Supporting Information for

Novel [1,5] Sigmatropic Rearrangements of Cyclohexadienones Generated from Fischer Carbene Complexes. A New Strategy for Installing the C-20 Angular Ethyl Group in *Aspidospermidine* Alkaloids

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Experimental Procedures and Spectral Data for All New Compounds.

Preparation of 1,3-Dimethyl indole (methoxy) carbene complex 8:

A solution of *t*-Butlyllithium (45 mL of a 1.7 M solution in pentane, 76.5 mmol) was added to a solution of 1,3-dimethylindole (10.02 g, 69 mmol) in 45 mL of THF cooled to -78 °C over a 45 minute period. The resulting bright yellow slurry was stirred cold for 30 minutes and then allowed to warm to room temperature. The slurry was re-cooled to -78 °C and $Cr(CO)_6$ (16 g, 73 mmol) was added as a solid in a single portion. The reaction was again allowed to stir for 30 minutes cold and then warmed to room temperature. The dark brown reaction mixture was then stirred for 22 hours. The solution was cooled to 0 °C and methyl triflate (8.2 mL, 72 mmol) was added. The reaction was stirred for 20 minutes cold, warmed to room temperature and stirred an additional hour. The deep red solution was filtered through silica and concentrated. The red oily residue was dissolved in hexane and allowed to stand in the freezer. The chromium carbene complex[1] was collected as deep red crystals (19.9 g, 73 %).

Spectral Data for **8:** [121573-95-3], Deep red crystals, mp = 102-104 °C, R_f = 0.61 (80:20 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H), 3.60 (s, 3 H), 4.22 (s, 3 H), 7.12 (m, 2 H), 7.24 (d, 1 H, 3.5 Hz), 7.53 (d, 1 H, 8.0 Hz); IR (NaCl, neat) 2063 m, 1933 br s, 1432 w, 1355 w, 1251 m, 1182 w, 1144 m, 932 m, 748 m, 698 m cm^{-1}; mass spectrum m/z (relative intensity) 379 (M^+, 7), 351 (57), 323 (65), 295 (25), 267 (84), 239 (100), 209 (100), 187 (85), 172 (100), 157 (27), 144 (98), 128 (30), 115 (38), 103 (46), 91 (28), 77 (48).

Carbazol-4-one 9a from the Reaction of Complex 8 with 1-Pentyne

1-Pentyne (400 µL, 4.06 mmol) was added to a solution of carbene complex **8** (1.028 g, 2.71 mmol) in 50 mL of argon sparged hexane. The reaction was heated at 55 °C for 90 minutes, concentrated and chromatographed on silica gel (95:5 hexane:EtOAc) to yield the carbazolone[2] **9a** as a deep red oil (638 mg, 83 %).

Spectral data for **9a:** [121573-83-9] Dark red oil, R_f = 0.43 (80:20 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, 7.3 Hz), 1.45-1.55 (m, 5 H), 2.1-2.35 (d of m, 2 H), 3.51 (s, 3 H), 3.64 (s, 3H), 6.67 (d, 1 H, 7.8 Hz), 6.84 (s, 1 H), 6.89 (t, 1 H, 7.2 Hz), 7.19 (t, 1 H, 7.8 Hz), 7.87 (d, 1 H, 7.4 Hz).

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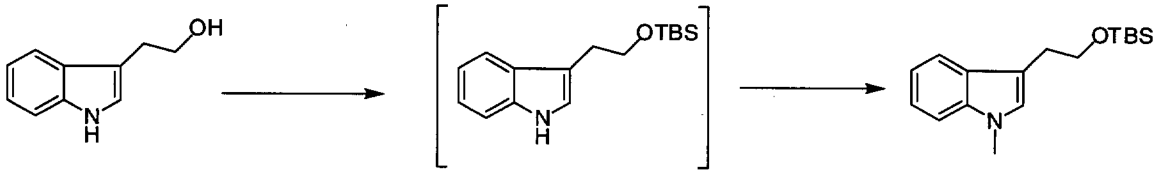
[1] Bauta, B. E.; Wulff, W. D.; Pavkovic, S. F.; Zaluzec, E. J. *J. Org. Chem.* **1989**, *54*, 3249.
[2] Bauta, B. E.; Wulff, W. D.; Pavkovic, S. F.; Zaluzec, E. J. *J. Org. Chem.* **1989**, *54*, 3249.

Preparation of N-Methyl-O-tertbutyldimethylsilyl-Tryptophol 45.



43 **44** **45**

t-Butyldimethylsilylchloride (37.9 g, 251 mmol) was added to a solution of tryptophol (33.8 g, 210 mmol) and imidazole (35.7 g, 524 mmol) in 100 mL of DMF cooled to 0 °C. The reaction was stirred cold for 30 minutes, warmed to room temperature and stirred for 1 hour. The reaction mixture was partially concentrated and poured into a water - ether mixture. The aqueous layer was back extracted once and the combined ether layers washed once with water, once with brine, and dried over anhy. $MgSO_4$. The ether was removed to yield the TBS protected tryptophol[3] as a red oil which was not purified further, but used directly. The TBS-tryptophol was dissolved in 200 mL of THF and added to a slurry of NaH (16.8 g of a 60 % dispersion in oil, 420 mmol) in 60 mL of THF cooled to 0 °C. When the evolution of H_2 subsided, the flask was fitted with a reflux condenser and methyl iodide (20 mL, 322 mmol) was added. The reaction was stirred at 0 °C for 15 minutes and then refluxed for 1 hour, cooled to room temperature and concentrated. The residue was extracted from water and ether. The ether layer was dried over anhy $MgSO_4$ and concentrated to yield a yellow oil.

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[3] Grotjahn, D. B.; Vollhardt, P. C.; *J. Am. Chem. Soc.*, **1986**, *108*, 2091.

The product was purified *via* vacuum distillation (135-147 °C / 0.1 mm Hg) to yield a water white oil (51.7 g, 85 %)

Spectral data for **44**: [101079-48-5] (light red oil) ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.90 (s, 9 H), 3.00 (t, 2 H, *J* = 7.1 Hz), 3.88 (t, 2 H, *J* = 7.4 Hz), 7.03 (d, 1 H, 2.1 Hz), 7.11-7.18 (m, 2 H), 7.33-7.36 (m, 1 H), 7.61 (d, 1 H, 7.7 Hz), 7.97 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.1, 15.5, 26.2, 29.2, 64.1, 111.2, 113.3, 119.1, 119.4, 122.0, 122.2, 127.9, 136.3.

Spectral data for **45:** Colorless oil, bp = 165-147 °C / 0.1mm Hg, R_f = 0.13 (95:5 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 6 H), 0.91 (s, 9 H), 2.98 (t, 2 H, 7.6 Hz), 3.73 (s, 3 H), 3.85 (t, 2 H, 7.5 Hz), 6.88 (s, 1 H), 7.10 (t, 1 H, 7.2 Hz), 7.18-7.29 (m, 2 H), 7.59 (d, 1 H, 7.9Hz); ^{13}C NMR ($CDCl_3$) δ -5.3, 18.4, 26.0, 28.9, 32.6, 64.1, 109.1, 111.4, 118.6, 118.9, 121.4, 126.9, 128.0, 136.8; IR (NaCl, neat) 3055 w, 2954 s, 2928 s, 2856 s, 1472 s, 1424 w, 1385 m, 1327 m, 1250 s, 1095 br s, 1005 m, 920 w, 835 s, 776 s, 737 s cm^{-1}; mass spectrum m/z (relative intensity) 289 (M^+, 21), 232 (96), 158 (63), 144 (100), 115 (10), 73 (15), 57 (10); elemental analysis calculated for $C_{17}H_{27}NOSi$: C = 70.53 %, H = 9.40 %, N = 4.84 %, found C = 71.1 %, H = 9.71 %, N = 4.58 %.

