Supporting Information (SI) for

Simultaneous Synthesis of both Rings of Chromenes via a Benzannulation/*o*-Quinone Methide Formation/Electrocyclization Cascade

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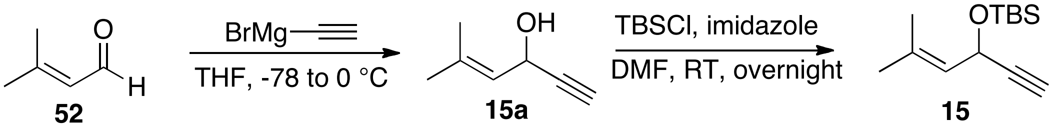
General Information

All reactions were carried out in flame-dried glassware under an atmosphere of argon unless otherwise indicated. All solvents were strictly dried prior to use: dichloromethane and acetonitrile were distilled over calcium hydride under nitrogen; tetrahydrofuran and ether were distilled from sodium and benzophenone; benzene and toluene were distilled from sodium under nitrogen. Hexanes and ethyl acetate were ACS grade and used as purchased. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded in KBr matrix (for solids) and on NaCl disc (for liquids) on a Nicolet IR/42 spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a Varian Inova 300 MHz or Varian Unity Plus 500 MHz or Varian Inova 600 MHz spectrometer using $CDCl_3$ as solvent. Low-resolution Mass Spectrometry and High Resolution Mass Spectrometry were performed at Michigan State University Mass Facility. Analytical thin-layer chromatography (TLC) was performed on Silicycle silica gel plates with F-254 indicator. Visualization was by short wave (254 nm) and long wave (365 nm) ultraviolet light, or by staining with phosphomolybdic acid in ethanol. Column chromatography was performed with silica gel 60 (230 – 450 mesh). All reagents were purified by simple distillation or crystallization with simple solvents unless otherwise indicated.

Preparation of the Enynes :

Preparation of Enyne (15):

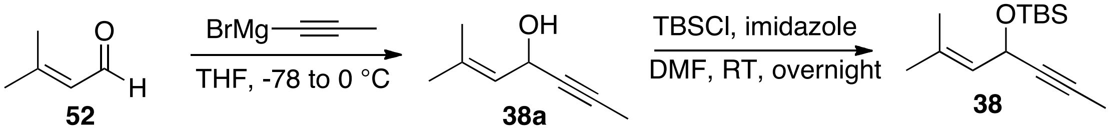


To a solution of 3-methylbut-2-enal **52** (10.00 mL, 10.46 g, 124.3 mmol) in 250 mL of THF at –78 °C was added ethynylmagnesium bromide (0.5 M in THF, 250.0 mL, 150.2 mmol). The reaction mixture was stirred for 3 hours at –78 °C and warmed to room temperature. After completion (as judged by TLC) the reaction mixture was then poured into 100 mL of saturated ammonium chloride solution. The aqueous layer was separated and extracted with ethyl acetate (100 mL x 3). The organic layers were combined and dried over magnesium sulfate. The solution was filtered through fluted filter paper and the solvent was removed under reduced pressure. The resulting alcohol **15a** (12.80 g, 116.2 mmol) was used in the next step without further purification.

A 500 mL single neck round bottom flask was charged with all of the compound **15a** (12.80 g, 116.2 mmol), imidazole (11.76 g, 172.9 mmol), TBSCl (17.89 g, 118.7 mmol) and dry DMF (390 mL). The mixture was stirred at room temperature for overnight. The solution was extracted with ether (250 mL x 2), saturated ammonium chloride solution (250 mL), and water (300 mL). Each aqueous layer was then back extracted with ether (150 mL x 3). The organic layers were combined and dried over magnesium sulfate. The crude product was purified by chromatography on silica gel with 5% ethyl acetate / hexane to give 19.84 g (87% yield, 94.90 mmol) of compound **15** as light yellow oil.

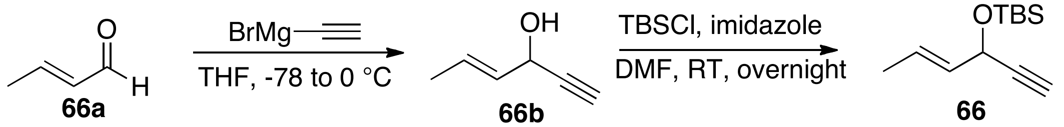
R_f = 0.82 (30% ethyl acetate / hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.09 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 1.66 (d, 3H, *J* = 1.3 Hz), 1.71 (d, 3H, *J* = 1.3 Hz), 2.40 (d, 1H, *J* = 2.5 Hz), 5.03 (dd, 1H, *J* = 8.5, 2.5 Hz), 5.29-5.33 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -4.67, -4.53, 18.08, 18.22, 25.54, 25.77, 59.84, 71.62, 85.12, 125.73, 134.29; IR (neat film) 3314, 2959, 2932, 2859, 1474, 1252, 1069, 837 cm^{-1}; mass spectrum *m/z* (% rel intensity) 225 $[M+1]^+$ (0.03), 224 M^+ (0.1), 209 (2), 167 (47), 91 (23), 83 (17), 75 (100), 61 (15); Anal calcd for $C_{13}H_{24}OSi$: C, 69.58; H, 10.78. Found; C, 69.38; H, 10.92.

Preparation of Enyne (38):



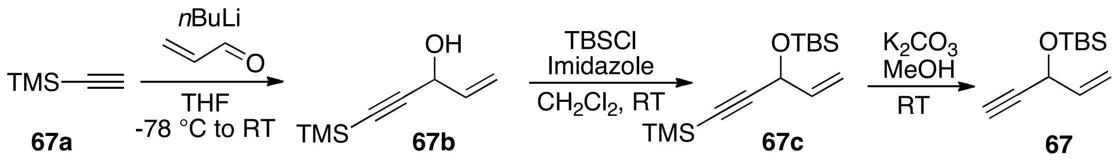
The compound **38** was prepared following the procedure described above for compound **15**. Compound **52** (2.00 mL, 1.74 g, 20.7 mmol) was reacted with propynyl magnesium bromide (0.5 M in THF, 50.0 mL, 25.0 mmol) in dry THF (50 mL). The entire crude product **38a** was used in the next step and reacted with tert-butyldimethylsilyl chloride (3.97 g, 26.4 mmol) and imidazole (2.60 g, 38.4 mmol) in dimethylformamide (115 mL). The final product **38** was obtained as a colorless oil in 98% yield (4.85 g, 20.4 mmol). R_f = 0.62 (5% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.87 (s, 9H), 1.63 (d, 3H, *J* = 1.5 Hz), 1.68 (d, 3H, *J* = 1.5 Hz), 1.79 (d, 3H, *J* = 2 Hz), 4.99 (dd, 1H, *J* = 8.5, 2.0 Hz), 5.28 (dt, 1H, *J* = 8.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -4.62, -4.47, 3.64, 17.99, 18.27, 25.52, 25.84, 60.21, 79.80, 80.52, 126.63, 133.12; IR (neat film) 2957, 2932, 2858, 1674, 1472, 1245 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{14}H_{26}OSi$ *m/z* 238.1753, meas 238.1761.

Preparation of Enyne (66):



The compound **66** was prepared following the procedure described above for compound **15**. Freshly distilled crotonaldehyde **66a** (1.00 mL, 0.850 g, 12.1 mmol) was reacted with ethynyl magnesium bromide (0.5 M in THF, 30.2 mL, 15.1 mmol) in dry THF (30 mL). The entire crude product **66b** was used in the next step and reacted with tert-butyldimethylsilyl chloride (2.18 g, 14.5 mmol) and imidazole (1.32 g, 19.3 mmol) in dimethylformamide (30 mL). The final product **66** was obtained as colorless oil in 74% yield (1.89 g, 9.00 mmol). R_f = 0.67 (5% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.11 (s, 3 H), 0.12 (s, 3H), 0.89 (s, 9H), 1.68-1.71 (m, 3H), 2.45 (d, 1H, *J* = 1.5 Hz), 4.80-4.83 (m, 1H), 5.50-5.56 (m, 1H), 5.76-5.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –4.83, –4.61, 17.39, 18.31, 25.78, 63.29, 72.96, 84.10, 127.02, 130.62; IR (neat film) 3312, 2958, 2930, 2833, 1652 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{12}H_{23}OSi$ (M^++H) *m/z* 211.1518, meas 211.1512.

