Supporting Information for

The advantages of covalently attaching organometallic catalysts to a carbon black support: Recyclable Rh(I) complexes that deliver enhanced conversion and product selectivity

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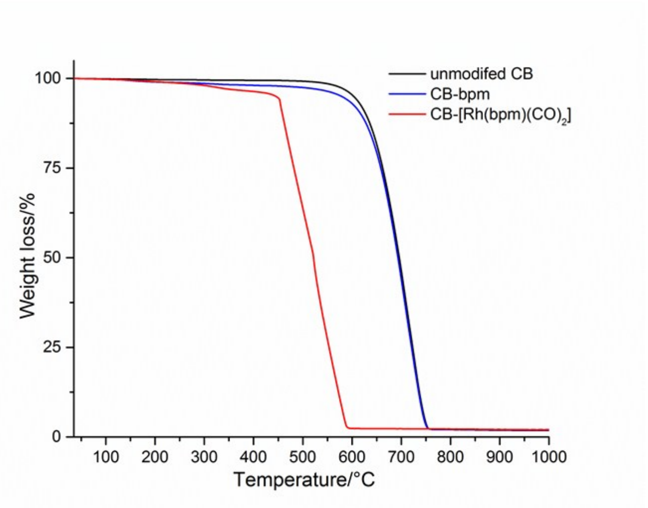


Figure S1. TGA curves for unmodified carbon black (CB, black trace), bpm-modified carbon black (CB-bpm, blue trace) and carbon black modified with Rh complex (CB-[Rh(bpm)(CO)$_2$], red trace) recorded under an atmosphere of air.

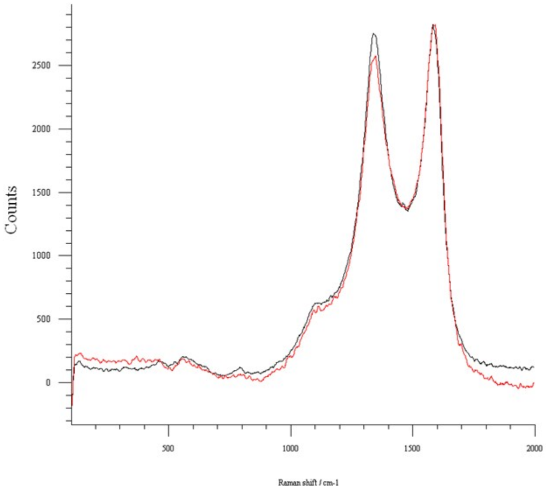


Figure S2. Raman spectra of unmodified Vulcan XC-72R (CB, red trace) and CB-[Rh(bpm)(CO)$_2$] (black trace).

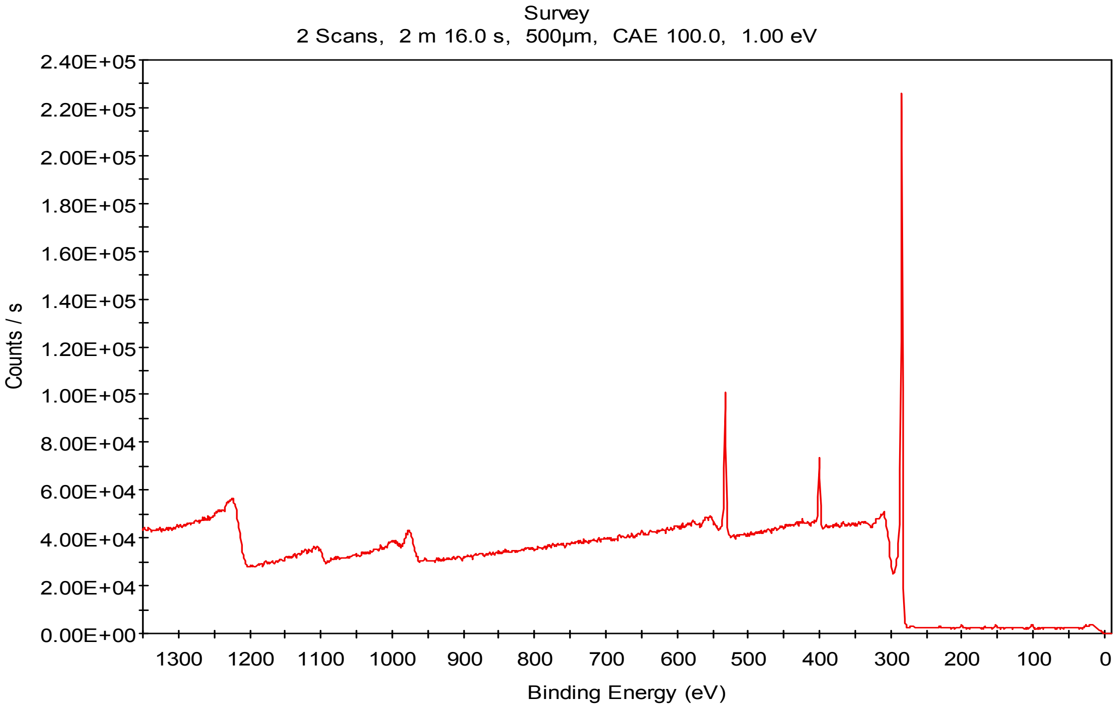


Figure S3. XP survey spectrum of GC-bpm.

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	At. %	SF Al Scof
C1s A	291.78	284.49	281.18	0.86	31622.8	55.07	1
C1s B	291.78	285.74	281.18	1.73	13780.09	24	1
C1s C	291.78	287.49	281.18	1.73	1788.56	3.12	1
C1s D	291.78	289.06	281.18	1.73	189.63	0.33	1
Cl2p3 A	205.08	200.21	194.74	1.22	175.19	0.2	1.51
Cl2p3 B	205.08	197.26	194.74	1.59	70.09	0.08	1.51
Si2p	105.28	101.71	98.58	1.24	318.7	0.67	0.817
N1s A	405.23	401.25	396.18	1.53	3469.17	3.4	1.8
N1s B	405.23	399.82	396.18	1.53	3966.46	3.88	1.8
O1s	537.48	532.64	527.38	2.14	14897.21	9.12	2.93
S2p3 A	173.18	167.8	165.18	1.9	88.74	0.14	1.11

Table S1. Peak table for the XP survey spectrum of GC-bpm.

