

Supporting Information

Recyclable Copper-Catalytic System For Performing Intramolecular *O*-Arylation Reactions In Aqueous Media. New Synthesis Of Xanthones.

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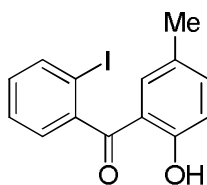
General Remarks

1. General procedures.

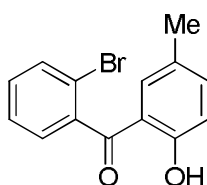
All reagents were purchased and used as received except when indicated. Chemical shifts (δ) are given in ppm downfield from Me₄Si and refer as internal standard to the residual solvent (unless indicated) CDCl₃: (δ = 7.26 for ¹H and 77.0 for ¹³C). Coupling constants, *J*, are reported in hertz (Hz). Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO₂, and the spots were located with UV light. Flash chromatography was carried out on SiO₂. Drying of organic extracts during work-up of reactions was performed over anhydrous Na₂SO₄. Evaporation of solvents was accomplished with a rotary evaporator.

*General procedure for the Friedel-Crafts acylation:*¹

A screw-capped tube was charged with graphite (8.3 mmol) and the corresponding benzoic acid (1 mmol) and put at 120°C in a prewarmed oil bath. Then, MsOH (7.5 mL) and the phenol derivative (1 mmol) were added and the stirring was kept until the reaction was finished (3-4 hours). After cooling down, the mixture was poured into water, extracted with EtOAc and washed with an aqueous solution of NaHCO₃ (5%). The organic layer was dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to render a brown residue which was then purified by flash chromatography (20 mol% EtOAc/hexane).

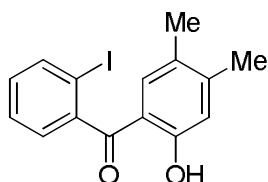


(2-Hydroxy-5-methylphenyl)(2-iodophenyl)methanone 2a: The general procedure was followed starting from 2-iodobenzoic acid (1.0 g, 4.03 mmol) and *p*-cresol (0.42 mL, 4.03 mmol) to afford the target 2-iodobenzophenone **2a** (580.1 mg, 42%) as a yellowish solid. Mp: 82-84°C (from hexane); IR $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1625, 1479, 1332 and 1238; $^1\text{H NMR}$ (300 MHz, CDCl_3 , SiMe_4) (δ_{H} , ppm): 2.18 (s, 3H, CH_3), 6.94-6.98 (m, 2H, H_{arom}), 7.17-7.28 (m, 2H, H_{arom}), 7.32 (dd, J 8.5 and 2.2 Hz, 1H, H_{arom}), 7.44-7.49 (m, 1H, H_{arom}), 7.91-7.94 (m, 1H, H_{arom}) and 11.78 (br s, 1H, OH); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , SiMe_4) (δ_{C} , ppm): 20.3 (CH_3), 91.8 ($\text{C}_{\text{arom-I}}$), 118.1 ($\text{C}_{\text{arom-H}}$), 118.2 ($\text{C}_{\text{arom-C}}$), 127.8, 127.9 ($\text{C}_{\text{arom-H}}$), 128.2 ($\text{C}_{\text{arom-C}}$), 131.1, 133.0, 138.3, 139.5 ($\text{C}_{\text{arom-H}}$), 143.3, 161.4 and 202.5 ($\text{C}_{\text{arom-C}}$); MS (CI) m/z : 339 ($\text{M}+1$, 100), 338 (M^+ , 31%), 231 (24) and 211 (14). HRMS (CI) [$\text{M}+1$]: calculated for $\text{C}_{14}\text{H}_{12}\text{IO}_2$, 338.9882; found, 338.9879.

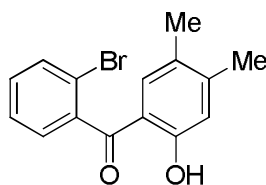


(2-Bromophenyl)(2-hydroxy-5-methylphenyl)methanone 2a': The general procedure was followed starting from 2-bromobenzoic acid (800.2 mg, 3.98 mmol) and *p*-cresol (0.41 mL, 3.98 mmol) to afford the target 2-bromobenzophenone **2a'** (548.1 mg, 47%) as yellowish solid. Mp: 67-69°C (from hexane); IR $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1625, 1479, 1338 and 1238; $^1\text{H NMR}$ (300 MHz, CDCl_3 , SiMe_4) (δ_{H} , ppm): 2.18 (s, 3H, CH_3), 6.95-6.98 (m, 2H, H_{arom}), 7.29-7.46 (m, 4H, H_{arom}), 7.65-7.68 (m, 1H, H_{arom}) and 11.77 (br s, 1H, OH); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , SiMe_4) (δ_{C} , ppm): 20.3 (CH_3), 118.1 ($\text{C}_{\text{arom-}}$

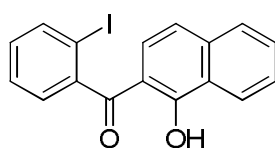
H), 118.7, 119.1 (C_{arom}-C), 127.2 (C_{arom}-H), 128.3 (C_{arom}-C), 128.4, 131.2, 132.9, 133.2, 138.3 (C_{arom}-H), 139.5, 161.3 and 201.1 (C_{arom}-C); MS (CI) m/z: 291 (M+1, 100), 290 (M⁺, 25%), 211 (22), 185 (18) and 183 (19). HRMS (CI) [M+1]: calculated for C₁₄H₁₂BrO₂, 291.0021; found, 291.0019. In a scale-up experiment, the general procedure was also followed (a round-bottom flask equipped with a condenser was employed) starting from 2-bromobenzoic acid (70.08 g, 0.35 mol) and *p*-cresol (35.91 mL, 0.35 mmol) to afford the target 2-bromobenzophenone **2a'** (48 g, 47%) as yellowish solid.



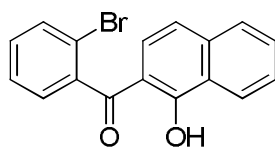
(2-Hydroxy-4,5-dimethylphenyl)(2-iodophenyl)methanone 2b: The general procedure was followed starting from 2-iodobenzoic acid (409.5 mg, 1.65 mmol) and 3,4-dimethylphenol (197.0 mg, 1.61 mmol) to afford the target 2-iodobenzophenone **2b** (243.3 mg, 42%) as white solid. Mp: 54-56°C (from hexane); IR ν_{\max} (film)/cm⁻¹ 1625, 1455, 1338 and 1255; ¹H NMR (300 MHz, CDCl₃, SiMe₄) (δ_{H} , ppm): 2.09 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 6.87 (s, 1H, H_{arom}), 6.88 (s, 1H, H_{arom}), 7.20 (ddd, *J* 7.9, 7.5 and 1.7 Hz, 1H, H_{arom}), 7.25-7.28 (m, 1H, H_{arom}), 7.47 (apparent dt, *J* 7.5 and 1.1 Hz, 1H, H_{arom}), 7.91-7.94 (m, 1H, H_{arom}) and 11.83 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃, SiMe₄) (δ_{C} , ppm): 18.7, 20.6 (CH₃), 91.9 (C_{arom}-I), 116.5 (C_{arom}-C), 118.9 (C_{arom}-H), 127.5 (C_{arom}-C), 127.7, 127.8, 130.9, 133.3, 139.4 (C_{arom}-H), 143.4, 148.2, 161.8 and 201.9 (C_{arom}-C); MS (CI) m/z: 353 (M+1, 100), 352 (M⁺, 28%), 230 (15) and 225 (12). HRMS (CI) [M+1]: calculated for C₁₅H₁₄IO₂, 353.0039; found, 353.0022.



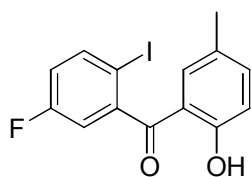
(2-Bromophenyl)(2-hydroxy-4,5-dimethylphenyl)methanone 2b': The general procedure was followed starting from 2-bromobenzoic acid (402.6 mg, 2.00 mmol) and 3,4-dimethylphenol (243.1 mg, 1.99 mmol) to afford the target 2-bromobenzophenone **2b'** (298.0 mg, 49%) as yellowish solid. Mp: 82-84°C (from hexane); IR ν_{max} (film)/ cm^{-1} 1631, 1337 and 1255; ^1H NMR (300 MHz, CDCl_3 , SiMe_4) (δ_{H} , ppm): 2.07 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 6.85 (s, 1H, H_{arom}), 6.91 (s, 1H, H_{arom}), 7.27-7.44 (m, 3H, H_{arom}), 7.64 (dd, J 7.8 and 0.9 Hz, 1H, H_{arom}) and 11.84 (br s, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3 , SiMe_4) (δ_{C} , ppm): 18.6, 20.5 (CH_3), 116.9 ($\text{C}_{\text{arom}}\text{-C}$), 118.8 ($\text{C}_{\text{arom}}\text{-H}$), 118.9 ($\text{C}_{\text{arom}}\text{-C}$), 127.1 ($\text{C}_{\text{arom}}\text{-H}$), 127.4 ($\text{C}_{\text{arom}}\text{-C}$), 128.3, 131.0, 133.0, 133.2 ($\text{C}_{\text{arom}}\text{-H}$), 139.5, 148.1, 161.6 and 200.3 ($\text{C}_{\text{arom}}\text{-C}$); MS (CI) m/z : 305 ($\text{M}+1$, 100), 304 (M^+ , 29%), 225 (24), 185 (15), 182 (15) and 149 (10). HRMS (CI) [$\text{M}+1$]: calculated for $\text{C}_{15}\text{H}_{14}\text{BrO}_2$, 305.0177; found, 305.0176.