Preparation of Enyne (67):

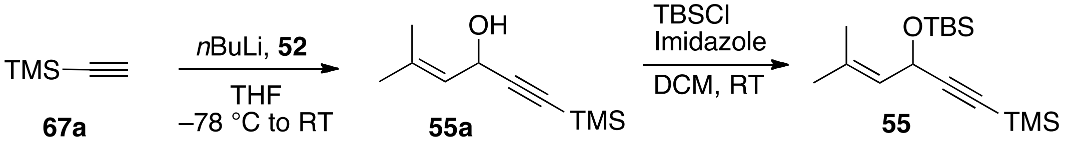


The compound **67b** was prepared following known literature method and spectroscopic properties were identical to those previously reported.[1a] To a solution of (trimethylsilyl) acetylene **67a** (2.00 g, 2.90 mL, 20.4 mmol) in dry THF (130 mL) at –78 °C was added dropwise a solution of n-butyllithium (2.5 M in hexanes, 8.16 mL, 20.4 mmol) under Ar atmosphere. After 15 minutes, freshly distilled ice-cold acrolein (1.40 g, 1.67 mL, 24.5 mmol) was introduced slowly. The resulting mixture was allowed to warm gradually to 0 °C over a period of 1.5 h. After stirring for an additional 1 h at room temperature, the mixture was quenched with ice-cold satd. NH_4Cl. The aqueous phase was extracted with Et_2O, dried with $MgSO_4$ and concentrated to dryness in *vacuo*. The crude compound **67b** was pure enough (from ^{1}HNMR) to be used in the next step without further purification.

All the crude compound **67b** was used in the next step along with tert-butyldimethylsilyl chloride (3.70 g, 24.7 mmol) and imidazole (2.20 g, 32.4 mmol) in dichloromethane (115 mL). The mixture was stirred for 16 h at room temperature. The crude product was concentrated in *vacuo* and directly chromatographed on silica gel (eluted with 100 : 1 hexane–ethyl acetate) to afford 4.85 g (18.1 mmol) of **67c** as colorless oil, giving 89% yield over two steps. The spectroscopic properties were identical to those reported in literature.[1b]

The deprotection of trimethylsilyl group from compound **67c** to the target enyne **67** was followed from known literature procedure.[1c] To a solution of **67c** (2.31 g, 8.62 mmol) in MeOH (20 mL), K_2CO_3 (2.38 g, 17.2 mmol) was added and the mixture was stirred for 4 h at room temperature. The reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The concentrated mixture was directly loaded onto a silica gel column, which was eluted with 1% Ethyl acetate/Hexane to give pure compound **67** (1.50 g, 7.65 mmol, 89% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.12 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 2.47 (d, 1H, J = 2.5 Hz), 4.86-4.88 (m, 1H), 5.15 (dt, 1H, J = 10, 1.5 Hz), 5.40 (dt, 1H, J = 17, 1.5 Hz), 5.89 (ddd, 1H, J = 17, 10, 4.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –4.94, –4.67, 18.30, 25.74, 63.44, 73.33, 83.42, 115.14, 137.40. The spectroscopic data match with the previously reported in the literature [1b].

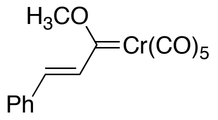
Preparation of Enyne (55):



The compound **55** was prepared following the same procedure previously described for compound **67c**. To a solution of (trimethylsilyl) acetylene **67a** (1.00 g, 1.45 mL, 10.2 mmol) in dry THF (65 mL) at –78 °C was added dropwise a solution of n-butyllithium (2.5 M in hexanes, 4.08 mL, 10.2 mmol) under Ar atmosphere. After 15 minutes, ice-cold 3-methylbut-2-enal (1.03 g, 1.18 mL, 12.24 mmol) was introduced slowly. The resulting mixture was allowed to warm gradually to 0 °C over a period of 1.5 h. After stirring for an additional 1 h at room temperature, the mixture was quenched with ice-cold satd. NH_4Cl. The aqueous phase was extracted with Et_2O, dried with $MgSO_4$ and concentrated to dryness in *vacuo*. The crude compound **55a** was pure enough (from ^{1}HNMR) to be used in the next step without further purification.

All the crude compound **55a** was used in the next step along with tert-butyldimethylsilyl chloride (3.40 g, 22.5 mmol) and imidazole (2.50 g, 36.0 mmol) in dichloromethane (57 mL). The mixture was stirred for 16 h at room temperature. The crude product was concentrated in *vacuo* and directly chromatographed on silica gel (eluted with 100 : 1 hexane–ethyl acetate) to afford 2.95 g (9.96 mmol) of **55** as colorless oil, giving 97% yield over two steps. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.10 (s, 3H), 0.11 (s, 3H), 0.13 (s, 9H), 0.88 (s, 9H), 1.65 (d, 3H, J = 1.5 Hz), 1.70 (d, 3H, J = 1.5 Hz), 5.01 (d, 1H, J = 8 Hz), 5.29 (dt, 1H, J = 8, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -4.51, -4.35, -0.16, 18.10, 18.30, 25.64, 25.84, 60.42, 88.19, 107.10, 125.73, 134.51; IR (neat film) 2959, 2930, 2898, 2858, 2172, 1673, 1472, 1250, 1063 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{16}H_{33}OSi_2$ (M$^+$+H) *m/z* 297.2070, meas 297.2062.

Preparation of the Carbene Complexes 14, 20, 37, 53, 68 –71: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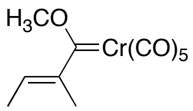
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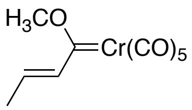
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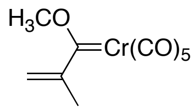
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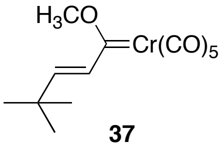
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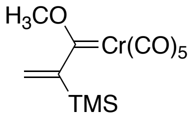
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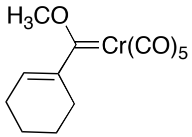
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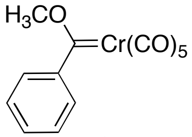
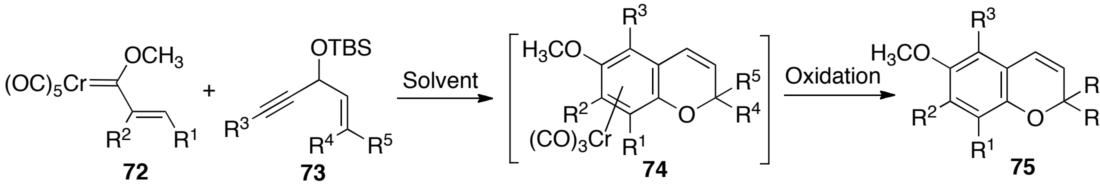
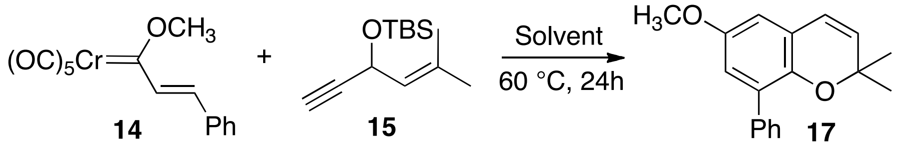

53

Carbene complexes 14[2], 20[3], 68[4], 69[5], 37[6], 70[7], 71[8] and 53[9] were prepared according to the literature methods.

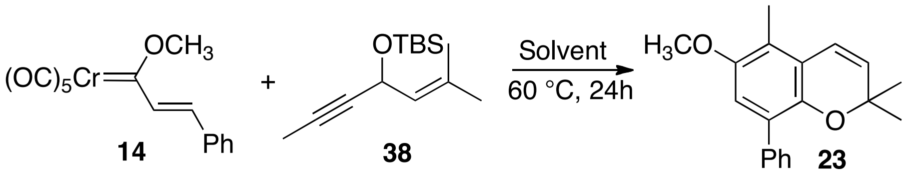
General Procedure for the Synthesis of Chromenes 17, 22-36, 46, 54:



The carbene complex **72** (0.26 mmol), enyne **73** (0.32 mmol), and solvent (8.00 mL) were added to a 25 mL Schlenk flask. The reaction mixture was deoxygenated by the freeze-pump-thaw method (3 cycles) and finally the flask was back-filled with argon. The reaction mixture was stirred and heated at 60 ºC for 24 hours. The solvent was removed under reduced pressure and the crude compound was dissolved in 8 mL of diethyl ether. To this mixture, water (8 mL) and 7.5 equiv. of $FeCl_3$.DMF complex were added and stirred under air. Upon completion of the oxidation of compound **74** (judged by TLC), the organic layer was separated. The aqueous layer was washed with ether (3 x 15 mL). Organic layers were combined, washed with brine and dried over magnesium sulfate. Column chromatography with 1% ethyl acetate / hexane gave pure compound **75**.

