Electronic Supplementary Information (ESI)

for

Inorganic clusters with a $[Fe_2MoOS_3]$ core —a functional model for acetylene reduction by nitrogenases

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Table S1 Reaction of **1** with BX_4^- and/or substrates in the presence or absence of X_2O (X = H or D). R = H or Ph. The yields were calculated based on **1**, BX_4^- and substrate.

entry	BX_4^- (8 eq.)	substrate (10 eq.)	X_2O (9 eq.)	ratio of H_2:HD:D_2	yield of dihydrogen (%)[†]			ratio of RC_2H_3: RC_2H_2D: RC_2HD_2: RC_2D_3	yield of styrene or ethylene (%)[‡]		
					based on **1**	based on BX_4^-	based on substrate		based on **1**	based on BX_4^-	based on substrate
1	BD_4^-	–	–	0:12:88	21	2.6	2.1	–	–	–	–
2	BH_4^-	–	–	100:0:0	25	3.1	2.5	–	–	–	–
3	BD_4^-	–	H_2O	1:89:10	78	9.8	7.8	–	–	–	–
4	BH_4^-	–	D_2O	16:83:1	56	7.0	5.6	–	–	–	–
5	BD_4^-	PhC≡CH	–	0:14:86	18	2.3	1.8	10:30:60:0	16	2.0	1.6
6	BH_4^-	PhC≡CH	–	100:0:0	19	2.4	1.9	100:0:0:0	25	3.1	2.5
7	BD_4^-	PhC≡CH	H_2O	0:88:12	58	7.3	5.8	4:85:11:0	70	8.8	7
8	BH_4^-	PhC≡CH	D_2O	24:76:0	35	4.4	3.5	25:74:1:0	77	9.6	7.7
9	BD_4^-	PhC≡CD	–	0:6:94	10	1.3	1	0:6:44:50	19	2.4	1.9
10	BH_4^-	PhC≡CD	–	100:0:0	11	1.4	1.1	0:98:2:0	15	1.9	1.5
11	BD_4^-	PhC≡CD	H_2O	0:89:11	63	7.9	6.3	0:1:84:15	72	9.0	7.2
12	BH_4^-	PhC≡CD	D_2O	25:75:0	26	3.3	2.6	0:26:73:1	60	7.5	6
13	BD_4^-	HC≡CH	–	5:25:70	29	3.6	2.9	23:27:50:0	8	1.0	0.8
14	BH_4^-	HC≡CH	–	100:0:0	19	2.4	1.9	100:0:0:0	9	1.1	0.9
15	BD_4^-	HC≡CH	H_2O	4:85:11	79	9.9	7.9	33:59:8:0	20	2.5	2
16	BH_4^-	HC≡CH	D_2O	34:66:0	56	7.0	5.6	51:47:2:0	18	2.3	1.8

[†] The yields of dihydrogen based on **1**: {(mol of dihydrogen)/(mol of **1**)} × 100.

The yields of dihydrogen based on BX_4^-: {(mol of dihydrogen)/(mol of BX_4^-)} × 100.

The yields of dihydrogen based on substrate: {(mol of dihydrogen)/(mol of substrate)} × 100.

[‡] The yields of styrene or ethylene based on **1**: {(mol of product)/(mol of **1**)} × 100.

The yields of styrene or ethylene based on BX_4^-: {(mol of product)/(mol of BX_4^-)} × 100.

The yields of styrene or ethylene based on substrate: {(mol of product)/(mol of substrate)} × 100.

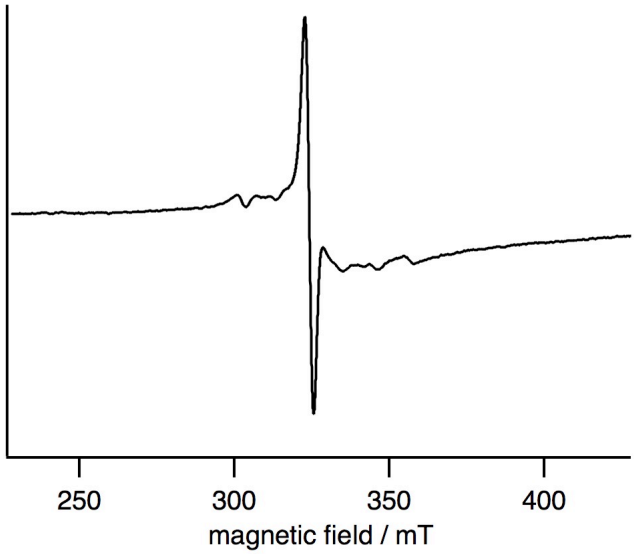

Fig. S1 An ESR spectrum of **1** in acetonitrile at −150 ºC (microwave frequency: 9.20 GHz, microwave power: 1.64 mW).

