Supporting Information

(Figures S1 – S5 and Table S1)

Non-innocent Ligand in Rhodium(III) Complex Catalyzed C–H Bond Amination with Tosyl Azide

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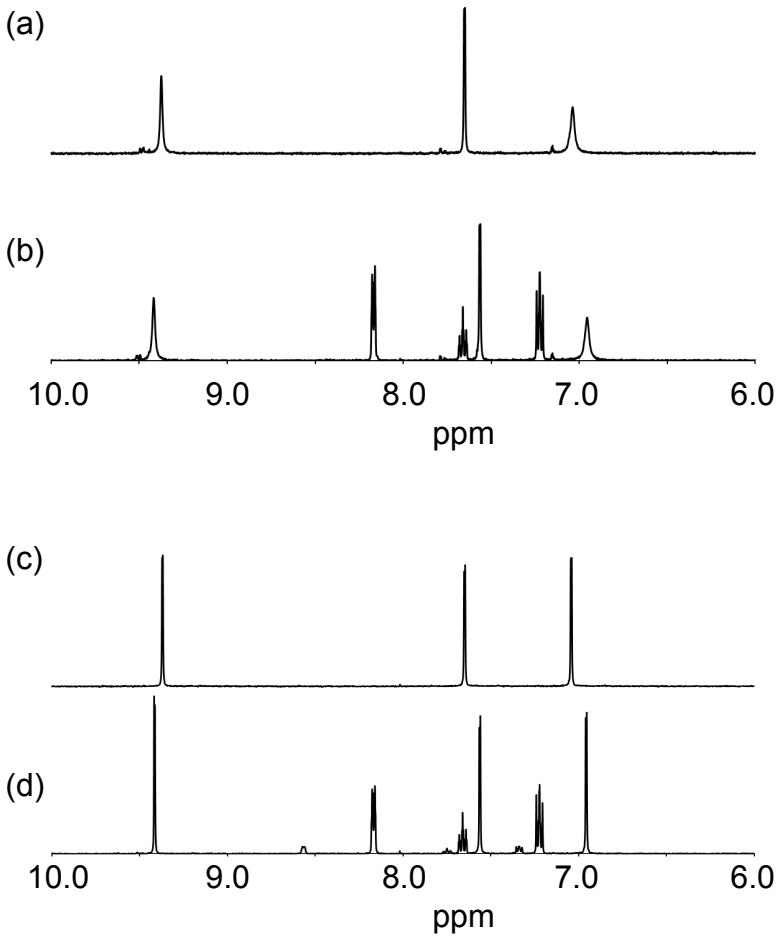


Figure S1. (a) ^{1}H NMR spectrum of $\mathbf{1}^{\mathbf{Cl/H_2O}}$ in acetone-d_6 and (b) that obtained upon addition of 1 equiv. of pyridine. (c) ^{1}H NMR spectrum of $\mathbf{1}^{\mathbf{Cl/THF}}$ in acetone-d_6 and (d) that obtained upon addition of 1 equiv. of pyridine

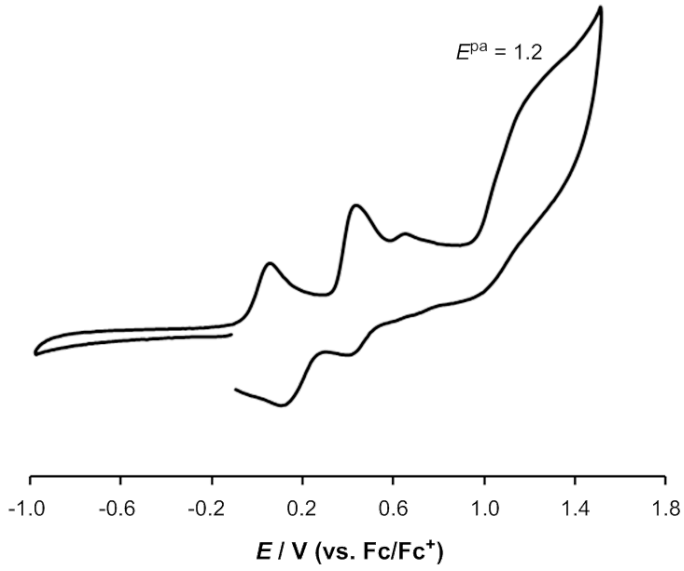


Figure S2. Cyclic voltammogram of **1**$^{Cl/AN}$ in CH_3CN solutions (1.0 mM) containing $^{n}Bu_4NPF_6$ (0.10 M) (working electrode: GC, counter electrode: Pt. Scan rate: 100 mV/s).

