Supporting Information for

Dinuclear Pt(II) and Au(III) complexes with cyclometallating tridentate ligands: luminescence enhancement for Au_2, aggregate-like emission for Pt_2, and Au-to-Pt energy transfer in a heterodimer

Rebeca Muñoz-Rodríguez[a], Elena Buñuel[a], J. A. Gareth Williams[b]*, Diego J. Cárdenas[a]*

[a] *Department of Organic Chemistry, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain.*
[b] *Department of Chemistry, University of Durham, Durham DH1 3LE, UK.*

1. Details of synthetic procedures

The following reagents were purchased: 2,7-di-tert-butyl-4,5-dibromo-9,9-dimethylxanthene (Aldrich), 2,6-dibromopyridine (Fluka), 4-*n*-butylphenylboronic acid (Aldrich), 2-bromopyridine (Aldrich), $K[AuCl_4]\cdot nH_2O$ (Strem Chemicals), $K_2[PtCl_4]$ (Alfa Aesar).

Synthesis of 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene (2)

2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene (**2**) was prepared from 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylxanthene (**1**) according to the published method and the spectral properties correspond to those reported.[1]

Synthesis of 2,7-di-*tert*-butyl-4,5-bis((trimethylsilyl)ethynyl)-9,9-dimethylxanthene (3)

Bis(triphenylphosphine)palladium (II) dichloride (490 mg) and copper (I) iodide (212 mg) were added successively to a solution of 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene (**1**) (2 g, 3.48 mmol) and trimethysilylacetylene (1.6 ml, 1.026 mg, 10.45 mmol) in triethylamine (16 ml) under argon at room temperature. The reaction mixture was stirred at 60ºC for 24 h and then concentrated *in vacuo*. The residue was diluted with H_2O (30 ml) and dichloromethane (30 ml). Separated the layers, the aqueous phase was extracted with dichloromethane (3 x 20 ml), and the combined organic phases were dried over magnesium sulfate and evaporated. The crude produced was purified by flash column chromatography on silica gel with hexane-EtOAc (30:1) as eluent to give a white solid Yield: 1.35 g (75%).

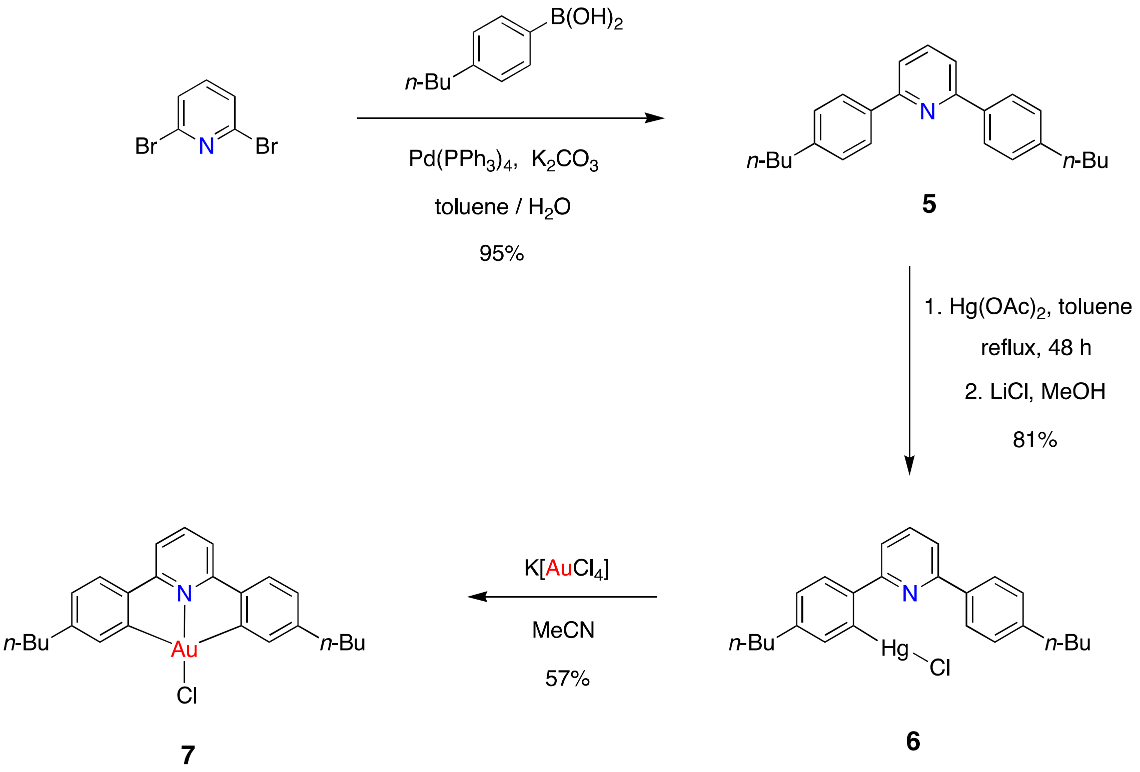
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.3 Hz, 2H), 7.34 (d, 2.3 Hz, 2H), 1.58 (s, 6H), 1.31 (s, 18H), 0.31 (s, 18H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 148.3 (C), 145.4 (C) 130.8 (CH), 129.6 (C), 123.7 (CH), 111.0 (C), 102.5 (C), 98.4 (C), 34.6 (C), 34.5 (C), 32.8 (CH_3), 31.5 (CH_3), 0.7 (CH_3).
HRMS TOF MS EI $[M]^+$: Calc. 514.3083; found 514.3087.

Synthesis of 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (4)

A solution of K_2CO_3 (150 mg, 1.09 mmol) in MeOH (3 ml) was added to a solution of 2,7-di-*tert*-butyl-4,5-bis((trimethylsilyl)ethynyl)-9,9-dimethylxanthene (**3**) (100 mg, 0.174 mmol) in CH_2Cl_2 (3 ml). After stirring at room temperature for 12h, the reaction mixture was concentrated *in vacuo*. The residue was diluted with H_2O (20 ml) and dichloromethane (20 ml). Separated the layers, the aqueous phase was extracted with dichloromethane (3 x 15 ml), and the combined organic phases were dried over magnesium sulfate and evaporated. The crude produced was purified by flash column chromatography on silica gel with hexane-EtOAc (30:1) as eluent to give a white solid Yield: 63 mg (98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.37 (m, 4H), 3.32 (s, 2H), 1.61 (s, 6H), 1.32 (s, 18H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 149.7 (C), 145.7 (C) 129.8 (C), 129.0 (CH), 123.7 (CH), 110.2 (C), 81.2 (CH), 79.9 (C), 34.8 (C), 34.6 (C), 32.2 (CH_3), 31.6 (CH_3).
HRMS ESI $[M+Na]^+$: Calc. 393.2197; found 393.2188.

Synthesis of Cyclometalated Au(III) Chloride Complex



2,6-Bis(4-*n*-butylphenyl)pyridine (H*n*BuC^N^C*n*BuH) (5)

This was synthesized by modification of a literature procedure.[2] A mixture of 2,6-dibromopyridine (0.550 g, 2.34 mmol), 4-n-butylphenylboronic acid (1.0 g, 5.62 mmol) and $Pd(PPh_3)_4$ (0.3% eq., 0.07 mmol) as catalyst, was heated at 120 ºC for 18 hours in a solvent mixture of toluene (50 ml) and an aqueous solution of K_2CO_3 (25 ml, 8.5 M). After cooling to room temperature the two layers were separated and the aqueous layer extracted three times with dichloromethane. The combined organic layers were washed with water until pH = 7, dried over magnesium sulfate and the solvent was evaporated. The crude produced was purified by flash column chromatography on silica gel with Hexane-Et_2O (30:1) as eluent to give a white solid. Yield: 0.760 g (95%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 4H), 7.77 (dd, *J* = 8.4, 1.4 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 4H), 2.68 (t, *J* = 7.6 Hz, 4H), 1.71-1.59 (m, 4H), 1.46-1.32 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 157.0 (C), 144.1 (C), 137.4 (C), 137.3 (C), 128.9 (CH), 128.9 (CH), 127.1 (CH), 118.2 (CH), 35.6 (CH_2), 33.8 (CH_2), 22.5 (CH_2), 14.1 (CH_3).
HRMS ESI $[M+H]^+$: Calc. 344.2377; found 344.2372.

[Hg(*n*BuC^N^C*n*BuH)Cl] (6)

This was synthesized by modification of a literature procedure.[3] A mixture of 2,6-bis(4-*n*-butylphenyl)pyridine (**5**) (0.750 g, 2.18 mmol) and mercury(II) acetate (0.696 g, 2.18 mmol) in absolute ethanol (14 mL) was heated under reflux for 24 h, and addicional mercury(II) acetate (0.696 g, 2.18 mmol) in absolute ethanol (5 mL) was then added. After 48 h a solution of lithium chloride (0.185 g, 4.367 mmol) in methanol (9 mL) was then added. The mixture was heated for 15 min and was then diluted with distilled water (30 mL) and EtOAc (30 ml). Separated the layers, the aqueous phase was extracted with EtOAc (5 x 30 ml), and the combined organic phases were dried over magnesium sulfate and evaporated. The crude produced was purified by flash column chromatography on silica gel with hexane-EtOAc (6:1) as eluent to give a white solid Yield: 1.027 g (81%).

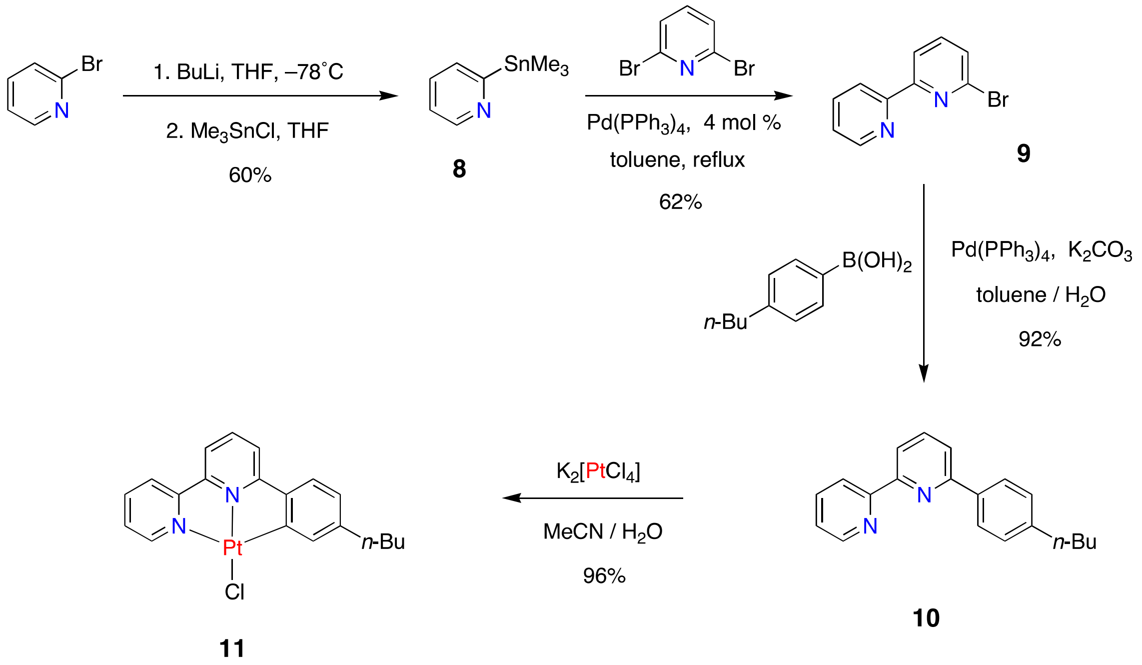
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.80 (m, 4H), 7.73 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.67 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 (dd, *J* = 7.8, 1.8 Hz, 2H), 2.75-2.63 (m, 4H), 1.74-1.59 (m, 4H), 1.47-1.33 (m, 4H), 0.96 (dt, *J* = 7.3, 1.7 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 158.3 (C), 157.7 (C), 148.8 (C), 144.7 (C), 144.5 (C), 140.9 (C), 138.4 (CH), 138.0 (CH), 136.0 (C), 129.2 (CH), 129.1 (CH), 128.1 (CH), 127.9 (CH), 120.6 (CH), 119.4 (CH), 35.6 (CH_2), 35.5 (CH_2), 33.7 (CH_2), 33.6 (CH_2), 22.5 (CH_2), 22.4 (CH_2), 14.2 (CH_2), 14.1 (CH_3).
HRMS ESI $[M]^+$: Calc. 579.1679; found 579.1658.

[Au(*n*BuC^N^C*n*Bu)Cl] (7)

This was synthesized by modification of a literature procedure.[3] A mixture of Hg(*n*BuC^N^C*n*BuH)Cl (**6**) (2.0 g, 3.46 mmol) and $K[AuCl_4]\cdot nH_2O$ (1.570 g, 4.152 mmol) in acetonitrile (200 mL) was refluxed for 24 h to afford a deep yellow solid. The solid was filtered and dried *in vacuo*. Yield: 1.132 g (57%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (t, J = 8.1 Hz, 1H), 7.70 (d, J = 1.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.01 (dd, J = 7.9, 1.3 Hz, 2H), 2.63 (t, J = 7.5 Hz, 4H), 1.71-1.56 (m, 4H), 1.46-1.31 (m. 4H), 0.95 (t, J = 7.2 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 170.6 (C), 165.2 (C), 147.9 (C), 145.2 (C), 142.7 (CH), 134.0 (CH), 127.4 (CH), 125.2 (CH), 116.2 (CH), 36.5 (CH_2), 33.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3).
HRMS ESI $[M+H]^+$: Calc. 574.1575; found 574.1570.

Synthesis of Cyclometalated Pt(II) Chloride Complex



The compounds **8** and **9** were prepared respectively according to the literature procedure and the spectral properties correspond to those reported.[4,5]

6-(4-n-butylphenyl)-2,2'-bipyridine (H*n*BuC^N^N) (10)

This was synthesized by modification of a literature procedure.[2] A mixture of 6-bromo-2,2'-bipyridine (**9**) (0.890 g, 3.79 mmol), 4-*n*-butylphenylboronic acid (0.675 g, 3.79 mmol) and $Pd(PPh_3)_4$ (0.3% eq., 0.11 mmol) as catalyst, was heated at 120 ºC for 20 hours in a solvent mixture of toluene (40 ml) and an aqueous solution of K_2CO_3 (19 ml, 8.5 M). After cooling to room temperature the two layers were separated and the aqueous layer extracted three times with dichloromethane. The combined organic layers were washed with water until pH = 7, dried over magnesium sulfate and the solvent was evaporated. The crude produced was purified by flash column chromatography on silica gel with Hexane-Et_2O (20:1) as eluent to give 1.010 g of a colorless oil containing 0.925 g of compound **9** and 0.085 g of unreacted starting material (calculated by ^{1}H NMR). Yield: 0.925 g (85%). An analytical sample of pure compound **10** could be isolated, which allowed the complete characterization of the product.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73-8.60 (m, 2H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.92-7.80 (m, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.37-7.28 (m, 3H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.73-1.58 (m, 2H), 1.48-1.31 (m, 2H), 0.95 (t, *J* = 7.32 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 156.7 (C), 156.6 (C), 155.8 (C), 149.2 (CH), 144.2 (C), 137.8 (CH), 137.1 (C), 137.0 (CH), 129.0 (CH), 127.0 (CH), 123.8 (CH), 121.4 (CH), 120.2 (CH), 119.1 (CH), 35.6 (CH_2), 33.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3).
HRMS ESI $[M+H]^+$: Calc. 289.1692; found 289.1699.

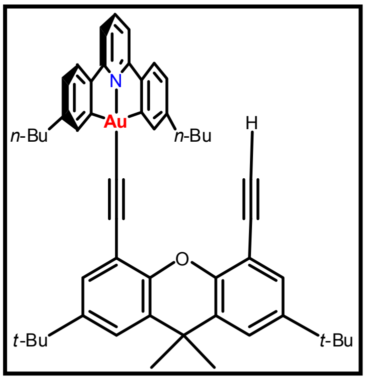
[Pt(*n*BuC^N^N)Cl] (11)

This was synthesized by modification of a literature procedure.[6] A solution of $K_2[PtCl_4]$ (1.251 g, 3.02 mmol) in water (65 ml) was treated with a solution of 6-(4-n-butylphenyl)-2,2'-bipyridine (**10**) (0.914 g, 3.17 mmol) in MeCN (65 ml). The reaction mixture was refluxed for 3 days and the MeCN was then evaporated *in vacuo*. The orange solid so obtained was collected by filtration, washed with water, water-EtOH (5:1) and diethyl ether, and dried *in vacuo*. Yield: 1.496 g (96%)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (d, *J* = 5.1 Hz, 1H), 7.96 (t, 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.61-7.38 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.88 (dd, *J* = 7.7, 1.3 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.72-1.57 (m, 2H), 1.48-1.32 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 166.9 (C), 157.4 (C), 154.4 (C), 148.9 (CH), 147.0 (C), 144.0 (C), 142.4 (C), 139.1 (CH), 138.3 (CH), 135.4 (CH), 127.2 (CH), 124.5 (CH), 124.4 (CH), 122.6 (CH), 118.3 (CH), 117.6 (CH), 36.4 (CH_2), 33.9 (CH_2), 22.8 (CH_2), 14.2 (CH_3).
HRMS ESI $[M+Na]^+$: Calc. 540.0786; found 540.0776.

Synthesis of mononuclear Au (III) complex (Au)

A sealed reaction tube was charged with [Au(*n*BuC^N^C*n*Bu)Cl] (**7**) (50 mg, 0.087 mmol), 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**4**) (38 mg, 0.105 mmol), Et_3N (0.5 mL) and CuI (27% eq., 0.023 mmol), followed by addition of anhydrous CH_2Cl_2 (7 mL). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 ºC for 24 hours and then concentrated *in vacuo*. The crude produced was purified by flash column chromatography on silica gel with Hexane-CH_2Cl_2 (2:1) as eluent to give a yellow solid. Yield: 67 mg (85%).

