Supporting Information Prepared for Organometallics

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pH-Dependent Aqueous Polymerization of Styrene Promoted by Water-Soluble Robust Ruthenium Hydride Complexes

A Table of Contents

Crystal Structure Determination of [(η^6-C_6Me_6)Ru^{II}(bpy)H]CF_3SO_3 {1(CF_3SO_3)}. An orange block crystal of $C_{23}H_{27}N_2O_3RuF_3S$ having approximate dimensions of 0.20 x 0.20 x 0.10 mm was mounted in a glass capillary. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: a = 13.371(6) Å, b = 13.509(6) Å, c = 13.777(7) Å, β = 107.313(6)°, V = 2375(1) Å^3. For Z = 4 and F.W. = 569.60, the calculated density is 1.59 g/cm^3. The systematic absences of $h0l$: $l \pm 2n$ and $0k0$: $k \pm 2n$ uniquely determine the space group to be: $P2_1/c$ (No. 14). The data were collected at a temperature of -50 ± 1°C to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A first sweep of data was done using ω scans from –70.0 to 110.0° in 0.50° step, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 20.0 sec/°. The detector swing angle was 19.7°. The crystal-to-detector distance was 45.19 mm. A second sweep of data was done using ω scans from –70.0 to 110.0° in 0.50° step, at χ = 45.0° and ϕ = 90.0°. The exposure rate was 20.0 sec/°. The detector swing angle was 19.7°. The crystal-to-detector distance was 45.19 mm. Of the 19190 reflections which were collected, 5430 were unique (R_{int} = 0.050); equivalent reflections were merged. Data were collected and processed using the CrystalClear program (Rigaku). Net intensities and sigmas were derived as follows:

$$F^2 = [\sum_{i=1}^{m} (P_i - mB_{ave})] \cdot Lp^{-1}$$

where P_i is the value in counts of the i^{th} pixel.
m is the number of pixels in the integration area.
B_{ave} is the background average.
Lp is the Lorentz and polarization factor.

$$B_{ave} = \frac{\sum_{j=1}^{n} B_j}{n}$$

where n is the number of pixels in the background area.
B_j is the value of the j^{th} pixel in counts.

$$\sigma^2(F^2_{hkl}) = [(\sum_{i=1}^{m} P_i) + m(\frac{\sum_{j=1}^{n} (B_{ave} - B_j)^2}{n - 1})] \cdot Lp^{-1} \cdot errmul + (erradd \cdot F^2)^2$$

where $erradd$ = 0.04, $errmul$ = 1.00

The linear absorption coefficient, μ, for Mo-Kα radiation is 8.0 cm^{-1}. A symmetry-related absorption correction using the program REQAB[1] was applied which resulted in

transmission factors ranging from 0.98 to 0.98. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR92)[2] and expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. The coordinates (*xyz*) of H1 were refined. The coordinates (*xyz*) of H2-H27 were fixed. The isotopic *B* of all hydrogen atoms were fixed. The final cycle of full-matrix least-squares refinement[4] was based on 5430 all reflections ($2\theta < 54.96$) and 302 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma(F_o^2 - F_c^2) / \Sigma F_o^2 = 0.069$$

$$R_W = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2} = 0.083$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.045 \qquad \text{for } I > 2.0\sigma(I) \text{ data}$$

The standard deviation of an observation of unit weight[5] was 1.01. The weighting scheme was based on counting statistics and included a factor ($p = 0.025$) to downweight the intense reflections. Plots of $\Sigma w(F_o^2 - F_c^2)^2$ versus F_o^2 reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.79 and –1.48 $e^-/Å^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in F_{calc};[7] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[8] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[9] All calculations were performed using the teXsan[10] crystallographic software package of Molecular Structure Corporation.

References and Notes

(1) Jacobson, R. *REQAB: Private communication:* 1995-1998.

(2) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.*, **1994,** *27*, 435.

(3) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF-94 program system: Technical Report of the Crystallography Laboratory*, University of Nijmegen: The Netherlands, 1994.

