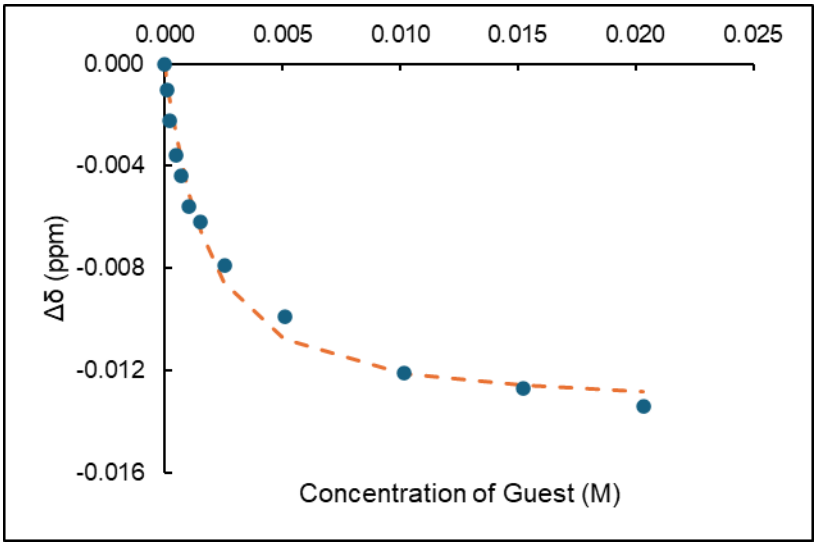
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.4765	0.0000
0.0011	0.0001	7.4764	-0.0001
0.0011	0.0002	7.4763	-0.0002
0.0011	0.0005	7.4758	-0.0007
0.0011	0.0007	7.4756	-0.0009
0.0011	0.0010	7.4754	-0.0011
0.0011	0.0015	7.4746	-0.0019
0.0011	0.0025	7.4734	-0.0031
0.0011	0.0050	7.4707	-0.0058
0.0011	0.0099	7.4667	-0.0098
0.0011	0.0149	7.4637	-0.0128
0.0011	0.0198	7.4614	-0.0151



The association constant K_a = 4.77 x 10^1 M^{-1}

24. Binding constant between Ph(DMIX)IOTf and DABCO in MeCN-d_3

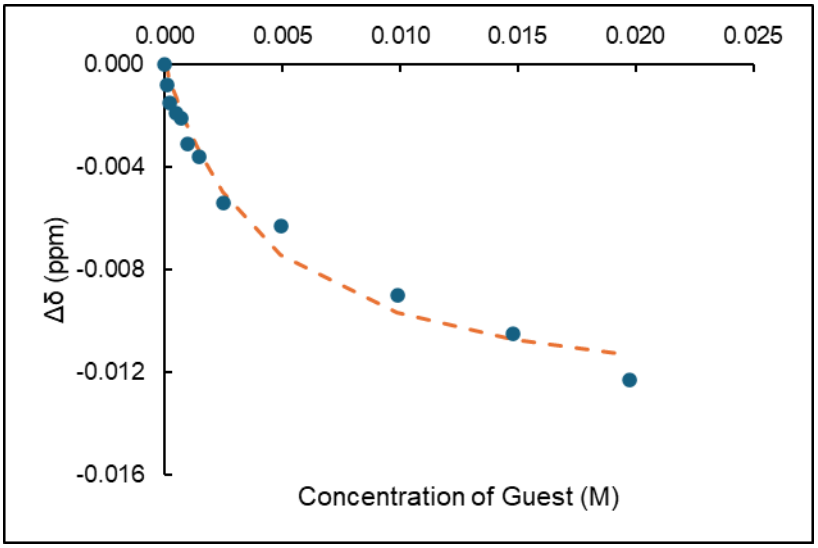
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5474	0.0000
0.0010	0.0001	7.5464	-0.0010
0.0010	0.0002	7.5452	-0.0022
0.0010	0.0005	7.5438	-0.0036
0.0010	0.0007	7.5430	-0.0044
0.0010	0.0010	7.5418	-0.0056
0.0010	0.0015	7.5412	-0.0062
0.0010	0.0025	7.5395	-0.0079
0.0010	0.0051	7.5375	-0.0099
0.0010	0.0102	7.5353	-0.0121
0.0010	0.0152	7.5347	-0.0127
0.0010	0.0203	7.5340	-0.0134



The association constant K_a = 9.20 x 10^2 M^{-1}

25. Binding constant between Ph(DMIX)IOTf and morpholine in MeCN-d_3

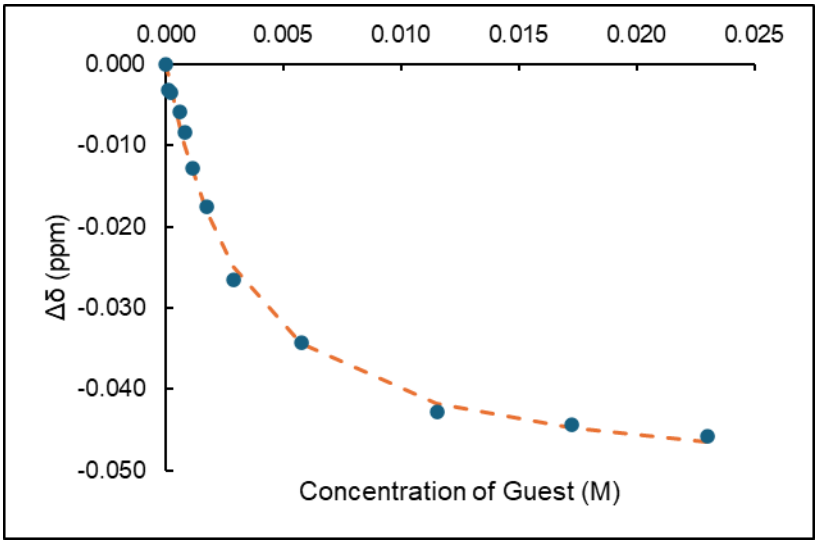
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5494	0.0000
0.0010	0.0001	7.5486	-0.0008
0.0010	0.0002	7.5479	-0.0015
0.0010	0.0005	7.5475	-0.0019
0.0010	0.0007	7.5473	-0.0021
0.0010	0.0010	7.5463	-0.0031
0.0010	0.0015	7.5458	-0.0036
0.0010	0.0025	7.5440	-0.0054
0.0010	0.0049	7.5431	-0.0063
0.0010	0.0099	7.5404	-0.0090
0.0010	0.0148	7.5389	-0.0105
0.0010	0.0197	7.5371	-0.0123



The association constant K_a = 2.80 x 10^2 M^{-1}

26. Binding constant between Ph(DMIX)IOTf and piperidine in MeCN-d_3

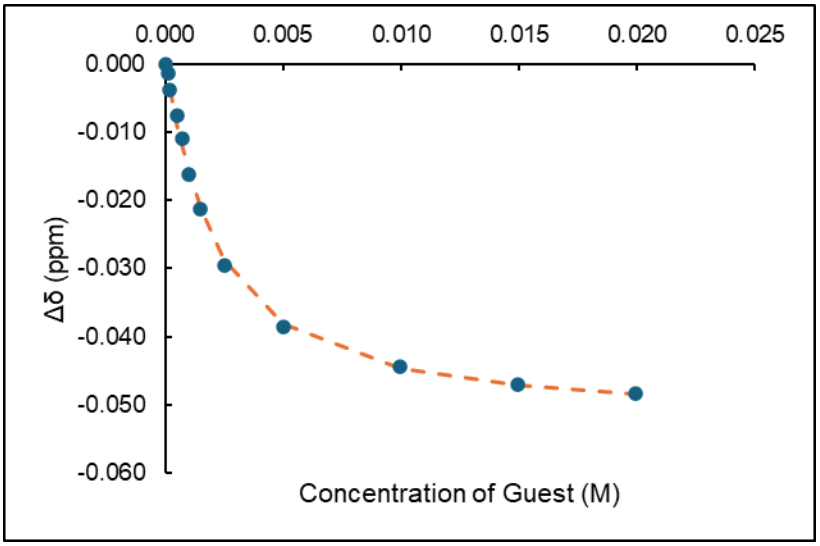
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5487	0.0000
0.0010	0.0001	7.5455	-0.0032
0.0010	0.0002	7.5452	-0.0035
0.0010	0.0006	7.5429	-0.0058
0.0010	0.0008	7.5403	-0.0084
0.0010	0.0012	7.5359	-0.0128
0.0010	0.0017	7.5312	-0.0175
0.0010	0.0029	7.5222	-0.0265
0.0010	0.0058	7.5144	-0.0343
0.0010	0.0115	7.5059	-0.0428
0.0010	0.0173	7.5044	-0.0443
0.0010	0.0230	7.5029	-0.0458



The association constant K_a = 3.82 x 10^2 M^{-1}

27. Binding constant between Ph(DMIX)IOTf and dibutyl amine in MeCN-d_3

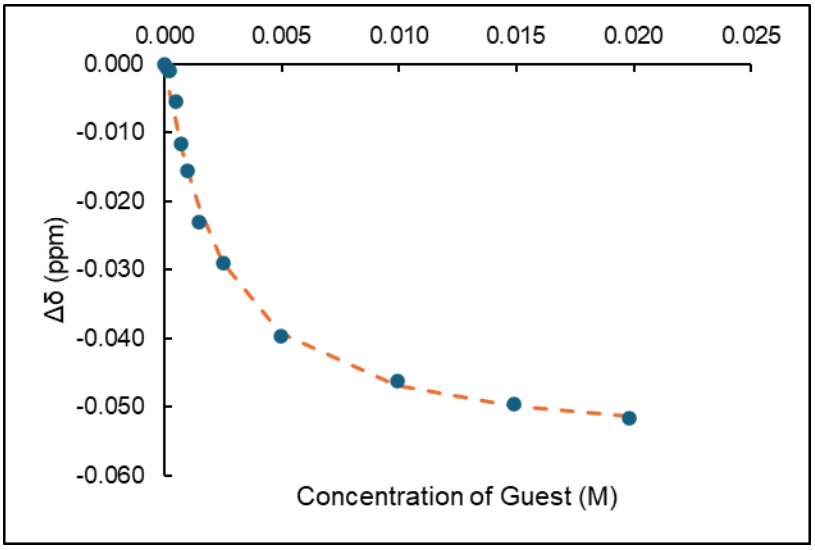
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5487	0.0000
0.0010	0.0001	7.5473	-0.0014
0.0010	0.0002	7.5449	-0.0038
0.0010	0.0005	7.5412	-0.0075
0.0010	0.0007	7.5378	-0.0109
0.0010	0.0010	7.5324	-0.0163
0.0010	0.0015	7.5275	-0.0212
0.0010	0.0025	7.5191	-0.0296
0.0010	0.0050	7.5102	-0.0385
0.0010	0.0100	7.5044	-0.0443
0.0010	0.0150	7.5016	-0.0471
0.0010	0.0199	7.5003	-0.0484



