Supporting information

Boosting gold(I) catalysis via weak interactions: new fine-tunable ImPy ligands

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General methods

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz).

^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm).

^{19}F-NMR spectra were recorded on a Varian 400 (377 MHz). Chemical shifts are reported in ppm from $CFCl_3$.

GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: m/z (rel. intense).

LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer.

Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer.

Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected.

Chromatographic purification was done with 240-400 mesh silica gel.

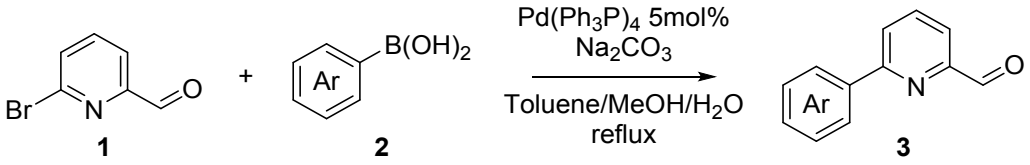
Anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Ethyl acetate was dried on activated 5Å molecular sieves.

Commercially available chemicals were purchased from Sigma Aldrich, Fluorochem and TCI and used without any further purification.

These compound were synthetized according to literature: **7**,[1] XX(PROBENZOIL)[2] , XX(2-phenylacetilene-benzaldeide)[3]

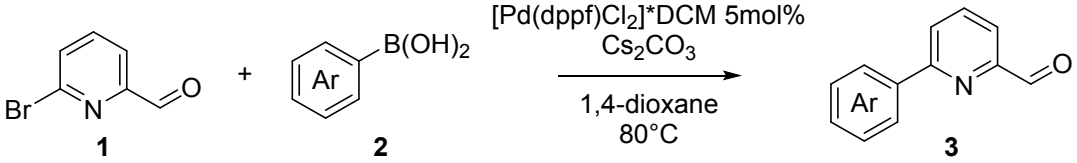
General procedure for 3a-f.

Procedure A)



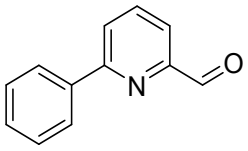
A 2 necked-round bottom flask equipped with a condenser was evacuated with vacuum and back-filled with N_2 (3 times). To a solution of 6-bromopyridine-2-carboxaldehyde (**1**, 279 mg, 1.5 mmol, 1 eq) dissolved in the minimum amount of toluene was added a solution of aryl boronic acid (**2**, 2.25mmol, 1.5 eq, 2.5 M in MeOH) and 1.5mL of aqueous solution of Na_2CO_3 (318mg, 3mmol, 2 eq, 2 M) followed by a degassing with N_2 under vigorous stirring (2 minutes). Then, 4.3mL of degassed toluene solution of $[(Ph_3P)_4Pd]$ (5 mol%, 86mg, 0.075 mmol, 20 mg/mL) was added and the mixture was heated to reflux. The reaction was monitored by TLC (10/1 *c*Hex/AcOEt). The reaction was cooled down to room temperature and extracted with DCM (2x15mL). The organic phase was dried over Na_2SO_4 and evaporated. The product was purified by flash chromatography with *n*Hexane/AcOEt 20/1 as eluent.[4]

Procedure B)

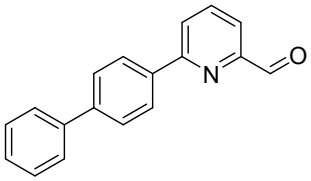


To a Schlenk tube 6-bromopyridine-2-carboxaldehyde (**1**, 186mg, 1mmol, 1 eq), aryl boronic acid (**2**, 1.5mmol, 1.5 eq), Cs_2CO_3 (978mg, 3mmol, 3eq) and 5mL 1,4-dioxane were added, and the mixture was degassed with N_2 flux. Then, $[Pd(dppf)Cl_2]$•DCM adduct (65mg, 0.075mmol, 5 mol%) was added and the mixture stirred at 80 °C overnight. After complete consumption of **1** by TLC, water was added and the biphasic mixture extracted with ethyl acetate (2x10mL). The product was purified by flash chromatography with *n*-Hex/AcOEt 10:1.[5]

6-Phenylpicolinaldehyde (**3a**), procedure A, yield 95%, white solid. ^1H, ^{13}C NMR, GC-MS(EI) spectra were in agreement with reported values.[2]



6-([1,1'-Biphenyl]-4-yl)picolinaldehyde (**3b**)*,* procedure A, yield 80%, white solid.



^1H-NMR (400 MHz, $CDCl_3$) δ =10.19 (d, J = 0.9 Hz, 1H), 8.17 (d, J = 8.4 Hz, 2H), 8.03 – 7.88 (m, 3H), 7.75 (d, J = 8.5 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.50 – 7.44 (m, 2H), 7.41 – 7.35 (m, 1H).

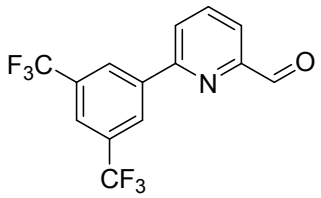
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 193.89, 157.50, 152.75 142.47, 140.35, 137.83, 136.91, 128.87, 127.71, 127.64, 127.40, 127.11, 124.32, 119.74.

GC-MS(EI): 259 (100%, M^{*+}); 230 (63%, -CHO); 202 (22%)

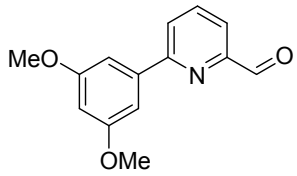
Melting point: 145-148 °C.

Elemental analysis, calc. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; found: C, 83.44; H, 4.97.

6-(3,5-bis(trifluoromethyl)phenyl)picolinaldehyde (**3c**), procedure B, yield 62%, white solid. ^{1}H, ^{13}C NMR, GC-MS were in agreement with reported values.[3]



6-(3,5-dimethoxyphenyl)picolinaldehyde (**3d**), procedure B, yield 32%, white solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ =10.12 (d, *J* = 1.1 Hz, 1H), 7.85 (s, 3H), 7.20 (dd, J = 2.3, 1.1 Hz, 2H), 6.53 (td, J = 2.3, 1.1 Hz, 1H), 3.84 (s, 6H).

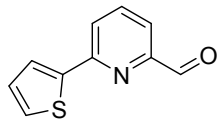
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 193.81, 161.26, 157.46, 152.52, 140.07, 137.75, 124.59, 119.93, 105.10, 101.65, 55.46.

GC-MS(EI): 243 (100%, M^{*+}), 213 (38%)

Melting point: 106-108 °C.

Elemental analysis, calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; found: C, 69.10; H, 5.24.

6-(Thiophen-2-yl)picolinaldehyde (**3e**), procedure A, yield 93%, pale yellow solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 10.04 (d, J = 1.0 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.62 (dt, J = 3.7, 1.2 Hz, 1H), 7.41 (dt, J = 5.0, 1.2 Hz, 1H), 7.09 (ddd, J = 4.9, 3.7, 1.0 Hz, 1H).

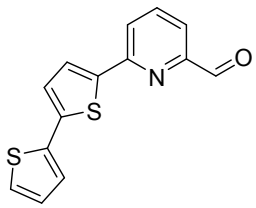
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 193.46, 153.12, 152.43, 143.45, 137.65, 128.51, 128.23, 125.67, 122.73, 119.35.

GC-MS(EI): 189 (100%, M^{*+}), 160 (88%, -CHO)

Melting point: 60-62 °C

Elemental analysis, calc. for $C_{10}H_7NOS$: C, 63.47; H, 3.73; found: C, 63.53; H, 3.70.

6-([2,2'-Bithiophen]-5-yl)picolinaldehyde (**3f**), procedure A, yield 68%, yellow solid



Note: boronic acid pinacol ester was used instead of boronic acid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 10.16 (s, 1H), 7.90 – 7.76 (m, 3H), 7.66 (d, J = 3.8 Hz, 1H), 7.28 (ddd, J = 6.3, 4.3, 1.1 Hz, 2H), 7.20 (dd, J = 4.2, 1.3 Hz, 1H), 7.08 – 7.02 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 193.36, 152.88, 152.46, 141.75, 140.44, 137.64, 137.08, 128.02, 126.34, 125.14, 124.55, 124.36, 122.44, 119.33.

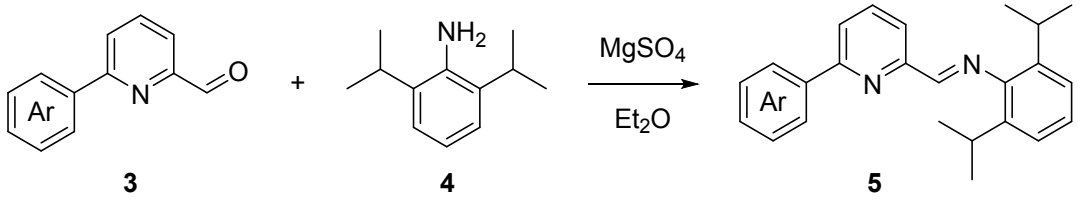
GC-MS(EI): 271 (100%, M^{*+}); 242 (25%, -CHO)

Melting point: 104-107 °C

Elemental Analysis, calc. for $C_{14}H_9NOS_2$: C, 61.97; H, 3.34; found: C, 62.07; H, 3.30.

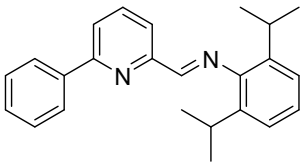
General procedure for 5a-f

Following reported literature,[1] a 2 necked-round bottom flask, under inert atmosphere, was charged with **3** (1.3 mmol, 1 eq), 0.5g of anhydrous $MgSO_4$, 10 mL diethyl ether and 2,6-diisopropylaniline (**4**, 293 µL 1.56 mmol, 1.2 eq). The reaction was stirred at room temperature overnight. The complete consumption of **3** was evaluated by GC-MS. Then $MgSO_4$ was filtered off and washed with diethyl ether. The organic phase was evaporated and the excess of **4** was distilled at 140 °C 0.2 mbar. Product **5** was used in the next steps without further purification.



3 **4** **5**

(E)-N-(2,6-Diisopropylphenyl)-1-(6-phenylpyridin-2-yl)methanimine (**5a**), quat. yield, yellow solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.40 (d, J = 0.8 Hz, 1H), 8.24 (dd, J = 7.6, 1.2 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.93 – 7.86 (m, 1H), 7.84 (dt, J = 7.9, 0.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H), 7.20 – 7.10 (m, 3H), 3.00 (hept, J = 6.9 Hz, 2H), 1.19 (d, J = 6.9 Hz, 12H).

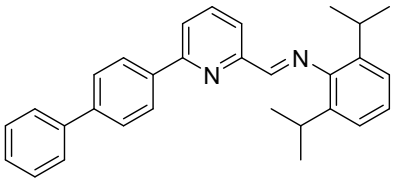
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 163.58, 157.34, 154.39, 148.51, 138.84, 137.38, 137.20, 129.22, 128.81, 126.98, 124.36, 122.99, 121.95, 119.34, 27.95, 23.40.

GC-MS(EI): 327 (100%, -CH_3); 342 (74%, M^{*+}); 156 (55%)

Melting point: 185-188 °C

Elemental Analysis, calc. for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; found: C, 84.14; H, 7.67.

(E)-1-(6-([1,1'-biphenyl]-4-yl)pyridin-2-yl)-N-(2,6-diisopropylphenyl)methanimine (**5b**), quant. yield, white solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 8.28 (dd, J = 7.1, 1.6 Hz, 1H), 8.21 – 8.14 (m, 2H), 7.96 – 7.84 (m, 2H), 7.79 – 7.72 (m, 2H), 7.69 – 7.65 (m, 2H), 7.48 (dd, J = 8.4, 6.9 Hz, 2H), 7.42 – 7.33 (m, 1H), 7.23 – 7.12 (m, 3H), 3.05 (hept, J = 6.9 Hz, 2H), 1.22 (d, J = 6.9 Hz, 12H).

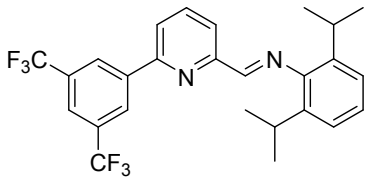
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 163.60, 156.91, 154.42, 148.54, 142.04, 140.54, 137.67, 137.48, 137.24, 128.87, 127.61, 127.56, 127.42, 127.12, 124.43, 123.05, 121.89, 119.41, 28.00, 23.45.

GC-MS(EI): 403 (100%, -CH_3); 418 (90%, M^{*+}); 245 (55%)

Melting point: 118-121°C

Elemental Analysis, calc. for $C_{30}H_{30}N_2$: C, 86.08; H, 7.22; found: C, 86.15; H, 7.26.

(E)-1-(6-(3,5-bis(trifluoromethyl)phenyl)pyridin-2-yl)-N-(2,6-diisopropylphenyl)methanimine (**5c**), quant. yield, yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54 (s, 2H), 8.41 (s, 1H), 8.35 (dd, *J* = 7.7, 1.1 Hz, 1H), 8.02 – 7.95 (m, 1H), 7.93 (d, *J* = 1.2 Hz, 2H), 7.18 (d, *J* = 6.2 Hz, 2H), 2.98 (hept, *J* = 6.8 Hz, 2H), 1.19 (dd, *J* = 6.8, 0.8 Hz, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 162.88, 154.85, 153.91, 148.26, 140.70, 138.00, 137.08, 132.18 (q, *J* = 33.1 Hz), 126.98, 124.57, 123.04, 121.95, 120.77, 27.99, 23.38.

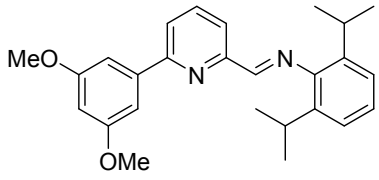
^{19}F-NMR (377 MHz, $CDCl_3$) δ = -62.89 (6F, s)

GC-MS(EI): 421 (100%), 478 (97%, M^{*+}), 463 (95%, -CH_3)

Melting point: 124-128 °C

Elemental Analysis, calc. for $C_{26}H_{24}F_6N_2$: C, 65.27; H, 5.06; found: C, 65.24; H, 5.01.

(E)-N-(2,6-diisopropylphenyl)-1-(6-(3,5-dimethoxyphenyl)pyridin-2-yl)methanimine (**5d**), quant. yield, viscous colorless oil.



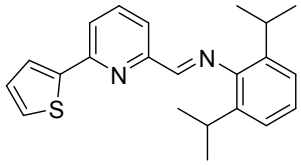
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 8.26 (dd, J = 7.7, 1.0 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.82 (dd, J = 7.8, 1.0 Hz, 1H), 7.26 (d, J = 2.3 Hz, 2H), 7.20 (d, J = 2.1 Hz, 1H), 7.18 (s, 1H), 7.16 – 7.11 (m, 1H), 6.57 (t, J = 2.3 Hz, 1H), 3.88 (s, 6H), 3.02 (hept, J = 6.8 Hz, 2H), 1.20 (d, J = 6.8 Hz, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.55, 161.23, 156.99, 154.27, 148.53, 140.90, 137.44, 137.19, 124.41, 123.02, 122.17, 119.63, 105.18, 101.36, 55.48, 27.97, 23.41.

GC-MS(EI): 387 (100%, -CH_3), 402 (75%, M^{*+}), 359 (32%, -$CH(CH_3)_2$)

Elemental Analysis, calc. for $C_{26}H_{30}N_2O_2$: C, 77.58; H, 7.51; found: C, 77.59; H, 7.45.

(E)-N-(2,6-Diisopropylphenyl)-1-(6-(thiophen-2-yl)pyridin-2-yl)methanimine (**5e**), quant. yield, yellow solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, J = 0.8 Hz, 1H), 8.16 (dd, J = 7.7, 1.0 Hz, 1H), 7.83 (td, J = 7.8, 0.8 Hz, 1H), 7.74 (dd, J = 7.8, 1.1 Hz, 1H), 7.67 (dd, J = 3.7, 1.1 Hz, 1H), 7.41 (dd, J = 5.0, 1.1 Hz, 1H), 7.21 – 7.10 (m, 4H), 3.00 (hept, J = 6.8 Hz, 2H), 1.20 (d, J = 6.9 Hz, 12H).

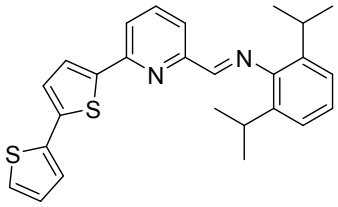
^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.24, 154.23, 152.55, 148.44, 144.26, 137.30, 137.16, 128.05, 127.86, 125.07, 124.37, 122.97, 120.27, 119.01, 27.93, 23.38.

GC-MS(EI): 333 (100%, -CH_3), 348 (81%, M^{*+}), 291 (50%)

Melting point: 115-119 °C

Elemental Analysis, calc. for $C_{22}H_{24}N_2S$: C, 75.82; H, 6.94; found: C, 75.86; H, 6.95.

(*E*)-1-(6-([2,2'-bithiophen]-5-yl)pyridin-2-yl)-N-(2,6-diisopropylphenyl)methanimine (**5f**), quant. yield, yellow solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.33 (d, J = 0.7 Hz, 1H), 8.14 (dd, J = 7.7, 1.0 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.71 (dd, J = 7.9, 1.0 Hz, 1H), 7.55 (dd, J = 5.7, 3.8 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.20 – 7.09 (m, 4H), 7.03 (dd, J = 5.1, 3.6 Hz, 1H), 2.98 (hept, J = 6.9 Hz, 2H), 1.19 (d, J = 6.8 Hz, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 163.13, 154.24, 152.28, 148.42, 142.73, 139.75, 137.25, 137.16, 127.94, 125.70, 124.84, 124.49, 124.41, 124.14, 122.98, 119.96, 119.01, 27.95, 23.39.

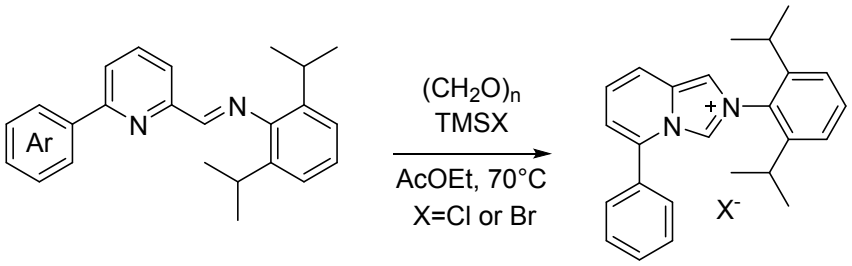
GC-MS(EI): GC-MS = 415 (100%, -CH_3); 430 (95%, M^{*+}).

Melting point: 148-151 °C

Elemental Analysis, calc. for $C_{26}H_{26}N_2S_2$: C, 72.52; H, 6.09; found: C, 72.42; H, 6.12.

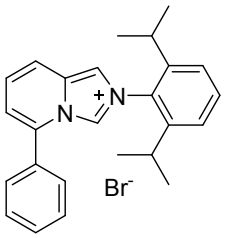
General procedure for 6a-f

In a 2 necked-round bottom flask, under inert atmosphere, **5** (1 mmol, 1 eq) was dissolved in 5mL of dried AcOEt and then paraformaldehyde (33 mg, 1.1 mmol, 1.1 eq) was added and heated at 70 °C. After 15 minutes at the same temperature TMSX (1.1 mmol, 1.1 eq., X = Br, 145 µL, or X = Cl, 138 µL) was added dropwise. The reaction was stirred at the same temperature until **5** was consumed. TLC *c*Hex/AcOEt 5:1. The reaction was cooled to 0 °C and filtered with a Gooch funnel. The solid was washed once with cold ethyl acetate and twice with diethyl ether. The solid was dried with vacuum and used without further purification.[6]



5 **6**

2-(2,6-Diisopropylphenyl)-5-phenylimidazo[1,5-a]pyridin-2-ium bromide (**6a**), yield 88%, pale yellow solid.



^{1}H-NMR (400 MHz, $CCDl_3$) δ = 9.04 (s, 1H), 8.73 (d, J = 9.3 Hz, 1H), 8.60 (d, J = 1.8 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.61 (dt, J = 3.3, 2.0 Hz, 2H), 7.59 (d, J = 1.9 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.19 (dd, J = 7.0, 1.1 Hz, 1H), 2.20 (hept, J = 6.7 Hz, 2H), 1.23 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.8 Hz, 6H).

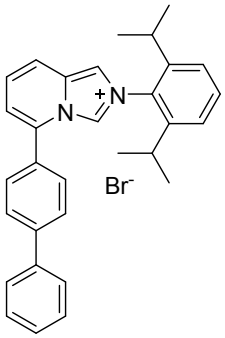
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 144.97, 134.70, 132.40, 132.15, 131.53, 130.73, 130.50, 130.30, 128.21, 126.33, 124.64, 122.28, 120.28, 119.89, 119.18, 28.66, 24.52, 24.26.

LC-MS(ESI+): 355.4 (-Br^-)

Melting point: 287-290 °C

Elemental Analysis, calc. for $C_{25}H_{27}BrN_2$: C, 68.96; H, 6.25; found: C, 68.87; H, 6.28.

5-([1,1'-Biphenyl]-4-yl)-2-(2,6-diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium bromide (**6b**), yield 78%, white solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.11 (d, J = 1.8 Hz, 1H), 8.78 (d, J = 9.3 Hz, 1H), 8.68 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.77 – 7.71 (m, 2H), 7.60 (d, J = 7.4 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.32 (d, J = 7.8 Hz, 2H), 7.24 – 7.21 (m, 1H), 2.23 (hept, J = 6.7 Hz, 2H), 1.25 (d, J = 6.7 Hz, 6H), 1.14 (d, J = 6.8 Hz, 6H).

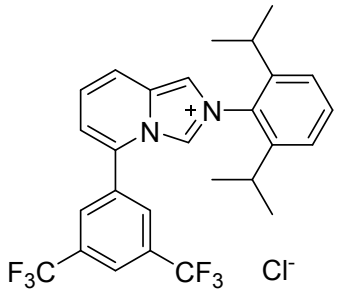
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 145.18, 144.23, 139.31, 134.68, 132.46, 132.13, 130.55, 129.60, 129.05, 128.85, 128.74, 128.34, 127.13, 126.73, 124.65, 122.44, 119.95, 119.77, 118.53, 28.64, 24.56, 24.38.

LC-MS(ESI+): 431.4 (-Br^-)

Melting point: 130-132 °C

Elemental Analysis, calc. for $C_{31}H_{31}BrN_2$: C, 72.79; H, 6.11; found: C, 72.72; H, 6.09.

5-(3,5-bis(trifluoromethyl)phenyl)-2-(2,6-diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**6c**), yield 90%, yellow solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.03 – 8.97 (m, 1H), 8.45 (s, 1H), 8.35 (d, *J* = 9.2 Hz, 1H), 8.27 (s, 2H), 8.00 (s, 1H), 7.52 (td, *J* = 8.2, 7.6, 2.3 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 4.9 Hz, 1H), 2.26 (hept, *J* = 6.6 Hz, 2H), 1.16 (d, *J* = 6.6 Hz, 6H), 1.10 (d, *J* = 6.6 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 145.23, 133.61, 133.43, 133.28, 132.15, 132.11, 130.37, 129.26, 126.37, 124.82, 124.62, 123.96, 123.82, 121.24, 121.21, 120.48, 118.06, 28.54, 24.33, 24.31.

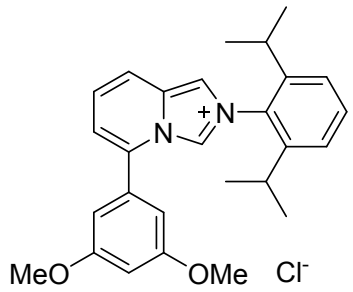
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.96.

LC-MS(ESI+): 491.4 (-Cl^-)

Melting point: decomposition at 230 °C

Elemental Analysis, calc. for $C_{27}H_{25}ClF_6N_2$: C, 61.54; H, 4.78; found: C, 61.57; H, 4.83.

2-(2,6-diisopropylphenyl)-5-(3,5-dimethoxyphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**6d**), yield 60%, pale yellow solid



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (dt, *J* = 7.2, 1.8 Hz, 1H), 8.66 (d, *J* = 1.9 Hz, 1H), 8.49 (t, *J* = 8.5 Hz, 1H), 7.51 (ddd, *J* = 19.9, 8.9, 6.9 Hz, 2H), 7.30 (dd, *J* = 7.9, 2.5 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 1H), 6.75 (dt, *J* = 3.2, 1.9 Hz, 2H), 6.58 (d, *J* = 2.6 Hz, 1H), 3.79 (d, *J* = 2.6 Hz, 6H), 2.19 (tt, *J* = 10.9, 5.2 Hz, 2H), 1.20 (dd, *J* = 6.9, 3.3 Hz, 6H), 1.10 (dd, *J* = 6.9, 2.2 Hz, 6H).

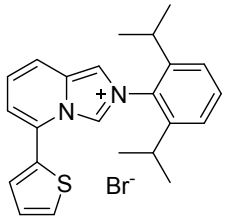
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 162.05, 145.11, 134.72, 132.46, 132.34, 132.18, 130.50, 126.44, 124.65, 122.53, 119.87, 119.57, 118.52, 106.26, 102.80, 55.74, 28.63, 24.58, 24.24.

LC-MS(ESI+): 415.4 (-Cl^-)

Melting point: decomposition at 200 °C

Elemental Analysis, calc. for $C_{27}H_{31}ClN_2O_2$: C, 71.91; H, 6.93; found: C, 71.98; H, 6.87.

2-(2,6-Diisopropylphenyl)-5-(thiophen-2-yl)imidazo[1,5-a]pyridin-2-ium bromide (**6e**), yield 90%, yellow solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.08 (dt, J = 1.8, 0.9 Hz, 1H), 9.01 (d, J = 1.9 Hz, 1H), 8.75 – 8.67 (m, 1H), 7.70 (dd, J = 3.7, 1.2 Hz, 1H), 7.63 (dd, J = 5.1, 1.1 Hz, 1H), 7.56 (t, J = 7.9 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.33 (ddd, J = 7.9, 3.6, 1.1 Hz, 3H), 7.27 (ddd, J = 5.0, 3.7, 0.9 Hz, 1H), 2.19 (hept, J = 6.6 Hz, 2H), 1.24 – 1.20 (m, 6H), 1.15 (dd, J = 6.9, 0.8 Hz, 6H).

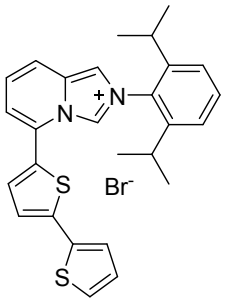
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 145.03, 132.35, 132.24, 130.75, 130.48, 130.29, 129.61, 129.02, 128.69, 126.00, 124.70, 123.03, 120.88, 120.58, 119.29, 28.73, 24.54, 24.39.

LC-MS(ESI+): 361.4 (-Br^-)

Melting point: decomposition at 245°C

Elemental Analysis, calc. for $C_{23}H_{25}BrN_2S$: C, 62.58; H, 5.71; found: C, 62.50; H, 5.73.

5-([2,2'-Bithiophen]-5-yl)-2-(2,6-diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium bromide (**6f**), yield 74%, yellow solid.



^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 9.61 – 9.56 (m, 1H), 8.57 (d, J = 1.8 Hz, 1H), 8.35 (dt, J = 9.3, 1.0 Hz, 1H), 7.73 (d, J = 3.9 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 7.54 (dd, J = 9.3, 7.1 Hz, 1H), 7.43 (d, J = 1.1 Hz, 1H), 7.41 (s, 1H), 7.39 (s, 1H), 7.37 (dd, J = 5.1, 1.2 Hz, 1H), 7.35 (d, J = 3.9 Hz, 1H), 7.32 (dd, J = 3.7, 1.2 Hz, 1H), 7.09 (dd, J = 5.1, 3.7 Hz, 1H), 2.21 (hept, J = 6.8 Hz, 2H), 1.22 (d, J = 5.2 Hz, 6H), 1.21 (d, J = 5.3 Hz, 6H).

^{13}C-NMR (100 MHz, CD_2Cl_2) δ = 145.04, 141.55, 135.20, 132.23, 131.17, 129.03, 128.74, 128.26, 126.47, 126.37, 125.52, 124.92, 124.69, 124.26, 124.15, 120.20, 119.08, 118.12, 28.75, 24.20, 24.08.

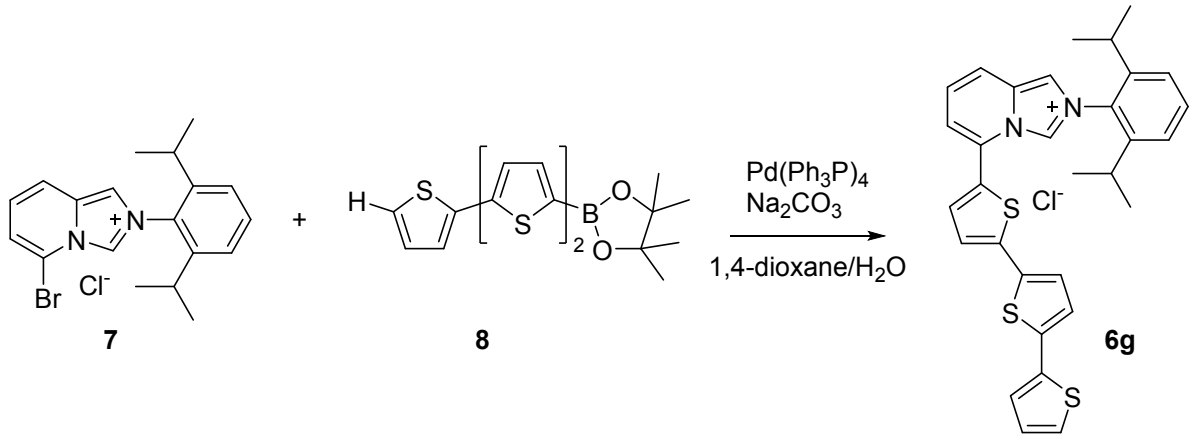
LC-MS(ESI+): 443.4 (-Br^-)

Melting point: 266-270 °C

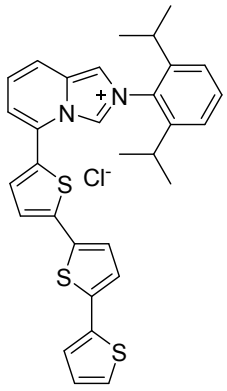
Elemental Analysis, calc. for $C_{27}H_{27}BrN_2S_2$: C, 61.94; H, 5.20; found: C, 61.93; H, 5.27.

Synthesis of 6g

A 2 necked-round bottom flask equipped with a condenser, under inert atmosphere, was charged with **7** (197 mg, 0.5 mmol), [$Pd(PPh_3)_4$] (29 mg, 5 mol%), **8** (224 mg, 0.6mmol) and 3.5mL of degassed 1,4-dioxane. The reaction was stirred at room temperature for 30 min, then 1.2mL of 0.5 M solution of Na_2CO_3 (1.2 eq) in degassed water was added and the reaction mixture heated at 80 °C. The reaction was monitored by TLC DCM/MeOH 10:1. After consumption of **7** the reaction mixture was extracted 3 times with CH_2Cl_2, dried on Na_2SO_4 and purified by flash chromatography with DCM/MeOH from 100/1 to 20/1 as an eluent.[7]



5-([2,2':5',2"-Terthiophen]-5-yl)-2-(2,6-diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**6g**), yield 69%, brown solid.



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.35 (d, J = 1.8 Hz, 1H), 8.94 (d, J = 1.8 Hz, 1H), 8.64 (d, J = 9.3 Hz, 1H), 7.72 (d, J = 3.9 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.46 (dd, J = 9.3, 7.1 Hz, 1H), 7.34 (t, J = 7.2 Hz, 3H), 7.29 (d, J = 3.9 Hz, 1H), 7.24 (d, J = 4.8 Hz, 1H), 7.16 (dd, J = 12.7, 3.7 Hz, 2H), 7.08 (d, J = 3.8 Hz, 1H), 7.03 – 6.99 (m, 1H), 2.20 (h, J = 6.7 Hz, 2H), 1.22 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 144.99, 141.02, 138.28, 136.35, 133.71, 132.28, 132.21, 131.35, 130.53, 128.54, 128.03, 126.12, 126.08, 125.21, 124.97, 124.66, 124.50, 124.32, 123.59, 120.41, 120.04, 118.96, 28.75, 24.50, 24.46.

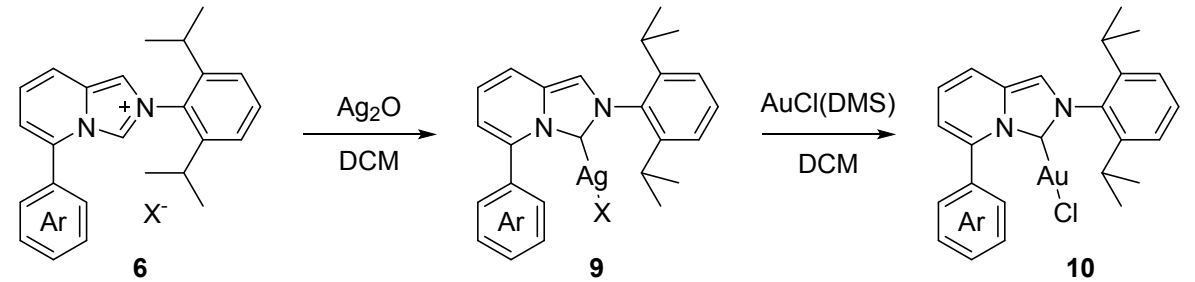
LC-MS(ESI+): 525.0 ($-Cl^-$)

Melting point: decomposition at 285°C

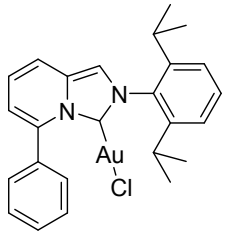
Elemental Analysis, calc. for $C_{31}H_{29}ClN_2S_3$: C, 66.35; H, 5.21; found: C, 66.41; H, 5.18.

General procedure for 10a-g

In a tow-necked round bottom flask, covered with aluminium foil to provide darkness, **6** (0.2 mmol, 1 eq) was dissolved in 1 mL of dry DCM and then Ag_2O (56 mg, 0.24 mmol, 1.1 eq) was added. The reaction mixture was stirred at room temperature overnight. TLC monitoring using *c*Hex/AcOEt 2:1. The reaction was filtered through Celite® pad and washed with DCM. The organic phase was then evaporated. The crude **9** was redissolved in 1 mL of dry DCM and transferred in a 2 necked-bottom flask covered with foil. [AuCl(DMS)] (59 mg, 0.2 mmol, 1 eq) was then added and stirred at room temperature for 5 h. After all Ag complex was completely consumed the reaction was filtered through Celite® pad and washed with DCM and evaporated. The residual solid was dried under vacuum to remove DMS.[8]



10a, yield over 2 steps 83%, pale orange solid.



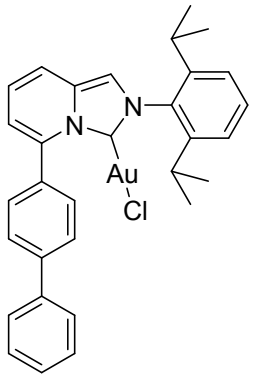
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.48 (m, 5H), 7.48 – 7.41 (m, 2H), 7.32 (s, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.05 (dd, J = 9.3, 6.6 Hz, 1H), 6.60 (dd, J = 6.6, 1.3 Hz, 1H), 2.18 (hept, J = 6.8 Hz, 2H), 1.22 (d, J = 6.8 Hz, 6H), 1.10 (d, J = 6.9 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 145.12, 135.63, 132.34, 132.09, 131.57, 130.61, 130.33, 130.30, 128.62, 127.37, 124.78, 123.55, 119.91, 118.36, 116.98, 28.68, 24.68, 24.57.

Melting point: decomposition at 195°C

Exact mass, calc for $C_{25}H_{26}AuClN_2$: 586.1450, found: 586.1455.

10b, yield over 2 steps 80%, white solid.



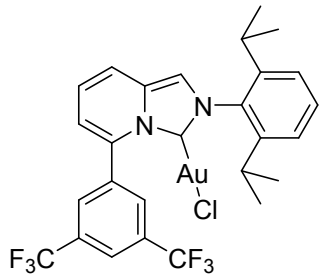
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 3H), 7.66 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.46 (dd, J = 8.5, 3.7 Hz, 2H), 7.40 (t, J = 7.8 Hz, 3H), 7.36 – 7.29 (m, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.07 (dd, J = 9.3, 6.7 Hz, 1H), 6.66 (dd, J = 6.7, 1.3 Hz, 1H), 2.26 – 2.14 (m, 2H), 1.24 (d, J = 6.8 Hz, 6H), 1.10 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.18, 144.19, 139.36, 135.44, 132.34, 132.16, 130.36, 129.35, 129.08, 129.04, 128.78, 128.29, 127.38, 127.21, 124.79, 123.46, 119.92, 118.24, 116.78, 28.66, 24.67, 24.59.

Melting Point: decomposition at 225°C

Exact mass, calc for $C_{31}H_{30}AuClN_2$: 662.1763, found: 662.1766.

