Electronic Supplementary Information

Position-Selective Intramolecular Aromatic C-H Bond Activation of 1,2,3-Triazol-5-ylidene (tzNHC) Ligands in (*p*-Cymene)Ruthenium(II) Complexes

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Contents

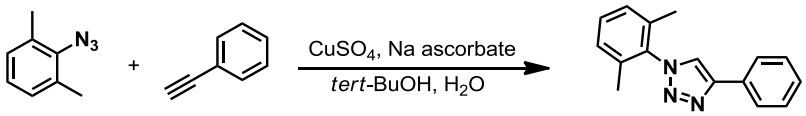
1. Experimental Procedures

1.1 General Procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under a nitrogen atmosphere by using a standard Schlenk tube or high vacuum techniques. CH_2Cl_2 was distilled over calcium hydride under nitrogen atmosphere prior to use. THF was distilled over sodium-benzophenone under nitrogen atmosphere prior to use. 2,6-dimethyl phenyl azide,[1] 2-methyl phenyl azido,[2] **1a**,[3] **1d**[4] were prepared according to literature procedures. Other reagents employed in this research were commercially available and used without further purification. Column chromatography was performed on silica gel (spherical, 60 μm) and alumina (spherical, 75 μm). The ^1H and ^{13}C NMR spectra recorded with a Varian Mercury-300 or Varian 400-MR spectrometer at ambient temperature. The chemical shifts were reported in δ units downfield from the internal reference (Me_4Si). All coupling constants were recorded in Hz. Elementary analysis were measured on a Perkin-Elmer 2400 series II CHN analyzer.

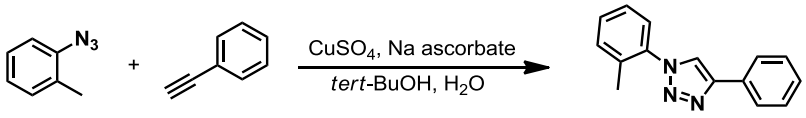
1.2 Synthesis of triazole and triazolium salt

1.2.1 Preparation of the 1-(2,6-xylyl)-4-phenyl-1,2,3-triazole.



The mixture of Phenylacetylene (0.37 mL, 3.3 mmol), 2,6-xylylazido (450 mg, 3.1 mmol), sodium ascorbate (1450 mg, 3.6 mmol), anhydrous copper sulfate (579 mg, 3.6 mmol), H_2O (5.0 mL) and *tert*-BuOH (20 mL) were charged in a 100 mL round-bottomed flask. After stirring at room temperature for 43 h under air, the mixture was extracted with ethyl acetate, washed with conc. NH_4Cl aq. dried over $MgSO_4$, and the volatile was removed under reduced pressure. The residual solid was purified by silica gel chromatograph (eluted with hexane first, then with ethyl acetate) to yield the 1-(2,6-xylyl)-4-phenyl-1,2,3-triazole as a white solid (721 mg, 2.89 mmol, 93%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 7.0 Hz, 2H, Ar), 7.87 (s, 1H, triazol C=CH), 7.5 (m, 2H, Ar), 7.4-7.3 (m, 2H, Ar) 7.21 (d, J = 7.7 Hz, 2H, Ar), 2.07 (s, 6H, xylyl-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 135.8, 135.4, 130.3, 130.0, 128.9, 128.4, 128.3, 125.7, 121.3 (s, Ar, triazole C=C), 17.3 (s, xylyl-CH_3). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.34; H, 6.04; N, 16.96%

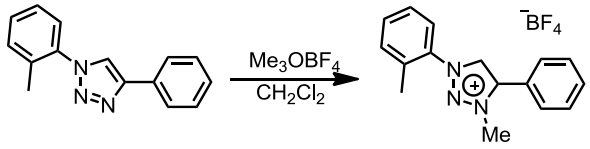
1.2.2 Preparation of the 1-(2-methyl phenyl)-4-phenyl-1,2,3-triazole.



