Neolignans and Sesquiterpenes from Leaves and Embryogenic Cultures of *Ocotea catharinensis* (Lauraceae)

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Foram isoladas de extratos de folhas de *Ocotea catharinensis* Mez (Lauraceae) quatorze neolignanas sendo nove benzofurânicas (incluindo três novas substâncias 1e, 2f e 4b), uma seco-benzofurânica inédita (3b), duas biciclo[3.2.1]octânicas (incluindo a nova 5c), dois novos dímeros biciclo[3.2.1]octânicos (7a e 7b) e ainda dois sesquiterpenos (incluindo o novo humulanol 9). Nos embriões somáticos de *O. catharinensis* foram identificadas sete neolignanas incluindo uma nova neolignana biciclo[3.2.1]octânea (4a).

The extracts from leaves of *Ocotea catharinensis* Mez (Lauraceae) were found to contain fourteen neolignans and two sesquiterpenes: nine benzofuran types (including three new compounds 1e, 2f and 4b), one new seco-benzofuran type (3b), two bicyclo[3.2.1]octane types (including the new compound 5c), two new dimers of bicyclo[3.2.1]octane type (7a and 7b) and two sesquiterpenes (including a new humulanol 9). In addition, seven neolignans were also showed to occur in somatic embryos of *O. catharinensis* including one new bicyclo[3.2.1]octane type (4a).

Keywords: *Ocotea catharinensis*, benzofuran neolignans, bicyclo[3.2.1]octane neolignans, humulane sesquiterpene, somatic embryos

Introduction

*Ocotea catharinensis* (Lauraceae) is a woody plant species found in southern Atlantic forest in Brazil, which produces excellent quality of timber. The extensive logging over the past thirty years associated with difficulties for propagation has led its natural population to be significant decrease. Since *O. catharinensis* has been included as endangered species, a somatic embryogenic system was developed aiming to a massive propagation.1,2

The *Ocotea* has been one of the most phytochemically investigated Lauraceous genus and their major secondary compounds were showed to be phenylpropanoid-derived including several sub-classes of neolignans.3 Previous phytochemical studies carried out in leaves of *O. catharinensis* collected at Horto Florestal (Serra da Cantareira), São Paulo State, Brazil, reported the occurrence of benzofuran (1b, 1c, 1d, 2b, 2c, 2d, 2e and 2h) and bicyclo[3.2.1]octane (5a, 5b and 5d) neolignans.4 Representatives of both sub-classes of neolignans have also been previously isolated from barks and woods of a specimen collected in São Paulo State,5,6 and also from wood and leaves of *O. porosa* (“imbuia”) collected in Rio Grande do Sul State, southern Brazil.7,9

This work describes the isolation and characterization of major secondary compounds from leaves collected at Vale do Itajaí, Santa Catarina State, Brazil and from embryogenic cultures developed from the same plant source. The extracts from leaves afforded seven new neolignans 1e, 2f, 3b, 4b, 5c, 7a, 7b, besides seven previously reported ones 1a,6,10 1d,8 2a,6,10,11 2d,4 2e,6 2g,12 5e.13 Additionally, a new sesquiterpene of humulane type (9), besides known
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Results and Discussion

The defatted fraction of hexane extracts from *O. catharinensis* leaves and from *O. catharinensis* somatic embryos were submitted to flash chromatography followed by prep. TLC and/or circular chromatography (Chromatotron®). This procedure yielded nine new compounds (1e, 2f, 3b, 4a, 4b, 5c, 7a, 7b and 9), besides armenin-B (1a), 6,10 5'-methoxyprosin (1d), 6 ferrearin-C (2a), 6,10,11 ferrearin-B (2b), 11,12 2d, 6 ferrearin-E (2e), 6 ferrearin-G (2g), 12 5e, 13 6e and spathulenol (8). 4,14

The molecular formula of compound 1e was determined by HRESI as C_{23}H_{30}O_{7}. Its 1H NMR spectrum was quite similar to that of armenin-B (1a) (C_{21}H_{24}O_{6}), previously isolated from *Licaria armeniaca* 10 and from...
Table 1. \(^1\)H and \(^{13}\)C NMR data of 1e, 2f, 3b, 4a, 4b and 6 [\(\delta, J\) (Hz), 200 MHz and 50 MHz, CDCl₃]

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*O. catharinsenis.* The only difference was assigned to the oxygenation pattern of the aromatic ring, which was determined as 3,4,5-trimethoxyphenyl in 1e instead of 3,4-methylenedioxyphenyl in 1a.

