Supplementary Materials: Solvent and substituent effects on the phosphine + CO2 reaction

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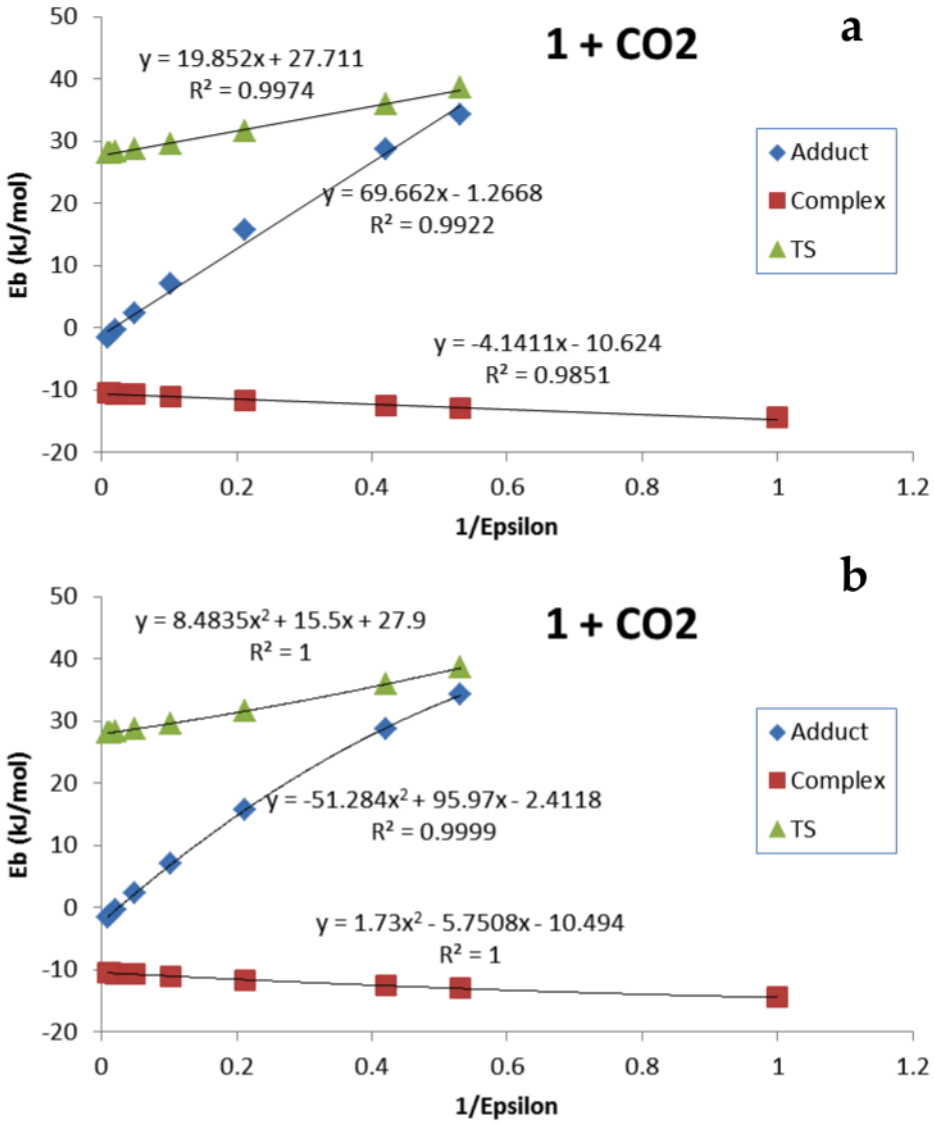

Fig. S1. Linear (a) and second order polynomial (b)relationships between the Eb and 1/ε for the stationary points in the **1** + CO_2 surface.

