SUPPORTING INFORMATION

Palladium-catalyzed Allylic Substitution with (η^6-arene–CH_2Z)$Cr(CO)_3$-based Nucleophiles

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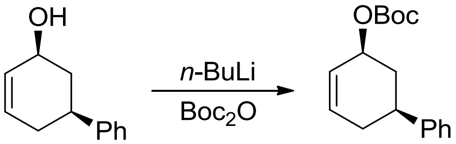
General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture sensitive solutions were handled under nitrogen and transferred via syringe. THF was freshly distilled from Na/benzophenone ketyl under nitrogen. Unless 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. The progress of all reactions was 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. Silica gel (230-400 mesh, Silicycle) was used for air-flashed chromatography. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained using a Brüker AM-500 Fourier-transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS) and all coupling constants are reported in hertz. The infrared spectra were obtained on KBr using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. Chromium-complexed masses were recorded with electrospray + (ES+) HRMS methods, and $[M]^+$ or $[M-(CO)_3]^+$ (unless otherwise stated) was confirmed by the presence of the characteristic chromium isotope pattern. Chromium-decomplexed masses were recorded with chemical ionization + (CI+) HRMS methods.

Caution: Care should be taken to avoid direct bright light exposure of reactions, as arene tricarbonylchromium complexes can decompose in solution under bright light and air.

Preparation of Allylic Electrophiles.

Compounds **2a**[1], **2b**[2], **2c**[3], **2d**[4], **2e**[5], **2f**[6], **2g**[1], **2i**[7], and **2k**[8] were prepared according to literature procedures.

Compound **2j** ((***rac***)**-*cis*-*tert*-butyl (5-phenyl-2-cyclohexenyl) carbonate**)



n-BuLi (2.2 mL of a 2.5 M solution in hexanes) was added to a solution of (*rac*)-*cis*-5-phenyl-2-cyclohexen-1-ol [9] (0.906 g, 5.20 mmol) in THF (4 mL) at –78 ℃. The mixture was warmed and stirred for 15 min at 0 ℃ before di-*tert*-butyl dicarbonate (1.135 g, 5.20 mmol) in THF (1.5 mL) was added. The resulting solution was stirred for 12 h at rt, quenched with saturated aqueous $NaHCO_3$, and then diluted with 75mL of EtOAc. The layers were separated and the organic layer was extracted with H_2O (3 x 15 mL), washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Silica gel chromatography using 5% to 10% CH_2Cl_2/hexanes afforded 1.166 g (82% yield) of the desired compound as a colorless oil. TLC R_f = 0.45 (CH_2Cl_2/hexanes = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.18 (m, 5H), 5.92 (m, 1H), 5.75 (m, 1H), 5.36 (m, 1H), 2.96 (m, 1H), 2.40 – 2.26 (m, 2H), 2.22 – 2.12 (m, 1H), 1.94 – 1.84 (td, *J* = 13.0 Hz, 10.5 Hz, 1H) 1.49 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 153.5, 145.3, 130.6, 128.8, 127.1, 126.9, 126.7, 82.2, 74.0, 39.3, 35.3, 33.7, 28.0 ppm; IR (thin film): λ_{max} 3031, 2980, 2931, 1737, 1455, 1369, 1276, 1255, 1164, 1091, 983.1, 867.2, 700.0 cm^{-1}; HRMS (ES^+) calc'd for $C_{17}H_{22}O_3Na^+$ 297.1467, observed 297.1479 $[MNa]^+$.

Preparation of (η^6-toluene)$Cr(CO)_3$ Derivatives.

Compounds **1a**[10], **1c**[11], **1d**[11], **1h**[12], **1k**[13], **1l**[14], **1m**[10], **1n**[15], **1o**[16] and **1p**[17] were prepared according to general literature procedures for the synthesis of arene tricarbonylchromium complexes from $Cr(CO)_6$ and the parent arene. The complexes were crystallized from diethyl ether and hexanes to afford yellow crystalline solids.

General Procedure A. Synthesis of (η^6-toluene)$Cr(CO)_3$ derivatives (**1b**, **1e**, **1f**, **1g**, **1i**, and **1q**): A solution of $Cr(CO)_6$ (1.10 g, 5.0 mmol), arene (1.2 – 5 equiv), and THF (3 mL) in 1,4-dioxane (8 mL) was heated under reflux (oil bath temp = 120 °C) under a nitrogen atmosphere for 3 – 5 days. The yellow–orange solution was allowed to cool, and completion of the reaction was verified by the absence of solid $Cr(CO)_6$ on the sides of the flask (from sublimation) after refluxing subsided. After cooling to rt, the solution was filtered through Celite, and then evaporated under reduced pressure. The yellow product was either recrystallized from diethyl ether and hexanes or purified by column chromatography eluting with EtOAc/hexanes.

1b - (η^6-4-isopropyltoluene)$Cr(CO)_3$: General Procedure A was applied to 4-isopropyltoluene (3.9 mL, 25 mmol) and $Cr(CO)_6$ (1.10 g, 5.0 mmol). The desired compound was recrystallized from hexanes at -78 °C and isolated as a yellow solid (1.16 g, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.36 (d, *J* = 6.8 Hz, 2H), 5.15 (d, *J* = 6.8 Hz, 2H), 2.57 (septet, *J* = 7.0 Hz, 1H), 2.16 (s, 3H), 1.21 (d, *J* = 7.0 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 234.0, 117.4, 108.8, 93.7, 92.9, 32.6, 23.7, 20.5 ppm; IR (thin film): λ_{max} 2973, 2932, 2876, *1941, 1867, 1828* (strong CO stretch), 1479, 1382, 1036, 845.2, 667.4, 632.9 cm^{-1}; HRMS (ES^+) calc'd for $C_{13}H_{15}O_3Cr^+$ 271.0426, observed 271.0422 $[MH]^+$.

1e - (2-(η^6-*p*-tolyl)pyridine)$Cr(CO)_3$: General Procedure A was applied to 2-(*p*-tolyl)pyridine (4.2 mL, 25 mmol) and $Cr(CO)_6$ (1.10 g, 5.0 mmol). The desired compound was recrystallized from diethyl ether and hexanes at –16 °C and isolated as a yellow solid (1.22 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (d, *J* = 5.0 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.23 (m, 1H), 6.27 (d, *J* = 6.5 Hz, 2H), 5.32 (d, *J* = 6.5 Hz, 2H), 2.25 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.0, 153.8, 149.7, 137.1, 123.4, 119.9, 109.6, 103.1, 93.5, 92.4, 20.8 ppm; IR (thin film): λ_{max} 3082, 2925, *1965, 1873* (strong CO stretch), 1587, 1466, 1427, 779.1, 664.9, 630.1 cm^{-1}; HRMS (ES^+) calc'd for $C_{15}H_{11}NO_3Cr^+$ 305.0144, observed 305.0141 $[M]^+$.

1f - (2-(η^6-*p*-tolyl)thiophene)$Cr(CO)_3$: General Procedure A was applied to 2-(*p*-tolyl)thiophene (784 mg, 4.5 mmol) and $Cr(CO)_6$ (0.99 g, 4.5 mmol). Silica gel chromatography using 5% to 20% EtOAc/hexanes afforded 1.066 g (77% yield) of the desired compound as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 6.5 Hz, 1H), 7.22 (d, *J* = 3.5 Hz, 1H), 7.01 (m, 1H), 5.78 (d, *J* = 6.5 Hz, 2H), 5.28 (d, *J* = 6.5 Hz, 2H), 2.20 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.1, 139.9, 128.0, 126.2, 124.9, 108.1, 101.2, 92.6, 92.3, 20.6 ppm; IR (thin film): λ_{max} 3079, *1946, 1879, 1855* (strong CO stretch), 714.1, 665.6, 627.0 cm^{-1}; HRMS (ES^+) calc'd for $C_{14}H_{11}O_3SCr^+$ 310.9834, observed 310.9825 $[MH]^+$.

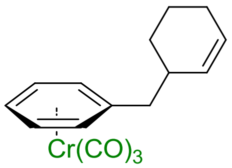
1g - (1-(η^6-*p*-tolyl)-1*H*-pyrrole)Cr(CO)$_3$: General Procedure A was applied to 1-(*p*-tolyl)-1*H*-pyrrole (2.2 g, 14 mmol) and $Cr(CO)_6$ (1.10 g, 5.0 mmol). Silica gel chromatography using 5% to 20% EtOAc/hexanes afforded 0.760 g (52% yield) of the desired compound as a yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ 6.95 (s, 2H), 6.28 (s, 2H), 5.63 (d, *J* = 6.0 Hz, 2H), 5.40 (d, *J* = 6.0 Hz, 2H), 2.17 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 232.8, 119.9, 115.7, 111.7, 105.7, 93.4, 85.5, 20.3 ppm; IR (thin film): λ_{max} 3132, 3082, 2922, *1949, 1883, 1852* (strong CO stretch), 1549, 1511, 1494, 1326, 733.3, 678.3, 665.6, 629.7 cm^{-1}; HRMS (ES^+) calc'd for $C_{14}H_{11}NO_3Cr^+$ 293.0144, observed 293.0142 $[M]^+$.

1i - (4-chloro-4'-η^6-methylbiphenyl)Cr(CO)$_3$: General Procedure A was applied to 4-chloro-4'-methylbiphenyl (1.01 g, 5.0 mmol) and $Cr(CO)_6$ (1.10 g, 5.0 mmol). Silica gel chromatography using 5% to 10% EtOAc/hexanes afforded 0.889 g (53% yield) of the desired compound as a yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.32 (m, 4H), 5.73 (d, *J* = 6.5 Hz, 2H), 5.30 (d, *J* = 6.5 Hz, 2H), 2.22 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.0, 135.3, 135.0, 129.2, 128.5, 108.8, 106.4, 93.7, 92.7, 20.6 ppm; IR (thin film): λ_{max} 3088, 2925, *1950, 1893, 1874* (strong CO stretch), 1470, 1099, 827.0, 665.7, 631.0 cm^{-1}; HRMS (ES^+) calc'd for $C_{16}H_{11}O_3ClCr^+$ 337.9802, observed 337.9789 $[M]^+$.

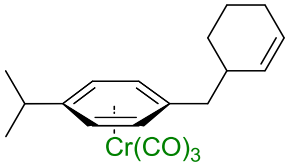
1q - (η^6-C_6H_5-CH_2-morpholine)Cr(CO)$_3$: General Procedure A was applied to 4-(phenylmethyl)-morpholine (1.54 g, 8.7 mmol) and $Cr(CO)_6$ (1.60 g, 7.25 mmol). The desired compound was recrystallized from diethyl ether and hexanes at –16 ℃ and isolated as a yellow solid (1.66 g, 73% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 5.40 – 5.30 (m, 4H), 5.28 – 5.22 (m, 1H), 3.76 – 3.63 (m, 4H), 3.24 (s, 2H), 2.57 – 2.44 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 232.9, 107.7, 94.0, 93.2, 91.6, 67.0, 62.1, 53.7 ppm; IR (thin film): λ_{max} 3066, 2971, 2867, 2817, *1961, 1877* (strong CO stretch), 1458, 1285, 1115, 1007, 865, 662, 630 cm^{-1}; HRMS (ES^+) calc'd for $C_{14}H_{16}NO_4Cr^+$ 314.0484, observed 314.0497 $[MH]^+$.

Procedure and Characterization for the Pd-catalyzed Allylic Substitution with (η^6-arene-CH_2Z)$Cr(CO)_3$-based Nucleophiles.

General Procedure B: An oven-dried reaction vial equipped with a stir bar was charged with (η^6-arene-CH_2Z)$Cr(CO)_3$ (0.10 mmol). To the reaction vial was added $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol, 3 equiv) under a nitrogen atmosphere followed by 0.5 mL of dry THF and the reaction mixture was stirred for 5 min. A solution of $Pd(COD)Cl_2$ (1.43 mg, 0.0050 mmol) and Xantphos (4.34 mg, 0.0075 mmol) in 0.5 mL THF was taken up by syringe and added to the reaction vial. After stirring for 5 min, the allylic electrophile (0.2 mmol, 2 equiv) was added to the reaction followed by NEt_3 (14 µL, 0.1 mmol, 1 equiv). The reaction mixture was stirred for 12 h. The reaction mixture was then quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional ethyl acetate and the solution was concentrated in vacuo. The crude material was loaded onto a silica gel column and purified by flash chromatography.

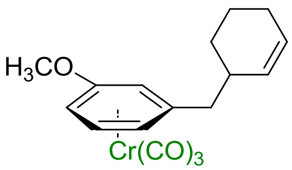


3a – (η^6-(2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$: The reaction was performed following General Procedure B with **1a** (22.8 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 µL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 µL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (29.7 mg, 96% yield) as a yellow solid. R_f = 0.45 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.74 (m, 1H), 5.55 (m, 1H), 5.39 (t, *J* = 6.0 Hz, 2H), 5.21 – 5.12 (m, 3H), 2.41 – 2.24 (m, 3H), 1.99 (m, 2H), 1.82 – 1.67 (m, 2H), 1.57 – 1.47 (m, 1H), 1.35 – 1.25 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.2, 129.6, 128.5, 112.0, 94.00, 93.97, 93.3, 93.2, 90.4, 42.0, 37.4, 28.6, 25.1, 22.3 ppm; IR (thin film): λ_{max} 3019, 2930, 2860, *1966*, *1877* (strong CO stretch), 1459, 662.5, 630.2 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{16}H_{16}O_3Cr^+$ 308.0505, observed 308.0492 [M]$^+$.

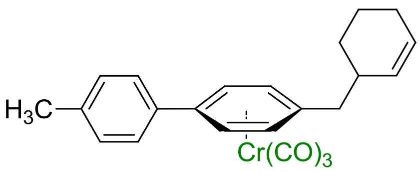


3b – (η^6-(2-cyclohexen-1-ylmethyl)-4-isopropylbenzene)$Cr(CO)_3$: The reaction was performed following General Procedure B with **1b** (27.0 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 µL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 µL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (31.0 mg, 89% yield) as a yellow solid. R_f = 0.60 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.73 (m, 1H), 5.56 (m, 1H), 5.34 (d, *J* = 6.0 Hz, 2H), 5.16 (d, *J* = 6.0 Hz, 2H), 2.59 (septet, *J* = 7.0 Hz, 1H), 2.40 – 2.23 (m, 3H), 1.99 (m, 2H), 1.83 – 1.68 (m, 2H), 1.59 – 1.47 (m, 1H), 1.37 –

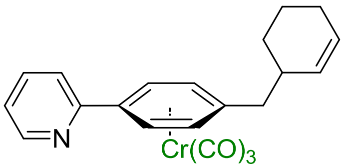
1.19 (m, 7H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.9, 130.0, 128.6, 117.9, 111.1, 93.42, 93.37, 93.32, 93.28, 41.9, 37.7, 32.6, 29.0, 25.4, 23.7, 21.2 ppm; IR (thin film): λ_{max} 3021, 2929, 2861, *1960*, *1877* (strong CO stretch), 1448, 722.3, 666.0, 627.4 cm^{-1}; HRMS (ES^+) calc'd for $C_{19}H_{22}O_3Cr^+$ 350.0974, observed 350.0973 $[M]^+$.



3c – (η^6-(2-cyclohexen-1-ylmethyl)-3-methoxybenzene)$Cr(CO)_3$: The reaction was performed following General Procedure B with **1c** (25.8 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (26.9 mg, dr = 1:1, 80% yield) as a yellow solid. R_f = 0.45 (EtOAc:hexanes = 1:9); ^1H NMR (500 MHz, $CDCl_3$): δ 5.74 (m, 1H), 5.61 – 5.49 (m, 2H), 5.07 – 4.98 (m, 2H), 4.75 (d, J = 6.0 Hz, 1H), 3.72 (s, 3H), 2.49 – 2.26 (m, 3H), 1.99 (m, 2H), 1.84 – 1.67 (m, 2H), 1.58 – 1.48 (m, 1H), 1.38 – 1.27 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.6, 143.79, 143.76, 129.9, 129.8, 128.8, 113.5, 95.0, 87.18, 87.16, 80.7, 80.5, 76.3, 76.2, 55.7, 42.5, 37.79, 37.76, 29.1, 28.9, 25.4, 21.23, 21.17 ppm; IR (thin film): λ_{max} 2931, *1959*, *1869* (strong CO stretch), 1537, 1460, 1267, 1150, 1030, 669.9, 629.7 cm^{-1}; HRMS (ES^+) calc'd for $C_{17}H_{19}O_4Cr^+$ 339.0688, observed 339.0722 $[MH]^+$.

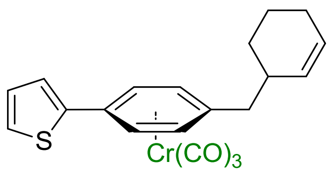


3d – (η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-tolyl)-benzene)$Cr(CO)_3$: The reaction was performed following General Procedure B with **1d** (31.8 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (38.0 mg, 90% yield) as a yellow solid. R_f = 0.45 (EtOAc:hexanes = 1:19); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.79 – 5.68 (m, 3H), 5.58 (m, 1H), 5.32 (d, J = 6.5 Hz, 2H), 2.44 – 2.28 (m, 6H), 1.99 (m, 2H), 1.86 – 1.68 (m, 2H), 1.60 – 1.48 (m, 1H), 1.38 – 1.28 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.4, 139.1, 133.7, 129.9, 129.7, 128.8, 127.1, 110.7, 108.9, 93.53, 93.49, 93.30, 93.28, 41.9, 37.8, 28.9, 25.4, 21.4, 21.2 ppm; IR (thin film): λ_{max} 3021, 2926, 2859, *1961*, *1880* (strong CO stretch), 1471, 1448, 817.2, 721.0, 661.4, 625.5 cm^{-1}; HRMS (ES^+) calc'd for $C_{23}H_{22}O_3Cr^+$ 398.0974, observed 398.0966 $[M]^+$.

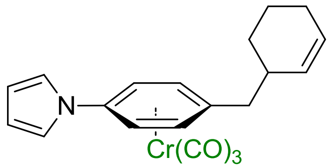


3e – (η^6-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$: The reaction was performed following General Procedure B with **1e** (30.5 mg, 0.1

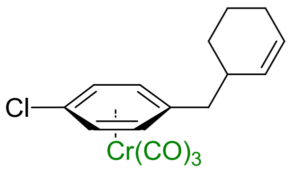
mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (29.4 mg, 77% yield) as a yellow solid. R_f = 0.20 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (d, *J* = 6.0 Hz, 1H), 7.73 (td, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 7.5 Hz, 5.0 Hz, 1H), 6.24 (d, *J* = 6.5 Hz, 2H), 5.75 (m, 1H), 5.58 (m, 1H), 5.34 (d, *J* = 6.5 Hz, 2H), 2.48 – 2.31 (m, 3H), 1.99 (m, 2H), 1.86 – 1.69 (m, 2H), 1.58 – 1.49 (m, 1H), 1.40 – 1.30 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.0, 153.8, 149.7, 137.1, 129.9, 128.8, 123.5, 120.1, 112.0, 103.8, 93.2, 93.1, 92.9, 92.8, 42.0, 37.7, 28.9, 25.4, 21.2 ppm; IR (thin film): λ_{max} 2927, 2858, *1963*, *1885* (strong CO stretch), 1587, 1462, 1432, 785.1, 661.9, 623.3 cm^{-1}; HRMS (ES^+) calc'd for $C_{21}H_{20}NO_3Cr^+$ 386.0848, observed 386.0837 $[MH]^+$.



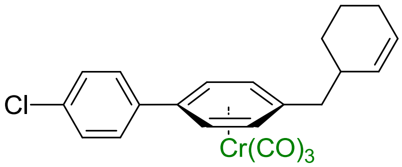
3f – (η^6-(2-cyclohexen-1-ylmethyl)-4-(2-thiophenyl)-benzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1f** (31.0 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (31.3 mg, 80% yield) as a yellow solid. R_f = 0.33 (EtOAc:hexanes = 1:19); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 7.23 (dd, *J* = 3.5 Hz, 1.0 Hz, 1H), 7.02 (dd, *J* = 5.0 Hz, 3.5 Hz, 1H), 5.79 – 5.72 (m, 3H), 5.58 (m, 1H), 5.30 (d, *J* = 6.5 Hz, 2H), 2.42 – 2.27 (m, 3H), 1.99 (m, 2H), 1.84 – 1.69 (m, 2H), 1.59 – 1.48 (m, 1H), 1.37 – 1.27 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.1, 139.9, 129.8, 128.8, 128.1, 126.3, 124.9, 110.4, 101.9, 93.12, 93.09, 91.83, 91.80, 41.9. 37.8, 28.9, 25.4, 21.2 ppm; IR (thin film): λ_{max} 3018, 2928, 2858, *1962*, *1881* (strong CO stretch), 1471, 1259, 852.1, 703.1, 660.2, 623.9 cm^{-1}; HRMS (ES^+) calc'd for $C_{20}H_{18}O_3SCr^+$ 390.0382, observed 390.0384 $[M]^+$.



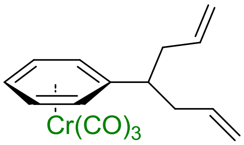
3g – (η^6-(2-cyclohexen-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1g** (29.3 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (27.5 mg, 74% yield) as a yellow solid. R_f = 0.50 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (t, *J* = 7.0 Hz, 2H), 6.29 (t, *J* = 7.0 Hz, 2H), 5.75 (m, 1H), 5.61 (d, *J* = 6.5 Hz, 2H), 5.56 (m, 1H), 5.41 (d, *J* = 6.5 Hz, 2H), 2.40 – 2.23 (m, 3H), 1.99 (m, 2H), 1.84 – 1.68 (m, 2H), 1.60 – 1.48 (m, 1H), 1.37 – 1.26 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 232.7, 129.7, 129.0, 119.9, 116.4, 111.8, 107.9, 93.8, 84.88, 84.86, 41.5, 37.8, 28.9, 25.4, 21.2 ppm; IR (thin film): λ_{max} 3018, 2929, 2859, *1965*, *1885* (strong CO stretch), 1543, 1492, 1326, 1065, 725.5, 665.7, 624.3 cm^{-1}; HRMS (ES^+) calc'd for $C_{20}H_{19}NO_3Cr^+$ 373.0770, observed 373.0771 $[M]^+$.



3h – (η^6-(2-cyclohexen-1-ylmethyl)-4-chlorobenzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1h** (26.3 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (15.3 mg, 45% yield) as a yellow solid. R_f = 0.67 (EtOAc:hexanes = 1:9); ^1H NMR (500 MHz, $CDCl_3$): δ 5.74 (m, 1H), 5.51 (m, 1H), 5.48 (d, *J* = 6.5 Hz, 2H), 5.27 (d, *J* = 6.5 Hz, 2H), 2.31 – 2.19 (m, 3H), 1.98 (m, 2H), 1.80 – 1.67 (m, 2H), 1.59 – 1.47 (m, 1H), 1.32 – 1.24 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 232.1, 129.5, 129.0, 110.5, 107.9, 93.7, 92.29, 92.27, 41.5, 37.7, 28.8, 25.3, 21.1 ppm; IR (thin film): λ_{max} 3084, 3019, 2929, 2859, *1971*, *1889* (strong CO stretch), 1452, 1087, 725.7, 659.1, 620.0 cm^{-1}; HRMS (ES^+) calc'd for $C_{16}H_{15}O_4Cr^+$ 323.0375, observed 323.0281 $[M-Cl+O]^+$.

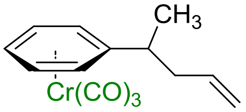


3i – (η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-chlorophenyl)-benzene) Cr(CO)$_3$: The reaction was performed following General Procedure B with **1i** (33.9 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (29.7 mg, 71% yield) as a yellow solid. R_f = 0.45 (EtOAc:hexanes = 1:19); ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.33 (m, 4H), 5.76 (m, 1H), 5.70 (d, *J* = 6.5 Hz, 2H), 5.58 (m, 1H), 5.31 (d, *J* = 6.5 Hz, 2H), 2.47 – 2.28 (m, 3H), 2.00 (m, 2H), 1.86 – 1.69 (m, 2H), 1.61 – 1.49 (m, 1H), 1.38 – 1.28 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.0, 135.3, 135.1, 129.8, 129.3, 128.9, 128.5, 111.1, 107.0, 93.3, 93.2, 93.13, 93.12, 41.9, 37.7, 28.9, 25.4, 21.2 ppm; IR (thin film): λ_{max} 3019, 2928, 2859, *1964*, *1886* (strong CO stretch), 1467, 1094, 1005, 830.0, 720.8, 664.8, 623.1 cm^{-1}; HRMS (ES^+) calc'd for $C_{22}H_{19}O_3ClCr^+$ 418.0428, observed 418.0447 $[M]^+$.

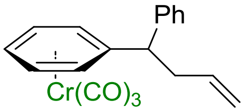


4ad – (η^6-(1-(2-propen-1-yl)-3-buten-1-yl)-benzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1a** (23.7 mg, 0.104 mmol), $LiN(SiMe_3)_2$

(100.4 mg, 0.60 mmol) and allyl *tert*-butyl carbonate (**2d**, 68 μL, 0.4 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (42 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:99) to give the product (25.9 mg, 81% yield) as a yellow solid. R_f = 0.60 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.75 (m, 2H), 5.31 – 5.16 (m, 5H), 5.11 – 4.99 (m, 4H), 2.46 (quint, *J* = 6.5 Hz, 1H), 2.40 – 2.29 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.4, 135.2, 118.1, 116.9, 93.4, 92.30, 92.26, 42.8, 38.8 ppm; IR (thin film): λ_{max} 3079, 2980, 2922, *1965*, *1867* (strong CO stretch), 1641, 1458, 1442, 1419, 997.0, 919.0, 814.6, 663.0, 631.1 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{13}H_{16}Cr^+$ 224.0657, observed 224.0658 $[M-(CO)_3]^+$.



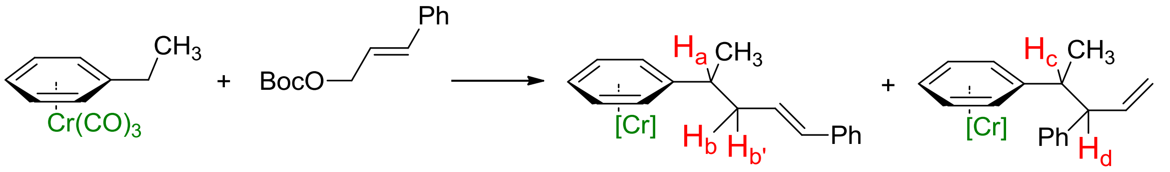
4kd – (η^6-(1-methyl-3-buten-1-yl)-benzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1k** (23.0 mg, 0.095 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and allyl *tert*-butyl carbonate (**2d**, 34 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (21 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:99) to give the product (23.0 mg, 86% yield) as a yellow solid. R_f = 0.50 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.75 (m, 1H), 5.35 – 5.21 (m, 5H), 5.08 – 4.98 (m, 2H), 2.58 – 2.49 (m, 1H), 2.39 – 2.30 (m, 1H), 2.25 – 2.16 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.4, 135.5, 118.5, 117.7, 93.8, 92.7, 92.6, 92.1, 91.6, 43.1, 38.1, 19.7 ppm; IR (thin film): λ_{max} 2959, 2924, 2853, *1974*, *1902* (strong CO stretch), 1462, 917.2, 812.9, 659.7, 628.1 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{11}H_{13}Cr^+$ 197.0422, observed 197.0424 $[M-H-(CO)_3]^+$.



4ld – (η^6-4,4-diphenyl-1-butene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1l** (29.6 mg, 0.097 mmol), $LiN(SiMe_3)_2$ (25.1 mg, 0.15 mmol) and allyl *tert*-butyl carbonate (**2d**, 25 μL, 0.15 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 3:97) to give the product (30.5 mg, 91% yield) as a yellow solid. R_f = 0.40 (EtOAc:hexanes = 1:19); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.15 (m, 5H), 5.67 (m, 1H), 5.51 – 4.95 (m, 7H), 3.68 (dd, *J* = 10.5 Hz, 5.0 Hz, 1H), 2.80 – 2.62 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.2, 142.0, 135.5, 128.9, 128.4, 127.4, 117.6, 116.4, 94.4, 92.5, 92.3, 92.2, 92.0, 49.9, 39.6 ppm; IR (thin film): λ_{max} 3083, 3030, 2927, *1965*, *1888* (strong CO stretch), 1494, 1454, 1417, 996.2, 919.4, 748.4, 703.0, 661.9, 630.1 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{16}H_{16}Cr^+$ 260.0657, observed 260.0670 $[M-(CO)_3]^+$.

Determination of Regioselectivity of **4ke**.

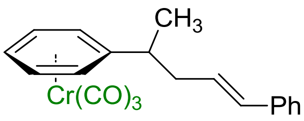
Ratio of linear:branched (L:B) was determined to be 77:23 at room temperature (or 85:15 at 0 °C) by ^{1}H NMR of the crude reaction mixture based on chemical shifts of indicated protons. The resonances for alkene C-H's and (η^6-arene) C-H's of the linear product overlap with those for the branched product.



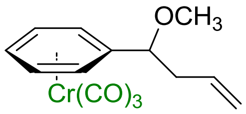
1k **2e**

Linear (**4ke**)
2.62 (m, 1H$_a$)
2.50 (m, 1H$_b$)
2.37 (m, 1H$_{b'}$)

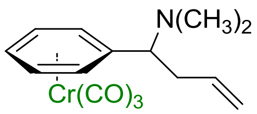
Branched
3.29, 3.19 (t, *J* = 8.7 Hz, 1H$_d$)
2.79, 2.73 (m, 1H$_c$)



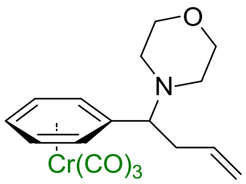
4ke – (η^6-*α*-(*E*)-cinnamyl-ethylbenzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1k** (24.2 mg, 0.10 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.30 mmol) and *tert*-butyl (*E*)-cinnamyl carbonate (**2e**, 46 μL, 0.20 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (21 μL, 0.1 mmol) at rt. The crude material was purified by flash chromatography on silica gel (eluted with CH$_2$Cl$_2$:hexanes = 5:95) to give the linear product (25.4 mg, 71% yield) as a yellow solid. R$_f$ = 0.30 (CH$_2$Cl$_2$:hexanes = 1:9); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.42 – 7.18 (m, 5H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.15 (dt, *J* = 16.0 Hz, 7.5 Hz, 1H), 5.40 – 5.20 (m, 5H), 2.68 – 2.57 (m, 1H), 2.55 – 2.45 (m, 1H), 2.42 – 2.32 (m, 1H), 1.28 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 233.4, 137.4, 132.9, 128.8, 127.5, 127.2, 126.3, 118.3, 93.7, 92.7, 92.6, 92.1, 91.5, 42.3, 38.6, 19.9 ppm; IR (thin film): λ_{max} 3082, 3026, 2969, 2930, *1962*, *1875* (strong CO stretch), 1529, 1495, 1460, 1420, 1379, 1157, 967.8, 815.0, 741.5, 693.8, 662.6, 631.7 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{17}H_{18}Cr^+$ 274.0814, observed 274.0830 [M-(CO)$_3$]$^+$.



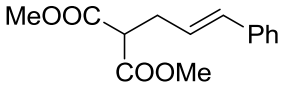
4od – (η^6-1-methoxy-1-phenyl-3-butene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1o** (24.2 mg, 0.094 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.30 mmol) and allyl *tert*-butyl carbonate (**2d**, 34 μL, 0.20 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (21 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95 to 10:90) to give the product (25.2 mg, 90% yield) as a yellow solid. R$_f$ = 0.33 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.80 (m, 1H), 5.55 (m, 1H), 5.35 – 5.21 (m, 4H), 5.12 – 5.03 (m, 2H), 3.94 (t, *J* = 6.0 Hz, 1H), 3.52 (s, 3H), 2.48 (m, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 233.1, 133.4, 118.5, 112.0, 93.1, 91.62, 91.58, 91.54, 91.42, 80.9, 58.5, 42.3 ppm; IR (thin film): λ_{max} 3082, 2984, 2935, 2831, *1965, 1888, 1867* (strong CO stretch), 1642, 1456, 1418, 1099, 997.4, 921.4, 818.0, 665.9, 631.8 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{11}H_{15}OCr^+$ 215.0528, observed 215.0523 $[MH-(CO)_3]^+$.