Preparation of 1-Methyl-TBS-Tryptophol carbene complex 10:

A solution of *t*-Butyllithium (20 mL of a 1.7M soln. in pentane, 34 mmol) was added over 15 minutes to a solution of N-methyl-O-tert-butyldimethylsilyl tryptophol **45** (9.182 g, 32 mmol) in 25 mL of ether cooled to -78 °C. The solution was stirred cold for 45 minutes and then allowed to warm to room temperature and stirr for an additional

90 minutes. The turbid yellow solution was re-cooled to -78 °C and chromium hexacarbonyl (7.0 g, 32 mmol) was added as a solid in a single portion. The reaction was kept at -78 °C for 4 hours and then allowed to warm to room temperature and stirred for 18 hours. The dark brown solution was cooled to 0 °C and methyl triflate (3.8 mL, 34 mmol) was added. The reaction was stirred at 0 °C for 20 minutes and room temperature for 1 hour. The reaction was concentrated and the carbene complex purified via column chromatography (pentane) to yield 11.046 g of a deep red oil which solidifies on standing (67 %).

Spectral data for **10:** Dark red crystals, softens 45 °C, mp = 62-65 °C, R_f = 0.58 (90:10 Hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 6 H), 0.85 (s, 9 H), 2.98 (t, 2 H, 7.1 Hz), 3.59 (s, 3 H), 3.82 (t, 2 H, 7.1 Hz), 4.28 (s, 3 H), 7.13-7.18 (m, 1 H), 7.25-7.33 (m, 2 H), 7.63 (d, 1 H, 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ -5.4, 18.4, 25.9, 29.2, 31.5, 63.6, 66.4, 107.7, 109.6, 120.1, 120.5, 123.4, 127.5, 137.4, 215.6, 224.7, 249.3 (2 aromatic carbons overlap); IR (NaCl, neat) 2954 br w, 2929 br w, 2063 s, 2052 m, 1934 br s, 1466 w, 1251 w, 1132 br w, 1095 br w, 835 w, 741w, 656 w cm^{-1}; mass spectrum m/z (relative intensity) 383 (M^+, 5), 355 (8), 303 (11), 289 (2), 262 (5), 246 (13), 232 (8), 216 (2), 172 (16), 158 (55), 144 (25), 126 (5), 89 (76), 75 (100), 59 (22); elemental analysis calculated for $C_{24}H_{29}NO_7SiCr$: C = 55.05 %, H = 5.58 %, N = 2.68 %, Cr = 9.93 %, found C = 55.16 %, H = 5.70 %, N = 2.66 %, Cr = 6.23 %.

Carbazolone 12 From the Reaction of Complex 10 with 1-Pentyne.

1-Pentyne (330 µL, 3.35 mmol) was added to a solution of carbene complex **10** (1.180 g, 2.25 mmol) in 45 mL of Argon sparged hexane. The reaction was heated at 45-55 °C for 90 minutes. The reaction was then cooled to room temperature, concentrated, and purified via column chromatography (95:5 hexane:EtOAc) to yield 510 mg of a deep red oil (53 %).

Spectral data for **12:** Deep red oil, R_f = 0.28 (95:5 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ -0.1 (s, 6 H), 0.85 (s, 9 H), 1.02 (t, 3 H, 7.2 Hz), 2.5-2.7 (m, 2 H), 2.1 (t, 2 H, 7.1 Hz), 2.2-2.5 (m, 2 H), 3.4-3.5 (m, 2 H), 3.6 (br s, 3 H), 3.75 (br s, 3 H), 6.8 (d, 1 H, 7.9 Hz), 6.95(br s, 1 H), 7.0-7.1 (m, 1 H), 7.35 (t, 1 H, 7.4 Hz), 7.95 (d, 1 H, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ -5.4, 13.9, 18.1, 22.4, 25.8, 30.8, 31.2, 48.1, 58.9, 60.8, 63.8, 106.7, 109.2, 119.9, 124.0, 125.1, 128.0, 129.7, 140.2, 146.9, 148.8, 200.9; IR (NaCl, neat) 2956, 2929, 2856, 1934, 1918, 1671, 1634, 1608, 1541, 1463, 1361, 1350, 1252, 1099*, 835, 776, 740 cm^{-1}; elemental analysis calculated for $C_{25}H_{37}NO_3Si$: C = 70.21 %, H = 8.72 %, N = 3.28 %, found C = 68.23 %, H = 8.70 %, N = 2.82 %.

Carbazolone 13 from the Reaction of Complex 10 with 1-Pentyne.

1-Pentyne (760 µL, 7.7 mmol) was added to a solution of carbene complex **10** (2.00 g, 3.82 mmol) in 77 mL of Argon sparged hexane. The reaction was heated at 55 °C for 48 hours. The reaction was then cooled to room temperature, concentrated, and purified via column chromatography (95:5 hexane:EtOAc) followed by recrystallization from hexane to yield 1.424 g of colorless crystals (38 %).

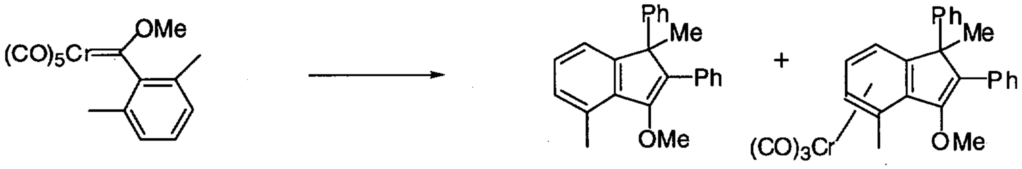
Spectral data for **13:** Colorless crystals, mp = 110-111 °C, R_f = 0.15 (95:5 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ -0.11 (s, 6 H), 0.77 (m, 12 H), 1.0-1.2 (m, 2 H), 1.45-1.55 (m, 1 H), 1.7-1.8 (m, 1 H), 1.95-2.05 (m, 1 H), 2.3-2.4 (m, 1H), 3.4-3.5 (m, 2 H), 3.81 (s, 3 H), 4.03 (s, 3 H), 5.20 (s, 1 H), 7.25-7.35 (m, 3 H), 8.25-8.30 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.5, -5.4, 14.4, 17.4, 18.1, 25.8, 32.4, 44.0, 44.3, 53.1, 54.9, 59.9, 109.5, 112.5, 112.9, 121.9, 123.0, 123.6, 124.2, 138.8, 142.0, 146.9, 196.9; IR (NaCl, neat) 2955 s, 2931 s, 2857 m, 1639 m, 1626 s, 1610 m, 1470* s, 1419 m, 1314 w, 1248 m, 1090 br m, 1010 w, 837 s, 7765 m, 751 m cm^{-1}; mass spectrum m/z (relative intensity) 427 (M^+ 23), 412 (14), 370 (32), 312 (26), 269 (100), 254 (11), 240 (16), 723 (28); elemental analysis calculated for $C_{25}H_{37}NO_3Si$: C = 70.21 %, H = 8.72 %, N = 3.28 %, found C = 70.40 %, H = 8.83 %, N = 3.18 %.

