Electronic Supplementary Information

Stoichiometric C-H Arylation of Tricarbonyl(arene)chromium Complexes Bearing Pyridine Directing Groups.

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Contents:

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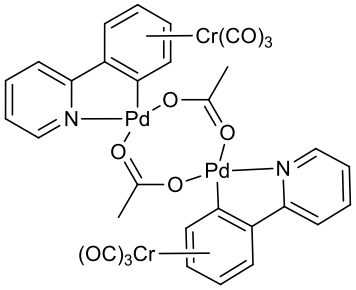
Experimental Procedures

2-(Tricarbonyl(η^6-phenyl)chromium(0))pyridine (**3**) was synthesised as previously reported.[1]

Palladacycle 4



A solution of Cr-complex **3** (0.20 g, 0.68 mmol) and $Pd(OAc)_2$ (0.15 g, 0.68 mmol) in dry degassed DCE (10.0 mL) was stirred for 20 h at room temperature. The resulting black precipitate formed was removed by filtration over celite and washing with $CHCl_3$. The solvent was removed *in vacuo* to afford a red-orange film which was treated with $CHCl_3$ to yield a red solid complex **4** and an unidentified but highly similar by-product in a 2:1 mixture (0.29 g, 91% based on **4**):

*Complex **4**:* A pure sample of compound **4** was obtained from spontaneous crystallisation from a $CDCl_3$ solution containing the obtained mixture of palladium complexes.

^{1}H-NMR (acetone-d_6, 400 MHz) δ 8.17 (d, J = 5.1 Hz, 2H, Ar-*H*), 8.01 (s, 2H, 2 C*H*Cl_3), 7.88 (dt, J = 7.8, 1.2 Hz, 2H, Ar-*H*), 7.52 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.15 (t, J = 6.3 Hz, 2H, Ar-*H*), 5.89 (d, J = 6.5 Hz, 2H, Ar-*H*), 5.41 (d, J = 6.3 Hz, 2H, Ar-*H*), 5.19 (d, J = 6.4 Hz, 2H, Ar-*H*), 5.17 (t, J = 6.6 Hz, 2H, Ar-*H*), 2.12 (s, 6H, CH_3)

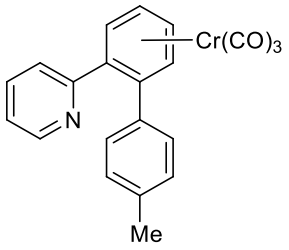
Unidentified Pd complex by-product:

^{1}H-NMR (acetone-d_6, 400 MHz) δ 8.11 (d, J = 5.1 Hz, 1H, Ar-*H*), 7.79 (dt, J = 7.9, 1.3 Hz, 1H, Ar-*H*), 7.47 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.07 (t, J = 6.2 Hz, 1H, Ar-*H*), 5.99 (d, J = 6.5 Hz, 1H, Ar-*H*), 5.47 (d, J = 6.4 Hz, 1H, Ar-*H*), 5.28 (t, J = 6.4 Hz, 1H, Ar-*H*), 5.22 (d, J = 6.4 Hz, 1H, Ar-*H*)

*Mixture of **4** and unidentified by-product:*

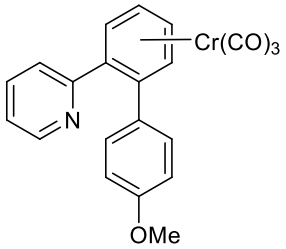
^{13}C-NMR (acetone-d_6, 100 MHz) δ 235.93, 235.82, 164.67, 151.98, 151.12, 141.30, 141.28, 125.52, 125.24, 120.26, 97.53, 96.75, 96.60, 96.55, 93.14, 92.97, 91.64, 91.44, 25.50, MS-EI (*m/z*): M^+ calcd for $C_{22}H_{16}N_2Pd$, 414.0348; found, 414.0350; Anal. Calc. for $C_{32}H_{22}Cr_2N_2O_{10}Pd$: C, 42.17; H, 2.43; N, 3.07. Found: C, 41.99; H, 2.50; N, 3.13.

2-(Tricarbonyl(η^6-6'-methylphenyl-phenyl)chromium(0))pyridine 7



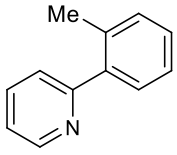
A stirring solution of complex **4** (0.05 g, 0.05 mmol), *p*-tolylphenyl boronic acid (0.04 g, 0.28 mmol), *p*-benzoquinone (0.06 g, 0.28 mmol) and 2M Na_2CO_3 (0.3 mL, 0.55 mmol) in DCE (1.0 mL) was heated to 60 ^{o}C for 20 minutes. The reaction mixture was allowed to cool to room temperature and filtered through a thin pad of celite (eluting with CH_2Cl_2). The filtrate was washed with brine (20.0 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (silica, hexanes : Et_2O : CH_2Cl_2 5 : 3 : 2) to yield product **7** as orange solid (0.019 g, 0.05 mmol, 91%). R_f 0.33 (hexanes : Et_2O : CH_2Cl_2 5 : 3 : 2); mp 107-111 ^{o}C; IR 1947, 1858 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.57 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.42 (*br* t, *J* = 7.5 Hz, 1H, Ar*H*), 7.16 (*br* t, *J* = 7.5 Hz, 1H, Ar*H*), 7.12 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.05 – 7.02 (m, 3H, Ar*H*), 6.02 (*br* s, 1H, Ar*H*), 5.52 (*br* s, 3H, Ar*H*), 2.32 (s, 3H, -C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 232.8, 154.9, 149.0, 138.4, 135.5, 133.3, 130.1, 129.6, 128.9, 126.4, 122.9, 113.8, 109.4, 94.9, 94.7, 92.1, 91.8, 91.7, 21.1; MS (ESI) m/z 382 $[M+H]^+$; HRMS (ESI) cal. for $C_{21}H_{15}CrNO_3$ [M] 382.0457, found $[M+H]^+$ 382.0535; Anal. Calc. for $C_{21}H_{15}CrNO_3$: C, 66.14; H, 3.96; N, 3.67. Found: C, 66.24; H, 3.87; N, 3.59.

2-(Tricarbonyl(η^6-6'-methoxyphenyl-phenyl)chromium(0))pyridine 8



A stirring solution of complex **4** (0.10 g, 0.11 mmol), *p*-methoxyphenyl boronic acid (0.083 g, 0.55 mmol), *p*-benzoquinone (0.06 g, 0.55 mmol) and 2M Na_2CO_3 (0.55 mL, 1.10 mmol) in DCE (2.0 mL) was heated to 60 ^oC for 20 minutes. The reaction mixture was allowed to cool to room temperature and filtered through a thin pad of celite (eluting with CH_2Cl_2). The filtrate was washed with brine (20.0 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (silica, hexanes : Et_2O : CH_2Cl_2 5 : 3 : 2) to yield product **8** as an orange gum (0.020 g, 0.058 mmol, 53%. R_f 0.38 (hexanes: Et_2O : CH_2Cl_2 5 : 3 : 2); IR 1953, 1862 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.63 (dd, *J* = 6.0, 4.4 Hz, 1H, ArH), 7.48 – 7.41 (m, 2H, ArH), 7.21 – 7.06 (m, 3H, ArH), 6.81 – 6.78 (m, 2H, ArH), 6.04 (d, *J* = 6.0 Hz, 1H, ArH), 5.55 – 5.54 (m, 3H, ArH), 3.82 (s, 3H, -OMe); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.7, 154.9, 149.0, 135.5, 131.4, 130.8 (2C), 128.3, 126.4, 122.8, 113.6 (2C), 109.5, 95.0, 94.4, 92.3, 91.7, 55.3; MS (ESI) m/z 398 $[M+H]^+$; HRMS (ESI) cal. for $C_{21}H_{15}CrNO_4$ $[M+H]^+$ 398.0406, found $[M+H]^+$ 398.0482; Anal. Calc. for $C_{21}H_{15}CrNO_4$: C, 63.48; H, 3.81; N, 3.53. Found: C, 58.46; H, 3.80; N, 3.91.

