Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Long-range proton-coupled electron transfer in phenol – Ru(2,2'-bipyrazine)$_3^{2+}$ dyads

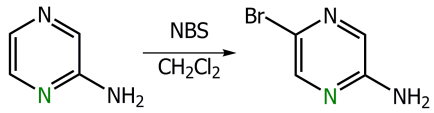
Catherine Bronner, and Oliver S. Wenger*

University of Basel, Department of Chemistry, Spitalstrasse 51, CH-4056 Basel, Switzerland

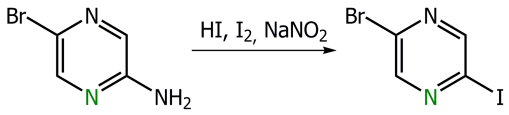
E-mail: oliver.wenger@unibas.ch

Supporting Information:

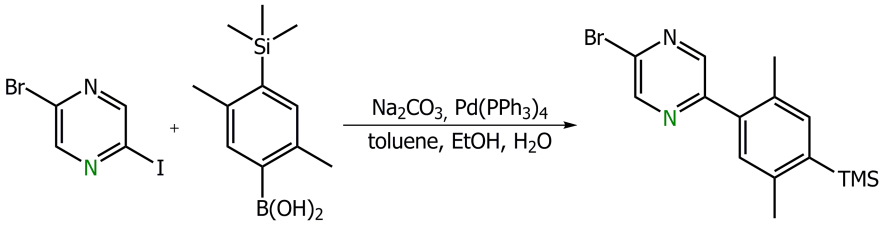
Syntheses of the two dyads



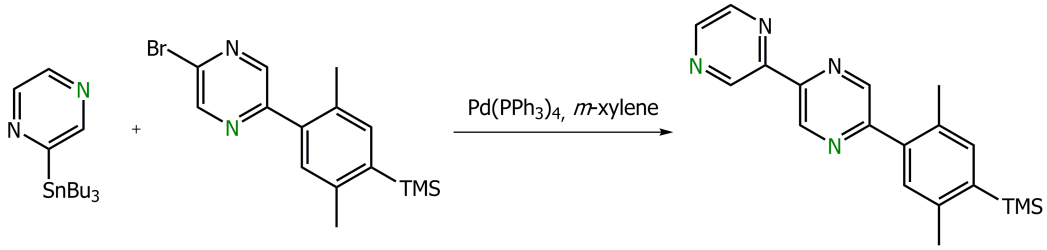
This synthesis followed a previously published protocol.[1] To a cooled suspension of 2-aminopyrazine (**1**) (20.0 g, 210 mmol) in dry CH_2Cl_2 (1 L), NBS (37.55 g, 211 mmol) was added. This suspension was stirred under N_2 and allowed to warm up gently to room temperature overnight. After 40h of stirring, the brown mixture was washed with saturated aqueous Na_2CO_3 (3 × 300 mL). Then the organic layer was washed with H_2O (3 × 300 mL) and dried over anhydrous $MgSO_4$. After purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95/5, R_f = 0.5), 5-bromo-2-aminopyrazine (**2**) was obtained as a brown solid (13.63 g, 78.3 mmol, 37 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.63 (s, 2H), 7.77 (d, J = 1.4 Hz, 1H), 8.08 (d, J = 1.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.2, 131.7, 144.2, 153.4 ppm. Elemental analysis: calculated C 27.61, H 2.32, N 24.15; measured C 27.52, H 2.18, N 24.31.



This synthesis followed a previously published protocol.[2] 5-bromo-2-aminopyrazine (**2**) (5.01 g, 28.8 mmol) was dissolved in aqueous HI (57 % in water, 40 mL) at 0 °C then I_2 (5.11 g, 20.10 mmol) was added as a solid over 1h. Solid $NaNO_2$ (8.38 g, 121 mmol) was then added in small amounts over a period of 3.5 hours. Then the reaction was quenched by addition of 10 % aqueous $Na_2S_2O_5$ solution (250 mL) and saturated aqueous Na_2CO_3 solution (150 mL). The resulting aqueous mixture was extracted with Et_2O (3 × 500 mL), and the organic layer was washed again with a 10 % aqueous $Na_2S_2O_5$ solution (1 × 500 mL) and H_2O (2 × 500 mL) before drying over $MgSO_4$. Purification by column chromatography (SiO_2, CH_2Cl_2/pentane 1/1, R_f = 0.6) afforded 2-iodo-5-bromopyrazine (**3**) (3.56 g, 12.5 mmol, 43 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, J = 1.4 Hz, 1H), 8.62 (d, J = 1.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.0, 140.5, 148.7, 152.8 ppm. Elemental analysis: calculated C 16.86, H 0.71, N 9.83; measured C 16.98, H 0.77, N 9.75.

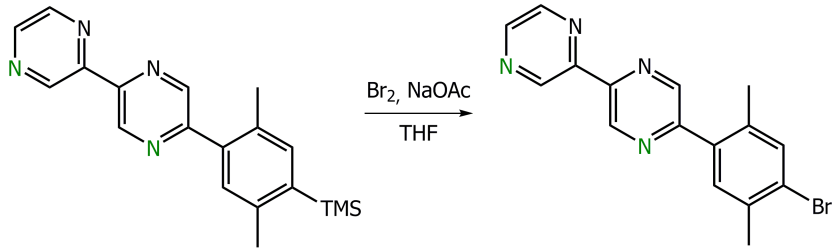


To 2-iodo-5-bromopyrazine (3.00 g, 10.5 mmol) in 395 mL toluene were added (2,5-dimethyl-4-(trimethylsilyl)phenyl)boronic acid (**4**)[3] (3.04 g, 13.7 mmol) in 53 mL EtOH and Na_2CO_3 (3.69 g, 34.86 mmol) in 24 mL H_2O. After bubbling N_2 through the solution for 1 hour, $Pd(PPh_3)_4$ (604 mg, 0.52 mmol) was added and the reaction mixture was refluxed under N_2 for 65 hours. Progress of the reaction was monitored by ^{1}H NMR in $CDCl_3$, and the reaction was stopped once there was no pyrazine starting material left. After cooling to room temperature, H_2O (200 mL) and CH_2Cl_2 (400 mL) were added. The organic layer was separated, dried over anhydrous $MgSO_4$ and evaporated. Pentane (~ 200 mL) was added and a yellow impurity was filtrated. Column chromatography of the filtrate (SiO_2, pentane to CH_2Cl_2/pentane 1/4 to pure CH_2Cl_2, R_f = 0.7 (in pure CH_2Cl_2)) gave the desired product (**5**) (1.667 g, 4.97 mmol, 47 %) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.36 (s, 9H), 2.37 (s, 3H), 2.48 (s, 3H), 7.22 (s, 1H), 7.39 (s, 1H), 8.48 (d, J = 1.5 Hz, 1H), 8.75 (d, J = 1.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.0, 20.0, 22.6, 130.9, 132.4, 136.0, 137.6, 138.9, 140.6, 141.6, 144.9, 146.6, 154.0 ppm. Elemental analysis: calculated C 53.73, H 5.71, N 8.35; measured C 54.03, H 5.97, N 8.15.

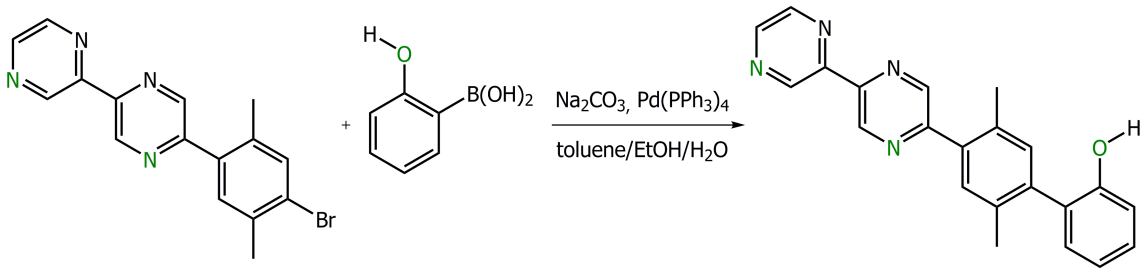


To compound **5** (218 mg, 0.65 mmol) in 2.5 mL *m*-xylene, 2-stannylpyrazine (**6**)[4] (200 µL, 0.63 mmol) was added. After 1 hour of bubbling N_2 through the solution, $Pd(PPh_3)_4$ (37 mg, 0.03 mmol) was added, and the mixture was deoxygenated for another 15 min. After refluxing for 66 hours under N_2, the solvent was evaporated and the mixture was purified by column chromatography (SiO_2, 1st column with CH_2Cl_2 / 3 % MeOH, 2nd column with EtOAc, R_f in CH_2Cl_2 = 0.3) to yield 168 mg of a white solid ($5 \cdot 10^{-4}$ mol, 77 %). Purification by recrystallization from hot EtOAc yielded a pure sample of **7** for the analytical measurements. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.37 (s, 9H), 2.44 (s, 3H), 2.50 (s, 3H), 7.33 (s, 1H), 7.42 (s, 1H), 8.66 – 8.69 (m, 2H), 8.81 (d, J = 1.5 Hz, 1H), 9.64 (dd, J = 5.4, 1.5 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.00, 20.1, 22.6, 131.1, 132.5, 137.1, 137.6, 140.5, 141.6,

142.6, 143.6, 144.03, 144.04, 145.2, 146.8, 149.7, 155.9 ppm. Elemental analysis: calculated (+ 0.09 EtOAc) C 67.90, H 6.69, N 16.36; measured C 67.81, H 6.47, N 16.63.

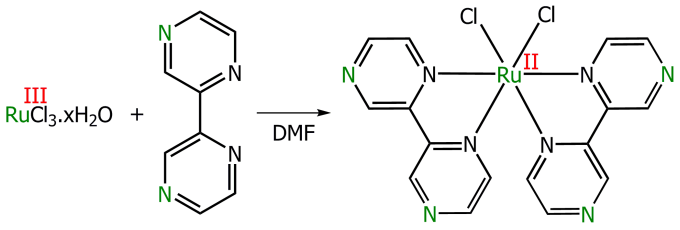


Compound **7** (100 mg, $3 \cdot 10^{-4}$ mol) was suspended with NaOAc (50 mg, $6.1 \cdot 10^{-4}$ mol) in 3 mL dry THF under N_2. Br_2 (61 µL, $1.2 \cdot 10^{-3}$ mol) was added slowly at 0 °C. Then the ice-bath was removed and the orange mixture is allowed to warm up to room temperature during 2.5 hours in the dark. NEt_3 (340 µL, $2.4 \cdot 10^{-3}$ mol) was then added and this gave a white mixture. Saturated aq. $Na_2S_2O_3$ (15 mL) was added subsequently, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. Purification by column chromatography (SiO_2, CH_2Cl_2 / 4 % MeOH, R_f = 0.5) followed by a recrystallization from hot CH_2Cl_2 yielded a white solid (53 mg, $1.5 \cdot 10^{-4}$ mol, 52 %). Product **8** can also be purified by washing the crude product with acetone. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.44 (s, 3H), 7.39 (s, 1H), 7.54 (s, 1H), 8.67 – 8.70 (m, 2H), 8.77 (d, J = 1.5 Hz, 1H), 9.64 (dd, J = 4.3, 1.5 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7, 22.3, 126.2, 131.9, 134.8, 135.6, 135.8, 142.4, 142.8, 143.4, 143.7, 143.9, 144.3, 145.1, 146.9, 154.8 ppm.

