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ARTICLE TYPE

One-pot Synthesis of Amides by Aerobic Oxidative Coupling of Alcohols or Aldehydes with Amines using Supported Gold and Base as Catalysts

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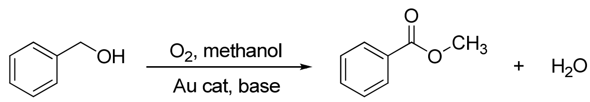
DOI: 10.1039/b000000x

Supporting information

Table S1 show the results from the initial experiments with formation of methyl benzoate by aerobic oxidation of benzyl alcohol using supported gold nanoparticles as catalyst.

Table S1. Formation of methyl benzoate by aerobic oxidation of benzyl alcohol in methanol using supported gold nanoparticles as catalyst[a]



Entry	Catalyst	Base	Conv. [%]	Sel. [%]	Yield [%]
1	Au/TiO_2	LiOMe	>99	84	84
2[b]	Au/TiO_2	LiOMe	>99	86	86
3[c]	Au/TiO_2	LiOMe	>99	89	89
4	Au/TiO_2	NaOMe	>99	87	87
5	Au/TiO_2	KOMe	>99	92	92
6	Au/TiO_2	$Zn(OMe)_2$	42	66	28
7	Au/TiO_2	$Mg(OMe)_2$	95	87	83
8	Au/TiO_2	$Ti(OMe)_4$	1	>99	1
9	Au/TiO_2	-	6	>99	6
10	TiO_2	KOMe	0	0	0
11	Au/Al_2O_3	KOMe	>99	87	87
12	Au/ZnO	KOMe	>99	87	87

[a] Reaction conditions: benzyl alcohol (5 mmol), methanol (50 mmol), anisol (0.5 mmol for internal standard), base (1.25 mmol based on methoxides), catalyst (197 mg), 1 atm O_2, room temperature, 24 h. [b] 75 mmol methanol. [c] 100 mmol methanol.

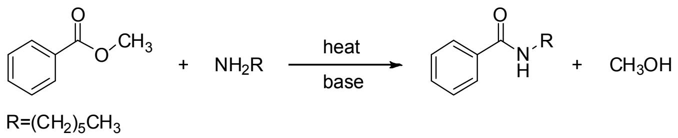
Entry 1-3 shows the effect of the amount of methanol on conversion and selectivity after 24 hours reaction at room temperature and 1 atm of oxygen employing LiOMe as the base and Au/TiO_2 as catalyst. The results show that the selectivity toward the methyl ester increased with increasing excess of methanol.

The results in Table S1 also shows that base was important for the conversion of substrate, as almost no conversion occurred in absence of base. The methoxide bases were chosen, because several of the base reagents were available as methanol solutions (the corresponding solvent), and because these reagents were likely to contain less contaminating water compared to similar reagents made from the corresponding metal hydroxides. In principle, however, hydroxide bases could also have been utilised. Entry 4-8 shows that the yield of methyl ester was dependent on the metal applied in the methoxide base. In general, the best results were obtained by employing the alkali metal methoxides. Lithium methoxide resulted in an overall yield of 84%, sodium methoxide in 87%, and potassium in 92% under identical reaction conditions. This trend in yield, going down in the periodic table, correlates to the typical order of basicity of the metal methoxides in methanol, where KOMe>NaOMe>LiOMe.[1]

Table S1 also shows the effect of changing the support material from TiO_2 to Al_2O_3 and ZnO. Full conversion was achieved with all catalysts, and the change of support only resulted in a slight decrease in selectivity. Although the support material is known to have an important effect in *e.g.* CO oxidation[2] the support had little effect under the given reaction conditions in this reaction. The Au/TiO_2 catalyst was therefore used throughout the rest of the study. The reaction with pure TiO_2 did not result in any conversion, which verified that the gold nanoparticles were required to obtain catalytic activity.

Table S2 compiles the results from the initial experiments with adding N-hexylamine to methyl benzoate under the same reaction conditions as for the esterification.

Table S2. Formation of N-hexylbenzamide from methyl benzoate and hexylamine[a]



Entry	Catalyst	Base	Temp. [°C]	Yield [%]
1	-	LiOMe	RT	82
2[b]	-	LiOMe	RT	69
3[c]	-	LiOMe	RT	59
4	-	NaOMe	RT	89
5	-	KOMe	RT	92
6	-	-	RT	0
7	-	LiOMe	65	>99
8	-	NaOMe	65	>99
9	-	KOMe	65	>99
10	Au/TiO_2	-	65	15
11	Au/TiO_2	KOMe	65	>99

[a] Reaction conditions: methyl benzoate (5 mmol), hexylamine (10 mmol), methanol (50 mmol), anisole (0.5 mmol), base (1.25 mmol based on methoxides), catalyst (197 mg), 24 h. [b] 75 mmol methanol. [c] 100 mmol methanol.

