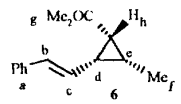
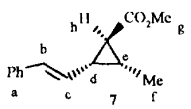
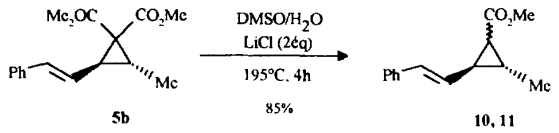
	δ in ppm, J in Hz							
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
	7.4–7.2 m	6.6 apparent s	6.6 apparent d J_{cd} = 2.9	2.18 ddd J_{dh} = 8.7 J_{de} = 5.9 J_{dc} = 2.9	1.67 m	1.36 d J_{fe} = 6.5	3.67 s	2.0 apparent t J_{hd} = J_{he} = 8.7
	7.3–7.2 m	6.59 d J_{bc} = 15.8	5.93 dd J_{cb} = 15.8 J_{cd} = 9	2.29 apparent td J_{dc} = J_{de} = 9 J_{dh} = 4.6	1.76 m	1.20 d J_{fe} = 6.4	3.69 s	1.55 apparent t J_{hd} = J_{he} = 4.6

be separated by chromatography on silica gel. We have tried to separate them on several HPLC columns without success.



5b **10, 11**

The decarboethoxylations of the 1:1 mixtures of cyclopropyl compounds **5e,f** and **5g,h** are currently under investigation in our laboratory. The results of these studies will be reported in due course.

Conclusion

This method allows the easy synthesis of *trans*- and *cis*-cyclopropanes **5** with a vinylic *E* configurated chain starting from the adequate configurations of the 1,4-functionalized ethylenic substrates **2**. This methodology implying alkylation and cyclopropanation is therefore a powerful tool for the synthesis of chiral cyclopropanes. The choice of the chirality of the propargylic alcohol is crucial, each one would provide a *cis*- and a *trans*-cyclopropane. Subsequently, the palladium-catalyzed reactions have emerged as a convergent route to chiral trisubstituted cyclopropanes. The decarboalkoxylations of **5** have provided functionalized trisubstituted cyclopropanes.

Experimental section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 or 200. MS data were recorded on a Hewlett Packard 5989 A instrument. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 589 nm. IR spectra were recorded on a IRFT 45 Bruker. Microanalysis were obtained from the Microanalysis Laboratory, at the Université Pierre-et-Marie-Curie.

General procedures

• *Formation of acetylenic compounds* **1**
An LDA solution (1.1 equiv) in THF, prepared by the addition of a butyllithium solution to diisopropylamine at −40 °C, was transferred via cannula to a THF solution of (*R*) or (*S*)-ethyl (1-methylprop-2-ynyl)carbonate (1.1 equiv) at −60 °C. The benzaldehyde (1 equiv) was then slowly added to the reddish solution. The solution was stirred for 1 h at −40 °C, treated with aqueous NH_4Cl. The aqueous phase was extracted by diethyl ether. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

• *Formation of ethylenic compounds* **2**
To a solution of **1** (1 equiv) in ethyl acetate was added Pd Lindlar (10% weight) and the reaction mixture was stirred under hydrogen atmosphere at rt for 6 h. After filtering through a short plug of silica gel using diethyl ether as the eluent, the solvent was evaporated under reduced pressure.

• *Alkylation*
$Pd(OAc)_2$ (10% molar) and dppe (1,2-bis(diphenylphosphino)ethane) (1.5 equiv/Pd) were stirred in THF at 30 °C during 30 min. The mixture was added to a THF solution of **2** (1 equiv) at rt. Dimethyl malonate (1.4 equiv) was added apart to a THF suspension of NaH (1.4 equiv, 60% in oil). After 15 min at rt, the catalyst was added to the anion of the dimethyl malonate. After 1 h the solution was treated by aqueous NH_4Cl. The aqueous phase was extracted with diethyl ether. The organic phase was concentrated under reduced pressure to afford the crude **3**, which was diluted in diethyl ether, dried over Na_2SO_4, and concentrated.

• *Formation of alkylated ethylenic compounds* **4**
To a CH_2Cl_2 solution of alcohol **3** (1 equiv) and pyridine (2 equiv) was slowly added 2,4-dichlorobenzoyl chloride (1.2 equiv) at 0 °C. The solution was stirred 1 h at 0 °C and 1 h at rt. After completion the reaction mixture was washed with aqueous HCl 5% and brine to pH 7. The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure.

• *Cyclopropanation*
$Pd(OAc)_2$ (10% molar) and dppe (1.5 equiv/Pd) were stirred in THF at 30 °C during 30 min. The mixture containing the catalyst was added to a THF solution of **4** (1 equiv) at rt. Then DBU (1.4 equiv) was slowly added. After 1 h at rt, the reaction mixture was treated with aqueous NH_4Cl. The aqueous phase was extracted with diethyl ether. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure.

• *Decarboalkoxylation*
To a solution of cyclopropane **5** in DMSO was added LiCl (2 equiv) and water. The mixture was refluxed (190 °C) for 4 h. After adding diethyl ether, the aqueous layer was

extracted with a mixture of pentane/diethyl ether. The organic layer was washed several times with water, dried over Na_2SO_4 and concentrated under reduced pressure.

■ *(1S)-Ethyl (4-hydroxy-1-methyl-4-phenylbut-2-ynyl) carbonate* **1a,b**

The reaction of (*S*)-ethyl (1-methylprop-2-ynyl)carbonate (1 g, 7.04 mmol) with the benzaldehyde (651 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) a colorless oil **1a,b** (952 mg, 60%). R_f = 0.4 (cyclohexane/ethyl acetate 8:2).

