Supporting Information

Novel Metal-Free Hydrogenation of the Carbon-Carbon Double Bond in Azulenoid Enones by Use of Cycloheptatriene and Protic Acid

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Figure 1. ^1H NMR spectrum for **2a**

Figure 2. ^{13}C NMR spectrum for **2a**

DU=/home/yamamura/35, USER=kimura, NAME=taka-Me-benzazredC, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.67cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY [Hz]	INTENSITY [PPM]	HISTOGRAM
1	1505.5	26210.600	208.4213	5.96 *****
2	10654.1	17826.473	141.7524	6.85 *****
3	10752.9	17735.863	141.0319	6.49 *****
4	11657.8	16906.604	134.4378	15.07 *****
5	11727.1	16843.051	133.9325	6.54 *****
6	11902.0	16682.836	132.6585	16.62 *****
7	12153.6	16452.211	130.8246	5.47 *****
8	12394.0	16231.935	129.0730	2.02 **
9	12469.6	16162.589	128.5216	14.16 *****
10	12505.0	16130.221	128.2642	1.99 **
11	12700.3	15951.228	126.8409	14.16 *****
12	12825.9	15836.075	125.9252	7.84 *****
13	12877.2	15789.126	125.5519	15.80 *****
14	12906.0	15762.662	125.3414	1.07 *
15	13192.1	15500.522	123.2570	16.95 *****
16	13337.0	15367.702	122.2008	17.44 *****
17	13535.4	15185.918	120.7553	13.92 *****
18	13898.0	14853.550	118.1124	16.90 *****
19	16907.9	12095.185	96.1784	0.82 *
20	19491.0	9727.942	77.3546	17.24 *****
21	19525.9	9695.956	77.1002	17.48 *****
22	19560.8	9663.979	76.8460	17.19 *****
23	24154.1	5454.438	43.3726	19.00 *****
24	25965.2	3794.706	30.1747	13.65 *****
25	27465.2	2419.972	19.2431	17.04 *****

Figure 3. ¹H NMR spectrum for 2b

Figure 4. ^{13}C NMR spectrum for **2b**

DU=/home/yamamura/35, USER=kimura, NAME=taka-naphtoazu2C, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.50cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY		INTENSITY	HISTOGRAM
		[Hz]	[PPM]		
1	1505.2	26210.920	208.4238	3.95	****
2	11155.2	17367.225	138.1006	2.87	***
3	11177.3	17346.914	137.9391	3.69	****
4	11189.1	17336.115	137.8532	3.32	***
5	11416.3	17127.914	136.1976	6.68	*****
6	11604.1	16955.842	134.8294	6.24	*****
7	11808.0	16768.984	133.3435	7.61	*****
8	12292.0	16325.364	129.8159	7.69	*****
9	12364.9	16258.605	129.2851	7.19	*****
10	12384.5	16240.626	129.1421	19.00	*****
11	12479.2	16153.870	128.4522	3.26	***
12	12495.5	16138.862	128.3329	18.70	*****
13	12621.8	16023.113	127.4125	2.93	***
14	12775.8	15882.049	126.2908	6.92	*****
15	12811.6	15849.222	126.0297	6.80	*****
16	12835.3	15827.497	125.8570	3.90	****
17	12896.3	15771.603	125.4125	10.58	*****
18	12924.9	15745.354	125.2038	7.10	*****
19	13049.3	15631.389	124.2976	7.18	*****
20	13188.5	15503.785	123.2829	6.69	*****
21	13271.9	15427.402	122.6755	7.48	*****
22	13732.5	15005.206	119.3183	6.38	*****
23	19480.8	9737.246	77.4286	7.56	*****
24	19515.7	9705.296	77.1745	7.69	*****
25	19550.6	9673.328	76.9203	7.60	*****
26	24117.0	5488.432	43.6429	9.08	*****
27	25754.2	3988.015	31.7119	0.51	*
28	25943.9	3814.193	30.3297	7.76	*****
29	27149.1	2709.732	21.5472	7.60	*****
30	27158.3	2701.278	21.4800	7.63	*****
31	28150.2	1792.194	14.2512	0.56	*