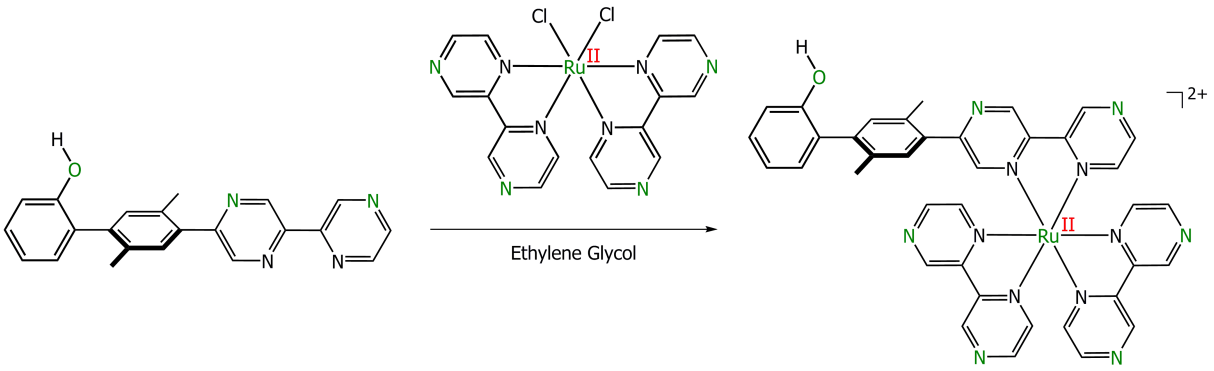


Compound **8** (84 mg, $2.5 \cdot 10^{-4}$ mol) in 20 mL toluene, phenol-2-boronic acid (**9**) (45 mg, $3.3 \cdot 10^{-4}$ mol) in 2.5 mL EtOH, and Na_2CO_3 (94 mg, $9 \cdot 10^{-4}$ mol) in 1 mL H_2O were mixed together and deoxygenated by bubbling N_2 through the solution for 45 min. $Pd(PPh_3)_4$ (14 mg, $1.2 \cdot 10^{-5}$ mol) was then added and the mixture was purged again with N_2 during 30 min before heating to reflux under N_2 for 3.5 days. After cooling to room temperature, CH_2Cl_2 (50 mL) and H_2O (50 mL) were added, and the organic phase was separated. The aqueous phase is extracted twice with CH_2Cl_2 (2 × 50 mL) and the combined organic phases were dried over $MgSO_4$ and evaporated. Purification by column chromatography (SiO_2, EtOAc, R_f = 0.8) and solubilization in hot CH_2Cl_2 followed by slow

evaporation of the solvent yielded yellow crystals of ligand **11** (40 mg, $1.1 \cdot 10^{-4}$ mol, 46 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3H), 2.46 (s, 3H), 6.98 – 7.04 (m, 2H), 7.16 (dd, J = 7.8, 1.8 Hz, 1H), 7.25 (s, 1H), 7.28 – 7.34 (m, 1H), 7.50 (d, J = 0.8 Hz, 1H), 8.67 – 8.71 (m, 2H), 8.86 (d, J = 1.5 Hz, 1H), 9.66 (dd, J = 13.7, 1.5 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.3, 19.9, 115.5, 120.5, 127.1, 129.3, 130.1, 132.1, 133.3, 134.4, 135.4, 136.4, 137.4, 142.4, 143.4, 143.8, 143.9, 145.0, 146.9, 149.4, 152.6, 155.3 ppm. Elemental analysis: calculated (+0.1 EtOAc) C 74.07, H 5.22, N 15.43; measured C 74.02, H 5.21, N 15.45.

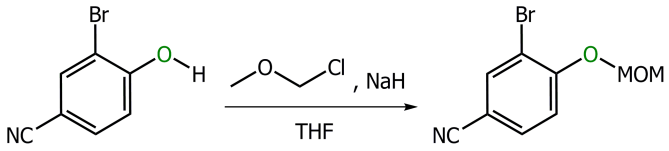


$RuCl_3 \cdot 3\ H_2O$ (155 mg, $7.5 \cdot 10^{-4}$ mol) and 2,2'-bipyrazine (254 mg, $1.6 \cdot 10^{-3}$ mol) were suspended in 20 mL dry DMF and deoxygenated by bubbling N_2 through the solution for 5 min. The mixture was heated to 150 °C for 16 hours under N_2. At room temperature, 200 mL Et_2O were added and the purple precipitate were filtrated and washed with Et_2O (50 mL) to yield the desired precursor complex (277 mg, $5.7 \cdot 10^{-4}$ mol, 76 %). The product was used without further purification.

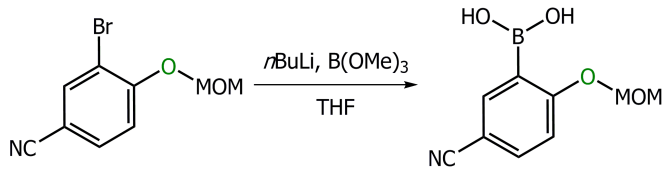


Ligand **11** (71 mg, $2 \cdot 10^{-4}$ mol) and the $[Ru(bpz)_2Cl_2]$ precursor (101 mg, $2.1 \cdot 10^{-4}$ mol) were suspended in 6 mL ethylene glycol. The mixture was heated to 135 °C for 15 hours under N_2. After cooling to room temperature, 20 mL of a saturated aqueous KPF_6 solution was added and the orange precipitate was filtrated. Purification by column chromatography (SiO_2, acetone to acetone/H_2O 100/10, to acetone/H_2O/sat. aq. KNO_3 100/10/1) followed by precipitation of the PF_6^- salt by adding a sat. aq. KPF_6 solution to the aqueous chromatography fractions (organic solvent component removed) afforded the complex (110 mg, $1 \cdot 10^{-4}$ mol, 52 %) as an orange powder. ^{1}H NMR (300 MHz,

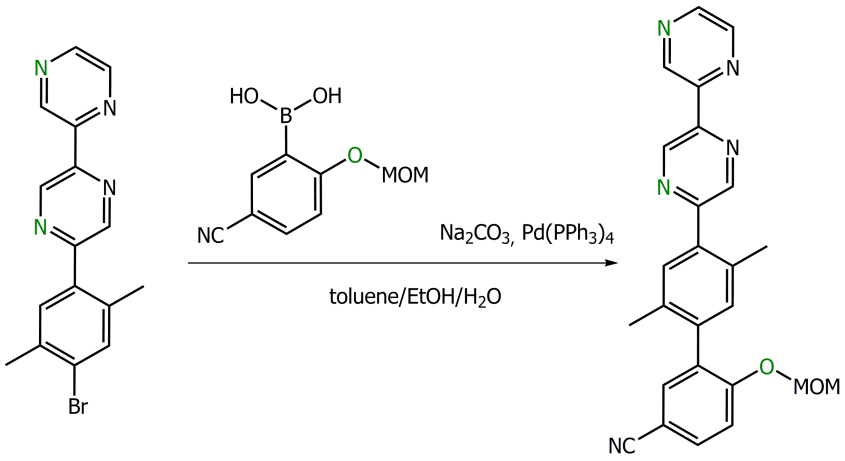
Acetonitrile-d_3): δ 2.14 (s, 3H), 2.22 (s, 3H), 6.86 – 7.03 (m, 3H), 7.04 – 7.17 (m, 2H), 7.27 (ddd, J = 8.0, 7.3, 1.8 Hz, 1H), 7.43 (s, 1H), 7.81 – 7.98 (m, 5H), 8.03 (dd, J = 3.2, 1.2 Hz, 1H), 8.61 – 8.75 (m, 5H), 9.75 – 9.89 (m, 6H) ppm. HRMS (ESI): $[M]^{2+}$ 386.0856 (calcd 386.0849). Elemental analysis: calculated (+ KPF_6, + 2/3 KNO_3) C 34.76, H 2.30, N 13.51; measured C 34.89, H 2.71, N 13.12.



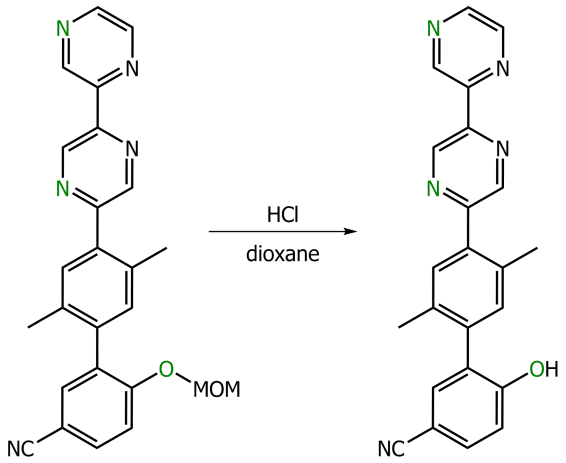
To a suspension of NaH (207 mg, $5.2 \cdot 10^{-3}$ mol) in 10 mL dry THF, 3-bromo-4-hydroxybenzonitrile (1 g, $5.1 \cdot 10^{-3}$ mol) in 6 mL dry THF was added slowly at 0 °C under N_2. After 15 min MOMCl (460 µL, $6.1 \cdot 10^{-3}$ mol) was added dropwise. The mixture was stirred for 45 min at 0 °C and then for 2 hours at room temperature. After pouring the beige reaction mixture onto 50 g of ice, the suspension was extracted with 50 mL EtOAc. The organic phase was washed with brine (100 mL) and water (50 mL) and dried over anhydrous $MgSO_4$ to afford the pure protected phenol as a beige crystalline powder (1.217 g, $5 \cdot 10^{-3}$ mol, 100 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.54 (s, 3H), 5.34 (s, 2H), 7.24 (d, J = 8.6 Hz, 1H), 7.58 (dd, J = 8.6, 2.0 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 56.7, 94.9, 106.4, 113.1, 115.5, 117.6, 132.8, 136.9, 157.4 ppm.



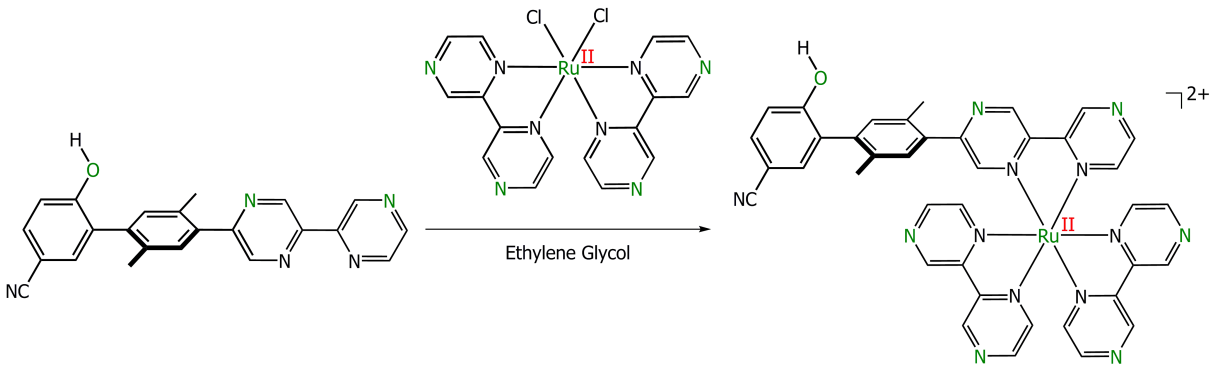
n-BuLi (870 µL, $2.2 \cdot 10^{-3}$ mol, 2.5 M in hexane) was added dropwise to a solution of the protected phenol (499 mg, $2.1 \cdot 10^{-3}$ mol) in 12 mL dry THF at -78 °C under N_2. After 2 hours, trimethylborate (260 µL, $2.3 \cdot 10^{-3}$ mol) was added and the mixture was allowed to warm up to room temperature EtOAc (50 mL) and H_2O (50 mL) were added and the organic phase was separated. The aqueous phase was extracted twice with EtOAc (2 × 50 mL), and the combined organic phases were washed with H_2O (60 mL) and brine (2 × 50 mL) and dried over anhydrous Na_2SO_4. The yellow oil was triturated with 30 mL of a EtOAc/cyclohexane 1/6 mixture to afford the boronic acid **10** (146 mg, $7 \cdot 10^{-4}$ mol, 34 %) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H), 5.35 (s, 2H), 5.72 (s, 2H), 7.22 (d, J = 8.7 Hz, 1H), 7.70 (dd, J = 8.7, 2.2 Hz, 1H), 8.18 (d, J = 2.3 Hz, 1H) ppm.