4pd – (η^6-*α*-allyl-*N,N*-dimethyl-benzylamine)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1p** (26.6 mg, 0.098 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and allyl *tert*-butyl carbonate (**2d**, 34 μL, 0.20 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (21 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 40:60) to give the product (28.6 mg, 94% yield) as a yellow solid. R$_f$ = 0.25 (EtOAc:hexanes = 4:6); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.92 (m, 1H), 5.40 – 5.24 (m, 5H), 5.21 – 5.09 (m, 2H), 3.41 (dd, *J* = 9.0 Hz, 5.5 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.49 – 2.40 (m, 1H), 2.24 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.0, 136.0, 117.0, 108.7, 95.9, 93.3, 92.3, 91.46, 91.36, 66.5, 40.8, 33.8 ppm; IR (thin film): λ_{max} 3078, 2938, 2827, 2783, *1965*, *1888*, *1867* (strong CO stretch), 1641, 1456, 998.7, 915.2, 662.5, 631.5 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{15}H_{18}NO_3Cr^+$ 312.0692, observed 312.0695 $[MH]^+$.

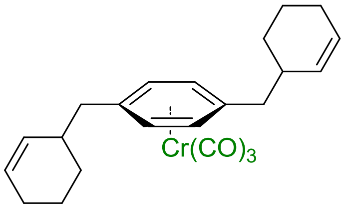


4qd – (η^6-4-(1-phenyl-3-butenyl)-morpholine)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1q** (31.0 mg, 0.10 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and allyl *tert*-butyl carbonate (**2d**, 34 μL, 0.20 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (21 μL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 30:70) to give the product (34.4 mg, 97% yield) as a yellow solid. R$_f$ = 0.55 (EtOAc:hexanes = 4:6); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.93 (m, 1H), 5.40 – 5.24 (m, 5H), 5.20 – 5.07 (m, 2H), 3.67 (m, 4H), 3.39 (dd, *J* = 9.0 Hz, 5.0 Hz, 1H), 2.66 – 2.54 (m, 3H), 2.49 – 2.38 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.0, 135.7, 117.1, 109.1, 95.5, 93.2, 92.2, 91.5, 91.4, 67.4, 66.8, 49.4, 33.7 ppm; IR (thin film): λ_{max} 3079, 2958, 2856, 2818, *1965, 1888, 1867* (strong CO stretch), 1641, 1454, 1292, 1116, 997.3, 916.6, 665.7, 630.9 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{17}H_{20}NO_4Cr^+$ 354.0797, observed 354.0794 $[MH]^+$.

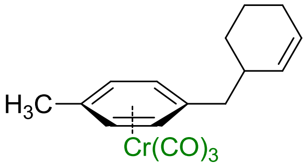


***α*-(*E*)-cinnamyl dimethyl malonate**: The reaction was performed following General Procedure B with dimethyl malonate (23 μL, 0.20 mmol), BSA (49 μL, 0.20 mmol) and *tert*-butyl (*E*)-cinnamyl carbonate (**2e**, 23 μL, 0.10 mmol) in the presence of 5 mol % Pd(COD)Cl_2/Xantphos catalyst and KOAc (1.0 mg, 10 mol %) in THF (1 mL) at rt for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95) to give the product (L:B > 20:1, 21.0 mg, 85%

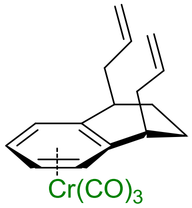
yield) as a colorless oil. R_f = 0.25 (EtOAc:hexanes = 1:9). The NMR spectral data match the previously published data.[18]



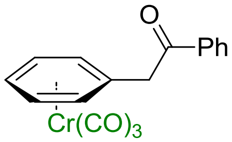
7 – (η^6-1,4-di(2-cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1m** (24.2 mg, 0.10 mmol), LiN(SiMe$_3$)$_2$ (100.4 mg, 0.60 mmol) and 2-cyclohexenyl mesitoate (**2k**, 94 µL, 0.40 mmol) in the presence of 10 mol % Pd catalyst and NEt$_3$ (28 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (31.3 mg, 78% yield) as a yellow solid. R_f = 0.50 (EtOAc:hexanes = 1:19); ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.74 (m, 2H), 5.55 (m, 2H), 5.23 (s, 4H), 2.38 – 2.20 (m, 6H), 2.05 – 1.91 (m, 4H), 1.83 – 1.66 (m, 4H), 1.58 – 1.47 (m, 2H), 1.35 – 1.23 (m, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 233.7, 130.0, 128.7, 109.9, 94.5, 41.9, 37.7, 29.0, 25.4, 21.2 ppm; IR (thin film): λ_{max} 2957, 2925, 2854, *1968, 1894* (strong CO stretch), 1728, 1463, 1378, 1287, 722.2, 665.4, 626.3 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{20}H_{26}Cr^+$ 318.1440, observed 318.1450 $[M-(CO)_3]^+$.



8 – (η^6-(2-cyclohexen-1-ylmethyl)-4-methylbenzene)Cr(CO)$_3$: The product was a byproduct from the preceding reaction. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (4.8 mg, 15% yield) as a yellow solid. R_f = 0.40 (EtOAc:hexanes = 1:19); ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.73 (m, 1H), 5.54 (m, 1H), 5.30 – 5.15 (m, 4H), 2.36 – 2.20 (m, 3H), 2.15 (s, 3H), 2.02 – 1.92 (m, 2H), 1.82 – 1.65 (m, 2H), 1.57 – 1.46 (m, 1H), 1.35 – 1.22 (m, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 233.8, 129.9, 128.7, 109.2, 107.6, 95.02, 95.00, 94.07, 94.04, 41.8, 37.7, 28.9, 25.4, 21.2, 20.5 ppm; IR (thin film): λ_{max} 2926, 2859, *1959, 1867* (strong CO stretch), 1448, 1381, 668.4, 631.7, 535.3 cm^{-1}; HRMS (ES$^+$) calc'd for $C_{14}H_{18}Cr^+$ 238.0814, observed 238.0867 $[M-(CO)_3]^+$.



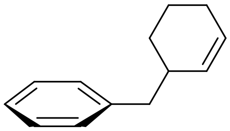
9 – (η^6-(*R,S*)-1,2,3,4-tetrahydro-1,4-di-2-propen-1-yl-naphthalene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1n** (26.8 mg, 0.10 mmol), LiN(SiMe$_3$)$_2$ (100.4 mg, 0.60 mmol) and allyl *tert*-butyl carbonate (**2d**, 68 µL, 0.40 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (42 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with Et$_2$O:hexanes = 5:95) to give the product (26.2 mg, 76% yield) as a yellow solid. R_f = 0.50 (EtOAc:hexanes = 1:19); ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.76 (m, 2H), 5.38 – 5.24 (m, 4H), 5.12 – 5.03 (m, 4H), 2.73 (m, 2H), 2.45 – 2.37 (m, 2H), 2.37 – 2.28 (m, 2H), 1.86 – 1.76 (m, 2H), 1.70 – 1.59 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 233.7, 135.6, 117.8, 113.6, 93.2, 92.2, 41.3, 36.6, 23.9 ppm; IR (thin film): λ_{max} 2934, *1959*, *1870* (strong CO stretch), 1458, 995.3, 917.6, 667.1, 630.7 cm^{-1}; HRMS (ES^+) calc'd for $C_{16}H_{20}Cr^+$ 264.0970, observed 264.0958 $[M-(CO)_3]^+$.



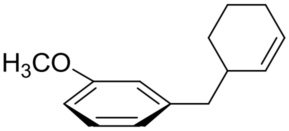
(η^6-benzyl phenyl ketone)$Cr(CO)_3$: The reaction was performed following General Procedure B with **1a** (23.2 mg, 0.102 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and 1-cyclohex-2-enyl benzoate (**2c**, 37 μL, 0.2 mmol) and NEt_3 (14 μL, 0.1 mmol) *in the absence of Pd catalyst*. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95 to 40:60) to give the product (33.2 mg, 98% yield) as a yellow solid. R_f = 0.33 (EtOAc:hexanes = 1:9). The NMR spectral data match the previously published data.[25]

Procedure and Characterization for the Tandem Allylic Substitution/Demetallation.

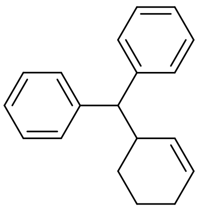
General Procedure C: The reaction was conducted according to General Procedure B described above. After 12 h, the reaction was quenched with two drops of H_2O, diluted with 10 – 20 mL of diethyl ether, and the solution was exposed to sunlight by placing it on the windowsill and stirring for 3 – 6 h. The demetallation step was monitored until TLC showed complete consumption of the (η^6-arene)$Cr(CO)_3$ product. During this time, a green precipitate formed as the chromium was oxidized. The reaction mixture was then filtered through a pad of $MgSO_4$ and silica, concentrated *in vacuo* and loaded directly onto a silica gel column.



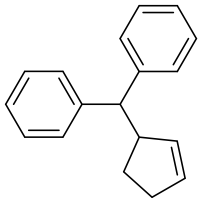
3'a – (2-cyclohexen-1-ylmethyl)-benzene: The reaction was performed following General Procedure C with **1a** (22.8 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the organic product (15.9 mg, 92% yield) as a colorless oil. R_f = 0.60 (EtOAc:hexanes = 1:19). The NMR spectral data match the previously published data.[19]



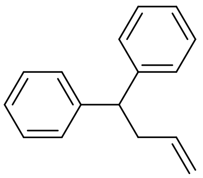
3'c – (2-cyclohexen-1-ylmethyl)-3-methoxybenzene: The reaction was performed following General Procedure C with **1c** (24.9 mg, 0.0965 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the organic product (14.2 mg, 73% yield) as a colorless oil. R_f = 0.67 (EtOAc:hexanes = 1:19); ^1H NMR (500 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.5 Hz, 1H), 6.80 – 6.66 (m, 3H), 5.69 (m, 1H), 5.57 (m, 1H), 3.80 (s, 3H), 2.61 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H) , 2.51 (dd, *J* = 13.2 Hz, 8.4 Hz, 1H), 2.37 (m, 1H), 1.98 (m, 2H), 1.76 – 1.66 (m, 2H), 1.53 – 1.46 (m, 1H), 1.31 – 1.19 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.7, 142.8, 131.5, 129.3, 127.6, 121.8, 115.1, 111.2, 55.3, 43.0, 37.3, 29.1, 25.6, 21.5 ppm; IR (thin film): λ_{max} 3017, 2925, 2854, 1601, 1585, 1488, 1454, 1260, 1153, 1044, 773.1, 697.0 cm^{-1}; HRMS (CI^+) calc'd for $C_{14}H_{18}O^+$ 202.1358, observed 202.1360 $[M]^+$.



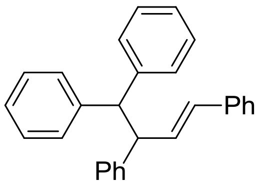
5lb – 3-(diphenylmethyl)-1-cyclohexene: The reaction was performed following General Procedure C with **1l** (30.4 mg, 0.10 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2b** (39 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the organic product (24.0 mg, 96% yield) as a colorless oil. R_f = 0.60 (EtOAc:hexanes = 3:97). The ^{1}H NMR spectrum matches the previously published report.[20] The ^{13}C NMR spectrum of the title compound was not reported before. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 144.4, 144.1, 130.2, 128.70, 128.65, 128.5, 128.4, 128.2, 126.32, 126.28, 58.4, 39.1, 28.5, 25.6, 21.7 ppm.



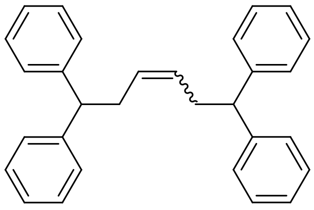
5lg – 3-(diphenylmethyl)-1-cyclopentene: The reaction was performed following General Procedure C with **1l** (30.4 mg, 0.10 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and *tert*-butyl 2-cyclopentenyl carbonate (**2g**, 40 μL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the organic product (20.8 mg, 89% yield) as a colorless oil. R_f = 0.60 (EtOAc:hexanes = 3:97). The ^{1}H NMR spectrum matches the previously published report.[20] The ^{13}C NMR spectrum of the title compound was not reported before. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.0, 144.7, 134.1, 131.6, 128.59, 128.56, 128.4, 128.3, 126.3, 58.4, 50.4, 32.2, 29.6 ppm.



5ld – 4,4-diphenyl-1-butene: The reaction was performed following General Procedure C with **1l** (30.4 mg, 0.10 mmol), $LiN(SiMe_3)_2$ (25.1 mg, 0.15 mmol) and allyl *tert*-butyl carbonate (**2d**, 25 μL, 0.15 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the organic product (18.9 mg, 91% yield) as a colorless oil. R_f = 0.75 (EtOAc:hexanes = 5:95). The NMR spectral data match the previously published data.[21]



5lf – (*E*)-1,1,2,4-tetraphenylbut-3-ene: The reaction was performed following General Procedure C with **1l** (30.4 mg, 0.10 mmol), $LiN(SiMe_3)_2$ (25.1 mg, 0.15 mmol) and (*E*)-1,3-diphenyl allyl acetate (**2f**, 30.3 mg, 0.12 mmol) in the presence of 5 mol % $[Pd(allyl)Cl]_2$ and 10 mol % DPPP. After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 1:9) to give the organic product (34.3 mg, 91% yield) as a white solid. R_f = 0.50 (EtOAc:hexanes = 5:95); m.p. = 119–120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 6.96 (m, 20H), 6.27 (dd, *J* = 15.5 Hz, 7.5 Hz, 1H), 6.17 (d, *J* = 15.5 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 4.31 (dd, *J* = 11.0 Hz, 7.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.5, 143.4, 143.1, 137.8, 133.2, 131.3, 128.9, 128.7, 128.6, 128.52, 128.47, 128.3, 127.2, 126.5, 126.3, 126.1, 57.6, 53.8 ppm; IR (thin film): λ_{max} 3060, 3026, 2907, 1599, 1494, 1450, 961.2, 742.3, 697.5 cm^{-1}; HRMS (CI$^+$) calc'd for $C_{28}H_{25}^+$ 361.1956, observed 361.1942 [MH]$^+$.

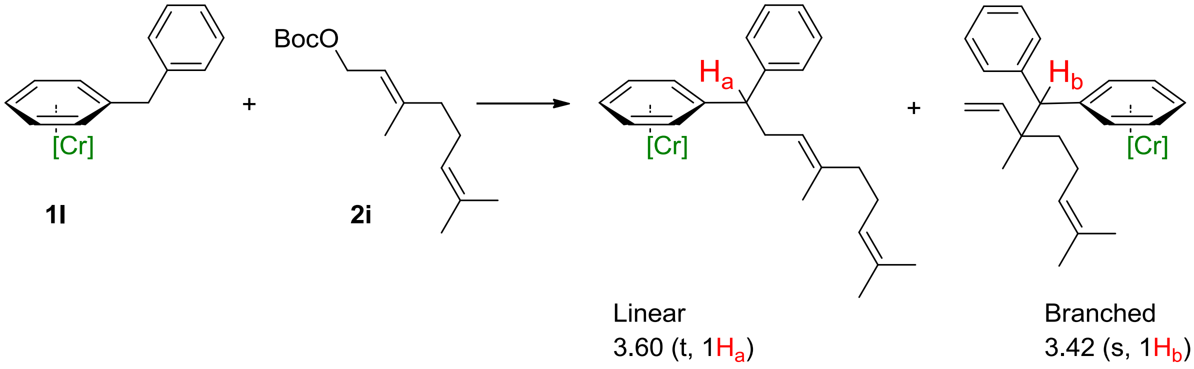


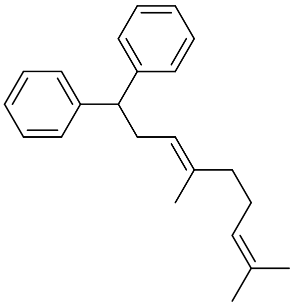
cis:*trans* = 2:1

5lh – 1,1,6,6-tetraphenylhex-3-ene (*cis*:*trans* = 2:1): The reaction was performed following General Procedure C with **1l** (68.4 mg, 0.225 mmol), LiN(SiMe$_3$)$_2$ (56.4 mg, 0.337 mmol) and *cis*-1,4-diacetoxy-2-butene (**2h**, 12 µL, 0.075 mmol) in the presence of 5 mol % [Pd(allyl)Cl]$_2$ and 10 mol % DPPP. After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the organic product (22.3 mg, 77% yield) as a white solid. R$_f$ = 0.50 (EtOAc:hexanes = 5:95); m.p. data for the title compound have been reported[22]; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29 – 7.09 (m, 10H), 5.35 – 5.24 (m, 2H), 3.86 – 3.76 (m, 2H), 2.76 – 2.60 (m, 4H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 144.9, 130.3, 129.1, 128.6, 128.5, 128.2, 126.4, 126.3, 51.8, 51.3, 39.0, 33.8 ppm; IR (thin film): λ_{max} 3060, 3025, 2923, 2852, 1599, 1493, 1450, 742.8, 698.5 cm^{-1}; HRMS (CI$^+$) calc'd for $C_{30}H_{29}^+$ 389.2269, observed 389.2287 [MH]$^+$.

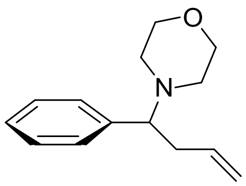
Determination of Regioselectivity of **5li**.

Ratio of linear:branched (L:B) was determined to be 78:22 by ^{1}H NMR of the crude reaction mixture based on chemical shifts of indicated protons.



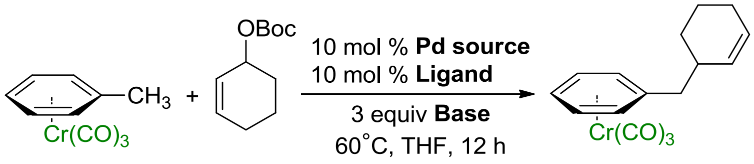


5li – *α*-geranyl-diphenylmethane: The reaction was performed following General Procedure C with **1l** (31.3 mg, 0.103 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.30 mmol) and *tert*-butyl geranyl carbonate (**2i**, 56 µL, 0.20 mmol) in the presence of 5 mol % Pd catalyst and NEt_3 (14 μL, 0.1 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the organic product (22.9 mg, 73% yield) as a colorless oil. R_f = 0.75 (EtOAc:hexanes = 5:95); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.13 (m, 10H), 5.07 (t, *J* = 6.5 Hz, 1H), 4.99 (t, *J* = 6.5 Hz, 1H), 3.94(t, *J* = 7.5 Hz, 1H), 2.73(t, *J* = 7.5 Hz, 2H), 2.01 – 1.94 (m, 2H), 1.94 – 1.87 (m, 2H), 1.64 (s, 3H), 1.54 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.2, 136.5, 131.5, 128.5, 128.3, 126.2, 124.5, 122.8, 51.7, 39.9, 34.5, 26.8, 25.9, 17.9, 16.3 ppm; IR (thin film): λ_{max} 3026, 2965, 2923, 2854, 1494, 1450, 1376, 748.6, 698.6 cm^{-1}; HRMS (CI$^+$) calc'd for $C_{23}H_{29}^+$ 305.2269, observed 305.2277 [MH]$^+$.



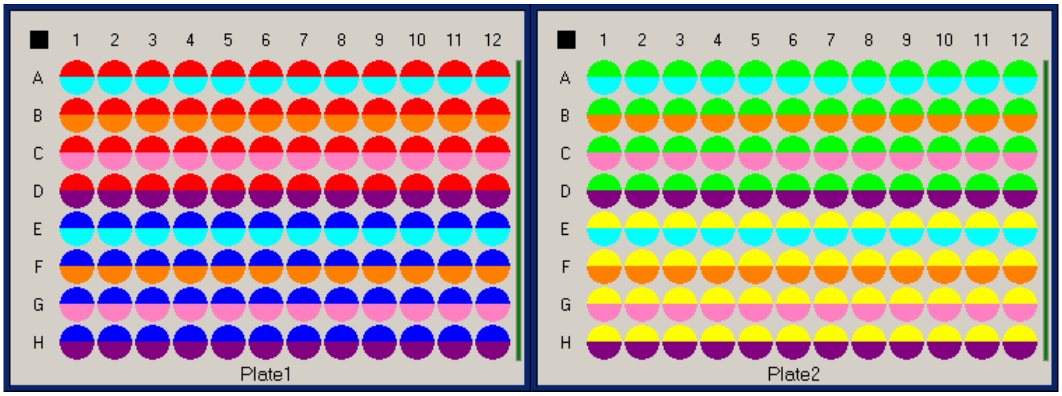
4'qd – 4-(1-phenyl-3-butenyl)-morpholine: The reaction was performed following General Procedure C with **1q** (0.939 g, 3.0 mmol), $LiN(SiMe_3)_2$ (1.506 g, 9.0 mmol) and allyl *tert*-butyl carbonate (**2d**, 1.0 mL, 6.0 mmol) in the presence of 5 mol % Pd catalyst and PMDTA (0.63 mL, 3.0 mmol). After demetallation, the crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:8 to EtOAc:hexanes = 3:7) to give the organic product (0.580 g, 89% yield) as a light yellow oil. R_f = 0.60 (EtOAc:hexanes = 3:7). The NMR spectral data match the previously published data.[23]

Microscale High-throughput Experimentation (HTE) for Catalyst Identification.



1 equiv **1a** 2 equiv **2a** **3a**

Ligand was used in a 2:1 ratio relative to Pd for monodentate ligands and 1:1 ratio for bidentate ligands.



12 **Ligand**s x 4 **Pd source**s x 4 **Base**s at 60 ℃ in THF (25 µL) at [**1a**] = 0.1 M on a 2.5 µmol scale.

12 **Ligand**s were:

1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE;

1,1'-BIS(DIISOPROPYLPHOSPHINO)FERROCENE;

1,3-BIS(DIPHENYLPHOSPHINO)PROPANE;

1,4-BIS(DIPHENYLPHOSPHINO)BUTANE;

BIS(2-DIPHENYLPHOSPHINOPHENYL)ETHER;

9,9-DIMETHYL-4,5-BIS(DIPHENYLPHOSPHINO)XANTHENE;

(R)-(+)-2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BINAPHTHYL;

(R)-(S)-Cy2PF-PtBu2;

N-PHENYL-2-(DI-T-BUTYLPHOSPHINO)PYRROLE;

2-DI-TERT-BUTYLPHOSPHINO-2',4',6'-TRIISOPROPYLBIPHENYL;

TRICYCLOHEXYLPHOSPHONIUM TETRAFLUOROBORATE;

TRI-O-TOLYLPHOSPHINE.

The 12 ligands were predosed in each column from 1 to 12 for both plates.

4 **Pd source**s were: $[Pd(allyl)Cl]_2$, $Pd_2(dba)_3$, $Pd(COD)Cl_2$ and $Pd(OAc)_2$.

Plate 1: A1-D12 = $[Pd(allyl)Cl]_2$ and E1-H12 = $Pd_2(dba)_3$.

Plate 2: A1-D12 = $Pd(COD)Cl_2$ and E1-H12 = $Pd(OAc)_2$.

4 **Base**s were: $LiN(SiMe_3)_2$, LDA, *t*-BuOK and $KN(SiMe_3)_2$.

Rows A & E = $LiN(SiMe_3)_2$; B & F = LDA; C & G = *t*-BuOK; D & H = $KN(SiMe_3)_2$ for both plates.

Experimental:

Set up:

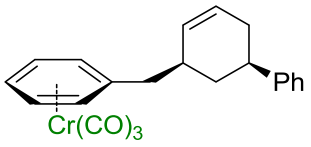
The screening was set up inside a glovebox under a nitrogen atmosphere. Two 96-well aluminum blocks containing 100 μL glass vials were predosed in each column from 1 to 12 for both plates. The solution or slurry of the Pd sources in 25 μL of THF (10 mol %) was dosed in each vial, and the solvent THF was removed using a Genevac vacuum centrifuge. Small perylene magnetic stirbars were added to the reaction vials. A stock solution containing **1a**, **2a**, and base in THF was prepared at [**1a**] = 0.1 M, and 25 μL of the stock solution was dosed in each vial using an Eppendorf multi-channel pipet. The 96-well plates were sealed and agitated at ~960 rpm for overnight at 60 ℃ (control with thermocouple) by using a tumble stirrer provided with heating element.

Work up:

The plates were cooled to room temperature, and then opened to air and 125 μL of acetonitrile (containing 0.25 μmol of biphenyl as internal standard) was syringed into each vial by means of an Eppendorf multi-channel pipet (to ensure complete solubilization of the reaction mixture). The plates were then covered again and the vials stirred for 15-20 minutes to extract the product and to ensure good homogenization. Portions of each reaction mixture (20 μL) were then transferred with the multi-channel pipet into 96-well HPLC blocks pre-filled with 750 μL of acetonitrile. The blocks were then mounted on HPLC instruments for analysis (no filtration necessary for the corresponding volumes and concentrations). Agilent 1200 Series HPLC instruments with reverse phase C–18 columns and acetonitrile/water as mobile phase were used. Data processing was done by using Agilent's ChemStation software and biphenyl as an internal standard.

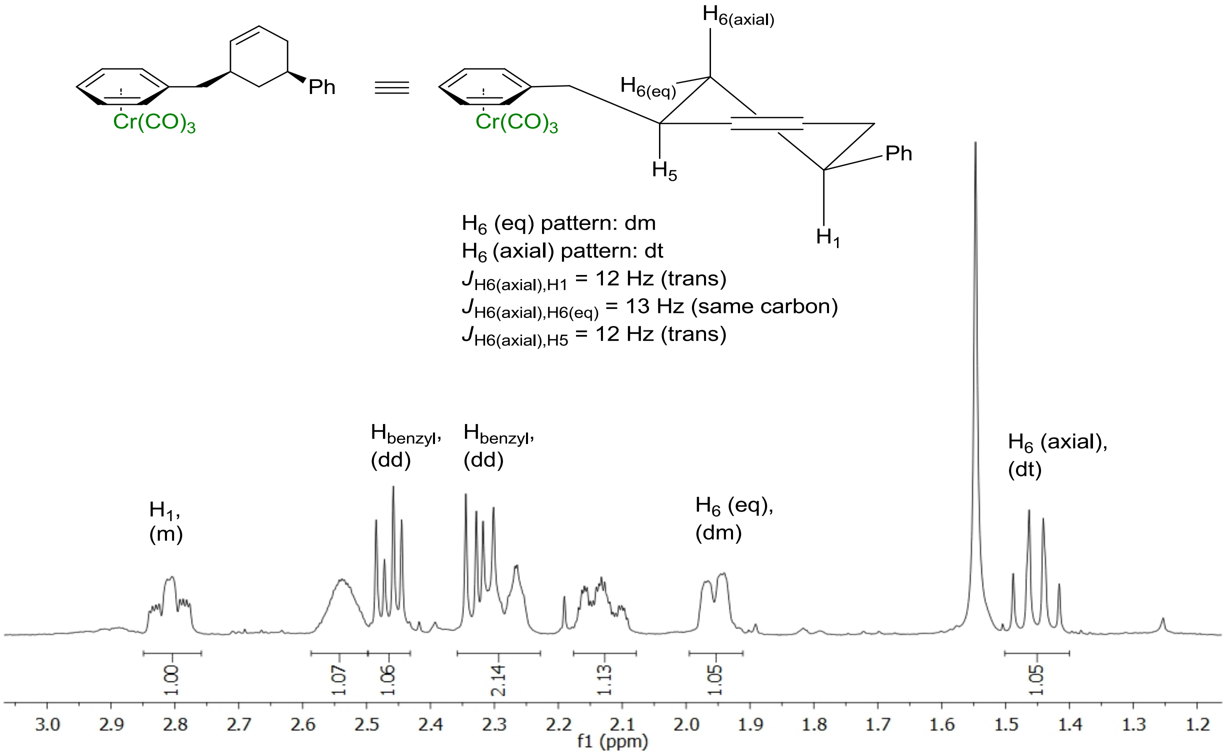
The lead hit from the screening was the combination of $Pd(COD)Cl_2$, $LiN(SiMe_3)_2$, and Xantphos, giving 36% yield of the desired product **3a**. A scale-up reaction on a 0.1 mmol scale using the General Procedure B for the Pd-catalyzed allylic substitution reaction proved successful with isolation of **3a** in 39% yield.

Determination of the Relative Stereochemistry of Compound 6.



6 – *cis*-(η^6-(5-phenyl-2-cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$: The reaction was performed following General Procedure B with **1a** (22.8 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.30 mmol) and *cis*-*tert*-butyl (5-phenyl-2-cyclohexenyl) carbonate (**2j**, 53 µL, 0.2 mmol) in the presence of 5 mol % Pd catalyst and NEt$_3$ (14 µL, 0.1 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (24.2 mg, 63% yield) as a yellow solid. R$_f$ = 0.45 (EtOAc:hexanes = 1:19); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.34 – 7.15 (m, 5H), 5.83 (m, 1H), 5.63 (m, 1H), 5.38 (m, 2H), 5.16 (m, 3H), 2.81 (m, 1H), 2.54 (m, 1H), 2.47 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 2.32 (dd, *J* = 13.5 Hz, 8.0 Hz, 1H), 2.27 (m, 1H), 2.13 (m, 1H), 1.96(dm, *J* = 13 Hz, 1H), 1.45 (dt, *J* = 13 Hz, 12 Hz, 12 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 233.3, 146.7, 129.8, 128.7, 128.3, 127.0, 126.5, 111.6, 94.14, 94.09, 93.4, 93.2, 90.5, 42.5, 40.6, 39.7, 36.9, 34.0 ppm; IR (thin film): λ$_{max}$ 3083, 3025, 2919, 2852, *1965*, *1878* (strong CO stretch), 1604, 1493, 1453, 1419, 1154, 758.8, 700.8, 662.6, 630.9 cm^{-1}; HRMS (ES$^+$) calc'd for C$_{19}$H$_{20}$Cr$^+$ 300.0970, observed 300.0966 [M-(CO)$_3$]$^+$.

The relative chemistry of the single diastereomer was established by ^{1}H NMR splitting patterns and coupling constants.[24] ^{1}H NMR spectrum of compound **6** is consistent with those of the starting alcohol (*cis*-5-phenyl-2-cyclohexen-1-ol) and carbonate (**2j**).



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Crystal Structure for 3a

Diffraction-quality single-crystals were obtained by slow evaporation of a diethyl ether/hexanes solution of **3a**.