Carbazol-4-one 14 from the Thermal Rearrangement of Carbazolone 9a.

Carbazolone **9a** (638 mg, 2.25 mmol) was dissolved 30 mL of xylenes and heated to reflux (~140 °C) for 2 days. The reaction was cooled to room temperature, concentrated and chromatographed (90:10 hexane:EtOAc) to yield 252 mg of **14** as colorless crystals (40 %) along with 153 mg of starting material **9a** (24 %) as a deep red oil.

Spectral data for **14:** Colorless crystals, mp = 134-135 °C, R_f = 0.31 (80:20 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3 H, 7.3 Hz), 1.0-1.2 (m, 2 H), 1.30 (s, 3 H), 1.45 (t of d, 1 H, 4.1 Hz, 12.8 Hz), 2.10 (t of d, 1 H, 4.9 Hz, 12.2 hz), 3.83 (s, 3 H), 4.06 (s, 3 H), 5.21 (s, 1 H), 7.25-7.40 (m, 3 H), 8.3-.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 18.3, 26.8, 32.2, 43.7, 50.4, 54.8, 109.4, 111.8, 113.9, 121.5, 122.8, 123.5, 124.3, 138.8, 141.9, 146.0, 197.7; IR (NaCl, neat) 2957 m, 2931 m, 2870 w, 1639 s, 1625 s, 1609 s, 1471* s, 1417 s, 1398 m, 1250 m, 1153 w, 1125 m, 1076 m, 1010 w, 901 w, 753 m cm^{-1}; mass spectrum m/z (relative intensity) 283 (M$^+$, 41), 268 (16), 240 (100), 226 (19), 212 (17), 197 (19), 182 (9), 168 (9), 158 (10), 144 (6); elemental analysis calculated for $C_{18}H_{21}NO_2$: C = 76.30 %, H = 7.47 %, N = 4.94 %, found C = 76.33 %, H = 77.4 %, N = 4.84 %.

Reaction of Complex 15 with Diphenylacetylene in Benzene.



15 **16a** **17a**

In 615 mL benzene (0.5 M) were combined 104.5 mg complex **63** (0.31 mmol) and 109.3 mg diphenylacetylene (0.61 mmol). These were heated after degassing at 110 °C for 19.75 h. Immediate chromatography on silica gel with gradient elution from 10 % benzene/hexane to 30 % benzene/hexane gave 53.0 mg indene **16a** (52.9 %), and 61.0 mg chromium tricarbonyl complexed indene **17a** (42.9 %). The following spectral data is consistent with published data.[4]

Spectral data for 3,7-Dimethyl-2,3-diphenyl-1-methoxy-1-indene **16a**. R_f = 0.73 (1:1:10). ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3H), 2.64 (s, 3H), 3.66 (s, 3H), 6.85 (d, 1H, J = 7 Hz), 7.00-7.20 (m, 12H).

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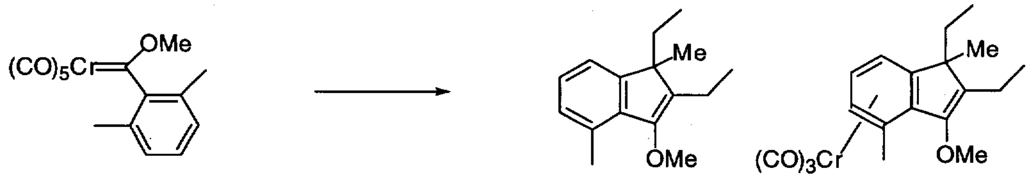
[4] Dötz, K. H.; Dietz, R.; Kappenstein, C.; Neugebauer, D.; Schubert, U. *Chem. Ber.*, **1979**, *112*, 3682.

Spectral data for (3,7-Dimethyl-2,3-diphenyl-1-methoxy-1-indenyl)tricarbonyl chromium (0) **17a**. R_f = 0.33 (1:1:10). ^{1}H NMR (CDCl$_3$) δ 1.68 (s, 3H), 2.50 (s, 3H), 3.89 (s, 3H), 4.89 (t, 1H, J = 6.3 Hz), 5.36 (d, 1H, J = 6.2 Hz), 5.64 (d, 1H, J = 6.1 Hz), 7.19-7.49 (m, 10H).

Reaction of Complex 15 with 3-Hexyne in Benzene.



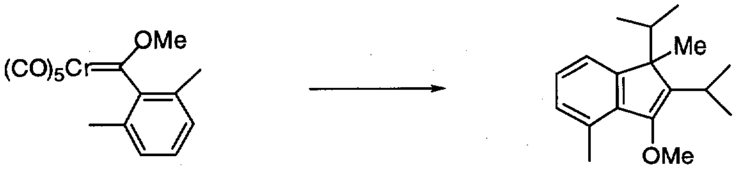
15 **16b** **17b**

A solution of 203.2 mg **15** (0.60 mmol) and 136 mL 3-hexyne (1.20 mmol) in 600 mL benzene (1.0 M) was deoxygenated by the freeze-thaw method. The reaction was heated under argon at 110 ^{o}C for 12 h 50 min, then opened to air overnight at room temperature. Chromatography with a 1:1:30 mixture of ether:methylene chloride:hexanes on silica gel gave 89.2 mg indene **16b**, 64.9 %, and 79.4 mg chromium tricarbonyl-complexed indene **17b**, 35 %.

Spectral data for 2,3-diethyl-3,7-dimethyl-1-methoxy-1-indene **16b**. R_f = 0.61 (1:1:20). ^{1}H NMR (CDCl$_3$) δ 0.36 (t, 3H, J = 7.4 Hz), 1.23 (t, 3H, J = 7.7 Hz), 1.25 (s, 3H), 1.76 (dq, 1H, J = 14 Hz, J =7.0 Hz), 1.83 (dq, 1H, J = 7.1 Hz, J = 14 Hz), 2.24 (dq, 1H, J = 7.5 Hz, J = 14.8 Hz), 2.36 (dq, 1H, J = 7.5 Hz, J =14.7 Hz), 2.54 (s, 3H), 3.78 (s, 3H), 6.95 (dd, 1H, J =6.4 Hz, J =1.6 Hz), 7.01-7.05 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 1.47, 8.83, 14.02, 17.53, 18.40, 24.8, 30.8, 60.8, 119.1, 125.1, 129.2, 129.5, 136.5, 137.9, 150.6, 155.0; IR (neat) 2964vs, 2931vs, 2873m, 1627m, 1461m, 1349m, 1282m, 1122m, 1032m, 767m cm^{-1}; mass spectrum m/z (% rel intensity) 230 M$^+$ (27), 215 (9), 202 (16), 201 (100), 186 (5), 171 (11), 128 (10); colorless oil.

Spectral data for (2,3-diethyl-3,7-dimethyl-1-methoxy-1-indene)chromium tricarbonyl complex **17b**. ^{1}H NMR (CDCl$_3$) δ 1.16 (t, 3H, J = 7.5 Hz), 1.20 (t, 3H, J = 7.6 Hz), 1.24 (s, 3H), 1.63 (dq, 1H, J = 14.2 Hz, J = 7.3 Hz), 1.84 (dq, 1H, J = 7.3 Hz, J =14.0 Hz), 2.26 (dq, 1H, J =14.9 Hz, J = 7.5 Hz), 2.32 (dq, 1H, J = 14.0 Hz, J = 7.5 Hz), 2.42 (s, 3H), 3.84 (s, 3H), 5.06 (t, 1H, J = 6.3 Hz), 5.23 (d, 1H, J = 6.3 Hz), 5.60 (d, 1H, J = 6.2 Hz); IR (neat) 2966w, 2931w, 1953vs, 1872vs cm^{-1}; lemon yellow oil.

