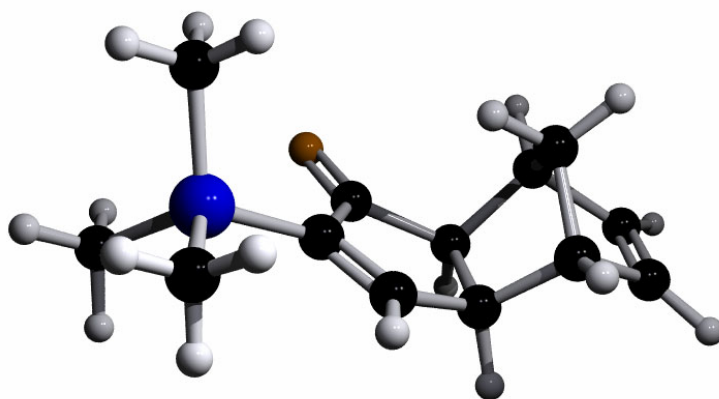


Tesi doctoral

Departament de Química Orgànica

**“Aplicacions sintètiques dels adductes de
Pauson-Khand del norbornadiè. Aproximació a
la síntesi de prostaglandines i fitoprostans.”**



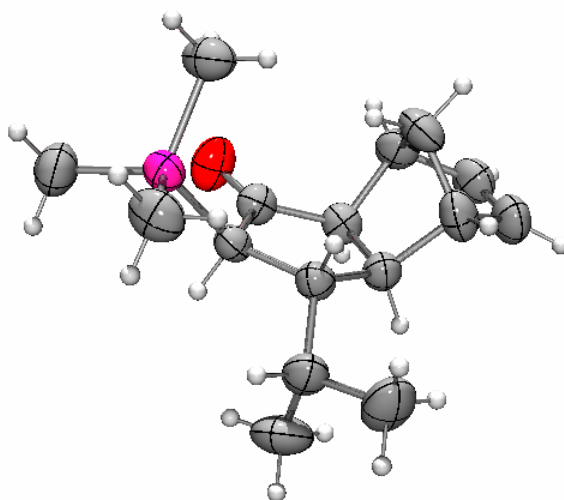
Agustí Lledó Ponsati



UNIVERSITAT DE BARCELONA



11. Apèndix I. Dades de difracció de raigs X

**Table 1.** Crystal data and structure refinement for **39**.

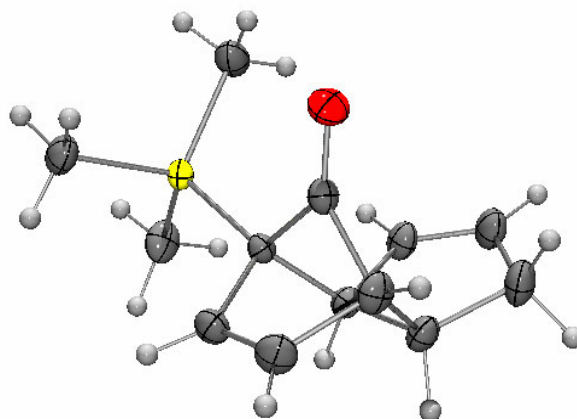
Identification code	ALP129	
Empirical formula	$C_{16}H_{26}OSi$	
Formula weight	262.46	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 8.689(7)$ Å	$\alpha = 92.825(14)^\circ$.
	$b = 9.239(7)$ Å	$\beta = 108.874(14)^\circ$.
	$c = 11.965(9)$ Å	$\gamma = 116.102(12)^\circ$.
Volume	$795.2(11)$ Å ³	
Z	2	
Density (calculated)	1.096 Mg/m ³	
Absorption coefficient	0.137 mm ⁻¹	
F(000)	288	
Crystal size	$0.44 \times 0.25 \times 0.07$ mm ³	
Theta range for data collection	2.52 to 28.31° .	
Index ranges	$-6 \leq h \leq 11$, $-12 \leq k \leq 12$, $-$	
	$15 \leq l \leq 11$	
Reflections collected	4739	
Independent reflections	3566 [R(int) = 0.0194]	
Completeness to theta = 28.31°	89.8 %	

Absorption correction	Semi-empirical
Max. and min. transmission	0.9905 and 0.9424
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3566 / 0 / 163
Goodness-of-fit on F^2	1.071
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0450, wR2 = 0.1180
R indices (all data)	R1 = 0.0649, wR2 = 0.1269
Largest diff. peak and hole	0.191 and $-0.161 \text{ e.}\text{\AA}^{-3}$

Table 2. Bond lengths [\AA] and angles [$^\circ$] for **39**.