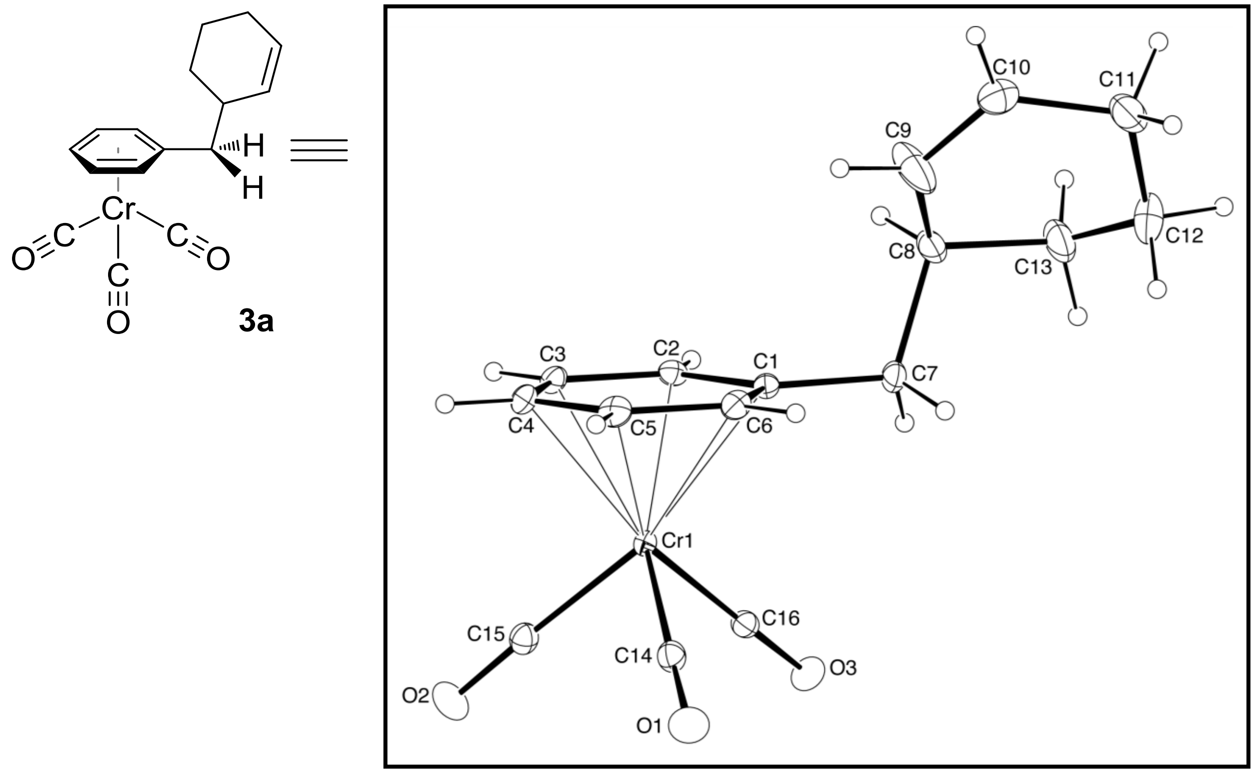

3a

Table 1. lists cell information, data collection parameters, and refinement data.

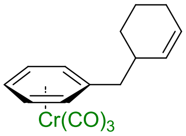
Table 1. Summary of Structure Determination of Compound 3a

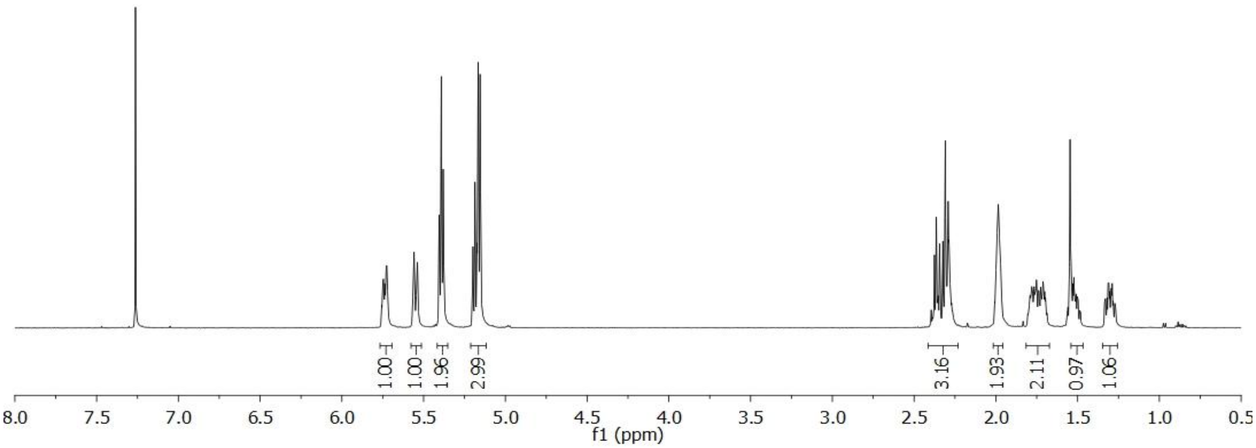
Empirical formula	$C_{16}H_{16}O_3Cr$
Formula weight	308.29
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Cell constants:	
a	5.9990(5) Å
b	11.8071(9) Å
c	19.7318(15) Å
β	92.184(4) °
Volume	1396.60(19) Å^3
Z	4
Density (calculated)	1.466 Mg/m^3
Absorption coefficient	0.822 mm^{-1}
F(000)	640

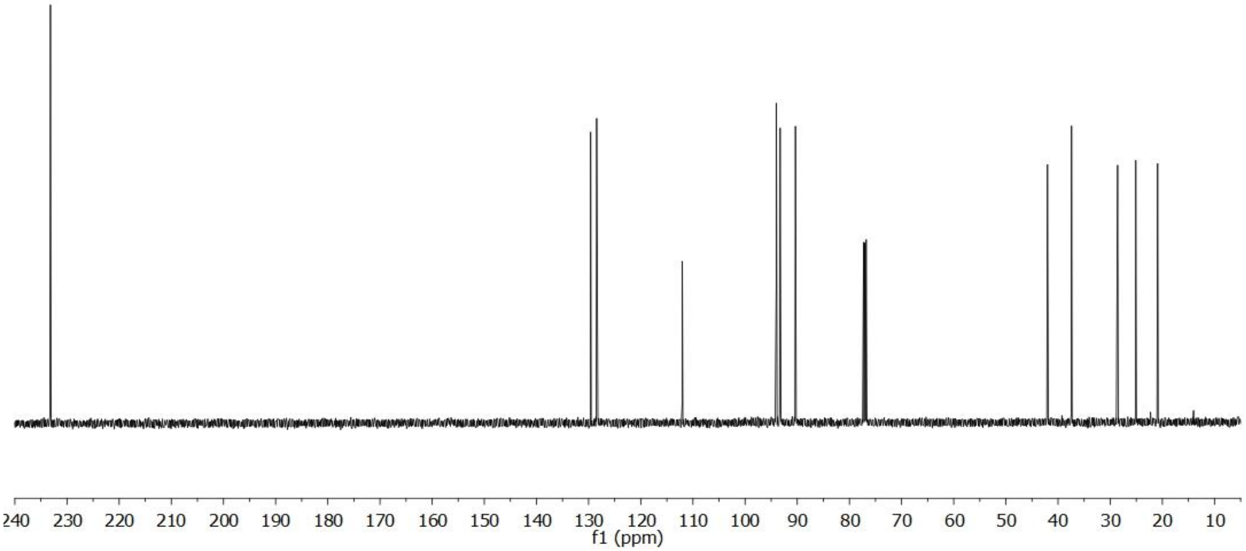
Crystal size	0.48 x 0.32 x 0.01 mm^3
Theta range for data collection	2.01 to 27.50 °
Index ranges	$-7 \le \eta \le 7$, $-15 \le \kappa \le 15$, $-25 \le \lambda \le 25$
Reflections collected	26318
Independent reflections	3209 [R(int) = 0.0267]
Completeness to theta = 27.50 °	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6477
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3209 / 0 / 182
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1014
R indices (all data)	R1 = 0.0462, wR2 = 0.1034
Largest diff. peak and hole	1.494 and -1.252 e.$Å^{-3}$

NMR Spectra.

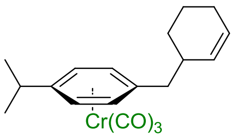
3a – (η^6-(2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$

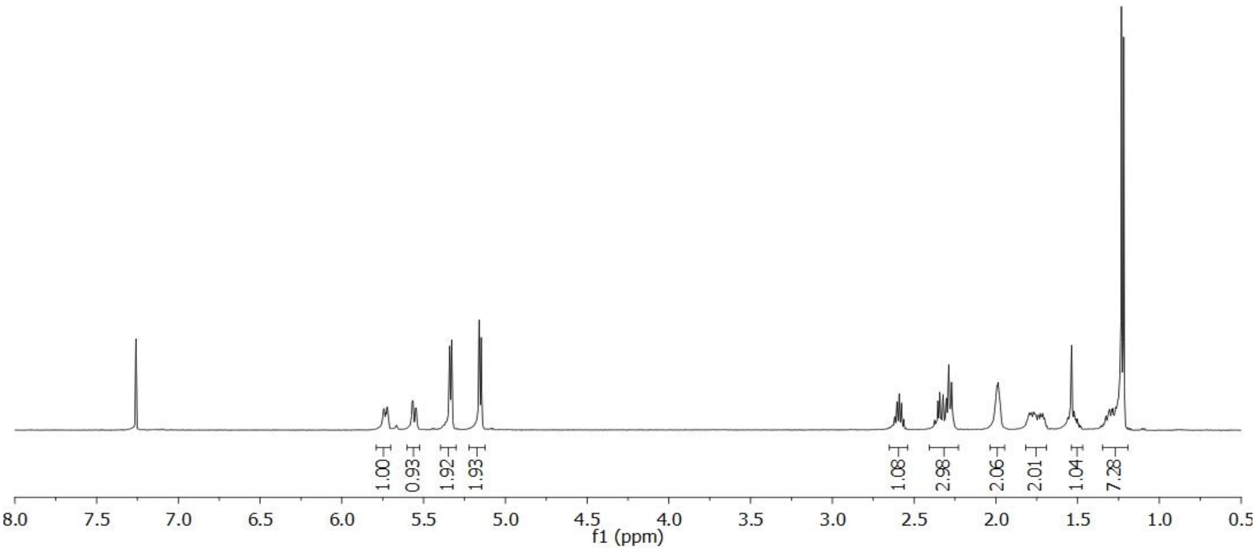


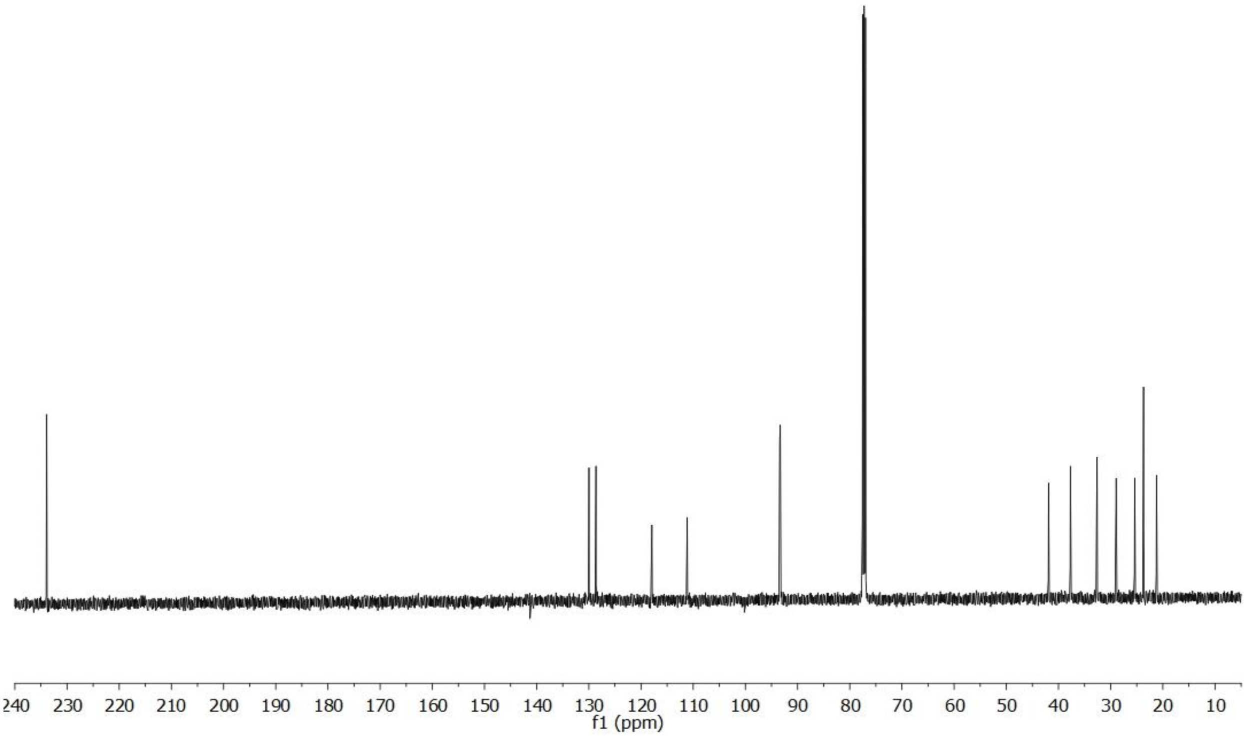




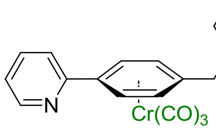
3b – (η^6-(2-cyclohexen-1-ylmethyl)-4-isopropylbenzene)Cr(CO)$_3$

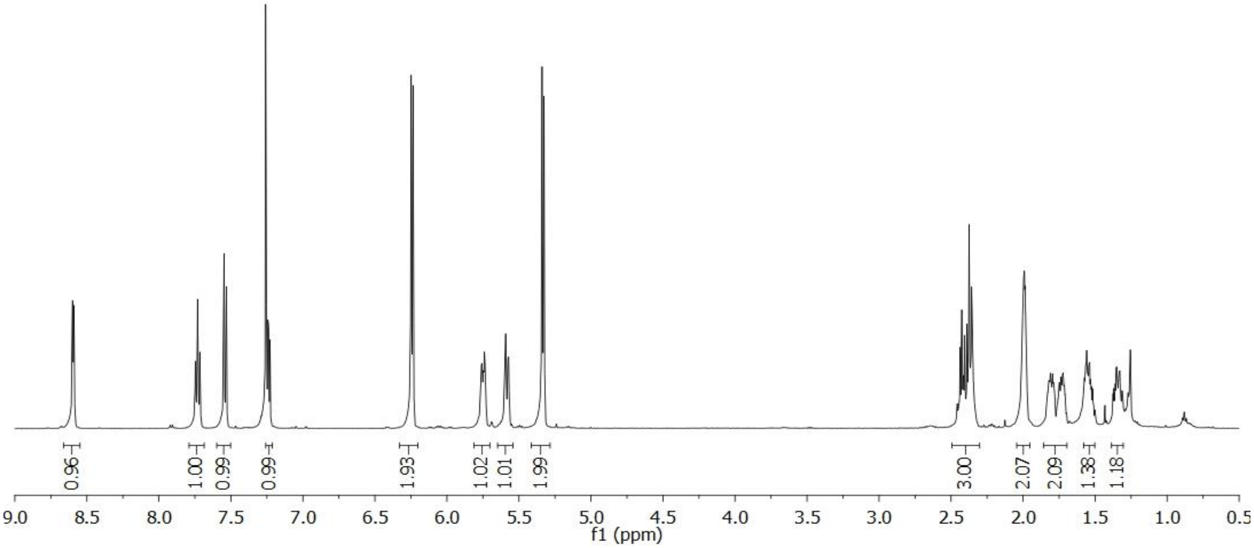


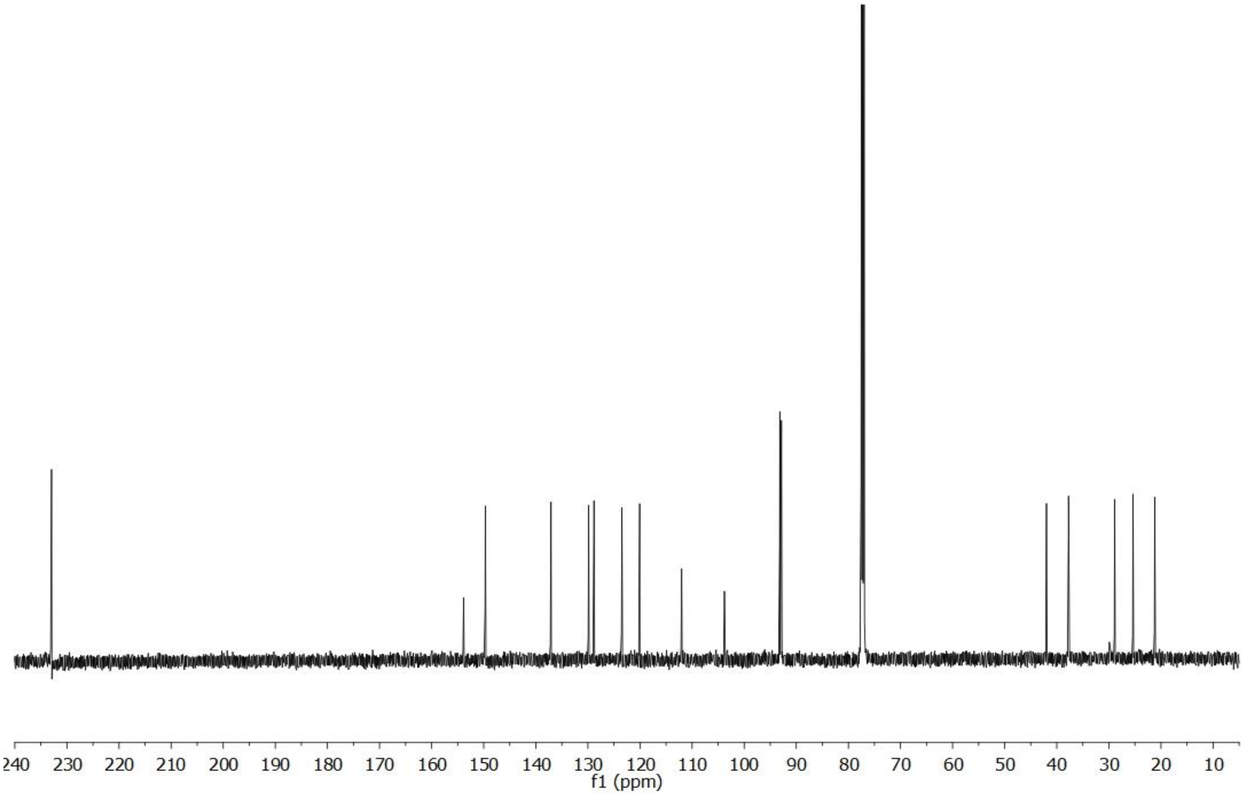




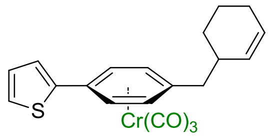
3e – (η^6-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$

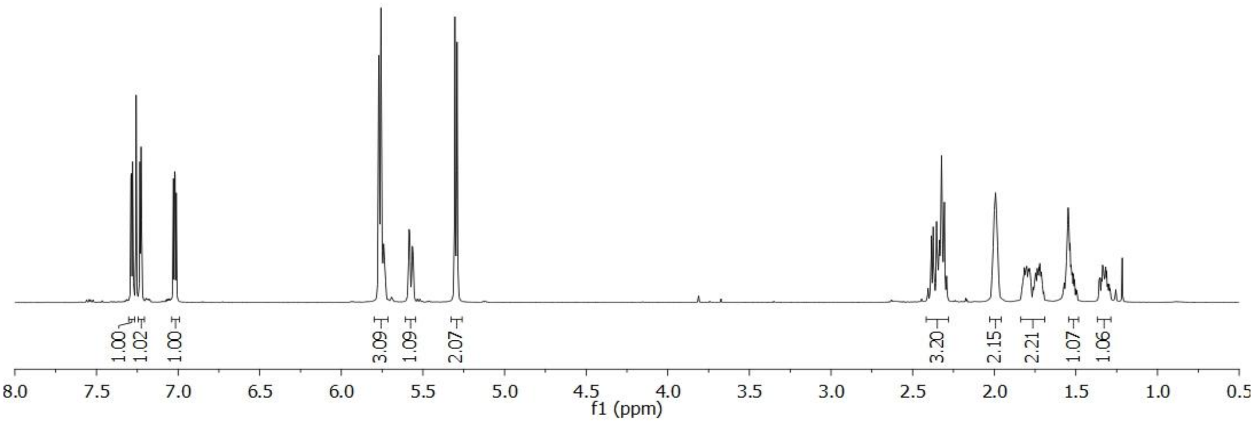


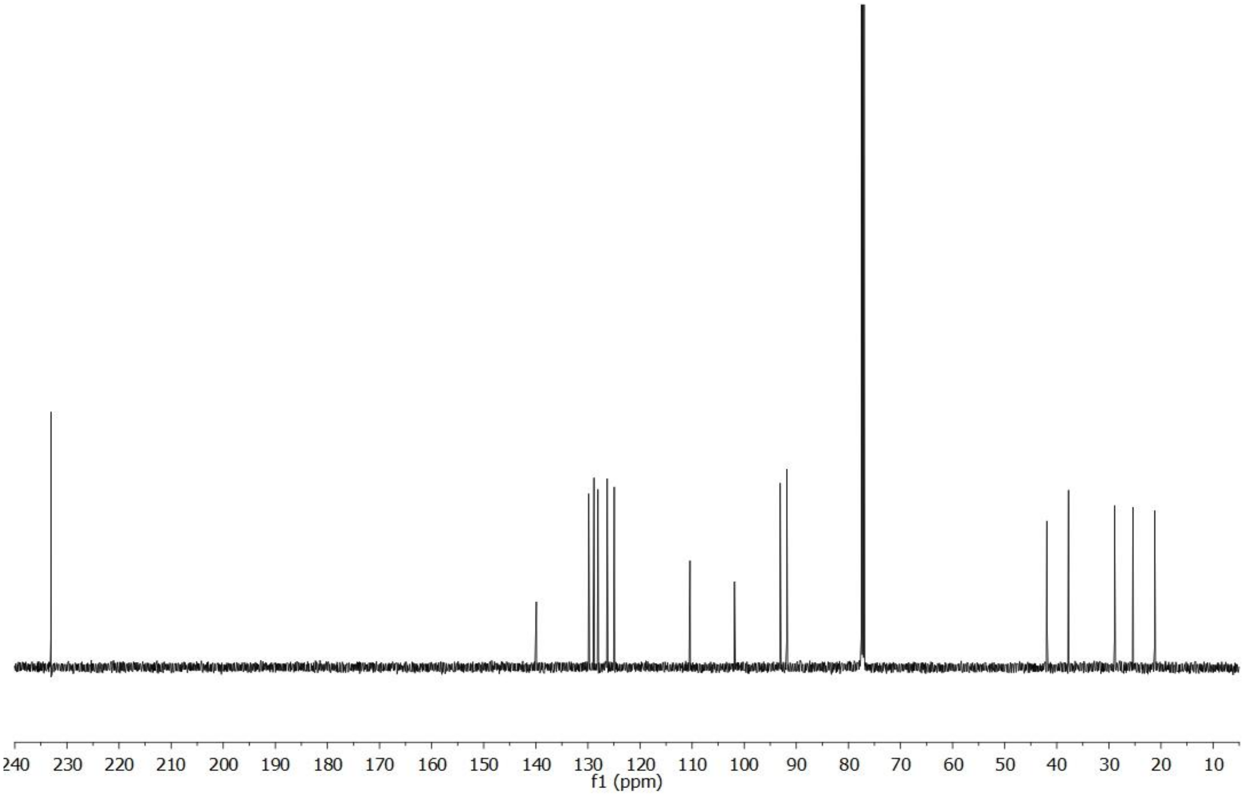




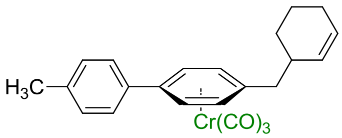
3f – (η^6-(2-cyclohexen-1-ylmethyl)-4-(2-thiophenyl)-benzene)Cr(CO)$_3$

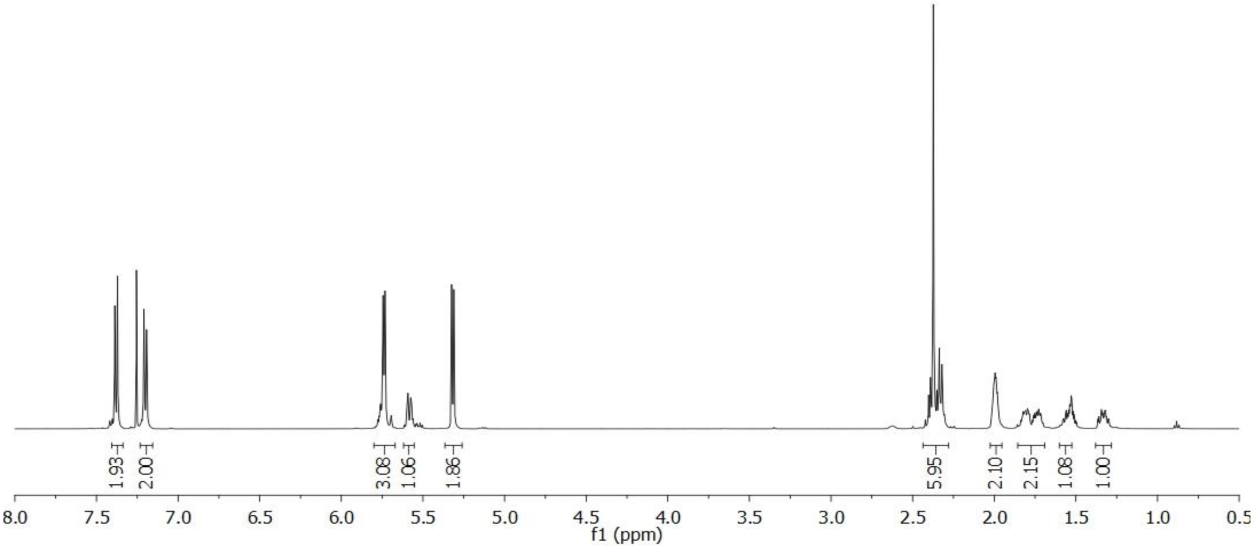


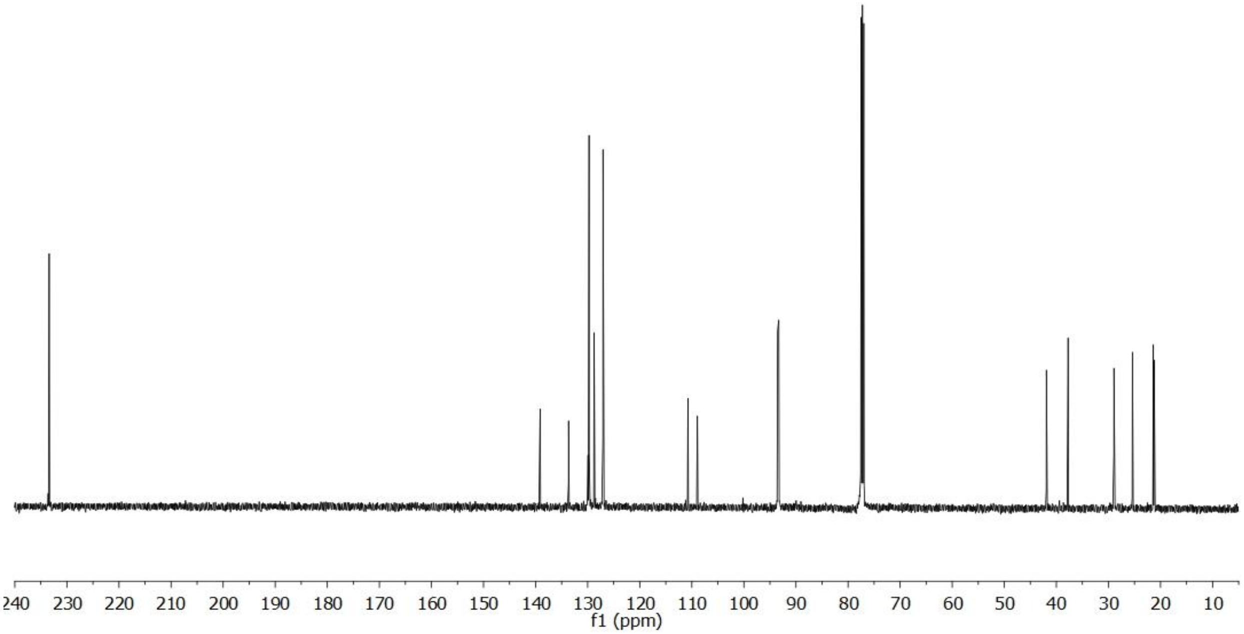




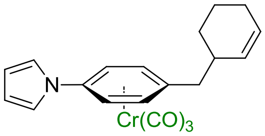
3d – (η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-tolyl)-benzene)Cr(CO)$_3$

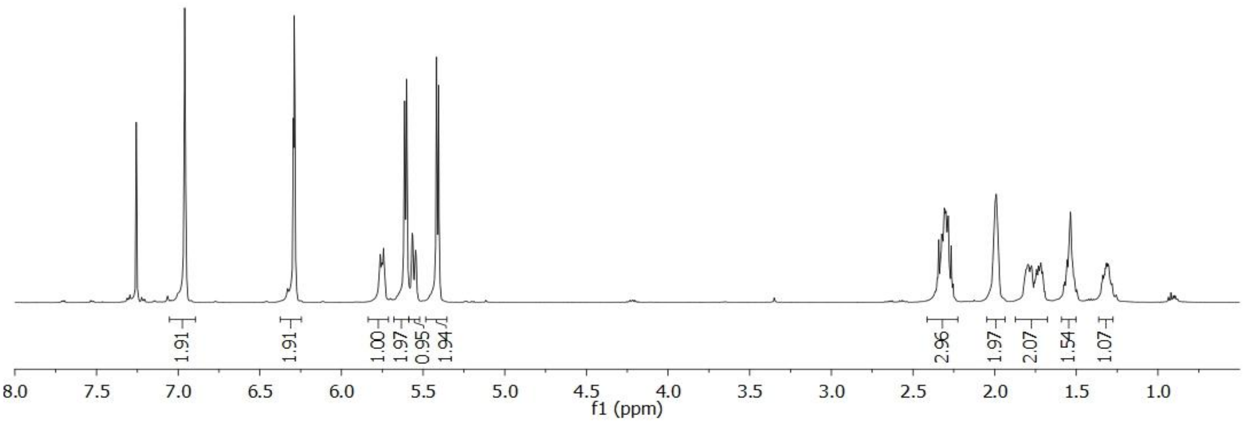


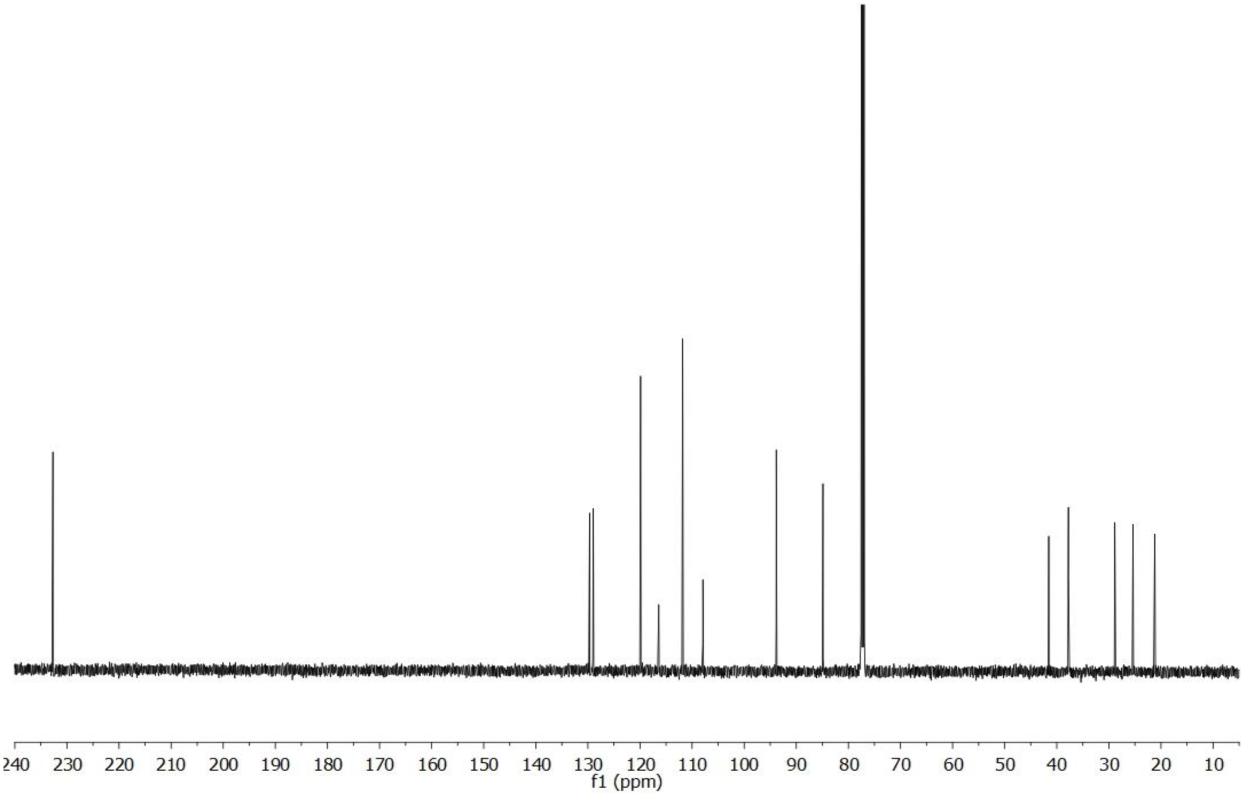




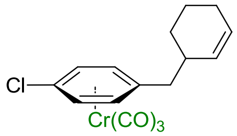
3g – (η^6-(2-cyclohexen-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)Cr(CO)$_3$

