An Efficient Synthesis of 2-Vinylic Cyclic 1,3-Alkadienes via the Cp*Ru(II)-Catalyzed Intermolecular Coupling Reactions of Alkynes and Cyclic Allenes

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Supporting Information

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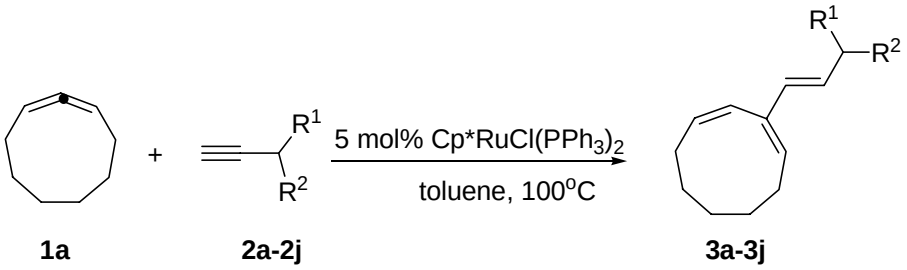
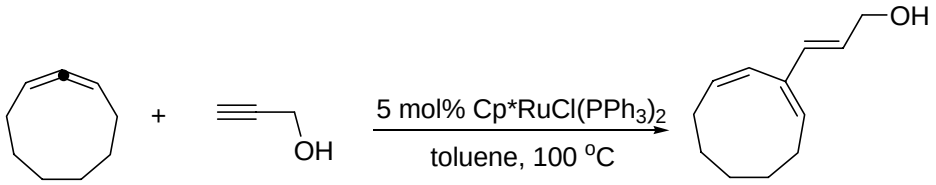
I. General Procedure I and Analytical Data for Compounds 3a-3j.



1a **2a-2j** **3a-3j**

Under an argon atmosphere, to a Schlenk tube with a screw cap were added $Cp^*RuCl(PPh_3)_2$ [1] (5 mol%), alkyne (**2a-2j)** (0.3 mmol), cyclonona-1,2-diene **1a** (0.25 mmol), and 2 mL of toluene. The resulting mixture was heated at 100 ^oC with stirring for 24 hours. After the reaction was complete as monitored by TLC, the solvent was evaporated and the mixture was purified via flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford pure products **3a**-**3j**.

(1) **2-(3-Hydroxyl-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3a**)

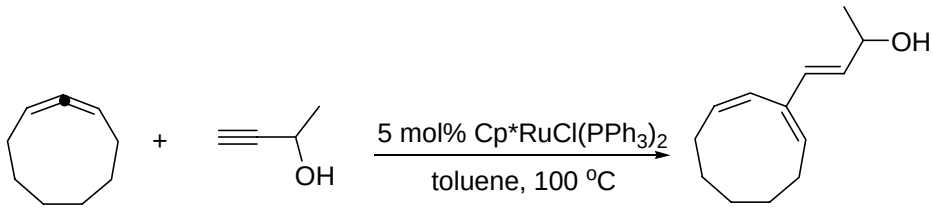


1a **2a** **3a**

The reaction of $Cp^*RuCl(PPh_3)_2$ (11 mg, 0.0136 mmol, 5.5 mol%), cyclonona-1,2-diene (**1a**) (30 mg, 0.246 mmol), and prop-2-yn-1-ol (**2a**) (18 μL, d = 0.945 g/mL, 17 mg, 0.300 mmol) in 2 mL of toluene afforded 37 mg (84%) of **3a**: Oil; ^1H NMR (300 MHz, $CDCl_3$): δ 6.27 (d, *J* = 15.3 Hz, 1 H), 5.93-5.76 (m, 2 H), 5.72-5.60 (m, 2 H), 4.17 (d, *J* = 6.0 Hz, 2 H), 2.21-2.13 (m, 2 H), 2.02-1.95 (m, 2 H),

1.63-1.52 (m, 2 H), 1.52-1.36 (m, 5 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 137.7, 134.3, 134.0, 133.9, 127.6, 126.4, 63.7, 29.8, 29.7, 29.4, 26.6, 25.8; IR (neat) *v* (cm^{-1}): 3353, 2924, 1674, 1454, 1440, 1088; MS (EI) *m/z* (%): 178 (M^+, 21.22), 91 (100); HRMS calcd. for $C_{12}H_{18}O$: 178.1358, found, 178.1356.

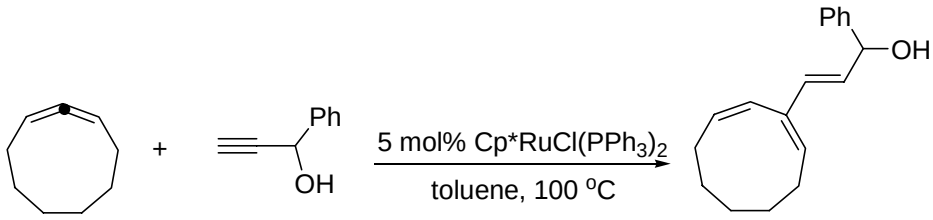
(2) **2-(3-Hydroxyl-1(*E*)-butenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3b**)



1a **2b** **3b**

The reaction of $Cp^*RuCl(PPh_3)_2$ (10 mg, 0.0111 mmol, 4.5 mol%), cyclonona-1,2-diene (**1a**) (31 mg, 0.254 mmol), and but-3-yn-2-ol (**2b**) (24 μL, d = 0.895 g/mL, 21 mg, 0.300 mmol) in 2 mL of toluene afforded 32 mg (67%) of **3b**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.22 (d, *J* = 15.6 Hz, 1 H), 5.92-5.76 (m, 2 H), 5.67 (t, *J* = 8.7 Hz, 1 H), 5.55(dd, *J* = 15.6, 6.6 Hz, 1 H), 4.38-4.32 (m, 1 H), 2.22-2.14 (m, 2 H), 2.04-1.96 (m, 2 H), 1.58-1.37 (m, 7 H), 1.28 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 137.6, 134.2, 133.9, 132.8, 131.9, 126.4, 68.8, 29.8, 29.7, 29.4, 26.6, 25.8, 23.4; IR (neat) *v* (cm^{-1}): 3339, 2924, 1643, 1454, 968; MS (EI) *m/z* (%): 192 (M^+, 3.09), 43 (100); HRMS calcd. for $C_{13}H_{20}O$: 192.1514, found, 192.1513.

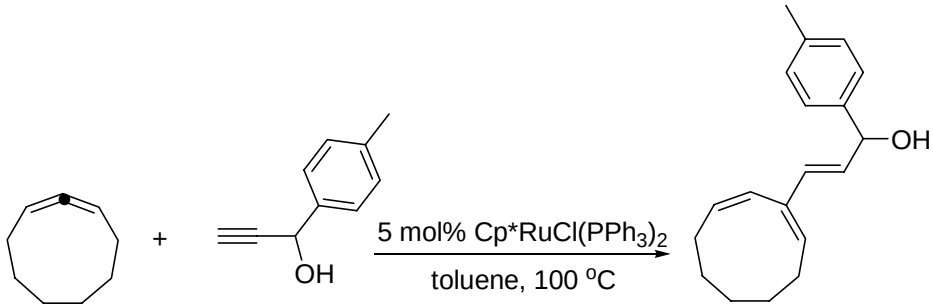
(3) **2-(3-Hydroxyl-3-phenyl-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3c**)



1a **2c** **3c**

The reaction of $Cp^*RuCl(PPh_3)_2$ (10 mg, 0.0123 mmol, 5.0 mol%), cyclonona-1,2-diene (**1a**) (31 mg, 0.254 mmol), and 1-phenylprop-2-yn-1-ol (**2c**) (40 mg, 0.303 mmol) in 2 mL of toluene afforded 42 mg (66%) of **3c**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5 H), 6.33 (d, *J* = 15.3 Hz, 1 H), 5.91-5.77 (m, 2 H), 5.76-5.65 (m, 2 H), 5.25 (d, *J* = 6.3, 1 H), 2.23-2.15 (m, 2 H), 2.04-1.96 (m, 3 H), 1.62-1.54 (m, 2 H), 1.52-1.40 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 143.2, 137.6, 134.5, 134.3, 133.3, 130.7, 128.4, 127.5, 126.3, 126.25, 75.1, 29.8, 29.7, 29.4, 26.6, 25.8; IR (neat) *v* (cm^{-1}): 3358, 2923, 1639, 1602, 1453, 1015; MS (EI) *m/z* (%): 254 (M^+, 1.78), 105 (100); HRMS calcd. for $C_{18}H_{22}O$: 254.1671, found, 254.1671.

(4) **2-(3-Hydroxyl-3-(*p*-tolyl)-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3d**)

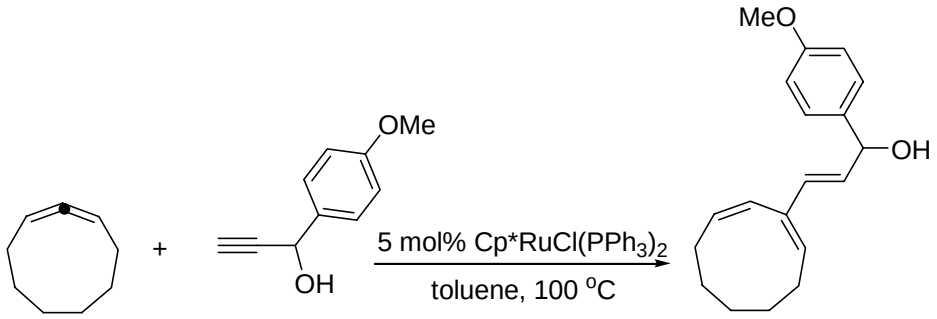


1a **2d** **3d**

The reaction of $Cp^*RuCl(PPh_3)_2$ (10 mg, 0.0123 mmol, 5.0 mol%), cyclonona-1,2-diene (**1a**) (30 mg, 0.246 mmol), and 1-*p*-tolylprop-2-yn-1-ol (**2d**) (44 mg, 0.301 mmol) in 2 mL of toluene afforded 40 mg (60%) of **3d**: Oil; ^{1}H NMR (300

MHz, $CDCl_3$): δ 7.26 (d, *J* = 7.9 Hz, 2 H), 7.15 (d, *J* = 7.9 Hz, 2 H), 6.32 (d, 15.3 Hz, 1 H), 5.90-5.76 (m, 2 H), 5.75-5.64 (m, 2 H), 5.22 (d, *J* = 6.6 Hz, 1 H), 2.34 (s, 3 H), 2.22-2.13 (m, 2 H), 2.03-1.94 (m, 2 H), 1.89 (s, 1 H), 1.50-1.54 (m, 2 H), 1.53-1.36 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 140.3, 137.7, 137.2, 134.33, 134.30, 133.1, 130.9, 129.1, 126.3, 126.2, 74.9, 29.8, 29.7, 29.4, 26.6, 25.8, 21.1; IR (neat) *v* (cm^{-1}): 3433, 2923, 1658, 1454, 1017; MS (EI) *m/z* (%): 268 (M^+, 3.63), 119 (100); HRMS calcd. for $C_{19}H_{24}O$: 268.1827, found, 268.1826.

(5) **2-(3-Hydroxyl-3-(*p*-methoxyphenyl)-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3e**)

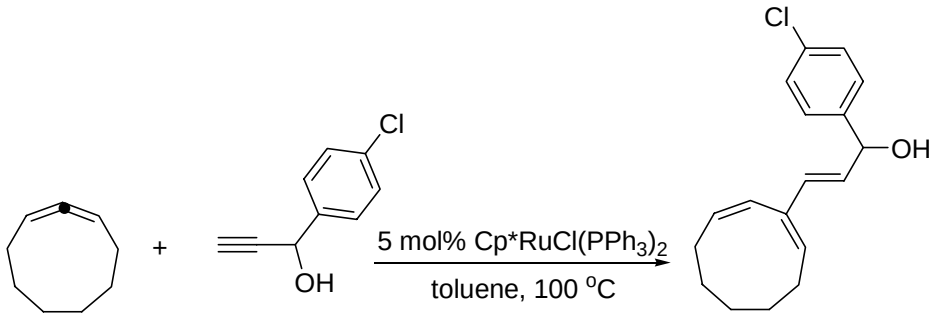


1a **2e** **3e**

The reaction of $Cp^*RuCl(PPh_3)_2$ (10 mg, 0.0123 mmol, 5 mol%), cyclonona-1,2-diene (**1a**) (30 mg, 0.246 mmol), and 1-(*p*-methoxyphenyl)prop-2-yn-1-ol (**2e**) (46 mg, 0.284 mmol) in 2 mL of toluene afforded 38 mg (53%) of **3e**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.24 (m, 2 H), 6.90-6.83 (m, 2 H), 6.30 (d, *J* = 15.3 Hz, 1 H), 5.91-5.73 (m, 2 H), 5.72-5.83 (m, 2 H), 5.19 (d, *J* = 6.9 Hz, 1 H), 3.79 (s, 3 H), 2.22-2.13 (m, 2 H), 2.07 (bs, 1 H), 2.03-1.95 (m, 2 H), 1.61-1.53 (m, 2 H), 1.51-1.38 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 158.9, 137.6, 135.4, 134.3, 132.9, 130.9, 127.6, 126.3, 113.8, 74.6, 55.2, 29.8, 29.7,

29.4, 26.6, 25.8; IR (neat) *v* (cm^{-1}): 3462, 2924, 1608, 1510, 1455, 1441, 1035; MS (EI) *m/z* (%): 284 (M^+, 1.66), 84 (100); HRMS calcd. for $C_{19}H_{24}O_2$: 284.1776, found, 284.1771.

