

Supporting Information

for

Domino ring-opening–ring-closing enyne metathesis vs enyne metathesis of norbornene derivatives with alkynyl side chains. Construction of condensed polycarbocycles

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Experimental and analytical data

Experimental section

General experimental methods are similar to [49].

Synthesis of diol 6. A solution of the known lactol **5** (1.1 g, 5.72 mmol) in anhydrous Et₂O (20 mL) was slowly added to a solution of propargyl magnesium bromide [prepared by adding propargyl bromide (1.97 mL, 22.89 mmol) to a mixture of magnesium turnings (550 mg, 22.88 mmol) and HgCl₂ (78 mg, 0.286 mmol) in Et₂O (20 mL)] at 0 °C for 30 min. The reaction was quenched by adding saturated aqueous solution of NH₄Cl (5 mL) and was filtered through celite. The celite was washed by Et₂O (3 × 30 mL). The combined filtrate was washed with brine (5 mL) and dried. The residue after evaporation of organic layer was purified by column chromatography (30% EA/PE) to provide the diol **6** (1.17 g, 88%) as an oil. ¹H NMR (300 MHz) δ 6.13-6.06 (2H, m), 4.02 (2H, brs), 3.58 (1H, q, *J* = 4.5 Hz), 3.51-3.43 (2H, m), 2.45-2.33 (4H, m), 2.11-2.01 (3H, m), 1.81-1.64 (3H, m), 1.49-1.35 (2H, m), 1.28-1.17 (1H, m); ¹³C NMR (75 MHz) δ 137.0, 135.0, 81.9, 73.4, 70.9, 67.4, 61.8, 61.1, 52.0, 51.7, 45.6, 36.5, 33.0, 28.7, 24.8; HRMS (ESI) *m/z* Calcd for C₁₅H₂₀O₂Na [M + Na]⁺ 255.1361, found 255.1363.

Synthesis of silyl ether 7a. In a similar manner to a procedure from [49] the diol **6** (1 g, 4.30 mmol) was silylated to afford the silyl ether **7a** (oil, 1.37 g, 92%) as an oil; ¹H NMR (300 MHz) δ 6.17 (1H, dd, *J* = 2.7, 5.7 Hz), 6.08 (1H, dd, *J* = 3, 5.7 Hz), 4.36 (1H, s), 3.58-3.49 (3H, m), 2.44-2.31 (4H, m), 2.21-2.14 (1H, m), 1.99 (1H, t, *J* = 2.7 Hz), 1.93-1.87 (1H, m), 1.85-1.64 (3H, m), 1.47-1.35 (2H, m), 1.26-1.16 (1H, m), 0.87 (9H, s), 0.07 (6H, s); ¹³C NMR (75 MHz) δ 136.2 (X 2), 83.0, 73.1, 69.3, 68.5, 62.9, 61.1, 52.0, 51.9, 45.8, 36.7, 33.2, 28.7, 25.9 (X3), 24.3, 18.3, -5.5, -5.6; HRMS (ESI) *m/z* Calcd for C₂₁H₃₄O₂SiNa [M + Na]⁺ 369.2226, found 369.2223.

Synthesis of norbornene derivative 7b. To a solution of the silyl ether **7a** (1.35 g, 3.90 mmol) in anhydrous DCM (15 mL) was added Et₃N (4.31 mL, 31.16 mmol), catalytic amount of 4-dimethylaminopyridine (DMAP) (10 mg) and acetic anhydride (1.47 mL, 15.58 mmol). The mixture was stirred for 72 h. On dilution with water (10 mL) the reaction mixture was extracted with Et₂O (3 × 50 mL). The combined extract was washed with brine and dried. The residue left after evaporation of solvent under vacuo was purified by column chromatography (10% EA/PE) to afford the acetate derivative **7b** as a colorless oil (1.17 g, 77%); IR: 2954, 1743, 1471, 1245 cm⁻¹; ¹H NMR (300 MHz) δ 6.26 (1H, dd, *J* = 3, 6 Hz), 6.17 (1H, dd, *J* = 3, 6 Hz), 4.73-4.70 (1H, m), 3.16-3.08 (2H, m), 2.74 (1H, s), 2.56-2.51 (1H, m), 2.50-2.43 (2H, m), 2.28-2.21 (1H, m), 2.01 (3H, m), 1.98-1.95 (1H, m), 1.83-1.67 (3H, m), 1.47-1.25 (4H, m), 0.88 (9H, s), -0.01 (3H, s), -0.02 (3H, s); ¹³C NMR (75 MHz) δ 170.0, 138.9, 135.1, 80.6, 74.4, 70.7, 67.0, 61.6, 61.1, 51.2, 49.4, 44.6, 36.6, 34.6, 27.8, 26.0 (X 3), 23.4, 21.3, 18.4, -5.4, -5.5; HRMS (ESI) *m/z* Calcd for C₂₃H₃₆O₃SiNa [M + Na]⁺ 411.2332, found 411.2330.

Synthesis of dinitrobenzoate derivative 13. A solution of the diene **11** (200 mg, 0.53 mmol) in DCM (10 mL) was treated with Et₃N (0.6 mL, 4.27 mmol), catalytic amount of DMAP (10 mg) and 3,5-dinitrobenzoyl chloride (493 mg, 2.14 mmol) was stirred at rt for 72 h. A saturated aqueous solution of NaHCO₃ (5 mL) was added to the reaction mixture. The reaction mixture was extracted with Et₂O (3 × 20 mL). The combined organic extract was washed with brine (5 mL) and dried. Evaporation of solvent under vacuo provided a viscous mass (178 mg). Without any purification and characterization this product was directly used for the next step. To a solution of this mass in THF (10 mL) was treated with 6 N HCl (20 mL) at rt for 3 h. The reaction mixture was extracted with diethyl ether (3 × 20 mL). The combined ether layer was washed with saturated NaHCO₃ (5 mL), brine (5 mL) and dried.

Evaporation of solvent under vacuo followed by column chromatography (20% EA/PE) of the residual mass provided the hydroxy-compound **13** (122mg, 51%) as a white solid which was crystallized (20% PE/DCM) to afford the pure compound **13**, m.p. 171-172 °C; IR: 2954, 1735, 1627, 1548 cm^{-1} ; ^1H NMR (300 MHz) δ 9.19 (1H, t, $J = 2.1$ Hz), 9.03-9.02 (2H, m), 6.39 (1H, dd, $J = 3, 6$ Hz), 6.35-6.34 (1H, m), 6.30-6.24 (1H, m), 5.34-5.28 (1H, m), 5.20-5.09 (2H, m), 4.94 (2H, d, $J = 6$ Hz), 3.38 (1H, d, $J = 10.2$ Hz), 3.15 (1H, d, $J = 10.2$ Hz), 2.80-2.75 (1H, m), 2.73-2.46 (4H, m), 2.06-1.28 (7H, m), 0.97-0.85 (1H, m); ^{13}C NMR (75 MHz) δ 161.5, 148.8, 142.4 (X 2), 138.6, 138.5, 135.2, 134.8, 129.3 (X 2), 122.2, 119.9, 114.0, 78.5, 66.9, 62.8, 61.0, 51.9, 50.2, 45.3, 36.3, 35.9, 34.6, 28.3; HRMS (ESI) m/z Calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_7$ $[\text{M} + \text{H}]^+$ 455.1818, found 455.1816.