The association constant K_a = 6.28 x 10^2 M^{-1}

28. Binding constant between Ph(DMIX)IOTf and butyl amine in MeCN-d_3

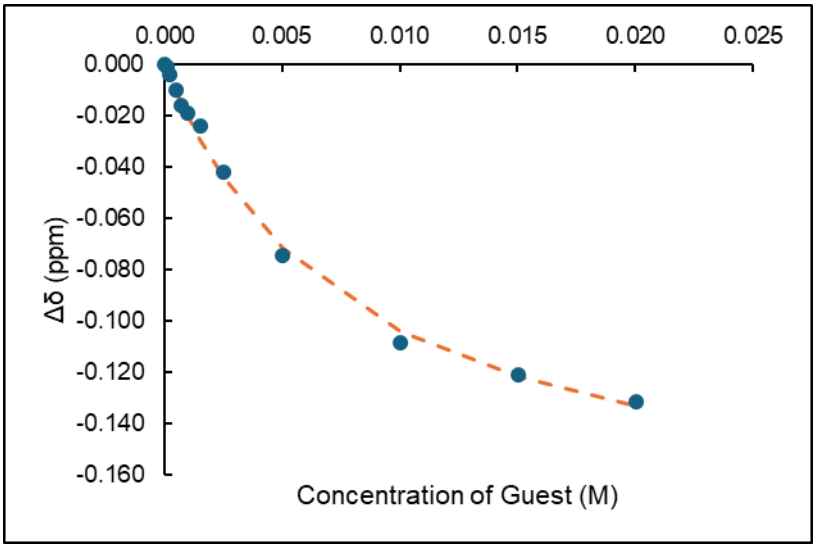
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5480	0.0000
0.0010	0.0001	7.5475	-0.0005
0.0010	0.0002	7.5471	-0.0009
0.0010	0.0005	7.5425	-0.0055
0.0010	0.0007	7.5364	-0.0116
0.0010	0.0010	7.5324	-0.0156
0.0010	0.0015	7.5249	-0.0231
0.0010	0.0025	7.5189	-0.0291
0.0010	0.0050	7.5084	-0.0396
0.0010	0.0099	7.5017	-0.0463
0.0010	0.0149	7.4984	-0.0496
0.0010	0.0198	7.4964	-0.0516



The association constant K_a = 5.38 x 10^2 M^{-1}

29. Binding constant between Ph_2IOTf and DABCO in DCM-d_2

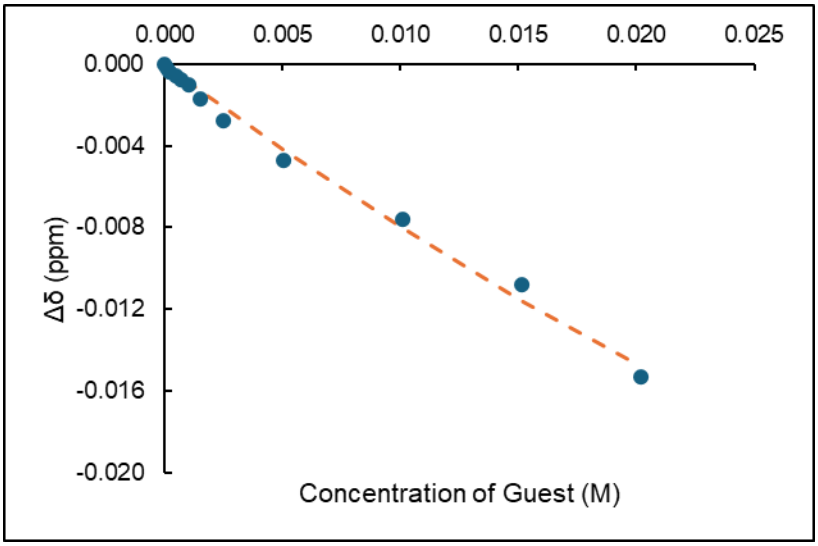
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5332	0.0000
0.0010	0.0001	7.5322	-0.0010
0.0010	0.0002	7.5291	-0.0041
0.0010	0.0005	7.5230	-0.0102
0.0010	0.0007	7.5171	-0.0161
0.0010	0.0010	7.5140	-0.0192
0.0010	0.0015	7.5091	-0.0241
0.0010	0.0025	7.4912	-0.0420
0.0010	0.0050	7.4588	-0.0744
0.0010	0.0100	7.4248	-0.1084
0.0010	0.0150	7.4122	-0.1210
0.0010	0.0201	7.4018	-0.1314



The association constant K_a = 1.40 x 10^2 M^{-1}

30. Binding constant between Ph_2IOTf and morpholine in DCM-d_2

[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5329	0.0000
0.0010	0.0001	7.5327	-0.0002
0.0010	0.0002	7.5325	-0.0004
0.0010	0.0005	7.5323	-0.0006
0.0010	0.0007	7.5321	-0.0008
0.0010	0.0010	7.5319	-0.0010
0.0010	0.0015	7.5312	-0.0017
0.0010	0.0025	7.5301	-0.0028
0.0010	0.0050	7.5282	-0.0047
0.0010	0.0101	7.5253	-0.0076
0.0010	0.0151	7.5221	-0.0108
0.0010	0.0202	7.5176	-0.0153

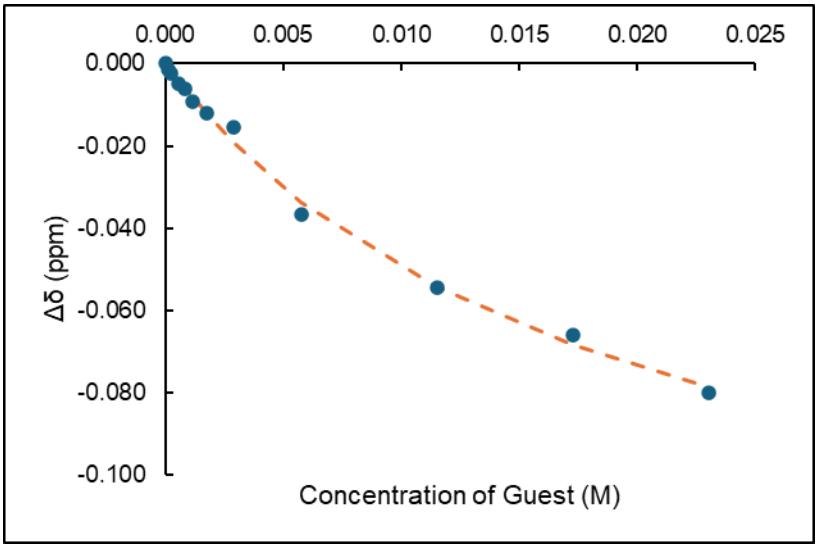


The association constant K_a = 9.68 M^{-1}

The association constant (K_a) calculated as the average of triplicate run = (1.28 ± 0.32) x 10^1 M^{-1}

31. Binding constant between Ph_2IOTf and piperidine in DCM-d_2

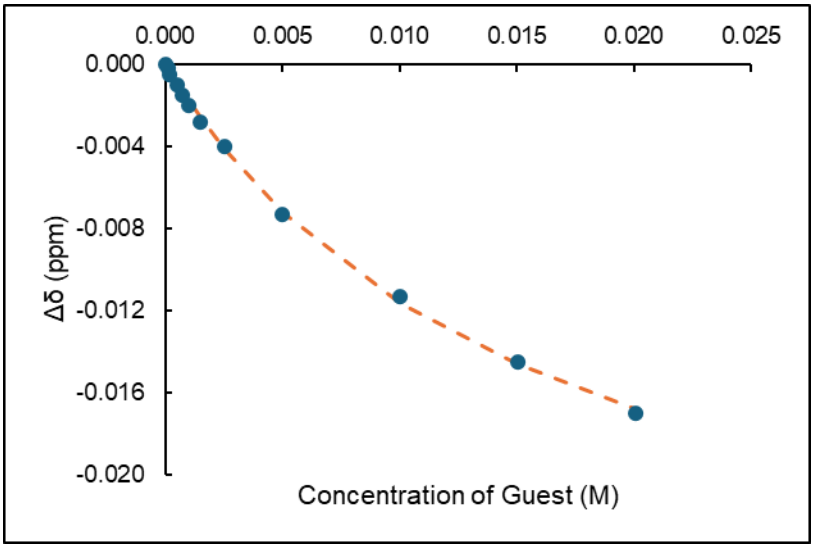
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5306	0.0000
0.0010	0.0001	7.5292	-0.0014
0.0010	0.0002	7.5281	-0.0025
0.0010	0.0006	7.5256	-0.0050
0.0010	0.0008	7.5244	-0.0062
0.0010	0.0012	7.5215	-0.0091
0.0010	0.0017	7.5187	-0.0119
0.0010	0.0029	7.5151	-0.0155
0.0010	0.0058	7.4940	-0.0366
0.0010	0.0115	7.4761	-0.0545
0.0010	0.0173	7.4647	-0.0659
0.0010	0.0230	7.4506	-0.0800



The association constant $K_a = 5.78 \times 10^1\ M^{-1}$

32. Binding constant between Ph_2IOTf and dibutyl amine in DCM-d_2

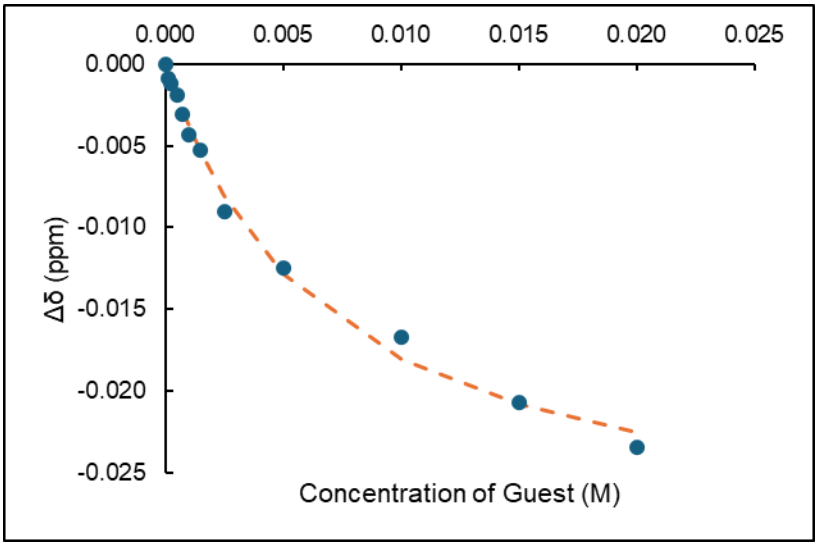
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5331	0.0000
0.0010	0.0001	7.5329	-0.0002
0.0010	0.0002	7.5326	-0.0005
0.0010	0.0005	7.5321	-0.0010
0.0010	0.0007	7.5316	-0.0015
0.0010	0.0010	7.5311	-0.0020
0.0010	0.0015	7.5303	-0.0028
0.0010	0.0025	7.5291	-0.0040
0.0010	0.0050	7.5258	-0.0073
0.0010	0.0100	7.5218	-0.0113
0.0010	0.0150	7.5186	-0.0145
0.0010	0.0201	7.5161	-0.0170



