Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

^{125}Te NMR Provides Evidence of Autoassociation of Organo-Ditellurides in Solution

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SUPPORTING INFORMATION

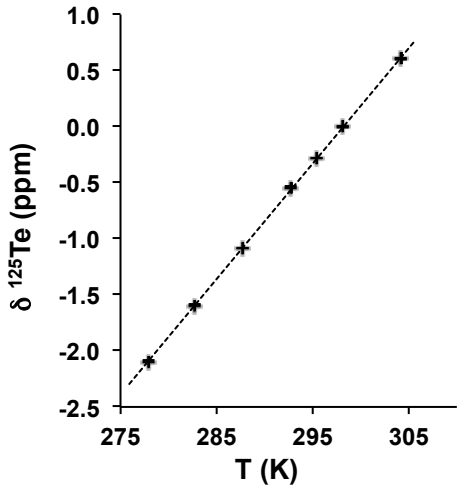


Figure S1. Temperature dependence of the ^{125}Te NMR line of $(CH_3)_2Te$ (standard).

Table S1. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **2** in water.*

T (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
315.0	-0.6 ± 0.1	710.8
307.7	-0.4 ± 0.1	710.2
296.2	-0.4 ± 0.1	709.4
288.5	-0.8 ± 0.1	709.0
279.8	-0.6 ± 0.1	708.4

*Standard errors calculated at 95% confidence range.

† Standard error ≤ 0.05 ppm unless otherwise stated.

At infinite dilution, when the effect of the diamagetic susceptibility if the sample is zero

$$\delta_0 = \frac{\sigma_{ref} - \sigma}{1 - \sigma_{ref}} = \frac{\nu - \nu_{ref}}{\nu_{ref}} = \frac{\nu}{\nu_{ref}} - 1$$

$$\nu = \frac{\gamma B}{2\pi}$$

in each case, reference and sample, at the nucleus:

$$B_{eff} = B_0 (1 - \sigma)$$

more preceisely and in order to account for the effect of concentration of the sample in cgs units:

$$B_{eff} = B_0 (1 + 4\pi\chi_v)(1 - \sigma)$$

$$\delta = \frac{(1 + 4\pi\chi_v)(1 - \sigma)}{(1 - \sigma_{ref})} - 1$$

for the sample in dilute solution, if ΔV of mixing is small and Wiedemann' s law holds:

$$\chi_v = \chi_{v,solvent} + (\chi_{v,sample} - \chi_{v,solvent})\, p$$

$$p = \frac{V_{sample}}{V_{sample} + V_{solvent}} = \frac{V_{sample}}{V} = \frac{m_{sample}}{\rho_{sample} V} = \frac{FW_{sample} n_{sample}}{\rho_{sample} V} = \frac{FW_{sample} C\, V}{\rho_{sample} V}$$

$$\chi_{\mathrm{v}} = \chi_{\mathrm{v},solvent} + \left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample} C}{\rho_{sample}}$$

$$\frac{d\delta}{dC} = \frac{d}{dC}\frac{\left(1+4\pi\chi_{\mathrm{v}}\right)\left(1-\sigma\right)}{\left(1-\sigma_{ref}\right)} - 1$$

$$\frac{d\delta}{dC} = \frac{\left(1-\sigma\right)}{\left(1-\sigma_{ref}\right)}\frac{d}{dC}\left(1+4\pi\chi_{\mathrm{v}}\right) = \frac{\left(1-\sigma\right)}{\left(1-\sigma_{ref}\right)}\frac{d}{dC}\left(4\pi\chi_{\mathrm{v}}\right)$$

$$\frac{d}{dC}\left(4\pi\chi_{\mathrm{v}}\right) = \frac{d}{dC}\left(\chi_{\mathrm{v},solvent} + \left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample} C}{\rho_{sample}}\right)$$

$$\frac{d}{dC}\left(4\pi\chi_{\mathrm{v}}\right) = 4\pi\left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample}}{\rho_{sample}}$$

$$\frac{d\delta}{dC} = 4\pi\frac{\left(1-\sigma\right)}{\left(1-\sigma_{ref}\right)}\left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample}}{\rho_{sample}}$$