Entry 1-3 in Table S2 shows the effect of the amount of methanol on conversion and selectivity after 24 hours reaction at room temperature and in presence of 20 mol% LiOMe. Increasing the amount of methanol from 50 mmol to 75 and 100 mmol led to a decrease in yield from 82% to 69% and 59%, respectively. Furthermore, KOMe was found to be the best base. This suggested that the basicity of the solution had an important effect on the reaction rate. Performing the reaction in absence of base did not result in any conversion. It is important to note that selectivity remained high and unaffected by the presence of base in all reactions.

Entry 7-11 show that is was possible to achieve full conversion in 24 hours by increasing the temperature from 25 to 65°C (refluxing temperature of methanol). Even at 65°C, however, the presence of base was still important

[1] P. Castilho, M. R. Crampton and J. Yarwood, *J. Chem. Soc.*, 1991, **5**, 639.
[2] N. Lopez, T. V. W. Janssens, B. S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J. K. Nørskov, *J. Catal.*, 2004, **223**, 232.

for the conversion of substrate. Performing the reaction in absence of base, but in presence of Au/TiO_2, resulted in only 15% yield. Conducting the reaction in presence of the gold catalyst had no apparent effect on the reaction outcome, see Table S2 entry 11.

Figure S1 shows the results from the second step in the combined one-pot reaction of N-hexylbenzamide. Here, benzyl alcohol was first oxidised to methyl benzoate at room temperature for 24 hours, before 10 or 25 mmol of hexane-1-amine was added and the temperature was increased to 65°C.

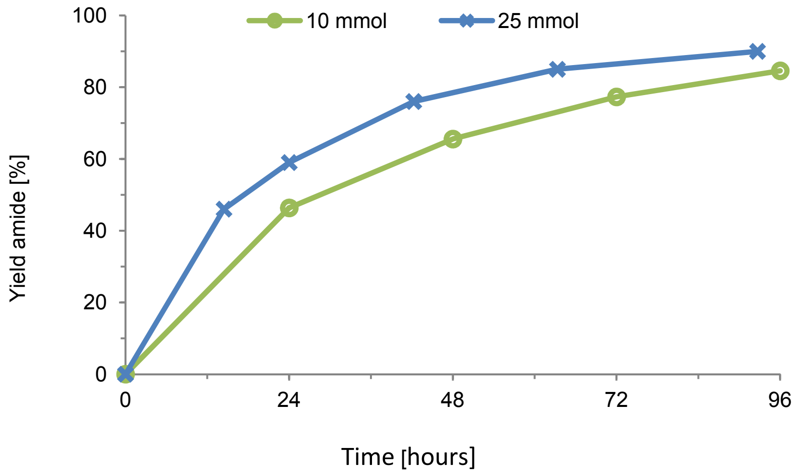
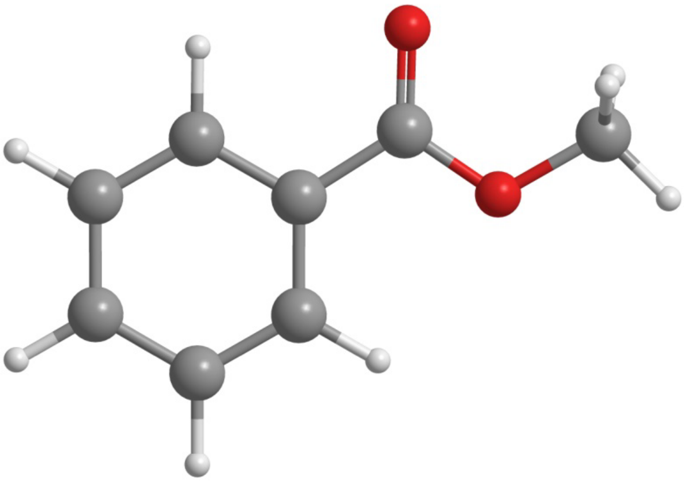


Figure S1. Yield of amide obtained in the one-pot synthesis of N-hexylbenzamide from benzyl alcohol and hexylamine as function of the time after addition of hexane-1-amine.