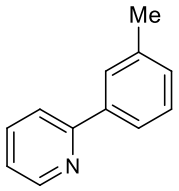
2-(2' -Methylphenyl)pyridine 12[2]



A solution of *o*-tolylboronic acid (0.50 g, 3.68 mmol) and K_3PO_4 (2.01 g, 9.48 mmol) in toluene : H_2O (10 : 1 mL) was added to a stirring solution of 2-bromopyridine (0.30 mL, 3.40 mmol), $Pd_2(dba)_3$ (0.092 g, 0.10 mmol) and SPhos (0.082 g, 0.20 mmol) in toluene (2.0 mL) and was heated under reflux for 3 h. The reaction mixture was

allowed to cool to room temperature and was diluted with H_2O (10.0 mL) and Et_2O (10.0 mL). The resulting layers were separated and the aqueous layer was extracted with Et_2O (2 x 15.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a crude yellow oil. The crude product was purified *via* column chromatography (silica, hexanes : EtOAc 3 : 1) to yield the titled compound **12** as a yellow oil (0.53 g, 3.12 mmol, 92%); R_f 0.39 (hexanes : EtOAc 3 : 1); IR 1585, 1467, 1424, 747 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.73 (d, *J* = 4.8 Hz, 1H, Ar*H*), 7.77 (dt, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 7.43 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.32–7.26 (m, 4H, Ar*H*), 2.40 (s, 3H, -C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 160.0, 149.2, 140.5, 136.1, 135.8, 130.8, 129.6, 128.3, 125.9, 124.1, 121.6, 20.3; MS (EI) m/z 168 [M^+]; HRMS (EI) calc. for $C_{12}H_{11}N$ [M^+] 169.0815, found [M^+] 169.0891.

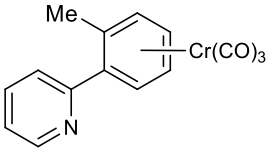
2-(3' -Methylphenyl)pyridine 13[2]



A solution of *m*-tolylboronic acid (0.50 g, 3.68 mmol) and K_3PO_4 (2.01 g, 9.48 mmol) in toluene : H_2O (13.0 : 1.0 mL) was added to a stirring solution of 2-bromopyridine (0.30 mL, 3.40 mmol), $Pd_2(dba)_3$ (0.092 g, 0.10 mmol) and SPhos (0.082 g, 0.20 mmol) in toluene (2.0 mL) and was heated under reflux for 3 h. The reaction mixture was allowed to cool to room temperature and was diluted with H_2O (10.0 mL) and Et_2O (10.0 mL). The resulting layers were separated and the aqueous layer was extracted with Et_2O (2 x 15.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford crude orange oil. The crude product was purified *via* column chromatography (silica, CH_2Cl_2 : EtOAc 40 : 1) to yield the titled compound **13** as a yellow oil (0.56 g, 3.31 mmol, 98%); R_f 0.34 (CH_2Cl_2 : EtOAc 40 : 1); IR 1584, 1565, 1460, 1432, 764 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.72 (d, *J* = 4.8 Hz, 1H, Ar*H*), 7.87 (s, 1H, Ar*H*), 7.80-7.74 (m, 3H, Ar*H*), 7.40 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.30-7.25 (m, 2H, Ar*H*), 2.47 (s, 3H, -C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 157.7, 149.6, 139.4, 138.4, 136.7, 129.7, 128.7, 127.7, 124.0,

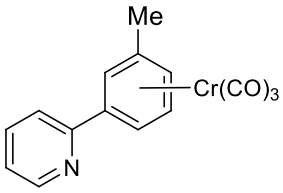
122.0, 120.7, 21.5; MS (EI) m/z 169 [M^+]; HRMS (EI) calc. for $C_{12}H_{11}N$ [M^+] 169.0891, found [M^+] 169.0888.

2-(Tricarbonyl(η^6-2' -methylphenyl)chromium(0))pyridine 14



2-(2′-methylphenyl)pyridine (**12**) (0.25 g, 1.48 mmol) was added to a stirring solution of hexacarbonylchromium(0) (0.39 g, 1.77 mmol) in a deoxygenated mixture of Bu_2O : THF (10.0 : 1.0, 22.0 mL) and heated under reflux for 24 hrs. The reaction mixture was cooled to room temperature and filtered through celite and the solvent evaporated under reduced pressure to yield the crude complex to give a yellow solid. This solid was recrystallised from hexanes/CH_2Cl_2 to afford the title complex **14** as yellow plates (0.29 g, 0.95 mmol, 64%); Rf 0.21 (CH_2Cl_2); mp 75-78 ^oC; IR 1944, 1874, 1843, 627 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.64 (*br* s, 1H, Ar*H*), 7.80 (*br* s, 1H, Ar*H*), 7.60 (*br* s, 1H, Ar*H*), 7.31 (*br* s, 1H, Ar*H*), 5.73 (*br* s, 1H, Ar*H*), 5.55 (*br* s, 1H, Ar*H*), 5.23 (*br* s, 2H, Ar*H*), 2.25 (s, 3H, -C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 155.6, 149.0, 136.9, 125.3, 123.0, 109.9, 109.8, 97.5, 95.1, 92.2, 88.5, 20.0; MS (EI) m/z 305 [M^+]; HRMS (EI) calc. for $C_{15}H_{11}CrNO_3$ [M^+] 305.0144, found [M^+] 305.0221.

2-(Tricarbonyl(η^6-3'-methylphenyl)chromium(0))pyridine 15

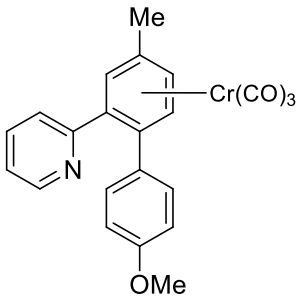


2-(3′-methylphenyl)pyridine (**13**) (0.57 g, 3.37 mmol) was added to a stirring solution of hexacarbonylchromium(0) (0.89 g, 4.04 mmol) in a deoxygenated mixture of Bu_2O : THF (10.0 : 1.0, 22.0 mL) and heated under reflux for 24 hrs. The reaction mixture was cooled to room temperature and filtered through celite rinsing with Et_2O. After washing with brine (50.0 mL), the ethereal layer was dried over Mg_2SO_4 and the

solvent evaporated under reduced pressure to yield the crude complex as yellow solid. This solid was purified by column chromatography (silica, hexane : Et_2O 1 : 1) and recrystallised from hexanes/CH_2Cl_2 to afford the title complex **15** as orange crystal blocks (0.420 g, 1.38 mmol, 41%); R_f 0.47 (CH_2Cl_2); mp 82-90 ^oC; IR 1939, 1853, 1584, 618 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.66 (*br* s, 1H, ArH), 7.79 (*br* t, *J* = 7.2 Hz, 1H, ArH), 7.60 (*br* d, *J* = 8.0 Hz, 1H, ArH), 7.30 (*br* s, 1H, ArH), 6.06 (s, 1H, ArH), 5.96 (d, *J* = 6.4 Hz, 1H, ArH), 5.63 (t, *J* = 6.4 Hz, 1H, ArH), 5.28 (d, *J* = 6.4 Hz, 1H, ArH), 2.35 (s, 3H, -Me); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 233.1, 153.9, 149.5, 136.9, 123.8, 120.4, 109.1, 107.0, 93.8, 92.3, 92.0, 88.8, 21.0; MS (EI) m/z 305 [M^+]; HRMS (EI) calc. for $C_{15}H_{11}CrNO_3$ [M^+] 305.0144, found [M^+] 305.0222; Anal. Calc. for $C_{15}H_{11}CrNO_3$: C, 59.02; H, 3.63; N, 4.59. Found: C, 59.12; H, 3.55; N, 4.61.