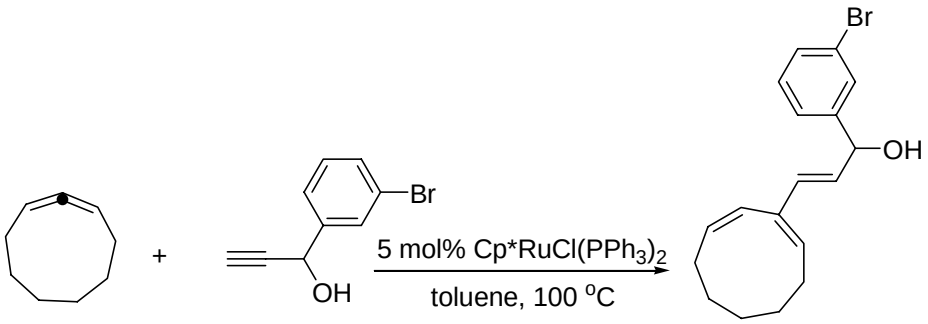
(6) **2-(3-Hydroxyl-3-(*p*-chlorophenyl)-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene (3f)**



1a **2f** **3f**

The reaction of $Cp^*RuCl(PPh_3)_2$ (9 mg, 0.0111 mmol, 4.4 mol%), cyclonona-1,2-diene (**1a**) (31 mg, 0.254 mmol), and 1-(*p*-chlorophenyl)prop-2-yn-1-ol (**2f**) (51 mg, 0.306 mmol) in 2 mL of toluene afforded 55 mg (76%) of **3f**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (s, 4 H), 6.31 (d, *J* = 15.3 Hz, 1 H), 5.89-5.77 (m, 2 H), 5.72 (t, *J* = 8.7 Hz, 1 H), 5.73 (dd, *J* = 15.3, 6.6 Hz, 1 H), 5.22 (d, *J* = 6.6 Hz, 1 H), 2.22-2.13 (m, 2 H), 2.02-1.94 (m, 3 H), 1.62-1.53 (m, 2 H), 1.51-1.37 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 141.6, 137.5, 135.0, 134.5, 133.8, 133.1, 130.3, 128.5, 127.6, 126.1, 74.4, 29.9, 29.7, 29.4, 26.6, 25.8; IR (neat) *v* (cm^{-1}): 3385, 2924, 1651, 1592, 1489, 1090, 1013; MS (EI) *m/z* (%): 290 (M^+ (^{37}Cl), 1.48), 288 (M^+ (^{35}Cl), 4.09), 139 (100.0); HRMS calcd. for $C_{18}H_{21}OCl$ (M^+ (^{35}Cl)): 288.1281, found, 288.1272.

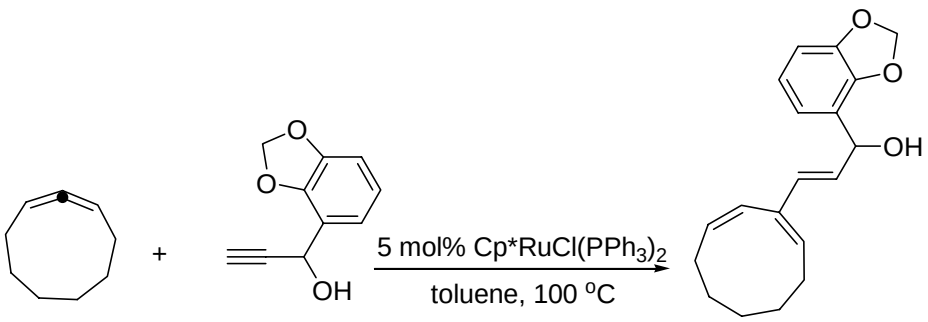
(7) **2-(3-Hydroxyl-3-(*m*-bromophenyl)-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3g**)



1a **2g** **3g**

The reaction of $Cp^*RuCl(PPh_3)_2$ (10 mg, 0.0123 mmol, 5.2 mol%), cyclonona-1,2-diene (**1a**) (29 mg, 0.238 mmol), and 1-(*m*-bromophenyl)prop-2-yn-1-ol (**2g**) (65 mg, 0.308 mmol) in 2 mL of toluene afforded 60 mg (72%) of **3g**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (s, 1 H), 7.41-7.36 (m, 1 H), 7.31-7.17 (m, 2 H), 6.32 (d, *J* = 15.9 Hz, 1 H), 5.90-5.70 (m, 2 H), 5.74 (t, *J* = 8.1 Hz, 1 H), 5.62 (dd, *J* = 15.3, 7.2 Hz, 1 H), 5.21 (dd, *J* = 6.9, 2.7 Hz, 1 H), 2.23-2.14 (m, 2 H), 2.03-1.94 (m, 3 H), 1.56-1.37 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 145.4, 137.4, 135.1, 134.6, 134.0, 130.4, 130.0, 129.97, 129.3, 126.1, 124.8, 122.5, 74.5, 29.9, 29.7, 29.3, 26.5, 25.8; IR (neat) *v* (cm^{-1}): 3321, 2923, 1630, 1590, 1570, 1454, 1186, 1070; MS (EI) *m/z* (%): 333 (M^+ (^{81}Br), 1.57), 331 (M^+ (^{79}Br), 1.29), 91 (100.0); HRMS calcd. for $C_{18}H_{21}OBr$ ((M^+ (^{79}Br))+1): 332.0776, found, 332.0786.

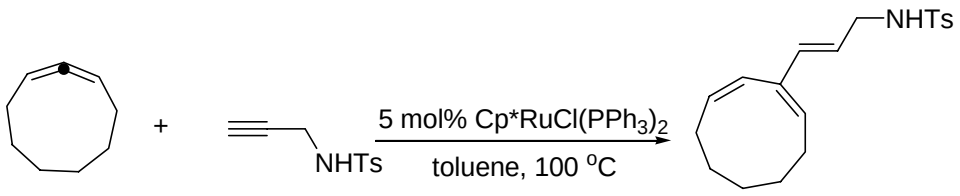
(8) **2-(3-Hydroxyl-3-(1,3-benzodioxol-4-yl)-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3h**)



1a **2h** **3h**

The reaction of $Cp^*RuCl(PPh_3)_2$ (9 mg, 0.0111 mmol, 4.7 mol%), cyclonona-1,2-diene (**1a**) (29 mg, 0.238 mmol), and 1-(1,3-benzo dioxol-4-yl)prop-2-yn-1-ol (**2h**) (53 mg, 0.301 mmol) in 2 mL of toluene afforded 43 mg (61%) of **3h**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.89-6.74 (m, 3 H), 6.30 (d, *J* = 15.6 Hz, 1 H), 5.94 (s, 2 H), 5.91-5.73 (m, 2 H), 5.71-5.61 (m, 2 H), 5.16 (d, *J* = 6.3 Hz, 1 H), 2.21-2.13 (m, 2 H), 2.03-1.92 (m, 3 H), 1.61-1.54 (m, 2 H), 1.51-1.37 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 147.6, 146.8, 137.6, 137.3, 134.5, 134.4, 133.1, 130.7, 126.3, 119.6, 108.0, 106.9, 100.9, 74.8, 29.8, 29.7, 29.4, 26.6, 25.8; IR (neat) *v* (cm^{-1}): 3412, 2923, 1607, 1503, 1487, 1442, 1247, 1040; MS (EI) *m/z* (%): 298 (M^+, 3.31), 280 (M^+-H_2O, 19.44), 84 (100); HRMS calcd. for $C_{19}H_{22}O_3$: 298.1569, found, 298.1569.

(9) **2-(3-(tosylamidol)-1(*E*)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3i**)

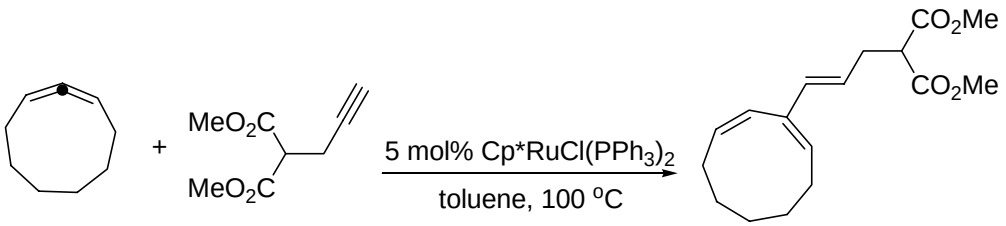


1a **2i** **3i**

The reaction of $Cp^*RuCl(PPh_3)_2$ (10 mg, 0.0123 mmol, 5 mol%), cyclonona-1,2-diene (**1a**) (30 mg, 0.246 mmol), and

N-(prop-2-ynyl)toluenesulfonamide (**2i**) (63 mg, 0.303 mmol) in 2 mL of toluene afforded 71 mg (87%) of **3i**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 6.07 (d, *J* = 15.3 Hz, 1 H), 5.81-5.69 (m, 2 H), 5.57 (t, *J* = 8.2 Hz, 1 H), 5.27 (dt, *J* = 15.3, 6.2 Hz, 1 H), 4.58 (t, *J* = 6.2 Hz, 1 H), 3.60 (t, *J* = 6.2 Hz, 2 H), 2.41 (s, 3 H), 2.17-2.08 (m, 2 H), 1.94-1.85 (m, 2 H), 1.56-1.48 (m, 2 H), 1.47-1.34 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 143.3, 137.3, 137.0, 135.5, 134.5, 134.4, 129.6, 127.1, 126.0, 123.0, 45.3, 29.7, 29.6, 29.3, 26.5, 25.8, 21.5; IR (neat) *v* (cm^{-1}): 3281, 2924, 1598, 1454, 1328, 1160, 1094; MS (EI) *m/z* (%): 331 (M^+, 0.76), 91 (100); HRMS calcd. for $C_{19}H_{25}NO_2S$: 331.1606, found, 331.1605.

(10) **2-(4,4-Bis(methoxycarbonyl)-1(*E*)-butenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3j**)

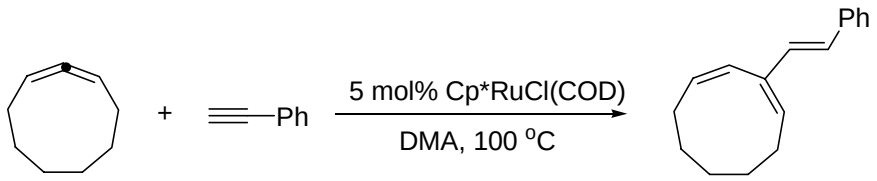


1a **2j** **3j**

The reaction of $Cp^*RuCl(PPh_3)_2$ (19 mg, 0.0234 mmol, 4.7 mol%), cyclonona-1,2-diene (**1a**) (61 mg, 0.500 mmol), and dimethyl 2-(prop-2-ynyl)malonate (**2j**) (101 mg, 0.594 mmol) in 4 mL of toluene afforded 74 mg (49 %) of **3j**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.12 (d, *J* = 15.6 Hz, 1 H), 5.87-5.75 (m, 2 H), 5.59 (t, *J* = 8.1 Hz, 1 H), 5.37 (dt, *J* = 15.3, 6.9 Hz, 1 H), 3.72 (s, 6 H), 3.42 (t, *J* = 7.6 Hz, 1 H), 2.65 (t, *J* = 7.6 Hz, 2 H), 2.18-2.10 (m, 2 H), 2.00-1.92 (m, 2 H), 1.59-1.51 (m, 2 H), 1.50-1.36 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 169.4, 137.9, 135.3, 134.1, 132.9, 126.5, 124.3, 52.4, 51.8, 32.0, 29.7, 29.3, 26.7, 25.9;

IR (neat) ν (cm^{-1}): 3479, 2932, 1736, 1438, 1159; MS (EI) *m/z* (%): 292 (M^+, 1.04), 84 (100); HRMS calcd. for $C_{17}H_{24}O_4$: 292.1675, found, 292.1680.