Compound **8** (131 mg, $3.8 \cdot 10^{-4}$ mol) in 30 mL toluene, the protected *p*-cyanophenol boronic acid **10** (88 mg, $4.3 \cdot 10^{-4}$ mol) in 4 mL EtOH, and Na_2CO_3 (129 mg, $1.2 \cdot 10^{-3}$ mol) in 1 mL H_2O were mixed together and deoxygenated by bubbling N_2 through the solution during 15 min. $Pd(PPh_3)_4$ (49 mg, $4.2 \cdot 10^{-5}$ mol) was then added, and the mixture was bubbled with N_2 for another 10 min prior to heating to reflux under N_2 for 18h. After cooling to room temperature, CH_2Cl_2 (50 mL) and H_2O (50 mL) were added, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic phases were dried over anhydrous Na_2SO_4 and evaporated. Purification by column chromatography (SiO_2, EtOAc, $R_f = 0.7$) yielded a pale yellow solid (123 mg, $2.9 \cdot 10^{-4}$ mol, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H), 2.45 (s, 3H), 3.41 (s, 3H), 5.18 (s, 2H), 7.12 (s, 1H), 7.31 (d, $J = 8.6$ Hz, 1H), 7.44 (s, 1H), 7.49 (d, $J = 2.1$ Hz, 1H), 7.65 (dd, $J = 8.6$, 2.2 Hz, 1H), 8.67 – 8.70 (m, 2H), 8.86 (d, $J = 1.5$ Hz, 1H), 9.66 (dd, $J = 9.7$, 1.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.4, 20.0, 56.5, 94.5, 105.2, 114.9, 118.9, 131.3, 132.2, 132.6, 133.4, 133.7, 134.6, 134.7, 136.1, 137.7, 142.4, 143.5, 143.9, 143.9, 145.1, 146.8, 149.5, 155.4, 157.9 ppm.



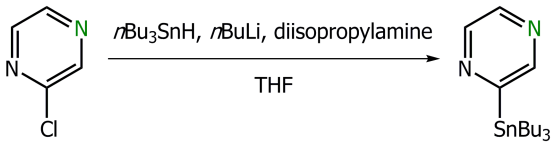
A 4 M solution of HCl in dioxane (3 mL) was added to a solution of the protected ligand (60 mg, $1.4 \cdot 10^{-3}$ mol) in 3 mL dioxane, and the yellow solution was stirred overnight. After neutralization with a saturated aqueous $NaHCO_3$ solution (25 mL), the mixture was extracted with CH_2Cl_2 (2 × 25 mL) and dried over anhydrous $MgSO_4$. Purification by column chromatography (SiO_2, EtOAc/Cyclohexane, 1/1, R_f = 0.3) yielded ligand **12** as a pale yellow solid (51 mg, $1.3 \cdot 10^{-4}$ mol, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 2.45 (s, 3H), 5.89 (s, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.20 (s, 1H), 7.48 – 7.51 (m, 2H), 7.62 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.66 – 8.71 (m, 2H), 8.84 (d, *J* = 1.5 Hz, 1H), 9.58 (d, *J* = 1.5 Hz, 1H), 9.67 (d, *J* = 1.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.2, 19.9, 104.2, 116.8, 119.0, 128.5, 132.4, 133.1, 133.7, 134.4, 134.8, 135.00, 135.2, 137.4, 142.5, 143.3, 143.7, 143.9, 145.0, 147.1, 149.4, 154.9, 156.7 ppm. Elemental analysis: calculated (+ 0.2 EtOAc + 0.2 cyclohexane) C 72.55, H 5.11, N 16.92 measured; C 72.55, H 5.27, N 17.04.



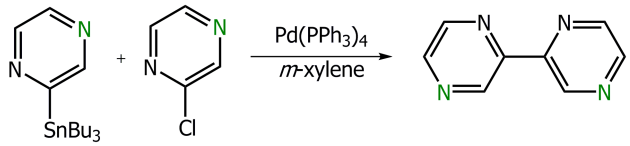
Ligand **12** (85 mg, $2.2 \cdot 10^{-4}$ mol) and the $[Ru(bpz)_2Cl_2]$ precursor (110 mg, $2.3 \cdot 10^{-4}$ mol) were suspended in 8 mL ethylene glycol. The mixture was heated to 135 °C under N_2 for 15 hours. After cooling to room temperature, saturated aqueous KPF_6 solution was added and the red precipitate was filtrated. Purification by column chromatography (SiO_2, acetone to acetone/H_2O 100/10, to acetone, H_2O/sat. aq. KNO_3 100/10/1) followed by precipitation of the PF_6^- salt by adding sat. aq. KPF_6 solution to the aqueous residues of the chromatography fractions (organic solvent components removed) afforded the CN-PhOH–Ru^{2+} dyad (118 mg, $1.1 \cdot 10^{-4}$ mol, 48 %) as a red powder. ^{1}H NMR (400 MHz, Acetone-d_6): δ 2.13 (s, 3 H), 2.22 (s, 3 H), 7.11 - 7.22 (m, 2 H), 7.38 (s, 1 H), 7.47 (d, *J* = 2.1 Hz, 1 H), 7.68 (dd, *J* = 8.5, 2.2 Hz, 1 H), 8.36 - 8.50 (m, 5 H), 8.58 (d, *J* = 3.3 Hz, 1 H), 8.78 (dt, *J* = 12.8, 3.6 Hz, 5 H), 10.18 (dd, *J* = 11.3, 8.2 Hz, 5 H), 10.27 (s, 1 H) ppm. HRMS (ESI): $[M]^{2+}$ 398.5826 (calcd 398.5825).

Elemental analysis: calculated (+2 H_2O) C 41.72, H 2.96, N 16.22; measured C 41.52, H 3.11, N 16.17.

Synthesis of 2,2'-bipyrazine



This synthesis followed a previously published protocol.[4] To a solution of diisopropylamine (1.9 mL, $13.5 \cdot 10^{-3}$ mol) in dry THF (50 mL), *n*-BuLi (1.6 M in hexane, 8.5 mL, $13.5 \cdot 10^{-3}$ mol) was added dropwise at 0°C under N_2. After 10 min, still at 0°C, $SnBu_3H$ (3.8 mL, $14.1 \cdot 10^{-3}$ mol) was added, and the mixture was stirred for 10 min. 2-chloropyrazine (1.5 g, $1.31 \cdot 10^{-2}$ mol) in 10 mL dry THF was added at -78 °C and this mixture was stirred at -78 °C under N_2 for 8 hours. The reaction was quenched at -40 °C by addition of a saturated aqueous KF solution (50 mL). The flask was stored in the fridge overnight. 30 mL H_2O were then added, and the organic and aqueous phases were separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic phases were dried over anhydrous $MgSO_4$. Purification by column chromatography (SiO_2, pentane/EtOAc, 9/1, $R_f = 0.5$) afforded 2-tributylstannylpyrazine as a colorless oil (1.47 g, $4 \cdot 10^{-3}$ mol, 30 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, $J = 7.3$ Hz, 9H), 1.04 – 1.20 (m, 6H), 1.28 – 1.39 (m, 6H), 1.46 – 1.62 (m, 6H), 8.29 – 8.41 (m, 1H), 8.54 (d, $J = 1.7$ Hz, 1H), 8.69 (dd, $J = 2.6$, 1.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.9, 13.6, 27.3, 29.0, 142.9, 146.7, 151.2, 169.9 ppm.



A solution of 2-chloropyrazine (57 µL, $6.4 \cdot 10^{-4}$ mol) and 2-tributylstannylpyrazine (200 µL, $6.3 \cdot 10^{-4}$ mol) in 2.5 mL *m*-xylene was deoxygenated by bubbling with N_2 for 40 min. $Pd(PPh_3)_4$ (39 mg, $3.4 \cdot 10^{-5}$ mol) was added and the mixture was bubbled with N_2 for 15 min. After 3 days at reflux under N_2, the solvent of the black reaction mixture was evaporated, and the residue was purified by column chromatography (SiO_2, EtOAc, $R_f = 0.5$). 2,2'-bipyrazine was obtained as a white solid in 100 % yield (100 mg, $6.3 \cdot 10^{-4}$ mol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, $J = 1.0$ Hz, 2H), 9.63 (d, $J = 1.0$ Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 143.8, 145.2, 149.4 ppm.

Experimental methods / apparatus

^{1}H and ^{13}C NMR spectra were measured on 300 MHz and 400 MHz Bruker Avance spectrometers. The ^{1}H and ^{13}C spectra were referenced relative to $SiMe_4$ by using the solvent signals as internal standards. High-resolution mass spectrometry was performed on a Bruker maXis 4G QTOF ESI mass spectrometer. Elemental analysis was conducted by Ms. Sylvie Mittelheisser at the Department of Chemistry, University of Basel on a Vario Micro Cube instrument from Elementar and by the Analytical Laboratory at the Institute for Inorganic Chemistry at the University of Göttingen using a Vario III CHNS analyzer from Elementar. X-ray diffraction measurement on the single crystal of ligand **11** (Figure 1) was performed on a Bruker APEX II diffractometer, equipped with a graphite monochromator centered on the path of Mo Kα radiation, by Dr. Pierre Dechambenoit at Université de Bordeaux, Centre de Recherche Paul Pascal. A single crystal was coated with Paratone N oil and mounted on a fiber loop, followed by data collection at 120 K. The program SAINT was used to integrate the data, which was thereafter corrected using SADABS.[9] The structure was solved with SHELXS-97 and refined by a full-matrix least-squares method on F^2 using SHELXL-97.[10] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions using suitable riding models. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Further details about the crystal structure refinement can be found in the CIF file (CCDC 951403). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. UV-Vis absorption was measured on a Shimadzu UV-1800 spectrophotometer. Steady-state luminescence was recorded using a Fluorolog 3 instrument from Horiba Jobin-Yvon. Time-resolved luminescence and transient absorption spectroscopy was performed using an LP920-KS instrument from Edinburgh Instruments with the frequency-doubled (or frequency-triplet) output from a Quantel Brilliant b laser as an excitation source. The duration of the excitation pulses was approximately 10 ns. Transient absorption spectra were generally recorded by time-averaging over a detection period of 200 ns. Detection either occurred immediately after pulsed excitation or with suitable delay times as indicated in the text and figure captions. The excitation wavelength was 532 nm unless otherwise indicated.

Quartz cuvettes from Starna and spectrophotometric (or HPLC) grade solvent was used for all optical spectroscopic experiments.

