

Synthesis of an Unsymmetrically Substituted, Dithienylethene-Containing 1,10-Phenanthroline Ligand and its Ruthenium(II) Complex

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Abstract: The synthesis of an unsymmetrically substituted 1,10-phenanthroline ligand and its corresponding ruthenium(II) complex is reported. Suzuki coupling has been employed under different conditions to get the target ligand.

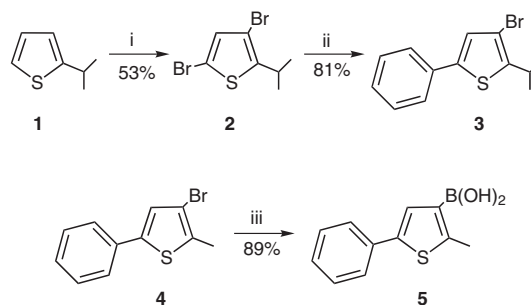
Key words: metal complexes, cross-coupling, heterocycles, ligands, ruthenium

Organic dithienylethene derivatives have been extensively reported because of their potential applications in the field of photochromic systems and photonic devices.¹ Metal complexes containing such derivatives as ligands are less common in literature.² In general, new properties like energy transfer processes from a metal complex to an incorporated photochromic unit can be observed if a dithienylethene-substituted phenanthroline ligand is coordinated to a ruthenium complex.³ Recently, Yam et al. published a 1,10-phenanthroline ligand fused with a photochromic dithienylethene moiety and its ruthenium(I) complex.⁴ In all the dithienylethene-phenanthroline systems reported so far, both thiophene moieties are identical. Here, we report the synthesis of an unsymmetrically substituted, dithienylethene containing 1,10-phenanthroline ligand **8** and its ruthenium(II) complex **Ru(8)**. The asymmetry was introduced by means of the two differently substituted thiophene units.

The thiophene moieties **3** and **5** were synthesized as shown in Scheme 1.

The precursor **3** was prepared from 2-isopropylthiophene (**1**)⁵ in a two-step reaction. Compound **1** was brominated in chloroform–acetic acid (1:1) over five hours to form 3,5-dibromo-2-isopropylthiophene (**2**). *n*-BuLi was added to a solution of compound **2** in anhydrous THF at –78 °C followed by the addition of tributyl borate. After warming to room temperature, Pd(PPh₃)₄, aqueous Na₂CO₃ (20 wt%) and iodobenzene were added to the mixture to obtain 3-bromo-5-phenyl-2-isopropylthiophene (**3**) (81%). The Suzuki coupling reaction was performed under deaerated conditions.

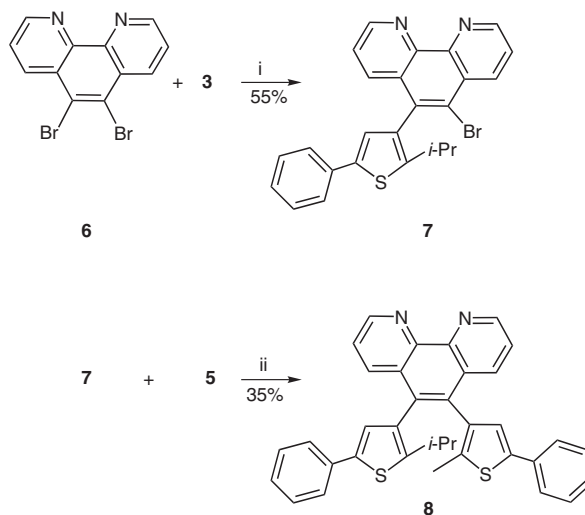
The precursor **5** was synthesized by reacting 3-bromo-2-methyl-5-phenylthiophene (**4**)⁶ with *n*-BuLi in THF at –78 °C. Then, tributyl borate was added to form the bo-



Scheme 1 Reagents and conditions: i) Br₂, 0 °C, CHCl₃–toluene (1:1); ii) *n*-BuLi, THF, –78 °C; tributyl borate; PhI, Pd(PPh₃)₄, aq Na₂CO₃, 70 °C, 24 h; iii) *n*-BuLi, THF, –78 °C; tributyl borate; concd HCl.

ronic ester, which was hydrolyzed with hydrochloric acid to yield 5-phenyl-2-methylthio-3-boronic acid (**5**).