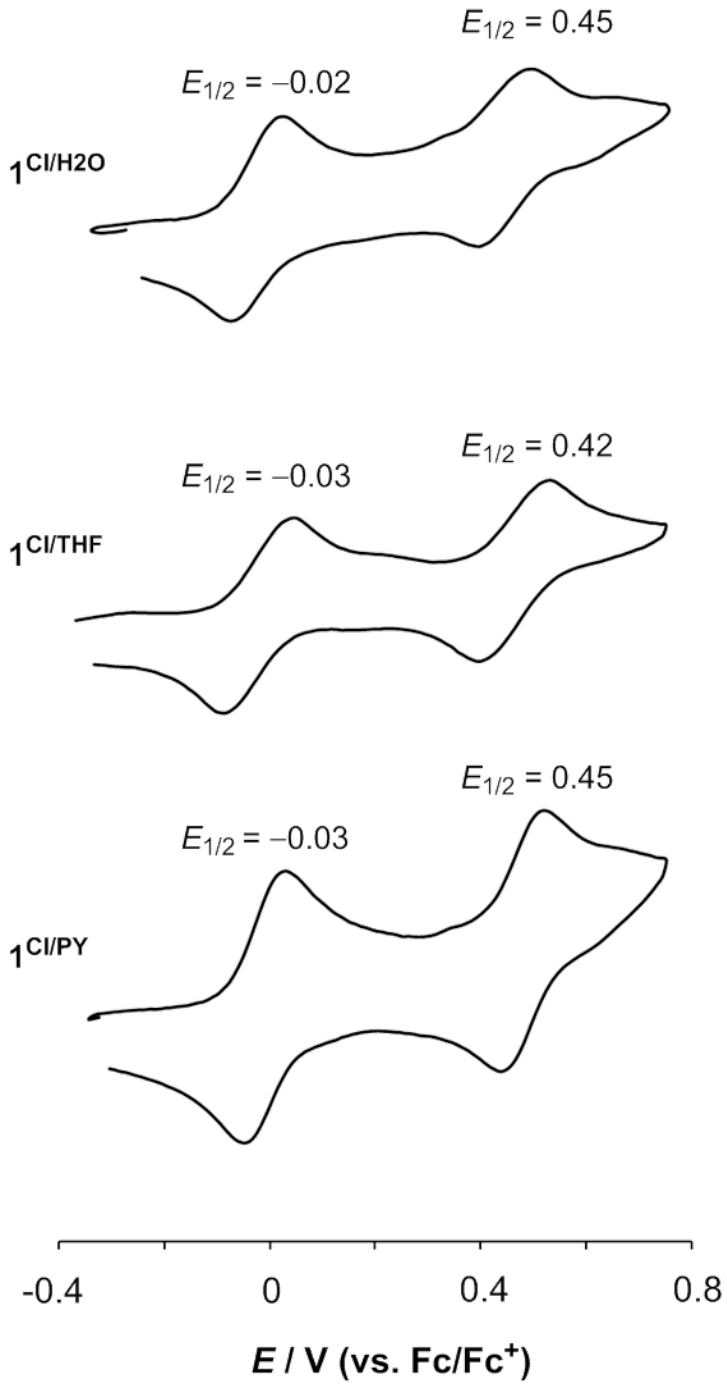
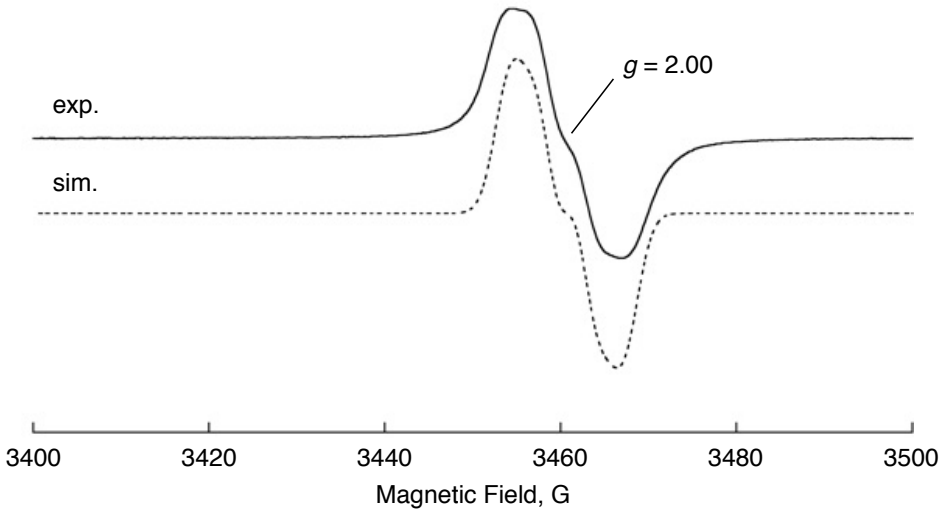


