SUPPORTING INFORMATION

A New Approach to Polyarylated Methanes via Cross-coupling of Tricarbonylchromium-Activated Organolithiums

Genette Itoko McGrew, Jesada Temaismithi, Patrick J. Carroll and Patrick J. Walsh*

P. Roy and Diana T. Vagelos Laboratories
Department of Chemistry, University of Pennsylvania
231 South 34th St., Philadelphia, PA 19104-6323

pwalsh@sas.upenn.edu

TABLE OF CONTENTS

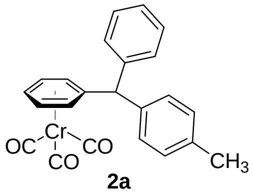
General Methods. All reactions were performed under nitrogen using oven-dried glassware. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. THF was freshly distilled from Na/benzophenone ketyl. Glyme and toluene were drawn from a Grubbs column. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich or Acros, and solvents were purchased from Fisher Scientific. Reactions were monitored by thin-layer chromatography using Whatman Partisil® K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wave ultra-violet light as well as by treatment with ceric ammonium molybdate (CAM) stain. NMR spectra were recorded in $CDCl_3$ on a Bruker 300 MHz Fourier-transform spectrometer. Chemical shifts are reported in ppm referenced to tetramethylsilane (TMS) or the $CHCl_3$ solvent residual peak at 7.26 ppm for ^1H and 77.23 ppm for $^{13}C\{^1H\}$; ^{19}F peaks were referenced to an external standard of trifluoroacetic acid in $CDCl_3$ at −76.55 ppm. Infrared spectra were obtained on NaCl using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. Chromium-complexed masses were recorded with Electrospray + (ES+) HRMS methods, and $[M]^+$ or $[M\text{ -}(CO)_3]^+$ was confirmed by the presence of the characteristic chromium isotope pattern. Decomplexed masses were recorded with Chemical Ionization + (CI+) HRMS methods, and $[M]^+$ or $[MH]^+$ were observed.

Compounds **1**, **3**, **6**, **9**, **11**, **15, 16**, **17**[a,b,c], **23**[d], and **24**[e] were prepared according to general literature procedure for the synthesis of arene tricarbonylchromium complexes from $Cr(CO)_6$ and parent arene, and were crystallized from dichloromethane and hexanes or purified by column chromatography eluting in diethyl ether in either pentane or hexanes to afford either yellow crystalline solids (**1**, **3**, **6**, **9**, **11**, **17**, **23**, and **24**), or viscous orange oils (**15** and **16**).

Caution: Care should be taken to avoid direct light exposure of reactions, as arene tricarbonylchromium complexes can decompose in solution under light. Compounds **15** and **16** require storage at or below 0 °C

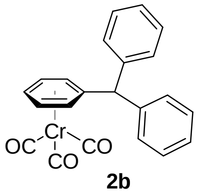
General procedures and characterizations for benzylic coupling reactions. The following procedures are representative of arene tricarbonylchromium coupling reactions with aryl bromides. Unless otherwise specified, chromatography was run in 2 – 50 % by volume diethyl ether in pentane.

General Procedure A:



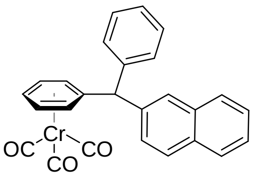
2a

2a – (4-C_6H_4-CH_3)PhCH(η^6-C_6H_5)Cr(CO)$_3$: An oven-dried glass reaction tube was charged with a small magnetic stirbar and **PhCH$_2$(η^6-C_6H_5)Cr(CO)$_3$ (1)** (44.5 mg, 0.146 mmol, 1.0 equiv), sealed with a septum, and purged with nitrogen. $PdCl_2(PPh_3)_2$ (3.2 mg, 0.0045 mmol, 3 mol %) and $LiN(SiMe_3)_2$ (38 mg, 0.23 mmol, 1.6 equiv) were dissolved in 1.0 mL of dry THF under a nitrogen atmosphere, forming an orange solution, to which neat 4-bromotoluene (28 μL, 0.23 mmol, 1.6 equiv) was added. The catalyst, base, and aryl bromide solution was taken up by syringe and added to **1**, which turned intensely red-orange. The reaction mixture was heated with stirring for 45 min at 57 ºC, then allowed to cool. The orange solution was quenched with two drops of aqueous 2N HCl and allowed to stir for 5 min. The golden solution was opened to air and diluted with 3 mL diethyl ether, then filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with an additional 1 mL diethyl ether and the solution was concentrated *in vacuo*, loaded directly onto a silica gel column, and eluted with 20% diethyl ether in pentane. The title compound **2a** (52.6 mg, 0.133 mmol, 91% yield) was obtained as a highly crystalline yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 3H), 7.19 – 7.12 (m, 4H), 7.06 (d, *J* = 6.3 Hz, 2H), 5.38 – 5.33 (m, 1H), 5.24 – 5.20 (m, 3H), 5.13 – 5.09 (m, 2H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.1, 141.8, 138.6, 137.0, 129.6, 129.5, 128.8, 127.3, 115.3, 95.55, 95.50, 93.2, 91.3, 54.6, 21.2; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; *meta*- and *meta'*- proton signals overlap with the benzylic proton; *meta- and meta'*- carbon signals overlap; IR 3027, 2923, 1963, 1877, 1512, 1494, 1453, 701, 661, 630 cm^{-1}. HRMS (ES+) calc'd for $C_{20}H_{18}Cr$ 310.0814, observed 310.0806 [M -(CO)$_3$]$^+$.



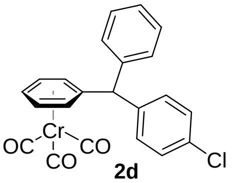
2b

2b – Ph$_2$CH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, **1 (**30.1 mg, 0.099 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (27 mg, 0.16 mmol, 1.6 equiv) and $PdCl_2(PPh_3)_2$ (2.5 mg, 0.0036 mmol, 3.6 mol %) in 0.8 mL THF and bromobenzene (17 μL, 0.16 mmol, 1.6 equiv) for 50 min at 56 ºC, yielding **2d** (34.6 mg, 0.091 mmol, 92% yield) as a bright yellow crystalline solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36 – 7.26 (m, 6H), 7.18 (m, 4H), 5.36 (t, *J* = 6.3 Hz, 1H), 5.24-5.20 (m, 3H), 5.11 (d, *J* = 6.3 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.1, 141.6, 129.6, 128.8, 127.4, 114.9, 95.6, 93.3, 91.2, 54.9; tricarbonylchromium-coordinated arene *meta*- protons overlap with the benzylic proton; IR 3085, 3053, 3028, 1963 and 1878 (strong CO stretch), 1626, 1568, 1495, 1452, 1415, 1301, 1268, 1213, 1184, 1081, 923, 826, 758, 741, 702, 662, 630, 619, 534 cm^{-1}; HRMS (ES+) calc'd for $C_{19}H_{16}Cr$ 296.0657, observed 296.0650 [M -(CO)$_3$]$^+$. Existing literature characterization corresponds with the characterization data for this compound.[f]



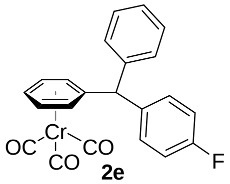
2c

2c – (2-naphthyl)PhCH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure A, **1** (15.2 mg, 0.050 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (12 mg, 0.070 mmol, 1.4 equiv) and PdCl$_2$(PPh$_3$)$_2$ (1.7 mg, 0.0025 mmol, 5 mol %) in 0.6 mL THF and 2-bromonaphthalene (12.3 mg, 0.060 mmol, 1.2 equiv) for 1 h at 57 ºC, yielding **2c** (19.5 mg, 0.045 mmol, 90% yield) as a pale yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.84 - 7.80 (m, 2H), 7.78 - 7.75 (m, 1H), 7.56 (br s, 1H), 7.50 - 7.45 (m, 2H), 7.37 - 7.28 (m, 4H), 7.26 - 7.23 (m, 2H), 5.41 - 5.36 (m, 2H), 5.28 - 5.20 (m, 2H), 5.17 - 5.11 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.1, 141.3, 139.4, 133.4, 132.6, 129.8, 128.8, 128.5, 128.3, 128.1, 127.9, 127.8, 127.5, 126.6, 126.4, 114.7, 95.8, 95.5, 93.4, 91.2, 55.0. Tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; *meta- and meta'*- carbon signals overlap; IR 3059, 3028, 1963 and 1877 (strong CO stretches), 1600, 1494, 1453, 1414, 816, 748, 702, 630, 660 cm^{-1}.

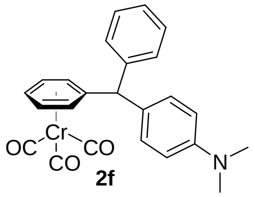


2d

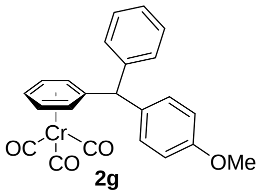
2d – (4-C$_6$H$_4$-Cl)PhCH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure A, **1** (45.8 mg, 0.151 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (40 mg, 0.24 mmol, 1.6 equiv) and PdCl$_2$(PPh$_3$)$_2$ (5.7 mg, 0.008 mmol, 5 mol %) in 2 mL THF and 1M 4-bromochlorobenzene THF solution (0.225 mL, 0.225 mmol, 1.5 equiv) for 6 h at 57 ºC, yielding **2d** (51.8 mg, 0.125 mmol, 83% yield), as a highly crystalline yellow solid after purification by silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.33 – 7.27 (m, 5H), 7.17 – 7.11 (m, 4H), 5.38 (t, *J* = 6.2 Hz, 1H), 5.23(m, 3H), 5.10 (d, *J* = 6.3 Hz, 1H), 5.05 (d, *J* = 6.3 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz) ppm 232.9, 141.24, 140.0, 133.4, 130.9, 129.5, 129.0, 128.9, 127.6, 114.2, 95.4, 95.2, 93.3, 91.2, 91.1, 54.3; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; *meta*- and *meta'*- proton signals overlap with the benzylic proton; IR 3080, 3027, 1964 and 1879 (strong CO stretch), 1625, 1568, 1491, 1454, 1184, 1091, 1015, 923, 813, 755, 661, 629, 619 cm^{-1}; HRMS (ES+) calc'd for $C_{19}H_{15}ClCr$ 330.0267, 330.0258 [M -(CO)$_3$]$^+$.


2e

2e – (4-C$_6$H$_4$-F)PhCH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure A, **1** (60.5 mg, 0.199 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (60.5 mg, 0.36 mmol, 1.8 equiv) and PdCl$_2$(PPh$_3$)$_2$ (7.6 mg, 0.01 mmol, 5 mol %) in 3 mL THF and 4-bromofluorobenzene (35 μL, 0.3 mmol, 1.5 equiv) for 6 h at 60 ºC, yielding **2e** (69.7 mg, 0.175 mmol, 88% yield) as a bright yellow crystalline solid after purification by silica gel chromatography. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37 – 7.24 (m, 3H), 7.17 – 7.13 (m, 4H), 7.02 (t, *J* = Hz, 2H), 5.37 (t, *J* = 6.2 Hz, 1H), 5.25 – 5.20 (m, 3H), 5.12 (d, *J* = 6.8 Hz, 1H), 5.05 (d, *J* = 6.6 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz) ppm 232.9, 162.1 (d, *J* = 347 Hz), 141.6, 131.13 (d, *J* = 8 Hz), 129.5, 128.9, 127.5, 115.7 (d, *J* = 21 Hz), 114.6, 95.5, 95.3, 93.4, 91.2, 91.1, 54.2; ^{19}F NMR (282 MHz) ppm −115.4 (m); tricarbonylchromium-coordinated arene carbons and protons exhibit diastereotopic signals; *meta*- and *meta'*- proton signals overlap with the benzylic proton; IR 3079, 3027, 2895, 2746, 1964 and 1877 (strong CO stretch), 1624, 1507, 1495, 1454, 1303, 1224, 1183, 1098, 922, 819, 741, 702, 661, 629, 619 cm^{-1}; HRMS (ES+) calc'd for $C_{19}H_{15}CrF$ 314.0563, observed 314.0549 [M -(CO)$_3$]$^+$.

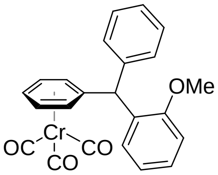

2f

2f – [4-C$_6$H$_4$-N(CH$_3$)$_2$]PhCH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure A, **1 (**30.2 mg, 0.099 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (27 mg, 0.16 mmol, 1.6 equiv) and PdCl$_2$(PPh$_3$)$_2$ (3.1 mg, 0.004 mmol, 4 mol %) in 1 mL THF and 4-bromo-*N*,*N*-dimethylaniline (29.9 mg, 0.15 mmol, 1.5 equiv) for 1 h at 52 ºC, yielding **2f** (38.2 mg, 0.090 mmol, 91% yield) as a shiny pale yellow flakes after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34 – 7.01 (m, 5H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.33 (t, *J* = 6.1 Hz, 1H), 5.25 – 5.20 (m, 2H), 5.16 – 5.08 (m, 3H), 2.94 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz) 233.3, 149.7, 142.4, 130.2, 129.5, 129.2, 128.7, 127.1, 116.3, 112.6, 95.7, 95.4, 93.1, 91.4, 54.0, 40.7 ppm; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; the *ortho'*- proton signal overlaps with the benzylic proton; *meta- and meta'*- carbon signals overlap; IR 3030, 2921, 2852, 2804, 1963 and 1878 (strong CO stretch), 611, 1520, 1452, 1352, 947, 702, 662, 630 cm^{-1}.