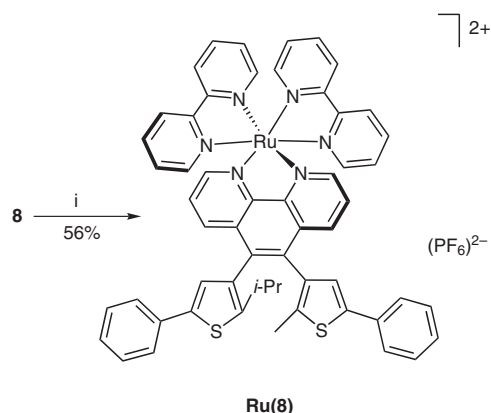
Synthesis of ligand **8** was performed as described in Scheme 2. 5,6-Dibromo-1,10-phenanthroline (**6**) was prepared by the procedure outlined by Mlochowsky.⁷ *n*-BuLi was added to a solution of precursor **3** in anhyd THF at –78 °C followed by the addition of tributyl borate. After warming to room temperature, Suzuki coupling was performed by adding Pd(PPh₃)₄ catalyst, aqueous Na₂CO₃ (20 wt%) and **6** to furnish 5-bromo-6-(2-isopropyl-5-thien-3-yl)-1,10-phenanthroline (**7**) in moderate yield. The homo disubstituted product, with two isopropyl sub-



Scheme 2 Reagents and conditions: i) **3**, *n*-BuLi, THF, –78 °C; tributyl borate; **6**, Pd(PPh₃)₄, aq Na₂CO₃, 70 °C, overnight; ii) Pd(PPh₃)₄, aq Na₂CO₃, 100 °C, 60 h.

stituents, was detected during the purification process in very poor yield (less than 1%) and analyzed by ^1H NMR and MS.⁸ Compound **5** was dissolved in ethanol–toluene (1:1) and $\text{Pd}(\text{PPh}_3)_4$, aqueous Na_2CO_3 (20 wt%), and **7** was added to carry out a second Suzuki coupling reaction to get ligand **8** in moderate yield.

For the formation of the metal complex, $[\text{Ru}(\text{bpy})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and ligand **8** were refluxed in methoxyethanol overnight. The solvent was removed and the residue was dissolved in water. The complex **Ru(8)** was precipitated with NH_4PF_6 and purified on silica gel preparative plate (Scheme 3).



Scheme 3 Reagents and conditions: i) $[\text{Ru}(\text{bpy})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, methoxyethanol, reflux, 7 h.

Ligand **8** and complex **Ru(8)** showed no photochromism unlike the symmetrically substituted analogue with a methyl group attached to each of the two thiophene moieties. The reason lies in the exclusive formation of the *syn*-isomer of ligand **8** which is photo-inert and undergoes no photocyclization reaction.⁹

To conclude, we have developed a synthetic strategy, involving Suzuki coupling and manipulation of solvent polarity, to get the asymmetrically substituted ligand **8**.

Column chromatography was performed using silica gel, 230–400 or 400–600 mesh size, from Chemie Brunschwig AG. Preparative plates (20 × 20 cm) with silica gel 60 F₂₅₄, having a layer thickness of 2 mm and aluminum sheets (for TLC) coated with silica gel 60 F₂₅₄ were purchased from Merck.

All products were characterized by ^1H NMR and ^{13}C NMR spectra, recorded on a Bruker Avance DRX-400 (400.13 MHz, for ^1H NMR and 100.62 MHz for ^{13}C NMR) and on a Bruker Avance DRX-360 spectrometer (360 MHz, for ^1H NMR and 90.55 MHz for ^{13}C NMR). Chemical shifts are given in ppm using the solvent itself as internal standard. The chemical shifts are expressed as δ values and the coupling constants (J) are given in Hertz.