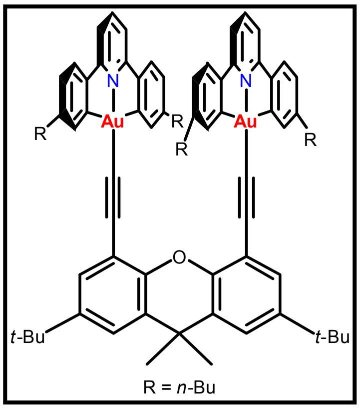


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.4 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.47 (d, *J* = 7.90 Hz, 2H), 7.43-7.37 (m, 3H), 7.33 (t, *J* = 2.7 Hz, 2H), 7.05 (dd, *J* = 8.0, 1.6 Hz, 2H), 2.83 (s, 1H), 2.62 (t, *J* = 7.6 Hz, 4H), 1.70-1.55 (m, 4H, partially buried under singlet CH_3 signal), 1.66 (s, 6H, CH_3), 1.41-1.25 (m, 4H, partially buried under *t*-Bu signals), 1.37 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu), 0.85 (t, *J* = 7.3 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 167.4 (C), 165.3 (C), 150.2 (C), 148.8 (C), 147.5 (C), 146.6 (C), 145.2 (C), 145.0 (C), 142.0 (CH), 138.1 (CH), 129.8 (C), 129.3

(C), 129.1 (CH), 128.5 (CH), 126.8 (CH), 125.0 (CH), 123.4 (CH), 121.4 (CH), 115.9 (CH), 114.8 (C), 110.6 (C), 96.7 (C), 96.6 (C), 82.5 (C), 79.9 (CH), 36.3 (CH_2), 34.9 (C), 34.6 (C), 34.5 (C), 33.5 (CH_2), 32.4 (CH_3), 31.7 (CH_3), 31.6 (CH_3), 22.7 (CH_2), 14.1 (CH_3).
HRMS ESI $[M+Na]^+$: Calc. 930.3871; found 930.3919.

Synthesis of homodinuclear Au (III) complex (Au_2)

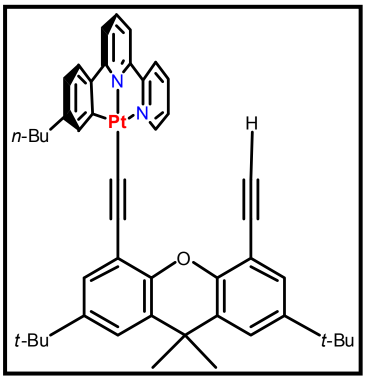
A sealed reaction tube was charged with [Au(*n*BuC^N^*Cn*Bu)Cl] (**7**) (59 mg, 0.103 mmol), 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**4**) (15 mg, 0.041 mmol), Et_3N (0.5 mL) and CuI (27% eq., 0.011 mmol), followed by addition of anhydrous CH_2Cl_2 (7 mL). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 ºC for 24 hours and then concentrated *in vacuo*. The crude produced was purified by flash column chromatography on silica gel with Hexane-CH_2Cl_2 (1:1) as eluent to give a yellow solid. Yield: 37 mg (79%).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.4 Hz, 4H), 7.59-7.50 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 7.8 Hz, 4H), 6.60 (dd, *J* = 7.8, 1.4 Hz, 4H), 2.60-2.15 (m. 8H), 1.73 (s, 6H), 1.61-1.42 (m, 8H), 1.37 (s, 18H), 1.36-1.19 (m, 8H), 0.82 (t, *J* = 7.3 Hz, 12H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 168.0 (C), 164.9 (C), 149.3 (C), 147.1 (C), 145.7 (C), 144.5 (C), 140.7 (CH), 138.4 (CH), 129.3 (CH), 128.9 (C), 125.9 (CH), 124.1 (CH), 121.1 (CH), 115.4 (C), 115.0 (CH), 97.2 (C), 95.4 (C), 36.2 (CH_2), 34.9 (C), 34.6 (C), 33.1 (CH_2), 32.8 (CH_3), 31.7 (CH_3), 22.9 (CH_2), 14.1(CH_3).
HRMS ESI $[M+H]^+$: Calc. 1445.5873; found 1445.5831.

Synthesis of mononuclear Pt (II) complex (Pt)

A sealed reaction tube was charged with [Pt(*n*BuC^N^N)Cl] (**11**) (70 mg, 0.135 mmol), 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**4**) (60 mg, 0.162 mmol), Et_3N (0.94 mL) and CuI (3% eq., 0.004 mmol), followed by addition of anhydrous CH_2Cl_2 (16 mL). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 ºC for 7 days and then concentrated *in vacuo*. The crude produced was purified by flash column chromatography on neutral Al_2O_3 with CH_2Cl_2-EtOAc (30:1) as eluent to give an orange solid. Yield: 31 mg (27%).

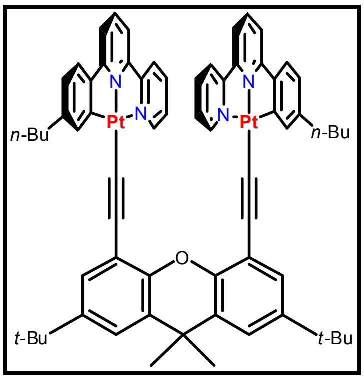


^{1}H NMR (300 MHz, $CDCl_3$) δ 9.53-9.40 (m, 1H), 8.02-7.92 (m, 2H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.79-7.69 (t, *J* = 8.0 Hz, 1H), 7.60-7.44 (m, 4H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.30-7.20 (m, 2H), 6.87 (dd, *J* = 7.9, 1.7 Hz, 1H), 2.83 (s, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.70-1.60 (m, 2H, partially buried under singlet CH_3 signal), 1.65 (s,

6H), 1.43-1.24 (m, 2H, partially buried under *t*-Bu signals), 1.35 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu), 0.88 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 166.1 (C), 158.0 (C), 154.6 (C), 153.1 (CH), 150.5 (C), 148.6 (C), 147.1 (C), 144.9 (C), 144.6 (C), 144.3 (C), 142.8 (C), 140.0 (CH), 138.6 (CH), 138.5 (CH), 130.2 (C), 129.5 (CH), 128.7 (C), 128.6 (CH), 127.8 (CH), 124.5 (CH), 123.9 (CH), 123.7 (CH), 122.4 (CH), 119.7 (CH), 118.2 (CH), 117.1 (CH), 116.7 (C), 110.7 (C), 110.3 (C), 101.8 (C), 82.1 (C), 80.6 (CH), 36.3 (CH_2), 34.8 (C), 34.6 (C), 34.5 (C), 33.6 (CH_2), 32.5 (CH_3), 31.8 (CH_3), 31.6 (CH_3), 22.8 (CH_2), 14.2 (CH_3).
HRMS ESI $[M+H]^+$: Calc. 852.3481; found 852.3487.

Synthesis of homodinuclear Pt (II) complex (Pt_2)

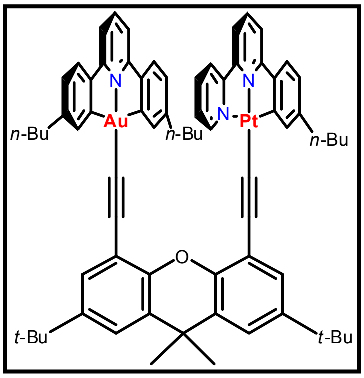
A sealed reaction tube was charged with [Pt(*n*BuC^N^N)Cl] (**11**) (58 mg, 0.113 mmol), 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**4**) (50 mg, 0.135 mmol), Et_3N (0.78 mL) and CuI (3% eq., 0.003 mmol), followed by addition of anhydrous CH_2Cl_2 (13 mL). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 ºC for 3 days and then concentrated *in vacuo*. The crude produced was purified by flash column chromatography on neutral Al_2O_3 with CH_2Cl_2-EtOAc (10:1) as eluent to give a dark-orange solid. Yield: 35 mg (22%).



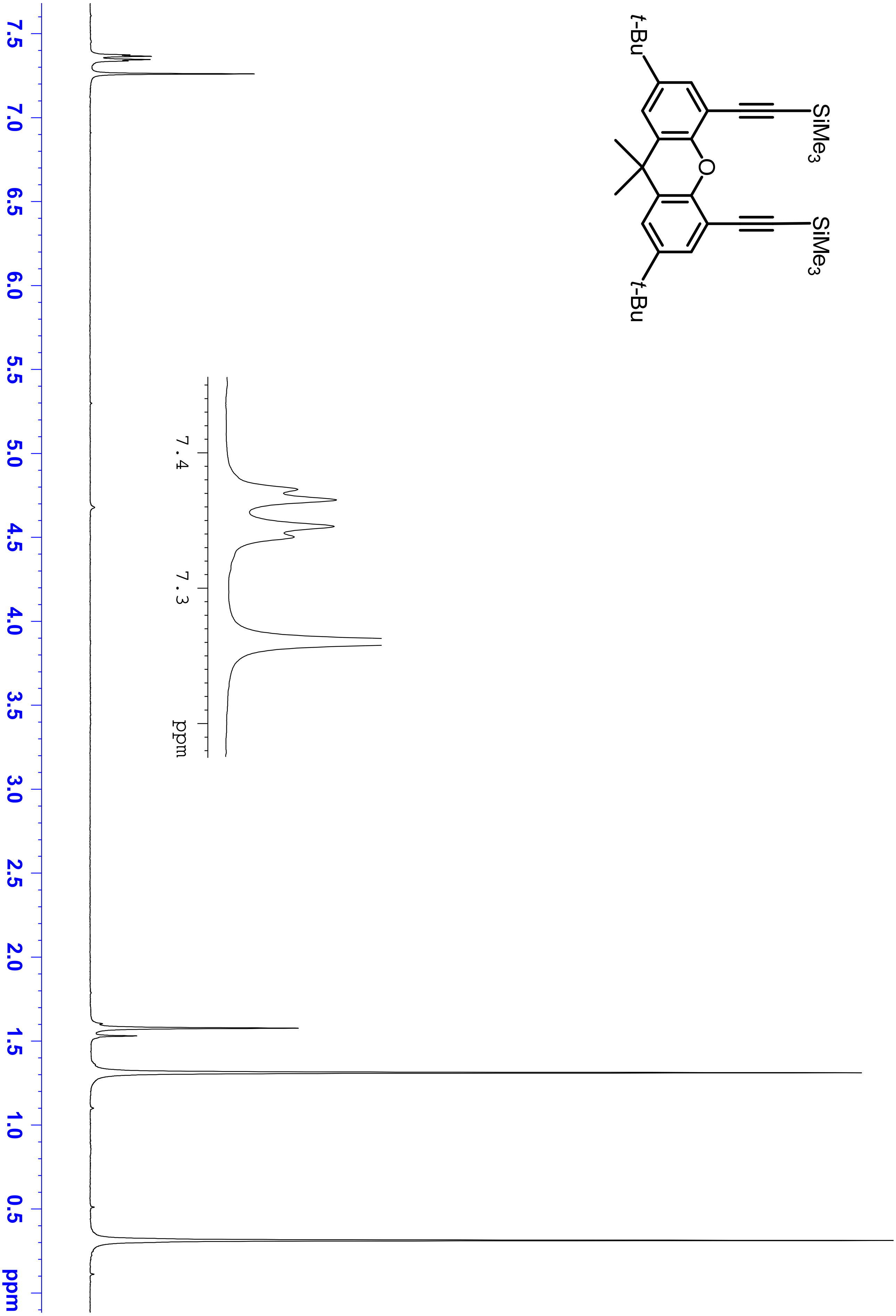
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75-9.59 (m, 2H), 7.48 (d, *J* = 2.2 Hz, 2H), 7.38-7.11 (m, 10H), 7.00-6.66 (m, 10H), 2.48 (t, *J* = 7.3 Hz, 4H), 1.73 (s, 6H), 1.68-1.53 (m, 4H), 1.50-1.30 (m, 4H, partially buried under *t*-Bu signal), 1.36 (s, 18H), 0.98 (t, *J* =7.2 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 164.5 (C), 156.4 (C), 155.0 (C), 154.6 (CH), 149.8 (C), 145.7 (C), 144.9 (C), 144.1 (C), 143.9 (C), 138.8 (CH), 137.1 (CH), 134.0 (CH), 129.0 (C), 128.3 (CH), 127.8 (CH), 123.7 (CH), 122.7 (CH), 121.1 (CH), 119.6 (CH), 117.1 (C), 116.7 (CH), 116.6 (CH), 112.5 (C), 101.1 (C), 36.2 (CH_2), 34.9 (C), 34.6 (C), 33.6 (CH_2), 33.0 (CH_3), 31.8 (CH_3), 22.9 (CH_2), 14.3 (CH_3).
HRMS ESI $[M]^+$: Calc. 1333.4580; found 1333.4604.

Synthesis of heterodinuclear Au (III) and Pt (II) complex (AuPt)

A sealed reaction tube was charged with mononuclear Au (III) complex (**Au**) (50 mg, 0.055 mmol), [Pt(*n*BuC^N^N)Cl] (**11**) (34 mg, 0.066 mmol), Et_3N (0.38 mL) and CuI (10% eq., 0.006 mmol), followed by addition of anhydrous CH_2Cl_2 (6 mL). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 ºC for 3 days and then concentrated *in vacuo*. The crude produced was purified by flash column chromatography on neutral Al_2O_3 with CH_2Cl_2-EtOAc (3:1) as eluent to give a red solid. Yield: 44 mg (58%).



