Supporting Information

Unsymmetrical Dicarbenes Based on *N*-Heterocyclic/Mesoionic Carbene Frameworks: A Stepwise Metallation Strategy for the Generation of a Dicarbene-Bridged Mixed-Metal Pd/Rh Complex

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Selected NMR Spectra

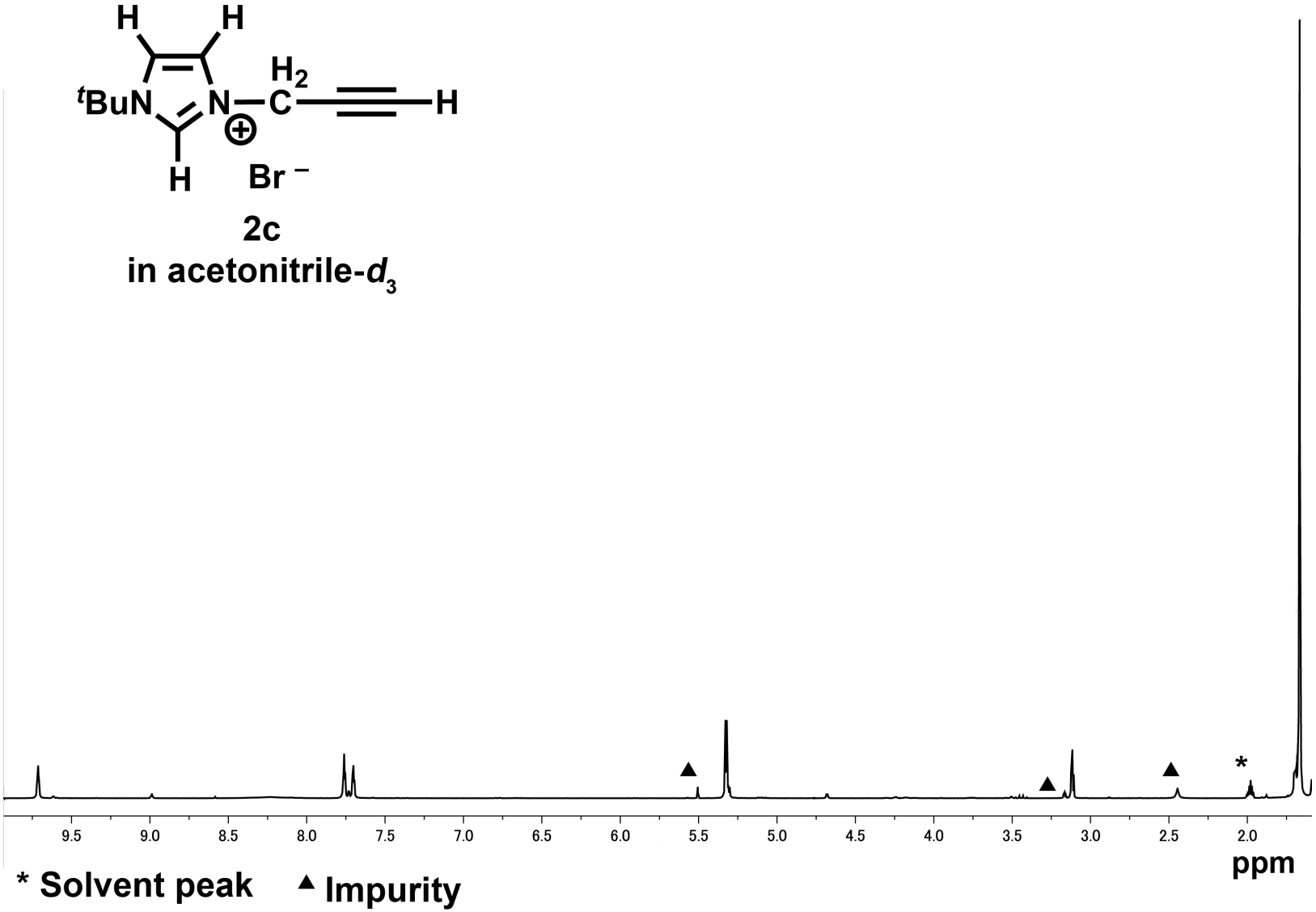

Figure S1 ^{1}H NMR spectrum (299.97 MHz, acetonitrile-d_3, 27.5 ºC) of compound **2c**.