The mixture of Phenylacetylene (0.85 mL, 7.7 mmol), 2-methyl phenyl azido (1.02 g, 7.7 mmol), sodium ascorbate (153 mg, 0.77 mmol), copper sulfate pentahydrate (96.3 mg, 0.39 mmol), H_2O (11.0 mL) and *tert*-BuOH (11.0 mL) were charged in a 100 mL round-bottomed flask. After stirring at room temperature for overnight under air, the mixture was extracted with ethyl acetate, washed with conc. NH_4Cl aq. dried over $MgSO_4$, and the volatile was

removed under reduced pressure. The residual solid was purified by silica gel chromatograph (eluted with hexane first then with ethyl acetate) to yield the compound as a white solid (1.51 g, 6.42 mmol, 83%). The compound was prepared by modified method for previous report which have been synthesized this compound.[2] Spectroscopic data also was compared to data for previous report.[5]

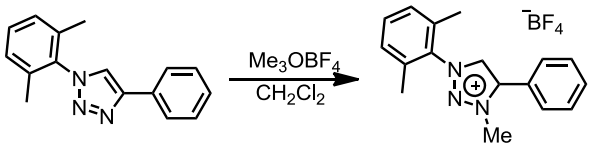
1.2.3 Preparation of the triazolium salt 1b



1b

The mixture of 1-(2-methyl phenyl)-4-phenyl-1,2,3-triazole (186 mg, 0.79 mmol), Me_3OBF_4 (159 mg, 1.03 mmol) and CH_2Cl_2 (10 mL) were charged in a 50 mL Schlenk tube. After stirring at room temperature for overnight, the reaction was quenched with MeOH, and the volatile was removed under reduced pressure. The residual solid was washed with Et_2O and dried to yield **1b** as a white solid (252 mg, 2.89 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H, triazolium CH), 7.8-7.7 (m, 3H, Ar), 7.6 (m, 3H), 7.6-7.5 (m, 1H, Ar), 7.43 (dd, *J* = 6.3, 6.3 Hz, 2H, Ph), 4.39 (s, 3H, N-CH_3), 2.38 (s, 3H, *o*-tolyl-CH_3). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 142.7 (triazolium CH), 134.2, 133.4, 132.1, 131.7, 130.4, 129.5, 129.5, 127.6, 126.2, 122.6 (s, Ar, triazole), 39.0 (s, N-CH_3), 17.0 (s, xylyl-CH_3).Anal. Calcd for $C_{16}H_{16}N_3$: C, 57.00; H, 4.78; N, 12.46. Found: C, 57.08; H, 4.75; N, 12.54%

1.2.4 Preparation of the triazolium salt 1c.

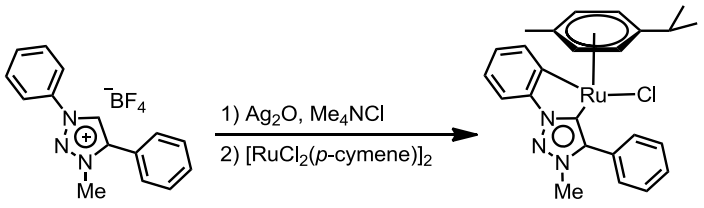


1c

The mixture of 1-xylyl-4-phenyl 1,2,3-triazole (125 mg, 0.50 mmol), Me_3OBF_4 (99.7 mg, 0.67 mmol) and CH_2Cl_2 10 mL were charged in a 50 mL Schlenk tube. After stirring at room temperature for overnight, the reaction was quenched with MeOH, and the volatile was removed under reduced pressure. The residual solid was washed with Et_2O and dried to yield **1c** as a white solid (161 mg, 0.46 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H, triazolium CH), 7.81 (dd, *J* = 6.7, 3.1Hz, 2H, Ar), 7.7-7.6 (m, 3H, Ar), 7.48 (d, *J* = 8.0 Hz, 1H, Ar), 7.3 (m, 2H, Ar), 4.47 (s, 3H, N-CH_3), 2.22 (s, 6H, xylyl-CH_3). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 143.2 (s, triazolium CH), 134.9, 133.7, 132.0, 131.7, 130.9, 129.7, 129.4, 129.1, 122.7 (s, Ar, triazole), 39.1 (s, N-CH_3), 16.9 (s, xylyl-CH_3). Anal. Calcd for $C_{17}H_{18}N_3$: C, 58.15; H, 5.17; N, 11.97. Found: C, 58.14; H, 5.06; N, 11.94%