Reaction of Complex 15 with Diisopropylacetylene in Benzene.



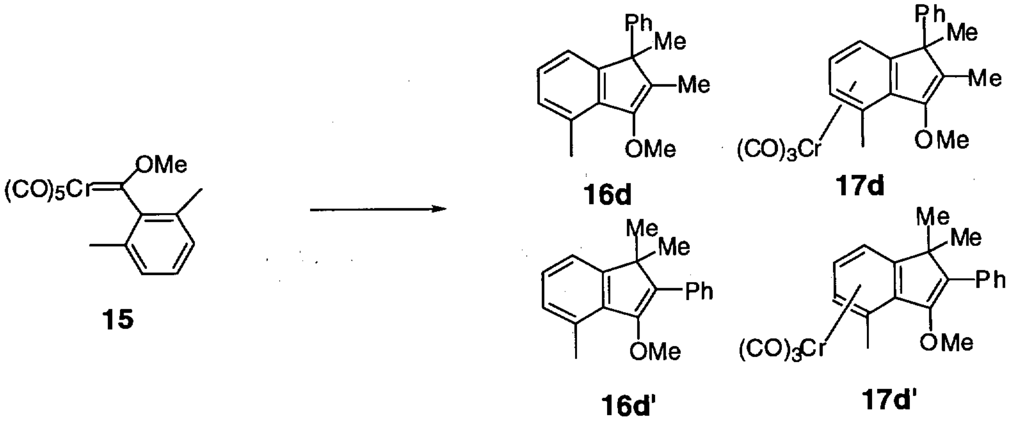
15

16c

In 1.1 mL benzene (0.5 M) were 180.6 mg complex **15** and 117.0 mg diisopropylacetylene (1.06 mmol) combined. After deoxygenation by the freeze-thaw method the reaction was heated under argon at 110 °C for 29 h and then at 130 °C for 5 h. Solvent was removed and 30 mL THF followed by 2.0 g FeCl$_3$-DMF complex (3.5 mmol) was added. After stirring for 20 min, the reaction was poured into ether and extracted with water. Chromatography in hexanes gave 108.8 mg indene **16c** as a white solid, 79 %.

Spectral data for 2,3-diisopropyl-3,7-dimethyl-1-methoxy-1-indene **16c**. R_f = 0.21 (hexanes). ^{1}H NMR (CDCl$_3$) δ 0.52 (d, 3H, J = 6.8 Hz), 1.08 (d, 3H, J = 6.9 Hz), 1.27 (s, 3H), 1.28 (d, 3H, J = obscured due to overlap), 1.36 (d, 3H, J = 7.0 Hz), 2.05 (septet, 1H, J = 6.8 Hz), 2.49 (septet, 1H, J = 7.0 Hz), 2.55 (s, 3H), 3.74 (s, 3H), 6.96 (d, 1H, J = 7.4 Hz), 7.00 (t, 1H, J = 7.4 Hz), 7.09 (d, 1H, J = 7.2 Hz); ^{13}C NMR (CDCl$_3$) δ 17.69, 17.94, 18.25, 21.27, 21.66, 23.24, 25.75, 33.25, 52.79, 60.93, 120.16, 124.15, 128.56, 129.06, 137.95, 142.81, 149.01, 154.18; IR (neat) 2962vs, 2933s, 2873m, 1627m, 1457m, 1371m, 1284s, 1033m, 768m cm^{-1}; mass spectrum m/z (% rel intensity) 258 M$^+$ (29), 215 (100), 185 (19), 141 (10), 83 (10); Calcd for C$_{18}$H$_{26}$O m/z 258.1984, found 258.1974; white solid, mp 36-7 °C.

Reaction of Complex 15 with 1-phenyl-1-propyne in benzene.



To 100.0 mg complex **15** (0.29 mmol) in 590 mL benzene (0.5 M) was added 74 mL 1-phenyl-1-propyne (0.59 mmol). After deoxygenation by the freeze-thaw method, the reaction was heated under argon to 110 °C for 28 h. Air oxidation overnight at room temperature followed by chromatography with a 1:1:40 mixture of

ether:methylene chloride:hexane gave 3 bands: indene **16d**, 51.0 mg, 66 %; indene **17d'** chromium tricarbonyl complex, 10.6 mg, 10.9 %; and indene **17d**, chromium tricarbonyl complex, 16.5 mg, 16.9 %.

The chromium tricarbonyl complex of indene **17d** was dissolved in ether and shaken with dilute CAN solution followed by brine. Drying, and solvent removal gave 8.2 mg recovered indene **16d**, clean by TLC and NMR. This amounts to a nearly quantitative oxidation, 97.3 %.

Similarly, 154.4 mg complex **15** and 115 mL phenylmethylacetylene were heated for 5.5 h at 110 ^{o}C. Crude NMR after CAN extractive treatment as above shows a 3:1 ratio of indenes **16d:16d'**. After chromatography with hexanes and a gradient to a 1:1:40 mixture of ether:methylene chloride:hexanes, however, 17.9 mg **16d'** (15 %) and 79.3 mg **16d** (66 %) were recovered (4.4 : 1 ratio).

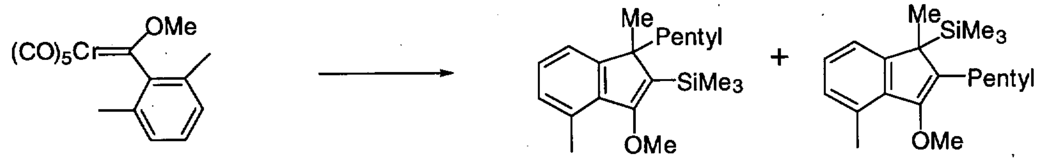
Spectral data for 1-methoxy-3-phenyl-2,3,7-trimethyl-1-indene **16d**. R_f = 0.49 (1:1:30). ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3H), 1.73 (s, 3H), 2.58 (s, 3H), 3.85 (s, 3H), 6.86 (t, 1H, J = 4.2 Hz), 6.97 (d, 2H, J = 4.2 Hz), 6.99-7.14 (m, 4H), 7.25 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.53, 25.03, 29.73, 47.73, 59.63, 98.93, 118.83, 125.73, 126.83, 127.83, 128.93, 129.13, 130.43, 131.23, 136.13, 152.13, 153.43; IR (neat) 2965s, 2932s, 1636s, 1494m, 1444m, 1344s, 1299s cm^{-1}; mass spectrum m/z (% rel intensity) 264 M$^+$ (88), 249 (100), 233 (54), 221 (13), 191 (12), 129 (11); calcd for $C_{19}H_{20}O$ *m/z* 264.1514, found *m/z* 264.1513; white solid.

Spectral data for (1-methoxy-3-phenyl-2,3,7-trimethyl-1-indene) chromium tricarbonyl complex **17d**. R_f = 0.20 (1:1:30). ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 3H), 1.90 (s, 3H), 2.42 (s, 3H), 4.05 (s, 3H), 4.86 (t, 1H, J = 6.2 Hz), 5.30 (d, 1H, J = 6.0 Hz), 5.61 (d, 1H, J = 6.5 Hz), 7.25-7.38 (m, 5H); IR (neat) 1954vs, 1872vs, 1637vw, 1445vw, 1305vw cm^{-1}; yellow oil.