Figure S3. Cyclic voltammograms of $\mathbf{1}^{\mathbf{Cl/H_2O}}$, $\mathbf{1}^{\mathbf{Cl/THF}}$, and $\mathbf{1}^{\mathbf{Cl/PY}}$ in acetone solutions (1.0 mM) containing $^{n}Bu_4NPF_6$ (0.10 M) (working electrode: GC, counter electrode: Pt. Scan rate: 100 mV /s).



Conditions
X-band: 9.6795 GHz
Modulation: 10.0 G
Microwave Power: 1.0 mW
Temp.: 333 K

Simulation Parameters
N: 3.6 G
H_1: 2.8 G
H_2: 1.5 G
Linewidth: 3.5 G

Simulated on WINEPR SimFonia, distributed by Bruker

Figure S4. EPR spectrum of **2** (5.0 mM) in chlorobenzene at 60 °C.

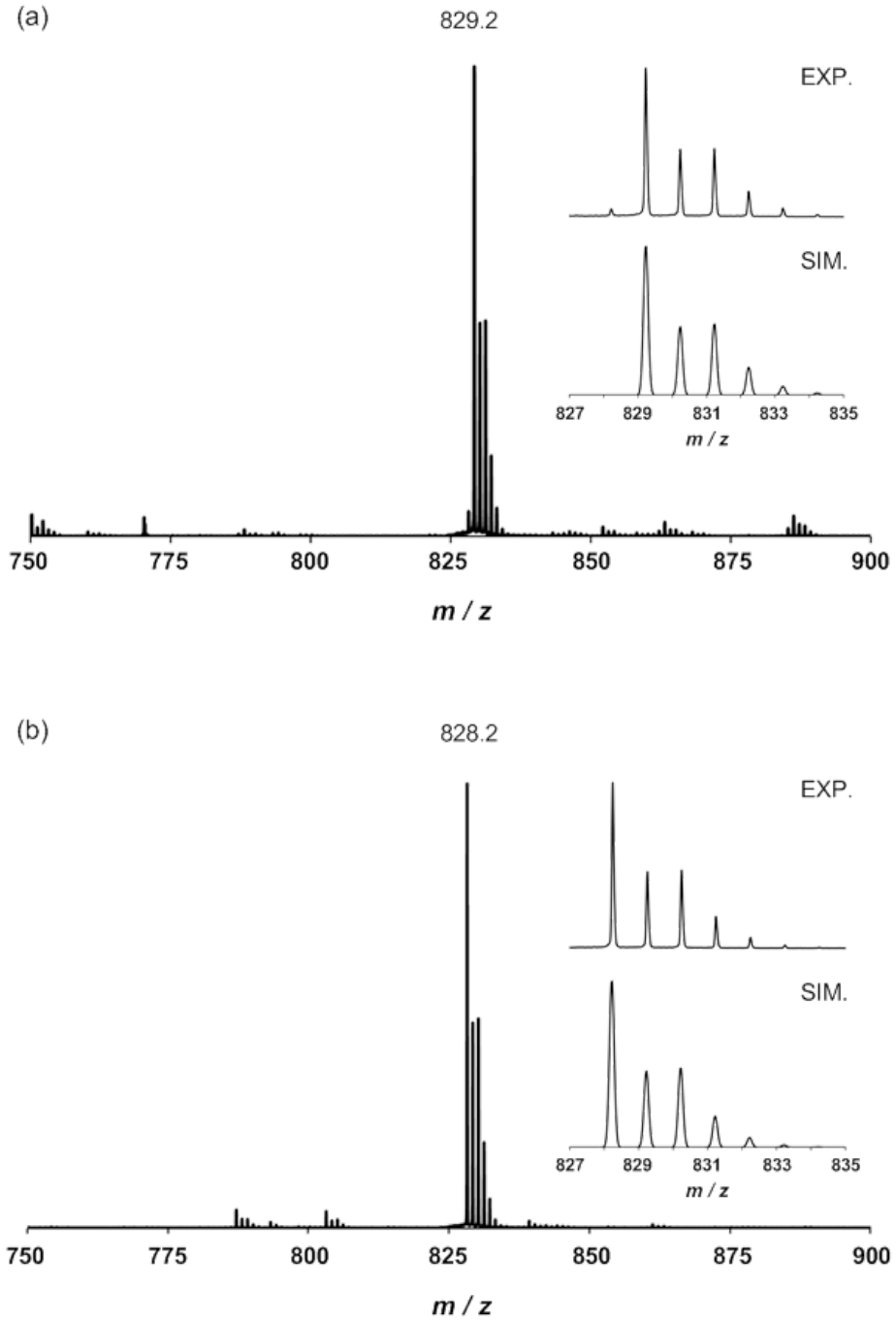


Figure S5. (a) ESI-MS spectrum of reaction mixture of $\mathbf{1}^{Cl/AN}$ and TsN_3 in D_2O/acetone. (b) ESI-MS spectrum of reaction mixture of $\mathbf{1}^{Cl/AN}$ and TsN_3 in CD_2Cl_2.

Table S1. Cartesian Coordinate of 2 Calcurated by DFT in the UB3LYP/def2TZVP Level Theory.