Si(1)-C(15)	1.848(2)	C(4)-C(5)	1.515(3)
Si(1)-C(16)	1.859(2)	C(4)-C(6)	1.556(3)
Si(1)-C(14)	1.862(2)	C(6)-C(7)	1.536(2)
Si(1)-C(9)	1.8939(19)	C(6)-C(10)	1.561(2)
O(1)-C(8)	1.211(2)	C(7)-C(8)	1.504(3)
C(1)-C(2)	1.501(3)	C(8)-C(9)	1.501(2)
C(1)-C(5)	1.525(3)	C(9)-C(10)	1.542(2)
C(1)-C(7)	1.561(2)	C(10)-C(11)	1.545(2)
C(2)-C(3)	1.308(3)	C(11)-C(13)	1.522(3)
C(3)-C(4)	1.513(3)	C(11)-C(12)	1.525(3)
C(15)-Si(1)-C(16)	109.09(11)	C(5)-C(4)-C(6)	101.18(14)
C(15)-Si(1)-C(14)	109.62(12)	C(4)-C(5)-C(1)	93.88(15)
C(16)-Si(1)-C(14)	109.21(11)	C(7)-C(6)-C(4)	101.94(14)
C(15)-Si(1)-C(9)	108.30(10)	C(7)-C(6)-C(10)	107.60(13)
C(16)-Si(1)-C(9)	109.40(10)	C(4)-C(6)-C(10)	114.60(16)
C(14)-Si(1)-C(9)	111.18(10)	C(8)-C(7)-C(6)	106.57(13)
C(2)-C(1)-C(5)	100.37(16)	C(8)-C(7)-C(1)	114.20(15)
C(2)-C(1)-C(7)	105.68(15)	C(6)-C(7)-C(1)	103.46(14)
C(5)-C(1)-C(7)	100.14(14)	O(1)-C(8)-C(9)	124.73(16)
C(3)-C(2)-C(1)	107.06(17)	O(1)-C(8)-C(7)	123.75(16)
C(2)-C(3)-C(4)	108.21(18)	C(9)-C(8)-C(7)	111.52(14)
C(3)-C(4)-C(5)	99.39(16)	C(8)-C(9)-C(10)	106.39(14)
C(3)-C(4)-C(6)	106.29(17)	C(8)-C(9)-Si(1)	113.18(12)

C(10)-C(9)-Si(1)	117.69(12)	C(13)-C(11)-C(12)	111.87(18)
C(9)-C(10)-C(11)	113.36(15)	C(13)-C(11)-C(10)	110.25(16)
C(9)-C(10)-C(6)	107.15(13)	C(12)-C(11)-C(10)	113.73(16)
C(11)-C(10)-C(6)	114.10(14)		

**Table 3.** Crystal data and structure refinement for **66**.

Identification code	alp2061g	
Empirical formula	$C_{13}H_{18}O_{Si}$	
Formula weight	218.36	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 6.3595(2)$ Å	$\alpha = 90^\circ$.
	$b = 7.6380(2)$ Å	$\beta = 91.4440(10)^\circ$.
	$c = 12.7412(4)$ Å	$\gamma = 90^\circ$.
Volume	$618.69(3)$ Å ³	
Z	2	
Density (calculated)	1.172 Mg/m ³	
Absorption coefficient	0.163 mm ⁻¹	
F(000)	236	
Crystal size	3.00 x 0.10 x 0.02 mm ³	
Theta range for data collection	1.60 to 31.49°.	
Index ranges	$-9 \leq h \leq 9, -10 \leq k \leq 10, -18 \leq l \leq 18$	
Reflections collected	9256	
Independent reflections	3877 [R(int) = 0.0457]	
Completeness to theta = 31.49°	96.0 %	
Absorption correction	SADABS (Bruker-AXS)	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3877 / 1 / 208
Goodness-of-fit on F^2	1.070
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0371, wR2 = 0.0918
R indices (all data)	R1 = 0.0406, wR2 = 0.0942
Absolute structure parameter	0.04(9)
Largest diff. peak and hole	0.282 and -0.327 e.Å ⁻³

Table 4 Bond lengths [Å] and angles [°] for **66**.

Si(1)-C(12)	1.8601(16)	C(2)-C(1)-C(10)	95.06(10)
Si(1)-C(11)	1.8646(16)	C(2)-C(1)-C(9)	105.50(11)
Si(1)-C(13)	1.8658(16)	C(10)-C(1)-C(9)	98.13(10)
Si(1)-C(1)	1.8911(13)	C(2)-C(1)-Si(1)	116.99(9)
O(1)-C(10)	1.2034(18)	C(10)-C(1)-Si(1)	119.53(9)
C(1)-C(2)	1.5285(17)	C(9)-C(1)-Si(1)	117.82(8)
C(1)-C(10)	1.5493(17)	C(3)-C(2)-C(1)	109.38(12)
C(1)-C(9)	1.5766(19)	C(2)-C(3)-C(4)	108.82(13)
C(2)-C(3)	1.339(2)	C(3)-C(4)-C(10)	95.88(12)
C(3)-C(4)	1.513(2)	C(3)-C(4)-C(5)	107.25(13)
C(4)-C(10)	1.537(2)	C(10)-C(4)-C(5)	100.72(11)
C(4)-C(5)	1.547(2)	C(4)-C(5)-C(6)	114.30(14)
C(5)-C(6)	1.550(2)	C(4)-C(5)-C(9)	103.07(11)
C(5)-C(9)	1.5789(19)	C(6)-C(5)-C(9)	106.15(11)
C(6)-C(7)	1.500(2)	C(7)-C(6)-C(5)	104.37(12)
C(7)-C(8)	1.329(2)	C(8)-C(7)-C(6)	112.86(13)
C(8)-C(9)	1.4992(19)	C(7)-C(8)-C(9)	113.15(13)
C(12)-Si(1)-C(11)	108.98(8)	C(8)-C(9)-C(1)	114.41(11)
C(12)-Si(1)-C(13)	109.38(8)	C(8)-C(9)-C(5)	103.44(11)
C(11)-Si(1)-C(13)	110.09(8)	C(1)-C(9)-C(5)	104.92(11)
C(12)-Si(1)-C(1)	108.05(6)	O(1)-C(10)-C(4)	130.69(13)
C(11)-Si(1)-C(1)	112.19(6)	O(1)-C(10)-C(1)	130.97(13)
C(13)-Si(1)-C(1)	108.09(7)	C(4)-C(10)-C(1)	98.29(11)

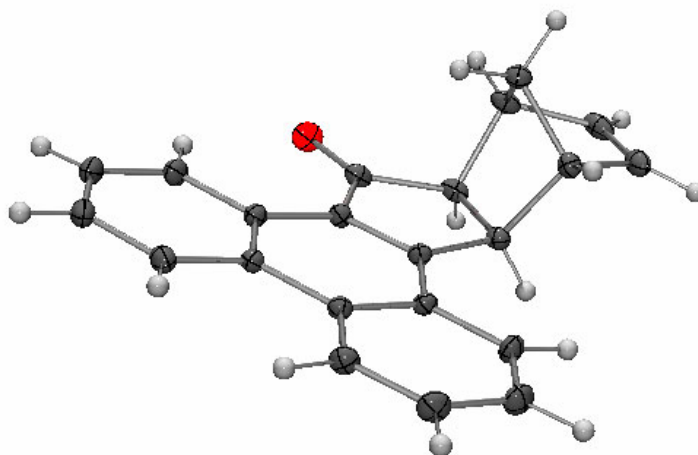


Table 5 Crystal data and structure refinement for **131**.