The association constant $K_a = 6.75 \times 10^1\ M^{-1}$

33. Binding constant between Ph_2IOTf and butyl amine in DCM-d_2

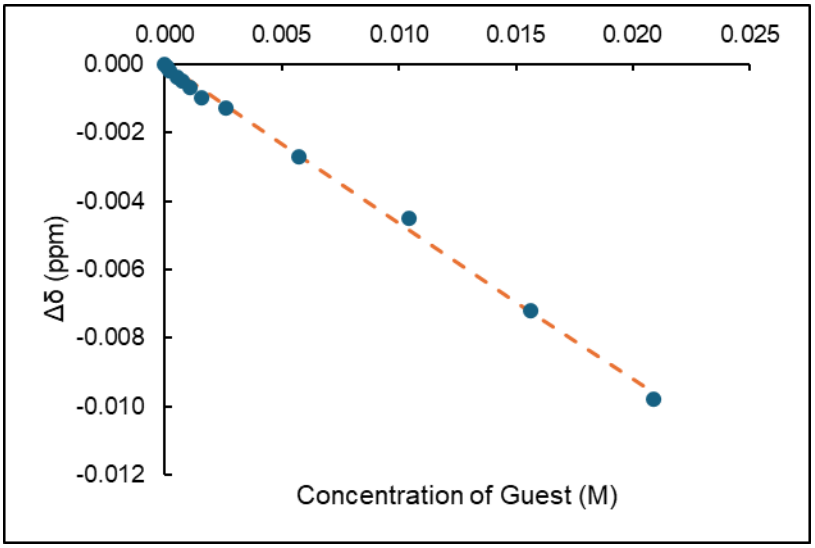
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.5332	0.0000
0.0010	0.0001	7.5323	-0.0009
0.0010	0.0002	7.5320	-0.0012
0.0010	0.0005	7.5313	-0.0019
0.0010	0.0007	7.5301	-0.0031
0.0010	0.0010	7.5289	-0.0043
0.0010	0.0015	7.5279	-0.0053
0.0010	0.0025	7.5242	-0.0090
0.0010	0.0050	7.5207	-0.0125
0.0010	0.0100	7.5165	-0.0167
0.0010	0.0150	7.5125	-0.0207
0.0010	0.0200	7.5098	-0.0234



The association constant K_a = 1.69 x 10^2 M^{-1}

34. Binding constant between Ph_2IOTf and aniline in DCM-d_2

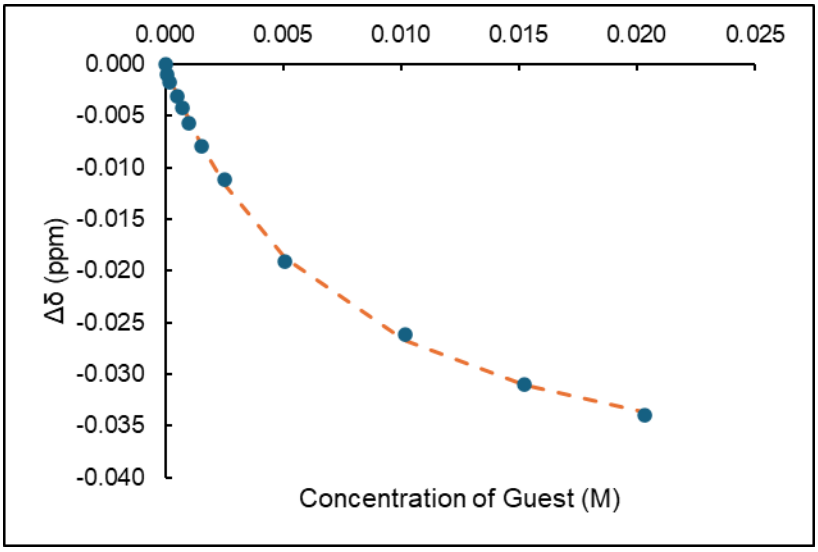
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0011	0.0000	7.5326	0.0000
0.0011	0.0001	7.5325	-0.0001
0.0011	0.0002	7.5324	-0.0002
0.0011	0.0005	7.5322	-0.0004
0.0011	0.0007	7.5321	-0.0005
0.0011	0.0010	7.5319	-0.0007
0.0011	0.0016	7.5316	-0.0010
0.0011	0.0026	7.5313	-0.0013
0.0011	0.0057	7.5299	-0.0027
0.0011	0.0104	7.5281	-0.0045
0.0011	0.0156	7.5254	-0.0072
0.0011	0.0209	7.5228	-0.0098



The association constant K_a = 1.54 M^{-1}

35. Binding constant between Ph_2IOTf and DABCO in acetone-d_6

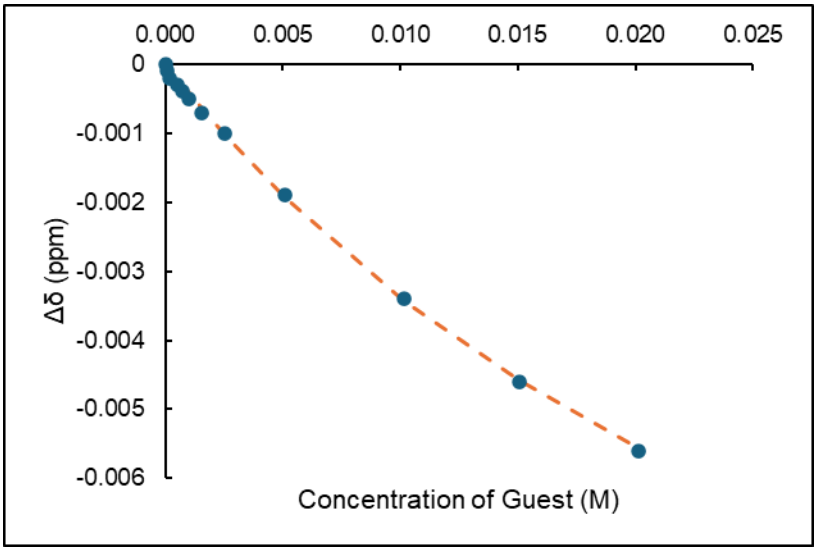
[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.6414	0.0000
0.0010	0.0001	7.6404	-0.0010
0.0010	0.0002	7.6397	-0.0017
0.0010	0.0005	7.6383	-0.0031
0.0010	0.0007	7.6372	-0.0042
0.0010	0.0010	7.6357	-0.0057
0.0010	0.0015	7.6335	-0.0079
0.0010	0.0025	7.6302	-0.0112
0.0010	0.0051	7.6223	-0.0191
0.0010	0.0102	7.6152	-0.0262
0.0010	0.0152	7.6104	-0.0310
0.0010	0.0203	7.6074	-0.0340



The association constant K_a = 1.56 x 10^2 M^{-1}

36. Binding constant between Ph_2IOTf and morpholine in acetone-d_6

[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
0.0010	0.0000	7.6385	0.0000
0.0010	0.0001	7.6384	-0.0001
0.0010	0.0002	7.6383	-0.0002
0.0010	0.0005	7.6382	-0.0003
0.0010	0.0007	7.6381	-0.0004
0.0010	0.0010	7.6380	-0.0005
0.0010	0.0015	7.6378	-0.0007
0.0010	0.0025	7.6375	-0.0010
0.0010	0.0051	7.6366	-0.0019
0.0010	0.0101	7.6351	-0.0034
0.0010	0.0150	7.6339	-0.0046
0.0010	0.0201	7.6329	-0.0056



The association constant $K_a = 2.99 \times 10^1\ M^{-1}$

Correlation Plots:

$$logK_a = s_I LA_I + LB_I \quad (equ.1)$$

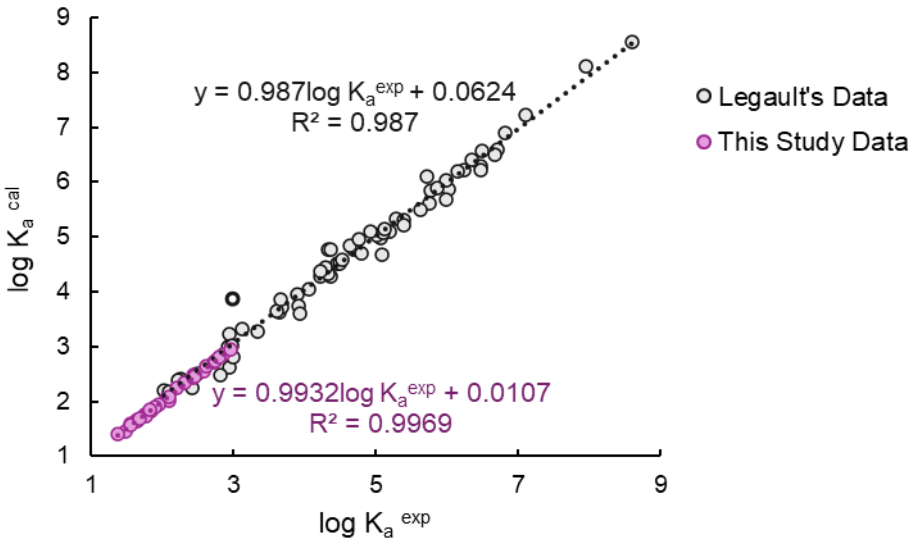


Fig S2: Comparative correlation plot of observed and calculated log K_a with (a) Legault's dataset[12] and (b) dataset from this study with the model developed by Legault based on equ. 1

Amines	LB	N	pKa(H)
Quinuclidine	2.25	20.54	9.80
DABCO	2.24	18.80	8.90
Piperidine	1.85	17.35	10.90
Morpholine	1.66	15.65	9.20
Dibutyl amine	2.09	14.51	-
Butyl amine	1.97	15.11	11.10
4-aminopyridine	2.21	14.99	-
Aniline	1.76	12.64	3.80

