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

The role of secondary interactions on the preferred conformers of the fenchone-ethanol complex

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Supplementary Information

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Table S1. D_e binding energies (kJ mol^{-1}), including BSSE corrections, for the twelve lower-energy conformers of fenchone-ethanol.

Conformer	B3LYP-D3BJ	MP2
*t*a1	44.8	23.6
*t*a2	45.3	23.6
g+a1	51.7	25.0
g+a2	51.3	24.7
g–a1	51.2	24.6
g–a2	51.8	25.1
*t*b	42.0	21.5
g+b	49.0	22.8
g–b	50.2	23.7
*t*c	39.3	19.9
g+c	47.5	21.2
g–c	47.3	20.7

Table S2. Measured frequencies and residuals (in MHz) of the rotational transitions of conformer ***g+a1*** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	$\nu_{obs}-\nu_{calc}$
4	1	4	3	1	3	2929.7690	-0.00165
4	0	4	3	0	3	2988.7638	-0.01622
4	1	3	3	1	2	3068.0403	-0.00789
5	1	5	4	1	4	3659.9537	-0.00305
5	0	5	4	0	4	3726.7165	0.00352
5	1	4	4	1	3	3832.4220	0.00092
6	1	6	5	1	5	4388.7790	-0.01147
6	0	6	5	0	5	4459.0944	-0.00849
6	1	5	5	1	4	4594.8561	-0.01055
7	1	7	6	1	6	5116.1325	-0.01116
7	0	7	6	0	6	5185.7673	0.00368
7	1	6	6	1	5	5354.8293	-0.00297
8	1	8	7	1	7	5841.9520	-0.00020
8	0	8	7	0	7	5907.1453	0.00145
8	1	7	7	1	6	6111.6820	0.00031
9	1	9	8	1	8	6566.2141	-0.00028
9	0	9	8	0	8	6624.2534	0.00303
9	1	8	8	1	7	6864.6950	-0.00404
10	1	10	9	1	9	7288.9845	0.00015
10	0	10	9	0	9	7338.3853	-0.00037
10	1	9	9	1	8	7613.1155	-0.00018
4	2	3	3	2	2	3000.4845	0.01642
4	2	2	3	2	1	3013.1568	-0.00171
5	2	4	4	2	3	3748.9453	0.00107
5	2	3	4	2	2	3774.0232	0.00289
6	2	4	5	2	3	4539.2900	-0.00255
7	2	6	6	2	5	5242.4165	0.00331
7	2	5	6	2	4	5308.9135	-0.01062
8	2	7	7	2	6	5986.9905	-0.00027
8	2	6	7	2	5	6082.2186	0.00124
9	2	8	8	2	7	6729.8659	-0.00506
9	2	7	8	2	6	6857.9009	0.00295
5	3	3	4	3	2	3755.8750	0.01184
5	3	2	4	3	1	3756.4926	0.01004
6	3	4	5	3	3	4508.2899	-0.00549
6	3	3	5	3	2	4509.9461	0.00420
7	3	5	6	3	4	5261.1685	-0.00332
7	3	4	6	3	3	5264.8520	-0.00468
8	3	6	7	3	5	6014.3842	0.00122
8	3	5	7	3	4	6021.6881	-0.00267
9	3	7	8	3	6	6767.7581	0.00141
9	3	6	8	3	5	6780.9869	0.00077
3	1	2	2	0	2	3057.1476	-0.00035
4	1	3	3	0	3	3879.1745	-0.00323
5	1	4	4	0	4	4722.8296	0.01081
6	1	5	5	0	5	5590.9713	-0.00116
7	1	6	6	0	6	6486.7133	0.01146
8	1	7	7	0	7	7412.6258	0.00589

Table S3. Measured frequencies and residuals (in MHz) of the rotational transitions of conformer ***g−a2*** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	$\nu_{obs}-\nu_{calc}$
4	1	4	3	1	3	2906.7780	-0.0050
4	0	4	3	0	3	2982.3193	-0.0024
4	1	3	3	1	2	3092.9040	0.0016
5	1	5	4	1	4	3629.7110	-0.0016
5	0	5	4	0	4	3712.2520	0.0000
5	1	4	4	1	3	3861.4606	-0.0068
6	1	6	5	1	5	4350.4655	-0.0025
6	0	6	5	0	5	4433.4579	-0.0027
6	1	5	5	1	4	4626.5433	-0.0073
7	1	7	6	1	6	5068.9203	-0.0004
7	0	7	6	0	6	5146.4577	-0.0062
7	1	6	6	1	5	5387.0950	0.0038
8	1	8	7	1	7	5785.0625	-0.0051
8	0	8	7	0	7	5852.9220	0.0024
8	1	7	7	1	6	6141.8745	0.0040
9	1	9	8	1	8	6499.0161	-0.0009
9	0	9	8	0	8	6555.0794	-0.0110
9	1	8	8	1	7	6889.5870	0.0201
4	2	2	3	2	1	3024.5479	-0.0042
5	2	3	4	2	2	3793.4975	-0.0059
6	2	4	5	2	3	4569.2621	-0.0074
7	2	5	6	2	4	5350.9238	-0.0001
8	2	6	7	2	5	6136.3589	-0.0064
5	2	4	4	2	3	3750.4088	0.0041
6	2	5	5	2	4	4496.4018	0.0180
7	2	6	6	2	5	5240.1561	0.0018
8	2	7	7	2	6	5981.4055	0.0163
5	3	2	4	3	1	3763.7210	-0.0033
6	3	3	5	3	2	4520.5543	0.0046
7	3	4	6	3	3	5280.2053	-0.0037
4	3	2	3	3	1	3008.5501	-0.0084
5	3	3	4	3	2	3762.3478	0.0171
6	3	4	5	3	3	4516.8579	0.0034
7	3	5	6	3	4	5271.9881	0.0143
8	3	6	7	3	5	6027.4024	-0.0045
9	3	7	8	3	6	6782.7505	-0.0109
4	1	3	3	0	3	3973.6242	-0.0001
5	1	4	4	0	4	4852.7704	0.0004
6	1	5	5	0	5	5767.0710	0.0023
7	1	6	6	0	6	6720.6940	-0.0053
2	2	0	1	1	0	3674.5379	0.0035
3	2	1	2	1	1	4387.8625	0.0049
4	2	2	3	1	2	5090.6556	0.0023
5	2	3	4	1	3	5791.2556	0.0013
7	2	5	6	1	5	7223.4163	-0.0134