Interestingly, the yield of amide after 24 hours and addition of 10 mmol amine was only 46%, which was considerable lower than the result expected from starting with pure methyl benzoate (Table S2, entry 9). The decrease in reaction rate may be related to the formation of water from the preceding oxidation step as the methoxide base is expected to be lost due to reaction with water under formation of methanol and hydroxide. After 96 hours, however, the reaction reached 94% conversion. The figure also shows that the reaction rate increased with excess of amine. Thus, after 96 hours, the reaction with 25 mmol added amine reached full conversion.

Supporting information

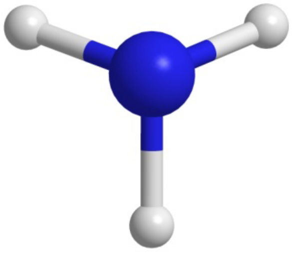
Ph_COOMe
Gradients converged
E_solv = -460.15071600209 a.u.



18

C	-4.59991	2.63970	1.69947
C	-3.37034	2.43378	1.05584
C	-3.11903	1.21456	0.40792
C	-4.08582	0.21172	0.40237
C	-5.31023	0.42016	1.04464
C	-5.56501	1.63299	1.69179
H	-4.79498	3.58141	2.20095
H	-2.16399	1.06773	-0.08588
H	-3.88604	-0.73019	-0.10126
H	-6.06514	-0.36184	1.04079
H	-6.51652	1.79399	2.19083
C	-2.29954	3.46897	1.02829
O	-1.21882	3.31832	0.47796
O	-2.63514	4.60051	1.67317
C	-1.63528	5.64383	1.68054
H	-0.72348	5.29521	2.17144
H	-1.40000	5.95398	0.65963
H	-2.07717	6.46930	2.23801

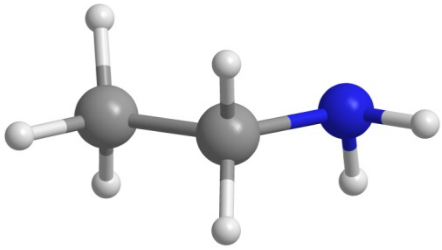
NH3
Gradients converged
E_solv = -56.57017374095 a.u.



4

H	0.09262	1.34237	-0.15223
N	-0.91792	1.41504	-0.03435
H	-1.25636	0.45299	-0.05688
H	-1.25430	1.83392	-0.90138

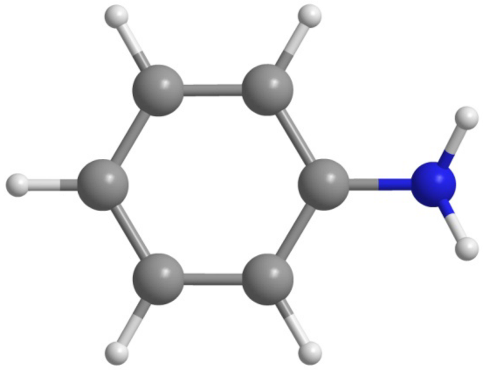
EtNH2
Gradients converged
E_solv = -135.19238605557 a.u.



10

H	0.11620	1.15796	-0.18664
N	-0.86151	1.41726	-0.04932
H	-1.34833	0.53338	0.10134
C	-1.36744	2.04196	-1.28433
H	-1.26573	1.38901	-2.16570
H	-2.44245	2.22062	-1.15806
C	-0.66279	3.36891	-1.55901
H	-0.83005	4.08212	-0.74478
H	0.41942	3.22629	-1.66543
H	-1.03243	3.81568	-2.48776

PhNH2
Gradients converged
E_solv = -287.62875503333 a.u.



14

H	-1.72901	1.54319	0.59203
N	-0.96124	1.39326	-0.05406
H	-0.07824	1.65774	0.36999
C	-1.58918	2.85659	-3.96568
C	-2.67384	2.53399	-3.14447
C	-2.47253	2.06378	-1.84728
C	-1.16955	1.90877	-1.33702
C	-0.08024	2.22254	-2.17200
C	-0.29313	2.69193	-3.46763
H	-3.69010	2.65278	-3.51359
H	-3.32493	1.81332	-1.21893
H	0.93337	2.09529	-1.79710
H	0.56439	2.93506	-4.09107
H	-1.75081	3.23124	-4.97263