2-(Tricarbonyl(η^6- 3´methyl--6'-methoxyphenyl-phenyl)chromium(0))pyridine

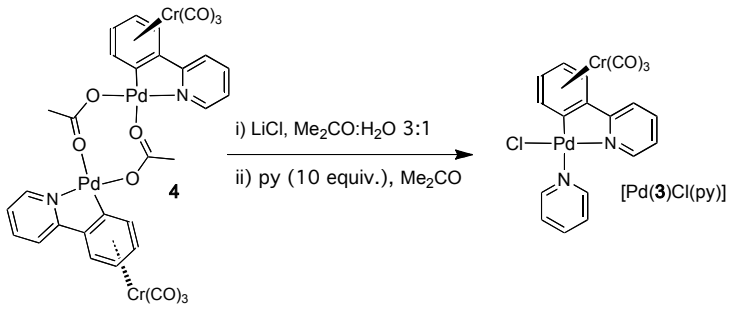
17



A solution of 2-(tricarbonyl(η^6-3´-methylphenyl)chromium(0))pyridine (**15**) (0.05 g, 0.16 mmol) and palladium acetate (0.036 g, 0.16 mmol) in DCE (3.0 mL) was left to stir for 1 h at ambient temperature. A solution of *p*-methoxyphenyl boronic acid (0.13 g, 0.82 mmol) and 2M Na_2CO_3 (0.8 mL, 1.60 mmol) in DCE (3.0mL) was added to the stirring palladacycle, immediately followed by a solution of *p*-benzoquinone (0.02 g, 1.60 mmol) in DCE (3.0 mL) and resulting mixture was stirred at rt for 3 h. The reaction mixture was filtered through a thin pad of $MgSO_4$ (eluting with CH_2Cl_2). The filtrate was concentrated under reduced pressure and purified by column chromatography (silica, hexane : Et_2O 1 : 1) to give the titled compound **17** as an orange gum (0.034 g, 0.082 mmol, 51%); R_f 0.20 (hexanes : Et_2O 1:1); IR 1950, 1862, 1515, 1249, 624 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.62 (*br* s, 1H, Ar*H*), 7.46 (*br* s, 1H, Ar*H*), 7.45 (*br* m, 4H, Ar*H*), 6.79 (*br* s, 2H, Ar*H*), 5.90 (*br* s, 1H, Ar*H*), 5.62 (*br* s, 1H, Ar*H)*, 5.37 (*br* s, 1H, Ar*H*), 3.79 (*br* s, 3H, -OCH_3), 2.34 (*br* s,

3H, -C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 233.3, 159.5, 154.9, 149.0, 135.4, 131.5, 130.7, 128.4, 126.6, 122.9, 113.6, 113.5, 111.0, 110.7, 108.8, 96.2, 94.9, 92.2, 55.3, 20.4; MS (EI) m/z 411 [M^+]; HRMS (EI) calc. for $C_{22}H_{17}CrNO_4$ [M^+] 411.0563, found [M^+] 411.0637.

Coordination Chemistry of 4



Pallacycle **4** (455 mg) was dissolved acetone (20 mL). LiCl (85 mg, 2.00 mmol, 2.0 eq) in acetone:H_2O (3:1, 20 mL) were introduced into the reaction vessel. After stirring at ambient temperature for 18h the solvents were evaporated under reduced pressure and the residue purified by column chromatography (silica, acetone:hexanes, 30:70 to 50:50 to 100:0). Recrystallisation of the resultant solid from acetone and acetone/hexanes afforded the product as orange solid, which was used immediately in the next step. The obtained chloride complex (26 mg, 0.03 mmol) and pyridine (24 µL, 0.30 mmol, 10.0 eq) were dissolved in acetone (2 mL). After 1 h at ambient temperature, the solution was filtered over celite, the solvents evaporated under reduced pressure and the residue washed with Et_2O. This afforded orange crystals (3 mg) that were suitable for X-ray diffraction analysis: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 9.25 (s, 1H, Ar-*H*), 8.99 (s, 2H, Ar-*H*), 7.94-7.85 (m, 2H, Ar-*H*), 7.54 (s, 2H, Ar-*H*), 7.42 (d, *J* = 6.9 Hz, 1H, Ar-*H*), 5.77 (s, 1H, Ar-*H*), 5.23 (s, 2H, Ar-*H*), 4.24 (s, 1H, Ar-*H*)

X-ray data

The structure of **4** was found to have crystallographic C_2 symmetry about an axis that bisects the Pd(1)···Pd(1A) and O(13)···O(13A) vectors. The position of the nitrogen atom of the C(6)-based pyridyl ring in the structure of **7**, and of the C(7)-based pyridyl ring in the structures of both **14** and **15**, was determined in each case by comparison of the thermal parameters and bond lengths when both possible *ortho* sites were refined as carbon atoms, and by the location from a ΔF map of a hydrogen atom bound to one of the two sites. The absolute structure of **15** was determined by a combination of *R*-factor tests [$R_1^+ = 0.0295$, $R_1^- = 0.0416$] and by use of the Flack parameter [$x^+ = +0.000(14)$].

Table S1. Crystal Data, Data Collection and Refinement Parameters for the structures of **4**, [Pd(**3**)Cl(py)], **7**, **14** and **15**.

data	**4**	[Pd(**3**)Cl(py)]	**7**
formula	$C_{32}H_{22}Cr_2N_2O_{10}Pd_2$	$C_{19}H_{13}ClCrN_2O_3Pd$	$C_{21}H_{15}CrNO_3$
solvent	$2CHCl_3$	—	—
formula weight	1150.05	511.16	381.34
colour, habit	orange blocks	orange blocky needles	yellow shards
crystal size / mm^3	0.29 × 0.21 × 0.14	0.50 × 0.18 × 0.13	0.25 × 0.16 × 0.05
temperature / K	173	173	173
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)
***a* / Å**	16.0719(3)	26.7584(5)	8.89230(17)
***b* / Å**	19.7859(2)	13.0677(2)	14.2567(3)
***c* / Å**	14.6400(3)	11.01544(19)	13.8089(3)
α / deg	—	—	—
β / deg	123.678(3)	104.3242(18)	94.6477(17)
γ / deg	—	—	—
***V* / Å^3**	3874.13(18)	3732.03(11)	1744.87(6)
Z	4 [b]	8	4
D_c / g cm^{-3}	1.972	1.820	1.452
radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ / mm^{-1}	1.933	1.711	0.676
2θ max / deg	65	66	64
no. of unique reflns			
measured (R_{int})	6472 (0.0199)	6366 (0.0208)	5390 (0.0279)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	5238	5064	4230
no. of variables	254	244	236
R_1(obs), wR_2(all) [a]	0.0260, 0.0727	0.0213, 0.0499	0.0372, 0.0982

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [b] The molecule has crystallographic C_2 symmetry.

Table S1. Continued

data	14	15
formula	$C_{15}H_{11}CrNO_3$	$C_{15}H_{11}CrNO_3$
solvent	—	—
formula weight	305.25	305.25
colour, habit	yellow blocks	yellow blocks
crystal size / mm^3	0.31 × 0.26 × 0.14	0.46 × 0.20 × 0.14
temperature / K	173	173
crystal system	orthorhombic	orthorhombic
space group	*Pbca* (no. 61)	$P2_12_12_1$ (no. 19)
***a* / Å**	7.62537(16)	7.00453(14)
***b* / Å**	12.3834(2)	8.13150(15)
***c* / Å**	27.5890(5)	24.1140(4)
α / deg	—	—
β / deg	—	—
γ / deg	—	—
***V* / Å^3**	2605.17(8)	1373.47(4)
Z	8	4
***D*$_c$ / g cm^{-3}**	1.557	1.476
radiation used	Mo-Kα	Mo-Kα
μ / mm^{-1}	0.883	0.838
2θ max / deg	62	65
no. of unique reflns		
measured (*R*$_{int}$)	3768 (0.0270)	4627 (0.0281)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	3352	4350
no. of variables	182	182
***R*$_1$(obs), *wR*$_2$(all)** [a]	0.0494, 0.1089	0.0295, 0.1007

Table 1 provides a summary of the crystallographic data for the structures of **4**, [Pd(**3**)Cl(py)], **7**, **14** and **15**. Data were collected using an Oxford Diffraction Xcalibur 3 diffractometer, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[3] The absolute structure of **15** was determined by a combination of *R*-factor tests [$R_1^+ = 0.0295$, $R_1^- = 0.0416$] and by use of the Flack parameter [$x^+ = +0.000(14)$]. CCDC 912626 to 912630.

