

Study of Metal-Free and Palladium-Catalysed Synthesis of Benzochromenes Via Direct C-H Arylation Using Unactivated Aryl Benzyl Ethers Derived from Essential Oils as Raw Materials

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1. Reagents

2-Bromobenzyl bromide: Was purchased from Alfa Aesar and used as received.

3,4,5-Trimethoxybenzaldehyde: Was purchased from Aldrich and used as received.

3,4-Dimethoxybenzaldehyde: Was purchased from Aldrich and used as received.

4-Hidroxicoumarin: Was purchased from Aldrich and used as received.

8-Hydroxyquinoline: Was purchased from Aldrich and used as received.

Acetone: Was purchased from Merck and used as received.

CH₂Cl₂: Was purchased from Alfa Aesar and used as received.

DMA anhydrous: Was purchased from Aldrich and used as received.

Eugenol: Was purchased from Merck and used as received.

Iodine: Was purchased from Aldrich and used as received.

Isoeugenol: Was purchased from Aldrich and used as received.

NaI: Was purchased from Aldrich and used as received.

P(*p*-FC₆H₄)₃: Was purchased from Aldrich and used as received.

PdCl₂(MeCN)₂: Was purchased from Aldrich and used as received.

Phenol: Was purchased from Merck and used as received.

Potassium carbonate: Was purchased from Alfa Aesar and used as received.

Pyridine: Was purchased from Aldrich and used as received.

Silica gel 60 (0.063-0.200 mm) 70-230 mesh: Was purchased from Merck and used as received.

***tert*-Butyl hydroperoxide:** Was purchased from Aldrich and used as received.

2. Characterization data of all synthesized bromo aryl benzyl ethers **8a-v**

General Procedure

To a mixture of K_2CO_3 (3 equiv.), NaI (0.5 equiv.) and the appropriate phenol (4 mmol) in acetone (0.5 M) was added 2-bromobenzyl bromide (2 mmol) and the system was heating to 60 °C for 24 hours. The reaction mixture was quenched with a $NaOH$ (2N) solution and was extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was separated, dried with Na_2SO_4 , and concentrated to afford the crude product, which was purified by silica gel flash chromatography to yield the corresponding bromo aryl benzyl ethers **8a-8v**.

1-Bromo-2-(phenoxyethyl)benzene (8a): White solid (0.51 g, 1.94 mmol, 97%) R_f [hexane-EtOAc 30:1] = 0.57; m.p.= 37-40°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 1597 $\nu_{(\text{C}=\text{C})}$, 1244 $\nu_{(\text{C}-\text{O}-\text{C})}$, 686-675 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, $CDCl_3$), $\delta_{(\text{ppm})}$: 7.63–7.57 (2H, m, 4- and 10-H_{Ar}), 7.39–7.31 (3H, m, 9-, 8- and 7-H_{Ar}), 7.21 (1H, td, J = 7.9, 1.7 Hz, 1-H_{Ar}), 7.05–7.00 (3H, m, 3-, 2- and 1a-H_{Ar}), 5.17 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, $CDCl_3$), $\delta_{(\text{ppm})}$: 158.5, 136.4, 132.7, 129.6 (2), 129.3, 128.9, 127.6, 122.3, 121.2, 115.0 (2), 69.3; HRMS (ESI+): m/z : calcd for $C_{13}H_{12}BrO$ ([M+H]⁺) 263.0066, found: 206.0065; calcd for $C_{13}H_{11}BrNaO$ ([M+Na]⁺) 284.9885, found: 284.9884.

3-((2-Bromobenzyl)oxy)phenol (8b): White solid (0.51 g, 1.84 mmol, 92 %); R_f [hexane EtOAc 30:1] = 0.33; m.p.= 67-69°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3367 $\nu_{(\text{O}-\text{H})}$, 3059 $\nu_{(=\text{CHAr})}$, 1593 $\nu_{(\text{C}=\text{C})}$, 1282 $\nu_{(\text{C}-\text{O}-\text{C})}$, 682 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, $CDCl_3$), $\delta_{(\text{ppm})}$: 7.59 (1H, d, J = 7.9 Hz, 10-H_{Ar}), 7.54 (1H, d, J = 7.7 Hz, 7-H_{Ar}), 7.33 (1H, td, J = 7.5, 1.2 Hz, 9-H_{Ar}), 7.20 (1H, dd, J = 7.7, 1.4 Hz, 8-H_{Ar}), 7.15 (1H, t, J = 8.1 Hz, 3-H_{Ar}), 6.59 (1H, dd, J = 8.3, 2.3 Hz, 2-H_{Ar}), 6.51 (1H, t, J = 2.3 Hz, 1a-H_{Ar}), 6.47 (1H, dd, J = 8.0, 2.3 Hz, 4-H_{Ar}), 5.24 (1H, s, 1-OH), 5.11 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, $CDCl_3$), $\delta_{(\text{ppm})}$: 159.8, 156.8, 136.2, 132.7, 130.3, 129.3, 129.0, 127.6, 122.4, 108.4, 107.4, 102.6, 69.5; HRMS (ESI+): m/z : calcd for $C_{13}H_{12}BrO_2$ ([M+H]⁺) 279.0015, found: 279.0014; calcd for $C_{13}H_{11}BrNaO_2$ ([M+Na]⁺) 300.9834, found: 300.9833.

1-Bromo-2-((4-methoxyphenoxy)methyl)benzene (8c): Colorless oil (0.58 g, 1.98 mmol, 99%); R_f [hexane-EtOAc 15:1] = 0.43; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3061 $\nu_{(=\text{CHAr})}$, 2997 $\nu_{(\text{OCH}_3)}$, 1504 $\nu_{(\text{C}=\text{C})}$, 1226 $\nu_{(\text{C}-\text{O}-\text{C})}$, 669 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, $CDCl_3$), $\delta_{(\text{ppm})}$: 7.64–7.54 (2H, m, 10- and 7-H_{Ar}), 7.35 (1H, td, J = 7.5, 1.2 Hz, 9-H), 7.19 (td, J = 7.8, 1.6 Hz, 8-H), 6.99–6.91 (2H, m, 3- and 4-H), 6.91–6.83 (2H, m, 1- and 1a-H), 5.11 (2H, s, 6-CH₂), 3.79 (3H, s, 3-OCH₃); ^{13}C NMR (101 MHz, $CDCl_3$), $\delta_{(\text{ppm})}$: 154.2, 152.7, 136.7, 132.6, 129.2, 128.9, 127.6, 122.3, 115.9 (2), 114.7 (2), 70.2, 55.7; HRMS (ESI+): m/z : calcd for $C_{14}H_{14}BrO_2$ ([M+H]⁺) 293.0172, found: 293.0170; calcd for $C_{14}H_{13}BrNaO_2$ ([M+Na]⁺): 314.9991, found 314.9989.

2-((2-Bromobenzyl)oxy)-1,4-dimethylbenzene (8d): White solid (0.57 g, 1.98 mmol, 99 %); R_f [hexane-EtOAc 30:1]= 0.40; m.p.= 49-50°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3049 $\nu_{(\text{=CHAr})}$, 2972 $\nu_{(\text{CH}_3)}$, 1510 $\nu_{(\text{C=C})}$, 1265 $\nu_{(\text{C-O-C})}$, 673 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.64 (1H, dd, $J=7.7, 1.3$ Hz, 10-H_{Ar}), 7.61 (1H, dd, $J=8.0, 1.1$ Hz, 7-H_{Ar}), 7.37 (1H, td, $J=7.6, 1.0$ Hz, 9-H_{Ar}), 7.21 (1H, td, $J=7.9, 1.6$ Hz, 8-H_{Ar}), 7.08 (1H, d, $J=7.8$ Hz, 3-H_{Ar}), 6.77-6.71 (2H, m, 2- and 1a-H_{Ar}), 5.13 (2H, s, 6-CH₂), 2.35 (3H, s, 4-CH₃), 2.31 (3H, s, 1-CH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 156.5, 137.0, 136.8, 132.6, 130.6, 129.1, 128.6, 127.6, 123.9, 122.1, 121.5, 112.5, 69.3, 21.5, 16.1; HRMS (ESI+): m/z : calcd for $\text{C}_{15}\text{H}_{16}\text{BrO}$ ($[\text{M}+\text{H}]^+$) 291.0379, found: 291.0378; calcd for $\text{C}_{15}\text{H}_{15}\text{BrNaO}$ ($[\text{M}+\text{Na}]^+$) 313.0198, found: 313.0197.

2-((2-Bromobenzyl)oxy)-1-isopropyl-4-methylbenzene (8e): White solid (0.51 g; 1.6 mmol, 80 %); R_f [hexane-EtOAc 30:1]= 0.30; m.p.= 37-40°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3055 $\nu_{(\text{=CHAr})}$, 2958 $\nu_{(\text{CH}_3)}$, 1504 $\nu_{(\text{C=C})}$, 1259 $\nu_{(\text{C-O-C})}$, 675 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.69-7.59 (2H, m, 10- and 7-H_{Ar}), 7.39 (1H, td, $J=7.6, 1.2$ Hz, 9-H_{Ar}), 7.22 (1H, td, $J=7.7, 1.0$ Hz, 8-H_{Ar}), 7.18 (1H, d, $J=7.7$ Hz, 3-H_{Ar}), 6.83 (1H, dd, $J=7.7, 1.5$ Hz, 2-H_{Ar}), 6.78 (1H, s, 1a-H_{Ar}), 5.14 (2H, s, 6-CH₂), 3.45 (1H, m, 11-CH), 2.37 (3H, s, 1-CH₃), 1.30 (3H, s, 12-CH₃), 1.28 (3H, s, 13-CH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 155.5, 137.0, 136.5, 134.3, 132.6, 129.1, 128.6, 127.6, 126.0, 122.1, 121.8, 112.7, 69.4, 26.7, 22.9 (2), 21.5; HRMS (ESI+): m/z : calcd for $\text{C}_{17}\text{H}_{20}\text{BrO}$ ($[\text{M}+\text{H}]^+$) 319.0692, found: 319.0690; calcd for $\text{C}_{17}\text{H}_{19}\text{BrNaO}$ ($[\text{M}+\text{Na}]^+$) 341.0511, found: 341.0509.

2-((2-Bromobenzyl)oxy)-4-isopropyl-1-methylbenzene (8f): White solid (0.57 g, 1.78 mmol, 89%), R_f [hexane-EtOAc 30:1]= 0.20; m.p.= 48-50°C. IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3053 $\nu_{(\text{=CHAr})}$, 2958 $\nu_{(\text{CH}_3)}$, 1512 $\nu_{(\text{C=C})}$, 1253 $\nu_{(\text{C-O-C})}$, 673 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.66 (1H, dd, $J=7.7, 1.5$ Hz, 10-H_{Ar}), 7.62 (1H, dd, $J=8.0, 1.1$ Hz, 7-H_{Ar}), 7.39 (1H, td, $J=7.6, 1.2$ Hz, 8-H_{Ar}), 7.22 (1H, td, $J=7.9, 1.7$ Hz, 9-H_{Ar}), 7.14 (1H, d, $J=7.5$ Hz, 3-H_{Ar}), 6.82 (1H, dd, $J=7.6, 1.5$ Hz, 2-H_{Ar}), 6.80 (1H, s, 1a-H_{Ar}), 5.17 (2H, s, 6-CH₂), 2.91 (1H, m, 11-CH), 2.33 (3H, s, 4-CH₃), 1.29 (3H, s, 13-CH₃), 1.27 (3H, s, 12-CH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 156.4, 148.1, 136.9, 132.5, 130.6, 129.1, 128.7, 127.6, 124.4, 122.2, 118.6, 110.1, 69.2, 34.2, 24.2 (2), 16.2; HRMS (ESI+): m/z : calcd for $\text{C}_{17}\text{H}_{20}\text{BrO}$ ($[\text{M}+\text{H}]^+$) 319.0692, found: 319.0690; calcd for $\text{C}_{17}\text{H}_{19}\text{BrNaO}$ ($[\text{M}+\text{Na}]^+$) 341.0511, found: 341.0509.

2-((2-Bromobenzyl)oxy)-4-isopropyl-1-methylbenzene (8f'): White solid (0.22 g, 0.68 mmol, 34%), R_f [hexane-EtOAc 30:1]= 0.20; m.p.= 48-50°C; it was prepared according to general procedure using the essential oil of *Plectranthus amboinicus* (0.60 g) as a starting material; spectral data were identical to **8f.**

1-((2-Bromobenzyl)oxy)-2,3-dimethylbenzene (8g): White solid (0.58 g; 1.96 mmol, 98 %); R_f [hexane-EtOAc 30:1]= 0.40; m.p.= 59-60°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3068 $\nu_{(\text{=CHAr})}$, 2918 $\nu_{(\text{CH}_3)}$, 1598 $\nu_{(\text{C=C})}$, 1257 $\nu_{(\text{C-O-C})}$, 675 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.61 (2H, t, J = 7.6 Hz, 10- and 7-H_{Ar}), 7.36 (1H, t, J = 7.4 Hz, 9-H_{Ar}), 7.20 (1H, t, J = 7.7 Hz, 8-H_{Ar}), 7.07 (1H, t, J = 7.9 Hz, 1-H_{Ar}), 6.83 (1H, d, J = 7.5 Hz, 2-H_{Ar}), 6.79 (1H, d, J = 8.3 Hz, 1a-H_{Ar}), 5.13 (2H, s, 6-CH₂), 2.32 (3H, s, 4-CH₃), 2.27 (3H, s, 3-CH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 156.4, 138.2, 137.0, 132.6, 129.1, 128.7, 127.6, 125.9, 125.6, 122.9, 122.2, 109.5, 69.7, 20.2, 12.0. HRMS (ESI+): m/z : calcd for $\text{C}_{15}\text{H}_{16}\text{BrO}$ ($[\text{M}+\text{H}]^+$) 291.0379, found: 291.0378; calcd for $\text{C}_{15}\text{H}_{15}\text{BrNaO}$ ($[\text{M}+\text{Na}]^+$) 313.0198, found: 313.0197.

1-Bromo-4,5-dimethoxy-2-(phenoxyethyl)benzene (8h): White solid (0.32 g, 1 mmol, 50%); R_f [hexane-EtOAc 30:1]= 0.30; m.p.= 52-56°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 2968 $\nu_{(\text{OCH}_3)}$, 1595 $\nu_{(\text{C=C})}$, 1224 $\nu_{(\text{C-O-C})}$, 692 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.35-7.26 (2H, m, 3- and 2-H_{Ar}), 7.05 (2H, d, J = 1.8 Hz, 10- and 7-H_{Ar}), 7.02-6.95 (3H, m, 4-, 1- and 1a-H_{Ar}), 5.07 (2H, s, 6-CH₂), 3.88 (3H, s, 8-OCH₃), 3.86 (3H, s, 9-OCH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 158.5, 149.2, 148.6, 129.6 (2), 128.2, 121.3, 115.4, 115.0 (2), 112.7, 111.9, 69.4, 56.3, 56.1; HRMS (ESI+): m/z : calcd for $\text{C}_{15}\text{H}_{16}\text{BrO}_3$ ($[\text{M}+\text{H}]^+$) 323.0277, found: 323.0276; calcd for $\text{C}_{15}\text{H}_{15}\text{BrNaO}_3$ ($[\text{M}+\text{Na}]^+$) 345.0097, found: 345.0095.

2-Bromo-3,4,5-trimethoxy-1-(phenoxyethyl)benzene (8i): Colorless oil (0.69 g, 1.98 mmol, 99%); R_f [hexane-EtOAc 30:1]= 0.40; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 2935 $\nu_{(\text{OCH}_3)}$, 1598 $\nu_{(\text{C=C})}$, 1234 $\nu_{(\text{C-O-C})}$, 690 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.33 (1H, d, J = 7.1 Hz, 1a-H_{Ar}), 7.31 (1H, d, J = 7.2 Hz, 4-H_{Ar}), 7.02-6.99 (3H, m, 3-, 2-and 1-H_{Ar}), 6.95 (1H, s, 7-H_{Ar}), 5.10 (2H, s, 6-CH₂), 3.93 (3H, s, 10-OCH₃), 3.90 (3H, s, 9-OCH₃), 3.85 (3H, s, 8-OCH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 158.5, 153.1, 151.0, 142.7, 132.0, 129.6 (2), 121.4, 115.0 (2), 108.5, 107.8, 69.6, 61.5, 61.1, 56.2; HRMS (ESI+): m/z : calcd for $\text{C}_{16}\text{H}_{18}\text{BrO}_4$ ($[\text{M}+\text{H}]^+$) 353.0383, found: 353.0381; calcd for $\text{C}_{16}\text{H}_{17}\text{BrNaO}_4$ ($[\text{M}+\text{Na}]^+$) 375.0202, found: 375.0200.

4-Allyl-1-((2-bromobenzyl)oxy)-2-methoxybenzene (8j): Colorless oil (0.53 g, 1.6 mmol, 80%); R_f [hexane-EtOAc 30:1]= 0.23; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3055 $\nu_{(\text{=CHAr})}$, 2958 $\nu_{(\text{OCH}_3)}$, 1504 $\nu_{(\text{C=C})}$, 1259 $\nu_{(\text{C-O-C})}$, 675 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.58 (2H, m, 10- and 7-H_{Ar}), 7.32 (1H, td, J = 7.7, 1.2 Hz, 9-H_{Ar}), 7.16 (1H, ddd, J = 7.9, 7.3, 1.7 Hz, 8-H_{Ar}), 6.79 (1H, d, J = 8.2 Hz, 1a-H_{Ar}), 6.77 (1H, d, J = 2.0 Hz, 3-H_{Ar}), 6.69 (1H, dd, J = 8.1, 2.0 Hz, 1-H_{Ar}), 5.98 (1H, ddt, J = 16.8, 10.1, 6.7 Hz, 12=CH), 5.22 (2H, s, 6-CH₂), 5.14-0.06 (2H, m, 13=CH₂), 3.92 (3H, s, 4-OCH₃), 3.35 (2H, d, J = 6.7 Hz, 11-CH₂); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 149.5, 146.1, 137.6, 136.6, 133.6, 132.5, 129.0, 128.6, 127.6, 121.8, 120.5, 115.8, 114.1, 112.4, 70.4, 56.0, 39.9; HRMS (ESI+): m/z : calcd for $\text{C}_{17}\text{H}_{18}\text{BrO}_2$ ($[\text{M}+\text{H}]^+$) 333.0485, found: 333.0483; calcd for $\text{C}_{17}\text{H}_{17}\text{BrNaO}_2$ ($[\text{M}+\text{Na}]^+$) 355.0304; found: 355.0302.

4-Allyl-1-((2-bromobenzyl)oxy)-2-methoxybenzene (8j'): Colorless oil (0.46 g, 1.4 mmol, 70%); R_f [hexane-EtOAc 30:1]= 0.23; it was prepared according to general procedure using the essential oil of *Eugenia caryophyllus* (0.91 g) as starting material; spectral data were identical to **8j**.

(E)-1-((2-Bromobenzyl)oxy)-2-methoxy-4-(prop-1-en-1-il)benzene (8k): White solid (0.46 g, 1.4 mmol, 70 %); R_f [hexane-EtOAc 30:1]= 0.30; m.p.= 56-61°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3007 $\nu_{(\text{=CHAr})}$, 2949 $\nu_{(\text{OCH}_3)}$, 1510 $\nu_{(\text{C=C})}$, 1259 $\nu_{(\text{C-O-C})}$, 675 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 7.58 (1H, d, $J= 7.9$ Hz, 7-H_{Ar}), 7.56 (1H, d, $J= 7.5$ Hz, 7-H_{Ar}), 7.31 (1H, td, $J= 7.5$, 1.2 Hz, 8-H_{Ar}), 7.16 (1H, td, $J= 7.8$, 1.5 Hz, 9-H_{Ar}), 6.94 (1H, d, $J= 1.7$ Hz, 3-H_{Ar}), 6.81 (1H, dd, $J= 8.5$, 1.9 Hz, 1-H_{Ar}), 6.77 (1H, d, $J= 8.3$ Hz, 1a-H_{Ar}), 6.34 (1H, dd, $J= 15.7$, 1.5 Hz, 11=CH), 6.19–6.05 (1H, m, 12=CH), 5.21 (2H, s, 6-CH₂), 3.93 (3H, s, 4-OCH₃), 1.87 (3H, dd, $J= 6.6$, 1.5 Hz, 13-CH₃); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 149.6, 146.8, 136.4, 132.5, 131.9, 130.5, 129.1, 128.6, 127.6, 124.2, 121.8, 118.6, 113.9, 109.1, 70.3, 56.0, 18.5; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₈BrO₂ ([M+H]⁺) 333.0485, found: 333.0483; calcd for C₁₇H₁₇BrNaO₂ ([M+Na]⁺) 355.0304; found: 355.0302.

2-((2-Bromobenzyl)oxy)benzaldehyde (8l): White solid (0.40 g, 1.40 mmol, 70 %); R_f [hexane-EtOAc 30:1]= 0.45; m.p.= 85-91°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 2916 $\nu_{(\text{=CHAr})}$, 1681 $\nu_{(\text{C=O})}$, 1597 $\nu_{(\text{C=C})}$, 1240 $\nu_{(\text{C-O-C})}$, 648 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 10.59 (1H, s, 4-CHO), 7.88 (1H, dd, $J= 7.7$, 1.8 Hz, 3-H_{Ar}), 7.61 (1H, dd, $J= 8.0$, 1.1 Hz, 10-H_{Ar}), 7.58–7.56 (1H, m, 2-H_{Ar}), 7.56-7.53 (1H, m, 1-H_{Ar}), 7.36 (1H, td, $J= 7.6$, 1.0 Hz, 8-H_{Ar}), 7.23 (1H, td, $J= 8.1$, 1.5 Hz, 9-H_{Ar}), 7.08 (1H, d, $J= 7.5$ Hz, 7-H_{Ar}), 7.09–7.02 (1H, m, 1a-H_{Ar}), 5.26 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 189.7, 160.8, 136.1, 135.5, 132.9, 129.8, 129.0, 128.8, 127.8, 125.3, 122.5, 121.4, 113.2, 70.1; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₂BrO₂ ([M+H]⁺) 291.0015, found: 291.0014; calcd for C₁₄H₁₁BrNaO₂ ([M+Na]⁺) 312.9835, found: 312.9833.

4-((2-Bromobenzyl)oxy)benzaldehyde (8m): White solid (0.52 g, 1.78 mmol, 89 %); R_f [hexane-EtOAc 30:1]= 0.50; m.p. = 54-58°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 2914 $\nu_{(\text{=CHAr})}$, 1681 $\nu_{(\text{C=O})}$, 1597 $\nu_{(\text{C=C})}$, 1240 $\nu_{(\text{C-O-C})}$, 648 $\nu_{(\text{C-Br})}$; ^1H NMR (400 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 9.90 (1H, s, 2-CHO), 7.89–7.81 (2H, m, 3- and 1-H_{Ar}), 7.61 (1H, d, $J= 8.0$ Hz, 10-H_{Ar}), 7.51 (1H, d, $J= 7.7$ Hz, 7-H_{Ar}), 7.35 (1H, t, $J= 7.5$ Hz, 8-H_{Ar}), 7.22 (1H, td, $J= 7.9$, 1.4 Hz, 9-H_{Ar}), 7.09 (2H, d, $J= 8.7$ Hz, 4- and 1a-H_{Ar}), 5.22 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 190.9, 163.5, 135.3, 132.9, 132.1 (2), 130.4, 129.7, 129.0, 127.8, 122.5, 115.3 (2), 69.7; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₂BrO₂ ([M+H]⁺) 291.0015, found: 291.0014; calcd for C₁₄H₁₁BrNaO₂ ([M+Na]⁺) 312.9835, found: 312.9833.

4-((2-Bromobenzyl)oxy)-3-methoxybenzaldehyde (8n**):** White solid (0.63 g, 1.98 mmol, 99 %); R_f [hexane-EtOAc 30:1]= 0.13; m.p.= 89-92°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3082 $\nu_{(\text{C}=\text{CHAr})}$, 2912 $\nu_{(\text{OCH}_3)}$, 1668 $\nu_{(\text{C}=\text{O})}$, 1587 $\nu_{(\text{C}=\text{C})}$, 1263 $\nu_{(\text{C}-\text{O}-\text{C})}$, 648 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 9.84 (1H, s, 13-CHO), 7.58 (1H, dd, $J= 8.0, 1.2$ Hz, 10-H_{Ar}), 7.52 (1H, d, $J= 7.6$ Hz, 7-H_{Ar}), 7.44 (1H, d, $J= 1.8$ Hz, 3-H_{Ar}), 7.40 (1H, dd, $J= 8.2, 1.9$ Hz, 1-H_{Ar}), 7.32 (1H, td, $J= 7.6, 1.0$ Hz, 8-H_{Ar}), 7.18 (1H, td, $J= 7.9, 1.6$ Hz, 9-H_{Ar}), 6.94 (1H, d, $J= 8.2$ Hz, 1a-H_{Ar}), 5.29 (2H, s, 6-CH₂), 3.96 (3H, s, 4-OCH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 191.0, 153.2, 150.0, 135.3, 132.7, 130.5, 129.5, 128.6, 127.8, 126.8, 121.9, 112.4, 109.4, 70.1, 56.1; HRMS (ESI+): *m/z*: calcd for $\text{C}_{15}\text{H}_{14}\text{BrO}_3$ ([M+H]⁺) 321.0120, found: 321.0119; calcd for $\text{C}_{15}\text{H}_{13}\text{BrNaO}_3$ ([M+Na]⁺) 342.9940, found: 342.9938.

3-((2-Bromobenzyl)oxy)-4-methoxybenzaldehyde (8o**):** White solid (0.63 g, 1.96 mmol, 98 %); R_f [hexane-EtOAc 30:1]= 0.13; m.p.= 85-86°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3066 $\nu_{(\text{C}=\text{CHAr})}$, 2941 $\nu_{(\text{OCH}_3)}$, 1680 $\nu_{(\text{C}=\text{O})}$, 1508 $\nu_{(\text{C}=\text{C})}$, 1265 $\nu_{(\text{C}-\text{O}-\text{C})}$, 640 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 9.81 (1H, s, 1-CHO), 7.60–7.52 (2H, m, 10-and 7-H_{Ar}), 7.48 (1H, dd, $J= 8.2, 1.8$ Hz, 2-H_{Ar}), 7.43 (1H, d, $J= 1.8$ Hz, 1a-H_{Ar}), 7.32 (1H, td, $J= 7.5, 1.2$ Hz, 9-H_{Ar}), 7.17 (1H, td, $J= 7.7, 1.7$ Hz, 8-H_{Ar}), 7.00 (1H, d, $J= 8.2$ Hz, 3-H_{Ar}), 5.21 (2H, s, 6-CH₂), 3.96 (3H, s, 4-OCH₃); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 190.8, 155.0, 148.4, 135.6, 132.7, 130.0, 129.4, 128.8, 127.6, 127.1, 122.3, 111.5, 110.9, 70.1, 56.2. HRMS (ESI+): *m/z*: calcd for $\text{C}_{15}\text{H}_{14}\text{BrO}_3$ ([M+H]⁺) 321.0120, found: 321.0119; calcd for $\text{C}_{15}\text{H}_{13}\text{BrNaO}_3$ ([M+Na]⁺) 344.9921 found: 344.9931.

1-((4-allyl-2-methoxyphenoxy)methyl)-2-bromo-3,4,5-trimethoxybenzene (8p**):** Colorless liquid (0.50 g, 1.2 mmol, 60%); R_f [hexane-EtOAc 10:1]= 0.26; ^1H NMR (400 MHz, CDCl_3) $\delta_{(\text{ppm})}$: 7.02 (1H, s, 7-H_{Ar}), 6.83 (1H, d, $J= 8.1$ Hz, 1a-H_{Ar}), 6.75 (1H, d, $J= 1.9$ Hz, 3-H_{Ar}), 6.69 (1H, dd, $J= 8.2, 2.0$ Hz, 1-H_{Ar}), 5.95 (1H, ddt, $J= 16.8, 10.1, 6.7$ Hz, 12=CH), 5.14 (1H, s, 6-CH₂), 5.11–5.04 (2H, m, 13=CH₂), 3.91 (3H, s, 10-OMe), 3.89 (3H, s, 8-OMe), 3.88 (3H, s, 9-OMe), 3.83 (3H, s, 4-OMe), 3.33 (2H, d, $J= 6.7$ Hz, 11-CH₂); ^{13}C NMR (101 MHz, CDCl_3) $\delta_{(\text{ppm})}$: 153.1, 150.8, 149.7, 146.34, 142.5, 137.6, 133.9, 132.4, 120.7, 115.8, 114.8, 112.6, 108.0, 107.6, 71.0, 61.1, 61.1, 56.2, 56.0, 39.9; HRMS (ESI+): *m/z*: calcd for $\text{C}_{20}\text{H}_{24}\text{BrO}_5$ ([M+H]⁺) 425.0783, found: 425.0782; calcd for $\text{C}_{20}\text{H}_{23}\text{BrNaO}_5$ ([M+Na]⁺) 447.0603, found: 447.0601.

1-((4-allyl-2-methoxyphenoxy)methyl)-2-bromo-3,4,5-trimethoxybenzene (8p'**):** Colorless liquid (0.46 g, 1.1 mmol, 55%); R_f [hexane-EtOAc 10:1]= 0.26; it was prepared according to general procedure from essential oil of *Eugenia caryophyllus* (0.91 g) as starting material; spectral data were identical to **8p**.

(E)-2-bromo-3,4,5-trimethoxy-1-((2-methoxy-4-(prop-1-en-1-yl)phenoxy)methyl)benzene (8q): Colorless liquid (0.81 g, 1.92 mmol, 96%); R_f [hexane-EtOAc 10:1]= 0.13; ^1H NMR (400 MHz, CDCl₃) δ (ppm): 6.99 (1H, s, 3-H_{Ar}), 6.91 (1H, d, J = 1.5 Hz, 1a-H_{Ar}), 6.87–6.83 (1H, m, 1-H_{Ar}), 6.80 (1H, s, 7-H_{Ar}), 6.32 (1H, dd, J = 15.7, 1.5 Hz, 11=CH), 6.11 (1H, dq, J = 15.7, 6.6 Hz, 12=CH), 5.15 (2H, s, 6-CH₂), 3.90 (6H, s, 9- and 10-OMe), 3.87 (3H, s, 8-OMe), 3.81 (3H, s, 4-OMe), 1.85 (3H, dd, J = 6.6, 1.5 Hz, 13-CH₃); ^{13}C NMR (101 MHz, CDCl₃) δ (ppm): 153.0, 150.7, 149.6, 146.8, 142.3, 132.1, 130.5, 129.4, 124.2, 118.7, 114.3, 109.0, 107.9, 107.4, 70.6, 61.1, 61.0, 56.1, 55.9, 18.4. HRMS (ESI+): m/z : calcd for C₂₀H₂₄BrO₅ ([M+H]⁺) 425.0784, found: 425.0782; calcd for C₂₀H₂₃BrNaO₅ ([M+Na]⁺) 447.0603, found: 447.0601.

1-((2-Bromobenzyl)oxy)naphthalene (8r): Pale yellow solid (0.57 g, 1.98 mmol, 99%); R_f [hexane-EtOAc 15:1]= 0.5; m.p.= 105–110°C; IR (KBr, $\nu_{\text{máx}}$ /cm⁻¹): 3053 $\nu_{(=\text{CHAr})}$, 1581 $\nu_{(\text{C}=\text{C})}$, 1276 $\nu_{(\text{C}-\text{O}-\text{C})}$, 669 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, CDCl₃), δ (ppm): 8.48–8.41 (1H, m, 1'-H_{Ar}), 7.91–7.82 (1H, m, 4'-H_{Ar}), 7.73 (1H, dd, J = 7.7, 1.4 Hz, 10-H_{Ar}), 7.66 (1H, dd, J = 8.0, 1.1 Hz, 7-H_{Ar}), 7.57–7.54 (2H, m, 3'- and 9-H_{Ar}), 7.51 (1H, d, J = 8.3 Hz, 2-H_{Ar}), 7.44–7.39 (2H, m, 2'- and 1-H_{Ar}), 7.23 (1H, dd, J = 7.6, 1.5 Hz, 9-H_{Ar}), 6.92 (1H, d, J = 7.5 Hz, 1a-H_{Ar}), 5.36 (2H, s, 6-CH₂); ^{13}C RMN (101 MHz, CDCl₃), δ (ppm): 154.1, 136.5, 134.7, 132.7, 129.3, 128.8, 127.7, 127.6, 126.6, 125.9, 125.8, 125.4, 122.3, 122.2, 120.8, 105.5, 69.6; HRMS (ESI+): m/z : calcd for C₁₇H₁₄BrO ([M+H]⁺) 313.0222, found: 313.0221; calcd for C₁₇H₁₃BrNaO ([M+Na]⁺) 335.0042, found: 335.0040.

4-((2-Bromobenzyl)oxy)-2H-chromen-2-one (8s): Pale yellow solid (0.65 g, 1.96 mmol, 98 %); R_f [hexane-EtOAc 5:1]= 0.30; m.p.= 165–170°C; IR (KBr, $\nu_{\text{máx}}$ /cm⁻¹): 3095 $\nu_{(=\text{CHAr})}$, 1716 $\nu_{(\text{C}=\text{O})}$, 1560 $\nu_{(\text{C}=\text{C})}$, 1242 $\nu_{(\text{C}-\text{O}-\text{C})}$, 663 $\nu_{(\text{C}-\text{Br})}$; ^1H NMR (400 MHz, DMSO-d₆), δ (ppm): 7.78 (1H, dd, J = 8.0, 1.4 Hz, 10-H_{Ar}), 7.78–7.68 (2H, m, 4- and 7-H_{Ar}), 7.66 (1H, ddd, J = 8.8, 7.4, 1.6 Hz, 8-H_{Ar}), 7.49 (1H, td, J = 7.5, 1.2 Hz, 2-H_{Ar}), 7.45–7.34 (2H, m, 1- and 3-H_{Ar}), 7.35 (1H, ddd, J = 8.2, 7.4, 1.1 Hz, 9-H_{Ar}), 6.10 (1H, s, 11a-H_{Ar}), 5.37 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, DMSO-d₆), δ (ppm): 164.5, 161.5, 152.7, 134.0, 132.9, 132.9, 131.2, 131.0, 128.1, 124.3, 123.5, 122.9, 116.5, 115.07, 91.3, 70.7; HRMS (ESI+): m/z : calcd for C₁₆H₁₂BrO₃ ([M+H]⁺) 330.9964, found: 330.9963; calcd for C₁₆H₁₁BrNaO₃ ([M+Na]⁺) 352.9780, found: 352.9782.

8-((2-Bromobenzyl)oxy)quinoline (8t): Pale yellow solid (0.51g, 1.64 mmol, 82 %); R_f [hexane-EtOAc 5:1]= 0.17; m.p.= 109–111°C; IR (KBr, $\nu_{\text{máx}}$ /cm⁻¹): 3061 $\nu_{(=\text{CHAr})}$, 1571 $\nu_{(\text{C}=\text{C})}$, 1265 $\nu_{(\text{C}-\text{O}-\text{C})}$; ^1H NMR (400 MHz, CDCl₃), δ (ppm): 8.90 (1H, dd, J = 4.2, 1.7 Hz, 3-H_{Ar}), 8.04 (1H, dd, J = 8.3, 1.7 Hz, 1-H_{Ar}), 7.54 (1H, dd, J = 7.7, 1.6 Hz, 10-H_{Ar}), 7.50 (1H, dd, J = 8.0, 1.1 Hz, 7-H_{Ar}), 7.35 (1H, dd, J = 8.3, 4.2 Hz, 2-H_{Ar}), 7.30–7.28 (2H, m, 8- and 12-H_{Ar}), 7.17 (1H, td, J = 7.5, 6.9, 1.5 Hz, 11-H_{Ar}), 7.06 (1H, td, J = 7.7, 1.7 Hz, 9-H_{Ar}), 6.87 (1H, dd, J =

6.4, 2.5 Hz, 11a-H_{Ar}), 5.41 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 155.2, 153.9, 149.5, 140.3, 136.0, 132.5, 129.5, 129.1, 128.6, 127.7, 126.6, 121.7, 120.2, 109.8, 100.0, 70.0. HRMS (ESI+): *m/z*: calcd for C₁₆H₁₃BrNO ([M+H]⁺) 314.0175, found: 314.0173; calcd for C₁₆H₁₂BrNNaO ([M+Na]⁺) 335.9994, found: 335.9993.

8-((2-Bromobenzyl)oxy)-2-methylquinoline (8u): Pale yellow solid (0.65g, 1.98 mmol, 99 %); *R*_f[hexane-EtOAc 5:1]= 0.27; m.p.= 110-115°C; IR (KBr, ν_{máx}/cm⁻¹): 3055 ν_(=CHAr), 2947 ν_(CH₃), 1587 ν_(C=C), 1261 ν_(C-O-C), 661 ν_(C-Br); ¹H NMR (400 MHz, CDCl₃), δ_(ppm): 8.01 (1H, d, *J*= 8.4 Hz, 1-H_{Ar}), 7.66 (1H, dd, *J*= 7.8, 1.8 Hz, 10-H_{Ar}), 7.58 (1H, dd, *J*= 7.9, 1.1 Hz, 7-H_{Ar}), 7.35 (1H, dd, *J*= 8.3, 1.3 Hz, 2-H_{Ar}), 7.34–7.29 (2H, m, 9- and 11-H_{Ar}), 7.28 (1H, dd, *J*= 7.0, 1.6 Hz, 12-H_{Ar}), 7.15 (1H, td, *J*= 7.9, 1.5 Hz, 8-H_{Ar}), 6.93 (1H, dd, *J*= 7.6, 1.2 Hz, 11a-H_{Ar}), 5.50 (2H, s, 6-CH₂), 2.82 (3H, s, 3-CH₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 158.3, 153.4, 139.9, 136.2, 136.2, 132.5, 128.9, 128.4, 127.8, 127.6, 125.6, 122.7, 121.4, 120.1, 110.3, 70.1, 25.9; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₄BrNO ([M+H]⁺) 328.0331, found: 328.0329; calcd for C₁₇H₁₅BrNNaO ([M+Na]⁺) 350.0150, found: 350.0149.

8-((2-Bromobenzyl)oxy)-5-chloroquinoline (8v): Pale yellow solid (0.68 g, 1.96 mmol, 98 %); *R*_f[hexane-EtOAc 5:1]= 0.20; m.p.= 140-143°C; IR (KBr, ν_{máx}/cm⁻¹): 3066 ν_(=CHAr), 1587 ν_(C=C), 1309 ν_(C-O-C), 742 ν_(C-Cl), 648 ν_(C-Br); ¹H NMR (400 MHz, CDCl₃), δ_(ppm): 9.01 (1H, dd, *J*= 4.2, 1.7 Hz, 3-H_{Ar}), 8.51 (1H, dd, *J*= 8.6, 1.7 Hz, 1-H_{Ar}), 7.58 (1H, dd, *J*= 8.2, 1.4 Hz, 10-H_{Ar}), 7.57 (1H, dd, *J*= 7.9, 1.2, 7-H_{Ar}), 7.54 (1H, dd, *J*= 8.3, 4.7 Hz, 2-H_{Ar}), 7.42 (1H, d, *J*= 8.4 Hz, 11-H_{Ar}), 7.25 (1H, td, *J*= 7.6, 1.2 Hz, 8-H_{Ar}), 7.19–7.09 (1H, m, 9-H_{Ar}), 6.86 (1H, d, *J*= 8.4 Hz, 11a-H_{Ar}), 5.46 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 153.1, 149.9, 140.8, 135.5, 133.0, 132.6, 129.3, 128.5, 127.8, 127.1, 126.4, 122.7, 122.5, 121.8, 109.7, 70.2; HRMS (ESI+): *m/z*: calcd for C₁₆H₁₂BrClNO ([M+H]⁺) 349.9764, found: 349.9774; calcd for C₁₆H₁₁BrClNNaO ([M+Na]⁺) 371.9583, found: 371.9581.

2-(Benzylxy)-3-bromo-1-isopropyl-4-methylbenzene (19): White solid (0.41 g, 1.3 mmol, 65%); *R*_f[hexane-EtOAc 30:1]= 0.63; m.p.= 85-90°C; ¹H NMR (400 MHz, CDCl₃), δ_(ppm): 7.59–7.52 (2H, m, 10a- and 7-H_{Ar}), 7.48–7.35 (5H, m, 10-, 9-, 8-, 3- and 2-H_{Ar}), 4.93 (2H, s, 6-CH₂), 3.32 (1H, h, *J*= 6.9 Hz, 11-CH), 2.60 (3H, s, 1-CH₃), 1.22 (3H, s, 12-CH₃), 1.20 (3H, s, 13-CH₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 152.4, 142.7, 136.8, 136.2, 129.6, 128.6(2), 128.3, 128.1(2), 121.5, 120.4, 75.3, 27.4, 24.1, 23.7(2); (ESI+): *m/z*: calcd for C₁₇H₂₀BrO ([M+H]⁺) 319.0692, found: 319.0690; calcd for C₁₇H₁₉BrNaO ([M+Na]⁺) 341.0511, found: 341.0509.

3. Characterization data of all synthesized 6H-Benzo[c]chromenes 9a-v

General procedure for intramolecular direct arylation

A crimper vial equipped with a magnetic stir bar was charged with bromo aryl benzyl ether (2 mmol), K₂CO₃ (3 equiv.), PivOH (30 mol%) as an additive, P(*p*-FPh)₃ (5 mol%) as a ligand and PdCl₂(MeCN)₂ (5 mol%). The vial was sealed and was purged three times with argon and 3 mL of degassed *N,N*-Dimethylacetamide (DMA) was added. Then, the reaction mixture was heated over 3 hours at 120°C. After cooling to room temperature, the crude mixture was loaded directly onto celite; then, purified by column chromatography (silica gel) using hexane/ethyl acetate mixtures as the eluent.

6H-Benzo[c]chromene (9a): Colorless oil (0.35 g, 1.92 mmol, 96 %); R_f [hexane-EtOAc 30:1]= 0.57; IR (KBr, ν_{máx}/cm⁻¹): 3068 ν_(=CHAr), 1609 ν_(C_{Ar}=C_{Ar}), 1244 ν_(C-O-C); ¹H NMR (400 MHz, CDCl₃) δ_(ppm): 7.76 (1H, dd, J= 7.7, 1.6 Hz, 4-H_{Ar}), 7.72 (1H, d, J= 7.7 Hz, 10-H_{Ar}), 7.40 (1H, td, J= 7.6, 1.3 Hz, 9-H_{Ar}), 7.32 (1H, dd, J= 7.5, 1.1 Hz, 8-H_{Ar}), 7.28 (1H, ddd, J= 8.0, 7.4, 1.7 Hz, 2-H_{Ar}), 7.17 (1H, dd, J= 7.4, 0.8 Hz, 7-H_{Ar}), 7.09 (1H, td, J= 7.6, 1.2 Hz, 3-H_{Ar}), 7.03 (1H, dd, J= 8.1, 1.3 Hz, 1-H_{Ar}), 5.15 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 154.8 (4a-C), 131.5 (10a-C), 130.1 (7a-C), 129.5 (2-C_{Ar}), 128.5 (9-C_{Ar}), 127.7 (8-C_{Ar}), 124.7 (7-C_{Ar}), 123.4 (4-C_{Ar}), 123.0 (1a-C), 122.2 (10-C_{Ar}), 122.1 (3-C_{Ar}), 117.4 (1-C_{Ar}), 68.5 (6-CH₂); COSY, [δ_H/δ_H]: 7.76/7.09 [4-H_{Ar}/3-H_{Ar}], 7.72/7.40 [10-H_{Ar}/9-H_{Ar}], 7.40/7.32 [9-H_{Ar}/8-H_{Ar}], 7.32/7.17 [8-H_{Ar}/7-H_{Ar}], 7.28/7.03 [2-H_{Ar}/1-H_{Ar}], 7.28/7.09 [2-H_{Ar}/3-H_{Ar}] 7.17/5.15 [7-H_{Ar}/6-CH₂]; HSQC, [δ_H/δ_C]: 7.76/123.4 [4-H_{Ar}/C_{Ar}-4], 7.72/122.2 [10-H_{Ar}/C_{Ar}-10], 7.40/128.5 [9-H_{Ar}/C_{Ar}-9], 7.32/127.7 [8-H_{Ar}/C_{Ar}-8], 7.28/129.5 [2-H_{Ar}/C_{Ar}-2], 7.17/124.7 [7-H_{Ar}/C_{Ar}-7], 7.09/122.1 [3-H_{Ar}/C_{Ar}-3], 7.03/117.4 [1-H_{Ar}/C_{Ar}-1], 5.15/68.5 [6-CH₂/C-6]; HMBC, [δ_H/δ_C]: 7.76/154.8 [4-H_{Ar}/C-4a], 7.72/123.4/127.7/131.4 [10-H_{Ar}/C_{Ar}-1/C_{Ar}-8/C-10a], 7.40/124.7/130.1 [9-H_{Ar}/C_{Ar}-7/C-7a], 7.32/122.2/131.4 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.28/123.0/122.1 [2-H_{Ar}/C-1a/C_{Ar}-3], 7.17/68.5/130.1 [7-H_{Ar}/C-6/C-7a], 7.09/117.4/123.0 [3-H_{Ar}/C_{Ar}-1/C-1a], 7.03/122.2/154.8 [1-H_{Ar}/C_{Ar}-10/C-4a], 5.15/124.7/131.4/154.8 [6-CH₂/C_{Ar}-7/C-10a/C-4a]; HRMS (ESI+): m/z: calcd for C₁₃H₁₁O ([M+H]⁺) 183.0804, found: 183.0803; calcd for C₁₃H₁₀NaO ([M+Na]⁺) 205.0623, found: 205.0622.

6H-Benzo[c]chromen-1-ol (9b): White solid (0.26 g, 1.34 mmol, 67 %); R_f [hexane-EtOAc 30:1]= 0.37; m.p.= 168-169°C; IR (KBr, ν_{máx}/cm⁻¹): 3361 ν_(-OH), 3257 ν_(=CHAr), 1587 ν_(C_{Ar}=C_{Ar}), 1234 ν_(C-O); ¹H NMR (400 MHz, CDCl₃) δ_(ppm): 8.33 (1H, d, J= 8.2 Hz, 10-H_{Ar}), 7.39 (1H, td, J= 7.9, 1.4 Hz, 9-H_{Ar}), 7.29 (1H, dd, J= 7.4, 1.1 Hz, 8-H_{Ar}), 7.19 (1H, dd, J= 7.4, 0.8 Hz, 7-H_{Ar}), 7.06 (1H, t, J= 8.1 Hz, 3-H_{Ar}), 6.65 (1H, dd, J= 8.1, 1.1 Hz, 4-H_{Ar}), 6.50

(1H, dd, $J= 8.1, 1.1$ Hz, 2-H_{Ar}), 5.43 (1H, s, 1-OH), 5.02 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 157.1 (4a-C), 153.8 (1-C), 132.0 (10a-C), 129.1 (3-C_{Ar}), 128.9 (7a-C), 128.4 (9-C_{Ar}), 127.2 (8-C_{Ar}), 126.1 (10-C_{Ar}), 124.7 (7-C_{Ar}), 111.8 (1a-C), 110.2 (2-C_{Ar}), 110.1 (4-C_{Ar}), 69.0 (6-CH₂); COSY, [δ_H/δ_H]: 8.33/7.39 [10-H_{Ar}/9-H_{Ar}] 7.39/7.29 [9-H_{Ar}/8-H_{Ar}], 7.29/7.19 [8-H_{Ar}/7-H_{Ar}], 7.05/6.65/6.50/5.02 [3-H_{Ar}/4-H_{Ar}/2-H_{Ar}/6-CH₂]; HSQC, [δ_H/δ_C]: 8.33/126.1 [10-H_{Ar}/C_{Ar}-10], 7.39/128.4 [9-H_{Ar}/C_{Ar}-9], 7.29/127.2 [8-H_{Ar}/C_{Ar}-8], 7.19/124.7 [7-H_{Ar}/C_{Ar}-7], 7.06/129.1 [3-H_{Ar}/C_{Ar}-3], 6.65/110.1 [4-H_{Ar}/C_{Ar}-4], 6.50/110.2 [2-H_{Ar}/C_{Ar}-2], 5.02/69.0 [6-CH₂/C-6]; HMBC, [δ_H/δ_C]: 8.33/111.8/132.0 [10-H_{Ar}/C-1a/C-10a], 7.39/124.7/128.9 [9-H_{Ar}/C_{Ar}-7/C-7a], 7.29/126.1/132.0 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.19/69.0/128.9 [7-H_{Ar}/C-6/C-7a], 7.06/153.8/157.1 [3-H_{Ar}/C-1/C-4a], 6.65/110.2/157.1 [4-H_{Ar}/C_{Ar}-2/C-4a], 6.50/110.1/153.8 [2-H_{Ar}/C_{Ar}-4/C-1a/C-1], 5.43/111.8/153.8 [1-OH/C-1a/C-1], 5.02/124.7/128.4/128.9/129.1/132.0/157.1 [6-CH₂/C_{Ar}-9/C-7a/C_{Ar}-3/C-10a/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₃H₁₁O₂ ([M+H]⁺) 199.0753, found: 199.0752; calcd for C₁₃H₁₀NaO₂ ([M+Na]⁺) 221.0673, found: 221.0672.

2-Methoxy-6H-benzo[c]chromene (9c): Colorless (0.25 g, 1.2 mmol, 60 %); R_f [hexane-EtOAc 30:1]= 0.57; IR (KBr, ν_{máx}/cm⁻¹): 3037 ν_(=CH_{Ar}), 2995 ν_(OCH₃), 2833 ν_(CH₂), 1570 ν_(C_{Ar}=C_{Ar}), 1494 ν_(CH₃), 1217 ν_(C-O-C); ¹H NMR (400 MHz, CDCl₃) δ_(ppm): 7.62 (1H, d, $J= 7.7$ Hz, 10-H_{Ar}), 7.34 (1H, td, $J= 7.8, 1.4$ Hz, 9-H_{Ar}), 7.25 (1H, td, $J= 7.5, 1.2$ Hz, 8-H_{Ar}), 7.22 (1H, d, $J= 3.0$ Hz, 1-H_{Ar}), 7.12 (1H, dd, $J= 7.4, 0.7$ Hz, 7-H_{Ar}), 6.90 (1H, d, $J= 8.9$ Hz, 4-H_{Ar}), 6.77 (1H, dd, $J= 8.8, 3.0$ Hz, 3-H_{Ar}), 5.03 (2H, s, 6-CH₂), 3.80 (3H, s, 2-OMe); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 154.8 (4a-C), 148.9 (2-C), 131.9 (10a-C), 130.2 (7a-C), 128.5 (9-C_{Ar}), 127.9 (8-C_{Ar}), 124.8 (7-C_{Ar}), 123.7 (1a-C), 122.1 (10-C_{Ar}), 118.0 (4-C_{Ar}), 115.0 (3-C_{Ar}), 108.4 (1-C_{Ar}), 68.6 (6-CH₂), 55.9 (2-OCH₃); COSY, [δ_H/δ_H]: 7.63/7.04 [1-H_{Ar}/2-H_{Ar}], 7.22–7.16/6.98 [3-H_{Ar}/4-H_{Ar}], 7.22–7.16/7.04 [3-H_{Ar}/2-H_{Ar}], 7.62/7.34 [10-H_{Ar}/9-H_{Ar}], 7.34/7.25 [9-H_{Ar}/8-H_{Ar}], 7.22/6.77 [1-H_{Ar}/3-H_{Ar}], 7.14/5.03 [7-H_{Ar}/6-CH₂], 6.90/6.77 [4-H_{Ar}/3-H_{Ar}], 6.77/3.80 [3-H_{Ar}/2-OMe]; HSQC, [δ_H/δ_C]: 7.62/122.1 [10-H_{Ar}/C_{Ar}-10], 7.34/128.5 [9-H_{Ar}/C_{Ar}-9], 7.25/127.9 [8-H_{Ar}/C_{Ar}-8], 7.22/108.4 [1-H_{Ar}/C_{Ar}-1], 7.12/124.8 [7-H_{Ar}/C_{Ar}-7], 6.90/118.0 [4-H_{Ar}/C_{Ar}-4], 6.77/115.0 [3-H_{Ar}/C_{Ar}-3], 5.03/68.6 [6-CH₂/C-6], 3.80/55.9 [2-OMe/C-2]; HMBC, [δ_H/δ_C]: 7.63/123.7/127.9/131.9 [10-H_{Ar}/C-1a/C_{Ar}-8/C-10a], 7.34/122.1/124.8/130.2 [9-H_{Ar}/C_{Ar}-10/C_{Ar}-7/C-7a], 7.25/122.1/131.9 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.22/115.0/148.9/154.8 [1-H_{Ar}/C_{Ar}-3/C-2/C-4a], 7.12/68.6/118.0/130.2 [7-H_{Ar}/C-6/C_{Ar}-4/C-7a], 6.90/123.7/148.8/154.8 [4-H_{Ar}/C-1a/C-2/C-4a], 6.77/108.4/148.9/154.8 [3-H_{Ar}/C_{Ar}-1/C-2/C-4a], 5.04/122.1/124.8/130.2/131.9 [6-CH₂/C_{Ar}-10/C_{Ar}-7/C-7a/C-10a], 3.81/148.9 [2-OMe/C-2]; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₃O₂ ([M+H]⁺) 213.0910, found: 213.0909; calcd for C₁₄H₁₂NaO₂ ([M+Na]⁺) 235.0729, found: 235.0728.

1,4-Dimethyl-6H-benzo[c]chromene(9d): Colorless oil (0.23 g, 1.1 mmol, 55 %); R_f [hexane-EtOAc 30:1]= 0.30; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3024 $\nu_{(\text{=CHAr})}$, 2951 $\nu_{(\text{CH}_3)}$, 1581 $\nu_{(\text{CAr=CAr})}$, 1450 $\nu_{(\text{CH}_3)}$, 1251 $\nu_{(\text{C-O-C})}$; ^1H NMR (400 MHz, CDCl₃) $\delta_{(\text{ppm})}$: 7.77 (1H, d, $J= 7.9$ Hz, 10-H_{Ar}), 7.40 (1H, td, $J= 7.7$, 1.7 Hz, 9-H_{Ar}), 7.31 (1H, td, $J= 7.3$, 1.1 Hz, 8-H_{Ar}), 7.26 (1H, d, $J= 7.4$ Hz 7-H_{Ar}), 7.04 (1H, d, $J= 7.7$ Hz, 3-H_{Ar}), 6.87 (1H, d, $J= 7.7$ Hz, 2-H_{Ar}), 4.97 (2H, s, 6-CH₂), 2.68 (3H, s, 1-CH₃), 2.28 (3H, s, 4-CH₃); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 154.5 (4a-C), 133.9 (10a-C), 132.8 (1a-C), 131.2 (7a-C), 129.9 (3-C_{Ar}), 127.8 (9-C_{Ar}), 126.8 (8-C_{Ar}), 126.5 (10-C_{Ar}), 124.8 (7-C_{Ar}), 124.8 (2-C_{Ar}), 124.1 (1-C_{Ar}), 123.0 (4-C_{Ar}), 69.1 (6-CH₂), 22.6 (1-CH₃), 16.0 (4-CH₃); COSY, [$\delta_{\text{H}}/\delta_{\text{H}}$]: 7.77/7.39 [10-H_{Ar}/9-H_{Ar}] 7.04/6.87/2.28 [3-H_{Ar}/2-H_{Ar}/4-CH₃], 6.87/2.68 [2-H_{Ar}/1-CH₃]; HSQC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.77/126.5 [10-H_{Ar}/C_{Ar}-10], 7.39/127.8 [9-H_{Ar}/C_{Ar}-9], 7.31/126.8 [8-H_{Ar}/C_{Ar}-8], 7.26/124.8 [7-H_{Ar}/C_{Ar}-7], 7.04/129.9 [3-H_{Ar}/C_{Ar}-3], 6.87/124.8 [2-H_{Ar}/C_{Ar}-2], 4.97/69.1 [6-CH₂/C-6], 2.68/22.6 [1-CH₃/CH₃-1], 2.28/16.0 [4-CH₃/CH₃-4]; HMBC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.78/123.0/126.8/133.9 [10-H_{Ar}/C-4/C_{Ar}-8/C-10a], 7.40/124.8/131.2 [9-H_{Ar}/C_{Ar}-7/C-7a], 7.31/126.5/133.9 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.27/69.1/127.8/131.2 [7-H_{Ar}/C-6/C_{Ar}-9/C-7a], 6.87/22.6/123.0/124.1 [2-H_{Ar}/CH₃-1/C-4/C-1], 4.97/124.8/131.1/133.9/154.5 [4-H_{Ar}/C_{Ar}-7/C-7a/C-10a/C-4a], 2.68/124.1/129.9/132.8 [1-CH₃/C-1/C_{Ar}-3/C-1a], 2.28/124.1/129.9/154.5 [4-CH₃/C-1/C_{Ar}-3/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₅H₁₅O ([M+H]⁺) 211.1117, found: 211.1116; calcd for C₁₅H₁₄NaO ([M+Na]⁺) 233.0937, found: 233.0935.

4-Isopropyl-1-methyl-6H-benzo[c]chromene (9e): White solid (0.38 g, 1.6 mmol; 80 %); R_f [hexane-EtOAc 30:1]= 0.30; m.p.= 56-60 °C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3049 $\nu_{(\text{=CHAr})}$, 2959 $\nu_{(\text{CH}_3)}$, 1606 $\nu_{(\text{CAr=CAr})}$, 1249 $\nu_{(\text{C-O-C})}$; ^1H NMR (400 MHz, CDCl₃) $\delta_{(\text{ppm})}$: 7.80 (1H, d, $J= 7.8$ Hz, 10-H_{Ar}), 7.43 (1H, td, $J= 7.6$, 1.7 Hz, 9-H_{Ar}), 7.33 (1H, td, $J= 7.3$, 1.2 Hz, 8-H_{Ar}), 7.29 (1H, d, $J= 7.5$ Hz, 7-H_{Ar}), 7.16 (1H, d, $J= 7.9$ Hz, 3-H_{Ar}), 6.97 (1H, d, $J= 7.9$ Hz, 2-H_{Ar}), 4.98 (2H, s, 6-CH₂), 3.39 (1H, m, 11-CH), 2.70 (3H, s, 1-CH₃), 1.31 (3H, s, 13-CH₃), 1.29 (3H, s, 12-CH₃); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 153.6 (4a-C), 134.7 (4-C), 134.1 (10a-C), 132.6 (1-C), 131.3 (7a-C), 127.7 (9-C_{Ar}), 126.7 (10-C_{Ar}), 126.6 (8-C_{Ar}), 125.3 (3-C_{Ar}), 125.1 (2-C_{Ar}), 124.7 (7-C_{Ar}), 123.2 (1a-C), 69.0 (6-CH₂), 27.1 (11-CH), 22.8 (13 and 12-CH₃), 22.6 (1-CH₃); COSY, [$\delta_{\text{H}}/\delta_{\text{H}}$]: 7.80/7.43 [10-H_{Ar}/9-H_{Ar}] 7.43/7.33 [9-H_{Ar}/8-H_{Ar}], 7.33/7.29 [8-H_{Ar}/7-H_{Ar}], 7.29/4.98 [7-H_{Ar}/6-CH₂] 7.16/6.97 [3-H_{Ar}/2-H_{Ar}], 6.97/2.70 [2-H_{Ar}/1-CH₃], 3.40/1.29/1.31 [11-CH/12-CH₃/13-CH₃]; HSQC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.80/126.6 [10-H_{Ar}/C_{Ar}-10], 7.43/127.7 [9-H_{Ar}/C_{Ar}-9], 7.33/126.7 [8-H_{Ar}/C_{Ar}-8], 7.29/124.7 [7-H_{Ar}/C_{Ar}-7], 7.16/125.1 [3-H_{Ar}/C_{Ar}-3], 6.97/125.3 [2-H_{Ar}/C_{Ar}-2], 4.98/69.0 [6-CH₂/C-6], 3.39/27.0 [11-CH/C-11], 2.70/22.6 [1-CH₃/CH₃-1], 1.31/22.8 [13-CH₃/C-13], 1.29/22.8 [12-CH₃/C-12]; HMBC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.80/123.2/126.7/134.7 [10-H_{Ar}/C-1a/C_{Ar}-8/C-10a], 7.43/124.7/126.6/131.2 [9-H_{Ar}/C_{Ar}-7/C_{Ar}-10/C-7a], 7.33/126.5/134.1 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.29/69.0/127.7/131.2 [7-

$\text{H}_{\text{Ar}}/\text{C}-6/\text{C}_{\text{Ar}}-9/\text{C}-7\text{a}$], 7.16/27.1/123.2/125.1/132.6/153.6 [3- H_{Ar} /C-11/C-1a/ $\text{C}_{\text{Ar}}-2/\text{C}-1/\text{C}-4\text{a}$], 6.97/22.6/123.2/125.1/132.6/134.7 [2- H_{Ar} /CH₃-1/ $\text{C}_{\text{Ar}}-3/\text{C}-1/\text{C}-10\text{a}$], 4.98/124.7/131.2/134.1/153.6 [6-CH₂/ $\text{C}_{\text{Ar}}-7/\text{C}-7\text{a}/\text{C}-4\text{a}$] 3.39/22.8/125.1/134.7/153.6 [11-CH/CH₃-12 and 13/ $\text{C}_{\text{Ar}}-3/\text{C}-4/\text{C}-4\text{a}$], 2.70/123.2/125.3/132.6 [1-CH₃/C-1a/ $\text{C}_{\text{Ar}}-2/\text{C}-1$], 1.29-1.31/27.1/134.7 [13 and 12-CH₃/C-11/C-4]; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₉O ([M+H]⁺) 239.1430, found: 239.1429; calcd for C₁₇H₁₈NaO ([M+Na]⁺) 261.1249, found: 261.1248.

4-Isopropil-1-methyl-6H-benzo[c]chromene (9e'): White solid (0.41 g, 1.74 mmol; 87 %); it was prepared according to general procedure from **19** (0.64 g, 2 mmol); spectral data were identical to **9e**.

1-Isopropil-4-methyl-6H-benzo[c]chromene (9f): Colorless oil (0.46 g, 1.92 mmol, 96 %); R_f [hexane-EtOAc 30:1]= 0.70; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3026 $\nu_{(\text{=CHAR})}$, 2960 $\nu_{(\text{CH}_3)}$, 1581 $\nu_{(\text{CAr=CAr})}$, 1257 $\nu_{(\text{C-O-C})}$; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.63 (1H, d, *J*= 7.9 Hz, 10- H_{Ar}), 7.41 (1H, td, *J*= 7.8, 7.3, 2.1 Hz, 9- H_{Ar}), 7.32 (2H, td, *J*= 7.1, 1.0 Hz, 8- and 7- H_{Ar}), 7.14 (1H, d, *J*= 7.9 Hz, 3- H_{Ar}), 7.05 (1H, d, *J*= 7.9 Hz, 2- H_{Ar}), 4.95 (2H, s, 6-CH₂), 3.79-3.67 (1H, m, 11-CH), 2.28 (3H, s, 4-CH₃), 1.38 (3H, s, 13-CH₃), 1.37 (3H, s, 12-CH₃); ¹³C NMR (101 MHz, CDCl₃), δ (ppm): 154.2 (4a-C), 144.4 (1-C), 134.4 (10a-C), 130.9 (7a-C), 130.4 (3-CAr), 127.9 (9-CAr), 127.0 (10-CAr), 126.7 (8-CAr), 125.0 (7-CAr), 123.3 (4-C), 122.2 (1a-C), 119.8 (2-CAr), 69.1 (6-CH₂), 29.4 (11-CH), 25.1 (13 and 12-CH₃), 16.0 (4-CH₃); COSY, [$\delta_{\text{H}}/\delta_{\text{H}}$]: 7.63/7.41 [10- $\text{H}_{\text{Ar}}/9\text{-H}_{\text{Ar}}$], 7.63/7.32 [10- $\text{H}_{\text{Ar}}/8\text{-H}_{\text{Ar}}$], 7.41/7.32 [9- $\text{H}_{\text{Ar}}/8\text{- and }7\text{-H}_{\text{Ar}}$], 7.32/4.95 [7- $\text{H}_{\text{Ar}}/6\text{-CH}_2$], 7.14/7.05 [3- $\text{H}_{\text{Ar}}/2\text{-H}_{\text{Ar}}$], 7.14/2.28 [3- $\text{H}_{\text{Ar}}/4\text{-CH}_3$], 3.71/1.39-1.37 [11-CH/13 and 12-CH₃], 1.39/1.37 [13-CH₃/12-CH₃]; HSQC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.63/127.0 [10- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-10$], 7.41/127.9 [9- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-9$], 7.32/125.0 [8- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-8$], 7.32/126.7 [7- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-7$], 7.14/130.4 [3- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-3$], 7.05/119.8 [2- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-2$], 4.95/69.1 [6-CH₂/C-6], 3.71/29.4 [11-CH/C-11], 2.28/16.0 [4-CH₃/C-4], 1.39-1.37/25.18 [13 and 12-CH₃/13 and 12-CH₃]; HMBC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.63/122.2/126.7/134.4 [10- $\text{H}_{\text{Ar}}/\text{C}-1\text{a}/\text{C}_{\text{Ar}}-8/\text{C}-10\text{a}$], 7.41/125.0/130.9 [9- $\text{H}_{\text{Ar}}/\text{C}-7/\text{C}-7\text{a}$], 7.32/126.7/127.0/130.8/134.4 [8 and 7- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}-8/\text{C}_{\text{Ar}}-10/\text{C}_{\text{Ar}}-7\text{a}/\text{C}-10\text{a}$], 7.14/16.0/144.4/154.2 [3- $\text{H}_{\text{Ar}}/\text{CH}_3-4/\text{C}-1/\text{C}-4\text{a}$], 7.05/29.4/123.3 [2- $\text{H}_{\text{Ar}}/\text{CH}-11/\text{C}-4$], 4.95/122.2/125.0/130.8/134.4 [6-CH₂/C-1a/C-7/C-10a/C-4a], 3.71/25.1/119.8/122.2/144.4 [11-CH/13 and 12-CH₃/C-1a/C-1], 2.28/123.3/130.4/154.1 [4-CH₃/C-4/C-3/C1/C-4a], 1.39-1.37/29.4/144.4 [13 and 12-CH₃/11-CH/C-1]. HRMS (ESI+): *m/z*: calcd for C₁₇H₁₉O ([M+H]⁺) 239.1430, found: 239.1429; calcd for C₁₇H₁₈NaO ([M+Na]⁺) 261.1249, found: 261.1248.