Identification code	alp288_0m	
Empirical formula	$C_{22}H_{16}O$	
Formula weight	296.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	$a = 5.4737(3)$ Å	$\alpha = 90^\circ$.
	$b = 15.2166(9)$ Å	$\beta = 90^\circ$.
	$c = 16.9657(11)$ Å	$\gamma = 90^\circ$.
Volume	$1413.09(15)$ Å ³	
Z	4	
Density (calculated)	1.393 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
F(000)	624	
Crystal size	0.50 x 0.20 x 0.15 mm ³	
Theta range for data collection	2.75 to 39.54°.	
Index ranges	$-9 \leq h \leq 9, -8 \leq k \leq 26, -30 \leq l \leq 29$	
Reflections collected	28155	
Independent reflections	8281 [R(int) = 0.0556]	
Completeness to theta = 39.54°	97.9 %	
Absorption correction	SADABS (Bruker-AXS)	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8281 / 0 / 208
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0516, wR2 = 0.1319
R indices (all data)	R1 = 0.0600, wR2 = 0.1363
Absolute structure parameter	0.2(10)
Largest diff. peak and hole	0.475 and -0.320 e.Å ⁻³

Table 6 Bond lengths [Å] and angles [°] for **131**.

C(1)-C(2)	1.4095(11)	C(18)-C(19)	1.3369(14)
C(1)-C(6)	1.4192(11)	C(19)-C(20)	1.5161(12)
C(1)-C(14)	1.4402(11)	C(20)-C(22)	1.5405(12)
C(2)-C(3)	1.3808(13)	C(20)-C(21)	1.5755(11)
C(3)-C(4)	1.4003(14)	C(2)-C(1)-C(6)	119.88(7)
C(4)-C(5)	1.3799(12)	C(2)-C(1)-C(14)	121.85(7)
C(5)-C(6)	1.4150(11)	C(6)-C(1)-C(14)	118.25(7)
C(6)-C(7)	1.4580(11)	C(3)-C(2)-C(1)	120.52(8)
C(7)-C(8)	1.4132(11)	C(2)-C(3)-C(4)	119.93(8)
C(7)-C(12)	1.4233(11)	C(5)-C(4)-C(3)	120.55(8)
C(8)-C(9)	1.3821(13)	C(4)-C(5)-C(6)	120.89(8)
C(9)-C(10)	1.4028(14)	C(5)-C(6)-C(1)	118.21(7)
C(10)-C(11)	1.3774(12)	C(5)-C(6)-C(7)	121.84(7)
C(11)-C(12)	1.4123(11)	C(1)-C(6)-C(7)	119.93(7)
C(12)-C(13)	1.4350(11)	C(8)-C(7)-C(12)	117.64(7)
C(13)-C(14)	1.3683(11)	C(8)-C(7)-C(6)	122.43(7)
C(13)-C(21)	1.5018(11)	C(12)-C(7)-C(6)	119.93(7)
C(14)-C(15)	1.4837(11)	C(9)-C(8)-C(7)	121.41(8)
C(15)-O(1)	1.2186(11)	C(8)-C(9)-C(10)	120.25(8)
C(15)-C(16)	1.5281(12)	C(11)-C(10)-C(9)	120.10(8)
C(16)-C(21)	1.5515(11)	C(10)-C(11)-C(12)	120.37(8)
C(16)-C(17)	1.5615(11)	C(11)-C(12)-C(7)	120.22(7)
C(17)-C(18)	1.5266(14)	C(11)-C(12)-C(13)	121.18(7)
C(17)-C(22)	1.5400(12)	C(7)-C(12)-C(13)	118.59(7)

C(14)-C(13)-C(12)	121.30(7)	C(18)-C(17)-C(22)	99.38(7)
C(14)-C(13)-C(21)	113.25(7)	C(18)-C(17)-C(16)	106.21(7)
C(12)-C(13)-C(21)	125.37(7)	C(22)-C(17)-C(16)	100.32(6)
C(13)-C(14)-C(1)	121.94(7)	C(19)-C(18)-C(17)	107.59(8)
C(13)-C(14)-C(15)	109.14(7)	C(18)-C(19)-C(20)	107.52(8)
C(1)-C(14)-C(15)	128.86(7)	C(19)-C(20)-C(22)	99.75(7)
O(1)-C(15)-C(14)	127.62(8)	C(19)-C(20)-C(21)	105.00(7)
O(1)-C(15)-C(16)	124.43(8)	C(22)-C(20)-C(21)	101.54(6)
C(14)-C(15)-C(16)	107.92(7)	C(13)-C(21)-C(16)	104.12(6)
C(15)-C(16)-C(21)	105.36(6)	C(13)-C(21)-C(20)	113.53(6)
C(15)-C(16)-C(17)	111.38(7)	C(16)-C(21)-C(20)	102.26(6)
C(21)-C(16)-C(17)	103.60(6)	C(17)-C(22)-C(20)	94.09(6)