When referring to CH_3CN/water mixtures in the text of the manuscript, this designates 4:1 (v:v) mixtures in the case of the CN-PhOH–Ru^{2+} dyad and 1:1 (v:v) mixtures in the case of the PhOH–Ru^{2+} dyad, respectively. For H/D kinetic isotope effect studies, the aqueous solvent component was heavy water (D_2O); this leads to rapid exchange of the phenolic protons by deuterons.[5]

All optical spectroscopic measurements were performed in aerated solutions.

Additional optical spectroscopic data

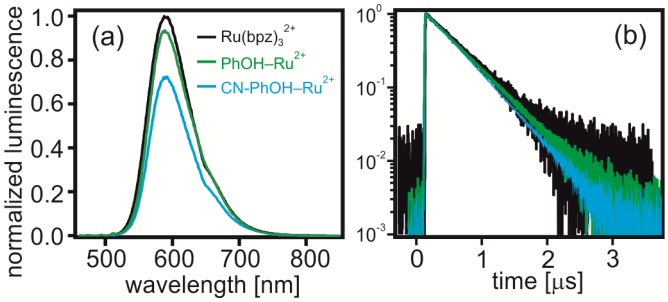


Figure S1. (a) Steady-state luminescence recorded from ~10^{-5} M (aerated) acetonitrile solutions of $Ru(bpz)_3^{2+}$, PhOH–Ru^{2+}, and CN-PhOH–Ru^{2+}. The spectra are corrected for differences in absorbance at the excitation wavelength. The spectrum of $Ru(bpz)_3^{2+}$ has been normalized to a maximum intensity of 1.0, the spectra of the two dyads have been scaled properly. (In one set of experiments, excitation occurred at 444 nm for PhOH–Ru^{2+} and $Ru(bpz)_3^{2+}$; in a second set of experiments, excitation occurred at 495 nm for CN-PhOH–Ru^{2+} and $Ru(bpz)_3^{2+}$). (b) Decays of the luminescence from the same three samples following excitation at 532 nm with pulses of ~10 ns duration. The detection wavelength was 600 nm for PhOH–Ru^{2+} whereas for $Ru(bpz)_3^{2+}$ and CN-PhOH–Ru^{2+} detection occurred at 610 nm.

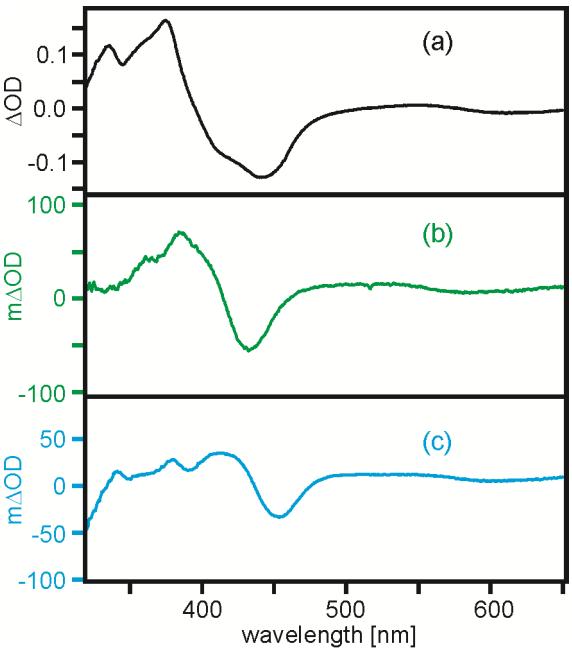


Figure S2. Transient absorption spectra obtained from ~10^{-5} M acetonitrile solutions of (a) $Ru(bpz)_3^{2+}$, (b) PhOH–Ru^{2+}, and (c) CN-PhOH–Ru^{2+}. Excitation occurred at 532 nm with pulses of

~10 ns in all three cases. The spectra were recorded by time-averaging the transient absorption signals over a 200 ns time period starting immediately after the laser pulses.

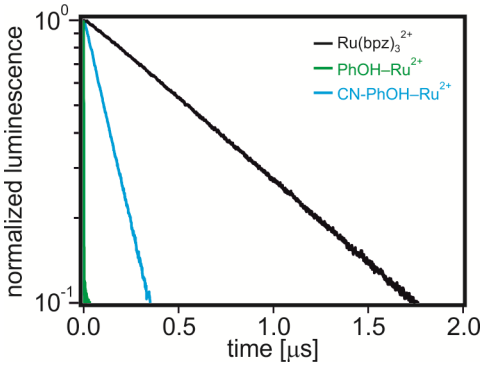
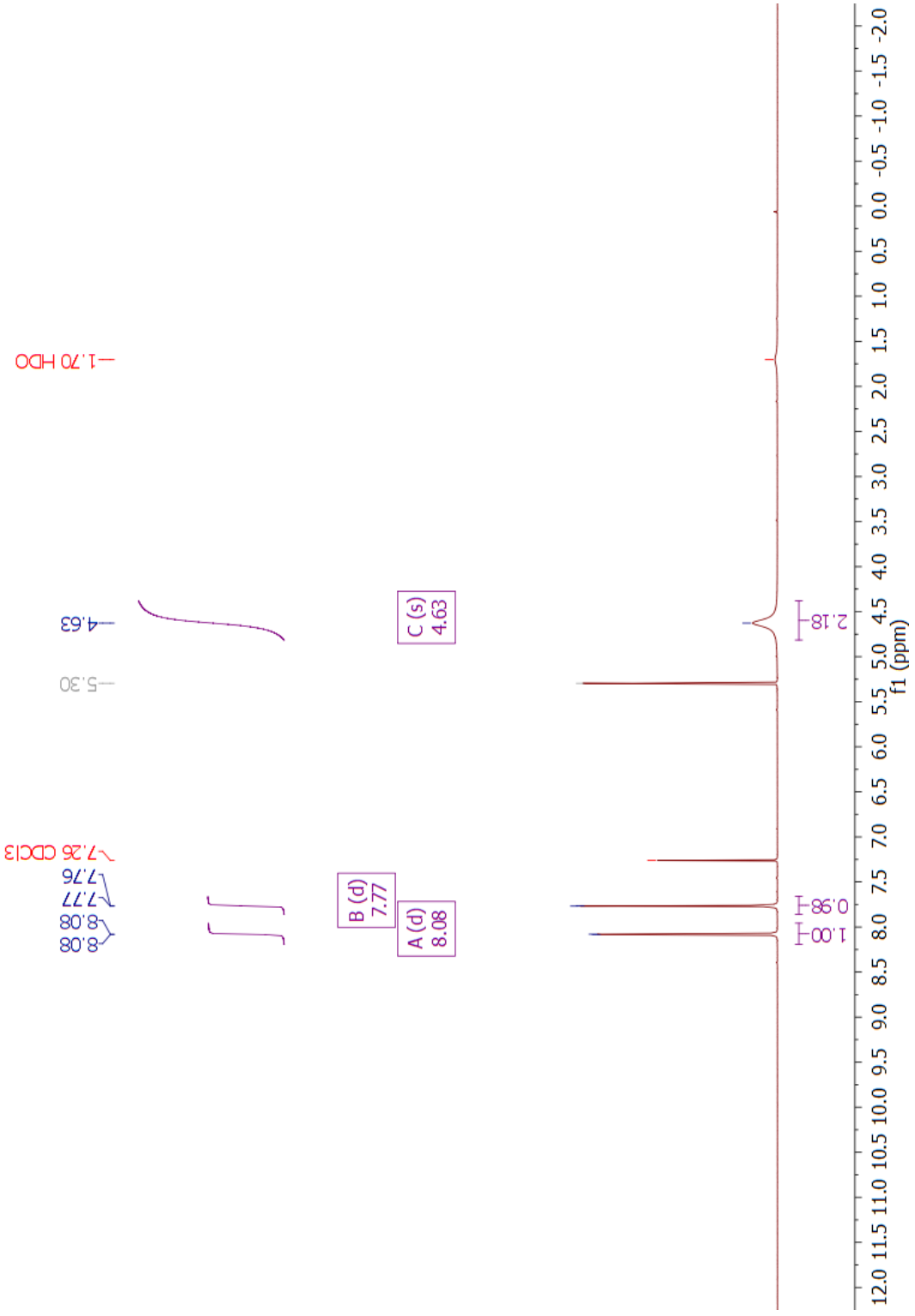


Figure S3. Normalized luminescence decays recorded after pulsed excitation of aerated ~10^{-5} M CH_3CN/H_2O solutions of $Ru(bpz)_3^{2+}$, $PhOH–Ru^{2+}$, and $CN\text{-}PhOH–Ru^{2+}$. The excitation wavelength was 532 nm. The duration of the pulses was ~10 ns. The detection wavelength was 600 nm for $Ru(bpz)_3^{2+}$ and $PhOH–Ru^{2+}$ and 610 nm for $CN\text{-}PhOH–Ru^{2+}$. The CH_3CN/H_2O solutions were 1:1 (v:v) in the case of $Ru(bpz)_3^{2+}$ and $PhOH–Ru^{2+}$, and 4:1 (v:v) in the case of $CN\text{-}PhOH–Ru^{2+}$. The decays were arbitrarily normalized to a value of 1.0 at t = 0.