Mass spectra were recorded on a HP 5988A Quadrupol (EI ionization, 70 eV) mass spectrometer. ESI and high-resolution mass spectra were recorded on a Bruker FTMS 4.7T BioAPEXII spectrometer.

GC-MS analyses were recorded on a ThermoQuest Finnigan VOYAGER GS/MS Trace GC 2000 Series equipped with an Optima-5-MS column (0.25 μm , 25 m × 0.32 mm, Macherey-Nagel).

2,4-Dibromo-5-isopropylthiophene (2)

2-Isopropylthiophene (**1**; 2 mL, 16 mmol) was dissolved in CHCl_3 –toluene (1:1, 10 mL). The solution was cooled to 0 °C and Br_2 (2.2 mL, 43 mmol) in CHCl_3 –toluene (1:1, 5 mL) was added dropwise over 5 h. Stirring was continued overnight at r.t. H_2O (20 mL) was added to the dark brown solution and the aqueous phase was extracted with CHCl_3 (3 × 10 mL). The combined organic fractions were neutralized (Na_2CO_3), dried (MgSO_4) and filtered. The solvent was removed and the brown oil thus-obtained was purified by column chromatography (silica, hexane) to yield **2** as a colorless oil; yield: 2.3 g (53%).

IR (film): 3094, 2954, 2920, 2850, 1723, 1522, 1456, 1384, 1364, 1294, 1122, 1104, 1024, 966, 808, 806 cm^{-1} .

^1H NMR (CDCl_3): δ = 6.97 (s, 1 H), 3.36 (sept, J = 6.8 Hz, 1 H), 1.32 (d, J = 6.8 Hz, 1 H).

^{13}C NMR (CDCl_3): δ = 148.9, 131.9, 109.0, 106.1, 30.4, 23.7.

MS (EI): m/z = 283.9 (M^+).

3-Bromo-2-isopropyl-5-phenylthiophene (3)

To anhyd THF (60 mL) containing **2** (2.5 g, 8.8 mmol), was added $n\text{-BuLi}$ (1.6 M in hexane, 6 mL, 9.6 mmol) at –78 °C under argon, and the solution was stirred for 1 h at the same temperature. Tributyl borate (3.5 mL, 13 mmol) was slowly added to the mixture and the stirring was continued for 1.5 h at –78 °C. After warming up the solution to r.t., aq 20 wt% Na_2CO_3 (22 mL), iodobenzene (1.8 g, 1 mL, 8.8 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.42 g, 0.38 mmol) were added. The mixture was refluxed at 70 °C for 24 h. The product was extracted with Et_2O and the organic fractions were dried (MgSO_4), filtered, and concentrated. The residue was purified by distillation (Kugelrohr-oven) to give **3** as a colorless oil; yield: 2.0 g (81%).

IR (film): 3058, 3024, 2960, 2864, 1940, 1866, 1790, 1598, 1496, 1384, 1362, 1194, 1100, 1072, 1032, 1016, 952, 904, 866, 816, 754, 688 cm^{-1} .

^1H NMR (CDCl_3): δ = 7.59 (d, 2 H, J = 7.7 Hz), 7.42 (dd, 2 H, J = 7.7, 7.3 Hz), 7.34 (t, 1 H, J = 7.3 Hz), 7.2 (s, 1 H), 3.44 (sept, 1 H, J = 6.8 Hz), 1.42 (d, J = 6.9 Hz, 6 H).

^{13}C NMR (CDCl_3): δ = 146.6, 140.8, 133.7, 129.0, 127.8, 125.5, 125.4, 107.5, 30.0, 23.9.

MS (EI): m/z = 281.9 (M^+).

