Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis of Formamides Containing Unsaturated Groups by N-Formylation of Amines using CO_2 with H_2

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1. Experimental section

Chemicals

4-dimethylaminopyridine, DBACO, TMG, potassium tert-butoxide, 4-methylpyridine, 4-methylmorpholine, tetramethylethylenediamine, $PdCl_2$, Chloroform-d, 3,3'-IMinodipropionitrile, 4'-piperazinoacetophenone, 1-allylpiperazine, diallylamine, 1-acetylpiperazine, 2-(1-cyclohexenyl)ethylamine, 1-Boc-piperazine, N-allylmethylamine, 1-benzoylpiperazine, 1,2,3,4-tetrahydroisoquinoline, benzonitrile, α-Al_2O_3, 1-phenyl-1-propyne, pyrrolidine, N-ethylpiperazine, butylamine, dibutylamine, 4-methylpiperidine, dihexylamine, n-octylamine, cyclohexylamine, morpholine, 1-methylpiperazine, cyclohexene, styrene, n-decane and tetrahydrofuran were purchased from J&K Scientific Ltd. $Cu(OAc)_2$, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, $RhCl_3$, desloratadine, benzylamine, dibenzylamine, hexamethyleneimine, N-methylbutylamine and N-methylbenzylamine was provided by Energy Chemical. Trans-1-cinnamylpiperazine, Pd/C, carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) and $Ru_3(CO)_{12}$ purchased from alfa aesar. $CuSO_4•5H_2O$, $Cu(NO_3)_2•3H_2O$, $CuCl_2•2H_2O$, $Ni(OAc)_2•4H_2O$, $Co(OAc)_2•4H_2O$, nitrobenzene, cyclohexanone and sodium tetrahydroborate was provided by Sinopharm Chemical Reagent Co., Ltd. The CO_2 (99.99%), H_2 (99.99%) and N_2 (99.99%) were provided by Beijing Analytical Instrument Company.

Characterization

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) at ambient temperature in $CDCl_3$. GC/MS analysis was conducted on Agilent 7890B GC+ 5977 MSD. Sample analysis was operated on an Agilent 6820 gas chromatography equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm), Agilent Technologies Singapore (Sales) Pte Ltd., Singapore.

N-Formylation of amines using H_2 and CO_2

The reaction was carried out in a Teflon-lined stainless-steel reactor of 10 mL in capacity with a magnetic stirrer. The pressure was determined by a pressure transducer (FOXBORO/ICT, Model 93), which could be accurate to ±0.025 MPa. In a typical experiment, 0.1 mmol of $Cu(OAc)_2$ and 2 mmol of 4-dimethylaminopyridine (DMAP) were loaded into the reactor. 1 mmol of substrate and 1.5 mL solvent (e.g. THF) were added. The reactor was sealed and purged with H_2 to remove the air at ambient temperature. The reactor was placed in an air bath at desired temperature. H_2 of 40 atm was added, and then CO_2 was charged until the total pressure reached 80 atm, and then the stirrer was started at 500 rpm. After reaction the reactor was placed in ice water and the gas was released. The reaction mixture was analyzed by GC-MS and GC with decane as an internal standard, or purified by flash column chromatography on silica gel to afford the desired product was characterized by ^1H NMR and ^{13}C NMR.

Prepare of Pd/Al_2O_3

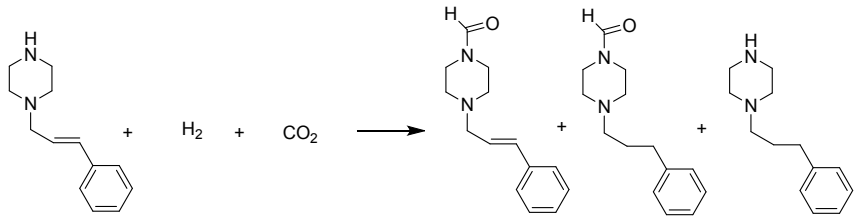
Suitable amount of H_2PdCl_4 (8 mg) were added into 50 mL distilled water and 400 mg α-Al_2O_3 was added to the solution under stirring. A freshly prepared solution of $NaBH_4$ (0.1 M, 20 mL) was then added under stirring to form a dark solution. After the mixture was further stirred for 3 h at 30 ^oC, it was centrifuged and washed by water, dried at 120 ^oC for 4 h and calcined at 350 ^oC for 4 h in air. A grey solid sample was obtained.[s1]

Compution

The geometrical optimizations TS were performed at the 6-31G* level. All calculations were performed with the Gaussian 09 programs. Frequencies were calculated at the same level to confirm each stationary point to be either a minimum (no imaginary frequency) or a saddle point (unique imaginary frequency).