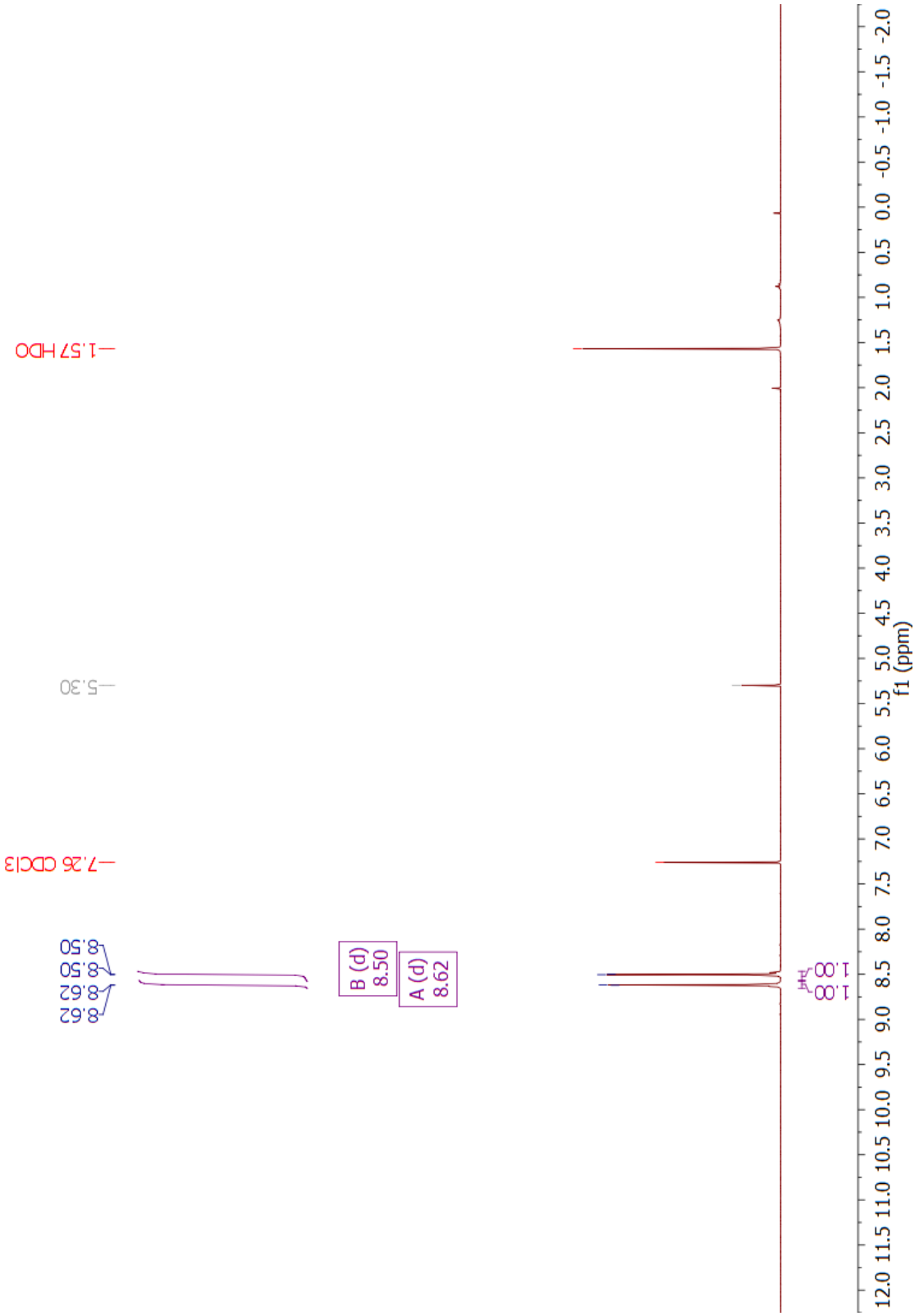
^{1}H NMR spectra of new key compounds

Compound **2**



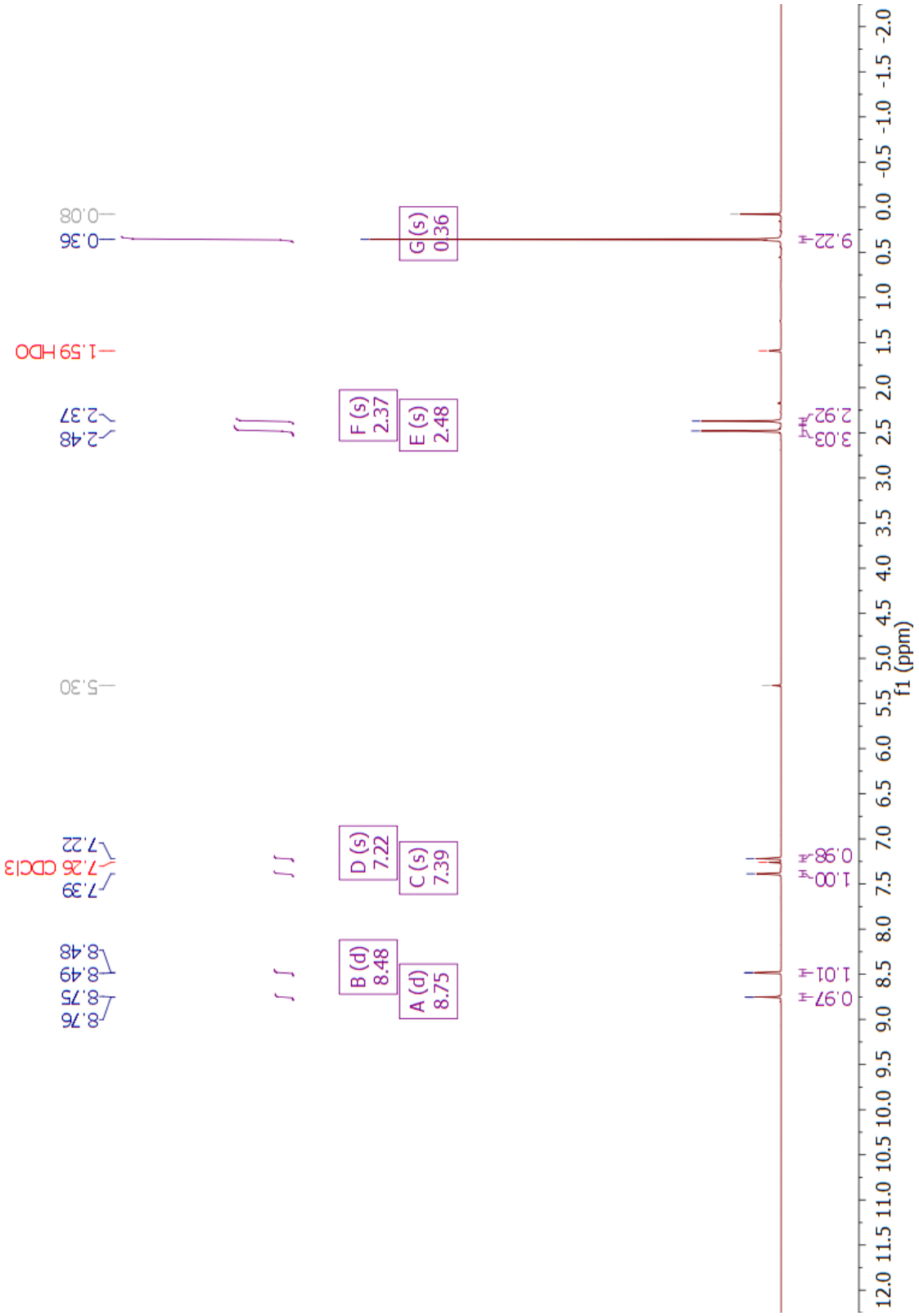
The signal at 5.30 ppm is due to CH_2Cl_2.

Compound **3**



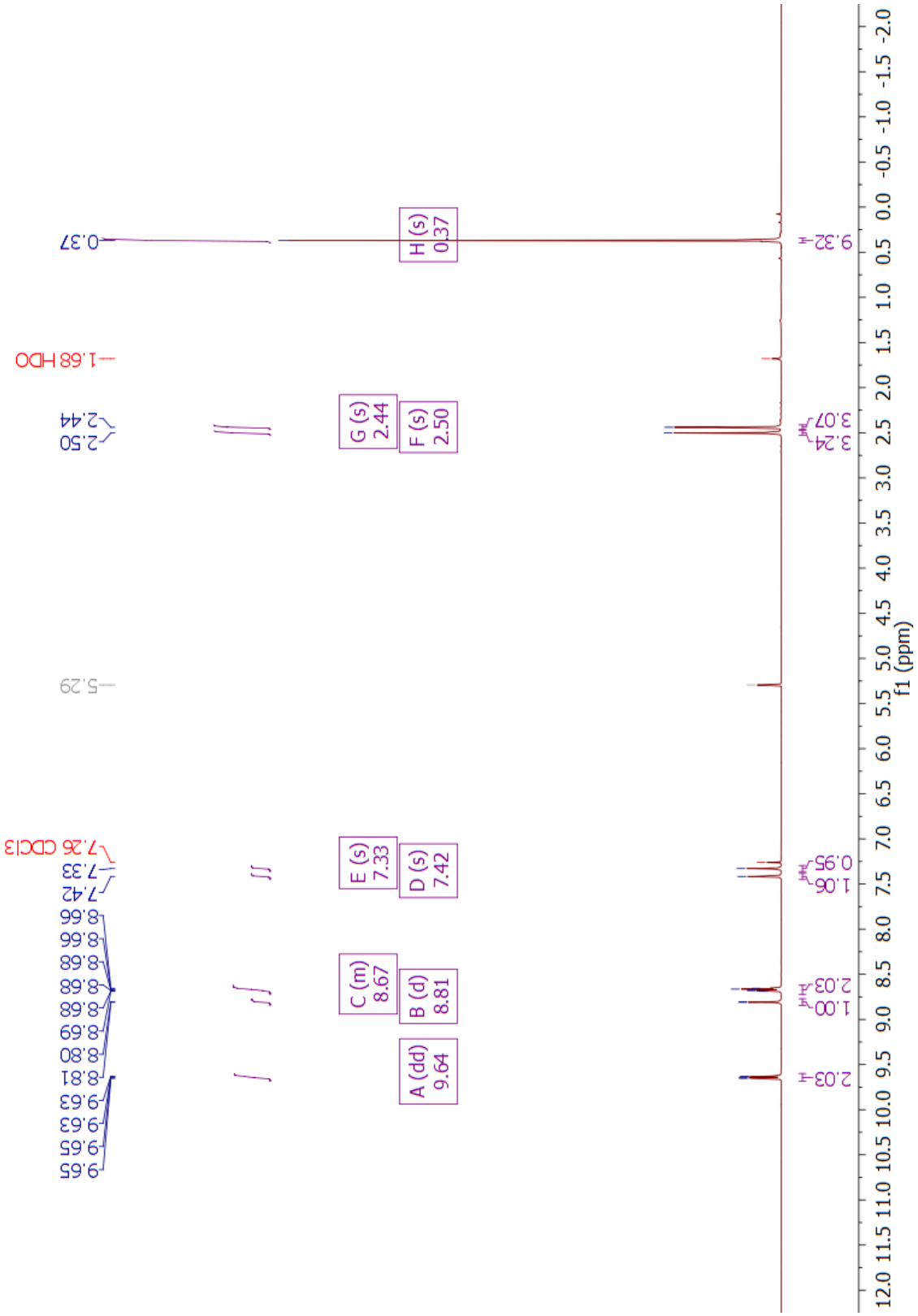
The unlabeled signal at 5.30 ppm is due to CH_2Cl_2.

Compound **5**



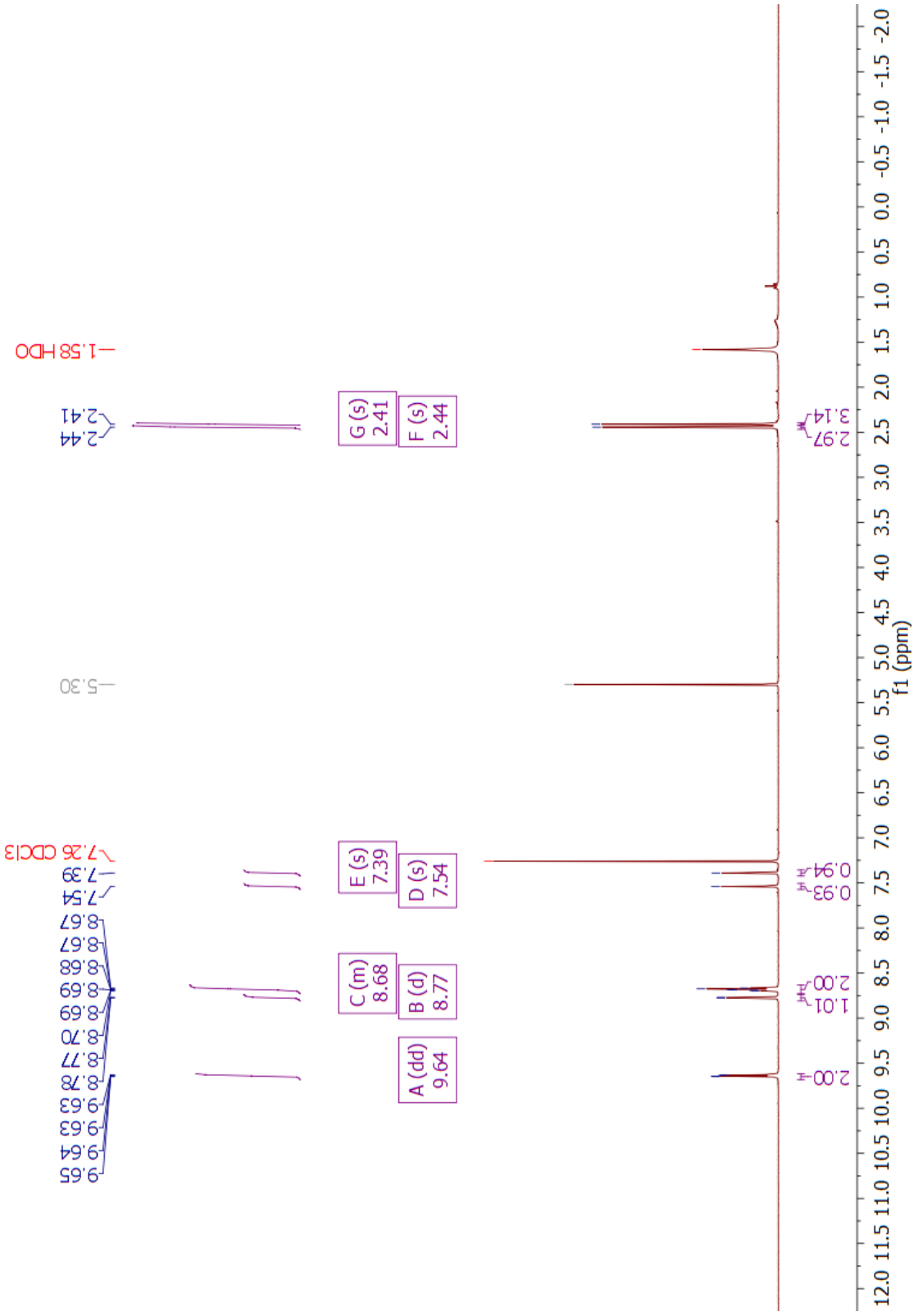
The unlabeled signals at 5.30 ppm and 0.08 ppm are attributed to CH_2Cl_2 and grease, respectively.