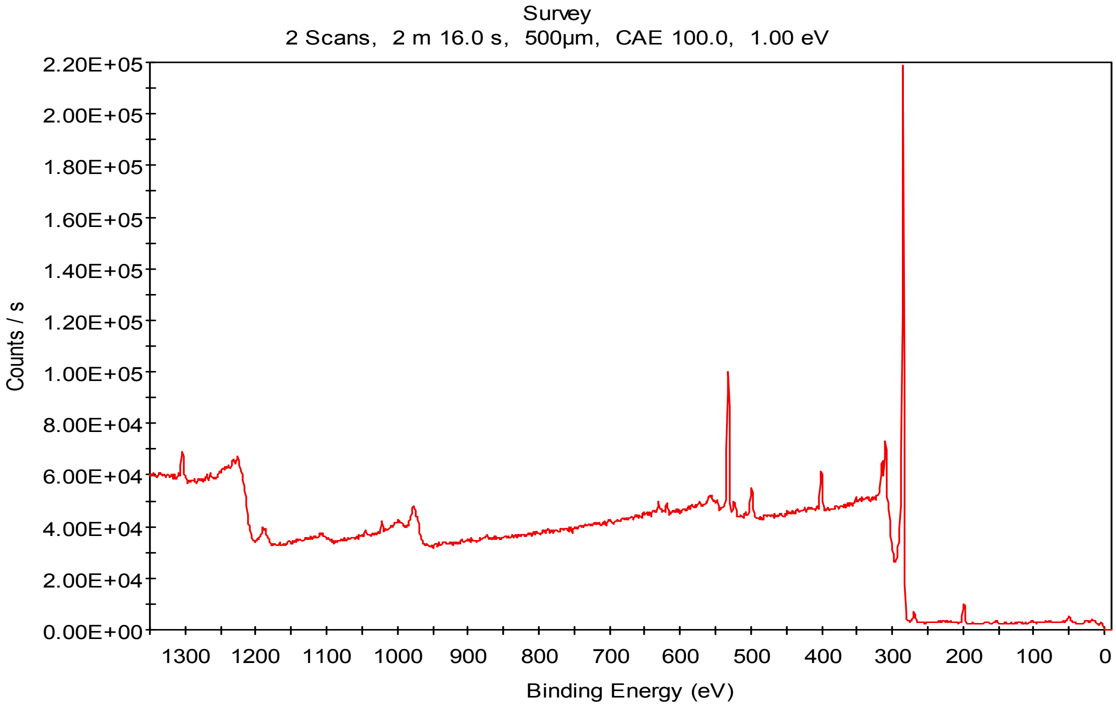


Figure S4. XP survey spectrum of GC-[Rh(bpm)(CO)$_2$].

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	At. %	SF Al Scof
C1s A	294.28	284.44	281.98	0.75	19311.46	37.27	1
C1s B	294.28	284.94	281.98	1.54	15854.33	30.6	1
C1s C	294.28	285.94	281.98	1.54	1621.1	3.13	1
C1s D	294.28	286.54	281.98	1.54	3584.25	6.92	1
C1s E	294.28	287.94	281.98	1.54	1451.21	2.8	1
C1s F	294.28	289.14	281.98	1.54	480.44	0.93	1
C1s G	294.28	290.76	281.98	2.89	1499.54	2.9	1
Cl2p3 A	203.78	198.17	193.98	1.41	900.31	1.14	1.51
Cl2p3 B	203.78	200.05	193.98	1.64	209.97	0.27	1.51
N1s A	404.41	401.45	396.78	1.73	2174.26	2.36	1.8
N1s B	404.41	399.93	396.78	1.73	1274.38	1.38	1.8
O1s A	537.68	532.35	528.68	2.63	12867.49	8.73	2.93
Rh3d5 A	318.89	310.08	307.37	1.91	4322.15	1	8.39
Zn2p3 A	1025.18	1022.13	1017.48	1.84	899.94	0.11	18.92
Si2p A	106.09	101.81	98.28	1.35	166.7	0.39	0.817
I3d5 A	635.78	619.4	615.58	1.77	794.98	0.08	19.87

Table S2. Peak table for the XP survey spectrum of GC-[Rh(bpm)(CO)$_2$].

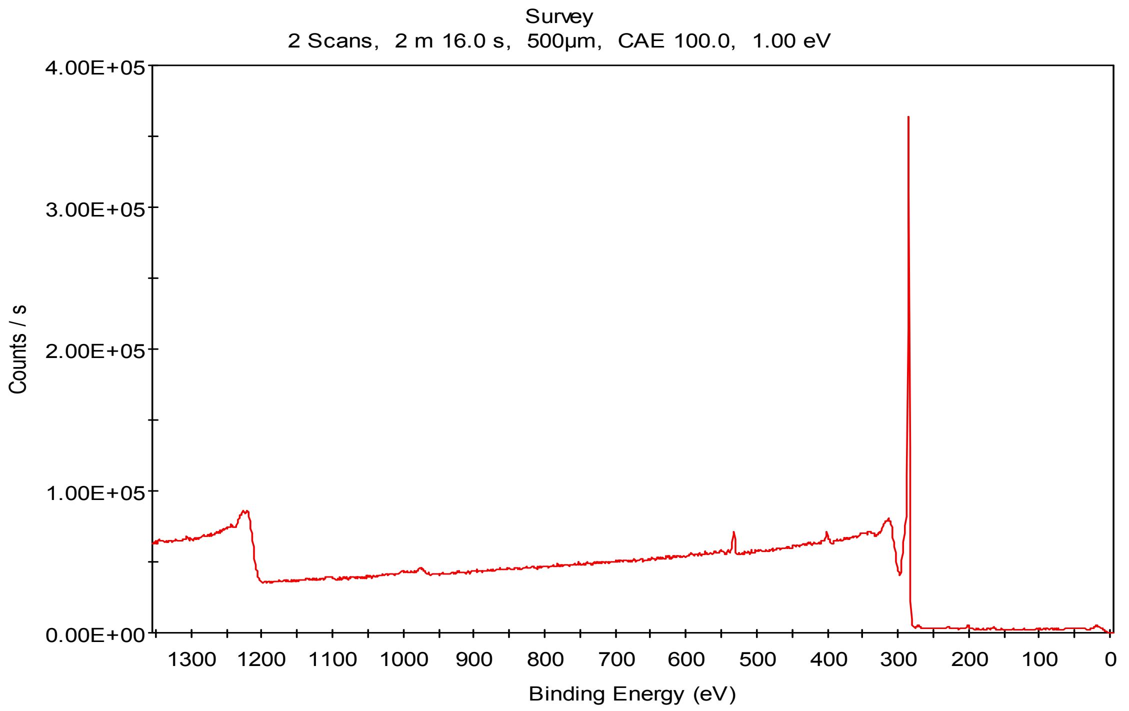


Figure S5. XP survey spectrum of CB-bpm.