1-Isopropil-4-methyl-6H-benzo[c]chromene (9f'): Colorless oil (0.45 g, 1.88 mmol, 94 %); R_f [hexane-EtOAc 30:1]= 0.70; it was prepared according to general procedure from **8f'** (0.64 g, 2 mmol); spectral data were identical to **9f**.

3,4-Dimethyl-6H-benzo[c]chromene (9g): Colorless oil (0.26 g, 1.22 mmol, 61 %); R_f [hexane-EtOAc 30:1]= 0.63; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3030 $\nu_{(\text{=CHAr})}$, 2916 $\nu_{(\text{CH}_3)}$, 1589 $\nu_{(\text{CAr=CAr})}$, 1199 $\nu_{(\text{C-O-C})}$; ^1H NMR (400 MHz, CDCl₃) $\delta_{(\text{ppm})}$: 7.67 (1H, d, $J=7.8$ Hz, 10-H_{Ar}), 7.50 (1H, d, $J=7.9$ Hz, 1-H_{Ar}), 7.36 (1H, td, $J=7.6$, 0.8 Hz, 9-H_{Ar}), 7.31–7.22 (1H, m, 8-H_{Ar}), 7.16 (1H, d, $J=7.5$ Hz, 7-H_{Ar}), 6.89 (1H, d, $J=7.9$ Hz, 2-H_{Ar}), 5.11 (2H, s, 6-CH₂), 2.31 (3H, s, 3-CH₃), 2.21 (3H, s, 4-CH₃); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 154.5 (4a-C), 133.9 (3-C), 132.8 (10a-C), 131.2 (7a-C), 129.9 (9-C_{Ar}), 127.8 (8-C_{Ar}), 126.8 (7-C_{Ar}), 126.5 (2-C_{Ar}), 124.8 (10 and 1-C_{Ar}), 124.1 (1a-C), 123.0 (4-C), 69.1 (6-CH₂), 22.6 (3-CH₃), 16.0 (4-CH₃); COSY, [$\delta_{\text{H}}/\delta_{\text{H}}$]: 7.67/7.36 [10-H_{Ar}/9-H_{Ar}] 7.50/6.89/2.31 [1-H_{Ar}/2-H_{Ar}/3-CH₃], 7.16/5.11/7.27 [7-H_{Ar}/6-CH₂/8-H_{Ar}]; HSQC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.67/124.8 [10-H_{Ar}/C_{Ar}-10], 7.50/124.8 [1-H_{Ar}/C_{Ar}-1], 7.36/129.9 [9-H_{Ar}/C_{Ar}-9], 7.27/127.8 [8-H_{Ar}/C_{Ar}-8], 7.16/126.8 [7-H_{Ar}/C_{Ar}-7], 6.89/126.5 [2-H_{Ar}/C_{Ar}-2], 5.11/69.1 [6-CH₂/C-6], 2.31/22.6 [3-CH₃/CH₃-3], 2.28/16.0 [4-CH₃/CH₃-4]; HMBC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.67/124.1/127.8/129.9/132.8 [10-H_{Ar}/C-1a/C_{Ar}-8/C_{Ar}-9/C-10a], 7.50/126.5/124.1 [1-H_{Ar}/C_{Ar}-2/C-1a], 7.36/126.8/127.8/132.8 [9-H_{Ar}/C_{Ar}-7/C_{Ar}-8/C-10a], 7.27/126.8/129.9/131.2/ [8-H_{Ar}/C_{Ar}-7/C_{Ar}-9/C-7a], 7.16/69.1/127.8/131.2 [7-H_{Ar}/C-6/C_{Ar}-8/C-7a], 6.89/22.31/123.0/124.1/124.8 [2-H_{Ar}/CH₃-3/C-4/C-1a/C_{Ar}-1], 5.11/126.8/131.2 /132.8/154.5 [6-CH₂/C_{Ar}-7/C-7a/C-10a/C-4a] 2.31/126.5/133.9/ [3-CH₃/C_{Ar}-2/C-3], 2.21/123.0/154.5 [4-CH₃/C-4/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₅H₁₅O ([M+H]⁺) 211.1117, found: 211.1116; calcd for C₁₅H₁₄NaO ([M+Na]⁺) 233.0937, found: 233.0936.

9,10-Dimethoxy-6H-benzo[c]chromene (9h): White solid (0.36 g, 1.5 mmol, 75 %); R_f [hexane-EtOAc 30:1]= 0.20; m.p.= 102–106°C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 2958 $\nu_{(\text{=CHAr})}$, 2916 $\nu_{(\text{OCH}_3)}$, 1600 $\nu_{(\text{CAr=CAr})}$, 1460 $\nu_{(\text{CH}_3)}$, 1280 $\nu_{(\text{C-O-C})}$; ^1H NMR (400 MHz, CDCl₃) $\delta_{(\text{ppm})}$: 7.63 (1H, dd, $J=7.7$, 1.6 Hz, 1-H_{Ar}), 7.22–7.16 (1H, m, 3-H_{Ar}), 7.19 (1H, s, 10-H_{Ar}) 7.04 (1H, td, $J=7.5$, 1.3 Hz, 2-H_{Ar}), 6.98 (1H, dd, $J=8.0$, 1.3 Hz, 4-H_{Ar}), 6.67 (1H, s, 7-H_{Ar}), 5.07 (2H, s, 6-CH₂), 3.97 (3H, s, 9-OMe), 3.91 (3H, s, 8-OMe); ^{13}C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 154.1 (4a-C), 149.3 (9-C), 149.0 (8-C), 128.7 (3-C_{Ar}), 124.1 (10a-C), 123.1 (7a-C), 122.9 (1a-C), 122.6 (1-C_{Ar}), 122.2 (2-C_{Ar}), 117.3 (4-C_{Ar}), 107.9 (7-C_{Ar}), 105.5 (8-C_{Ar}), 68.2 (6-CH₂), 56.2 (9-OMe), 56.1 (8-OMe); COSY, [$\delta_{\text{H}}/\delta_{\text{H}}$]: 7.63/7.04 [1-H_{Ar}/2-H_{Ar}], 7.22–7.16/6.98 [3-H_{Ar}/4-H_{Ar}], 7.22–7.16/7.04 [3-H_{Ar}/2-H_{Ar}], 7.19/3.97 [10-H_{Ar}/9-OMe], 6.67/5.07 [7-H_{Ar}/6-CH₂], 6.67/3.91 [7-H_{Ar}/8-OMe]; HSQC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.63/122.6 [1-H_{Ar}/C_{Ar}-1], 7.22–7.16/128.6 [3-H_{Ar}/C_{Ar}-3], 7.19/105.5 [8-H_{Ar}/C_{Ar}-8], 7.04/122.2 [2-H_{Ar}/C_{Ar}-2], 6.98/117.3 [4-H_{Ar}/C_{Ar}-4], 6.67/107.9 [7-H_{Ar}/C_{Ar}-7], 5.08/68.2 [6-CH₂/C-6], 3.97/56.2 [9-OMe/C-9], 3.91/56.1 [8-OMe/C-8]; HMBC, [$\delta_{\text{H}}/\delta_{\text{C}}$]: 7.63/122.8/128.6/154.1 [1-H_{Ar}/C-1a/C_{Ar}-3/C-4a], 7.19/154.1 [3-H_{Ar}/C-4a], 7.21/124.1/149.0 [10-H_{Ar}/C-10a/C-8], 7.04/123.1/117.3 [2-H_{Ar}/C-7a/C_{Ar}-4], 6.98/122.6 [4-H_{Ar}/C_{Ar}-1], 6.68/68.5/122.9/149.3 [7-H_{Ar}/C-6/C-1a/C-9], 5.07/107.9/129.1/154.1 [6-CH₂/C_{Ar}-7/C-10a/C-4a], 3.97/149.3 [9-OMe/C-9], 3.91/149.0 [8-

$\text{CH}_3/\text{C}-8]$; HRMS (ESI+): m/z : calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3$ ($[\text{M}+\text{H}]^+$) 243.1016, found: 243.1015; calcd for $\text{C}_{15}\text{H}_{14}\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$) 265.0837, found: 265.0835.

8,9,10-Trimethoxy-6H-benzo[c]chromene (9i): Yellow pale liquid (0.42 g, 1.2 mmol, 60%); R_f [hexane-EtOAc 30:1]= 0.40; ^1H NMR (400 MHz, CDCl_3) $\delta_{(\text{ppm})}$: 8.22 (dd, $J= 7.9, 1.6$ Hz, 4-H_{Ar}), 7.09 (tdd, $J= 7.3, 1.7, 0.6$ Hz, 3-H_{Ar}), 6.95 (tdd, $J= 7.3, 1.4, 0.6$ Hz, 2-H_{Ar}), 6.90 (dd, $J= 8.0, 1.4$ Hz, 1-H_{Ar}), 6.41 (1H, s, 7-H_{Ar}), 4.83 (2H, s, 6-CH₂), 3.82 (3H, s, 10-OMe), 3.78 (3H, s, 1H, 8-OMe), 3.74 (3H, s, 9-OMe); ^{13}C NMR (101 MHz, CDCl_3) $\delta_{(\text{ppm})}$: 154.4 (4a-C), 153.0 (8-C_{Ar}), 151.6 (9-C_{Ar}), 142.7 (10-C_{Ar}), 128.9 (10a-C), 128.3 (3-C_{Ar}), 127.1(4-C_{Ar}), 122.2 (2-C_{Ar}), 121.9 (7a-C), 117.0 (1-C_{Ar}), 116.5 (1a-C), 104.3 (7-C_{Ar}), 68.8 (6-CH₂), 61.1 (10-OMe), 60.4 (8-OMe), 56.1 (9-OMe); COSY, $[\delta_{\text{H}}/\delta_{\text{H}}]$: 8.22/7.09 [4-H_{Ar}/3-H_{Ar}], 8.35/6.95 [4-H_{Ar}/2-H_{Ar}] 7.09/8.22 [3-H_{Ar}/4-H_{Ar}], 7.09/6.95 [3-H_{Ar}/2-H_{Ar}], 7.09/6.90 [3-H_{Ar}/1-H_{Ar}], 6.95/8.22 [2-H_{Ar}/4-H_{Ar}], 6.95/7.09 [2-H_{Ar}/3-H_{Ar}], 6.90/7.09 [1-H_{Ar}/2-H_{Ar}], 6.41/4.83 [7-H_{Ar}/6-CH₂], 6.41/3.78 [7-H_{Ar}/8-OMe], 4.83/6.41 [6-CH₂/7-H_{Ar}], 3.78/6.41 [8-OMe/7-H_{Ar}]; HSQC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 8.22/127.1 [4-H_{Ar}/C_{Ar}-4], 7.09/128.3 [3-H_{Ar}/C_{Ar}-3], 6.95/122.2 [2-H_{Ar}/C_{Ar}-2], 6.90/117.0 [1-H_{Ar}/C_{Ar}-1], 6.41/104.3 [7-H_{Ar}/C_{Ar}-7], 4.83/68.8 [6-CH₂/C-6], 3.82/61.1 [10-OMe/C-], 3.78/60.4 [8-OMe/C-8], 3.74/56.1 [9-OMe/C-9]; HMBC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 8.22/116.5/128.3/154.4 [4-H_{Ar}/C-1a/C_{Ar}-3/C-4a], 7.09/117.0/127.1/154.4 [3-H_{Ar}/C_{Ar}-1/C_{Ar}-4/C-4a], 6.95/117.0/122.2/127.1 [2-H_{Ar}/C_{Ar}-1/C_{Ar}-2/C_{Ar}-4], 6.90/122.2/128.3/154.4 [1-H_{Ar}/C_{Ar}-2/C_{Ar}-3/C_{Ar}-4a], 6.41/68.8/116.5/142.7/151.6/153.0 [7-H_{Ar}/C-6/C-1a/C_{Ar}-10/C_{Ar}-9/C_{Ar}-8], 4.83/104.3/116.5/128.9/142.7/151.6/153.0/154.4 [6-CH₂/C_{Ar}-7/C-1a/C-10a/C_{Ar}-10/C_{Ar}-9/C_{Ar}-8/C-4a], 3.82/151.6 [10-OMe/C_{Ar}-10], 3.78/152.9 [8-OMe/C_A-8], 3.74/142.7 [9-OMe/C_{Ar}-9]; HRMS (ESI+): m/z : calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$ ($[\text{M}+\text{H}]^+$) 273.1121, found: 273.1119; calcd for ($[\text{M}+\text{Na}]^+$) 295.0940, found: 295.0939.

2-Allyl-4-methoxy-6H-benzo[c]chromene (9j): Colorless oil (0.30 g, 1.2 mmol, 60%); R_f [hexane-EtOAc 30:1]= 0.40; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3001 $\nu_{(=\text{CHAR})}$, 2906 $\nu_{(\text{OCH}_3)}$, 1573 $\nu_{(\text{CAr=CAr})}$, 1438 $\nu_{(\text{CH}_3)}$, 1280 $\nu_{(\text{C-O-C})}$; ^1H NMR (400 MHz, CDCl_3) $\delta_{(\text{ppm})}$: 7.68 (1H, d, $J= 7.4$ Hz, 10-H_{Ar}), 7.35 (1H, dd, $J= 7.5, 1.2$ Hz, 9-H_{Ar}), 7.29 (1H, dd, $J= 7.4, 1.1$ Hz, 8-H_{Ar}), 7.18 (1H, d, $J= 1.7$ Hz, 1-H_{Ar}), 7.16 (1H, d, $J= 7.5$ Hz, 7-H_{Ar}), 6.71 (1H, d, $J= 1.8$ Hz, 3-H_{Ar}), 6.01 (1H, ddt, $J= 16.8, 10.1, 6.7$ Hz, 12=CH), 5.16 (2H, s, 6-CH₂), 5.18-5.11 (2H, m, 13=CH₂), 3.91 (3H s, 4-OMe), 3.40 (2H, d, $J= 6.7$ Hz, 11-CH₂); ^{13}C NMR (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 148.9 (4-C), 142.2 (4a-C), 137.6 (12=CH), 133.5 (2-C), 131.5 (10a-C), 128.4 (9-C_{Ar}), 127.8 (8-C), 124.7 (7-C_{Ar}), 123.5 (1a-C) 122.4 (10-C_{Ar}), 116.0 (13=CH₂), 115.2 (1-C_{Ar}), 113.3 (7a-C), 112.1 (3-C_{Ar}), 68.9 (6-CH₂), 56.1 (4-OMe), 40.3 (11-CH₂); COSY, $[\delta_{\text{H}}/\delta_{\text{H}}]$: 7.68/7.35 [10-H_{Ar}/9-H_{Ar}], 7.35/7.29 [9-H_{Ar}/8-H_{Ar}], 7.29/7.16 [8-H_{Ar}/7-H_{Ar}], 7.18/6.71 [1-H_{Ar}/3-H_{Ar}], 7.16/5.16 [7-H_{Ar}/6-CH₂], 6.71/3.91 [3-H_{Ar}/4-OMe], 6.01/5.18-5.11 [12=CH/13=CH₂], 6.01/3.40 [12-CH/11-CH₂] 5.18-5.11/3.40 [13=CH₂/11-CH₂]; HSQC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 7.63/122.4

[10-H_{Ar}/C_{Ar}-10], 7.35/128.4 [9-H_{Ar}/C_{Ar}-9], 7.29/127.8 [8-H_{Ar}/C_{Ar}-8], 7.18/115.2 [6-H_{Ar}/C_{Ar}-7], 7.16/124.7 [7-H_{Ar}/C_{Ar}-7], 6.71/112.1 [3-H_{Ar}/C_{Ar}-3], 6.01/137.6 [12=CH/C=H-12], 5.18-5.11/116.0 [13=CH₂/C=H₂-13], 5.16/68.9 [6-CH₂/C-6], 3.91/56.16 [4-OMe/4-OMe], 3.40/40.3 [11-CH₂/C-11]; HMBC, $[\delta_H/\delta_C]$: 7.68/123.5/127.8/131.5 [10-H_{Ar}/C-1a/C_{Ar}-8/C-10a], 7.35/124.7 [9-H_{Ar}/C-7], 7.30/122.4/131.5 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.18/40.3/112.1/142.2 [1-H_{Ar}/CH₂=11/C_{Ar}-3/C-4a], 6.71/40.3/115.2/142.2/148.9 [3-H_{Ar}/C_{Ar}-1/C-4a/C-4], 4.95/122.2/125.0/130.8/134.4/154.1 [6-CH₂/C-1a/C-7/C-10a/C-4a], 5.16/124.7/142.2 [6-CH₂/C_{Ar}-7/C-4a], 3.91/148.9 [4-OMe/C-4], 3.40/112.1/133.5/137.6 [11-CH₂/C_{Ar}-3/C-2/C=H₂-12]; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₇O₂ ([M+H]⁺) 253.1223, found: 253.1221; calcd for C₁₇H₁₆NaO₂ ([M+Na]⁺) 275.104250, found: 275.1041.

2-Allyl-4-methoxy-6H-benzo[c]chromene (9j'): Colorless oil (0.35 g, 1.38 mmol, 69%); *R_f* [hexane-EtOAc 30:1]= 0.40; it was prepared according to general procedure from **8j'** (0.66 g, 0.2 mmol); spectral data were identical to **9j**.

(E)-4-Methoxy-2-(prop-1-en-1-il)-6H-benzo[c]chromene (9k): Colorless oil (0.30 g, 1.2 mmol, 61 %); *R_f* [hexane-EtOAc 30:1]= 0.40; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3018 $\nu_{(=\text{CHAr})}$, 2960 $\nu_{(\text{OCH}_3)}$, 1591 $\nu_{(\text{CAr}=\text{CAr})}$, 1438 $\nu_{(\text{CH}_3)}$, 1143 $\nu_{(\text{C-O-C})}$; ¹H NMR (400 MHz, CDCl₃) $\delta_{(\text{ppm})}$: 7.68 (1H, d, *J*= 7.2 Hz, 10-H_{Ar}), 7.36 (1H, td, *J*= 7.6, 1.3 Hz, 9-H_{Ar}), 7.29 (1H, d, *J*= 1.7 Hz, 1-H_{Ar}), 7.27 (1H, dd, *J*= 7.4, 1.0 Hz, 8-H_{Ar}), 7.15 (1H, d, *J*= 7.4 Hz, 7-H_{Ar}), 6.88 (1H, d, *J*= 1.8 Hz, 3-H_{Ar}), 6.41 (1H, dd, *J*= 15.7, 1.8 Hz, 11=CH), 6.19 (1H, dq, *J*= 15.7, 6.6 Hz, 12=CH), 5.17 (2H, s, 6-CH₂), 3.92 (3H, s, 4-OMe), 1.91 (3H, dd, *J*= 6.6, 1.6 Hz, 13-CH₃); ¹³C NMR (101 MHz, CDCl₃), $\delta_{(\text{ppm})}$: 148.9 (4-C), 142.9 (4a-C), 131.7 (2-C), 131.2 (1a-C), 130.7 (11=CH), 129.9 (7a-C), 128.4 (9-C_{Ar}), 127.7 (8-C_{Ar}), 124.6 (12=CH), 124.4 (7-C_{Ar}), 123.3 (10a-C), 122.2 (10-C_{Ar}), 113.2 (1-C_{Ar}), 108.6 (3-C_{Ar}), 68.8 (6-CH₂), 55.9 (4-OMe), 18.4 (13-CH₃); COSY, $[\delta_H/\delta_H]$: 7.68/7.36 [10-H_{Ar}/9-H_{Ar}], 7.36/7.27 [9-H_{Ar}/8-H_{Ar}], 7.29/6.88 [1-H_{Ar}/3-H_{Ar}], 7.27/7.15 [8-H_{Ar}/7-H_{Ar}], 7.15/5.17 [7-H_{Ar}/6-CH₂], 6.88/3.92 [3-H_{Ar}/4-OMe], 6.41/1.91 [11=CH/13-CH₃]; HSQC, $[\delta_H/\delta_C]$: 7.68/122.2 [10-H_{Ar}/C_{Ar}-10], 7.37/128.4 [9-H_{Ar}/C_{Ar}-9], 7.29/113.2 [1-H_{Ar}/C_{Ar}-1], 7.27/127.7 [8-H_{Ar}/C_{Ar}-8], 7.15/124.4 [7-H_{Ar}/C_{Ar}-7], 6.88/108.6 [3-H_{Ar}/C_{Ar}-3], 6.41/130.7 [11=CH/C-11], 6.19/124.6 [12=CH/C-12], 5.17/68.83 [6-CH₂/C-6], 3.92/55.9 [4-OMe/4-OMe], 1.91/18.4 [13-CH₃/C-13]; HMBC, $[\delta_H/\delta_C]$: 7.68/123.3/127.7 [10-H_{Ar}/C-10a/C_{Ar}-8], 7.36/124.4/129.9 [9-H_{Ar}/C_{Ar}-7/C-7a], 7.29/108.6/131.2/142.9/148.7 [1-H_{Ar}/C_{Ar}-3/C-2/C-4a/C-4], 7.27/122.2 [8-H_{Ar}/C_{Ar}-10], 7.15/68.8/129.9 [7-H_{Ar}/C-6/C-7a], 6.88/113.2/130.7/142.9/148.9 [3-H_{Ar}/C-1/C-11/C-4a/C-4], 6.41/108.6/113.2/124.6 [11=CH/C_{Ar}-3/C_{Ar}-1/C-12], 5.17/124.4/131.2/142.9 [6-CH₂/C_{Ar}-7/C-1a/C-4a], 3.92/148.9 [4-OMe/C-4], 1.91/124.6/130.7 [13-CH₃/C-12/C-11]; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₇O₂ ([M+H]⁺) 253.1223, found: 253.1222; calcd for C₁₇H₁₆NaO₂ ([M+Na]⁺) 275.1042, found: 275.1041.

6H-Benzo[c]chromeno-4-carbaldehyde (9l): White solid (0.25 g, 1.2 mmol, 60 %); R_f [hexane-EtOAc 30:1]= 0.83; m.p.= 50-53 °C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3068 $\nu_{(\text{=CHAr})}$, 1678 $\nu_{(\text{C=O})}$, 1597 $\nu_{(\text{CAr=CAr})}$, 1238 $\nu_{(\text{C-O})}$; ^1H NMR (400 MHz, CDCl₃) δ (ppm): 10.50 (1H, s, 4-CHO), 7.94 (1H, dd, J = 7.7, 1.7 Hz, 1-H_{Ar}), 7.78 (1H, dd, J = 7.8, 1.7 Hz, 3-H_{Ar}), 7.69 (1H, d, J = 7.7 Hz, 10-H_{Ar}), 7.41 (1H, td, J = 7.6, 1.2 Hz, 9-H_{Ar}), 7.34 (1H, td, J = 7.5, 1.2 Hz, 8-H_{Ar}), 7.19 (1H, dd, J = 7.5, 0.8 Hz, 7-H_{Ar}), 7.12 (1H, td, J = 7.7, 0.6 Hz, 2-H_{Ar}), 5.24 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, CDCl₃), δ (ppm): 189.5 (4-CHO), 157.5 (4a-C), 130.7 (7a-C), 129.2 (1-CAr), 128.9 (9-CAr), 128.8 (1a-C), 128.5 (8-CAr), 127.9 (3-CAr), 125.3 (4-C), 124.8 (7-CAr), 124.1 (10a-C), 122.2 (10-CAr), 121.9 (2-CAr), 68.7 (6-CH₂); COSY, $[\delta_{\text{H}}/\delta_{\text{H}}]$: 7.94/7.78 [1-H_{Ar}/3-H_{Ar}] 7.94/7.12 [1-H_{Ar}/2-H_{Ar}], 7.78/7.12 [3-H_{Ar}/2-H_{Ar}], 7.69/7.41 [10-H_{Ar}/9-H_{Ar}] 7.34/7.19 [8-H_{Ar}/7-H_{Ar}], 7.19/5.24 [7-H_{Ar}/6-CH₂]; HSQC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 10.50/189.5 [4-CHO/C-HO-4], 7.94/129.2 [1-H_{Ar}/CAr-1], 7.78/127.9 [3-H_{Ar}/CAr-3], 7.69/122.2 [10-H_{Ar}/CAr-10], 7.41/128.9 [9-H_{Ar}/CAr-9], 7.34/128.4 [8-H_{Ar}/CAr-8], 7.19/124.8 [7-H_{Ar}/CAr-7], 7.12/121.9 [2-H_{Ar}/CAr-2], 5.24/68.7 [6-CH₂/C-6]; HMBC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 10.50/125.3/127.9 [4-CHO/C-4/CAr-3], 7.94/127.9/157.5 [1-H_{Ar}/CAr-3/C-4a], 7.78/129.2/157.5/189.4 [3-H_{Ar}/CAr-1/C-4a/CHO-4], 7.69/124.1/129.2 [10-H_{Ar}/C-10a/CAr-1], 7.41/124.8/128.8 [9-H_{Ar}/CAr-7/C-1a], 7.34/122.2/130.7 [8-H_{Ar}/CAr-10/C-7a], 7.19/68.7/128.8/128.9 [7-H_{Ar}/C-6/C-1a/CAr-9], 7.12/125.3 [2-H_{Ar}/C-4], 5.24/124.8/129.2/130.7/157.3 [6-CH₂/CAr-7/CAr-1/C-7a/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₁O₂ ([M+H]⁺) 211.0753, found: 211.0752; calcd for C₁₄H₁₀NaO₂ ([M+Na]⁺) 233.0573, found: 233.0572.

6H-Benzo[c]chromene-2-carbaldehyde (9m): White solid (0.32 g, 1.54 mmol; 77 %); R_f [hexane-EtOAc 30:1]= 0.57; m.p.= 60-62 °C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3059 $\nu_{(\text{=CHAr})}$, 1693 $\nu_{(\text{C=O})}$, 1600 $\nu_{(\text{CAr=CAr})}$, 1249 $\nu_{(\text{C-O})}$; ^1H NMR (400 MHz, CDCl₃) δ (ppm): 9.94 (1H, s, 2-CHO), 8.25 (1H, d, J = 2.0 Hz, 1-H_{Ar}), 7.77 (1H, d, J = 7.8 Hz, 10-H_{Ar}), 7.74 (1H, dd, J = 8.4, 2.0 Hz, 3-H_{Ar}), 7.40 (1H, td, J = 7.6, 1.2 Hz, 9-H_{Ar}), 7.33 (1H, td, J = 7.5, 1.2 Hz, 8-H_{Ar}), 7.15 (1H, d, J = 7.5 Hz, 7-H_{Ar}), 7.07 (1H, d, J = 8.3 Hz, 4-H_{Ar}), 5.20 (2H, s, 6-CH₂); ^{13}C NMR (101 MHz, CDCl₃), δ (ppm): 191.0 (2-CHO), 159.9 (2-C), 131.6 (3-CAr), 131.1 (4a-C), 130.6 (10a-C), 128.9 (9-CAr), 128.7 (7a-C), 128.6 (8-CAr), 125.1 (1-CAr), 124.8 (7-CAr), 123.2 (1a-C), 122.3 (10-CAr), 118.2 (4-CAr), 68.7 (6-CH₂); COSY, $[\delta_{\text{H}}/\delta_{\text{H}}]$: 9.94/8.25 [2-CHO/1-H_{Ar}] 8.25/7.74 [1-H_{Ar}/3-H_{Ar}], 7.77/7.40 [10-H_{Ar}/9-H_{Ar}], 7.74/7.07 [3-H_{Ar}/4-H_{Ar}] 7.33/7.15 [8-H_{Ar}/7-H_{Ar}], 7.15/5.20 [7-H_{Ar}/6-CH₂]; HSQC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 9.94/191.0 [2-CHO/C-HO-2], 8.25/125.1 [1-H_{Ar}/CAr-1], 7.77/122.3 [10-H_{Ar}/CAr-10], 7.74/131.6 [3-H_{Ar}/CAr-3], 7.40/128.9 [9-H_{Ar}/CAr-9], 7.33/128.6 [8-H_{Ar}/CAr-8], 7.15/124.8 [7-H_{Ar}/CAr-7], 7.07/118.2 [4-H_{Ar}/CAr-4], 5.20/68.7 [6-CH₂/C-6]; HMBC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 9.94/125.1/131.1 [2-CHO/CAr-1/C-4a], 8.25/128.7/131.6 /159.9/190.0 [1-H_{Ar}/C-7a/CAr-3/C-2/CHO-2], 7.77/125.1/159.9/190.9 [10-H_{Ar}/CAr-1/C-2/CHO-2], 7.74/123.2/128.6/130.6 [3-H_{Ar}/C-1a/CAr-8/C-10a],

7.40/124.8/125.1/128.6/128.7 [9-H_{Ar}/C_{Ar}-7/C_{Ar}-1/C_{Ar}-8/C-7a], 7.33/122.3/130.6 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.15/68.7/128.6 /128.7/128.9 [7-H_{Ar}/C-6/C_{Ar}-8/C-7a/C_{Ar}-9], 7.07/123.2/131.1/159.9 [4-H_{Ar}/C-1a/C-4a/C-2], 5.20/124.8/128.7/130.6/131.1 [6-CH₂/C_{Ar}-7/C-7a/C-10a/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₁O₂ ([M+H]⁺) 211.0753, found: 211.0752; calcd for C₁₄H₁₀NaO₂ ([M+Na]⁺) 233.0573, found: 233.0572.

4-Methoxy-6H-benzo[c]chromene-2-carbaldehyde (9n): White solid (0.36 g, 1.5 mmol, 75 %); *R_f* [hexane-EtOAc 30:1]= 0.20; m.p.= 89-92 °C; IR (KBr, ν_{máx}/cm⁻¹): 3007 ν(=CH_{Ar}), 2983 ν(OCH₃), 2848 ν(CH₂), 1680 ν(C=O), 1589 ν(C_{Ar}=C_{Ar}), 1388 ν(CH₃), 1139 ν(C-O-C); ¹H NMR (400 MHz, CDCl₃) δ_(ppm): 9.90 (1H, s, 2-CHO), 7.83 (1H, d, *J*= 1.6 Hz, 1-H_{Ar}), 7.71 (1H, d, *J*= 7.7 Hz, 10-H_{Ar}), 7.39 (1H, td, *J*= 7.7, 1.5 Hz, 9-H_{Ar}) 7.35 (1H, d, *J*= 1.6 Hz, 3-H_{Ar}), 7.32 (1H, td, *J*= 7.5, 1.2 Hz, 8-H_{Ar}), 7.15 (1H, d, *J*= 7.5 Hz, 7-H_{Ar}), 5.25 (2H, s, 6-CH₂), 3.94 (3H, s, 4-OCH₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 191.0 (2-CHO), 149.7 (4-C), 149.2 (7a-C), 130.5 (1a-C), 130.3 (2-C), 128.8(4a-C), 128.6 (8 and 9-C_{Ar}), 124.8 (7-C_{Ar}), 123.4 (10a-C), 122.4 (10-C_{Ar}), 120.2 (1-C_{Ar}), 109.6 (3-C_{Ar}), 69.0 (6-CH₂), 56.2 (4-OMe); COSY, [δ_H/δ_H]: 9.90/7.83 [2-CHO/1-H_{Ar}], 7.71/7.39 [10-H_{Ar}/9-H_{Ar}], 7.35/3.94 [3-H_{Ar}/4-OMe], 7.32/7.15 [8-H_{Ar}/7-H_{Ar}], 7.15/5.25 [7-H_{Ar}/6-CH₂], 7.15/5.17 [7-H_{Ar}/6-CH₂]; HSQC, [δ_H/δ_C]: 9.90/191.0 [2-CHO/C-HO-2], 7.83/120.2 [1-H_{Ar}/C_{Ar}-1], 7.71/122.4 [10-H_{Ar}/C_{Ar}-10], 7.39/128.6 [9-H_{Ar}/C_{Ar}-9], 7.35/109.6 [3-H_{Ar}/C_{Ar}-3], 7.32/128.6 [8-H_{Ar}/C_{Ar}-8], 7.15/124.8 [7-H_{Ar}/C_{Ar}-7], 5.25/69.0 [6-CH₂/C-6], 3.94/56.2 [4-OMe/4-OMe]; HMBC, [δ_H/δ_C]: 9.90/109.6/130.3/130.5 [2-CHO/C_{Ar}-3/C-2/C-1a], 7.83/109.6/128.8/149.1/191.0 [1-H_{Ar}/C_{Ar}-3/C-4a/C-7a/CHO-2], 7.71/123.4/128.8/130.3 [10-H_{Ar}/C-10a/C-4a/C_{Ar}-2], 7.39/124.8/128.8 [9-H_{Ar}/C_{Ar}-7/C-4a], 7.35/120.2/149.1/191.0 [3-H_{Ar}/C_{Ar}-1/C-7a/C-HO-2], 7.32/122.4 [8-H_{Ar}/C_{Ar}-10], 7.15/69.0/109.6/128.8 [7-H_{Ar}/C-6/C_{Ar}-3/C-4a], 5.25/124.8/130.3/130.5 [6-CH₂/C_{Ar}-7/C_{Ar}-2/C-1a], 3.94/149.7 [4-OMe/C-4]; HRMS (ESI+): *m/z*: calcd for C₁₅H₁₃O₃ ([M+H]⁺) 241.0859, found: 241.0858; calcd for C₁₅H₁₂NaO₃ ([M+Na]⁺) 263.0678, found: 263.0677.

4-Methoxy-6H-benzo[c]chromene-1-carbaldehyde (9o): White solid (0.31 g, 1.3 mmol, 65 %); *R_f* [hexane-EtOAc 30:1]= 0.40; m.p.= 108-113°C; IR (KBr, ν_{máx}/cm⁻¹): 3089 ν(=CH_{Ar}), 2974 ν(OCH₃), 2841 ν(CH₂), 1666 ν(C=O), 1587 ν(C_{Ar}=C_{Ar}), 1435 ν(CH₃), 1298 ν(C-O-C); ¹H NMR (400 MHz, CDCl₃) δ_(ppm): 10.24 (1H, s, 1-CHO), 7.71 (1H, d, *J*= 8.6 Hz, 2-H_{Ar}), 7.41 (2H, ddd, *J*= 6.6, 4.9, 1.5 Hz, 10- and 9-H_{Ar}), 7.31 (1H, dd, *J*= 4.8 Hz, 8-H_{Ar}), 7.31 (1H, d, *J*= 8.9 Hz, 7-H_{Ar}), 6.97 (1H, *J*= 8.6 Hz, 3-H_{Ar}) 5.11 (2H, s, 6-CH₂), 3.97 (3H, s, 4-OCH₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 190.7 (1-CHO), 153.2 (4-C), 145.1 (7a-C), 133.2 (10a-C), 129.1 (8-C_{Ar}), 128.7 (10-C_{Ar}), 128.5 (9-C_{Ar}), 127.4 (1a-C), 126.9 (1-C), 126.4 (4a-C), 125.4 (7-C_{Ar}), 124.1 (2-C_{Ar}), 110.7 (3-C_{Ar}), 69.5 (6-CH₂), 56.3 (4-OMe); COSY, [δ_H/δ_H]: 7.71/6.97 [2-H_{Ar}/3-H_{Ar}], 7.31/5.10 [7-H_{Ar}/6-CH₂], 7.41/7.31 [8-H_{Ar}/9-H_{Ar}], 6.97/3.97 [3-H_{Ar}/4-OMe];

HSQC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 10.24/190.7 [1-CHO/C-HO-1], 7.71/124.1 [2-H_{Ar}/C_{Ar}-2], 7.41/128.5/128.7 [9-10-H_{Ar}/C_{Ar}-9/C_{Ar}-10], 7.31/129.1 [8-H_{Ar}/C_{Ar}-8], 7.31/125.4 [7-H_{Ar}/C_{Ar}-7], 6.97/110.7 [3-H_{Ar}/C_{Ar}-3], 5.11/69.5 [6-CH₂/C-6], 3.97/56.3 [4-OMe/4-OMe]; HMBC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 10.24/124.1/126.4/126.9 [1-CHO/C_{Ar}-2/C-4a/C-1], 7.71/110.7/126.9/153.2/190.7 [2-H_{Ar}/C_{Ar}-3/C-1/C-4/CHO-1], 7.41/126.4/126.9/133.2 [10- and 9-H_{Ar}/C-4a/C-1/C-10a], 7.31/128.7/133.2 [8-H_{Ar}/C_{Ar}-10/C-10a], 7.31/69.5 [7-H_{Ar}/C-6], 6.97/126.4/145.1/153.2 [3-H_{Ar}/C-4a/C-7a/C-4], 5.11/125.5/126.4/133.2/145.1 [6-CH₂/C_{Ar}-7/C-10a/C-7a], 3.97/153.2 [4-OMe/C-4]; HRMS (ESI+): *m/z*: calcd for C₁₅H₁₃O₃ ([M+H]⁺) 241.0859, found: 241.0858; calcd for C₁₅H₁₂NaO₃ ([M+Na]⁺) 263.0678, found: 263.0677.

2-Allyl-4,8,9,10-tetramethoxy-6H-benzo[c]chromene (9p): White solid (0.52, 1.52 mmol, 76%); *R_f* [hexane-EtOAc 30:1]= 0.53; m.p.= 175-177°C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.94 (1H, d, *J*= 1.9 Hz, 1-H_{Ar}), 6.85 (1H, d, *J*= 1.7 Hz, 3-H_{Ar}), 6.52 (1H, s, 7-H_{Ar}), 6.17 (1H, dq, *J*= 15.6, 6.6 Hz, 12=CH), 5.15–5.06 (2H, m, 13=CH₂), 4.98 (2H, s, 6-CH₂), 3.87 (6H, s, 10- and 4-OMe), 3.82 (3H, s, 8-OMe), 3.80 (3H, s, 9-OMe), 3.38 (2H, d, *J*= 6.7 Hz, 11-CH₂); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 153.0, 151.6, 148.6, 142.7, 137.8, 131.6, 131.2, 124.0, 119.1, 117.2, 115.6, 107.9, 104.3, 69.2, 61.1, 60.5, 56.0 (3), 40.4; HRMS (ESI+): *m/z*: calcd for C₂₀H₂₃O₅ ([M+H]⁺) 343.1540, found: 343.1538; calcd for C₂₀H₂₂NaO₅ ([M+Na]⁺) 365.1359, found: 365.1357.

2-Allyl-4,8,9,10-tetramethoxy-6H-benzo[c]chromene (9p'): White solid (0.53, 1.54 mmol, 77%); *R_f* [hexane-EtOAc 30:1]= 0.53; m.p.= 175-177°C; it was prepared according to general procedure from **8p'** (0.86 g, 2 mmol); spectral data were identical to **9p**.

(E)-4,8,9,10-tetramethoxy-2-(prop-1-en-1-yl)-6H-benzo[c]chromene (9q): White solid (0.61 g, 1.8 mmol, 90%); *R_f* [hexane-EtOAc 30:1]= 0.54; m.p.= 170-175°C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.93 (1H, d, *J*= 1.6 Hz, 3-H_{Ar}), 6.84 (1H, d, *J*= 1.6 Hz, 1-H_{Ar}), 6.51 (1H, s, 7-H_{Ar}), 6.41–6.35 (1H, m, 12=CH), 6.16 (1H, dq, *J*= 15.7, 6.5 Hz, 11=CH), 4.97 (2H, s, 6-CH₂), 3.90 (3H, s, 10-OMe), 3.89 (3H, s, 8-OMe), 3.85 (3H, s, 9-OMe), 3.81 (3H, s, 4-OMe), 1.87 (3H, dd, *J*= 6.6, 1.3 Hz, 13-CH₃); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 152.9, 151.5, 148.5, 142.7, 131.5, 131.2, 128.8, 123.9, 122.4, 117.1, 116.3, 107.9, 104.2, 69.1, 61.0, 60.4, 56.0 (2), 55.9 (2), 18.4; HRMS (ESI+): *m/z*: calcd for C₂₀H₂₃O₅ ([M+H]⁺) 343.1540, found: 343.1538; calcd for C₂₀H₂₂NaO₅ ([M+Na]⁺) 365.1359, found: 365.1357.

6H-Dibenzo[c,h]chromene (9r): Pale yellow solid (0.43 g, 1.86 mmol, 93 %); *R_f* [hexane-EtOAc 30:1]= 0.53; m.p.= 83-85 °C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3051 $\nu_{(\text{C}-\text{H})}$, 2850 $\nu_{(\text{CH}_2)}$, 1583 $\nu_{(\text{C}\equiv\text{C}-)}$, 1257 $\nu_{(\text{C}-\text{O}-\text{C})}$; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.35–8.27 (1H, m, 1'-H_{Ar}), 7.86 (1H, d, *J*= 8.6 Hz, 2-H_{Ar}), 7.84 (1H, m, 3'-H_{Ar}), 7.76 (1H, d, *J*= 7.7 Hz, 10-H_{Ar}), 7.56 (1H, d, *J*= 8.6 Hz, 1-H_{Ar}), 7.56–7.48 (2H, m, 2'- and 4'-H_{Ar}), 7.44 (1H, td, *J*= 7.6, 1.4 Hz, 9-H_{Ar}),

7.32 (1H, td, $J=7.4$, 1.1 Hz, 8-H_{Ar}), 7.23 (1H, d, $J=7.5$ Hz, 7-H_{Ar}), 5.34 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_{ppm} : 150.4 (4a-C), 134.4 (4-C), 130.8 (3-C_{Ar}), 130.7 (10a-C), 128.6 (9-C_{Ar}), 127.7 (2'-C_{Ar}), 127.4 (8-C_{Ar}), 126.7 (4'-C_{Ar}), 125.9 (3'-C_{Ar}), 125.4 (1a-C), 124.7 (7-C_{Ar}), 122.3 (1'-C_{Ar}), 122.0 (10-C_{Ar}), 121.6 (1-C_{Ar}), 121.0 (2-C_{Ar}), 117.2 (7a-C), 69.0 (6-CH₂); COSY, [δ_H/δ_H]: 8.83/7.84/7.56-7.48 [1'-H_{Ar}/3'-H_{Ar}/2-H_{Ar}] 7.87/7.56 [2-H_{Ar}/1-H_{Ar}], 7.84/7.56-7.48 [3'-H_{Ar}/4'- and 2'-H_{Ar}], 7.76/7.43 [10-H_{Ar}/9-H_{Ar}] 7.32/7.23 [8-H_{Ar}/7-H_{Ar}], 7.23/5.34 [7-H_{Ar}/6-CH₂]; HSQC, [δ_H/δ_C]: 8.31/122.3 [1'-H_{Ar}/C_{Ar}-1'], 7.86/121.0 [2-H_{Ar}/C_{Ar}-2], 7.84/127.7 [3'-H_{Ar}/C_{Ar}-3'], 7.76/122.0 [10-H_{Ar}/C_{Ar}-10], 7.56/121.6 [1-H_{Ar}/C_{Ar}-1], 7.53-7.48/125.9/126.7 [2' and 4'-H_{Ar}/C_{Ar}-2'/C_{Ar}-4'], 7.43/128.6 [9-H_{Ar}/C_{Ar}-9], 7.32/127.4 [8-H_{Ar}/C_{Ar}-8], 7.23/124.7 [7-H_{Ar}/C_{Ar}-7], 5.34/69.0 [6-CH₂/C-6]; HMBC, [δ_H/δ_C]: 8.31/126.7/134.4 [1'-H_{Ar}/C_{Ar}-4'/C-4], 7.87/121.6/130.8/134.4 [2-H_{Ar}/C_{Ar}-1/C-3/C-4], 7.84/125.9 [3'-H_{Ar}/C_{Ar}-2'], 7.76/117.2/127.4/130.7 [10-H_{Ar}/C-7a/C_{Ar}-8/C-10a], 7.53-7.48/122.3/127.7 [4' and 2'-H_{Ar}/C_{Ar}-1'/C_{Ar}-3'], 7.43/122.0/124.7/130.7 [9-H_{Ar}/C_{Ar}-10/C_{Ar}-7/C-10a], 7.32/122.0/130.7 [8-H_{Ar}/C_{Ar}-10/C-10a] 7.23/69.0/117.2/128.6/130.7 [7-H_{Ar}/C-6/C-7a/C_{Ar}-9/C-10a], 5.34/117.2/124.7/150.4 [6-CH₂/C-7a/C_{Ar}-7/C-1a/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₃O ([M+H]⁺) 233.0960, found: 233.0959; calcd for C₁₇H₁₂NaO ([M+Na]⁺) 255.0780, found: 255.0779.

6*H*,11*H*-Isochromeno[4,3-*c*]chromen-11-one (9s): White solid (0.49 g, 1.96 mmol, 98 %); R_f [hexane-EtOAc 30:1]= 0.20; m.p.= 136-137 °C; IR (KBr, ν_{máx}/cm⁻¹): 2916 ν(_{=CH_{Ar}}), 2848 ν(CH₂), 1699 ν(C=O), 1608 ν(C_{Ar}=C_{Ar}), 1282 ν(C-O-C); ¹H NMR (400 MHz, CDCl₃) δ_(ppm): 8.53 (1H, d, $J=8.6$ Hz, 10-H_{Ar}), 7.83 (1H, dd, $J=7.9$, 1.5 Hz, 1-H_{Ar}), 7.54 (1H, ddd, $J=8.8$, 7.3, 1.6 Hz, 3-H_{Ar}), 7.39 (1H, td, $J=7.9$, 1.3 Hz, 9-H_{Ar}), 7.35-7.23 (3H, m, 2-,4-, and 8-H_{Ar}), 7.10 (1H, d, $J=7.4$ Hz, 7-H_{Ar}), 5.37 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_{ppm} : 161.2 (11-C=O), 160.2 (5a-C), 152.8 (12a-C), 132.5 (3-C_{Ar}), 129.0 (9-C_{Ar}), 128.2 (4-C_{Ar}), 127.4 (4a-C), 126.6 (10a-C), 124.8 (10-C_{Ar}), 124.1 (7-C_{Ar}), 124.0 (8-C_{Ar}), 123.1 (1-C_{Ar}), 116.5 (2-C_{Ar}), 115.2 (11a-C), 102.6 (7a-C), 69.7 (6-CH₂); COSY, [δ_H/δ_H]: 8.53/7.39 [10-H_{Ar}/9-H_{Ar}] 7.83/7.35-7.23 [1-H_{Ar}/2-H_{Ar}], 7.54/7.35-7.23 [3-H_{Ar}/2-H_{Ar}], 7.35-7.23/7.10 [8-H_{Ar}/7-H_{Ar}] 7.10/5.37 [7-H_{Ar}/6-CH₂]; HSQC, [δ_H/δ_C]: 8.53/124.8 [10-H_{Ar}/C_{Ar}-10], 7.83/123.1 [1-H_{Ar}/C_{Ar}-1], 7.54/132.5 [3-H_{Ar}/C_{Ar}-3], 7.39/129.0 [9-H_{Ar}/C_{Ar}-9], 7.35-7.23/116.5 [2-H_{Ar}/C_{Ar}-2], 7.35-7.23/124.0 [8-H_{Ar}/C_{Ar}-8], 7.35-7.23/128.2 [4-H_{Ar}/C_{Ar}-4], 7.10/124.1 [7-H_{Ar}/C_{Ar}-7], 5.37/69.7 [6-CH₂/C-6]; HMBC, [δ_H/δ_C]: 8.53/102.6/126.6/129.0 [10-H_{Ar}/C-7a/C-10a/C_{Ar}-9], 7.83/116.5/132.5/161.2 [1-H_{Ar}/C_{Ar}-2/C_{Ar}-3/C-5a], 7.54/116.5/123.1/152.8 [3-H_{Ar}/C_{Ar}-2/C-12a], 7.39/124.0/124.1/126.6 [9-H_{Ar}/C_{Ar}-8/C_{Ar}-7/C-10a], 7.35-7.23/115.2 /124.1/124.8/127.4/161.2 [2-, 4- and 8-H_{Ar}/C_{Ar}-2/C_{Ar}-7/C_{Ar}-10/C-4a/C-5a], 7.10/69.7/102.6/126.6/127.4 [7-H_{Ar}/C-6/C-7a/C-10a/C-4a], 5.37/102.6/124.1/161.2 [6-

$\text{CH}_2/\text{C-7a/C}_{\text{Ar}}\text{-7/C-5a}]; \text{HRMS (ESI+): } m/z: \text{calcd for C}_{16}\text{H}_{11}\text{O}_3 ([\text{M}+\text{H}]^+) 251.0702, \text{found: } 251.0701; \text{calcd for C}_{16}\text{H}_{10}\text{NaO}_3 ([\text{M}+\text{Na}]^+) 273.0522, \text{found: } 273.0520.$

12-Chloro-6H-isochromeno[4,3-h]quinoline (9v): Pale yellow solid (0.52 g, 1.96 mmol, 98 %); R_f [hexane-EtOAc 30:1]= 0.17; m.p.= 172-175 °C; IR (KBr, $\nu_{\text{máx}}/\text{cm}^{-1}$): 3057 $\nu_{(\text{=CH}_{\text{Ar}})}$, 2850 $\nu_{(\text{CH}_2)}$, 1587 $\nu_{(\text{CAr=CAr})}$, 1288 $\nu_{(\text{C-O-C})}$, 761 $\nu_{(\text{C-Cl})}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta_{(\text{ppm})}$: 8.94 (1H, dd, $J= 4.2, 1.7$ Hz, 3- H_{Ar}), 8.47 (1H, dd, $J= 8.5, 1.6$ Hz, 1- H_{Ar}), 7.94 (1H, s, 11- H_{Ar}), 7.66 (1H, d, $J= 7.6$ Hz, 10- H_{Ar}), 7.48 (1H, dd, $J= 8.5, 4.2$ Hz, 2- H_{Ar}), 7.39 (1H, td, $J= 7.6, 1.2$ Hz, 9- H_{Ar}), 7.33 (1H, td, $J= 7.4, 1.1$ Hz, 8- H_{Ar}), 7.20 (1H, dd, $J= 7.5$ Hz, 7- H_{Ar}), (2H, s, 6- CH_2); $^{13}\text{C NMR}$ (101 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 150.5 (3- C_{Ar}), 149.2 (5a-C), 140.8 (4a-C), 133.1 (1- C_{Ar}), 130.8 (7a-C), 128.9 (10a-C), 128.8 (8- C_{Ar}), 128.7 (9- C_{Ar}), 126.8 (12-C), 124.9 (7- C_{Ar}), 123.7 (1a-C), 122.3 (2- C_{Ar}), 122.1 (10- C_{Ar}), 121.7 (11- C_{Ar}), 121.1 (11a-C), 69.2 (6- CH_2); COSY, $[\delta_{\text{H}}/\delta_{\text{H}}]$: 8.94/7.48 [3- $\text{H}_{\text{Ar}}/2\text{-H}_{\text{Ar}}$] 8.47/7.48 [1- $\text{H}_{\text{Ar}}/2\text{-H}_{\text{Ar}}$], 7.66/7.39 [10- $\text{H}_{\text{Ar}}/9\text{-H}_{\text{Ar}}$], 7.39/7.20 [9- $\text{H}_{\text{Ar}}/7\text{-H}_{\text{Ar}}$] 7.33/7.20 [8- $\text{H}_{\text{Ar}}/7\text{-H}_{\text{Ar}}$], 7.20/5.41 [7- $\text{H}_{\text{Ar}}/6\text{-CH}_2$]; HSQC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 8.94/150.53 [3- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-3}]$, 8.47/133.1 [1- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-1}]$, 7.94/121.7 [11- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-11}]$, 7.66/122.1 [10- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-10}]$, 7.48/122.3 [2- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-2}]$, 7.39/128.7 [9- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-9}]$, 7.33/128.8 [8- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-8}]$, 7.20/124.9 [7- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-7}]$, 5.41/69.2 [6- $\text{CH}_2/\text{C-6}]$; HMBC, $[\delta_{\text{H}}/\delta_{\text{C}}]$: 8.94/122.3/133.1/140.8 [3- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-2/C}_{\text{Ar}}\text{-1/C-4a}]$, 8.47/123.7/140.8/150.5 [1- $\text{H}_{\text{Ar}}/\text{C-1a/C-4a/C}_{\text{Ar}}\text{-3}]$, 7.94/123.7/126.8/149.2 [11- $\text{H}_{\text{Ar}}/\text{C-1a/C-12/C-5a}]$, 7.66/121.1/128.7/128.8/128.9/130.8 [10- $\text{H}_{\text{Ar}}/\text{C-11a/C}_{\text{Ar}}\text{-9/C}_{\text{Ar}}\text{-8/C-10a/C-7a}]$, 7.48/133.1/150.8 [2- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-1/C}_{\text{Ar}}\text{-3}]$, 7.40/124.9/128.8 [9- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-7/C}_{\text{Ar}}\text{-8}]$, 7.33/122.1/130.8 [8- $\text{H}_{\text{Ar}}/\text{C}_{\text{Ar}}\text{-10/C}_{\text{Ar}}\text{-7/C-7a}]$, 7.20/69.2/128.7/128.8/128.9 [7- $\text{H}_{\text{Ar}}/\text{C-6/C}_{\text{Ar}}\text{-9/C}_{\text{Ar}}\text{-8/C-10a}]$, 5.41/124.9/130.8/149.2 [6- $\text{CH}_2/\text{C}_{\text{Ar}}\text{-7/C-7a/C-5a}]$. HRMS (ESI+): m/z : calcd for $\text{C}_{16}\text{H}_{11}\text{ClNO} ([\text{M}+\text{H}]^+)$ 268.0524, found: 268.0538; calcd for $\text{C}_{16}\text{H}_{10}\text{ClNNaO} ([\text{M}+\text{Na}]^+)$ 290.0343, found: 290.0341.

4. Characterization data of all synthesized synthesized phenanthridin-6(5H)-one 16a-b and 17b

General Procedure

To a mixture of K_2CO_3 (3 equiv.), NaI (0.5 equiv.) and *N*-methylaniline (4 mmol) in acetone (0.5 M) was added the 2-bromobenzyl bromide (2 mmol) and the reaction was heated to 60°C for 24 hours. The reaction mixture was quenched with a NaOH (2N) solution and was extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was separated, dried with Na_2SO_4 , and concentrated to afford the crude product, which was purified by silica gel flash chromatography to yield the corresponding *N*-(2-bromobenzyl)-aniline.

***N*-(2-bromobenzyl)aniline (16a):** Yellow liquid (0.21 g, 0.8 mmol, 40%); R_f [hexane-EtOAc 10:1]= 0.6; $^1\text{H NMR}$ (400 MHz, CDCl_3), $\delta_{(\text{ppm})}$: 7.57 (1H, dd, $J= 7.9, 1.2$ Hz, 10- H_{Ar}), 7.41

(1H, dd, $J=7.6, 1.5$ Hz, 7-H_{Ar}), 7.22–7.09 (4H, m, 9-, 8-, 3- and 1-H_{Ar}), 6.72 (1H, tt, $J=7.3, 1.1$ Hz, 2-H_{Ar}), 6.62 (2H, dt, $J=7.7, 1.1$ Hz, 4- and 1a-H_{Ar}), 4.41 (2H, s, 6-CH₂); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 147.8, 138.3, 132.9, 129.(2), 129.3, 128.8, 127.7, 123.4, 117.9, 113.0 (2), 48.5.

N-(2-bromobenzyl)-N-methylaniline (16b): Yellow liquid (0.55 g, 1.98 mmol, 99 %); R_f [hexane-EtOAc 30:1] = 0.7; IR (KBr, ν_{máx/cm⁻¹}): 3061 ν_(CH₃), 1598 ν_(C=C), 1253 ν_(C-N), 688 ν_(C-Br); ¹H NMR (400 MHz, CDCl₃), δ_(ppm): 7.59 (1H, d, $J=8.0$ Hz, 10-H_{Ar}), 7.23 (3H, dd, $J=8.8, 7.3$ Hz, 9-, 1- and 3-H_{Ar}), 7.14 (2H, d, $J=7.6$ Hz, 8- and 7-H_{Ar}), 6.73 (1H, t, $J=7.2$ Hz, 2-H_{Ar}), 6.68 (2H, d, $J=8.1$ Hz, 1a- and 4-H_{Ar}), 4.56 (2H, s, 6-CH₂), 3.11 (3H, s, 11-CH₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 132.9 (2), 129.3 (2), 128.5, 127.9, 127.6, 122.8, 116.6, 111.9, 57.5, 53.5, 38.9, 29.8; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₅BrN ([M+H]⁺) 276.0382, found: 276.0381; calcd for C₁₄H₁₄BrNNa ([M+Na]⁺) 298.0201, found: 298.0200.

General procedure for intramolecular direct arylation

A crimped vial equipped with a magnetic stir bar was charged with *N*-(2-bromobenzyl)-*N*-methylaniline (2 mmol), K₂CO₃ (3 equiv.), PivOH (30 mol%) as an additive, P(*p*-FPh)₃ (5 mol%) as a ligand and PdCl₂(MeCN)₂ (5 mol%). The vial was sealed and was purged three times with argon and 3 mL of degassed *N,N*-Dimethylacetamide (DMA) was added. Then, the reaction mixture is heated over 3 hours at 120°C. After cooling to room temperature, the crude mixture was loaded directly onto celite; then, purified by column chromatography (silica gel) using hexane/ethyl acetate mixtures as the eluent. **5-methylphenanthridin-6(5H)-one (17b):** Yellow liquid (0.20 g, 0.99 mmol, 45 %); R_f [hexane-EtOAc 30:1] = 0.24; IR (KBr, ν_{máx/cm⁻¹}): 3072 ν_(CH₃), 1643 ν_(C=O), 1585 ν_(C_{Ar}=C_{Ar}), 1348 ν_(C-N), 688 ν_(C-Br); ¹H NMR (400 MHz, CDCl₃), δ_(ppm): 8.54 (1H, dd, $J=8.1, 1.5$ Hz, 7-H_{Ar}), 8.26 (2H, dd, $J=8.2, 2.6$ Hz, 10- and 1-H_{Ar}), 7.75 (1H, ddd, $J=8.4, 7.1, 1.5$ Hz, 8-H_{Ar}), 7.60–7.51 (2H, m, 9- and 3-H_{Ar}), 7.40 (1H, d, $J=8.3$ Hz, 4-H_{Ar}), 7.31 (1H, ddd, $J=8.2, 7.2, 1.2$ Hz, 2-H_{Ar}), 3.80 (3H, s, 11-CH₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 161.7 (6-C=O), 138.0 (4a-C), 133.6 (6a-C), 132.5 (8-C_{Ar}), 129.6 (9-C_{Ar}), 128.9 (7-C_{Ar}), 128.0 (3-C_{Ar}), 125.6 (10a-C), 123.3 (10-C_{Ar}), 122.5 (2-C_{Ar}), 121.7 (1-C_{Ar}), 119.3 (1a-C), 115.1 (4-C_{Ar}), 30.1 (11-CH₃); COSY, [δ_H/δ_H]: 8.54 / 7.75 [7-H_{Ar}/8-H_{Ar}] 8.54/7.61-7.51 [7-H_{Ar}/9-H_{Ar}], 8.26/7.75 [10-H_{Ar}/8-H_{Ar}], 8.25/7.31 [1-H_{Ar}/2-H_{Ar}], 7.75/7.61-7.51 [8-H_{Ar}/9-H_{Ar}], 7.61-7.51/7.40 [3-H_{Ar}/4-H_{Ar}], 7.61-7.51/7.31 [3-H_{Ar}/2-H_{Ar}], 7.40/7.31 [4-H_{Ar}/2-H_{Ar}], 7.41/3.80 [4-H_{Ar}/CH₃-11]; HSQC, [δ_H/δ_C]: 8.54/128.9 [7-H_{Ar}/C_{Ar}-7], 8.26/121.7/123.3 [10- and 1-H_{Ar}/C_{Ar}-1/C_{Ar}-10], 7.75/132.5 [8-H_{Ar}/C_{Ar}-8], 7.61-7.51/128.0/129.6 [9- and 3-H_{Ar}/C_{Ar}-3/C_{Ar}-9], 7.40/115.1 [4-H_{Ar}/C_{Ar}-4], 7.30/122.5 [2-H_{Ar}/C_{Ar}-2], 3.80/30.1 [11-CH₃/C_{Ar}-11]; HMBC, [δ_H/δ_C]: 8.54/132.5/133.6 [7-H_{Ar}/C_{Ar}-8/C-6a], 8.26/119.3/125.6/128.0/129.6/133.6/138.0 [10- and 1-H_{Ar}/C-1a/C-10a/C_{Ar}-3/C_{Ar}-9/C-6a].

6a/C-4a], 7.75/128.9/133.6 [8-H_{Ar}/C_{Ar}-7/C-6a], 7.61–7.51/121.7/123.3/125.6/138.06 [9-H_{Ar} and 3-H_{Ar}/C_{Ar}-1/C_{Ar}-10/C-10a/C-4a], 7.40/119.3/122.5 [4-H_{Ar}/C-1a/C_{Ar}-2], 7.31/115.1/119.3 [2-H_{Ar}/C_{Ar}-4/C-1a], 3.80/138.0/161.7 [11-CH₃/C-4a/C-6]; HRMS (ESI+): *m/z*: calcd for C₁₄H₁₄N ([M+H]⁺) 196.1120, found: 196.1119; calcd for C₁₄H₁₃NNa ([M+Na]⁺) 218.0940, found: 218.0939.

5. Characterization data of all synthesized *6H-benzo[c]chromen-6-ones* 18a-b

General procedure for oxidation of benzylic methylenes to *6H-benzo[c]chromene*

To a solution of the appropriate *6H-benzo[c]chromene* (4 mmol), *tert*-butylhydroperoxide (TBHP) (70% aqueous solution, 4 equiv.), iodine (I₂, 10 mol%) and pyridine (Py, 10 mol%) were sealed in a 10 mL tube. The solution was stirred at 80 °C for 24 hours. TLC monitoring confirmed the end of the reaction and the mixture was treated with saturated solution of NaHCO₃, then extracted three times with CH₂Cl₂ (3 x 20 mL) and organic layer was separated, dried with Na₂SO₄, and concentrated to afford the crude product, which was purified by silica gel flash chromatography to yield the corresponding *6H-benzo[c]chromen-6-ones*.

6-(*Tert*-butilperoxy)-*6H-benzo[c]chromene* (Int.): White solid (0.32 g, 1.20 mmol, 60 %); R_f [hexane-EtOAc 30:1]= 0.20; NMR (400 MHz, CDCl₃) δ_(ppm): 7.85 (1H, d, *J*= 7.9 Hz, 4-H_{Ar}), 7.84 (1H, dd, *J*= 7.8, 1.6 Hz, 7-H_{Ar}), 7.52 (1H, ddd, *J*= 7.9, 6.9, 1.9 Hz, 3-H_{Ar}), 7.41–7.37 (2H, m, 2- and 1-H_{Ar}), 7.31 (1H, ddd, *J*= 8.2, 7.3, 1.6 Hz, 9-H_{Ar}), 7.18 (1H, dd, *J*= 8.2, 1.0 Hz, 10-H_{Ar}), 7.11 (1H, ddd, *J*= 7.8, 7.3, 1.3 Hz, 8-H_{Ar}), 6.54 (1H, s, 6-CH), 1.21 (9H, s, 11-(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃), δ_(ppm): 150.9 (4a-C), 130.3 (3-C_{Ar}), 130.0 (10a-C), 129.7 (9-C_{Ar}), 127.8 (1- and 2-C_{Ar}), 126.2 (1a-C), 122.9 (4-C_{Ar}), 122.3 (8-C_{Ar}), 122.0 (7-C_{Ar}), 120.8 (7a-C), 118.8 (10-C_{Ar}), 100.0 (6-CH), 81.5 (11-C-(CH₃)₃), 26.6 (11-(CH₃)₃); COSY, [δ_H/δ_H]: 7.85/7.52 [4-H_{Ar}/3-H_{Ar}], 7.84/7.11 [7-H_{Ar}/8-H_{Ar}], 7.84/6.54 [7-H_{Ar}/6-CH], 7.52/7.40 [3-H_{Ar}/1- and 2-H_{Ar}], 7.30/7.18 [9-H_{Ar}/10-H_{Ar}]; HSQC, [δ_H/δ_C]: 7.85/122.9 [4-H_{Ar}/C_{Ar}-4], 7.84/122.01 [7-H_{Ar}/C_{Ar}-7], 7.52/130.3 [3-H_{Ar}/C_{Ar}-3], 7.41–7.37/127.8 [1- and 2-H_{Ar}/C_{Ar}-1/C_{Ar}-2], 7.31/129.7 [9-H_{Ar}/C_{Ar}-9], 7.18/118.8 [10-H_{Ar}/C_{Ar}-10], 7.11/122.3 [8-H_{Ar}/C_{Ar}-8], 6.54/100.0 [6-CH/C-6], 1.21/26.6 [11-(CH₃)₃/C-11]; HMBC, [δ_H/δ_C]: 7.85/126.2/127.8/150.9 [4-H_{Ar}/C-1a/C_{Ar}-2/C-4a], 7.84/120.8/129.7 [7-H_{Ar}/C-7a/C_{Ar}-9], 7.52/127.8 [3-H_{Ar}/C_{Ar}-2], 7.41–7.37/126.2 [1- and 2-H_{Ar}/C-1a], 7.31/122.3 [9-H_{Ar}/C_{Ar}-8], 7.18/120.8 [10-H_{Ar}/C-7a], 7.11/118.8/120.8 [8-H_{Ar}/C_{Ar}-10/C-7a], 6.54/122.0/129.7/150.9 [6-CH/C_{Ar}-7/C-10a/C-4a]; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₉O₃ ([M+H]⁺) 271.1328, found: 271.1327; calcd for C₁₇H₁₈NaO₃ ([M+Na]⁺) 293.1148, found: 293.1146.

