Table S1: Heats of formation (kcal/mol) for the molecules in the training set. Standard MNDO values are compared with results from the connection atom treatment, with one methyl group replaced by a connection atom (column ACA).

Molecule	MNDO	ACA	ACA-MNDO
ethane	-19.7	-19.6	0.2
propane	-24.9	-25.5	-0.5
propene	5.0	5.4	0.4
cis-butane	-26.5	-28.5	-2.1
trans-butane	-29.7	-29.8	-0.1
isobutane	-26.8	-28.0	-1.2
but-1-ene	-0.1	-1.0	-0.8
trans-2-butene	-5.1	-4.1	1.0
isobutene	-2.0	-2.5	-0.5
pentane	-34.4	-34.5	-0.1
neopentane	-24.6	-26.9	-2.3
1,2-dimethylcyclopropene	39.2	38.5	-0.8
toluene	13.6	14.0	0.5
ethanol	-63.0	-60.3	2.7
1-propanol	-67.7	-67.9	-0.1
2-propanol	-65.1	-61.9	3.2
tert-butanol	-64.3	-62.1	2.2
diethylether	-62.0	-58.6	3.4
diethylperoxide	-38.9	-35.8	3.2
propionaldehyde	-47.5	-46.6	1.0
propionic acid	-105.6	-103.5	2.1
acetylacetone	-83.4	-81.5	1.9
acetylaceton enol	-83.9	-82.9	1.0
methyl acetate	-93.7	-93.9	-0.2
acetic anhydride	-132.6	-132.5	0.1
ethylamine	-13.2	-10.5	2.8
propylamine	-18.2	-18.8	-0.6
tert-butylamine	-15.5	-17.0	-1.5
propionitrile	13.8	13.1	-0.7

Table S2: Heats of formation (kcal/mol) for the molecules in the training set. Standard AM1 values are compared with results from the connection atom treatment, with one methyl group replaced by a connection atom (column ACA)

Molecule	AM1	ACA	ACA-AM1
ethane	-17.4	-18.2	-0.8
propane	-24.3	-25.6	-1.3
propene	6.6	6.4	-0.2
cis-butane	-27.8	-30.6	-2.7
trans-butane	-31.1	-31.1	0.0
isobutane	-29.4	-30.9	-1.6
but-1-ene	0.2	-1.4	-1.7
trans-2-butene	-3.3	-2.2	1.1
isobutene	-1.2	-2.6	-1.4
pentane	-38.0	-37.8	0.2
neopentane	-32.8	-34.7	-1.9
1,2-dimethylcyclopropene	54.6	55.2	0.6
toluene	14.4	15.2	0.8
ethanol	-62.7	-61.6	1.1
1-propanol	-69.5	-69.5	0.1
2-propanol	-69.5	-66.5	3.0
tert-butanol	-71.6	-69.2	2.4
diethylether	-64.4	-61.3	3.1
diethylperoxide	-36.7	-33.3	3.4
propionaldehyde	-47.7	-48.9	-1.3
propionic acid	-109.0	-108.3	0.7
acetylacetone	-85.5	-80.0	5.5
acetylaceton enol	-84.9	-83.6	1.3
methyl acetate	-96.4	-95.7	0.7
acetic anhydride	-131.6	-129.7	1.9
ethylamine	-15.1	-14.7	0.4
n-propylamine	-22.1	-22.3	-0.2
tert-butylamine	-21.3	-25.3	-4.0
propionitrile	13.0	10.5	-2.6

Table S3: Heats of formation (kcal/mol) for the molecules in the training set. Standard PM3 values are compared with results from the connection atom treatment, with one methyl group replaced by a connection atom (column ACA).

Molecule	PM3	ACA	ACA-PM3
ethane	-18.1	-18.4	-0.2
propane	-23.6	-24.1	-0.5
propene	6.4	7.4	1.0
cis-butane	-29.1	-29.4	-0.3
trans-butane	-25.1	-26.4	-1.3
isobutane	-29.5	-30.2	-0.7
but-1-ene	1.5	-0.1	-1.5
trans-2-butene	-3.8	-2.6	1.2
isobutene	-3.3	-3.6	-0.2
pentane	-34.5	-34.8	-0.3
neopentane	-35.8	-36.7	-0.9
1,2-dimethylcyclopropene	46.7	47.1	0.4
toluene	14.1	13.8	-0.3
ethanol	-56.9	-55.5	1.4
1-propanol	-62.2	-62.7	-0.5
2-propanol	-65.8	-64.5	1.3
tert-butanol	-71.3	-70.3	0.9
diethylether	-57.4	-56.0	1.5
diethylperoxide	-40.0	-39.6	0.4
propionaldehyde	-48.6	-49.5	-0.9
propionic acid	-106.3	-107.3	-0.9
acetylacetone	-91.6	-91.6	0.0
acetylaceton enol	-88.8	-88.4	0.4
methyl acetate	-94.1	-95.7	-1.6
acetic anhydride	-135.0	-136.7	-1.8
ethylamine	-12.5	-12.5	0.0
n-propylamine	-17.9	-18.4	-0.5
tert-butylamine	-25.2	-26.8	-1.6
propionitrile	18.5	16.0	-2.6