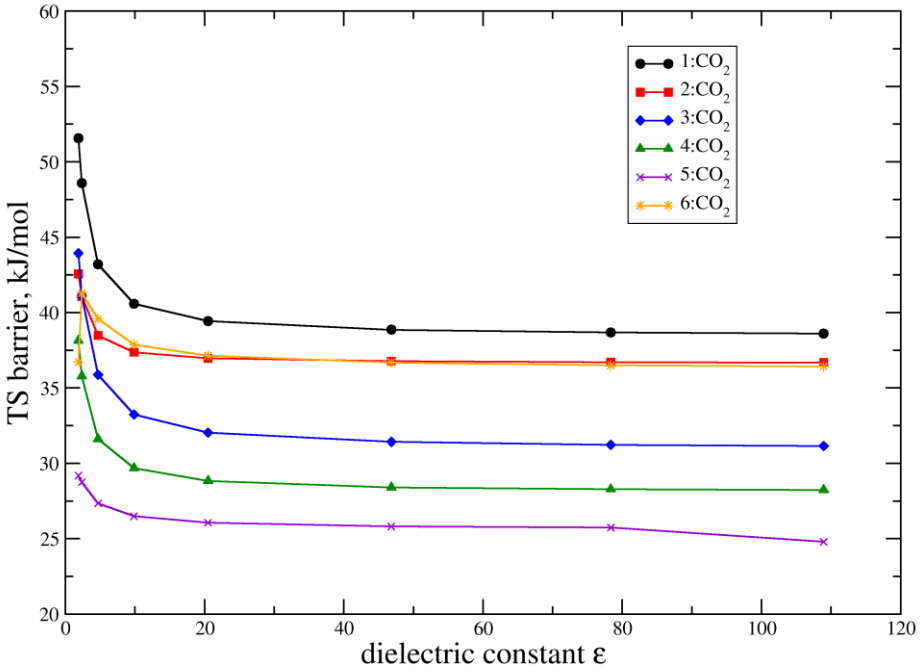

Fig. S2. Evolution of the transition barriers *vs*. the dielectric constant of the solvent.