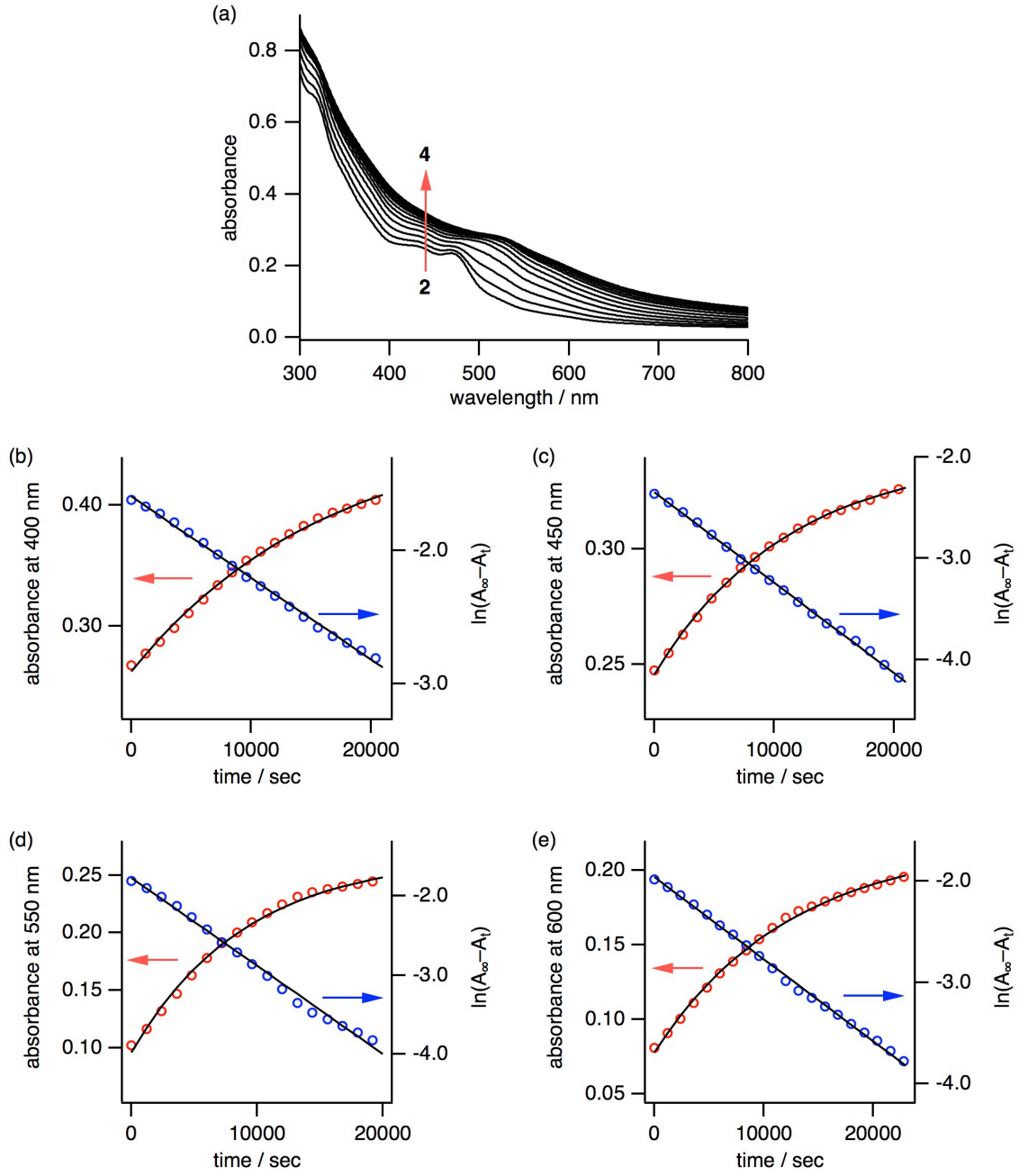

Fig. S2 (a) A UV-vis spectral change from **2** (0.27 mM) to **4** in the reaction of **1** with 2 equivalents of PPh_4BH_4 in acetonitrile under an N_2 atmosphere at –10 °C (2400 sec interval). Time course of the absorbance changes at (b) 400 nm, (c) 450 nm, (d) 550 nm and (e) 600 nm and the first-order kinetic plots (1200 sec interval). The solid lines indicate the first-order kinetic fittings.