Synthesis of diol 15. In a similar manner to a procedure from [49] the lactol **5** (1.0 g, 5.20 mmol) in THF (20 mL) was added to a solution of lithium (trimethylsilyl) acetylide. The crude product obtained as above was dissolved in dry MeOH (15 mL) and then K_2CO_3 (1.44 g, 10.40 mmol) was added to it. The mixture was stirred for 2 h and was filtered through celite. The celite bed was washed with Et_2O (20 mL). Then the filtrate was evaporated under vacuo and the residue was purified by column chromatography (30% EA/PE) to afford the diol **15** (1.02 g, 90%) as a liquid; ^1H NMR (300 MHz) δ 6.18 (1H, s), 6.12 (1H, s), 4.86 (1H, brs), 4.22 (1H, brs), 4.16 (1H, s), 3.46 (2H, dd, $J = 11.4, 35.7$ Hz), 2.67 (1H, s), 2.42 (1H, s), 2.36 (1H, s), 2.31-2.25 (1H, m), 2.07-2.01 (1H, m), 1.83-1.76 (2H, m), 1.74-1.61 (1H, m), 1.54-1.37 (3H, m); ^{13}C NMR (75 MHz) δ 136.6, 136.2, 84.3, 72.9, 67.7, 67.4, 63.0, 60.0, 52.9, 52.3, 45.5, 36.7, 34.6, 28.6; HRMS $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 219.1385, found 219.1386.

Synthesis of silyl ether 16. In a similar manner to a procedure from [49] the diol **15** (995 mg, 4.56 mmol) was converted to the silyl ether **16** as colorless oil (1.44 g, 95%); ^1H NMR (300

MHz) δ 6.19 (1H, s), 6.07-6.06 (1H, m), 4.70 (1H, s), 4.15 (1H, s), 3.55 (1H, d, J = 10.5, Hz), 3.41 (1H, d, J = 10.5 Hz), 2.66 (1H, s), 2.37-2.32 (3H, m), 1.91-1.63 (4H, m), 1.50-1.32 (3H, m), 0.84 (9H, s), 0.04 (3H, s), 0.03 (3H, s). ^{13}C NMR (75 MHz) δ 136.6, 135.9, 84.3, 71.9, 68.7, 67.3, 63.3, 60.0, 52.9, 52.2, 45.6, 36.9, 34.6, 28.6, 25.8 (X 3), 18.1, -5.6, -5.7; HRMS: $\text{C}_{20}\text{H}_{32}\text{O}_2\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 355.2069, found 355.2068.

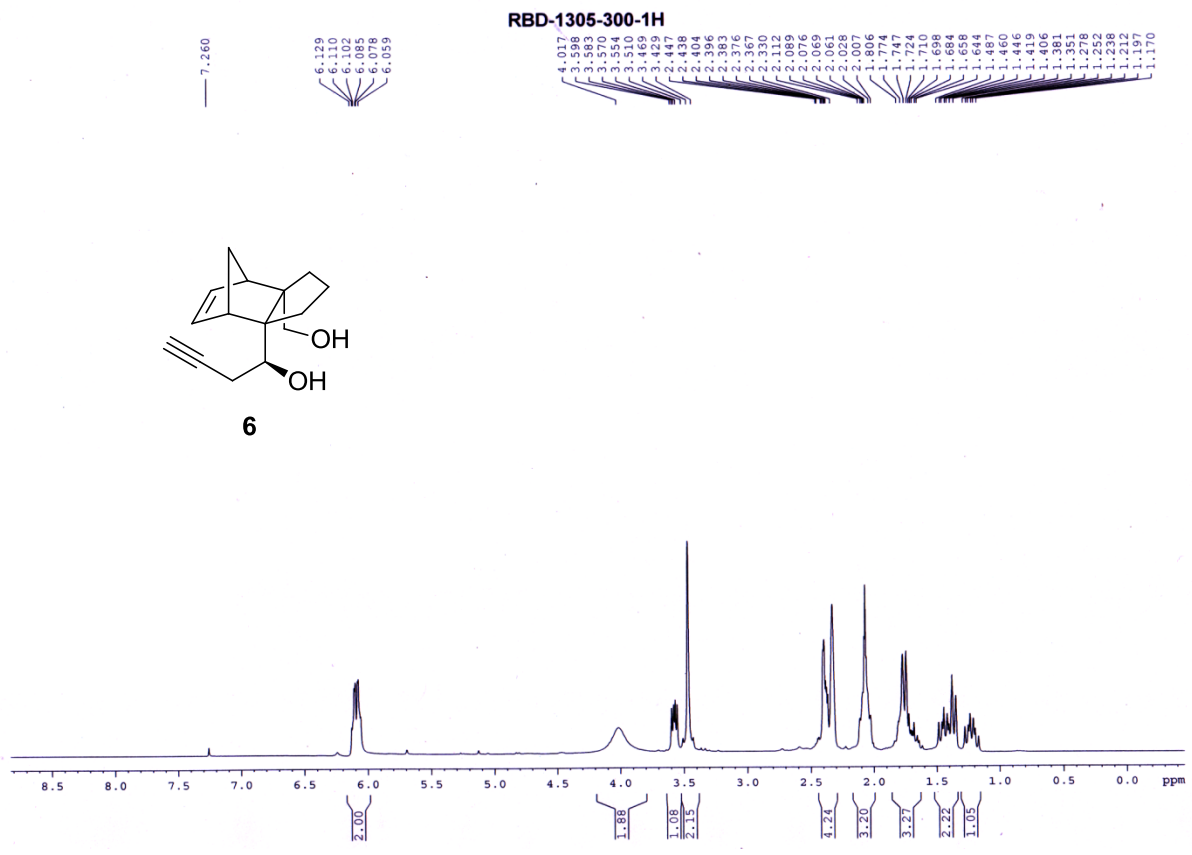
Synthesis of acetate 17. Following the procedure described for synthesis of the acetyl derivative **7b**, the carbinol **16** (800 mg, 2.41 mmol) was converted to the norbornene derivative **17** as colorless oil (739 mg, 83%) using acetic anhydride (0.91 mL, 9.62 mmol) and Et_3N (2.66 mL, 19.24 mmol) after purification by column chromatography (10% EA/PE). The acetate displayed the following spectral data: IR: 2955, 1747, 1469, 1228 cm^{-1} ; ^1H NMR (300 MHz) δ 6.22-6.21 (2H, m), 4.85 (1H, d, J = 1.8 Hz), 3.18 (1H, d, J = 8.7 Hz), 2.98 (1H, dd, J = 9, 1.5 Hz), 2.72 (2H, dd, J = 11.1, 1.2 Hz), 2.39 (1H, d, J = 2.1 Hz), 2.29-2.27 (1H, m), 2.01 (3H, s), 1.98-1.92 (1H, m), 1.82-1.68 (3H, m), 1.56-1.23 (3H, m), 0.86 (9H, s), -0.04 (6H, s); ^{13}C NMR (75 MHz) δ 169.5, 138.4, 135.6, 81.2, 73.2, 69.0, 66.2, 61.5, 60.1, 51.9, 49.8, 44.4, 36.5, 36.0, 27.5, 25.9 (X 3), 21.0, 18.3, -5.4, -5.6; HRMS: $\text{C}_{22}\text{H}_{35}\text{O}_3\text{Si}$ $[\text{M} + \text{H}]^+$ 375.2355, found 375.2351.