Spectral data for 1-methoxy-2-phenyl-3,3,7-trimethyl-1-indene **16d'**. R$_f$ = 0.64 (1:1:30). ^{1}H NMR (CDCl$_3$) δ 1.29 (s, 6H), 2.57 (s, 3H), 3.58 (s, 3H), 7.00 (d, 1H, J = 7.2 Hz), 7.10-7.16 (m, 2H), 7.27-7.36 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 18.58, 25.04, 47.70, 59.64, 118.78, 125.73, 126.80, 127.78, 128.96, 129.14, 130.44, 131.23, 135.94, 136.11, 152.13, 153.43; IR (neat), 2961s, 2926s, 1627s, 1492m, 1460s, 1444m, 1349s, 1317s, 983m, 758s, 703s cm^{-1}; mass spectrum m/z (% rel intensity) 264 M$^+$ (98), 249 (100), 233 (61), 219 (16), 191 (26), 189 (19), 129 (20), 91 (19); Anal calc for $C_{19}H_{20}O$: C, 86.32%; H, 7.63%; Found: C, 86.59%; H, 7.65%; off-white solid, mp 47 ^{o}C.

Spectral data for (1-methoxy-2-phenyl-3,3,7-trimethyl-1-indene) chromium tricarbonyl complex **17d'**. R$_f$ = 0.27 (1:1:30). ^{1}H NMR (CDCl$_3$) δ 1.28 (s, 3H), 1.36 (s, 3H), 2.46 (s, 3H), 3.47 (s, 3H), 5.11 (t, 1H, J = 6.3 Hz), 6.23 (d, 1H, J = 6.3 Hz), 6.66 (d, 1H, J = 6.5 Hz), 7.28-7.37 (m, 5H); IR (neat) 1955vs, 1874vs, 1689vw, 1327vw cm^{-1}; yellow oil.

Reaction of Complex 15 with 1-trimethylsilyl-1-heptyne in benzene.



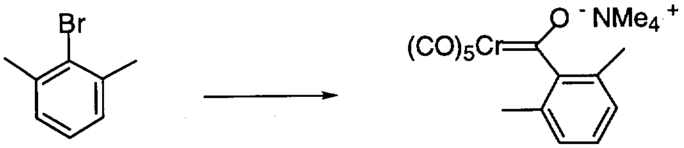
15 **16e** **16e'**

In 1 mL benzene were dissolved 170 mg complex **15** (0.5 mmol) and 168.1 mg 1-trimethylsilyl-1-heptyne (1.0 mmol). After degassing by the freeze thaw method, the reaction was heated under agron at 145 ^{O}C for 48 h. The solvent was removed and the residue treated in 20 mL THF with 1.90 g ferric chloride/DMF complex (3.5 mmol) for 30 min at room temperature. Extraction with ether and water washing, drying, and chromatography in hexanes gave 123.5 mg indene **16e** (78.1 %) and 9.3 mg of the isomeric indene **16e'** (6 %).

Spectral data for 1-methoxy-3,7-dimethyl-3-n-pentyl-2-trimethylsilyl-1-indene **16e**. ^{1}H NMR (CDCl$_3$) δ .30 (s, 9H), 0.49-0.54 (m, 1H), 0.77 (t, 3H, J = 7.1 Hz), 0.86-0.94 (m, 1H), 1.05-1.17 (m, 4H), 1.32 (s, 3H), 1.83-1.87 (m, 2H), 2.55 (s, 3H), 3.71 (s, 3H), 6.96 (d, 1H, J = 7.1 Hz), 7.04-7.10 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 0.90, 14.05, 17.99, 22.39, 23.62, 26.04, 32.23, 38.82, 52.72, 61.36, 118.51, 125.93, 128.83, 129.70, 134.53, 136.64, 155.73, 167.68; IR (neat) 2955s, 2930s, 1550s, 1281s, 1247s, 837vs, 758s cm^{-1}; mass spectrum m/z (% rel intensity) 316 M^{+} (15), 301 (99), 245 (83), 231 (59), 215 (12), 89 (19), 73 (100).

Spectral data for 1-methoxy-3,7-dimethyl-2-n-pentyl-3-trimethylsilyl-1-indene **16e'**. ^{1}H NMR (CDCl$_3$) δ -0.11 (s, 9H), 0.88-0.93 (m, 3H), 1.30-1.40 (m, 4H), 1.46 (s, 3H), 1.61-1.64 (m, 2H), 2.17-2.24 (m, 1H), 2.51-2.55 (m, 1H), 2.58 (s, 3H), 3.76 (s, 3H), 6.93 (d, 1H, J = 7.4 Hz), 7.01 (t, 1H, J = 7.5 Hz), 7.08 (d, 1H, J = 7.5 Hz); IR (neat) 2956s, 2930s, 1261m, 1248s, 1045m, 839vs cm^{-1}; mass spectrum m/z (% rel intensity) 316 M^{+} (9), 301 (100), 243 (10), 171 (10), 83 (30), 73 (98); Calcd for $C_{20}H_{32}OSi$ *m/z* 316.2269, Found *m/z* 316.2252; colorless oil.

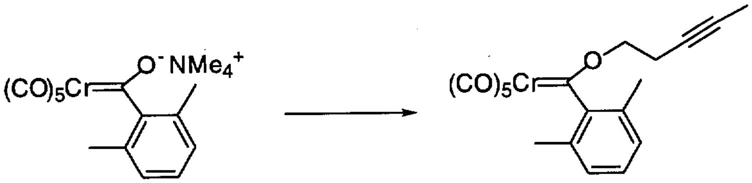
Preparation of 2,6-dimethylphenyl(oxidocarbene)pentacarbonyl chromium (0) tetramethylammonium salt 46.



A solution of 1.33 mL 2-bromo-*m*-xylene (10 mmol) in 10 mL ether was treated with 12.4 mL *t*-BuLi (1.7 M in pentane, 21 mmol) at -78 ^{o}C for 30 min, then warmed to RT for 30 min. The yellow solution was transferred via canula into a slurry of 2.42 g $Cr(CO)_6$ (11 mmol) in 20 mL ether at 0 ^{o}C, then warmed to RT for 1 h. The solvent was then removed *in vacuo* to leave a brown oil residue, which was taken up in water and filtered through Celite to remove undissolved solids. The aqueous layer was then shaken twice with hexanes (discarded), and treated with solid tetramethylammonium bromide until precipitation of the yellow salt was no longer observed. After standing for 5 min, the salt was filtered off onto a pad of Celite and washed with water and hexanes. The collection flask was changed and the solids washed through with dichloromethane. After drying ($MgSO_4$), the solvent was removed to leave **46** as a yellow crystalline solid, 3.36 g, 84 %, which was pure by NMR assay.

Spectral data for **46:**^{1}H NMR (d$_6$-acetone) δ 2.17 (s, 6H), 3.36 (s, 12H), 6.79 (s, 3H).

Preparation of Complex 18.