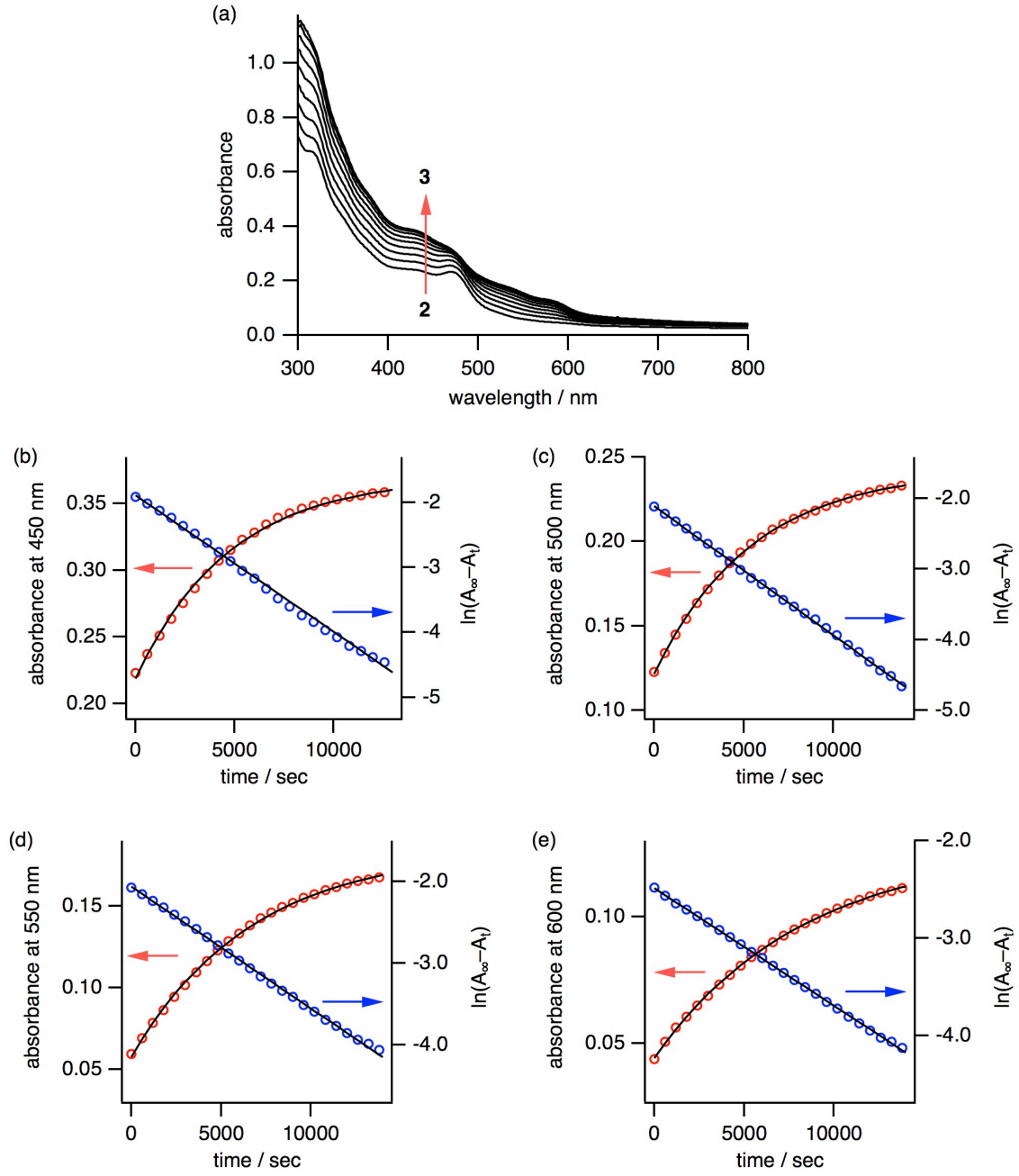

Fig. S3 (a) A UV-vis spectral change from **2** (0.27 mM) to **3** in the reaction of **1** with 2 equivalents of PPh_4BH_4 in HC≡CH-saturated acetonitrile under an HC≡CH atmosphere at –10 °C (1200 sec interval). Time course of the absorbance changes at (b) 450 nm, (c) 500 nm, (d) 550 nm and (e) 600 nm and the pseudo-first-order kinetic plots (600 sec interval). The solid lines indicate the pseudo-first-order kinetic fittings.