2g

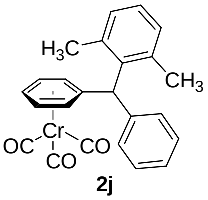
2g – (4-C$_6$H$_4$-OCH$_3$)PhCH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure A, **1** (44.8 mg, 0.147 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (39 mg, 0.23 mmol, 1.6 equiv) and

$PdCl_2(PPh_3)_2$ (4.2 mg, 0.006 mmol, 4 mol %) in 1 mL THF and 4-bromoanisole (32 μL, 0.25 mmol, 1.7 equiv) for 45 min at 56 ºC, yielding **2g** (56.7 mg, 0.138 mmol, 94% yield) as a yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.17 (d, *J* = 6.9 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7Hz, 2H), 5.35 (t, *J* = 6.6 Hz, 1H), 5.25 – 5.19 (m, 3H), 5.12 – 5.09 (m, 2H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.1, 158.9, 142.1, 133.6, 130.6, 129.5, 128.8, 127.3, 115.5, 114.2, 95.51, 95.48, 93.2, 91.3, 55.5, 54.1; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; *meta*- and *meta'*- proton signals overlap with the benzylic proton; *meta- and meta'*- carbon signals overlap; IR 3085, 3064, 3030, 3003, 2956, 2934, 2907, 2838, 1962 and 1875 (strong CO stretch), 1609, 1510, 1496, 1454, 1302, 1255, 1180, 1112, 1077, 1033, 922, 818, 741, 703, 662, 629, 619 cm^{-1}; HRMS (ES+) calc'd for $C_{20}H_{18}CrO$ 326.0763, observed 326.0933 [M -(CO)$_3$]$^+$.



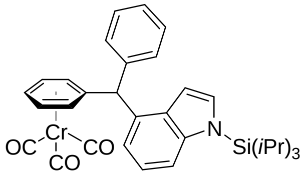
2h

2h – (2-C_6H_4-OCH_3)PhCH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, **1** (44.0 mg, 0.145 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (38 mg, 0.23 mmol, 1.6 equiv) and $PdCl_2(PPh_3)_2$ (4 mg, 0.006 mmol, 4 mol %) in 1 mL THF and 2-bromoanisole (31 μL, 0.25 mmol, 1.7 equiv) for 1 h at 54 ºC, yielding **2h** (54.0 mg, 0.132 mmol, 91% yield) as a highly crystalline yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 6H), 6.94 – 6.86 (m, 3H), 5.63 (s, 1H), 5.37 (t, *J* = 6.1 Hz, 1H), 5.28 (d, *J* = 7.0 Hz), 5.16 (t, *J* = 6.5 Hz, 2H), 5.08 (d, *J* = 6.5 Hz), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.2, 141.2, 130.8, 130.2, 129.6, 128.6, 128.5, 127.1, 120.4, 114.4, 111.1, 96.2, 96.1, 93.8, 90.42, 90.39, 55.6, 47.9; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3064, 3028, 2936 and 2838 (strong CO stretch), 1962, 1878, 1598, 1491, 1454, 1248, 1029, 755, 702, 662, 630 cm^{-1}.



2j

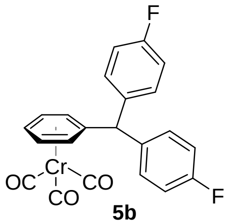
2j – [2,6-C_6H_3-$(CH_3)_2$]PhCH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, **1** (60.5 mg, 0.199 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (50.3 mg, 0.30 mmol, 1.5 equiv) and $PdCl_2(PPh_3)_2$ (6.8 mg, 0.01 mmol, 5 mol %) in 3.5 mL THF with 1-bromo-2,6-dimethylbenzene (55 μL, 0.4 mmol, 2 equiv) for 24 h at 58 ºC, yielding **2j** (65.3 mg, 0.16 mmol, 81% yield) as a yellow solid after silica gel chromatography eluting with 10% diethyl ether in pentane (5.7 mg, 10% of starting material **1** also isolated). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 3H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05 (broad d, *J* = 7.2 Hz, 2H), 5.84 (s, 1H), 5.30 – 5.25 (m, 4H), 5.09 (d, *J* = 6.3 Hz, 1H), 2.16 (very broad s, 6H); ^{13}C{^{1}H} NMR (75 MHz) ppm 133.4, 138.5, 137.2, 129.6, 128.9, 127.7, 127.5, 116.6, 95.16, 92.7, 92.2, 91.6, 49.5. tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; *meta- and meta'-* carbon signals overlap; signals from the non-axial carbons of the xylyl group were not observed in the $^{13}C\{^1H\}$ NMR due to the hindered rotation. IR 3064, 3022, 2962, 2914, 2743, 1961 and 1873 (strong CO stretch), 1625, 1495, 1467, 1455, 1301, 1214, 1183, 1097, 1078, 924, 821, 772, 738, 662, 629, 619 cm^{-1}; HRMS (ES+) calc'd for $C_{21}H_{20}Cr$ 324.097, observed 324.0985 [M -(CO)$_3$]$^+$.



2k

2k – [1-(triisopropylsilyl)-1*H*-indol-4-yl]PhCH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, **1** (30.4 mg, 0.100 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (25 mg, 0.15 mmol, 1.5 equiv) and PdCl$_2$(PPh$_3$)$_2$ (5 mg, 0.005 mmol, 7 mol %) in 1 mL THF and 4-bromo-1-TIPS-indole (45 mg, 0.13 mmol, 1.3 equiv) for 40 min at 58 ºC, yielding **2k** (51.4 mg, 0.089 mmol, 89% yield) as a shiny pale yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 (d, *J* = 8.3 Hz, 1H), 7.31 - 7.24 (m, 5H), 7.17 (d, *J* = 3.3 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 2.6 Hz, 1H), 5.62 (s, 1H), 5.45 (d, *J* = 6.9 Hz, 1H), 5.38 (t, *J* = 6.2 Hz, 1H), 5.23 - 5.18 (m, 2H), 5.01 (d, *J* = 6.6 Hz, 1H), 1.67 (septet, *J* = 7.5 Hz, 3H), 1.12 (d, *J* = 7.5 Hz, 18H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.3, 141.2, 140.6, 134.9, 131.5, 131.2, 129.7, 128.6, 127.3, 121.1, 120.1, 115.3, 113.1, 103.5, 96.9, 95.7, 93.7, 91.0, 90.8, 52.8, 18.4, 13.1; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3062, 3027, 2949, 2869, 1966 and 1883 (strong CO stretch), 1600, 1426, 1283, 1148, 1016, 883, 751, 631, 661 cm^{-1}.

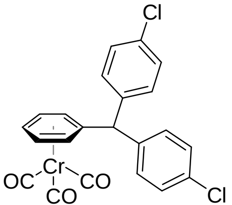
5a – Ph$_2$CH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, 45.8 mg (0.201 mmol, 1.0 equiv) of **(η^6-toluene)Cr(CO)$_3$ (3)** was reacted with 93.5 mg (0.57 mmol, 2.8 equiv) LiN(SiMe$_3$)$_2$ and 5.4 mg of PdCl$_2$(PPh$_3$) in 2 mL THF with 64 μL of bromobenzene (0.6 mmol, 3 equiv) for 5 h at 57 ºC, yielding 68.9 mg (0.181 mmol, 90% yield) of **5a**. All appearances and characterization data match that of **2b**.



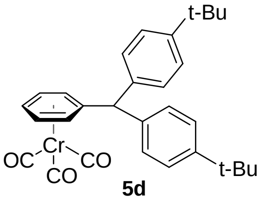
5b

5b – (4-C_6H_4-F)$_2$CH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, **3** (45.5 mg, 0.199 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (97 mg, 0.58 mmol, 2.9 equiv) and PdCl$_2$(PPh$_3$)$_2$ (5.1 mg, 0.007 mmol, 4 mol %) of in 2.5mL THF with 4-bromofluorobenzene (66 μL, 0.6 mmol, 3 equiv) for 5.5 h to yield **5b** (68.7 mg, 0.165 mmol, 83% yield) as a deep yellow solid after silica gel chromatography eluting with 13% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.15 – 7.11 (m, 4H), 7.06 – 7.00 (t, *J* = 8.5 Hz, 4H), 5.39 (t, *J* = 6.1 Hz, 1H), 5.25 – 5.20 (m, 3H), 5.06 (d, *J* = 6.2

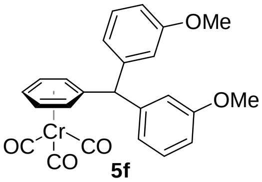
Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 232.8, 62.1 (d, J = 246.5 Hz), 137.2, 131.0 (d, J = 8.0 Hz), 115.8 (d, J = 21.4 Hz), 114.2, 95.2, 93.4, 91.1, 53.4; ^{19}F NMR (282 MHz) ppm −118.1 (m); tricarbonylchromium-coordinated arene *meta*- proton signals overlap with the benzylic proton; IR 3074, 3044, 1966 and 1880 (strong CO stretch), 1631, 1605, 1506, 1457, 1321, 1302, 1268, 1225, 1185, 1159, 1100, 924, 824, 661, 629 cm^{-1}; HRMS (ES+) calc'd for $C_{19}H_{14}CrF_2$ 332.0469, observed 332.0460 [M -(CO)$_3$]$^+$.


5c

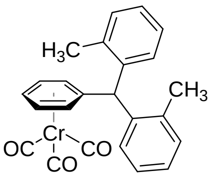
5c – $(4\text{-}C_6H_4\text{-}Cl)_2CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure A, **2** (11.4 mg, 0.050 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (34 mg, 0.20 mmol, 4 equiv) and $PdCl_2(PPh_3)_2$ (3.9 mg, 0.005 mmol, 10 mol %) in 0.6 mL THF and 1M 4-bromochlorobenzene THF solution (0.125 mL, 0.125 mmol, 2.5 equiv) for 2 h at 53 ºC to yield **5c** (17.5 mg, 0.039 mmol, 78%) as a highly crystalline yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H), 5.38 (t, J = 6.2 Hz, 1H), 5.23 (t, J = 6.3Hz, 2H), 5.18 (s, 1H), 5.04 (d, J = 6.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 232.7, 139.6, 133.6, 130.8, 129.1, 113.5, 95.0, 93.3, 91.1, 53.6; IR 3090, 3027, 1965 and 1881 (strong CO stretch), 1490, 1405, 1092, 1014, 810, 659, 629 cm^{-1}.


5d

5d – $[4\text{-}C_6H_4\text{-}C(CH_3)_3]_2CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure A, **3** (34 mg, 0.149 mmol, 1.0 equiv) of was reacted with $LiN(SiMe_3)_2$ (70 mg , 0.42 mmol, 2.8 equiv) and $PdCl_2(PPh_3)_2$ (10.9 mg, 0.015 mmol, 10 mol %) in 4 mL THF with 4-*tert*-butyl-bromobenzene (65 μL, 0.45 mmol, 3 equiv) for 5 h at 46 ºC to yield **5d** (60.0 mg, 0.122 mmol, 82% yield) as a pale yellow solid after silica gel chromatography eluting with 3% diethyl ether in pentane. ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 4H), 7.10 (d, J = 8.4 Hz, 4H), 5.34 (t, J = 6.2 Hz, 1H), 5.22 (t, J = 6.3 Hz, 2H), 5.16 – 5.13 (m, 3H), 1.30 (S, 18H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.3, 150.1, 138.7, 129.2, 125.6, 115.9, 95.6, 93.1, 91.3, 54.1, 34.7, 31.6; tricarbonylchromium-coordinated arene *ortho*- proton signals overlap with the benzylic proton; IR 3028, 2965, 2905, 2870, 1960 and 1880 (strong CO stretch), 1476, 1461, 1365, 1265, 704, 667, 623 cm^{-1}. HRMS (ES+) calc'd for $C_{27}H_{32}Cr$ 408.1909, found 408.1901 [M -(CO)$_3$]$^+$.

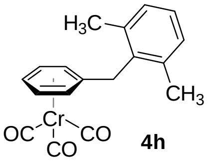

5f

5e – $(3\text{-}C_6H_4\text{-}OCH_3)_2CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure A, **3** (34.8 mg, 0.153 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (96 mg, 0.57 mmol, 3.7 equiv) and $PdCl_2(PPh_3)_2$ (8.3 mg, 0.012 mmol, 8 mol %) in 3 mL THF and 3-bromoanisole (57 μL, 0.45 mmol, 3 equiv) for 1.5 h at 57 ºC to yield **5f** (57.7mg, 0.131 mmol, 86% yield) as a yellow solid after silica gel chromatography eluting with 15% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.5 Hz, 2H), 6.82 – 6.73 (m, 6H), 5.36 (t, *J* = 6.1 Hz, 1H), 5.23 (t, *J* = 6.4 Hz, 2H), 5.17 – 5.13 (m, 3H), 3.79 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.1, 159.9, 143.0, 129.7, 122.0, 115.6, 114.9, 112.7, 95.5, 93.3, 91.3, 55.4, 54.9; tricarbonylchromium-coordinated arene *ortho*- proton signals overlap with the benzylic proton; IR 3079, 3005, 2940, 2837, 1961 and 1874 (strong CO stretch), 1598, 1584, 1488, 1455, 1266, 1049, 759, 662, 631 cm^{-1}; HRMS (ES+) calc'd for $C_{21}H_{20}CrO_2$ 356.0868, observed 356.0866 $[M -(CO)_3]^+$.