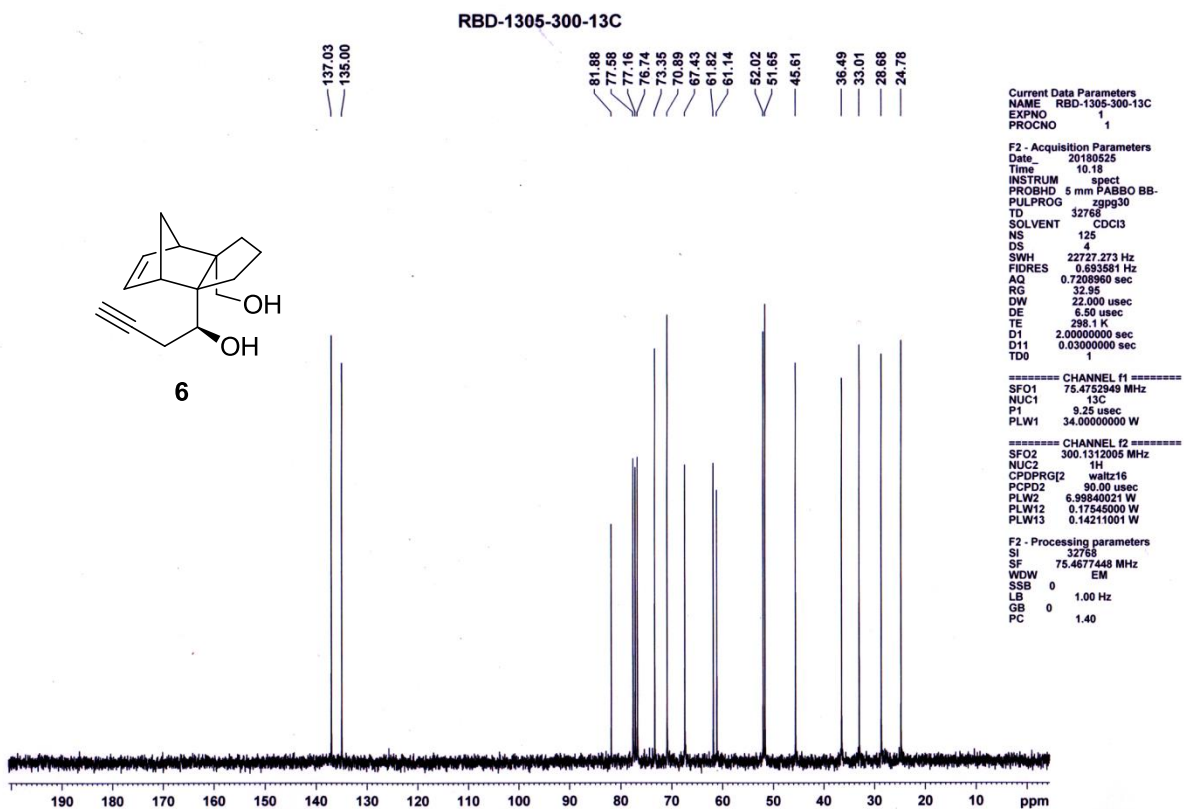
Synthesis of the diyne 18. In a similar manner to a procedure from [49] the norbornene derivative **17** (600 mg, 1.60 mmol) was subjected to cleavage to afford the corresponding bis-aldehyde. A solution of methyl triphenyl phosphonium bromide (2.29 g, 6.41 mmol) in THF (20 mL) was treated with KHMDS [0.5 (M) in toluene] (16.0 mL, 8.01 mmol) at 0 °C for 30 min. To it a solution of the bis-aldehyde obtained above in THF (10 mL) was added at 0 °C for 1 h. The reaction was quenched by saturated aqueous NH_4Cl (5 mL). The resulting mixture was extracted with Et_2O (3 \times 30 mL). The combined ether layer was washed with brine (5 mL) and dried. Solvent was evaporated under reduced pressure and purified by

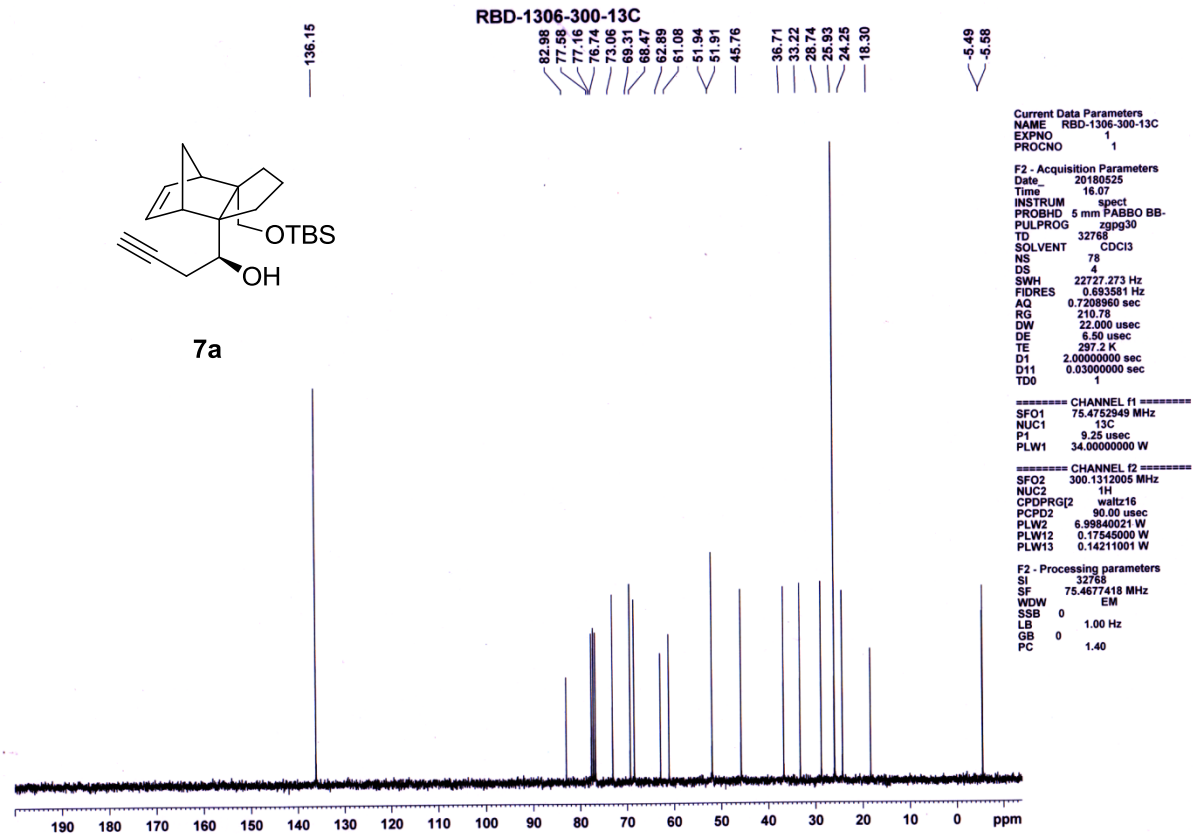
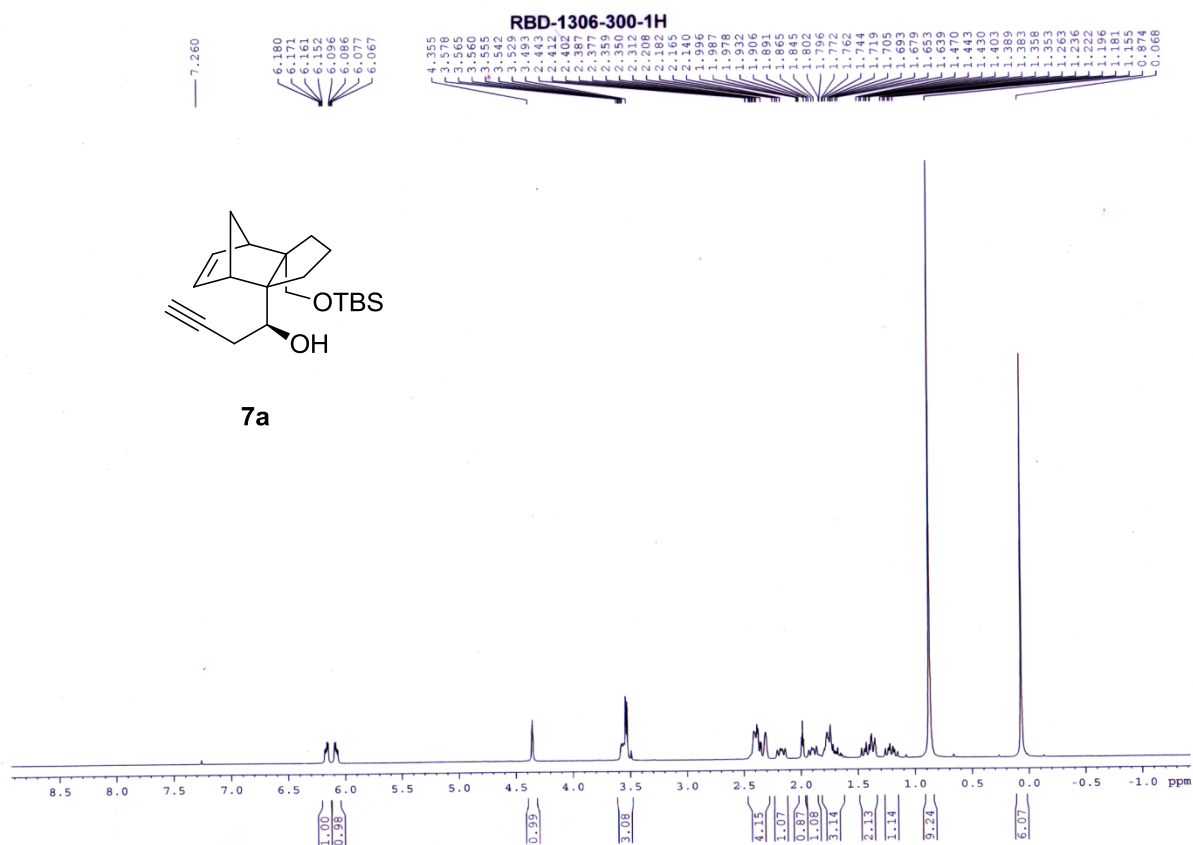
column chromatography (8% EA/PE) to afford the dienyne **18** (420 mg, 66%) as an oil; IR: 2954, 1743, 1471, 1238 cm^{-1} ; ^1H NMR (400 MHz) δ 6.24-6.11 (1H, m), 5.90-5.87 (1H, m), 5.76 (1H, s), 5.01-4.93 (4H, m), 4.03 (1H, d, $J = 10.4$ Hz), 3.52 (1H, d, $J = 10.4$ Hz), 2.47 (1H, d, $J = 2.4$ Hz), 2.34-2.26 (2H, m), 2.02 (3H, s), 1.77-1.61 (7H, m), 1.54-1.51 (1H, m), 0.90 (9H, s), 0.06 (3H, s), 0.03 (3H, s); ^{13}C NMR (100 MHz) δ 169.5, 139.3, 139.1, 115.0, 114.7, 82.1, 75.2, 67.2, 64.2, 60.6, 60.5, 54.1, 53.2, 38.9, 37.6, 36.4, 26.0 (X 3), 21.8, 21.1, 18.4, -5.5, -5.6; HRMS (ESI) m/z Calcd for $\text{C}_{24}\text{H}_{38}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 425.2488, found 425.2487.