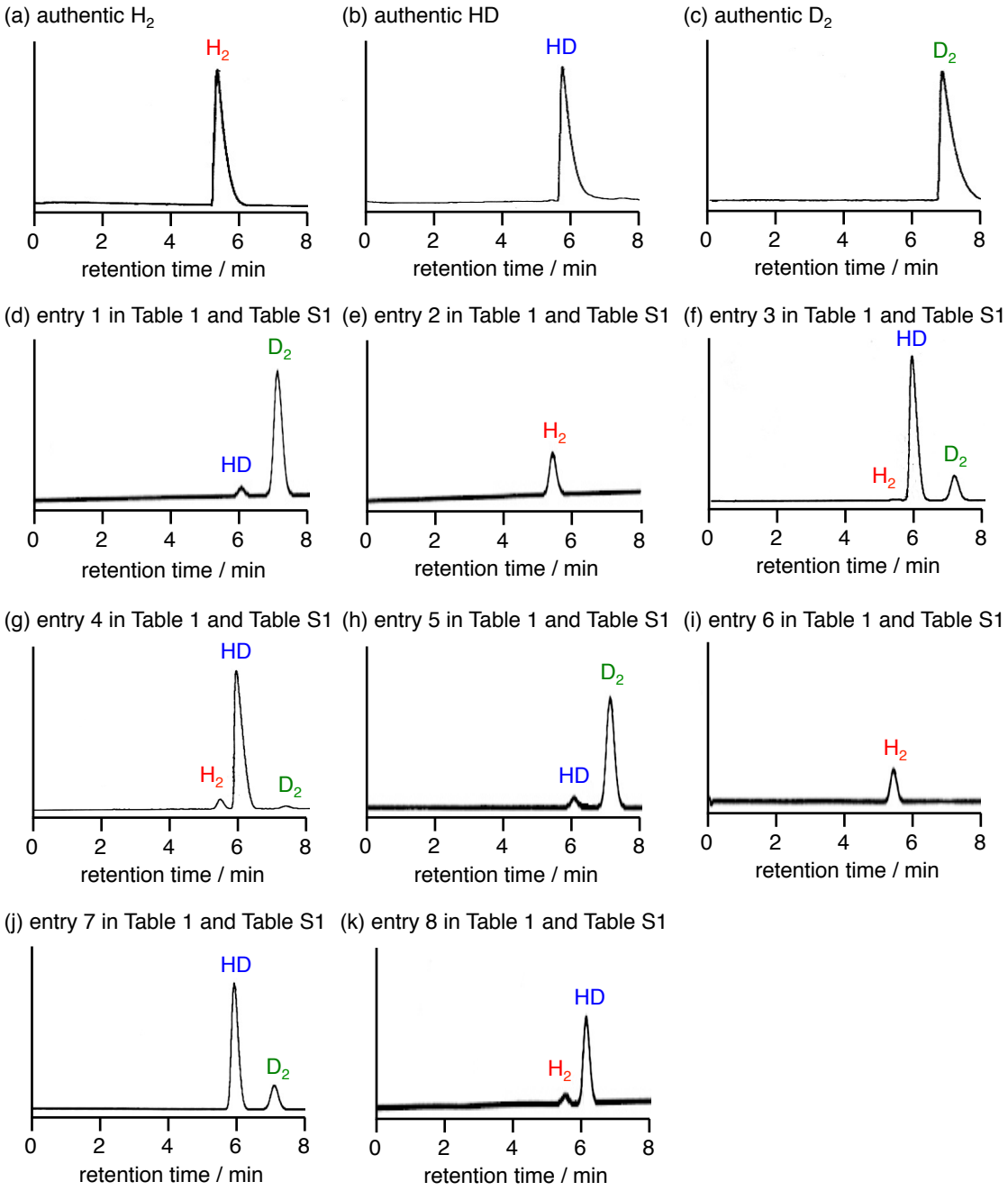

Fig. S4 Gas chromatograms of authentic (a) H_2, (b) HD and (c) D_2 gases. Gas chromatograms obtained from the reaction of **1** with (d) BD_4^- (entry 1), (e) BH_4^- (entry 2), (f) BD_4^- with H_2O (entry 3), (g) BH_4^- with D_2O (entry 4), (h) BD_4^- with PhC≡CH (entry 5), (i) BH_4^- with PhC≡CH (entry 6), (j) BD_4^- with PhC≡CH and H_2O (entry 7) and (k) BH_4^- with PhC≡CH and D_2O (entry 8). The ratios of H_2 : HD : D_2 were determined based on those peak areas. The detection sensitivities of H_2 : HD : D_2 are 1 : 3.4 : 4.9, which were determined by using authentic H_2, HD and D_2 gases.

