Electronic Supplementary Information for Dalton Transactions


# Supporting Information

# for

# 2,2':6,2''-Terpyridine meets 2,6-*bis*(1*H*-1,2,3-triazol-4-yl)pyridine: Tuning the electropical properties of ruthenium(II) complexes

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# Experimental Section

### *Instrumentation*

The 1D ($^{1}$H and $^{13}$C) and 2D NMR (gCOSY) spectra were recorded in deuterated solvents (Cambridge Isotope Laboratories Inc.) at 25 °C on a Varian Mercury 400 MHz instrument and are reported in ppm *vs.* TMS as internal standard. Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-ToF MS) was performed on a Voyager-DE PRO biospectrometry workstation (Applied Biosystems) time-of-flight mass spectrometer, with dithranol as matrix. Elemental analyses were obtained on a EuroVector EuroEA3000 elemental analyser for CHNS-O. UV/vis spectra were measured on a Perkin-Elmer Lambda-45 spectrometer, photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Absolute quantum yields were evaluated on a Hamamatsu Photonic Multi-Channel Analyzer C10027. For these three techniques a concentration of $10^{-6}$ M in degassed acetonitrile (1 cm cuvette) at 25 °C was used. Low temperature photoluminescence experiments were performed in dilute *n*-butyronitrile solutions on a Edinburgh Instruments FS 920 fluorescence spectrometer. Electrochemical experiments were carried out using an Autolab PGSTAT30 potentiostat at a scan rate of 100 mV/s. For this, a standard three-electrode configuration was used, with a platinum disk working electrode, a platinum-rod auxillary electrode and an Ag/AgCl-reference electrode. Ferrocene was added at the end of each experiment as an internal standard. The potentials are quoted *vs.* the $Fc/Fc^{+}$ couple. The solvent was $CH_2Cl_2$, containing tetra-*n*-butylammonium hexafluorophosphate (*n*-$Bu_4NPF_6$, 0.1 M).

### *General Methods*

All reagents were purchased from commercial sources and used without further purification unless specified. The solvents were received from Biosolve and were dried and distilled according to standard procedures. The synthesis of the precursor complexe $Ru(DMSO)_4Cl_2$,[1] the *mono*-terpyridine complexes $Ru(R^2\text{-tpy})Cl_3$ ($R^2$ = H, 4-Br-$C_6H_4$)[2] and the homoleptic complex $[Ru(R^2\text{-tpy})_2](PF_6)_2$ (**7**, $R_2$ = H)[2a] was carried out according to literature procedures.

[1] E. Duliere, M. Devillers, J. Marchand-Brynaert, *Organometallics* **2003**, *22*, 804.

[2] (a) A. Winter, J. Hummel, N. Risch, *J. Org. Chem.* **2006**, *71*, 4862. (b) O. Schmelz, M. Rehahn, *e-Polymers* **2002**, 47.

Chromatographic separations were performed on silica gel ($SiO_2$ 60, 0.040–0.063 mm, Merck KGaA) and aluminium oxide (neutral, 0.063–0.200 mm, Macherey & Nagel). Preparative layer chromatography (PLC) was performed on silica gel ($SiO_2$ 60 on 20 × 20 cm glass plates, 1 mm layer thickness, Merck). Preparative size exclusion chromatography was performed on BioRad S-X3 beads swollen with $CH_2Cl_2$.

***Safety Comment***

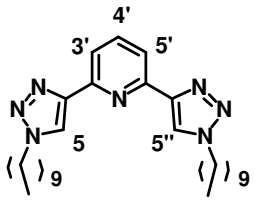
Sodium azide is very toxic, personal protection precautions should be taken. As low molecular weight organic azides are potential explosives, care must be taken during their handling. Generally, when the total number of carbon ($N_C$) plus oxygen ($N_O$) atoms is less than the total numbers of nitrogen atoms ($N_N$) by a ratio of three, *i.e.* $(N_C + N_O)/N_N \leq 3$, the compound is considered as an explosive hazard. Therefore, the compounds were prepared prior to use and used immediately.

***General procedure for the Click reaction with aliphatic azides***

A suspension of sodium azide (1.2 eq.) and an alkyl bromide (1 eq.) in ethanol/water (8 mL, 2:1 ratio) in a 20 mL microwave vail equipped with a magnetic stirrerwas heated under microwave irradiation at 125 °C for 1 h. The formation of the alkyl azide was monitored by GC-MS. Subsequently, aqueous solutions of $CuSO_4 \times 5\ H_2O$ (46 mg, 10 mol-%) and sodium ascorbate (360 mg, 100 mol-%), additional ethanol (5 mL) and 2,6-diethynylpyridine (1 eq.) were added. The reaction mixture was then heated under microwave irradiation at 100 °C for 1 h, whereupon a precipitate was formed. The precipitation was completed by adding water (10 mL). After filtration and thoroughly washing with water (200 mL), the precipitate was dissolved in $CH_2Cl_2$ and dried over $Na_2SO_4$. The solvent was removed *in vacuo* and the crude product was purified using column chromatography (alumina, $CH_2Cl_2$/EtOAc as eluent). When applicable, deviations from this general protocol are given below.[3]

[3] (a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.*, **2002**, *41*, 2596; T. R. Chan, R. Hilgraf, K. B. Sharpless, V. V. Fokin, *Org. Lett.*, **2004**, *6*, 2853.

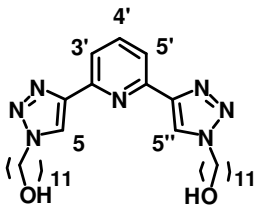
***2,6-Bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine, (tripy, $R^1 = C_{10}H_{21}$)***




Following the general procedure, sodium azide (184 mg, 2.83 mmol), 1-bromodecane (0.49 mL, 522 mg, 2.36 mmol), $CuSO_4 \times 5\ H_2O$ (39 mg, 0.16 mmol), sodium ascorbate (312 mg, 1.57 mmol) and 2,6-diethynylpyridine (100 mg, 0.79 mmol) in DMSO (15 mL) were reacted to yield the desired product as a white solid (369 mg, 95%) after column chromatography (alumina, $CH_2Cl_2$/EtOAc as eluent).

$^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.21 (s, 2H, $H^{5,5''}$), 8.06 (d, $^3J$ = 7.6 Hz, 2H, $H^{3',5'}$), 7.87 (t, $^3J$ = 7.6 Hz, 1H, $H^{4'}$), 4.42 (t, $^3J$ = 7.2 Hz, 4H, $H^{alkyl}$), 1.97 ($m_c$, 4H, $H^{alkyl}$), 1.40–1.25 (m, 28H, $H^{alkyl}$), 0.88 (t, $^3J$ = 6.8 Hz, 6H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 150.3, 148.1, 137.6, 121.9, 118.8, 50.5, 31.8, 30.2, 29.5, 29.4, 29.2, 29.0, 26.4, 22.6, 13.8 ppm. MS (MALDI-TOF, dithranol): *m/z* = 494.59 ($[M + H]^+$). Elem. anal. calcd. for $C_{29}H_{47}N_7$ (493.73): C, 70.55%; H, 9.59%; N, 19,86%; found: C, 70.42%; H, 9.80%; N, 19.85%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 303 (10,000) nm.

***2,6-Bis(11-undecanol-1-yl-1H-1,2,3-triazol-4-yl)pyridine, (tripy, $R^1 = C_{11}H_{22}OH$)***

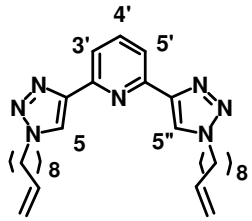



Following the general procedure, sodium azide (184 mg, 2.83 mmol), 11-bromo-1-undecanol (593 mg, 2.36 mmol), $CuSO_4 \times 5\ H_2O$ (25 mg, 0.16 mmol), sodium ascorbate (312 mg, 1.57 mmol) and 2,6-diethynylpyridine (100 mg, 0.79 mmol) were reacted at room temperature for 24 h. Due to the decreased solubility of the product, a modified workup was employed: After precipitation of the crude product with water (10 mL) and subsequent filtration, washing thoroughly with water (200 mL) and acetone (3 × 10 mL), the remaining copper salts were removed by refluxing the crude product with an excess of hydroxyethylenediaminetriacetic acid (HEDTA) in dichloromethane/methanol (25 mL, 2:1 ratio) for 2 h. The solution was concentrated *in vacuo* and water (20 mL) was added. The precipitate was filtered and

susequently washed thoroughly with water (25 mL), acetone (2 mL) and diethyl ether (5 mL) to afford the desired product as a white powder (297 mg, 68%).

$^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.20 (s, 2H, $H^{5,5''}$), 8.06 (d, $^3J$ = 8 Hz, 2H, $H^{3',5'}$), 7.87 (t, $^3J$ = 8 Hz, 1H, $H^{4'}$), 4.43 (t, $^3J$ = 7.2 Hz, 4H, $H^{alkyl}$), 3.58 ($m_c$, 4H, $H^{alkyl}$), 1.99 ($m_c$, 4H, $H^{alkyl}$), 1.53 (br s, 2H, $H^{OH}$), 1.38–1.30 (m, 32H, $H^{alkyl}$) ppm. A $^{13}$C NMR spectrum was not measured due to the low solubility. MS (MALDI-TOF, dithranol): *m/z* = 554.37 ($[M + H]^+$). Elem. anal. calcd. for $C_{31}H_{51}N_7O_2$ (553.78): C, 67.23%; H, 9.28%; N, 17.7%; found: C, 67.37%; H, 9.53%; N, 17.52%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 303 (8,000) nm.

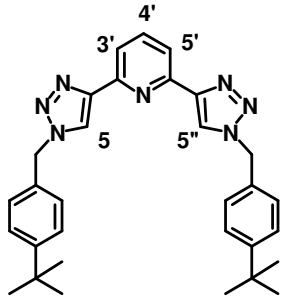
***2,6-Bis(1-(10-decenyl)-1H-1,2,3-triazol-4-yl)pyridine (tripy, $R^1 = C_8H_{16}CH{=}CH_2$)***




Following the general procedure, sodium azide (184 mg, 2.83 mmol), 10-bromo-1-decene (0.47 mL, 517 mg, 2.36 mmol), $CuSO_4 \times 5\ H_2O$ (39 mg, 0.16 mmol), sodium ascorbate (312 mg, 1.57 mmol) and 2,6-diethynylpyridine (100 mg, 1.57 mmol) were reacted at room temperature for 18 h to yield the desired product as a white solid (218 mg, 56%) after gel filtration (alumina, dichloromethane) and size exclusion chromatography (Bio-Beads SX-8, $CH_2Cl_2$ as eluent).

$^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.26 (s, 2H, $H^{5,5''}$), 8.08 (d, $^3J$ = 8.0 Hz, 2H, $H^{3',5'}$), 7.87 (t, $^3J$ = 8.0 Hz, 1H, $H^{4'}$), 5.87–5.77 (m, 2H, $H^{olefin}$), 5.02–4.91 (m, 4H, $H^{olefin}$), 4.38 (t, $^3J$ = 7.2 Hz, 4H, N-C$H_2$), 2.04 ($m_c$, C$H_2$-CH=CH$_2$, 4H), 1.92 ($m_c$, 4H, N-CH$_2$-C$H_2$), 1.40–1.29 (m, 20H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 150.3, 148.1, 139.2, 137.7, 122.0, 118.8, 113.9, 50.4, 33.7, 30.2, 29.2, 29.0, 28.9, 28.8, 26.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 490.19 ($[M + H]^+$). Elem. anal. calcd. for $C_{29}H_{43}N_7$ (489.70): C, 71.13%; H, 8.85%; N, 20.02%; found: C, 71.08%; H, 9.01%; N, 20.04%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 302 (11,000), 240 (30,500) nm.

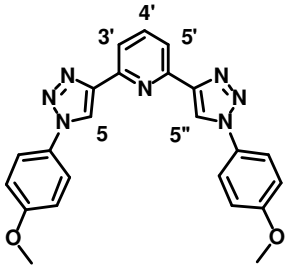
***2,6-Bis(1-(4-$^t$butyl)benzyl-1H-1,2,3-triazol-4-yl)pyridine (tripy, $R^1$ = 4-$^t$Bu-$C_6H_4$-$CH_2$)***




Following the general procedure, sodium azide (184 mg, 2.83 mmol), 4-*t*butyl-benzylbromide (0.43 mL, 536 mg, 2.36 mmol), $CuSO_4 \times 5\ H_2O$ (39 mg, 0.16 mmol), sodium ascorbate (312 mg, 1.57 mmol) and 2,6-diethynylpyridine (100 mg, 1.57 mmol) were reacted in to yield the desired product as a white solid (367 mg, 92%) after column chromatography (alumina, $CH_2Cl_2$, gradient with EtOAc as eluent).

$^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.10 (s, 2H, $H^{5,5''}$), 8.05 (d, $^3J$ = 8 Hz, 2H, $H^{3',5'}$), 7.86 (t, $^3J$ = 8 Hz, 1H, $H^{4'}$), 7,42 (d, $^3J$ = 8.4 Hz, 2H, $H^{AA'/BB'}$), 7.27 (d, $^3$J = 8.4 Hz, 2H, $H^{BB'/AA'}$), 5.55 (s, 4H, C$H_2$), 1.32 (s, 18H, C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CH_2Cl_2$): $\delta$ = 151.9, 150.1, 148.5, 137.6, 131.9, 127.8, 126.0, 122.0, 118.9, ~52 (with solvent), 34.5, 31.0 ppm. MS (MALDI-TOF, dithranol): *m/z* = 506.18 ([M + H]$^+$). Elem. anal. calcd. for $C_{31}H_{35}N_7$ (505.66): C, 73.63%; H, 6.98%; N, 19.39%; found: C, 73.46%; H, 6.86%; N, 19.34%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 303 (10,000) nm.

***2,6-Bis(1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine, (tripy, $R^1$ = 4-MeO-$C_6H_4$)***



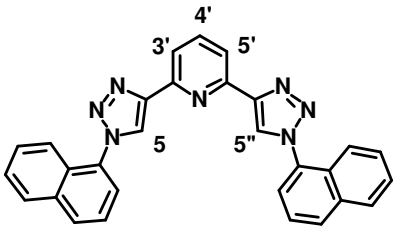

A 50 mL two-neck round bottom flask was equipped with a magnetic stirrer, an argon inlet and a reflux condenser and was loaded with ethanol/water (15 mL, 7:3 ratio), 4-bromoanisole (0.3 mL, 442 mg, 2.36 mmol, 3 equiv.), CuI (45 mg, 0.24 mmol, 10 mol-%), sodium ascorbate (23 mg, 0.12 mmol, 5 mol-%), *N*,*N*'-dimethylethylendiamine (0.04 mL, 31 mg, 0.354 mmol, 15 mol-%) and sodium azide (307 mg, 4.72 mmol).[4] Stirring at room

[4] C.-Z. Tao, X. Cui, J. Li, A.-X. Liu, L. Liu, Q.-X. Guo, *Tetrahedron Lett.* **2007**, *48*, 3525.

temperature under argon for 30 min resulted in a blue solution. After refluxing the reaction micture under argon for 2 h, further sodium ascorbate (23 mg) and 2,6-diethynylpyridine (100 mg, 0.79 mmol) were added. The reaction mixture was refluxed for 4 h and then stirred at room temperature for 12 h. The workup (see the General Procedure above), followed by gel filtration (silica, $CH_2Cl_2$/EtOAC (3:1 ratio) as eluent) and reprecipitation into diethyl ether yielded the desired product (215 mg, 62%).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.58 (s, 2H, $H^{5,5''}$), 8.19 (d, $^3J$ = 7.6 Hz, 2H, $H^{3',5'}$), 7.92 (t, $^3J$ = 8 Hz, 1H, $H^{4'}$), 7.72 (d, $^3J$ = 8.8 Hz, 2H, $H^{AA'/BB'}$), 7.04 (d, $^3J$ = 8.8 Hz, 2H, $H^{BB'/AA'}$), 3.88 (s, 6H, $H^{methoxy}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.0, 149.5, 148.0, 138.4, 130.4, 122.2, 120.7, 119.9, 114.8, 55.7 ppm. MS (MALDI-TOF, dithranol): *m/z* 426.29 ($[M + H]^+$). Elem. anal. calcd. for $C_{29}H_{19}N_7O_2$ (425.44): C, 64.93%; H, 4.50%; N, 23.05%; found: C, 65.02%; H, 4.70%; N, 23.18%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 303 (8,000) nm.

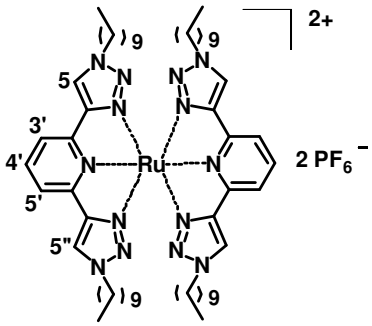
***2,6-Bis(1-(naphth-1-yl)-1H-1,2,3-triazol-4-yl)pyridine (tripy, $R^1$ = naphth-1-yl)***




1-Naphthylboronic acid (406 mg, 2.36 mmol, 3 equiv.) and sodium azide (184 mg, 2.83 mmol, 3.6 equiv.) were dissolved in methanol (15 mL). After addition of $CuSO_4 \times 5\ H_2O$ (38 mg, 0.24 mmol) the resulting brown solution was stirred at room temperature for 12 h with the flask open to the air. The obtained green solution containing the 1-azidonaphthalene was transferred into a 20 mL microwave vail, water (5 mL), an aqueous solution of sodium ascorbate (474 mg, 2.39 mmol) and 2,6-diethynylpyridine (100 mg, 0.79 mmol) were added and the mixture was heated under microwave irradiation at 100 °C for 2 h. Subsequently, aqueous solutions of $CuSO_4 \times 5\ H_2O$ (25 mg, 0.16 mmol) and sodium ascorbate (312 mg, 1.57 mmol) were added and the mixture was heated further under microwave irradiation at 100 °C for 2 h. After the usual workup (see general procedure for the click reaction with aliphatic azides) gel filtration (alumina, EtOAc as eluent), column chromatography (alumina, $CH_2Cl_2$, gradient with EtOAc as eluent) and precipitation with pentane yielded the product as an off-white solid (226 mg, 62%).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.57 (s, 2H, $H^{5,5''}$), 8.29 (d, $^3J$ = 8 Hz, 2H, $H^{3',5'}$), 7.99–7.91 (m, 5H, $H^{4',naphthyl}$), 7.70 (d, $^3J$ = 8.4 Hz, 2H, $H^{naphthyl}$), 7.61-7.48 (m, 8H, $H^{naphthyl}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 150.0, 148.3, 138.0, 134.1, 134.0, 130.5, 128.4, 128.3, 127.9, 127.1, 125.0, 123.5, 122.3, 119.7 ppm. MS (MALDI-TOF, dithranol): *m/z* = 612.25 ([M + H]$^+$). Elem. anal. calcd. for $C_{29}H_{19}N_7$ (465.51): C, 74.82%; H, 4.11%; N, 21.06%; found: C, 74.73%; H, 4.26%; N, 21.32%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 294 (22,000) nm.

***[Ru(R$^1$-tripy)$_2$](PF$_6$)$_2$ (R$^1$ = C$_{10}$H$_{21}$): Bis[2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine] ruthenium(II) hexafluorophosphate (8)***



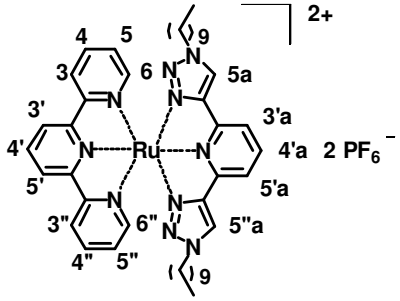

A 100 mL two-neck round bottom flask with a magnetic stirrer and a reflux condenser was securated three times. Degassed methanol (5 mL) and ethylene glycol (10 mL) were added. In the counterflow of argon, $Ru(DMSO)_4Cl_2$ (38 mg, 0.08 mmol)[5] and a concentrated solution of **R$^1$-tripy** (R$^1$ = $C_{10}H_{21}$, 85 mg, 0.17 mmol) in degassed acetone were added. The suspension was refluxed under argon for 2.5 h. After cooling to room temperature, water (15 mL) and then an excess of $NH_4PF_6$ (100 mg) was added. The formed yellow precipitate was filtered off, thoroughly washed with water (10 mL), dissolved in $CH_2Cl_2$ and dried over $Na_2SO_4$. The solution was concentrated *in vacuo* and the crude product was purified by size exclusion column chromatography (BioBeads SX-3, $CH_2Cl_2$ as eluent) to yield **8** as a yellow powder (89 mg, 75%).

$^1$H NMR (400 MHz, $d_6$-acetone): $\delta$ = 9.18 (s, 4H, $H^{5,5''}$), 8.50–8.41 (m, 6H, $H^{3',4',5'}$), 4.40 (t, $^3J$ = 7.4 Hz, 8H, $H^{alkyl}$), 1.77 (m, 8H, $H^{alkyl}$), 1.30–1.00 (m, 56H, $H^{alkyl}$), 0.86 (t, $^3J$ = 7.0 Hz, 12H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 150.7, 149.4, 137.7, 125.2, 119.8, 52.1, 31.6, 29.2, 29.1, 29.0, 28.9, 28.3, 25.5, 22.4, 13.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1233.59 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{58}H_{94}F_{12}N_{14}P_2Ru$ (1378.46): C, 50.54%; H, 6.87%; N, 14.23%; found: C, 50.50%; H, 6.91%; N, 13.94%. UV-vis ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 394 (15,500), 285 (60,500), 255 (27,000), 226 (45,500) nm.

***General procedure for the synthesis of the complexes [($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$***

To a suspension of ($R^2$-tpy)$RuCl_3$ (1 equiv.)[2] and **$R^1$-tripy** (1 equiv.) in methanol (15 mL) *N*-ethyl morpholine (10 drops) was added and the reaction mixture was stirred under reflux for 24 h. The mixture was filtered hot and then an excess of $NH_4PF_6$ (100 mg) was added. After stirring for 30 min, water (10 mL) was added and the formed precipitate was filtered off and washed thoroughly with water (10 mL). The precipitate was dissolved in $CH_2Cl_2$ and the solution evaporated after drying over $Na_2SO_4$ to give the desired complex. When applicable, deviations from this general protocol are given below.