2-Methyl-5-phenylthio-3-boronic Acid (5)

$n\text{-BuLi}$ (1.6 M in hexane, 6.2 mL, 9.9 mmol, 1.1 equiv) was added slowly to a stirred solution of 3-bromo-2-methyl-5-phenylthiophene (**4**; 2.27 g, 9.0 mmol, 1 equiv) in anhyd THF (65 mL) at –78 °C under argon. After 60 min, tributyl borate (3.6 mL, 13.5 mmol, 1.5 equiv) was added, and the stirring continued at –78 °C for 5 h followed by warming up to r.t. After 15 h, the mixture was added to 1.2 N HCl (26 mL) and stirred. The THF layer was separated and extracted with aq 1 N NaOH (4 × 7 mL). The combined aqueous phases were then filtered to remove trace of solids, and then acidified to pH 1 at 0 °C with conc. HCl. The resulting precipitates were filtered, washed with 0.01 N HCl and dried under vacuum, to yield **5** as a white powder; yield: 1.52 g (89%).

IR (KBr): 3336, 3060, 3022, 2970, 2862, 1932, 1858, 1780, 1598, 1540, 1498, 1466, 1438, 1378, 1308, 1286, 1178, 1120, 1046, 992, 848 cm^{-1} .

^1H NMR ($\text{DMSO}-d_6$): δ = 2.60 (s, 3 H), 7.24 (tt, J = 7.4, 1.1 Hz, 1 H), 7.38 (dd, J = 7.4, 8.3 Hz, 1 H), 7.53 (dd, J = 8.3, 1.3 Hz, 1 H), 7.61 (s, 1 H), 7.95 (s, 2 H).

^{13}C NMR (CDCl_3): δ = 15.7, 124.9, 126.9, 129.1, 129.8, 134.1, 138.6, 148.6

MS (EI): m/z = 218.3 (M^+).

5-Bromo-6-(2-isopropyl-5-phenylthien-3-yl)-1,10-phenanthroline (7)

To anhyd THF (3 mL) containing 3-bromo-2-isopropylthiophene (**3**; 120 mg, 0.43 mmol, 2 equiv), was added *n*-BuLi (1.6 M in hexane, 0.3 mL, 0.48 mmol, 2.25 equiv) at -78°C under argon, and the resulting solution was stirred for 1 h at the same temperature. Tributyl borate (0.2 mL, 0.74 mmol, 3.5 equiv) was slowly added to the mixture followed by stirring for another 1.5 h at -78°C . After warming the solution up to r.t., aq 20 wt% Na_2CO_3 (1 mL), 5,6-dibromophenanthroline (**6**; 72 mg, 0.21 mmol, 1 equiv), and $\text{Pd}(\text{PPh}_3)_4$ (25 mg, 0.021 mmol, 10%) were added to the mixture and refluxed overnight at 70°C . The crude product was washed with Et_2O and filtered to yield **7**; yield: 113 mg (58%).

IR (KBr): 3058, 2954, 2922, 2862, 1924, 1954, 1748, 1596, 1586, 1558, 1508, 1416, 1470, 906, 844, 802, 760, 738, 694 cm^{-1} .

^1H NMR (CDCl_3): δ = 9.26 (dd, J = 4.1, 1.4 Hz, 1 H), 9.23 (dd, J = 4.5, 1.4 Hz, 1 H), 8.84 (dd, J = 8.6, 1.4 Hz, 1 H), 8.01 (dd, J = 8.2, 1.4 Hz, 1 H), 7.78 (dd, J = 8.2, 4.5 Hz, 1 H), 7.64 (d, J = 7.7 Hz, 2 H), 7.59 (dd, J = 8.4, 4.3 Hz, 1 H), 7.38 (dd, J = 7.5, 7.5 Hz, 2 H), 7.21 (t, J = 7.2 Hz, 1 H), 7.12 (s, 1 H), 2.78 (sept, J = 6.8 Hz, 1 H), 1.28 (d, J = 6.8 Hz, 3 H) 1.12 (d, J = 6.8 Hz, 3 H).

^{13}C NMR (CDCl_3): δ = 151.2, 150.9, 149.5, 141.8, 137.9, 137.3, 135.5, 134.5, 133.3, 134.0, 129.9, 129.3, 129.1, 128.7, 127.8, 126.1, 125.6, 125.1, 124.4, 124.4, 124.1, 29.6, 25.3, 24.9.