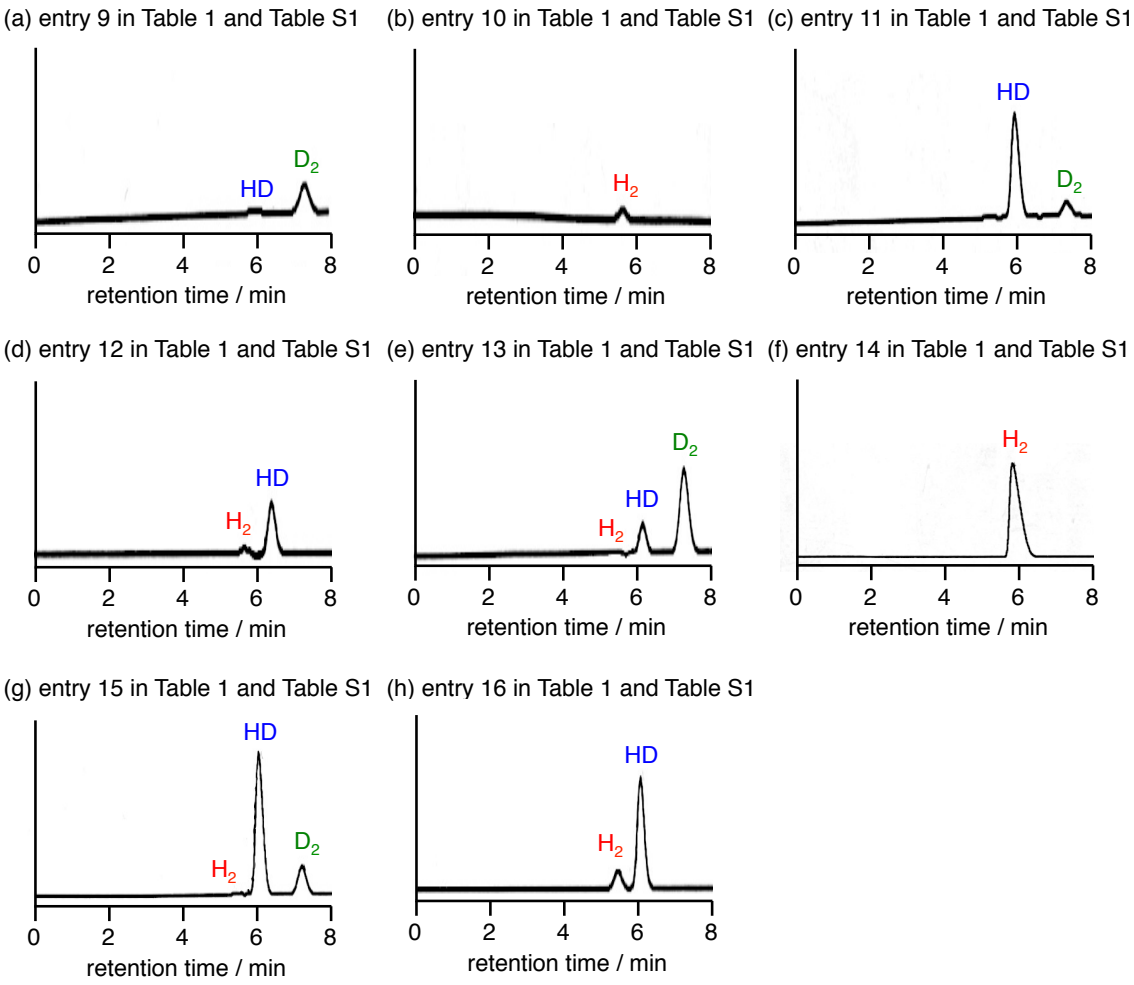

Fig. S5 Gas chromatograms obtained from the reaction of **1** with (a) BD_4^- with PhC≡CD (entry 9), (b) BH_4^- with PhC≡CD (entry 10), (c) BD_4^- with PhC≡CD and H_2O (entry 11), (d) BH_4^- with PhC≡CD and D_2O (entry 12), (e) BD_4^- with HC≡CH (entry 13), (f) BH_4^- with HC≡CH (entry 14), (g) BD_4^- with HC≡CH and H_2O (entry 15) and (h) BH_4^- with HC≡CH and D_2O (entry 16). The ratios of H_2 : HD : D_2 were determined based on those peak areas. The detection sensitivities of H_2 : HD : D_2 are 1 : 3.4 : 4.9, which were determined by using authentic H_2, HD and D_2 gases.