(1-Hydroxynaphthalen-2-yl)(2-iodophenyl)methanone 2d: The general procedure was followed starting from 2-iodobenzoic acid (601.6 mg, 2.42 mmol) and 1-naphthol (248.8 mg, 2.42 mmol) to afford the target 2-iodobenzophenone **2d** (443.4 mg, 49%) as white solid.²

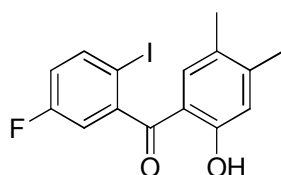


(2-Bromophenyl)(1-hydroxynaphthalen-2-yl)methanone 2d': The general procedure was followed starting from 2-bromobenzoic acid (611.7 mg, 3.04 mmol) and 1-naphthol (430.3 mg, 2.98 mmol) to afford the target 2-bromobenzophenone **2d'** (416.2 mg, 42%) as white solid. Mp: 88-100°C (from hexane); IR ν_{\max} (film)/cm⁻¹ 1608, 1455, 1331 and 1279; ¹H NMR (300 MHz, CDCl₃, SiMe₄) (δ_{H} , ppm): 7.11-7.19 (m, 2H, H_{arom}), 7.36-7.42 (m, 2H, H_{arom}), 7.44-7.49 (m, 1H, H_{arom}), 7.53-7.59 (m, 1H, H_{arom}), 7.63-7.76 (m, 3H, H_{arom}), 8.52-8.56 (m, 1H, H_{arom}) and 13.74 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃, SiMe₄) (δ_{C} , ppm): 112.8 (C_{arom}-C), 118.5 (C_{arom}-H), 119.2 (C_{arom}-C), 124.5 (C_{arom}-H), 125.1 (C_{arom}-C), 126.0, 126.8, 127.3, 127.5, 128.4, 130.7, 131.1, 133.1 (C_{arom}-H), 137.6, 139.6, 163.9 and 200.8 (C_{arom}-C); MS (CI) m/z: 329 (M+3, 100), 328 (M+2, 70), 327 (M+1, 90), 326 (M⁺, 58%), 247 (58), 185 (20), 183 (18) and 171 (13). HRMS (CI) [M+1]: calculated for C₁₇H₁₂BrO₂, 327.0021; found, 327.0018.

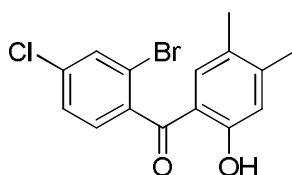


(5-Fluoro-2-iodophenyl)(2-hydroxy-5-methylphenyl)methanone 2e: The general procedure was followed starting from 5-fluoro-2-iodobenzoic acid (404.0 mg, 1.52 mmol) and *p*-cresol (0.16 mL, 1.50 mmol) to afford the target 2-iodobenzophenone **2e** (168.8 mg, 31%) as white solid. Mp: 56-58°C (from hexane); IR ν_{\max} (film)/cm⁻¹ 1631, 1478, 1331 and 1255; ¹H NMR (300 MHz, CDCl₃, SiMe₄) (δ_{H} , ppm): 2.21 (s, 3H, CH₃), 6.93-7.05 (m, 4H, H_{arom}), 7.34-7.37 (m, 1H, H_{arom}), 7.87 (dd, *J* 8.7 and 5.1 Hz, 1H, H_{arom}) and 11.60 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃, SiMe₄) (δ_{C} , ppm): 20.4

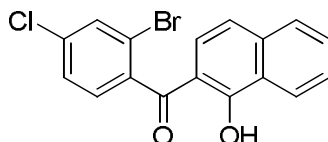
(CH₃), 85.0 (d, *J* 3.6 Hz, C_{arom}-I), 115.6 (d, *J* 23.7 Hz, C_{arom}-H), 117.8 (C_{arom}-C), 118.4, 118.8 (d, *J* 21.6 Hz) (C_{arom}-H), 128.6 (C_{arom}-C), 132.8, 138.8, 141.2 (d, *J* 7.5 Hz) (C_{arom}-H), 144.9 (d, *J* 6.4 Hz), 161.6 (C_{arom}-C), 162.4 (d, *J* 251.0 Hz) (C_{arom}-F) and 201.0 (C_{arom}-C); MS (CI) *m/z*: 357 (M+1, 100), 356 (M⁺, 30%), 249 (23) and 229 (16). HRMS (CI) [M+1]: calculated for C₁₄H₁₁FIO₂, 356.9788; found, 356.9774.



(5-Fluoro-2-iodophenyl)(2-hydroxy-4,5-dimethylphenyl)methanone 2f: The general procedure was followed starting from 5-fluoro-2-iodobenzoic acid (400.7 mg, 1.51 mmol) and 3,4-dimethylphenol (183.7 mg, 1.50 mmol) to afford the target 2-iodobenzophenone **2f** (278.2 mg, 50%) as white solid. Mp: 124-126°C (from hexane); IR ν_{\max} (film)/cm⁻¹ 1633 and 1332; ¹H NMR (300 MHz, CDCl₃, SiMe₄) (δ_{H} , ppm): 2.11, 2.28 (s, 3H, CH₃), 6.96 (s, 1H, H_{arom}), 6.87 (s, 1H, H_{arom}), 6.93-7.04 (m, 2H, H_{arom}), 7.87 (dd, *J* 8.6, 5.1 Hz, 1H, H_{arom}) and 11.65 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃, SiMe₄) (δ_{C} , ppm): 18.7, 20.6 (CH₃), 85.0 (d, *J* 3.7 Hz) (C_{arom}-I), 115.5 (d, *J* 23.7 Hz) (C_{arom}-H), 116.0 (C_{arom}-C), 118.5 (d, *J* 21.7 Hz), 119.1, (C_{arom}-H), 127.7 (C_{arom}-C), 133.0, 141.1 (d, *J* 7.5 Hz) (C_{arom}-H), 145.1 (d, *J* 6.3 Hz), 148.6, 161.9 (C_{arom}-C), 162.4 (d, *J* 250.9 Hz) (C_{arom}-F) and 200.2 (d, *J* 1.4 Hz) (C_{arom}-C); MS (CI) *m/z*: 371 (M+1, 100), 370 (M⁺, 28%) and 249 (15). HRMS (CI) [M+1]: calculated for C₁₅H₁₃FIO₂, 370.9944; found, 370.9930.

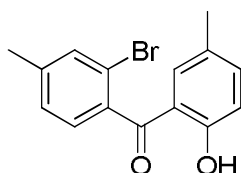


(2-Bromo-4-chlorophenyl)(2-hydroxy-4,5-dimethylphenyl)methanone 2g: The general procedure was followed starting from 4-chloro-2-bromobenzoic acid (508.0 mg, 2.15 mmol) and 3,4-dimethylphenol (259.4 mg, 2.12 mmol) to afford the target 2-bromobenzophenone **2g** (339.0 mg, 46%) as white solid. Mp: 85-87°C (from hexane); IR ν_{max} (film)/ cm^{-1} (ν , cm^{-1}) 1631 and 1333; ^1H NMR (300 MHz, CDCl_3 , SiMe_4) (δ_{H} , ppm): 2.10 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 6.86 (s, 1H, H_{arom}), 6.88 (s, 1H, H_{arom}), 7.25 (d, J 8.1 Hz, H_{arom}), 7.42 (dd, J 8.2, 1.9 Hz, 1H, H_{arom}), 7.69 (d, J 1.9 Hz, 1H, H_{arom}) and 11.70 (br s, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3 , SiMe_4) (δ_{C} , ppm): 18.7, 20.6 (CH_3), 116.8 ($\text{C}_{\text{arom}}\text{-C}$), 119.0 ($\text{C}_{\text{arom}}\text{-H}$), 119.8 ($\text{C}_{\text{arom}}\text{-C}$), 127.5 ($\text{C}_{\text{arom}}\text{-H}$), 127.7 ($\text{C}_{\text{arom}}\text{-C}$), 129.3, 132.9, 133.0 ($\text{C}_{\text{arom}}\text{-H}$), 136.3, 138.1, 148.5, 161.7 and 199.3 ($\text{C}_{\text{arom}}\text{-C}$); MS (CI) m/z : 341 ($\text{M}+3$, 100), 340 ($\text{M}+2$, 53), 339 ($\text{M}+1$, 81), 338 (M^+ , 33%), 261 (10), 259 (31), 219 (16) and 149 (16). HRMS (CI) [M^+]: calculated for $\text{C}_{15}\text{H}_{12}\text{BrClO}_2$, 337.9709; found, 337.9724.