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	At. %	SF Al Scof
C1s A	294.98	284.53	281.38	0.78	35165.95	45.94	1
C1s B	294.98	285.03	281.38	1.64	22138.2	28.92	1
C1s C	294.98	286.63	281.38	1.64	4835.52	6.32	1
C1s D	294.98	288.03	281.38	1.64	2382.84	3.11	1
C1s E	294.98	289.23	281.38	1.64	667.32	0.87	1
C1s F	294.98	290.74	281.38	3.32	6469.56	8.46	1
C1s G	294.98	283.75	281.38	0.78	2525.77	3.3	1
Cl2p3 A	205.98	200.51	197.38	1.18	320.51	0.28	1.51
N1s A	403.98	399.65	396.78	1.33	710.43	0.52	1.8
N1s B	403.98	401.15	396.78	1.33	680.91	0.5	1.8
O1s A	536.98	531.76	528.58	2.05	1510.71	0.69	2.93
O1s B	536.98	533.01	528.58	2.05	1913.88	0.88	2.93
S2p3 A	167.38	163.9	161.78	0.9	182.85	0.21	1.11

Table S3. Peak table for the XP survey spectrum of CB-bpm

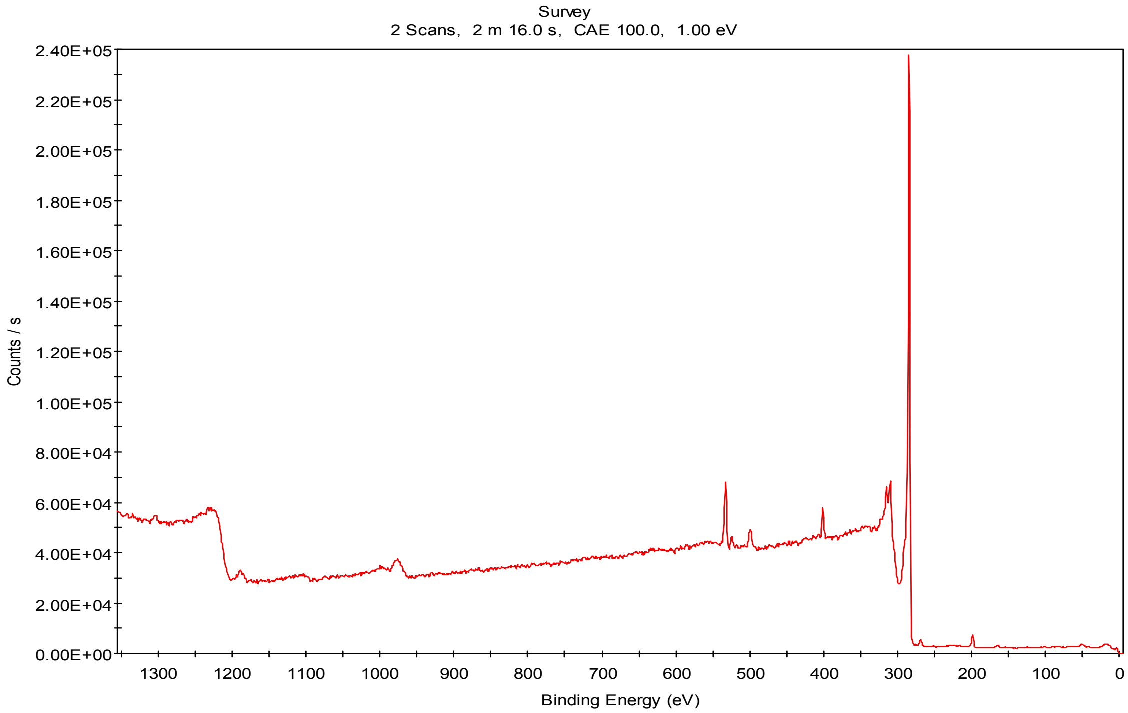


Figure S6. XP survey spectrum of CB-[Rh(bpm)(CO)$_2$].

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	At. %	SF Al Scof
C1s A	292.38	284.43	281.08	0.88	29916.07	51.33	1
C1s B	292.38	284.95	281.08	1.54	15342.41	26.33	1
C1s C	292.38	285.95	281.08	1.54	2315.01	3.97	1
C1s D	292.38	286.55	281.08	1.54	2141.77	3.68	1
C1s E	292.38	287.95	281.08	1.54	1008	1.73	1
C1s F	292.38	289.15	281.08	1.54	709.94	1.22	1
C1s G	292.38	290.74	281.08	1.81	1011.91	1.74	1
Cl2p3 A	204.08	198.06	195.22	1.42	693.4	0.78	1.51
Cl2p3 B	204.08	199.84	195.22	1.42	150.03	0.17	1.51
N1s A	404.93	399.98	394.88	1.77	841.67	0.81	1.8
N1s B	404.93	401.47	394.88	1.77	2110.78	2.04	1.8
O1s	539.05	532.08	527.08	2.54	7931.73	4.78	2.93
Rh3d5 A	317.9	310.16	305.91	1.73	4930.41	1.01	8.39
Rh3d5 B	317.9	308.1	305.91	1.73	1002.23	0.21	8.39
S2p3 A	167.77	163.78	161.08	0.88	137.38	0.21	1.11

Table S4. Peak table for the XP survey spectrum of CB-[Rh(bpm)(CO)$_2$].

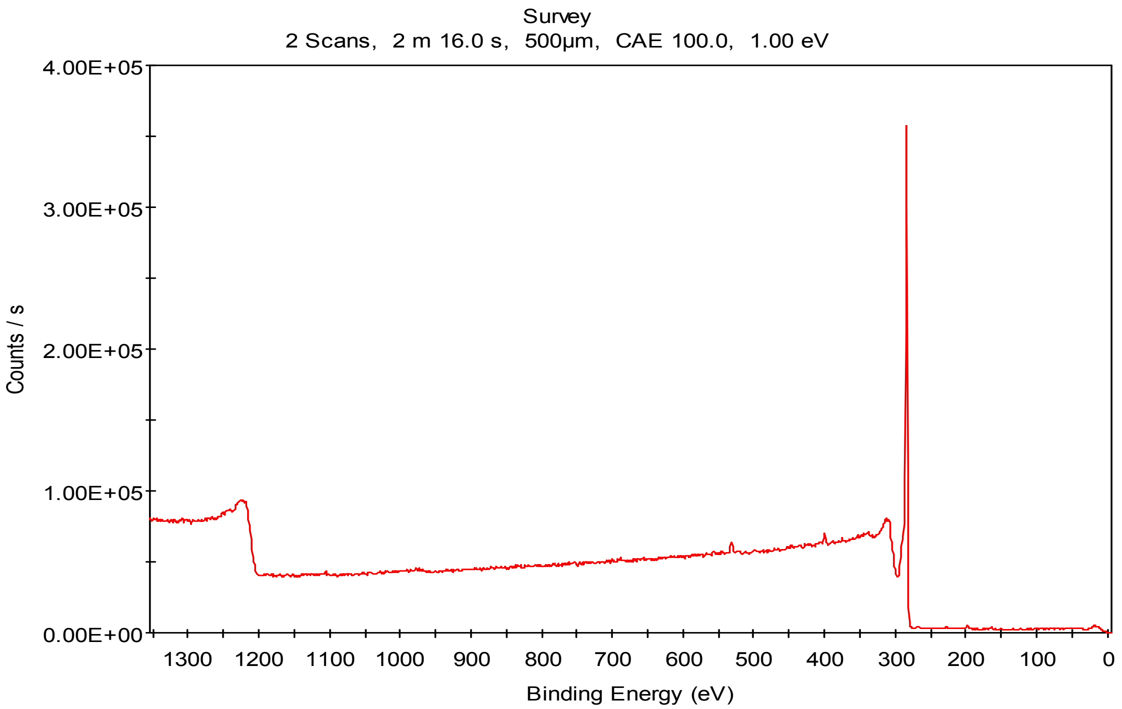


Figure S7. XP survey spectrum of CB-[Rh(bpm)(CO)$_2$] after 2 catalytic cycles.