The \(^1\)H NMR spectra of 2f (C$_2$H$_5$O$_2$H) and of ferrearin-E (2e) (C$_{21}$H$_{29}$O$_6$) isolated from *O. catharinsenis* were similar. The difference between both compounds consisted of an additional methoxyl group at B-position (C-5', $\delta$ 169.3) of 2f.

The molecular formula of compound 3b was determined by HRESI as C$_{22}$H$_{26}$O$_4$. All the \(^1\)H NMR data was similar to that of a neolignan 3a (C$_{21}$H$_{26}$O$_5$) previously isolated from *O. porosa.* Nevertheless, the \(^1\)H and \(^{13}\)C NMR spectra indicated that 3b contained a methoxyl group at C-3' ($\delta$H 3.58, $\delta$C 55.7) which was evidenced by the signal of C-3' at $\delta$C 152.8 instead of $\delta$C 132.7 in 3a. Its absolute configuration was determined as 8S,1'R,5'R based on the signal of optical rotation ([\(\alpha\)]$_D^{25}$ = $-$17° (MeOH, $c$ = 0.92 g/100mL) and comparison with reported data for (−)-megaphone in which X-ray crystallographic studies was carried out.

The compounds 4a and 4b were characterized as hexahydrobenzofuran neolignans by analysis of their \(^1\)H and \(^{13}\)C NMR spectra and comparison with 4c which was previously isolated from *O. porosa.* The aromatic rings were determined as 3,4-methylenedioxyphenyl and 5-methoxy-3,4-methylenedioxyphenyl for 4a and 4b, respectively. The relative stereochemistry between methyl and aryl groups...
was deduced from the anisotropic shielding effect caused by aromatic ring on cis methyl hydrogens as observed in the 'H NMR spectra. The methyl (H-9) signals of 4a (trans) and 4b (cis) were observed at δ 0.84 (d, 6.8 Hz) and 0.57 (d, 7.5 Hz), respectively. The placement of hydroxyl group at C-2' and methoxyl group at C-3' were possible by comparison of 13C NMR data and those described for 4c.9

The molecular formula of compound 5e was determined by HRESI as C13H20O4. Its 'H NMR were similar to that observed for previously reported 5e (C18H24O4) isolated from Aniba simulans,13 but with a 3,4-methylenedioxy for 5e instead of 5-methoxy-3,4-methylenedioxy observed for 5e.

Compounds 7a and 7b had their structures determined by analysis of their IR, MS and NMR spectra. The IR spectra of 7a/7b exhibited absorption bands at 1766 and 1714 cm⁻¹, assignable to two carbonyl groups for each compound. Their 'H and 13C NMR spectra resembled those of 5e/5e, respectively. Nevertheless, the 13C NMR signals associated to the olefinic double bond at C5′-C6′ were replaced by signals of quaternary carbinolic and methine signals at δ 88.4/52.6 (7a) and δ 88.4/52.7 (7b), respectively. The EIMS of 7a/7b showed molecular ion at m/z 370 and 400, but the chemical ionization mass spectrometry (CIMS) provided a molecular ion peak (M + H)⁺ at m/z 741 and m/z 801, respectively. These molecular ions combined with 'H and 13C NMR (PND and DEPT 135°) suggested a molecular formula C13H20O4 and C14H24O4 compatible with dimeric structures. Thus, the fragmentary ion peaks found at m/z 371 of 7a and 401 of 7b were assigned to the cleavage into monomers indicating that 7a and 7b were symmetric dimers of 5a and 5e. Based on similarities to 5a and 5e all 'H and 13C NMR data were assigned with the aid of 'H-'H COSY and HETCOR spectra (Table 2).