Figure 5. ^1H NMR spectrum for **2c**

CC(=O)OCC1=C2C(=C1)C3=CC=CC=C3C=C2C4=CC=CC=C4

DU=/home/yamamura/35, USER=kimura, NAME=taka-naphto1C, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=1.74cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY		INTENSITY	HISTOGRAM
		[Hz]	[PPM]		
1	1500.2	26214.586	208.4530	7.60	*
2	10550.9	17920.135	142.4972	7.12	*
3	10982.8	17524.326	139.3498	6.34	*
4	11497.9	17052.270	135.5961	16.70	**
5	11575.9	16980.811	135.0279	7.82	*
6	11854.4	16725.531	132.9980	13.90	**
7	11871.0	16710.340	132.8772	16.40	**
8	12084.0	16515.111	131.3248	8.75	*
9	12165.8	16440.205	130.7291	16.22	**
10	12170.9	16435.484	130.6916	7.97	*
11	12256.8	16356.733	130.0654	16.41	**
12	12581.9	16058.863	127.6968	16.64	**
13	12990.0	15684.785	124.7222	8.88	*
14	13004.2	15671.793	124.6189	15.82	**
15	13107.3	15577.305	123.8675	14.82	**
16	13146.9	15541.071	123.5794	16.97	**
17	13303.9	15397.188	122.4353	16.59	**
18	13355.5	15349.844	122.0588	4.93	*
19	13811.9	14931.606	118.7331	16.49	**
20	19501.3	9717.620	77.2725	162.30	*****
21	19536.1	9685.666	77.0184	166.89	*****
22	19571.0	9653.691	76.7642	165.70	*****
23	24034.1	5563.520	44.2400	19.00	**
24	25955.6	3802.628	30.2377	13.47	**
25	27475.2	2409.990	19.1637	17.39	**
26	30104.9	-0.003	-0.0000	6.58	*

Figure 7. ^1H NMR spectrum for **2d**

Current Data Par
NAME taka-ace-
EXPNO
PROCNO

F2 - Acquisition
Date_ 200
Time 16.29

INSTRUM av500
PROBHD 5 mm BBO BE-1H
PULPROG zgpg30

TD 65536
SOLVENT CDCl3

NS 1024
DS 4

SWH 30030.029 Hz
FIDRES 0.458222 Hz

AQ 1.0912410 sec
RG 2896.3

DW 16.650 usec
DE 6.00 usec

TE 300.5 K
D1 2.00000000 sec

dl1 0.03000000 sec
MCREST 0.00000000 sec

MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C

P1 9.00 usec
PL1 1.00 dB

SFO1 125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16

NUC2 1H
PCPD2 80.00 usec

PL2 0.00 dB
PL12 15.14 dB

PL13 15.14 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768

WDW EM
SSB 0

LB 1.00 Hz
GB 0

PC 1.00

DU=/home/yamamura/35, USER=kimura, NAME=taka-ace-Me-redC, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.34cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY [Hz]	INTENSITY [PPM]	HISTOGRAM
1	1525.5	26182.238	208.1957	7.46 *****
2	9289.2	19067.227	151.6186	5.76 *****
3	10210.1	18223.270	144.9077	7.96 *****
4	10953.8	17541.717	139.4881	5.74 *****
5	11336.0	17191.443	136.7028	15.51 *****
6	11630.9	16921.133	134.5533	7.48 *****
7	11726.2	16833.857	133.8593	6.80 *****
8	11781.0	16783.574	133.4595	16.27 *****
9	11847.0	16723.160	132.9791	15.86 *****
10	12127.0	16466.494	130.9382	6.49 *****
11	12175.0	16422.545	130.5887	8.91 *****
12	12178.2	16419.607	130.5653	6.97 *****
13	12483.2	16140.095	128.3427	14.79 *****
14	12487.8	16135.893	128.3093	1.38 *
15	12555.0	16074.282	127.8194	16.10 *****
16	12631.5	16004.131	127.2615	13.65 *****
17	13083.3	15590.116	123.9694	14.19 *****
18	13155.0	15524.441	123.4471	16.31 *****
19	13167.0	15513.387	123.3592	16.81 *****
20	13224.0	15461.205	122.9443	9.53 *****
21	13331.3	15362.812	122.1619	13.98 *****
22	13772.2	14958.759	118.9490	14.68 *****
23	19488.4	9720.228	77.2932	18.61 *****
24	19523.3	9688.268	77.0391	19.28 *****
25	19558.2	9656.276	76.7847	19.06 *****
26	24035.9	5552.670	44.1537	19.00 *****
27	25960.1	3789.269	30.1315	15.73 *****
28	27298.8	2562.418	20.3758	16.30 *****
29	30094.8	-0.004	-0.0000	2.64 ***

