

SUPPORTING INFORMATION ACCOMPANYING:

Tandem Suzuki Coupling-Norbornadiene Insertion Reactions. A Convenient Route to 5,6-Diarylnorbornene Compounds.

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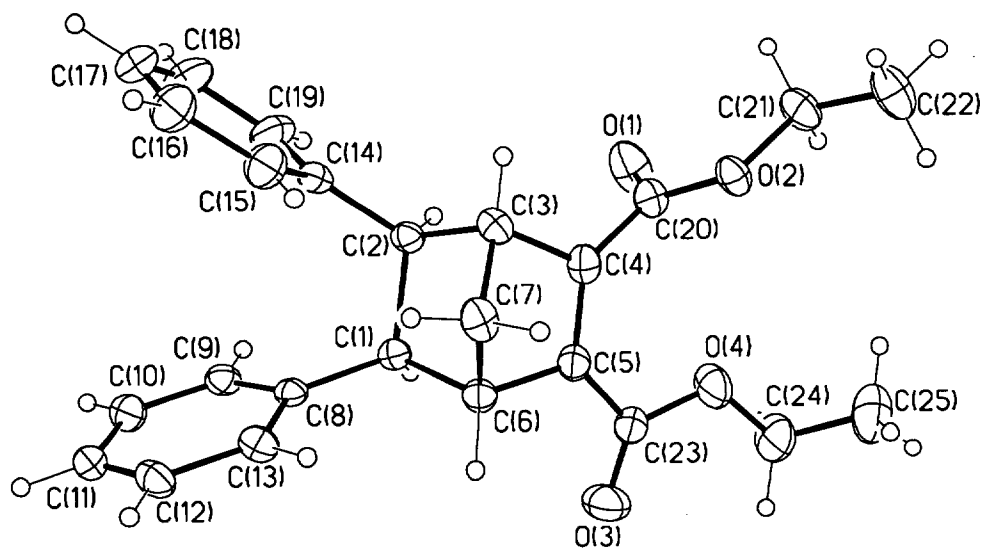


Figure 1S. ORTEP diagram of **1a**. Thermal ellipsoids at 30% probability.

Crystallographic characterization footnote:

For $C_{25}H_{26}O_4$: monoclinic, $P2_1/c$, $a = 15.240(4)$, $b = 7.7029(17)$, $c = 18.493(4)$ Å, $\beta = 104.757(4)^\circ$, $V = 2099.3(8)$ Å³, $Z = 4$, $Z' = 1$, $T = 173(2)$ K, $D_{\text{calc}} = 1.235$ g cm⁻³, colorless block, $GOF = 1.512$, $R(F) = 6.60\%$ for 4059 observed independent reflections ($4^\circ \times 2^\circ \times 52^\circ$).

Table 1S. Crystal data and structure refinement.

Identification code	wcu01	
Empirical formula	C ₂₅ H ₂₆ O ₄	
Formula weight	390.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.240(4) Å	α = 90°.
	b = 7.7029(17) Å	β = 104.757(4)°.
	c = 18.493(4) Å	γ = 90°.
Volume	2099.3(8) Å ³	
Z	4	
Density (calculated)	1.235 g/cm ³	
Absorption coefficient	0.083 mm ⁻¹	
F(000)	832	
Crystal size	0.50 x 0.40 x 0.20 mm ³	
Theta range for data collection	2.34 to 26.00°.	
Index ranges	-18 ≤ h ≤ 18, -8 ≤ k ≤ 9, -15 ≤ l ≤ 22	
Reflections collected	8391	
Independent reflections	4059 [R(int) = 0.0267]	
Completeness to theta = 26.00°	98.2 %	
Absorption correction	Empirical from SADABS	
Max. and min. transmission	0.9837 and 0.9598	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4059 / 0 / 262	
Goodness-of-fit on F ²	1.512	
Final R indices [I > 2σ(I)]	R1 = 0.0660, wR2 = 0.1947	
R indices (all data)	R1 = 0.0888, wR2 = 0.2147	
Largest diff. peak and hole	0.348 and -0.289 e.Å ⁻³	