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65-9.49 (m, 1H), 7.72 (bs, 2H), 7.47-7.18 (m, 9H), 7.02-6.93 (m, 2H), 6.89-6.65 (m, 9H), 2.56-2.38 (m, 6H), 1.77-1.49 (m, 6H, partially buried under singlet CH_3 signal), 1.72 (s, 6H), 1.49-1.20 (m, 6H, partially buried under *t*-Bu signals), 1.37 (s, 9H), 1.34 (s, 9H), 0.97 (t, J = 7.3 Hz, 3H), 0.80 (t, J = 7.3 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135) δ 167.9 (C), 165.3 (C), 164.6 (C), 157.1 (C), 154.4 (C), 153.8 (CH), 150.4 (C), 149.7 (C), 146.7 (C), 146.2 (C), 145.9 (C), 144.7 (C), 144.3 (C), 144.1 (C), 143.2 (C), 140.4 (CH), 139.2 (CH), 138.3 (CH), 137.0 (CH), 136.9 (CH), 129.6 (C), 128.7 (C), 128.0 (CH), 127.5 (CH), 127.4 (CH), 125.6 (CH), 124.2 (CH), 123.7 (CH), 122.5 (CH), 121.3 (CH), 121.1 (CH), 119.0 (CH), 117.6 (C), 117.1 (CH), 116.2 (CH), 115.3 (CH), 115.1 (C), 112.8 (C), 101.2 (C), 98.9 (C), 95.6 (C), 36.4 (CH_2), 36.3 (CH_2), 34.9 (C), 34.6 (C), 33.3 (CH_2), 33.2 (CH_2), 32.5 (CH_3), 31.8 (CH_3), 23.0 (CH_2), 22.9 (CH_2), 14.3 (CH_3), 14.1 (CH_3).
HRMS ESI $[M+Na]^+$: Calc. 1412.5060; found 1412.5061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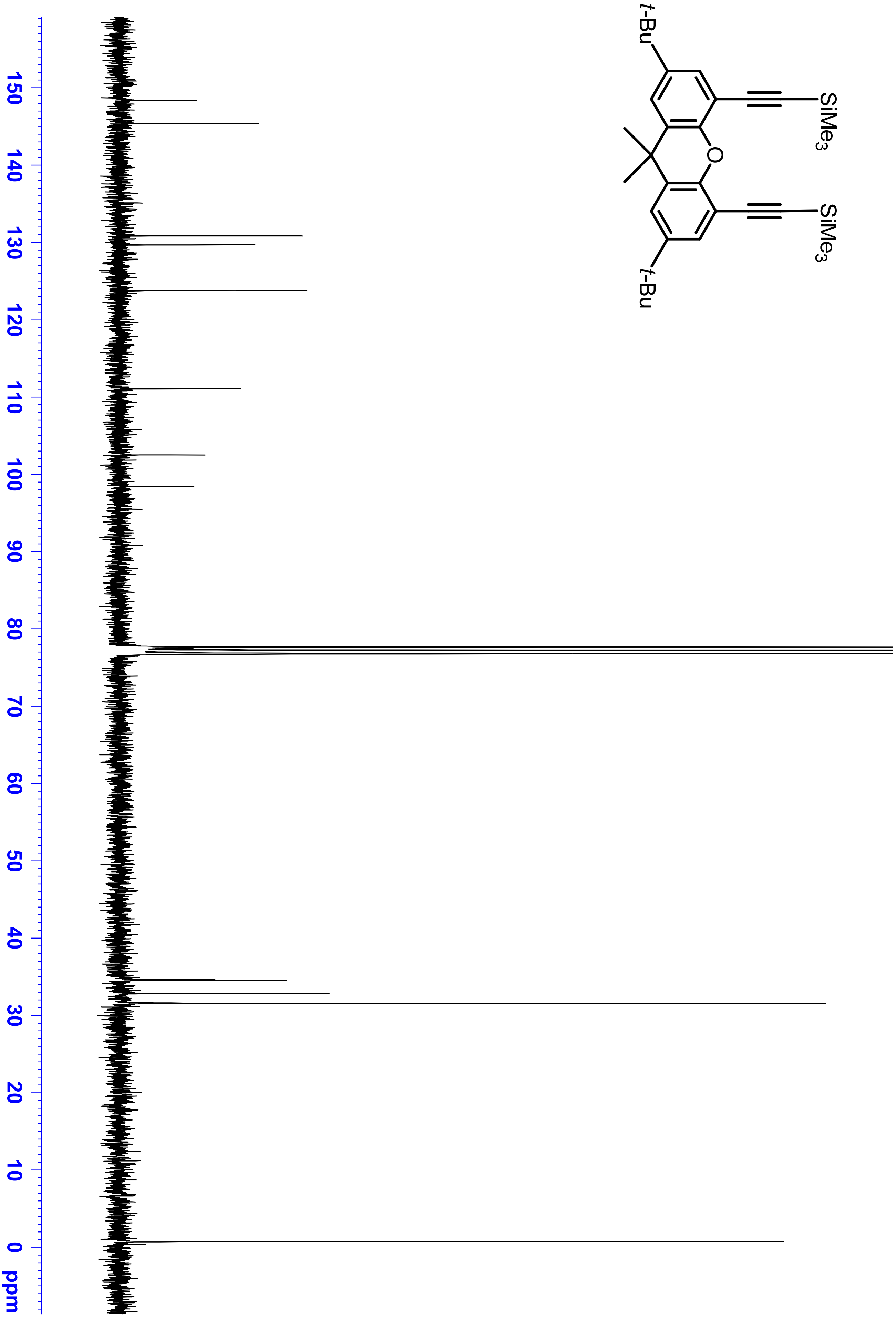
SiMe$_3$
O
SiMe$_3$
t-Bu
7.4
7.3
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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O
SiMe3
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20