$$\frac{\left(1-\sigma\right)}{\left(1-\sigma_{ref}\right)} - 1 = \frac{\left(1-\sigma\right) - \left(1-\sigma_{ref}\right)}{\left(1-\sigma_{ref}\right)} = \frac{\sigma_{ref} - \sigma}{1-\sigma_{ref}} = \delta_0$$

$$\frac{d\delta}{dC} = 4\pi\left(\delta_0 + 1\right)\left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample}}{\rho_{sample}}$$

as $\delta_0 \ll 1$

$$\frac{d\delta}{dC} \approx 4\pi\left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample}}{\rho_{sample}}$$

or in SI units

$$\frac{d\delta}{dC} \approx \mu_0\left(\chi_{v,sample} - \chi_{\mathrm{v},solvent}\right)\frac{FW_{sample}}{\rho_{sample}}$$

From literature* data for $Te(OH)_6$:

$\rho_{Te(OH)6}$ = 3,070 g/L

$FW_{Te(OH)6}$ = 229.644040 g/mol

$\chi_{v,H2O} = -7.203\times10^{-7}$

$\chi_{v,Te(OH)6} = -1.2\times10^{-6}$

$$\frac{d\delta}{dC} = -0.5 \text{ ppm L mol}^{-1}$$

* O. Lindqvist, *Acta Chem. Scand*. 1970, **24**, 3178-88.

Table S2. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **2** in hexane.*

Temperature (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
308.2	11.9 ± 0.2	421.6
296.6	11.8 ± 0.1	419.0
288.9	12.6 ± 0.4	417.3
280.1	13.3 ± 0.3	415.3
272.7	14.6 ± 0.5	413.5

*Standard errors calculated at 95% confidence range.

† Standard error ≤ 0.05 ppm unless otherwise stated.

Table S3. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **2** in toluene.*

Temperature (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
307.7	7.3 ± 0.2	422.2
296.3	7.6 ± 0.1	419.4
288.7	7.5 ± 0.2	417.5
279.9	8.0 ± 0.3	415.2
272.6	8.5 ± 0.4	413.2

*Standard errors calculated at 95% confidence range.

† Standard error ≤ 0.05 ppm unless otherwise stated.

Table S4. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **2** in dichloromethane.*

Temperature (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
295.6	4.52 ± 0.09	420.4
287.2	4.91 ± 0.10	418.9
280.3	5.04 ± 0.04	417.7

*Standard errors calculated at 95% confidence range.

† Standard error ≤ 0.05 ppm unless otherwise stated.

Table S5. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **3** in hexane.*

Temperature (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
307.8	8.7 ± 0.3	345.2
296.2	9.3 ± 0.2	343.9
289.2	9.8 ± 0.3	343.1
281.3	10.1 ± 0.3	342.2
274.6	10.6 ± 0.3	341.5

*Standard errors calculated at 95% confidence range.

† Standard error ≤ 0.05 ppm unless otherwise stated.

Table S6. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **3** in toluene.*

Temperature (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
308.0	3.11 ± 0.05	348.7
297.6	3.5 ± 0.2	347.3
288.6	3.0 ± 0.1	346.2
279.9	2.6 ± 0.2	345.2
272.5	3.1 ± 0.1	344.3

*Standard errors calculated at 95% confidence range.

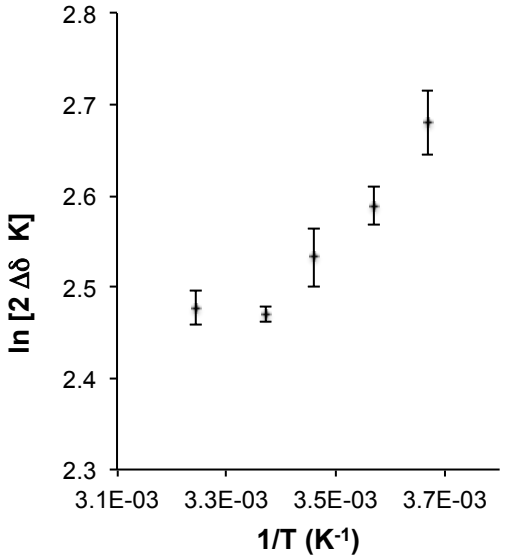
† Standard error ≤ 0.05 ppm unless otherwise stated.