6H-Benzo[c]chromen-6-one (18a): White solid (0.35 g, 1.80 mmol, 90 %); R_f [hexane-EtOAc 30:1]= 0.30; NMR (400 MHz, CDCl₃) δ (ppm): 8.39 (1H, dd, J = 8.0, 1.2 Hz, 4-H_{Ar}), 8.11 (1H, d, J = 8.1 Hz, 10-H_{Ar}), 8.05 (1H, dd, J = 7.9, 1.4 Hz, 9-H_{Ar}), 7.82 (1H, ddd, J = 8.0, 7.3, 1.4 Hz, 8-H_{Ar}), 7.57 (1H, ddd, J = 8.2, 7.3, 1.1 Hz, 2-H_{Ar}), 7.47 (1H, ddd, J = 8.4, 7.2, 1.5 Hz, 3-H_{Ar}), 7.37–7.34 (1H, m, 1-H_{Ar}), 7.33–7.31 (1H, m, 7-H_{Ar}); ¹³C RMN (101 MHz, CDCl₃), δ (ppm): 161.3, 151.3, 134.9, 134.8, 130.7, 130.5, 129.0, 124.6, 122.8, 121.8, 121.3, 118.1, 117.9; HRMS (ESI+): *m/z*: calcd for C₁₃H₉O₂ ([M+H]⁺) 197.0597, found: 197.0596; calcd for C₁₃H₈NaO₂ ([M+Na]⁺) 219.0416, found: 219.0415.

1-Isopropil-4-methyl-6H-benzo[c]chromen-6-one(18b): Pale yellow solid (0.37 g, 1.48 mmol, 74 %); R_f [hexane-EtOAc 30:1]= 0.36; NMR (400 MHz, CDCl₃) δ (ppm): 8.40 (1H, dd, J = 7.9, 1.3 Hz, 10-H_{Ar}), 8.10 (1H, d, J = 8.4 Hz, 7-H_{Ar}), 7.74 (1H, ddd, J = 8.4, 7.3, 1.6 Hz, 8-H_{Ar}), 7.51 (1H, ddd, J = 8.0, 7.2, 0.9 Hz, 9-H_{Ar}), 7.23 (2H, d, 6.3 Hz, 3- and 2-H_{Ar}), 3.85–3.76 (1H, m, 12-CH), 2.40 (3H, s, 11-CH₃), 1.37 (3H, s, 13-CH₃), 1.36 (3H, s, 14-CH₃); ¹³C RMN (101 MHz, CDCl₃), δ (ppm): 161.5, 149.7, 145.0, 135.7, 134.0, 131.2, 130.6, 128.0, 126.9, 124.0, 122.6, 122.5, 116.6, 30.2, 24.7(2), 16.2; HRMS (ESI+): *m/z*: calcd for C₁₇H₁₇O₂ ([M+H]⁺) 253.1223, found: 253.1221; calcd for C₁₇H₁₆NaO₂ ([M+Na]⁺) 275.1042, found: 275.1041.

6. Extraction and characterization of the essential oils of clove (*Eugenia caryophyllus*) and oregano (*Plectranthus amboinicus*)

The essential oil (EO) of clove was obtained by microwave-assisted hydrodistillation (MWHD) from the dried flower buds in 12.8 ± 0.2% yield as a pale-yellow color and with a spicy odor. The main identified compounds were eugenol (71.8 %), eugenyl acetate (18.4 %) and the *trans*-β-caryophyllene (7.5 %), as revealed by the obtained chromatogram accurate by GC-FID Figure ESI1.

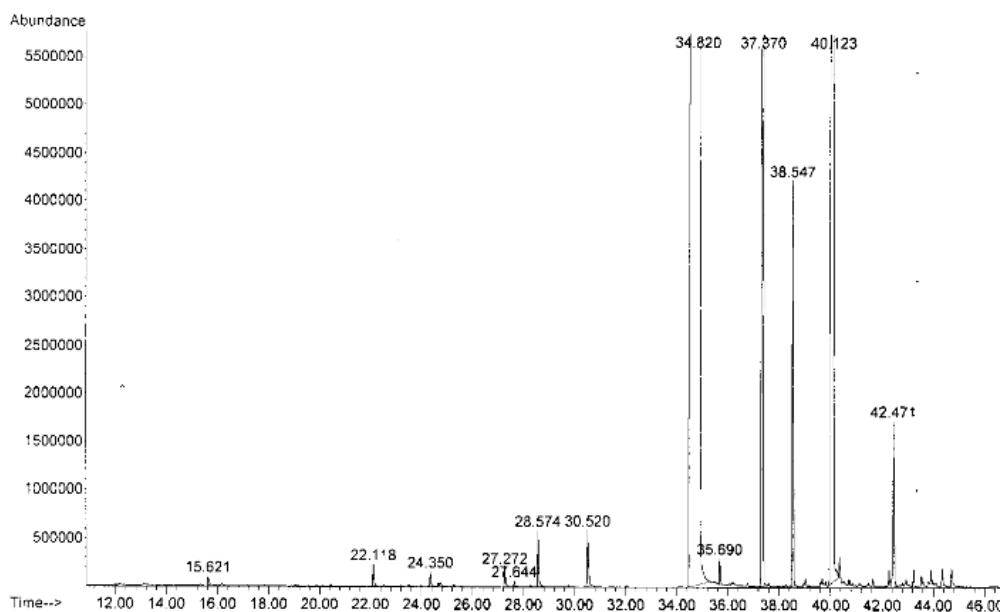


Figure ESI 1. Profile (chromatographic pattern) of the secondary metabolites present in the EO from clove obtained by GC-FID in a GC capillary column DB-5 (60 m).

Besides eugenol and eugenyl acetate, other compounds were identified and quantified by GC-MS using an internal standard (Istd). Their retention times and percentage, in the 98.2% of the Total Ionic Current (TIC), are described in Table ES1.

Table ESI-1: Compounds detected after MWHD of *E. caryophyllus* by GC-FID

Peak ^a	RT, min	Compound	Percentage (%)
1	15.62	2-Heptanone	<0.1
2	22.12	2-Heptyl acetate	0.1
3	24.35	2-Nonanone	<0.1
4	27.27	Benzyl acetate	0.1
5	27.65	Ethyl benzoate	<0.1
6	28.57	Methyl salicylate	0.2
7	30.52	Chavicol	0.2
8	34.82	Eugenol	71.8
9	35.69	α -Copaene	0.1
10	37.37	<i>trans</i> - β -Caryophyllene	7.5
11	38.55	α -Humulene	1.1
12	40.12	Eugenyl acetate	18.4
13	42.47	Caryophyllene oxide	0.5

^aPeaks detected in the Profile (chromatographic pattern) obtained by GC-FID.

The EO of oregano was obtained by MWHD from the dried leaves in 1% yield as a pale yellow color. The main identified compounds were carvacrol (67.1 %), *trans*- β -caryophyllene (8.8 %) and γ -terpinene (7.4 %), as revealed the obtained chromatogram accurate by GC-FID Figure ESI2.

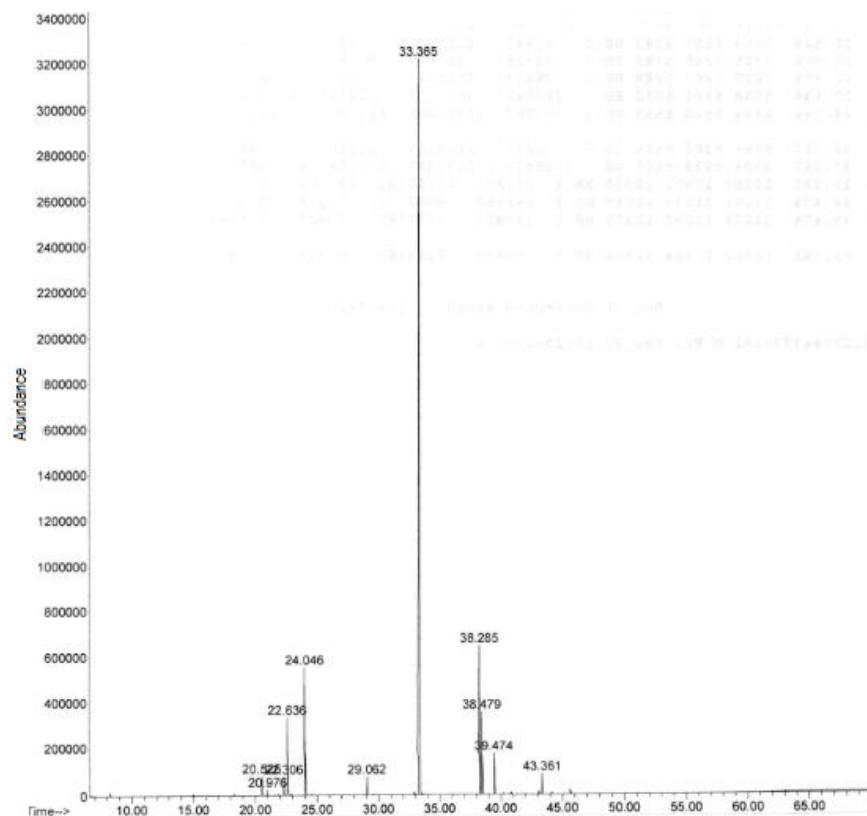


Figure ESI 2. Profile (chromatographic pattern) of the secondary metabolites present in the EO from oregano obtained by GC-FID in a GC capillary column DB-5 (60 m).

With carvacrol and *trans*- β -caryophyllene, other compounds were identified and quantified by GC-MS using an internal standard (Istd). Their retention times and percentage, in the 98.2% of the Total Ionic Current (TIC), are described in Table ES2.

Table ESI-2: Compounds detected after MWHD of leaves from *P. amboinicus* by GC-FID

Peak ^a	RT, min	Compound	Percentage (%)
1	20.53	1-Octen-3-ol	1.1
2	20.98	β -Mircene	0.3
3	22.31	α -Terpinene	1.0
4	22.64	<i>p</i> -Cymene	4.6
5	24.05	γ -Terpinene	7.4
6	29.06	Terpinen-4-ol	1.1
7	33.37	Carvacrol	67.1
8	38.29	<i>trans</i> - β -Caryophyllene	8.8
9	38.48	<i>trans</i> - α -Bergamotene	4.9
10	39.47	α -Humulene	2.4
11	43.36	Caryophyllene oxide	1.2

^aPeaks detected in the Profile (chromatographic pattern) obtained by GC-FID.

7. Copies of ^1H NMR and ^{13}C NMR charts of 8a-v.

Figure ESI 3. ^1H -NMR spectrum of *1-bromo-2-(phenoxyethyl)benzene* **8a**

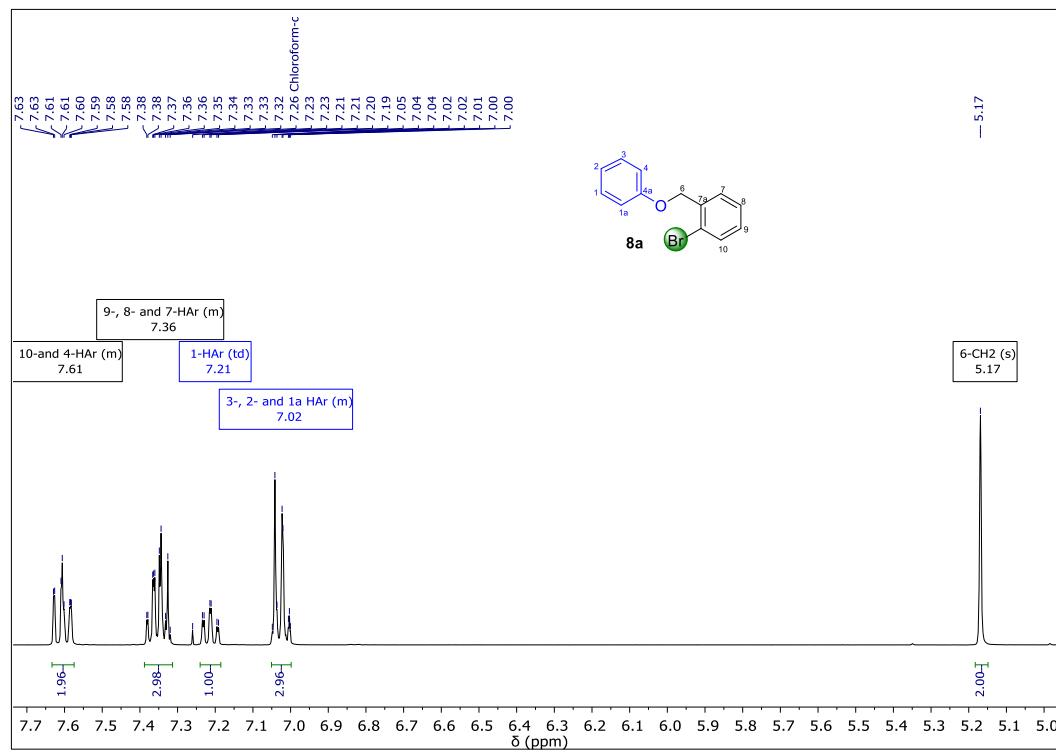


Figure ESI 4. ^{13}C -NMR spectrum of *1-bromo-2-(phenoxyethyl)benzene* **8a**

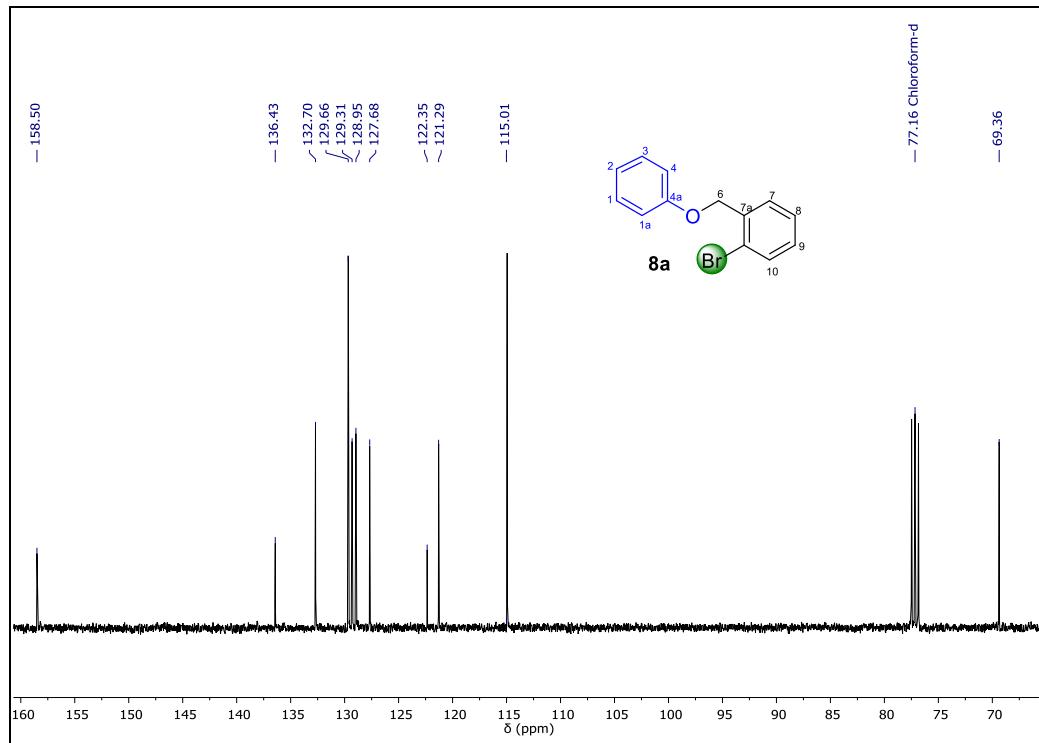


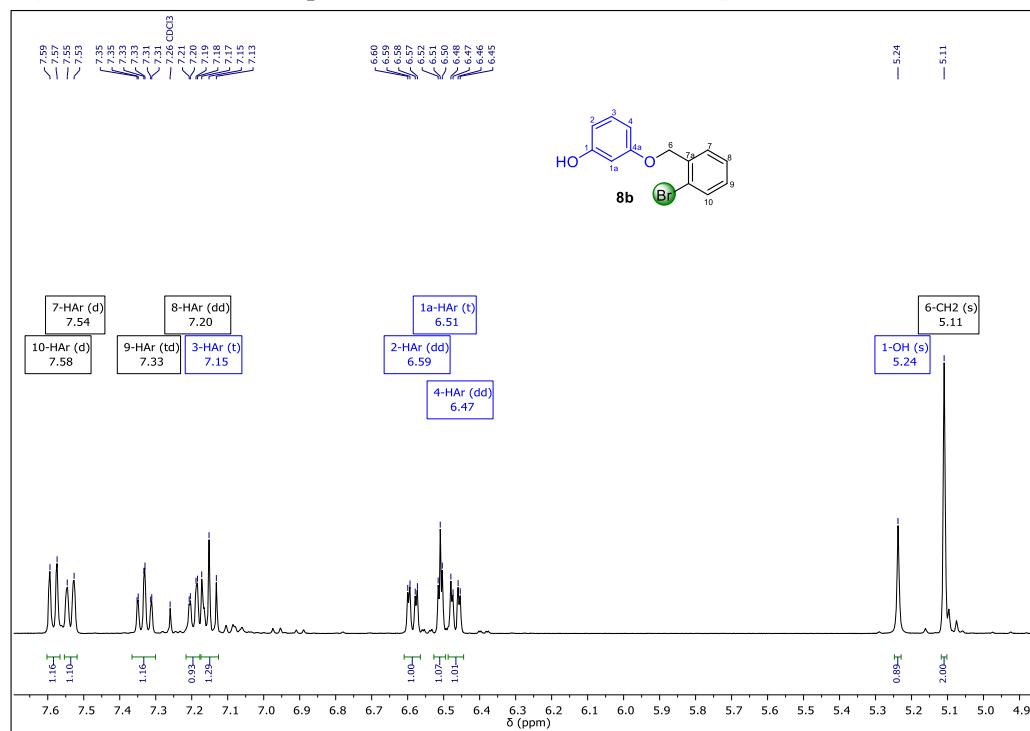
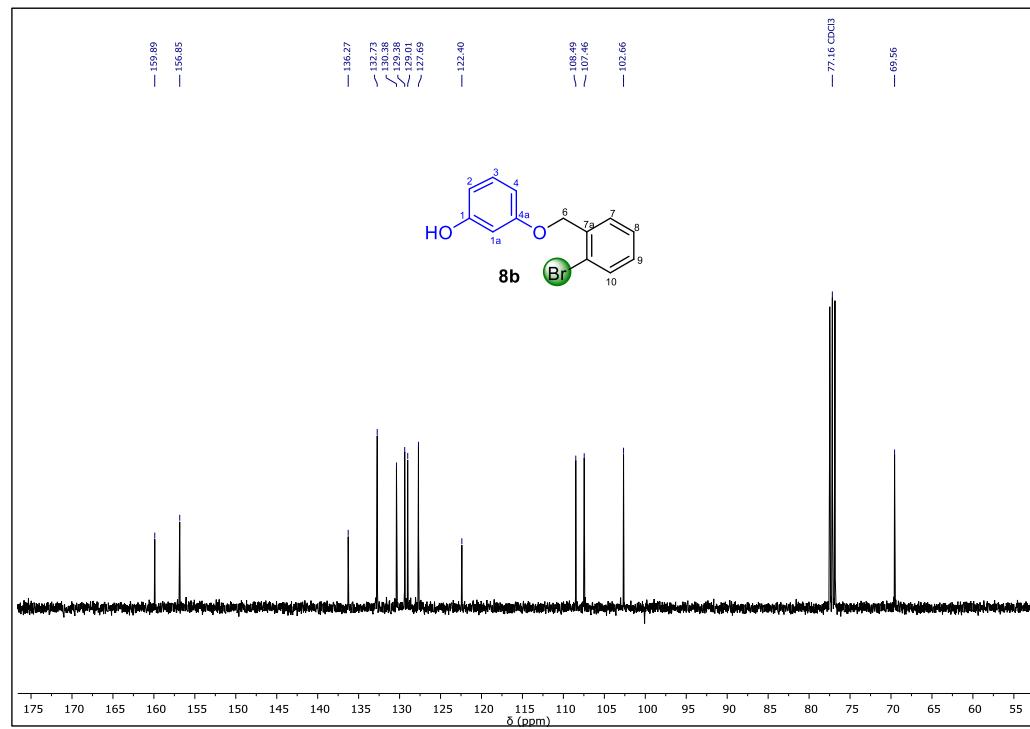
Figure ESI 5. ^1H -NMR spectrum of 3-((2-bromobenzyl)oxy)phenol **8b****Figure ESI 6.** ^{13}C -NMR spectrum of 3-((2-bromobenzyl)oxy)phenol **8b**

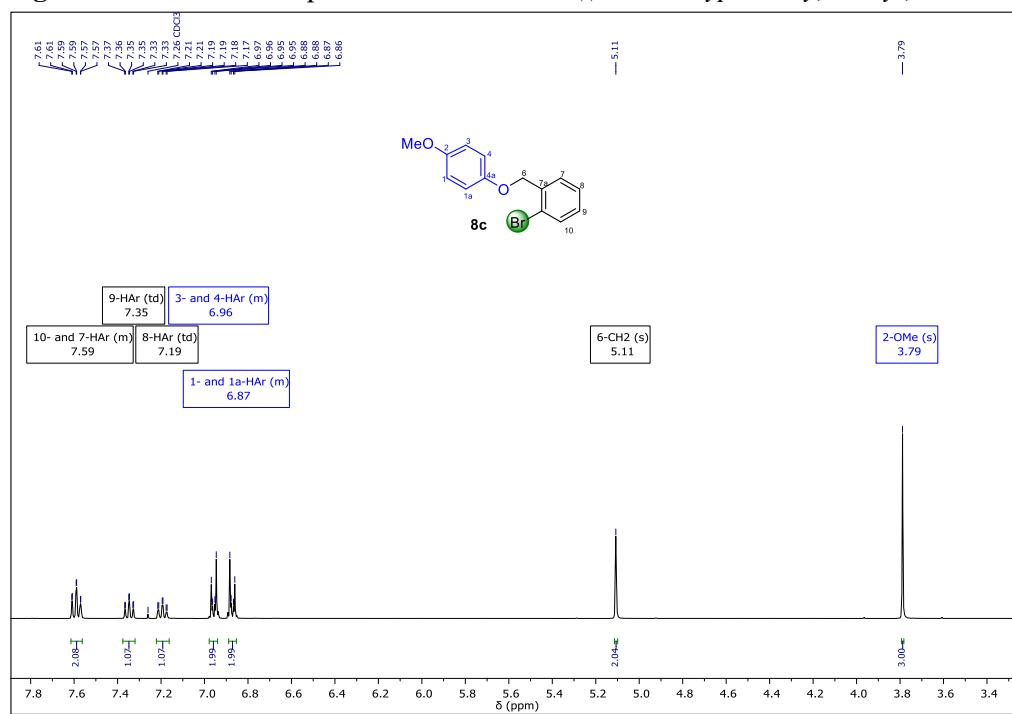
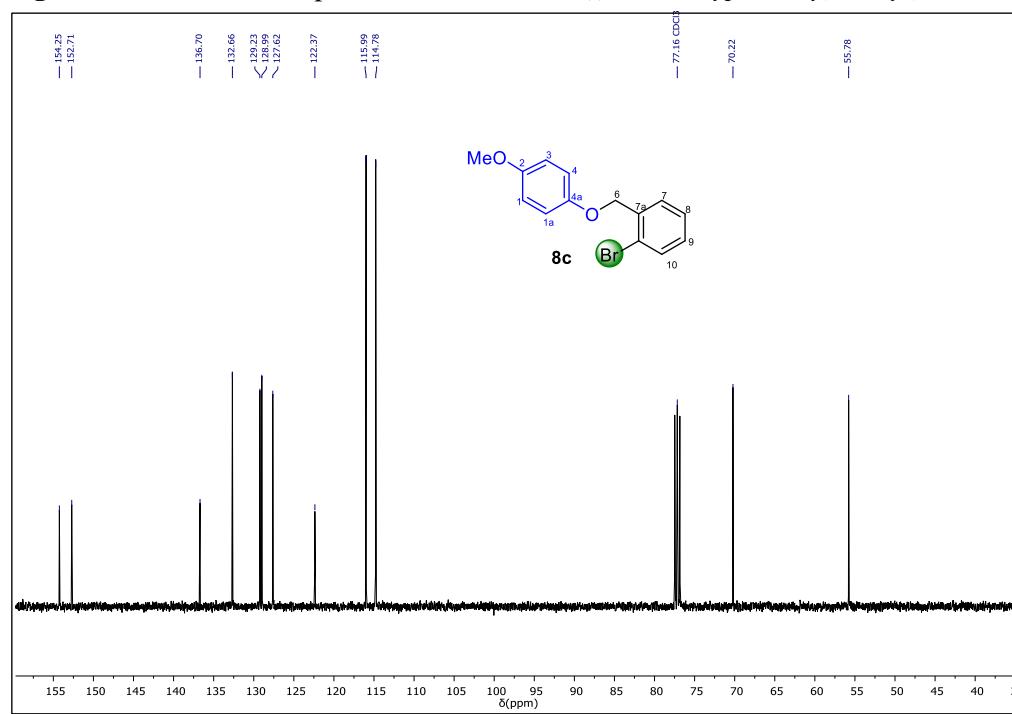
Figure ESI 7. ^1H -NMR spectrum of *1-bromo-2-((4-methoxyphenoxy)methyl)benzene* **8c****Figure ESI 8.** ^{13}C -NMR spectrum of *1-bromo-2-((4-methoxyphenoxy)methyl)benzene* **8c**

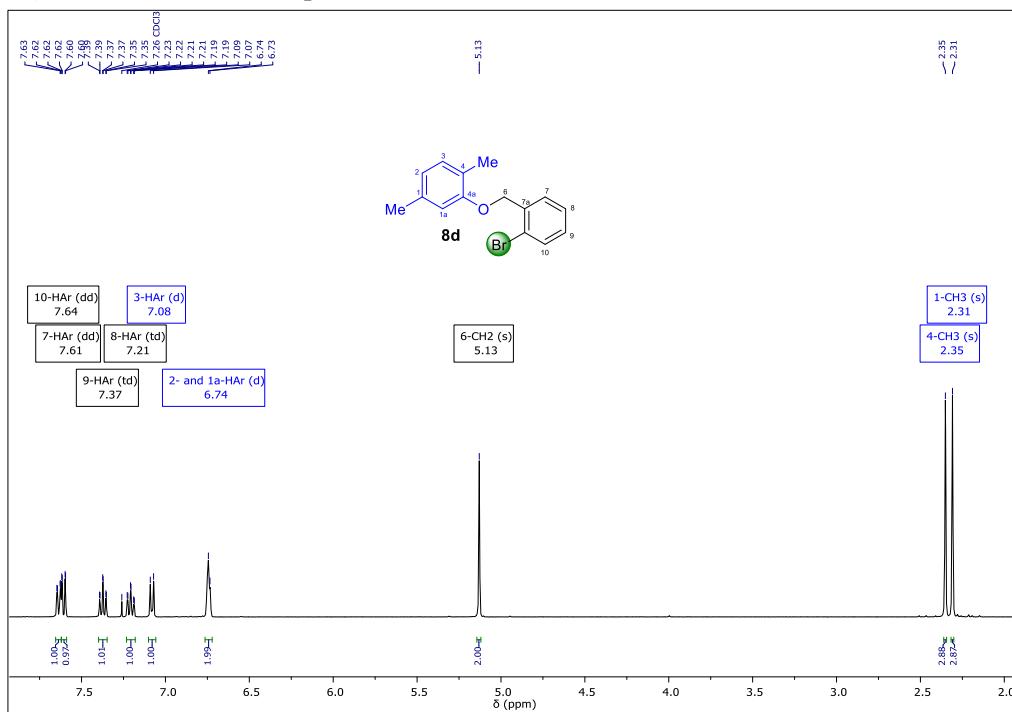
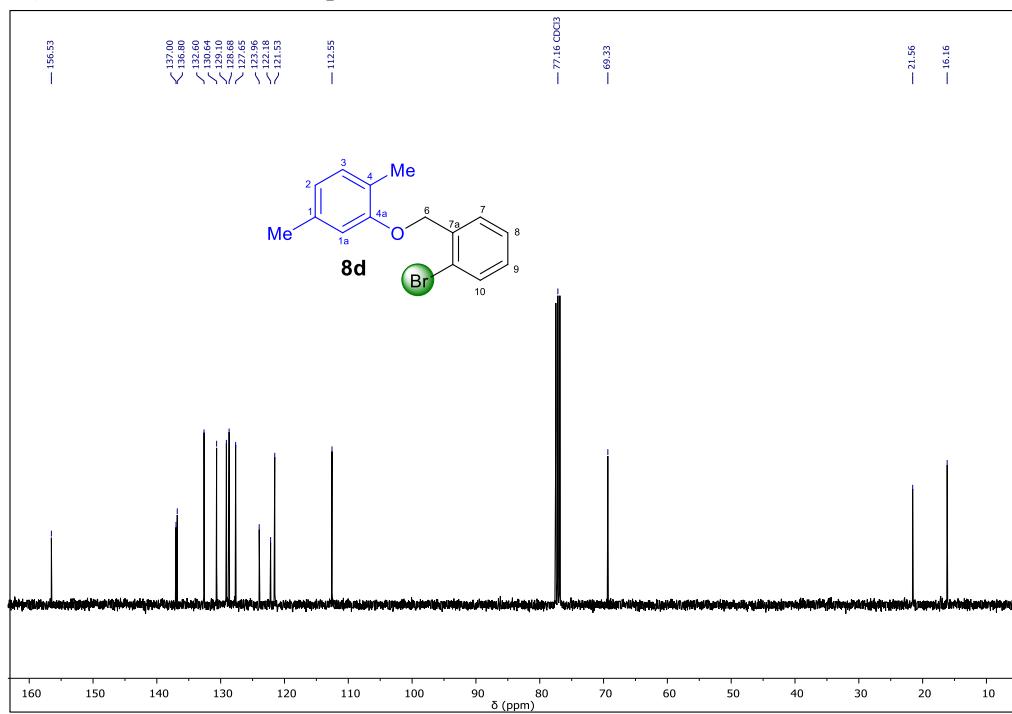
Figure ESI 9. ^1H -NMR spectrum of 2-((2-bromobenzyl)oxy)-1,4-dimethylbenzene **8d****Figure ESI 10.** ^{13}C -NMR spectrum of 2-((2-bromobenzyl)oxy)-1,4-dimethylbenzene **8d**

Figure ESI 11. ^1H -NMR spectrum of 2-((2-bromobenzyl)oxy)-1-isopropyl-4-methylbenzene **8e**

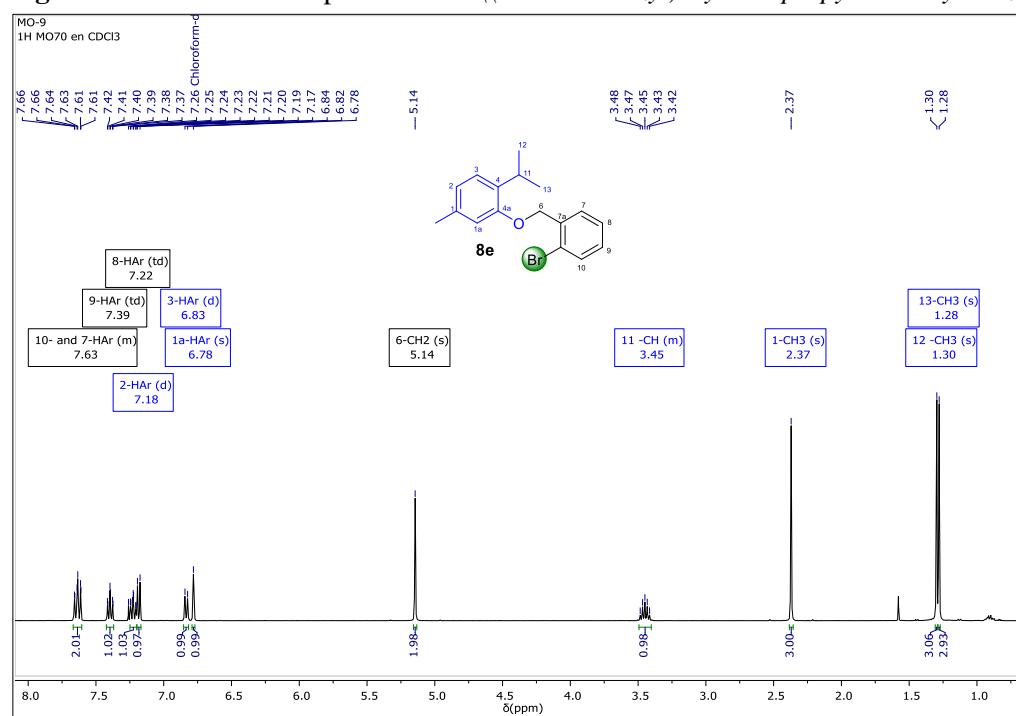


Figure ESI 12. ^{13}C -NMR spectrum of 2-((2-bromobenzyl)oxy)-1-isopropyl-4-methylbenzene **8e**

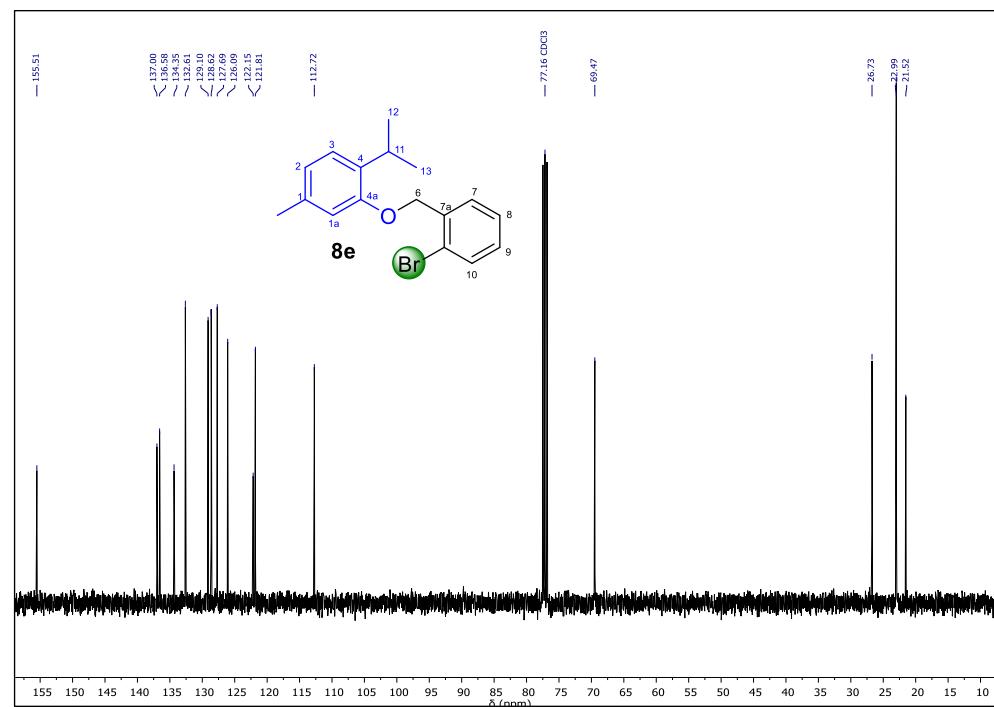


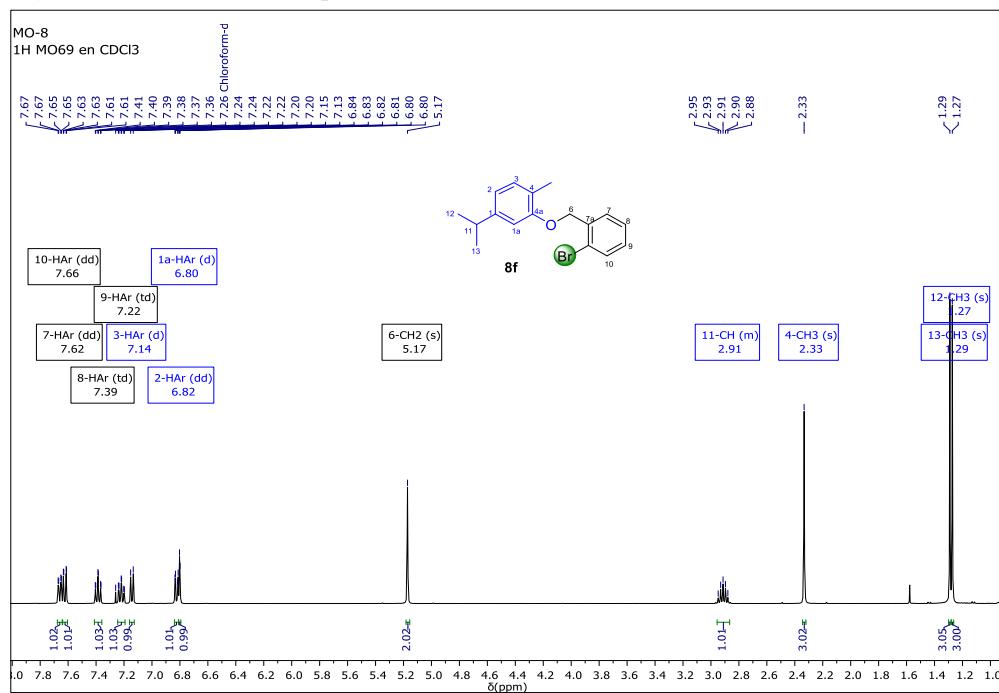
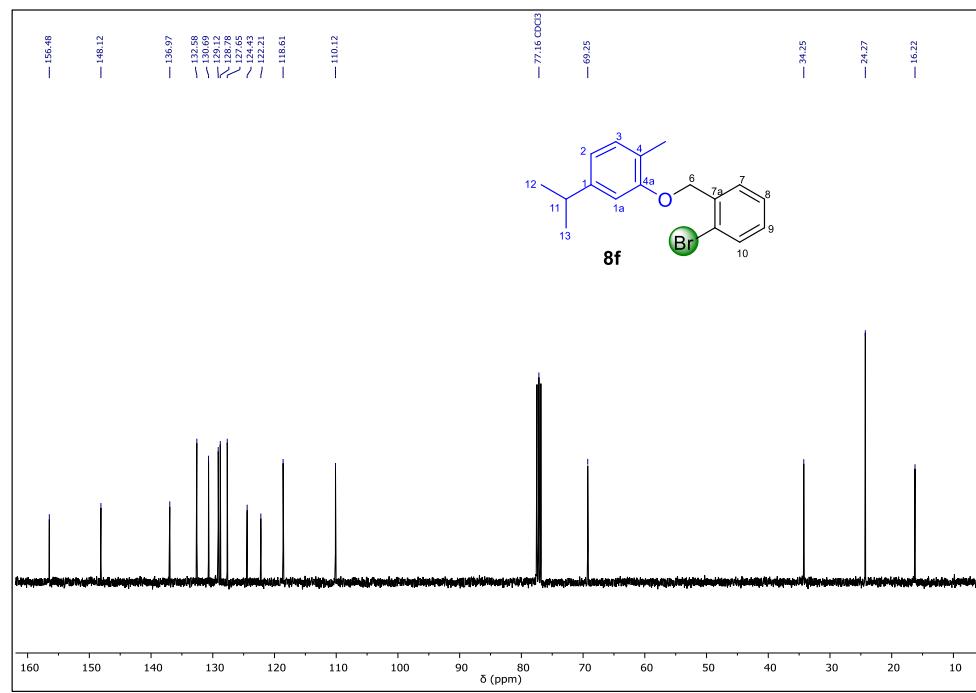
Figure ESI 13. ^1H -NMR spectrum of 2-((2-bromobenzyl)oxy)-4-isopropyl-1-methylbenzene **8f****Figure ESI 14.** ^{13}C -NMR spectrum of 2-((2-bromobenzyl)oxy)-4-isopropyl-1-methylbenzene **8f**

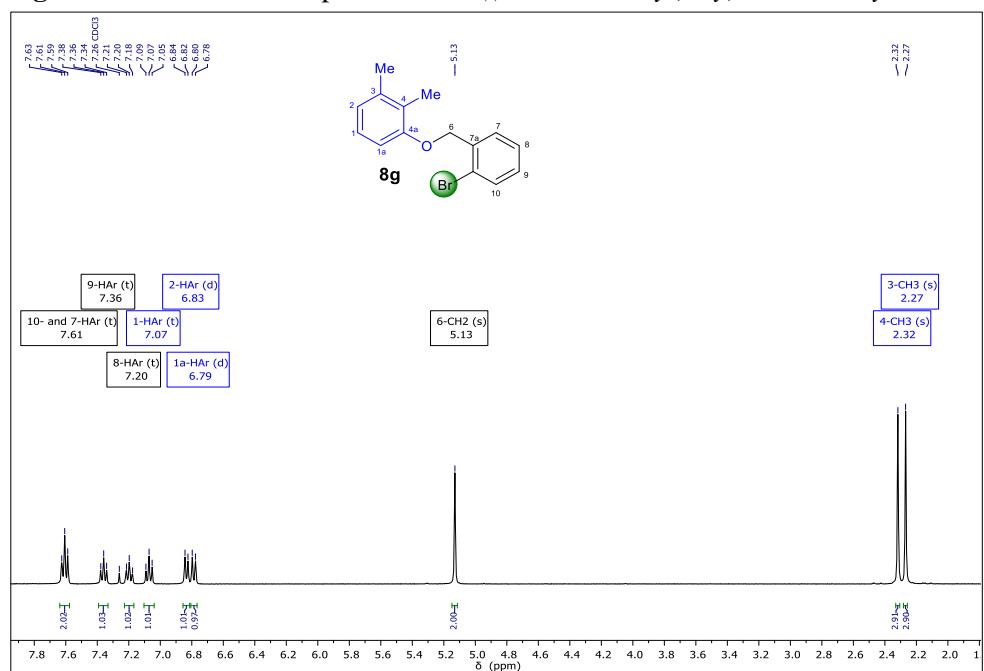
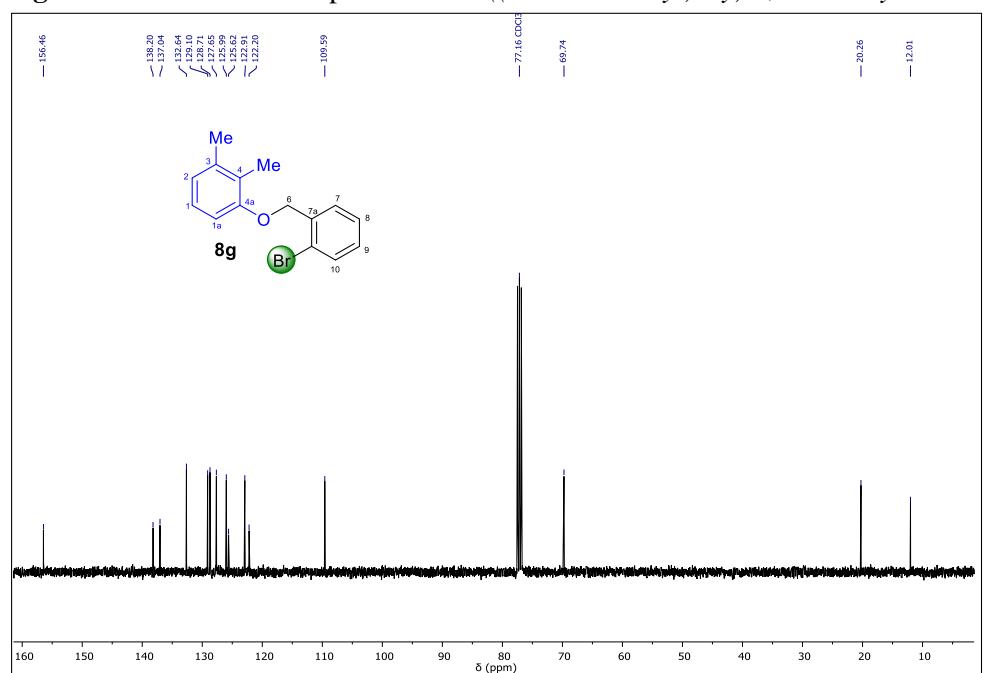
Figure ESI 15. ^1H -NMR spectrum of *1-((2-bromobenzyl)oxy)-2,3-dimethylbenzene* **8g****Figure ESI 16.** ^{13}C -NMR spectrum of *1-((2-bromobenzyl)oxy)-2,3-dimethylbenzene* **8g**

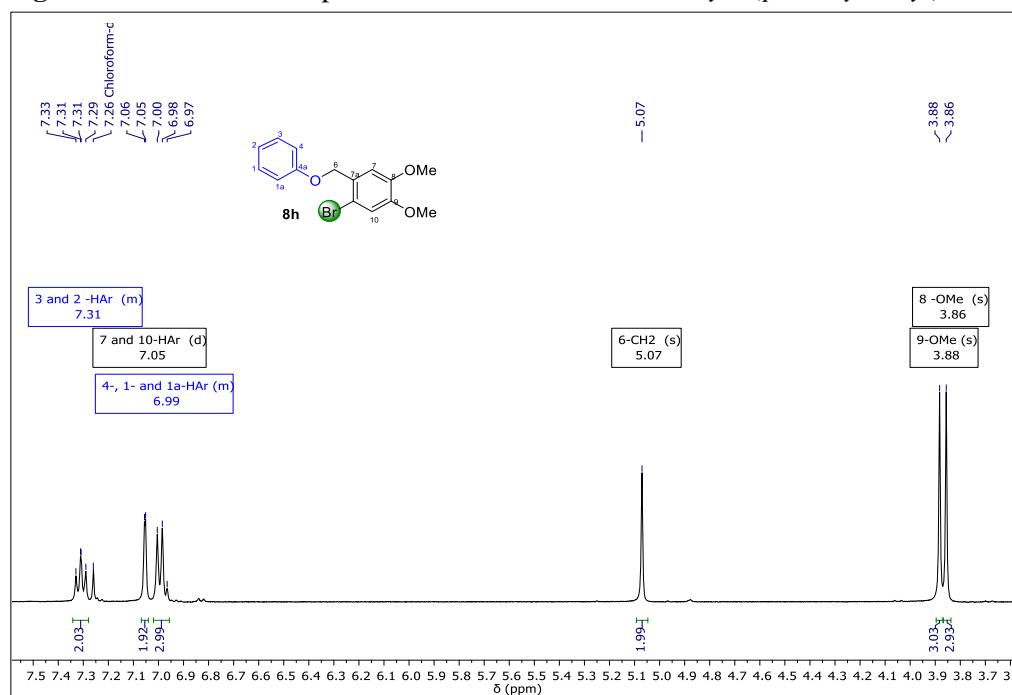
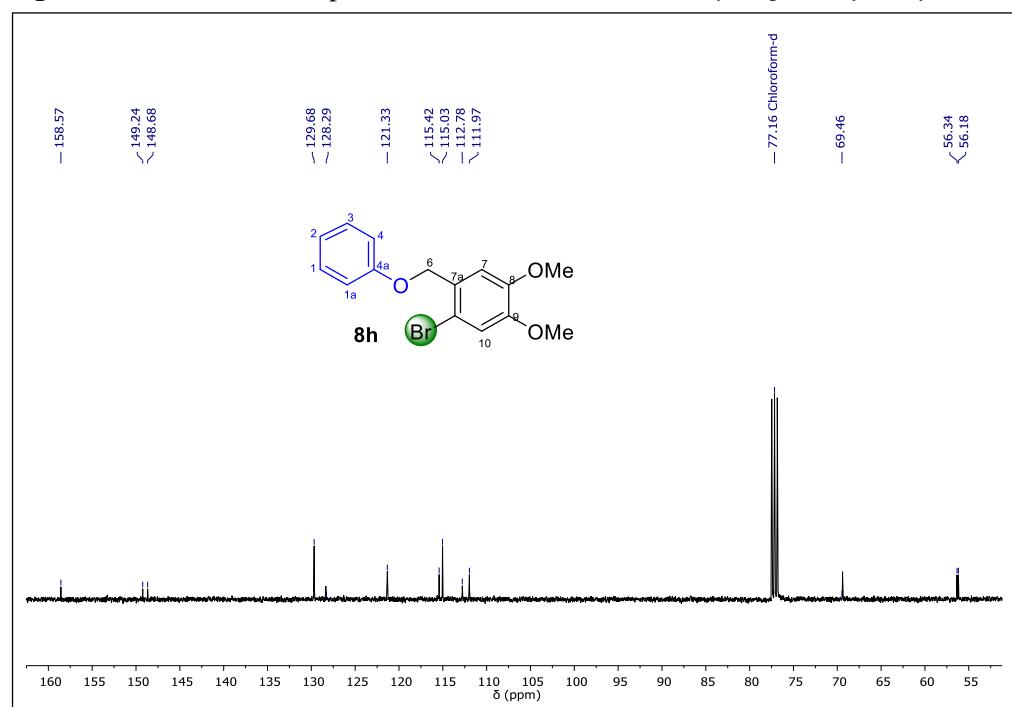
Figure ESI 17. ^1H -NMR spectrum of *1-bromo-4,5-dimethoxy-2-(phenoxyethyl)benzene* **8h****Figure ESI 18.** ^{13}C -NMR spectrum of *1-bromo-4,5-dimethoxy-2-(phenoxyethyl)benzene* **8h**

Figure ESI 19. ^1H -NMR spectrum of 2-bromo-3,4,5-trimethoxy-1-(phenoxyethyl)benzene **8i**

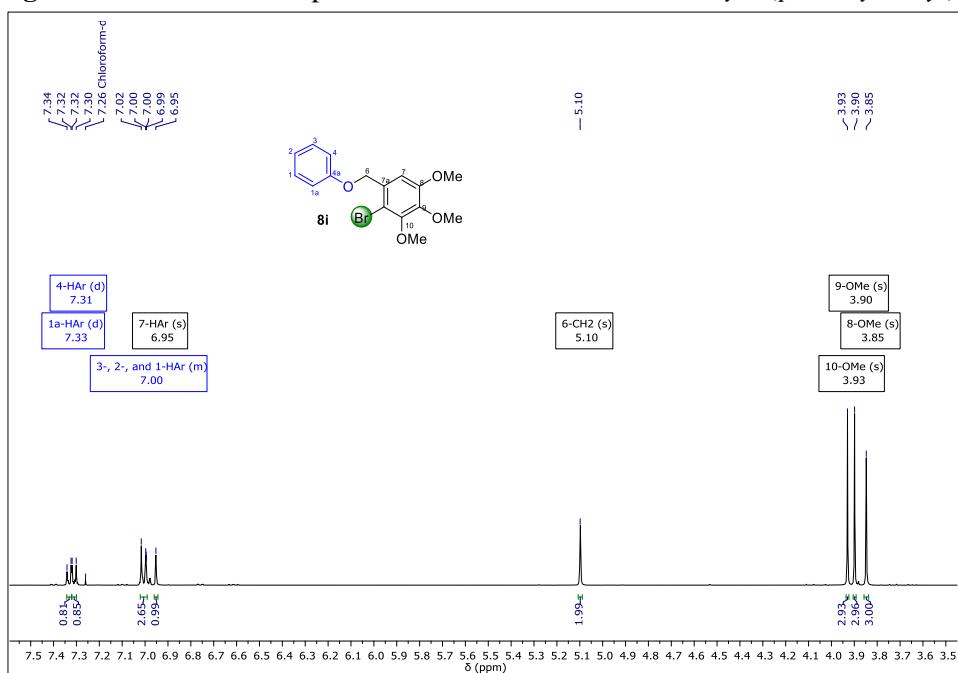


Figure ESI 20. ^{13}C -NMR spectrum of 2-bromo-3,4,5-trimethoxy-1-(phenoxyethyl)benzene **8i**

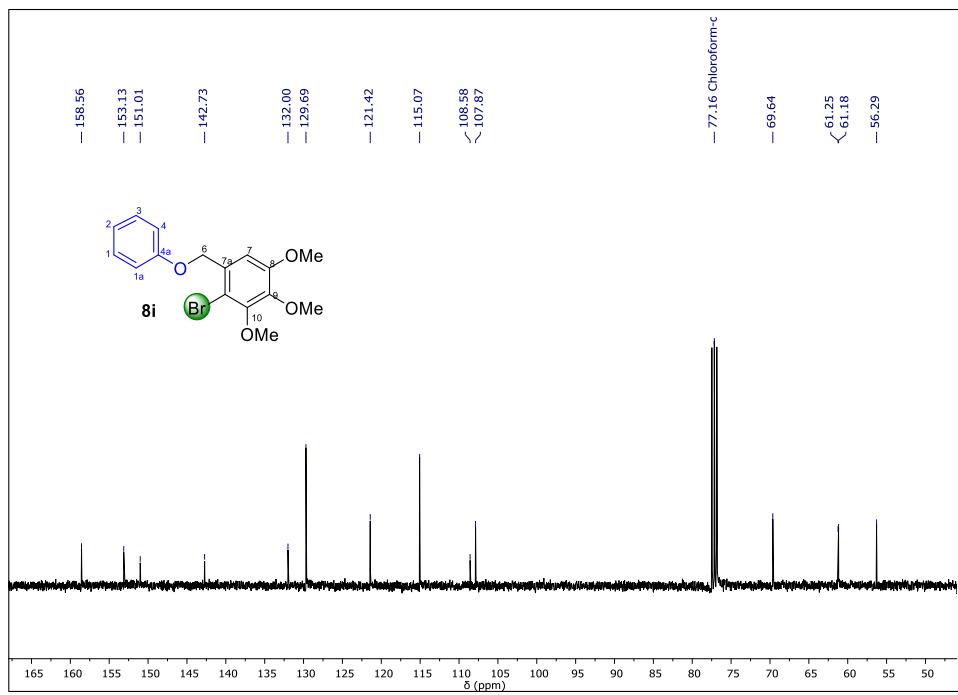


Figure ESI 21. ^1H -NMR spectrum of 4-allyl-1-((2-bromobenzyl)oxy)-2-methoxybenzene **8j**

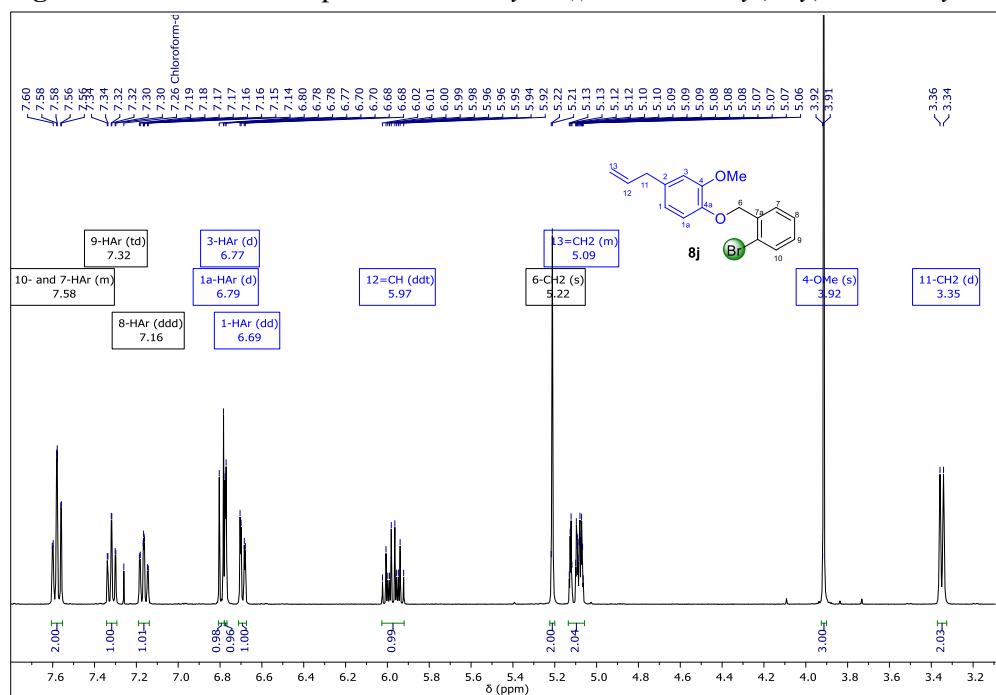


Figure ESI 22 ^{13}C -NMR spectrum of 4-allyl-1-((2-bromobenzyl)oxy)-2-methoxybenzene **8j**

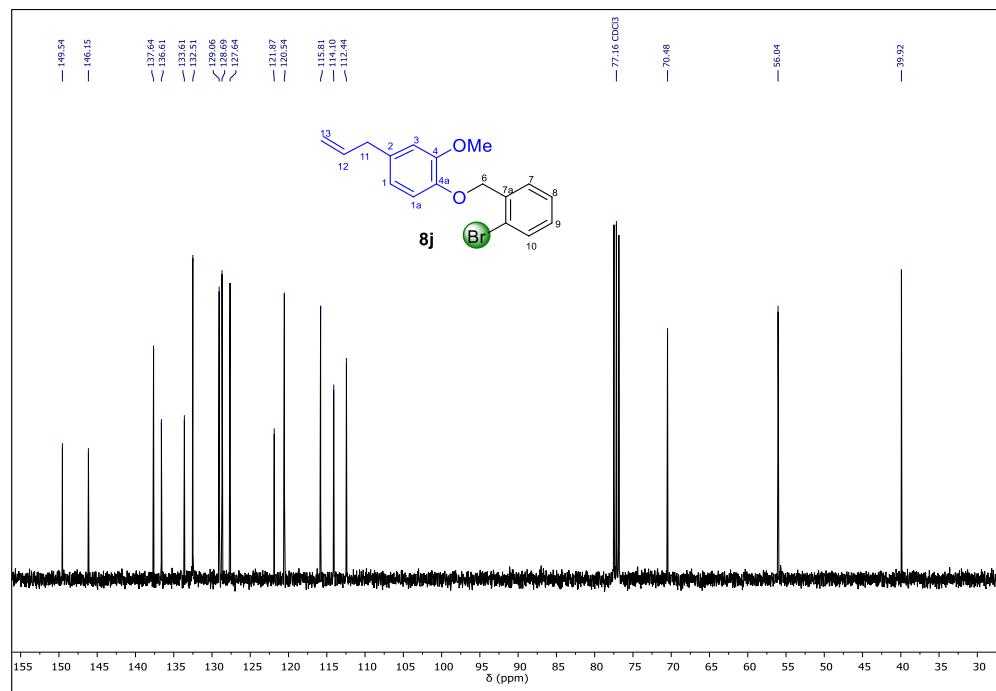


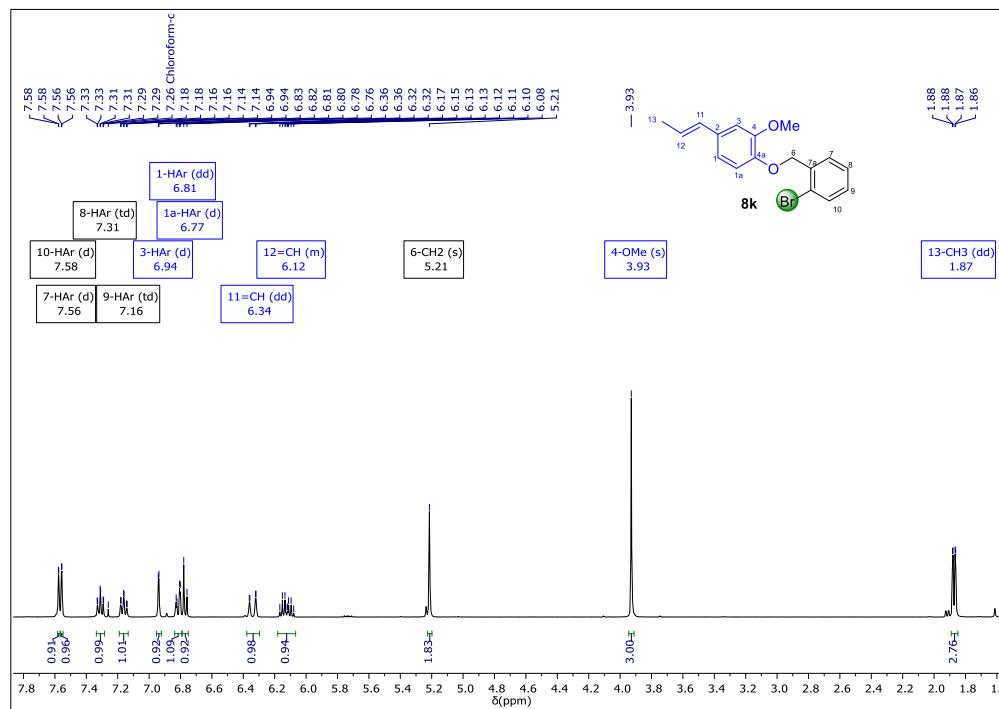
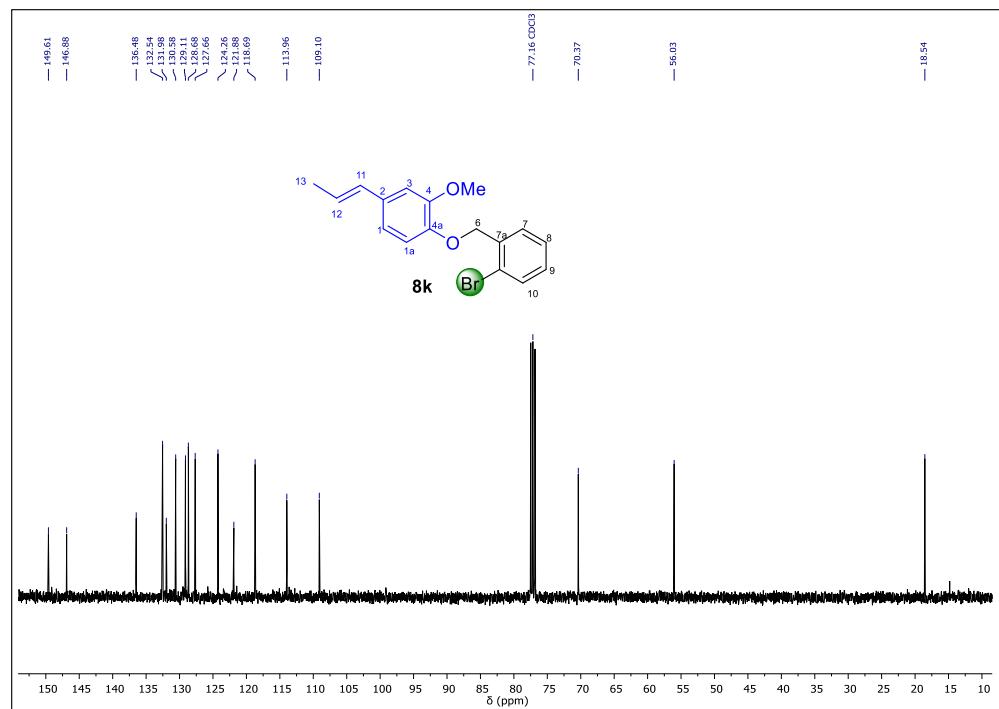
Figure ESI 23. ^1H -NMR spectrum of (*E*)-1-((2-bromobenzyl)oxy)-2-methoxy-4-(prop-1-en-1-*il*)benzene **8k****Figure ESI 24.** ^{13}C -NMR spectrum of (*E*)-1-((2-bromobenzyl)oxy)-2-methoxy-4-(prop-1-en-1-*il*)benzene **8k**

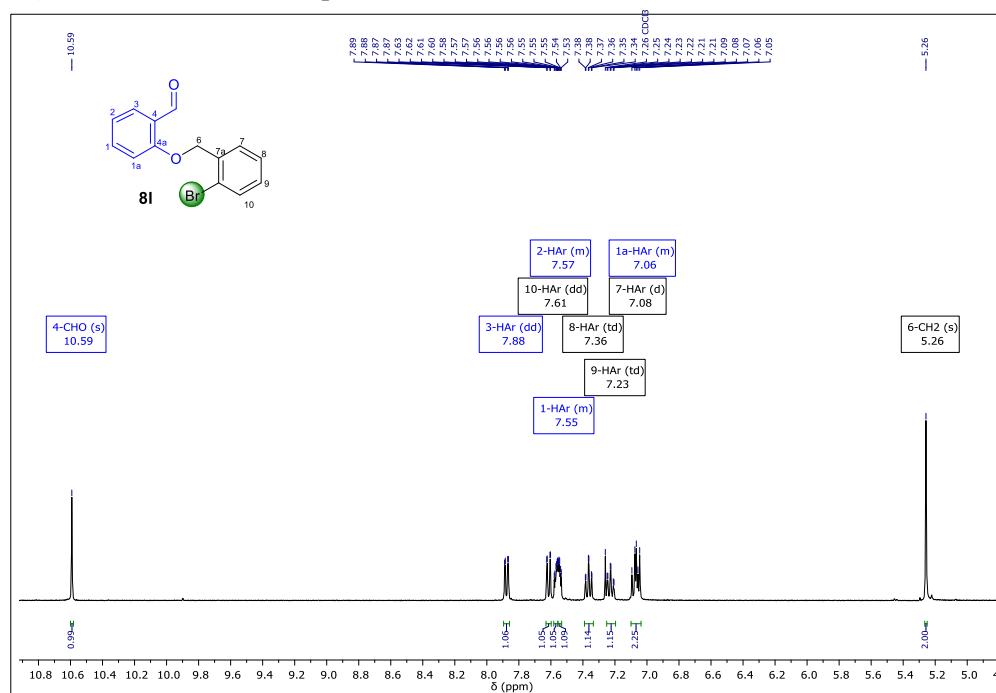
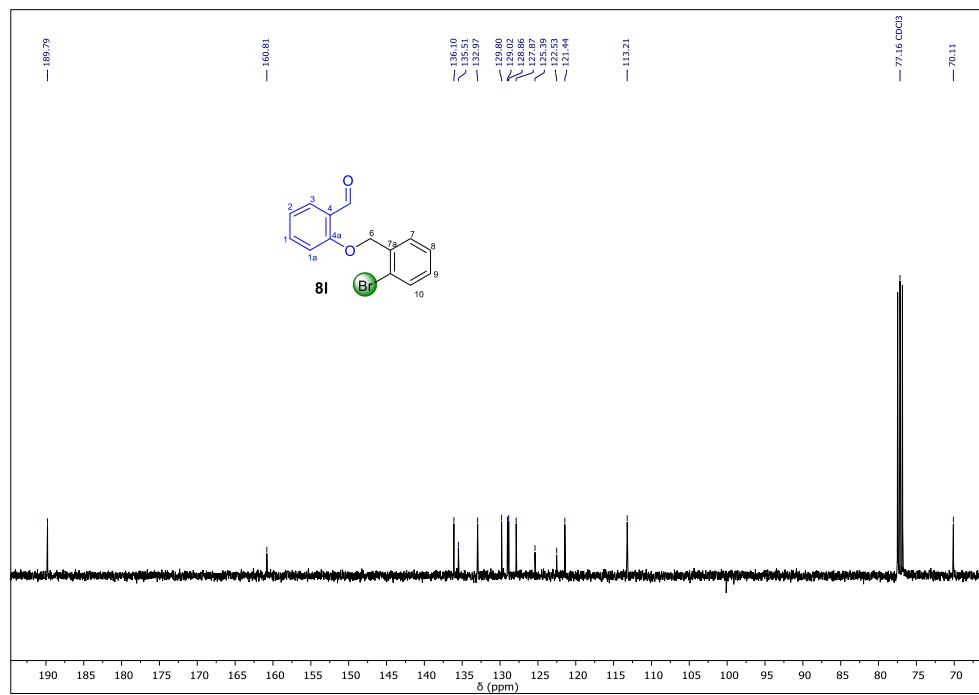
Figure ESI 25. ^1H -NMR spectrum of 2-((2-bromobenzyl)oxy)benzaldehyde **8I****Figure ESI 26.** ^{13}C -NMR spectrum of 2-((2-bromobenzyl)oxy)benzaldehyde **8I**