Table S4. Measured frequencies and residuals (in MHz) of the rotational transitions of conformer ***g*−*b*** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	$\nu_{obs}-\nu_{calc}$
3	1	3	2	1	2	2599.2188	-0.00294
3	0	3	2	0	2	2668.4197	-0.00752
3	1	2	2	1	1	2771.8215	0.00386
4	1	4	3	1	3	3460.2420	-0.00265
4	0	4	3	0	3	3535.8087	0.00010
4	1	3	3	1	2	3689.0394	0.00537
5	1	5	4	1	4	4317.4343	-0.00170
5	1	4	4	1	3	4599.6152	0.00397
6	1	6	5	1	5	5170.6715	-0.01891
6	0	6	5	0	5	5230.0019	0.00159
6	1	5	5	1	4	5500.8707	-0.00333
7	1	7	6	1	6	6020.2650	-0.00087
7	0	7	6	0	6	6064.7576	0.00119
8	1	8	7	1	7	6866.6748	-0.00354
8	0	8	7	0	7	6897.4600	-0.00736
8	1	7	7	1	6	7263.6780	0.00623
9	1	9	8	1	8	7710.5829	0.01712
9	0	9	8	0	8	7730.6457	0.00256
3	2	1	2	2	0	2709.0826	0.01287
4	2	3	3	2	2	3580.9729	0.00229
4	2	2	3	2	1	3630.1480	0.01310
5	2	4	4	2	3	4469.7744	-0.00008
5	2	3	4	2	2	4562.1812	0.00633
6	2	5	5	2	4	5354.3800	0.00061
6	2	4	5	2	3	5501.3243	0.00339
7	2	6	6	2	5	6234.1050	-0.00582
7	2	5	6	2	4	6441.3737	-0.01330
8	2	7	7	2	6	7108.4594	-0.00202
8	2	6	7	2	5	7376.4862	-0.01363
4	3	1	3	3	0	3596.1935	0.00880
5	3	3	4	3	2	4496.0668	0.00758
6	3	4	5	3	3	5398.3397	0.00354
6	3	3	5	3	2	5413.9175	0.00125
7	3	5	6	3	4	6300.3817	-0.00234
7	3	4	6	3	3	6334.2125	-0.00082
8	3	5	7	3	4	7264.9594	0.00520
8	3	6	7	3	5	7201.0502	0.00584
6	4	3	5	4	2	5394.7461	-0.00215
6	4	2	5	4	1	5395.2238	-0.00327
7	4	4	6	4	3	6298.6230	0.01051
7	4	3	6	4	2	6300.1711	-0.02138
8	4	5	7	4	4	7204.1965	0.00053
8	4	4	7	4	3	7208.4753	0.00238

Table S5. Measured frequencies and residuals (in MHz) of the rotational transitions of the $^{13}C_1$-ethanol isotopologue of conformer ***g*+a1** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	*J"*	$K"_{-1}$	$K"_{+1}$	ν_{obs}	$\nu_{obs}-\nu_{calc}$
3	0	3	2	0	2	2216.1280	-0.0040
3	1	2	2	1	1	2270.7595	0.0013
4	1	4	3	1	3	2891.4584	0.0024
4	1	3	3	1	2	3026.1844	-0.0002
5	1	5	4	1	4	3612.1862	0.0005
5	0	5	4	0	4	3677.8235	-0.0017
5	1	4	4	1	3	3780.2470	-0.0012
6	1	6	5	1	5	4331.6311	-0.0004
6	0	6	5	0	5	4401.1088	-0.0026
6	1	5	5	1	4	4532.5040	0.0006
7	1	7	6	1	6	5049.6715	0.0041
7	0	7	6	0	6	5118.8915	-0.0045
7	1	6	6	1	5	5282.4370	0.0014
8	1	8	7	1	7	5766.2295	0.0030
8	0	8	7	0	7	5831.5340	-0.0049
8	1	7	7	1	6	6029.4505	-0.0023
9	1	9	8	1	8	6481.3045	0.0042
9	0	9	8	0	8	6539.9280	-0.0087
9	1	8	8	1	7	6772.8910	0.0035
10	0	10	9	0	9	7245.2950	-0.0039
10	1	9	9	1	8	7512.0250	0.0065
4	2	3	3	2	2	2960.2905	0.0009
5	2	4	4	2	3	3698.8140	0.0012
6	2	5	5	2	4	4436.3000	-0.0062
7	2	6	6	2	5	5172.5750	0.0055
8	2	7	7	2	6	5907.4170	0.0075
9	2	8	8	2	7	6640.6555	0.0119
4	2	2	3	2	1	2972.2648	0.0021
5	2	3	4	2	2	3722.4895	0.0000
6	2	4	5	2	3	4476.9235	0.0002
7	2	5	6	2	4	5235.5773	0.0096
8	2	6	7	2	5	5997.8230	-0.0062
9	2	7	8	2	6	6762.5584	-0.0028
10	2	8	9	2	7	7528.2730	-0.0071
4	3	2	3	3	1	2963.5557	0.0051
5	3	3	4	3	2	3705.3487	-0.0019
6	3	4	5	3	3	4447.6165	-0.0026
7	3	5	6	3	4	5190.3186	-0.0002
8	3	6	7	3	5	5933.3537	0.0013
9	3	7	8	3	6	6676.5668	0.0026
6	3	3	5	3	2	4449.1187	-0.0046
7	3	4	6	3	3	5193.6865	0.0003
8	3	5	7	3	4	5940.0250	-0.0094