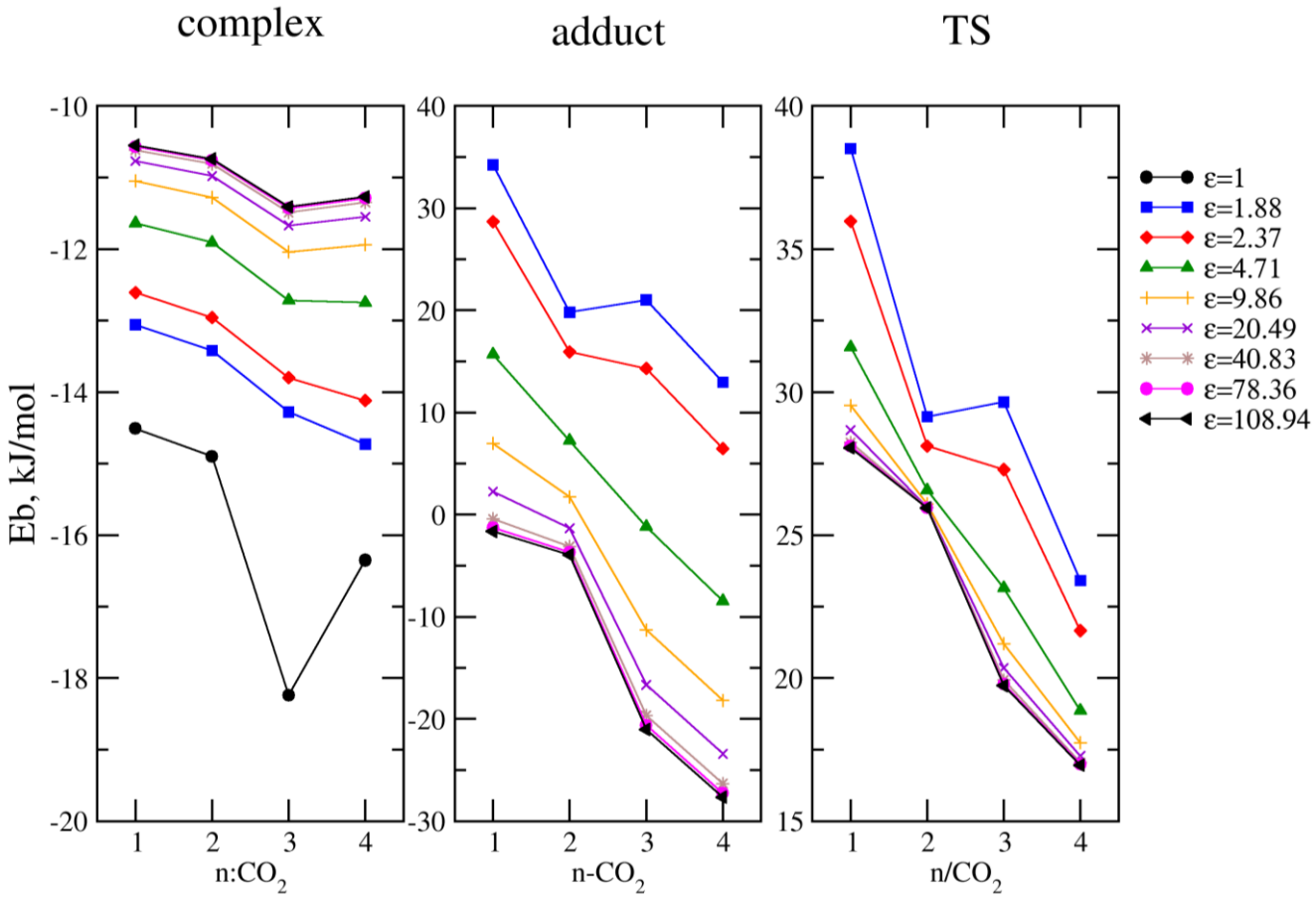

Fig. S3. Evolution of the transition barriers *vs*. the complexes **1**, **2**, **3** and **4**.

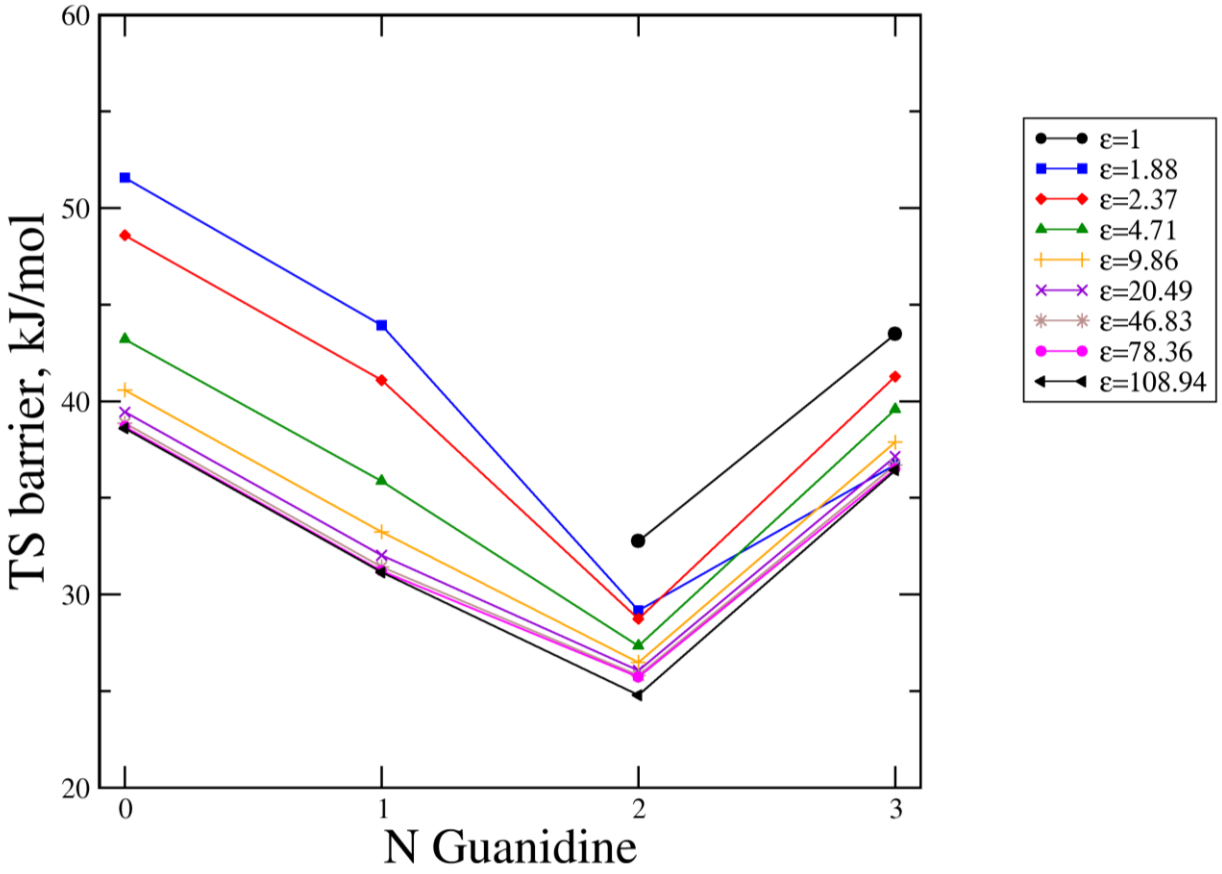

Fig. S4. Evolution of the transition barriers *vs*. the number of guanidine substituent for complexes **1**, **3**, **5** and **6**.