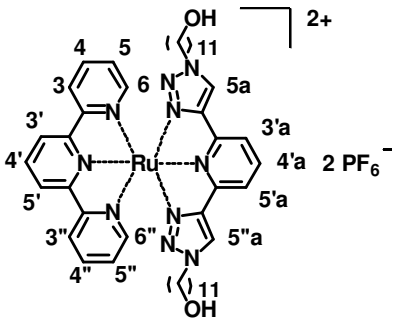
***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = $C_{10}H_{21}$, $R^2$ = H): [2,6-Bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine] [2,2':6',2''-terpyridine] ruthenium(II) hexafluorophosphate (1)***




Following the general procedure, ($R^2$-tpy)$RuCl_3$ ($R^2$ = H,[2a] 44 mg, 0.1 mmol) and **$R^1$-tripy** ($R^1$ = $C_{10}H_{21}$, 49 mg (0.1 mmol) were reacted to yield **1** (91 mg, 81%) as an orange-red solid after reprecipitation into diethyl ether.

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.68 (s, 2H, $H^{5a,5''a}$), 8.64 (d, $^3J$ = 8 Hz, 2H, $H^{3',5'}$), 8.46 (d, $^3J$ = 8 Hz, 2H, $H^{3',3''}$, 2H), 8.40–8.31 (m, H4, $H^{4',3'a,4'a,5'a}$), 7.96 (dt, $^3J$ = 8 Hz, 2H, $H^{4',4''}$), 7.47 (dd, $^3J$ = 6.4 Hz, 2H, $H^{6',6''}$), 7.25 (dt, $^3J$ = 6.6 Hz, 2H, $H^{5',5''}$), 4.18 (t, $^3J$ = 7.2 Hz, 4H, $H^{alkyl}$), 1.65 ($m_c$, 4H, $H^{alkyl}$), 1.30–0.93 (m, 28H, $H^{alkyl}$), 0.88 (t, $^3J$ = 7.0 Hz, 6H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 158.1, 156.5, 152.9, 149.6, 149.3, 138.1, 137.5, 136.1, 127.6, 125.5, 124.0, 122.8, 120.6, 52.1, 31.6, 29.1, 29.0, 28.9, 28.98, 28.3, 25.5, 22.4, 13.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 973.46 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{44}H_{58}F_{12}N_{10}P_2Ru$ (1118.00): C, 47.27%; H, 5.23%; N, 12.53%; found: C, 47.46%; H, 5.44%; N, 12.46%. UV-vis ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 432 (11,500), 356 (5,500), 303 (39,000), 286 (41,500), 226 (41,500) nm.

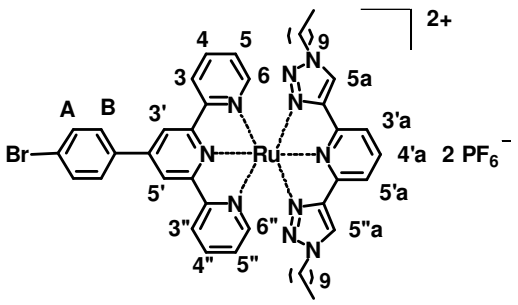
***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = $C_{11}H_{22}OH$, $R^2$ = H): [2,6-Bis(11-undecanol-1-yl-1H-1,2,3-triazol-4-yl)pyridine] [2,2':6',2''-terpyridine] ruthenium(II) hexafluorophosphate (2)***




Following the general procedure, ($R^2$-tpy)$RuCl_3$ ($R^2$ = H,[2a] 60 mg, 0.14 mmol) and **$R^1$-tripy** ($R^1$ = $C_{11}H_{22}OH$, 75 mg, 0.14 mmol) were reacted to yield **2** (144 mg, 90%) as an orange-red solid.

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.66 (d, $^3J$ = 8 Hz, 2H, $H^{3',5'}$, 2H), 8.64 (s, 2H, $H^{5a,5''a}$), 8.47 (d, $^3J$ = 8 Hz, 2H, $H^{3,3''}$), 8.33 ($m_c$, 4H, $H^{4',3'a,4'a,5'a}$), 7.96 (dt, $^3J$ = 8 Hz, 2H, $H^{4',4''}$), 7.45 (dd, $^3J$ = 5.2 Hz, 2H, $H^{6',6''}$), 7.25 (dt, $^3J$ = 6.6 Hz, 2H, $H^{5',5''}$), 4.17 (t, $^3J$ = 7.0 Hz, 4H, $H^{alkyl}$), 3.48 ($m_c$, 4H, $H^{alkyl}$), 2.47 (t, $^3J$ = 5.2 Hz, 2H, $H^{OH}$), 1.64 ($m_c$, 4H, $H^{alkyl}$), 1.48 ($m_c$, 4H, $H^{alkyl}$), 1.35–0.90 (m, 28H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 158.2, 156.5, 152.8, 149.6, 149.3, 138.1, 137.5, 136.1, 127.5, 125.4, 124.0, 122.8, 120.6, 61.6, 52.1, 32.6, 29.2, 29.1, 29.0, 28.9, 28.8, 28.2, 25.6, 25.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1033.33 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{46}H_{62}F_{12}N_{10}O_2P_2Ru$ (1178.05): C, 46.90%; H, 5.30%; N, 11.89%; found: C, 46.96%; H, 5.66%; N, 11.82%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 435 (10,000), 356 (4,500), 305 (36,000), 287 (37,500) nm.

***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = $C_{10}H_{21}$, $R^2$ = 4-Br-$C_6H_4$): [2,6-Bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine] [4'-(4-bromophenyl)-2,2':6',2''-terpyridine] ruthenium(II) hexafluorophosphate (3)***

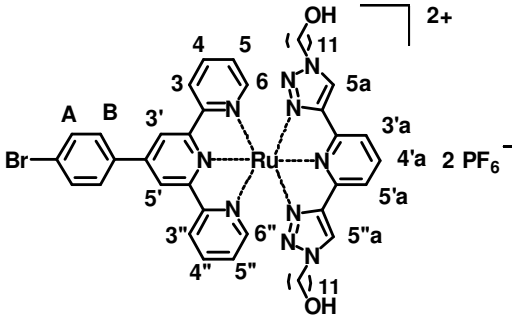



Following the general procedure, ($R^2$-tpy)$RuCl_3$ ($R^2$ = 4-Br-$C_6H_4$,[2b] 98 mg, 0.16 mmol) and **$R^1$-tripy** ($R^1$ = $C_{10}H_{21}$, 81 mg (0.16 mmol) were reacted to yield **3** (111 mg, 53%) as orange-red solid after subsequent column chromatography (alumina, $CH_2Cl_2$/acetone, elution of the

product with $CH_2Cl_2$/methanol, 1:1), gel filtration (silica, $CH_3CN$, elution of the product with $CH_3CN$/water 9:1, sat. with $KNO_3$) and reprecipitation into diethyl ether.

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.86 (s, 2H, $H^{5a,5''a}$), 8.68 (s, 2H, $H^{3',5'}$), 8.53 (d, $^3J$ = 8 Hz, 2H, $H^{3',3''}$), 8.37 ($m_c$, 3H, $H^{3'a4'a,5'a}$), 8.09 (d, $^3J$ = 8.4 Hz, 2H, $H^{AA'/BB'}$), 7.95 (dt, $^3J$ = 8 Hz, 2H, $H^{4',4''}$), 7.86 (d, $^3J$ = 8.4 Hz, 2H, $H^{BB'/AA'}$), 7.50 (dd, $^3J$ = 5.6 Hz, 2H, $H^{6',6''}$), 7.27 (dt, $^3J$ = 6.8 Hz, 2H, $H^{5',5''}$), 4.19 (t, $^3J$ = 7.2 Hz, 4H, $H^{alkyl}$), 1.66 ($m_c$, 4H, $H^{alkyl}$), 1.30–0.93 (m, 28H, $H^{alkyl}$), 0.86 (t, $^3J$ = 7.0 Hz, 6H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 158.2, 156.8, 153.0, 149.6, 149.3, 147.1, 138.1, 137.6, 135.7, 132.6, 129.7, 127.6, 125.5, 124.5, 124.2, 120.6, 120.5, 52.1, 31.6, 29.1, 29.0, 28.9, 28.2, 25.5, 22.4, 13.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1129.05 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{50}H_{61}BrF_{12}N_{10}P_2Ru$ (1272.99): C, 47.18%; H, 4.83%; N, 11%; found: C, 47.11%; H, 4.63%; N, 10.91%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 456 (16,500), 438 (16,000), 356 (6,500), 287 (67,000) nm.

***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = $C_{11}H_{22}OH$, $R^2$ = 4-Br-$C_6H_4$): [2,6-Bis(11-undecanol-1-yl-1H-1,2,3-triazol-4-yl)pyridine] [4'-(4-bromophenyl)-2,2':6',2''-terpyridine] ruthenium(II) hexafluorophosphate (4)***

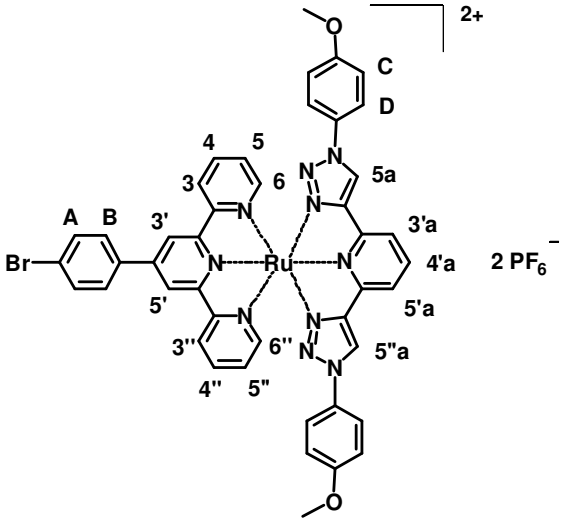



Following the general procedure, ($R^2$-tpy)$RuCl_3$ ($R^2$ = 4-Br-$C_6H_4$,[2b] 97 mg, 0.16 mmol) and **$R^1$-tripy** ($R^1$ = $C_{11}H_{22}OH$, 90 mg, 0.16 mmol) were reacted to yield **4** (91 mg, 42%) as an orange-red solid after purification by column chromatography (alumina, $CH_2Cl_2$/acetone 1:1).

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.89 (s, 2H, $H^{5a,5''a}$), 8.66 (s, 2H, $H^{3',5'}$), 8.59 (d, $^3J$ = 8 Hz, 2H, $H^{3',3''}$), 8.35 ($m_c$, 3H, $H^{3'a,4'a,5'a}$), 8.11 (d, $^3J$ = 8.4 Hz, 2H, $H^{AA'/BB'}$), 7.97 (dt, $^3J$ = 8 Hz, 2H, $H^{4',4''}$), 7.91 (d, $^3J$ = 8.4 Hz, 2H, $H^{BB'/AA'}$), 7.48 (dd, $^3J$ = 5.6 Hz, 2H, $H^{6',6''}$), 7.26 (dt, $^3J$ = 6.8 Hz, 2H, $H^{5',5''}$), 4.18 (t, $^3J$ = 7.0 Hz, 4H, $H^{alkyl}$), 3.47 ($m_c$, 4H, $H^{alkyl}$), 2.47 (t, $^3J$ = 5.4 Hz, 2H, $H^{OH}$), 1.65 ($m_c$, 4H, $H^{alkyl}$), 1.45 ($m_c$, 4H, $H^{alkyl}$), 1.34–0.91 (m, 28H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 158.2, 156.8, 153.0, 149.6, 149.3, 147.1, 138.1, 137.6, 135.7, 132.6, 129.7, 127.6, 125.5, 124.5, 124.2, 120.6, 120.5, 61.6, 52.1, 32.6, 29.2, 29.1, 29.0, 28.9, 28.2, 25.6, 25.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1187.14 ([M -

$PF_6]^+$). Elem. anal. calcd. for $C_{52}H_{65}BrF_{12}N_{10}O_2P_2Ru$ (1333.04): C, 46.85%; H, 4.91%; N, 10.51%; found: C, 46.63%; H, 4.99%; N, 10.54%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 456 (16,500), 438 (16,000), 356 (6,500), 287 (67,000) nm.

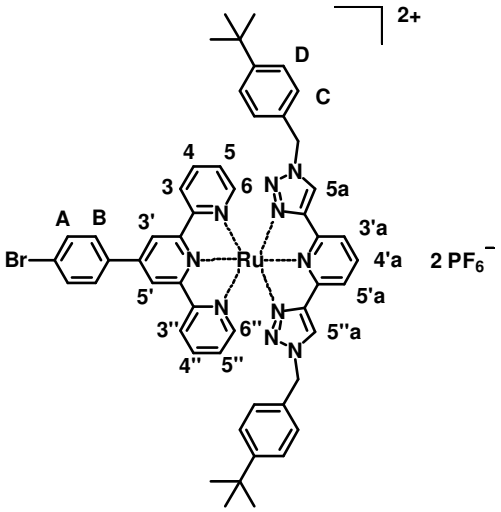
***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = 4-MeO-$C_6H_4$, $R^2$ = 4-Br-$C_6H_4$): [2,6-Bis(1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine] [4'-(4-bromophenyl)-2,2':6',2''-terpyridine] ruthenium(II) hexafluorophosphate (5)***




Following the general procedure, ($R^2$-tpy)$RuCl_3$ ($R^2$ = 4-Br-$C_6H_4$,[2b] 135 mg, 0.23 mmol) and **$R^1$-tripy** ($R^1$ = 4-MeO-$C_6H_4$, 100 mg, 0.23 mmol) were reacted to yield **5** (145 mg, 53%) as an orange-red solid after purification by column chromatography (silica, $CH_3CN$/water 9:1, sat. with $KNO_3$). Single crystals were obtained by slow diffusion of diethyl ether into a concentrated solution of **5** in $CH_3CN$.

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 9.08 (s, 2H, $H^{5a,5''a}$), 8.92 (s, 2H, $H^{3',5'}$), 8.62 (d, $^3J$ = 8.0 Hz, 2H, $H^{3',3''}$), 8.43 ($m_c$, 3H, $H^{3'a,4'a,5'a}$), 8.12 (d, $^3J$ = 8.4 Hz, 2H, $H^{AA'/BB'}$), 8.02 (dt, $^3J$ = 8.0 Hz, 2H, $H^{4',4''}$), 7.93 (d, $^3J$ = 8.4 Hz, 2H, $H^{BB'/AA'}$), 7.57 (dd, $^3J$ = 5.6 Hz, 2H, $H^{6',6''}$), 7.44 (d, $^3J$ = 9.2 Hz, 2H, $H^{CC'/DD'}$), 7.30 (dt, $^3J$ = 6.4 Hz, 2H, $H^{5',5''}$), 7.02 (d, $^3J$ = 9.2 Hz, 2H, $H^{DD'/CC'}$), 3.80 (s, 3H, $H^{methoxy}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 160.8, 158.3, 156.8, 153.2, 150.0, 149.5, 147.4, 138.2, 137.8, 135.9, 132.6, 129.7, 129.1, 127.6, 124.4, 124.3, 123.6, 122.4, 120.9, 120.8, 114.9, 55.5 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1061.34 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{44}H_{33}BrF_{12}N_{10}O_2P_2Ru$ (1204.70): C, 43.87%; H, 2.76%; N, 11.63%; found: C, 44.03%; H, 2.84%; N, 11.53%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 456 (14,500), 435 (13,500), 300 (73,000) nm.

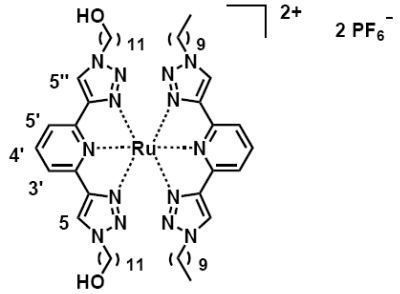
***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = 4-$^t$Bu-$C_6H_4$-$CH_2$, $R^2$ = 4-Br-$C_6H_4$): [2,6-Bis(1-(4-$^t$butyl-benzyl)-1H-1,2,3-triazol-4-yl)pyridine] [4'-(4-bromophenyl)-2,2':6',2''-terpyridine] ruthenium(II) hexafluorophosphate (6)***




Following the general procedure, ($R^2$-tpy)$RuCl_3$ ($R^2$ = 4-Br-$C_6H_4$,[2b] 106 mg, 0.18 mmol), **$R^1$-tripy** ($R^1$ = 4-$^t$Bu-$C_6H_4$-$CH_2$, 90 mg, 0.18 mmol) were reacted to yield **6** as an orange-red solid (66 mg, 28%) after purification by column chromatography (silica, $CH_3CN/H_20$ 9:1, saturated with $KNO_3$).

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.75 (s, 2H, $H^{5a,5''a}$), 8.57 (s, 2H, $H^{3'a,5'a}$), 8.38 (m, 3H, $H^{3',5',4'a}$), 8.12 (d, $^3J$ = 8.0 Hz, 2H, $H^{3,3''}$), 7.81 (d, $^3J$ = 8 Hz, 2H, $H^{AA'/BB'}$), 7.77 (dt, $^3J$ = 8.0 Hz, 2H, $H^{4,4''}$), 7.62 (d, $^3J$ = 8 Hz, 2H, $H^{BB'/AA'}$), 7.48 (dd, $^3J$ = 5.6 Hz, 2H, $H^{6,6''}$), 7.23 (dt, $^3J$ = 6.8 Hz, 2H, $H^{5,5''}$), 7.19 (d, $^3J$ = 8 Hz, 4H, $H^{CC'/DD'}$), 6.98 (d, $^3J$ = 8 Hz, 4H, $H^{DD'/CC'}$), 5.36 (s, 2H, C$H_2$), 1.11 (s, 18H, C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 157.8, 156.8, 153.2, 152.1, 149.7, 149.5, 146.3, 138.1, 137.7, 134.7, 132.6, 130.4, 129.1, 128.1, 127.6, 126.0, 125.9, 124.7, 123.8, 121.0, 119.7, ~55 (with solvent), 34.1, 30.3 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1139.17 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{52}H_{49}BrF_{12}N_{10}P_2Ru$ (1284.92): C, 48.61%; H, 3.84%; N, 10.9%; found: C, 48.4%; H, 4.13%; N, 10.82%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 455 (17,500), 435 (16,500), 357 (6,000), 288 (73,000) nm.

***[($R^1$-tripy)Ru(tripy-$R^{1'}$)]($PF_6$)$_2$ ($R^1$ = $C_{10}H_{21}$, $R^{1'}$ = $C_{11}H_{22}OH$): [2,6-Bis(11-undecanol-1-yl-1H-1,2,3-triazol-4-yl)pyridine] [2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine] ruthenium(II) hexafluorophosphate (6)***




A suspension of $RuCl_3 \times H_2O$ (57 mg, 0.2 mmol) and **$R^1$-tripy** ($R^1$ = $C_{10}H_{21}$, 100 mg, 0.2 mmol) in methanol (40 mL) was refluxed till TLC monitoring indicated the full consumption of the ligand. After 20 h, **$R^{1'}$-tripy** ($R^{1'}$ = $C_{11}H_{22}OH$, 112 mg, 0.2 mmol) and *N*-ethyl morpholine (5 drops) were added and the reaction mixture was refluxed till TLC monitoring indicated also the consumption of the second ligand. After 3 days, the reaction mixture was purified (see General Procedure above) by column chromatography (silica, $CH_3CN$/water 95:5, sat. with $KNO_3$) yielding **6** (165 mg, 57%).

$^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.67 (s, 4H, $H^{5,5''}$), 8.26 ($m_c$, 6H, $H^{3',4',5'}$), 4.23 (t, $^3J$ = 7.2 Hz, 8H, $H^{alkyl}$), 3.49 (t, $^3J$ = 6.4 Hz, 4H, $H^{alkyl}$), 2.51 (s, 1H, $H^{OH}$), 1.70 ($m_c$, 8H, $H^{alkyl}$), 1.47 ($m_c$, 4H, $H^{alkyl}$), 1.30–1.00 (m, 56H, $H^{alkyl}$), 0.89 (t, $^3J$ = 7.2 Hz, 6H, $H^{alkyl}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 150.7, 149.4, 137.8, 125.2, 119.8, 61.6, 52.1, 32.6, 31.6, 29.3, 29.2, 29.1, 29.00, 28.4, 28.3, 25.7, 25.6, 22.4, 13.4 ppm. MS (MALDI-TOF, dithranol): *m/z* = 1293.61 ([M - $PF_6$]$^+$). Elem. anal. calcd. for $C_{60}H_{98}F_{12}N_{14}O_2P_2Ru$ (1438.51): C, 50.10%; H, 6.87%; N, 13.63%; found: C, 50.28%; H, 7.09%; N, 13.37%. UV-vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$/L·mol$^{-1}$·cm$^{-1}$) = 395 (18,000), 286 (63,000), 256 (32,500) nm.

# X-Ray crystallographic data

### *Crystal structure determination*

The intensity data for the compound were collected with a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation. The data were corrected for Lorentz and polarization effects, but not for absorption effects.[5,6] The structure was solved by direct methods (SHELXS[7]) and refined by full-matrix least squares techniques against $Fo^2$ (SHELXL-97[8]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. CCDC-691377 contains the supplementary crystallographic data for **5**. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; deposit@ccdc.cam.ac.uk).

