Electronic Supplementary Information

for

Orthopalladated imidazolones and thiazolones: synthesis, photophysical properties and photochemical reactivity

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Contents

Experimental Section

Materials and Measurements. Solvents were obtained from commercial sources and were used without further purification. All reactions were performed without special precautions against air and moisture. IR spectra were measured in solid state on a Perkin-Elmer Spectrum One spectrophotometer. Electrospray ionization (ESI^+) mass spectra were recorded using Bruker Esquire3000 plus™ or Amazon Speed ion-trap mass spectrometers equipped with standard ESI sources. High-resolution mass spectra-ESI (HRMS-ESI) were recorded using either a Bruker MicroToF-Q™ system equipped with an API-ESI source and a Q-ToF mass analyzer, or a TIMS-TOF system, both allowing a maximum error in the measurement of 5 ppm. Acetonitrile was used as solvent. For all types of MS measurements, samples were introduced in a continuous flow of 0.2 mL/min and nitrogen served both as the nebulizer gas and the dry gas. The ^1H, ^{13}C and ^{19}F NMR spectra of the isolated products were recorded in $CDCl_3$, CD_2Cl_2 or dmso-d_6 solutions at 25 °C (other conditions were specified) on Bruker AV300, AV400 or Bruker AV500 spectrometers (δ in ppm, J in Hz) at ^1H operating frequencies of 300.13, 400.13 and 500.13 MHz, respectively. The ^1H and ^{13}C NMR spectra were referenced using the solvent signal as internal standard, while ^{19}F NMR spectra were referenced to $CFCl_3$. The assignment of ^1H NMR peaks has been performed through standard 2D ^1H–COSY (2K points in t_2 using a spectral width of 10 ppm; 128 t_1 experiments were recorded and zero-filled to 1K; for each t_1 value four scans were signal-averaged using a recycle delay of 1 s) and selective 1D ^1H-SELNOE experiments. Typical mixing times in the case of selective 1D-SELNOE experiments were in the range 0.5-2 s, as a function of the irradiated signal. These values of optimized mixing times were set equal to the longitudinal relaxation time T_1, determined using the inversion–recovery sequence. The ^{13}C NMR peaks were identified using standard ^1H–^{13}C edited-HSQC and ^1H–^{13}C HMBC 2D-experiments. In both cases 4K points in t_2 using spectral widths of 10 ppm (^1H) and 200 ppm (^{13}C) were used, with averaged values of the coupling constants $^1J_{CH}$ = 145 Hz and long-range $^nJ_{CH}$ = 10 Hz. Typically, 128 t_1 experiments were recorded and zero-filled to 2K. For each t_1 value 8 (HSQC) or 32 (HMBC) scans were signal-averaged using a recycle delay of 1 s. Absorption spectra were measured on a Thermo Scientific Evolution 600BB spectrophotometer. The steady-state excitation–emission spectra were measured on a Jobin-Yvon Horiba Fluorolog FL-3-11 spectrofluorimeter. All measurements were carried out at room temperature on solutions of 10^{-5}M concentration using quartz cuvettes of 1 cm path length. The measurement of the quantum yield values (Φ_{PL}) was carried out using the absolute method on a Quantaurus-QY C11347 spectrometer. The oxazolones **1a-1e** were prepared using the Erlenmeyer–Plöchl method, by reaction of hippuric acid with the corresponding aldehydes in acetic anhydride.[1] The new imidazolones **2a-2e** and the known thiazolones **3a-3e** were prepared from the corresponding oxazolones **1** by published methods.[2,3]

X-ray Crystallography and Structural Data. Single crystals of **4c, 11a** and **11b** of suitable quality for X-ray diffraction measurements were grown by slow diffusion of *n*-pentane into CH_2Cl_2 or $CHCl_3$ solutions of the crude products at –18 °C for several weeks. One selected single crystal of each compound was mounted at a MicroMount (MiTeGen) in a random orientation, covered with perfluorinated oil (magic oil) and placed under a cold stream of N_2 gas. Crystallographic measurements were carried out at 100 K on a Bruker APEXD8 Venture CCD diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection is based on narrow frame ω and ϕ scans. The diffraction frames were integrated using the program SAINT[4] and the integrated intensities were corrected for absorption with SADABS.[5] The structures were solved by direct methods with SHELXS[6] and refined with SHELXL, [7] included in Olex2 program.[8] All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of **4c** and **11b** were included in the model in calculated positions and refined as riding atoms, with an isotropic displacement parameters equal to 1.2–1.5 times the equivalent isotropic displacement parameter of their parent atoms. Non-disordered hydrogen atoms of **11a** were included in observed positions and freely refined. Special details on disordered or solvent treatment are described below. **CCDC 2332942-2332944** contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for complex 4c: $C_{42}H_{30}Cl_4F_6N_4O_6Pd_2$; Mr = 1155.25; orange prism, 0.140 × 0.160 × 0.260 mm^3; monoclinic *C2/c*; a = 24.7871(14) Å, b = 10.8791(7) Å, c = 16.2545(10) Å, β = 101.132(2)°; V = 4300.7(5) Å^3, Z = 4, D_c= 1.784 g/cm^3; μ = 1.164 cm^{-1}; min. and max. absorption correction factors: 0.7002 and 0.7457; $2\theta_{max}$ = 56.602°; 109048 reflections measured, 5340 unique; R_{int} = 0.0272; number of data/restraint/parameters 5340/1/299; R_1 = 0.0195 [5318 reflections, $I > 2\sigma(I)$], *wR2* =

0.0491 (all data); largest difference peak 0.608 e·Å^{-3}. Two fluorine atoms of a CF_3 fragment have been found to be disordered. They have bene included in the model in three sets of positions and isotropically refined.

Crystal data for complex 11a: $C_{36}H_{18}F_8N_2O_6Pd_2S_2{\cdot}2(CHCl_3)$; Mr = 1242.18; orange prism, 0.140 × 0.170 × 0.190 mm^3; orthorhombic *Pbcn*; *a* = 22.7038(8) Å, *b* = 11.4463(5) Å, *c* = 16.6779(7) Å; *V* = 4334.2(3) Å^3, *Z* = 4, D_c= 1.904 g/cm^3; μ = 1.380 cm^{-1}; min. and max. absorption correction factors: 0.7010 and 0.7457; $2\theta_{max}$ = 56.608°; 88200 reflections measured, 5375 unique; R_{int} = 0.0361; number of data/restraint/parameters 5375/0/347; R_1 = 0.0235 [5203 reflections, $I > 2\sigma(I)$], *wR2* = 0.0586 (all data); largest difference peak 0.764 e·Å^{-3}.

Crystal data for complex 11b: $C_{36}H_{18}Cl_2F_6N_2O_6Pd_2S_2{\cdot}2(CH_2Cl_2)$; Mr = 1206.23; orange block, 0.090 × 0.095 × 0.130 mm^3; orthorhombic *Pbcn*; *a* = 24.4713(8) Å, *b* = 11.0368(4) Å, *c* = 15.9675(5) Å; *V* = 4312.6(3) Å^3, *Z* = 4, D_c= 1.857 g/cm^3; μ = 1.377 cm^{-1}; min. and max. absorption correction factors: 0.6806 and 0.7464; $2\theta_{max}$ = 64.192°; 65746 reflections measured, 7464 unique; R_{int} = 0.0351; number of data/restraint/parameters 7464/0/262; R_1 = 0.0293 [6717 reflections, $I > 2\sigma(I)$], *wR2* = 0.0782 (all data); largest difference peak 0.688 e·Å^{-3}. Attempts to interpret solvent as disordered dichloromethane lead to unrealistic geometrical parameters. Therefore, its contribution to the calculated structure factors have been calculated with a solvent mask. Two fluorine atoms of a CF_3 fragment have been found to be disordered, they have been included in the model in two sets of positions and refined with complementary occupancy factors.

Computational Details. All calculations were carried out within the Density Functional Theory (DFT),[9] using the Gaussian16 program package.[10] First, in order to characterize the ground electronic state of the selected complexes, geometry optimizations and harmonic frequency calculations were performed by using the M06-2X[11] exchange-correlation functionals, combined with the 6-31+G(d,p) basis set for the non-metal atom,[12] def2SVP basis set and the corresponding pseudopential was used for Pd center.[13] All the calculations included the integral equation formalism variant of the polarizable continuum model (IEF-PCM) with the SMD solvation model (solvent = dichloromethane) to account for solvent effects.[14] Finally, in order to study the photoabsorption process Time-Dependent Density Functional Theory (TDDFT)[15] was used, at the same levels of theory used in the characterization of the ground states. Vertical transitions were calculated for absorption properties. The molecular orbitals representations were generated by *PyMOL*[16] using Paton Research Group openly accessible display settings.[17]

General synthesis of New Imidazolones 2a-2e

All (*Z*)-4-aryliden-1-propyl-2-phenyl-5(4*H*)-imidazolones **2a-e** have been prepared from the corresponding oxazolones **1a-1e** following methods reported in the literature.[2]

(*Z*)-4-(4-fluorobenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2a)

(*Z*)-4-(4-fluorobenzylidene)-2-phenyl-5(4*H*)-oxazolone **1a** (2.11 g, 7.9 mmol) was suspended in pyridine (6 mL) and treated with *n*-propylamine (0.65 mL, 7.9 mmol) with strong stirring for 20 minutes at 25 °C. A white precipitate formed. After this time, bis(trimethylsilyl)acetamide (BSA, 3.85 mL, 15.8 mmol) was added, and the resulting mixture was stirred while heated at 110 °C for 15 h. The resulting dark suspension was allowed to cool to room temperature and treated with 15 mL of ethyl acetate. This mixture was washed with brine (5×15 mL), dried over anhydrous $MgSO_4$, filtered to remove any remaining solid, and evaporated to dryness. The resulting brown oil was treated with 10 mL of *n*-hexane giving **2a** as an orange solid, which was filtered, washed with additional *n*-hexane (10 mL) and dried by suction. Orange solid. Obtained: 1.67 g, yield: 68%. ^{1}H NMR ($CDCl_3$, 400.16 MHz): δ 8.24 (dd, 2H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.75 Hz, H_2/H_6, C_6H_4), 7.78 (dd, 2H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.6 Hz, H_o, C_6H_5), 7.58 – 7.52 (m, 3H, H_m, H_p, C_6H_5), 7.20 (s, 1H, =CH), 7.10 (dd, 2H, $^3J_{HH}$ = 8.7 Hz, H_3/H_5, C_6H_4), 3.74 (t, 2H, $^3J_{HH}$ = 7.5 Hz, NCH_2), 1.59 (sext, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2), 0.84 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 171.72 (C=O), 163.89 (d, $^1J_{CF}$ = 252.86 Hz, CF, C_6H_4), 163.00 (CN), 138.67 (C=), 134.69 (d, $^3J_{CF}$ = 8.34 Hz, C_2/C_6, C_6H_4), 131.46 (C_p, C_6H_5), 130.78 (d, $^4J_{CF}$ = 3.13 Hz, C_i, C_6H_4), 129.88 (C_i, C_6H_5), 128.99 (C_m, C_6H_5), 128.40 (C_o, C_6H_5), 127.41 (d, $^5J_{CF}$ = 1.34 Hz, =CH), 115.99 (d, $^2J_{CF}$ = 21.88 Hz, C_3/C_5, C_6H_4), 43.46 (NCH_2), 22.68 (CH_2), 11.11 (CH_3). ^{19}F NMR (376.49 MHz, $CDCl_3$) δ -108.42 (s, CF). HRMS (ESI$^+$) m/z calcd for $C_{19}H_{18}FN_2O$ $[M+H]^+$: 309.1403, found: 309.1405.

(*Z*)-4-(4-chlorobenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2b)

Imidazolone **2b** was prepared following the same experimental procedure than the described for **2a**, but starting from the corresponding oxazolone **1b**. Therefore, (*Z*)-4-(4-chlorobenzylidene)-2-phenyl-oxazol-5(4*H*)-one **1b** (2.19 g, 7.7 mmol) was reacted with *n*-propylamine (0.64 mL, 7.7 mmol) and bis(trimethylsilyl)acetamide (3.77 mL, 15.4 mmol) in pyridine (6 mL) to give **2b** as an orange solid. Obtained: 1.845 g, yield: 74%. ^{1}H NMR ($CDCl_3$, 400.16 MHz): δ 8.16 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, H_2/H_6, C_6H_4), 7.79 (dd, 2H, $^{3}J_{HH}$ = 6.7 Hz, $^{3}J_{HH}$ = 1.4 Hz, H_o, C_6H_5), 7.62 – 7.54 (m, 3H, H_m, H_p, C_6H_5), 7.38 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, H_3/H_5, C_6H_4), 7.18 (s, 1H, =CH), 3.75 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, NCH_2), 1.59 (sext, 2H, $^{3}J_{HH}$ = 7.4 Hz, CH_2), 0.85 (t, 3H,$^{3}J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$) δ 171.68 (C=O), 163.31 (CN), 139.40 (C=), 136.38 (C_i, C_6H_4), 133.73 (C_2/C_6, C_6H_4), 132.99 (C_i, C_6H_5), 131.58 (C_p, C_6H_5), 129.87 (CCl), 129.12 (C_m, C_6H_5), 129.05 (C_o, C_6H_5), 128.47 (C_3/C_5, C_6H_4), 127.14 (=CH), 43.54 (NCH_2), 22.72 (CH_2), 11.17 (CH_3). HRMS (ESI^+) m/z calcd for $C_{19}H_{18}ClN_2O$ $[M+H]^+$: 325.1108, found: 325.1100.

(*Z*)-4-(3,4-dichlorobenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2c)

Imidazolone **2c** was prepared following the same experimental procedure than the described for **2a**, but starting from the corresponding oxazolone **1c**. Therefore, (*Z*)-4-(3,4-dichlorobenzylidene)-2-phenyl-oxazol-5(4*H*)-one (2.27 g, 7.2 mmol) was reacted with *n*-propylamine (0.58 mL, 7.2 mmol) and bis(trimethylsilyl)acetamide (3.50 mL, 14.4 mmol) in pyridine (6 mL) to give **2c** as an orange solid. Obtained: 1.984 g, yield: 77%. ^{1}H NMR ($CDCl_3$, 400.16 MHz): δ 8.36 (d, 1H, $^{3}J_{HH}$ = 1.9 Hz, H_2, C_6H_3), 8.04 (dd, 1H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.8 Hz, H_6, C_6H_3), 7.79 (m, 2H, H_o, C_6H_5), 7.61 – 7.53 (m, 3H, H_m, H_p, C_6H_5), 7.47 (d, 1H, $^{3}J_{HH}$ = 8.4, H_5, C_6H_3), 7.26 (s, 1H, =CH), 3.75 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, NCH_2), 1.60 (sext, 2H, $^{3}J_{HH}$ = 7.4 Hz, CH_2), 0.85 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$) δ 171.53 (C=O), 164.00 (CN), 134.50 (C=), 134.19 (C_i, C_6H_3), 133.71 (C_2, C_6H_3), 132.98 (C_i, C_6H_5), 131.77 (C_p, C_6H_5), 131.46 (C_6, C_6H_3), 130.74 (C_5, C_6H_3), 129.66 (CCl), 129.08 (C_m, C_6H_5), 128.51 (C_o, C_6H_5), 125.39 (=CH), 43.62 (NCH_2), 22.72 (CH_2), 11.16 (CH_3). HRMS (ESI^+) m/z calcd for $C_{19}H_{17}Cl_2N_2O$ $[M+H]^+$: 359.0718, found: 359.0730; m/z calcd for $C_{19}H_{16}Cl_2N_2NaO$ $[M+Na]^+$: 381.0532, found: 381.0538.

(Z)-4-(3,4-dimethoxybenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2d)

Imidazolone **2d** was prepared following the same experimental procedure than the described for **2a**, but starting from the corresponding oxazolone **1d**. Therefore, (*Z*)-4-(3,4-dimethoxybenzylidene)-2-phenyl-oxazol-5(4*H*)-one (1.42 g, 4.6 mmol) was reacted with *n*-propylamine (0.37 mL, 4.6 mmol) and bis(trimethylsilyl)acetamide (2.25 mL, 9.2 mmol) in pyridine (6 mL) to give **2d** as an orange solid. Obtained: 1.475 g, yield: 92%. ^{1}H NMR ($CDCl_3$, 400.16 MHz): δ 8.19 (d, 1H, $^{3}J_{HH}$ = 1.9 Hz, H_2, C_6H_3), 7.78 (dd, 1H, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{HH}$ = 1.8 Hz, H_o, C_6H_5), 7.65 (dd, 2H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.8 Hz, H_6, C_6H_3), 7.59 – 7.53 (m, 3H, H_m, H_p, C_6H_5), 7.23 (s, 1H, =CH), 6.89 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz, H_5, C_6H_3), 3.93 (OCH_3), 3.92 (OCH_3), 3.75 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, NCH_2), 1.59 (sext, 2H, $^{3}J_{HH}$ = 7.4 Hz, CH_2), 0.84 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$) δ 171.77 (C=O), 161.48 (CN), 151.42 (C_3, C_6H_3), 149.11 (C_4, C_6H_3), 137.46 (C=), 131.21 (C_p, C_6H_5), 130.27 (C_i, C_6H_5), 129.06 (=CH), 128.94 (C_m, C_6H_5), 128.33 (C_o, C_6H_5), 127.79 (C_i, C_6H_3), 127.44 (C_6, C_6H_3), 114.56 (C_2, C_6H_4), 110.98 (C_5, C_6H_3), 56.02 (OCH_3), 55.96 (OCH_3), 43.46 (NCH_2), 22.54 (CH_2), 11.16 (CH_3). HRMS (ESI^+) m/z calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1709, found: 351.1689.

(Z)-4-(2,4-dimethoxybenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2e)

Imidazolone **2e** was prepared following the same experimental procedure than the described for **2a**, but starting from the corresponding oxazolone **1e**. Therefore, (*Z*)-4-(2,4-dimethoxybenzylidene)-2-phenyl-oxazol-5(4*H*)-one (1.03 g, 3.33 mmol) was reacted with *n*-propylamine (0.274 mL, 3.33 mmol) and bis(trimethylsilyl)acetamide (1.63 mL, 6.66 mmol) in pyridine (6 mL) to give **2e** as an orange solid. Obtained: 0.728 g, yield: 71%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.93 (d, 1H, $^{3}J_{HH}$ = 8.8 Hz, H_6, C_6H_3), 7.82 – 7.76 (m, 2H, =CH, H_o, C_6H_5), 7.56 – 7.50 (m, 3H, H_m, C_6H_5, H_p, C_6H_5), 6.58 (dd, 1H, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 2.4 Hz, H_5, C_6H_3), 6.43 (d, 1H, $^{3}J_{HH}$ = 2.4, H_3, C_6H_3), 3.88 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.74 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, NCH_2), 1.58 (sext, 2H, $^{3}J_{HH}$ = 7.4 Hz, CH_2), 0.83 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$) δ 171.76 (C=O), 163.38 (C_4, C_6H_3), 161.12 (C_2, C_6H_3), 160.94 (CN), 136.70 (C=), 134.95 (C_6, C_6H_3), 131.00 (C_p, C_6H_5), 130.47 (C_i, C_6H_5), 128.90 (C_m, C_6H_5), 128.44 (C_o, C_6H_5), 123.15 (=CH), 116.95 (C_i, C_6H_3), 106.12 (C_5, C_6H_4), 97.81 (C_3, C_6H_3), 55.73 (OCH_3), 55.57 (OCH_3), 43.33 (NCH_2), 22.57 (CH_2), 11.18 (CH_3). HRMS (ESI^+) m/z calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1709, found: 351.1705.

General synthesis of Thiazolones 3a-3e

All (*Z*)-4-aryliden-2-phenyl-5(4*H*)-thiazolones **3a-3e** have been prepared from the corresponding oxazolones **1a-1e** following methods reported in the literature.[3]

General method for the orthopalladation of imidazolones 2 and thiazolones 3. All orthopalladation reactions have been performed in the same way, following methods published in the literature.[18] In some instances, these procedures have been adapted to a particular case, which will be detailed.

Synthesis of orthopalladated 4a

To a suspension of $Pd(OAc)_2$ (0.218 g, 0.97 mmol) in CF_3CO_2H (4 mL), imidazolone **2a** (0.300 g, 0.97 mmol) was added. The resulting suspension was heated at 75 °C for 2 h. During this time, the color of the suspension changes from orange-brown to yellow. After the reaction time, the suspension was cooled to room temperature and treated with water (25 mL). The precipitated solid of **4a** was filtered, washed with additional water (3 × 15 mL) until the smell of CF_3CO_2H was not detected and dried by suction. Yellow solid. Obtained: 0.412 g, yield 81%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 7.52 (t, 2H, $^3J_{HH}$ = 7.5 Hz, H_p, C_6H_5), 7.50 (s, 2H, =CH), 7.44 (t, 4H, $^3J_{HH}$ = 8.0 Hz, H_m, C_6H_5), 7.26 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HF}$ = 6.1 Hz, 2H, H_2, C_6H_3), 7.17 (d, broad, 4H, $^3J_{HH}$ = 8.4 Hz, H_o, C_6H_5), 6.91 (ddd, 2H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HF}$ = 8.0 Hz, $^3J_{HH}$ = 2.4 Hz, H_3, C_6H_3), 6.86 (dd, 2H, $^3J_{HF}$ = 10.5 Hz, $^4J_{HH}$ = 2.5 Hz, H_5, C_6H_3), 3.46 (ddd, 2H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 5.7 Hz, NCH_2), 3.19 (ddd, 2H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 6.1 Hz, NCH_2), 1.28, 1.14 (m, 4H, CH_2), 0.63 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 165.24 (C=O), 164.87 (CN), 164.52 (q, $^2J_{CF}$ = 38.5 Hz, CF_3CO_2), 161.44 (d, $^1J_{CF}$ = 259.7 Hz, CF), 138.75 (C=), 134.90 (=CH), 134.15 (d, $^2J_{CF}$ = 8.7 Hz C_2, C_6H_3), 132.67 (C_p, C_6H_5), 129.14 (C_m, C_6H_5), 128.69 (C_o, C_6H_5), 128.33 (d, $^3J_{CF}$ = 2.6 Hz, C_6, C_6H_3), 126.51 (d, $^4J_{CF}$ = 1.6 Hz C_i, C_6H_3), 126.36 (C_i, C_6H_5), 121.00 (d, $^3J_{CF}$ = 22.0 Hz, C_5, C_6H_3), 114.6 (q, $^1J_{CF}$ = 287.9 Hz, CF_3), 112.76 (d, $^2J_{CF}$ = 22.0 Hz, C_3, C_6H_3), 43.67 (NCH_2), 21.82 (CH_2), 10.94(CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.40 (s, CF_3), -106.10 (dt, $^3J_{FH}$ = 10.6 Hz, $^4J_{FH}$ = 7.0 Hz, CF). HRMS (ESI^+) m/z calcd for $C_{42}H_{32}F_8N_4NaO_6Pd_2$ $[M+Na]^+$: 1075.0161, found: 1075.0170.

Synthesis of orthopalladated 4b

Orthopalladated **4b** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding imidazolone **2b**. Therefore, **2b** (0.3 g, 0.93 mmol) was reacted with $Pd(OAc)_2$ (0.208 g, 0.93 mmol) in CF_3CO_2H (4 mL) at 75 °C to give **4b** as a yellow solid. Obtained: 0.474 g, yield: 95%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 7.53 (t, 2H, $^3J_{HH}$ = 7.5 Hz, H_p, C_6H_5), 7.47 – 7.43 (m, 6H, =CH, H_m, C_6H_5), 7.13 – 7.20 (m, 8H, H_3, C_6H_3, H_2, C_6H_3 H_o, C_6H_5), 7.11 (d, 2H, $^3J_{HH}$ = 0.9 Hz, H_5, C_6H_3), 3.46 ddd, 2H, $^3J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 6.1 Hz, NCH_2), (ddd, 2H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 5.7 Hz, NCH_2), 1.27, 1.14 (m, 4H, CH_2), 0.64 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 165.24 (CN), 165.55 (C=O), 164.52 (q, $^2J_{CF}$ = 39.2 Hz, CF_3CO_2), 136.77 (C=), 135.25 (CCl), 134.40 (=CH), 133.85 (C_5, C_6H_3), 133.23 (C_2, C_6H_3), 132.71 (C_p, C_6H_5), 129.15(C_m, C_6H_5), 128.78 (C_6, C_6H_3), 128.71 (C_o, C_6H_5), 128.41 (C_i, C_6H_3), 126.29 (C_i, C_6H_5), 125.55 (C_3, C_6H_3), 114.6 (q, $^1J_{CF}$ = 289.3 Hz, CF_3), 43.66 (NCH_2), 21.74 (CH_2), 10.96 (CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.43 (CF). HRMS (ESI^+) m/z calcd for $C_{40}H_{34}Cl_2F_3N_4O_6Pd_2$ $[M\text{-}CF_3CO_2\text{+}2H]^+$: 972.9979, found: 972.9930.

Synthesis of orthopalladated 4c

Orthopalladated **4c** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding imidazolone **2c**. Therefore, **2c** (0.187 g, 0.84 mmol) was reacted with $Pd(OAc)_2$ (0.300 g, 0.84 mmol) in CF_3CO_2H (4 mL) at 75 °C to give **4c** as a yellow solid. Obtained: 0.435 g, yield: 91%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 7.55 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H_p, C_6H_5), 7.47 (t, 4H, $^3J_{HH}$ = 8.0 Hz, H_m, C_6H_5), 7.39 (s, 2H, =CH), 7.32 (s, 2H, H_2, C_6H_2), 7.20 (d, broad, 4H, $^3J_{HH}$ = 7.7 Hz, H_o, C_6H_5), 7.17 (s, 2H, H_5, C_6H_2) 3.52 (ddd, 4H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 6.1 Hz, NCH_2), 3.27 (ddd, 4H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 5.7 Hz, NCH_2), 1.33, 1.14 (m, 4H, CH_2), 0.66 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 166.51 (CN), 165.02 (C=O), 135.21 (C_5, C_6H_2), 133.32 (C=), 133.01 (=CH), 132.96 (C_p, C_6H_5), 132.78 (C_i, C_6H_2), 132.23 (C_2, C_6H_2), 129.79 (C_6, C_6H_2), 129.69 (CCl), 129.61 (CCl), 129.28 (C_m, C_6H_5), 128.71 (C_o, C_6H_5), 126.04 (C_i, C_6H_5), 114.44 (q, $^1J_{CF}$ = 288.2 Hz, CF_3), 43.91 (NCH_2), 22.09 (CH_2), 10.95 (CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.48 (CF). HRMS (ESI^+) m/z calcd for $C_{42}H_{30}Cl_4F_6N_4NaO_6Pd_2$ $[M+Na]^+$: 1174.8791, found: 1174.8823.

Synthesis of orthopalladated 4d

Orthopalladated **4d** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding imidazolone **2d**. Therefore, **2d** (0.300 g, 0.86 mmol) was reacted with $Pd(OAc)_2$ (0.192 g, 0.86 mmol) in CF_3CO_2H (4 mL) at 75 °C to give **4d** as a yellow solid. Obtained: 0.384 g, yield: 78%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 7.46 (m, 3H, =CH, H_p, C_6H_5), 7.34 (t, 4H, $^3J_{HH}$ =7.6 Hz, H_m, C_6H_5), 7.12 (d, broad, 4H, $^3J_{HH}$ = 7.2 Hz, H_o, C_6H_5), 6.80 (d, 2H, H_2, C_6H_3), 6.68 (d, 1H, H_5, C_6H_3), 3.93 (s, 6H, OCH_3 (C_4)), 3.87 (s, 6H, OCH_3 (C_3)), 3.46 (ddd, 2H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.4 Hz, NCH_2), 3.15 (ddd, 2H, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 5.5 Hz, NCH_2), 1.21 – 1.12 (m, 2H, CH_2), 1.05 (ddt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2), 0.57 (t, 6H,$^3J_{HH}$ = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 164.91 (C=O), 163.87 (q, $^2J_{CF}$ = 38.4 Hz, CF_3CO_2), 163.12 (CN), 149.08 (C_3, C_6H_3), 147.01 (C_4, C_6H_3), 135.71 (=CH), 132.22 (C_p, C_6H_5), 129.66 (C_i, C_6H_5), 128.80 (C_o, C_6H_5), 128.76 (C_m, C_6H_5), 127.21 (C=), 126.78 (C_i, C_6H_3),122.29 (C_6, C_6H_3), 115.71 (C_5, C_6H_3), 113.87 (C_2, C_6H_3), 56.10 (OCH_3), 55.81 (OCH_3), 43.16 (NCH_2), 21.65 (CH_2), 10.84 (CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.07 (CF). HRMS (ESI$^+$) m/z calcd for $C_{46}H_{42}F_6N_4NaO_{10}Pd_2$ $[M+Na]^+$: 1159.0772, found: 1159.0775.

Synthesis of orthopalladated 4e

Orthopalladated **4e** was prepared following an adaptation of the experimental procedure described for **4a**, and starting from the corresponding imidazolone **2e**. Therefore, **2e** (0.728 g, 1.34 mmol) was reacted with $Pd(OAc)_2$ (0.300 g, 1.34 mmol) in CF_3CO_2H (4 mL) at room temperature for 17h to give **4e** as an orange solid. Obtained: 0.717 g, yield: 94 %. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.11 (s, 2H, =CH), 7.44 (t, 2H, $^3J_{HH}$ = 7.5 Hz, H_p, C_6H_5), 7.34 (t, 4H, $^3J_{HH}$ =7.9 Hz, H_m, C_6H_5), 7.03 (d, broad, 4H, $^3J_{HH}$ = 7.4 Hz, H_o, C_6H_5), 6.33 (d, 2H, $^3J_{HH}$ = 2.2, H_5, C_6H_3), 6.25 (d, 1H, $^3J_{HH}$ = 2.2 Hz, H_3, C_6H_3), 3.91 (s, 6H, OCH_3, C_2), 3.80 (s, 6H, OCH_3, C_4), 3.52 (ddd, 2H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 6.4 Hz, NCH_2), 3.15 (ddd, 2H, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 5.6 Hz, NCH_2), 1.31 – 1.18 (m, 2H, CH_2), 1.16 – 1.05 (m, 2H, CH_2), 0.60 (t, 6H,$^3J_{HH}$ = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 164.02 (C=O), 163.65 (q, $^2J_{CF}$ = 38.1 Hz, CF_3CO_2), 162.16 (CN), 160.29 (C_4, C_6H_3), 158.59 (C_2, C_6H_3), 140.35 (C_i, C_6H_3), 131.69 (C_p, C_6H_5), 129.00 (=CH), 128.63 (C_o, C_6H_5), 128.43 (C_m, C_6H_5), 127.17 (C_i, C_6H_5), 126.30 (C=), 113.54 (C_6, C_6H_3), 109.29 (C_5, C_6H_3), 96.04 (C_3, C_6H_3), 55.66 (OCH_3 (C_2)), 55.32 (OCH_3 (C_4)), 42.98 (NCH_2), 21.55 (CH_2), 10.80 (CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.04 (s, CF_3). HRMS (ESI$^+$) m/z calcd for $C_{46}H_{42}F_6N_4NaO_{10}Pd_2$ $[M+Na]^+$: 1159.0772, found: 1159.0754.

Synthesis of orthopalladated 11a

Orthopalladated **11a** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding thiazolone **3a**. Therefore, **3a** (0.378 g, 1.34 mmol) was reacted with $Pd(OAc)_2$ (0.300 g, 1.34 mmol) in CF_3CO_2H (7 mL) at 75 °C for 3 h to give **11a** as a yellow solid. Obtained: 0.644 g, yield: 95%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.04 (d, 4H, $^3J_{HH}$ = 7.2 Hz, H_o, C_6H_5) 7.59 (t, 2H, $^3J_{HH}$ = 7.26 Hz, H_p, C_6H_5), 7.55 – 7.50 (m, 6H, =CH, H_m, C_6H_5), 7.35 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HF}$ = 6.0 Hz, 2H, H_2, C_6H_3), 6.91 (ddd, 2H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 2.5 Hz, H_3, C_6H_3), 6.86 (dd, 2H, $^3J_{HF}$ = 9.8 Hz, $^4J_{HH}$ = 2.5 Hz, H_5, C_6H_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 184.22 (C=O), 175.76 (CN), 162.39 (d, $^1J_{CF}$ = 264.4 Hz, CF), 141.20 (d, $^3J_{CF}$ = 7.2 Hz, C_6, C_6H_3), 138.62 (=CH), 137.49 (C=), 135.60 (d, $^2J_{CF}$ = 9.1 Hz C_2, C_6H_3), 134.10 (C_p, C_6H_5), 131.85 (C_i, C_6H_5), 129.32 (C_m, C_6H_5), 129.02 (C_o, C_6H_5), 127.70 (d, $^4J_{CF}$ = 1.9 Hz C_i, C_6H_3), 120.8 (d, $^3J_{CF}$ = 21.4 Hz, C_5, C_6H_3), 113.97 (d, $^2J_{CF}$ = 23.1 Hz, C_3, C_6H_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.95 (s, CF_3), -102.89 (tt, $^3J_{FH}$ = 9.7 Hz, $^4J_{FH}$ = 7.6 Hz, CF). HRMS (ESI$^+$) m/z calcd for $C_{34}H_{20}F_5N_2O_4Pd_2S_2$ $[M-CF_3CO_2+2H]^+$: 890.8854, found: 890.8809.

Synthesis of orthopalladated 11b

Orthopalladated **11b** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding thiazolone **3b**. Therefore, **3b** (0.400 g, 1.34 mmol) was reacted with $Pd(OAc)_2$ (0.300 g, 1.34 mmol) in CF_3CO_2H (7 mL) at 75 °C for 3 h to give **11b** as an orange solid. Obtained: 0.673 g, yield: 95%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.04 (d, 4H, $^3J_{HH}$ = 7.3 Hz, H_o, C_6H_5) 7.60 (t, 2H, $^3J_{HH}$ = 7.46 Hz, H_p, C_6H_5), 7.54 (t, 4H, H_m, C_6H_5), 7.48 (s, 2H, =CH), 7.24 (d, $^3J_{HH}$ = 8 Hz, 2H, H_2, C_6H_3), 7.20 (d, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, H_3, C_6H_3), 6.91 (d, 2H, $^4J_{HH}$ = 1.8 Hz, H_5, C_6H_3). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 184.24 (C=O), 176.45 (CN), 139.10 (C_6, C_6H_3), 137.93 (C=), 137.16 (CCl), 138.23 (=CH), 134.40 (C_2, C_6H_3), 134.21 (C_p, C_6H_5), 133.57 (C_5, C_6H_3), 131.90 (C_i, C_6H_5), 129.58 (C_i, C_6H_3), 129.34 (C_m, C_6H_5), 129.02 (C_o,

C_6H_5), 126.68 (C_3, C_6H_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -75.02 (s, CF_3). HRMS (ESI^+) m/z calcd for $C_{36}H_{18}Cl_2F_6N_2NaO_6Pd_2S_2$ $[M+Na]^+$: 1056.7855, found: 1056.7848.

Synthesis of orthopalladated 11c

Orthopalladated **11c** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding thiazolone **3c**. Therefore, **3c** (0.445 g, 1.34 mmol) was reacted with $Pd(OAc)_2$ (0.300 g, 1.34 mmol) in CF_3CO_2H (7 mL) at 75 °C for 3 h to give **11c** as an orange solid. Obtained: 0.670 g, yield: 90%. ^1H NMR (CD_2Cl_2, 500.13 MHz): δ 8.12 (d, 4H, $^3J_{HH}$ = 7.7 Hz, H_o, C_6H_5), 7.79 (t, 4H, $^3J_{HH}$ = 7.7 Hz, H_p, C_6H_5), 7.67 (t, 2H, $^3J_{HH}$ = 7.7 Hz, H_m, C_6H_5), 7.45 (s, 2H, H_2, C_6H_2), 7.43 (s, 2H, =CH), 7.25 (s, 2H, H_5, C_6H_2). $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2) δ 183.91 (C=O), 177.90 (CN), 136.15 (=CH), 134.58 (C_p, C_6H_5), 134.46, 133.22 (C_2, C_5, C_6H_2), 134.17 (C_i, C_6H_5), 130.77 ($C_{3,4}Cl$, C_6H_2), 130.39 ($C_{3,4}Cl$, C_6H_2), 129.20 (C_m, C_6H_5), 128.96 (C_o, C_6H_5). Due to the insolubility of the product, even in CD_2Cl_2, some ^{13}C were not observed (=C, C_1 and C_6 of C_6H_2). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -75.36 (CF). HRMS (ESI^+) m/z calcd for $C_{32}H_{19}Cl_4N_2O_2Pd_2S_2$ $[M-2CF_3CO_2+3H]^+$: 878.7712, found: 878.7758.

Synthesis of orthopalladated 11d

Orthopalladated **5d** was prepared following the same experimental procedure than the described for **4a**, but starting from the corresponding thiazolone **3d**. Therefore, **3d** (0.435 g, 1.34 mmol) was reacted with $Pd(OAc)_2$ (0.300 g, 1.34 mmol) in CF_3CO_2H (7 mL) at 75 °C for 3 h to give **11d** as a red solid. Obtained: 0.653 g, yield: 88%. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 8.01 (d, 4H, $^3J_{HH}$ = 7.1 Hz, H_o, C_6H_5) 7.62 – 7.46 (m, 8H, H_p, C_6H_5, H_m, C_6H_5, =CH), 6.90 (s, 2H, H_2, C_6H_2), 6.70 (s, 2H, H_5, C_6H_2), 3.97 (s, 6H, OCH_3 (C_4)), 3.88 (s, 6H, OCH_3 (C_3)). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 184.26 (C=O), 173.47 (CN), 150.89 (C_3, C_6H_3), 147.69 (C_4, C_6H_3), 139.82 (=CH), 133.51 (C_p, C_6H_5), 132.20 (C_i, C_6H_5), 129.06, (C_o, C_6H_5), 129.00 (C_m, C_6H_5), 136.36 (C=), 115.40 (C_5, C_6H_3), 115.22 (C_2, C_6H_3), 133.41 (C_i, C_6H_3), 123.76 (C_6, C_6H_3), 56.31 (OCH_3 (C_3)), 56.08 (OCH_3 (C_4)). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.64 (s, CF_3). HRMS (ESI^+) m/z calcd for $C_{40}H_{28}F_6N_2NaO_{10}Pd_2S_2$ $[M+Na]^+$: 1108.9057, found: 1108.9050.

Reactivity of orthopalladated 4e, synthesis of luminiscent mononuclear and dinuclear derivatives 5e-9e

Synthesis of mononuclear 5e

A suspension of orthopalladated **4a** (0.100 g, 0.088 mmol) in CH_2Cl_2 (10 mL) was reacted with pyridine (14.2 μL, 0.176 mmol) for 30 minutes at room temperature. During this time the initial suspension gradually dissolved. After the reaction time any remaining solid was filtered, and the resulting solution was evaporated to dryness, giving **5e** as a deep red solid. Obtained: 0.086 g, yield: 93%. Compound **5e** was characterized in solution at 233K as the mixture of the *cis*- and *trans*-isomers (1:1 molar ratio). Signals at room temperature are broad and preclude a correct characterization. ^1H NMR (CD_2Cl_2, 400.13 MHz, 233K): δ 9.73 (d, $^3J_{HH}$ = 5.6 Hz, 1H, H_o, py), 8.52 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H_o, py), 8.10 (s, 1H, H_v), 8.00 (m, 2H, H_o, Ph), 7.85 – 7.72 (m, 4H, H_o + H_p, py), 7.67-7.58 (m, 3H, H_v + H_o Ph), 7.55 (m, 2H, H_p, Ph), 7.46 – 7.37 (m, 2H, H_m, py), 7.36 – 7.22 (m, 4H, H_m py + H_m Ph), 7.06 – 6.95 (m, 2H, H_m, Ph), 6.18 (s, br, 1H, C_6H_2), 6.16 (s, br, 1H, C_6H_2), 5.66 (s, br, 1H, C_6H_2), 5.64 (s, br, 1H, C_6H_2), 3.89, 3.87 (2s, 6H, 2 OMe), 3.66 (t, $^3J_{HH}$ = 7.6 Hz, 2H, NCH_2, Pr), 3.59 (t, $^3J_{HH}$ = 7.6 Hz, 2H, NCH_2, Pr), 3.51, 3.50 (2s, 6H, 2 OMe), 1.45 (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2, Pr), 1.33 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2, Pr), 0.73 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3, Pr), 0.65 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH_3, Pr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.77 MHz, 233K) δ 165.51, 165.12 (C=N), 162.47, 161.94 (C=O), 161.11, 160.82, 160.17, 159.29 (C-O, C_3+C_5, C_6H_2), 153.13, 152.64 (C_o, py), 148.76, 148.25 (=C), 139.47, 137.96 (C_p, py), 138.62, 132.10, 131.67, 131.41 (=CH + C_p Ph), 129.60, 129.24, 128.93, 128.48 (C_o + C_m, Ph), 127.52, 127.46, 127.19, 126.45 (C_1 + C_2, C_6H_2), 126.69 (2C, C_m, py), 115.77, 115.56 (C_i, Ph), 114.75, 114.24 (C_6, C_6H_2), 94.48, 94.34 (C_4, C_6H_2), 55.92, 55.76, 55.48, 55.34 (OMe), 43.55 ($2NCH_2$, Pr), 22.68, 22.12 (CH_2, Pr), 10.95, 10.85 (CH_3, Pr). Peaks assigned to CF_3CO_2 in the APT spectrum could not be assigned, despite the use of low temperatures and long accumulation trials. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -74.51, -74.94. HRMS (ESI^+) m/z calcd for $C_{28}H_{25}F_3N_3O_5Pd$ $[M]^+$: 646.0781, found: 646.0801.

Synthesis of dinuclear 6e

To a suspension of **4e** (1.11 g, 0.976 mmol) in MeOH (15 mL) at room temperature, LiCl (0.340 g, 1.952 mmol) was added. The resulting mixture was stirred for 30 min, then filtered. The orange solid collected of **6e** was washed with additional MeOH (5 mL) and Et_2O (3 × 5 mL), and dried by suction. Orange solid. Obtained: 0.599 g, yield 63%. This compound resulted too insoluble in the usual NMR solvents, therefore it was characterized by IR and HRMS. HRMS (ESI^+) m/z calcd for $C_{42}H_{42}Cl_2N_4O_6Pd_2$ $[M]^+$: 980.0551, found: 980.0567. IR (ν, cm^{-1}): 1710 (νC=O, heterocycle), 1570 (νC=N, heterocycle), 334 (νPd-Cl).

Synthesis of mononuclear 7e

To a suspension of **6e** (0.100 g, 0.102 mmol) in CH_2Cl_2 (10 mL) pyridine (16.4 μL, 0.204 mmol) was added, and the resulting mixture was stirred for 30 minutes at room temperature. After this time any remaining solid was filtered, and the resulting solution was evaporated to dryness, giving **7e** as a deep red solid. Obtained: 0.091 g, yield: 98%. Compound **7e** was characterized in solution at 233K as the mixture of the *C-trans-Cl* and *C-trans-py* isomers (4:1 molar ratio). Only the major isomer could be fully characterized due to extensive overlapping of peaks. Signals at room temperature are broad and preclude a correct characterization. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 233K): δ 8.78 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, H_o, py), 8.18 (s, 1H, H_{vinyl}), 8.00 (m, 2H, H_o, Ph), 7.85 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H_p, py), 7.51 (tt, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H_p, Ph), 7.41 (m, 2H, H_m, py), 7.20 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H_6, C_6H_2), 6.98 (t, $^3J_{HH}$ = 8 Hz, 2H, H_m, Ph), 6.18 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H_4, C_6H_2), 3.89, 3.87 (2s, 2 OMe), 3.60 (t, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2, Pr), 1.33 (q, $^3J_{HH}$ = 7.5 Hz, CH_2, Pr), 0.66 (t, $^3J_{HH}$ = 7.2Hz, CH_3, Pr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.4 MHz, 233 K) δ 165.39 (C=N), 161.00 (C=O), 160.19, 159.90 (C-O, C_3+C_5, C_6H_2), 153.14 (C_o, py), 150.25 (=C), 139.10 (C_p, py), 132.03, 131.38 (=CH + C_p Ph), 128.98 (C_o, Ph), 127.93, 126.51 (C_1 + C_2, C_6H_2), 125.34 (C_m, Ph), 124.58 (C_m, py), 117.30 (C_6, C_6H_2), 115.95 (C_i, Ph), 94.78 (C_4, C_6H_2), 55.76 (2C overlapped, OMe), 43.45 (NCH_2, Pr), 22.25 (CH_2, Pr), 10.89 (CH_3, Pr). HRMS (ESI^+) m/z calcd for $C_{26}H_{26}N_3O_3Pd$ $[M\text{-}Cl+H]^+$: 534.1004, found: 534.1004.

Synthesis of mononuclear 8e

To a suspension of **6e** (0.100 g, 0.102 mmol) in CH_2Cl_2 (5 mL) and acetone (1 mL), $AgBF_4$ (0.040 g, 0.204 mmol) was added. The resulting mixture was stirred at room temperature for 30 min with exclusion of light, then filtered over Celite to remove the precipitated AgCl. The clear solution thus obtained was treated with pyridine (32.8 μL, 0.408 mmol) and further stirring at room temperature for additional 30 minutes. After this time the resulting solution was evaporated to dryness, affording an orange solid characterized as **8e**. Obtained: 0.138 g, yield 97%. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 233K): δ 8.79 (d, $^3J_{HH}$ = 5.4 Hz, 2H, H_o, py), 8.29 (s, 1H, =CH), 8.12 (d, $^3J_{HH}$ = 5.0 Hz, 2H, H_o, py), 7.73 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H_p, py), 7.52 – 7.35 (m, 7H, H_m py, H_o+H_m+H_p, Ph), 7.04 (dd, $^3J_{HH}$ =7.8 Hz, $^3J_{HH}$ =6.0 Hz, 2H, H_m py), 6.15 (d, $^3J_{HH}$ = 2.1 Hz, 1H, H_6, C_6H_2), 5.78 (d, $^3J_{HH}$ = 2.2 Hz, 1H, H_4, C_6H_2), 3.88 (s, 3H, OMe), 3.63 (t, $^3J_{HH}$ = 7.6 Hz, 2H, NCH_2), 3.51 (s, 3H, OMe), 1.39 (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2), 0.69 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3). This product was too insoluble at low temperature to obtain reliable ^{13}C NMR data. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -152.26 (s, BF_4). HRMS (ESI^+) m/z calcd for $C_{21}H_{21}N_2O_3Pd$ $[M\text{-}2py]^+$: 455.0587, found: 455.0606.

Synthesis of 9e

Tl(acac) (0.062 g, 0.204 mmol) was added to a stirring suspension of Orthopalladate of (Z)-4-(2,4-dimethoxybenzylidene)-2-phenyl-1H-thiazol-5(4*H*)-one (Cl) (0.1 g, 0.102 mmol) in CH_2Cl_2 (5 mL) at room temperature. The mixture was stirred for 30 minutes then the precipitated TlCl was removed by filtration. The clear solution was evaporated to dryness, and the solid residue was washed with cold *n*-hexane (3 × 3 mL) and dried by suction. Orange solid. Obtained: 0.088 g, yield 82%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.22 (s, 1H, =CH), 7.87 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.9 Hz, H_o, C_6H_5), 7.56 – 7.47 (m, 3H, H_p, C_6H_5, H_m, C_6H_5), 7.03 (d, 1H, $^4J_{HH}$ = 2.3 Hz, H_3, C_6H_2), 6.20 (d, 1H, $^4J_{HH}$ = 2.3 Hz, H_5, C_6H_2), 5.05 (s, 1H, CH, acac), 3.90 (s, 3H, $OCH_3(C_4)$), 3.84 (s, 3H, $OCH_3(C_2)$), 3.69 (t, 2H, $^3J_{HH}$ = 7.7 Hz, NCH_2), 1.94 (s, 3H, CH_3, acac), 1.51 (sext, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2), 1.18 (s, 3H, CH_3, acac), 0.76 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 187.30 (C-O, acac), 185.40 (C-O, acac), 166.16 (CN), 161.58, (C_4, C_6H_2), 160.42 (C=O), 159.99 (C_2, C_6H_2), 150.68 (C_i, C_6H_2), 131.51 (=CH), 131.17

(C_p, C_6H_5), 129.13 (C_i, C_6H_5), 128.92 (C_o, C_6H_5), 128.68 (C=), 126.39 (C_m, C_6H_5), 116.23 (C_6, C_6H_2), 110.77 (C_3, C_6H_2), 99.05 (CH, acac), 95.88 (C_5, C_6H_2), 55.74 ($OCH_3(C_2)$), 55.50 ($OCH_3(C_4)$), 43.70 (NCH_2), 27.48 (CH_3, acac), 26.22 (CH_3, acac), 22.34 (CH_2), 11.12 (CH_3). HRMS (ESI^+) m/z calcd for $C_{26}H_{29}N_2O_5Pd$ $[M+H]^+$: 555.1111, found: 555.1112.

General method for the [2+2]-photocycloaddition of orthopalladated complexes 4 and 11. Synthesis of cyclobutanes 10 and 12. All photocycloadditions have been performed in the same way, following methods published in the literature.[19-22] In some instances these procedures have been adapted to a particular case, which will be detailed.

Synthesis of cyclobutane derivative 10a by [2+2] cycloaddition of orthopalladated 4a

A stirred suspension of orthopalladated **4a** (0.300 g, 0.28 mmol) in 10 mL CH_2Cl_2 was irradiated with blue light (465 nm; Kessil lamp, 40W) for 24h. During the reaction time the initial suspension gradually dissolved. After the reaction time any remaining solid was filtered through a Celite bed. The resulting clear solution was evaporated to dryness, giving **10a** as a yellow solid. Obtained: 0.298 g, yield 99%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 7.65 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H_p, C_6H_5), 7.54 (t, 4H, $^3J_{HH}$ = 7.9 Hz, H_m, C_6H_5), 7.39 (d, 4H, $^3J_{HH}$ = 7.0 Hz, H_o, C_6H_5), 6.75 (dd, 2H, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 2.5 Hz, H_2, C_6H_3), 6.72 – 6.64 (m, 4H, H_3, C_6H_3, H_5, C_6H_3), 4.94 (s, 2H, CH cyclobut), 3.61 (ddd, 2H, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.7 Hz, NCH_2, Pr), 3.26 (ddd, 2H, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 6.1 Hz, NCH_2, Pr), 1.45 – 1.28 (m, 4H, CH_2, Pr), 0.69 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3, Pr). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 179.36 (C=O), 172.91 (C=N), 159.45 (d, $^1J_{CF}$ = 252.9 Hz, CF), 138.17 (d, $^2J_{CF}$ = 5.9 Hz, C_6, C_6H_3), 132.65 (C_p, C_6H_5), 129.11 (C_m, C_6H_5), 129.04 (C_5, C_6H_3), 128.41 (C_o, C_6H_5), 126.75 (C_i, C_6H_5), 125.42 (d, $^4J_{CF}$ = 2.6 Hz, C_i, C_6H_3), 120.40 (d, $^3J_{CF}$ = 19.4 Hz, C_2, C_6H_3), 112.12 (d, $^2J_{CF}$ = 22.3 Hz, C_3, C_6H_3), 71.04 (C cyclobut), 58.87 (CH cyclobut), 44.16 (NCH_2), 21.76 (CH_2), 10.89 (CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -75.00 (s, 3F, CF_3), -112.82 (tt, $^3J_{FH}$ = 14.9 Hz, $^4J_{FH}$ = 9.1 Hz, 1F, CF). HRMS (ESI^+) m/z calcd for $C_{42}H_{32}F_8N_4NaO_6Pd_2$ $[M+Na]^+$: 1075.0156, found: 1075.0154.

Synthesis of cyclobutane derivative 10b by [2+2] cycloaddition of orthopalladated 4b

Cyclobutane **10b** was obtained following the same experimental procedure than that described for **4a**, but starting from orthopalladated **4b** (0.300 g, 0.28 mmol). Yellow solid. Obtained: 0.264 g, yield 88%. ^{1}H NMR ($CDCl_3$, 500.13 MHz, r.t.): δ 7.66 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H_p, C_6H_5), 7.55 (t, 4H, $^3J_{HH}$ = 7.9 Hz, H_m, C_6H_5), 7.41 (d, 4H, $^3J_{HH}$ = 7.0 Hz, H_o, C_6H_5), 7.04 (d, 2H, $^4J_{HH}$ = 2.1 Hz, H_5, C_6H_3), 6.94 (dd, 2H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.1 Hz, H_3, C_6H_3), 6.64 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H_2, C_6H_3), 4.92 (s, 2H, CH cyclobut), 3.61 (ddd, 2H, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 7.95 Hz, $^3J_{HH}$ = 6.8 Hz, NCH_2, Pr), 3.27 (ddd, 2H, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.0 Hz, NCH_2, Pr), 1.46 – 1.28 (m, 4H, CH_2, Pr), 0.69 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3, Pr). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$, r.t.): δ 179.29 (C=O), 173.06 (C=N), 137.52 (C_i, C_6H_3), 133.42 (C_5, C_6H_3), 132.72 (C_p, C_6H_5), 131.96 (C_6, C_6H_3), 129.14 (C_m, C_6H_5), 129.02 (C_2, C_6H_3), 128.44 (C_o, C_6H_5), 128.05 (CCl), 126.68 (C_i, C_6H_5), 125.21 (C_3, C_6H_3), 71.53 (C cyclobut), 58.89 (CH cyclobut), 44.21 (NCH_2), 21.77 (CH_2), 10.91 (CH_3). ^{19}F NMR (470.55 MHz, $CDCl_3$, r.t.): δ -75.09 (s, CF_3). HRMS (ESI^+) m/z calcd for $C_{42}H_{32}Cl_2F_6N_4NaO_6Pd_2$ $[M+Na]^+$: 1106.9565, found: 1106.9583.

Synthesis of cyclobutane derivative 10c by [2+2] cycloaddition of orthopalladated 4c

Cyclobutane **10c** was obtained following the same experimental procedure than that described for **4a**, but starting from orthopalladated **4c** (0.300 g, 0.26 mmol). Yellow solid. Obtained: 0.249 g, yield 83%. ^{1}H NMR ($CDCl_3$, 500.13 MHz, r.t.): δ 7.69 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H_p, C_6H_5), 7.58 (t, $^3J_{HH}$ = 7.9 Hz, 4H, H_m, C_6H_5), 7.44 (d, $^3J_{HH}$ = 7.1 Hz, 4H, H_o, C_6H_5), 7.12 (s, 2H, H_5, C_6H_3), 6.84 (s, 2H, H_2, C_6H_3), 4.87 (s, 2H, CH cyclobut), 3.63 (ddd, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.7 Hz, 2H, NCH_2, Pr), 3.31 (ddd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.1 Hz, 2H, NCH_2, Pr), 1.39 – 1.29 (m, 4H, CH_2, Pr), 0.71 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3, Pr). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 178.88 (C=O), 173.72 (C=N), 134.91 (C_5, C_6H_3), 134.65 (C_i, C_6H_3), 132.94 (C_p, C_6H_5), 130.20 (C_6, C_6H_3), 129.42 (CCl), 129.25 (C_m, C_6H_5), 129.18 (C_2, C_6H_3), 129.12 (CCl), 128.40 (C_o, C_6H_5), 126.50 (C_i, C_6H_5), 70.31 (C cyclobut), 58.34 (CH cyclobut), 44.38 (NCH_2), 21.68 (CH_2), 10.78 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.05 (s, CF_3). HRMS (ESI^+) m/z calcd for $C_{42}H_{30}Cl_4F_6N_4NaO_6Pd_2$ $[M+Na]^+$: 1174.8786, found: 1174.8776.

Synthesis of cyclobutane derivative 12b by [2+2] cycloaddition of orthopalladated 11b

Cyclobutane **12b** was obtained following the same experimental procedure than that described for **4a**, but starting from orthopalladated **11b** (0.300 g, 0.29 mmol). Yellow solid. Obtained: 0.296 g, yield 99%. A second minor component was detected, probably due to the [2+2] coupling of the cisoid isomer (head-to-head 1,2-orientation), but it could not be fully characterized. Therefore, only the cyclobutane arising from the head-to-tail cycloaddition (1,3-coupling) was characterized. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.30 (d, 4H, $^{3}J_{HH}$ = 7.0 Hz, H_o, C_6H_5), 7.67 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, H_p, C_6H_5), 7.61 (t, 4H, $^{3}J_{HH}$ = 7.2 Hz, H_m, C_6H_5), 7.12 (d, $^{4}J_{HH}$ = 2.1 Hz, 2H, H_5, C_6H_3), 7.04 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 2.1 Hz, 2H, H_3, C_6H_3), 6.83 (d, $^{3}J_{HH}$ = 8.0 Hz, H_2, C_6H_3), 5.12 (s, 2H, CH cyclobut). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$) δ 199.91 (C=O), 180.12 (C=N), 137.32 (C_1, C_6H_3), 133.82 (C_5, C_6H_3), 133.29 (C_p, C_6H_5), 133.09 (C_4-Cl, C_6H_3) 132.69 (C_i, C_6H_5), 130.11 (C_2, C_6H_3), 129.25 (C_m, C_6H_5), 127.62 (C_6, C_6H_3),127.77 (C_o, C_6H_5), 125.86 (C_3, C_6H_3), 84.16 (C, cyclobut), 62.39 (CH, cyclobut). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -75.14 (s, CF_3). HRMS (ESI^+) m/z calcd for $C_{36}H_{18}Cl_2F_6N_2NaO_6Pd_2S_2$ $[M+Na]^+$: 1056.7855, found: 1056.7841.

Synthesis of cyclobutane derivative 12c by [2+2] cycloaddition of orthopalladated 11c

Cyclobutane **12c** was obtained following the same experimental procedure than that described for **4a**, but starting from orthopalladated **11c** (0.300 g, 0.27 mmol). Yellow solid. Obtained: 0.278 g, yield 93%. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 8.36 (d, 4H, $^{3}J_{HH}$ = 6.9 Hz, H_o, C_6H_5), 7.70 (t, 2H, $^{3}J_{HH}$ = 7.4 Hz, H_p, C_6H_5), 7.64 (t, 4H, $^{3}J_{HH}$ = 7.9 Hz, H_m, C_6H_5), 7.22 (s, 2H, H_5, C_6H_3), 7.00 (s, 2H, H_2, C_6H_3), 5.05 (s, 2H, CH cyclobut). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$) δ 199.52 (C=O), 181.29 (C=N), 134.75 (C_5, C_6H_3), 134.48 (C_1, C_6H_3), 134.13 (C_p, C_6H_5), 131.49 ($C_{3,4}$-Cl, C_6H_3), 131.42 ($C_{3,4}$-Cl, C_6H_3), 132.48 (C_i, C_6H_5), 130.04 (C_2, C_6H_3), 129.36 (C_m, C_6H_5), 128.94 (C_6, C_6H_3),127.47 (C_o, C_6H_5), 84.18 (C, cyclobut), 61.82 (CH, cyclobut). ^{19}F NMR (470.55 MHz, $CDCl_3$) δ -75.08 (s, CF_3). HRMS (ESI^+) m/z calcd for $C_{36}H_{16}Cl_4F_6N_2NaO_6Pd_2S_2$ $[M+Na]^+$: 1124.7075, found: 1124.7078.