(4) Least-Squares:

Function minimized: $\Sigma w(F_o^2 - F_c^2)^2$ where

$$w = 1/[\sigma^2(F_o^2)] = [\sigma^2_c(F_o^2) + (p(\text{Max}(F_o^2,0) + 2F_o^2)/3)^2]^{-1}$$

$\sigma_c(F_o^2)$ = e.s.d. based on counting statistics

p = p-factor

(5) Standard deviation of an observation of unit weight:

$$[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(6) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*, Vol. IV; The Kynoch Press: Birmingham, England, 1974; Table 2.2 A.

(7) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.*, **1964,** *17*, 781.

(8) Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*, Vol C; Wilson, A. J. C., Eds.; Kluwer Academic Publishers, Boston, 1992; Table 4.2.6.8, pages 219-222.

(9) Creagh, D. C.; Hubbell, J. H. In *International Tables for Crystallography*, Vol C; Wilson, A. J. C., Eds.; Kluwer Academic Publishers, Boston, 1992; Table 4.2.4.3, pages 200-206.

(10) *teXsan: Crystal Structure Analysis Package;* Molecular Structure Corporation, The Woodlands, TX, 1985 and 1999.

Table (S1). Summary of crystal data, data collection parameters, and structure solution and refinement for [(η^6-C_6Me_6)Ru^{II}(bpy)H]CF_3SO_3 {**1**(CF_3SO_3)}

Crystal Data	
empirical formula	$C_{23}H_{27}N_2O_3RuF_3S$
formula weight	569.60
crystal color, habit	orange, block
crystal dimensions/mm	0.20 x 0.20 x 0.10
crystal system	monoclinic
lattice type	primitive
no. of reflections used for unit cell determination (2θ range/deg)	5424 (6.1 - 55.0)
lattice parameters	
a/Å	13.371(6)
b/Å	13.509(6)
c/Å	13.777(7)
β/deg	107.313(6)
V/Å^3	2375(1)
space group	$P2_1/c$ (No. 14)
Z value	4
D_{calc}/g cm^{-3}	1.592
F_{000}	1160
μ(MoKα)/cm^{-1}	7.99

Table (S1) (continued). Summary of crystal data, data collection parameters, and structure solution and refinement for **1**(CF_3SO_3)

Data Collection	
diffractometer	Rigaku/MSC Mercury CCD
voltage/kV, current/mA	50, 40
radiation (wavelength, λ/Å)	MoKα (0.7107)
monochromator	graphite
detector aperture/mm	70 x 70
data images/exposures	720
ω oscillation range	
(χ = 45.0, ϕ = 0.0 and 90.0)/deg	–70.0 - 110.0
exposure rate/sec deg^{-1}	20.0
detector swing angle/deg	19.66
crystal to detector distance/mm	45.19
$2\theta_{max}$/deg	55.0
temperature/˚C	–50.0
collimator diameter/mm	0.5
range of *h, k, l*	$-17 \le h \le 17$
	$-17 \le k \le 14$
	$-17 \le l \le 12$
no. of reflections measured	total: 19190
	unique: 5430 (R_{int} = 0.050)
extinction parameters	not refined
corrections for decay	not applied
Lorentz-polarization corrections	applied
absorption corrections method	empirical
transmission factor	0.9750 - 0.9840

Table (S1) (continued). Summary of crystal data, data collection parameters, and structure solution and refinement for **1**(CF_3SO_3)

Solution and Refinement	
structure solution	direct methods (SIR92)
refinement	full-matrix least-squares
function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
least squares weights	$1/[\sigma^2(F_o^2)]$
p-factor	0.025
anomalous dispersion	all non-hydrogen atoms
atoms refined anisotropically	all non-hydrogen atoms
coordinates of hydrogen atom: H1	refined
coordinates of hydrogen atoms: H2-H27	fixed
isotropic *B* of all hydrogen atoms	fixed
no. of reflections (all, $2\theta < 54.96^\circ$)	5430
no. of parameters	302
reflection/parameter ratio	17.98
$R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$	0.069
$R_w = [\{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}]^{1/2}$	0.083
$R1 = \Sigma \, \|\|F_o\| - \|F_c\|\| \, / \, \Sigma \, \|F_o\|$ {for $I > 2.0\sigma(I)$ data}	0.045
no. of reflections to calc *R*1	3757
goodness of fit indicator	
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(N_o - N_v)]^{1/2}$	1.01
(N_o = number of observations, N_v = number of variables)	
max shift/error in final cycle	0.000
maximum peak in final diff. map/e$^-$Å^{-3}	1.79
minimum peak in final diff. map/e$^-$Å^{-3}	–1.48