***[($R^2$-tpy)Ru(tripy-$R^1$)]($PF_6$)$_2$ ($R^1$ = 4-MeO-$C_6H_4$, $R^2$ = 4-Br-$C_6H_4$) (5)***

Empirical formula: $C_{44}H_{33}BrN_{10}O_2Ru \cdot 2(F_6P) \cdot 2(C_2H_3N)$,

Color of crystal: red-brown prism

Crystal system: triclinic

Space group: $P\bar{1}$

Crystal size: $0.05 \times 0.04 \times 0.04$ mm$^3$

Data: $\mu$ (Mo-$K_\alpha$) = 12.2 cm$^{-1}$, T = 183 K, F(000) = 1288, 18915 reflections in h(-13/13), k(-20/17), l(-20/21), measured in the range $1.65° \le \Theta \le 27.48°$, completeness $\Theta_{max}$ = 98.2%,11802 independent reflections, $R_{int}$ = 0.0474, 8528 reflections with $F_o > 4\sigma(F_o)$, 707 parameters, 0 restraints, $R1_{obs}$ = 0.0632, $wR^2_{obs}$ = 0.1407, $R1_{all}$ = 0.0984, $wR^2_{all}$ = 0.1576, GOOF = 1.077, largest difference peak and hole: 1.338 / -1.225 e Å$^{-3}$

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[5] COLLECT, Data Collection Software, Nonius B.V., the Netherlands, **1998**.

[6] Z. Otwinowski, W. Minor, *Processing of X-Ray Diffraction Data Collected in Oscillation Mode* in *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, ed. C. W. Carter, R. M. Sweet, pp. 307–326, Academic Press **1997**.

[7] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[8] G. M. Sheldrick, SHELXL-97 (release 97-2), University of Göttingen, Germany, **1997**.

Cell dimensions: a = 10.4011(4) Å

b = 15.6521(7) Å

c = 16.4051(6) Å

α = 101.112(2) °

β = 93.416(3)°

γ = 90.460(2)°

Molecules/cell: Z = 2

Volume: V = 2615.49(18) $Å^3$

Calculated density: $\rho_{calcd.}$ = 1.634 $g \cdot cm^{-3}$

Molecular weight: $M_r$ = 1286.83 $g \cdot mol^{-1}$

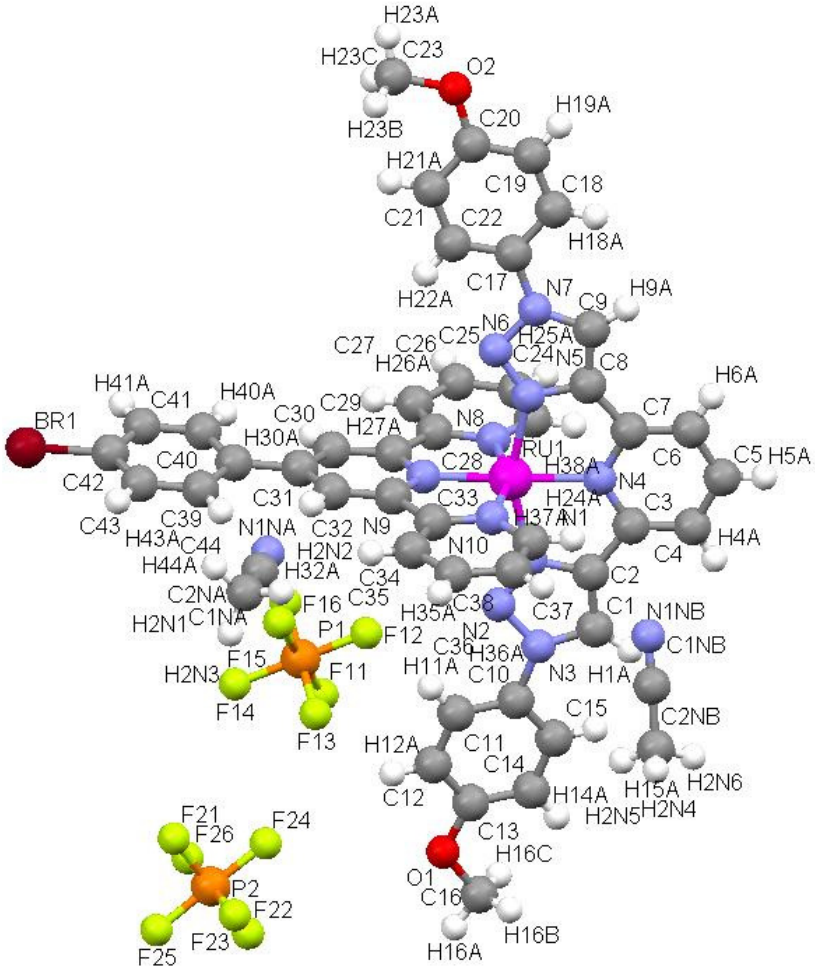


**Figure 1.** Schematic representation of the X-ray crystal structure of **5**, including the $PF_6^-$ counterion and the coordinated $CH_3CN$ molecules.

# $^{1}$H and $^{13}$C NMR spectra

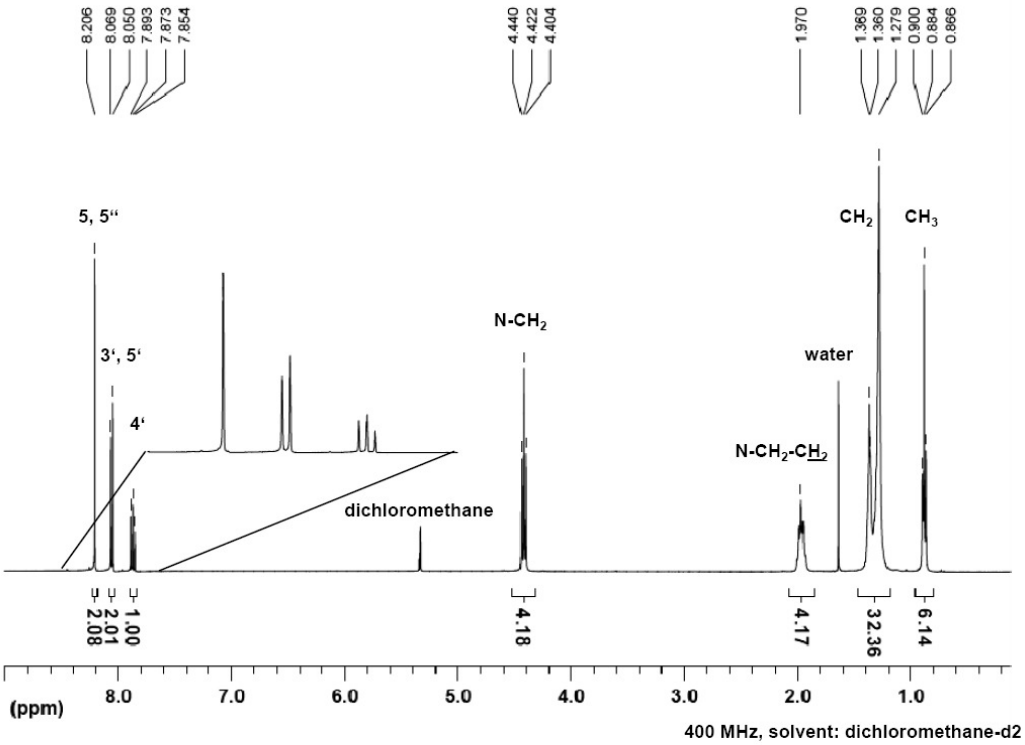


**Figure 2.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$) of **R$^{1}$-tripy** ($R^1 = C_{10}H_{21}$).

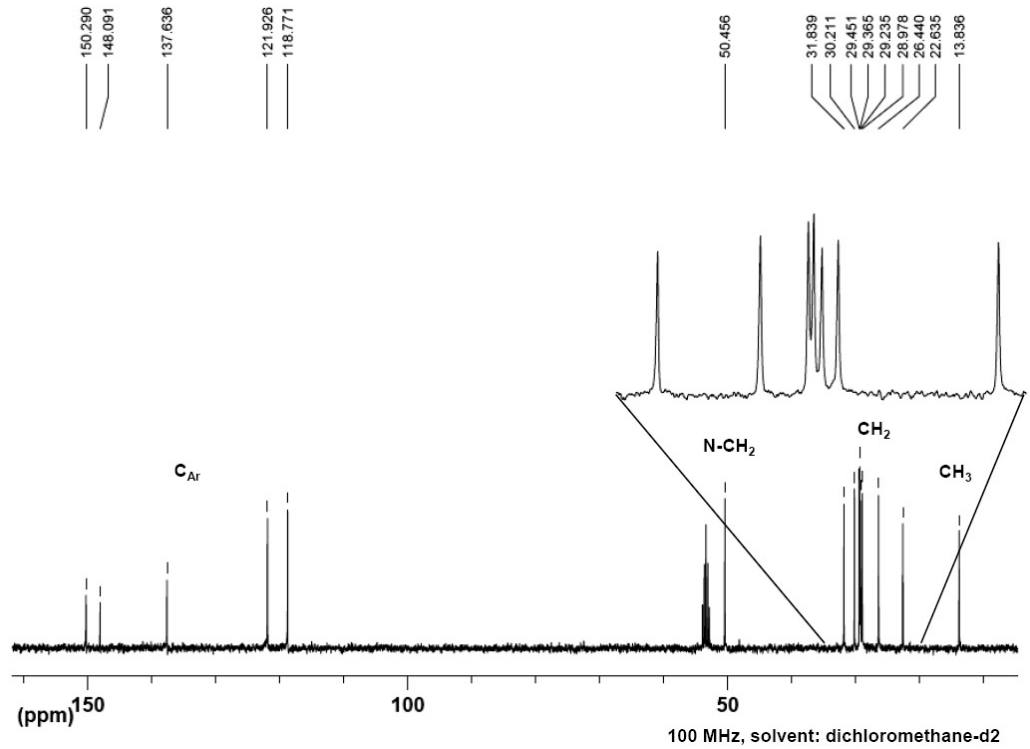


**Figure 3.** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$) of **R$^{1}$-tripy** ($R^1 = C_{10}H_{21}$).

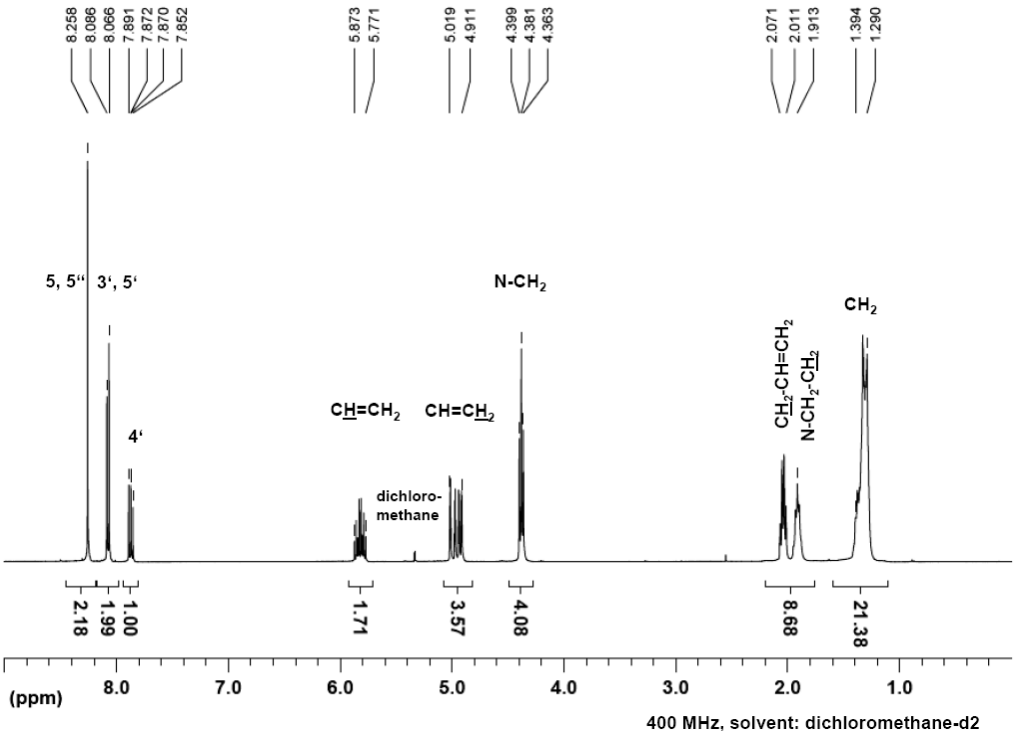


**Figure 4.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$) of **R$^{1}$-tripy** ($R^1 = C_{11}H_{22}OH$).

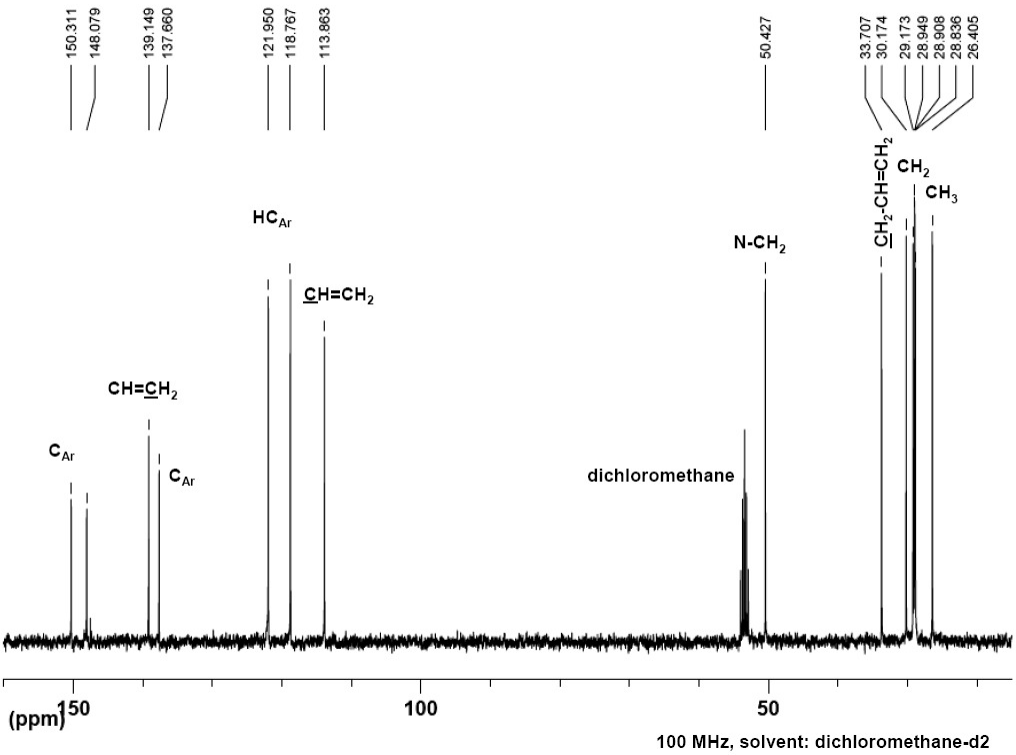


**Figure 5.** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$) of **R$^{1}$-tripy** ($R^1 = C_{11}H_{22}OH$).

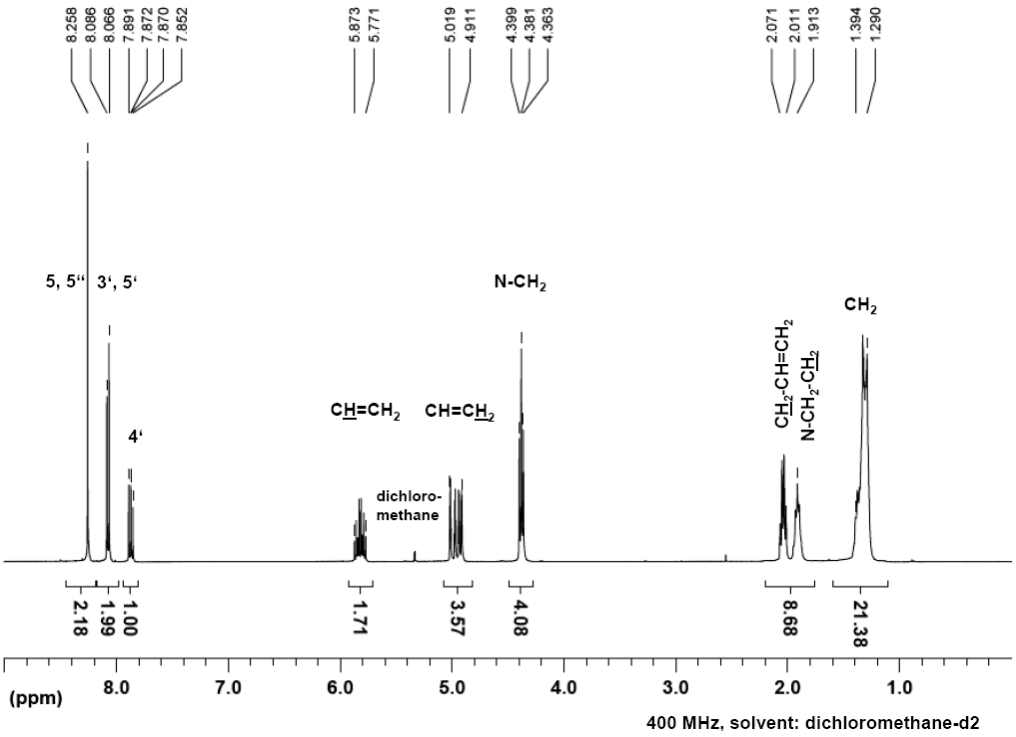


**Figure 6.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$) of **R$^{1}$-tripy** ($R^1 = C_8H_{16}CH{=}CH_2$).

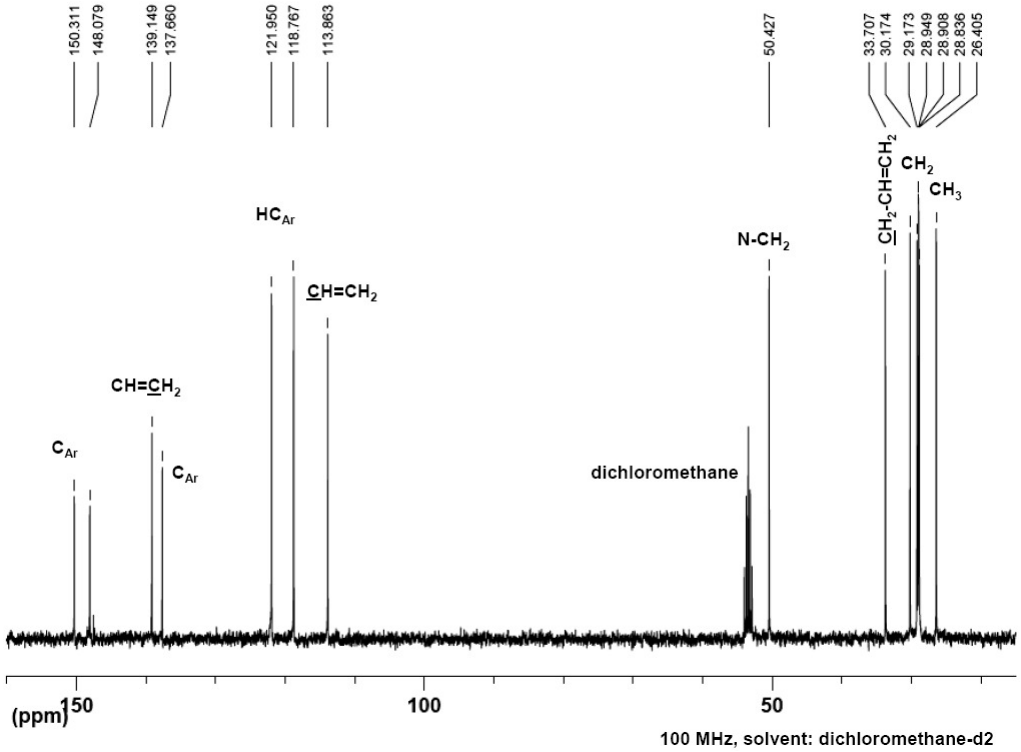


**Figure 7.** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$) of **R$^{1}$-tripy** ($R^1 = C_8H_{16}CH{=}CH_2$).

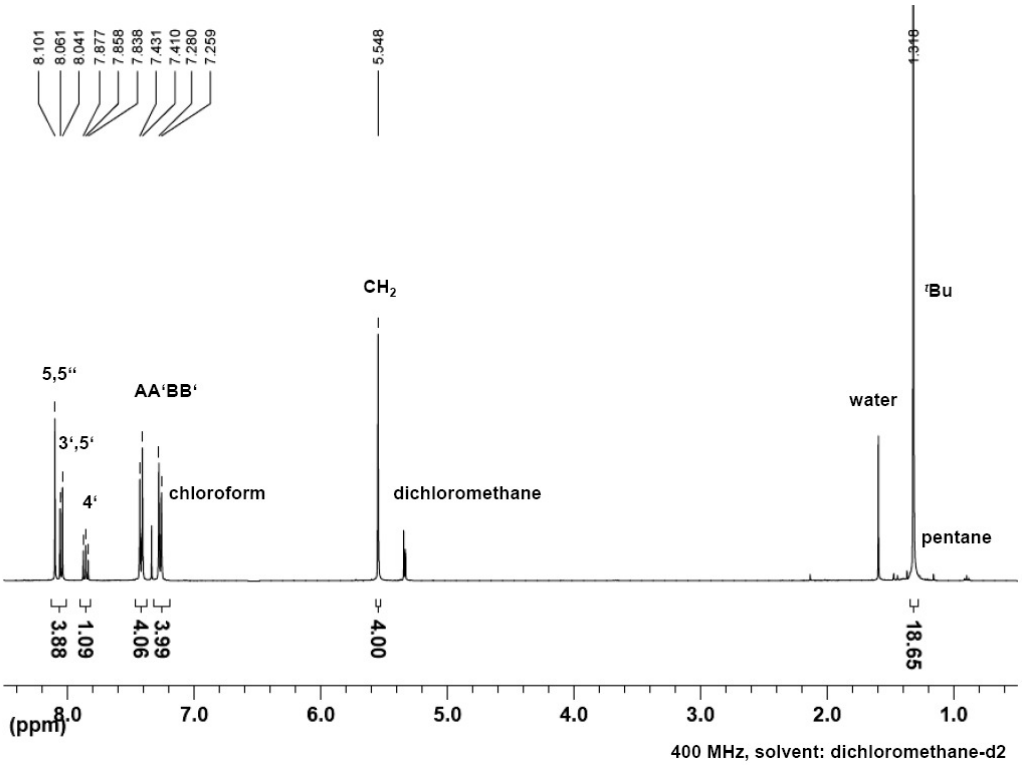


**Figure 8.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$) of **R$^{1}$-tripy** ($R^1$ = 4-$^{t}$Bu-$C_6H_4$-$CH_2$).