2. Optimization of reaction conditions

Table S1 Optimization of condition for the catalytic N-formylation reaction of 1-cinnamylpiperazine[a]



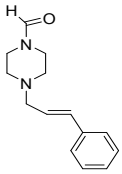
2a 3a 3a' 3a''

Entry	T (^oC)	Solvent	$Cu(OAc)_2$ (mol%)[b]	DMAP (equiv)[b]	Yield (%)[c]
1	70	THF	10	2	2
2	80	THF	10	2	51
3	90	THF	10	2	91
4	90	water	10	2	0
5	90	toluene	10	2	85
6	90	cyclohexane	10	2	61
7	90	acetonitrile	10	2	53
8	90	1,4-dioxane	10	2	83
9	90	ethanol	10	2	3
10	90	THF	5	2	67

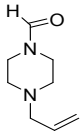
11	90	THF	2	2	33
12	90	THF	10	1	25
13	90	THF	10	0.5	16

[a]Reaction conditions: trans-1-cinnamylpiperazine (1 mmol), P_{CO2}=P_{H2}= 40 atm, solvent (1.5 mL), 6 h. [b]The amount based on the substrate, [c]Yield of **3a** was determined by GC.

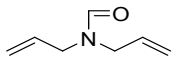
3. Characterization data for the N-formylation products



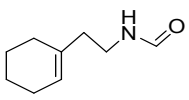
4-cinnamylpiperazine-1-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (s, 1H), 7.38-7.21 (m, 5H), 6.56-6.51 (m, 1H), 6.27-6.20 (m, 1H), 3.59-3.56 (t, J =5.1 Hz, 2H), 3.40-3.37 (t, J =5.1 Hz, 2H), 3.18-3.16 (m, 2H), 2.51-2.45 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ160.52, 136.47, 133.33, 128.42, 127.49, 126.15, 125.65, 60.70, 53.28, 52.17 45.44, 39.77.



4-allylpiperazine-1-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 1H), 5.89-5.79 (m, 1H), 5.23-5.17 (m, 2H), 3.59-3.56 (t, J =5.1 Hz, 2H), 3.40-3.38 (t, J =5.1 Hz, 2H), 3.04-3.01 (t, J =5.5 Hz, 2H), 2.47-2.44 (t, J = 5.1 Hz, 2H), 2.43-2.41 (t, J = 5.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ160.67, 134.35, 118.45, 61.53, 53.33, 52.20, 45.60, 39.93.

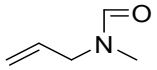


N,N-diallylcarboxamide:^{1}H NMR ($CDCl_3$,400 MHz) δ 8.13 (s, 1H), 5.79-5.66 (m, 2H), 5.26-5.14 (m, 4H), 3.95-3.94 (m, 2H), 3.83-3.81 (m, 2H). ^{13}C NMR ($CDCl_3$,100 MHz) δ162.51, 133.10, 132.12, 118.55, 118.08, 58.44, 49.25, 44.32.

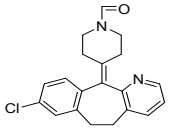


N-(2-cyclohex-1-enyl-ethyl)-formamide:^{1}H NMR ($CDCl_3$,400 MHz) δ 8.16 (s, 0.79H), 8.06-7.97 (m, 0.21H), 5.49 (s, 1.72H), 5.30 (s, 0.24H), 3.40-3.27 (m, 2H),2.17-2.13 (s,

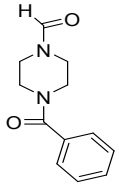
2H), 2.01-2.00 (s, 2H), 1.93-1.91 (m, 2H), 1.66-1.52 (m, 4H). ^{13}C NMR ($CDCl_3$,100 MHz) δ164.35, 161.07, 134.23, 133.20, 124.63, 123.64, 37.35, 35.72, 28.00, 27.75, 25.12, 25.08, 22.69, 22.66, 22.22, 22.15.



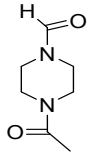
N-methyl-N-allyl-formamide: ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.08 (s, 1H), 5.79-5.69 (m, 1H), 5.30-5.18 (m, 2H), 3.96-3.94 (d, J= 6.0Hz, 1H), 3.84-3.82(d, J= 5.7Hz, 1H), 2.91(s, 1H), 2.84 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ162.67, 132.87, 131.86, 118.45, 118.06, 51.98, 46.61, 33.96, 29.45.