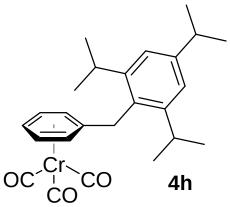
5g

5f – $(2\text{-}C_6H_4\text{-}CH_3)_2CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure A, **3** (45 mg, 0.197 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (94 mg, 0.56 mmol, 2.8 equiv) and $PdCl_2(PPh_3)_2$ (13 mg, 0.018 mmol, 9 mol %) in 4.2 mL THF and 2-bromotoluene (75 μL, 0.6 mmol, 3 equiv) for 12 h at 58 ºC to yield 70.7 mg (0.173 mmol, 88% yield) of **5g** as a yellow solid after silica gel chromatography eluting with 10% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 6H), 6.93 (d, *J* = 7.4 Hz, 2H), 5.52 (t, *J* = 6.1 Hz, 1H), 5.45 (s, 1H), 5.29 (d, *J* = 6.3 Hz, 2H), 5.11 (t, *J* = 6.3 Hz, 2H), 2.41 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.0, 140.0, 137.2, 131.2, 129.4, 127.2, 126.1, 111.9, 97.5, 95.8, 88.8, 47.5, 19.9; IR 3073, 3020, 2945, 2913, 1963 and 1877 (strong CO stretch), 1628, 1492, 1461, 1297, 1213, 1183, 1101, 1056, 923, 823, 742, 729, 663, 629 cm^{-1}.



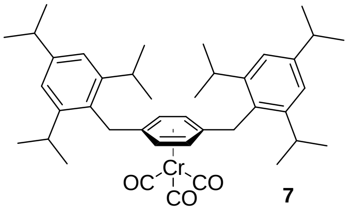
4h

4g – $[2,6\text{-}C_6H_3\text{-}(CH_3)_2]CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure A, **3** (91.4 mg, 0.401 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (98.5 mg, 0.59 mmol, 1.5 equiv) and $PdCl_2(PPh_3)_2$ (15.5 mg, 0.022 mmol, 5 mol %) in 4 mL THF and 1-bromo-2,6-dimethybenzene (0.11 mL, 0.8 mmol, 2 equiv) for 8 h at 63 ºC to yield **4h** (114 mg. 0.343 mmol, 86% yield) as a fluffy yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane . ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (m, 3H), 5.32 (t, *J* = 6.3 Hz, 2H), 5.21 (m, 3H), 3.91 (s, 2H), 2.33 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.4, 137.3, 134.6, 128.8, 127.4, 111.4, 93.9, 92.8, 91.8, 33.7, 20.7; tricarbonylchromium-coordinated arene *ortho*- and *para*- proton signals overlap; IR 3074, 3041, 2944, 1971 and 1858 (strong CO stretch), 1625, 1502, 1462, 1300, 1213, 1184, 1097, 923, 820, 775, 736, 672, 632, 616 cm^{-1}; HRMS (ES+) calc'd for $C_{15}H_{16}Cr$ 248.0657, observed 248.0653 $[M -(CO)_3]^+$.



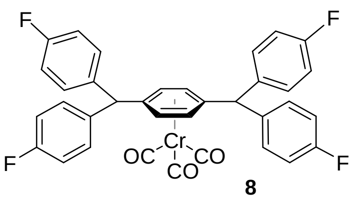
4h

4h – (2,4,6-C_6H_2-^{i}Pr$_3$)CH(η^6-C_6H_5)Cr(CO)$_3$: Using the general procedure, **3** (45.5 mg 0.199 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (50 mg, 0.30 mmol, 1.5 equiv) and PdCl$_2$(PPh$_3$)$_2$ (8.5 mg, 0.012 mmol, 6 mol %) in 1.5 mL THF and 2,4,6-triisopropylbromobenzene (74 μL, 0.4 mmol, 2 equiv) for 12 h at 63 ºC to yield **4h** (69.4 mg, 0.162 mmol, 87% yield) as a fluffy pale yellow solid after column chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.02 (s, 2H), 5.33 (t, *J* = 6.4 Hz, 2H), 5.19 (m, 3H), 3.95 (s, 2H), 3.09 (m, *J* = 6.8 Hz, 2H), 2.89 (m, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.4, 148.2, 147.7, 128.5, 121.6, 113.7, 94.1, 92.8, 91.7, 34.4, 31.5, 30.2, 24.5, 24.2; tricarbonylchromium-coordinated arene *ortho*- and *para*- proton signals overlap; IR (CH$_2$Cl$_2$ film) 2962, 2928, 2869, 1965 and 1882 (strong CO stretch), 1607, 1574, 1526, 1457, 1384, 1363, 1153, 879, 664, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{22}H_{30}Cr$ 346.1753, observed 346.1765 [M -(CO)$_3$]$^+$.



7

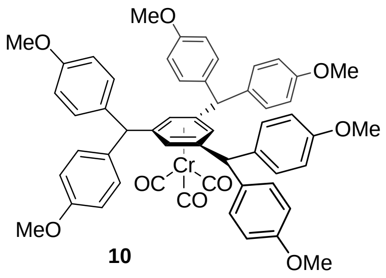
7 – 1,4-[2,4,6-C_6H_2-^{i}Pr$_3$CH$_2$]$_2$(η^6-C_6H_4)Cr(CO)$_3$: Using general procedure A, **(η^6-*p*-xylene)Cr(CO)$_3$ (6)** (23.9 mg, 0.099 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (82 mg, 0.49 mmol, 4.9 equiv) and PdCl$_2$(PPh$_3$)$_2$ (8.4 mg, 0.012 mmol, 12 mol %) in 2.4 mL THF and 2,4,6-triisopropylbromobenzene (56 μL, 0.3 mmol, 3 equiv) for 24 h at 55 ºC to yield **7** (46.4 mg, 0.072 mmol, 73% yield) as a fluffy pale yellow solid after silica gel chromatography eluting with 3% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.97 (s, 4H), 5.20 (s, 4H), 3.88 (s, 4H), 3.04 (m, *J* = 6.8Hz, 4H), 2.87 – 2.82 (m, *J* = 6.9Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 12H), 1.15 (d, *J* = 6.9 Hz, 24 H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.8, 148.1, 147.6, 128.6, 121.5, 112.2, 94.0, 34.4, 31.0, 30.1, 24.2, 24.2; IR 3058, 2962, 2928, 2869, 1962 and 1882 (strong CO stretch), 1608, 1462, 1384, 1363, 1101, 878, 667, 625 cm^{-1}; HRMS (ES+) calc'd for $C_{38}H_{54}Cr$ 562.3631, found 562.3657 [M -(CO)$_3$]$^+$.



8

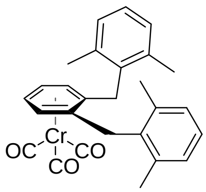
8 – 1,4-[(4-C_6H_4-F)$_2$CH]$_2$(η^6-C_6H_4)Cr(CO)$_3$: Using general procedure A, **6** (12.1 mg, 0.050 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (75.6 mg, 0.45 mmol, 9.0 equiv) and PdCl$_2$(PPh$_3$)$_2$ (3.6 mg, 0.005 mmol, 10 mol %) in 1.0 mL THF and 4-bromofluorobenzene (33 μL, 0.3 mmol, 6 equiv) for 20 h at 58 – 60 ºC to yield **8** (21.5 mg, 0.035 mmol, 70% yield) as a highly crystalline pale yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.12 (m, 4H), 7.02 (t, *J* = Hz, 4H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz) ppm 232.8, 162.1 (d, *J* = 247 Hz), 137.1, 130.9 (d, *J* = 8 Hz), 115.9

(d, J = 22 Hz), 114.6, 93.7, 35.0 ; ^{19}F NMR (282 MHz) ppm −117.9 (m); IR 3112, 3077, 3044, 2884, 2747, 1963 and 1876 (strong CO stretch), 1766, 1630, 1567, 1505, 1468, 1300, 1223, 1183, 1159, 1100, 924, 826, 737, 665, 622 cm^{-1}. HRMS (ES+) calc'd for $C_{32}H_{22}CrF_4$ 618.0910, found 618.0919 [M]$^+$.



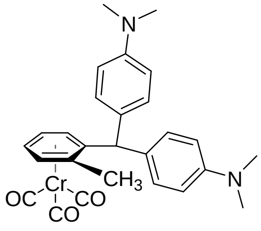
10

10 – 1,3,5-[(4-C_6H_4-OCH_3)$_2$CH]$_3$(η^6-C_6H_3)Cr(CO)$_3$: Using general procedure A, **(η^6-mesitylene)Cr(CO)$_3$ (9)** (25.5 mg (0.099 mmol, 1.0 equiv) was reacted with LiN($SiMe_3$)$_2$ (188 mg, 1.1 mmol, 11 equiv) and $PdCl_2(PPh_3)_2$ (14.1 mg, 0.02 mmol, 20 mol %) in 2.6 mL of THF and 4-bromoanisole (0.125 mL, 1.0 mmol, 10 equiv) for 5 h at 55 ºC to yield **10** (38.6 mg, 0.043 mmol, 43% yield) as a yellow crystalline solid after silica gel chromatography eluting with 40% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (d, J = 8.6 Hz, 12H), 6.81 (d, J = 8.6 Hz, 2H), 4.94 (s, 3H), 4.93 (s, 3H), 3.81 (s, 18H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.4, 158.6, 134.4, 130.3, 113.9, 113.6, 97.6, 55.5, 53.0; the tricarbonylchromium-coordinated arene proton signal overlaps with the benzylic proton sigmal; IR 3071, 3000, 2953, 2932, 2903, 2835, 1956 and 1874 (strong CO stretch), 1766, 1611, 1509, 1464, 1302, 1250, 1179, 1112, 1035, 925, 830, 736, 667, 625 cm^{-1}; HRMS (ES+) calc'd for $C_{54}H_{48}CrO_9$ 892.2703, found 892.2746 [M]$^+$. *X-ray crystal structure was determined for this compound; see **S28**.*



12

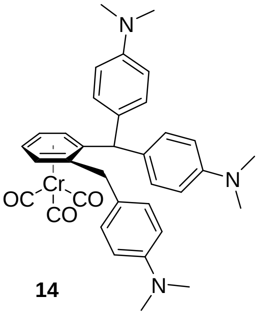
12 – 1,2-[(2,6-C_6H_3-Me_2)CH_2]$_2$(η^6-C_6H_4)Cr(CO)$_3$: Using general procedure A, **(η^6-*o*-xylene)Cr(CO)$_3$ (11)** (12.2 mg, .0504 mmol, 1.0 equiv) was reacted with LiN($SiMe_3$)$_2$ (50 mg, 0.30 mmol, 6 equiv) and $PdCl_2(PPh_3)_2$ (4.9 mg, 7 μmol, 14 mol %) in 0.75 mL THF and 2-bromo-*m*-xylene (20 μL, 0.15 mmol, 3 equiv) for 5 h at 62 ºC to yield **12** (19.3 mg, 0.0428 mmol, 85% yield) as a pale yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (m, 6H), 5.10 (dd, J = 4.7, 2.9 Hz, 2H), 4.87 (dd, J = 4.6, 3.0 Hz, 2H), 4.11 (s, 1H), 2.37 (s, 12H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.7, 137.6, 133.9, 128.8, 127.5, 109.9, 92.9, 92.1, 31.1, 20.3; IR 2923, 2853, 1952 and 1869 (strong CO stretch), 1470, 1434, 1381, 1027, 769, 666 cm^{-1}; HRMS (ES+) calc'd for 450.1287 $C_{27}H_{26}CrO_3$, found 450.1274 [M]$^+$.



13

13 – 1-[(4-C_6H_4-NMe_2)$_2$CH]-2-Me-(η^6-C_6H_4)Cr(CO)$_3$: Using general procedure A, **(η^6-*o*-xylene)Cr(CO)$_3$ (11)** (12.1 mg, 0.050 mmol, 1 equiv) was reacted with LiN($SiMe_3$)$_2$ (26 mg, 0.15 mmol, 3 equiv) and $PdCl_2(PPh_3)_2$ (4.2 mg, 6 μmol, 12 mol %)

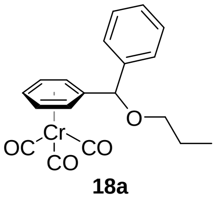
in 0.7 mL THF and 4-bromo-*N*,*N*-dimethylaniline (30 mg, 0.15 mmol, 3 equiv) for 10 h at 48 ºC to yield **13** (15.4 mg, 0.032 mmol, 64% yield) as a yellow solid after silica gel chromatography eluting with 40% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, J = 8.8 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.67 (m, 4H), 5.39 (dt, *J* = 1.1, 6.3 Hz, 1H), 5.19 (s, 1H), 5.11 - 5.06 (m, 2H), 4.92 (dd, *J* = 0.7, 6.2 Hz, 1H), 2.93 (s, 6 H), 2.92 (s, 6H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.9, 149.7, 149.4, 130.7, 130.4, 129.7, 128.7, 116.4, 112.7, 112.5, 110.3, 96.2, 94.6, 93.1, 89.8, 50.8, 40.8, 19.5; diastereotopic carbon signals on dimethylamino group overlap (40.8 ppm); IR 3074, 2922, 2854, 2804, 1958 and 1873 (strong CO stretche), 1611, 1520, 1352, 1227, 1203, 1166, 947, 816, 667, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{24}H_{29}N_2$ 345.2331, found 345.2324 $[MH - Cr(CO)_3]^+$.