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	At. %	SF Al Scof
C1s A	294.28	284.49	281.98	0.87	40571.99	47.63	1
C1s B	294.28	284.99	281.98	1.54	26313.47	30.89	1
C1s C	294.28	285.99	281.98	1.54	2128.84	2.5	1
C1s D	294.28	286.59	281.98	1.54	4871.43	5.72	1
C1s E	294.28	287.99	281.98	1.54	2259.64	2.65	1
C1s F	294.28	289.19	281.98	1.54	1196.74	1.41	1
C1s G	294.28	290.91	281.98	2.65	5134.27	6.03	1
Cl2p3 A	203.78	198.04	193.98	1.51	382.61	0.3	1.51
Cl2p3 B	203.78	200.59	193.98	1.59	63.44	0.05	1.51
N1s A	404.41	401.49	396.78	1.73	757.81	0.5	1.8
N1s B	404.41	400.02	396.78	1.73	1202.94	0.79	1.8
O1s A	539.18	532.53	528.16	2.77	2446.18	1.01	2.93
S2p3 A	167.88	163.87	160.83	0.9	196.4	0.21	1.11
Rh3d5 A	317.68	310.07	307.88	2.51	2307.6	0.32	8.39

Table S5. Peak table for the XP survey spectrum of CB-[Rh(bpm)(CO)$_2$] after 2 catalytic cycles.

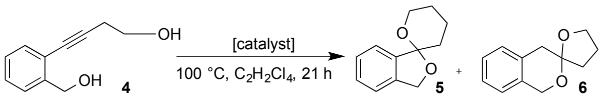
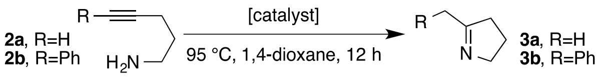
Entry	Catalyzed reaction	Catalytic run	Catalyst sample weight, mg	[Rh], mg/L	Rh, wt %
1	N/A	0	42.2	16.90	1.00
2		1	2.5	0.90	0.90
3		2	1.7	0.59	0.88
4		3	2.1	0.71	0.85
5		4	1.3	0.43	0.83
6		1	2.0	0.73	0.91
7		2	2.2	0.77	0.88
8		3	1.9	0.64	0.85
9		4	2.3	0.76	0.83

Table S6. Summary of ICP-MS analysis of catalyst samples recovered after completion of every catalytic run

Example of calculation for entry 1:

m_{Rh} = 16.9 mg/L × 0.025 L = 0.4225 mg;

Rh wt % = (0.4225/42.2) × 100% = 1.0 %.

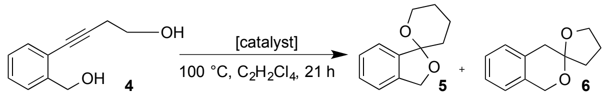
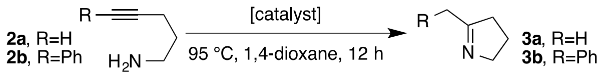
Entry	Catalyzed reaction	Catalytic run	[Rh], mg/L	Rh, wt %
1		1	1.87	9.1
2		2	0.42	2.0
3		3	0.47	2.3
4		4	0.44	2.1
5		1	1.77	8.8
6		2	0.41	2.0
7		3	0.46	2.3
8		4	0.48	2.4

Table S7. Summary of ICP-MS analysis of residues obtained after evaporation of mother liquors recovered after completion of every catalytic run.

Example of calculation for entry 5

m_{Rh} = 1.77 mg/L × 0.025 L = 0.04425 mg;

Rh wt % = [(0.04425 mg)/(50.0 mg × 0.01)] × 100% = 8.8 %

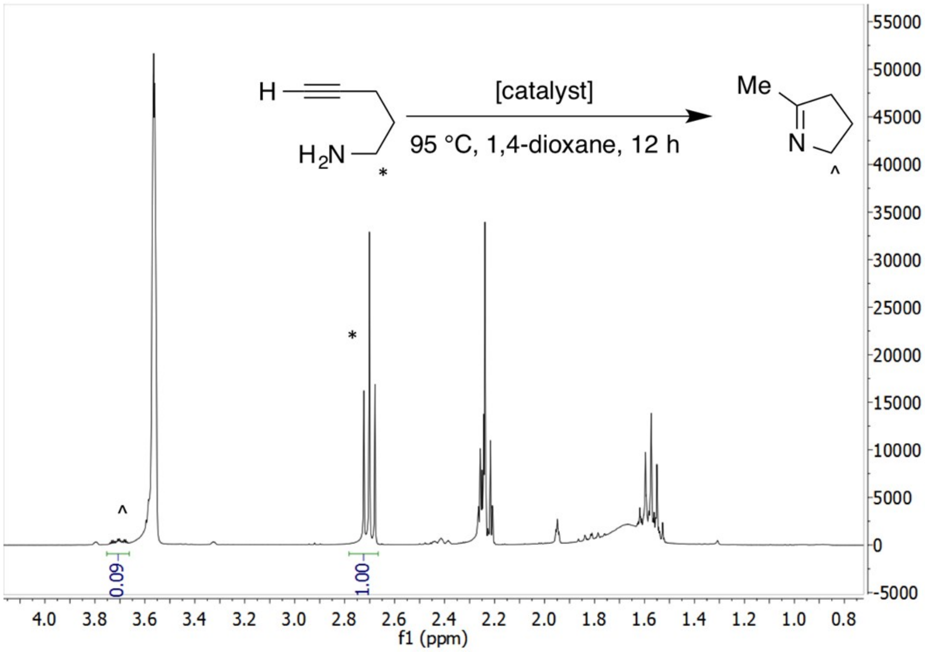


Figure S8. ^{1}H NMR spectrum of the residues recovered after completion of hydroamination of pent-4-yn-1-amine using CB-[Rh(bpm)(CO)$_2$] (table 1, entry 1).