Table S1. Electron density properties (au) of the intermolecular BCP in the stationary points of the **1** + CO_2 energy profile.

1:CO_2 (P···O BCP)

Solvent	ϱ_{BCP}	$\nabla^2\varrho_{BCP}$	H_{BCP}
Gas	0.0087	0.0260	0.0009
Hexane	0.0086	0.0257	0.0009
Toluene	0.0084	0.0254	0.0009
Chloroform	0.0081	0.0246	0.0009
Octanol	0.0079	0.0240	0.0009
Acetone	0.0078	0.0236	0.0009
DMSO	0.0077	0.0234	0.0009
Water	0.0077	0.0233	0.0009
Formamide	0.0077	0.0234	0.0009

1-CO_2 (P···C BCP)

Solvent	ϱ_{BCP}	$\nabla^2\varrho_{BCP}$	H_{BCP}
Hexane	0.1454	-0.2717	-0.1004
Toluene	0.1489	-0.2968	-0.1063
Chloroform	0.1539	-0.3445	-0.1189
Octanol	0.1556	-0.3649	-0.1324
Acetone	0.1560	-0.3343	-0.1410
DMSO	0.1561	-0.3146	-0.1428
Water	0.1561	-0.3084	-0.1432
Formamide	0.1561	-0.3062	-0.1433

1/CO_2 (P···C BCP)

Solvent	ϱ_{BCP}	$\nabla^2\varrho_{BCP}$	H_{BCP}
Hexane	0.0901	-0.0395	-0.0393
Toluene	0.0836	-0.0220	-0.0337
Chloroform	0.0724	0.0044	-0.0248
Octanol	0.0670	0.0153	-0.0209
Acetone	0.0645	0.0199	-0.0192
DMSO	0.0633	0.0221	-0.0183
Water	0.0629	0.0228	-0.0180
Formamide	0.0627	0.0231	-0.0179

Table S2. Binding energies (kJ·mol^{-1}) and Linear relationship R^2 vs. 1/ε of all the stationary points.

1 + CO_2

Solvent	Complex	Adduct	TS
Gas	-14.51		
Hexane	-13.06	34.24	38.51
Toluene	-12.61	28.68	35.97
Chloroform	-11.64	15.67	31.57
Octanol	-11.05	6.98	29.53
Acetone	-10.77	2.25	28.67
DMSO	-10.62	-0.41	28.24
Water	-10.57	-1.28	28.11
Formamide	-10.55	-1.64	28.05
R^2	0.985	0.992	0.997

2 + CO_2

Solvent	Complex	Adduct	TS
Gas	-14.90	32.56	34.54
Hexane	-13.42	19.81	29.14
Toluene	-12.96	15.93	28.11
Chloroform	-11.91	7.25	26.57
Octanol	-11.28	1.73	26.09
Acetone	-10.98	-1.33	25.98
DMSO	-10.81	-3.10	25.96
Water	-10.76	-3.68	25.95
Formamide	-10.74	-3.93	25.95
R^2	0.98	0.98	0.96

3 + CO_2

Solvent	Complex	Adduct	TS
Gas	-18.24		
Hexane	-14.28	21.01	29.65
Toluene	-13.80	14.30	27.29
Chloroform	-12.72	-1.18	23.15
Octanol	-12.04	-11.28	21.20
Acetone	-11.67	-16.66	20.36
DMSO	-11.49	-19.65	19.93
Water	-11.43	-20.62	19.79
Formamide	-11.41	-21.02	19.74
R^2	0.99	0.99	1.00

4 + CO_2

Solvent	Complex	Adduct	TS
Gas	-16.35	33.39	33.43
Hexane	-14.73	12.96	23.41
Toluene	-14.12	6.46	21.66
Chloroform	-12.75	-8.46	18.86
Octanol	-11.94	-18.19	17.74
Acetone	-11.55	-23.41	17.28
DMSO	-11.35	-26.32	17.05
Water	-11.29	-27.26	16.99
Formamide	-11.27	-27.66	16.96
R^2	0.97	0.97	0.97