In order to determine the relative stereochemistry at the cyclobutane ring, NOESY spectra showed cross-peaks between H-8 and H-7', H-7' and H-6', H-6' and OMe-5'. Thus, among the cyclobutane syn-adducts at C-5' and C-6' four dimers would be expected (Figure 1). Dimers III and IV having cis configuration at the cyclobutane would involve a considerable steric hindrance between the bulky groups of bicyclooctane neolignan, which would prevent such arrangement. For these reason, dimers I and II having trans configuration were considered as the mostly probable structures.

The molecular formula of 9 (C17H18O) was deduced from MS and 13C NMR (PND and DEPT 135°) spectral data. The spectral characteristics of compound 9 were closely related to those of α-humulane17 except for the existence of a hydroxyl group (IR νmax/cm⁻¹: 3425) and two double bonds instead of three. All the 'H and 13C NMR signals were assigned by 'H-'H

![Figure 1. Possible structure of dimers for 7a/7b.](image-url)
Initiation and multiplication of embryogenic cultures

Embryogenic cultures were initiated from mature zygotic embryos of *O. catharinensis* according to described methodology.1,2

The somatic embryos produced at early cotyledonary stage (2-3 mm length) were inoculated in Woody Plant Medium (WPM, Sigma Co., USA) supplemented with 22.7 g L\(^{-1}\) sorbitol, 2 g L\(^{-1}\) Phytagel, 20 g L\(^{-1}\) sucrose and 400 mg L\(^{-1}\) glutamine (pH 5.8) and maintained at 25 °C and with photon flux of 22 µmol m\(^{-2}\) s\(^{-1}\) provided by fluorescent tubes under 16 h photoperiod.2,18 After four weeks cultivation the somatic embryos at mature stage (≥5 mm) were transferred to Petri dishes (6 cm), spread over two filter papers, and maintained at 25 °C for 4 days for desiccation.

Extraction and isolation of the constituents from leaves

Dried and powdered leaves (395.0 g) were exhaustively extracted with hexane at room temp. Evaporation of the
hexane under a reduced pressure gave a residue, which was partitioned between hexane and MeOH-H₂O (9:1). The hydroalcoholic phase was concentrated under reduced pressure yielding 2.4 g. This residue was submitted to flash chromatography column (silica gel, 150 g) and eluted with hexane-EtOAc mixtures at increasing polarities (7:3 to 0:1), yielding 120 fractions (30 mL each). Frs. 29-32 (33.0 mg) submitted to prep. TLC (silica gel, hexane-EtOAc, 4:1) gave spathulenol B (7.0 mg) and humula-4,8-dien-2-ol 9 (17.0 mg). Frs. 33-41 (76.0 mg) was also fractionated by prep. TLC (silica gel, cyclohexane-MeOH, 94.5:5:0:0.5) and afforded 2d (5.5 mg) and 2a (4.9 mg). Frs. 44-59 (60.0 mg) submitted to prep. TLC (silica gel, cyclohexane-Me₂CO, 97:3) followed by prep. TLC (silica gel, CHCl₃, EtOAc-iso-PrOH, 94.5:5:0:0.5) yielded 4b (5.0 mg) and 6 (5.0 mg). Frs. 60 (24.0 mg) and 61-65 (440.0 mg) submitted to flash chromatography column (silica gel, 150 g) and eluted with CHCl₃-MeOH at increasing polarity (1:1 to 0:1), affording 160 fractions (20 mL each). Fr. 1 (18.0 mg) submitted to prep. TLC (cyclohexane-Me₂CO, 95:5) yielded 2a (5.0 mg) and 6 (5.0 mg). Frs. 2-12 (7.0 mg) submitted to prep. TLC (cyclohexane-Me₂CO, 95:5) gave 2a (1.0 mg) and 2e (2.0 mg). Frs. 13-21 (20.5 mg) submitted to prep. TLC (cyclohexane-Me₂CO, 95:5) gave 2b (3.0 mg), 2a (4.0 mg) and 1c (3.0 mg). Frs. 22-54 (43.0 mg) purified by prep. TLC (CH₂Cl₂-Me₂CO, 9:1) yielded 4a (3.0 mg) and 6 (4.0 mg). Frs. 145-158 (29.0 mg) fractionated by prep. TLC (CHCl₃-MeOH, 9:1) yielded 1d (7.0 mg).