II. General Procedure II and Analytical Data for Compound 3k. Synthesis of 2-(2-Phenyl-(*E*)-ethenyl)cyclonona-1(*Z*), 3(*Z*)-diene (3k)



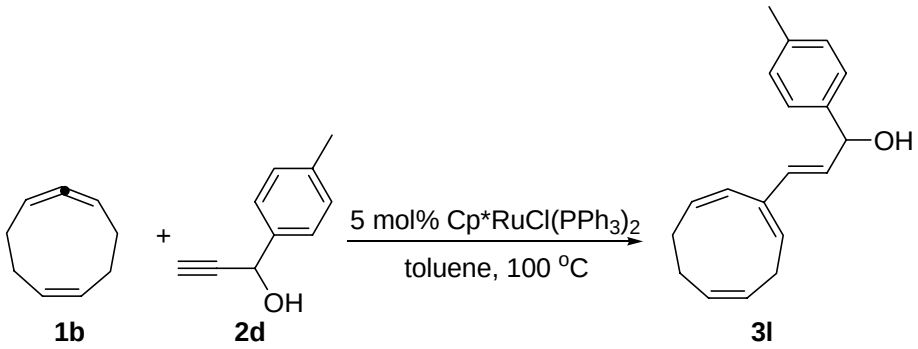
1a **2k** **3k**

Under an argon atmosphere, to a Schlenk tube with a screw cap were added Cp*RuCl(COD)[2] (5 mg, 0.0122 mmol, 4.8 mol%), ethynylbenzene **2k** (36 μL, d = 0.883 g/mL, 32 mg, 0.300 mmol), and cyclonona-1,2-diene **1a** (31 mg, 0.254 mmol) and 2 mL of DMA. The resulting mixture was heated at 100 ℃ with stirring for 24 hours. After the reaction was complete as monitored by TLC, water (5 mL) was added, and the mixture was extracted with ether (2×6 mL). Organic extracts were dried (Na_2SO_4) and filtrated. After evaporation, the residue was purified via flash chromatography on silica gel (petroleum ether) to afford 27 mg (50%) of **3k**: Oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.36 (m, 2 H), 7.32-7.24 (m, 2 H), 7.19-7.14 (m, 1 H), 6.81 (d, J = 16.0 Hz, 1 H), 6.38 (d, J = 16.0 Hz, 1 H), 6.02 (d, J = 10.8 Hz, 1 H), 5.90 (dt, J = 10.8, 8.1 Hz, 1 H), 5.81 (t, J = 8.4 Hz, 1 H), 2.27-2.21 (m, 2 H), 2.07-2.00 (m, 2 H), 1.65-1.59 (m, 2 H), 1.53-1.42 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 138.6, 137.8, 134.7, 134.6, 131.3, 128.5, 128.0, 126.9, 126.4, 126.2, 30.0,

29.7, 29.4, 26.8, 25.9; IR (neat) *v* (cm^{-1}): 3023, 2924, 1600, 1493, 1448; MS (EI) *m/z* (%): 224 (M^+, 40.21), 91 (100); HRMS calcd. for $C_{17}H_{20}$: 224.1565; found, 224.1557.

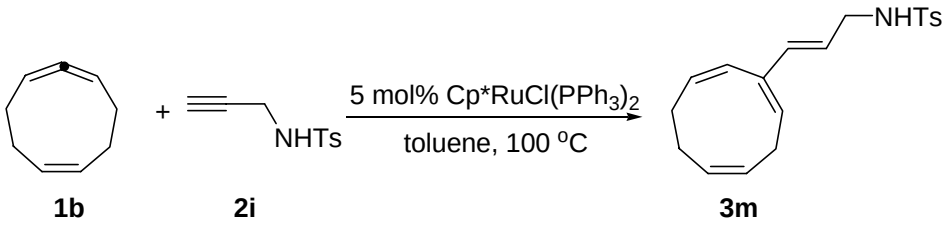
III. **General Procedure I and Analytical Data for Compounds 3l and 3m.**

(1) **3-(3-Hydroxyl-3-(*p*-tolyl)-1(*E*)-propenyl)cyclonona-1(Z), 3(Z), 6(Z)-triene** (**3l**)



Following General procedure I, the reaction of $Cp^*RuCl(PPh_3)_2$ (9 mg, 0.0111 mmol, 4.5 mol%), 1-*p*-tolylprop-2-yn-1-ol **2d** (36 mg, 0.246 mmol), and 1,2,6-cyclononatriene **1b** (62 mg, 0.517 mmol) in 2 mL of toluene was heated to 100 ℃. The reaction was monitored by TLC. After complete consumption of starting material, the solvent was evaporated and the mixture was purified via flash chromatography on silica gel (petroleum ether/ ethyl acetate) to afford pure product 40 mg (60%) of **3l**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 6.37 (d, *J* = 15.6 Hz, 1 H), 5.85-5.58 (m, 6 H), 5.23 (d, *J* = 6.9 Hz, 1 H), 2.61 (t, *J* = 7.8 Hz, 2 H), 2.35 (s, 3 H), 2.20-2.03 (m, 5 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 140.2, 137.2, 135.0, 134.6, 133.5, 132.1, 131.1, 129.1, 129.05, 126.7, 126.2, 123.6, 75.0, 29.8, 29.5, 24.4, 21.1; IR (neat) *v* (cm^{-1}): 3372, 2917, 1640, 1512, 1453, 1015; MS (EI) *m/z* (%): 266 (M^+, 1.57), 91 (100); HRMS calcd. for $C_{19}H_{22}O$: 266.1671; found, 266.1660.

(2) **3-(3-(Tosylamidol)-1(*E*)-propenyl)cyclonona-1(Z), 3(Z), 6(Z)-triene** (**3m**)

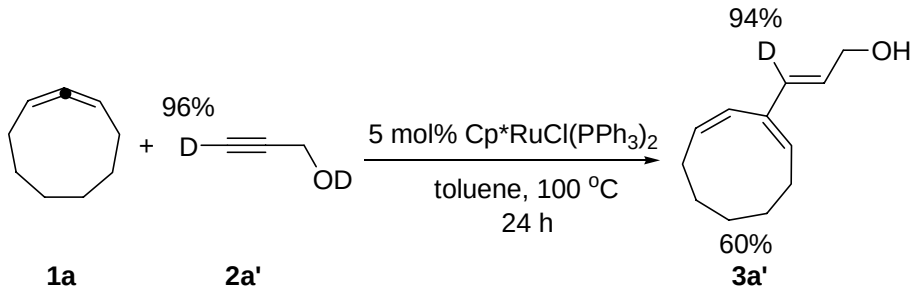


1b **2i** **3m**

Following General procedure I, the reaction of $Cp^*RuCl(PPh_3)_2$ (9 mg, 0.0111 mmol), 1,2,6-cyclononatriene (**1b**) (61 mg, 0.508 mmol), and N-(prop-2-ynyl)toluenesulfonamide (**2i**) (52 mg, 0.248 mmol) in 2 mL of toluene afforded 41 mg (50 %) of **3m**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 6.13 (d, *J* = 15.6 Hz, 1 H), 5.76-5.51 (m, 5 H), 5.33 (dt, *J* = 15.3, 6.3 Hz, 1 H), 4.63 (t, *J* = 6.0 Hz, 1 H), 3.61 (t, *J* = 6.0 Hz, 2 H), 2.57-2.49 (m, 2 H), 2.41 (s, 3 H), 2.13-1.98 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 143.3, 137.1, 136.0, 134.7, 134.6, 132.1, 129.6, 129.2, 127.1, 126.6, 123.3, 45.3, 29.7, 29.4, 24.4, 21.5; IR (neat) *v* (cm^{-1}): 3282, 2940, 1643, 1598, 1326, 1159, 1094; MS (ESI) *m/z* 368 $[M+K]^+$, 352 $[M+Na]^+$; HRMS (MALDI/DHB): Calcd. for $C_{19}H_{23}NO_2SNa^+$ $[M+Na^+]$ 352.1337; Found: 335.1342.

IV. General Procedure I and analytical data for compounds 3a'and 3b.

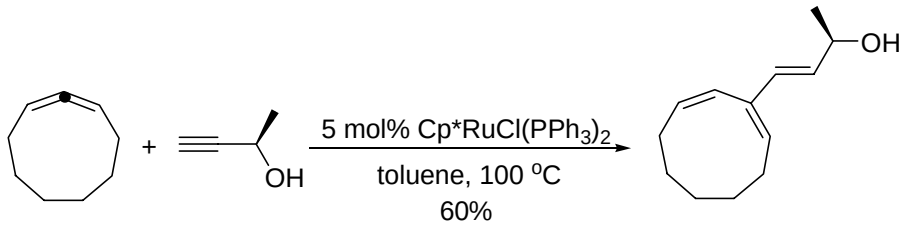
(1) **2-(3-Hydroxyl-1(*E*)-(D)-propenyl)cyclonona-1(*Z*), 3(*Z*)-diene** (**3a'**)



1a **2a'** **3a'**

Following General procedure I, the reaction of $Cp^*RuCl(PPh_3)_2$ (9 mg, 0.0111 mmol), cyclonona-1,2-diene (**1a**) (31 mg, 0.254 mmol), and 3,O-dideuterioprop-2-yn-1-ol[3] (**2a'**) (19 μL, 19 mg, 0.327 mmol) in 2 mL of toluene afforded 27 mg (60 %) of **3a'**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.26 (d, *J* = 15.6 Hz, 0.04 H), 5.92-5.76 (m, 2 H), 5.71-5.61 (m, 2 H), 4.17 (d, *J* = 5.7 Hz, 2 H), 2.21-2.13 (m, 2 H), 2.03-1.95 (m, 2 H), 1.62-1.52 (m, 2 H), 1.51-1.37 (m, 5 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 137.6, 134.2, 133.8, 133.3 (t, *J* = 23.6 Hz, *C*D=CH),[4] 127.5, 126.3, 63.4, 29.7, 29.66, 29.3, 26.6, 25.8; IR (neat) *v* (cm^{-1}): 3326, 2923, 2220 ($v_{=C\text{-}D}$),[4] 1941, 1628, 1454, 1011, 975; MS (EI) *m/z* (%): 179 (M^+, 14.00), 92 (100); HRMS calcd. for $C_{12}H_{17}DO$: 179.1420; found, 179.1423.

(2) **2-(3(*R*)-Hydroxyl-1(*E*)-butenyl)cyclonona-1(*Z*), 3(*Z*)-diene (*R*-3b)**.



1a **(*R*)-2b** *ee*: 98% **(*R*)-3b** *ee*: 97%

Following General procedure I, the reaction of $Cp^*RuCl(PPh_3)_2$ (19 mg, 0.0234 mmol), cyclonona-1,2-diene (**1a**) (61 mg, 0.500 mmol), and (*R*)-but-3-yn-2-ol (*R*-**2b**)

(47 μL, d = 0.895 g/mL, 42 mg, 0.600 mmol) in 4 mL of toluene afforded 57 mg (60 %, 97% ee) of ***R*-3b**. HPLC conditions: AD-H column; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 95/5, λ = 230 nm, $[\alpha]^{20}_{D} = +2.5^{o}$ (c = 0.95, $CHCl_3$).

References:

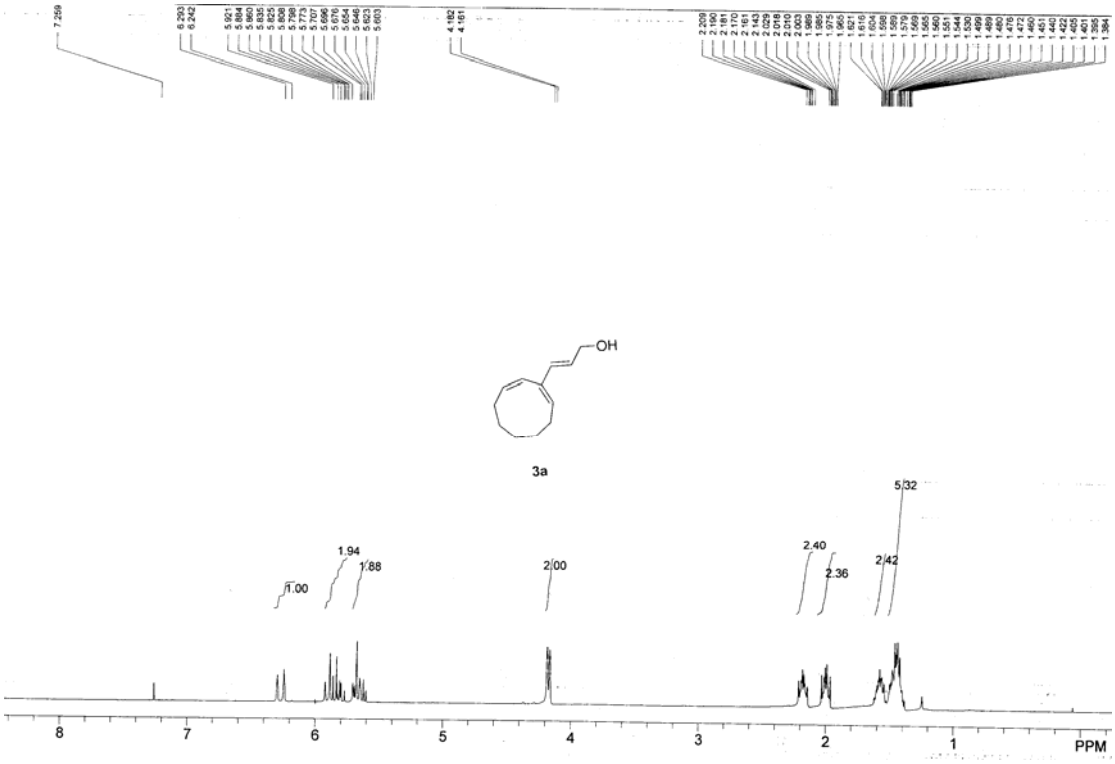
1. (a) P. J. Fagan, W. S. Mahoney, J. C. Calabrese, I. D. Williams, *Organometallics* 1990, **9**, 1843. (b) M. S. Chinn, D. M. Heinekey, *J. Am. Chem. Soc.* 1990, **112**, 5166.