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0
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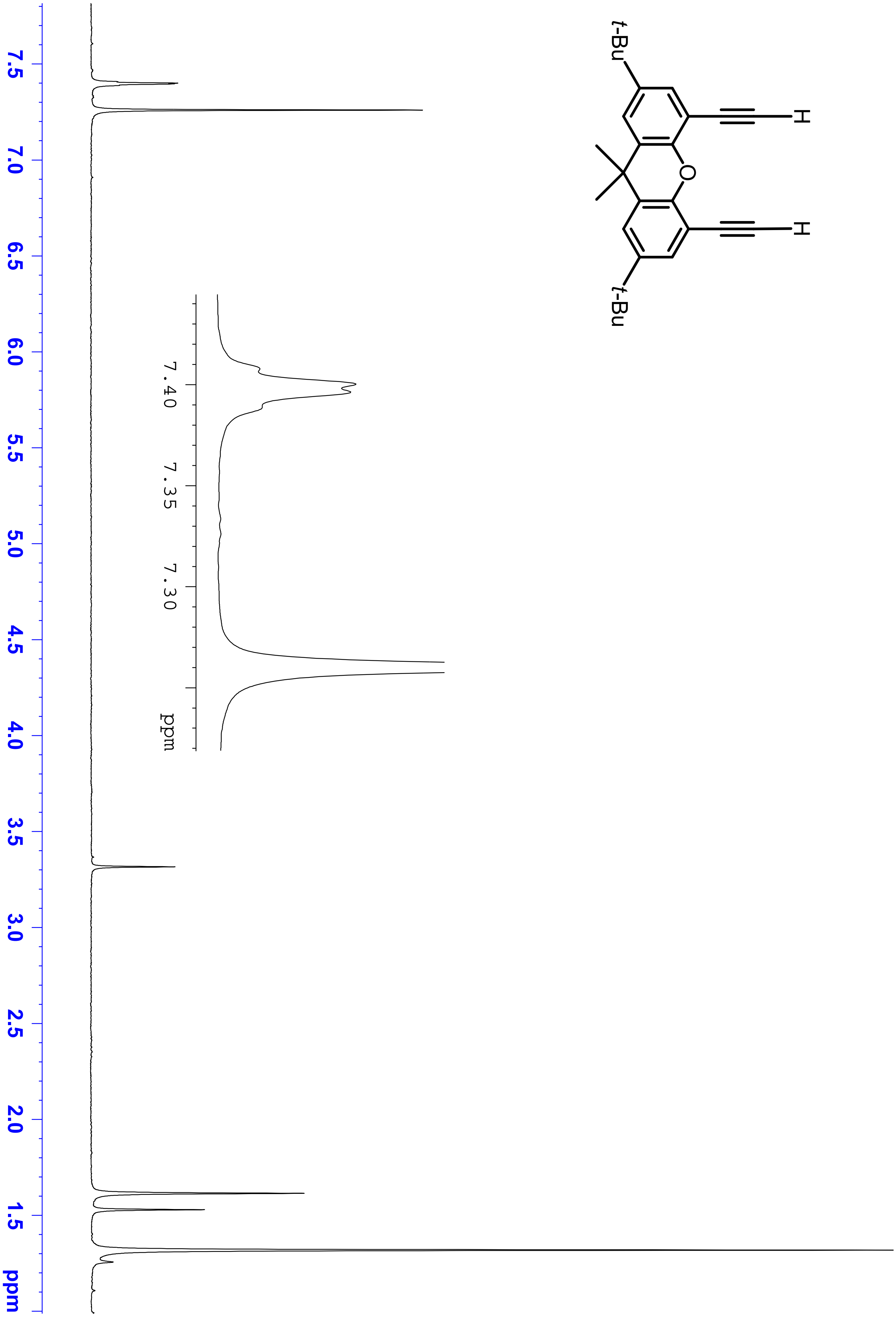
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O
H
t-Bu
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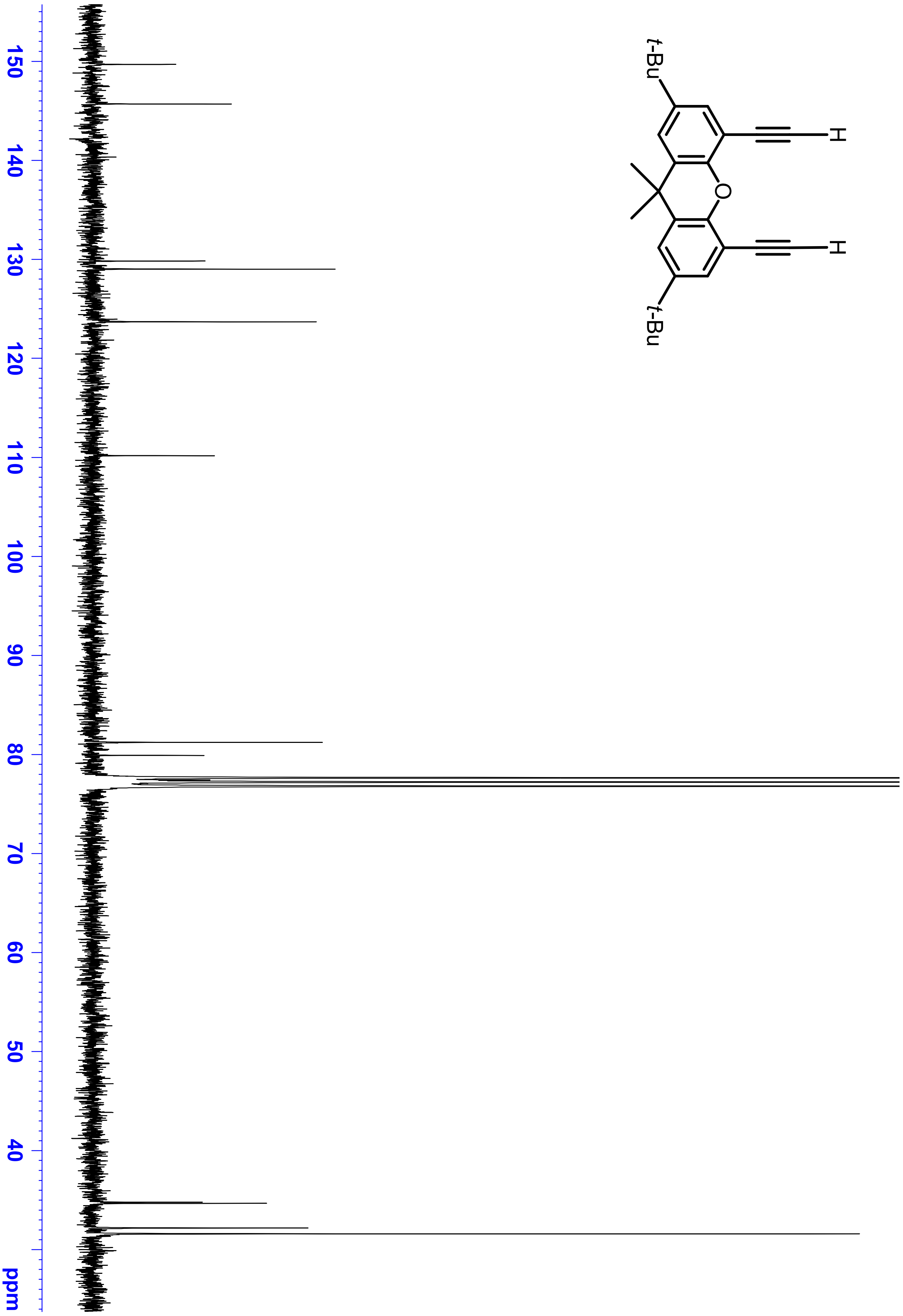
2.0
1.5
ppm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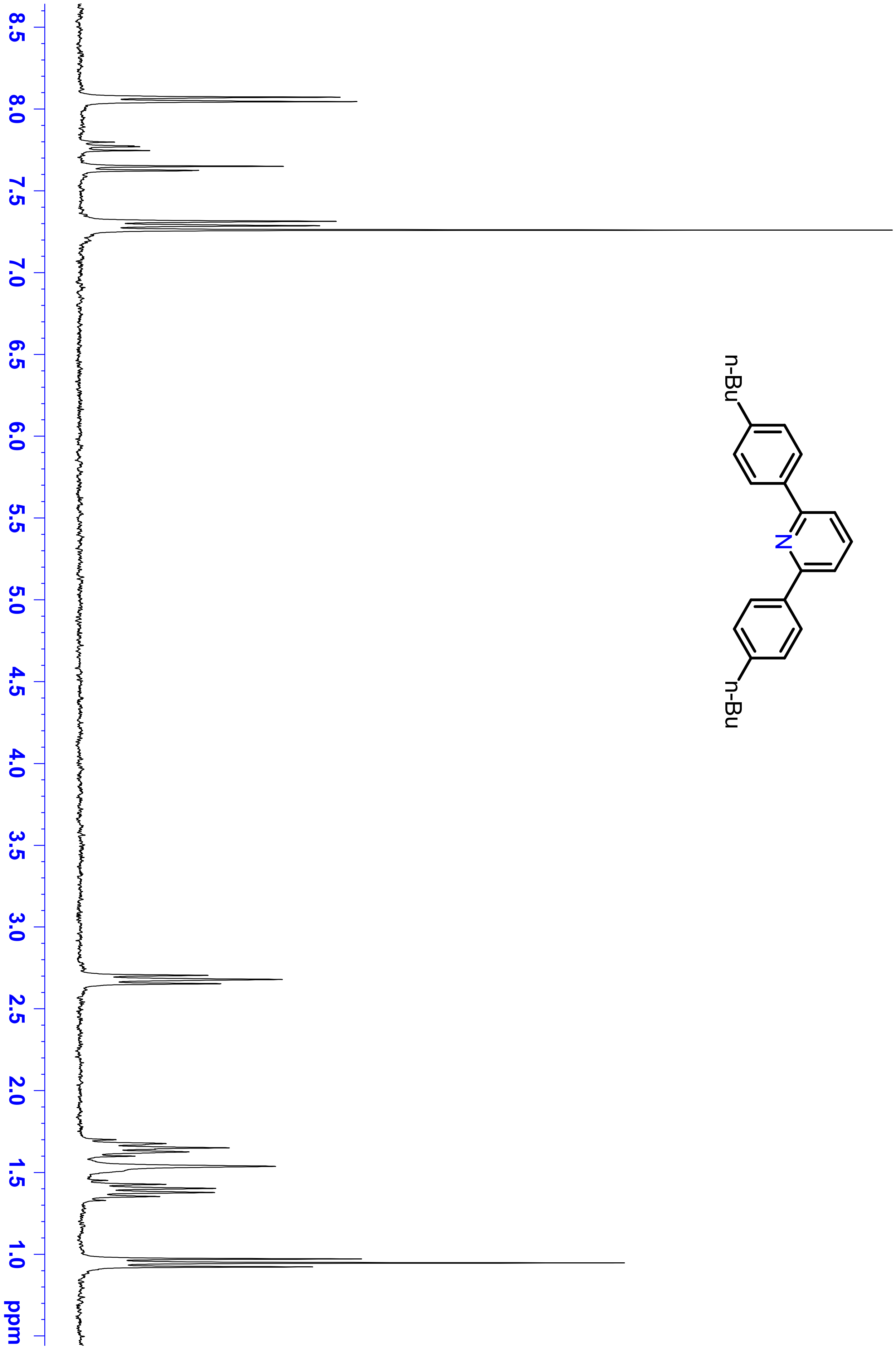
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2.5
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1.5
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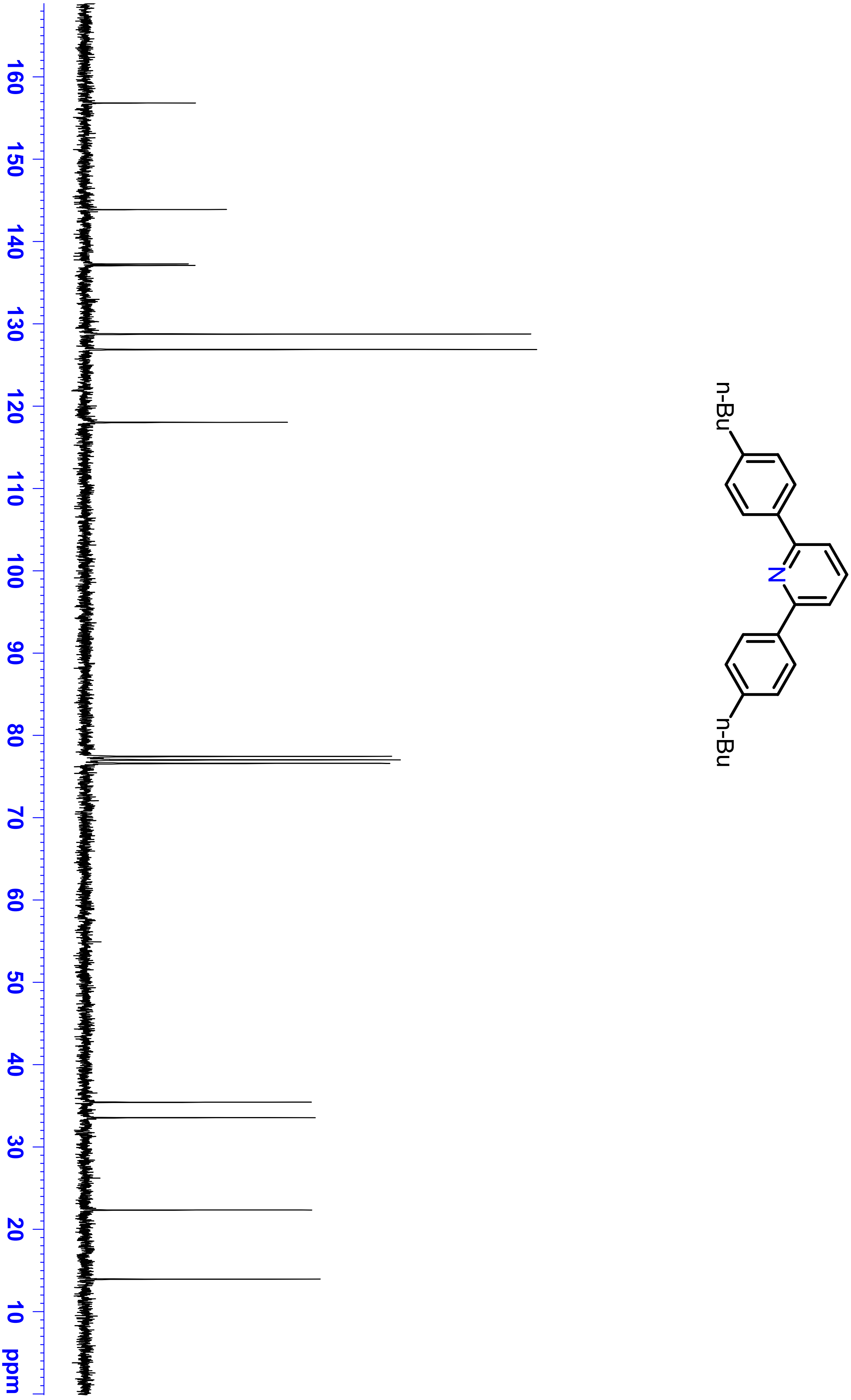
ppm
n-Bu
N
n-Bu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10
ppm
n-Bu
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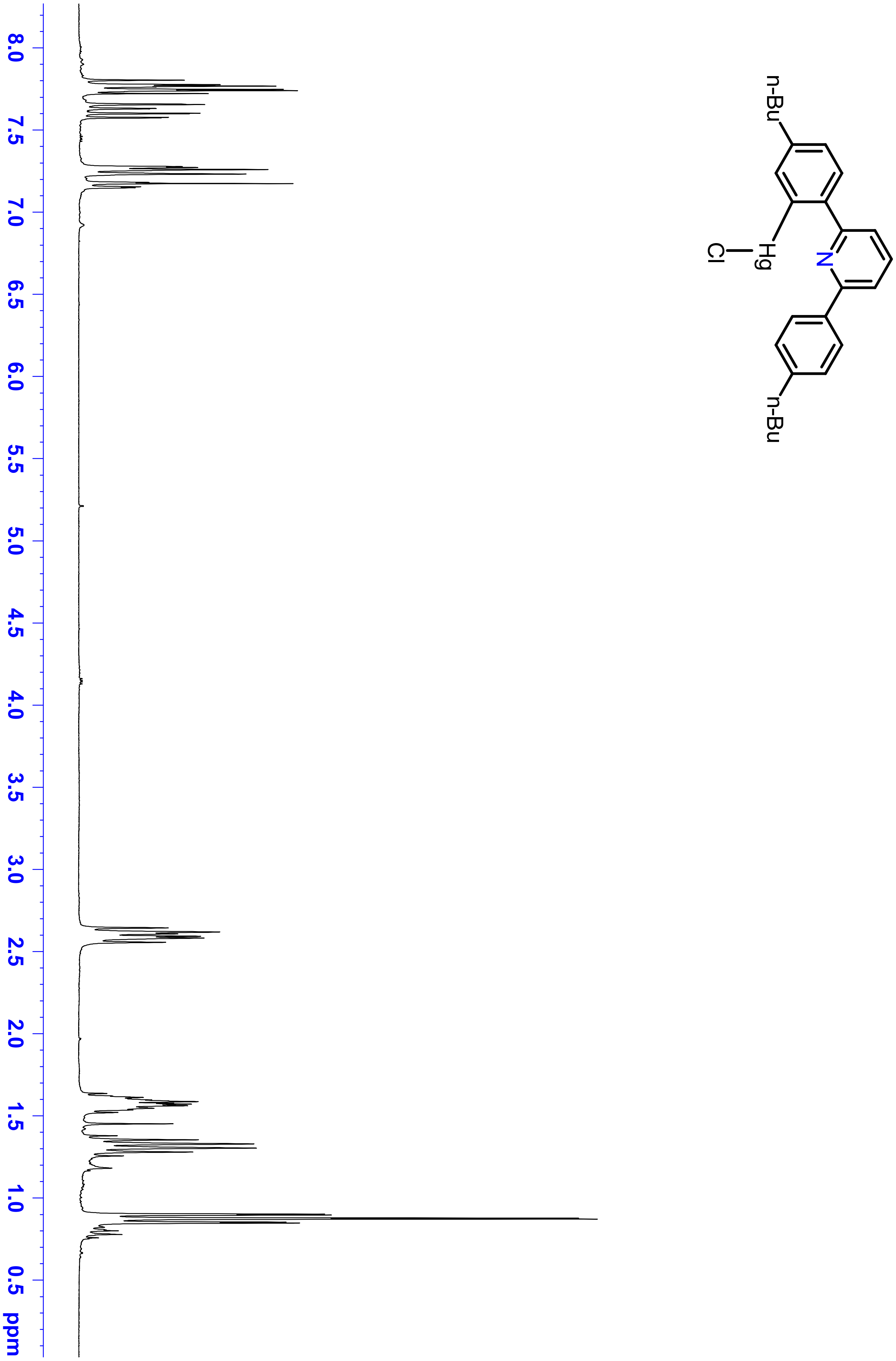
n-Bu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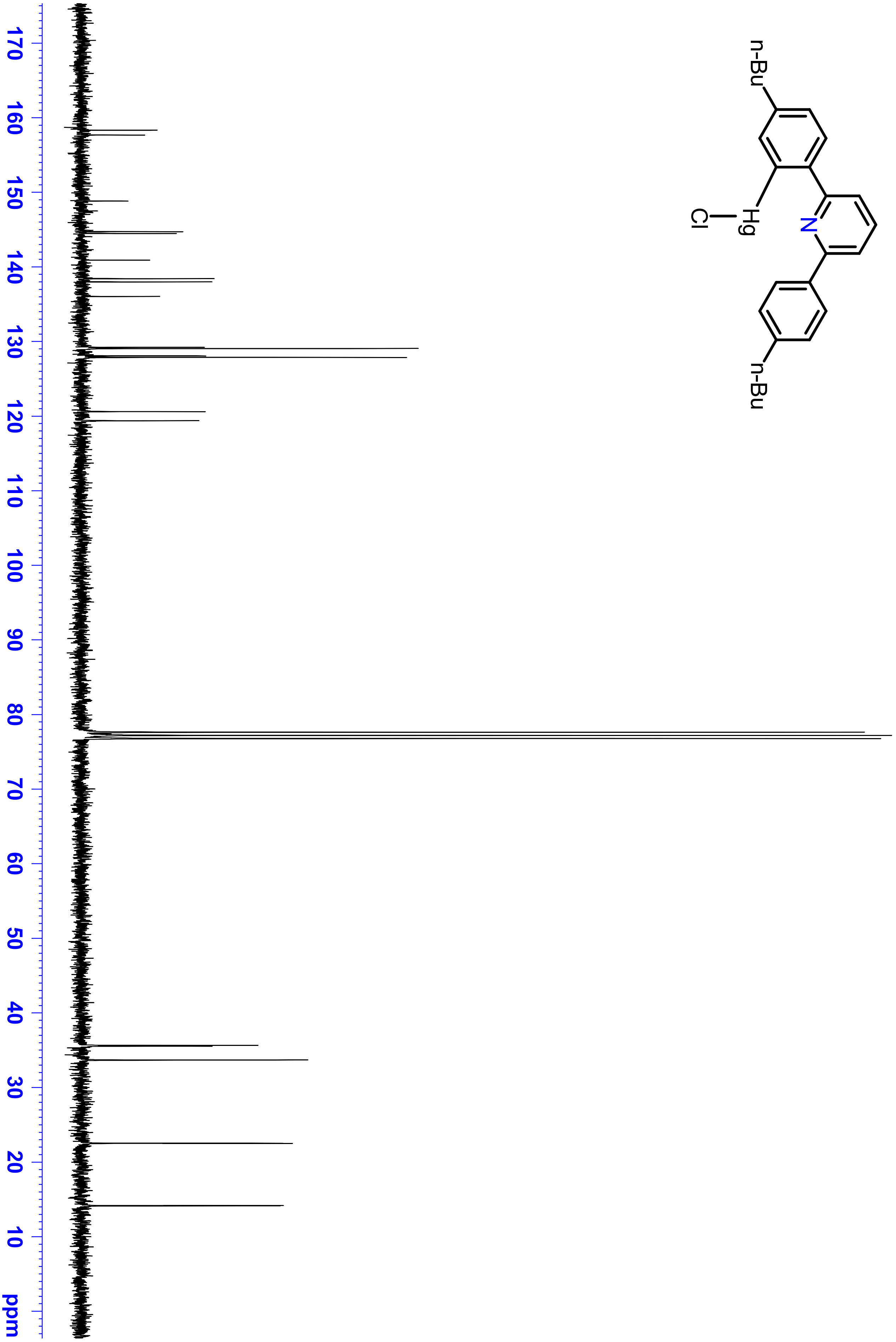
ppm
n-Bu
Hg
Cl
N
n-Bu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ppm
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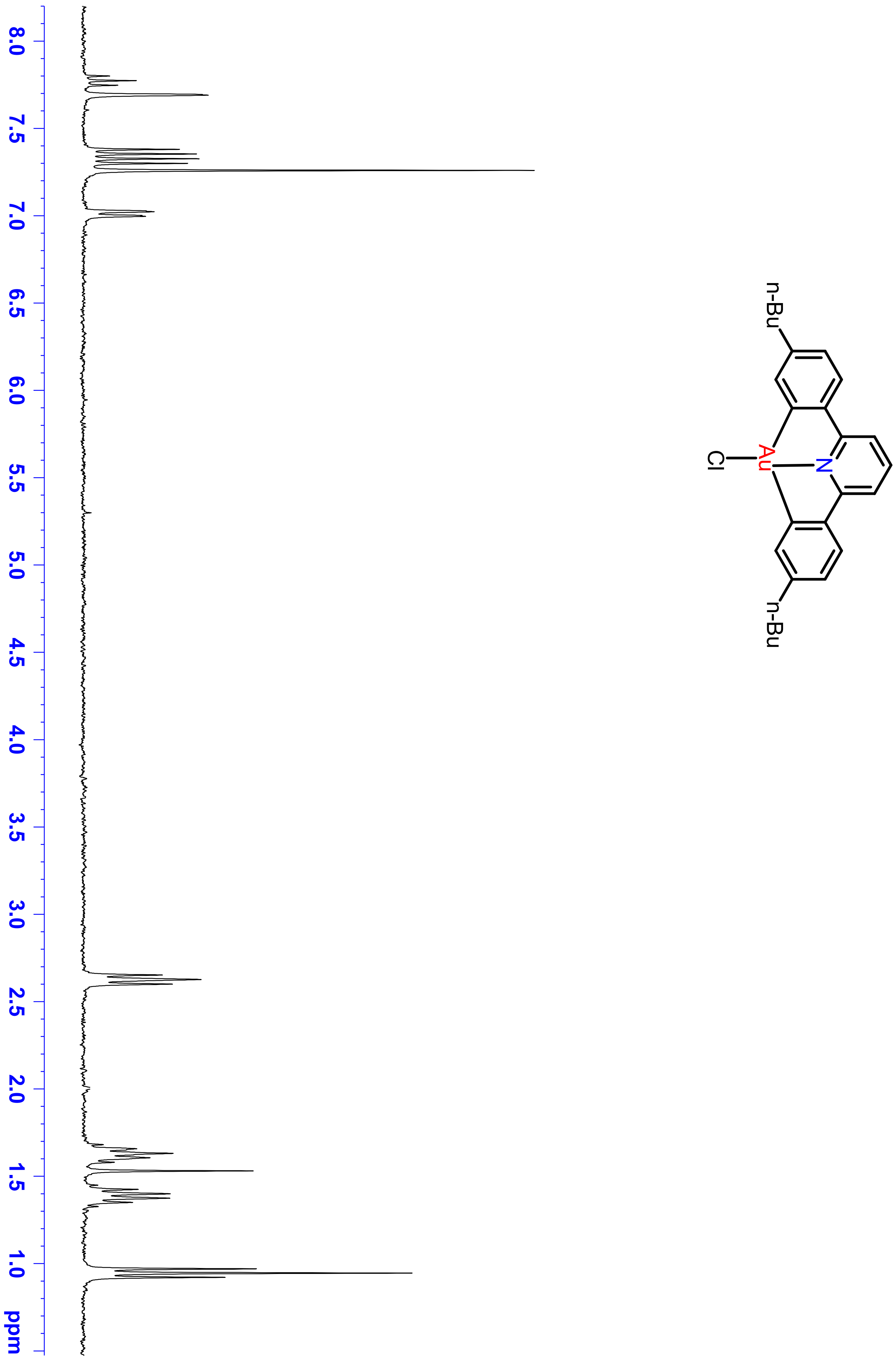
Hg
Cl
N
n-Bu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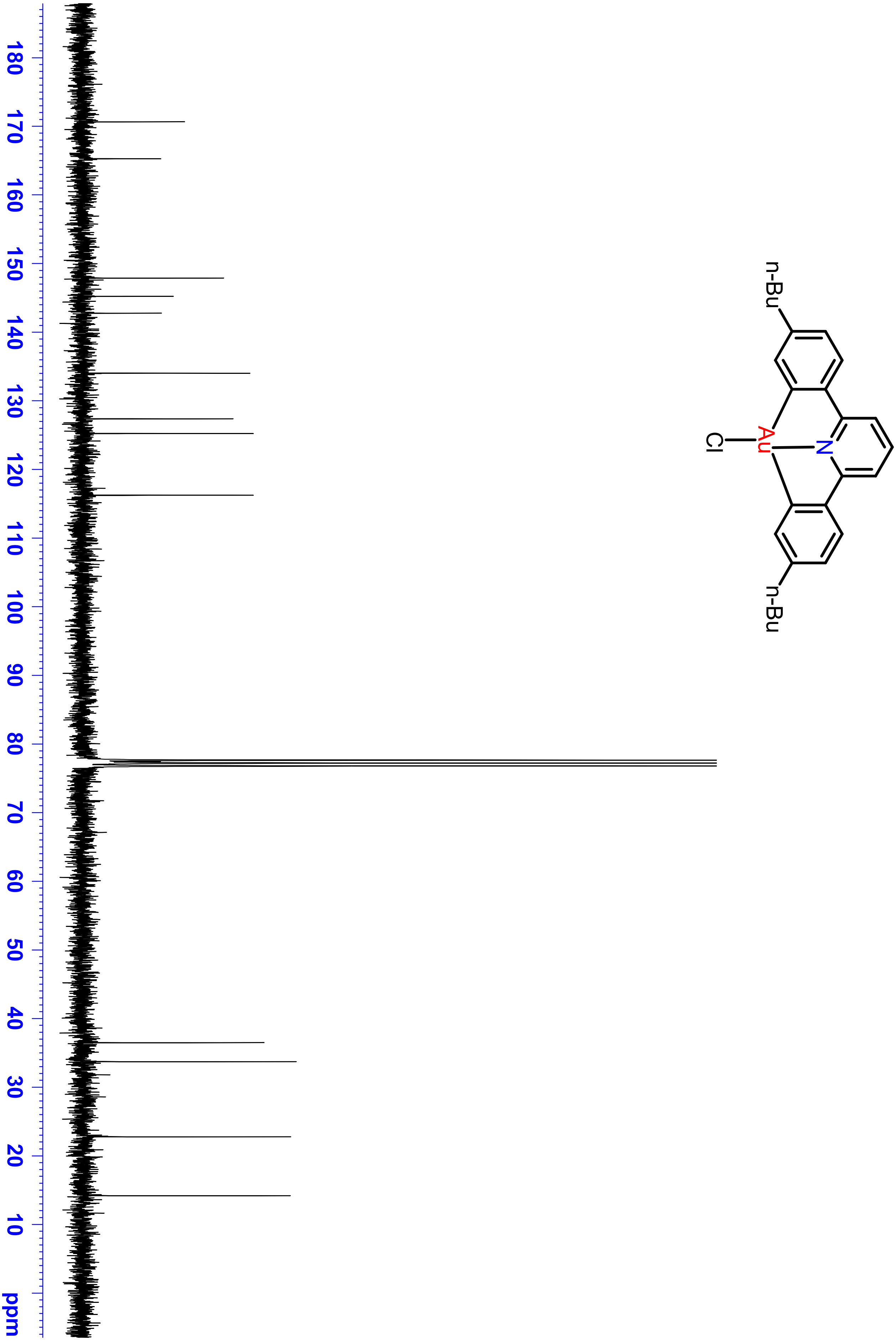
2.0
1.5
1.0
ppm
n-Bu
n-Bu
Au
N
Cl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80
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60
50
40
30
20
10
ppm
n-Bu
Cl
Au
N
n-Bu