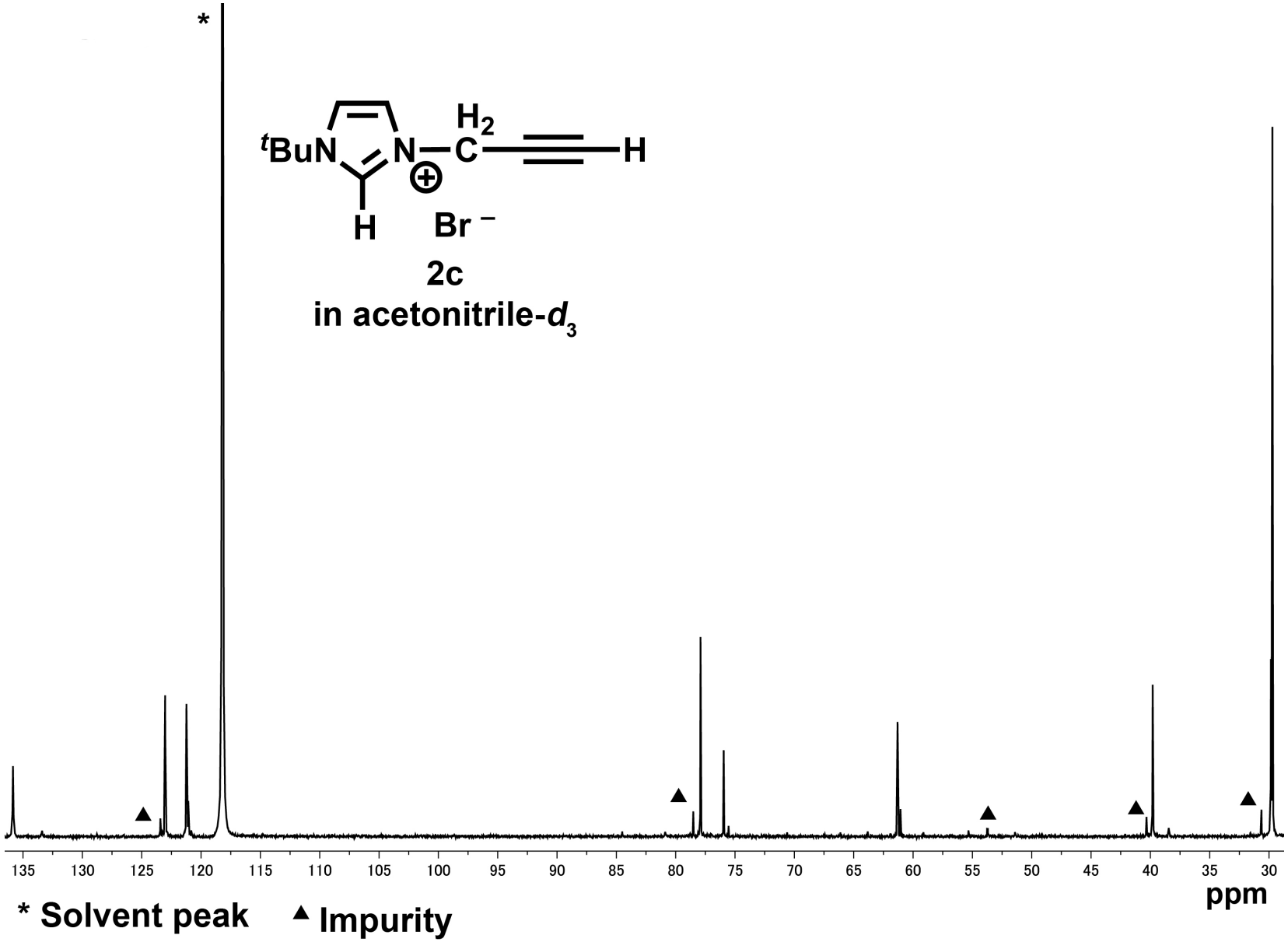

Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum (100.58 MHz, acetonitrile-d_3, –0.1 ºC) of compound **2c**.

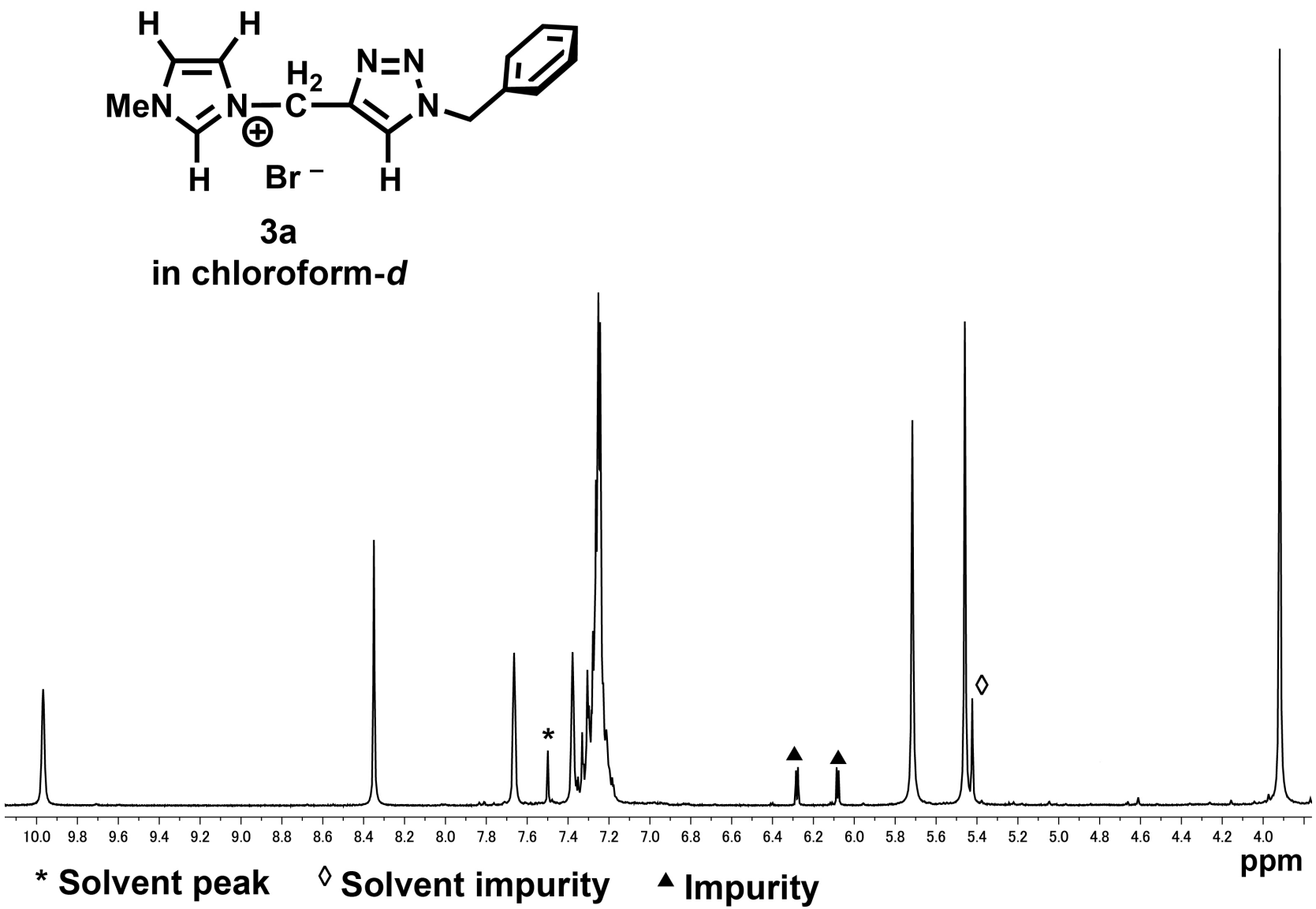

Figure S3 ^{1}H NMR spectrum (299.97 MHz, chloroform-*d*, 27.5 ºC) of compound **3a**.