Compound **7**



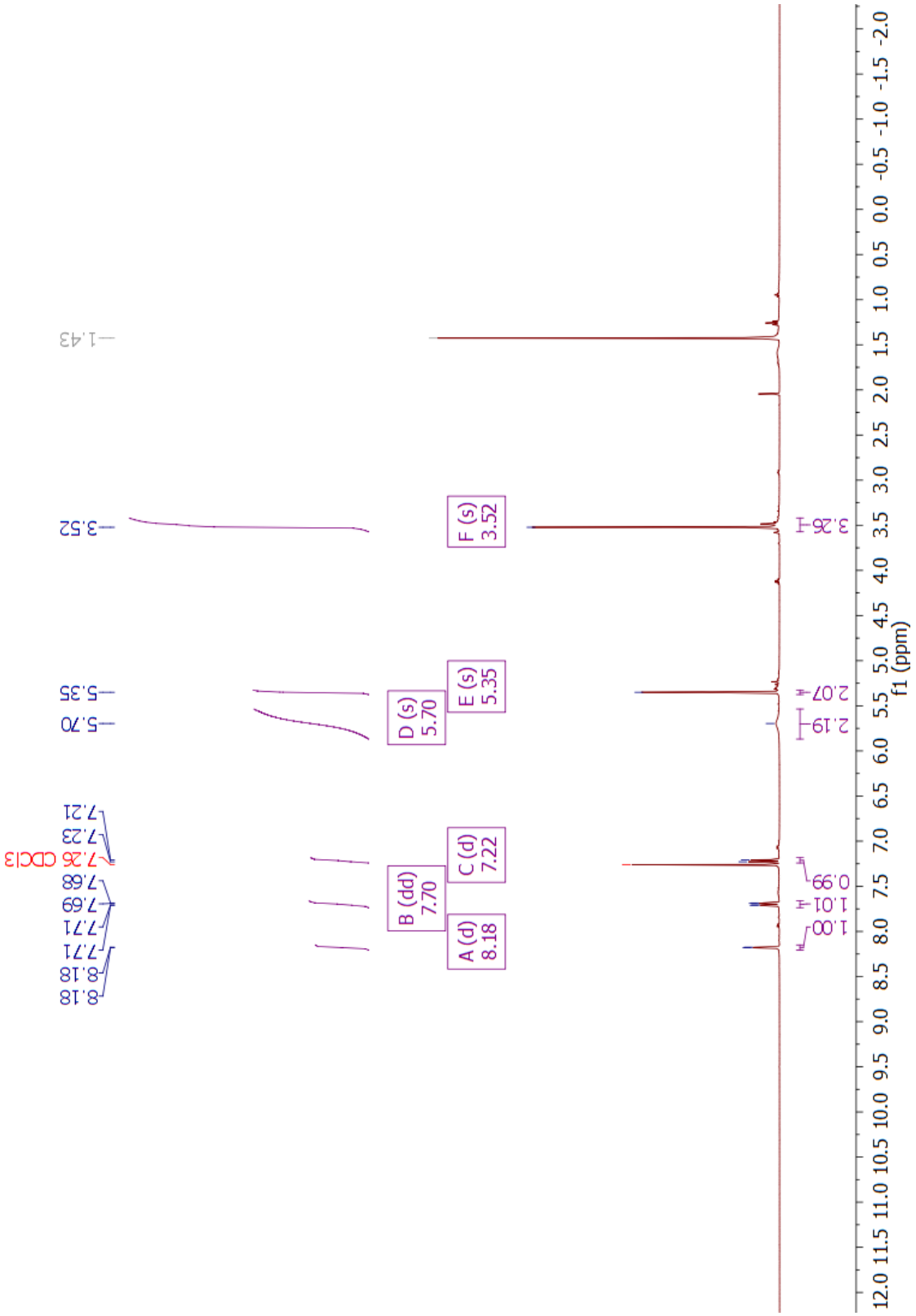
The unlabeled signal at 5.29 ppm is attributed to CH_2Cl_2.

Compound **8**



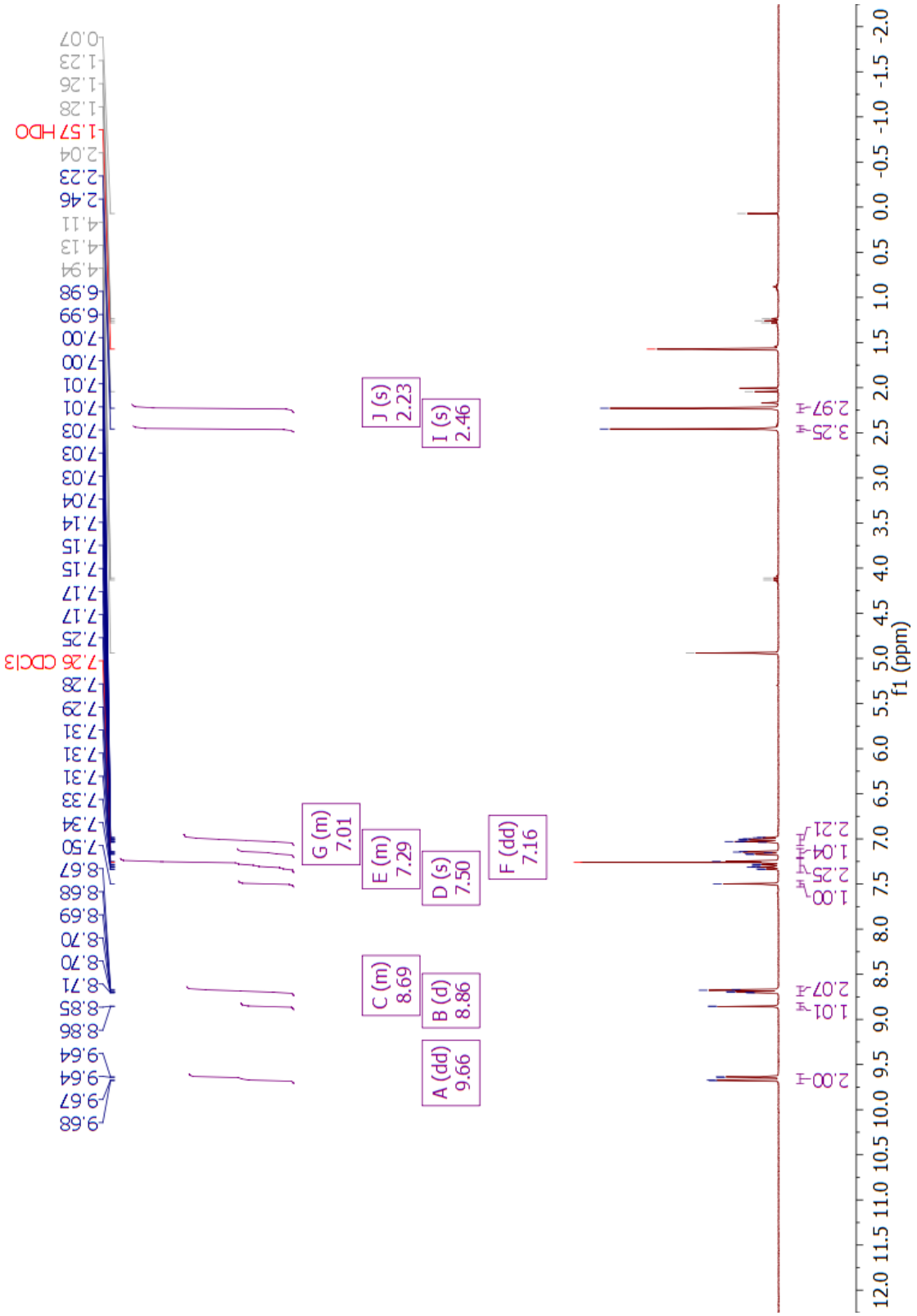
The unlabeled signal at 5.30 ppm is due to CH_2Cl_2.