Table (S2). Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}/Å^2) of non-hydrogen atoms for [(η^6-C_6Me_6)Ru^{II}(bpy)H]CF_3SO_3 {**1**(CF_3SO_3)}, where $B_{eq} = 8/3\pi^2\{U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)cos\ \gamma + 2U_{13}(aa^*cc^*)cos\ \beta + 2U_{23}(bb^*cc^*)cos\ \alpha\}$

atom	*x*	*y*	*z*	B_{eq}
Ru(1)	0.23781(2)	0.24076(2)	0.42324(2)	2.124(6)
S(1)	0.26885(8)	-0.24144(8)	0.62277(9)	3.79(2)
F(1)	0.3123(3)	-0.1312(3)	0.4857(3)	8.4(1)
F(2)	0.1527(3)	-0.1269(3)	0.4826(3)	8.1(1)
F(3)	0.2127(4)	-0.2526(3)	0.4258(3)	11.8(2)
O(1)	0.3608(3)	-0.2989(2)	0.6284(3)	5.01(9)
O(2)	0.2876(3)	-0.1565(2)	0.6888(3)	5.39(10)
O(3)	0.1771(3)	-0.2977(2)	0.6213(3)	5.49(9)
N(1)	0.3118(2)	0.1535(2)	0.3412(2)	2.25(7)
N(2)	0.1212(3)	0.1428(2)	0.3484(2)	2.39(7)
C(1)	0.3697(3)	0.2281(3)	0.5698(3)	2.90(9)
C(2)	0.2805(4)	0.1919(3)	0.5914(3)	3.11(10)
C(3)	0.1880(3)	0.2504(3)	0.5639(3)	2.84(8)
C(4)	0.1866(3)	0.3468(3)	0.5219(3)	2.87(9)
C(5)	0.2784(4)	0.3832(3)	0.5022(3)	2.92(9)
C(6)	0.3700(3)	0.3248(3)	0.5257(3)	2.86(9)
C(7)	0.4680(4)	0.1656(4)	0.5942(4)	5.2(1)
C(8)	0.2813(5)	0.0934(3)	0.6432(4)	5.8(2)
C(9)	0.0910(4)	0.2117(4)	0.5860(3)	5.4(1)
C(10)	0.0910(4)	0.4125(4)	0.5055(4)	5.3(1)
C(11)	0.2804(4)	0.4858(3)	0.4574(4)	5.1(1)
C(12)	0.4712(4)	0.3664(4)	0.5134(4)	5.1(1)
C(13)	0.4076(3)	0.1693(3)	0.3313(3)	3.09(10)
C(14)	0.4553(3)	0.1055(3)	0.2820(3)	3.22(10)
C(15)	0.4026(3)	0.0211(3)	0.2391(3)	3.22(10)
C(16)	0.3037(3)	0.0038(3)	0.2468(3)	2.90(9)
C(17)	0.2589(3)	0.0712(2)	0.2970(3)	2.21(8)
C(18)	0.1521(3)	0.0641(3)	0.3021(3)	2.39(8)
C(19)	0.0836(4)	-0.0126(3)	0.2606(3)	3.03(9)
C(20)	-0.0187(4)	-0.0074(3)	0.2615(3)	3.7(1)
C(21)	-0.0517(3)	0.0755(3)	0.3017(3)	3.8(1)
C(22)	0.0189(3)	0.1480(3)	0.3437(3)	3.4(1)
C(23)	0.2350(5)	-0.1878(5)	0.4972(5)	5.8(2)

Table (S2) (continued). Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}/Å^2) of non-hydrogen atoms for **1**(CF_3SO_3), where $B_{eq} = 8/3\pi^2\{U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)cos\ \gamma + 2U_{13}(aa^*cc^*)cos\ \beta + 2U_{23}(bb^*cc^*)cos\ \alpha\}$