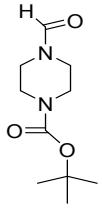
N-formyl desloratadine: ^{1}H NMR ($CDCl_3$,400 MHz) δ8.39-8.36 (m, 1H), 8.06 (s, 1H), 7.42 (s, 1H),7.16-7.0 (m, 4H),3.35-3.20 (m, 2H),3.1-3.0 (m, 2H),2.9-2.6 (m, 4H),2.3-2.4 (m, 4H).



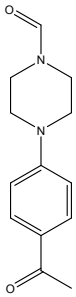
4-benzoyl-1-piperazinecarboxaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (s, 1H), 7.41 (m, 5H), 3.73-3.40 (m, 8H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.24, 159.82, 134.03, 128.87, 127.43, 125.85, 44.20, 38.69.



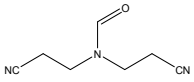
1-formyl-4-acetylpiperazine: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (s, 1H), 3.63-3.36 (m, 8H), 2.13 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ168.542, 160.37, 160.29, 46.13, 44.99, 44.89, 44.47, 41.23, 40.07, 39.37, 20.70.



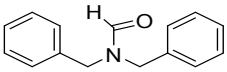
1-Boc-4-formylpiperazine: ^{1}HNMR ($CDCl_3$, 400 MHz) δ8.08 (s, 1H), 3.53-3.35 (m, 8 H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$,100 MHz) δ160.69, 154.20, 80.25, 45.24, 39.75, 28.17.



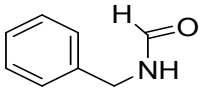
4-(4-acetylphenyl)piperazine-1-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (s, 1H), 7.84 (d, J = 8.70 Hz, 2H), 6.86 (d, J =8.70 Hz, 2H), 3.64 (t, J = 5.04 Hz, 2H), 3.49 (t, J = 5.52, 2H), 3.30 (dt, J = 17.06, 5.21 Hz, 4H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.91, 160.55, 153.40, 129.99, 127.80, 113.85, 48.01, 46.77, 44.56, 39.16, 25.84.



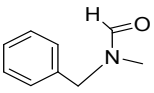
N,N-bis-(2-cyano-ethyl)-formamide: ^{1}HNMR ($CDCl_3$, 400 MHz) δ8.23 (s, 1H), 3.72-3.66 (m, 4 H), 2.78-2.68 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ163.07, 117.90, 117.39, 44.33, 43.66, 15.96.



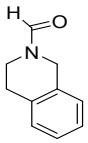
N,N-dibenzylformamide:^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (s, 1H), 7.43-7.26 (m, 10H), 4.51 (s, 2H), 4.33 (s, 2H). ^{13}C NMR (CDCl3, 100 MHz) δ 161.24, 134.60, 134.31, 127.27, 127.08, 126.73, 126.62, 126.17, 125.99,48.51, 42.93.



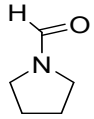
N-benzylformamide: ^{1}H NMR (400 MHz, $CDCl_3$)δ8.23 (s, 1H), 8.15 (d, J = 11.9 Hz, 1H), 7.21-7.40 (m, 5H), 6.07 (s, 1H), 4.46 (d, J = 5.9 Hz, 2H), 4.39 (d, J = 6.5 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.07, 160.83 , 137.71, 128.8, 128.6, 127.6, 127.5, 127.0, 45.7, 41.9



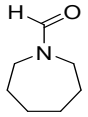
N-benzyl-N-methylformamide: ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.29-8.16 (m, 1H), 7.39-7.19 (m, 5H), 4.51-4.37 (m, 2H), 2.82-2.76 (m, 3H).^{13}C NMR (100 MHz,$CDCl_3$) δ 161.55, 161.40, 135.02,134.84, 127.68, 127.50, 127.40, 126.98, 126.82, 126.40, 126.31, 52.12, 46.44, 32.83, 28.15.



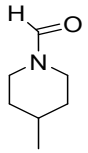
3,4-dihydro-2(1H)-isoquinolinecarbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 and 8.16 (m,1H), 7.16-7.08 (d,J=30.8 Hz, 4H), 4.63-4.48(m,2H), 3.73-3.59 (m, 2H), 2.85 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ160.83, 160.33, 133.55, 132.86, 131.58, 130.96, 128.32, 128.18, 126.25, 125.87, 125.75, 125.69, 125.16, 46.43, 42.38, 41.44, 37.16, 28.90, 27.13.



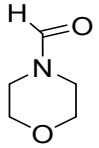
N-formylpyrrolidine: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H),3.46-3.38 (d, J = 30.2 Hz,4H), 2.00-1.88 (m, 4H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 159.97, 45.19, 42.28, 24.10, 23.42.



