Ab initio and 2nd ab initio values are W1U and CBS-APNO results when all species consist of no more than four heavy atoms, CBS-APNO and G3B3 results, respectively, when at least one species of five or more heavy atoms is involved.

*Contribution to the error function as defined by eq. (6) in the paper.

Ab initio and literature isodesmic reaction heats (kJ/mol), their differences and their contributions to the error function

AMINE/ALCOHOL CYCLE	Ab initio	2nd ab initio	Literature / (kJ mol^{-1})	*Lit–Calc*	ε^*
MeNH$_2$ + H$_2$O → MeOH + **NH$_3$**	16.5	14.6	17.8	1.3	3.648
MeNH$_2$ + EtOH → MeOH + **EtNH$_2$**	5.0	5.0	9.6	4.6	21.438
MeNH$_2$ + PrOH → MeOH + **PrNH$_2$**	4.0	4.7	4.9	0.9	0.636
MeNH$_2$ + BuOH → MeOH + **BuNH$_2$**	4.8	5.7	5.0	0.2	0.029
MeNH$_2$ + *i*-BuOH → MeOH + ***i*-BuNH$_2$**	5.9	6.0	7.1	1.2	0.465
EtNH$_2$ + PrOH → EtOH + **PrNH$_2$**	-1.1	-1.0	-4.7	-3.6	9.143
EtNH$_2$ + BuOH → EtOH + **BuNH$_2$**	-0.2	0.6	-4.6	-4.4	9.086
EtNH$_2$ + *i*-BuOH → EtOH + ***i*-BuNH$_2$**	0.9	0.9	-2.5	-3.4	3.538
PrNH$_2$ + BuOH → PrOH + **BuNH$_2$**	0.7	1.0	0.1	-0.6	0.172
PrNH$_2$ + *i*-BuOH → PrOH + ***i*-BuNH$_2$**	1.9	1.3	2.2	0.3	0.026
BuNH$_2$ + *i*-BuOH → BuOH + ***i*-BuNH$_2$**	1.1	0.3	2.1	1.0	0.251
BuNH$_2$ → ***i*-BuNH$_2$**	-8.3	-9.2	-6.8	1.5	0.730
				Sum =	**49.2**

AMINE/ALKANE CYCLE	Ab initio	2nd ab initio	Literature / (kJ mol^{-1})	*Lit–Calc*	ε^*
MeNH$_2$ + MeH -> EtH + **NH$_3$**	-34.5	-34.1	-31.9	2.6	2.956
MeNH$_2$ + PrH -> EtH + **EtNH$_2$**	-7.9	-7.7	-3.2	4.7	13.768
MeNH$_2$ + BuH -> EtH + **PrNH$_2$**	-7.4	-7.5	-6.8	0.6	0.233
MeNH$_2$ + PeH -> EtH + **BuNH$_2$**	-7.1	-7.1	-5.3	1.8	0.958
MeNH$_2$ + *i*-PeH -> EtH + ***i*-BuNH$_2$**	-8.1	-8.6	-5.4	2.7	2.018
EtNH$_2$ + BuH -> PrH + **PrNH$_2$**	0.4	0.2	-3.6	-4.0	7.439
EtNH$_2$ + PeH -> BuH + **PrNH$_2$**	0.6	1.0	-2.1	-2.7	1.929
EtNH$_2$ + *i*-PeH -> *i*-BuH + **PrNH$_2$**	-0.4	-0.5	-2.2	-1.8	0.793
PrNH$_2$ + PeH -> BuH + **BuNH$_2$**	0.4	0.4	1.5	1.1	0.270
PrNH$_2$ + *i*-PeH -> BuH + ***i*-BuNH$_2$**	-0.6	-1.1	1.4	2.0	0.872
BuNH$_2$ + *i*-PeH -> PeH + ***i*-BuNH$_2$**	-1.0	-1.5	-0.1	0.9	0.165
MeNH$_2$ + H$_2$ -> MeH + **NH$_3$**	-98.7	-99.2	-96.9	1.8	2.801
				Sum =	**34.2**