Table S6. Measured frequencies and residuals (in MHz) of the rotational transitions of the $^{13}C_2$-ethanol isotopologue of conformer ***g*+a1** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	$\nu_{obs}-\nu_{calc}$
3	1	3	2	1	2	2170.8130	0.0042
3	2	2	2	2	1	2221.5980	0.0130
3	2	1	2	2	0	2226.3303	0.0005
3	1	2	2	1	1	2270.8850	-0.0012
4	1	4	3	1	3	2893.0489	-0.0032
4	2	3	3	2	2	2961.1616	0.0004
4	2	2	3	2	1	2972.9590	-0.0001
4	1	3	3	1	2	3026.3755	0.0003
5	1	5	4	1	4	3614.2042	-0.0022
5	0	5	4	0	4	3679.2356	0.0011
5	2	4	4	2	3	3699.9213	-0.0007
5	2	3	4	2	2	3723.2538	-0.0006
5	1	4	4	1	3	3780.5190	-0.0010
6	1	6	5	1	5	4334.0907	-0.0006
6	0	6	5	0	5	4402.9666	0.0006
6	2	5	5	2	4	4437.6669	0.0010
6	3	4	5	3	3	4448.8091	-0.0006
6	3	3	5	3	2	4450.2854	0.0007
6	2	4	5	2	3	4477.6974	-0.0017
6	1	5	5	1	4	4532.8817	0.0000
7	1	7	6	1	6	5052.5812	0.0002
7	0	7	6	0	6	5121.2591	-0.0004
7	2	6	6	2	5	5174.2009	0.0058
7	3	5	6	3	4	5191.6906	0.0074
7	3	4	6	3	3	5194.9848	-0.0009
7	2	5	6	2	4	5236.3030	0.0005
7	1	6	6	1	5	5282.9498	-0.0037
8	1	8	7	1	7	5769.6037	-0.0042
8	0	8	7	0	7	5834.4574	-0.0036
8	2	7	7	2	6	5909.3169	-0.0016
8	3	6	7	3	5	5934.8840	-0.0013
8	3	5	7	3	4	5941.4383	-0.0010
8	2	6	7	2	5	5998.4896	0.0020
8	1	7	7	1	6	6030.1500	-0.0027
9	1	9	8	1	8	6485.1632	0.0012
9	0	9	8	0	8	6543.4487	0.0023
9	2	8	8	2	7	6642.8496	-0.0058
9	3	7	8	3	6	6678.2620	-0.0012
9	3	6	8	3	5	6690.1389	-0.0009
9	2	7	8	2	6	6763.1277	-0.0033
9	1	8	8	1	7	6773.8196	-0.0025
10	1	10	9	1	9	7199.2819	-0.0032
10	0	10	9	0	9	7249.4094	0.0054
10	2	9	9	2	8	7374.6469	0.0061
10	3	8	9	3	7	7421.6110	-0.0007
10	3	7	9	3	6	7441.6285	-0.0049
10	1	9	9	1	8	7513.2834	0.0323
10	2	8	9	2	7	7528.7822	0.0084

Table S7. Measured frequencies and residuals (in MHz) of the rotational transitions of the $^{13}C_1$-ethanol isotopologue of conformer ***g*−a2** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	$\nu_{obs}-\nu_{calc}$
3	1	3	2	1	2	2153.8395	0.0045
3	0	3	2	0	2	2214.7946	0.0058
3	1	2	2	1	1	2289.8218	-0.0002
4	1	4	3	1	3	2869.4592	-0.0010
4	0	4	3	0	3	2943.4850	-0.0011
4	1	3	3	1	2	3050.4925	-0.0014
5	1	5	4	1	4	3583.2708	-0.0001
5	0	5	4	0	4	3664.5803	-0.0004
5	1	4	4	1	3	3808.7490	-0.0009
6	1	6	5	1	5	4295.0187	-0.0003
6	0	6	5	0	5	4377.3462	-0.0004
6	1	5	5	1	4	4563.7531	-0.0004
7	1	7	6	1	6	5004.5702	-0.0025
7	0	7	6	0	6	5082.1607	0.0005
7	1	6	6	1	5	5314.5233	0.0019
8	1	8	7	1	7	5711.9185	0.0021
8	0	8	7	0	7	5780.4831	0.0000
8	1	7	7	1	6	6059.9220	-0.0003
9	1	9	8	1	8	6417.1434	0.0033
9	0	9	8	0	8	6474.4135	0.0019
9	1	8	8	1	7	6798.7210	0.0011
10	1	10	9	1	9	7120.4160	-0.0013
10	0	10	9	0	9	7166.0241	-0.0013
10	1	9	9	1	8	7529.6955	0.0038
11	1	11	10	1	10	7821.9762	-0.0019
11	0	11	10	0	10	7856.9030	-0.0056
4	2	3	3	2	2	2962.5420	0.0034
5	2	4	4	2	3	3700.5354	-0.0003
6	2	5	5	2	4	4436.7870	0.0022
7	2	6	6	2	5	5170.9663	0.0114
9	2	8	8	2	7	6631.8526	0.0049
10	2	9	9	2	8	7358.0650	0.0084
4	2	2	3	2	1	2983.2212	-0.0045
5	2	3	4	2	2	3741.1393	-0.0021
6	2	4	5	2	3	4505.5917	-0.0021
7	2	5	6	2	4	5275.8185	-0.0041
8	2	6	7	2	5	6049.9505	-0.0028
9	2	7	8	2	6	6825.4207	-0.0108
10	2	8	9	2	7	7599.6443	-0.0086
4	3	2	3	3	1	2968.1785	0.0015
5	3	3	4	3	2	3711.7700	0.0012
6	3	4	5	3	3	4456.0856	0.0005
7	3	5	6	3	4	5200.9926	0.0024
8	3	6	7	3	5	5946.2340	0.0025
9	3	7	8	3	6	6691.4525	0.0004
10	3	8	9	3	7	7436.2219	0.0091
4	3	1	3	3	0	2968.5363	-0.0037
5	3	2	4	3	1	3713.0352	-0.0007
6	3	3	5	3	2	4459.4420	-0.0034
7	3	4	6	3	3	5208.4836	-0.0003
8	3	5	7	3	4	5961.0135	0.0013
9	3	6	8	3	5	6717.9887	-0.0038
10	3	7	9	3	6	7480.3645	-0.0032
5	4	2	4	4	1	3709.8287	0.0027
5	4	1	4	4	0	3709.8287	-0.0089
7	4	4	6	4	3	5197.5318	0.0045
8	4	5	7	4	4	5942.6497	-0.0052
10	4	7	9	4	6	7435.7648	-0.0017
7	4	3	6	4	2	5197.6981	-0.0027