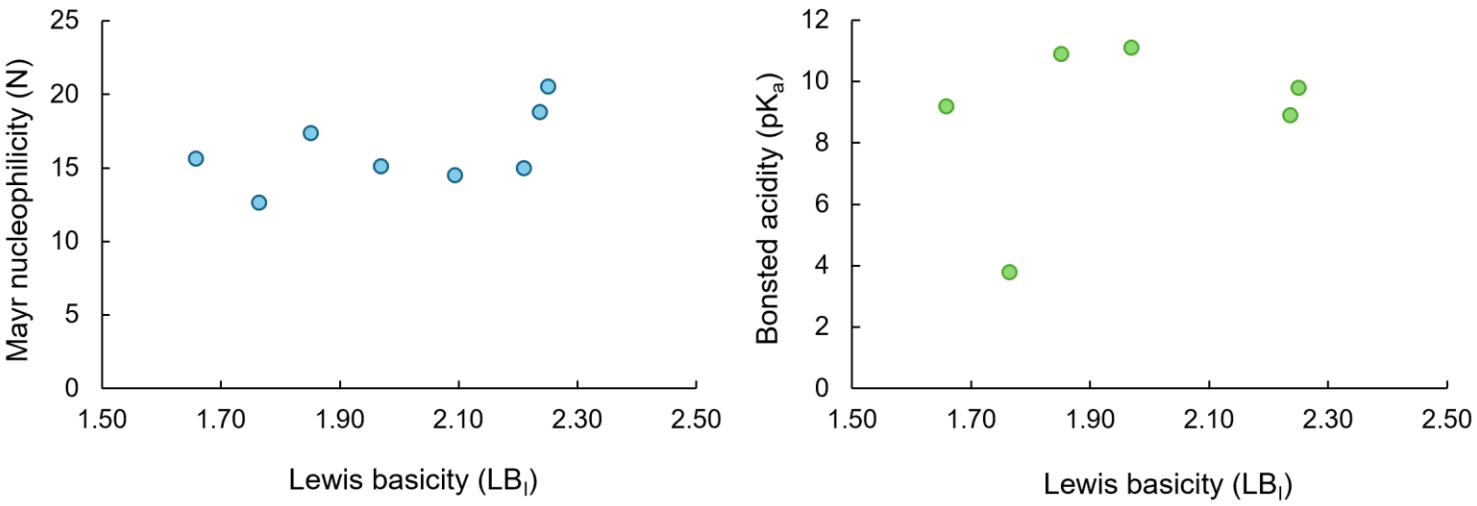
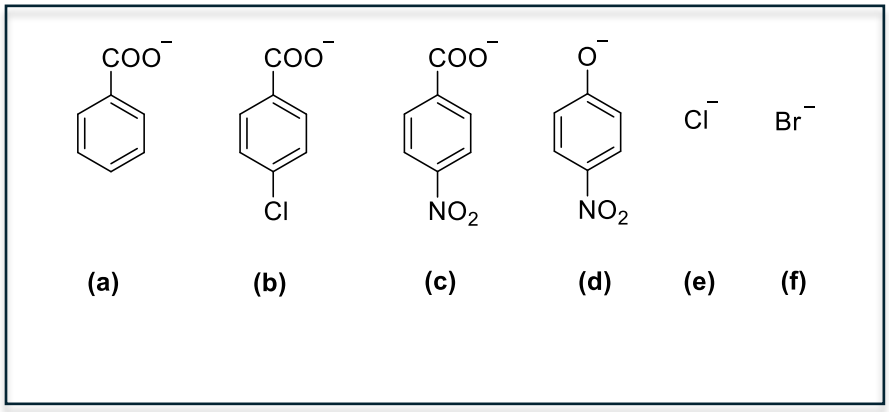


Fig S3: Correlation plot of Lewis basicity (LB_1) with (a) Mayr Nucleophilicity (N) and (b) Bronsted acidity



Lewis bases	LB_I	pK_a	pK_a
a	5.33	11.10	4.20
b	4.78	-	3.99
c	4.52	-	3.44
d	3.96	10.80	7.10
e	4.71	1.80	-8.00
f	4.29	0.90	-9.00

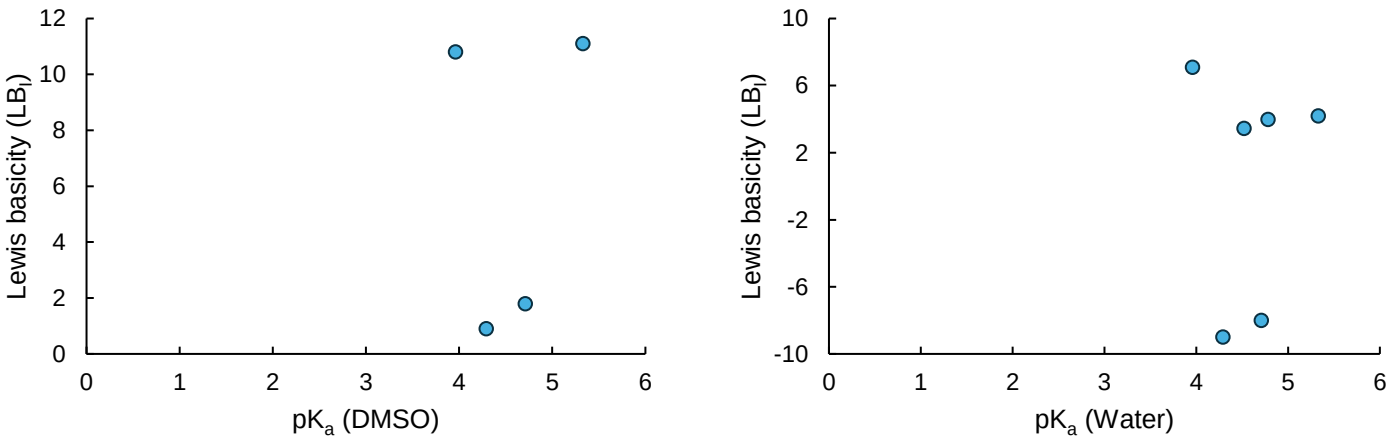


Fig S4: Correlation plot of Lewis basicity (LB_I) with (a) pK_a in DMSO and (b) pK_a in Water

The reference Lewis bases, and their corresponding Lewis basicity (LB_I) values used in this plot are taken from Legault's iodonium Lewis acidity scale.

Amines	Solvent	E^t_n	K_a
DABCO	DCM-d_2	3.10	1.40×10^2
	Acetone-d_6	5.10	1.56×10^2
	MeCN-d_3	5.80	1.64×10^2
Morpholine	DCM-d_2	3.10	9.68
	Acetone-d_6	5.10	2.99×10^1
	MeCN-d_3	5.80	4.38×10^1

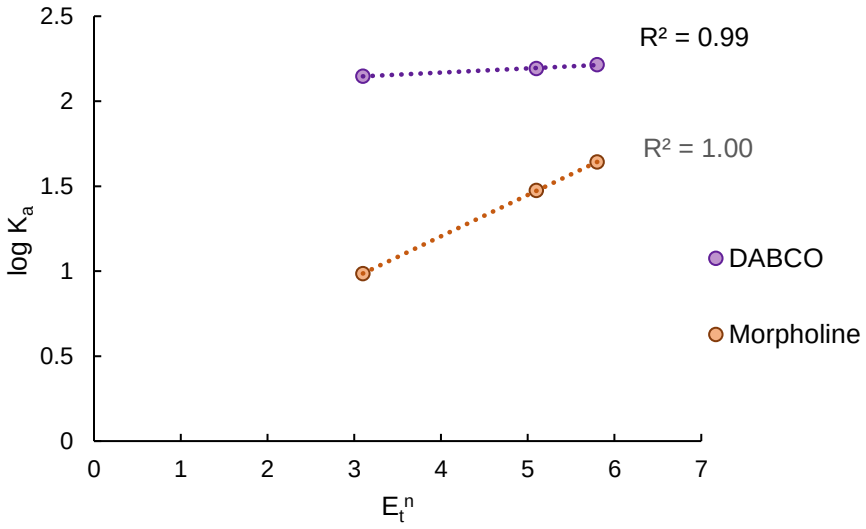


Fig S5: Correlation plot of log K_a of amines (5 and 6) with iodonium (1) in different solvent polarity (E_t^n)

The equilibrium constants (K_a) used in this plot are from this study.

Control study:

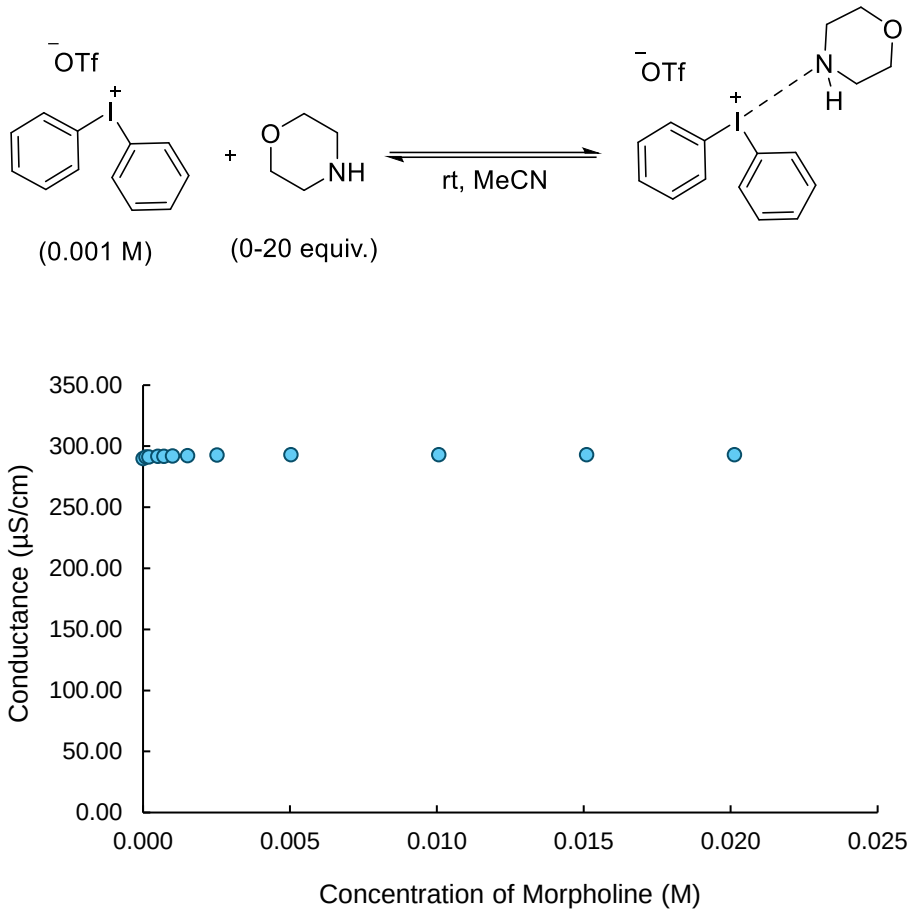


Fig S6: Conductivity analysis of morpholine binding to diphenyliodonium triflate in MeCN

There was no significant change in conductivity observed upon the addition of increasing equivalents of morpholine to a 0.001 M solution of Ph2IOTf in MeCN.