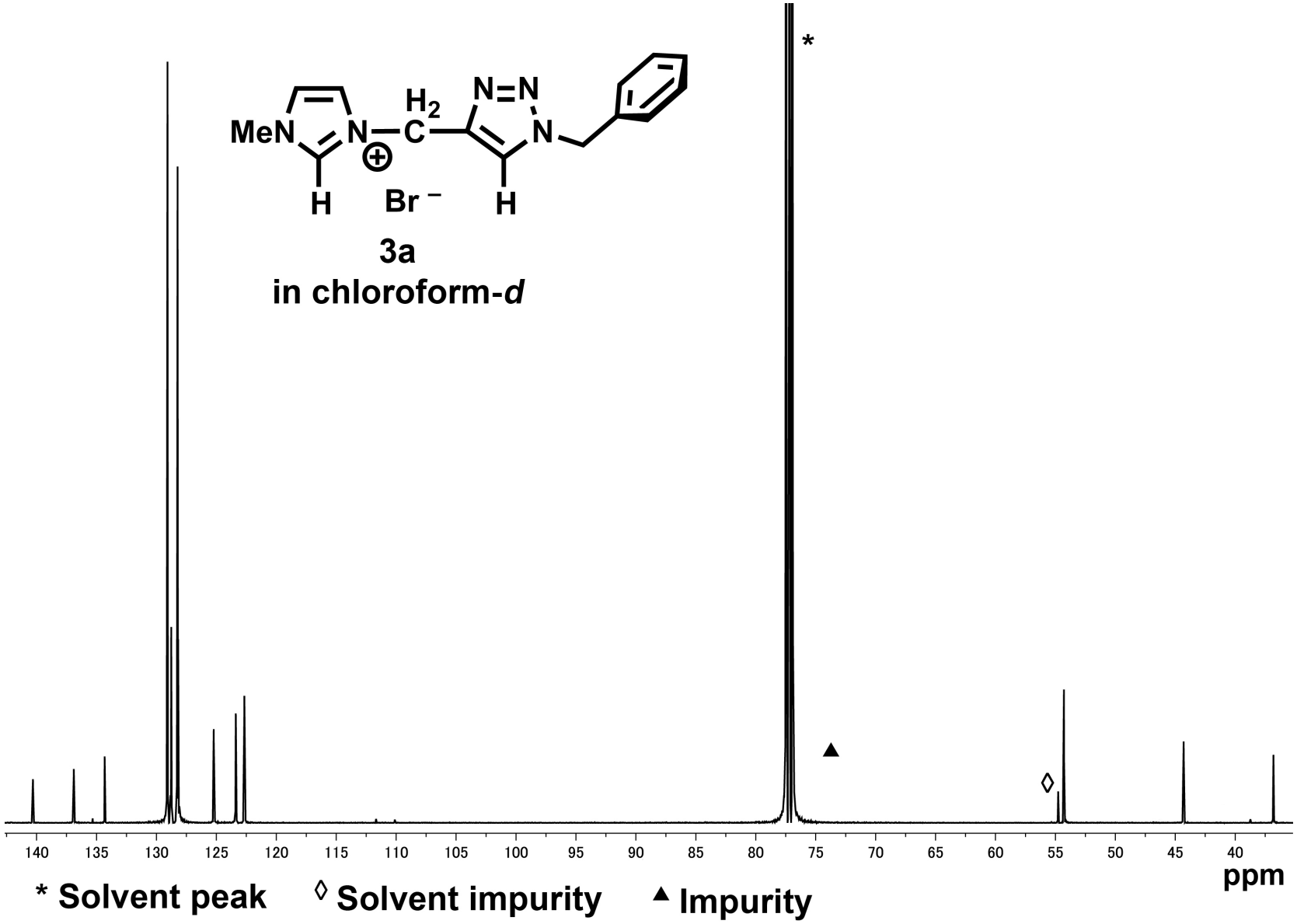

Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum (125.69 MHz, chloroform-*d*, 27.7 ºC) of compound **3a**.

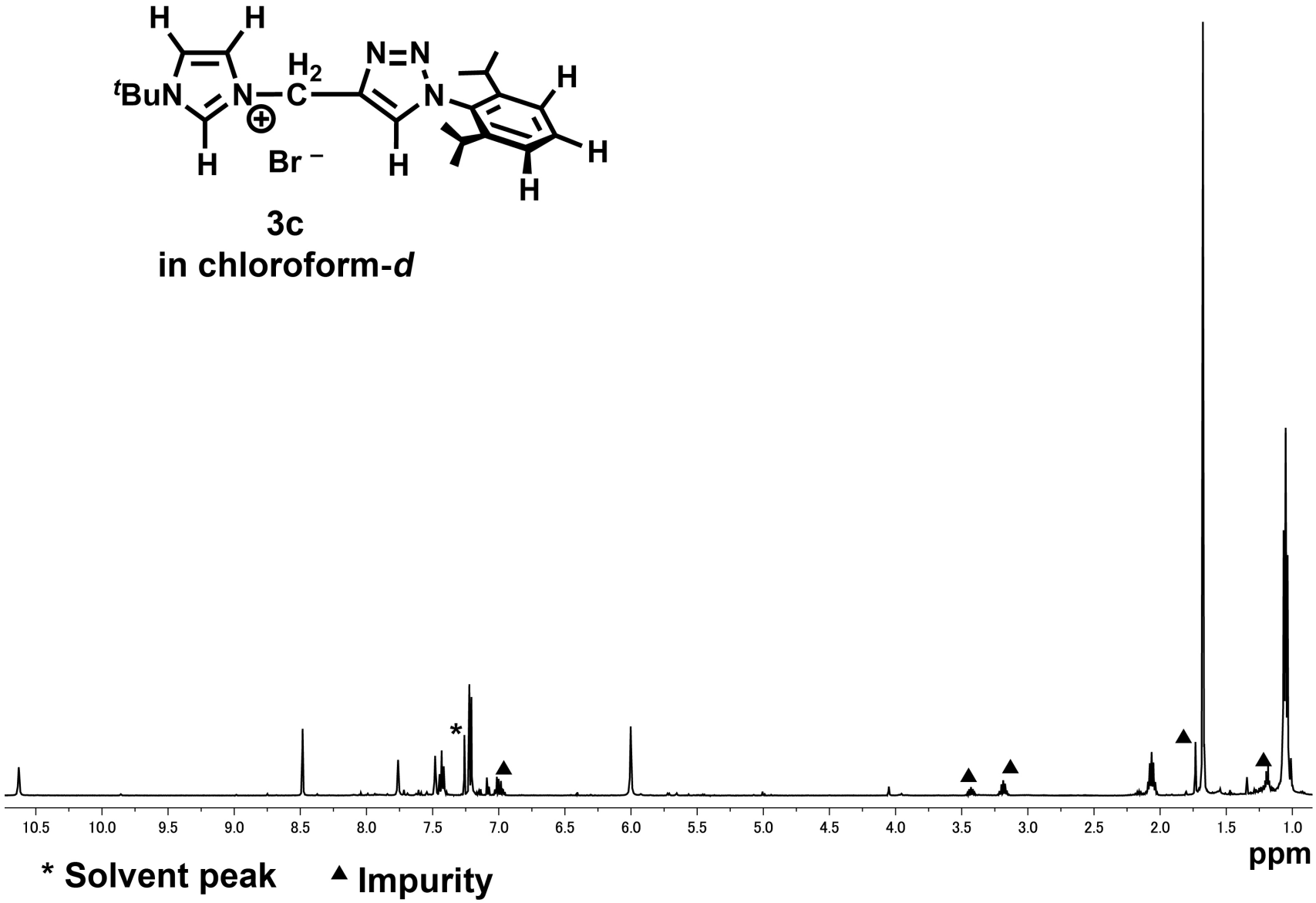

Figure S5 ^{1}H NMR spectrum (498.12 MHz, chloroform-*d*, 27.5 ºC) of compound **3c**.