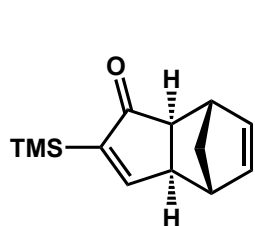
12. Apèndix II. Publicacions

El treball realitzat en el transcurs de la present tesi doctoral ha portat a l'elaboració i publicació dels següents articles:

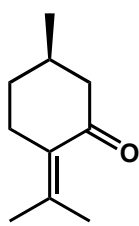
- **“PuPHOS: A Synthetically Useful Chiral Bidentate Ligand for the Intermolecular Pauson-Khand Reaction”**. Xavier Verdaguer, Agustí Lledó, Cristina López-Mosquera, Miguel A. Maestro, Miquel A. Pericàs i Antoni Riera. *Journal of Organic Chemistry* **2004**, *69*, 8053-8061.
- **“Total Synthesis and Biological Activity of 13,14-Dehydro-12-Oxo-Phytodienoic Acids (Deoxy-J₁-Phytosteranes)”**. Mazhar Iqbal, Paul Evans, Agustí Lledó, Xavier Verdaguer, Miquel A. Pericàs, Antoni Riera, Christiane Loeffler, Alok K. Sinha, Martin J. Mueller. *ChemBioChem* **2005**, *6*, 276-280.
- **“Cobalt Catalyzed Norbornadiene Intermolecular Pauson-Khand Reaction: Kinetic and Mechanistic Studies”**. Rafel Cabot, Agustí Lledó, Marc Revés, Antoni Riera, Xavier Verdaguer. En revisió.
- **“Photochemistry of Norbornadiene-Pauson-Khand Cycloadducts: Photochemical Rearrangement through a Bis-allyl Diradical”**. Agustí Lledó, Xavier Verdaguer, Jordi Benet-Bucholtz, Albert Solé, Santiago Olivella, Antoni Riera. En revisió (*Journal of the American Chemical Society*).

Índex d'estructures

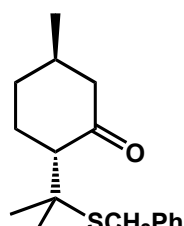
Índex d'estructures.