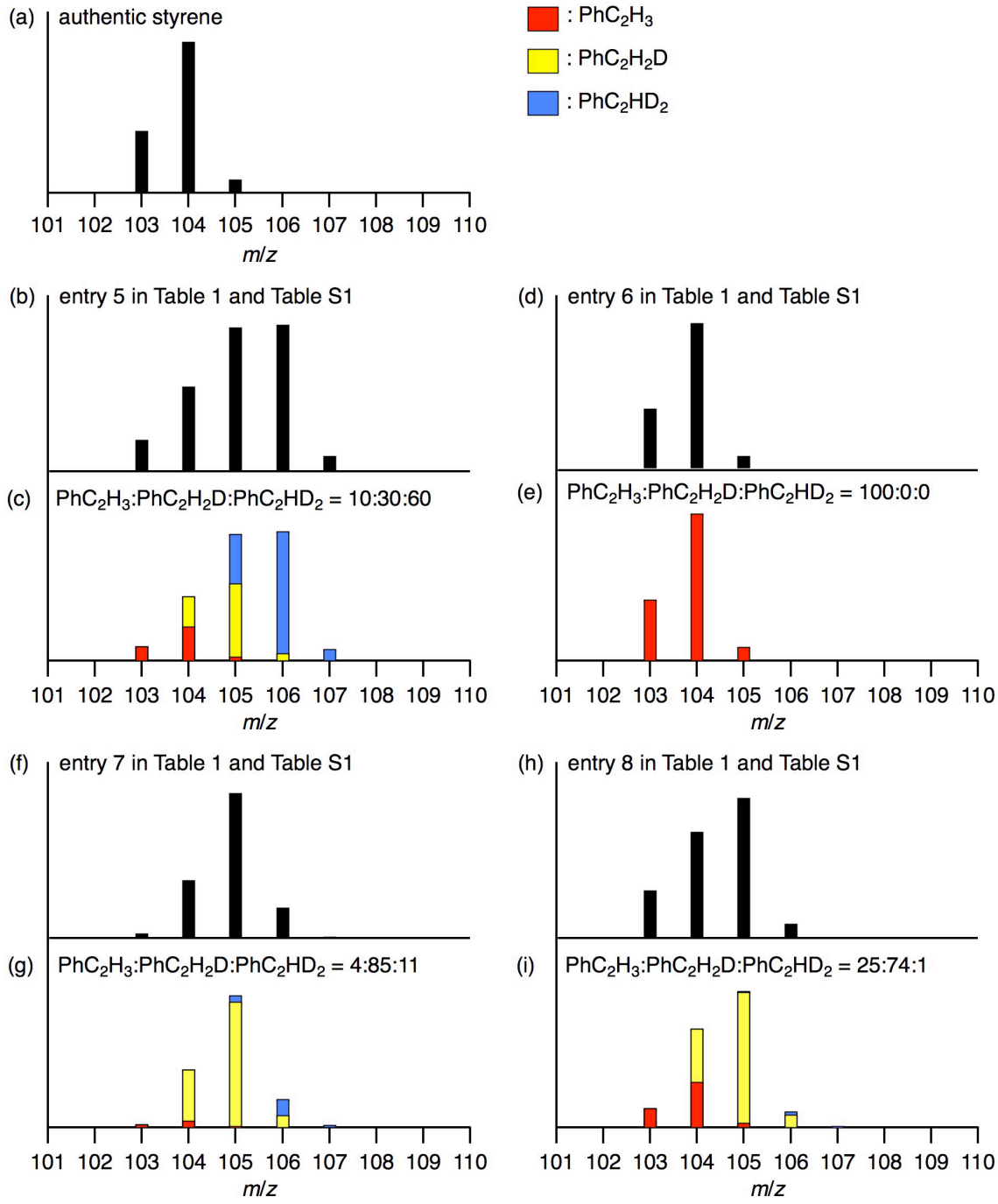

Fig. S6 (a) A GC mass spectrum of authentic $PhCH{=}CH_2$. GC mass spectra obtained from the reduction of $PhC{\equiv}CH$ by **1** with (b) BD_4^- (entry 5), (d) BH_4^- (entry 6), (f) BD_4^- with H_2O (entry 7) and (h) BH_4^- with D_2O (entry 8). Calculated distributions obtained from combination of PhC_2H_3, PhC_2H_2D and PhC_2HD_2 as (c) 10 : 30 : 60, (e) 100 : 0 : 0, (g) 4 : 85 : 11 and (i) 25 : 74 : 1. The ratios of PhC_2H_3 : PhC_2H_2D : PhC_2HD_2 were determined based on those peak areas as the same sensitivities of PhC_2H_3, PhC_2H_2D and PhC_2HD_2.