Table 2S. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	9915(1)	5637(3)	2478(1)	71(1)
O(2)	10286(1)	7050(2)	3571(1)	43(1)
O(3)	8086(1)	2326(3)	3691(2)	81(1)
O(4)	9460(1)	3453(2)	3885(1)	70(1)
C(1)	6936(1)	5598(3)	2261(1)	32(1)
C(2)	7545(1)	6950(3)	1950(1)	34(1)
C(3)	8110(2)	7821(3)	2689(1)	40(1)
C(4)	8761(2)	6416(3)	3065(1)	41(1)
C(5)	8273(2)	5221(3)	3317(1)	42(1)
C(6)	7296(2)	5829(3)	3122(1)	39(1)
C(7)	7453(2)	7799(3)	3196(1)	43(1)
C(8)	5924(1)	5827(2)	1955(1)	32(1)
C(9)	5525(2)	5210(3)	1240(1)	39(1)
C(10)	4609(2)	5359(4)	926(2)	50(1)
C(11)	4055(2)	6147(3)	1315(2)	48(1)
C(12)	4436(2)	6766(3)	2020(2)	44(1)
C(13)	5358(2)	6599(3)	2345(1)	40(1)
C(14)	7045(2)	8173(3)	1350(2)	41(1)
C(15)	6569(2)	9606(3)	1484(2)	60(1)
C(16)	6104(2)	10635(4)	901(3)	82(1)
C(17)	6120(2)	10290(5)	183(3)	90(1)
C(18)	6584(3)	8868(6)	36(2)	87(1)
C(19)	7038(2)	7826(4)	612(2)	62(1)
C(20)	9711(2)	6288(3)	3000(2)	44(1)
C(21)	11233(2)	7039(4)	3552(2)	53(1)
C(22)	11752(2)	7922(5)	4229(2)	71(1)
C(23)	8577(2)	3510(3)	3639(1)	47(1)
C(24)	9872(2)	1869(4)	4243(2)	75(1)
C(25)	10674(3)	2352(5)	4792(2)	89(1)

Table 3S. Bond lengths [Å] and angles [°].

O(1)-C(20)	1.196(3)
O(2)-C(20)	1.325(3)
O(2)-C(21)	1.453(3)
O(3)-C(23)	1.199(3)
O(4)-C(23)	1.307(3)
O(4)-C(24)	1.453(3)
C(1)-C(8)	1.512(3)
C(1)-C(6)	1.557(3)
C(1)-C(2)	1.596(3)
C(2)-C(14)	1.507(3)
C(2)-C(3)	1.568(3)
C(3)-C(4)	1.512(3)
C(3)-C(7)	1.535(3)
C(4)-C(5)	1.340(3)
C(4)-C(20)	1.486(3)
C(5)-C(23)	1.472(4)
C(5)-C(6)	1.513(3)
C(6)-C(7)	1.537(3)
C(8)-C(13)	1.391(3)
C(8)-C(9)	1.391(3)
C(9)-C(10)	1.373(3)
C(10)-C(11)	1.382(4)
C(11)-C(12)	1.370(4)
C(12)-C(13)	1.386(3)
C(14)-C(15)	1.378(4)
C(14)-C(19)	1.387(4)
C(15)-C(16)	1.380(4)
C(16)-C(17)	1.361(6)
C(17)-C(18)	1.368(6)
C(18)-C(19)	1.373(5)
C(21)-C(22)	1.466(4)
C(24)-C(25)	1.425(5)
C(20)-O(2)-C(21)	115.92(19)

C(23)-O(4)-C(24)	118.3(2)
C(8)-C(1)-C(6)	115.42(17)
C(8)-C(1)-C(2)	114.87(17)
C(6)-C(1)-C(2)	102.01(17)
C(14)-C(2)-C(3)	115.90(19)
C(14)-C(2)-C(1)	116.23(17)
C(3)-C(2)-C(1)	101.89(17)
C(4)-C(3)-C(7)	99.51(19)
C(4)-C(3)-C(2)	104.13(18)
C(7)-C(3)-C(2)	103.24(18)
C(5)-C(4)-C(20)	128.4(2)
C(5)-C(4)-C(3)	107.1(2)
C(20)-C(4)-C(3)	123.3(2)
C(4)-C(5)-C(23)	127.6(2)
C(4)-C(5)-C(6)	107.7(2)
C(23)-C(5)-C(6)	124.2(2)
C(5)-C(6)-C(7)	99.36(19)
C(5)-C(6)-C(1)	106.04(18)
C(7)-C(6)-C(1)	102.12(18)
C(3)-C(7)-C(6)	93.89(17)
C(13)-C(8)-C(9)	117.4(2)
C(13)-C(8)-C(1)	124.4(2)
C(9)-C(8)-C(1)	118.25(19)
C(10)-C(9)-C(8)	121.7(2)
C(9)-C(10)-C(11)	120.4(2)
C(12)-C(11)-C(10)	118.8(2)
C(11)-C(12)-C(13)	121.1(2)
C(12)-C(13)-C(8)	120.6(2)
C(15)-C(14)-C(19)	117.3(3)
C(15)-C(14)-C(2)	124.0(2)
C(19)-C(14)-C(2)	118.7(2)
C(14)-C(15)-C(16)	120.5(3)
C(17)-C(16)-C(15)	121.2(3)
C(16)-C(17)-C(18)	119.3(3)
C(17)-C(18)-C(19)	119.8(4)
C(18)-C(19)-C(14)	121.8(3)