atom	*x*	*y*	*z*	B_{eq}
H(1)	0.200(3)	0.300(3)	0.327(3)	4.3(8)
H(2)	0.2974	0.0424	0.6028	7.0
H(3)	0.3326	0.0944	0.7080	7.0
H(4)	0.2143	0.0814	0.6515	7.0
H(5)	0.0705	0.1509	0.5512	6.5
H(6)	0.0360	0.2586	0.5637	6.5
H(7)	0.1056	0.2013	0.6571	6.5
H(8)	0.0373	0.3770	0.5227	6.4
H(9)	0.0667	0.4321	0.4361	6.4
H(10)	0.1091	0.4696	0.5473	6.4
H(11)	0.2134	0.5158	0.4450	6.1
H(12)	0.3315	0.5252	0.5040	6.1
H(13)	0.2972	0.4804	0.3953	6.1
H(14)	0.4584	0.4302	0.4835	6.2
H(15)	0.5222	0.3710	0.5782	6.2
H(16)	0.4962	0.3237	0.4709	6.2
H(17)	0.5210	0.2004	0.5752	6.2
H(18)	0.4913	0.1522	0.6650	6.2
H(19)	0.4532	0.1051	0.5575	6.2
H(20)	0.4441	0.2278	0.3600	3.7
H(21)	0.5234	0.1190	0.2774	3.9
H(22)	0.4340	-0.0246	0.2046	3.9
H(23)	0.2664	-0.0541	0.2176	3.5
H(24)	0.1074	-0.0684	0.2318	3.6
H(25)	-0.0660	-0.0601	0.2349	4.5
H(26)	-0.1229	0.0820	0.3002	4.6
H(27)	-0.0050	0.2049	0.3709	4.1

Table (S3). Anisotropic displacement parameters for [(η^6-C_6Me_6)Ru^{II}(bpy)H]CF_3SO_3 {**1**(CF_3SO_3)}. The general temperature factor expression: $\exp\{-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)\}$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	0.0264(1)	0.0261(2)	0.0273(1)	-0.0016(2)	0.0067(1)	-0.0024(1)
S(1)	0.0355(6)	0.0407(6)	0.0686(7)	0.0025(5)	0.0168(5)	0.0122(6)
F(1)	0.082(3)	0.125(3)	0.129(3)	0.000(2)	0.055(3)	0.058(2)
F(2)	0.063(2)	0.115(3)	0.124(3)	0.019(2)	0.018(2)	0.066(2)
F(3)	0.215(5)	0.152(4)	0.067(2)	0.003(4)	0.018(3)	-0.018(3)
O(1)	0.044(2)	0.050(2)	0.098(3)	0.014(2)	0.023(2)	0.011(2)
O(2)	0.060(3)	0.064(2)	0.082(3)	0.000(2)	0.024(2)	-0.009(2)
O(3)	0.042(2)	0.060(2)	0.106(3)	-0.009(2)	0.020(2)	0.026(2)
N(1)	0.029(2)	0.032(2)	0.026(2)	-0.002(1)	0.010(1)	-0.003(1)
N(2)	0.027(2)	0.035(2)	0.027(2)	-0.004(1)	0.006(1)	-0.004(1)
C(1)	0.033(2)	0.042(2)	0.030(2)	0.008(2)	0.001(2)	-0.005(2)
C(2)	0.054(3)	0.030(2)	0.033(2)	-0.002(2)	0.011(2)	-0.001(2)
C(3)	0.034(2)	0.051(2)	0.023(2)	-0.011(2)	0.008(2)	-0.007(2)
C(4)	0.033(2)	0.041(2)	0.029(2)	0.012(2)	0.001(2)	-0.008(2)
C(5)	0.048(3)	0.028(2)	0.030(2)	-0.005(2)	0.004(2)	-0.006(2)
C(6)	0.032(2)	0.041(2)	0.035(2)	-0.007(2)	0.010(2)	-0.008(2)
C(7)	0.047(3)	0.081(3)	0.061(3)	0.025(3)	0.004(3)	0.004(3)
C(8)	0.117(5)	0.044(3)	0.066(4)	0.002(3)	0.035(4)	0.015(2)
C(9)	0.054(3)	0.112(4)	0.042(3)	-0.019(3)	0.020(3)	-0.004(3)
C(10)	0.059(4)	0.086(4)	0.054(3)	0.031(3)	0.012(3)	-0.011(3)
C(11)	0.089(4)	0.030(2)	0.061(3)	-0.006(2)	0.002(3)	0.000(2)
C(12)	0.054(4)	0.075(3)	0.071(4)	-0.031(3)	0.027(3)	-0.026(3)
C(13)	0.033(3)	0.046(2)	0.039(2)	-0.007(2)	0.012(2)	-0.004(2)
C(14)	0.029(2)	0.055(3)	0.038(2)	0.004(2)	0.011(2)	-0.003(2)
C(15)	0.039(3)	0.045(2)	0.038(2)	0.010(2)	0.010(2)	-0.002(2)
C(16)	0.043(3)	0.031(2)	0.035(2)	0.001(2)	0.009(2)	-0.002(2)
C(17)	0.031(2)	0.028(2)	0.023(2)	0.001(2)	0.005(2)	0.002(1)
C(18)	0.034(2)	0.031(2)	0.025(2)	-0.002(2)	0.006(2)	0.001(2)
C(19)	0.044(3)	0.035(2)	0.033(2)	-0.011(2)	0.007(2)	-0.002(2)
C(20)	0.046(3)	0.054(3)	0.038(3)	-0.023(2)	0.007(2)	-0.008(2)
C(21)	0.031(3)	0.075(3)	0.041(3)	-0.013(2)	0.013(2)	-0.011(2)
C(22)	0.034(3)	0.055(3)	0.039(2)	-0.004(2)	0.009(2)	-0.013(2)
C(23)	0.063(4)	0.086(4)	0.074(4)	0.008(3)	0.022(3)	0.023(3)