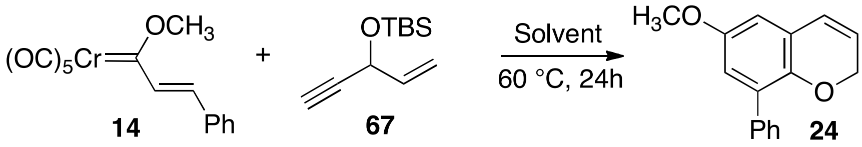


Compound 17: The carbene complex **14** (0.30 g, 0.88 mmol) was reacted with enyne **15** (0.221 g, 1.06 mmol) in 27 mL of dichloromethane. The reaction gave 0.18 g (76% yield, 0.67 mmol) of compound **17** as light yellow oil. This reaction was conducted in five other solvents, which were acetonitrile, hexane, benzene, THF and toluene and gave 95%, 70%, 74%, 65% and 62% yields respectively. These yields in the first four solvents were the average of two runs. The reaction in toluene was done at 80 °C for 24 h. The reaction was also done in toluene in presence of 5 equiv. of Hunig's base at 80 °C for 24 h and the yield was 35%. The reaction didn't need an oxidative workup when acetonitrile was the solvent. $R_f = 0.25$ (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.41 (s, 6H), 3.79 (s, 3H), 5.66 (d, 1H, $J = 9.5$ Hz), 6.33 (d, 1H, $J = 9.5$ Hz), 6.57 (d, 1H, $J = 3$ Hz), 6.77 (d, 1H, $J = 3$ Hz), 7.31 (t, 1H, $J = 7$ Hz), 7.40 (t, 2H, $J = 7.5$ Hz), 7.57 (dd, 2H, $J = 8$ Hz, $J = 1$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.49, 55.74, 75.88, 111.06, 115.45, 122.59, 122.73, 126.80, 127.84, 129.37, 130.17, 131.86, 138.08, 143.68, 153.41; IR (neat film) 3100, 3050, 2975, 2936, 2890, 1750, 1597, 1489, 1437, 1424, 1321, 1199 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{18}H_{18}O_2$ *m/z* 266.1307, meas 266.1304.

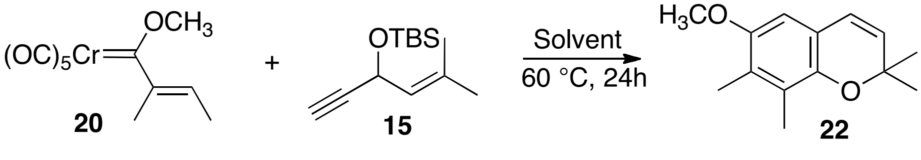


Compound 23: The carbene complex **14** (0.30 g, 0.88 mmol) was reacted with enyne **38** (0.251 g, 1.06 mmol) in 27 mL of dichloromethane. The reaction gave 0.171 g

(69% yield, 0.611 mmol) of compound **23** as a light yellow oil. The reaction was also conducted in acetonitrile and gave 66% yield. R_f = 0.27 (1% Ethyl acetate / Hexane); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.42 (s, 6H), 2.25 (s, 3H), 3.82 (s, 3H), 5.74 (d, 1H, *J* = 8.5 Hz), 6.62 (d, 1H, *J* = 8.5 Hz), 6.76 (s, 1H), 7.32 (t, 1H, *J* = 6 Hz), 7.42 (t, 2H, *J* = 6 Hz), 7.59 (dd, 2H, *J* = 7, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 10.76, 27.23, 56.15, 74.70, 112.47, 119.93, 121.42, 121.87, 126.50, 126.98, 127.81, 129.38, 131.81, 138.63, 143.60, 151.57; IR (neat film) 3054, 2973, 2931, 2855, 1463, 1388, 1212, 1100 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{19}H_{21}O_2$ (M^++H) *m/z* 281.1542, meas 281.1545.

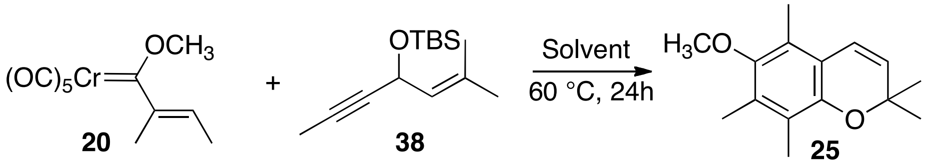


Compound 24: The carbene complex **14** (0.30 g, 0.88 mmol) was reacted with enyne **67** (0.207 g, 1.06 mmol) in 27 mL of acetonitrile. The reaction gave 0.10 g (47% yield, 0.42 mmol) of compound **24** as light yellow oil. R_f = 0.11 (1% Ethyl acetate / Hexane); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 3.80 (s, 3H), 4.73-4.74 (m, 2H), 5.86-5.89 (m, 1H), 6.47 (dd, 1H, *J* = 10, 1.5 Hz), 6.59 (d, 1H, *J* = 2.5 Hz), 6.78 (d, 1H, *J* = 2.5 Hz), 7.35 (t, 1H, *J* = 7 Hz), 7.44 (t, 2H, *J* = 7.5 Hz), 7.57 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 55.64, 65.23, 111.25, 115.28, 123.17, 123.83, 125.02, 127.09, 127.98, 129.26, 129.96, 137.73, 144.72, 153.70; IR (neat film) 3062, 2965, 2952, 2836, 1598, 1471, 1435, 1429, 1319, 1199 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{16}H_{13}O_2$ (M^+–H) *m/z* 237.0916, meas 237.0910.

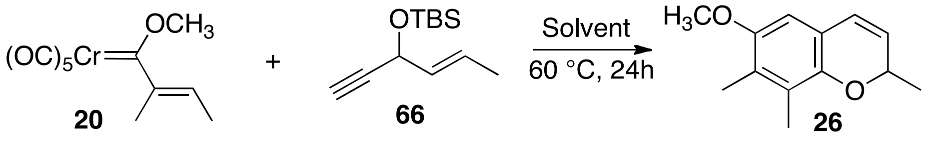


Compound 22: The carbene complex **20** (0.300 g, 1.03 mmol) was reacted with enyne **15** (0.278 g, 1.24 mmol) in 27 mL of dichloromethane. The reaction gave 0.199 g

(88% yield, 0.913 mmol) of compound **22** as a light yellow oil. This reaction was conducted in three other solvents including acetonitrile, benzene and THF and gave 65%, 73% and 74% yields, respectively. The yield in acetonitrile was an average of three runs. $R_f = 0.27$ (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 (s, 6H), 2.12 (s, 6H), 3.75 (s, 3H), 5.55 (d, 1H, J = 10 Hz), 6.25 (d, 1H, J = 10 Hz), 6.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.58, 12.03, 27.57, 56.00, 75.37, 105.99, 118.31, 122.83, 125.51, 126.16, 130.15, 144.62, 151.40; IR (neat film) 3040, 2973, 2932, 2859, 1637, 1577, 1462, 1422, 1261 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{14}H_{19}O_2$ (M^++H) *m/z* 219.1385, meas 219.1382.

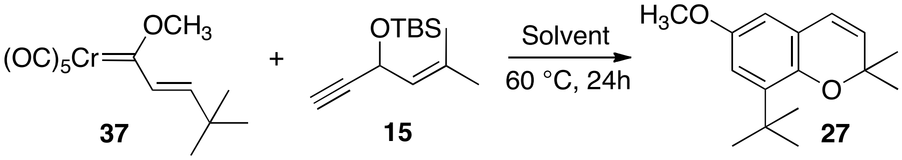


Compound 25: The carbene complex **20** (0.300 g, 1.03 mmol) was reacted with enyne **38** (0.285 g, 1.24 mmol) in 27 mL of dichloromethane. The reaction gave 0.201 g (84% yield, 0.866 mmol) of compound **25** as a light yellow oil. Repeat of this reaction in the same solvent gave 84% yield again. This reaction was also conducted in acetonitrile and gave 87% yield. $R_f = 0.25$ (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 6H), 2.07 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 3.60 (s, 3H), 5.59 (d, 1H, J = 10 Hz), 6.46 (d, 1H, J = 10 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.13, 11.53, 12.76, 27.57, 60.29, 74.65, 117.98, 119.93, 122.77, 123.11, 129.98, 146.79, 150.26 (1 sp^2 C not located); IR (neat film) 3050, 2977, 2936, 2898, 1640, 1597, 1462, 1406, 1387, 1289, 1217, 1090 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{15}H_{20}O_2$ *m/z* 232.1463, meas 232.1461.