Figure 1. ^1H NMR spectrum for **2e**

Figure 10. ^{13}C NMR spectrum for **2e**

Current data set:

NAME = takahashi2c EXPNO = 1 PROCNO = 1
 USER = kimura DU = /home/yamamura/35

MI=0.00 cm, MAXI=10000.00 cm, PC=1.400
 F1=215.000 ppm, F2=-5.000 ppm

Peak-Nr	Frequency [Hz]	Frequency [ppm]	Intensity [cm]	Integral
1	26186.539	208.2299	6.05	
Int-Reg: 1	208.4898	207.9433		2.66434
2	19203.420	152.7016	4.93	
Int-Reg: 2	153.1277	152.5228		2.21046
3	17197.117	136.7479	5.42	
Int-Reg: 3	136.9351	136.4105		2.27197
4	17047.172	135.5556	14.02	
5	17031.547	135.4313	0.26	
Int-Reg: 4	135.9805	134.9530		6.12115
6	16783.059	133.4554	0.27	
7	16760.377	133.2751	14.48	
8	16731.836	133.0481	5.21	
9	16707.520	132.8547	15.72	
10	16681.893	132.6510	0.28	
Int-Reg: 5	133.4736	132.3951		14.6785
11	16359.296	130.0857	16.42	
12	16335.256	129.8946	0.25	
Int-Reg: 6	130.3036	129.7207		6.07663
13	16249.086	129.2094	4.24	
14	16222.745	128.9999	0.14	
Int-Reg: 7	129.6332	128.6421		1.75438
15	15439.697	122.7733	0.17	
16	15411.858	122.5519	14.94	
17	15404.455	122.4930	0.45	
18	15378.631	122.2877	0.12	
Int-Reg: 8	122.9871	121.6390		6.62344
19	15216.398	120.9977	7.31	
20	15205.686	120.9125	14.68	
21	15194.312	120.8220	0.34	
Int-Reg: 9	121.2819	120.4293		8.8207
22	14886.846	118.3771	0.24	
23	14862.948	118.1871	0.15	
24	14833.793	117.9553	13.96	
Int-Reg: 10	118.5272	117.5580		6.77558
25	9722.750	77.3133	8.78	
26	9690.775	77.0590	8.95	
27	9658.785	76.8047	8.86	
Int-Reg: 11	77.8929	76.4062		22.5996
28	5595.337	44.4930	0.21	
29	5578.130	44.3561	19.00	
30	5559.921	44.2113	0.13	
Int-Reg: 12	44.6333	44.0722		7.00619
31	3786.435	30.1089	13.63	
Int-Reg: 13	30.3719	29.7671		4.91969

32	2633.722	20.9428	0.12	
33	2609.626	20.7512	0.16	
34	2593.284	20.6213	18.98	
35	2568.417	20.4235	0.13	
Int-Reg:	14	21.0514	20.3008	7.47735