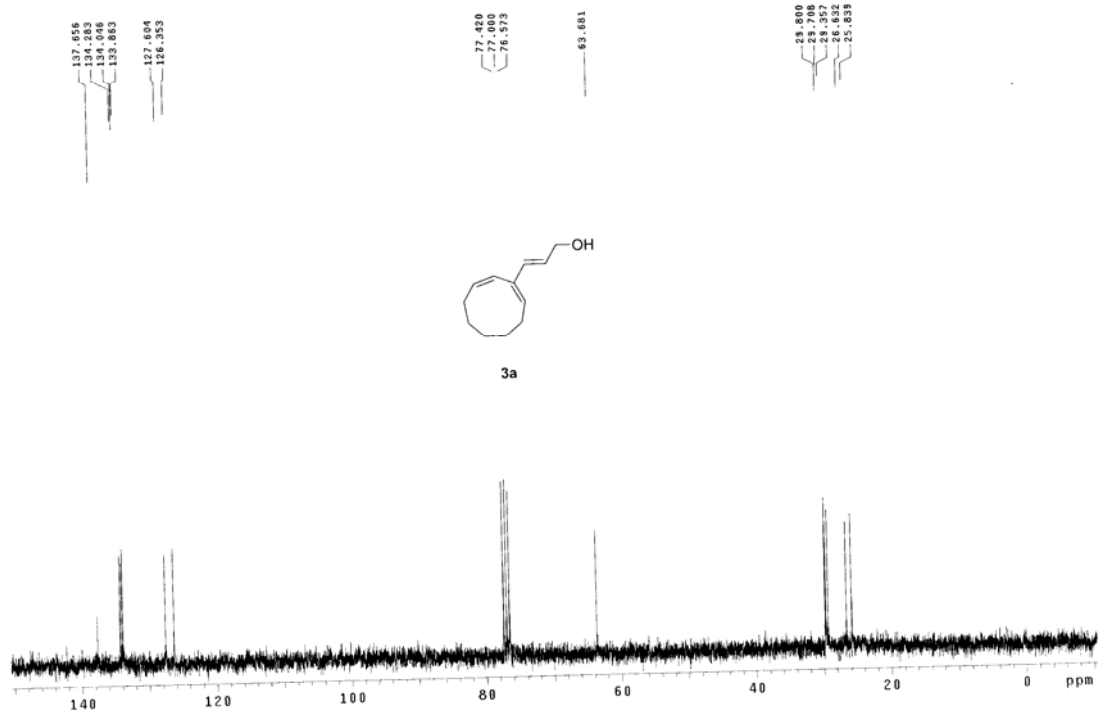
2. N. Oshima, H.Suzuki, and Y. Moro-oka, *Chem. Lett.* 1984, 1161.

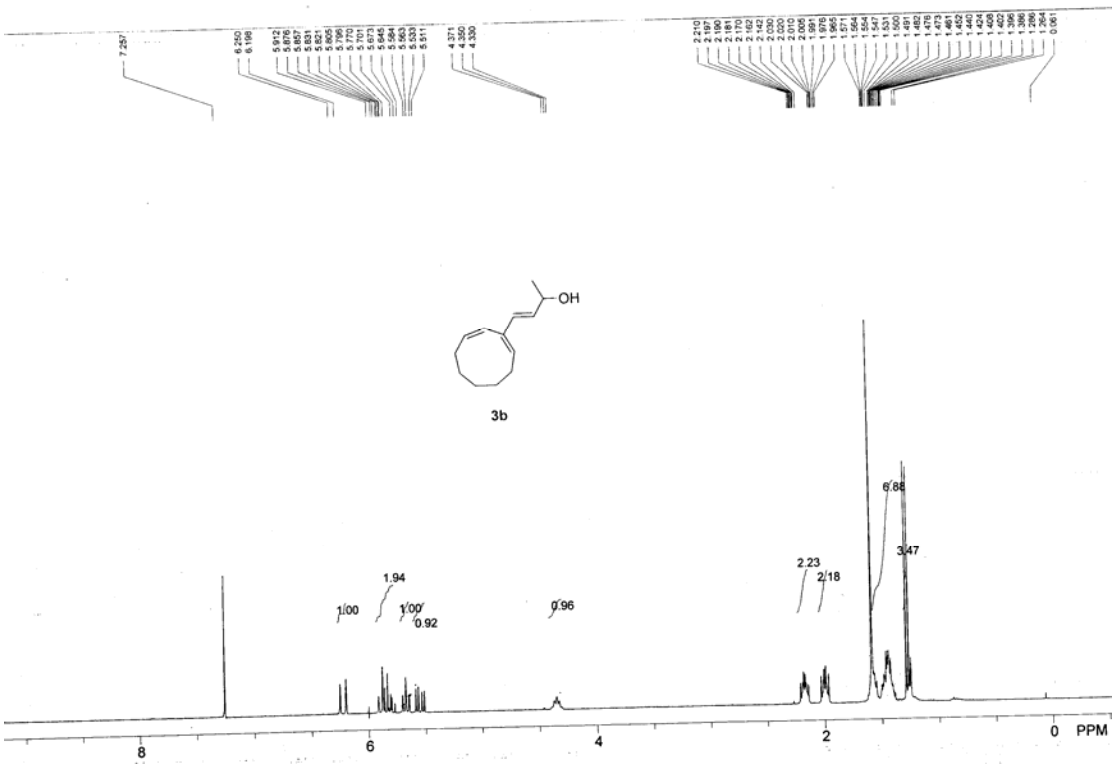
3. W. C. Eckhoff, C. E. Miller, C. F. Billera, P. S. Engel, R.F. Curl, *J. Mol. Spectrosc.* 1997, **186**, 193.

4. H. G. Korth, H. Trill, and R. Sustmann, *J. Am. Chem. Soc.* 1981, **103**, 4483.

V. ^{1}H NMR and ^{13}C NMR spectra for compounds 3a-3m and 3a'.



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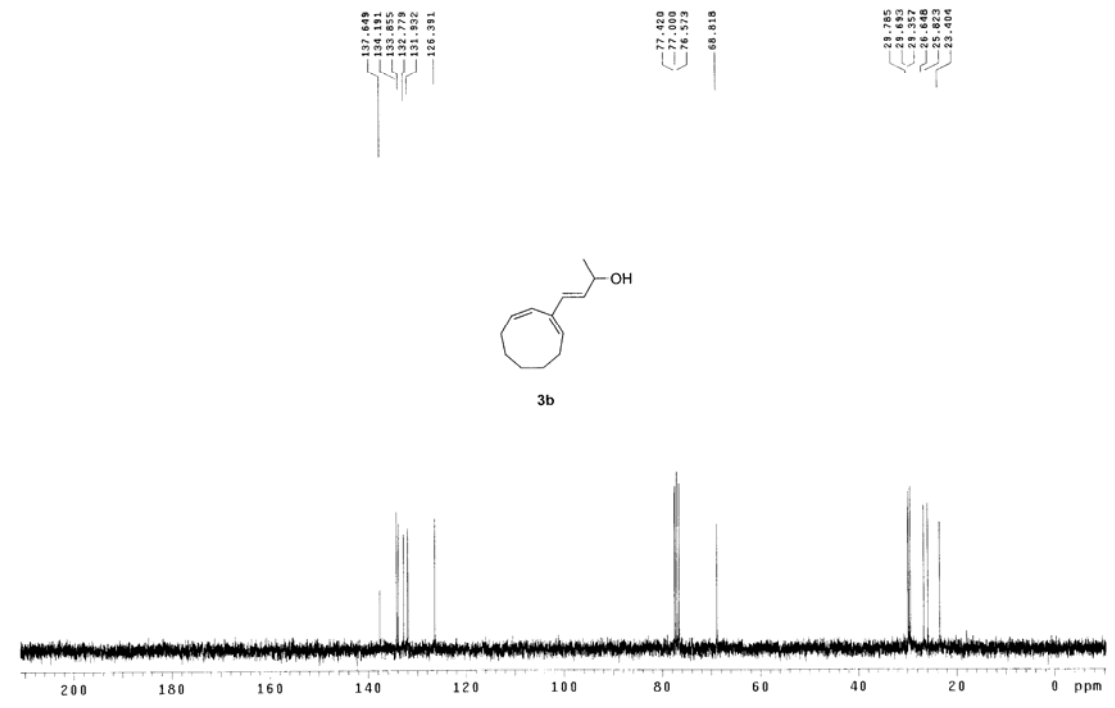
2.18
6.88
3.47
8
6
4
2
0 PPM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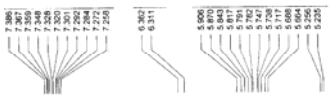
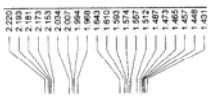
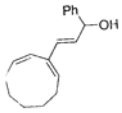
160
140
120
100
80
60
40
20
0 ppm



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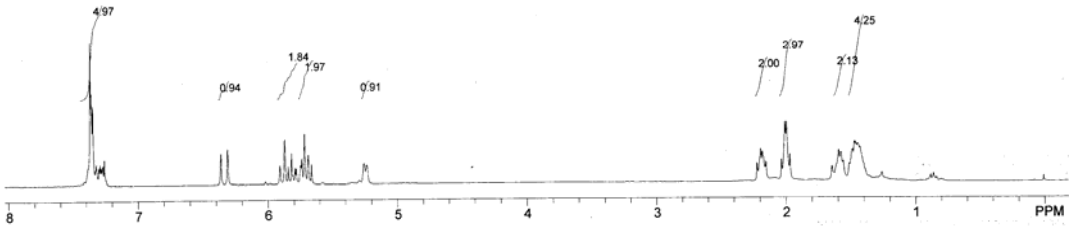
OH

3c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1.97
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2.97
2.13
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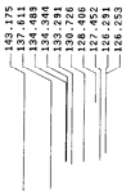
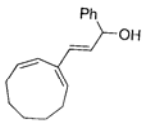
8
7
6
5
4
3
2
1
PPM

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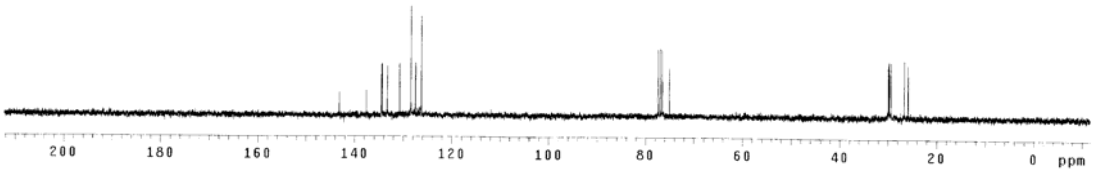
OH