10c, yield over 2 steps 77%, pale yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 7.92 (m, 2H), 7.55 (d, J = 9.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.40 (s, 1H), 7.25 – 7.19 (m, 2H), 7.09 (dd, J = 9.3, 6.7 Hz, 1H), 6.71 (d, J = 6.8 Hz, 1H), 2.15 (hept, 6.6 Hz, 2H), 1.25 – 1.20 (d, J = 6.6 Hz, 6H), 1.11 (d, J = 6.6 Hz, 6H).

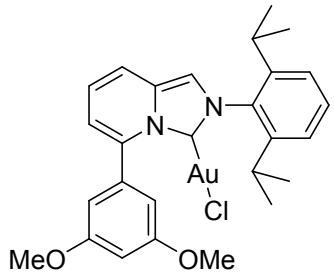
^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.09, 145.03, 136.36, 135.89, 135.07, 132.41, 132.07, 131.44, 130.78, 129.99, 124.18, 123.28, 118.56, 117.90, 117.67, 114.32, 28.48, 24.35, 24.17.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.96 (s, 6F).

Melting Point: decomposition at 175 °C.

Exact mass, calc for $C_{27}H_{24}AuClF_6N_2$: 722.1198, found: 722.1199.

10d, yield over 2 steps 75%, white solid.



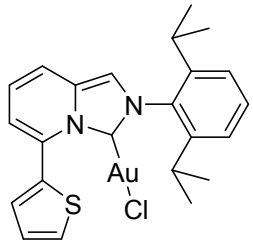
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 7.40 (m, 2H), 7.31 (s, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.03 (dd, J = 9.3, 6.7 Hz, 1H), 6.73 – 6.69 (m, 2H), 6.65 – 6.60 (m, 2H), 3.81 (s, 7H), 2.18 (hept, J = 6.7 Hz, 2H), 1.24 (d, J = 6.8 Hz, 6H), 1.10 (d, J = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.09, 145.06, 139.69, 135.57, 135.25, 131.57, 130.54, 124.06, 123.49, 117.03, 116.00, 113.51, 108.48, 102.18, 55.54, 28.40, 24.41, 24.23.

Melting point: decomposition at 160 °C.

Exact mass, calc for $C_{27}H_{30}AuClN_2O_2$: 646.1661, found: 646.1668.

10e, yield over 2 steps 92%, pale yellow solid.



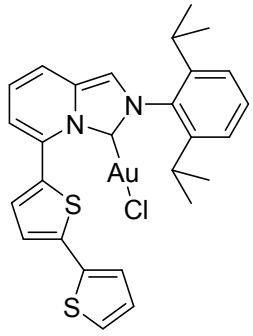
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.60 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.52 – 7.38 (m, 3H), 7.33 (d, *J* = 1.3 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.01 (ddd, *J* = 8.1, 6.7, 1.4 Hz, 1H), 6.76 (dd, *J* = 6.7, 1.4 Hz, 1H), 2.22 – 2.15 (m, 2H), 1.23 (d, *J* = 7.2 Hz, 6H), 1.09 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.11, 135.52, 133.78, 132.54, 131.55, 130.76, 130.60, 128.49, 127.73, 124.07, 123.10, 119.14, 118.17, 114.02, 28.39, 24.46, 24.22.

Melting point: decomposition at 210 °C.

Exact mass, calc for $C_{23}H_{24}AuClN_2S$: 592.1014, found: 592.1021.

10f, yield over 2 steps 87%, dark yellow solid.



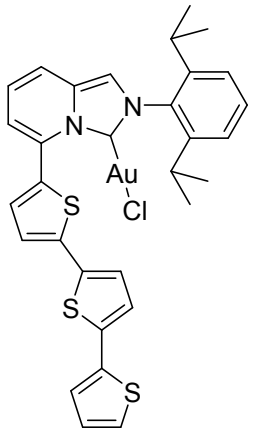
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.40 (m, 2H), 7.35 (d, J = 3.7 Hz, 1H), 7.32 (s, 2H), 7.27 – 7.18 (m, 4H), 7.05 – 6.98 (m, 1H), 6.97 (dd, J = 5.3, 3.7 Hz, 1H), 6.79 (dd, J = 6.8, 1.2 Hz, 1H), 2.20 (hept, J = 6.9 Hz, 2H), 1.25 (d, J = 6.8 Hz, 6H), 1.10 (d, J = 6.9 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 145.11, 140.50, 136.38, 135.52, 132.19, 131.55, 130.62, 127.79, 125.35, 125.30, 124.58, 124.09, 123.11, 119.18, 118.19, 114.08, 28.41, 24.47, 24.27.

Melting point: decomposition 235 °C.

Exact mass, calc for $C_{27}H_{26}AuClN_2S_2$: 674.0891, found: 674.0886.

10g, yield over 2 steps 80%, brown solid.



^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.59 – 7.51 (m, 2H), 7.41 (s, 1H), 7.39 (d, J = 3.8 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.22 (dd, J = 3.6, 1.2 Hz, 1H), 7.19 (d, J = 3.8 Hz, 1H), 7.12 (d, J = 3.8 Hz, 1H), 7.06 (d, J = 6.7 Hz, 1H), 7.05 – 7.02 (m, 2H), 6.84 (dd, J = 6.7, 1.2 Hz, 1H), 2.24 (hept, J = 6.9 Hz, 2H), 1.26 (d, J = 6.8 Hz, 6H), 1.13 (d, J = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ = 145.27, 139.86, 137.10, 136.89, 135.71, 135.23, 132.71, 131.79, 131.72, 131.59, 130.56, 127.91, 125.68, 125.64, 124.70, 124.42, 124.39, 124.23, 124.07, 124.04, 123.93, 123.05, 123.01, 119.35, 118.39, 114.32, 28.38, 24.13, 23.89.

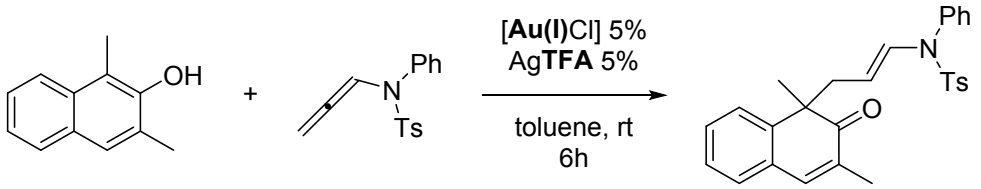
Melting point: 248-252°C.

Exact mass, calc for $C_{31}H_{28}AuClN_2S_3$: 756.0769, found: 756.0765

[Au(I)]-catalysed dearomatization of β-naphthol

In a two-necked round bottom flask under inert atmosphere, [Au(I)Cl] (2.5 x 10^{-3} mmol, 5 mol%) and AgTFA (0.55 mg, 5 mol%) were added and dissolved in 1 mL of dry toluene and stirred. The glassware was covered in aluminium foil to provide darkness. After 15 minutes, 1,3-dimethyl naphth-2-ol (**12**, 8.6 mg, 0.05 mmol) and *N*-phenyl-*N*-tosyl allenammide (**13**, 21.3 mg, 0.075 mmol) were added. The reaction was stirred at room temperature for 6 h. After that time, the mixture was charged directly in column for purification by flash chromatography using *n*-Hex:AcOEt 9 to 1 as eluent.[9]

Table S1.



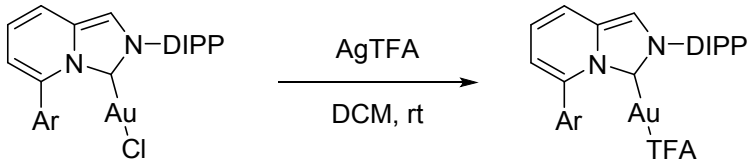
12 **13** **14**

Catalyst	Yield 14 (%)[a]
10a	35
10b	70
10c	95
10d	22
10e	87
10f	30
10g	70

a) Determined after flash chromatography.

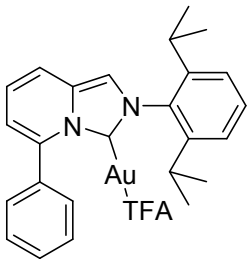
General procedure for the synthesis of [Au(I)]-TFA complexes 11a-d

The counterion metathesis was carried in a two-necked round bottom flask under inert atmosphere and in darkness. The gold(I) chloride complex **10** (0.015 mmol, 1 eq) was dissolved in 0.5 mL of dry DCM, then 3.3 mg of AgTFA (0.015 mmol, 1 eq) was added. The reaction was stirred for 1 h at room temperature in the dark. The reaction was filtered through a pad of Celite® and washed with 1.5 mL of dry DCM. The organic phase was evaporated affording the desired product without any further purification in almost quantitative yields.



10 **11**

11a, yield 96%, brown powder.

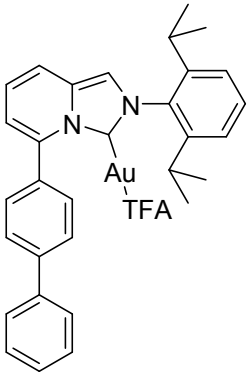


^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.53 (m, 2H), 7.53 – 7.43 (m, 5H), 7.35 (s, 1H), 7.24 (s, 2H), 7.08 (dd, *J* = 9.3, 6.7 Hz, 1H), 6.64 (dd, *J* = 6.7, 1.2 Hz, 1H), 2.17 (hept, *J* = 6.9 Hz, 2H), 1.24 (d, *J* = 6.7 Hz, 6H), 1.11 (d, *J* = 6.9 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -74.29 (s, 3F).

Exact mass, calc. for $C_{27}H_{26}AuF_3N_2O_2$: 664,1612; found: 664.1604.

11b, yield 98%, orange powder.

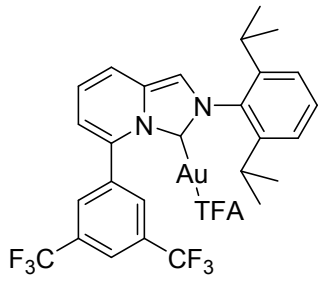


^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.86 (q, *J* = 8.3 Hz, 4H), 7.62 – 7.56 (m, 2H), 7.56 – 7.47 (m, 2H), 7.45 – 7.33 (m, 4H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.15 (dd, *J* = 9.3, 6.7 Hz, 1H), 6.74 (dd, *J* = 6.7, 1.2 Hz, 1H), 2.25 (hept, *J* = 7.1 Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.10 (d, *J* = 6.8 Hz, 6H).

^{19}F-NMR (377 MHz, $CDCl_3$) δ = -73.23 (s, 3F).

Exact mass, calc. for $C_{33}H_{30}AuF_3N_2O_2$: 740,1925; found: 740.1933.

11c, yield 98%, pale yellow powder.



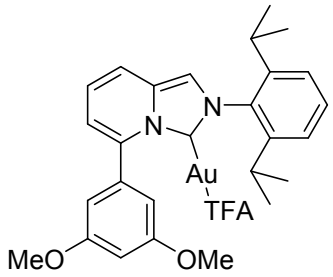
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (s, 2H), 7.97 (s, 1H), 7.56 (dd, J = 9.3, 1.2 Hz, 1H), 7.46 (s, 0H), 7.43 (d, J = 1.2 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.15 – 7.09 (m, 1H), 6.75 (dd, J = 6.7, 1.2 Hz, 1H), 2.14 (hept, J = 7.0 Hz, 2H), 1.25 (d, J = 7.0 Hz, 6H), 1.12 (d, J = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.05, 156.04, 145.03, 136.30, 135.57, 134.89, 132.85, 132.51, 132.18, 131.84, 131.76, 130.97, 129.97, 129.93, 129.89, 129.86, 124.30, 124.23, 124.13, 123.46, 121.52, 118.53, 118.04, 114.71, 28.56, 24.42, 24.09.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -63.21(s, 6F), -74.46 (s, 3F).

Exact mass, calc. for $C_{29}H_{24}AuF_9N_2O_2$: 800,1360; found: 800.1357.

11d, yield 93%, pale yellow powder.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.35 (s, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 7.08 (dd, *J* = 9.3, 6.7 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 2H), 6.68 (dd, *J* = 6.7, 1.2 Hz, 1H), 6.52 (t, *J* = 2.3 Hz, 1H), 3.80 (s, 6H), 2.22 (hept, *J* = 6.8 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 7H), 1.10 (d, *J* = 6.8 Hz, 6H).

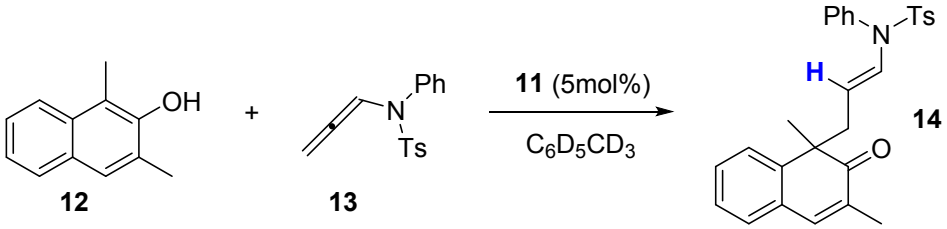
^{19}F NMR (377 MHz, $CDCl_3$) δ = -73.67.

Exact mass, calc. for $C_{29}H_{30}AuF_9N_2O_4$: 724,1823; found: 724,1830.

Kinetic experiments

Dried NMR tubes were charged with 6 mg of 1,3-dimethylnapht-2-ol (**12**, 0.035 mmol, 15 mg allenamide (**13**, 0.053 mmol), **11** (1.75 μmol, 5 mol%) and 0.035mmol of internal standard. Subsequently 0.7 mL of d^8-toluene were added (t = 0 min). NMR spectra were then collected periodically. To evaluate the progress of the reaction we focused to the diagnostic peaks of C*H* in beta position of the enamide moiety of **14** (δ = 3.99 ppm, dt, 1H).

Table S2. *Concentration of **14** (μmol) over time*



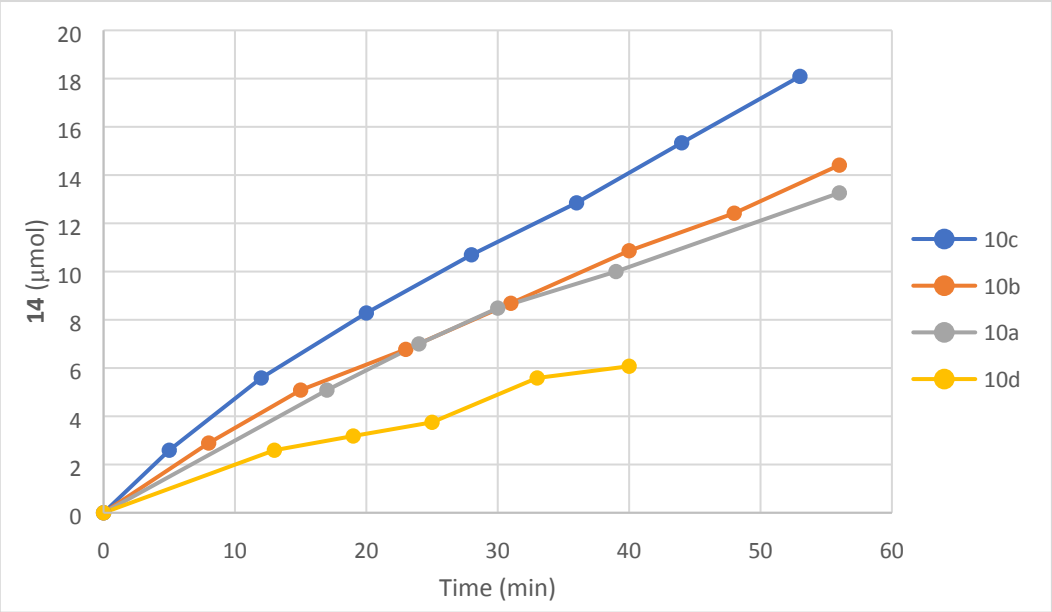
By ^{1}H-NMR integration μmol of **14** are calculated and reported by time.

11a	
Time (min)	**14** (μmol)
0	0
17	5,085
24	7,000
30	8,485
39	10,000
56	13,261

11b	
Time (min)	**14** (μmol)
0	0
8	2,890
15	5,085
23	6,774
31	8,684
40	10,862
48	12,419
56	14,412

11c	
Time (min)	**14** (μmol)
0	0
5	2,593
12	5,588
20	8,282
28	10,694
36	12,848
44	15,337
53	18,092

11d	
Time (min)	**14** (μmol)
0	0
13	2,592
19	3,181
25	3,750
33	5,588
40	6,0743



Graphic 1. *Plot of µmol of* ***14*** *by time*

Table S3. *Velocity and statistics of fitting*

The initial velocity of each catalyst is calculated by a linear regression considering initial stage of the curves:

11a	
V µmol/min	0,294
δ	0,002
R^2	0,9998

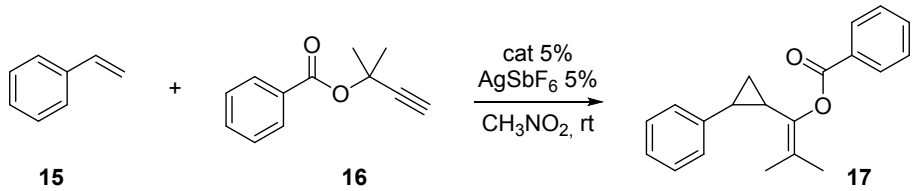
11b	
V µmol/min	0,343
δ	0,007
R^2	0,9992

11c	
V µmol/min	0,47
δ	0,01
R^2	0,9984

11d	
V µmol/min	0,17
δ	0,01
R^2	0,9930

General procedure for the cyclopropanation reaction

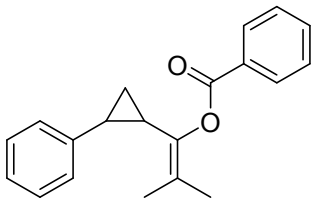
In a two neck round bottomed flask, under nitrogen atmosphere, the [Au] complex (5 mol%) was dissolved in 1 mL of nitromethane (ACS reagent grade). The flask was covered with aluminium foil to provide darkness. $AgSbF_6$ (1.7 mg, 5 mol%) is added and the reaction was let stirring for 10 min. Then styrene (45 µL, 0.4 mmol, 4 eq) add **16** (18.8 mg, 0.1 mmol) were added subsequently. After 30 min the reaction was monitored by TLC and solvent evaporated. Final product **17** was purified by flash chromatography using *n*-hexane:AcOEt 30/1 as eluent phase.[10]



15 **16** **17**

Catalyst	Yield 17 (%)[a]	*Cis/trans*[b]
10a	79	10/1
10c	88	7/1
10d	64	7.3/1

a) Determined after flash chromatography. b) Determined by NMR on the reaction crude.



17, colourless viscous oil. [10]

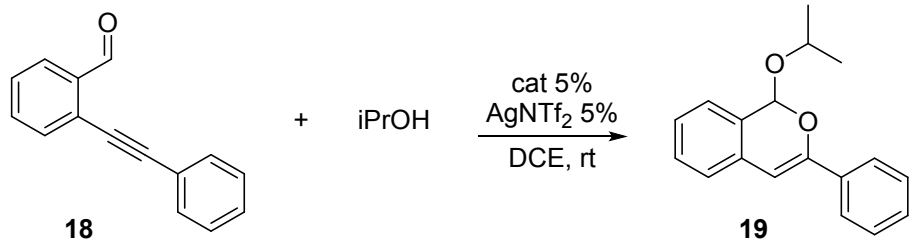
^{1}H NMR *cis*-**17** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 2.42 – 2.22 (m, 2H), 1.63 (s, 3H), 1.47 (s, 3H), 1.28 (dt, *J* = 13.6, 5.1 Hz, 1H), 1.09 (q, *J* = 5.9 Hz, 1H).

^{13}C *cis*-**17** NMR (100 MHz, $CDCl_3$) δ 164.65, 139.34, 138.55, 133.03, 129.86, 129.79, 128.31, 127.63, 127.61, 125.58, 123.48, 23.76, 21.41, 18.65, 17.62, 11.70.

GC-MS(EI): 105 (100%), 170 (14%), 292 (3%, $M^{\bullet+}$)

General procedure for alkynilbenzaldehyde cyclization

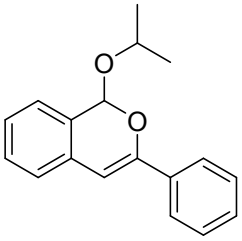
In a two neck round bottomed flask, under nitrogen atmosphere, the [Au] catalyst (10 µmol, 5 mol%) was dissolved in 1 mL of dichloroethane. The flask was covered with foil to provide darkness. $AgNTf_2$ (3.9mg, 10µmol) is added and the reaction was let stirring for 10 minutes. Then isopropanol (15 µL, 0.2 mmol) and **18** (41.2mg, 0.2mmol, 1eq) were added subsequently. After 2 hours the reaction was monitored by TLC and solvent evaporated. Final product **19** was purified by flash chromatography using *n*-hexane:AcOEt 30/1 as eluent phase.[11]



18 **19**

Catalyst	Yield 19 (%)
10a	41

10c	68
10d	13



18, pale yellow solid. [11]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (dt, *J* = 6.5, 1.4 Hz, 4H), 7.44 – 7.38 (m, 4H), 7.35 (tt, *J* = 7.6, 1.8 Hz, 4H), 7.29 – 7.19 (m, 6H), 6.61 (s, 2H), 6.32 (s, 2H), 4.38 (hept, *J* = 6.2 Hz, 2H), 1.32 (d, *J* = 6.1 Hz, 6H), 1.19 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.50, 134.80, 130.38, 129.15, 128.62, 128.41, 127.62, 126.64, 125.54, 124.86, 124.57, 100.38, 96.95, 69.84, 23.57, 21.97.

GC-MS (EI): 105 (100%), 207 (58%, -OiPr), 266 (45%, $M^{\bullet+}$)

Photophysical studies

The photophysical properties of T3-ImPy imidazolium salt ad gold(I) complex (**6g** and **10g**) were also investigated: Figure 6 reports the absorption and emission spectra of the selected compounds in air-equilibrated dichloromethane solution. The broad shape of the absorption band is similar for both the species and the maxima are located between 370 and 400 nm: gold complex **10g** is slightly blue-shifted with respect to **6g**; the same trend can be observed also in the emission spectra. The corresponding lifetimes are sub-nanosecond (below the equipment resolution, Table 3), demonstrating that the emission bands peaked at 510-545 nm are fluorescence for all the three investigated compounds. The higher emission quantum yield (Table 3) was measured for compound **6g**, 6.4%, while a significant lower value was recorded for gold complex **10g** (0.2%). The loss of the fluorescence quantum yield can be tentatively assigned to a higher efficiency of the non-radiative inter system crossing deactivation of the fluorescent excited state promoted by heavy atom effect. In the solid state, **6g** shows fluorescence bands (**Figure S1**) very similar to the one observed in dichloromethane solution, while **10g** is not luminescent. No phosphorescence was detected at 77 K in rigid matrix.

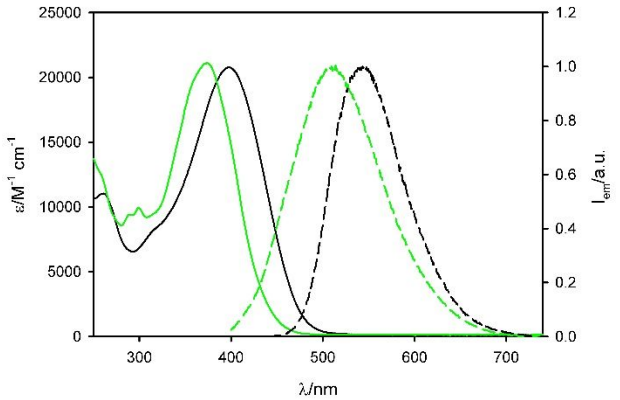


Figure S1. Absorption (left, solid lines) and emission spectra (right, dashed lines) of **6g** (black line) and **10g** (green line) in air-equilibrated dichloromethane solution at 298 K.

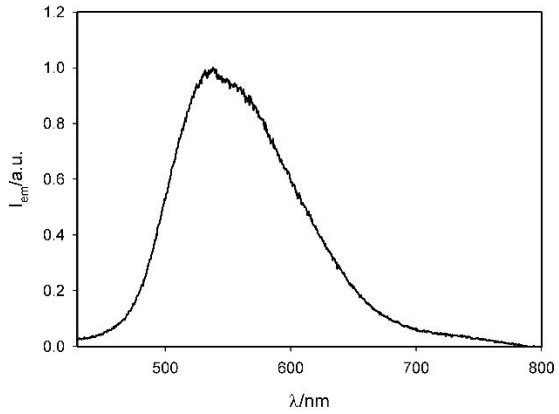


Figure S2. Solid state emission spectra of **6g** at 298 K.

The photophysical properties of the investigated compounds are reminiscent of those reported for α-terthiophene (Table 3)[12] in terms of shape, emission quantum yields and lifetimes, but a significant red-shift is observed for the lowest-energy absorption band and the fluorescence band, demonstrating that the functionalization with imidazo[1,5-a]pyridin-3-ylidene affects the electronic properties by extending the conjugation.

Table S4. Photophysical properties of the compound **6g** and **10g** in DCM at 298 K.

	Absorption		emission		
	λ (nm)	ε · 10^{-4} (M^{-1} cm^{-1})	λ (nm)	ϕ_{em}	τ^a (ns)
α-terthiophene	354[b]	1.15[c]	411, 431[b]	0.06[d]	0.17[d]
6g	398	2.08	545	0.064	< 0.5
10g	374	2.11	509	0.002	< 0.5

[a] The emission intensity decays were fitted by a biexponential functions: for all the compounds a longer lifetime (ca. 1 ns) is observed, corresponding to a very low fraction of emitted light (<7%) and likely due to a different conformation of the molecules in solution. [b] See ref. 8a. [c] See ref. 8b. [d] See ref. 8c.

Crystal Structure Determination for 10a-10g

The X-ray intensity data were measured on a Bruker Apex II CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.5° ω steps. The software SMART[3] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program,[13] and an empirical absorption correction was applied using SADABS.[14] The structures were solved by direct methods (SIR 2014)[15] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[16] using anisotropic thermal parameters for all non-hydrogen atoms. The aromatic, methyl and methine hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters *U(H)* = 1.2 *Ueq*(C) and allowed to ride on their carrier carbons. In the asymmetric units of three crystal structures one toluene (**10b)**, one CH_3CN (**10b'**) and one CH_2Cl_2 (**10c**) solvent molecules are present, respectively. Moreover in the asymmetric unit of **10c** two indipendent molecules have been found. In the SbF_6^- anion of **10b'** four fluorine atoms are disordered over two positions with relative occupancies of 0.62 and 0.38, respectively.

Crystal data and experimental details of the data collection for the Pn-series (**10a-10d**), **10b'** and Tn-series (**10e-10g**) are reported in **Table S5**, **Table S7** and **Table S9** respectively. Molecular drawings were generated using Mercury.[17]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 2091513-2091520. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

Table S5. Crystal data and experimental details for **10a-10d**

Compound	**10a**	**10b**	**10c**	**10d**
Formula	$C_{25}H_{26}AuClN_2$	$C_{31}H_{30}AuClN_2 \bullet C_6H_5CH_3$	$2(C_{27}H_{24}AuClF_6N_2) \bullet CH_2Cl_2$	$C_{27}H_{30}AuClN_2O_2$
Fw	586.89	755.12	1530.72	646.94
T, K	296(2)	296(2)	100(2)	296(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
Crystal symmetry	Monoclinic	Monoclinic	Triclinic	triclinic
Space group	Cc	$P2_1/c$	P-1	P-1
a, Å	14.603(5)	11.3017(7)	12.8783(5)	8.581(1)
b, Å	13.510(3)	25.342(2)	15.0377(6)	10.434(2)
c, Å	11.732(3)	11.6502(8)	15.6241(6)	15.176(3)
α	90	90	91.396(1)	104.303(5)
β	97.942(13)	100.307(2)	107.936(1)	91.153(7)
γ	90	90	99.023(1)	98.151(6)
Cell volume, $Å^3$	2292.4(1)	3282.9(4)	2834.6(2)	1301.3(4)
Z	4	4	2	2
D_c, Mg m^{-3}	1.701	1.528	1.793	1.651
μ(Mo-K_α), mm^{-1}	6.547	4.591	5.438	5.781
F(000)	1144	1504	1484	636
Crystal size/ mm	0.34 x 0.28 x 0.20	0.34 x 0.21 x 0.17	0.22 x 0.17 x 0.14	0.21 x 0.16 x 0.07
θ limits, °	2.063 to 28.360	1.950 to 25.999	1.687 to 25.500	2.152 to 30.595
Reflections collected	20699	58242	37649	29642
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	5664 [R(int) = 0.0537]	6434 [R(int) = 0.0561]	10531 [R(int) = 0.0326]	7975 [R(int) = 0.0435]
Goodness-of-fit-on F^2	0.898	1.218	1.105	1.027
R_1 (F)[a], wR_2 (F^2) [I > 2σ(I)][b]	R1 = 0.0286, wR2 = 0.0745	R1 = 0.0259, wR2 = 0.0544	R1 = 0.0388, wR2 = 0.0883	R1 = 0.0248, wR2 = 0.0580
Largest diff. peak and hole, e. $Å^{-3}$	0.541 and -2.425	0.639 and -1.342	2.817 and -2.043	1.048 and -1.107

[a)] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S3. ORTEP drawing of **10a** (top) and **10b** (bottom)**.** Thermal ellipsoid are drawn at 30% of the probability level.

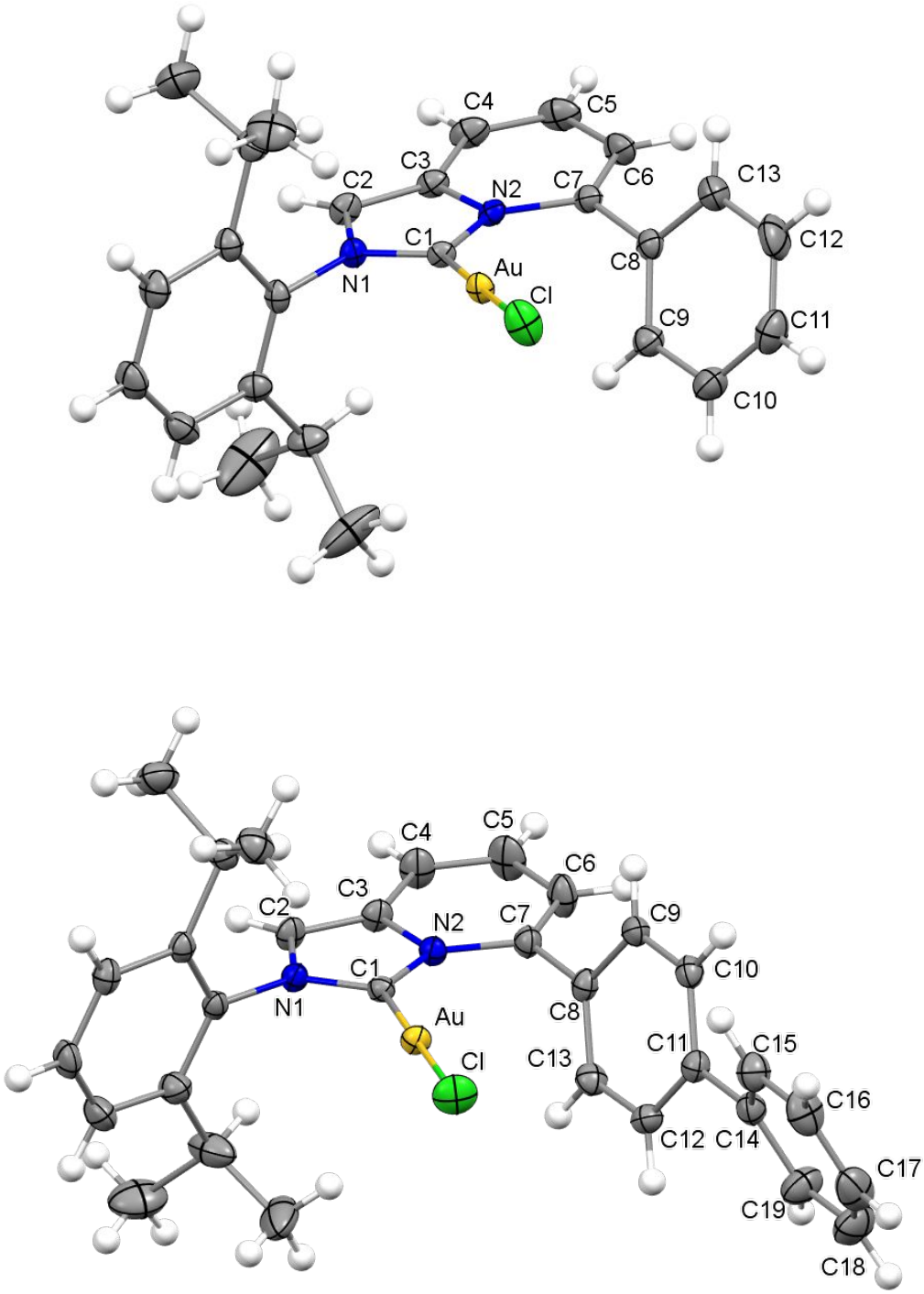


Figure S4. ORTEP drawing of one of the two independent molecules of **10c** (top) and **10d** (bottom). Thermal ellipsoid are drawn at 30% of the probability level.

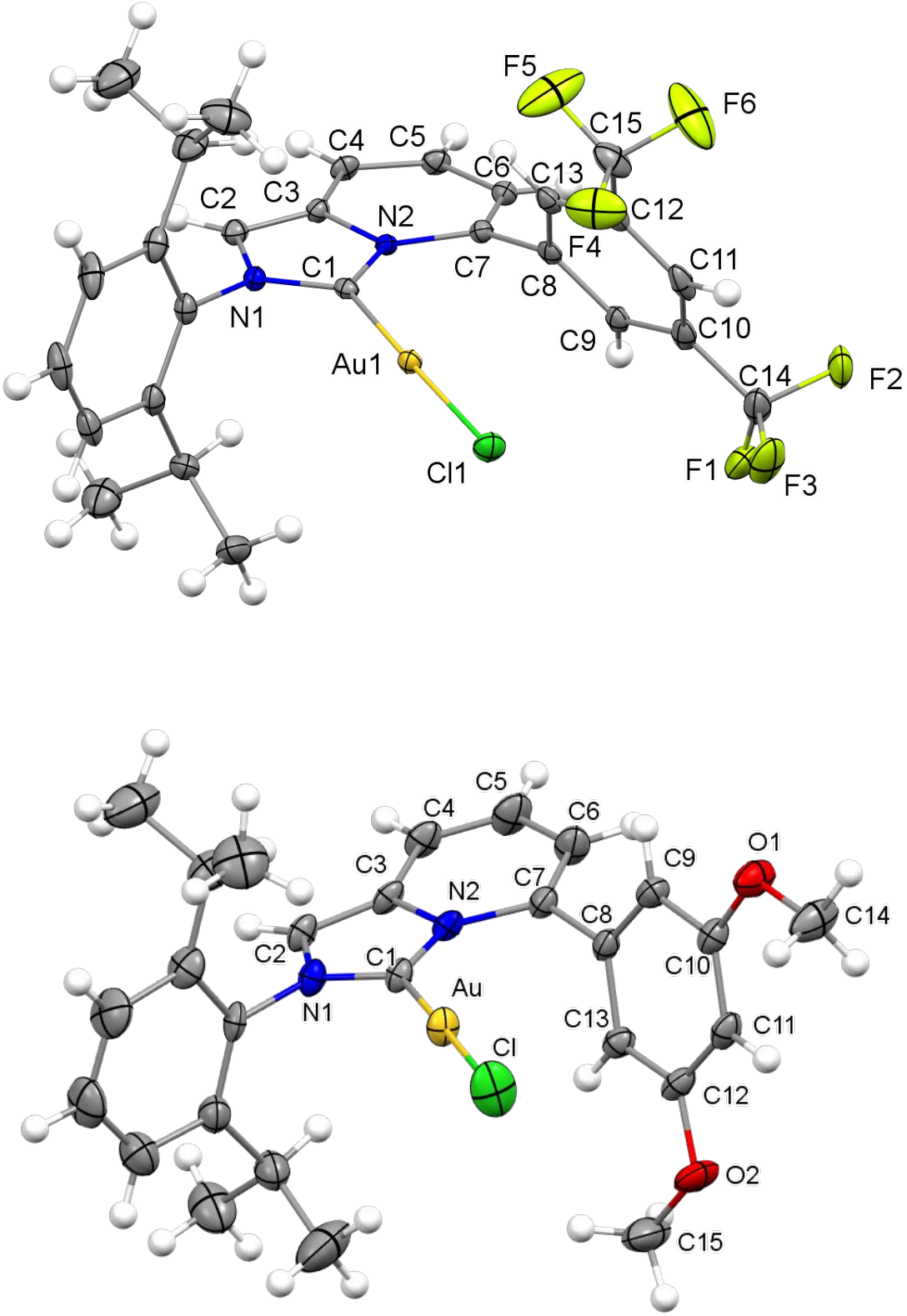


Table S6. Relevant hydrogen bonding for the P_n-series **10a-10d**.

10a

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C6-H6	2.89	132.0	3.580(9)	Cl[a]
C2-H2	2.80	148.8	3.629(9)	Cl[b]

Symmetry operation used to generate equivalent atoms: [a] x+1/2, y+1/2, z; [b] x+1/2, -y+3/2, z-1/2.