Figure 11. ^1H NMR spectrum for **2f**

Figure 12. ^{13}C NMR spectrum for **2f**

DU=/home/yamamura/35, USER=kimura, NAME=taka-thioisomerC, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.84cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY	[PPM]	INTENSITY	HISTOGRAM
		[Hz]			
1	1518.7	26198.543	208.3254	6.31	*****
2	9141.6	19212.598	152.7746	4.82	****
3	11330.1	17206.943	136.8261	6.06	*****
4	11492.9	17057.750	135.6397	15.70	*****
5	11806.1	16770.721	133.3573	15.94	*****
6	11837.0	16742.381	133.1320	6.47	*****
7	11864.8	16716.855	132.9290	15.72	*****
8	12242.9	16370.387	130.1739	16.67	*****
9	12364.9	16258.560	129.2847	4.45	****
10	12394.2	16231.735	129.0714	0.89	*
11	13277.4	15422.308	122.6350	14.07	*****
12	13492.0	15225.632	121.0711	7.59	*****
13	13502.9	15215.636	120.9916	17.15	*****
14	13910.8	14841.843	118.0193	16.14	*****
15	19492.9	9726.212	77.3408	22.67	*****
16	19527.7	9694.245	77.0866	22.89	*****
17	19562.6	9662.300	76.8326	22.31	*****
18	24005.7	5590.431	44.4540	16.74	*****
19	25960.4	3799.070	30.2094	11.87	*****
20	27265.9	2602.628	20.6956	19.00	*****

Figure 13. ^1H NMR spectrum for **2g**

Figure 13. ^{13}C NMR spectrum for **2g**

DU=/home/yamamura/35, USER=kimura, NAME=taka-benzthioredC, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.45cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY	INTENSITY	HISTOGRAM
		[Hz]	[PPM]	
1	1538.0	26180.838	208.1846	8.16 ***
2	9921.0	18498.299	147.0947	5.82 **
3	10048.2	18381.746	146.1678	6.05 **
4	11168.1	17355.418	138.0067	6.98 ***
5	11281.2	17251.715	137.1821	13.17 *****
6	11749.8	16822.328	133.7677	13.65 *****
7	11889.2	16694.574	132.7518	14.57 *****
8	11946.1	16642.416	132.3371	6.78 **
9	12087.9	16512.436	131.3035	6.05 **
10	12584.0	16057.754	127.6880	4.97 **
11	12735.1	15919.279	126.5868	14.58 *****
12	12997.1	15679.211	124.6778	15.31 *****
13	13066.0	15616.029	124.1754	16.16 *****
14	13119.2	15567.301	123.7880	14.34 *****
15	13379.7	15328.534	121.8893	13.98 *****
16	13389.0	15320.059	121.8219	9.11 ***
17	13475.7	15240.614	121.1902	13.64 *****
18	19455.1	9760.780	77.6157	0.51
19	19499.0	9720.566	77.2959	54.16 *****
20	19533.9	9688.588	77.0416	55.01 *****
21	19568.8	9656.628	76.7875	53.72 *****
22	24007.0	5589.276	44.4448	19.00 *****
23	25948.9	3809.632	30.2934	14.21 *****
24	27312.6	2559.825	20.3552	14.45 *****
25	30103.4	2.224	0.0177	1.02

Figure 15. ^{13}C NMR spectrum for **2h**

Figure 16. ^{13}C NMR spectrum for **2h**

DU=/home/yamamura/35, USER=kimura, NAME=taka-benzofuran-redC, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.34cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY	INTENSITY	HISTOGRAM
		[Hz]	[PPM]	
1	1536.4	26174.885	208.1373	5.95 *****
2	7203.2	20981.646	166.8417	4.40 ****
3	8003.8	20247.889	161.0070	6.08 *****
4	10906.6	17587.691	139.8537	5.81 *****
5	11595.1	16956.703	134.8362	15.25 *****
6	11903.9	16673.637	132.5853	15.90 *****
7	12031.1	16557.086	131.6585	15.35 *****
8	12393.8	16224.730	129.0157	0.53 *
9	12504.9	16122.934	128.2062	0.71 *
10	12519.1	16109.876	128.1024	6.36 *****
11	12906.1	15755.229	125.2823	0.39
12	13053.6	15620.080	124.2076	14.46 *****
13	13095.9	15581.250	123.8989	7.07 *****
14	13161.0	15521.609	123.4246	18.10 *****
15	13166.0	15517.082	123.3886	18.49 *****
16	13247.3	15442.507	122.7956	14.45 *****
17	13620.1	15100.859	120.0789	15.78 *****
18	14286.9	14489.807	115.2199	5.04 *****
19	14745.4	14069.595	111.8785	14.70 *****
20	15257.0	13600.748	108.1503	7.83 *****
21	19491.2	9720.331	77.2941	20.34 *****
22	19526.1	9688.340	77.0397	20.89 *****
23	19561.0	9656.354	76.7853	20.57 *****
24	24152.1	5448.912	43.3286	19.00 *****
25	25972.9	3780.215	30.0595	13.89 *****
26	27542.3	2342.004	18.6231	17.08 *****
27	30097.8	0.002	0.0000	1.44 *

