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COBALT METALLOCYCLES

I. ONE-STEP AND STEPWISE SYNTHESIS OF COBALTACYCLOPENTADIENE COMPLEXES FROM ACETYLENES

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Summary

 $(\pi$ -Cyclopentadienyl) (triphenylphosphine) cobaltacyclopentadiene complexes having a variety of substituents have been prepared from substituted acetylenes and $(\pi$ -cyclopentadienyl)bis(triphenylphosphine)cobalt. In some cases monoacetylene complexes have been isolated and by addition of other acetylenes to the monoacetylene complexes, cobalt metallocycles consisting of two different acetylene units have been prepared. The structures of all cobaltacyclopentadiene isomers have been determined by NMR spectra and/or by degradation to organic compounds.

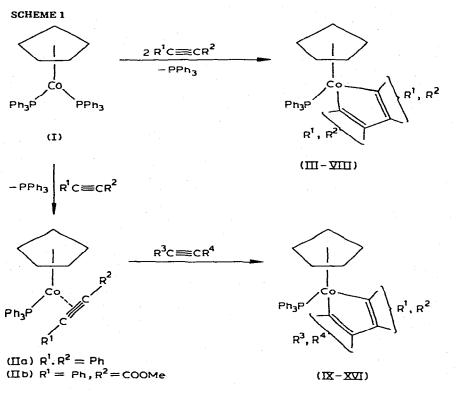
After the discovery of ferracyclopentadiene complexes, which are prepared by the reaction of iron carbonyl with acetylenes [1], many metallocyclopentadiene complexes have been prepared from acetylenes [2]. However, only few examples are known of the synthesis of complexes bearing different substituents in their metallocycles [1,2b,2d,2k]. Some metallocyclopentadiene complexes have been used as starting materials for the synthesis of 5- or 6-membered organic ring compounds [2b,3] and control of substitution in these organic ring compounds has been achieved by using cobaltacyclopentadiene complexes having various substituents at the desired positions in the metallocycle [3].

In the present paper, we report details of the synthesis of such substituted cobaltacyclopentadiene complexes. They are prepared in one step by the reaction of $(\pi$ -cyclopentadienyl)bis(triphenylphosphine)cobalt with two molar equivalents of a substituted acetylene or, by a stepwise procedure, with isolation of intermediate (π -acetylene)cobalt complexes. By the stepwise method two different acetylenes can be incorporated into the metallocycle.