Table (S4). Bond lengths (*l*/Å)

atom	atom	distance	atom	atom	distance
Ru(1)	N(1)	2.077(3)	Ru(1)	N(2)	2.071(3)
Ru(1)	C(1)	2.257(4)	Ru(1)	C(2)	2.312(4)
Ru(1)	C(3)	2.233(3)	Ru(1)	C(4)	2.219(4)
Ru(1)	C(5)	2.197(3)	Ru(1)	C(6)	2.218(4)
S(1)	O(1)	1.436(3)	S(1)	O(2)	1.439(3)
S(1)	O(3)	1.439(3)	S(1)	C(23)	1.805(6)
F(1)	C(23)	1.332(6)	F(2)	C(23)	1.341(6)
F(3)	C(23)	1.283(6)	N(1)	C(13)	1.345(5)
N(1)	C(17)	1.360(4)	N(2)	C(18)	1.366(4)
N(2)	C(22)	1.352(5)	C(1)	C(2)	1.400(6)
C(1)	C(6)	1.441(5)	C(1)	C(7)	1.514(6)
C(2)	C(3)	1.421(5)	C(2)	C(8)	1.509(6)
C(3)	C(4)	1.424(5)	C(3)	C(9)	1.511(6)
C(4)	C(5)	1.421(6)	C(4)	C(10)	1.517(6)
C(5)	C(6)	1.411(5)	C(5)	C(11)	1.520(5)
C(6)	C(12)	1.521(6)	C(13)	C(14)	1.366(5)
C(14)	C(15)	1.378(5)	C(15)	C(16)	1.377(6)
C(16)	C(17)	1.383(5)	C(17)	C(18)	1.454(5)
C(18)	C(19)	1.388(5)	C(19)	C(20)	1.373(6)
C(20)	C(21)	1.379(6)	C(21)	C(22)	1.365(6)
Ru(1)	H(1)	1.51(4)	C(7)	H(17)	0.95
C(7)	H(18)	0.95	C(7)	H(19)	0.95
C(8)	H(2)	0.95	C(8)	H(3)	0.95
C(8)	H(4)	0.95	C(9)	H(5)	0.95
C(9)	H(6)	0.95	C(9)	H(7)	0.95
C(10)	H(8)	0.95	C(10)	H(9)	0.95
C(10)	H(10)	0.95	C(11)	H(11)	0.95
C(11)	H(12)	0.95	C(11)	H(13)	0.95
C(12)	H(14)	0.95	C(12)	H(15)	0.95
C(12)	H(16)	0.95	C(13)	H(20)	0.95
C(14)	H(21)	0.95	C(15)	H(22)	0.95
C(16)	H(23)	0.95	C(19)	H(24)	0.95
C(20)	H(25)	0.95	C(21)	H(26)	0.95
C(22)	H(27)	0.95			