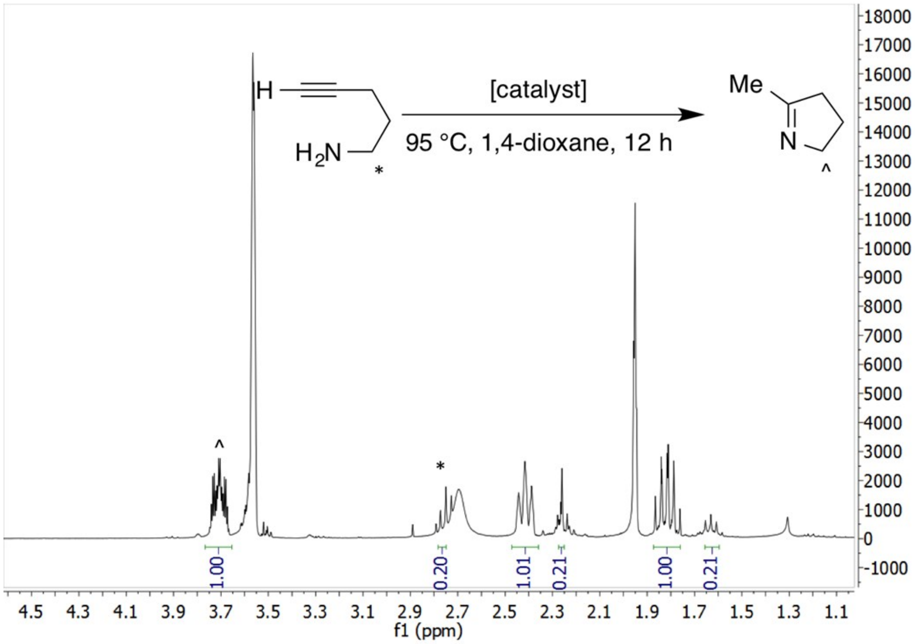


Figure S9 ^{1}H NMR spectrum of the residues recovered after completion of hydroamination of pent-4-yn-1-amine using CB-[Rh(bpm)(CO)$_2$] (table 1, entry 2).

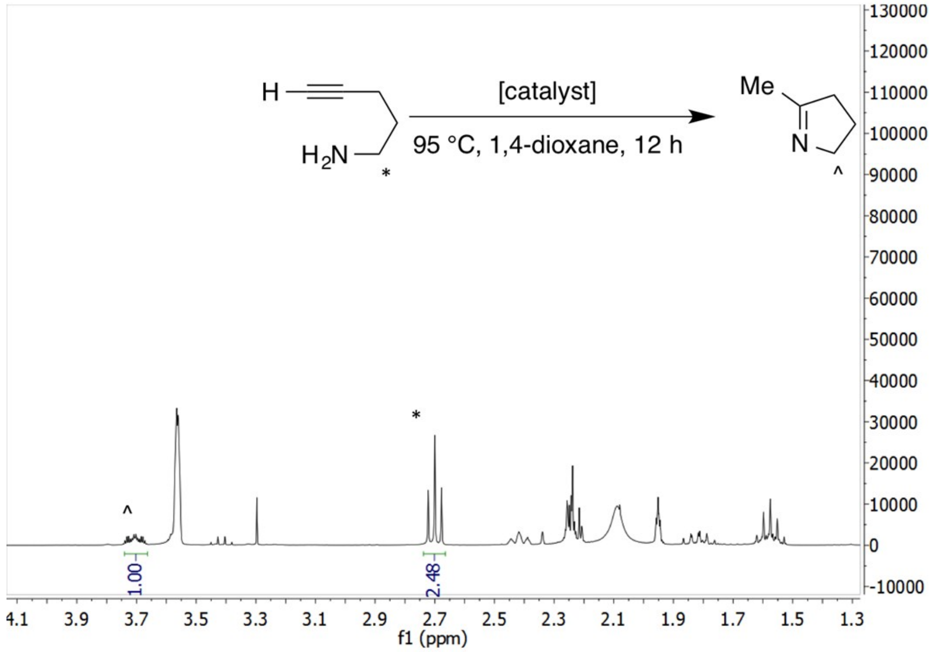


Figure S10. ^{1}H NMR spectrum of the residues recovered after completion of hydroamination of pent-4-yn-1-amine using CB-[Rh(bpm)(CO)$_2$] (table 1, entry 4).

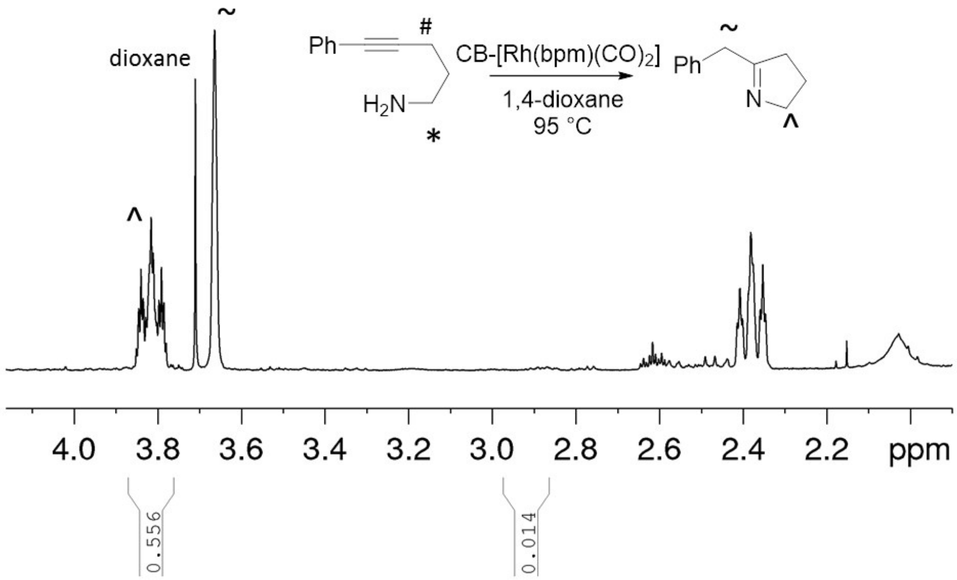


Figure S11. ^{1}H NMR spectrum of the residues recovered after completion of the first run of hydroamination of 5-phenyl-4-pentyn-1-amine using CB-[Rh(bpm)(CO)$_2$] as a catalyst (Table 1, entry 7)