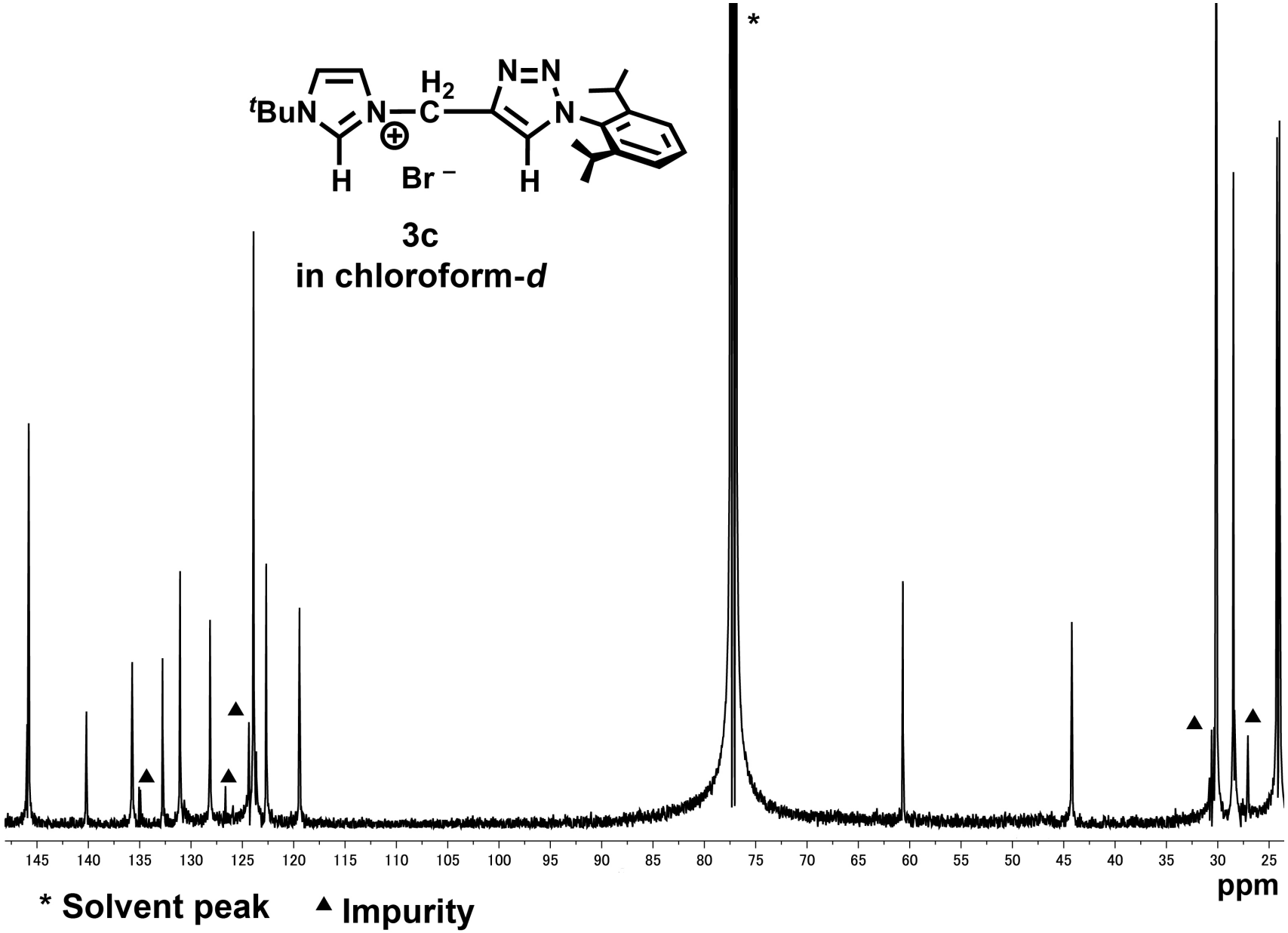

Figure S6 $^{13}C\{^{1}H\}$ NMR spectrum (125.69 MHz, chloroform-*d*, 27.5 ºC) of compound **3c**.

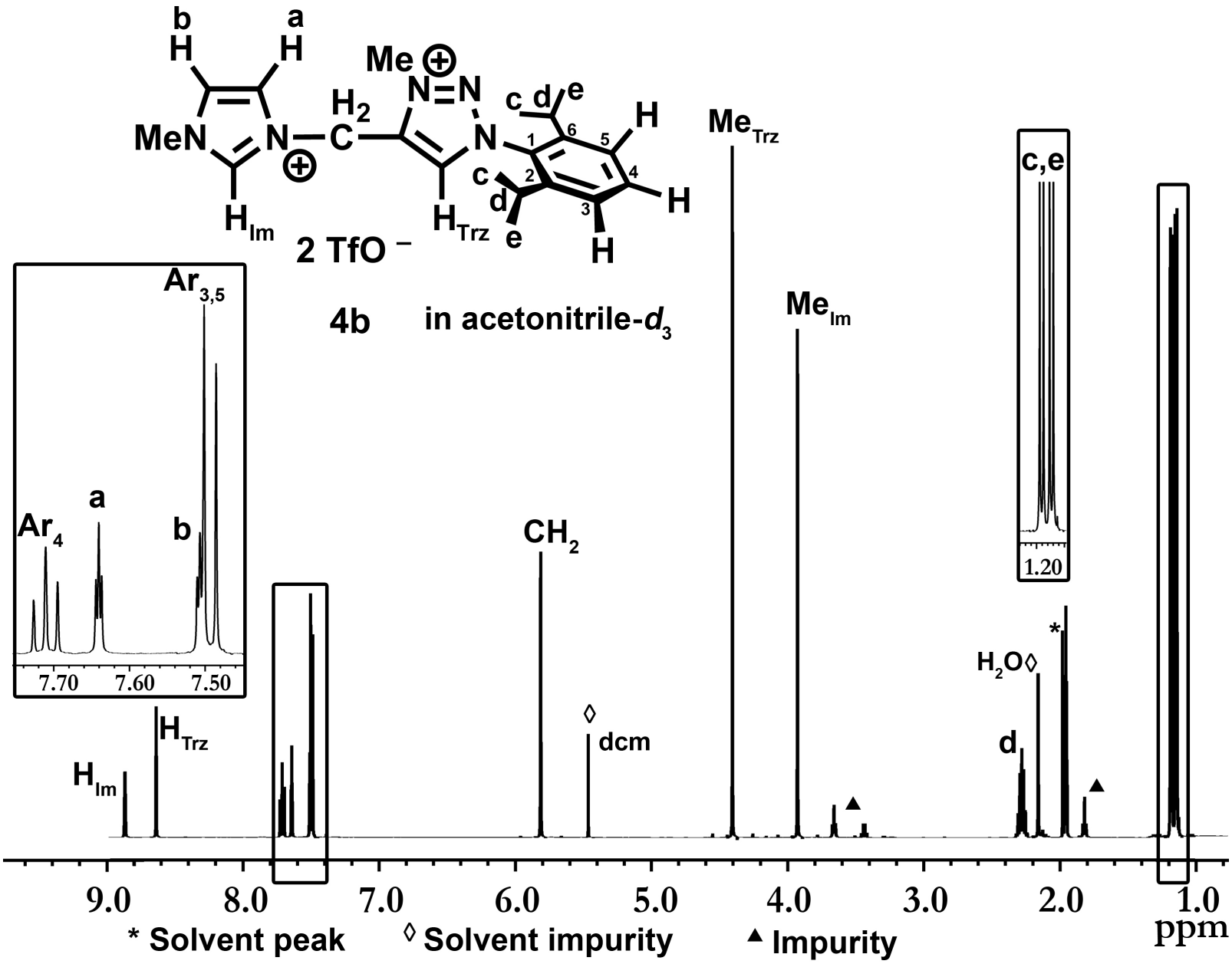

Figure S7. ^{1}H NMR spectrum (498.12 MHz, acetonitrile-d_3, 26.1 °C) of complex **4b** with expanded olefinic/aromatic and ^{i}Pr regions.