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
n-Bu
N
N


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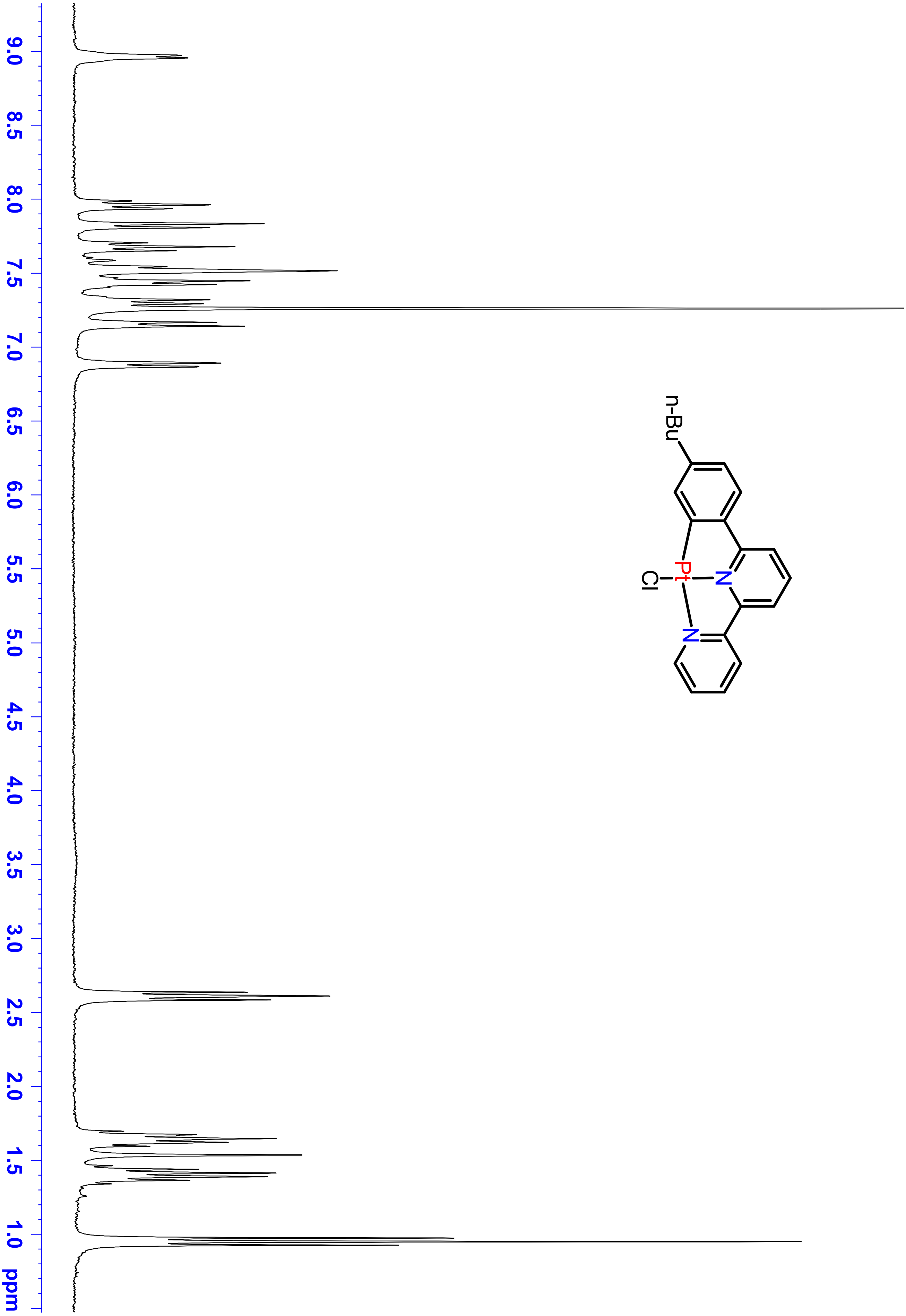
120
110
100
90
80
70
60
50
40
30
20
ppm
n-Bu
N
N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5.5
5.0
4.5
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3.5
3.0
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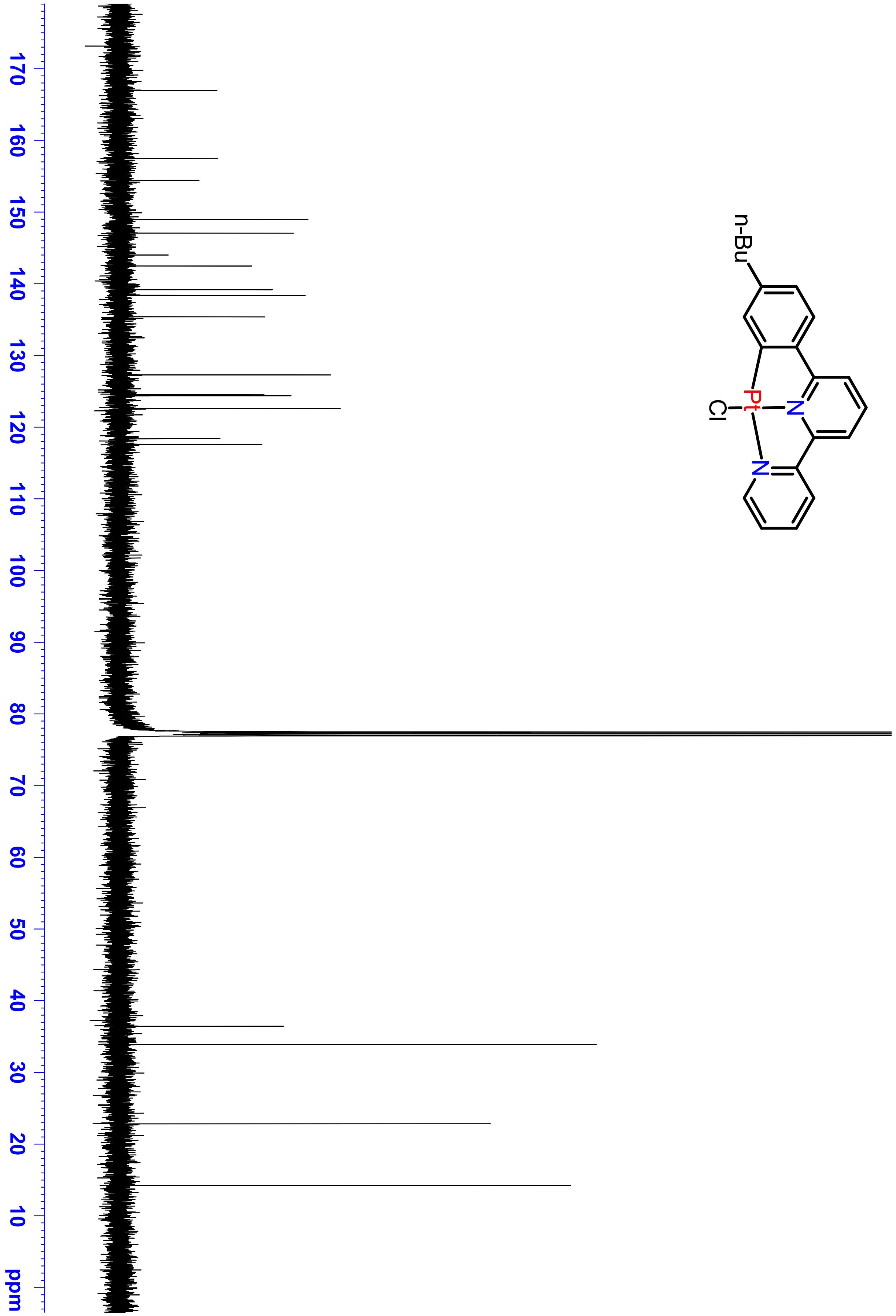
2.0
1.5
1.0
ppm
n-Bu
Pt
Cl
N
N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10
ppm
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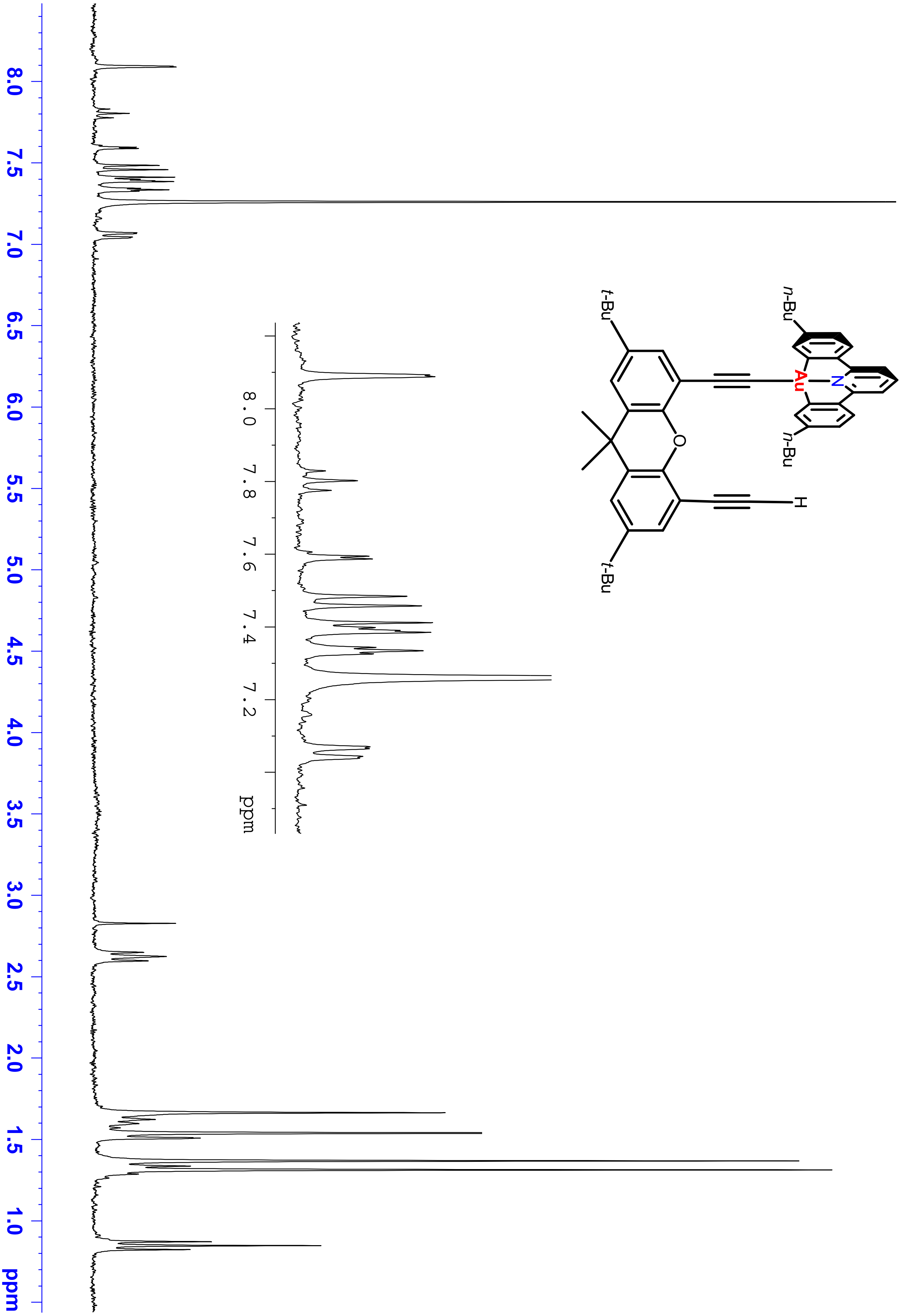
Pt
Cl
N
N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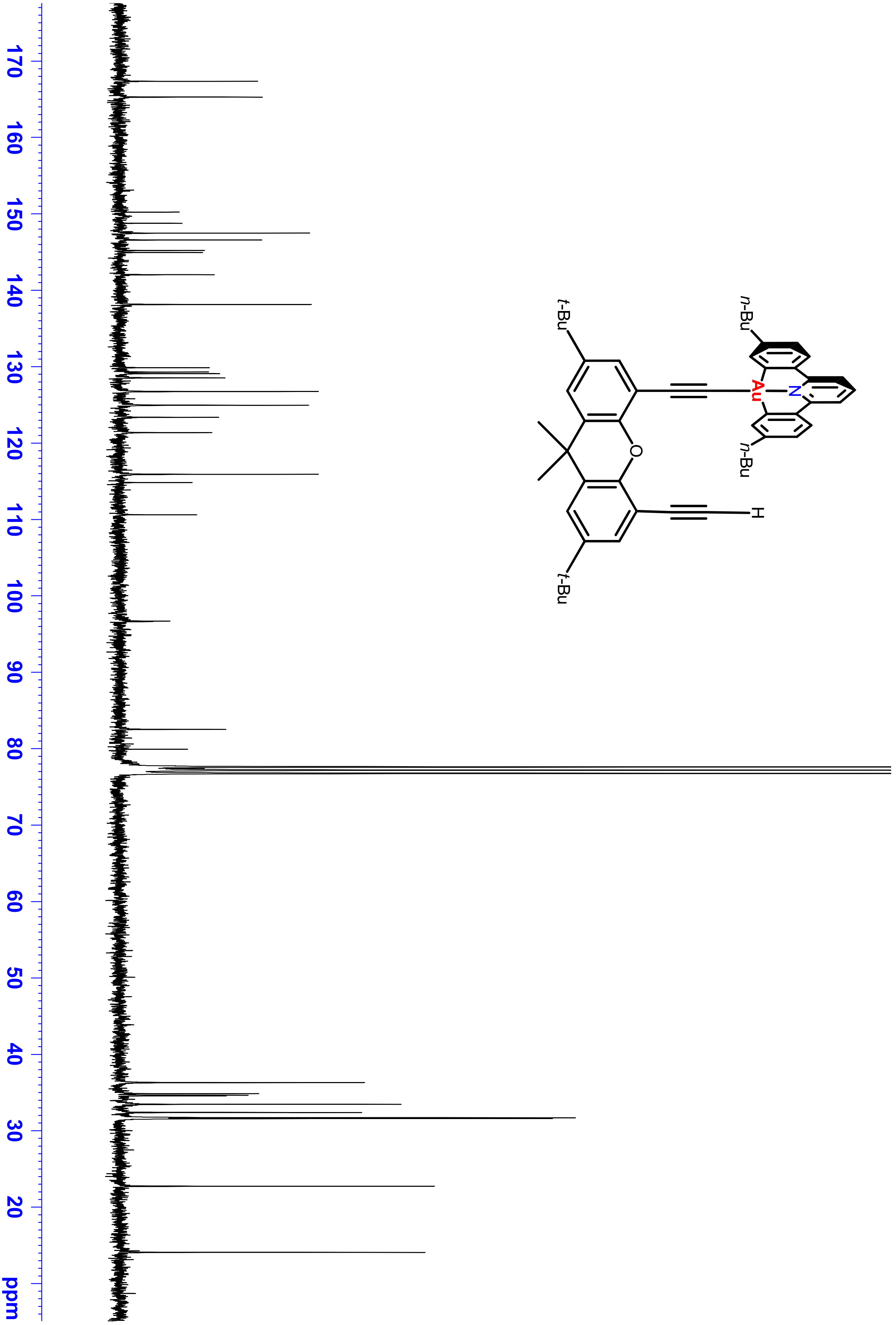
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
8.0
7.8
7.6
7.4
7.2
ppm
t-Bu
t-Bu
O
H
Au
N
n-Bu
n-Bu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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
t-Bu
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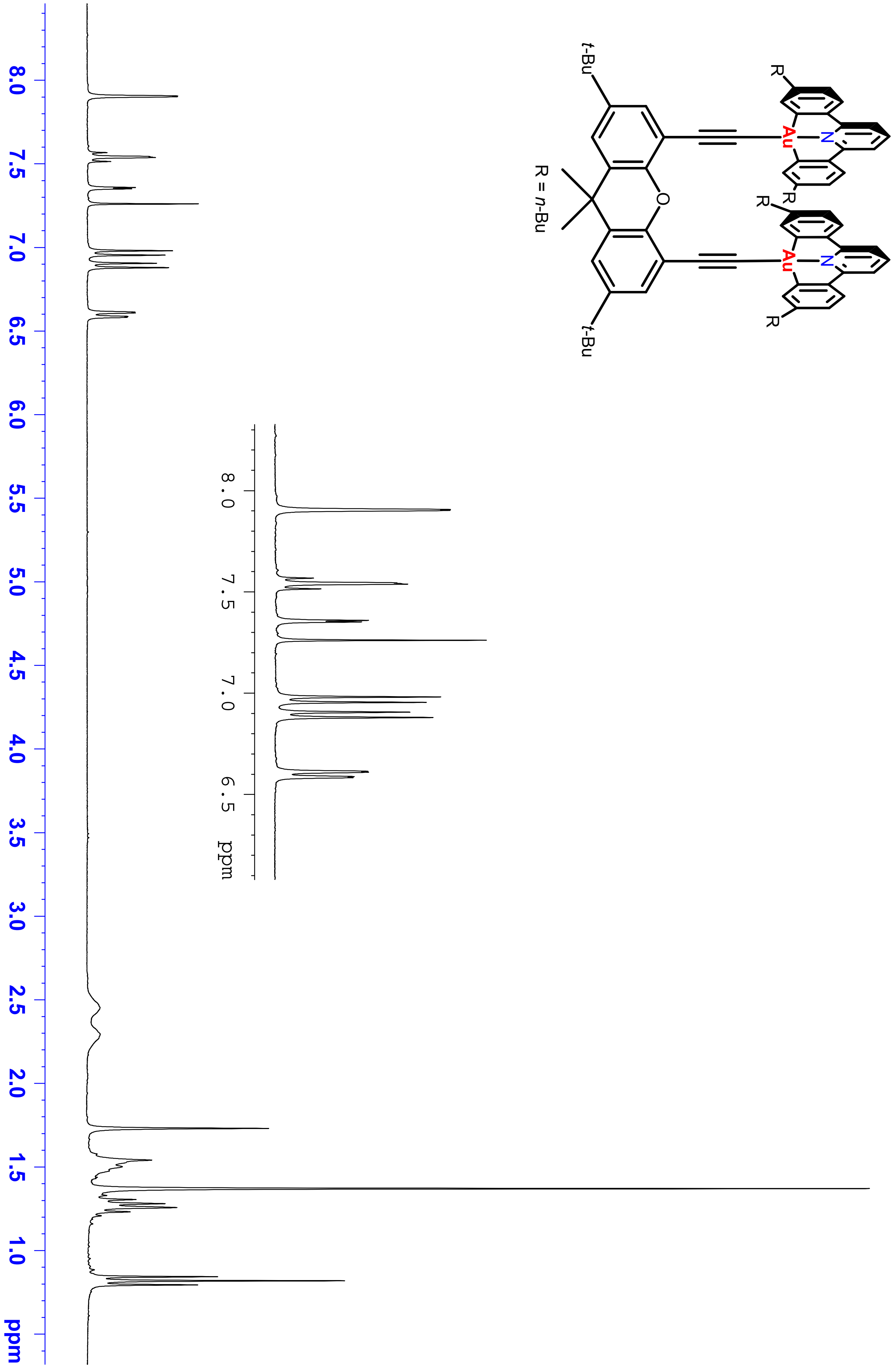
O
H
n-Bu
n-Bu
Au
N