References

1. A. Berger, J. –P. Djuckic, M. Pfeffer, *Organometallics*, 2003, **22**, 5243.
2. V. Martínez-Barrasa, A. García de Viedma, C. Burgos, J. Alvarez-Builla, *Org. Lett*. 2000, **2**, 3933.
3. G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

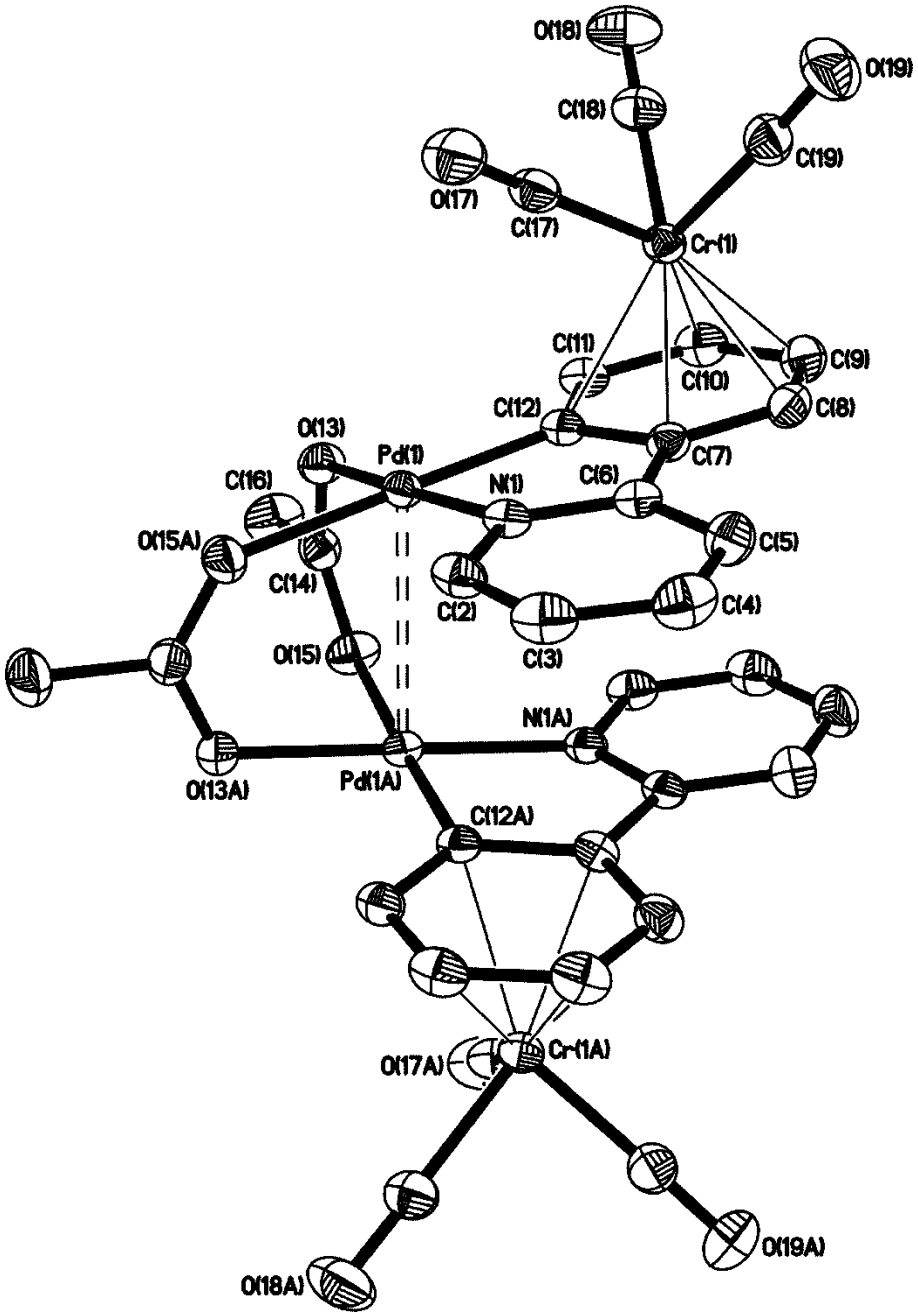


Fig. S1 The crystal structure of **4** (50% probability ellipsoids).

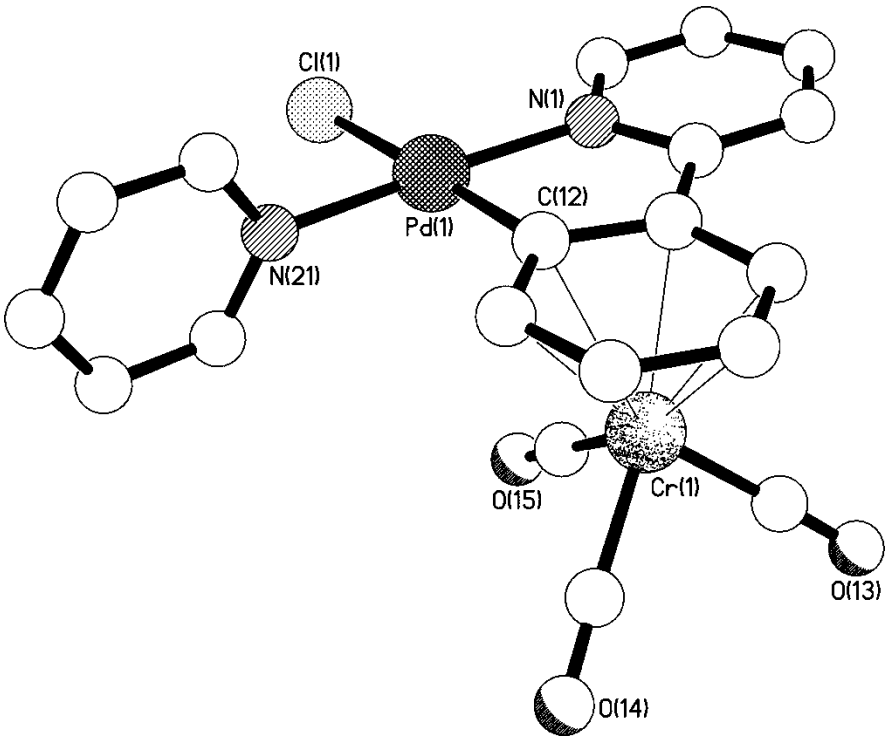


Fig. S2 The crystal structure of [Pd(**3**)Cl(py)].

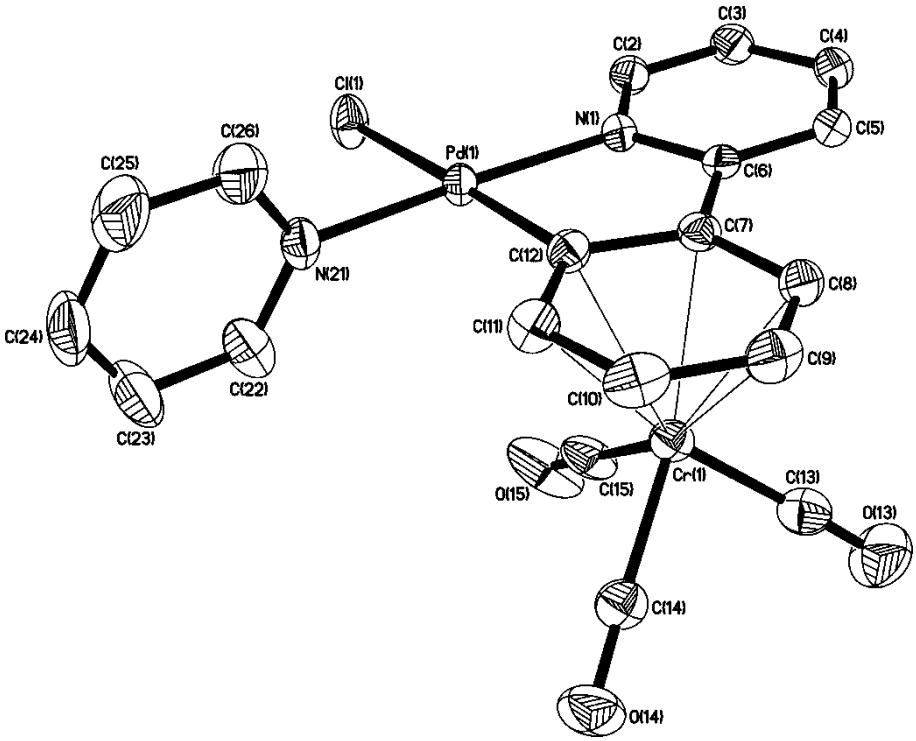


Fig. S3 The crystal structure of [Pd(**3**)Cl(py)] (50% probability ellipsoids).