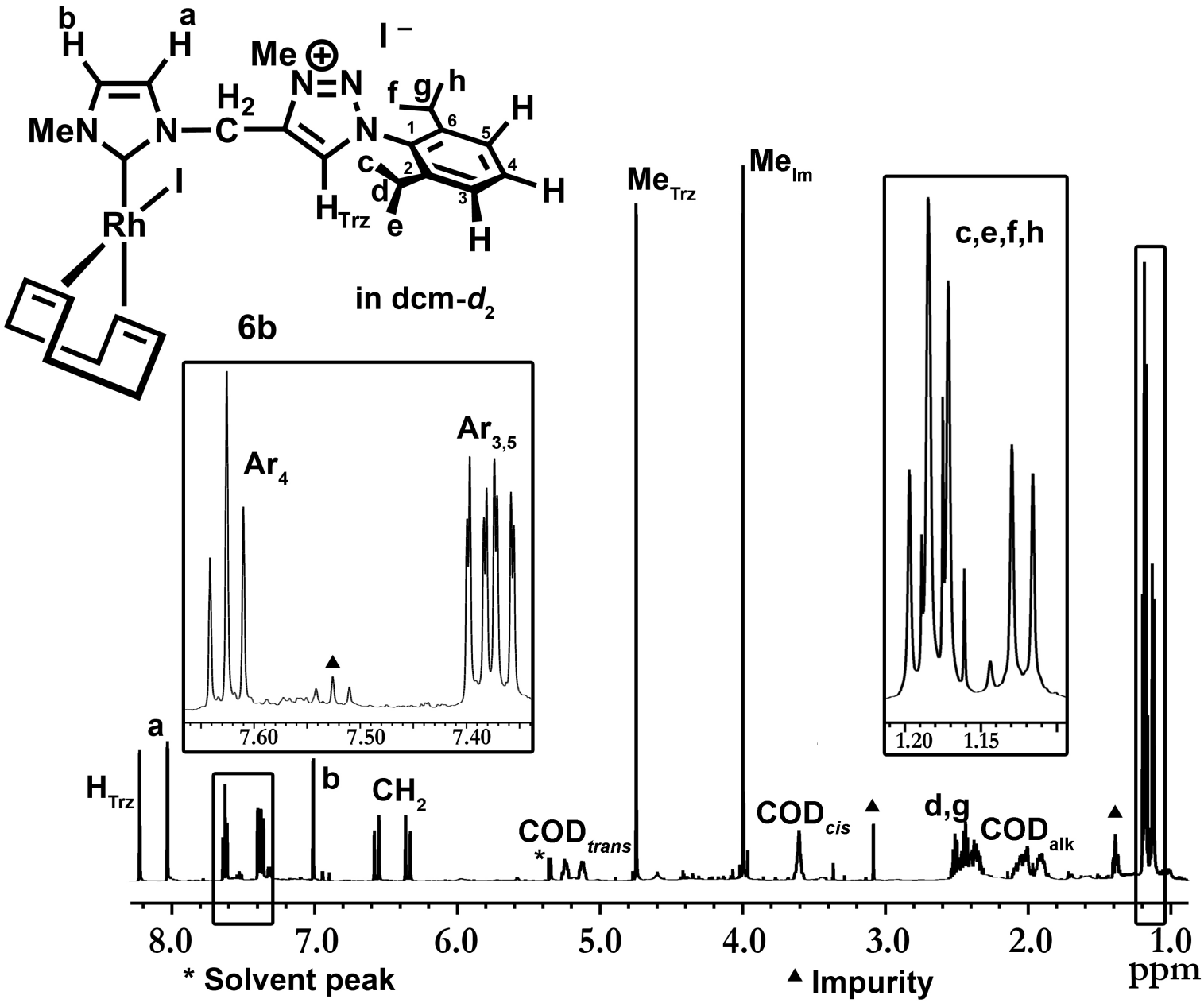

Figure S8. ^{1}H NMR spectrum (499.82 MHz, acetonitrile-d_3, 27.7 °C) of complex **6b** with expanded aromatic and ^{i}Pr regions.

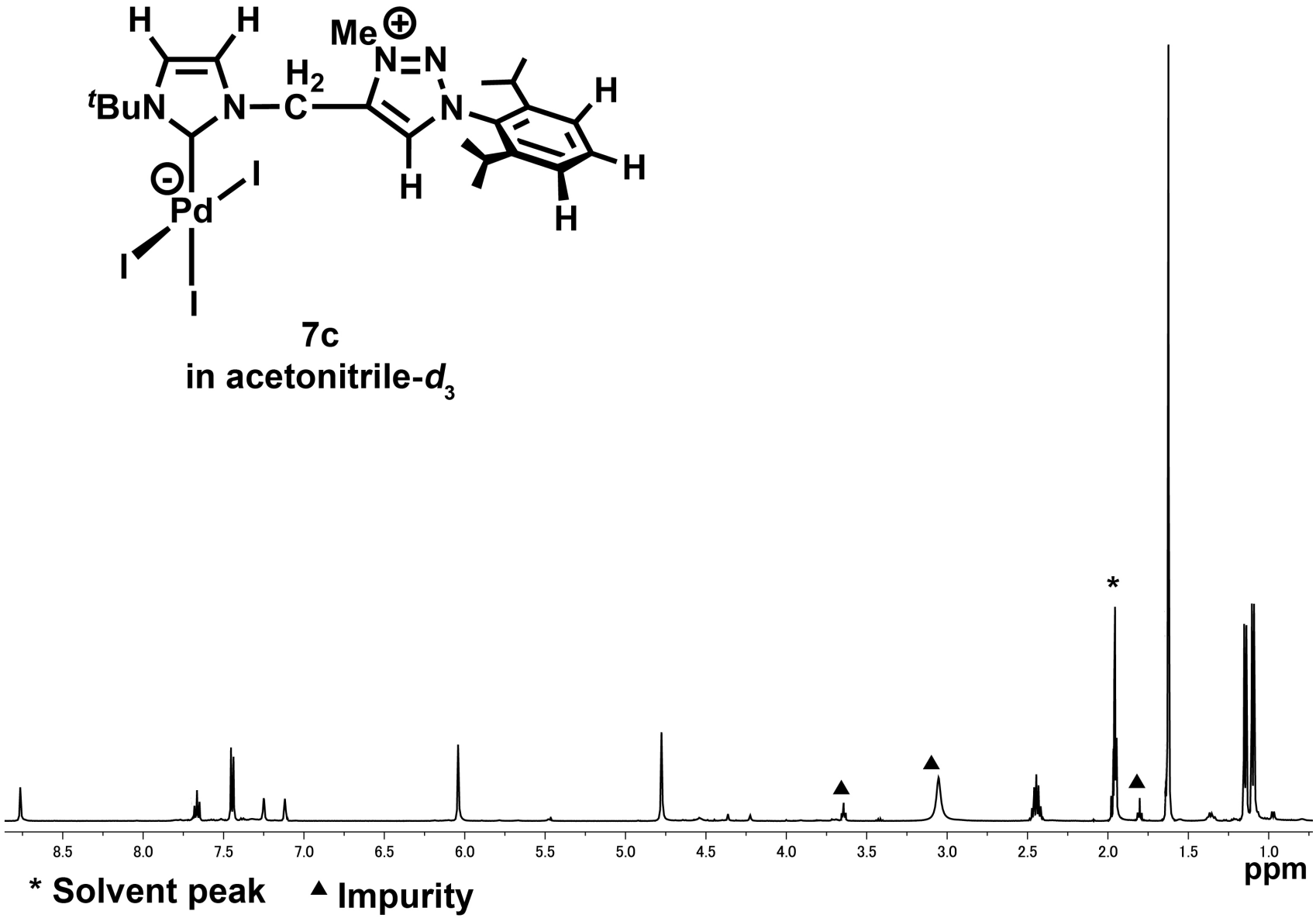

Figure S9 ^{1}H NMR spectrum (498.12 MHz, acetonitrile-d_3, 26.1 ºC) of compound **7c**.