5 + CO_2

Solvent	Complex	Adduct	TS
Gas	-22.20	-5.75	10.56
Hexane	-20.08	-16.61	9.09
Toluene	-19.35	-20.00	9.39
Chloroform	-17.64	-20.91	9.70
Octanol	-16.56	-27.89	9.93
Acetone	-16.03	-31.74	10.03
DMSO	-15.75	-33.95	10.06
Water	-15.66	-34.68	10.07
Formamide	-15.62	-34.99	9.17
R^2	0.97	0.93	0.90

6 + CO_2

Solvent	Complex	Adduct	TS
Gas	-26.20	-2.51	17.28
Hexane	-21.82	-15.26	14.90
Toluene	-21.91	-19.36	19.37
Chloroform	-21.96	-28.60	17.62
Octanol	-21.87	-34.42	16.01
Acetone	-21.81	-35.42	15.33
DMSO	-21.74	-37.96	14.95
Water	-21.75	-38.82	14.74
Formamide	-21.75	-39.19	14.68
	0.70	0.98	0.24

Table S3. Interatomic distances (Å) in the stationary points.

Solvent	**1**:CO_2 (P···O)	**2**:CO_2 (P···O)	**3**:CO_2 (P···O)	**4**:CO_2 (P···O)	**5**:CO_2 (N···C)	**6**:CO_2 (N···C)
Gas	3.306	3.275	3.274	3.275	2.937	3.023
Hexane	3.323	3.296	3.287	3.293	2.949	3.066
Toluene	3.332	3.301	3.292	3.301	2.952	3.068
Chloroform	3.349	3.316	3.301	3.320	2.963	3.074
Octanol	3.362	3.327	3.320	3.333	2.969	3.078
Acetone	3.370	3.336	3.327	3.345	2.986	3.080
DMSO	3.374	3.339	3.330	3.346	2.990	3.082
Water	3.375	3.339	3.331	3.347	2.991	3.082
Formamide	3.374	3.340	3.332	3.347	2.993	3.082

P···C Interatomic distances (Å) in the TSs.

Solvent	**1**/CO_2	**2**/CO_2	**3**/CO_2	**4**/CO_2	**5**/CO_2	**6**/CO_2
Gas		2.185		2.093	2.279	2.324
Hexane	2.206	2.289	2.274	2.295	2.363	2.387
Toluene	2.245	2.314	2.312	2.333	2.383	2.431
Chloroform	2.318	2.362	2.383	2.403	2.425	2.466
Octanol	2.358	2.386	2.421	2.442	2.440	2.481
Acetone	2.377	2.397	2.440	2.462	2.458	2.489
DMSO	2.387	2.403	2.450	2.472	2.464	2.495
Water	2.390	2.405	2.453	2.475	2.466	2.496
Formamide	2.391	2.406	2.454	2.476	2.467	2.497

P-C distances (Å) in the adducts.

Solvent	**1**/CO_2	**2**/CO_2	**3**/CO_2	**4**/CO_2	**5**/CO_2	**6**/CO_2
Gas		1.982		2.037	1.929	1.923
Hexane	1.959	1.946	1.946	1.941	1.918	1.913
Toluene	1.946	1.939	1.935	1.931	1.915	1.911
Chloroform	1.926	1.927	1.919	1.916	1.908	1.905
Octanol	1.917	1.921	1.911	1.909	1.903	1.902
Acetone	1.914	1.918	1.908	1.906	1.901	1.906
DMSO	1.912	1.917	1.907	1.904	1.900	1.905
Water	1.911	1.916	1.906	1.904	1.900	1.904
Formamide	1.911	1.916	1.906	1.903	1.899	1.904

Table S4. Free Gibbs energies (ΔG) obtained with respect to the entrance channel (isolated monomers) and with respect to the complex configuration.