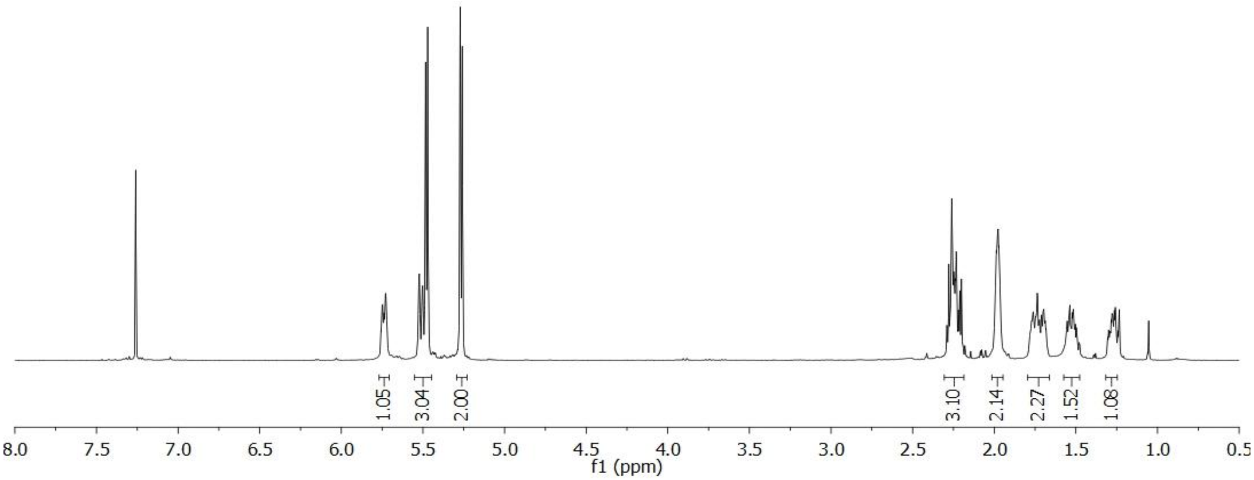


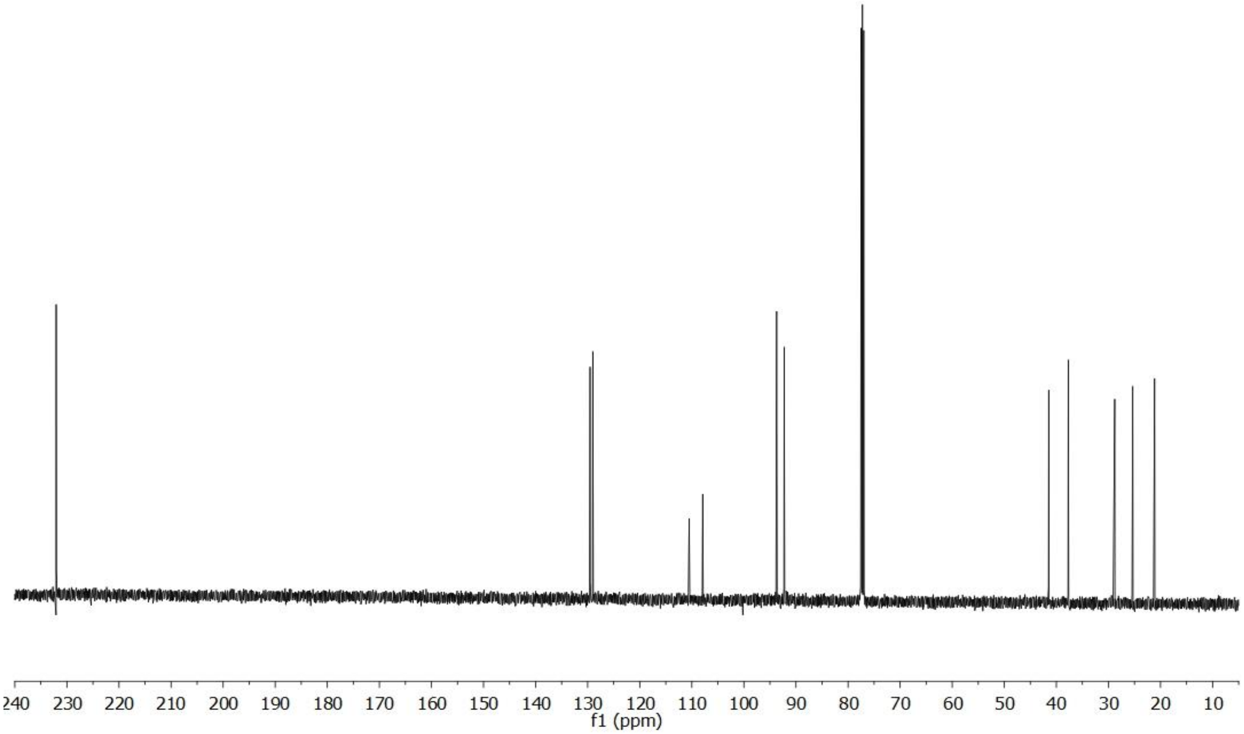




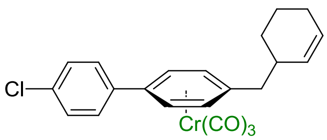
3h – (η^6-(2-cyclohexen-1-ylmethyl)-4-chlorobenzene)Cr(CO)$_3$

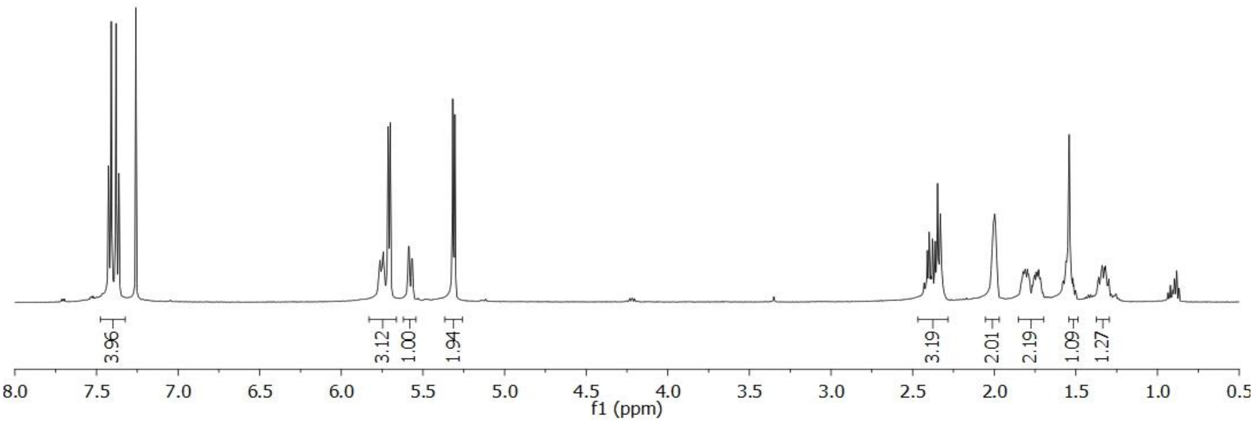


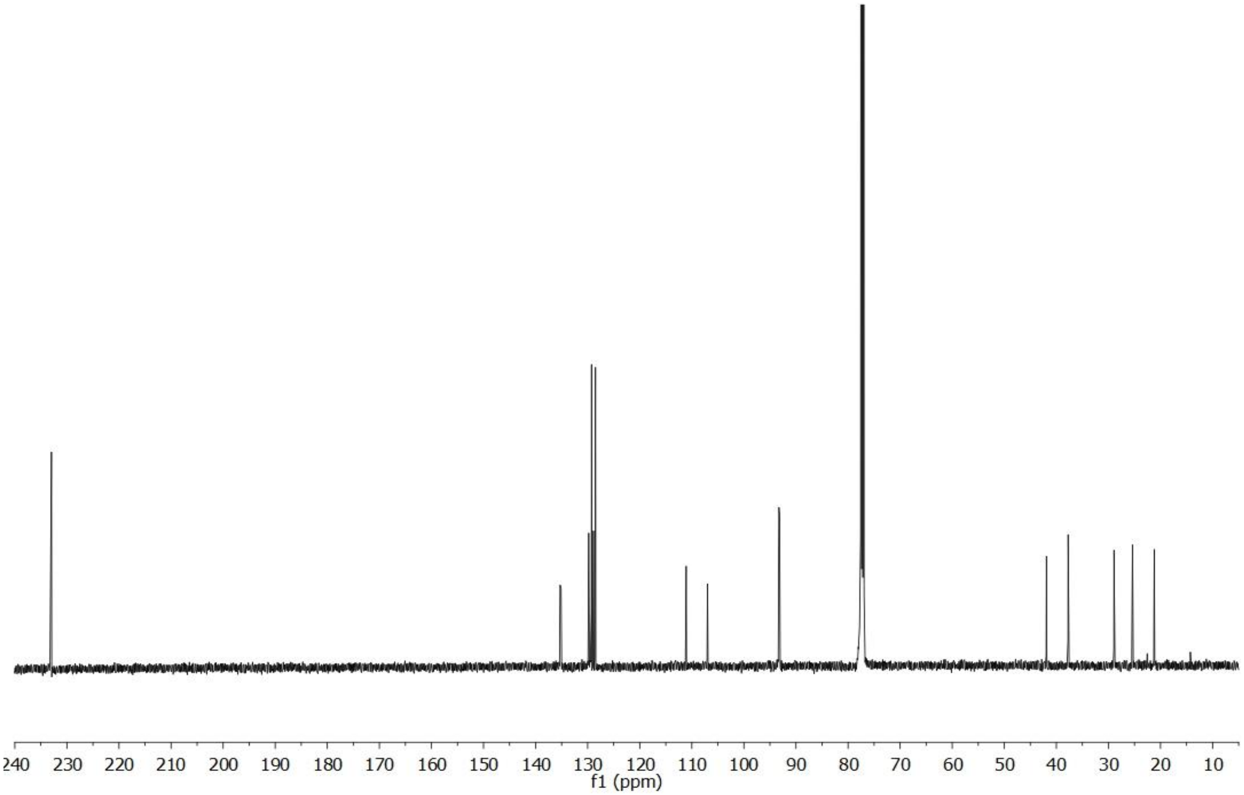




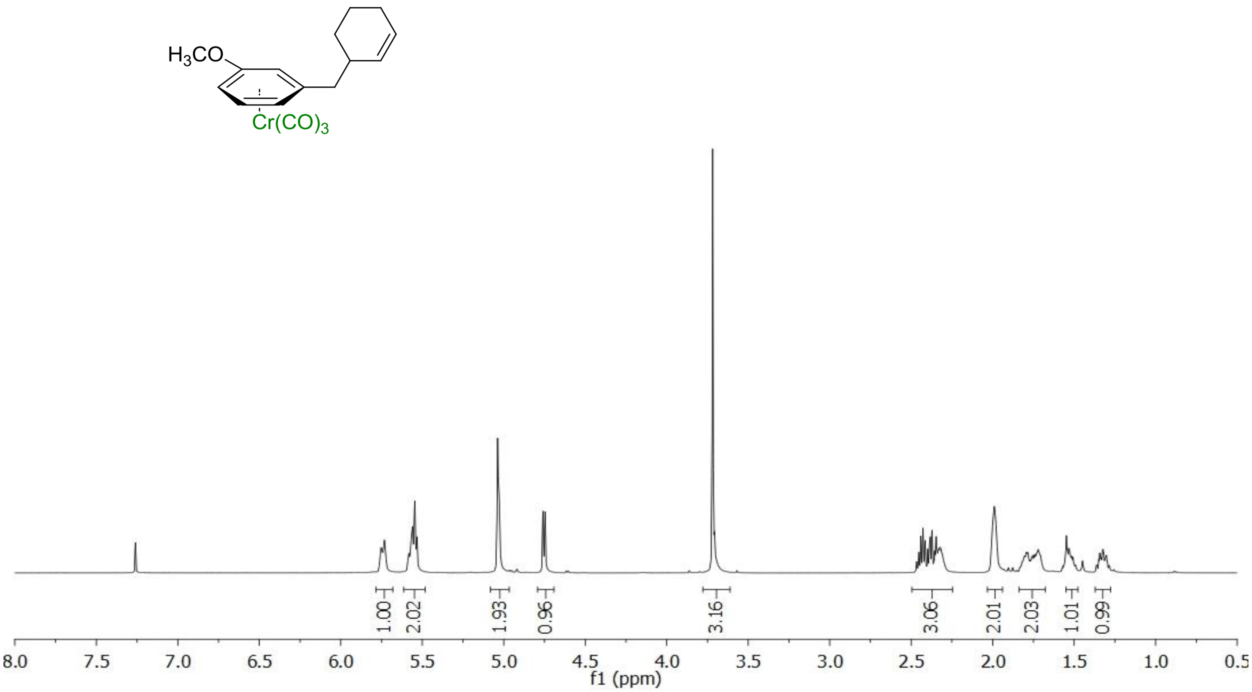
3i – (η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-chlorophenyl)-benzene)Cr(CO)$_3$

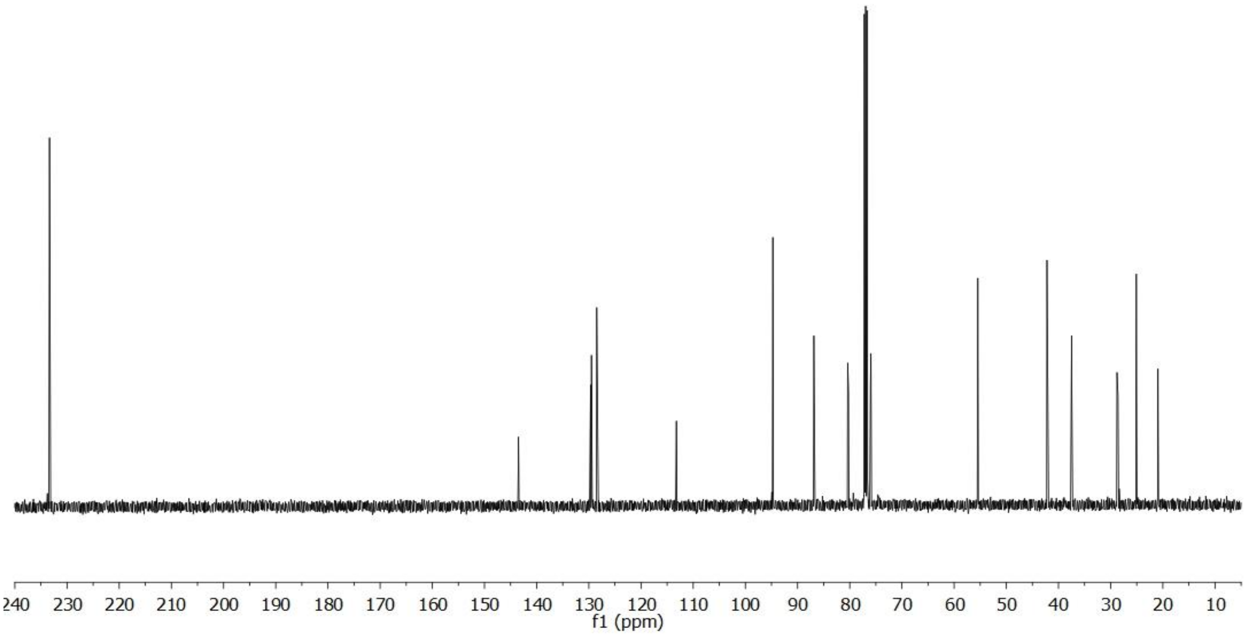




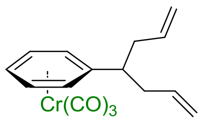


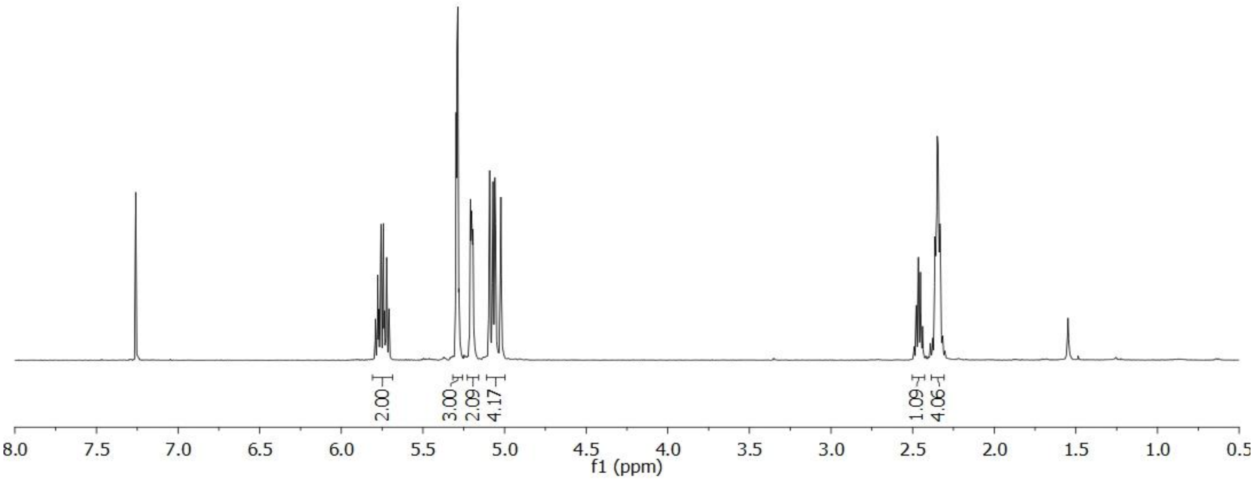
3c – (η^6-(2-cyclohexen-1-ylmethyl)-3-methoxybenzene)$Cr(CO)_3$

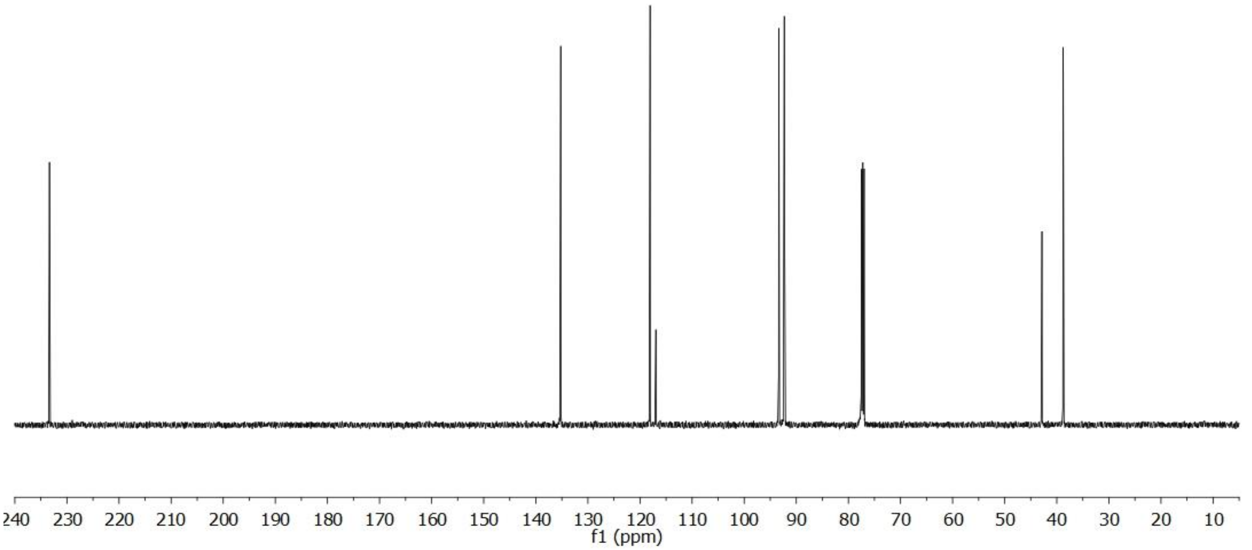




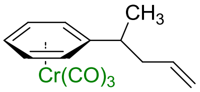
4ad – (η^6-(1-(2-propen-1-yl)-3-buten-1-yl)-benzene)Cr(CO)$_3$

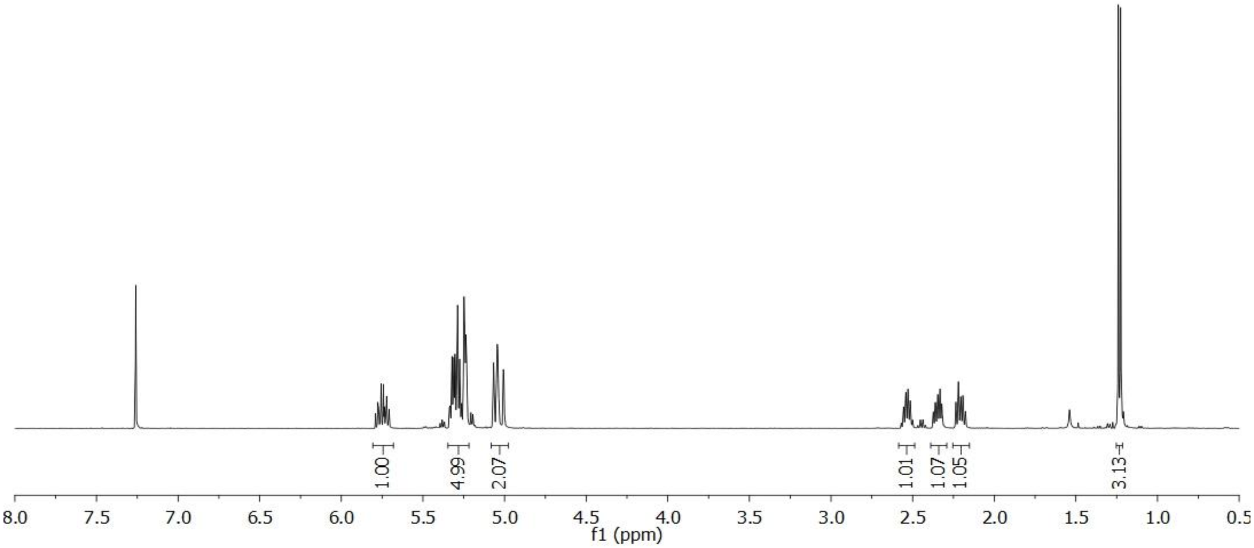


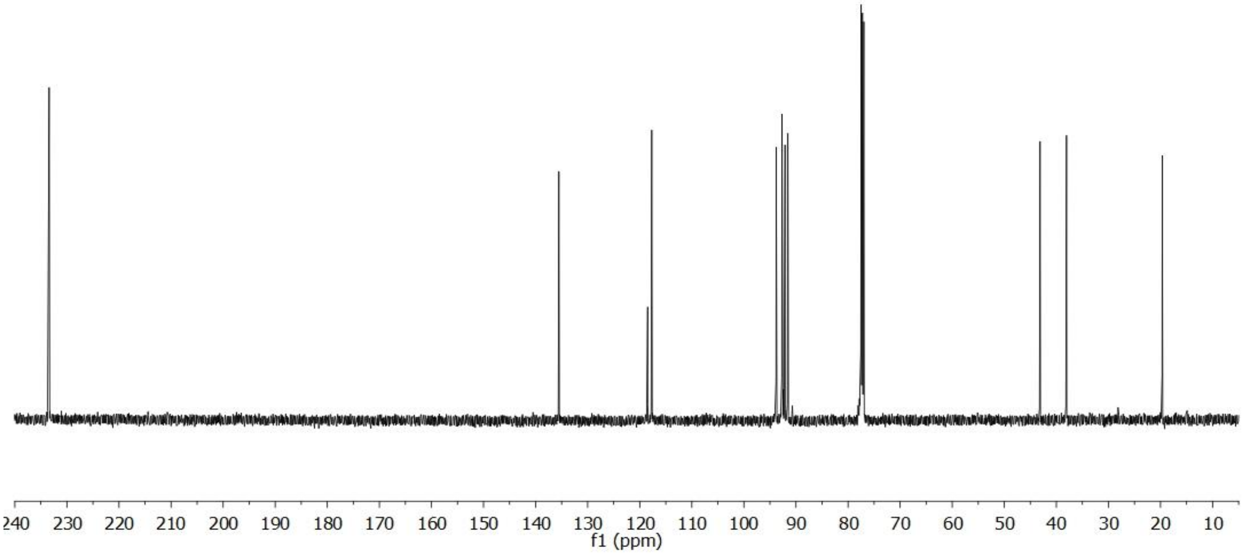




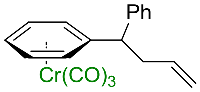
4kd – (η^6-(1-methyl-3-buten-1-yl)-benzene)Cr(CO)$_3$

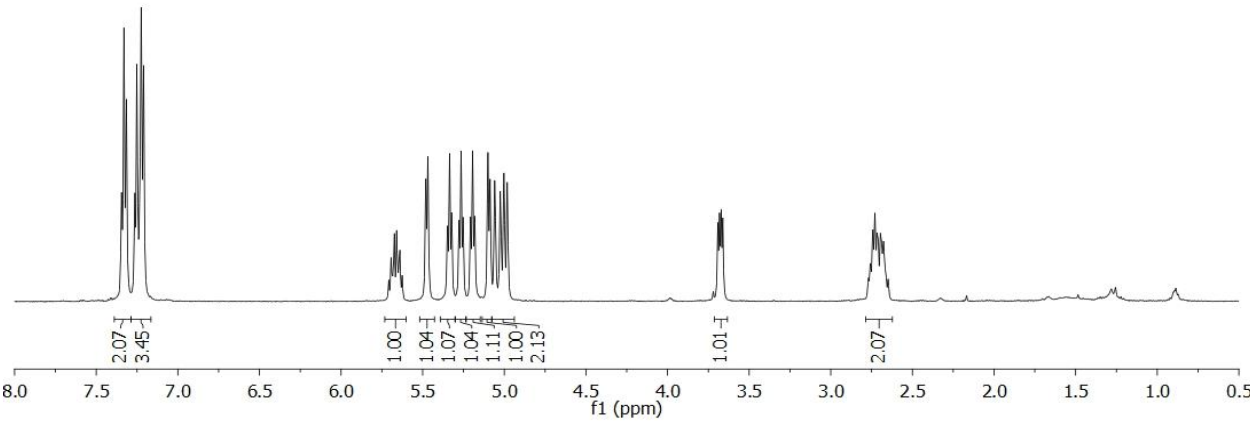


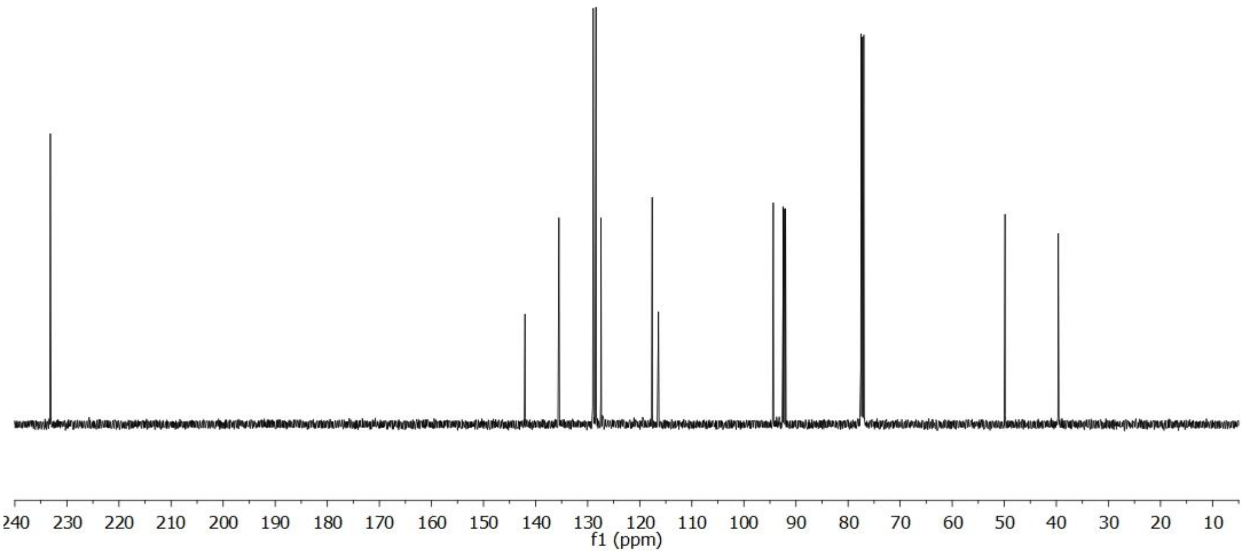




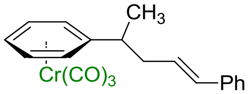
4ld – (η^6-4,4-diphenyl-1-butene)Cr(CO)$_3$