8	4	4	7	4	3	5943.1207	-0.0093
9	4	5	8	4	4	6689.8707	0.0087
10	4	6	9	4	5	7438.2006	-0.0011
6	5	2	5	5	1	4451.3914	-0.0085
6	5	1	5	5	0	4451.3914	-0.0088
7	5	3	6	5	2	5194.5860	0.0013
9	5	5	8	5	4	6682.8332	0.0153
9	5	4	8	5	3	6682.8332	-0.0070
10	5	6	9	5	5	7428.0368	0.0043
3	1	2	2	0	2	3095.5463	-0.0003
5	1	4	4	0	4	4796.5115	-0.0040
6	1	5	5	0	5	5695.7039	0.0156
7	1	6	6	0	6	6632.8628	-0.0003
2	2	0	1	1	0	3668.3330	-0.0017
3	2	1	2	1	1	4372.3787	0.0027
4	2	2	3	1	2	5065.7805	0.0008
5	2	3	4	1	3	5756.4332	0.0060
6	2	4	5	1	4	6453.2657	-0.0054
7	2	5	6	1	5	7165.3321	-0.0081

Table S8. Measured frequencies and residuals (in MHz) of the rotational transitions of the $^{13}C_2$-ethanol isotopologue of conformer ***g*−a2** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	$\nu_{obs}-\nu_{calc}$
3	1	3	2	1	2	2154.0379	-0.0019
3	0	3	2	0	2	2215.0790	-0.0019
3	2	2	2	2	1	2223.5046	0.0018
3	2	1	2	2	0	2231.9270	-0.0012
3	1	2	2	1	1	2290.3238	-0.0021
4	1	4	3	1	3	2869.7135	0.0009
4	0	4	3	0	3	2943.7918	-0.0007
4	2	3	3	2	2	2963.0110	-0.0007
4	3	2	3	3	1	2968.7080	0.0079
4	3	1	3	3	0	2969.0658	-0.0029
4	2	2	3	2	1	2983.8770	-0.0021
5	1	5	4	1	4	3583.5567	0.0007
5	0	5	4	0	4	3664.8444	0.0012
5	2	4	4	2	3	3701.1034	0.0011
5	4	1	4	4	0	3710.4811	-0.0088
5	3	3	4	3	2	3712.4326	0.0002
5	3	2	4	3	1	3713.7162	-0.0027
5	2	3	4	2	2	3742.0500	-0.0021
5	1	4	4	1	3	3809.5160	0.0006
6	1	6	5	1	5	4295.3210	0.0000
6	0	6	5	0	5	4377.5156	0.0005
6	2	5	5	2	4	4437.4299	0.0015
6	5	1	5	5	0	4452.1912	0.0113
6	3	4	5	3	3	4456.8909	-0.0002
6	3	3	5	3	2	4460.3011	-0.0024
6	2	4	5	2	3	4506.7922	-0.0015
6	1	5	5	1	4	4564.6043	0.0007
7	1	7	6	1	6	5004.8768	0.0001
7	0	7	6	0	6	5082.2093	-0.0002
7	2	6	6	2	5	5171.6648	0.0084
7	4	4	6	4	3	5198.4700	0.0025
7	4	3	6	4	2	5198.6431	-0.0017
7	3	5	6	3	4	5201.9377	0.0008
7	3	4	6	3	3	5209.5434	-0.0025
7	2	5	6	2	4	5277.3102	-0.0045
7	1	6	6	1	5	5315.4139	0.0036
8	1	8	7	1	7	5712.2107	0.0011
8	0	8	7	0	7	5780.4222	0.0020
8	2	7	7	2	6	5903.4742	0.0008
8	4	5	7	4	4	5943.7502	0.0029
8	4	4	7	4	3	5944.2245	-0.0085
8	3	6	7	3	5	5947.3134	0.0010
8	3	5	7	3	4	5962.3150	-0.0024
8	2	6	7	2	5	6051.6911	-0.0124
8	1	7	7	1	6	6060.7866	-0.0046
9	1	9	8	1	8	6417.4165	0.0038
9	0	9	8	0	8	6474.2704	0.0016
9	2	8	8	2	7	6632.6058	0.0073
9	4	5	8	4	4	6691.1383	0.0016
9	3	7	8	3	6	6692.6569	0.0019
9	3	6	8	3	5	6719.5825	-0.0075
9	1	8	8	1	7	6799.5006	0.0031
9	2	7	8	2	6	6827.3705	-0.0039
10	1	10	9	1	9	7120.6655	0.0025
10	0	10	9	0	9	7165.8463	0.0022
10	2	9	9	2	8	7358.8070	0.0106
10	4	7	9	4	6	7437.1762	-0.0004
10	3	8	9	3	7	7437.5238	0.0046
10	4	6	9	4	5	7439.6652	-0.0004

10	3	7	9	3	6	7482.3058	-0.0054
10	1	9	9	1	8	7530.3115	0.0128
10	2	8	9	2	7	7601.6970	-0.0101
11	1	11	10	1	10	7822.1910	-0.0025
11	0	11	10	0	10	7856.7158	-0.0084
3	1	2	2	0	2	3092.9491	-0.0023
2	2	1	1	1	1	3702.0787	-0.0009
4	1	3	3	0	3	3929.0105	-0.0007
3	2	1	2	1	1	4362.8790	-0.0025
3	2	2	2	1	2	4488.6870	-0.0028
5	1	4	4	0	4	4794.7365	0.0024
5	2	3	4	1	3	5747.3447	-0.0014
3	3	0	2	2	0	5884.4286	0.0022
3	3	1	2	2	1	5886.4828	0.0040
6	2	4	5	1	4	6444.6217	-0.0026
4	3	1	3	2	1	6621.5700	0.0030
4	3	2	3	2	2	6631.6618	-0.0143
7	1	6	6	0	6	6632.3923	0.0025
6	2	5	5	1	5	6982.9260	0.0023
7	2	5	6	1	5	7157.3331	-0.0023
5	3	2	4	2	2	7351.4101	0.0033
5	3	3	4	2	3	7381.1010	0.0042
8	1	7	7	0	7	7610.9742	0.0027
7	2	6	6	1	6	7859.2724	0.0133
8	2	6	7	1	6	7893.6146	-0.0139