14

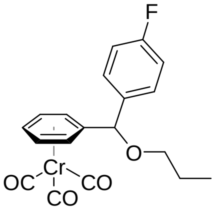
14 –1-[(4-C_6H_4-NMe_2)$_2$CH]-2-[(4-C_6H_4-NMe_2)CH_2](η^6-C_6H_4)$Cr(CO)_3$: Using general procedure A, **(η^6-*o*-xylene)$Cr(CO)_3$ (11)** (12.3 mg, 0.0508 mmol, 1 equiv) was reacted with $LiN(SiMe_3)_2$ (39 mg, 0.25 mmol, 5 equiv) and $PdCl_2(PPh_3)_2$ (5 mg, 7 µmol, 14 mol %) in 0.75 mL THF and 4-bromo-*N*,*N*-dimethylaniline (42 mg, 0.2 mmol, 4 equiv) for 24 h at 48 ºC to yield **12** (14.6 mg, 0.024 mmol, 48% yield) as a pale yellow solid after silica gel chromatography eluting with 40% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.71 - 6.63 (m, 6H), 5.38 (s, 1H), 5.27 (dt, *J* = 1.1, 6.3 Hz, 1H), 5.11 (dt, *J* = 1.1, 6.3 Hz, 1H), 4.90 (dd, *J* = 0.9, 6.4 Hz, 1H), 4.66 (dd, *J* = 1.0, 6.2 Hz, 1H), 3.88 (d, *J* = 16.6, Hz, 1H), 3.42 (d, *J* = 16.7 Hz, 1H), 2.94 (s, 6H), 2.93 (s, 6H), 2.92 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 234.0, 149.73, 149.69, 149.5, 130.9, 130.8, 130.3, 129.8, 129.0, 124.3, 116.5, 115.1, 112.9, 112.5, 95.6, 94.0, 92.8, 90.6, 50.4, 50.83, 40.79, 35.9; diastereotopic carbons on dimethylamino groups overlap (112.9, 40.8 ppm); IR 2917, 2850, 2800, 1957 and 1870 (strong CO stretches), 1613, 1520, 1444, 1351, 1202, 1164, 947, 811, 667, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{32}H_{38}N_3$ 464.3066, found 464.3051 $[MH - Cr(CO)_3]^+$.

General Procedure B (for sensitive liquid substrates):



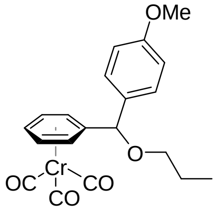
18a

18a – ^{n}PrOPhCH(η^6-C_6H_5)$Cr(CO)_3$: An oven-dried reaction tube was charged with a small magnetic stirbar, $PdCl_2(PPh_3)_2$ (8.5 mg, 0.012 mmol, 6 mol %) and $LiN(SiMe_3)_2$ (13 mg, 0.08 mmol, 0.4 equiv) under nitrogen and sealed with a septum. 1.4 mL of dry THF was added via syringe with stirring, forming a red-orange solution to which neat bromobenzene (27 μL, 0.26 mmol, 1.3 equiv) was added. The catalyst, base, and aryl bromide solution was allowed to stir for 5 min, and neat **^{n}PrOCH$_2$(η^6-C_6H_5)Cr(CO) (15)** (44 μL, 0.20 mmol, 1.0 equiv) was added. The reaction mixture was heated with stirring at 57 ºC. A separate portion of LiN(SiMe$_3$)$_2$ (54 mg, 0.32 mmol, 1.6 equiv) was dissolved in 0.35 mL dry THF and added via syringe over 1.5 h. The reaction mixture was heated for an additional 30 min before cooling to room temperature and quenching with 2 drops H_2O. The orange solution was then opened to air, diluted with 3 mL diethyl ether, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional diethyl ether and the resulting solution was concentrated *in vacuo,* loaded onto a silica gel column and eluted with 6% diethyl ether in pentane. The result was **18a** (58.9 mg, 0.162 mmol, 81% yield) as an orange oil. Upon storage at 0 ºC, product crystallized as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 5.70 (broad d, *J* = 6.3 Hz, 1H), 5.34 (dt, *J* = 1.4 Hz, 6.2 Hz, 1H), 5.26 - 5.17 (m, 2H), 5.12 - 5.09 (m, 1H), 5.00 (s, 1H), 3.49 - 3.36 (m, 2H), 1.65 (sextet, *J* = 7.0 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.2, 140.5, 129.0, 128.7, 127.4, 113.9, 92.3, 92.2, 91.9, 91.7, 91.6, 81.5, 71.6, 55.6, 23.2, 10.9; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3031, 2965, 2936, 2876, 1965 and 1881 (strong CO stretches), 1455, 1100, 1075, 753, 703, 661, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{16}H_{18}CrO$ 278.0763, found 278.0753 [M -(CO)$_3$]$^+$.



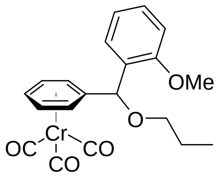
18b

18b – ^{n}PrO(4-C_6H_4-F)CH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure B, **15** (88 μl, 0.40 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (28 mg, 0.16 mmol, 0.25 equiv) and PdCl$_2$(PPh$_3$)$_2$ (16 mg, 0.022 mmol, 5.5 mol %) in 2.5 mL THF and 4-bromofluorobenzene (70 μL, 0.64 mmol, 1.6 equiv) and heated at 57 ºC. More LiN(SiMe$_3$)$_2$ (108 mg, 0.64 mmol, 1.6 equiv) dissolved in 0.7 mL THF was added over 1h. The reaction was allowed to proceed for an additional 1.8 h, and yielded **18b** (115 mg, 0.30 mmol, 75% yield) as a viscous orange oil after silica gel chromatography eluting with 6% diethyl ether in pentane. Upon storage at 0 ºC, **18b** became a crystalline yellow-orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.33 (m, 2H), 7.07 (apparent t, *J* = 8.4 Hz, 2H), 5.65 (d, *J* = 6.2 Hz, 1H), 5.33 (t, *J* = 5.9 Hz, 1H), 5.27 - 5.18 (m, 2H), 5.09 (d, *J* = 6.2 Hz, 1H), 5.00 (s, 1H), 33.48 - 3.34 (m, 2H), 1.65 (sextet, *J* = 6.9 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.0, 162.9 (d, *J* = 247 Hz), 136.2 (d, *J* = 3 Hz), 129.1 (d, *J* = 8.3 Hz), 115.9 (d, *J* = 21.9), 113.5, 92.4, 92.0, 91.9, 91.8, 91.7, 80.8, 71.7, 23.2, 10.9; ^{19}F NMR (282 MHz) ppm −113.3 (m); tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3088, 2966, 2937, 2877, 1967 and 1885 (strong CO stretch), 1604, 1508, 1456, 1224, 1157, 1090, 823, 810, 660, 630 cm^{-1}.



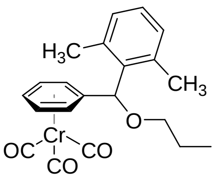
18c

18c – ^{n}PrO(4-C$_6$H$_4$-OMe)CH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure B, **15** (22 μl, 0.10 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (8 mg, 0.05 mmol, 0.5 equiv) and PdCl$_2$(PPh$_3$)$_2$ (3.5 mg, 0.005 mmol, 5 mol %) in 0.7 mL THF and 4-bromoanisole (18 μL, 0.15 mmol, 1.5 equiv) and heated at 58 ºC. More LiN(SiMe$_3$)$_2$ (24 mg, 0.15 mmol, 1.5 equiv) dissolved in 0.3 mL THF was added over 30 min. The reaction was allowed to proceed for an additional 1 h, and yielded **14c** (31.4 mg, 0.080 mmol, 80% yield) as an orange oil after silica gel chromatography eluting with 20% diethyl ether in pentane. Upon storage at 0 °C, **18c** became a yellow-orange solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.69 (d, *J* = 6.5 Hz, 1H), 5.36 - 5.32 (m, 1H), 5.23 - 5.20 (m, 2H), 5.09 (br d, *J* = 5.7 Hz, 1H), 4.97 (s, 1H), 3.81 (s, 3H), 3.43 - 3.38 (m, 2H), 1.64 (sextet, *J* = 7.0 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.2, 159.9, 132.5, 128.7, 114.4, 114.3, 92.3, 92.2, 92.1, 91.1, 91.7, 81.0, 71.4, 55.5, 23.2, 10.9; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3087, 2964, 2936, 2876, 1965 and 1882 (strong CO stretches), 1610, 1510, 1457, 1248, 1172, 1095, 1033, 661, 631 cm^{-1}.



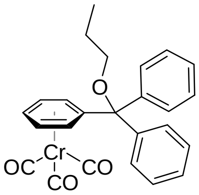
18d

18d – ^{n}PrO(2-C$_6$H$_4$-OMe)CH(η^6-C$_6$H$_5$)Cr(CO)$_3$: Using general procedure B, **15** (22 μl, 0.10 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (7 mg, 0.042 mmol, 0.4 equiv) and PdCl$_2$(PPh$_3$)$_2$ (4.9 mg, 0.007 mmol, 7 mol %) in 0.8 mL THF and 2-bromoanisole (20 μL, 0.16 mmol, 1.6 equiv) and heated at 58 ºC. More LiN(SiMe$_3$)$_2$ (24 mg, 0.15 mmol, 1.5 equiv) dissolved in 0.2 mL THF was added over ~50 min. The reaction was allowed to proceed for an additional 1.7 h, and yielded **18d** (30.3 mg, 0.077 mmol, 77% yield) as an orange oil after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 (dd, *J* = 1.7, 7.6 Hz, 1H), 7.30 - 7.27 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.70 (d, *J* = 6.4 Hz, 1H), 5.52 (s, 1H), 5.41 (d, *J* = 6.3 Hz, 1H), 5.29 (dt, *J* = 1.4, 6.3 Hz, 1H), 5.24 - 5.15 (m, 2H), 3.88 (s, 3H), 3.47 - 3.38 (m, 2H), 1.65 (sextet, *J* = 7.0 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.4, 157.1, 129.43, 129.36, 127.2, 121.2, 114.5, 110.8, 92.5, 92.2, 91.9, 91.8, 91.6, 74.1, 71.6, 55.6, 23.2, 10.9; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3080, 2964, 2937, 2877, 1964 and 1882 (strong CO stretch), 1600, 1489, 1463, 1242, 1112, 1090, 1027, 757, 662, 631 cm^{-1}.



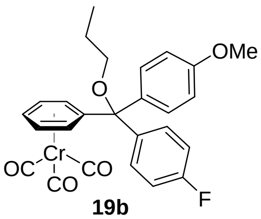
18e

18e – ^{n}PrO(2,6-$C_6H_3Me_2$)CH(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure B, **15** (22 µl, 0.10 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (8 mg, 0.05 mmol, 0.5 equiv) and PdCl$_2$(PPh$_3$)$_2$ (5.6 mg, 0.008 mmol, 8 mol %) in 1.0 mL THF and 2-bromo-*m*-xylene (20 µL, 0.15 mmol, 1.5 equiv) and heated at 58 ºC. More LiN(SiMe$_3$)$_2$ (26 mg, 0.15 mmol, 1.5 equiv) dissolved in 0.2 mL THF was added over ~40 min. The reaction was allowed to proceed for an additional 4.8 h, and yielded **18e** (22.5 mg, 0.058 mmol, 58% yield) as a yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.13 (t, *J* = 7.5 Hz, 1H), 7.02 (br. d, *J* = 7.3 Hz, 2H), 6.12 (d, *J* = 6.3 Hz, 1H), 5.82 (s, 1H), 5.49 - 5.44 (m, 1H), 5.24 - 5.20 (m, 2H), 4.87 (broad d, *J* = 5.7 Hz, 1H), 3.44 - 3.38 (m, 1H), 3.36 - 3.30 (m, 1H), 2.6 - 2.1 (very br. s, 6H), 1.64 (sextet, 7.3 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.4, 137.9, 136.1, 130.4, 128.6, 113.9, 92.8, 92.5, 92.4, 92.1, 91.1, 76.6, 71.0, 23.3, 20.9, 11.0; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; non-axial carbons on the xylyl group exhibit diminished signals due to the hindered rotation; IR 3071, 2965, 2934, 2877, 1965 and 1881 (strong CO stretches), 1471, 1456, 1104, 1088, 774, 663, 629 cm^{-1}.



19a

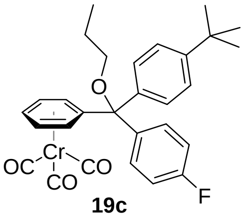
19a – ^{n}PrOPh$_2$C(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure B, **15** (19 µl, 0.085 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (58 mg, 0.35 mmol, 4.1 equiv) and PdCl$_2$(PPh$_3$)$_2$ (6 mg, 0.009 mmol, 10 mol %) in 0.8 mL THF and bromobenzene (32 µL, 0.30 mmol, 3.5 equiv) and heated at 55 ºC for 16 h, and yielded **19a** (27.1 mg, 0.062 mmol, 73% yield) as a pale yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.43 - 7.35 (m, 10H), 5.71 (d, *J* = 6.0 Hz, 2H), 5.46 (t, *J* = 6.2 Hz, 1H), 5.04 (t, *J* = 6.5 Hz, 2H), 3.09 (t, *J* = 6.7 Hz, 2H), 1.69 (sextet, *J* = 7.0 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 232.9, 141.2, 129.8, 128.2, 128.0, 118.7, 95.8, 95.4, 87.9, 84.4, 66.3, 23.2, 11.0; IR 3060, 3028, 2964, 2935, 2875, 1965 and 1887 (strong CO stretches), 1492, 1447, 1074, 1029, 753, 706, 660, 651, 633 cm^{-1}. HRMS (ES+) calc'd for $C_{25}H_{22}CrO$ 438.0923 found 438.091 [M]$^+$.