TABLE 1 Com- bound Gom- R ¹ R ² Yield MIR (6 pm) in CDCl ₃ Com- R ¹ R ² Yield MIR (6 pm) in CDCl ₃ Com- R ¹ R ² Yield MIR (6 pm) in CDCl ₃ Com- R ¹ R ² Yield MIR (6 pm) in CDCl ₃ Com- R ¹ R ² Yield MIR (6 pm) in CDCl ₃ V Com- C-CR ² -CR	TABLE 1 Communication Mainter State Mainter State<	ABLE 1 $OBALTACYCLOPENTADIENE$ Dm - $Co-CR^1=CR^2-CR^3=C$ bm - $Co-CR^1=CR^2-CR^3=C$ v $CoOMe$ v $CoOMe$ v Ch_2OMe r R^1 r R^2 <tr< th=""><th>YieldM.p.Analysis found (calcd.) (%)NMR (6 ppm) in CDCl3\mathbb{R}^4(%)(%)(%)NMR (6 ppm) in CDCl3\mathbb{R}^4(%)(%)CHC5H5\mathbb{R}^6(%)CHC5H50-M6PhB81193-19482.67(62.47)$b.50(5.43)$$b.66$$3.56$COOMe14216-21763.56(62.70)$b.66(5.43)$$b.66$$3.56$COOMe14216-21772.26(73.00)$5.27(5.144)$$4.97$$3.213.16$Ph29216-21772.26(73.00)$5.27(5.144)$$4.92$$3.06$Ph29216-21772.26(73.00)$5.27(5.544)$$4.93$$3.46$COOMe29216-21773.26(73.00)$5.27(5.544)$$4.93$$3.46$Ph50102-10668.26(66.102)6.11(60.08)$4.96$$3.46$Ph541174-17680.36(61.02)6.11(60.08)$4.94$$3.57$$3.40$Ph541174-17680.36(61.02)6.11(60.08)$4.96$$3.43$Ph575.006.30(5.42)$4.96$$3.45$$5.50(5.42)$$6.00$Ph27180-18276.447(61.00)$6.04(5.94)$$4.96$$3.43$Ph27180-18276.447(61.00)$6.04(5.94)$$4.96$$3.43$Ph27180-18276.447(76.10)$5.00(5.42)$$4.96$$3.43$Ph671061174-17676.447(76.10)5.0</th><th>TABL</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></tr<>	YieldM.p.Analysis found (calcd.) (%)NMR (6 ppm) in CDCl3 \mathbb{R}^4 (%)(%)(%)NMR (6 ppm) in CDCl3 \mathbb{R}^4 (%)(%)CHC5H5 \mathbb{R}^6 (%)CHC5H50-M6PhB81193-19482.67(62.47) $b.50(5.43)$ $b.66$ 3.56 COOMe14216-21763.56(62.70) $b.66(5.43)$ $b.66$ 3.56 COOMe14216-21772.26(73.00) $5.27(5.144)$ 4.97 $3.213.16$ Ph29216-21772.26(73.00) $5.27(5.144)$ 4.92 3.06 Ph29216-21772.26(73.00) $5.27(5.544)$ 4.93 3.46 COOMe29216-21773.26(73.00) $5.27(5.544)$ 4.93 3.46 Ph50102-10668.26(66.102)6.11(60.08) 4.96 3.46 Ph541174-17680.36(61.02)6.11(60.08) 4.94 3.57 3.40 Ph541174-17680.36(61.02)6.11(60.08) 4.96 3.43 Ph575.006.30(5.42) 4.96 3.45 $5.50(5.42)$ 6.00 Ph27180-18276.447(61.00) $6.04(5.94)$ 4.96 3.43 Ph27180-18276.447(61.00) $6.04(5.94)$ 4.96 3.43 Ph27180-18276.447(76.10) $5.00(5.42)$ 4.96 3.43 Ph671061174-17676.447(76.10) 5.0	TABL											
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PhCOOMePh26 $218-219$ $73.26(73.09)$ $5.28(5.14)$ 4.75 3.32 COOMeMeMeCOOMePh26 $218-219$ $73.26(73.09)$ $5.28(5.54)$ 4.94 3.57 3.46 COOMeMeCOOMeMeCOOMeMe 56 $102-104$ $68.33(68.04)$ $5.56(5.54)$ 4.94 3.57 3.46 PhMePh 56 $1174-176$ $80.96(61.02)$ $6.11(6.08)^\circ$ 4.64 3.57 3.46 PhPhCOOMeAmePh 54 $1174-176$ $73.41(73.08)$ $5.57(5.14)$ 4.96 $3.463.20$ PhPhCH20MeCH20Me48 $119-121$ $73.41(73.08)$ $5.27(5.14)$ 4.96 $3.463.20$ PhPhCH20MeCH20Me48 $119-121$ $73.41(73.08)$ $5.27(5.14)$ 4.95 $3.463.20$ PhPhPhCOOMe40 $174-176$ $73.44(76.10)$ $6.04(5.63)$ 4.96 $3.463.20$ PhPhPhMePh27 $1190-121$ $73.41(73.08)$ $5.56(6.43)$ 4.95 $3.463.20$ PhPhMePh27 $1190-121$ $73.44(76.10)$ $6.04(5.63)$ 4.72 $3.463.20$ PhPhMePhMePh $149-151$ $76.96(76.66)$ $5.56(6.42)$ 4.96 $3.463.20$ PhPhMePhPhPhPhPh $120-12218$ $76.86(76.66)$ $5.56(6.42)$	VI-2 Ph COOMe COOMe Ph 26 218-219 73.26(73.0b) 5.28(5.14) 4.75 3.32 VII-1 COOMe Me Me COOMe Ph 56 $(5.16.14)$ 5.77(5.54) 4.98 3.46 1.50(2.Hz) VII-1 COOMe Me Ph 56 $(1.02.14)$ 5.77(5.54) 4.98 3.46 1.50(2.Hz) VII-2 COOMe Me Ph 56 $(1.02.14)$ 5.77(5.54) 4.98 3.46 1.50(2.Hz) VII-2 COOMe Me Ph 56 $(1.02.14)$ 5.77(5.54) 4.98 3.46 3.20 1.51(1.Hz) VII-2 COOMe Me Ph 56 $(1.02.14)$ 5.57(5.54) 4.98 3.46 3.20 1.51(1.Hz) VII-2 COOMe Me Ph 56 $(1.02.14)$ 5.57(5.54) 4.98 3.46 3.20 1.51(1.Hz) VII-2 Ph Ph 21 $(1.4-176)$ 80.96(81.02) 5.11(1.9) 4.95 3.46 3.20 1.51(1.Hz) VII-2 Ph Ph 21 $(1.4-176)$ 80.96(81.02) 5.11(1.9) 4.95 3.46 3.20 1.51(1.Hz) VII-2 Ph Ph 21 $(1.4-176)$ 80.96(81.05) 5.27(5.54) 4.98 3.46 3.20 1.51(1.Hz) VII-2 Ph Ph 21 $(1.4-176)$ 80.96(81.05) 5.50(5.44) 4.85 3.18 3.10^{\circ} VII-1 Ph Ph 21 $(1.4-176)$ 80.96(81.05) 5.50(5.44) 4.85 3.18 3.10^{\circ} VII-2 Ph Ph 21 $(1.4-176)$ 80.96(81.05) 5.50(5.44) 4.85 3.18 3.10^{\circ} VII-2 Ph Ph 21 $(1.4-176)$ 76.96(76.86) 5.50(5.44) 4.85 3.18 3.10^{\circ} 1.50(1.Hz) VII-2 Ph Ph 21 $(1.4-176)$ 76.96(76.86) 5.50(5.42) 7.72 $(1.2-176)$ 78.72 $(1.2-176)$ 79.72 $(1.2-176)$ 79.72 $(1.2-176)$ 79.92 $(1.2-176)$ 70.91 $(1.2-176)$	VI-2 Ph COOMe COOMe Ph 26 218–219 73.26(73.09) 5.28(5.14) 4.75 3.32 VII-1 COOMe Me COOMe Ph 26 118–119 73.26(73.09) 5.28(5.14) 4.75 3.32 VII-1 COOMe Me COOMe Ph 50 118–104 68.33(68.04) 5.57(5.54) 4.94 3.57 3.40 11.50(2 Hz) VIII Ph Me Me 7000Me 70 1165(2 Hz) 4.96 3.57 3.53 4.00 11.61(1 Hz) X Ph Ph 27 2.67 2.96 XII Ph Ph 27 2.67 2.66 XII Ph Ph 27 2.66 XII Ph Ph 27 180-121 73.41(76.10) 5.44(5.54) 4.95 3.18 3.10 ⁶ XII Ph Ph 3.17 180(5.44) 4.82 3.18 3.10 ⁶ XIII Ph Ph 14 2000Me 48 119–121 73.41(76.10) 5.64(5.64) 4.85 3.18 3.10 ⁶ XIII Ph Ph 14 2000Me 48 119–121 73.41(76.10) 5.64(5.34) 4.82 3.18 3.10 ⁶ XIII Ph Ph 14 2000Me 48 119–121 73.41(76.10) 5.64(5.64) 4.82 3.18 3.10 ⁶ XIII Ph Ph 14 2000Me 48 119–121 73.41(76.10) 5.64(5.64) 4.82 3.18 3.10 ⁶ XIII Ph Ph Ph 27 180(5.113) 5.61(5.48) 4.72 3.17 11.82(2 Hz) XV-1 Ph Ph Ph 2000Me 68 180-182 75.88(76.13) 5.61(5.48) 4.72 3.17 11.82(2 Hz) XV-1 Ph Ph Ph 2000Me 68 180-182 75.88(76.13) 5.61(5.48) 4.72 3.17 11.82(2 Hz) XV-1 Ph Ph Ph 2000Me 98 180-182 75.88(76.13) 5.61(5.43) 4.72 3.17 11.82(2 Hz) XV-1 Ph Ph Ph 2000Me 98 180-182 75.88(76.13) 5.51(5.29) 4.90 3.22 XV-1 Ph Ph Ph 2000Me 98 180-182 70.67(7.081) 5.51(5.29) 4.90 3.22 XV-1 Ph Ph Ph 2000Me 98 180-182 70.67(7.081) 5.51(5.29) 4.90 3.22 XV-1 Ph Ph Ph 2000Me 99 202-203 70.59(70.81) 5.50(5.32) 4.89 3.30 1.18(2 Hz) XV-1 COOMe Ph 2000Me Ph 2000Me 91 202-203 70.59(70.81) 5.40(5.32) 4.89 3.30 3.16 1.183(2 Hz) XV-1 COOMe Ph 2000Me Ph 2000Me 91 202-203 70.59(70.81) 5.40(5.32) 4.89 3.30 1.18(2 Hz) XV-1 COOMe Ph 2000Me	VI-2 Ph COOMe COOMe Ph 26 218-219 73.26(73.09) 5.28(5.14) 4.75 3.32 VII-1 COOMe Me Ke COOMe Ph 26 218-219 73.26(73.09) 5.28(5.54) 4.98 3.46 1.50(2 Hz) VII-2 COOMe Me Ke COOMe Ph 50 158-160 65.26(65.04) 4.98 3.46 1.50(2 Hz) VIII Ph Me Me Ke 50 6101.02) 6.11(6.08) 4.64 3.57 3.40 1.65(1 Hz) X Ph Ph COOMe 48 119-121 73.41(73.08) 5.27(6.14) 4.95 3.46 3.20 XI Ph Ph 21 27.41(73.08) 5.27(6.14) 4.95 3.46 3.20 XI Ph Ph 21 27.41(73.08) 5.59(6.44) 4.85 3.18 3.10 ⁶ XI Ph Ph H COOMe 48 119-121 73.41(73.08) 5.69(6.46) 4.85 3.18 3.10 ⁶ XI Ph Ph H COOMe 48 119-121 73.41(73.08) 5.69(6.46) 4.85 3.18 3.10 ⁶ XI Ph Ph H COOMe 48 119-121 73.41(73.08) 5.69(6.46) 4.85 3.18 3.10 ⁶ XI Ph Ph Ph H 2000Me 48 119-121 73.41(73.08) 5.69(6.46) 4.85 3.18 3.10 ⁶ XII Ph Ph Ph Ph Ph Ph 27 218 78.114(1.06) 5.69(6.46) 4.82 3.13 3.10 ⁶ XII Ph Ph Ph Ph Ph Ph 27 2.96 7.70 XV-1 Ph Ph Ph Ph 2000Me 68 180-182 76.8(76.13) 5.61(6.48) 4.80 3.17 1.82(2 Hz) XV-1 Ph Ph Ph Ph Ph 2000Me 68 180-182 76.8(76.13) 5.61(6.48) 4.80 3.17 1.82(2 Hz) XV-1 Ph Ph Ph Ph 2000Me 9 2.17-218 78.18(77.80) 5.24(5.29) 4.90 3.22 1.56(2 Hz) XV-1 Ph Ph Ph Ph 2000Me 9 2.17-218 78.18(77.80) 5.24(5.29) 4.90 3.32 1.58(2 Hz) XV-1 Ph Ph Ph 2000Me 9 2.202 70.67(70.81) 5.24(5.29) 4.90 3.32 1.58(2 Hz) XV-2 COOMe Ph 2000Me Ph 2000Me 9 2.02-203 70.57(70.81) 5.24(5.32) 4.80 3.30 1.184(2 Hz) XV-2 COOMe Ph 2000Me Ph 30 179-182 70.57(70.81) 5.24(5.32) 4.80 3.30 1.186(2 Hz) XV-2 COOMe Ph 2000Me Ph 2000Me 9 2.0007(70.81) 5.24(5.32) 4.80 3.37 (VAB 10 6.6 - 6.6 0.018 Ph 10.41, 6A - 6_B 0.08 Ppm), 4A 2000Me 2000Me Ph 2000M	1-17	£	COOMe	E	COOMe	29	215-217	72,92(73,00)	5,27(5,14)	4,92	3.06 3.03	
$ \begin{array}{lcccccccccccccccccccccccccccccccccccc$	VII-1 COOMe Me Me COOMe 9 102–104 68.33(08.04) 5.77(5.54) 4.98 3.46 1.50(2 Hz) VII-2 COOMe Me COOMe Me 50 158–160 68.25(654) 4.94 3.57 3.40 1.56(2 Hz) VII-2 COOMe Me COOMe Ph 54 1174–176 76.47(5.10) 6.56(5.64) 4.95 3.18 3.10 f X Ph Ph COOMe COOMe 48 119–121 73.41(73.08) 5.57(5.14) 4.95 3.18 3.10 f X Ph Ph 21 Ph 21 Ph 21 73.41(73.08) 5.57(5.44) 4.95 3.18 3.10 f X Ph Ph 21 Ph 21 Ph 21 73.41(73.08) 5.56(5.63) 4.72 1.51(1 Hz) X Ph Ph 21 Ph 21 Ph 21 73.41(73.08) 5.56(5.63) 4.72 1.51(1 Hz) X Ph Ph 21 Ph 21 Ph 21 73.41(73.08) 5.56(5.63) 4.72 1.51(1 Hz) X Ph Ph 21 Ph 21 Ph 21 76.96(5.66) 5.59(5.42) 4.85 3.18 3.10 f X Ph Ph 21 Ph 21 2000e 48 149–151 76.96(5.63) 4.72 4.89 3.43 1.7 1.50(1 Hz) X Ph Ph Ph 21 COOMe 48 149–151 76.96(5.63) 4.72 4.89 3.43 1.7 1.50(1 Hz) X Ph Ph Ph 21 COOMe 68 180–182 75.88(76.11) 5.65(5.63) 4.72 2.95 4.72 1.52(2 Hz) X Ph Ph Ph 21 Ph 21 2000e 9 202–203 70.59(5.41) 5.50(5.42) 5.07 2.96 1.63(2 Hz) X V-1 Ph Ph 2000e Ph 29 170-7178(77.89) 5.50(5.32) 5.03 3.34 3.16 1.63(2 Hz) X V-2 COOMe Ne Ph 2000me 9 202–203 70.67(70.81) 5.24(5.32) 4.99 3.13 1.86(2 Hz) X V-2 COOMe Ne Ph 29 170-600 8.60 (17.60) 5.60(5.32) 5.03 3.34 3.16 1.63(2 Hz) X V-2 COOMe Ne Ph 2000me 9 202–203 70.67(70.81) 5.24(5.32) 4.99 3.10 1.86(2 Hz) X V-2 COOMe Ne Ph 2000me 9 202–203 70.67(70.81) 5.24(5.32) 4.89 3.16 1.63(2 Hz) X V-4 50 0.68 0 Ph 2000 2.00 3.10 1.142 0.67(70.81) 5.24(5.32) 4.89 3.34 3.16 1.63(2 Hz) X V-4 50 0.68 0 Ph 2000 2.00 2.00 3.00 1.70 2.90 4.90 3.22 (JA B DAITECH Centered at 3.97 (JA B DAITECH CENTERED CENTERED CENTERED CENTERED CENTERED CENTERED ENDERED CENTERED ENDERED ENDE	VII-1 COOMe Me Me COOMe 9 102–104 68.33(08.04) 5.77(5.54) 4.98 3.46 1.56(2 Hz) VII-2 COOMe Me COOMe Me COOMe 9 102–104 68.33(08.04) 5.57(5.54) 4.94 3.57 3.40 1.56(2 Hz) VII-2 COOMe Me COOMe 76 1 14–176 80.96(81.02) 5.57(5.64) 4.94 3.57 3.40 1.56(1 Hz) X Ph Ph COOMe 70 14 119–121 73.41(73.0B) 5.27(5.14) 4.95 3.46 3.20 1.51(1 Hz) X Ph Ph 3 18 3.10 ⁶ 1.56(5.64) 4.85 3.18 3.10 ⁶ 1.56(1 Hz) X Ph Ph 3 18 27 180–182 81.14(81.05) 5.63(5.44) 4.85 3.18 3.10 ⁶ 1.56(1 Hz) X Ph Ph 3 18 Ph 27 180–182 81.14(81.05) 5.63(5.44) 4.85 3.18 3.10 ⁶ 1.56(1 Hz) X Ph Ph H COOMe 48 149–151 76.96(76.86) 5.59(6.42) 4.72 1.50(1 Hz) X Ph Ph Ph 3 27 180–182 81.14(81.05) 5.63(5.44) 4.85 3.18 3.10 ⁶ 1.56(1 Hz) X Ph Ph Ph 2 27 180–182 71.58(76.16) 5.65(6.63) 4.72 1.50(1 Hz) X Ph Ph Ph Ph 2 200Me 68 180–182 75.68(76.86) 5.50(5.42) 4.90 3.17 1.82(2 Hz) X Ph Ph Ph Ph 2 200Me 68 180–182 75.68(76.96) 5.07 2.96 X V-1 Ph Ph Ph 2 3.031.6 1.68(76.59) 5.50(5.52) 4.90 3.22 X V-2 Ph Ph 2 000Me Ph 2 200Me 9 202–203 77.78(77.89) 5.24(5.52) 4.90 3.23 3.16 1.63(2 Hz) X V-2 COOMe Me Ph 200Me 9 202–203 77.78(77.89) 5.24(5.32) 4.90 3.20 1.68(2 Hz) X V-2 COMe Me Ph 200Me 9 202–203 77.76(70.81) 5.60(5.62) 4.89 3.22 X V-2 Ph Ph 2 000Me 9 202–203 77.78(77.891) 5.24(5.32) 4.90 3.30 3.16 1.68(2 Hz) X V-2 COMe Me Ph 200Me 9 202–203 77.76(70.81) 5.24(5.32) 4.90 3.30 3.16 1.68(2 Hz) X V-2 COMe Me Ph 200Me 9 202–203 77.7081 5.24(5.32) 4.80 3.30 3.16 1.68(2 Hz) X V-2 COMe Me Ph 200Me 9 202–203 77.7081 5.24(5.32) 4.80 3.30 3.16 1.68(2 Hz) X V-2 COMe Me Ph 200Me 9 200-67(70.81) 5.24(5.32) 4.80 3.30 7.0/AB 1.66(7 4.66, 5.60) 5.00 5.00 5.00 5.00 5.00 5.00 5.00 5.	VII-1 COOMe Me Ge COOMe 9 192-194 66.33(66.04) 5.77(5.54) 4.98 3.46 1.50(2 Hz) VII-2 COOMe Me COOMe Me E0 158-160 68.25(6.04) 5.57(5.54) 4.94 3.57 3.40 1.55(2 Hz) VIII Ph Me Me COOMe COOMe 48 119-121 73.34(73.08) 5.27(5.14) 4.95 3.46 3.20 I.51(1 Hz) X Ph Ph COOMe COMe 48 119-121 73.41(76.10) 5.04(5.94) 4.85 3.46 3.20 XI Ph Ph H COOMe 48 119-121 73.41(76.10) 5.04(5.94) 4.85 3.43.310° XI Ph Ph H A COOMe 48 119-121 76.65(5.64) 4.85 3.46 3.20 XI Ph Ph H COOMe 48 119-121 76.65(5.63) 4.72 4.86 3.20 XI Ph Ph H COOMe 48 119-121 76.65(5.63) 4.72 4.86 3.18.310° XI Ph Ph H COOMe 48 119-121 76.65(5.63) 4.72 4.72 11.52(2 Hz) XI Ph Ph Ph H COOMe 48 119-151 76.96(5.63) 4.72 4.72 3.17 1.52(2 Hz) XI Ph Ph Ph Ph Ph Ph Ph Ph COOMe 68 180-182 75.80(61.35) 5.61(6.43) 3.17 1.52(2 Hz) XV-1 Ph Ph Ph Ph Ph COOMe 68 180-182 75.80(61.36) 5.61(6.43) 3.17 1.52(2 Hz) XV-1 Ph	V1-2	<u>ب</u>	COOMe	COOMe	h	26	218-219	73,26(73,09)	5,28(5,14)	4.75	3.32	•