BnNH2
Gradients converged
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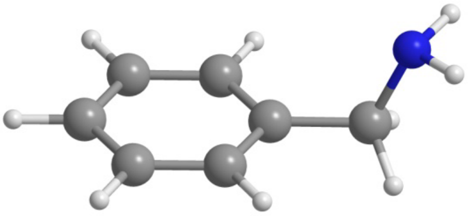
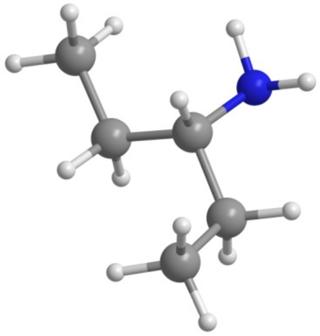
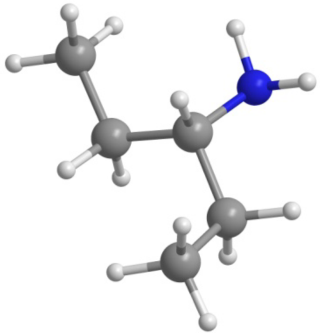


17

H	-0.45743	0.61798	0.02194
N	-1.00868	1.47342	0.04007
H	-1.90983	1.19653	0.42379
C	-1.19379	1.97170	-1.34665
H	-0.68308	1.30992	-2.05462
H	-2.25597	1.95099	-1.61366
C	0.28890	6.00873	-1.93738
C	-1.03103	5.79648	-1.53084
C	-1.50505	4.49620	-1.33862
C	-0.67272	3.38693	-1.54769
C	0.65071	3.61427	-1.95194
C	1.13014	4.91257	-2.14465
H	0.65735	7.01915	-2.09579
H	-1.69327	6.64393	-1.37010
H	-2.53679	4.34151	-1.02851
H	1.31199	2.76695	-2.12356
H	2.15802	5.06869	-2.46327

1_ethyl_propylamine
Gradients converged
E_solv = -253.14237871042 a.u.

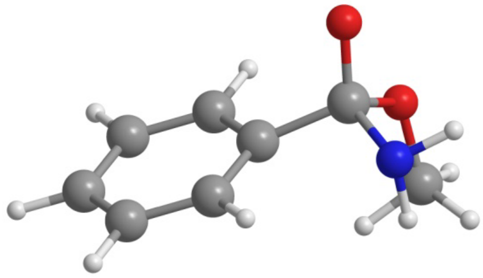




19

H	0.79808	0.56392	-2.83039
C	-1.14780	1.43463	-2.32668
H	-2.05225	1.72085	-2.87590
H	-1.42379	0.57341	-1.70297
C	-0.06709	1.01308	-3.32987
H	0.29121	1.86716	-3.91702
H	-0.45588	0.26810	-4.03192
C	-1.85858	2.92953	-0.38704
H	-1.43037	3.56371	0.40102
H	-2.16708	1.99900	0.10823
C	-3.07785	3.64105	-0.98147
H	-3.56576	3.04219	-1.75762
H	-3.82531	3.84965	-0.20877
H	-2.79061	4.59789	-1.43265
C	-0.75295	2.60578	-1.40982
H	-0.61431	3.49723	-2.04908
H	0.75217	3.08865	-0.11151
H	1.25287	2.16489	-1.33878
N	0.48691	2.28144	-0.67658

Ph_CO_OMe_ONH2
Gradients converged
E_solv = -516.18370586541 a.u.



21

C	-5.20151	1.47201	-0.30303
C	-5.83552	2.69723	-0.53962
C	-7.22397	2.75878	-0.64583
C	-8.01764	1.60862	-0.51663
C	-7.37025	0.39012	-0.27615
C	-5.97659	0.31853	-0.17238
H	-4.11841	1.42052	-0.22248
H	-5.24425	3.60475	-0.64263
H	-7.71736	3.70701	-0.83286
H	-7.96610	-0.51280	-0.18692
H	-5.49756	-0.64157	0.00858
C	-9.53437	1.70625	-0.82187
O	-9.77629	1.85326	-2.08709
O	-10.03356	2.98108	-0.11392
C	-10.00053	2.99798	1.29249
H	-10.25454	4.01065	1.62966
H	-9.00846	2.74645	1.69846
H	-10.73094	2.30785	1.74777
H	-10.18763	0.53442	0.78512
N	-10.24593	0.54694	-0.23299
H	-11.23020	0.68021	-0.46702