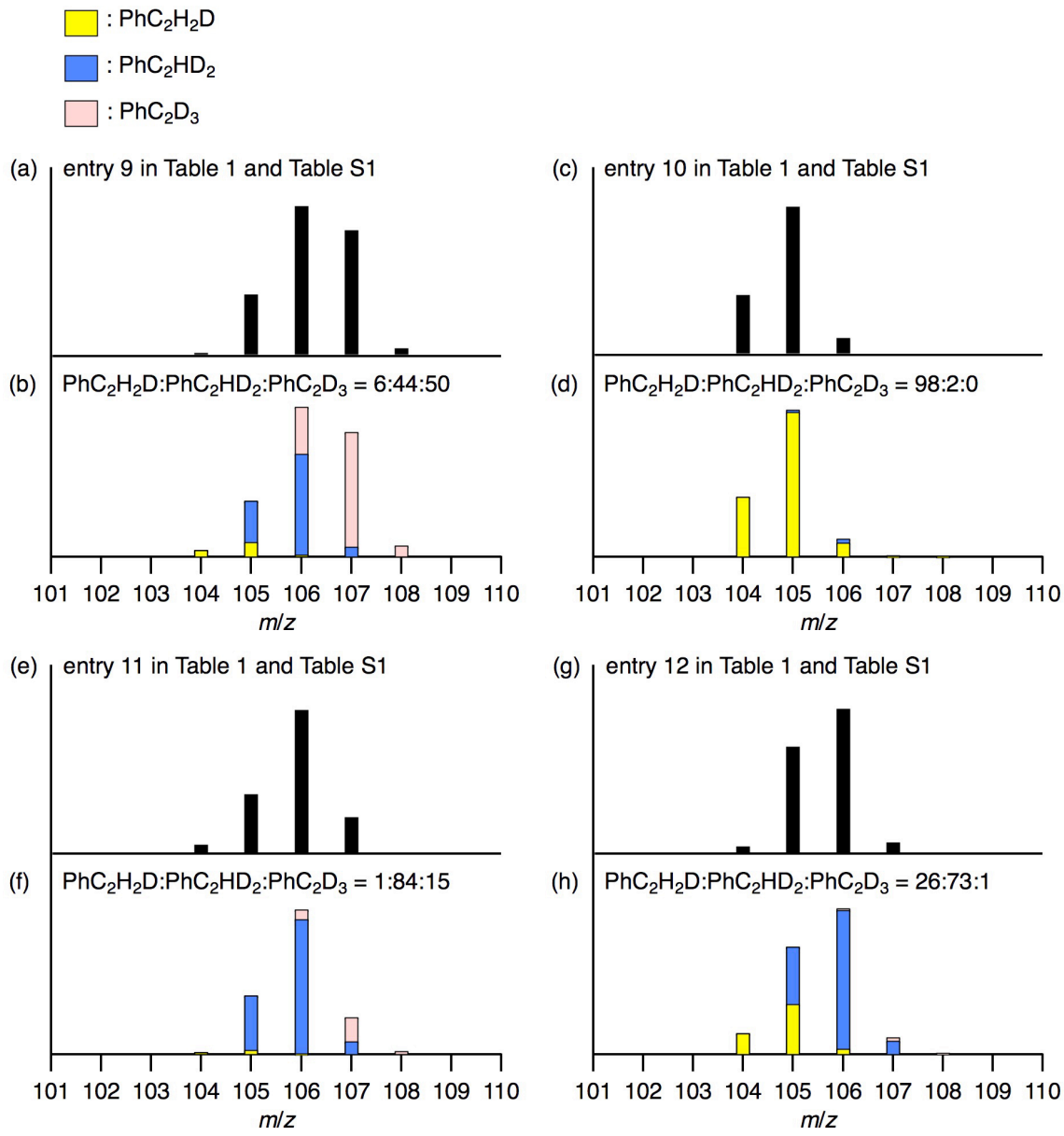

Fig. S7 GC mass spectra obtained from the reduction of PhC≡CD by **1** with (a) BD_4^- (entry 9), (c) BH_4^- (entry 10), (e) BD_4^- with H_2O (entry 11) and (g) BH_4^- with D_2O (entry 12). Calculated distributions obtained from combination of PhC_2H_2D, PhC_2HD_2 and PhC_2D_3 as (b) 6 : 44 : 50, (d) 98 : 2 : 0, (f) 1 : 84 : 15 and (h) 26 : 73 : 1. The ratios of PhC_2H_2D : PhC_2HD_2 : PhC_2D_3 were determined based on those peak areas as the same sensitivities of PhC_2H_2D, PhC_2HD_2 and PhC_2D_3.