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3.- NMR spectra of all new compounds: imidazolones 2 and thiazolones 3

(*Z*)-4-(4-fluorobenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2a)

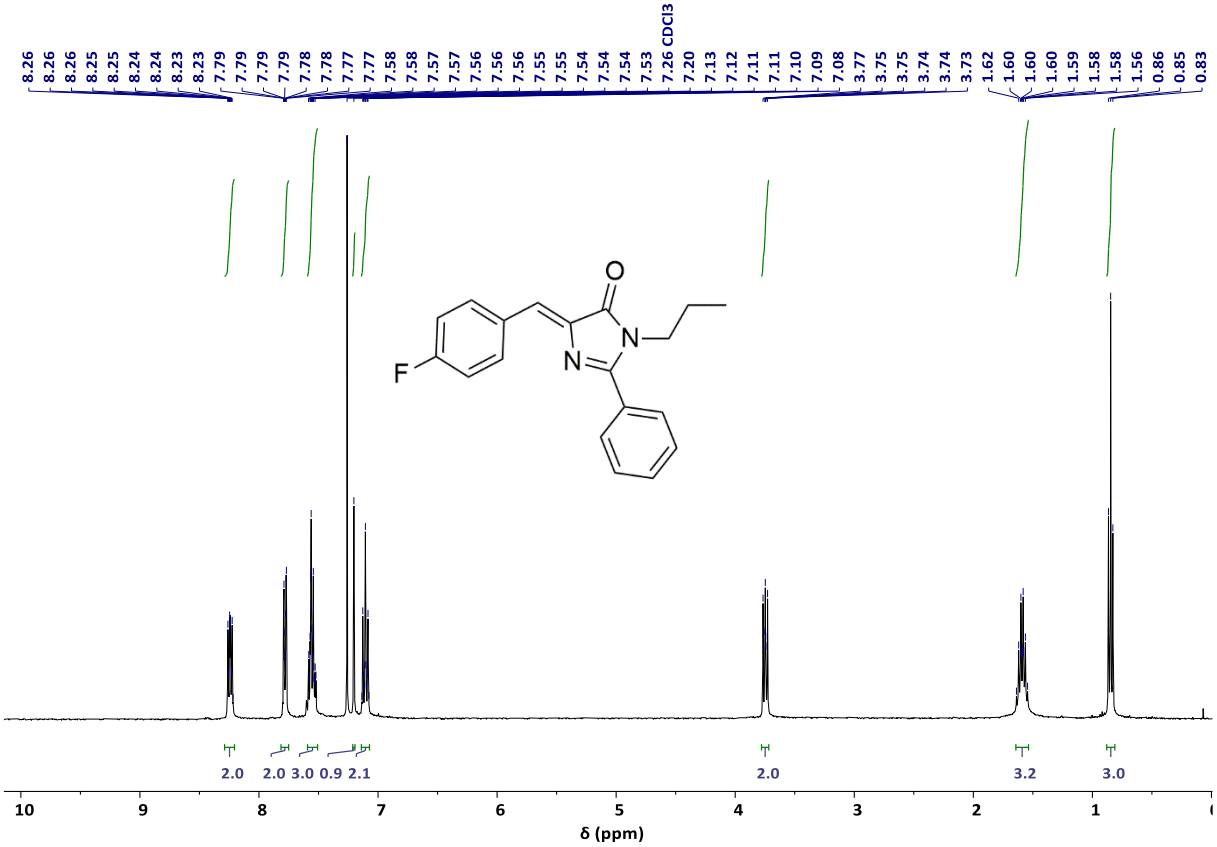

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **2a**

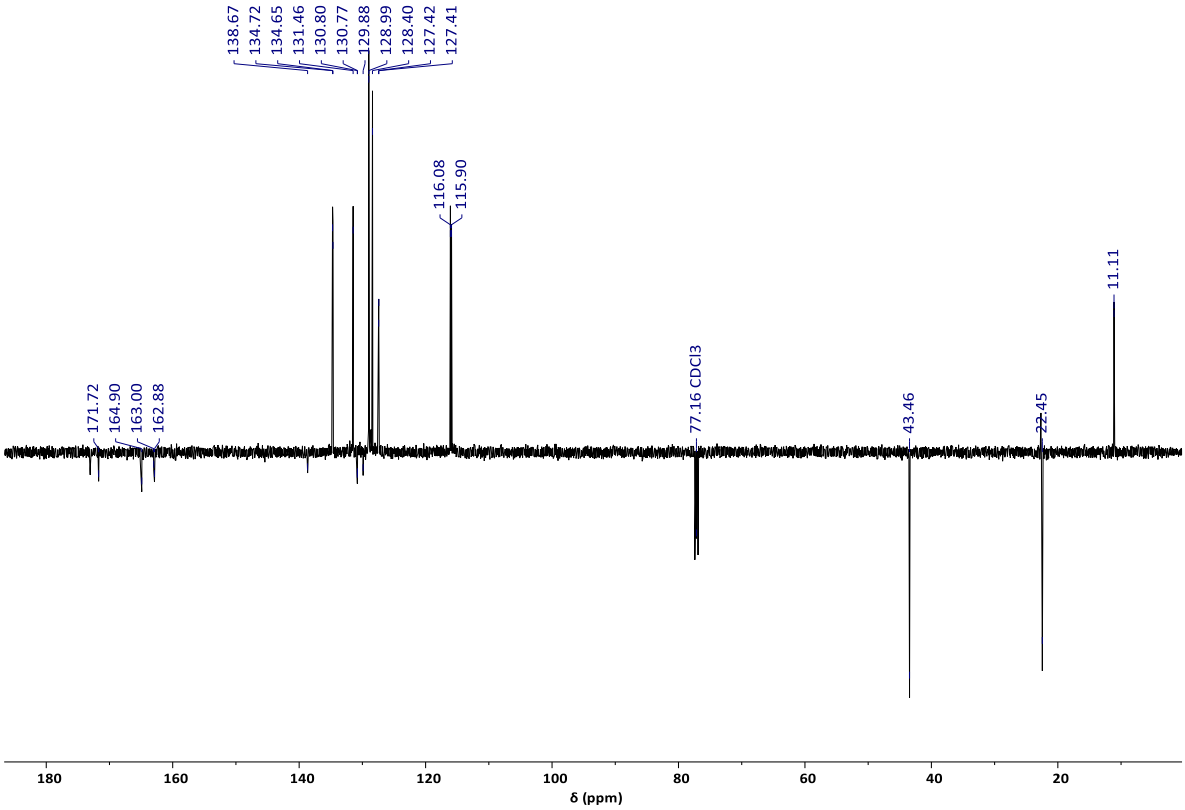

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **2a**

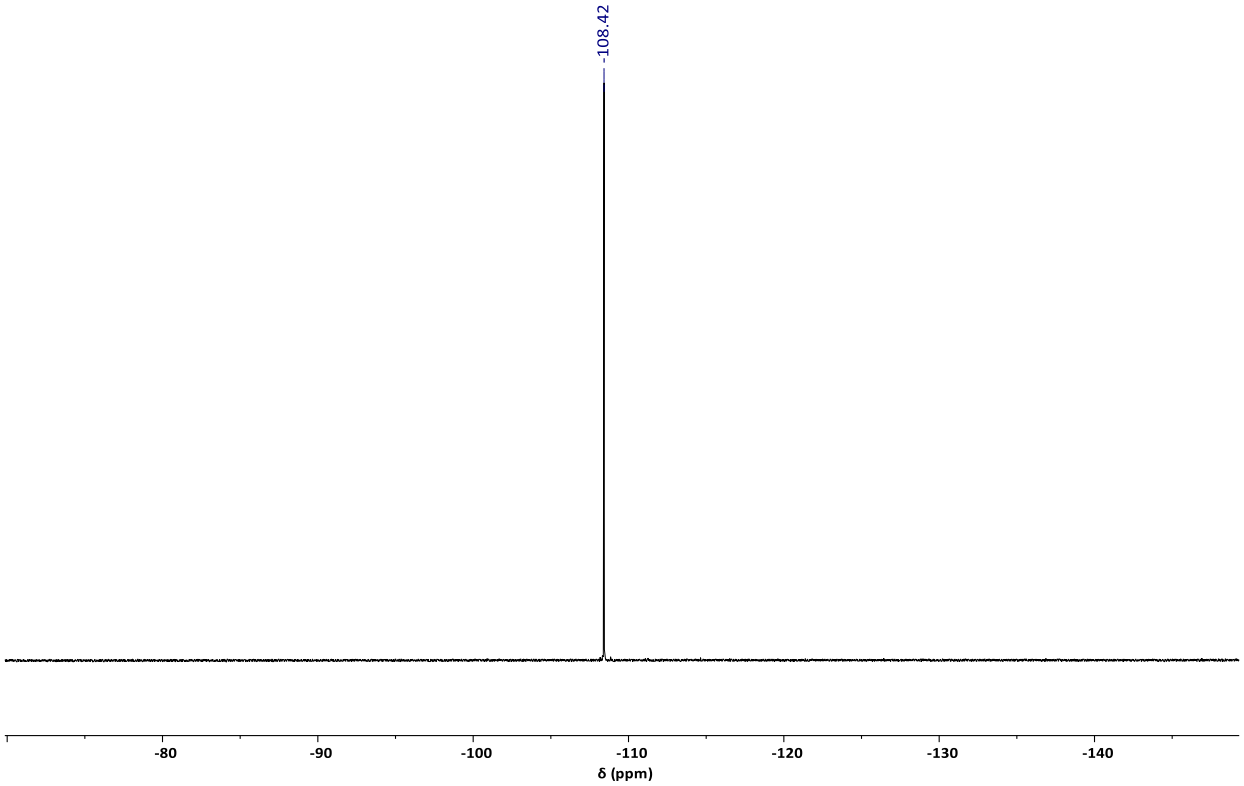

Figure S3. $^{19}F\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 376.49 MHz, r. t.) of **2a**

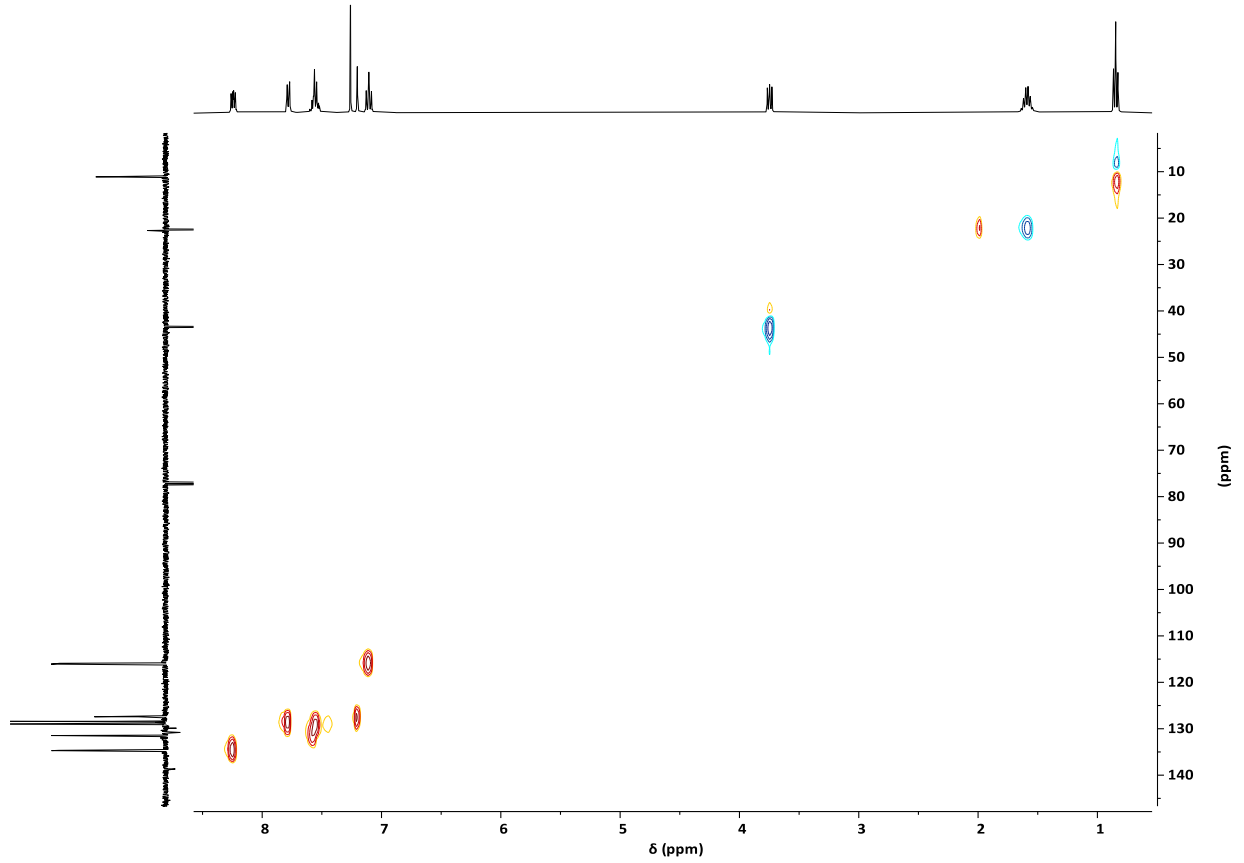

Figure S4. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **2a.**

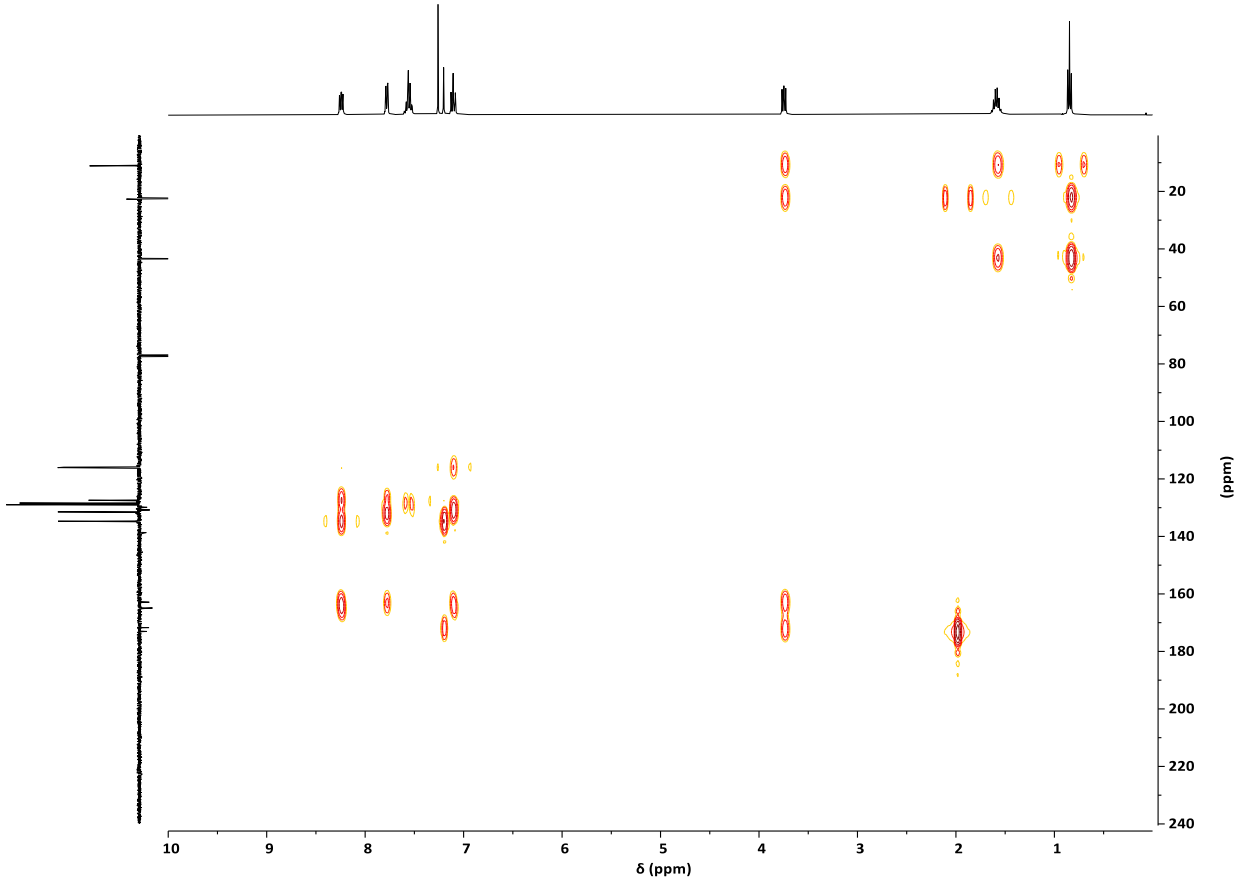

Figure S5. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **2a.**

(*Z*)-4-(4-chlorobenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2b)

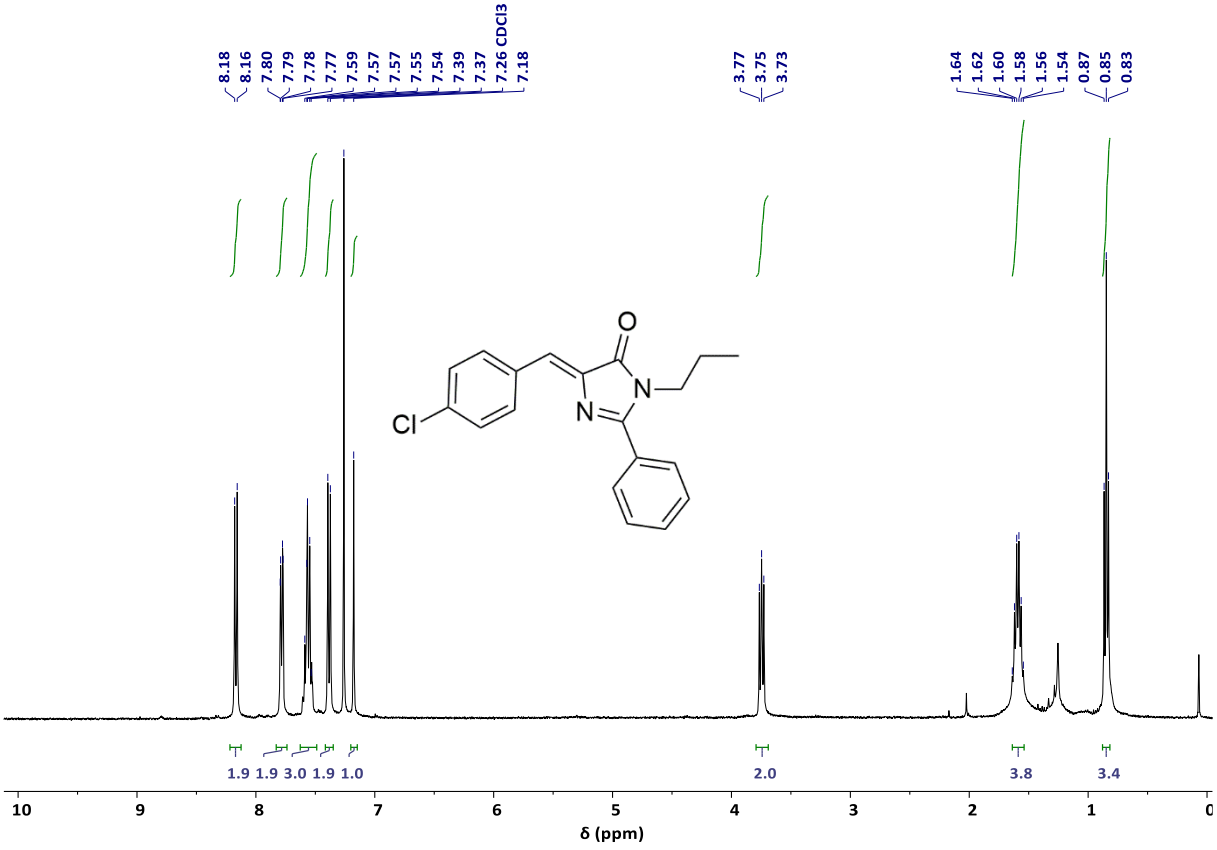

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **2b**

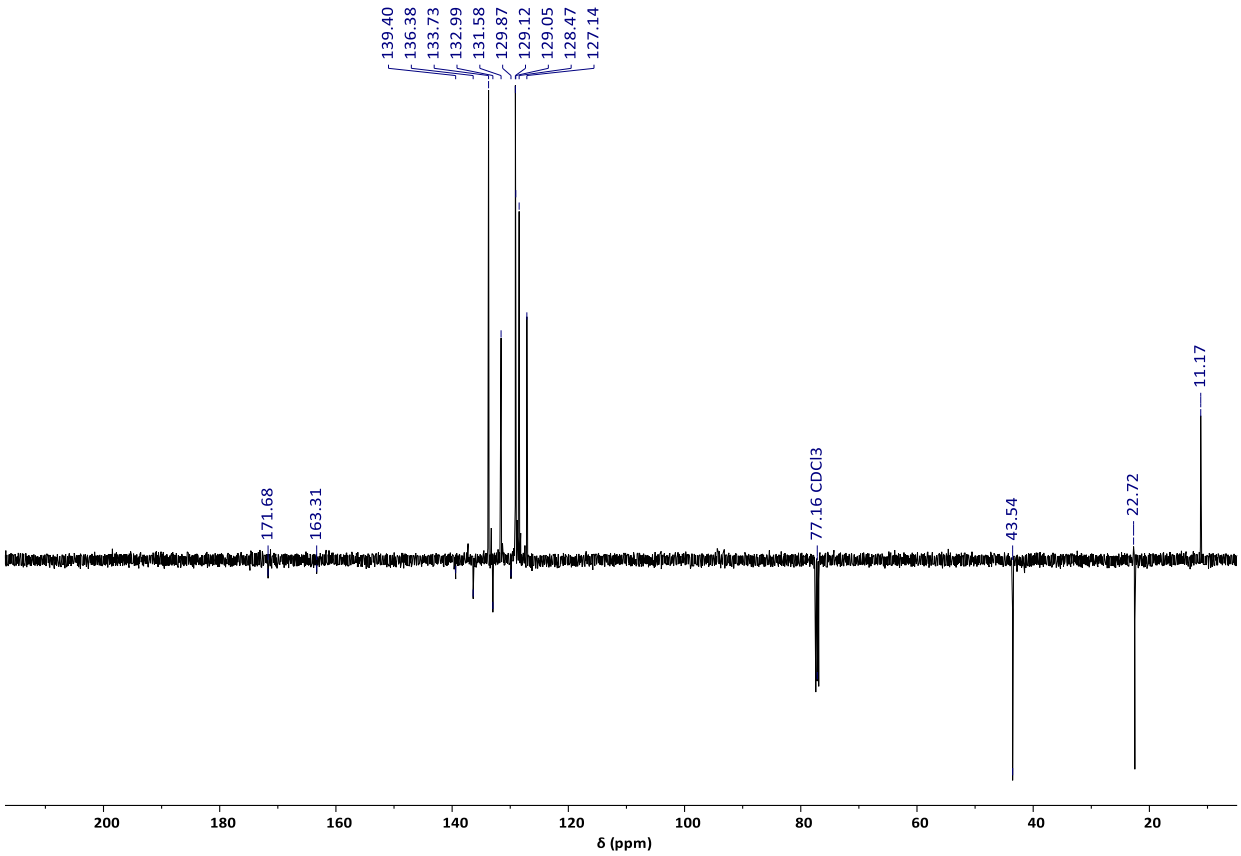

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **2b**

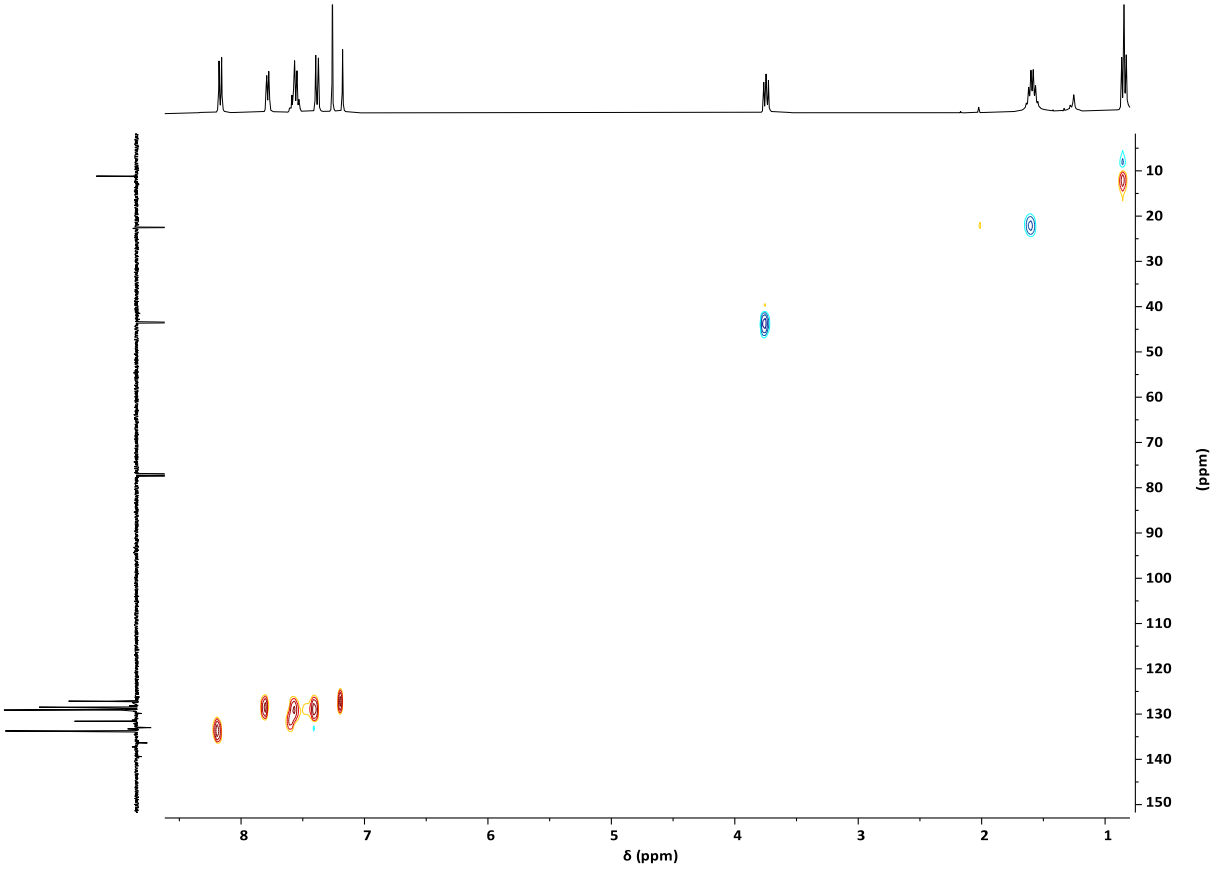

Figure S8. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **2b.**

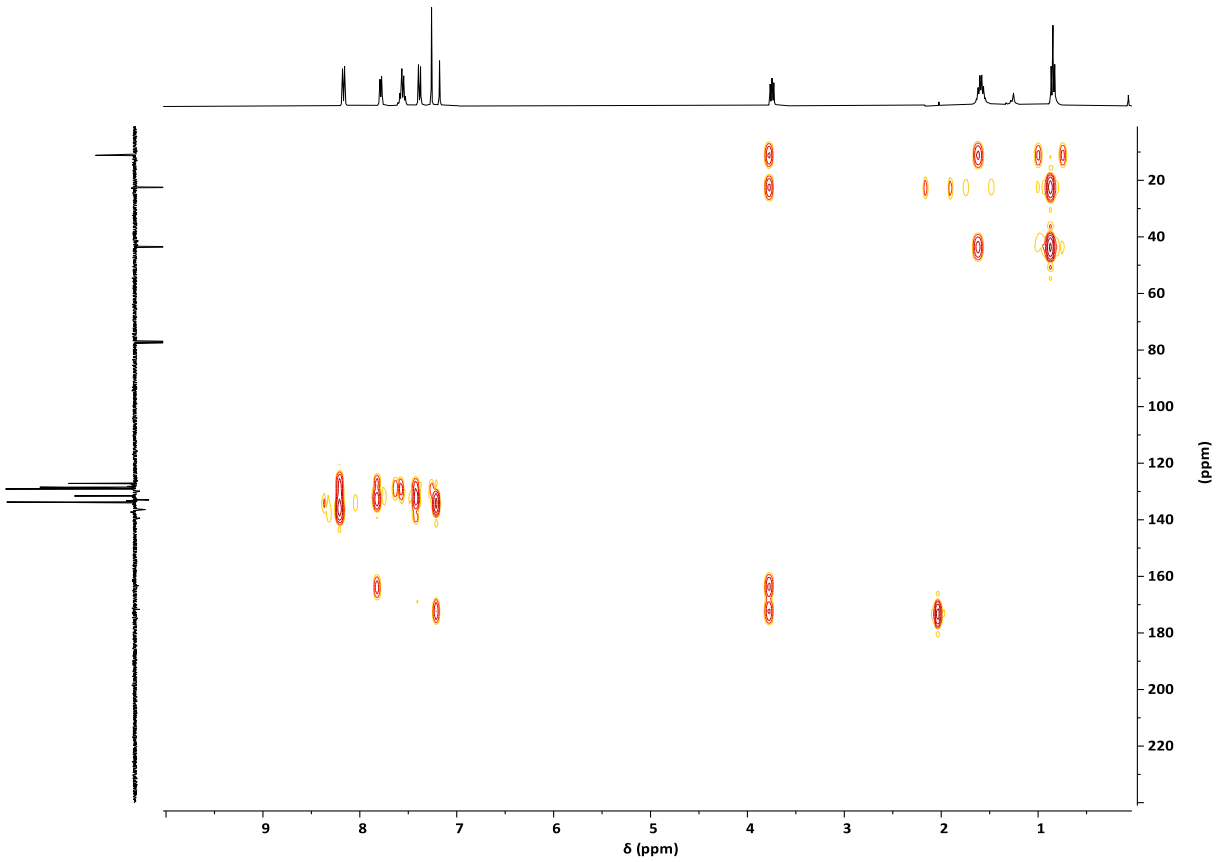

Figure S9. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **2b.**

(*Z*)-4-(3,4-dichlorobenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2c)

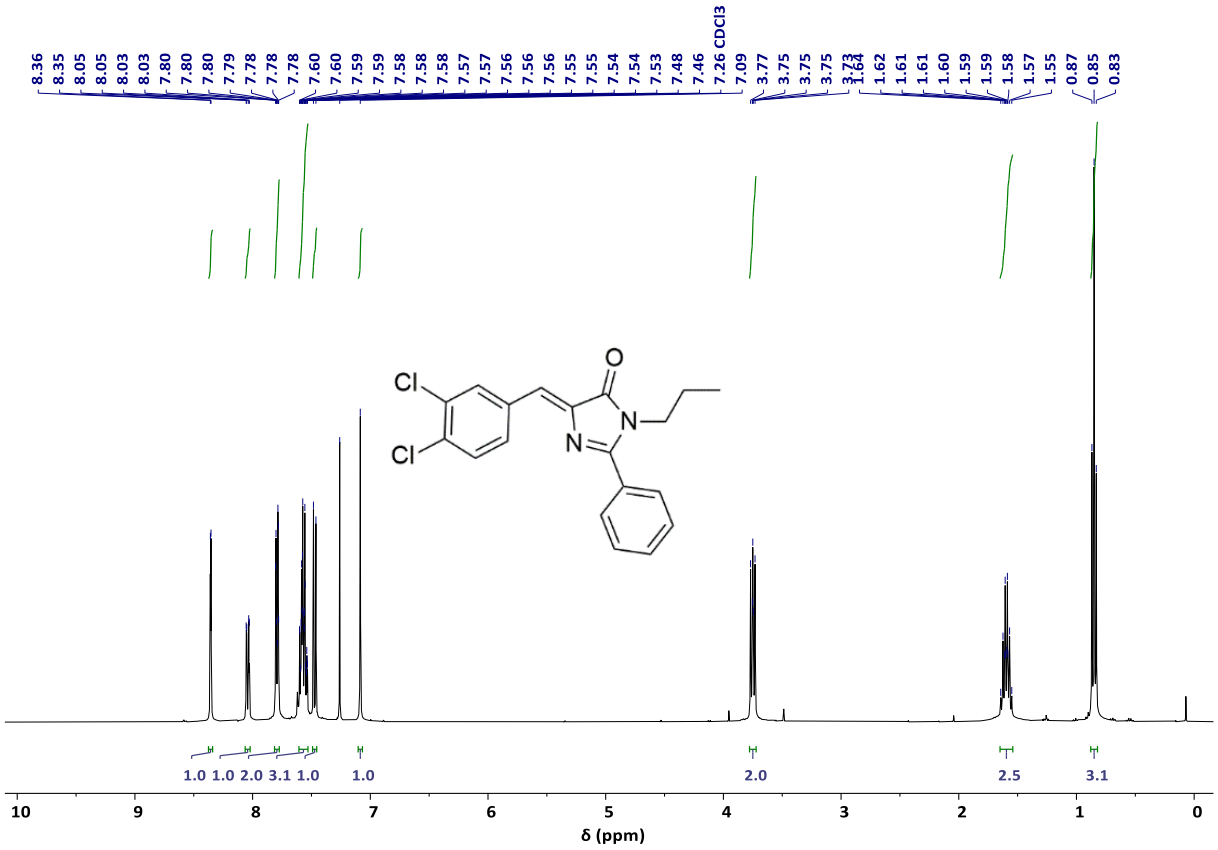

Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **2c**

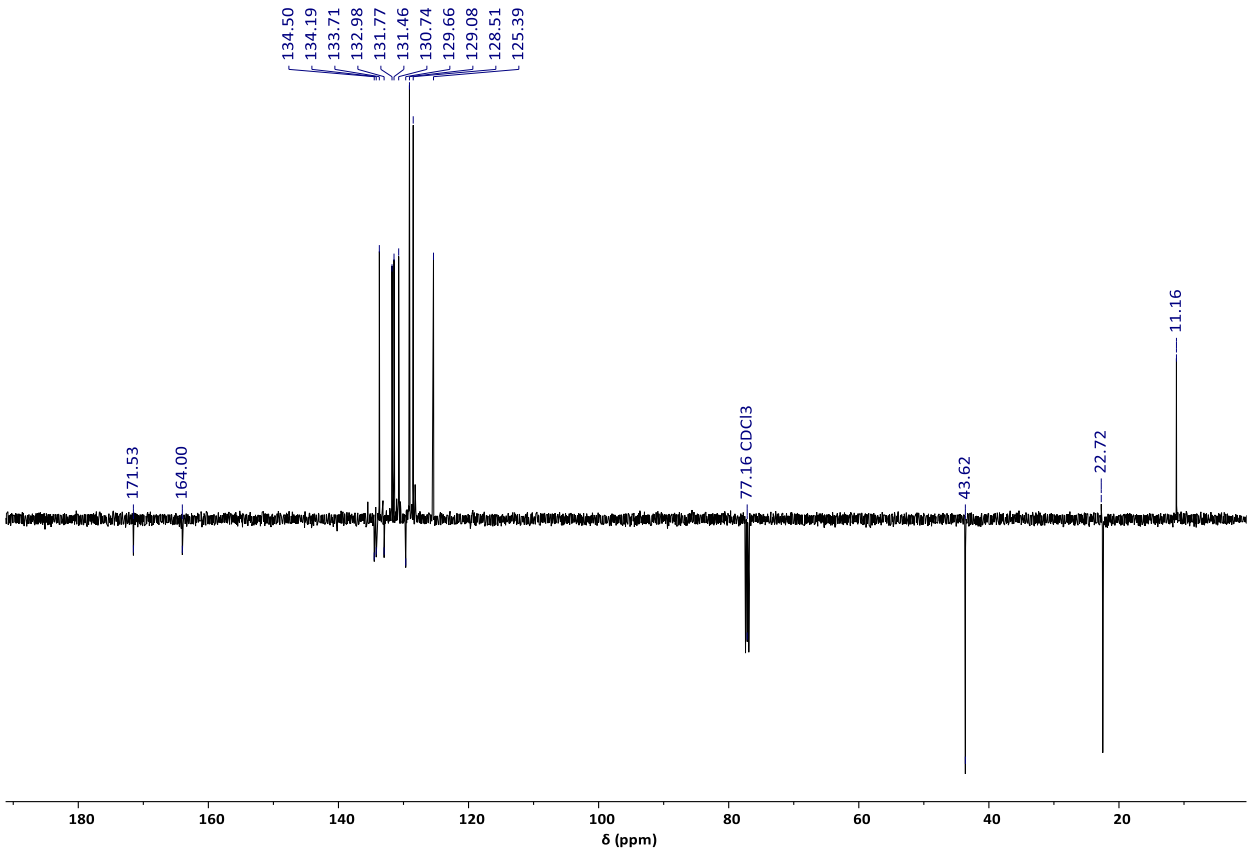

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **2c**

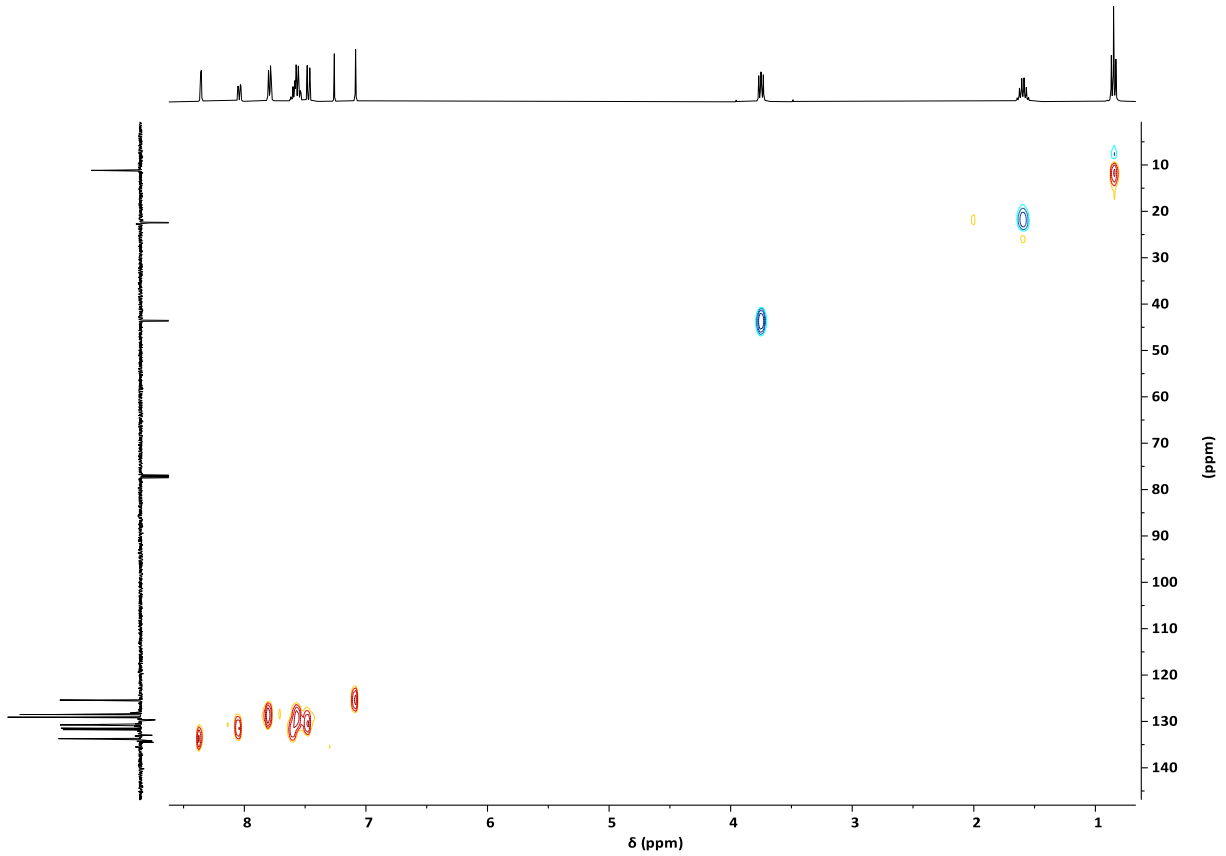

Figure S12. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **2c.**

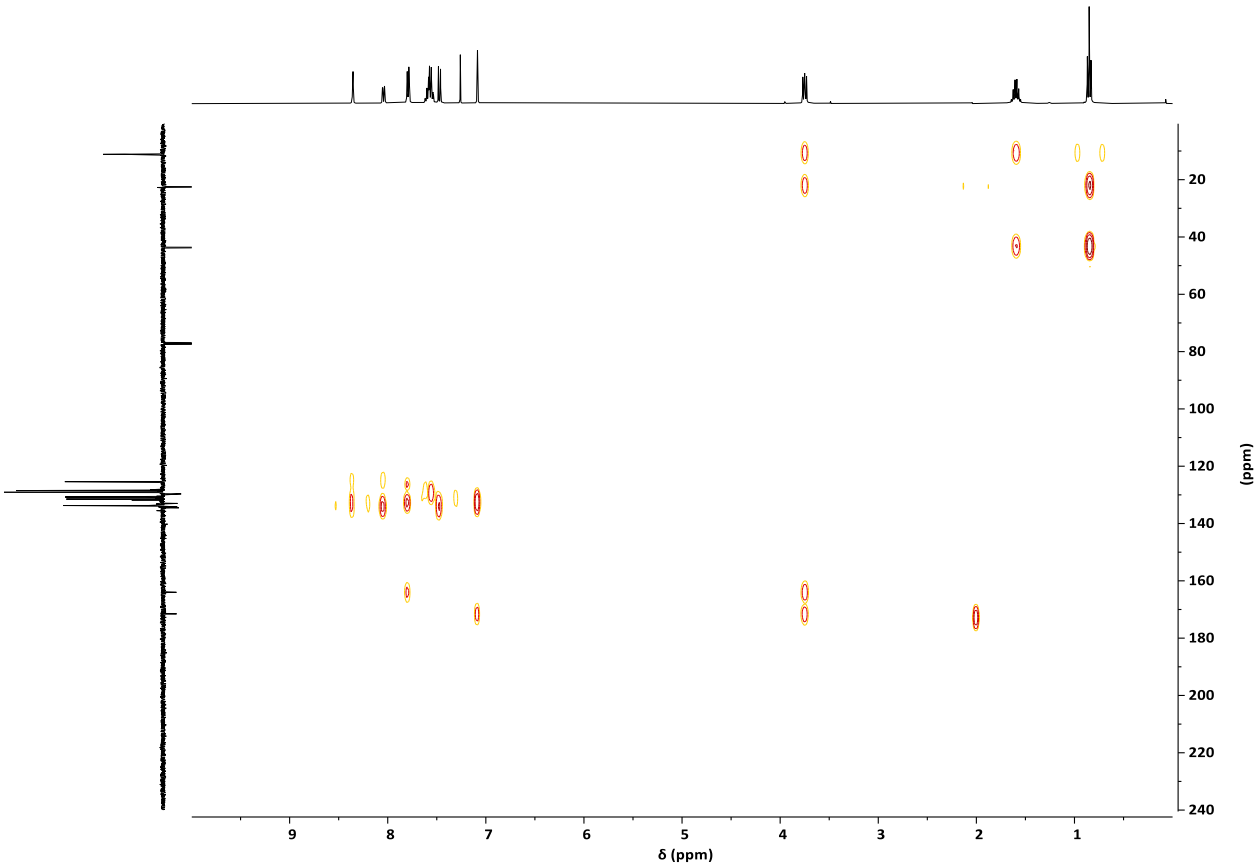

Figure S13. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **2c.**

(*Z*)-4-(3,4-dimethoxybenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2d)

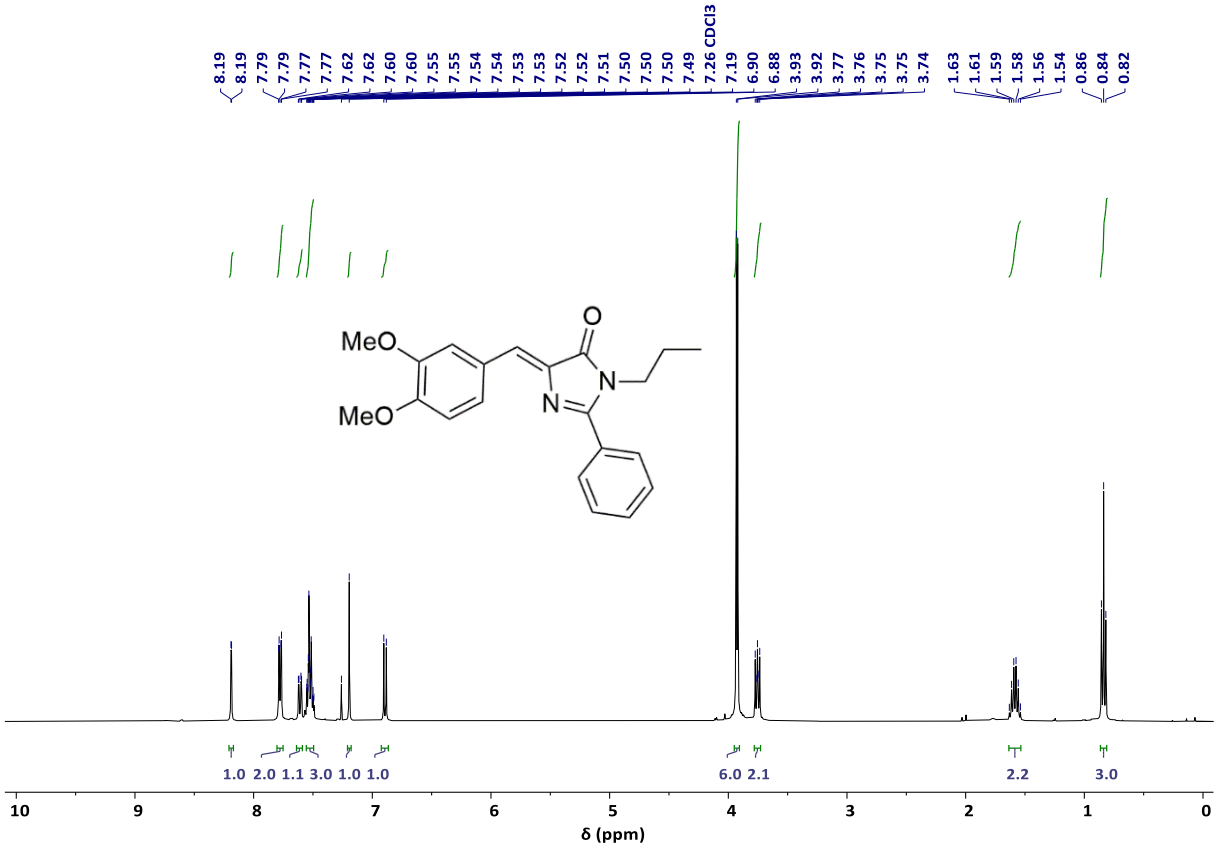

Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **2d**

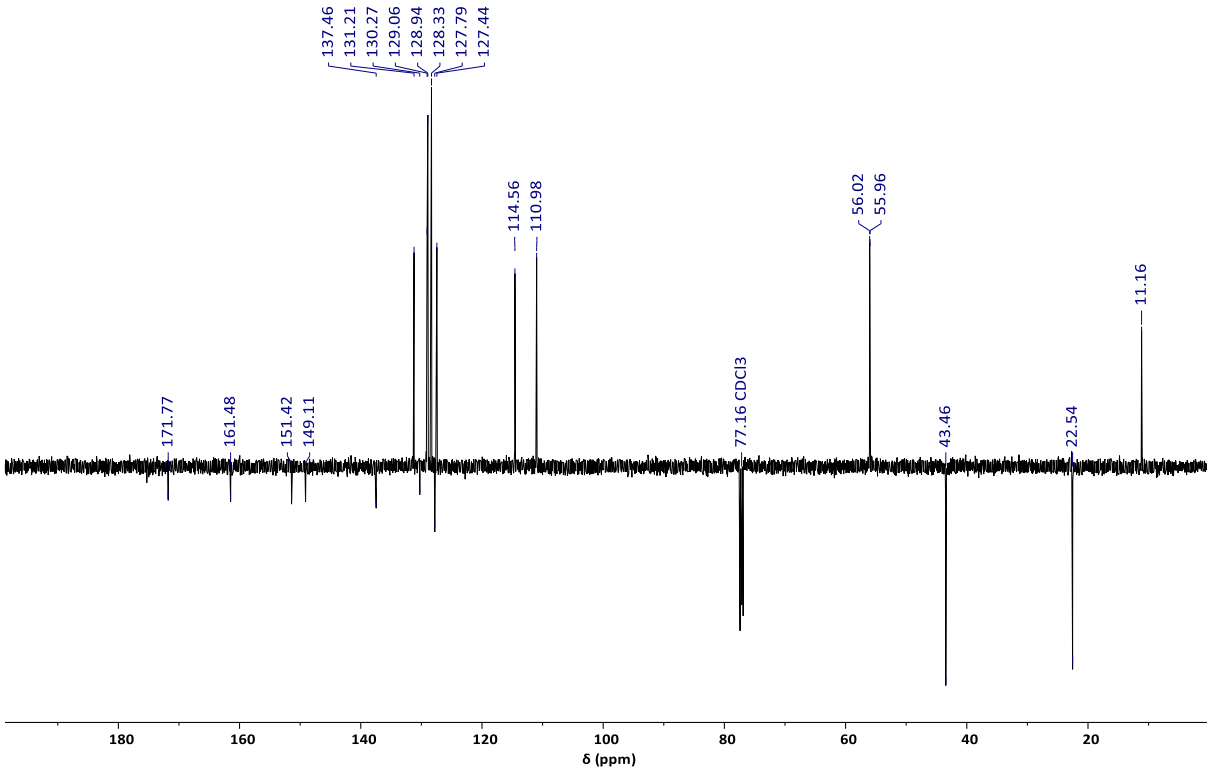

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **2d**

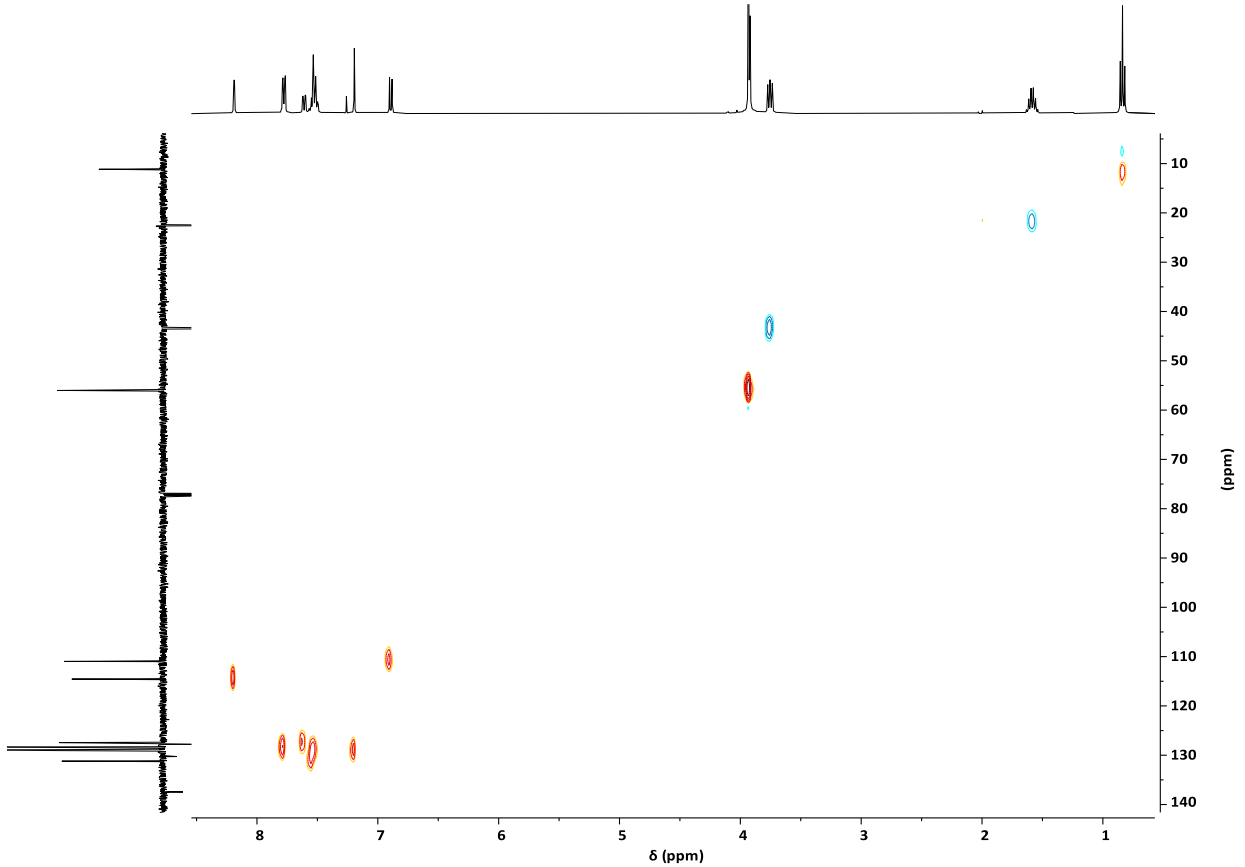

Figure S16. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **2d**

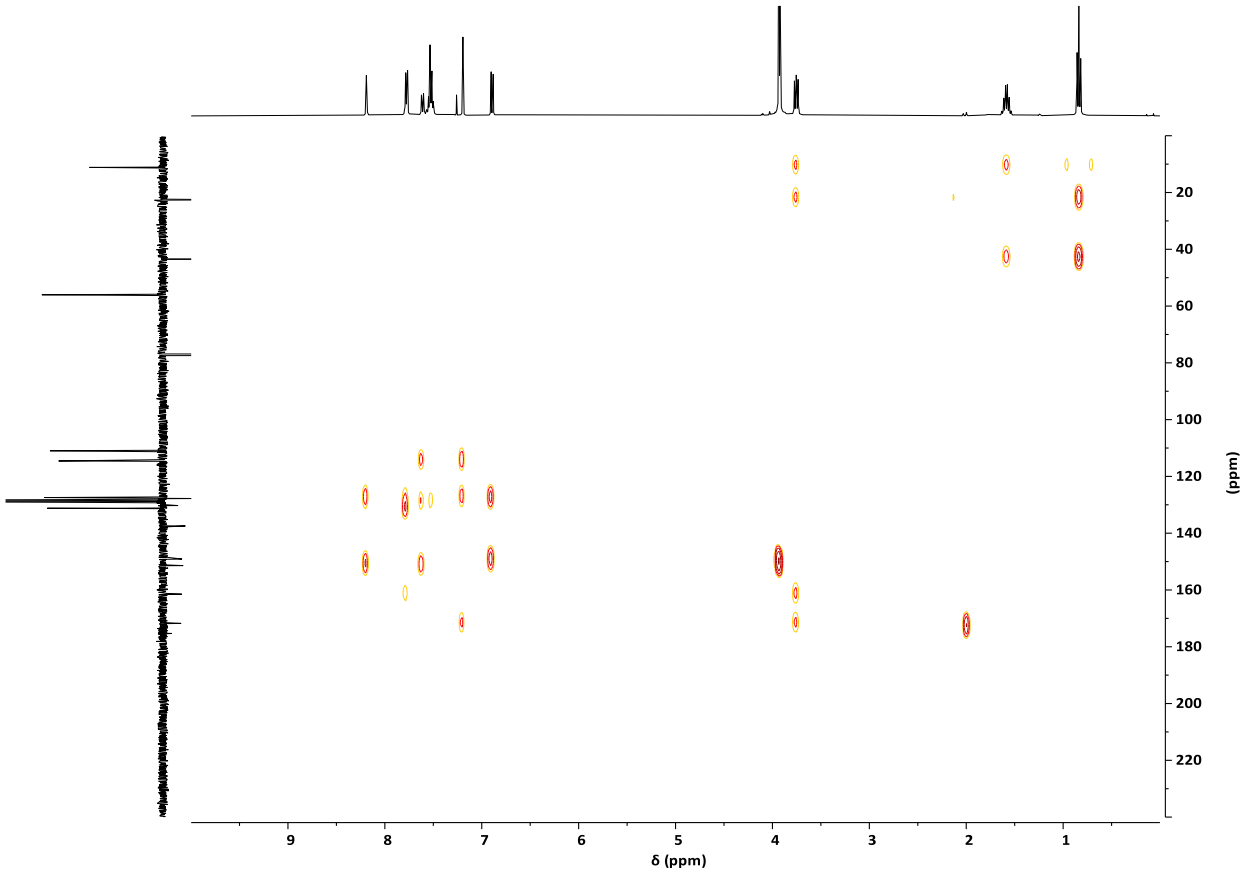

Figure S17. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **2d**

(*Z*)-4-(2,4-dimethoxybenzylidene)-1-(propyl)-2-phenyl-imidazol-5(4*H*)-one (2e)

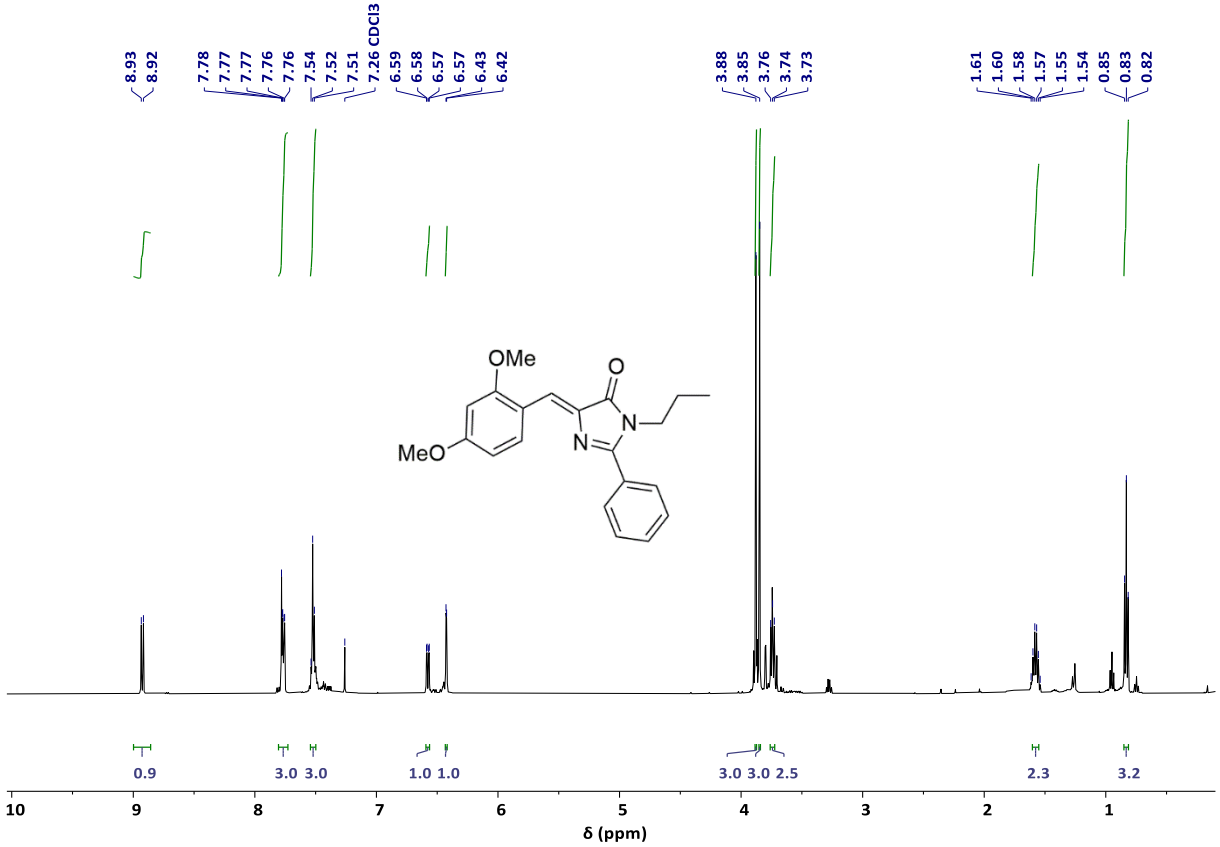

Figure S18. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **2e**

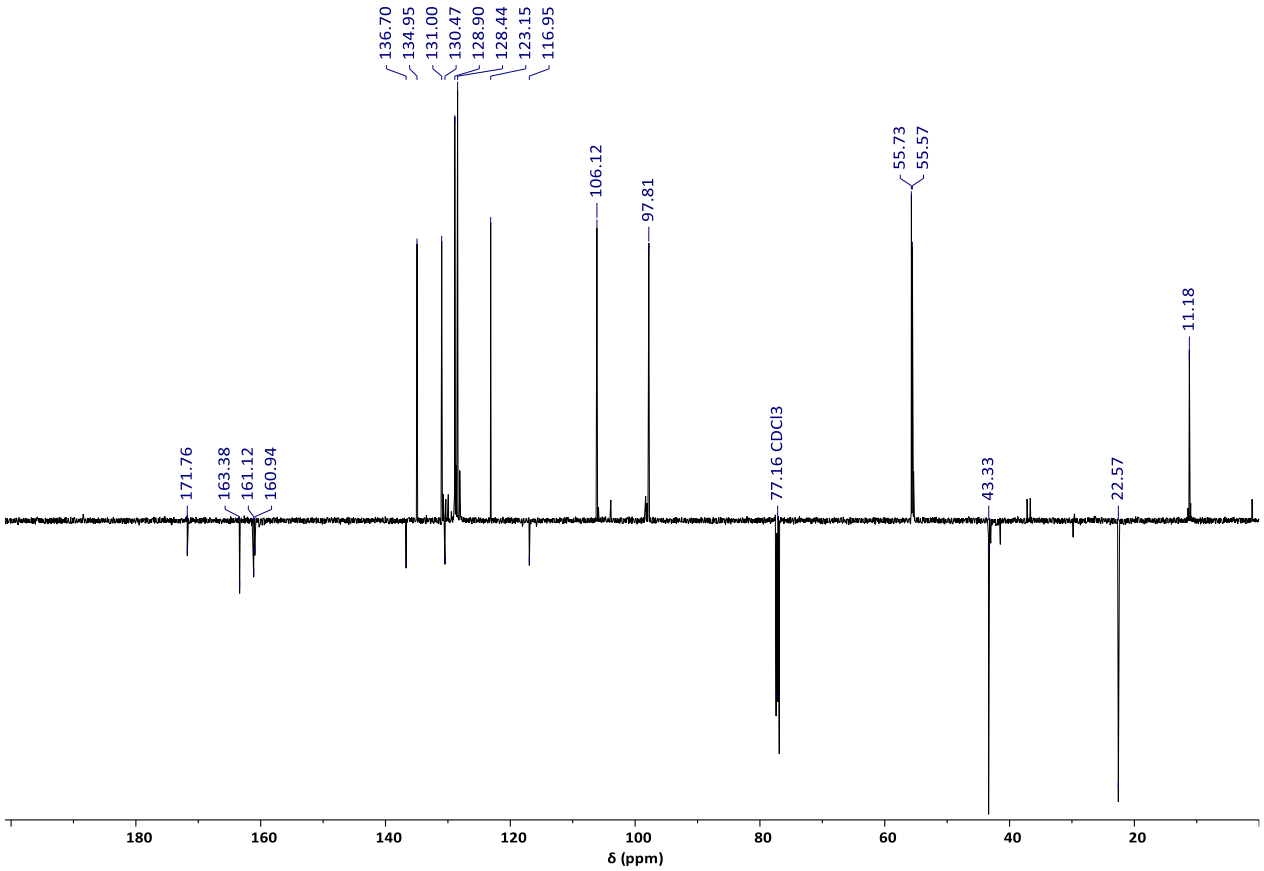

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **2e**

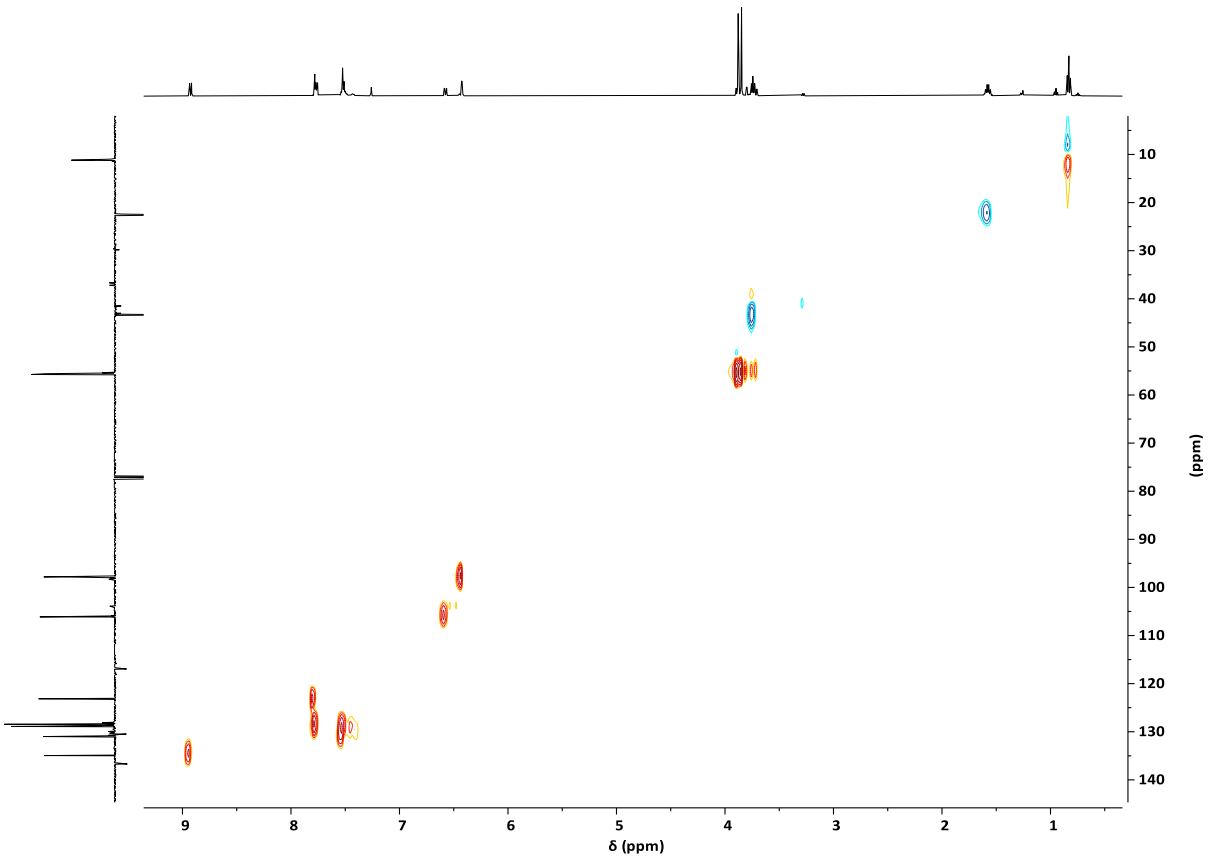

Figure S20. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **2e.**

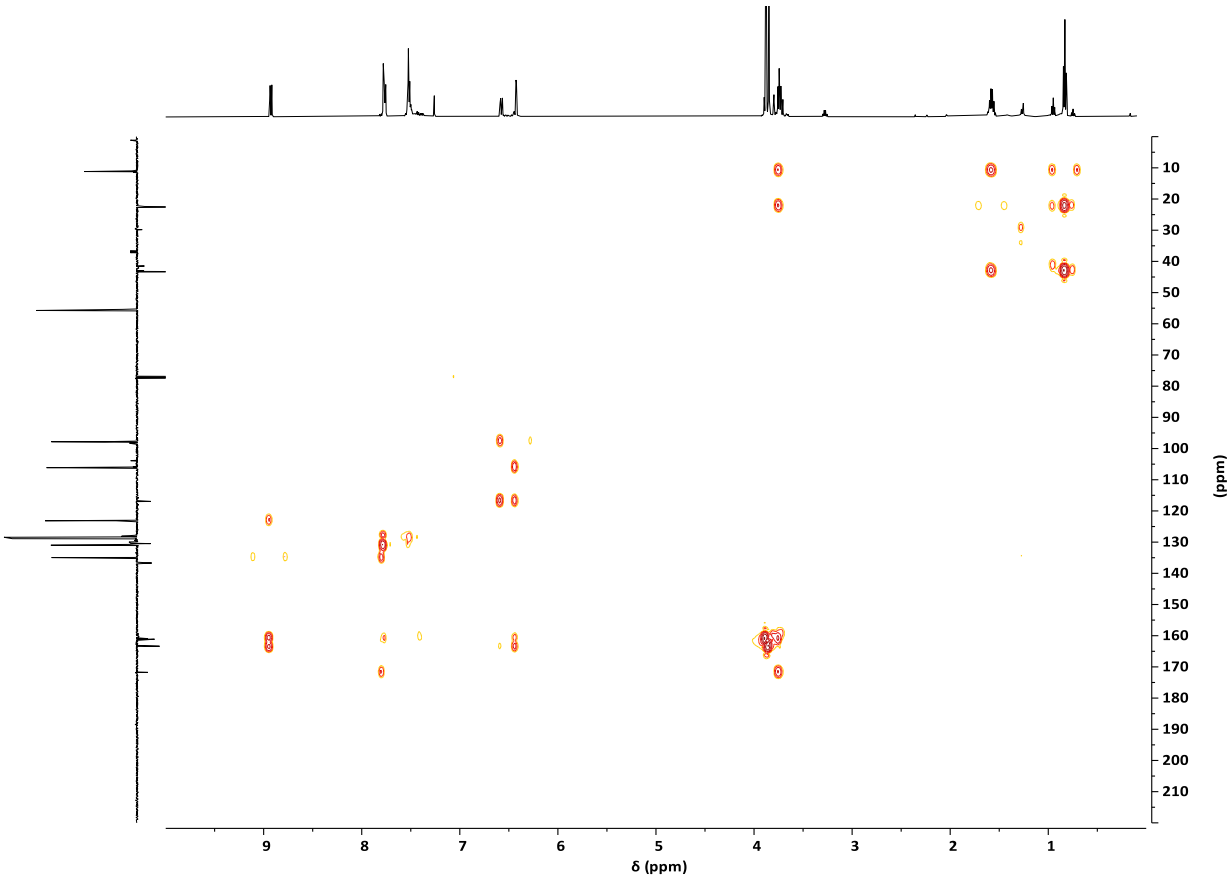

Figure S21. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **2e.**

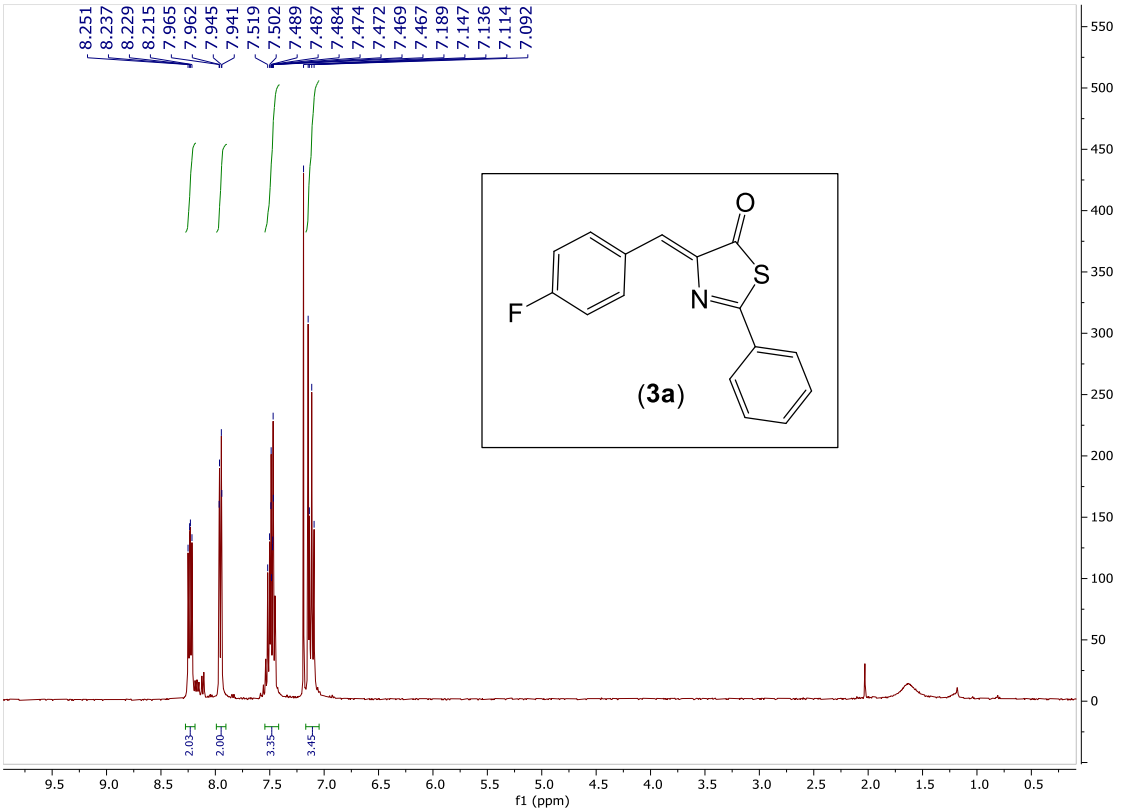

Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **3a**

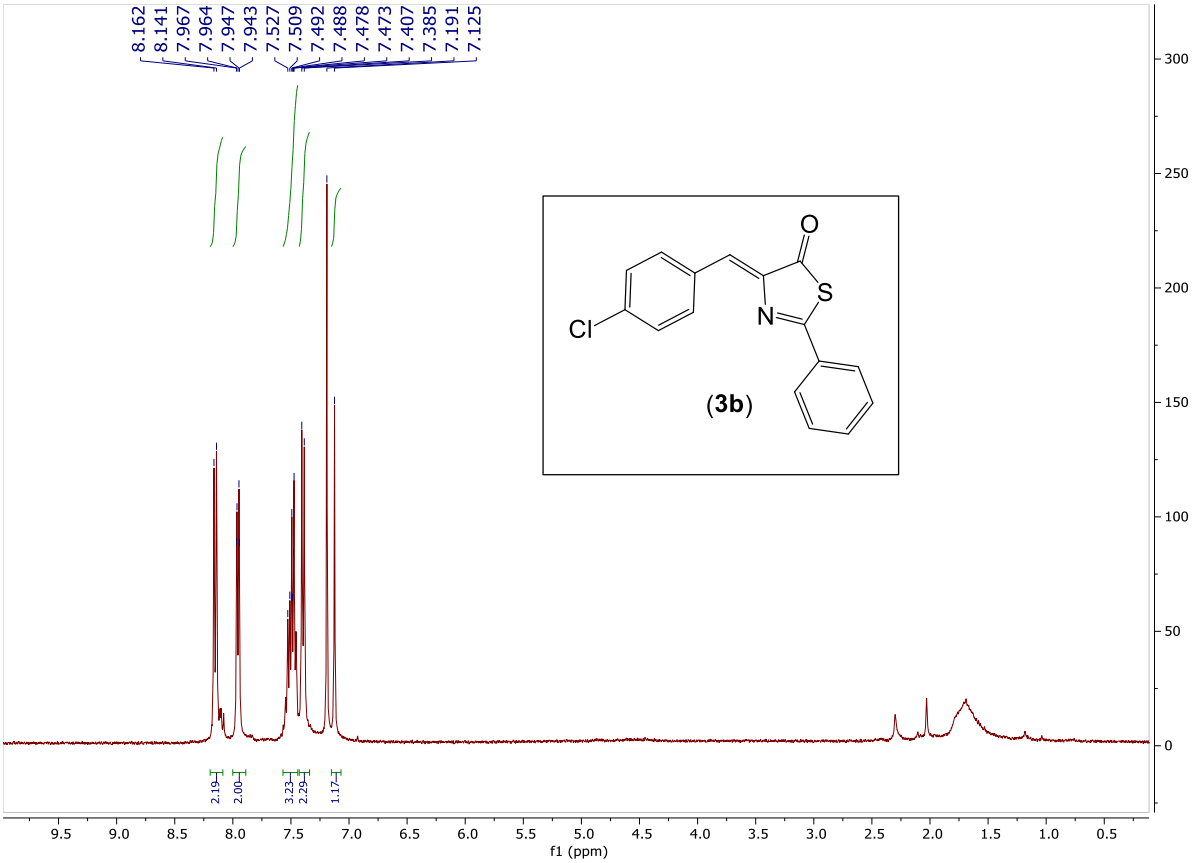

Figure S23. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **3b**

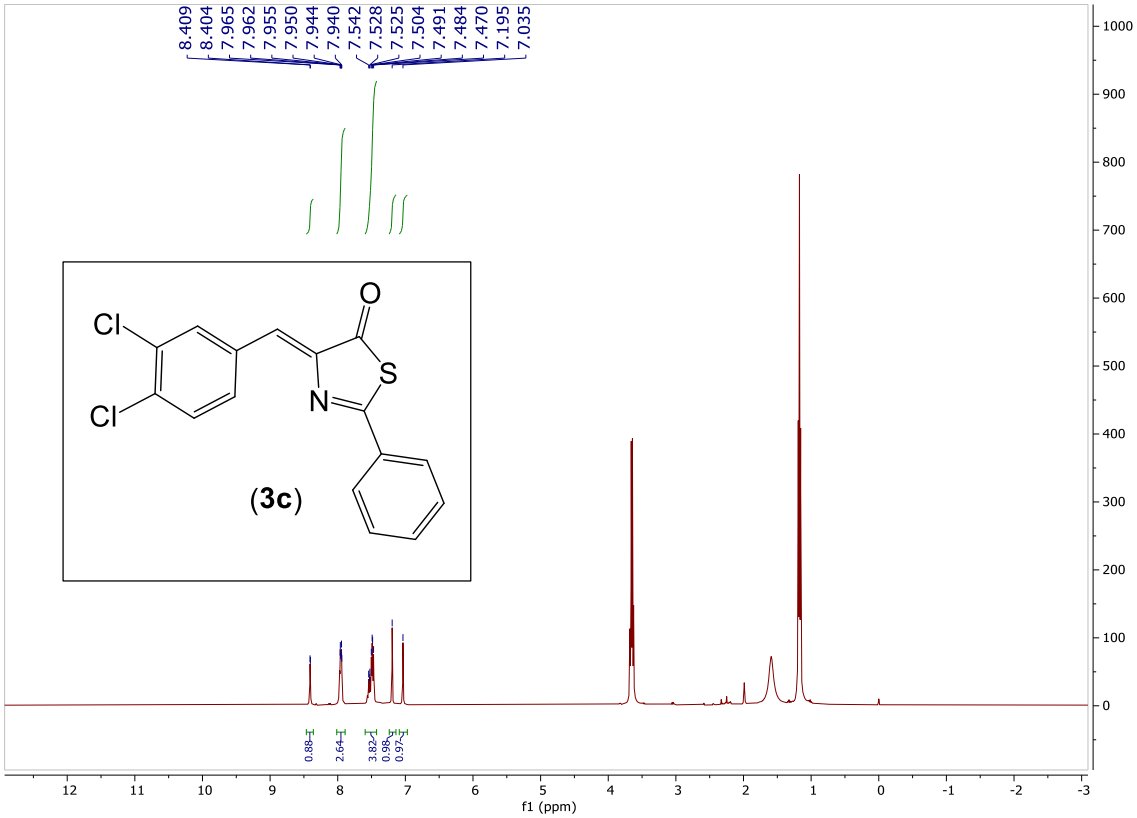

Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **3c**. (peaks at 1.2 ppm and 3.6 ppm are due to residual ethanol, solvent used to wash the product).