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	VII-2 COOMe Me COOMe Me 50 158-160 68.25(68.04) 5.55(6.54) 4.94 3.57 3.40 1.65(2 Hz) VIII Ph Me Me COOMe Ph 54 174-176 80.96(81.02) 6.11(6.08) c 4.64 1.61(1 Hz) X Ph Ph CH20Me CH30Me 48 119-121 73.41(73.08) 5.27(6.14) 4.95 3.46 3.20 1.61(1 Hz) X Ph Ph 31 Ph 33 Ph 27 180-182 81.14(61.10) 5.04(5.94) 4.85 3.18 3.10 e XII Ph Ph 34 Ph 48 149-151 73.41(73.08) 5.59(6.42) e 4.86 3.20 XII Ph Ph 34 Ph 34 Ph 27 180-182 81.14(61.10) 5.66(5.63) 4.86 3.34 3.10 e XII Ph Ph 94 Ph 27 180-182 76.86(7.6.86) 5.59(6.42) e 4.89 3.43 XIV Ph Ph Ph 94 Ph 94 e 700Me 68 180-182 75.86(7.6.86) 5.59(6.42) e 4.89 3.17 1.85(2 Hz) XV-1 Ph Ph Ph Ph 200Me 68 180-182 75.86(7.6.86) 5.00(7.29) e 4.90 3.22 XV-1 Ph Ph Ph 200Me Ph 200Me 9 202-203 70.59(7.0.81) 5.22(5.29) 4.90 3.22 XV-1 Ph Ph 200Me Ph 200Me 9 202-203 70.59(7.0.81) 5.24(5.32) 4.90 3.22 XV-1 Ph Ph 200Me Ph 200Me 9 202-203 70.59(7.0.81) 5.24(5.32) 4.90 3.22 XV-1 Ph 200Me Ne Ph 200Me 9 202-203 70.59(7.0.81) 5.24(5.32) 4.90 3.22 XV-1 Ph 200Me Ne Ph 200Me 9 202-203 70.59(7.0.81) 5.24(5.32) 4.90 3.22 1.63(2 Hz) XV-2 Ph 200Me Ne Ph 200Me 9 202-203 70.59(7.0.81) 5.24(5.32) 4.80 3.16 1.66(2 Hz) XV-1 Ph 200Me Ne Ph 200Me 9 202-203 70.59(7.0.81) 5.24(5.32) 4.80 3.30 3.16 1.66(2 Hz) XV-1 Ph 200Me Ne Ph 200Me 9 202-203 70.56(7.0.81) 5.24(5.32) 4.80 3.30 3.16 1.66(2 Hz) XV-1 Ph 200Me Ne Ph 200Me 9 202-203 70.56(7.0.81) 5.24(5.32) 4.80 3.30 3.16 1.66(2 Hz) XV-2 Ph 200Me Ne Ph 200Me 9 202-203 70.56(7.0.81) 5.24(5.32) 4.80 3.30 3.16 1.66(2 Hz) XV-2 Ph 200Me 13.37 Ph 200Me 9 202-203 70.56(7.0.81) 5.24(5.32) 4.80 3.30 3.16 1.66(2 Hz) XV-2 Ph 200Me 13.37 Ph 200Me 9 202-203 70.57(7.0.81) 5.24(5.32) 4.80 3.30 4.166 Ph 50.48 Ph 70 4.60	VII:2 COOMe Me COOMe Me 50 158-160 68.25(6.54) 4.94 3.57 3.40 1.66(2 Hz) 2 YII:2 COOMe Me Ph E4 1174-176 80.96(61.02) 6.11(6.08) $^{\circ}$ 4.64 3.57 3.40 1.66(2 Hz) 1.51(1 Hz) 1.7 Ph Ph 2006 COOMe 48 119-121 73.41(73.08) 5.27(6.14) 4.95 3.46 3.20 1.61(1 Hz) 1.51(1 Hz) 1.7 Ph Ph 31 Ph 27 119-121 73.41(76.10) 5.63(6.44) 4.85 3.18 3.10^{\circ} 1.61(1 Hz) XII Ph Ph 14 COOMe COOMe 48 119-121 73.41(76.10) 5.63(6.44) 4.85 3.18 3.10^{\circ} 1.61(1 Hz) XII Ph Ph 14 COOMe 700 48 114-176 76.47(6.10) 5.63(6.44) 4.85 3.18 3.10^{\circ} 1.60(1 Hz) XII Ph Ph 14 COOMe 48 149-151 76.96(76.86) 5.59(6.43) 4.72 1.80 1.62(1 Hz) 1.82(2 Hz) XV1 Ph Ph Ph Ph 27 180-182 71.68(75.66) 5.59(5.44) 4.89 3.43 1.60(1 Hz) XV1 Ph Ph Ph Ph Ph 27 000Me 48 149-151 76.96(76.86) 5.59(5.32) 2.9 4.90 3.17 1.82(2 Hz) XV1 Ph Ph Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV1 Ph Ph Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV1 Ph Ph Ph Ph Ph COOMe 9 202-203 70.59(5.29) 5.07 2.96 1.63(2 Hz) XV1 Ph Ph Ph Ph COOMe Ph 200 77.89(5.39(5.22) 4.90 3.22 XV1 1.82(2 Hz) XV1 COOMe Ne Ph 20 2000 77.69(1) 5.24(5.32) 4.90 3.22 XV1 1.82(2 Hz) XV1 COOMe Ne Ph 20 2000 77.69(1) 5.24(5.32) 4.90 3.22 2.00 7.96 7.77.80 1.63(7.63) 5.24(5.32) 4.90 3.22 2.00 7.77.80 1.63(7.14) 5.24(5.32) 4.30 3.34.3.16 1.63(2 Hz) XV1 2.000Me Ne Ph 20 200Me Ne Ph 20 200Me Ne Ph 20 200Me Ne Ph 20 2010 7.77.80 1.5.24(5.32) 4.30 3.34.3.16 1.63(2 Hz) XV1 2.000Me Ne Ph 20 200Me Ne Ph 20 201 70.60 5.24(5.32) 4.30 3.30 7.4A 1.66(2 Hz) 5.24(5.32) 4.30 3.30 7.4A 1.66(2 Hz) 1.6	VII-2 COOMe Me COOMe Me 60 168-160 68.25(68.04) $5.55(5.54)$ 4.94 3.57 3.40 1.65(2 Hz) 2 VII-2 Ph Me Me Ph 64 174-176 80.96(61.02) 6.11(6.08) 646 4.64 1.61(1 Hz) 1.51(1 Hz) 1.71 Ph Ph COOMe COOMe 48 119-121 73.41(73.08) 6.24(5.94) 4.95 3.46.3.20 1.61(1 Hz) 1.51(1 Hz) 1.71 Ph Ph 21 Ph 21 1.4-176 76.44(76.10) 5.63(5.4.4) 4.95 3.18.3.10 e 1.61(1 Hz) 1.51(1 Ph Ph 21 Ph 21 Ph 21 1.31(1.73.08) 5.63(5.4.4) 4.85 3.18.3.10 e 1.61(1 Hz) 1.71 Ph Ph 14 Ph 21 Ph 21 1.41(1.71.06) 5.63(5.4.4) 4.82 3.13.3.10 e 1.61(1 Hz) 1.71 Ph Ph 14 COOMe 48 11.4-176 76.46(76.86) 5.63(5.4.4) 4.82 3.13 3.10 e 1.61(1 Hz) 1.71 Ph Ph Ph Me Ph 27 180-182 71.46(76.86) 5.63(5.4.4) 4.82 3.13 3.10 e 1.61(1 Hz) 1.71 Ph Ph Ph Ph Ph 200 Me 48 149-151 76.96(76.86) 5.63(5.4.4) 4.82 3.17 1.82(2 Hz) 1.71 Ph Ph Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) 1.82(2 Hz) 1.71 Ph Ph Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.68) 3.13 1.63(2 Hz) 1.82(2 Hz) 1.71 Ph Ph Ph Ph Ph Ph COOMe 98 180-182 75.88(76.13) 5.61(5.68) 3.343.16 1.63(2 Hz) 1.82(2 Hz) 1.71 COOMe Ph 20 000 Ph 202-203 77.78(77.89) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) 1.82(2 Hz) 1.71 COOMe Ph 20 000 Ph 202-203 77.78(77.89) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) 1.82(2 Hz) 1.71 COOMe Ph 20 2.00 Ph 202-203 77.78(77.89) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) 1.64(2 Hz) 1.70^{6} under reduced pressure. ^b Solvated with $\int Ph COOMe Ph 202-203 77.76(77.89) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) 1.65(0.74) 1.66(7.56) 1.66(7.56) 1.60(7.70.81) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) 1.66(7 Hz) 1.66$	1-11/	COOMe	Me	Me	COOMe	6 .	102-104	68.33(68.04)	5.77(5.54)	4,9.8	3,46	1.50(2 Hz)
Ph Me Ph 54 174-176 80.96(81.02) 6.11(6.08) ^C 4.64 Ph CH20Me CH20Me CH30Me 4.8 119-121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 Ph CH20Me CH20Me CH20Me 4.0 174-176 78.47(6.10) 6.04(5.94) 4.85 3.46.3.20 Ph Ph CH20Me CH20Me 4.0 174-176 78.47(6.10) 6.04(5.94) 4.85 3.46.3.20 Ph Ph H COOMe 27 180-182 81.14(81.06) 5.63(5.42) 4.85 3.46.3.20 Ph Ph H COOMe 48 119-151 76.96(76.86) 5.59(5.42) 4.82 3.43 Ph Me Ph Me Ph Me COOMe 68 180-181 76.96(76.86) 5.50(5.42) 4.82 3.43 Ph Me Ph Me Ph Me Ph 72.96(7.613) 5.51(5.42) 4.90 <th< td=""><td>VIII Ph Me Me We Ph 54 $174-176$ 80.96(81.02) 6.11(6.08)^c 4.64 1.61(1 Hz) X Ph Ph COOMe COOMe 48 119-121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 XI Ph Ph CH2OMe CH2OMe 40 174-176 76.44(76.10) 6.04(5.94) 4.85 3.18.3.10^c XI Ph Ph X Ph 27 180-182 81.14(81.05) 5.63(5.44) 4.85 3.18.3.10^c XIII Ph Ph Me Ph 27 180-182 81.14(81.05) 5.63(5.44) 4.85 3.18.3.10^c XIII Ph Ph Me Ph 200Me 48 149-151 76.96(76.86) 5.69(6.42) 4.85 3.18.3.10^c XIII Ph Ph Me Ph 200Me 48 149-151 76.96(76.86) 5.69(5.43) 4.72 1.80(1.14z) XIII Ph Ph Ph 200Me 68 180-182 81.14(81.05) 5.63(5.48) 4.89 3.17 1.82(2.14z) XV-1 Ph Ph Ph 200Me 68 180-182 75.88(76.13) 5.61(5.49) 4.90 3.22 XV-1 Ph Ph COOMe Ph 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-1 Ph Ph 200Me Ph 339 1.00-182 70.56(70.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2.14z) XV-2 Ph Ph 200Me Ph 30 1790-182 70.67(70.81) 5.24(5.32) 4.90 3.22 XV-1 Ph Ph 200Me Ph 30 3.20 7.04 9.03 3.20 1.63(2.14z) XV-1 Ph Ph 200Me Ph 30 9.179-182 70.47,0181) 5.24(5.32) 4.90 3.22 (12) XV-1 Ph Ph 200Me Ph 30 0.160(5.32) 5.03 3.34 3.16 1.66(2.14z) XV-1 Ph Ph 200Me Ph 30 0.170 4.1176 4.646.^c Solvated with $\frac{1}{2}$CH3.013, $\frac{1}{4}$ PM of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6.44 8.74 10.02 (10.81) 5.24(5.32) 4.90 3.20 3.16 1.66(2.14z) $\frac{1}{2}$ Ph 6B 0.21 PPM) and a one hroad singlet at 3.73 Pm.^c PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6.44 8.74 0.03 Pm M</td><td>VIII Ph Me Me We Ph 54 174–176 80.96(61.02) 6.11(6.08) ^c 4.64 1.61(1 Hz) X Ph Ph CH₂OMe C0OMe 48 119–121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 X Ph Ph CH₂OMe CH₂OMe 40 174–176 76.47(76.10) 6.04(5.94) 4.85 3.18.3.10^e X Ph Ph H COOMe 48 1190–121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 X Ph Ph H COOMe 48 149–151 73.61(5.64) 4.82 3.18.3.10^e X Ph Ph Me Ph Me 27 180–182 81.14(61.06) 5.65(5.63) 4.72 1.50(1 Hz) X Ph Ph Me Ph Me 27 180–182 75.86(7.6.18) 5.56(5.63) 4.72 1.82(2 Hz) X Ph Ph Ph Me 200Me 68 180–182 75.86(7.6.18) 5.61(5.48) 4.80 3.17 1.82(2 Hz) X Ph Ph Ph 2 200Me 9 2017 181.40(1.71) 5.65(5.63) 4.72 1.62(2 Hz) X V-1 Ph Ph 2 200Me 9 202–203 70.59(7.0.81) 5.24(5.29) 4.90 3.22 X V-2 Ph Ph COOMe Ph 39 1170–182 70.56(7.0.81) 5.24(5.29) 4.90 3.22 X V-1 Ph 2 200Me 9 202–203 70.59(7.0.81) 5.24(5.29) 4.90 3.22 X V-1 Ph 2 COOMe Ph 39 170–182 70.67(7.81) 5.4(5.32) 5.03 3.34 3.16 1.63(2 Hz) X V-2 Ph 2 Ph 2 COOMe 9 202–203 70.59(7.0.81) 5.24(5.32) 4.89 3.30 3.16 1.66(2 Hz) X V-1 Ph 2 COOMe 9 202–203 70.59(7.0.81) 5.24(5.32) 4.80 3.20 3.16 1.66(2 Hz) X V-2 Ph 2 Ph</td><td>VIII Ph Me Me Ph 114-176 80.96(81.02) 6.11(6.08) $^{\circ}$ 4.64 1.61(1.Hz) IX Ph Ph COOMe COOMe 48 119-121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 XI Ph Ph 33 Ph 27 114(61.06) 5.63(5.44) 4.85 3.18.3.10 $^{\circ}$ XIII Ph Ph H COOMe 48 149-151 76.47(76.10) 5.04(5.93) 4.72 1.50(1.Hz) XIII Ph Ph Me Ph 87 149-151 76.96(76.86) 5.53(5.44) 4.86 3.17 1.50(1.Hz) XIII Ph Ph Me Ph 87 149-151 76.96(76.86) 5.53(5.44) 4.89 3.17 1.82(2.Hz) XIII Ph Ph Me Ph 87 169-171 81.40(81.17) 5.65(5.63) 4.72 1.50(1.Hz) XV-1 Ph Ph Ph Me Ph 87 169-171 81.40(81.17) 5.65(5.63) 4.72 1.50(1.Hz) XV-1 Ph Ph</td><td>VII-2</td><td>COOMe</td><td>Me</td><td>COOMe</td><td>Me</td><td>60</td><td>158-160</td><td>68,25(68,04)</td><td>-</td><td>4,94</td><td>3.57 3.40</td><td>1.65(2 Hz)2</td></th<>	VIII Ph Me Me We Ph 54 $174-176$ 80.96(81.02) 6.11(6.08) ^c 4.64 1.61(1 Hz) X Ph Ph COOMe COOMe 48 119-121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 XI Ph Ph CH2OMe CH2OMe 40 174-176 76.44(76.10) 6.04(5.94) 4.85 3.18.3.10 ^c XI Ph Ph X Ph 27 180-182 81.14(81.05) 5.63(5.44) 4.85 3.18.3.10 ^c XIII Ph Ph Me Ph 27 180-182 81.14(81.05) 5.63(5.44) 4.85 3.18.3.10 ^c XIII Ph Ph Me Ph 200Me 48 149-151 76.96(76.86) 5.69(6.42) 4.85 3.18.3.10 ^c XIII Ph Ph Me Ph 200Me 48 149-151 76.96(76.86) 5.69(5.43) 4.72 1.80(1.14z) XIII Ph Ph Ph 200Me 68 180-182 81.14(81.05) 5.63(5.48) 4.89 3.17 1.82(2.14z) XV-1 Ph Ph Ph 200Me 68 180-182 75.88(76.13) 5.61(5.49) 4.90 3.22 XV-1 Ph Ph COOMe Ph 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-1 Ph Ph 200Me Ph 339 1.00-182 70.56(70.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2.14z) XV-2 Ph Ph 200Me Ph 30 1790-182 70.67(70.81) 5.24(5.32) 4.90 3.22 XV-1 Ph Ph 200Me Ph 30 3.20 7.04 9.03 3.20 1.63(2.14z) XV-1 Ph Ph 200Me Ph 30 9.179-182 70.47,0181) 5.24(5.32) 4.90 3.22 (12) XV-1 Ph Ph 200Me Ph 30 0.160(5.32) 5.03 3.34 3.16 1.66(2.14z) XV-1 Ph Ph 200Me Ph 30 0.170 4.1176 4.646. ^c Solvated with $\frac{1}{2}$ CH3.013, $\frac{1}{4}$ PM of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6.44 8.74 10.02 (10.81) 5.24(5.32) 4.90 3.20 3.16 1.66(2.14z) $\frac{1}{2}$ Ph 6B 0.21 PPM) and a one hroad singlet at 3.73 Pm. ^c PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6.44 8.74 0.03 Pm M	VIII Ph Me Me We Ph 54 174–176 80.96(61.02) 6.11(6.08) ^c 4.64 1.61(1 Hz) X Ph Ph CH ₂ OMe C0OMe 48 119–121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 X Ph Ph CH ₂ OMe CH ₂ OMe 40 174–176 76.47(76.10) 6.04(5.94) 4.85 3.18.3.10 ^e X Ph Ph H COOMe 48 1190–121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 X Ph Ph H COOMe 48 149–151 73.61(5.64) 4.82 3.18.3.10 ^e X Ph Ph Me Ph Me 27 180–182 81.14(61.06) 5.65(5.63) 4.72 1.50(1 Hz) X Ph Ph Me Ph Me 27 180–182 75.86(7.6.18) 5.56(5.63) 4.72 1.82(2 Hz) X Ph Ph Ph Me 200Me 68 180–182 75.86(7.6.18) 5.61(5.48) 4.80 3.17 1.82(2 Hz) X Ph Ph Ph 2 200Me 9 2017 181.40(1.71) 5.65(5.63) 4.72 1.62(2 Hz) X V-1 Ph Ph 2 200Me 9 202–203 70.59(7.0.81) 5.24(5.29) 4.90 3.22 X V-2 Ph Ph COOMe Ph 39 1170–182 70.56(7.0.81) 5.24(5.29) 4.90 3.22 X V-1 Ph 2 200Me 9 202–203 70.59(7.0.81) 5.24(5.29) 4.90 3.22 X V-1 Ph 2 COOMe Ph 39 170–182 70.67(7.81) 5.4(5.32) 5.03 3.34 3.16 1.63(2 Hz) X V-2 Ph 2 Ph 2 COOMe 9 202–203 70.59(7.0.81) 5.24(5.32) 4.89 3.30 3.16 1.66(2 Hz) X V-1 Ph 2 COOMe 9 202–203 70.59(7.0.81) 5.24(5.32) 4.80 3.20 3.16 1.66(2 Hz) X V-2 Ph 2 Ph	VIII Ph Me Me Ph 114-176 80.96(81.02) 6.11(6.08) $^{\circ}$ 4.64 1.61(1.Hz) IX Ph Ph COOMe COOMe 48 119-121 73.41(73.08) 5.27(5.14) 4.95 3.46.3.20 XI Ph Ph 33 Ph 27 114(61.06) 5.63(5.44) 4.85 3.18.3.10 $^{\circ}$ XIII Ph Ph H COOMe 48 149-151 76.47(76.10) 5.04(5.93) 4.72 1.50(1.Hz) XIII Ph Ph Me Ph 87 149-151 76.96(76.86) 5.53(5.44) 4.86 3.17 1.50(1.Hz) XIII Ph Ph Me Ph 87 149-151 76.96(76.86) 5.53(5.44) 4.89 3.17 1.82(2.Hz) XIII Ph Ph Me Ph 87 169-171 81.40(81.17) 5.65(5.63) 4.72 1.50(1.Hz) XV-1 Ph Ph Ph Me Ph 87 169-171 81.40(81.17) 5.65(5.63) 4.72 1.50(1.Hz) XV-1 Ph	VII-2	COOMe	Me	COOMe	Me	60	158-160	68,25(68,04)	-	4,94	3.57 3.40	1.65(2 Hz)2