3c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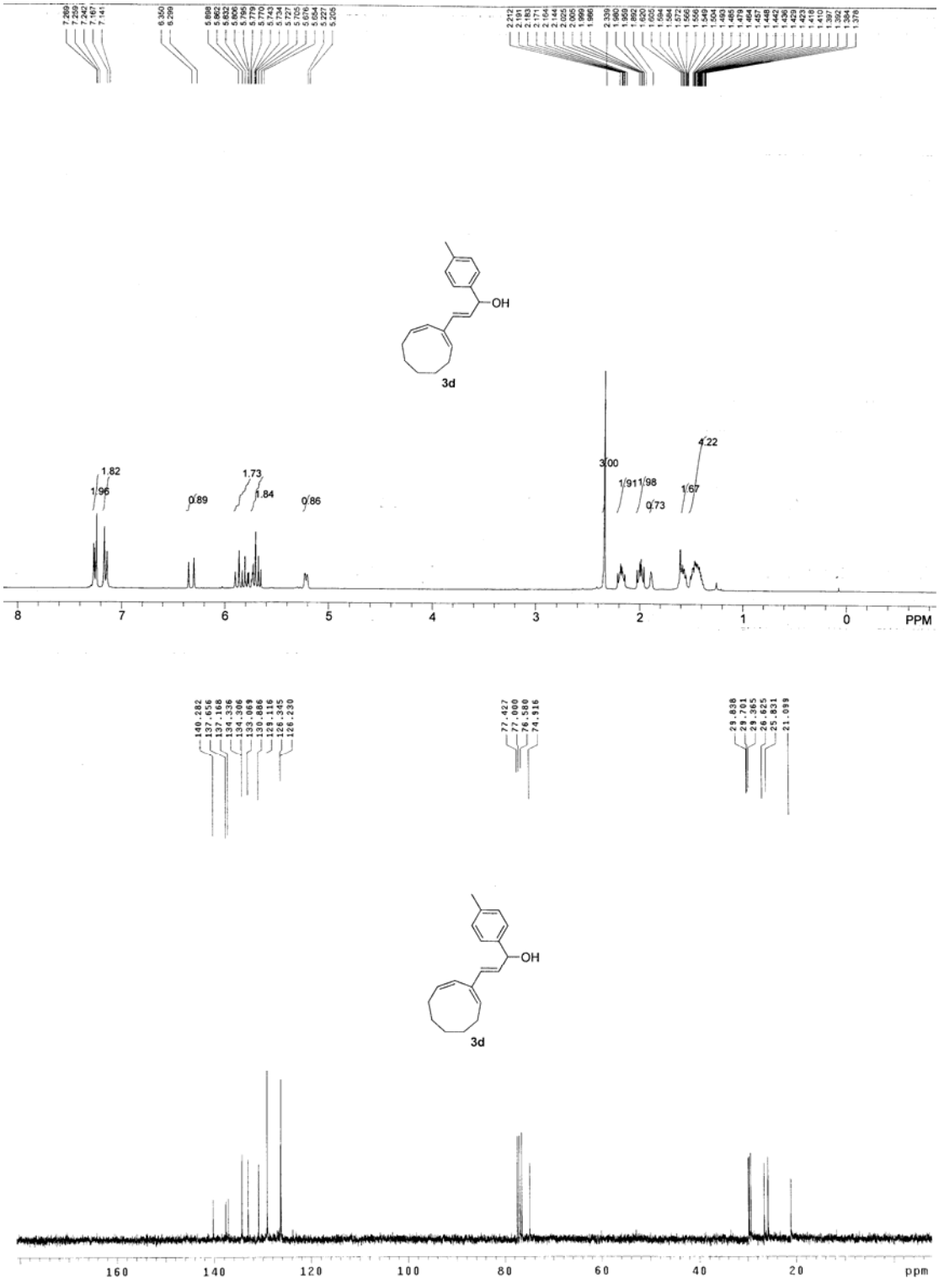
120
100
80
60
40
20
0
ppm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3.00
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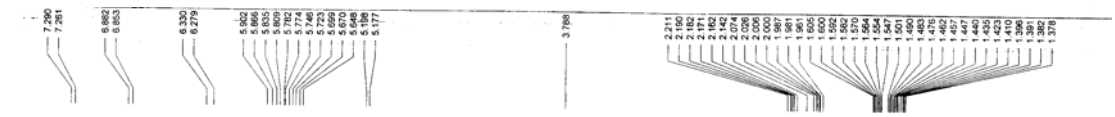
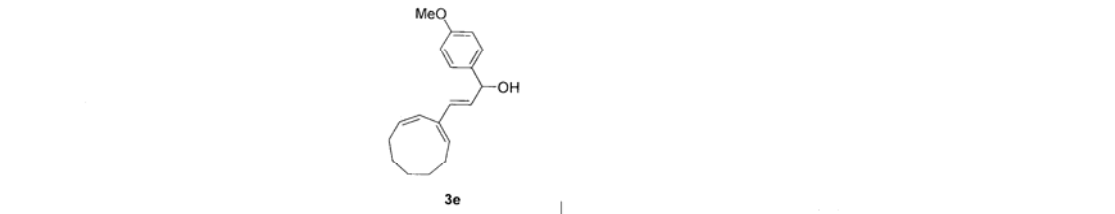
1.67
4.22
PPM
OH
3d
ppm

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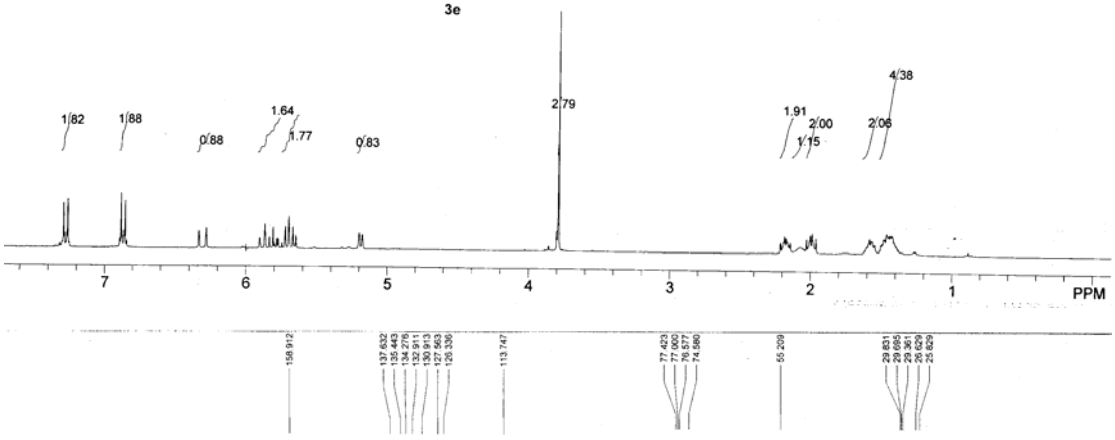
OH

3e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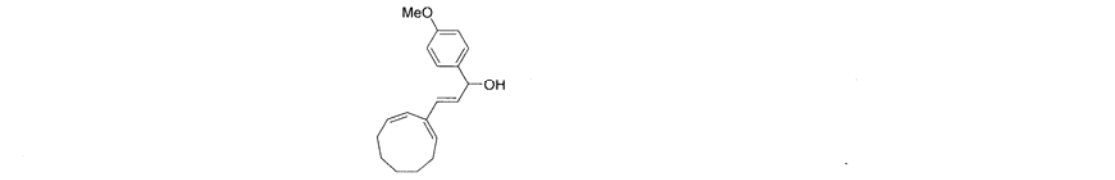
7
6
5
4
3
2
1
PPM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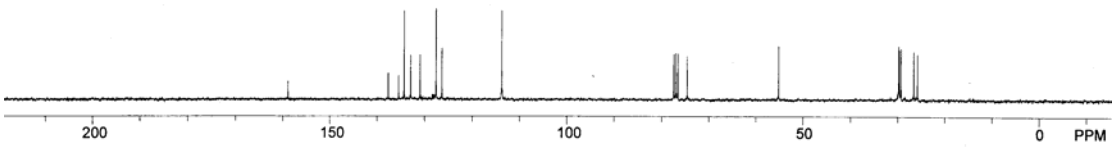
OH