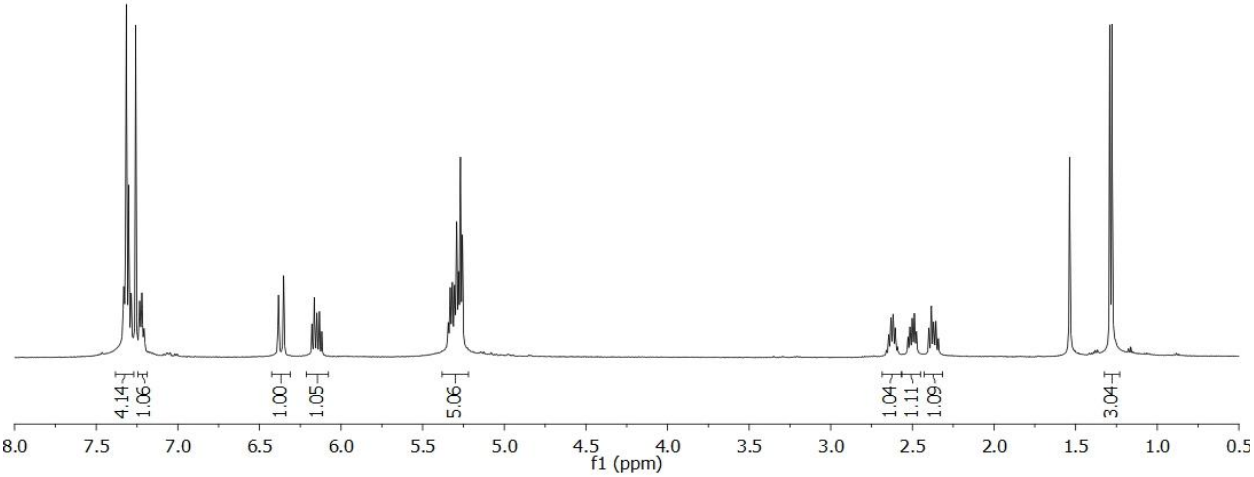


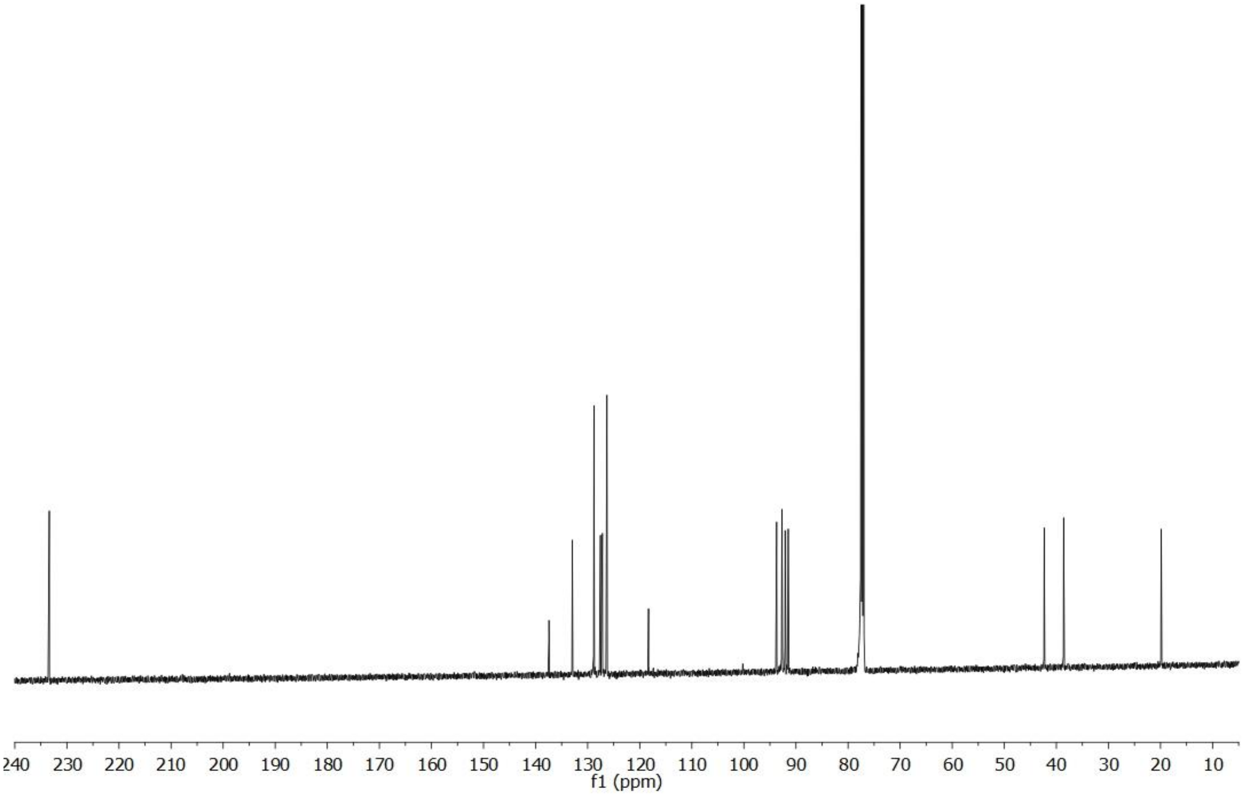




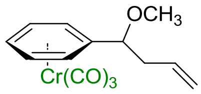
4ke – (η^6-*α*-(*E*)-cinnamyl-ethylbenzene)Cr(CO)$_3$

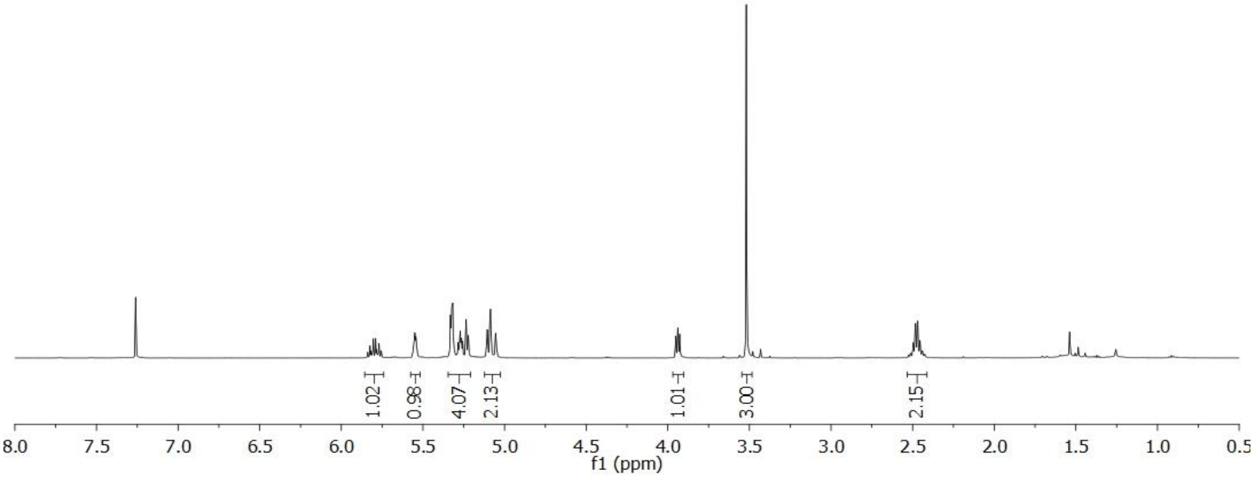


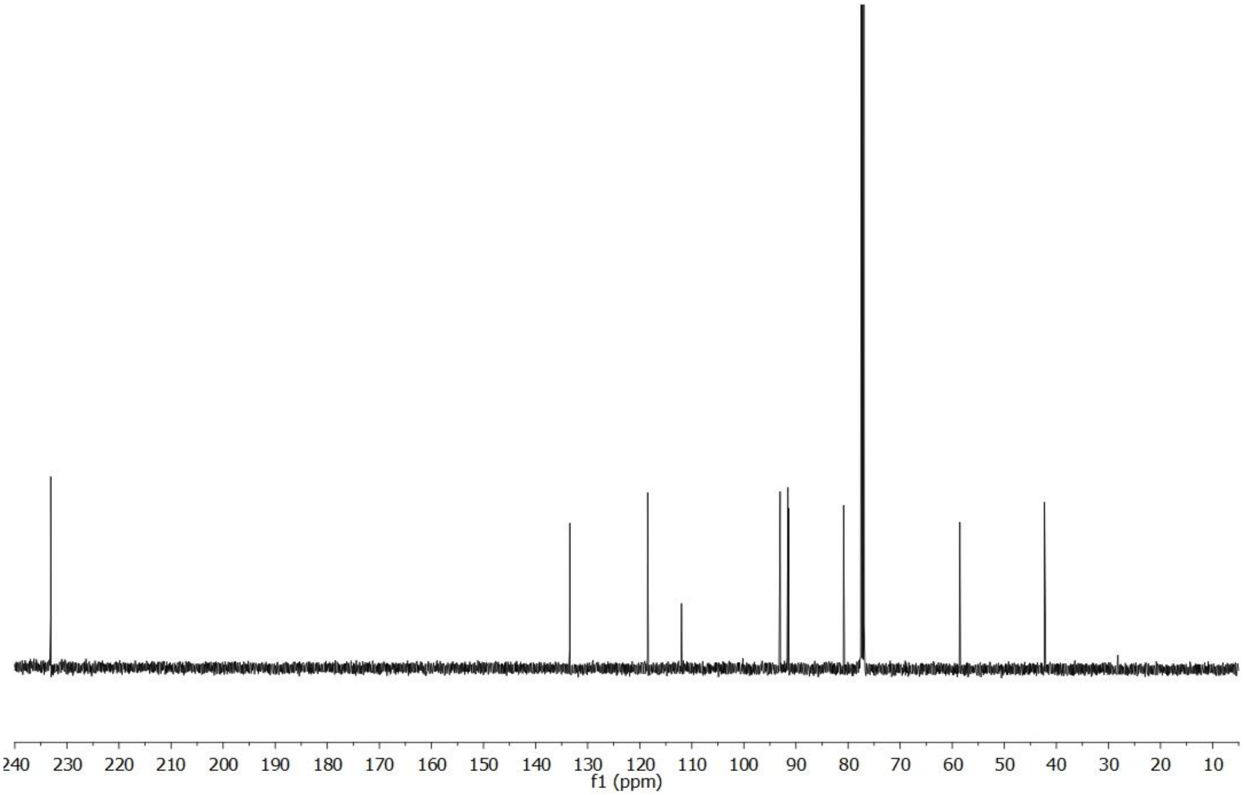




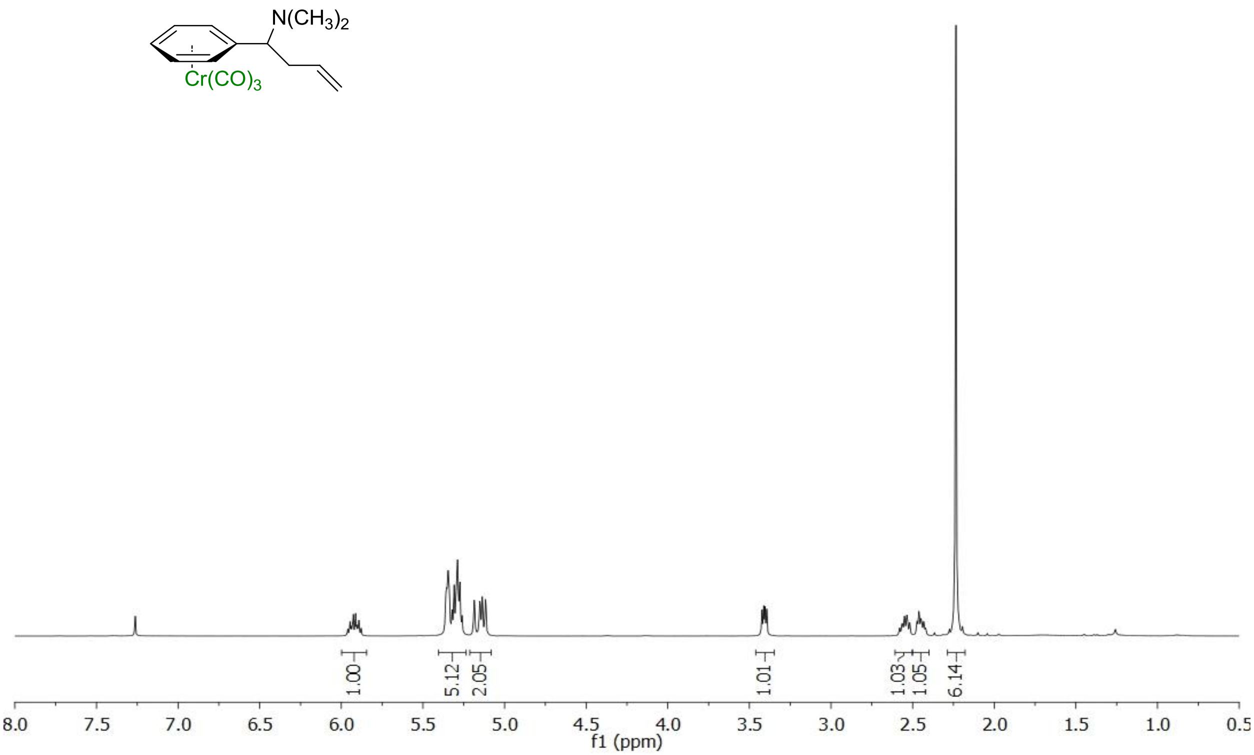
4od – (η^6-1-methoxy-1-phenyl-3-butene)Cr(CO)$_3$

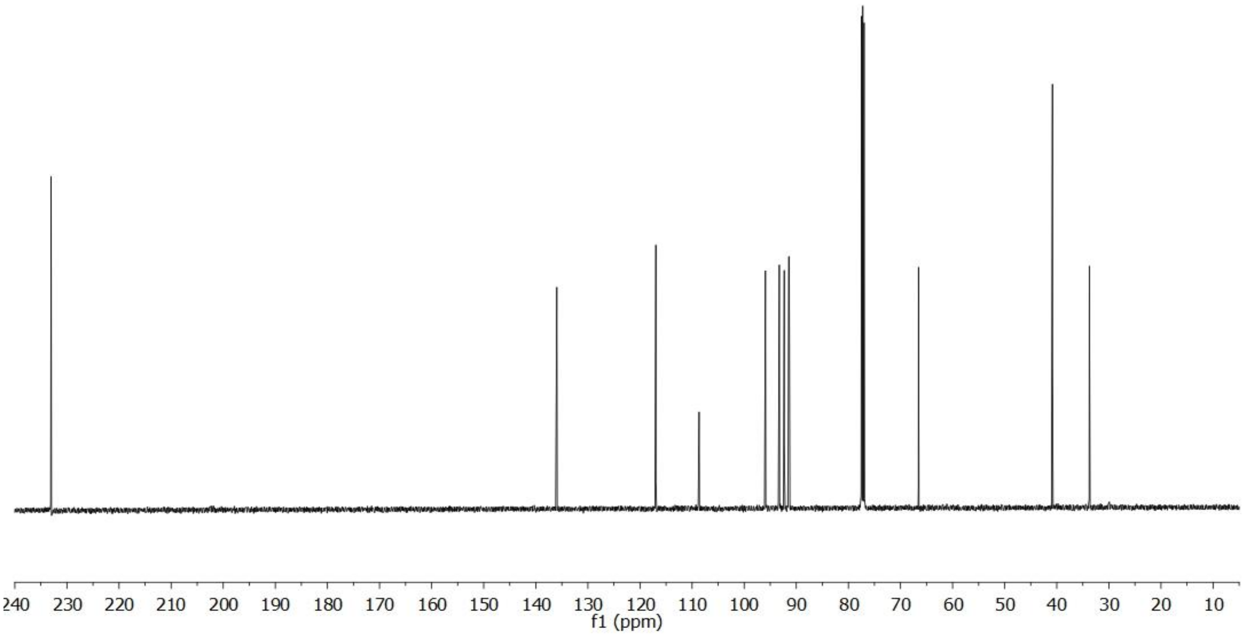




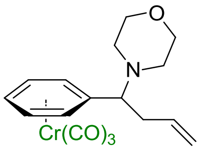


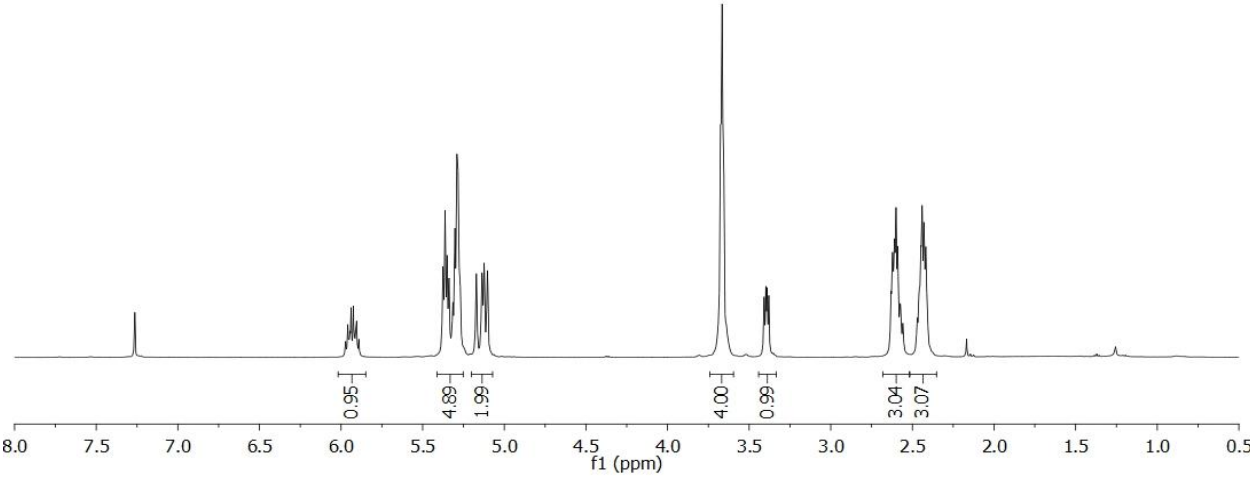
4pd – (η^6-*α*-allyl-*N*,*N*-dimethyl-benzylamine)Cr(CO)$_3$

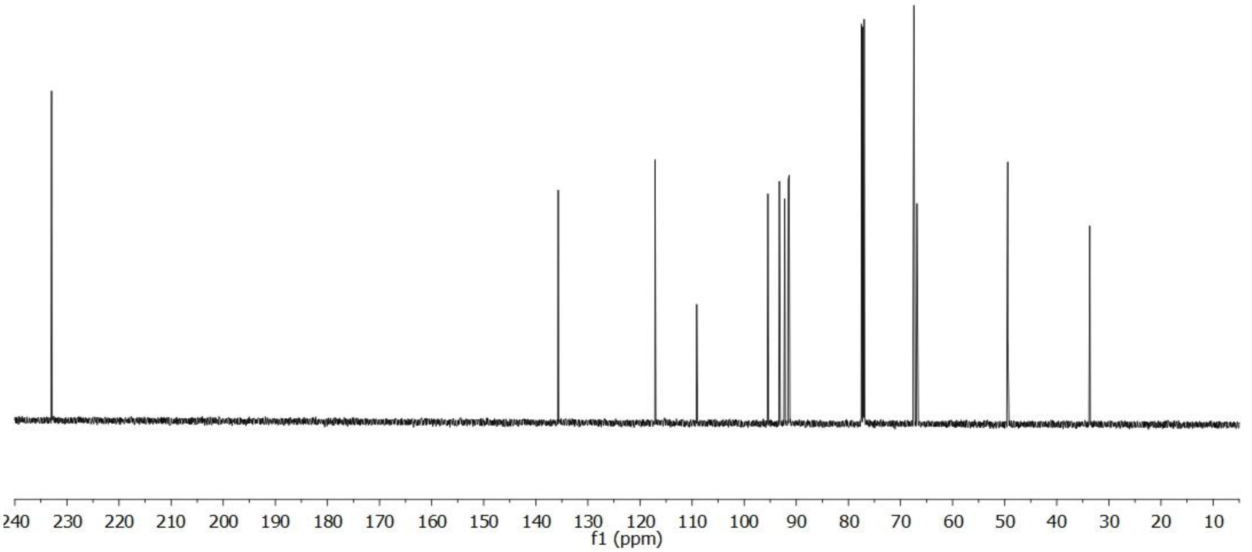




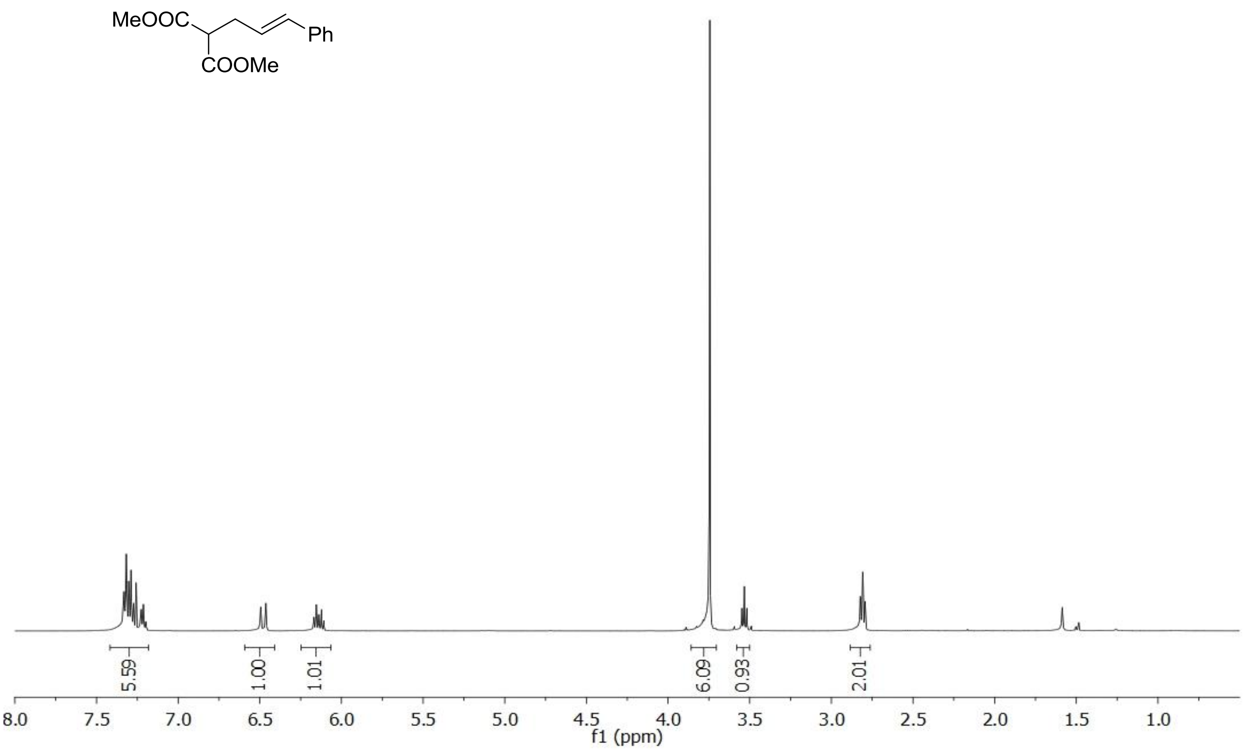
4qd – (η^6-4-(1-phenyl-3-butenyl)-morpholine)Cr(CO)$_3$

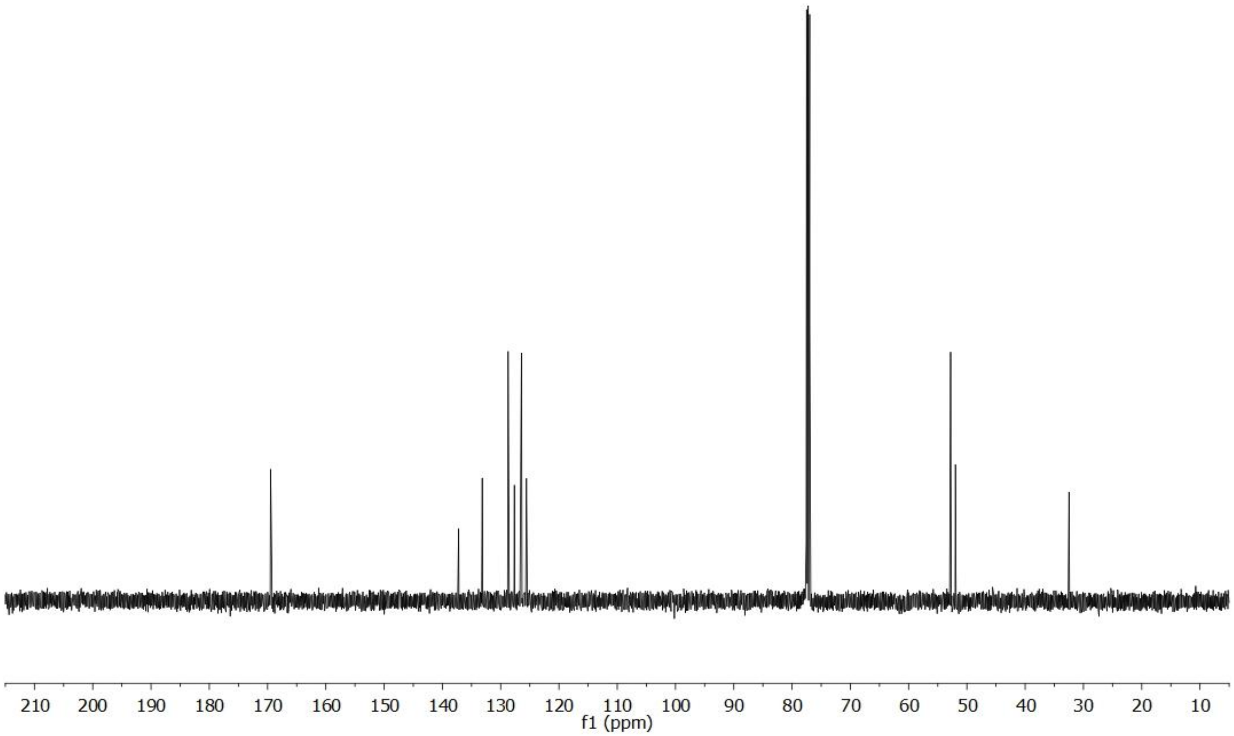




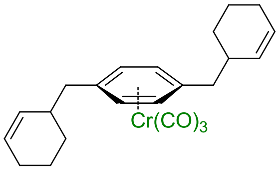


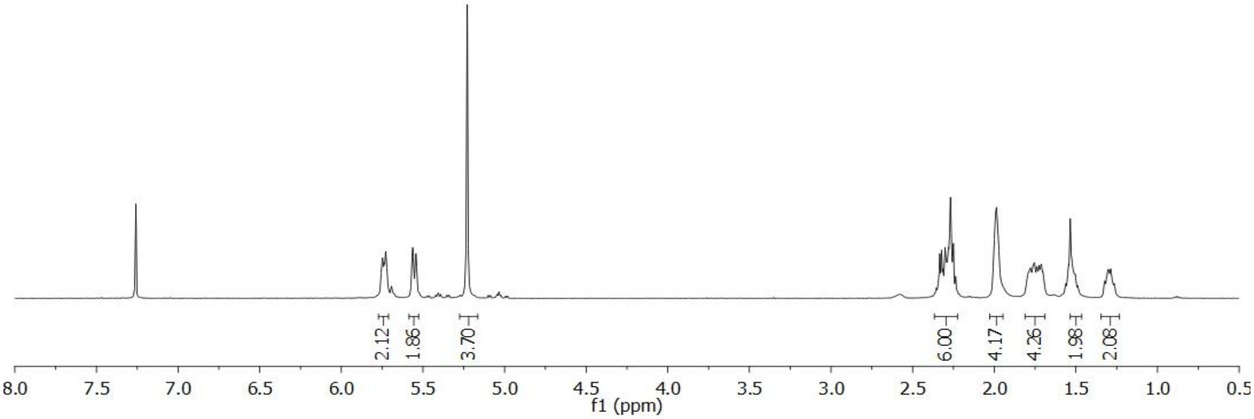
α-(*E*)-cinnamyl dimethyl malonate

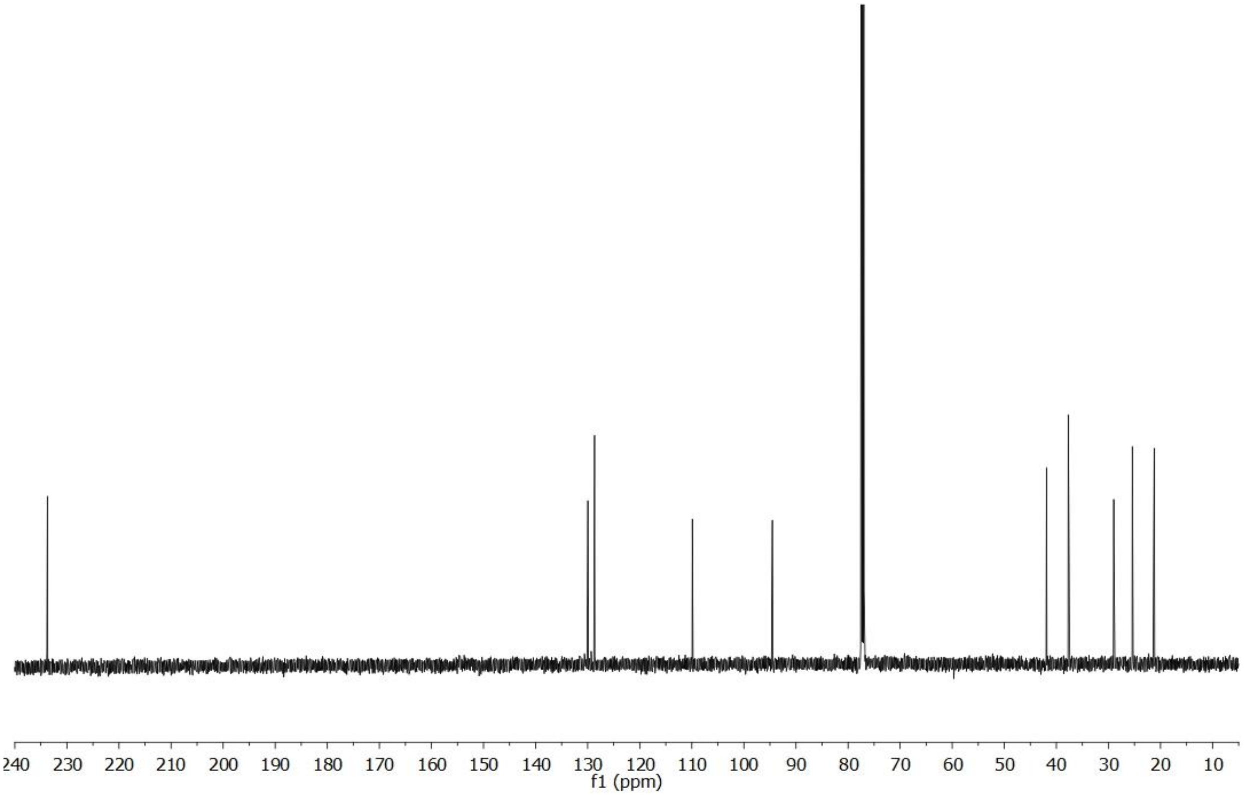




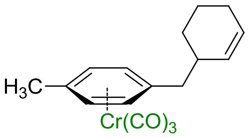
7 – (η^6-1,4-di(2-cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$