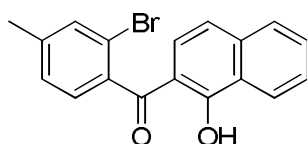


(2-Bromo-4-chlorophenyl)(1-hydroxynaphthalen-2-yl)methanone 2h: The general procedure was followed starting from 4-chloro-2-bromobenzoic acid (603.2 mg, 2.56 mmol) and 1-naphthol (367.3 mg, 2.55 mmol) to afford the target 2-bromobenzophenone **2h** (434.0 mg, 47%) as white solid. Mp: 104-106°C (from hexane); IR ν_{max} (film)/ cm^{-1} 1608, 1461, 1332 and 1273; ^1H NMR (300 MHz, CDCl_3 , SiMe_4) (δ_{H} , ppm): 7.09 (d, J 8.8 Hz, 1H, H_{arom}), 7.18 (d, J 8.5 Hz, 1H, H_{arom}), 7.30 (d, J 8.2 Hz, 1H, H_{arom}), 7.44 (dd, J 8.2, 1.9 Hz, 1H, H_{arom}), 7.56 (ddd, J 8.2, 6.8, 1.4 Hz, 1H, H_{arom}), 7.63-7.68 (m, 1H, H_{arom}), 7.71 (d, J 1.9 Hz, 1H, H_{arom}), 7.72-7.75 (m, 1H, H_{arom}), 8.51-8.55 (m, 1H, H_{arom}) and 13.65 (br s, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3 , SiMe_4)

(δ_C , ppm): 112.6 ($C_{\text{arom-C}}$), 118.6 ($C_{\text{arom-H}}$), 119.9 ($C_{\text{arom-C}}$), 124.6 ($C_{\text{arom-H}}$), 125.0 ($C_{\text{arom-C}}$), 126.2, 126.4, 127.5, 127.7, 129.4, 130.8, 132.9 ($C_{\text{arom-H}}$), 136.5, 137.7, 138.0, 164.1 and 199.7 ($C_{\text{arom-C}}$); MS (CI) m/z : 363 ($M+3$, 94), 362 ($M+2$, 55), 361 ($M+1$, 100) and 360 (M^+ , 38%). HRMS (CI) [$M+1$]: calculated for $C_{17}H_{11}BrClO_2$, 360.9631; found, 360.9633.

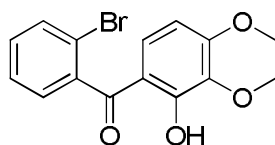


(2-Bromo-4-methylphenyl)(2-hydroxy-5-methylphenyl)methanone 2i: The general procedure was followed starting from 2-bromo-4-methylbenzoic acid (411.5 mg, 1.91 mmol) and *p*-cresol (0.19 mL, 1.86 mmol) to afford the target 2-bromobenzophenone **2i** (239.1 mg, 30%) as white solid. Mp: 82-84°C (from hexane); IR ν_{max} (film)/ cm^{-1} 1625, 1478, 1337 and 1238; ^1H NMR (300 MHz, CDCl_3 , SiMe_4) (δ_{H} , ppm): 2.18 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 6.95 (d, J 8.5 Hz, 1H, H_{arom}), 7.00-7.01 (m, 1H, H_{arom}), 7.17-7.24 (m, 2H, H_{arom}), 7.29-7.32 (m, 1H, H_{arom}), 7.48-7.49 (m, 1H, H_{arom}) and 11.82 (br s, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3 , SiMe_4) (δ_{C} , ppm): 20.3, 21.0 (CH_3), 118.0 ($C_{\text{arom-H}}$), 118.9, 119.0 ($C_{\text{arom-C}}$), 127.9 ($C_{\text{arom-H}}$), 128.1 ($C_{\text{arom-C}}$), 128.4, 133.0, 133.6, 138.1 ($C_{\text{arom-H}}$), 141.8, 161.2 and 201.3 ($C_{\text{arom-C}}$); MS (CI) m/z : 307 ($M+3$, 97), 305 ($M+1$, 100), 304 (M^+ , 27%), 225 (25), 199 (21), 197 (22) and 135 (12). HRMS (CI) [$M+1$]: calculated for $C_{15}H_{14}BrO_2$, 305.0177; found, 305.0187.



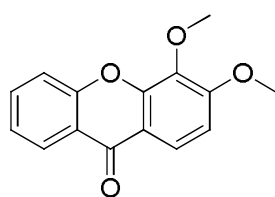
(2-Bromo-4-methylphenyl)(1-hydroxynaphthalen-2-yl)methanone 2j: The general procedure was followed starting from 2-bromo-4-methylbenzoic acid (526.9 mg, 2.45

mmol) and 1-naphthol (402.3 mg, 2.80 mmol) to afford the target 2-bromobenzophenone **2j** (398.1 mg, 48%) as white solid. Mp: 116-119°C (from hexane); IR ν_{\max} (film)/cm⁻¹ 1602, 1455, 1331 and 1279; ¹H NMR (300 MHz, CDCl₃, SiMe₄) (δ_{H} , ppm): 2.42 (s, 3H, CH₃), 7.16-7.25 (m, 4H, H_{arom}), 7.51-7.54 (m, 4H, H_{arom}), 8.52 (d, *J* 8.1 Hz, 1H, H_{arom}) and 13.79 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃, SiMe₄) (δ_{C} , ppm): 21.0 (CH₃), 112.9 (C_{arom}-C), 118.3 (C_{arom}-H), 119.0 (C_{arom}-C), 124.5 (C_{arom}-H), 125.1 (C_{arom}-C), 125.9, 126.9, 127.4, 128.0, 128.4, 130.5, 133.5 (C_{arom}-H), 136.7, 137.6, 141.8, 163.8 and 201.0 (C_{arom}-C); MS (CI) *m/z*: 343 (M+3, 92), 342 (M+2, 55), 341 (M+1, 100), 340 (M⁺, 26%), 261 (19) and 199 (18). HRMS (CI) [M⁺ + 1]: calculated for C₁₈H₁₄BrO₂, 341.0177; found, 341.0162.

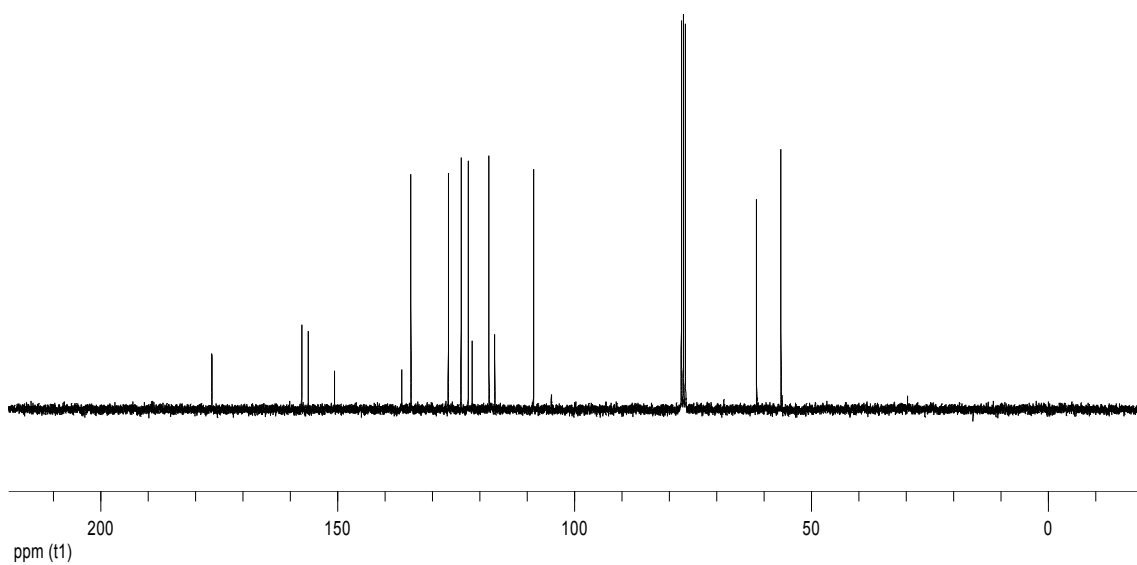
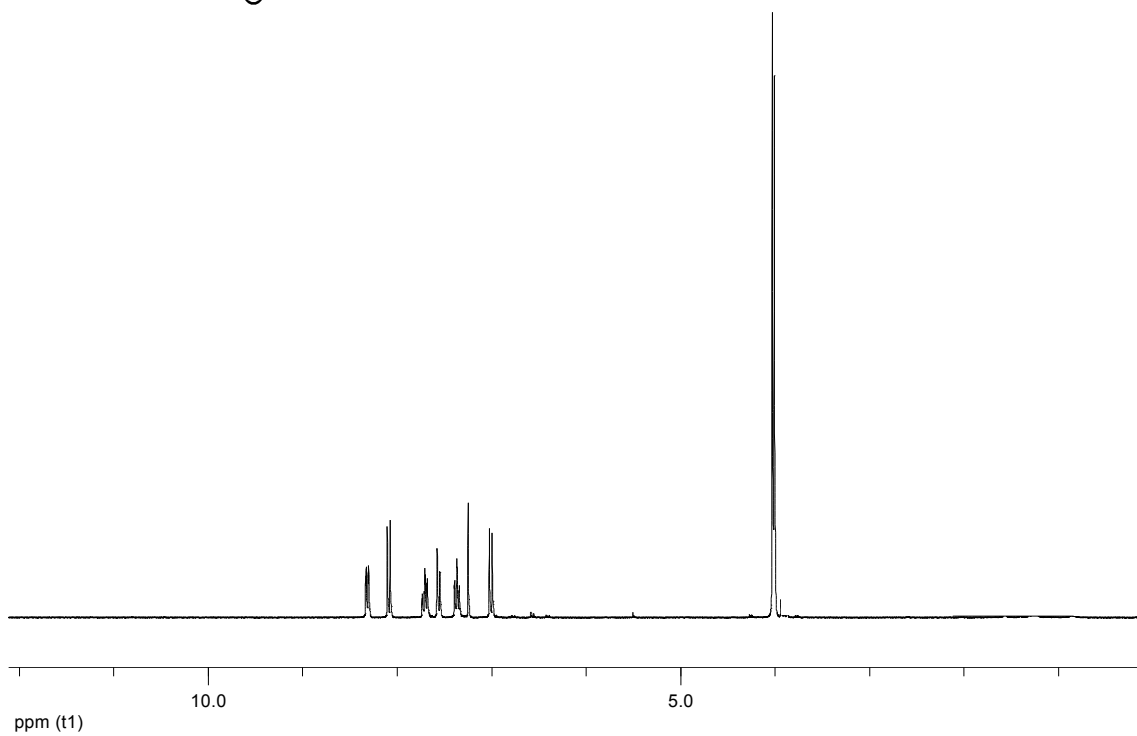