Ph COOMe 48 119-121 73.41(73.08) $5.27(5.14)$ 4.95 $3.463.20$ Ph CH2OMe CH2OMe CH2OMe CH30Me CH40Me CH40Me CH40Me CH30Me CH40Me CH40Me CH40Me CH40Me <td>IX Ph Ph COOMe COOMe 48 119-121 73.41(73.08) $5.27(5.14)$ 4.95 3.463.20 XI Ph Ph COMe CP120Me 40 174-176 76.44(76.10) 6.04(5.94) 4.85 3.183.10° XII Ph Ph H COOMe 48 1149-151 76.96(76.86) 5.69(5.44) 4.85 3.183.10° XIII Ph Ph Me Ph COOMe 48 149-151 76.96(76.86) 5.69(5.42) 4.89 3.43 XII Ph Ph Me Ph COOMe 48 149-151 76.96(76.86) 5.69(5.43) 4.72 3.17 1.82(2.12) XIV Ph Ph Me Ph COOMe 68 180-182 75.88(76.13) 5.61(5.63) 4.72 3.17 1.82(2.12) XV-1 Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.63) 4.72 3.17 1.82(2.12) XV-1 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 33 177 1.95(7.0.81) 5.61(5.32) 5.03 3.343.16 1.63(2.12) XV-2 Ph Ph COOMe Ph 33 170.56(70.81) 5.60(5.32) 5.03 3.343.16 1.63(2.12) XV-2 Ph Ph COOMe Ph 30 179-182 70.57(70.81) 5.24(5.32) 4.90 3.22 XV-2 Ph Ph COOMe Ph 30 179-182 70.57(70.81) 5.24(5.32) 4.90 3.22 XV-2 Ph Ph COOMe Ph 30 0.167(70.81) 5.24(5.32) 4.90 3.23 1.6 1.66(2.12) XV-1 Ph Ph COOMe Ph 30 0.177 0.11 1.2.67 -0's appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 J_{AB} 0.03 number 7.65 0.03 number 7.65 0.03 number 12 200 120.10 11 Hz. 6A - 6B 0.48 ppm)</td> <td>IX Ph Ph COOMe COMe 48 119-121 73.41(73.0B) $5.27(5.14)$ 4.95 3.463.20 XI Ph Ph COMe CH20Me 40 174-176 76.44(76.10) 6.04(5.94) 4.85 3.183.10° XI Ph Ph CH20Me CH20Me 40 174-176 76.44(76.10) 5.04(5.94) 4.85 3.183.10° XII Ph Ph H COOMe 48 149-151 76.96(76.86) 5.59(6.43) 4.82 1.83.10° XII Ph Ph Me Ph COOMe 48 149-151 76.96(76.86) 5.59(6.63) 4.72 1.82(2 H2) XII Ph Ph Me Ph COOMe 68 180-182 75.88(76.13) 5.66(5.63) 4.72 1.82(2 H2) XV-1 Ph Ph Ph COOMe 98 180-182 75.88(76.13) 5.66(5.63) 4.72 1.82(2 H2) XV-1 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 2000Me 9 202-203 70.59(7.081) 5.60(5.32) 5.03 3.343.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 170-182 70.59(7.0.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 170-182 70.59(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) 5.2 - 5.03 13.00 17.6 - 5.00.08 Ph 200 - 0.80 170 170-0.5 appear as an AB pattern centered at 3.97 (J_{AB} 10 5.2 - 5.00 10 Hz, $\delta_A - \delta_B 0.08 Ph M$.</td> <td>IX Ph Ph COOMe COOMe 48 119-121 73.41(73.08) $5.27(6.14)$ 4.95 3.463.20 XI Ph Ph CH20Me CH20Me 40 114-176 76.44(76.10) 6.04(6.94) 4.85 3.183.110^e XII Ph Ph H COOMe 48 1190-182 81.14(81.06) 5.63(6.44) 4.82 3.183.110^e XII Ph Ph Me Ph 67 180-182 81.14(81.06) 5.63(6.43) 4.72 1.50(1.142) XIV Ph Ph Me Ph 67 180-181 81.40(81.171) 5.65(6.63) 4.72 1.82(2.142) XV-1 Ph Ph Ph 200Me 68 180-182 75.88(7.6.13) 5.51(5.49) 4.90 3.22 XV-1 Ph Ph Ph 200Me 9 217-218 78.18(77.89) 5.52(5.29) 4.90 3.22 XV-1 Ph Ph COOMe Ph 2000Me 68 217-218 78.18(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 200Me 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34.81.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 39 1170⁻¹¹²² 70.59(70.81) 5.4(5.32) 4.89 3.30.31.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 2000Me 9 202-203 70.59(70.81) 5.4(5.32) 5.03 3.34.81.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 30 177-178(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 30 177-112 70.59(70.81) 5.4(5.32) 5.03 3.34.81.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 30 177.78(77.89) 5.22(5.29) 4.90 3.22 XV-1.2 COOMe Me Ph 2002Me 9 202-203 70.59(70.81) 5.4(5.32) 4.89 3.30.31.6 1.66(2.142) XV-2 COOMe Ne Ph 2000Me 9 2022-203 70.59(70.81) 5.4(5.32) 4.89 3.30.31.6 1.66(2.142) XV-2 Ph Ph 200Me Ph 30 1170^o under reduced pressure. ^b Solvated with $\frac{1}{2}CH_2Cl_2$, ^d PMI of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 $5_A - 5_B 0.21 ppm)$ and as one broad singlet at 3.73 ppm.^e PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.92 (J_{AB} 10) $5_A - 5_B 0.21 ppm)$ and as one broad singlet at 3.73 ppm.^e PMR of $-CH_2-O$'s appear as two AB pattern sentered at 3.92 (J_{AB} 10) and at 3.76 ppm (J_{AB} 10 Hz, $\delta_A - \delta_B 0.08 ppm$).</td> <td>IIIA</td> <td>£</td> <td>Me</td> <td>Me</td> <td>Ъh</td> <td>54</td> <td>174-176</td> <td>80.96(81.02)</td> <td>-</td> <td>4,64</td> <td></td> <td>1.61(1 Hz)</td>	IX Ph Ph COOMe COOMe 48 119-121 73.41(73.08) $5.27(5.14)$ 4.95 3.463.20 XI Ph Ph COMe CP120Me 40 174-176 76.44(76.10) 6.04(5.94) 4.85 3.183.10° XII Ph Ph H COOMe 48 1149-151 76.96(76.86) 5.69(5.44) 4.85 3.183.10° XIII Ph Ph Me Ph COOMe 48 149-151 76.96(76.86) 5.69(5.42) 4.89 3.43 XII Ph Ph Me Ph COOMe 48 149-151 76.96(76.86) 5.69(5.43) 4.72 3.17 1.82(2.12) XIV Ph Ph Me Ph COOMe 68 180-182 75.88(76.13) 5.61(5.63) 4.72 3.17 1.82(2.12) XV-1 Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.63) 4.72 3.17 1.82(2.12) XV-1 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 33 177 1.95(7.0.81) 5.61(5.32) 5.03 3.343.16 1.63(2.12) XV-2 Ph Ph COOMe Ph 33 170.56(70.81) 5.60(5.32) 5.03 3.343.16 1.63(2.12) XV-2 Ph Ph COOMe Ph 30 179-182 70.57(70.81) 5.24(5.32) 4.90 3.22 XV-2 Ph Ph COOMe Ph 30 179-182 70.57(70.81) 5.24(5.32) 4.90 3.22 XV-2 Ph Ph COOMe Ph 30 0.167(70.81) 5.24(5.32) 4.90 3.23 1.6 1.66(2.12) XV-1 Ph Ph COOMe Ph 30 0.177 0.11 1.2.67 -0's appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 J_{AB} 0.03 number 7.65 0.03 number 7.65 0.03 number 12 200 120.10 11 Hz. 6A - 6B 0.48 ppm)	IX Ph Ph COOMe COMe 48 119-121 73.41(73.0B) $5.27(5.14)$ 4.95 3.463.20 XI Ph Ph COMe CH20Me 40 174-176 76.44(76.10) 6.04(5.94) 4.85 3.183.10° XI Ph Ph CH20Me CH20Me 40 174-176 76.44(76.10) 5.04(5.94) 4.85 3.183.10° XII Ph Ph H COOMe 48 149-151 76.96(76.86) 5.59(6.43) 4.82 1.83.10° XII Ph Ph Me Ph COOMe 48 149-151 76.96(76.86) 5.59(6.63) 4.72 1.82(2 H2) XII Ph Ph Me Ph COOMe 68 180-182 75.88(76.13) 5.66(5.63) 4.72 1.82(2 H2) XV-1 Ph Ph Ph COOMe 98 180-182 75.88(76.13) 5.66(5.63) 4.72 1.82(2 H2) XV-1 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 2000Me 9 202-203 70.59(7.081) 5.60(5.32) 5.03 3.343.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 170-182 70.59(7.0.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 170-182 70.59(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) XV-2 Ph Ph COOMe Ph 30 0.08 Ph 30 0.08 Ph 30 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 H2) 5.2 - 5.03 13.00 17.6 - 5.00.08 Ph 200 - 0.80 170 170-0.5 appear as an AB pattern centered at 3.97 (J _{AB} 10 5.2 - 5.00 10 Hz, $\delta_A - \delta_B 0.08 Ph M$.	IX Ph Ph COOMe COOMe 48 119-121 73.41(73.08) $5.27(6.14)$ 4.95 3.463.20 XI Ph Ph CH20Me CH20Me 40 114-176 76.44(76.10) 6.04(6.94) 4.85 3.183.110 ^e XII Ph Ph H COOMe 48 1190-182 81.14(81.06) 5.63(6.44) 4.82 3.183.110 ^e XII Ph Ph Me Ph 67 180-182 81.14(81.06) 5.63(6.43) 4.72 1.50(1.142) XIV Ph Ph Me Ph 67 180-181 81.40(81.171) 5.65(6.63) 4.72 1.82(2.142) XV-1 Ph Ph Ph 200Me 68 180-182 75.88(7.6.13) 5.51(5.49) 4.90 3.22 XV-1 Ph Ph Ph 200Me 9 217-218 78.18(77.89) 5.52(5.29) 4.90 3.22 XV-1 Ph Ph COOMe Ph 2000Me 68 217-218 78.18(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 200Me 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34.81.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 39 1170 ⁻¹¹²² 70.59(70.81) 5.4(5.32) 4.89 3.30.31.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 2000Me 9 202-203 70.59(70.81) 5.4(5.32) 5.03 3.34.81.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 30 177-178(77.89) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph COOMe Ph 30 177-112 70.59(70.81) 5.4(5.32) 5.03 3.34.81.6 1.63(2.142) XV-2 Ph Ph COOMe Ph 30 177.78(77.89) 5.22(5.29) 4.90 3.22 XV-1.2 COOMe Me Ph 2002Me 9 202-203 70.59(70.81) 5.4(5.32) 4.89 3.30.31.6 1.66(2.142) XV-2 COOMe Ne Ph 2000Me 9 2022-203 70.59(70.81) 5.4(5.32) 4.89 3.30.31.6 1.66(2.142) XV-2 Ph Ph 200Me Ph 30 1170 ^o under reduced pressure. ^b Solvated with $\frac{1}{2}CH_2Cl_2$, ^d PMI of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 $5_A - 5_B 0.21 ppm)$ and as one broad singlet at 3.73 ppm. ^e PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.92 (J_{AB} 10) $5_A - 5_B 0.21 ppm)$ and as one broad singlet at 3.73 ppm. ^e PMR of $-CH_2-O$'s appear as two AB pattern sentered at 3.92 (J_{AB} 10) and at 3.76 ppm (J_{AB} 10 Hz, $\delta_A - \delta_B 0.08 ppm$).	IIIA	£	Me	Me	Ъh	54	174-176	80.96(81.02)	-	4,64		1.61(1 Hz)
Ph CH_2OMe CH_2OMe <thch_2ome< th=""> <thch_2ome< th=""> <thch_2o< td=""><td>X Ph Ph CH₂OMe CH₂OMe 40 174–176 76.44(76.10) 6.04(6.94) 4.85 3.18 3.10^e XI Ph Ph CH₂OMe CH₂OMe 40 174–176 76.46(6.69) 5.66(6.64) 4.85 3.18 3.10^e XII Ph Ph H COOMe 48 149–151 76.96(76.86) 5.69(6.42) 4.82 3.43 1.50(1 Hz) XII Ph Ph Me Ph COOMe 48 1490–151 76.86(76.13) 5.61(5.63) 4.72 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 68 1800–182 75.88(76.13) 5.61(5.63) 4.72 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 79 2.17–218 77.80 5.30(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 5.03 3.34 3.16 1.63(2 Hz) XV-2 Ph Ph COOMe Ph 30 17.90–182 70.56(7.0.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2 Hz) XV-1 COOMe Me Ph COOMe Ph 30 17.90–182 70.67(70.81) 5.24(5.32) 4.90 3.22 XV1-1 COOMe Me Ph COOMe Ph 30 17.90–182 70.56(7.0.81) 5.24(5.32) 4.90 3.22 XV1-2 COOMe Me Ph COOMe 9 202–203 70.56(70.81) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.57(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.56(7.03) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.56(7.0.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.57(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.57(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph 200 Network Ph R of $-CH_2-O^{14}$ PM R of $-CH_2-O^{14}$ PM Ph $-CH_2-$</td><td>X Ph Ph CH₂OMe CH₂OMe 40 174–176 76.44(76.10) 6.04(5.94) 4.85 3.18 3.10^e XI Ph Ph CH₂OMe CH₂OMe 40 174–176 76.44(76.10) 5.63(5.44) 4.85 3.18 3.10^e XII Ph Ph H COOMe 48 149–151 76.96(76.86) 5.63(5.43) 4.82 1.50(1.12) XII Ph Ph Me COOMe 48 149–151 76.96(76.86) 5.63(5.63) 4.72 1.82(2 Hz) XV-1 Ph Ph Me COOMe 68 180–182 75.88(76.13) 5.61(5.48) 4.80 3.17 1.82(2 Hz) XV-1 Ph Ph 20000 68 217–218 76.86(7.13) 5.61(5.48) 4.80 3.17 1.82(2 Hz) XV-1 Ph Ph 20000 9 2.77–218 77.80(5.29) 4.90 3.22 XV1-1 COOMe Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 5.03 3.343.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.60(6.32) 5.03 3.343.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 177-0°s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 $-\delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm.^a PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 $-\delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm.^a PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 $-\delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm.^a PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.92 (J_{AB} 10</td><td>XI Ph Ph CH₂OMe CH₂OMe 40 174–176 76.44(76.10) 6.04(5.94) 4.85 3.18 3.10^e XII Ph Ph 3 Ph 21 Ph 21 Ph 22 Ph 22 Ph 23 Ph 4.82 1.14(61.06) 5.63(5.44) 4.82 3.43 1.50(1.Hz) XII Ph Ph Ph 9 Ph 23 Ph 24 Ph 27 1.80–182 81.14(61.06) 5.63(5.44) 4.89 3.43 1.50(1.Hz) XIV Ph Ph Ph 26 COOMe 48 140–151 76.96(76.86) 5.50(5.43) 4.72 1.82(2.Hz) XIV Ph Ph Ph 26 COOMe 68 180–182 75.88(76.13) 5.61(5.49) 4.89 3.17 1.82(2.Hz) XV-1 Ph Ph Ph 20 0.09 Ph 20 0.00 Ph 20 0.182 75.88(76.13) 5.61(5.49) 4.89 3.17 1.82(2.Hz) XV-1 Ph Ph 20 0.00 Ph 20 0.00 Ph 20 0.00 Ph 20 0.120 0.1778(77.89) 5.22(5.29) 4.90 3.22 XV1-1 COOMe Me Ph 20 0.00 Ph 20 0.00 Ph 20 0.00 Ph 20 0.00 Ph 20.00 P</td><td>×</td><td>£</td><td>Ph</td><td>COOMe</td><td>COOMe</td><td>48</td><td>119-121</td><td>73,41(73,08)</td><td>5.27(5.14)</td><td>4,96</td><td>3.46 3,20</td><td></td></thch_2o<></thch_2ome<></thch_2ome<>	X Ph Ph CH ₂ OMe CH ₂ OMe 40 174–176 76.44(76.10) 6.04(6.94) 4.85 3.18 3.10 ^e XI Ph Ph CH ₂ OMe CH ₂ OMe 40 174–176 76.46(6.69) 5.66(6.64) 4.85 3.18 3.10 ^e XII Ph Ph H COOMe 48 149–151 76.96(76.86) 5.69(6.42) 4.82 3.43 1.50(1 Hz) XII Ph Ph Me Ph COOMe 48 1490–151 76.86(76.13) 5.61(5.63) 4.72 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 68 1800–182 75.88(76.13) 5.61(5.63) 4.72 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 79 2.17–218 77.80 5.30(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 5.03 3.34 3.16 1.63(2 Hz) XV-2 Ph Ph COOMe Ph 30 17.90–182 70.56(7.0.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2 Hz) XV-1 COOMe Me Ph COOMe Ph 30 17.90–182 70.67(70.81) 5.24(5.32) 4.90 3.22 XV1-1 COOMe Me Ph COOMe Ph 30 17.90–182 70.56(7.0.81) 5.24(5.32) 4.90 3.22 XV1-2 COOMe Me Ph COOMe 9 202–203 70.56(70.81) 5.24(5.32) 4.99 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.57(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.56(7.03) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.56(7.0.