10b

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C4-H4	2.86	149.7	3.687(4)	Cl[a]

Symmetry operation used to generate equivalent atoms: [a] x+1, y, z.

10c

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C6-H6	2.99	127.4	3.643(6)	Cl1B
C4-H4	2.80	136.2	3.544(6)	Cl1B[a]
C2B-H2B	2.84	129.7	3.524(6)	Cl1[b]
C1S-H1S1	2.55	136.7	3.34(2)	F3[b]
C1S-H1S2	2.90	158.1	3.83(2)	Cl1[c]

Symmetry operation used to generate equivalent atoms: [a] -x+1, -y+1, -z+1; [b] -x+1, -y, -z+1; [c] x-1, y, z-1

10d

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C15-H15B	2.78	132.9	3.508(8)	Cl[a]

Symmetry operation used to generate equivalent atoms: [a] -x+1, -y, -z+1.

Table S7. Crystal data and experimental details for **10b'.**

Compound	**10b'**
Formula	$C_{33}H_{33}AuF_6N_3Sb{\bullet}CH_3CN$
Fw	945.39
T, K	296(2)
λ, Å	0.71073
Crystal symmetry	Triclinic
Space group	P-1
a, Å	11.464(5)
b, Å	13.676(4)
c, Å	13.934(4)
α	99.58(2)
β	109.15(2)
γ	112.69(2)
Cell volume, Å^3	1793.1(1)
Z	2
D_c, Mg m^{-3}	1.751
μ(Mo-K_α), mm^{-1}	4.900
F(000)	916
Crystal size/ mm	0.28 x 0.14 x 0.07
θ limits, °	1.935 to 26.388
Reflections collected	24348
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	7188 [R(int) = 0.0334]
Goodness-of-fit-on F^2	1.053
R_1 (F)[a], wR_2 (F^2) [$I > 2\sigma(I)$][b]	R1 = 0.0259, wR2 = 0.0561
Largest diff. peak and hole, e. Å^{-3}	0.515 and -0.693

[a)]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.[b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S5. ORTEP drawing of **10b'**. Thermal ellipsoid are drawn at 30% of the probability level.

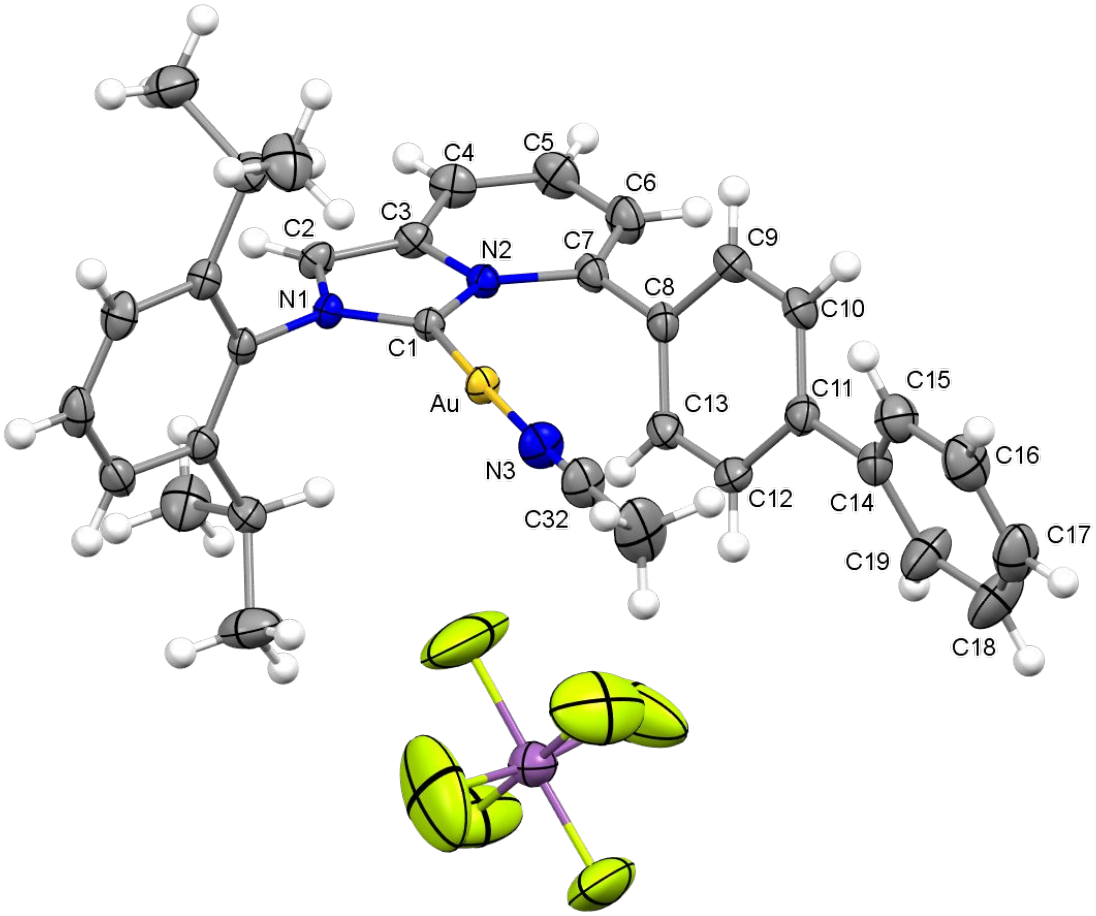


Table S8. Relevant hydrogen-bonding of **10b'**.

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C6-H6	2.60	161.0	3.49(2)	F5B[a]
C6-H6	2.32	155.9	3.19(2)	F4[a]
C33-H33A	2.52	129.0	3.211(8)	F6
C33-H33B	2.57	150.2	3.44(3)	F4B[b]
C2S-H2S1	2.20	140.3	3.00(3)	F5

Symmetry operation used to generate equivalent atoms: [a] x-1, y, z; [b] -x+1, -y+1, -z+1.

Table S9. Crystal data and experimental details for the T_n-series (**10e-10g**).

Compound	**10e**	**10f**	**10g**
Formula	$C_{23}H_{24}AuClN_2S$	$C_{27}H_{26}AuClN_2S_2$	$C_{31}H_{28}AuClN_2S_3$
Fw	592.92	675.03	757.15
T, K	296(2)	296(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal symmetry	Monoclinic	Monoclinic	Triclinic
Space group	Cc	C2/c	P-1
a, Å	14.5656(3)	26.832(1)	9.9008(4)
b, Å	13.4438(3)	9.3547(4)	11.8021(5)
c, Å	11.6052(2)	21.9411(9)	12.8588(5)
α, °	90	90	90.483(1)
β, °	97.303(1)	106.099(2)	99.696(1)
γ, °	90	90	93.561(1)
Cell volume, Å^3	2254.06(8)	5291.4(4)	1478.0(1)
Z	4	8	2
D_c, Mg m^{-3}	1.747	1.695	1.701
μ(Mo-K_α), mm^{-1}	6.748	5.837	5.303
F(000)	1152	2640	744
Crystal size/ mm	0.28 x 0.22 x 0.20	0.20 x 0.16 x 0.10	0.11 x 0.08 x 0.06
θ limits, °	2.069 to 26.398	1.580 to 28.355	1.607 to 26.000
Reflections collected	18724	38550	19132
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	4606 [R(int) = 0.0372]	6546 [R(int) = 0.0513]	5731 [R(int) = 0.0297]
Goodness-of-fit-on F^2	1.055	0.861	1.046
R_1 (F)[a], wR_2 (F^2) [$I > 2\sigma(I)$][b]	R1 = 0.0184, wR2 = 0.0487	R1 = 0.0458, wR2 = 0.1053	R1 = 0.0196, wR2 = 0.0483
Largest diff. peak and hole, e. Å^{-3}	0.991 and -0.355	2.313 and -1.041	1.034 and -0.653

[a)] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b)] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S6. ORTEP drawing of **10e** (top) and **10f** (bottom)**.** Thermal ellipsoid are drawn at 30% of the probability level.

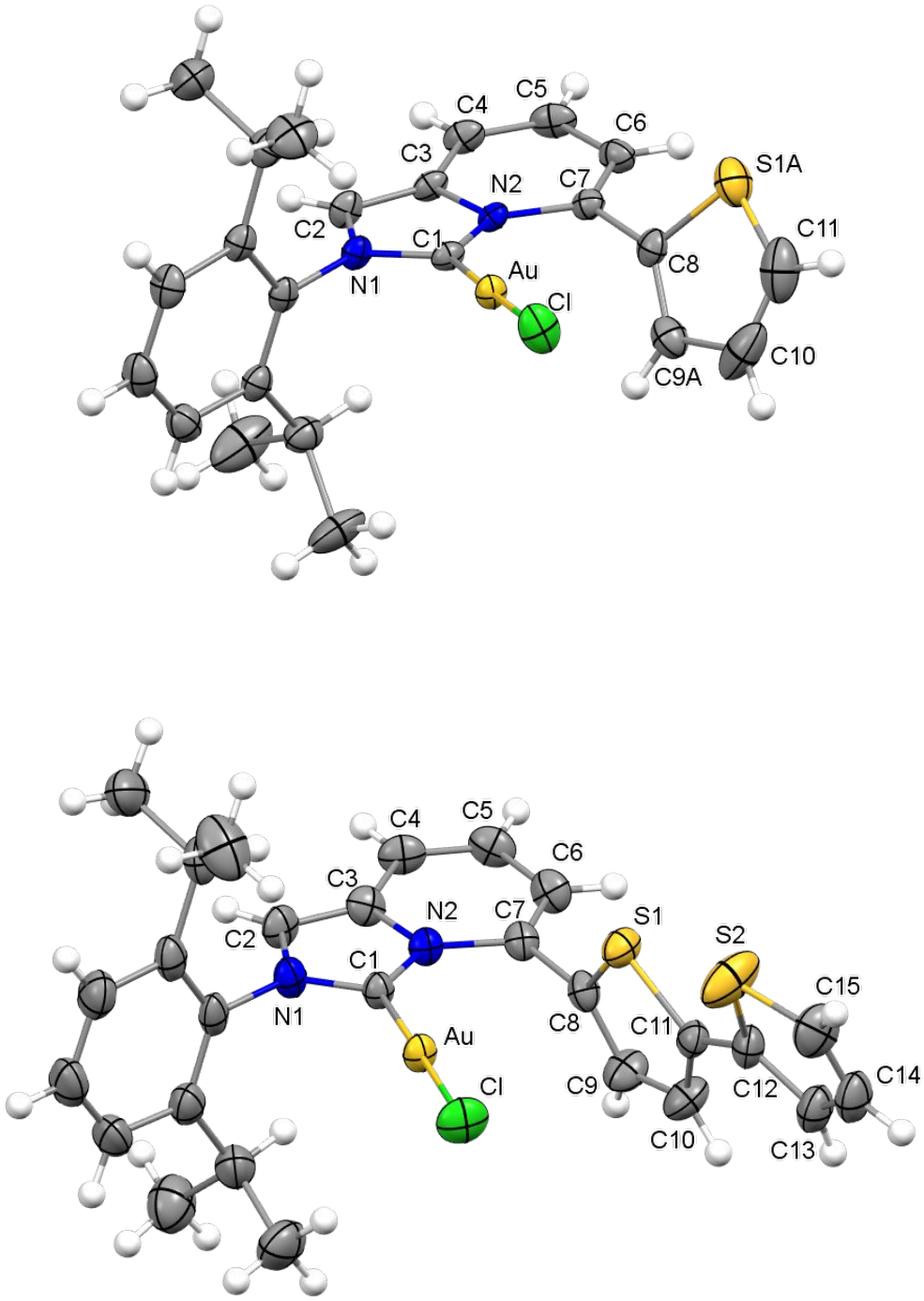


Figure S7. ORTEP drawing of **10g.** Thermal ellipsoid are drawn at 30% of the probability level.

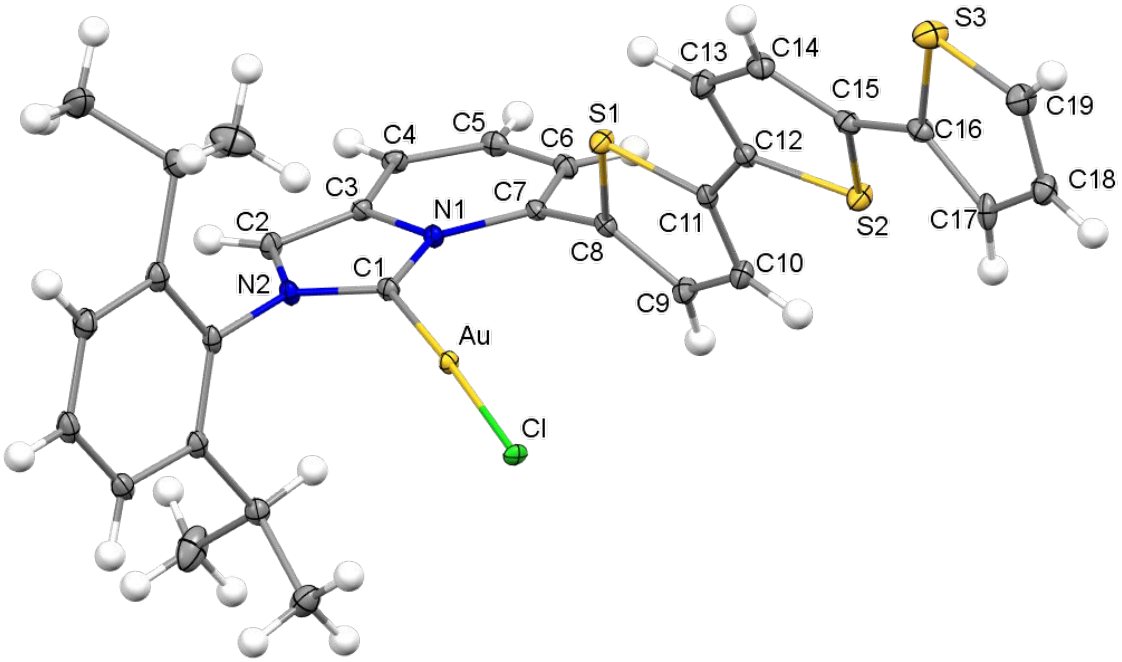


Table S10. Relevant hydrogen-bonding T_n-series.

10e

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C2-H2	2.74	148.0	3.562(7)	Cl[a]
C6-H6	2.84	134.0	3.554(8)	Cl[b]

Symmetry operation used to generate equivalent atoms: [a] x+1/2, -y+3/2, z-1/2; [b] x+1/2, y+1/2, z.

10f

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C4-H4	2.71	169.1	3.628(7)	Cl[a]
C13-H13	2.87	159.0	3.75(1)	Cl[b]

Symmetry operation used to generate equivalent atoms: [a] x, -y+1, z+1/2; [b] -x+3/2, -y+3/2, -z+1.

sulphur-sulphur	d [Å]
S1-S2	3.301

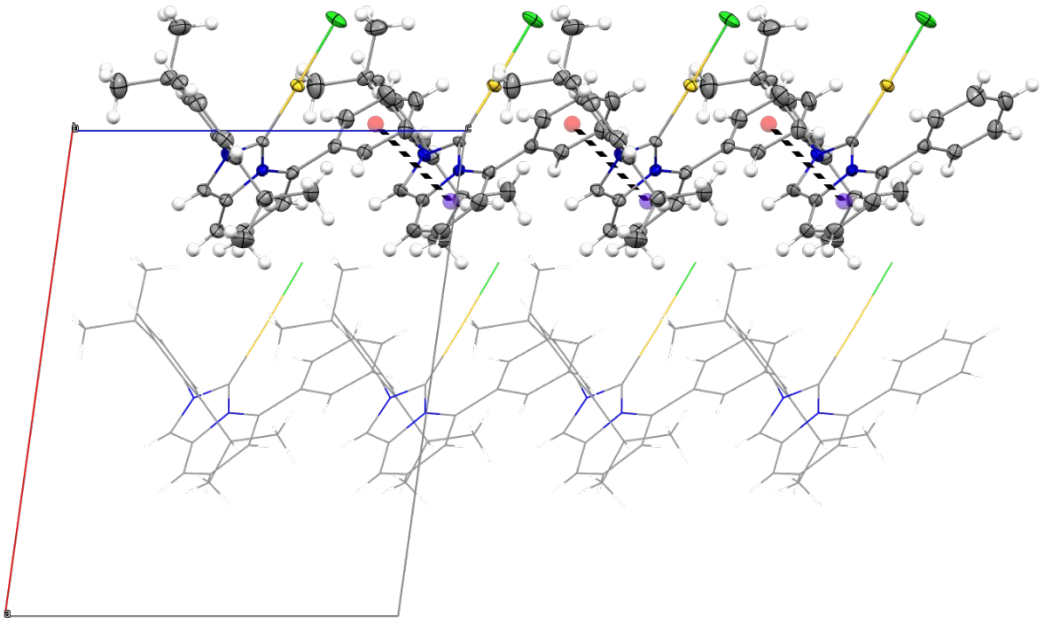
10g

D-H	d (H…A) [Å]	<DHA [°]	d (D…A)	A
C4-H4	2.88	137.2	3.621(3)	Cl[a]
C9-H9	2.80	153.0	3.656(3)	Cl[b]
C2-H2	2.74	137.6	3.490(3)	Cl[a]
C13-H13	3.03	144.8	3.825(4)	S1[c]

Symmetry operation used to generate equivalent atoms: [a] x+1, y, z; [b] -x+1, -y+1, -z+2; [c] -x+1, -y+1, -z+1.

Arene-arene π-π interactions

Figure S8. View down the *b* axis of the crystal packing of **10a** showing intermolecular π-π interactions (black dashed lines) between terminal phenyls and pyridine rings belonging to adjacent molecules (centroid-centroid distance 3.745 Å) generating zig-zag chains.



For T_n-series, π-π interactions were observed for **10e** and **10g**.

Figure S9. View down the *b* axis of the crystal packing of **10e** showing intermolecular π-π interactions (black dashed lines) between terminal thienyls and pyridine rings belonging to adjacent molecules (centroid-centroid distance 3.737 Å) generating zig-zag chains.

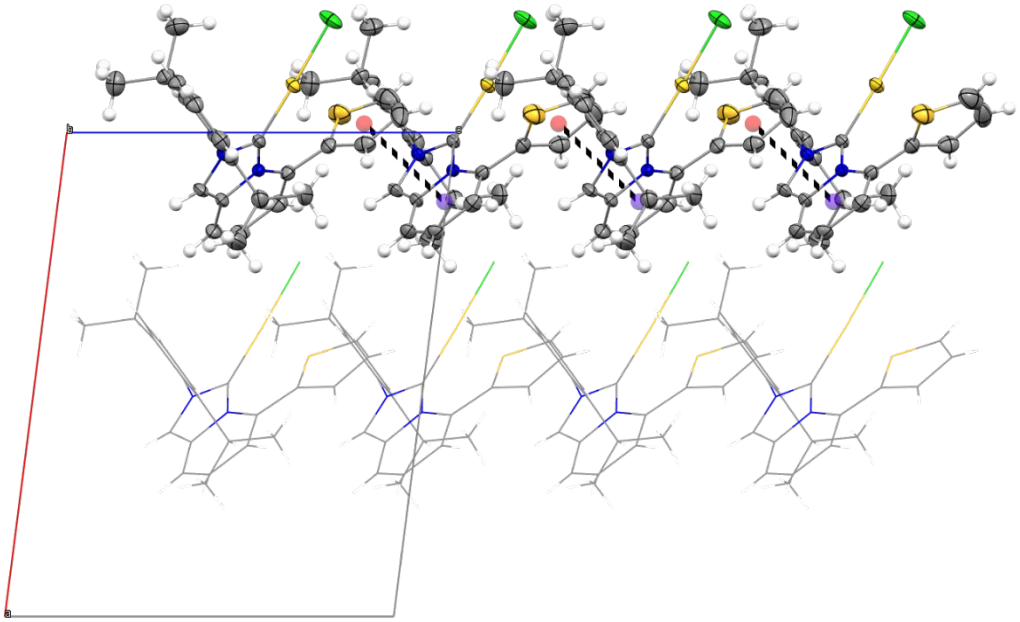
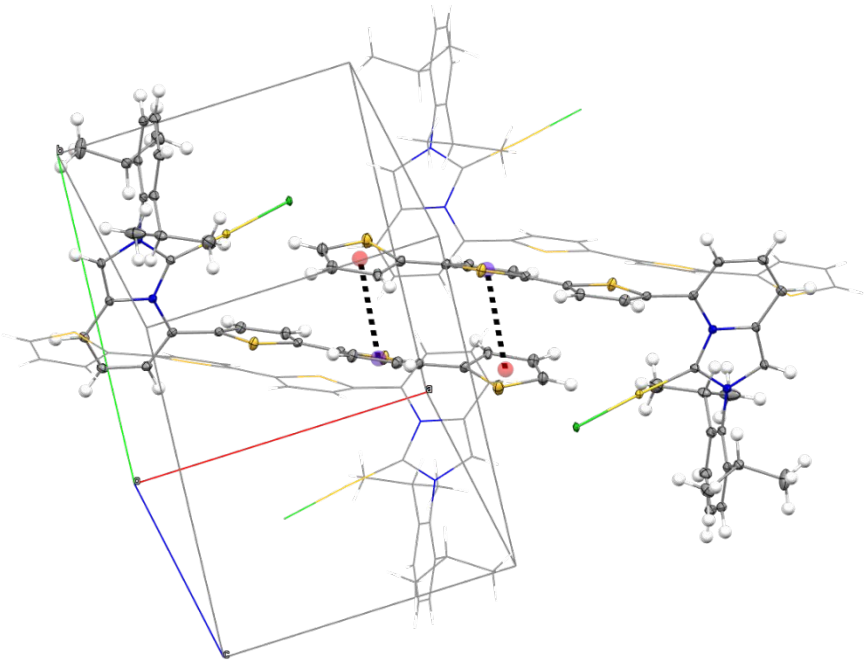


Figure S10. Arbitrary view of the crystal packing of **10g** showing two intermolecular π-π interactions (black dashed lines) involving the second and the third thienyl ring of one molecule and the third and second thienyl ring, respectively of the adjacent molecule (centroid-centroid distances 3.922 Å) generating dimeric units.



DIPP-ImPy dihedral angles

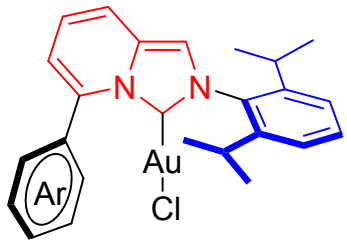


Table S11. Dihedral angles between DIPP (blue) and ImPy scaffold (red).

10	Dihedral angle [°]
10a	86.93
10b	84.06
10c	86.75
10d	87.89
10e	85.41
10f	93.94
10g	94.65

Cartesian coordinates for computed analysis

10a:

SCF Energy: E(RB3LYP) = -1673.90985081 A.U.
Zero-point correction= 0.450855 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.387954
Sum of electronic and thermal Free Energies= -1673.521897

C	-0.045074	3.068178	0.046776
C	0.507926	4.377705	0.001123
C	1.862818	4.516479	-0.073573
C	2.699373	3.353295	-0.069813
C	2.201430	2.082466	-0.006173
N	0.801851	1.926890	0.025179
H	-0.165651	5.228007	0.017651
H	2.319546	5.499884	-0.118648
H	3.777342	3.470495	-0.087960
C	3.109482	0.904278	0.067330
C	-1.329631	2.586215	0.077283
N	-1.240657	1.212178	0.058936
H	-2.275677	3.103302	0.097928
C	-2.405110	0.348814	0.067846
C	0.048844	0.773895	0.019099
Au	0.577736	-1.167668	-0.111144
Cl	1.101110	-3.470841	-0.292036
C	3.324459	0.244246	1.289395
C	4.265686	-0.782806	1.378190
C	4.996817	-1.166408	0.248173
C	4.789220	-0.512544	-0.969563
C	3.853291	0.522541	-1.059350
H	2.763322	0.543811	2.170392
H	4.426717	-1.284340	2.328602
H	5.725318	-1.969661	0.318268
H	5.354405	-0.804952	-1.850432
H	3.695744	1.034622	-2.004848
C	-2.993384	0.004104	-1.165766
C	-4.131471	-0.813666	-1.125223
C	-4.656338	-1.260275	0.086933
C	-4.053718	-0.893812	1.289800
C	-2.914171	-0.077359	1.311256
C	-2.448323	0.484531	-2.508029
H	-4.612397	-1.106012	-2.054380
H	-5.538261	-1.895594	0.094239
H	-4.475041	-1.247684	2.226468
C	-2.284476	0.316441	2.644699
H	-1.402978	0.931439	2.440062
C	-3.249826	1.171427	3.491728
C	-1.802475	-0.918192	3.432962
H	-1.300707	-0.602223	4.355686
H	-2.639579	-1.568430	3.713899
H	-1.094460	-1.511574	2.843814
H	-2.756691	1.490815	4.417822
H	-3.569858	2.068849	2.949280

H	-4.148008	0.606347	3.768545
H	-1.544961	1.072730	-2.321151
C	-2.040203	-0.695391	-3.412909
C	-3.455038	1.408616	-3.224349
H	-1.594534	-0.318932	-4.341661
H	-1.304805	-1.337781	-2.916038
H	-2.904401	-1.313560	-3.684061
H	-3.021407	1.786856	-4.158028
H	-4.379062	0.874385	-3.476318
H	-3.722943	2.269098	-2.599995

10c:

SCF Energy: E(RB3LYP) = -2348.02274547 A.U.
Zero-point correction= 0.459135 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.383470
Sum of electronic and thermal Free Energies= -2347.639275

C	1.490791	1.457293	2.756680
C	1.140918	2.139721	3.954666
C	-0.176939	2.363870	4.225502
C	-1.180963	1.880964	3.323972
C	-0.875734	1.206533	2.176840
N	0.480731	1.010810	1.861852
H	1.934957	2.471878	4.615122
H	-0.479397	2.888816	5.125516
H	-2.228760	2.022783	3.565275
C	-1.950433	0.650997	1.307493
C	2.686332	1.119043	2.174321
N	2.389311	0.511453	0.975242
H	3.700249	1.273724	2.507242
C	3.408375	0.028236	0.063523
C	1.048326	0.436114	0.747157
Au	0.223701	-0.289666	-0.943768
Cl	-0.668396	-1.120990	-2.969637
C	-2.753380	1.510182	0.552954
C	-3.829973	0.999439	-0.182690
C	-4.122976	-0.362077	-0.163310
C	-3.322500	-1.217834	0.601956
C	-2.243576	-0.721939	1.331435
H	-2.532972	2.572824	0.533228
C	-4.687625	1.957878	-0.968319
H	-4.956317	-0.753504	-0.734991
C	-3.673072	-2.682008	0.675327
H	-1.633012	-1.393013	1.925620
C	3.844979	-1.305518	0.193197
C	4.846558	-1.738148	-0.687328
C	5.386637	-0.879302	-1.643828
C	4.936687	0.437048	-1.739173
C	3.936635	0.925496	-0.886647
C	3.281829	-2.266024	1.237094
H	5.208414	-2.760419	-0.623868

H	6.161361	-1.236944	-2.317105
H	5.367944	1.094748	-2.488493
C	3.470918	2.373861	-1.009415
H	2.667329	2.539091	-0.285460
C	4.606200	3.359993	-0.664058
C	2.888126	2.668868	-2.406230
H	2.504025	3.695498	-2.443035
H	3.648499	2.568869	-3.189909
H	2.064270	1.986441	-2.642764
H	4.234855	4.391151	-0.704086
H	5.001580	3.179135	0.342418
H	5.438465	3.275898	-1.373183
H	2.508427	-1.741095	1.805860
C	2.609897	-3.488664	0.580161
C	4.367128	-2.703482	2.242483
H	2.162000	-4.129631	1.349220
H	1.818685	-3.180345	-0.112254
H	3.333727	-4.093650	0.021250
H	3.927717	-3.345473	3.015491
H	5.165019	-3.271697	1.749460
H	4.824953	-1.838863	2.737263
F	-5.551724	1.330546	-1.797458
F	-5.435598	2.749507	-0.147964
F	-3.943004	2.800766	-1.729115
F	-2.617364	-3.451713	1.030332
F	-4.651016	-2.918858	1.597303
F	-4.139174	-3.158563	-0.504051

10d:

SCF Energy: E(RB3LYP) = -1902.96369214 A.U.
Zero-point correction= 0.515987 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.446958
Sum of electronic and thermal Free Energies= -1902.516734

C	0.974562	3.087194	0.344354
C	0.601500	4.455367	0.453610
C	-0.722833	4.780204	0.417806
C	-1.707763	3.745595	0.306985
C	-1.383530	2.421247	0.222154
N	-0.017765	2.077971	0.212902
H	1.382654	5.201880	0.551194
H	-1.043813	5.814456	0.488694
H	-2.760530	4.005380	0.318914
C	-2.439585	1.371216	0.182258
C	2.182994	2.438781	0.294345
N	1.910405	1.099681	0.123763
H	3.189894	2.820298	0.352170
C	2.949417	0.095498	0.009257
C	0.573684	0.843449	0.061309
Au	-0.213482	-0.981855	-0.280379
Cl	-1.042627	-3.157494	-0.717312

C	-3.226551	1.241527	-0.958568
C	-4.286883	0.314646	-0.968278
C	-4.558287	-0.457007	0.159913
C	-3.762633	-0.305132	1.310706
C	-2.700405	0.600676	1.333478
H	-3.032481	1.835705	-1.845573
O	-4.996672	0.247615	-2.131500
H	-5.364988	-1.179404	0.187028
O	-4.119200	-1.096473	2.364229
H	-2.084961	0.728752	2.215067
C	3.411922	-0.527886	1.185705
C	4.434900	-1.476581	1.047196
C	4.970954	-1.782226	-0.203217
C	4.495007	-1.140966	-1.346272
C	3.473017	-0.184331	-1.269152
C	2.852196	-0.208038	2.569181
H	4.817095	-1.982930	1.929062
H	5.762659	-2.522264	-0.287078
H	4.923163	-1.388229	-2.313570
C	2.980578	0.508112	-2.537053
H	2.160707	1.179678	-2.265348
C	4.089918	1.373889	-3.169765
C	2.417816	-0.501929	-3.557157
H	2.016435	0.029742	-4.428422
H	3.193572	-1.189857	-3.914171
H	1.610138	-1.098017	-3.118199
H	3.699747	1.905417	-4.046164
H	4.469355	2.118903	-2.460497
H	4.937011	0.760305	-3.499494
H	2.056718	0.534552	2.454648
C	2.220368	-1.451347	3.227232
C	3.928676	0.414353	3.482423
H	1.771986	-1.179802	4.190724
H	1.436630	-1.879045	2.592184
H	2.968103	-2.231068	3.415184
H	3.489969	0.688566	4.449509
H	4.747418	-0.289627	3.674034
H	4.358883	1.318134	3.035110
C	-6.073052	-0.687775	-2.224111
H	-6.476711	-0.572979	-3.230853
H	-5.714546	-1.714401	-2.085793
H	-6.853871	-0.464115	-1.487355
C	-3.345985	-1.030402	3.563562
H	-3.798460	-1.751815	4.245170
H	-2.302401	-1.307356	3.374955
H	-3.391187	-0.028418	4.007225

Intermediate **Aa**:

SCF Energy: E(RB3LYP) = -1464.17372032 A.U.
Zero-point correction= 0.583904 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.513004
Sum of electronic and thermal Free Energies= -1463.660716

C	0.854387	-3.432181	0.317851
C	1.715719	-4.562083	0.378191
C	3.064285	-4.363275	0.317752
C	3.586110	-3.031619	0.241311
C	2.785569	-1.924251	0.206931
N	1.391768	-2.122006	0.207545
H	1.275178	-5.550181	0.458305
H	3.751704	-5.202315	0.350067
H	4.659526	-2.877516	0.249222
C	3.364360	-0.553695	0.224825
C	-0.510471	-3.282601	0.297833
N	-0.760422	-1.935918	0.160126
H	-1.300260	-4.014807	0.354077
C	-2.101238	-1.389806	0.090488
C	0.380688	-1.194327	0.092322
Au	0.419973	0.836283	-0.311049
C	4.125927	-0.100811	-0.863085
C	4.772524	1.138154	-0.806194
C	4.674061	1.928689	0.342088
C	3.922612	1.479000	1.434317
C	3.266935	0.248079	1.376022
H	4.210968	-0.719285	-1.752563
H	5.356290	1.479741	-1.656697
H	5.184029	2.887206	0.389339
H	3.852491	2.083644	2.334720
H	2.696053	-0.103466	2.231154
C	-2.729009	-1.004024	1.292197
C	-4.034382	-0.500430	1.199607
C	-4.681212	-0.395388	-0.031444
C	-4.034759	-0.796405	-1.200197
C	-2.728901	-1.306466	-1.169012
C	-2.053296	-1.123583	2.655654
H	-4.553692	-0.191812	2.102577
H	-5.694713	-0.005420	-0.079581
H	-4.554052	-0.715341	-2.150928
C	-2.054325	-1.752794	-2.463458
H	-1.038768	-2.082713	-2.225277
C	-2.789253	-2.954453	-3.093134
C	-1.927620	-0.592203	-3.470786
H	-1.386885	-0.927935	-4.363868
H	-2.910348	-0.228056	-3.793613
H	-1.377929	0.249647	-3.034573
H	-2.255804	-3.295097	-3.988668
H	-2.852224	-3.796043	-2.393490
H	-3.809986	-2.687670	-3.392262

H	-1.048029	-1.528706	2.506472
C	-1.890962	0.252962	3.331254
C	-2.808092	-2.105704	3.575119
H	-1.353865	0.145524	4.281372
H	-1.323287	0.939952	2.693086
H	-2.863016	0.712283	3.547402
H	-2.269702	-2.223128	4.523252
H	-3.817594	-1.745099	3.806036
H	-2.900754	-3.094537	3.111288
C	0.400966	2.852380	-0.850790
C	-0.047364	3.654078	0.257501
C	0.819651	3.354135	-2.025758
H	0.603845	3.728365	1.128218
N	-1.207042	4.245313	0.392484
H	1.163371	2.709062	-2.829645
H	0.859514	4.426934	-2.221488
C	-1.578435	4.929570	1.639860
C	-2.247613	4.234614	-0.645133
H	-3.181255	3.880614	-0.198988
H	-2.393121	5.252118	-1.019312
H	-1.949381	3.581282	-1.462392
H	-1.853515	5.963264	1.412809
H	-2.436530	4.420802	2.089365
H	-0.737455	4.917232	2.333582

Intermediate **Ac**:

SCF Energy: *E(RB3LYP) =* -2138.28671996 *A.U.*
Zero-point correction= *0.592365 (Hartree/Particle)*
Thermal correction to Gibbs Free Energy= *0.510086*
Sum of electronic and thermal Free Energies= *-1463.660716*

C	-1.274658	-3.450823	1.014054
C	-0.857076	-4.759730	1.381629
C	0.477589	-5.040772	1.415273
C	1.429741	-4.010762	1.124113
C	1.057525	-2.739415	0.791701
N	-0.315523	-2.452037	0.697183
H	-1.613176	-5.502066	1.614248
H	0.831616	-6.031155	1.681265
H	2.489856	-4.225421	1.203422
C	2.072930	-1.671115	0.587638
C	-2.502193	-2.863435	0.831302
N	-2.268033	-1.576027	0.405461
H	-3.497387	-3.260702	0.952567
C	-3.333302	-0.641517	0.097190
C	-0.939858	-1.290695	0.301916
Au	-0.190989	0.480485	-0.466383
C	2.967771	-1.755796	-0.481767
C	3.993640	-0.811259	-0.617745
C	4.144726	0.213464	0.312355

C	3.251820	0.289841	1.388532
C	2.219777	-0.635945	1.526683
H	2.861965	-2.555111	-1.208583
C	4.943696	-0.942966	-1.780836
H	4.945270	0.936864	0.209049
C	3.395855	1.417657	2.377104
H	1.542632	-0.575027	2.371439
C	-3.807097	0.195617	1.127570
C	-4.848704	1.077685	0.806860
C	-5.392670	1.115258	-0.476676
C	-4.907224	0.265056	-1.469675
C	-3.866820	-0.637802	-1.207554
C	-3.241097	0.168378	2.544706
H	-5.242687	1.739853	1.572608
H	-6.201777	1.805136	-0.702241
H	-5.345678	0.301154	-2.462838
C	-3.368396	-1.567058	-2.311068
H	-2.548966	-2.169891	-1.908442
C	-4.473391	-2.543938	-2.764081
C	-2.802980	-0.777622	-3.508835
H	-2.401692	-1.469518	-4.259123
H	-3.577614	-0.171872	-3.994036
H	-1.994274	-0.108500	-3.193518
H	-4.074439	-3.244976	-3.506931
H	-4.862704	-3.125932	-1.920583
H	-5.314802	-2.012080	-3.224141
H	-2.448770	-0.585012	2.584012
C	-2.601176	1.519348	2.923767
C	-4.313277	-0.246114	3.573268
H	-2.148897	1.456268	3.920822
H	-1.817872	1.797596	2.208909
H	-3.345371	2.324581	2.944803
H	-3.867709	-0.319075	4.572580
H	-5.127748	0.486338	3.622987
H	-4.749796	-1.219957	3.322608
C	0.521886	2.232671	-1.346892
C	0.303574	3.357433	-0.472799
C	1.174396	2.309393	-2.520428
H	0.860669	3.387729	0.463128
N	-0.564869	4.323704	-0.624154
H	1.330036	1.433137	-3.143720
H	1.600001	3.243007	-2.891749
C	-0.764693	5.344927	0.415607
C	-1.441440	4.452425	-1.797119
F	5.816524	0.086132	-1.864209
F	5.682160	-2.083129	-1.701542
F	4.282367	-1.001590	-2.967236
F	2.765861	1.168900	3.548457
F	4.692570	1.683854	2.667069
F	2.867942	2.581743	1.893995
H	-2.473981	4.552118	-1.451306