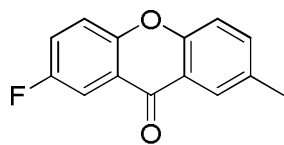
(2-Bromophenyl) (2-hydroxy-3,4-dimethoxyphenyl)methanone 2c.³ Freshly distilled SOCl₂ (1.1 mL, 14.8 mmol) was added dropwise to a stirred solution of 2-bromobenzoic acid (900.0 g, 4.48 mmol) in anhydrous PhMe (14.4 mL) under argon. The reaction mixture was heated at 135°C for 3.5 h, and after cooling, the solvent was removed under reduced pressure. The resultant brown oil was dissolved in anhydrous CH₂Cl₂ (7.2 mL), cooled at 0°C, and a solution of 1,2,3-trimethoxybenzene (941.4 mg, 5.61 mmol) in the same solvent (2.0 mL) was added dropwise under argon. Anhydrous AlCl₃ (895.4 mg, 6.72 mmol) was added in small portions at this temperature, and stirring was continued for 15 min. The reaction mixture was heated to reflux for 4 h, and after cooling to ambient temperature, was poured onto a mixture of crushed ice and 12M HCl (6 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were washed with saturated

aqueous NaHCO₃ (1 x 10 mL), dried over anhydrous Na₂SO₄, filtered off, and the solvent was evaporated under reduced pressure. The brown oil residue was then purified by flash chromatography (30 mol% EtOAc/hexane) to afford 2-bromobenzophenone **2c** (797.7 mg, 53%) as a white solid. Mp: 118-120°C (from hexane); IR ν_{\max} (film)/cm⁻¹ 1620, 1502, 1437, 1284 and 1102; ¹H NMR (300 MHz, CDCl₃, SiMe₄) (δ_{H} , ppm): 3.89 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 6.39 (d, *J* 9.1 Hz, 1H, H_{arom}), 6.95 (d, *J* 9.1 Hz, 1H, H_{arom}), 7.24-7.42 (m, 3H, H_{arom}), 7.62 (dd, *J* 7.8, 1.1 Hz, 1H, H_{arom}) and 12.17 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃, SiMe₄) (δ_{C} , ppm): 56.1, 60.7 (OCH₃), 103.2 (C_{arom}-H), 114.6, 119.1 (C_{arom}-C), 127.1, 128.4, 130.1, 131.0, 133.0 (C_{arom}-H), 136.5, 139.4, 157.6, 159.2 and 199.7 (C_{arom}-C); MS (CI) *m/z*: 339 (M+3, 96), 338 (M+2, 54), 337 (M+1, 100), 336 (M⁺, 39%) and 183 (11). HRMS (CI) [M+1]: calculated for C₁₅H₁₄BrO₄, 337.0075; found, 337.0067.

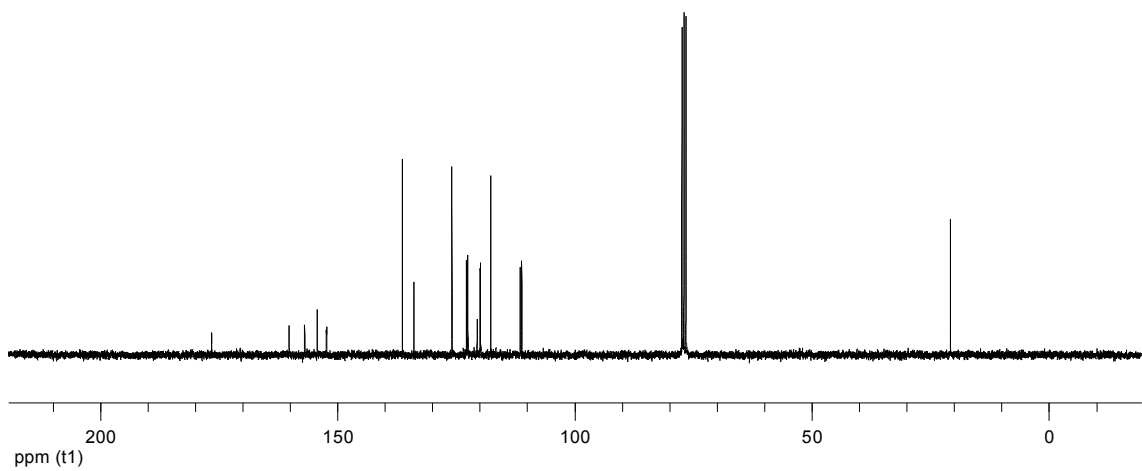
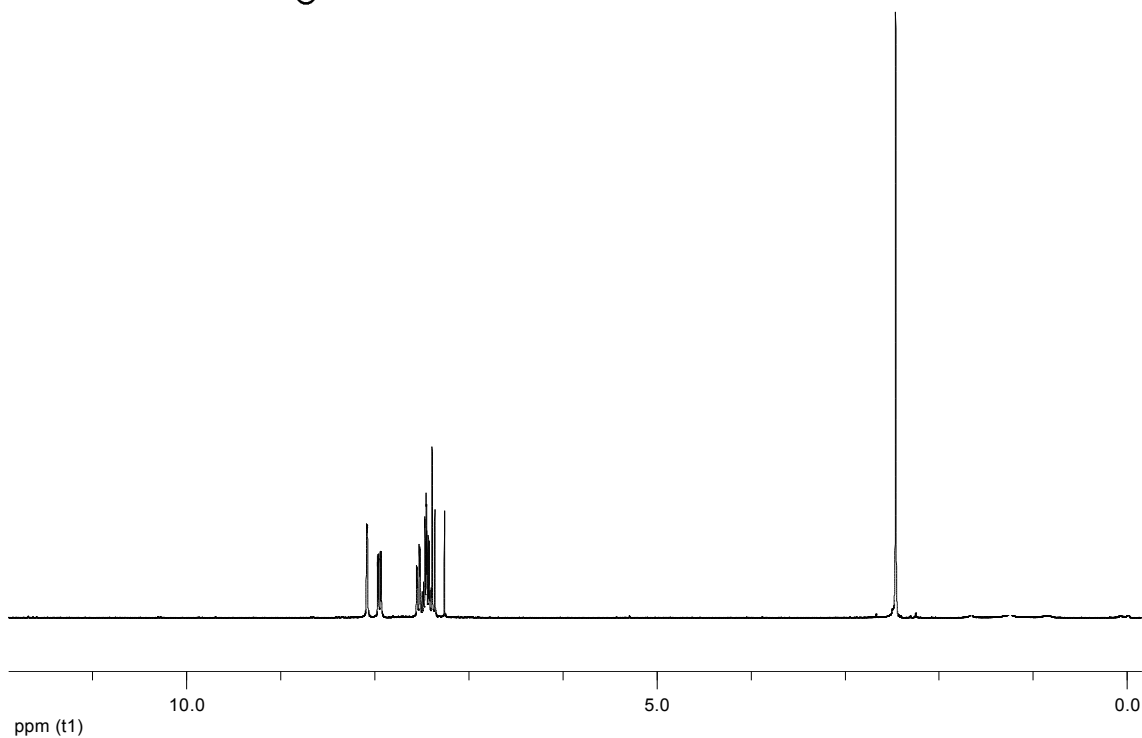


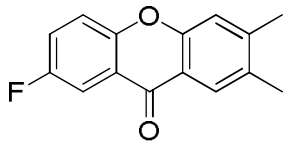
3,4-Dimethoxyxanthen-9-one (1c)