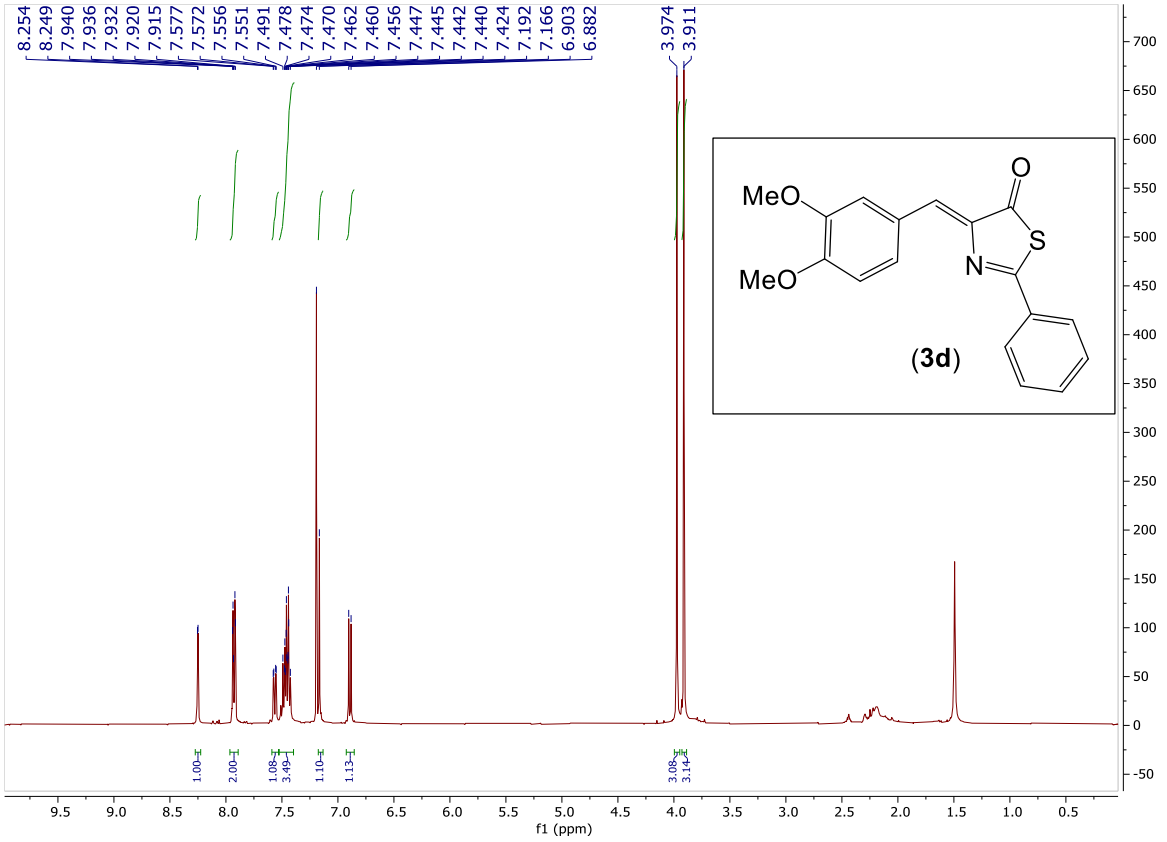

Figure S25. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, r. t.) of **3d**

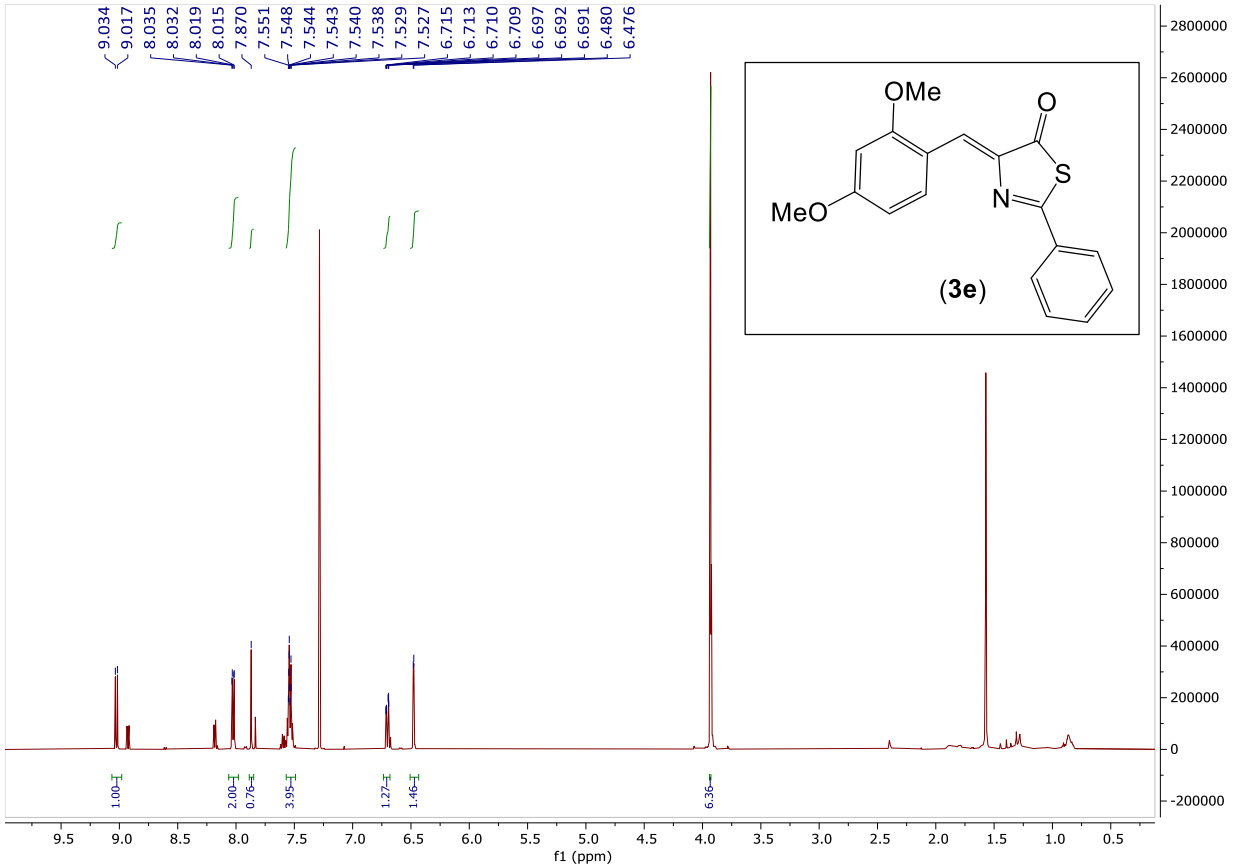

Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **3e**

4.-NMR spectra of all new compounds: orthopalladated compounds from imidazolones (4) and thiazolones (5)