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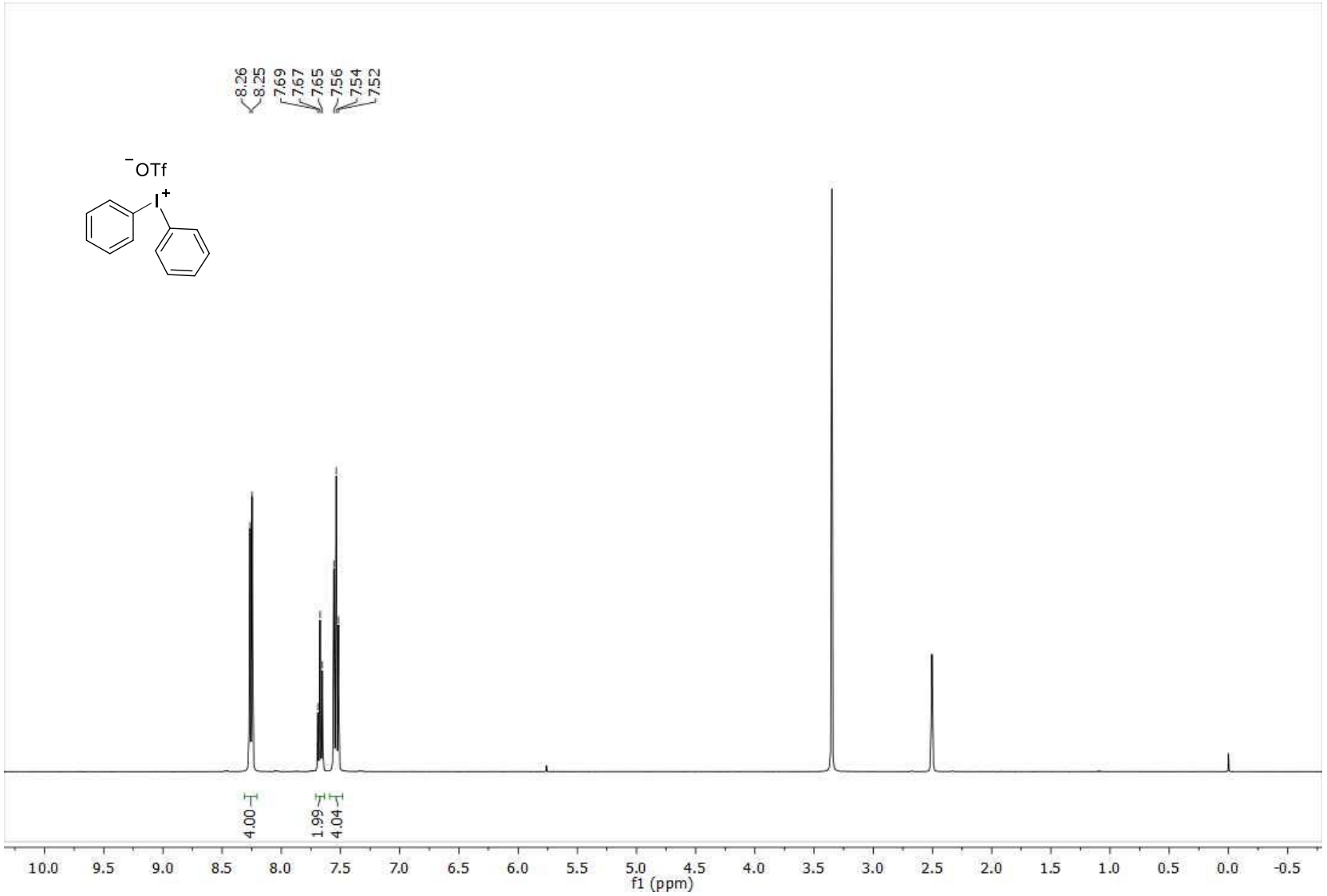
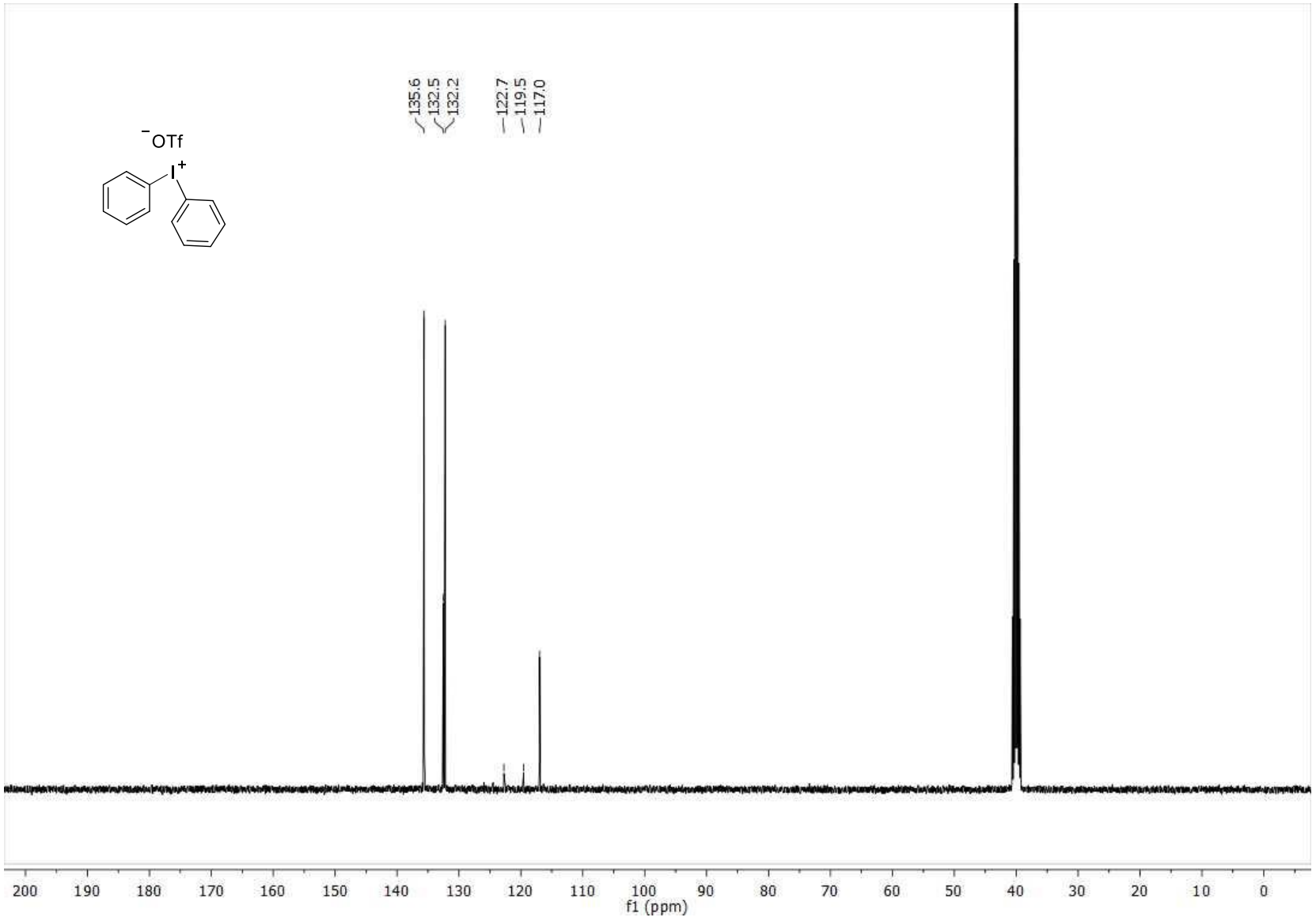
^{1}H,$^{13}C\{^{1}H\}$, $^{19}F\ \{^{1}H\}$ NMR spectra:

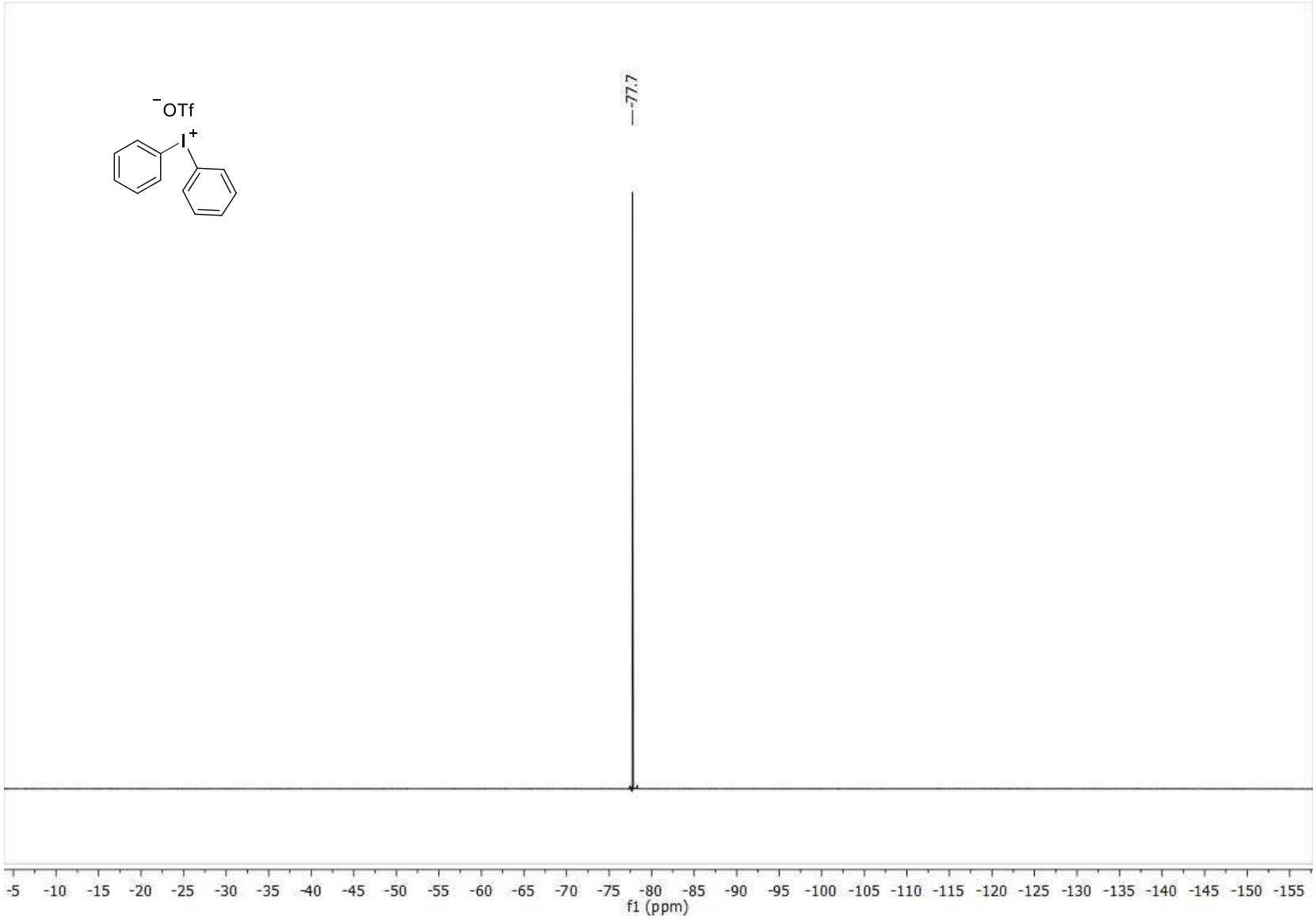
^{1}H NMR of compound **1** at 400 MHz in DMSO-d_6 at 298 K