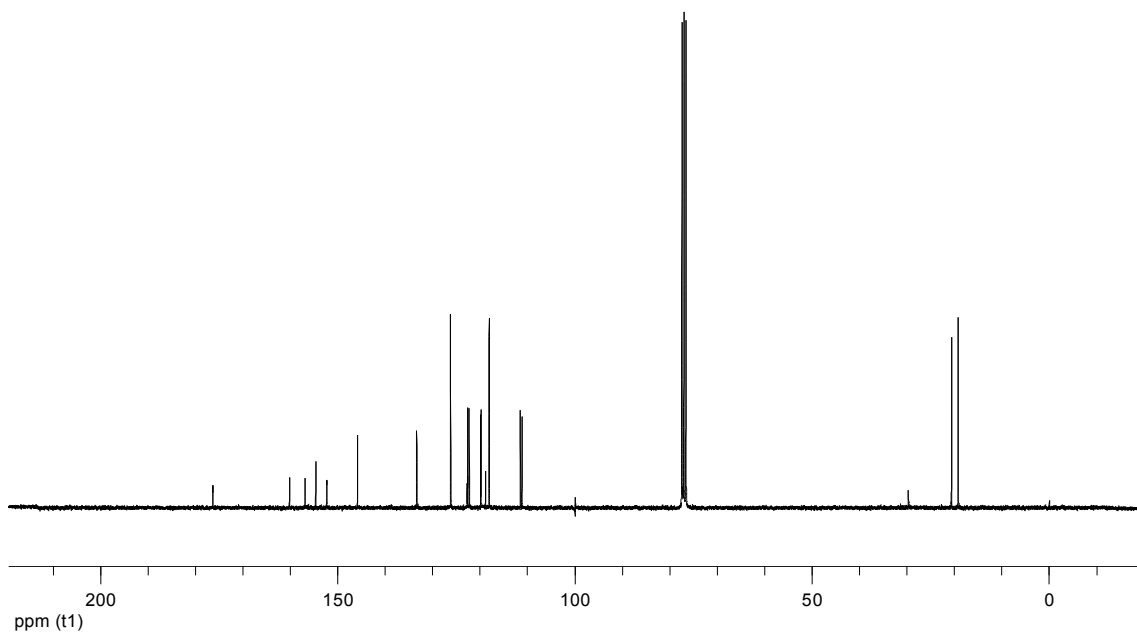
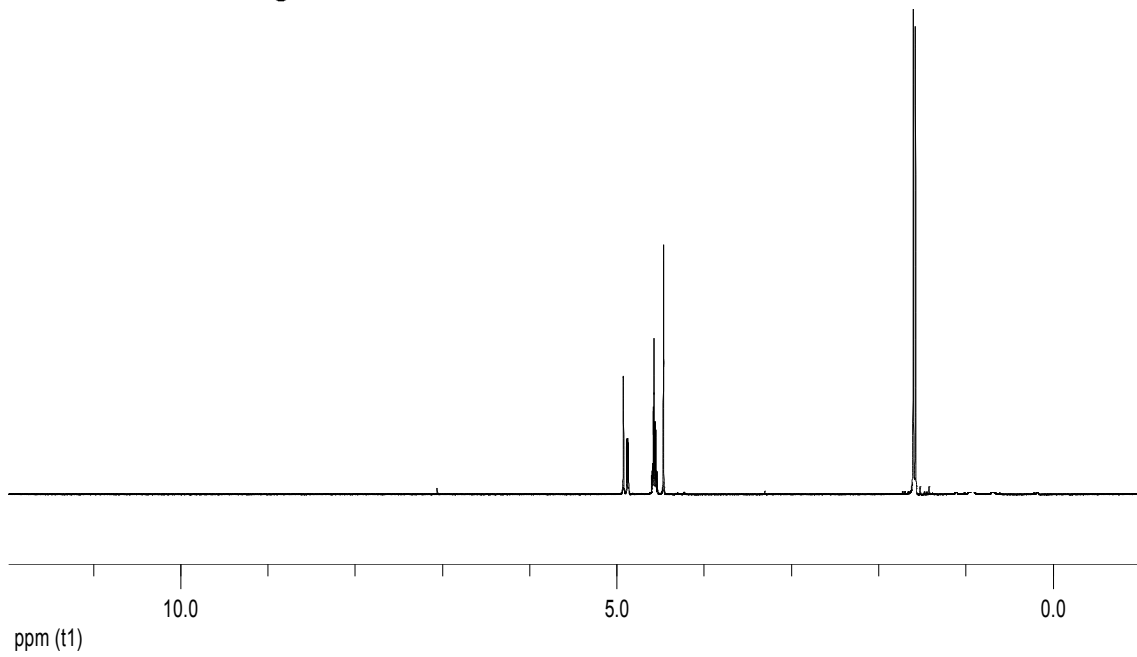


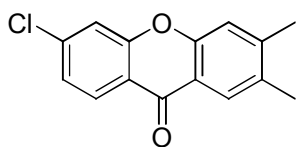
2-Fluoro-7-methylxanthen-9-one (1e)



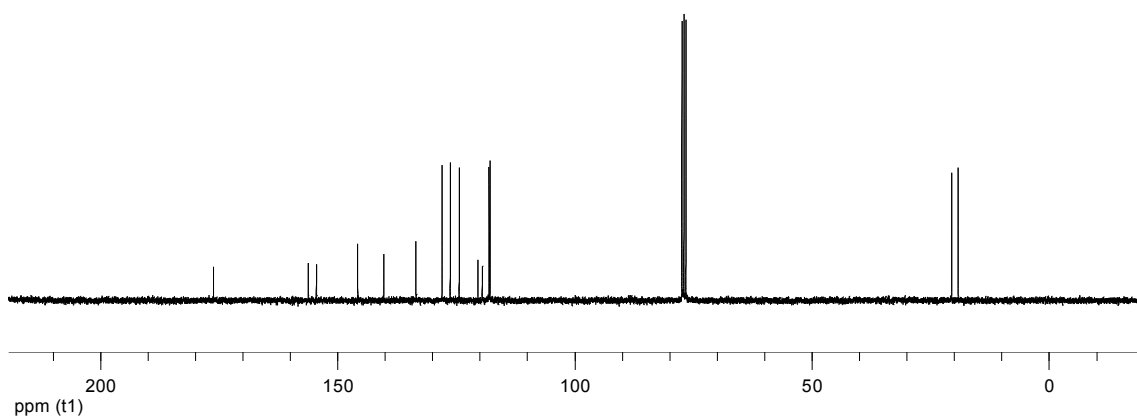
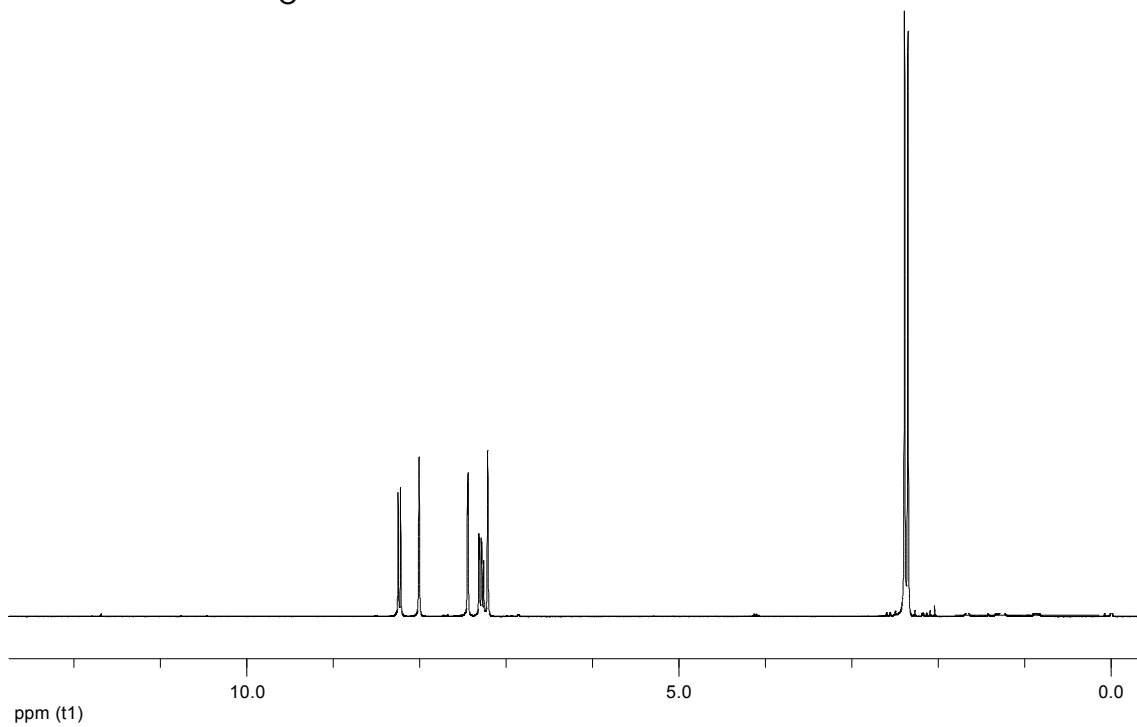


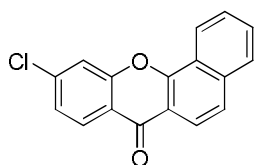
2-Fluoro-6,7-dimethylxanthen-9-one (1f)