Crystal data for compound **13**

Compound reference	13
Chemical formula	$\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_7$
Formula Mass	454.47
Crystal system	Triclinic
$a/\text{\AA}$	8.25(2)
$b/\text{\AA}$	10.46(2)
$c/\text{\AA}$	13.93(3)
$\alpha/^\circ$	77.91(4)
$\beta/^\circ$	76.47(4)
$\gamma/^\circ$	85.92(4)
Unit cell volume/ \AA^3	1142(5)
Temperature/K	293(2)
Space group	$P1, \bar{1}$
No. of formula units per unit cell, Z	2
Radiation type	MoK α
Absorption coefficient, μ/mm^{-1}	0.098
No. of reflections measured	3415
No. of independent reflections	2381
R_{int}	0.0399
Final R_I values ($I > 2\sigma(I)$)	0.1576
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.4564
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Goodness of fit on F^2	1.845
CCDC number	1847091







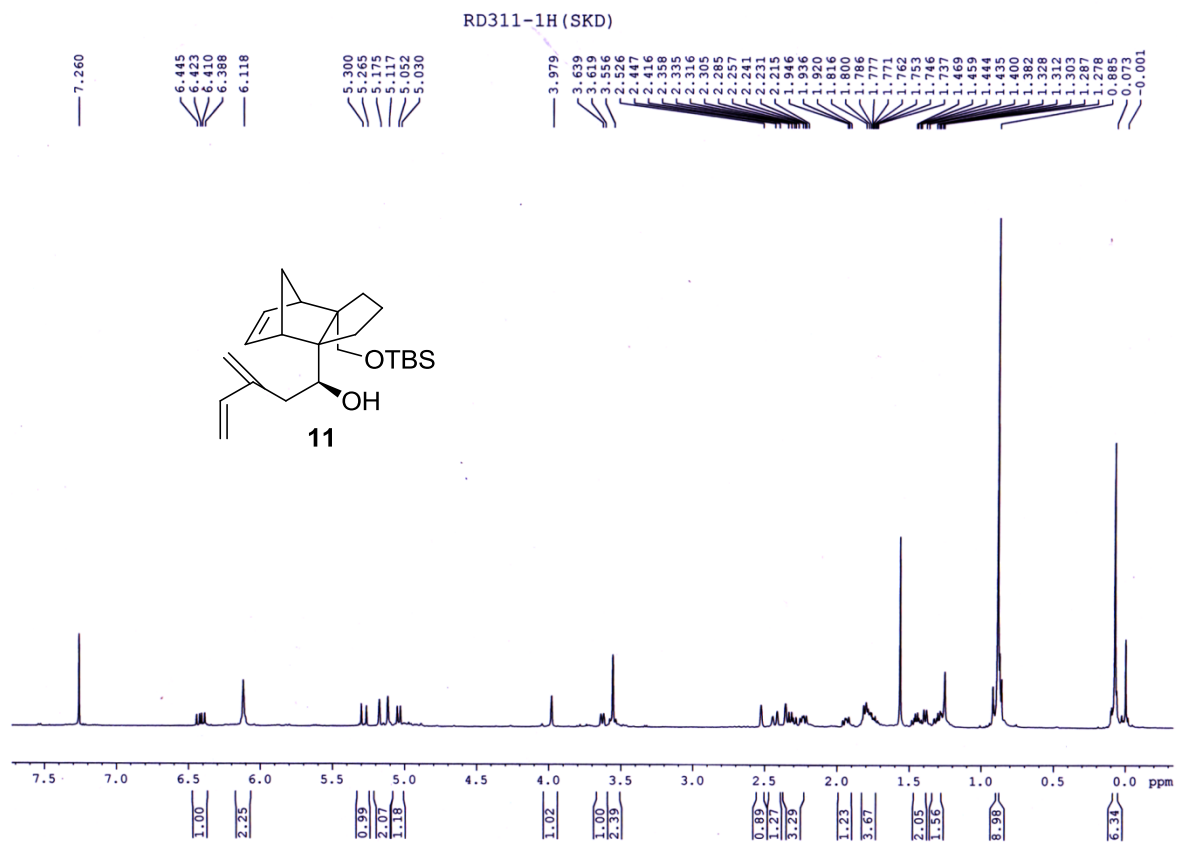
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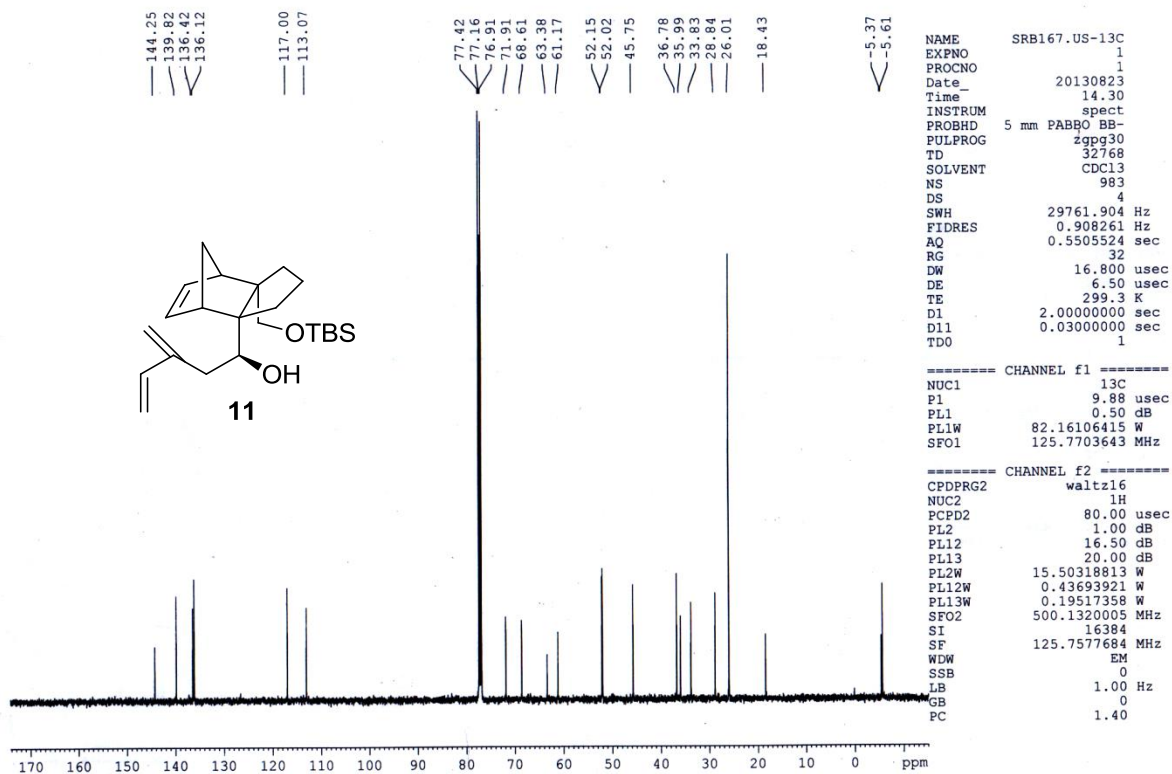
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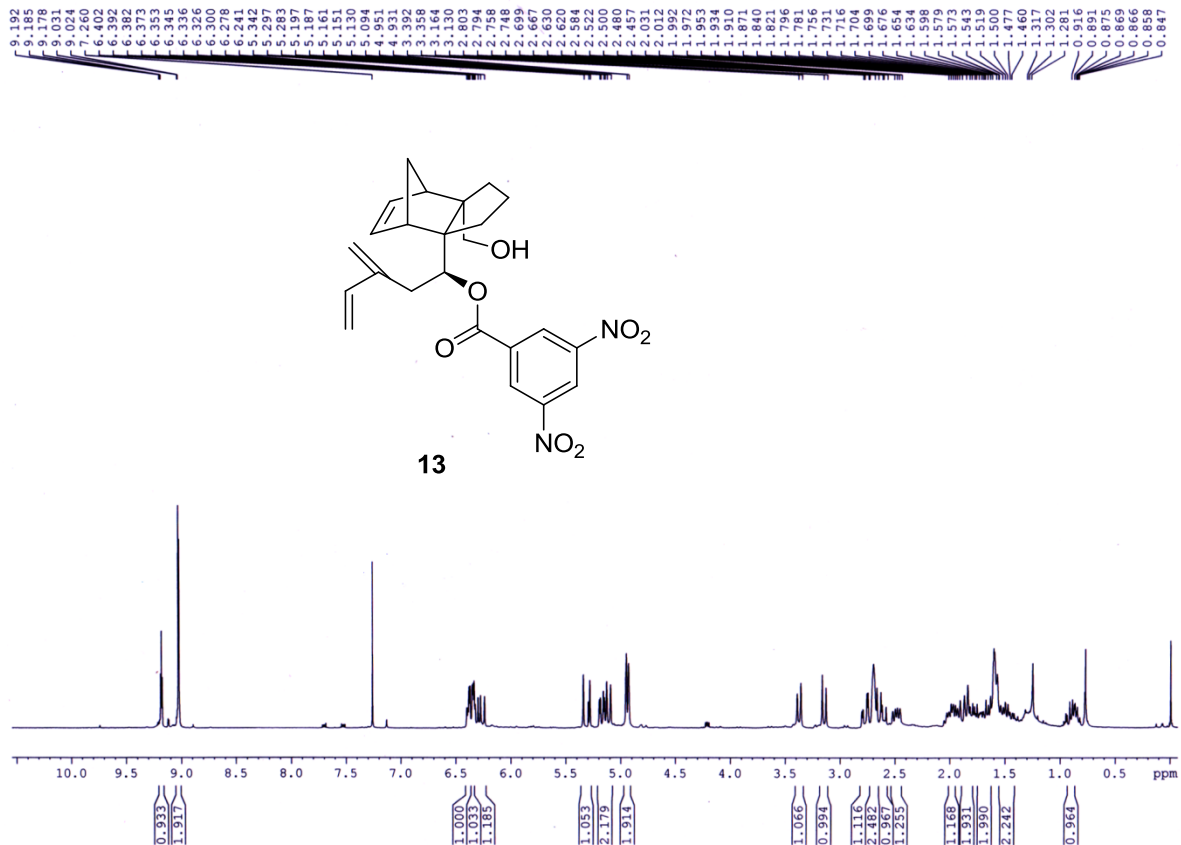
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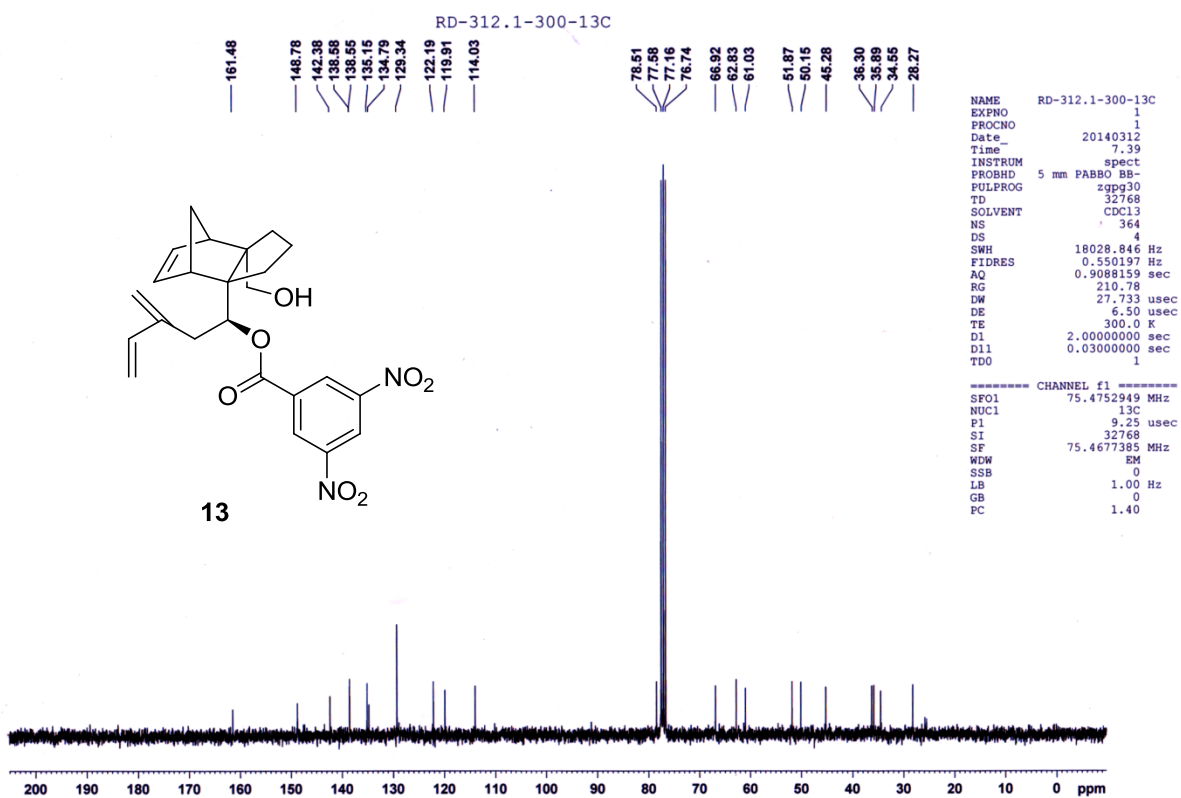