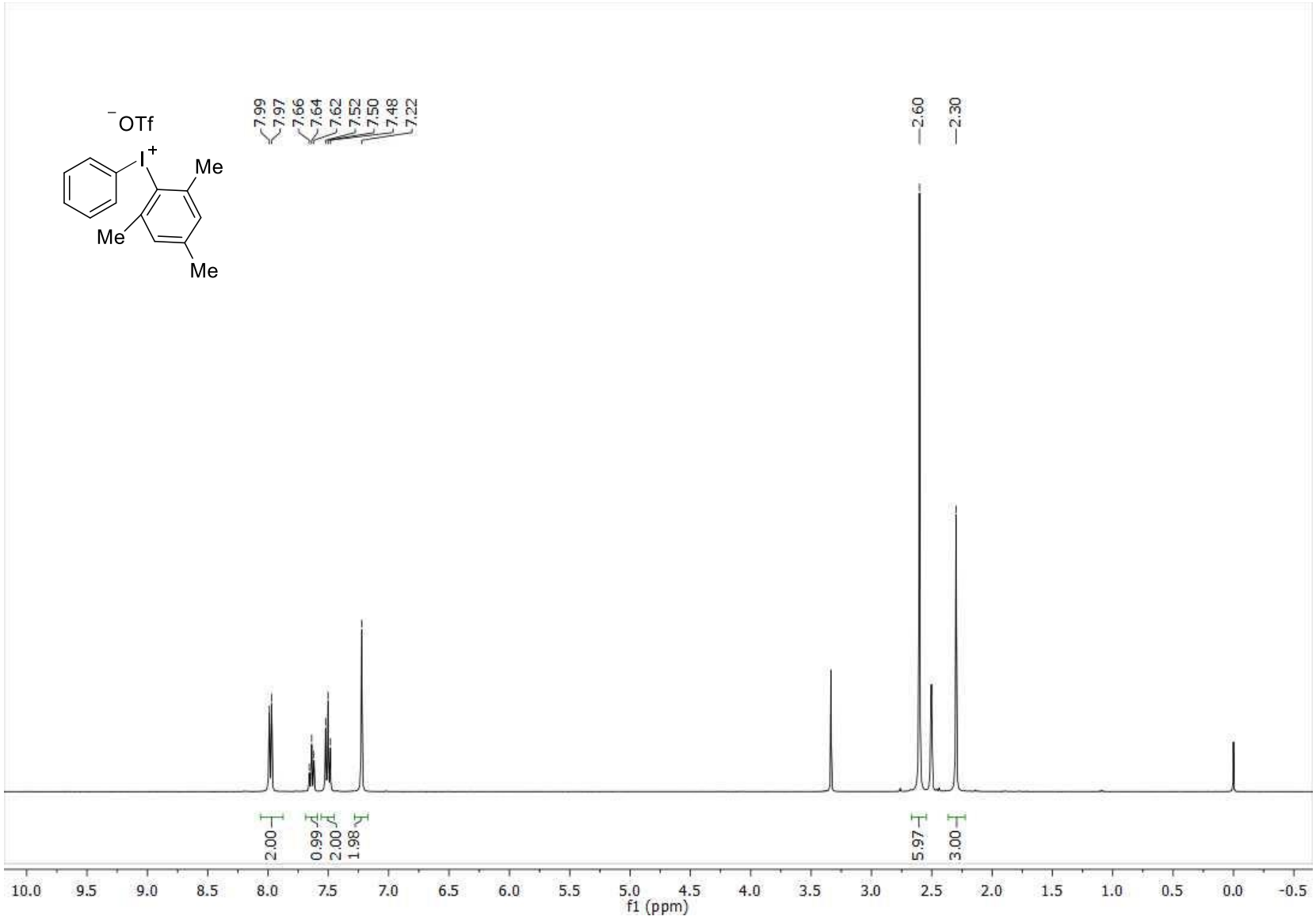
$^{13}C\{^{1}H\}$ NMR of compound **1** at 101 MHz in DMSO-d_6 at 298 K



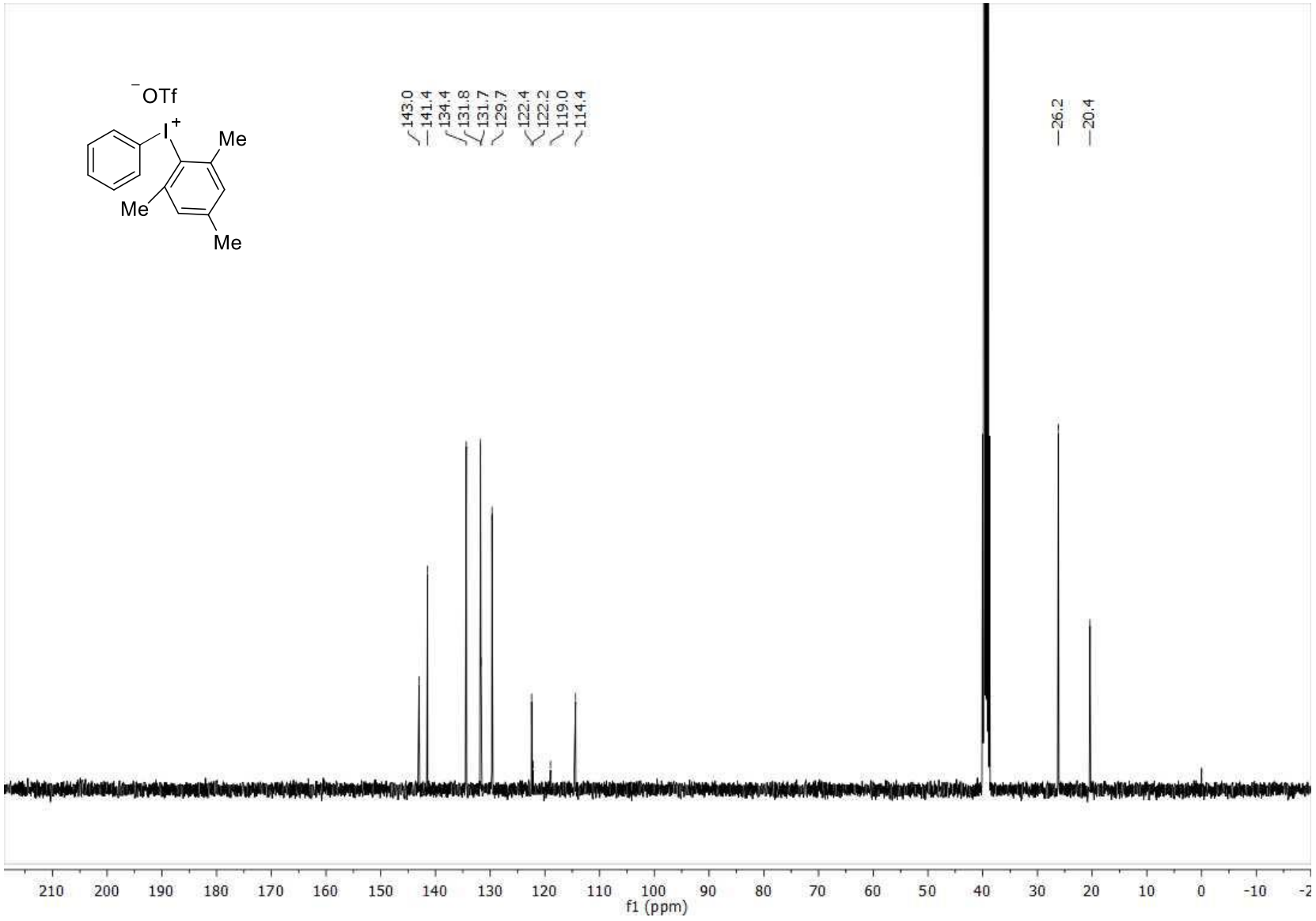
$^{19}F\{^{1}H\}$ NMR of compound **1** at 376 MHz in DMSO-d_6 at 298 K



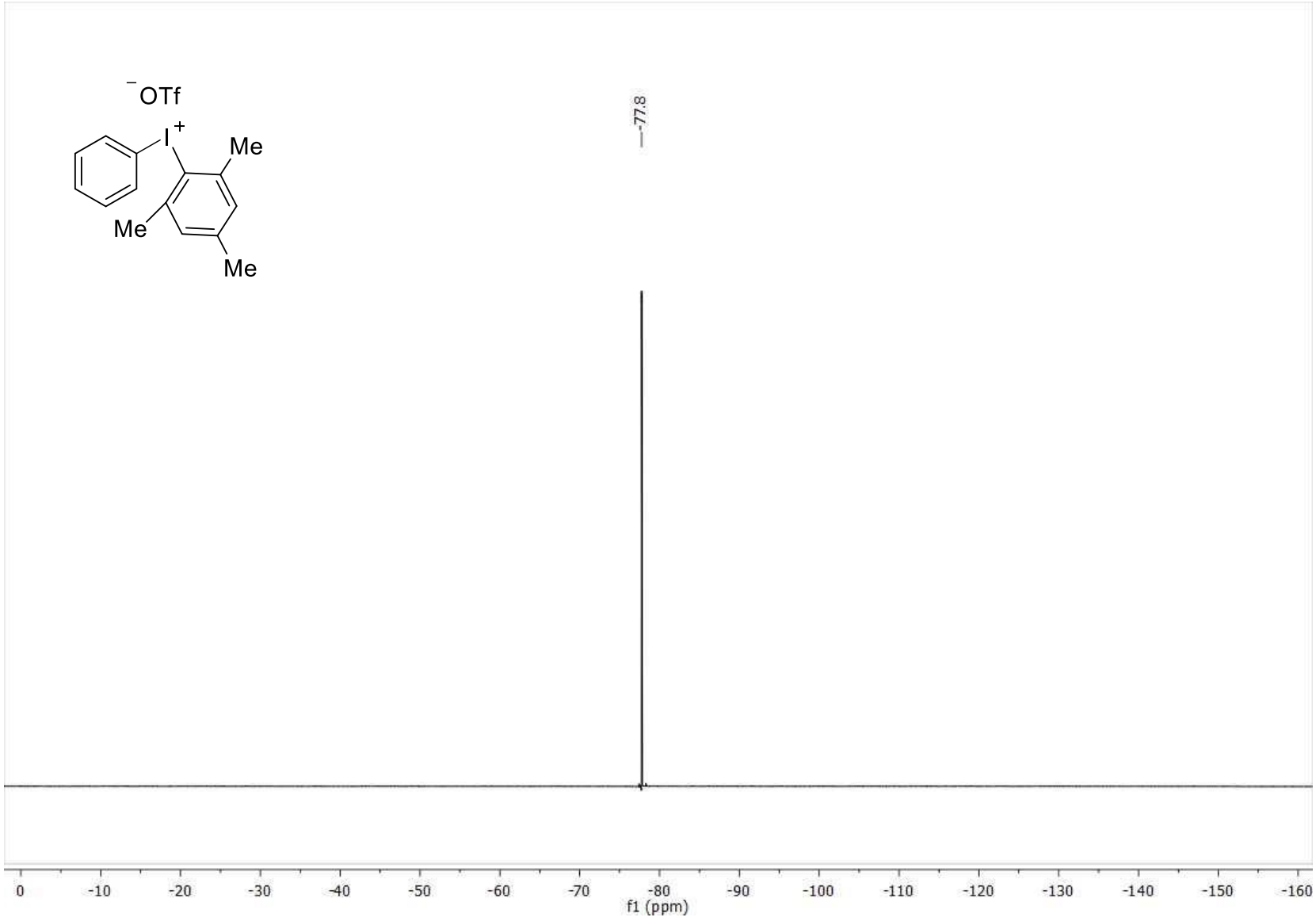
^{1}H NMR of compound **3** at 400 MHz in DMSO-d_6 at 298 K