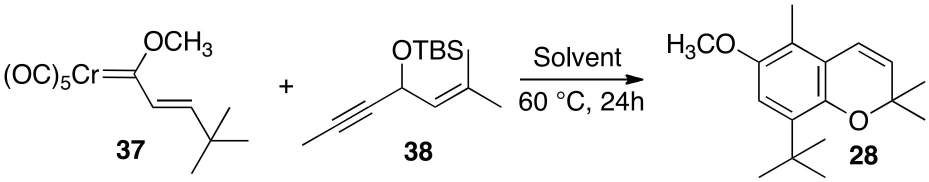
Compound 26: The carbene complex **20** (0.300 g, 1.03 mmol) was reacted with enyne **66** (0.260 g, 1.24 mmol) in 27 mL of dichloromethane. The reaction gave 0.147 g

(70% yield, 0.721 mmol) of compound **26** as a light yellow oil. R_f = 0.21 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.41 (d, 3H, *J* = 5.5 Hz), 2.12 (s, 6H), 3.75 (s, 3H), 4.86-4.91 (m, 1 H), 5.63 (dd, 1H, *J* = 8.5, 2.5 Hz), 6.32 (dd, 1H, *J* = 8.5, 1.5 Hz), 6.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.71, 12.05, 20.90, 56.11, 71.04, 106.19, 119.03, 124.36, 125.36, 126.38, 126.41, 145.27, 151.62; IR (neat film) 3050, 2974, 2931, 2845, 1608, 1579, 1463, 1425, 1386, 1321, 1228, 1109 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{13}H_{17}O_2$ (M^++H) *m/z* 205.1229, meas 205.1221.



Compound 27: The carbene complex **37** (0.094 g, 0.296 mmol) was reacted with enyne **15** (0.081 g, 0.362 mmol) in 9 mL of dichloromethane. The reaction gave 0.057 g (78% yield, 0.232 mmol) of compound **27** as a light yellow oil. This reaction was also conducted in acetonitrile and gave 78% yield. R_f = 0.36 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.40 (s, 9H), 1.45 (s, 6H), 3.76 (s, 3H), 5.60 (d, 1H, *J* = 10 Hz), 6.27 (d, 1H, *J* = 10 Hz), 6.42 (d, 1H, *J* = 3 Hz), 6.76 (d, 1H, *J* = 3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.34, 29.66, 34.66, 55.50, 75.54, 108.20, 113.47, 121.96, 123.16, 130.80, 138.81, 145.25, 152.88; IR (neat film) 3041, 2961, 2873, 2835, 1599, 1468, 1429, 1205 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{16}H_{23}O_2$ (M^++H) *m/z* 247.1698, meas 247.1701.

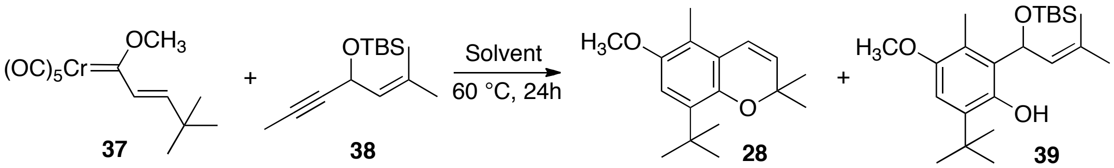
Reaction of complex 37 and enyne 38 with triflic acid workup:



Compound 28: The carbene complex **37** (0.30 g, 0.94 mmol) was reacted with enyne **38** (0.269 g, 1.13 mmol) in 27 mL of acetonitrile. The crude reaction mixture was then

treated with few drops of trifluoromethane sulfonic acid. The reaction gave 0.159 g (65% yield, 0.649 mmol) of compound **28** as a light yellow oil. $R_f = 0.32$ (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 9H), 1.41 (s, 6H), 2.14 (s, 3H), 3.76 (s, 3 H), 5.65 (d, 1H, *J* = 10 Hz), 6.52 (d, 1H, *J* = 10 Hz), 6.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.56, 27.18, 29.84, 34.66, 56.54, 74.43, 110.17, 120.16, 120.31, 121.15, 130.93, 135.13, 145.40, 150.91; IR (neat film) 2960, 2926, 1595, 1409, 1382 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{17}H_{24}O_2$ *m/z* 260.1776, meas 260.1774.

Reaction of complex 37 and enyne 38 without triflic acid workup:

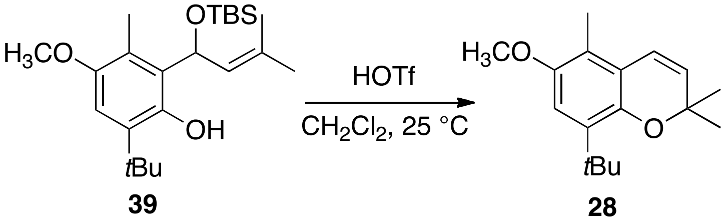


The carbene complex **37** (0.30 g, 0.94 mmol) was reacted with enyne **38** (0.269 g, 1.13 mmol) in 27 mL of dichloromethane. The reaction gave 0.187 g (76% yield, 0.719 mmol) of compound **28** as a light yellow oil as the major product. A side product **39** was also formed in the reaction and the ratio of compound **28** to compound **39** was 84:16. The ratio of compound **28** to compound **39** was tested in this reaction with isopropanol as additive. With 10 equivalents of isopropanol, the ratio was 91:9. With 50 equivalents of isopropanol the ratio remained the same. In presence of 100 equivalents of isopropanol the ratio was ≥ 95:5. The reaction was repeated again and the yield of compound **28** for the second run was 72%. The reaction was also performed in dichloromethane in presence of 10 equiv. of aniline as an additive and gave 86% yield of product **28** with no trace of side product. When the reaction was conducted in acetonitrile the ratio of compound **28** to compound **39** was 38:62.

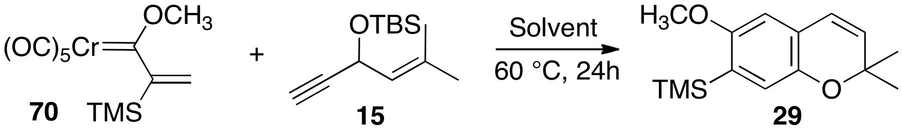
Isolation and Characterization of Compound 39: The side product **39** was purified from compound **28** by column chromatography using 40% $CHCl_3$-Hexane. In some cases column chromatography had to be repeated two or three times to get a pure fraction of compound **39**. $R_f = 0.63$ (40% Chloroform / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.02 (s, 3H), 0.11 (s, 3H), 0.86 (s, 9H), 1.40 (s, 9 H), 1.68 (s, 3H), 1.80 (s, 3H), 2.10 (s, 3H), 3.74 (s, 3H), 5.58-5.63 (m, 1H), 5.73 (d, 1H, J = 10 Hz), 6.75 (s, 1H), 8.74 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ –5.19, –4.73, 10.91, 18.01, 18.42, 25.58, 25.86, 29.55, 34.90, 56.66, 70.64, 109.94, 120.50, 124.59, 127.53, 133.77, 134.99, 149.51, 149.77; HRMS (TOF MS ES$^-$) calcd for $C_{23}H_{39}O_3Si$ (M$^+$–H) *m/z* 391.2668, meas 391.2656.

Compound **39** was subjected to deuterium exchange and the ^{1}H NMR spectrum of compound **39 OD** was taken. ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.02 (s, 3H), 0.11 (s, 3H), 0.86 (s, 9H), 1.40 (s, 9 H), 1.68 (s, 3H), 1.80 (s, 3H), 2.08 (s, 3H), 3.74 (s, 3H), 5.58-5.63 (m, 1H), 5.73 (d, 1H, J = 10 Hz), 6.75 (s, 1H).