Ph_CO_OMe_ONHEt
Gradients converged
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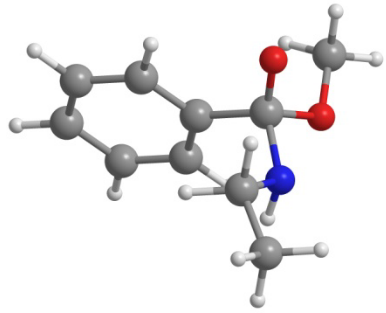
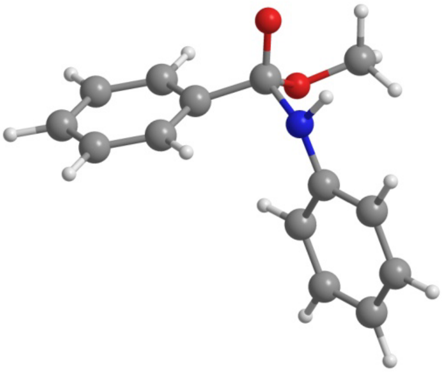


27

C	-6.12069	2.09300	-1.05563
C	-6.47362	2.36704	0.26778
C	-7.81104	2.29042	0.66348
C	-8.81833	1.95259	-0.24349
C	-8.45119	1.67627	-1.56840
C	-7.11691	1.74262	-1.97307
H	-5.08093	2.14633	-1.36895
H	-5.70705	2.63504	0.99206
H	-8.11074	2.47754	1.68950
H	-9.22123	1.39021	-2.27959
H	-6.85174	1.51645	-3.00380
C	-10.29784	1.93962	0.24237
O	-10.44659	1.88184	1.52631
O	-10.95548	0.79117	-0.51806
C	-10.62256	-0.47156	0.00925
H	-9.57905	-0.75929	-0.19936
H	-10.76752	-0.49876	1.09647
H	-11.27927	-1.21790	-0.45408
N	-11.04152	3.08436	-0.40220
C	-10.77923	4.38003	0.22261
H	-10.93450	4.24372	1.29555
H	-9.73324	4.71618	0.10374
C	-11.72375	5.45761	-0.31128
H	-11.54493	6.41630	0.18854
H	-11.58871	5.61523	-1.38856
H	-12.76943	5.17558	-0.14630
H	-10.77286	3.13482	-1.38533

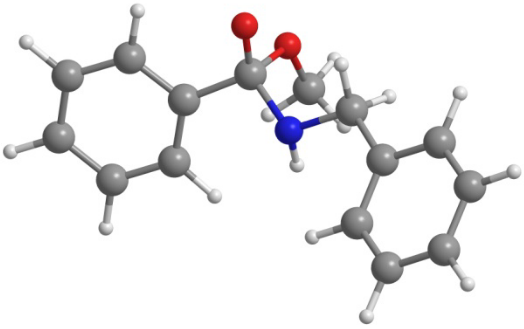
Ph_CO_OMe_ONHPh
Gradients converged
E_solv = -747.24501868850 a.u.



31

C	-4.99218	2.87109	-0.76007
C	-5.89714	2.42318	-1.72505
C	-7.25141	2.28505	-1.40936
C	-7.73356	2.59336	-0.13105
C	-6.81253	3.03333	0.83108
C	-5.45810	3.17268	0.52338
H	-3.93815	2.98284	-1.00344
H	-5.54872	2.18074	-2.72695
H	-7.95277	1.93793	-2.16203
H	-7.17107	3.26774	1.82761
H	-4.76369	3.51894	1.28614
C	-9.25224	2.64583	0.16253
O	-9.74059	3.84198	0.01988
O	-9.35452	2.10356	1.55996
C	-10.65680	2.22841	2.09108
H	-11.36138	1.51120	1.64250
H	-11.05269	3.23934	1.93590
H	-10.60214	2.02795	3.16682
N	-10.00790	1.69880	-0.73373
H	-10.85092	2.16776	-1.04469
C	-10.27366	-2.51277	-0.66866
C	-11.25382	-1.73397	-1.29371
C	-11.16939	-0.34470	-1.29070
C	-10.09079	0.32294	-0.66315
C	-9.11041	-0.47222	-0.02796
C	-9.20874	-1.86200	-0.03746
H	-10.34057	-3.59742	-0.67004
H	-12.09620	-2.21270	-1.78923
H	-11.93769	0.24886	-1.78376
H	-8.28389	0.01315	0.47485
H	-8.43707	-2.44563	0.46129

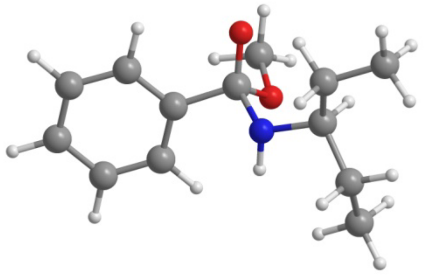
Ph_CO_OMe_ONHBn
Gradients converged
E_solv = -786.54806332327 a.u.