R
R
R
R
Au
Au
N
N
O
t-Bu
t-Bu
R = n-Bu
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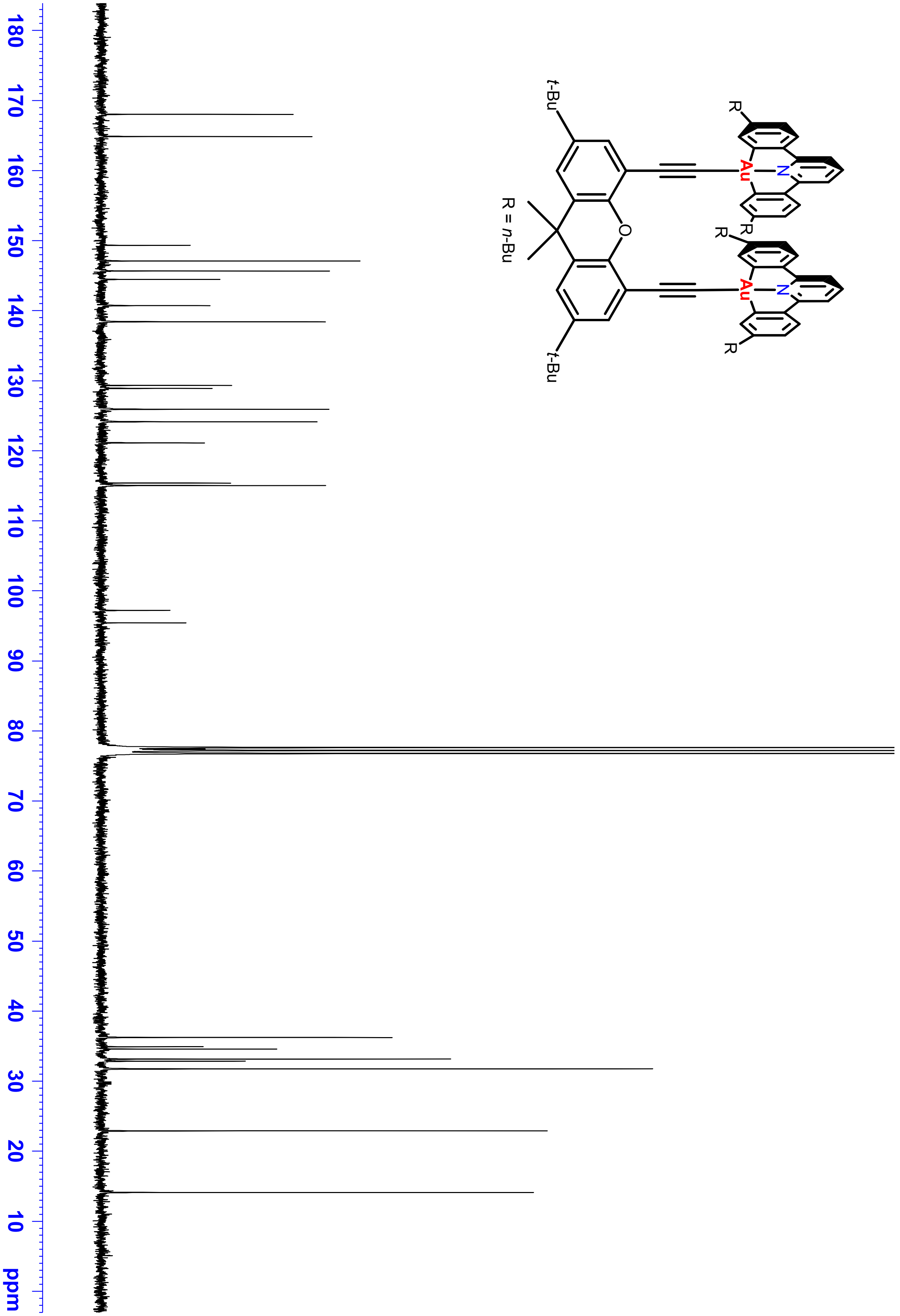
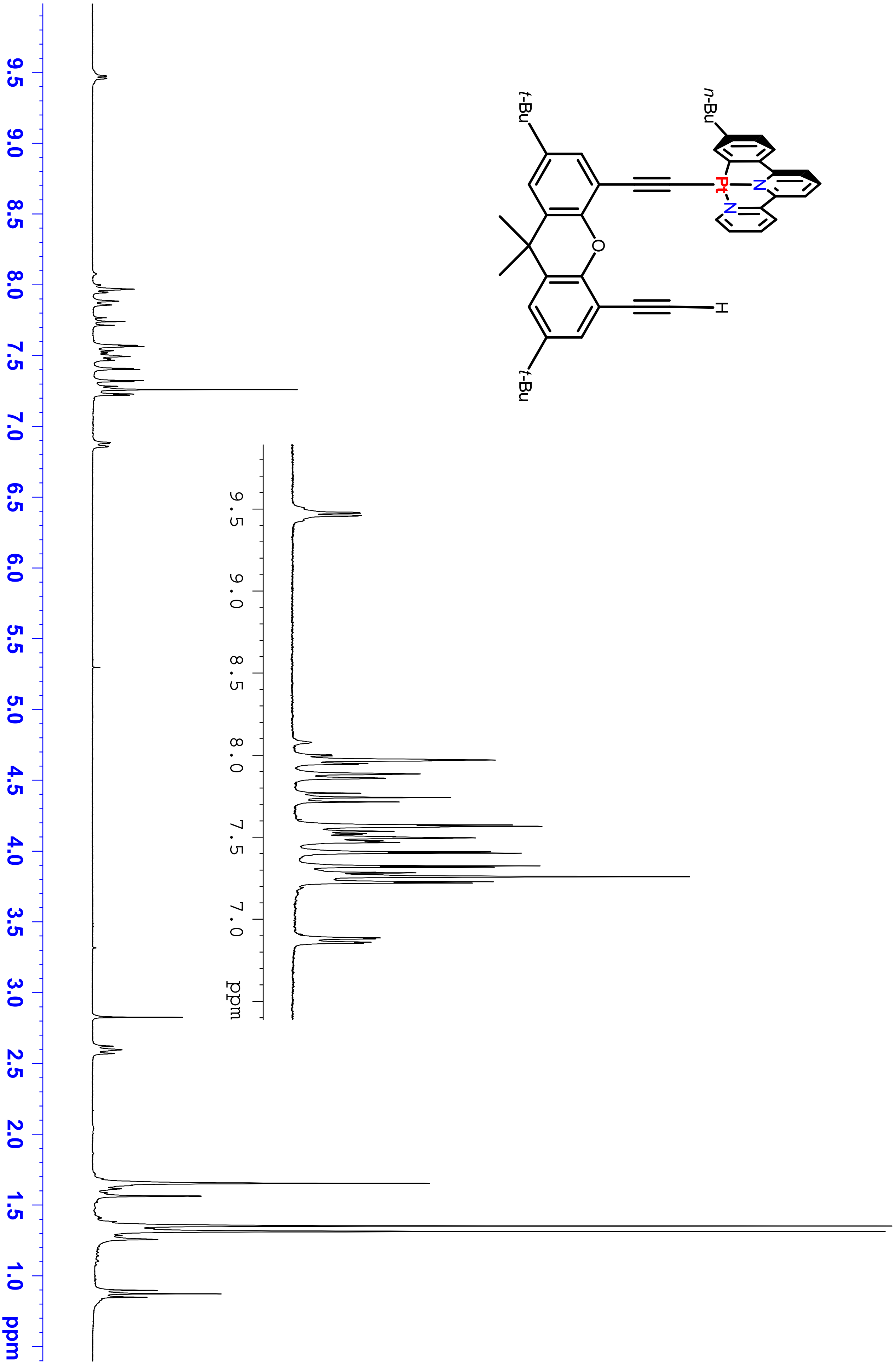
7.5
7.0
6.5
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
t-Bu
t-Bu
R = n-Bu
O
Au
N
Au
N
R
R
R
R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8.5
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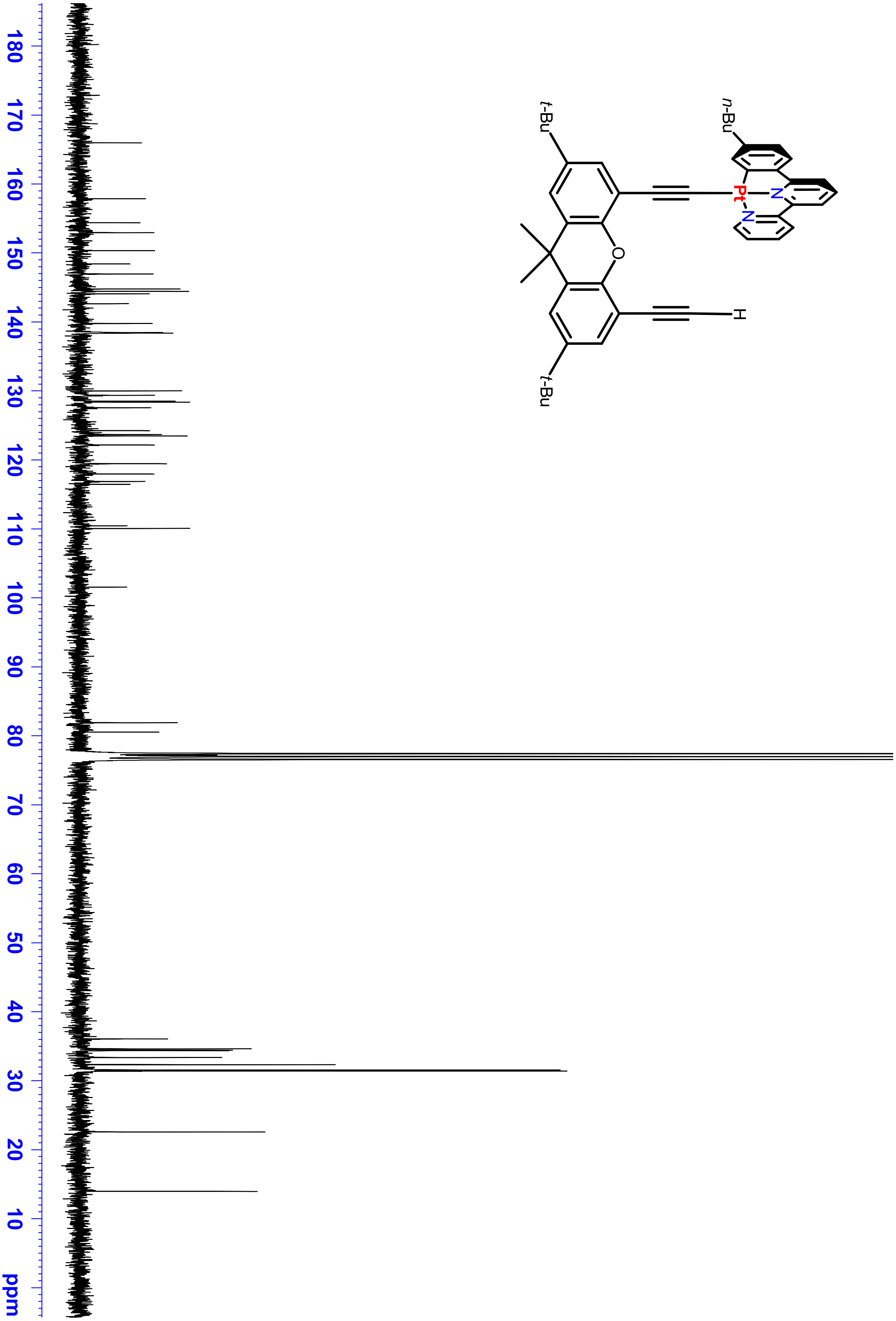
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
9.5
9.0
8.5
8.0
7.5
7.0
ppm
t-Bu
t-Bu
n-Bu
Pt
N
N
O
H


180
170
160
150
140
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50
40
30
20
10
ppm
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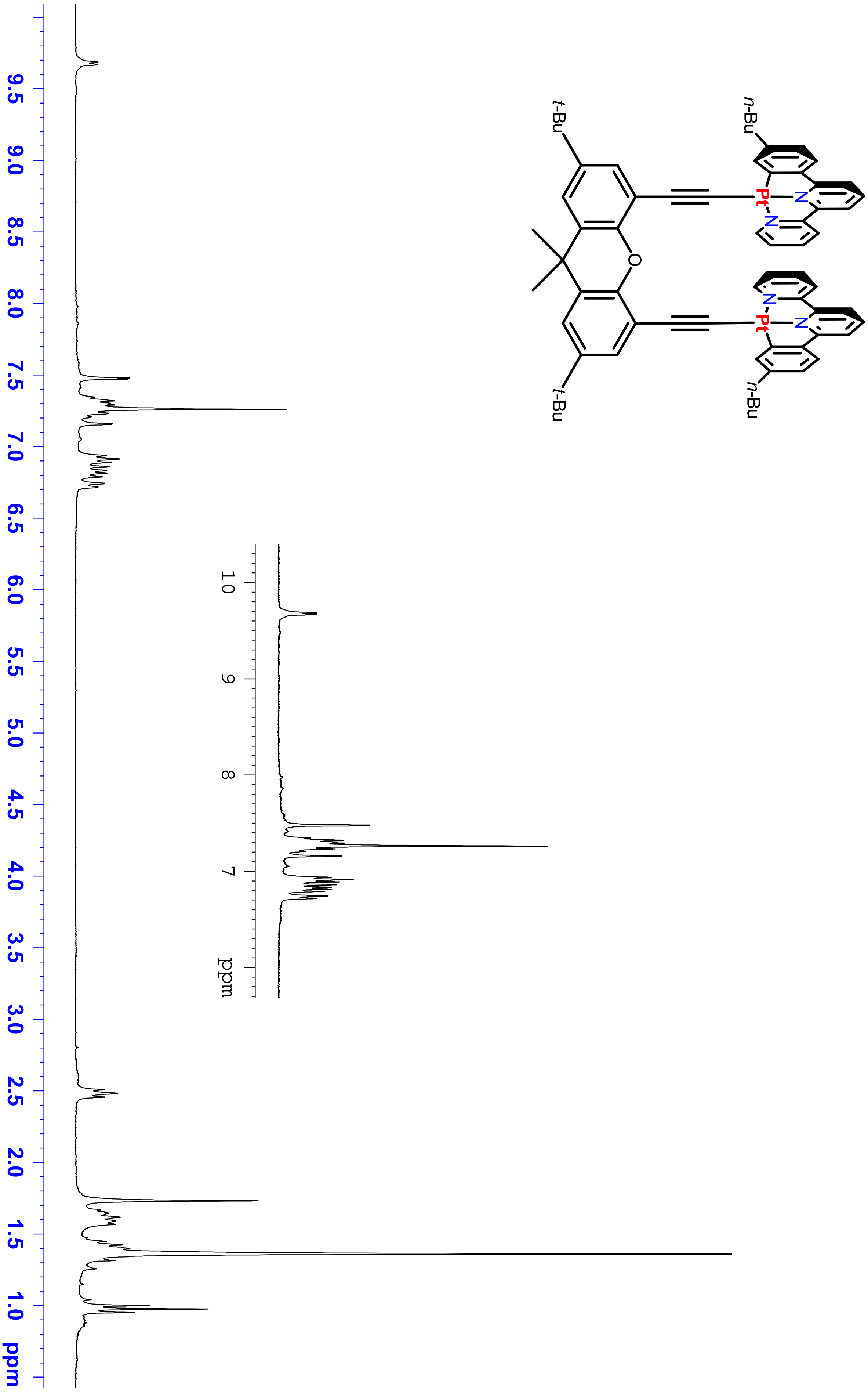
O
H
n-Bu
Pt
N
N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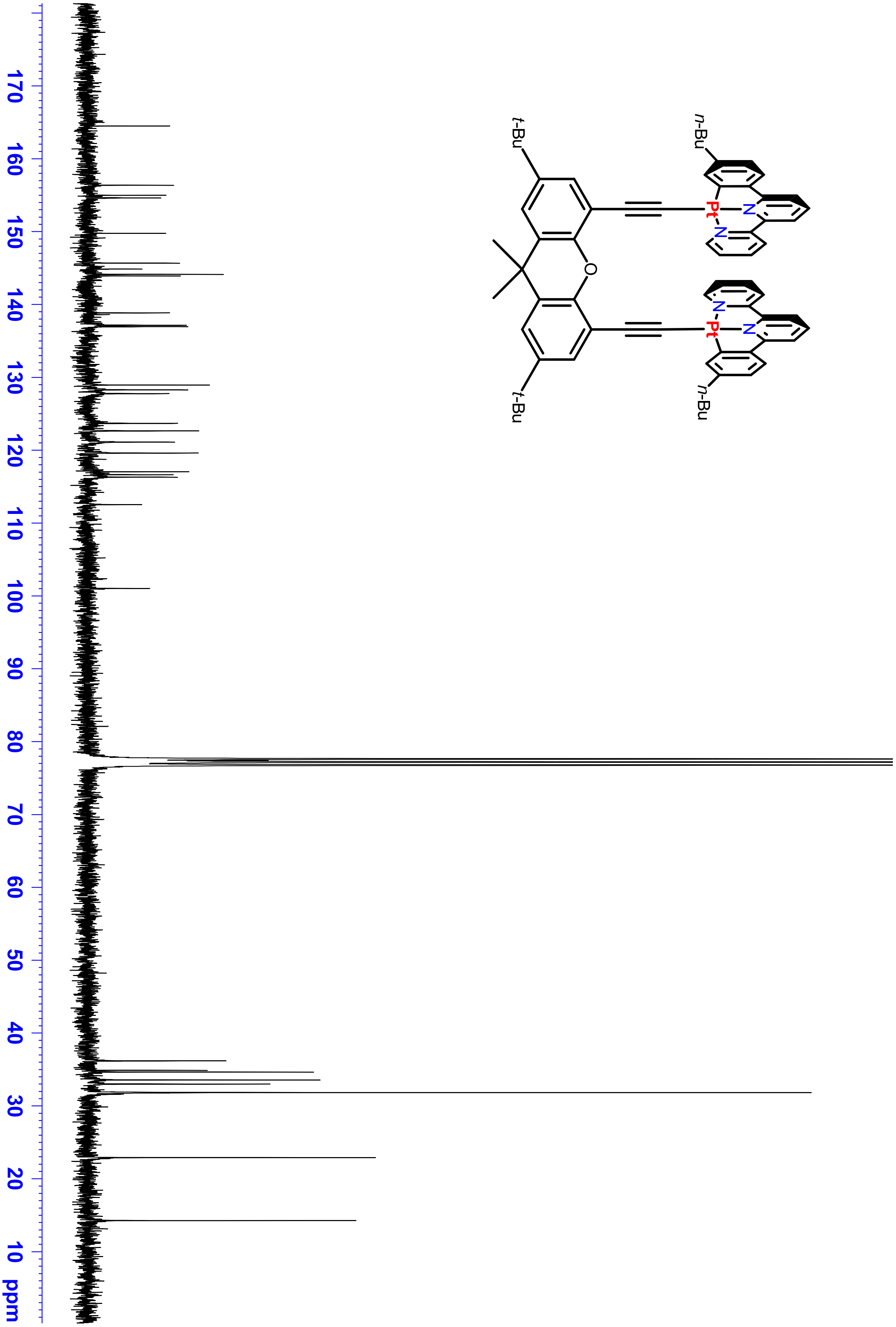
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10
9
8
7
ppm
t-Bu
t-Bu
n-Bu
n-Bu
O
Pt
Pt
N
N
N
N



170
160
150
140
130
120
110
100
90
80
70
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50
40
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20
10
ppm
t-Bu
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O
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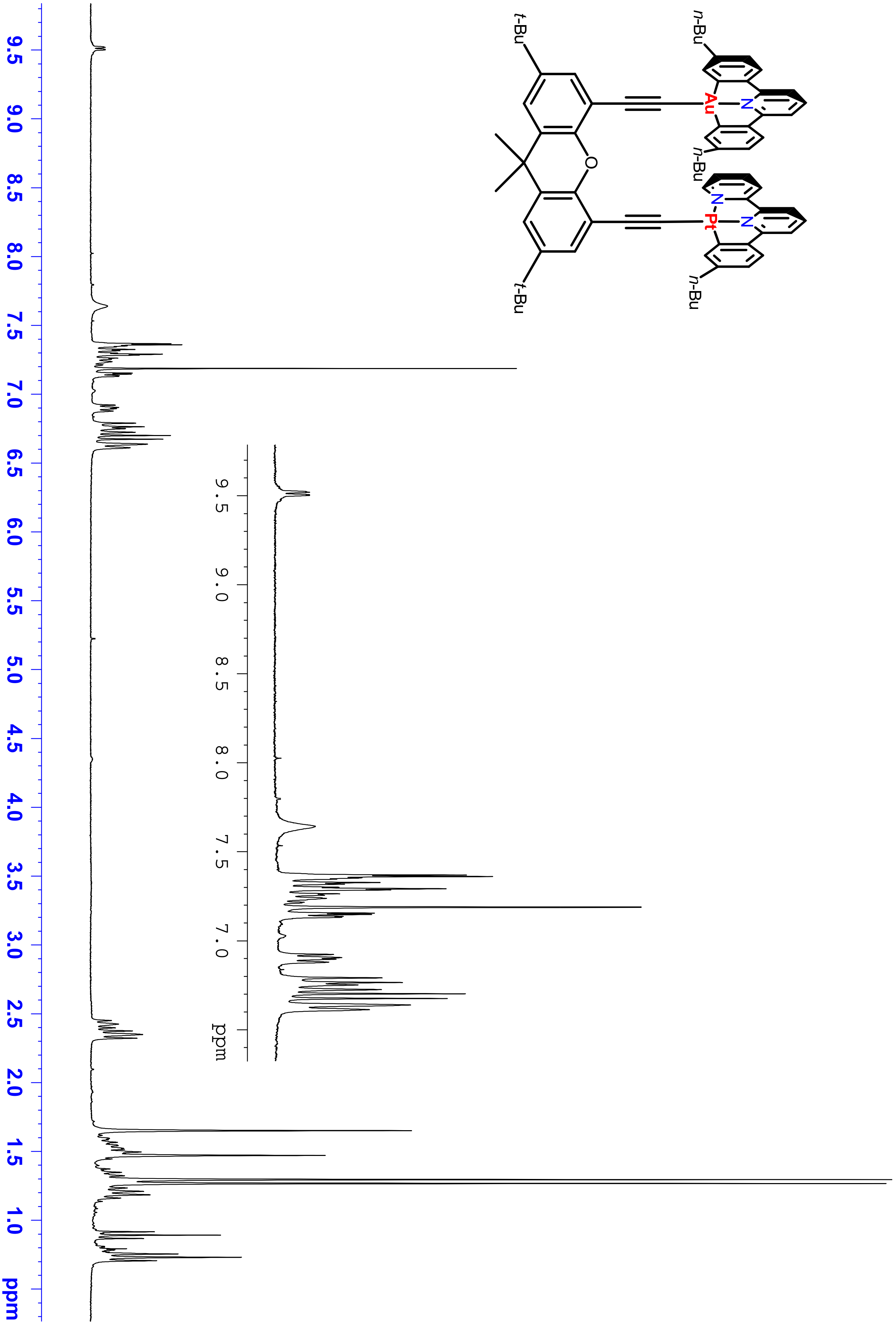
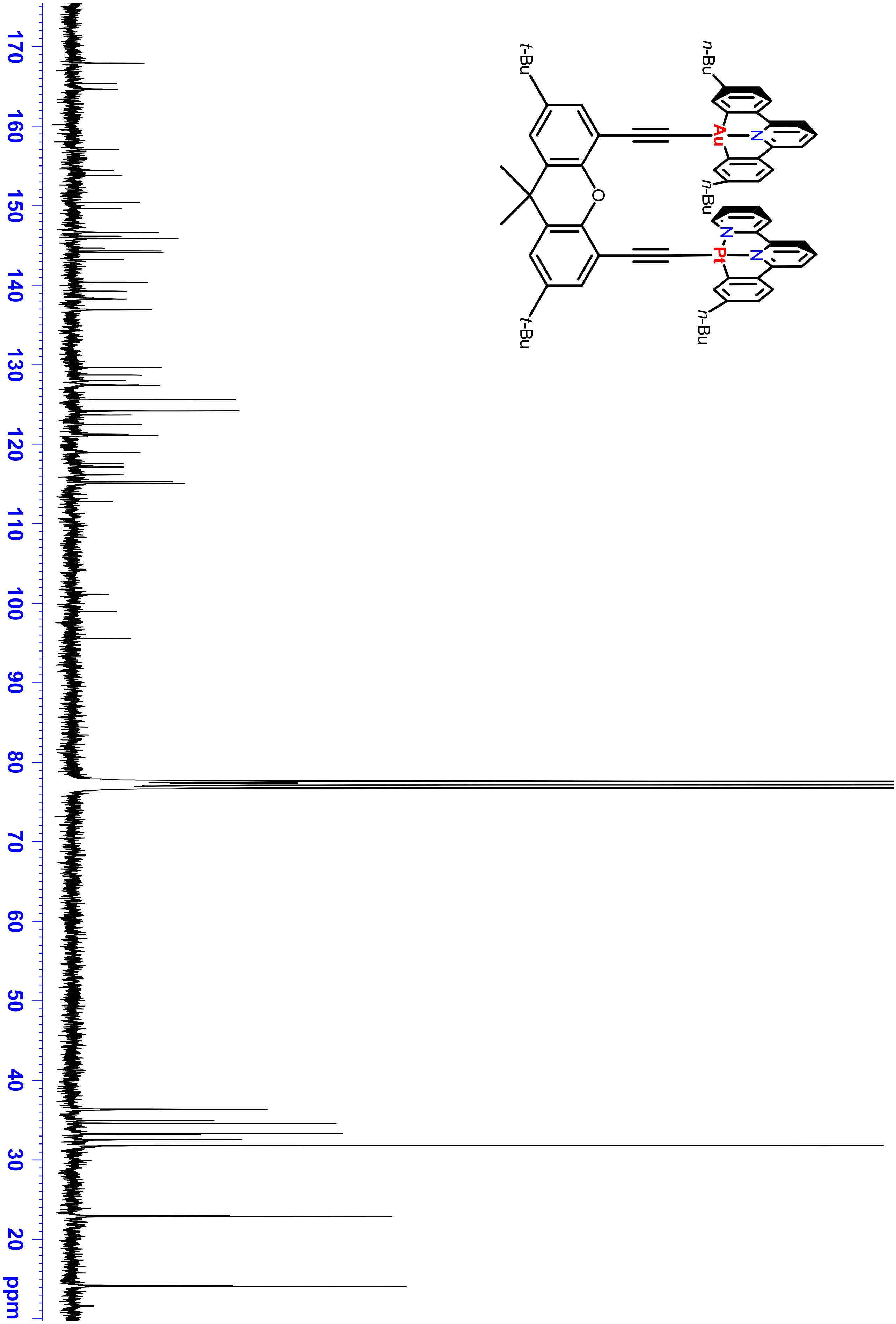
Pt
Pt
N
N
N
N