Viscous oil; IR (film) νmax/cm⁻¹: 3469, 2925, 1707, 1695, 1500, 1446, 1371, 1218, 1087, 1033, 925, 816, 772; 1H and 13C NMR, see Table 1; HRESIMS m/z: 419.2090 [M+H⁺] (calcld for C20H18O6, 419.2071); EIMS (70 eV) m/z (rel. int.): 418(M⁺, 34), 388(19), 377(100), 349(87), 317(29), 285(13), 208(44), 181(23), 91(13).

**rel(7R,8S,1'R,2'S)-2'-Hydroxy-3,4,5'-(trimethoxy-3'-oxo)Δ₁,3,5,5',8'-1,7,0.6'-neolignan (1e)**

Viscous oil; IR (film) νmax/cm⁻¹: 3455, 2936, 2849, 1739, 1654, 1586, 1457, 1451, 1142, 1072, 762; 1H and 13C NMR, see Table 1; HRESIMS m/z: 419.2090 [M+H⁺] (calcld for C20H18O6, 419.2071); EIMS (70 eV) m/z (rel. int.): 418(M⁺, 34), 388(19), 377(100), 349(87), 317(29), 285(13), 208(44), 181(22), 91(13).

**rel(7R,8S,1'R,2'S)-2'-Hydroxy-3,5'-(trimethoxy-3'-oxo)Δ₁,3,5,5',8'-1,7,0.6'-neolignan (2f)**

Viscous oil; [α]D ᵃ = −130° (MeOH, c = 0.20 g/100mL); IR (film) νmax/cm⁻¹: 3435, 2936, 2849, 1739, 1664, 1588, 1511, 1457, 1251, 1142, 1012, 762; 1H and 13C NMR, see Table 1; EIMS (70 eV) m/z (rel. int.): 374(M⁺, 7), 194(17), 167(100), 166(66), 165(76), 139(56), 95(17), 77(21), 69(18).

**rel(8S, 1'R, 5'R)-3',4',5'-Tetramethoxy-7,2'-dioxo-Δ₁,3,5,5',8'-1,7,0.6'-neolignan (3b)**

Viscous oil; [α]D ᵃ = −17° (MeOH, c = 0.92 g/100mL); IR (film) νmax/cm⁻¹: 2957, 2914, 2860, 2348, 1739, 1620, 1511, 1457, 1371, 1263, 1229, 1144, 1023, 766; 1H and 13C NMR, see Table 1; HRESIMS m/z: 389.1983 [M+H⁺] (calcld for C₂₅H₂₀O₁₀, 389.1966); EIMS (70 eV) m/z (rel. int.): 388(M⁺, 4), 352(30), 339(23), 324(10), 316(3), 165(100), 137(6).

**rel(7S,8S,1'R,2'S)-2'-Hydroxy-3,4-methylenedioxy-5',3'-5',5'-trimethoxy-Δ₁,3,5,5',8'-1,7,0.2'-neolignan (4a)**

Viscous oil; 1H NMR see Table 1.

**rel(7R,8S,1'R,2'S)-2'-Hydroxy-3,4-methylenedioxy-5',3'-5',5'-trimethoxy-Δ₁,3,5,5',8'-1,7,0.2'-neolignan (4b)**

Viscous oil; 1H and 13C NMR, see Table 1.