Table (S5). Bond angles (ϕ/deg)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Ru(1)	N(2)	77.1(1)	N(1)	Ru(1)	C(1)	94.1(1)
N(1)	Ru(1)	C(2)	111.6(1)	N(1)	Ru(1)	C(3)	145.0(1)
N(1)	Ru(1)	C(4)	169.7(1)	N(1)	Ru(1)	C(5)	132.8(1)
N(1)	Ru(1)	C(6)	102.6(1)	N(2)	Ru(1)	C(1)	132.0(1)
N(2)	Ru(1)	C(2)	104.0(1)	N(2)	Ru(1)	C(3)	95.4(1)
N(2)	Ru(1)	C(4)	113.2(1)	N(2)	Ru(1)	C(5)	147.6(1)
N(2)	Ru(1)	C(6)	169.5(1)	C(1)	Ru(1)	C(2)	35.7(1)
C(1)	Ru(1)	C(3)	65.4(1)	C(1)	Ru(1)	C(4)	78.6(1)
C(1)	Ru(1)	C(5)	67.1(1)	C(1)	Ru(1)	C(6)	37.5(1)
C(2)	Ru(1)	C(3)	36.4(1)	C(2)	Ru(1)	C(4)	66.4(1)
C(2)	Ru(1)	C(5)	78.6(1)	C(2)	Ru(1)	C(6)	66.1(1)
C(3)	Ru(1)	C(4)	37.3(1)	C(3)	Ru(1)	C(5)	67.2(1)
C(3)	Ru(1)	C(6)	78.7(1)	C(4)	Ru(1)	C(5)	37.5(1)
C(4)	Ru(1)	C(6)	67.2(1)	C(5)	Ru(1)	C(6)	37.3(1)
O(1)	S(1)	O(2)	114.2(2)	O(1)	S(1)	O(3)	115.4(2)
O(1)	S(1)	C(23)	103.6(2)	O(2)	S(1)	O(3)	114.7(2)
O(2)	S(1)	C(23)	103.5(2)	O(3)	S(1)	C(23)	103.2(3)
Ru(1)	N(1)	C(13)	125.9(2)	Ru(1)	N(1)	C(17)	116.0(2)
C(13)	N(1)	C(17)	118.0(3)	Ru(1)	N(2)	C(18)	116.2(3)
Ru(1)	N(2)	C(22)	126.3(3)	C(18)	N(2)	C(22)	117.4(3)
Ru(1)	C(1)	C(2)	74.3(2)	Ru(1)	C(1)	C(6)	69.8(2)
Ru(1)	C(1)	C(7)	129.5(3)	C(2)	C(1)	C(6)	121.1(4)
C(2)	C(1)	C(7)	119.7(4)	C(6)	C(1)	C(7)	119.2(4)
Ru(1)	C(2)	C(1)	70.0(2)	Ru(1)	C(2)	C(3)	68.8(2)
Ru(1)	C(2)	C(8)	133.7(3)	C(1)	C(2)	C(3)	118.5(3)
C(1)	C(2)	C(8)	121.5(4)	C(3)	C(2)	C(8)	119.9(4)
Ru(1)	C(3)	C(2)	74.8(2)	Ru(1)	C(3)	C(4)	70.8(2)
Ru(1)	C(3)	C(9)	130.6(3)	C(2)	C(3)	C(4)	121.5(4)
C(2)	C(3)	C(9)	119.1(4)	C(4)	C(3)	C(9)	119.3(4)
Ru(1)	C(4)	C(3)	71.9(2)	Ru(1)	C(4)	C(5)	70.4(2)
Ru(1)	C(4)	C(10)	133.3(3)	C(3)	C(4)	C(5)	119.1(3)
C(3)	C(4)	C(10)	120.3(4)	C(5)	C(4)	C(10)	120.4(4)
Ru(1)	C(5)	C(4)	72.0(2)	Ru(1)	C(5)	C(6)	72.2(2)