Acid Rearrangement of Compound 39 to 28:

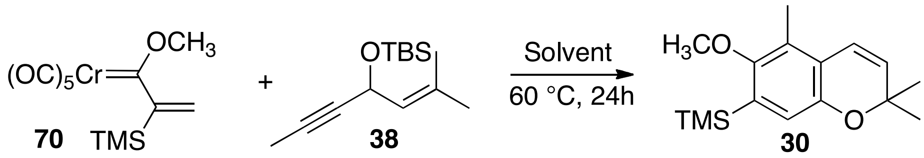


Compound **39** (0.043 g, 0.110 mmol) was taken up in a 25 mL round bottom flask in 5 mL of dichloromethane and few drops of trifluoromethanesulfonic acid was added. The reaction mixture was stirred for 10 minutes. The reaction was then quenched with saturated aqueous sodium carbonate solution (10 mL). The aqueous phase was extracted with dichloromethane (5 mL x 2). The organic layers were combined and dried with MgSO$_4$ and concentrated to dryness in *vacuo*. The compound **28** was obtained in quantitative yield (0.028 g, 0.110 mmol) and was analytically pure.

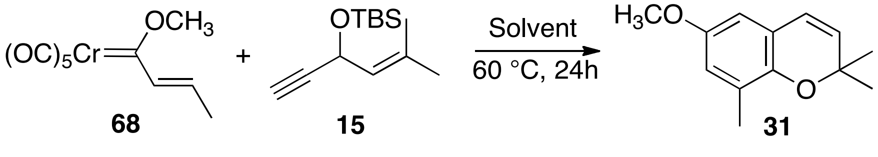


Compound 29: The carbene complex **70** (0.30 g, 0.90 mmol) was reacted with enyne **15** (0.242 g, 1.08 mmol) in 27 mL of dichloromethane. The reaction gave 0.152 g

(65% yield, 0.580 mmol) of compound **29** as a light yellow oil. The reaction was repeated two more times and both times the yield was 52%. This reaction was also conducted in acetonitrile and gave 23% yield. $R_f = 0.27$ (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.22 (s, 9H), 1.40 (s, 6H), 3.73 (s, 3H), 5.59 (d, 1H, *J* = 10 Hz), 6.27 (d, 1H, *J* = 10 Hz), 6.45 (s, 1H), 6.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –0.94, 27.80, 55.64, 75.84, 107.60, 122.29, 122.39, 122.44, 129.03, 131.57, 146.22, 158.53; IR (neat film) 3040, 2964, 2936, 2856, 1630, 1670, 1479, 1463, 1409, 1349, 1261, 1248, 1199, 1164 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{15}H_{23}O_2Si$ (M^++H) *m/z* 263.1467, meas 263.1470.

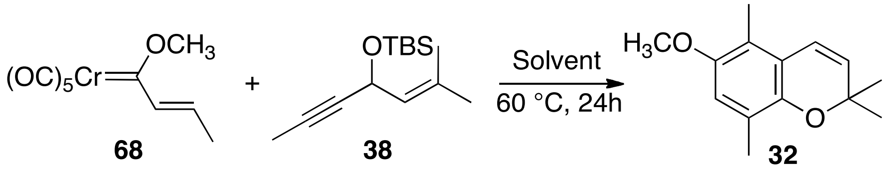


Compound 30: The carbene complex **70** (0.30 g, 0.90 mmol) was reacted with enyne **38** (0.256 g, 1.08 mmol) in 27 mL of dichloromethane. The reaction gave 0.215 g (87% yield, 0.779 mmol) of compound **30** as a light yellow oil. The reaction was repeated again and the yield was 81%. This reaction was also conducted in acetonitrile and gave 35% yield. $R_f = 0.26$ (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.26 (s, 9H), 1.40 (s, 6 H), 2.22 (s, 3H), 3.64 (s, 3H), 5.64 (d, 1H, *J* = 10 Hz), 6.48 (d, 1H, *J* = 10 Hz), 6.67 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –0.14 11.87, 27.75, 61.44, 74.97, 119.51, 119.83, 122.06, 125.49, 131.37, 132.80, 148.46, 157.62; IR (neat film) 3050, 2977, 2955, 1620, 1590, 1456, 1391, 1368, 1289, 1248 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{16}H_{24}O_2Si$ *m/z* 276.1546, meas 276.1553.

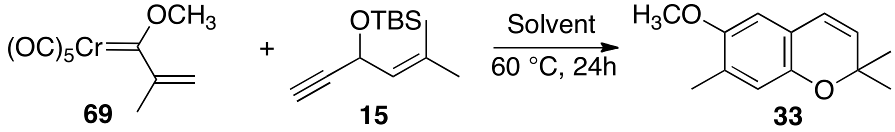


Compound 31: The carbene complex **68** (0.300 g, 1.08 mmol) was reacted with enyne **15** (0.292 g, 1.30 mmol) in 27 mL of acetonitrile. The reaction gave 0.185 g (83%

yield, 0.907 mmol) of compound **31** as a light yellow oil. The reaction in acetonitrile didn't need the oxidative workup. This reaction was also conducted in dichloromethane and gave 41% yield. R_f = 0.25 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.39 (s, 6H) 2.16 (s, 3 H), 3.73 (s, 3H), 5.61 (d, 1H, *J* = 10 Hz), 6.25 (d, 1H, *J* = 10 Hz), 6.39 (d, 1 H, *J* = 3 Hz), 6.55 (d, 1H, *J* = 3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.59, 27.61, 55.57, 75.49, 108.69, 115.94, 121.30, 122.69, 126.42, 131.44, 144.80, 153.03; IR (neat film) 3040, 2974, 2935, 2838, 1592, 1465, 1207 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{13}H_{16}O_2$ *m/z* 204.1150, meas 204.1145.

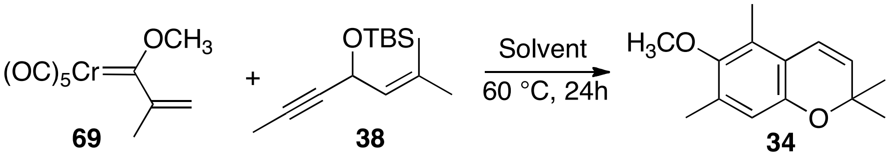


Compound 32: The carbene complex **68** (0.300 g, 1.08 mmol) was reacted with enyne **38** (0.310 g, 1.30 mmol) in 27 mL of dichloromethane. The reaction gave 0.145 g (61% yield, 0.665 mmol) of compound **32** as a light yellow oil. This reaction was also conducted in acetonitrile and gave 48% yield. The reaction in acetonitrile didn't need the oxidative workup. R_f = 0.27 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 6H) 2.14 (s, 3H), 2.16 (s, 3H), 3.75 (s, 3H), 5.67 (d, 1H, *J* = 10 Hz), 6.52 (d, 1H, *J* = 10 Hz), 6.53 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.49, 15.64, 27.41, 56.24, 74.38, 113.08, 119.61, 119.97, 120.47, 122.82, 131.44, 144.76, 151.08; IR (neat film) 3060, 2975, 2930, 2880, 1591, 1466, 1412, 1390, 1260, 1213, 1110 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{14}H_{18}O_2$ *m/z* 218.1307, meas 218.1305.

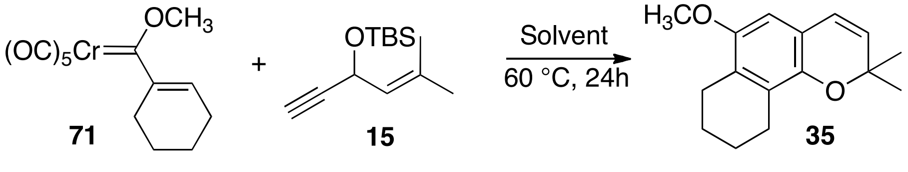


Compound 33: The carbene complex **69** (0.300 g, 1.08 mmol) was reacted with enyne **15** (0.292 g, 1.30 mmol) in 27 mL of dichloromethane. The reaction gave 0.10 g (45% yield, 0.490 mmol) of compound **33** as a light yellow oil. This reaction was also

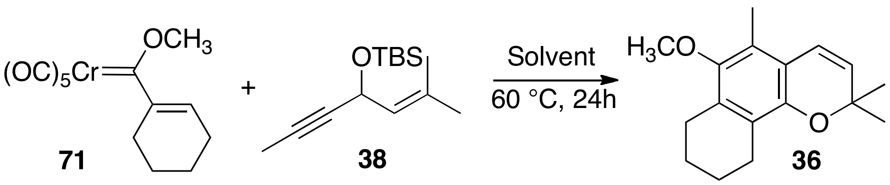
conducted in three other solvents, which were acetonitrile, hexane and benzene and gave 26%, 55% and 38% yields respectively. The yield in acetonitrile was the average of two runs. R_f = 0.25 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 (s, 6H), 2.14 (s, 3H), 3.75 (s, 3H), 5.53 (d, 1H, J = 9.5 Hz), 6.25 (d, 1H, J = 9.5 Hz), 6.45 (s, 1H), 6.58 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.20, 27.62, 55.90, 75.64, 108.19, 118.57, 119.01, 122.36, 127.51, 130.19, 146.25, 151.87; IR (neat film) 3039, 2973, 2925, 2859, 1701, 1498, 1465,1418, 1362, 1207 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{13}H_{17}O_2$ (M^++H) *m/z* 205.1229, meas 205.1236.