Table S7. Fitted concentration coefficients and δ_0 ^{175}Te NMR (ppm) at selected temperatures for **4** in dichloromethane.*

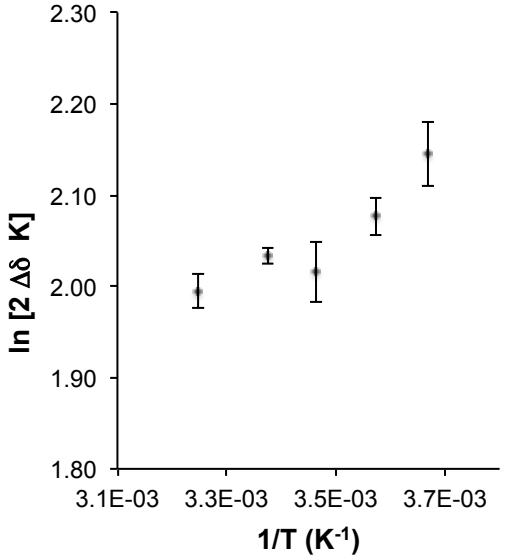
Temperature (± 0.1K)	Coefficient (ppm L mol^{-1})	δ_0 (ppm†)
296.0	-7 ± 1	418.0
291.9	-9 ± 2	415.9
287.3	-11 ± 2	414.1
280.0	-13 ± 2	410.9

*Standard errors calculated at 95% confidence range.

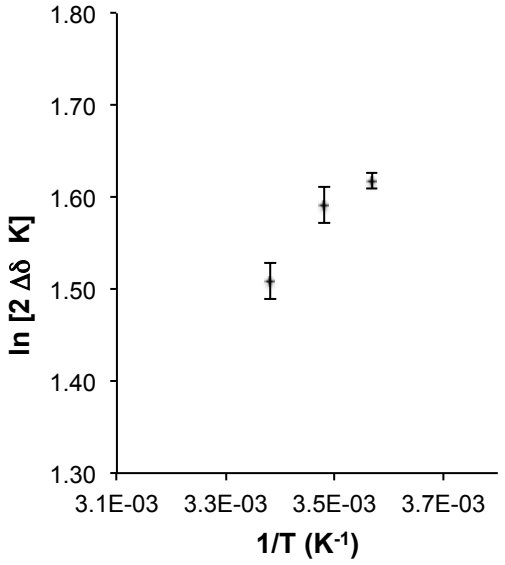
† Standard error ≤ 0.05 ppm unless otherwise stated.



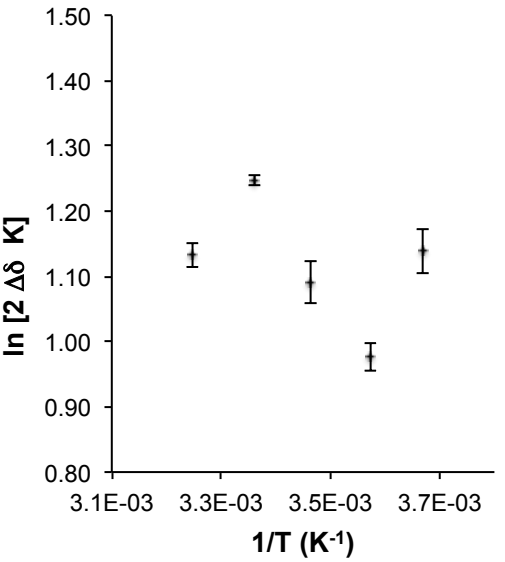
2 in hexane, $\Delta H = -4.1 \pm 0.9$ J mol^{-1}, $r^2 = 0.88$



2 in toluene, $\Delta H = -2.8 \pm 0.7$ J mol^{-1}, $r^2 = 0.83$



2 in CH_2Cl_2, $\Delta H = -5 \pm 1$ J mol^{-1}, $r^2 = 0.94$



3 in toluene, $r^2 = 0.18$.

Figure S2. Van't Hoff plots for the proposed equilibrium of autoassociation of **2** or **3** in selected solvents. Estimated values of ΔH are given for those cases with reasonably high correlation, as noted by the squared linear correlation coefficient (R^2).