n-Bu
n-Bu
n-Bu
n-Bu
t-Bu
t-Bu
Au
Pt
N
N
N
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
9.5
9.0
8.5
8.0
7.5
7.0
ppm


170
160
150
140
130
120
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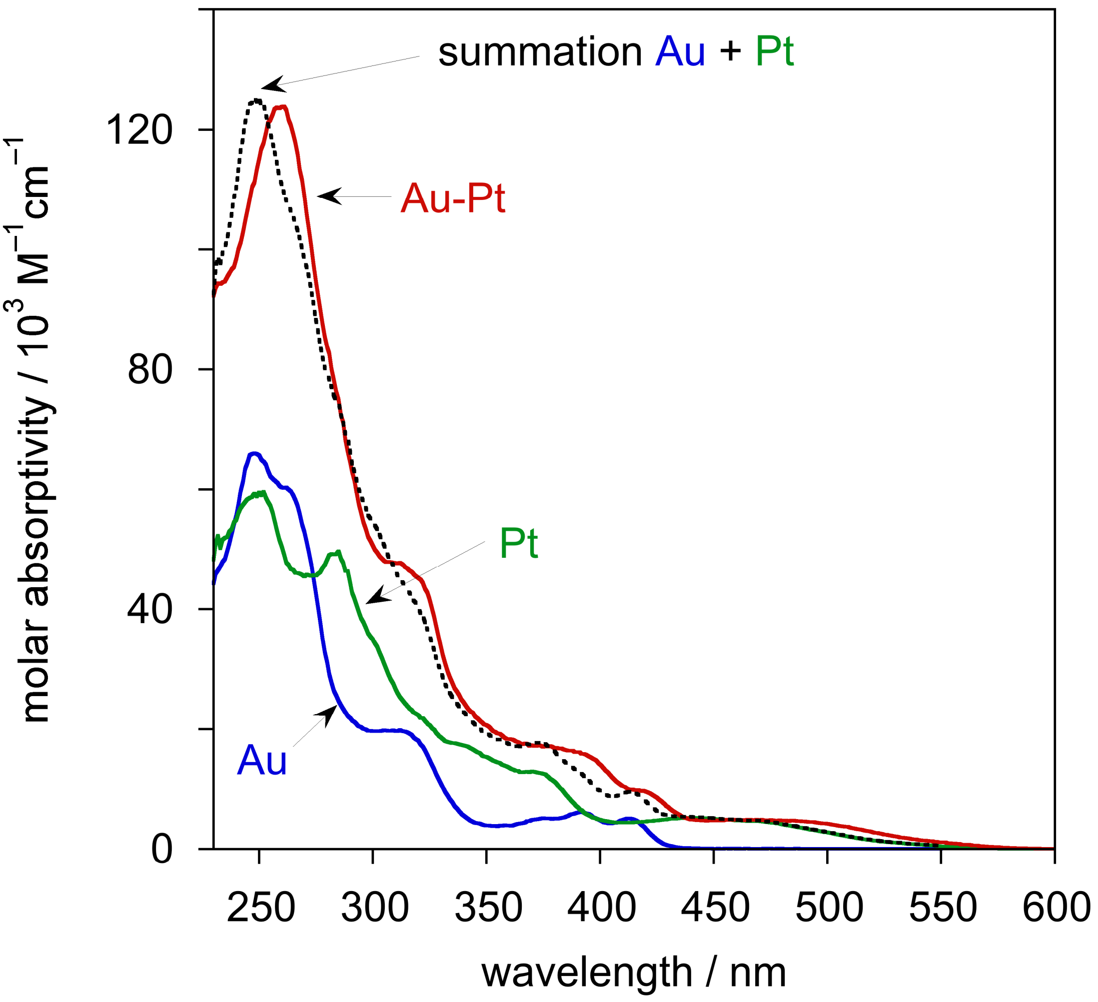
100
90
80
70
60
50
40
30
20
ppm
t-Bu
t-Bu
n-Bu
n-Bu
n-Bu
n-Bu
O
Au
N
N
Pt
N

2. Details of procedures and instrumentation for photophysical measurements

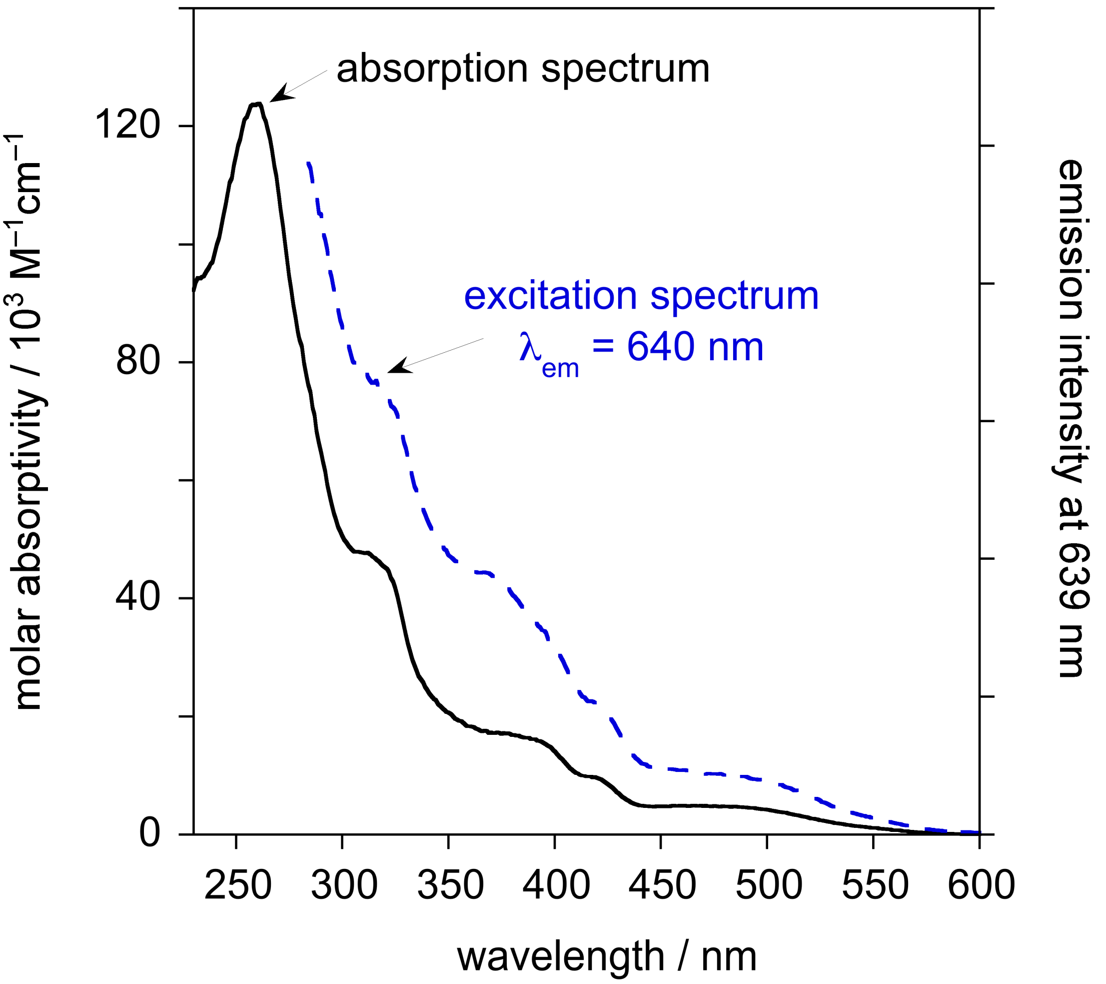
Absorption spectra were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm pathlength. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube; the spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. The emission spectrum of Pt_2 at room temperature extends beyond the range of the R928; the spectrum shown in Fig. 2 was recorded using a silicon photodiode detector. Samples for emission measurements were contained within quartz cuvettes of 1 cm pathlength modified with appropriate glassware to allow connection to a high-vacuum line. Degassing was achieved via a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77K was $< 10^{-2}$ mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using $[Ru(bpy)_3]Cl_2$ in aqueous solution ($\Phi = 0.028$) as the standard.[7]

The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting (TCSPC), following excitation at 374.0 nm with an EPL-375 pulsed diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is ±10% or better. The lifetimes of **Au** and **Au$_2$** at 77 K were determined by multichannel scaling using the same detector following excitation with a pulsed xenon lamp.

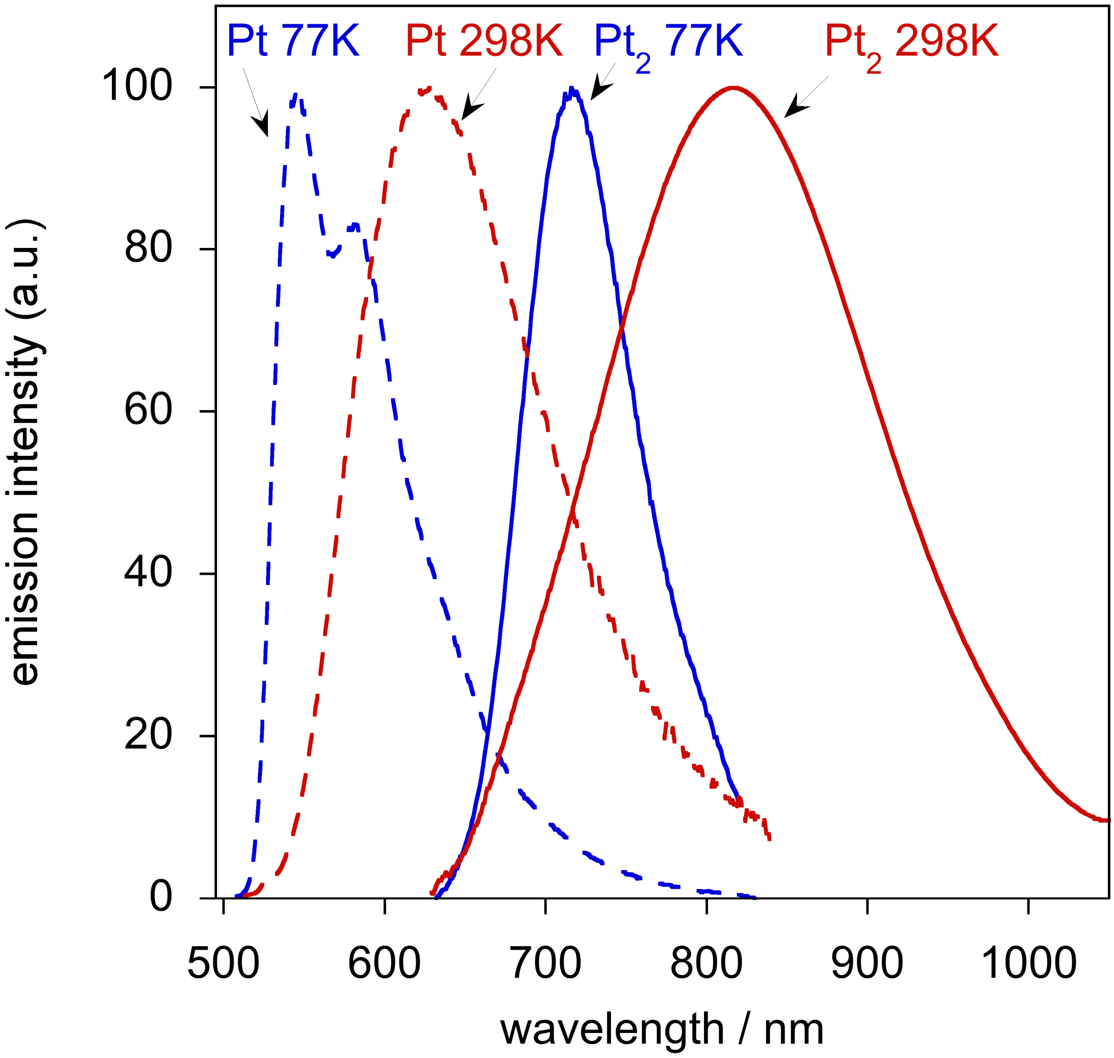
3. Additional absorption and emission spectra



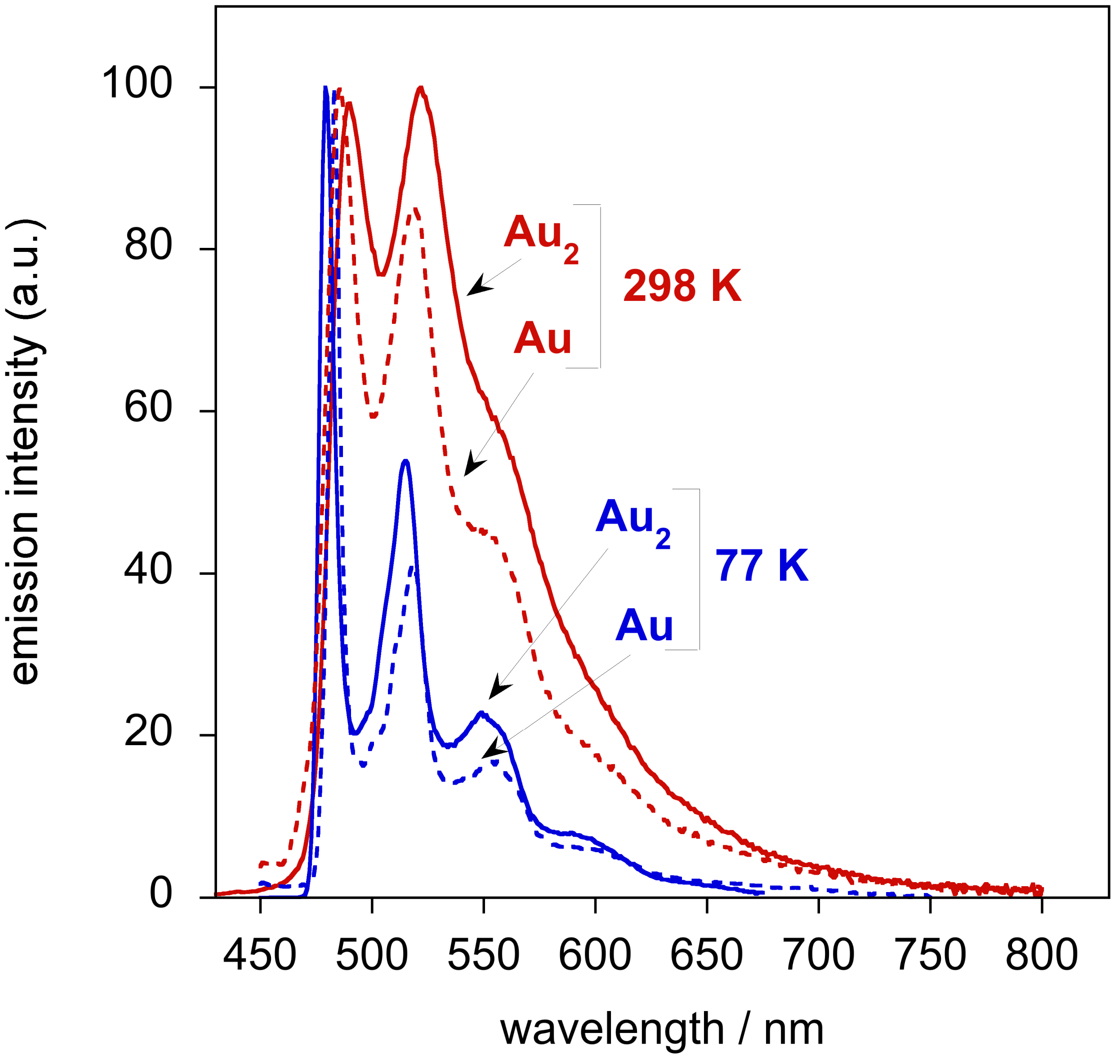
***3.1** Absorption spectra of the homonuclear complexes **Au** (blue line) and **Pt**, and of the heterodimer **AuPt**, in CH_2Cl_2 at 298 K. The dotted line shows the sum of **Au**+**Pt**, highlighting the similarity to the spectrum of **AuPt**.*