RADICAL CYCLE	Ab initio	2nd ab initio	Literature / (kJ mol^{-1})	*Lit–Calc*	ε^*
H + CH$_4$ → H$_2$ + **CH$_3$**	3.0	2.8	3.1	0.1	0.008
H + C$_2$H$_6$ → H$_2$ + **C$_2$H$_5$**	-13.5	-13.4	-13.3	0.2	0.095
H + C$_3$H$_8$ → H$_2$ + **C$_3$H$_7$**	-11.7	-11.6	-12.5	-0.8	1.215
H + C$_3$H$_8$ → H$_2$ + ***i*-C$_3$H$_7$**	-24.6	-24.4	-23.3	1.3	3.544
CH$_3$ + C$_2$H$_6$ → CH$_4$ + **C$_2$H$_5$**	-16.5	-16.2	-16.4	0.1	0.018
CH$_3$ + C$_3$H$_8$ → CH$_4$ + **C$_3$H$_7$**	-14.8	-14.3	-15.6	-0.8	0.788
CH$_3$ + C$_3$H$_8$ → CH$_4$ + ***i*-C$_3$H$_7$**	-27.7	-27.2	-26.4	1.3	1.824
C$_2$H$_5$ + C$_3$H$_8$ → C$_2$H$_6$ + **C$_3$H$_7$**	1.8	1.8	0.8	-1.0	1.138
C$_2$H$_5$ + C$_3$H$_8$ → C$_2$H$_6$ + ***i*-C$_3$H$_7$**	-11.2	-11.0	-10.0	1.2	1.709
C$_3$H$_7$ → ***i*-C$_3$H$_7$**	-12.9	-12.9	-10.8	2.1	4.509
				Sum =	**14.8**

ALCOHOL/ALKANE CYCLE	Ab initio	2nd ab initio	Literature / (kJ mol^{-1})	*Lit–Calc*	ε^*
MeOH + MeH → EtH + H$_2$O	-51.0	-48.7	-49.7	1.2	0.753
MeOH + PrH → EtH + EtOH	-12.9	-12.7	-12.8	0.1	0.002
MeOH + BuH → EtH + PrOH	-11.3	-11.5	-11.7	-0.4	0.082
MeOH + PeH → EtH + BuOH	-11.8	-12.9	-10.3	1.5	0.798
MeOH + *i*-PeH → EtH + *i*-BuOH	-14.0	-14.6	-12.5	1.5	0.763
EtOH + BuH → PrH + PrOH	1.6	1.2	1.1	-0.5	0.109
PrOH + PeH → BuH + BuOH	-0.3	-0.6	1.4	1.7	0.972
PrOH + *i*-PeH → BuH + *i*-BuOH	-2.5	-2.4	-0.8	1.7	0.933
BuOH + *i*-PeH → PeH + *i*-BuOH	-2.2	-1.8	-2.2	0.0	0.000
BuOH → *i*-BuOH	-7.7	-7.7	-8.9	-1.2	0.520
i-PeH → PeH	5.8	6.2	6.7	0.9	0.274
				Sum =	**5.2**

Ab initio isodesmic reaction heats (kJ/mol) with the new amine and alkyl radical heats of formation, their differences and their contributions to the error function

AMINE/ALCOHOL CYCLE	Ab initio	2nd ab initio	New Exp / (kJ mol^{-1})	*New–Calc*	ε^*
MeNH$_2$ + H$_2$O → MeOH + **NH$_3$**	16.5	14.6	16.2	-0.3	0.176
MeNH$_2$ + EtOH → MeOH + **EtNH$_2$**	5.0	5.0	5.4	0.4	0.170
MeNH$_2$ + PrOH → MeOH + **PrNH$_2$**	4.0	4.7	4.6	0.5	0.247
MeNH$_2$ + BuOH → MeOH + **BuNH$_2$**	4.8	5.7	5.6	0.8	0.367
MeNH$_2$ + *i*-BuOH → MeOH + ***i*-BuNH$_2$**	5.9	6.0	6.3	0.4	0.056
EtNH$_2$ + PrOH → EtOH + **PrNH$_2$**	-1.1	-1.0	-0.8	0.3	0.069
EtNH$_2$ + BuOH → EtOH + **BuNH$_2$**	-0.2	0.6	0.2	0.4	0.089
EtNH$_2$ + *i*-BuOH → EtOH + ***i*-BuNH$_2$**	0.9	0.9	0.9	0.0	0.000
PrNH$_2$ + BuOH → PrOH + **BuNH$_2$**	0.7	1.0	1.0	0.3	0.030
PrNH$_2$ + *i*-BuOH → PrOH + ***i*-BuNH$_2$**	1.9	1.3	1.8	-0.1	0.005
BuNH$_2$ + *i*-BuOH → BuOH + ***i*-BuNH$_2$**	1.1	0.3	0.7	-0.4	0.046
BuNH$_2$ → ***i*-BuNH$_2$**	-8.3	-9.2	-8.2	0.1	0.005
				Sum =	**1.3**