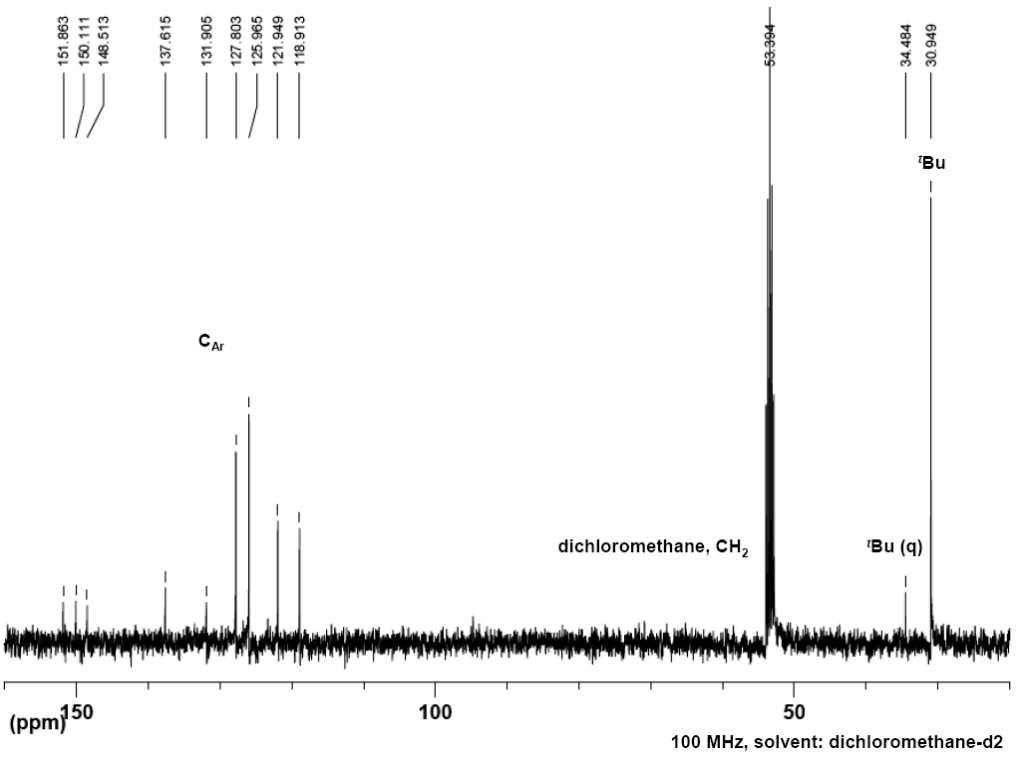


**Figure 9.** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$) of **R$^{1}$-tripy** ($R^1$ = 4-$^{t}$Bu-$C_6H_4$-$CH_2$).