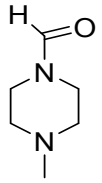
1-(formyl)-hexahydro-1H-azepine: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 3.41-3.33 (d, J = 31.3 Hz, 4H), 1.68 (s, 4H), 1.53 (s, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.49, 46.36, 42.05, 28.99, 26.72, 25.64, 25.59.



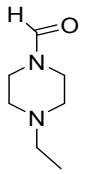
4-methyl-1-formylpiperidine: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 4.33-4.30 (m, 1H),3.57-3.54 (m, 1H), 3.01 (s, 1H),2.59 (s, 1H), 1.65-1.62 (m, 3H), 1.18-1.03 (m, 2H), 0.93 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ159.41, 44.78, 38.54, 33.42, 32.03, 29.93, 20.44.



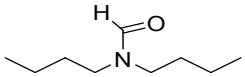
N-formylmorpholine: ^{1}H NMR (400 MHz, $CDCl_3$) δ8.05 (s, 1H), 3.70-3.68 (t, J = 4.9 Hz, 2H), 3.66-3.64 (t, J = 4.9 Hz, 2H), 3.57-3.54 (t, J = 4.9Hz, 2H), 3.43-3.40 (t, J = 4.9 Hz, 2H).^{13}C NMR (100 MHz,$CDCl_3$) δ 160.31, 66.68, 65.84,45.22, 40.02.



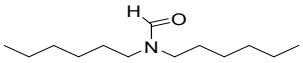
4-formyl-1-methylpiperazine: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 3.54 (s, 2H), 3.36 (s, 2H), 2.44 – 2.35 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.90, 52.43, 51.47, 44.84, 43.72, 39.17.



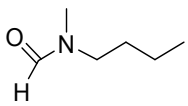
4-ethyl-1-formylpiperazine: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.52 (s, 2H), 3.36 (s, 2H), 2.39-2.35 (m, 6H), 1.06 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.24, 51.77, 50.77, 50.58, 44.12, 38.45, 10.57.



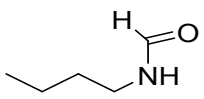
N,N-dibutylformamide: ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.04 (s, 1H)3.29-3.27 (t, J = 5.8 Hz, 2H), 3.20-3.18 (t, J = 5.8 Hz, 2H),1.51 (s, 4H),1.32-1.29 (m, 4H), 0.94-0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ161.76, 46.26, 40.94, 29.85, 28.52, 19.26, 18.74, 12.93, 12.77.



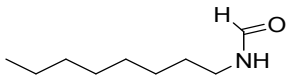
N,N-dihexylformamide:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.28 (t, J=6.4 Hz, 2H), 3.18 (t, J=6.9 Hz, 2H), 1.52 (s, 4H), 1.29 (s, 12H), 0.89 (m, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 47.4, 42.1, 31.5, 31.4, 28.6, 27.3, 26.6, 26.1, 22.6, 22.5, 14.0, 14.0.



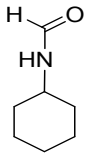
N-butyl-N-methylformamide: ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.03 (s, 1H),3.33-3.29(t, J = 6.0 Hz, 0.55H), 3.23-3.19 (t, J = 6.0 Hz,1.22H),2.91 (s, 1.0H), 2.83 (s, 2H), 1.52-1.50(m,2H), 1.29-1.26 (m, 2H), 0.94-0.91 (t, J = 5.8 Hz, 3H).^{13}C NMR (100 MHz,$CDCl_3$) δ161.71, 161.58, 48.38, 42.95, 33.65, 29.17, 27.88, 18.62, 17.87, 12.97, 12.81.



N-butylformamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-7.91 (m, 1H), 5.78 (s, 1H), 3.44-3.07 (m, 2H), 1.59-1.45 (m, 2H), 1.43-1.28 (m, 2H), 0.94 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.77, 46.17, 39.94, 34.71, 33.27, 31.36, 21.72.



N-octylformamide:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-7.91 (m, 1H), 5.53 (d, J = 149.5 Hz, 1H), 3.25 (m, 2H), 1.49 (m, 2H), 1.29 (d, J = 10.8 Hz, 9H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.57, 161.13, 77.35, 77.03, 76.71, 41.75, 38.20, 31.70, 31.65, 31.24, 29.52, 28.88, 28.78, 26.79, 26.34, 22.54, 14.01.



N-cyclohexylformamide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09(s, 1H),5.54 (br, 1H), 5.89-5.29 (m, 1H), 3.96-2.75 (m, 1H), 1.99-1.85 (m, 2H), 1.80-1.57 (m, 3H), 1.44 -1.25 (m, 3H), 1.24-1.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.50, 160.26, 50.93, 47.09, 34.71, 33.05, 25.43, 25.04, 24.73.