AMINE/ALKANE CYCLE	Ab initio	2nd ab initio	New Exp / (kJ mol^{-1})	*New–Calc*	ε^*
MeNH$_2$ + MeH -> EtH + **NH$_3$**	-34.5	-34.1	-33.5	0.9	0.398
MeNH$_2$ + PrH -> EtH + **EtNH$_2$**	-7.9	-7.7	-7.4	0.5	0.141
MeNH$_2$ + BuH -> EtH + **PrNH$_2$**	-7.4	-7.5	-7.1	0.3	0.057
MeNH$_2$ + PeH -> EtH + **BuNH$_2$**	-7.1	-7.1	-4.7	2.4	1.688
MeNH$_2$ + *i*-PeH -> EtH + ***i*-BuNH$_2$**	-8.1	-8.6	-6.2	1.9	1.026
EtNH$_2$ + BuH -> PrH + **PrNH$_2$**	0.4	0.2	0.3	-0.2	0.011
EtNH$_2$ + PeH -> BuH + **PrNH$_2$**	0.6	1.0	2.7	2.1	1.086
EtNH$_2$ + *i*-PeH -> *i*-BuH + **PrNH$_2$**	-0.4	-0.5	1.2	1.6	0.624
PrNH$_2$ + PeH -> BuH + **BuNH$_2$**	0.4	0.4	2.4	2.0	0.929
PrNH$_2$ + *i*-PeH -> BuH + ***i*-BuNH$_2$**	-0.6	-1.1	1.0	1.5	0.525
BuNH$_2$ + *i*-PeH -> PeH + ***i*-BuNH$_2$**	-1.0	-1.5	-1.5	-0.4	0.038
MeNH$_2$ + H$_2$ -> MeH + **NH$_3$**	-98.7	-99.2	-98.5	0.2	0.040
				Sum =	**6.6**

RADICAL CYCLE	Ab initio	2nd ab initio	New Exp / (kJ mol^{-1})	*New–Calc*	ε^*
H + CH$_4$ → H$_2$ + **CH$_3$**	3.0	2.8	3.1	0.1	0.008
H + C$_2$H$_6$ → H$_2$ + **C$_2$H$_5$**	-13.5	-13.4	-13.5	-0.1	0.011
H + C$_3$H$_8$ → H$_2$ + **C$_3$H$_7$**	-11.7	-11.6	-12.0	-0.3	0.156
H + C$_3$H$_8$ → H$_2$ + ***i*-C$_3$H$_7$**	-24.6	-24.4	-24.8	-0.2	0.056
CH$_3$ + C$_2$H$_6$ → CH$_4$ + **C$_2$H$_5$**	-16.5	-16.2	-16.6	-0.1	0.020
CH$_3$ + C$_3$H$_8$ → CH$_4$ + **C$_3$H$_7$**	-14.8	-14.3	-15.1	-0.3	0.127
CH$_3$ + C$_3$H$_8$ → CH$_4$ + ***i*-C$_3$H$_7$**	-27.7	-27.2	-27.9	-0.2	0.057
C$_2$H$_5$ + C$_3$H$_8$ → C$_2$H$_6$ + **C$_3$H$_7$**	1.8	1.8	1.5	-0.2	0.061
C$_2$H$_5$ + C$_3$H$_8$ → C$_2$H$_6$ + ***i*-C$_3$H$_7$**	-11.2	-11.0	-11.3	-0.1	0.015
C$_3$H$_7$ → ***i*-C$_3$H$_7$**	-12.9	-12.9	-12.8	0.1	0.013
				Sum =	**0.5**