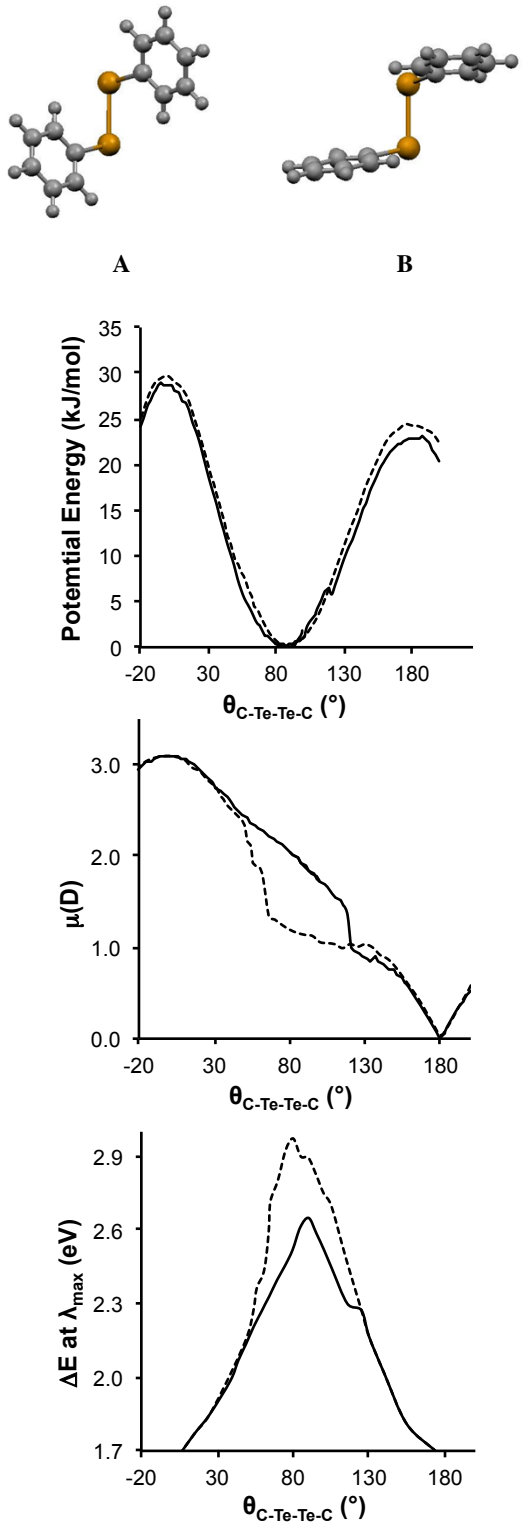


Figure S3. a) Molecular conformations of Ph-Te-Te-Ph, **1**, at the minima of two trajectories of minimum potential energy. b) Potential energy profiles; c) dipole moments; d) energy of first electronic excitation for trajectories A (--) and B (—).

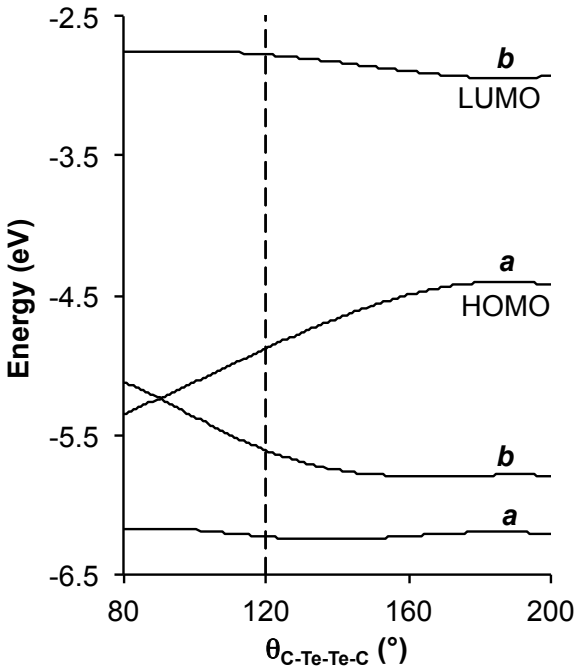


Figure S4. Walsh diagram for the frontier orbitals of **1** as a function of the C-Te-Te-C dihedral angle.