Table S9. Measured frequencies and residuals (in MHz) of the rotational transitions of the $^{13}C_1$-ethanol isotopologue of conformer ***g*−b** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	*J"*	$K"_{-1}$	$K"_{+1}$	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	2565.2240	0.0010
3	0	3	2	0	2	2633.2107	-0.0014
3	1	2	2	1	1	2733.2397	0.0055
4	1	4	3	1	3	3415.2332	-0.0036
4	0	4	3	0	3	3490.1437	-0.0005
4	1	3	3	1	2	3638.0545	0.0077
5	1	5	4	1	4	4261.6155	-0.0059
5	0	5	4	0	4	4333.1676	-0.0063
5	1	4	4	1	3	4536.7039	0.0052
6	1	6	5	1	5	5104.2410	-0.0051
6	0	6	5	0	5	5164.7287	-0.0057
6	1	5	5	1	4	5426.7227	-0.0020
7	1	7	6	1	6	5943.3199	-0.0001
7	0	7	6	0	6	5989.4827	0.0025
7	1	6	6	1	5	6305.3064	-0.0063
8	1	8	7	1	7	6779.3140	0.0117
8	1	7	7	1	6	7169.8238	0.0047
3	2	2	2	2	1	2652.2502	0.0042
3	2	1	2	2	0	2671.2942	0.0084
4	2	3	3	2	2	3532.5639	0.0023
4	2	2	3	2	1	3578.7322	0.0028
4	3	2	3	3	1	3545.2090	-0.0010
5	2	4	4	2	3	4409.6781	0.0029
5	2	3	4	2	2	4496.7956	0.0022
5	3	3	4	3	2	4434.3670	0.0010
6	2	5	5	2	4	5282.8531	0.0012
6	2	4	5	2	3	5422.1361	0.0003
6	3	4	5	3	3	5324.2315	-0.0029
6	2	4	5	2	3	5422.1361	0.0003
7	2	6	6	2	5	6151.4438	-0.0040
7	2	5	6	2	4	6349.0534	-0.0104

Table S10. Measured frequencies and residuals (in MHz) of the rotational transitions of the $^{13}C_2$-ethanol isotopologue of conformer ***g*−b** of fenchone-ethanol.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	2571.7070	-0.0070
3	0	3	2	0	2	2640.1849	0.0006
3	2	2	2	2	1	2659.9057	0.0040
3	1	2	2	1	1	2741.8389	0.0093
4	1	4	3	1	3	3423.7131	-0.0070
4	0	4	3	0	3	3498.7569	-0.0035
4	2	3	3	2	2	3542.6326	0.0012
4	3	2	3	3	1	3555.7289	0.0007
4	3	1	3	3	0	3557.3792	0.0057
4	2	2	3	2	1	3590.3909	0.0063
4	1	3	3	1	2	3649.2712	0.0082
5	0	5	4	0	4	4343.1336	-0.0039
5	2	4	4	2	3	4422.0449	0.0019
5	3	3	4	3	2	4447.5777	-0.0014
5	2	3	4	2	2	4511.9493	0.0081
5	1	4	4	1	3	4550.2851	0.0060
6	1	6	5	1	5	5116.4040	-0.0069
6	0	6	5	0	5	5175.9985	-0.0057
6	2	5	5	2	4	5297.3811	0.0026
6	5	1	5	5	0	5332.2208	-0.0036
6	5	2	5	5	1	5332.2208	0.0016
6	4	3	5	4	2	5336.5424	-0.0009
6	4	2	5	4	1	5336.9914	-0.0017
6	3	4	5	3	3	5340.1248	0.0039
6	3	3	5	3	2	5355.0099	0.0003
6	2	4	5	2	3	5440.6602	0.0040
6	1	5	5	1	4	5442.2988	-0.0005
7	1	7	6	1	6	5957.2156	-0.0006
7	0	7	6	0	6	6002.2311	-0.0050
7	2	6	6	2	5	6167.9806	0.0025
7	3	4	6	3	3	6264.8504	-0.0030
7	1	6	6	1	5	6322.3992	-0.0010
7	2	5	6	2	4	6370.5610	-0.0059
8	1	8	7	1	7	6794.8988	0.0011
8	0	8	7	0	7	6826.2732	-0.0019
8	3	5	7	3	4	7184.8207	-0.0060
8	1	7	7	1	6	7187.8917	-0.0037
8	2	6	7	2	5	7295.8982	-0.0115
9	1	9	8	1	8	7630.0783	0.0079
9	0	9	8	0	8	7650.6759	0.0032
9	2	8	8	2	7	7893.1912	0.0091
3	1	3	2	1	2	2571.7070	-0.0070
3	0	3	2	0	2	2640.1849	0.0006

Table S11. Experimental spectroscopic parameters of the single substituted $^{13}C_1$-ethanol conformers of fenchone-ethanol complex.

	$^{13}C_1$-I	$^{13}C_1$-II	$^{13}C_1$-III
A(MHz)[a]	1076.696(22)[e]	1106.13199(63)	930.597(12)
B(MHz)	387.02067(44)	393.20002(12)	470.08912(36)
C(MHz)	353.30343(42)	347.85084(14)	413.99879(33)
Δ_J(kHz)	0.2293(10)	0.1127(67)	0.1096(28)
Δ_{JK}(kHz)	0.295(43)	0.171(54)	0.247 (41)
δ_J(kHz)	-0.0420(14)	-	-
a/*b*/*c*[b]	y/n/n	y/n/y	y/n/n
N[c]	43	78	31
σ(kHz)[d]	5	5	5

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK} and δ_{JK} are the centrifugal distortion constants.
[b] *a*, *b* and *c* represent the type of transitions observed in the rotational spectrum.
[c] N is the number of the fitted transitions.
[d] σ is the rms deviation of the fit.
[e] Standard error in parentheses in units of the last digit.

Table S12. Experimental spectroscopic parameters of the single substituted $^{13}C_2$-ethanol conformers of fenchone-ethanol complex.

	$^{13}C_2$-I	$^{13}C_2$-II	$^{13}C_2$-III
A(MHz)[a]	1072.382(25)[e]	1102.92519(37)	926.640(10)
B(MHz)	386.95221(44)	393.31118(13)	471.71815(26)
C(MHz)	353.58768(42)	347.86197(14)	414.92110(30)
Δ_J(kHz)	0.2493(10)	0. 12172(73)	0.1201(17)
Δ_{JK}(kHz)	0.304(19)	0. 1474(76)	0.126(15)
δ_{JK}(kHz)	-0.0462(14)	-	-
a/*b*/*c*[b]	y/n/n	y/n/y	y/n/n
N[c]	46	84	41
σ(kHz)[d]	5	5	5

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK} and δ_{JK} are the centrifugal distortion constants.
[b] *a*, *b* and *c* represent the type of transitions observed in the rotational spectrum.
[c] N is the number of the fitted transitions.
[d] σ is the rms deviation of the fit.
[e] Standard error in parentheses in units of the last digit.