19b

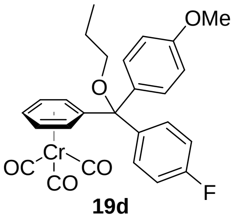
19b – ^{n}PrO(4-C_6H_4-F)$_2$C(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure B, **11** (22 µl, 0.10 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (7 mg, 0.04 mmol, 0.4 equiv) and PdCl$_2$(PPh$_3$)$_2$ (7 mg, 0.01 mmol, 10 mol %) in 0.6 mL THF and 4-bromofluorobenzene (43 µL, 0.04 mmol, 4 equiv) and heated at 56 ºC. More LiN(SiMe$_3$)$_2$ (70 mg, 0.42 mmol, 44.2 equiv) dissolved in 0.2 mL THF was added over 30 min. The reaction was allowed to proceed for an additional for 40 h, and yielded **19b** (27.4 mg, 0.058 mmol, 58% yield) as a pale yellow solid after silica gel chromatography eluting with 4% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.38 (m, 4H), 7.06 (t, *J* = 8.6 Hz, 4H), 5.65 (d, *J* = 6.4 Hz, 2H), 5.49 (t, *J* = 6.1 Hz, 1H), 5.04 (t, *J* = 6.4 Hz, 2H), 3.04 (t, *J* = 6.6 Hz, 2H), 1.68 (sextet, *J* = 7.0 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 232.6, 162.6 (d, *J* = 248.3 Hz), 137.02 (d, *J* = 3 Hz), 131.82 (d, *J* = 8.3 Hz), 118.07, 115.03 (d, *J* = 21.1 Hz), 95.53, 95.49, 87.8, 83.7, 66.3, 23.2, 11.0; ^{19}F NMR (282 MHz) ppm −113.8 (m); IR 3070, 2965, 2936, 2876, 1968 and 1889 (strong CO stretches), 1604, 1507, 1228, 1159, 1078, 831, 816, 657, 628 cm^{-1}.

General procedure C (for sensitive solid substrates):



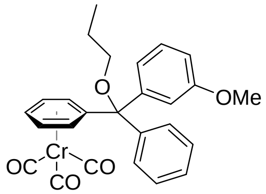
19c

19c – ^{n}PrO(4-C$_6$H$_4$-F)(4-C$_6$H$_4$-^{t}Bu)C(η^{6}-C$_6$H$_5$)Cr(CO)$_3$: An oven-dried reaction tube was charged with small magnetic stirbar and **^{n}PrO(4-C$_6$H$_4$-F)CH(η^{6}-C$_6$H$_5$)Cr(CO)$_3$ (18b)** (19 mg**,** 0.050 mmol, 1.0 equiv), sealed with a septum, and purged with nitrogen. PdCl$_2$(PPh$_3$)$_2$ (3.2 mg, 0.0046 mmol, 9 mol %) and LiN(SiMe$_3$)$_2$ (8 mg, 0.04 mmol, 0.8 equiv) was dissolved in 0.6 mL of dry THF in a nitrogen atmosphere, forming an orange solution, to which neat 4-*tert*-butylbromobenzene (20 μL, 0.15 mmol, 3 equiv) was added. The catalyst, base, and aryl bromide solution was taken up by syringe and added to **18b**, which turned deep red. The reaction mixture was heated with stirring at 58 ºC. A separate portion of LiN(SiMe$_3$)$_2$ (43 mg, 0.26 mmol, 5.2 equiv) was dissolved in 0.2 mL dry THF and added to the reaction mixture via syringe over 20 min, and then allowed to stir for an additional 24 before cooling to room temperature and quenching with 2 drops H$_2$O. The golden solution was then opened to air, diluted with 3 mL diethyl ether, and filtered over a pad of MgSO$_4$ and silica. The pad was rinsed with additional diethyl ether and the solution was concentrated *in vacuo*, loaded directly onto a silica gel column, and eluted with 3% diethyl ether in pentane. The result was **19c** (20.5 mg, 0.040 mmol, 80% yield) as a pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.45 - 7.41 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.27 (d overlapping with solvent pk, *J* = 7.3 Hz, 2H), 7.06 (apparent t, *J* = 8.7 Hz, 2H), 5.79 (d, *J* = 6.8 Hz, 1H), 5.60 (d, *J* = 6.7 Hz, 1H), 5.47 (t, *J* = 6.2 Hz, 1H), 5.06 - 5.01 (m, 2H), 3.06 (apparent dt, *J* = 2.4, 6.6 Hz, 2H), 1.68 (sextet, *J* = 7.1 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 232.9, 162.5 (d, *J* = 247 Hz), 151.3, 138.0, 137.4 (d, *J* = 3.8 Hz), 131.6 (d, *J* = 8.3 Hz), 129.5, 125.0, 118.8, 114.8 (d, *J* = 21 Hz), 95.9, 95.8, 95.5, 87.8, 87.7, 83.8, 66.2, 34.8, 31.5, 23.2, 11.1 ; ^{19}F NMR (282 MHz) ppm −114.3 (m); tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 3089, 2964, 2873, 1969 and 1893 (strong CO stretch), 1604, 1507, 1229, 1159, 1079, 830, 657, 626 cm^{-1}; HRMS (ES+) calc'd for $C_{29}H_{29}CrOF$ d512.1455, found 512.1478 $[M]^+$.



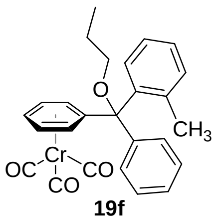
19d

19d – ^{n}PrO(4-C_6H_4-F)(4-C_6H_4-OMe)C(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure C, **18b** (19 mg, 0.050 mmol, 1.0 equiv) was combined with $LiN(SiMe_3)_2$ (13 mg, 0.08 mmol, 1.6 equiv) and $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol, 10 mol %) in 0.55 mL THF and 4-bromoanisole (19 μL, 0.15 mmol, 3.0 equiv) and heated at 55 ºC. More $LiN(SiMe_3)_2$ (20 mg, 0.12 mmol, 2.4 equiv) dissolved in 0.15 mL THF was added over 40 min. The reaction was allowed to proceed for an additional 16 h, and yielded **19d** (16.7 mg, 0.0343 mmol, 69 % yield) as a pale yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 5.5, 8.5 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.06 (apparent t, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.77 (d, *J* = 6.6 Hz, 1H), 5.55 (d, *J* = 6.6 Hz, 1H), 5.48 (t, *J* = 6.1 Hz, 1H), 5.08 - 5.00 (m, 2H), 3.82 (s, 3H), 3.11 - 2.99 (m, 2H), 1.67 (sextet, *J* = 7.0 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm .9, 162.4 (d, *J* = 248.0 Hz), 159.5, 137.6 (d, *J* = 3.4 Hz), 132.9, 131.4 (d, *J* = 8.1 Hz), 131.2, 118.9, 114.9 (d, *J* = 21.3 Hz), 113.4, 95.7, 95.6, 95.4, 88.0, 87.8, 83.7, 66.2, 55.6, 23.2, 11.1; ^{19}F NMR (282 MHz) ppm −114.3 (m); tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 2963, 2934, 2875, 1967 and 1889 (strong CO stretches), 1605, 1508, 1254, 1227, 1184, 1160, 1077, 1033, 830, 658, 628 cm^{-1}.



19e

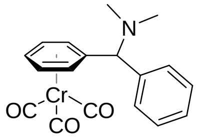
19e – ^{n}PrOPh(3-C_6H_4-OMe)C(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure A, **18a** (18 mg, 0.050 mmol, 1.0 equiv) was combined with $LiN(SiMe_3)_2$ (40 mg, 0.25 mmol, 5.0 equiv) and $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol, 10 mol %) in 0.65 mL THF and 3-bromoanisole (18 μL, 0.15 mmol, 3.0 equiv) and heated at 58 ºC for 24 h, and yielded **19e** (14.4 mg, 0.0307 mmol, 61% yield) as a pale yellow solid after silica gel chromatography eluting with 10% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.33 (m, 5H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.09 (br s, 1H), 6.94 - 6.88 (m, 2H), 5.79 (d, *J* = 6.8 Hz, 1H), 5.66 (d, *J* = 6.7 Hz, 1H), 5.46 (t, *J* = 6.2 Hz, 1H), 5.08 - 5.01 (m, 2H), 3.82 (s, 3H), 3.18 - 3.02 (m, 2H), 1.69 (sextet, *J* = 7.0 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 232.9, 159.5, 142.9, 141.0, 129.9, 128.7, 128.2, 127.9, 122.5, 118.7, 115.5, 113.7, 95.8, 95.7, 95.4, 88.0, 87.9, 84.4, 66.4, 55.5, 23.2, 11.1; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 2963, 2926, 2873, 1964 and 1883 (strong CO stretches), 1598, 1488, 1448, 1254, 1075, 1029, 706, 657, 632 cm^{-1}.



19f

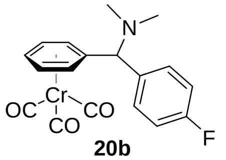
19f – ^{n}PrOPh(2-C_6H_4-Me)C(η^6-C_6H_5)Cr(CO)$_3$: Using general procedure C, **18a** (18 mg, 0.050 mmol, 1.0 equiv) was combined with LiN(SiMe$_3$)$_2$ (17 mg, 0.10 mmol, 2.0 equiv) and PdCl$_2$(PPh$_3$)$_2$ (3.5 mg, 0.005 mmol, 10 mol %) in 0.6 mL THF and 2-bromotoluene (18 μL, 0.15 mmol, 3.0 equiv) and heated at 58 ºC. More LiN(SiMe$_3$)$_2$ (33 mg, 0.20 mmol, 4.0 equiv) dissolved in 0.2 mL THF was added over 2h. The reaction was allowed to proceed for an additional 40 h, and yielded **15f** (13.3 mg, 0.0293 mmol, 59% yield) as a pale yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.46 - 7.39 (m, 3H), 7.36 - 7.18 (m, 5H), 7.15 - 7.12 (m, 1H), 5.78 (d, *J* = 6.4 Hz, 1H), 5.63 (d, *J* = 6.4 Hz, 1H), 5.47 (t, *J* = 6.2 Hz, 1H), 5.08 - 5.03 (m, 2H), 3.26 (dt, *J* = 8.9, 6.5 Hz, 1H), 2.90 (dt, *J* = 8.9, 7.0 Hz, 1H), 1.80 (s, 3H), 1.79 - 1.72 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm, 144.3, 140.2, 138.5, 132.7, 129.8, 128.5, 128.02, 128.03, 127.8, 125.6, 118.2, 97.5, 95.7, 95.6, 87.4, 87.3, 84.7, 67.6, 23.3, 22.5, 11.0; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; propoxy methylene protons exhibit diastereotopic signals in the ^{1}H NMR; IR 3022, 2963, 2930, 2873, 1966 and 1887 (strong CO stretches), 1448, 1074, 750, 706, 659, 632 cm^{-1}.

General procedure D (for liquid substrates):

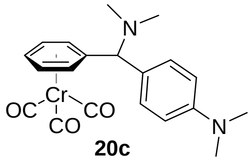


20a

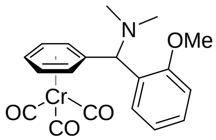
20a – Me$_2$NPhCH(η^6-C_6H_5)Cr(CO)$_3$: An oven-dried reaction tube was charged with small magnetic stirbar, PdCl$_2$(PPh$_3$)$_2$ (4.2 mg, 0.006 mmol, 6 mol %) and LiN(SiMe$_3$)$_2$ (38 mg, 0.23 mmol, 2.3 equiv) under nitrogen and sealed with a septum. 0.7 mL of dry THF was added via syringe with stirring, forming a red solution to which neat bromobenzene (17 μL, 0.16 mmol, 1.6 equiv) was added. The catalyst, base, and aryl bromide solution was allowed to stir for 5 min, and neat **Me$_2$NCH$_2$(η^6-C_6H_5)Cr(CO) (16)** (21 μL, 0.10 mmol, 1.0 equiv) was added dropwise and then heated at 56 ºC with stirring for 6 h. The dark reaction mixture was cooled to room temperature and quenched with 2 drops H$_2$O. The brownish orange solution was then opened to air and diluted with 3 mL diethyl ether, then filtered over a pad of MgSO$_4$ and silica. The pad was rinsed with additional diethyl ether and the solution was concentrated *in vacuo*, loaded directly onto a silica gel column and eluted with 50% diethyl ether in pentane. The result was **20a** (28.6 mg, 0.082 mmol, 82% yield) as an orange oil which solidified on standing. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.39-7.28 (m, 5H), 5.91 - 5.88 (m, 1H), 5.33 - 5.26 (m, 3H), 5.17 - 5.12 (m, 1H), 4.14 (s, 1H), 2.24 (s, 6H) ; ^{13}C{^{1}H} NMR (75 MHz) ppm 233.0, 140.0, 129.0, 128.6, 128.1, 114.0, 95.1, 94.5, 93.6, 91.0, 90.5, 73.4, 44.3; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 2946, 2864, 2823, 2781, 1962 and 1876 (strong CO stretches), 1611, 1521, 1454, 1353, 1016, 812, 663, 632 cm^{-1}; HRMS (ES+) calc'd for $C_{15}H_{17}Cr$ 263.0766, found 263.0757 $[M -(CO)_3]^+$.