O(1)-C(20)-O(2)	125.0(2)
O(1)-C(20)-C(4)	123.5(2)
O(2)-C(20)-C(4)	111.4(2)
O(2)-C(21)-C(22)	107.5(2)
O(3)-C(23)-O(4)	123.7(2)
O(3)-C(23)-C(5)	125.1(2)
O(4)-C(23)-C(5)	111.2(2)
C(25)-C(24)-O(4)	107.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 4S. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	50(1)	100(2)	66(1)	-32(1)	21(1)	-3(1)
O(2)	28(1)	52(1)	50(1)	-3(1)	12(1)	1(1)
O(3)	56(1)	72(1)	117(2)	42(1)	28(1)	1(1)
O(4)	44(1)	53(1)	99(2)	22(1)	-5(1)	4(1)
C(1)	33(1)	30(1)	34(1)	1(1)	13(1)	3(1)
C(2)	31(1)	36(1)	39(1)	2(1)	14(1)	2(1)
C(3)	33(1)	39(1)	47(1)	-4(1)	11(1)	-1(1)
C(4)	38(1)	45(1)	38(1)	-2(1)	6(1)	2(1)
C(5)	36(1)	52(1)	36(1)	3(1)	7(1)	1(1)
C(6)	35(1)	50(1)	34(1)	1(1)	12(1)	0(1)
C(7)	40(1)	51(1)	39(1)	-13(1)	9(1)	1(1)
C(8)	34(1)	26(1)	37(1)	3(1)	12(1)	-1(1)
C(9)	41(1)	44(1)	36(1)	0(1)	16(1)	-2(1)
C(10)	45(2)	63(2)	38(1)	4(1)	6(1)	-8(1)
C(11)	34(1)	51(1)	58(2)	19(1)	10(1)	1(1)
C(12)	35(1)	38(1)	64(2)	3(1)	21(1)	2(1)
C(13)	40(1)	38(1)	46(1)	-6(1)	17(1)	0(1)
C(14)	32(1)	41(1)	52(2)	10(1)	14(1)	-5(1)
C(15)	54(2)	46(1)	77(2)	14(1)	14(2)	10(1)
C(16)	63(2)	54(2)	123(4)	37(2)	13(2)	11(2)
C(17)	66(2)	91(3)	102(3)	64(3)	-2(2)	-11(2)
C(18)	96(3)	102(3)	61(2)	39(2)	20(2)	-8(2)
C(19)	71(2)	67(2)	52(2)	21(2)	25(2)	0(2)
C(20)	37(1)	47(1)	46(2)	-1(1)	8(1)	2(1)
C(21)	31(1)	62(2)	69(2)	-3(1)	18(1)	0(1)
C(22)	37(1)	87(2)	88(3)	-16(2)	14(2)	-2(2)
C(23)	39(1)	59(2)	40(1)	8(1)	7(1)	2(1)
C(24)	62(2)	60(2)	92(3)	25(2)	-1(2)	14(1)
C(25)	83(2)	83(2)	82(3)	3(2)	-13(2)	14(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

	x	y	z	U(eq)
H(1A)	7100	4402	2129	38
H(2A)	7977	6264	1737	41
H(3A)	8388	8971	2630	47
H(6A)	6907	5325	3431	46
H(7A)	6895	8481	2990	52
H(7B)	7743	8168	3715	52
H(9A)	5895	4671	962	47
H(10A)	4355	4919	437	60
H(11A)	3422	6256	1099	57
H(12A)	4062	7320	2290	53
H(13A)	5605	7016	2838	48
H(15A)	6561	9887	1983	71
H(16A)	5766	11600	1003	99
H(17A)	5813	11030	-212	109
H(18A)	6591	8603	-464	104
H(19A)	7355	6839	503	74
H(21A)	11308	7651	3101	64
H(21B)	11450	5831	3540	64
H(22A)	12396	7933	4233	107
H(22B)	11672	7306	4671	107
H(22C)	11534	9118	4233	107
H(24A)	9448	1259	4482	90
H(24B)	10025	1084	3869	90
H(25A)	10969	1310	5046	133
H(25B)	10515	3129	5159	133
H(25C)	11090	2950	4549	133