Table S13. Comparison between substitution and equilibrium B3LYP-D3BJ/6-311++G(d,p) coordinates determined for the C_1 of ethanol.

	r_s	r_e											
	$^{13}C_1$-I	*t*a1		*t*a2		*g*+a1		*g*+a2		*g*–a1		*g*–a2	
			Δ[c]		Δ		Δ		Δ		Δ		Δ
|*a*|[a]	4.26767(37)[b]	3.866	0.4	4.075	0.2	4.175	0.1	4.057	0.2	4.073	0.2	4.172	0.1
|*b*|	0.3643(43)	0.710	-0.3	0.806	-0.4	0.411	0.0	0.093	0.3	0.208	0.2	0.169	0.2
|*c*|	0.1641(96)	0.480	-0.3	0.102	0.1	0.213	0.0	0.393	-0.2	0.503	-0.3	0.488	-0.3
	r_s	r_e											
	$^{13}C_1$-II	*t*a1		*t*a2		*g*+a1		*g*+a2		*g*–a1		*g*–a2	
			Δ		Δ		Δ		Δ		Δ		Δ
|*a*|	4.24665(37)	3.866	0.4	4.075	0.2	4.175	0.1	4.057	0.2	4.073	0.2	4.172	0.1
|*b*|	0.1989(80)	0.710	-0.5	0.806	-0.6	0.411	-0.2	0.093	0.1	0.208	0.0	0.169	0.0
|*c*|	0.4752(33)	0.480	0.0	0.102	0.4	0.213	0.3	0.393	0.1	0.503	0.0	0.488	0.0
	r_s	r_e											
	$^{13}C_1$-III	*t*b		*g*+b		*g*–b							
			Δ		Δ		Δ						
|*a*|	3.93108(41)	3.308	0.6	3.260	0.7	3.917	0.0						
|*b*|	0.20379(79)	0.800	-0.6	0.095	0.1	0.290	0.0						
|*c*|	0.127(13)	0.021	0.1	0.711	-0.6	0.064	0.0						

[a] *a*, *b* and *c* are coordinates in angstroms of the C_1 carbon atom of ethanol in their absolute values.
[b] Standard error in parentheses in units of the last digit.
[c] Calculated differences between substitution and equilibrium coordinates.

Table S14. Comparison between substitution and equilibrium B3LYP-D3BJ/6-311++G(d,p) coordinates determined for the C_2 of ethanol.

	r_s	r_e											
	$^{13}C_2$-I	*t*a1		*t*a2		*g*+a1		*g*+a2		*g*–a1		*g*–a2	
			Δ[c]		Δ		Δ		Δ		Δ		Δ
|*a*|[a]	4.09557(37)[b]	5.167	-1.1	5.344	-1.2	3.947	0.1	4.607	-0.5	4.629	0.5	4.035	0.1
|*b*|	0.62584(43)	0.068	0.6	0.006	0.6	0.645	0.0	1.121	-0.5	1.176	-0.5	0.943	-0.3
|*c*|	1.30526(96)	0.399	0.9	0.082	1.2	1.278	0.0	0.347	1.0	0.186	1.1	0.819	0.5
	r_s	r_e											
	$^{13}C_2$-II	*t*a1		*t*a2		*g*+a1		*g*+a2		*g*–a1		*g*–a2	
			Δ		Δ		Δ		Δ		Δ		Δ
|*a*|	4.14172(38)	5.167	-1.0	5.344	-1.2	3.947	0.2	4.607	-0.5	4.629	-0.5	4.035	0.1
|*b*|	0.9306(17)	0.068	0.9	0.006	0.9	0.645	0.3	1.121	-0.2	1.176	-0.2	0.943	0.0
|*c*|	0.8533(18)	0.399	0.5	0.082	0.7	1.278	-0.4	0.347	0.5	0.186	0.7	0.819	0.0
	r_s	r_e											
	$^{13}C_2$-III	*t*b		*g*+b		*g*–b							
			Δ		Δ		Δ						
|*a*|	3.3199(11)	4.482	-1.1	3.848	-0.5	3.230	0.1						
|*b*|	1.3180(27)	0.359	1.0	1.139	0.2	1.182	0.1						
|*c*|	0.8379(43)	0.834	0.0	0.038	0.8	0.967	-0.1						

[a] *a*, *b* and *c* are coordinates in angstroms of the C_1 carbon atom of ethanol in their absolute values.
[b] Standard error in parentheses in units of the last digit.
[c] Calculated differences between substitution and equilibrium coordinates.

Table S15 Calculated energies in Hartree at different levels of theory of the lower-energy conformers of fenchone-ethanol.

Conformer	MP2/6-311G++(d,p)		M062X/6-311G++(d,p)		B3LYP-D3BJ/6-311G++(d,p)	
	E(h)	E+ZPC(h)	E(h)	E+ZPC(h)	E(h)	E+ZPC (h)
*t*a1	-619.319654	-618.993585	-620.8717541	-620.5466451	-621.2225426	-620.9003176
*t*a2	-619.3196034	-618.9936094	-620.8716684	-620.5468524	-621.2225823	-620.9005063
g+a1	-619.3200179	-618.9937579	-620.872125	-620.546738	-621.2229222	-620.9005102
g+a2	-619.3198612	-618.9936732	-620.8719915	-620.5467255	-621.2227725	-620.9003595
g–a1	-619.3198301	-618.9936111	-620.8718587	-620.5467927	-621.222728	-620.900275
g–a2	-619.3200577	-618.9938197	-620.8721397	-620.5467937	-621.2229526	-620.9006786
*t*b	-619.3194941	-618.9936801	-620.8712201	-620.5457851	-621.2215676	-620.8995096
g+b	-619.3199483	-618.9939133	-620.8716967	-620.5468647	-621.2220599	-620.8998619
g–b	-619.3201437	-618.9939407	-620.8718288	-620.5465378	-621.2224042	-620.9002152
*t*c	-619.3186447	-618.9930527	-620.8711281	-620.5458891	-621.2204224	-620.8986144
g+c	-619.3190733	-618.9931293	-620.871874	-620.546546	-621.2214833	-620.8989693
g–c	-619.3187749	-618.9929229	-620.8711557	-620.5462477	-621.2212483	-620.8992793

Figure S1. Potential energy barriers of fenchone-ethanol obtained by scanning the $\angle C_2^{et}C_1^{et}O^{et}O^f$ dihedral angle for the **a** (top), **b** (middle) and **c** (bottom) interaction sites.