3e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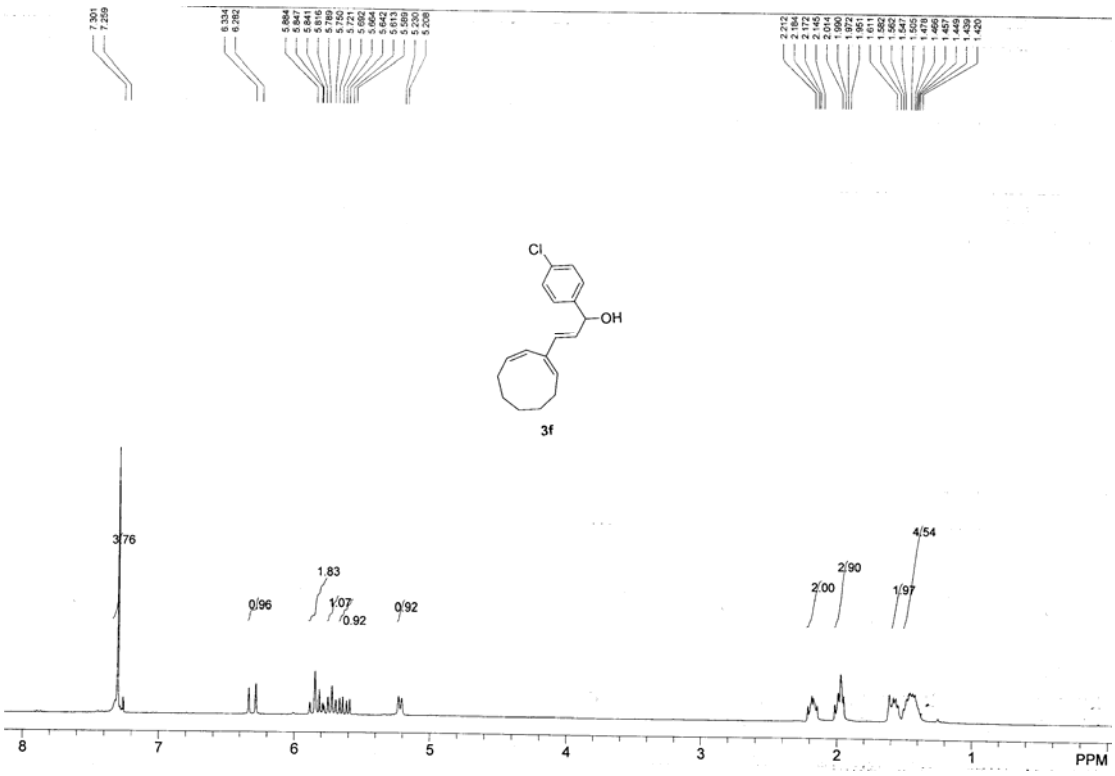
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5.642
5.593
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5.230
5.208
2.212
2.184
2.172
2.145
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1.951
1.691
1.582
1.562
1.547
1.535
1.478
1.466
1.457
1.449
1.439
1.420
Cl
OH
3f
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1.83
0.96
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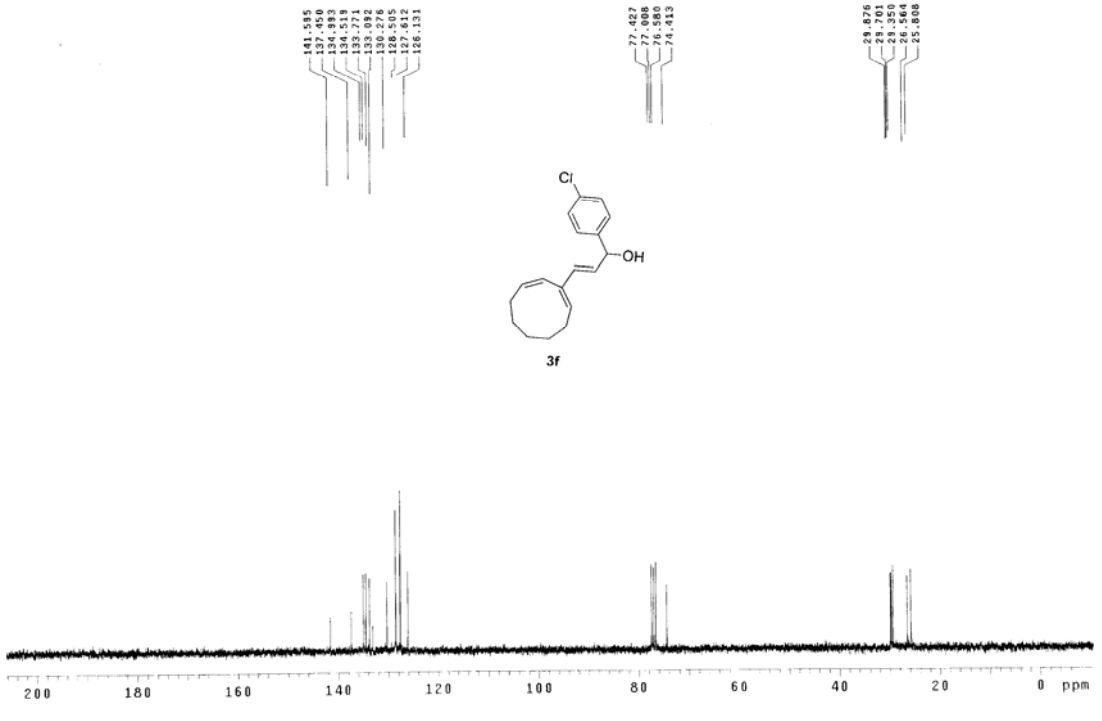
7
6
5
4
3
2
1
PPM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29.701
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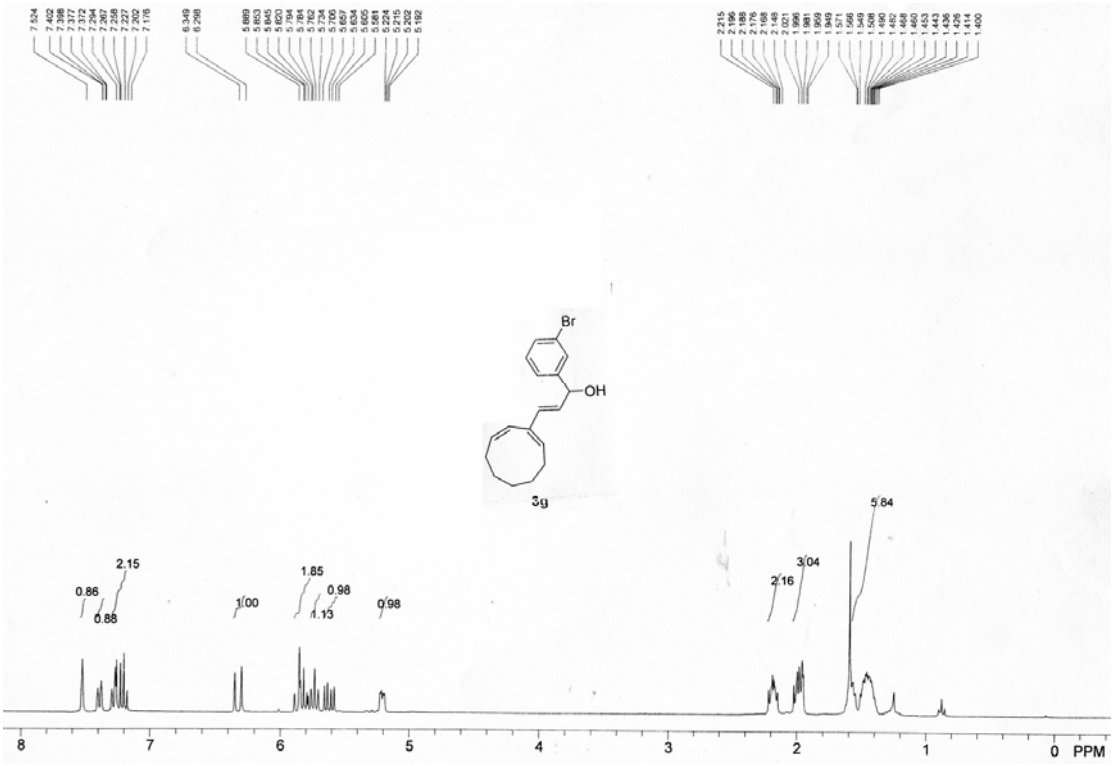
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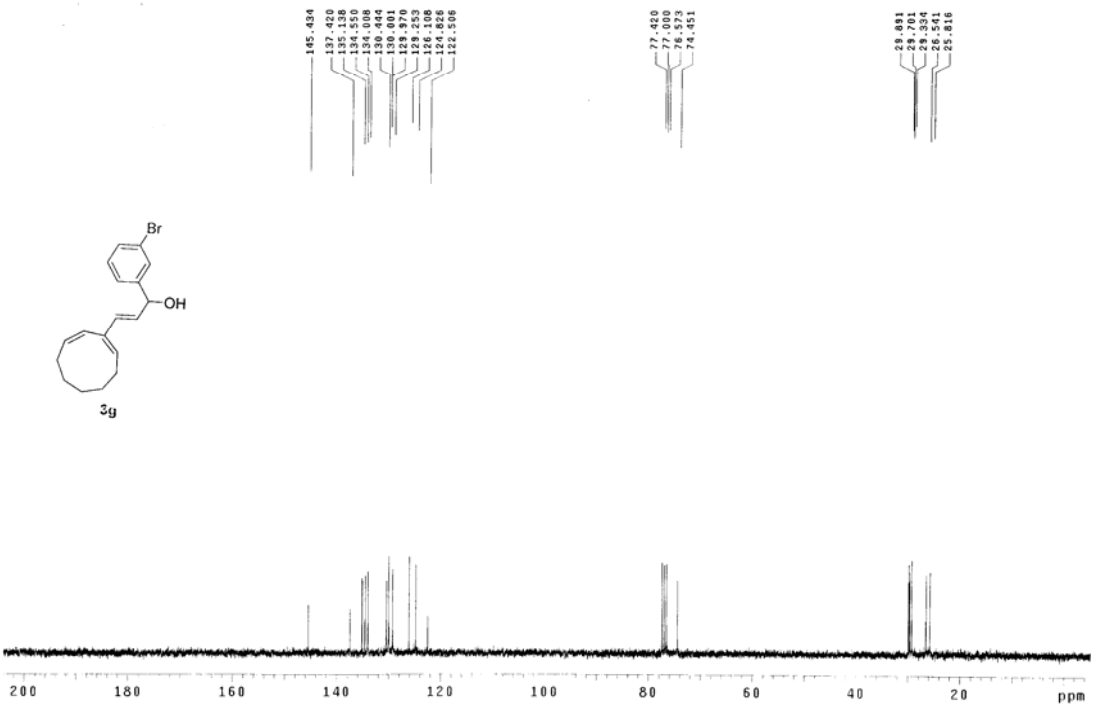
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120
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80
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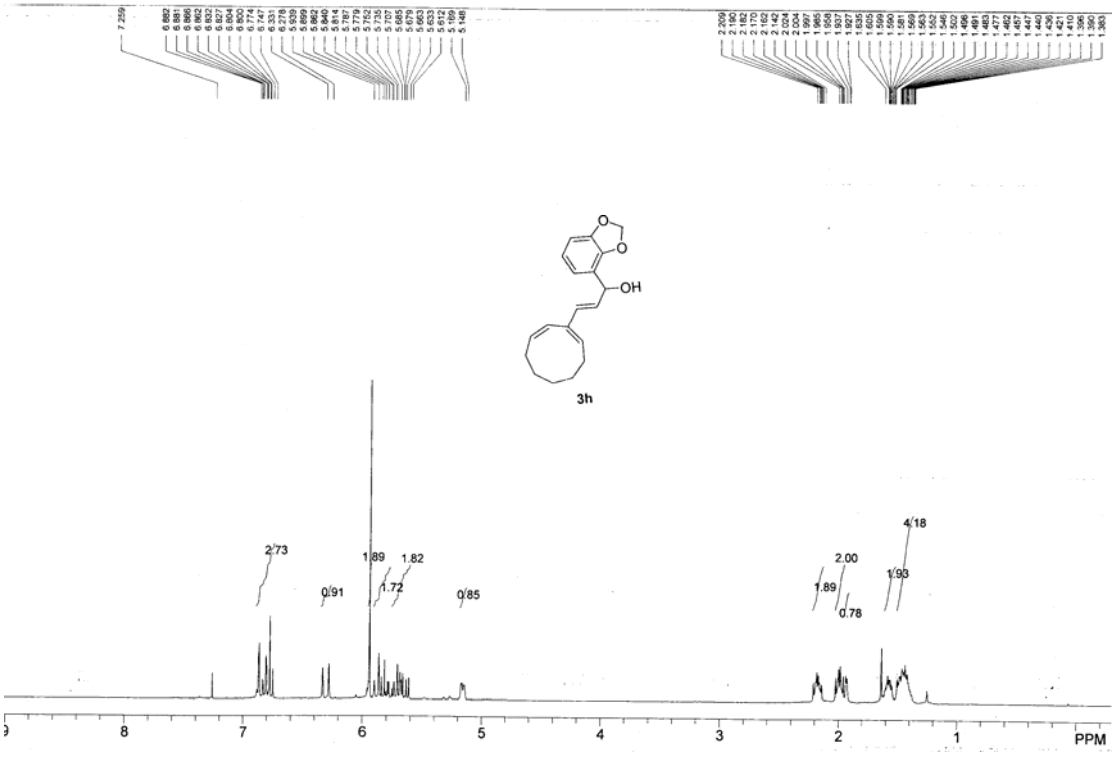
20
ppm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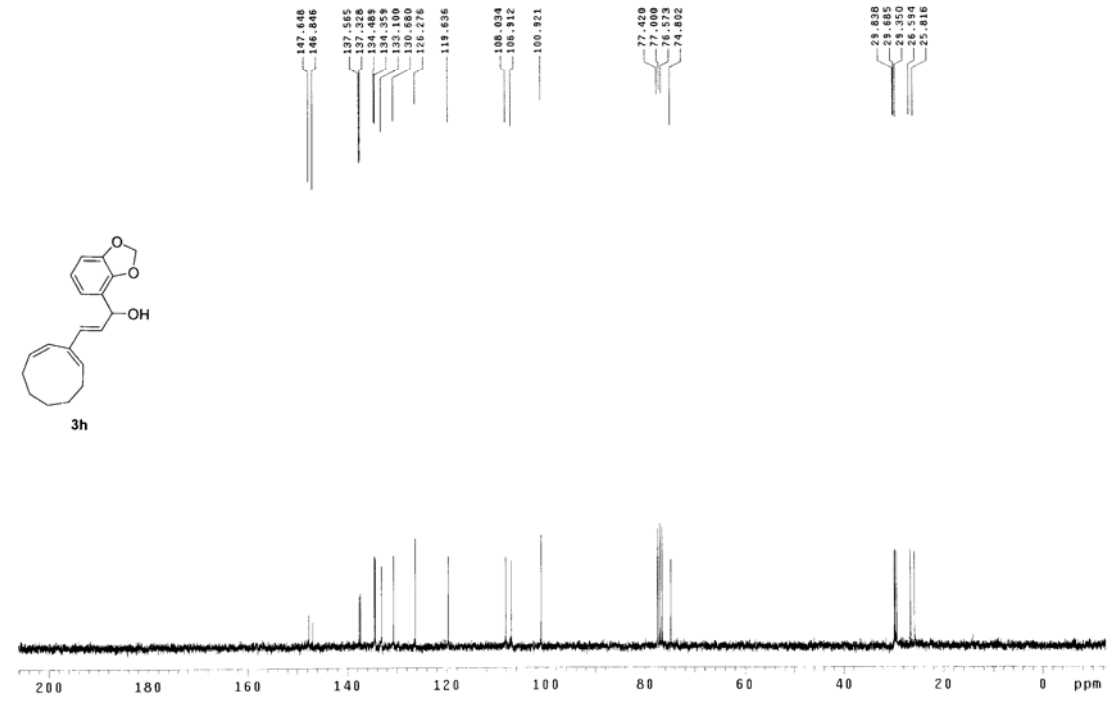