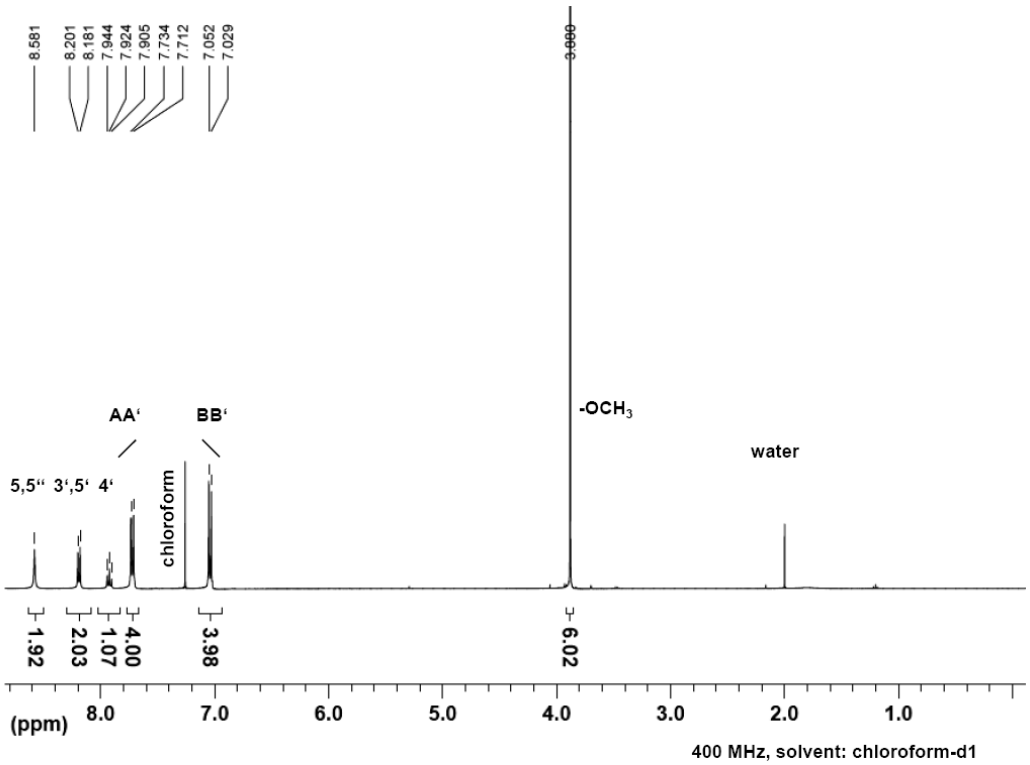


**Figure 10.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **$R^1$-tripy** ($R^1$ = 4-MeO-$C_6H_4$).

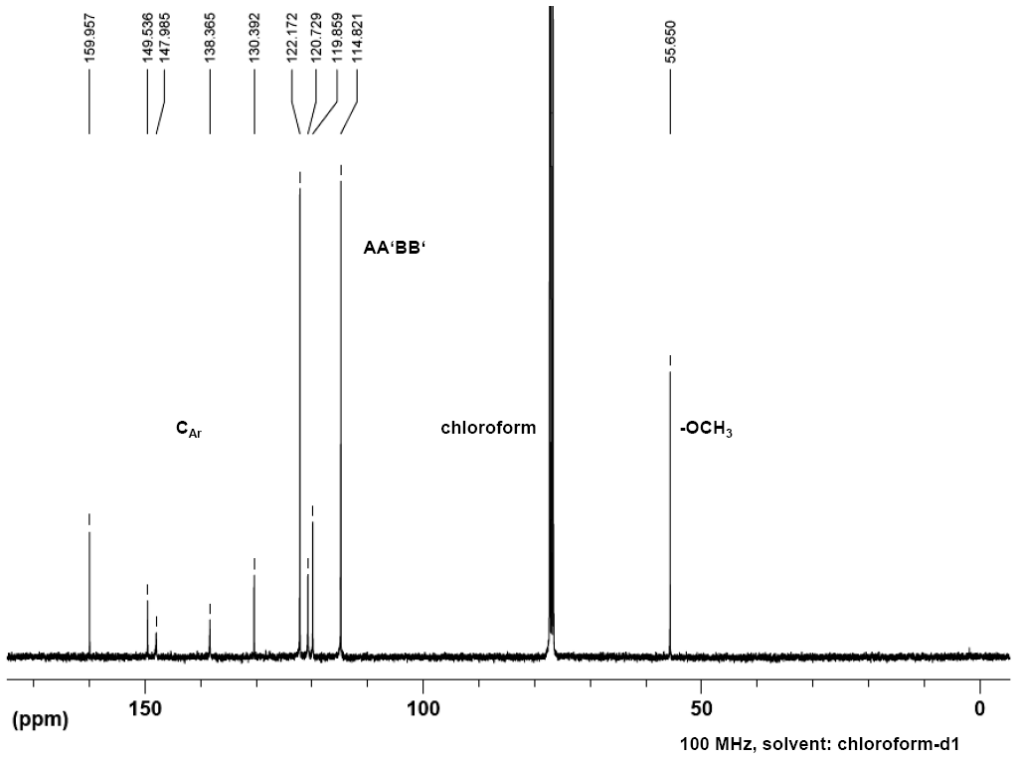


**Figure 11.** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$) of **$R^1$-tripy** ($R^1$ = 4-MeO-$C_6H_4$).

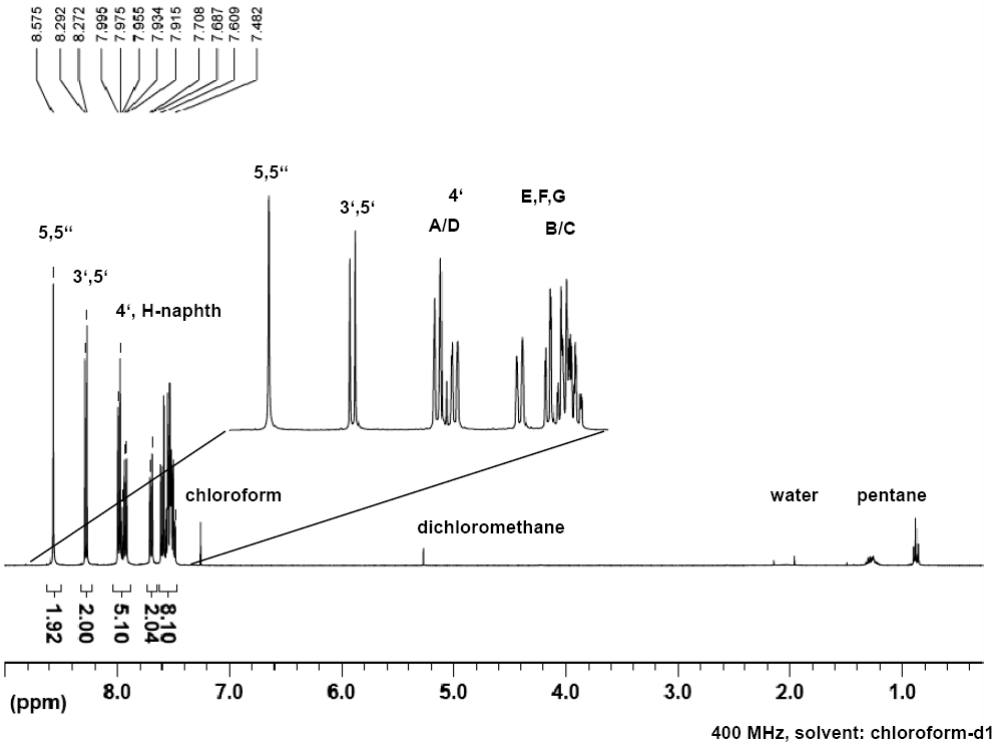


**Figure 12.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **$R^1$-tripy** ($R^1$ = naphth-1-yl).

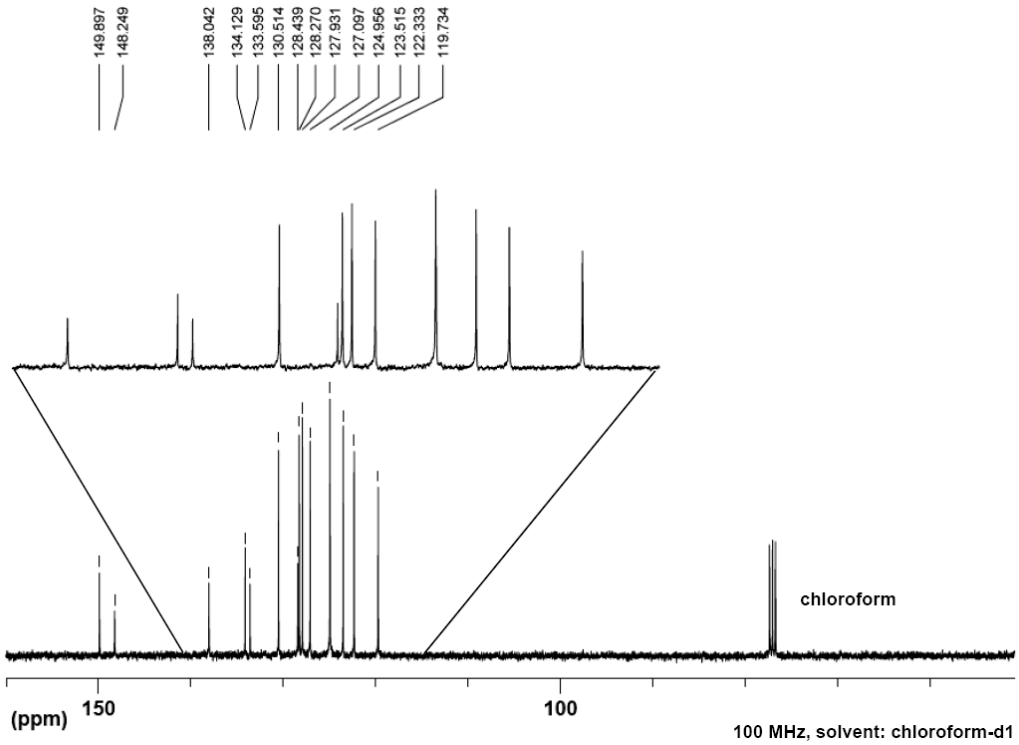


**Figure 13.** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$) of **$R^1$-tripy** ($R^1$ = naphth-1-yl).

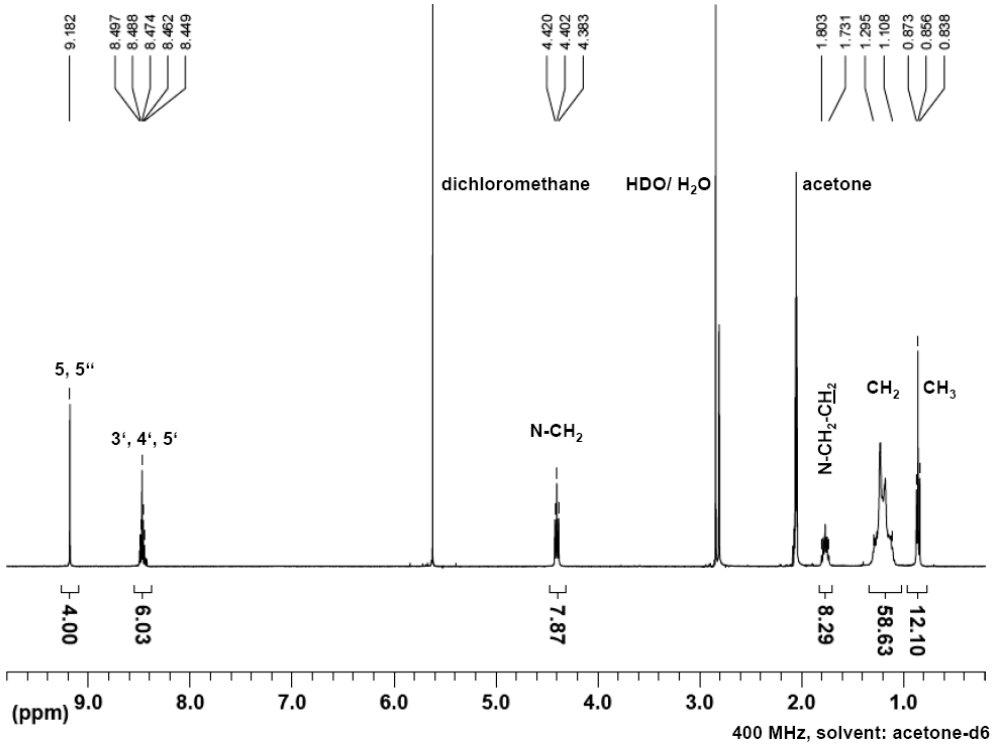


**Figure 14.** $^{1}$H NMR spectrum (400 MHz, $d_6$-acetone) of **9**.

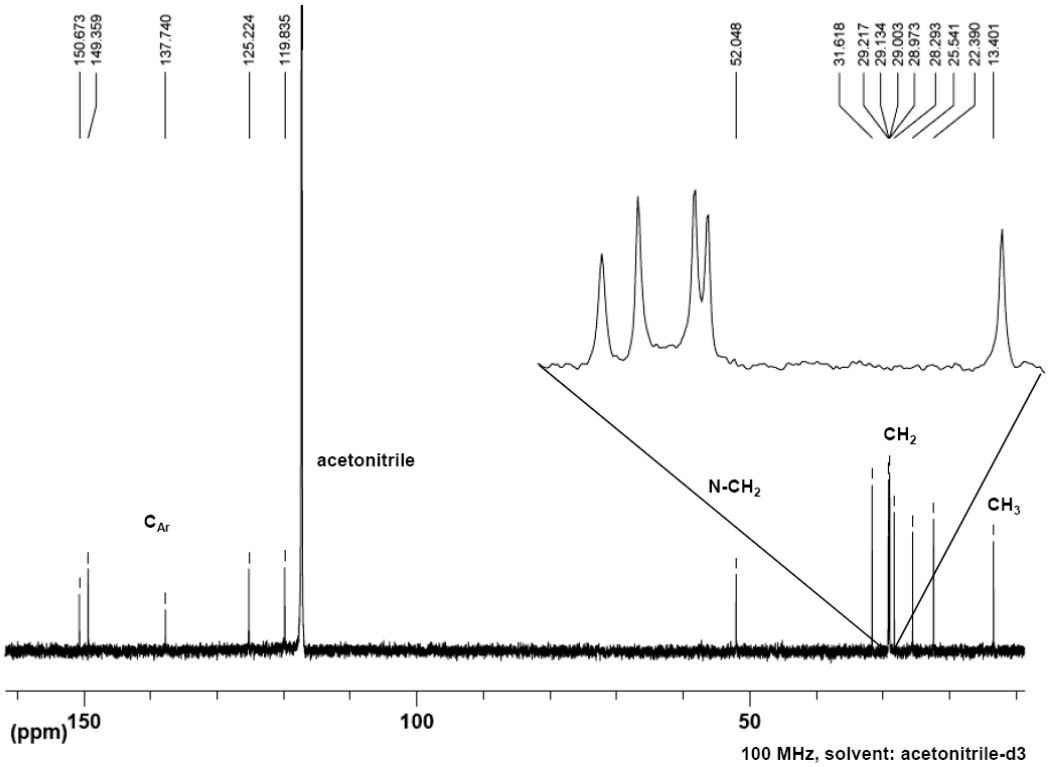


**Figure 15.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **9**.

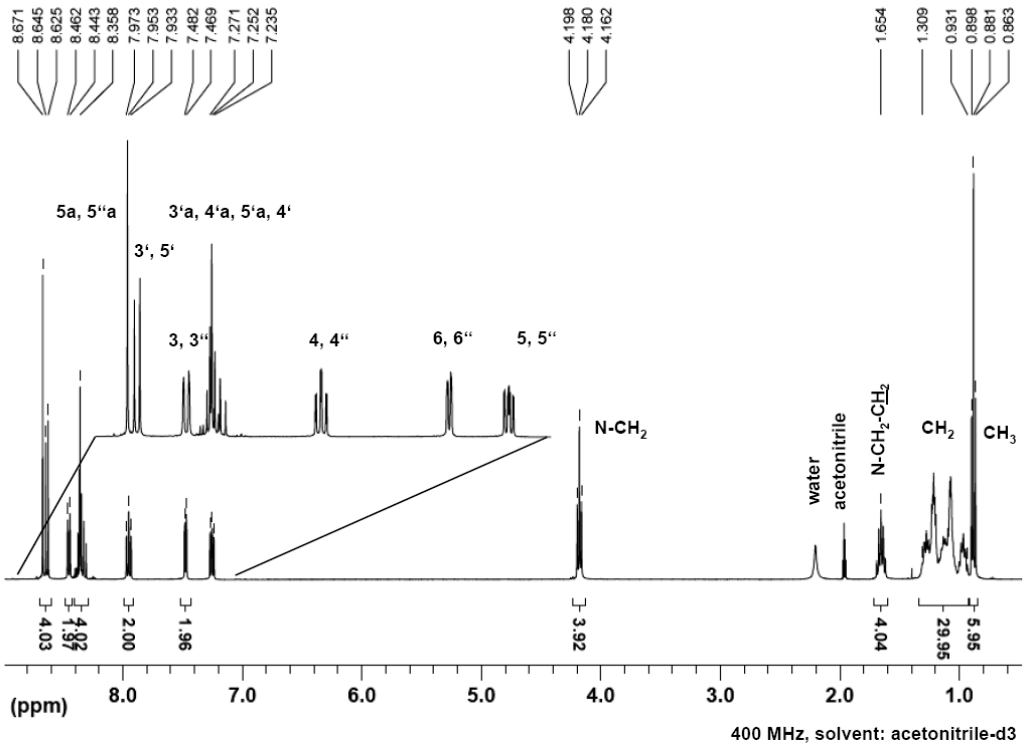


**Figure 16.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **1**.

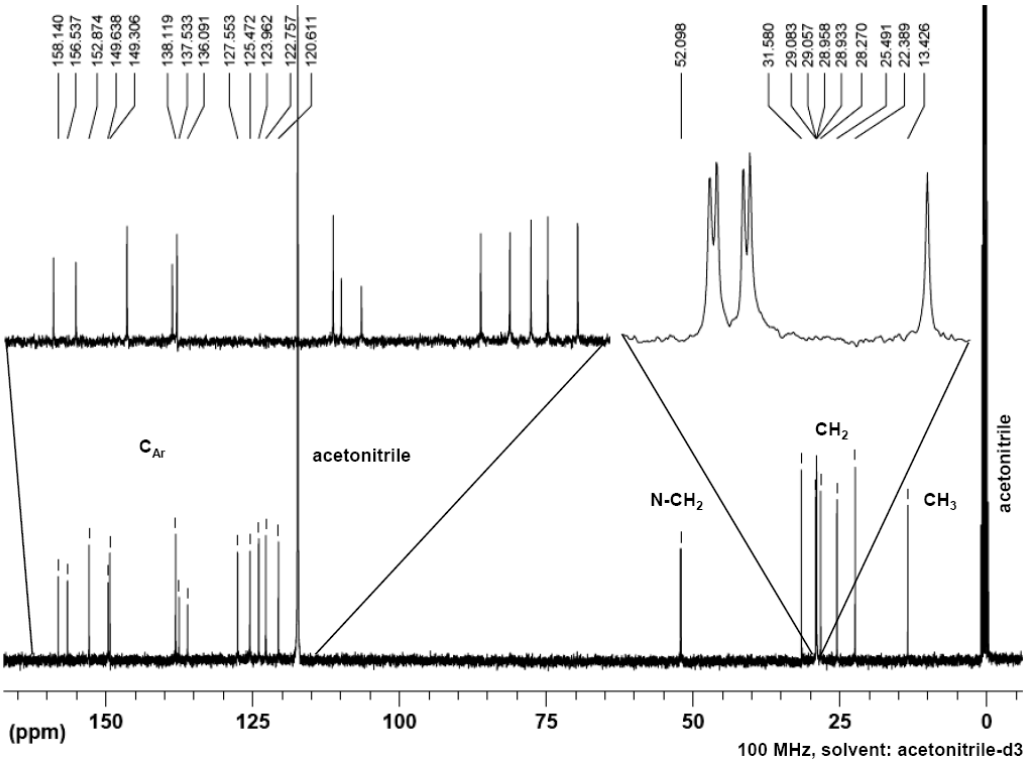


**Figure 17.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **1**.

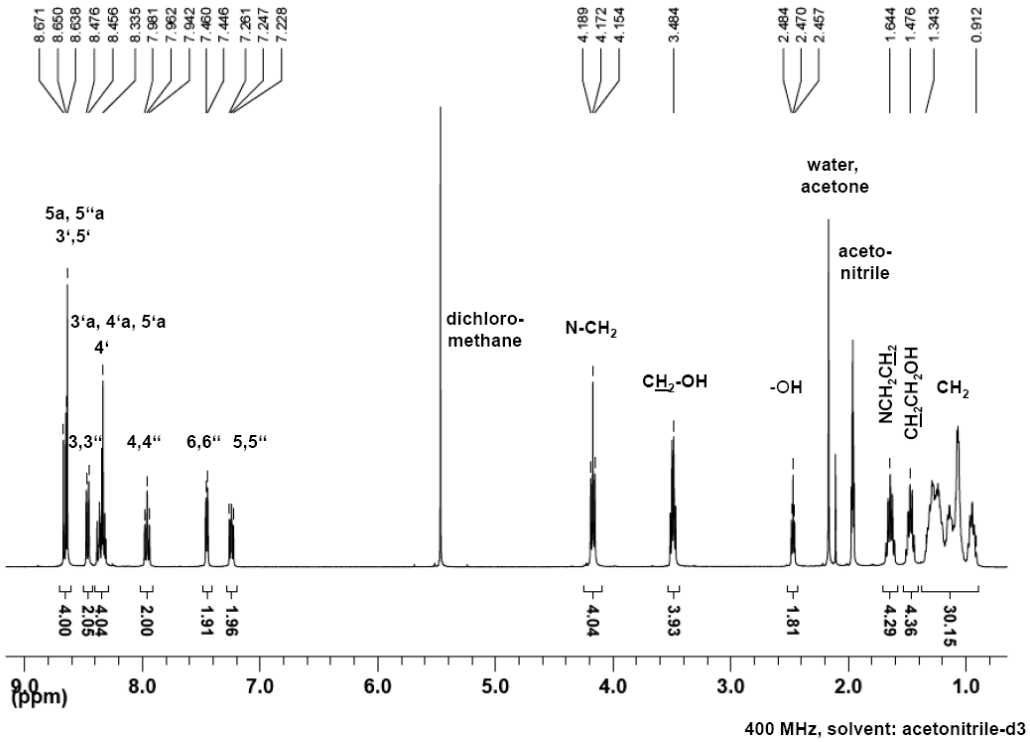


**Figure 18.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **2**.

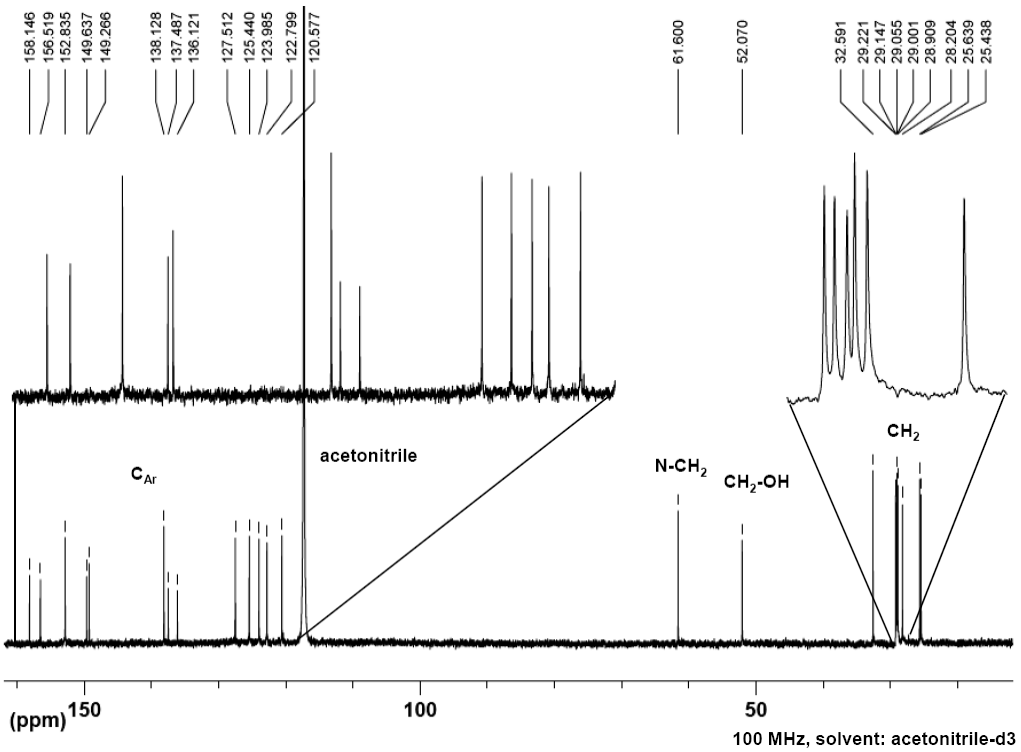