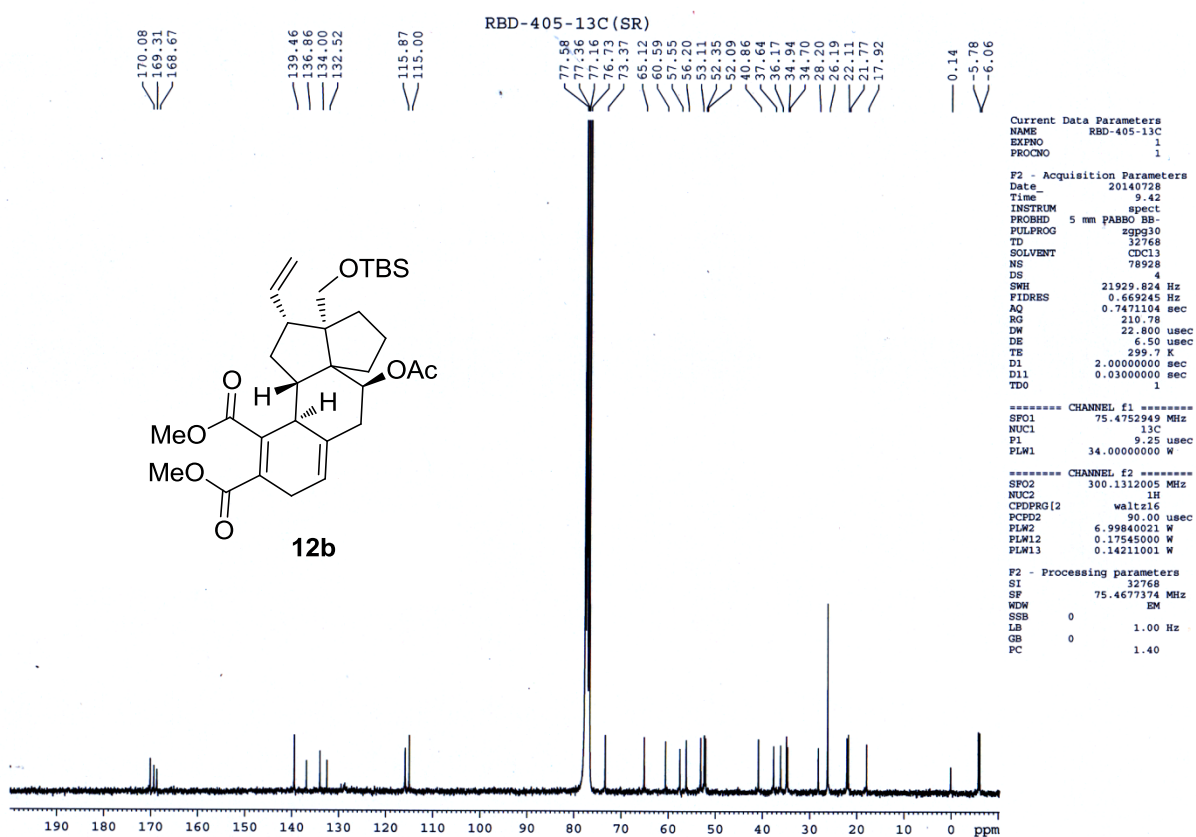
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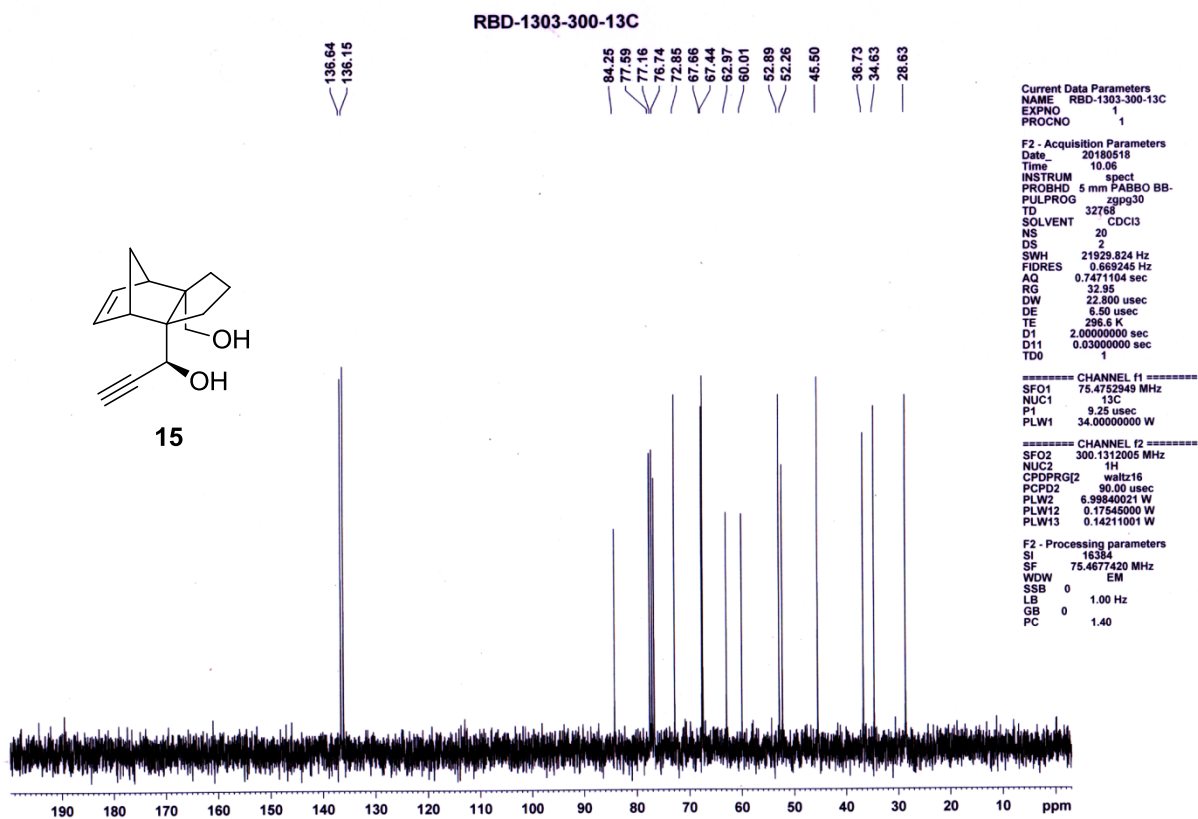
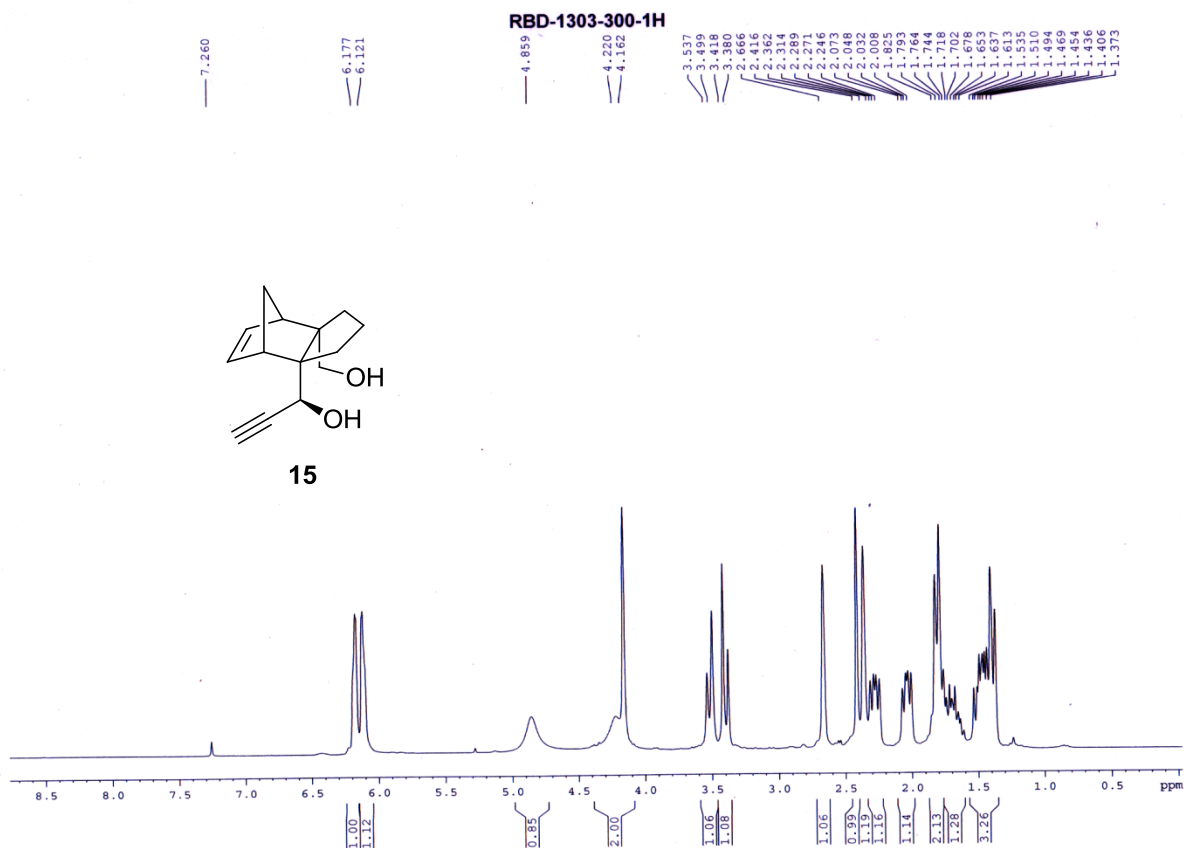