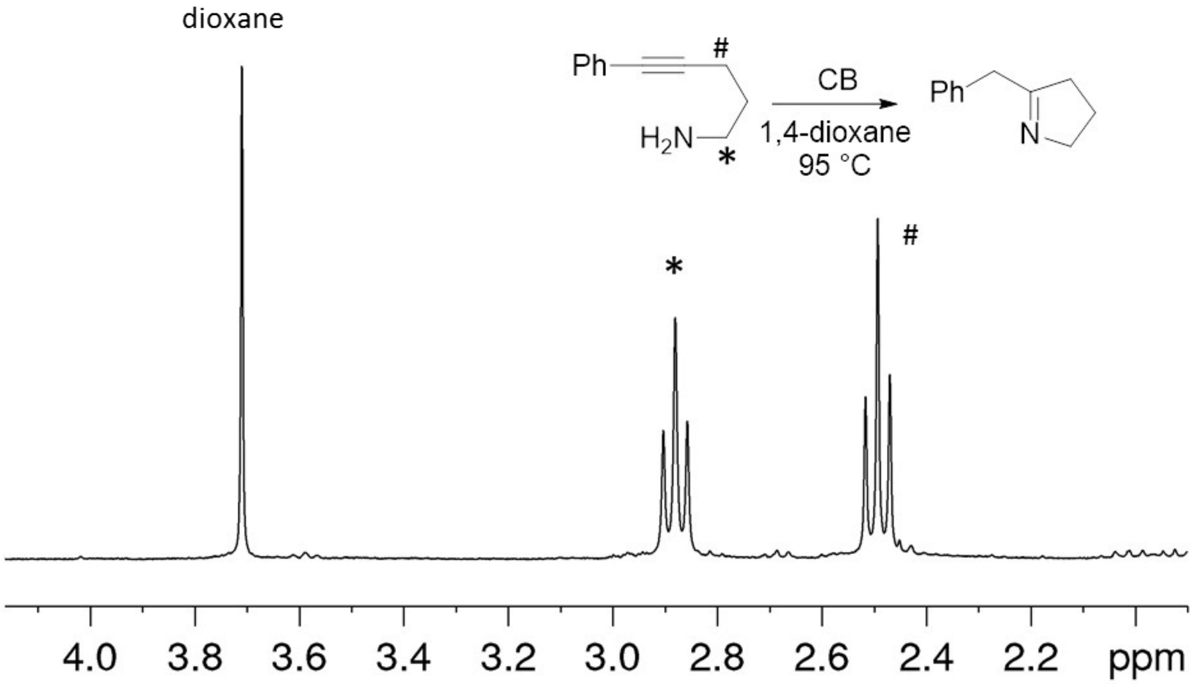


Figure S12. ^{1}H NMR spectrum of the residues recovered after completion of hydroamination of 5-phenyl-4-pentyn-1-amine using unmodified carbon black as a catalyst (table 1, entry 8).

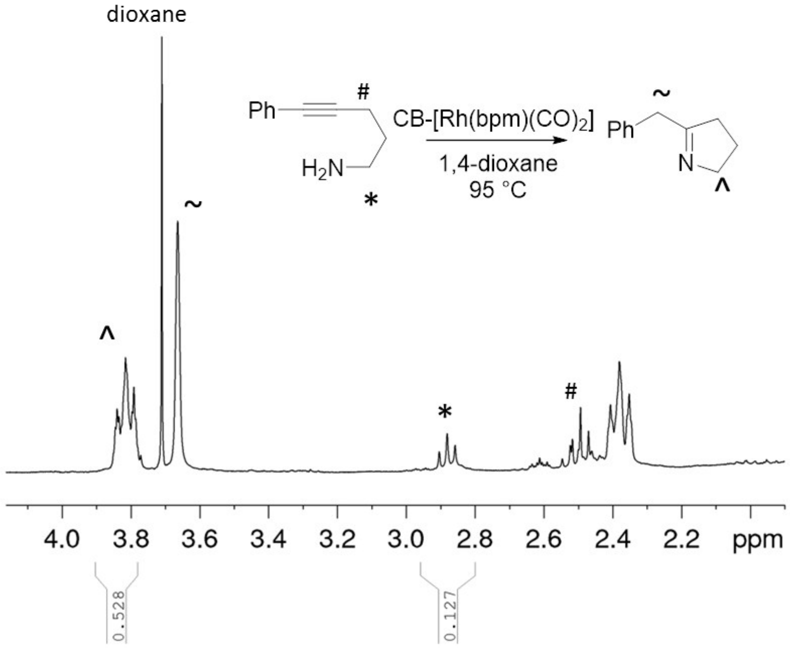


Figure S13. ^{1}H NMR spectrum of the residues recovered after completion of the second run of hydroamination of 5-phenyl-4-pentyn-1-amine using CB-[Rh(bpm)(CO)$_2$] as a catalyst (Table 2, entry 2).

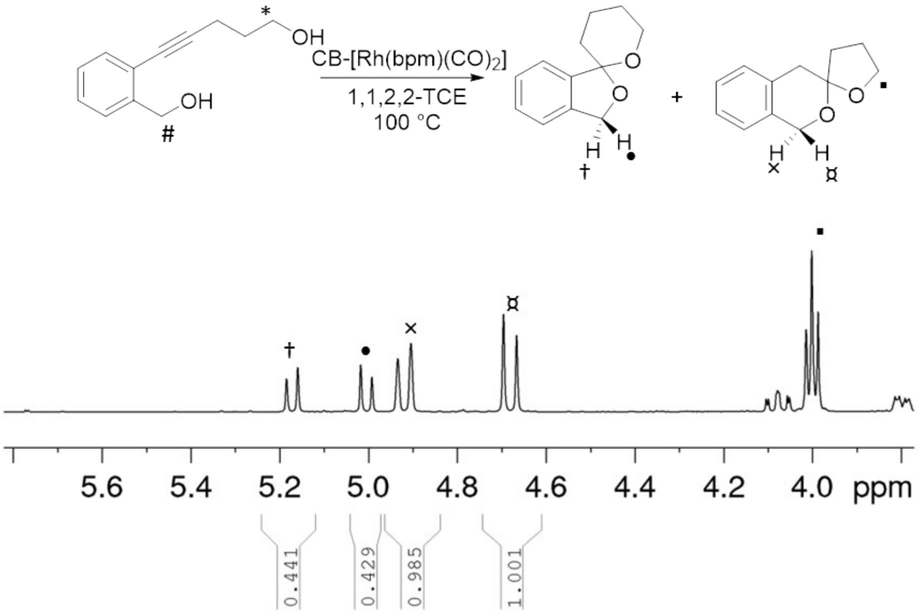


Figure S14. ^{1}H NMR spectrum of the compounds recovered after completion of the first run of hydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol using CB-[Rh(bpm)(CO)$_2$] as a catalyst (Table 3, entry 2).

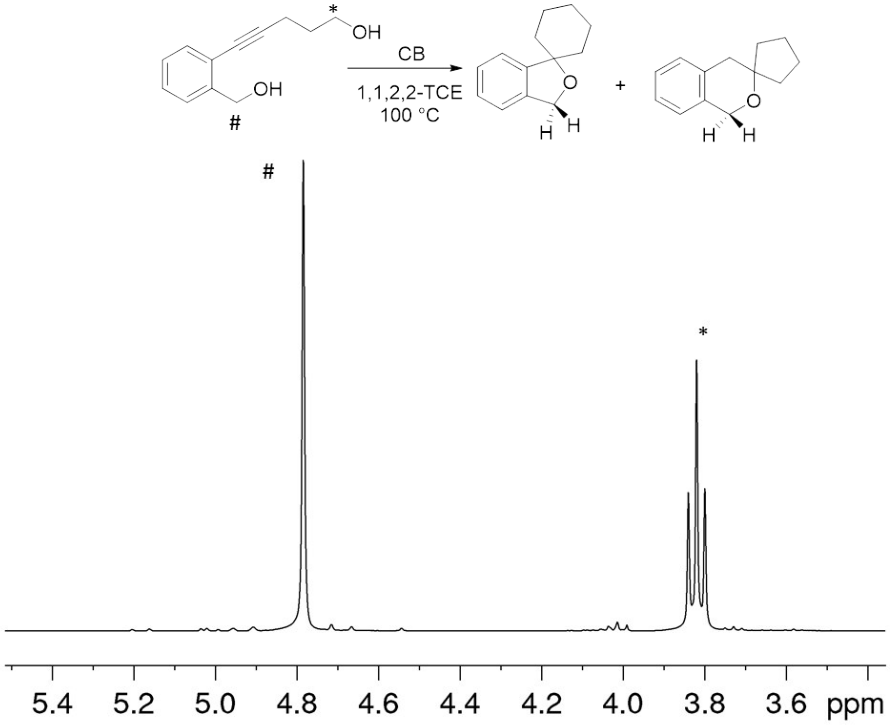


Figure S15. ^{1}H NMR spectrum of the residues recovered after completion of hydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol using unmodified carbon black as a catalyst (Table 3, entry 3).