Orthopalladated compound 4a

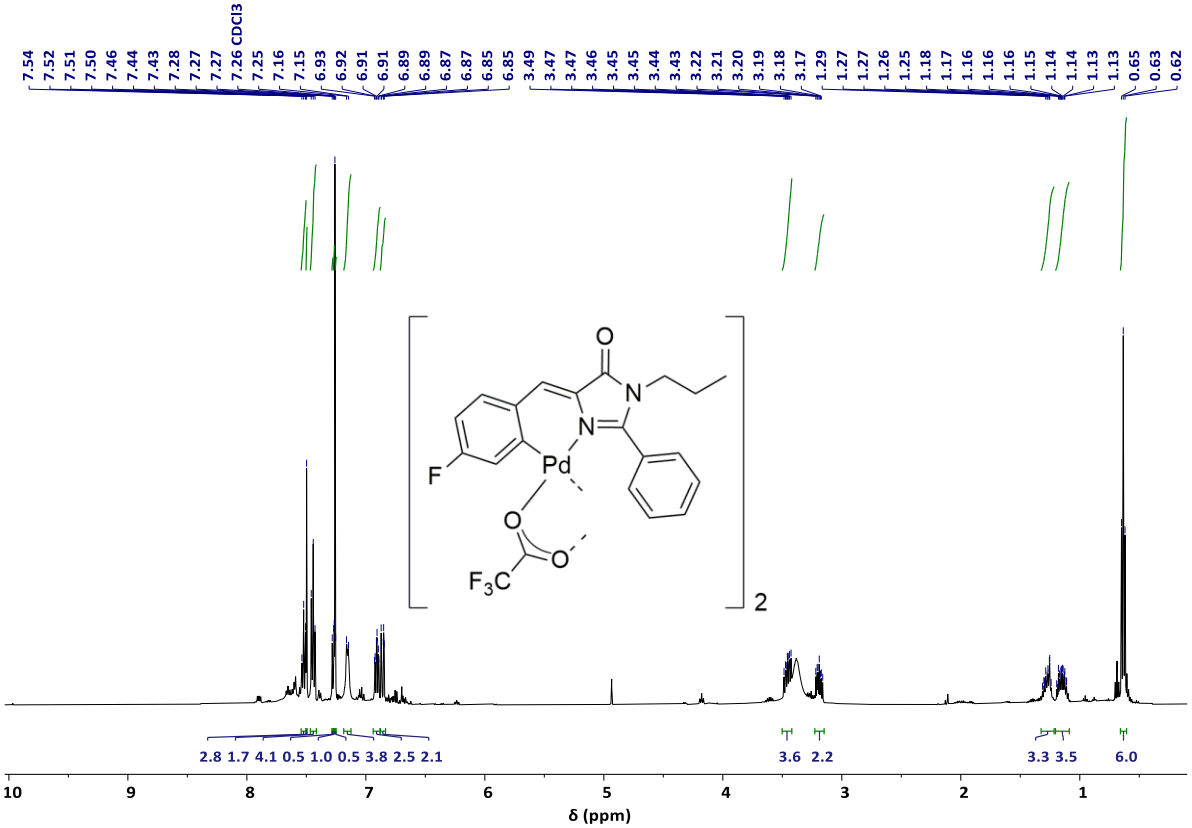

Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **4a**

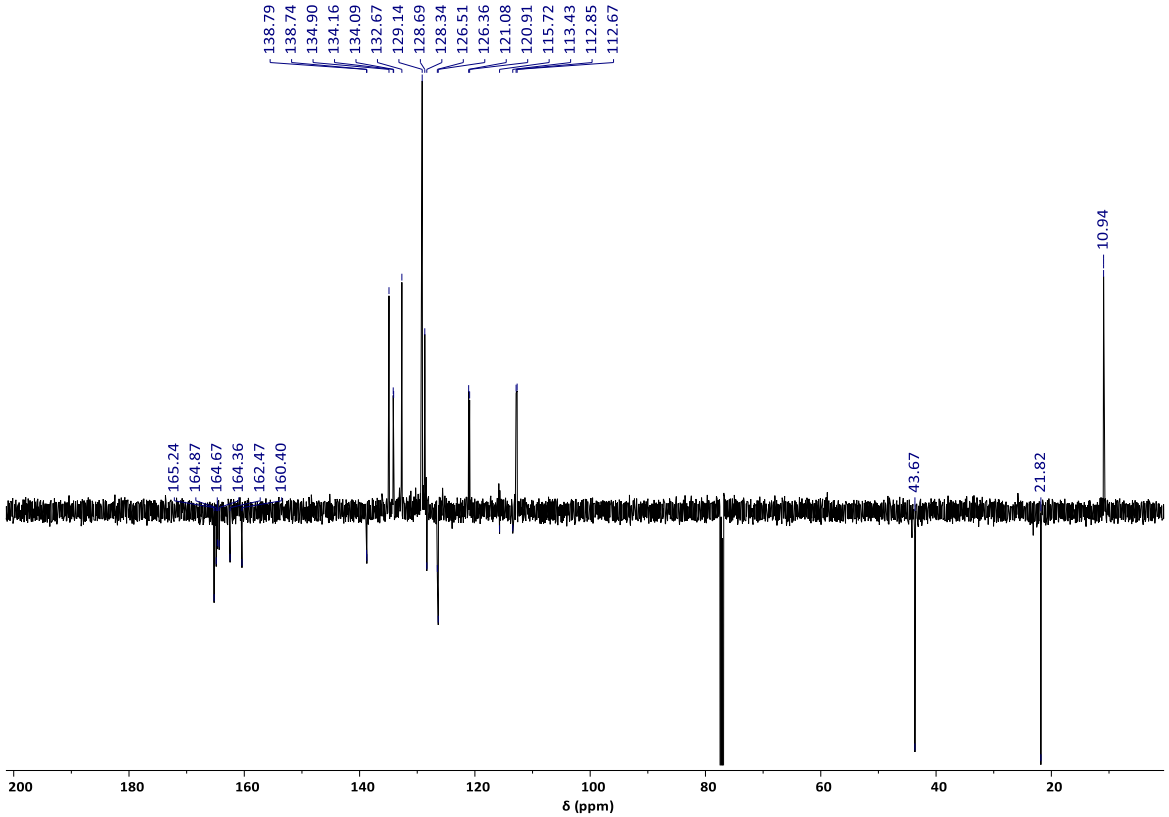

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **4a**

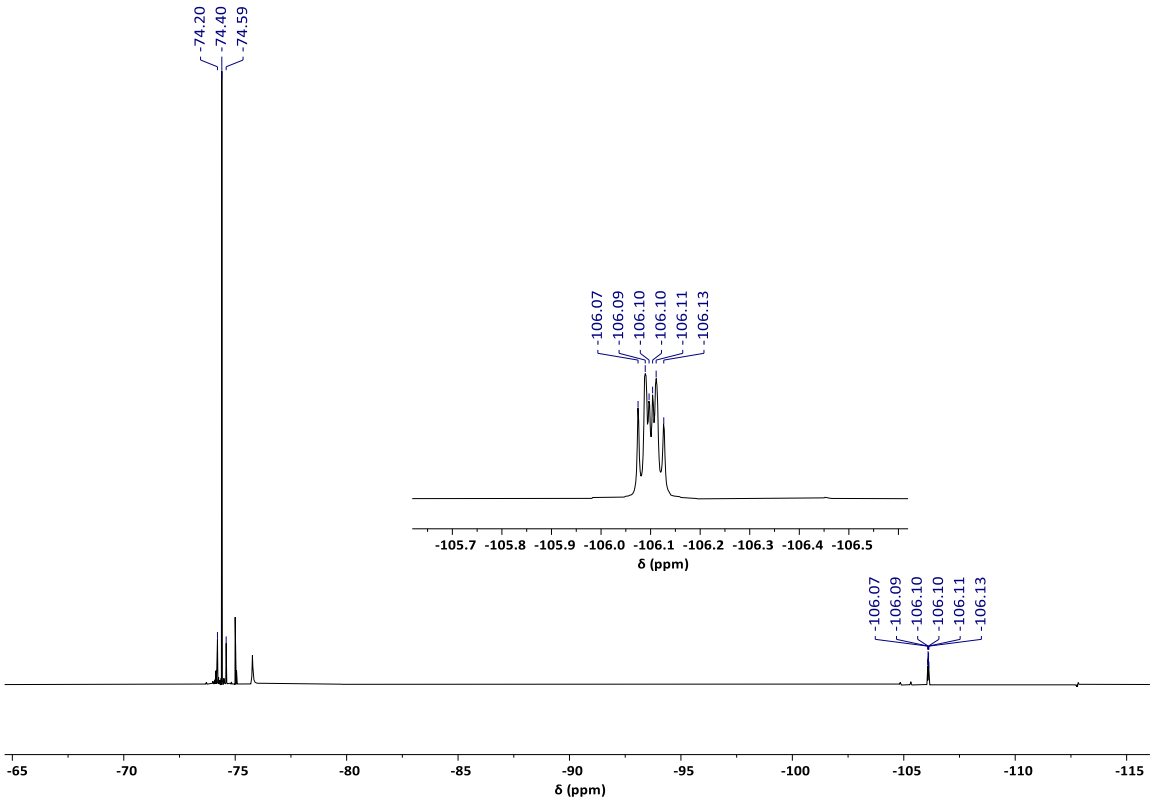

Figure S29. ^{19}F NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **4a**

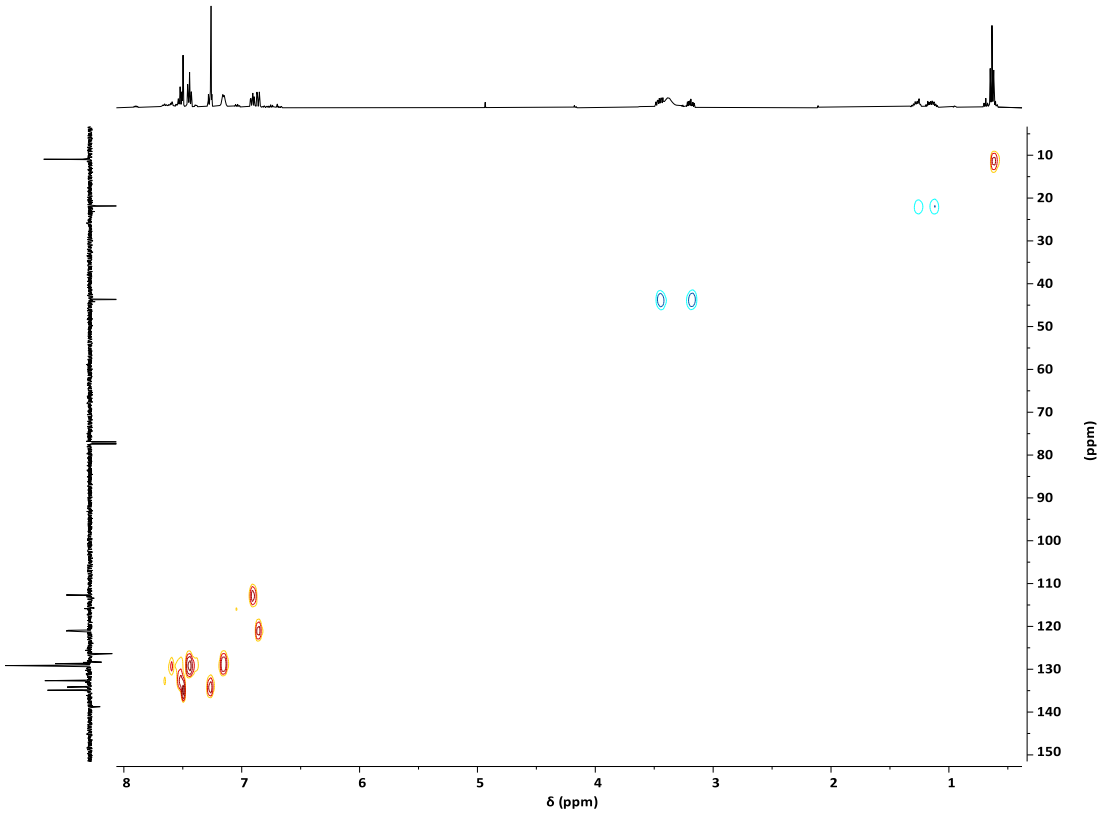

Figure S30. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **4a.**

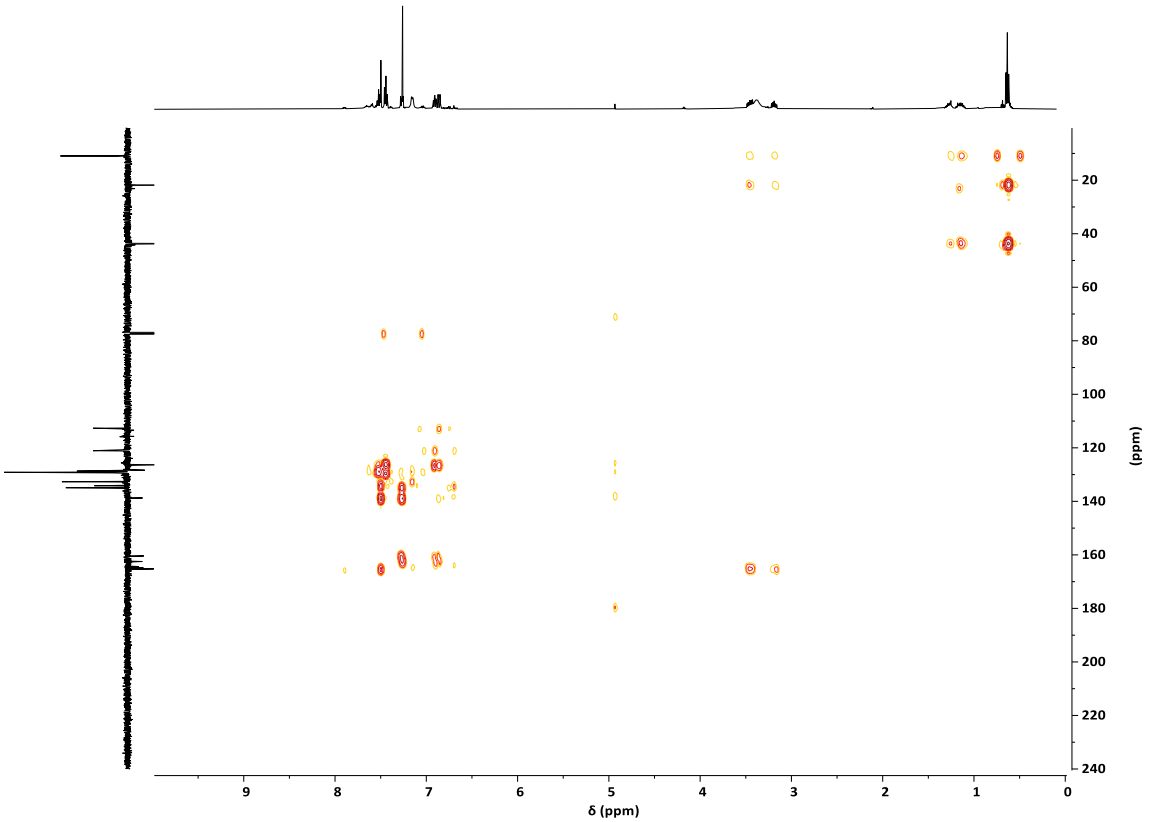

Figure S31. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **4a.**

Orthopalladated compound 4b

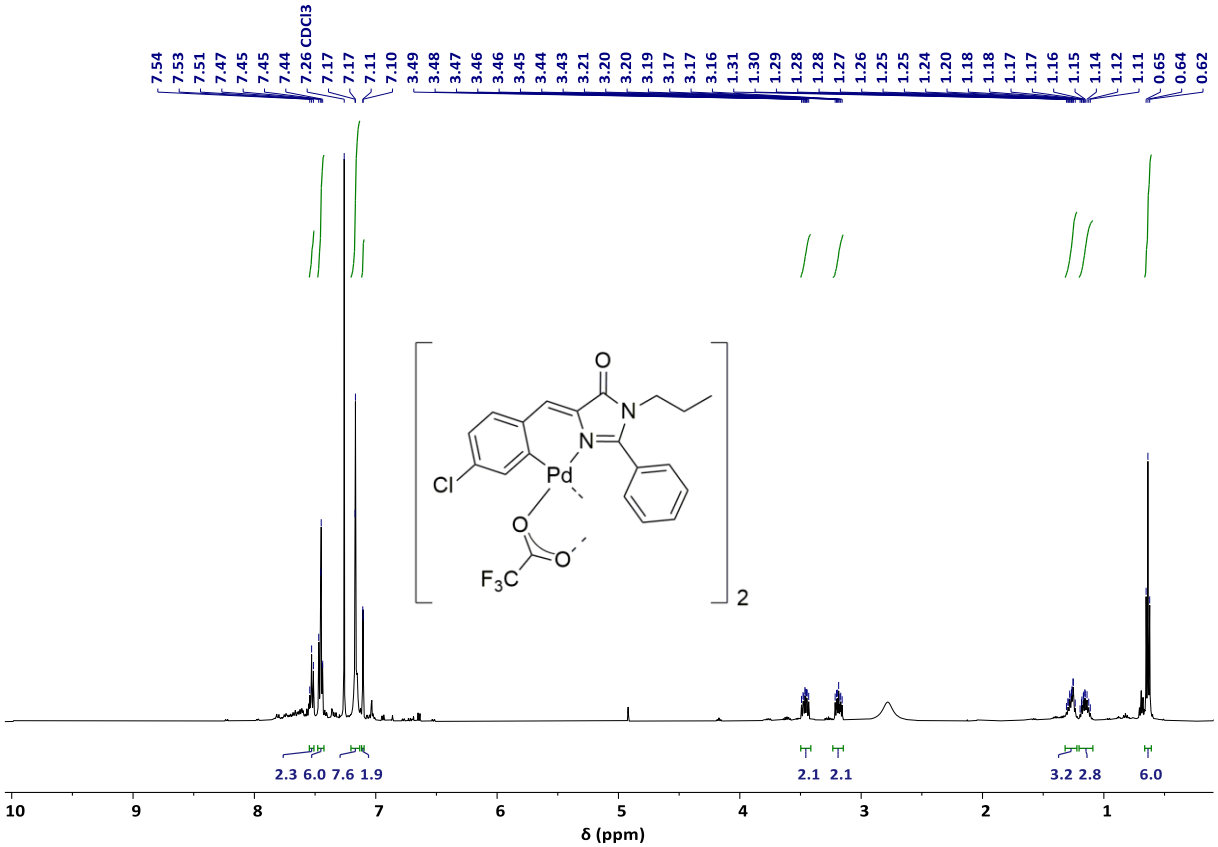

Figure S32. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **4b**

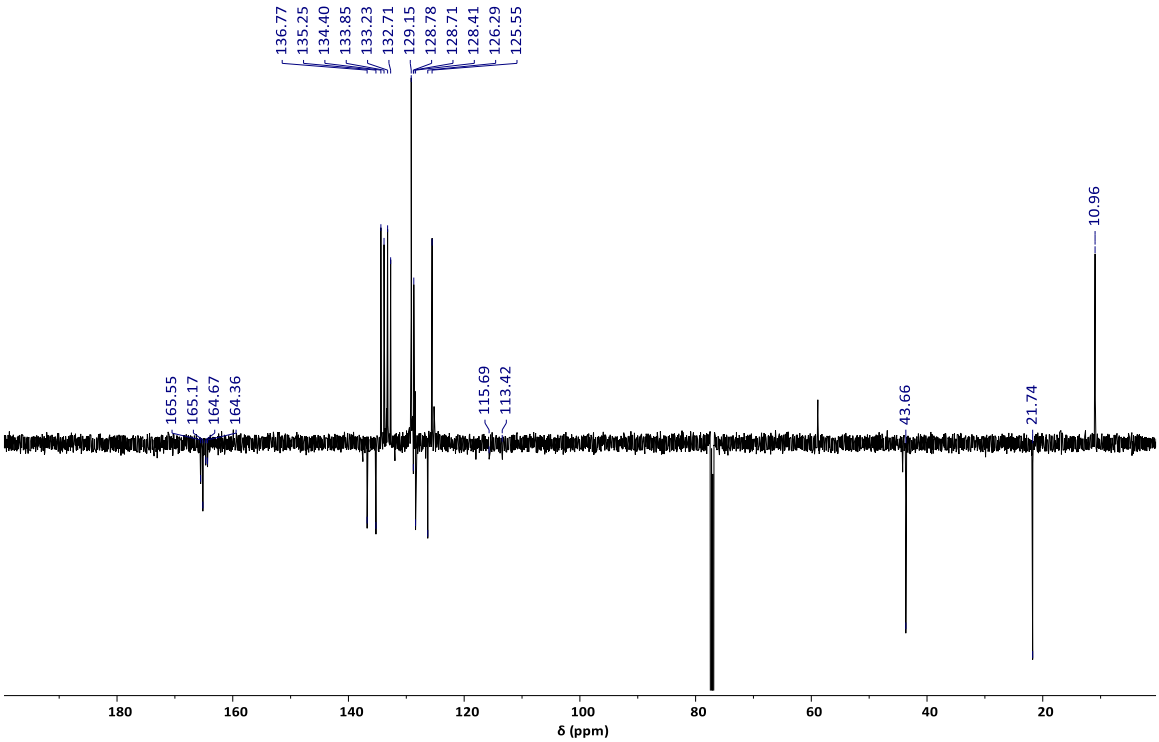

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **4b**

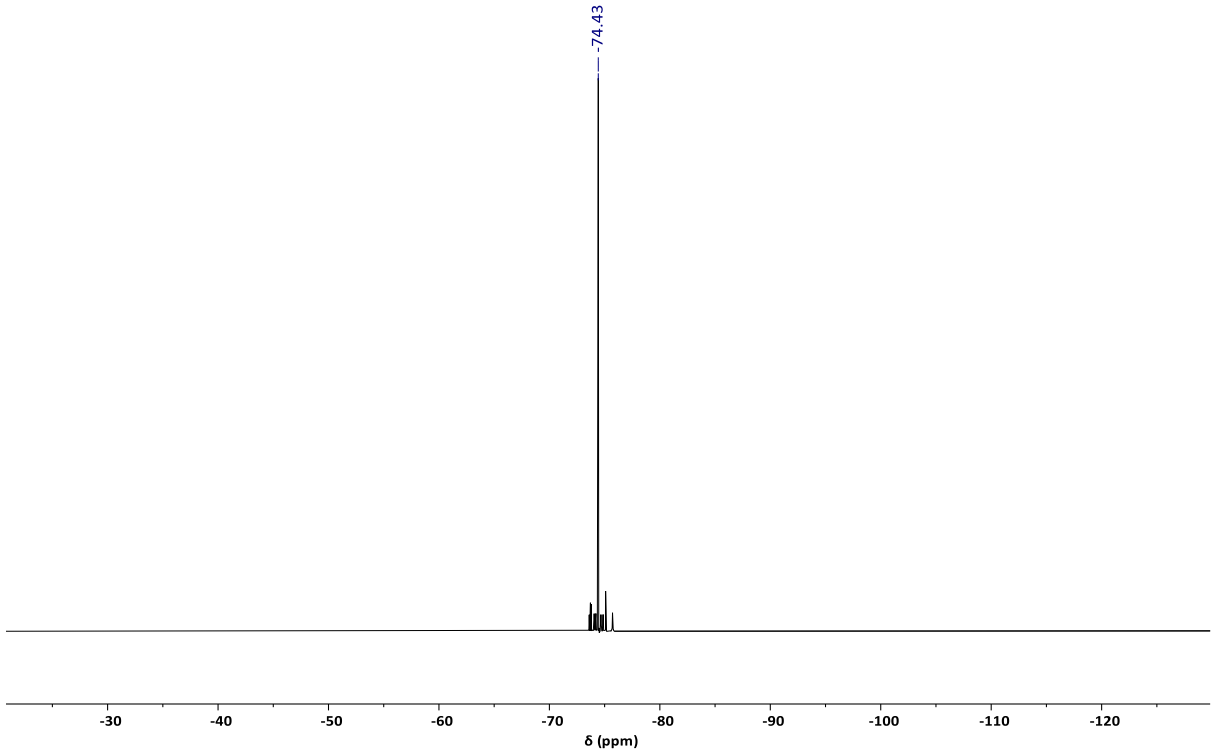

Figure S34. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **4b**

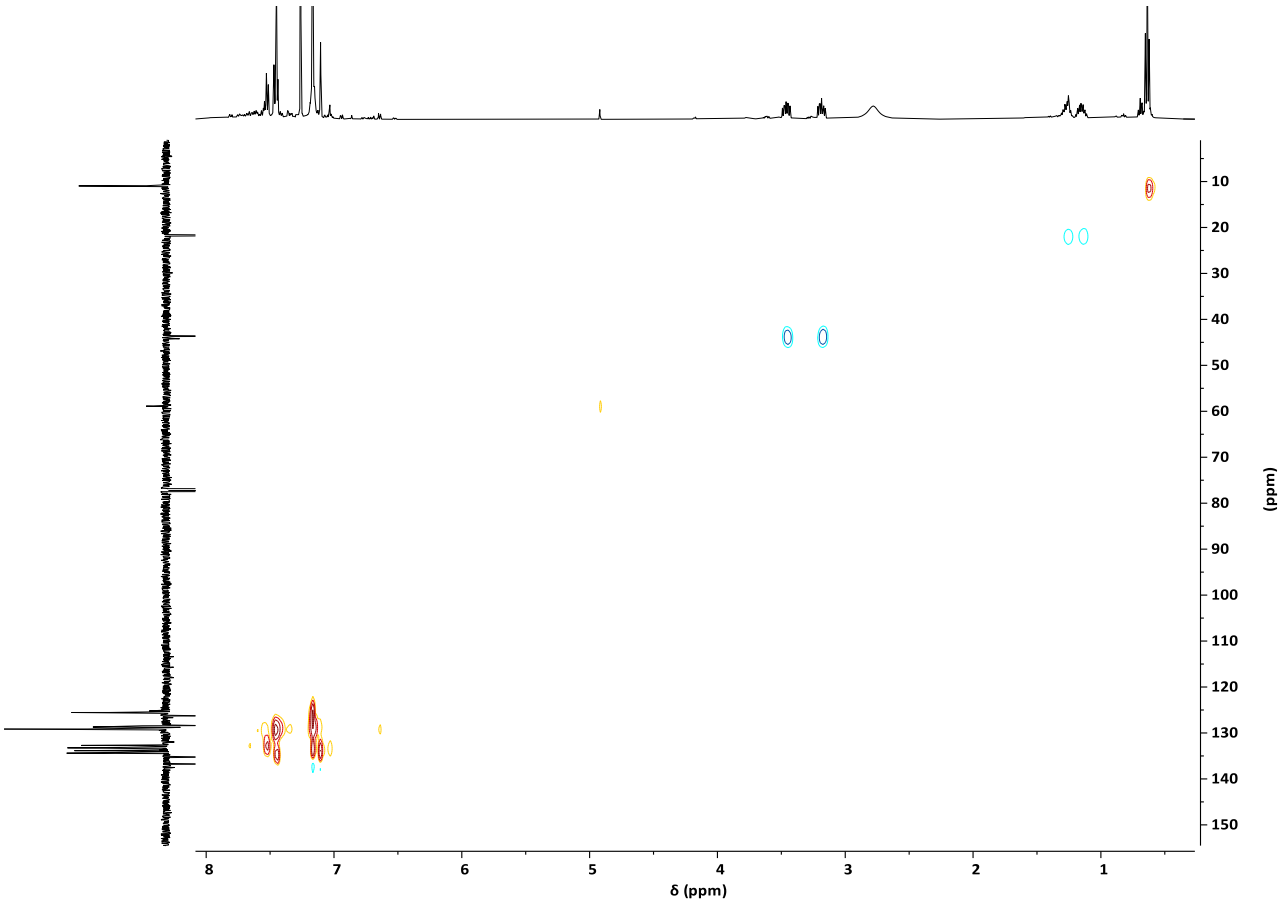

Figure S35. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **4b**

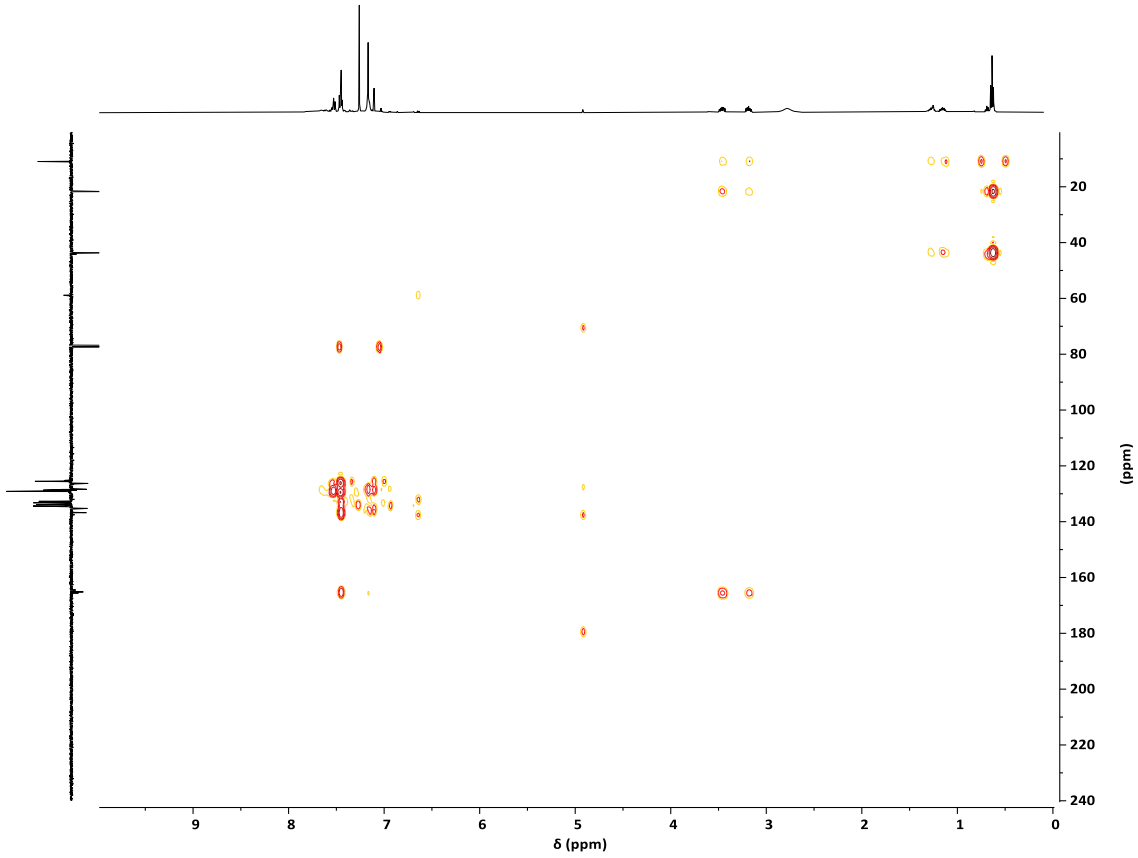

Figure S36. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **4b**

Orthopalladated compound 4c

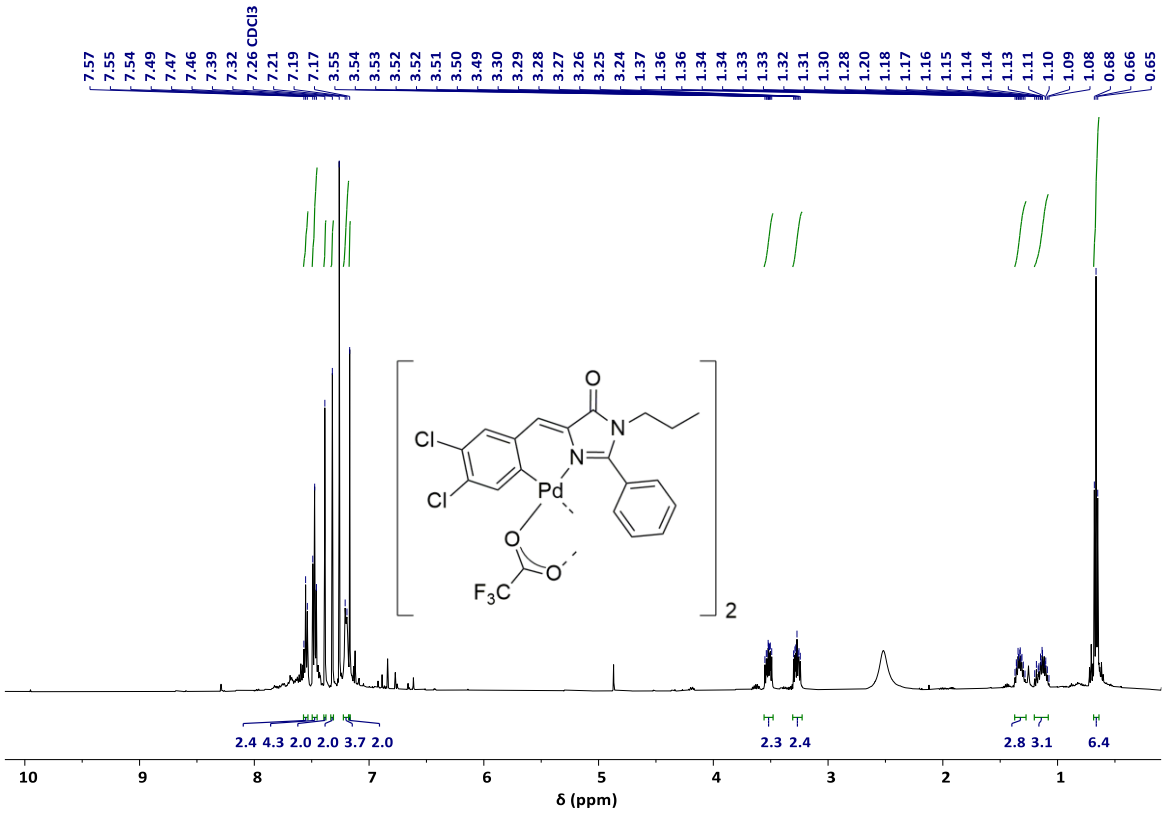

Figure S37. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **4c**

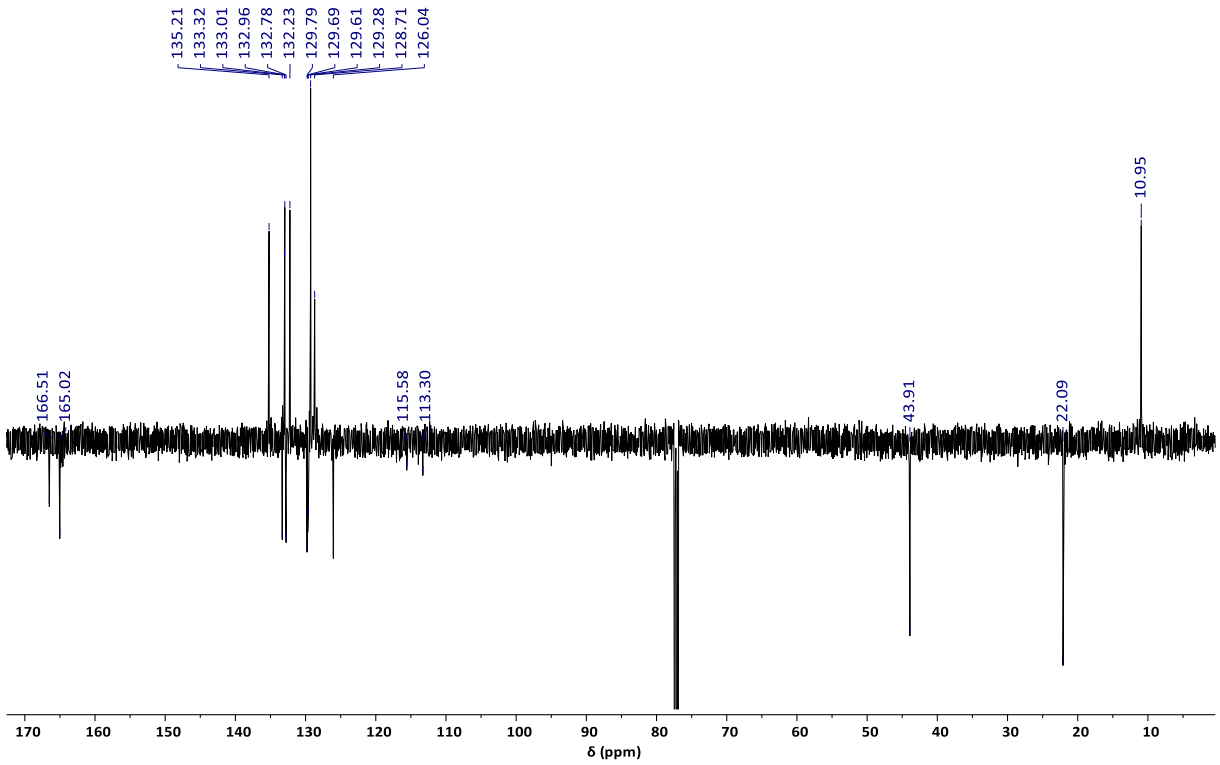

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **4c**

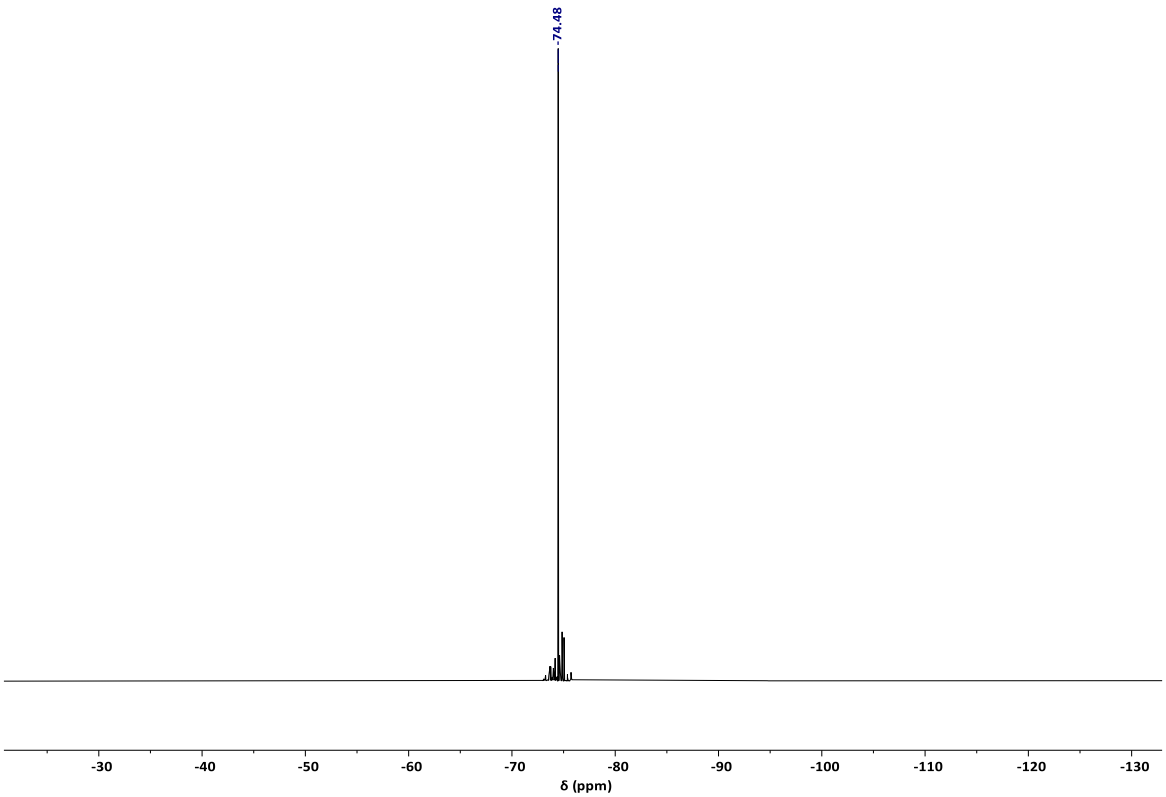

Figure S39. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **4c**

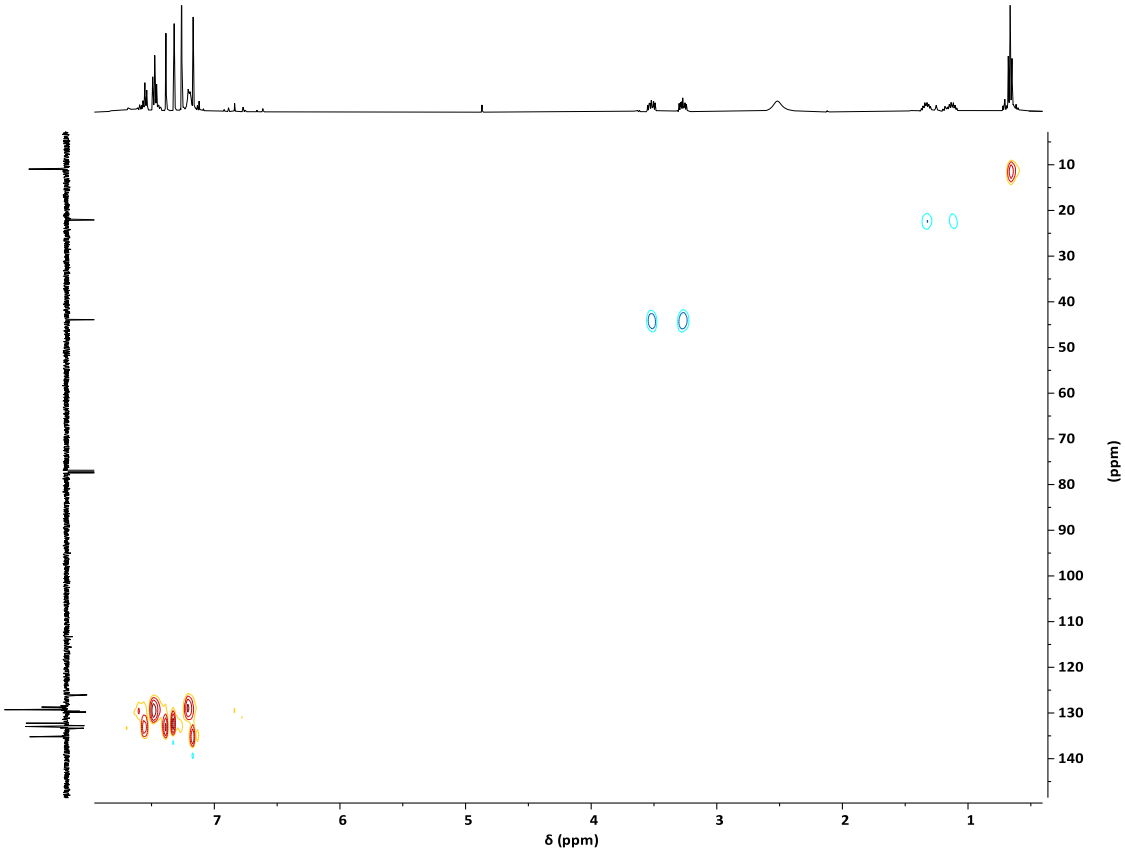

Figure S40. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **4c**

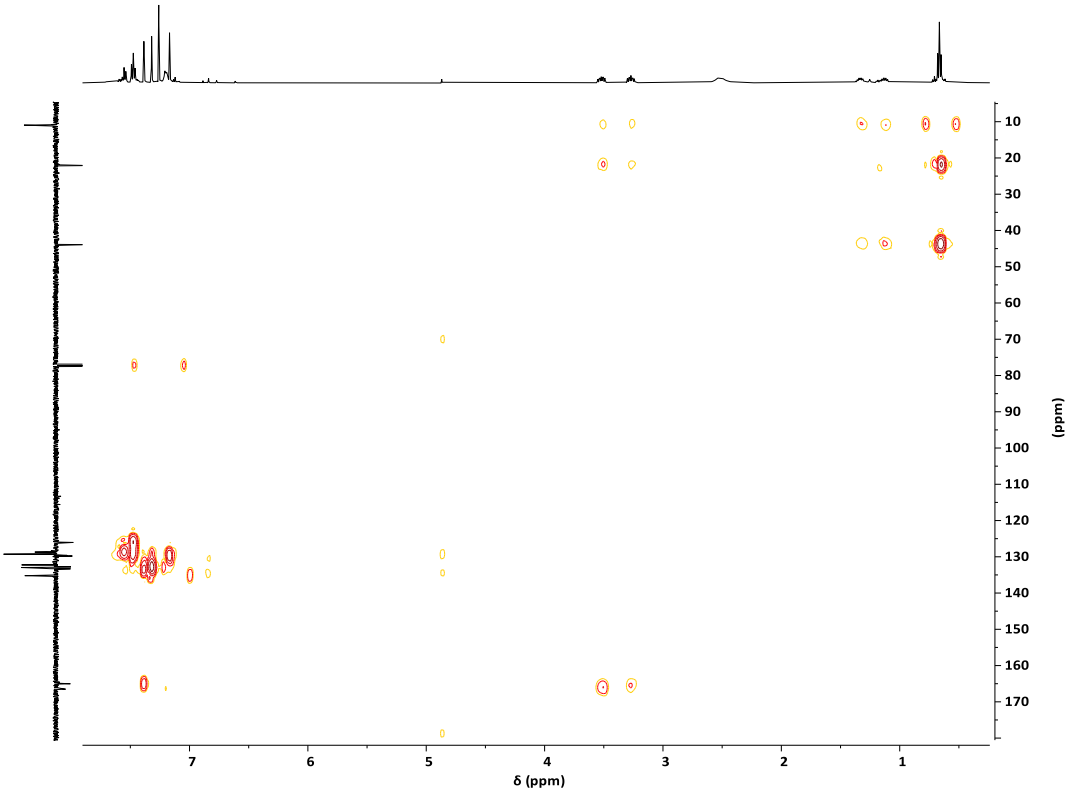

Figure S41. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **4c**

Orthopalladated compound 4d

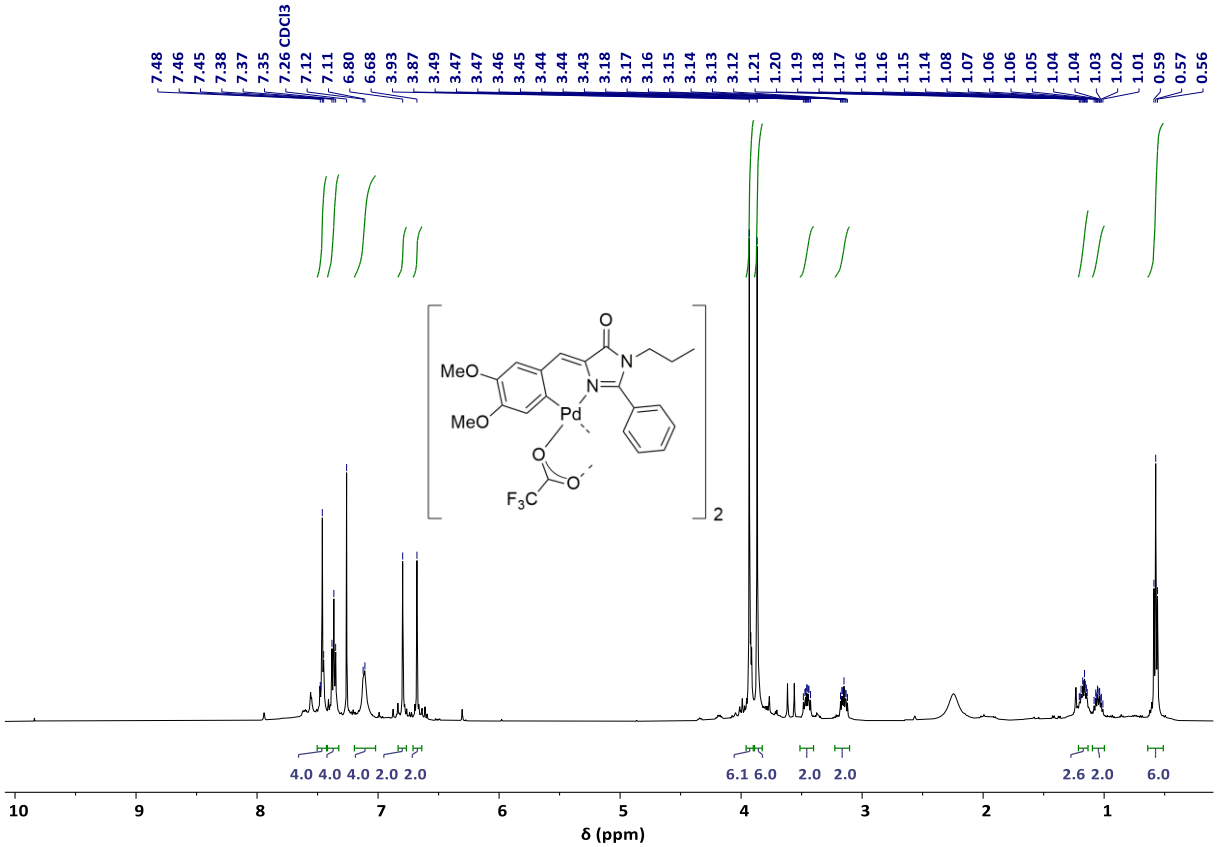

Figure S42. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **4d**

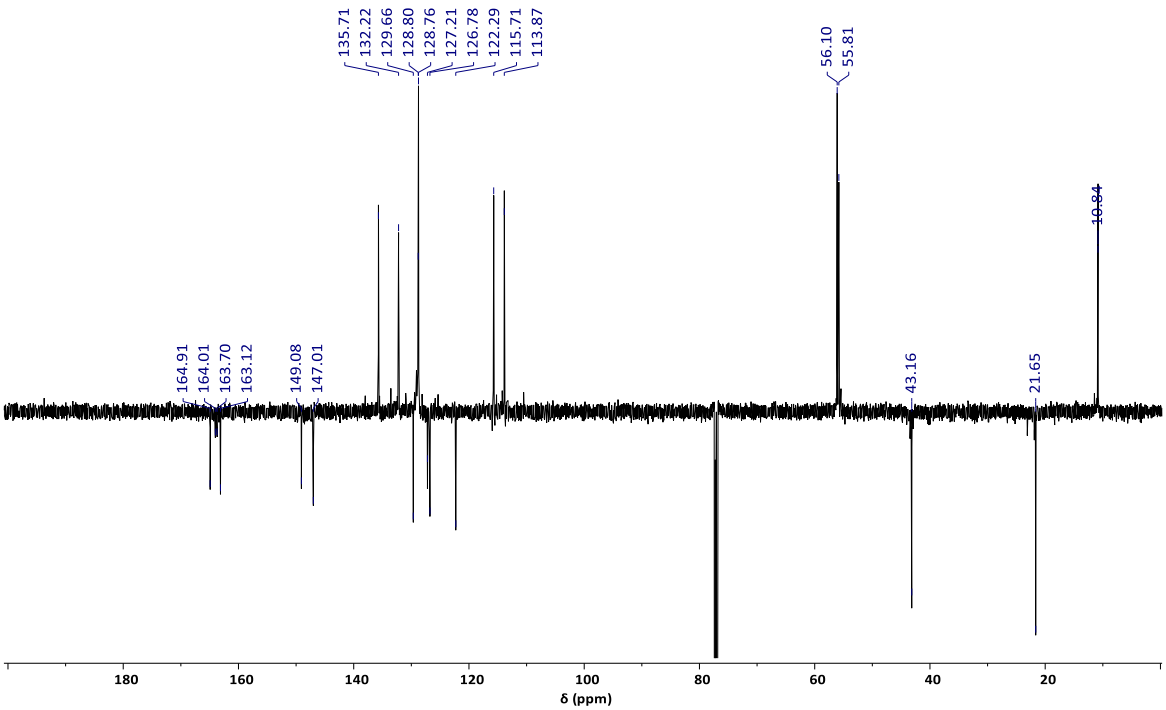

Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **4d**

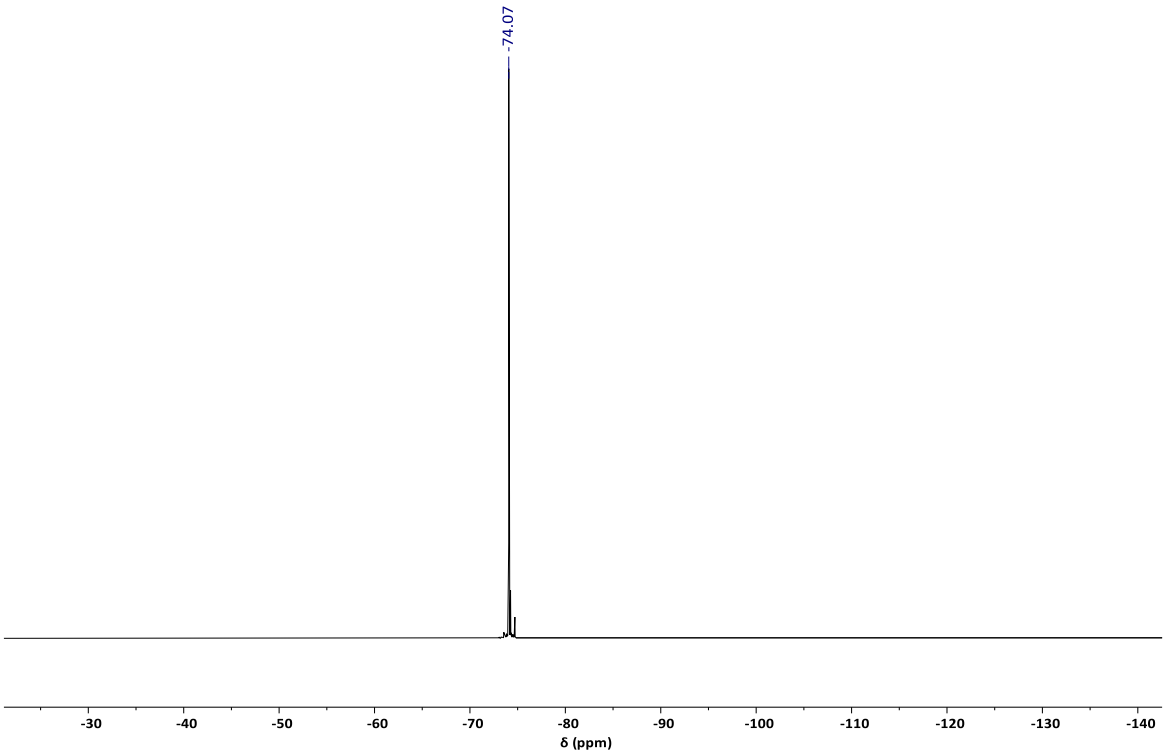

Figure S44. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **4d**

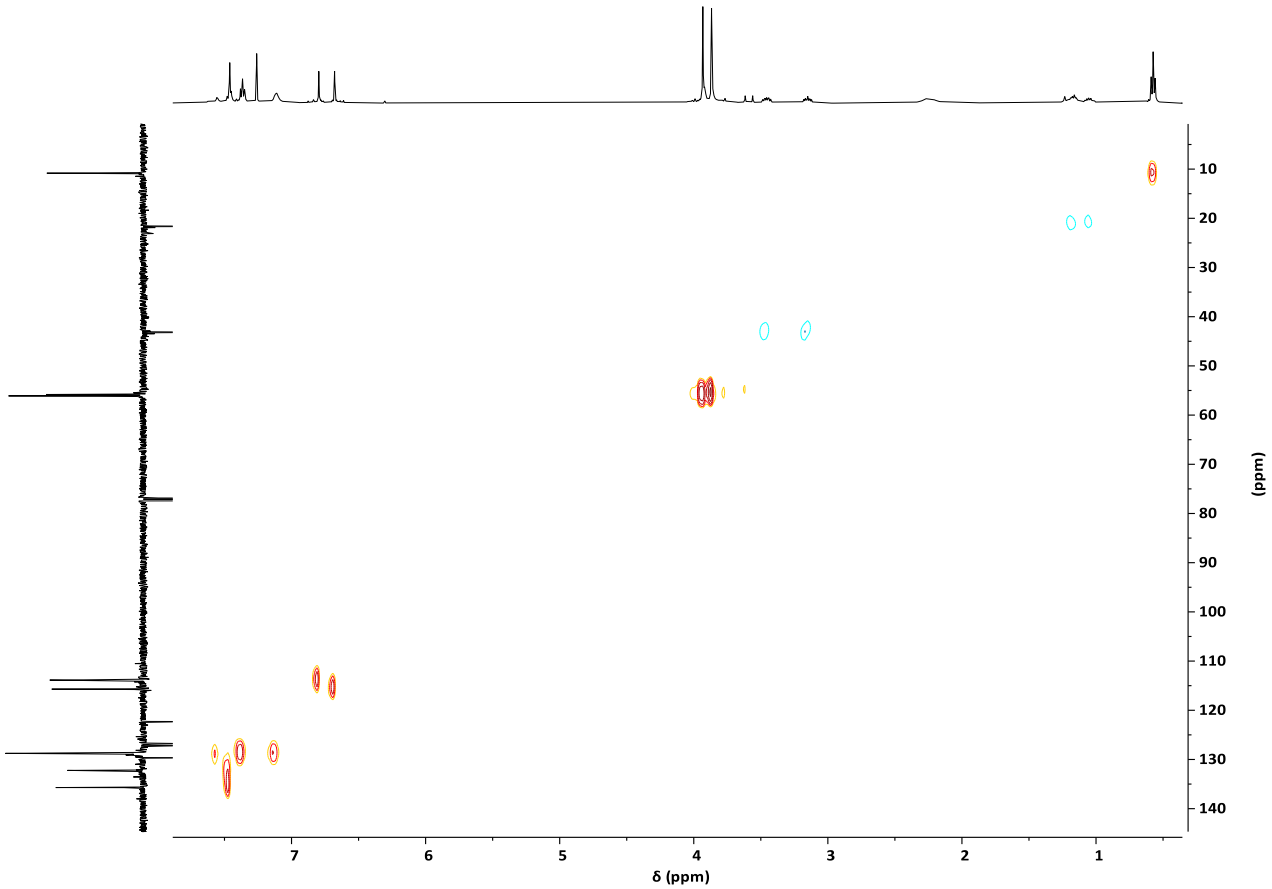

Figure S45. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **4d**

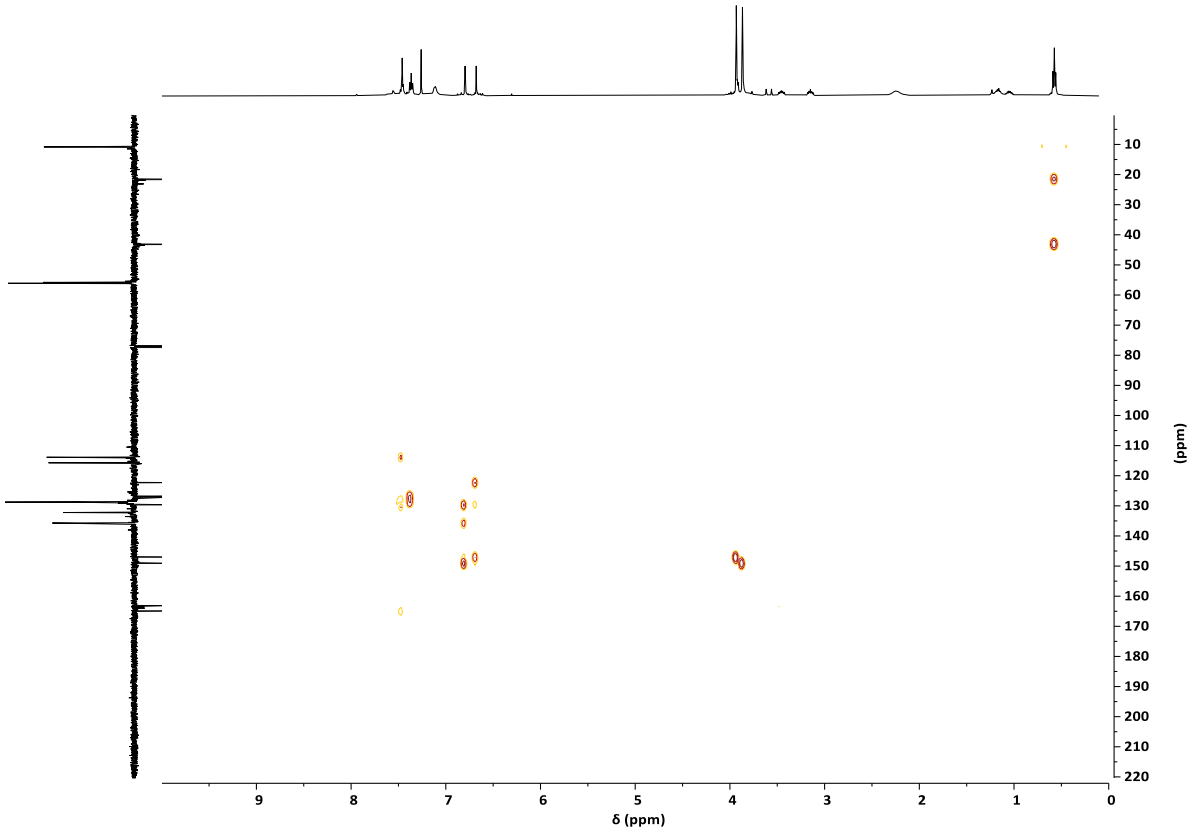

Figure S46. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **4d**

Orthopalladated compound 4e

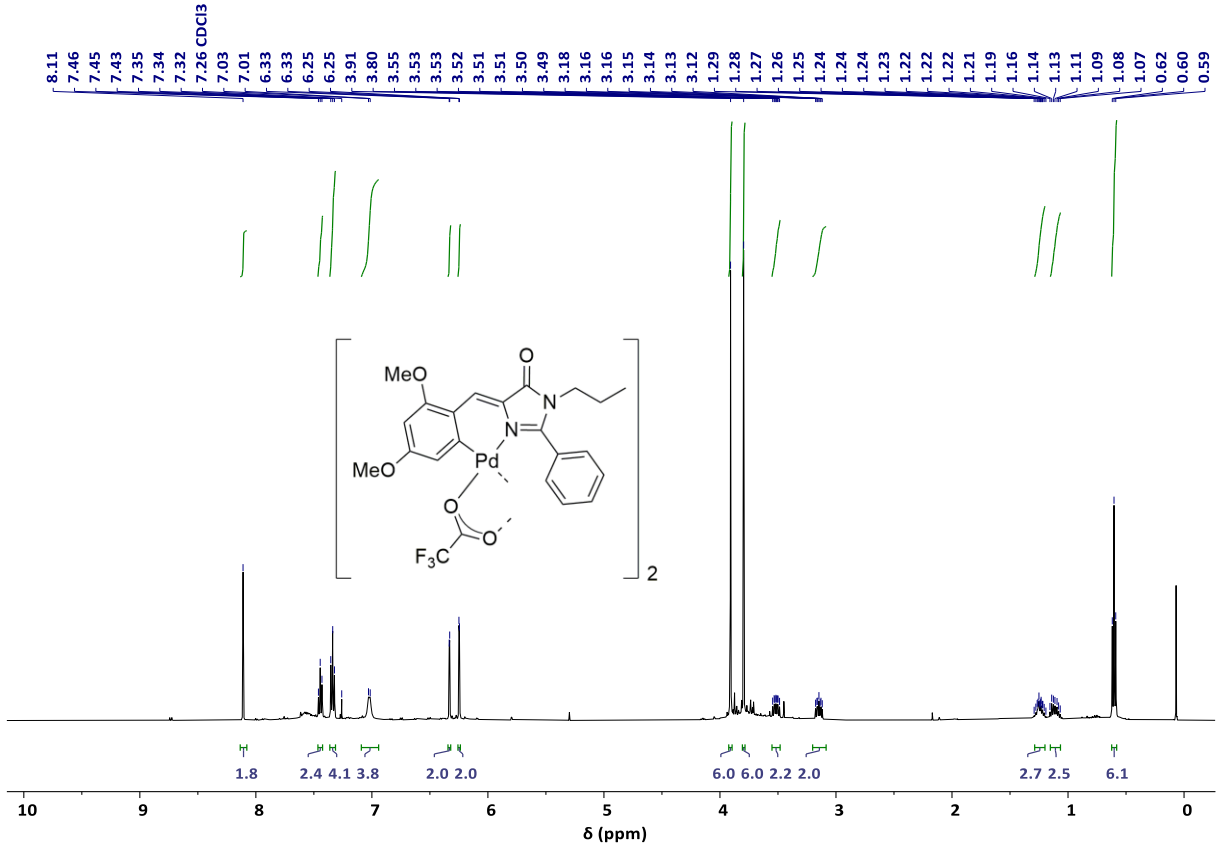

Figure S47. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **4e**

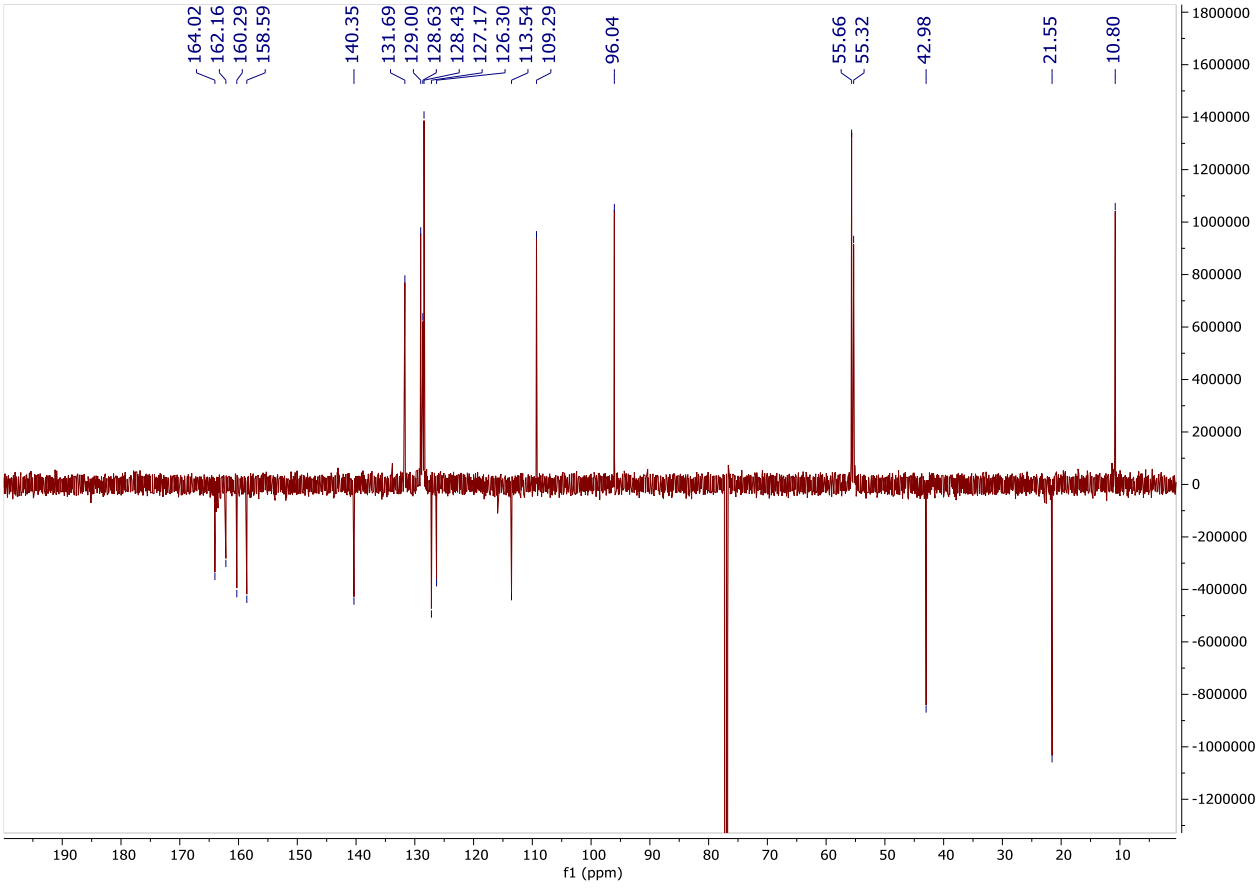

Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **4e**

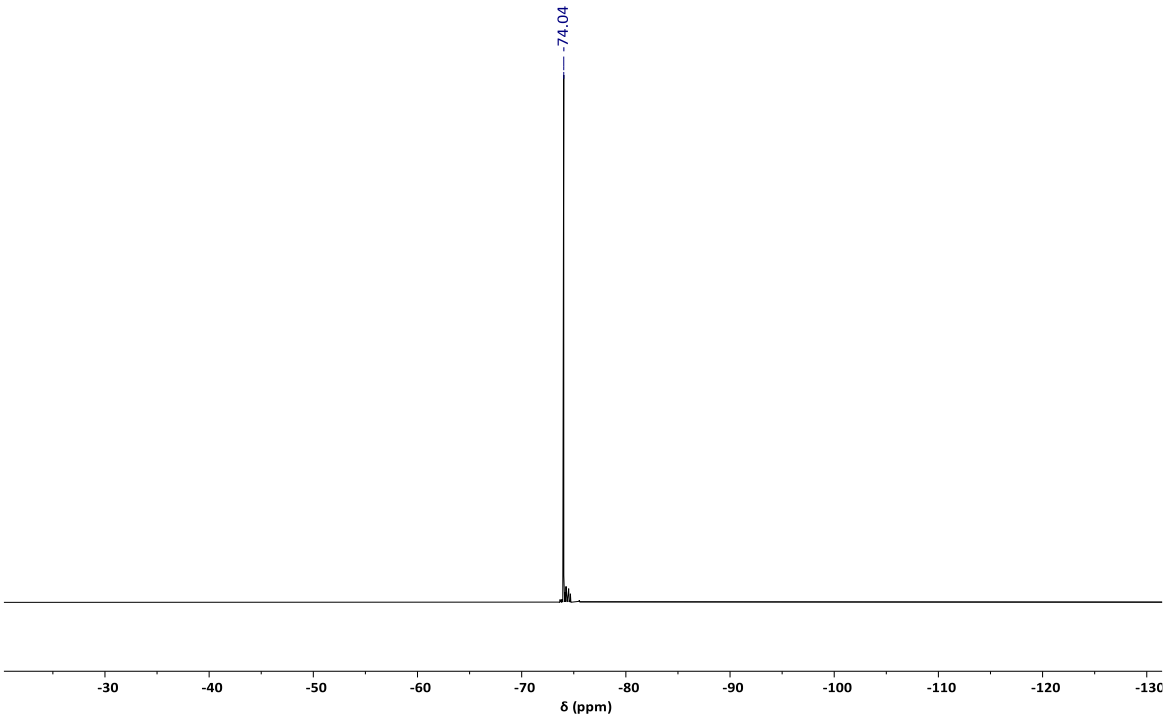

Figure S49. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **4e**

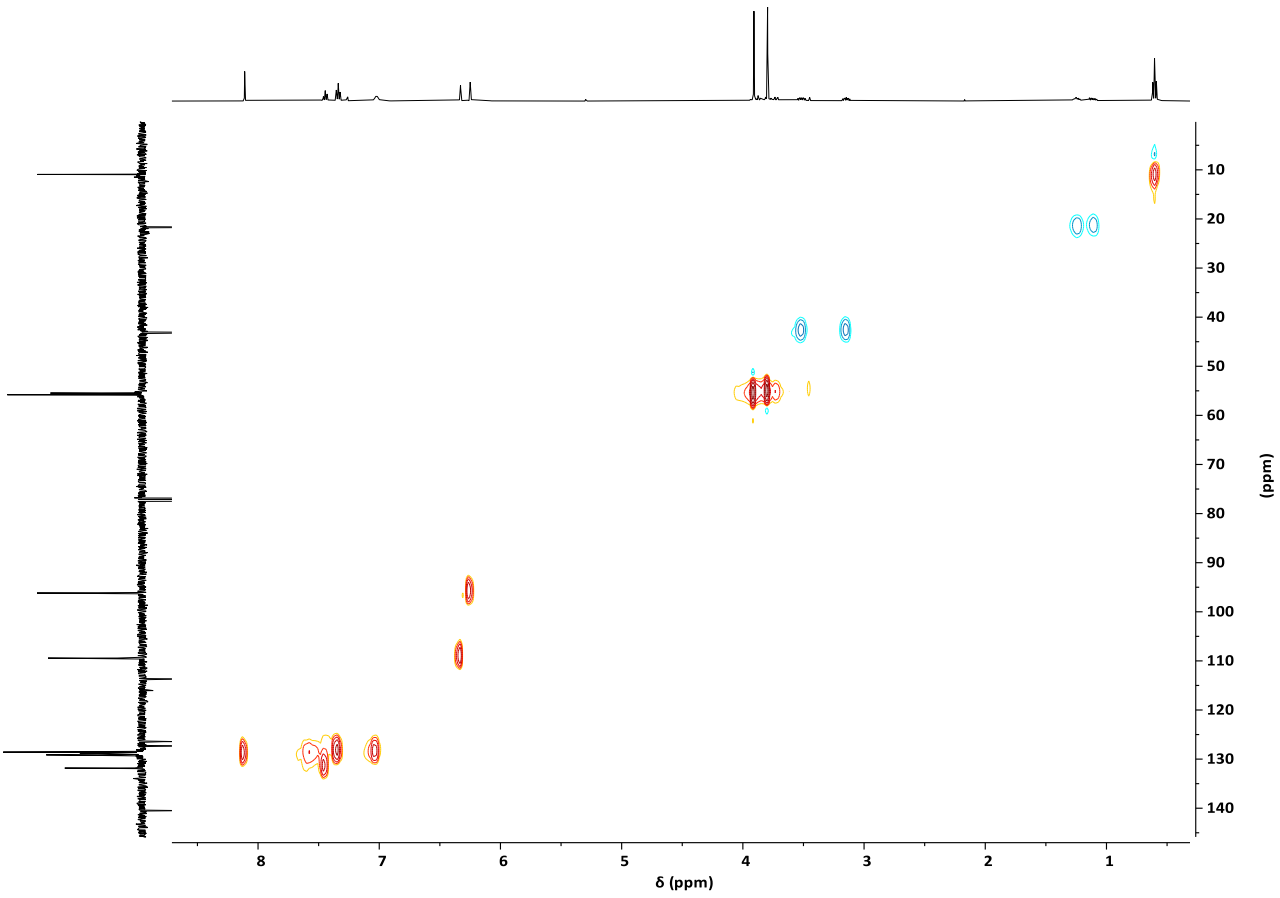

Figure S50. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **4e**

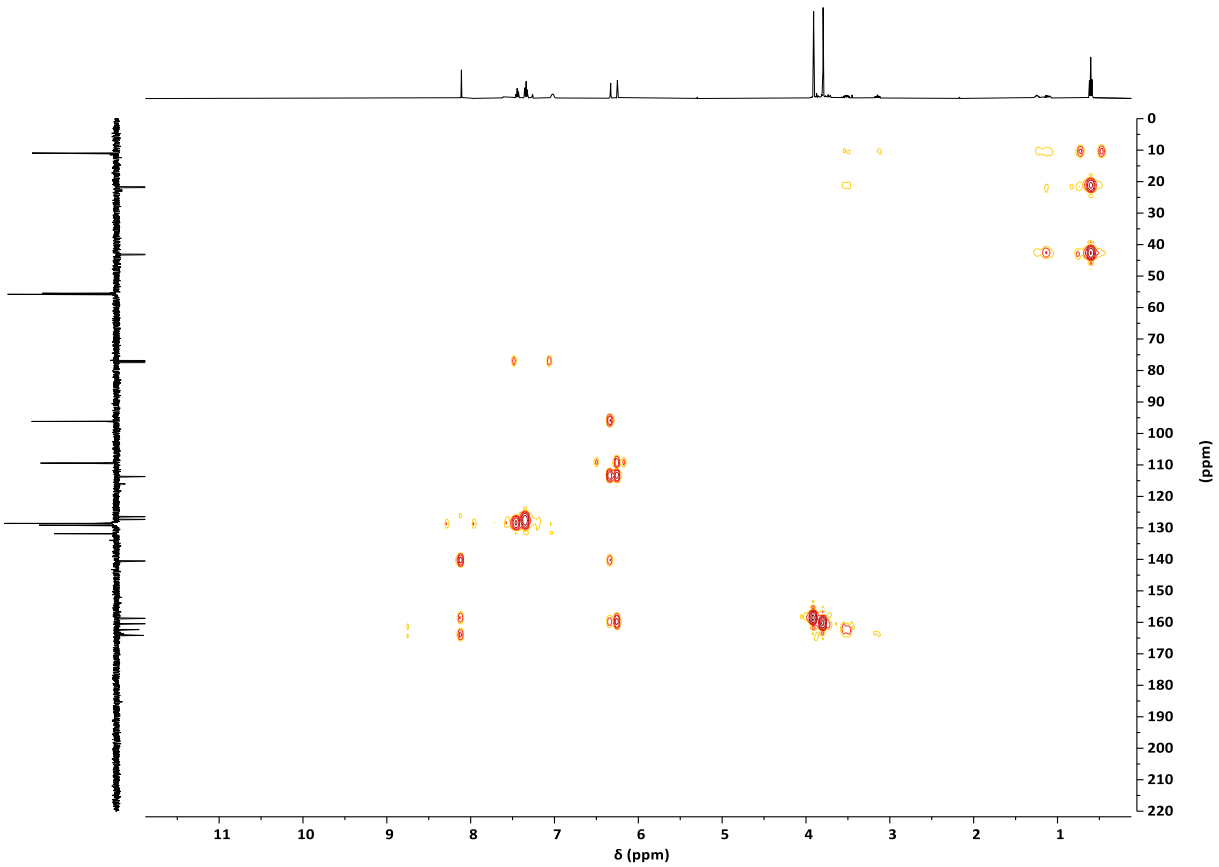

Figure S51. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **4e**

Orthopalladated compound 11a

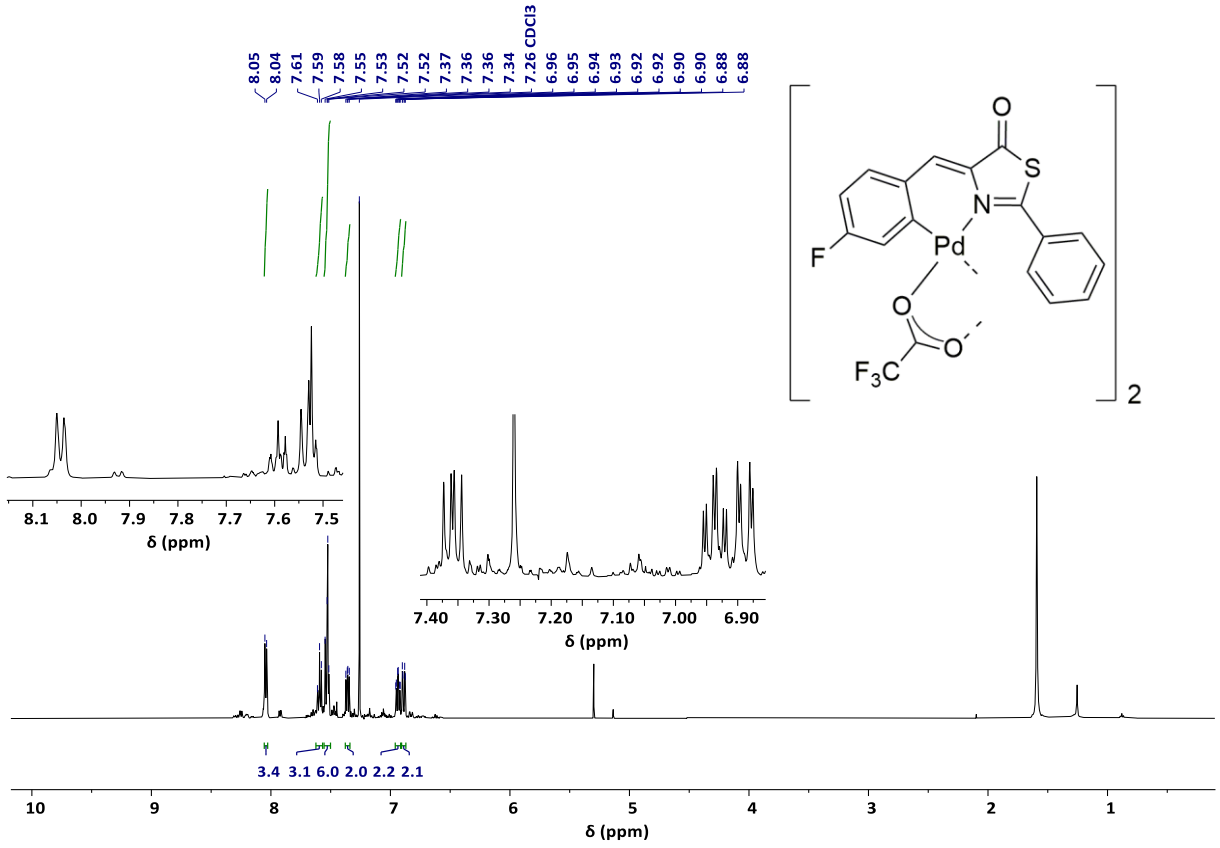

Figure S52. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **11a**

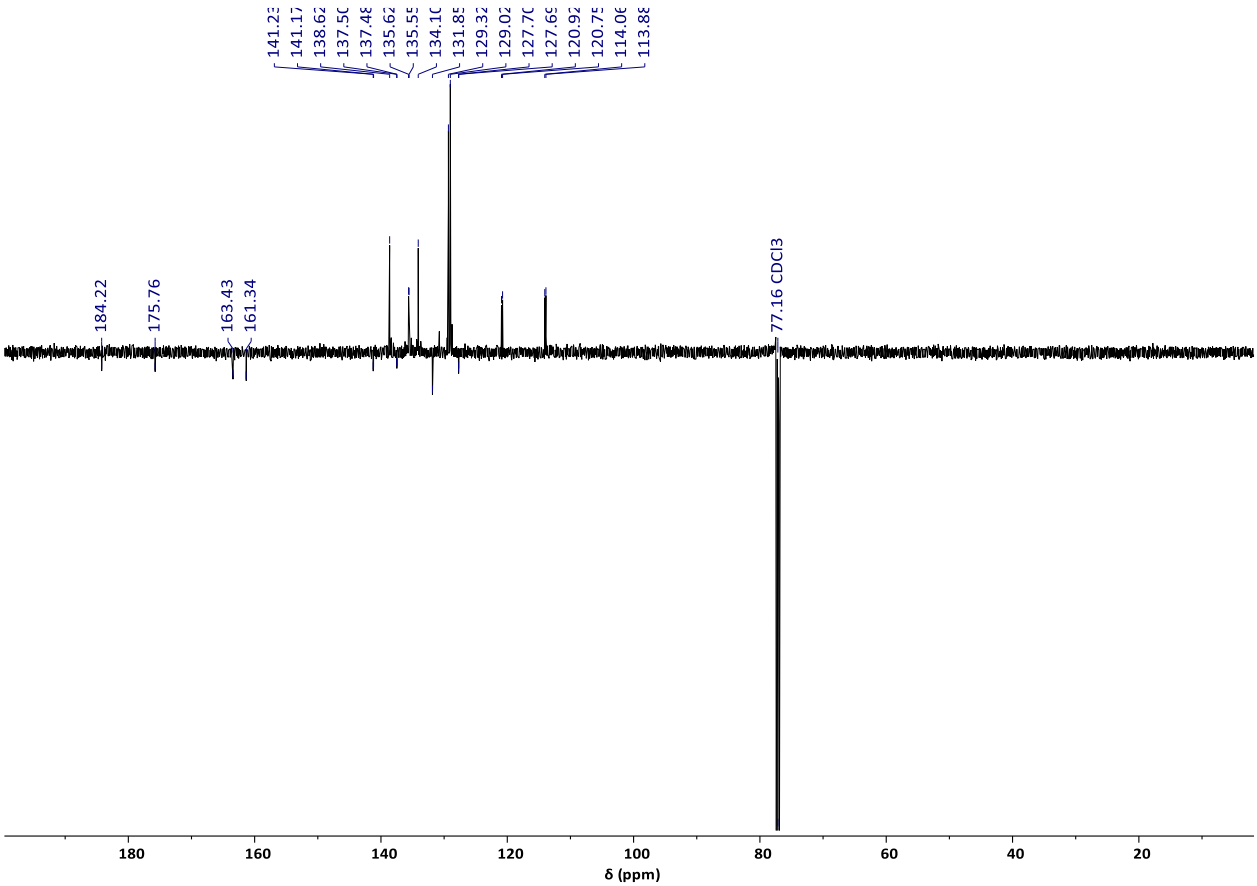

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **11a**

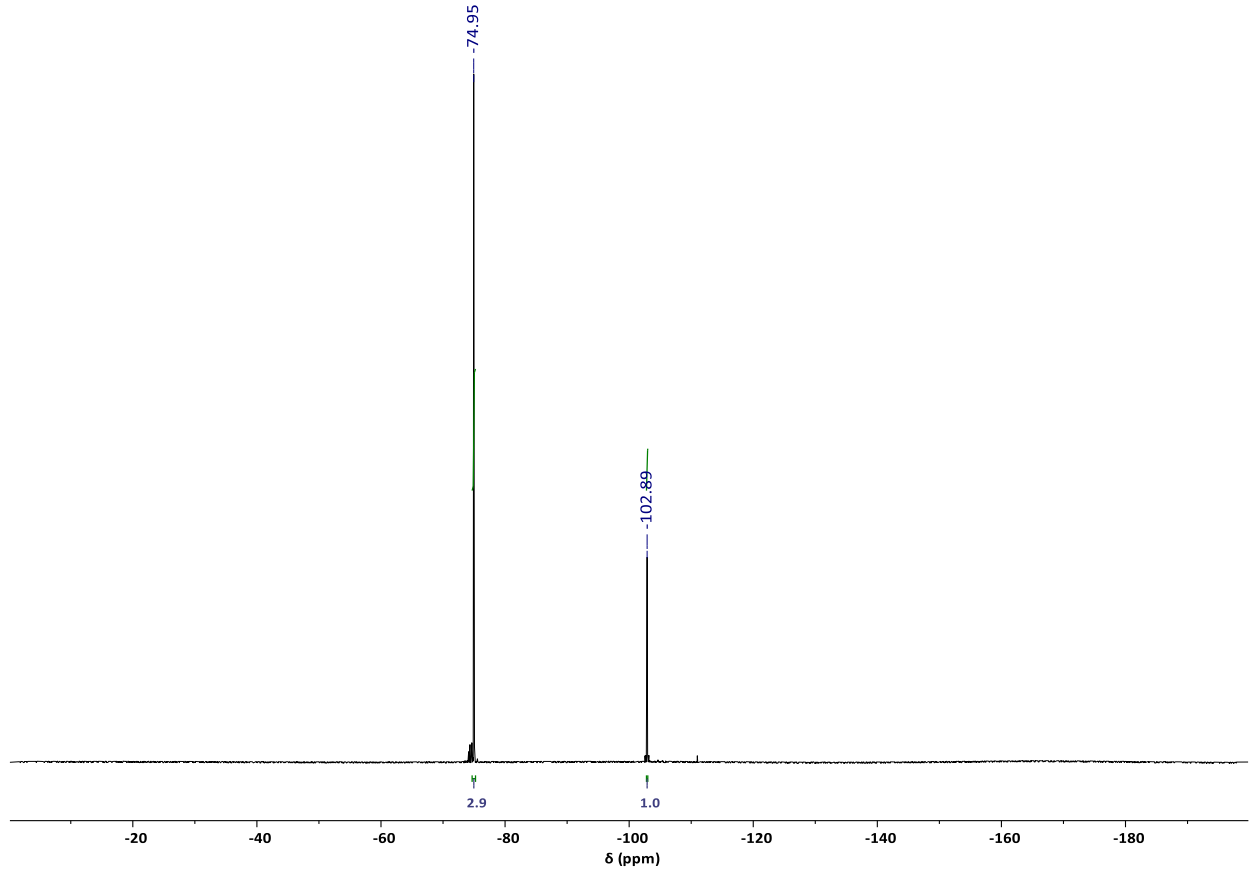

Figure S54. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **11a**

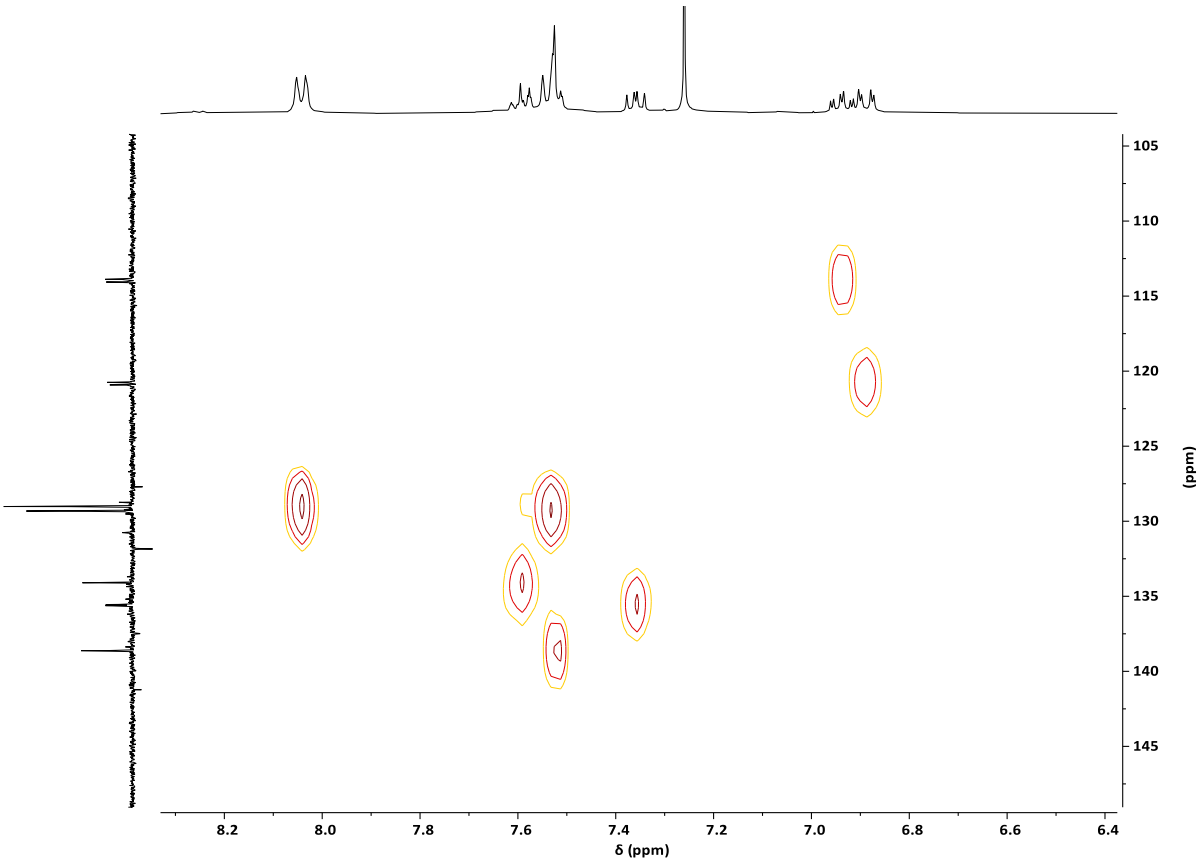

Figure S55. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of **11a**

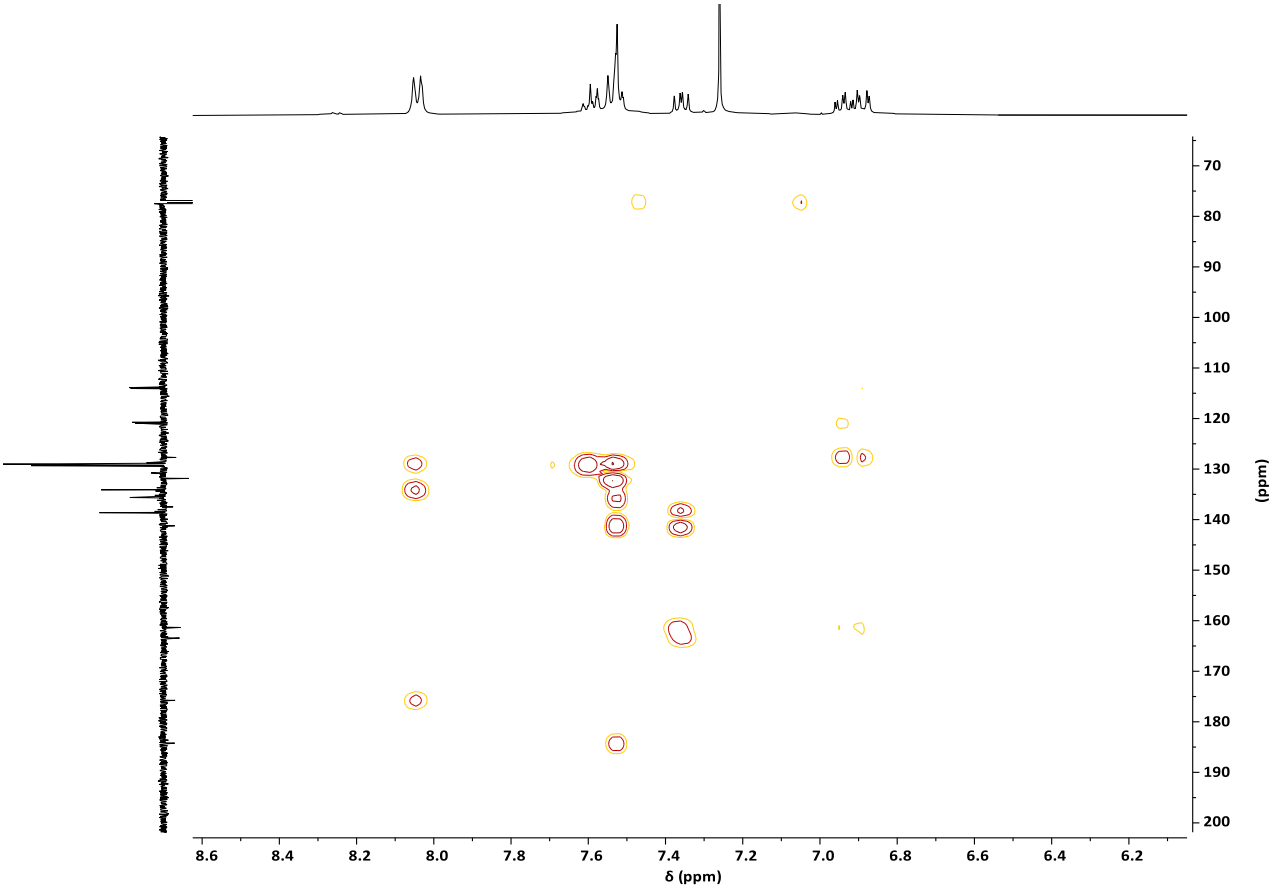

Figure S56. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of **11a**

Orthopalladated compound 11b

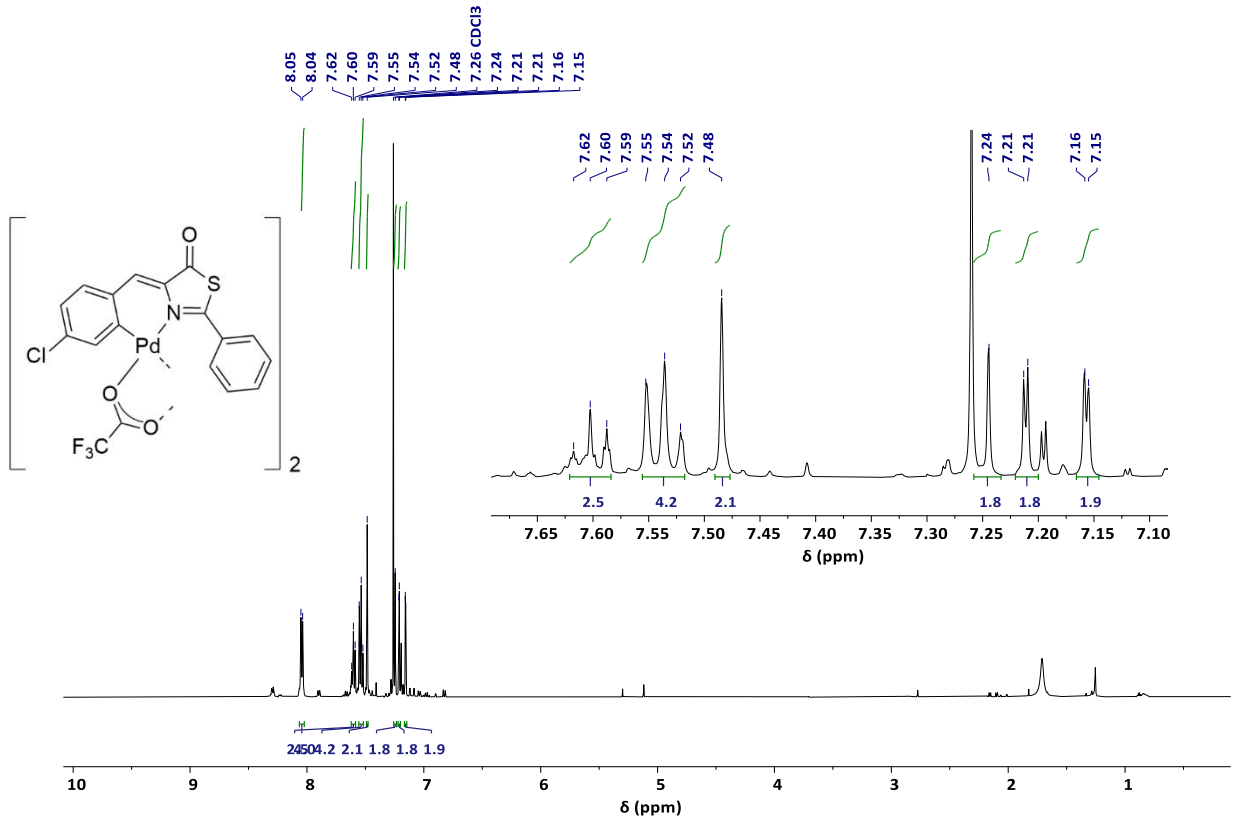

Figure S57. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **11b**

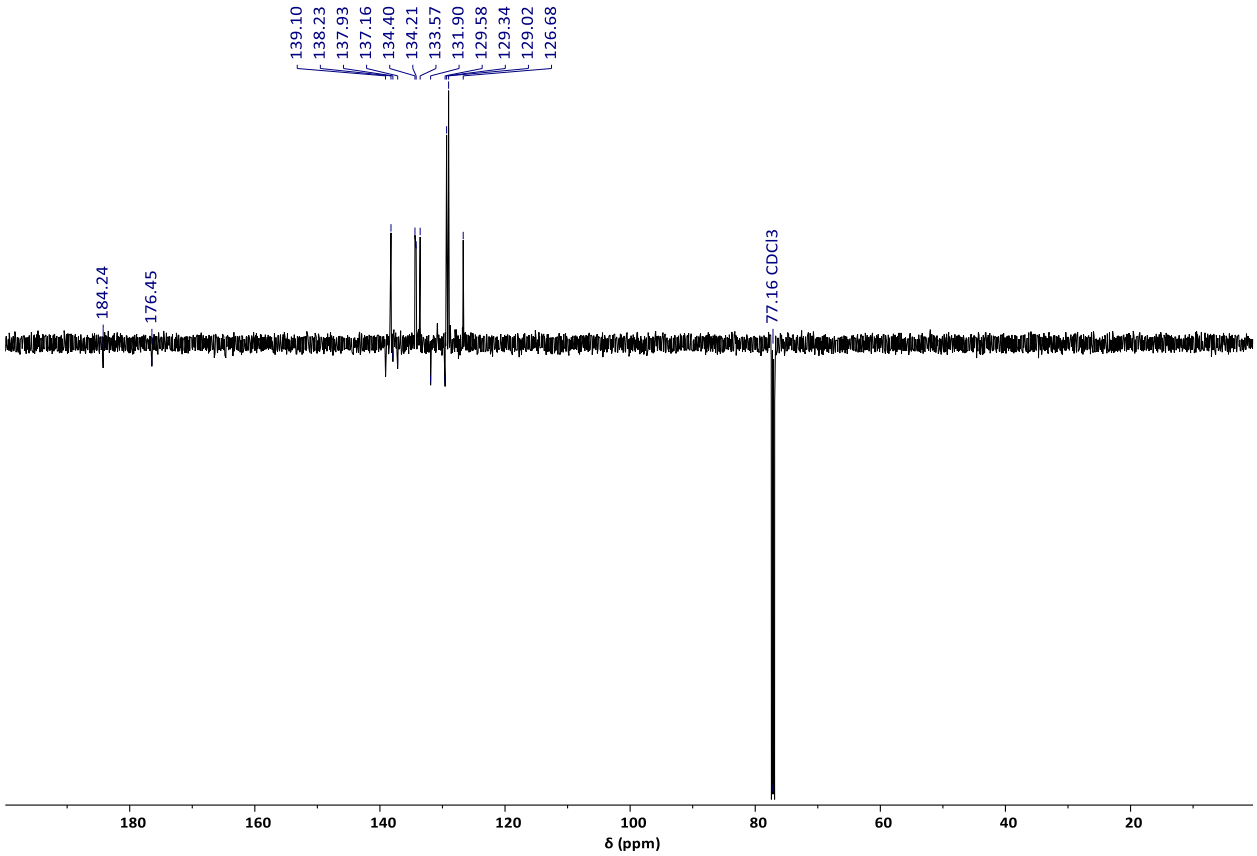

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **11b**

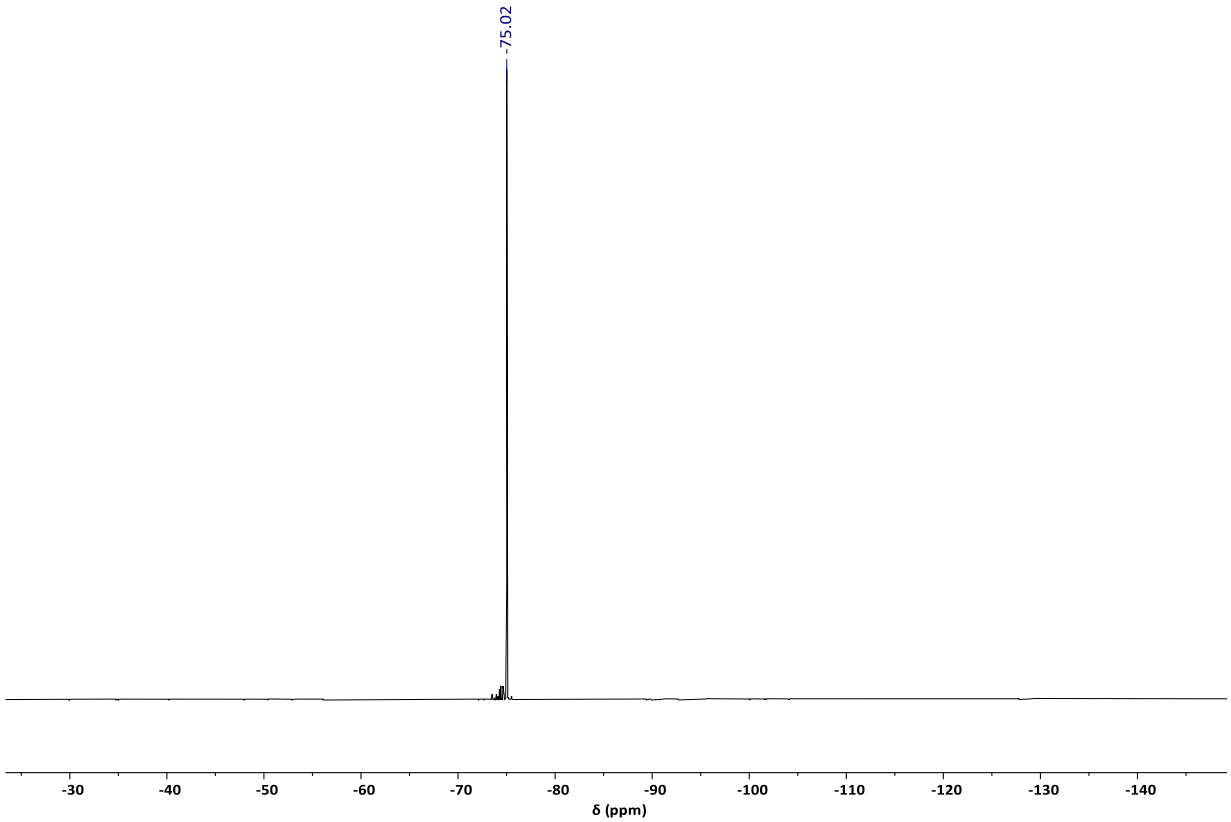

Figure S59. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **11b**

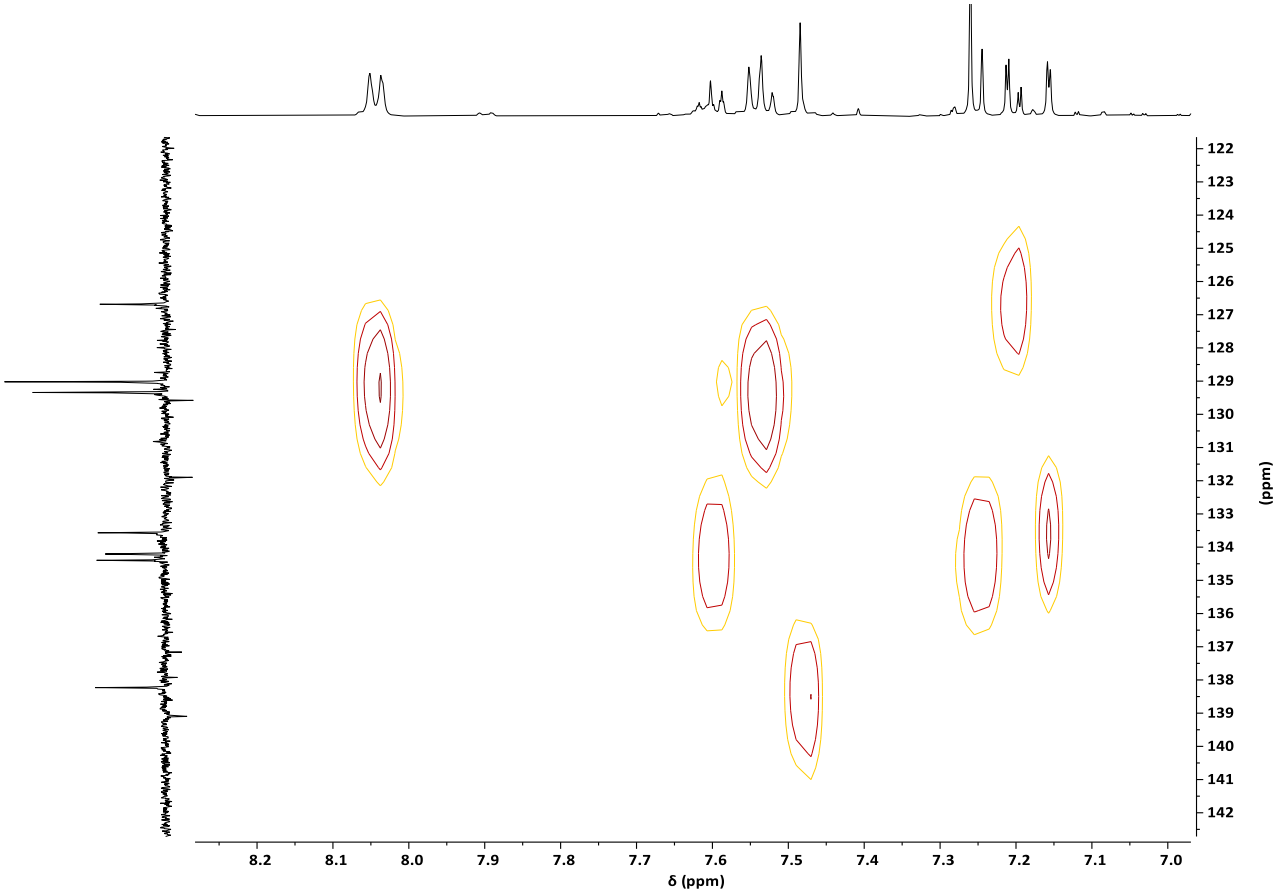

Figure S60. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of **11b**

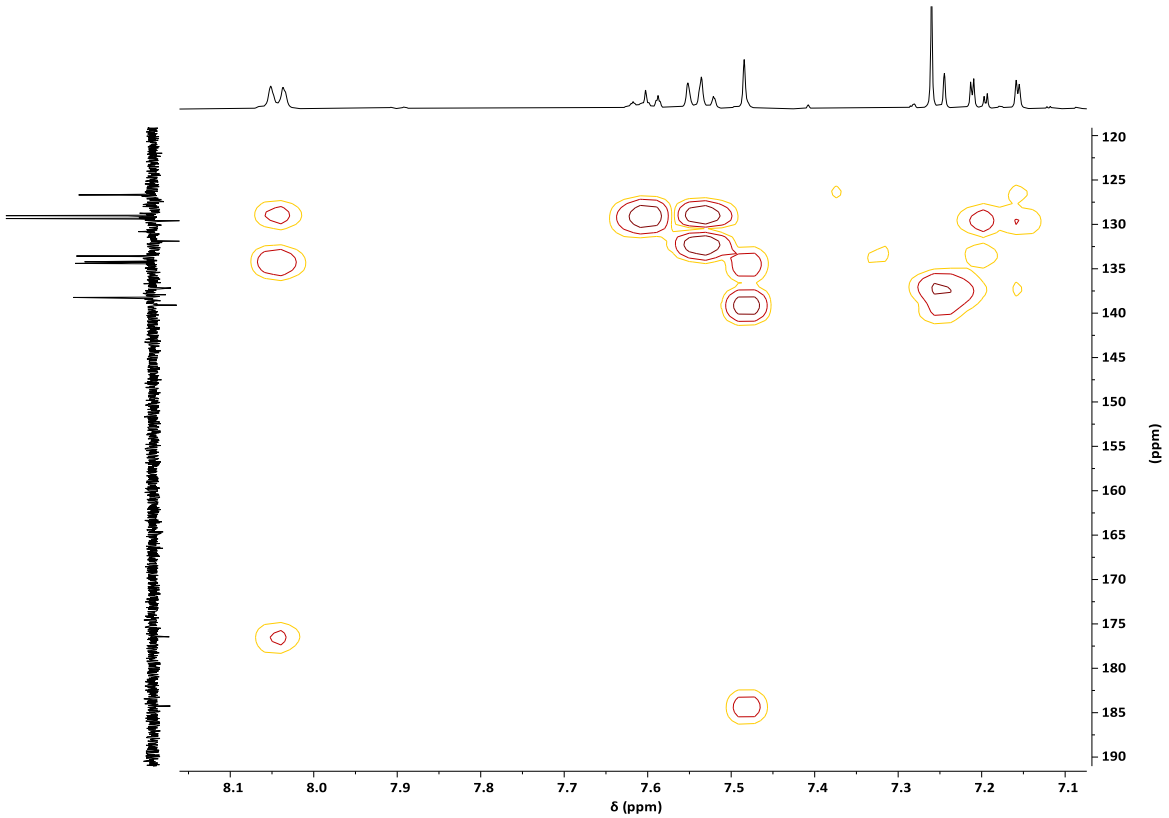

Figure S61. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of **11b**

Orthopalladated compound 11c

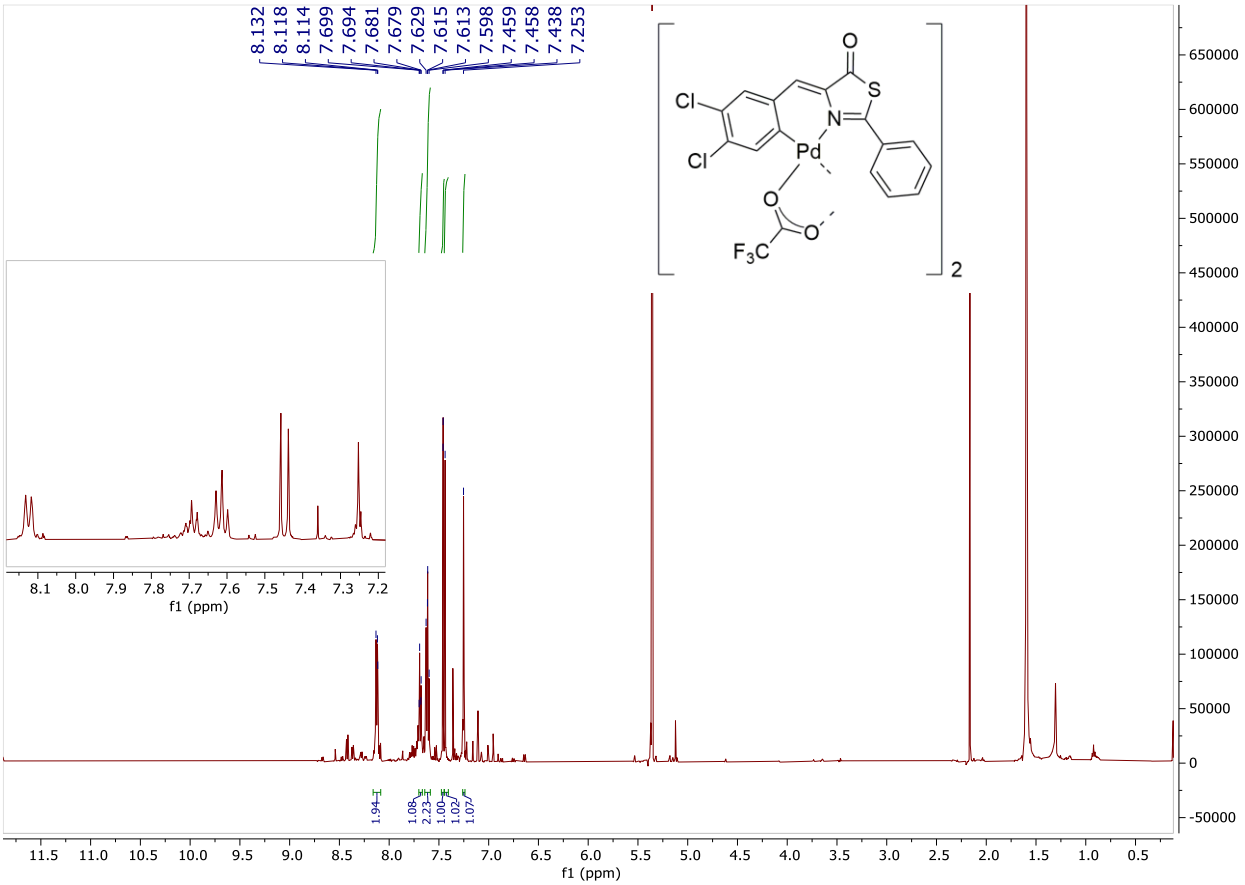

Figure S62. ^{1}H NMR spectrum (CD_2Cl_2, 500.13 MHz, r. t.) of **11c**

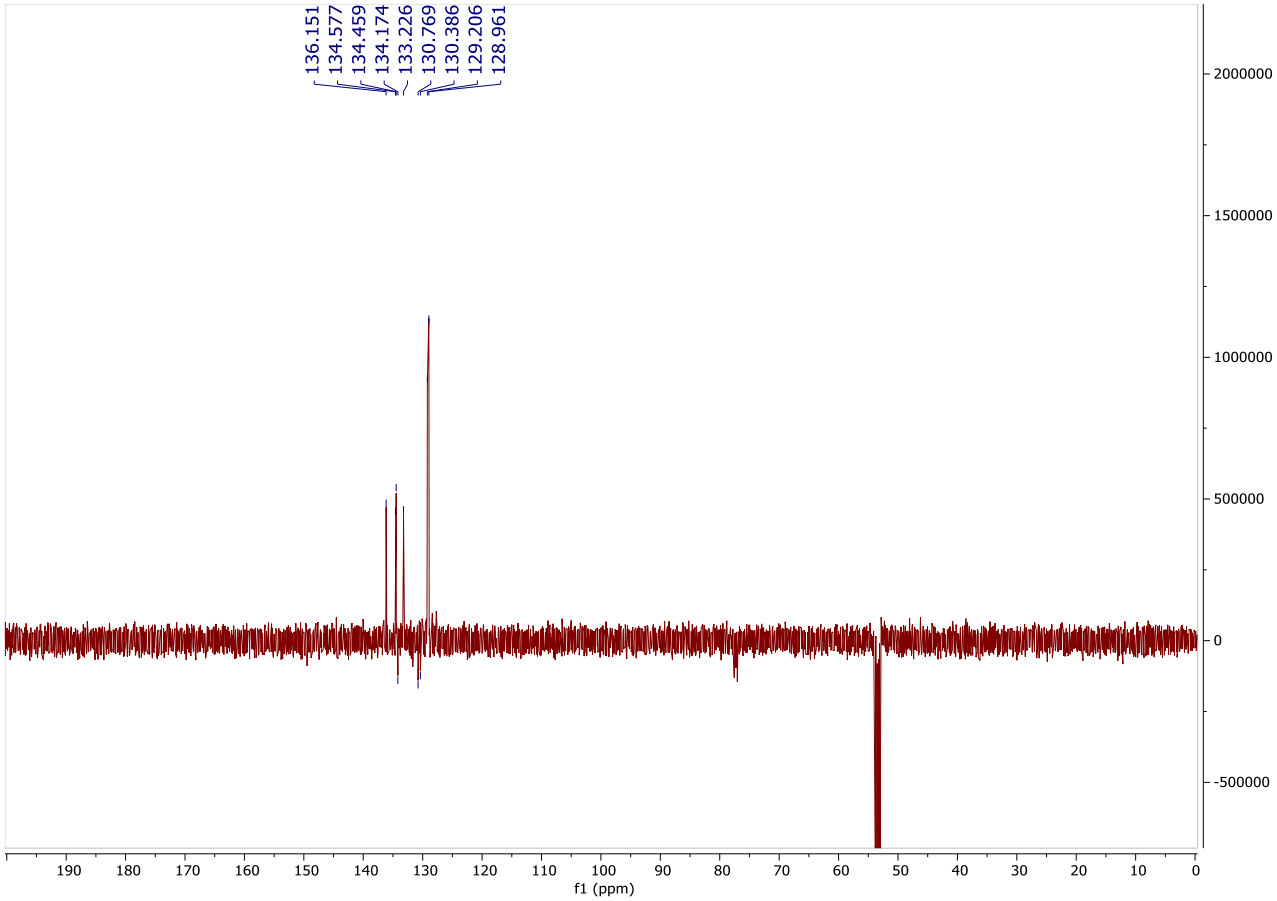

Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum (APT, CD_2Cl_2, 125.77 MHz, r. t.) of **11c**

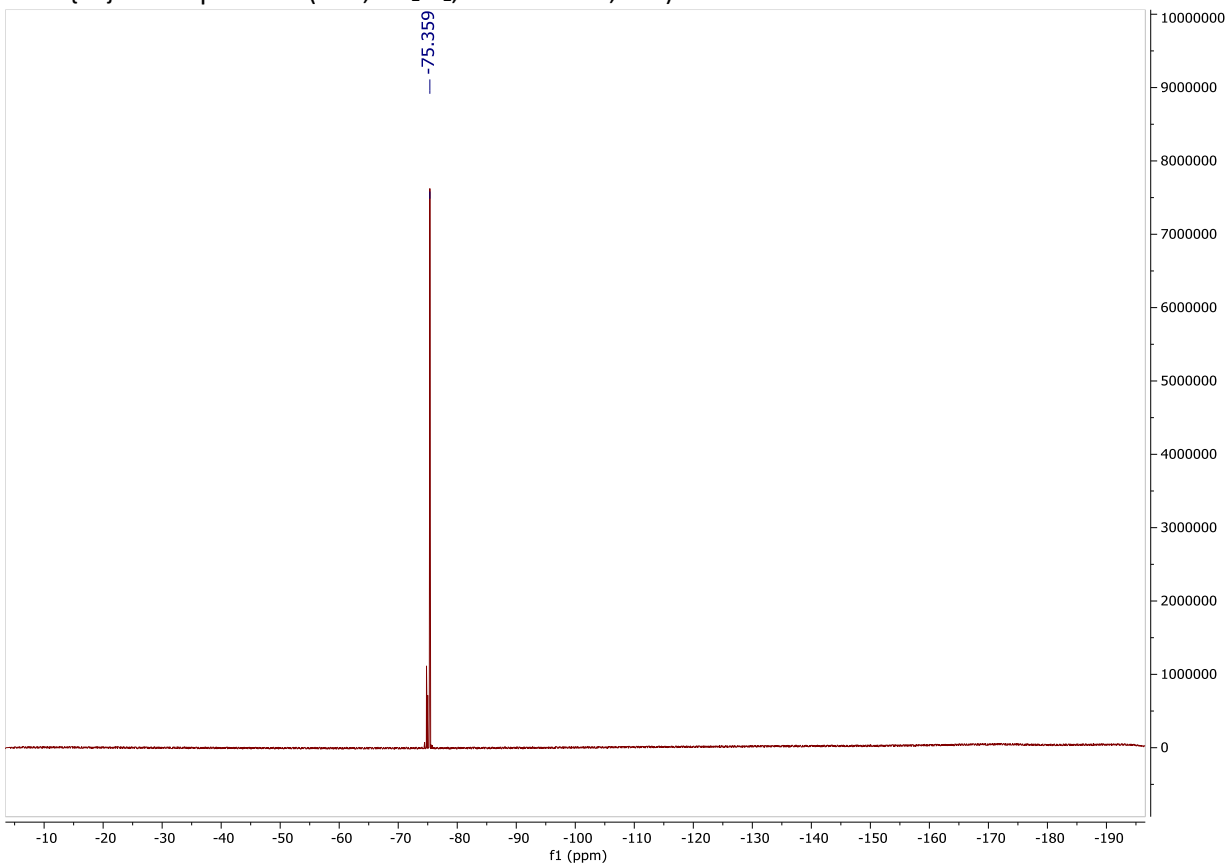

Figure S64. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 470.55 MHz, r. t.) of **11c**

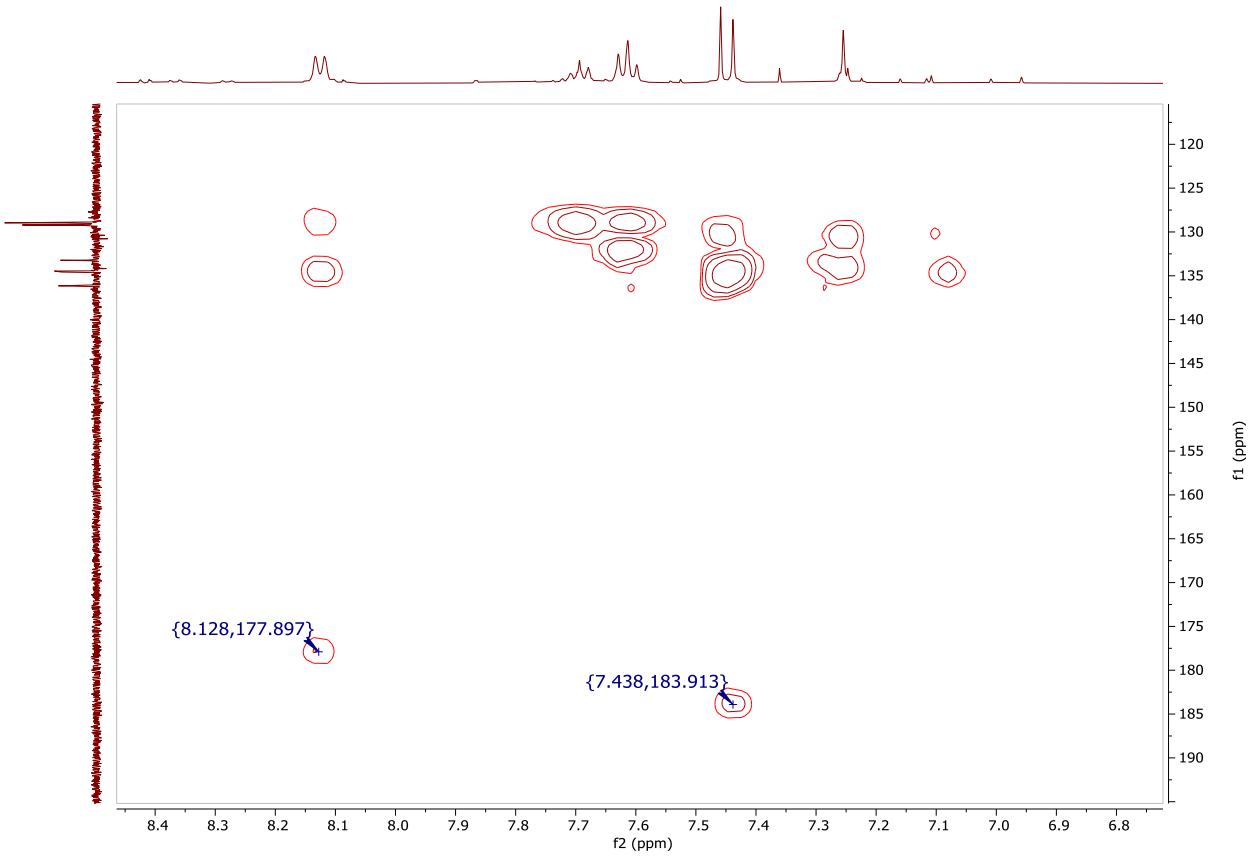

Figure S65. ^{1}H-^{13}C HMBC correlation spectrum (CD_2Cl_2, r.t.) of compound **11c**