The potential energy surface was evaluated by continuously varying C-Te-Te-C torsion angle from -20° to 200° while all other internal dimensions were fully optimized. The resulting potential energy surface is displayed in Figure S3. Two trajectories were identified by these calculations; they differ only by the orientation of the aromatic rings, as illustrated in Figure 3a. The trajectories are numerically different, but the differences are small enough (< 2.1 kJ/mol) to be blurred by thermal effects. In each case there is a well-defined minima at 90° but changes of up to 30° from the minimum would cost less than 5 kJ/mol. Indeed, most of the structurally characterized diaryl ditellurides do exhibit C-Te-Te-C dihedral angle values ranging from 60° to 120°. The maxima at 0° and 180° are the result of repulsion between lone-pairs on the tellurium atoms. The energy difference between the maxima is due to the steric interaction between aromatic rings at small C-Te-Te-C dihedral angles. The small maximum and minimum in surface B at 116 and 121°, respectively, are the result of an abrupt rotation around the C-Te bonds that takes place once the distance between phenyl rings is big enough.

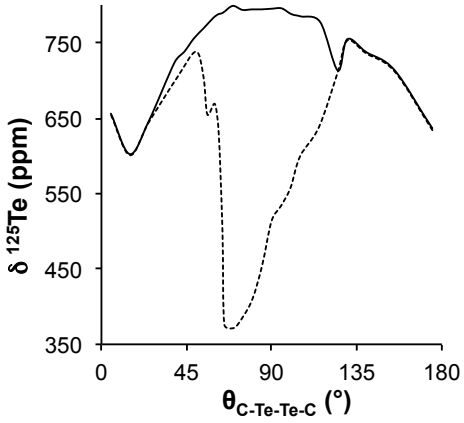


Figure S5. Effect of the dihedral angle on the ^{125}Te NMR chemical shift of **1** along trajectories A (---) and B (—).

Table S8. A comparison of optimized structures of **1** in gas phase and selected solvents modeled by the COSMO method.

Medium	$d_{Te\text{-}Te}$ (Å)	$\theta_{C\text{-}Te\text{-}Te}$ (°)	$\theta_{C\text{-}Te\text{-}Te\text{-}C}$ (°)	$\theta_{Ph\text{-}Ph}$ (°)
gas phase	2.732	101.10	88.89	23.23
hexanes	2.741	100.32	84.74	22.56
CCl_4	2.740	100.38	86.30	18.42
C_6H_6	2.739	100.56	85.78	22.71
toluene	2.741	100.41	85.34	23.12
Et_3N	2.740	100.38	86.25	17.72
CS_2	2.749	100.47	85.31	22.68
Et_2O	2.741	100.33	86.11	18.44
THF	2.742	100.42	88.11	18.77
DCM	2.740	99.99	85.85	18.16
Py	2.738	100.23	87.03	18.58
i-PrOH	2.741	100.32	87.07	21.63
$MeNO_2$	2.740	100.37	87.17	22.02
MeOH	2.741	100.36	86.44	22.69
ACN	2.739	100.51	87.59	21.81
DMSO	2.742	100.32	87.11	22.25