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**Extraction and isolation of the constituents from somatic embryos**

The desiccated somatic embryos (400.0 g) were frozen in Me₂CO with dry ice, ground and extracted with 500 mL MeOH-H₂O (4:1). The hydroalcoholic extracts was concentrated and successively partitioned with hexane and CHCl₃ (3 x 200 mL, each). The CHCl₃ residue (360.0 mg) was submitted to flash chromatography column (silica gel, 150 g) and eluted with CHCl₃-Me₂CO at increasing polarity (1:1 to 0:1), affording 160 fractions (20 mL each). Fr. 1 (18.0 mg) submitted to prep. TLC (cyclohexane-Me₂CO, 95:5) yielded 2a (5.0 mg) and 6 (5.0 mg). Frs. 2-12 (7.0 mg) submitted to prep. TLC (cyclohexane-Me₂CO, 95:5) gave 2a (1.0 mg) and 2e (2.0 mg). Frs. 13-21 (20.5 mg) submitted to prep. TLC (cyclohexane-Me₂CO, 95:5) gave 2b (3.0 mg), 2a (4.0 mg) and 1c (3.0 mg). Frs. 22-54 (43.0 mg) purified by prep. TLC (CH₂Cl₂-Me₂CO, 9:1) yielded 4a (3.0 mg) and 6 (4.0 mg). Frs. 145-158 (29.0 mg) fractionated by prep. TLC (CHCl₃-MeOH, 9:1) yielded 1d (7.0 mg).
rel(7S,8R,1'R,3'R)-4'-Hydroxy-3,4-methylenedioxy-3',5'-dimethoxy-2',4'-dioxo-Δ^{3,5,5',8',11,7,3'}-neolignan (5c)

Viscous oil; [α]_{D}^{21} = -18° (MeOH, c = 3.75 g/100mL); IR (film) ν_{max}/cm^{-1}: 1765, 1698, 1504, 1491, 1247, 1094, 1039. 1H and 13C NMR, see Table 2; HRESIMS m/z: 371.1496 [M+H]+ (calcd for C_{24}H_{23}O_{8}, 371.1496); EIMS (70 eV) m/z (rel. int.): 370 (M+, 22), 329(80), 287(12), 269(9), 208(100), 149(82), 137(73), 77(31).

rel(7S,8R,1'R,3'R)-4'-Hydroxy-3,4-methylenedioxy-3',5'-trimethoxy-2',4'-dioxo-Δ^{3,5,5',8',11,7,3'}-neolignan (5e)

Viscous oil; [α]_{D}^{21} = -29° (MeOH, c = 4.48 g/100mL); 1H and 13C NMR, see Table 2; EIMS (70 eV) m/z (rel. int.): 400 (M+, 52), 359(21), 331(10), 288(14), 219(100), 208(45), 207(43), 193(18), 192(66), 180(53), 165(34), 137(23), 91(14), 77(16).

7a (Dimer of 5c)

Viscous oil; [α]_{D}^{21} = +220° (MeOH, c = 0.07 g/100mL); IR (film) ν_{max}/cm^{-1}: 2922, 1766, 1714, 1513, 1453, 1137, 1094,1044; 1H and 13C NMR, see Table 2; CIMS m/z (rel. int.): 741(M+, 1), 579(1), 419(15), 391(91), 371(100), 341(18), 209(28), 163(37), 57(27).

7b (Dimer of 5e)

Viscous oil; [α]_{D}^{21} = + 57° (MeOH, c = 0.62 g/100mL); IR (film) ν_{max}/cm^{-1}: 1767, 1714, 1505, 1491, 1445, 1240, 1039; 1H and 13C NMR, see Table 2; CIMS m/z (rel. int.): 801(M+, 1), 609(18), 429(76), 419(85), 401(100), 371(11), 209(17), 193(11).

rel(8R)-Humulan-1,4-dien-8-ol (9)

Solid amorphous. Found: C, 80.89 %, H, 11.65% (C_{21}H_{23}O requires: C, 81.02%, H, 11.79%); IR (film) ν_{max}/cm^{-1}: 3425, 2946, 1707, 1464, 1371, 1022, 762; 1H and 13C NMR, see Table 3; EIMS (70 eV) m/z (rel. int.): 344(M+, 27), 303(9), 271(12), 189(100), 179(26), 178(76), 166(25), 165(66), 151(59), 137(19), 115(15), 107(27), 91(35), 77(33).