20b

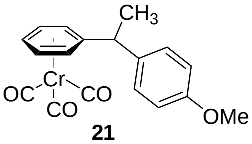
20b – $Me_2N(4\text{-}C_6H_4\text{-}F)CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure D, **16** (21 μl, 0.10 mmol, 1.0 equiv) was combined with $LiN(SiMe_3)_2$ (37 mg, 0.23 mmol, 2.3 equiv) and $PdCl_2(PPh_3)_2$ (4.9 mg, 0.007 mmol, 5 mol %) in 0.85 mL THF and 4-bromofluorobenzene (18 μL, 0.16 mmol, 1.6 equiv) and heated at 58 ºC for 5 h, yielding **20b** (22.7 mg, 0.062 mmol, 62% yield) as a yellow solid after silica gel chromatography eluting with 40% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 - 7.27 (m, 2H), 7.08 - 7.02 (m, 2H), 5.85 (d, *J* = 6.4 Hz, 1H), 5.34 (tt, *J* = 6.1, 1.1 Hz, 1H), 5.30 - 5.24 (m, 2H), 5.17 - 5.12 (m, 1H), 4.10 (s, 1H), 2.22 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 232.8, 162.5 (d, *J* = 246.8 Hz), 136.0 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 7.5 Hz), 115.6 (d, *J* = 24.2 Hz), 113.6, 95.5, 94.4, 93.9, 90.7, 90.2, 72.9, 44.3; $^{19}F\{^1H\}$ NMR (282 MHz) ppm −114.2 (s); tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; ; IR 2925, 2851, 2825, 2780, 1965, 1881, 1605, 1506, 1455, 1223, 1157, 1014, 820, 660, 631 cm^{-1}.


20c

20c – $Me_2N(4\text{-}C_6H_4\text{-}NMe_2)CH(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure D, **16** (21 μl, 0.10 mmol, 1.0 equiv) was combined with $LiN(SiMe_3)_2$ (38 mg, 0.23 mmol, 2.3 equiv) and $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol, 5 mol %) in 0.7 mL THF and 4-bromo-N,N-dimethylaniline (28 mg, 0.16 mmol, 1.6 equiv) and heated at 55 ºC for 4 h, yielding **20c** (30.1 mg, 0.077 mmol, 77% yield) as a yellow solid after silica gel chromatography eluting with 40% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.92 (br. d, *J* = 6.5 Hz, 1H), 5.36 (dt, *J* = 1.1, 6.4 Hz, 1H) 5.28 - 5.17 (m, 3H), 4.15 (s, 1H), 2.95 (s, 6H), 2.23 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.3, 150.3, 130.1, 127.4, 115.6, 112.3, 94.26, 9.24, 92.9, 91.8, 91.5, 72.4, 44.1, 40.7; IR cm^{-1}; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 2950, 2867, 2824, 2780, 1963 and 1875 (strong CO stretches), 1454, 1015, 755, 705, 661, 630 cm^{-1}.

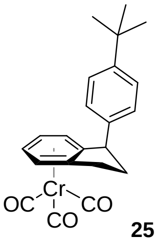

20d

20d – $Me_2NCH(2\text{-}C_6H_4\text{-}OMe)(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure D, **16** (21 μl, 0.10 mmol, 1.0 equiv) was combined with $LiN(SiMe_3)_2$ (34 mg, 0.20 mmol, 2 equiv) and $PdCl_2(PPh_3)_2$ (4.2 mg, 0.006 mmol, 6 mol %) in 0.7 mL THF and 2-bromoaniline (22 μL, 0.17 mmol, 1.7 equiv) and heated at 58 ºC for 5 h, yielding **20d** (27.2 mg, 0.072 mmol, 72% yield) as a yellow solid after silica gel chromatography eluting with 30 – 40% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 - 7.22 (m, 2H), 6.96 - 6.91 (m, 2H), 5.91 (d, *J* = 6.7 Hz, 1H), 5.39 (d, *J* = 6.6 Hz, 1H), 5.32 (tt *J* = 1.1, 6.2 Hz, 1H), 5.25 (dt, *J* = 1.4, 6.3 Hz, 1H), 5.11 (dt, *J* = 1.4, 6.3 Hz, 1H), 4.68 (s, 1H), 3.85 (s, 3H), 2.23 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz) ppm 33.0, 157.4, 129.3, 129.0, 128.9, 120.5, 114.9, 111.1, 95.9, 94.7, 93.9, 90.6, 89.9, 64.9, 55.6, 44.5; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; IR 2924, 2822, 2771, 1962 and 1881 (strong CO stretch), 1489, 1456, 1243, 1027, 755, 700, 662 cm^{-1}.



21

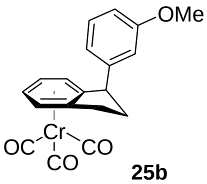
21 – $CH_3CH(4\text{-}C_6H_4\text{-}OCH_3)(\eta^6\text{-}C_6H_5)Cr(CO)_3$: Using general procedure C, **$CH_3CH_2(\eta^6\text{-}C_6H_5)Cr(CO)_3$ (17)** (24.4 mg, 0.10 mmol, 1.0 equiv) was combined with $LiN(SiMe_3)_2$ (13 mg, 0.08 mmol, 0.8 equiv) and $PdCl_2(PPh_3)_2$ (5.8 mg, 0.008 mmol, 8 mol %) in 0.85 mL of dry THF and 4-bromoanisole (19 μL, 0.15 mmol, 1.5 equiv) and heated at 58 ºC. More $LiN(SiMe_3)_2$ (20 mg, 0.12 mmol, 1.2 equiv) dissolved in 0.15 mL THF was added over 30 min. The reaction was allowed to proceed for an additional 3.5 h and yielded **21** (24.5 mg, 0.070 mmol, 70% yield) as a yellow-orange oil after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.43 (d, *J* = 6.3 Hz, 1H), 5.38 - 5.34 (m, 1H), 5.29 - 5.21 (m, 2H), 5.10 (d, *J* = 6.1 Hz, 1H), 3.86 - 3.77 (m, 4H), 1.56 (d, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.4, 158.8, 136.6, 128.6, 117.9, 114.3, 94.4, 92.8, 92.5, 92.1, 91.4, 55.5, 43.1, 21.3; tricarbonylchromium-coordinated protons and carbons exhibit diastereotopic signals; methoxy signal overlaps with the benzylic proton signal; IR 3089, 2971, 2936, 2838, 1962 and 1877 (strong CO stretch), 1611, 1511, 1457, 1247, 1180,1031, 835, 662, 630 cm^{-1}. HRMS (ES+) calc'd for $C_{15}H_{16}CrO$ 264.0606, found 264.0608 $[M\ \text{-}(CO)_3]^+$.



25a

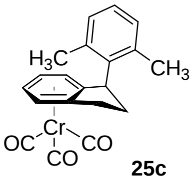
25a – 1-(4-C_6H_4-^{t}Bu)(η^6-indane)$Cr(CO)_3$: Using general procedure C, **23** (22.5 mg, 0.0885 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (13 mg, .078 mmol, 0.88 equiv) and $PdCl_2(PPh_3)_2$ (4.8 mg, 0.0068 mmol, 7.6 mol %) in 0.8 mL THF and 4-bromo-*tert*-butylbenzene (16 μL, 0.12 mmol, 1.3 equiv) and heated at 58 ºC. More $LiN(SiMe_3)_2$ (21 mg, 0.13 mmol, 1.5 equiv) dissolved in 0.2 mL THF was added over 3 h. The reaction was allowed to proceed for an additional 2 h, and yielded **25a** (0.0497 mmol, 19.2 mg, or 56% yield) as a fluffy yellow solid after silica gel chromatography eluting with 3% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.53 (d, *J* = 6.4 Hz, 1H), 5.39 (d, *J* = 6.4 Hz, 1H), 5.31 (dt, *J* = 6.2, 1.0 Hz, 1H), 5.21 (dt, *J* = 6.2, 1.0 Hz, 1H), 4.18

(dd, J = 8.5, 1.6 Hz, 1H), 3.08 - 3.00 (m, 1H), 2.79 - 2.70 (m, 1H), 2.66 - 2.54 (m, 1H) 2.10 - 2.02 (m, 1H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.6, 150.0, 141.4, 126.8, 125.9, 116.6, 114.9, 92.5, 91.9, 91.5, 90.3, 49.3, 34.7, 33.3, 31.6, 30.8; IR 3087, 3028, 2964, 2868, 1963 and 1877 (strong CO stretches), 1510, 1452, 1434, 1365, 1270, 1017, 830, 670, 631 cm^{-1}. HRMS (ES+) calc'd for $C_{22}H_{22}CrO_3$ 386.0974, found 386.0981 $[M]^+$.



25b

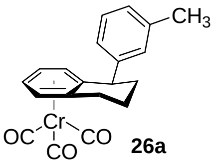
25b – 1-(3-C_6H_3OMe)(η^6-indane)Cr(CO)$_3$: Using general procedure C, **23** (61.3 mg, 0.241 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (25 mg, .15 mmol, 0.62 equiv) and PdCl$_2$(PPh$_3$)$_2$ (17.5 mg, 0.025 mmol, 10 mol %) in 2 mL THF and 3-bromoanisole (48 μL, 0.38 mmol, 1.6 equiv) and heated at 55 ºC. More LiN(SiMe$_3$)$_2$ (50 mg, 0.30 mmol, 1.2 equiv) dissolved in 0.5 mL THF was added over 3h. The reaction was allowed to proceed for an additional 1 h, and yielded **25b** (0.128 mmol, 46.0 mg, or 53% yield) as a fluffy yellow solid after silica gel chromatography eluting with 6% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.22 (t, J = 7.9 Hz, 1H), 6.77 (ddd, J = 8.3, 2.5, 1.8 Hz, 1H), 6.68 (d, J = 7.7 Hz, 1H), 6.62 (t, J = 1.9 Hz, 1H), 5.52 (d, J = 6.3 Hz, 1H), 5.39 (d, J = 6.3 Hz, 1H), 5.31 (dt, J = 0.9, 6.2 Hz, 1H), 5.22 (dt, J = 0.9, 6.2 Hz, 1H), 4.18 (dd, J = 8.6, 1.5 Hz, 1H), 3.75 (s, 3H), 3.09 - 2.97 (m, 1H), 2.80 - 2.69 (m, 1H), 2.66 - 2.56 (m, 1H), 2.09 - 2.02 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.6, 160.1, 146.1, 130.1, 119.6, 116.2, 114.9, 113.6, 111.8, 92.5, 91.9, 91.4, 90.3, 55.4, 49.8, 33.2, 30.8; IR 3081, 2924, 2851, 1958 and 1866 (strong CO stretches), 1599, 1488, 1451, 1265, 1050, 777, 701, 670, 629 cm^{-1}.



25c

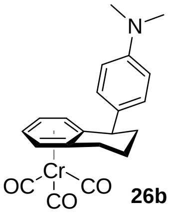
25c – 1-(2,6-$C_6H_3Me_2$)(η^6-indane)Cr(CO)$_3$: Using general procedure A, **23** (25.3 mg, 0.099 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (67 mg, 0.40 mmol, 4.2 equiv) and PdCl$_2$(PPh$_3$)$_2$ (4.8 mg, 0.007 mmol, 7 mol %) in 1 mL THF and 1-bromo-2,6-dimethylbenzene (41 μL, 0.3 mmol, 3 equiv) for 10 h at 55 ºC to yield **25c** (0.047 mmol, 17 mg, or 47% yield) as a yellow solid after silica gel chromatography eluting with 3% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.07 (d, J = 4.5 Hz, 2H), 6.98 – 6.96 (m, 1H), 5.61 (d, J = 6.1 Hz, 1H), 5.24 (m, 3H), 5.04 (t, J = 9.0 Hz, 1H), 3.15 (t, J = 7.9 Hz, 2H), 2.66 (m, 1H), 2.48 (s, 3H), 2.16 (m, 1H), 1.96 (s, 3H) ;$^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.9, 139.5, 137.5, 136.0, 130.7, 128.7, 127.2, 119.4, 115.7, 92.2, 91.7, 91.2, 90.4, 45.6, 31.8, 30.1, 21.6, 21.5; methyl carbons and protons on the xylyl moiety exhibit diastereotopic signals; IR 2962, 1957 and 1867 (strong CO stretch), 1469, 1449, 1084, 773, 667, 631 cm^{-1}.

General procedure E:



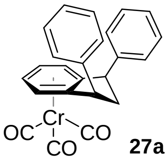
26a

26a – 1-(3-C_6H_4-Me)(η^6-tetrahydronaphthalene)Cr(CO)$_3$: An oven-dried glass reaction tube was charged with a small magnetic stirbar and **(η^6-tetrahydronaphthalene)Cr(CO)$_3$ (24)** (19.9 mg, 0.0742 mmol, 1.0 equiv), sealed with a septum, purged with nitrogen, and dissolved in 0.3 ml toluene. $PdCl_2(PPh_3)_2$ (3.6 mg, 5 μ mmol, 7 mol %) and $LiN(SiMe_3)_2$ (38 mg, 0.23 mmol, 3 equiv) were dissolved in 0.45 mL of dry THF under a nitrogen atmosphere, forming an orange solution, to which 3-bromotoluene (15 μL, 0.12 mmol, 1.6 equiv) was added. The catalyst, base, and aryl bromide THF solution was taken up by syringe and added to the toluene solution of **24**, which turned red-orange. The reaction mixture was heated with stirring for 4.5 h at 58 °C, then allowed to cool and quenched with one drop of aqueous 2N HCl and allowed to stir for 5 min. The pale orange solution was opened to air and diluted with 2 mL diethyl ether and filtered over a pad of $MgSO_4$ and silica which was rinsed with an additional 1 mL diethyl ether. After concentration *in vacuo* and purification by silica gel flash chromatography eluting with 6% diethyl ether in pentane, **26a** (14.7 mg, 0.041 mmol, 55% yield) was obtained as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.94 - 6.89 (m, 2H), 5.31 - 5.27 (m, 2H), 5.18 - 5.14 (ddd, *J* = 2.1, 5.3, 6.6 Hz, 1H), 5.06 (d, *J* = 6.7 Hz, 1H), 3.95 (dd, *J* = 5.8, 8.1 Hz, 1H), 2.82 - 2.67 (m, 2H), 2.33 (s, 3H), 2.20 - 2.12 (m, 1H), 1.87 - 1.69 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.8, 145.5, 138.6, 129.4, 128.8, 127.8, 125.7, 112.1, 110.5, 95.3, 93.4, 92.6, 91.6, 44.5, 32.5, 29.1, 21.7, 20.5; IR 3019, 2939, 2862, 1957 and 1868 (strong CO stretch), 1606, 1456, 788, 704, 667, 632, 536 cm^{-1}; HRMS (ES+) calc'd for $C_{20}H_{18}CrO_3$ 358.0661, found 358.0660 [M]$^+$.