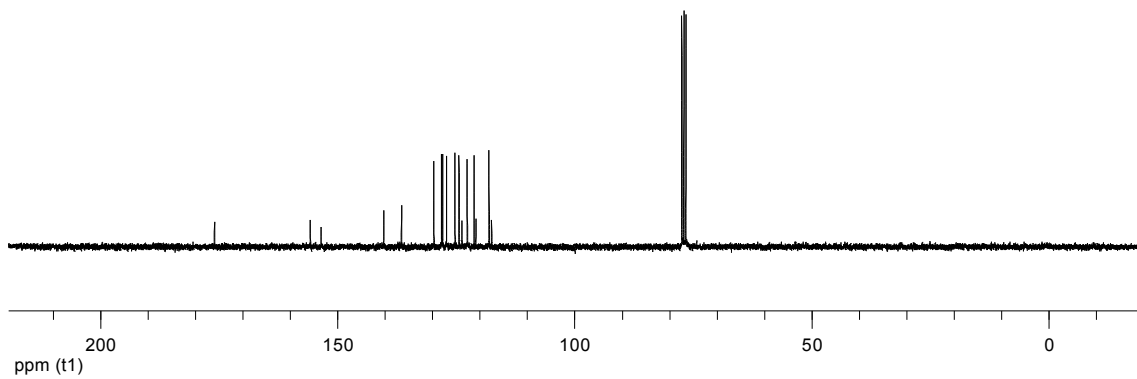
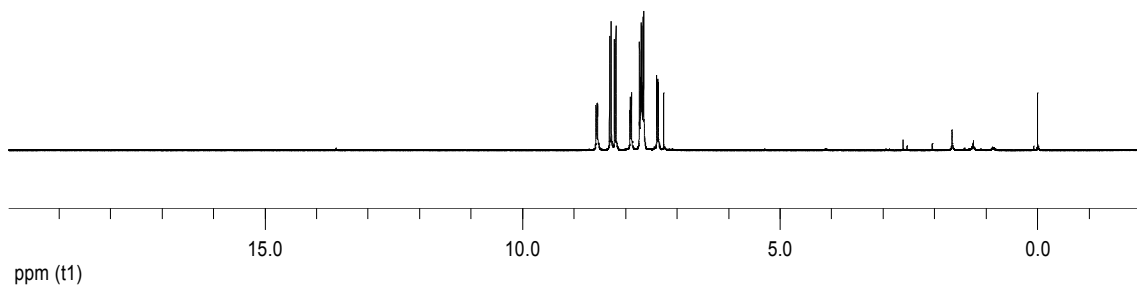


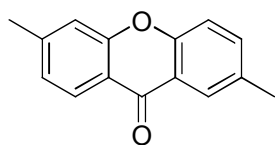
3-Chloro-6,7-dimethylxanthen-9-one (1g)



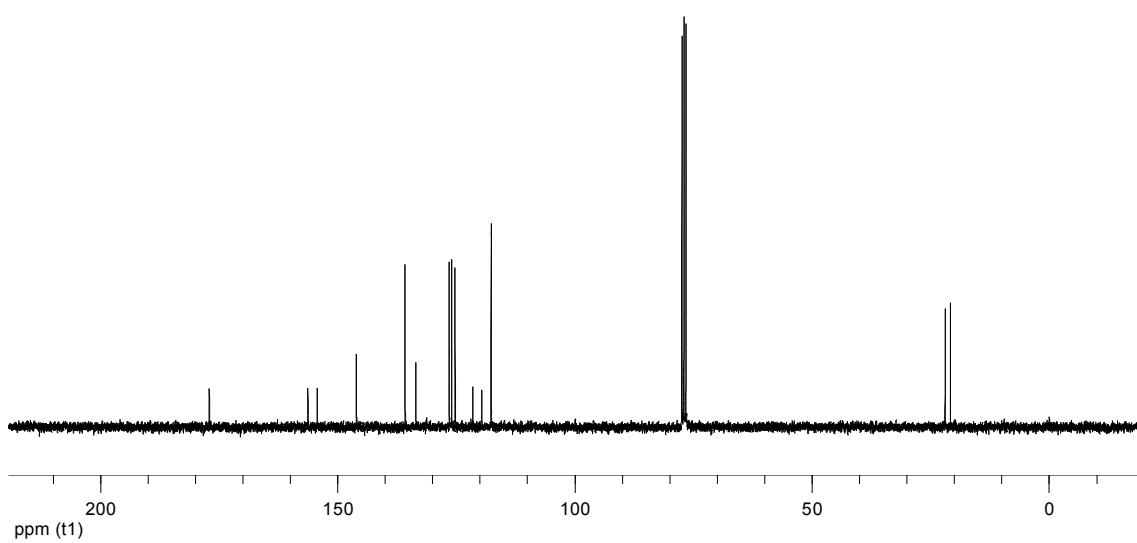
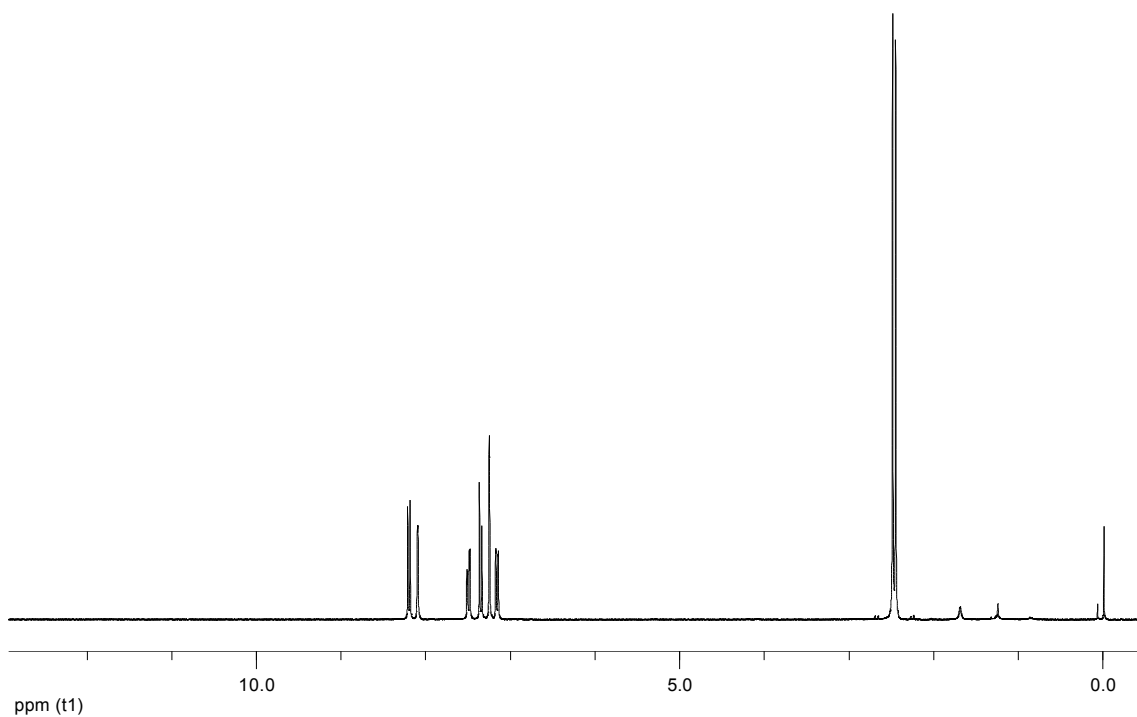


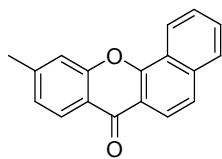
10-Chloro-7H-benzo[*c*]xanthen-7-one (1h)



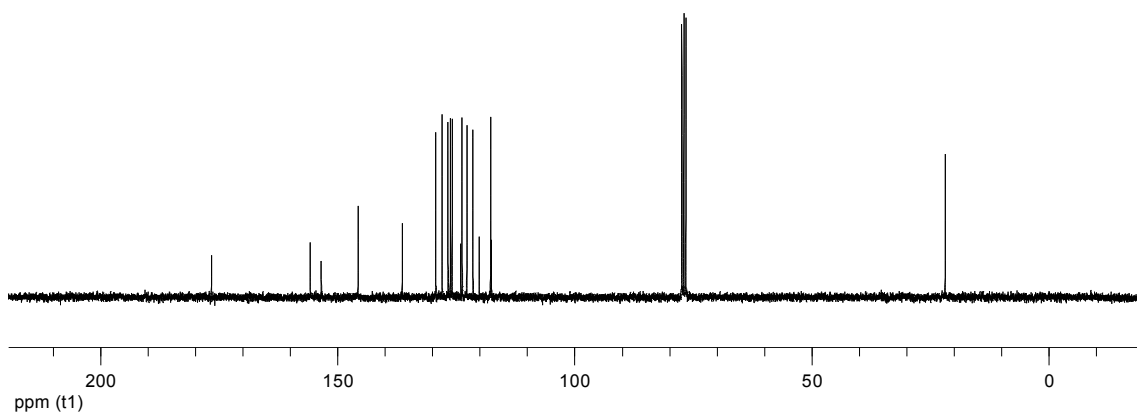
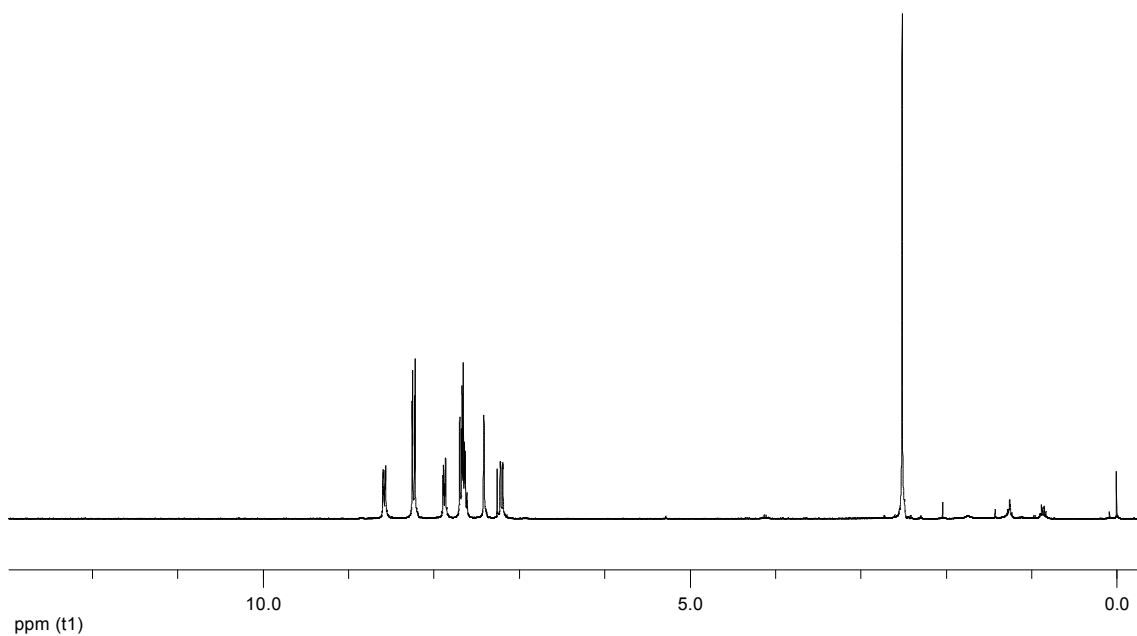