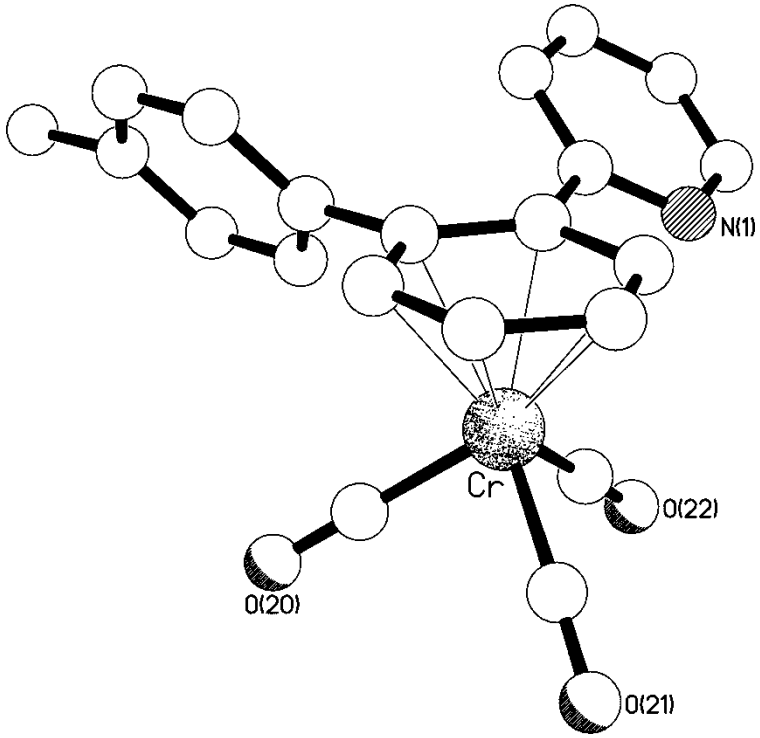


Fig. S4 The crystal structure of **7**.

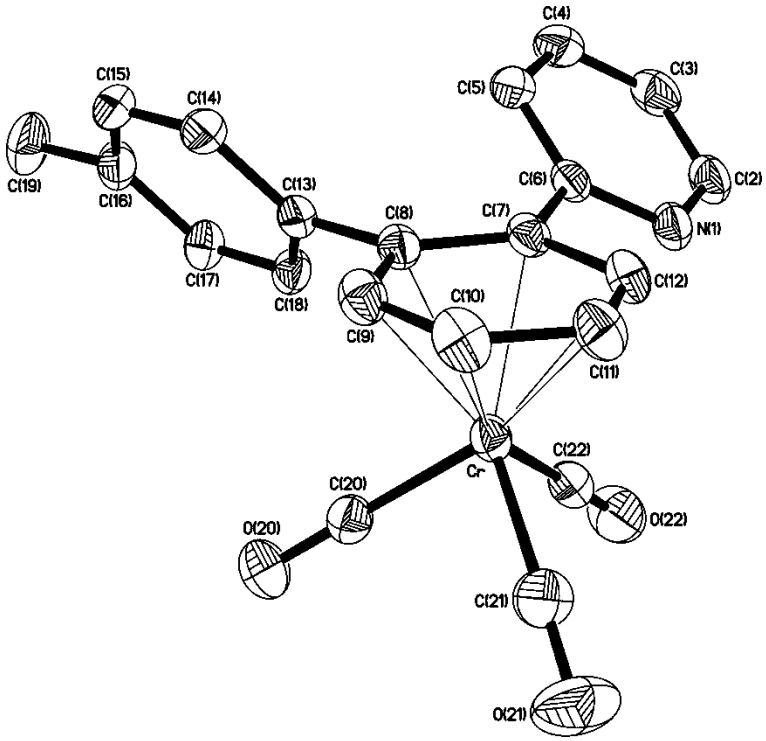


Fig. S5 The crystal structure of **7** (50% probability ellipsoids).

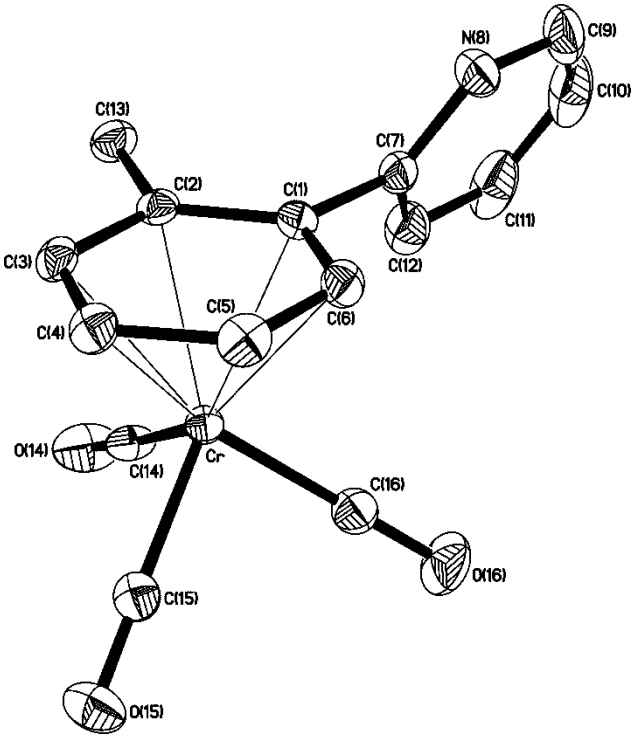


Fig. S6 The crystal structure of **14** (50% probability ellipsoids).

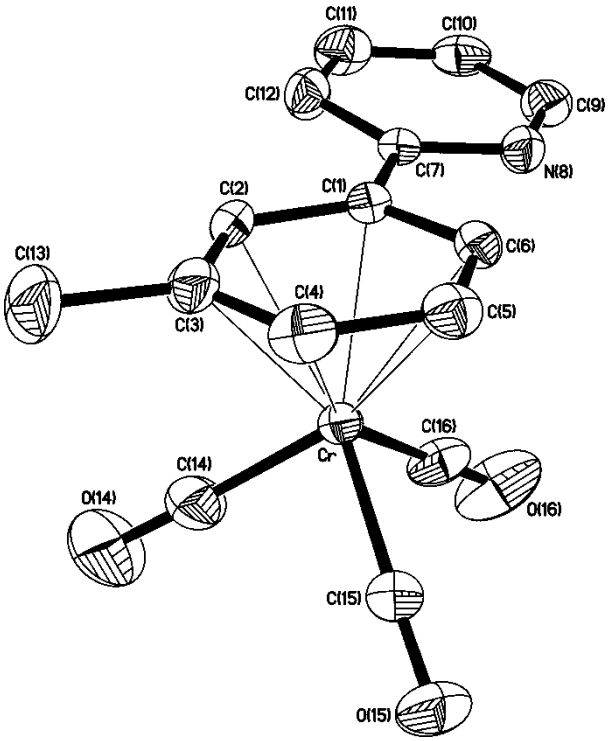


Fig. S7 The crystal structure of **15** (50% probability ellipsoids).