1.3 Synthesis of ruthenium NHC complexes

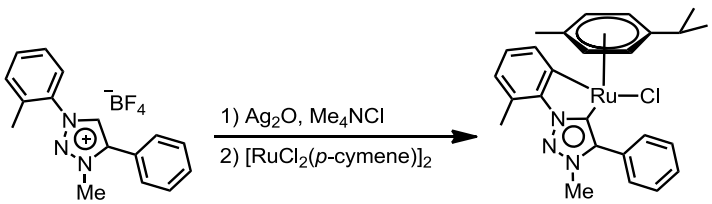
1.3.1 Synthesis of ruthenium complex 2a.



2a

The mixture of a triazolium salt **1a** (171 mg, 0.53 mmol), Ag_2O (74.3 mg, 0.32 mmol), Me_4NCl (69.7 mg, 0.64 mmol) and CH_2Cl_2/CH_3CN (1:1, 20 mL) were charged in a 50 mL Schlenk tube. After stirring at room temperature for 2 h, the volatile was removed under reduced pressure. The residual solid was extracted with CH_2Cl_2 and filtered, and the volatile was removed under reduced pressure. To this residue, $[RuCl_2(p\text{-cymene})]_2$ (162 mg, 0.26 mmol) and CH_2Cl_2 15 mL were added. After stirring for 3h at room temperature, the volatile was concentrated in reduced pressure and purified by alumina column chromatography (CH_2Cl_2/acetone = 9/1) to yield **2a** as a yellow solid (142 mg, 0.28 mmol, 53%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2 and Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.4, 1.1 Hz, 1H, Ar), 7.9 (m, 2H, Ar), 7.6 (m, 4H, Ar), 7.12 (ddd, *J* = 7.4, 7.3, 1.4 Hz, 1H, Ar), 7.02 (ddd, *J* = 7.6, 7.5, 1.4Hz, 1H, Ar), 5.26 (d, *J* = 7.0 Hz, *p*-cymene ring), 5.25 (d, *J* = 7.0 Hz, 1H, *p*-cymene ring), 4.83 (d, *J* = 5.8 Hz, 1H, *p*-cymene ring), 4.80 (d, *J* = 5.8 Hz, 1H, *p*-cymene ring), 4.11 (s, 3H, N-CH_3), 2.14 (sep, 1H, *J* = 6.9 Hz, *p*-cymene-C*H*$(CH_3)_2$), 1.94 (s, 3H, *p*-cymene-CH_3), 0.81 (d, *J* = 6.9 Hz, 3H, *p*-cymene-CH(C*H*$_3)_2$), 0.81 (d, *J* = 6.9 Hz, 3H, *p*-cymene-CH(C*H*$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0 (s, Ru-C(Ar)), 166.3 (s, carbene carbon), 145.7 144.9, 142.0, 130.6, 129.7, 128.9, 128.7, 127.4, 122.3, 113.8 (s, Ph, triazole), 102.1, 99.6, 89.7, 89.6, 88.4, 84.3 (s, *p*-cymene ring), 37.0, 30.9, 23.1, 21.5, 18.9 (s, *p*-cymene-CH_3, *p*-cymene-CH(*C*$H_3)_2$, N-CH_3). Anal. Calcd for $C_{25}H_{26}ClN_3Ru$: C, 59.46; H, 5.19; N, 8.32. Found: C, 59.42; H, 5.11; N, 8.28%