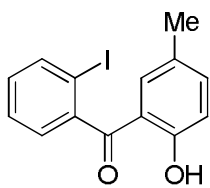
2,6-Dimethylxanthen-9-one (1i)



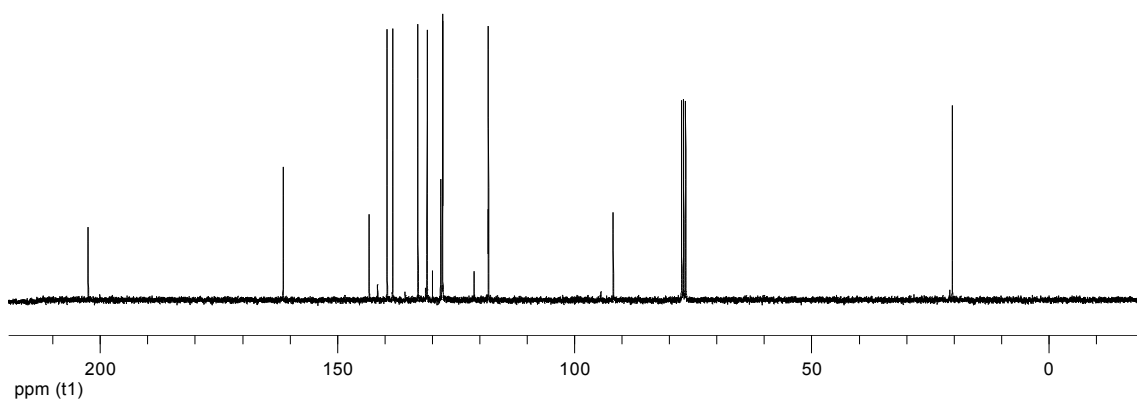
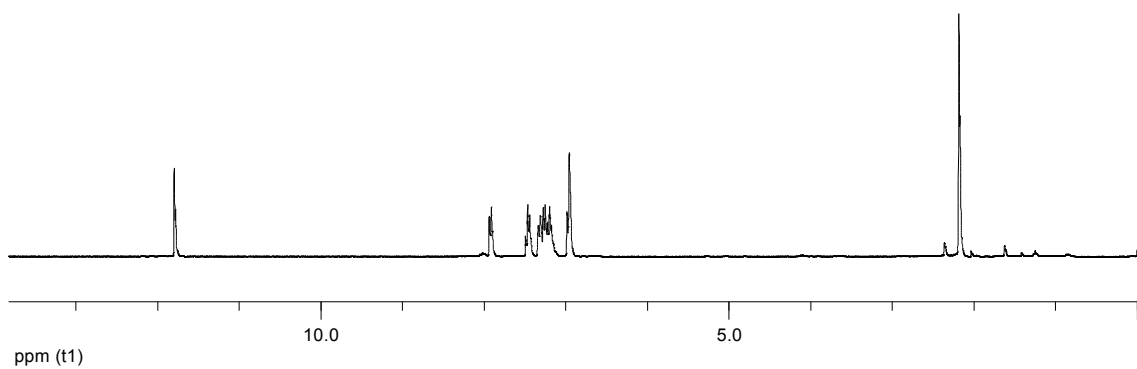


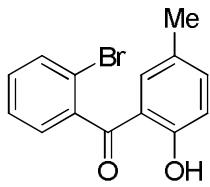
10-Methyl-7H-benzo[*c*]xanthen-7-one (1j)



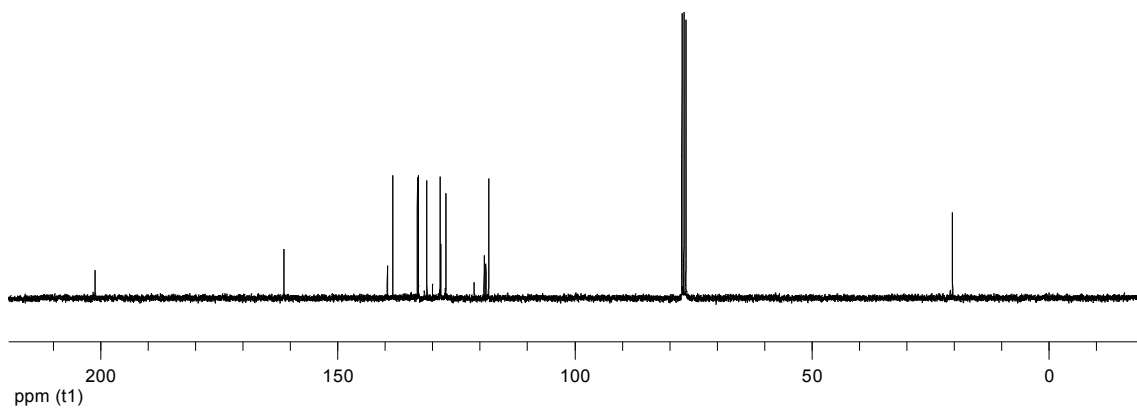
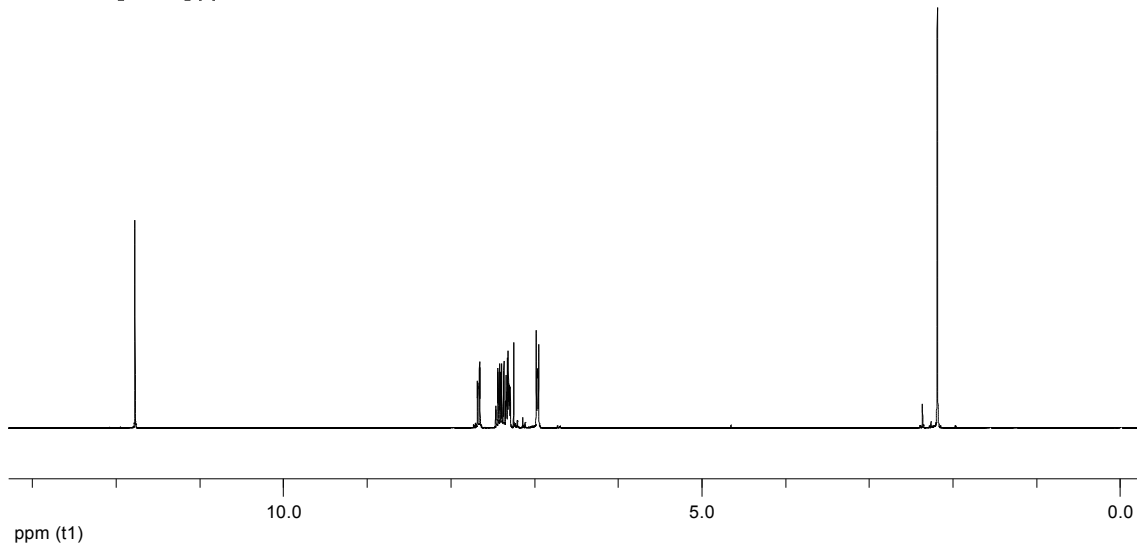


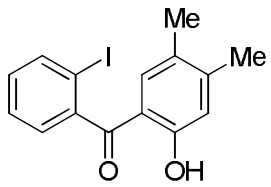
(2-Hydroxy-5-methylphenyl)(2-iodophenyl)methanone (2a)