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.57(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 30 17.90–182 70.57(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph 200 Network Ph R of $-CH_2-O^{14}$ PM R of $-CH_2-O^{14}$ PM Ph $-CH_2-$	X Ph Ph CH ₂ OMe CH ₂ OMe 40 174–176 76.44(76.10) 6.04(5.94) 4.85 3.18 3.10 ^e XI Ph Ph CH ₂ OMe CH ₂ OMe 40 174–176 76.44(76.10) 5.63(5.44) 4.85 3.18 3.10 ^e XII Ph Ph H COOMe 48 149–151 76.96(76.86) 5.63(5.43) 4.82 1.50(1.12) XII Ph Ph Me COOMe 48 149–151 76.96(76.86) 5.63(5.63) 4.72 1.82(2 Hz) XV-1 Ph Ph Me COOMe 68 180–182 75.88(76.13) 5.61(5.48) 4.80 3.17 1.82(2 Hz) XV-1 Ph Ph 20000 68 217–218 76.86(7.13) 5.61(5.48) 4.80 3.17 1.82(2 Hz) XV-1 Ph Ph 20000 9 2.77–218 77.80(5.29) 4.90 3.22 XV1-1 COOMe Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 5.03 3.343.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.60(6.32) 5.03 3.343.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph 20000 9 177-0°s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 $-\delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ^a PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 $-\delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ^a PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 $-\delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ^a PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.92 (J_{AB} 10	XI Ph Ph CH ₂ OMe CH ₂ OMe 40 174–176 76.44(76.10) 6.04(5.94) 4.85 3.18 3.10 ^e XII Ph Ph 3 Ph 21 Ph 21 Ph 22 Ph 22 Ph 23 Ph 4.82 1.14(61.06) 5.63(5.44) 4.82 3.43 1.50(1.Hz) XII Ph Ph Ph 9 Ph 23 Ph 24 Ph 27 1.80–182 81.14(61.06) 5.63(5.44) 4.89 3.43 1.50(1.Hz) XIV Ph Ph Ph 26 COOMe 48 140–151 76.96(76.86) 5.50(5.43) 4.72 1.82(2.Hz) XIV Ph Ph Ph 26 COOMe 68 180–182 75.88(76.13) 5.61(5.49) 4.89 3.17 1.82(2.Hz) XV-1 Ph Ph Ph 20 0.09 Ph 20 0.00 Ph 20 0.182 75.88(76.13) 5.61(5.49) 4.89 3.17 1.82(2.Hz) XV-1 Ph Ph 20 0.00 Ph 20 0.00 Ph 20 0.00 Ph 20 0.120 0.1778(77.89) 5.22(5.29) 4.90 3.22 XV1-1 COOMe Me Ph 20 0.00 Ph 20 0.00 Ph 20 0.00 Ph 20 0.00 Ph 20.00 P	×	£	Ph	COOMe	COOMe	48	119-121	73,41(73,08)	5.27(5.14)	4,96	3.46 3,20	
Ph Ph Ph 27 180–182 81,14(81.06) 6.63(6,44) 4.82 Ph Ph H COOMe 48 149–151 76.96(76.86) 5.58(6,42) 4.82 Ph Ph H COOMe 48 149–151 76.96(76.86) 5.58(6,42) 4.89 3.43 Ph Ph Me Ph 67 159–171 81.40(81.17) 5.66(5.63) 4.72 4.89 3.17 Ph Ph Me COOMe 68 180–182 75.88(76.13) 5.61(5.48) 4.89 3.17 Ph Ph Ph COOMe 68 180–182 75.88(75.13) 5.61(5.48) 4.89 3.17 Ph Ph Ph COOMe 5 217–218 75.38(75.19) 5.07 2.96 Ph Ph COOMe 9 200 77.78(77.89) 5.22(5.29) 4.90 3.22 COOMe Me Ph 200 177.78(77.89) 5.22(5.29)	XI Ph Ph 34	XI Ph Ph 3 Ph 3 Ph 27 180-182 81.14(81.06) $5.63(5,44)$ 4.82 XII Ph Ph 3 Ph 3 Ph 27 180-182 81.14(81.06) $5.63(5,44)$ 4.82 XII Ph Ph H COOMe 48 149-151 76.86(5.63) 4.72 1.80 1.50(1.12) TV Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5,48) 4.89 3.17 1.82(2.12) XV-2 Ph Ph COOMe Ph 43 210 77.18(77.80(5.39(5.29) 4.90 3.22 XV-1 COOMe Ph 2000 9 202-203 70.59(7.0.81) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph 2000 Ph 2000 9 202-203 70.59(70.81) 5.22(5.29) 4.90 3.22 XV-2 Ph Ph 2000 Ph 2000 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30.8.16 1.63(2.12) XV-2 Ph 2000 Me Ph 2000 Ph 30 170-1182 70.67(70.81) 5.24(5.32) 4.89 3.30.8.16 1.68(2.12) XV-2 COOMe Me Ph 2000 Ph 30 170-1182 70.69(7.0.81) 5.24(5.32) 4.89 3.30.8.16 1.68(2.12) XV-2 COOMe Me Ph 2000 Ph 30 170-1182 70.67(70.81) 5.24(5.32) 4.89 3.30.8.16 1.68(2.12) XV-2 COOMe Me Ph 2000 Ph 30 170-1182 70.67(70.81) 5.24(5.32) 4.89 3.30.8.16 1.68(2.12) XV-6 Dh 41 170° under reduced pressure. ^b Solvated with $\frac{1}{2}$ CH ₂ -0's appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 J_{AB} 10 Hz, $\delta_{A} - \delta_{B}$ 0.08 Ppm).	XI Ph Ph 3 Ph 3 Ph 27 180-182 81.14(61.06) 5.63(5,44) 4.82 XII Ph Ph 3 Ph 3 Ph 27 150(1 Hz) 76.96(76.86) 5.59(5.42) 4 4.89 3.43 XII Ph Ph Ph Me Ph 67 169-171 81.40(81.17) 5.65(5.63) 4.72 1.50(1 Hz) XV-1 Ph Ph Ph COOMe 48 140-182 75.88(76.13) 5.61(5,43) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5,43) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe Ph 2.90 3.22 (5.29) 4.90 3.22 (5.29) 4.90 3.22 XV-1 COOMe Me Ph 20 Ph 2.0 77.78(77.89) 5.24(5.32) 4.99 3.30 3.16 1.83(2 Hz) XV-2 COOMe Me Ph COOMe Ph 20 77.78(77.89) 5.24(5.32) 4.90 3.22 (5.29) 1.86(2 Hz) XV-2 COOMe Me Ph 20 202-203 70.59(7.0.81) 5.24(5.32) 4.90 3.22 (5.29) 1.86(2 Hz) XV-2 COOMe Me Ph 20 200 Ph 39 179-182 70.67(70.81) 5.24(5.32) 4.90 3.20 1.86(2 Hz) XV-2 COOMe Me Ph 20 200 Ph 30 170-91 Ph 10 Ph 20 Ph 20 20 Ph 20 P	×	£	5	CH2OMe	CH ₂ OMe	40	174-176	76.44(76.10)	6.04(5,94)	4,85	3,18 3,10 6	
Ph H COOMe 48 149-151 76.96(76.86) 5.59(6.42) 4.89 3.43 Ph Me Ph GOOMe 48 149-171 81.40(81.17) 5.66(5.63) 4.72 4.72 Ph Me Ph 67 169-171 81.40(81.17) 5.66(5.63) 4.72 Ph Ph Me COOMe 68 180182 75.88(76.13) 5.61(5.48) 4.89 3.17 Ph Ph Ph COOMe 68 180182 75.88(77.89) 5.38(5.29) 5.07 2.96 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.24(5.32) 5.03 3.34 3.16 COOMe Me Ph 30 179-182 70.67(70.81) 5.24(5.32) 4.80 3.30 3.16	XII Ph Ph H COOME 4B 149-151 76.96(76.86) 5.56(5.42) 4.89 3.43 XII Ph Ph M COOME 4B 149-151 76.96(76.86) 5.56(5.43) 4.72 1.50(1 Hz) XIV Ph Ph Me Ph COOME 68 180-171 81.40(61.17) 5.66(5.63) 4.72 1.82(2 Hz) XV-1 Ph Ph COOME 5 217-218 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph COOME 9 220-203 70.59(70.81) 5.26(5.29) 4.90 3.22 XV-1 COOME Me Ph COOME 9 202-203 70.59(70.81) 5.24(5.29) 4.90 3.22 XV-2 COOME Me Ph COOME 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOME Me Ph COOME 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOME Me Ph COOME 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOME Me Ph COOME 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOME Me Ph COOME 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-6 Didd at 170° under reduced presure. ^b Solvated with fCH_2CI_2 . ^d PM of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 5.4 f_{AB} 7.0 m def 3.70 pm and so ne broked singlet at 3.73 ppm. ^c PMR of $-CH_2-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6.4 f_{AB} 7.6 no 0.8 nom.	XII Ph Ph Ph H COOMe 4B 149-151 76.96(76.86) 5.59(5.42) ⁶ 4.89 3.43 XII Ph Ph Me Ph Me Ph 67 169-171 81.40(81.17) 5.65(5.63) 4.72 1.50(1 Hz) XIV Ph Ph Me COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph COOMe 6 217-218 78.18(77.89) 5.07 2.96 XV-2 Ph Ph COOMe 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2 Hz) XV1-1 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.4(5.32) 4.89 3.303.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 2022-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 200 Ph	XII FIN FIN FIN FIN H COOME 4B 140-151 76,96(76,80) 5,59(6,42) 74,89 3,43 XII FIN FIN FIN ME FIN ME FIN 67 169-171 81,40(81.17) 5,66(6,63) 4,72 1.50(1 Hz) XIV FIN FIN FIN ME COOME 68 180-182 75,88(76.13) 5,61(5,48) 4,89 3,17 1.82(2 Hz) XV-1 FIN FIN FIN COOME 6 217-218 78,18(77,89) 5,23(5,29) 4,90 3,22 XV-1 FIN FIN COOME FIN 43 210 77,78(77,89) 5,22(5,29) 4,90 3,22 XV-2 COOME ME FIN COOME 9 202-203 70,59(70,81) 5,24(5,32) 4,89 3,30,3,16 1.63(2 Hz) XV-2 COOME ME FIN COOME 9 202-203 70,59(70,81) 5,24(5,32) 4,89 3,30,3,16 1.63(2 Hz) XV-2 COOME ME FIN COOME 9 202-203 70,59(70,81) 5,24(5,32) 4,89 3,30,3,16 1.63(2 Hz) XV-2 COOME ME FIN COOME 9 202-203 70,59(70,81) 5,24(5,32) 4,89 3,30,3,16 1.63(2 Hz) XV-6 Difed at 170° under reduced pressure. ^b Solvated with $\frac{1}{7}CH_2Cl_2$, ^d PMI of $-CH_2-0$'s appear as an AB pattern centered at 3,97 (J_{AB} 10 6 $A - 6_B 0,21$ Ppm) and at one broad singlet at 3,73 ppm. ^c PMR of $-CH_2-0$'s appear as an AB pattern centered at 3,97 (J_{AB} 10 and at 3.76 ppm (J_{AB} 10 Hz, $\delta_A - \delta_B 0.08$ ppm).	×	£	4 4	. 1	Ph 	21	180-182	81,14(81,06)		4,82		-
Ph Me Ph 67 169–171 81.40(81.17) 5.65(5.63) 4.72 Ph Me COOMe 68 180–182 7.5.88(76.13) 5.61(5.48) 4.89 3.17 Ph Ph Ph COOMe 68 180–182 7.5.88(76.13) 5.61(5.48) 4.89 3.17 Ph Ph Ph COOMe 5 2.17–218 78.18(77.89) 5.38(5.29) 5.07 2.96 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.22(5.29) 4.90 3.22 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.24(5.32) 5.03 3.34.8.16 COOMe Me COOMe Ph 30 179–182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16	XIII Ph Ph Me Ph Me Ph 67 169–171 81.40(81.17) 5.65(5.63) 4.72 1.50(1 Hz) XIV Ph Ph Me COOMe 68 180–182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 5 217–218 78.18(77.89(5.39(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph 23.2 70.56(70.81) 5.22(5.29) 4.90 3.22 XV-1 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.24(5.32) 5.03 3.34 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 202–203 70.56(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 202–203 70.56(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 200–200 70.50(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 9 200–200 70.50(70.81) 5.24(5.32) 4.89 3.30 3.16 1.63(2 Hz) XV-2 COOMe Me Ph 2000Me 7.500 8 me 7.50	XIII Ph Ph Me Ph Me Ph 67 169–171 B1.40(B1.17) 5.65(5.63) 4.72 1.50(1 Hz) XIV Ph Ph Me Ph COOMe 68 180–182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 68 180–182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV1-1 COOMe Me Ph COOMe 6 217–218 78.18(77.89) 5.29(5.9) 5.07 2.96 XV1-1 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.60(5.32) 5.03 3.34.8.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202–203 70.59(70.81) 5.24(5.32) 4.89 3.30.3.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202–203 70.56(7.0.81) 5.24(5.32) 4.89 3.30.3.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202–203 70.57(70.81) 5.24(5.32) 4.89 3.30.3.16 1.68(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202–203 70.57(70.81) 5.24(5.32) 4.89 3.30.3.16 1.68(2 Hz) XV1-2 COOMe Me 7 at 3.73 ppm. ⁶ PMR of $-CH_2-0$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6 $A - 5B$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ⁶ PMR of $-CH_2-0$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 and at 3.76 ppm (J_{AB} 10 Hz, $\delta_A - \delta_B$ 0.08 ppm).	XIII Ph Ph Me Ph Me 7 169-171 81.40(61.17) 5.66(5.63) 4.72 1.50(1 Hz) XIV Ph Ph Me COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-2 Ph Ph COOMe 6 5 217-218 78.18(77.80) 5.22(5.29) 4.90 3.22 XV1-1 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.22(5.29) 4.90 3.22 XV1-2 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.24(5.32) 4.90 3.20 1.88(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.24(5.32) 4.90 3.20 1.88(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.83(2 Hz) XV1-2 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.30 3.16 1.83(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 39 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30 3.16 1.83(2 Hz) XV1-2 COOMe Me Ph COOMe Ph 20 20 Prove 200 70.50 Prove 200.70 Prove 200 1.80(7 Prove 200 Pro	IX	5	hh	H	COOMe	4 8	149-151	76,96(76,86)		4,89	3,43	