MS (ESI): m/z = 461.1 ($\text{M}^+ + 1$).

HRMS: m/z calcd for $\text{C}_{25}\text{H}_{20}\text{BrN}_2\text{S}$ ($\text{M}^+ + 1$): 459.0525; found: 459.0525.

6-(2-Isopropyl-5-phenylthien-3-yl)-5-(2-methyl-5-phenylthien-3-yl)-1,10-phenanthroline (8)

A deaerated mixture of toluene (2 mL), EtOH (2 mL) and aq 2 M Na_2CO_3 (0.4 mL) was added to a flask containing the boronic acid **5** (150 mg, 0.69 mmol, 7.9 equiv), bromophenanthroline **7** (40 mg, 0.087 mmol, 1 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (130 mg, 0.06 mmol, 69%). Two immiscible phases were formed. The mixture was heated at 100°C under argon for 60 h and then the solvents were removed in vacuo. The residual solid was further purified by column chromatography (SiO_2 , CH_2Cl_2 – Et_3N , 100:2) to give a white-brown solid, which was then washed with Et_2O to afford the colorless product **8**; yield: 17 mg (35%).

IR (KBr): 3056, 3020, 2956, 2864, 1654, 1596, 1560, 1508, 1438, 1178, 1118, 808, 746, 722, 692, 540 cm^{-1} .

^1H NMR (CDCl_3): δ = 1.01 (d, J = 6.8 Hz, 3 H), 1.02 (d, J = 6.8 Hz, 3 H), 2.18 (s, 3 H), 2.64 (sext, J = 6.8 Hz, 1 H), 6.92 (s, 1 H), 7.20 (dd, J = 6.6, 1.0 Hz, 2 H), 7.21 (s, 1 H), 7.33 (dd, J = 7.8, 7.3 Hz, 2 H), 7.39 (dd, J = 7.5, 7.5 Hz, 2 H), 7.44–7.50 (m, 1 H), 7.60 (d, J = 7.1 Hz, 2 H), 7.63–7.78 (m, 3 H), 8.18 (d, J = 8.3 Hz, 1 H), 8.23 (d, J = 8.3 Hz, 1 H), 9.26–9.36 (m, 2 H).

^{13}C NMR (CDCl_3): δ = 14.6, 24.5, 26.1, 29.0, 125.6, 125.6, 125.8, 126.5, 127.2, 127.4, 128.0, 128.4, 128.5, 128.8, 128.9, 129.4, 131.9, 131.9, 132.0, 132.1, 132.5, 133.0, 133.6, 134.2, 134.3, 134.8, 136.2, 140.5, 140.6, 149.9, 149.9, 151.1.

MS (ESI): m/z = 553.18 ($\text{M}^+ + 1$).

HRMS: m/z calcd for $\text{C}_{36}\text{H}_{29}\text{N}_2\text{S}_2$ ($\text{M}^+ + 1$): 553.1766; found: 553.1763.

Metal Complex Ru(8)

To a 10-mL, one-necked, round-bottom flask were added the ligand **8** (15 mg, 27.2 μmol , 1 equiv), $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (15 mg, 29.9 μmol , 1.1 equiv) and methoxyethanol (5 mL). The solution was refluxed for 7 h at 120°C under argon. The solvent was removed in vacuo and the residue was suspended in a solution of NH_4PF_6 (5 mL, 10 g/150 mL). The precipitate was collected by fil-

tration and purified on a silica gel plate (MeCN – MeOH – H_2O / KNO_3 , 100:10:10:1) to afford **Ru(8)** as a red powder; yield: 19 mg (56%).

IR (KBr): 3076, 2958, 2922, 2852, 1704, 1660, 1602, 1466, 1446, 1426, 838, 762, 558 cm^{-1} .