IR (neat): 3 400, 2 970, 2 225, 1 750.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.55–7.52 (m, 2H), 7.40–7.36 (m, 3H), 5.50 (2d, 1H, *J* = 6.2 Hz), 5.42 (qd, 1H, *J* = 6.7, 1.6 Hz), 4.22 (q, 2H, *J* = 7.1 Hz), 2.44 (2d, 1H, *J* = 6.2 Hz), 1.58 (d, 3H, *J* = 6.7 Hz), 1.30 (t, 3H, *J* = 7.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 154.1, 139.9, 128.5, 128.4, 126.6, 85.1, 84.3, 64.3, 64.2, 64.0, 21.2, 14.1.

MS (CI, NH_3) *m/e*: 266 (M + 18).

Anal calc for $C_{14}H_{16}O_4$: C, 67.73; H, 6.49. Found: C, 67.63; H, 6.53.

■ *(1R)-Ethyl (4-hydroxy-1-methyl-4-phenylbut-2-ynyl) carbonate* **1c,d**

The reaction of (*R*)-3-carboethoxy-but-1-yne (1 g, 7.04 mmol) with the benzaldehyde (651 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) a colorless oil **1c, d** (1.35 g, 85%). R_f = 0.5 (cyclohexane/ethyl acetate 8:2).

IR and MS as for **1a,b**.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.55–7.52 (m, 2H), 7.40–7.36 (m, 3H), 5.50 (2d, 1H, *J* = 6.2 Hz), 5.42 (qd, 1H, *J* = 6.7, 1.6 Hz), 4.22 (q, 2H, *J* = 7.1 Hz), 2.38 (2d, 1H, *J* = 6.2 Hz), 1.58 (d, 3H, *J* = 6.7 Hz), 1.30 (t, 3H, *J* = 7.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 154.1, 139.9, 128.5, 128.4, 126.6, 85.0, 84.3, 64.4, 64.0, 63.9, 21.2, 14.1.

Anal calc for $C_{14}H_{16}O_4$: C, 67.73; H, 6.49. Found: C, 67.62; H, 6.52.

■ *(1S)-Ethyl (4-hydroxy-1-methyl-4-phenylbut-2-enyl) carbonate* **2a,b**

The semi-hydrogenation of the mixture **1a,b** (509 mg, 2.05 mmol) gave after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **2a** (243 mg) and **2b** (243 mg); yield: 95%. R_{fa} = 0.3, R_{fb} = 0.4 (cyclohexane/ethyl acetate 8:2).

2a, α_D^{20} = −34.5° (*c* = 1, $CHCl_3$).

IR (neat): 3 450, 1 750, 1 650.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.47–7.26 (m, 5H), 5.80 (dq, 1H, *J* = 9.2, 6.3 Hz), 5.75 (ddd, 1H, *J* = 11, 7.8, 0.7 Hz), 5.61 (d, 1H, *J* = 7.8 Hz), 5.54 (ddd, 1H, *J* = 11, 9.2, 1 Hz), 4.18 (q, 2H, *J* = 7.1 Hz), 2.70 (broad s, 1H), 1.40 (d, 3H, *J* = 6.3 Hz), 1.30 (t, 3H, *J* = 7.1 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 154.4, 142.7, 134.2, 130.1, 128.3, 127.3, 125.7, 70.5, 63.6, 20.6, 14.0.

Anal calc for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.07; H, 7.28.

2b, α_D^{20} = +106.5° (*c* = 1.1, $CHCl_3$).

IR as for **2a**.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 5H), 5.80 and 5.48 (2ddd, 2H, *J* = 10, 0.5 Hz), 5.72 (m, 2H), 4.20 (q, 2H, *J* = 7.1 Hz), 3.29 (d, 1H, *J* = 2.2 Hz), 1.38 (d, 3H, *J* = 6.3 Hz), 1.33 (t, 3H, *J* = 7.1 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 154.7, 142.1, 135.9, 129.2, 128.2, 127.2, 125.7, 70.2, 68.6, 63.8, 20.1, 14.0.

Anal calc for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.19; H, 7.27.

■ *(1R)-Ethyl (4-hydroxy-1-methyl-4-phenylbut-2-enyl) carbonate* **2c,d**

The semi-hydrogenation of the mixture **1c,d** (950 mg, 3.83 mmol) gave after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **2c** (387 mg) and **2d** (387 mg); yield: 81%.

2c, α_D^{20} = +30° (*c* = 1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR and IR as for **2a**.

Anal calc for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.07; H, 7.35.

2d, α_D^{20} = −101° (*c* = 1.1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR and IR as for **2b**.

Anal calc for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.09; H, 7.28.

■ *Dimethyl (1R,4R)-((E)-4-hydroxy-1-methyl-4-phenylbut-2-enyl) malonate* **3a**

The alkylation of **2a** (128 mg, 0.51 mmol) by dimethyl malonate (82 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 7:3) **3a** (107 g, 69%). R_f = 0.3 (cyclohexane/ethyl acetate 7:3).

α_D^{20} = +8.1° (*c* = 1.3, $CHCl_3$).

IR (neat): 3 450, 1 735, 1 670.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 5H), 5.75–5.72 (m, 2H), 5.15 (dd, 1H, *J* = 6, 3.5 Hz), 3.69 and 3.53 (2s, 6H), 3.31 (d, 1H, *J* = 8.7 Hz), 3.00 (m, 1H), 2.28 (d, 1H, *J* = 3.5 Hz), 1.09 (d, 3H, *J* = 6.8 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.5, 168.4, 142.8, 133.6, 132.4, 128.4, 127.5, 126.0, 74.7, 57.5, 52.3, 52.1, 36.8, 18.1.

■ *Dimethyl (1R,4S)-((E)-4-hydroxy-1-methyl-4-phenylbut-2-enyl) malonate* **3b**

The alkylation of **2b** (191 mg, 0.76 mmol) by dimethyl malonate (122 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 7:3) **3b** (177 mg, 79%). R_f = 0.3 (cyclohexane/ethyl acetate 7:3).