Diethyl 1,4,5,6,7-pentamethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate

(6b). A 50 mL round-bottomed flask was charged with 0.716 g (4.21 mmol) of diethyl acetylenedicarboxylate and 1.00 g (7.35 mmol) of pentamethylcyclopentadiene. The reaction evolved a considerable amount of heat in the first few minutes. It was then left overnight at room temperature to ensure completion, and the crude product was distilled in a kugelrohr apparatus under a 5 mtorr dynamic vacuum. After a brief forerun at an oven temperature of 50 °C (to remove residual pentamethylcyclopentadiene), the product distilled at an oven temperature of 80 °C to yield 0.984 g (3.49 mmol, 83%) of **6b** as a pale-yellow oil which was a roughly 50:50 mixture of two isomers: ¹H NMR (300 MHz, CDCl₃) δ 4.15-4.25 (m, 4H), 2.35 and 2.12 (q, *J* = 6.3 Hz, 1H), 1.69 and 1.64 (s, 6H), 1.25-1.32 (m, 12H), 0.86 and 0.71 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.2, 166.0, 155.5, 151.2, 146.3, 140.9, 81.6, 80.4, 63.2, 63.0, 60.5, 60.4, 14.2, 11.7, 11.4, 11.2, 10.0, 9.8. Anal. Calcd. for C₁₈H₂₆O₄: C, 70.56; H, 8.55; Found: C, 70.77; H, 8.84.

General Procedure for Microscale Experiments. A stock solution that was 0.5 M in iodobenzene and 1,4-dimethoxybenzene, along with the appropriate amounts of diethyl norbornadiene-2,3-dicarboxylate and 2-phenyl-1,3,2-dioxaborinane, was prepared in THF and degassed via three freeze-pump-thaw cycles. A separate stock solution of 1.32 M K₂CO₃ in water was similarly prepared. Catalyst, phosphine, and additional reagents were weighed separately into 4 mL reaction vials charged with micro-stirbars. The solutions and vials were brought into a nitrogen-purged glove bag, where the vials were charged with 500 μL of each stock solution. The vials were then sealed with teflon-lined serum caps, removed from the glove bag, and placed in a 60 °C oil bath overnight.

Afterwards the reactions were extracted with 3 x 2 mL of CH₂Cl₂. The organic phases were pooled, dried over Na₂SO₄, and samples were injected directly onto an HPLC using 15% ethyl acetate in hexanes as an eluent.

Kinetics Experiment. A stock solution that was 0.50 M in iodobenzene, 0.50 M in 1,4-dimethoxybenzene, 0.55 M in diethyl norbornadiene-2,3-dicarboxylate and 0.55 M in 2-phenyl-1,3,2-dioxaborinane, was prepared in THF and degassed via three freeze-pump-thaw cycles. Separate stock solutions of 1.32 M K₂CO₃ in water and 0.12 M Pd(OAc)₂ in THF were similarly prepared and degassed. A 100 mL Schlenk flask was charged with 94.4 mg (0.36 mmol) of triphenylphosphine along with a stirbar and evacuated. A second identical flask was charged with a stirbar and similarly evacuated. Both flasks were backfilled with nitrogen, fitted with septa, and placed in a water bath that was equilibrated at 49.8 ± 0.2 °C. To each flask was then added 5.0 mL of the reactant stock (2.5 mmol), 5.0 mL of the base stock (6.6 mmol), and 1.0 mL of the catalyst stock (0.12 mmol). The reactions were run under static nitrogen while stirring, and 50 µL aliquots were periodically removed via syringe. These aliquots were treated with 1 mL of CH₂Cl₂ and extracted with 1 mL of 5% NaCN. After removal of the aqueous phase, they were dried over Na₂SO₄ and injected directly onto an HPLC using 15% ethyl acetate in hexanes as an eluent.