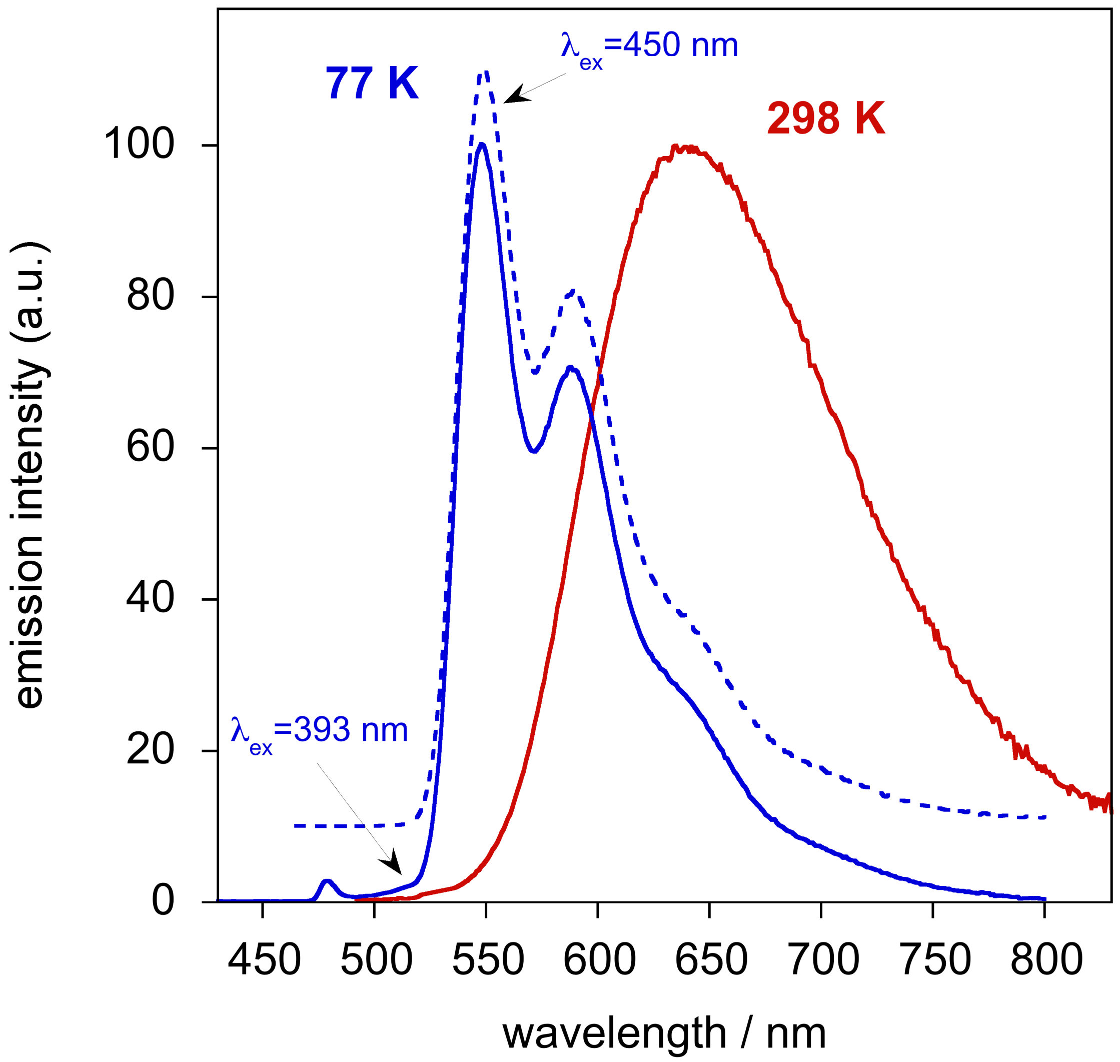
3.2 *Absorption (solid black line) and excitation (dashed blue line) spectra of* ***AuPt*** *in* CH_2Cl_2 *at 298 K, showing the close match between the spectra, supporting the conclusion that rapid energy transfer from the Au unit to the Pt unit occurs.*



*3.3 Comparison of the emission spectra of **Pt** and **Pt_2** at 298 K (in CH_2Cl_2; dashed and solid red line respectively) and at 77 K (in diethyl ether / isopentane / ethanol, 2:2:1 by volume; dashed and solid blue lines respectively).*

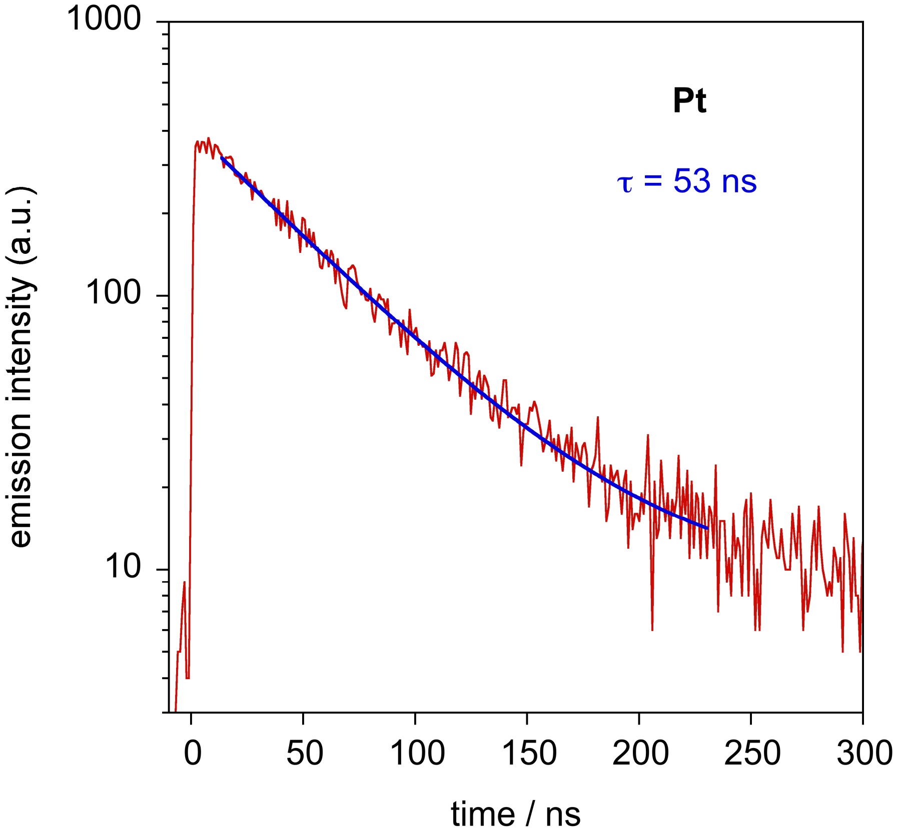


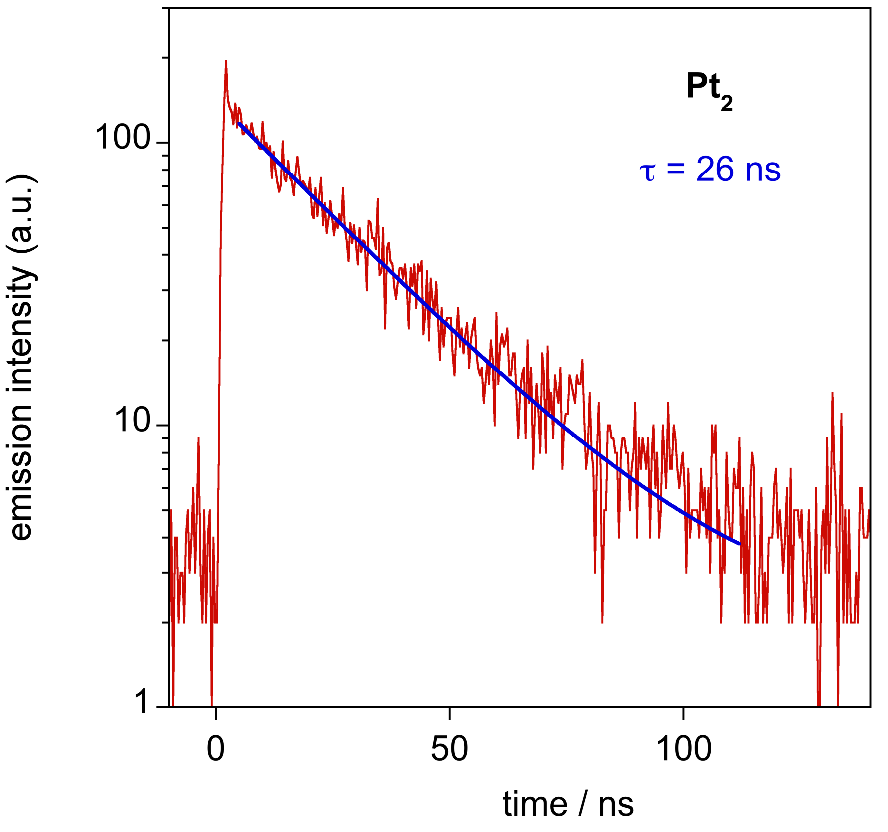
3.4 *Comparison of the emission spectra of* ***Au*** *and* ***Au$_2$*** *at 298 K (in CH_2Cl_2; dashed and solid red line respectively) and at 77 K (in diethyl ether / isopentane / ethanol, 2:2:1 by volume; dashed and solid blue lines respectively).*

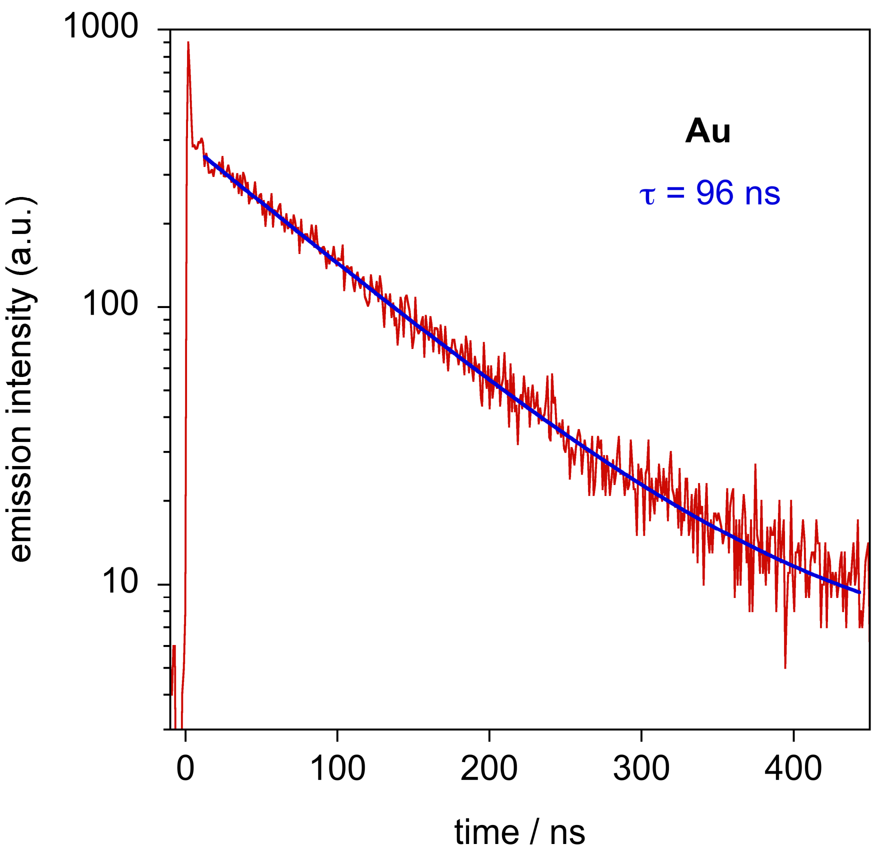


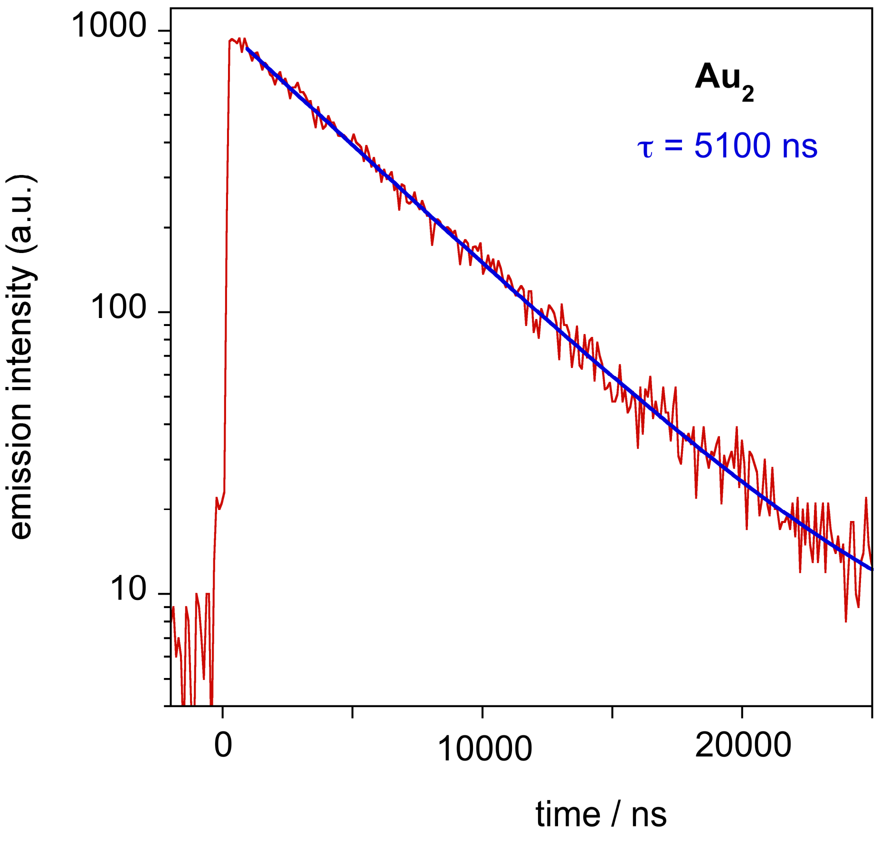
__3.5__ Emission spectra of __AuPt__ at 298 K (solid red line) and at 77 K (in diethyl ether / isopentane / ethanol, 2:2:1 by volume; blue lines). The offset dashed blue line shows the spectrum upon excitation at 450 nm, at which wavelength, only the Pt unit will be excited. The solid blue line shows the spectrum recorded following excitation at 393 nm. At this wavelength, the Au and Pt units should absorb equally (based on the molar absorptivies for __Au__ and __Pt__), but the spectrum shows only a scarcely detectable band for __Au__ emission at 480 nm.

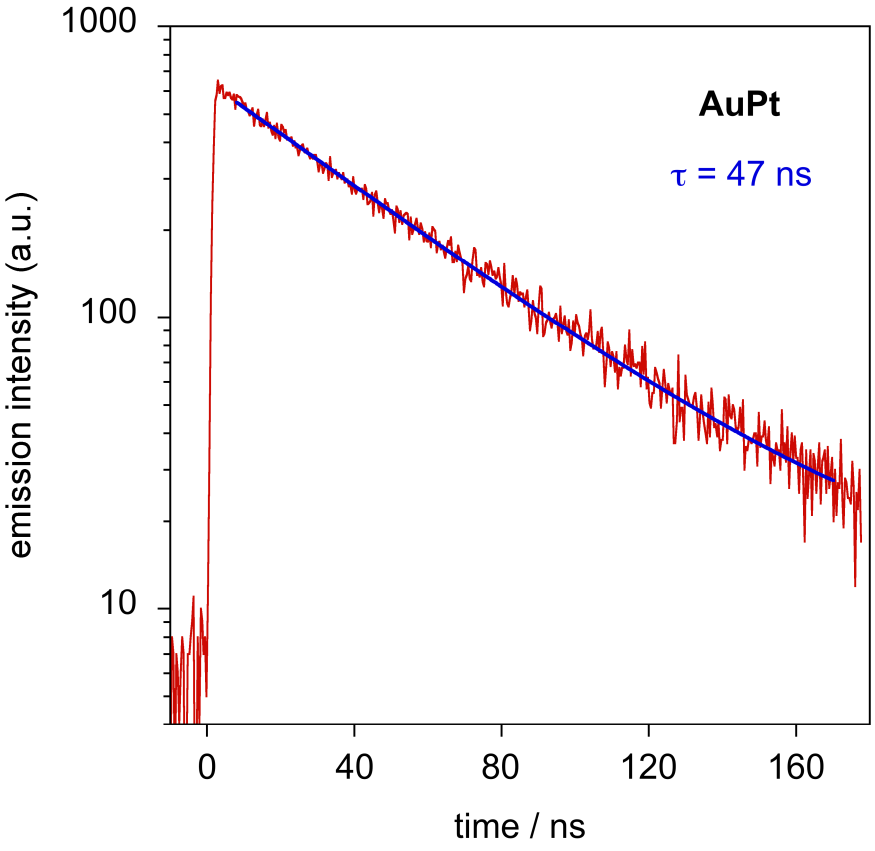
4. Representative luminescence decays in solution in CH_2Cl_2 at 298 K






Au
τ = 96 ns
emission intensity (a.u.)
1000
100
10
0
100
200
300
400
time / ns


Au$_2$
τ = 5100 ns
emission intensity (a.u.)
1000
100
10
0
10000
20000
time / ns



References

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