**Figure 19.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **2**.

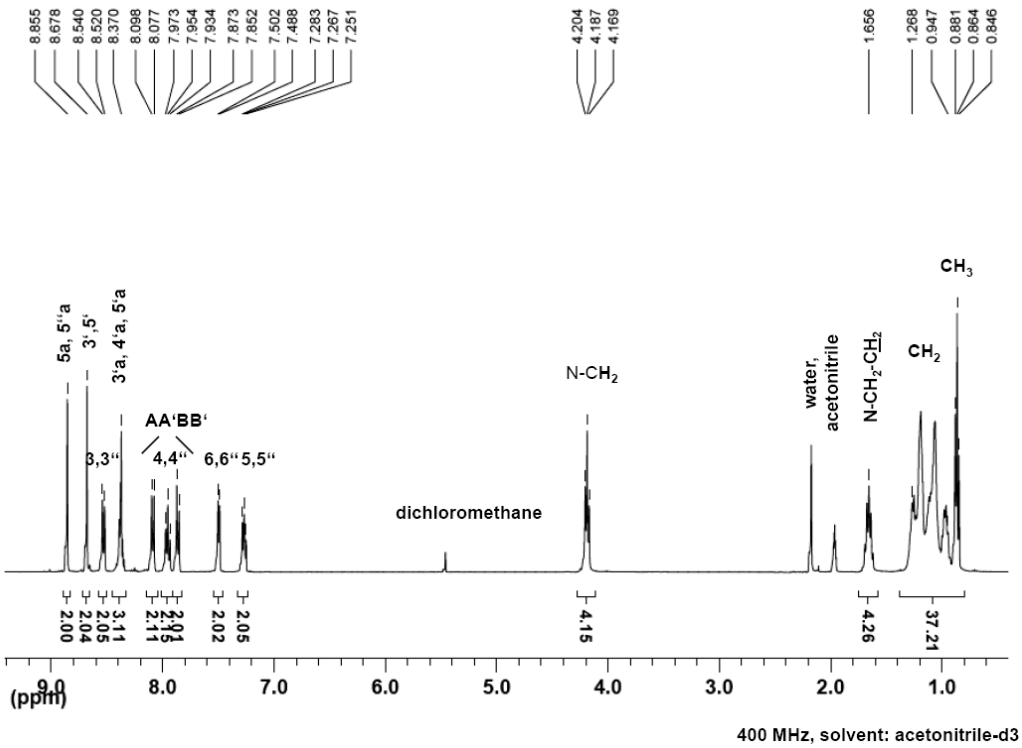


**Figure 20.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **3**.

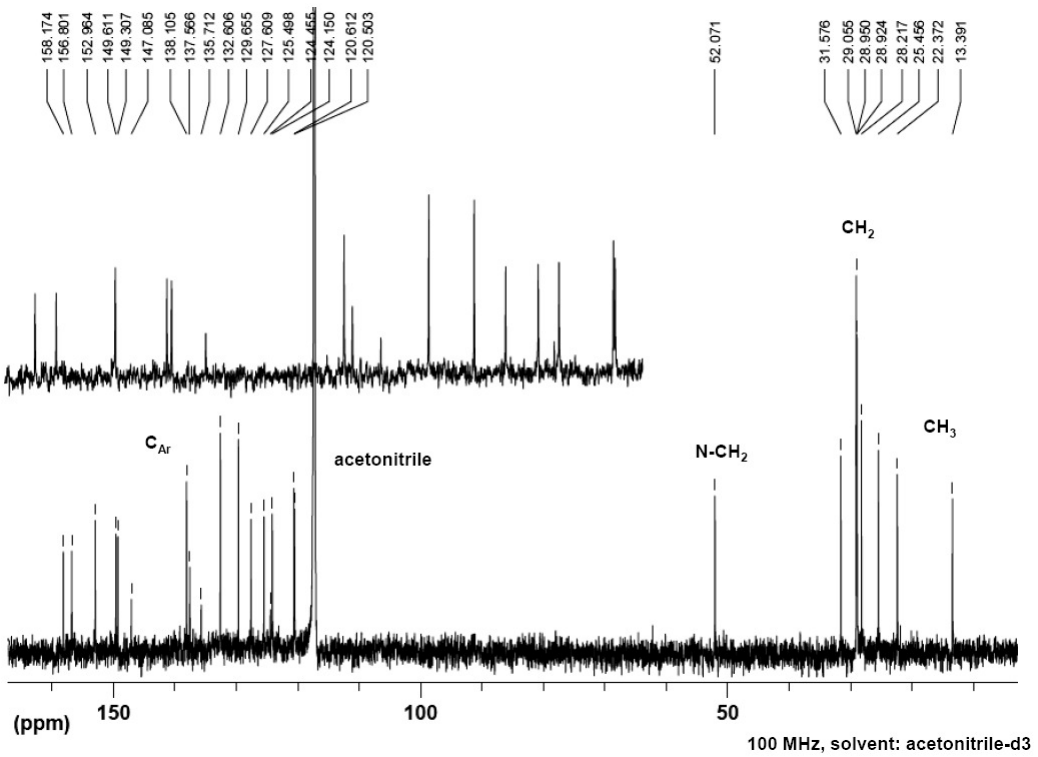


**Figure 21.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **3**.

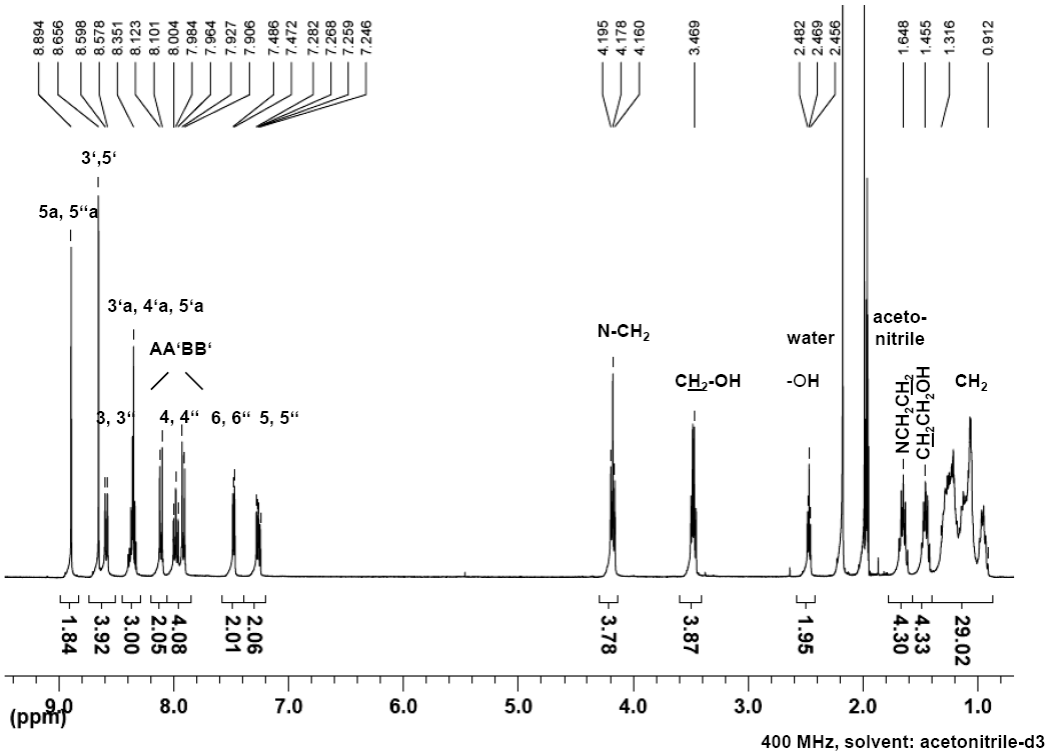


**Figure 22.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **4**.

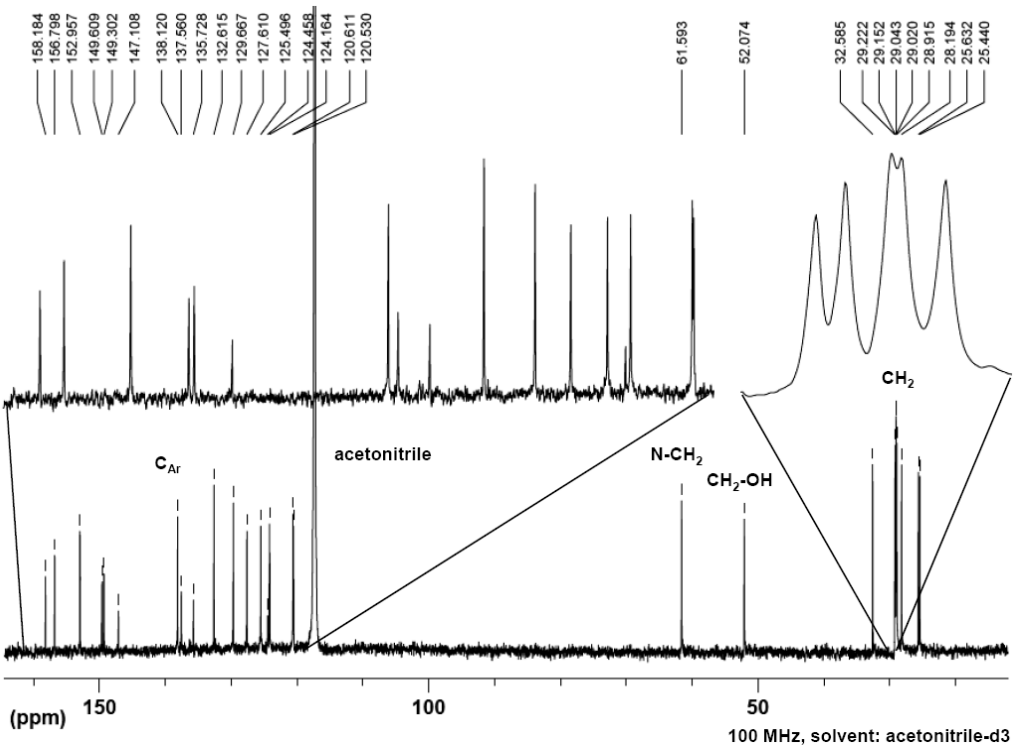


**Figure 23.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **4**.

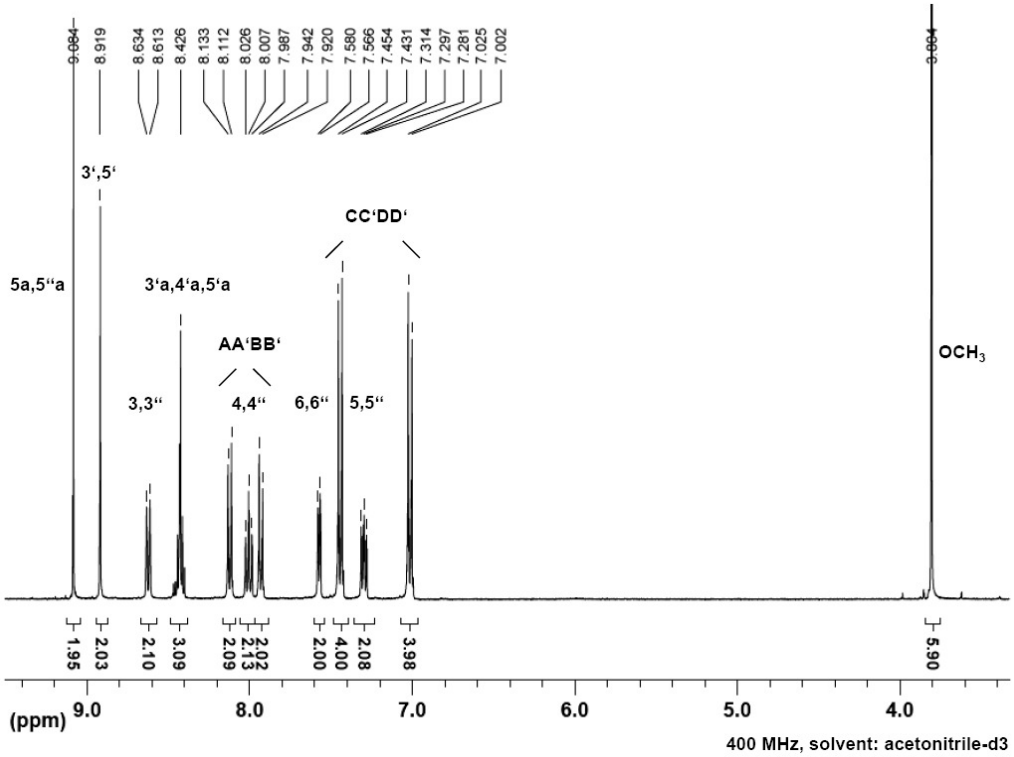


**Figure 24.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **5**.

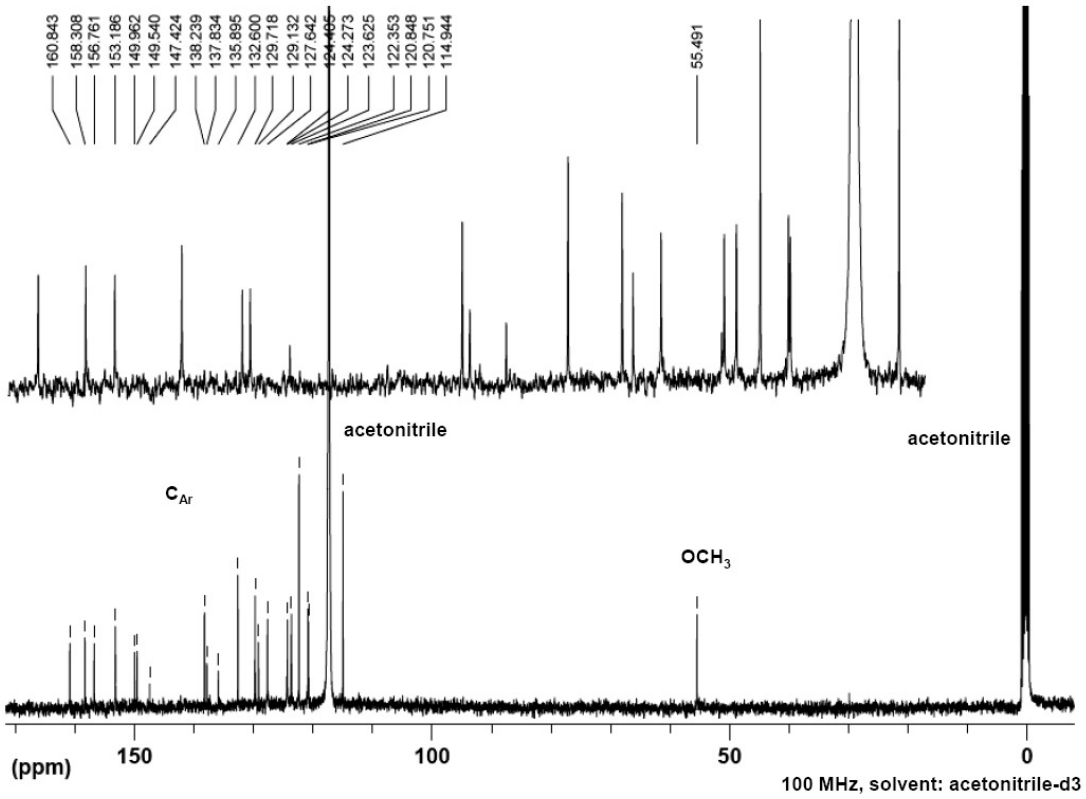


**Figure 25.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **5**.

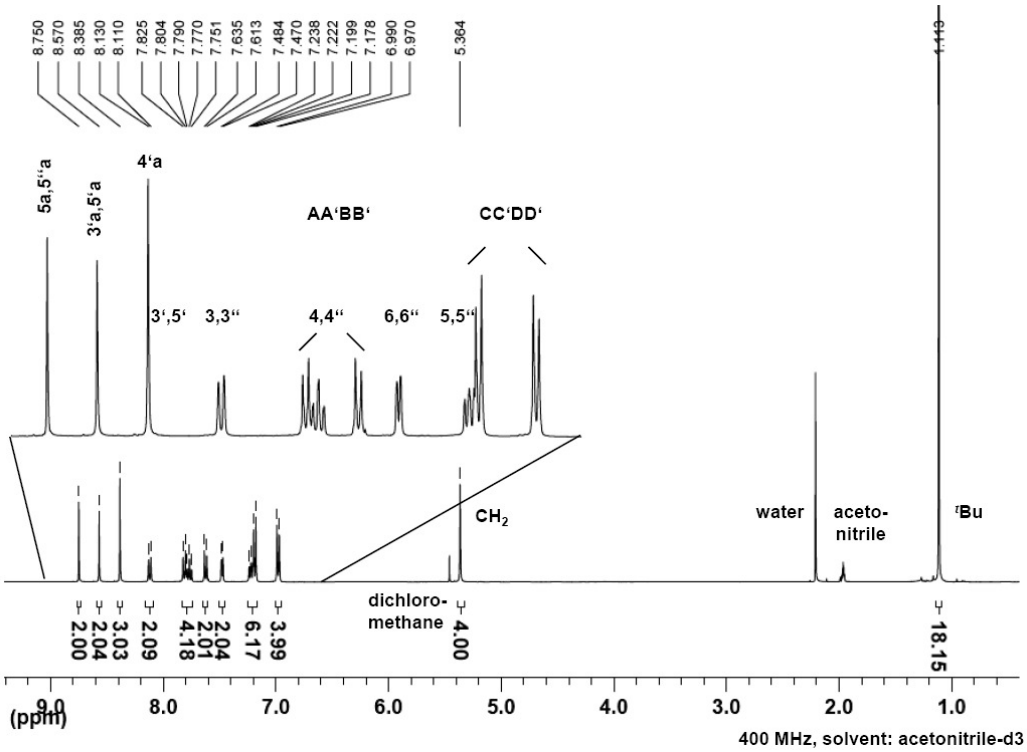


**Figure 26.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **6**.

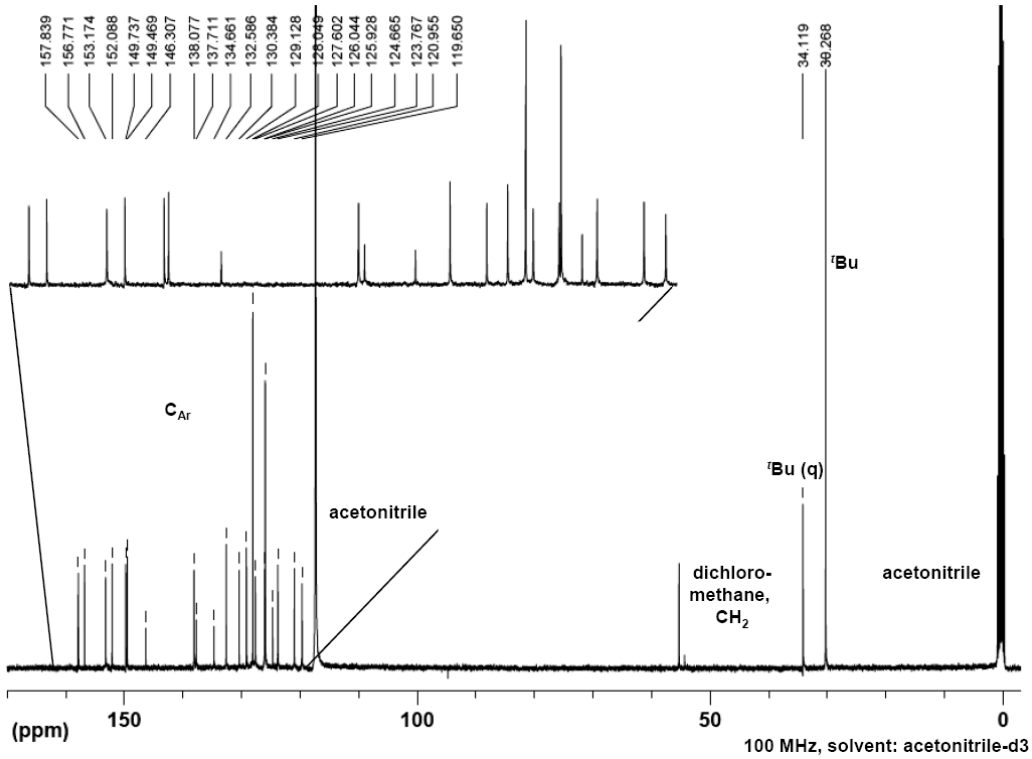


**Figure 27.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **6**.

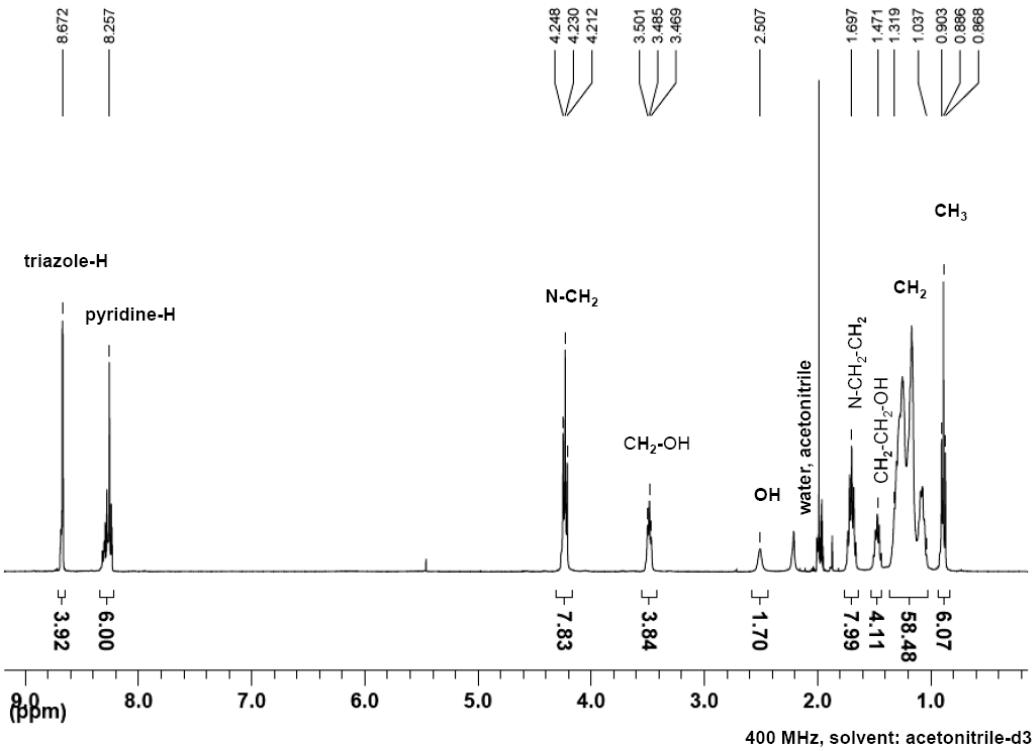


**Figure 28.** $^{1}$H NMR spectrum (400 MHz, $CD_3CN$) of **7**.

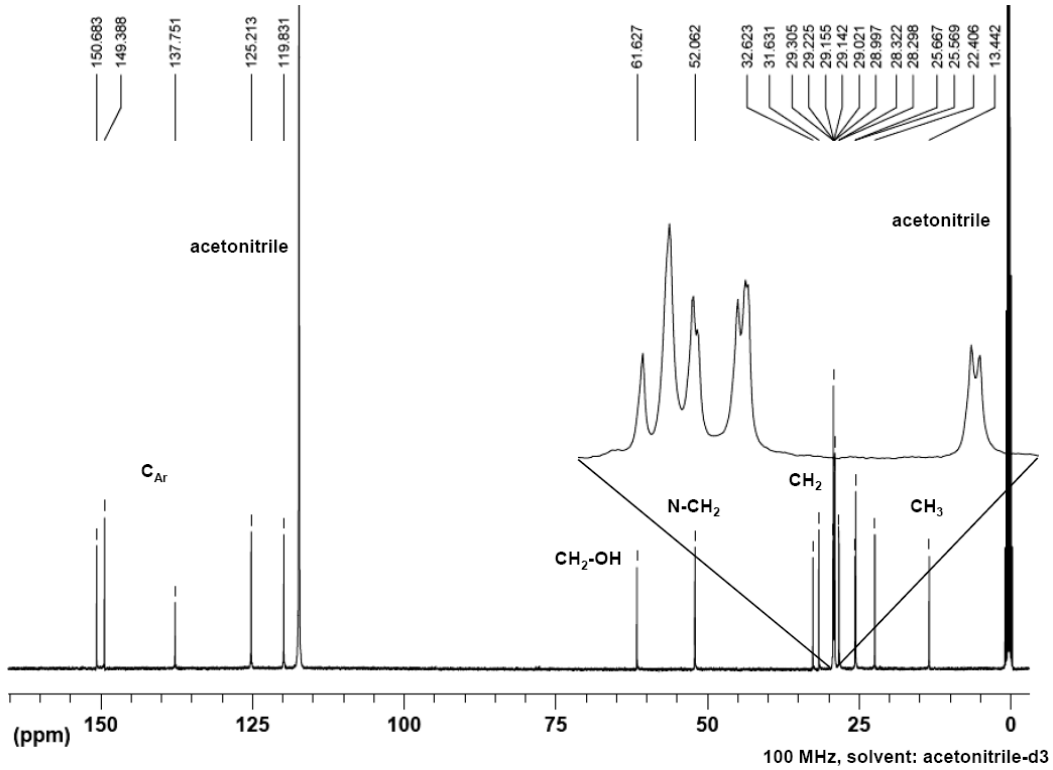


**Figure 29.** $^{13}$C NMR spectrum (100 MHz, $CD_3CN$) of **7**.

# $^{1}$H-$^{1}$H gCOSY NMR spectra

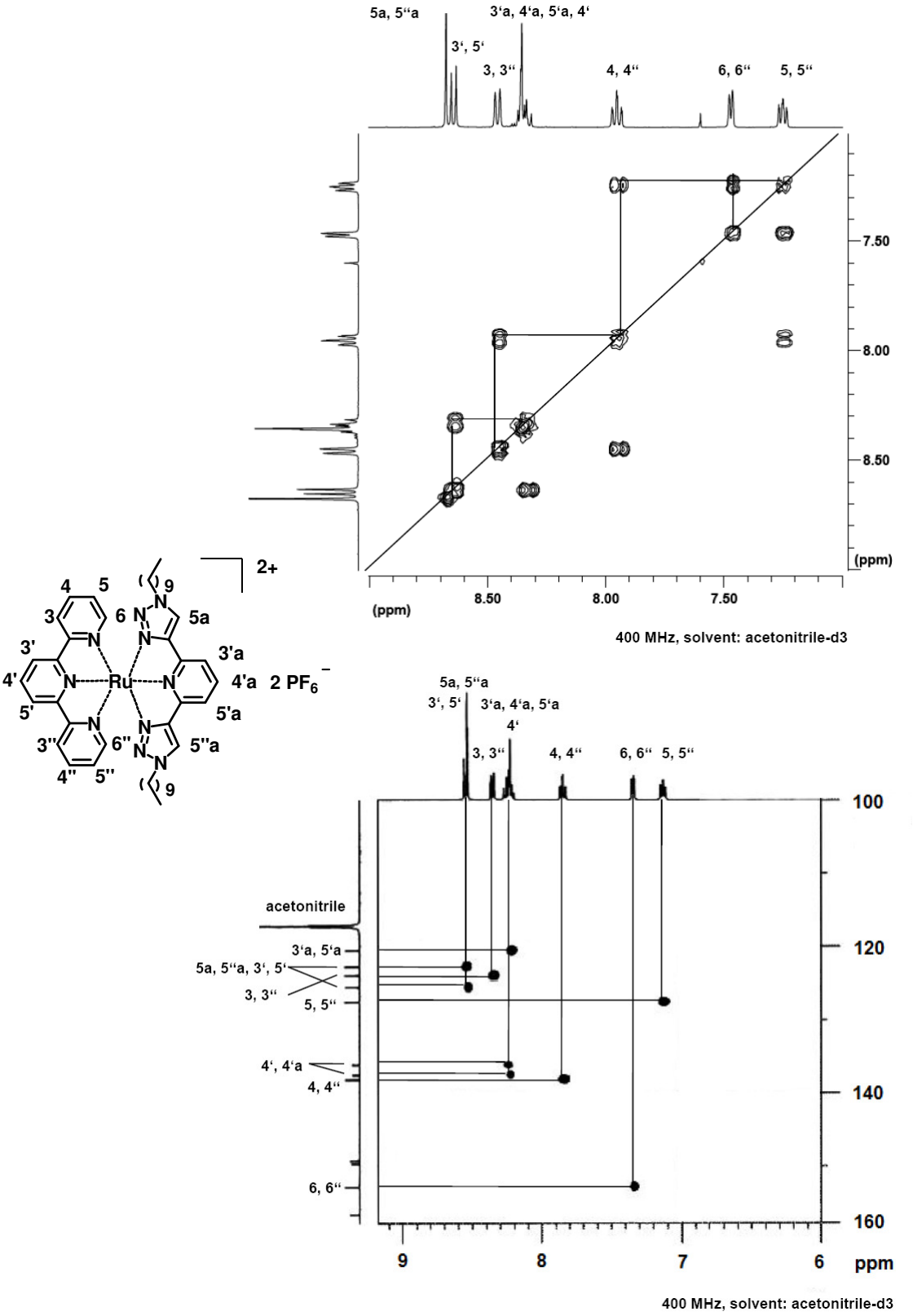