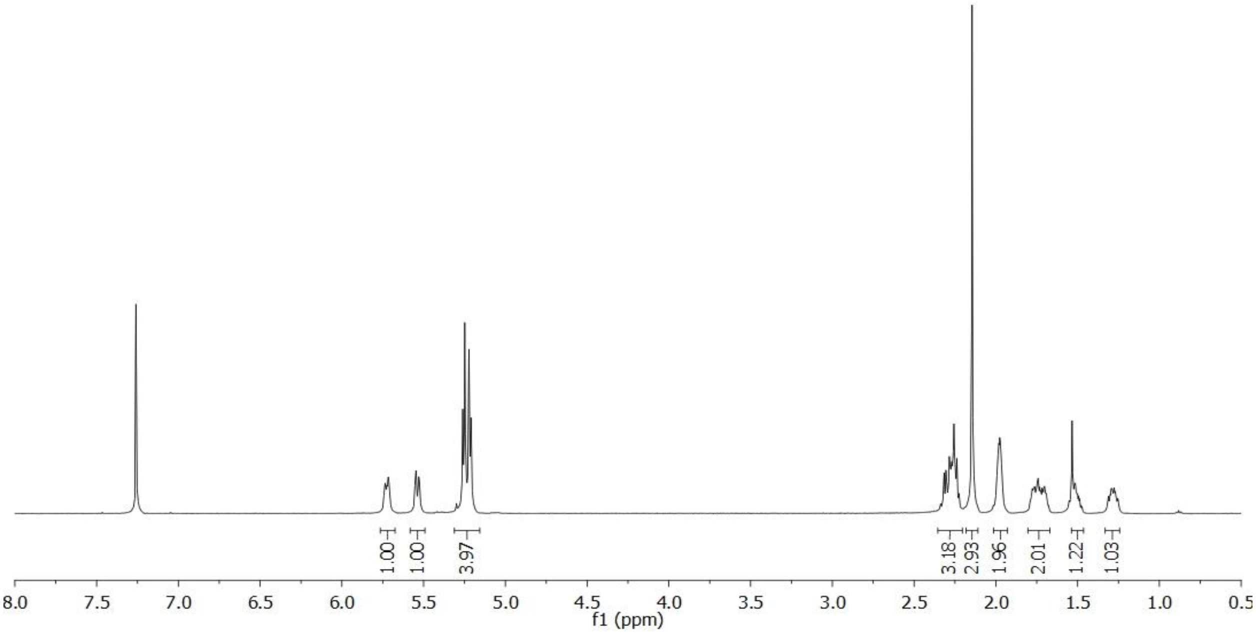


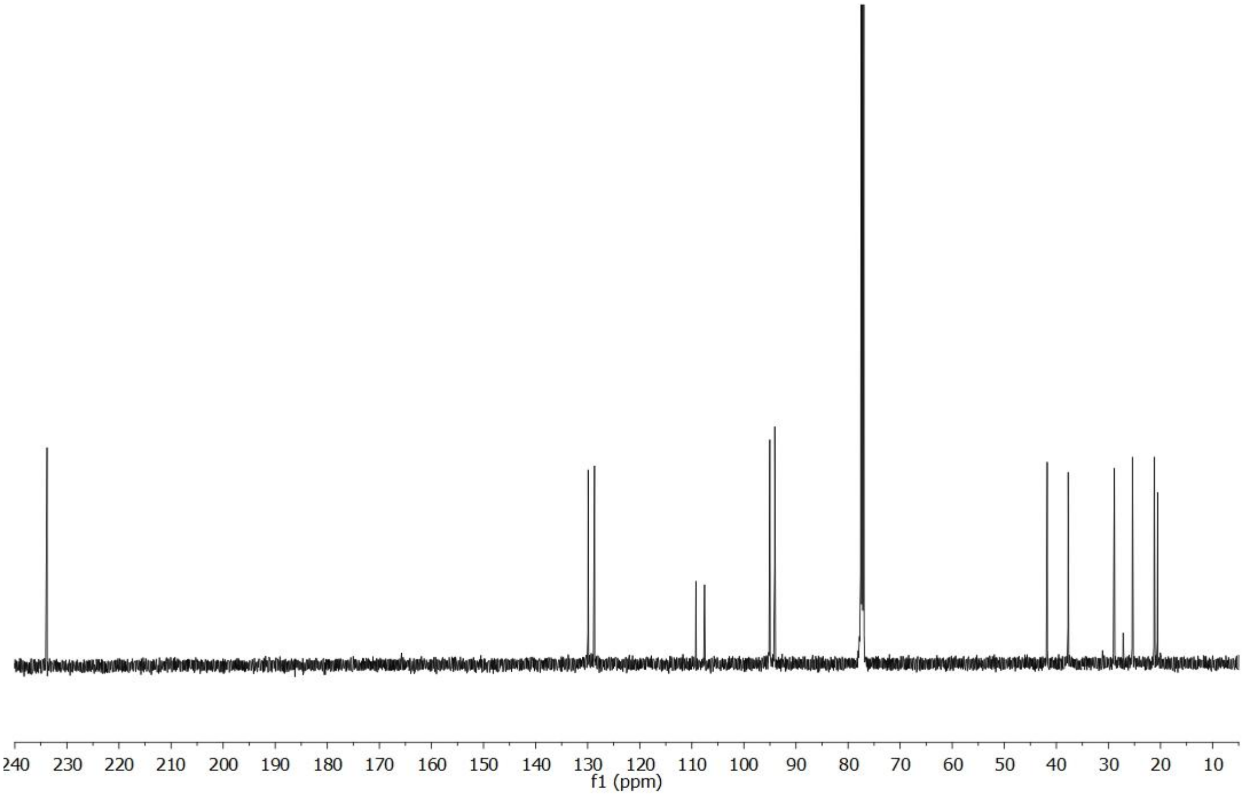




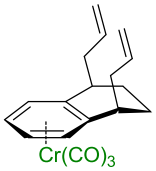
8 – (η^6-(2-cyclohexen-1-ylmethyl)-4-methylbenzene)Cr(CO)$_3$

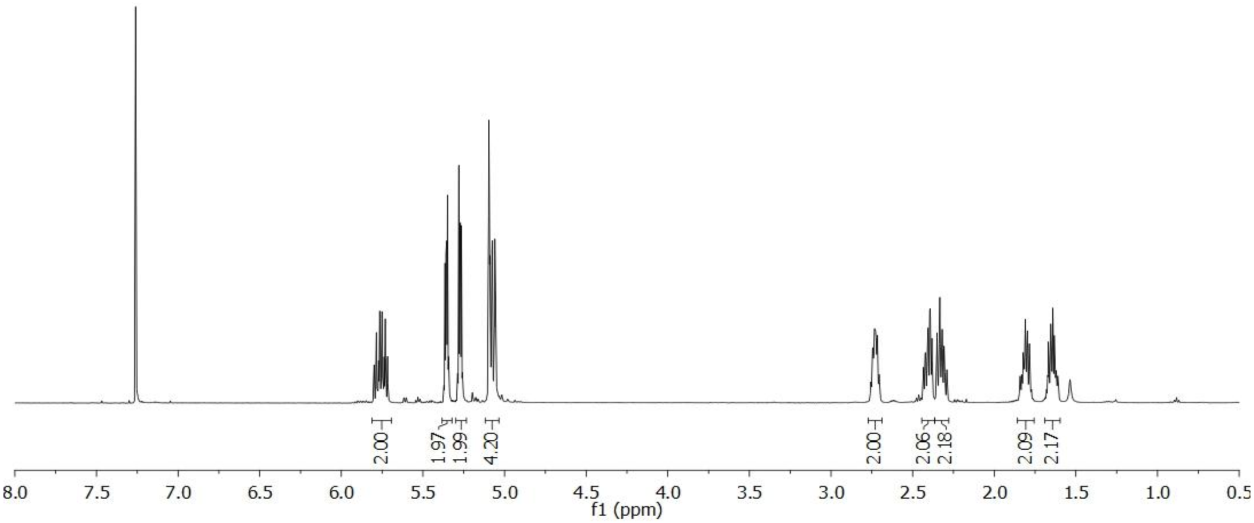


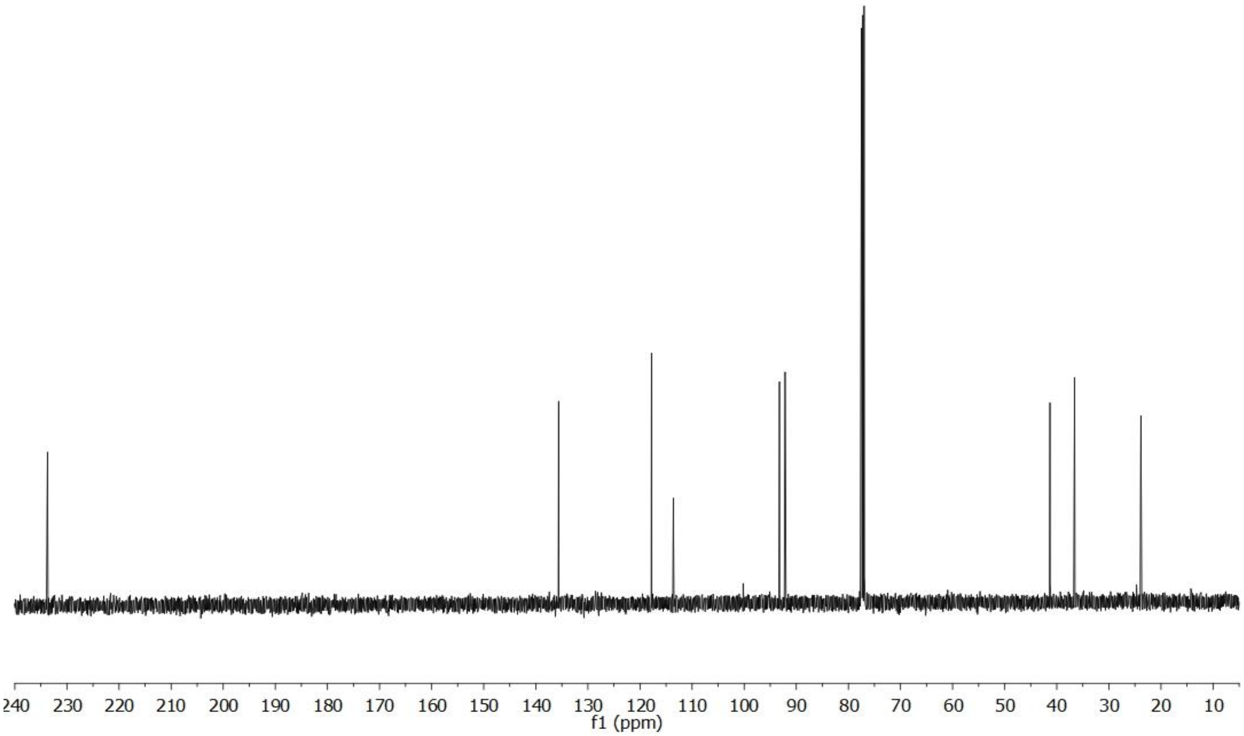




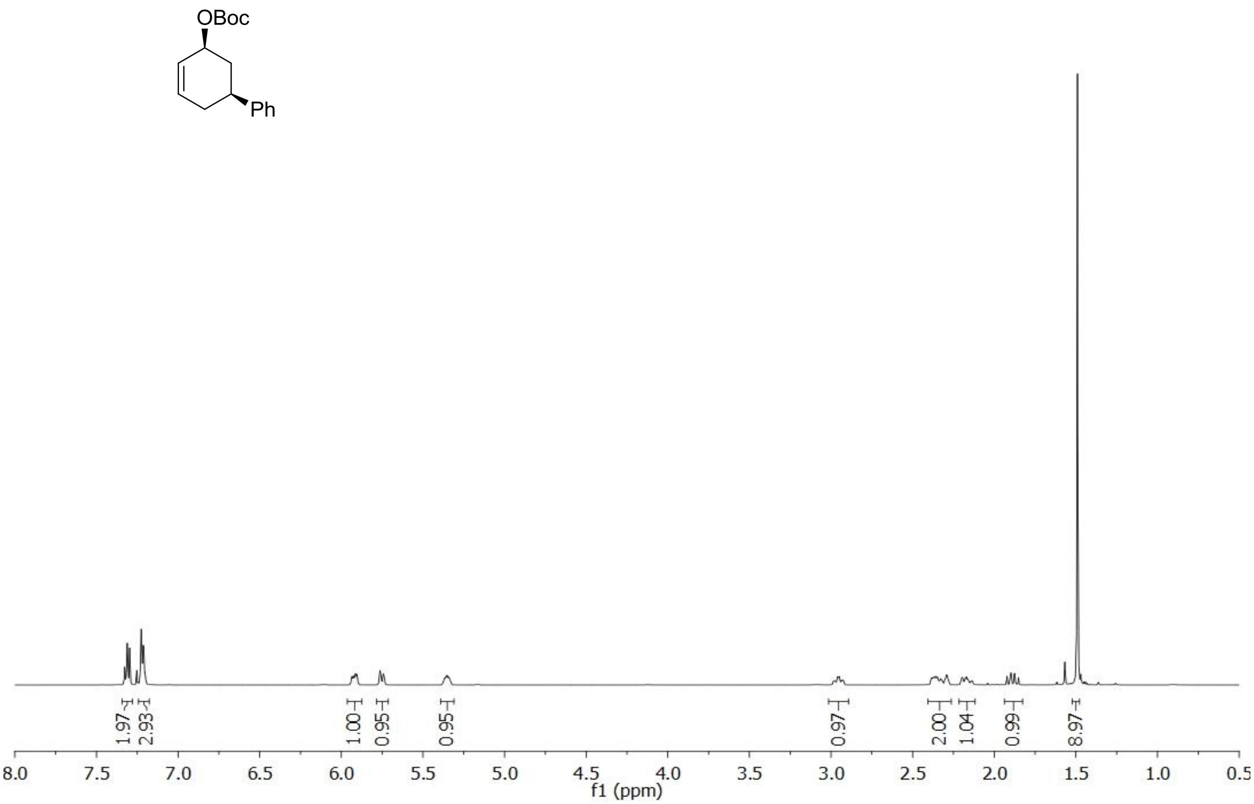
9 – (η^6-(*R*,*S*)-1,2,3,4-tetrahydro-1,4-di-2-propen-1-yl-naphthalene)Cr(CO)$_3$

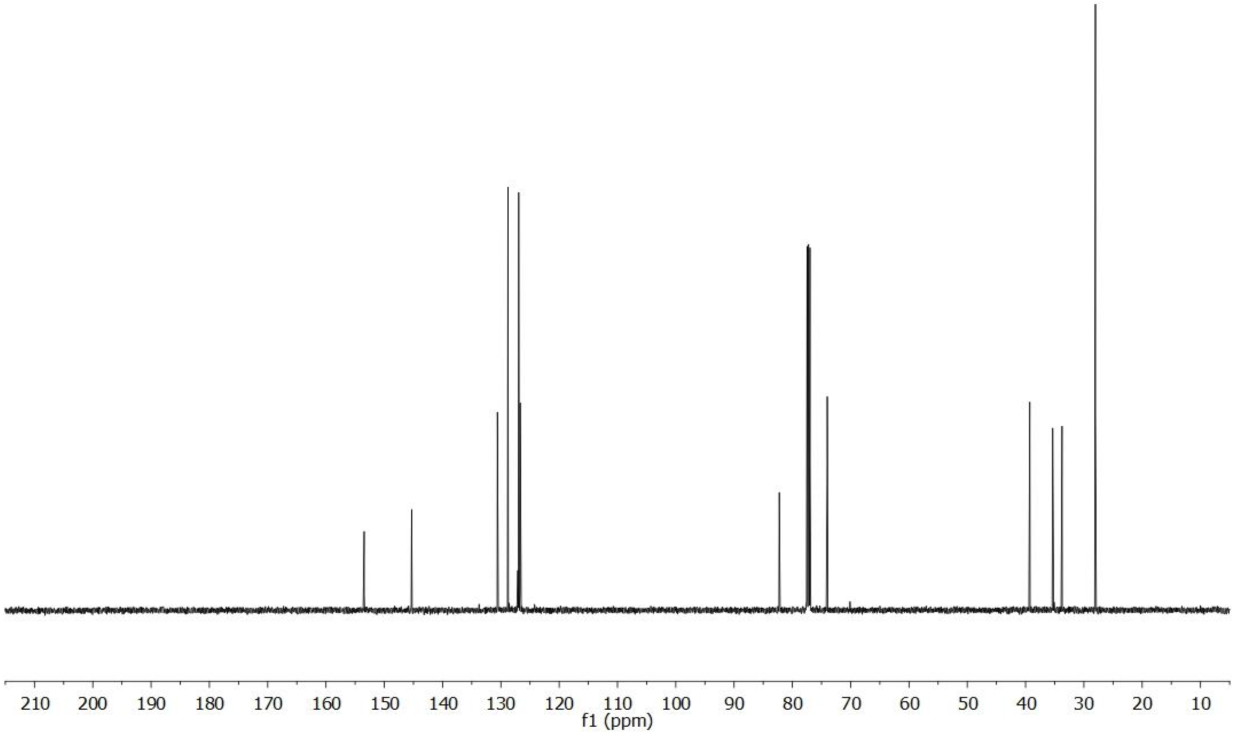




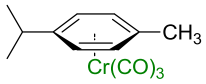


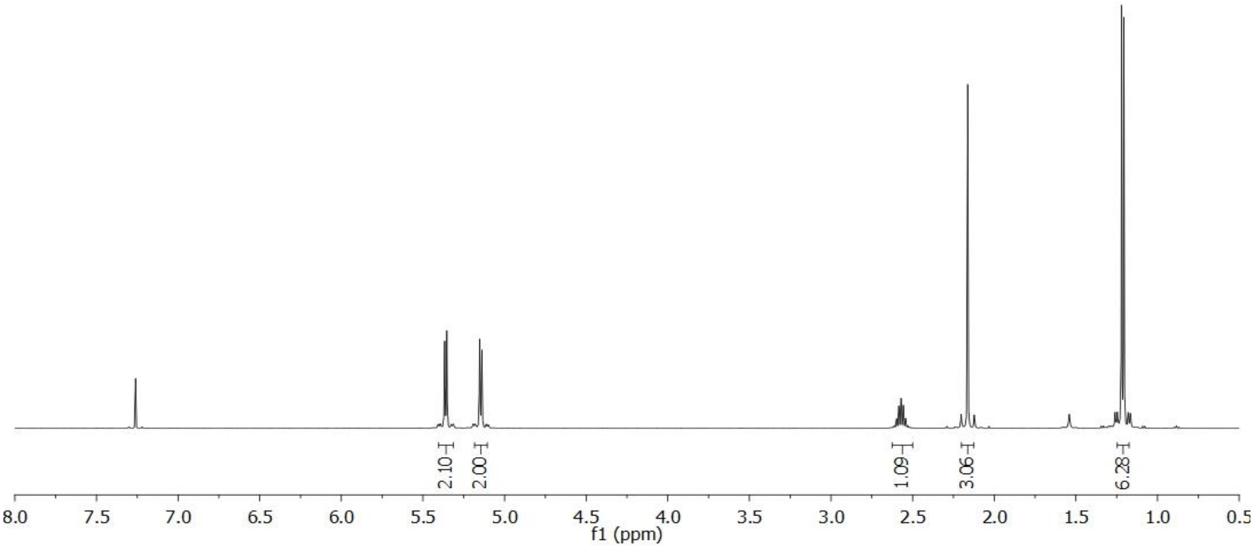
Compound **2j** ((***rac***)-***cis-tert*-butyl (5-phenyl-2-cyclohexenyl) carbonate**)

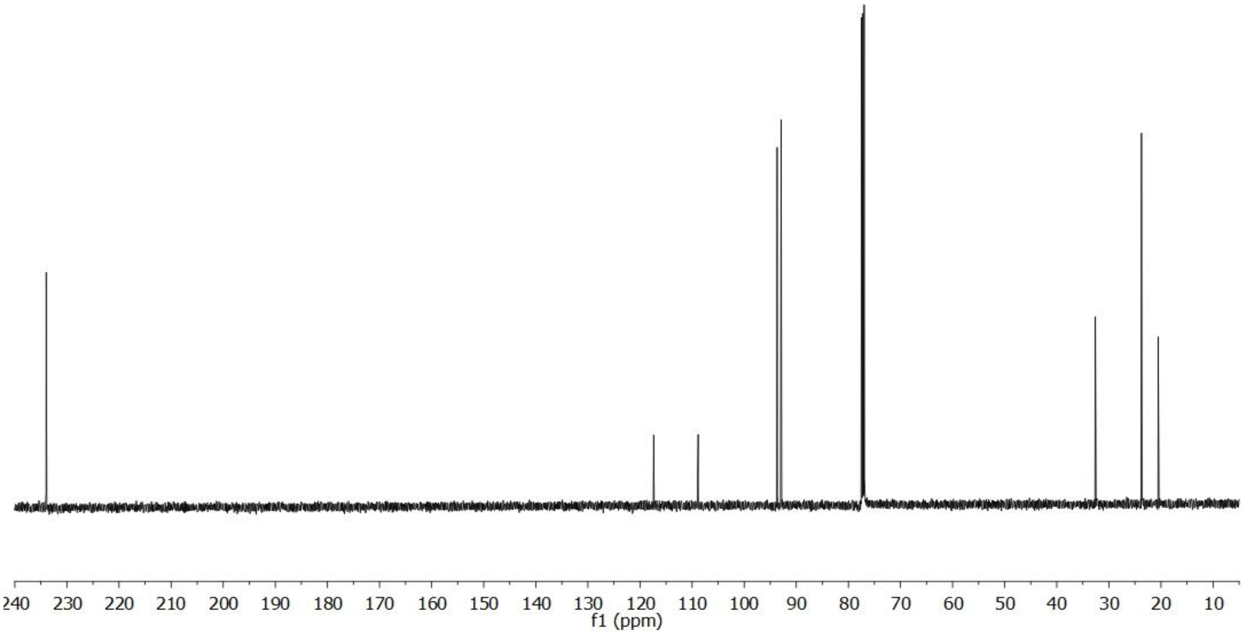




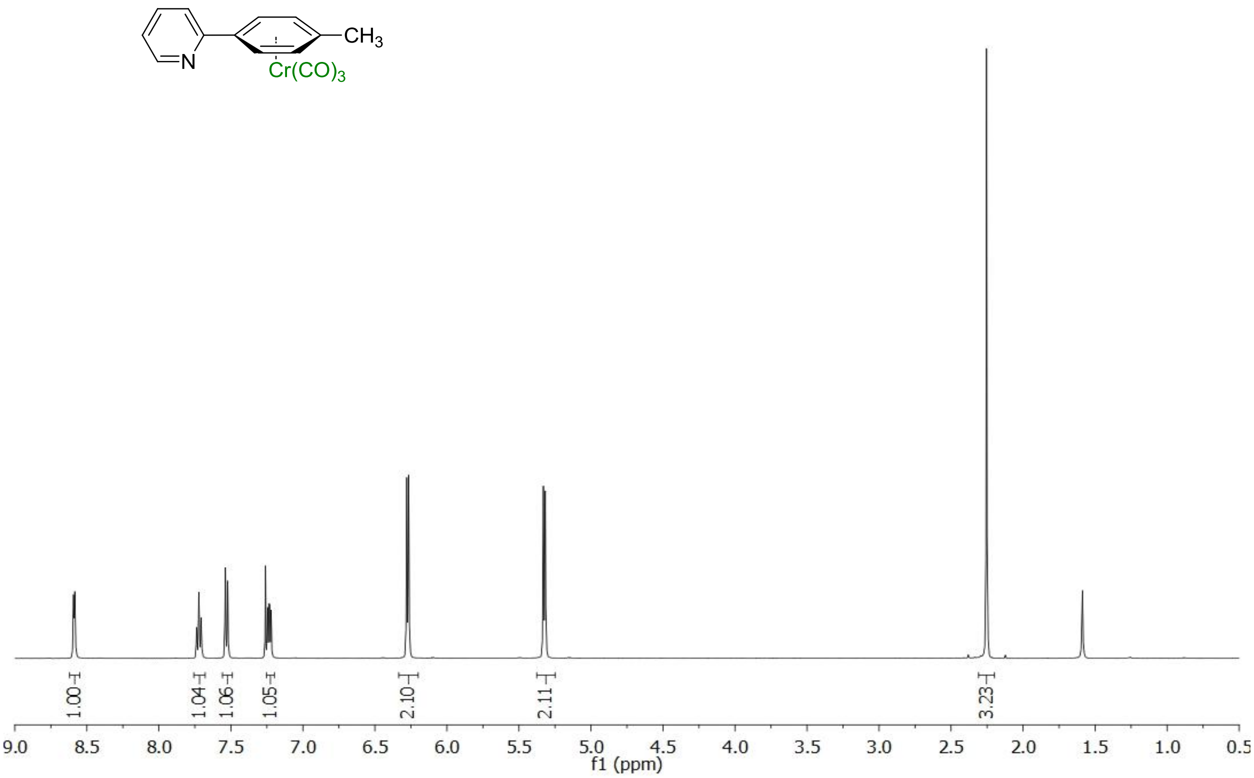
1b - (η^6-4-isopropyltoluene)Cr(CO)$_3$

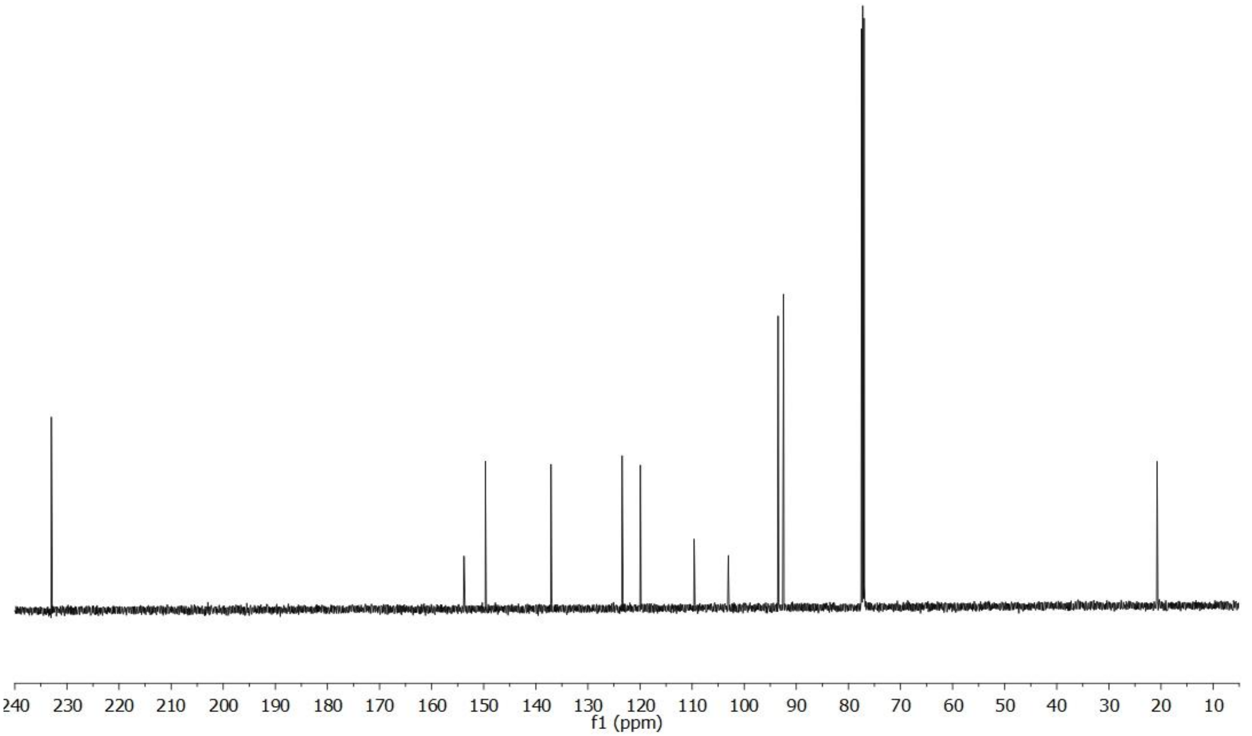




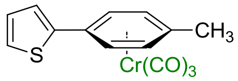


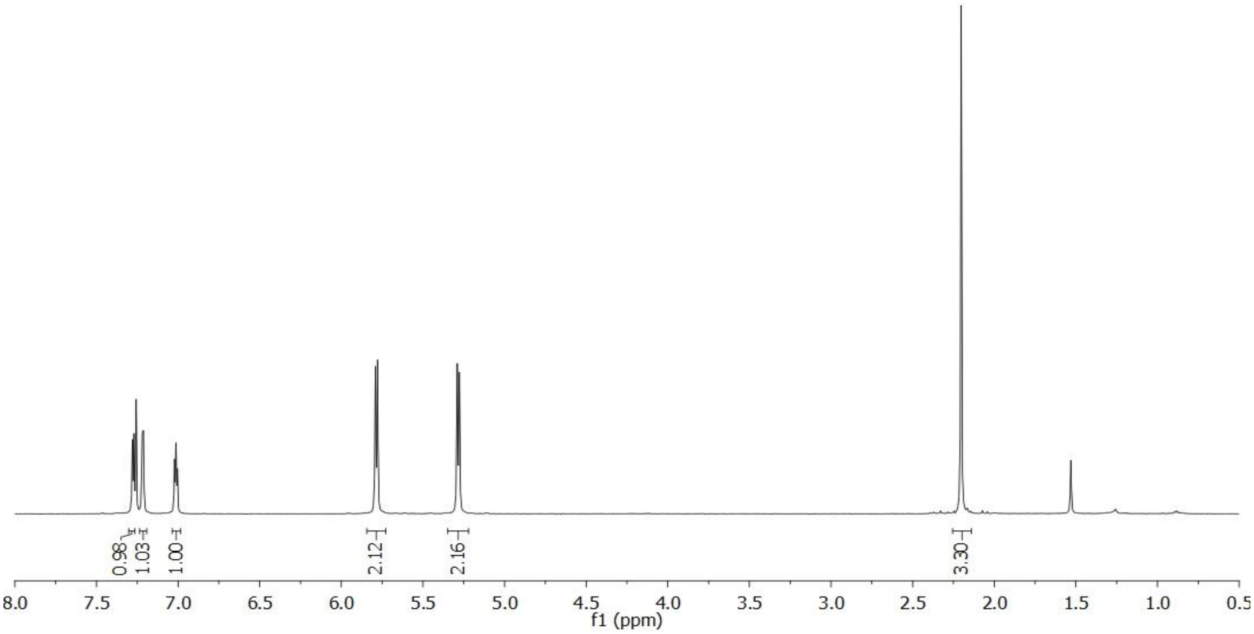
1e - (2-(η^6-*p*-tolyl)pyridine)Cr(CO)$_3$

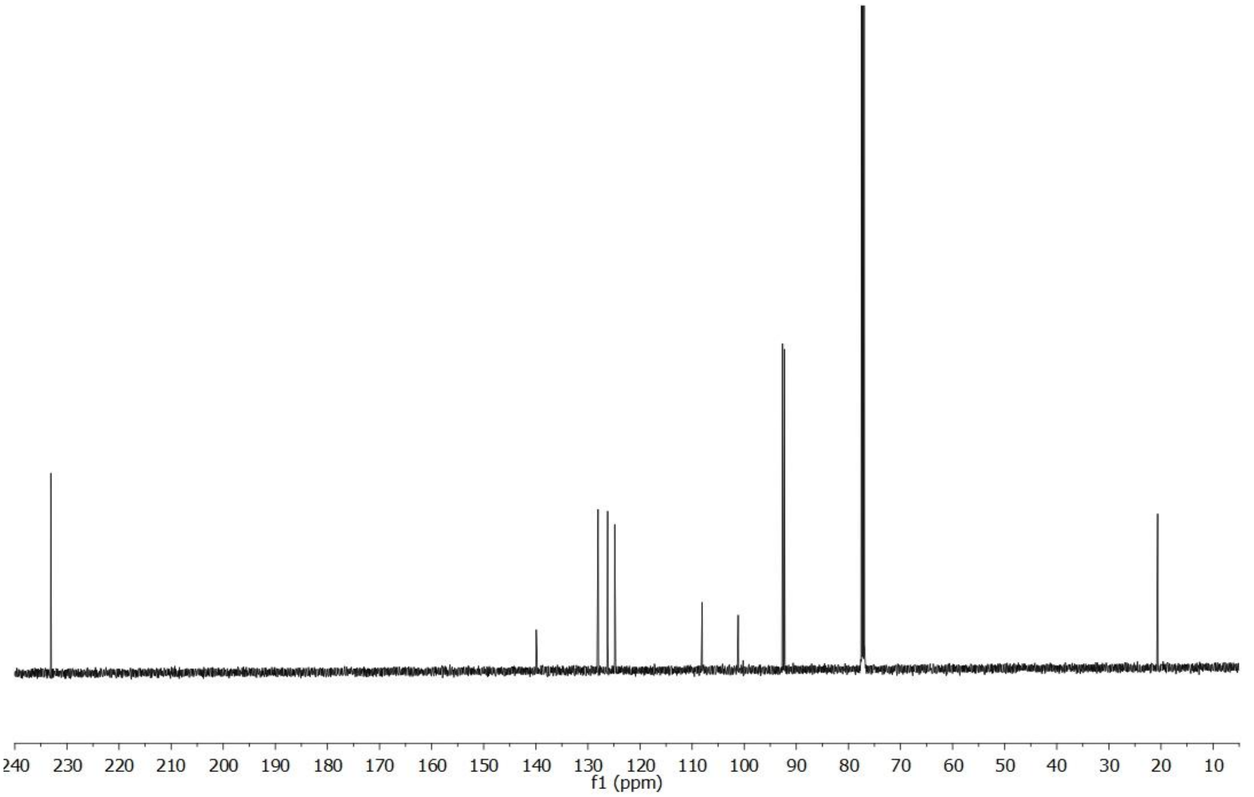




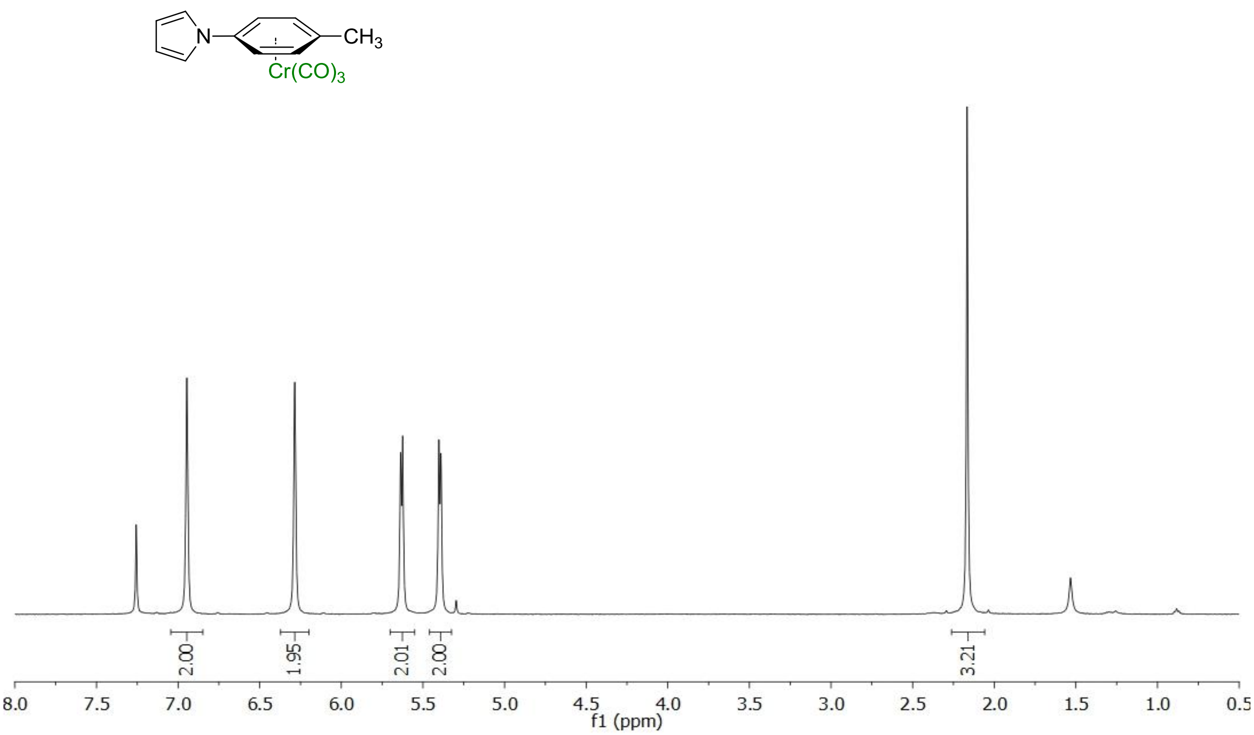
1f - (2-(η^6-*p*-tolyl)thiophene)Cr(CO)$_3$