α_D^{20} = +30.5° (*c* = 1, $CHCl_3$).

IR as for **3a**.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 5H), 5.74 (d, 1H, *J* = 4.1 Hz), 5.73 (d, 1H, *J* = 3.2 Hz), 5.14 (d, 1H, *J* = 3.2 Hz), 3.70 and 3.60 (2s, 6H), 3.32 (d, 1H, *J* = 8.7 Hz), 3.00 (m, 1H), 2.28 (s, 1H), 1.09 (d, 3H, *J* = 6.8 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.5, 142.8, 133.5, 132.1, 128.3, 127.5, 126.4, 74.3, 57.5, 52.3, 52.1, 36.6, 18.0.

Anal calc for $C_{16}H_{20}O_5$: C, 65.74; H, 6.89. Found: C, 65.29; H, 6.89.

■ *Dimethyl (1S,4S)-((E)-4-hydroxy-1-methyl-4-phenylbut-2-enyl) malonate* **3c**

The alkylation of **2c** (140 mg, 0.56 mmol) by dimethyl malonate (90 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 7:3) **3c** (125 mg, 80%).

α_D^{20} = −8.7° (*c* = 1.2, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR and IR as for **3a**.

■ *Dimethyl (1S,4R)-((E)-4-hydroxy-1-methyl-4-phenylbut-2-enyl) malonate* **3d**

The alkylation of **2d** (100 mg, 0.4 mmol) by dimethyl malonate (64 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 7:3) **3b** (90 mg, 80%).

α_D^{20} = −32° (*c* = 0.3, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR and IR as for **3b**.

Anal calc for $C_{16}H_{20}O_5$: C, 65.74; H, 6.89. Found: C, 65.59; H, 7.05.

■ *Dimethyl (1R,4R)-((E)-4-(2,4-dichlorobenzoyl)-1-methyl-4-phenylbut-2- enyl) malonate* **4a**

The reaction of the alcohol **3a** (66 mg, 0.23 mmol) with 2,4-dichlorobenzoyl chloride (38 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) **4a** (65 mg, 60%). R_f = 0.3 (cyclohexane/ethyl acetate 7:3).

α_D^{20} = +5.1° (*c* = 1.3, $CHCl_3$).

IR (neat) 1 765, 1 740, 1 650, 800.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.83 (d, 1H, *J* = 8.4 Hz), 7.48 (d, 1H, *J* = 2 Hz), 7.42–7.35 (m, 5H), 7.30 (dd, 1H, *J* = 8.4, 2 Hz), 6.43 (dd, 1H, *J* = 3.1, 2.1 Hz), 5.81 (m, 2H), 3.69 and 3.52 (2s, 6H), 3.30 (d, 1H, *J* = 9 Hz), 3.00 (m, 1H), 1.12 (d, 3H, *J* = 6.7 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.3, 168.2, 163.5, 138.7, 138.3, 135.2, 134.9, 132.5, 130.9, 129.1, 128.5, 128.3, 128.2, 126.9, 77.3, 57.3, 52.3, 52.1, 37.0, 18.0.

MS (CI, NH_3) *m/e*: 482 (M + 18).

■ *Dimethyl (1R,4S)-((E)-4-(2,4-dichlorobenzoyl)-1-methyl-4-phenylbut-2-enyl) malonate* **4b**

The reaction of the alcohol **3b** (150 mg, 0.51 mmol) with 2,4-dichlorobenzoyl chloride (87 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) **4b** (226 mg, 94%). R_f = 0.5 (cyclohexane/ethyl acetate 8:2).

α_D^{20} = +24° (*c* = 1.1, $CHCl_3$).

IR and MS as for **4a**.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.84 (d, 1H, *J* = 8.5 Hz), 7.47 (d, 1H, *J* = 2 Hz), 7.47–7.35 (m, 5H), 7.30 (dd, 1H, *J* = 8.5, 2 Hz), 6.43 (dd, 1H, *J* = 3.7, 1.5 Hz), 5.81 (m, 2H), 3.69 and 3.52 (2s, 6H), 3.30 (d, 1H, *J* = 9 Hz), 3.00 (m, 1H), 1.12 (d, 3H, *J* = 6.7 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.3, 168.2, 163.5, 138.6, 138.3, 135.0, 134.9, 132.5, 130.9, 129.0, 128.5, 128.3, 128.2, 127.0, 126.9, 77.1, 57.3, 52.3, 52.1, 36.7, 17.9.

Anal calc for $C_{23}H_{22}O_6Cl_2$: C, 59.37; H, 4.76. Found: C, 59.35; H, 4.79.

■ *Dimethyl (1S,4S)-((E)-4-(2,4-dichlorobenzoyl)-1-methyl-4-phenylbut-2-enyl) malonate* **4c**

The reaction of the alcohol **3c** (100 mg, 0.34 mmol) with 2,4-dichlorobenzoyl chloride (58 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) **4c** (134 mg, 84%).

α_D^{20} = −5.6° (*c* = 1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR, IR and MS as for **4a**.

Anal calc for $C_{23}H_{22}O_6Cl_2$: C, 59.37; H, 4.76. Found: C, 59.30; H, 4.77.

■ *Dimethyl (1S,4R)-((E)-4-(2,4-dichlorobenzoyl)-1-methyl-4-phenylbut-2-enyl) malonate* **4d**

The reaction of the alcohol **3d** (170 mg, 0.58 mmol) with 2,4-dichlorobenzoyl chloride (98 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) **4d** (216 mg, 80%).

α_D^{20} = −20.6° (*c* = 1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR, IR and MS as for **4b**.

■ *Dimethyl (2R,3S)-2-methyl-3-(1-(E)-2-phenylethenyl) cyclopropane-1,1-dicarboxylate* **5a**

The cyclopropanation of **4a** (65 mg, 0.14 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **5a** (34.5 mg, 90%). R_f = 0.6 (cyclohexane/ethyl acetate 8:2).