^1H NMR (CD_3CN): δ = 1.00–1.07 (m, 3 H), 1.09–1.15 (m, 3 H), 1.00–1.07 (m, 3 H), 2.19–2.33 (m, 3 H), 2.71–2.85 (m, 1 H), 2.90–3.07 (m, 1 H), 7.05–7.29 (m, 3 H), 7.30–7.38 (m, 3 H), 7.39–7.46 (m, 4 H), 7.47–7.53 (m, 3 H), 7.55–7.61 (m, 2 H), 7.62–7.79 (m, 5 H), 7.87–7.92 (m, 2 H), 8.03–8.10 (m, 2 H), 8.11–8.18 (m, 4 H), 8.22–8.37 (m, 2 H), 8.51–8.61 (m, 4 H).

MS (ESI): m/z = 1111.18 ($\text{M}^+ - \text{PF}_6^-$).

HRMS: m/z calcd for $\text{C}_{56}\text{H}_{44}\text{N}_6\text{RuS}_2$ ($\text{M}^{2+} - 2\text{PF}_6^-$): 483.1051; found: 483.1052.

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References

- (1) (a) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85.
(b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
- (2) (a) Adamo, V.; Belser, P. *Chimia* **2003**, *57*, 169. (b) Chen, B.; Wang, M.; Wu, Y.; Tian, H. *Chem. Commun.* **2002**, 1060. (c) Fernandez-Acebes, A.; Lehn, J.-M. *Adv. Mater.* **1998**, *10*, 1519. (d) Fernandez-Acebes, A.; Lehn, J.-M. *Chem. Eur. J.* **1999**, *5*, 3285. (e) Frayse, S.; Coudret, C.; Launay, J.-P. *Eur. J. Inorg. Chem.* **2000**, 1581. (f) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779. (g) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Coord. Chem. Rev.* **2005**, *249*, 1327. (h) Konaka, H.; Wu, L. P.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y. *Inorg. Chem.* **2003**, *42*, 1928. (i) Matsuda, K.; Takayama, K.; Irie, M. *Inorg. Chem.* **2004**, *43*, 482. (j) Matsuda, K.; Takayama, K.; Irie, M. *Chem. Commun.* **2001**, 363. (k) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1727. (l) Murguly, E.; Norsten, T. B.; Branda, N. R. *Angew. Chem. Int. Ed.* **2001**, *40*, 1752. (m) Samachetty, H. D.; Branda, N. R. *Chem. Commun.* **2005**, 2840. (n) Sud, D.; McDonald, R.; Branda, N. R. *Inorg. Chem.* **2005**, *44*, 5960. (o) Takeshita, M.; Irie, M. *J. Org. Chem.* **1998**, *63*, 6643. (p) Takeshita, M.; Irie, M. *Tetrahedron Lett.* **1998**, *39*, 613.
- (3) Belser, P.; De Cola, L.; Hartl, F.; Adamo, V.; Bozic, B.; Iyer, Y. C. V. M.; Jukes, R. T. F.; Kühni, J.; Querol, M.; Roma, S.; Salluce, N. *Adv. Funct. Mater.* **2006**, *16*, 195.
- (4) Yam, V. W.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 12734.
- (5) Detty, M. R.; Hays, D. S. *Heterocycles* **1995**, *40*, 925.
- (6) (a) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871. (b) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 285. (c) Lantz, R.; Hornfeldt, A. B. *Chem. Scr.* **1972**, *2*, 9.
- (7) Mlochowski, J. *J. Rocz. Chem.* **1974**, *48*, 2145.
- (8) ^1H NMR (CDCl_3): δ = 9.34 (d, J = 4.1 Hz, 2 H), 8.29 (d, J = 8.3 Hz, 2 H), 7.71 (dd, J = 8.3, 4.3 Hz, 2 H), 7.46 (d, J = 6.0 Hz, 4 H), 7.30 (dd, J = 7.3, 6.1 Hz, 4 H), 7.25 (t, J = 7.1 Hz, 2 H), 2.75 (sept, J = 6.8 Hz, 2 H), 1.18 (d, J = 6.8 Hz, 3 H) 1.06 (d, J = 6.8 Hz, 3 H). MS (ESI $^+$): m/z = 581.2 ($\text{M}^+ + 1$).
- (9) Kühni, J.; Adamo, V.; Belser, P. *Chimia*, submitted for publication.