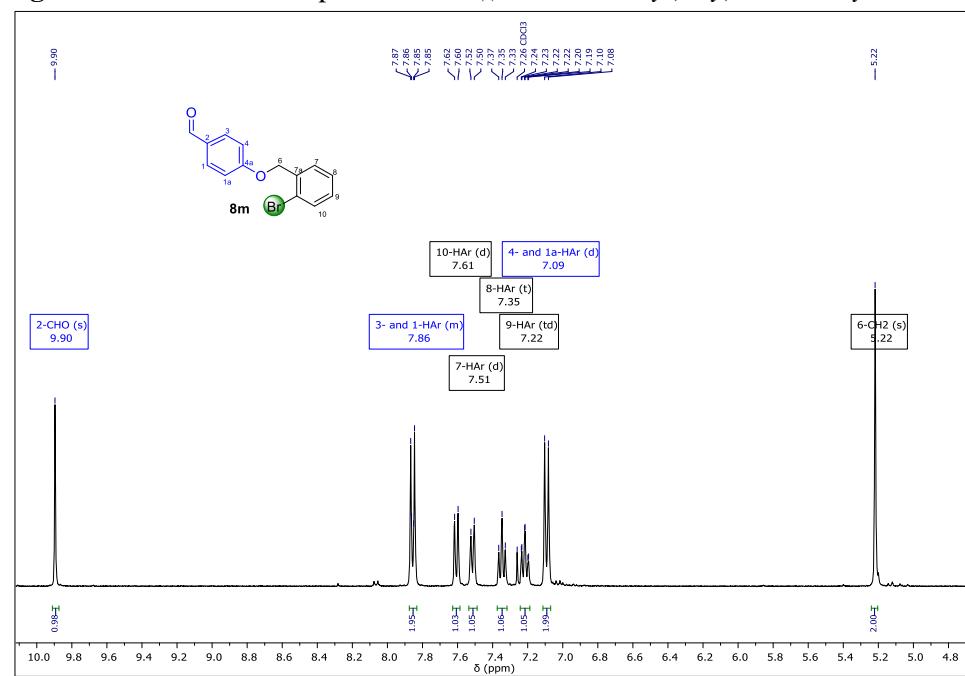
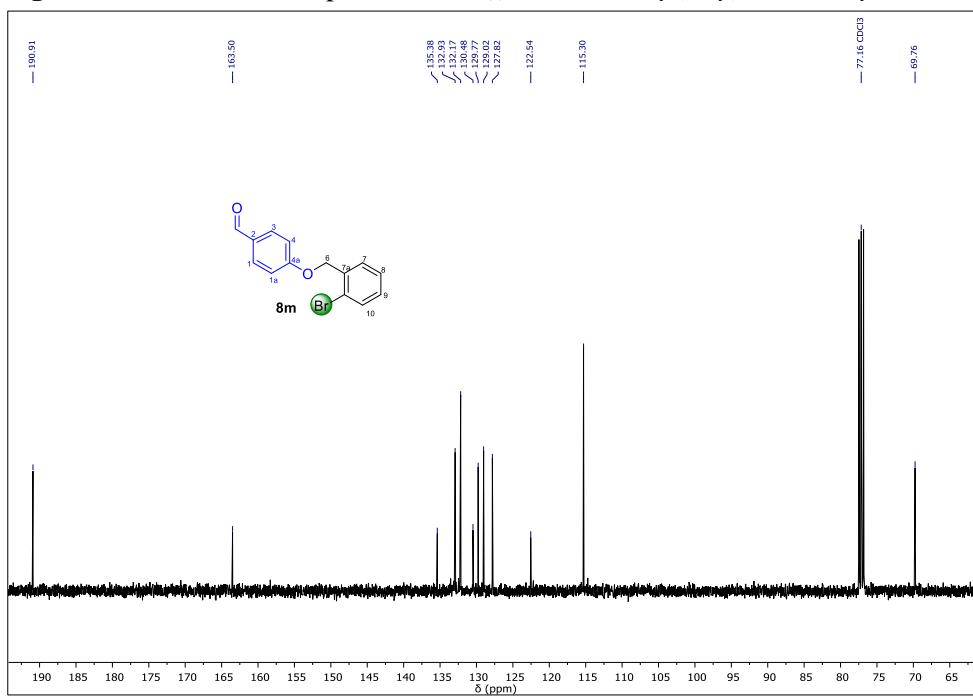
Figure ESI 27. ^1H -NMR spectrum of 4-((2-bromobenzyl)oxy)benzaldehyde **8m****Figure ESI 28.** ^{13}C -NMR spectrum of 4-((2-bromobenzyl)oxy)benzaldehyde **8m**

Figure ESI 29. ^1H -NMR spectrum of 4-((2-bromobenzyl)oxy)-3-methoxybenzaldehyde **8n**

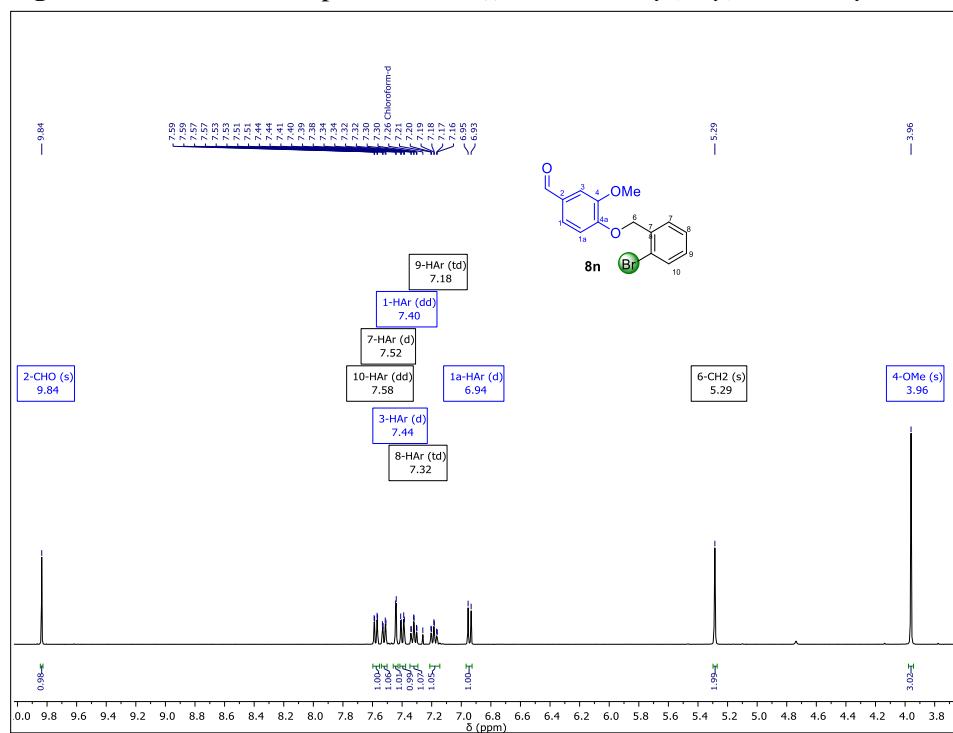


Figure ESI 30. ^{13}C -NMR spectrum of 4-((2-bromobenzyl)oxy)-3-methoxybenzaldehyde **8n**

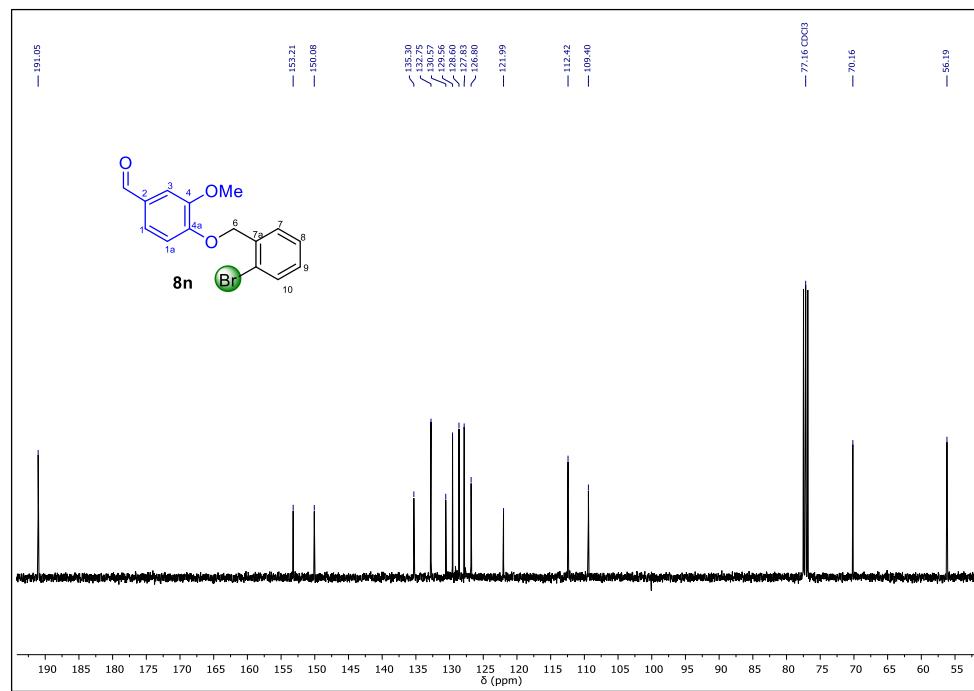


Figure ESI 31. ^1H -NMR spectrum of 3-((2-bromobenzyl)oxy)-4-methoxybenzaldehyde **8o**

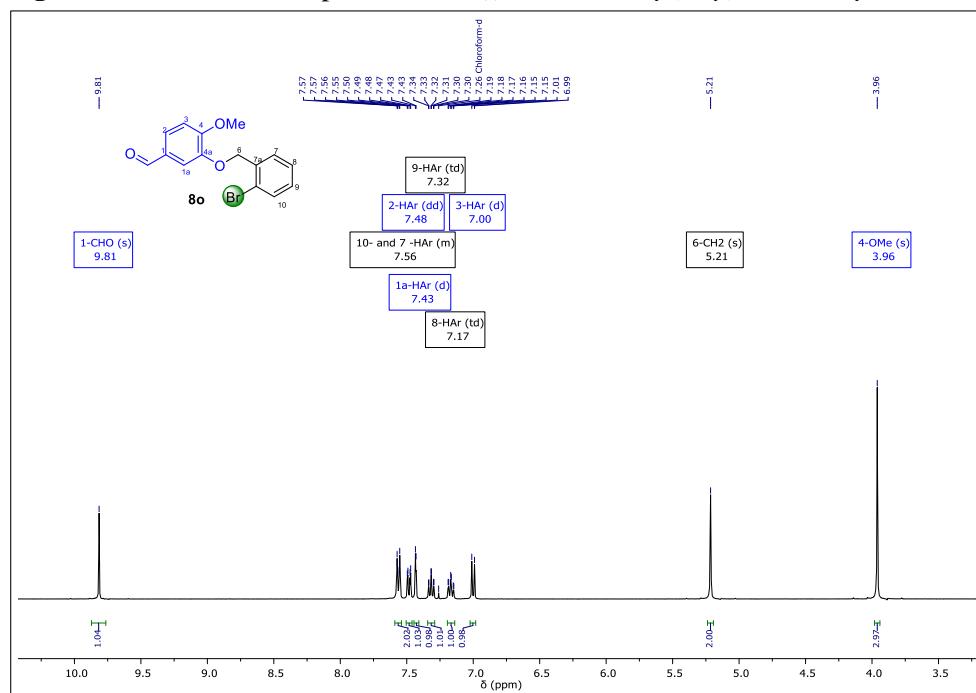


Figure ESI 32. ^{13}C -NMR spectrum of 3-((2-bromobenzyl)oxy)-4-methoxybenzaldehyde **8o**

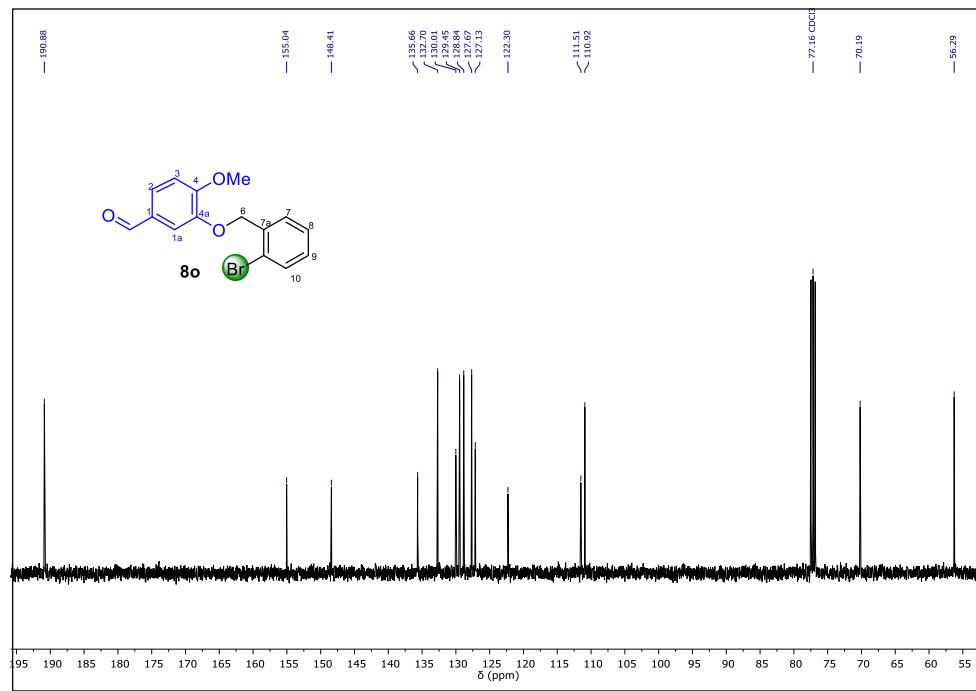


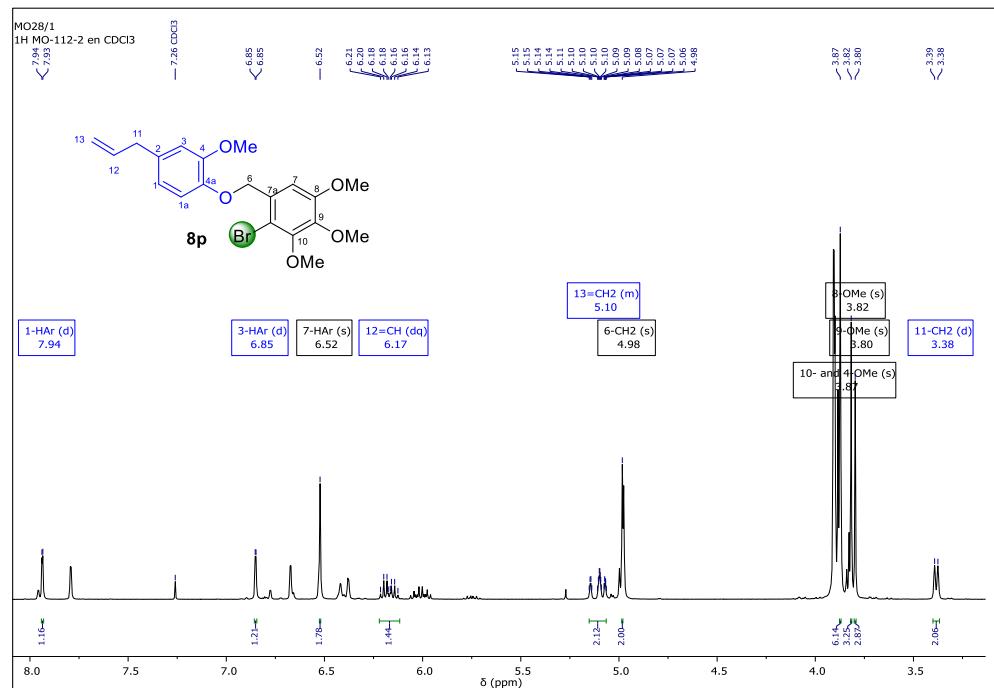
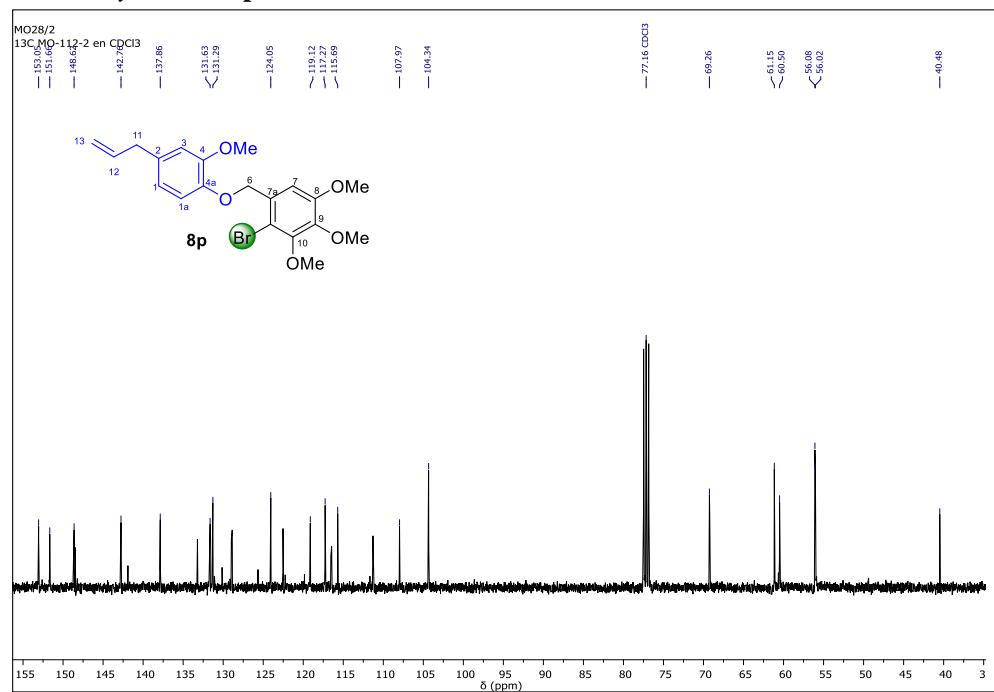
Figure ESI 33. ^1H -NMR spectrum of *1-((4-allyl-2-methoxyphenoxy)methyl)-2-bromo-3,4,5-trimethoxybenzene* **8p****Figure ESI 34.** ^{13}C -NMR spectrum of *1-((4-allyl-2-methoxyphenoxy)methyl)-2-bromo-3,4,5-trimethoxybenzene* **8p**

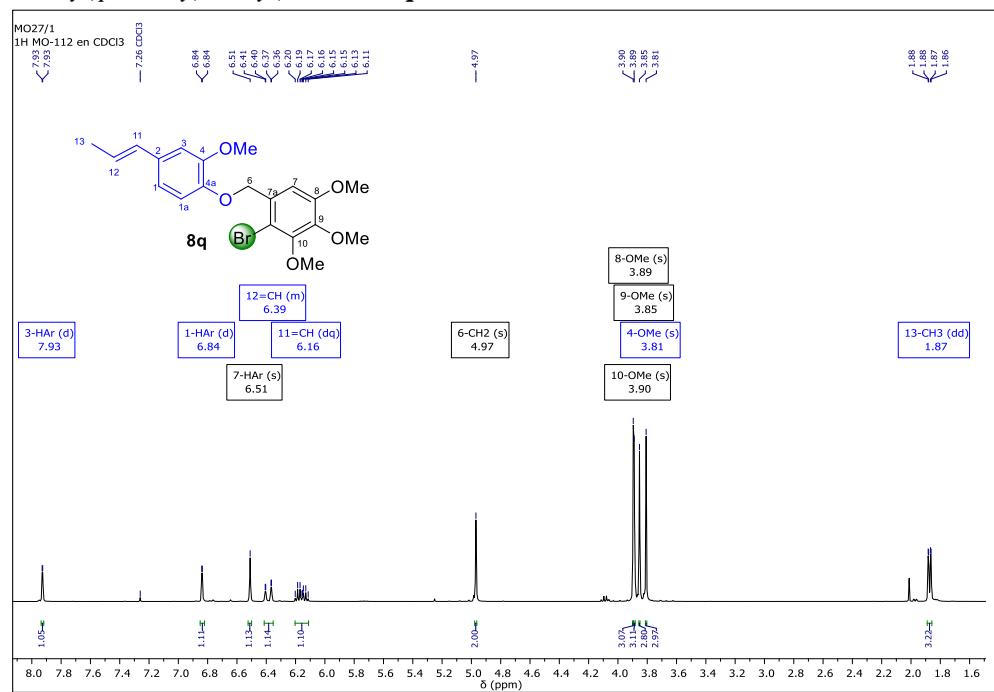
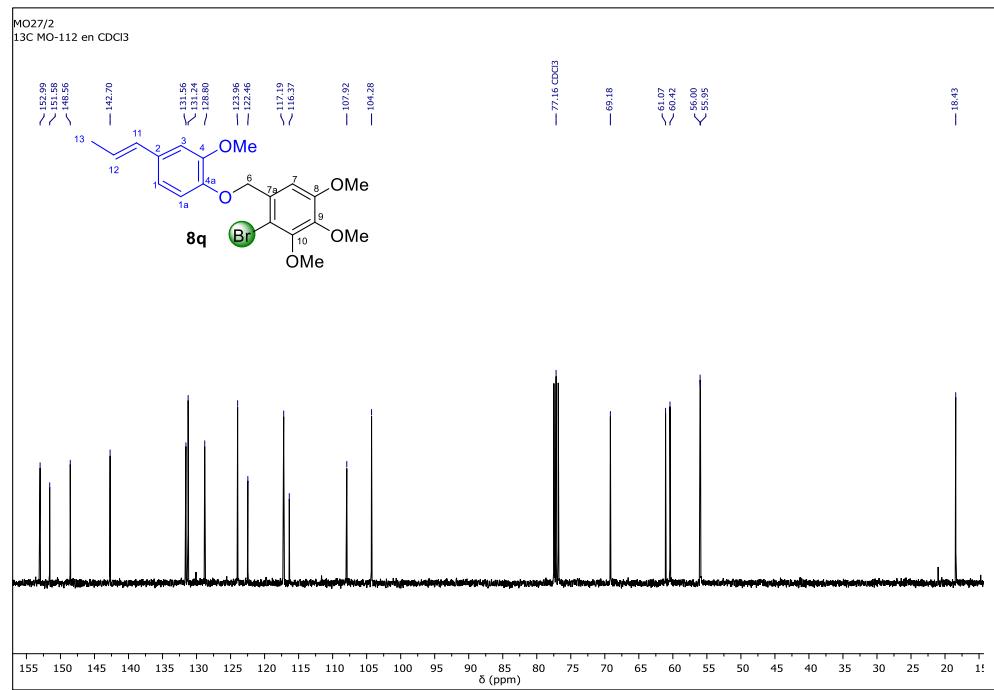
Figure ESI 35. ^1H -NMR spectrum of (*E*)-2-bromo-3,4,5-trimethoxy-1-((2-methoxy-4-(prop-1-en-1-yl)phenoxy)methyl)benzene **8q****Figure ESI 36.** ^{13}C -NMR spectrum of (*E*)-2-bromo-3,4,5-trimethoxy-1-((2-methoxy-4-(prop-1-en-1-yl)phenoxy)methyl)benzene **8q**

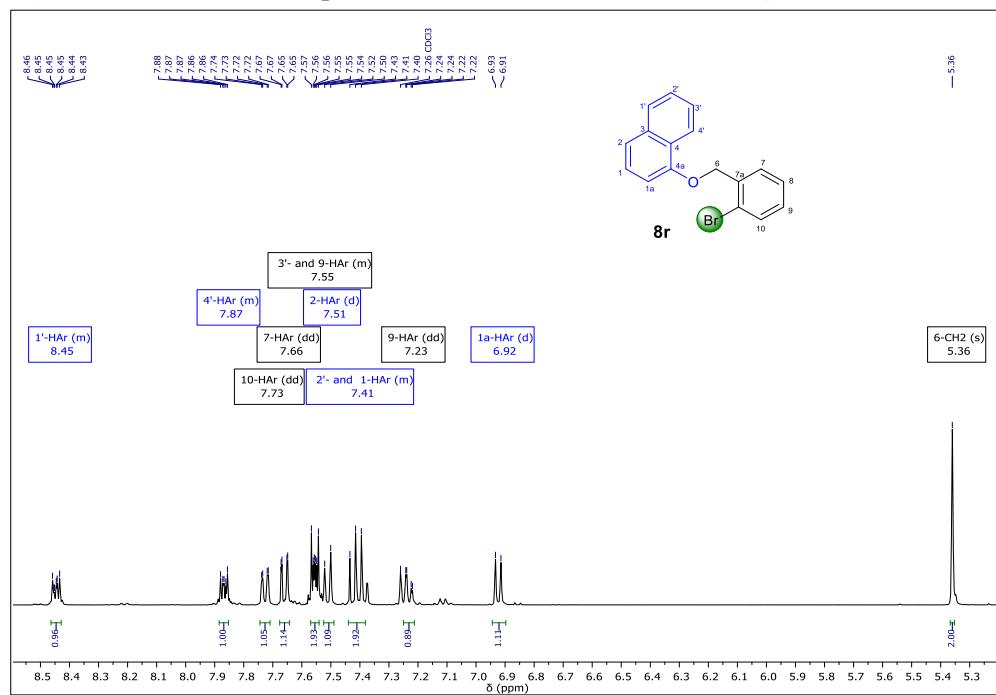
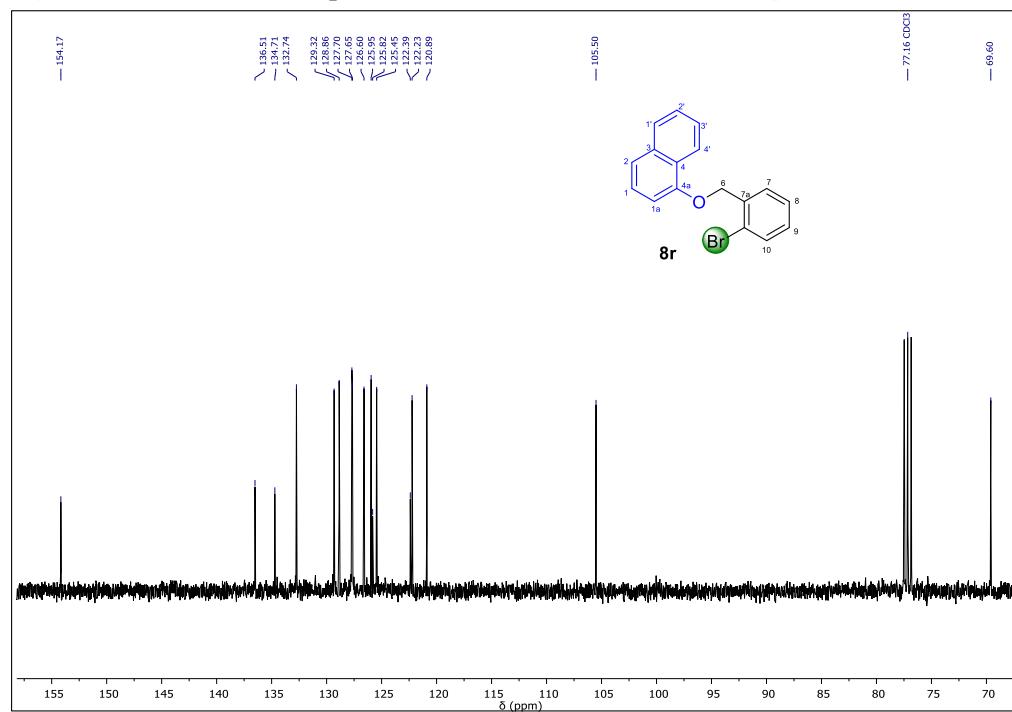
Figure ESI 37. ^1H -NMR spectrum of *1-((2-bromobenzyl)oxy)napthalene* **8r****Figure ESI 38.** ^{13}C -NMR spectrum of *1-((2-bromobenzyl)oxy)napthalene* **8r**

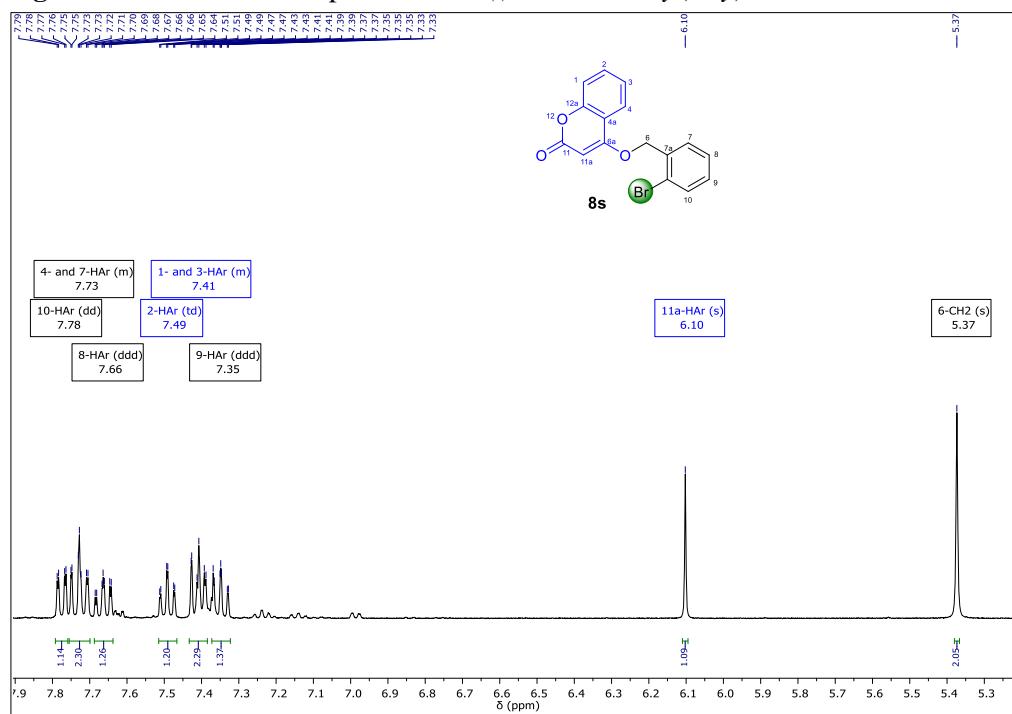
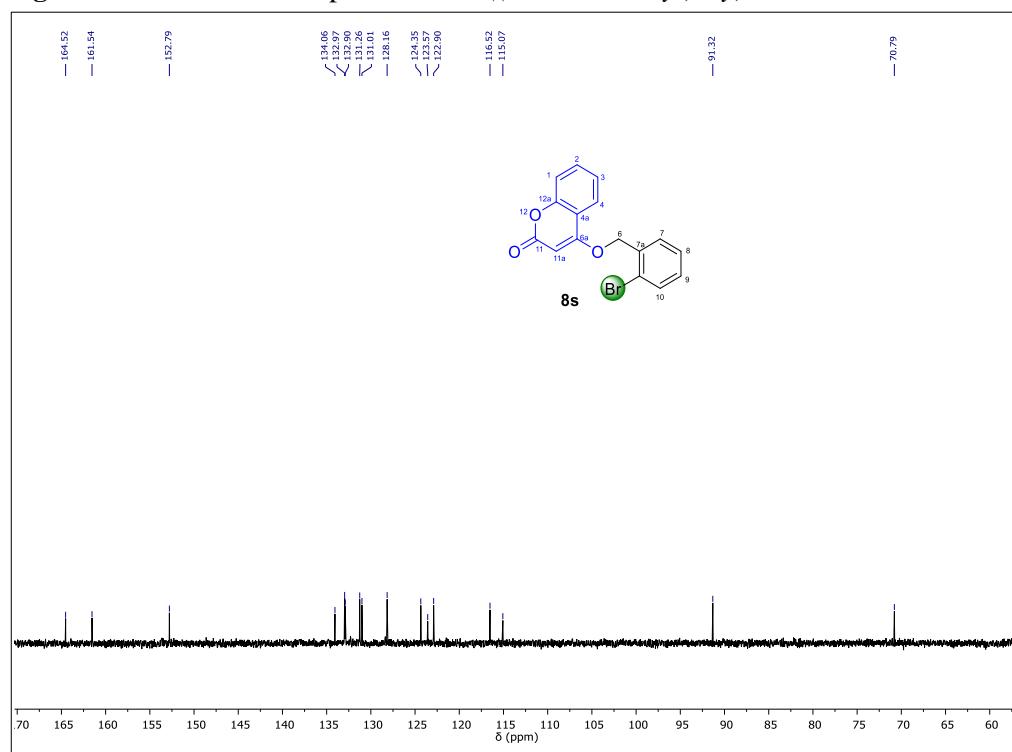
Figure ESI 39. ^1H -NMR spectrum of 4-((2-bromobenzyl)oxy)-2*H*-chromen-2-one **8s****Figure ESI 40.** ^{13}C -NMR spectrum of 4-((2-bromobenzyl)oxy)-2*H*-chromen-2-one **8s**

Figure ESI 41. ^1H -NMR spectrum of *8-((2-bromobenzyl)oxy)quinoline 8t*

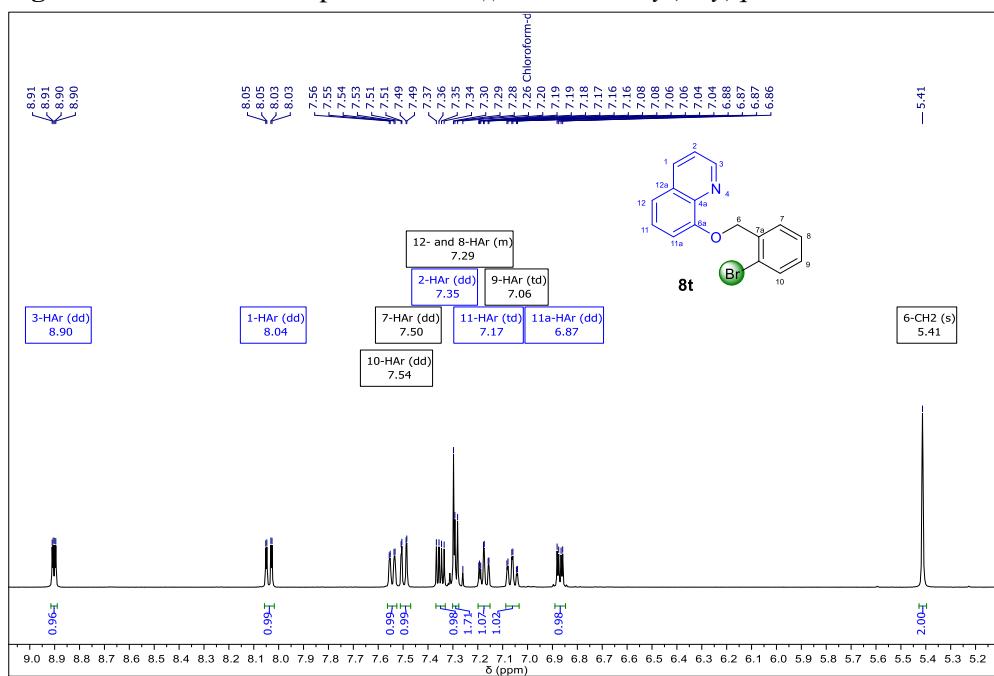


Figure ESI 42. ^{13}C -NMR spectrum of *8-((2-bromobenzyl)oxy)quinoline 8t*

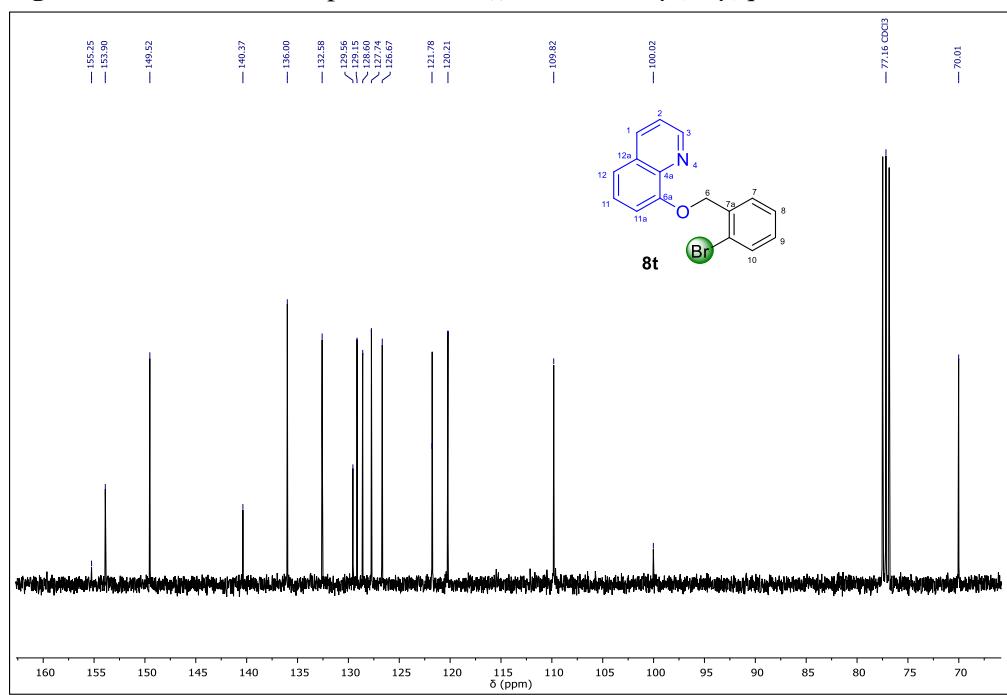


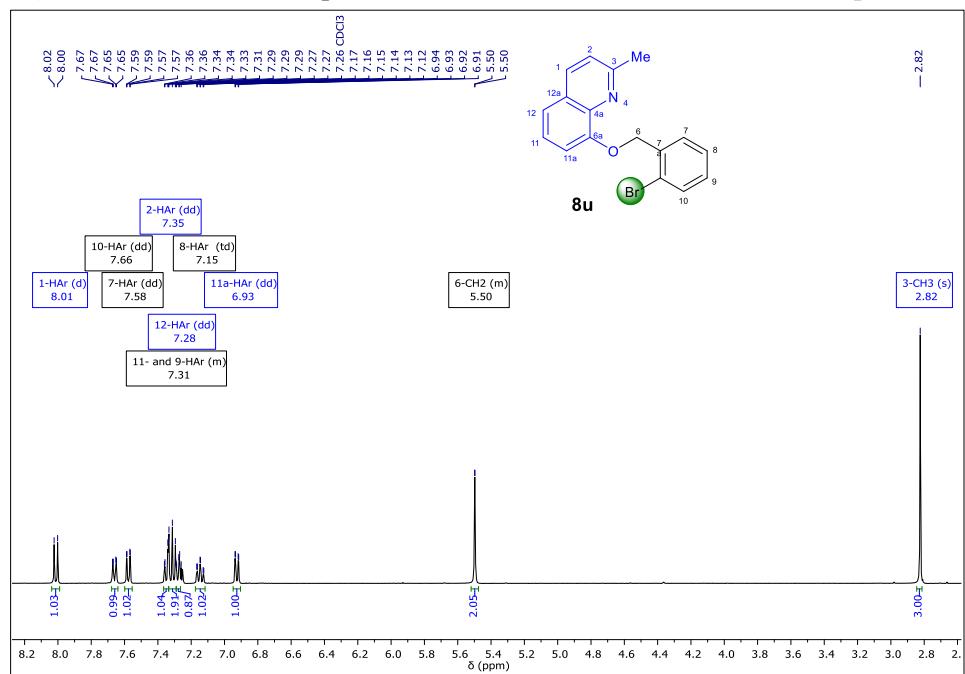
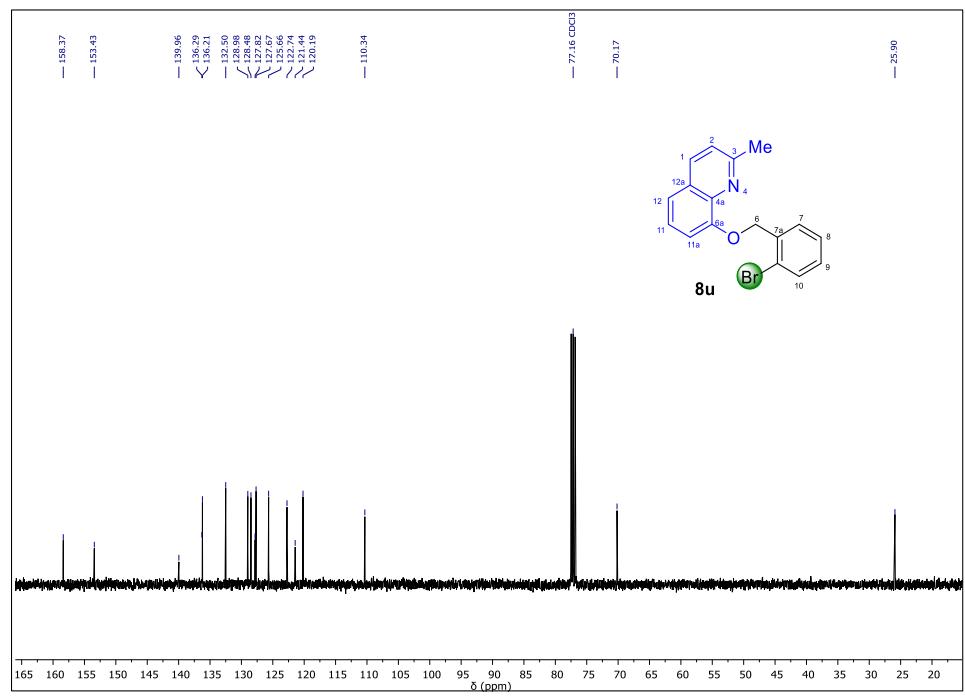
Figure ESI 43. ^1H -NMR spectrum of 8-((2-bromobenzyl)oxy)-2-methylquinoline **8u****Figure ESI 44.** ^{13}C -NMR spectrum of 8-((2-bromobenzyl)oxy)-2-methylquinoline **8u**

Figure ESI 45. ^1H -NMR spectrum of 8-((2-bromobenzyl)oxy)-5-chloroquinoline **8v**

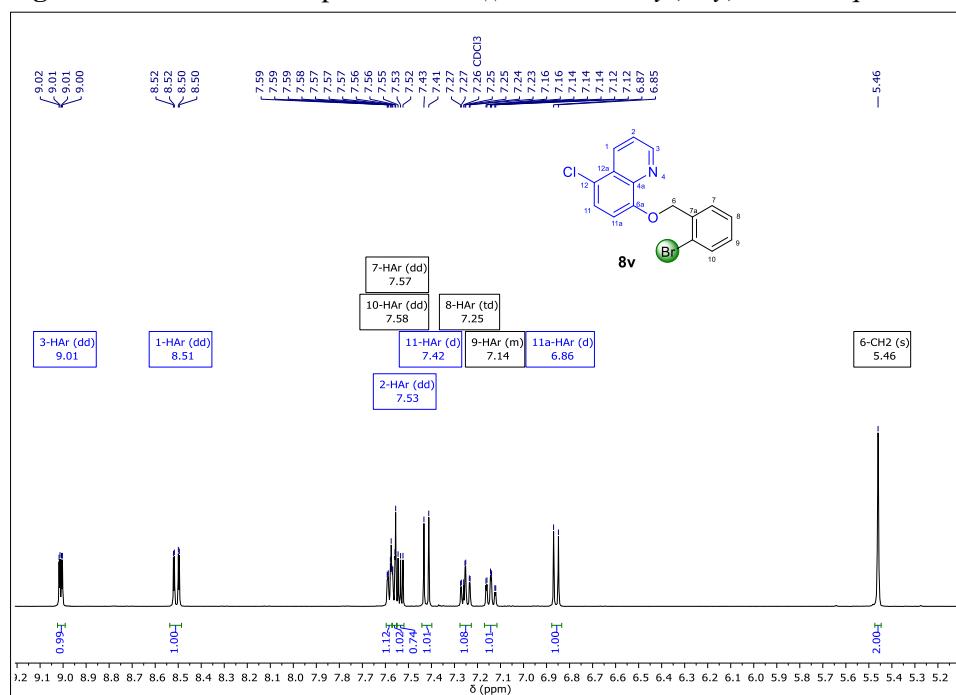


Figure ESI 46. ^{13}C -NMR spectrum of 8-((2-bromobenzyl)oxy)-5-chloroquinoline **8v**

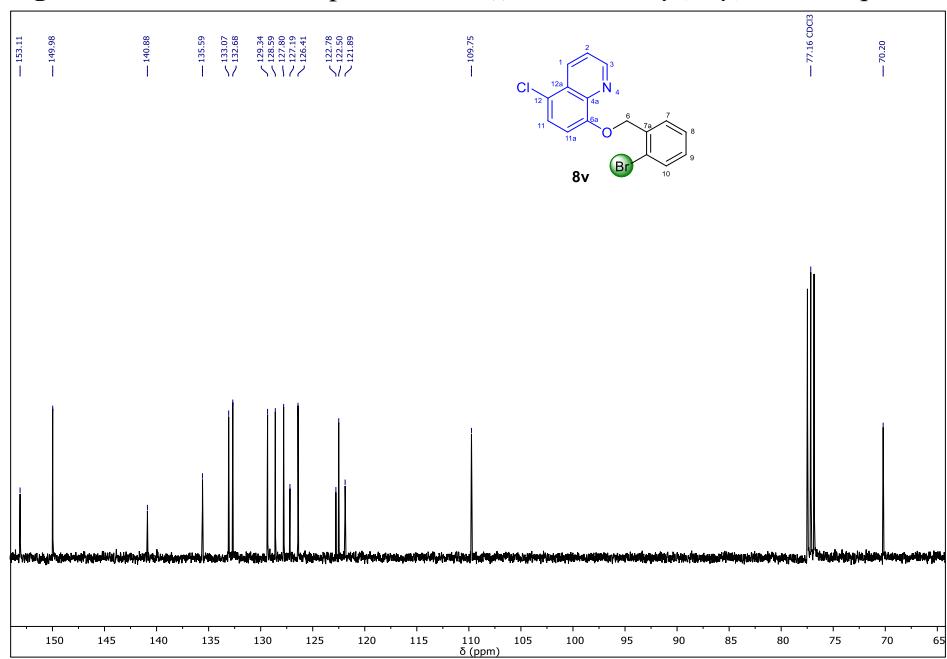


Figure ESI 47. ^1H -NMR spectrum of 2-(benzyloxy)-3-bromo-1-isopropyl-4-methylbenzene **19**

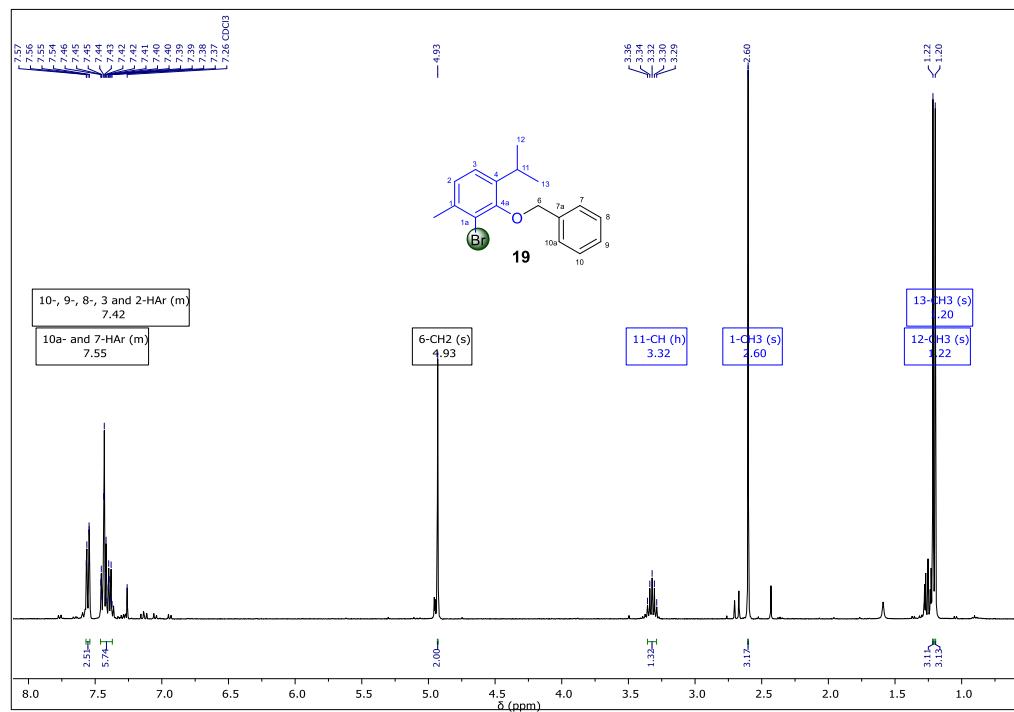
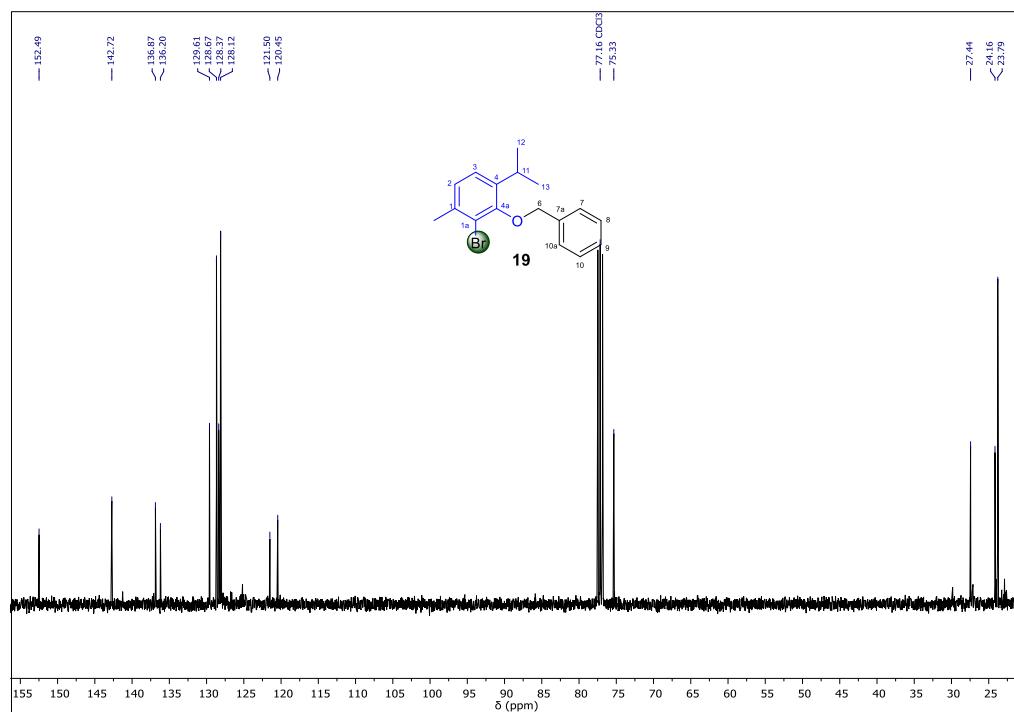


Figure ESI 48. ^{13}C -NMR spectrum of 2-(benzyloxy)-3-bromo-1-isopropyl-4-methylbenzene **19**



8. Copies of ^1H NMR, ^{13}C NMR, COSY, HSQC and HMBC charts of 9a-v.

Figure ESI 49. ^1H -NMR spectrum of 6H-benzo[c]chromene 9a

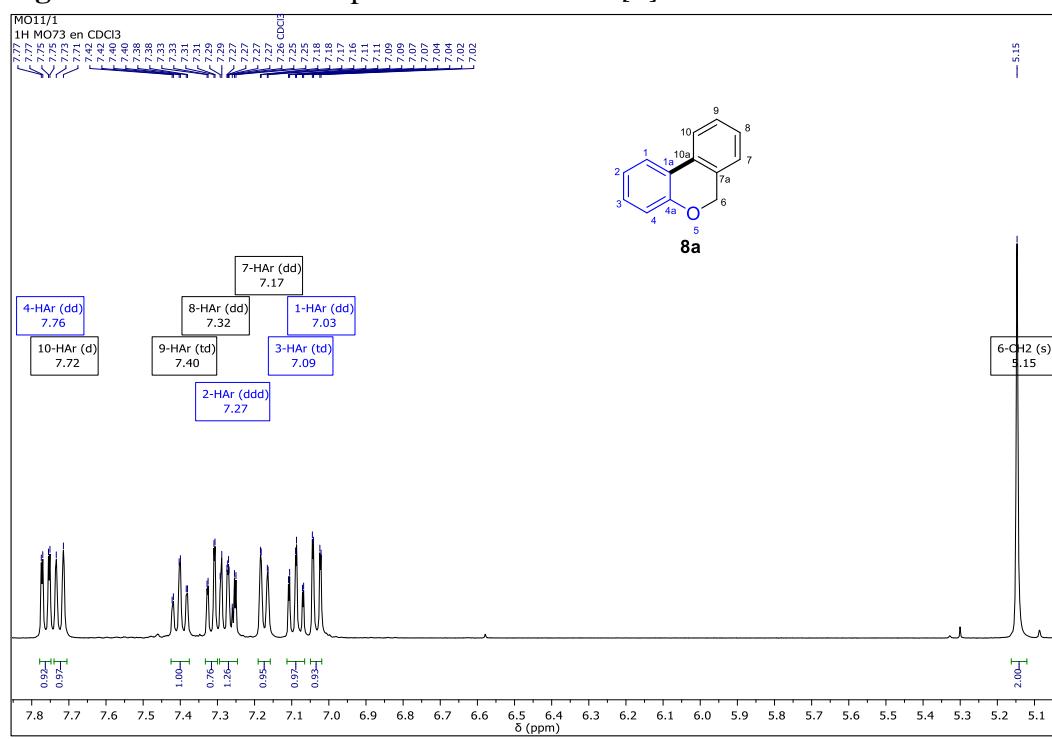


Figure ESI 50. ^{13}C -NMR spectrum of 6H-benzo[c]chromene 9a

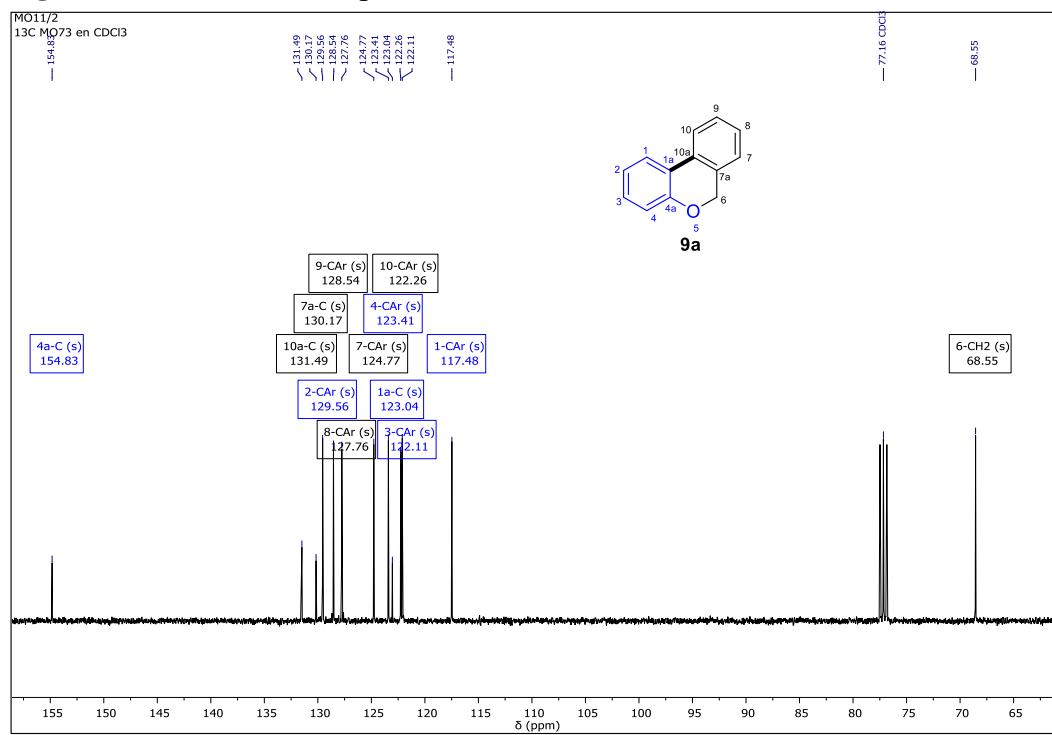


Figure ESI 51. COSY spectrum of *6H-benzo[c]chromene 9a*

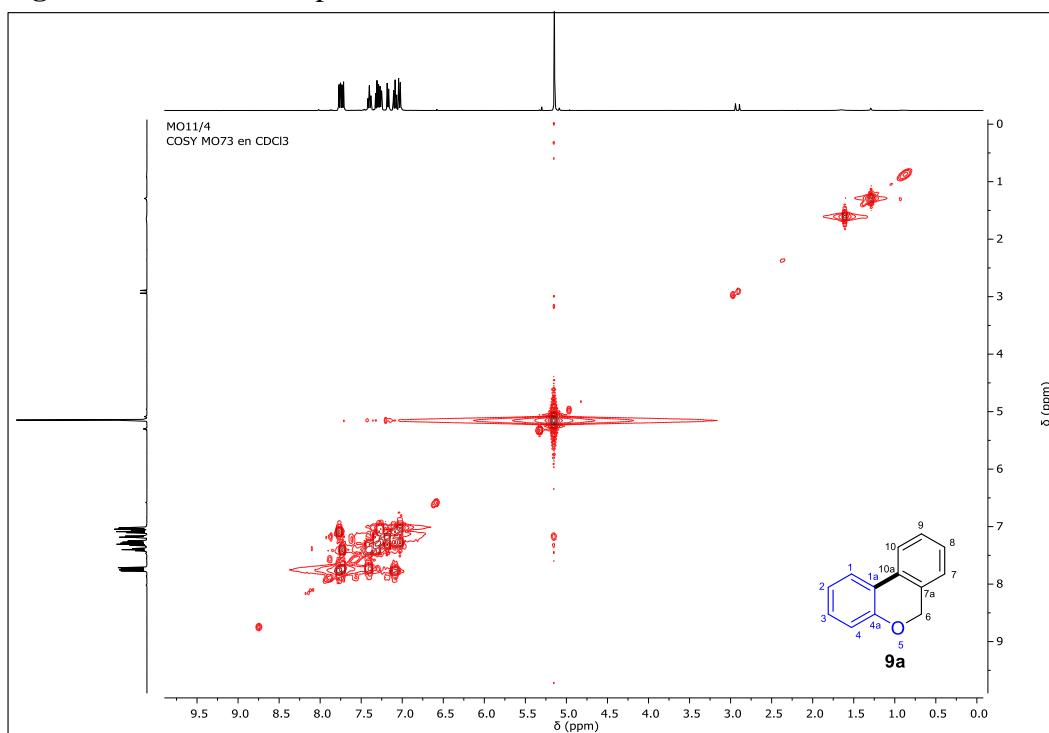


Figure ESI 52. HSQC spectrum of *6H-benzo[c]chromene 9a*

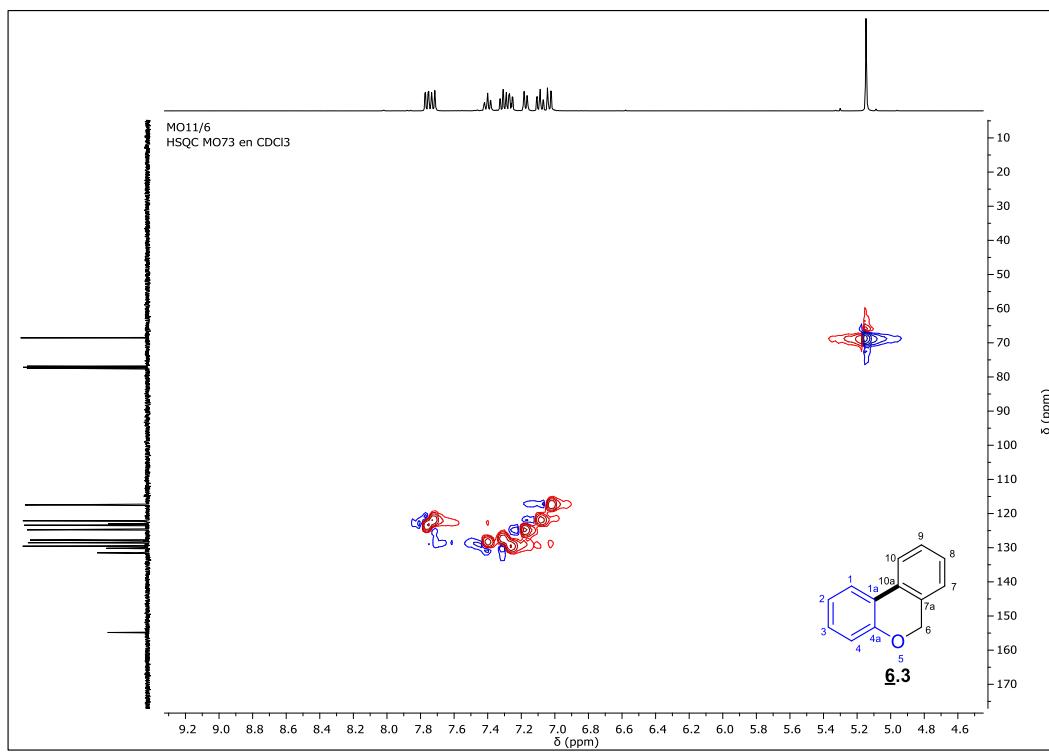


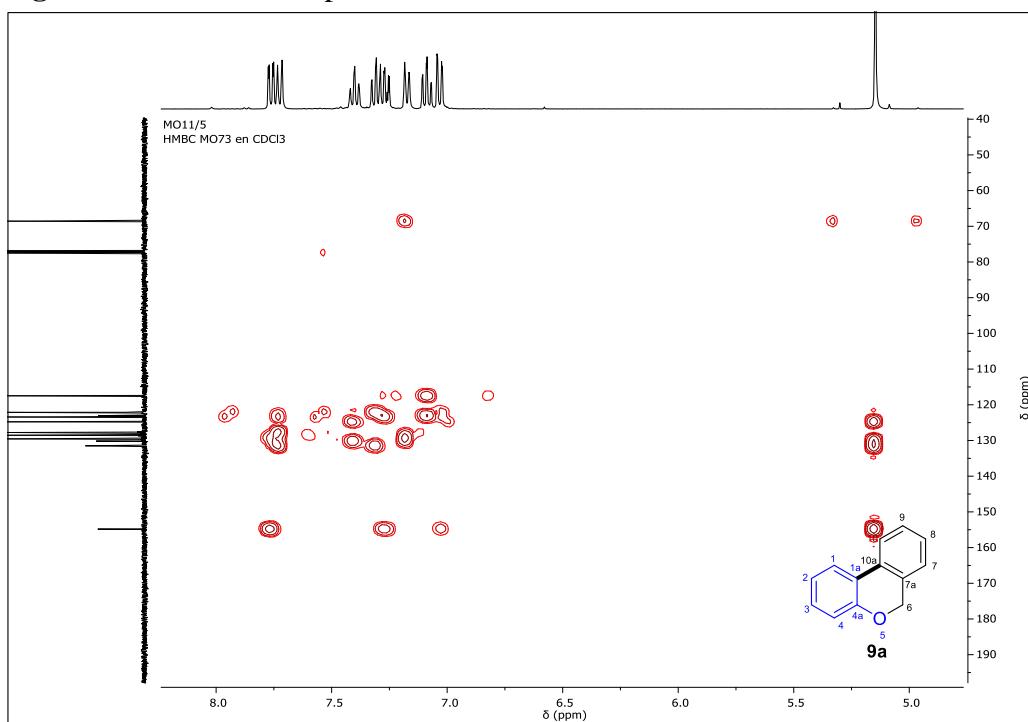
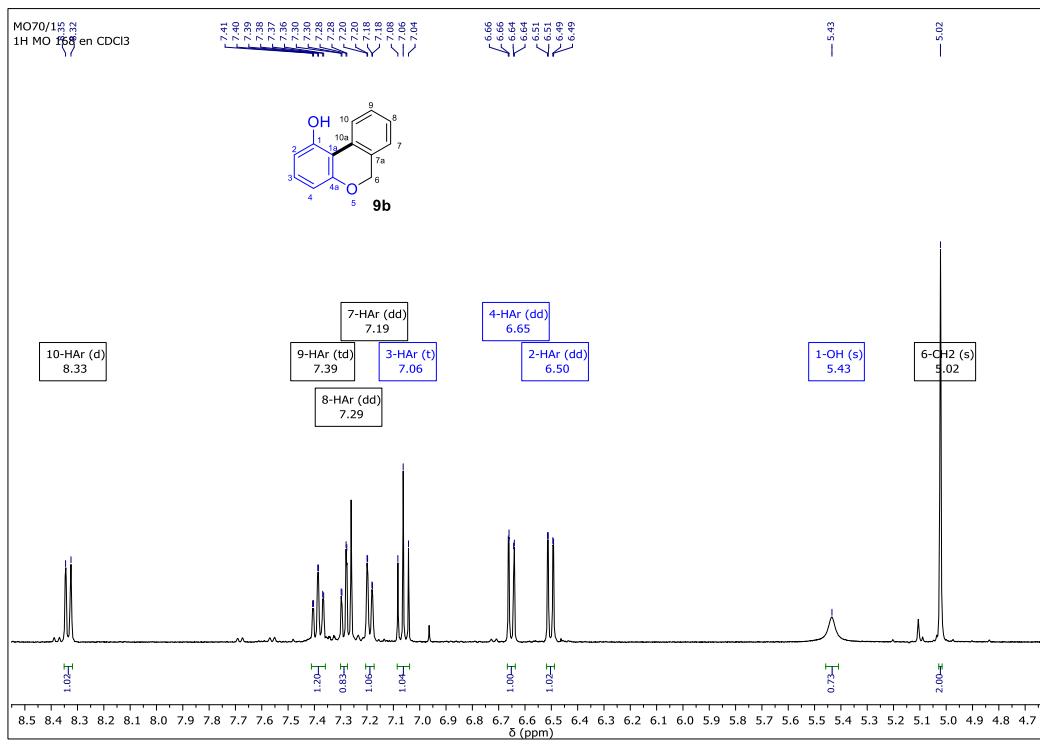
Figure ESI 53. HMBC spectrum of *6H-benzo[c]chromene* **9a****Figure ESI 54.** ¹H-NMR spectrum of *6H-benzo[c]chromen-1-ol* **9b**