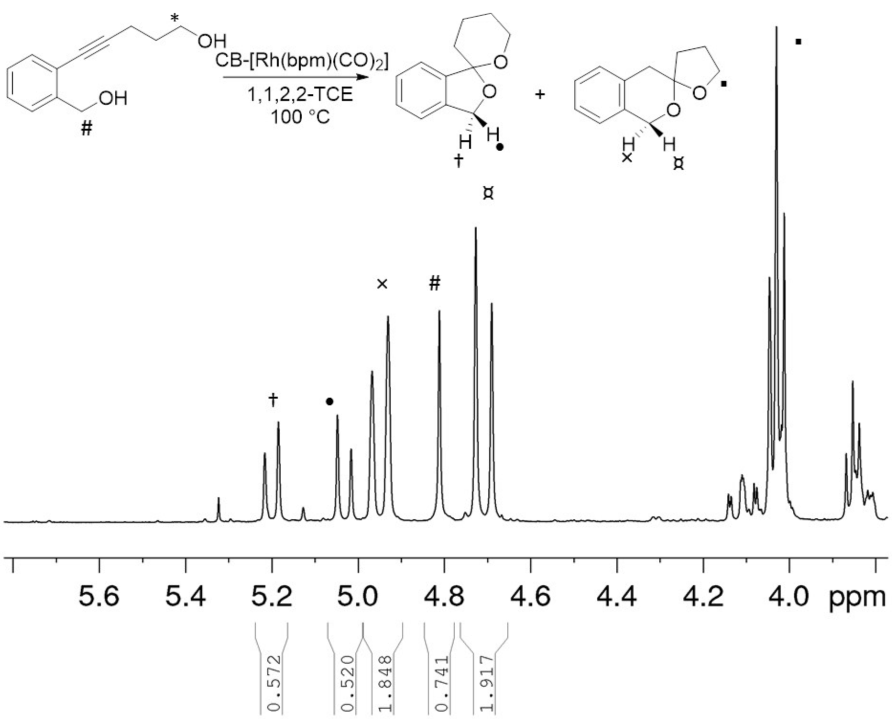
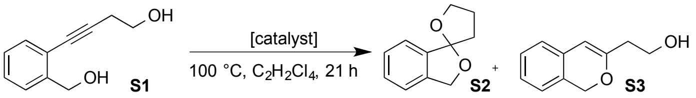


Figure S16. ^{1}H NMR spectrum of the residues recovered after completion of the second run of hydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol using CB-[Rh(bpm)(CO)$_2$] as a catalyst (Table 4, entry 2).



	Catalyst (Rh mol%)	*Conversion (%)*	*Ratio **S3**:**S2***	*TON*
1	CB-[Rh(bpm)(CO)$_2$] (4.6)	>98	3:17	21
2	CB + [Rh(CO)$_2$Cl]$_2$ (4.6) cycle 1	73	1:10	16
3	CB + [Rh(CO)$_2$Cl]$_2$ (4.6) cycle 2	30	3:17	7

Table S8. Dihydroalkoxylation of S1 using heterogeneous and homogeneous [Rh(bpm)(CO)$_2$]-based catalysts.

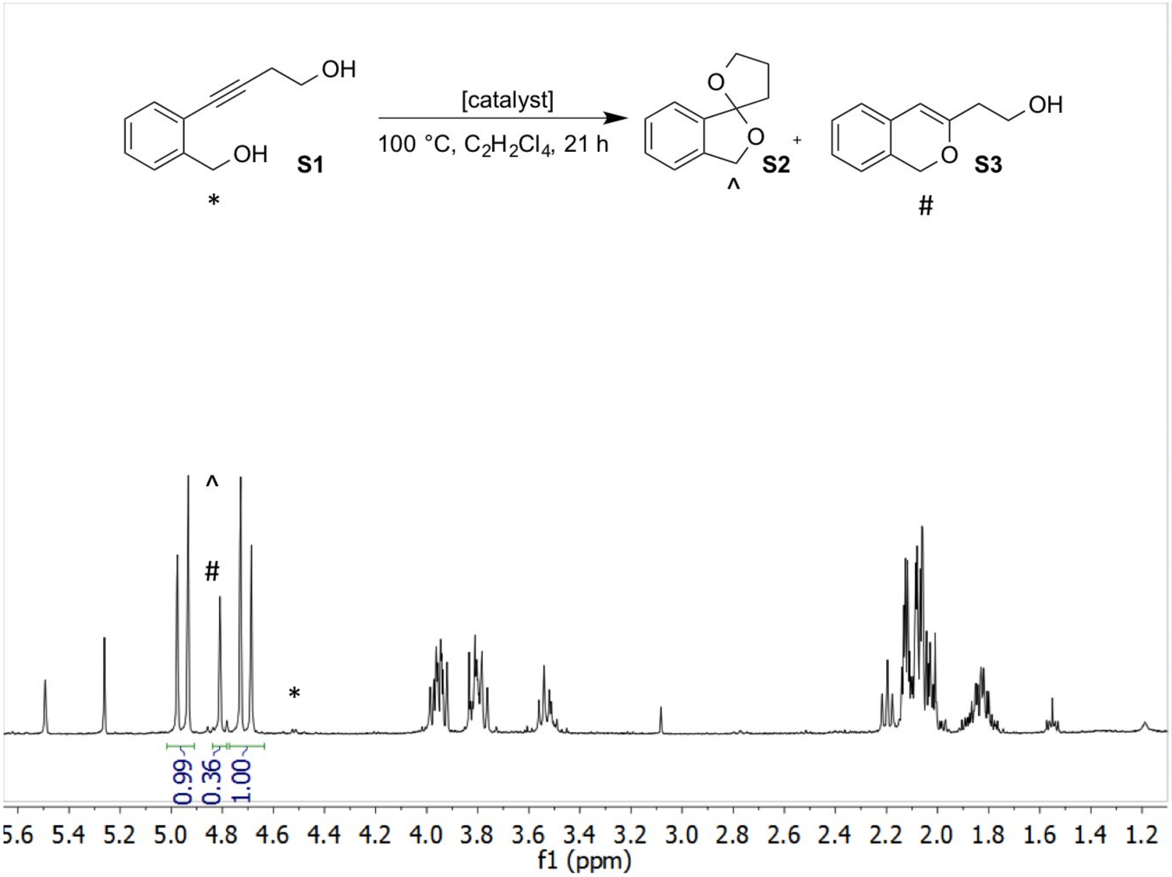


Figure S17 (table S8 entry 1)