4. Cartesian coordinate and energy of transition state at the B3LYP /6-31G* level

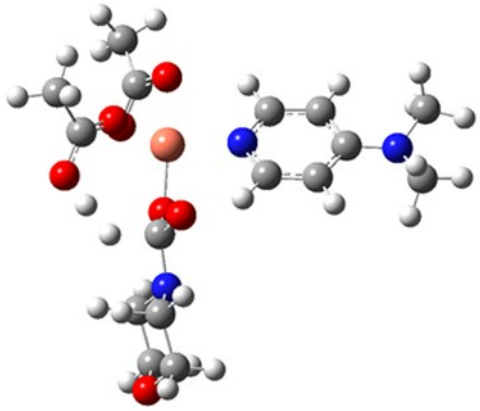


Figure S1. transition state for OAc- assisted hydrogen cracking

transition state:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29		-0.000001973	0.000001992	0.000001368

2	6	0.000000099	-0.000000167	-0.000000197
3	6	0.000000135	-0.000000061	0.000000133
4	6	0.000000000	-0.000000759	-0.000001612
5	1	0.000000181	-0.000000981	-0.000001339
6	6	0.000000058	-0.000000270	-0.000000846
7	1	0.000000015	0.000000237	0.000000720
8	6	-0.000000012	-0.000001221	-0.000002099
9	1	-0.000000004	-0.000000963	-0.000002182
10	1	-0.000000042	-0.000000183	-0.000000838
11	7	0.000000407	-0.000000615	-0.000001081
12	7	0.000000170	0.000000338	-0.000000856
13	6	-0.000000324	-0.000001761	-0.000004655
14	1	-0.000000610	-0.000000791	-0.000003318
15	1	-0.000000352	-0.000001494	-0.000004350
16	1	0.000000693	-0.000001890	-0.000003232
17	6	-0.000000338	-0.000000788	-0.000002581
18	1	-0.000000306	-0.000000312	-0.000002360
19	1	0.000000130	-0.000000903	-0.000002261
20	1	-0.000000222	-0.000000717	-0.000002808
21	8	-0.000000090	0.000000809	0.000004730
22	8	0.000001619	-0.000000227	0.000002118
23	6	-0.000000292	-0.000001767	0.000002708
24	6	-0.000000951	0.000001360	0.000003388
25	8	-0.000000487	-0.000001105	0.000000449
26	8	0.000000759	0.000001016	0.000001940
27	6	0.000001677	-0.000001432	0.000003548
28	1	0.000001739	-0.000002061	0.000003233
29	1	0.000001679	-0.000001587	0.000003629
30	1	0.000001467	-0.000001405	0.000003882
31	6	-0.000000211	0.000001208	0.000002519
32	1	0.000001133	0.000000214	0.000004657
33	1	0.000000402	0.000001723	0.000002472
34	1	-0.000000606	0.000002043	0.000004299
35	8	0.000000231	0.000000408	-0.000001457
36	6	-0.000002127	-0.000000186	-0.000000551
37	8	0.000001384	-0.000002630	-0.000000449
38	6	-0.000000679	0.000001421	-0.000000399
39	6	0.000000250	-0.000000334	-0.000000501
40	6	-0.000000903	0.000001866	-0.000001095
41	1	-0.000000593	0.000001367	0.000000549
42	6	-0.000000353	0.000000298	-0.000001671
43	1	0.000000130	-0.000000626	-0.000001057
44	1	-0.000001199	0.000001993	-0.000001693
45	1	-0.000000393	0.000000046	-0.000001898

46	7	-0.000002332	0.000001254	0.000000585
47	8	-0.000000836	0.000001411	-0.000001379
48	1	-0.000001306	0.000002587	-0.000000780
49	1	-0.000000854	0.000001973	0.000000083
50	1	-0.000000025	-0.000000200	-0.000000260
51	1	-0.000000610	0.000000440	-0.000002246
52	1	-0.000001034	-0.000003186	0.000003684
53	1	0.000005707	0.000004617	0.000001354

-

SCF- Energy:B3LYP (PCM, THF)/6-31G* = -2956.149565 (a.u.)

5. Full citation of Gaussian program (Reference 44 details)

Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

6. References

S1. X. J. Cui, Y. Zhang, Y. Q. Deng and F. Shi, *Chem. Commun.*, 2014, **50**, 189-191.

S2. M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.*, 2002, **117**, 43-54.