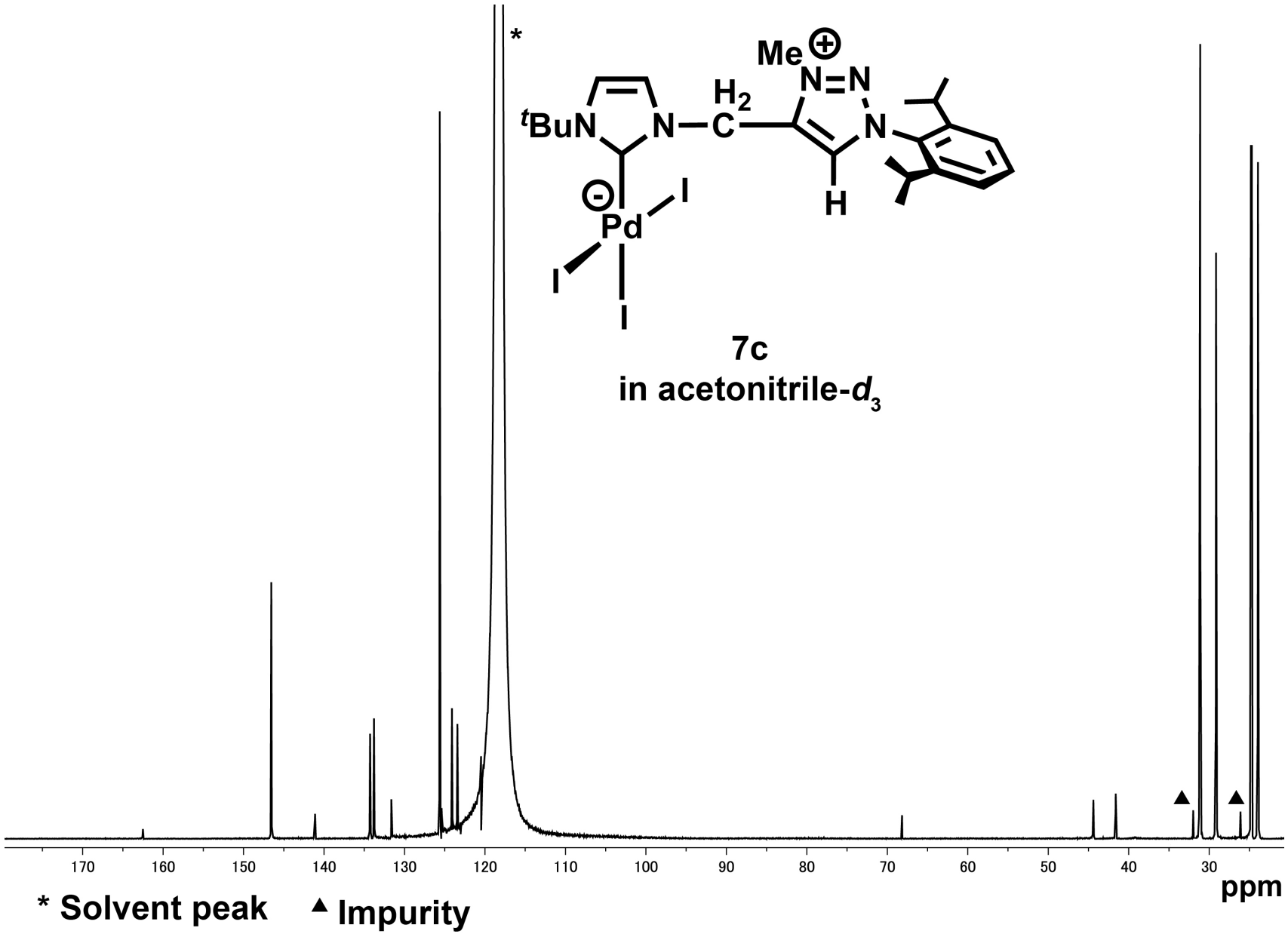

Figure S10 $^{13}C\{^{1}H\}$ NMR spectrum (125.69 MHz, acetonitrile-d_3, 27.7 ºC) of compound **7c**.