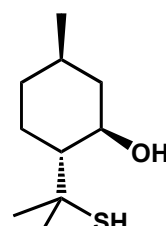
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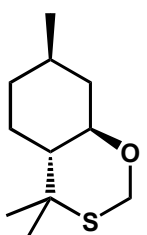
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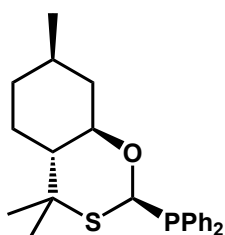
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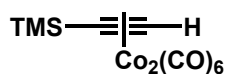
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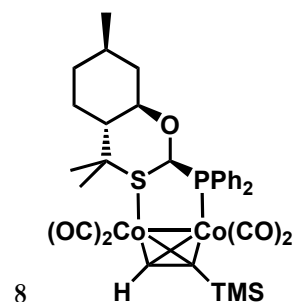
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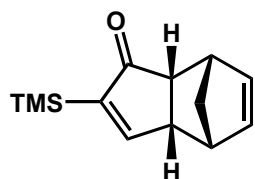
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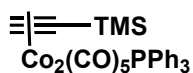
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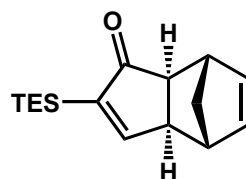
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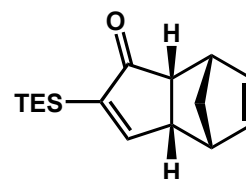
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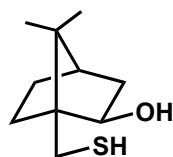
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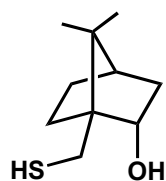
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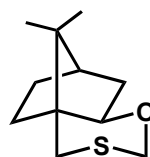
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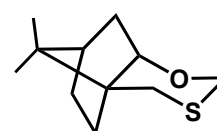
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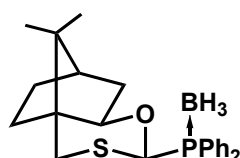
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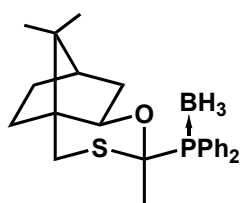
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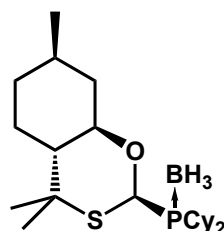
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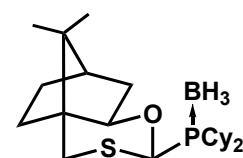
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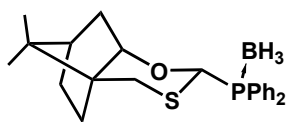
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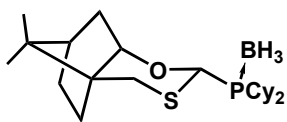
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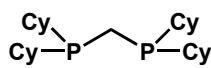
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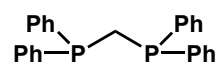
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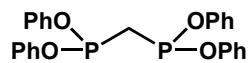
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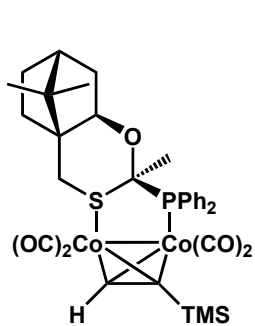
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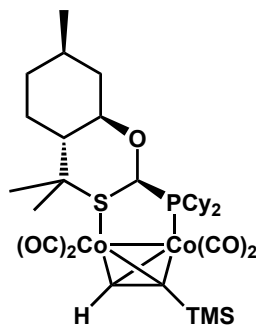
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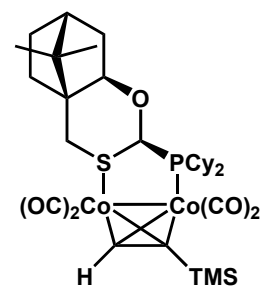