1.3.2 Synthesis of ruthenium complexes 2b.

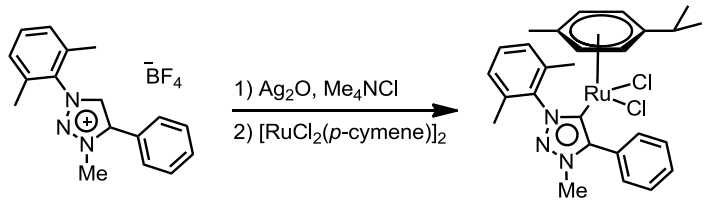


1b **2b**

Complex 2b was prepared from triazolium salt **1b** (80.7 mg, 0.24 mmol), Ag_2O (33.9 mg, 0.15 mmol), Me_4NCl (31.6 mg, 0.29 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (73.9 mg, 0.12 mmol) in the same manner as that for **2a** except for purification method. Complex **2b** was isolated by recrystallization from CH_2Cl_2/Et_2O as an orange solid (50.3 mg, 0.10 mmol, 40%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from 1,2-$C_2H_4Cl_2$ and Et_2O. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.9 Hz, 1H, *o*-tolyl), 7.9 (m, 2H, Ph), 7.6 (m, 3H,

Ph), 6.98 (dd, 1H, *J* = 7.4, 7.4 Hz, *o*-tolyl), 6.80 (d, *J* = 7.2 Hz, 1H, *o*-tolyl), 5.21 (s, 2H, *p*-cymene ring), 4.80 (d, *J* = 5.8 Hz, 1H, *p*-cymene ring), 4.74 (d, *J* = 5.8 Hz, 1H, , *p*-cymene ring), 4.11 (s, 3H, N-CH_3), 2.62 (s, 3H, *o*-tolyl-CH_3), 2.12 (sep, *J* = 6.9 Hz, 1H, *p*-cymene-C*H*(CH_3)$_2$), 1.92 (s, 3H, *p*-cymene-CH_3), 0.80 (d, *J* = 6.9 Hz, 3H, *p*-cymene-CH(C*H*$_3$)$_2$), 0.73 (d, *J* = 6.9 Hz, 3H, *p*-cymene-CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2 (s, Ru-C(Ar)), 167.6 (s, carbene carbon), 144.5, 143.6, 139.7, 130.8, 129.6, 128.9, 128.8, 126.6, 126.1, 125.9 (s, Ar, triazole), 102.1, 99.5, 90.1, 88.6, 84.7 (s, *p*-cymene ring), 37.1, 30.8, 23.0, 21.5, 20.8, 18.9 (s, *p*-cymene-*C*H(CH_3)$_2$, *p*-cymene-*C*H(CH_3)$_2$, N-CH_3, *o*-tolyl-CH_3). Anal. Calcd for $C_{26}H_{28}ClN_3Ru\cdot0.25CH_2Cl_2$: C, 58.36; H, 5.32; N, 7.78. Found: C, 58.46; H, 5.21; N, 7.88%

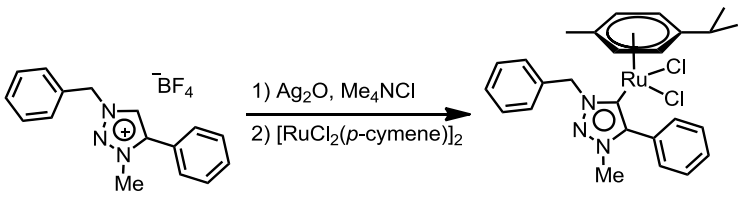
1.3.3 Synthesis of ruthenium complexes 3c.



1c **3c**

Complex **3c** was prepared from triazolium salt **1c** (231 mg, 0.66 mmol), Ag_2O (92.6 mg, 0.40 mmol), Me_4NCl (86.6 mg, 0.79 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (203 mg, 0.33 mmol) in the same manner as that for **2b**. Complex **3c** was isolated as an orange solid (300 mg, 0.53 mmol, 80%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2 and Et_2O. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 (m, 2H, Ar), 7.6 (m, 3H, Ar), 7.23 (t, *J* = 7.5 Hz, 1H, Ar), 7.05 (d, *J* = 7.5 Hz, 2H, Ar), 5.13 (d, *J* = 5.9 Hz, 2H, *p*-cymene ring), 4.22 (d, 2H, *J* = 5.9 Hz , *p*-cymene ring), 3.97 (s, 3H, N-CH_3), 2.85 (sep, *J* = 6.9 Hz, 1H, *p*-cymene-C*H*(CH_3)$_2$), 1.80 (s, 3H, *p*-cymene-CH_3), 1.16 (d, *J* = 6.9 Hz, 6H, *p*-cymene-CH(C*H*$_3$)$_2$). ^{13}C NMR NMR (300 MHz, $CDCl_3$) δ 162.4 (s, carbene carbon), 147.7, 140.1, 135.4, 131.8, 130.1, 129.8, 129.3, 128.6, 127.3 (s, Ar, triazole), 106.6, 97.0, 88.6, 80.4 (*p*-cymene ring), 37.6, 30.3, 22.4, 18.5, 18.4 (s, *p*-cymene-CH(*C*H$_3$)$_2$, *p*-cymene-*C*H(CH_3)$_2$, N-CH_3, xylyl). Anal. Calcd for Calcd for $C_{27}H_{31}Cl_2N_3Ru\cdot1/3CH_2Cl_2$: C, 54.91; H, 5.34; N, 7.03. Found: C, 54.63; H, 5.27; N, 6.99%