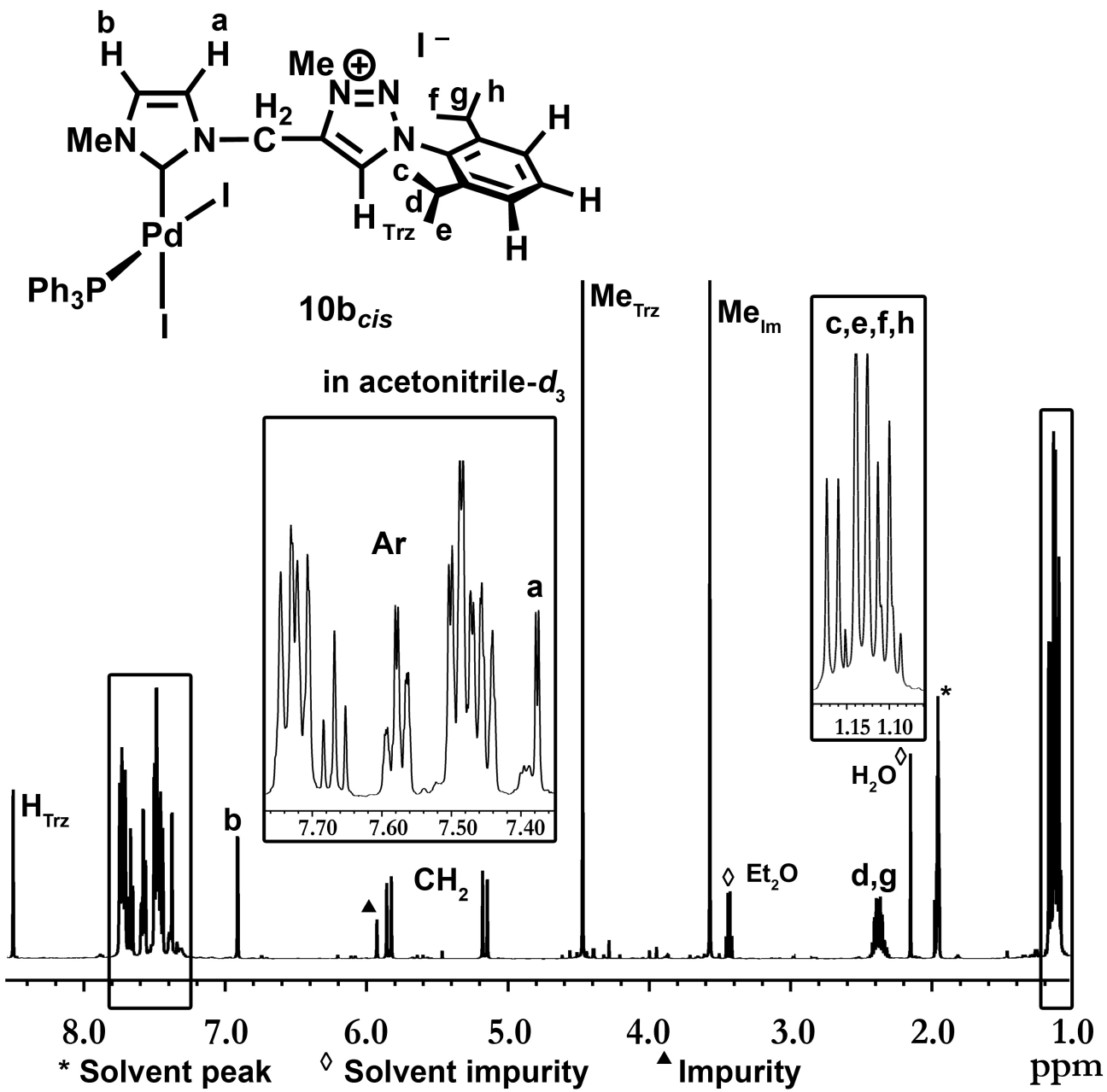

Figure S11 ^{1}H NMR spectrum (499.82 MHz, acetonitrile-d_3, 27.7 °C) of complex **10b**$_{cis}$ with expanded olefinic/aromatic and ^{i}Pr regions.

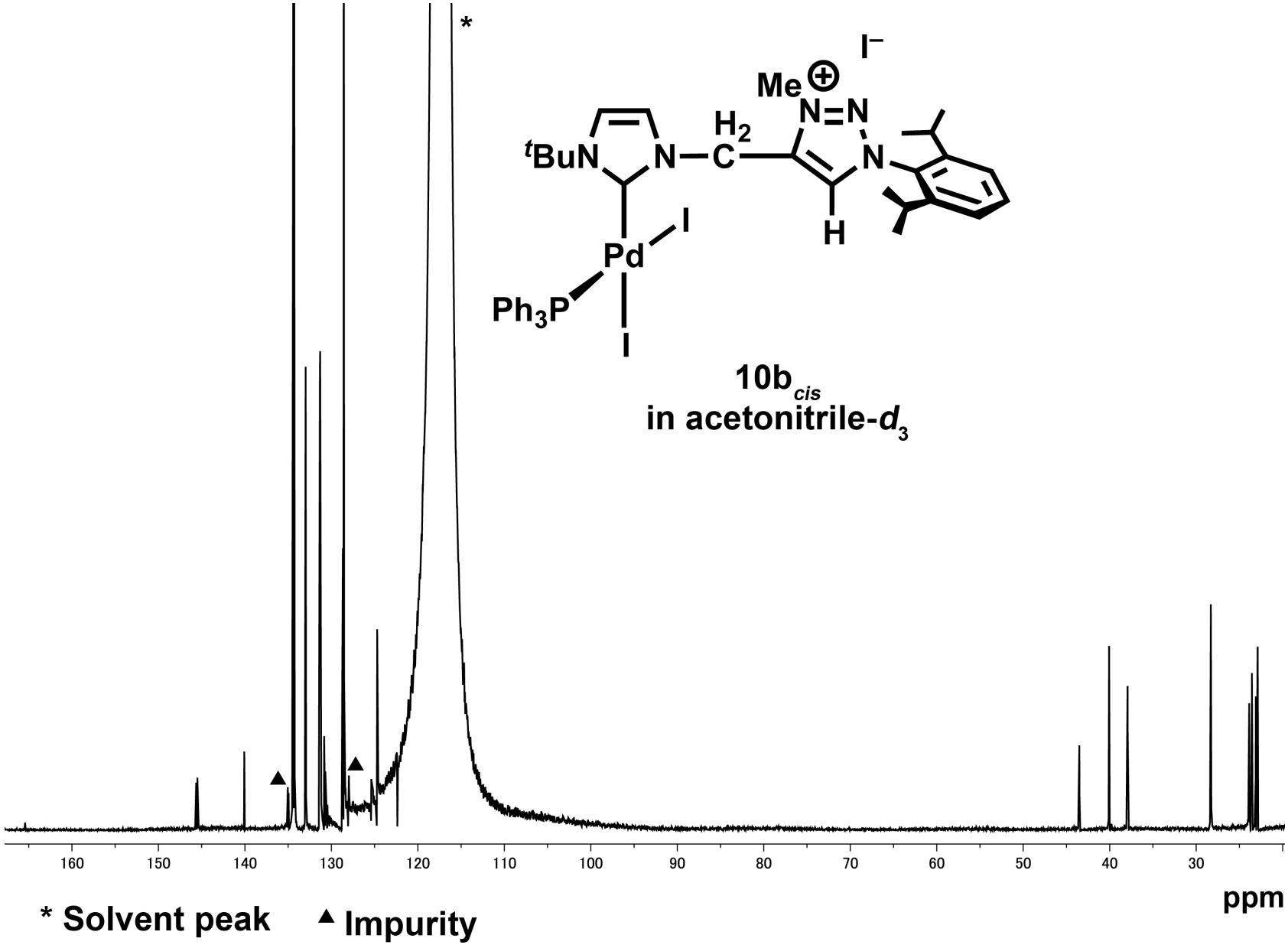

Figure S12 ^{1}H NMR spectrum (125.69 MHz, acetonitrile-d_3, 27.7 ºC) of compound **10b**$_{cis}$.