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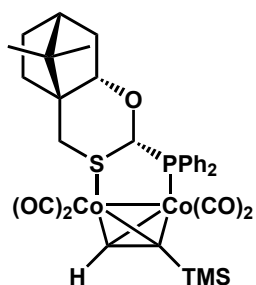
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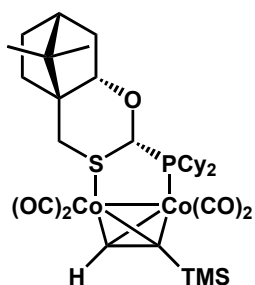
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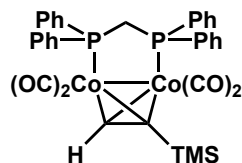
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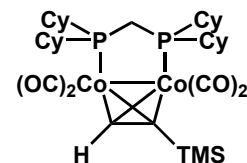
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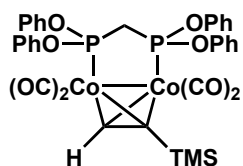
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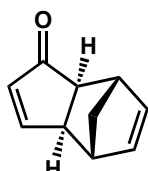
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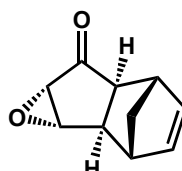
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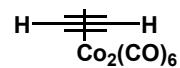
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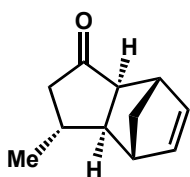
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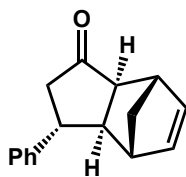
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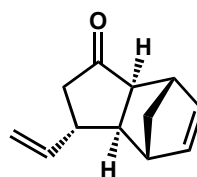
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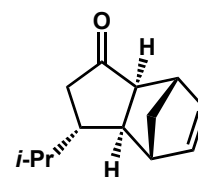
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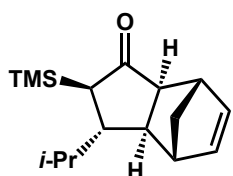
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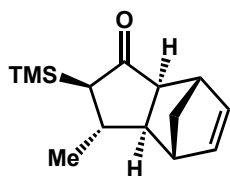
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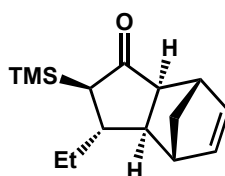
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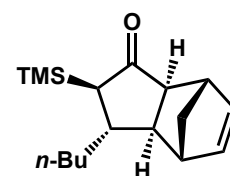
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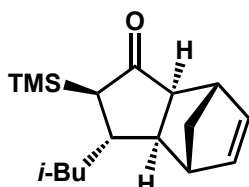
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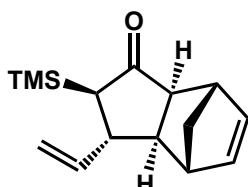
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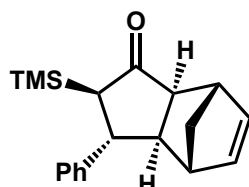
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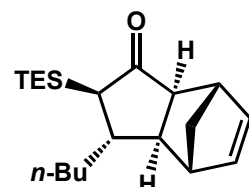
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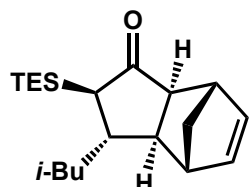
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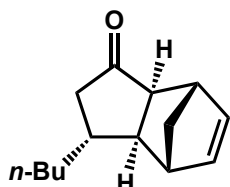
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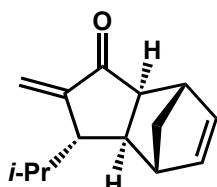
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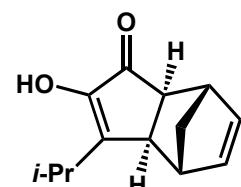
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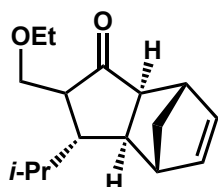