Figure 17. ¹H NMR spectrum for **2j**

No title

DU=/home/yamamura/35, USER=kimura, NAME=taka-guaaz-red-c, EXPNO=1, PROCNO=1
 F1=215.000ppm, F2=-5.000ppm, MI=0.28cm, MAXI=10000.00cm, PC=1.400

#	ADDRESS	FREQUENCY		INTENSITY	HISTOGRAM
		[Hz]	[PPM]		
1	1521.3	26196.113	208.3061	2.07	*
2	10201.0	18241.668	145.0540	4.01	***
3	11015.3	17495.402	139.1198	7.91	*****
4	11044.5	17468.619	138.9069	3.94	***
5	11217.7	17309.953	137.6452	3.12	**
6	11617.8	16943.293	134.7296	7.54	*****
7	11803.3	16773.256	133.3775	7.38	*****
8	11961.1	16628.639	132.2275	2.69	**
9	12731.1	15923.006	126.6165	4.38	***
10	12784.0	15874.470	126.2305	9.30	*****
11	13046.0	15634.357	124.3212	4.78	***
12	19501.0	9718.736	77.2814	28.62	*****
13	19535.9	9686.771	77.0272	29.11	*****
14	19570.7	9654.825	76.7732	28.45	*****
15	19770.9	9471.422	75.3148	0.42	
16	23654.0	5912.730	47.0168	10.20	*****
17	24939.2	4734.931	37.6512	9.34	*****
18	25977.9	3782.988	30.0815	6.10	****
19	26425.4	3372.879	26.8204	7.90	*****
20	26626.0	3189.051	25.3587	9.20	*****
21	26734.1	3090.049	24.5714	19.00	*****
22	27574.9	2319.459	18.4439	0.39	
23	28343.0	1615.528	12.8463	7.85	*****
24	30106.0	-0.128	-0.0010	0.75	*

List of elemental analyses and MS(m/z)

2a: Calcd for $C_{18}H_{16}O$: C 87.06, H 6.49. Found: C 87.12, H 6.35.

m/z: 248(M⁺).

2b: Calcd for $C_{22}H_{18}O$: C 88.56, H 6.08. Found: C 88.66, H 5.93.

m/z: 298(M⁺).

2c: Calcd for $C_{22}H_{18}O$: C 88.56, H 6.08. Found: C 88.32, H 6.14.

m/z: 298(M⁺).

2d: Calcd for $C_{24}H_{18}O$: C 89.41, H 5.63. Found: C 89.28, H 5.74.

m/z: 322(M⁺).

2e: Calcd for $C_{16}H_{14}OS$: C 75.55, H 5.55. Found: C 75.26, H 5.47.

m/z: 254(M⁺).

2f: Calcd for $C_{16}H_{14}OS$: C 75.55, H 5.55. Found: C 75.38, H 5.64.

m/z: 254(M⁺).

2g: Calcd for $C_{20}H_{16}OS$: C 78.91, H 5.38. Found: C 79.12, H 5.24.

m/z: 304(M⁺).

2h: Calcd for $C_{20}H_{16}O_2$: C 83.31, H 5.59. Found: C 83.18, H 5.35.

m/z: 288(M⁺).

2j: Calcd for $C_{19}H_{24}O$: C 85.03, H 9.01. Found: C 85.26, H 8.88.

m/z: 268(M⁺).