34

C	-4.53261	2.15328	1.46613
C	-5.51387	1.95533	2.43884
C	-6.84607	2.29939	2.18146
C	-7.22468	2.85097	0.94875
C	-6.22629	3.03596	-0.01680
C	-4.89700	2.69703	0.23032
H	-3.49859	1.88144	1.66448
H	-5.24609	1.52535	3.40134
H	-7.58499	2.11329	2.95592
H	-6.53693	3.43537	-0.97672
H	-4.14592	2.84702	-0.54278
C	-8.66859	3.26702	0.54844
O	-8.85927	3.37798	-0.72402
O	-8.84209	4.70440	1.14676
C	-8.86389	4.87620	2.54097
H	-9.68790	4.33281	3.03442
H	-9.01198	5.94431	2.74912
H	-7.92628	4.57038	3.03257
N	-9.64348	2.36127	1.21684
H	-9.53017	2.37394	2.22728
C	-11.02691	2.66725	0.86988
H	-11.01726	2.89828	-0.20017
H	-11.40270	3.57993	1.36436
C	-13.92281	-0.47960	1.61463
C	-12.60307	-0.64101	2.03754
C	-11.65807	0.36259	1.79972
C	-12.01318	1.54425	1.14027
C	-13.34524	1.69439	0.72032
C	-14.29065	0.69555	0.95025
H	-14.65783	-1.25990	1.79597
H	-12.30330	-1.55121	2.55193
H	-10.62682	0.22386	2.10994
H	-13.63884	2.60450	0.19964
H	-15.31428	0.83003	0.60827

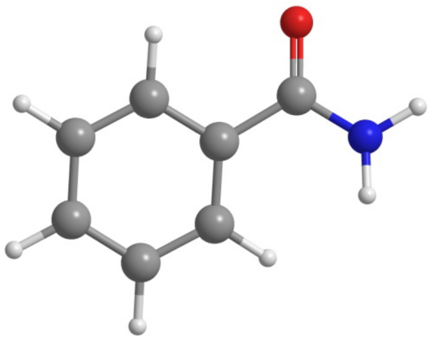
Ph_CO_OMe_1ethylpropylamine
Gradients converged
E_solv = -712.75583215245 a.u.



36

C	-6.23915	0.24101	-1.91563
C	-5.65621	1.23162	-1.12204
C	-6.46502	2.12802	-0.41939
C	-7.85866	2.06631	-0.49285
C	-8.43123	1.05484	-1.27777
C	-7.63319	0.15424	-1.98760
H	-5.61611	-0.45949	-2.46682
H	-4.57273	1.30485	-1.05053
H	-6.03747	2.90542	0.20665
H	-9.51270	0.95771	-1.31971
H	-8.09813	-0.62100	-2.59314
C	-8.69950	3.11401	0.30905
O	-8.01721	3.84871	1.12491
O	-9.76643	2.23774	1.03230
C	-9.23075	1.54957	2.13486
H	-10.05654	1.10335	2.70447
H	-8.67244	2.22537	2.79561
H	-8.54618	0.73576	1.83903
N	-9.52119	3.85070	-0.69115
H	-10.07745	3.15236	-1.17846
C	-10.44495	4.88251	-0.16982
H	-10.84269	4.57947	0.81193
C	-11.62889	5.04010	-1.14386
H	-12.21331	5.91773	-0.84674
H	-11.22616	5.26787	-2.14137
C	-12.57800	3.83883	-1.23002
H	-12.07864	2.93039	-1.58502
H	-13.01120	3.61006	-0.25032
H	-13.40318	4.04140	-1.92159
C	-9.69039	6.21562	0.01070
H	-8.80263	5.98178	0.60240
H	-9.33359	6.54789	-0.97477
C	-10.48781	7.34460	0.67415
H	-11.31584	7.69830	0.05019
H	-10.91425	7.02588	1.63259
H	-9.84407	8.20902	0.87352

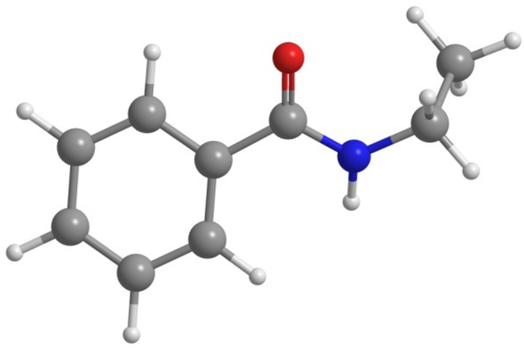
Ph_COONH2
Gradients converged
E_solv = -400.98460062942 a.u.