Acknowledgments

The authors acknowledge FAPESP, CNPq, CAPES and International Foundation for Science (Sweden) for financial support.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.org.br, as PDF file.

References


Received: October 1, 2008
Web Release Date: March 20, 2009

FAPESP helped in meeting the publication costs of this article.
Neolignans and Sesquiterpenes from Leaves and Embryogenic Cultures of *Ocotea catharinensis* (Lauraceae)

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Figure S1. $^1$H NMR spectrum of 1a (200 MHz, CDCl$_3$).

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Figure S2. $^{13}$C NMR spectrum of 1a (50 MHz, CDCl$_3$).

Figure S3. DEPT 135 $^{13}$C NMR spectrum of 1a (50 MHz, CDCl$_3$).
Figure S4. $^1$H NMR spectrum of 1b (200 MHz, CDCl$_3$).

Figure S5. $^1$H NMR spectrum of 1c (200 MHz, CDCl$_3$).
Figure S6. $^{13}$C NMR spectrum of 1c (50 MHz, CDCl$_3$).

Figure S7. DEPT $^{13}$C NMR spectrum of 1c (50 MHz, CDCl$_3$).
Figure S8. $^1$H NMR spectrum of 1e (200 MHz, CDCl$_3$).

Figure S9. $^{13}$C NMR spectrum of 1e (50 MHz, CDCl$_3$).
Figure S10. DEPT 135 $^{13}$C NMR spectrum of 1e (50 MHz, CDCl$_3$).

Figure S11. HRESIMS spectrum of 1e.
Figure S12. $^1$H NMR spectrum of 2a (200 MHz, CDCl$_3$).

Figure S13. $^{13}$C NMR spectrum of 2a (50 MHz, CDCl$_3$).
Figure S14. DEPT 135 $^{13}$C NMR spectrum of 2a (50 MHz, CDCl$_3$).

Figure S15. $^1$H NMR spectrum of 2b (200 MHz, CDCl$_3$).
Figure S16. $^{13}$C NMR spectrum of 2b (50 MHz, CDCl$_3$).

Figure S17. DEPT 135 $^{13}$C NMR spectrum of 2b (50 MHz, CDCl$_3$).
Figure S18. $^1$H NMR spectrum of 2c (200 MHz, CDCl$_3$).

Figure S19. $^{13}$C NMR spectrum of 2c (50 MHz, CDCl$_3$).
Figure S20. DEPT 135 $^{13}$C NMR spectrum of 2c (50 MHz, CDCl$_3$).

Figure S21. 2D COSY $^{13}$C NMR spectrum of 2c (200 MHz, CDCl$_3$).
Figure S22. $^1$H NMR spectrum of 2d (200 MHz, CDCl$_3$).

Figure S23. $^{13}$C NMR spectrum of 2d (50 MHz, CDCl$_3$).
Figure S24. DEPT 135 $^{13}$C NMR spectrum of 2d (50 MHz, CDCl$_3$).

Figure S25. $^1$H NMR spectrum of 2f (200 MHz, CDCl$_3$).
Figure S26. $^{13}$C NMR spectrum of 2f (50 MHz, CDCl$_3$).

Figure S27. DEPT 135 $^{13}$C NMR spectrum of 2f (50 MHz, CDCl$_3$).
Figure S28. $^1$H NMR spectrum of 2g (200 MHz, CDCl$_3$).

Figure S29. $^{13}$C NMR spectrum of 2g (50 MHz, CDCl$_3$).
Figure S30. $^1$H NMR spectrum of 2h (200 MHz, CDCl$_3$).

Figure S31. $^{13}$C NMR spectrum of 2h (50 MHz, CDCl$_3$).
Figure S32. DEPT 135 $^{13}$C NMR spectrum of $2h$ (50 MHz, CDCl$_3$).

Figure S33. $^1$H NMR spectrum of $3b$ (200 MHz, CDCl$_3$).
Figure S34. $^{13}$C NMR spectrum of 3b (50 MHz, CDCl$_3$).