NMR data

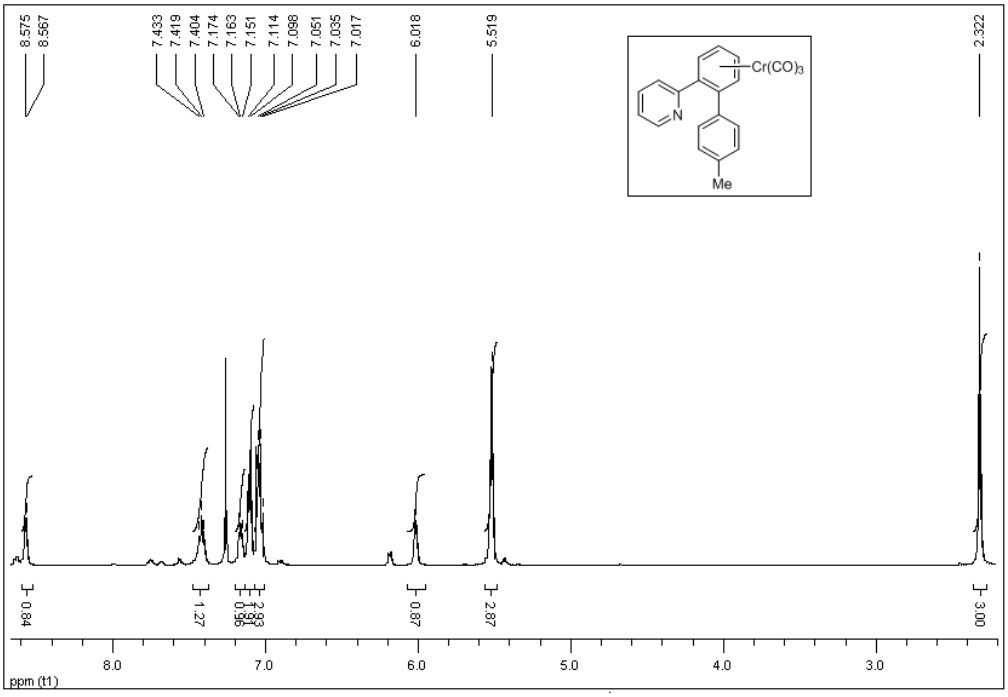


Fig. S8 ^{1}H NMR spectrum of compound **7**

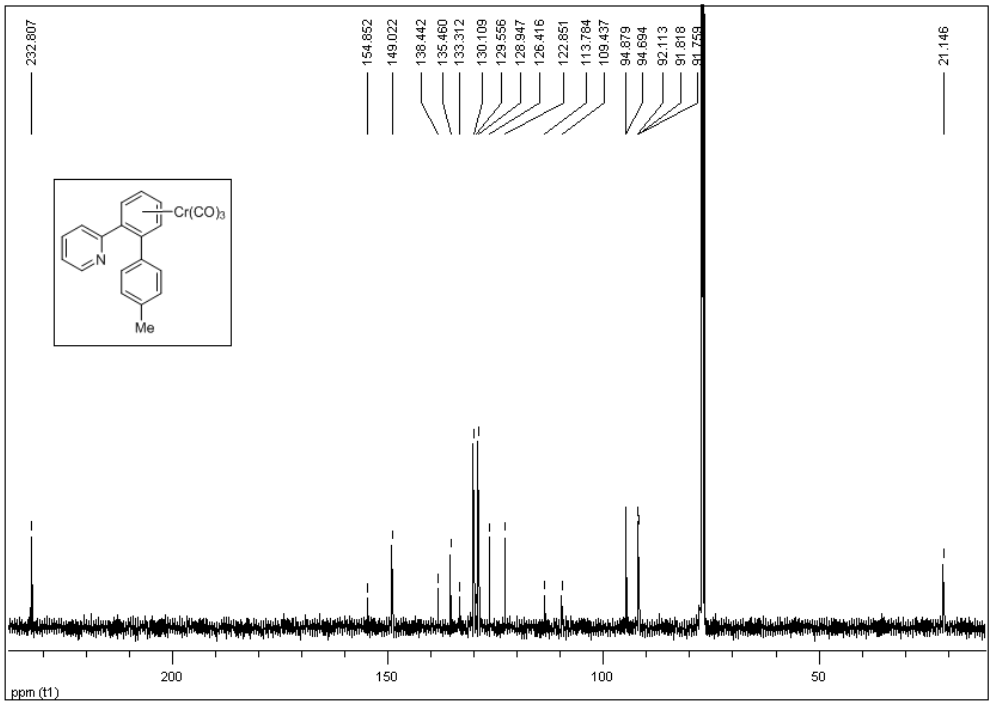


Fig. S9 ^{13}C NMR spectrum of compound **7**

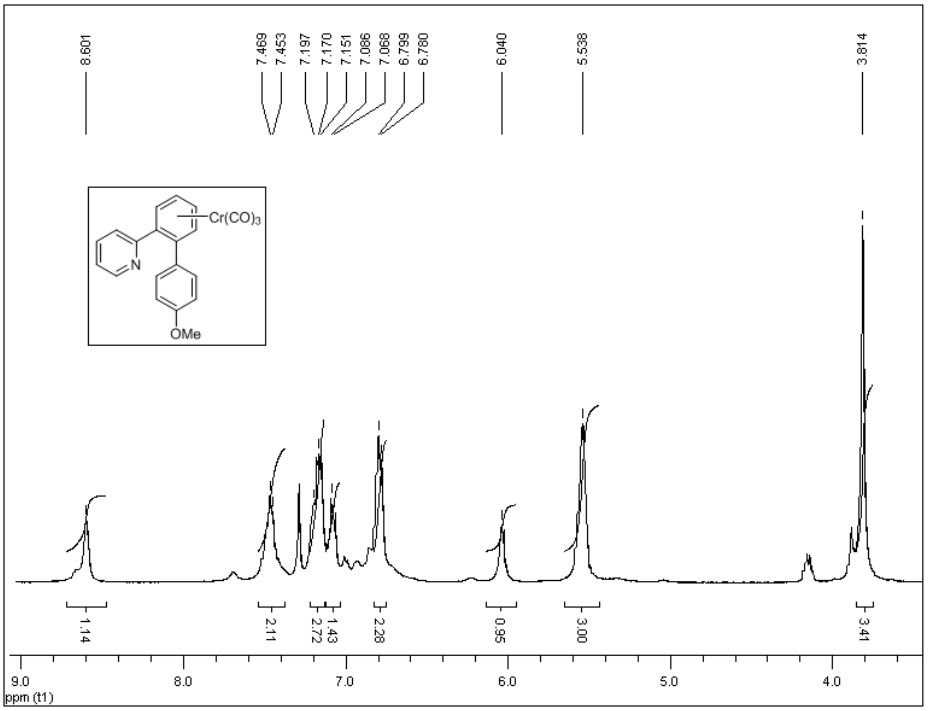


Fig. S10 ^{1}H NMR spectrum of compound **8**

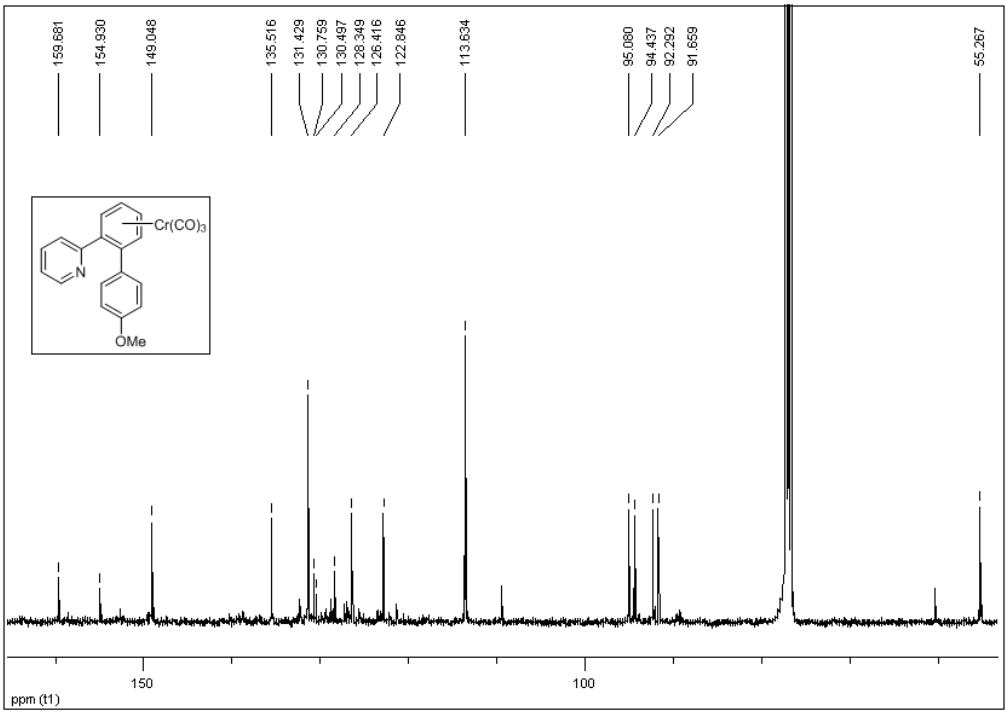


Fig. S11 ^{13}C NMR spectrum of compound **8**