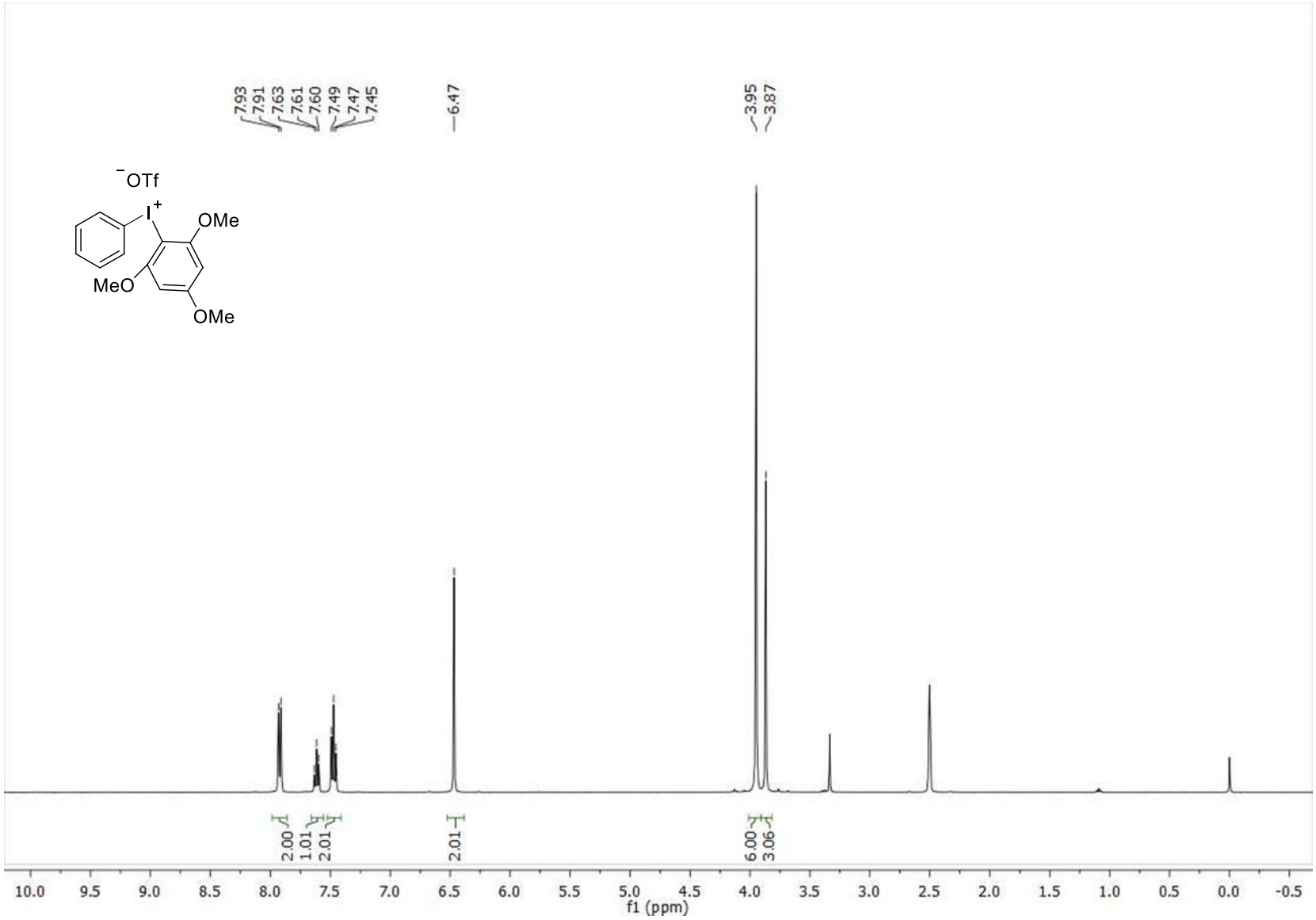
$^{13}C\{^{1}H\}$ NMR of compound **3** at 101 MHz in DMSO-d_6 at 298 K



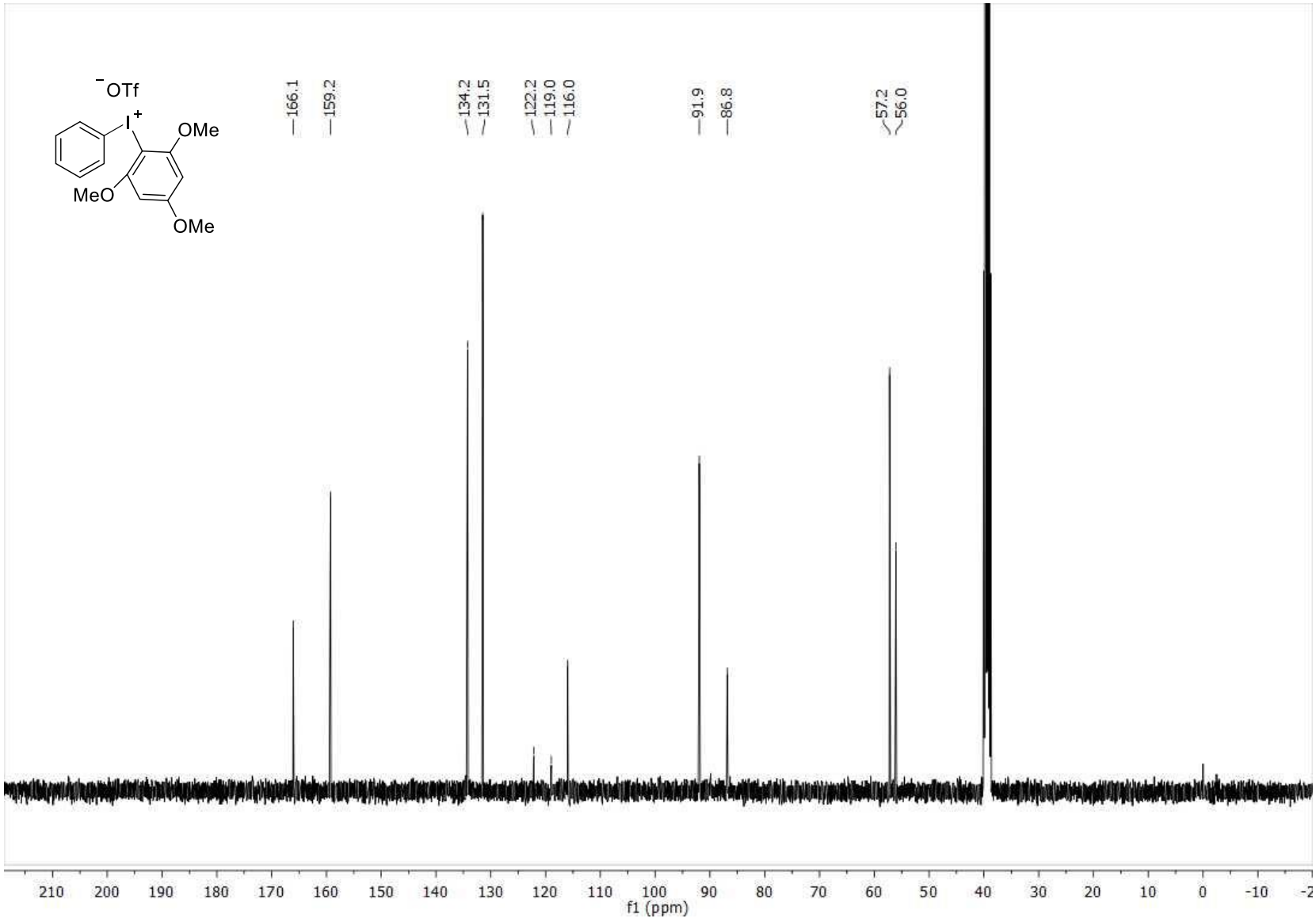
$^{19}F\{^{1}H\}$ NMR of compound **3** at 376 MHz in DMSO-d_6 at 298 K