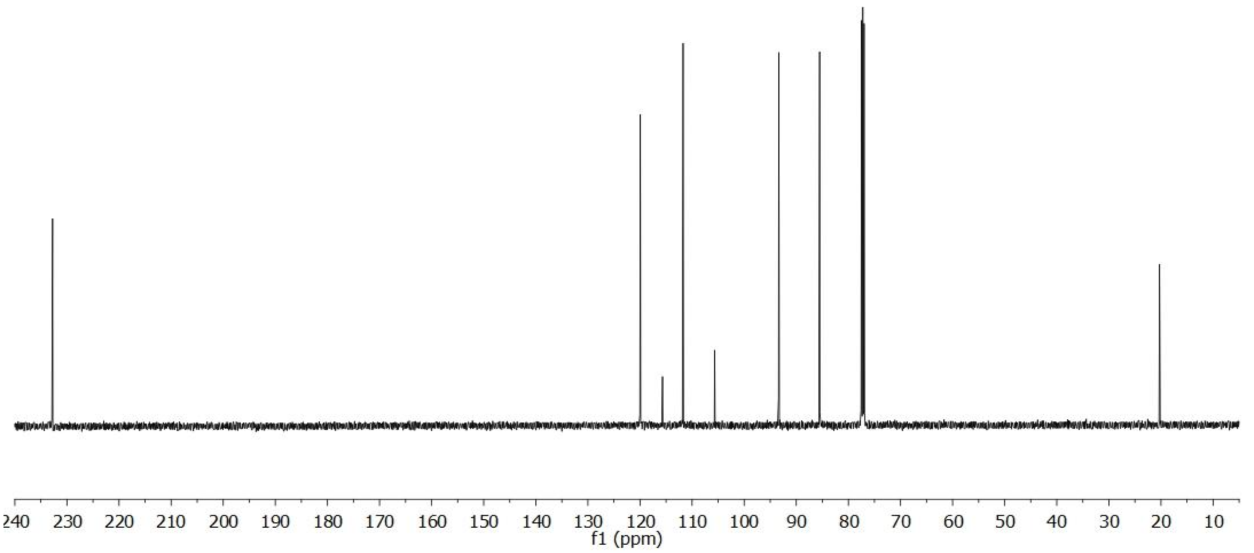




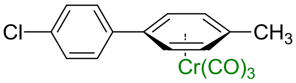


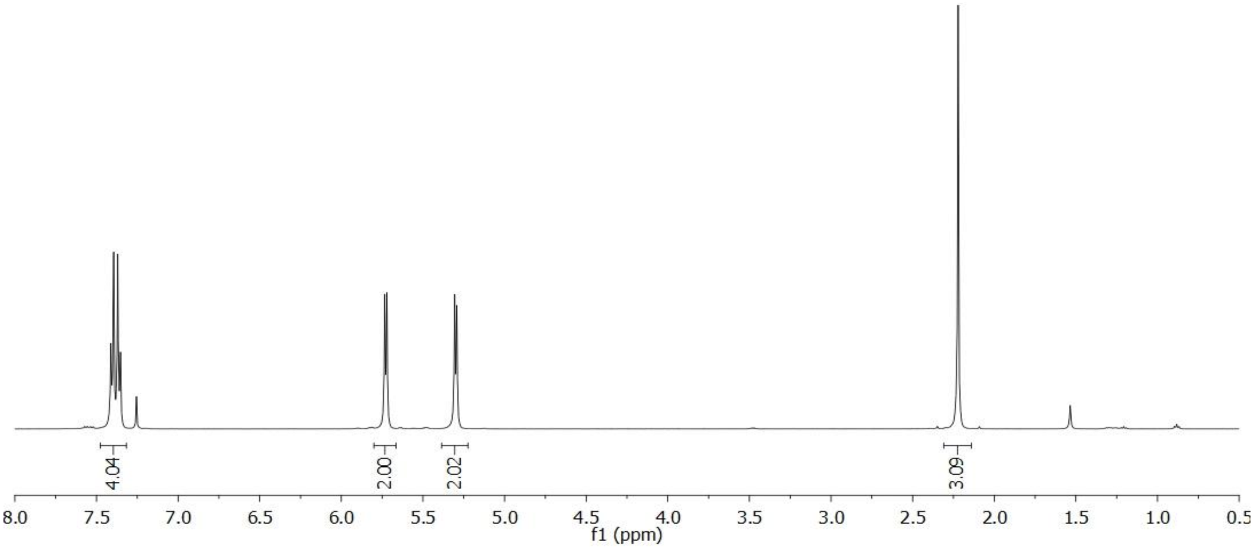
1g - (1-(η^6-*p*-tolyl)-1*H*-pyrrole)Cr(CO)$_3$

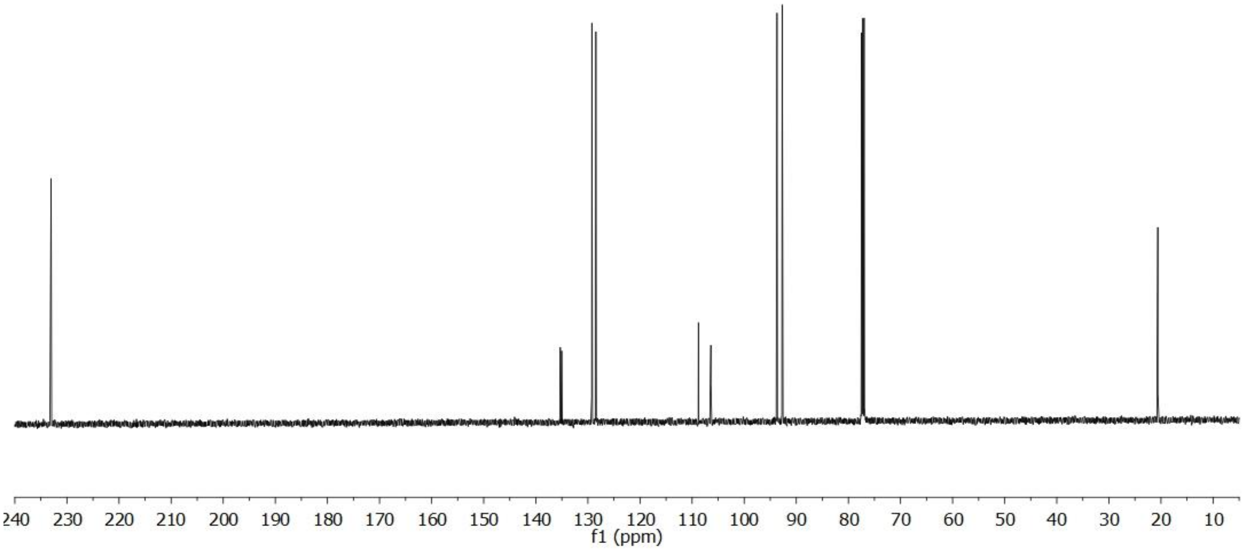




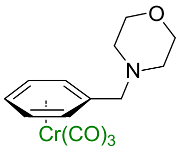
1i - (4-chloro-4’-η^6-methylbiphenyl)Cr(CO)$_3$

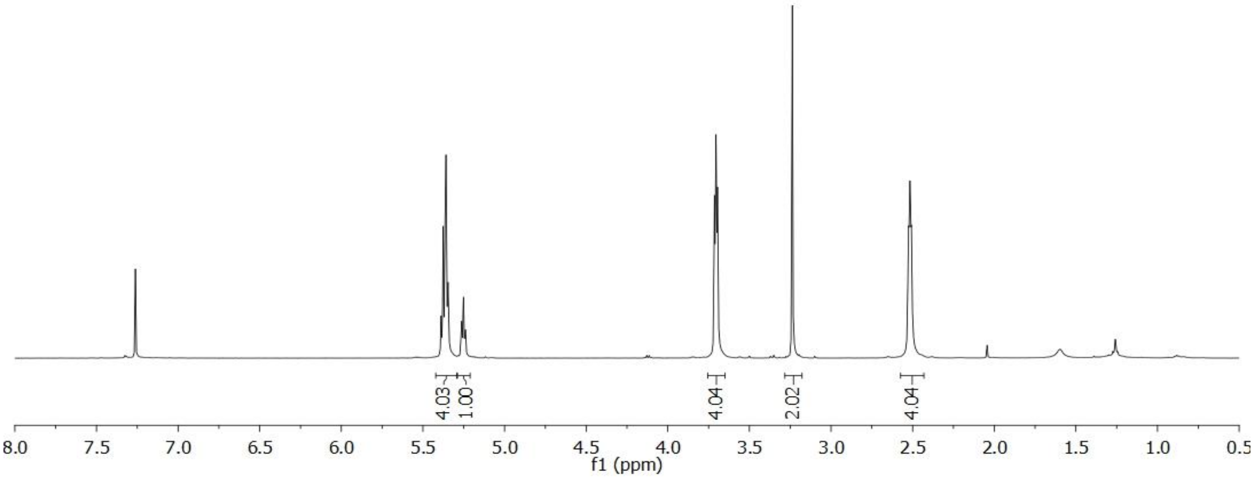


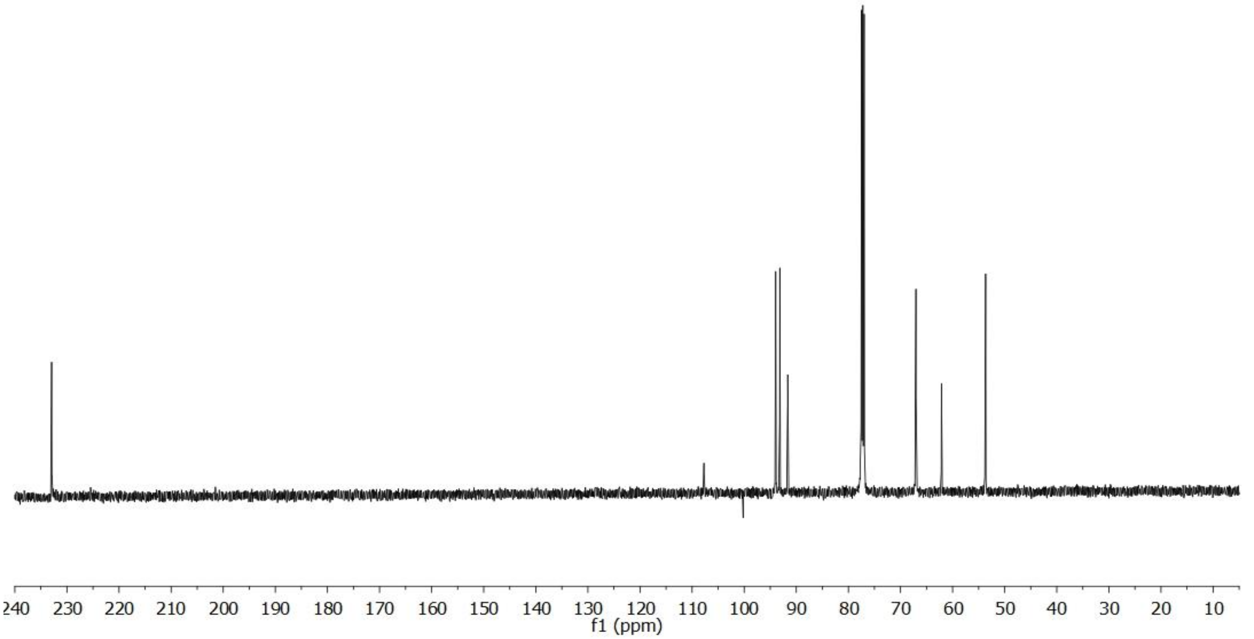




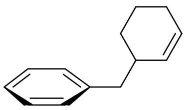
1q - (η^6-C_6H_5-CH_2-morpholine)Cr(CO)$_3$

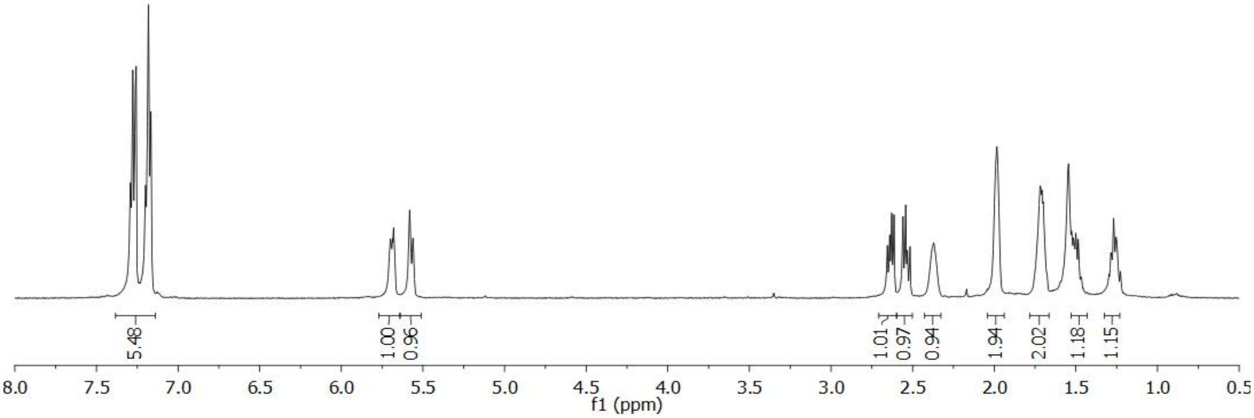


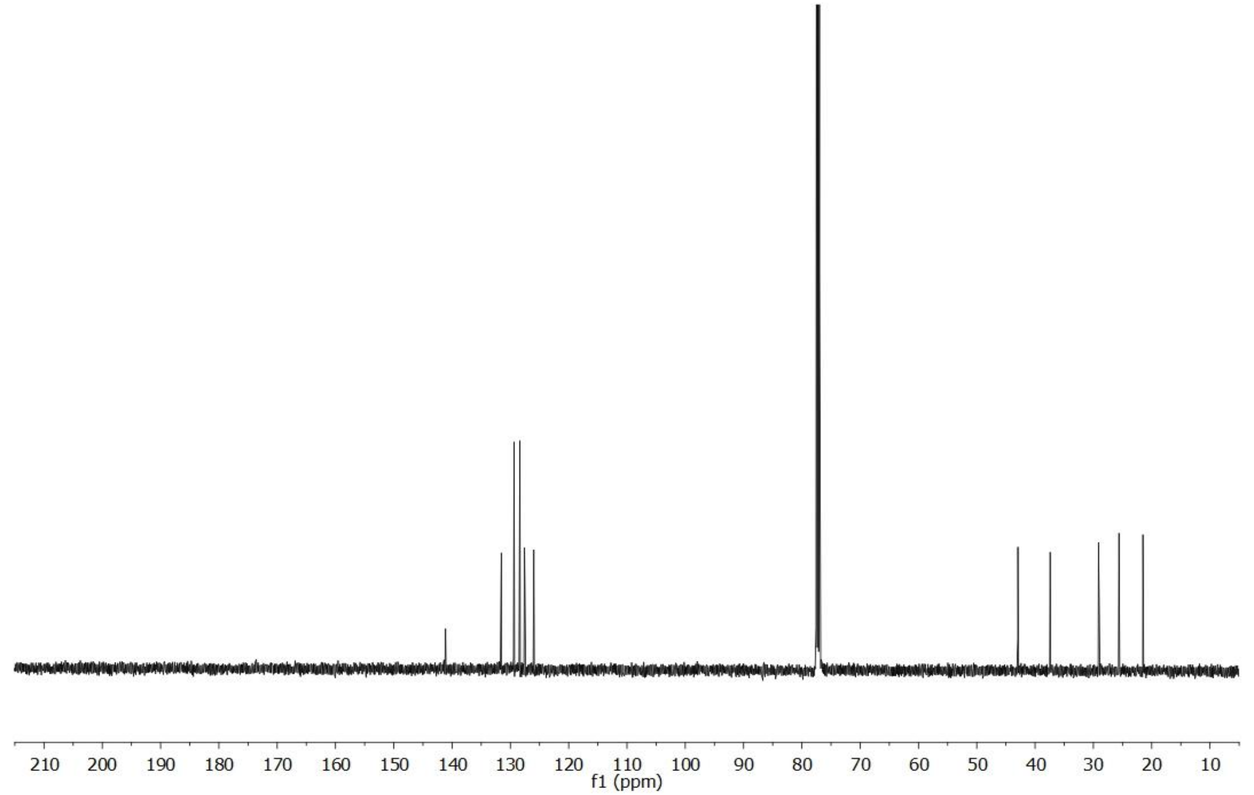




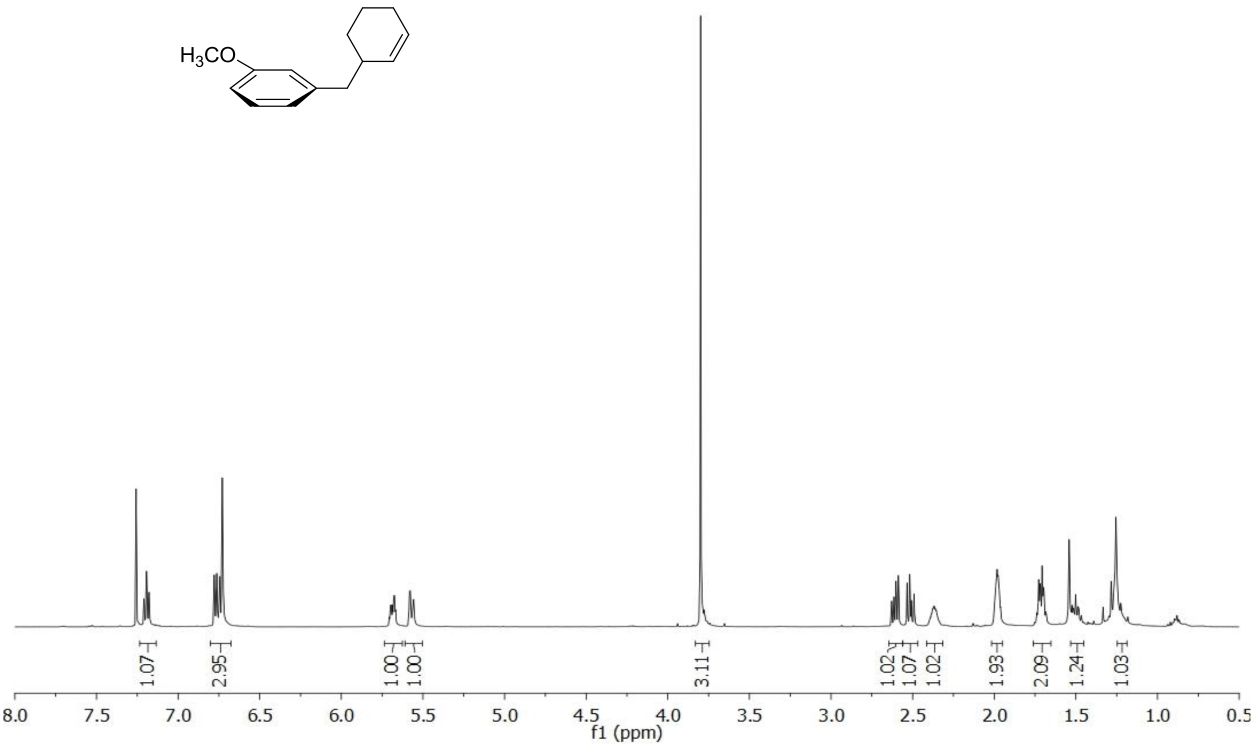
3’a – 2-cyclohexen-1-ylmethyl)-benzene

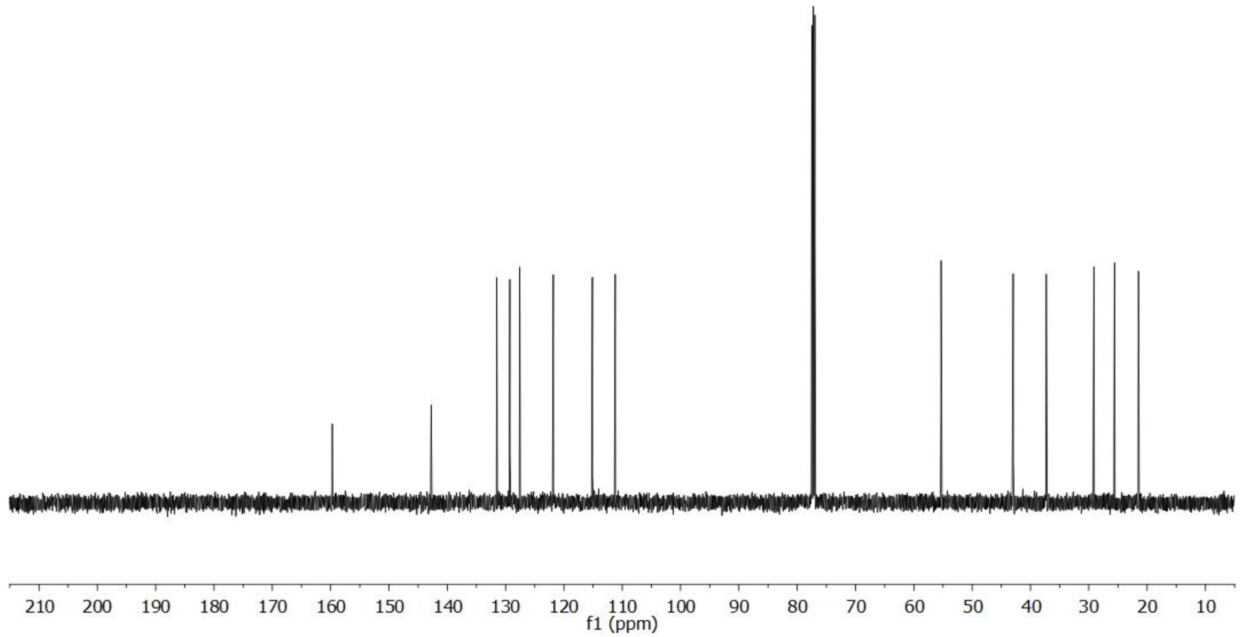




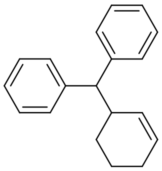


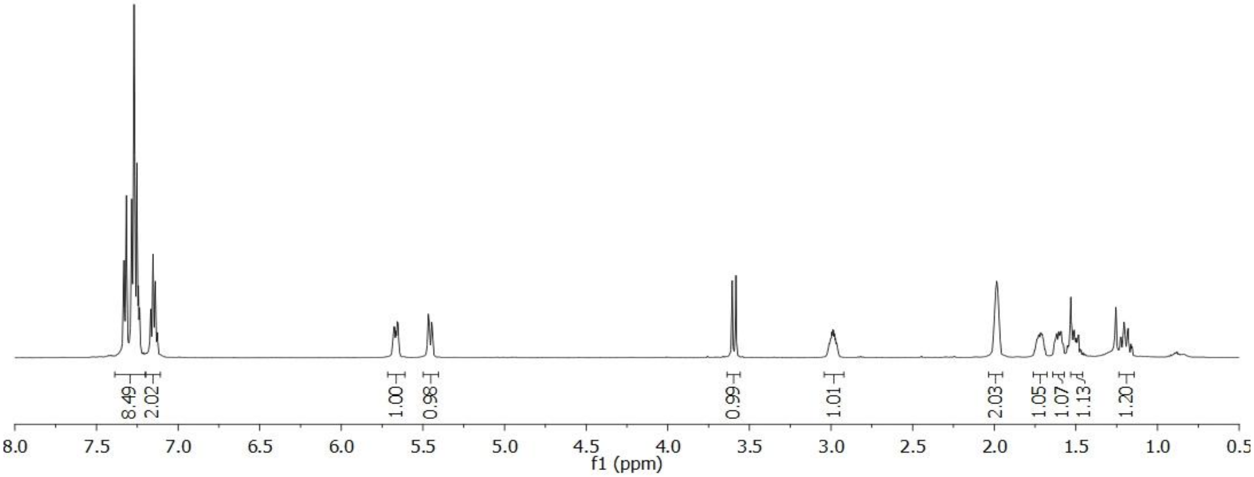
3’c – (2-cyclohexen-1-ylmethyl)-3-methoxybenzene