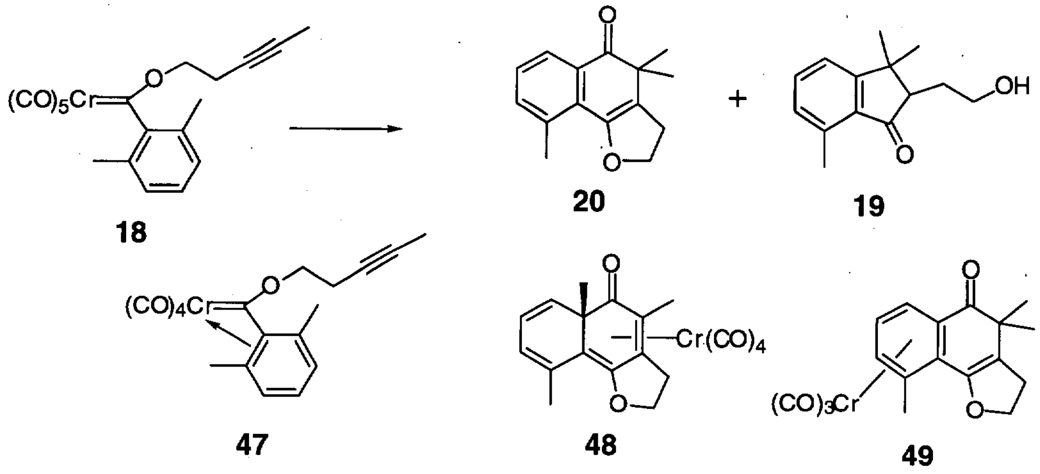


46 **18**

In 20 mL dichloromethane at 0 ^{o}C under nitrogen were combined 1.0 mL trifluoromethansulfonic anhydride (6.0 mmol) and 526 mL pyridine (6.5 mmol). After 5 min, 553 mL 3-pentyn-1-ol was added and the reaction slurry stirred for 20 min at 0 ^{o}C. To this was added 2.0 g ammonium salt **46** (5.0 mmol) and stirring continued for 30 min. The red solution was poured into ether and washed with brine and NaHCO$_3$. After drying, the organic layer was stripped and the residue taken up in hexanes. Again it was filtered through Celite and concentrated. Chromatography with a 1:1:20 mixturre of ether:methylene chloride:hexanes gave 1.467 g complex **18** as a red oil (75 %, contains a small amount of alkynol impurity by NMR) which could be crystallized from chloroform/hexanes at -78 ^{o}C to give an orange solid.

Spectral data for Complex **18**. R$_f$ = 0.41 (1:1:20). ^{1}H NMR (CDCl$_3$) δ 1.74 (t, 3H, J = 2.5 Hz), 2.15 (s, 6H), 2.72 - 2.84 (br s, 2H), 3.94 - 4.08 (br s, 2H), 7.0 - 7.13 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 3.32, 19.33, 19.87, 73.54, 77.71, 102.57, 126.42, 128.10, 128.33, 150.24, 216.27, 224.47, 362.50; IR (CHCl$_3$) 2064vs, 1991s, 1932vs, 1142m cm^{-1}; mass spectrum m/z (% rel intensity) Molecular ion not observed, 364 M^+- CO (2), 336 (M^+-2CO, 7) 308 (M^+-3CO, 2), 280 (M^+-4CO, 16), 252 (M^+-5CO, 43), 213 (11), 185 (28), 84 (100), 52 (64); Calcd for $C_{19}H_{16}CrO_6$ - CO, *m/z* 364.0403, measd *m/z* 364.0395; orange solid, mp 75-6 °C.

Thermolysis of Complex 18



A deoxygenated solution of 180.0 mg complex **18** (0.46 mmol) in 90 mL benzene (0.005 M) was heated under argon at 110 °C for 16 h. An organometallic species tentatively identified as the naphthalenone-tricarbonyl complex **49**, co-elutes with the product and persists after stirring in air overnight. Thus, the solvent was removed from the entire reaction mixture and the residue dissolved in 30 mL THF and treated with 1.75 g $FeCl_3$-DMF (3.2 mmol) for 30 min at room temperature. The solution was washed with water and brine, then dried ($MgSO_4$). Chromatography (5 % to 20 % EtOAc in hexanes) gave 39.0 mg naphthalenone **20** (0.17 mmol, 37 %) and 18.8 mg indanone **19**. The latter compound was repurified by preparative TLC in 20 % EtOAc in hexanes to give 16.6 mg **19**, (0.076 mmol, 17 %).

If the reaction was stopped before complete conversion and chromatographed under the same solvent conditions, an orange band and a purple band could be eluted off the column. The purple band was somewhat air sensitive and decomposed to the orange band before solvent could be removed. Upon dissolution in benzene and heating at 110 °C, the purple proceeded mainly to naphthalenone **20**. The orange band could be separated into two components which are tentatively proposed to be the aryl chelate **47** and cyclohexadienone tetracarbonyl complex **48** The orange band also proceeded to product upon resubmission to reaction conditions.

Spectral data for Naphthalenone **20**. R_f = 0.40 (10% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6H), 2.56 (s, 3H), 2.75 (t, 2H, J = 9.4 Hz), 4.46 (t, 2H, J = 9.4 Hz), 7.16 (t, 1H, J = 7.6 Hz), 7.29 (d, 1H, J = 6.9 Hz), 7.86 (d, 1H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 21.65, 24.82, 29.37, 44.56, 69.32, 118.49, 126.14, 127.27, 129.68, 130.13, 133.61, 137.35, 147.00, 204.14; IR (neat) 1672vs, 1589s, 1082s cm^{-1}; mass spectrum m/e (% rel intensity) 228 M$^+$ (19), 213 (100), 185 (15), 170 (5); Calcd for $C_{15}H_{16}O_2$ *m/e* 228.1150, measd *m/e* 228.1145; yellow solid.

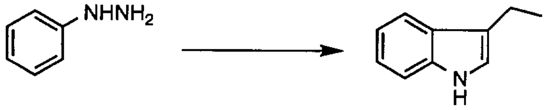
Spectral data for Indanone **19**. R_f = (). ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 3H), 1.44 (s, 3H), 1.79-1.91 (m, H), 2.50 (dd, 1H, J = 4.2 Hz, J = 9.4 Hz), 2.59 (s, 3H), 3.75 - 3.83 (m, 1H), 3.93 - 3.98 (m, 1H), 7.10 (d, 1H, J = 7.4 Hz), 7.29 (d, 1H, J = 7.6 Hz), 7.46 (t, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 18.46, 26.79, 27.90, 28.52, 41.64, 60.29, 62.71, 120.55, 129.37, 131.48, 134.50, 138.82, 163.62, 209.85; IR ($CHCl_3$) 3400 broad s, 2963m, 1702vs, 1594s cm^{-1}.

Spectral data for Naphthalenone tricarbonyl chromium complex **49**. ^{1}H NMR (CDCl$_3$) δ 1.29 (s, 3H), 1.41 (s, 3H), 2.31 (s, 3H), 2.71-2.79 (m, 2H), 4.83-4.99 (m, 2H), 5.03 (t, 1H, J = 6.3 Hz), 5.20 (d, 1H, J = 6.4 Hz), 5.61 (d, 1H, J = 6.3 Hz).

Spectral data for Cyclohexadienone tetracarbonyl chromium complex **48**. ^{1}H NMR (CDCl$_3$) δ 1.08 (s, 3H), 1.91 (s, 3H), 2.20 (s, 3H), 2.50 - 3.02 (m, 2H), 4.31 - 4.48 (m, 1H), 5.24 - 5.30 (m, 1H), 5.78 (d, 1H, J = 6 Hz), 5.98 (dd, 1H, J = 9.4 Hz, 5.78 Hz), 6.57 (d, 1H, J = 9.4 Hz).