Orthopalladated compound 11d

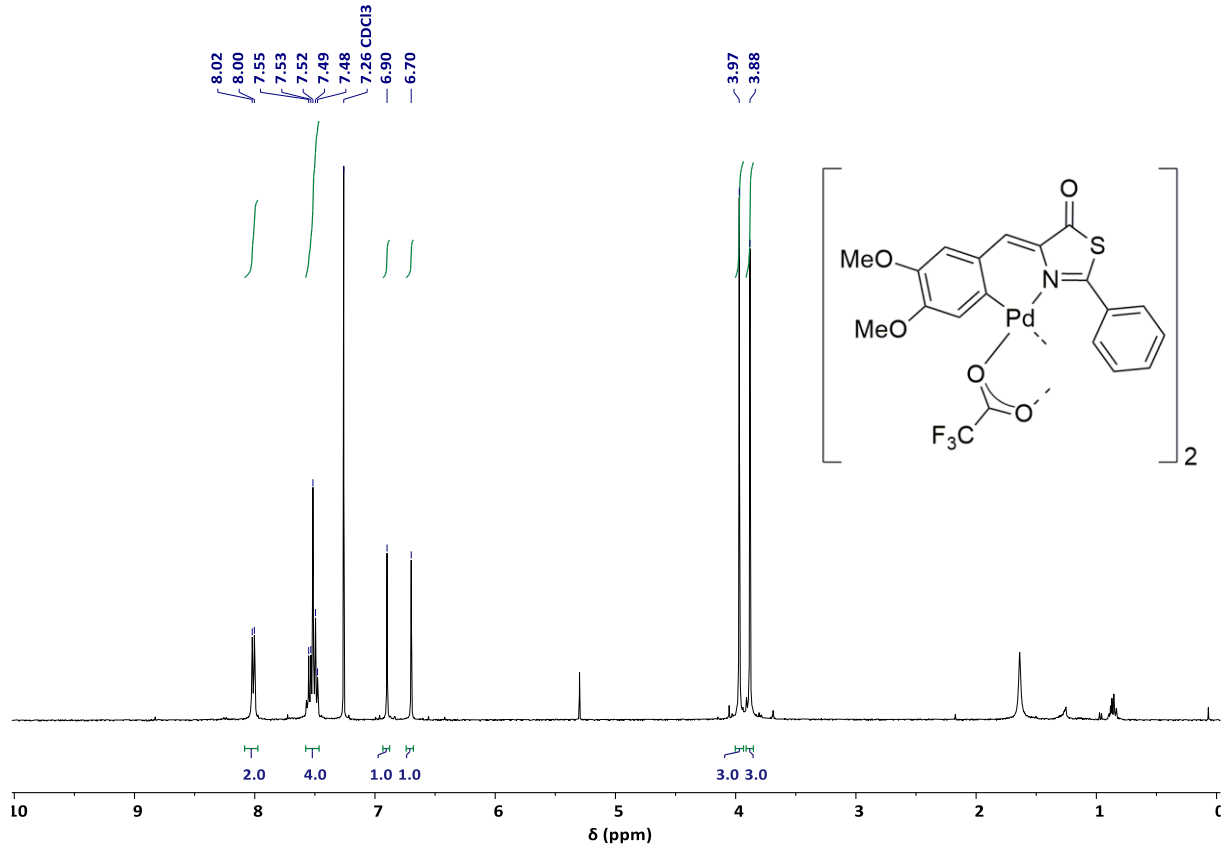

Figure S66. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, r. t.) of **11d**

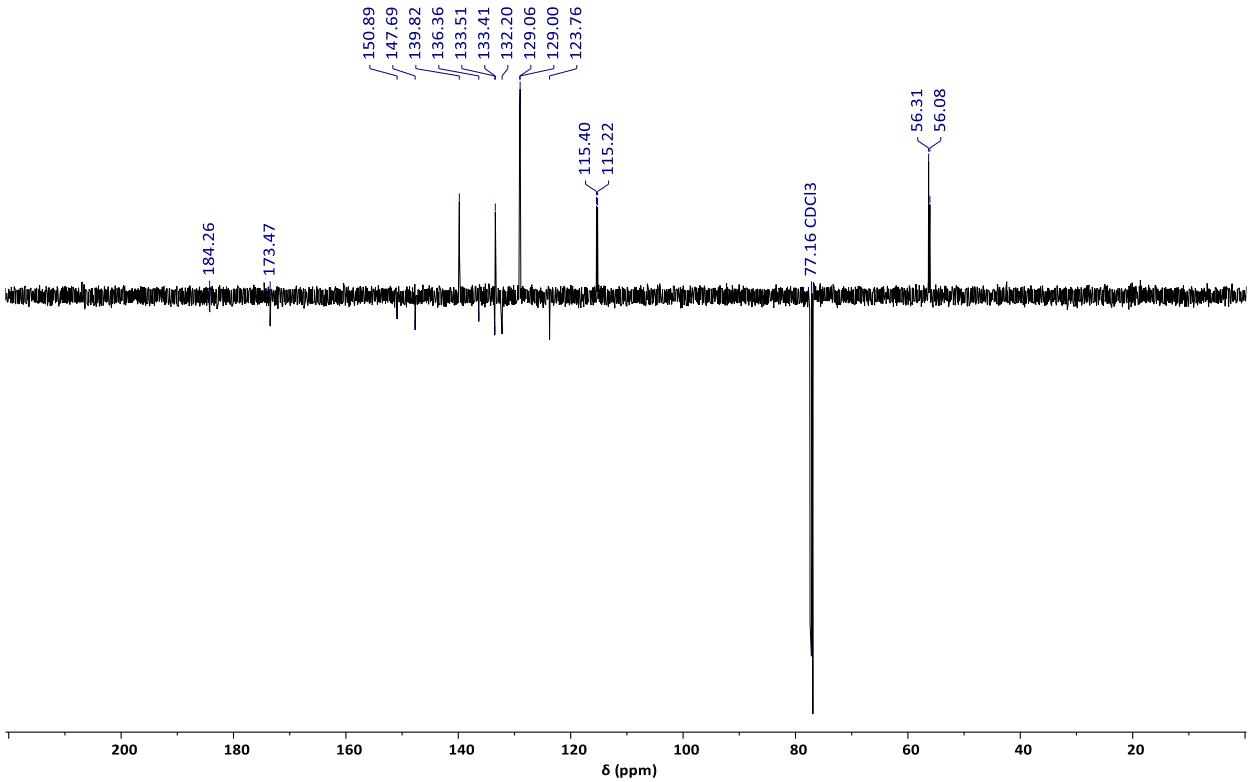

Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **11d**

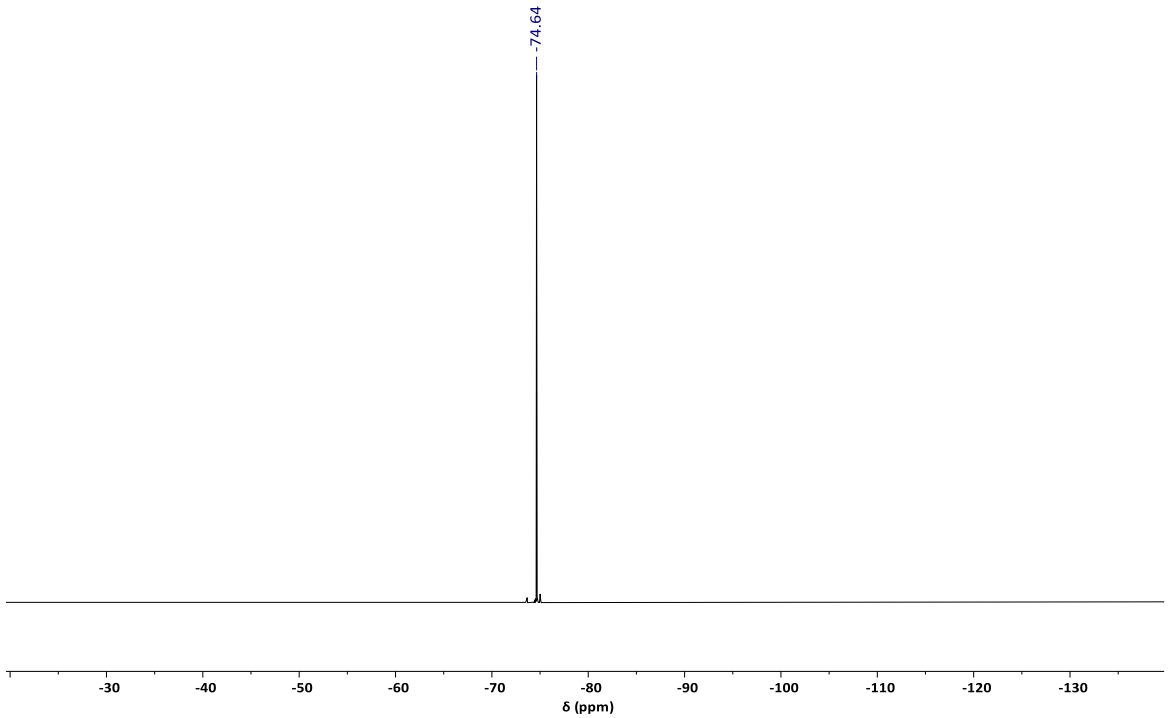

Figure S68. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **11d**

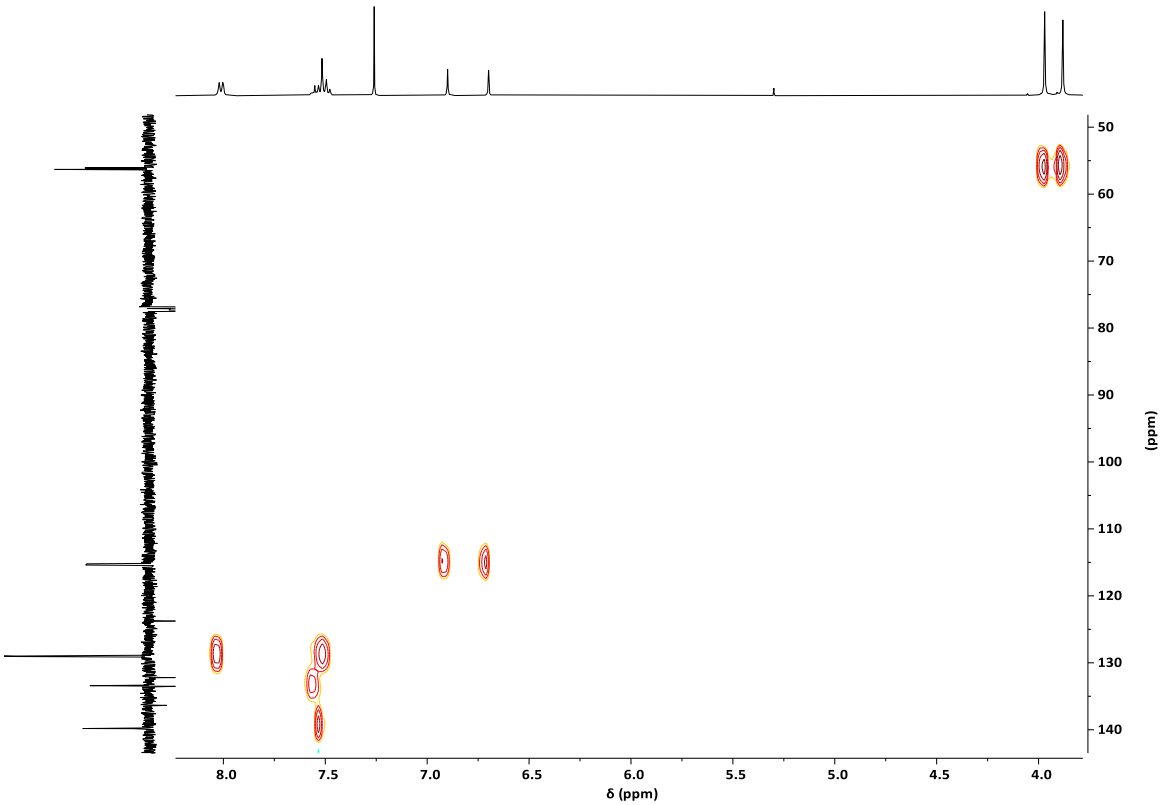

Figure S69. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **11d**

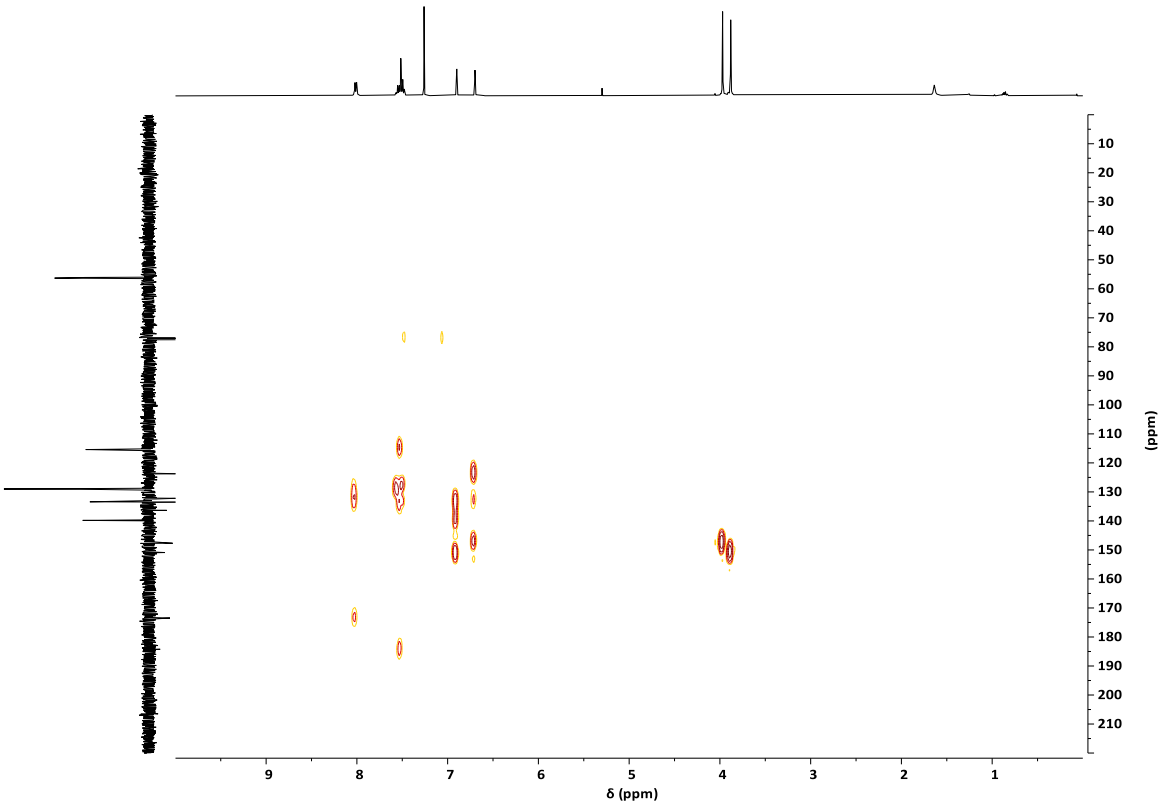

Figure S70. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **11d**

5.- Reactivity of orthopalladated 4e, synthesis of luminiscent mononuclear and dinuclear derivatives 5e-9e

Orthopalladated compound 5e

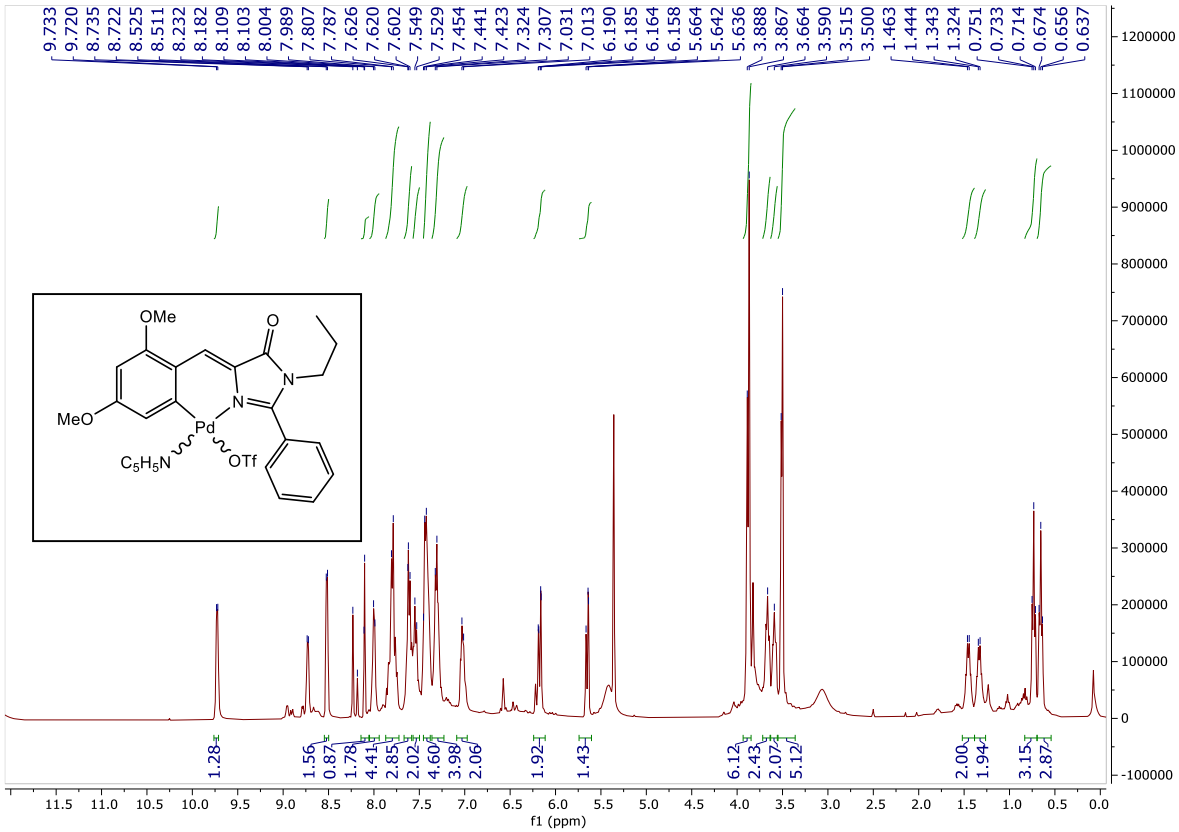

Figure S71. ^{1}H NMR spectrum (CD_2Cl_2, 400.13 MHz, 233 K) of **5e**

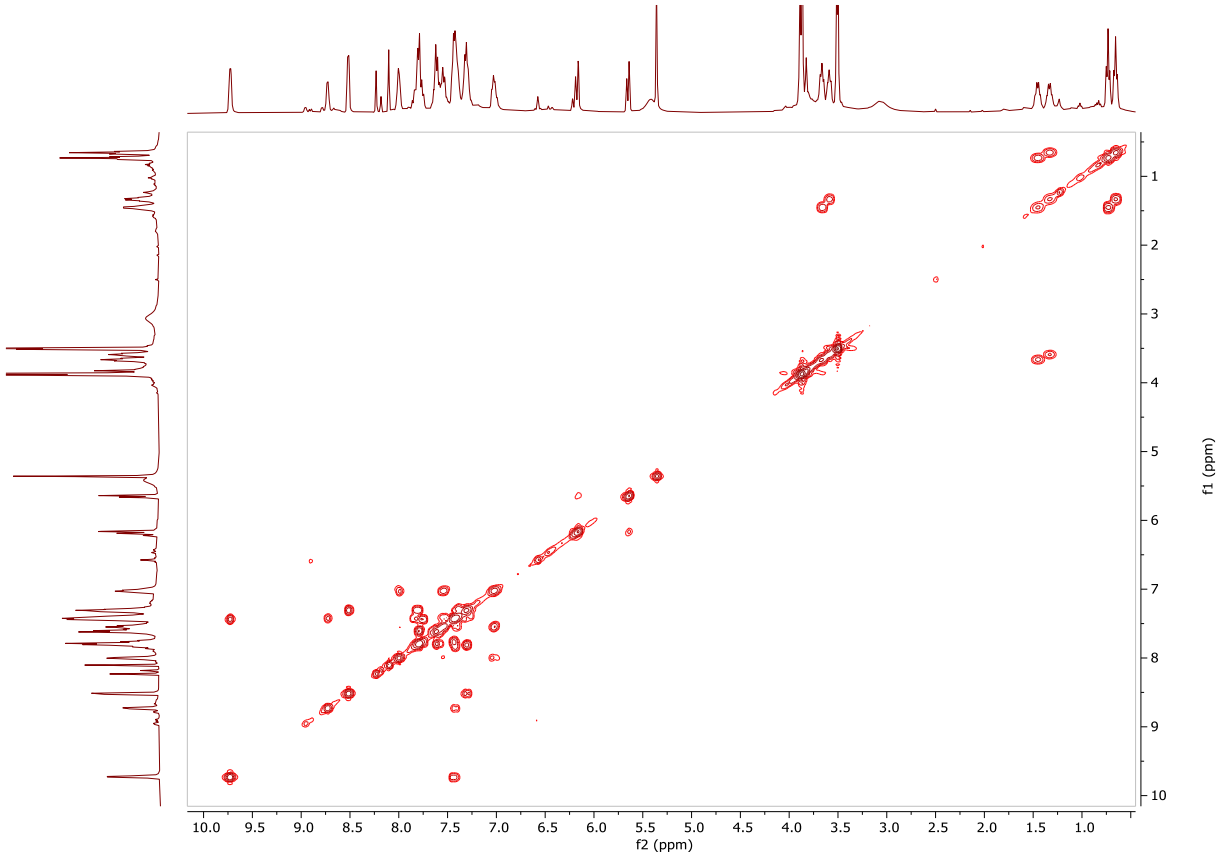

Figure S72. ^{1}H-^{1}H COSY correlation spectrum (CD_2Cl_2, 233 K) of **5e**.

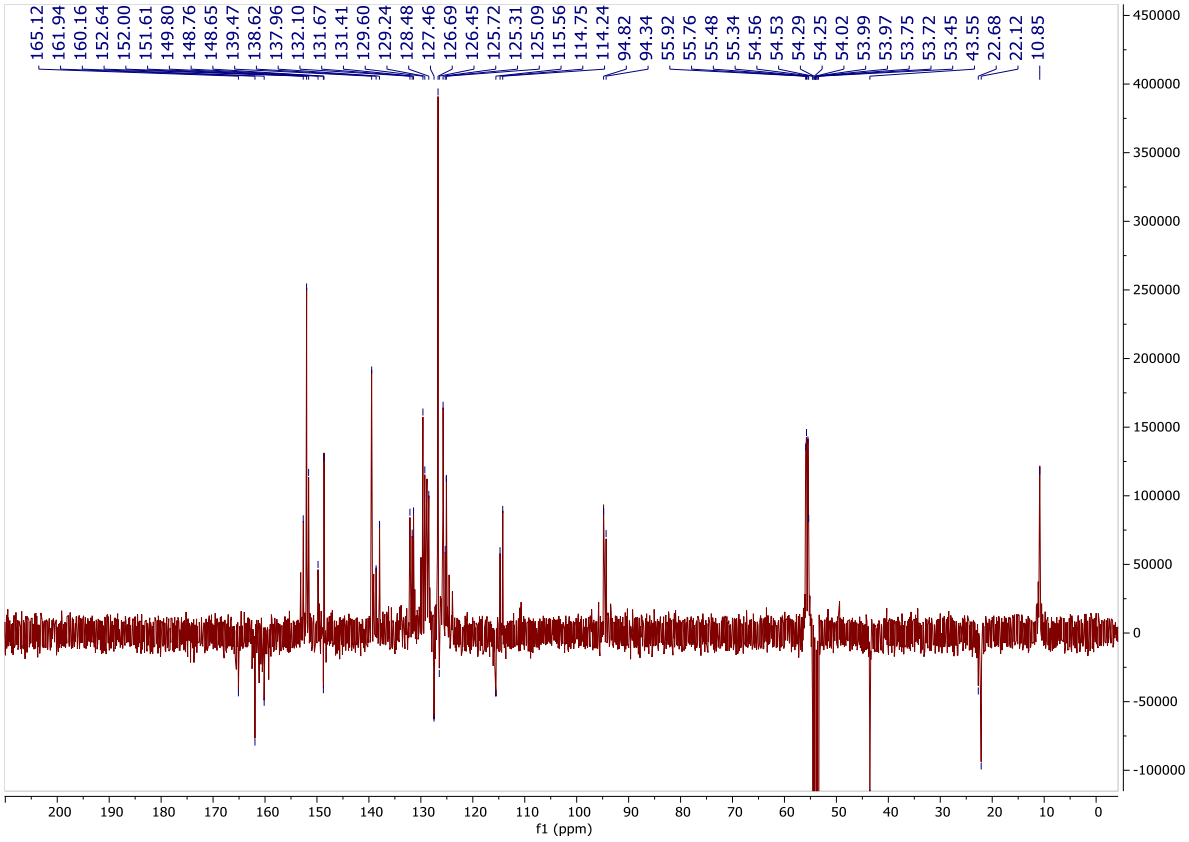

Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum (APT, CD_2Cl_2, 125.77 MHz, 233 K) of **5e**.

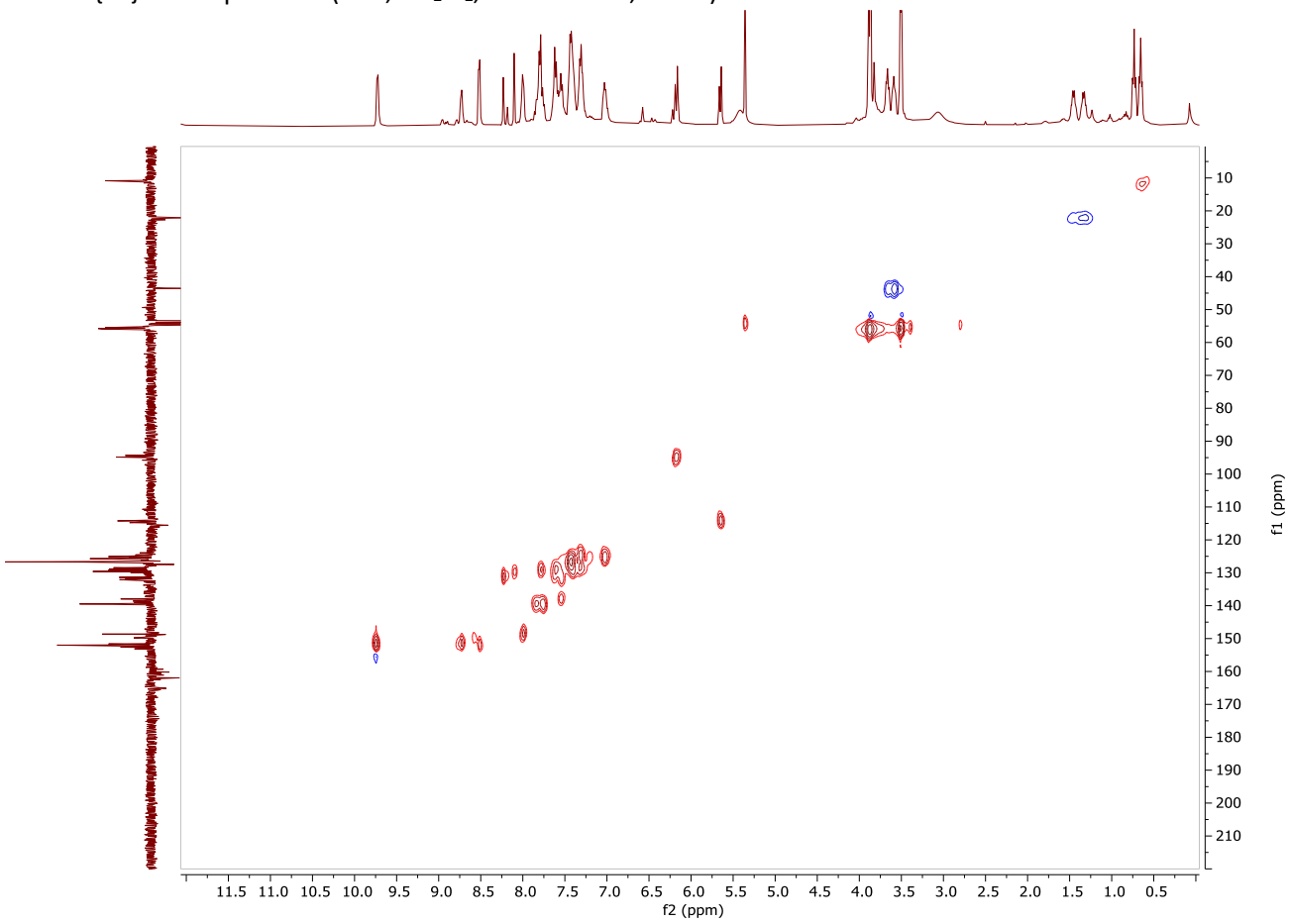

Figure S74. ^{1}H-^{13}C HSQC correlation spectrum (CD_2Cl_2, 233K) of **5e**

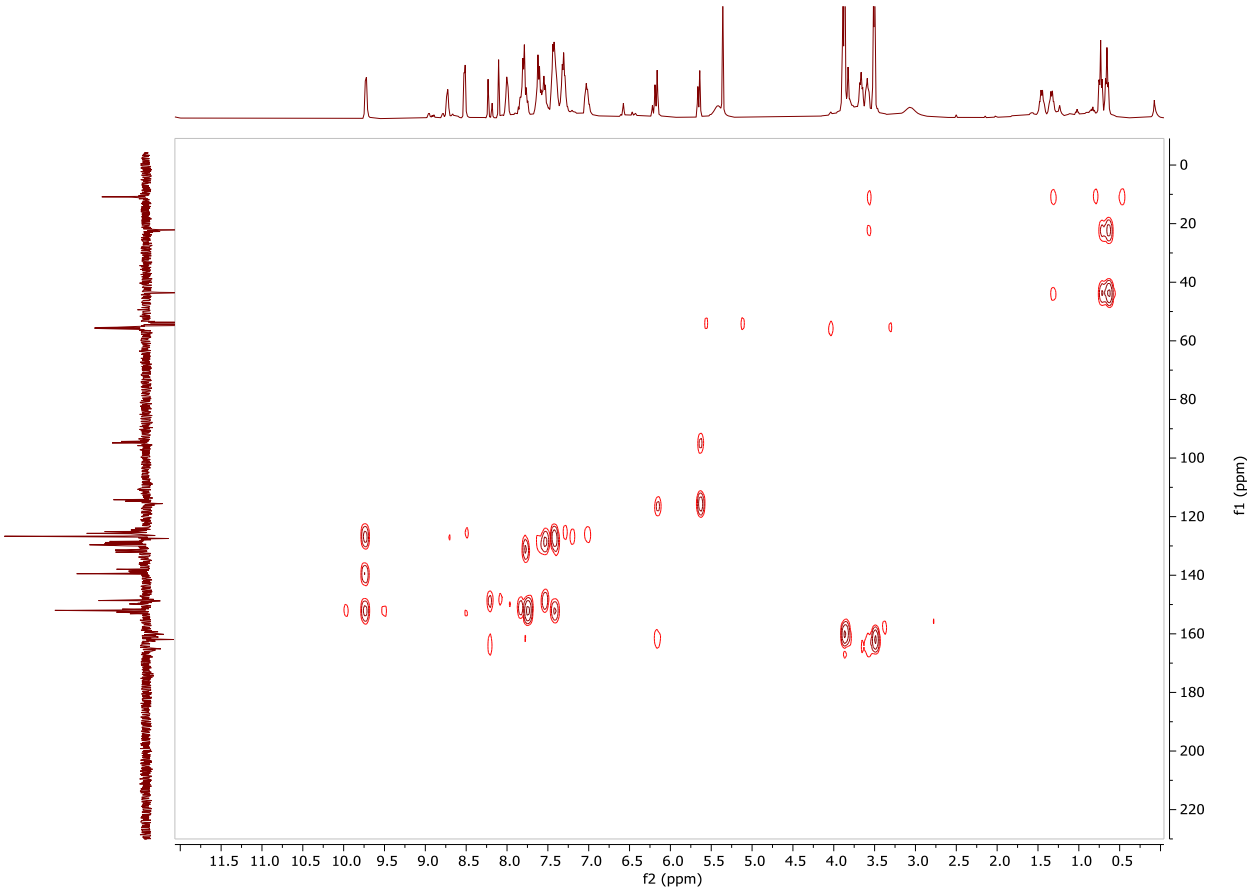

Figure S75. ^{1}H-^{13}C HMBC correlation spectrum (CD_2Cl_2, 233K) of **5e**

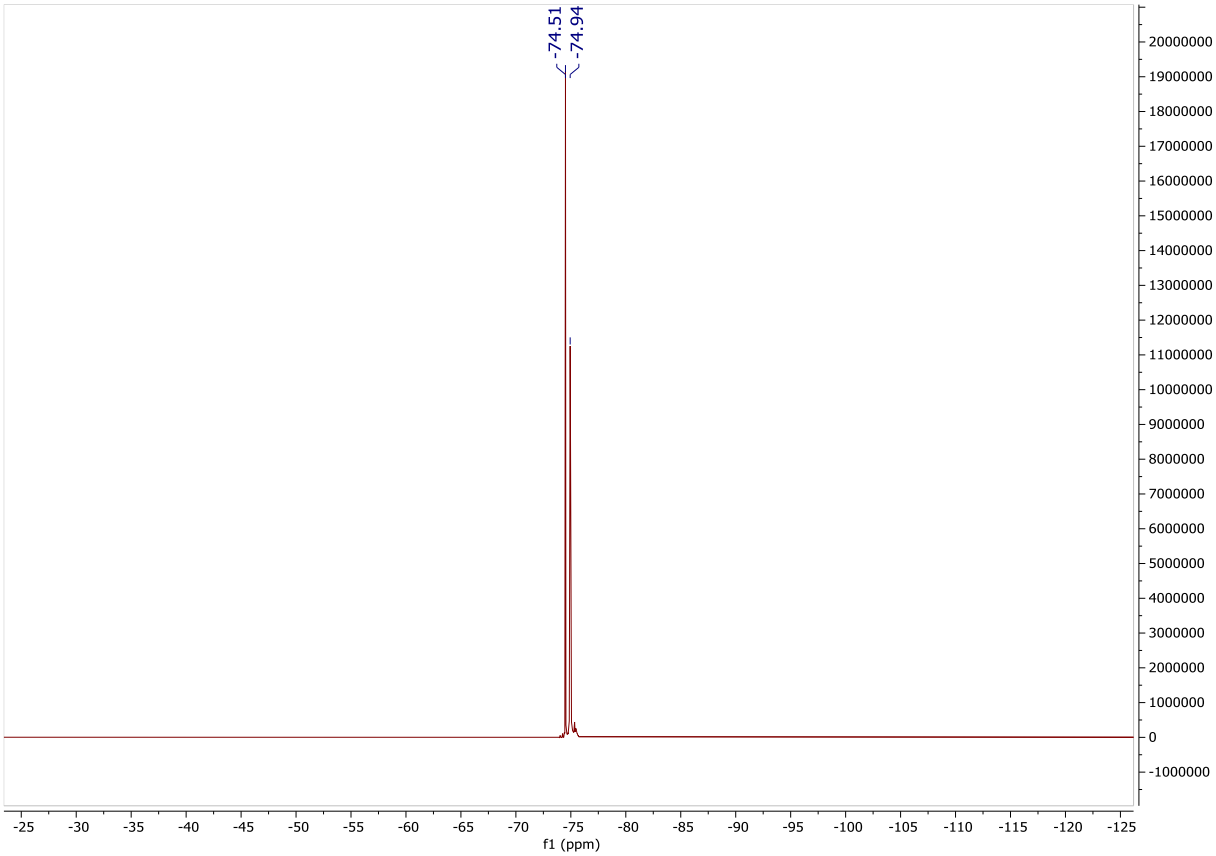

Figure S76. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 376.49 MHz, 233K) of **5e**

Orthopalladated compound 6e

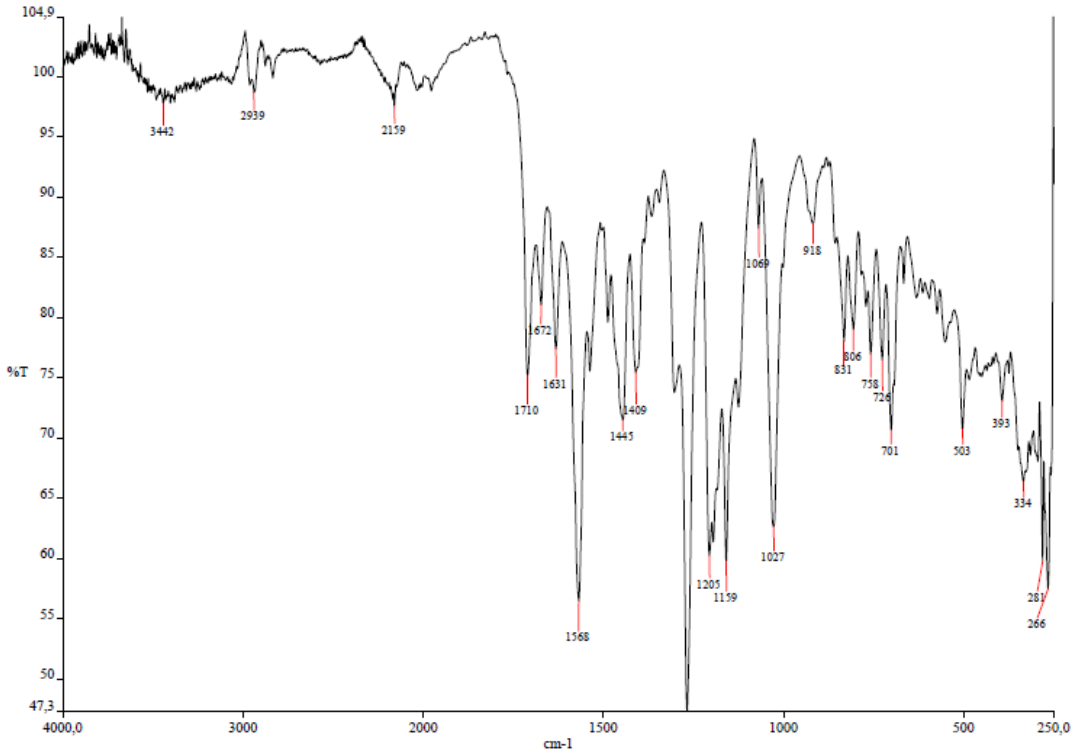

Figure S77: IR spectrum of **6e**

Orthopalladated compound 7e

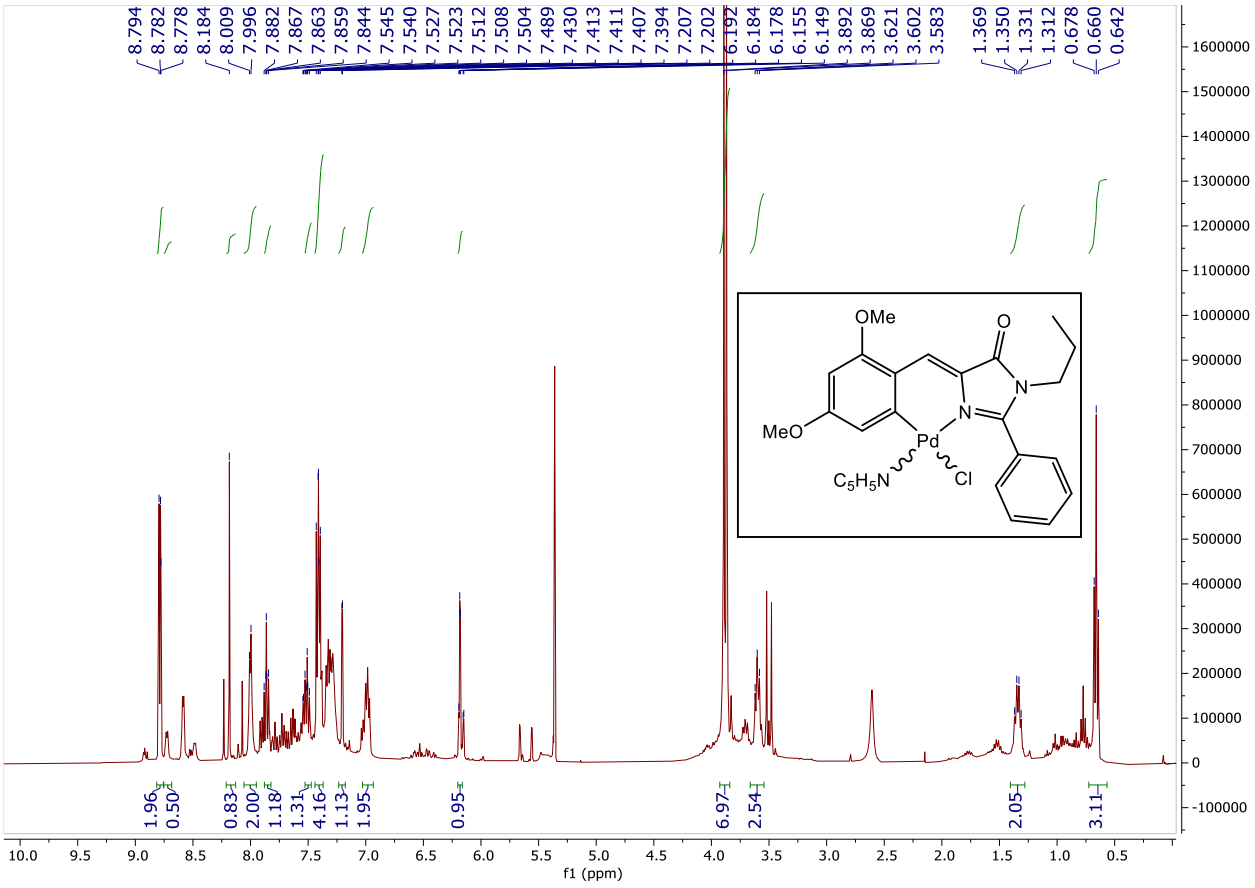

Figure S78. ^{1}H NMR spectrum (CD_2Cl_2, 400.13 MHz, 233 K) of **7e**

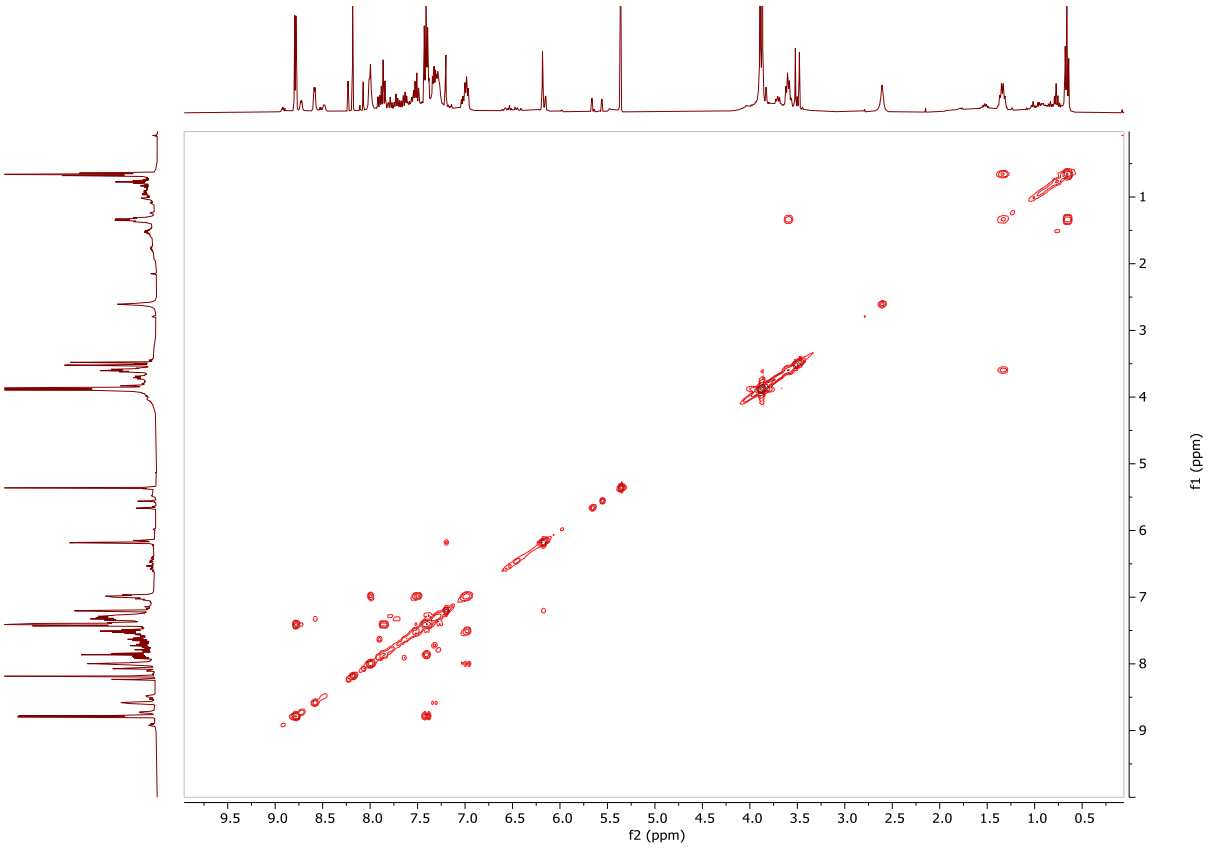

Figure S79. ^{1}H-^{1}H COSY correlation spectrum (CD_2Cl_2, 233 K) of **7e**.

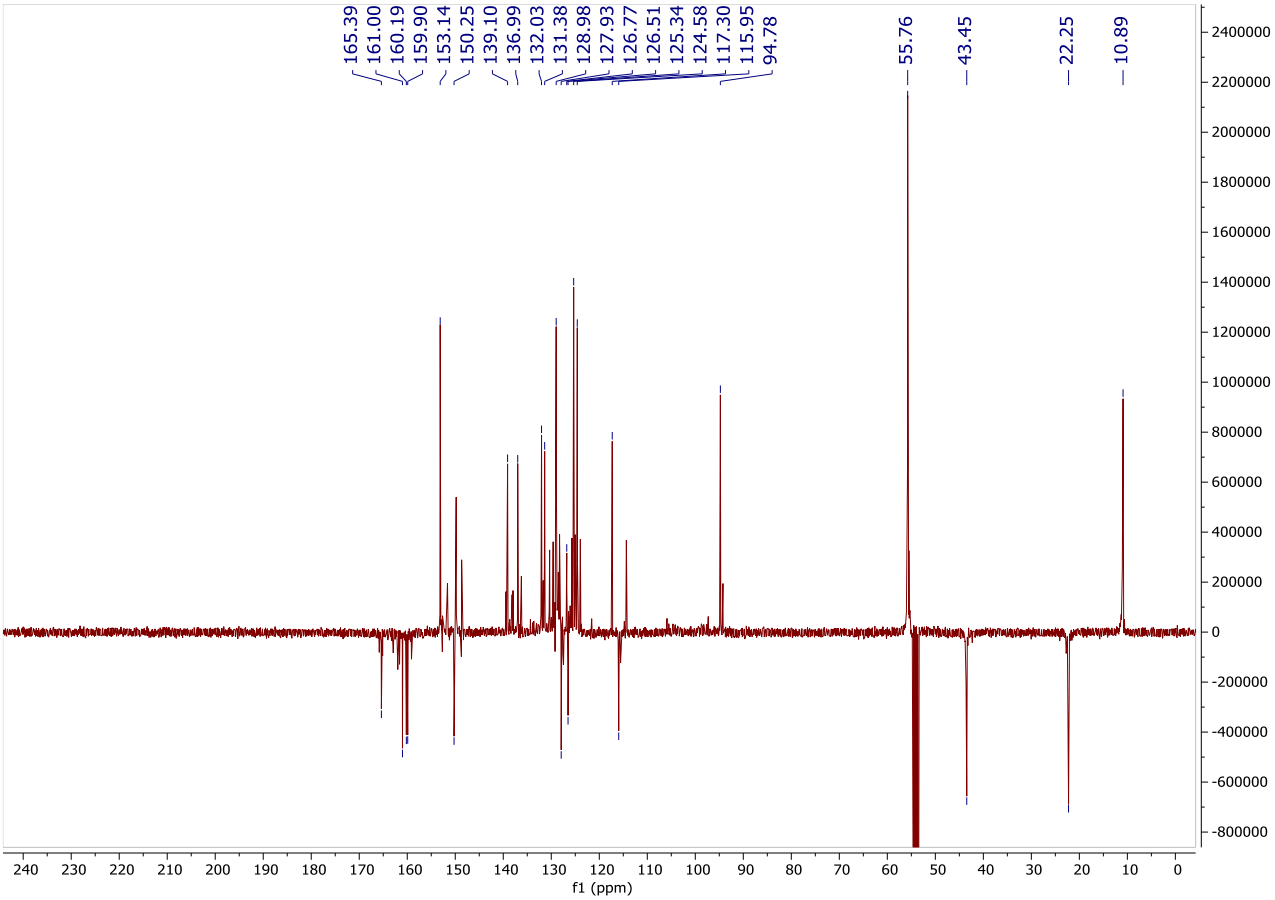

Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum (APT, CD_2Cl_2, 125.77 MHz, 233 K) of **7e**.

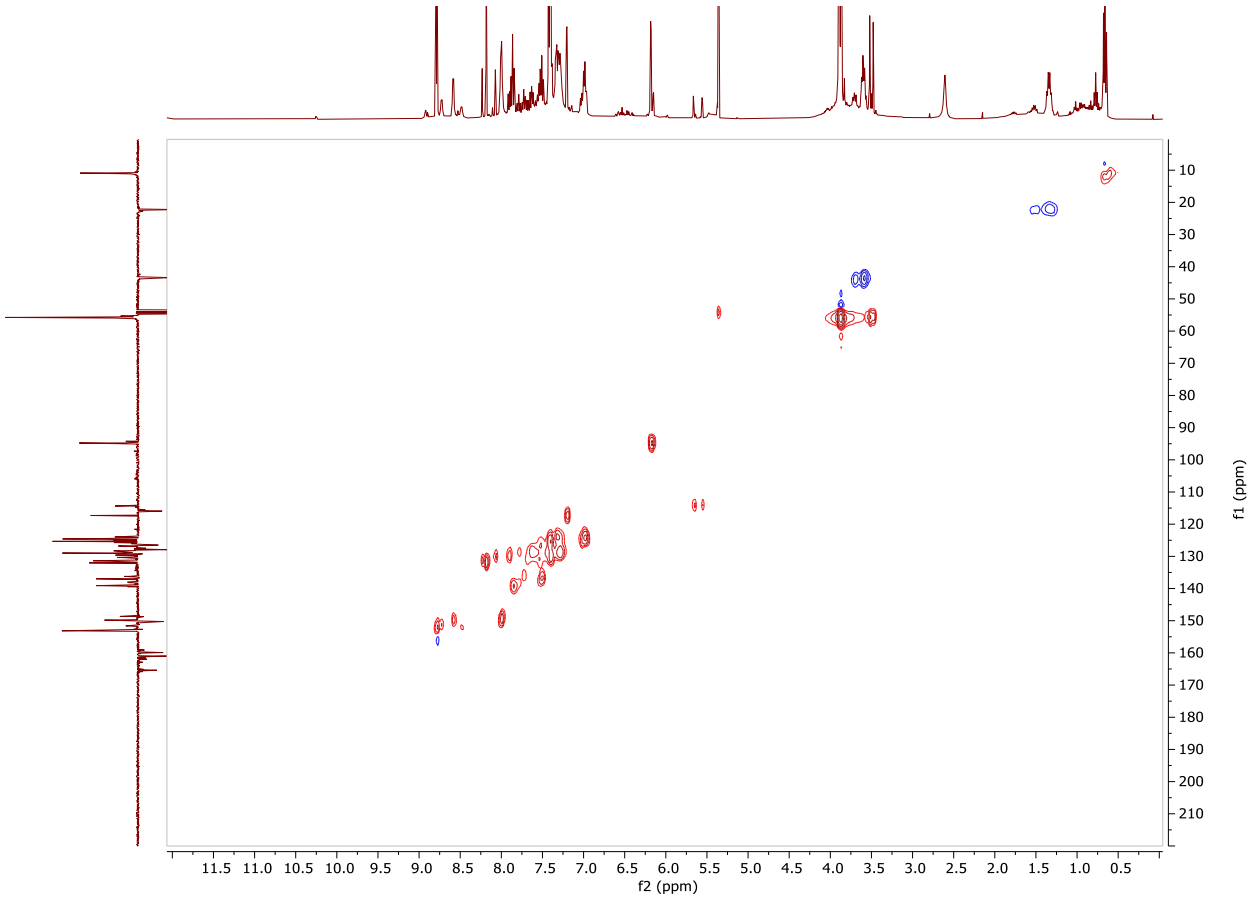

Figure S81. ^{1}H-^{13}C HSQC correlation spectrum (CD_2Cl_2, 233K) of **7e**

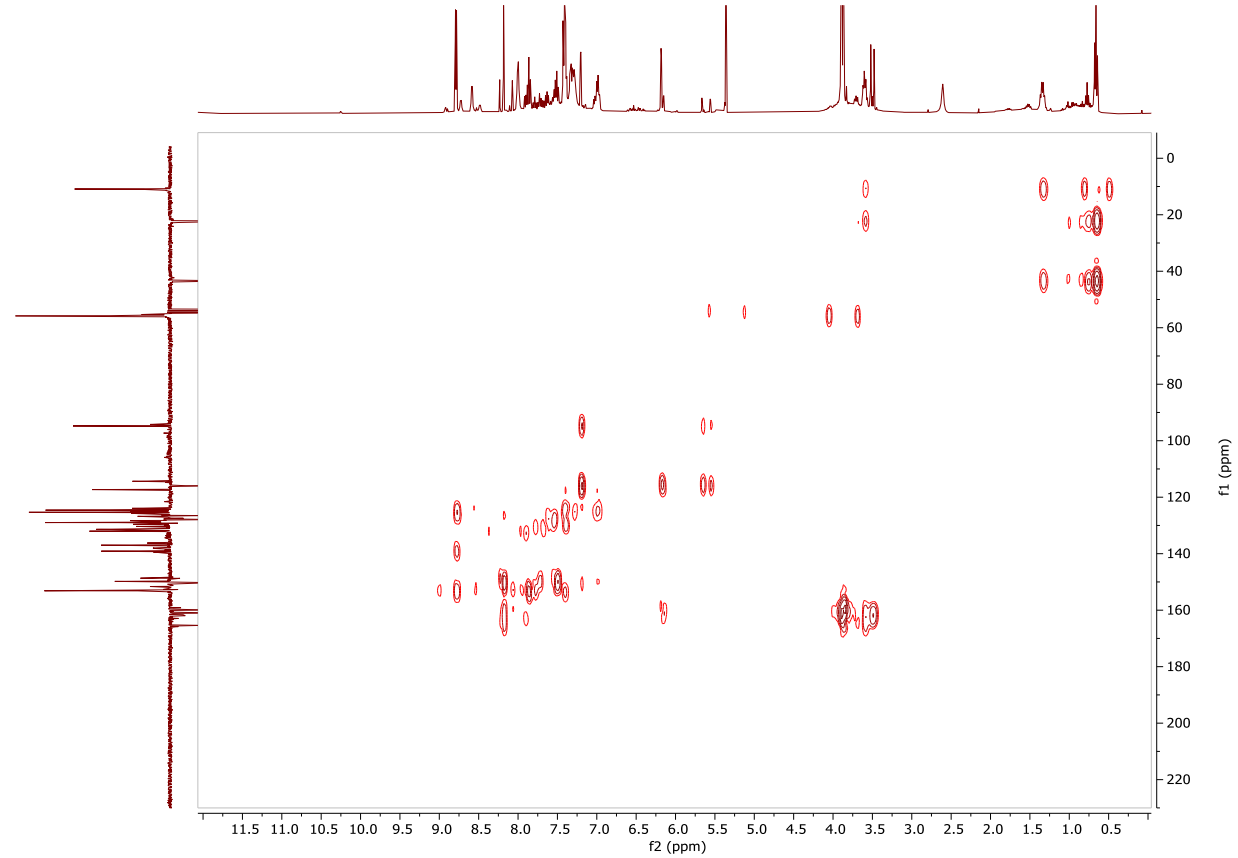

Figure S82. ^{1}H-^{13}C HMBC correlation spectrum (CD_2Cl_2, 233K) of **7e**

Synthesis of 8e

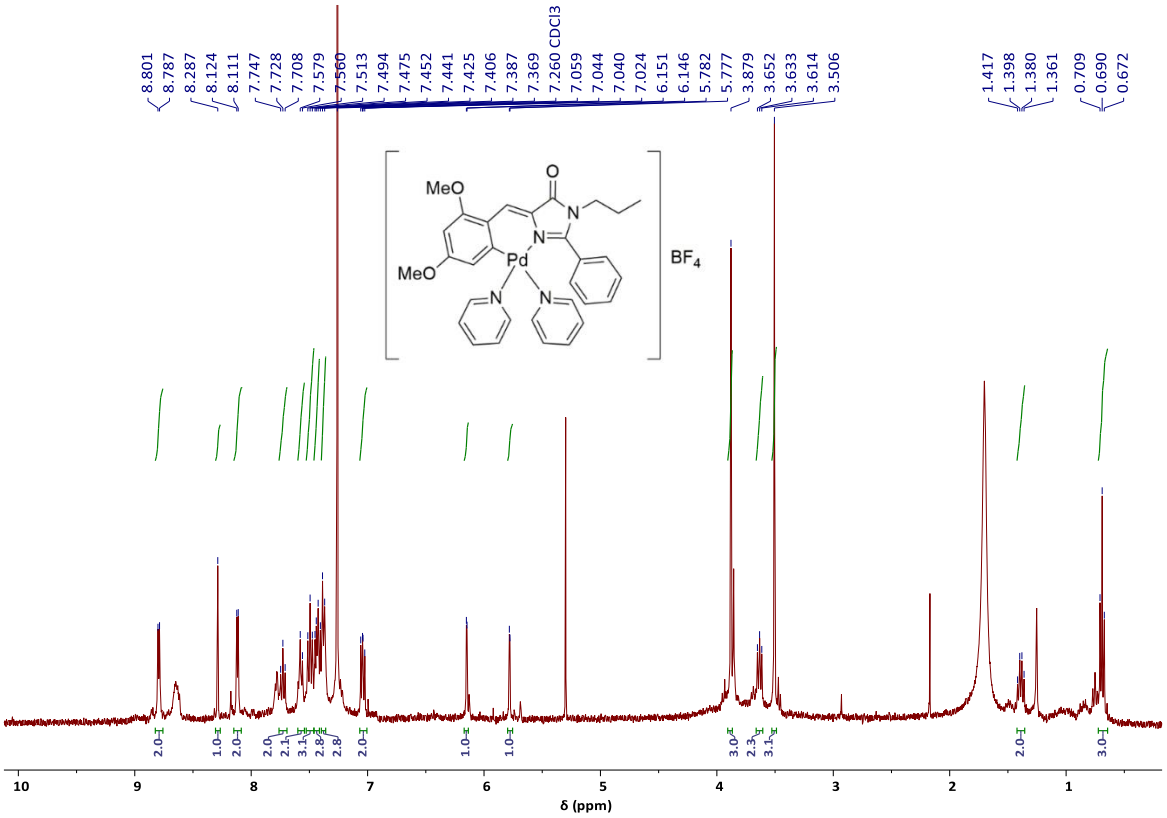

Figure S83. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 233 K) of **8e**

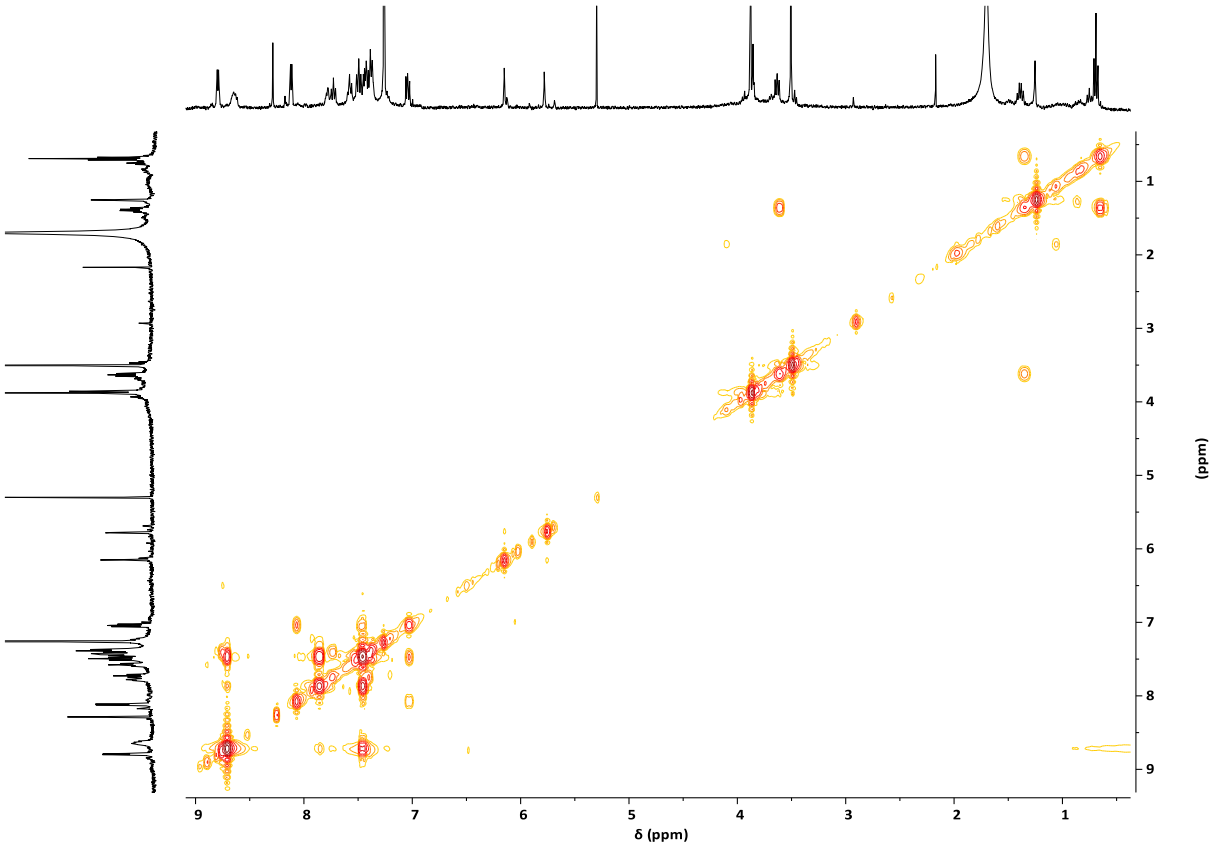

Figure S84. ^{1}H-^{1}H COSY correlation spectrum ($CDCl_3$, 233 K) of compound **8e**