		x	y	z
1	Rh1	0.0659	-1.7633	0.1551
2	Cl2	0.8679	-3.3845	1.6482
3	S3	-0.5757	0.2941	-2.4985
4	O4	-1.8423	-1.9849	0.8607
5	O5	0.4672	-0.3055	1.5102
6	O6	2.5488	-4.7562	-3.6441
7	O7	4.1503	-3.4510	-2.9964
8	O8	-1.6811	0.2258	-3.4278
9	O9	0.6723	-0.3217	-2.8505
10	N10	-0.1802	-3.1997	-1.2326
11	H11	-1.0768	-3.6594	-1.3156
12	N12	1.9654	-1.4299	-0.3767
13	N13	2.9732	-3.8304	-2.9376
14	N14	-1.0213	-0.3422	-1.0273
15	C15	0.7520	-3.6588	-2.0060
16	H16	0.5241	-4.4657	-2.6929
17	C17	2.0809	-3.1859	-2.0291
18	C18	2.6170	-2.1366	-1.2509
19	H19	3.6644	-1.9310	-1.4242
20	C20	-2.2697	-0.1253	-0.5133
21	C21	-3.1923	0.8614	-0.9229
22	H22	-2.9170	1.5261	-1.7207
23	C23	-4.4241	0.9775	-0.3221
24	C24	-4.7686	0.0736	0.7214
25	H25	-5.7367	0.1903	1.1838
26	C26	-3.9429	-0.9265	1.1702
27	C27	-2.6546	-1.0466	0.5403
28	C28	-5.4419	2.0499	-0.7336
29	C29	-4.9297	2.9376	-1.8770
30	H30	-4.7125	2.3553	-2.7740
31	H31	-5.6922	3.6760	-2.1354
32	H32	-4.0251	3.4791	-1.5957
33	C33	-6.7446	1.3695	-1.2071
34	H34	-7.1919	0.7552	-0.4249
35	H35	-7.4797	2.1239	-1.5003
36	H36	-6.5539	0.7269	-2.0688
37	C37	-5.7525	2.9587	0.4751
38	H38	-6.1674	2.3961	1.3123
39	H39	-4.8479	3.4592	0.8254
40	H40	-6.4801	3.7253	0.1948
41	C41	-4.3425	-1.8854	2.3020
42	C42	-5.7410	-1.5650	2.8544
43	H43	-5.9762	-2.2671	3.6568
44	H44	-5.7954	-0.5575	3.2730
45	H45	-6.5180	-1.6643	2.0927
46	C46	-3.3393	-1.7724	3.4713
47	H47	-3.6391	-2.4450	4.2797
48	H48	-2.3309	-2.0362	3.1628
49	H49	-3.3238	-0.7547	3.8684
50	C50	-4.3694	-3.3397	1.7808
51	H51	-4.6846	-4.0134	2.5822