Table (S5) (continued). Bond angles (ϕ/deg)

atom	atom	atom	angle	atom	atom	atom	angle
Ru(1)	C(5)	C(11)	129.0(3)	C(4)	C(5)	C(6)	120.1(3)
C(4)	C(5)	C(11)	120.8(4)	C(6)	C(5)	C(11)	119.0(4)
Ru(1)	C(6)	C(1)	72.7(2)	Ru(1)	C(6)	C(5)	70.6(2)
Ru(1)	C(6)	C(12)	133.2(3)	C(1)	C(6)	C(5)	119.5(4)
C(1)	C(6)	C(12)	119.7(4)	C(5)	C(6)	C(12)	120.5(4)
N(1)	C(13)	C(14)	123.3(4)	C(13)	C(14)	C(15)	118.7(4)
C(14)	C(15)	C(16)	119.2(4)	C(15)	C(16)	C(17)	119.7(4)
N(1)	C(17)	C(16)	121.1(4)	N(1)	C(17)	C(18)	114.8(3)
C(16)	C(17)	C(18)	124.0(3)	N(2)	C(18)	C(17)	114.2(3)
N(2)	C(18)	C(19)	121.3(4)	C(17)	C(18)	C(19)	124.5(3)
C(18)	C(19)	C(20)	119.7(4)	C(19)	C(20)	C(21)	118.9(4)
C(20)	C(21)	C(22)	119.4(4)	N(2)	C(22)	C(21)	123.0(4)
S(1)	C(23)	F(1)	111.2(4)	S(1)	C(23)	F(2)	110.5(4)
S(1)	C(23)	F(3)	113.3(4)	F(1)	C(23)	F(2)	105.1(5)
F(1)	C(23)	F(3)	108.2(5)	F(2)	C(23)	F(3)	108.1(6)
N(1)	Ru(1)	H(1)	85(1)	N(2)	Ru(1)	H(1)	83(1)
C(1)	Ru(1)	H(1)	143(1)	C(2)	Ru(1)	H(1)	162(1)
C(3)	Ru(1)	H(1)	128(1)	C(4)	Ru(1)	H(1)	96(1)
C(5)	Ru(1)	H(1)	86(1)	C(6)	Ru(1)	H(1)	106(1)
C(1)	C(7)	H(17)	109.5	C(1)	C(7)	H(18)	109.5
C(1)	C(7)	H(19)	109.4	H(17)	C(7)	H(18)	109.5
H(17)	C(7)	H(19)	109.5	H(18)	C(7)	H(19)	109.5
C(2)	C(8)	H(2)	109.5	C(2)	C(8)	H(3)	109.5
C(2)	C(8)	H(4)	109.4	H(2)	C(8)	H(3)	109.5
H(2)	C(8)	H(4)	109.5	H(3)	C(8)	H(4)	109.5
C(3)	C(9)	H(5)	109.4	C(3)	C(9)	H(6)	109.5
C(3)	C(9)	H(7)	109.4	H(5)	C(9)	H(6)	109.5
H(5)	C(9)	H(7)	109.4	H(6)	C(9)	H(7)	109.5
C(4)	C(10)	H(8)	109.5	C(4)	C(10)	H(9)	109.5
C(4)	C(10)	H(10)	109.5	H(8)	C(10)	H(9)	109.5
H(8)	C(10)	H(10)	109.5	H(9)	C(10)	H(10)	109.4
C(5)	C(11)	H(11)	109.4	C(5)	C(11)	H(12)	109.5
C(5)	C(11)	H(13)	109.5	H(11)	C(11)	H(12)	109.5

Table (S5) (continued). Bond angles (ϕ/deg)

atom	atom	atom	angle	atom	atom	atom	angle
H(11)	C(11)	H(13)	109.4	H(12)	C(11)	H(13)	109.5
C(6)	C(12)	H(14)	109.5	C(6)	C(12)	H(15)	109.4
C(6)	C(12)	H(16)	109.5	H(14)	C(12)	H(15)	109.5
H(14)	C(12)	H(16)	109.5	H(15)	C(12)	H(16)	109.5
N(1)	C(13)	H(20)	118.4	C(14)	C(13)	H(20)	118.3
C(13)	C(14)	H(21)	120.6	C(15)	C(14)	H(21)	120.6
C(14)	C(15)	H(22)	120.4	C(16)	C(15)	H(22)	120.4
C(15)	C(16)	H(23)	120.1	C(17)	C(16)	H(23)	120.1
C(18)	C(19)	H(24)	120.2	C(20)	C(19)	H(24)	120.2
C(19)	C(20)	H(25)	120.5	C(21)	C(20)	H(25)	120.5
C(20)	C(21)	H(26)	120.3	C(22)	C(21)	H(26)	120.3
N(2)	C(22)	H(27)	118.5	C(21)	C(22)	H(27)	118.5