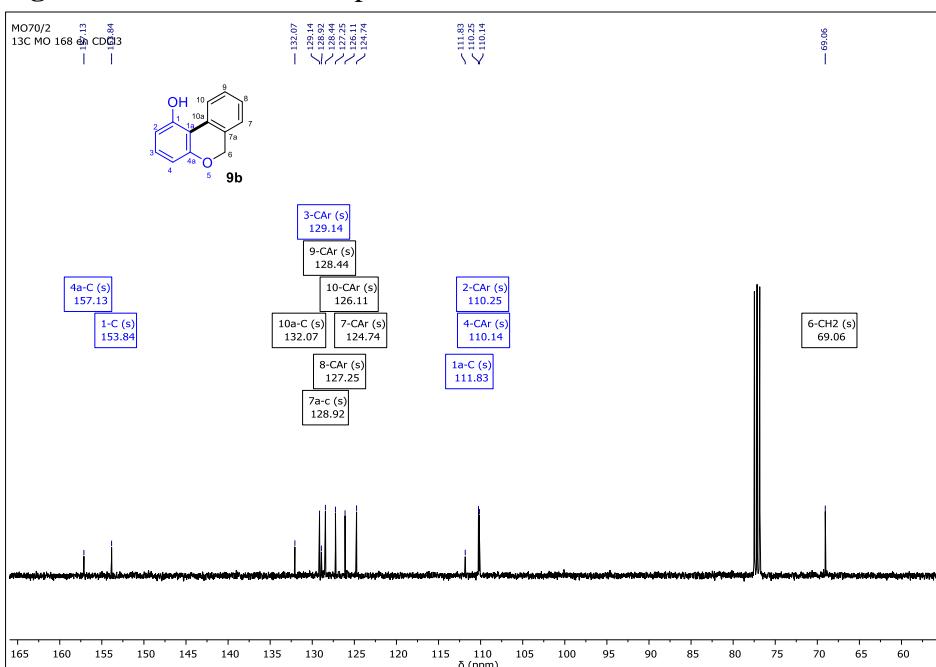
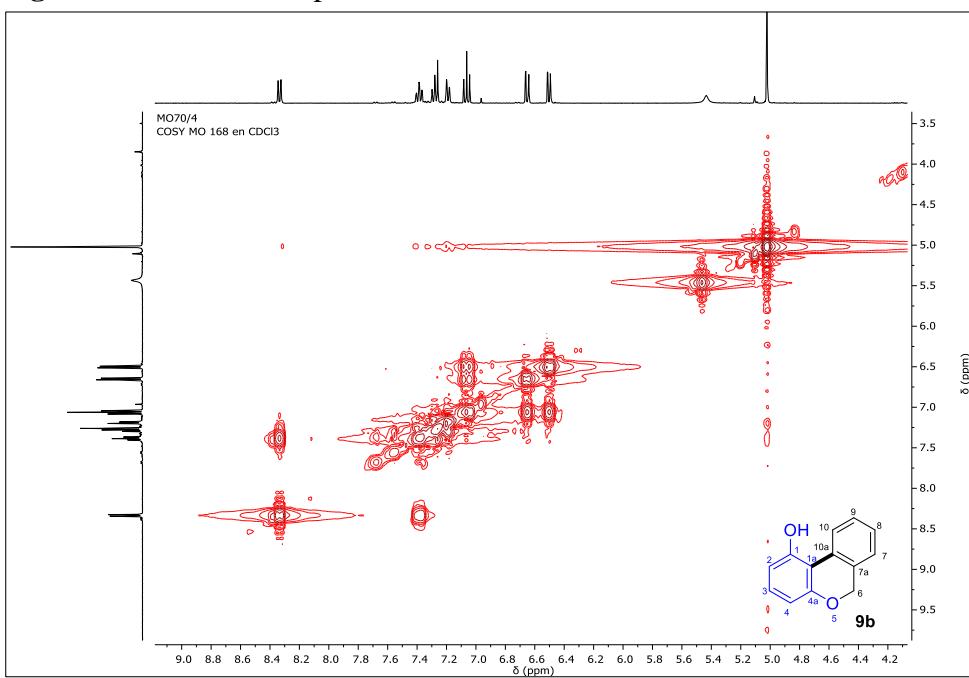
Figure ESI 55. ^{13}C -NMR spectrum of *6H-benzo[c]cromen-1-ol* **9b****Figure ESI 56.** COSY spectrum of *6H-benzo[c]cromen-1-ol* **9b**

Figure ESI 57. HSQC spectrum of *6H-benzo[c]cromen-1-ol* **9b**

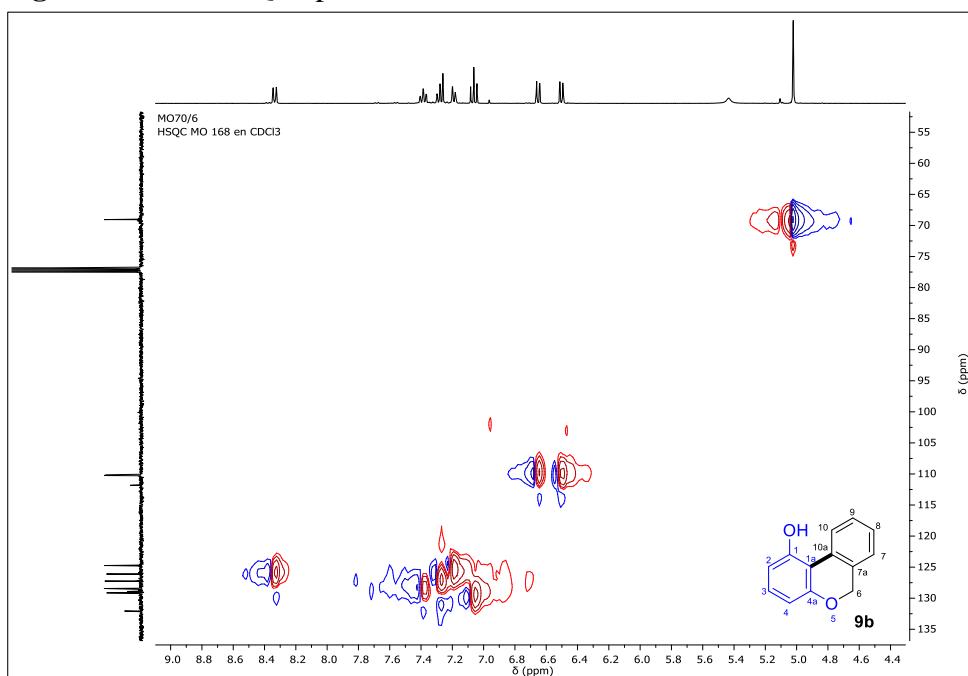


Figure ESI 58. HMBC spectrum of *6H-benzo[c]cromen-1-ol* **9b**

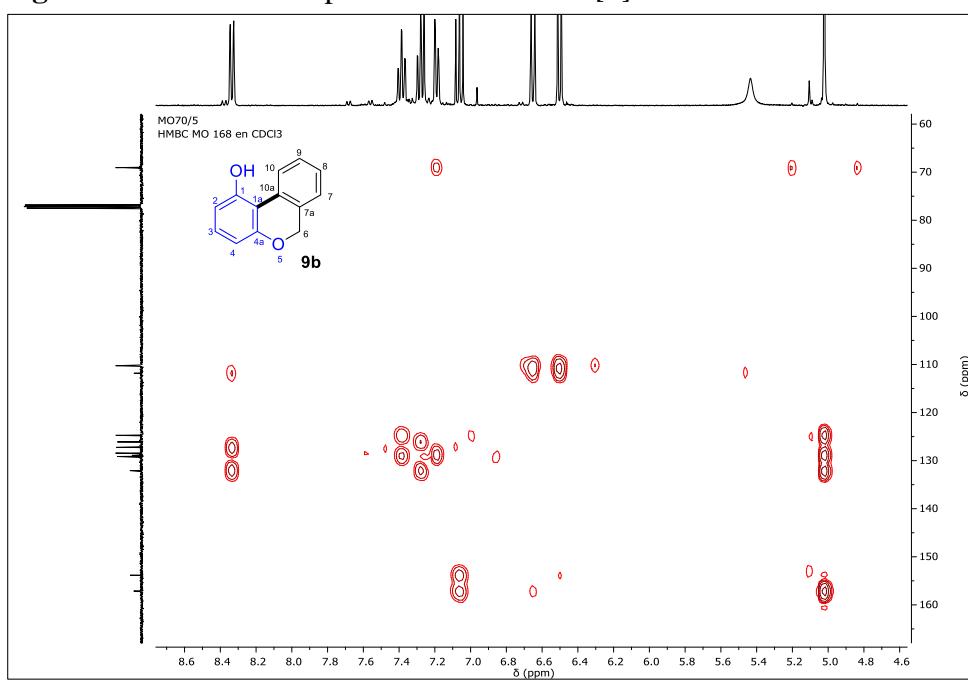


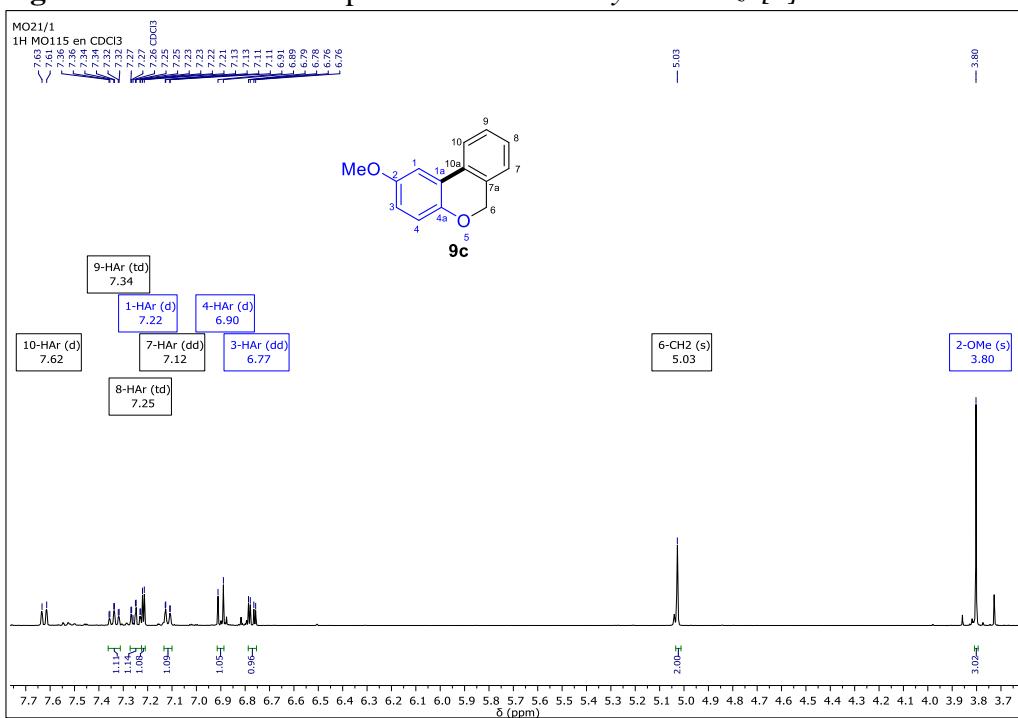
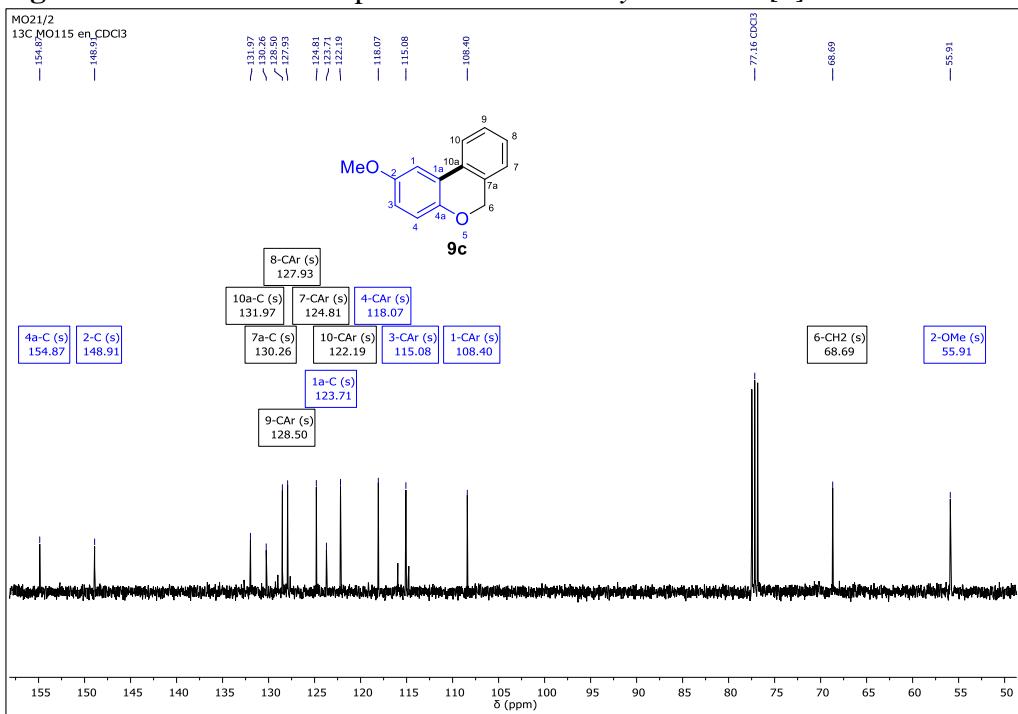
Figure ESI 59. ^1H -NMR spectrum of 2-methoxy-6H-benzo[c]chromene **9c****Figure ESI 60.** ^{13}C -NMR spectrum of 2-methoxy-6H-benzo[c]chromene **9c**

Figure ESI 61. COSY spectrum of 2-methoxy-6H-benzo[c]chromene **9c**

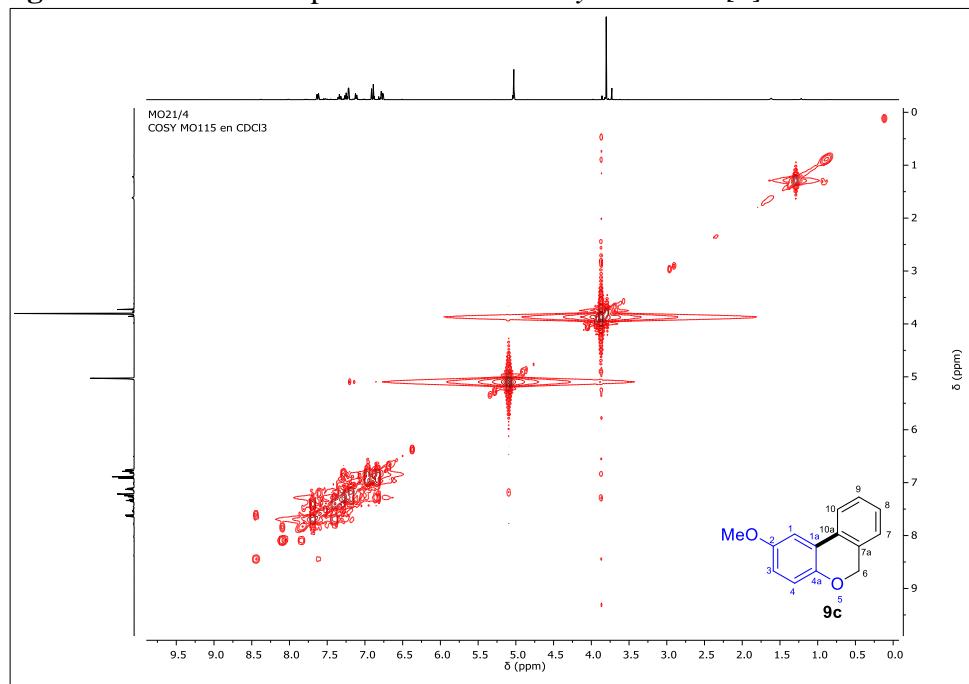


Figure ESI 62. HSQC spectrum of 2-methoxy-6H-benzo[c]chromene **9c**

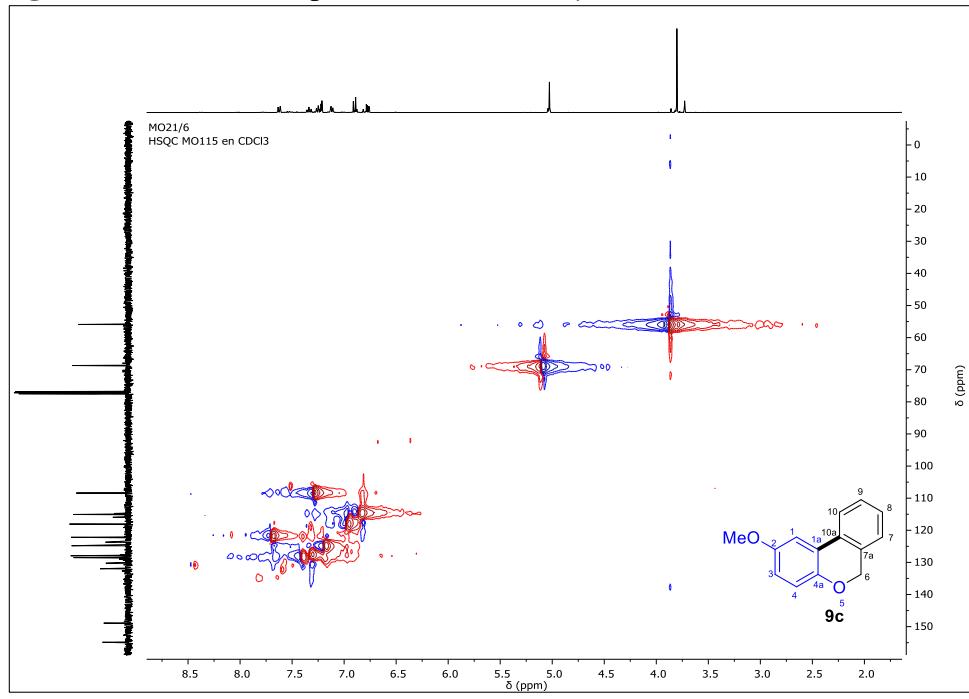


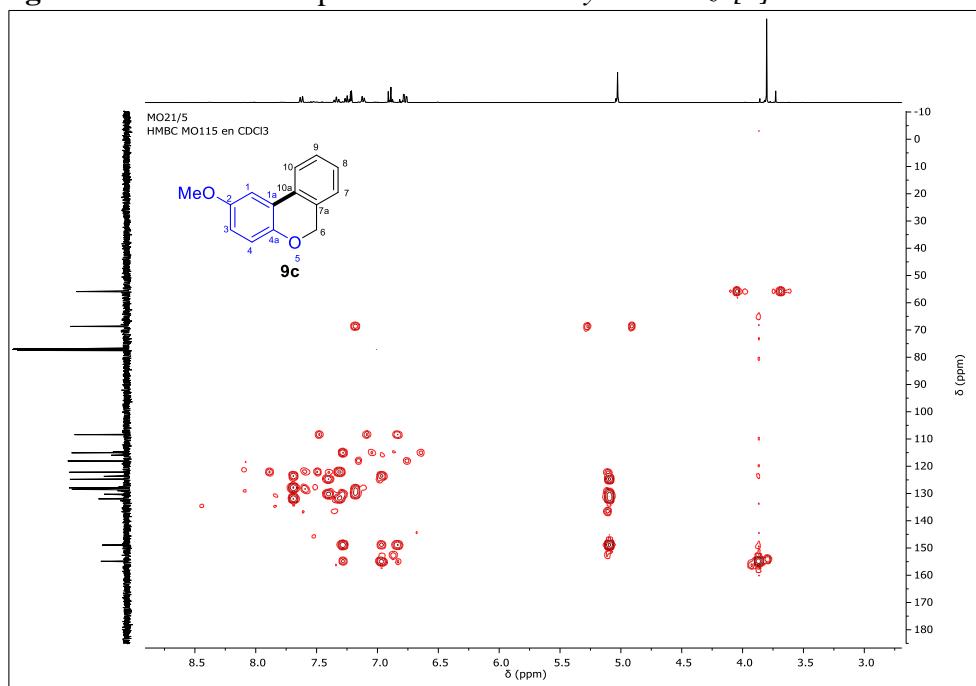
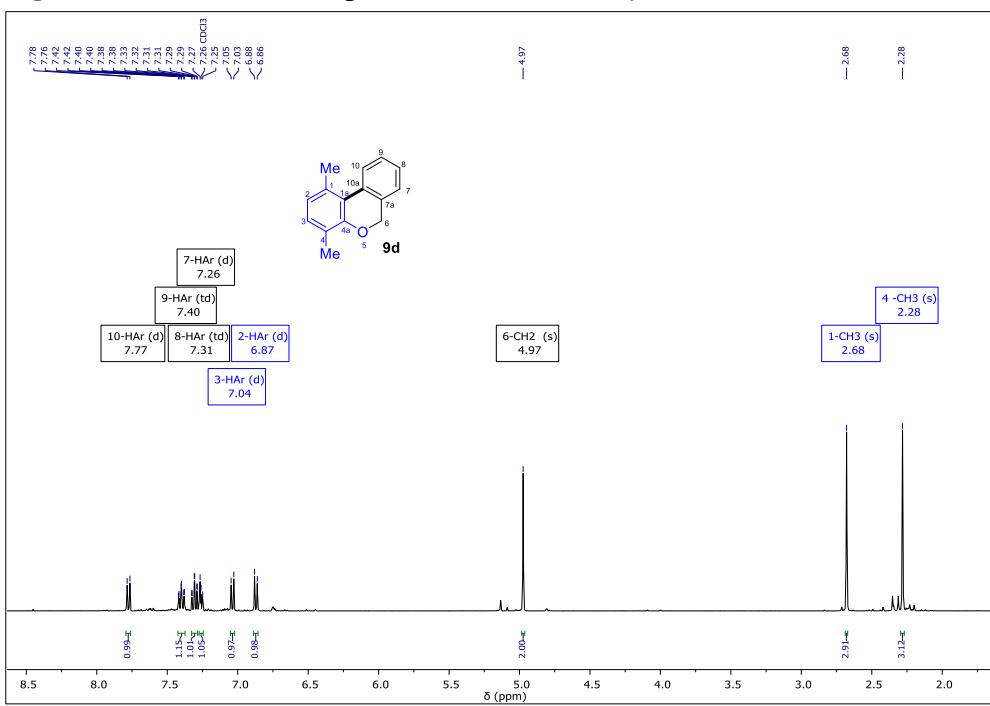
Figure ESI 63. HMBC spectrum of *2-methoxy-6H-benzo[c]chromene* **9c****Figure ESI 64.** ^1H -NMR spectrum of *1,4-dimethyl-6H-benzo[c]chromene* **9d**

Figure ESI 65. ^{13}C -NMR spectrum of *1,4-dimethyl-6H-benzo[c]chromene 9d*

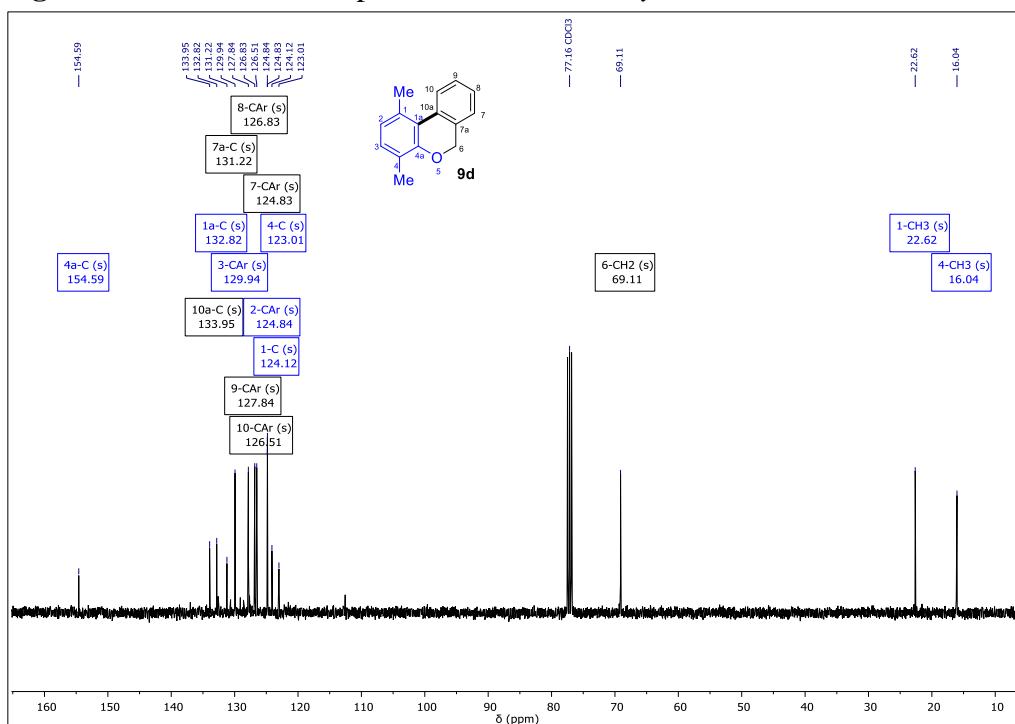


Figure ESI 66. COSY spectrum of *1,4-dimethyl-6H-benzo[c]chromene 9d*

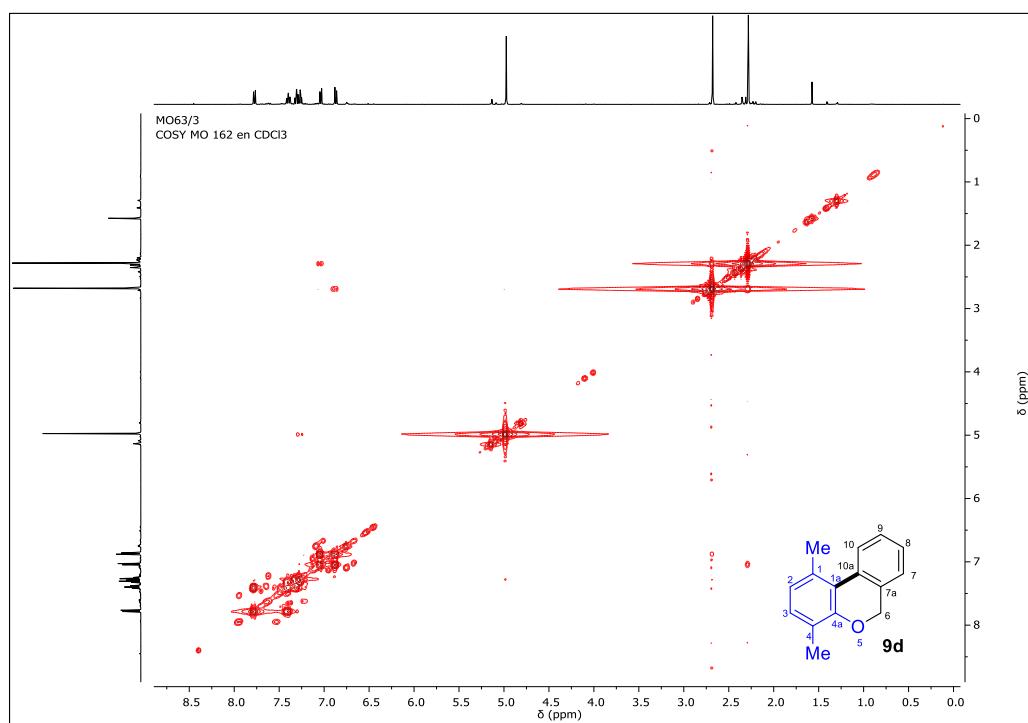


Figure ESI 67. HSQC spectrum of *1,4-dimethyl-6H-benzo[c]chromene 9d*

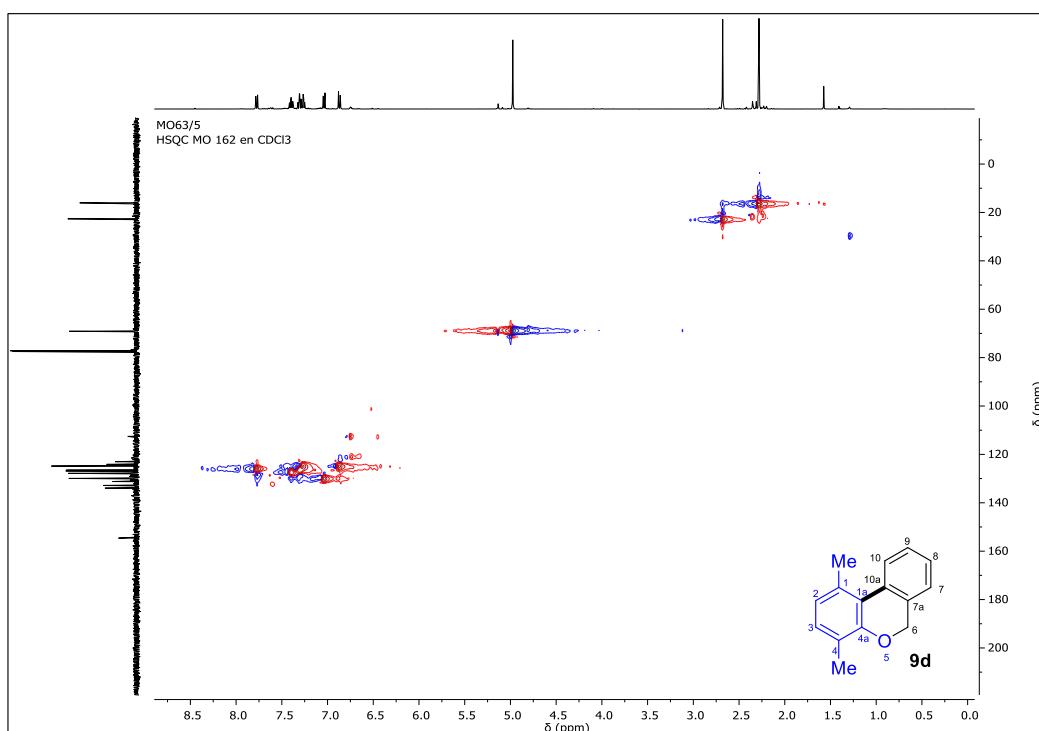


Figure ESI 68. HMBC spectrum del *1,4-dimethyl-6H-benzo[c]chromene 9d*

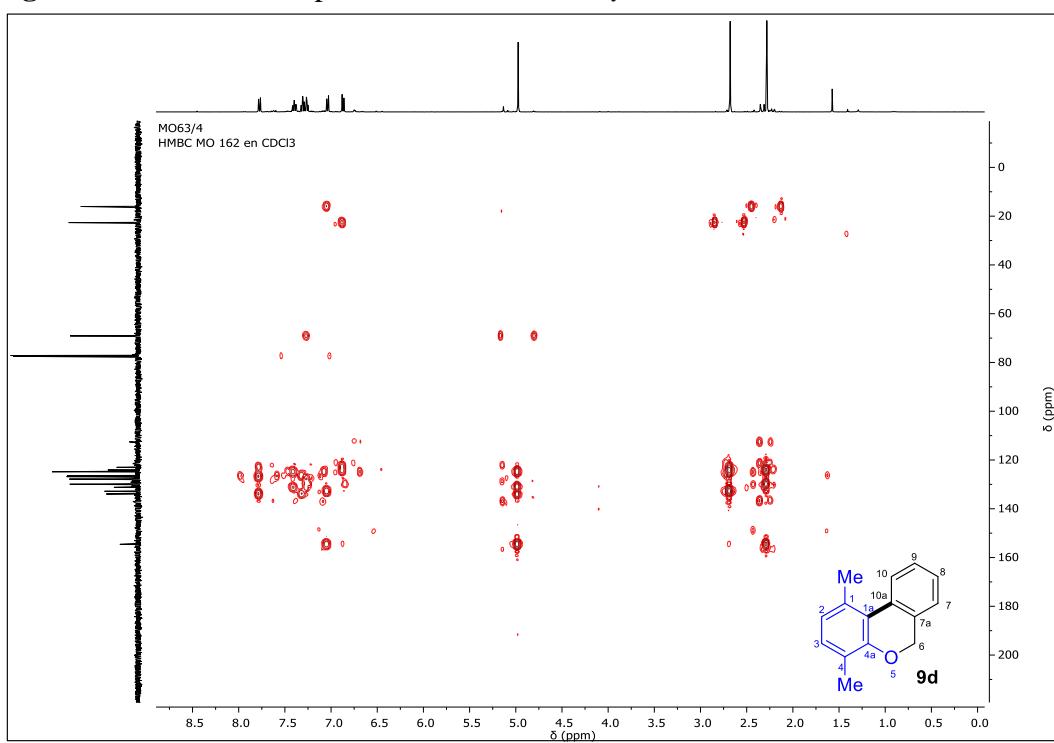


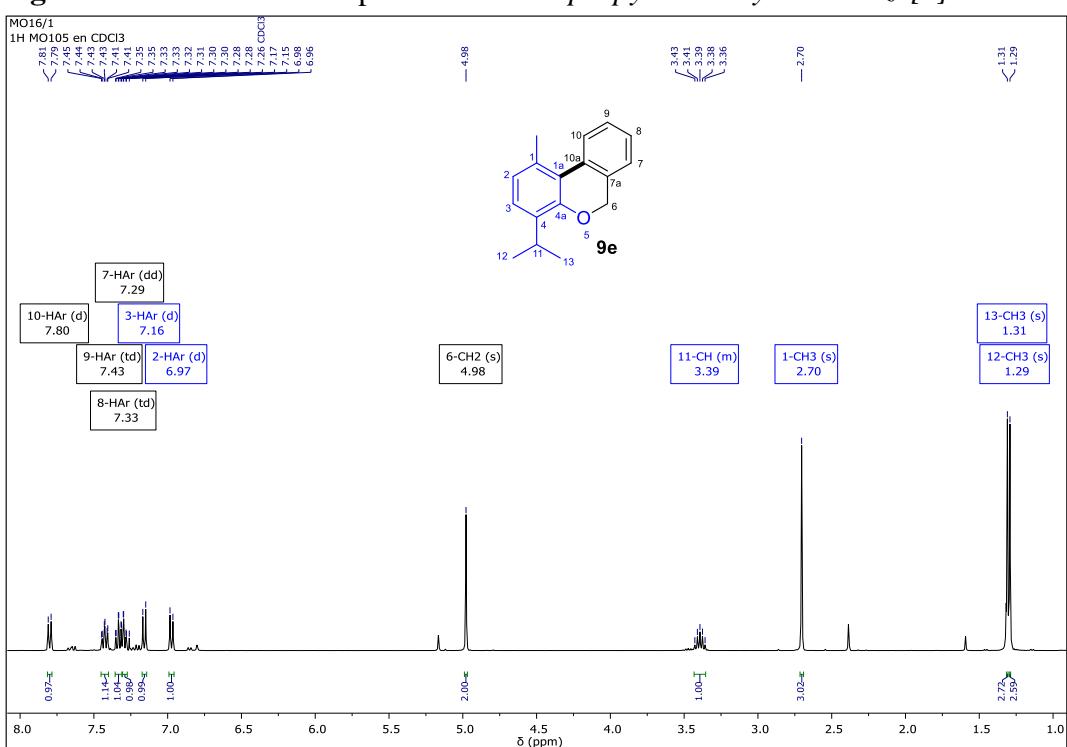
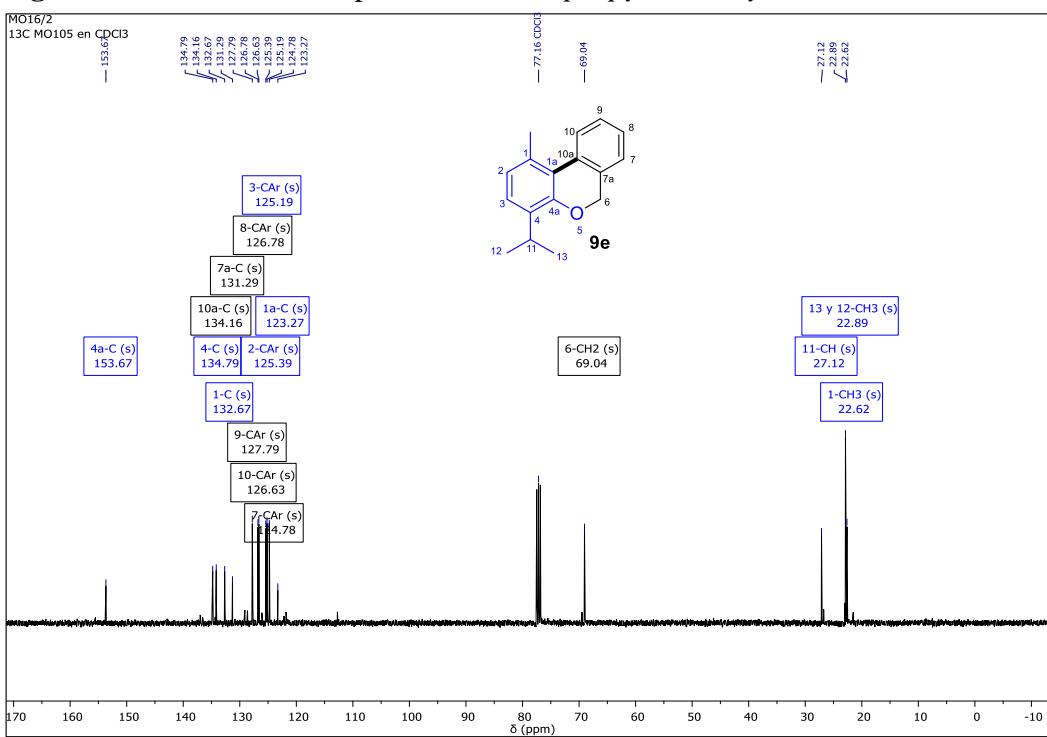
Figure ESO 69. ^1H -NMR spectrum of 4-isopropyl-1-methyl-6H-benzo[c]chromene **9e**.**Figure ESI 70.** ^{13}C -NMR spectrum of 4-isopropyl-1-methyl-6H-benzo[c]chromene **9e**

Figure ESI 71. COSY spectrum of *4-isopropyl-1-methyl-6H-benzo[c]chromene 9e*

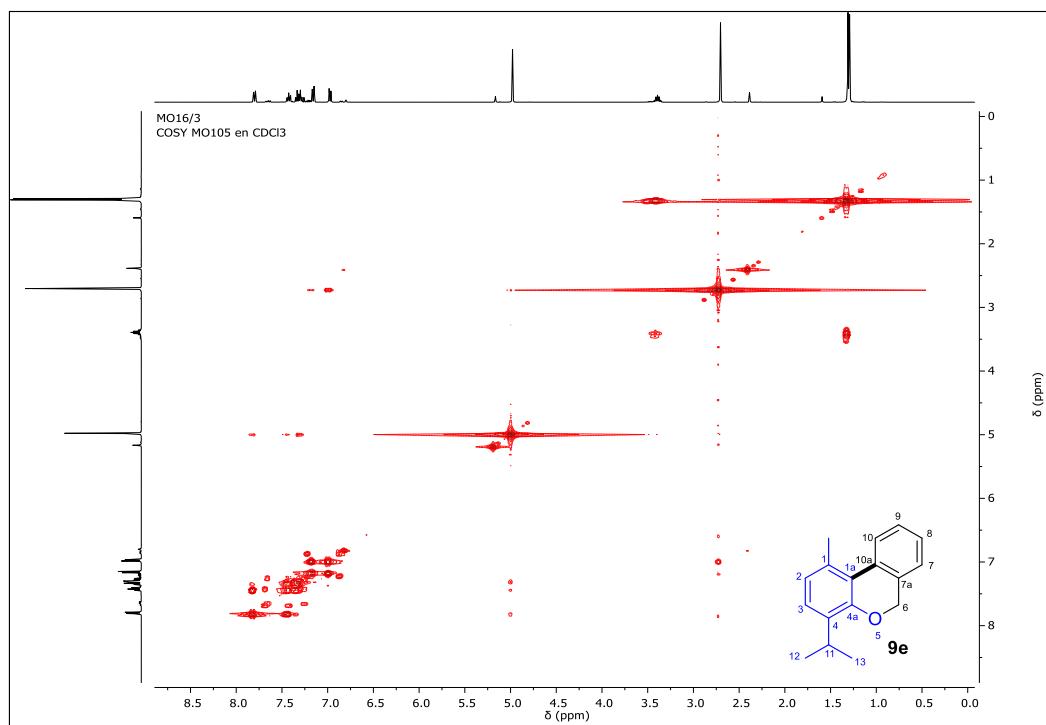


Figure ESI 72. HSQC spectrum of *4-isopropyl-1-methyl-6H-benzo[c]chromene 9e*

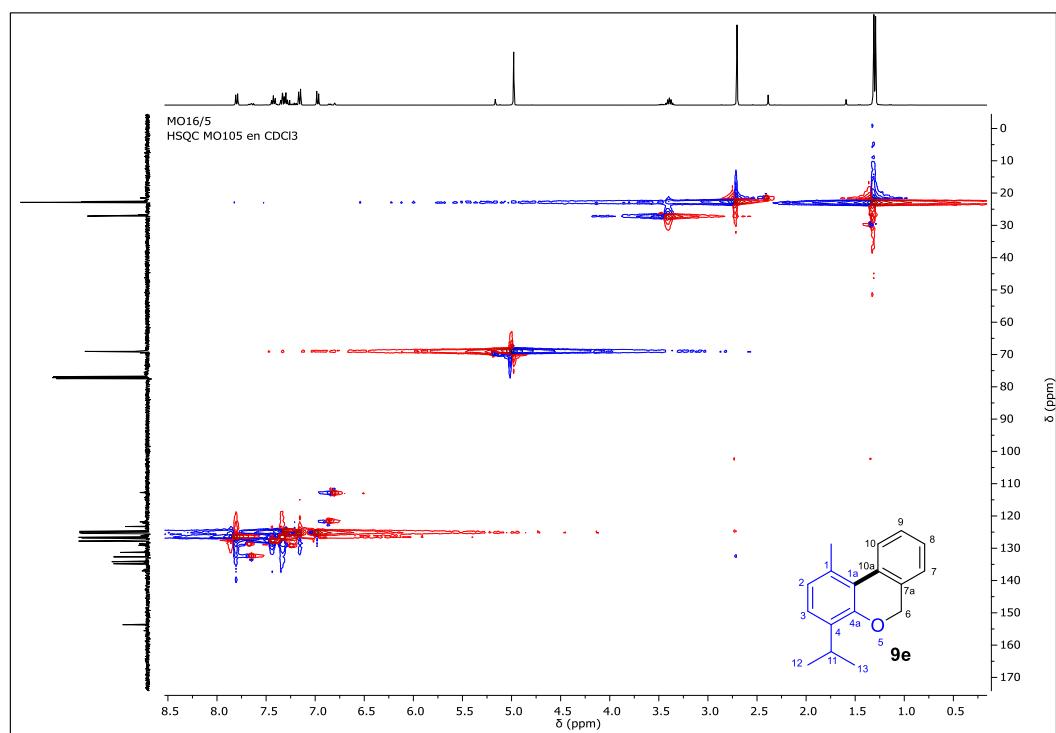


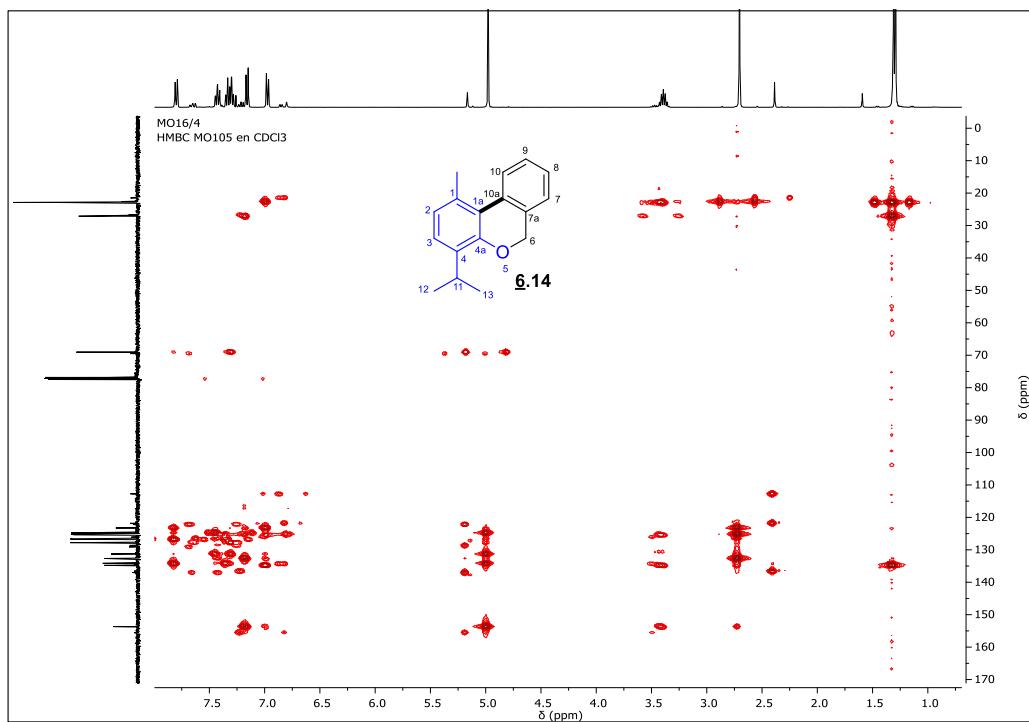
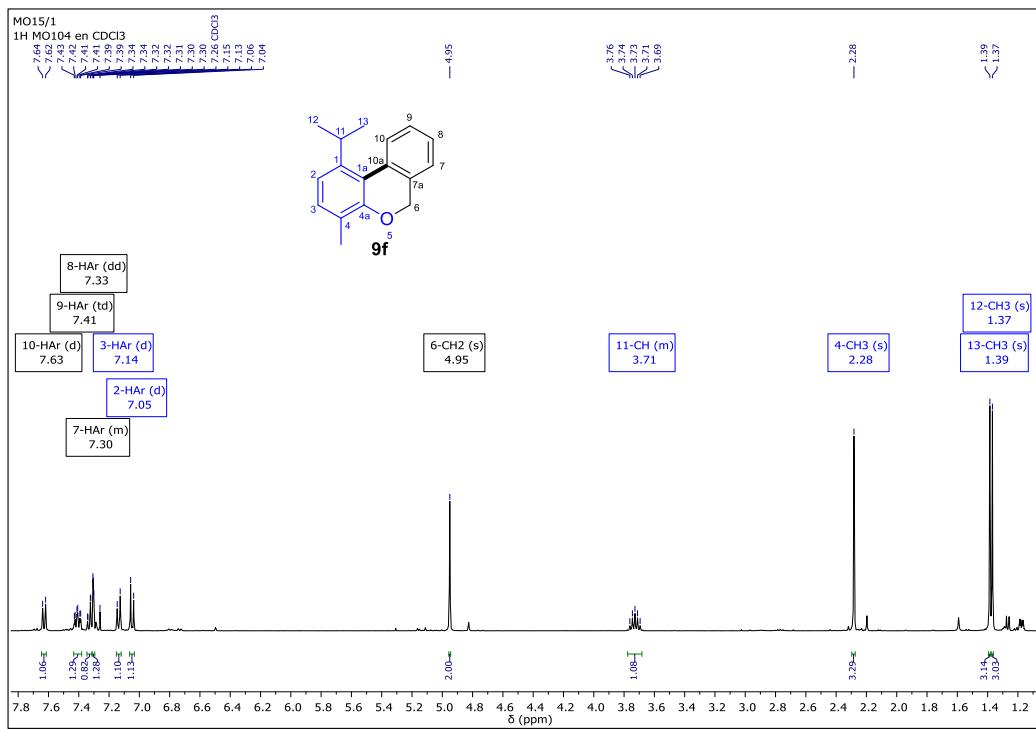
Figure ESI 73. HMBC spectrum *4-isopropyl-1-methyl-6H-benzo[c]chromene* **9e****Figure ESI 74.** ¹H-NMR spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromene* **9f**

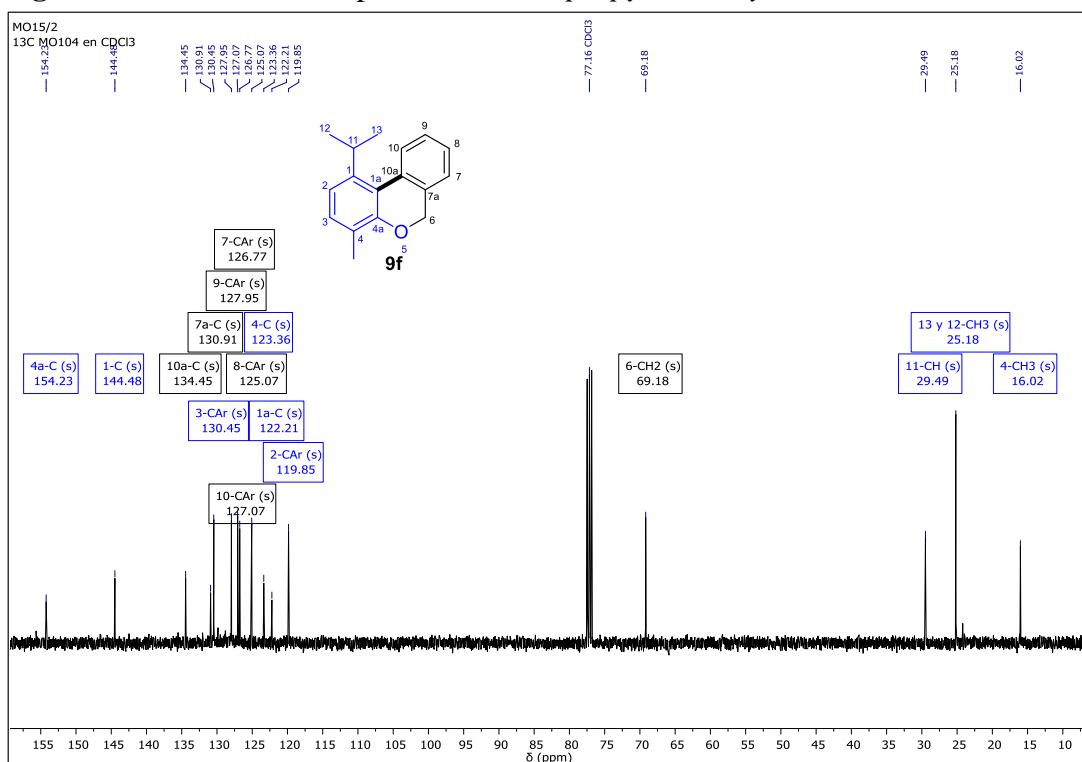
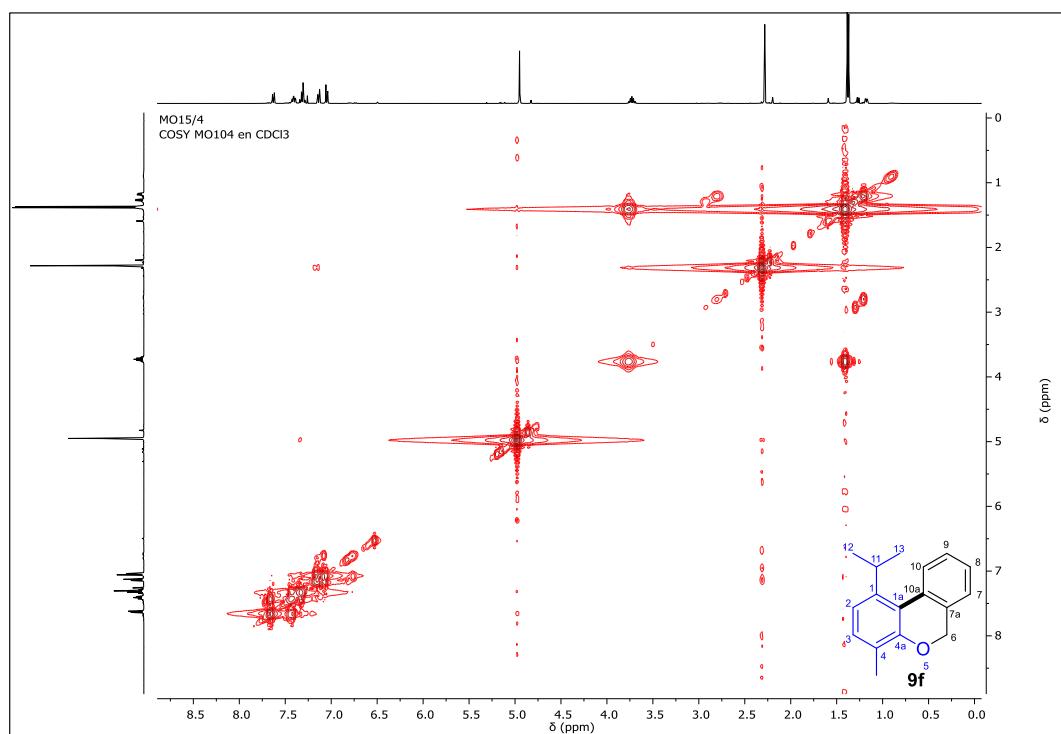
Figure ESI 75. ^{13}C -NMR spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromene* **9f****Figure ESI 76.** COSY spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromene* **9f**

Figure ESI 77. HSQC spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromene 9f*

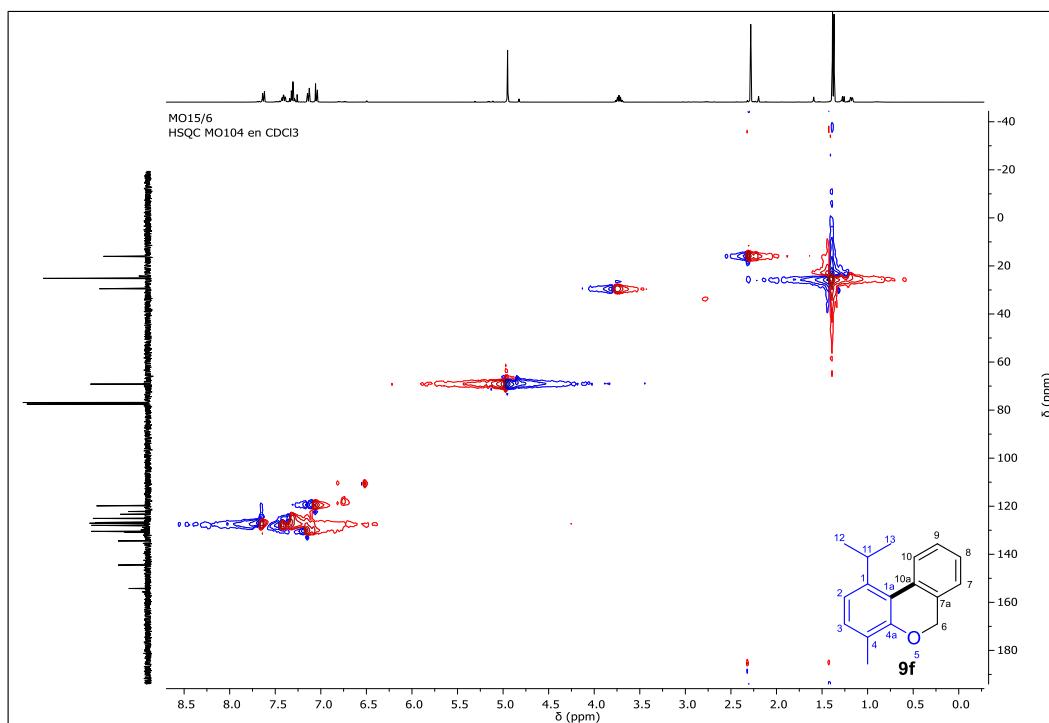


Figure ESI 78. HMBC spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromene 9f*

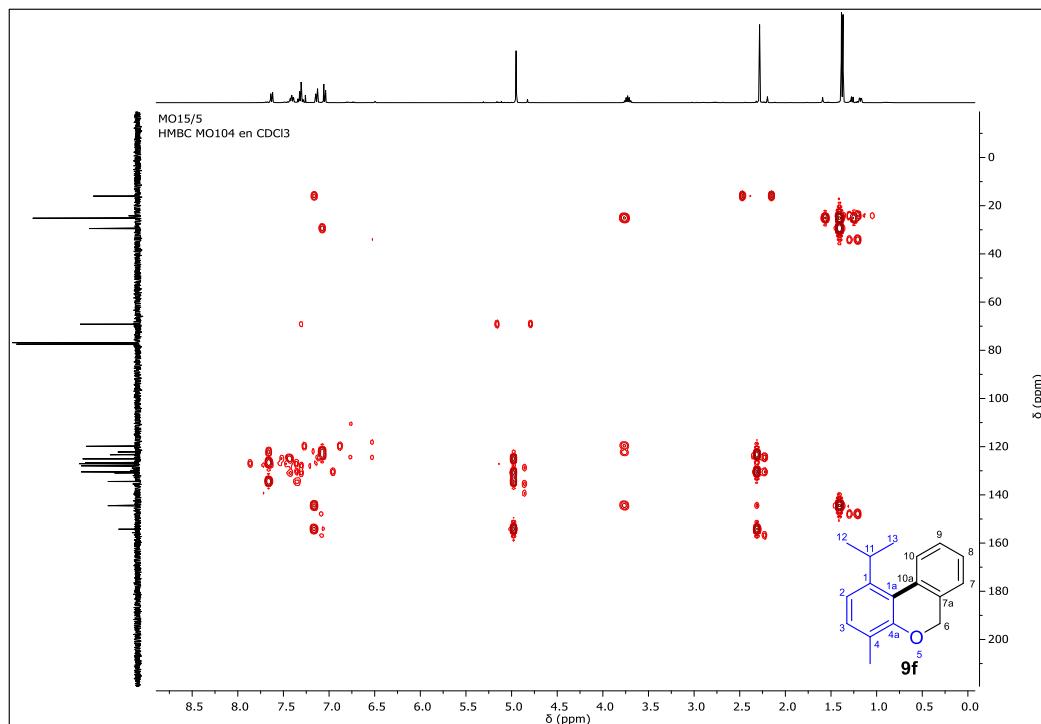


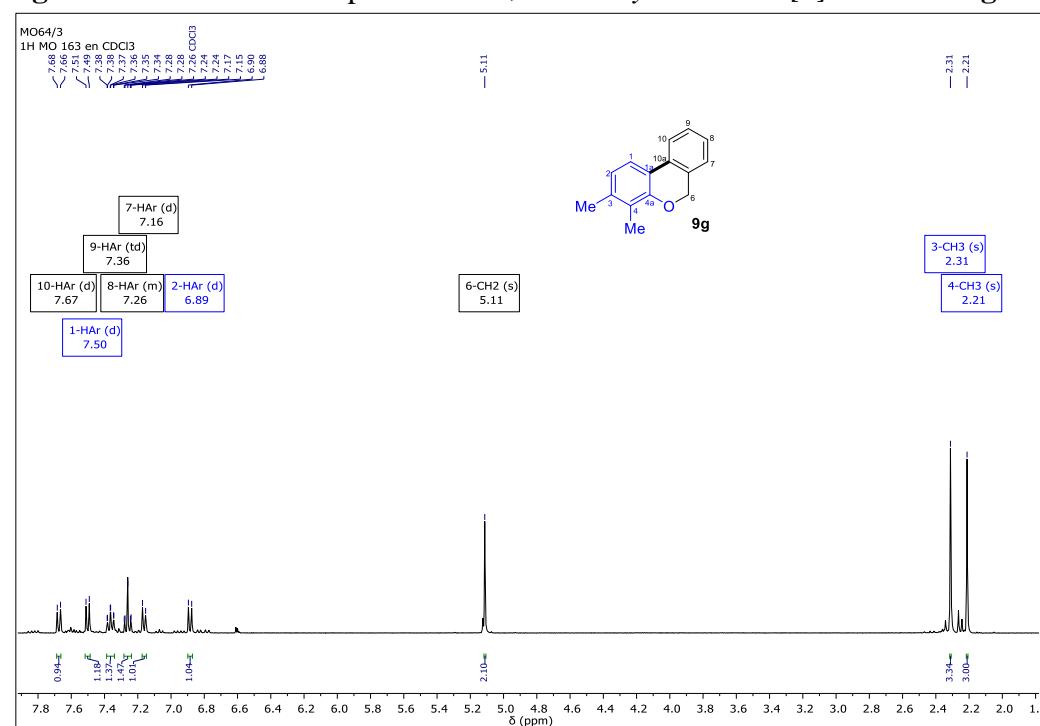
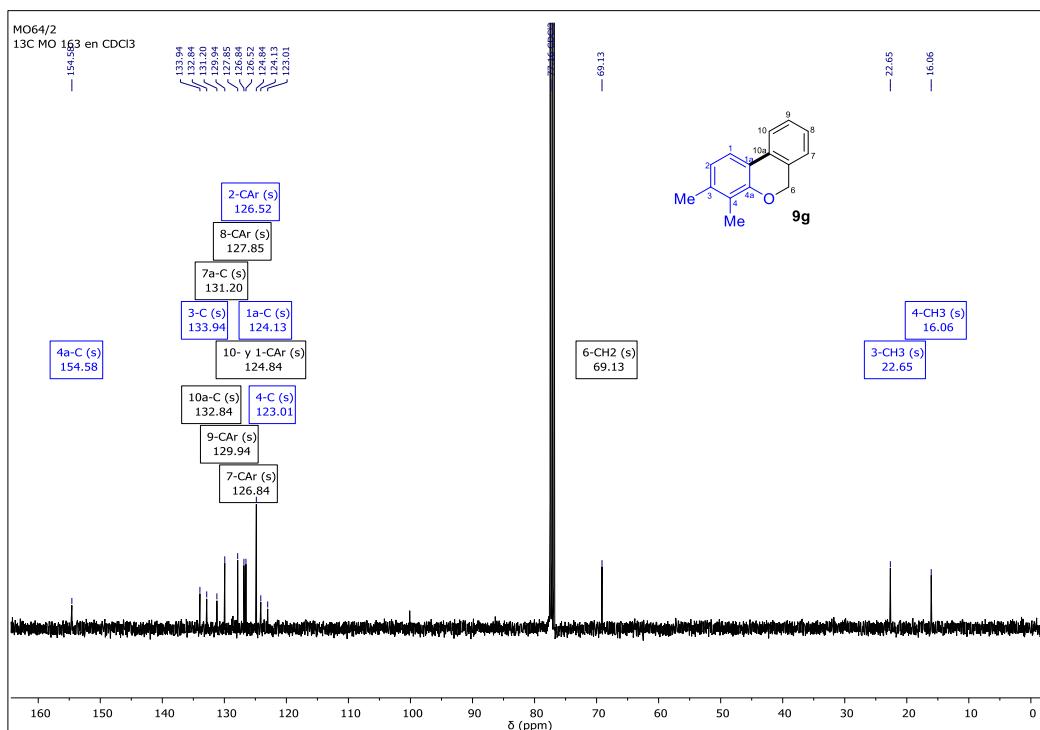
Figure ESI 79. ^1H -NMR spectrum of 3,4-dimethyl-6H-benzo[c]chromene **9g****Figure ESI 80.** ^{13}C -NMR spectrum of 3,4-dimethyl-6H-benzo[c]chromene **9g**