Spectral data for Aryl Chelate complex **47**. 1^{1}H NMR (CDCl$_3$) δ 0.70 (s, 3H), 1.75 (t, 3H, J = 2.0 Hz), 2.17 (s, 3H), 2.7 - 2.85 (m, 2H), 3.84 (d, 1H, J = 7.4 Hz), 4.42-4.58 (m, 1H), 5.02 - 5.07 (m, 1H), 5.19 - 5.24 (obscured t, 1H), 5.93 (d, 1H, J = 5.3 Hz).

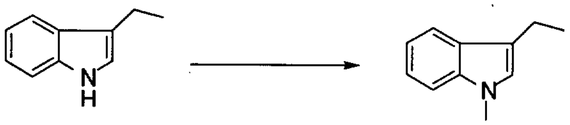
Preparation of 3–Ethyl–Indole 50.



A solution of phenylhydrazine (65 mL, 661 mmol) in xylenes (~150 mL) was slowly added over the course of an hour to a slurry of zinc chloride (100 g, 734 mmol) and butyraldehyde (60 mL, 666 mmol) in xylenes (~300 mL). The reaction was then heated to reflux with a Dean-Stark trap for 4 hours. The majority of the xylenes was then distilled off and the residue extracted from ether and water. The organic layer was dried over anhy $MgSO_4$, concentrated and distilled to yield 38.4 g (40 %) of the 3-ethyl-indole[5] as a light yellow oil.

Spectral data for 3–Ethyl–Indole **50**: [1484-19-1], light yellow oil, bp = 95-110 °C/1 mm Hg, $R_f = 0.41$ (80:20 hexane:EtOAc); ^1H NMR ($CDCl_3$) δ 1.3 (t, 3 H, *J* = 6.1 Hz), 2.77 (q, 2 H, *J* = 6.0 Hz), 6.82 (s, 1 H), 7.1 (t, 1 H, *J* = 7.6 Hz), 7.15 (t, 1 H, *J* = 7.4 Hz), 7.25 (d, 1 H, *J* = 7.9 Hz), 7.55 (d, 1 H, *J* = 8.2 Hz) 7.75 (br s, 1 H).

Preparation of 3–Ethyl–1–Methyl–Indole 51.



3-Ethyl indole **50** (37.612 g, 259 mmol) was dissolved in ~100 mL of THF and slowly added to a slurry of NaH (13 g of a 60 % dispersion in oil, 325 mmol) in ~400 mL THF. When the evolution of H_2 subsided (~1 hour), the flask was fitted with a reflux condenser and methyl iodide (21 mL, 338 mmol) was added. The reaction was stirred for 2 hours, carefully quenched with satd. $NaHCO_3$ solution, and concentrated. The residue was extracted from water and ether. The ether layer was dried over anhy $MgSO_4$ and concentrated to yield a yellow oil. The product was purified *via* vacuum distillation (76-96 °C / 0.2 mm Hg) to yield a water white oil[6] (34.86 g, 85 %).

Spectral data for 3–Ethyl–1–Methyl–Indole **51**: [45999-11-9], light yellow oil, bp = 71-75 °C/0.7 mm Hg, $R_f = 0.36$ (95:5 hexane:EtOAc); ^1H NMR ($CDCl_3$) δ 1.3 (t, 3 H, *J*

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[5] Cornforth, R. H.; Robinson, Sir R., *J. Chem. Soc.*, **1942**, 680.

= 6.2 Hz), 2.72 (q, 2 H, J = 6.0 Hz), 3.65 (s, 3 H), 6.7 (s, 1 H), 7.04 (t, 1 H, J = 7.3 Hz), 7.16 (t, 1 H, J = 7.1 Hz), 7.2 (d, 1 H, J = 8.0 Hz), 7.55 (d, 1 H, J = 8.2 Hz).

Preparation of Carbene complex 37

A solution of *t*-butyllithium (1.7M in pentane, 44 mL, 75mM) was added dropwise over a period of twenty minutes to a stirred solution of 3-ethyl-1-methyl-indole **51** (11.742 g, 74 mM) in 150 mL THF cooled with dry-ice/acetone. The resulting clear orange solution was stirred cold for 40 minutes and allowed to warm to room temperature over a one hour period. The anion solution was re-cooled to -78 ° and $Cr(CO)_6$ (16.22 g, 74 mM) was added as a solid in a single portion. The reaction was stirred on the dry-ice bath for 4-5 hours and allowed to warm to room temp solwly as the CO_2 sublimed. The stirring was continued for a total of 18 hours. The resulting black lithium acylate solution was re-cooled with ice water and freshly distilled methyl triflate (8.4 mL, 74 mM) was added. The resulting deep red solution was stirred for 30 minutes on the ice bath followed by 60 minutes at room temperature. The reaction was then concentrated, redissolved in ether, and filtered through a pad of Celite. Removal of the ether yielded a red oily solid that was recrystallized from pentane (15.1 g, 52 %).

Spectral data for **37:** Dark purple-black crystals, mp = 86-92 °C, R_f = 0.42 (90:10 hexane:EtOAc); ^1H NMR ($CDCl_3$) δ 1.26 (t, 3 H, 7.5 Hz), 2.71 (q, 2 H, 7.5 Hz), 3.58 (s, 3 H), 4.22 (s, 3 H), 7.1-7.3 (m, 3 H), 7.63 (d, 1 H, 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ

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[6] Snyder, H. R.; Eliel, E. L.; Carnahan, R. E., *J. Am. Chem.Soc.*, **1951**, *73*, 970.

15.5, 18.3, 31.5, 66.1, 109.6, 112.3, 120.0, 120.5, 123.4, 127.0, 137.8, 144.3, 215.7, 224.8, 349.3; IR (NaCl, neat) 2063 s, 1937* s, 1460 w, 1232 w, 1131 w, 741 w, 646 m cm^{-1}; mass spectrum m/z (relative intensity) 393 (M$^+$, 2), 365 (6), 337 (7), 309 (3), 281 (11), 253 (45), 223 (34), 201 (5), 195 (6), 186 (11), 182 (6), 170 (11), 158 (11), 143 (6), 128 (3), 115 (6), 80 (6), 52 (100), 42 (5); elemental analysis calculated for $C_{18}H_{15}NO_6Cr$: C = 55.0 %, H = 3.84 %, N = 3.56 %, found C = 55.23 %, H = 4.15 %, N = 3.52 % Cr = 14.17, 13.16, 13.23 %.

Carbamic acid (4-pentynyl) phenylmethyl ester, 39

Oxalyl chloride (20 mL, 229 mmol) was added dropwise over a period of 30 minutes to a solution of 5-hexyn-1-oic acid (23.885 g, 213 mmol) and DMF (~8 drops) in 80 mL of benzene. The reaction was stirred for 1 hour at room temperature, concentrated to remove HCl, and re-dissolved in 80 mL of benzene. Azidotrimethylsilyl chloride (30 mL, 226 mmol) was added to this solution over a 45 minute period and the reaction was stirred at room temperature for 18 hours followed by 1 hour at reflux. The reaction was then concentrated to ~ 1/2 its origional volume and benzyl alcohol (24 mL, 231 mmol) was added and the reaction refluxed for 2 hours. The reaction was then concentrated and fractionally vacuum distilled to remove residual benzyl alcohol followed by the product as a light yellow oil (37.36 g, 81 %, 130-145°C / ~1mm Hg).