Ph Me COOMe 68 180182 75.88(76.13) 5.61(6.48) 4.80 3.17 Ph Ph Ph COOMe 5 217218 78.18(77.89) 5.39(5.29) 5.07 2.96 Ph Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34.3.16 COOMe Me Ph COOMe Ph 202-203 70.59(70.81) 5.50(5.32) 5.03 3.34.3.16 COOMe Me COOMe Ph 39 179182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16	XIV Ph Ph Ph Me COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 6 217-218 78.18(77.89(5.39(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph 23.2 XV-2 Ph Ph COOMe Ph 23.0 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.24(5.32) 5.03 3.343.16 1.63(2 Hz) XV-2 COOMe Me Ph 200Me 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV-2 COOMe Me Ph 200Me 9 202-203 70.59(70.81) 5.24(5.32) 4.89 3.303.16 1.63(2 Hz) XV-2 COOMe Me Ph 200Me 9 202-203 70.50(70.81) 5.24(5.32) 4.89 3.303.16 1.66(2 Hz) XV-2 COOMe Me Ph 200Me 9 200Me 9 202-203 70.50(70.81) 5.24(5.32) 4.89 3.303.16 1.66(2 Hz) XV-2 COOMe Me Ph 200Me 9 200Me 9 202-203 70.50(70.81) 5.24(5.32) 4.89 3.303.16 1.66(2 Hz) XV-2 COOMe Me Ph 200Me 7 Ph 200Me 7 Ph 200Me 13.73 Ph 200Me 7 Ph 200	XIV Ph Ph Ph Me COOMe 68 180-182 75.88(76.13) 5.61(5.48) 4.89 3.17 1.82(2 Hz) XV-1 Ph Ph Ph COOMe 6 217-218 78.18(77.89(5.39(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph C3 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-1 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.60(6.32) 5.03 3.34 3.16 1.63(2 Hz) XV-2 COOMe Me Ph COOMe 9 202-203 70.69(70.81) 5.24(5.32) 4.89 3.30.3.16 1.63(2 Hz) XV-2 COOMe Me Ph COOMe 9 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.66(2 Hz) XV-2 COOMe Me Ph COOMe 9 202-203 70.50(7,0.81) 5.24(5.32) 4.89 3.30.3.16 1.66(2 Hz) XV-2 COOMe Me Ph COOMe 9 202-203 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.66(2 Hz) a Dried at 170° under reduced pressure. ^b Solvated with $C_{6}H_{6.}$ ^c Solvated with $\frac{1}{2}CH_{2}Cl_{2.}^{4}$ PMR of $-CH_{2}-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 $^{5}A - ^{5}B_{0.21}$ ppm (J_{AB} 10 Hz, $\delta_{A} - ^{5}B_{0.08}$ ppm).	XIV Ph Ph Ph Me COOMe 68 180-182 75.88 (76.13) 5.61 (5.48) 4.89 3.17 1.82 (2 Hz) XV-1 Ph Ph Ph COOMe 65 217-218 78.18 (77.89 (5.396) 5.07 2.96 XV-2 Ph Ph COOMe Ph COOMe 77.78 (77.89 (5.396) 5.07 2.96 1.63 (2 Hz) XV-1 COOMe Me Ph COOMe Ph 200 3.22 XV-1 COOMe Me Ph 2000 3.22 (5.30 3.34 3.16 1.63 (2 Hz) XV-2 COOMe Me Ph 2000 9 202-203 70.69 (70.81) 5.24 (5.32) 4.90 3.20 3.16 1.63 (2 Hz) XV-2 COOMe Me Ph 2000 Ph 39 179-182 70.67 (70.81) 5.24 (5.32) 4.90 3.20 3.16 1.63 (2 Hz) XV-2 COOMe Me Ph 2000 Ph 39 179-182 70.67 (70.81) 5.24 (5.32) 4.89 3.30 3.16 1.63 (2 Hz) XV-2 COOMe Me Ph 2000 Ph 39 170^{-01} 20.67 (70.81) 5.24 (5.32) 4.89 3.30 3.16 1.63 (2 Hz) XV-2 V-2 (2 D) Ph at at 170° under reduced pressure. ^b Solvated with $f_{C}H_{5}C_{12}$, ^d PMR of $-CH_{2}$ -0's appear as an AB pattern centered at 3.97 ($J_{A}B$ 10 hz, $\delta_{A} - \delta_{B}$ 0.08 ppm), ^e PMR of $-CH_{2}$ -0's appear as two AB patterns centered at 3.92 ($J_{A}B$ 10 Hz, $\delta_{A} - \delta_{B}$ 0.08 ppm).	IIIX	£.;	E.	Me	Ph	67	169-171	81.40(81.17)	5,65(5,63)	4.72		1.69(1 Hz)
Ph Ph COOMe 5 217-218 78.18(77.89(6.39(6.29) 5.07 2.96 Ph COOMe Ph COOMe Ph 4.3 210 77.78(77.89) 6.22(6.29) 4.90 3.22 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.60(6.32) 5.03 3.34.8.16 COOMe Me COOMe Ph 30 179-182 70.67(70.81) 5.24(5.32) 4.80 3.30.3.16	XV-1 Ph Ph Ph COOMe 5 217-218 78.18(77.89(5.39(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph COOMe Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV1-1 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.26(5.32) 5.03 3.34 3.16 1.63(2.Hz) XV1-2 COOMe Me COOMe Ph 29 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30 3.16 1.66(2.Hz) 2 Dried at 170° under reduced pressure. ^b Solvated with $6H_6.^c$ Solvated with $\frac{1}{2}CH_2CI_3.^d$ PMR of $-CH_2-OI$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 $6A - 6B$ 0.21 ppm) and a one hroad singlet at 3.73 ppm. ^c PMR of $-CH_2-OI$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 and 4.3.76 nom $(J_2, 0)$ 0.8 nom)	XV-1 Ph Ph Ph COOMe b 217-218 78.18(77.89(5.39(5.29) 5.07 2.96 XV-2 Ph Ph COOMe Ph 43 210 77.18(77.89) 5.22(5.29) 4.90 3.22 XV1-1 COOMe Me Ph COOMe 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34.3.16 1.63(2.Hz) XV1-2 COOMe Me Ph COOMe 9 202-203 70.67(70.81) 5.4(5.32) 4.89 3.30.3.16 1.66(2.Hz) XV1-2 COOMe Me Ph COOMe Ph 39 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.66(2.Hz) a Dried at 170° under reduced pressure. ^b Solvated with $6H_6$. ^c Solvated with $\frac{1}{2}$ CH ₂ Cl ₃ . ^d PMR of -CH ₂ -O's appear as an AB pattern centered at 3.97 (J_{AB} 10 5 $\mathbf{A} - \delta_{\mathbf{B}}$ 0.21 ppm) and at one broad singlet at 3.73 ppm. ^c PMR of -CH ₂ -O's appear as two AB patterns centered at 3.92 (J_{AB} 10 and at 3.76 ppm (J_{AB} 10 Hz, $\delta_{\mathbf{A}} - \delta_{\mathbf{B}}$ 0.08 ppm).	XV-1 Ph Ph Ph COOMe $5 \ 217-218 \ 78.18(77.80(5.39(5.29) 5.07 \ 2.96$ XV-2 Ph Ph COOMe Ph COOMe Ph COOMe Ph $3.22 \ 70.507 \ 2.96$ XV1-1 COOMe Me Ph COOMe Ph $3.210 \ 77.78(77.89) \ 5.22(6.29) \ 4.90 \ 3.22 \ 3.34 \ 3.16 \ 1.63(2 \ Hz)$ XV1-2 COOMe Me Ph COOMe Ph $3.003.16 \ 1.63(2 \ Hz)$ XV1-2 COOMe Me Ph COOMe Ph $3.033.16 \ 1.63(2 \ Hz)$ $2 \ Dried at 170^6$ under reduced pressure. b Solvated with $\int_{0}^{2} CH_{2}Cl_{2}$. $^{d} PMR$ of $-CH_{2}-0$'s appear as an ΛB pattern centered at 3.97 $(J_{AB} \ 10 \ Hz, \delta_{A} - \delta_{B} \ 0.08 \ ppm)$, and at one broad singlet at $3.73 \ ppm$. $^{c} PMR$ of $-CH_{2}-0$'s appear as two ΛB patterns centered at $3.92 \ (J_{AB} \ 10 \ Hz, \delta_{A} - \delta_{B} \ 0.48 \ ppm)$, and at $3.76 \ ppm$.	VIX	£	- 	Me	COOMe	68	180182	75.88(76.13)	5,61(5,48)	4,89	3.17	1.82(2 Hz)
Fin Pin COOMe Pin 430 3,22 COOMe Me Pin COOMe 9 202-203 70,59(70,81) 5,50(5,32) 5,03 3,34,3,16 COOMe Me COOMe Pin 200 179-182 70,58(70,611) 5,50(5,32) 4,90 3,22 COOMe Me COOMe Pin 30 179-182 70,58(70,611) 5,24(5,32) 4,89 3,30,3,16	XV-2 Fn Fn COOME Ph COOME Ph 43 210 77.78(77.89) 5.22(5.29) 4.90 3.22 XV-2 KV-2 COOME Me Ph COOME Ph 2020-203 70.59(70.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2 Hz) XV-2 COOME Me Ph COOME Ph 39 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30 3.16 1.66(2 Hz) $XV-2$ COOME Me COOME Ph 29 1.70° Under reduced pressure. ^b Solvated with $6H_6$. ^c Solvated with $\frac{1}{2}$ CH ₂ Cl ₂ . ^d PMR of -CH ₂ -O's appear as an AB pattern centered at 3.97 (J_{AB} 10 δ_{A} - δ_{B} 0.24 ppm) and are not broad singlet at 3.73 ppm. ^c PMR of -CH ₂ -O's appear as two AB pattern sentered at 3.92 (J_{AB} 10 δ_{A} - δ_{B} 0.48 ppm)	XV-2 FIN FIN COOME FIN COOME FIN 43 210 77.18(77.49) 5.22(5.29) 4.90 3.22 XVI-1 COOME ME FN COOME PN 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34 3.16 1.63(2 Hz) XVI-2 COOME ME COOME FN 29 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.66(2 Hz) d Dried at 170° under reduced pressure. ^b Solvated with $6H_{6.}$ ^c Solvated with $\frac{1}{2}$ CH ₂ (1 ₃ . ^d PMR of -CH ₂ -O's appear as an AB pattern centered at 3.97 (J_{AB} 10 6 $\Delta - ^{6}$ $_{B}$ 0.21 ppm) and as one bross finglet at 3.73 ppm. ^d PMR of -CH ₂ -O's appear as two AB patterns centered at 3.92 (J_{AB} 11 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 11 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 11 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 11 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm (J_{AB} 10 Hz, $\delta_{A} - ^{6}$ $_{B}$ 0.48 ppm)	XV-2 FIN FIN COOME FIN COOME FIN 4.3 210 71.78(77,89) 5.226.29) 4.90 3.22 XVI-1 COOME Me FIN COOME P1 202-203 70.69(70.81) 5.60(6.32) 5.03 3.34 3.16 1.63(2 Hz) XVI-2 COOME Me COOME FN 29 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.68(2 Hz) 0 Dried at 170 ⁶ under reduced pressure. ^b Solvated with C ₆ H ₆ . ^c Solvated with $\frac{1}{3}$ CH ₂ Cl ₂ . ^d PMR of -CH ₂ -O's appear as an AB pattern centered at 3.97 (J _{AB} 10 $\delta_{A} - \delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ^c PMR of -CH ₂ -O's appear as two AB patterns centered at 3.92 (J _{AB} 11 Hz, $\delta_{A} - \delta_{B}$ 0.48 ppm), and at 3.76 ppm (J _{AB} 10 Hz, $\delta_{A} - \delta_{B}$ 0.08 ppm).	I-AX	£ 1	5 . 1	Ph	COOMe	<u>ب</u> م	217-218	78,18(77,89(6,39(6,29)	5,07	2,96	
COOME ME Ph COOME 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.34.3.16 COOME ME COOME Ph 39 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16	XVI-1 CUOME Me Ph CUOME 9 202-203 70.59(70.81) 5.60(5.32) 5.03 3.343.16 1.63(2.Hz) XVI-2 COOME Me COOME Ph 39 170-182 70.67(70.81) 5.24(5.32) 4.89 3.303.16 1.86(2.Hz) 0 Dried at 170° under reduced presure. ^b Solvated with $6H_{6.}^{c}$ Solvated with $\frac{1}{2}$ CH ₂ Cl ₃ . ^d PMR of -CH ₂ -O's appear as an AB pattern centered at 3.97 (J_{AB} 10 6 A 2 B 0.21 ppm) and are one broad singlet at 3.73 ppm. ^e PMR of -CH ₂ -O's appear as two AB pattern sentered at 3.92 (J_{AB} 11 Hz. $\delta_{A} - \delta_{B}$ 0.48 ppm)	XVI-1 CUOMe Me Ph COOMe 9 202-203 70.69(70.81) 5.60(5.32) 5.03 3.343.16 1.63(2 Hz) XVI-2 COOMe Me COOMe Ph 39 179-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.86(2 Hz) a Dried at 170° under reduced pressure. ^b Solvated with $G_{\rm H6.}^{c}$ Solvated with $\frac{1}{2}$ CH ₃ Cl ₃ . ^d PMR of -CH ₃ -O's appear as an AB pattern centered at 3.97 ($J_{\rm AB}$ 10 6 Δ - 6 B 0.21 ppm) and as one broad singlet at 3.73 ppm. ^c PMR of -CH ₂ -O's appear as two AB patterns centered at 3.92 ($J_{\rm AB}$ 10 and at 3.76 ppm ($J_{\rm AB}$ 10 Hz, $\delta_{\rm A} - \delta_{\rm B}$ 0.08 ppm).	XVI-1 CUOMe Me Ph CUOMe Ph 202-203 70.59 (70.81) $5.60(5.32)$ 5.03 3.34 3.16 1.63 (2 Hz) XVI-2 COOMe Me COOMe Ph 39 179-182 70.67 (70.81) $5.24(5.32)$ 4.89 3.30 3.16 1.66 (2 Hz) 2 Dried at 170 ⁶ under reduced pressure. ^b Solvated with $G_{\rm FH6}$. ^c Solvated with ${}_{\rm J}{\rm CH}_{\rm J}{\rm CI}_{\rm J}$, ^d PMR of -CH ₂ -O's appear as an AB pattern centered at 3.97 (JAB 10 $\delta_{\rm A} - \delta_{\rm B}$ 0.08 ppm), ^e PMR of -CH ₂ -O's appear as two AB patterns centered at 3.92 (JAB 11 Hz, $\delta_{\rm A} - \delta_{\rm B}$ 0.48 ppm) and at 3.76 ppm (JAB 10 Hz, $\delta_{\rm A} - \delta_{\rm B}$ 0.08 ppm).	XV-2	E	£ :	COOMe	Ph 1	43	210	77,78(77,89)	5.22(5.29)	4,90	3,22	
COOMe Me COOMe Ph 39 179-182 70.67(70.81) 5,24(5,32) 4.89 3,303,16	XVI-2 COOMe Me COOMe Ph 39 170-182 70.87(70.81) 5.24(5.32) 4.89 3.303.16 1.86(2.11z) 0 Dried at 170° under reduced presure. ^b Solvated with $_{6}$ H ₆ . ^c Solvated with $\frac{1}{2}$ CH ₂ Ol, d PMR of $-$ CH ₂ $-$ O's appear as an AB pattern centered at 3.97 ($_{A}$ B 10 6 A $^{-}$ 6 B 0.21 ppm) and are one broad singlet at 3.73 ppm. ^c PMR of $-$ CH ₂ O's appear as two AB patterns centered at 3.92 ($_{A}$ A B 11 Hz. $_{6}$ A $^{-}$ 6 B 0.48 ppm) and $_{4}$ 2 A for the center of at 3.97 ($_{A}$ A prices at 3.62 ($_{A}$ A prices at 3.62 ($_{A}$ A prices at 3.62 ($_{A}$ A prices at 3.63 C prices at	XVI-2 COOMe Me COOMe Ph 39 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.86(2.112) ^a Dried at 170° under reduced presure. ^b Solvated with C_{6H_6} . ^c Solvated with $\frac{1}{2}$ CH ₃ Cl ₃ . ^d PMR of -CH ₃ -O's appear as an AB pattern centered at 3.97 (J_{AB} 10 5A - 5B 0.21 ppm) and as one broad singlet at 3.73 ppm. ^e PMR of -CH ₂ -O's appear as two AB patterns centered at 3.92 (J_{AB} 11 Hz, 5A - 5B 0.48 ppm) and at 3.76 ppm (J_{AB} 10 Hz, 5A - 5B 0.08 ppm).	XVI-2 COOMe Me COOMe Ph 39 170-182 70.67(70.81) 5.24(5.32) 4.89 3.30.3.16 1.86(2 Hz) ^a Dried at 170° under reduced pressure. ^b Solvated with GeH_6 . ^c Solvated with $\frac{1}{2}CH_2Cl_2$. ^d PMR of $-CH_2-0$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 6 $A_{-}-6$ B_0 ,21 ppm) and at one broad singlet at 3.73 ppm. ^d PMR of $-CH_2-0$'s appear as two AB patterns centered at 3.97 (J_{AB} 10 and at 3.76 ppm (J_{AB} 10 Hz. $\delta_A - \delta_B$ 0.08 ppm). and at 3.76 ppm (J_{AB} 10 Hz. $\delta_A - \delta_B$ 0.08 ppm).	I-IAX	COOMe	Me	h	COOMe	њ.	202-203	70,59(70,81)	5.60(5,32)	6.03	3,343,16	1.63(2 Hz)
	^a Dried at 170° under reduced pressure. ^b Solvated with $C_{6}H_{6}$. ^c Solvated with $\frac{1}{2}CH_{2}Cl_{3}$. ^d PMR of $-CH_{2}-O$'s appear as an AB pattern centered at 3.97 (J_{AB} 10 $\delta_{A} - \delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ^e PMR of $-CH_{2}-O$'s appear as two AB patterns centered at 3.92 (J_{AB} 11 Hz, $\delta_{A} - \delta_{B}$ 0.48 ppm) and 44 3.76 non $H_{2} - 0$ 0.08 nom.	^a Dried at 170° under reduced presure. ^b Solvated with C_{6H_6} . ^c Solvated with $\frac{1}{2}$ CH ₃ Cl ₃ . ^d PMR ofCH ₂ -O's appear as an AB pattern centered at 3.97 (J_{AB} 10 $\delta_{A} - \delta_{B}$ 0.21 ppm) and as one broad singlet at 3.73 ppm. ^e PMR ofCH ₂ -O's appear as two AB patterns centered at 3.92 (J_{AB} 11 Hz, $\delta_{A} - \delta_{B}$ 0.48 ppm) and at 3.76 ppm (J_{AB} 10 Hz, $\delta_{A} - \delta_{B}$ 0.48 ppm)	^a Dried at 170° under reduced presure. ^b Solvated with CeHe. ^c Solvated with $\frac{1}{2}$ CH ₂ Cl ₂ . ^d PMR ofCH ₂ -O's appear as an AB pattern centered at 3.97 (J _{AB} 10 6A6B 0.21 ppm) and as one broad singlet at 3.73 ppm. ^e PMR ofCH ₂ -O's appear as two AB patterns centered at 3.92 (J _{AB} 11 Hz, 5A - 6B 0.48 ppm) and at 3.76 ppm (J _{AB} 10 Hz, 5A - 6B 0.48 ppm).	XVI-2	COOMe	Me	COOMe	РЧ	30	179-182	70,67(70,81)	5,24(5.32)	4.89	3,30 3,16	1,86(2 Hz)