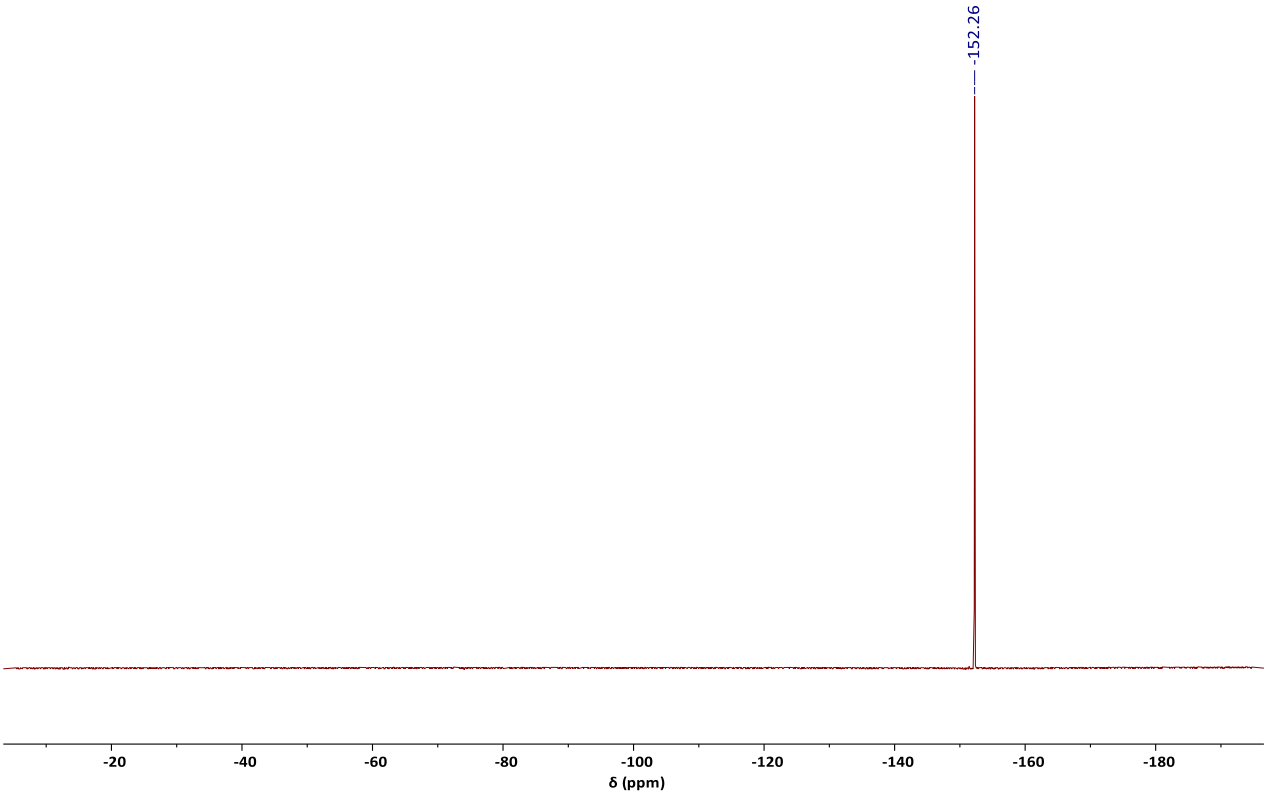

Figure S85. ^{19}F NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **8e**

Synthesis of 9e

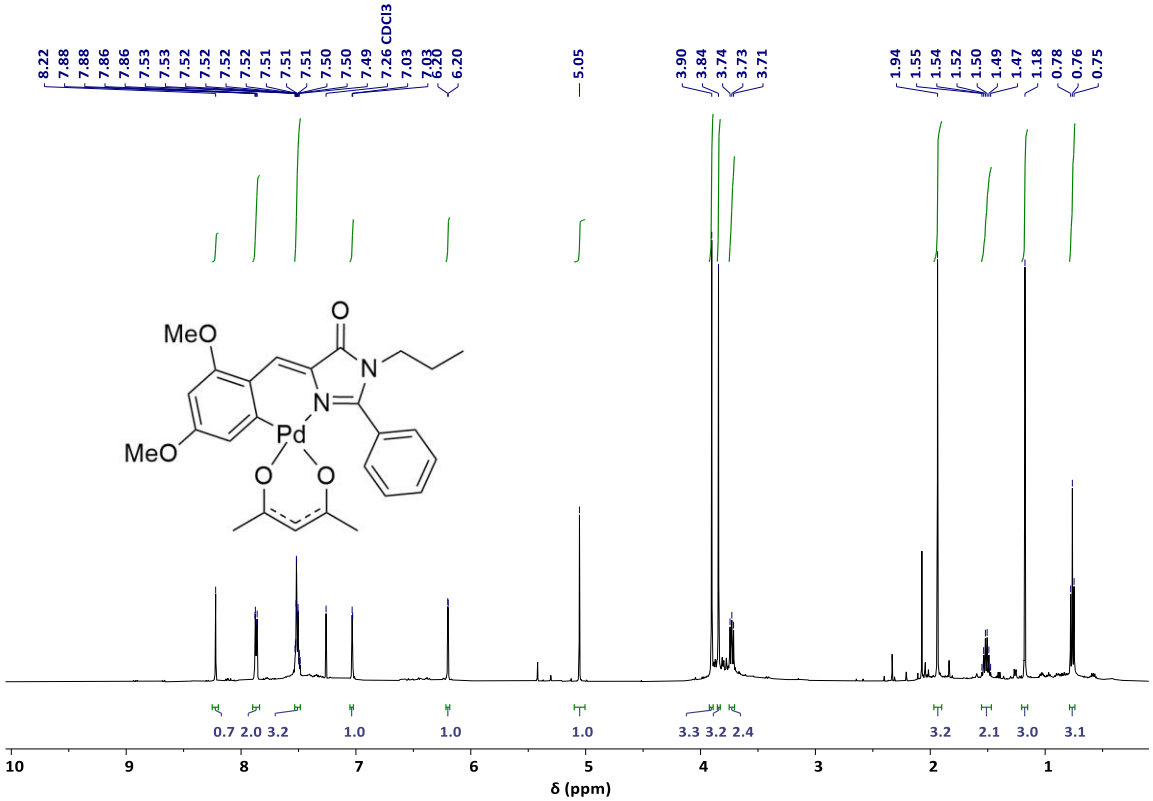

Figure S86. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **9e**

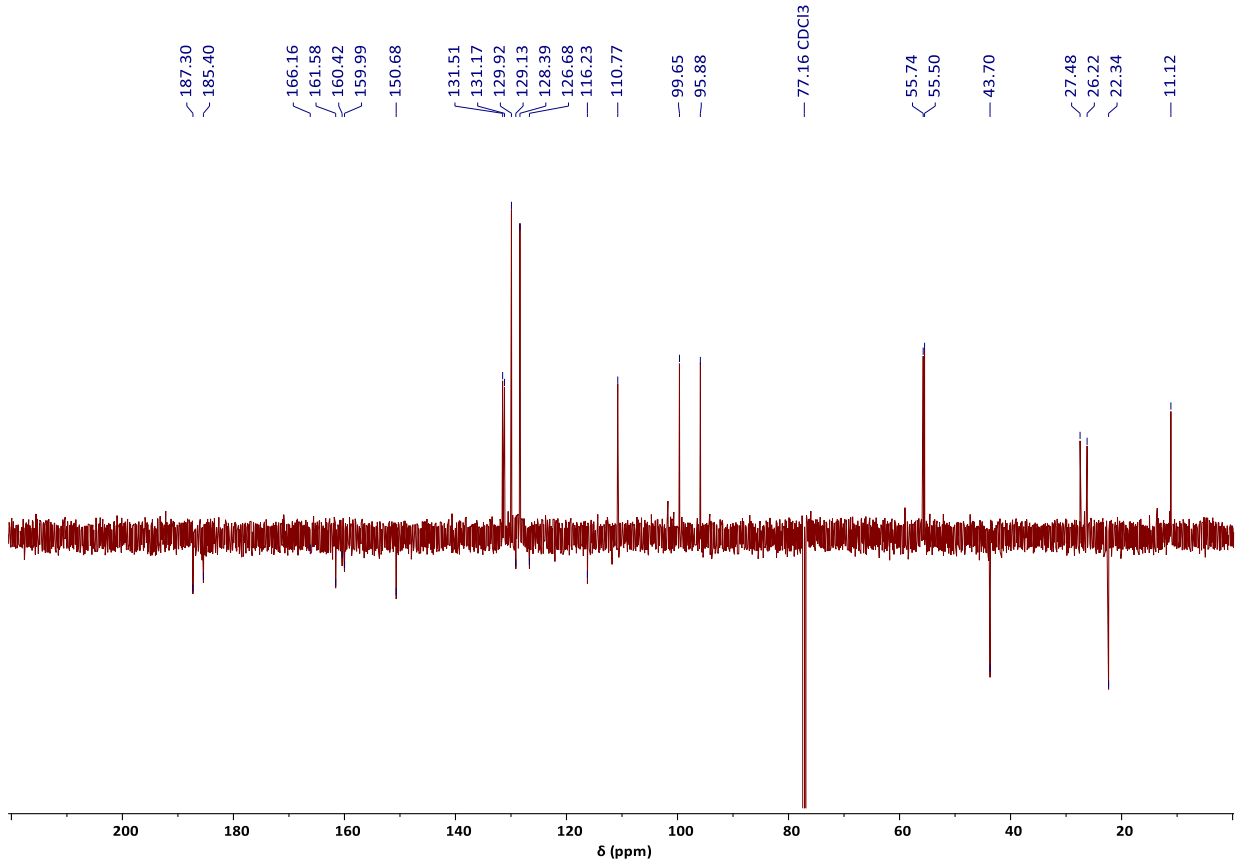

Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **9e**

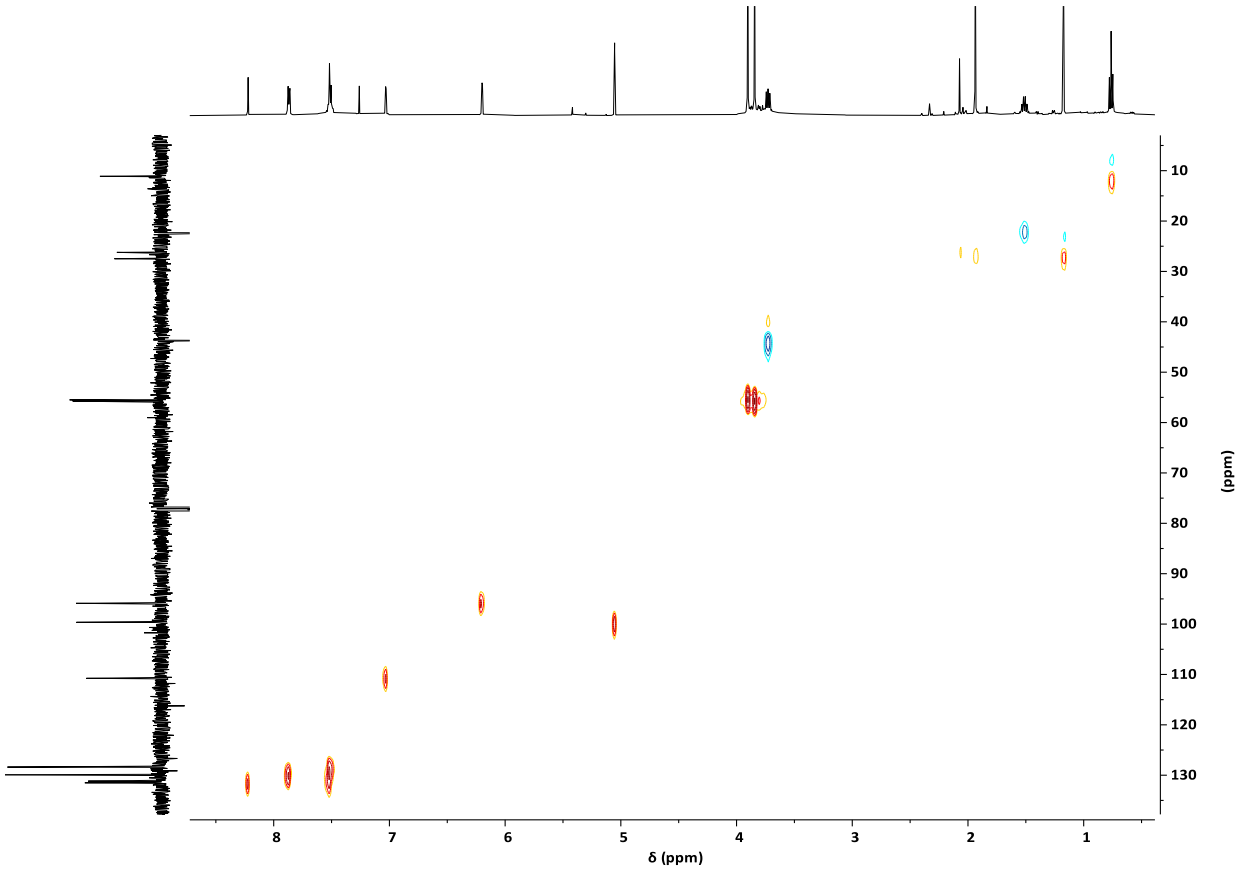

Figure S88. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **9e**

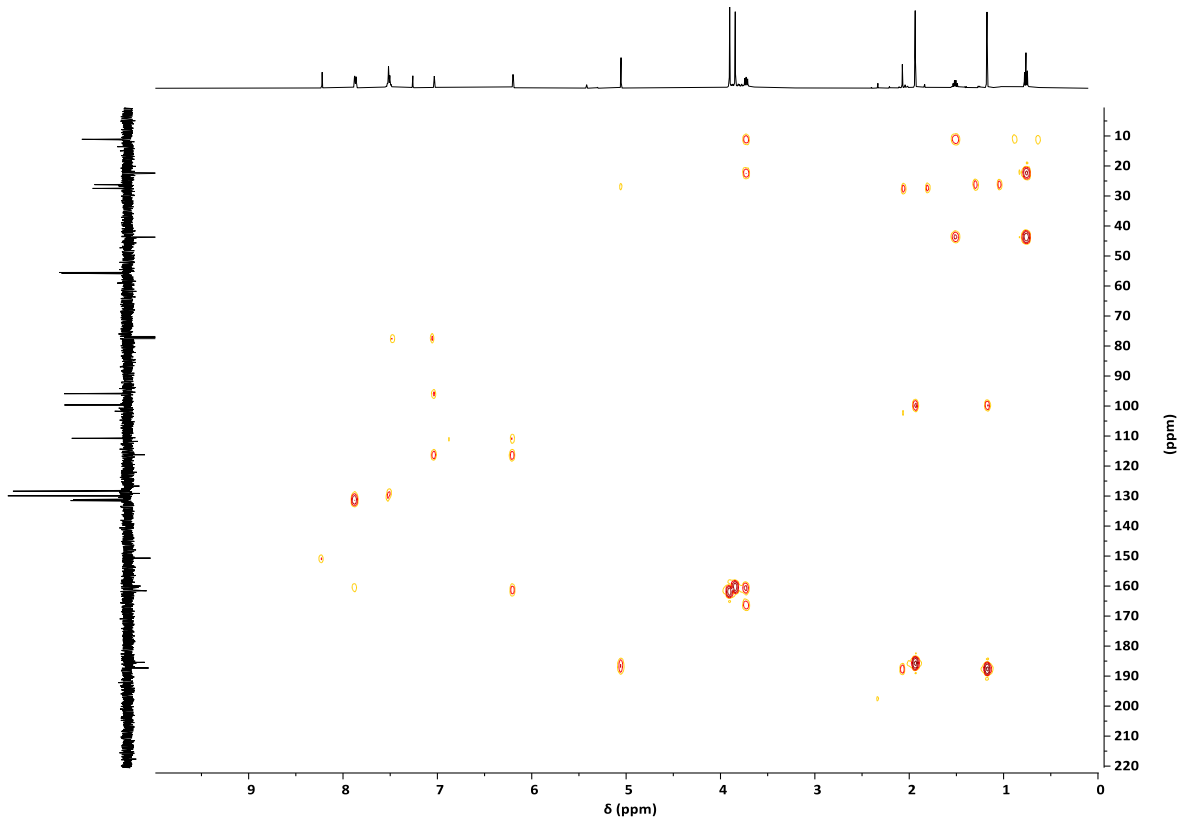

Figure S89. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **9e**

6.- [2+2] photocyclocycloaddition of 4 and 11: synthesis of the truxillic cyclobutane derivatives 10 and 12