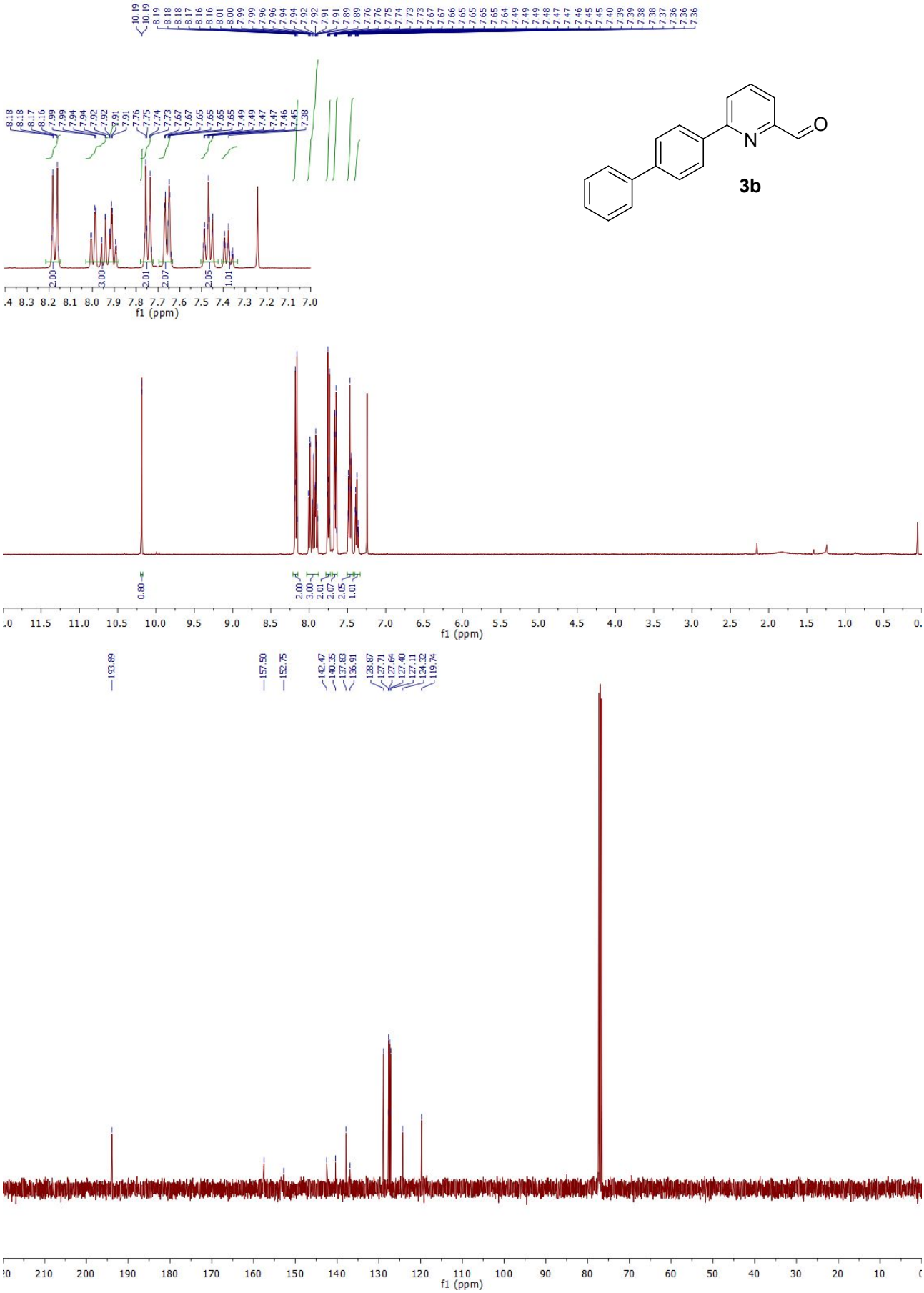
H	-1.163135	5.350447	-2.356072
H	-1.340169	3.576534	-2.434384
H	-0.625653	6.335558	-0.025613
H	-1.783490	5.266439	0.806830
H	-0.047198	5.198181	1.223215

Intermediate **Ad**:

SCF Energy: *E(RB3LYP) = -1693.22730199 A.U.*
Zero-point correction= *0.648764 (Hartree/Particle)*
Thermal correction to Gibbs Free Energy= *0.571061*
Sum of electronic and thermal Free Energies= *-1692.656241*

C	-1.018890	-3.516949	0.557161
C	-0.648221	-4.878951	0.730177
C	0.675682	-5.207794	0.700735
C	1.662057	-4.182175	0.537483
C	1.338401	-2.862671	0.392608
N	-0.025803	-2.518695	0.369390
H	-1.429282	-5.618951	0.868869
H	0.995002	-6.238168	0.818964
H	2.714298	-4.443316	0.560844
C	2.393381	-1.814640	0.309884
C	-2.225916	-2.866458	0.481932
N	-1.947588	-1.540095	0.240153
H	-3.233836	-3.240591	0.566181
C	-2.980614	-0.536040	0.081883
C	-0.610764	-1.290419	0.157465
Au	0.193803	0.548416	-0.349468
C	3.226836	-1.771943	-0.811888
C	4.291277	-0.859462	-0.847244
C	4.535849	-0.000935	0.233936
C	3.692221	-0.062200	1.354594
C	2.620093	-0.960674	1.397697
H	3.064736	-2.432911	-1.656963
O	5.048105	-0.881274	-1.982320
H	5.360642	0.697253	0.204755
O	3.847465	0.726563	2.459371
H	1.995010	-0.998397	2.283738
C	-3.421755	0.156876	1.227268
C	-4.435316	1.109302	1.048618
C	-4.984594	1.350280	-0.210436
C	-4.532104	0.638899	-1.321337
C	-3.519981	-0.324421	-1.203292
C	-2.850601	-0.096966	2.619747
H	-4.802993	1.666055	1.906100
H	-5.771958	2.090823	-0.325425
H	-4.974316	0.833212	-2.294411
C	-3.056224	-1.098580	-2.434385
H	-2.243096	-1.765743	-2.133547
C	-4.186702	-1.983107	-3.000382
C	-2.491707	-0.160187	-3.519906
H	-2.114587	-0.748477	-4.365106

H	-3.259886	0.521362	-3.904532
H	-1.665139	0.443306	-3.127852
H	-3.814855	-2.573197	-3.846637
H	-4.568547	-2.677580	-2.242912
H	-5.028506	-1.378105	-3.358006
H	-2.078875	-0.868082	2.538950
C	-2.172268	1.163511	3.193086
C	-3.929847	-0.632762	3.582806
H	-1.720331	0.938484	4.166674
H	-1.381806	1.523374	2.524196
H	-2.893327	1.976762	3.339338
H	-3.483318	-0.865134	4.557034
H	-4.725028	0.104375	3.746282
H	-4.392091	-1.547129	3.193072
C	0.938077	2.396661	-0.971087
C	0.730870	3.375071	0.064089
C	1.588887	2.638602	-2.122500
H	1.295775	3.263085	0.989146
N	-0.139068	4.353059	0.072377
H	1.731525	1.862383	-2.869248
H	2.025077	3.612077	-2.352776
C	-0.327288	5.200252	1.259467
C	-1.027841	4.657314	-1.057805
H	-2.056881	4.704864	-0.690716
H	-0.753202	5.628348	-1.480225
H	-0.935744	3.885757	-1.819428
H	-0.209996	6.248588	0.972332
H	-1.335227	5.048448	1.657442
H	0.411260	4.943803	2.019458
C	4.972823	1.604067	2.533702
H	4.901638	2.090732	3.507285
H	5.913801	1.044722	2.471730
H	4.938533	2.362829	1.742802
C	6.166741	0.001473	-2.087908
H	6.609308	-0.201297	-3.063840
H	5.848902	1.049779	-2.040458
H	6.904177	-0.200271	-1.302014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10.19
8.19
8.18
8.18
8.18
8.17
8.16
8.16
8.01
8.00
7.99
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7.96
7.96
7.94
7.94
7.92
7.92
7.91
7.91
7.89
7.76
7.76
7.75
7.74
7.73
7.73
7.67
7.67
7.66
7.65
7.65
7.65
7.65
7.64
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
2.00
3.00
2.01
2.07
2.05
1.01
f1 (ppm)
O
N
3b
0.80
2.00
3.00
2.01
2.07
2.05
1.01
f1 (ppm)
193.89
157.50
152.75
142.47
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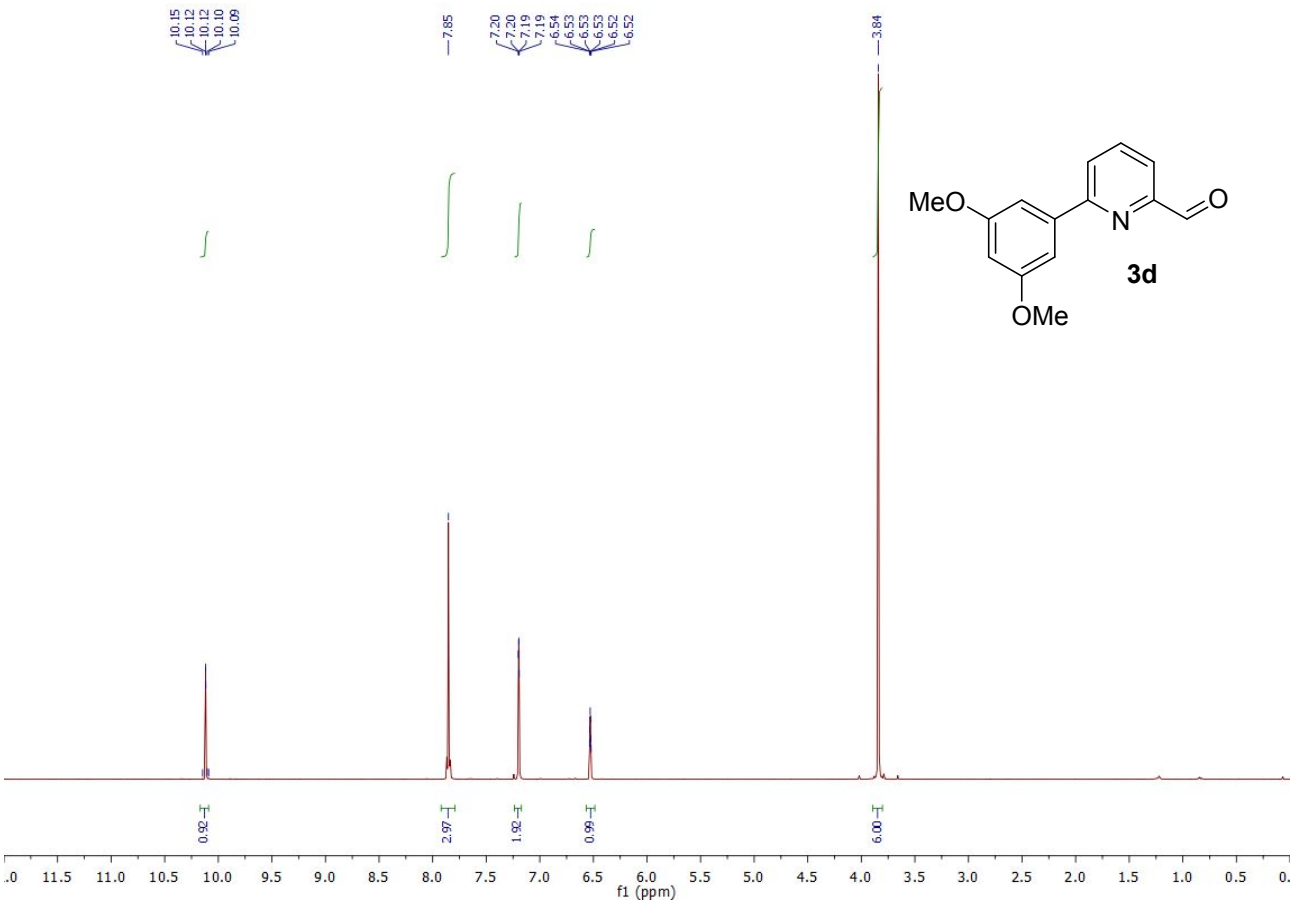
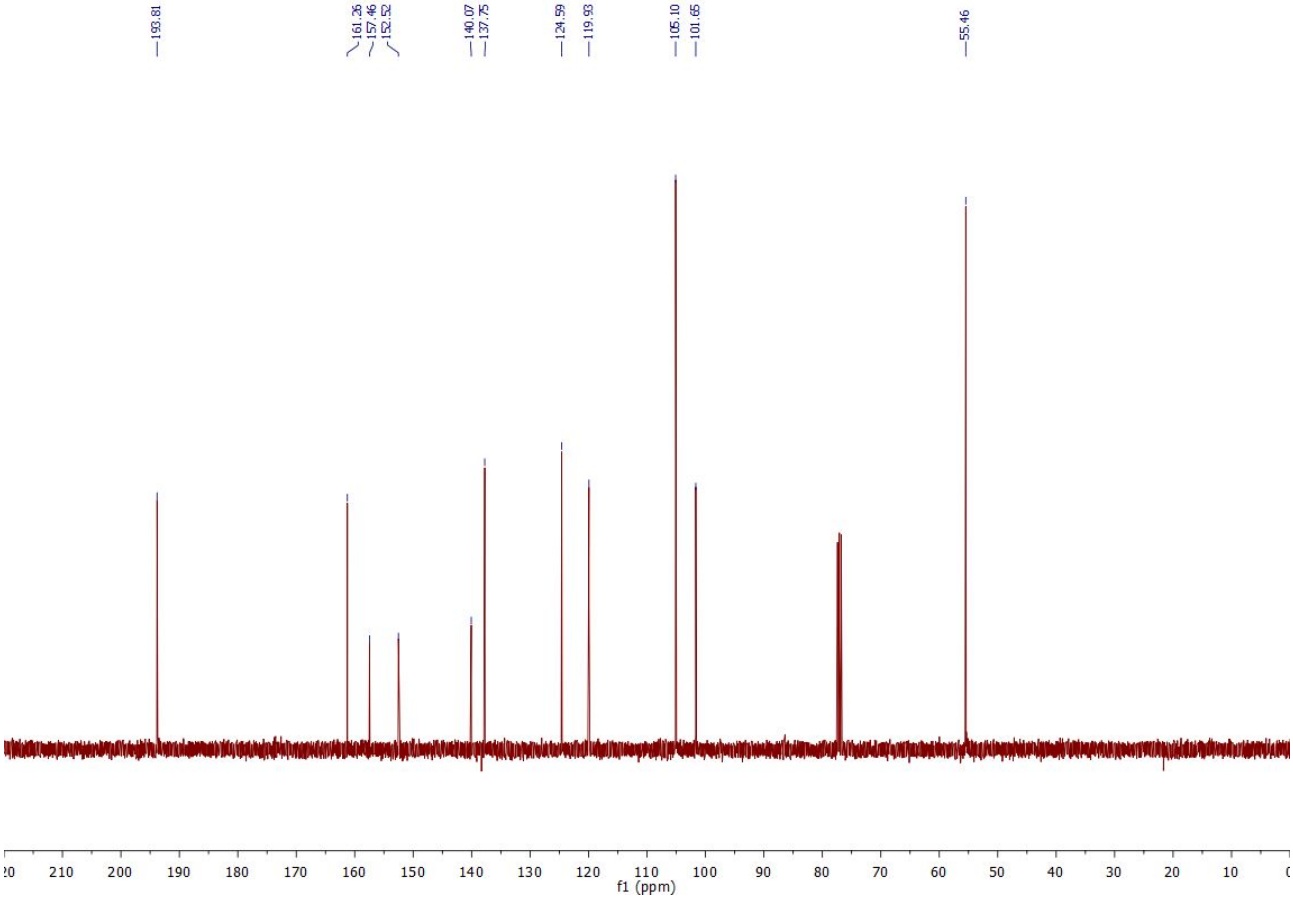
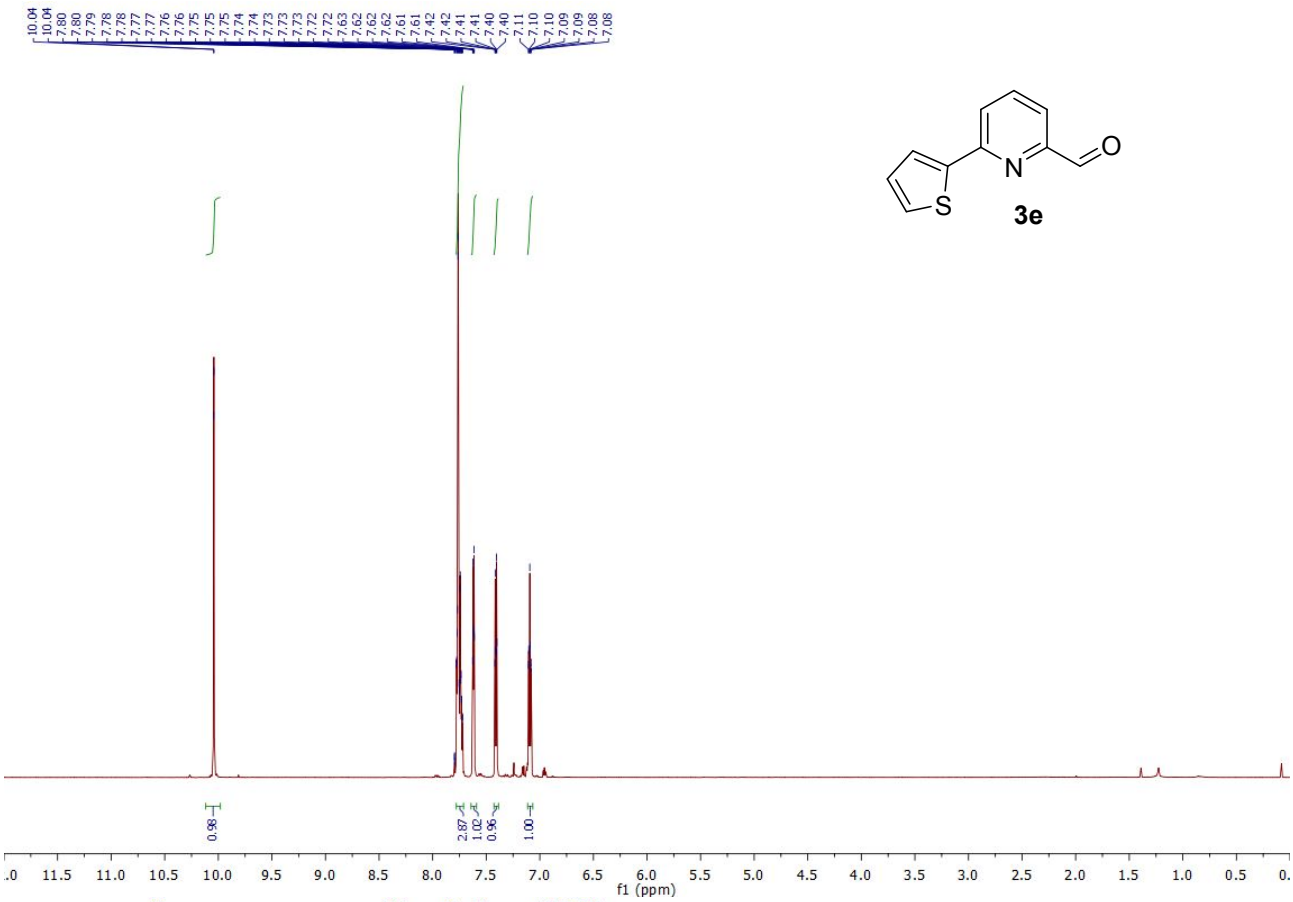
136.91
128.87
127.71
127.64
127.40
127.11
124.32
119.74
f1 (ppm)


10.15
10.12
10.12
10.10
10.09
7.85
7.20
7.20
7.19
7.19
6.54
6.53
6.53
6.52
6.52
3.84
MeO
N
O
OMe
3d
0.92
2.97
1.92
0.99
6.00
f1 (ppm)


193.81
161.26
157.46
152.52
140.07
137.75
124.59
119.93
105.10
101.65
55.46
f1 (ppm)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10.04
7.80
7.80
7.79
7.79
7.78
7.78
7.77
7.77
7.76
7.76
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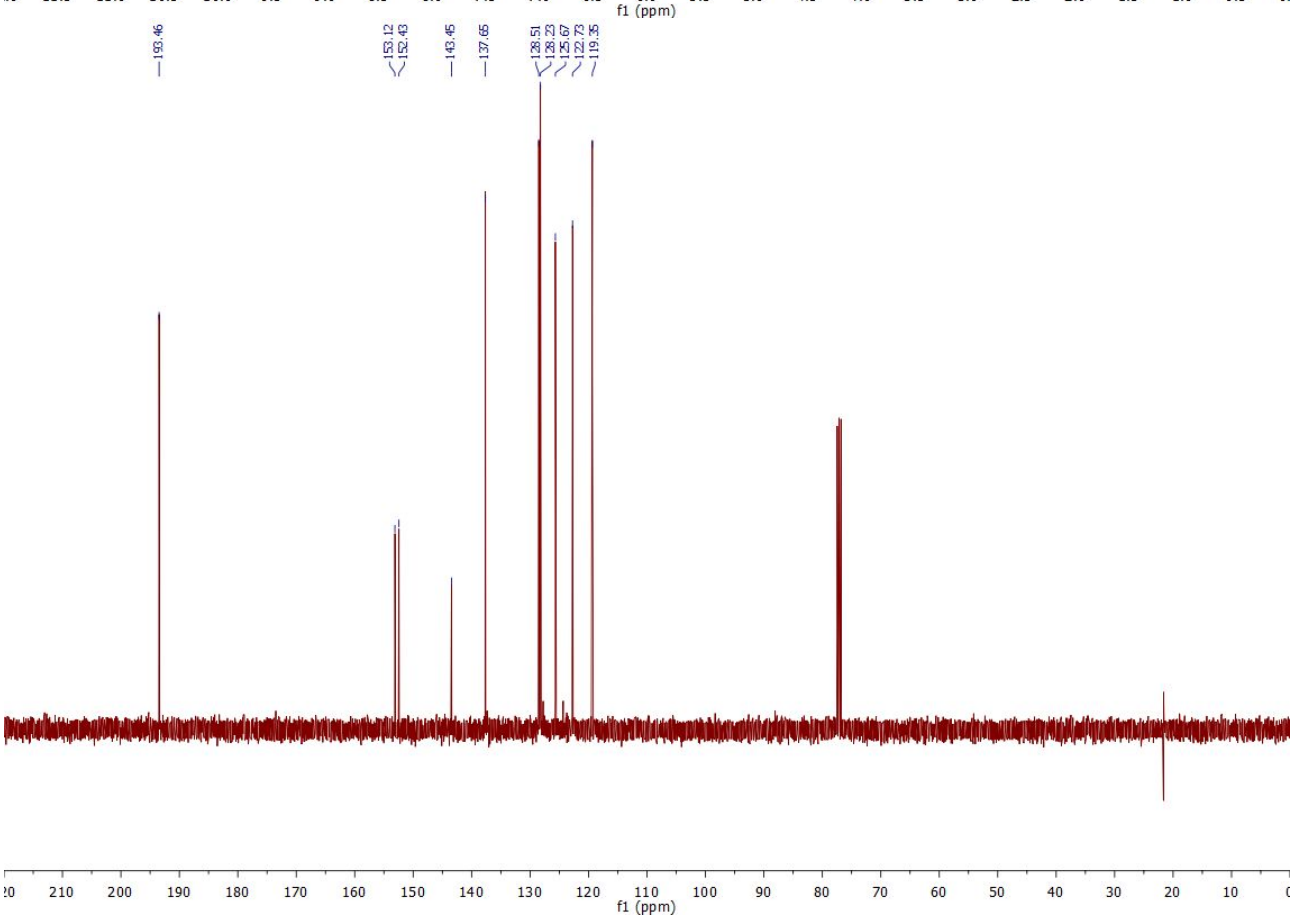
7.75
7.75
7.74
7.74
7.73
7.73
7.73
7.72
7.72
7.63
7.62
7.62
7.61
7.61
7.42
7.42
7.41
7.41
7.40
7.40
7.11
7.10
7.10
7.09
7.09
7.08
7.08
0.98
2.87
1.02
0.96
1.00
f1 (ppm)

O
N
S

3e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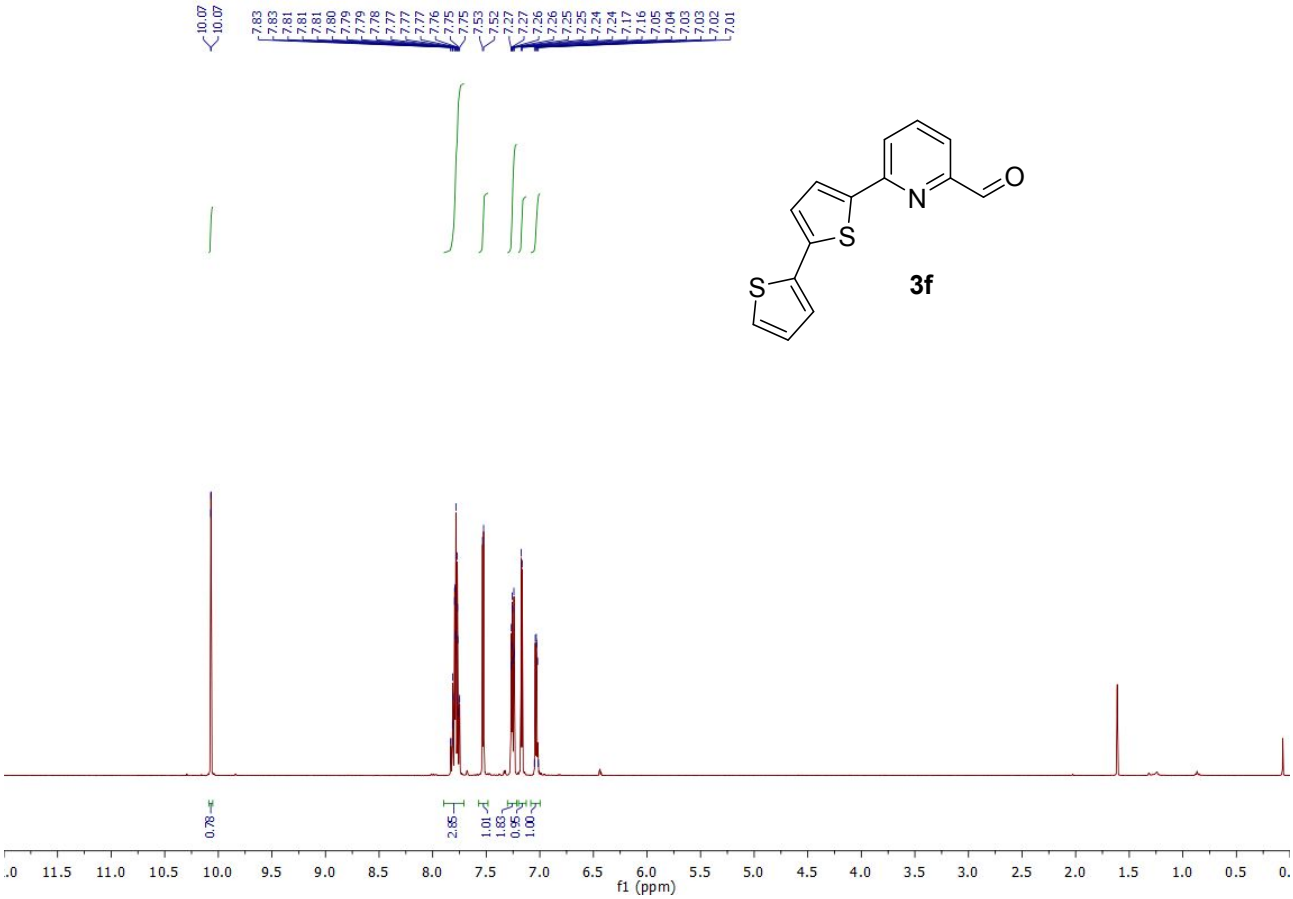
153.12
152.43
143.45
137.65
128.51
128.23
125.67
122.73
119.35
f1 (ppm)


10.07
10.07
7.83
7.83
7.81
7.81
7.81
7.80
7.79
7.79
7.78
7.77
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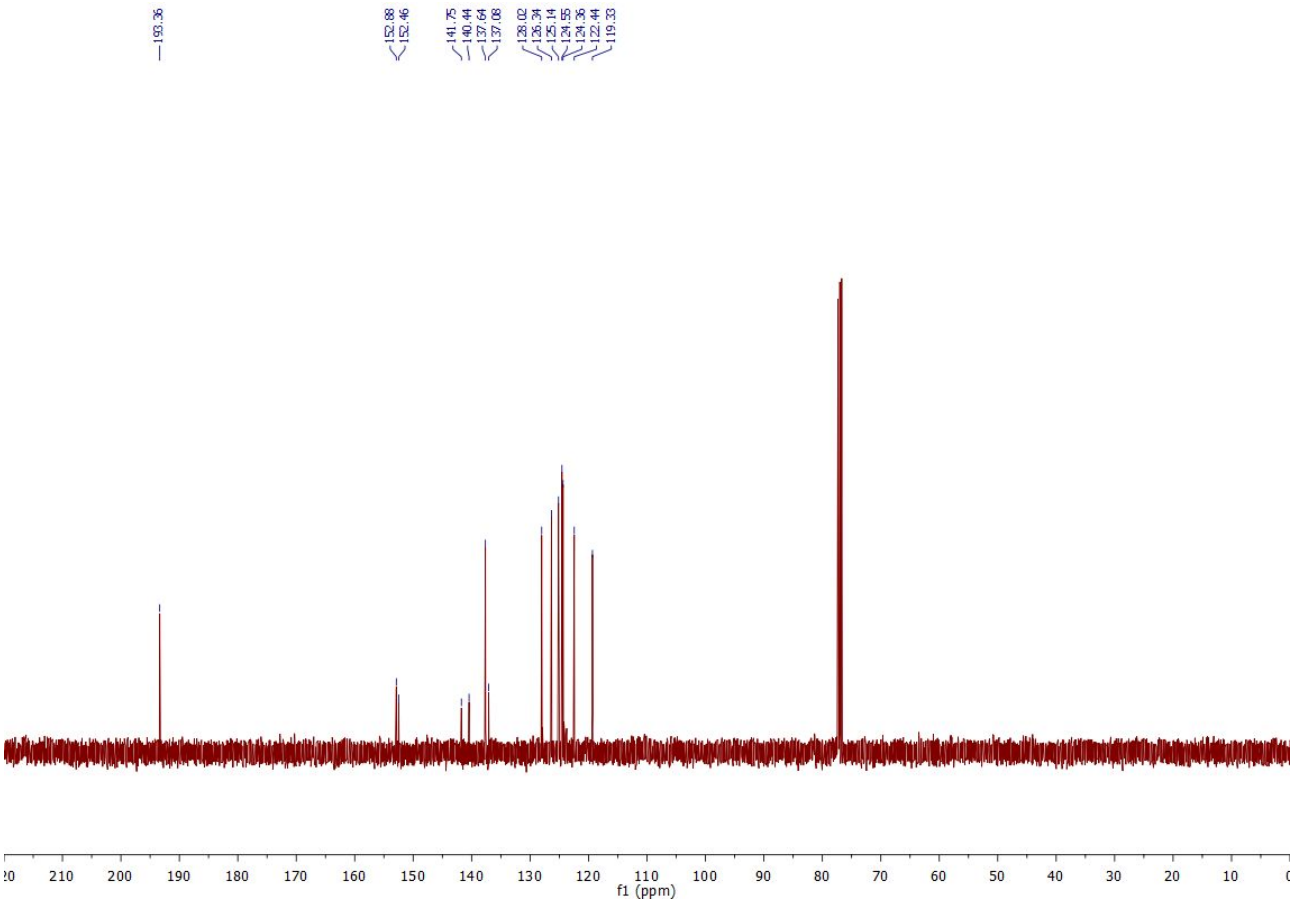
7.77
7.77
7.76
7.75
7.75
7.53
7.52
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.17
7.16
7.05
7.04
7.03
7.03
7.02
7.01
O
N
S
S
3f
0.78
2.85
1.01
1.83
0.95
1.00
f1 (ppm)