Compound **10**



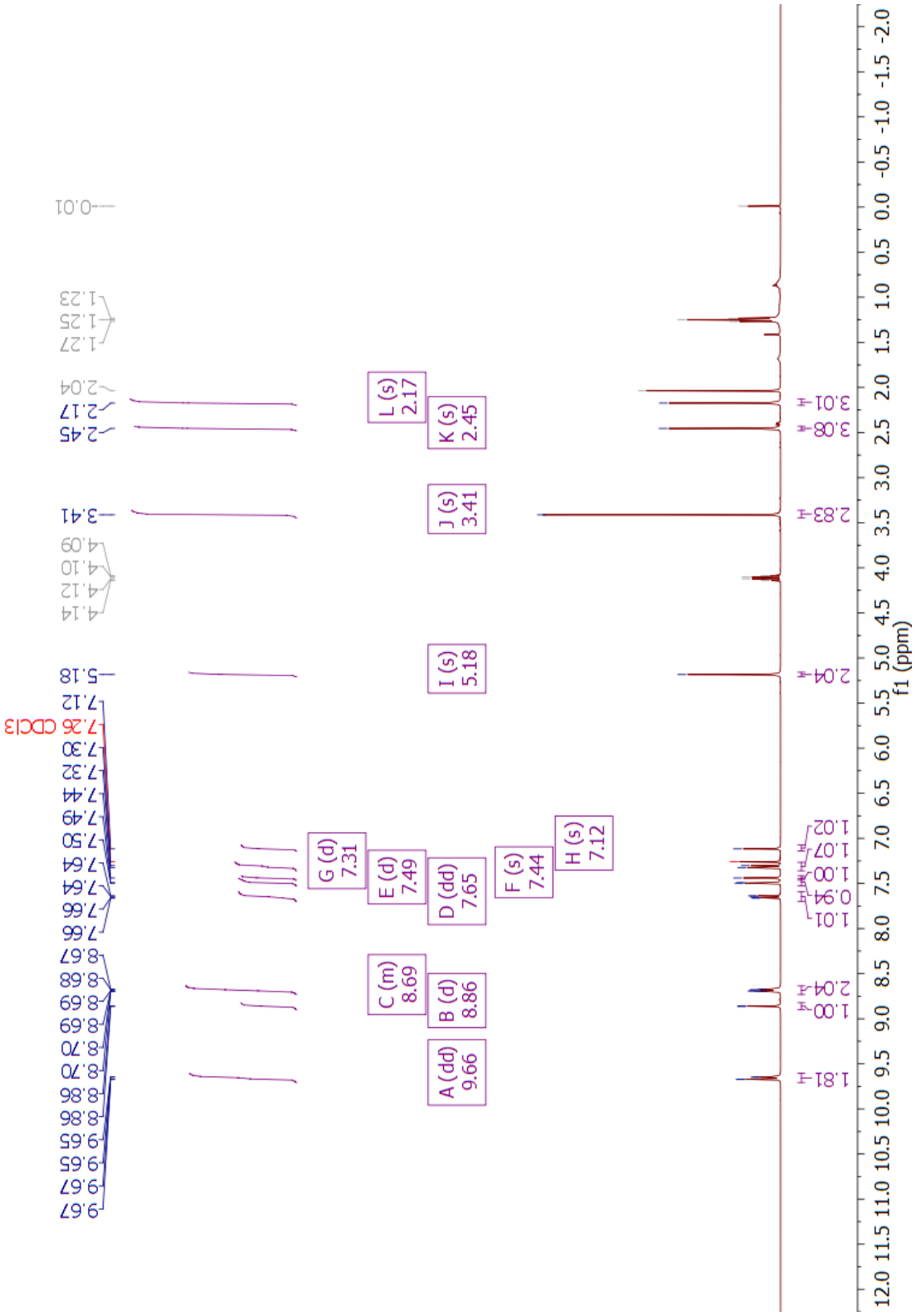
The unlabeled signal at 1.43 ppm is due to cyclohexane.

Ligand **11**



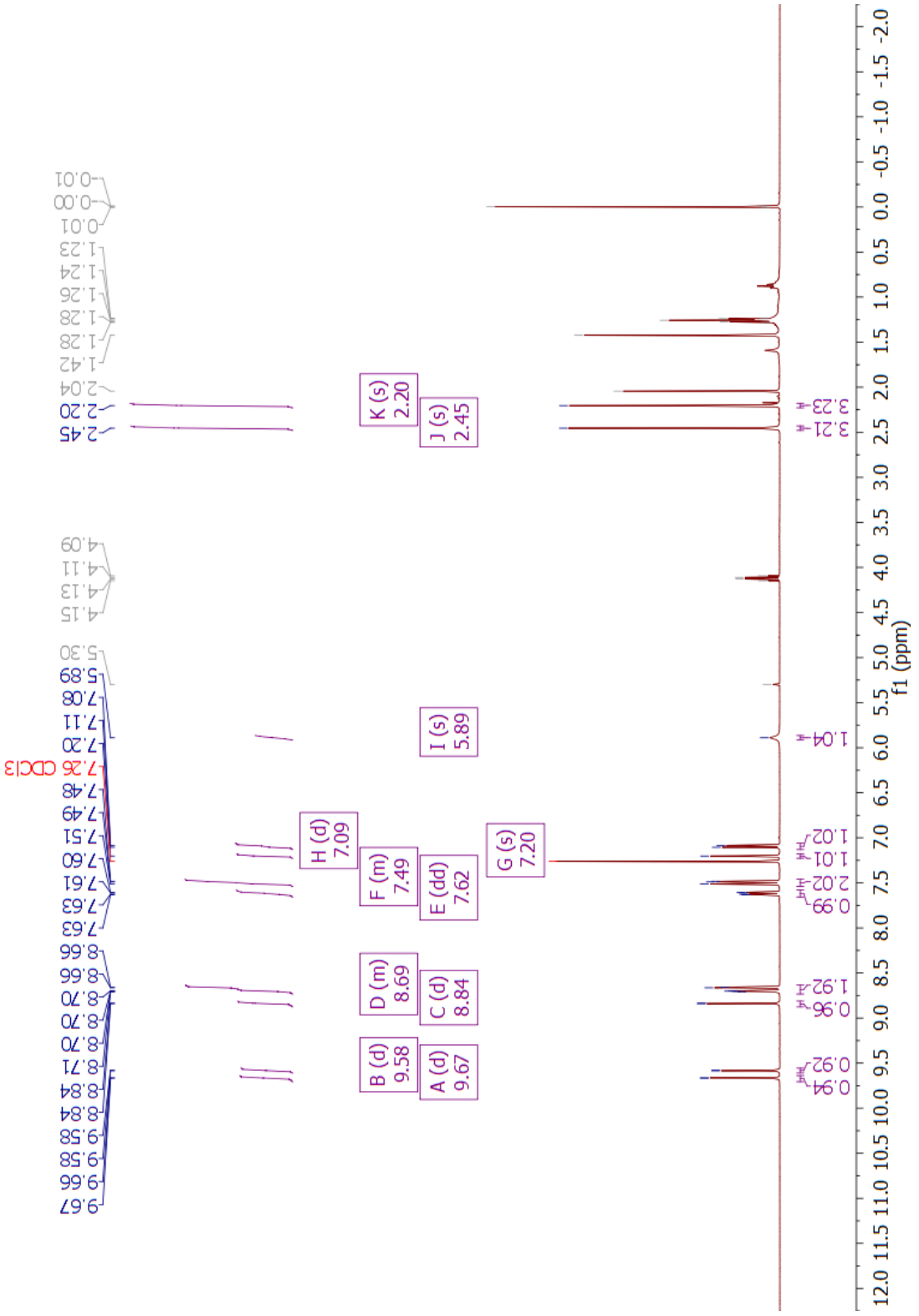
The unlabeled signals at 1.25 ppm, 2.05 ppm, 4.11 pm are due to ethyl acetate. The unlabeled signals at 0.07 ppm and 4.94 ppm are attributed to grease and CH_2Cl_2, respectively.

Ligand **12** before MOM-deprotection



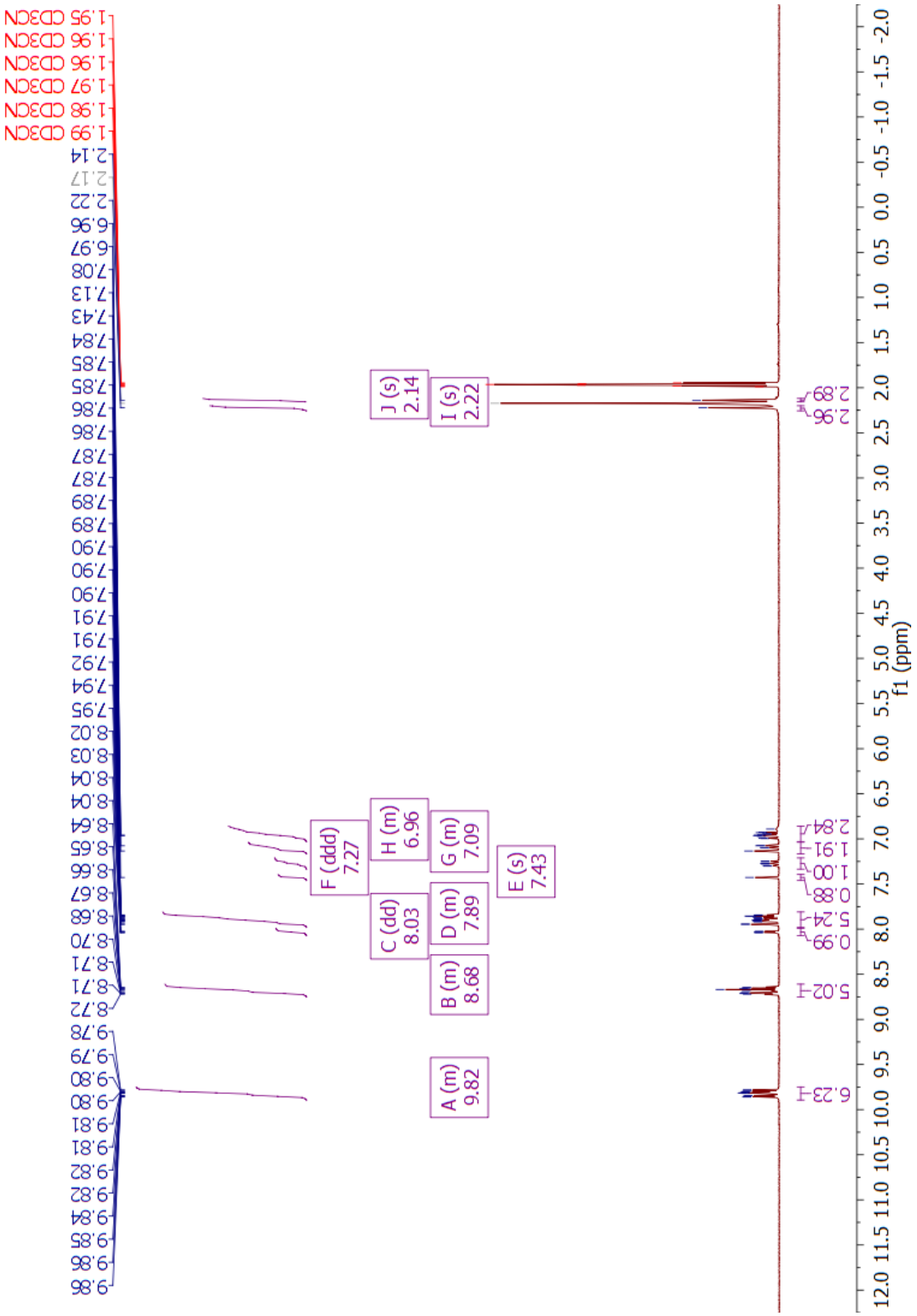
The unlabeled signals at 1.25 ppm, 2.05 ppm, 4.11 pm are due to ethyl acetate. The unlabeled signal at 0.01 is attributed to grease.