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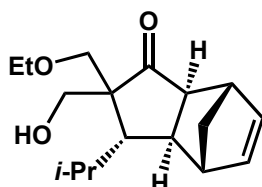
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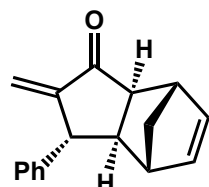
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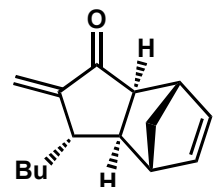
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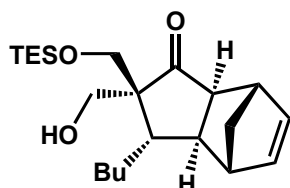
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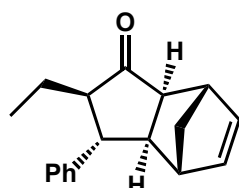
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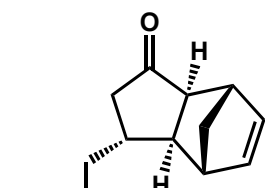
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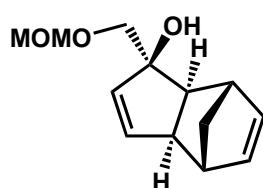
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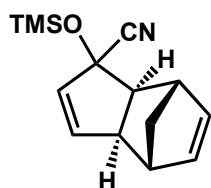
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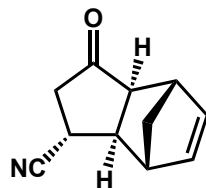
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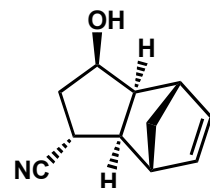
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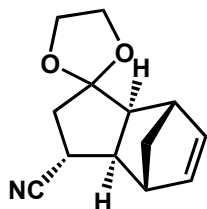
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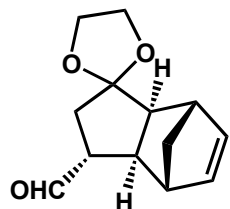
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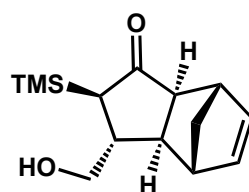
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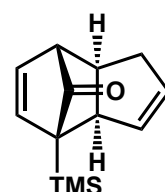
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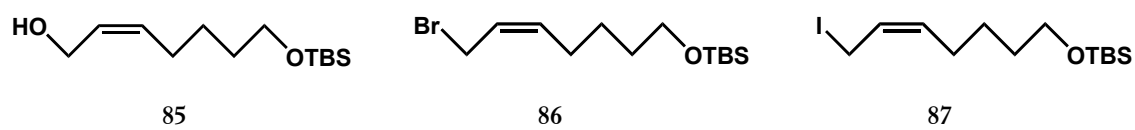
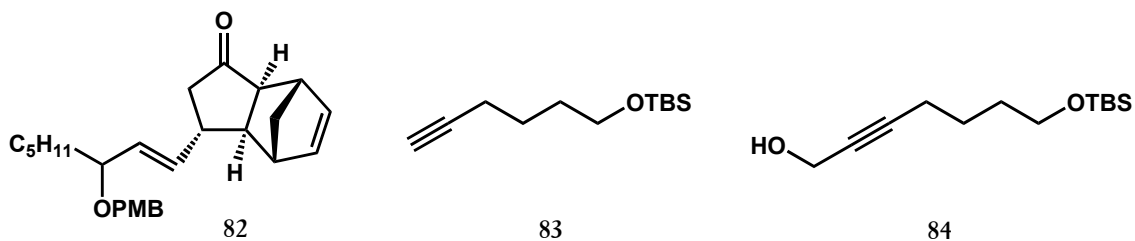
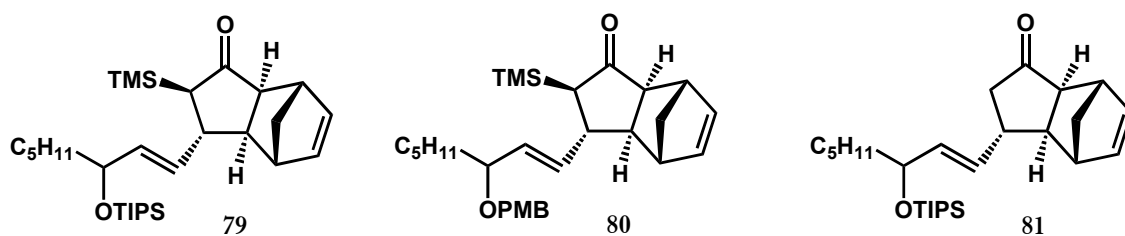
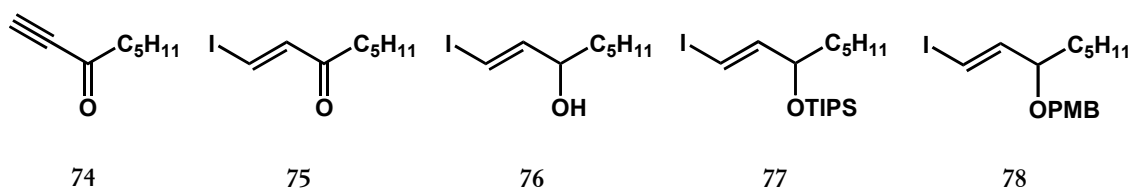
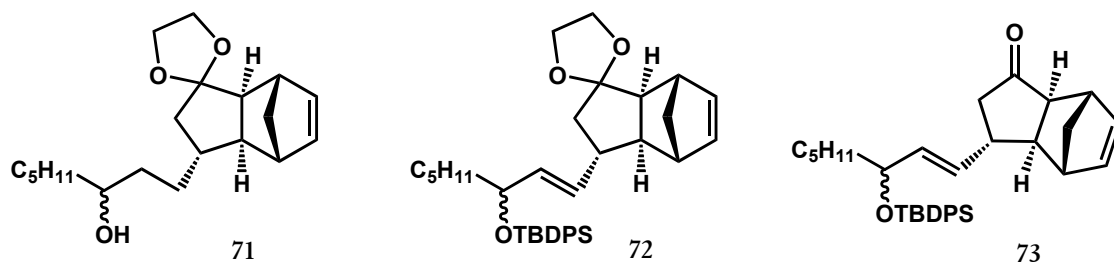
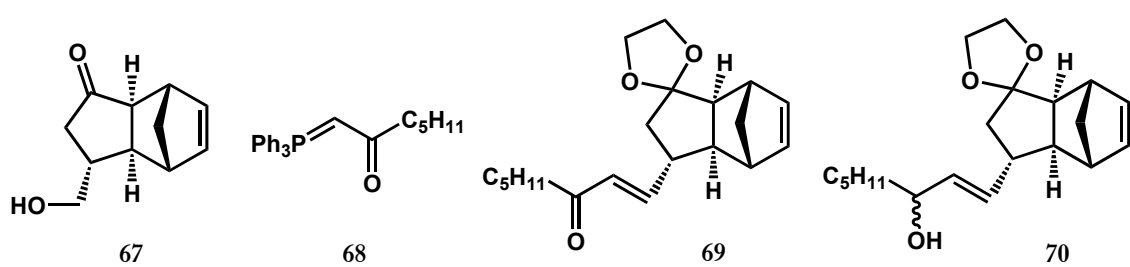
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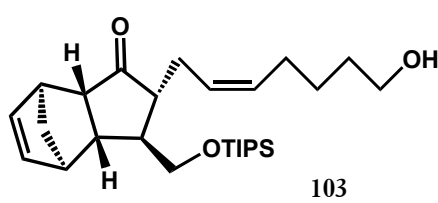
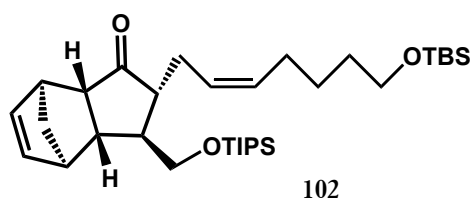
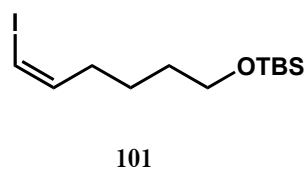
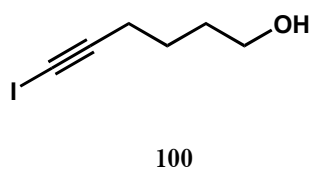
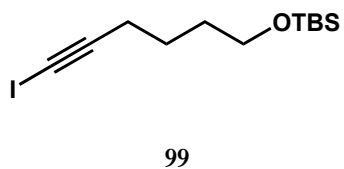
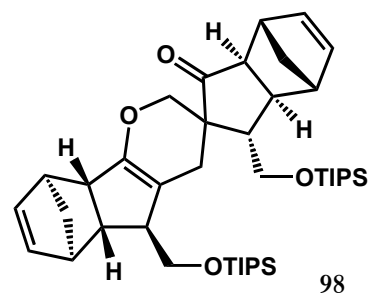
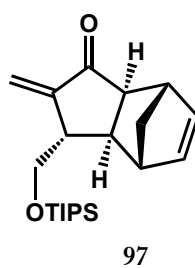
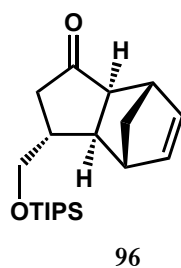
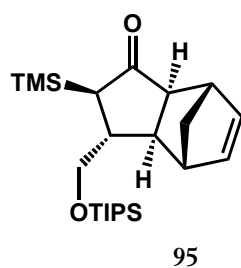
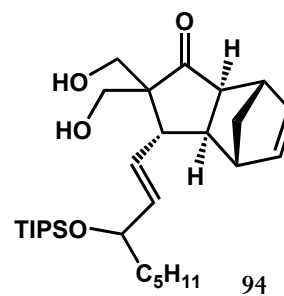
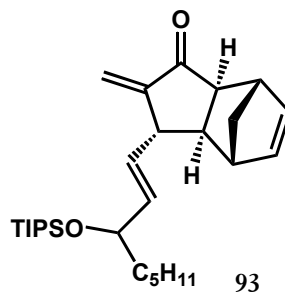
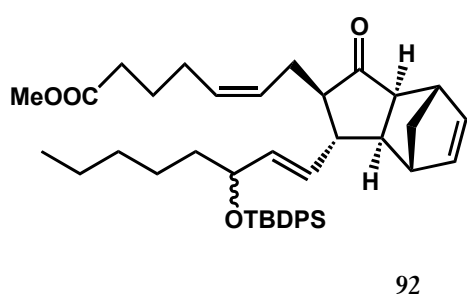
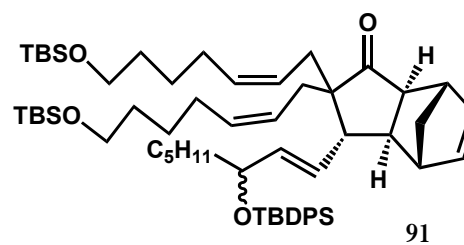
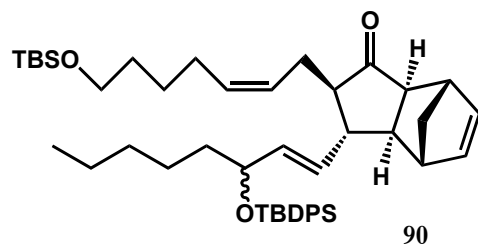
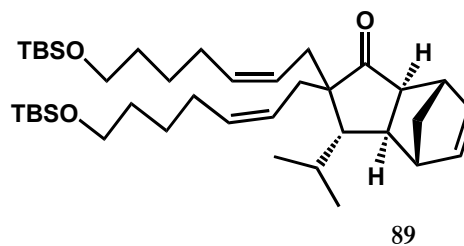
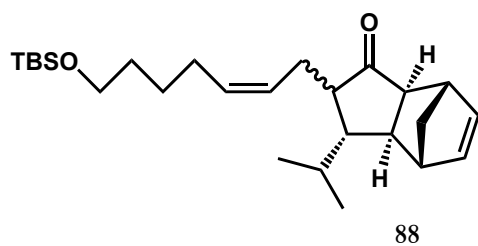