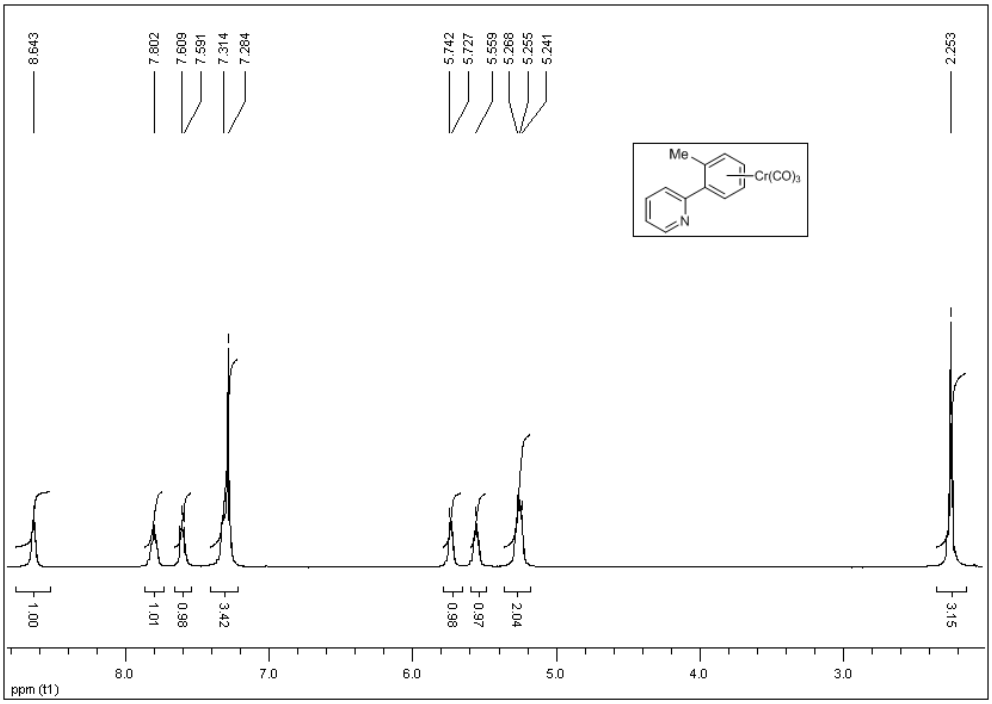


Fig. S12 ^{1}H NMR spectrum of compound **14**

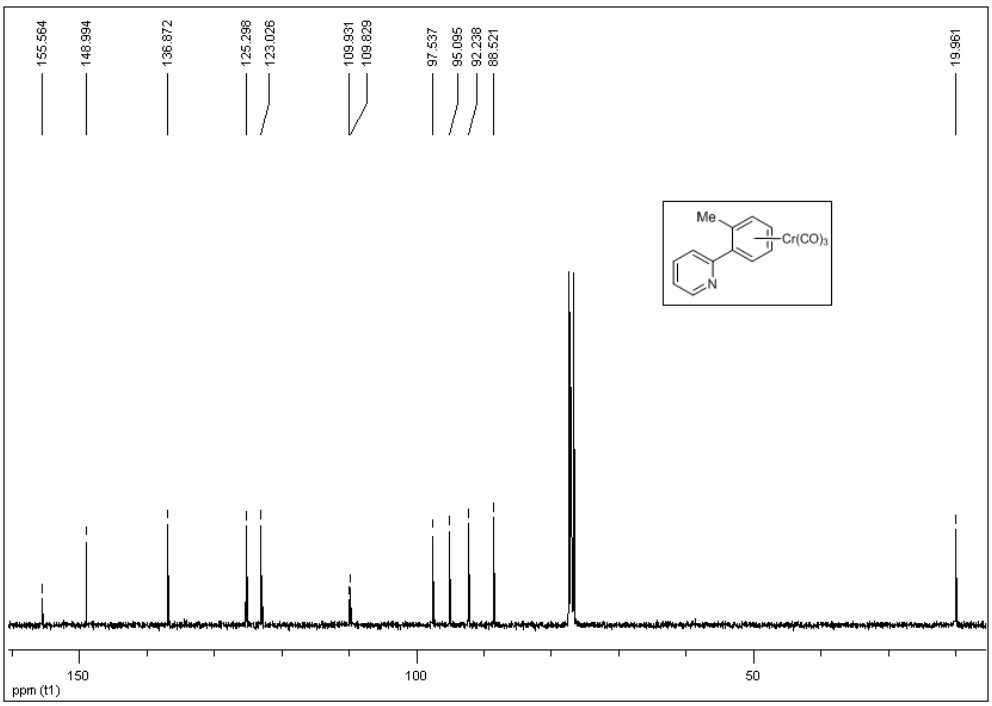


Fig. S13 ^{13}C NMR spectrum of compound **14**

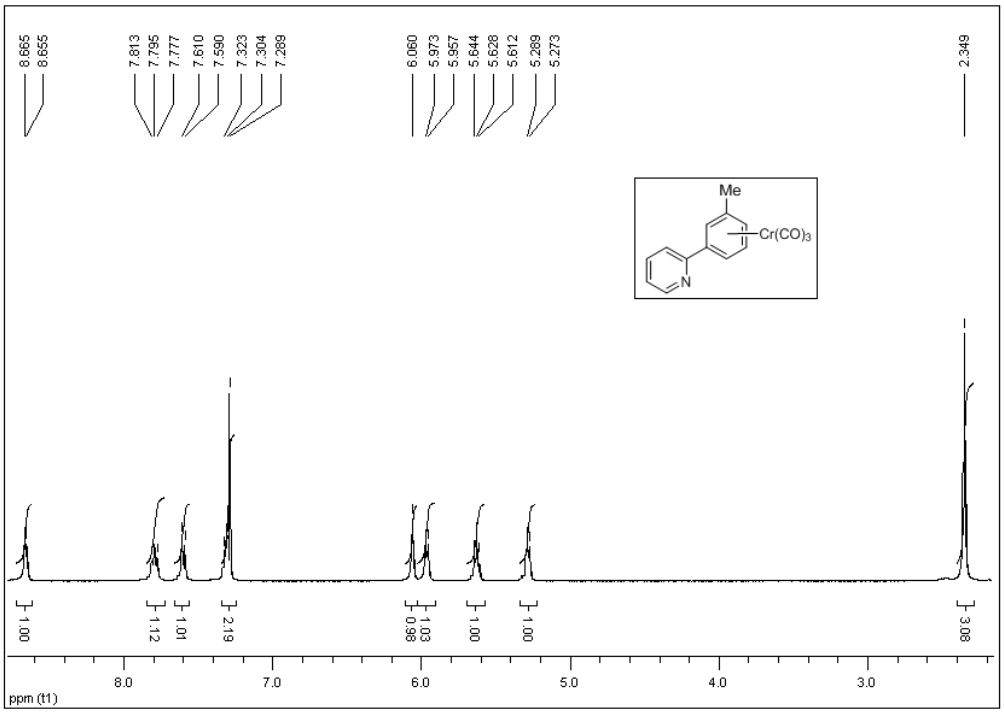


Fig. S14 ^{1}H NMR spectrum of compound **15**

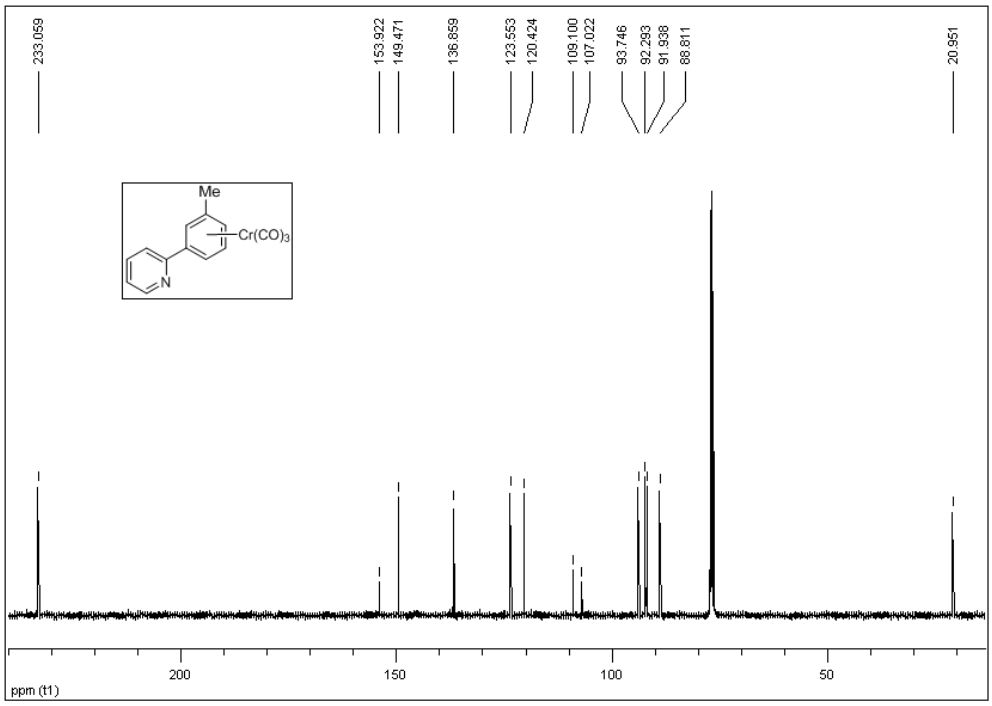