193.36
152.88
152.46
141.75
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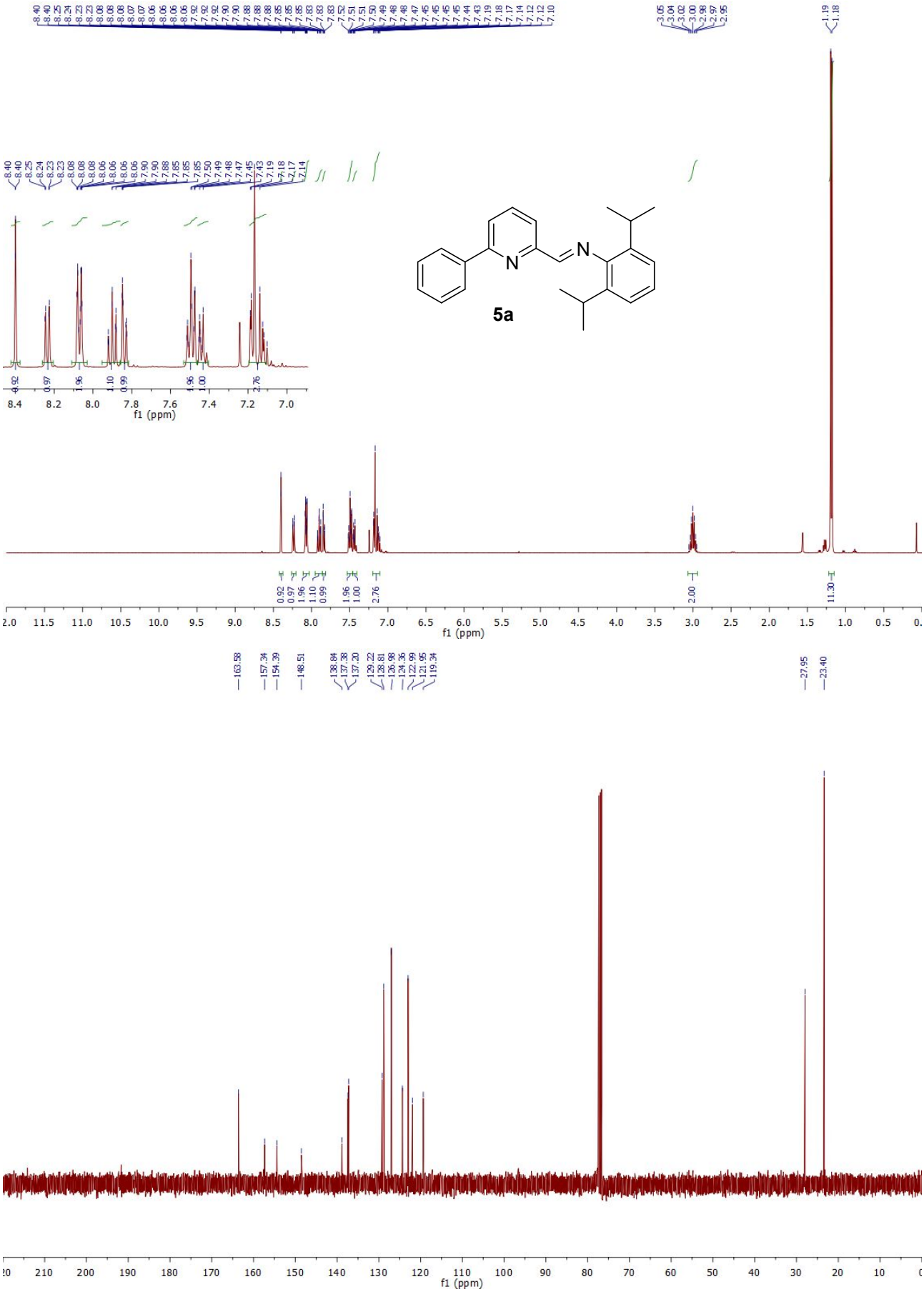
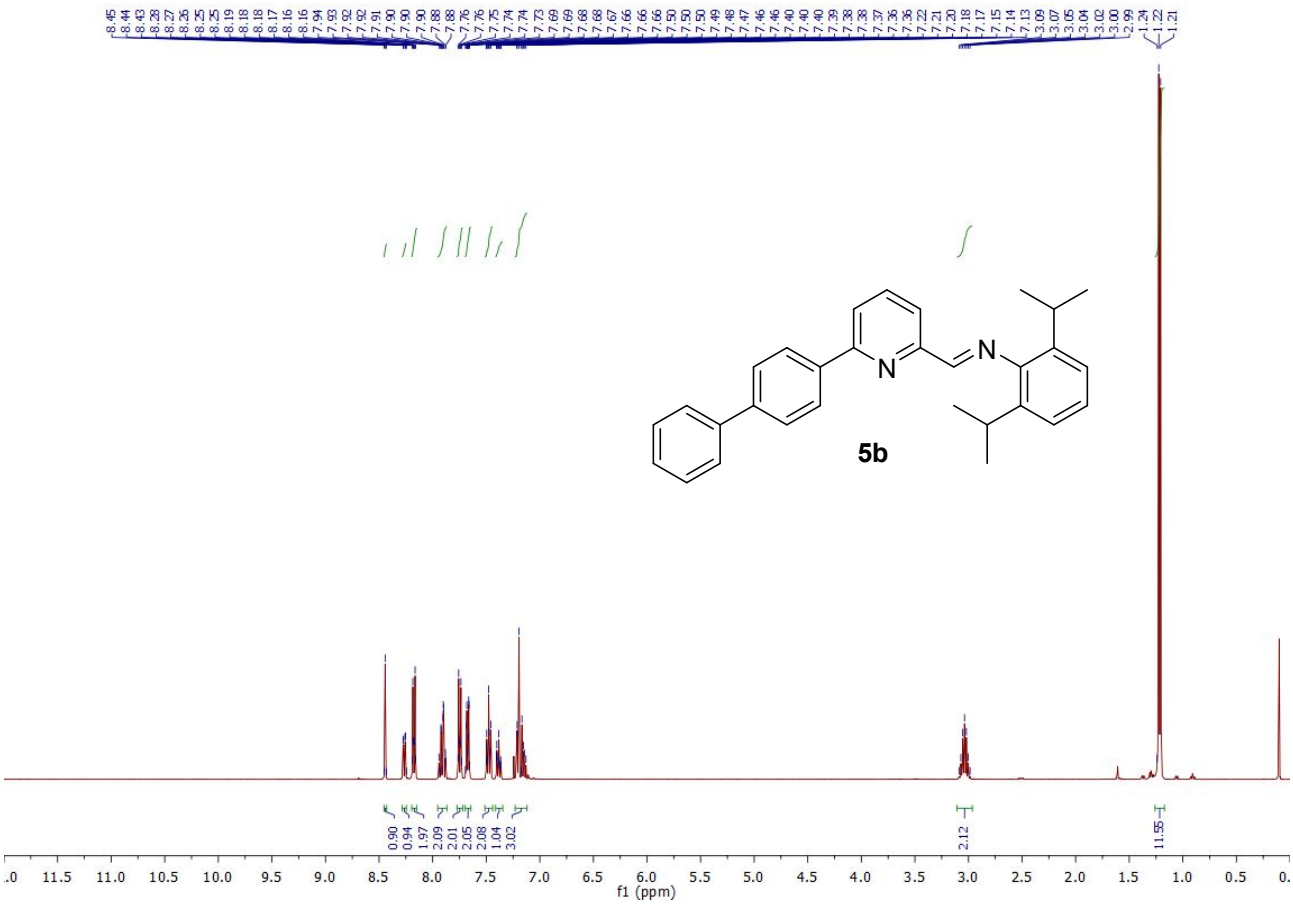
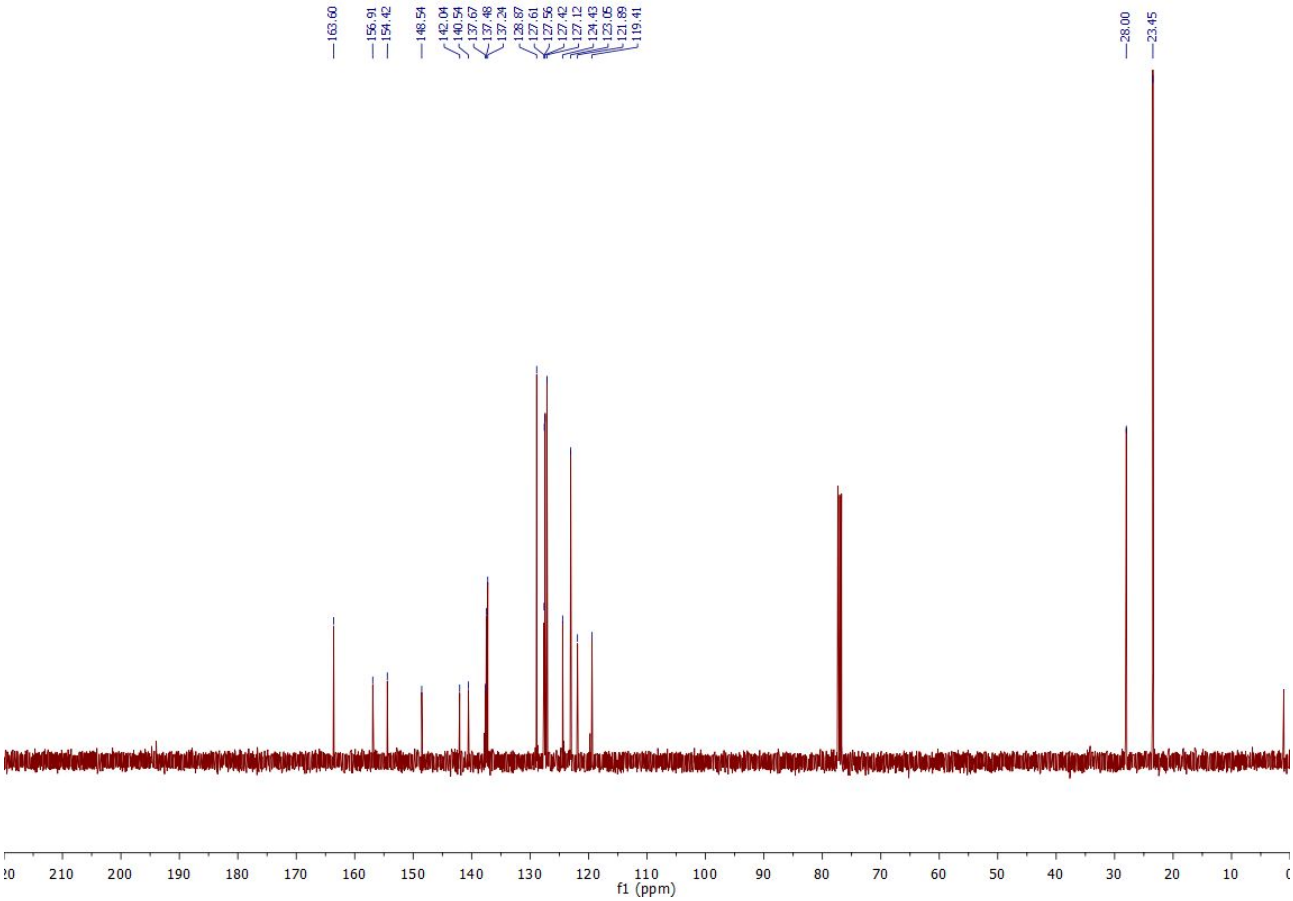
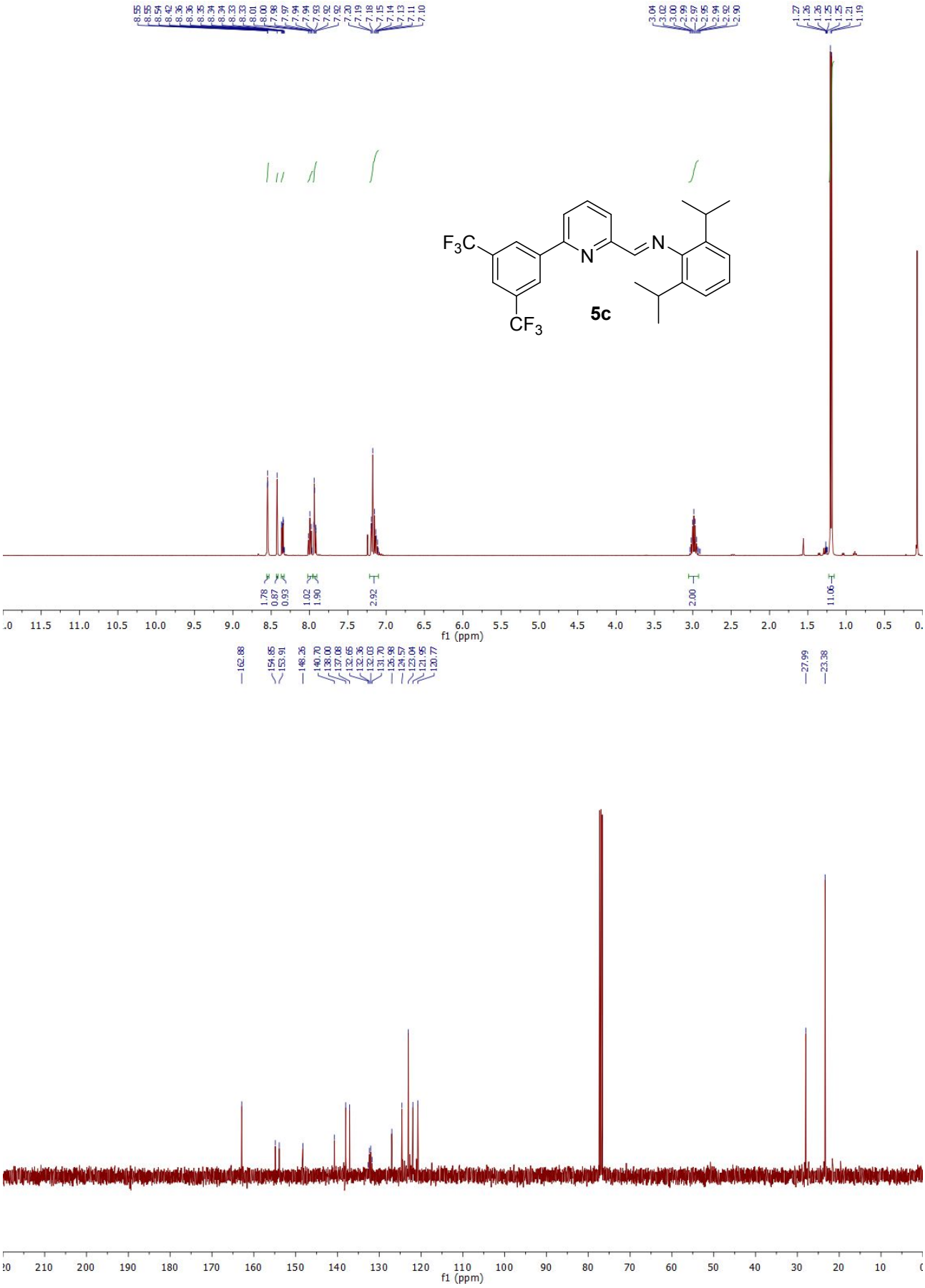
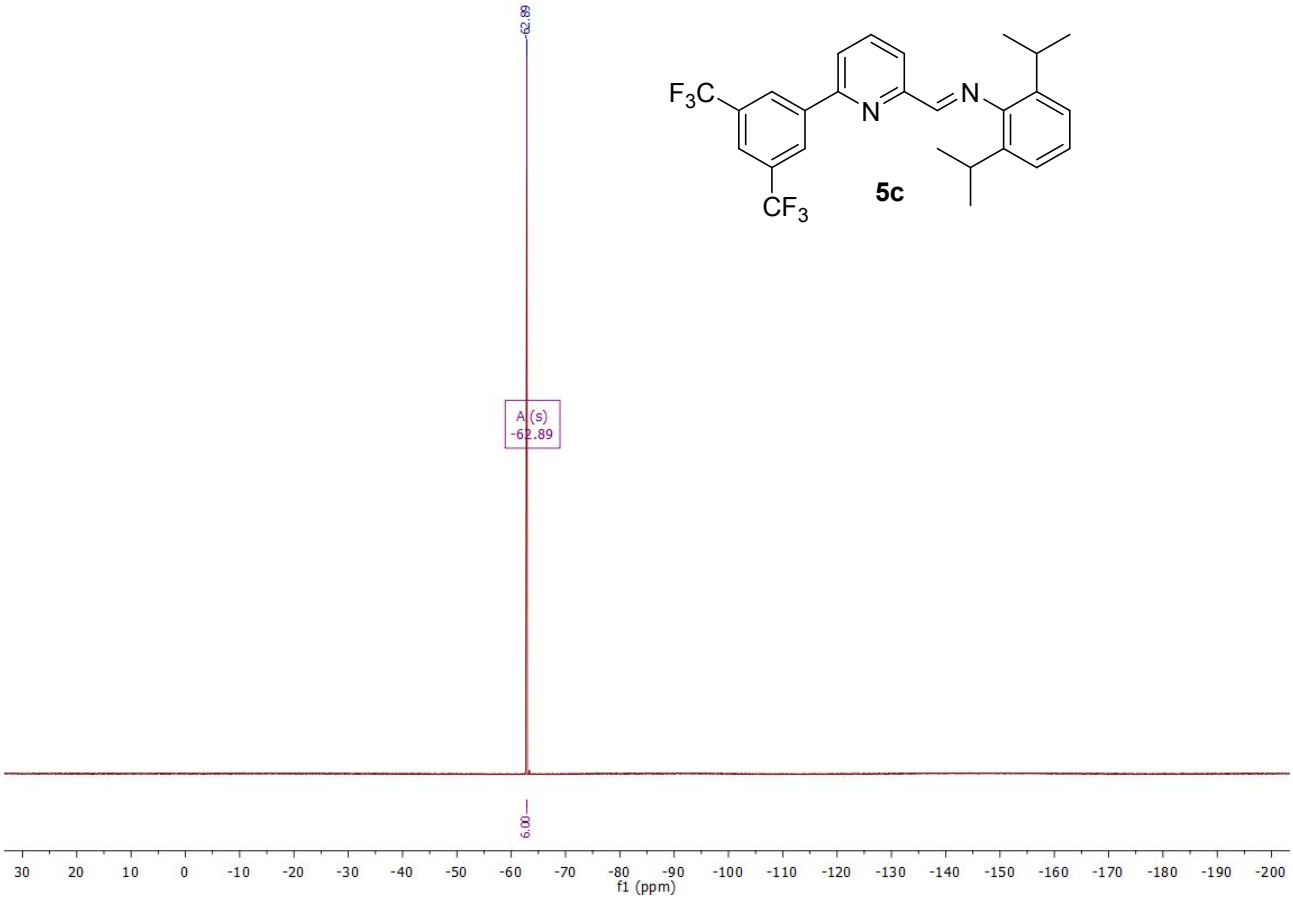
137.08
128.02
126.34
125.14
124.55
124.36
122.44
119.33
f1 (ppm)


5a
f1 (ppm)


8.45 8.44 8.43 8.28 8.27 8.26 8.25 8.25 8.19 8.18 8.18 8.17 8.16 8.16 7.94 7.93 7.92 7.92 7.91 7.90 7.90 7.90 7.88 7.88 7.76 7.76 7.75 7.74 7.74 7.73 7.69 7.69 7.68 7.68 7.67 7.66 7.66 7.50 7.50 7.50 7.49 7.48 7.47 7.46 7.46 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.36 7.22 7.21 7.20 7.18 7.17 7.15 7.14 7.13 3.09 3.07 3.05 3.04 3.02 3.00 2.99 1.24 1.22 1.21
N
N
5b
0.90 0.94 1.97 2.09 2.01 2.05 2.08 1.04 3.02 2.12 11.55
f1 (ppm)

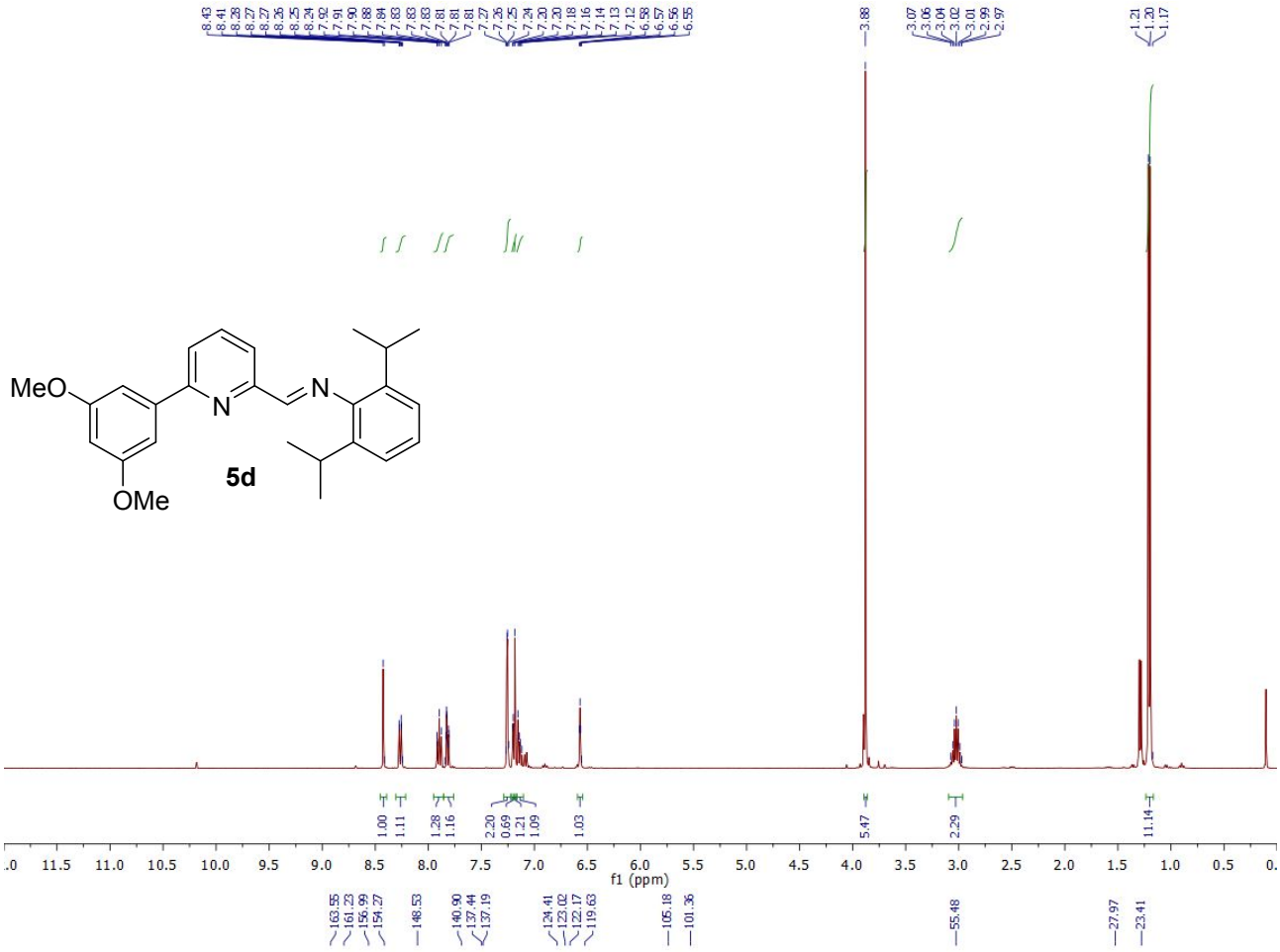

163.60 156.91 154.42 148.54 142.04 140.54 137.67 137.48 137.24 128.87 127.61 127.56 127.42 127.12 124.43 123.05 121.99 119.41 28.00 23.45
f1 (ppm)

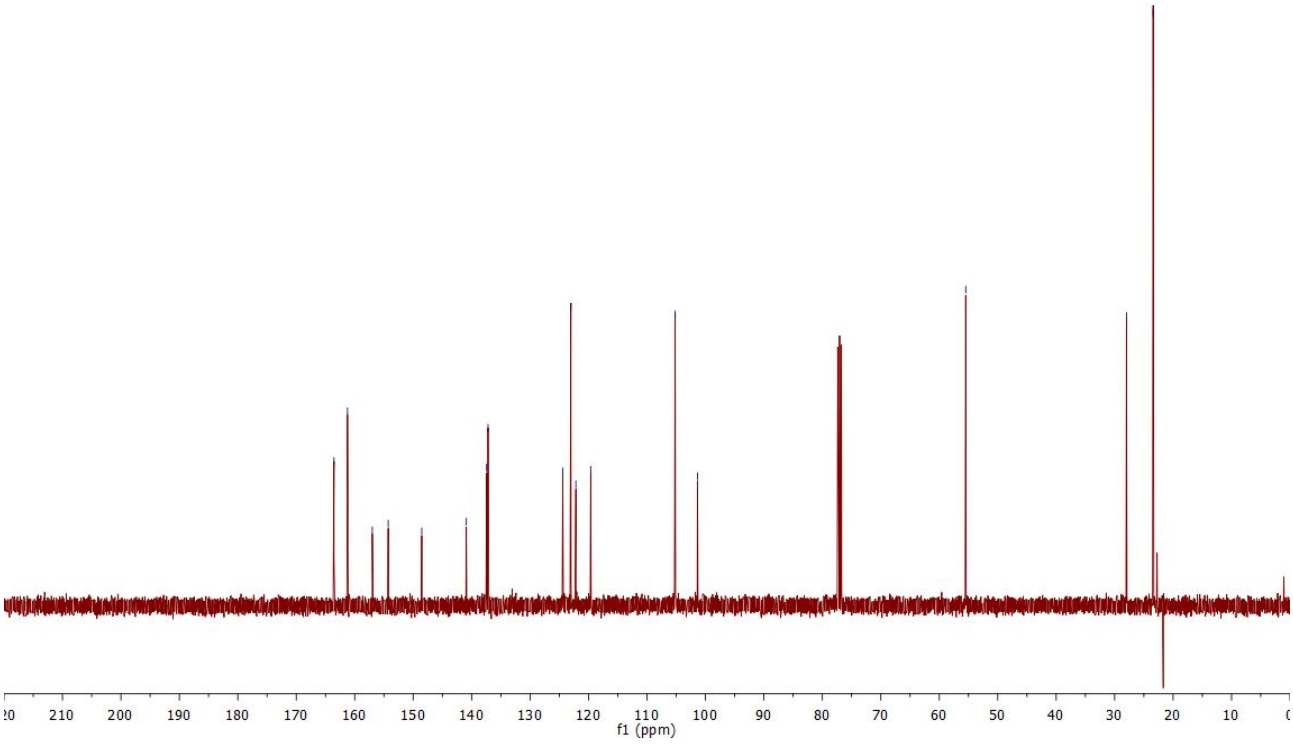

F3C
CF3
N
N
5c
f1 (ppm)
f1 (ppm)


-62.89
A (s)
-62.89
6.00
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

F3C
CF3
N
N

5c


MeO
N
N
OMe
5d
f1 (ppm)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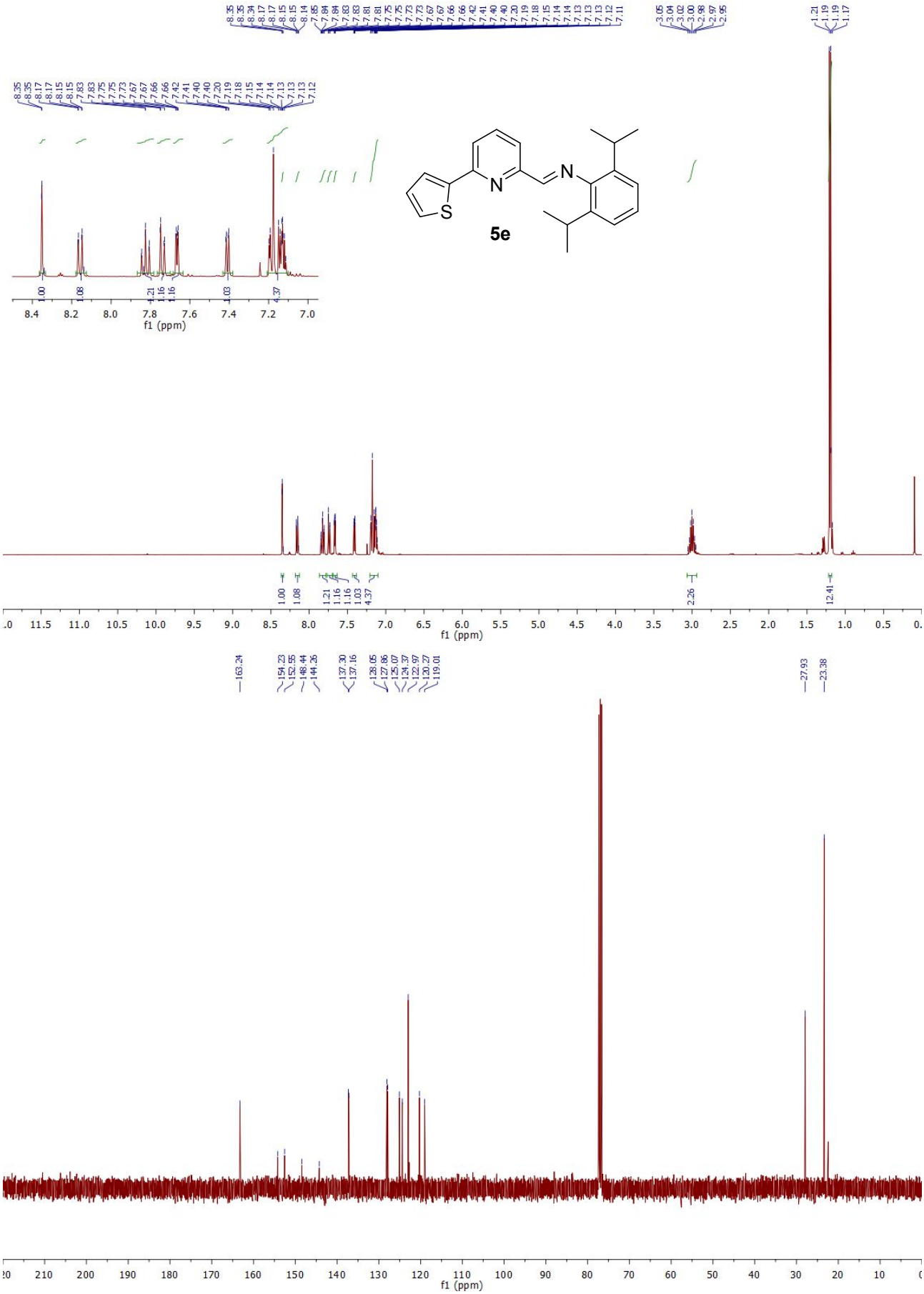
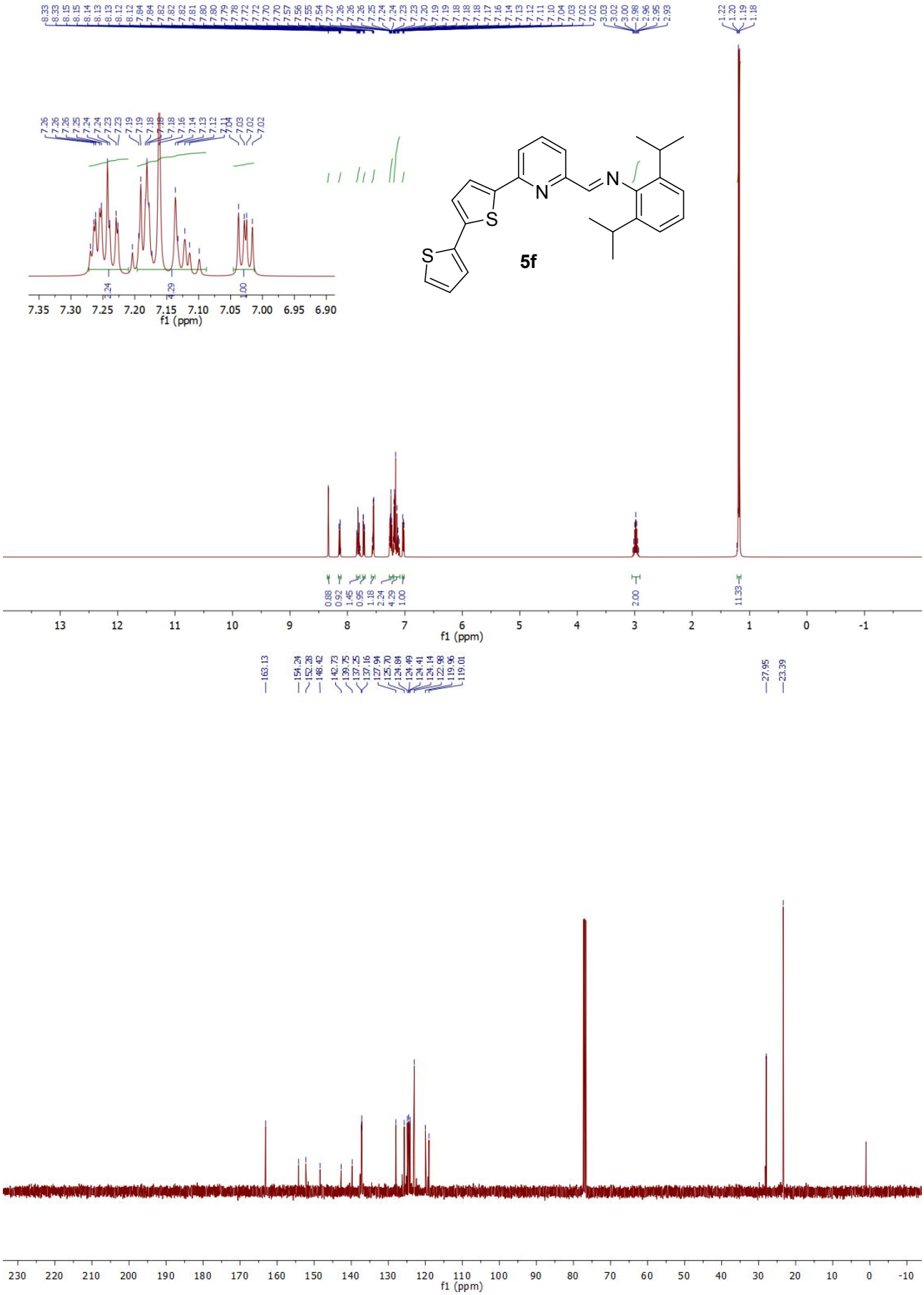
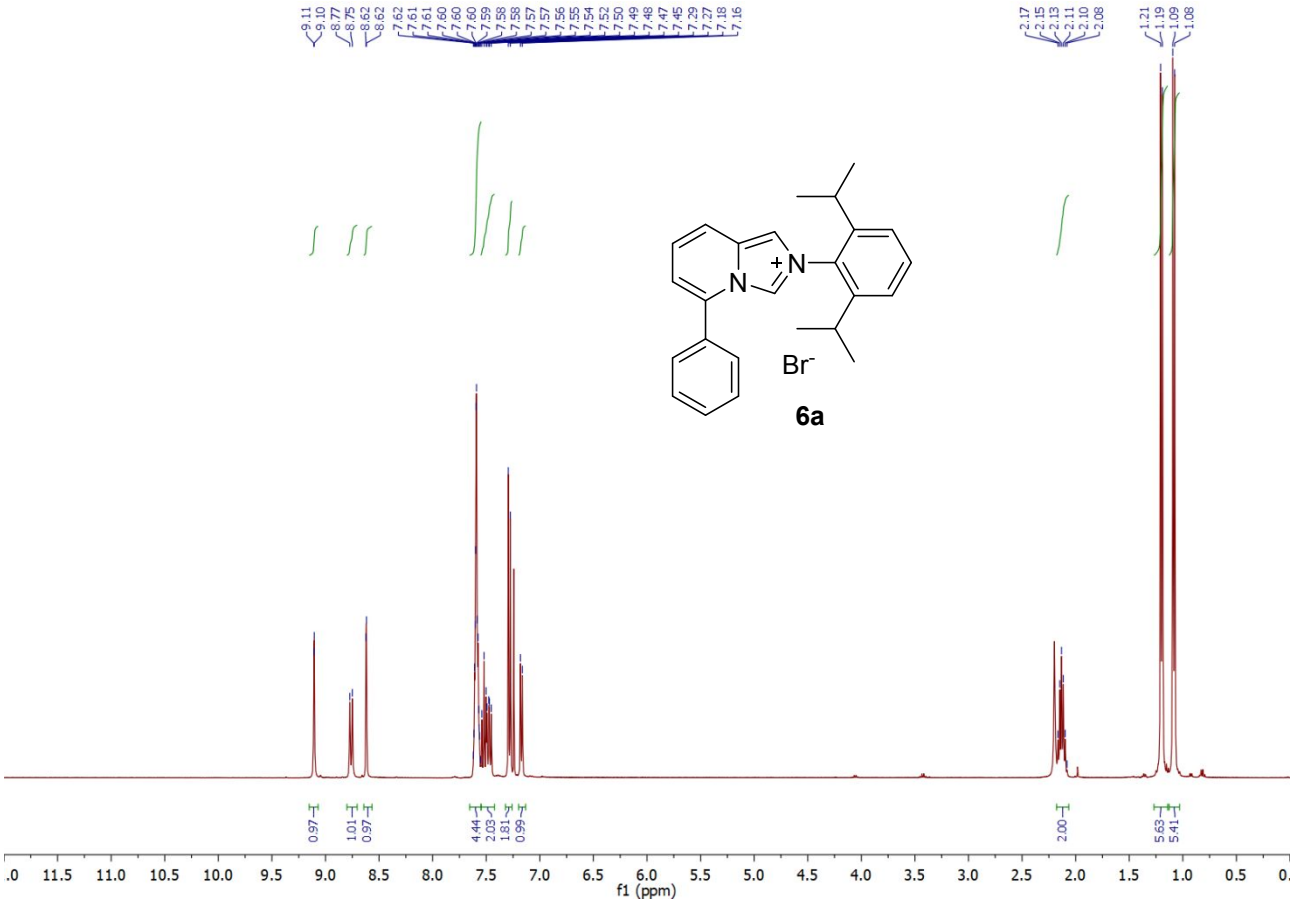
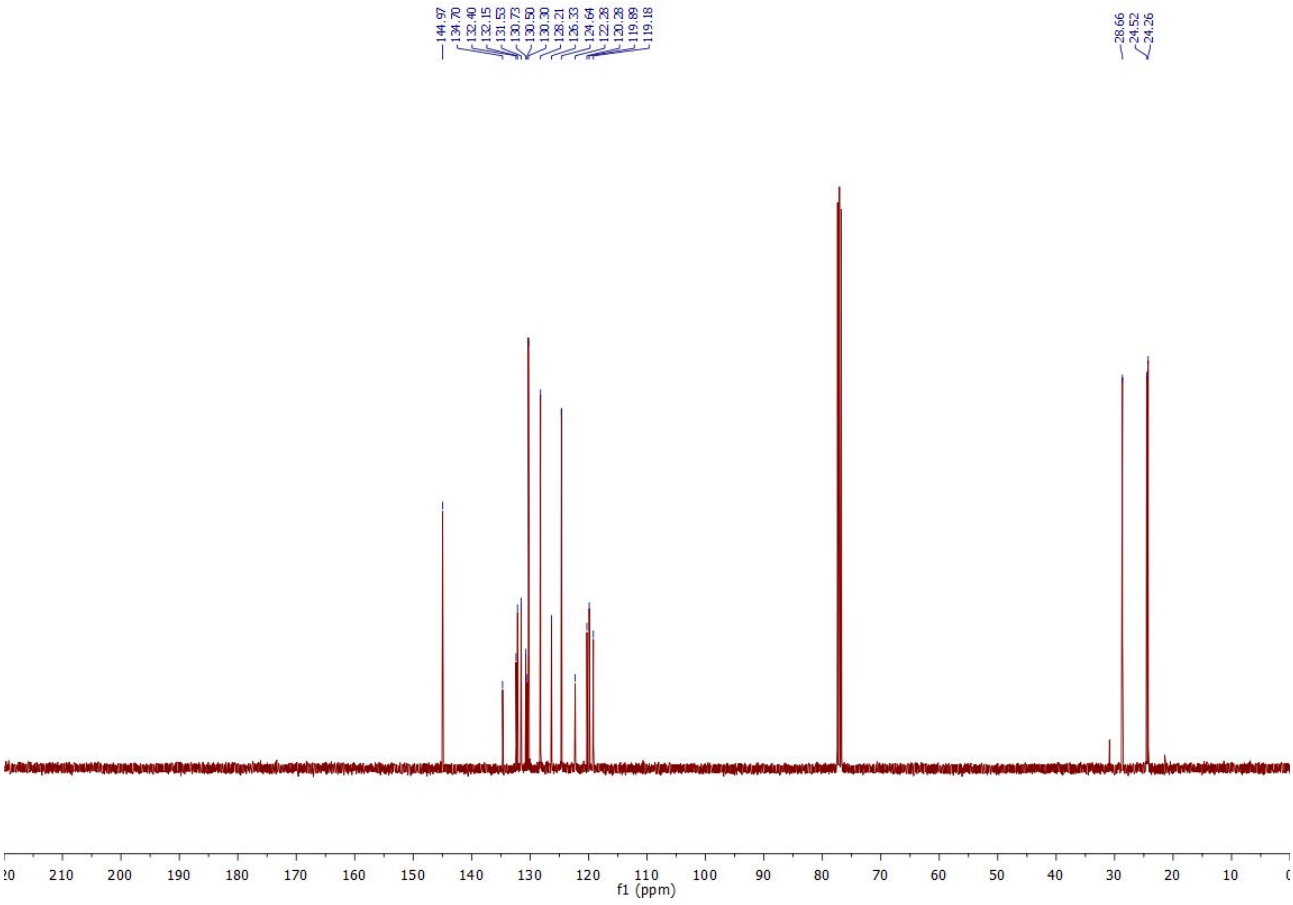
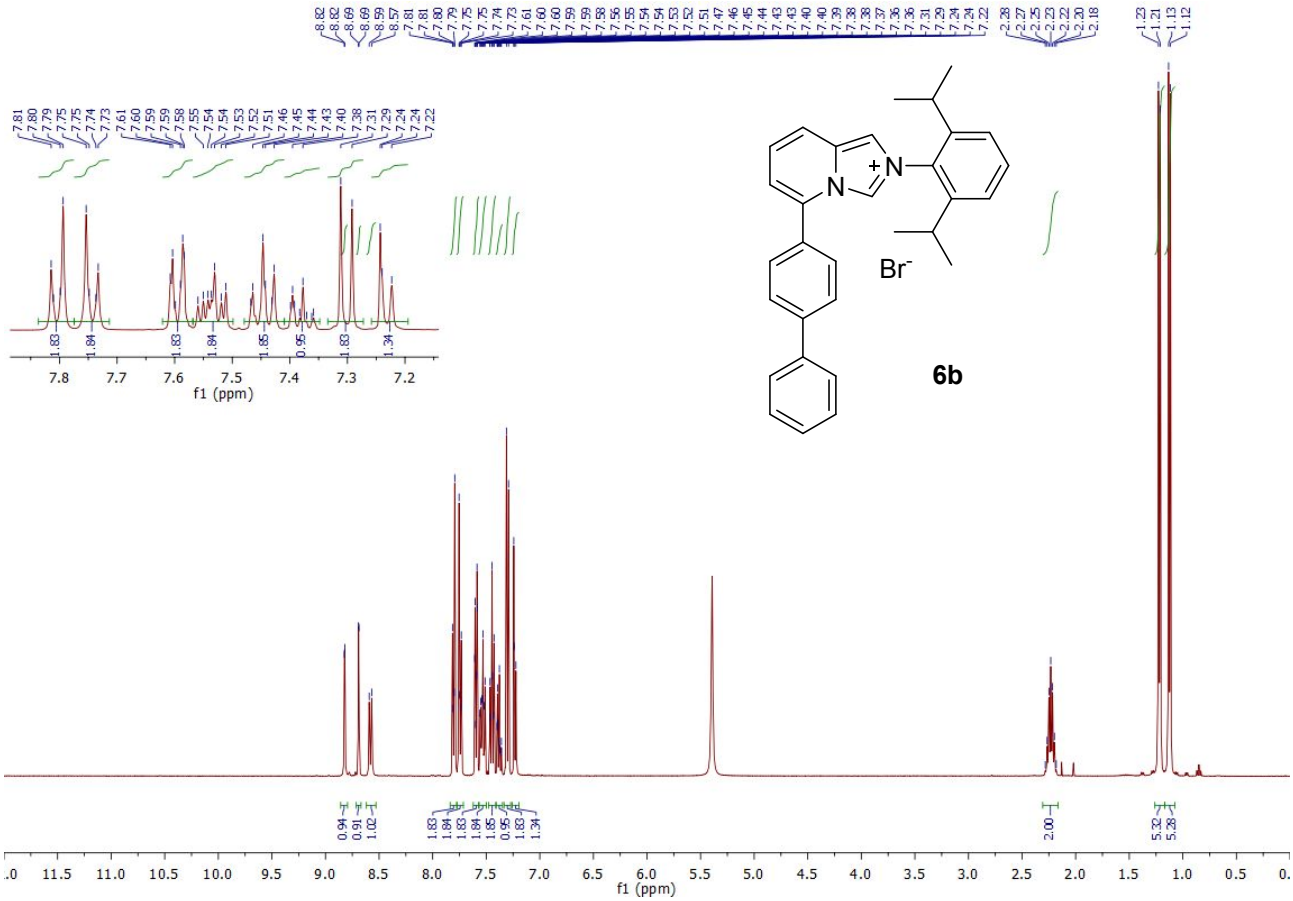
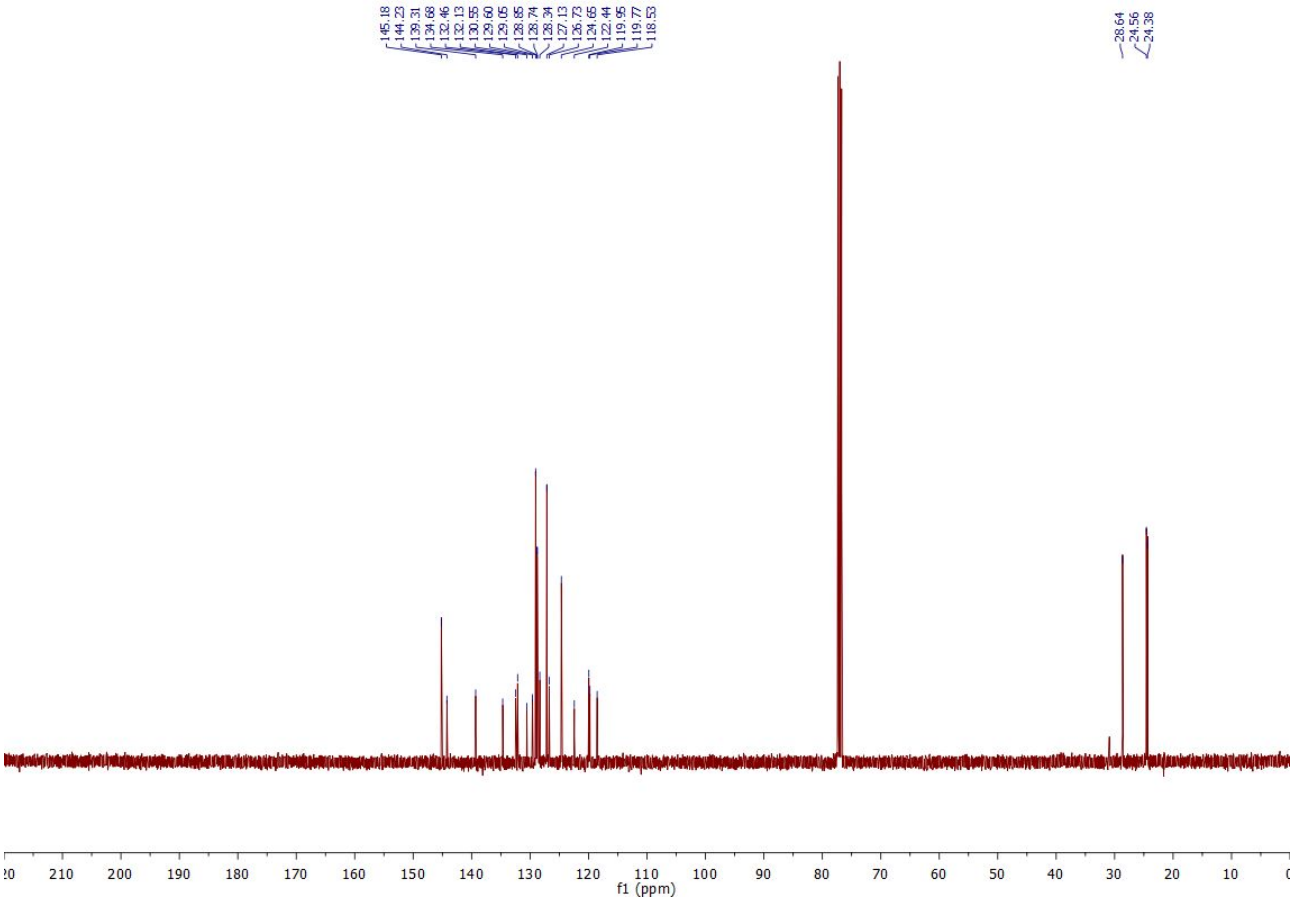