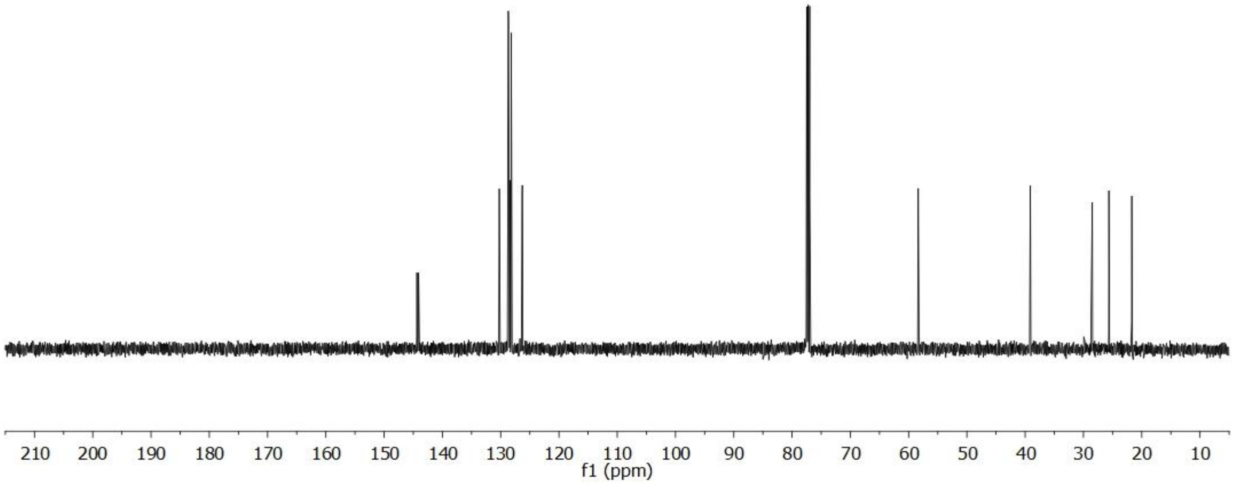




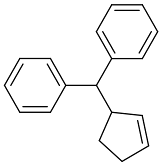
5lb – 3-(diphenylmethyl)-1-cyclohexene

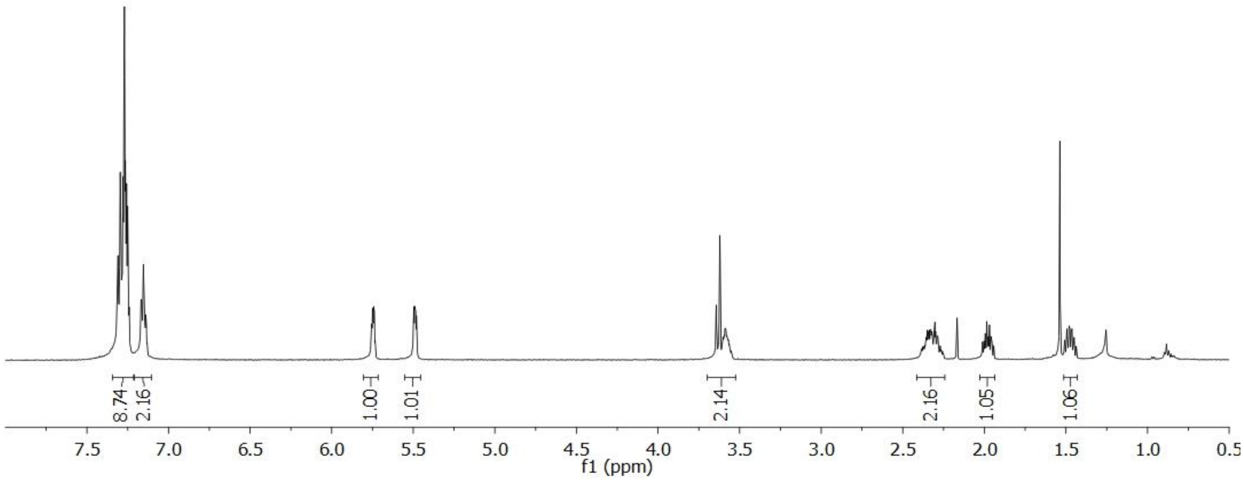


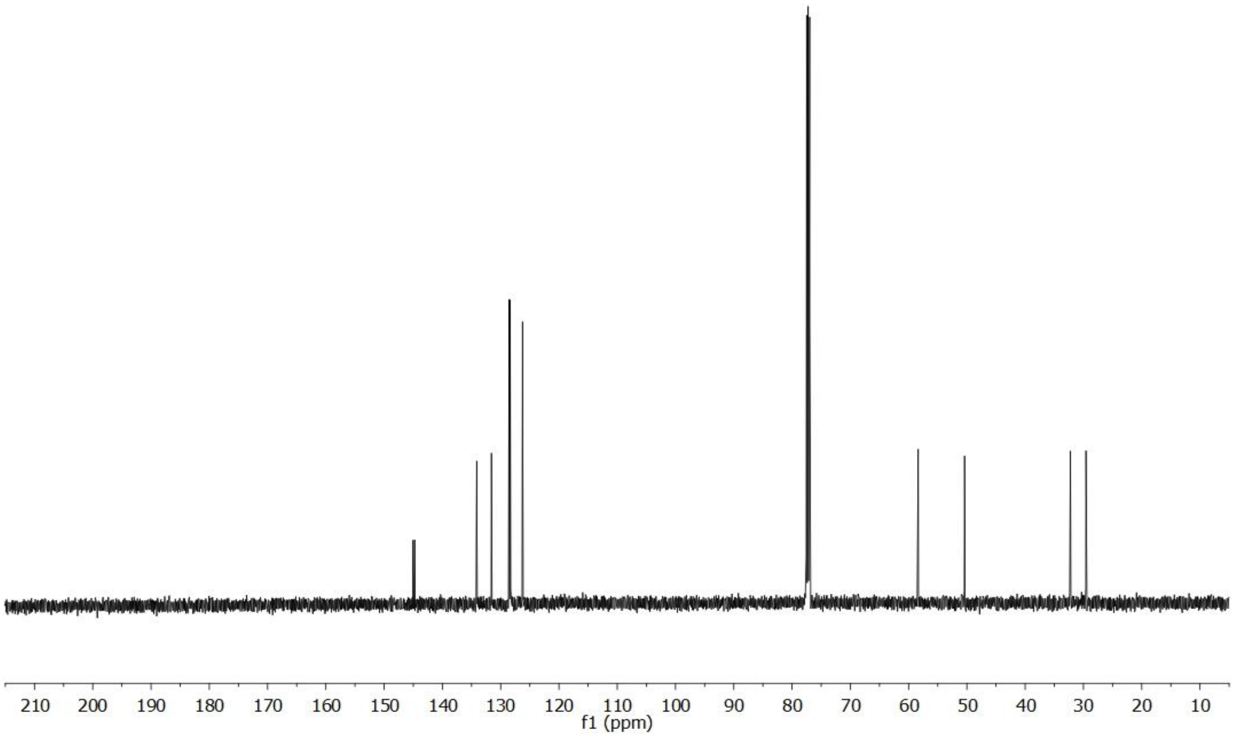




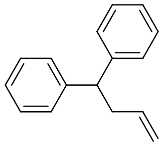
5lg – 3-(diphenylmethyl)-1-cyclopentene

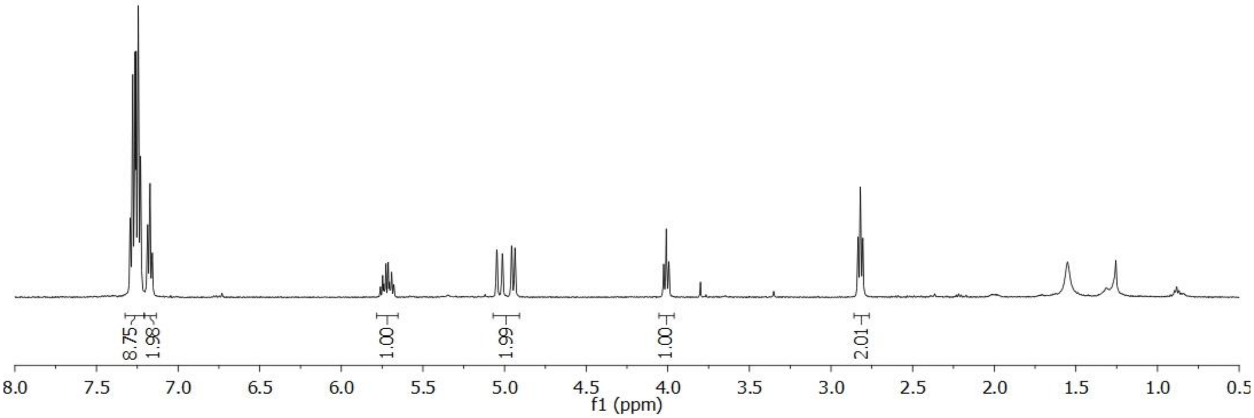


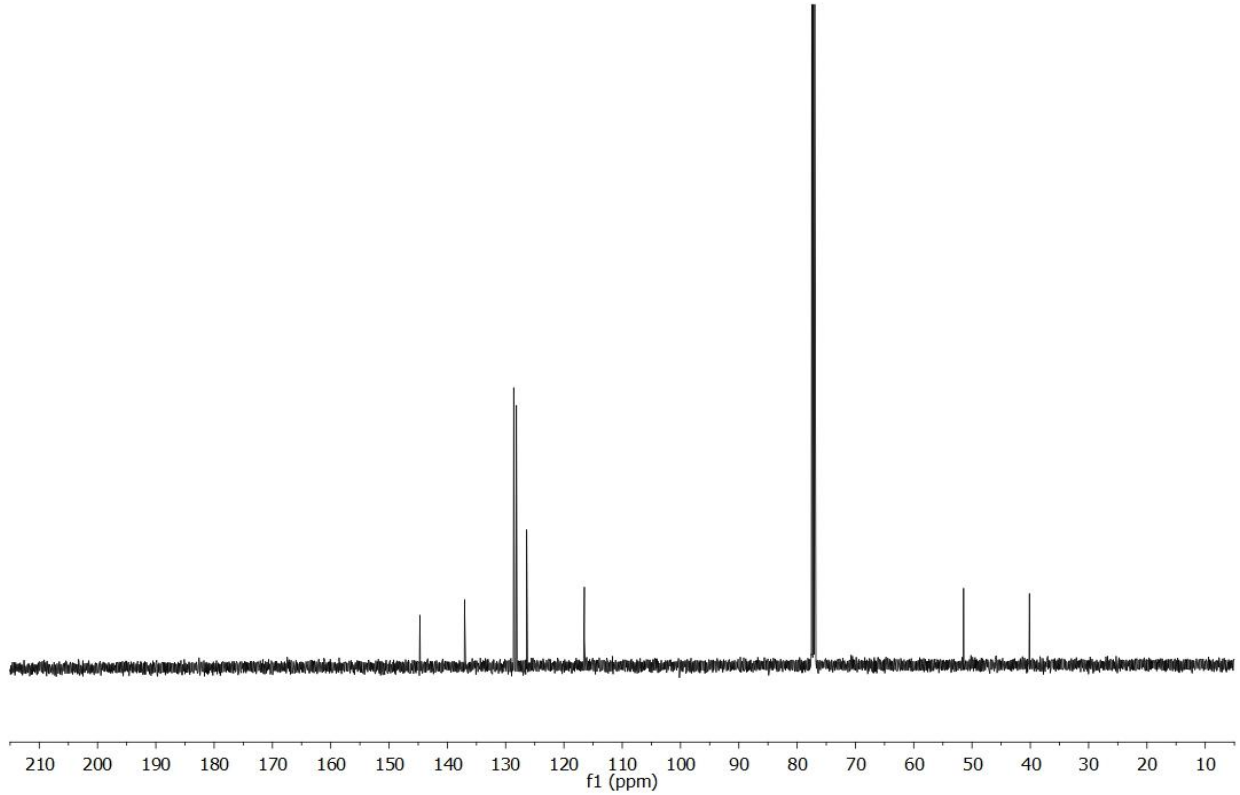




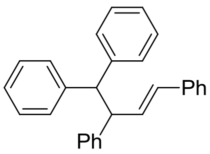
5ld – 4,4-diphenyl-1-butene

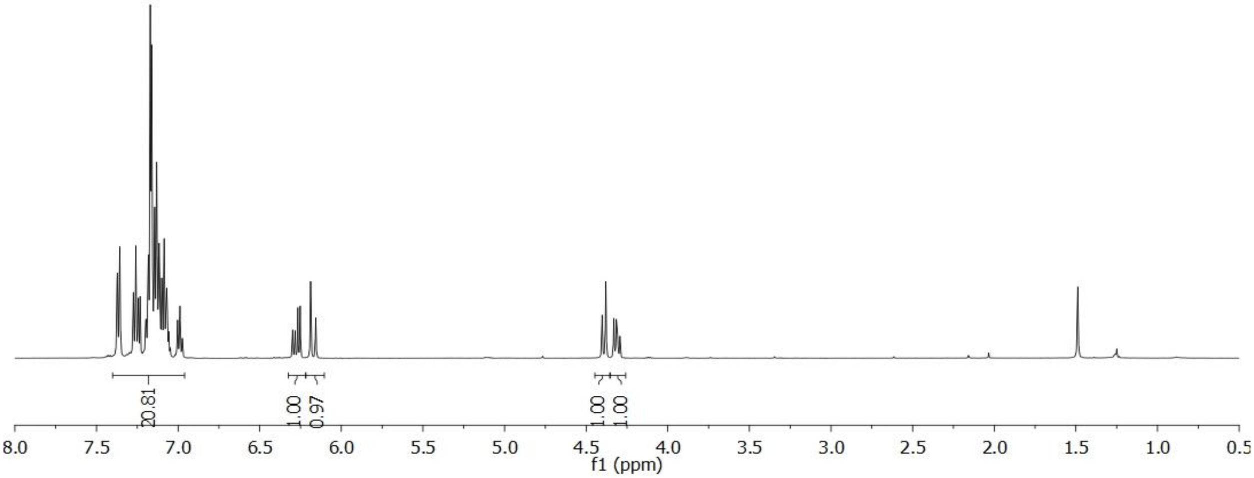


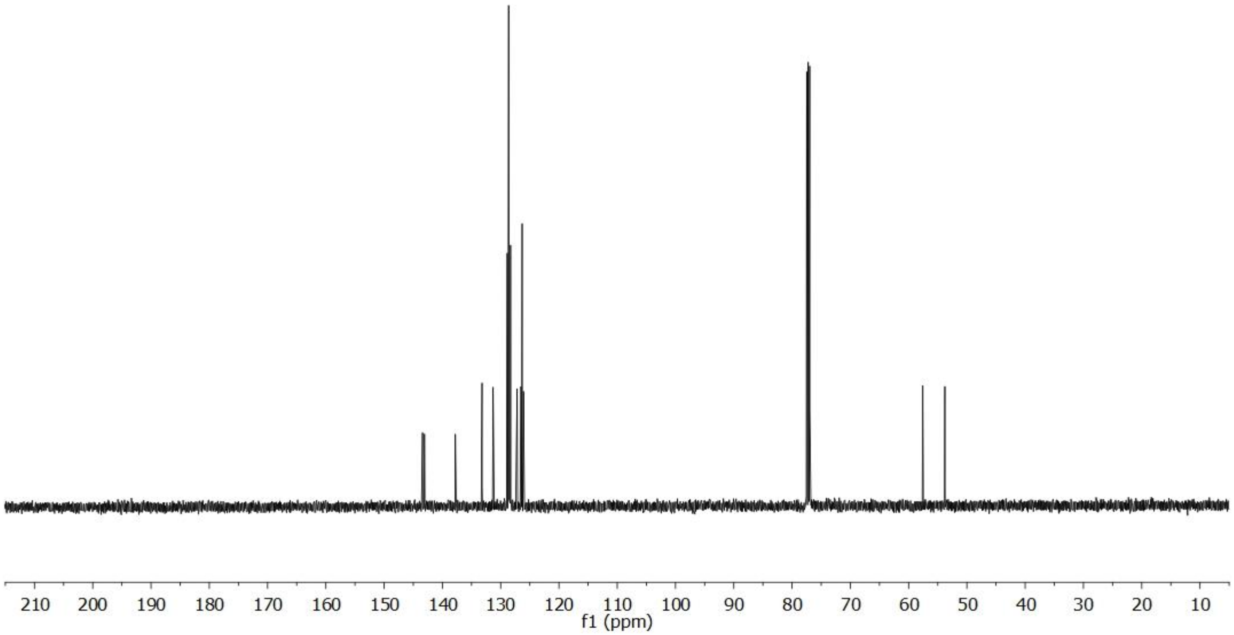




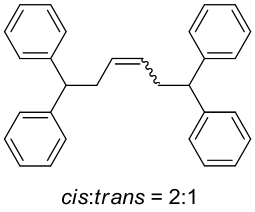
5lf – (*E*)-1,1,2,4-tetraphenylbut-3-ene

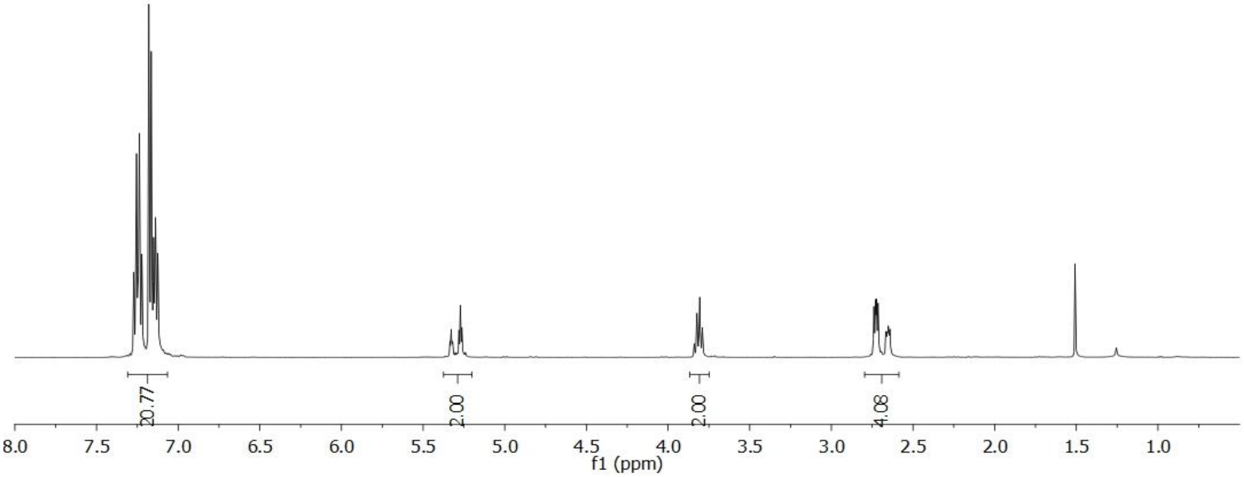


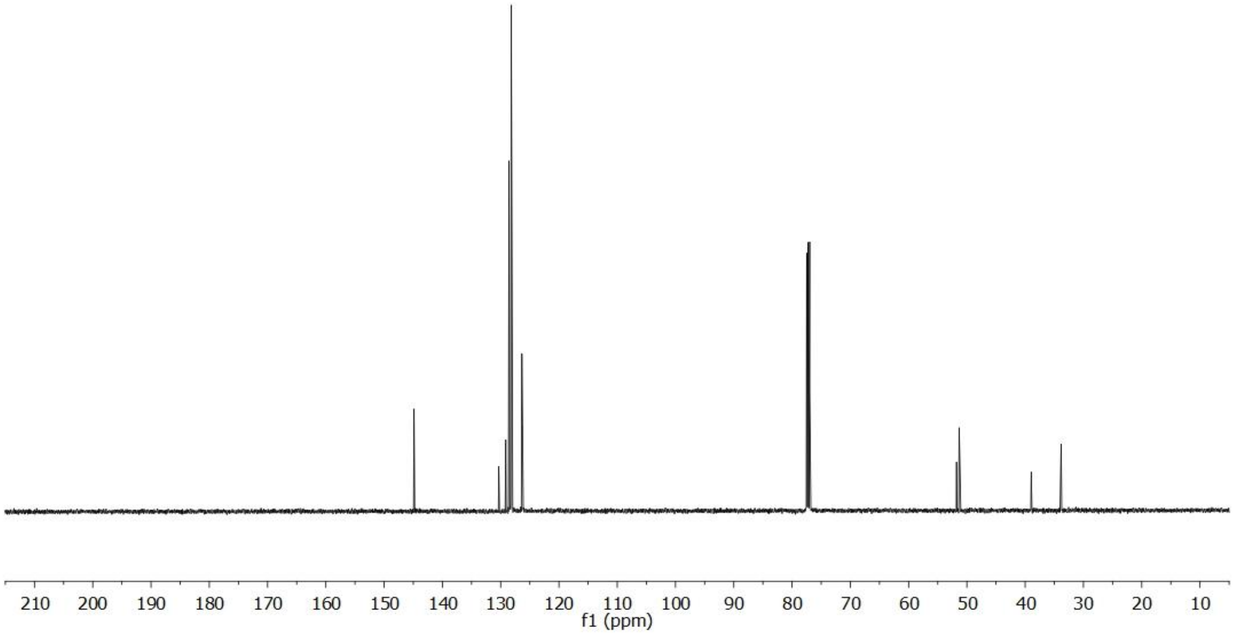




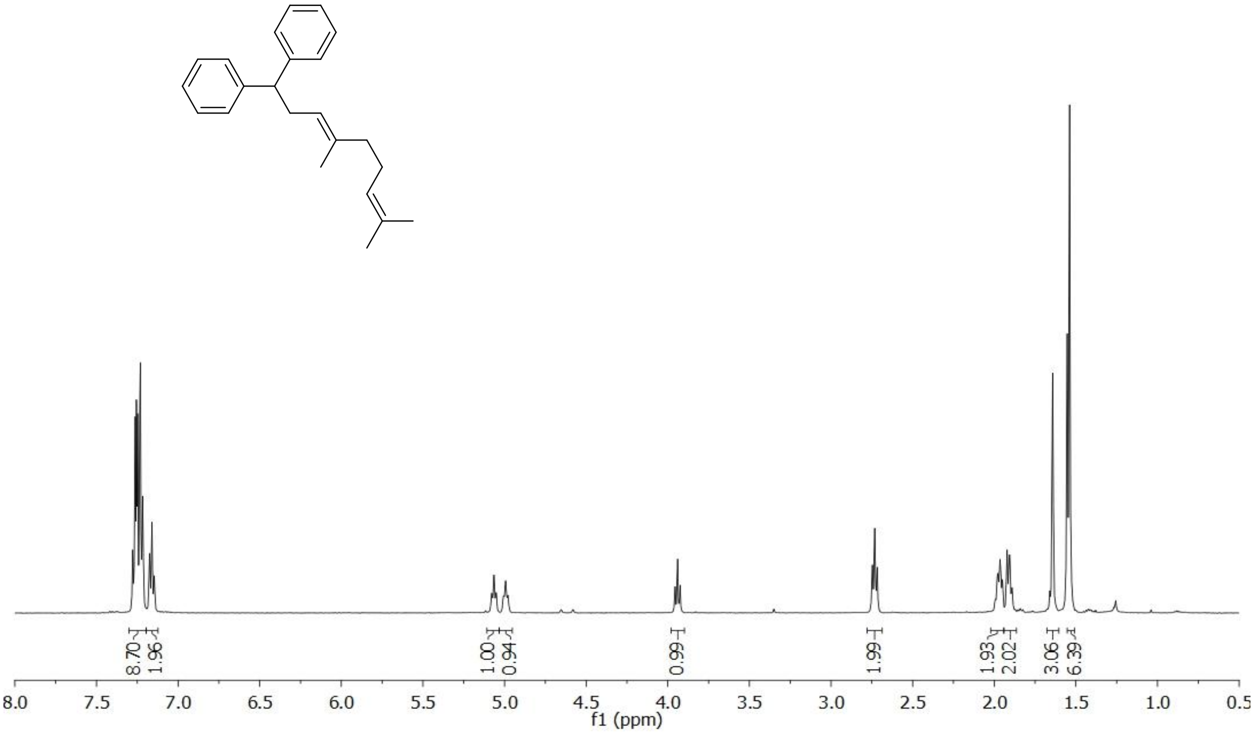
5lh – 1,1,6,6-tetraphenylhex-3-ene (*cis*:*trans* = 2:1)

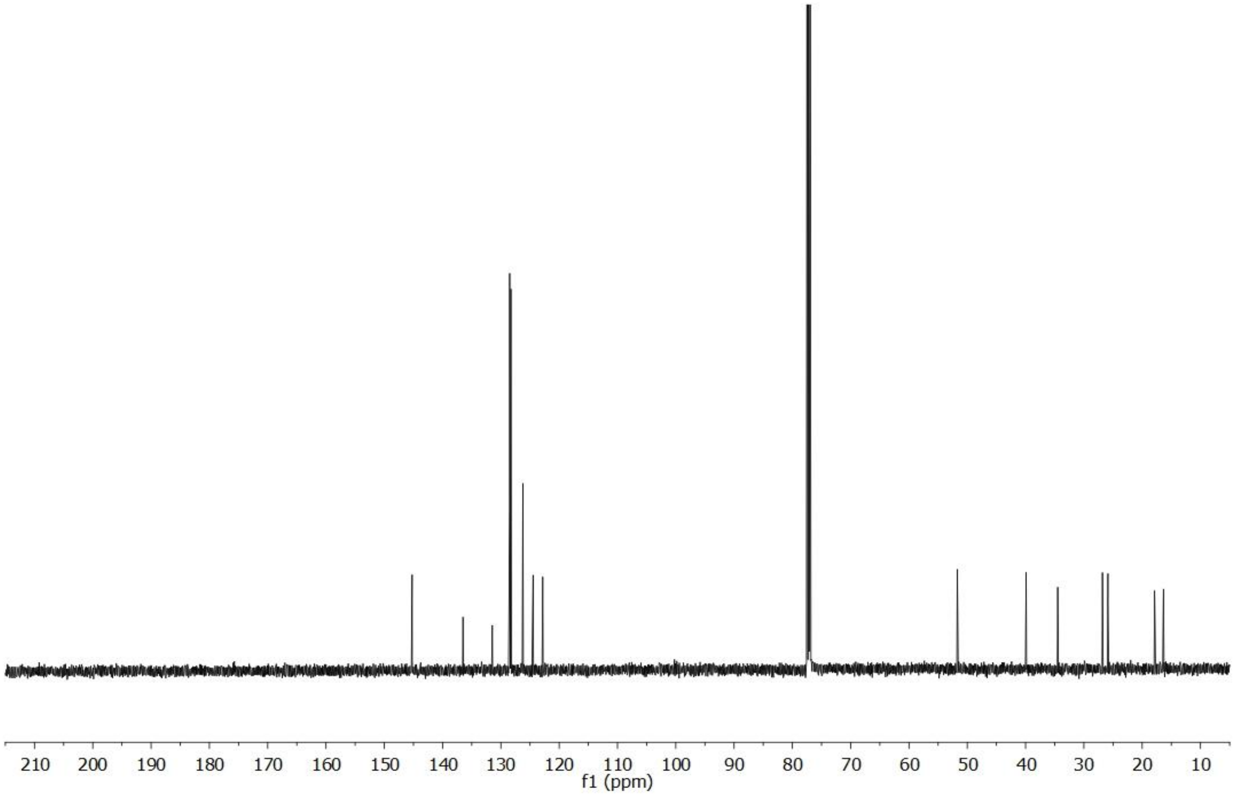




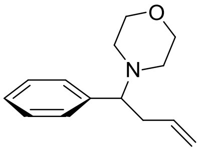


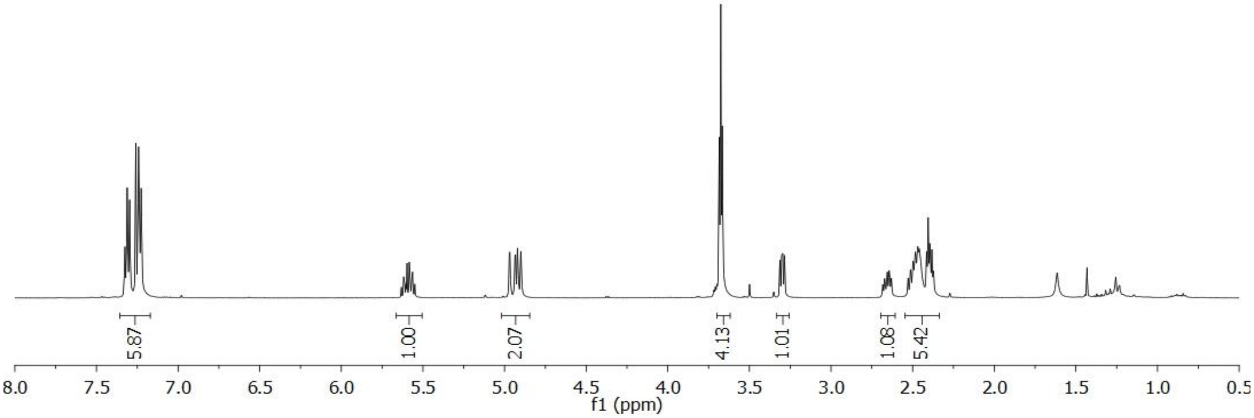
5li – α-geranyl-diphenylmethane

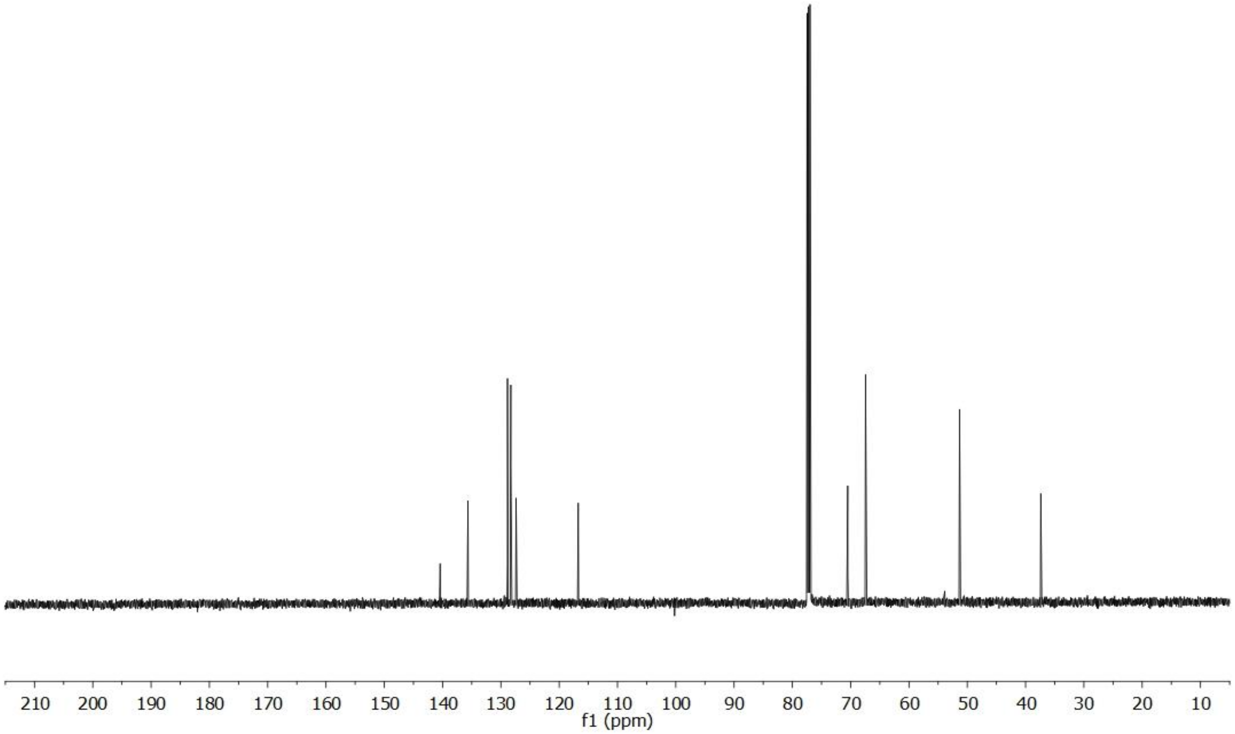




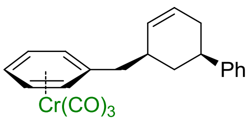
4’qd – 4-(1-phenyl-3-butenyl)-morpholine

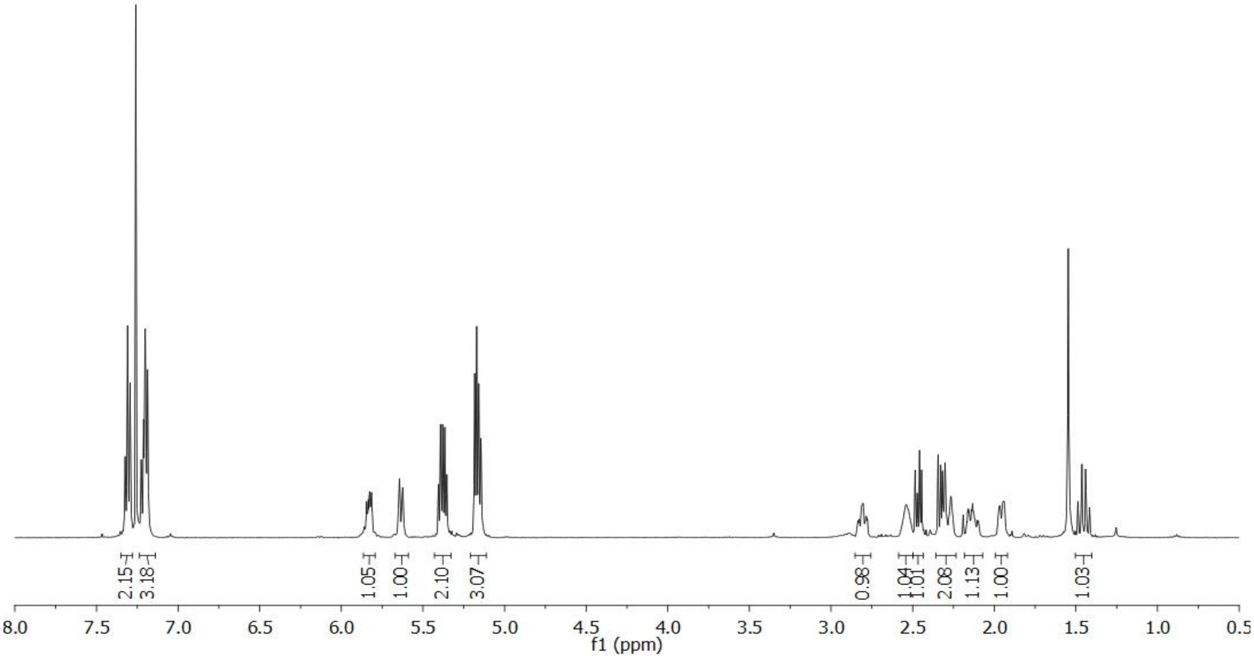


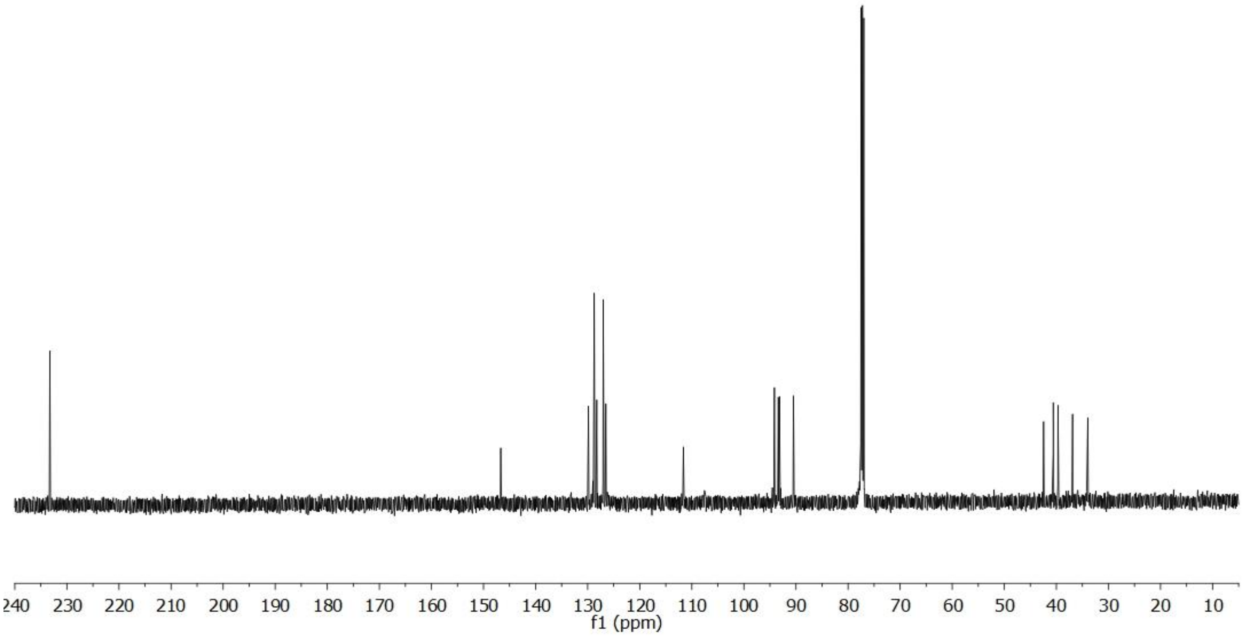




6 – *cis*-(η^6-(5-phenyl-2-cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$







(η^6-benzyl phenyl ketone)$Cr(CO)_3$