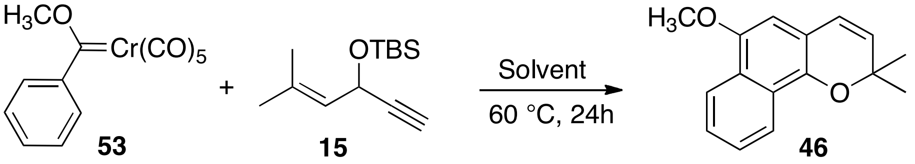
Compound 34: The carbene complex **69** (0.300 g, 1.08 mmol) was reacted with enyne **38** (0.31 g, 1.3 mmol) in 27 mL of dichloromethane. The reaction gave 0.16 g (68% yield, 0.73 mmol) of compound **34**. A repeat of the reaction gave the same yield. This reaction was also conducted in three other solvents, which were acetonitrile, hexane and benzene and gave 34%, 74% and 57% yields respectively. R_f = 0.25 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 (s, 6H), 2.20 (s, 6H), 3.63 (s, 3H), 5.58 (d, 1H, J = 10 Hz), 6.45 (d, 1H, J = 10 Hz), 6.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.27, 16.27, 27.60, 60.10, 74.90, 116.02, 118.52, 119.57, 126.30, 129.94, 131.21, 148.73, 150.66; IR (neat film) 3045, 2975, 2933, 2860, 1634, 1608, 1476, 1470, 1407, 1256 cm^{-1}; HRMS (TOF MS EI$^+$) calcd for $C_{14}H_{18}O_2$ *m/z* 218.1307, meas 218.1304.



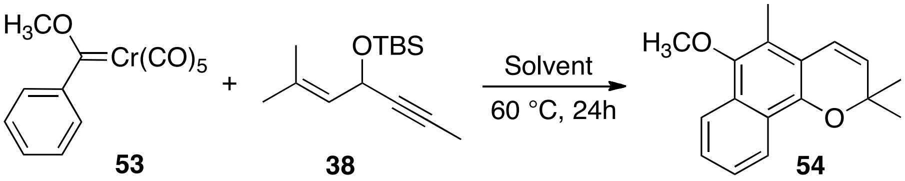
Compound 35: The carbene complex **71** (0.30 g, 0.95 mmol) was reacted with enyne **15** (0.255 g, 1.14 mmol) in 27 mL of dichloromethane. The reaction gave 0.167 g (72% yield, 0.684 mmol) of compound **35** as a light yellow oil. This reaction was also conducted in acetonitrile and gave 65% yield. The reaction in acetonitrile didn't need the oxidative workup. R_f = 0.36 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 6H), 1.70-1.72 (m, 4H), 2.57-2.63 (m, 4H), 3.74 (s, 3H), 5.53 (d, 1H, *J* = 8 Hz), 6.24 (d, 1H, *J* = 8 Hz), 6.32 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.28, 22.41, 23.18, 23.60, 27.73, 55.65, 75.40, 104.80, 117.51, 122.77, 126.51, 127.04, 129.86, 144.19, 151.04; IR (neat film) 3039, 2970, 2931 2867, 1636, 1607, 1577, 1259, 1434, 1424, 1328, 1271, 1107 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{16}H_{21}O_2$ (M$^+$+H) *m/z* 245.1542, meas 245.1533.



Compound 36: The carbene complex **71** (0.30 g, 0.95 mmol) was reacted with enyne **38** (0.271 g, 1.14 mmol) in 27 mL of dichloromethane. The reaction gave 0.196 g (80% yield, 0.759 mmol) of compound **36**. This reaction was also conducted in acetonitrile that gave 68% yield. The reaction in acetonitrile didn't need the oxidative workup. R_f = 0.27 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 6H), 1.70-1.72 (m, 4H), 2.18 (s, 3H), 2.56-2.59 (m, 2H), 2.67-2.71 (m, 2H), 3.62 (s, 3H), 5.57 (d, 1H, *J* = 8 Hz), 6.46 (d, 1H, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.26, 22.72, 22.82, 23.20, 24.23, 27.97, 60.19, 74.90, 117.53, 120.03, 122.96, 123.87, 129.83, 131.22, 146.80, 149.92; IR (neat film) 3096, 2974, 2932, 2858, 1638, 1596, 1452, 1415, 1322, 1268 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{23}O_2$ (M$^+$+H) *m/z* 259.1698, meas 259.1705.

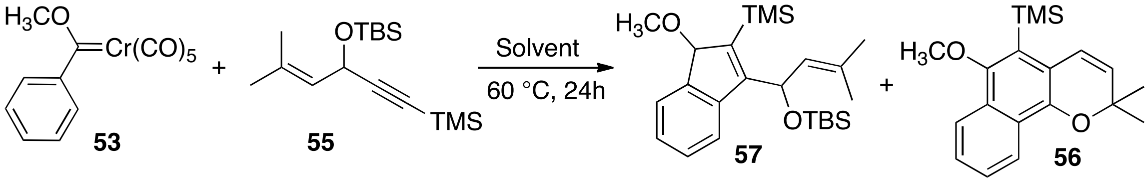


Lapachenole 46: The carbene complex **53** (0.30 g, 0.96 mmol) was reacted with enyne **15** (0.258 g, 1.15 mmol) in 20 mL of toluene in presence of 10 equiv. of aniline as additive. The reaction was run at 60 °C for 24 h. The reaction gave 0.11 g (48% yield, 0.46 mmol) of compound **46** as a light yellow oil. The compound was dissolved in a little pentane and was allowed to evaporate slowly. This process left a layer of waxy crystal. $R_f = 0.23$ (1% Ethyl acetate / Hexane); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.48 (s, 6H), 3.94 (s, 3H), 5.64 (d, 1H, $J = 9.5$ Hz), 6.39 (d, 1H, $J = 9.5$ Hz), 6.50 (s, 1H), 7.40-7.47 (m, 2H), 8.14 (d, 2H, $J = 8.30$ Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 27.52, 55.74, 76.16, 102.47, 114.74, 121.66, 121.78, 123.02, 125.43, 125.82, 125.88, 125.98, 129.89, 141.88, 149.22; IR (neat film) 3067, 3041, 2973, 2933, 2863, 2834, 1644, 1598, 1457, 1370 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{16}H_{17}O_2$ (M^++H) *m/z* 241.1229, meas 241.1217.



5-Methyl-Lapachenole 54: The carbene complex **53** (0.30 g, 0.96 mmol) was reacted with enyne **38** (0.274 g, 1.15 mmol) in 20 mL of toluene in presence of 10 equiv. of aniline as additive. The reaction was run at 60 °C for 24 h. The reaction gave 0.21 g (85% yield, 0.82 mmol) of compound **54** as a light yellow oil. This reaction was also conducted in toluene without aniline and gave 80% yield. $R_f = 0.22$ (1% Ethyl acetate / Hexane); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.50 (s, 6H), 2.41 (s, 3H), 3.85 (s, 3H), 5.69 (d, 1H, $J = 10$ Hz), 6.61 (d, 1H, $J = 10$ Hz), 7.38-7.46 (m, 2H), 7.98 (d, 1H, $J = 8.30$

Hz), 8.18 (d, 1H, J = 8.06 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.70, 27.47, 61.42, 75.51, 115.39, 119.97, 121.57, 122.22, 122.44, 124.66, 126.13, 128.04, 129.68, 144.57, 146.88; IR (neat film) 3069, 2975, 2934, 2843, 1643, 1455, 1378, 1360 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{19}O_2$ (M$^+$+H) *m/z* 255.1385, meas 255.1377.