1.3.4 Synthesis of ruthenium complexes 3d.

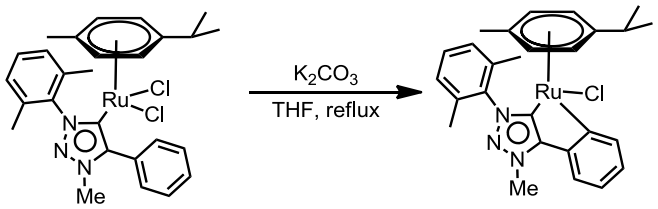


1d **3d**

Complex **3d** was prepared from **1d** (186 mg, 0.55 mmol), Ag_2O (77.3 mg, 0.33 mmol), Me_4NCl (72.3 mg, 0.66 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (169 mg, 0.28 mmol) in the same manner as that for **2b**. Complex **3d** was isolated as an orange solid (297 mg, 0.53 mmol, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 6.5, 3.1 Hz, 2H, Ar), 7.5 (m, 3H, Ar), 7.4-7.3 (m, 5H, Ar), 6.28 (s, 2H, Bn-CH_2), 5.13 (d, *J* = 6.0 Hz, 2H, *p*-cymene ring), 4.74 (d, *J* = 6.0

Hz, 2H, *p*-cymene ring), 3.74 (s, 3H, N-CH_3), 2.47 (sep, *J* = 6.9 Hz, 1H, *p*-cymene-C*H*$(CH_3)_2$), 1.59 (s, 3H, *p*-cymene-CH_3), 1.07 (d, *J* = 6.9 Hz, 6H, *p*-cymene-CH(C*H*$_3)_2$). ^{13}C NMR (75MHz, $CDCl_3$) δ 161.3 (s, carbene carbon), 148.5, 136.4, 131.9, 129.7, 128.6, 128.5, 127.9 (s, Ar, triazole), 105.5, 96.4, 84.7, 83.2 (s, *p*-cymene ring), 57.1 (s, Bn-CH_2), 37.1, 30.3, 22.4, 17.9 (s, *p*-cymene-*C*H_3, *p*-cymene-*C*H$(CH_3)_2$, *p*-cymene-CH(*C*$H_3)_2$, N-CH_3). Anal. Calcd for Calcd for $C_{26}H_{29}Cl_2N_3Ru\cdot0.2CH_2Cl_2$: C, 54.97; H, 5.18; N, 7.34. Found: C, 55.26; H, 5.25; N, 7.49%