52	H52	-5.0798	-3.4420	0.9563
53	H53	-3.3875	-3.6547	1.4370
54	C54	2.5496	-0.4019	0.4029
55	C55	3.8480	0.0796	0.2222
56	H56	4.4499	-0.3242	-0.5770
57	C57	4.3630	1.0677	1.0462
58	C58	3.5314	1.5523	2.0707
59	H59	3.9324	2.3090	2.7292
60	C60	2.2314	1.1175	2.2896
61	C61	1.7054	0.1241	1.4107
62	C62	5.7845	1.6299	0.8860
63	C63	5.7217	3.1501	0.6260
64	H64	6.7286	3.5653	0.5204
65	H65	5.1688	3.3612	-0.2919
66	H66	5.2266	3.6777	1.4425
67	C67	6.5406	0.9836	-0.2845
68	H68	7.5414	1.4158	-0.3600
69	H69	6.6550	-0.0932	-0.1479
70	H70	6.0344	1.1522	-1.2368
71	C71	6.5965	1.3735	2.1733
72	H72	7.6103	1.7738	2.0756
73	H73	6.1335	1.8438	3.0419
74	H74	6.6699	0.3032	2.3755
75	C75	1.3761	1.6607	3.4470
76	C76	0.1059	2.3462	2.8988
77	H77	-0.4886	1.6534	2.3085
78	H78	-0.5071	2.7164	3.7264
79	H79	0.3696	3.1993	2.2683
80	C80	0.9754	0.4985	4.3823
81	H81	0.4299	-0.2715	3.8419
82	H82	1.8633	0.0406	4.8248
83	H83	0.3457	0.8722	5.1957
84	C84	2.1294	2.6986	4.2951
85	H85	1.4787	3.0393	5.1041
86	H86	3.0296	2.2802	4.7506
87	H87	2.4167	3.5769	3.7120
88	C88	-0.2400	2.0319	-2.2218
89	C89	-0.9040	2.9840	-2.9842
90	H90	-1.6466	2.6666	-3.7031
91	C91	-0.5951	4.3308	-2.8245
92	H92	-1.1129	5.0688	-3.4266
93	C93	0.3685	4.7444	-1.9071
94	C94	1.0255	3.7676	-1.1528
95	H95	1.7819	4.0610	-0.4343
96	C96	0.7339	2.4217	-1.3059
97	H97	1.2624	1.6843	-0.7184
98	C98	0.6986	6.2024	-1.7241
99	H99	0.1466	6.8264	-2.4277
100	H100	0.4528	6.5379	-0.7131
101	H101	1.7652	6.3875	-1.8730

E(UB3LYP): –3118.50288735 hartree, <S^2>: 0.7575