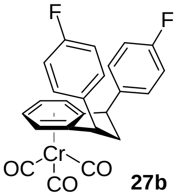


26b

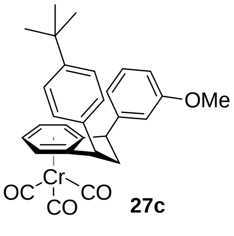
26b – 1-(4-C_6H_4-NMe_2)(η^6-tetrahydronaphthalene)Cr(CO)$_3$: Using general procedure E, a solution of **(η^6-tetrahydronaphthalene)Cr(CO)$_3$ (24)** (20.1 mg, 0.075 mmol, 1 equiv) in 0.3 ml Toluene was reacted with $LiN(SiMe_3)_2$ (32 mg, 0.19 mmol, 2.5 equiv) and $PdCl_2(PPh_3)_2$ (3.2 mg, 4.5 μmol, 6 mol %) of in 0.45 mL THF and 4-bromo-*N*,*N*-dimethylaniline (25 mg, 0.12 mmol, 1.6 equiv) for 6 h at 60 °C to yield **26b** (12.9 mg, 0.033 mmol, 44% yield) as a yellow-orange oil after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.30 - 5.24 (m, 2H), 5.17 - 5.13 (m, 1H), 5.11 (d, *J* = 6.3 Hz, 1H), 3.89 (dd, *J* = 5.7, 8.0 Hz, 1H), 2.94 (s, 6H), 2.81 - 2.67 (m, 2H), 2.17 - 2.08 (m, 1H), 1.88 - 1.65 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.9, 149.7, 133.3, 129.3, 113.0, 112.9, 110.5, 95.5, 93.5, 92.6, 91.6, 43.5, 40.8, 32.4, 29.1, 20.5; IR 2921, 2850, 1954 and 1865 (strong CO stretch), 1610, 1520, 1446, 1348, 814, 666, 631, 534 cm^{-1}; HRMS (ES+) calc'd for $C_{18}H_{22}N$ 252.1752, found 252.1736 $[MH - Cr(CO)_3]^+$.


27a

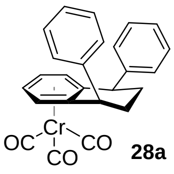
27a – 1,3-*cis*-Ph$_2$(η^6-indane)Cr(CO)$_3$: Using general procedure A, **24** (25.5 mg, 0.100 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (83 mg, 0.50 mmol, 5 equiv) and $PdCl_2(PPh_3)_2$ (4.3 mg, 0.006 mmol, 6 mol %) in 1 mL THF and bromobenzene (52 μL, 0.5 mmol, 5 equiv) for 5 h at 52 °C to yield **27a** (30.8 mg, 0.076 mmol, or 76%) as a yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 6H), 7.25 (m, 4H), 5.39 (dd, *J* = 4.5, 2.7 Hz, 2H), 5.22 (dd, *J* = 4.6, 3.0 Hz, 2H), 4.48 (t, *J* = 8.4 Hz, 2H), 3.11 (dt, *J* = 13.5, 8.4 Hz, 1H), 2.20 (dt, *J* = 13.5, 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.8, 143.5, 129.3, 128.4, 127.6, 119.0, 92.2, 91.8, 50.1, 45.8. IR 3081, 3027, 2970, 2935, 2856, 1956 and 1877 and 1867 (strong CO stretch), 1602, 1494, 1450, 1427, 1263, 1152, 1078, 803, 760, 747, 696, 667, 632 cm^{-1}. HRMS (ES+) calc'd for $C_{21}H_{18}Cr$ 322.0814, found 322.0819 $[M -(CO)_3]^+$.


27b

27b – 1,3-*cis*-(4-C$_6$H$_4$-F)$_2$(η^6-Indane)Cr(CO)$_3$: Using general procedure A, **24** (12.6 mg, 0.049 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (43 mg, 0.26 mmol, 5.1 equiv) and $PdCl_2(PPh_3)_2$ (3.6 mg, 0.005 mmol, 10 mol %) in 1.2 mL of THF and 4-bromofluorobenzene (27.5 μL, 0.25 mmol, 5 equiv) for 16 h at 53 °C to yield **27b** (12.1 mg, 0.030 mmol, or 61% yield) as a yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (m, 4H), 7.03 (t, *J* = 8.7 Hz, 4H), 5.36 (dd, *J* = 4.7, 2.7 Hz, 2H), 5.23 (dd, *J* = 4.8, 3.0 Hz, 2H), 4.45 (t, *J* = 8.3 Hz, 2H), 3.09 (dt, *J* = 13.5, 8.3 Hz, 1H), 2.10 (dt, 13.5, 8.3 Hz) ;$^{13}C\{^1H\}$ NMR (75 MHz) ppm 233.3, 162.1 (d, *J* = 246 Hz), 138.9 (d, *J* = 2.9 Hz), 129.6 (d, *J* = 8.0 Hz), 118.0, 116.0 (d, *J* = 21.4 Hz), 91.9, 91.3, 49.0, 45.8; ^{19}F NMR (282 MHz) ppm −118.3 (m); IR 3079, 3041, 2934, 1962 and 1875 (strong CO stretch), 1605, 1509, 1225, 1159, 1098, 834, 667, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{21}H_{16}CrF_2$ 358.0625, found 358.0617 $[M -(CO)_3]^+$. *X-ray crystal structure was determined for this compound; see **S29**.*

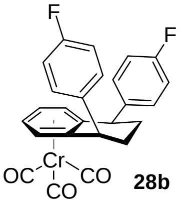

27c

27c – 1,3-*cis*-Ph(3-C$_6$H$_4$-OMe)(η^6-indane)Cr(CO)$_3$: Using general procedure A, **25b** (35.9 mg, 0.0996 mmol, 1.0 equiv) was reacted with $LiN(SiMe_3)_2$ (33 mg, 0.20 mmol, 2.0 equiv) and $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol, 10 mol %) in 1.0 mL THF and 4-bromo-*tert*-butylbenzene (22 μL, 0.15 mmol, 1.5 equiv) for 5 h at 57 °C to yield **27c** (40.1 mg, 0.0815 mmol, or 82%) as a yellow solid after silica gel chromatography eluting with 10% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.26 (t, 7.9 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.84 - 6.79 (m, 2H), 6.72 - 6.71 (m, 1H), 5.44 - 5.40 (m, 2H), 5.24 - 5.21 (m, 2H), 4.49 - 4.41 (m, 2H), 3.75 (s, 3H), 3.09 (dt 13.5, 8.5 Hz, 1H), 2.20 (dt, 13.5, 8.2 Hz, 1H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.6, 160.2, 150.3, 145.1, 140.3, 130.1, 127.8, 125.0, 120.5, 118.71, 118.66, 114.0, 112.5, 92.0, 91.9, 91.7, 91.5, 55.4, 49.9, 49.3, 45.1, 34.7, 31.5; IR 3027, 2963, 1962 and 1878 (strong CO stretch), 1600, 1455, 1268, 1050, 667, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{26}H_{28}CrO$ 408.1545, found 408.1526 [M -(CO)$_3$]$^+$.



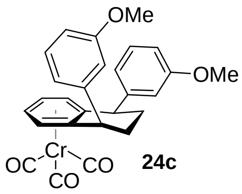
28a

28a – 1,4-*cis*-Ph$_2$(η^6-tetrahydronaphthalene)Cr(CO)$_3$: Using general procedure A, **(η^6-tetrahydronaphthalene)Cr(CO)$_3$ (24)** (13.3 mg, 0.050 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (42 mg, 0.25 mmol, 5 equiv) and PdCl$_2$(PPh$_3$)$_2$ (3.5 mg, 0.005 mmol, 10 mol %) of in 1 mL THF and bromobenzene (26 μL, 0.25 mmol, 5 equiv) for 12 h at 52 ºC to yield **28a** (18.4 mg, 0.044 mmol, 88% yield) as a yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36 (m, 4H), 7.28 (m, 2H), 7.21 (m, 4H), 5.23 (m, 2H), 5.17 (m, 2H), 4.10 (t, *J* = 6.3 Hz, 2H), 2.11 (m, 2H), 1.86 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.6, 145.3, 128.9, 128.7, 127.1, 112.3, 94.8, 92.2, 44.5, 28.9.; IR 3085, 3029, 2937, 2855, 1951 and 1875 and 1856 (strong CO stretch), 1600, 1492, 1416, 1443, 1077, 1054, 1029, 831, 755, 700, 667, 635 cm^{-1}; HRMS (ES+) calc'd for $C_{22}H_{20}Cr$ 336.0970, found 336.0968 [M -(CO)$_3$]$^+$.



28b

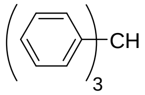
28b – 1,4-*cis*-(4-C$_6$H$_4$-F)$_2$(η^6-tetrahydronaphthalene)Cr(CO)$_3$: Using general procedure A, **20** (13.4 mg, 0.050 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (42 mg, 0.25 mmol, 5 equiv) and PdCl$_2$(PPh$_3$)$_2$ (2.6 mg, 0.0037 mmol, 7 mol %) in 1 mL THF and 4-bromofluorobenzene (28 μL, 0.25 mmol, 5 equiv) for 5 h at 55 – 57 ºC to yield **28b** (14.6 mg, 0.033 mmol, 64% yield) as a yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.14 (m, 4H), 7.05 (t, *J* = 8.7 Hz, 4H), 5.25 (dd, *J* = 4.9, 2.9 Hz, 2H), 5.12 (dd, *J* = 4.8, 2.9 Hz, 2H), 4.08 (t, *J* = 6.2 Hz, 2H), 2.10 (m, 2H), 1.80 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.3, 161.9 (d, *J* = 246 Hz), 140.9, 130.0 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 21.3 Hz), 111.8, 94.6, 92.3, 43.7, 28.9; ^{19}F NMR (282 MHz) ppm −118.7 (m); IR 3077, 3041, 2940, 2863, 1960 and 1871 (strong CO stretch), 1626, 1567, 1508, 1457, 1301, 1224, 1184, 1159, 1097, 924, 828, 736, 667, 628 cm^{-1}; HRMS (ES+) calc'd for $C_{22}H_{18}Cr$ 372.0782, found 372.0773 [M -(CO)$_3$]$^+$.



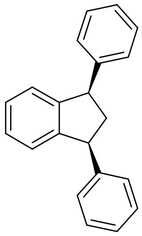
24c

24c – 1,4-*cis*-(3-C_6H_4-OCH_3)$_2$(η^6-tetrahydronaphthalene)Cr(CO)$_3$: Using general procedure A, **20** (13.6 mg, 0.051 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (42 mg, 0.25 mmol, 4.9 equiv) and PdCl$_2$(PPh$_3$)$_2$ (2.7 mg, 0.0037 mmol, 7 mol %) in 1 mL THF and 3-bromoanisole (32 μL, 0.25 mmol, 5 equiv) for 5 h at 55 ºC to yield **24c** (17.6 mg, 0.037 mmol, 73% yield) as a yellow solid after silica gel chromatography eluting with 20% diethyl ether in pentane. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.27 (t, *J* = 8.0 Hz, 2H), 6.78 (m, 6H), 5.24 (m, 2H), 5.18 (m, 2H), 4.06 (t, *J* = 6.2 Hz), 3.80 (s, 6H), 2.09 (m, 2H), 1.87 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz) ppm 233.5, 160.0, 146.9, 129.9, 121.1, 114.8, 112.2, 112.1, 94.8, 92.3, 55.4, 44.4, 28.8; IR 3000, 2939, 2835, 1959 and 1874 (strong CO stretch), 1599, 1584, 1487, 1455, 1266, 1149, 1046m 783, 700, 667, 630 cm^{-1}; HRMS (ES+) calc'd for $C_{24}H_{24}CrO_2$ 396.1181, found 396.1149 [M -(CO)$_3$]$^+$.

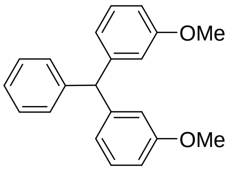
Procedure and characterization for decomplexation:



Triphenylmethane: **Ph$_2$CH(η^6-C_6H_5)Cr(CO)$_3$ (2a) (**64.5 mg, 0.170 mmol) was dissolved in 1.5 mL CHCl$_3$ and 10 mL diethyl ether and placed in bright sunlight for 3 h, until the clear yellow solution became a muddy purple-brown color. This suspension was filtered and concentrated under reduced pressure. The dark residue was diluted with 1:10 CHCl$_3$ in hexanes and filtered again over a pad of MgSO$_4$ and silica gel, and solvent was evaporated from the colorless solution *in vacuo*, yielding **triphenylmethane** (40.5 mg, 0.166 mmol, 98% yield) as a white crystalline solid, with no further purification necessary. All characterization data is consistent with triphenylmethane, a well-known compound.