**Figure 30.** $^{1}$H-$^{1}$H gCOSY NMR spectrum (400 MHz, $CD_3CN$) of **1**.

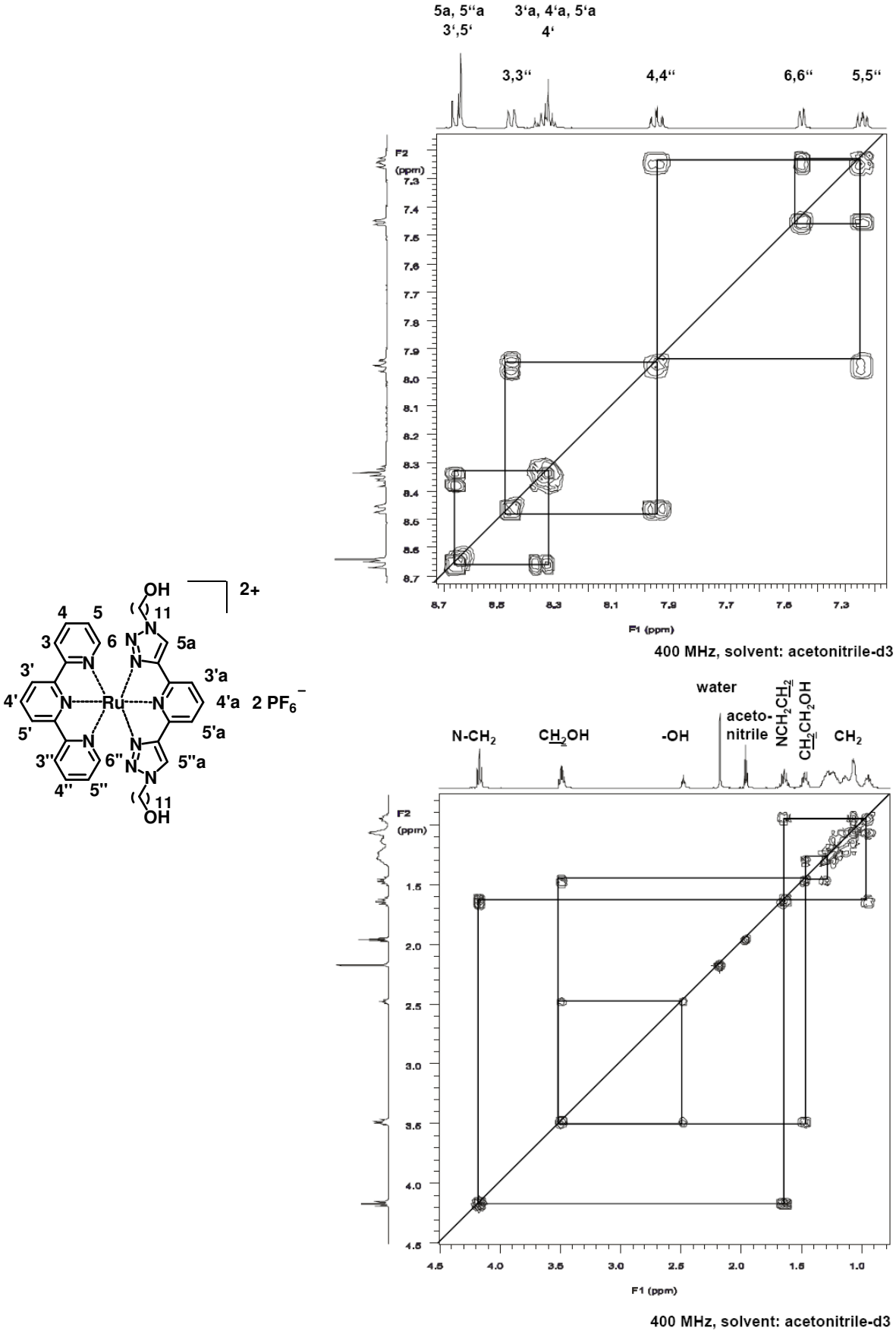


**Figure 31.** $^{1}$H-$^{1}$H gCOSY NMR spectrum (400 MHz, $CD_3CN$) of **2**.

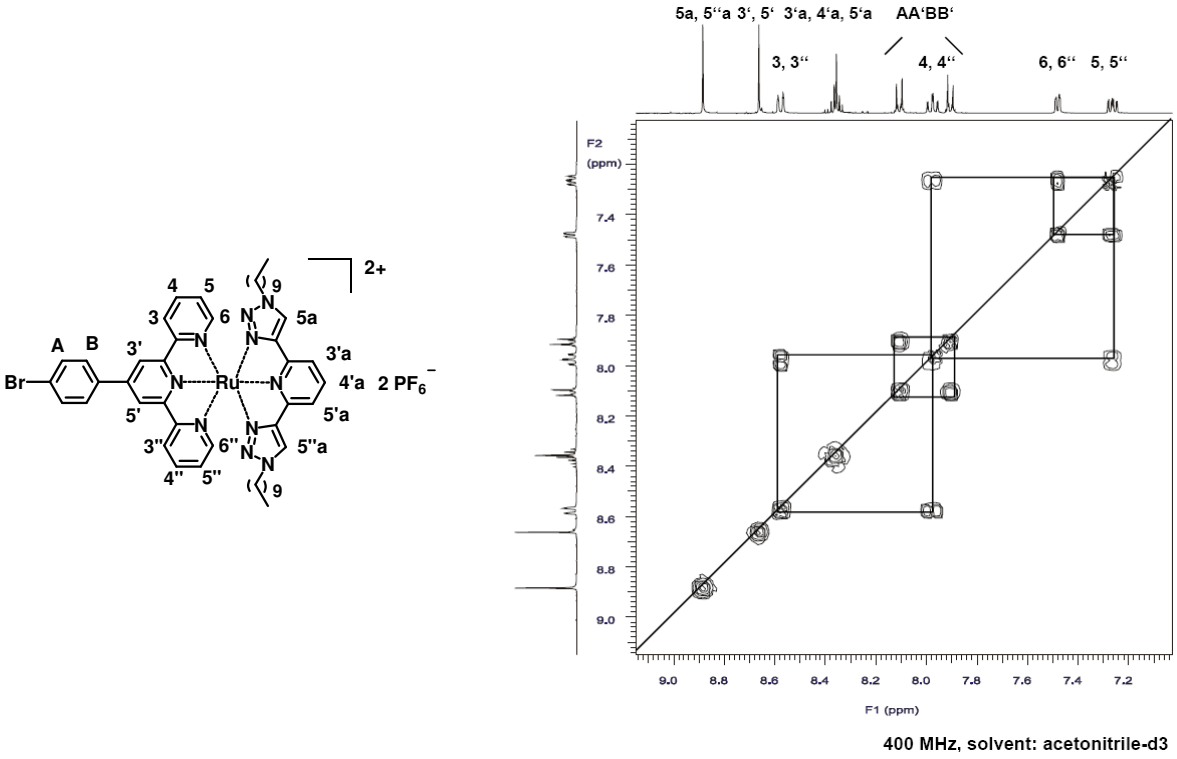


**Figure 32.** $^{1}$H-$^{1}$H gCOSY NMR spectrum (400 MHz, $CD_3CN$) of **3**.

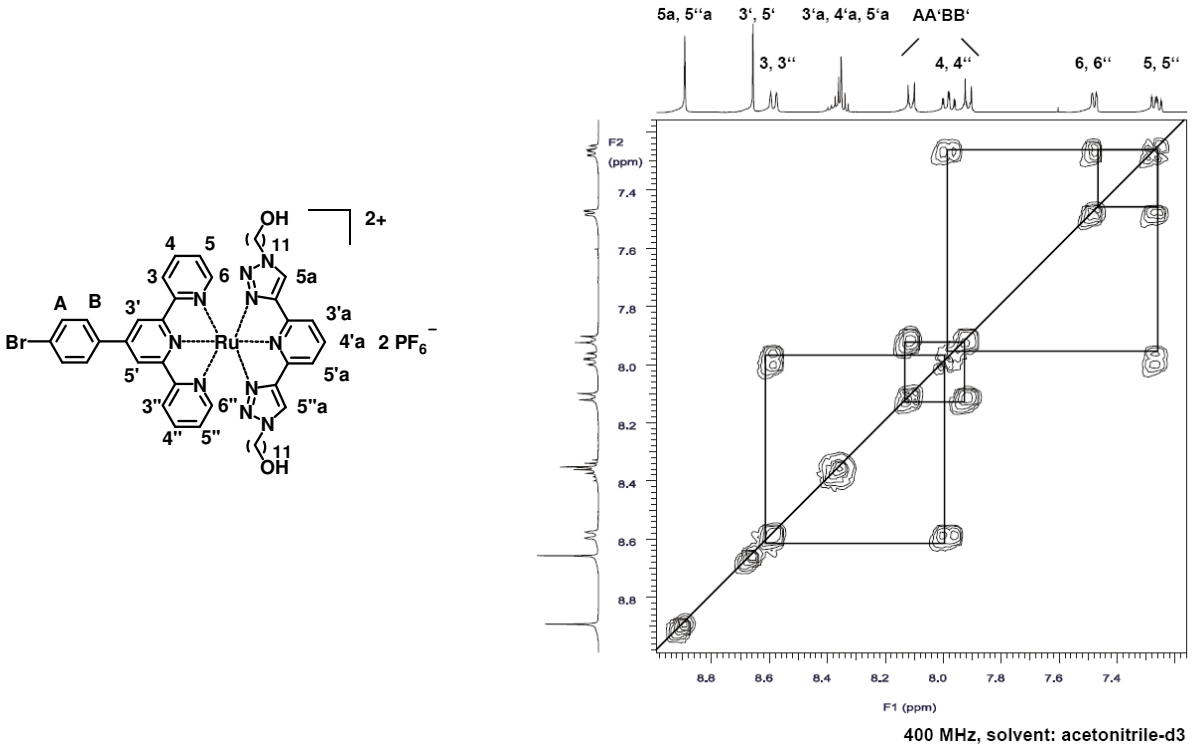


**Figure 33.** $^{1}$H-$^{1}$H gCOSY NMR spectrum (400 MHz, $CD_3CN$) of **4**.

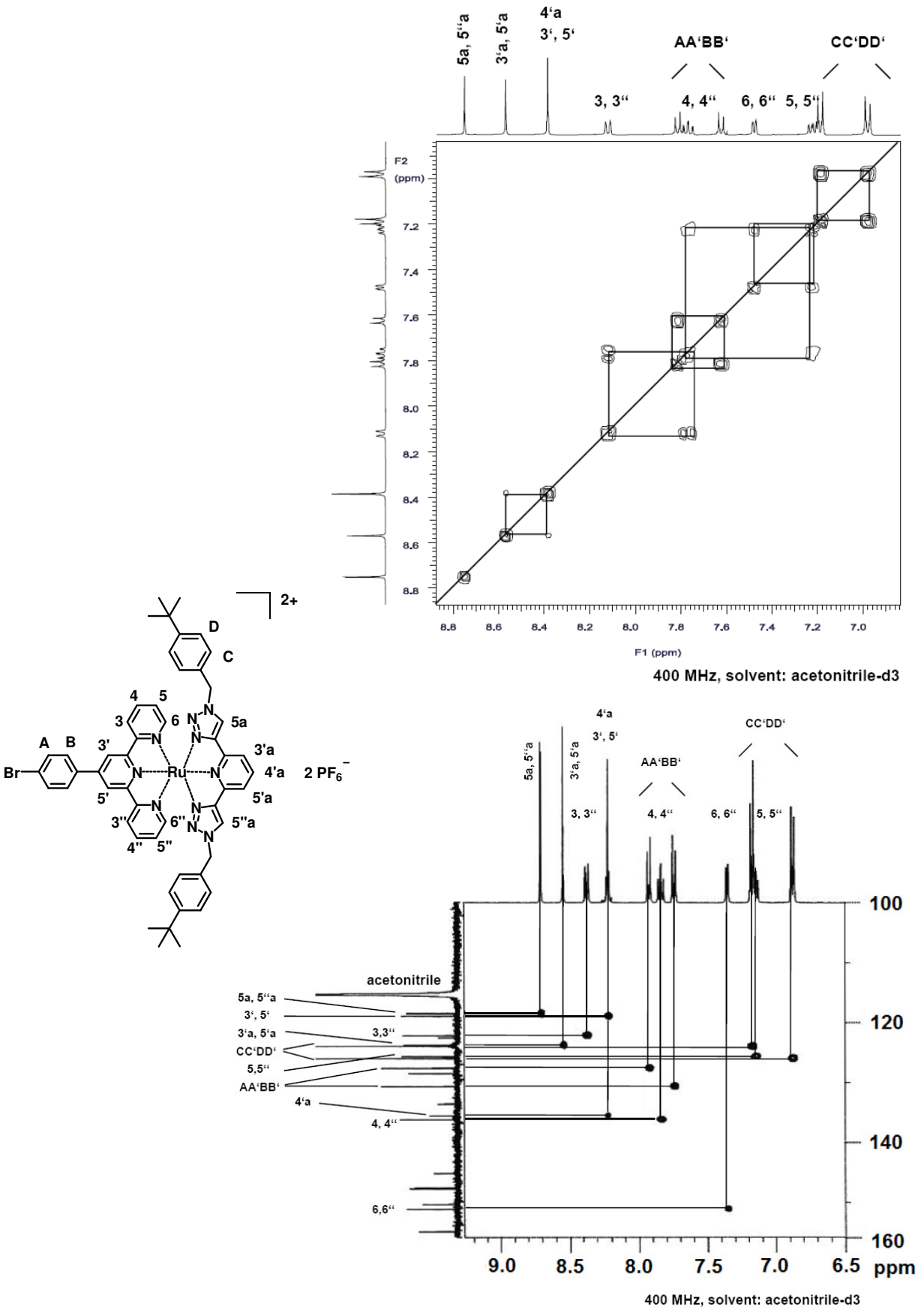


**Figure 34.** $^{1}$H-$^{1}$H gCOSY NMR spectrum (400 MHz, $CD_3CN$) of **6**.

## MALDI-TOF mass spectra

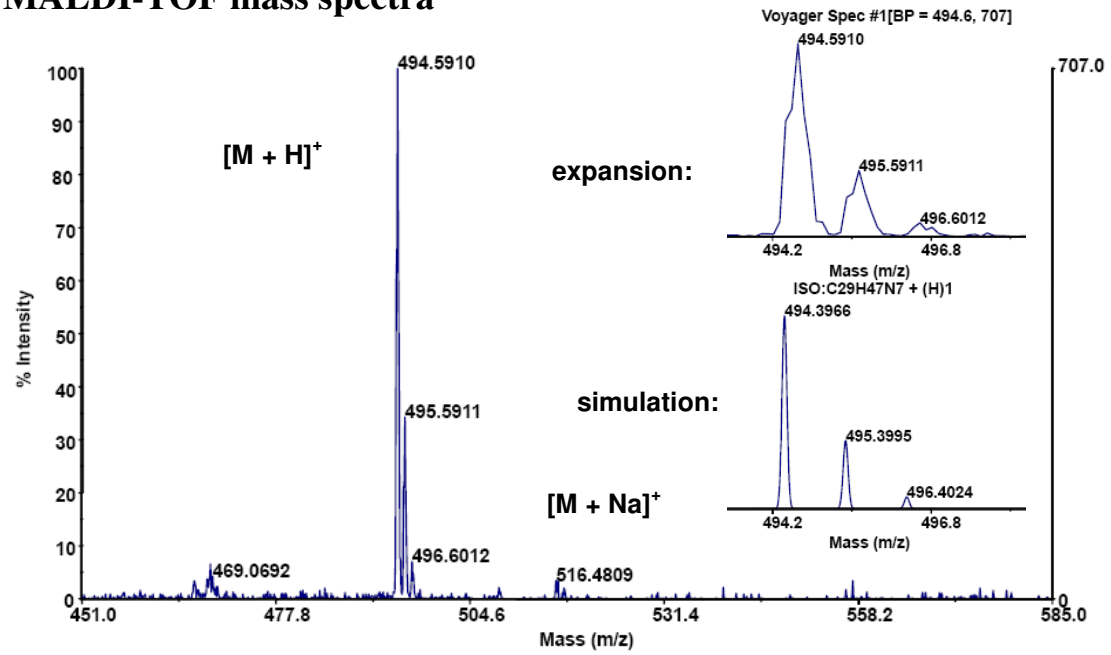


**Figure 35.** MALDI-TOF mass spectrum (dithranol as matrix) of **$R^1$-tripy** ($R^1 = C_{10}H_{21}$).

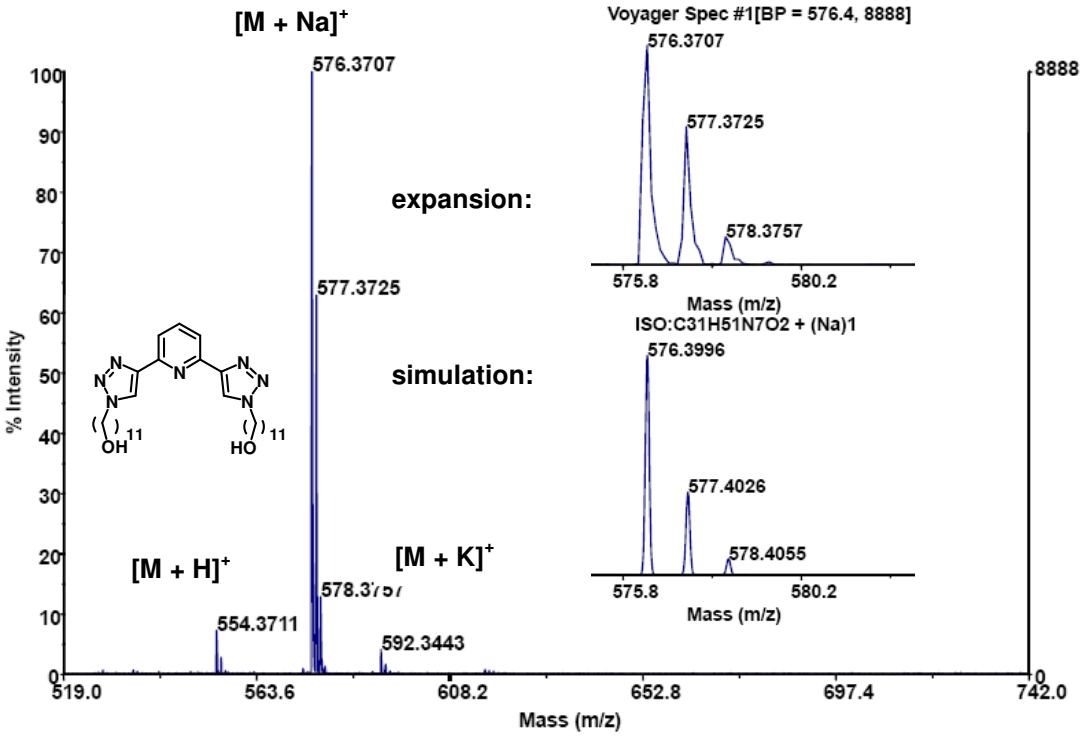


**Figure 36.** MALDI-TOF mass spectrum (dithranol as matrix) of **$R^1$-tripy** ($R^1 = C_{12}H_{22}OH$).

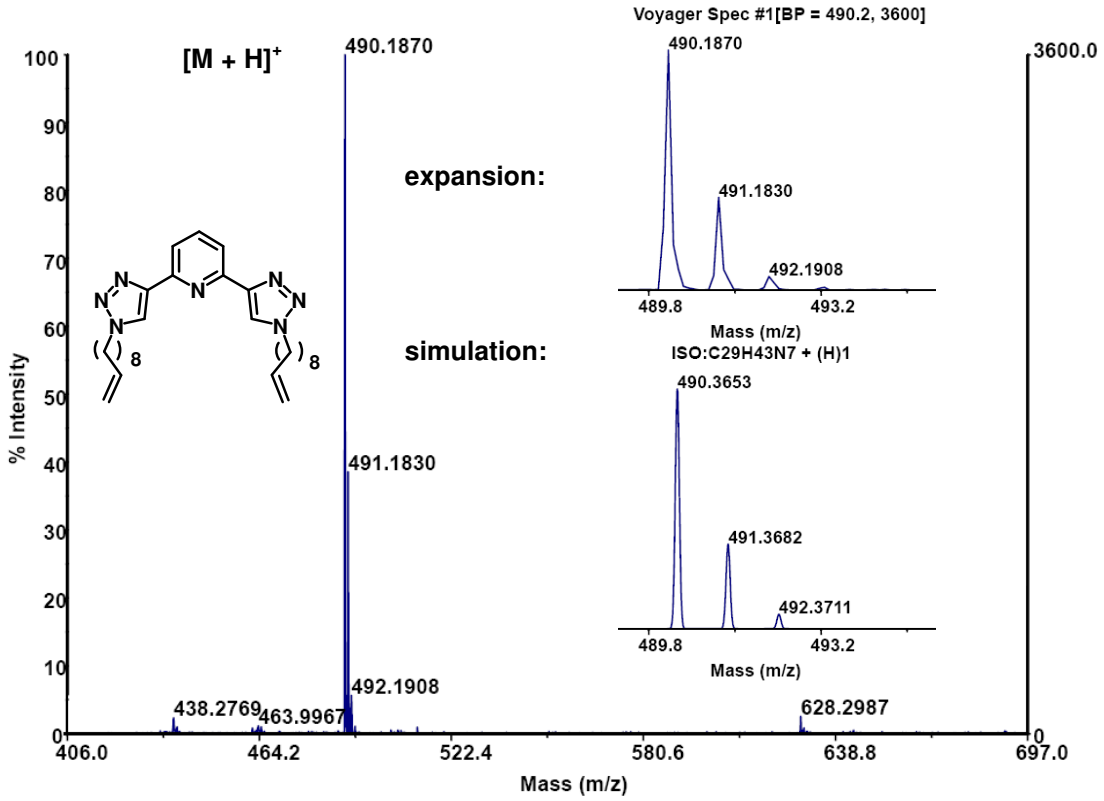


**Figure 37.** MALDI-TOF mass spectrum (dithranol as matrix) of **R[1]-tripy** ($R^1$ = $C_8H_{16}C{=}CH_2$).

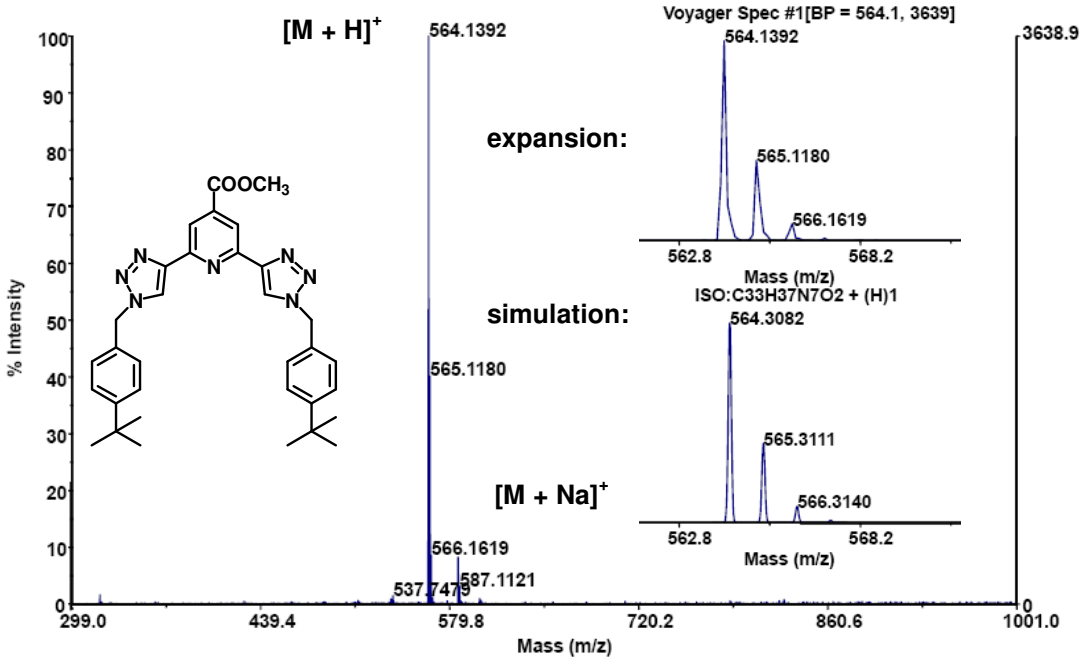


**Figure 38.** MALDI-TOF mass spectrum (dithranol as matrix) of **R[1]-tripy** ($R^1$ = 4-$^t$Bu-$C_6H_4$-$CH_2$).

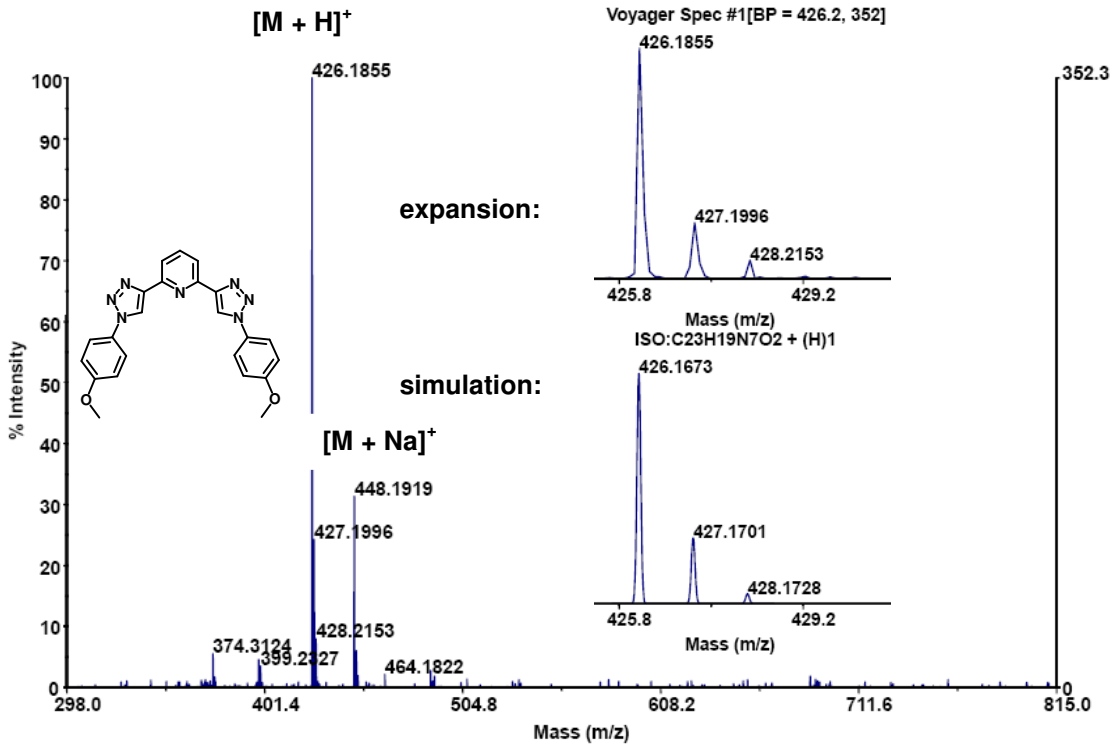