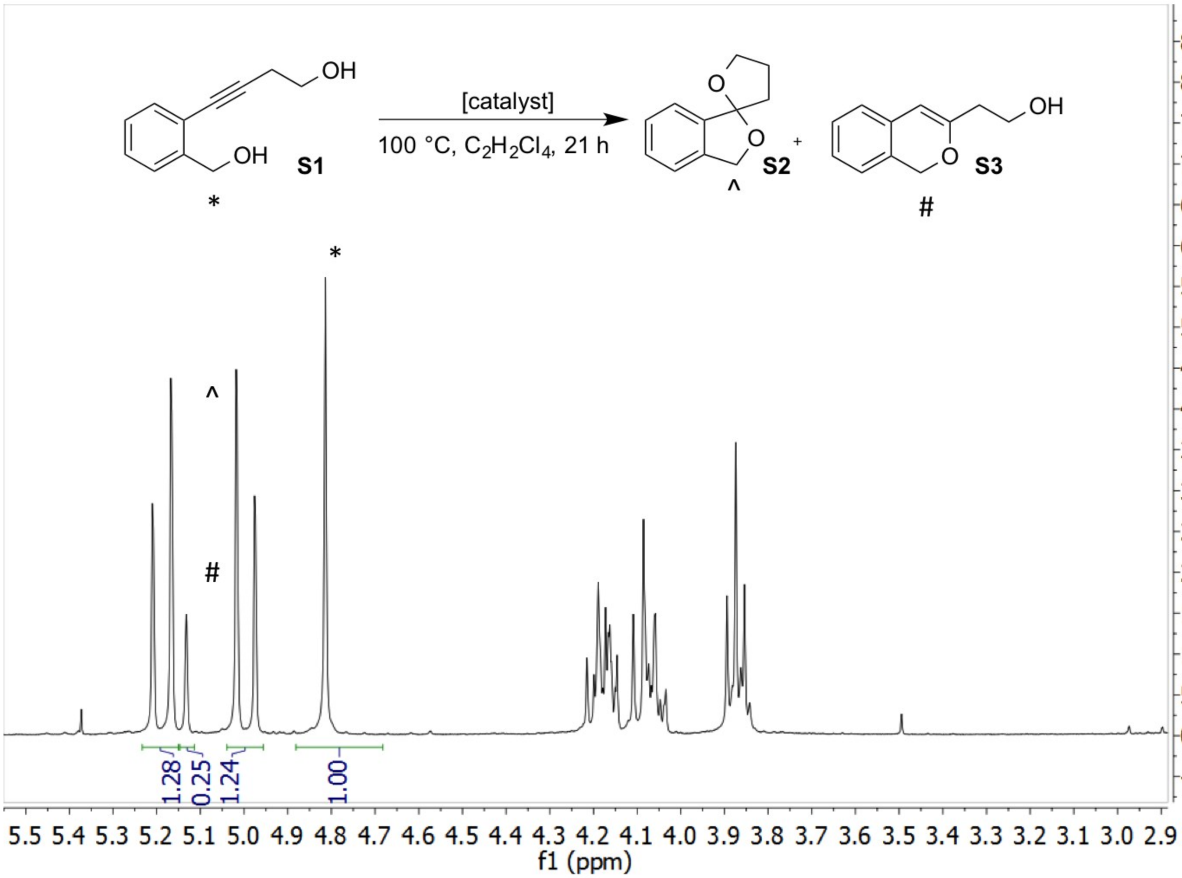


Figure S18 (table S8 entry 2)

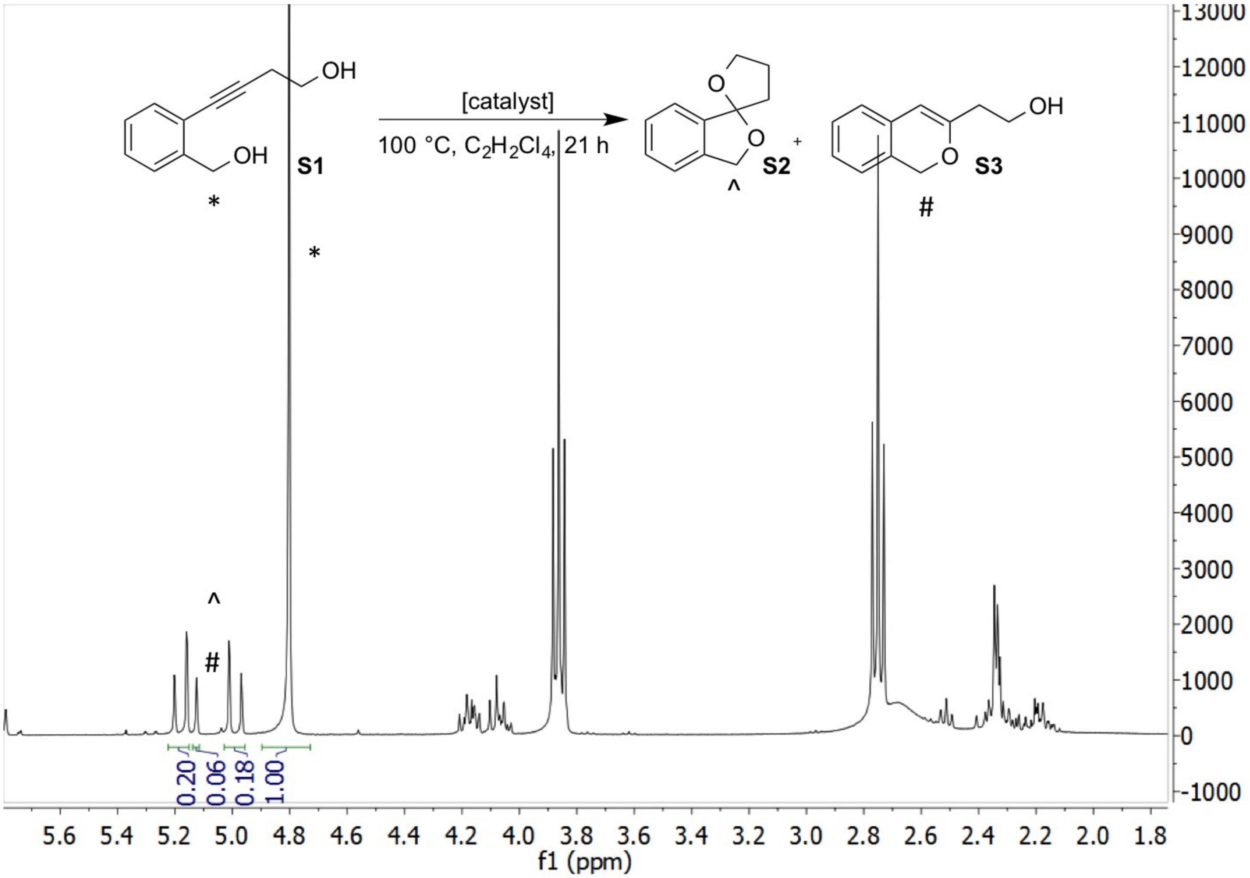


Figure S19 (table S8 entry 3)