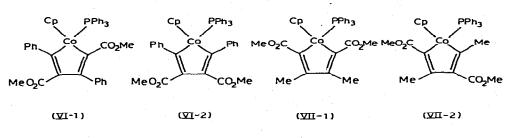
Results and discussion

The reaction is illustrated in Scheme 1 and all the cobaltacyclopentadiene complexes thus obtained are summarized in Table 1. They are very stable at room temperature and their solutions can be handled in air. However, they react easily with diverse reagents at 70–110°C [3]. In particular, the substituted thiophenes and benzenes derived from them are helpful for the determination of the position of each substituent in the parent cobalt metallocycles.



The reaction of $(\pi$ -cyclopentadienyl)bis(triphenylphosphine)cobalt (I) with an equimolar amount of diphenylacetylene or methyl phenylpropiolate gave the $(\pi$ -acetylene)cobalt complex (IIa, IIb) in good yield, whereas, a similar reaction with excess of acetylene afforded cobaltacyclopentadiene complexes (III-VIII).

In the one-step synthesis using methyl phenylpropiolate, the resulting complex contained only two of the three possible isomers and these were separated by column chromatography. Complex VI-1, which was eluted faster than the other, shows two methyl PMR absorptions and was assigned the structure $(\pi$ -cyclopentadienyl)(triphenylphosphine)-2,4-diphenyl-3,5-dimethoxycarbonylcobaltacyclopentadiene. The other isomer, VI-2, which revealed only one kind of methyl resonance in the PMR spectrum and gave 2,5-diphenyl-3,4-dimethoxycarbonylthiophene [4] on treatment with sulfur, was assigned as 2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene.



$$Cp = C_s H_s$$

The reaction of I with an excess of methyl methylpropiolate also gave two isomers. Complex VII-1, which was eluted faster than the other from an alumina column, has only two kinds of methyl resonances at δ 1.50 (d, J 2 Hz, C--CH₃) and 3.46 (s, O--CH₃) ppm and gave 2,5-dimethoxycarbonyl-3,4-dimethylthiophene [5] on treatment with sulfur. It was, therefore, assigned the structure 2,5-dimethoxycarbonyl-3,4-dimethylcobaltacyclopentadiene. Another complex, VII-2, which shows four methyl resonances at δ 1.65 (d, J 2 Hz, C--CH₃), 2.47 (s, C--CH₃), 3.40 (s, O--CH₃), and 3.57 (s, O--CH₃) ppm, was assigned as 2,4-dimethoxycarbonyl-3,5-dimethylcobaltacyclopentadiene derivative.

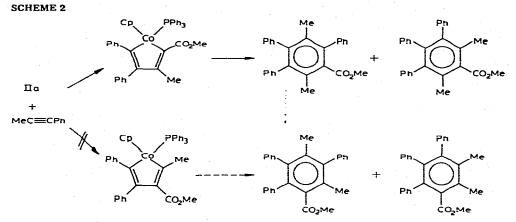
It is noteworthy that the methyl proton resonances at δ 1.50 in VII-1 and at 1.65 in VII-2 appear as doublets due to coupling with the ³¹P nucleus, whereas the other C—CH₃ resonance in VII-2 appears as a singlet. The finding that the long-range ¹H-³¹P coupling occurs only in the methyl group attached to 3- or 4-position of the cobaltacyclopentadiene ring supplies a method for the structural elucidation of other related complexes. The structure of VIII, which was the sole product in the reaction of I with methylphenylacetylene, was determined on this basis as that of 2,5-diphenyl-3,4-dimethylcobaltacyclopentadiene since the methyl resonance appears as a single doublet at δ 0.61 (J 1 Hz) ppm. This structure was further supported by the thiophene and benzene derivatives derived by the reaction of VIII with sulfur or dimethyl acetylenedicarboxylate: the melting points of the thiophene (159°C) and the benzene (126—127°C) derivatives obtained differed from those of known 2,5-dimethyl-3,4-diphenyl-thiophene (m.p. 113—114°C) [6] and 1,2-dimethoxycarbonyl-3,6-dimethyl-4,5-diphenylbenzene (m.p. 212°C) [7].

Cobaltacyclopentadiene complexes also were prepared from IIa and IIb. The reaction of IIa with dimethyl acetylenedicarboxylate and 1,4-dimethoxybutyne-2 gave IX and X, respectively. The reaction of IIa with unsymmetrical acetylenes, such as phenylacetylene, methyl propiolate, methylphenylacetylene, and methyl methylpropiolate, gave only one isomer (complexes XI—XIV, respectively) of the possible two.

From complexes XI and XII known thiophenes [4a,8,9] were derived by treatment with sulfur, thereby determining the positions of substituents in these metallocycles as indicated in Table 1. The structures of XIII and XIV could be deduced from their PMR spectra: doublet peaks of C-CH₃ groups with coupling constant 1 Hz in XIII and 2 Hz in XIV indicated that the C-CH₃ groups were attached to the β -carbon of the cobaltacycle. The structure of XIV was further confirmed by its reaction with methylphenylacetylene, which gave a ca. 1 : 1

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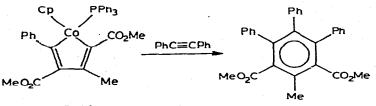
mixture of benzene derivatives (Scheme 2). In the PMR spectrum, one of the benzene isomers showed a single peak due to the C--CH₃ group at δ 2.09 ppm and the other isomer showed resonances at δ 2.05 and 1.80 ppm. The alternate structure for XIV would not give benzenes having such a resonance pattern (Scheme 2).



The reaction of IIa with methyl phenylpropiolate gave both isomers, XV-1 (5% yield) and XV-2 (43%). Based on the melting point of the thiophene derived from XV-2, which was consistent with that of authentic 2,3,5-triphenyl-4-methoxycarbonylthiophene [4a], the structures of both isomers were deduced as shown in Table 1.

The reaction of IIb with methyl methylpropiolate yielded only two isomers, XVI-1 and XVI-2. Their PMR spectra show doublet peaks attributable to C— CH₃ groups with a coupling constant of 2 Hz, suggesting that the methyl group is bonded to the β -carbon of the metallocycle in both isomers. As the melting point of the thiophene obtained from XVI-1 coincided with that of literature value [4a], XVI-1 was determined to be the 2,5-dimethoxycarbonyl-3-methyl-4-phenylcobaltacyclopentadiene derivative. The structure of XVI-2 was confirmed by a PMR spectrum of the benzene derivative prepared by its reaction with diphenylacetylene. Only one of the four possible isomers should give a benzene having a single O—methyl resonance and that was the case (Scheme 3).

SCHEME 3

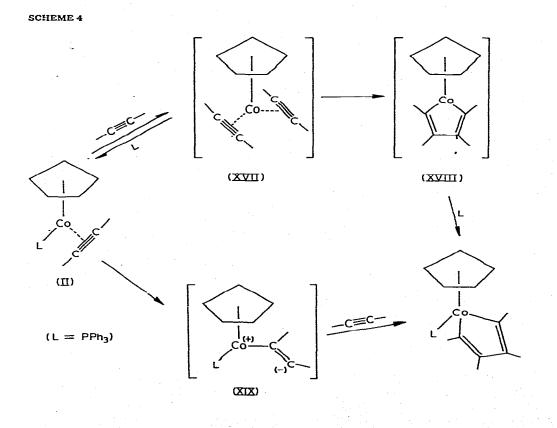


(XVI-2)

Obviously, the first step of the cobaltacyclopentadiene formation from I is replacement of one of the phosphines by an acetylene molecule to form a π -

acetylene complex II. For further reaction of II with an acetylene, two alternatives may be proposed (Scheme 4). In the first of these (path-1), an attacking acetylene replaces the other phosphine to give a bis(acetylene) complex (XVII), which undergoes oxidative coupling to form a coordinatively unsaturated Co^{III} metallocycle XVIII. Similar types of intermediate have been proposed in the reaction of "titanocene" with olefins [10] or diphenylacetylene [11]. The second path includes a thermally excited, ionic *monohapto*-acetylene intermediate XIX [1f,1j] to supply a vacant coordination site for an attacking acetylene molecule.

It is difficult to distinguish between these alternatives, but path-1 seems more probable by the following reasoning, although the ionic monohapto-acetylene intermediate might be important in other systems in which a much polar molecule is incorporated into a metallocycle [12]. (1) Polar solvents such as dichloromethane or pyridine did not enhance the rate of the reaction, $IIa + Ph_2C_2 \rightarrow III$, which could be observed easily by disappearance of the characteristic green color of IIa. (2) The reactions of IIa with methyl phenylpropiolate, and of IIb with diphenylacetylene, gave cobaltacyclopentadienes XV-1 and XV-2 in virtually identical ratio. The result, together with that of 1, suggests that a polar intermediate XIX is improbable. (3) Addition of free triphenylphosphine to a reaction system of IIa with diphenylacetylene markedly decreased the rate. The observation can be interpreted by the reasonable assumption that XVII \rightarrow XVIII



162

is the rate determining step of path-1 and that preliminary equilibrium is attained between II and XVII. To accomodate this observation, the ligand (triphenylphosphine) should not participate in the oxidative coupling reaction of the bisacetylene complex.