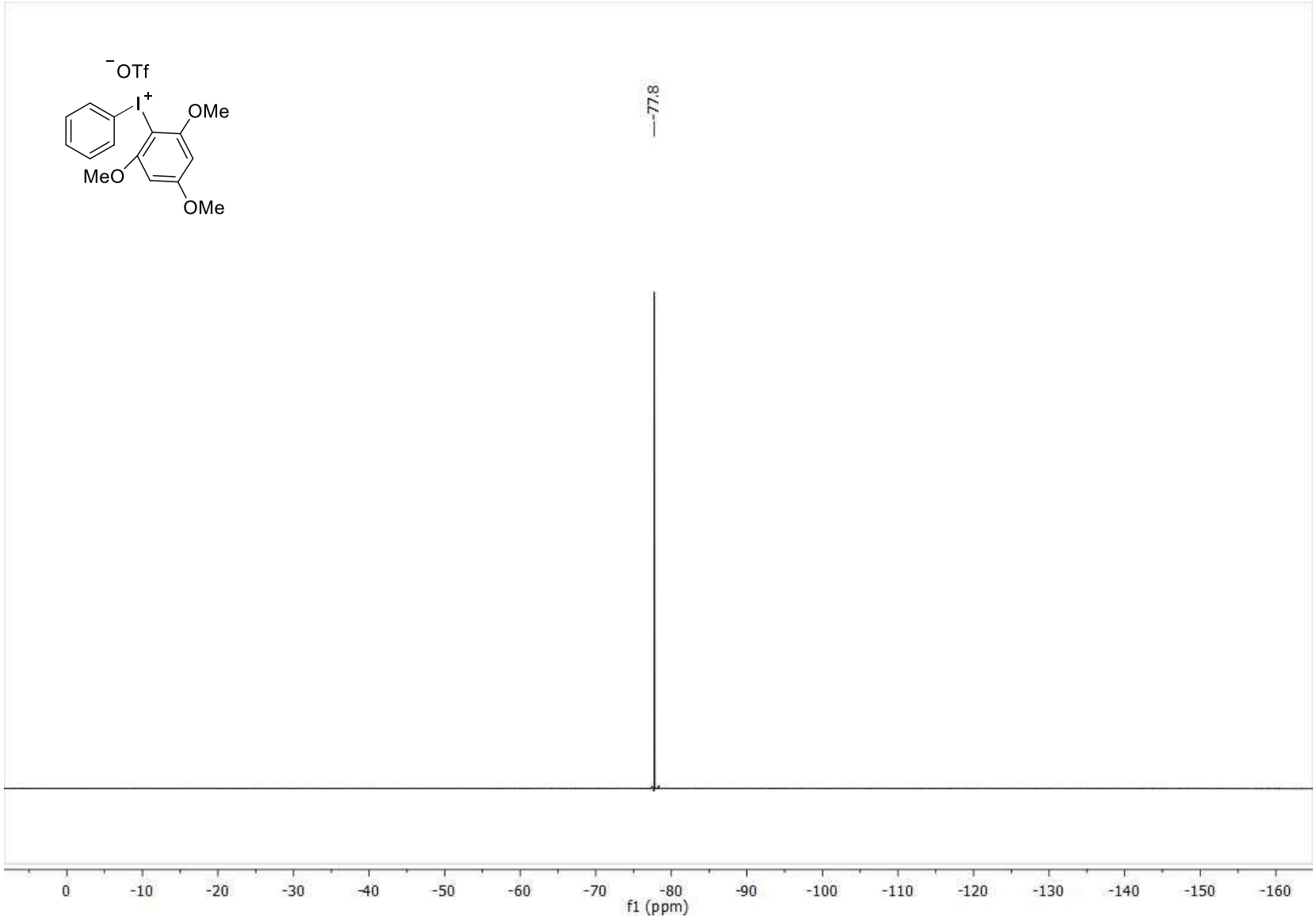
^{1}H NMR of compound **11** at 400 MHz in DMSO-d_6 at 298 K



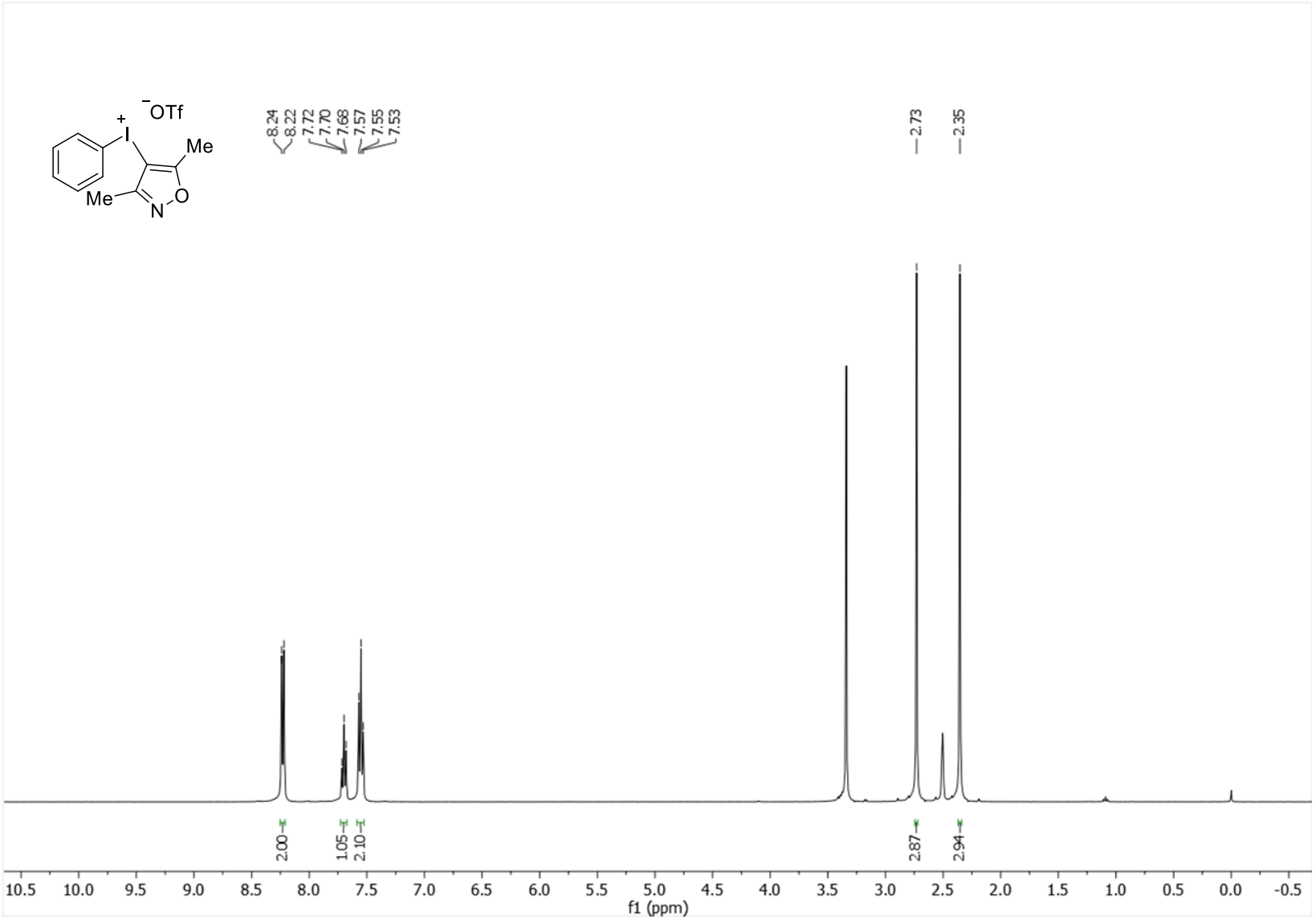
$^{13}C\{^{1}H\}$ NMR of compound **11** at 101 MHz in DMSO-d_6 at 298 K



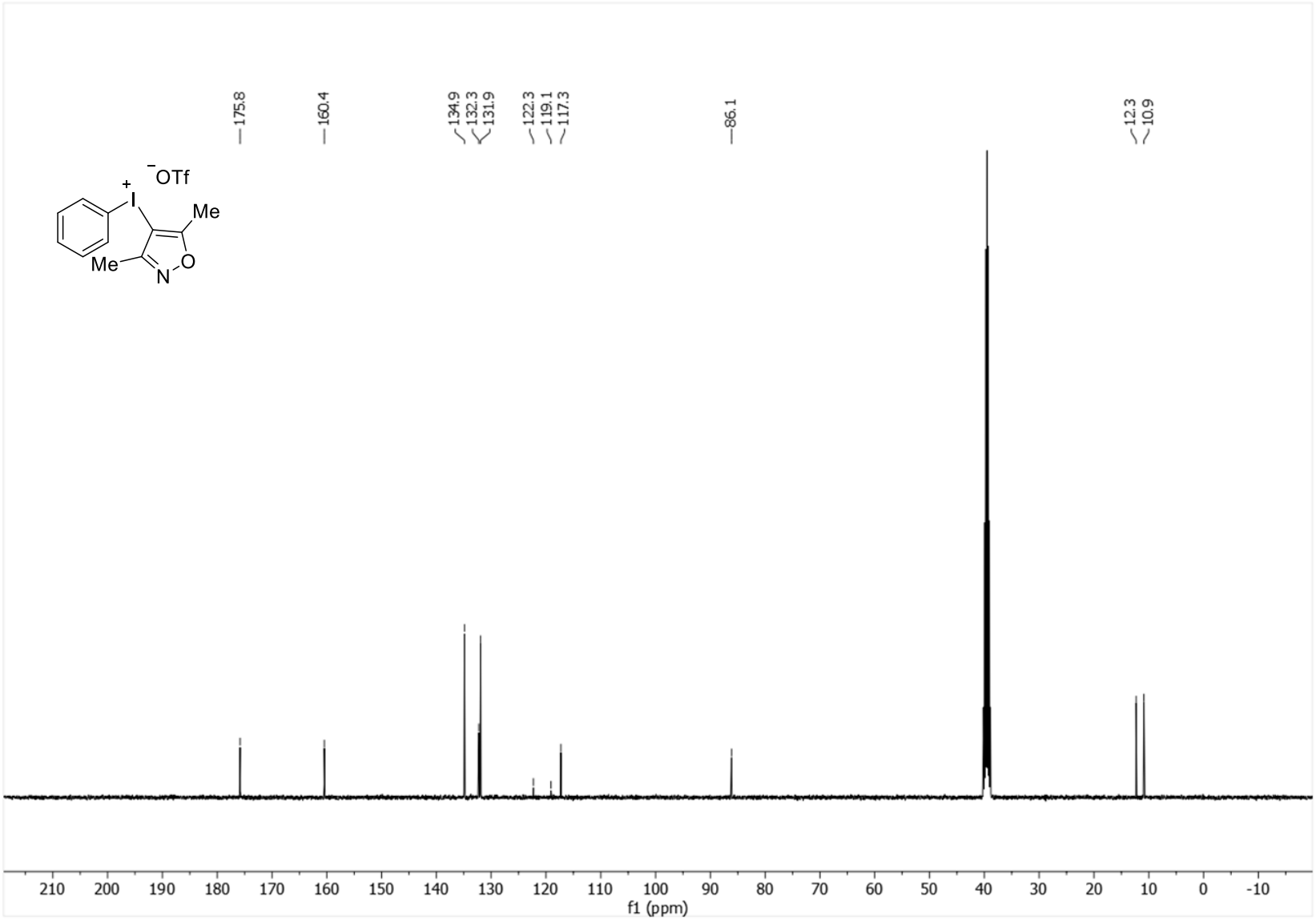
$^{19}F\{^{1}H\}$ NMR of compound **11** at 376 MHz in DMSO-d_6 at 298 K



^{1}H NMR of compound **12** at 400 MHz in DMSO-d_6 at 298 K



$^{13}C\{^{1}H\}$ NMR of compound **12** at 101 MHz in DMSO-d_6 at 298 K



$^{19}F\{^{1}H\}$ NMR of compound **12** at 376 MHz in DMSO-d_6 at 298 K