**Figure 39.** MALDI-TOF mass spectrum (dithranol as matrix) of **$R^1$-tripy** ($R^1$ = 4-MeO-$C_6H_4$).

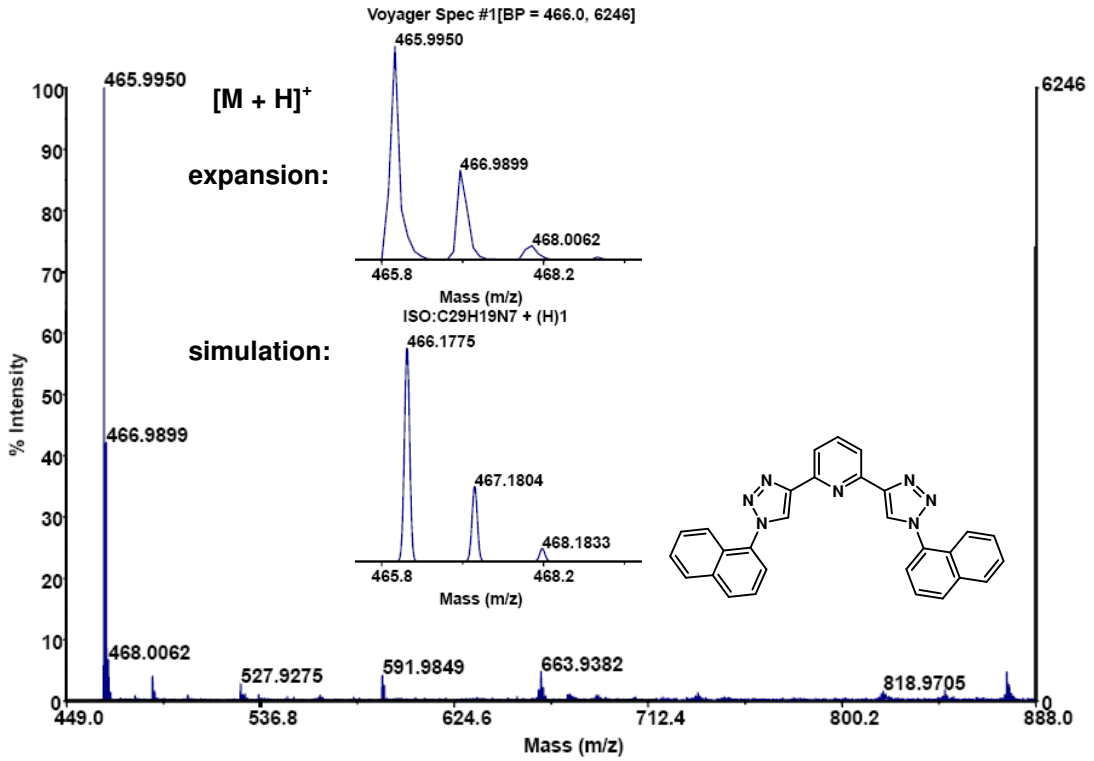


**Figure 40.** MALDI-TOF mass spectrum (dithranol as matrix) of **$R^1$-tripy** ($R^1$ = naphth-1-yl).

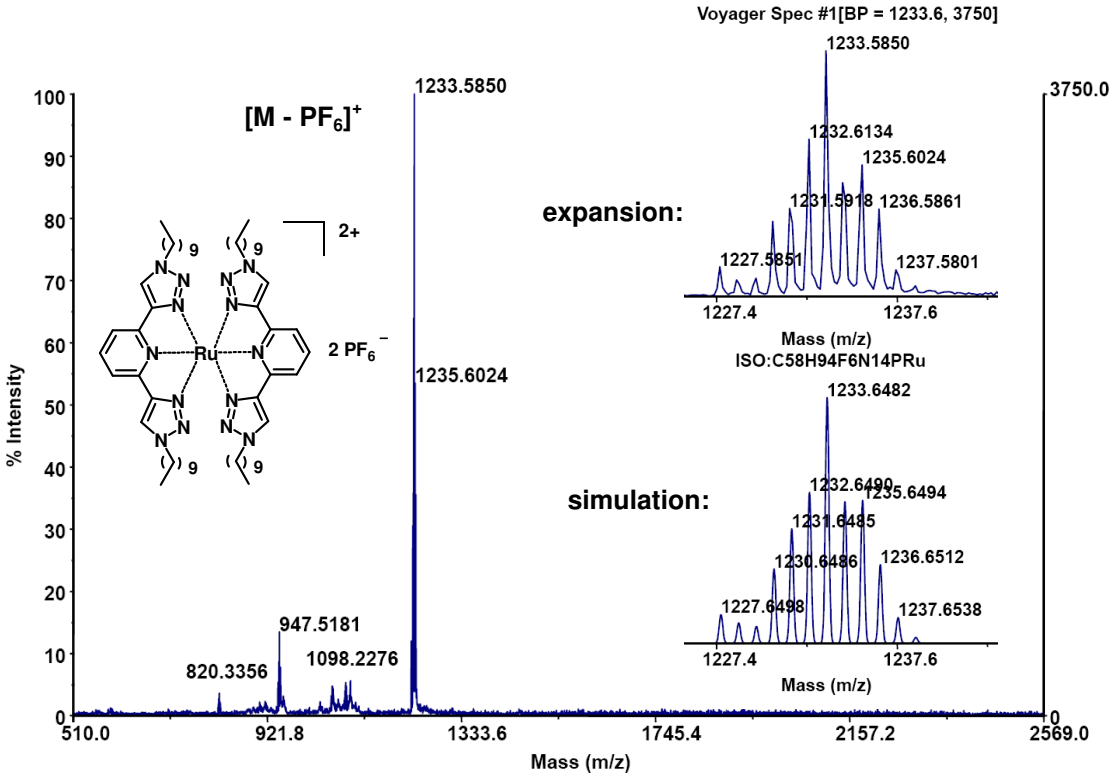


**Figure 41.** MALDI-TOF mass spectrum (dithranol as matrix) of **9**.

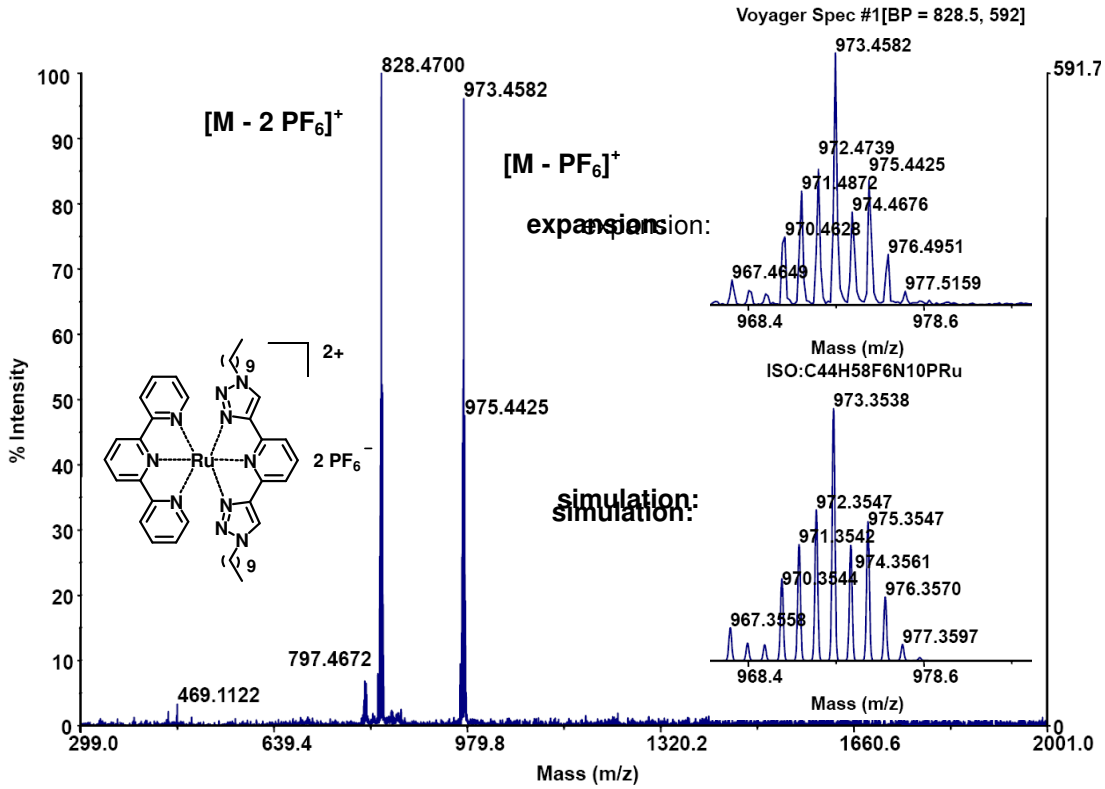


**Figure 42.** MALDI-TOF mass spectrum (dithranol as matrix) of **1**.

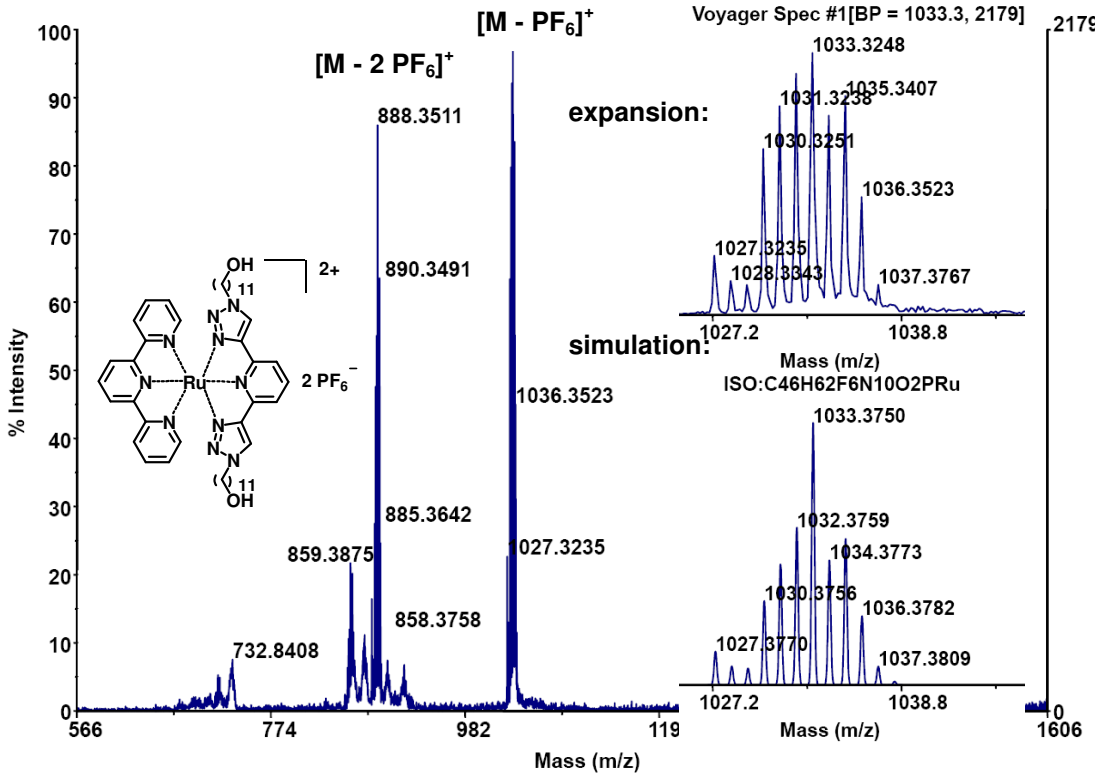


**Figure 43.** MALDI-TOF mass spectrum (dithranol as matrix) of **2**.

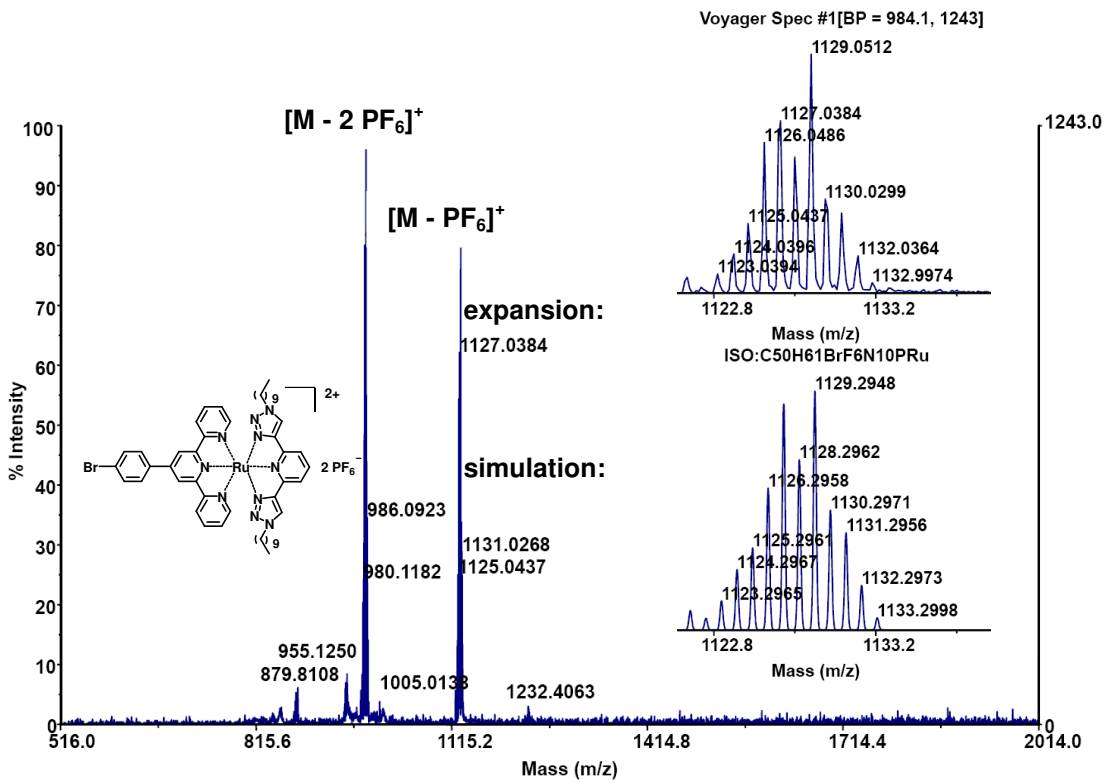


**Figure 44.** MALDI-TOF mass spectrum (dithranol as matrix) of **3**.

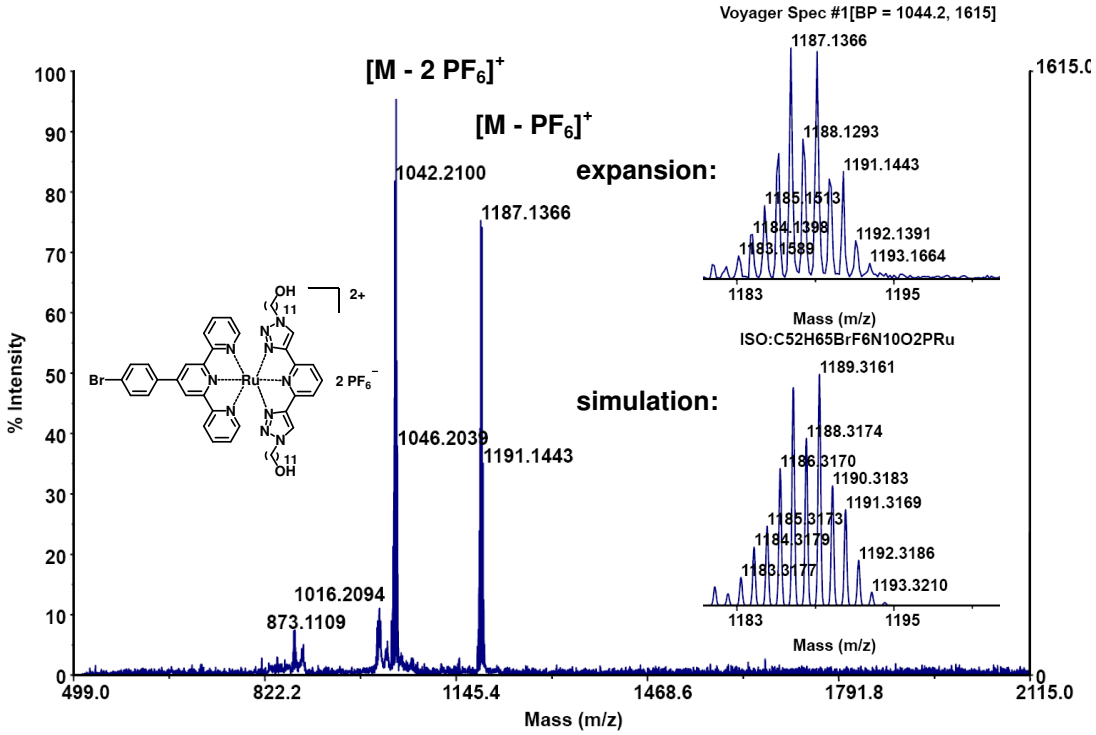


**Figure 45.** MALDI-TOF mass spectrum (dithranol as matrix) of **4**.

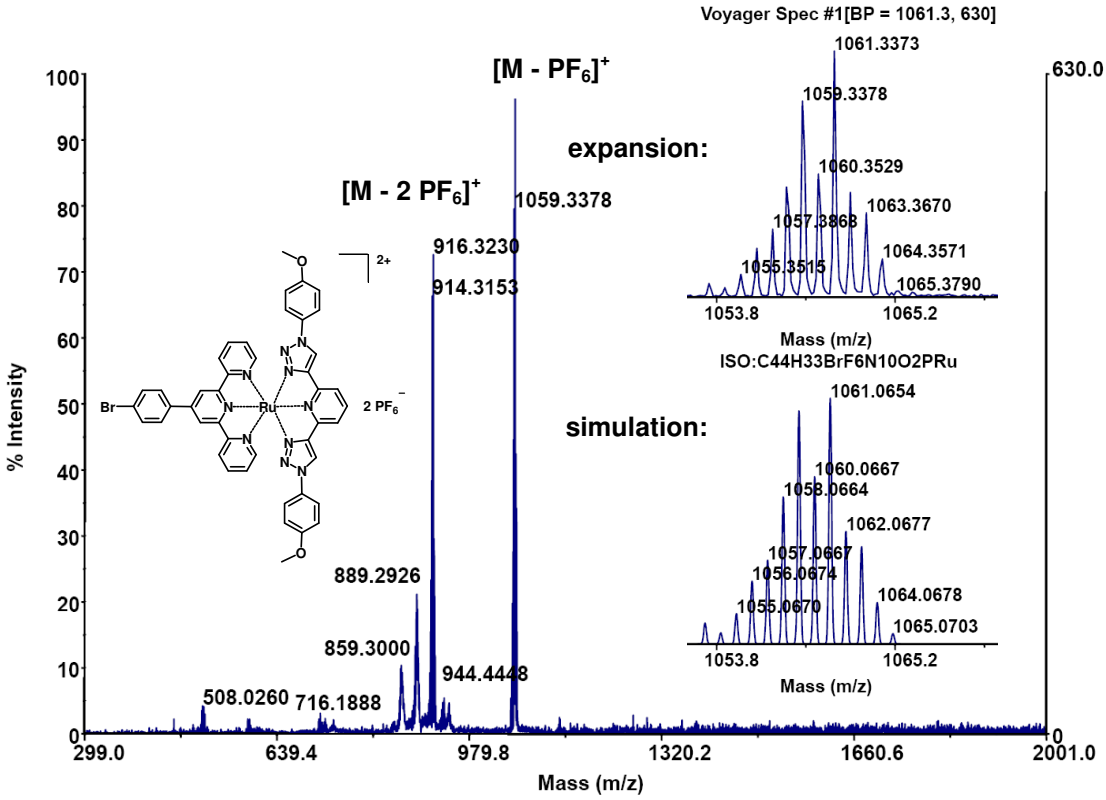


**Figure 46.** MALDI-TOF mass spectrum (dithranol as matrix) of **5**.

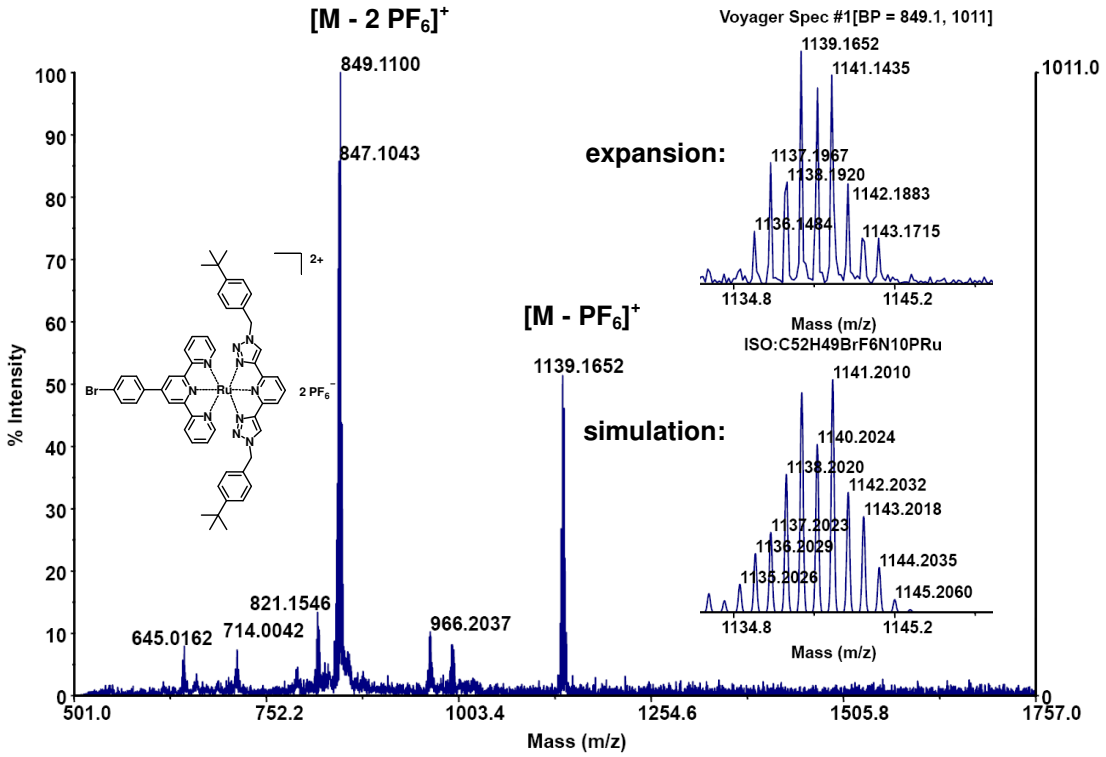


**Figure 47.** MALDI-TOF mass spectrum (dithranol as matrix) of **6**.

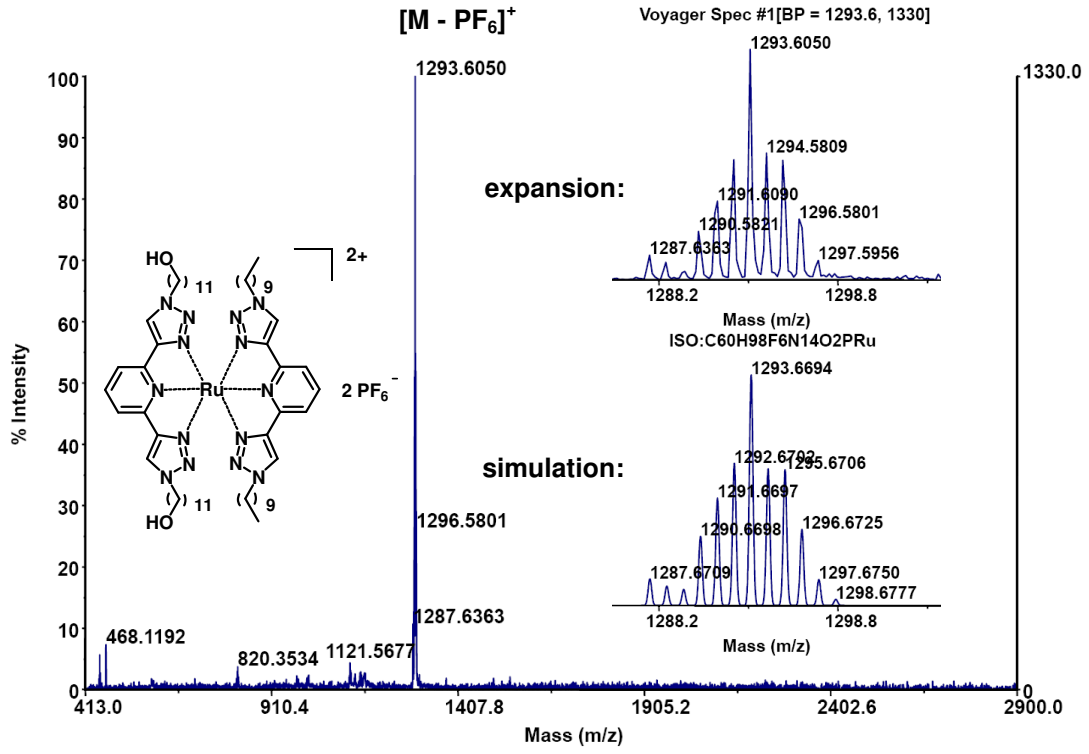


**Figure 48.** MALDI-TOF mass spectrum (dithranol as matrix) of **7**.