α_D^{20} = +160° (*c* = 1.1, $CHCl_3$).

IR (neat): 1 740, 1 670.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 5H), 6.68 (d, 1H, *J* = 15.7 Hz), 6.02 (dd, 1H, *J* = 15.7, 9.9 Hz), 3.78 and 3.75 (2s, 6H), 2.57 (dd, 1H, *J* = 9.9 Hz), 2.08 (dq, 1H, *J* = 9.9, 6.7 Hz), 1.26 (d, 3H, *J* = 6.7 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 170.4, 166.9, 136.8, 133.8, 128.2, 127.1, 125.8, 122.5, 52.5, 52.0, 38.8, 34.8, 26.8, 9.7.

MS (EI, 70 eV) *m/e*: 274 ($M^{+\cdot}$).

Anal calc for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.04; H, 6.71.

■ *Dimethyl (2R,3R)-2-methyl-3-(1-(E)-2-phenylethenyl)cyclopropane-1,1-dicarboxylate* **5b**

The cyclopropanation of **4b** (130 mg, 0.28 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **5b** (69 mg, 90%). R_f = 0.6 (cyclohexane/ethyl acetate 8:2).

α_D^{20} = −72° (*c* = 1.1, $CHCl_3$).

IR and MS as for **5a**.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 5H), 6.63 (d, 1H, *J* = 15.7 Hz), 5.86 (dd, 1H, *J* = 15.7, 9 Hz), 3.78 et 3.72 (2s, 6H), 2.57 (dd, 1H, *J* = 9, 7.5 Hz), 2.21 (dq, 1H, *J* = 7.5, 6.3 Hz), 1.18 (d, 3H, *J* = 6.3 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 168.2, 167.9, 136.6, 133.0, 128.2, 127.1, 125.7, 124.5, 52.3, 41.9, 36.7, 27.5, 12.2.

Anal calc for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.99; H, 6.69.

■ *Dimethyl (2S,3R)-2-methyl-3-(1-(E)-2-phenylethenyl) cyclopropane-1,1-dicarboxylate* **5c**

The cyclopropanation of **4c** (120 mg, 0.26 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **5c** (59 mg, 83%).

α_D^{20} = −153° (*c* = 1.1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR, IR and MS as for **5a**.

Anal calc for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.12; H, 6.69.

■ *Dimethyl (2S,3S)-2-methyl-3-(1-(E)-2-phenylethenyl) cyclopropane-1,1-dicarboxylate* **5d**

The cyclopropanation of **4b** (88 mg, 0.19 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **5b** (56 mg, 87%).

α_D^{20} = +57° (*c* = 1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR, IR and MS as for **5b**.

■ *Methyl (2R,3S)-2-methyl-3-(1-(E)-2-phenylethenyl) cyclopropane-1-carboxylate* **6, 7**

The decarbomethoxylation of **5a** (25 mg, 0.09 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **6** (10 mg) and **7** (10 mg), yield: 96%. R_{f-6} = 0.72, R_{f-7} = 0.67 (cyclohexane/ethyl acetate 8:2).

6, α_D^{20} = +54° (*c* = 0.7, $CHCl_3$).

IR (neat): 1 735, 1 675.

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 171.3, 137.3, 131.8, 128.2, 126.7, 125.7, 124.2, 51.0, 27.9, 23.9, 20.9, 7.6.

MS (CI, NH_3) *m/e*: 216 (M + 1), 234 (M + 18).

7, α_D^{20} = +114° (*c* = 0.6, $CHCl_3$).

IR and MS as for **6**.

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 173.6, 136.9, 132.1, 128.3, 126.9, 125.8, 125.6, 51.5, 30.7, 29.0, 22.9, 12.5.

Anal calc for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.02; H, 7.75.

■ *Methyl (2S,3R)-2-methyl-3-(1-(E)-2-phenylethenyl) cyclopropane-1-carboxylate* **8, 9**

The decarbomethoxylation of **5c** (33 mg, 0.12 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **8** (12 mg) and **9** (12 mg); yield: 92%.

8, α_D^{20} = −48.5° (*c* = 0.4, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR as for **6**.

9, α_D^{20} = −129° (*c* = 1, $CHCl_3$).

^{1}H-NMR, ^{13}C-NMR as for **7**.

■ *Methyl (2R,3R)-2-methyl-3-(1-(E)-2-phenylethenyl) cyclopropane-1-carboxylate* **10, 11**

The decarbomethoxylation of **5b** (49 mg, 0.18 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **10, 11** (33 mg, 85%). R_f = 0.72 (cyclohexane/ethyl acetate 8:2).

IR as for **7, 8**.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.36–7.16 (m, 5H), 6.55, 6.50 (2d, 1H, J = 15.8 Hz), 6.53, 5.77 (2dd, 1H, J = 15.8, 12, 8.6 Hz), 3.70, 3.68 (s, 3H), 2.08–1.43 (m, 3H), 1.30, 1.19 (d, 3H, J = 6.1, 5.6 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 172.0, 171.8, 137.0, 136.8, 130.6, 130.1, 129.5, 128.2, 128.2, 127.1, 126.8, 126.7, 125.6, 125.5, 51.4, 51.3, 33.3, 31.6, 29.0, 27.2, 24.0, 23.4, 17.2, 11.3.

MS (GC, DB 1701, $T_{initial}$ = 90 °C, T_{final} = 250 °C, 5 °C/min): t = 13.97 min, 14.83 min, m/e: 216 ($M^{+\cdot}$).

■ tert-*Butyl ethyl (1R,4S)-((E)-4-hydroxy-1-methyl-4-phenylbut-2-enyl) malonate* **3e,f**

The alkylation of **2b** (100 mg, 0.4 mmol) by *tert*-butyl ethyl malonate (106 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 7:3) **3e,f** (60 mg, 43%). R_f = 0.48 (cyclohexane/ethyl acetate 7:3).