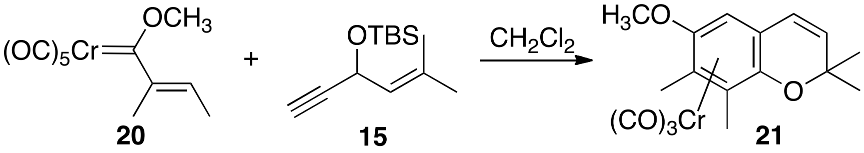


Compound 57: The carbene complex **53** (0.30 g, 0.96 mmol) was reacted with enyne **55** (0.341 g, 1.15 mmol) in 20 mL of toluene in presence of 10 equiv. of aniline as additive. The reaction was run at 60 °C for 24 h. The reaction gave 0.26 g (65% yield, 0.62 mmol) of compound **57** (1.14:1.00 mixture of diastereomers **57a** and **57b**) as light yellow oil. Compounds **57a** and **57b** were separated by preparative TLC. This reaction was also conducted in toluene in presence of 10 equiv. of aniline as additive and gave 62% yield of compound **57** as major product. However the crude ^{1}H NMR spectrum revealed a trace amount of another compound, which is tentatively identified as compound **56**.

Compound 57a: ^{1}H NMR ($CDCl_3$, 500 MHz) δ –0.05 - –0.03 (m, 6H), 0.13 (s, 9H), 0.83 (s, 9H), 1.64 (s, 3H), 1.71 (s, 3H), 3.30 (s, 3H), 5.34 (d, 1H, *J* = 1.2 Hz), 6.00 (s, 1H), 7.13-7.26 (m, 3H), 7.34 (dd, 2H, *J* = 7.9, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –0.22, 18.01, 19.29, 25.60, 25.67, 27.39, 57.07, 77.25 (overlapped with $CDCl_3$), 87.41, 119.42, 120.51, 124.39, 127.38, 127.49, 128.59, 128.86, 135.54, 138.31, 160.41; IR (neat film) 3059, 2956, 2930, 2899, 2858, 1590, 1472, 1253, 1198, 1166 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{24}H_{41}O_2Si_2$ (M$^+$+H) *m/z* 417.2645, meas 417.2627.

Compound 57b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ –0.27 (s, 9H), 0.14 (s, 6H), 0.94 (s, 9H), 1.74 (s, 3H), 1.86 (s, 3H), 3.22 (s, 3H), 5.50-5.71 (m, 1H), 6.28 (s, 1H), 7.26-7.32 (m, 2H), 7.32-7.37 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –4.86, 0.57, 18.44, 19.25, 25.96, 28.02, 56.39, 77.45, 87.17, 121.21, 123.94, 126.00, 128.05, 128.58, 129.60, 130.31, 137.15, 137.78, 158.69; IR (neat film) 3060, 2957, 2931, 2857, 1589, 1257, 1196, 1165 cm^{-1}; HRMS (TOF MS ES^{+}) calcd for $C_{24}H_{41}O_2Si_2$ (M^{+}+H) *m/z* 417.2645, meas 417.2631.

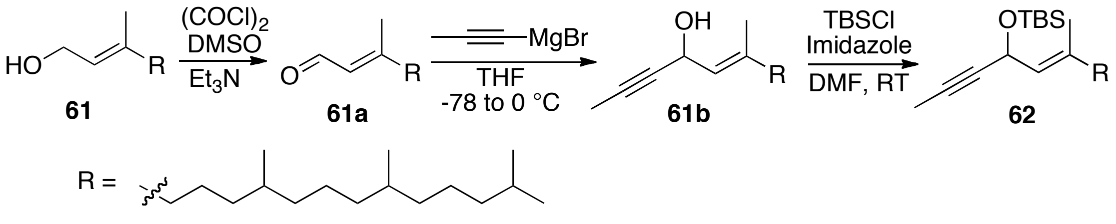
Preparation and Isolation of the Intermediate Chromium Tricarbonyl Complex (21):



To a 100 mL Schlenk flask was added carbene complex **20** (0.300 g, 1.03 mmol), alkyne **15** (0.278 g, 1.24 mmol), and dichloromethane (10 mL). The contents of the flask were heated for 24 hours at 45 °C. The solvent was quickly removed under reduced pressure at room temperature and loaded onto a silica gel column. The column was eluted with 4:1 pentane : ether. The compound **21** was collected and most of the solvent was removed below room temperature under a nitrogen purge through the solution. Finally rest of the solvent was removed under reduced pressure in a rotavapor without applying any heat. Yield = 61%; bright yellow crystal, mp 125 °C; R_f = 0.35 (4:1 pentane / ether); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.37 (s, 3H), 1.50 (s, 3H), 2.16 (s, 3H), 2.22 (s, 3H), 3.68 (s, 3H), 4.98 (s, 1H), 5.64 (d, 1 H, *J* = 10 Hz), 6.05 (d, 1H, *J* = 10 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.48, 12.76, 25.65, 29.45, 56.39, 72.47, 78.31, 85.62, 98.39, 98.62, 120.06, 128.15, 132.85, 135.31, 235.22; IR (neat film) 2975, 2928, 2855, 1945, 1874, 1458 cm^{-1}; HRMS (TOF MS ES^{+}) calcd for $C_{17}H_{19}O_5Cr$ (M^{+}+H) *m/z* 355.0638, meas 355.0624.

Synthesis of Vitamin E:

Preparation of Enyne (62):



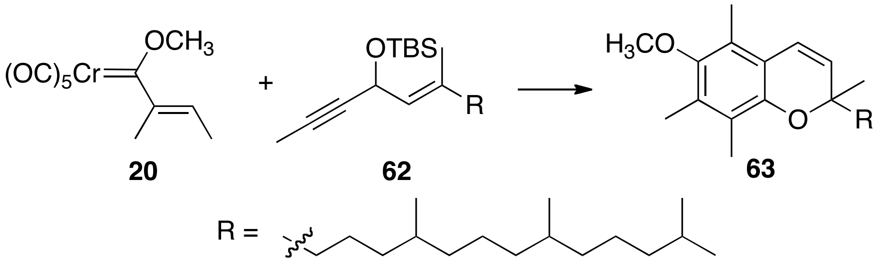
In dichloromethane (60 mL), DMSO (1.57 g, 1.43 mL, 20.1 mmol) was treated with oxalyl chloride (0.93 g, 0.65 mL, 7.41 mmol) at -78 °C for 5 minutes. Then (all-rac)-phytol **61** (2.00 g, 2.35 mL, 6.74 mmol, from Sigma-Aldrich) was added and the reaction mixture was stirred for 15 minutes. Triethyl amine (4.75 g, 6.54 mL, 47.0 mmol) was added. The reaction was warmed to room temperature over an hour. The solution was poured into 100 mL of 1M HCl. The solution was extracted with ethyl acetate (3 x 100 mL). The organic layers were combined and washed with brine (50 mL). The brine layer was back extracted with 3 x 25 mL of ethyl acetate. The organic layers were combined and dried and neutralized over solid sodium bicarbonate and magnesium sulfate. The solvent was removed under reduced pressure and crude aldehyde **61a** was used without further purification.

To all of the crude aldehyde from the above oxidation, was added propynyl magnesium bromide (0.5 M in THF, 19.8 mL, 9.87 mmol) over 10 minutes in THF (20 mL) at -78 °C. The solution was warmed to 0 °C and stirred for 1 h. After completion (as judged by TLC) the reaction mixture was then poured into 20 mL of saturated ammonium chloride solution. The aqueous layer was separated and extracted with ethyl acetate (20 mL x 3). The organic layers were combined and dried over magnesium sulfate. The solution was filtered through and the solvent was removed under reduced pressure in a rotavapor. All of the crude alcohol was used in the next step.

The alcohol **61b** was reacted with TBSCl (1.25 g, 8.29 mmol), imidazole (0.820 g, 12.1 mmol) in dry DMF (110 mL). The mixture was stirred at room temperature for overnight. The solution was extracted with ether (100 mL x 2), saturated ammonium chloride solution (100 mL), and water (100 mL). Each aqueous layer was then back extracted with ether (25 mL x 3). The organic layers were combined and dried over magnesium sulfate. The crude product was purified by chromatography on silica gel with 5% ethyl acetate / hexane. The final enyne **62** was prepared in 86% yield (2.61 g, 5.82 mmol) over 3 steps following the procedure described above for compound **10** as a light yellow oil. R_f= 0.66 (5% Ethyl Acetate - Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.82-0.86 (m, 12H), 0.88 (s, 9H), 0.99-1.55 (m, 22H), 1.80

(d, 3H, J = 2 Hz), 1.94 (t, 2H, J = 5 Hz), 5.00-5.04 (m, 1H), 5.27-5.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –4.59, –4.54, –4.40, –4.33, 3.72, 16.37, 16.38, 18.31, 19.64, 19.65, 19.68, 19.70, 19.72, 19.75, 22.62, 22.71, 23.22, 24.42, 24.44, 24.46, 24.80, 24.81, 24.89, 25.88, 25.91, 26.03, 26.05, 27.97, 32.54, 32.65, 32.67, 32.68, 32.70, 32.75, 32.77, 32.79, 32.80, 36.60, 36.69, 36.70, 37.31, 37.37, 37.41, 37.46, 39.37, 39.53, 59.90, 60.25, 79.72, 80.57, 126.27, 126.84, 136.90, 136.91; IR (neat film) 1597, 1463, 1376, 1259, 1089, 1037 cm^{-1}; HRMS (TOF MS ES$^+$) calcd for $C_{29}H_{56}OSi$ *m/z* 448.4100, meas 448.4119.