Figure ESI 81. COSY spectrum of *3,4-dimethyl-6H-benzo[c]chromene 9g*

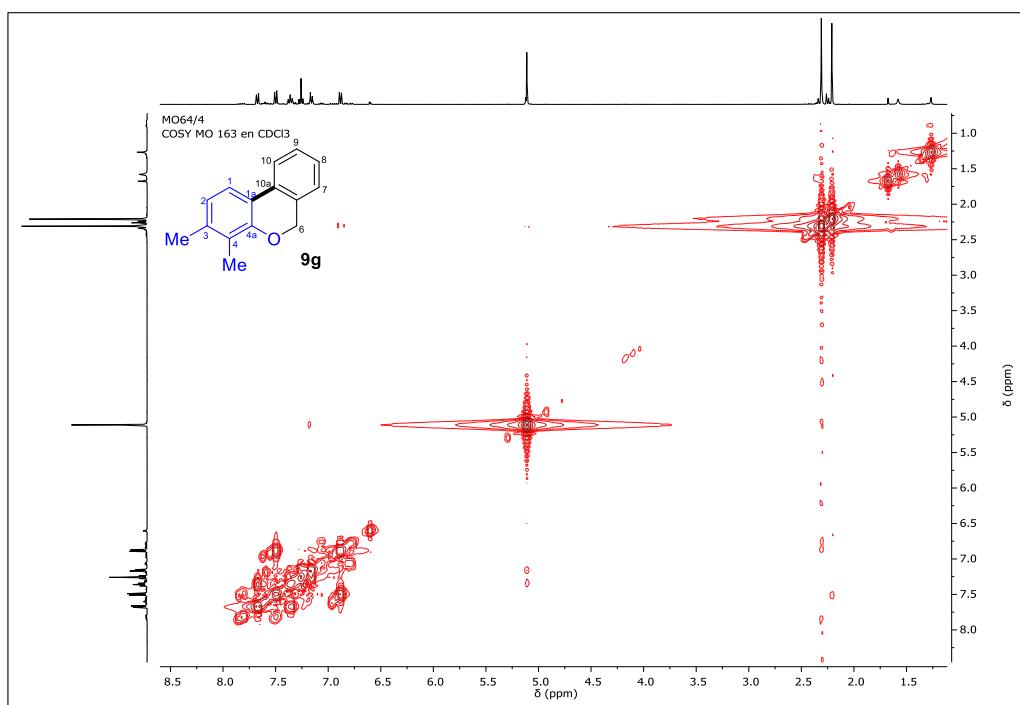


Figure ESI 82. HSQC spectrum of *3,4-dimethyl-6H-benzo[c]chromene 9g*

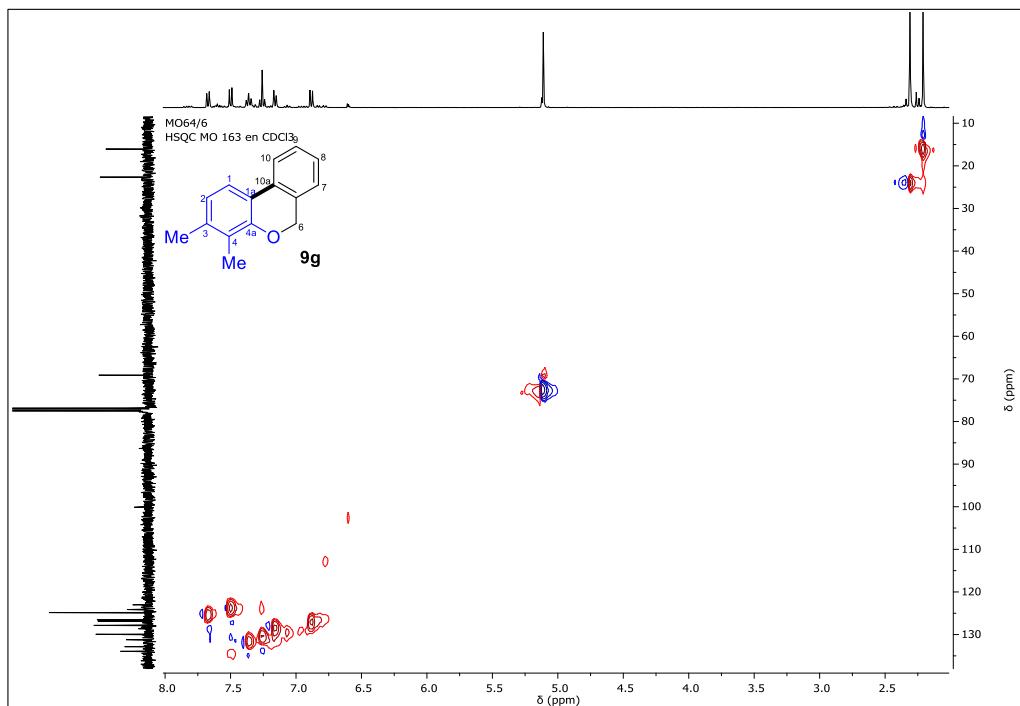


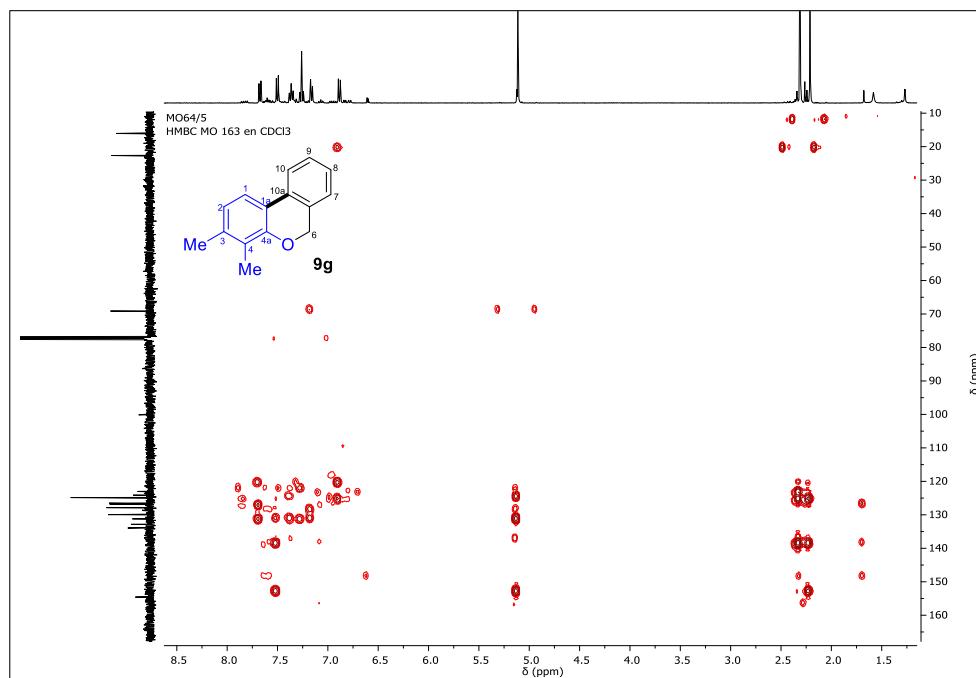
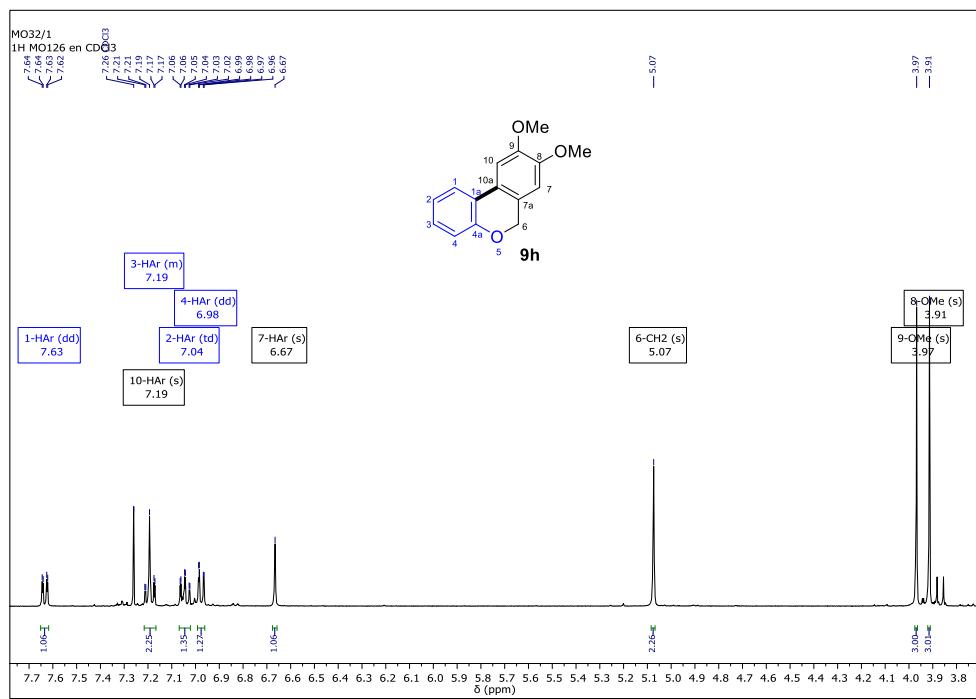
Figure ESI 83. HMBC spectrum of *3,4-dimethyl-6H-benzo[c]chromene 9g***Figure ESI 84.** ¹H-NMR spectrum of *9,10-dimethoxy-6H-benzo[c]chromene 9h*

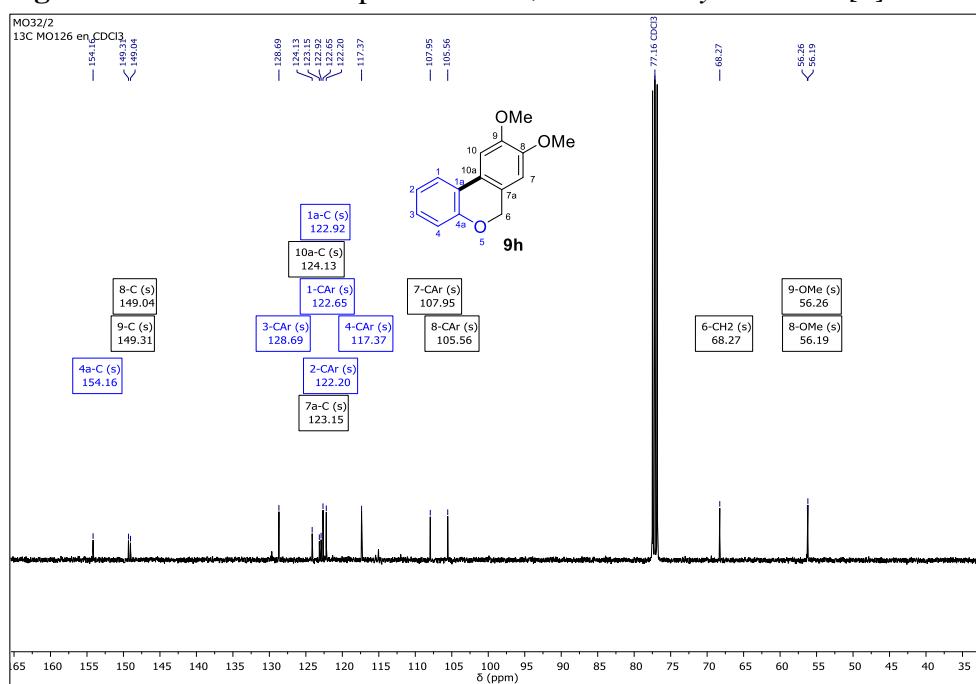
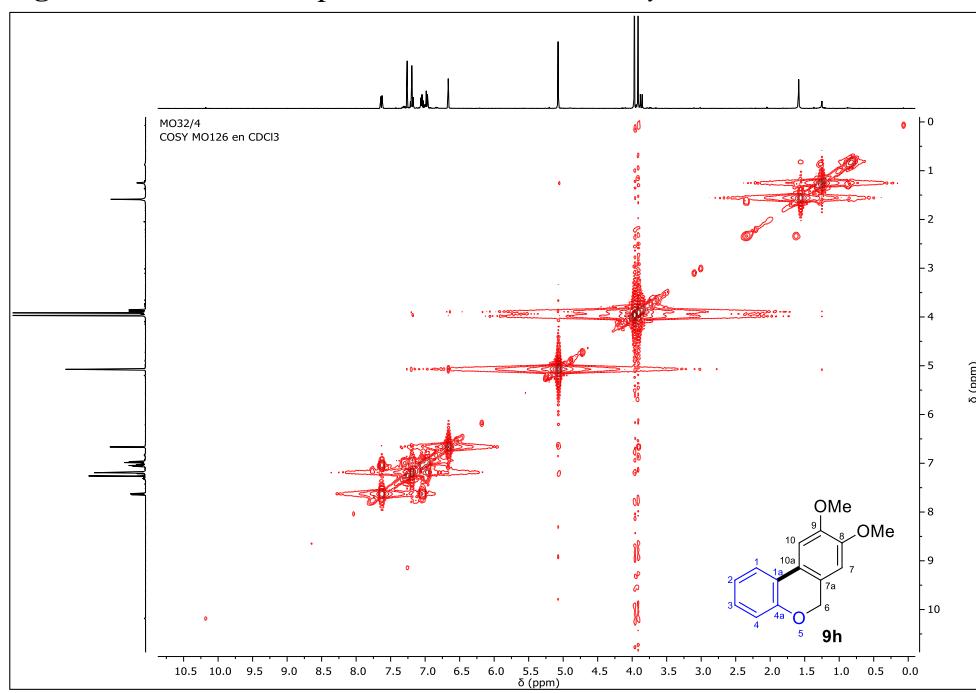
Figure ESI 85. ^{13}C -NMR spectrum of 9,10-dimethoxy-6H-benzo[c]chromene **9h****Figure ESI 86.** COSY spectrum of 9,10-dimethoxy-6H-benzo[c]chromene **9h**

Figure ESI 87. HSQC spectrum of *9,10-dimethoxy-6H-benzo[c]chromene 9h*

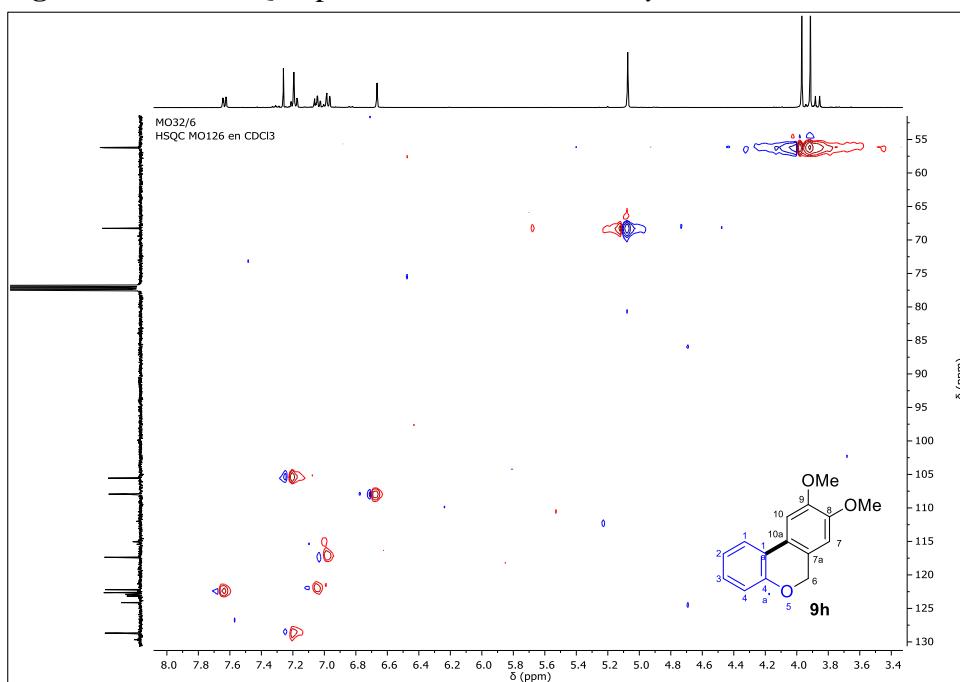


Figure ESI 88. HMBC spectrum of *9,10-dimethoxy-6H-benzo[c]chromene 9h*

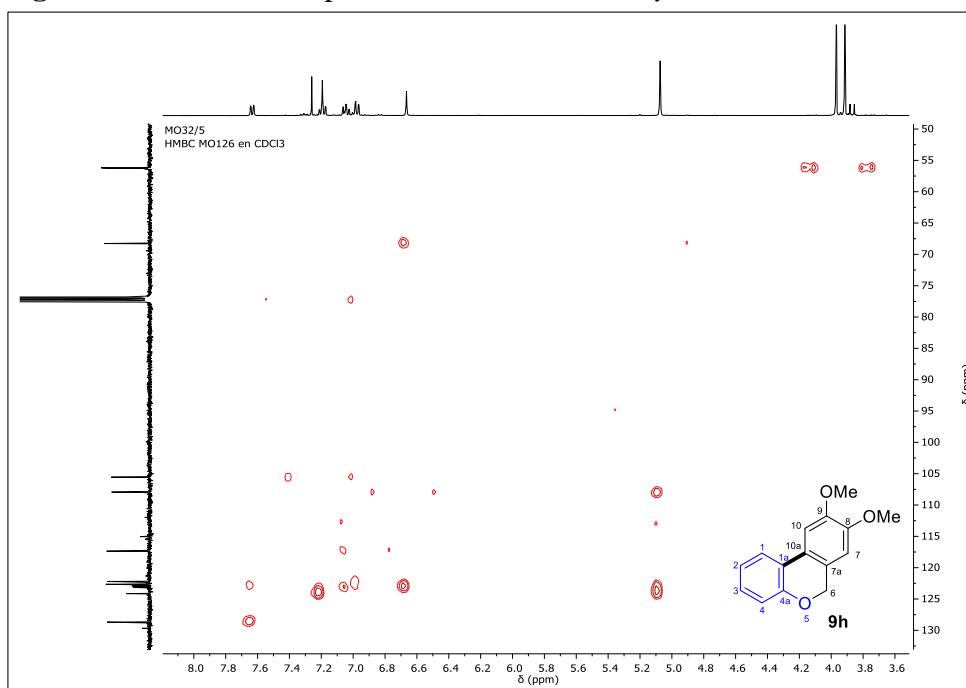


Figure ESI 89. ^1H -NMR spectrum of 8,9,10-trimethoxy-6H-benzo[c]chromene **9i**

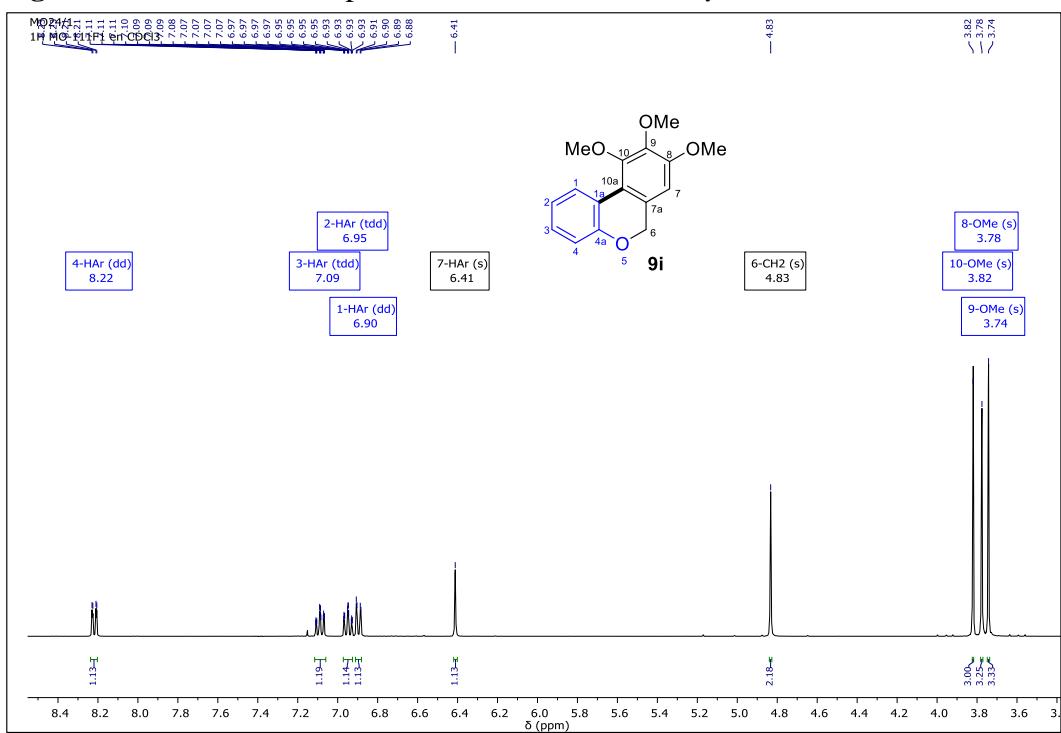


Figure ESI 90. ^{13}C -NMR spectrum of 8,9,10-trimethoxy-6H-benzo[c]chromene **9i**

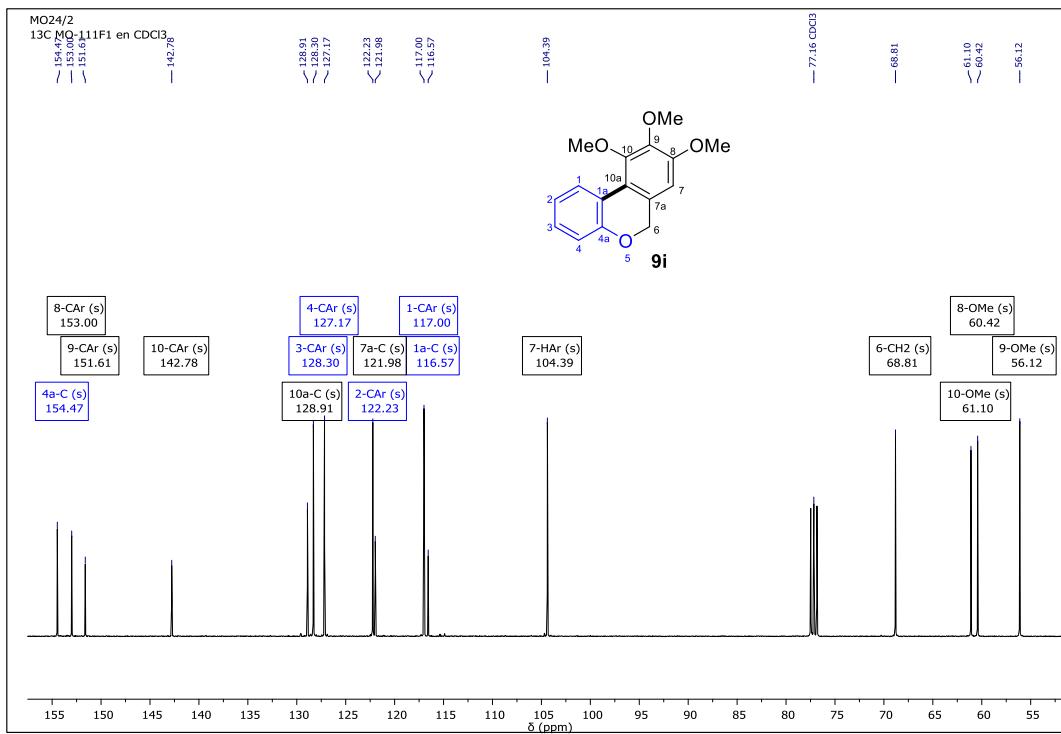


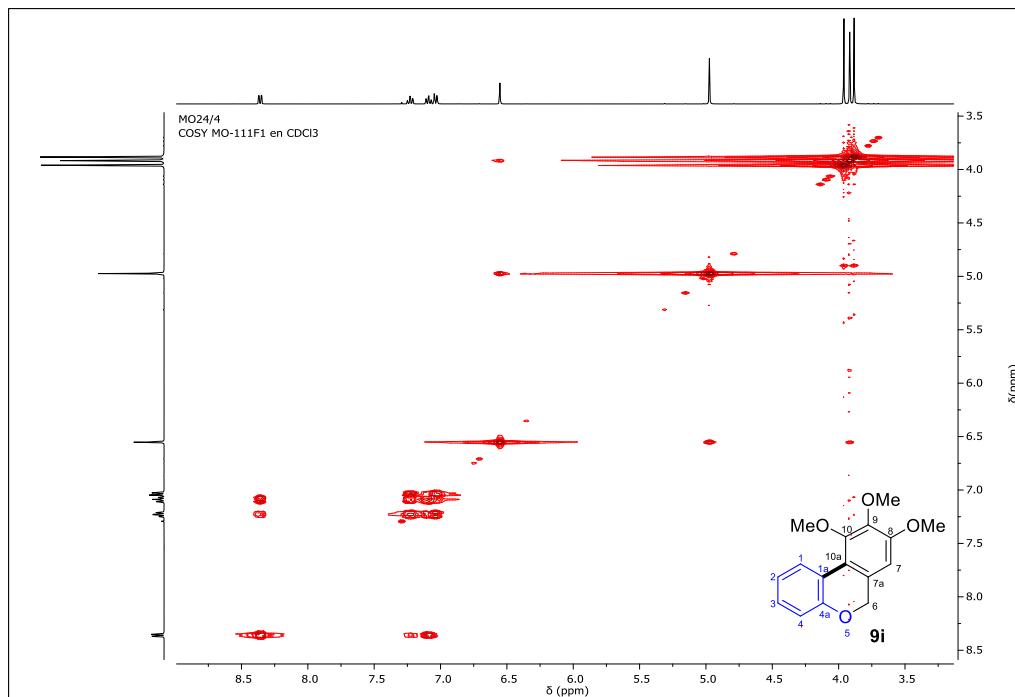
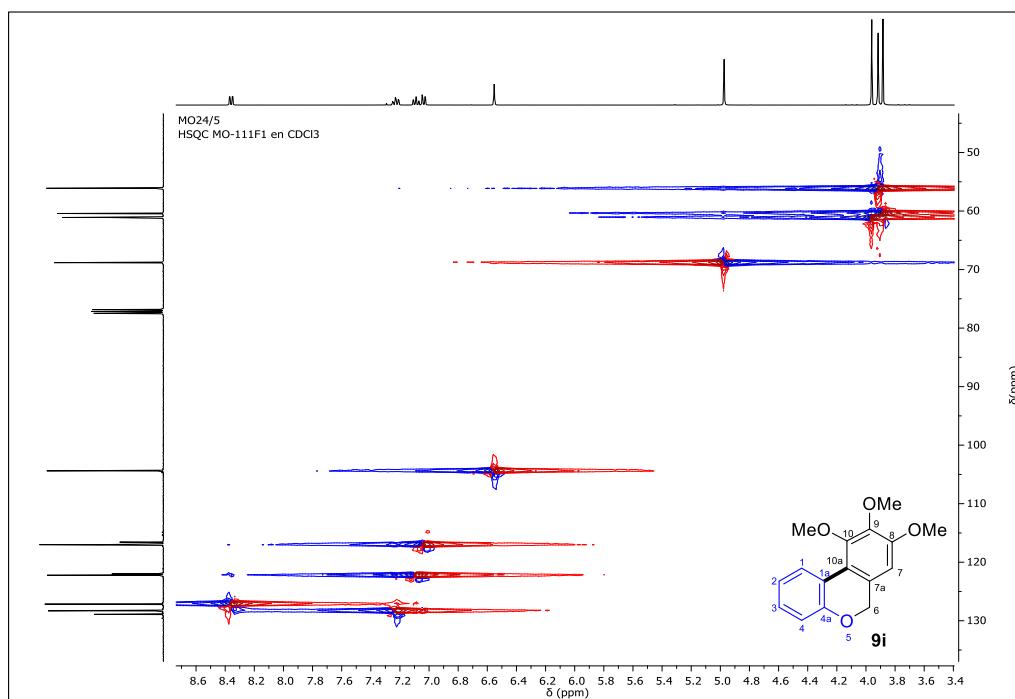
Figure ESI 91. COSY spectrum of *8,9,10-trimethoxy-6H-benzo[c]chromene* **9i****Figure ESI 92.** HSQC spectrum of *8,9,10-trimethoxy-6H-benzo[c]chromene* **9i**

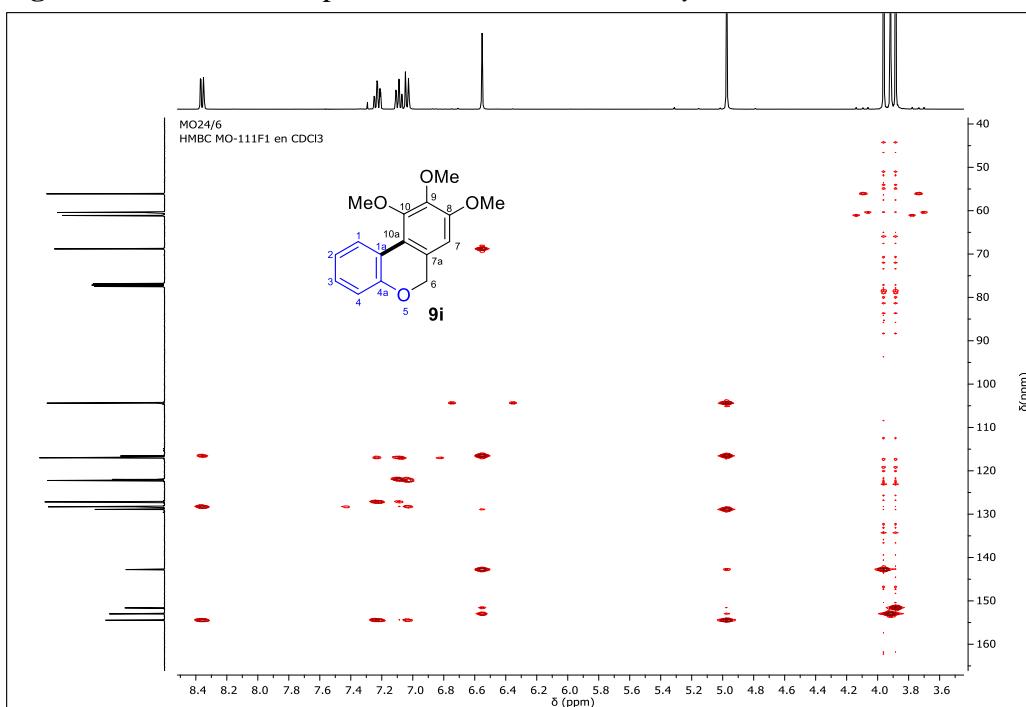
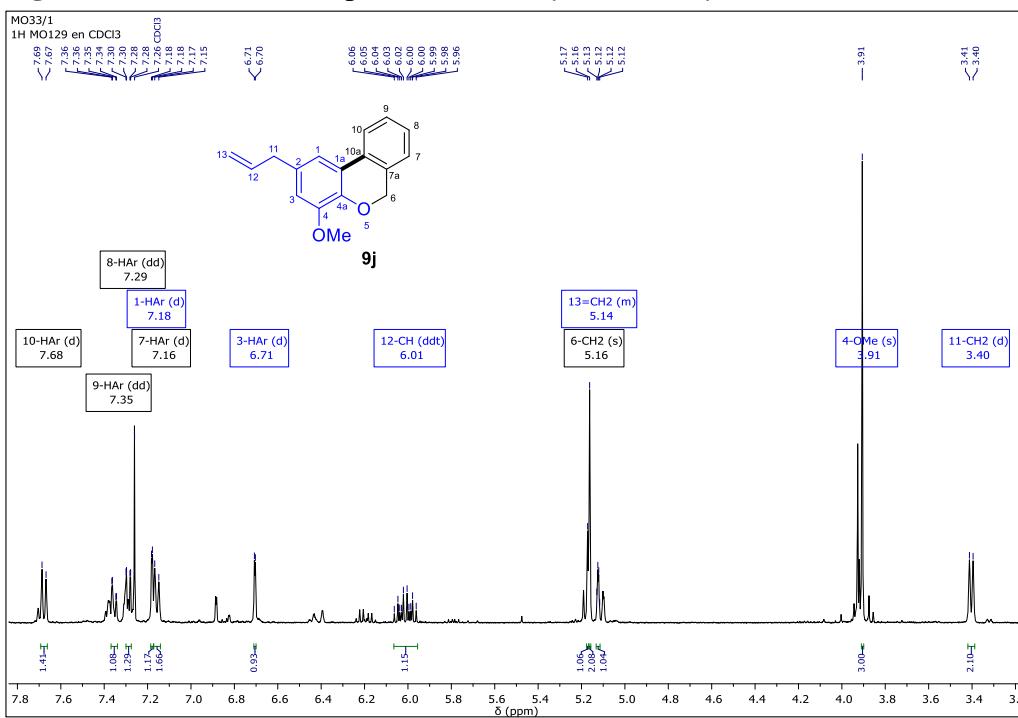
Figure ESI 93. HMBC spectrum of *8,9,10-trimethoxy-6H-benzo[c]chromene* **9i****Figure ESI 94.** ¹H-NMR spectrum of *2-allyl-4-methoxy-6H-benzo[c]chromene* **9j**

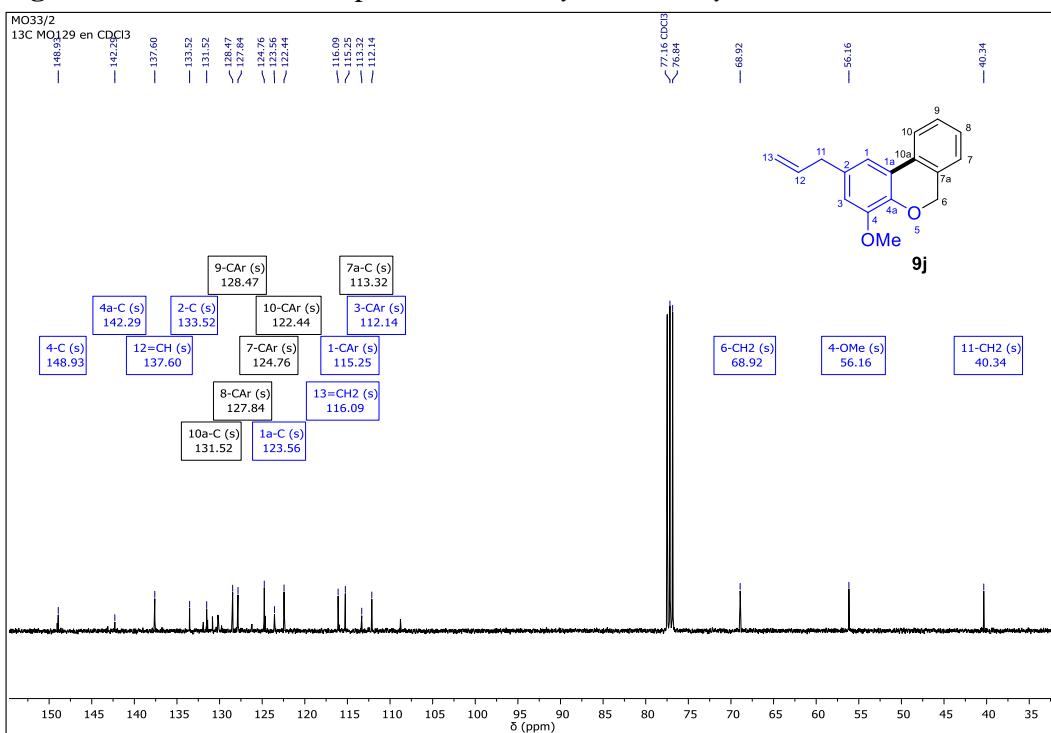
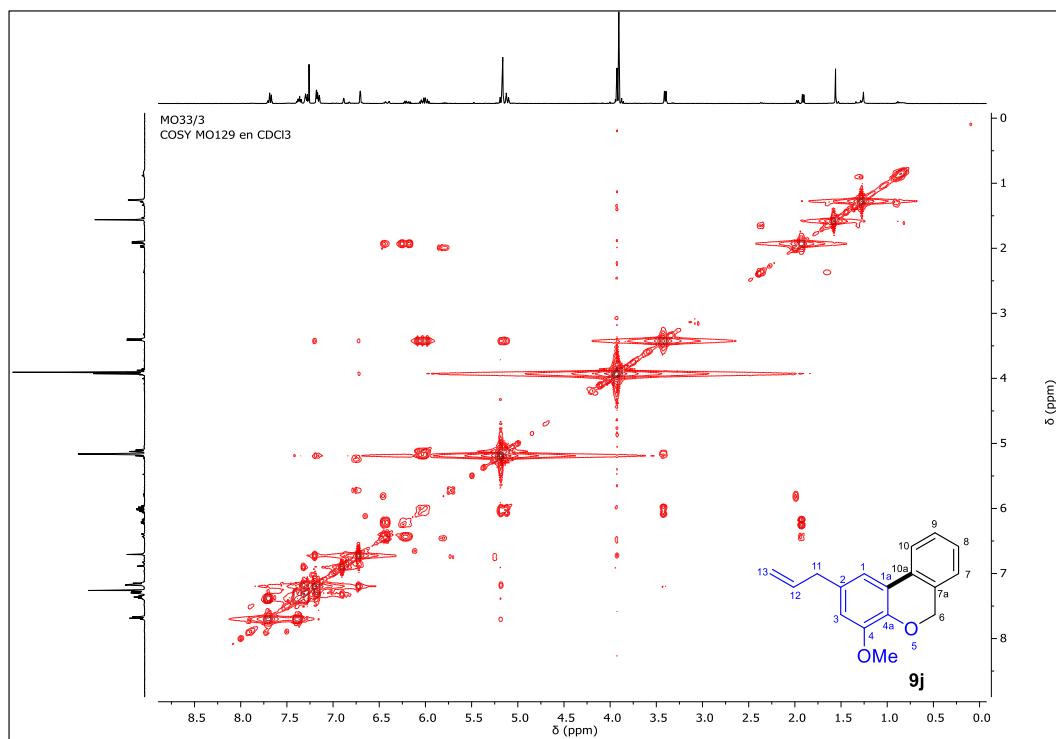
Figure ESI 95. ^{13}C -NMR spectrum of 2-allyl-4-methoxy-6H-benzo[c]chromene **9j****Figure ESI 96.** COSY spectrum of 2-allyl-4-methoxy-6H-benzo[c]chromene **9j**

Figure ESI 97. HSQC spectrum of *2-allyl-4-methoxy-6H-benzo[c]chromene 9j*

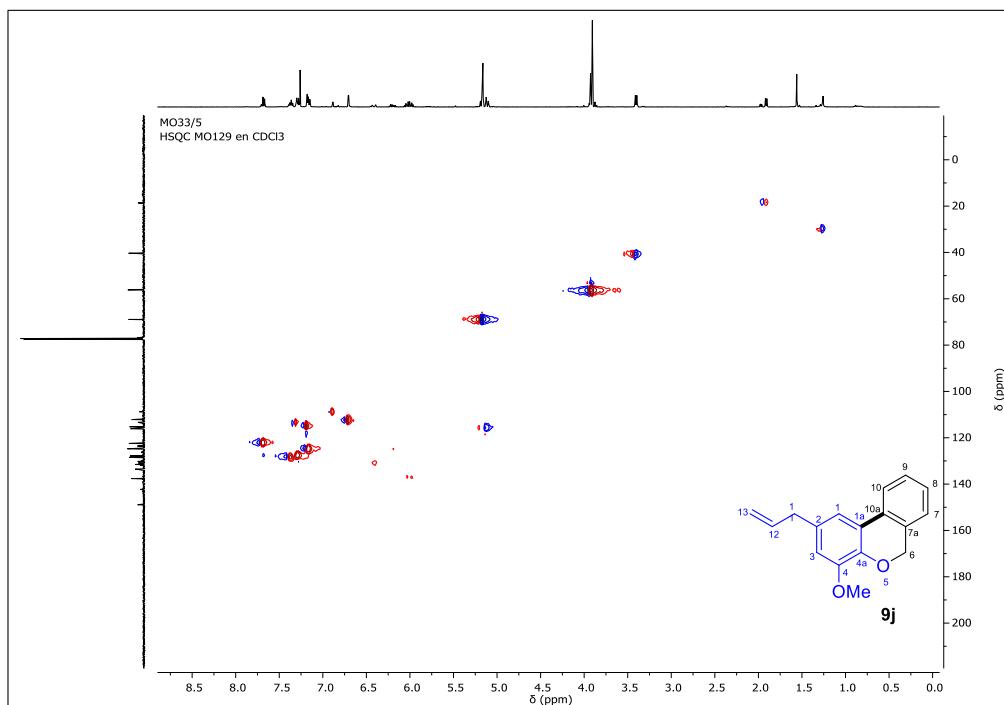


Figure ESI 98. HMBC spectrum of *2-allyl-4-methoxy-6H-benzo[c]chromene 9j*

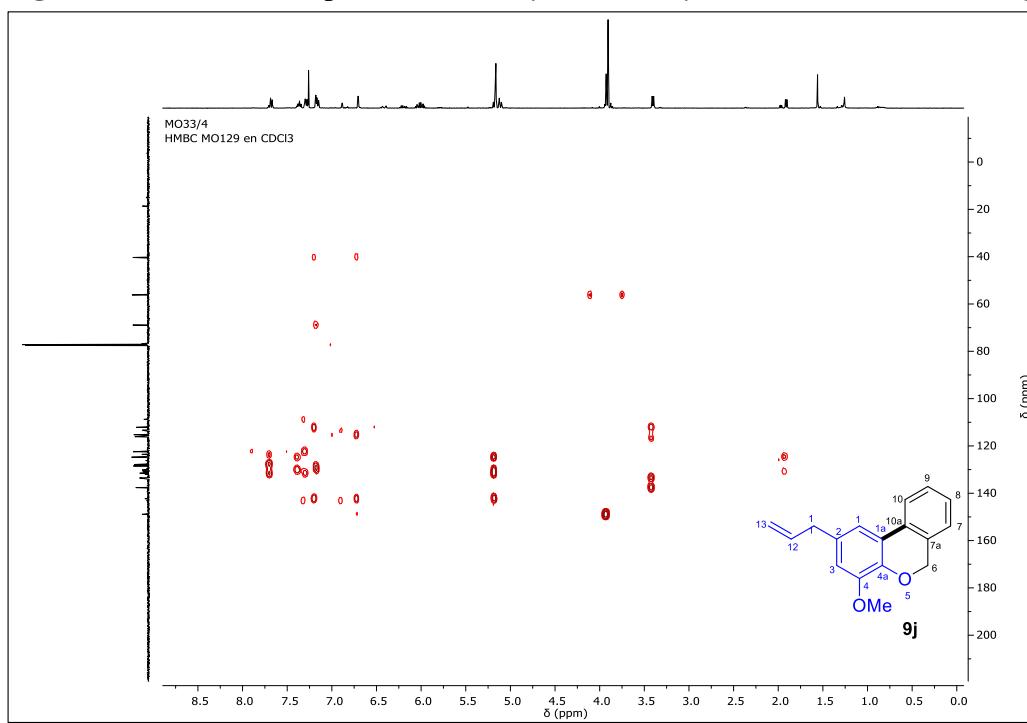


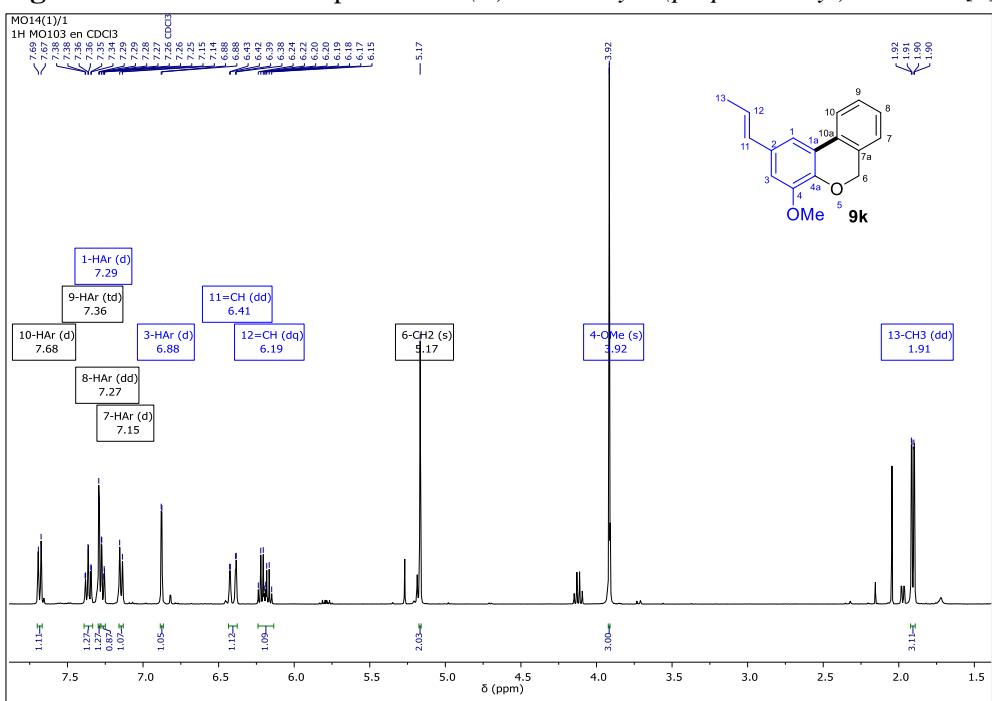
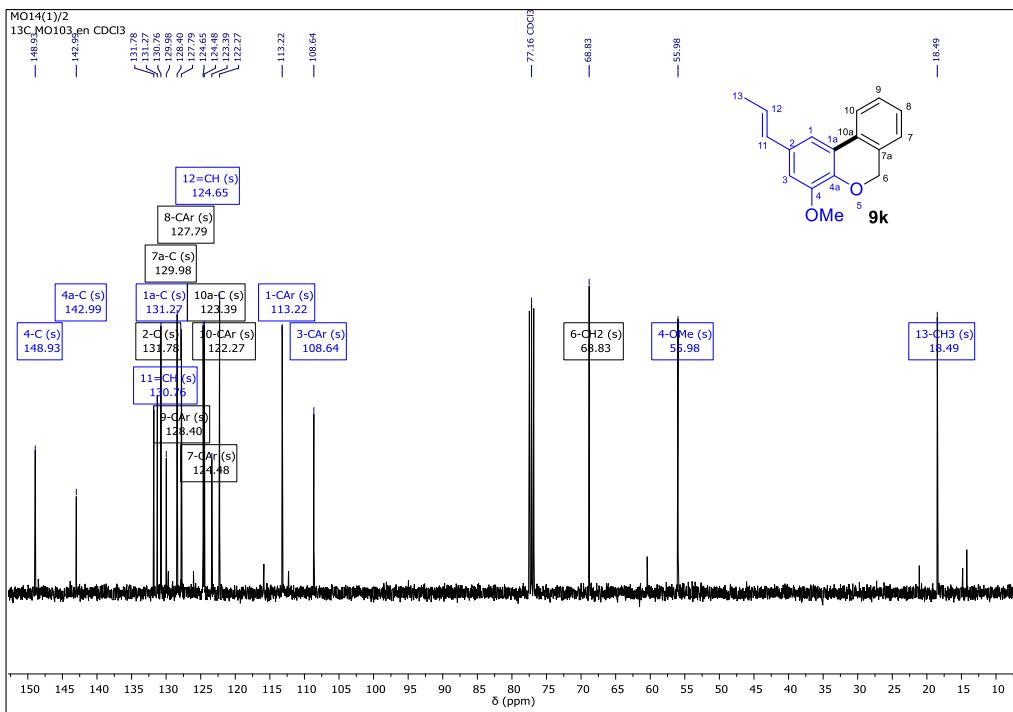
Figure ESI 99. ^1H -NMR spectrum of (*E*)-4-methoxy-2-(prop-1-en-1-yl)-6*H*-benzo[*c*]chromene **9k****Figure ESI 100.** ^{13}C -NMR spectrum of (*E*)-4-methoxy-2-(prop-1-en-1-yl)-6*H*-benzo[*c*]chromene **9k**

Figure ESI 101. COSY spectrum of (*E*)-4-methoxy-2-(prop-1-en-1-yl)-6H-benzo[*c*]chromene **9k**

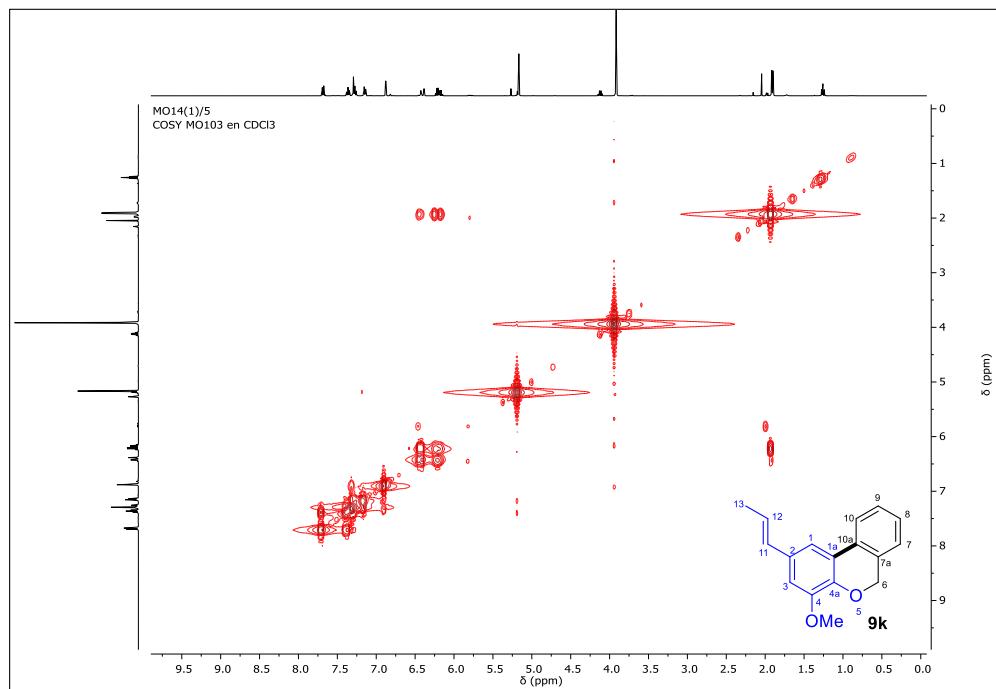


Figure ESI 102. HSQC spectrum of (*E*)-4-methoxy-2-(prop-1-en-1-yl)-6H-benzo[*c*]chromene **9k**

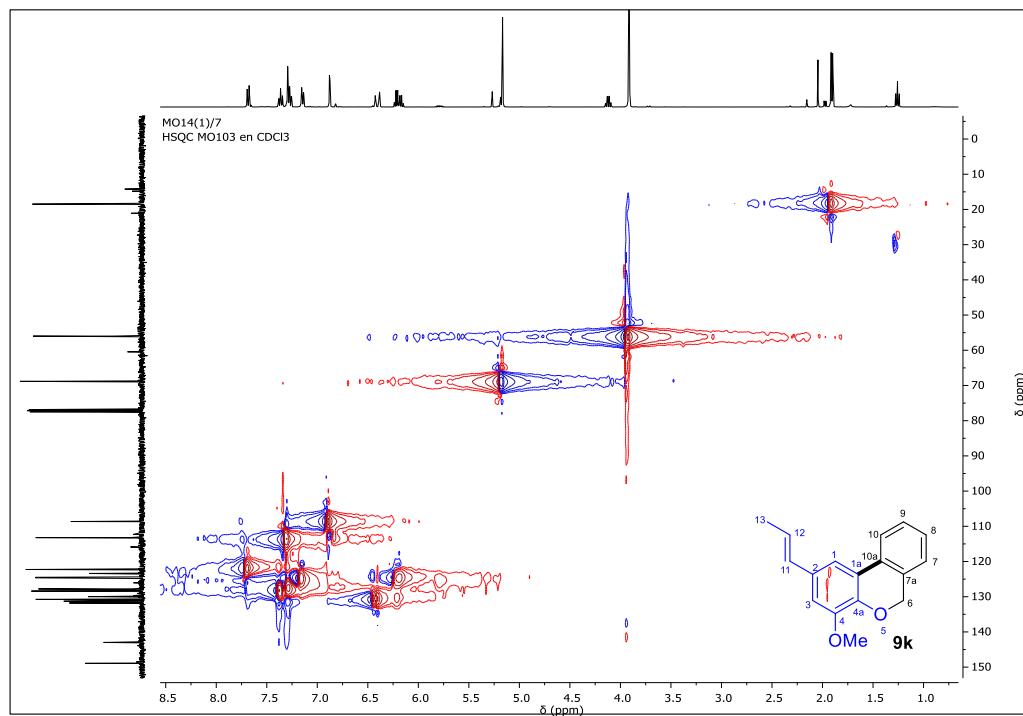


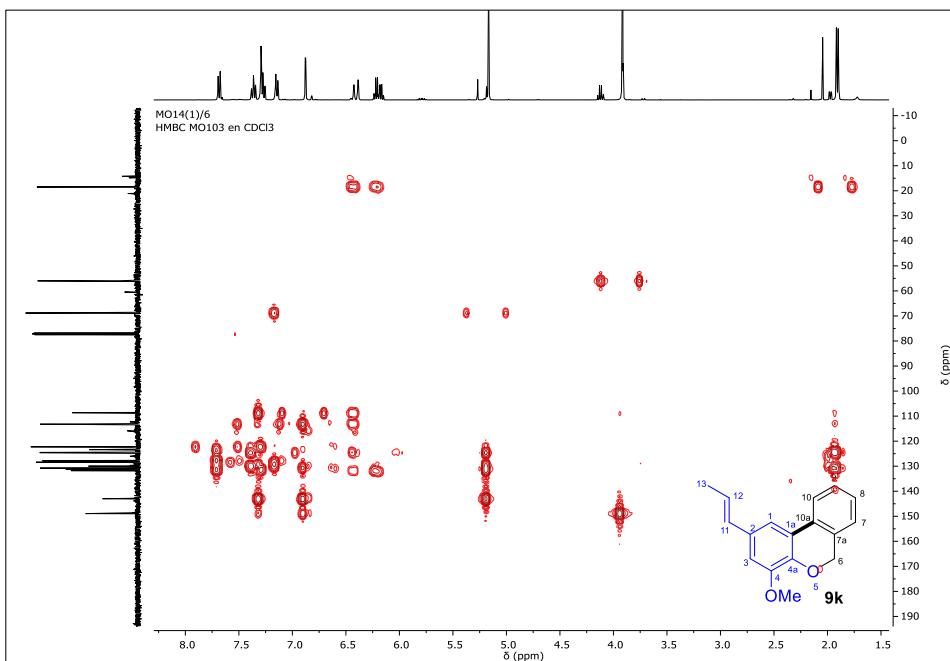
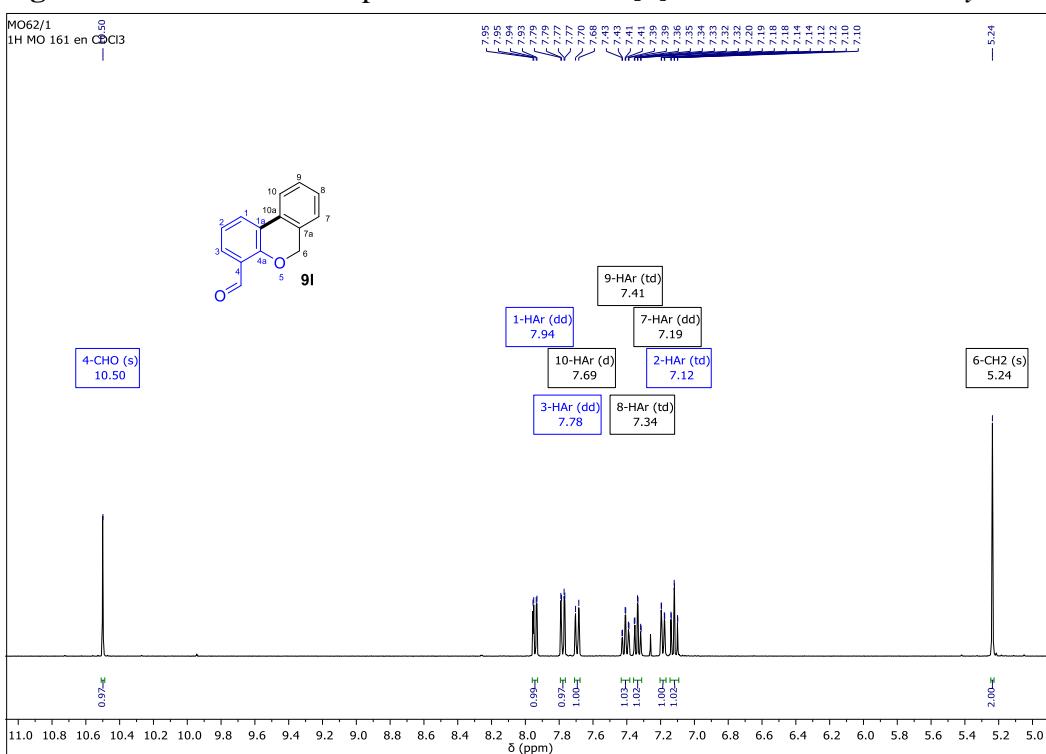
Figure ESI 103. HMBC spectrum of (*E*)-4-methoxy-2-(prop-1-en-1-yl)-6*H*-benzo[*c*]chromene **9k****Figure ESI 104.** ¹H-NMR spectrum of 6*H*-benzo[*c*]chromene-4-carbaldehyde **9l**

Figure ESI 105. ^{13}C -NMR spectrum of *6H-benzo[c]chromene-4-carbaldehyde* **9I**

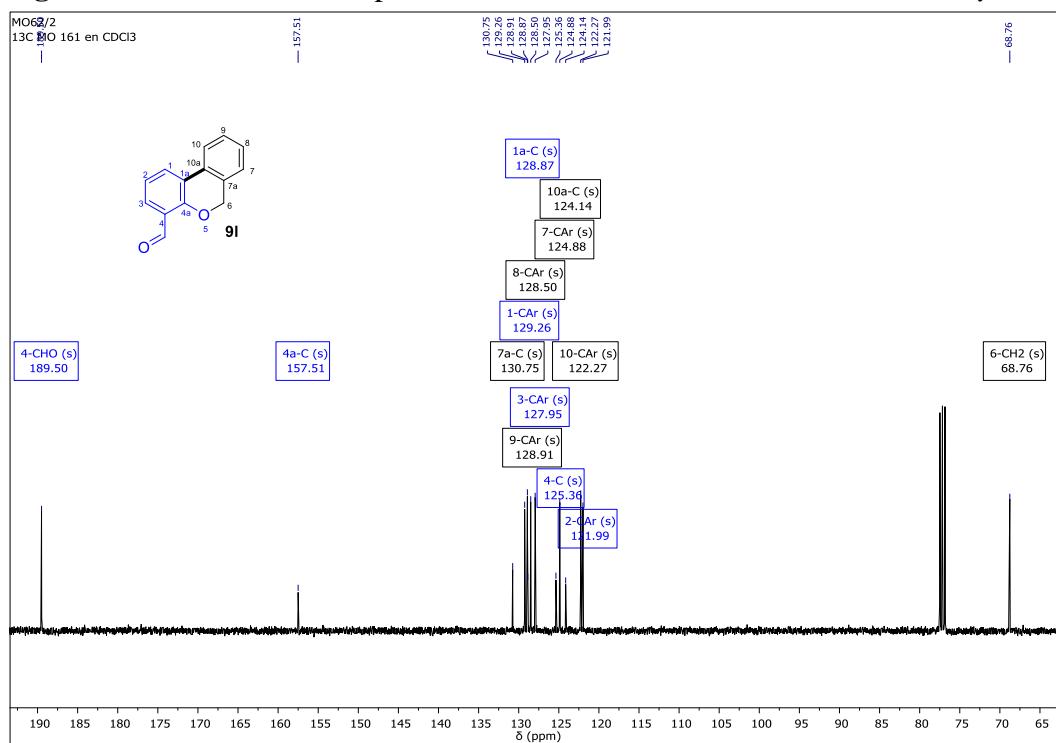


Figure ESI 106. COSY spectrum of *6H-benzo[c]chromene-4-carbaldehyde* **9I**

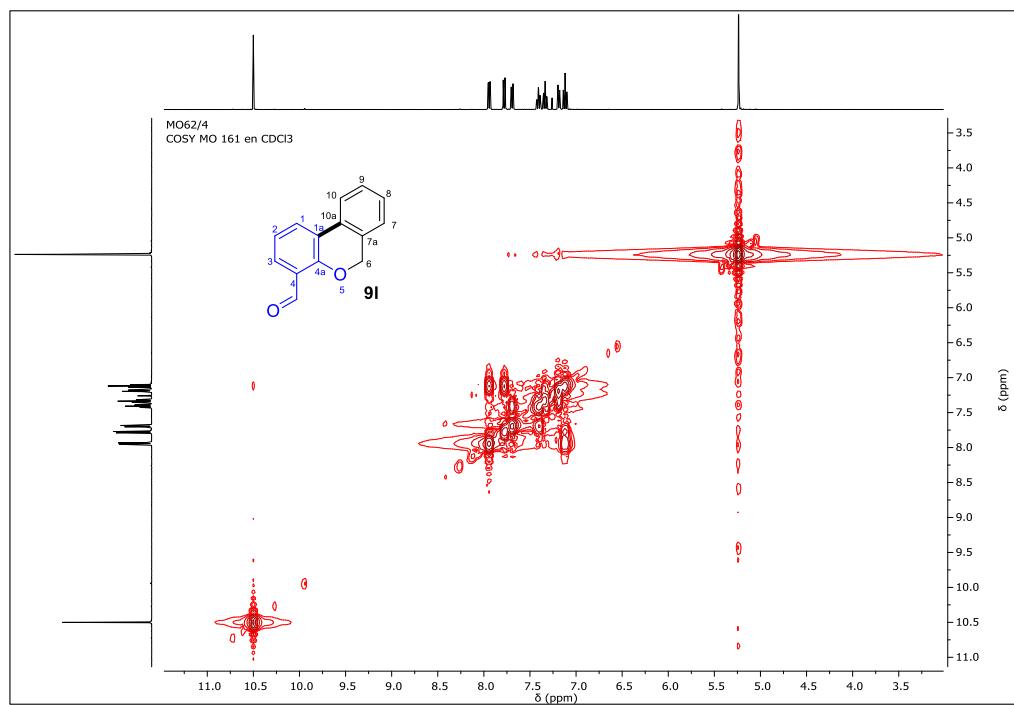


Figure ESI 107. HSQC spectrum of *6H-benzo[c]chromene-4-carbaldehyde* **9I**

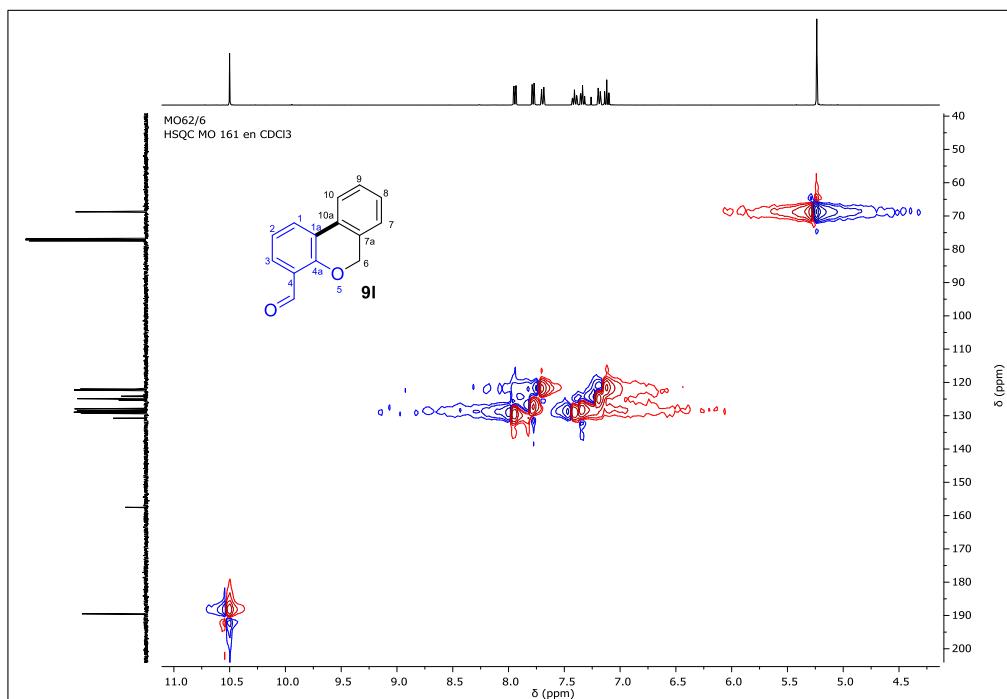


Figure ESI 108. HMBC spectrum of *6H-benzo[c]chromene-4-carbaldehyde* **9I**

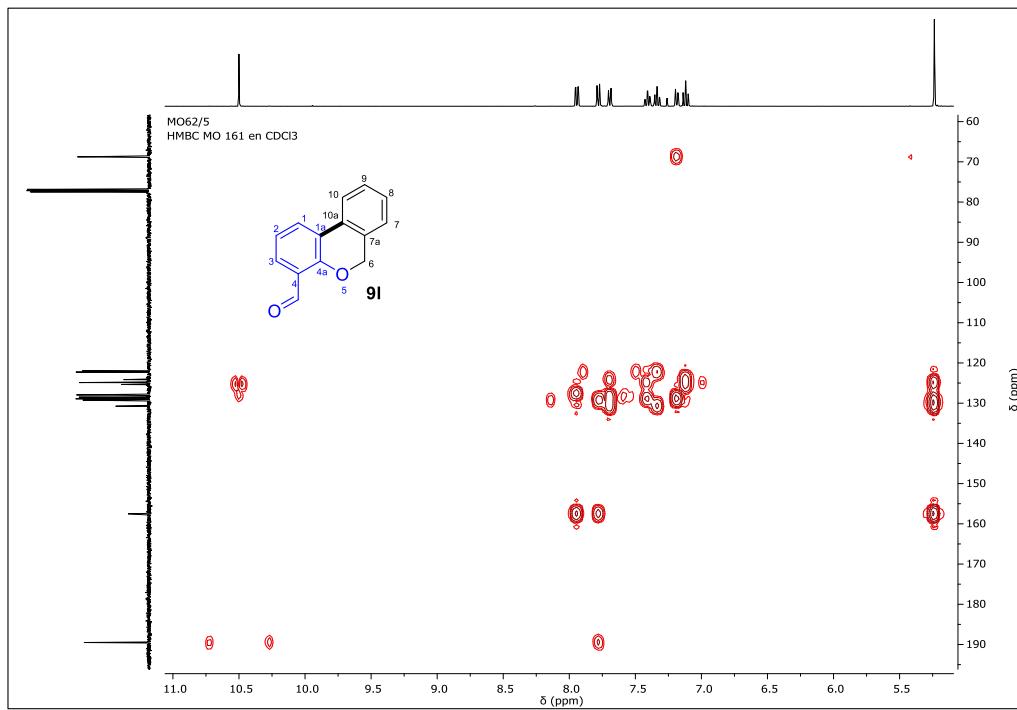


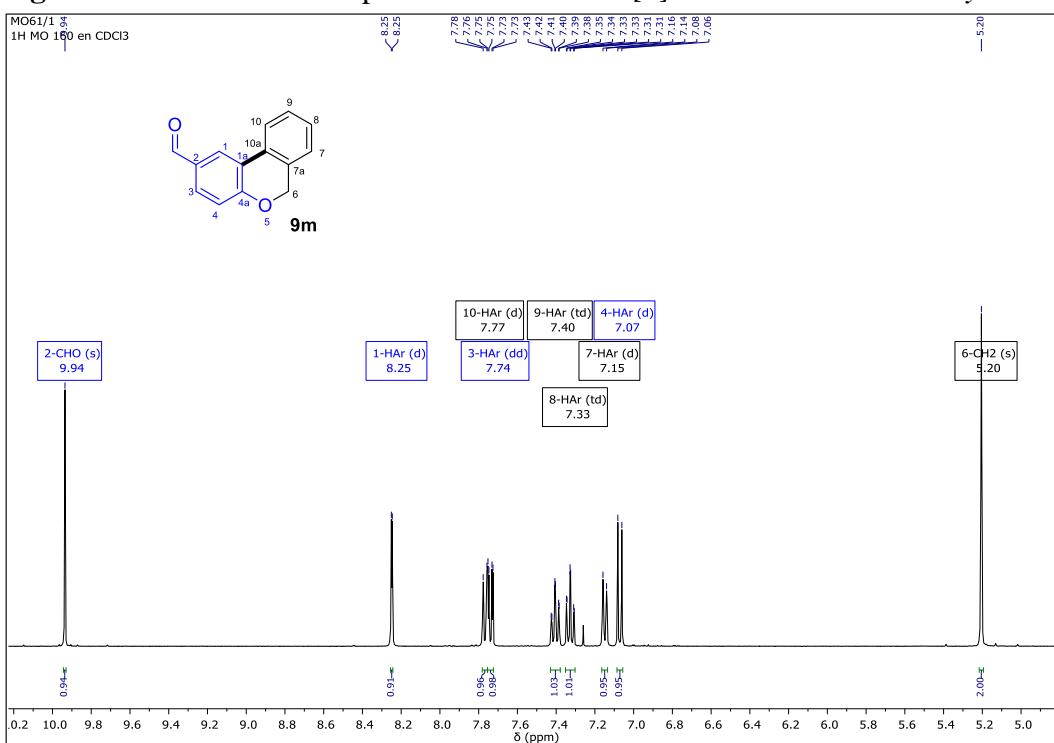
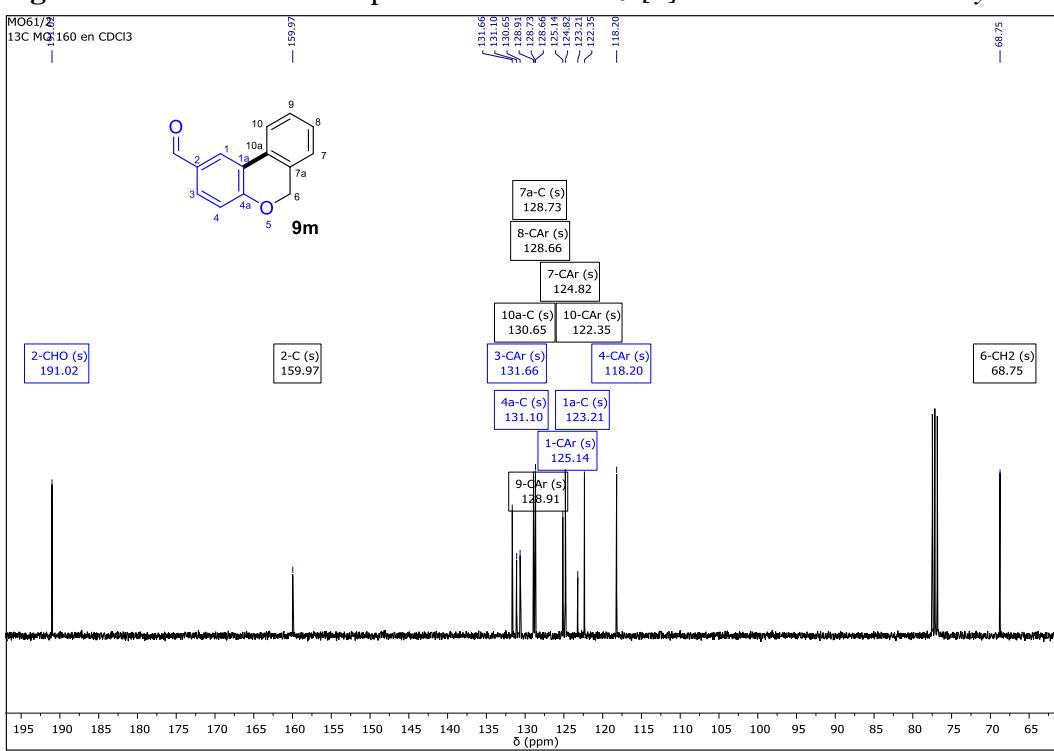
Figure ESI 109. ^1H -NMR spectrum of 6H-benzo[c]chromene-2-carbaldehyde **9m****Figure ESI 110.** ^{13}C -NMR spectrum of 6H-benzo[c]chromene-2-carbaldehyde **9m**