Fig. S15 ^{13}C NMR spectrum of compound **15**

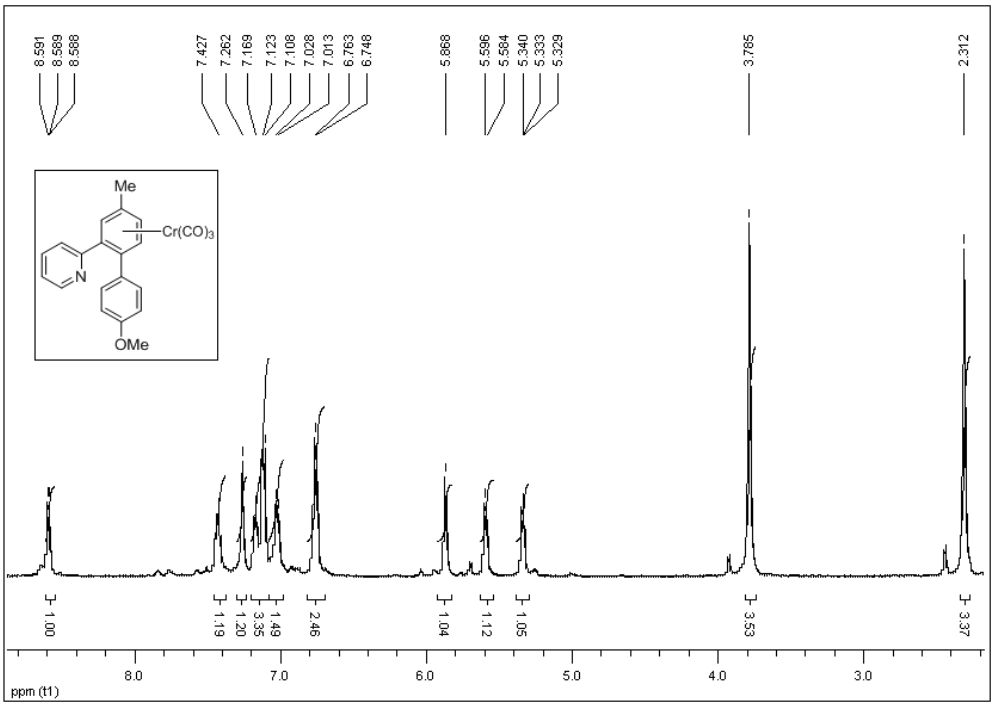


Fig. S16 ^{1}H NMR spectrum of compound **17**

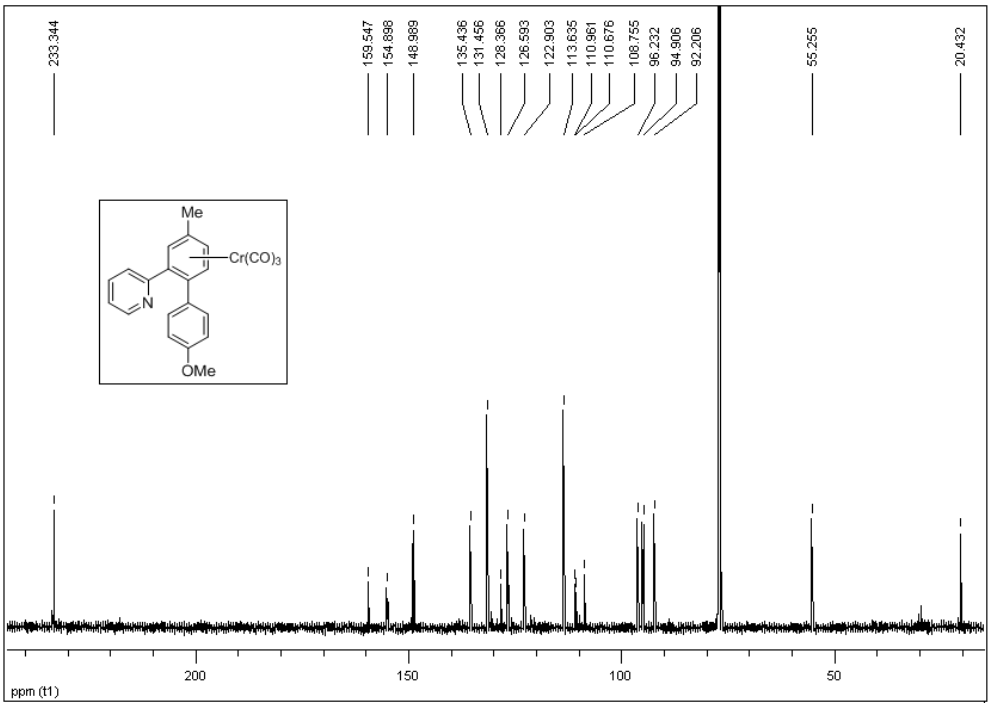


Fig. S17 ^{13}C NMR spectrum of compound **17**

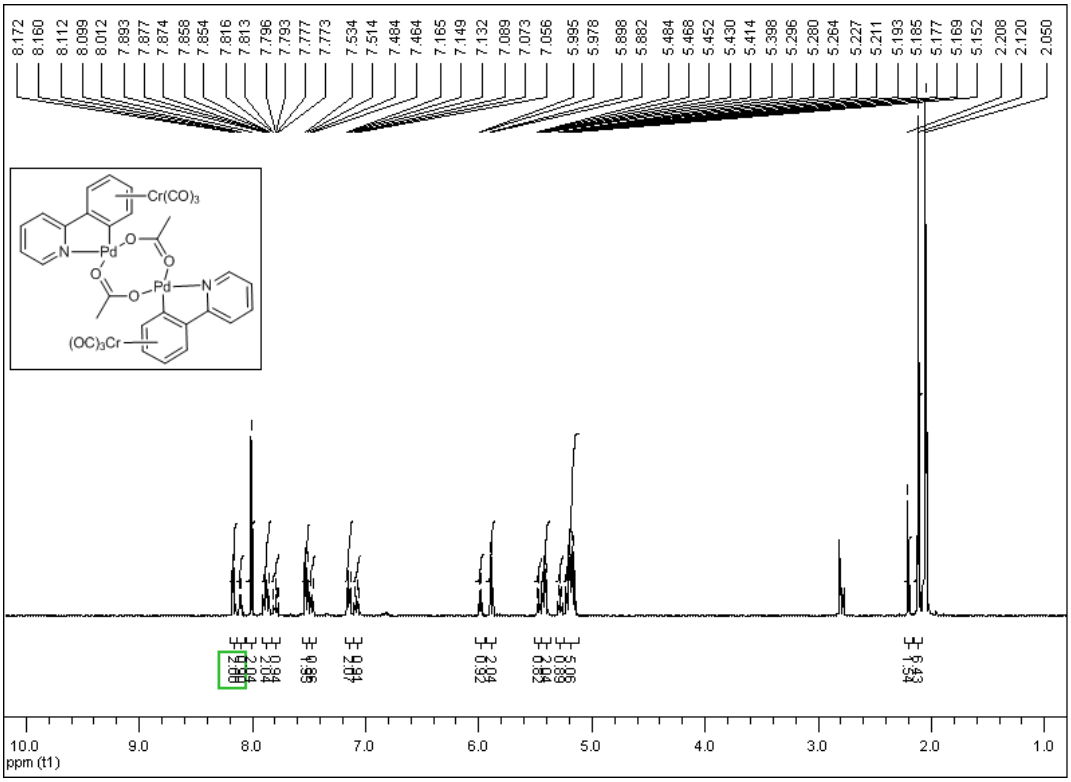


Fig. S18 ^{1}H NMR spectrum of palladacycle **4** and the unidentified by-product