IR (neat): 3 450, 1 740, 1 730, 1 670.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.36–7.25 (m, 5H), 5.78–5.74 (m, 2H), 5.15 (m, 1H), 4.18, 4.11 (2q, 2H, J = 7.1 Hz), 3.19 (2d, 1H, J = 8.6 Hz), 2.95 (m, 1H), 1.91 (d, 1H, J = 2.7 Hz), 1.45, 1.42 (2s, 9H), 1.26, 1.22 (2t, 3H, J = 7.1 Hz), 1.12, 1.11 (2d, 3H, J = 6.7 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.5, 167.3, 142.8, 133.4, 133.0, 128.3, 127.4, 126.1, 81.8, 81.7, 74.7, 74.6, 61.0, 60.9, 58.6, 58.5, 36.2, 36.1, 27.8, 18.0, 17.9, 14.0.

MS (CI, NH_3) m/e: 366 (M + 18).

■ tert-*Butyl ethyl (1R,4R)-((E)-4-hydroxy-1-methyl-4-phenylbut-2-enyl) malonate* **3g,h**

The alkylation of **2a** (45 mg, 0.18 mmol) by the *tert*-butyl ethyl malonate (50 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 7:3) **3g,h** (50 mg, 80%). R_f = 0.51 (cyclohexane/ethyl acetate 7:3).

IR and MS as for **3e,f**.

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.36–7.23 (m, 5H), 5.79–5.73 (m, 2H), 5.15 (m, 1H), 4.16, 4.01 (2q, 2H, J = 7.1 Hz), 3.18, 3.16 (2d, 1H, J = 8.6 Hz), 2.93 (m, 1H), 1.96 (broad s, 1H), 1.42, 1.37 (2s, 9H), 1.26, 1.22 (2t, 3H, J = 7.1 Hz), 1.12, 1.11 (2d, 3H, J = 6.7 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 168.4, 167.3, 167.2, 167.1, 142.8, 133.2, 133.0, 132.9, 128.3, 127.5, 126.1, 126.0, 81.8, 81.6, 74.8, 60.9, 60.8, 58.6, 58.5, 36.4, 36.3, 27.8, 27.7, 18.1, 14.0, 13.9.

■ tert-*Butyl ethyl (1R,4S)-((E)-4-(2,4-dichlorobenzoyl)-1-methyl-4-phenylbut-2- enyl) malonate* **4e,f**

The reaction of the mixture **3e,f** (55 mg, 0.16 mmol) with 2,4-dichlorobenzoyl chloride (27 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) **4e,f** (106 mg, 100%). R_f = 0.62 (cyclohexane/ethyl acetate 8:2).

IR (neat): 1 760, 1 735, 1 650, 800.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.83 (d, 1H, J = 8.5 Hz), 7.46 (d, 1H, J = 2 Hz), 7.41–7.26 (m, 6H), 6.43 (m, 1H), 5.83 (m, 2H), 4.1 (2q, 2H, J = 7.1 Hz), 3.18 (d, 1H, J = 8.7 Hz), 2.96 (m, 1H), 1.42, 1.35 (2s, 9H), 1.23, 1.16 (2t, 3H, J = 7.1 Hz), 1.1, 1.09 (2d, 3H, J = 6.7 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 168.5, 168.4, 167.3, 167.2, 159.5, 138.9, 138.4, 135.9, 135.2, 133.7, 132.7, 131.8, 131.1, 128.5, 128.3, 127.5, 127.1, 82.0, 81.9, 77.3, 61.2, 61.1, 58.6, 58.5, 36.5, 36.4, 28.0, 27.9, 18.0, 14.2.

MS (CI, NH_3) m/e: 538 (M + 18).

■ tert-*Butyl ethyl (1R,4R)-((E)-4-(2,4-dichlorobenzoyl)-1-methyl-4-phenylbut-2-enyl) malonate* **4g,h**

The reaction of the mixture **3g,h** (50 mg, 0.14 mmol) with 2,4-dichlorobenzoyl chloride (25 μL) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 8:2) **4g,h** (56 mg, 76%). R_f = 0.68 (cyclohexane/ethyl acetate 8:2).

IR and MS as for **4e,f**.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.82, 7.81 (2d, 1H, J = 8.4 Hz), 7.46, 7.42 (2d, 1H, J = 1.9 Hz), 7.39–7.26 (m, 6H), 6.43 (m, 1H), 5.82 (m, 2H), 3.98 (2q, 2H, J = 7.1 Hz), 3.16, 3.15 (2d, 1H, J = 8.7 Hz), 2.95 (m, 1H), 1.41, 1.33 (2s, 9H), 1.23, 1.16 (2t, 3H, J = 7.1 Hz), 1.1, 1.09 (2d, 3H, J = 6.7 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 168.5, 168.3, 167.3, 167.1, 163.7, 138.9, 138.4, 136.2, 135.1, 132.7, 132.6, 131.1, 128.8, 128.6, 128.3, 127.3, 127.2, 127.0, 82.0, 81.9, 77.6, 77.4, 61.1, 61.0, 58.7, 58.6, 36.7, 36.6, 27.9, 27.8, 18.2, 18.1, 14.2, 14.1.

■ tert-*Butyl ethyl (2R,3R)-2-methyl-3-(1-(E)-2-phenylethenyl)cyclopropane-1,1-dicarboxylate* **5e,f**

The cyclopropanation of **4e,f** (80 mg, 0.15 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **5e,f** (37 mg, 74%). R_f = 0.66 (cyclohexane/ethyl acetate 8:2).