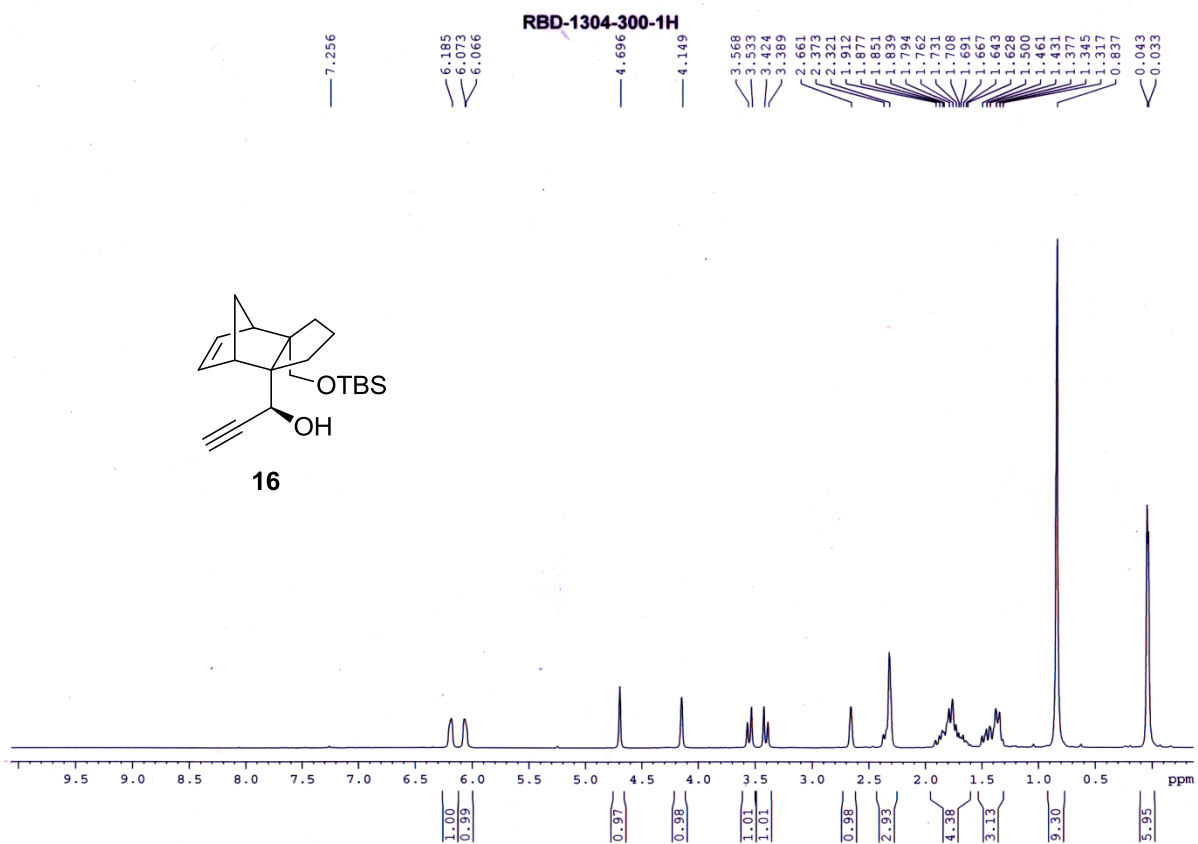
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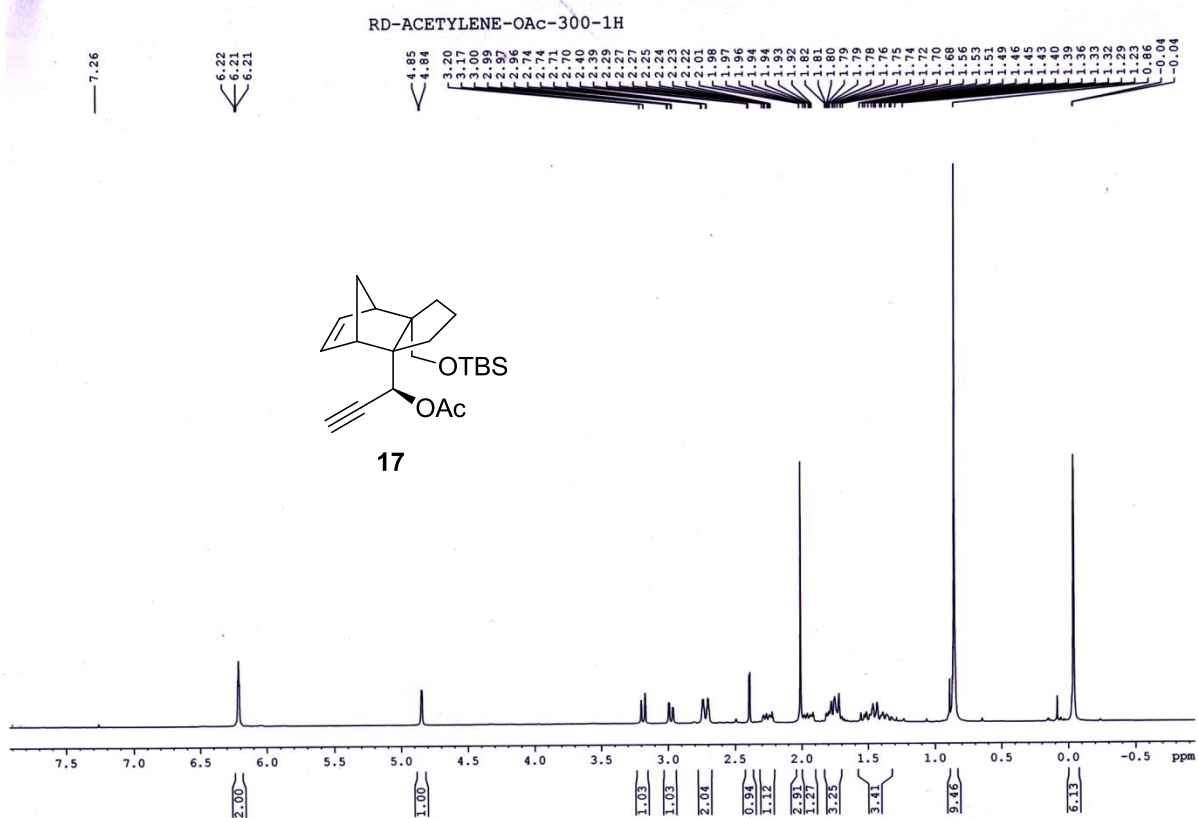
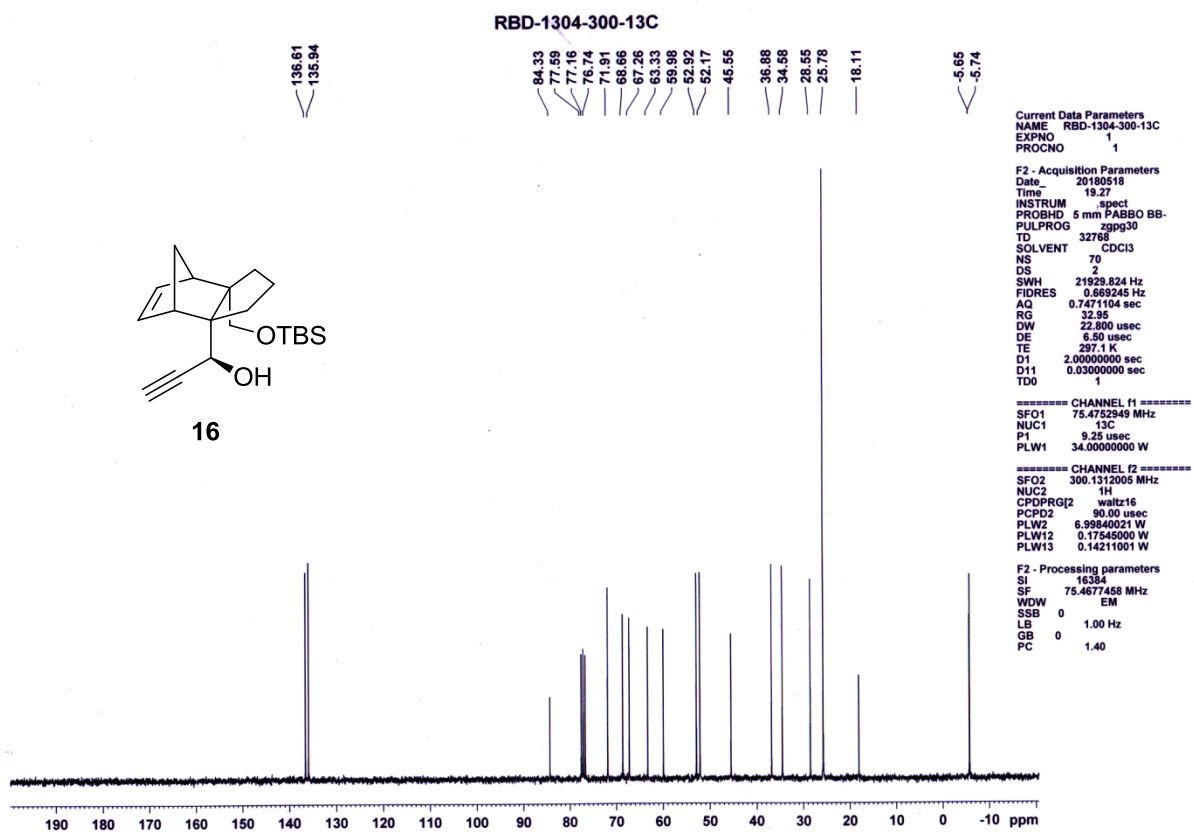