Ligand **12**



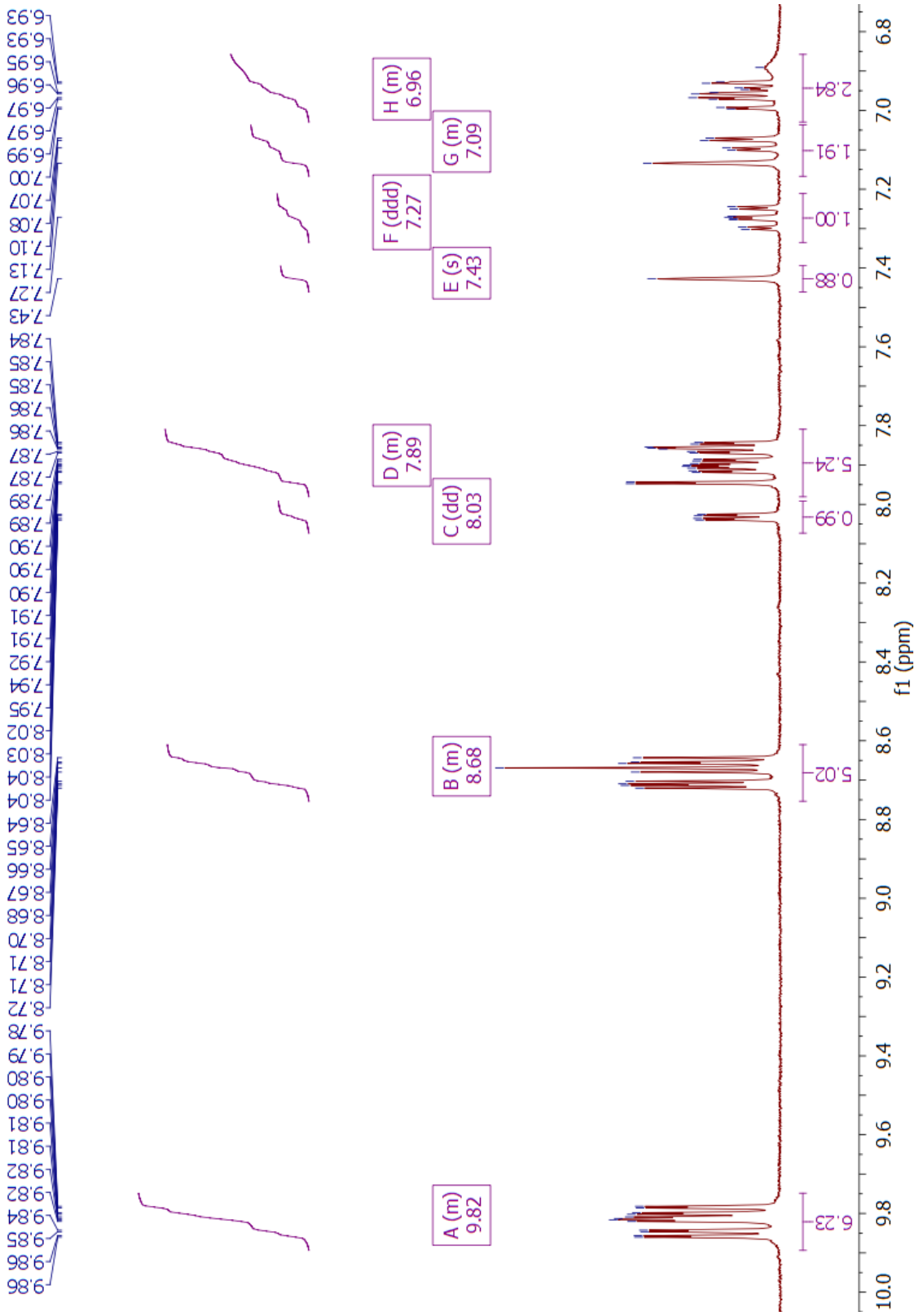
The unlabeled signals at 1.25 ppm, 2.05 ppm, 4.11 ppm are due to ethyl acetate. The unlabeled signal at 0.01 ppm is attributed to grease. The unlabeled signal at 5.32 ppm is due to CH_2Cl_2. The unlabeled signal at 1.42 ppm is assigned to cyclohexane.

PhOH–Ru^{2+}

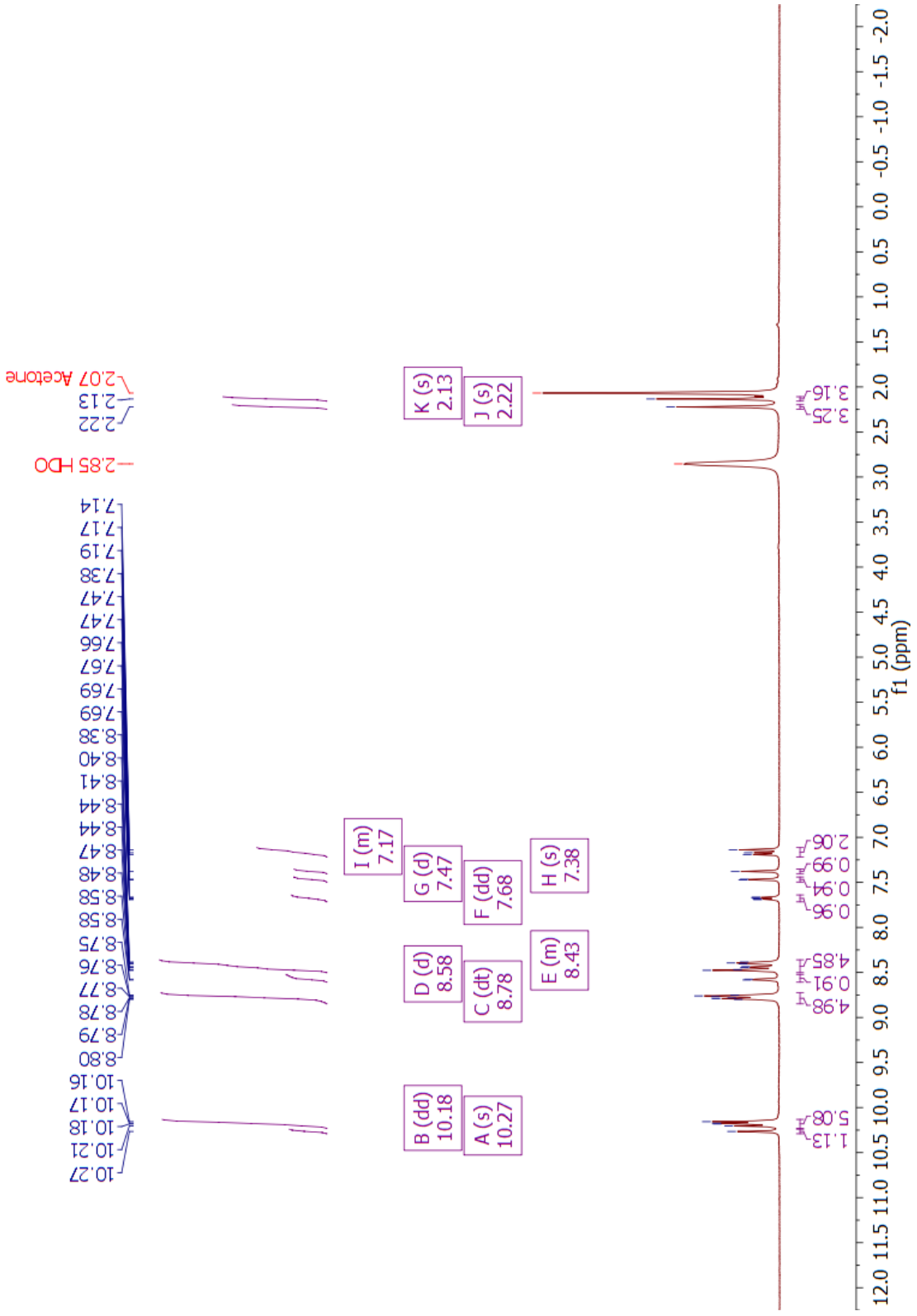


The unlabeled signal at 2.17 ppm is attributed to acetone.

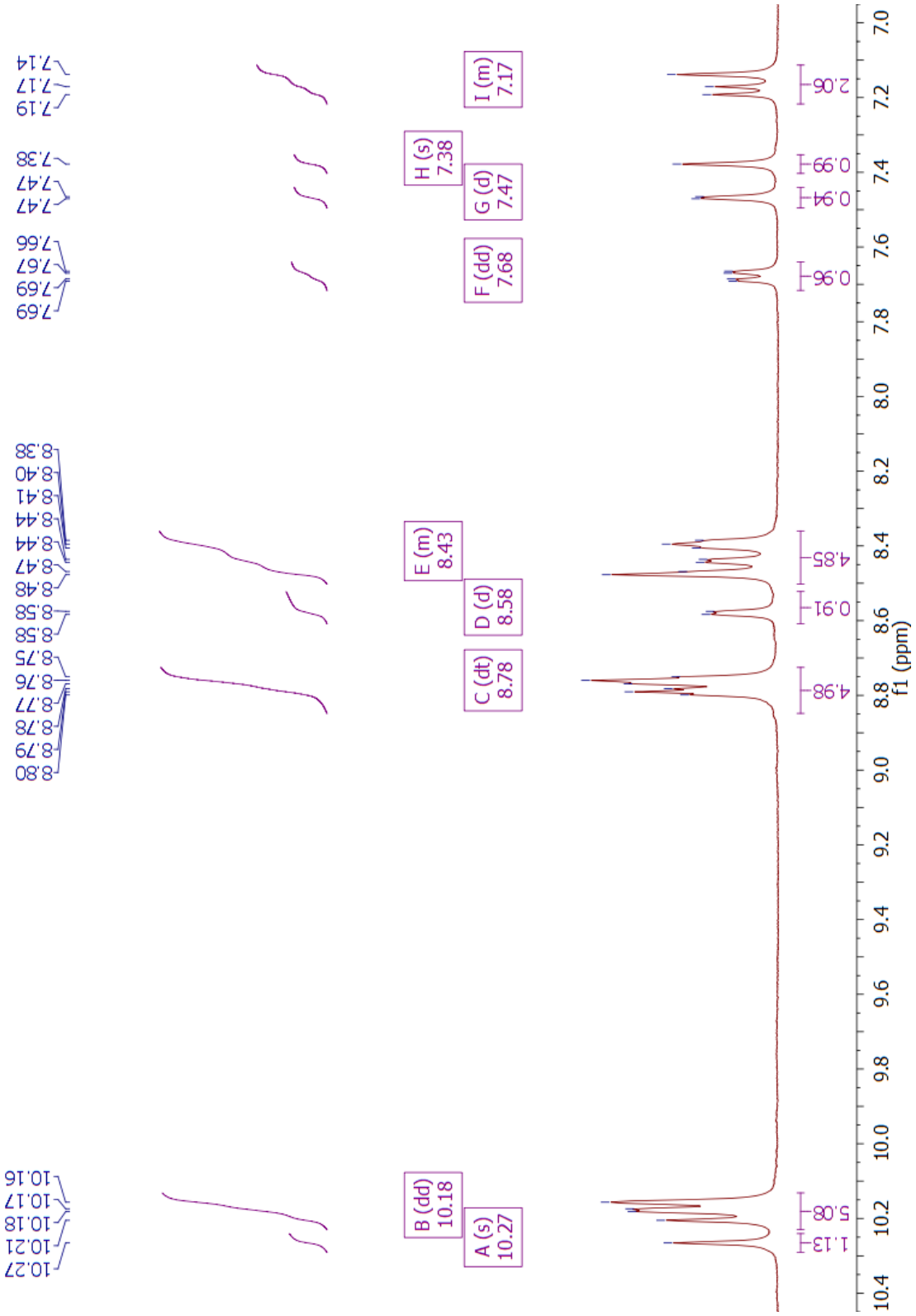
Zoom in the aromatic region of PhOH–Ru^{2+}



CN-PhOH–Ru^{2+}


Acetone
HDO
K (s) 2.13
J (s) 2.22
I (m) 7.17
G (d) 7.47
F (dd) 7.68
H (s) 7.38
D (d) 8.58
C (dt) 8.78
E (m) 8.43
B (dd) 10.18
A (s) 10.27
f1 (ppm)

Zoom in the aromatic region of CN-PhOH–Ru^{2+}



References

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(2) Dales, N.; Zhang, Z. US Patent, WO 2008/0245390 A2. 2008.

(3) Hanss, D.; Wenger, O. S., *Inorg. Chem.* **2009,** *48*, 671.

(4) Darabantu, M.; Boully, L.; Turck, A.; Ple, N., *Tetrahedron* **2005,** *61*, 2897.

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(6) APEX2 Software Suite; Bruker AXS, Madison, WI, 2009.

(7) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.