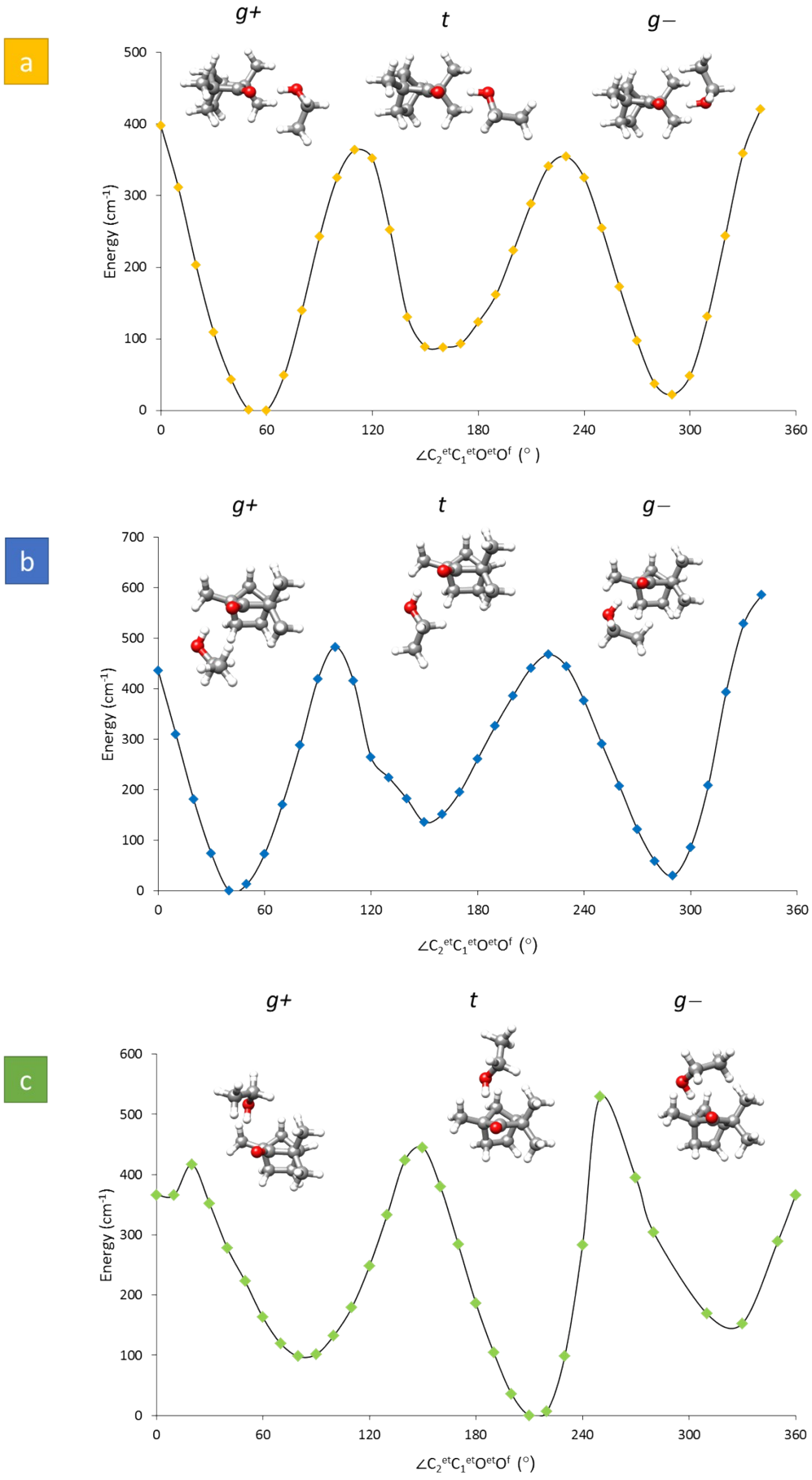

Figure S2. Potential energy barriers (M062X/6-311++G(d,p)) for the complex of fenchone with *trans* ethanol obtained by scanning the $\angle C_1^{et}O^{et}O^{f}C_2^{f}$ dihedral angle for the **a** (top), **b** (middle) and **c** (bottom) interaction sites. Minima not indicated were found not to be realminima once the structures were optimised without any constrains.