Figure ESI 111. COSY spectrum of *6H-benzo[c]chromene-2-carbaldehyde 9m*

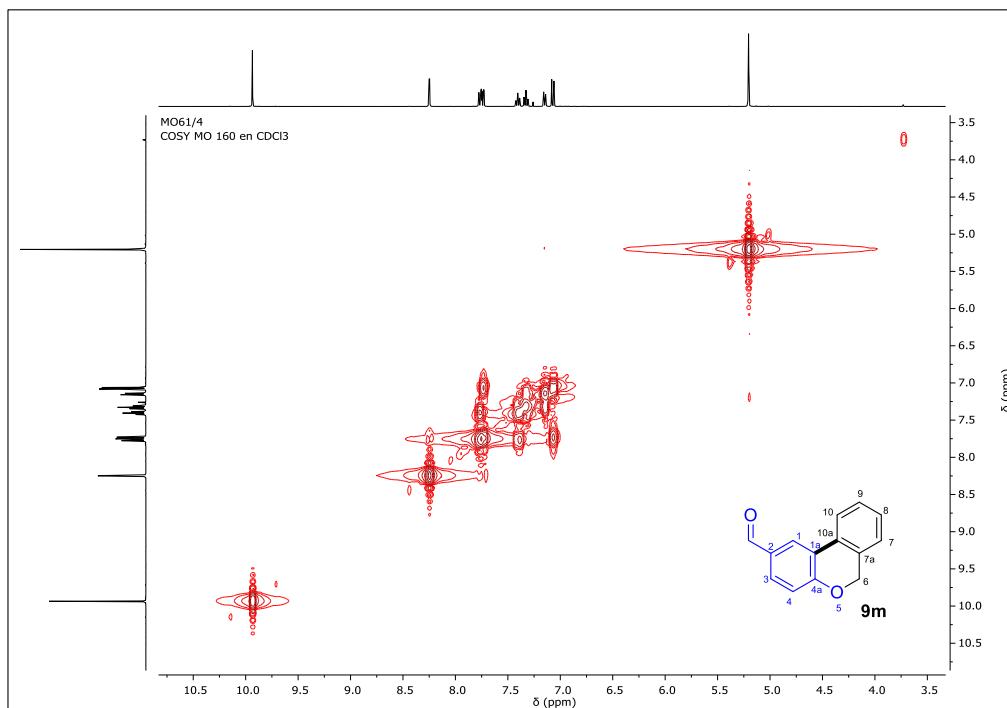


Figure ESI 112. HSQC spectrum of *6H-benzo[c]chromene-2-carbaldehyde 9m*

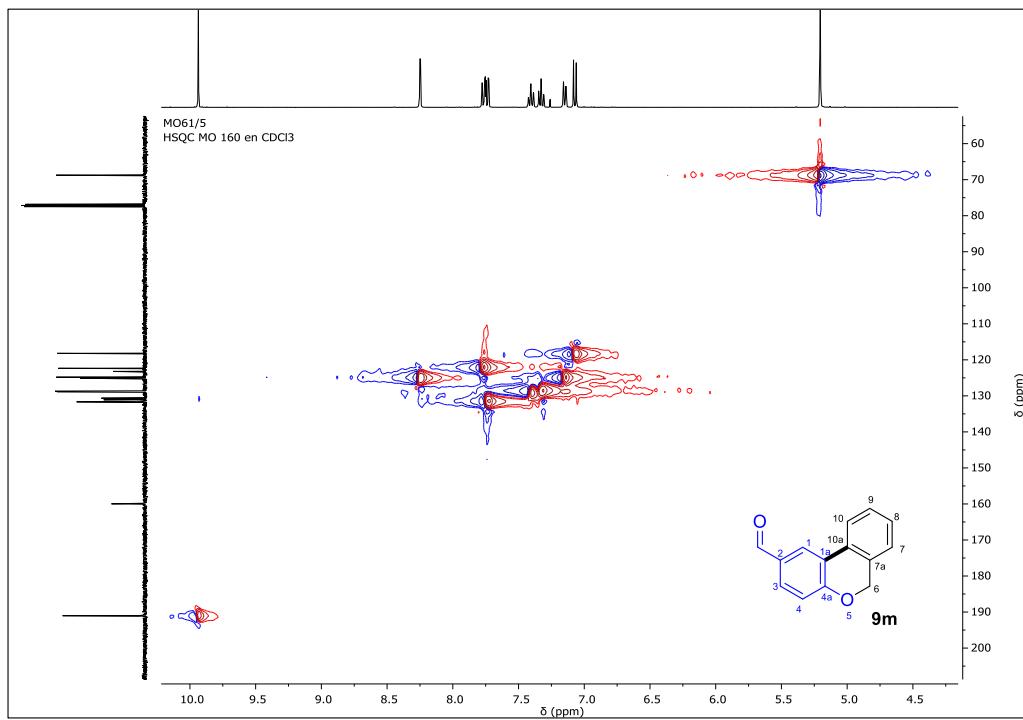


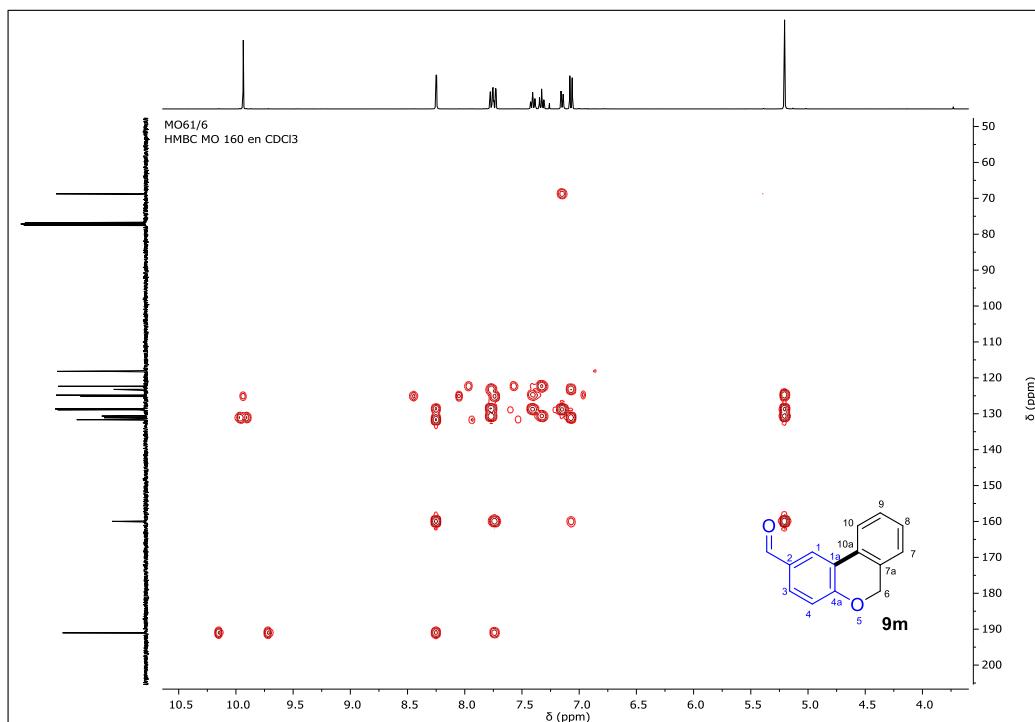
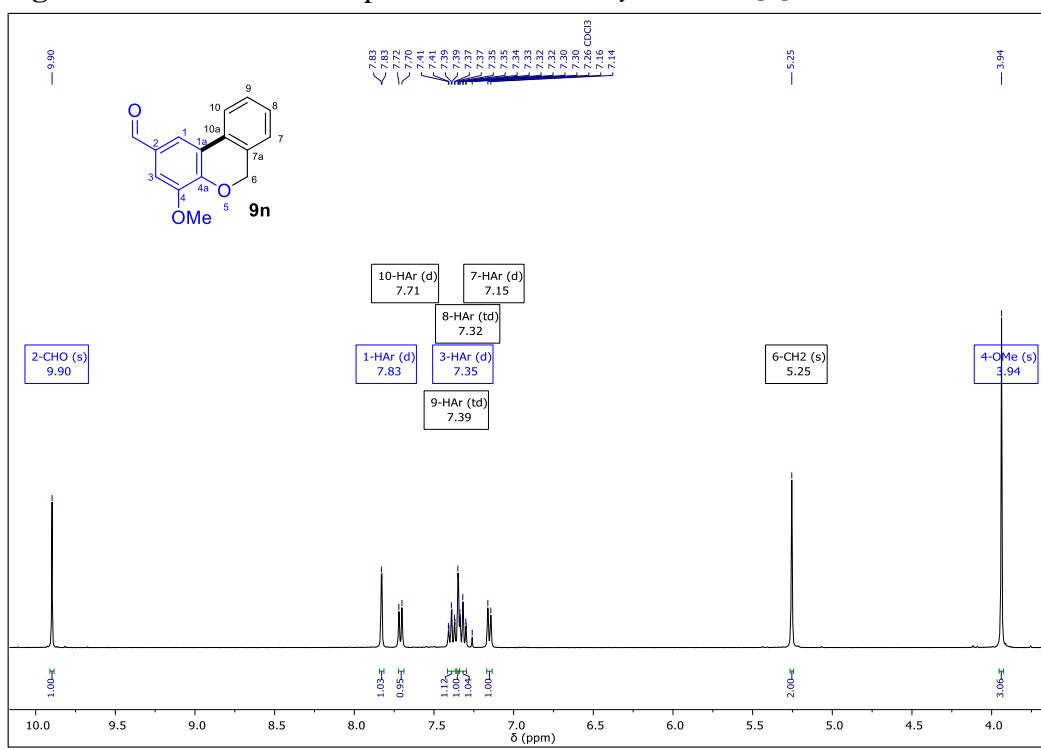
Figure ESI 113. HMBC spectrum of *6H*-benzo[*c*]chromene-2-carbaldehyde **9m****Figure ESI 114.** ^1H -NMR spectrum of 4-methoxy-6*H*-benzo[*c*]chromene-2-carbaldehyde **9n**

Figure ESI 115. ^{13}C -NMR spectrum of 4-methoxy-6H-benzo[c]chromene-2-carbaldehyde **9n**

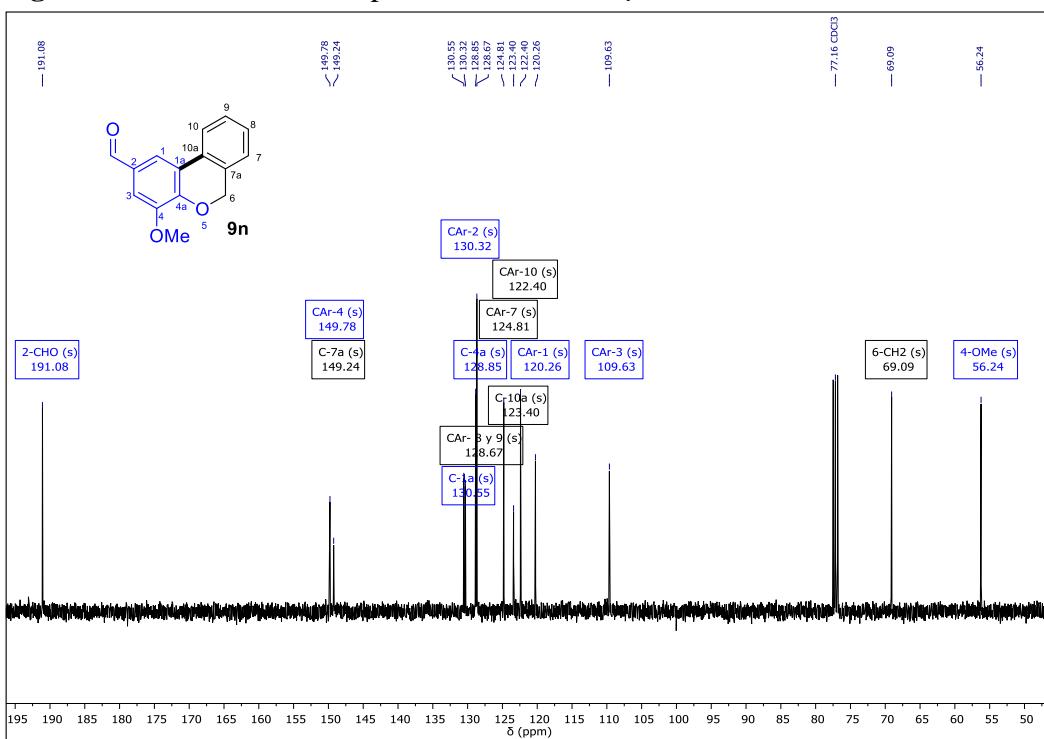


Figure ESI 116. COSY spectrum of 4-methoxy-6H-benzo[c]chromene-2-carbaldehyde **9n**

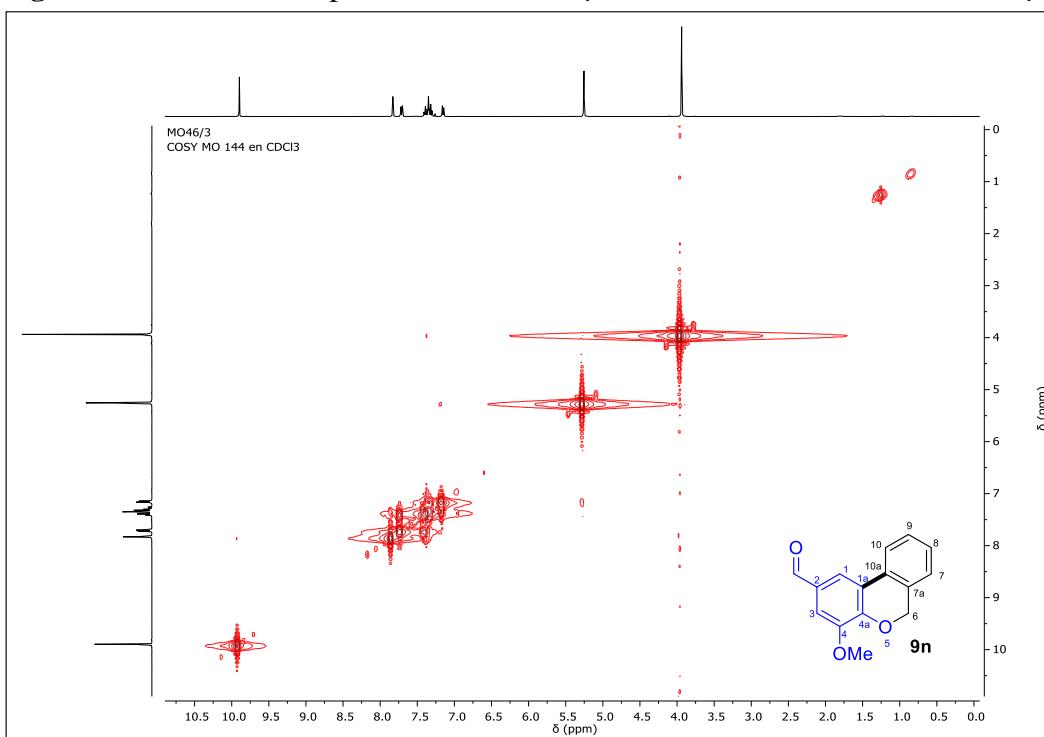


Figure ESI 117. HSQC spectrum of *4-methoxy-6H-benzo[c]chromene-2-carbaldehyde 9n*

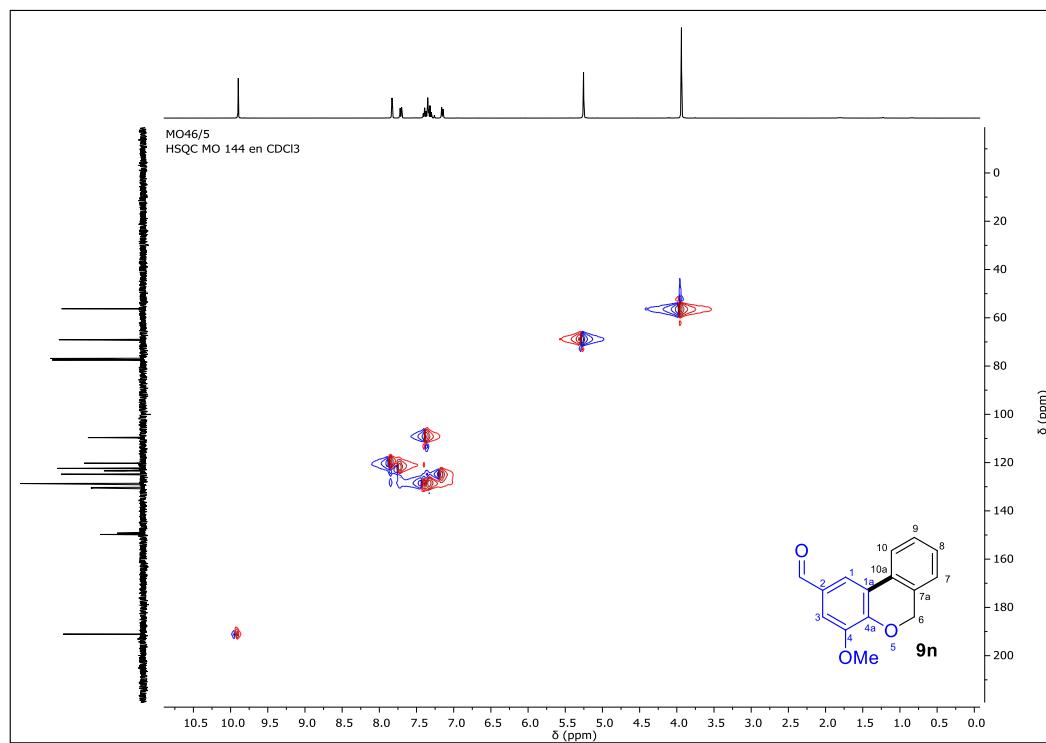


Figure ESI 118. HMBC spectrum of *4-methoxy-6H-benzo[c]chromene-2-carbaldehyde 9n*

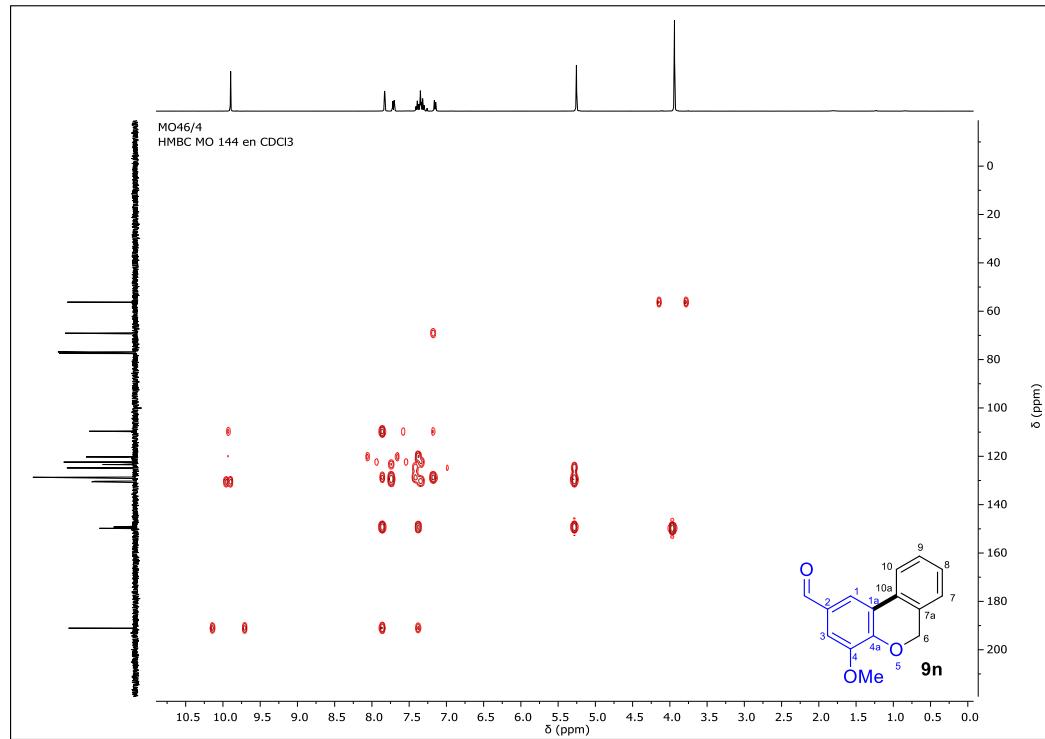


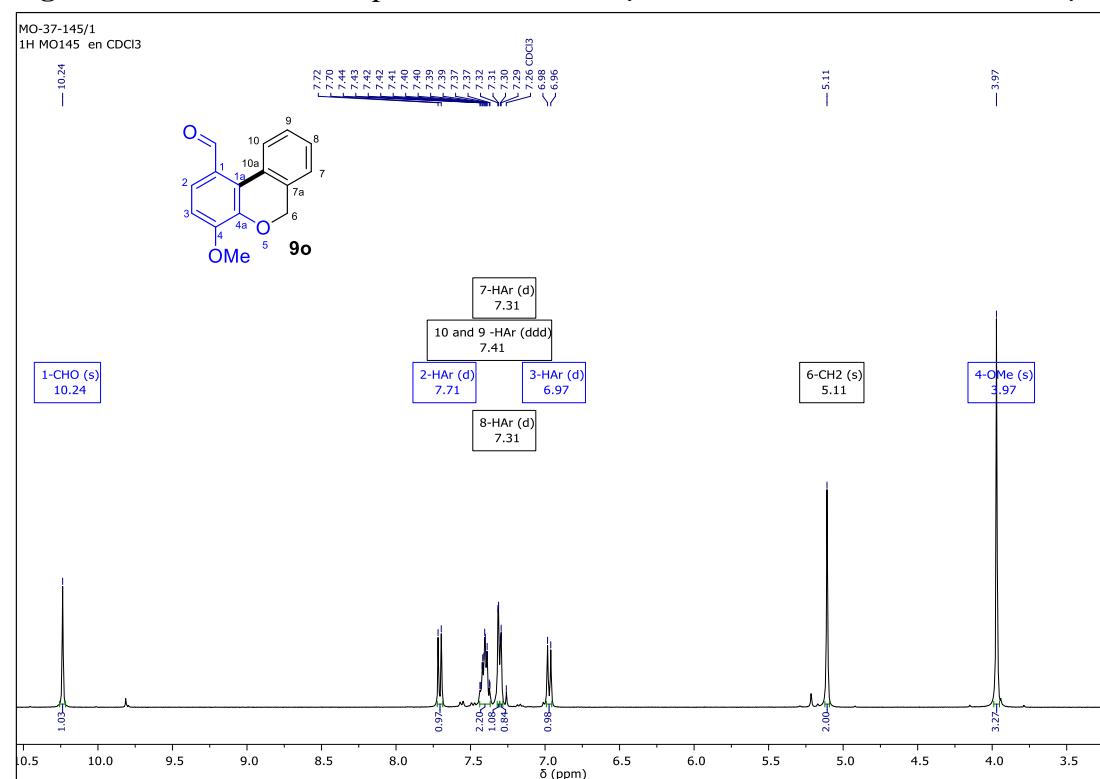
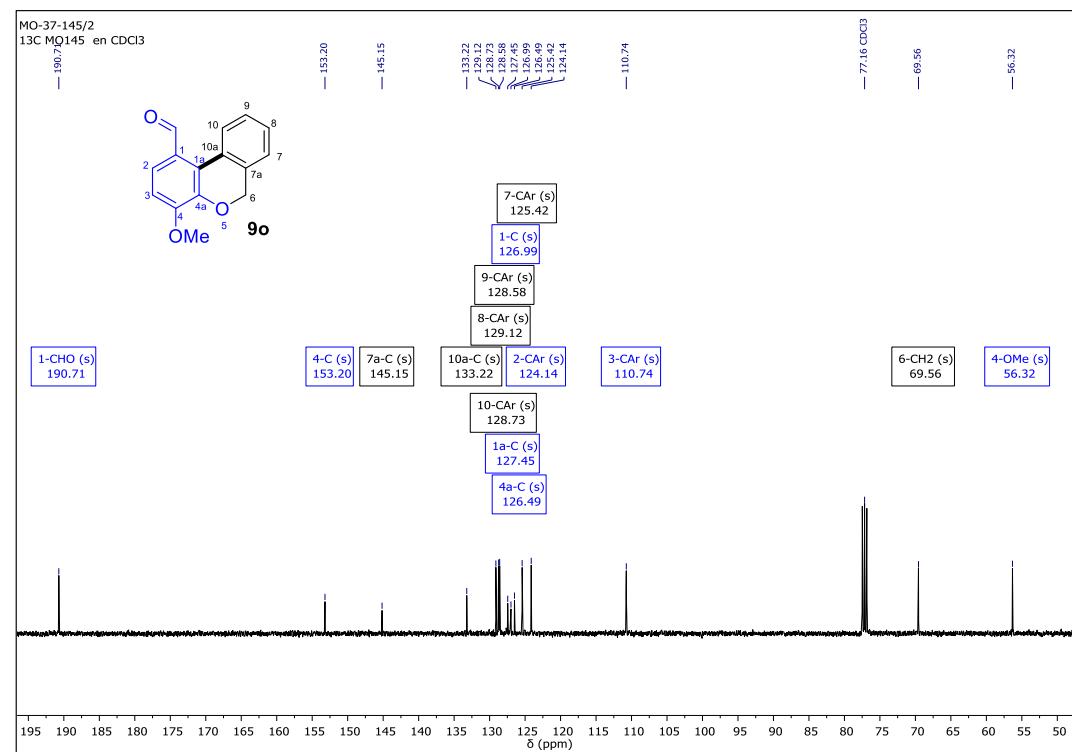
Figure ESI 119. ^1H -NMR spectrum of 4-methoxy-6H-benzo[c]chromene-1-carbaldehyde **9o****Figure ESI 120.** ^{13}C -NMR spectrum of 4-methoxy-6H-benzo[c]chromene-1-carbaldehyde **9o**

Figure ESI 121. COSY spectrum of *4-methoxy-6H-benzo[c]chromene-1-carbaldehyde* **9o**

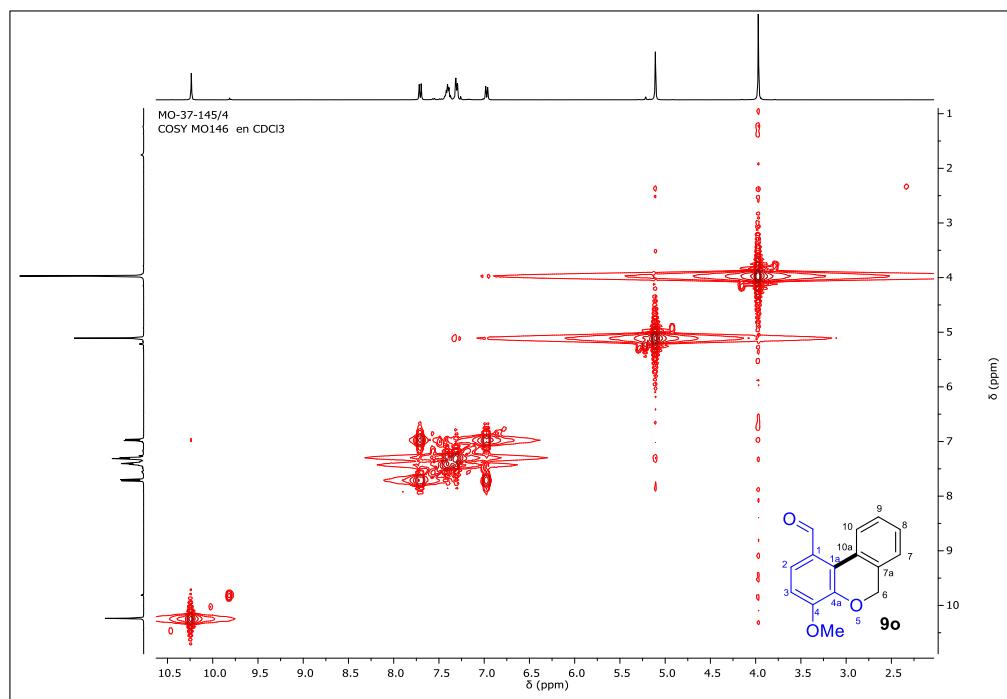


Figure ESI 122. HSQC spectrum of *4-methoxy-6H-benzo[c]chromene-1-carbaldehyde* **9o**

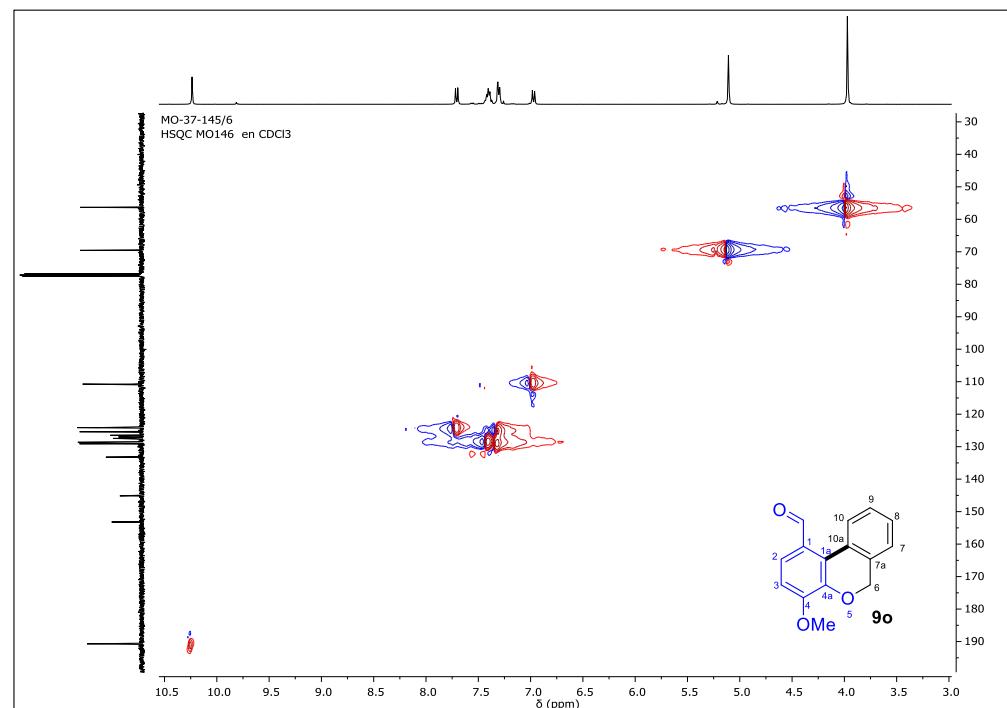


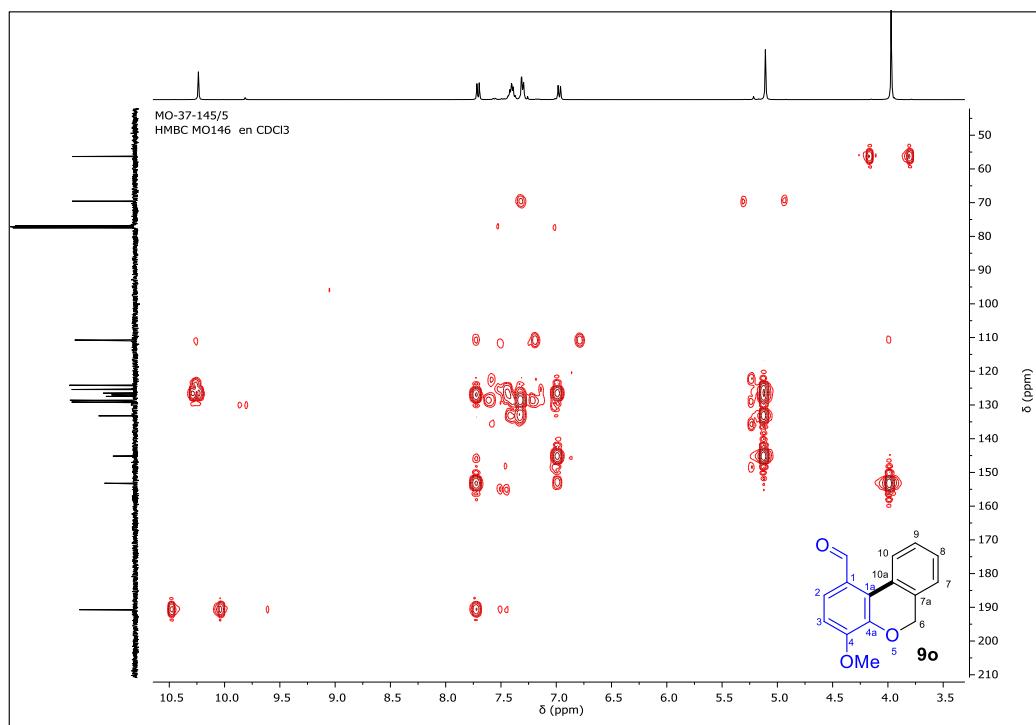
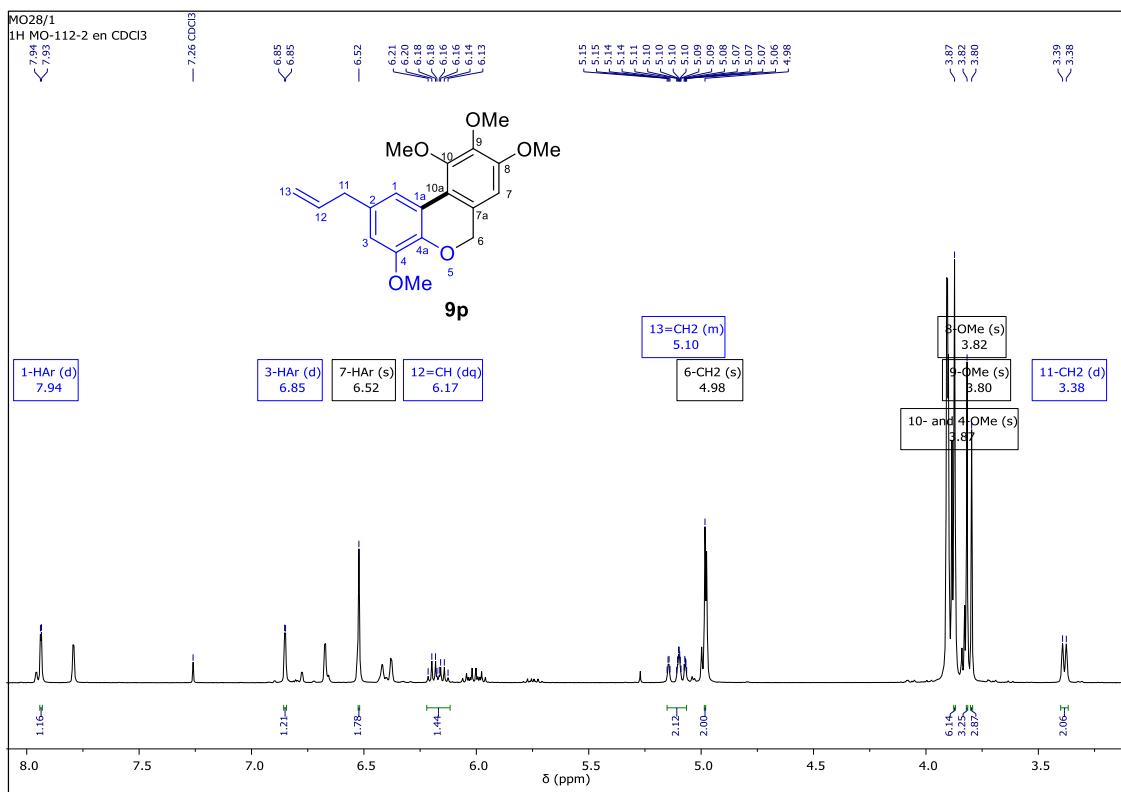
Figure ESI 123. HMBC spectrum of 4-methoxy-6H-benzo[c]chromene-1-carbaldehyde **9o****Figure ESI 124.** ^1H -NMR spectrum of 2-allyl-4,8,9,10-tetramethoxy-6H-benzo[c]chromene **9p**

Figure ESI 125. ^{13}C -NMR spectrum of 2-allyl-4,8,9,10-tetramethoxy-6H-benzo[c]chromene **9p**

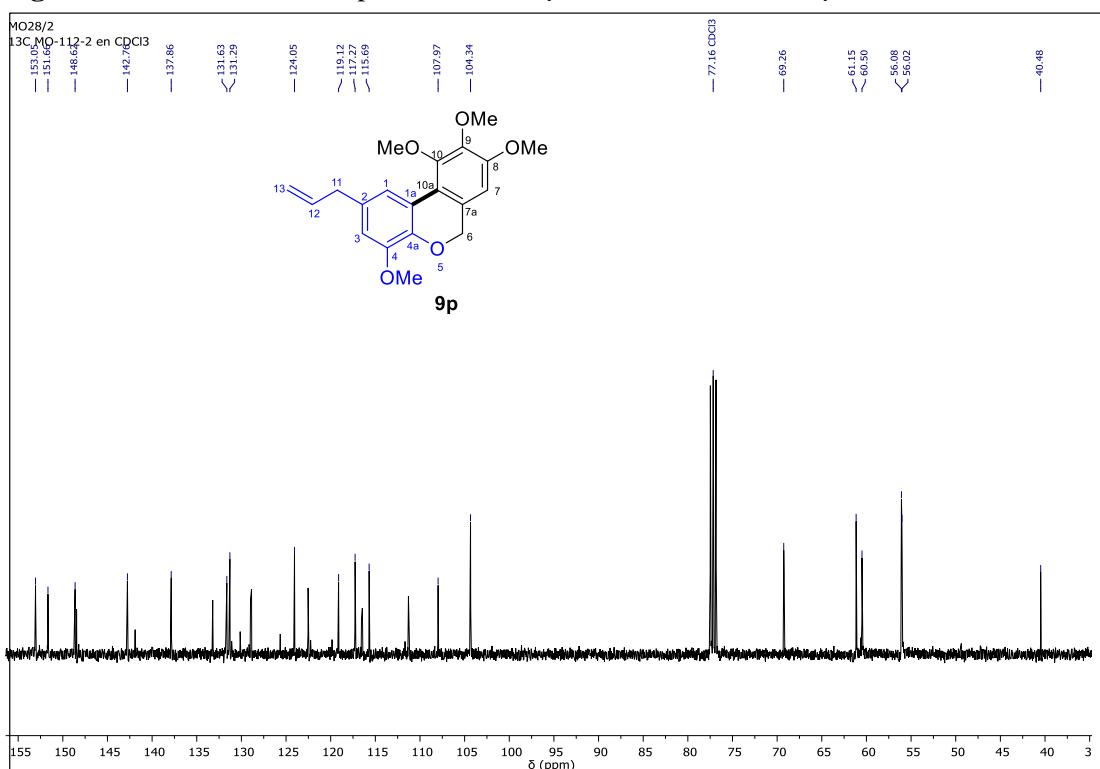


Figure ESI 126. ^1H -NMR spectrum of (*E*)-4,8,9,10-tetramethoxy-2-(prop-1-en-1-yl)-6H-benzo[c]chromene **9q**

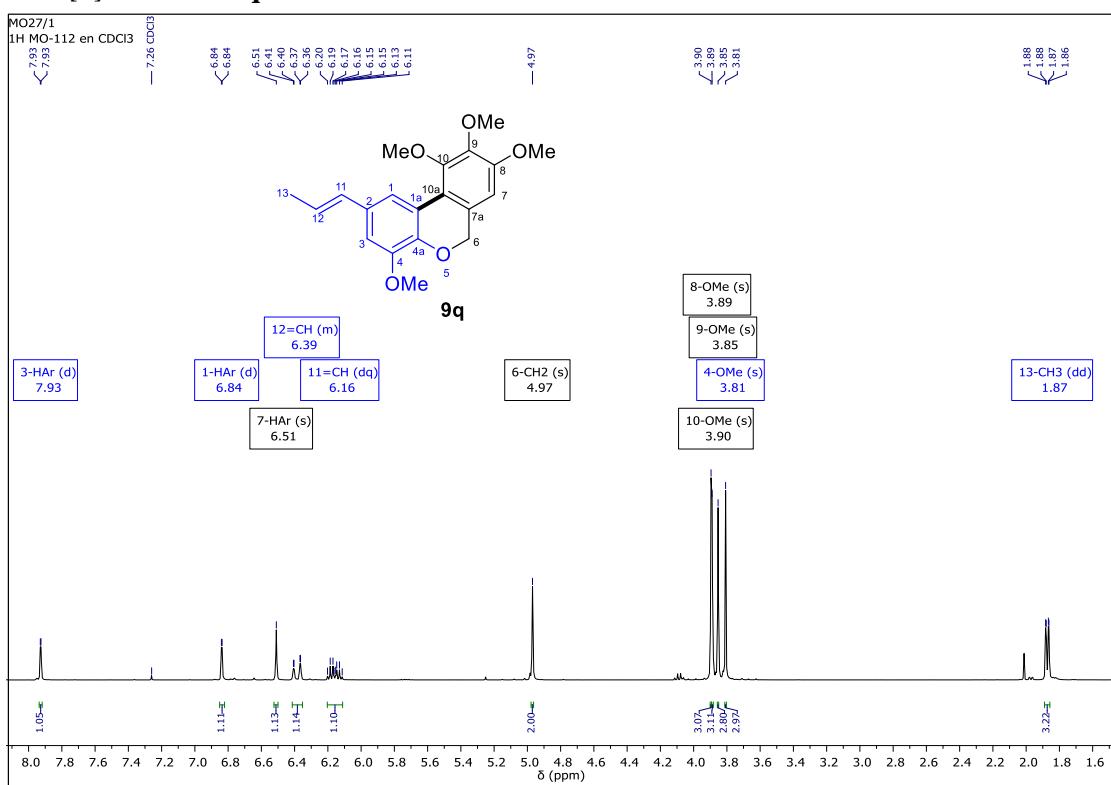


Figure ESI 127. ^{13}C -NMR spectrum of (*E*)-4,8,9,10-tetramethoxy-2-(*prop*-1-en-1-yl)-6*H*-benzo[*c*]chromene **9q**

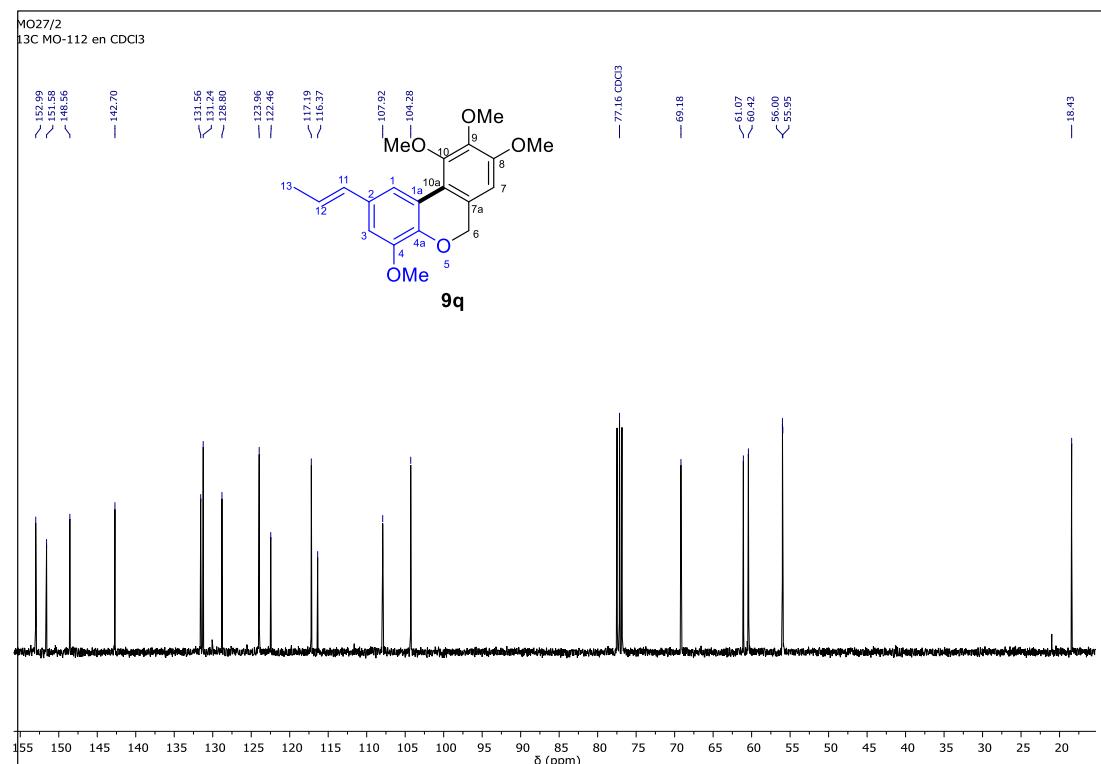


Figure ESI 128. ^1H -NMR spectrum of 6*H*-dibenzo[*c,h*]chromene **9r**

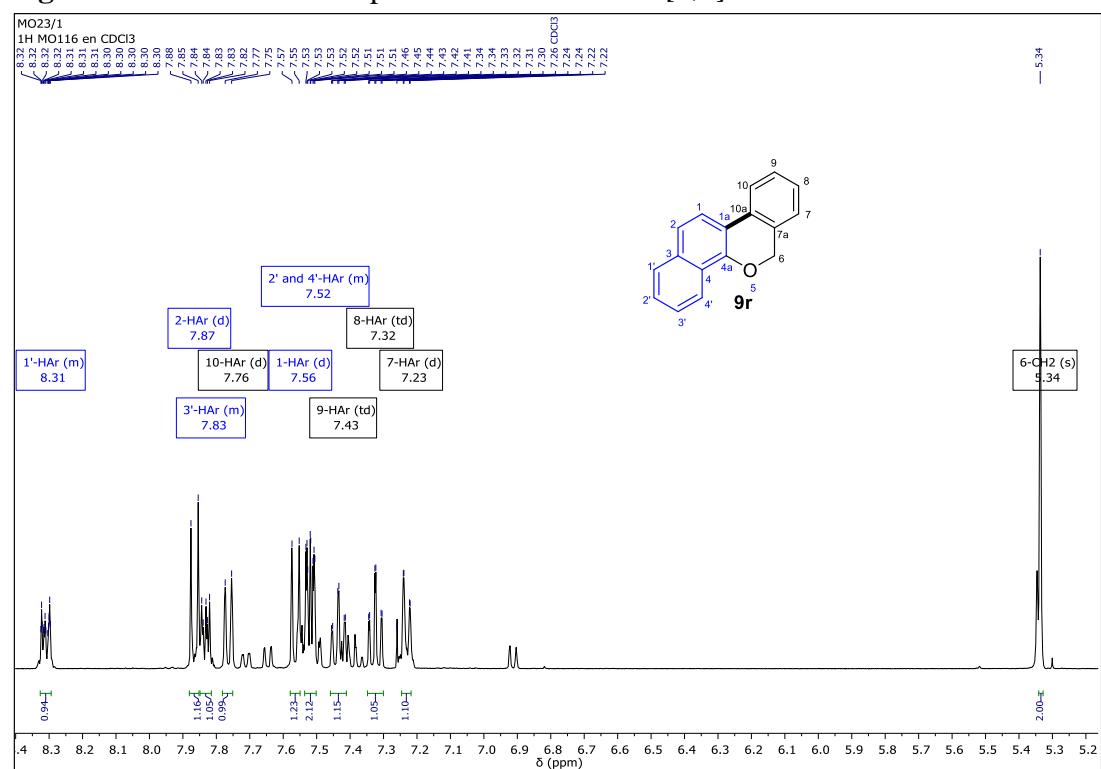


Figure ESI 129. ^{13}C -NMR spectrum of *6H-dibenzo[c,h]chromene 9r*

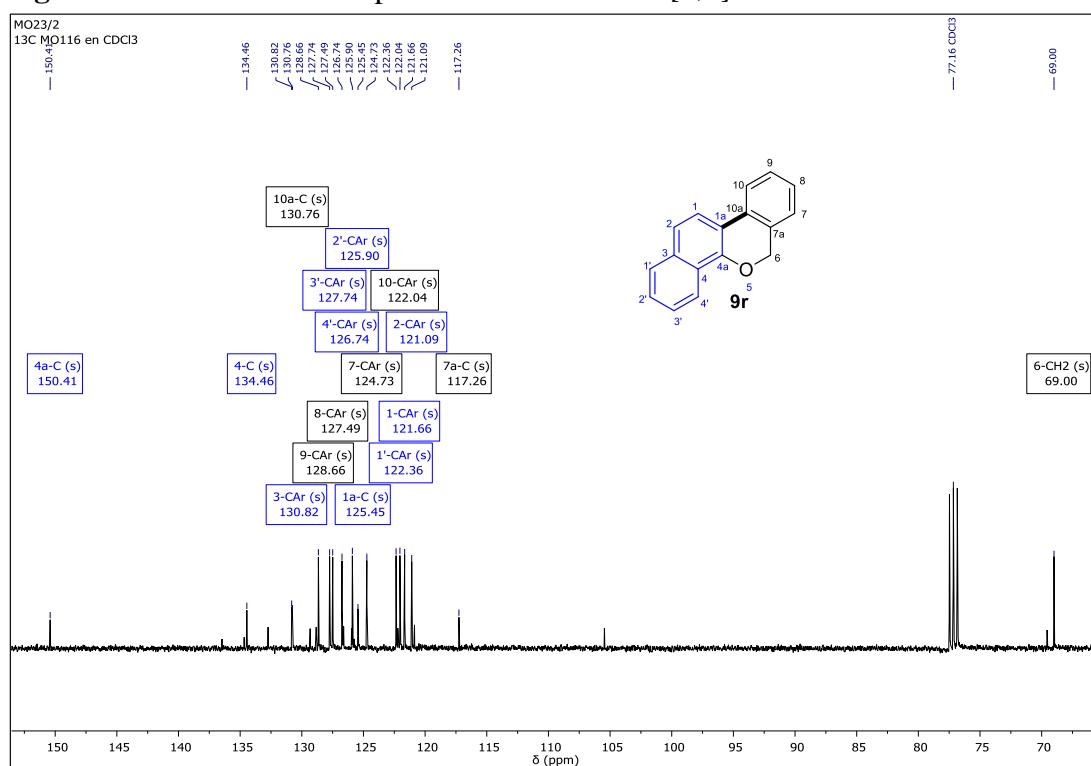


Figure ESI 130. COSY spectrum of *6H-dibenzo[c,h]chromene 9r*

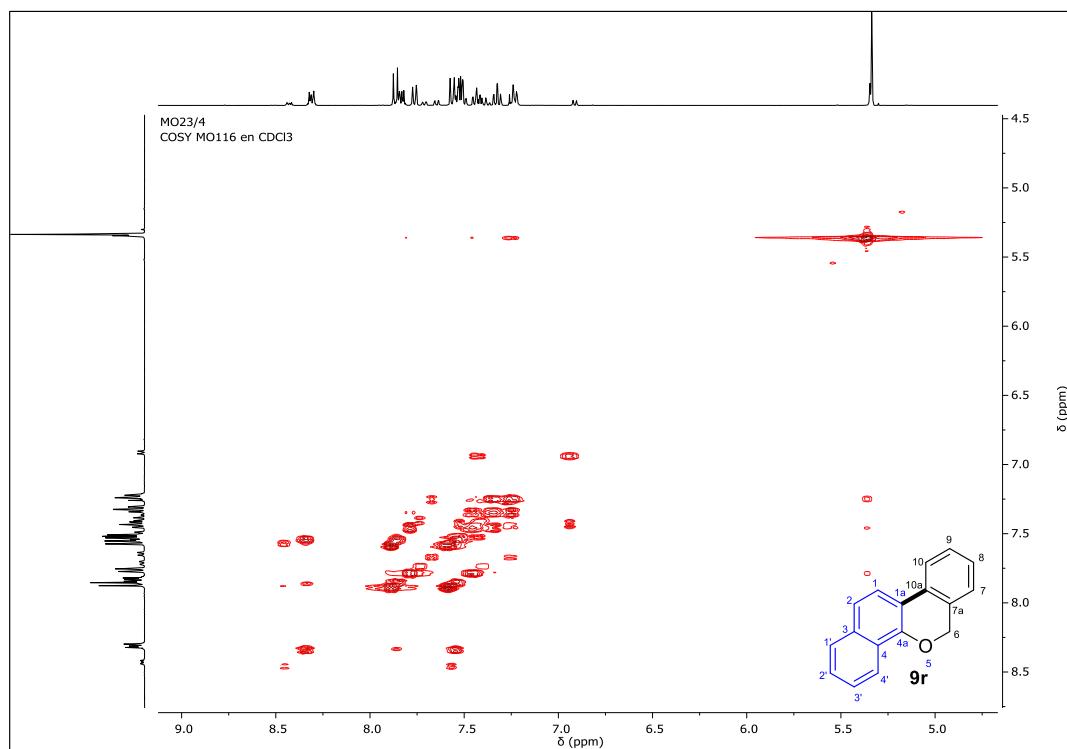


Figure ESI 131. HSQC spectrum of *6H-dibenzo[c,h]chromene 9r*

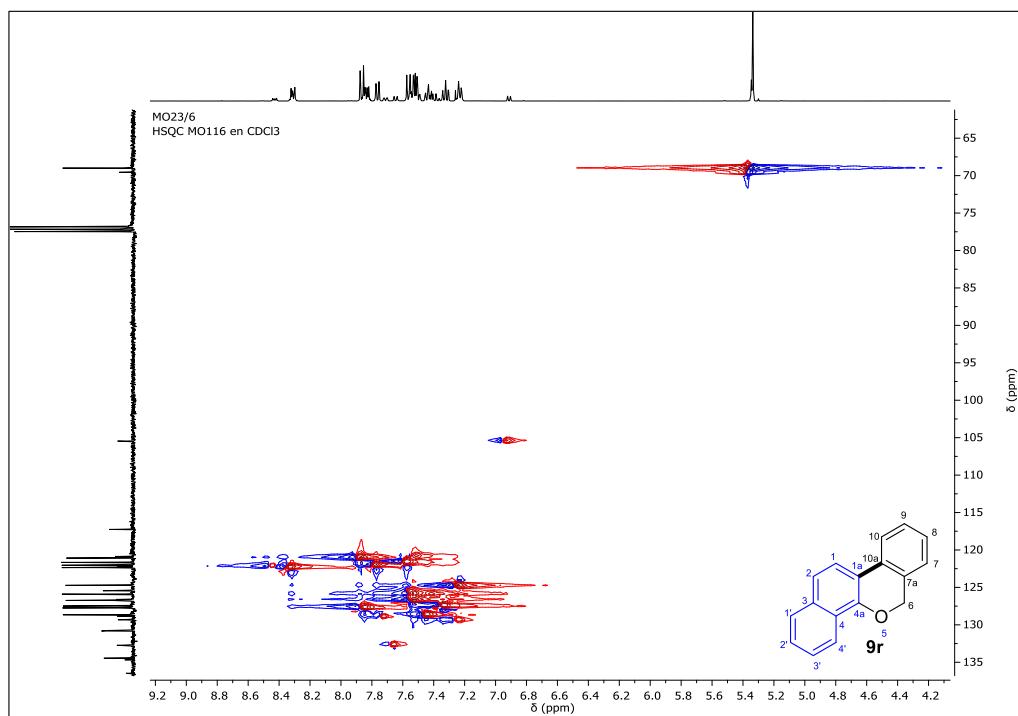


Figure ESI 132. HMBC spectrum of *6H-dibenzo[c,h]chromene 9r*

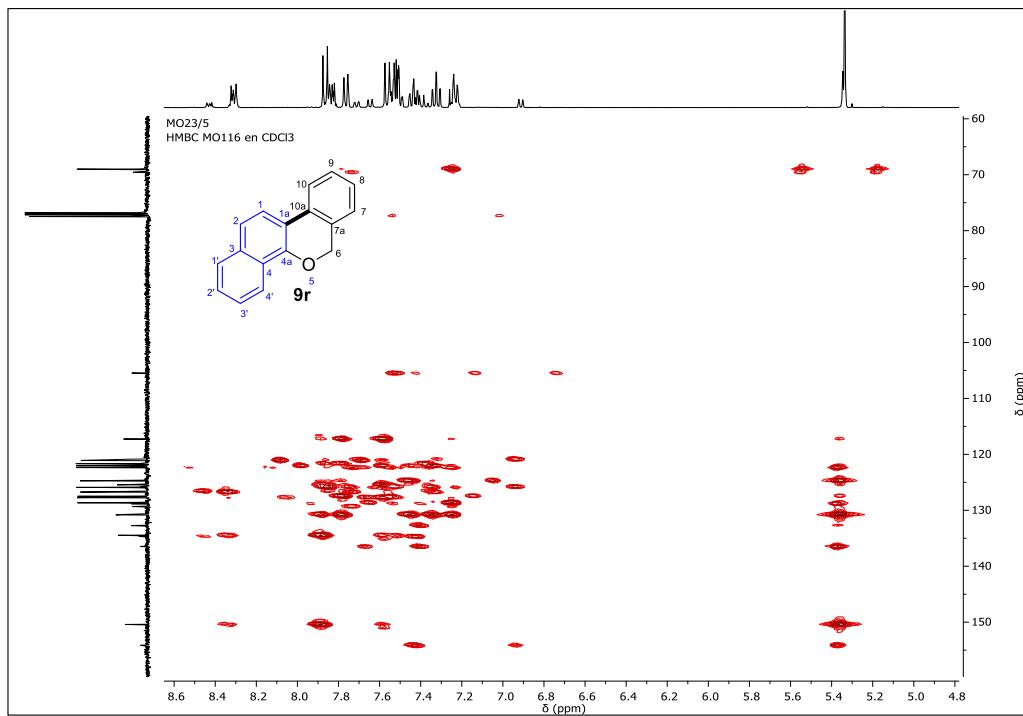


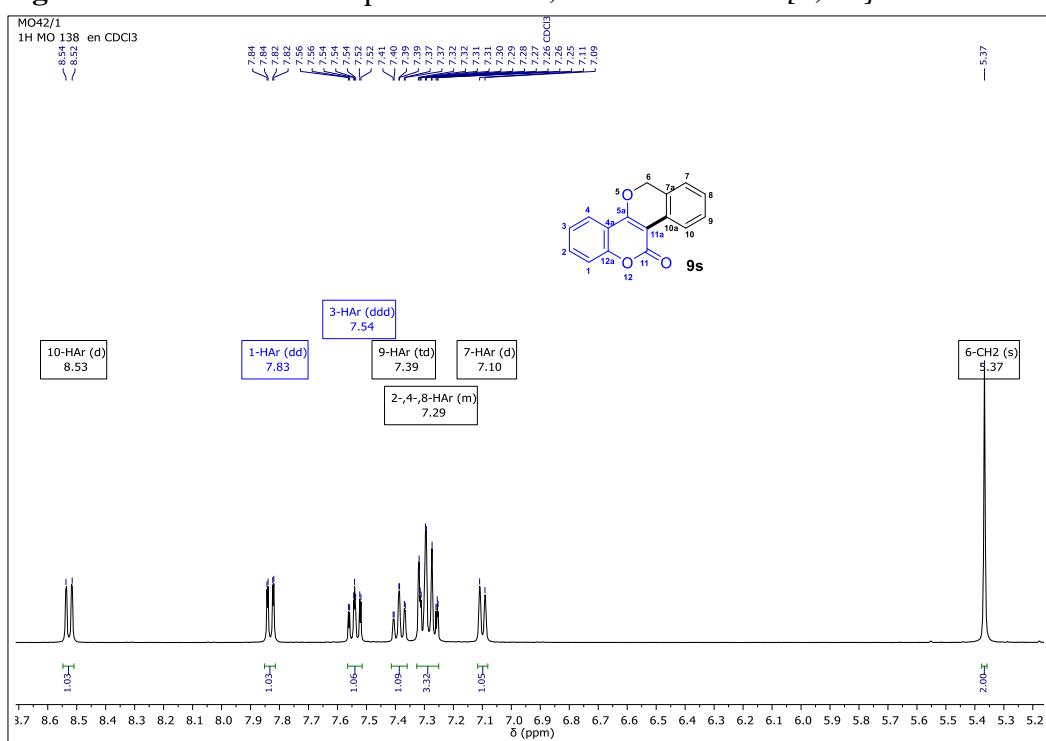
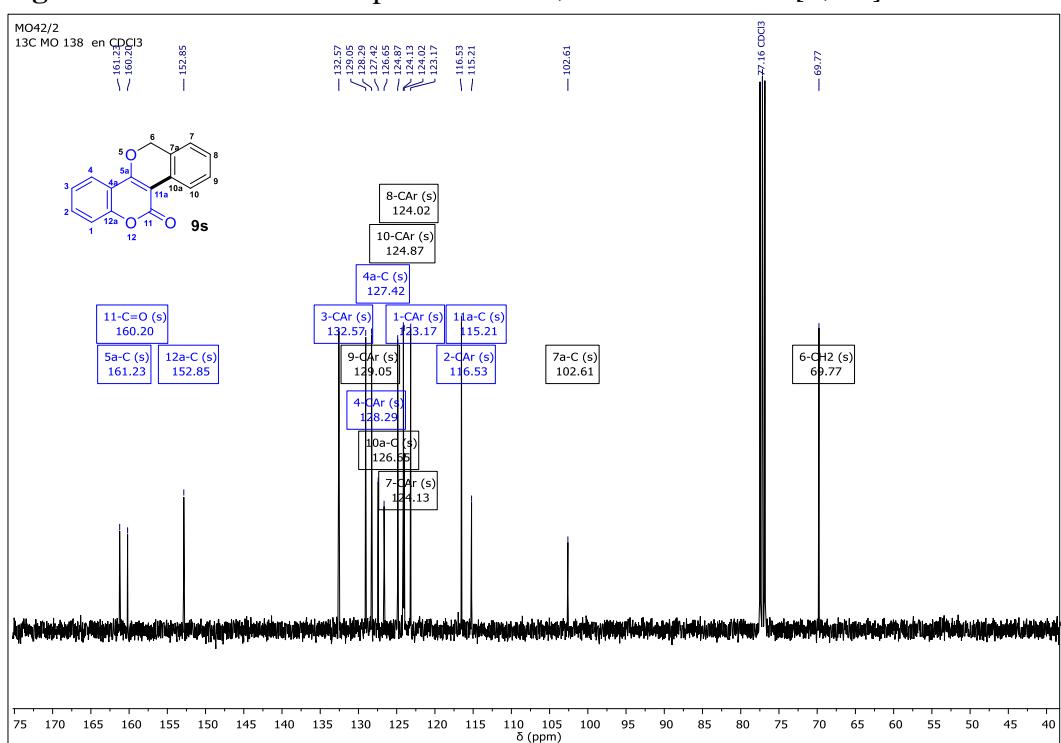
Figure ESI 133. ^1H -NMR spectrum of *6H,11H-isochromene[4,3-c]chromen-11-one* **9s****Figure ESI 134.** ^{13}C -NMR spectrum of *6H,11H-isochromene[4,3-c]chromen-11-one* **9s**