IR (neat): 1 735, 1 650.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.29–7.18 (m, 5H), 6.62 (d, 1H, J = 15.8 Hz), 5.87, 5.85 (2dd, 1H, J = 15.8, 9, 9.2 Hz), 4.4–4.0 (4dq, 2H, J = 7.2 Hz), 2.49, 2.45 (2t apparent, 1H, J = 9 Hz), 2.11 (m, 1H), 1.48, 1.41 (2s, 9H), 1.30, 1.24 (2t, 3H, J = 7.2 Hz), 1.19, 1.16 (2d, 3H, J = 6.1 Hz).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 168.2, 167. 8, 166.9, 166.5, 136.8, 136.7, 132.5, 128.2, 127.0, 125.7, 125.6, 125.0, 124.9, 81.5, 81.4, 61.0, 43.1, 43.0, 35.8, 35.7, 27.7, 26.7, 26.5, 14.0, 13.9, 12.0.

■ tert-*Butyl ethyl (2R,3S)-2-methyl-3-(1-(E)-2-phenylethenyl)cyclopropane-1,1-dicarboxylate* **5g,h**

The cyclopropanation of **4g,h** (56 mg, 0.11 mmol) afforded after chromatography (SiO_2, cyclohexane/ethyl acetate 9:1) **5g,h** (29 mg, 82%). R_f = 0.73 (cyclohexane/ethyl acetate 8:2).

IR as for **5e,f**.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.36–7.17 (m, 5H), 6.67, 6.65 (2d, 1H, J = 15.8 Hz), 6.06, 6.04 (2dd, 1H, J = 15.8, 10 Hz), 4.27–4.14 (m, 2H), 2.48, 2.46 (2t apparent, 1H, J = 10 Hz), 1.99 (m, 1H), 1.48, 1.46 (2s, 9H), 1.34–1.23 (m, 6H).

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 170.8, 169.3, 167.1, 165.8, 137.4, 133.6, 133.5, 128.6, 127.3, 126.1, 123.5, 82.1, 81.6, 61.6, 61.0, 40.3, 40.2, 34.6, 34.4, 28.1, 26.7, 26.4, 14.4, 14.2, 10.1, 10.0.

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Oxidation potentials and electron spin resonance spectra of 1,2,3,4-dibenzocycl[2.2.3]azines and their radical cations. A novel peripheral 18π system

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Summary — Oxidation potentials of 1,2,3,4-dibenzocycl[2.2.3]azines **2a–d** were obtained by cyclic voltammetry, which shows remarkably large effect of the substituents at the 2 position, ranging from +0.59 to +0.85 V vs NHE. In contrast to the parent cycl[2.2.3]azine **1**, the radical cation species were readily generated from the 1,2,3,4-dibenzocycl[2.2.3]azines **2a–c** upon oxidation with $AgClO_4$. The simulated hyperfine coupling constants were obtained from ESR spectra of these radical cations. Among these dibenzocyclazines, only the benzoyl-substituted one formed the radical anion. The effect of substitution on the the spin densities in these radical cations and the oxidation potentials are discussed qualitatively by means of simple MO theory, suggesting the important role of the peripheral 18π conjugation and the lesser contribution of the central nitrogen to the conjugation in this system.

cyclazine / electron spin resonance / oxidation potential / molecular orbital theory

Résumé — Potentiels d'oxydation et résonance paramagnétique électronique de 1,2,3,4-dibenzocycl[2.2.3]azines et de leurs cations radicaux. Un nouveau système 18π périphérique. *Les potentiels d'oxydation des 1,2,3,4-dibenzocycl[2.2.3]azines* **2a–d** *sont obtenus par voltamétrie cyclique qui montre de remarquables et importants effets du substituant en position C2 allant de +0,59 à +0,85 V vs NHE. En contraste avec la cycl[2.2.3]azine* **1**, *les espèces cations radicaux sont rapidement générées à partir des 1,2,3,4-dibenzocycl[2.2.3]azines* **2a–c** *par oxydation avec $AgClO_4$. Les constantes de couplages hyperfines simulées sont obtenues par spectroscopie RPE de ces cations-radicaux. Parmi ces dibenzocyclazines, seuls les dérivés benzoylés donnent l'anion radical. Les effets de substitution sur la densité de spin dans ces cations radicaux et les potentiels d'oxydation sont discutés qualitativement au moyen de la simple théorie OM, suggérant le rôle important de la conjugaison 18π périphérique et la moindre contribution de l'azote central dans la conjugaison de ce système.*

cyclazine / RPE / potentiel d'oxydation / théorie des orbitales moléculaires

Since Boekelheide et al reported the first synthesis of cycl[2.2.3]azine [1], the chemistry of cyclazines has attracted much attention particularly in their synthetic and physicochemical aspects [2, 3]. Specifically, peripheral conjugate heterocyclic systems such as bridged heteroannulenes and cyclazines are desired in order to obtain experimental evidence regarding recognition of the net energy changes associated with π-electron delocalization. Cycl[2.2.3]azine **1** [4] is a typical example, giving a peripheral 10π electron conjugate system. The radical anion $\mathbf{1}^{\cdot-}$ has been extensively studied by ESR spectroscopy [5a–c]. Furthermore, cycl[3.3.3]azine and its aza derivatives were thoroughly studied by means of theoretical calculations as well as spectroscopic methods (UV-vis, XPS, NMR, ESR) [3d, 5d]. Since several 1,2,3,4-dibenzocycl[2.2.3]azines have been prepared, albeit in low yields [6], by "a surprising sequence of reactions involving (i) cycloaddition of pyridinium dicyanomethanides with benzyne; (ii) elimination of hydrogen cyanide; (iii) cycloaddition of 6-cyanobenzindolidines with benzyne; and (iv) elimination of hydrogen cyanide" [7], we now report an electron spin resonance (ESR) study of the radical cations of the 1,2,3,4-dibenzocycl[2.2.3]azines along with their oxidation potentials obtained by cyclic voltammetry.