5e
f1 (ppm)


5f
f1 (ppm)


9.11
9.10
8.77
8.75
8.62
8.62
7.62
7.61
7.61
7.61
7.60
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.56
7.55
7.54
7.52
7.50
7.49
7.48
7.47
7.45
7.29
7.27
7.18
7.16
2.17
2.15
2.13
2.11
2.10
2.08
1.21
1.19
1.09
1.08
N
N
Br-
6a
0.97
1.01
0.97
4.44
2.03
1.81
0.99
2.00
5.63
5.41
f1 (ppm)


144.97
134.70
132.40
132.15
131.53
130.73
130.50
130.30
128.21
126.33
124.64
122.28
120.28
119.89
119.18
28.66
24.52
24.26
f1 (ppm)


6b
Br-
f1 (ppm)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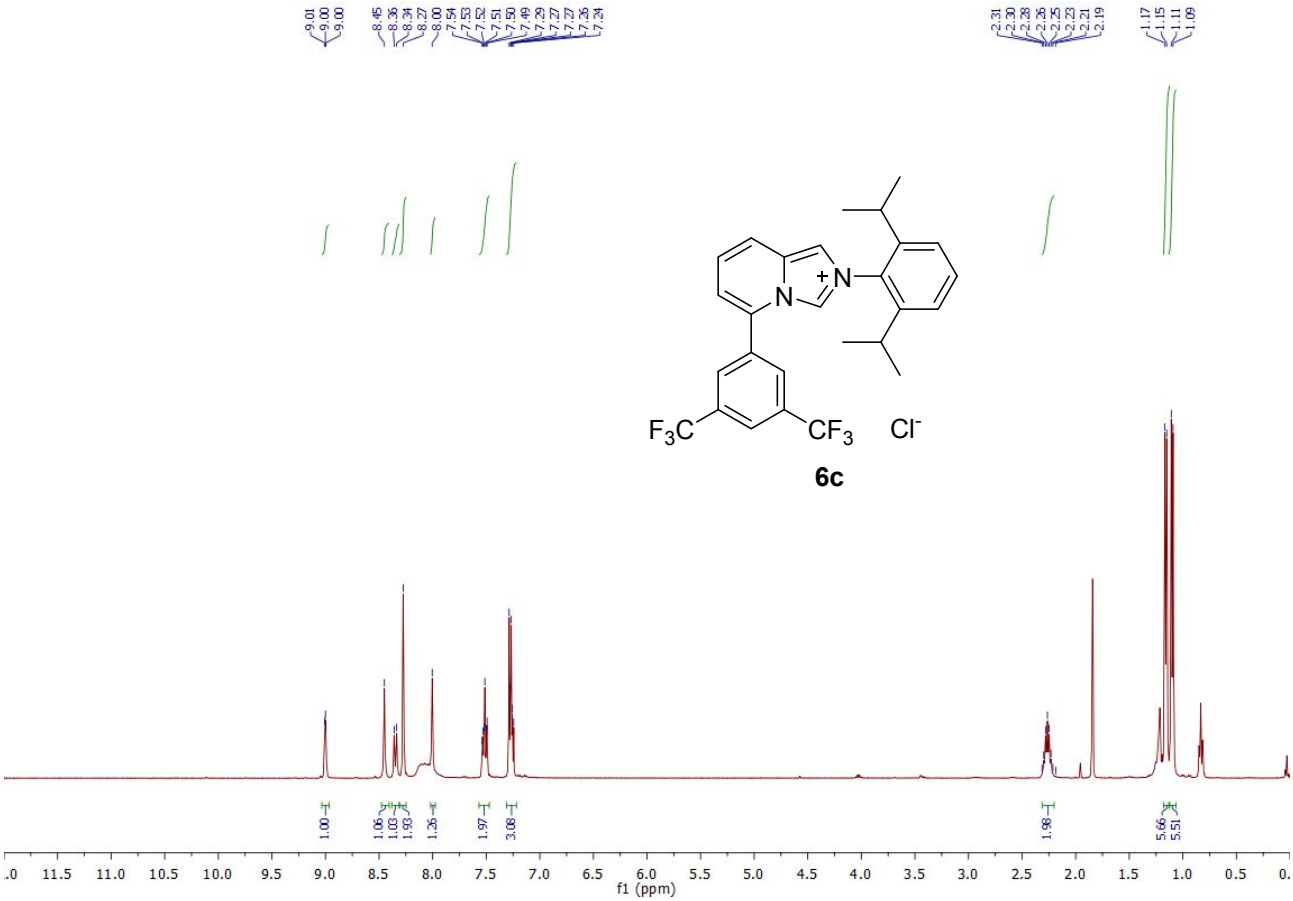
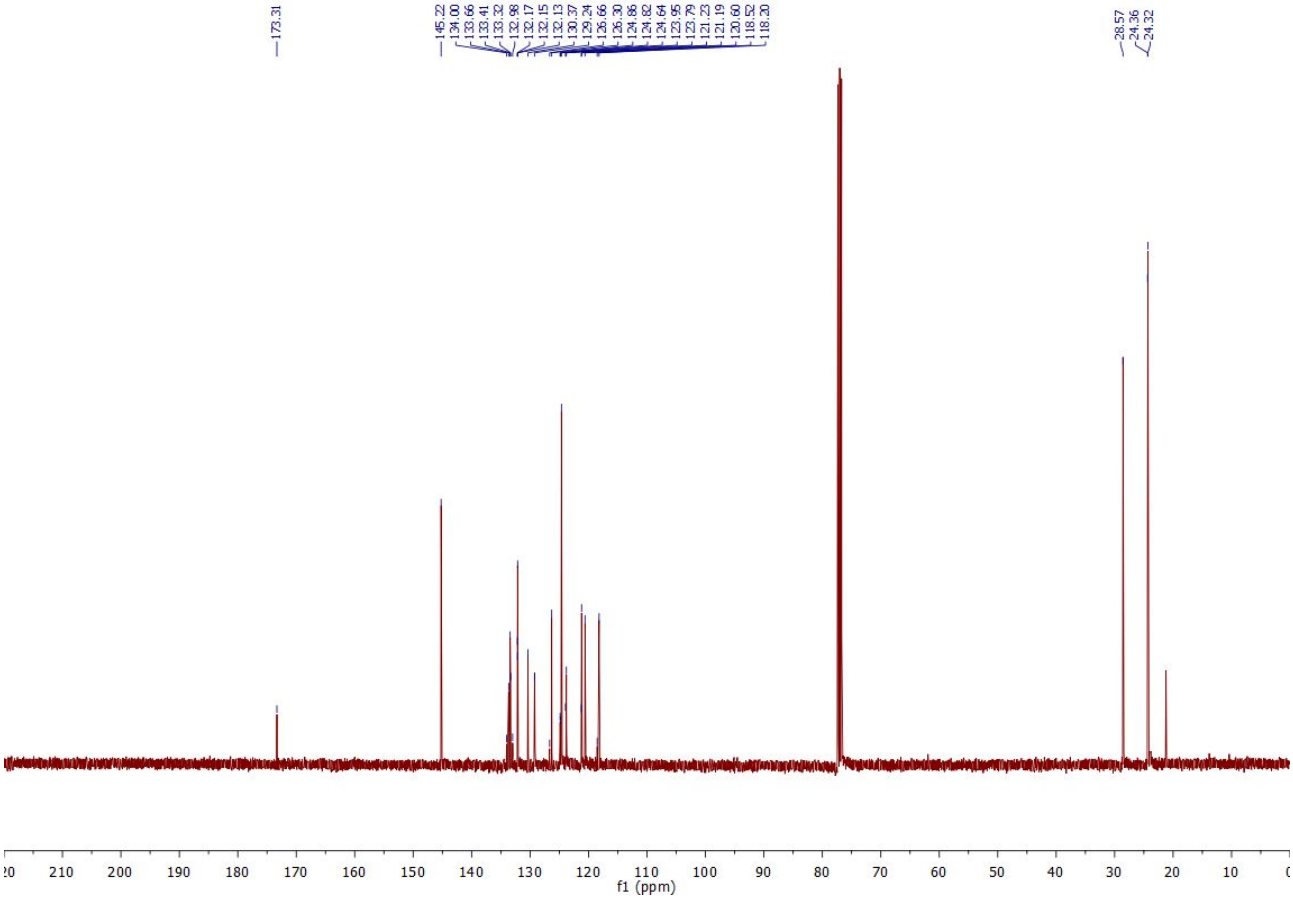
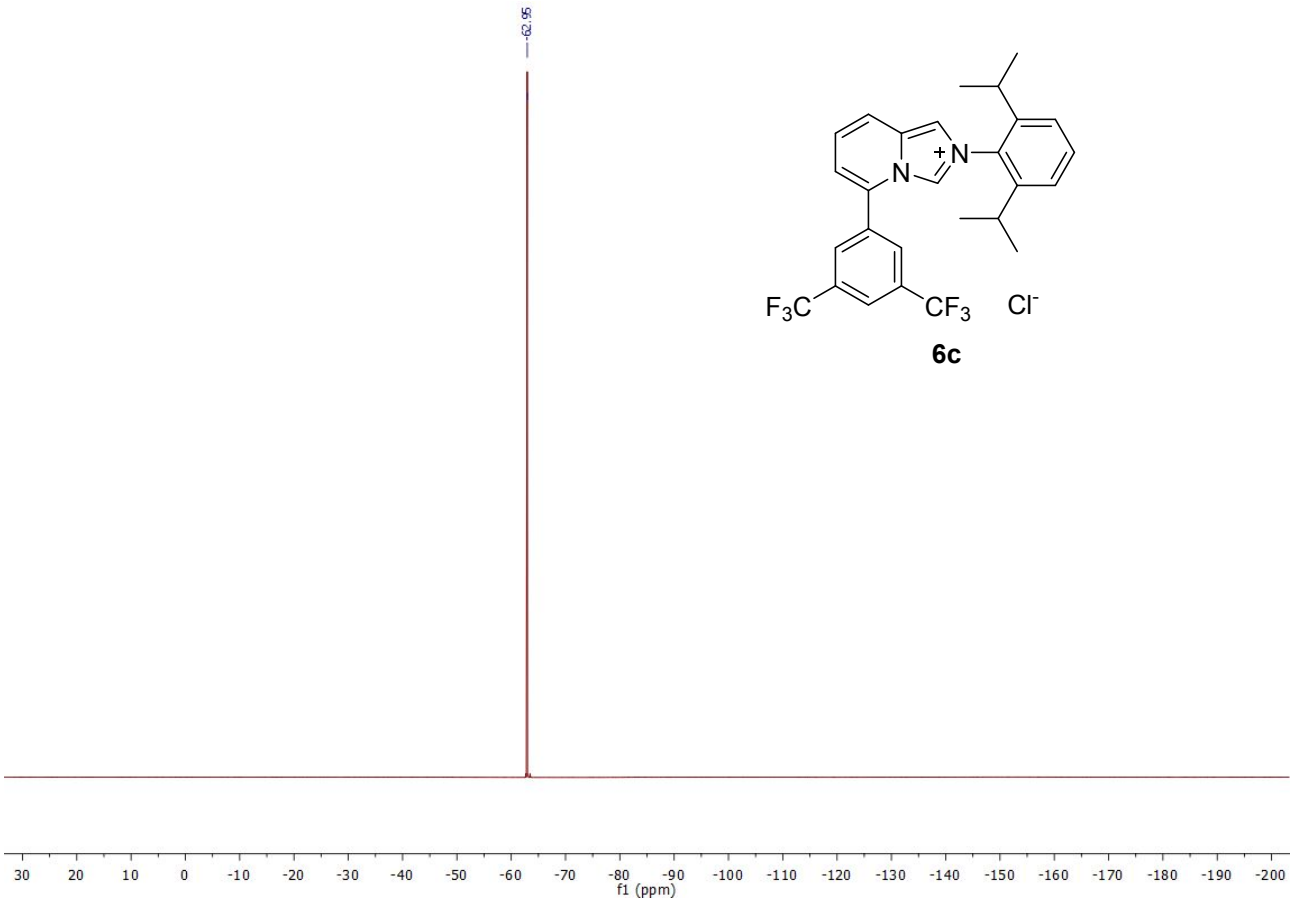

9.01
9.00
9.00
8.45
8.36
8.34
8.27
8.00
7.54
7.53
7.52
7.51
7.50
7.49
7.29
7.27
7.27
7.25
7.24
2.31
2.30
2.28
2.26
2.25
2.23
2.21
2.19
1.17
1.15
1.11
1.09
N
+
N
F3C
CF3
Cl-
1.00
1.06
1.03
1.93
1.26
1.97
3.08
1.98
5.66
5.51
f1 (ppm)

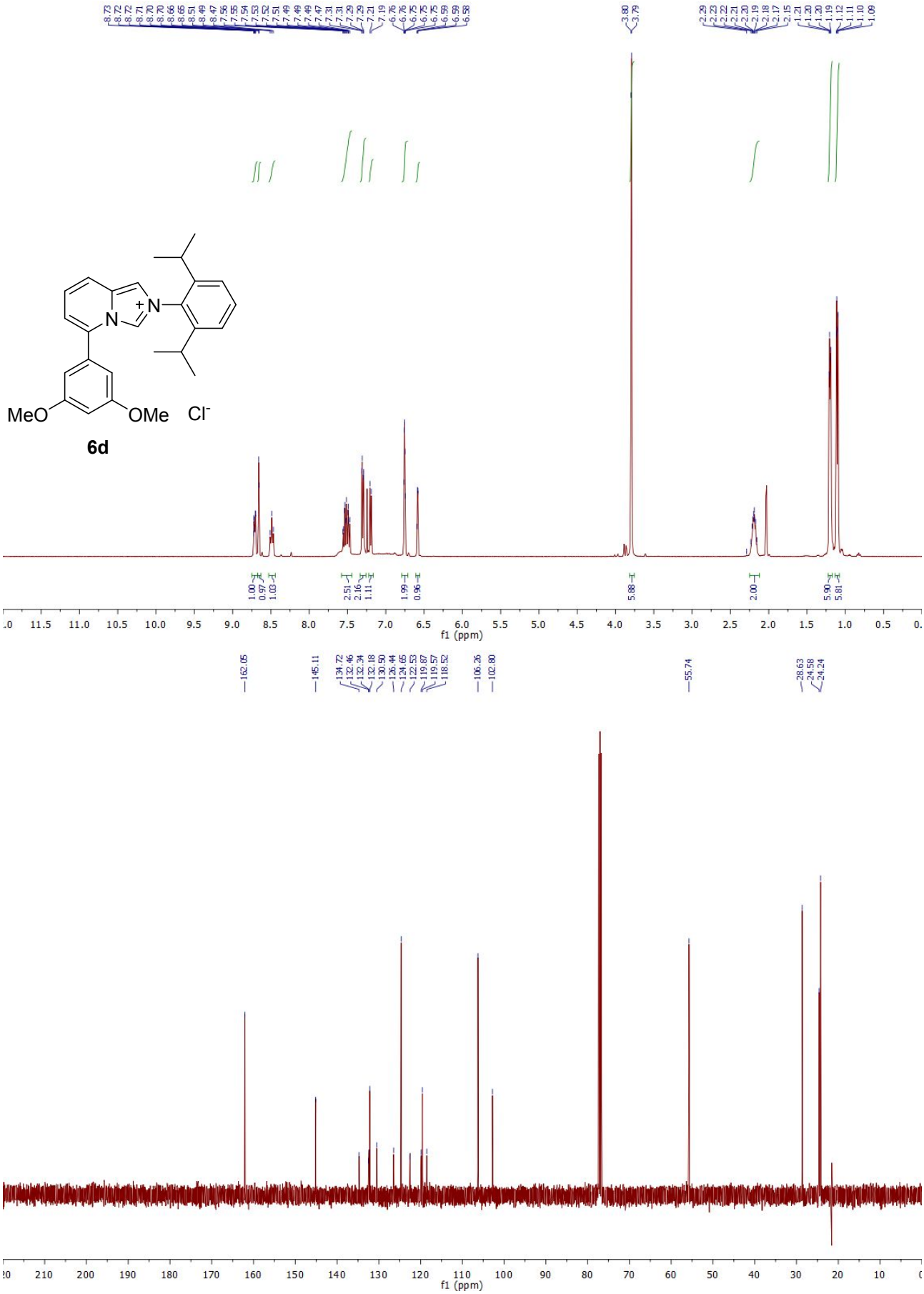
6c

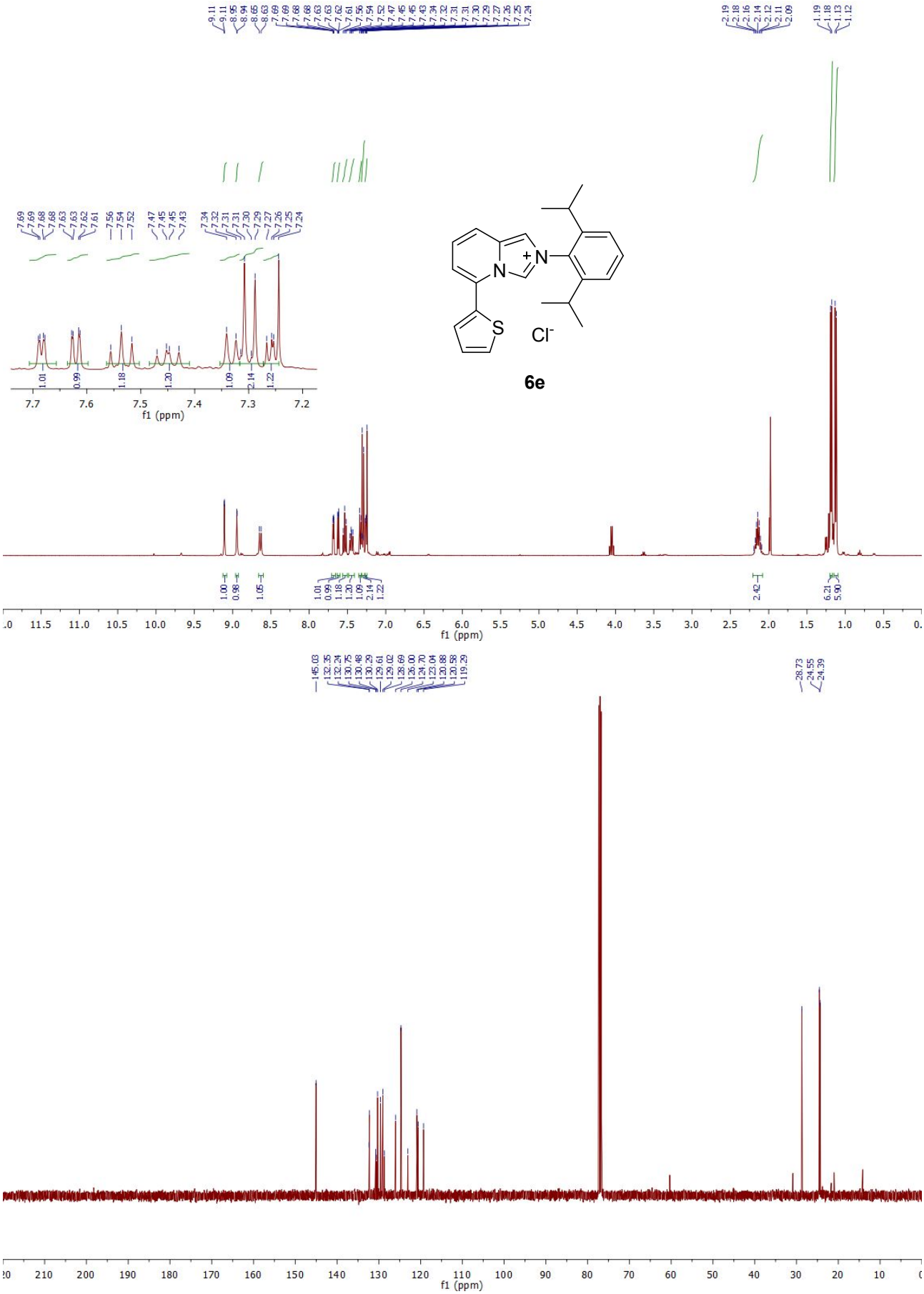

173.31
145.22
134.00
133.66
133.41
133.32
132.98
132.17
132.15
132.13
130.37
129.24
126.66
126.30
124.86
124.82
124.64
123.95
123.79
121.23
121.19
120.60
118.52
118.20
28.57
24.36
24.32
f1 (ppm)


-62.95
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

N
+N
F3C
CF3
Cl-

6c


MeO
OMe
Cl-
6d
f1 (ppm)
f1 (ppm)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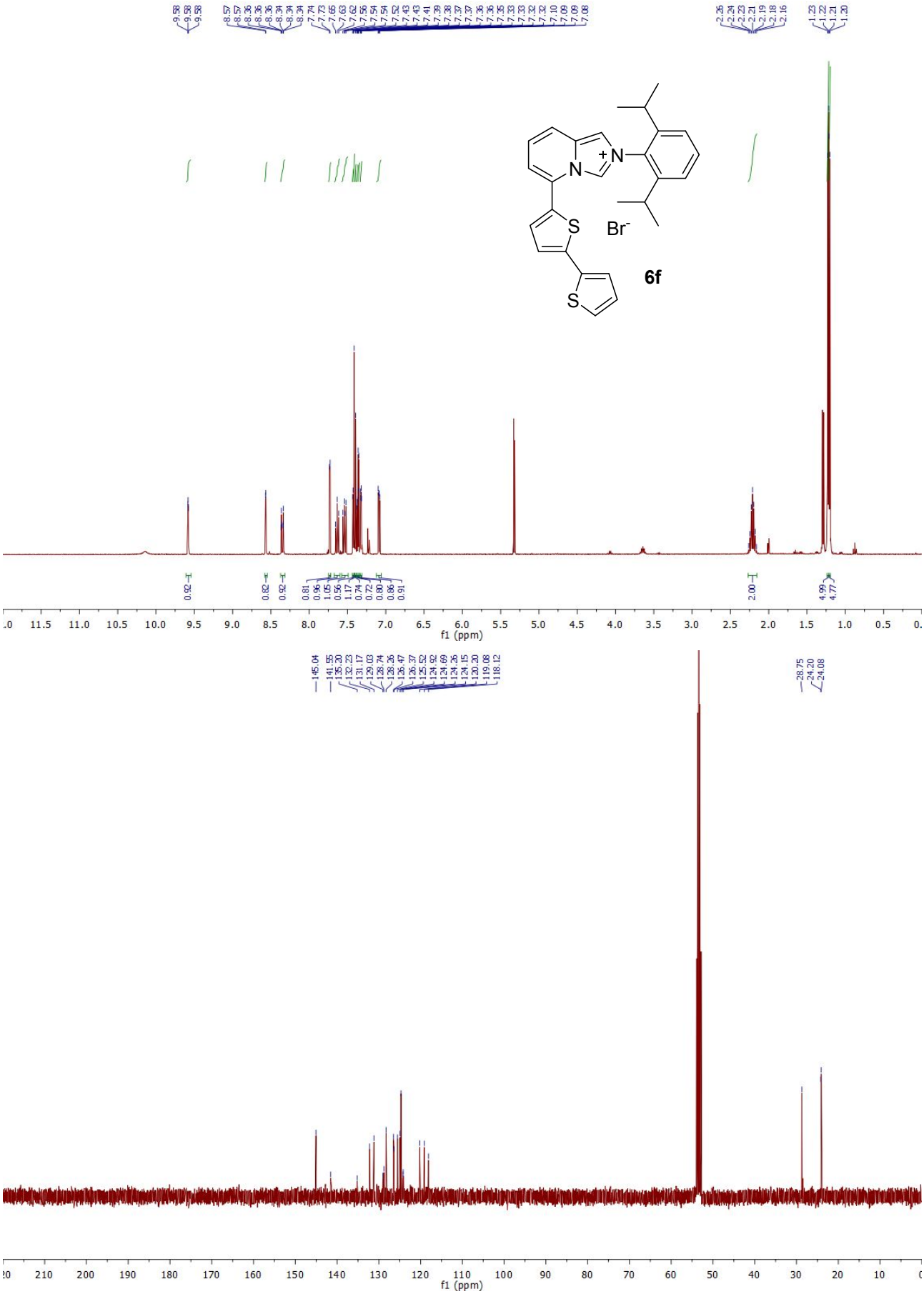
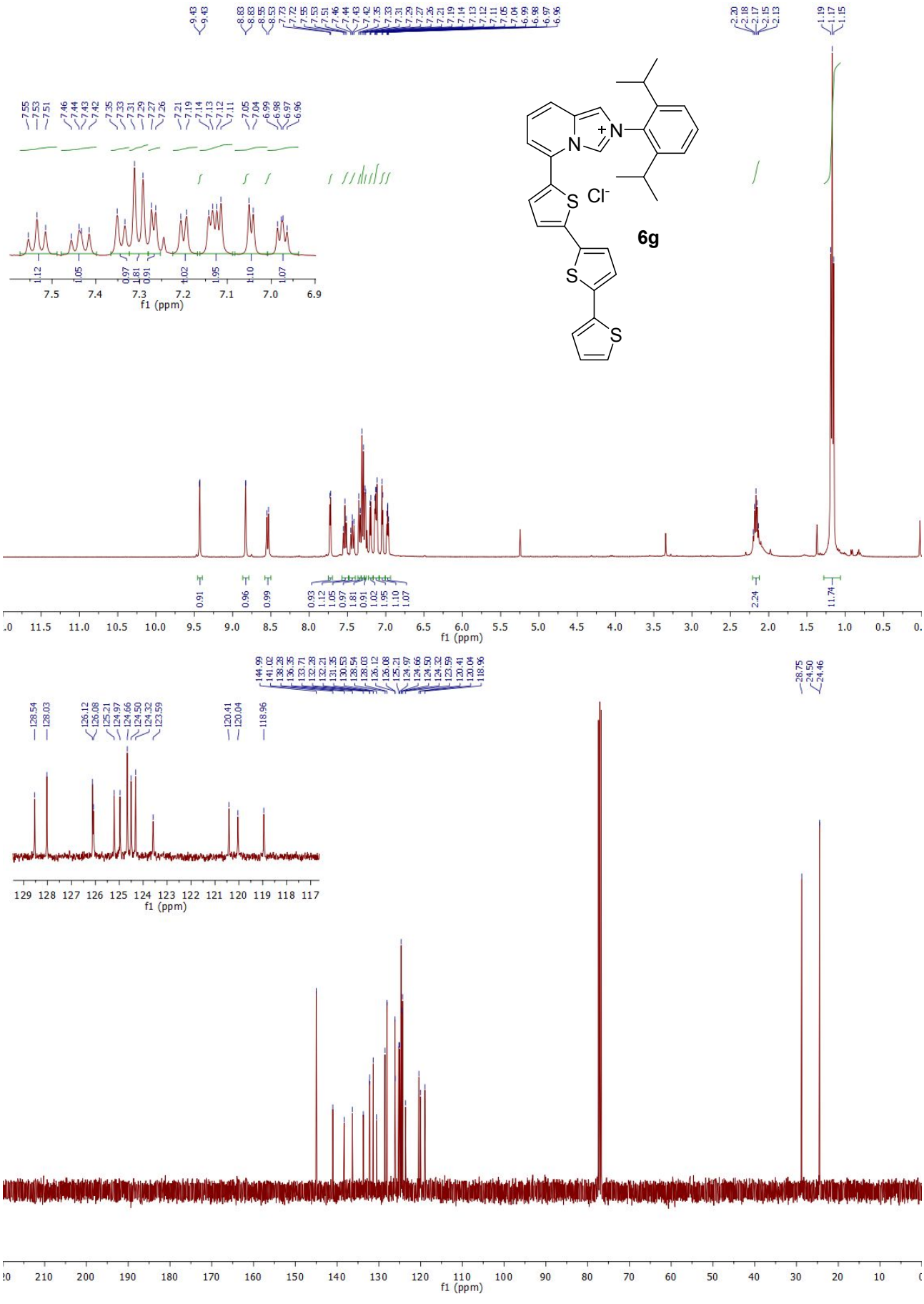
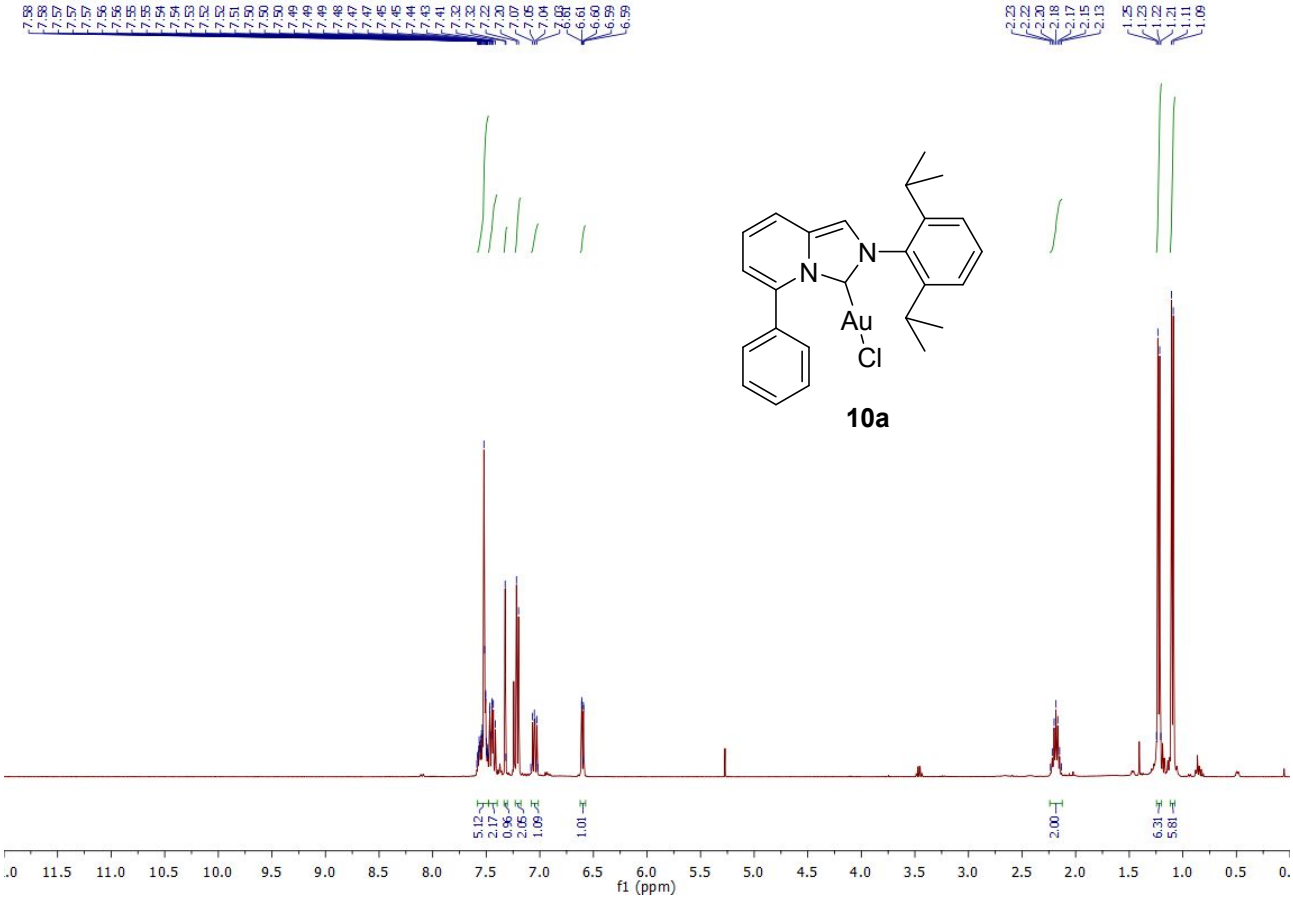
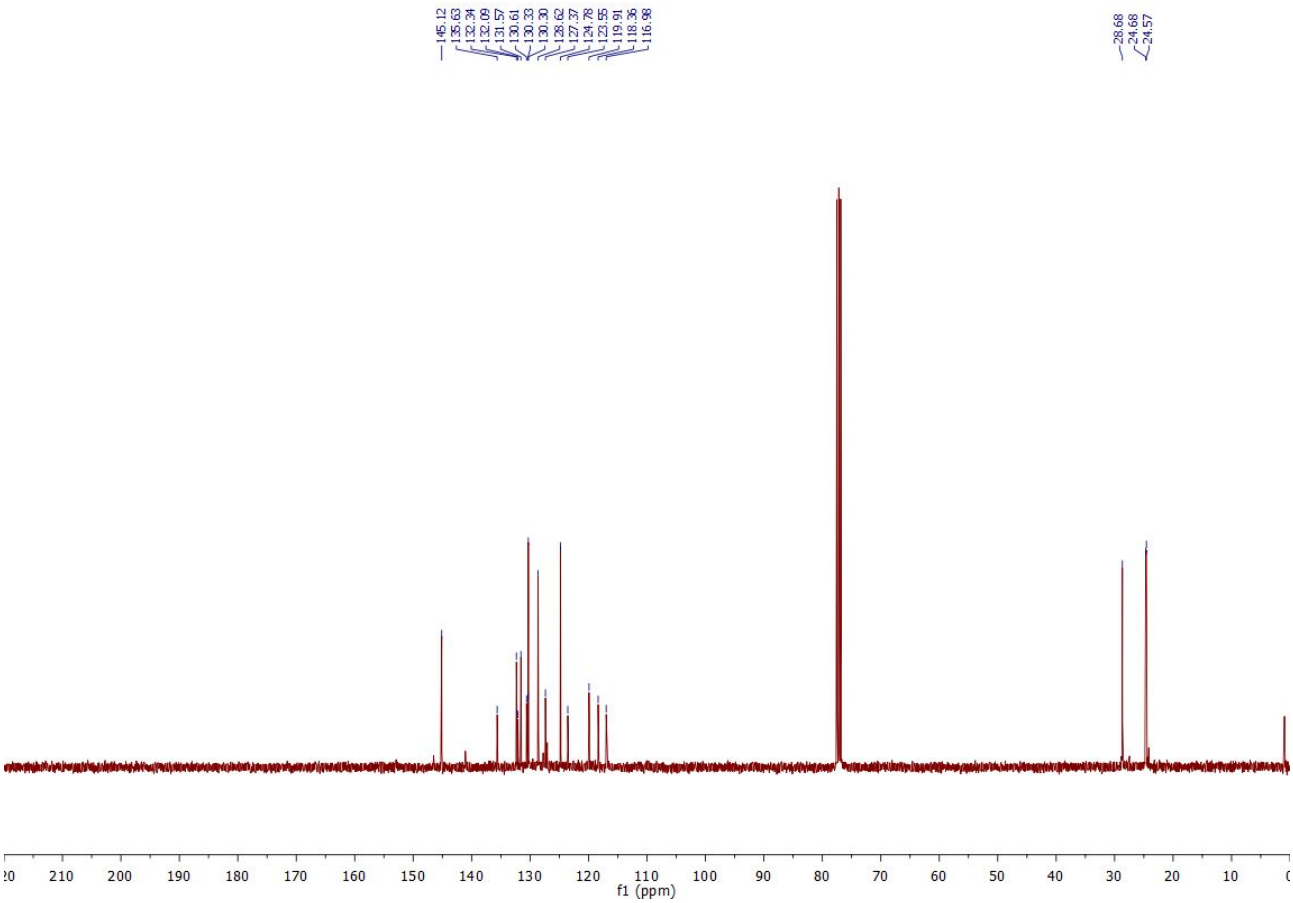
8.95
8.94
8.65
8.63
7.69
7.68
7.63
7.62
7.61
7.56
7.54
7.52
7.47
7.45
7.43
7.34
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.24
2.19
2.18
2.16
2.14
2.12
2.11
2.09
1.19
1.18
1.13
1.12
N
N
S
Cl-
6e
f1 (ppm)
145.03
132.35
132.24
130.75
130.48
130.29
129.61
129.02
128.69
126.00
124.70
123.04
120.88
120.58
119.29
28.73
24.55
24.39