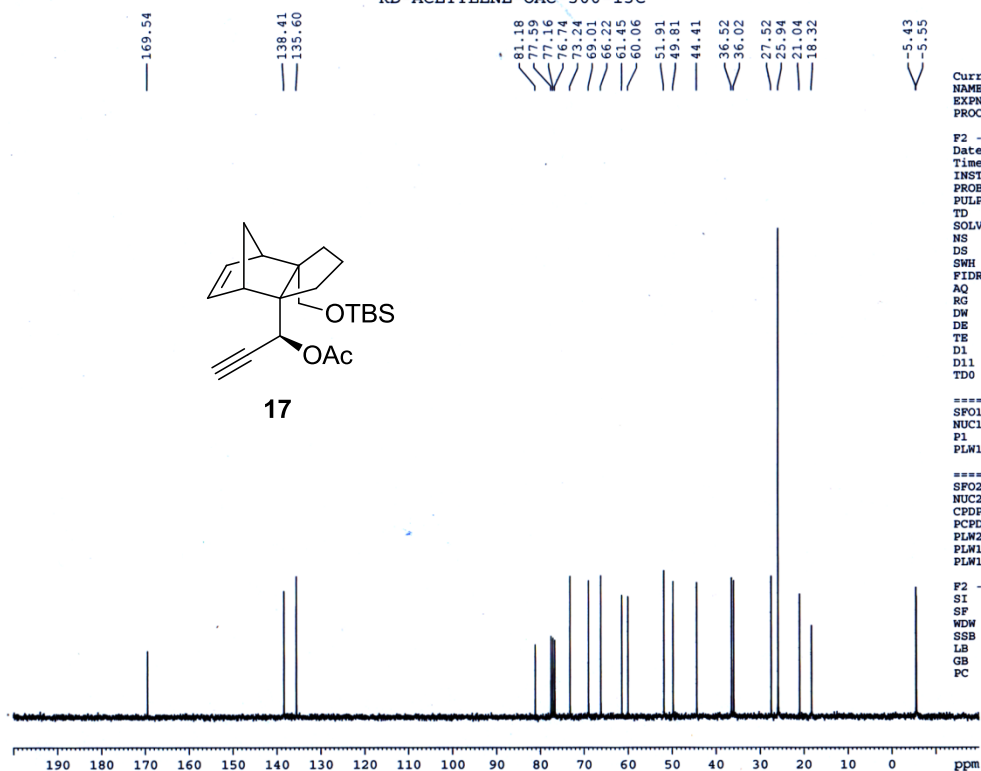








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