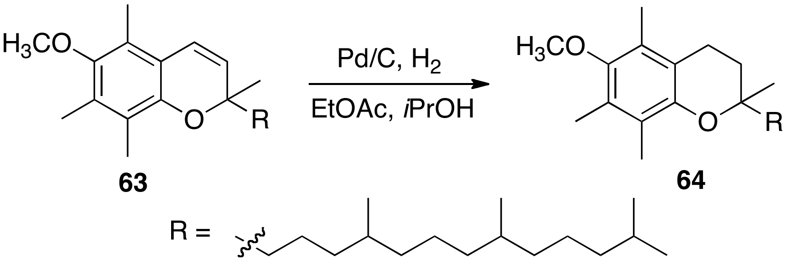
Preparation of Compound (63):



To a 100 mL single neck flask that had been modified by replacement of the joint with a threaded high vacuum Teflon valve was added carbene complex **20** (0.300 g, 1.03 mmol), alkyne **62** (0.556 g, 1.24 mmol), and dichloromethane (27 mL). The contents of the flask were heated for 24 hours at 60 °C. The solvent was removed under reduced pressure and dissolved in 15 mL ether and also 15 mL of water was added. In that reaction mixture $FeCl_3$.DMF complex (1.85 g, 7.75 mmol) was added. The mixture was stirred for 2 hours. The oxidation was monitored by TLC. After the oxidation was complete, the organic layer was separated and the water layer was washed with 3 x 20 mL of ether. All the organic layers were combined and dried with magnesium sulfate. The solvent was removed and the crude compound was purified by column chromatography using 1% ethyl acetate/hexane as the eluent. The yield of the product **63** was 85% (0.39 g, 0.88 mmol). The reaction was repeated in acetonitrile and the yield was 73%. Light yellow oil; R_f = 0.30 (1% Ethyl Acetate - Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.8-0.86 (m, 12H), 1.00-1.62 (m, 24H), 2.67 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 3.60 (s, 3H), 5.56 (d, 1H, J = 10 Hz), 6.48 (d, 1H, J = 10 Hz); ^{13}C

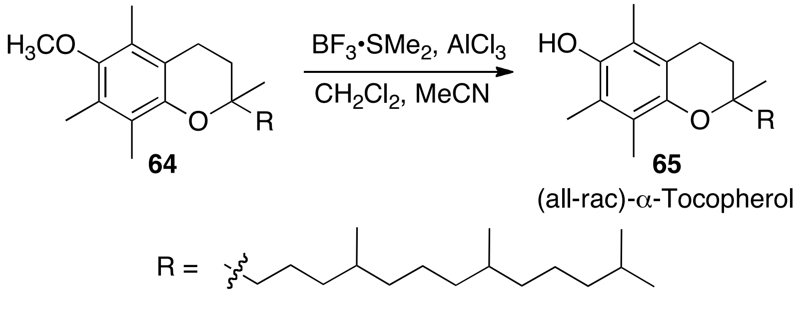
NMR ($CDCl_3$, 125 MHz) δ 11.13, 11.54, 12.78, 19.57, 19.62, 19.64, 19.67, 19.74, 21.37, 21.39, 21.40, 22.62, 22.71, 24.42, 24.44, 24.46, 24.79, 24.81, 25.63, 27.97, 32.67, 32.70, 32.77, 32.79, 37.29, 37.30, 37.34, 37.36, 37.39, 37.45, 39.37, 40.92, 40.95, 60.32, 117.86, 120.14, 122.60, 123.10, 129.44, 129.46, 129.99, 146.87, 150.12; IR (neat film) 3010, 2951, 2927, 2867, 1460, 1407, 1381, 1265 cm^{-1}; HRMS (TOF MS ES^+) calcd for $C_{30}H_{51}O_2$ (M^++H) *m/z* 443.3889, meas 443.3868.

Preparation of compound 64:



A 10 mL single neck flask was charged with compound **63** (0.20 g, 0.45 mmol), ethyl acetate (6 mL), isopropanol (6 mL), and 10 % Pd on carbon (0.096 g). The flask was fitted with a septum and then high vacuum was applied very briefly through a needle and as soon as the solvent began to bubble, vacuum was replaced with hydrogen introducing hydrogen filled balloon. The reaction was stirred for overnight at room temperature. The reaction mixture was filtered through Celite and the organic solvent was removed under reduced pressure to give compound **64** in 100% yield (0.20 g, 0.45 mmol) as a colorless oil. R_f = 0.28 (1% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.81-0.86 (m, 12H), 1.00-1.58 (m, 24H), 1.70-184 (m, 2H), 2.06 (s, 3H), 2.12 (s, 3H), 2.17 (s, 3H), 2.56 (t, 2H, *J* = 5.6 Hz), 3.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.64, 11.68, 11.73, 11.77, 12.51, 12.54, 19.59, 19.62, 19.66, 19.68, 19.74, 20.64, 21.04, 22.62, 22.71, 23.88, 23.89, 24.44, 24.81, 27.97, 29.70, 31.24, 31.29, 32.68, 32.70, 32.77, 32.79, 37.29, 37.34, 37.37, 37.39, 37.42, 37.46, 37.50, 37.57, 37.59, 39.38, 40.07, 40.11, 60.27, 60.32, 60.37, 60.43, 74.75, 74.76, 117.50, 122.87, 125.67, 127.70, 147.77, 149.38; IR (neat film) 2927, 2867, 1459, 1404, 1380, 1257, 1090 cm^{-1}; HRMS (TOF MS ES^{+}) calcd for $C_{30}H_{53}O_2$ (M^{+}+H) *m/z* 445.4046, meas 445.4043.

Preparation of compound (all-rac)-〈-Tocopherol 65:



The final cleavage of the methoxy ether was performed with a method developed for the conversion of **64** to vitamin E.[10] To a solution of compound **64** (0.100 g, 0.225 mmol) in dichloromethane (2.5 mL) and acetonitrile (1.7 mL) were added boron trifluoride-dimethylsulfide complex (0.420 mL, 3.99 mmol) and anhydrous aluminum chloride (0.300 g, 2.25 mmol) at 0 ºC. The reaction mixture was stirred for 6 h at room temperature. The solvent was evaporated in rotavapor. The mixture was neutralized by adding ice-cold sat. aqueous $NaHCO_3$ (10 mL) and extracted with ethyl acetate (15 mL x 3). The organic phases were combined and washed with water and brine and dried with Na_2SO_4. After evaporation of the volatiles in rotavapor, the residue was purified by flash chromatography using Hexane/ethyl acetate (v/v, 5:1) as eluent to provide compound **65** (vitamin E) as light yellow oil (0.083 g, yield 86%). R_f = 0.16 (5% Ethyl acetate / Hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.80-0.89 (m, 12H), 1.02-1.59 (m, 24H), 1.72-1.84 (m, 2H), 2.10 (s, 6H), 2.15 (s, 3H), 2.60 (t, 2H, *J* = 6.84 Hz), 4.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.26, 11.76, 12.19, 19.59, 19.63, 19.65, 19.68, 19.70, 19.74, 20.76, 21.04, 21.05, 21.07, 22.62, 22.71, 23.79, 24.44, 24.80, 24.81, 27.97, 31.50, 31.55, 32.68, 32.69, 32.70, 32.71, 32.78, 32.79, 37.28, 37.33, 37.39, 37.40, 37.41, 37.45, 37.46, 37.47, 37.50, 37.56, 37.59, 39.37, 39.81, 39.88, 74.51, 117.34, 118.45, 121.00, 122.61, 144.52, 145.55; IR (neat film) 3469, 2926, 2867, 1461, 1379, 1261, 1085 cm^{-1}; HRMS (TOF MS ES^{+}) calcd for $C_{29}H_{51}O_2$ (M^{+}+H) m/z 431.3889, meas 431.3881.

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