Figure ESI 135. COSY spectrum of *6H,11H-isochromene[4,3-c]chromen-11-one* **9s**

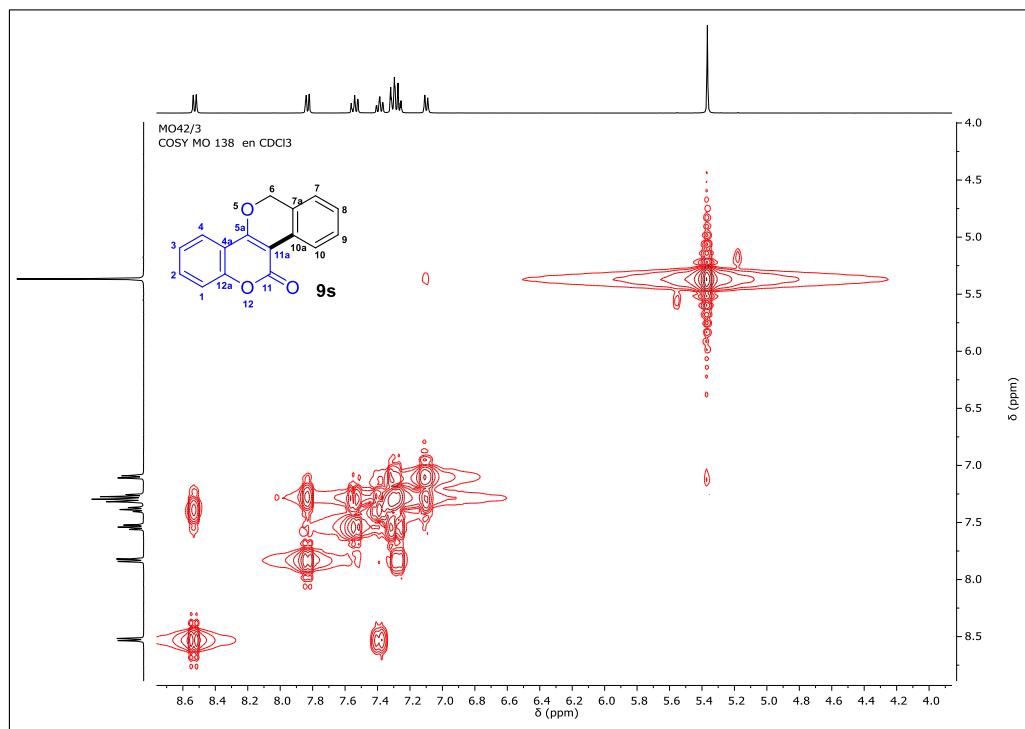


Figure ESI 136. HSQC spectrum of *6H,11H-isochromene[4,3-c]chromen-11-one* **9s**

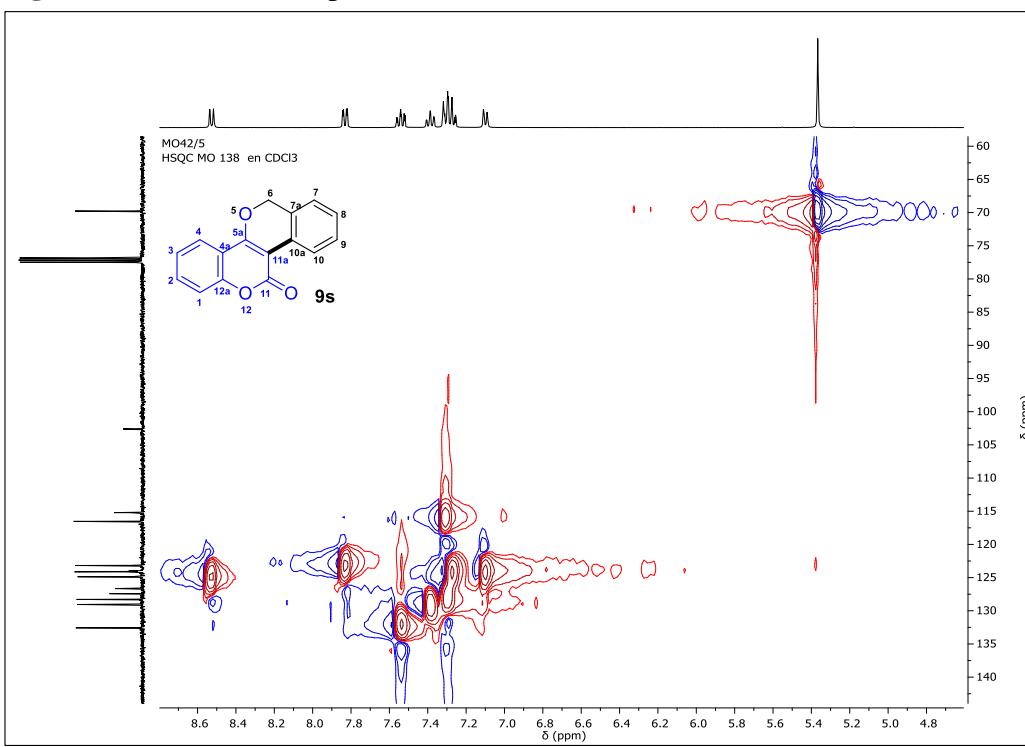


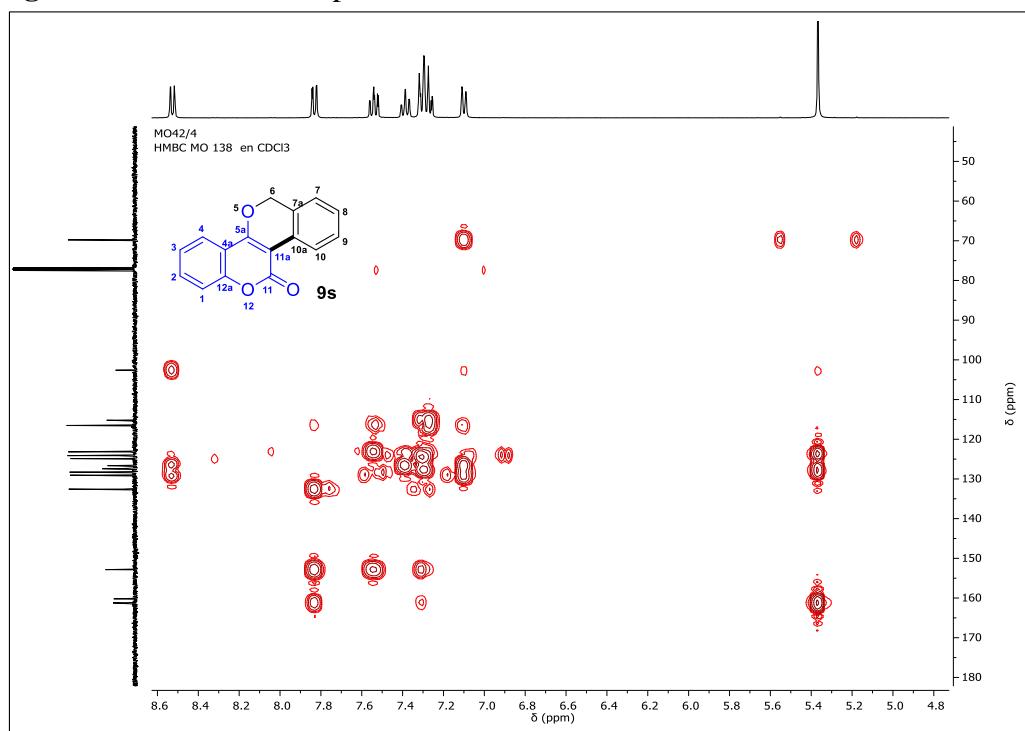
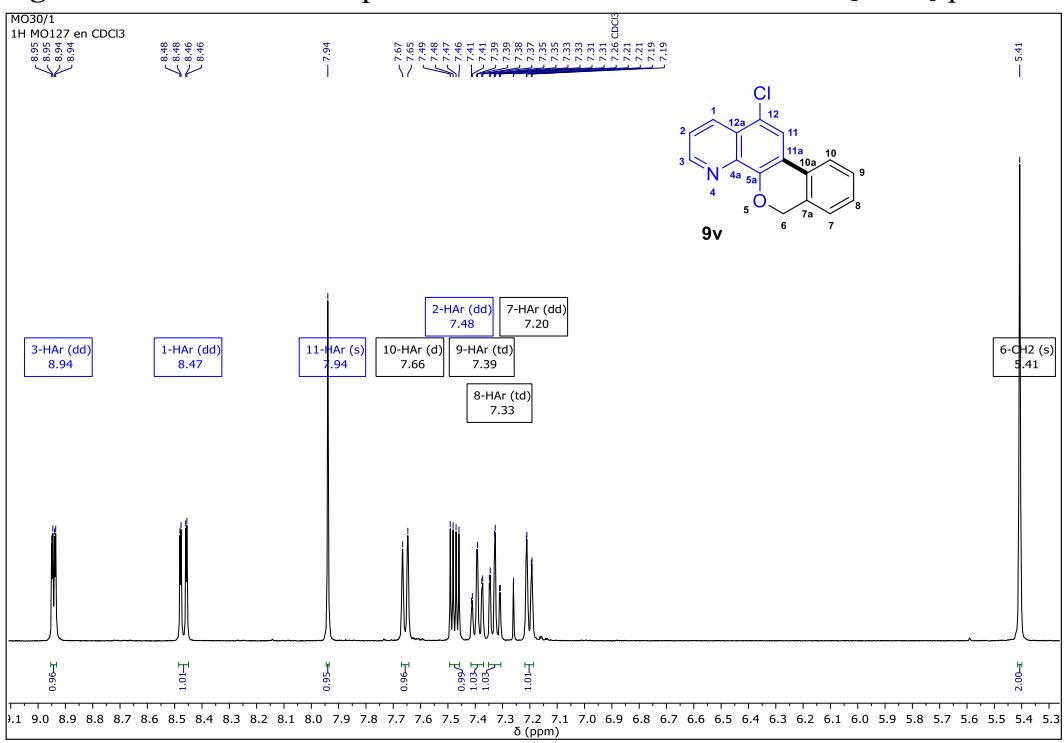
Figure ESI 137. HMBC spectrum of *6H,11H-isochromene[4,3-c]chromen-11-one* **9s****Figure ESI 138.** ^1H -NMR spectrum of *12-chloro-6H-isochromene[4,3-h]quinoline* **9v**

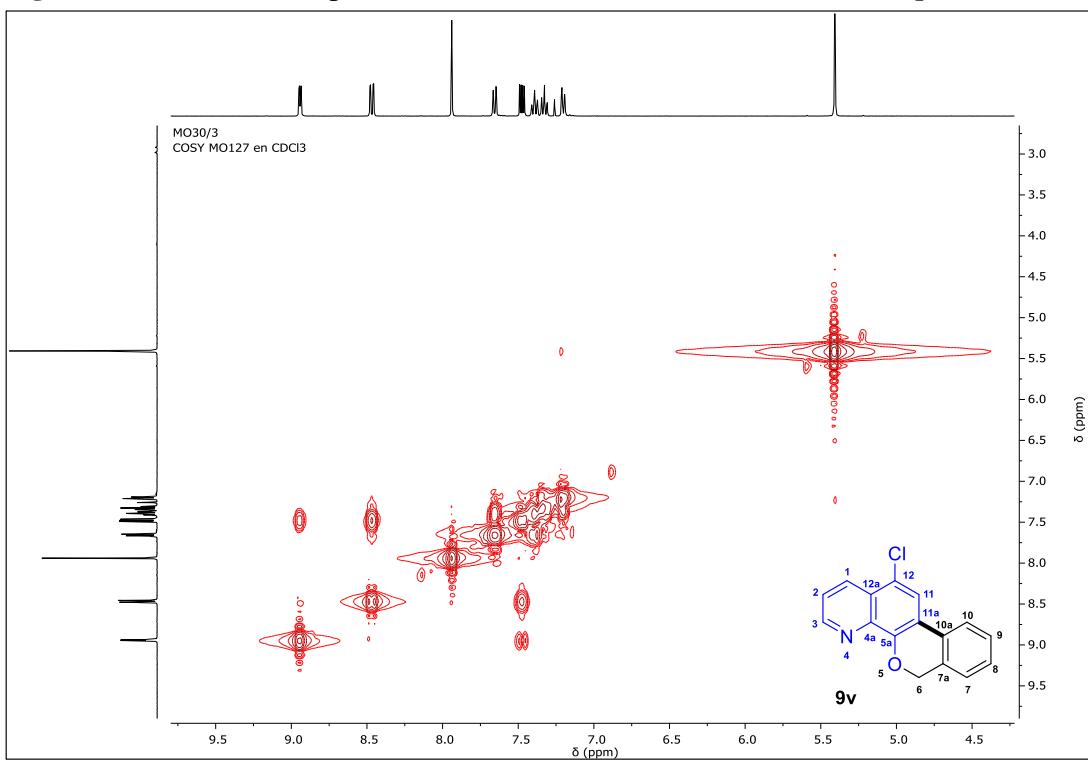
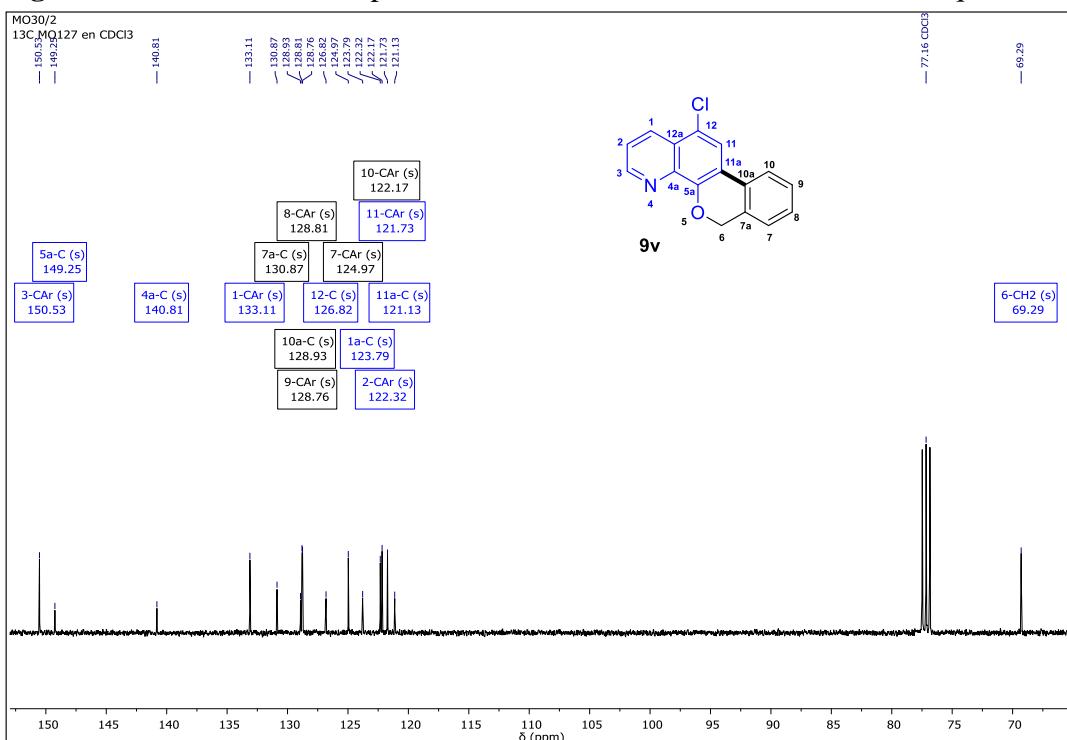
Figure ESI 139. ^{13}C -NMR spectrum of 12-choro-6H-isochromene[4,3-h]quinoline **9v**

Figure ESI 141. HSQC spectrum of *12-chloro-6H-isochromene[4,3-h]quinoline* **9v**

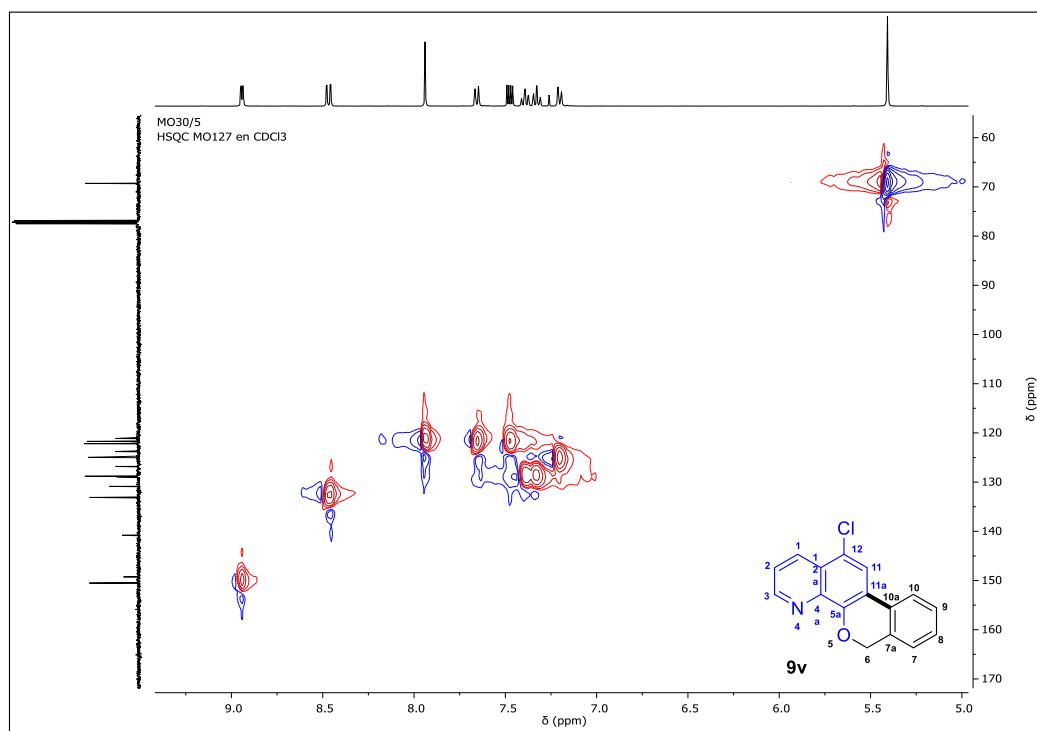
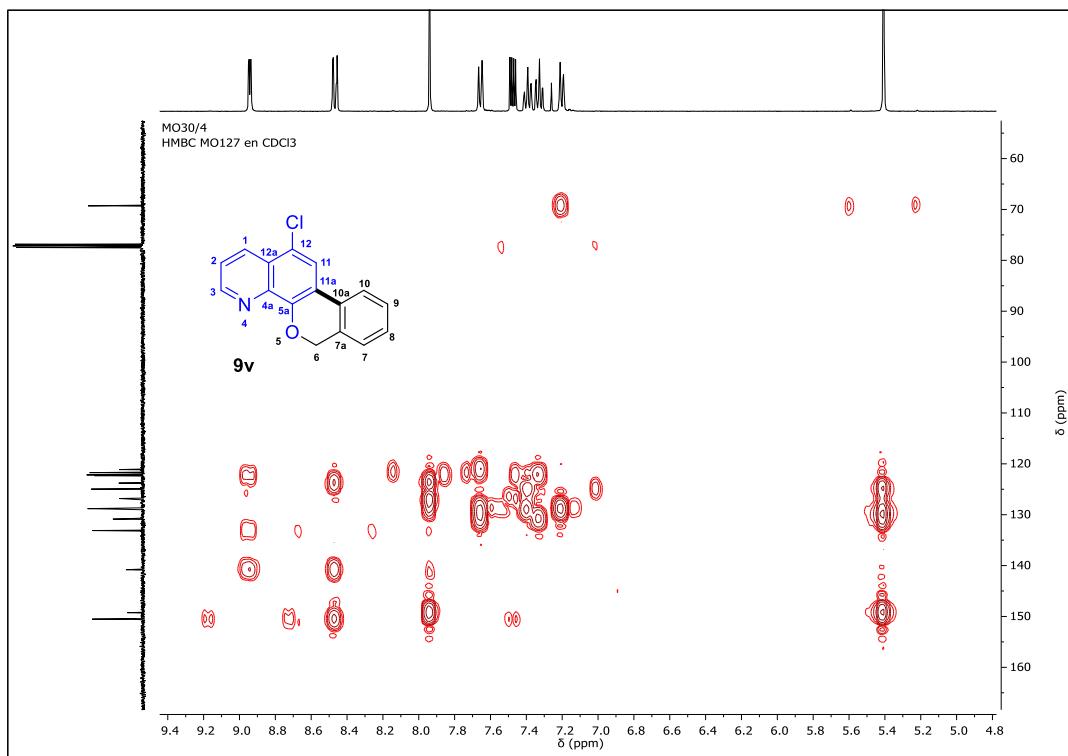


Figure ESI 142. HMBC spectrum of *12-chloro-6H-isochromene[4,3-h]quinoline* **9v**



9. Copies of ^1H NMR, ^{13}C NMR, COSY, HSQC and HMBC charts of **16a-b and **17b****

Figure ESI 143. ^1H -NMR spectrum of *N*-(2-bromobenzyl)aniline **16a**

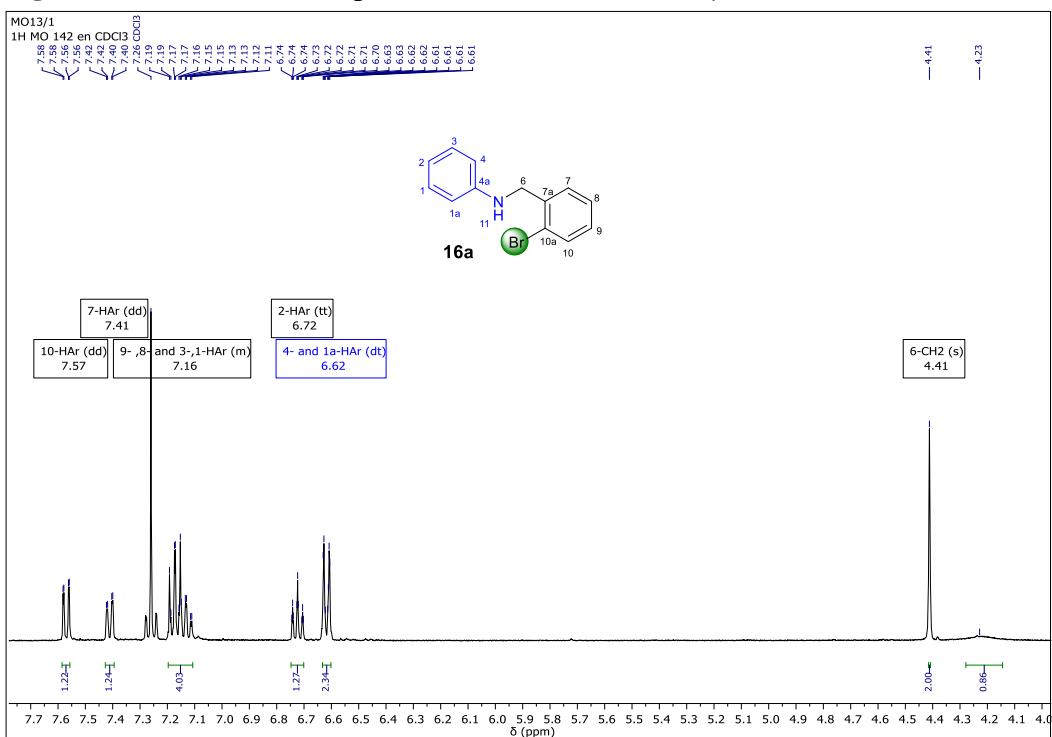


Figure ESI 144. ^{13}C -NMR spectrum of *N*-(2-bromobenzyl)aniline **16a**

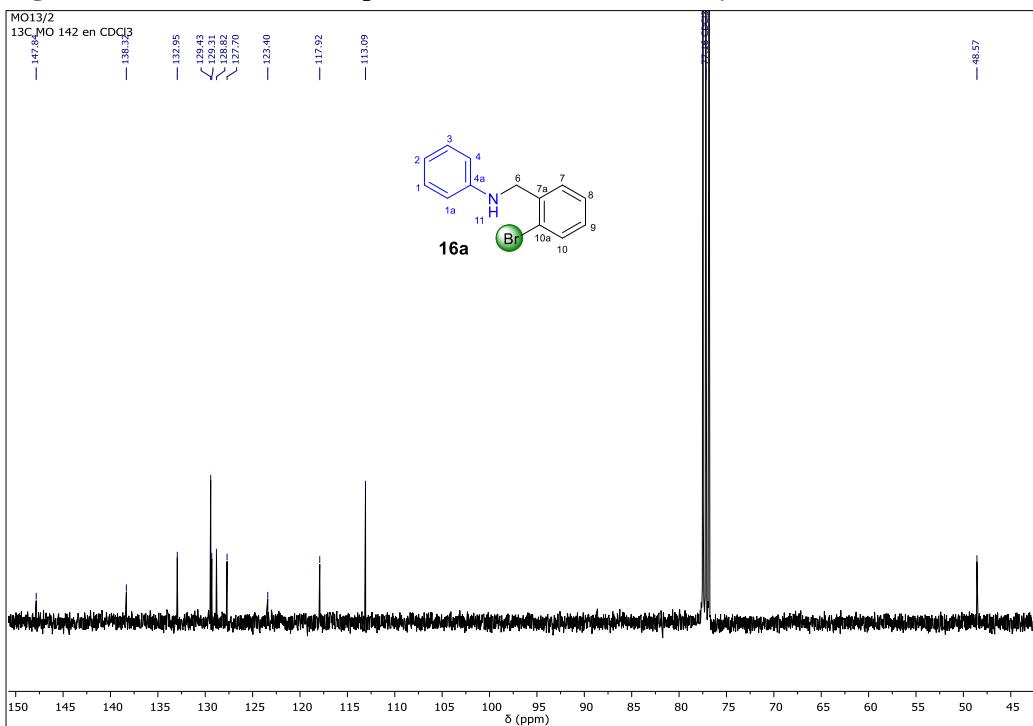


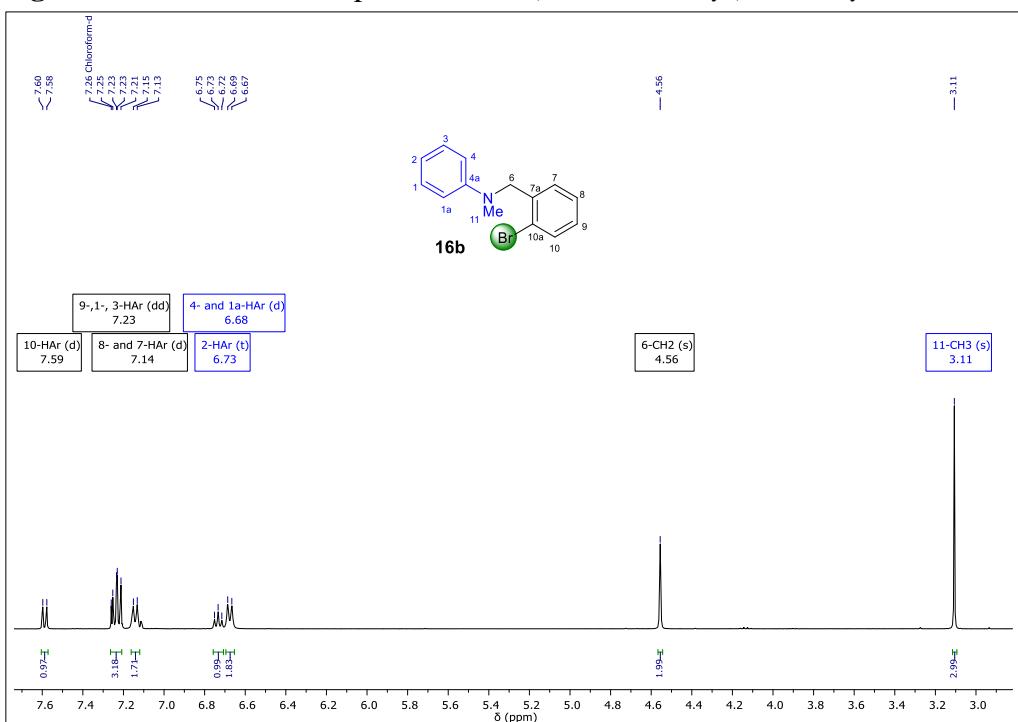
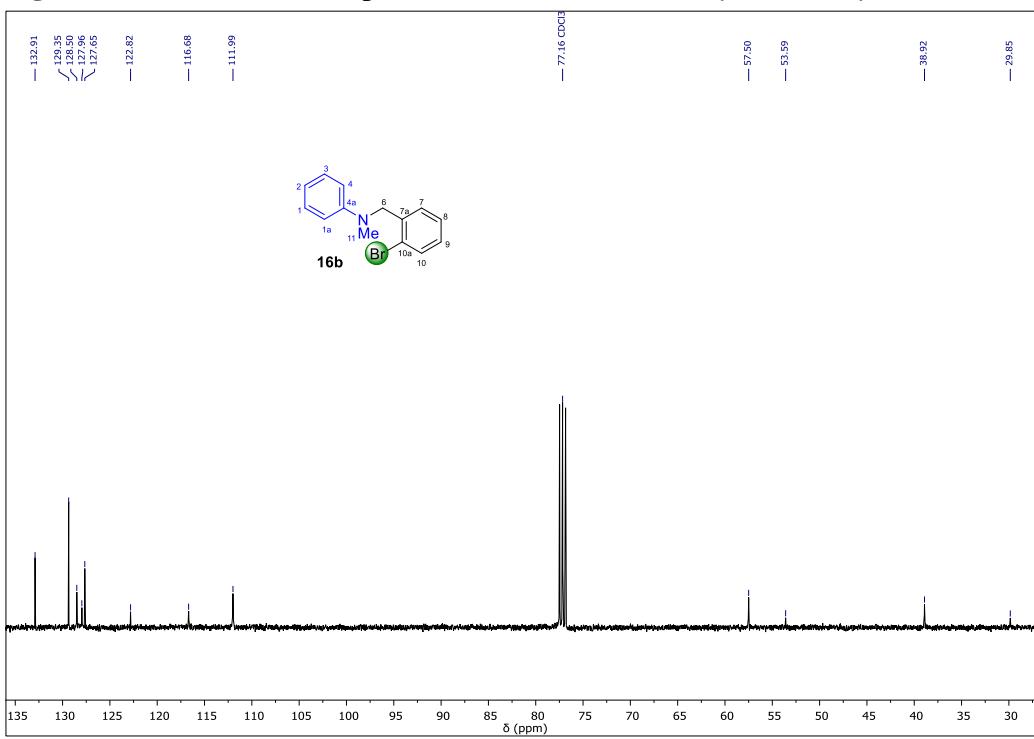
Figure ESI 145. ^1H -NMR spectrum of *N*-(2-bromobenzyl)-*N*-methylaniline **16b****Figure ESI 146.** ^{13}C -NMR spectrum of *N*-(2-bromobenzyl)-*N*-methylaniline **16b**

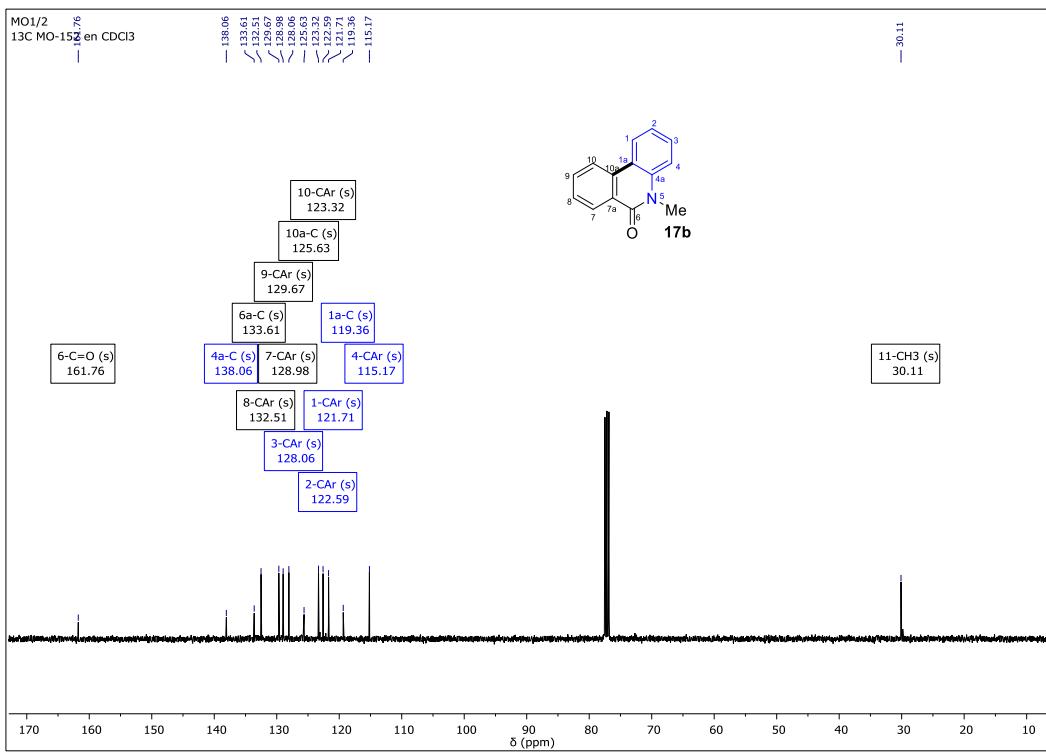
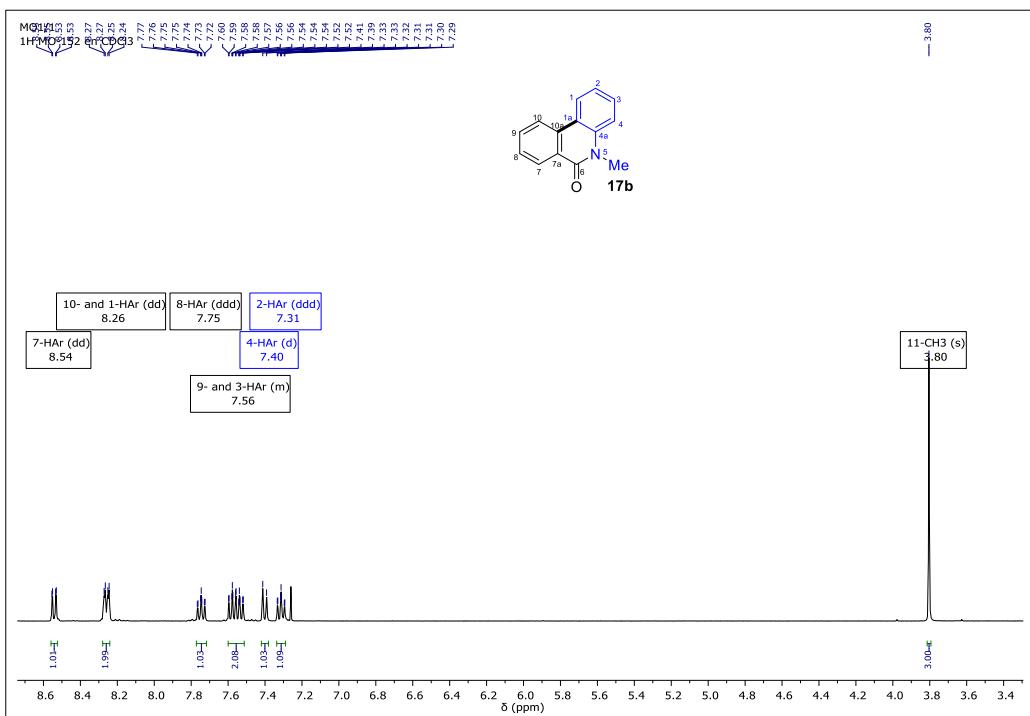
Figure ESI 147. ^1H -NMR spectrum of 5-methylphenanthridin-6(5H)-one **17b**

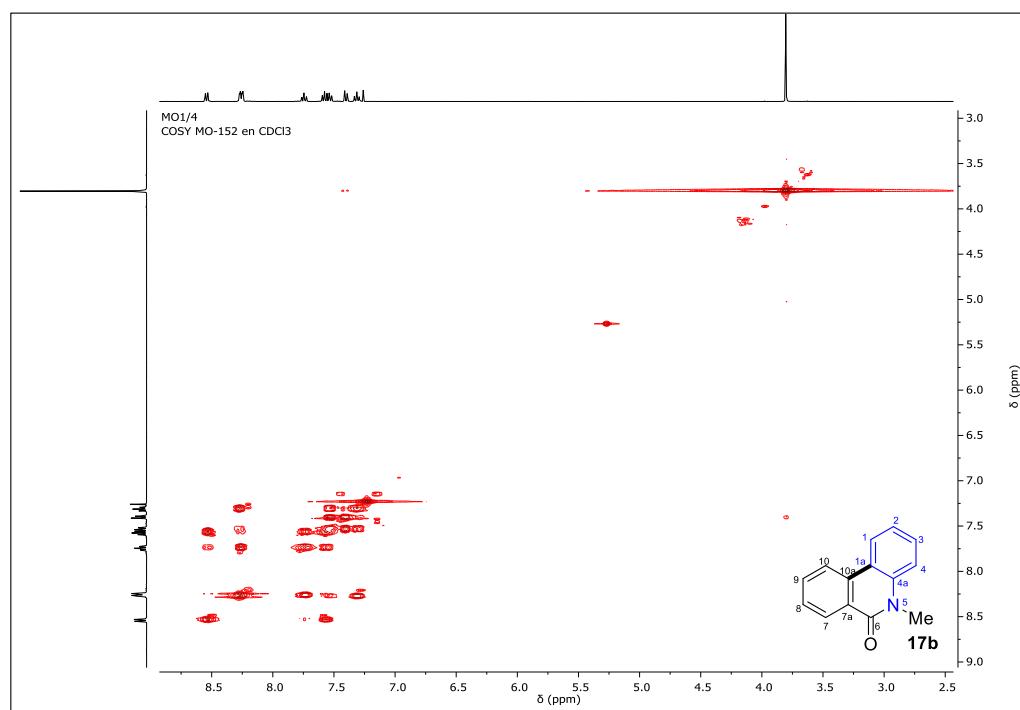
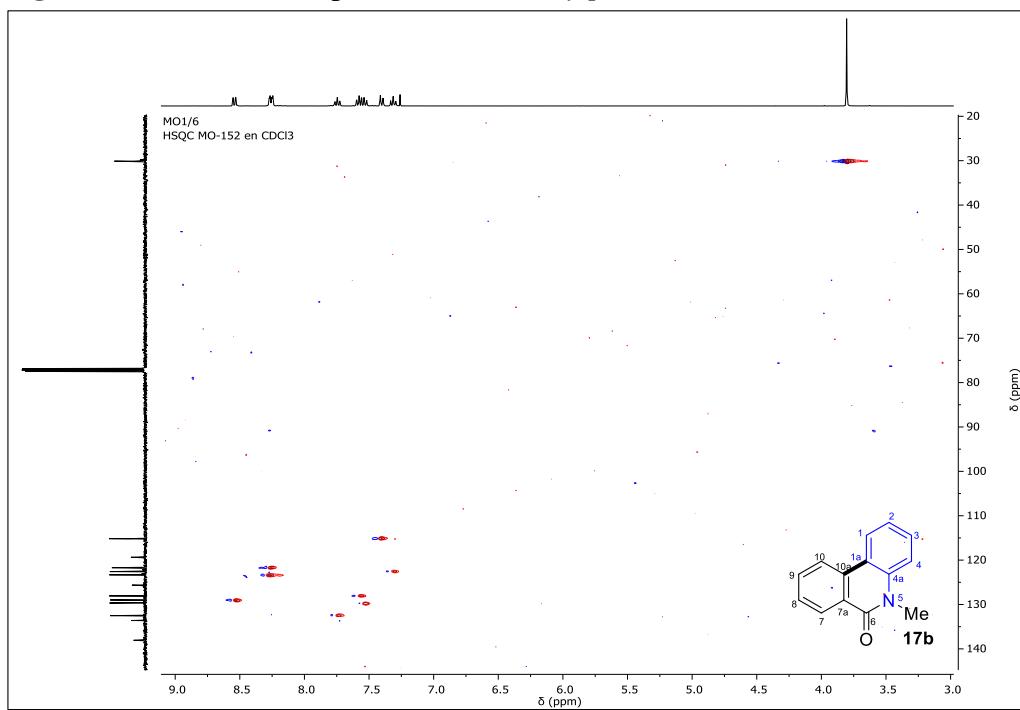
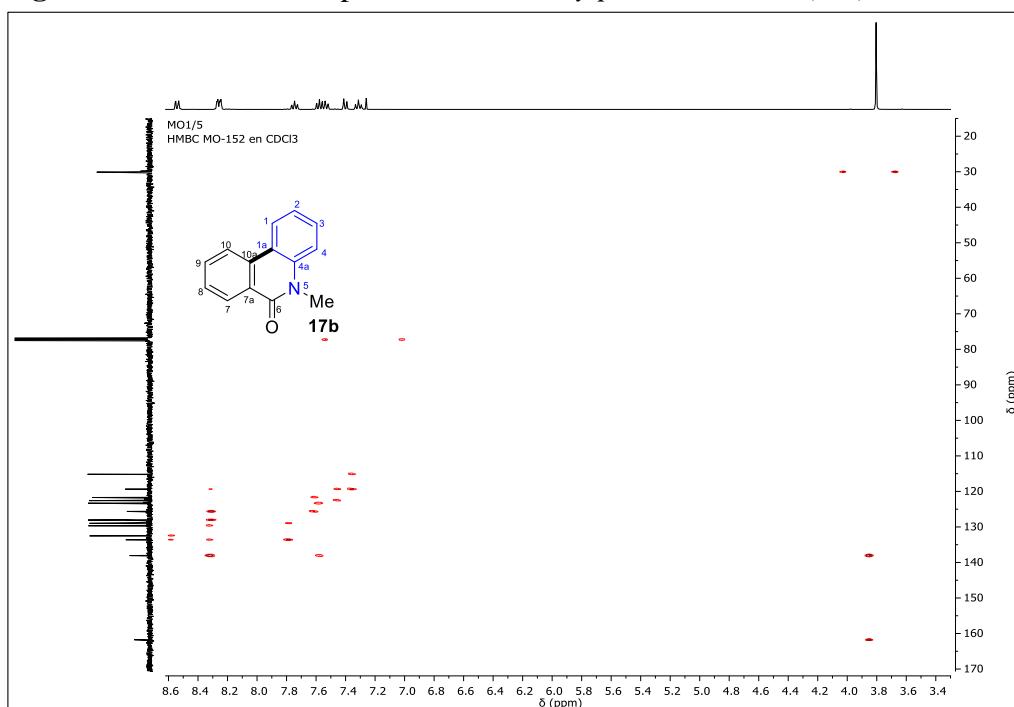
Figure ESI 149. COSY spectrum of *5-methylphenanthridin-6(5H)-one* **17b****Figure ESI 150.** HSQC spectrum of *5-methylphenanthridin-6(5H)-one* **17b**

Figure ESI 151. HMBC spectrum of *5-methylphenanthridin-6(5H)-one* **17b**



10. Copies of ^1H NMR, ^{13}C NMR, COSY, HSQC and HMBC charts of 18a-b.

Figure ESI 152. ^1H -NMR spectrum of 6-(*tert*-butylperoxy)-6*H*-benzo[*c*]chromene Int

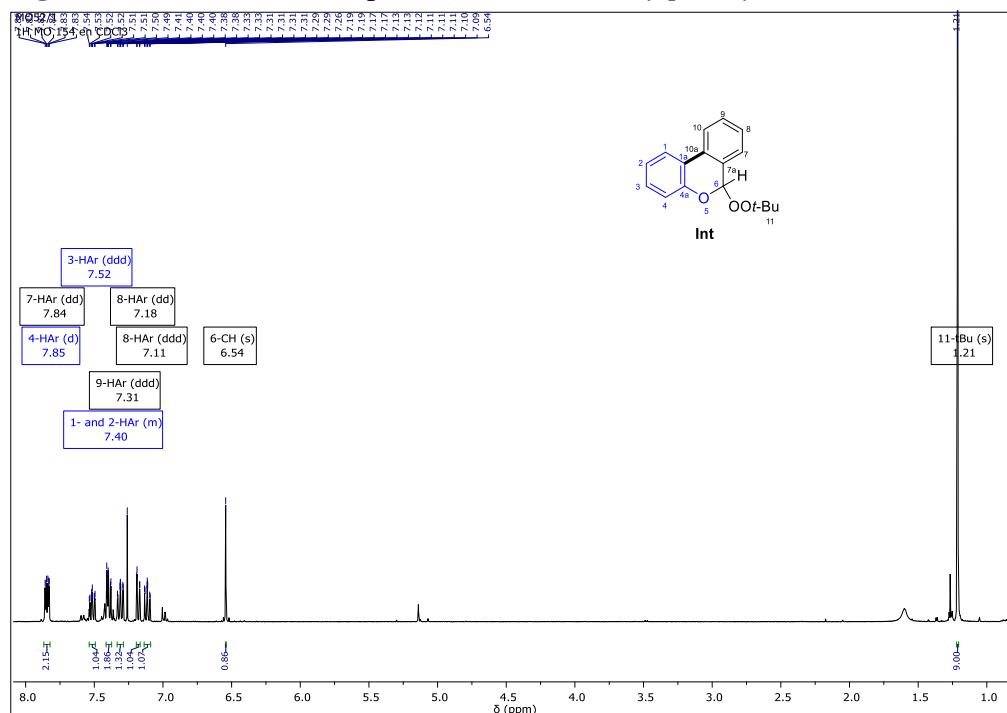


Figure ESI 153. ^{13}C -NMR spectrum of 6-(*tert*-butylperoxy)-6*H*-benzo[*c*]chromene Int

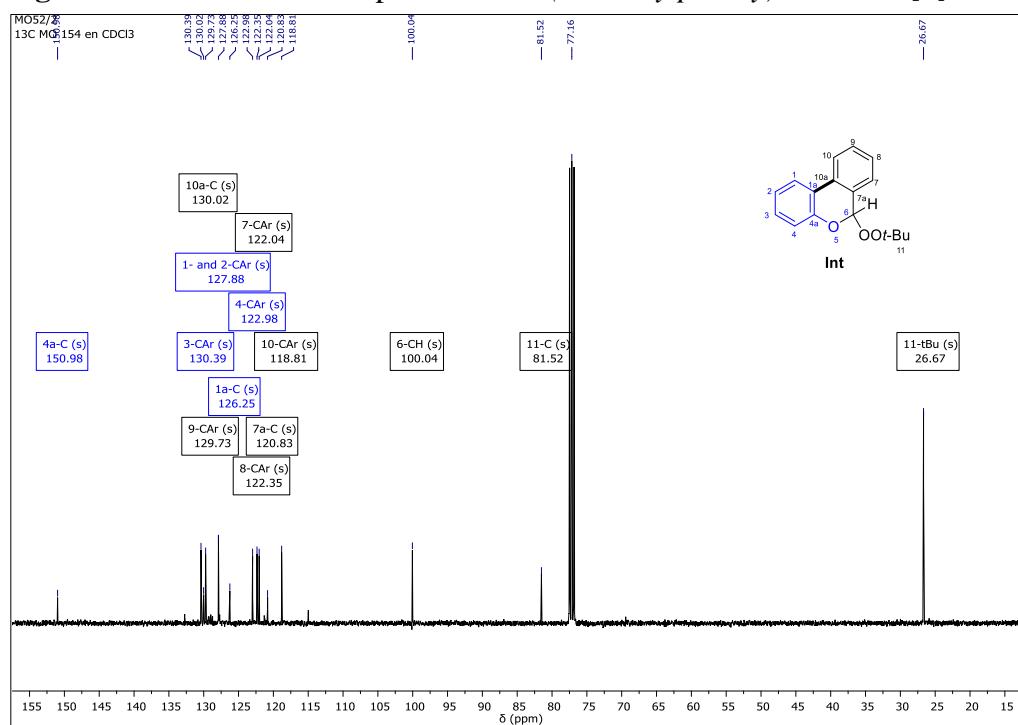


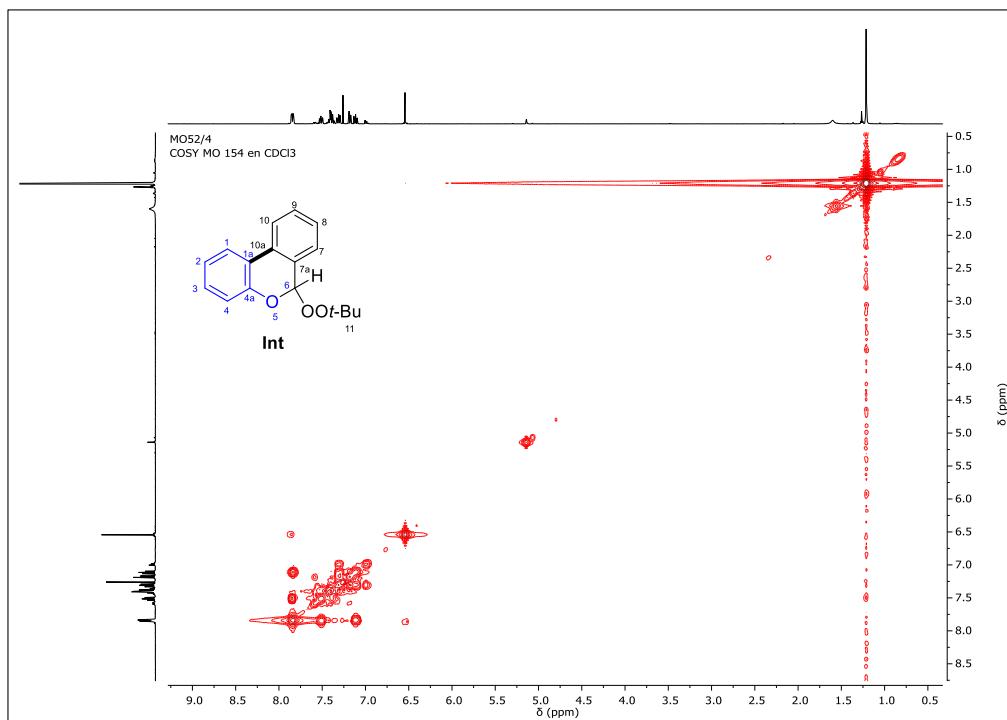
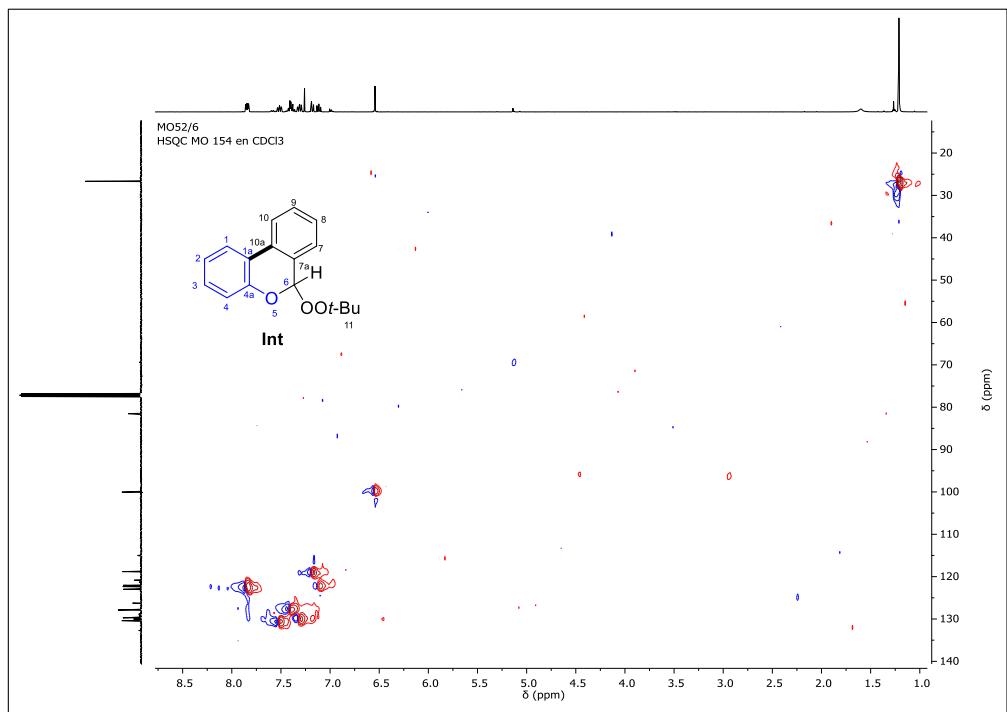
Figure ESI 154. COSY spectrum of *6-(tert-butylperoxy)-6H-benzo[c]chromene* **Int****Figure ESI 155.** HSQC spectrum of *6-(tert-butylperoxy)-6H-benzo[c]chromene* **Int**

Figure ESI 156. HMBC spectrum of *6-(tert-butylperoxy)-6H-benzo[c]chromene Int*

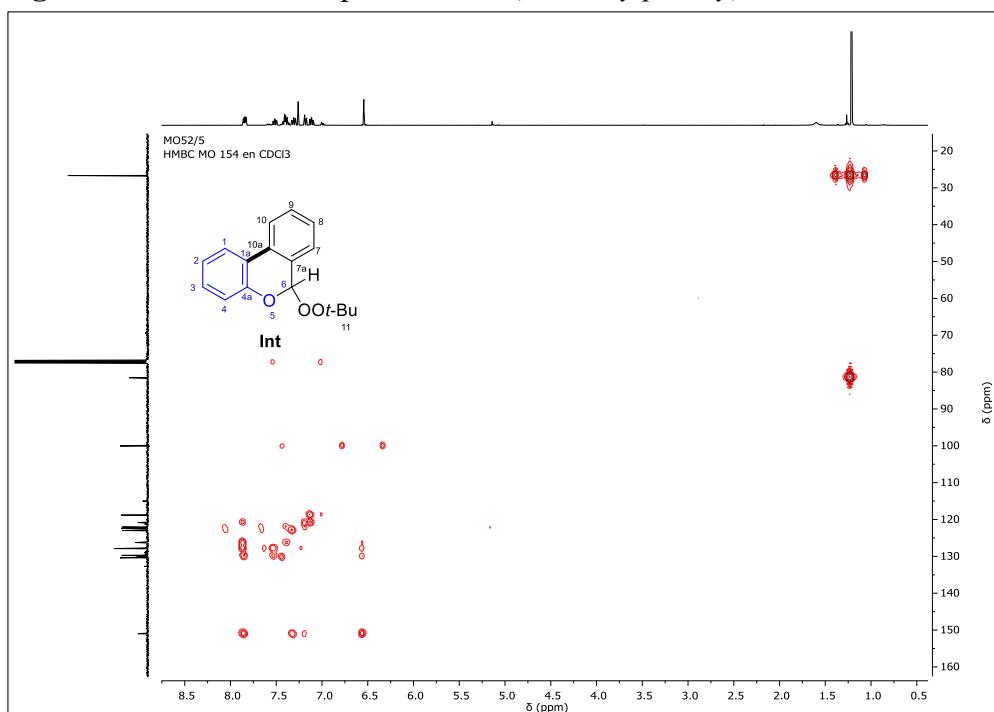


Figure ESI 157. ^1H -NMR spectrum of *6H-benzo[c]chromen-6-one 18a*

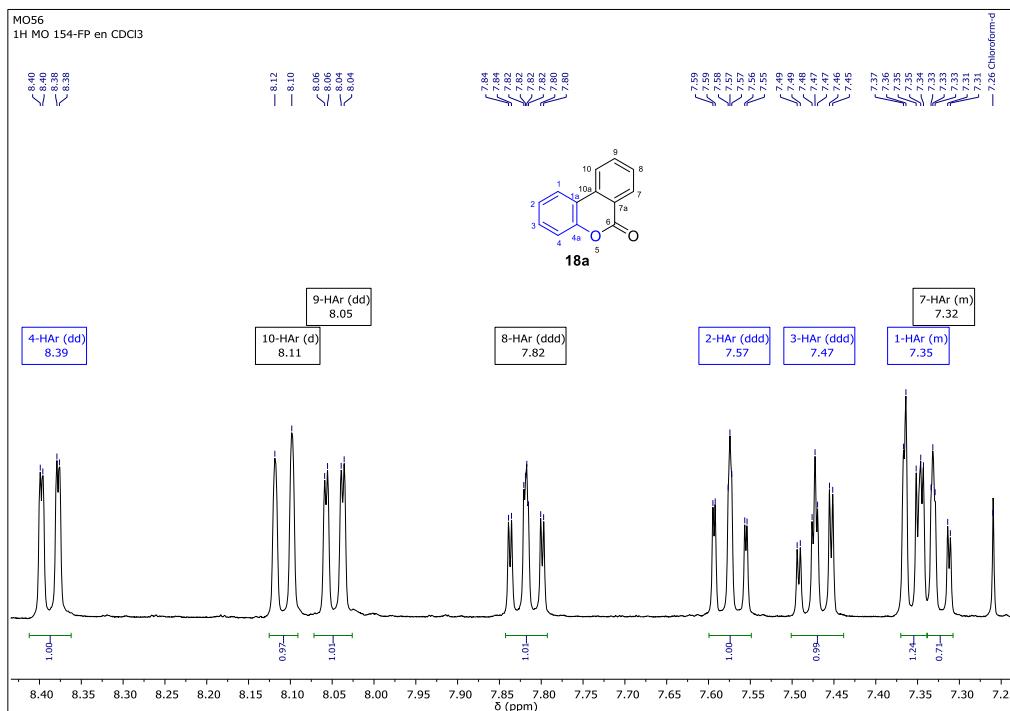


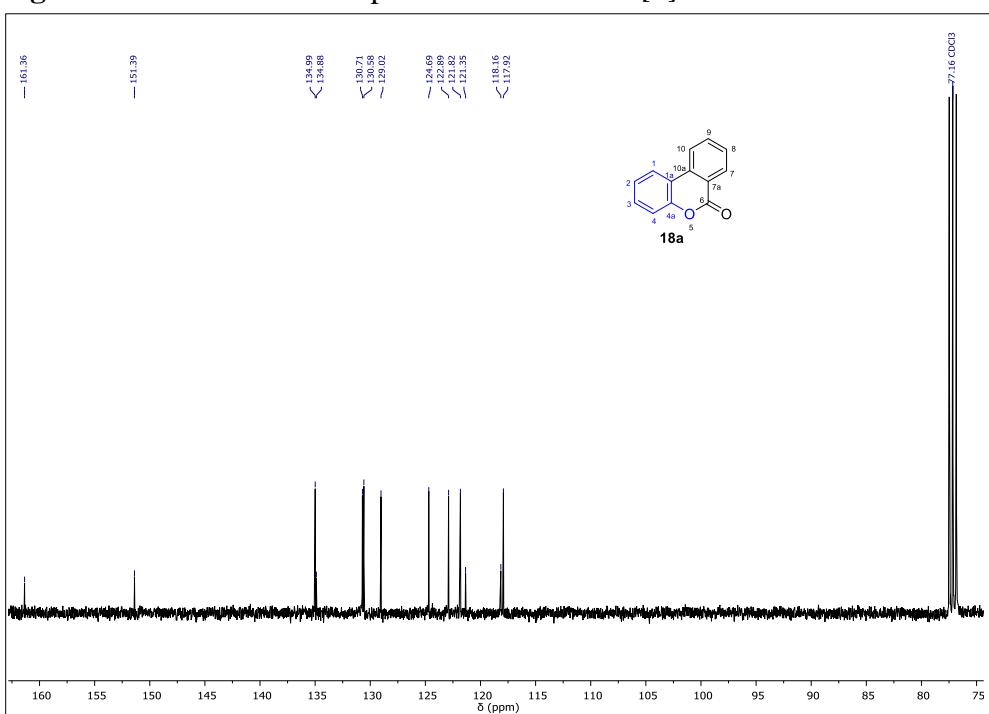
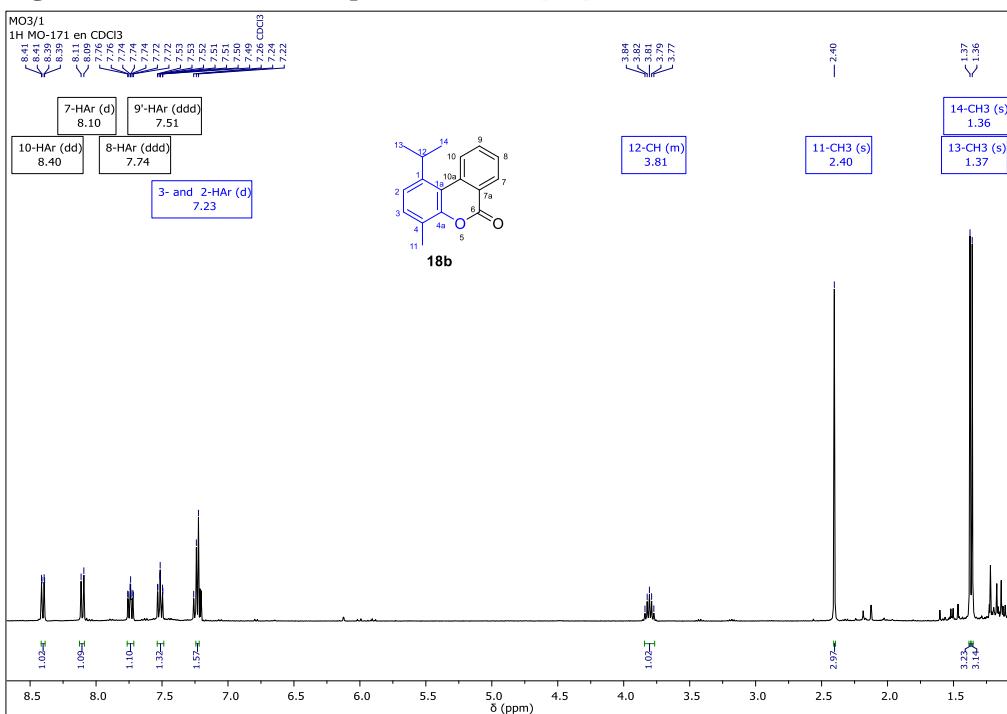
Figure ESI 158. ^{13}C -NMR spectrum of *6H-benzo[c]chromen-6-one* **18a****Figure ESI 159.** ^1H -NMR spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromen-6-one* **18b**

Figure ESI 160. ^{13}C -NMR spectrum of *1-isopropyl-4-methyl-6H-benzo[c]chromen-6-ona* **18b**