16

C	-4.78569	2.80062	1.22670
C	-3.43149	2.47070	1.07197
C	-3.06264	1.12126	0.96401
C	-4.03039	0.11919	0.98774
C	-5.37967	0.45547	1.13494
C	-5.75397	1.79568	1.25995
H	-5.09260	3.83471	1.35549
H	-2.01080	0.87537	0.86028
H	-3.73511	-0.92247	0.89409
H	-6.13595	-0.32468	1.15820
H	-6.79951	2.05955	1.39143
C	-2.33266	3.49499	1.04395
O	-1.16245	3.17792	1.30151
H	-1.93753	5.46789	0.71944
N	-2.66706	4.76611	0.72278
H	-3.58883	5.03941	0.41559

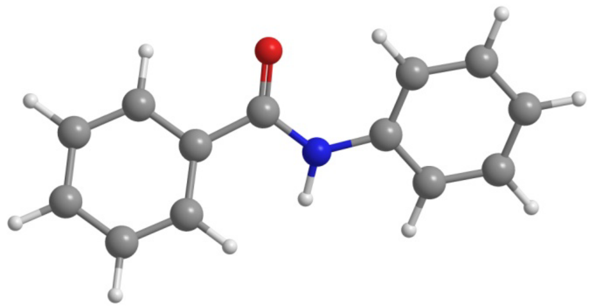
Ph_COONHEt
Gradients converged
E_solv = -479.61208239360 a.u.



22

C	-3.28084	1.24555	1.06036
C	-3.46582	2.63566	1.08702
C	-4.65988	3.17719	0.58924
C	-5.64519	2.34805	0.05677
C	-5.45313	0.96345	0.02957
C	-4.27244	0.41451	0.53630
H	-2.38247	0.80047	1.47948
H	-4.80212	4.25252	0.62857
H	-6.56341	2.77960	-0.33336
H	-6.22385	0.31452	-0.37851
H	-4.12654	-0.66232	0.53299
C	-2.45476	3.58838	1.66280
O	-2.80165	4.69632	2.10064
N	-1.16453	3.17645	1.69242
H	-0.89960	2.34117	1.18775
C	-0.09573	4.01448	2.23455
H	-0.48963	4.52087	3.11956
H	0.70648	3.34884	2.56575
C	0.43605	5.04551	1.23544
H	1.23126	5.64056	1.69697
H	0.84636	4.55937	0.34420
H	-0.36287	5.72411	0.92377

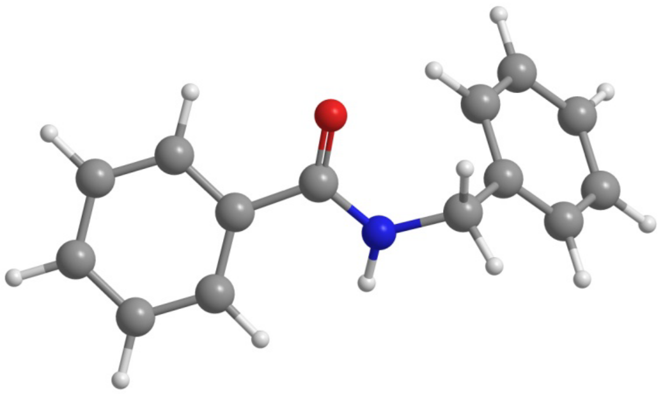
Ph_COONHPh
Gradients converged
E_solv = -632.03858004310 a.u.