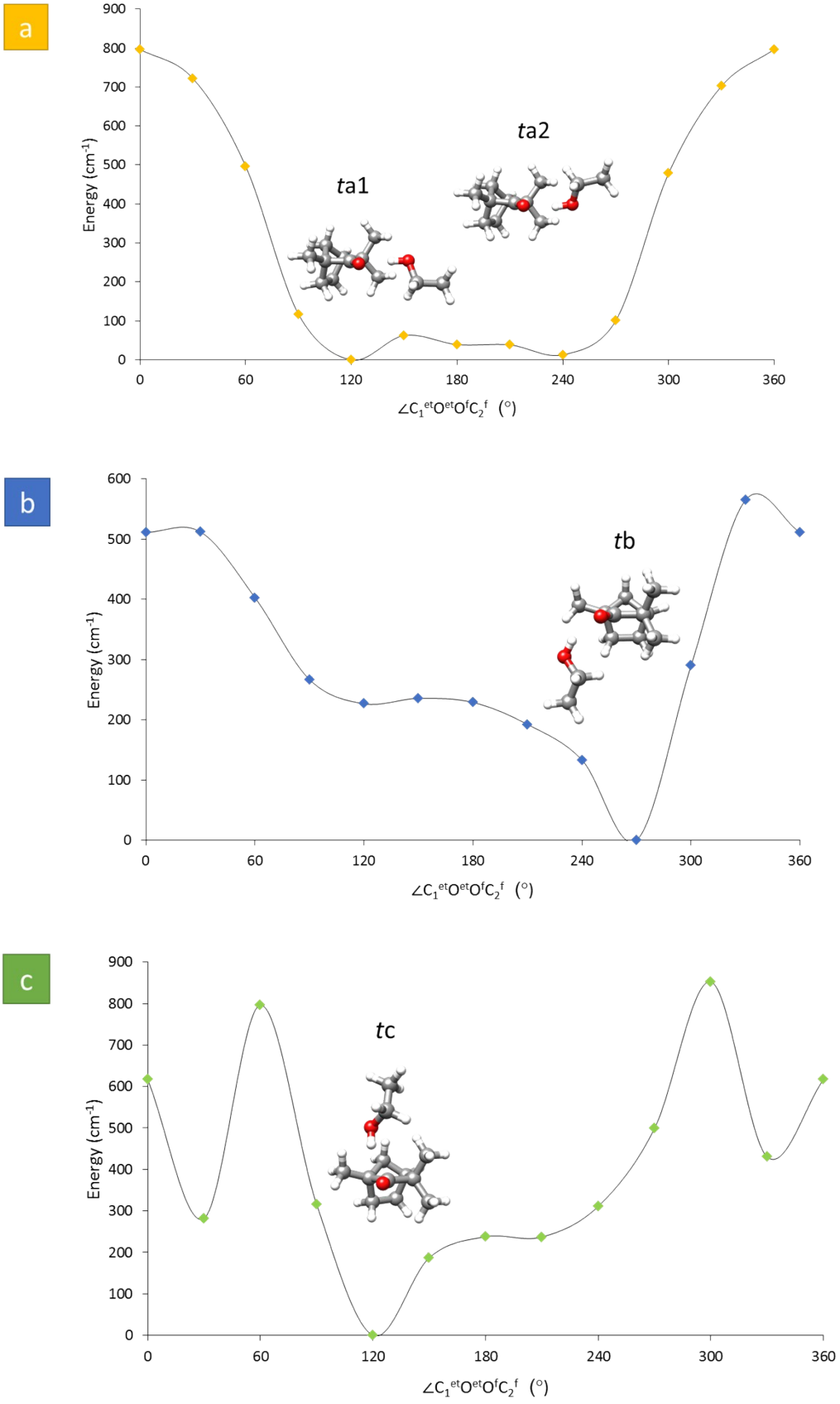

Figure S3. Potential energy barriers (M062X/6-311++G(d,p)) for the complex of fenchone with *g*+ ethanol obtained by scanning the $\angle C_1^{et}O^{et}O^{f}C_2^{f}$ dihedral angle for the **a** (top), **b** (middle) and **c** (bottom) interaction sites. Minima not indicated were found not to be realminima once the structures were optimised without any constrains.

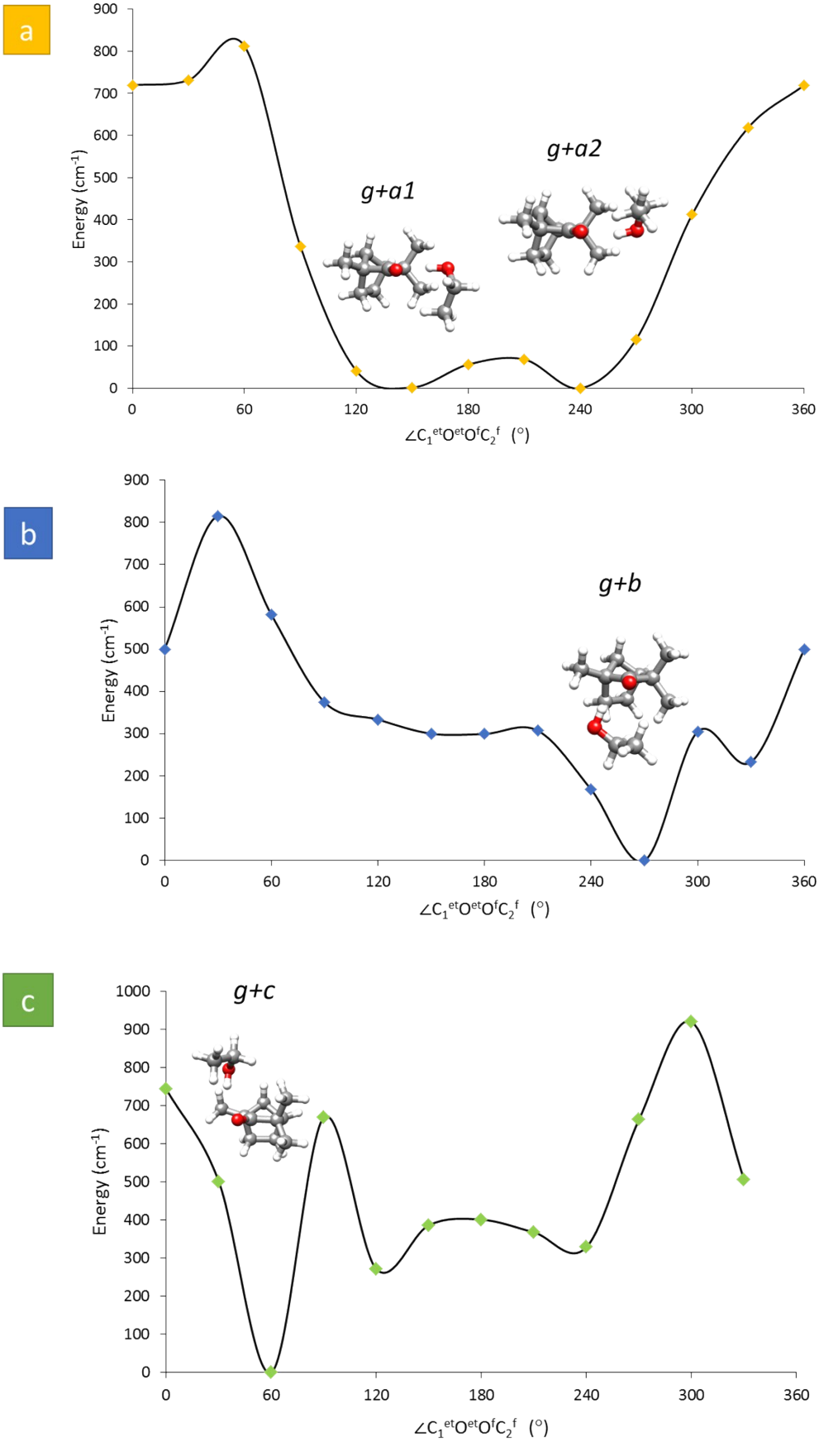

Figure S4. Potential energy barriers (M062X/6-311++G(d,p)) for the complex of fenchone with *g*− ethanol obtained by scanning the $\angle C_1^{et}O^{et}O^{f}C_2^{f}$ dihedral angle for the **a** (top), **b** (middle) and **c** (bottom) interaction sites. Minima not indicated were found not to be realminima once the structures were optimised without any constrains.