Results and discussion

Oxidation potentials

The oxidation potentials of **2a–c** were determined by conventional cyclic voltammetry [8] from the reference of the oxidation potential of ferrocene peak (0.400 V

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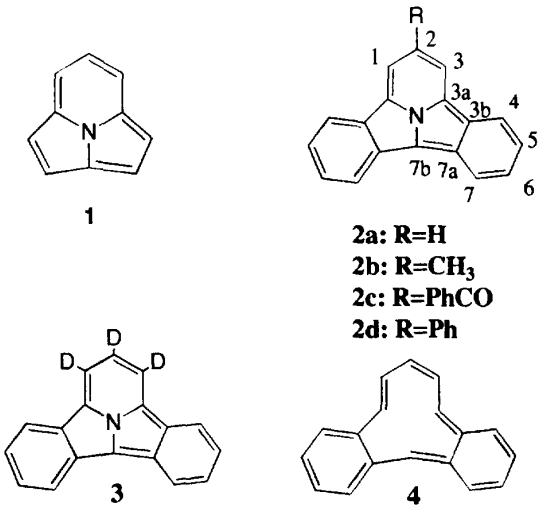

Scheme 1

vs NHE), indicating substituent effect at the position 2 (table I). For example, the voltammogram of **2a** showed a low oxidation peak, +0.70 vs NHE. Sweeping toward a reductive area up to −1.2 V exhibited no appreciable wave. As described below, the cyclazine **2a** is easily oxidized compared with cycl[2.2.3]azine **1**. The oxidation potential for **2a** of 0.70 V vs NHE seems to be small enough to produce a radical cation by a chemical reaction, in agreement with the ESR experiments described below. The oxidation potentials vary from 0.59 to 0.85 V vs NHE depending on the substituents. This effect can be discussed on the basis of the MO theory described in a later section. The Coulomb integral (α_C) at the substituted position was modified a little by taking into account the electron-donating or electron-withdrawing tendencies. (The parameter h changed between −0.2 to +0.2 depending on the electron-donating or electron-withdrawing substituents.) The Coulomb integral α_C is increased in units of the resonance integral β as

$$\alpha_C = \alpha + h\beta \qquad (1)$$

Table I. Oxidation potentials[a] of **2**.

Compound	*Oxidation potential (V)*
2a	0.70
2b	0.59
2c	0.85
2d	0.64

[a] A small amount of ferrocene was added and the position of the waves of the compounds under consideration was directly compared to that of ferrocenium/ferrocene peak (0.400 V vs NHE) as an internal standard.

Thus the HOMO energy level is stabilized for the cyclazine with the electron-withdrawing substituents ($h > 0$), resulting in large oxidation potentials. For instance, **2c** (R = PhCO) had oxidation potentials up to 0.85 V vs NHE, whereas **2b** (R = CH_3) had that of 0.59 V vs NHE. In the case of **2c**, the formation of a radical anion by alkaline metal reduction became relatively feasible as well as the formation of a radical cation as was shown in the ESR studies. The present data disclose the low oxidation potentials and remarkable substituent effect at position 2. These facts were more emphasized by the following ESR data exhibiting a particular spin density at position 2.

ESR measurements and hyperfine coupling constants

The ESR spectra of the radical cations contain several characteristic properties of dibenzocycl[2.2.3]azine. The most resolved ESR spectrum was given by the parent compound **2a** (R = H) as shown in figure 1. The other compounds showed broader ESR spectra probably due to the small hyperfine interactions. The key points of the spectral analyses are: 1) the hyperfine coupling constant (hfcc) determination from the non-overlapping wing-spectrum as inserted in figure 1; and 2) the comparison of the overall spectrum widths of the spectra of **2a** with that of dibenzocycl[2.2.3]azine-1,2,3-d_3 **3**.

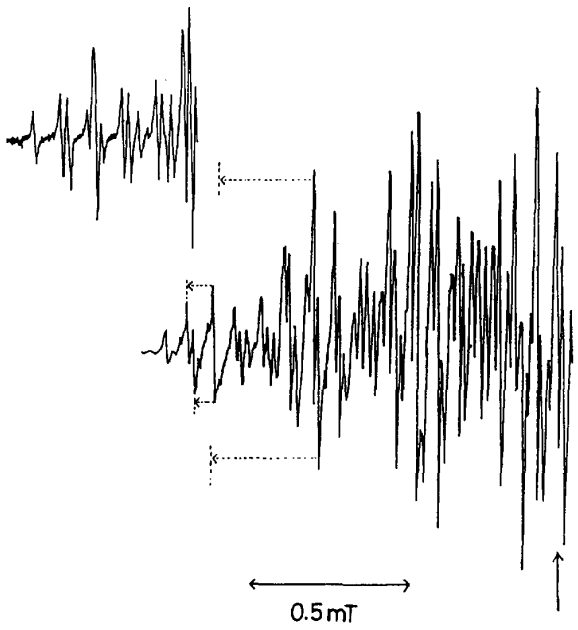

Fig 1. ESR spectrum of the radical cation **2a**$^{\cdot+}$: solvent, CH_2Cl_2; counterion: ClO_4^-; room temperature.

The first analysis established the hfccs and their equivalent proton numbers except for the proton at position 2 (table II). The second confirmed the proton hfcc at position 2, which is especially large, implying a large spin density at that position. The hfccs thus obtained for **2a** then suggest those for the D-substituted compound **3**. Comparing the nuclear magnetic moments of H and D, the deuteron hfcc is expected to be 0.063 mT. Based on this value and the remaining proton hfccs, the broad ESR spectrum of the D-substituted radical of cation of **3** was computer-simulated, as shown in figure 2. In the case of compounds other than **2b**, the hyperfine contribution from position 2 is so small that the ESR spectra is very similar, as shown in figure 3a for **2c**. The spectrum was also simulated as shown in

Table II. Simulated hyperfine coupling constants for the radical ions of **2** and **3** and predicted hyperfine coupling constants of $\mathbf{2a}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$.