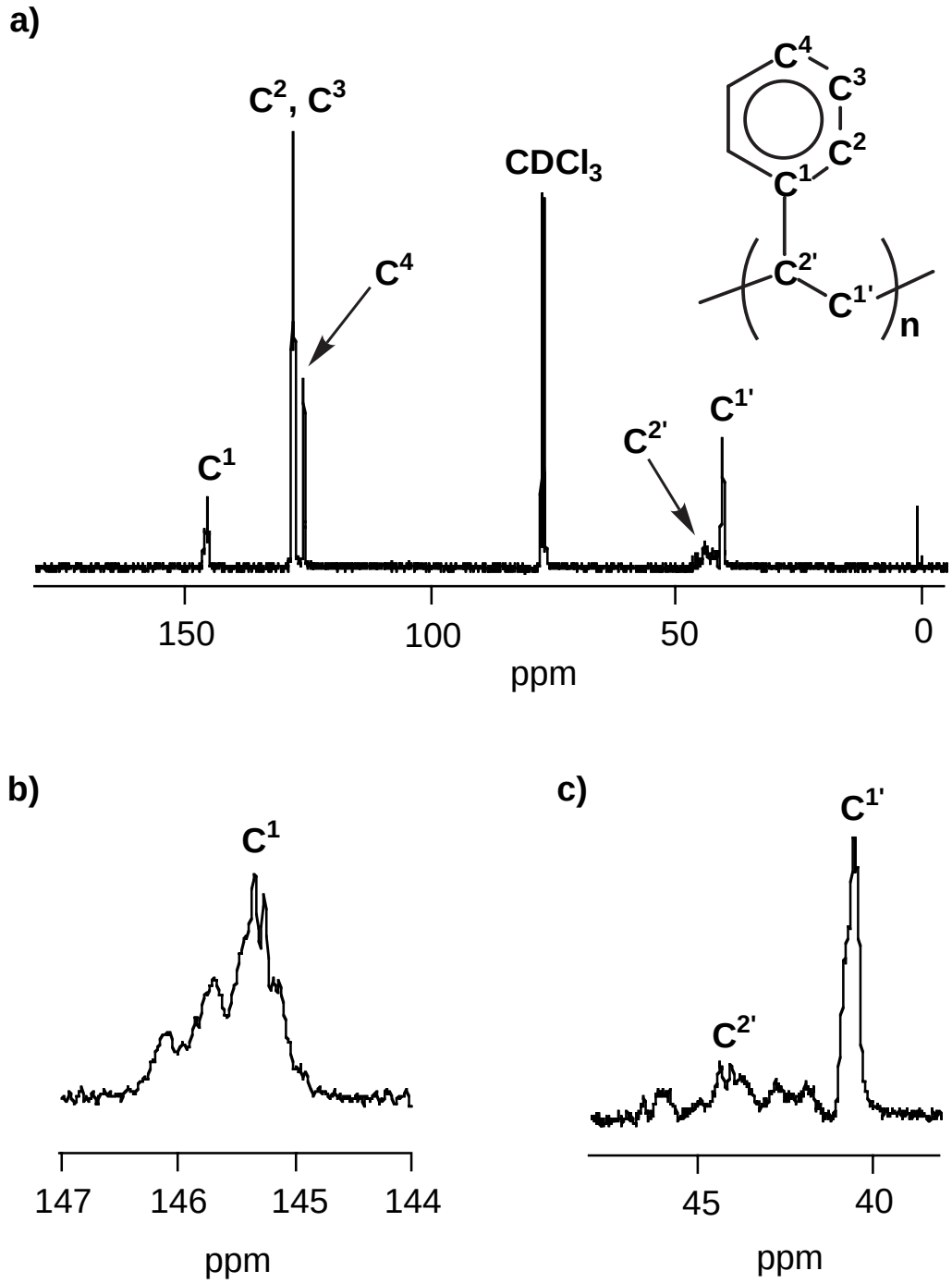

Figure (S6). (a) ^{13}C NMR spectra of the isolated polystyrene. (b) The signals assigned to C^1. (c) The signals assigned to $C^{1'}$ and $C^{2'}$.