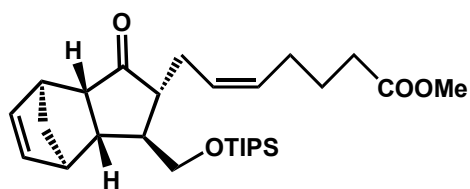
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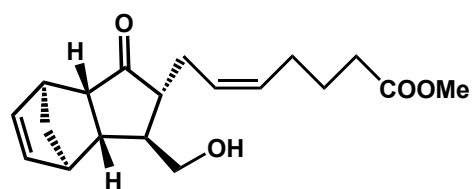
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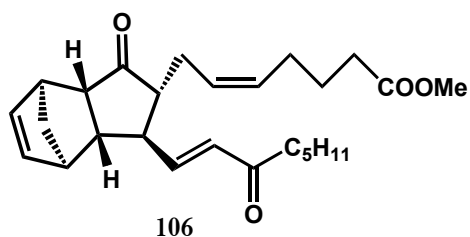




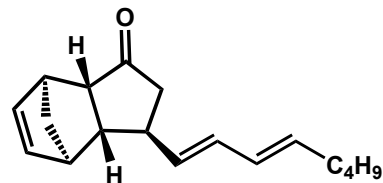
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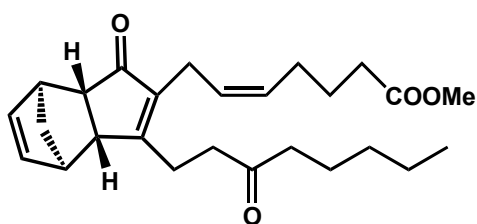
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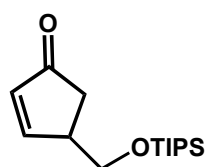
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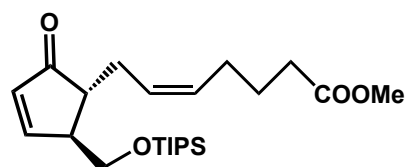
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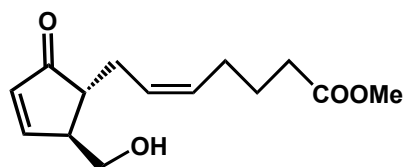
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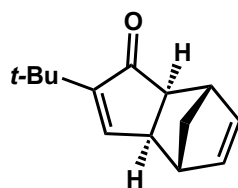
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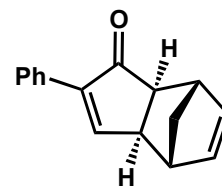
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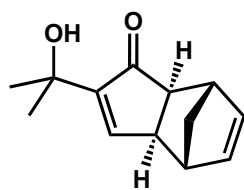
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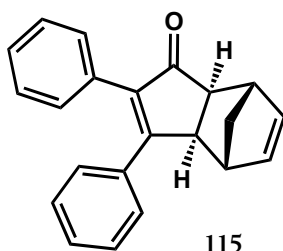
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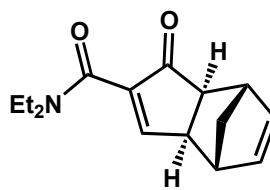
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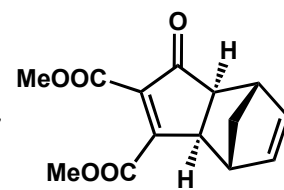
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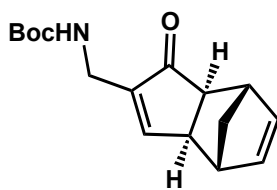
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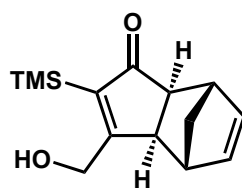
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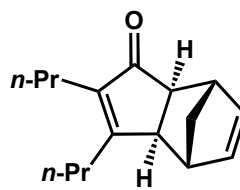
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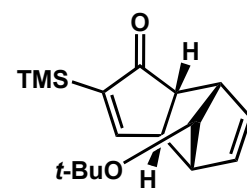
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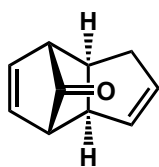
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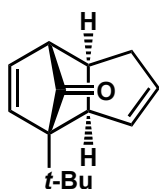
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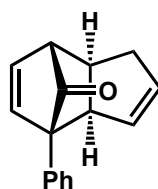
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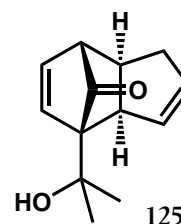
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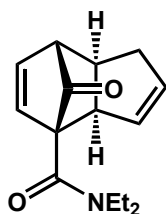
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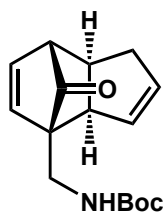
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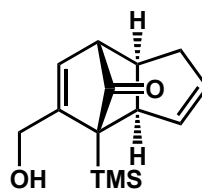
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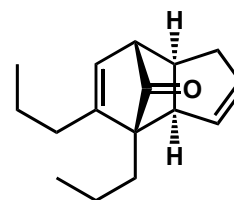
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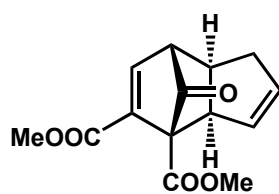
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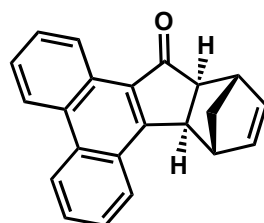
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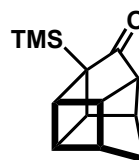
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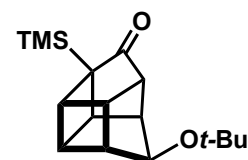
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