	$2a^{\bullet+}$		$4^{\bullet+}$	$2a^{\bullet+}$	$3^{\bullet+}$	$2c^{\bullet+}$	$2d^{\bullet+}$	$2c^{\bullet-}$	*Assignment*
	Hückel[a]	*McLachlan*	*McLachlan*						
1H	0.217	0.293	0.477	0.415	0.052	–	–	–	2
/1D	0.033	0.045	0.073						
2H	0.263	0.325	0.233	0.334	0.327	0.309	0.329	0.311	7, 8
2H	0.206	0.240	0.136	0.318	0.312	0.288	0.310	0.290	5, 10
2H	0.108	0.060	0.116	0.268	0.253	0.232	0.240	0.233	4, 11
2H	0.067	0.086	0.016	0.087	0.067	0.077	0.077	0.078	6, 9
2H	0.029	0.051	0.136	0.069	0.061	0.069	0.077	0.060	1, 3
1N				0.000	0.015	0.018	0.015	0.015	

[a] Calculated using the reported parameters in ref [6].

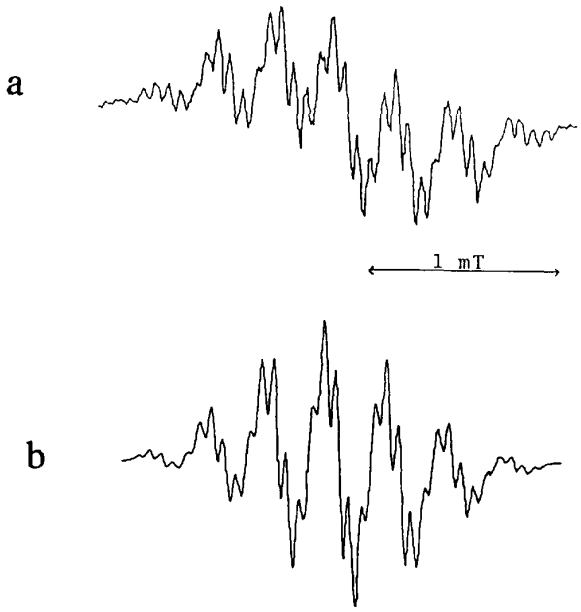

Fig 2. a) ESR spectrum of the radical cation $\mathbf{3}^{\bullet+}$: solvent: CH_2Cl_2; counterion: ClO_4^-; room temperature. b) Computer-simulated spectrum; for coupling constants see table I.

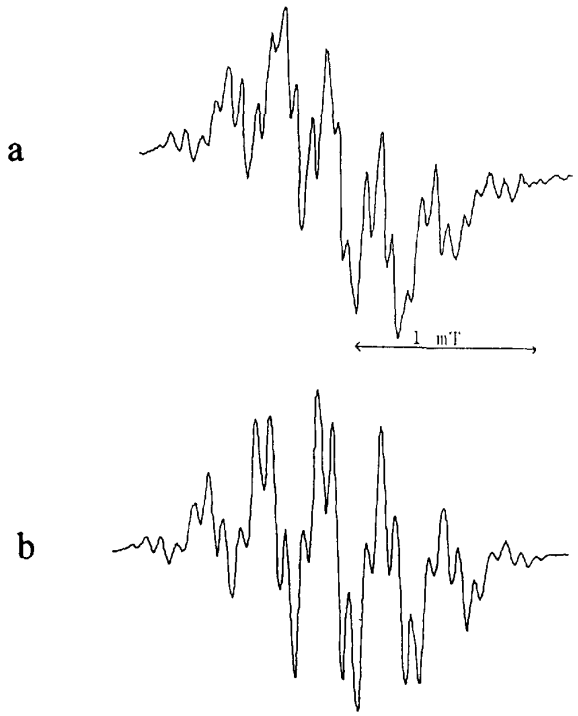

Fig 3. a) ESR spectrum of the radical cation $\mathbf{2c}^{\bullet+}$: solvent: CH_2Cl_2; counterion: ClO_4^-; room temperature. b) Computer-simulated spectrum; for coupling constants see table I.

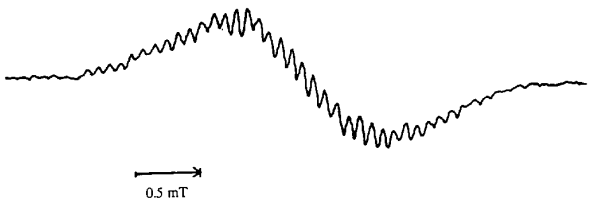

Fig 4. ESR spectrum of the radical cation $\mathbf{2b}^{\bullet+}$: solvent: CH_2Cl_2; counterion: ClO_4^-; room temperature.

figure 3b. The hfccs obtained by computer simulation are summarized in table II.

On the other hand, in the case of **2b** (R = CH_3) the spectrum became broad and lacked fine spectral characteristics (fig 4); the spectral analysis was therefore impossible. In an attempted formation of a radical anion of **2**, only **2c** exhibited a comparatively strong and well-resolved spectrum (fig 5). The spectral pattern itself was similar to that of the cation species, suggesting similar HOMO and LUMO. This will be discussed later. In summary, the hfccs of the dibenzocycl[2.2.3]azines **2** have several remarkable properties: 1) the proton in position 2 has the largest hfcc; 2) the spin density is substantially delocalized on the dibenzo group, which contributes to the aromatic stabilization of the molecule; and 3) the nitrogen hfcc is negligibly small, suggesting a peripheral 18π system.

The first finding is substantially correlated to the large substituent effect on the oxidation potentials at position 2. Concerning point (3) the small hfccs, which are comparable with the linewidth, these were considered as correct for reproduction of the broad spectra. Except for position 2, the hfccs were assigned from the MO calculations, referring to the order of the spin den-