Truxillic derivative 10a

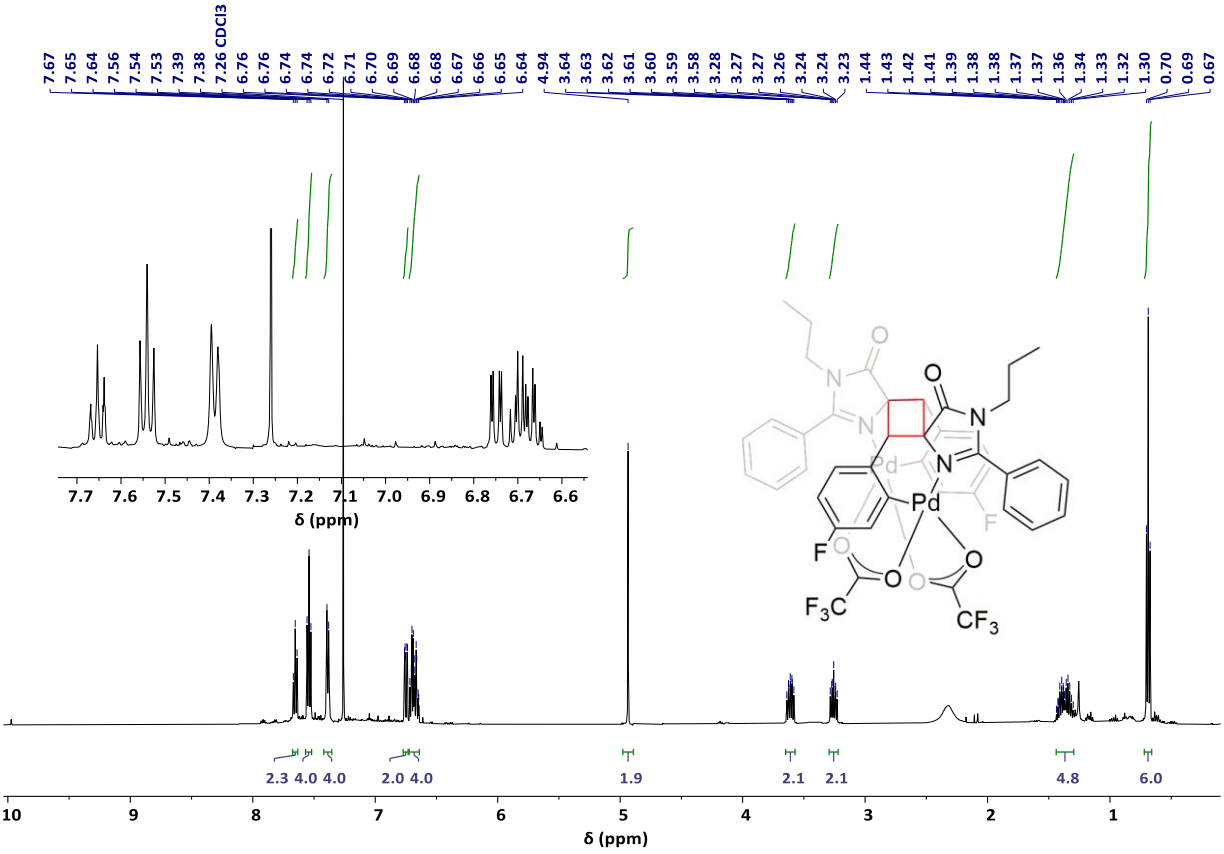

Figure S90. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **10a**

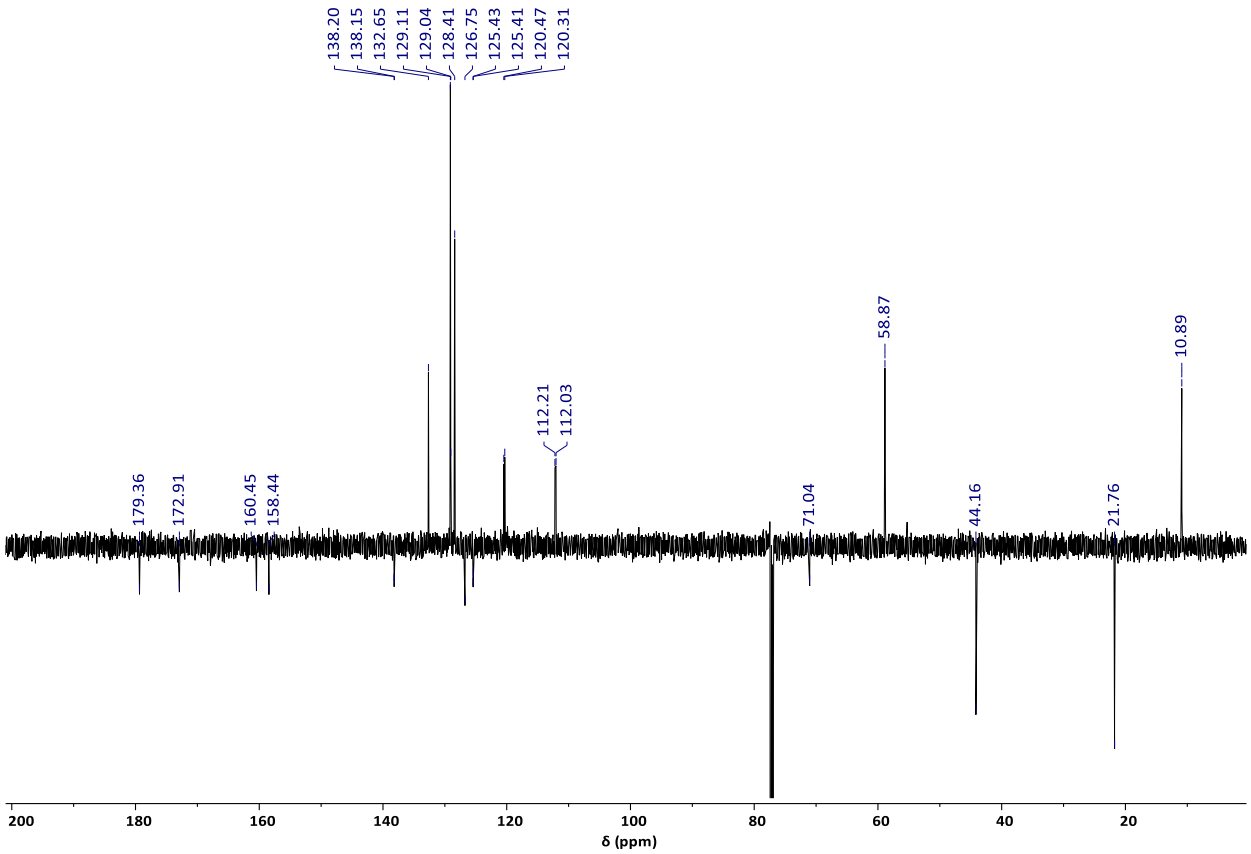

Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **10a**

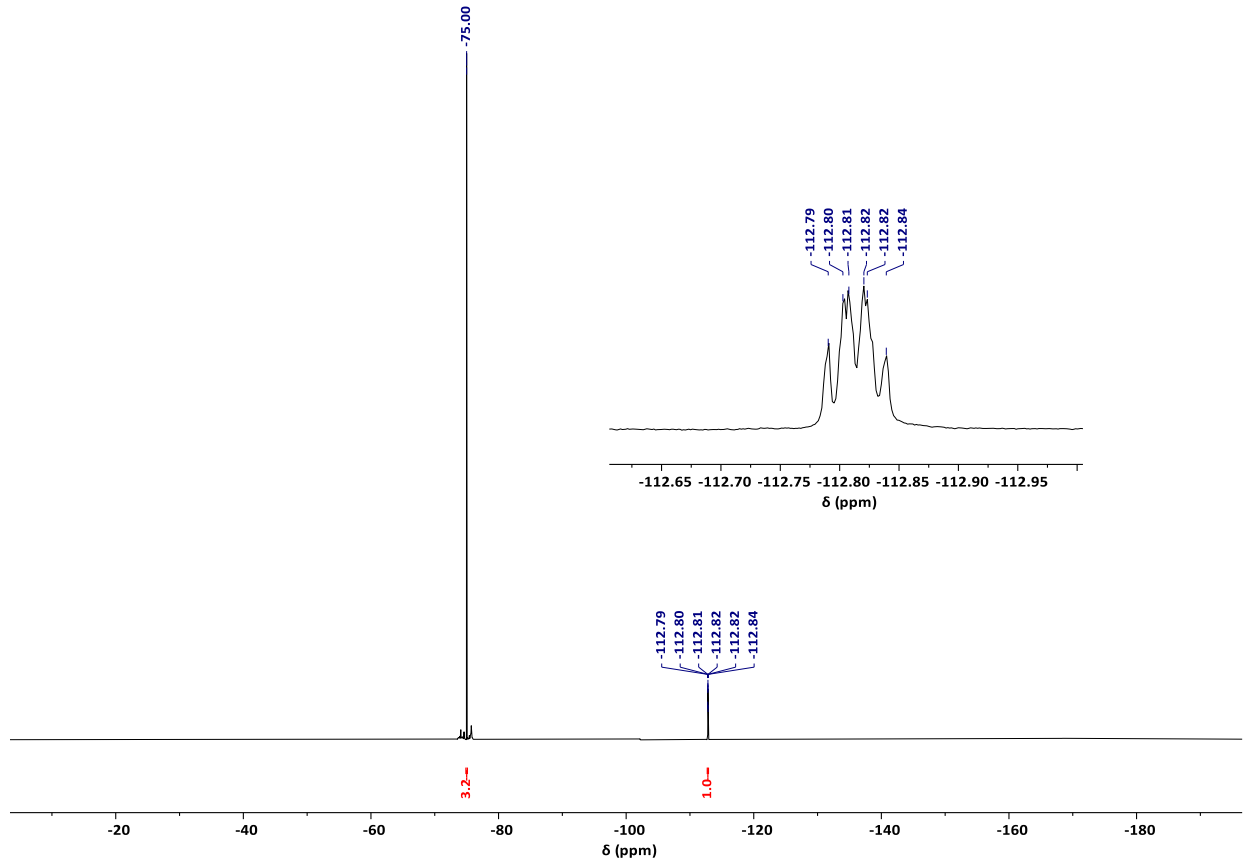

Figure S92. ^{19}F NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **10a**

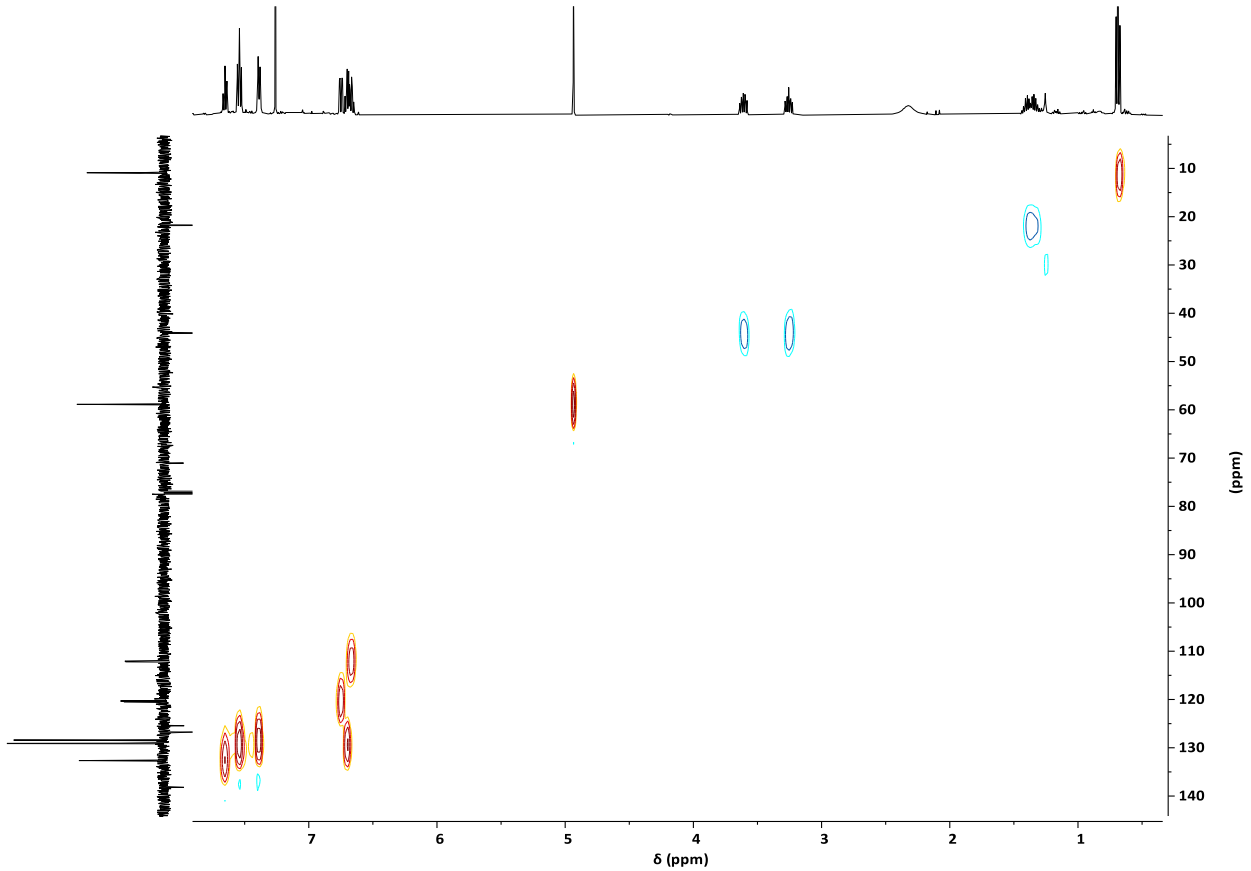

Figure S93. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **10a**

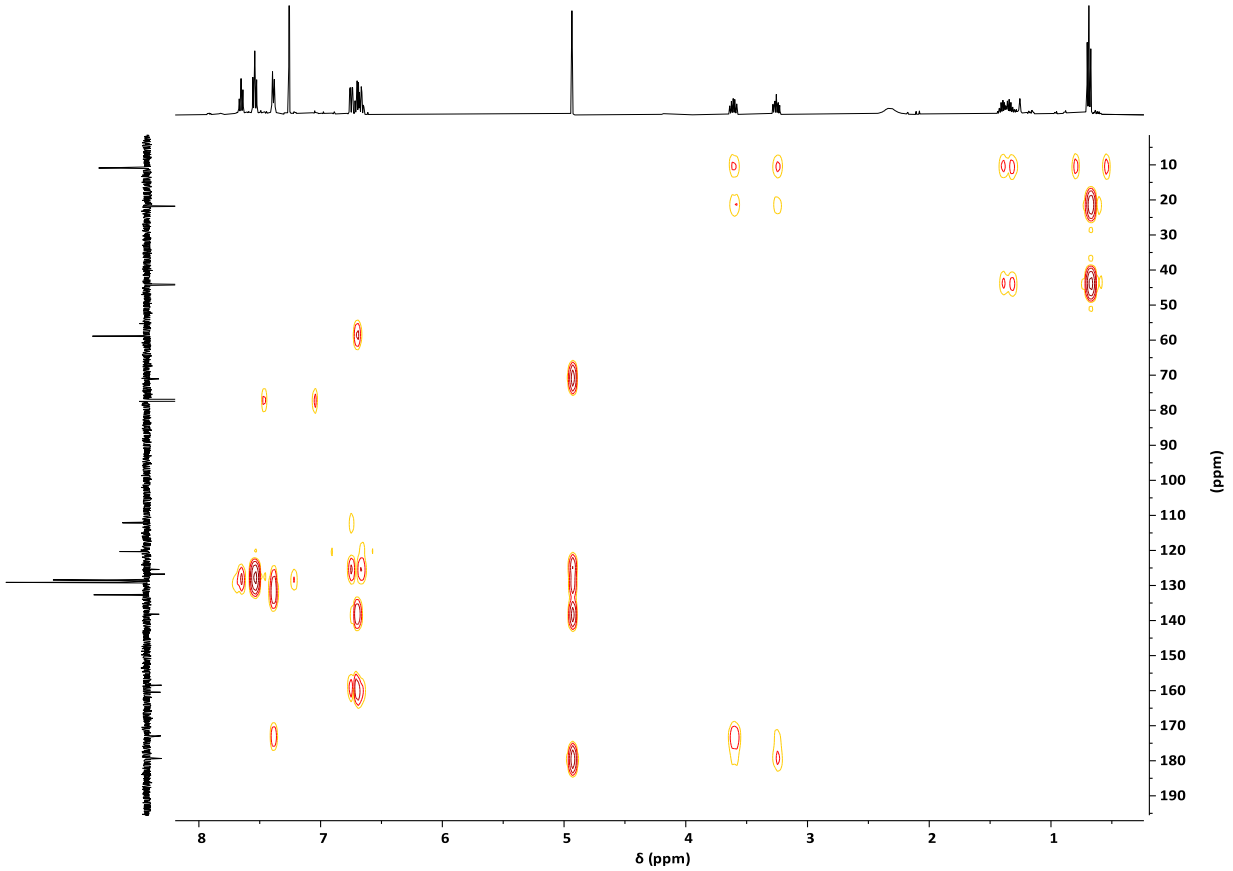

Figure S94. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **10a**

Truxillic derivative 10b

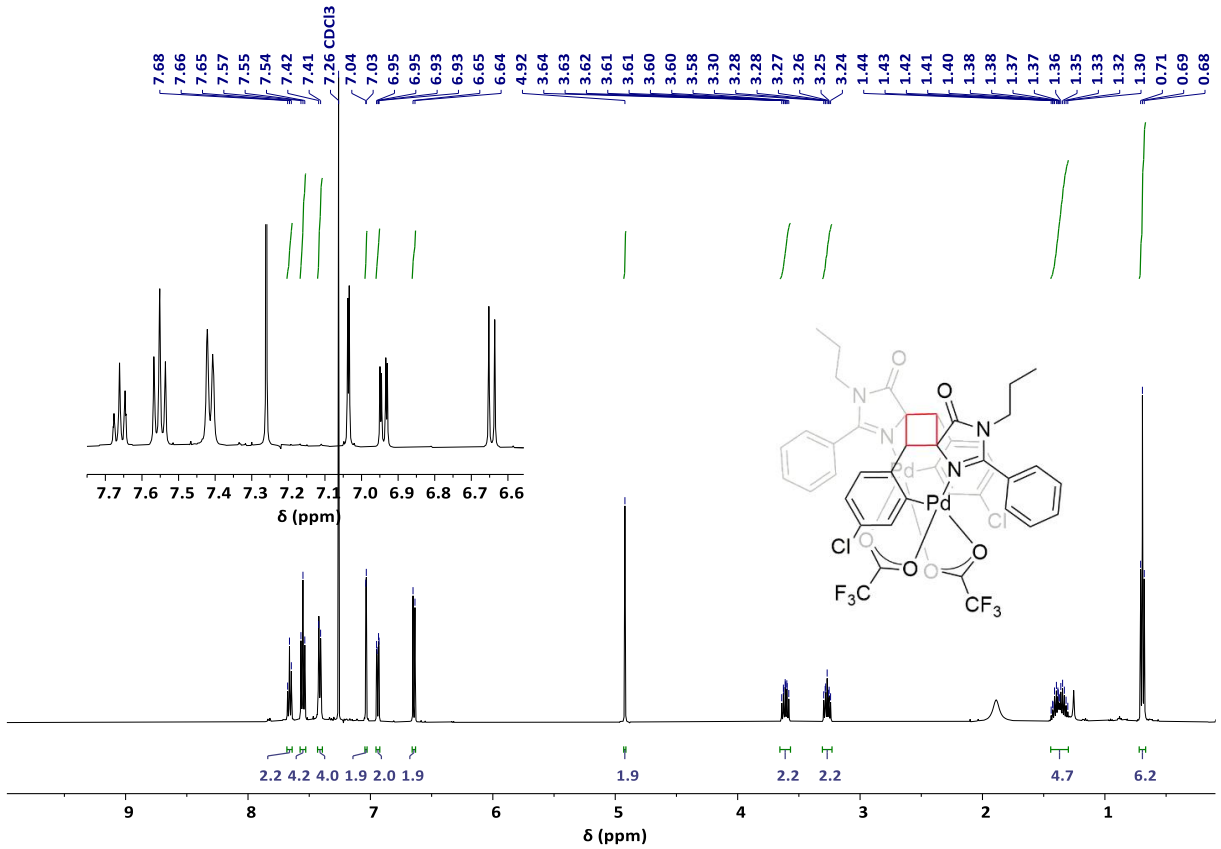

Figure S95. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **10b**

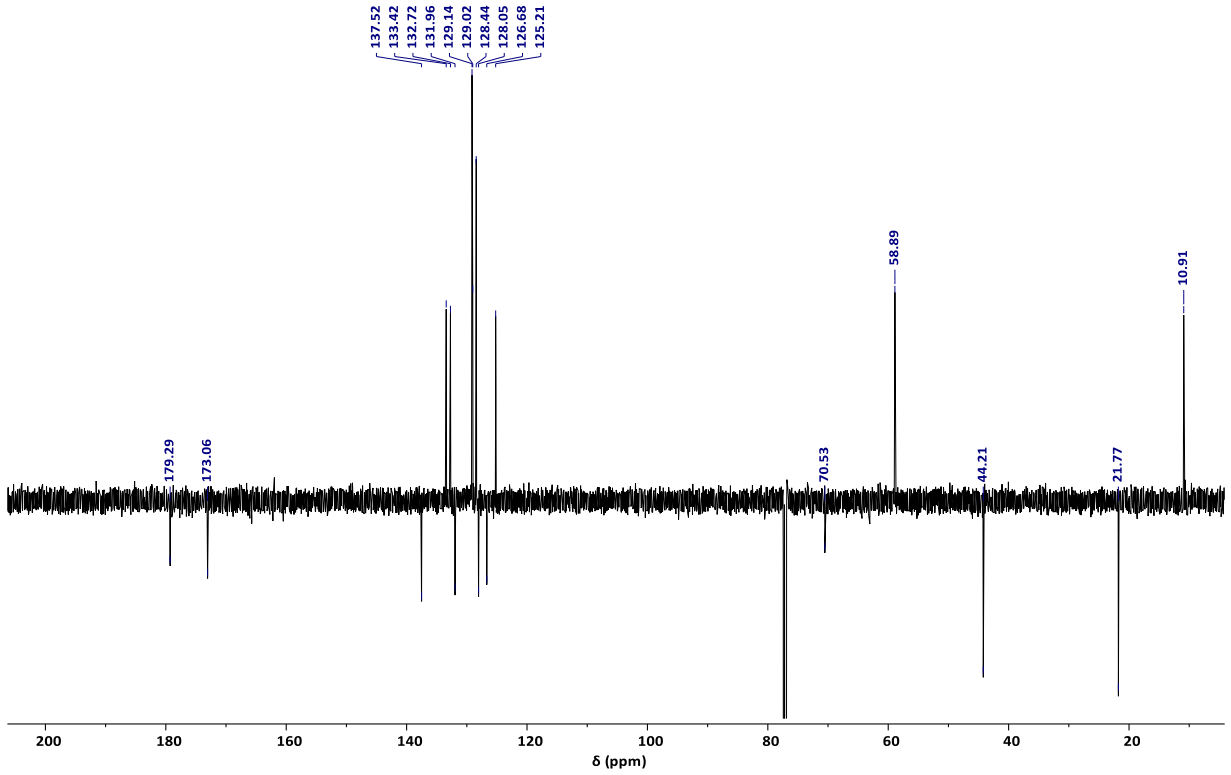

Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **10b**

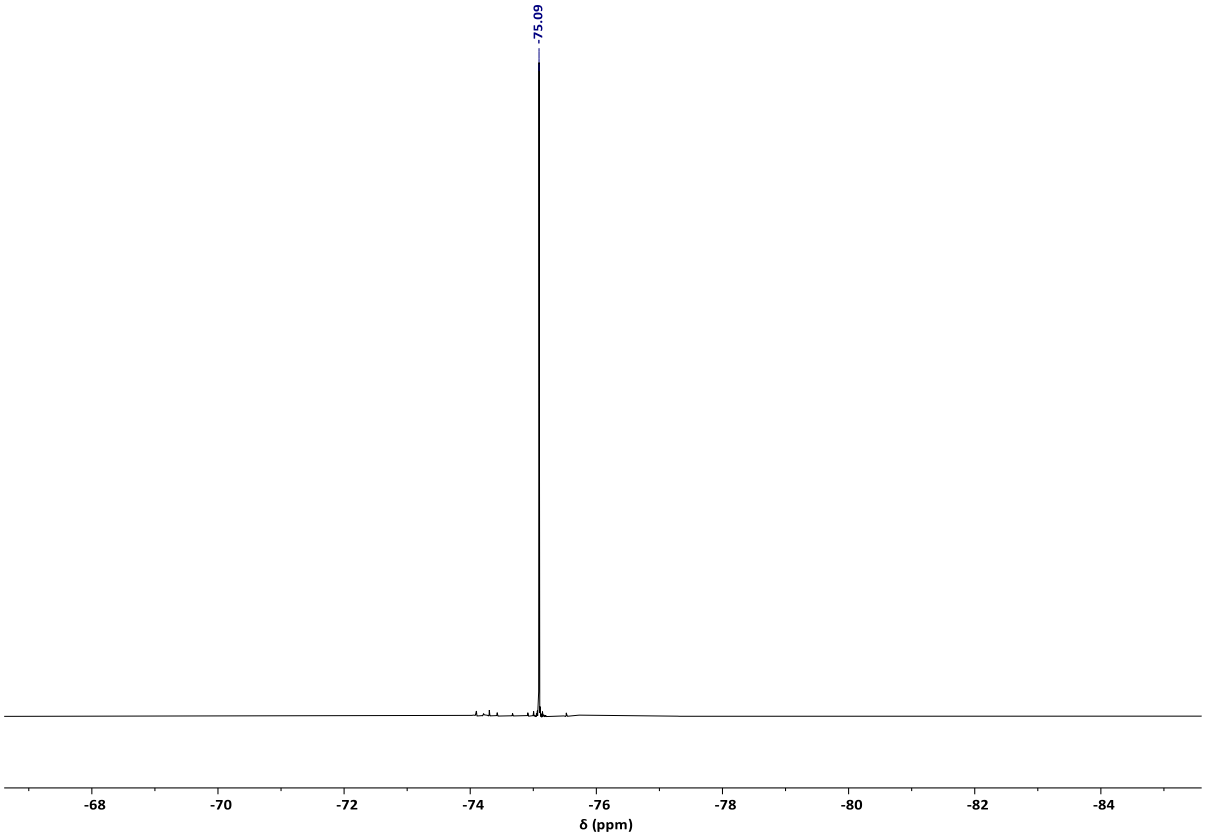

Figure S97. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **10b**

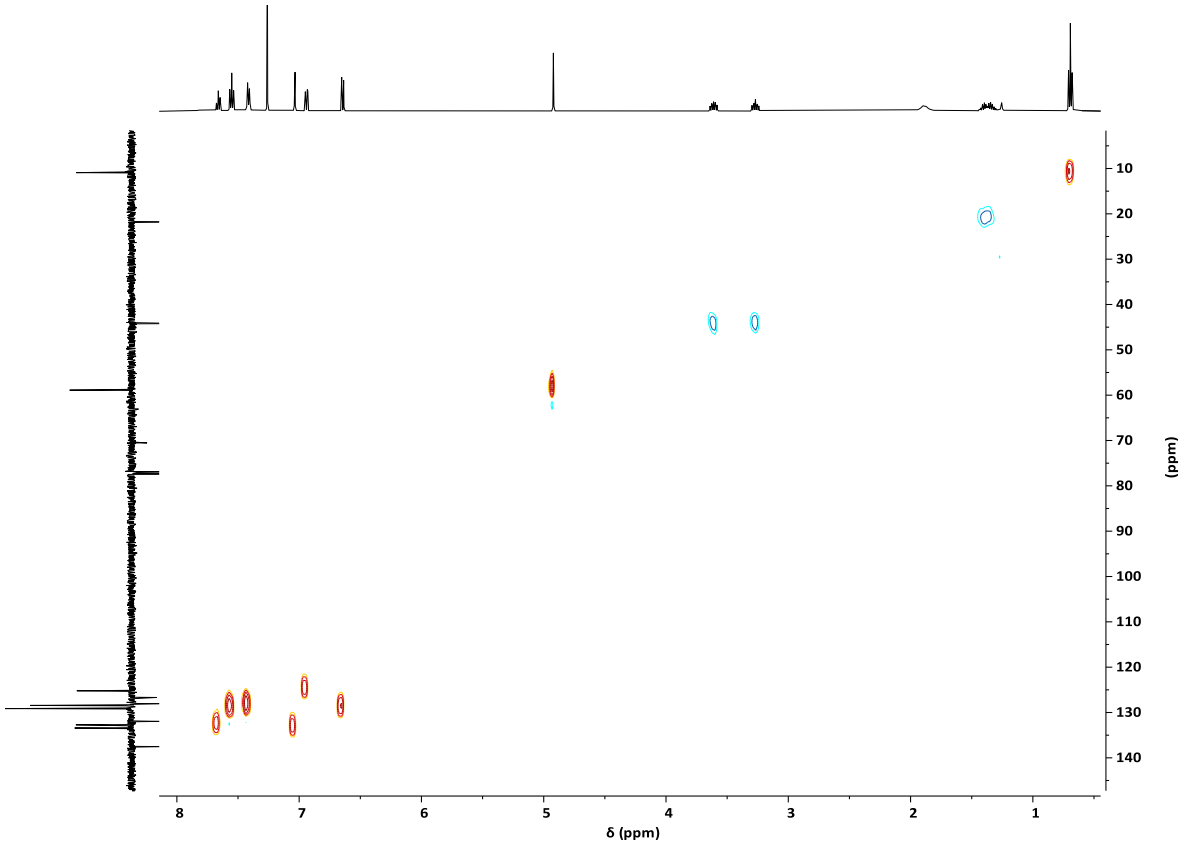

Figure S98. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **10b**

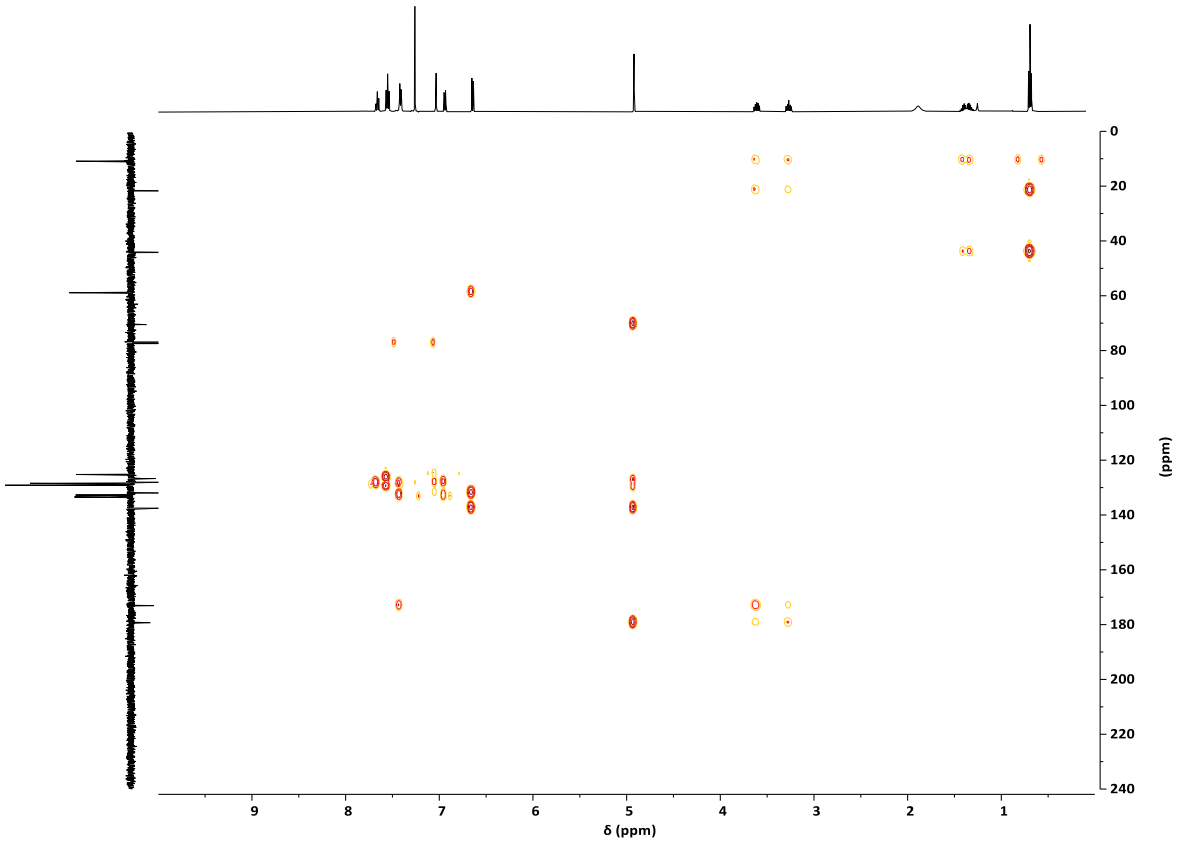

Figure S99. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **10b**

Truxillic derivative 10c

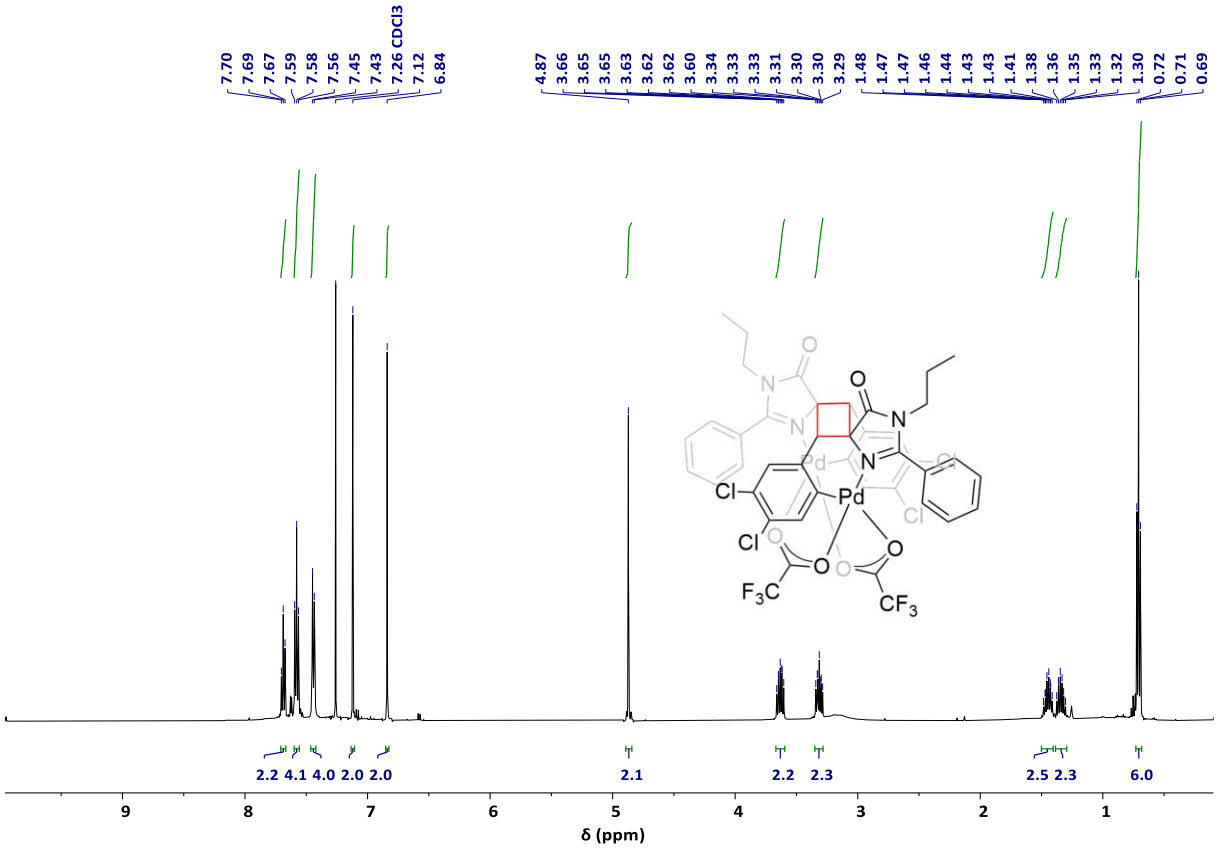

Figure S100. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **10c**

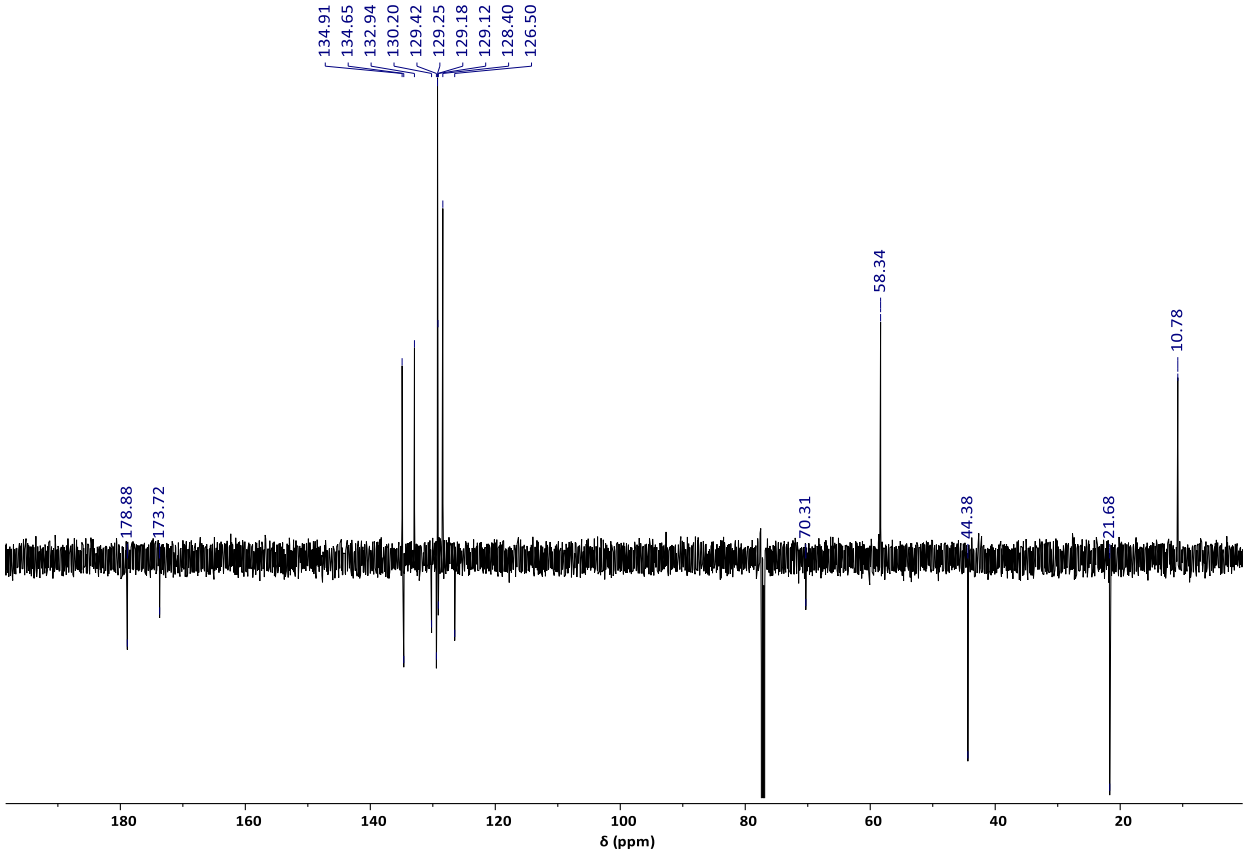

Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **10c**

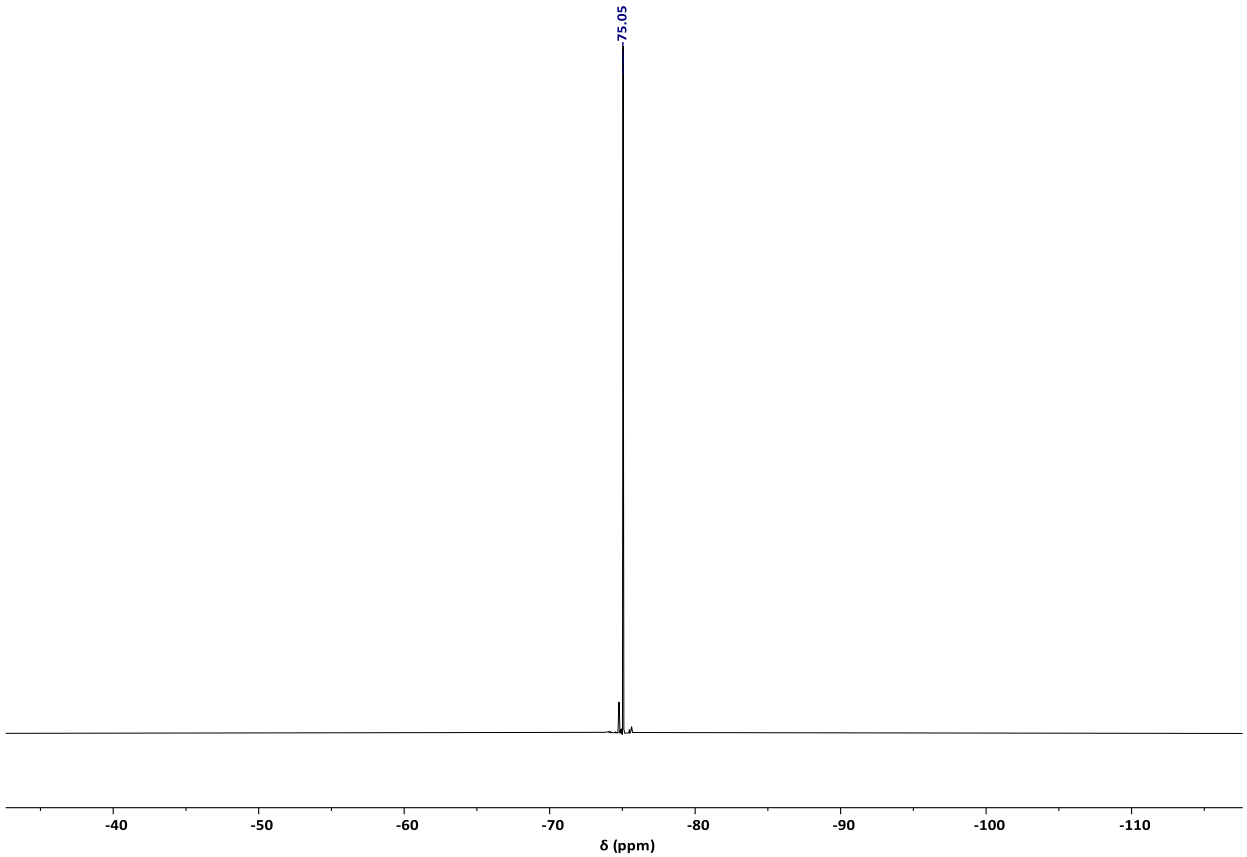

Figure S102. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **10c**

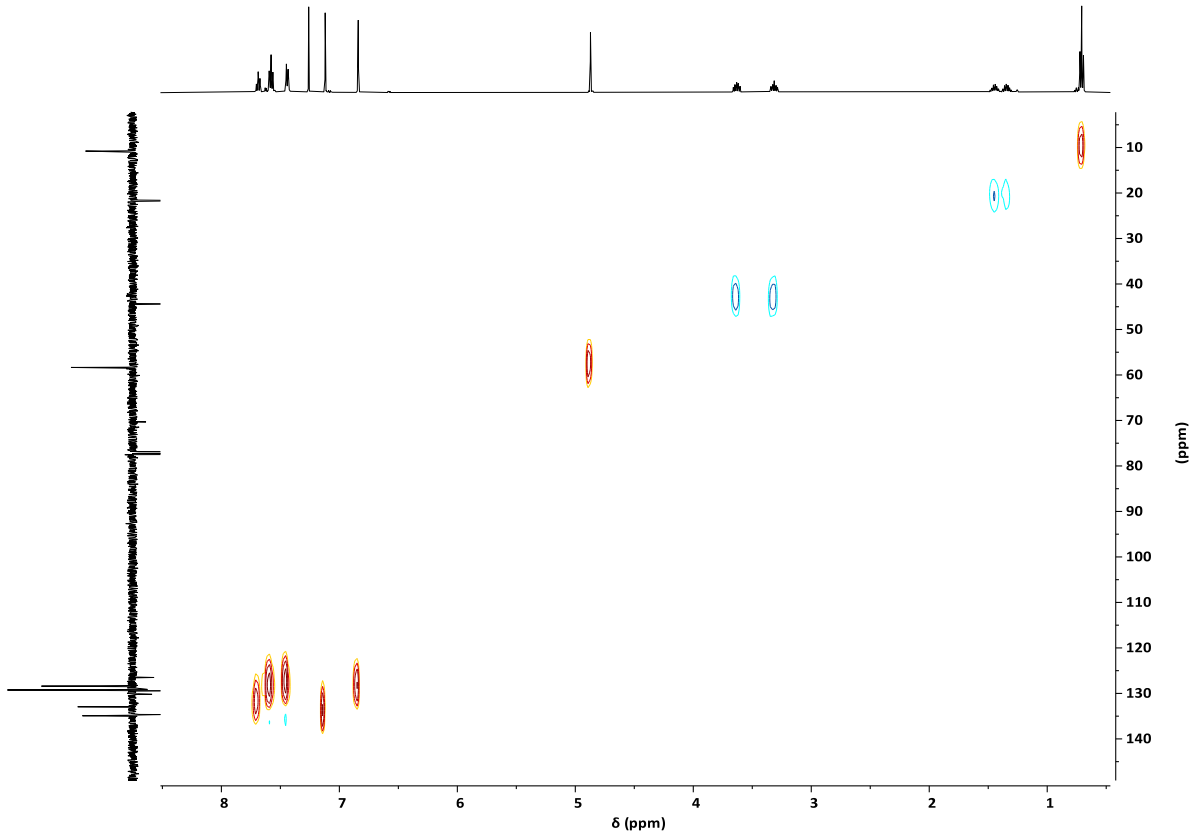

Figure S103. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **10c**

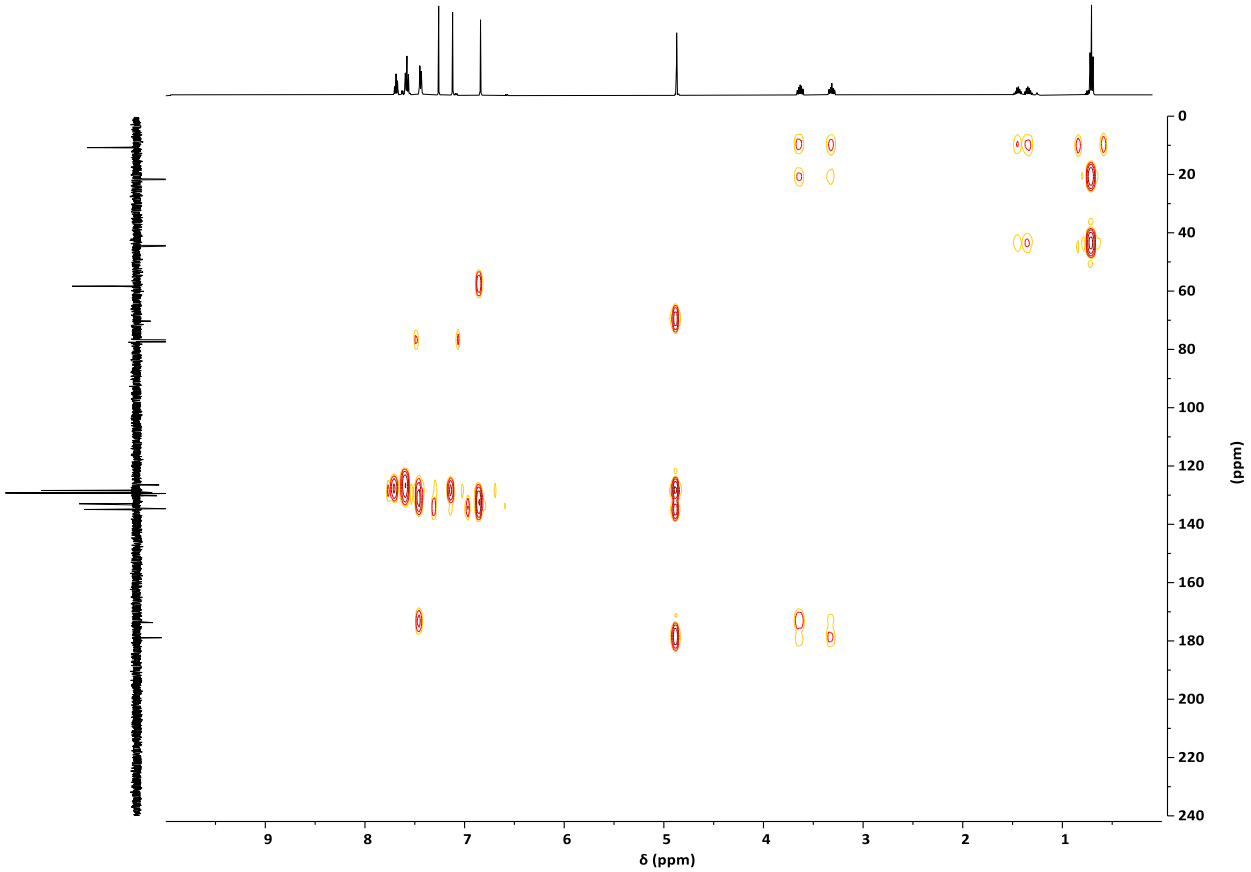

Figure S104. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **10c**

Truxillic derivative 12b

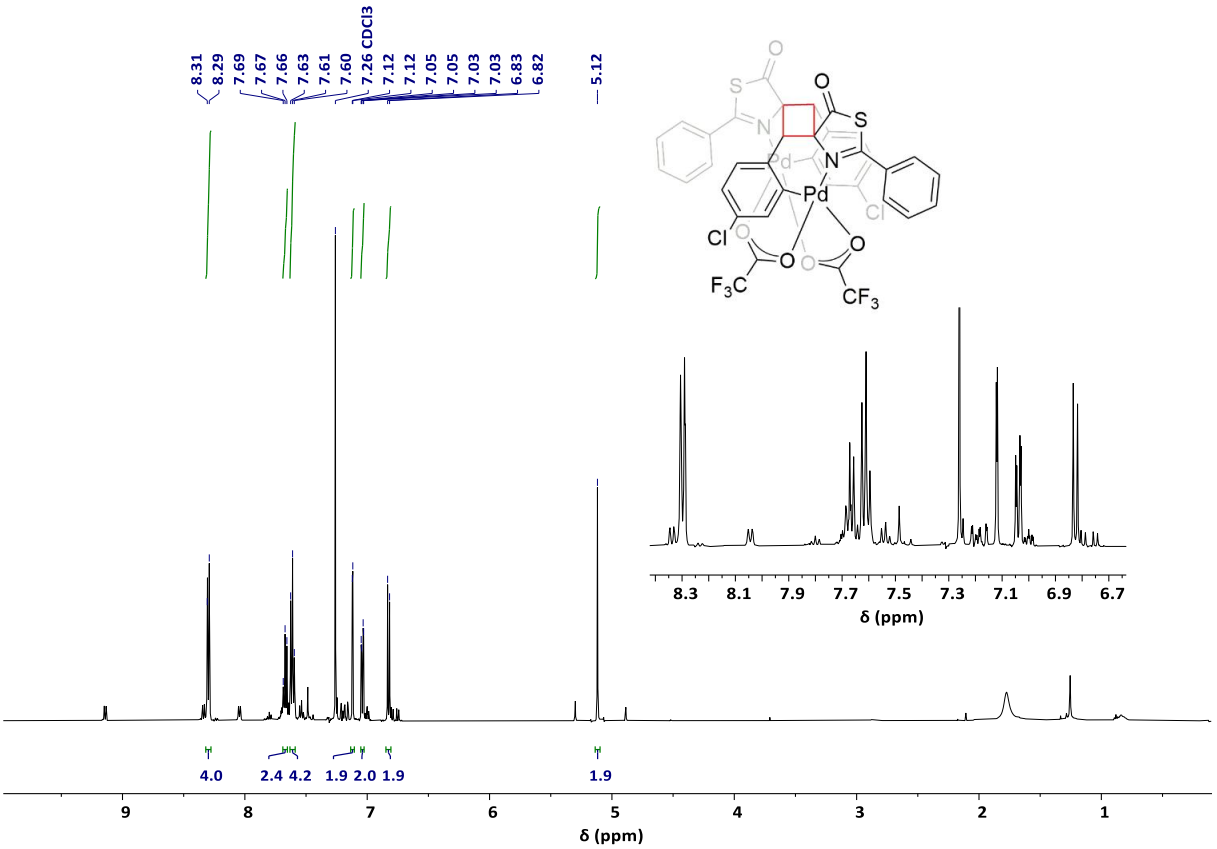

Figure S105. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **12b**

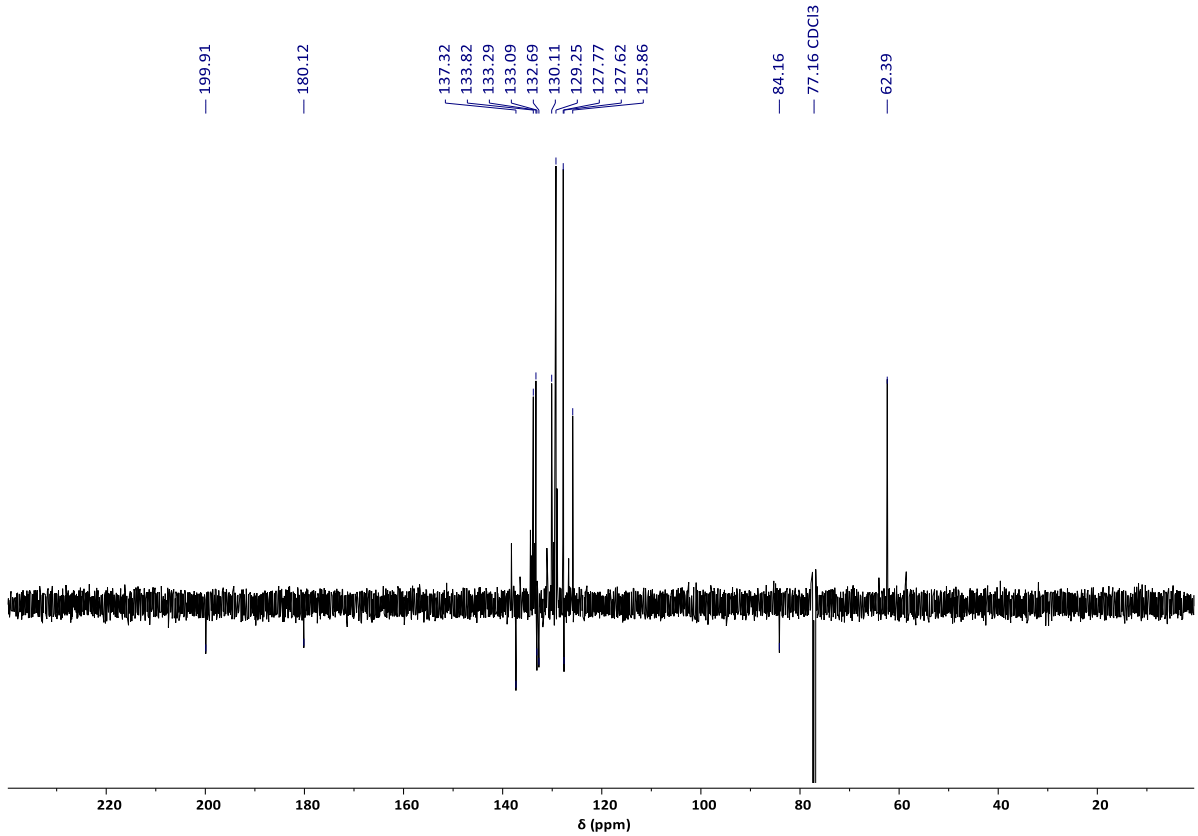

Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **12b**

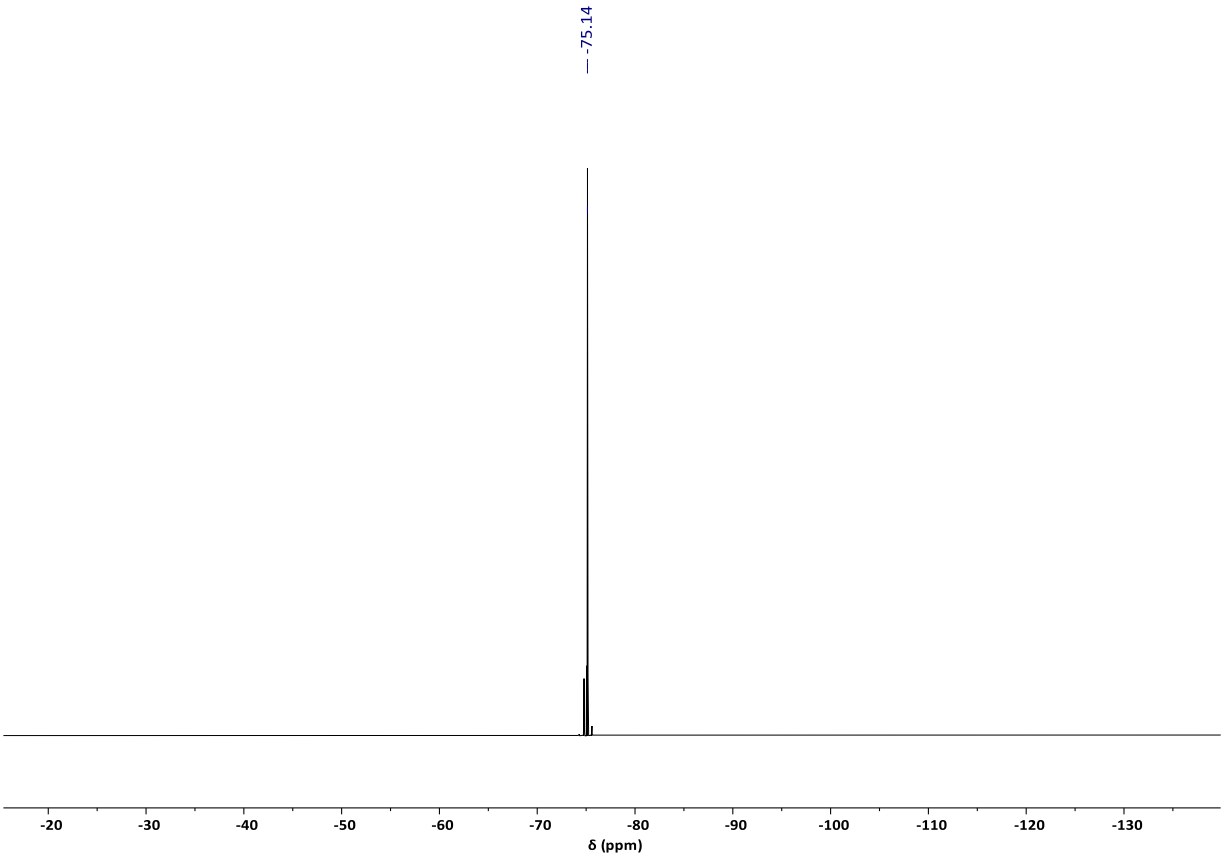

Figure S107. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **12b**

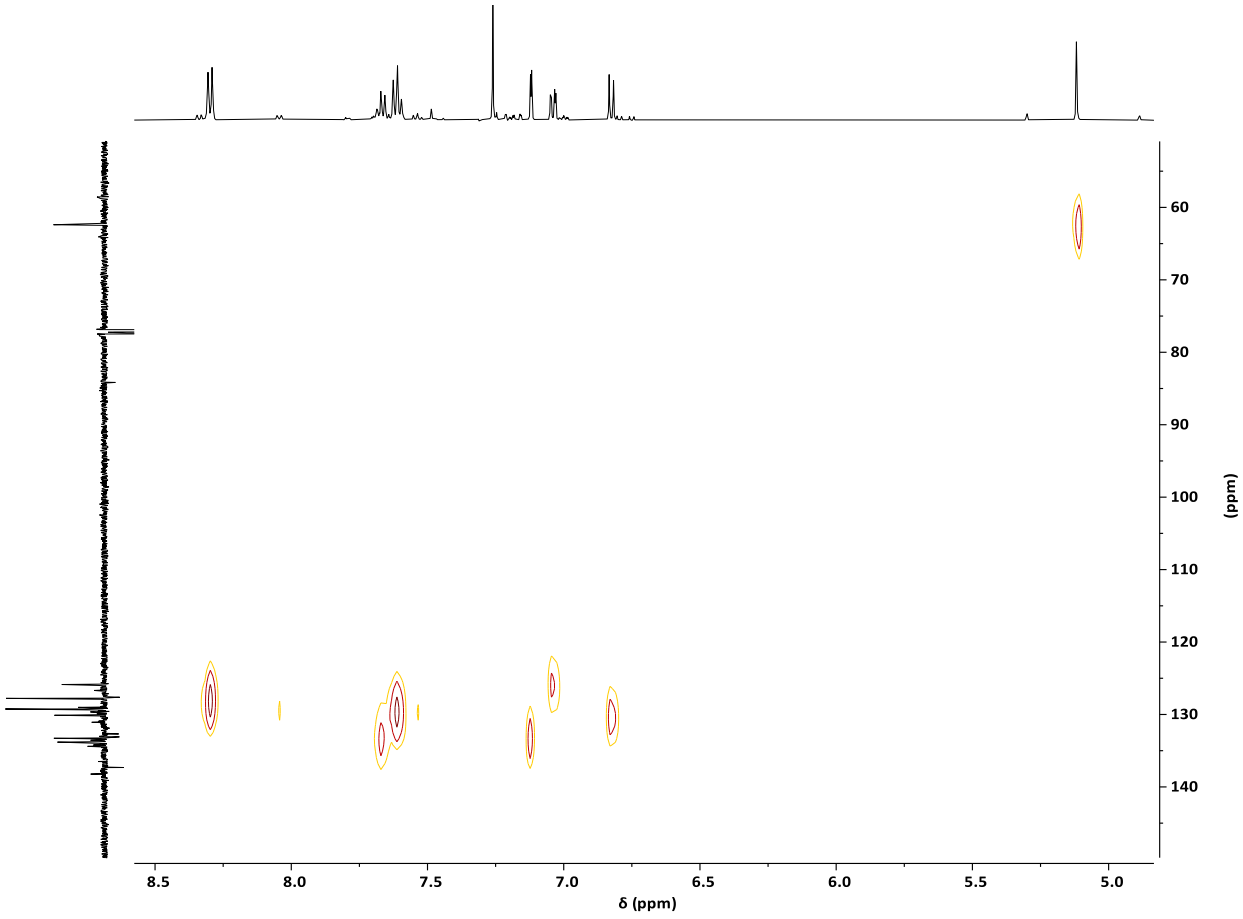

Figure S108. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **12b**

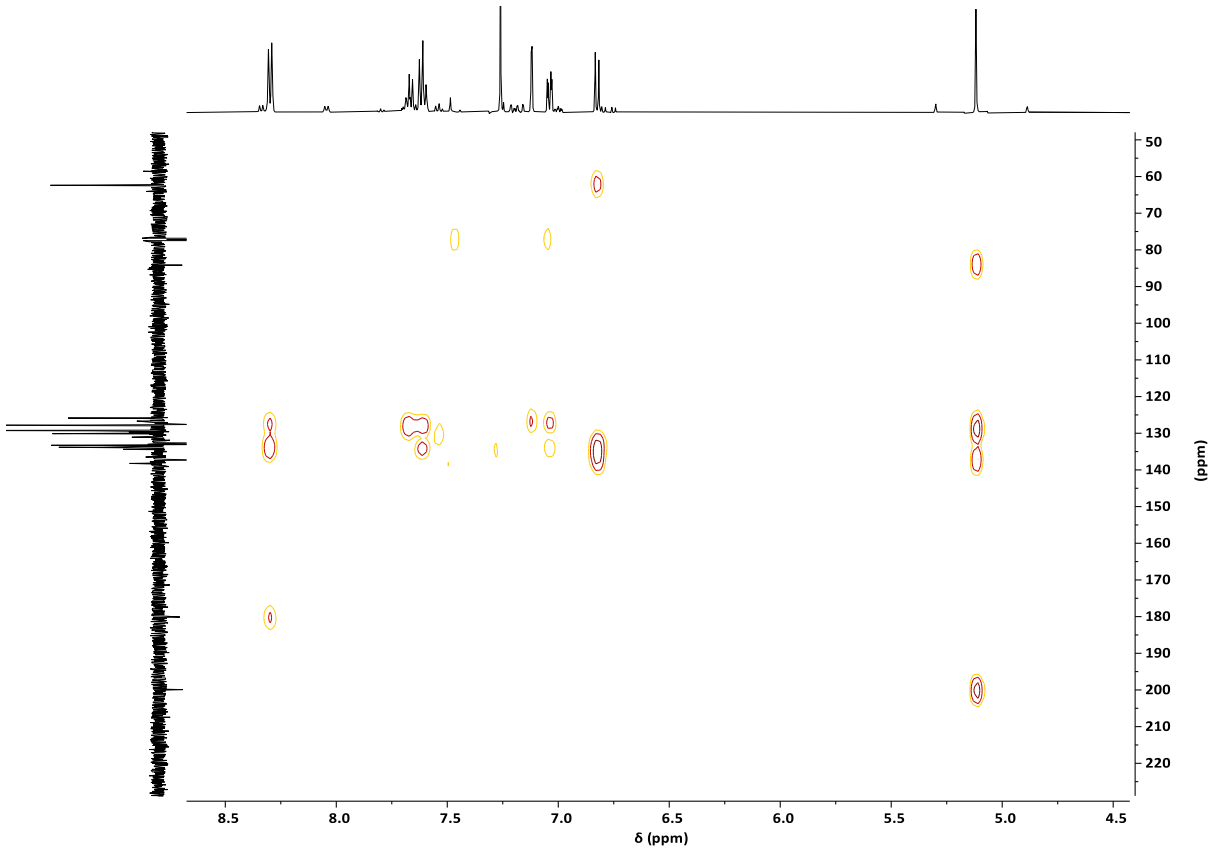

Figure S109. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **12b**

Truxillic derivative 12c

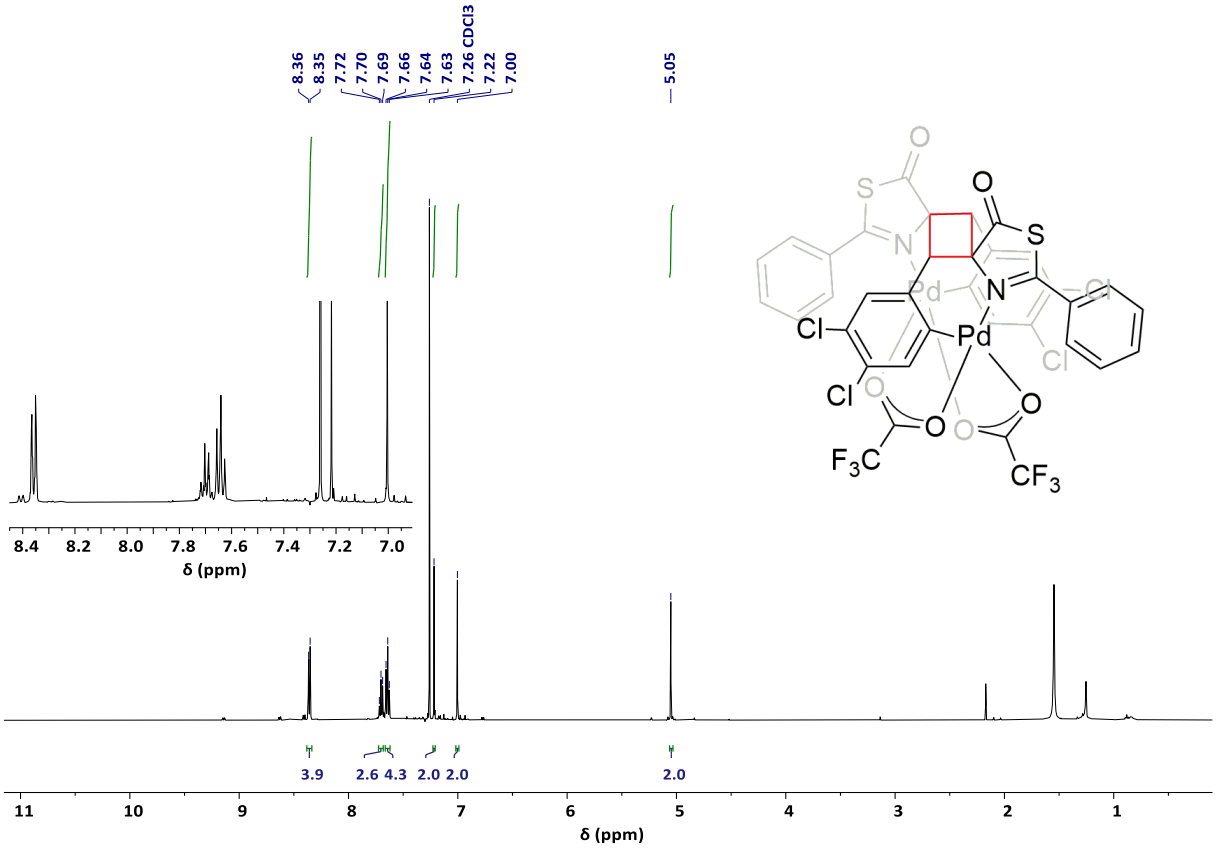

Figure S110. ^{1}H NMR spectrum ($CDCl_3$, 500.13 MHz, r. t.) of **12c**

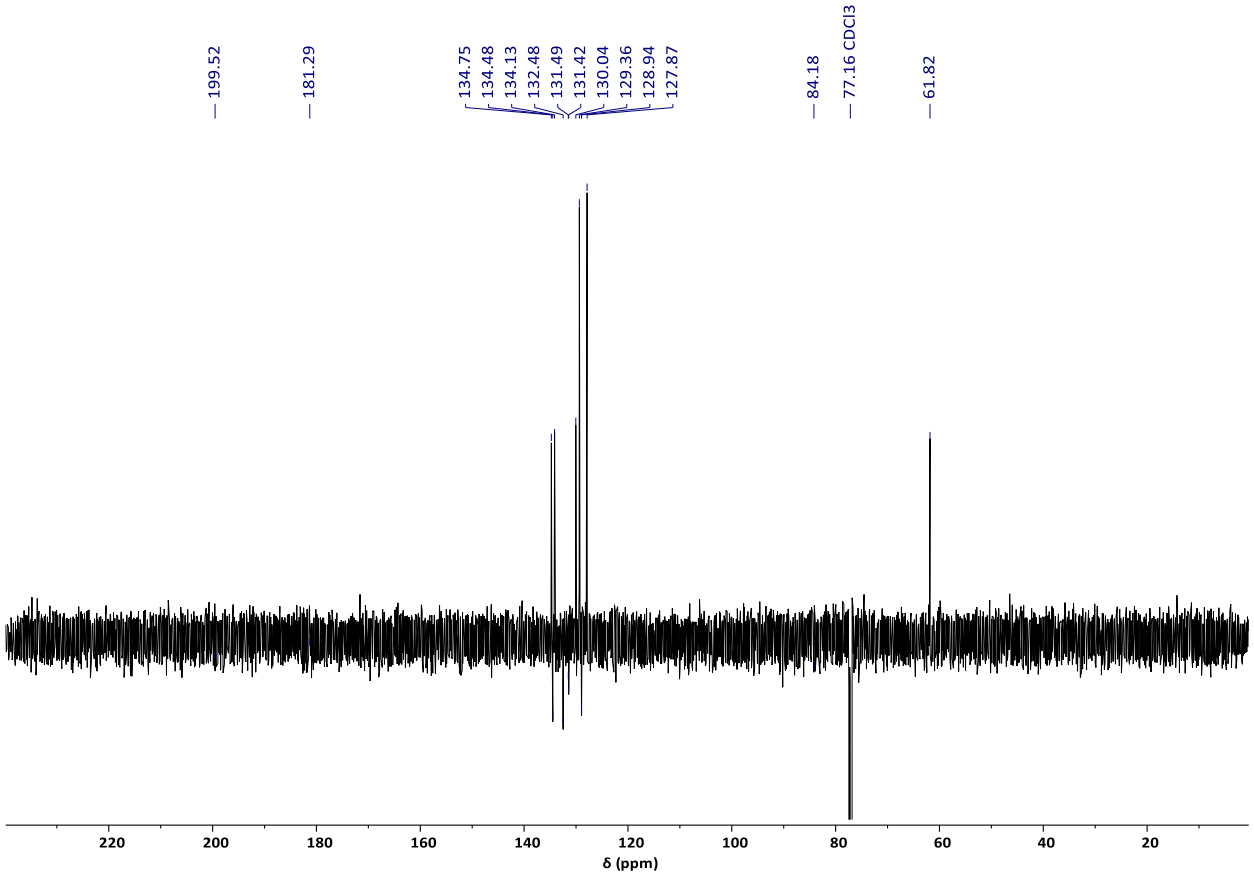

Figure S111. $^{13}C\{^{1}H\}$ NMR spectrum (APT, $CDCl_3$, 125.77 MHz, r. t.) of **12c**

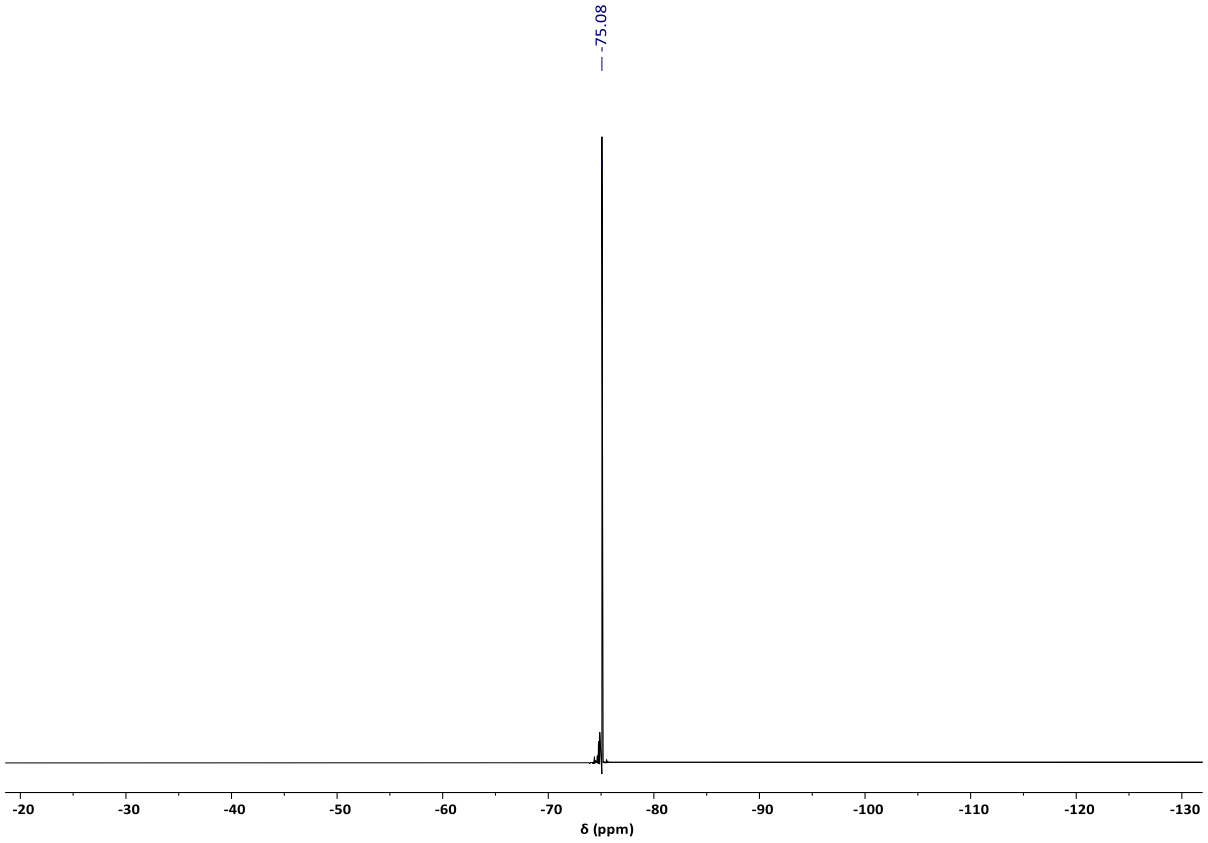

Figure S112. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 470.55 MHz, r. t.) of **12c**

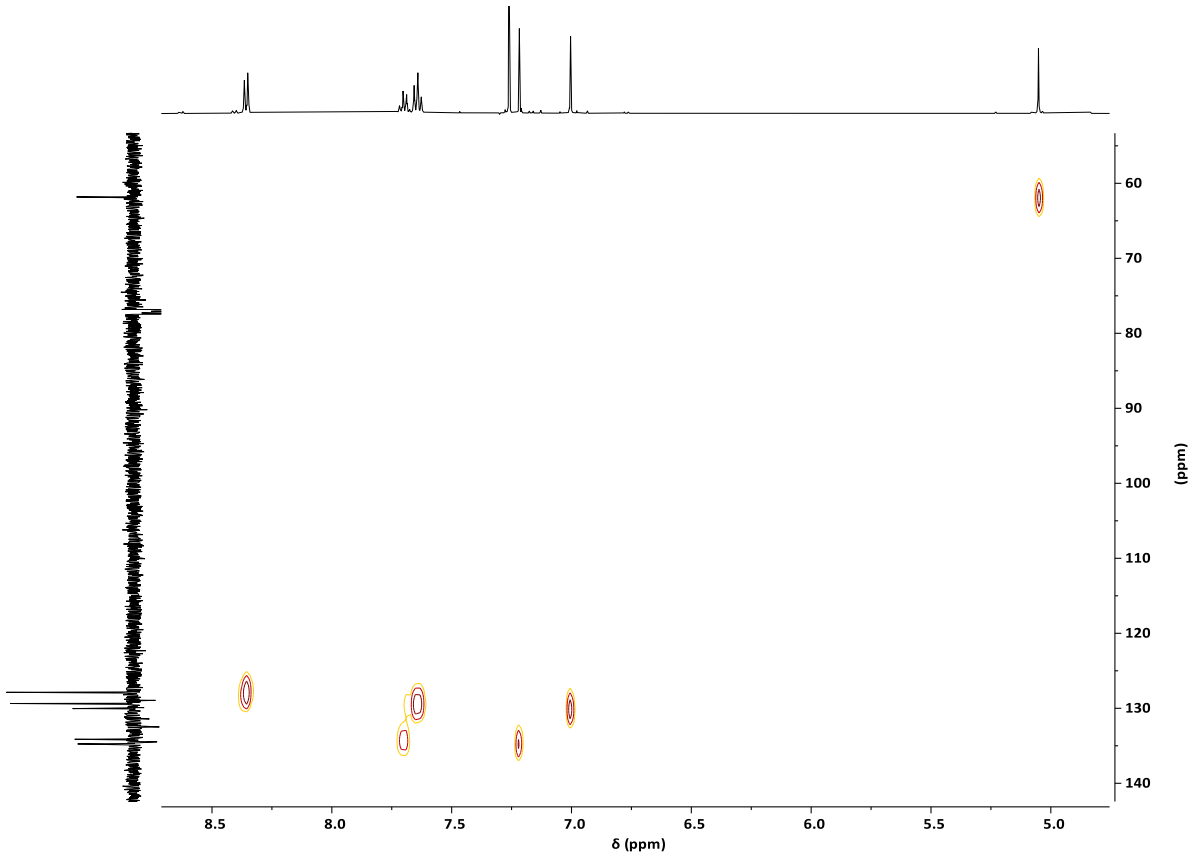

Figure S113. ^{1}H-^{13}C HSQC correlation spectrum ($CDCl_3$, r.t.) of compound **12c**

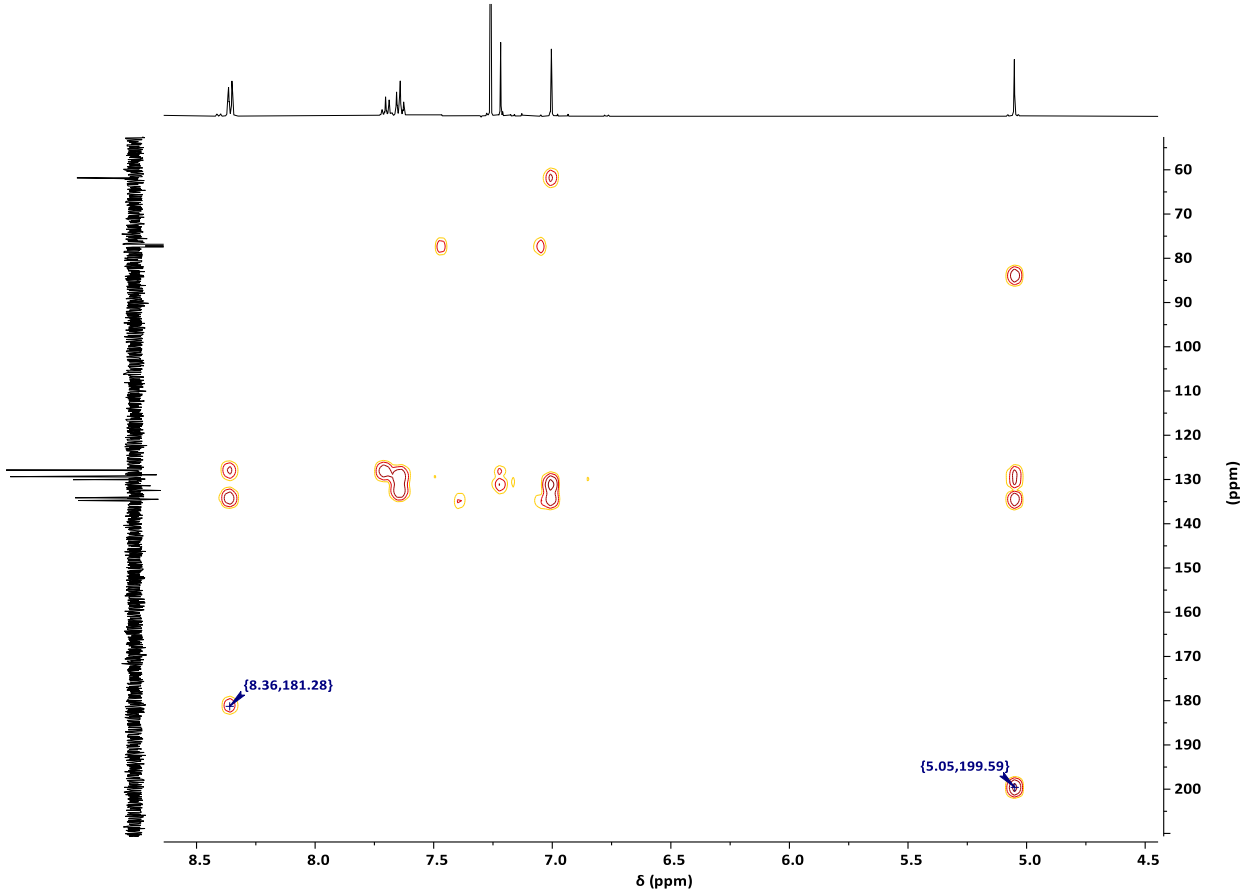

Figure S114. ^{1}H-^{13}C HMBC correlation spectrum ($CDCl_3$, r.t.) of compound **12c**

7.- Absorption spectra of imidazolones (2) and luminescent derivatives 5e-9e

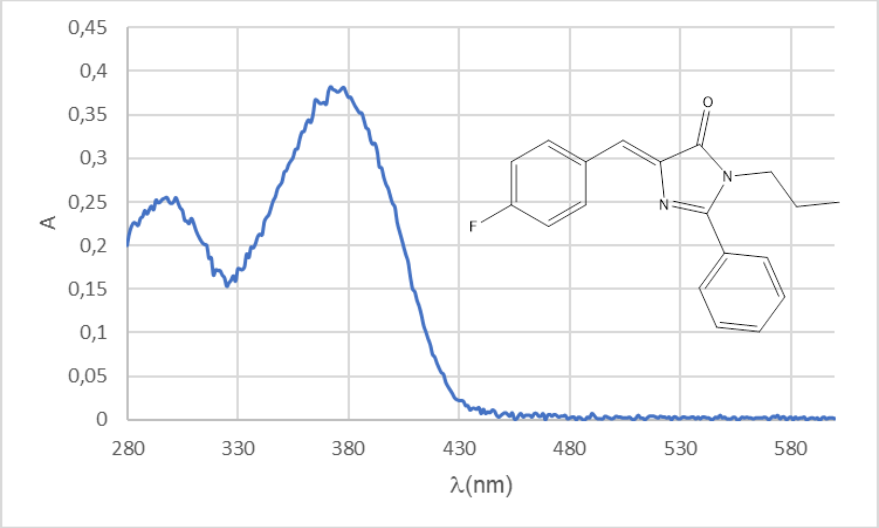

Figure S115. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2a**

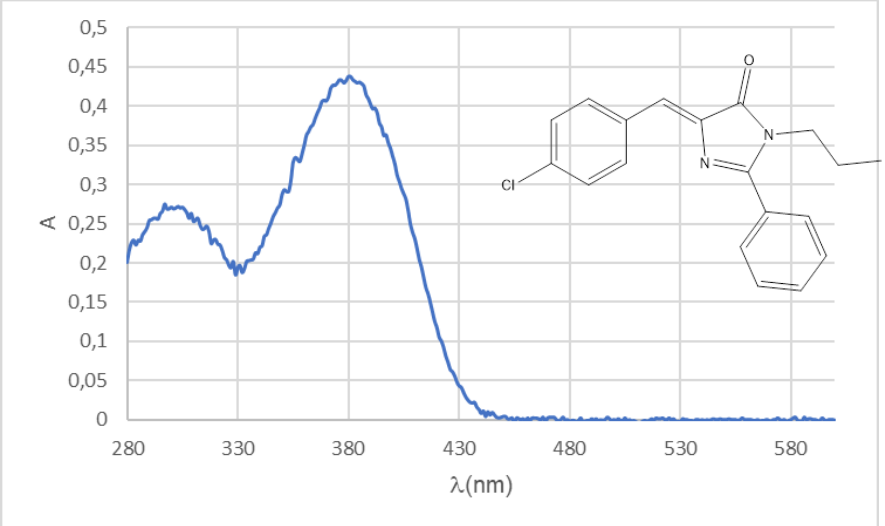

Figure S116. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2b**

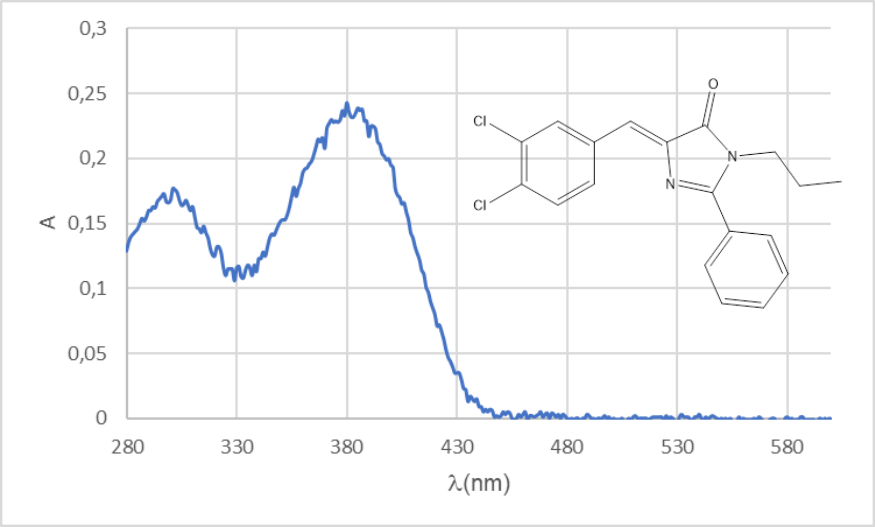

Figure S117. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2c**

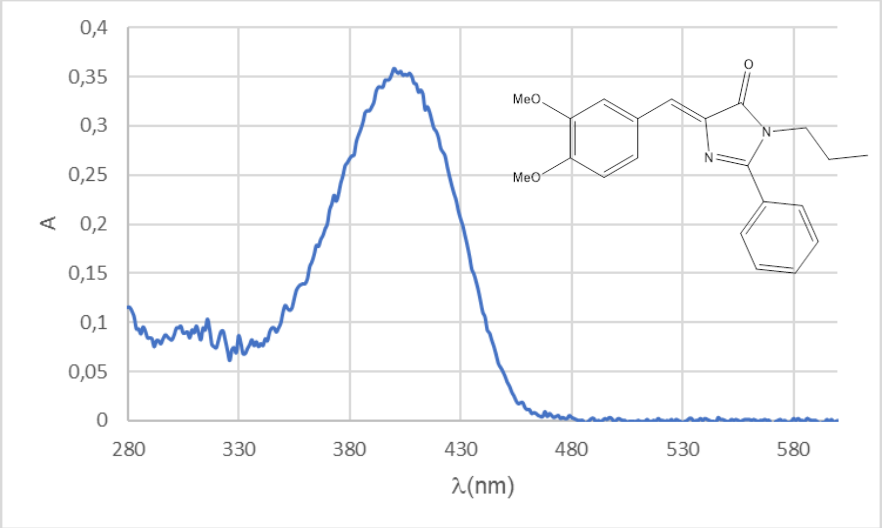

Figure S118. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2d**

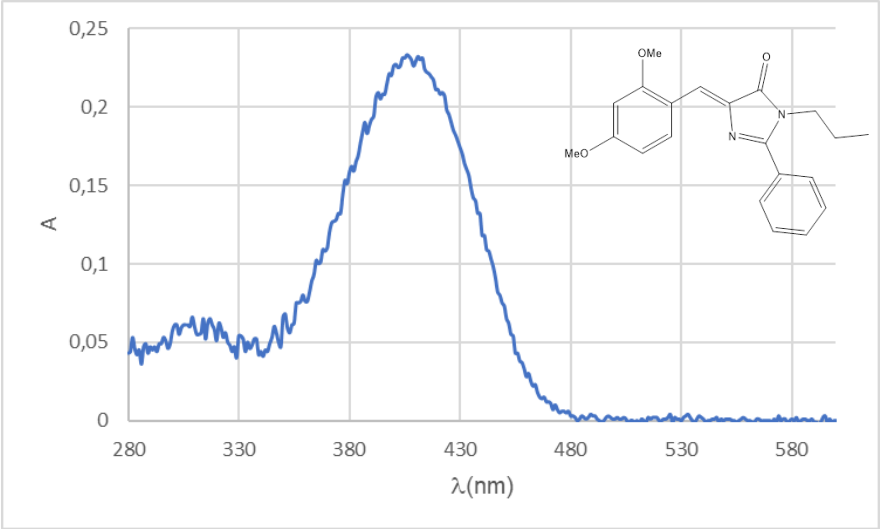

Figure S119. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2e**

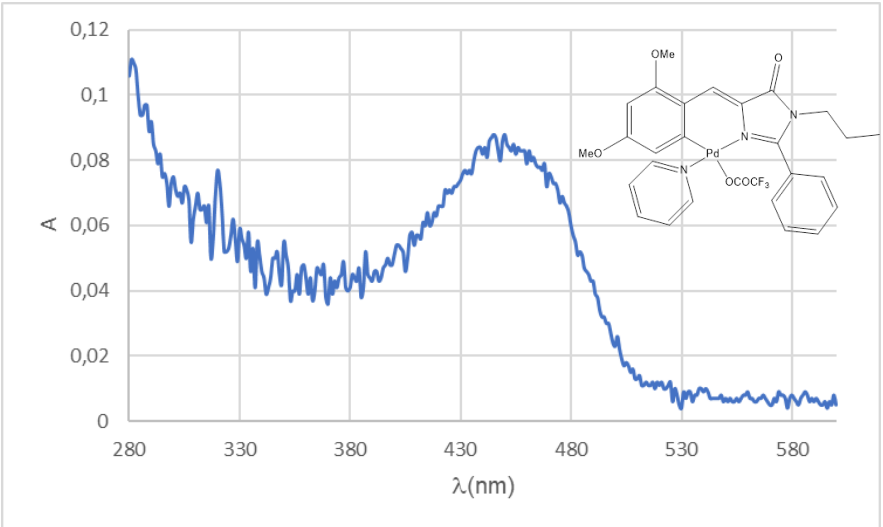

Figure S120. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **5e**

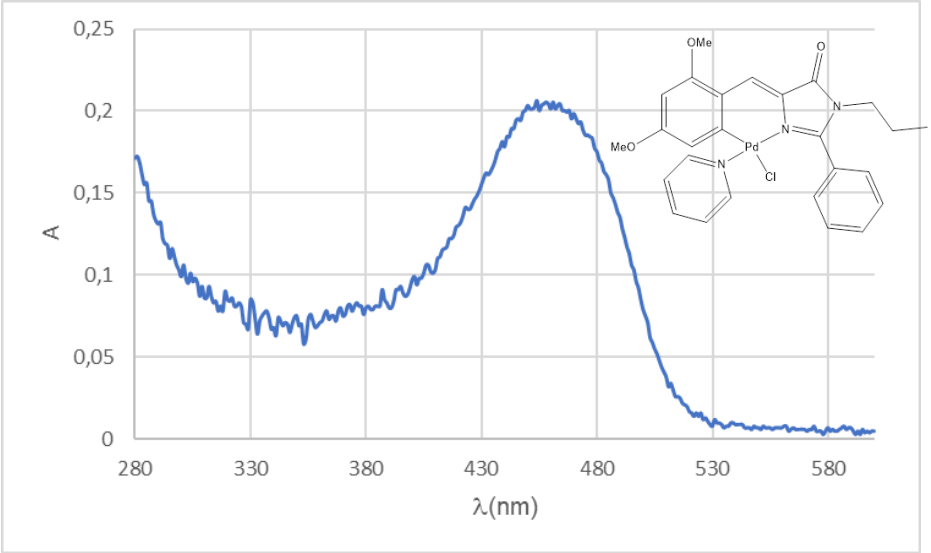

Figure S121. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **7e**

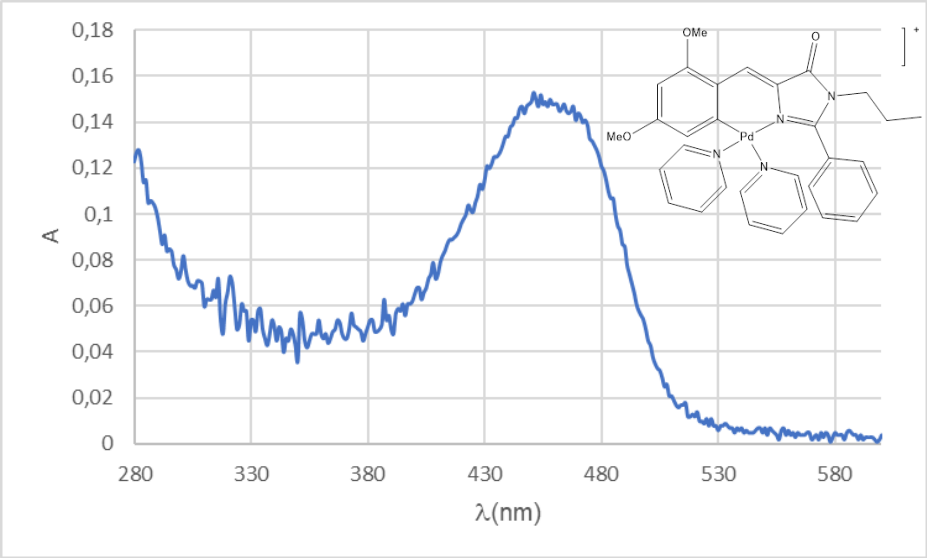

Figure S122. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **8e**

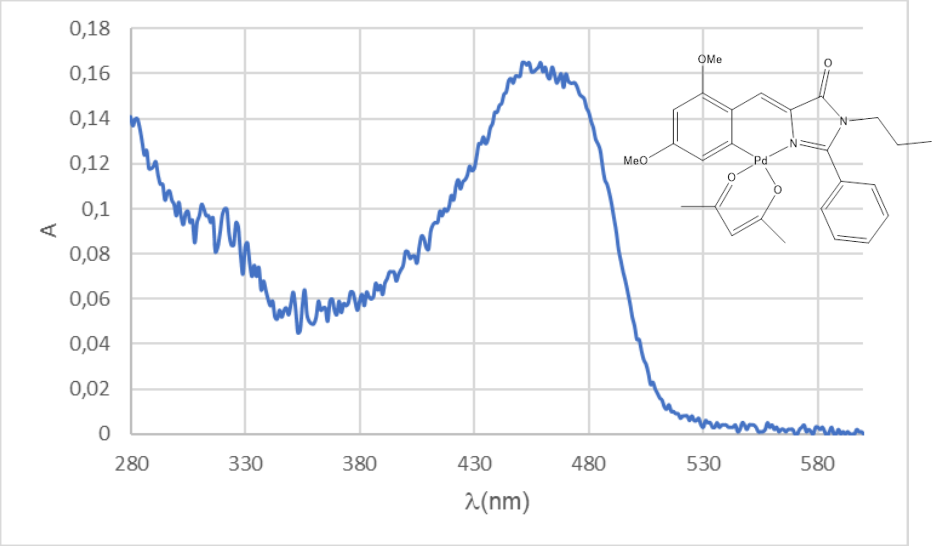

Figure S123. Absorption spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **9e**

8.- Excitation-emission spectra of imidazolones (2) and luminescent derivatives 5e-9e

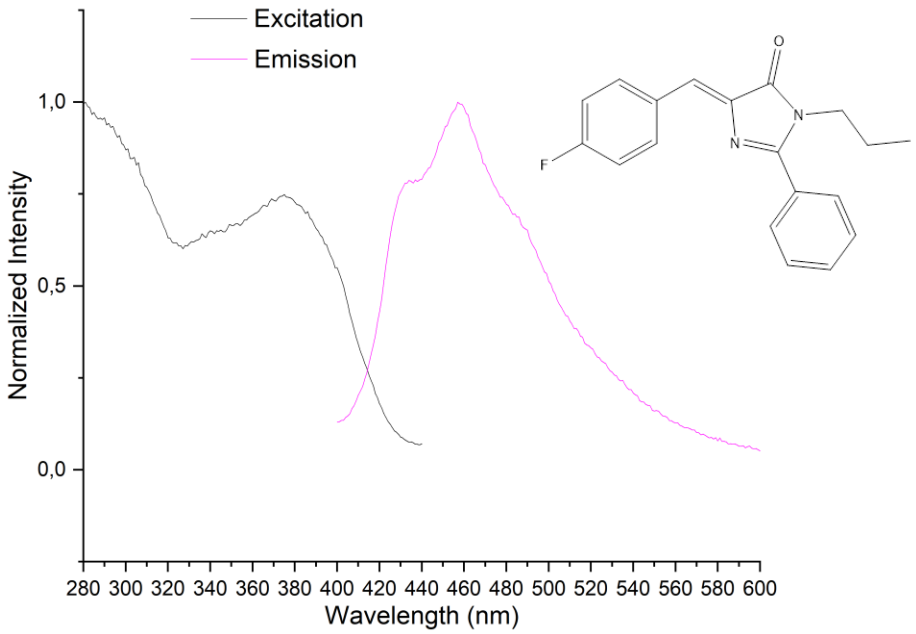

Figure S124. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2a**

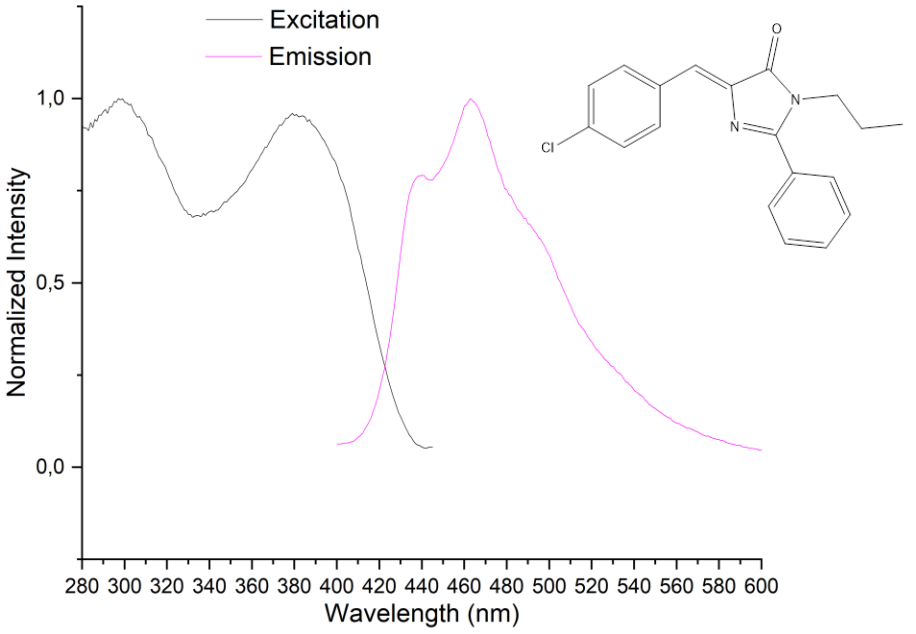

Figure S125. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2b**

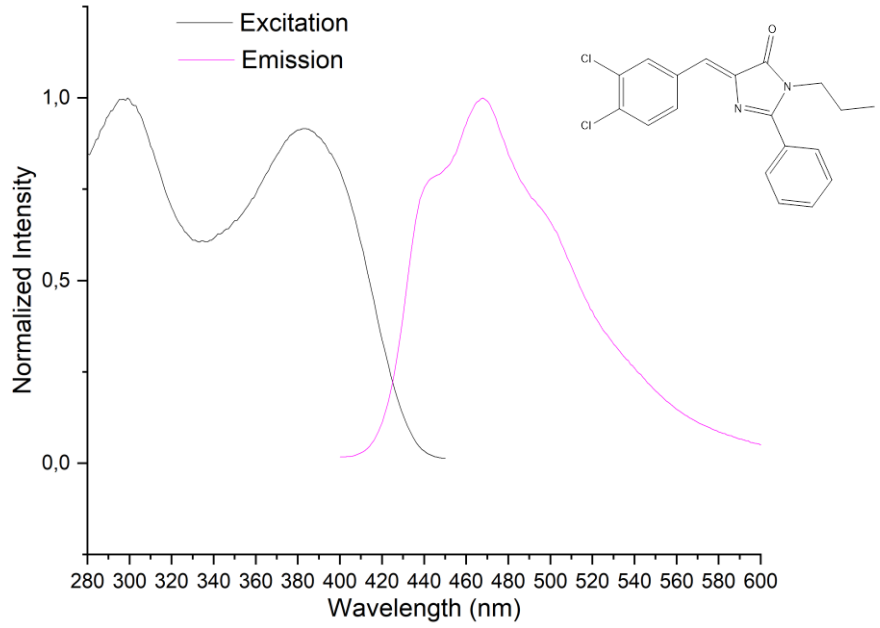

Figure S126. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2c**

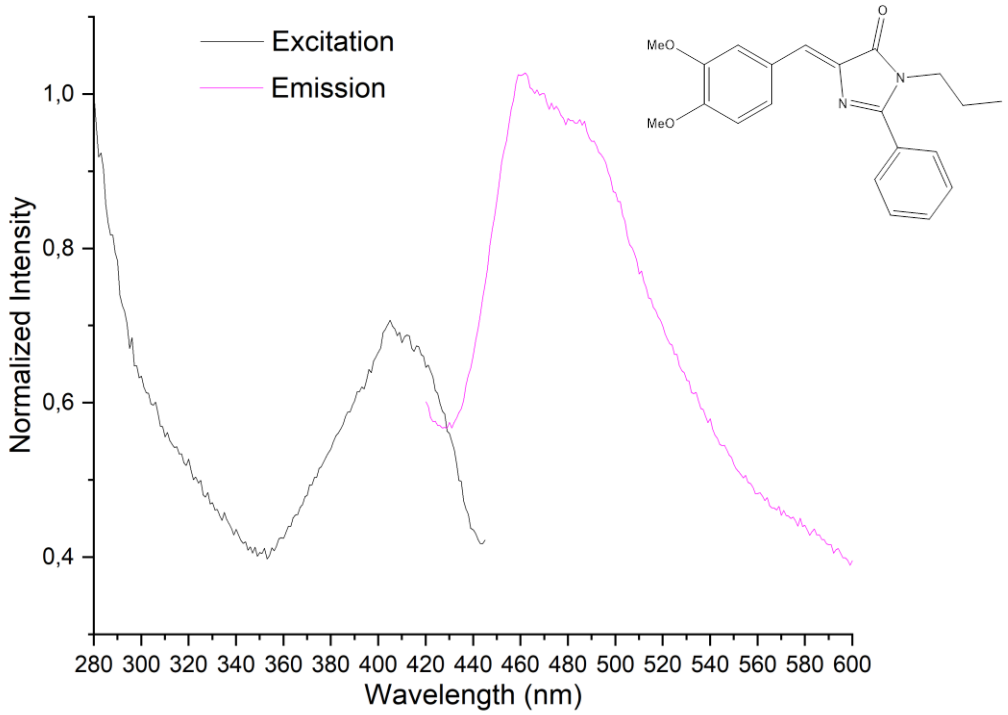

Figure S127. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2d**

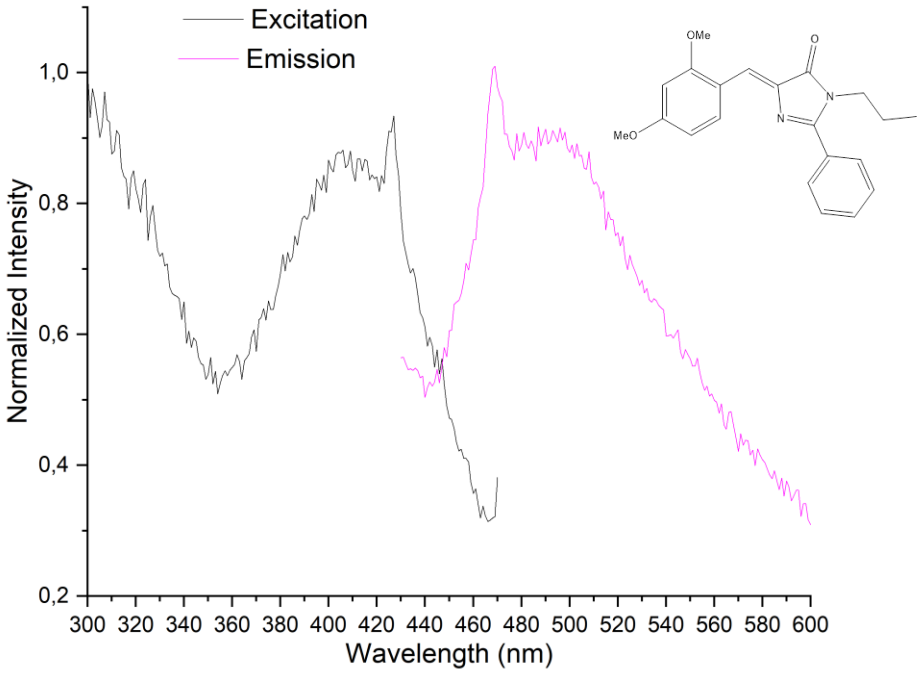

Figure S128. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of imidazolone **2e**

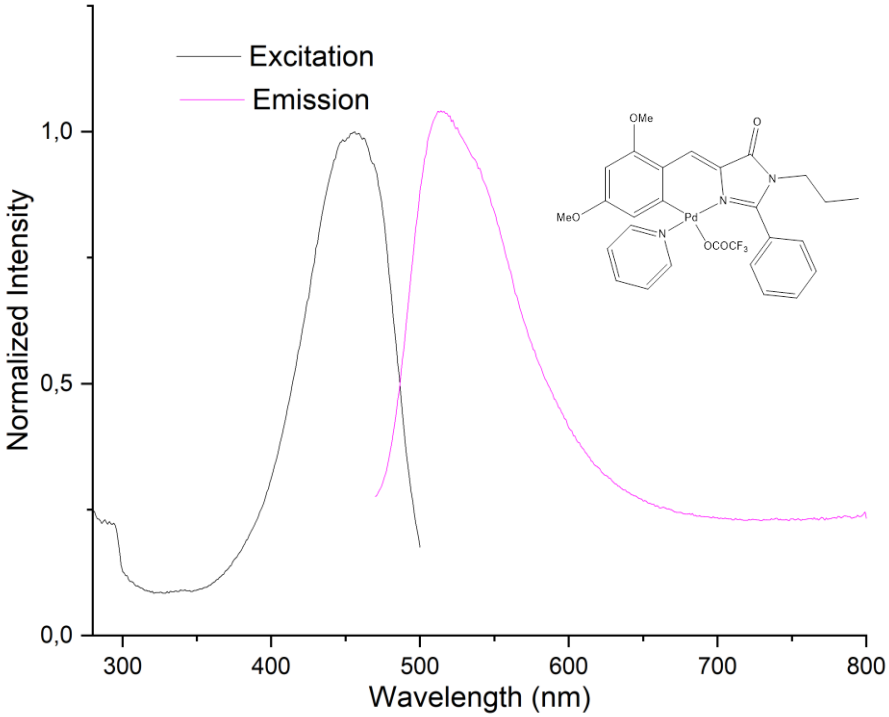

Figure S129. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **5e**

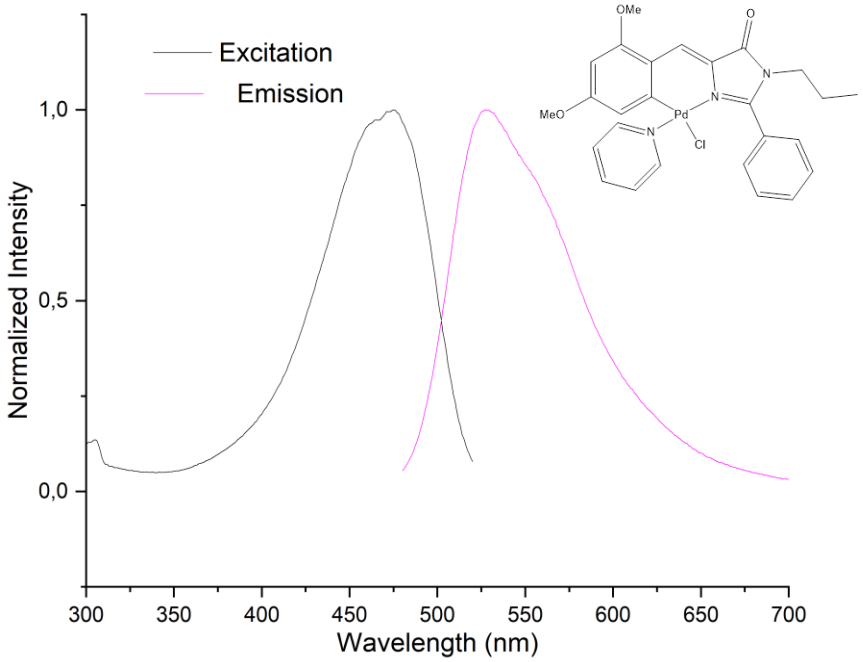

Figure S130. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **7e**

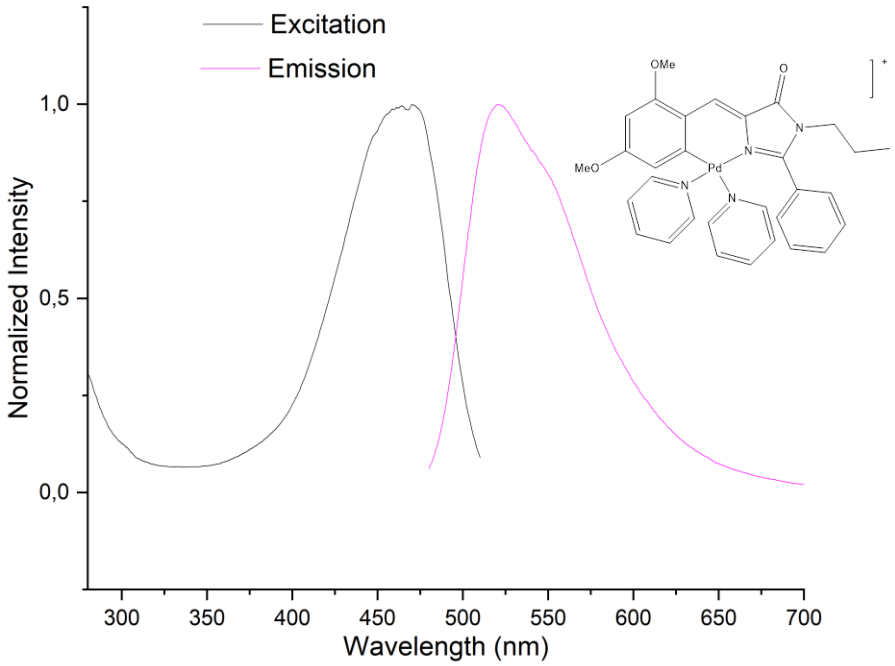

Figure S131. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **8e**

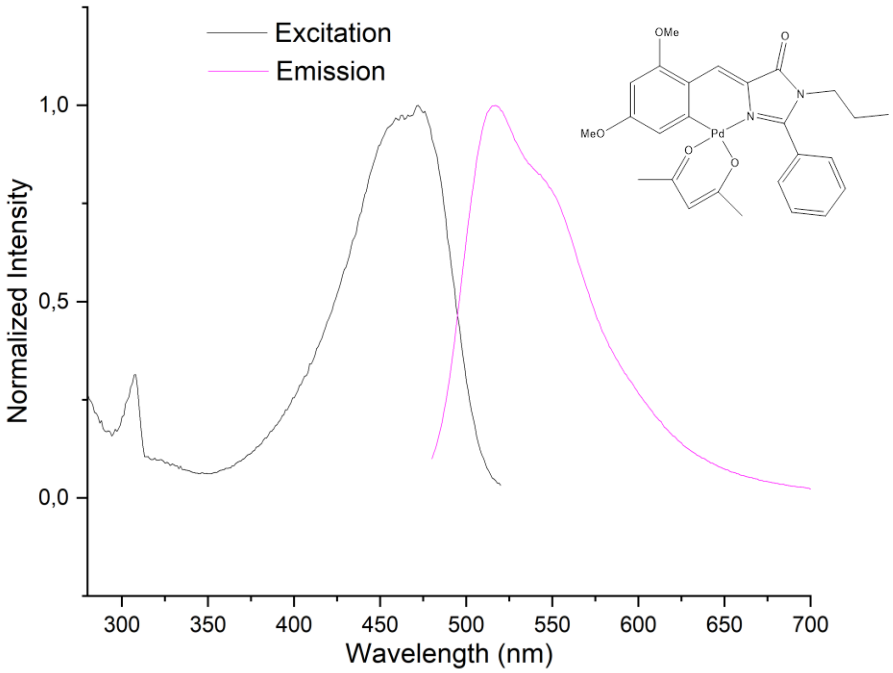

Figure S132. Excitation-emission spectrum (CH_2Cl_2, 10^{-5} M, r.t.) of orthopalladated **9e**