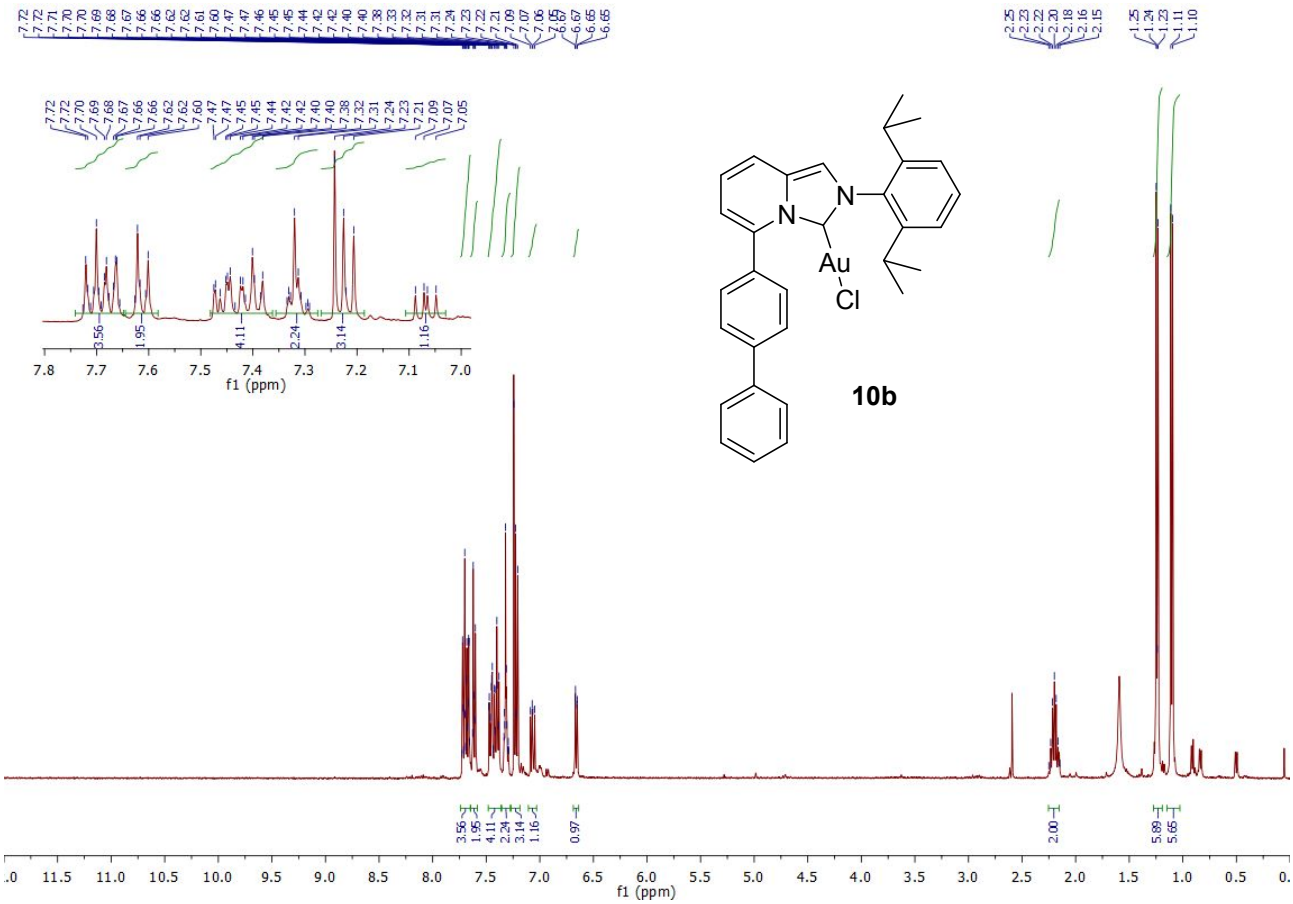

9.58
9.58
9.58
8.57
8.57
8.36
8.36
8.36
8.34
8.34
8.34
7.74
7.73
7.65
7.63
7.62
7.56
7.54
7.54
7.52
7.43
7.43
7.41
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.33
7.33
7.32
7.32
7.10
7.09
7.09
7.08
2.26
2.24
2.23
2.21
2.19
2.18
2.16
1.23
1.22
1.21
1.20
N
N
S
S
Br-
6f
0.92
0.82
0.92
0.81
0.96
1.05
0.56
1.17
0.74
0.72
0.80
0.86
0.91
2.00
4.99
4.77
f1 (ppm)
145.04
141.55
135.20
132.23
131.17
129.03
128.74
128.26
126.47
126.37
125.52
124.92
124.69
124.26
124.15
120.20
119.08
118.12
28.75
24.20
24.08
f1 (ppm)

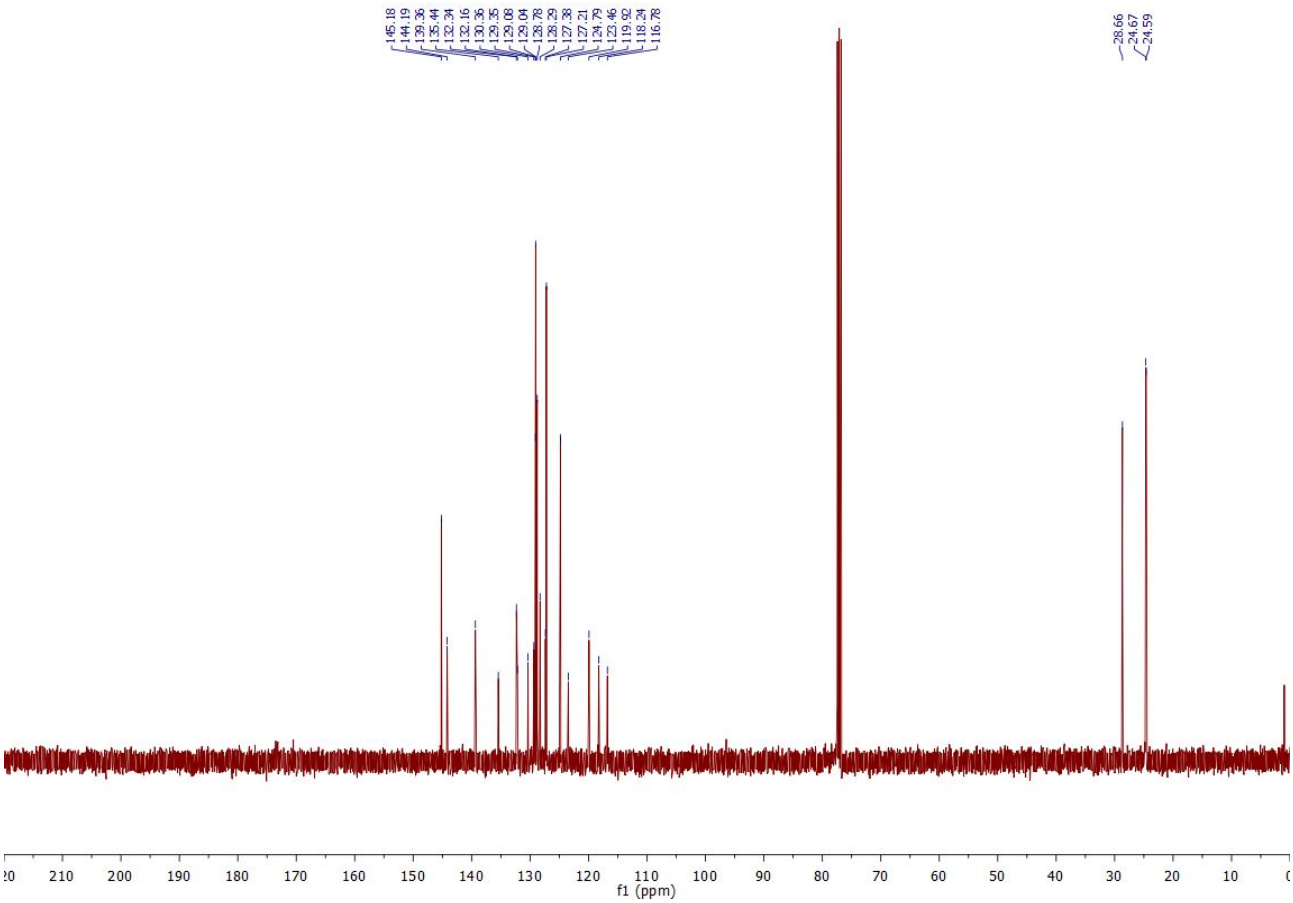

6g
f1 (ppm)

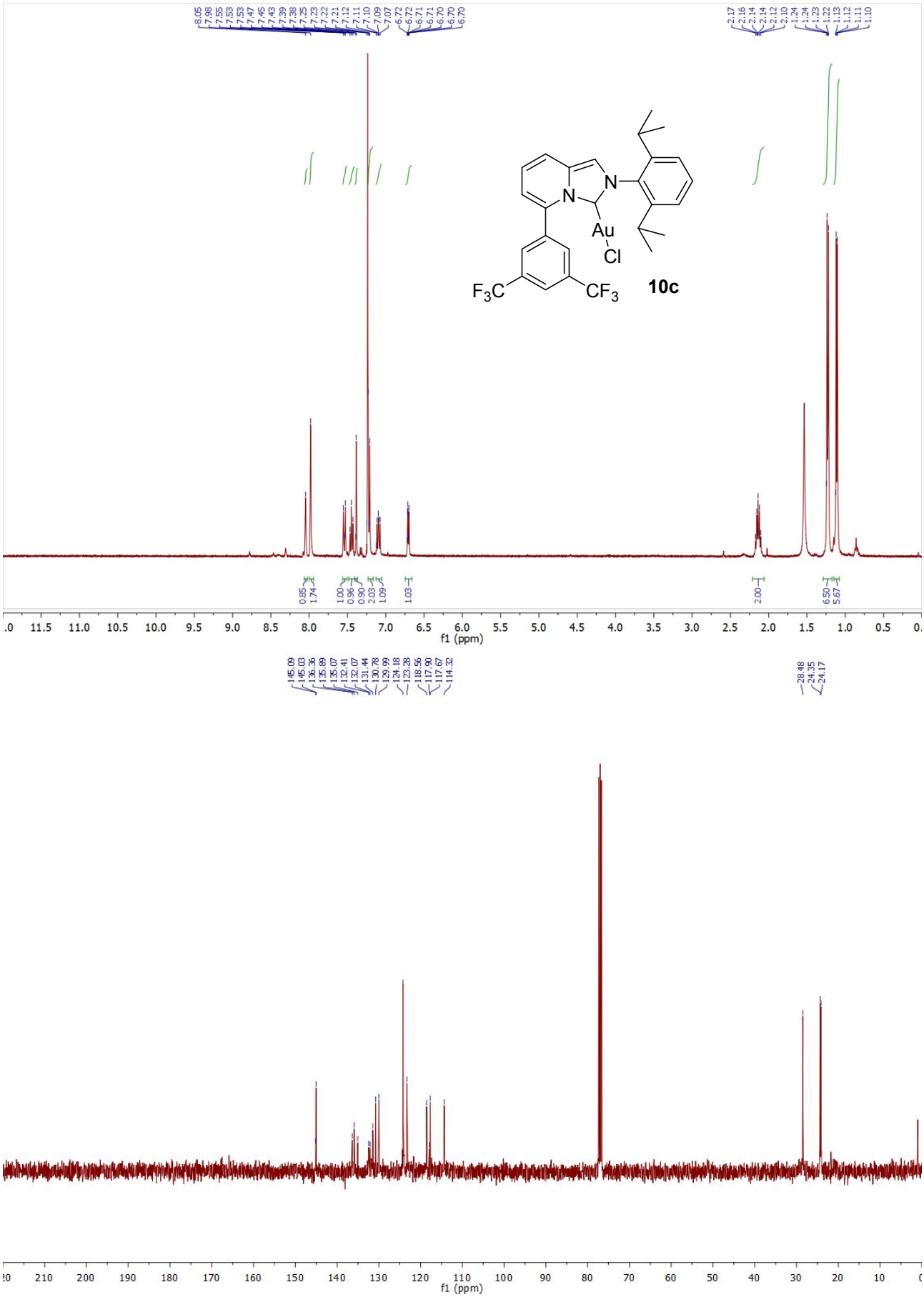


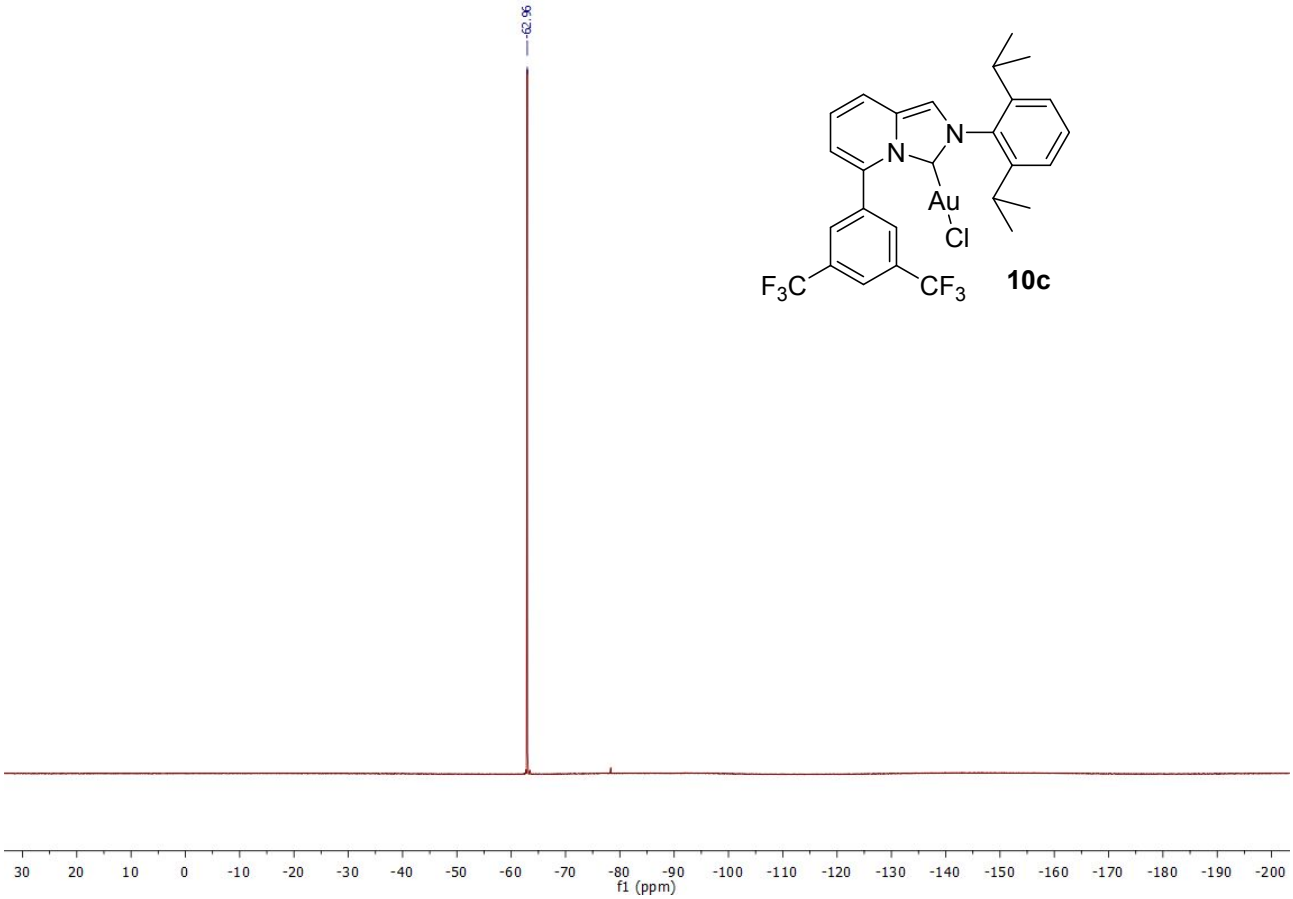
10a

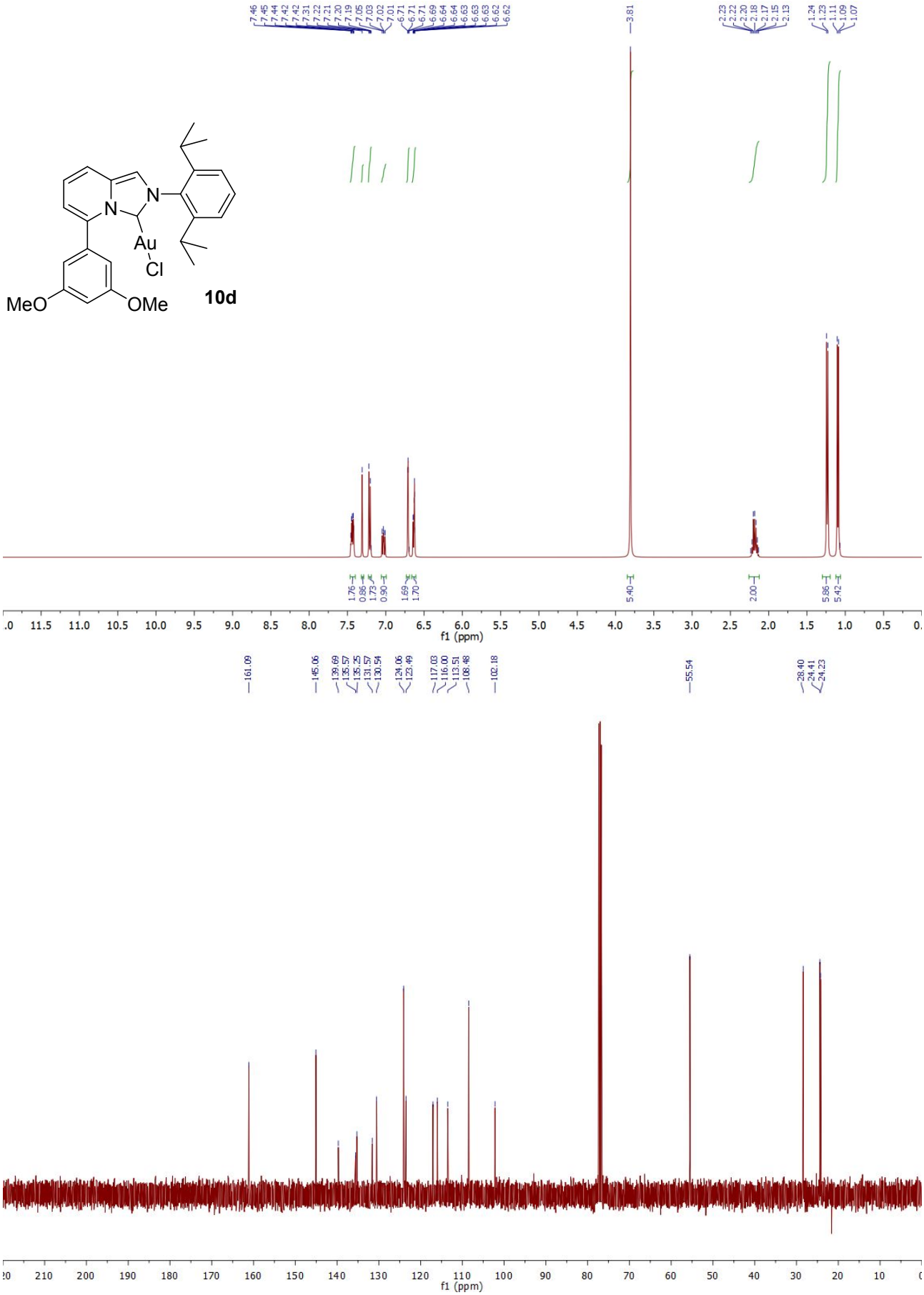


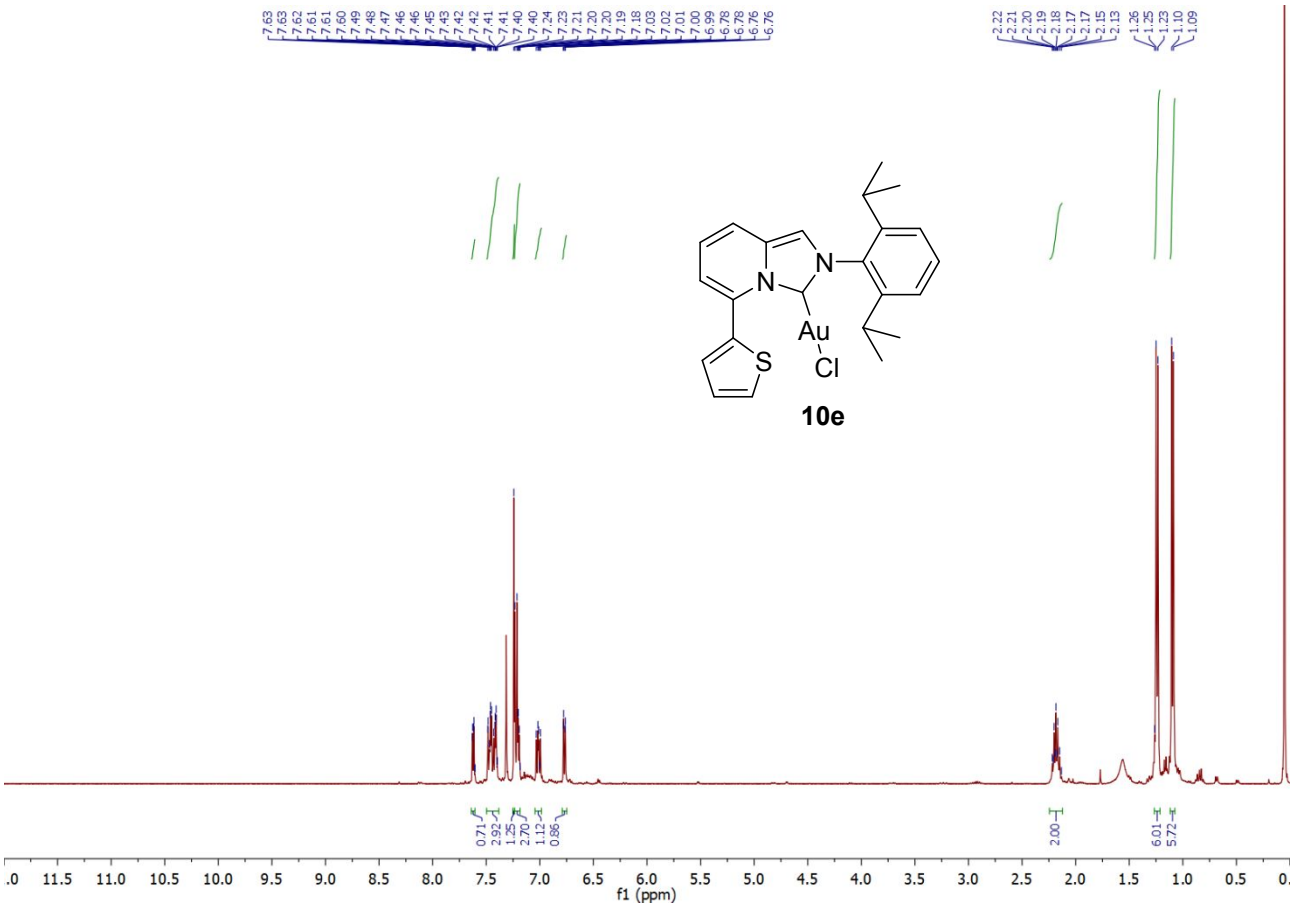

N
N
Au
Cl
10b
f1 (ppm)


f1 (ppm)

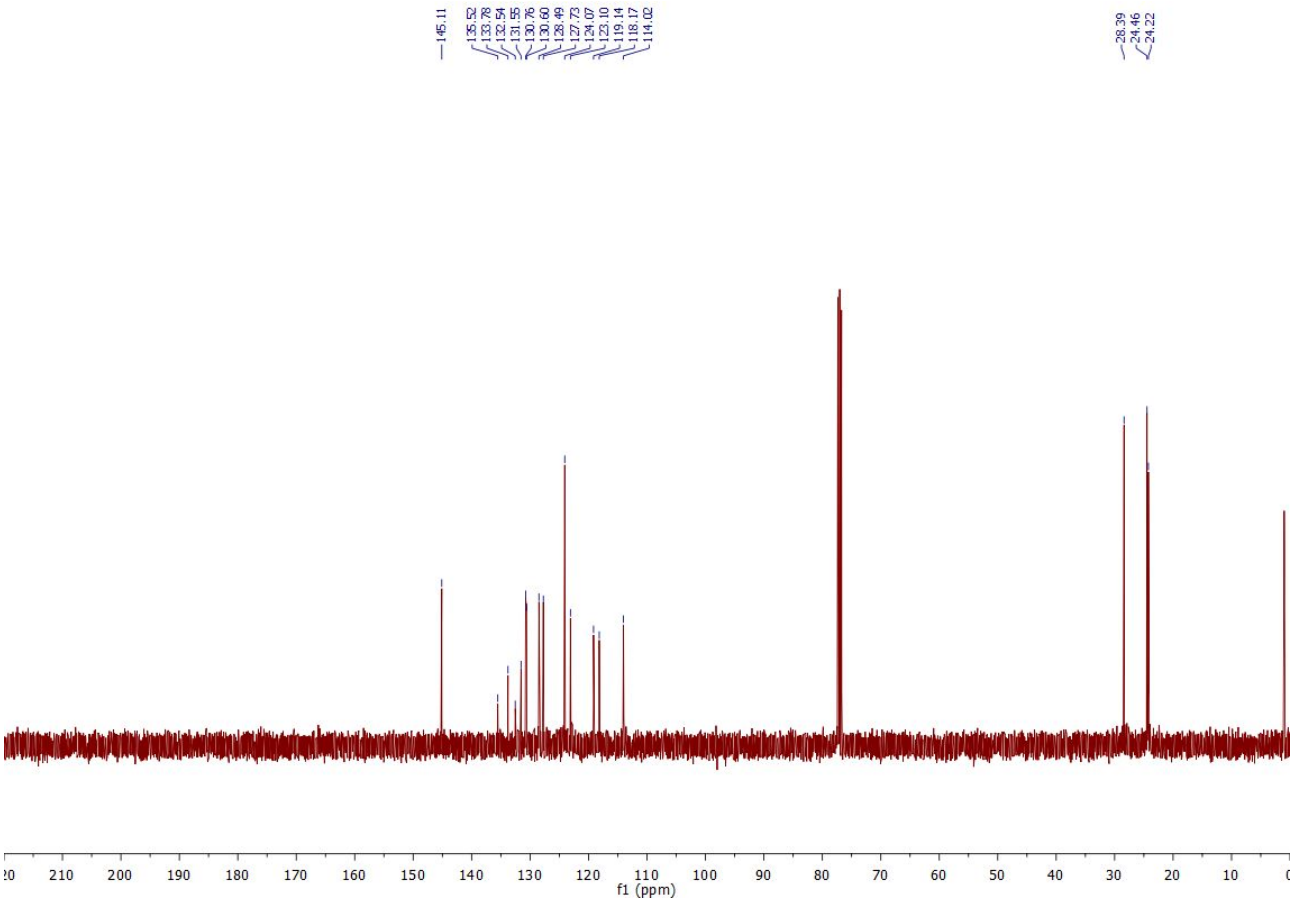

N
N
Au
Cl
F3C
CF3
10c
f1 (ppm)
f1 (ppm)

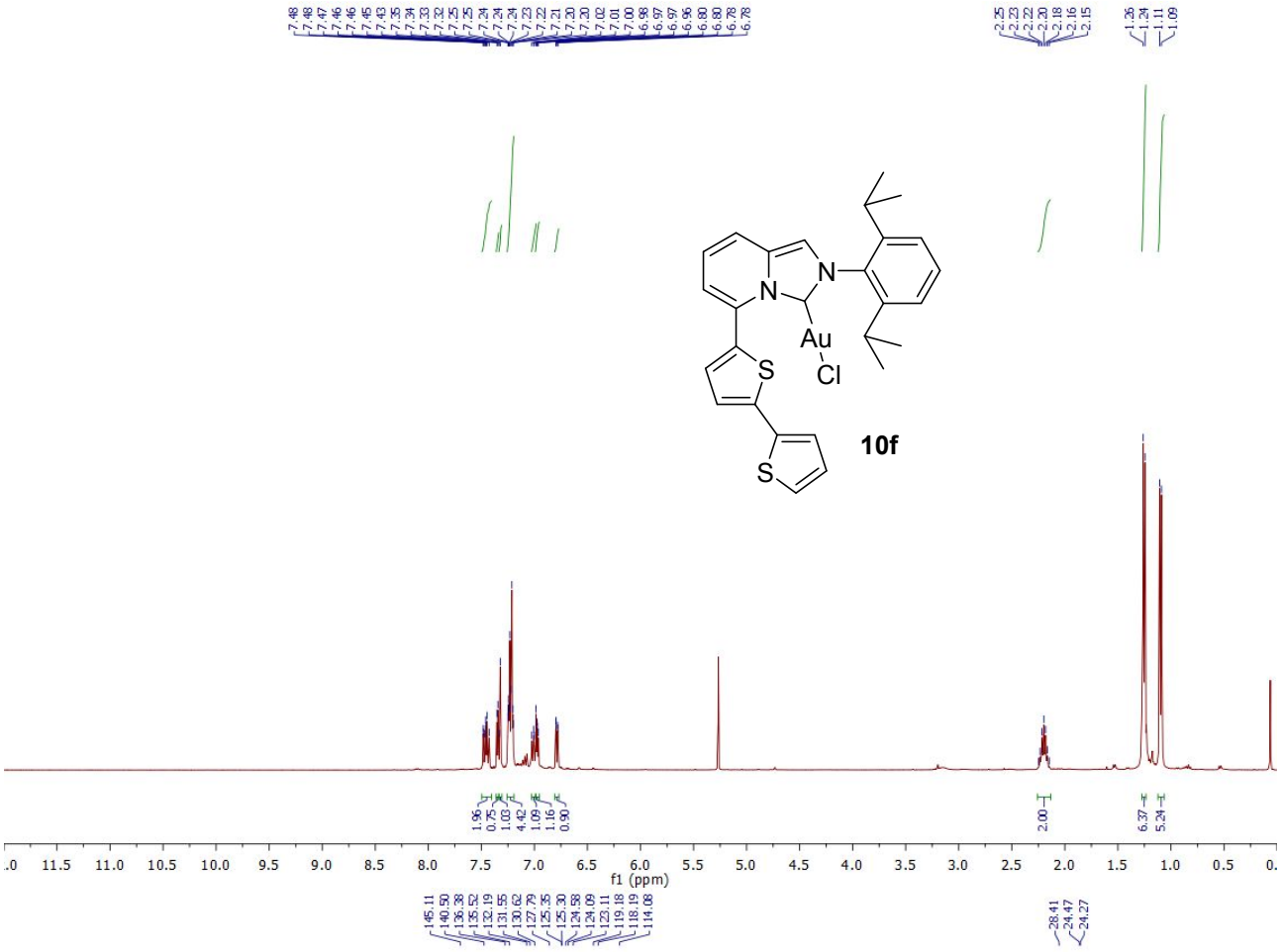

-62.96
N
N
Au
Cl
F3C
CF3
10c
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