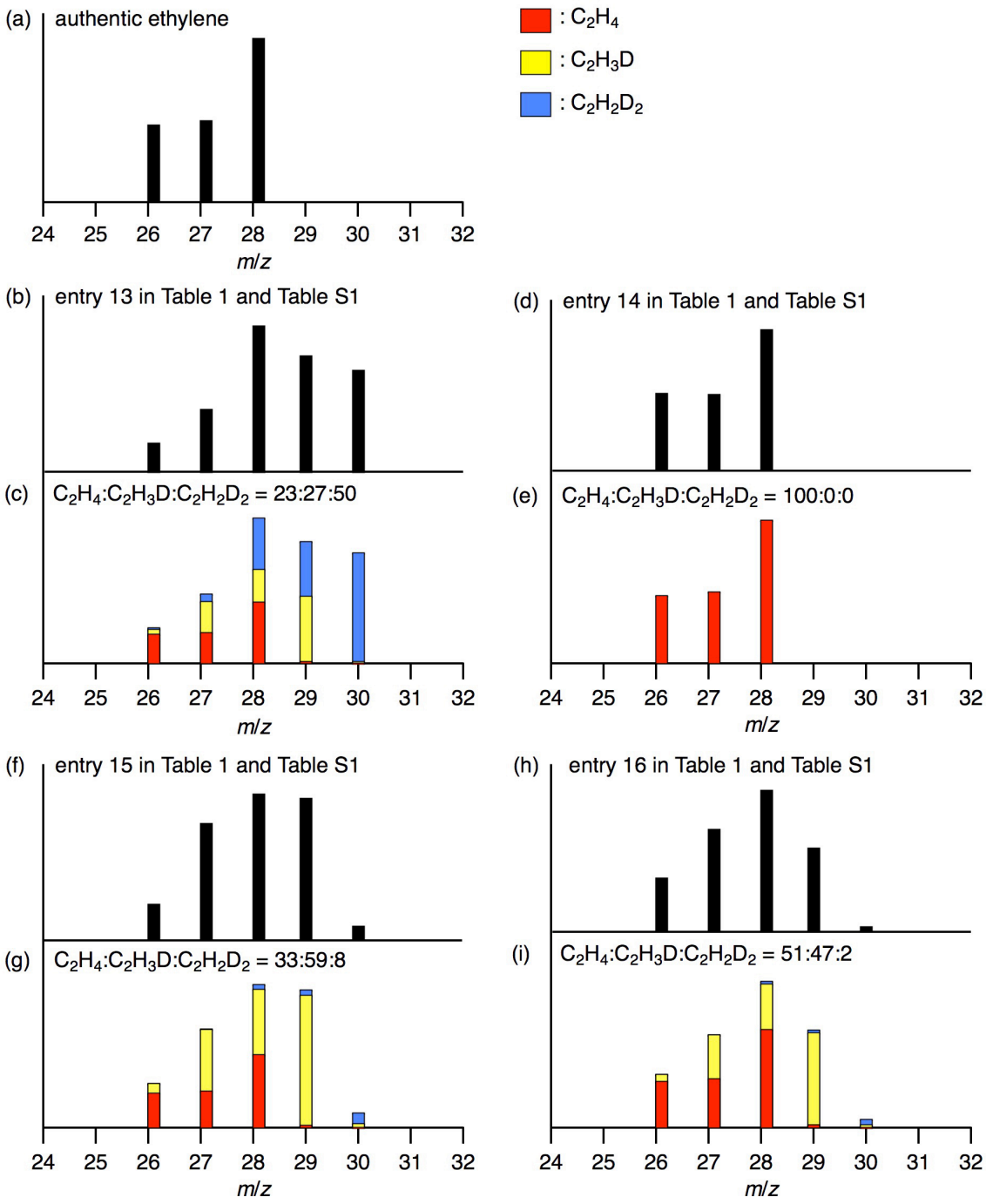

Fig. S8 (a) A GC mass spectrum of authentic CH_2=CH_2 gas. GC mass spectra obtained from the reduction of HC≡CH by and **1** with (b) BD_4^- (entry 13), (d) BH_4^- (entry 14), (f) BD_4^- with H_2O (entry 15) and (h) BH_4^- with D_2O (entry 16). Calculated distributions obtained from combination of C_2H_4, C_2H_3D and $C_2H_2D_2$ as (c) 23 : 27 : 50, (e) 100 : 0 : 0, (g) 33 : 59 : 8 and (i) 51 : 47 : 2. The ratios of C_2H_4 : C_2H_3D : $C_2H_2D_2$ were determined based on those peak areas as the same sensitivities of C_2H_4, C_2H_3D and $C_2H_2D_2$.