Figure S35. DEPT $^{13}$C NMR spectrum of 3b (50 MHz, CDCl$_3$).
**Figure S36.** COSY $^{13}$C NMR spectrum of 3b (50 MHz, CDCl$_3$).

**Figure S37.** HRESIMS spectrum of 3b.
Figure S38. $^1$H NMR spectrum of 4a (200 MHz, CDCl$_3$).

Figure S39. $^1$H NMR spectrum of 4b (200 MHz, CDCl$_3$).
Figure S40. $^{13}$C NMR spectrum of 4b (50 MHz, CDCl$_3$).

Figure S41. $^1$H NMR spectrum of 5a (200 MHz, CDCl$_3$).
**Figure S42.** $^{13}$C NMR spectrum of 5a (50 MHz, CDCl$_3$).

**Figure S43.** DEPT 135 $^{13}$C NMR spectrum of 5a (50 MHz, CDCl$_3$).
Figure S44. HETCOR $^{13}$C NMR spectrum of $5a$ (50 MHz, CDCl$_3$).

Figure S45. $^1$H NMR spectrum of $5b$ (200 MHz, CDCl$_3$).
Figure S46. $^{13}$C NMR spectrum of 5b (50 MHz, CDCl$_3$).

Figure S47. DEPT $^{13}$C NMR spectrum of 5b (50 MHz, CDCl$_3$).
Figure S48. COSY $^{13}$C NMR spectrum of 5b (50 MHz, CDCl$_3$).

Figure S49. HETCOR $^{13}$C NMR spectrum of 5b (50 MHz, CDCl$_3$).
Figure S50. $^1$H NMR spectrum of 5c (200 MHz, CDCl$_3$).

Figure S51. $^{13}$C NMR spectrum of 5c (50 MHz, CDCl$_3$).
Figure S52. COSY $^{13}$C NMR spectrum of 5c (50 MHz, CDCl$_3$).

Figure S53. HETCOR $^{13}$C NMR spectrum of 5c (50 MHz, CDCl$_3$).
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Figure S54. HRESIMS spectrum of 5c.

Figure S55. $^1$H NMR spectrum of 5d (200 MHz, CDCl$_3$).
Figure S56. $^{13}$C NMR spectrum of 5d (50 MHz, CDCl$_3$).

Figure S57. DEPT 135 $^{13}$C NMR spectrum of 5d (50 MHz, CDCl$_3$).
Figure S58. $^1$H NMR spectrum of 5e (200 MHz, CDCl$_3$).

Figure S59. $^{13}$C NMR spectrum of 5e (50 MHz, CDCl$_3$).
Figure S60. DEPT 135 $^{13}$C NMR spectrum of 5e (50 MHz, CDCl$_3$).

Figure S61. $^1$H NMR spectrum of 6 (200 MHz, CDCl$_3$).
Figure S62. $^1$H NMR spectrum of 7a (200 MHz, CDCl$_3$).

Figure S63. $^{13}$C NMR spectrum of 7a (50 MHz, CDCl$_3$).
Figure S64. COSY $^{13}$C NMR spectrum of 7a (50 MHz, CDCl$_3$).

Figure S65. HETCOR $^{13}$C NMR spectrum of 7a (50 MHz, CDCl$_3$).
Figure S66. EIMS spectrum of 7a (70 eV).

Figure S67. $^1$H NMR spectrum of 7a (200 MHz, CDCl$_3$).
Figure S69. DEPT 135 $^{13}$C NMR spectrum of 5e (50 MHz, CDCl$_3$).
Figure S70. $^1$H NMR spectrum of 8 (200 MHz, CDCl$_3$).

Figure S71. $^{13}$C NMR spectrum of 8 (50 MHz, CDCl$_3$).
Figure S72. $^1$H NMR spectrum of 9 (200 MHz, CDCl$_3$).

Figure S73. $^{13}$C NMR spectrum of 9 (50 MHz, CDCl$_3$).
Figure S74. COSY $^{13}$C NMR spectrum of 9 (50 MHz, CDCl$_3$).

Figure S75. HETCOR $^{13}$C NMR spectrum of 9 (50 MHz, CDCl$_3$).