

Supplementary Information

Author file of Reference 66, GAUSSIAN 03:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, J. R. M. M. A.; Cheeseman, J. A.; Vreven, T.; Kudin, K. N.; J. C. M. Burant, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, M. S. B.; Cossi, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; M. E. Hada, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; T. H. Nakajima, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, H. P. C. J. E.; Hratchian, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; R. S. Gomperts, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; C. O. Pomelli, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; P. D. Salvador, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, M. C. F. A. D.; Strain, O.; Malick, D. K.; Rabuck, A. D.; K. F. Raghavachari, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; S. C. Clifford, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, I. M. P.; Komaromi, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.

Author file for Reference 56, ADF2010:

E. J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A.W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, J. W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodríguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev,

Test of Meta GGA:TPSS on Intermediates 1 and 2:

Meta GGA:TPSS (full electron basis set)

	Doublet	Quartet	Sextet
1	105.56	72.89	0.00
2	-32.81	-46.68	38.35

ZORA+PW91/TZ2P (full electron basis set)

	Doublet	Quartet	Sextet
1	93.17	76.46	0.00
2	-31.91	-42.27	41.41

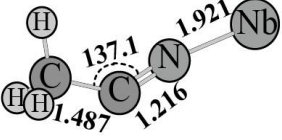
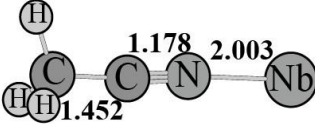
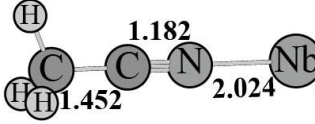
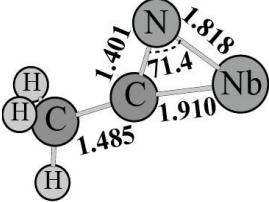
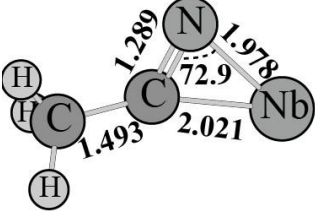
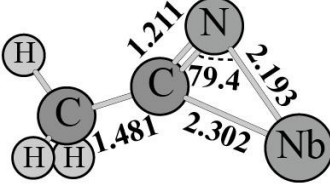
ZORA+PW91/TZ2P (with frozen cores)

	Doublet	Quartet	Sextet
1	139.85	58.54	0.00
2	1.29	-33.70	41.97

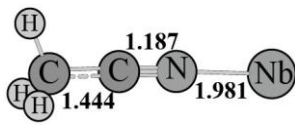
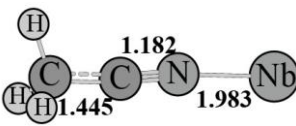
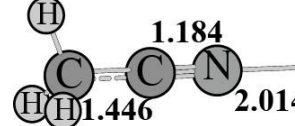
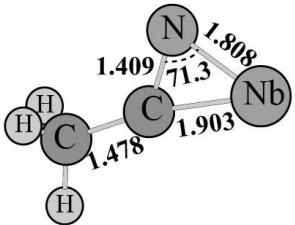
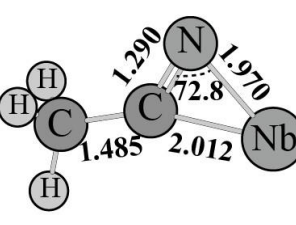
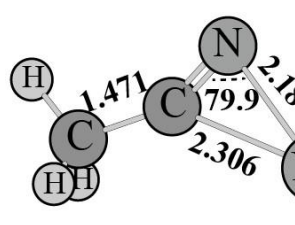
B3LYP (C+A)