9.- HRMS spectra of selected compounds

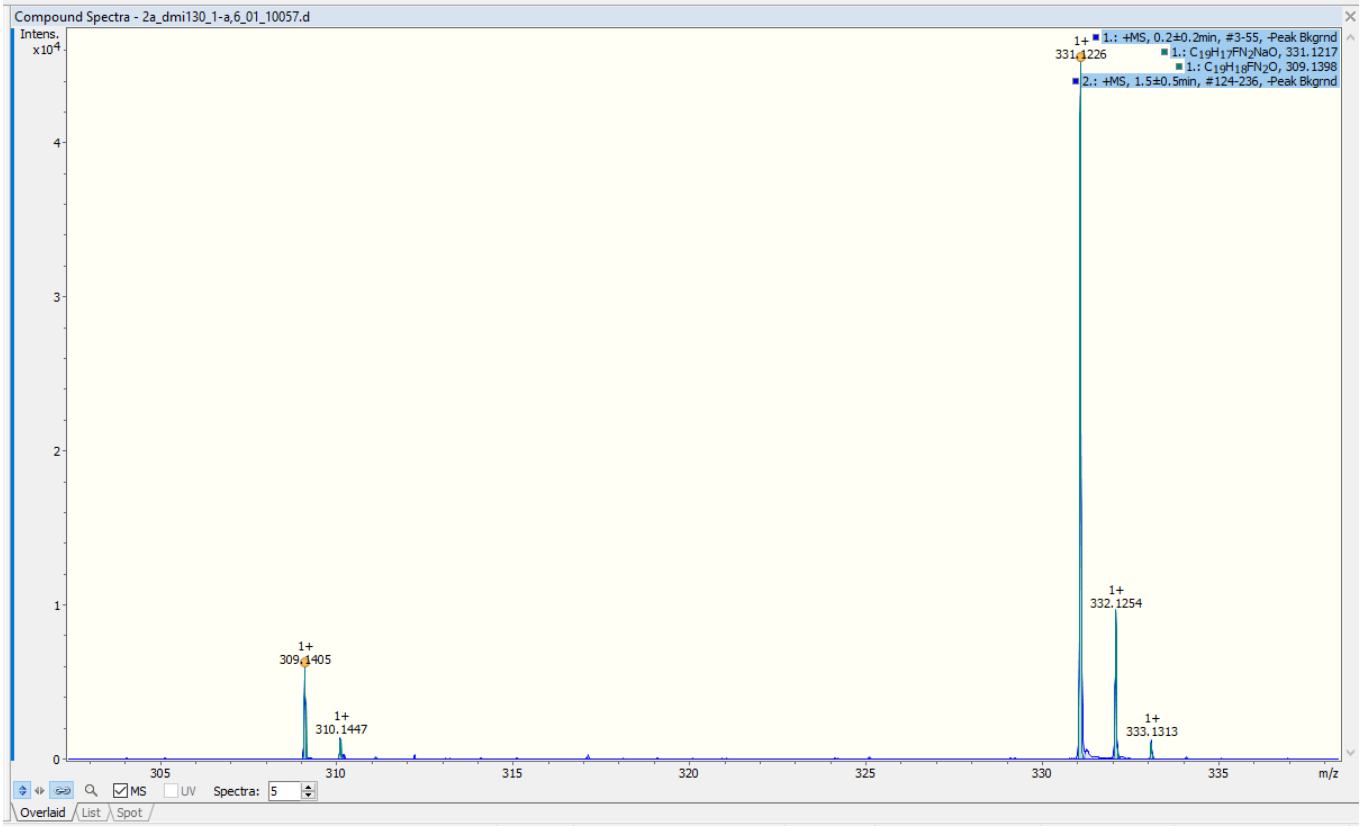

Figure S133. HRMS spectrum (ESI$^+$) of **2a**

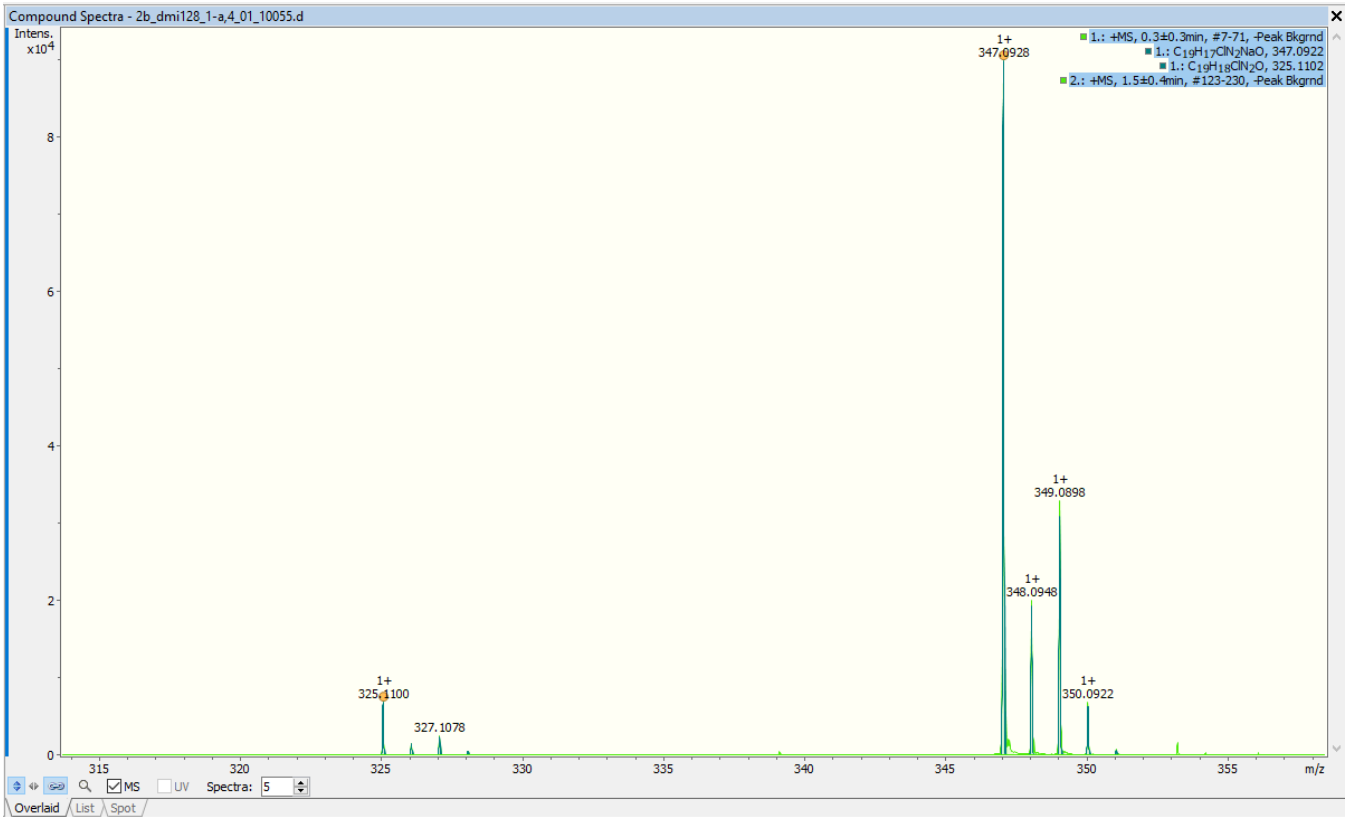

Figure S134. HRMS spectrum (ESI$^+$) of **2b**

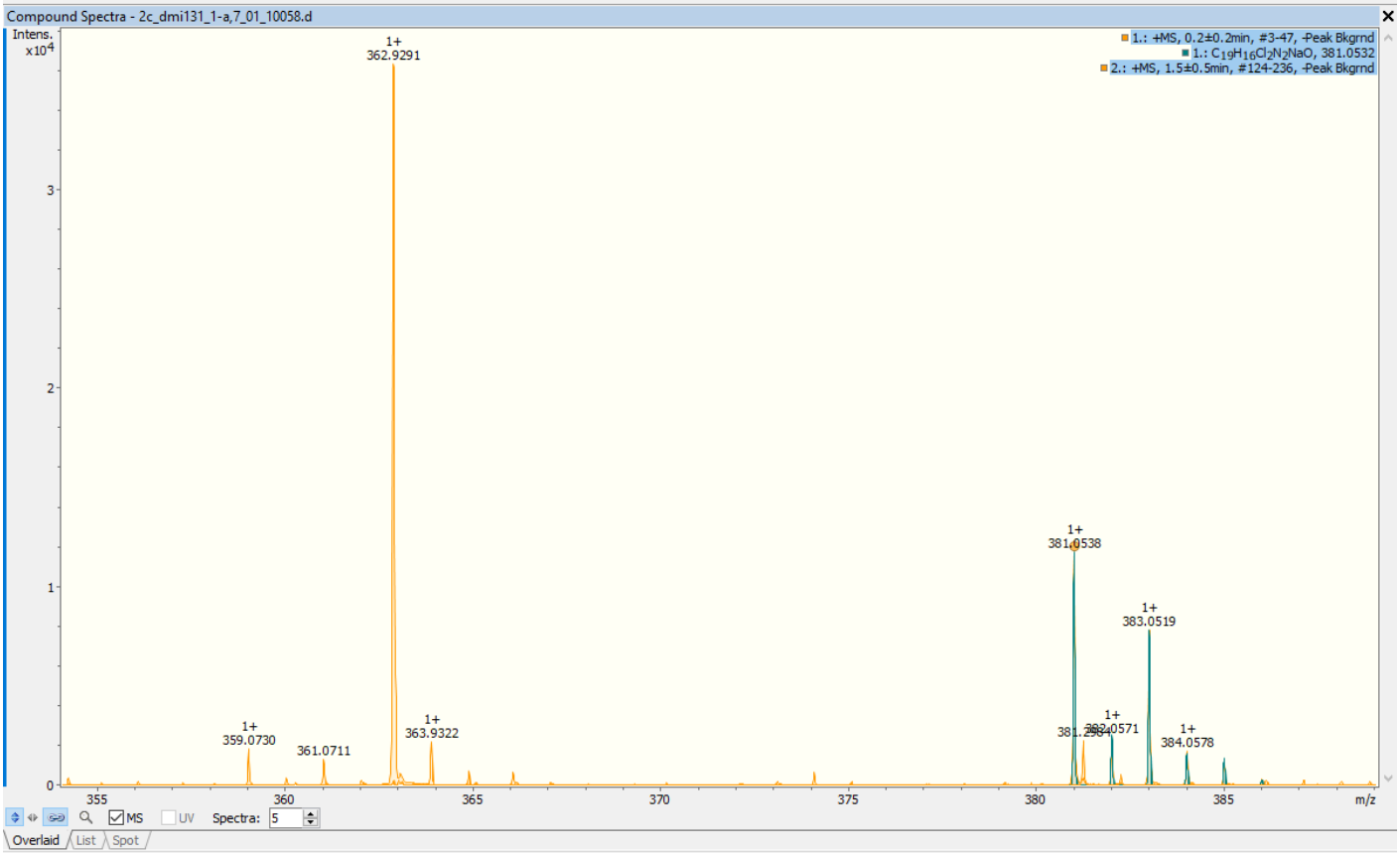

Figure S135. HRMS spectrum (ESI$^+$) of **2c**

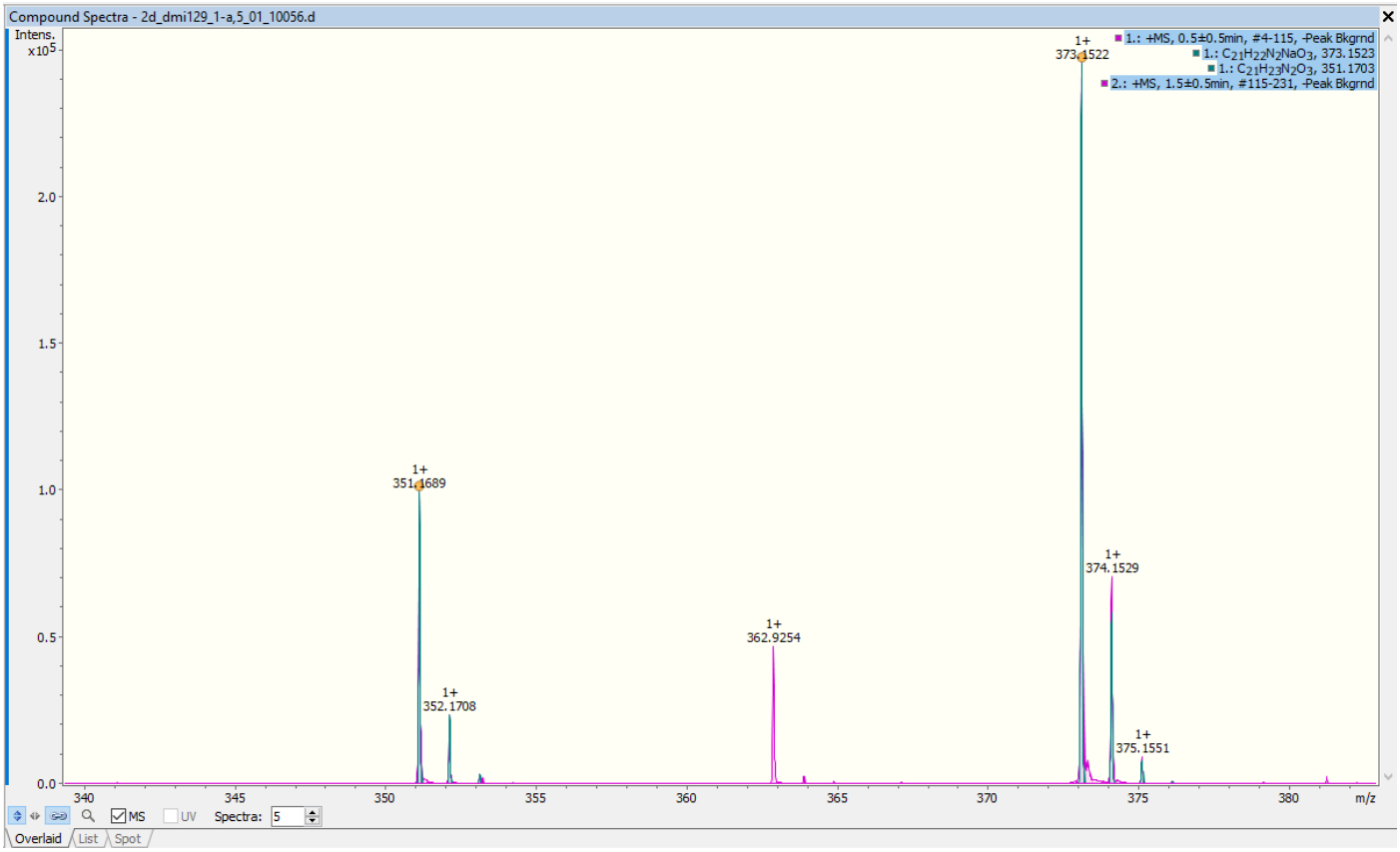

Figure S136. HRMS spectrum (ESI$^+$) of **2d**

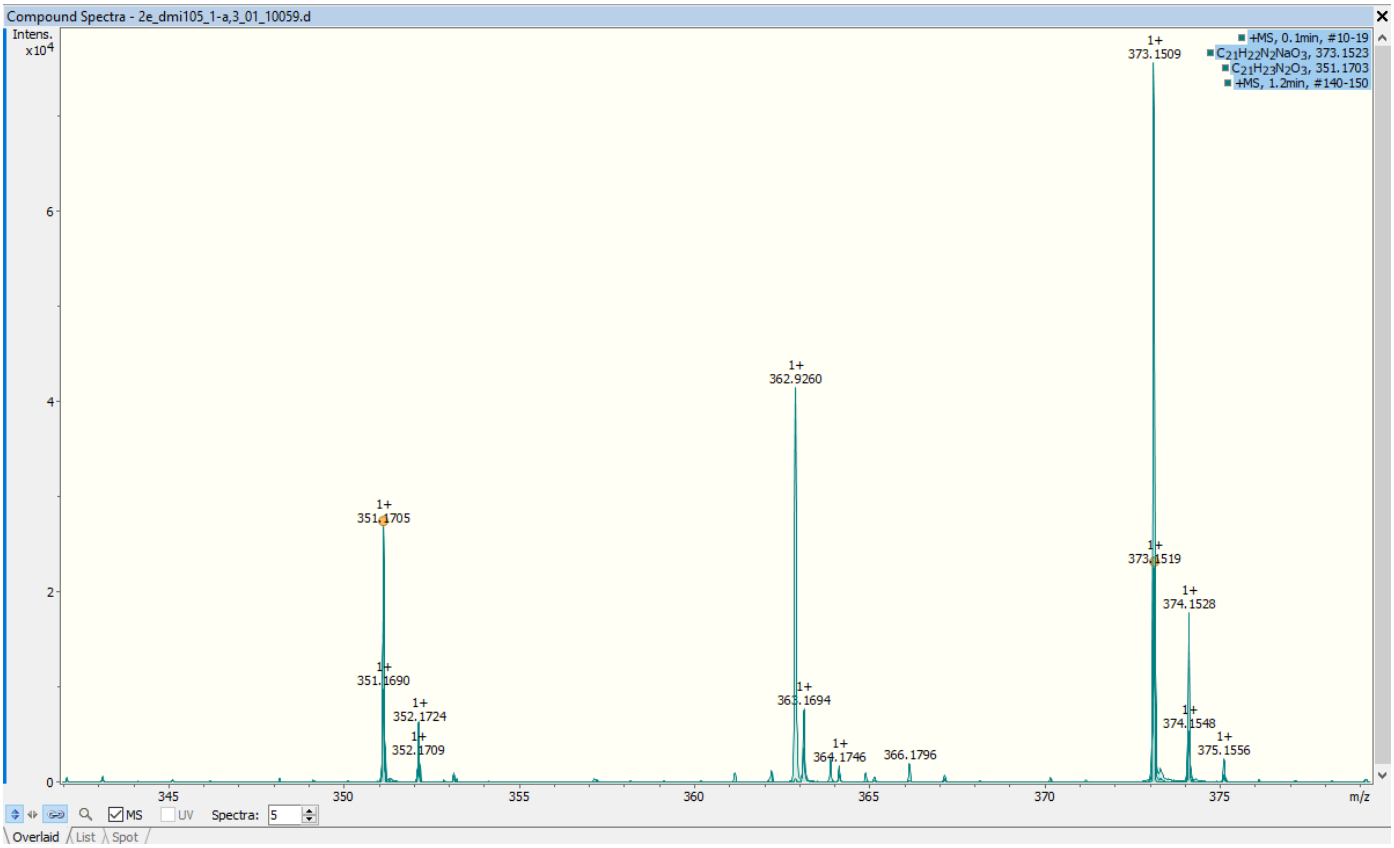

Figure S137. HRMS spectrum (ESI$^+$) of **2e**

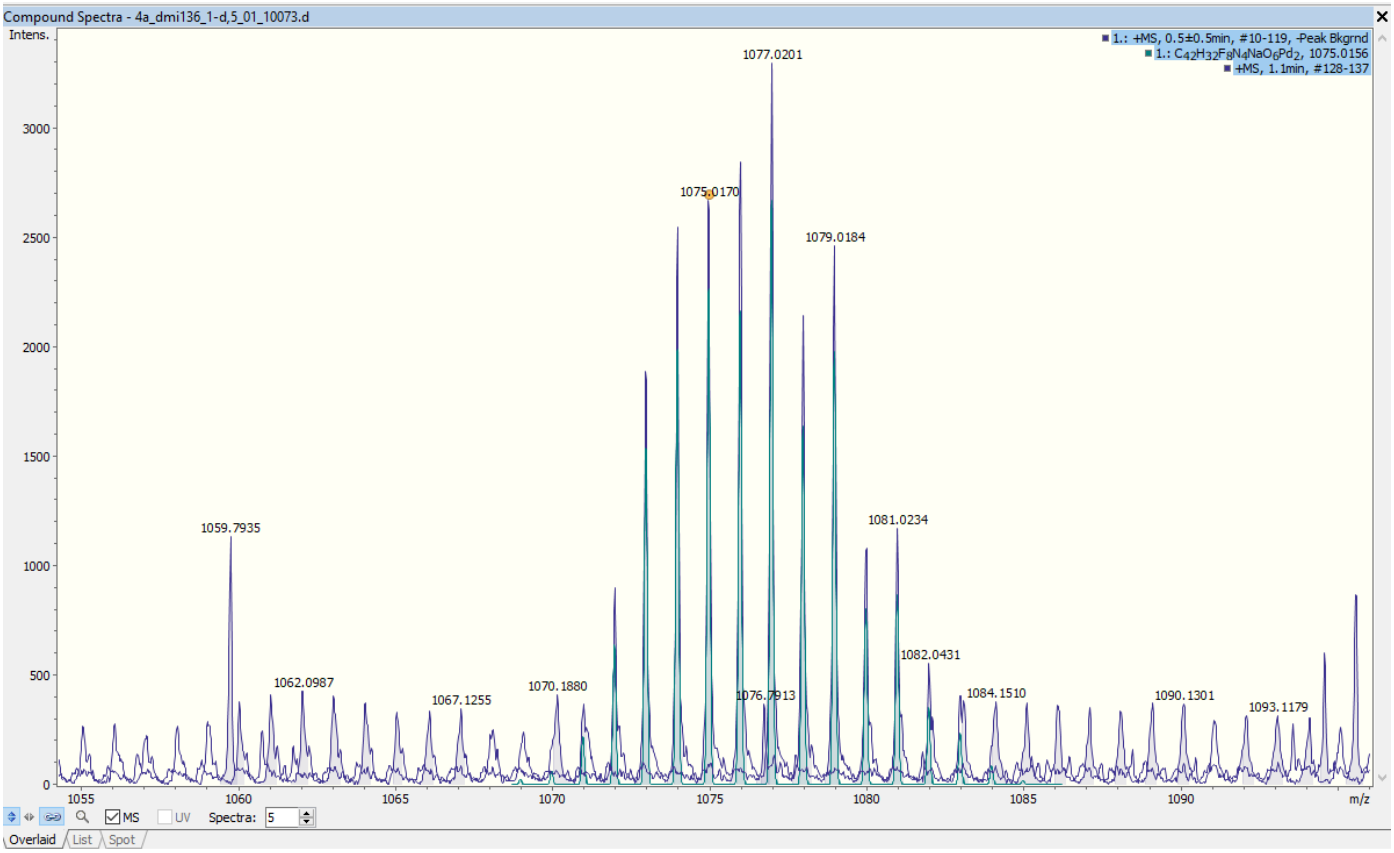

Figure S138. HRMS spectrum (ESI$^+$) of **4a**

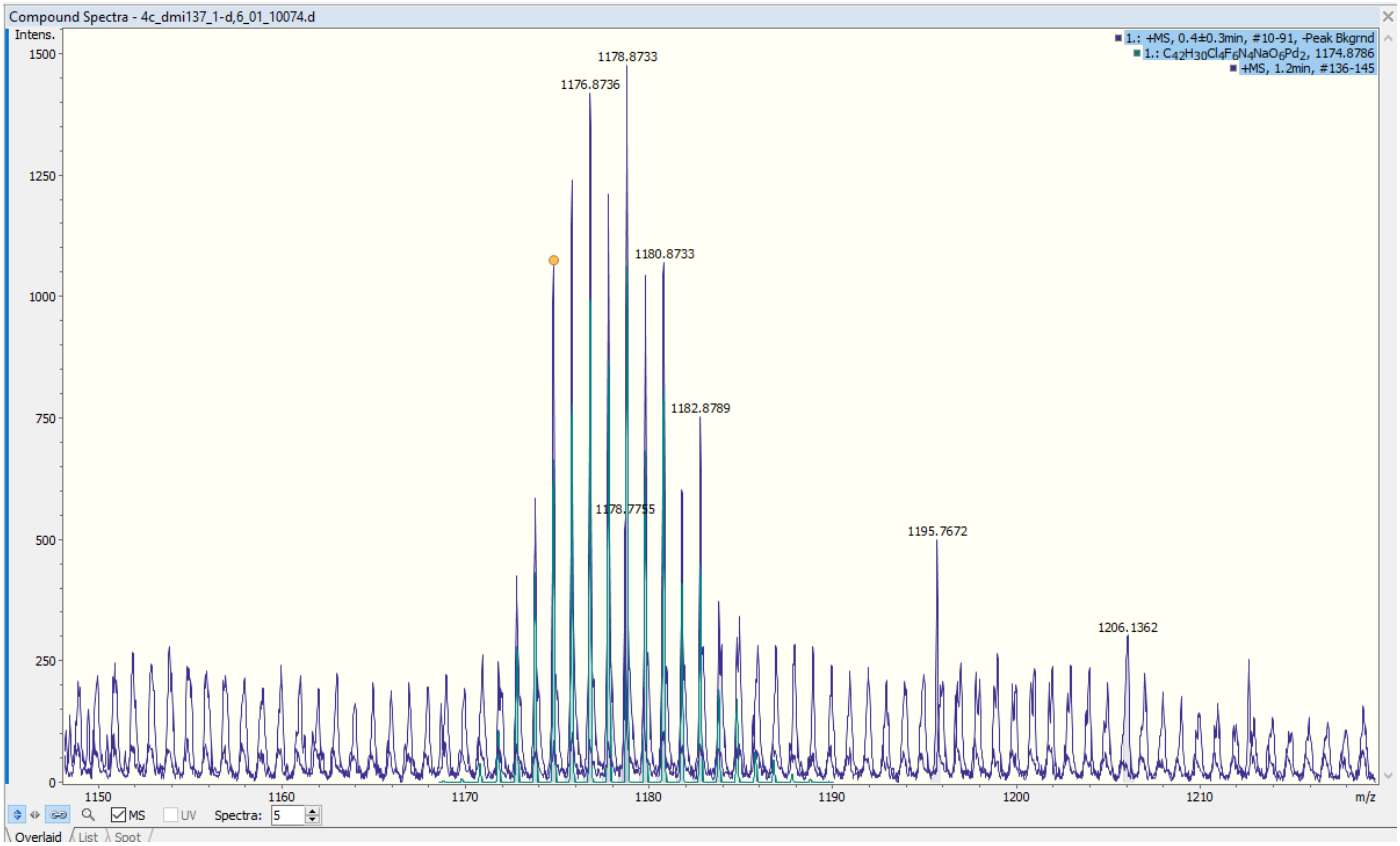

Figure S139. HRMS spectrum (ESI$^+$) of **4c**

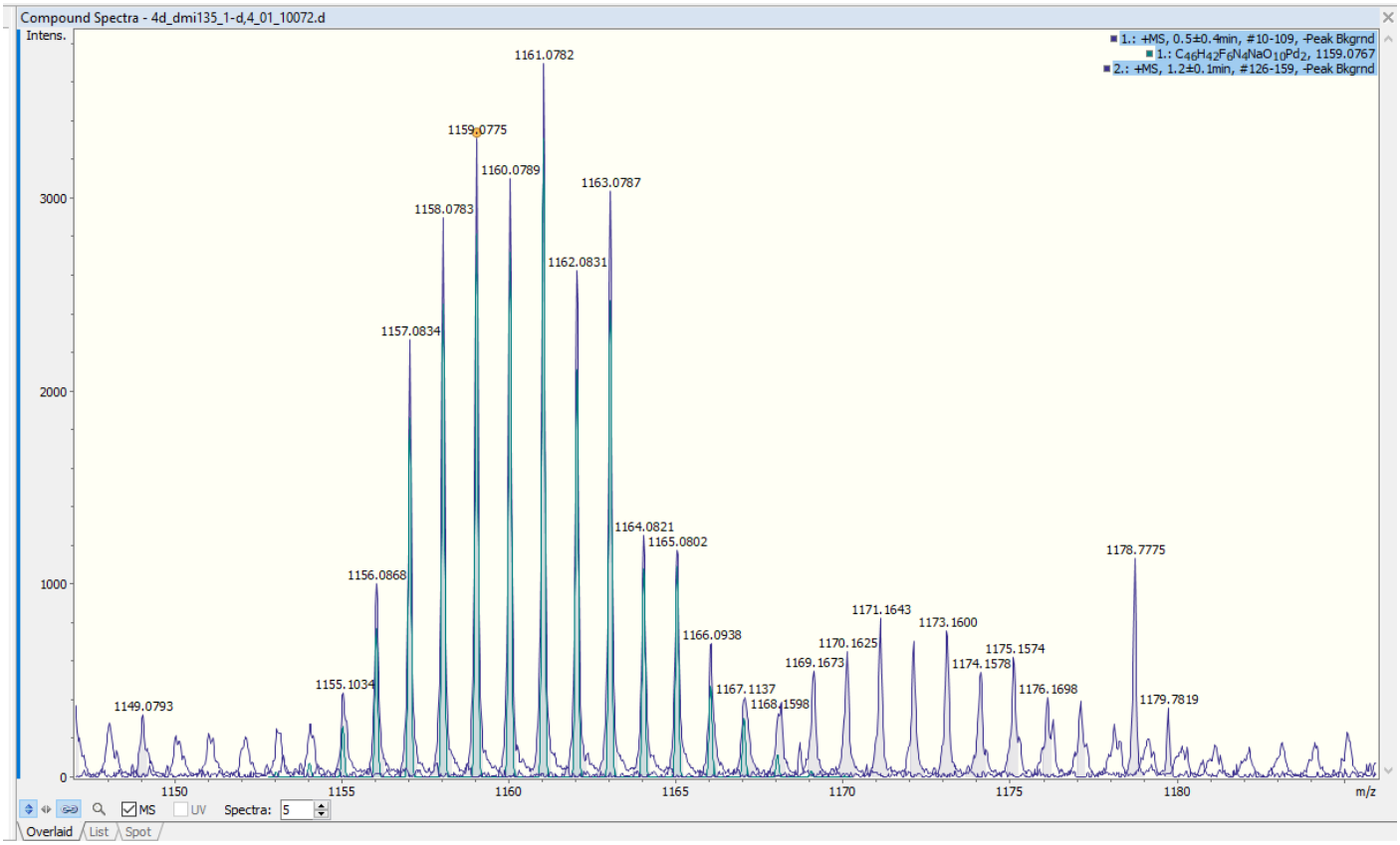

Figure S140. HRMS spectrum (ESI$^+$) of **4d**

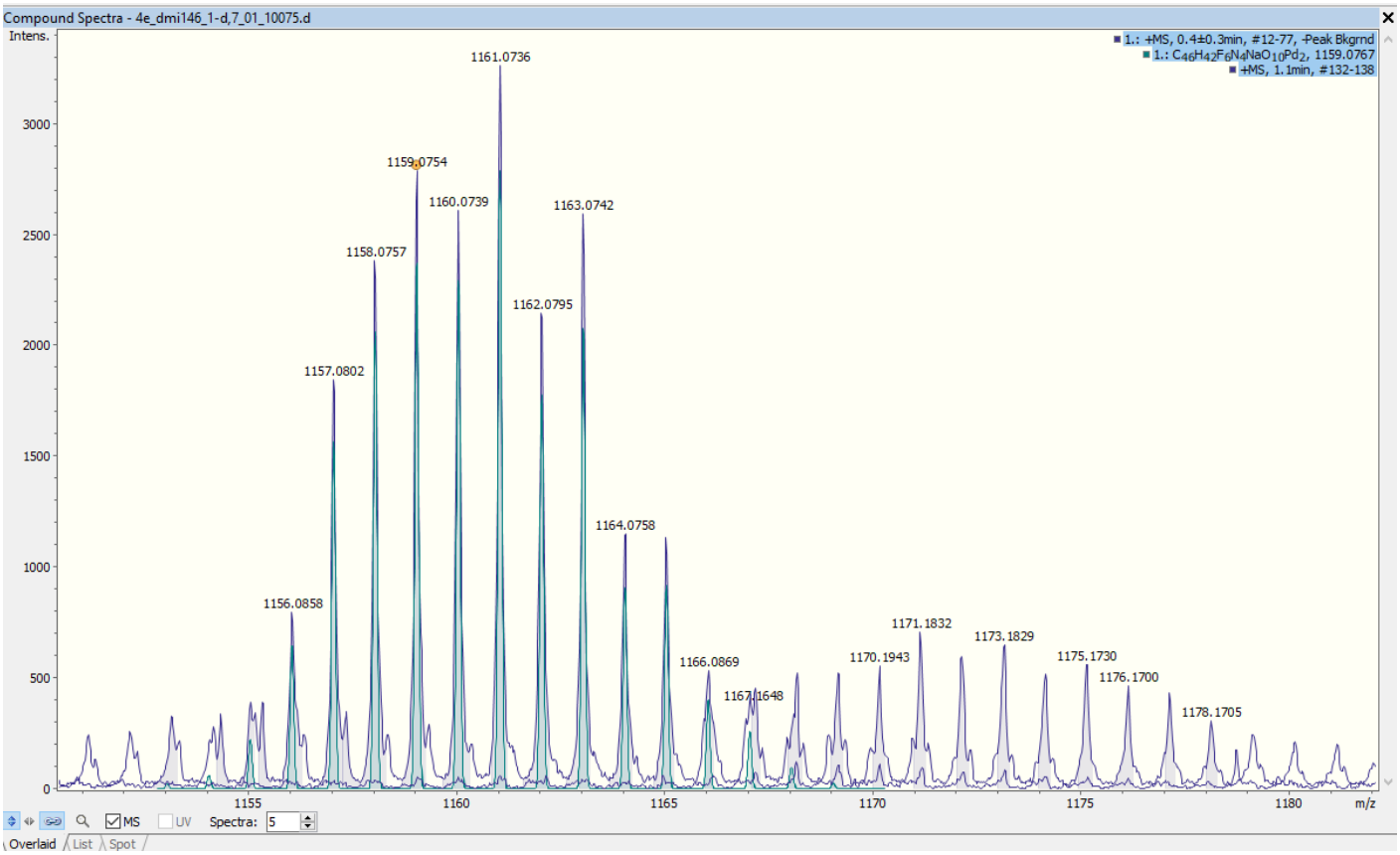

Figure S141. HRMS spectrum (ESI$^+$) of **4e**

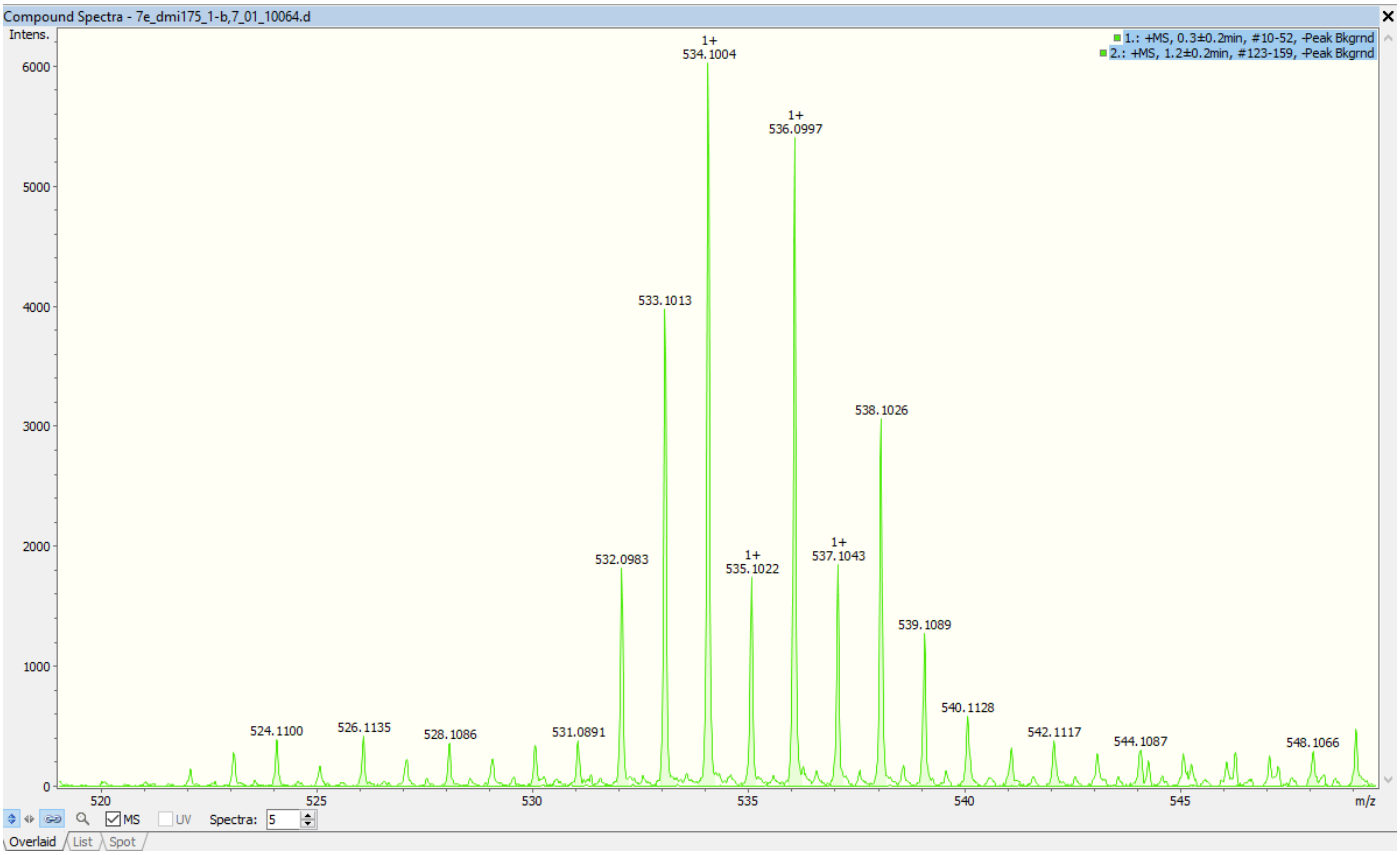

Figure S142. HRMS spectrum (ESI$^+$) of **7e**

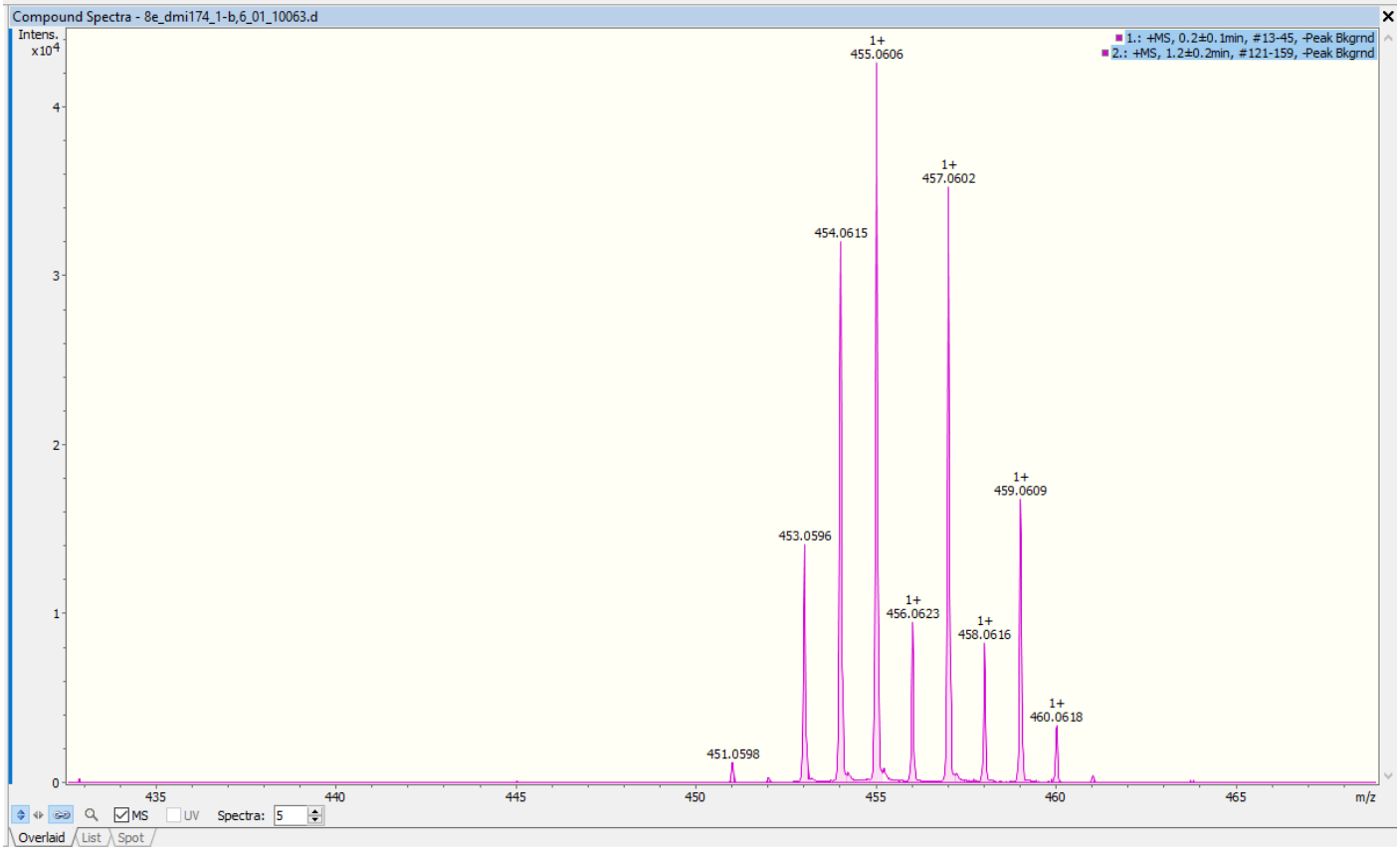

Figure S143. HRMS spectrum (ESI$^+$) of **8e**

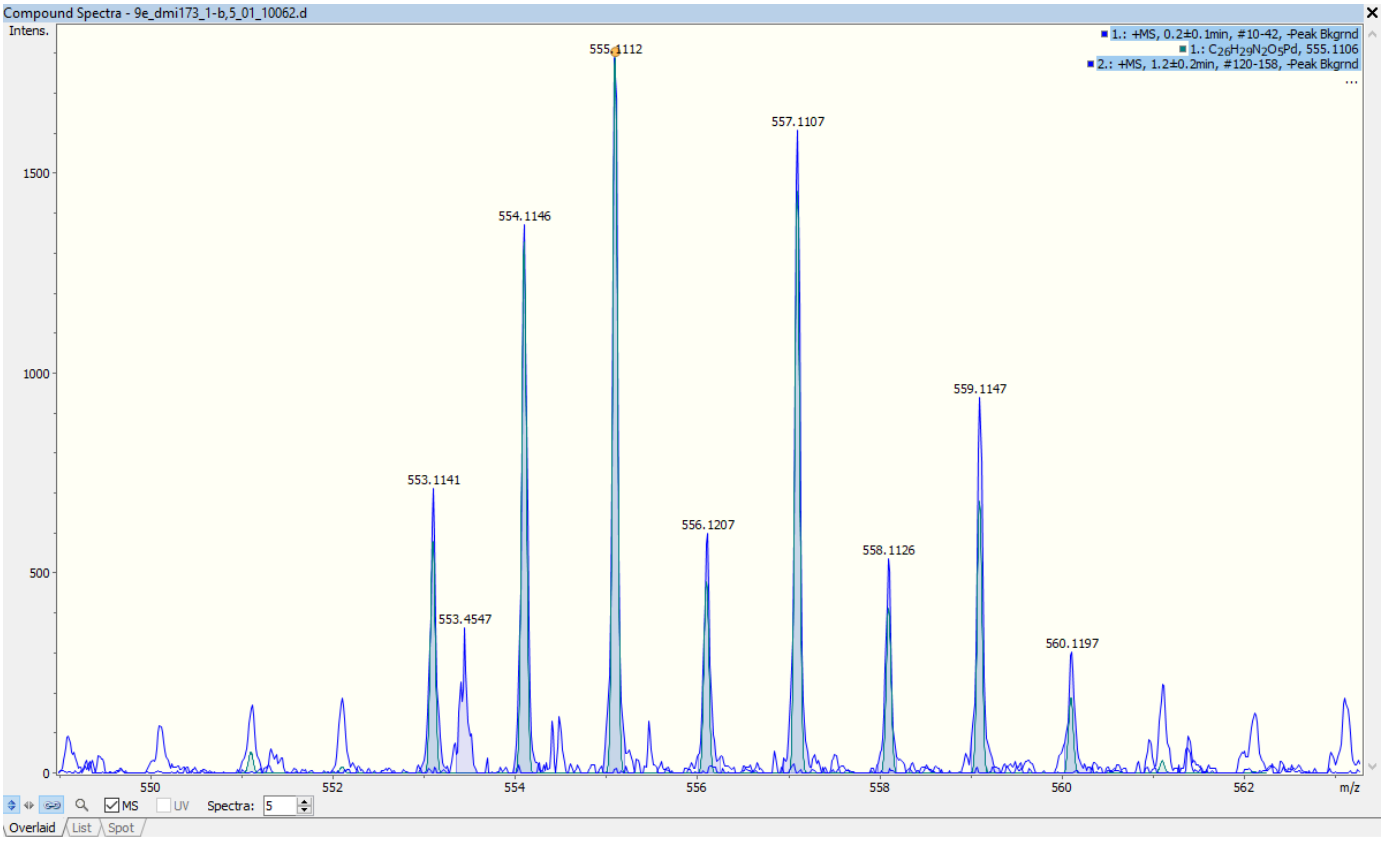

Figure S144. HRMS spectrum (ESI$^+$) of **9e**

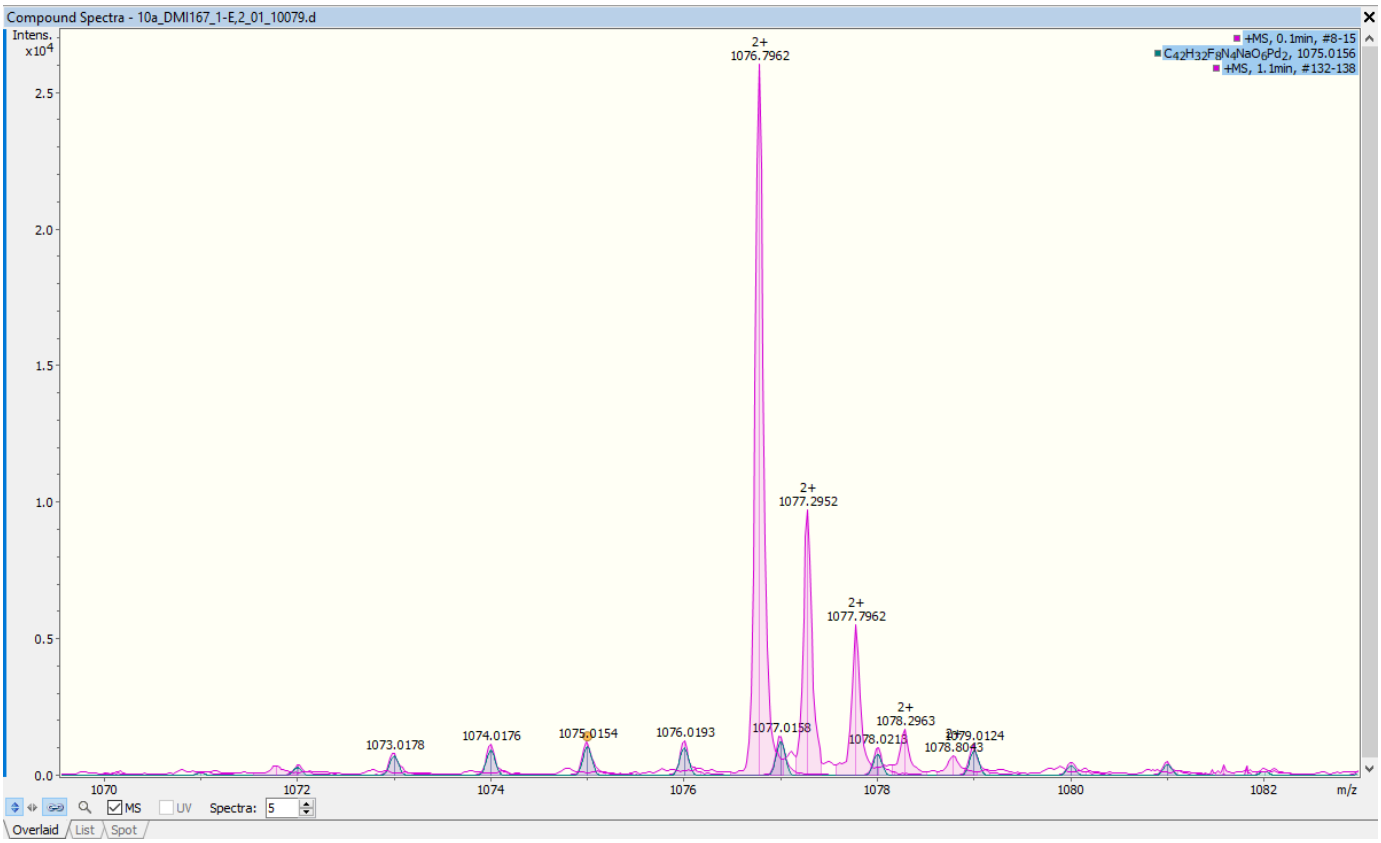

Figure S145. HRMS spectrum (ESI$^+$) of **10a**

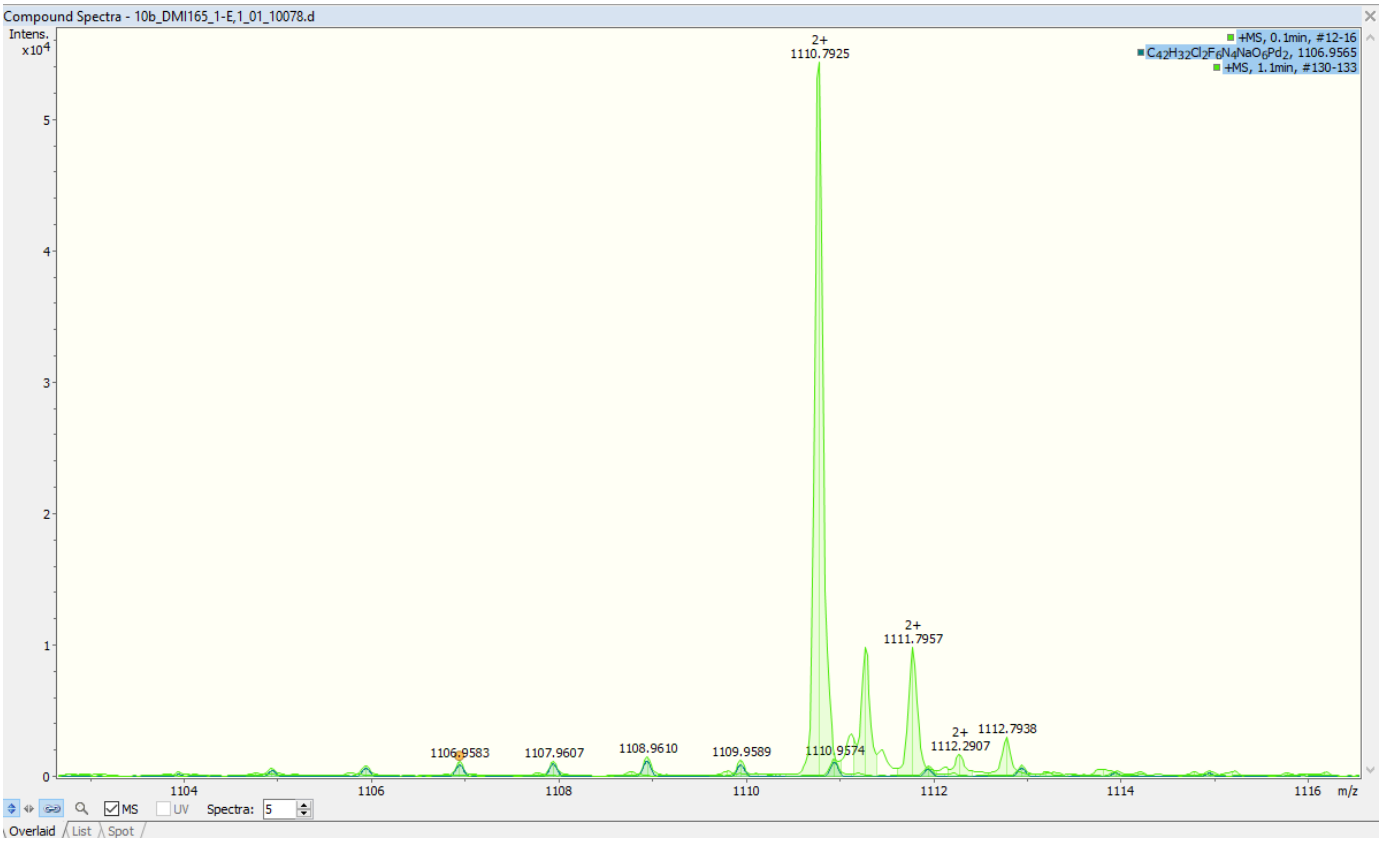

Figure S146. HRMS spectrum (ESI$^+$) of **10b**

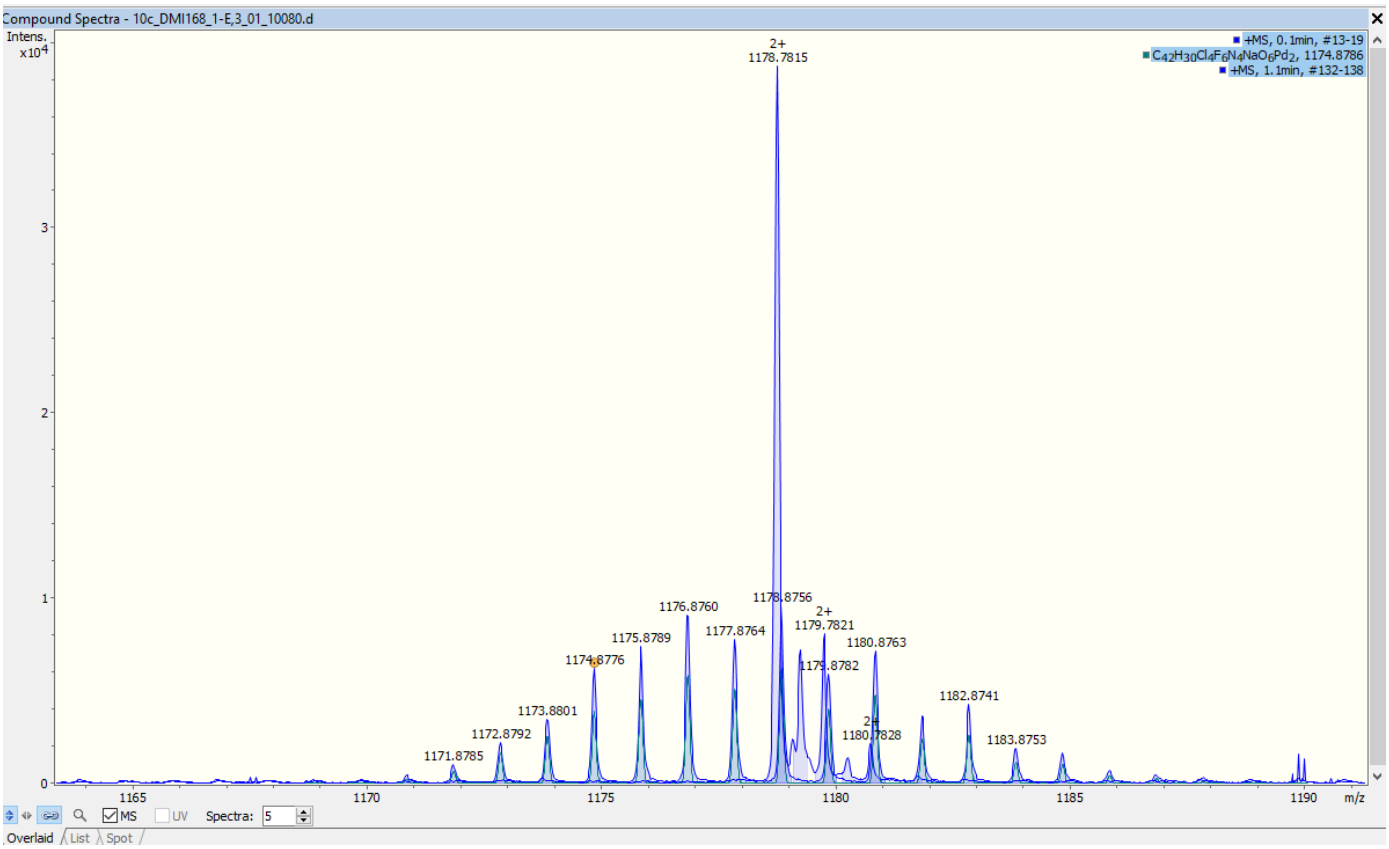

Figure S147. HRMS spectrum (ESI⁺) of **10c**

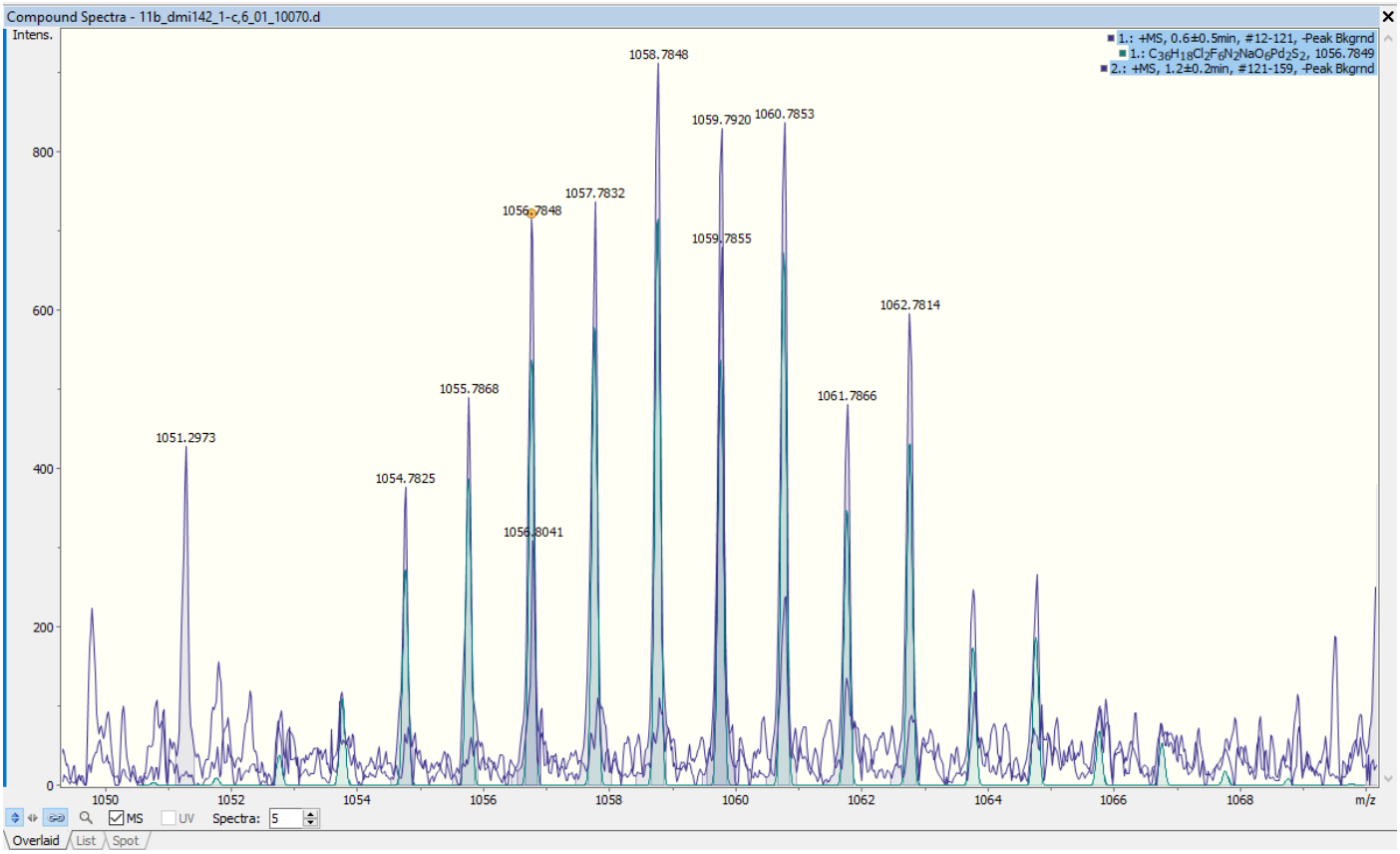

Figure S148. HRMS spectrum (ESI⁺) of **11b**

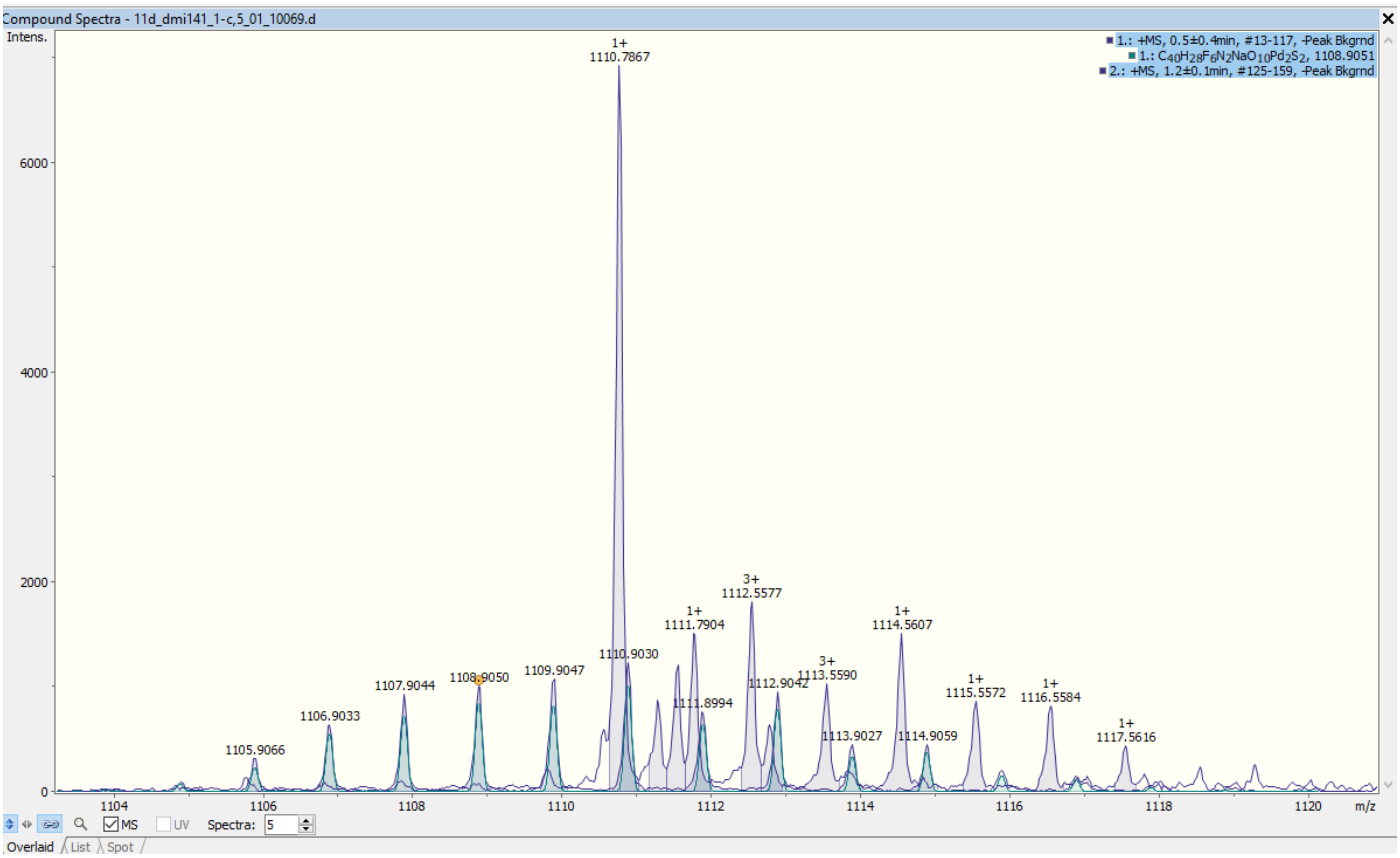

Figure S149. HRMS spectrum (ESI$^+$) of **11d**

10.- Computational results

In this section the supplementary information regarding the computational results will be provided. The ground state optimized geometries will be given for the selected complexes calculated with M06-2X functional.

Cartesian Coordinates

Complex 5e:

	X	Y	Z
O	-1.31736	4.13799	-1.74304
C	-1.24417	3.10110	-1.11153
N	-2.32788	2.44117	-0.50805
C	-3.64522	3.05980	-0.40430
C	-3.85575	3.74375	0.94396
C	-5.23607	4.38826	1.02349
C	-1.85093	1.34258	0.16458
C	-2.69969	0.44597	0.96020
C	-3.87943	-0.08641	0.43157
C	-4.62652	-0.98249	1.18725
C	-4.21451	-1.32772	2.47362
C	-3.04252	-0.79043	3.00217
C	-2.27799	0.09044	2.24428
N	-0.55494	1.20578	0.04245
C	-0.09019	2.27378	-0.73118
C	1.20694	2.57608	-0.95354
C	2.32807	1.86393	-0.38764
C	3.58858	2.53069	-0.37626
O	3.63374	3.71790	-1.02311
C	4.86067	4.42776	-1.03137
C	4.68045	1.98779	0.27995
C	4.53285	0.76489	0.94591
O	5.64424	0.31435	1.56913
C	5.57810	-0.94669	2.21456
C	3.31649	0.07656	0.92549
C	2.21873	0.60112	0.23653
Pd	0.61075	-0.52408	0.05593
O	-1.07612	-1.89501	-0.14552
C	-1.87624	-1.70809	-1.10772
C	-2.96568	-2.80134	-1.23053
F	-2.58260	-3.72530	-2.13054
F	-4.12995	-2.29274	-1.65921
F	-3.20588	-3.44159	-0.08171
O	-1.90062	-0.82443	-1.96130
N	1.78185	-2.28062	-0.17773
C	1.37872	-3.39826	0.44579
C	2.05799	-4.60285	0.31761
C	3.18093	-4.65718	-0.50080
C	3.58507	-3.50266	-1.16401
C	2.86293	-2.33291	-0.97186
H	-3.68640	3.78932	-1.21706
H	-4.41829	2.31137	-0.58646
H	-3.73680	3.00282	1.74310
H	-3.07150	4.49616	1.08107

H	-5.38256	4.88246	1.98607
H	-5.36442	5.13709	0.23638
H	-6.02405	3.63829	0.90616
H	-4.16256	0.13470	-0.59213
H	-5.52028	-1.42632	0.76228
H	-4.80334	-2.02453	3.06089
H	-2.72026	-1.06185	4.00167
H	-1.35671	0.50866	2.63797
H	1.40332	3.48096	-1.51983
H	5.64893	3.84504	-1.51872
H	4.67671	5.33885	-1.59798
H	5.17231	4.68423	-0.01374
H	5.64585	2.47472	0.30929
H	4.84415	-0.93740	3.02676
H	5.32285	-1.73960	1.50286
H	6.57085	-1.12834	2.62298
H	3.23223	-0.88168	1.42093
H	0.47861	-3.31132	1.04272
H	1.70227	-5.47663	0.84972
H	3.72937	-5.58476	-0.62441
H	4.44597	-3.49830	-1.82138
H	3.15106	-1.40482	-1.45192

Complex 7e:

	X	Y	Z
O	2.47114	3.47715	-1.76565
C	2.23094	2.39831	-1.24764
N	3.19043	1.50460	-0.75178
C	4.59651	1.88549	-0.60100
C	4.95815	2.22456	0.84459
C	4.09460	3.34074	1.42523
C	2.53709	0.41379	-0.21898
C	3.21662	-0.69641	0.46342
C	2.67741	-1.15660	1.66993
C	3.28669	-2.21111	2.34422
C	4.42537	-2.81544	1.81040
C	4.95662	-2.36226	0.60151
C	4.35905	-1.30053	-0.07110
N	1.23565	0.51036	-0.33402
C	0.95417	1.74569	-0.92574
C	-0.26339	2.33497	-0.96579
C	-1.45769	1.81069	-0.34858
C	-2.52787	2.72151	-0.12817
O	-2.39100	3.94610	-0.68418
C	-3.41088	4.91441	-0.47430
C	-3.63765	2.37369	0.64181
C	-3.68209	1.09161	1.19738
O	-4.69642	0.65675	1.97574
C	-5.76598	1.54978	2.26028
C	-2.66413	0.15734	0.95000
C	-1.56638	0.48977	0.16667
Pd	-0.28069	-0.92688	-0.34542
Cl	1.19519	-2.78321	-1.22989

N	-1.86745	-2.30118	-0.50279
C	-2.86839	-2.11095	-1.37531
C	-3.89760	-3.03179	-1.53169
C	-3.89476	-4.18162	-0.74671
C	-2.85542	-4.37437	0.15960
C	-1.85404	-3.41453	0.24535
H	4.71754	2.76555	-1.23818
H	5.23547	1.09586	-0.99733
H	6.01263	2.52176	0.84971
H	4.88017	1.32394	1.46458
H	4.40284	3.57749	2.44747
H	3.03761	3.05296	1.45894
H	4.17531	4.25329	0.82517
H	1.78838	-0.68177	2.07559
H	2.87095	-2.56303	3.28319
H	4.89657	-3.64241	2.33290
H	5.83114	-2.84405	0.17578
H	4.75152	-0.97861	-1.03018
H	-0.30203	3.33285	-1.39262
H	-4.36816	4.57110	-0.88011
H	-3.51686	5.14717	0.59045
H	-3.08636	5.80524	-1.01131
H	-4.43522	3.08228	0.81369
H	-6.28457	1.84599	1.34228
H	-6.45117	0.99811	2.90324
H	-5.40446	2.43851	2.78811
H	-2.78817	-0.83444	1.37256
H	-2.83739	-1.19359	-1.95392
H	-4.68224	-2.83990	-2.25470
H	-4.68848	-4.91613	-0.84094
H	-2.80879	-5.25458	0.79072
H	-1.01463	-3.52937	0.92291

Complex 8e:

	X	Y	Z
O	1.19591	4.20036	-1.74515
C	1.23311	3.12320	-1.18278
N	2.38990	2.53080	-0.63794
C	3.63462	3.28175	-0.47467
C	3.81925	3.78801	0.95572
C	2.62485	4.60004	1.44945
C	2.03330	1.34973	-0.03735
C	2.97854	0.49970	0.70090
C	4.19977	0.11658	0.13748
C	5.06366	-0.69810	0.86140
C	4.71966	-1.11736	2.14637
C	3.50180	-0.73590	2.70627
C	2.62479	0.06667	1.98310
N	0.75382	1.09316	-0.16269
C	0.17143	2.16852	-0.84072
C	-1.15717	2.38259	-0.97686
C	-2.19917	1.56918	-0.40662
C	-3.50087	2.13860	-0.34527

O	-3.65882	3.32280	-0.97362
C	-4.92541	3.95989	-0.91933
C	-4.53748	1.51706	0.34775
C	-4.27550	0.30397	0.98655
O	-5.19452	-0.37389	1.70203
C	-6.49356	0.18374	1.82840
C	-3.01325	-0.30469	0.89450
C	-1.98084	0.29870	0.19388
Pd	-0.29416	-0.70120	-0.07788
N	-1.36587	-2.51950	-0.20310
C	-1.19998	-3.47781	0.72088
C	-1.83801	-4.70743	0.63709
C	-2.67407	-4.95465	-0.44712
C	-2.84553	-3.96043	-1.40470
C	-2.17794	-2.75383	-1.24505
N	1.54086	-1.85570	-0.63823
C	2.18707	-2.71252	0.16115
C	3.31336	-3.41415	-0.25028
C	3.78823	-3.21670	-1.54275
C	3.12039	-2.32405	-2.37526
C	2.00160	-1.66466	-1.88249
H	4.47887	2.66847	-0.79225
H	3.54352	4.12043	-1.16934
H	4.72666	4.39996	0.96809
H	4.00240	2.93856	1.62346
H	2.39745	5.42031	0.76214
H	1.72802	3.97676	1.53359
H	2.82385	5.02336	2.43613
H	4.45317	0.42151	-0.87339
H	6.00315	-1.01181	0.41928
H	5.40104	-1.74620	2.70965
H	3.23515	-1.06143	3.70598
H	1.67359	0.37502	2.40670
H	-1.44348	3.30592	-1.47054
H	-5.20574	4.18692	0.11394
H	-5.69801	3.33871	-1.38313
H	-4.81719	4.88629	-1.48019
H	-5.51633	1.97006	0.39744
H	-6.45468	1.16345	2.31515
H	-7.05916	-0.50907	2.44871
H	-6.97760	0.27863	0.85111
H	-2.89816	-1.26791	1.37854
H	-0.54732	-3.23653	1.55360
H	-1.67870	-5.44824	1.41091
H	-3.18659	-5.90561	-0.54180
H	-3.48884	-4.10663	-2.26364
H	-2.29309	-1.94422	-1.95708
H	1.79831	-2.82229	1.16868
H	3.80685	-4.09031	0.43757
H	4.66675	-3.74685	-1.89433
H	3.45438	-2.13617	-3.38853
H	1.45131	-0.95513	-2.49437