When asymmetrically substituted acetylenes are used, the positions of the substituents in the final cobalt metallocycle will be governed by arrangements of the two acetylene molecules in the bisacetylene intermediate XVII, which might largely be affected by a dipole—dipole interaction between them. Which carbon of each acetylene unit is bonded to cobalt in the oxidative coupling step to give the more thermodynamically stable isomer, would be another important factor in determining regioselectivity of the final product.

Experimental

All reactions were performed under nitrogen.Melting points are uncorrected and determined on a Mitamura micromelting point apparatus. For column chromatography, Sumitomo Activated Alumina KCG-30 was used. IR spectra were obtained on a Shimazu IR-27G spectrophotometer. PMR spectra were recorded on a Varian HA-100 or a JEOL-60 spectrometer in CDCl₃ unless otherwise stated. Mass spectra were obtained on a Niphondenshi JPS-IS spectrometer at 75 eV.

$(\pi$ -Cyclopentadienyl)bis(triphenylphosphine)cobalt (I)

The following improved method was employed instead of the known published method [13].

To freshly prepared chlorotris(triphenylphosphine)cobalt [14] (12 g, 13.6 mmol) suspended in benzene (160 ml) was added a tetrahydrofuran solution of sodium cyclopentadienide (1 mmol solution, 20 ml) at room temperature, and the resulting dark-red solution was stirred for 30 min. Excess of sodium cyclopentadienide then was hydrolyzed with water (10 ml) at 0°C and the organic layer was dried over sodium sulfate. Concentration of the filtered solution under pressure (to ca. 30 ml), followed by addition of hexane (30 ml), gave dark-red crystals of the desired complex in 24 h (6.9 g, 70% yield).

$(\pi$ -Acetylene)cobalt complexes (III)

 $(\pi$ -Cyclopentadienyl) $(\pi$ -diphenylacetylene)(triphenylphosphine)cobalt (IIa). The known method [15] was improved as follows. Diphenylacetylene (0.9 g, 5 mmol) was added to a solution of I (3.6 g, 5 mmol) in benzene (25 ml) and the reaction mixture was allowed to stand at room temperature. After 1 h, hexane (50 ml) was added to precipitate shiny black crystals of the title compound which were separated by decantation and washed with hexane (2.4 g, 85%). The crystals should be stored in a refrigerator.

 $(\pi$ -Cyclopentadienyl) $(\pi$ -methyl phenylpropiolate)(triphenylphosphine)cobalt (IIb). To a solution of I (1.3 g, 1.8 mmol) in benzene (50 ml) was added methyl phenylpropiolate (0.3 g, 1.9 mmol) at 0°C and the solution was allowed to stand overnight at room temperature. After concentration, the residue was

CODALI				40			1		C	כ	ŭ	
complex	R ¹	\mathbf{R}^2	R ³	2						¢	<i>c</i> .	
		¦ .	I				0Me	CMe	,		1	
V1-2	£	COOMe	COOMe	hh	58	166167 ª	3,80		68,43	4,48	9,18	
	•								(68.17)	(4,68)	(01.6)	
VII-1	COOMe	Me	Me	COOMe	31	$(167 - 168)^{4}$ 168 - 169 d	3.86	2,46	52,61	5.27	13.85	
						(110 -171) ^e	(3,85)	(2,44) ^C	~	(5,30)	(14.05)	
						(171.5-172.5)						
AIII V	Ph Ph	Me	Me	Чď	20	159 #		2,22	81,99	5,96	12.17	
						-			(81.77)	(01'9)	(12.13)	
1	Ha.	Ph	H	Чd	24	139 -140			84,62	4,96		
						(142 143) ^b			(84,58)	(5.16)		
=	Ph	- 	н	COOMe	46	96,5	3.89		73,50	4,80		
				-					(13.44)	(4,79)		
	H	Ч	H	COOEL	22	78			73,98	5,30		
						(11.5)			(14,00)	(6.23)		
XV-2	£	문	COOMe	Чď	76	138 -130	3,48		78,06	4.71	8,66	
						(138 139)	•		(11.81)	(4,90)	(8,66)	
1-1VX	COOMe	Me	Ph	COOMe	31	136 /		000	61.78	4,92		
•						(134.5–135) ⁰	3.90	1	(62,05)	(4,86)		
V1-2	COOMe	Me	COOMe	4d	41	97 - 98	3.67	0 64	62,38	4,87	10,95	
							3.86	F0.2	(62,05)	(4,86)	(11,04)	

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164

TABLE 2 THIOPHENES chromatographed on Al₂O₃ (2 × 15 cm). A brown-red band was eluted with benzene. Concentration and addition of hexane gave chocolate-brown crystals of the title complex (0.73 g, 74%), m.p. 131–133°C (dec.). Found: C, 72.64; H, 5.20; mol. wt. 521 (vapor pressure osmometry in benzene). $C_{33}H_{28}O_2PCo$ calcd.: C, 72.53; H, 5.16%; mol. wt. 546.5. PMR (C_6D_6): δ 3.57 (s, CH₃); 4.74 (s, C_5H_5); 7–8 (multiplet, Ph) ppm. IR (nujol mull): 1820 ν (C=C) cm⁻¹.

Cobaltacyclopentadiene complexes (III-XVI)

 $(\pi$ -Cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetramethoxycarbonylcobaltacyclopentadiene (IV). To a solution of I (1.5 g, 2.1 mmol) in benzene (20 ml) was added dimethyl acetylenedicarboxylate (1.1 g, 8 mmol in 10 ml of benzene) dropwise under ice-cooling. The mixture was allowed to stand overnight at room temperature and then was chromatographed on Al₂O₃. An orangered band was eluted with 1 : 1 benzene/ethyl acetate. Removal of the solvent in vacuo and treatment of the residue with benzene/hexane gave orange-red crystals of IV (solvated with $\frac{1}{2}$ mol of benzene, 0.25 g, 14%). The solvated benzene could be removed by heating the crystals in vacuo at 170°C for 30 min.

 $(\pi$ -Cyclopentadienyl)(triphenylphosphine)-2,4-diphenyl-3,5-dimethoxycarbonylcobaltacyclopentadiene (VI-1) and $(\pi$ -cyclopentadienyl)(triphenylphosphine)-2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene (VI-2). To a solution of I (6.0 g, 8.3 mmol) in benzene (90 ml) was added methyl phenylpropiolate (3.0 g, 18.8 mmol) and the mixture was allowed to stand overnight. After concentration, the reaction mixture was chromatographed on Al₂O₃. Two bands separated on elution with 25 : 1 benzene/tetrahydrofuran. The first red-brown band was collected, concentrated and hexane was added to give redbrown crystals of VI-1 (1.7 g, 29%). From the second orange band, which was eluted with 10 : 1 benzene/tetrahydrofuran, orange-brown crystals of VI-2 were obtained (1.5 g, 26%).

By similar procedures, VII-1, VII-2, and VIII were prepared and isolated.

 $(\pi$ -Cyclopentadienyl)(triphenylphosphine)-2,3-diphenyl-4-methyl-5-methoxycarbonylcobaltacyclopentadiene (XIV). To a solution of IIa (0.56 g, 1 mmol) in benzene (20 ml) was added methyl methylpropiolate (0.15 ml). After 1 h, the mixture was concentrated and chromatographed on Al₂O₃. A brown band eluted with 10 : 1 benzene/dichloromethane was collected and concentrated. Addition of hexane gave brown crystals of XIV (0.45 g, 68%).

By similar procedures, were obtained IX, X, XI, XII, XIII, XV-1, and XV-2. $(\pi$ -Cyclopentadienyl)(triphenylphosphine)-2,5-dimethoxycarbonyl-3-methyl-4-phenylcobaltacyclopentadiene (XVI-1) and (π -cyclopentadienyl)(triphenylphosphine)-2,4-dimethoxycarbonyl-3-methyl-5-phenylcobaltacyclopentadiene (XVI-2). Methyl methylpropiolate (0.25 ml) was added to a solution of IIb (1.1 g, 2 mmol) in benzene (30 ml). After it had stood overnight, the reaction mixture was concentrated and chromatographed on Al₂O₃ to give mainly three zones, red-violet, yellow, and orange in color. From the first zone, which was eluted with 1 : 1 benzene/dichloromethane, dark-red crystal, which did not contain the triphenylphosphine ligand and of as yet unknown structure, were obtained (0.014 g, m.p. 136-138°C). Collection and concentration of the second band, which was eluted with dichloromethane, followed by addition of hexane, gave orange-red crystals of XVI-1 (0.12 g, 9%). From the third zone, which was eluted with 4:1 benzene/ethyl acetate, brown crystals of XVI-2 were obtained by similar work-up (0.50 g, 39%).

Reaction with sulfur

Reaction of VI-2 with sulfur. A mixture of VI-2 (0.20 g, 0.365 mmol) and elemental sulfur (80 mg) in benzene (30 ml) was heated at 150° C for 6 h in a sealed tube. After concentration, the reaction mixture was chromatographed on Al₂O₃ (2 × 15 cm). After the column was eluted with benzene (200 ml) and further with 1 : 1 benzene/dichloromethane (100 ml), the eluate with dichloromethane was collected and concentrated. The residue was crystallized from hexane to give colorless crystals of 2,5-diphenyl-3,4-dimethoxycarbonylthiophene.

Other reactions of cobaltacyclopentadiene complexes with sulfur were carried out similarly; Table 2 compares physical properties of thiophenes thus obtained with those listed in the literature.

Reaction with acetylenes

Reaction of VIII with dimethyl acetylenedicarboxylate. A mixture of VIII (0.21 g, 0.32 mmol) and dimethyl acetylenedicarboxylate (0.15 ml) in benzene (10 ml) was heated at 70°C in a sealed tube. After 20 h, the reaction mixture was chromatographed on Al_2O_3 and the eluate with 1 : 1 benzene/dichloromethane was collected. Evaporation of the solvent and recrystallization of the residue from benzene/hexane gave colorless crystals of 1,2-dimethoxycarbonyl-3,6-diphenyl-4,5-dimethylbenzene (0.014 g, 13%) m.p. 126–127°C. Found: C, 77.24; H, 5.90. C₂₄H₁₂O₄ calcd.: C, 76.98; H, 5.92%.

Reaction of XVI-2 with diphenylacetylene. By a similar procedure to that described above, crystals of 1,2-dimethoxycarbonyl-2-methyl-4,5,6-triphenyl-benzene were obtained (50 mg, 36%) from XVI-2 (205 mg, 0.29 mmol) and diphenylacetylene (0.33 g), m.p. 204–205°C. Found: C, 79.92; H, 5.60; mol. wt. 436 (mass spectrum). $C_{29}H_{24}O_4$ calcd.: C, 79.79; H, 5.54%; mol. wt. 436.5. PMR: δ 2.38 (C–CH₃); 3.45 (O–CH₃) ppm.

References

- 1 W. Hübel and E.H. Braye, J. Inorg. Nucl. Chem., 10 (1959) 250.
- 2 (a) J.P. Collman, J.W. Kang, W.F. Little and M.F. Sullivan, Inorg. Chem., 7 (1968) 1298 and references therein; (b) E. Müller, Synthesis, (1974) 761 and references therein; (c) C.T. Sears Jr. and F.G.A. Stone, J. Organometal. Chem., 11 (1968) 644; (d) P.M. Maitlis and S. McVey, ibid., 19 (1969) 169; (e)
 H. Yamazaki and N. Hagihara, ibid., 21 (1970) 431; (f) K. Burt, M. Cooke and M. Green, J. Chem. Soc. A, (1970) 2981; (g) Ts. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, J. Chem. Soc. Chem. Commun., (1972) 629; (h) S.A. Gardner, P.S. Andrews and M.D. Rausch, Inorg. Chem., 12 (1973) 2396; (i) J.L. Davidson, R. Herak, L. Manojlovic-Muir, K.W. Muir and D.W.A. Sharp, J. Chem. Soc. Chem. Commun., (1973) 865; (i) K. Moseley- and P.M. Maitlis, J. Chem. Soc. Dalton, (1974) 169; (k) W.H. Baddley and G.B. Tupper, J. Organometal. Chem., 67 (1974) C16; (l) J.J. Eisch and J.E. Galle, ibid., 96 (1975) C19; (m) J.J. Eisch and J.E. Galle, ibid., 96 (1975) C23.
- 3 (a) Y. Wakatsuki and H. Yamazaki, J. Chem. Soc. Chem. Commun. (1973) 280; (b) Y. Wakatsuki, T. Kuramitsu and H. Yamazaki, Tetrahedron Lett., (1974) 4549; (c) P. Hong and H. Yamazaki, Synthesis, (1977) 50.

- 4 (a) H. Gotthardt and B. Cristl, Tetrahedron Lett., (1968) 4747; (b) K.T. Potts, E. Houghton and U.P. Singh, J. Chem. Soc., D, (1969) 1129.
- 5 (a) H. Wynberg and D.J. Zwanenburg, J. Org. Chem., 29 (1964) 1919; (b) O. Dann, K.J. Bamberg and H. Sucker, Pharmazie, 23 (1968) 135.
- 6 W. Hübel and E.H. Braye, U.S. patent 3,280,017 (1966); Chem. Abstr., 66 (1967) 2462t.
- 7 C.F.H. Allen and J. Vanallan, J. Amer. Chem. Soc., 64 (1942) 1260.
- 8 M. Dodson and J.Y. Fan, J. Org. Chem., 36 (1971) 2708.
- 9 S. Hauptmann, M. Weissenfels, M. Scholz, E.M. Werner and H.J. Köhler, Tetrahedron Lett., (1968) 1317.
- 10 J.X. McDermott, M.E. Wilson and G.M. Whitesides, J. Amer. Chem. Soc., 98 (1976) 6529.
- 11 J.W. Lauher and R. Hoffmann, J. Amer. Chem. Soc., 98 (1976) 1729.
- 12 Y. Wakatsuki and H. Yamazaki, J. Amer. Chem. Soc., 95 (1973) 5781.
- 13 H. Yamazaki and N. Hagihara, Bull. Chem. Soc. Japan, 44 (1971) 5781.
- 14 M. Aresta, M. Rossi and A. Sacco, Inorg. Chim. Acta, 3 (1969) 227.
- 15 H. Yamazaki and N. Hagihara, J. Organometal. Chem., 21 (1970) 431.
- 16 J.L. Melles and H.J. Backer, Rec. Trav. Chim., 72 (1953) 314.
- 17 Y.L. Goldfarb and V.P. Litvinov, Zh. Obshch. Khim., 30 (1960) 2719.
- 18 B.M. Trost and R. Atkins, Tetrahedron Lett., (1968) 1225.