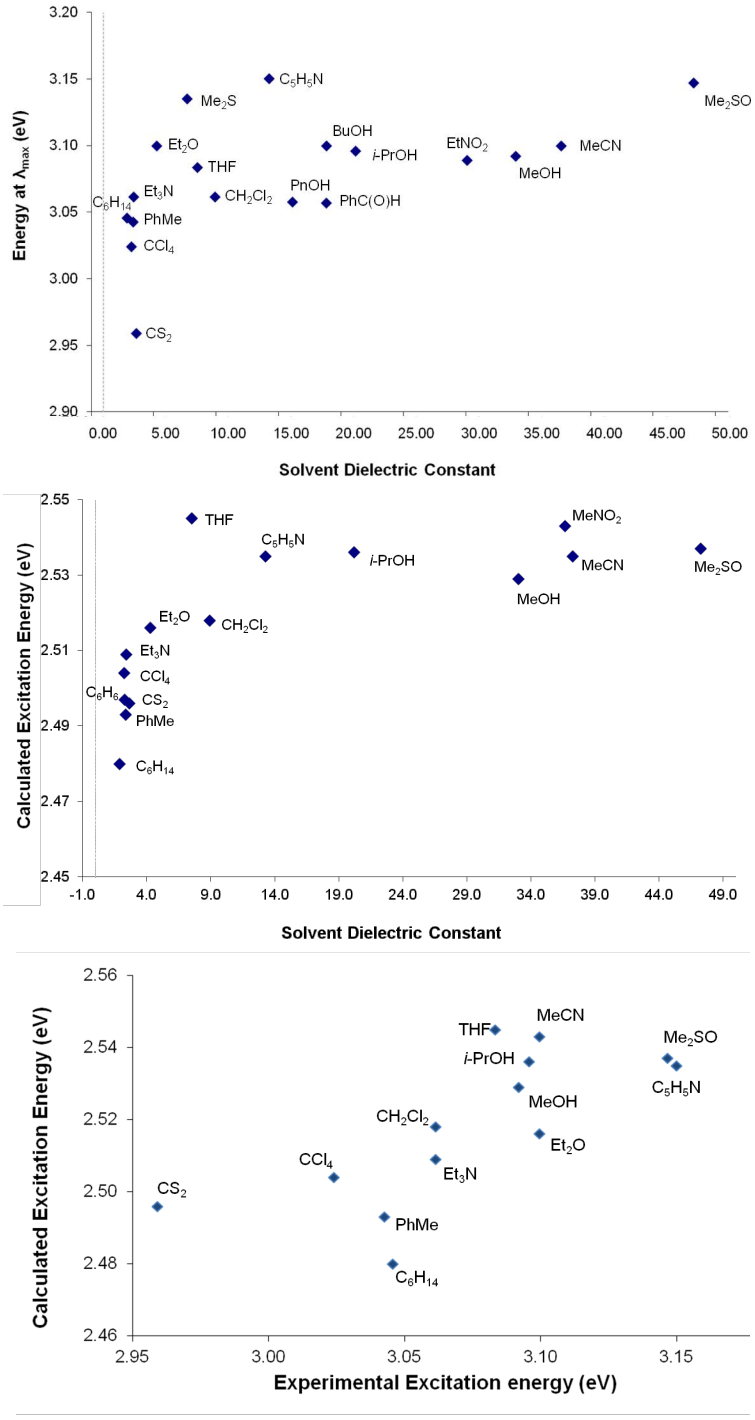


Figure S6. a) Experimentally determined energy of excitation of **2** (0.137 M, 303.0 K) dissolved in media of different dielectric constant. b) Calculated energy (COSMO-TD-DFT) for the first excitation of **1** in solvents of different dielectric constant. c) Comparison of excitation energies calculated for 1 and experimentally measured for **2** in a several solvents.

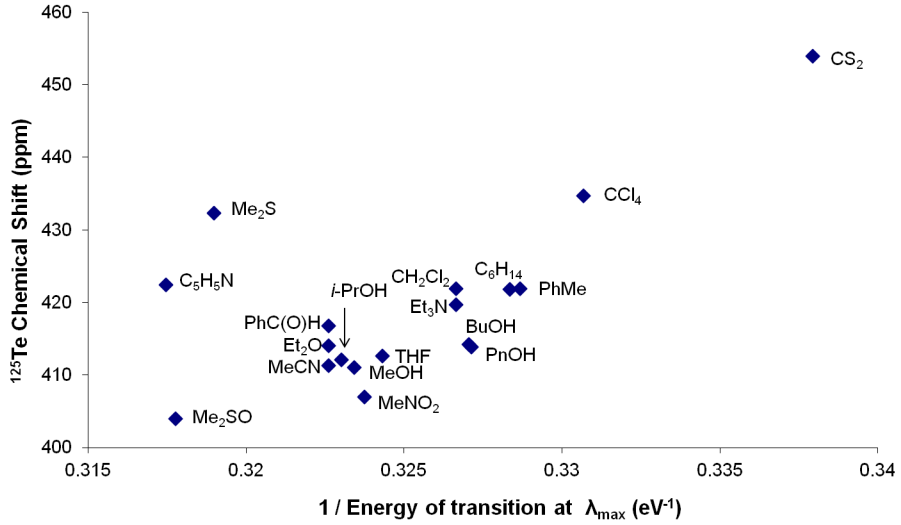


Figure S7. Experimental ^{125}Te chemical shift as a function of excitation energy for **2** in different solvents.