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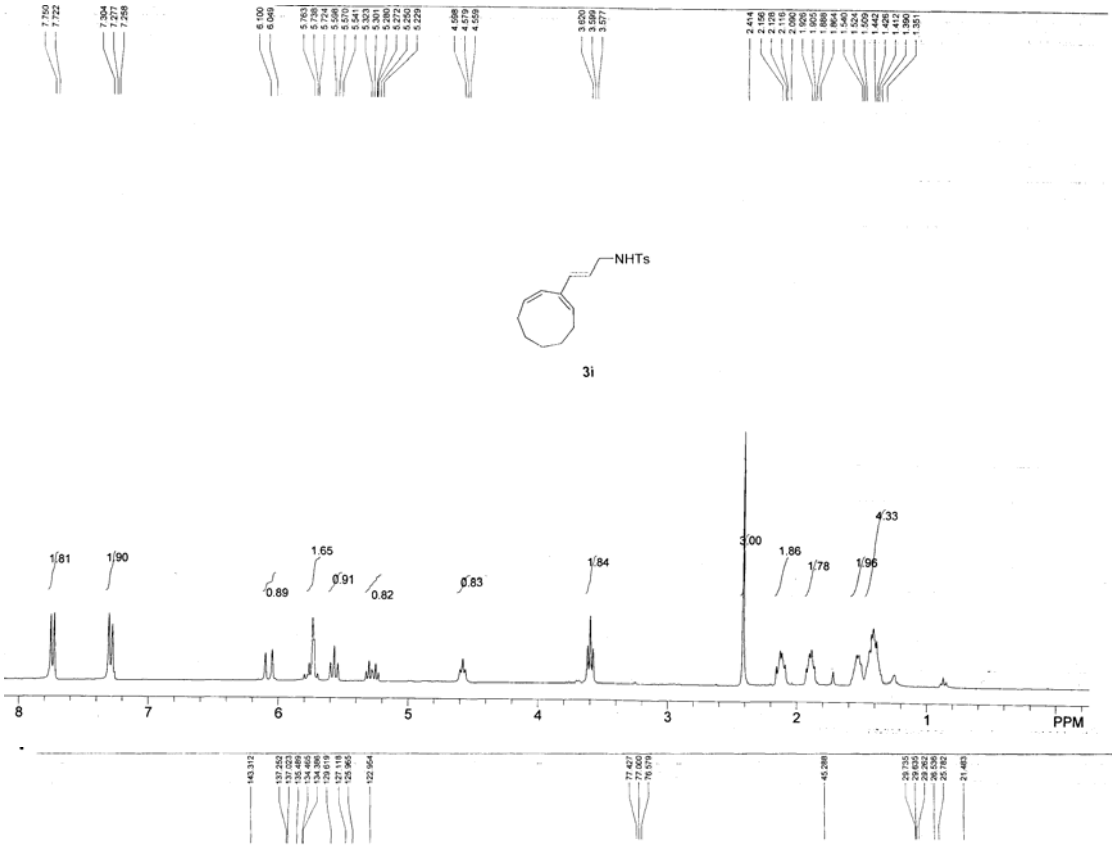
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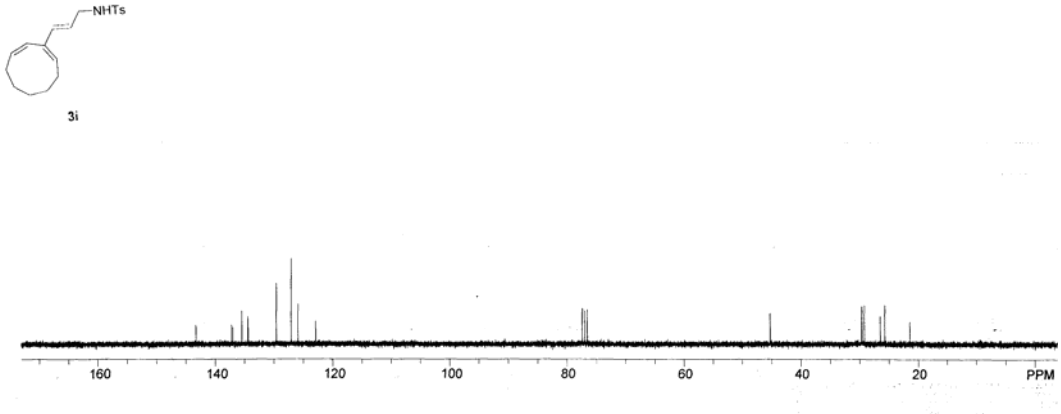
6
5
4
3
2
1
PPM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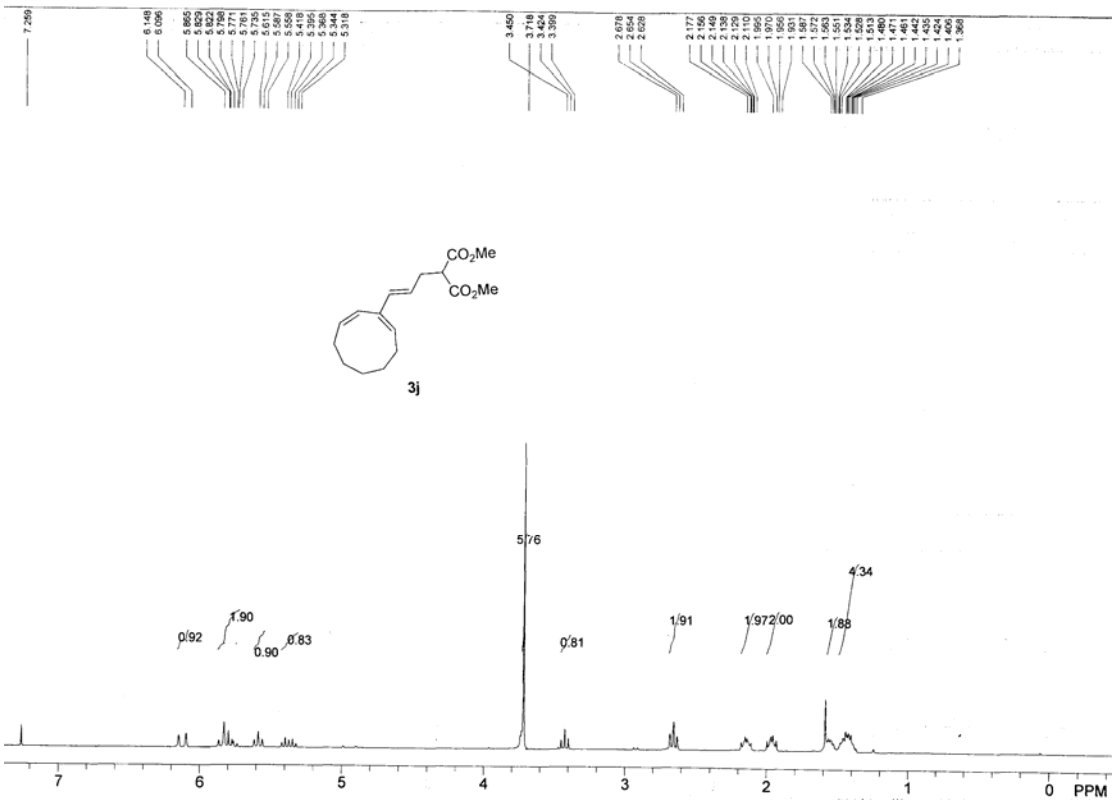
PPM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2.678
2.654
2.628
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1.442
1.435
1.424
1.405
1.368
CO2Me
CO2Me
3j
5.76
4.34
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0.92
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6
5
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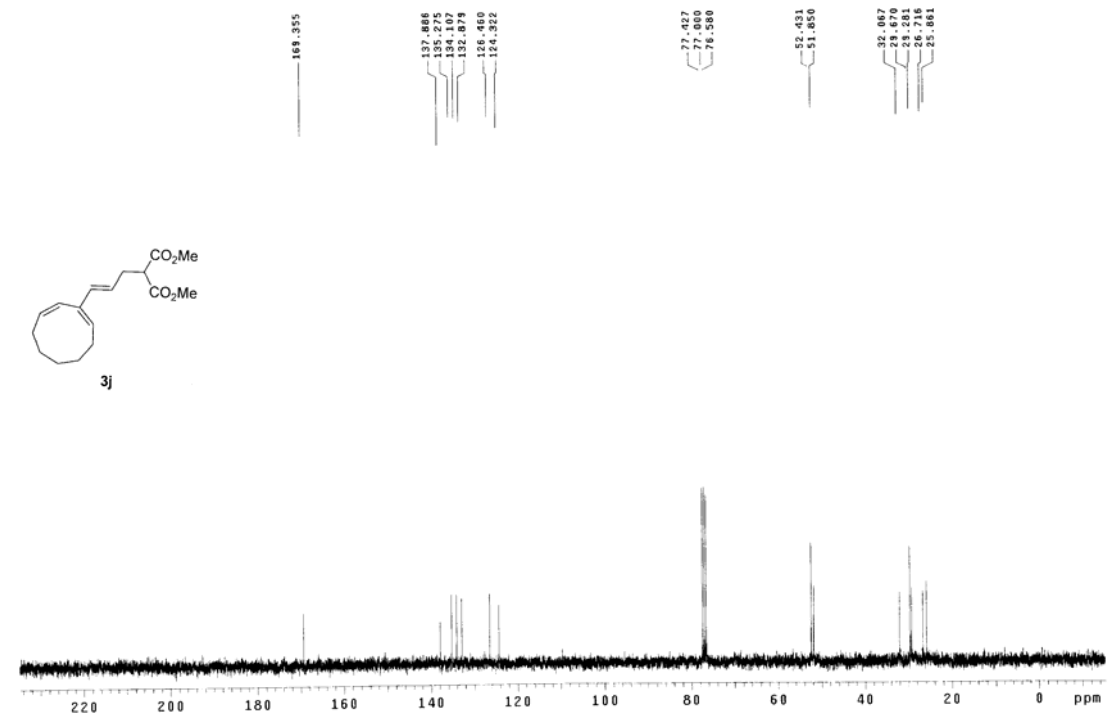
0
PPM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29.670
23.281
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CO2Me
3j
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200
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140
120
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60
40
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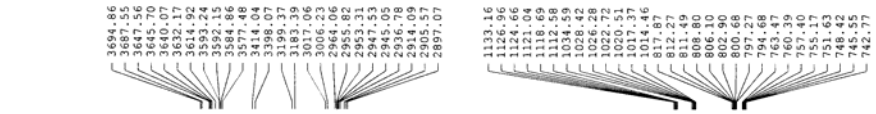
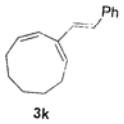
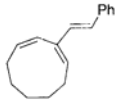
0
ppm