	Doublet	Quartet	Sextet
1	80	40	0
2	-5	-30	35

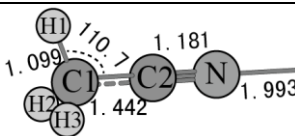
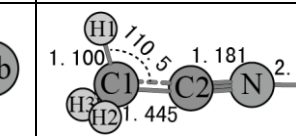
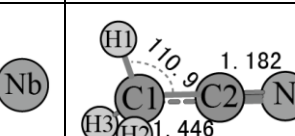
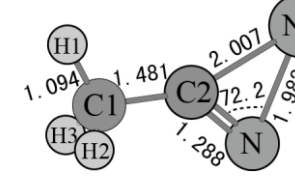
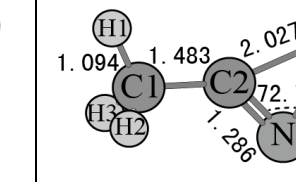
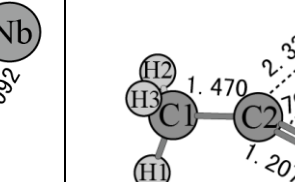
Meta GGA:TPSS (full electron basis set)

	Doublet	Quartet	Sextet
1			
2			

ZORA+PW91/TZ2P (full electron basis set)

	Doublet	Quartet	Sextet
1			
2			

ZORA+PW91/TZ2P (with frozen cores)

	Doublet	Quartet	Sextet
1			
2			

Optimized structures and energies (without ZPE correction) of some intermediates, at TZ2P/PW91 level (ADF2010)

Species	Cartesians				Energy(kJ/mol)
⁶ 1	C	0.000000	0.000000	-1.113467	-3996.51
	H	0.513619	-0.889613	-1.505775	
	H	0.513619	0.889613	-1.505775	
	H	-1.027237	0.000000	-1.505775	
	C	0.000000	0.000000	0.332526	
	N	0.000000	0.000000	1.514180	
	Nb	0.000000	0.000000	3.558158	
⁴ 2	C	-0.439195	-0.416857	0.000000	-4031.64
	H	-0.973307	-0.792154	0.885299	
	H	0.581188	-0.811488	0.000000	
	H	-0.973307	-0.792154	-0.885299	
	C	-0.470162	1.065957	0.000000	

	N	-1.445823	1.905070	0.000000	
	Nb	0.242230	2.963675	0.000000	
⁴ 3	C	0.482001	-0.341698	-0.429890	-4012.70
	H	1.400966	-0.904792	-0.612984	
	H	0.621793	0.557657	0.174177	
	Nb	-1.506935	-1.504586	-0.018462	
	N	-1.459302	-0.537060	-2.039860	
	C	-0.417711	-0.250401	-1.496429	
	H	-2.457008	-0.906681	1.393012	
⁴ 4	C	1.580290	0.481412	-0.000531	-4019.62
	H	1.382965	1.547425	0.138250	
	H	1.952706	0.310362	-1.036721	
	H	2.371060	0.135060	0.691252	
	Nb	0.073758	-1.019329	0.009360	
	N	-1.949735	-0.798443	-0.054503	
	C	-3.134630	-0.897077	0.011563	
² 5	C	0.530493	0.528202	0.000000	-3997.63
	H	0.855840	1.567486	0.000000	
	H	1.358877	-0.239452	0.000000	
	Nb	-0.729020	-0.874665	0.000000	
	N	-2.771437	-0.623516	0.000000	
	C	-3.912386	-0.288397	0.000000	
	H	0.126052	-2.457206	0.000000	
PCP1	C	-0.035162	0.012012	0.018440	Sextet: -3912.99 Quartet: -3913.35
	H	1.065310	0.054200	0.083470	
	H	-0.428684	1.035710	-0.007139	
	H	-0.423516	-0.472964	0.922988	
	C	-0.442518	-0.730735	-1.173957	
	N	-0.178500	-1.370778	-2.163371	
	Nb	-1.850441	-2.026589	-3.119567	
PCP2	C	0.051097	0.099263	-0.163056	Quartet: -3920.79 Doublet: -3921.92
	H	0.607769	0.291650	-1.111225	
	H	-0.523634	0.960776	0.175270	
	Nb	0.429882	-1.790940	0.146220	
	N	0.120322	-2.805643	1.891335	
	C	0.042287	-3.502481	2.852789	
	H	-1.022071	-0.994190	-0.642694	