26

C	-3.93676	3.22531	-0.84660
C	-3.00533	2.66332	0.04029
C	-3.39862	1.60031	0.86644
C	-4.70084	1.10254	0.79602
C	-5.61675	1.65626	-0.10133
C	-5.23207	2.71989	-0.92378
H	-3.62821	4.05779	-1.47071
H	-2.71118	1.18119	1.59611
H	-5.00227	0.28931	1.45029
H	-6.62961	1.26603	-0.15478
H	-5.94270	3.15583	-1.62090
C	-1.63755	3.28053	0.08060
O	-1.46655	4.46151	-0.23872
N	-0.62118	2.45309	0.48007
C	3.49981	3.19399	1.02054
C	2.63230	4.26724	0.81129
C	1.26416	4.06416	0.62281
C	0.74978	2.75727	0.63921
C	1.62190	1.67572	0.84919
C	2.98396	1.89508	1.03964
H	4.56265	3.36573	1.16636
H	3.01872	5.28329	0.79383
H	0.60242	4.90166	0.45560
H	1.22724	0.66190	0.86242
H	3.64329	1.04635	1.20043
H	-0.85044	1.47040	0.56456

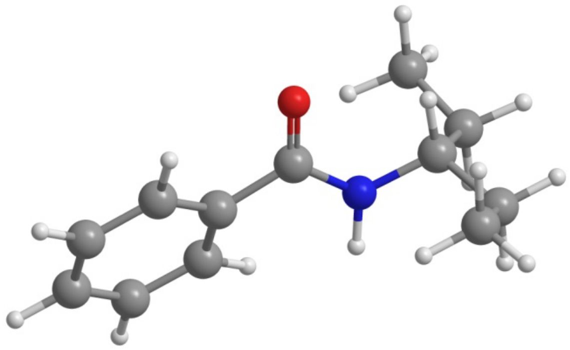
Ph_COONHBn
Gradients converged
E_solv = -671.35331185980 a.u.



29

C	-3.33265	3.18590	-1.01405
C	-2.92123	2.03385	-0.32866
C	-3.88778	1.20828	0.26450
C	-5.24282	1.52763	0.16241
C	-5.64464	2.67014	-0.53433
C	-4.68563	3.49970	-1.12305
H	-2.57818	3.82837	-1.45602
H	-3.59216	0.33285	0.83624
H	-5.98415	0.88892	0.63503
H	-6.70040	2.91701	-0.61271
H	-4.99235	4.39140	-1.66359
C	-1.44351	1.77077	-0.23827
O	-0.62704	2.69801	-0.35450
N	-1.05791	0.48964	-0.01880
H	-1.74323	-0.25130	-0.08445
C	0.34524	0.10232	0.13234
H	0.87895	0.98923	0.48247
H	0.40630	-0.65799	0.91700
C	2.13265	-1.37299	-3.52549
C	1.74756	-0.03229	-3.42023
C	1.17658	0.44173	-2.23963
C	0.97690	-0.41787	-1.14848
C	1.36543	-1.75697	-1.26211
C	1.94153	-2.23388	-2.44379
H	2.57923	-1.74174	-4.44546
H	1.89775	0.64425	-4.25812
H	0.88023	1.48347	-2.15517
H	1.21915	-2.43188	-0.42122
H	2.23934	-3.27695	-2.51730

PhCOO1ethylpropylamine
Gradients converged
E_solv = -597.56228925487 a.u.
31



C	-3.83889	1.82326	-0.07024
C	-3.13557	2.89871	0.49191
C	-3.63902	4.19911	0.33940
C	-4.81833	4.41725	-0.37500
C	-5.50402	3.34152	-0.94475
C	-5.01139	2.04247	-0.79075
H	-3.45398	0.81794	0.06766
H	-3.13533	5.04586	0.79775
H	-5.20607	5.42700	-0.47894
H	-6.42205	3.51359	-1.50077
H	-5.54280	1.20116	-1.22828
C	-1.89208	2.57768	1.27867
O	-1.73846	1.45261	1.77537
N	-0.97122	3.56623	1.40331
C	0.26873	3.43301	2.17806
H	0.25438	2.41273	2.57262
C	1.50010	3.60161	1.26965
H	1.47496	4.60257	0.81617
H	2.39147	3.57959	1.90843
H	-1.10866	4.42800	0.89031
C	0.28840	4.42521	3.35616
H	1.25472	4.31941	3.86441
H	0.26171	5.45018	2.96095
C	-0.84631	4.22284	4.36313
H	-0.80896	3.22129	4.80550
H	-0.78248	4.95025	5.17863
H	-1.82561	4.33918	3.88801
C	1.62313	2.53450	0.17909
H	0.75111	2.53779	-0.48262
H	1.70526	1.53269	0.61489
H	2.51129	2.70408	-0.43787