3k



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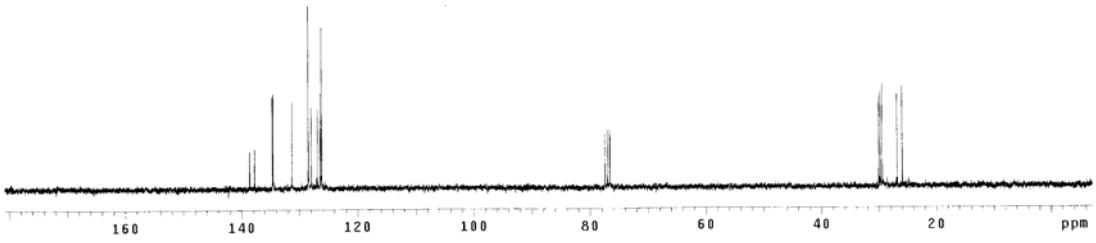
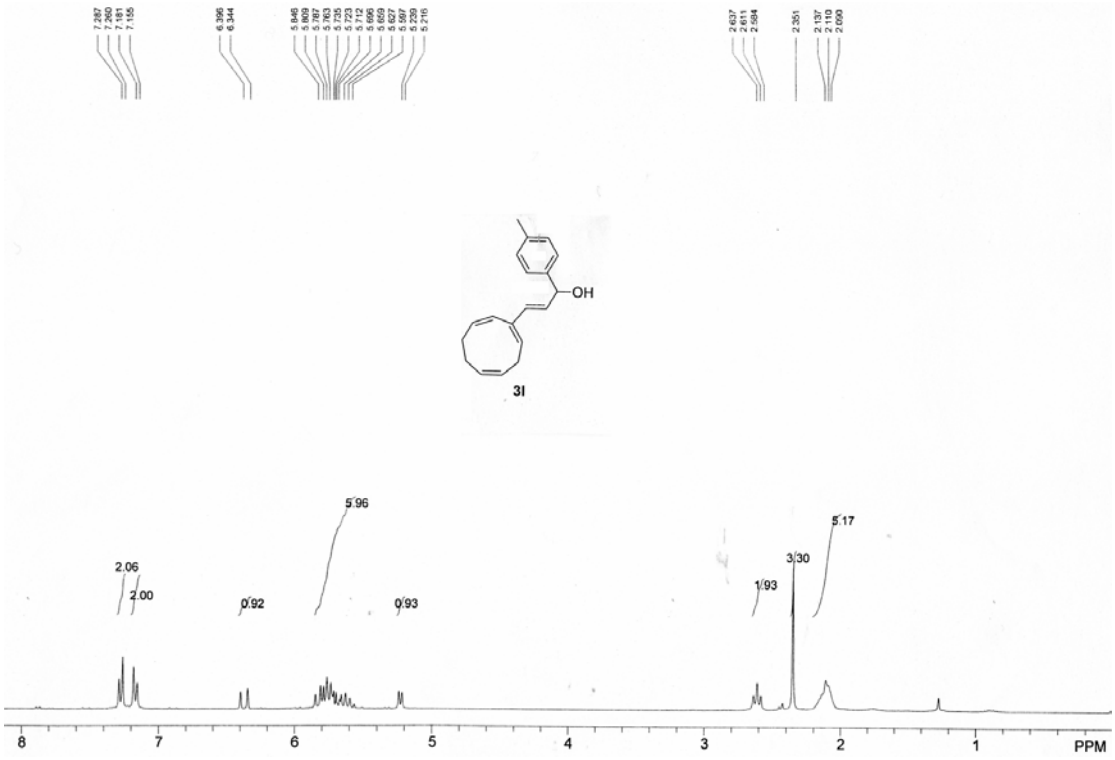
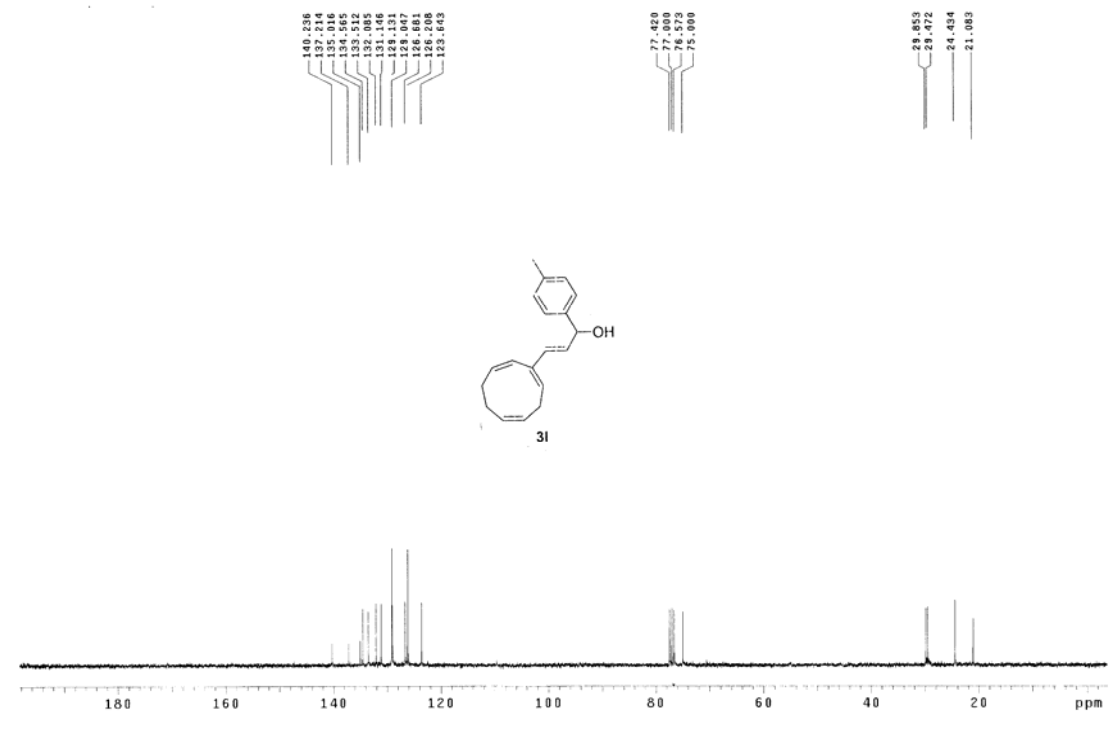
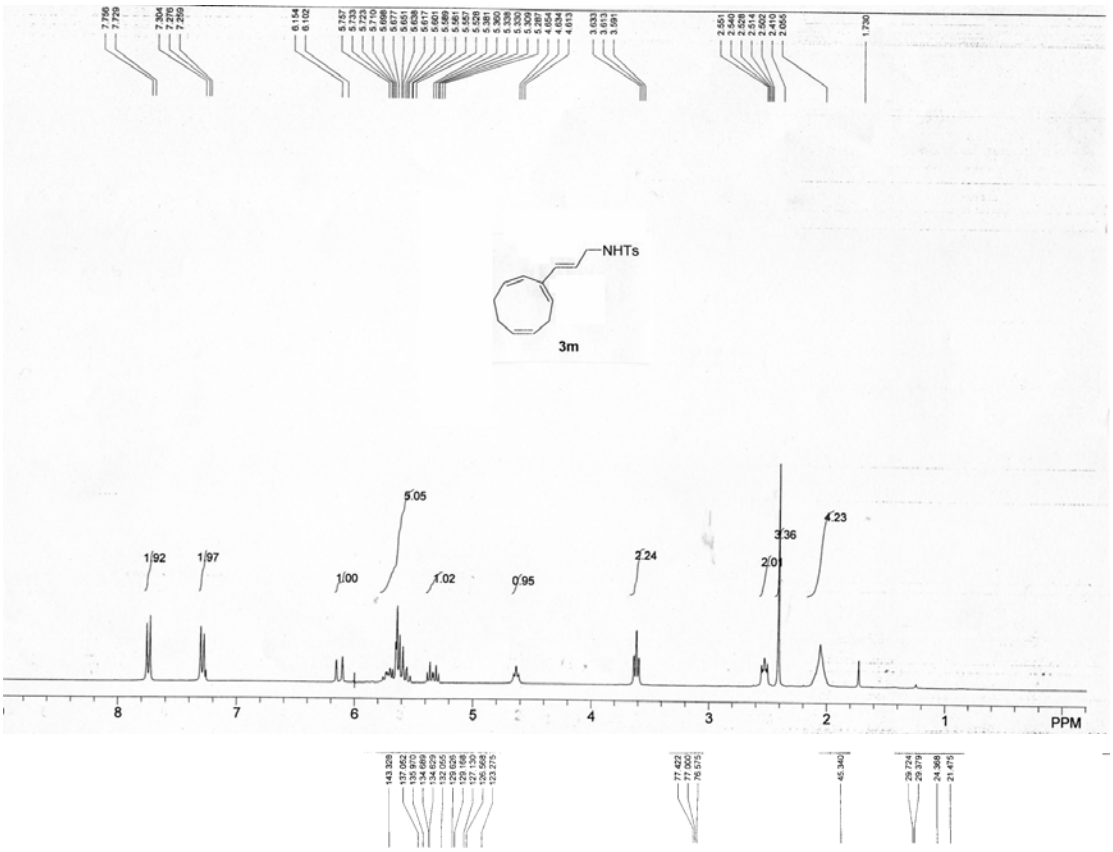
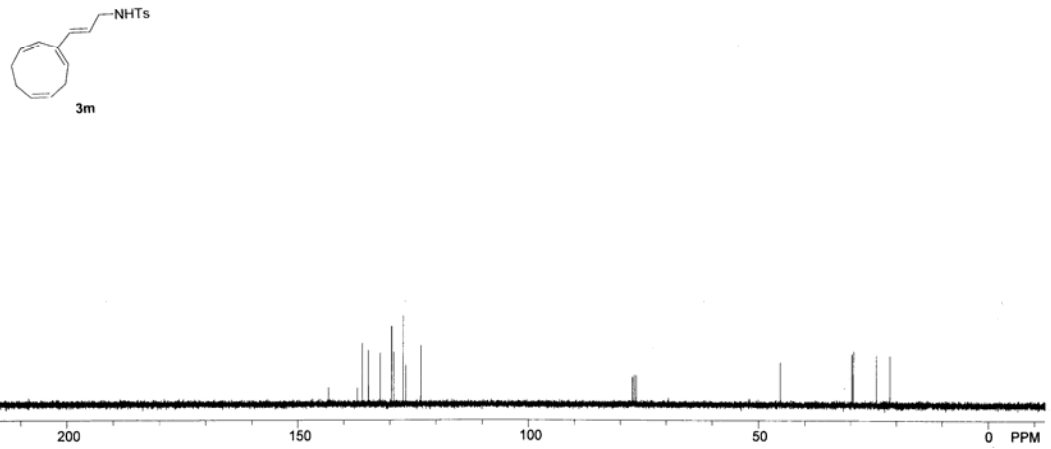
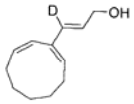



OH
3l
5.96
2.06
2.00
0.92
0.93
1.93
3.30
5.17
PPM

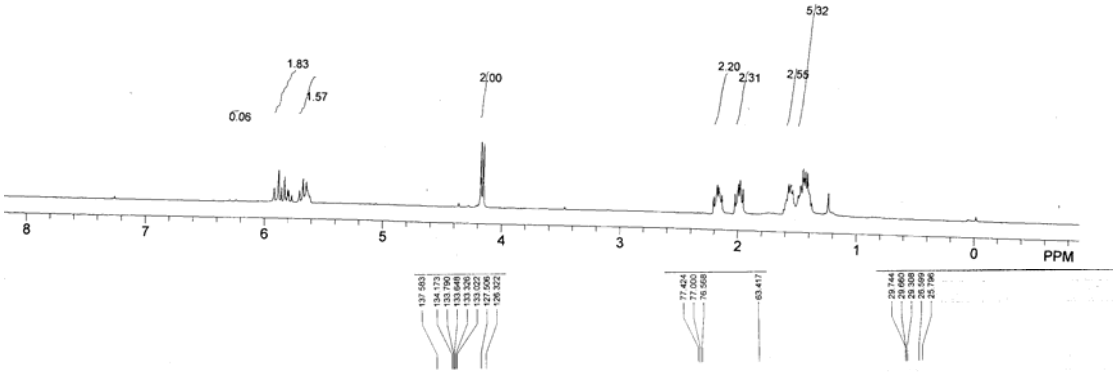

OH
3l
ppm

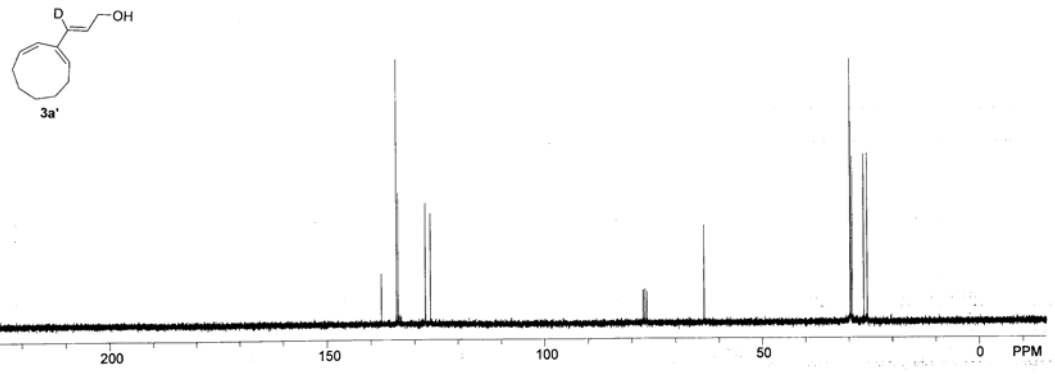

NHTs
3m
1.92
1.97
1.00
5.05
1.02
0.95
2.24
2.01
3.36
4.23
8
7
6
5
4
3
2
1
PPM


NHTs
3m
200
150
100
50
0
PPM



3a'

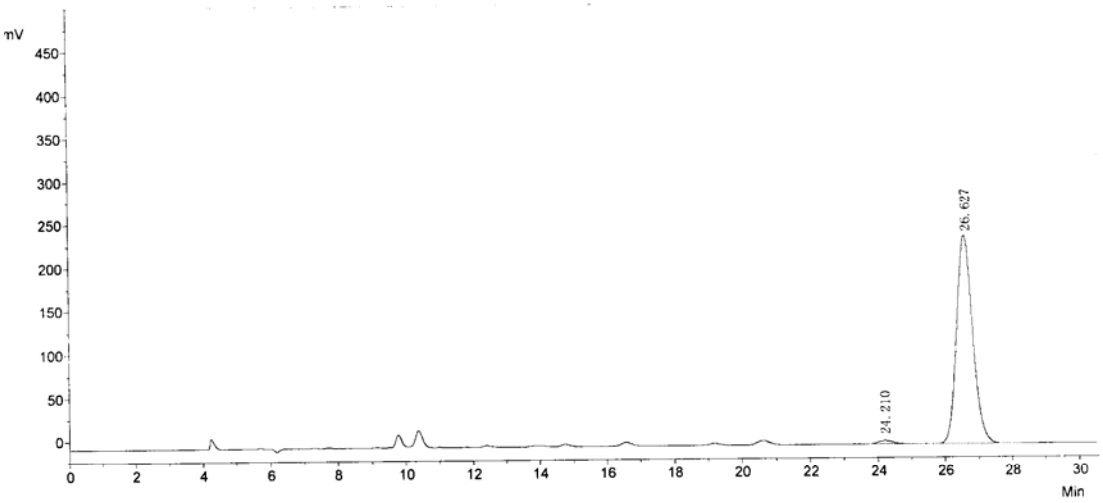




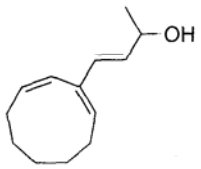
3a'

VI. HPLC data for compound (*R*)-3b.

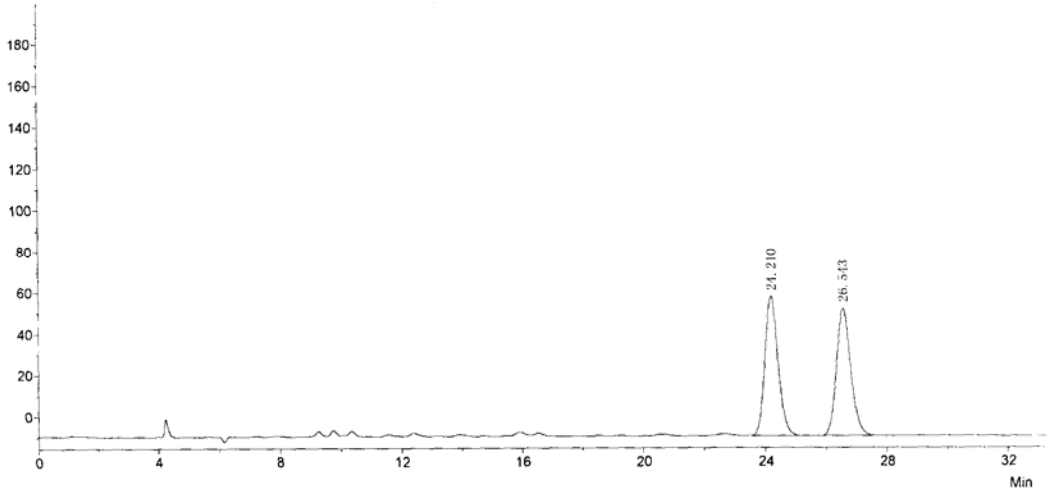
(*R*)-3b



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	24.210	4266.0	136174.5	1.6757
2	2	26.627	236487.3	7990374.9	98.3243
Total			240753.3	8126549.4	100.0000



3b



PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	24.210	66884.5	2006685.4	49.9324
2	26.543	61047.4	2012119.7	50.0676
11		127931.9	4018805.1	100.0000

PH 95:5 0.7 230nm