1.3.5 Synthesis of ruthenium complexes 4c.



3c **4c**

The mixture of the ruthenium complex **3c** (89.5 mg, 0.16 mmol), K_2CO_3 (35.0 mg, 0.25 mmol) and THF 5 mL were charged in a 20 mL Schlenk tube. After stirring at reflux for 6 h, the volatile was removed under reduced pressure. The residual solid was extracted with CH_2Cl_2 and filtered. The volatile was removed under reduced pressure and the residue was recrystallized (CH_2Cl_2/Et_2O) to yield **4c** as a yellow solid (61.6 mg, 0.12 mmol, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.4, Hz, 1H, Ph), 7.47 (dd, *J* = 7.6, 7.6 Hz, 1H, Ph), 7.4-7.3 (m, 3H, xylyl), 7.06 (dd, *J* = 7.4, 7.2 Hz, 1H, Ph), 6.96 (dd, *J* = 7.6, 7.6 Hz, 1H, Ph), 5.53 (d, *J* = 6.0 Hz, 1H, *p*-cymene ring), 4.91 (d, 1H, *J* = 6.0 Hz , *p*-cymene ring), 4.55 (d, 1H, *J* = 5.5 Hz , *p*-cymene ring), 4.28 (d, 1H, *J* = 5.5 Hz , *p*-cymene ring), 4.27 (s, 3H, N-CH_3), 2.39 (s, 3H, *p*-cymene-CH_3), 2.30 (sep, *J* = 6.9 Hz, 1H, *p*-cymene-C*H*$(CH_3)_2$), 2.10 (s, 3H, xylyl-CH_3), 1.82 (s, 3H, xylyl-CH_3), 0.92 (d, *J* = 6.9 Hz, 3H, *p*-cymene-CH(C*H*$_3)_2$), 0.52 (d, *J* = 6.9 Hz, 3H, *p*-cymene-CH(C*H*$_3)_2$). ^{13}C NMR NMR (300 MHz $CDCl_3$) δ 180.8, 178.4 (s, Ru-C(Ar), carbene carbon), 152.9 (s, triazle), 142.2, 138.1, 137.9, 136.5, 135.2, 130.2, 128.9, 127.8, 127.4, 121.8, 120.8 (s, Ar), 100.9, 99.8, 93.6, 90.8, 89.5, 75.9 (s, *p*-cymene ring), 37.3, 30.6, 23.9, 20.7, 18.9, 18.4, 17.6 (s, *p*-cymene-*C*H$(CH_3)_2$, *p*-cymene-CH(*C*$H_3)_2$, xylyl, N-CH_3). HR-MS (ESI) calcd for $C_{27}H_{30}ClN_3Ru$ [M+Na]+ 556.1069, found 556.1068.

2. X-ray Crystallographic data

Crystal data for **2a**: $C_{25}H_{26}ClN_3Ru$, M = 505.02, monoclinic, a = 7.9014(19), b = 23.660(6), c = 11.737(3) Å, V = 2187.0(9) Å^3, T = 123 K, space group P2$_1$/n (no. 14), Z = 4, μ(Mo–Kα) = 8.562 cm^{-1}, 16427 measured reflections, 4990 unique reflections. $R1$ = 0.0303, $wR2$ = 0.0703, for 4550 reflections. For **2b**·CH_2Cl_2: $C_{28}H_{32}Cl_3N_3Ru$, M = 618.01, monoclinic, a = 29.7166(6), b = 11.3579(2), c = 21.1834(4) Å, V = 5507(2) Å^3, T = 198 K, space group C2/c (no. 15), Z = 8, μ(Mo–Kα) = 8.822 cm^{-1}, 25744 measured reflections, 6277 unique reflections. $R1$ = 0.0365, $wR2$ = 0.0917, for 5904 reflections. For **3c**·2CH_2Cl_2: $C_{29}H_{35}Cl_6N_3Ru$, M = 739.40, monoclinic, a = 22.430(5), b = 13.091(3), c = 23.693(3) Å, V = 6449(3) Å^3, T = 123 K, space group P2$_1$/n (no. 14), Z = 8, μ(Mo–Kα) = 10.070 cm^{-1}, 48952 measured reflections, 14715 unique reflections. $R1$ = 0.0779, $wR2$ = 0.2052, for 11198 reflections. For **4c**·CH_2Cl_2: $C_{28}H_{32}Cl_3N_3Ru$, M = 618.01, monoclinic, a = 10.8748(3), b = 9.4047(2), c = 26.8586(6) Å, V = 2739.6(2) Å^3, T = 198 K, space group P2$_1$/n (no. 14), Z = 4, μ(Mo–Kα) = 8.867 cm^{-1}, 25313 measured reflections, 6266 unique reflections. $R1$ = 0.0302, $wR2$ = 0.0541, for 5599 reflections. CCDC numbers: 901766 (**2a**), 901767 (**2b**), 901768 (**3c**) and 901934 (**4c**).

3. References

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