Spectral data for **39**: Off white crystals, mp = 25-27 °C, bp = 130-145°C / ~1mm Hg, R_f = 0.15 (90:10 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.70 (pentet, 2 H, 6.7 Hz), 1.97 (s, 1 H), 2.21 (br t, 2 H, 5.7 Hz), 3.27 (q, 2 H, 6.4 hz), 5.07 (s, 2 H), 5.13 (br s, 1 H), 7.32

(s, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.7, 28.3, 39.9, 66.5, 69.0, 83.2, 127.9, 128.1, 128.3, 136.4, 156.3; IR (NaCl, neat) 3598 br m, 2941 br w, 1700* s, 1533 m, 1256 s, 1137 w, 1006 br w, 737 w, 697 m, 630 br m cm^{-1}; mass spectrum m/z (relative intensity) 217 (M^+, 12), 172 (7), 108 (83), 91 (100), 79 (17), 65 (20); elemental analysis calculated for $C_{13}H_{15}NO_2$: C = 71.9%, H = 6.96%, N = 6.45%, found C = 71.21 %, H = 7.13 %, N = 6.65 %.

The Reaction of Complex 37 with Alkyne 39.

The carbene complex **37** (1.095 g, 2.78 mmol) and alkyne **39** (920 mg, 4.23 mmol) were dissolved in 56 mL of Argon sparged xylenes and heated under N_2 at 55 °C for 90 minutes followed by heating at 140 °C for 1 hour. The reaction is concentrated and the residue is chromatographed (70:30 hexane:EtOAc) to yield the carbazolone **41** as colorless crystals (756 mg, 61 %). If the reaction is stopped after heating for only 90 minutes at 55 °C, the carbazolone **40** can be isolated.

Spectral data for **40**: deep red oil, R_f = 0.47 (50:50 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.69 (t, 3 H, 7.2 Hz), 1.6-1.75 (m, 2 H), 1.75-1.85 (m, 2 H), 2.2-2.4 (d of m, 2 H), 3.1-3.2 (m, 2 H), 3.50 (s, 3 H), 3.62 (s, 3 H), 5.06 (s, 2 H), 5.14 (br s, 1 H), 6.67 (d, 1 H, 7.8 Hz), 6.8-6.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.5, 25.6, 29.8, 31.2, 40.1, 41.1, 61.0, 63.6, 66.4, 106.7, 120.0, 122.1, 125.2, 127.0, 127.8, 127.9, 128.0, 128.4, 129.8, 136.7, 141.1, 146.8, 150.5, 156.4, 200.9; IR (NaCl, neat) 3350 br w, 2931 br w, 1717 s, 1663 w, 1627 m, 1608 m, 1534 s, 1456 m, 1352 m, 1244 s, 1123 m, 1099 m, 1012 br w, 754 m, 698 w cm^{-1}; mass spectrum m/z (relative intensity) 446 (23), 338 (51), 323 25), 310

(10), 281 (65), 266 (9), 254 (100), 240 (25), 226 (9), 210 (10), 196 (11), 182 (10), 167 (10), 158 (19), 108 (43), 91 (98), 79 (45), 65 (11), 51 (18).

Spectral data for **41:** colorless crystals, mp = 150-153 °C, R_f = 0.35 (50:50 hexane:EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.67 (t, 3H, 7.4 Hz), 1.1-1.3 (m, 2H), 1.3-1.6 (m, 2 H), 2.0-2.2 (m, 2 H), 3.06 (q, 2 H, 6.5 Hz), 3.84 (s, 3 H), 4.06 (s, 3 H), 4.75 (br s, 1 H), 5.04 (s, 2 H), 5.10 (s, 1 H), 7.2-7.4 (m, 8 H), 8.31 (d, 1 H, 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 8.8, 25.1, 32.4, 34.5, 37.9, 41.0, 54.9, 55.0, 66.2, 109.5, 111.8, 113.2, 121.6, 123.1, 123.7, 123.8, 127.8, 128.3, 136.5, 138.7, 142.3, 147.8, 156.2, 197.5; IR (NaCl, neat) 3319 br m, 3055 br w, 2961 m, 2933 m, 2874 w, 1718 s, 1623 s, 1607 s, 1529 br m, 1472* s, 1419 m, 1399 m, 1308 m, 1250 s, 1172 w, 1128 m, 1076 w, 1101 m, 880 m, 752 s, 725 s, 698 m cm^{-1}; mass spectrum m/z (relative intensity) 446 (M^+, 25), 38 (44), 323 (23), 310 (8), 281 (60), 266 (9), 256 (100), 254 (95), 240 (21), 226 (9), 211 (11), 196 (11), 182 (10), 167 (11), 158 (20), 146 (6), 128 (5), 114 (5), 108 (41), 102 (4), 91 (81), 79 (51), 77 (32), 65 (11), 56 (16), 51 (18), 41 (9); elemental analysis calculated for $C_{27}H_{30}N_2O_4$: C = 72.62 %, H = 6.77 %, N = 6.27 %, found C = 72.60 %, H = 6.92 %, N = 6.18 %.

Reduction of 41 with Ammonium Formate.

A 100 mL 3-neck round bottom flask with a reflux condenser was charged with carbazolone **41** (2.382 g, 5.3 mmol) and 10 % palladium on carbon (570 mg, 10 mol %). An argon atmosphere was established and 15 mL of methanol was added. A solution of ammonium formate (1.68 g, 26.6 mmol) in 5 mL of methanol was added to the reaction and it was heated at reflux for 18 hours. The reaction was then cooled, filtered through Celite, and poured into ethyl acetate and water. The organic layer was washed 2 times with water and once with brine. The organic layer was then dried over anhy. $MgSO_4$. The imine crystalized upon solvent removal (1.447 g, 92 %). The structure of the imine was confirmed by a series of ^1H NMR homonuclear decoupling experiments and by an X-ray crystal structure of its reduction product (to be reported separately).

Spectral data for **42**: yellow crystals, mp = 127-131 °C, R_f = 0.56 (80:20 hexane:EtOAc, TEA treated silica); ^1H NMR ($CDCl_3$) δ 0.80 (t, 3 H, 7.3 Hz), 1.18 (t of d, 1 H, 13.4 & 2.3 Hz), 1.3-1.4 (m, 2 H), 1.5-1.8 (m, 4 H), 1.85 (br d, 1 H, 12.9 Hz), 2.25 (d, 1 H, 14.9 Hz), 2.86 (t of d, 1 H, 13.1 &3.6 Hz), 3.25 (d of d), 1 H, 13.2 &4.2 Hz), 3.50 (s, 3 H), 3.63 (s, 3 H), 3.83 (s, 1 H), 4.29 (d, 1H, 4.9 Hz), 6.95 (t, 1 H, 7.6 Hz), 7.10 (t, 1 H, 7.3 Hz), 7.19 (d, 1 H, 7.5 Hz), 7.96 (d, 1 H, 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 7.1, 17.4, 21.7, 29.2, 33.1, 34.4, 34.6, 46.9, 56.4, 64.1, 70.8, 108.5, 111.6, 118.3, 121.0, 121.5, 125.6, 133.1, 137.4; IR (NaCl, neat) 2924 br s, 2847 m, 2811 w, 1462 br s, 1416 w, 1376 s, 1327 w, 1228 w, 1229 m, 1190 w, 1146 w, 1107 m, 1078 s, 1010 w, 743* s cm^{-1}.