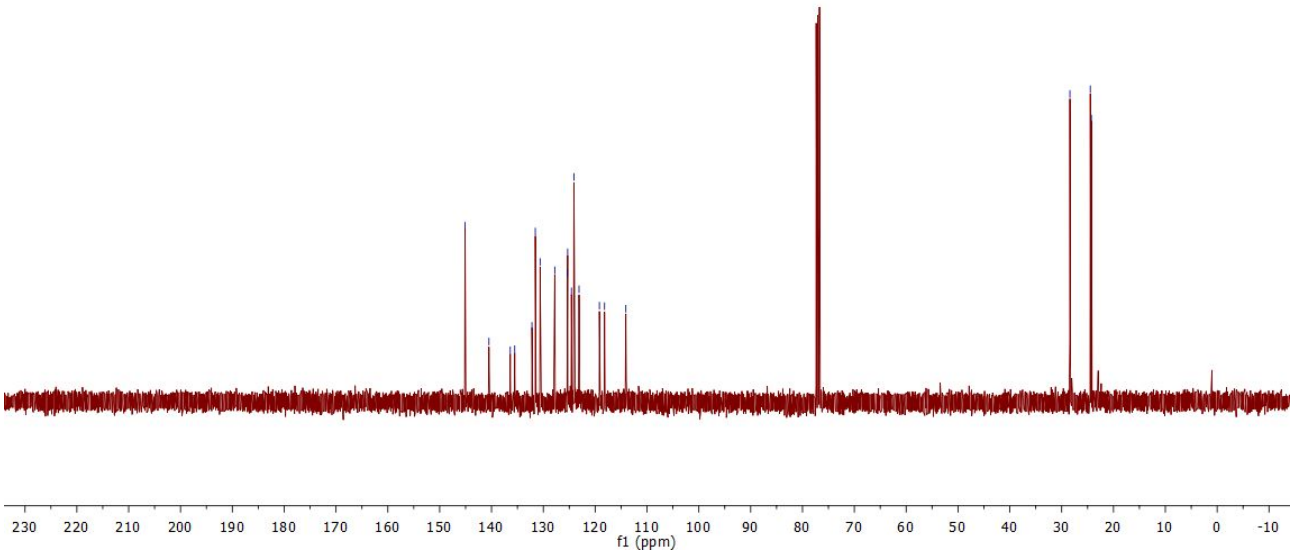

MeO
OMe
Au
Cl
N
N
10d
f1 (ppm)
f1 (ppm)

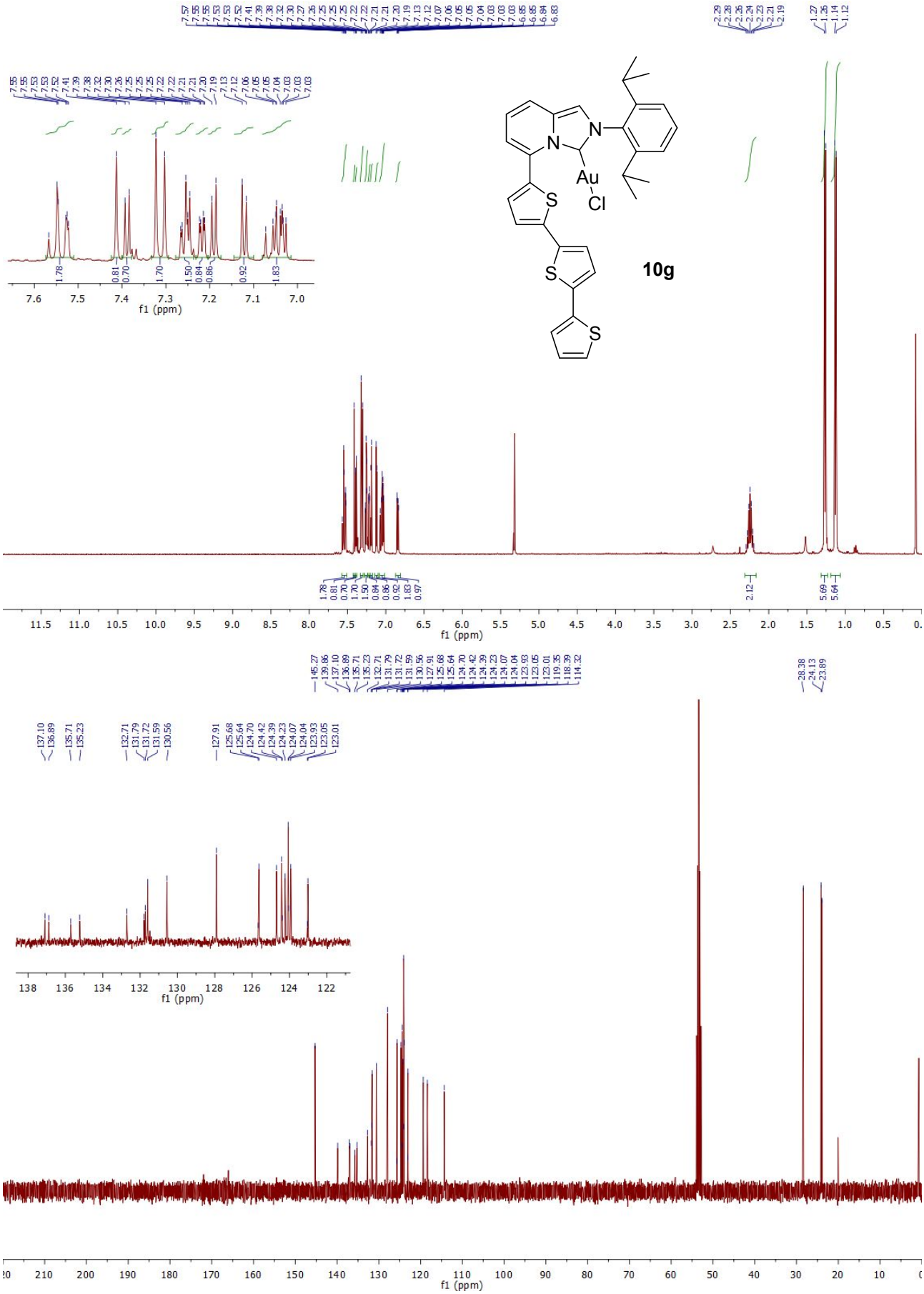

7.63 7.62 7.61 7.60 7.49 7.48 7.47 7.46 7.45 7.43 7.42 7.41 7.40 7.24 7.23 7.21 7.20 7.19 7.18 7.03 7.02 7.01 7.00 6.99 6.78 6.76
2.22 2.21 2.20 2.19 2.18 2.17 2.15 2.13 1.26 1.25 1.23 1.10 1.09
N
N
Au
Cl
S
0.71 2.92 1.25 2.70 1.12 0.86 2.00 6.01 5.72
f1 (ppm)

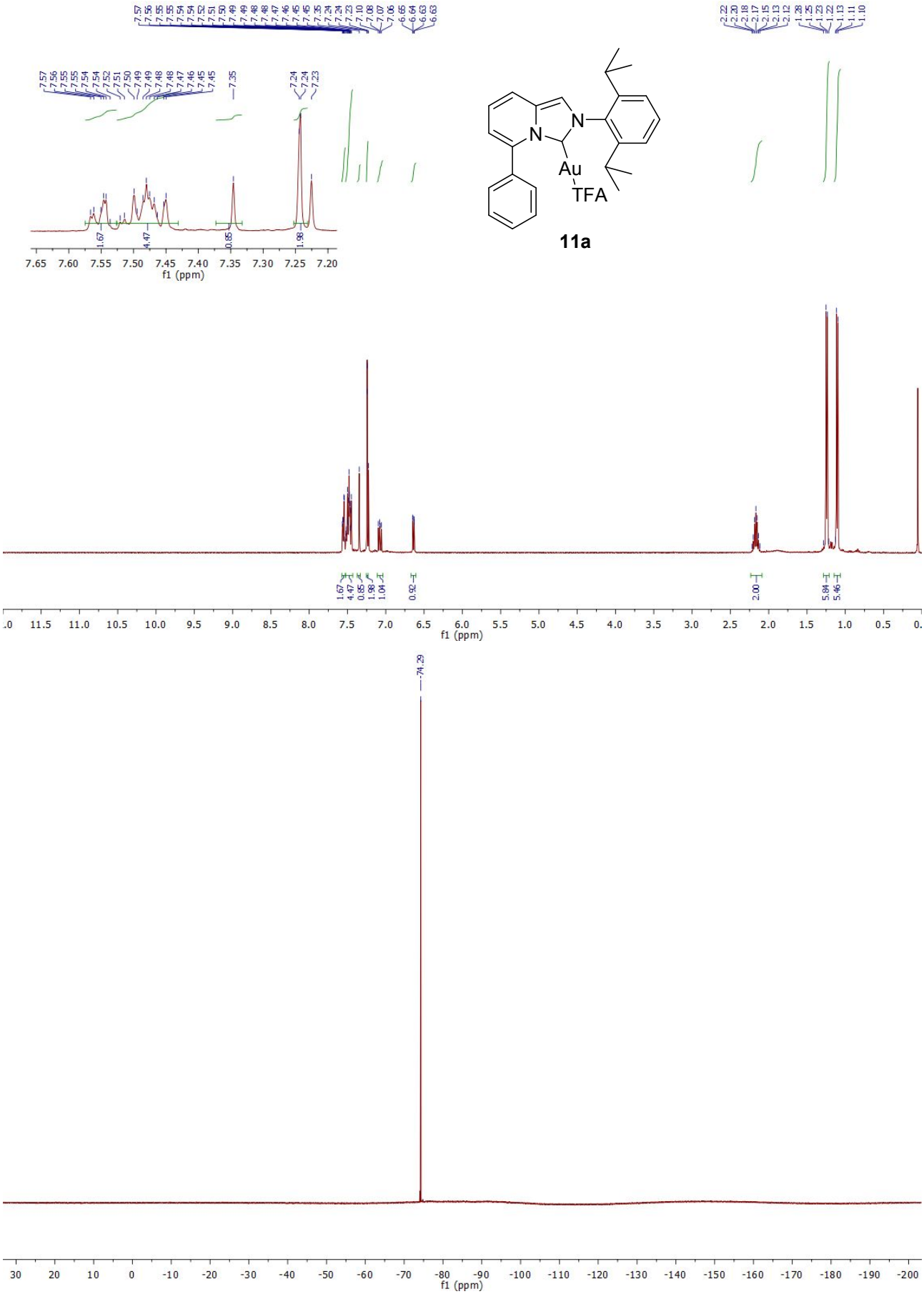
10e

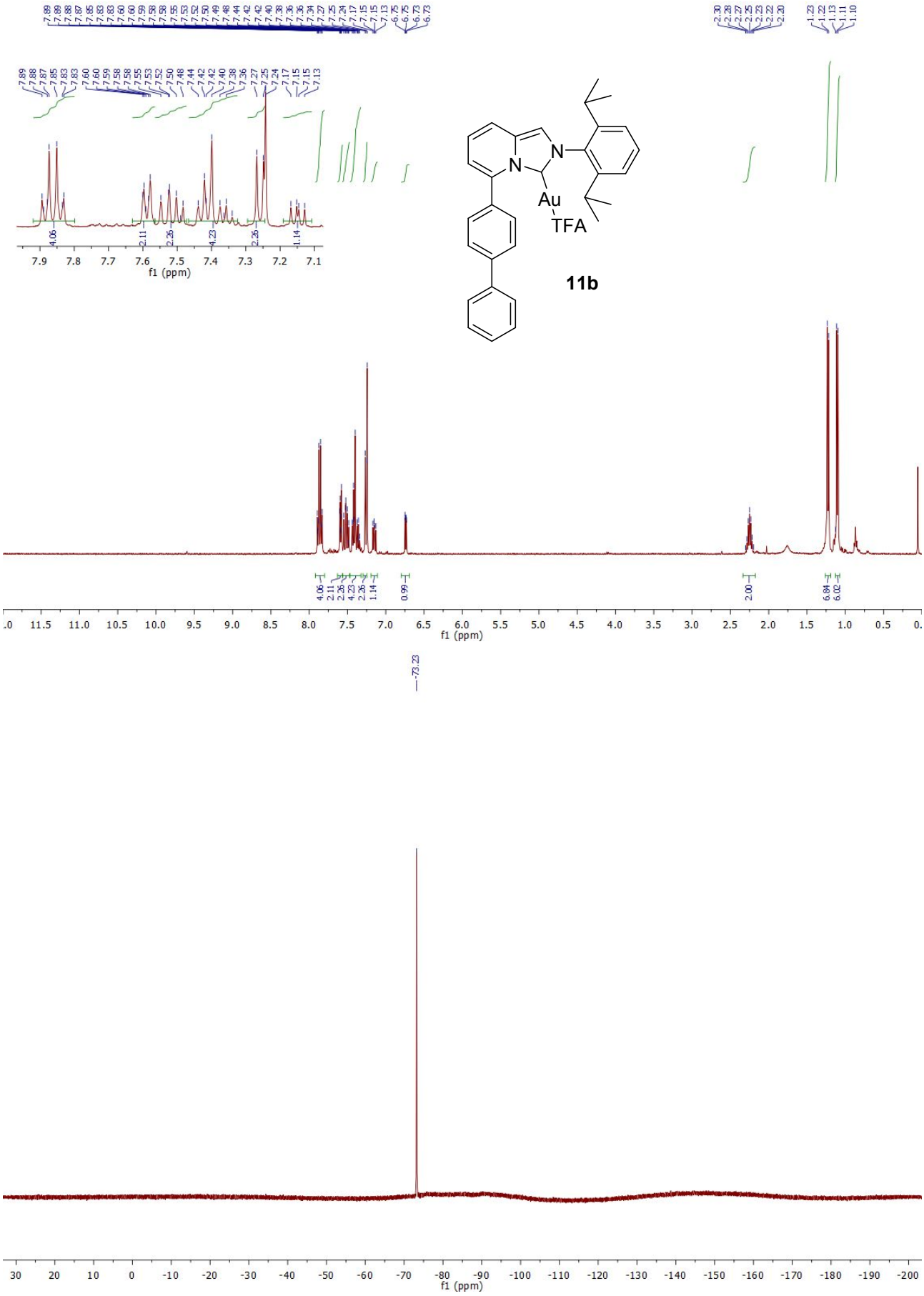

145.11 135.52 133.78 132.54 131.55 130.76 130.60 128.49 127.73 124.07 123.10 119.14 118.17 114.02
28.39 24.46 24.22
f1 (ppm)

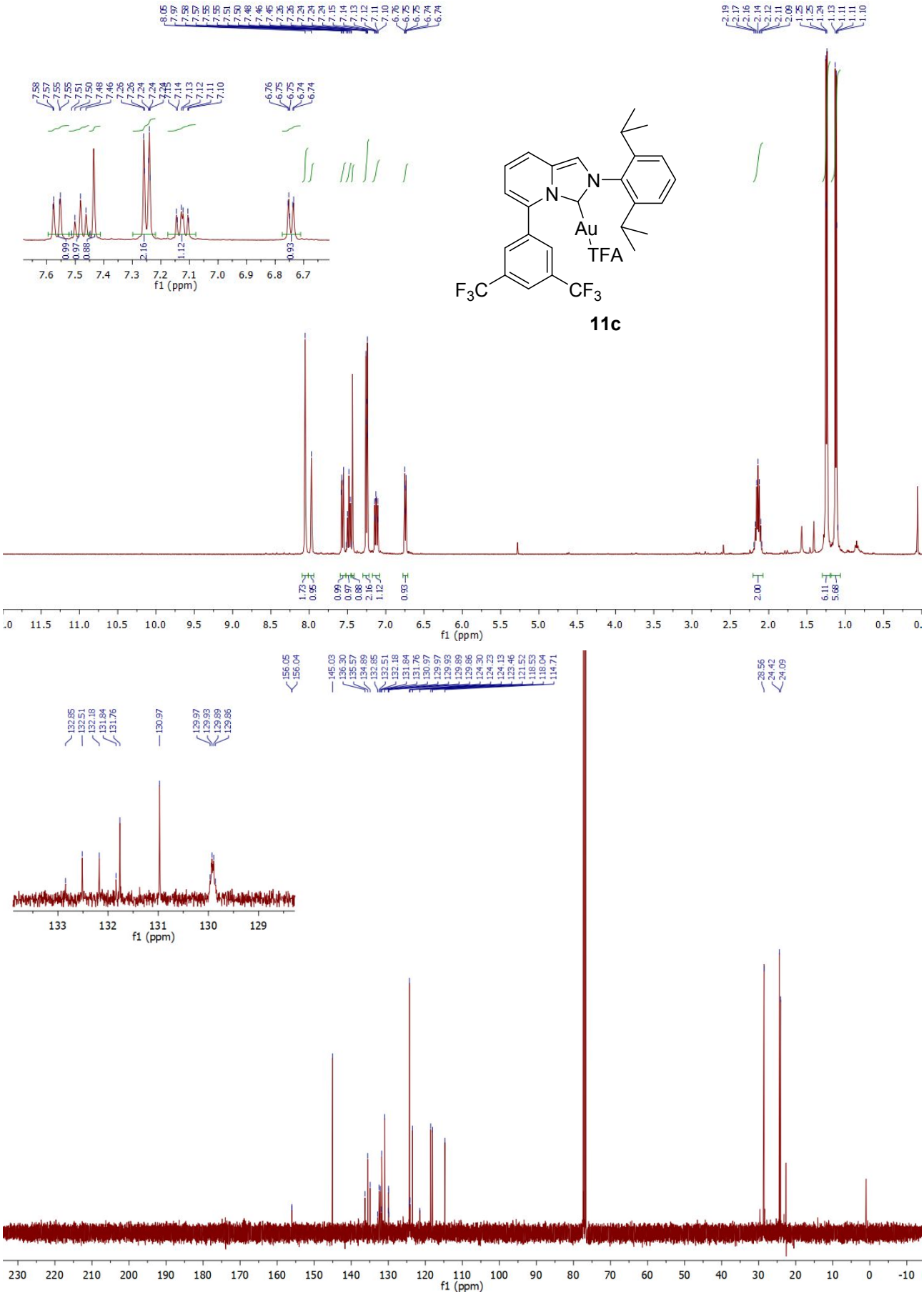

N
N
Au
Cl
S
S
10f
f1 (ppm)

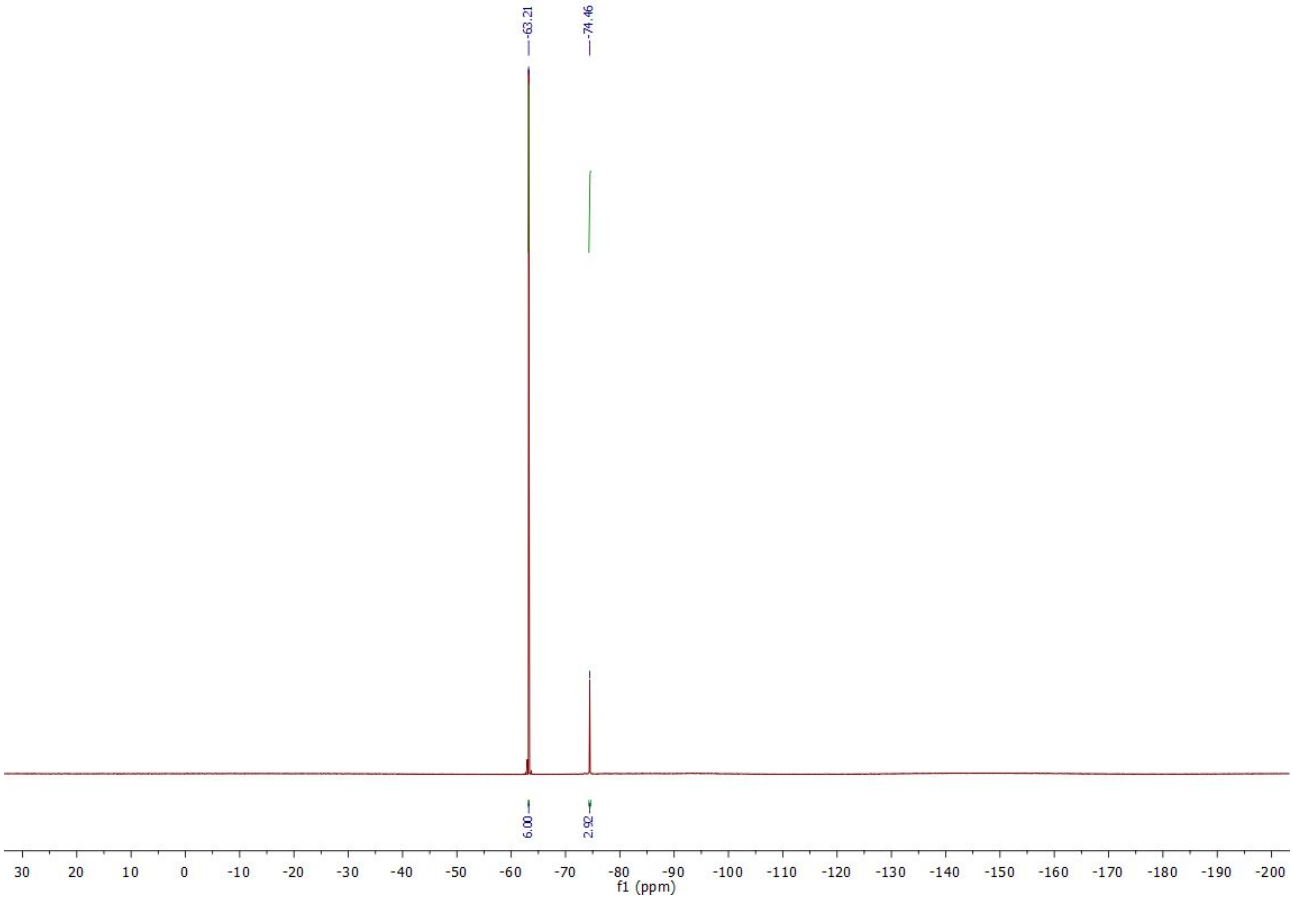

f1 (ppm)

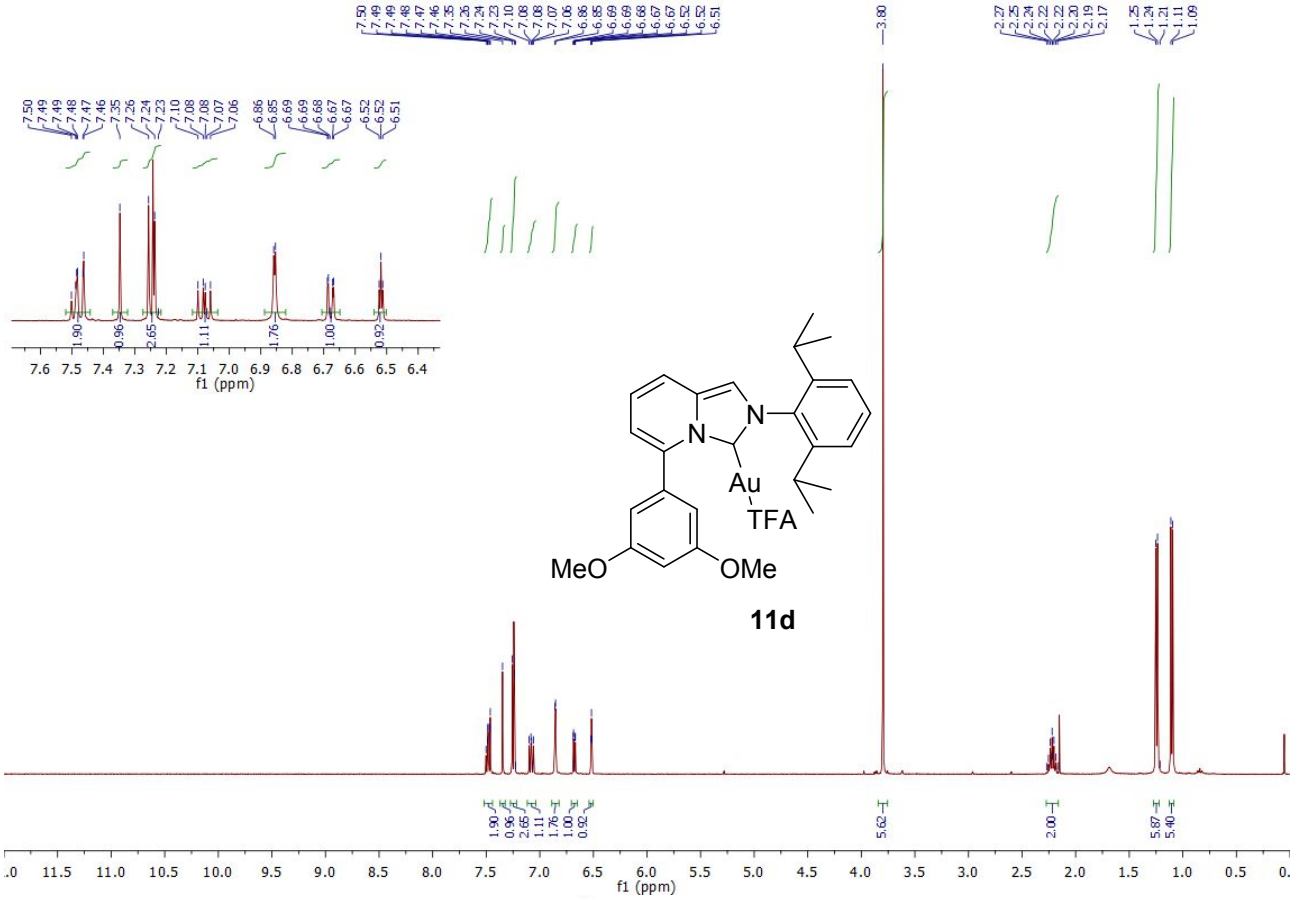

N
N
Au
Cl
S
S
S
10g
f1 (ppm)


N
N
Au
TFA
11a
f1 (ppm)
f1 (ppm)
f1 (ppm)

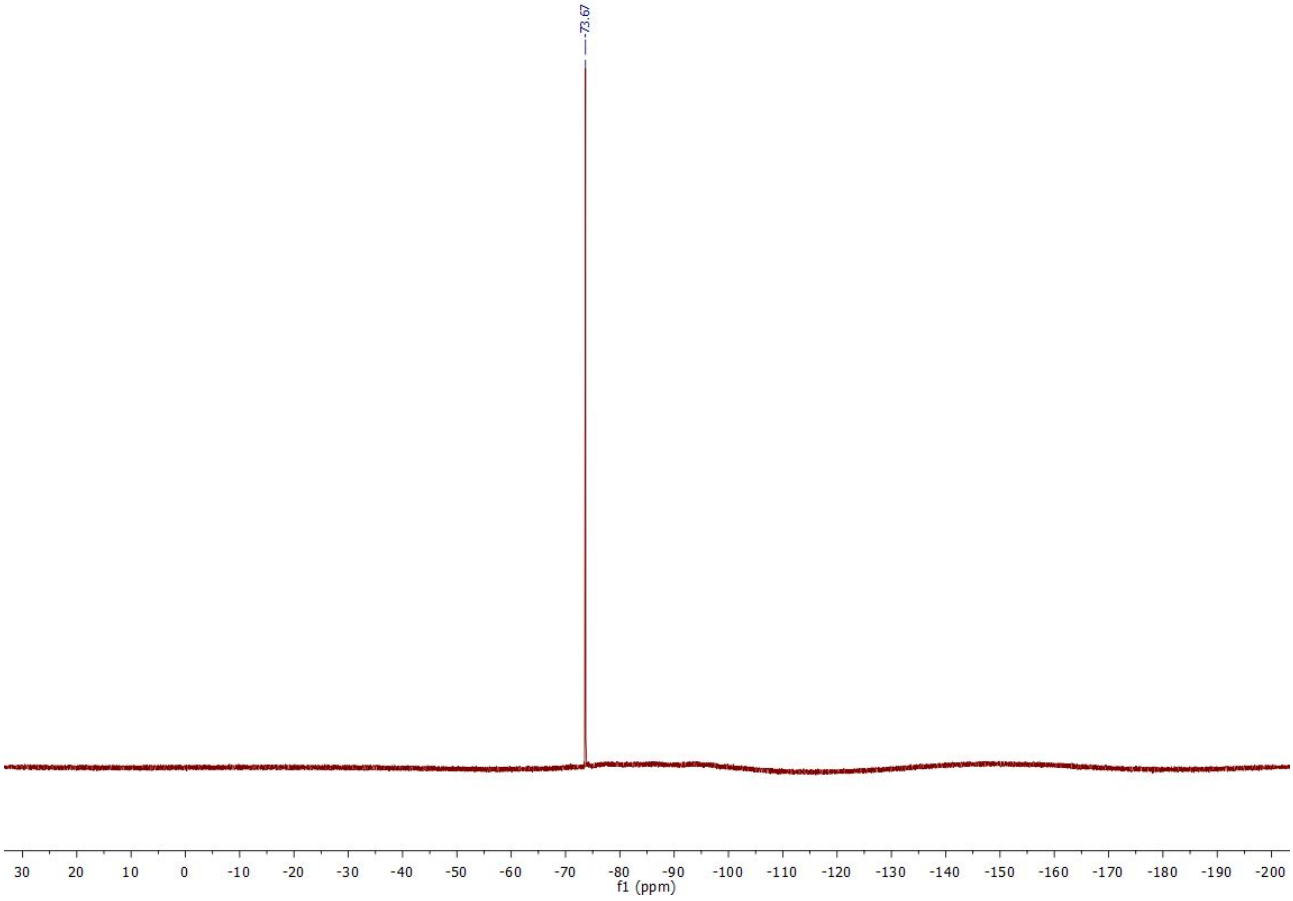

Au
TFA
11b
f1 (ppm)
-73.23
f1 (ppm)

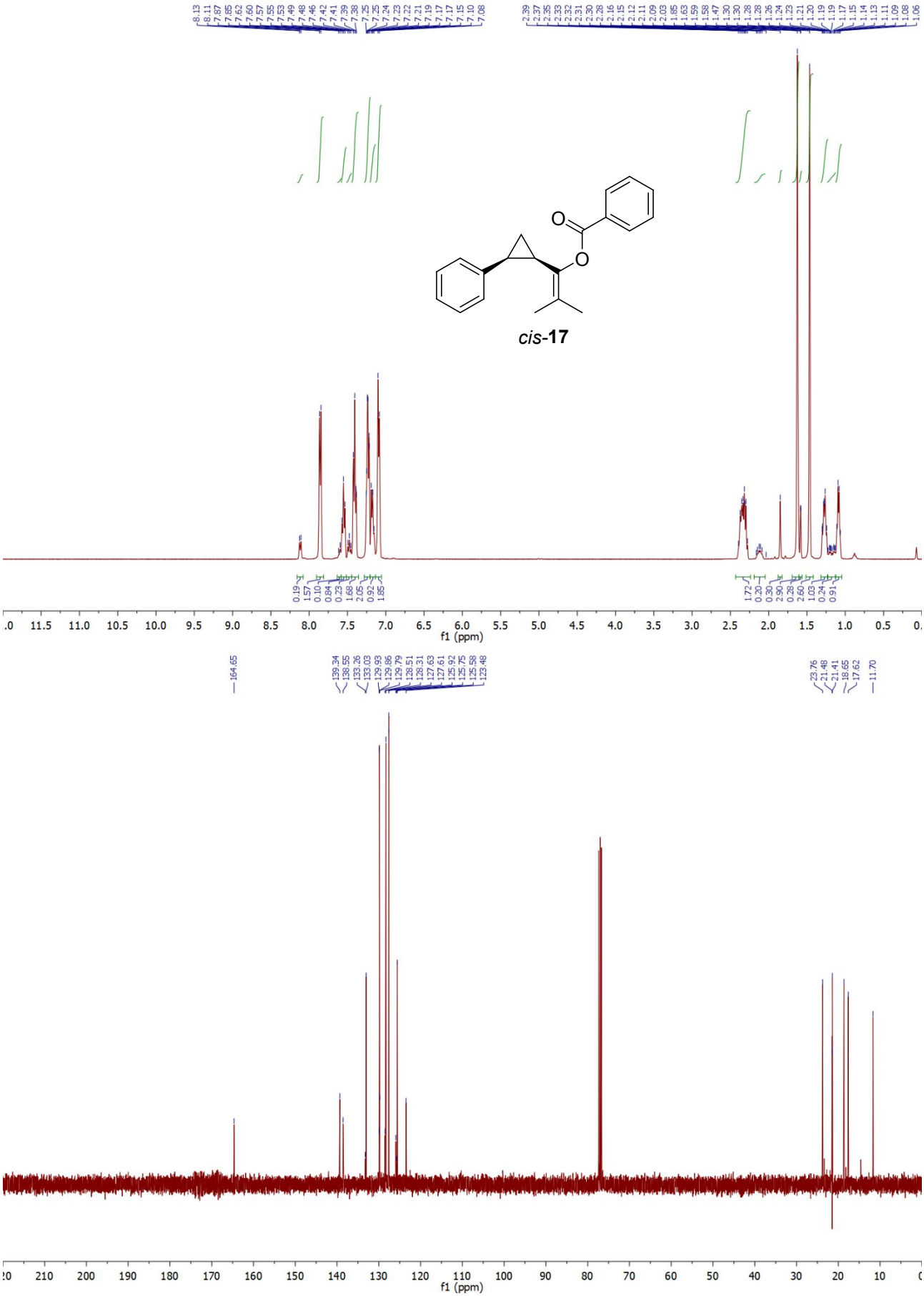

Au
TFA
F_3C
CF_3
11c
f1 (ppm)


-63.21
-74.46
6.00
2.92
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

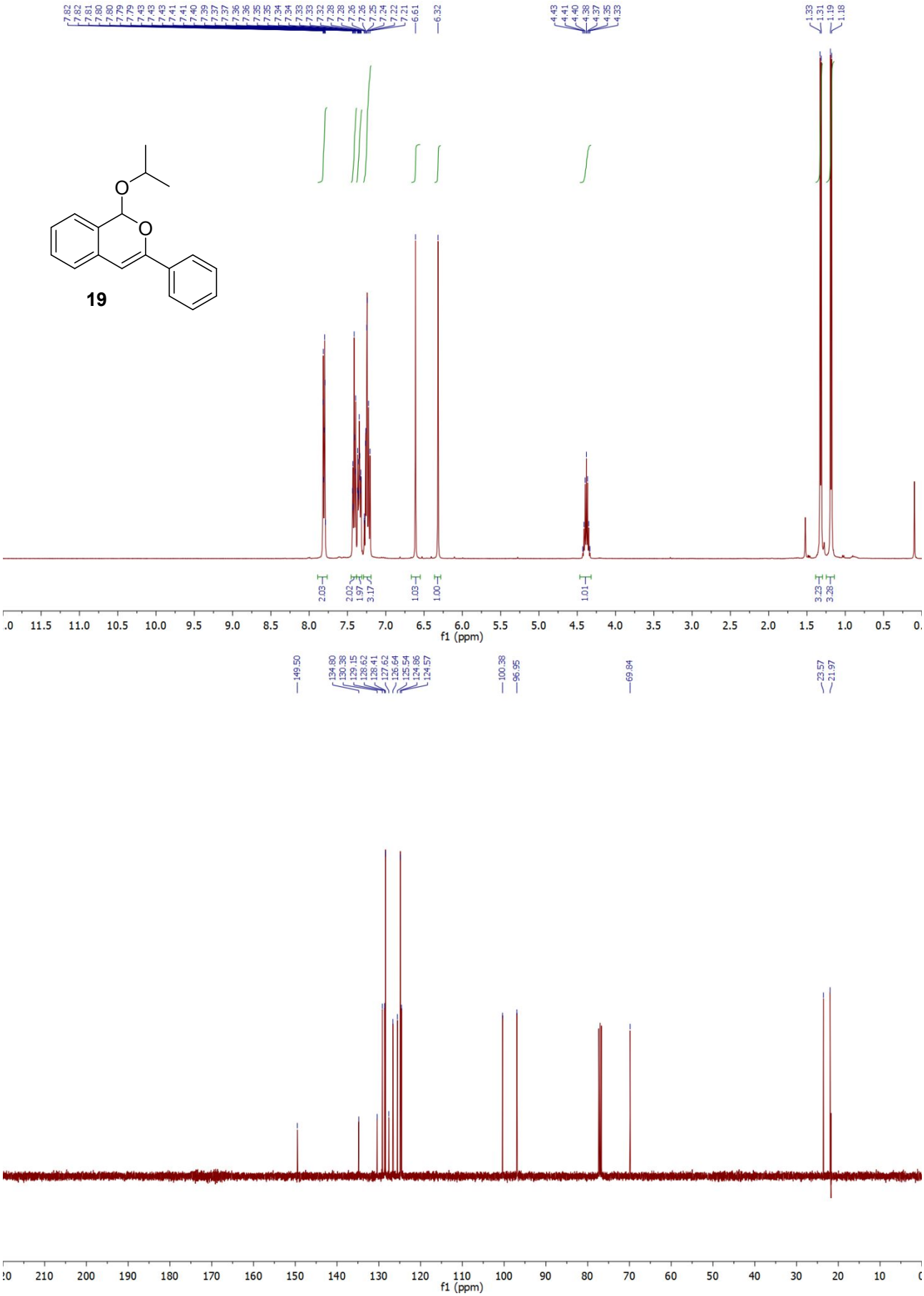


11d





cis-**17**


19
f1 (ppm)
f1 (ppm)

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