25 – *cis*-1,3-diphenylindane: Using general procedure A, **(η^6-indane)Cr(CO)$_3$ (19)** (0.127 g, 0.499 mmol, 1.0 equiv) was reacted with LiN(SiMe$_3$)$_2$ (0.42 g, 2.51 mmol, 5.0 equiv) and PdCl$_2$(PPh$_3$)$_2$ (24 mg, 0.034 mmol, 7 mol %) of in 5 mL THF and bromobenzene (0.26 mL, 2.50 mmol, 5.0 equiv) for 5 h at 53 ºC resulted in a deep red solution, which was quenched with 7 drops of aqueous 2N HCl solution, diluted with 6 mL diethyl ether and 1 mL CHCl$_3$ then filtered over a pad of MgSO$_4$ and silica gel. The red solution was placed in sun light for 5 h, and monitored for complete decomplexation by TLC. The cloudy solution was filtered, concentrated *in vacuo*, and chromatographed on silica gel with 6% diethyl ether in pentane to yield ***cis*-1,3-diphenylindane** (0.106 g, 0.392 mmol, 79% yield) as a highly crystalline white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 10H), 7.16 (dd, *J* = 5.6, 3.2 Hz, 2H), 6.95 (ddd, *J* = 5.0, 3.1, 0.5 Hz, 2H), 4.35 (dd, *J* = 11.1, 7.2 Hz, 2H), 2.96 (dt, *J* = 12.5, 7.2 Hz, 1H), 2.14 (dt, *J* = 12.5, 11.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 147.4, 144.6, 128.8, 128.7, 127.0, 126.8, 124.9, 51.0, 48.2. IR 3082, 3061, 3022, 2934, 2865, 1599, 1492, 1454, 1476, 1344, 1073, 1029, 906, 768, 749, 735, 701 cm^{-1}. HRMS (CI+) calc'd for $C_{21}H_{18}$ 270.1409, found 270.1409 $[M]^+$. Characterization data of this product is consistent with existing literature data.[g]



26 – 3,3'-(phenylmethylene)bis(methoxybenzene): For the large-scale reaction, a 50 mL Shlenk flask was charged with a stirbar and $LiN(SiMe_3)_2$ (2.51 g, 15 mmol, 3 equiv) and $PdCl_2(PPh_3)_2$ (139 mg, 0.20 mmol, 4 mol %) under nitrogen. Base and catalyst were dissolved in 28 mL of dry THF, and 3-bromoanisole (1.9 mL, 15 mmol, 3 equiv) was added. **(η^6-toluene)Cr(CO)$_3$ (3)** (1.14 g, 5.0 mmol, 1.0 equiv) was added to the stirring brownish-orange solution in one portion, then heated at 55 ºC for 5 h. The reaction was quenched with 0.2 mL of 2N HCl added dropwise, and solids formed in the stirred solution. The flask was opened to air and diluted with 20 mL Et_2O and 3 mL $CHCl_3$, filtered over a pad of $MgSO_4$ and silica gel, rinsed with diethyl ether, and the yellowish-orange clear solution was exposed to 12 h of sunlight. Precipitating solids were filtered from the brownish green suspension twice during the decomplexation process, and progress was monitored by TLC. The suspension was again filtered, concentrated in vacuo, and loaded onto a short silica gel column and eluted with hexanes, slowly increasing polarity to 3.5% diethyl ether in hexanes to yield **3,3'-(phenylmethylene)bis(methoxybenzene)** (1.42 g, 4.66 mmol, 93%) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 7H), 6.80 – 6.71 (m, 6H), 5.51 (s, 1H), 3.76 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz) ppm 159.8, 145.6, 143.8, 129.6, 129.4, 128.5, 126.6, 122.2, 115.8, 111.6, 57.0, 55.3. IR 3058, 3025, 3000, 2955, 2937, 2834, 1597, 1583, 1486, 1464, 1452, 1434, 1314, 1263, 1151, 1050, 878, 776, 758, 732, 697 cm^{-1}. HRMS (CI+) calc'd for $C_{21}H_{21}O_2$ 305.1542, found 305.1546 $[MH]^+$.

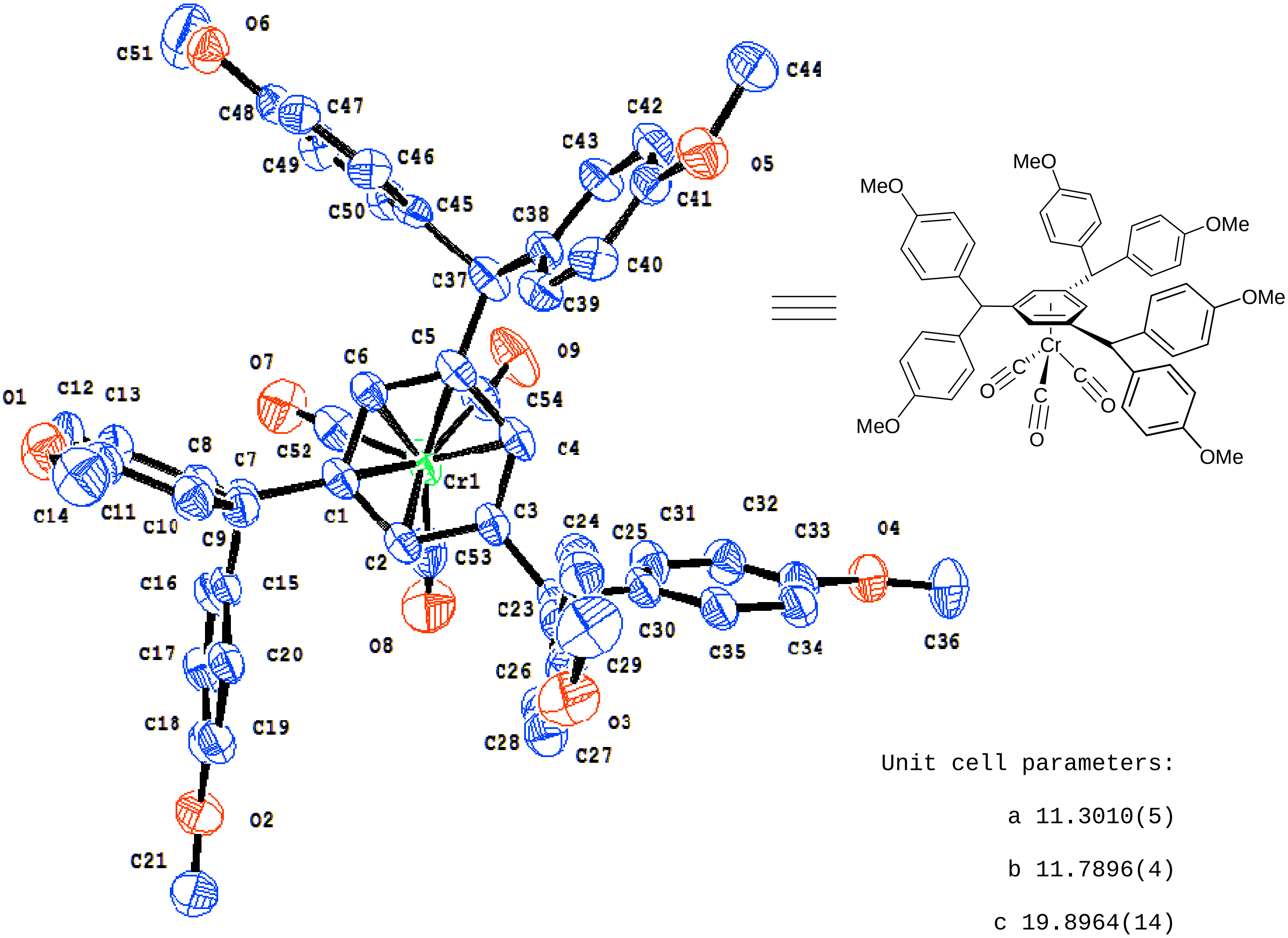
References.

---

[a] D. J. Cram, D. I. Wilkinson, *J. Am. Chem. Soc.* **1960**, *82*, 5721-5723.
[b] J. D. Woolins, Ed.; In *Inorganic Experiments;* VCH: Weinheim, **1994**, 194-195.
[c] C. A. L. Mahaffy, P. L. Pauson, *Inorg. Synth.* **1990**, *28*, 136-140.
[d] Ohlsson and Bengt et al, *J. Organomet. Chem.* **1989**, *365*, 243-267.
[e] Cambie, Richard C. et al, *J. Organomet. Chem.* **1988**, *342*, 315-337.
[f] V. S. Kaganovich, M. I. Rybinskaya, *Russ. Chem. Bull.* **1993**, *42*, 1734-1737.
[g] G. Farnia, G. Sandona, F. Marcuzzi, G. Melloni, *J. Chem. Soc. , Perkin Trans. 2,* **1988**, 247-254.

Full reference for "SB 209670, a rationally designed potent nonpeptide endothelin receptor antagonist": E. H. Ohlstein, P. Nambi, S. A. Douglas, R. M. Edwards, M. Gellai, A. Lago, J. K. Leber, R. D. Cousins, A. M. Gao, J. S. Frazee, C. E. Peishoff, J. W. Bean, D. S. Eggleston, N. A. Elshourbagy, C. Kumar, J. A. Lee, T. L. Yue, C. Louden, D. P. Brooks, J. Weinstock, G. Feuerstein, G. Poste, R. R. Ruffolo, J. G. Gleason, J. D. Elliott, *Proc. Natl. Acad. Sci. U. S. A.* **1994**, *91*, 8052-8056.

10



Unit cell parameters:

a 11.3010(5)

b 11.7896(4)

c 19.8964(14)

alpha 72.920(6)

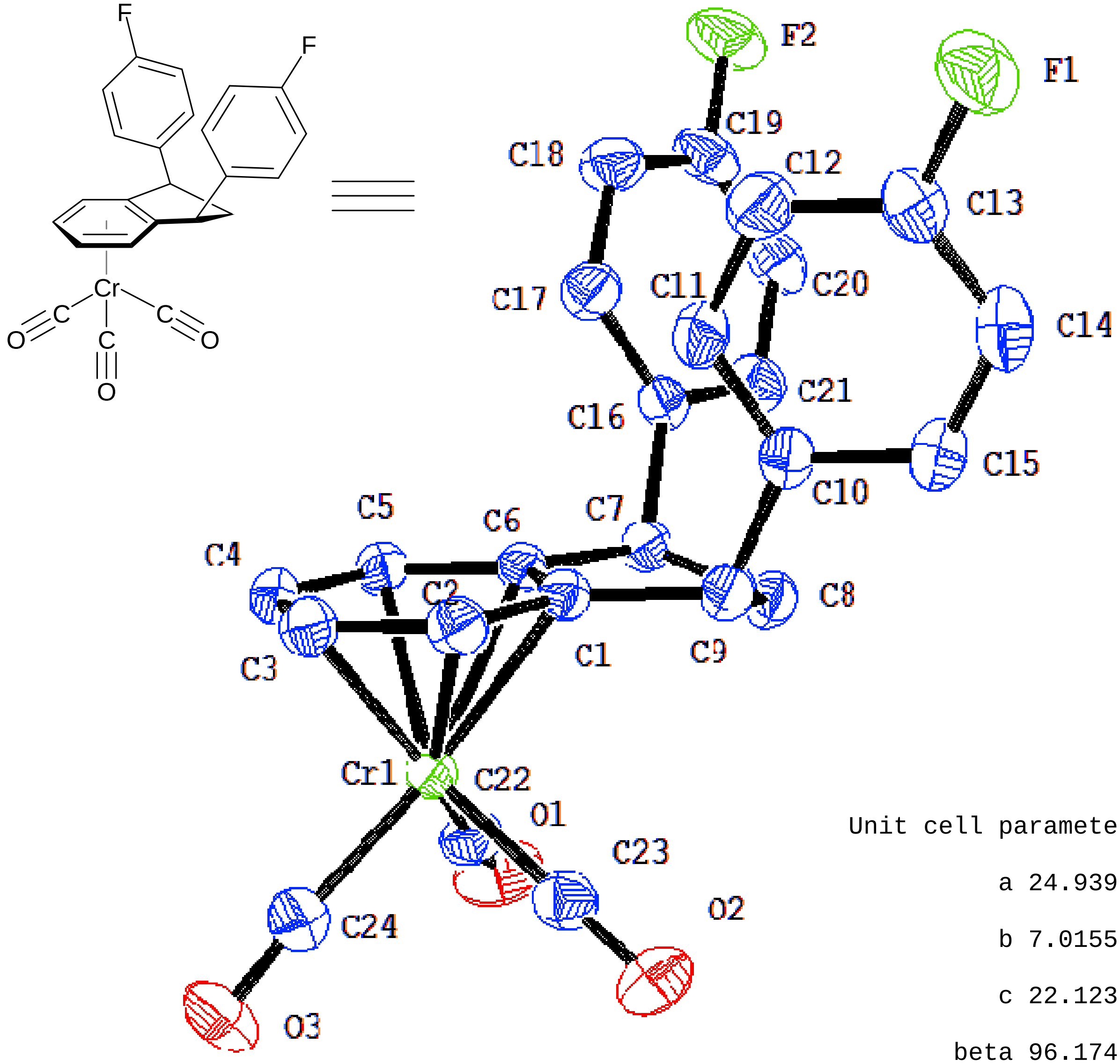
beta 82.244(7)

gamma 63.018(5)

space group P-1

CCDC 775771 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

27b



Unit cell parameters:

a 24.939(2)

b 7.0155(6)

c 22.123(2)

beta 96.174(2)

space group C2/c

CCDC 765716 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.