	w.r.t. isolated monomers			w.r.t. complex		
Solvent	**1**:CO_2	**1**/CO_2	**1**-CO_2	**1**:CO_2	**1**/CO_2	**1**-CO_2
Gas Phase	12.1					
n-Hexane	13.0	71.5	73.1	0.0	58.5	60.1
Toluene	13.2	69.0	67.6	0.0	55.8	54.4
Chloroform	14.4	63.9	51.3	0.0	49.4	36.8
n-Octanol	15.1	61.2	51.3	0.0	46.1	36.2
Acetone	14.9	59.6	38.9	0.0	44.7	24.0
DMSO	14.3	57.5	37.0	0.0	43.2	22.7
Water	13.9	57.5	36.6	0.0	43.6	22.7
Formamide	13.9	57.4	36.4	0.0	43.5	22.5
	w.r.t. isolated monomers			w.r.t. complex		
Solvent	**2**:CO_2	**2**/CO_2	**2**-CO_2	**2**:CO_2	**2**/CO_2	**2**-CO_2
Gas Phase	14.5	72.5	75.7	0.0	57.9	61.2
n-Hexane	15.3	63.0	63.6	0.0	47.7	48.3
Toluene	15.6	61.9	59.7	0.0	46.3	44.1
Chloroform	16.3	60.7	51.1	0.0	44.4	34.9
n-Octanol	16.8	59.8	45.2	0.0	43.1	28.5
Acetone	17.9	59.5	43.1	0.0	41.6	25.3
DMSO	17.8	59.3	42.4	0.0	41.5	24.6
Water	17.8	59.3	42.2	0.0	41.4	24.4
Formamide	17.7	59.2	42.1	0.0	41.5	24.4
	w.r.t. isolated monomers			w.r.t. complex		
Solvent	**3**:CO_2	**3**/CO_2	**3**-CO_2	**3**:CO_2	**3**/CO_2	**3**-CO_2
Gas Phase	11.0					
n-Hexane	16.3	69.7	63.5	0.0	53.3	47.2
Toluene	16.9	66.8	57.7	0.0	49.9	40.8
Chloroform	18.7	60.7	44.3	0.0	41.9	25.6
n-Octanol	19.8	59.8	35.4	0.0	40.1	15.7
Acetone	19.5	57.3	28.8	0.0	37.8	9.3
DMSO	19.2	55.7	25.5	0.0	36.4	6.3
Water	19.2	55.1	24.4	0.0	35.9	5.2
Formamide	19.2	54.9	24.2	0.0	35.7	5.0
	w.r.t. isolated monomers			w.r.t. complex		
Solvent	**4**:CO_2	**4**/CO_2	**4**-CO_2	**4**:CO_2	**4**/CO_2	**4**-CO_2
Gas Phase	14.6	75.3	73.2	0.0	60.8	58.6
n-Hexane	12.7	63.9	60.0	0.0	51.3	47.4
Toluene	12.9	61.1	54.5	0.0	48.2	41.6
Chloroform	14.5	56.4	39.8	0.0	41.9	25.3
n-Octanol	13.9	53.8	29.6	0.0	39.9	15.7
Acetone	13.1	53.5	23.8	0.0	40.4	10.7
DMSO	16.2	53.3	20.3	0.0	37.1	4.1
Water	16.9	53.4	19.5	0.0	36.5	2.6
Formamide	17.1	53.4	19.3	0.0	36.2	2.2

	w.r.t. isolated monomers			w.r.t. complex		
Solvent	**5**:CO_2	**5**/CO_2	**5**-CO_2	**5**:CO_2	**5**/CO_2	**5**-CO_2
Gas Phase	10.9	57.7	46.7	0.0	46.8	35.8
n-Hexane	12.8	54.7	35.9	0.0	42.0	23.1
Toluene	13.1	54.0	32.0	0.0	40.9	18.9
Chloroform	10.6	50.7	30.6	0.0	40.1	20.0
n-Octanol	14.2	53.2	24.1	0.0	38.9	9.9
Acetone	15.2	51.0	19.3	0.0	35.9	4.1
DMSO	16.5	51.3	17.0	0.0	34.8	0.6
Water	16.7	51.4	16.1	0.0	34.7	-0.6
Formamide	16.6	51.5	15.7	0.0	34.9	-0.8
	w.r.t. isolated monomers			w.r.t. complex		
Solvent	**6**:CO_2	**6**/CO_2	**6**-CO_2	**6**:CO_2	**6**/CO_2	**6**-CO_2
Gas Phase	8.6	61.0	45.2	0.0	52.4	36.5
n-Hexane	14.7	55.9	33.8	0.0	41.1	19.0
Toluene	15.8	57.1	30.4	0.0	41.3	14.6
Chloroform	17.8	55.9	20.6	0.0	38.1	2.9
n-Octanol	14.7	54.4	12.5	0.0	39.7	-2.2
Acetone	15.2	53.8	10.0	0.0	38.6	-5.3
DMSO	15.1	52.6	7.4	0.0	37.5	-7.8
Water	15.1	52.4	6.8	0.0	37.3	-8.4
Formamide	15.9	53.0	7.3	0.0	37.1	-8.6