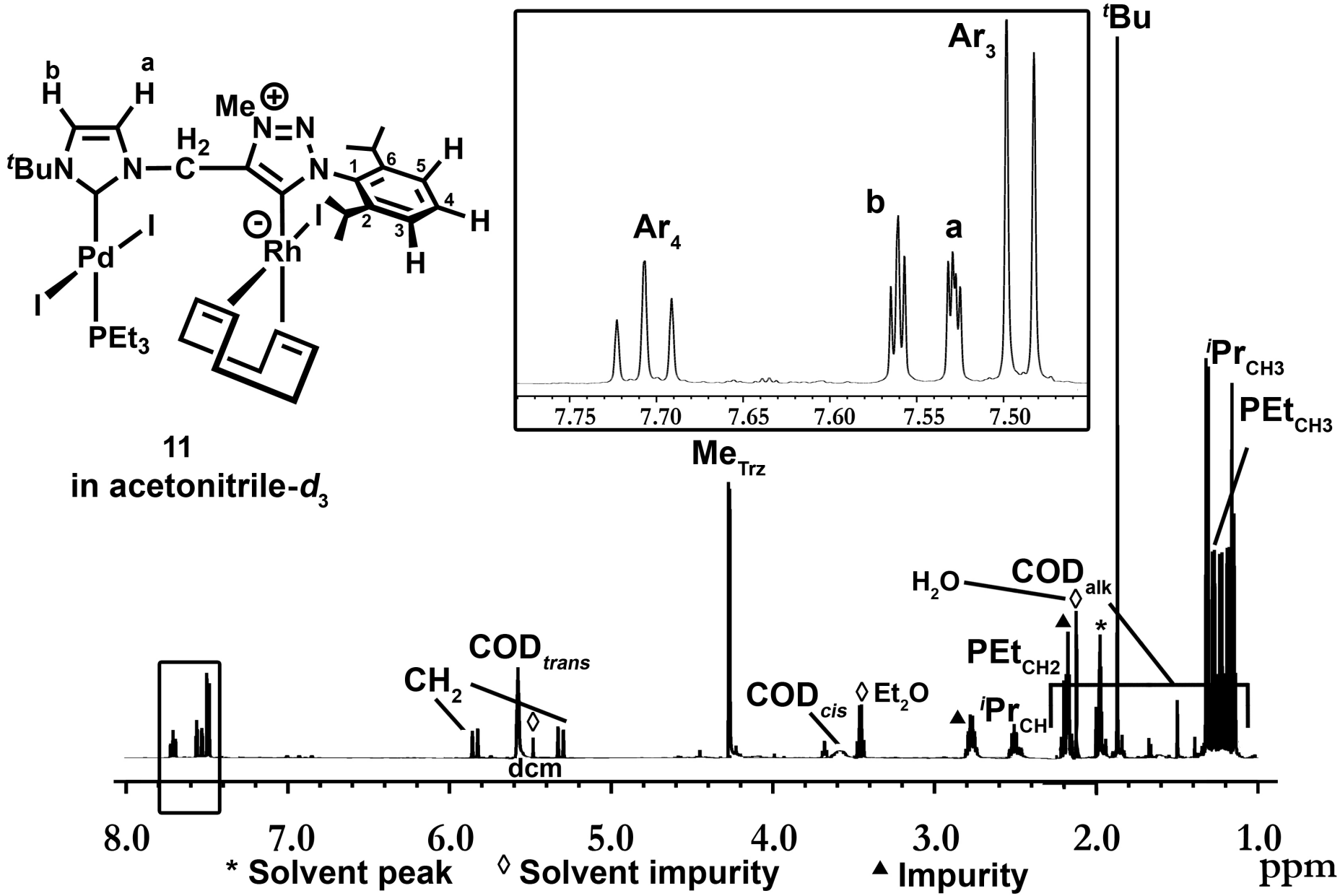

Figure S13 ^{1}H NMR spectrum (399.80 MHz, acetonitrile-d_3, 26.5 °C) of complex **11** with expanded olefinic/aromatic region.

Crystallographic Section

Crystallographic experimental details for compounds 4b, 5b, 7b, and $10b_{cis}$

Table S1. Crystallographic Data

Compound	**4b**	**5b**	**7b • 4CH$_3$CN**	**10b$_{cis}$ • 2CH$_3$CN**
Formula	$C_{22}H_{29}F_6N_5O_6S_2$	$C_{22}H_{30}I_2N_5O_2Rh$	$C_{28}H_{40}I_3N_9Pd$	$C_{42}H_{49}I_3N_7PPd$
Formula weight	637.62	753.22	989.79	1169.95
Crystal dimensions (mm)	0.47 × 0.44 × 0.04	0.27 × 0.25 × 0.05	0.60 × 0.11 × 0.09	0.48 × 0.28 × 0.06
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
Unit cell parameters[a]				
a (Å)	15.5497 (7)	10.1647 (5)	30.70 (2)	13.782 (3)
b (Å)	14.4945 (7)	10.4449 (5)	17.50 (1)	15.694 (3)
c (Å)	12.9298 (6)	13.1034 (6)	15.149 (9)	22.394 (5)
α (°)		76.4620 (5)		79.906 (3)
β (°)	102.3006 (6)	72.6898 (5)	119.530 (7)	88.010 (3)
γ (°)		78.6303 (5)		86.666 (3)
V (Å^3)	2847.3 (2)	1279.0 (1)	7079 (7)	4759 (2)
Z	4	2	8	4
ρ_{calcd} (g cm^{-3})	1.487	1.956	1.857	1.633
μ (mm^{-1})	0.272	3.109	3.173	2.405
Diffractometer	Bruker D8/APEX II CCD[b]			
Radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)			
Temperature (°C)	–100			
Scan type	ω scans (0.3°) (15 s exp)	ω scans (0.3°) (20 s exp)		
2θ max (°)	52.80	54.96	52.80	55.28
Total data collected	22483 (–19 ≤ h ≤ 19, –18 ≤ k ≤ 18, –16 ≤ l ≤ 16)	11340 (–13 ≤ h ≤ 13, –13 ≤ k ≤ 13, –17 ≤ l ≤ 16)	26866 (–38 ≤ h ≤ 38, –21 ≤ k ≤ 21, –18 ≤ l ≤ 18)	42692 (–17 ≤ h ≤ 17, –20 ≤ k ≤ 20, –29 ≤ l ≤ 29)
Independ reflns (R_{int})	5831 (0.0287)	5814 (0.0127)	7143 (0.0871)	21838 (0.0299)
Obsd reflns [$F_o^2 \geq 2\sigma(F_o^2)$]	4762	5305	4484	16825
Restraints/params	0 / 372	0 / 292	6[c] / 288	0 / 951
Goodness-of-fit (S)[d] [all data]	1.021	1.036	1.080	1.031
Final R indices[e]				
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0361	0.0172	0.0734	0.0351
wR_2 [all data]	0.0968	0.0436	0.2186	0.0924
Largest diff peak, hole (e Å^{-3})	0.322, –0.332	0.533, –0.401	2.100, –1.451	1.063, –0.870

[a] Obtained from least-squares refinement of 7376 reflections with 4.66° < 2θ < 43.22° for **4b**; 9930 reflections with 4.64° < 2θ < 54.96° for **5b**; 2599 reflections with 4.68° < 2θ < 37.90° for **7b**; 6916 reflections with 4.50° < 2θ < 41.80° for **10b$_{cis}$**.

[b] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

[c] The C–C distances within the disordered isopropyl group were restrained to be the same by use of the *SHELXL* **SAME** instruction.

[d] $S = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$; for **4b**, $a_0 = 0.0435$, $a_1 = 1.7352$; for **5b**, $a_0 = 0.0211$, $a_1 = 0.5336$; for **7b**, $a_0 = 0.1220$, $a_1 = 0$; for **10b$_{cis}$**, $a_0 = 0.0419$, $a_1 = 2.5075$.

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Least squares planes analysis

Table S2. Dihedral Angle Results for **7b**

Planes	Dihedral description	Angle (º)
1 – 2	Pd sq. plane – NHC plane	86.1(3)
2 – 3	NHC plane – MIC(H)$^+$ plane	78.8(4)
3 – 4	MIC(H)$^+$ plane – Ph_{Dipp} plane	82.1(4)

Table S3. Dihedral Angle Results for **10b**$_{cis}$

Planes	Dihedral description	Angle (º)
1 – 2	Pd sq. plane – NHC plane	86.25(9)
2 – 3	NHC plane – MIC(H)$^+$ plane	82.1(2)
3 – 4	MIC(H)$^+$ plane – Ph_{Dipp} plane	82.1(1)