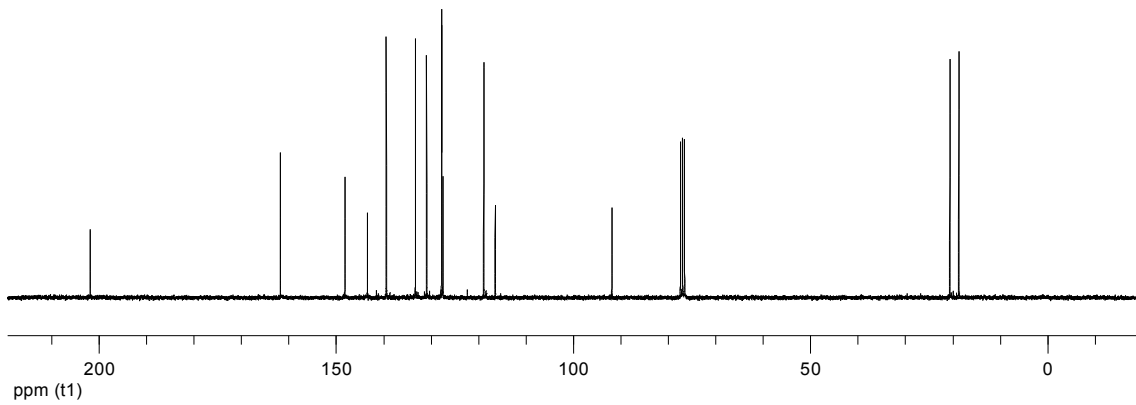
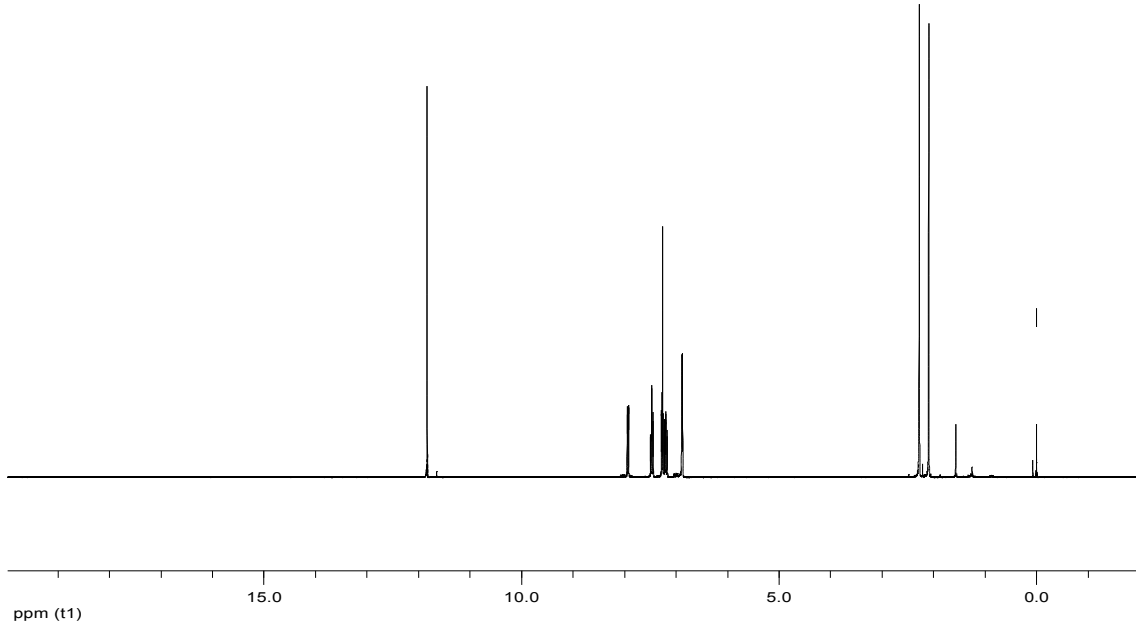


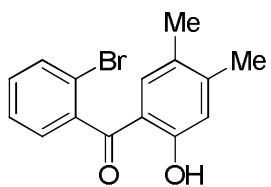
(2-Bromophenyl)(2-hydroxy-5-methylphenyl)methanone (2a')



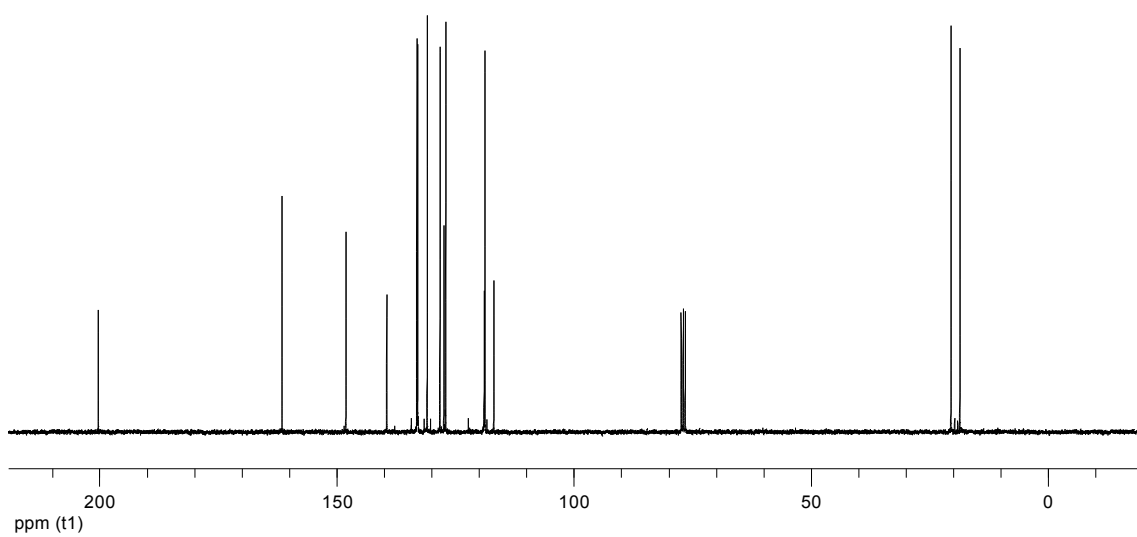
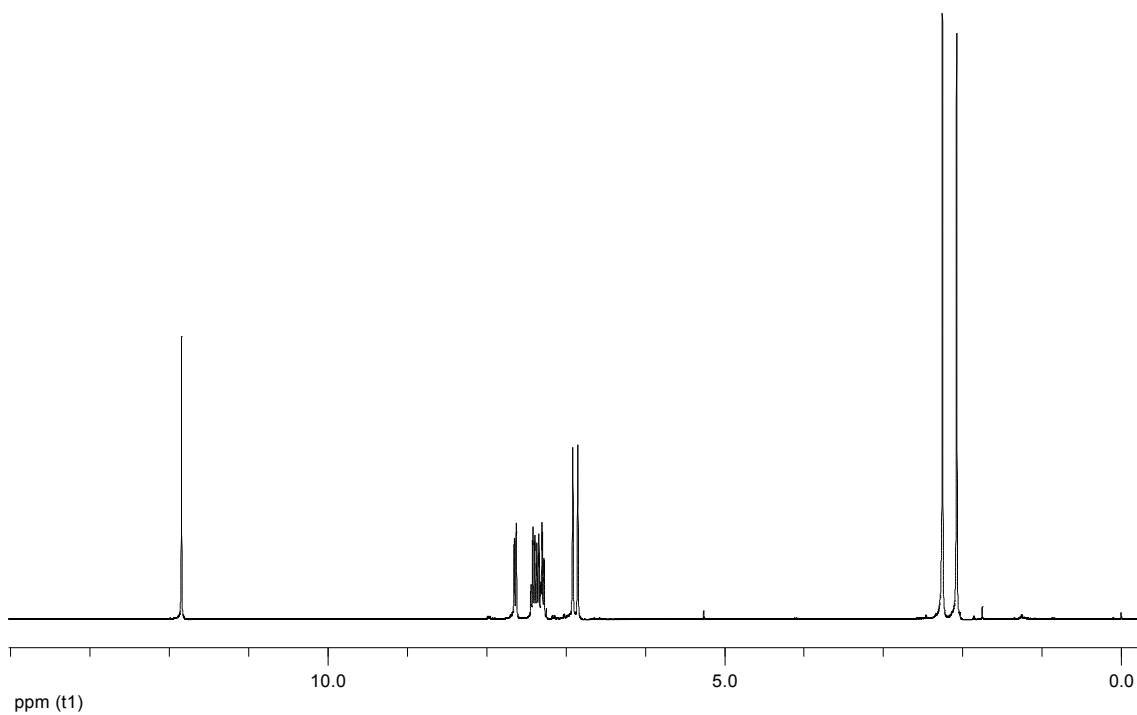


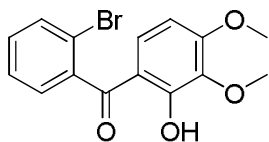
(2-Hydroxy-4,5-dimethylphenyl)(2-iodophenyl)
methanone (2b)



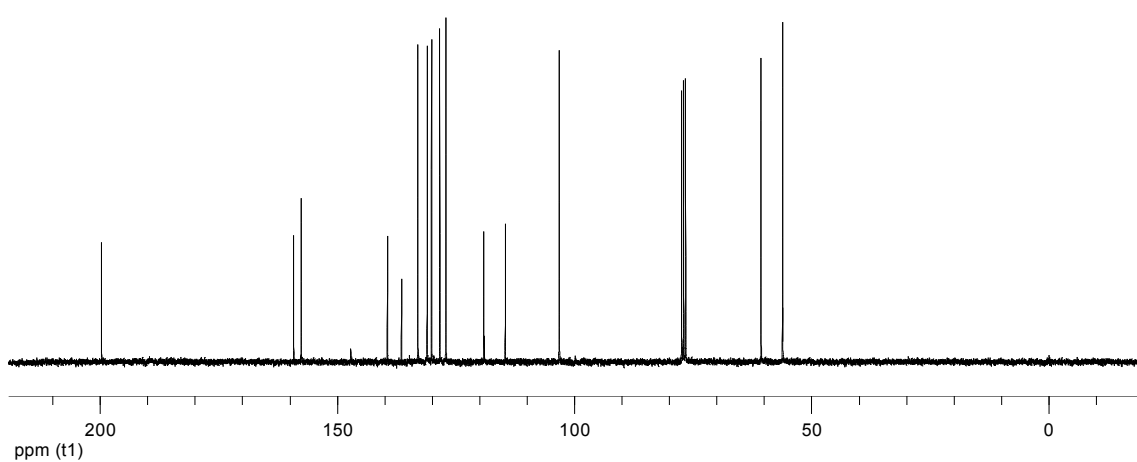
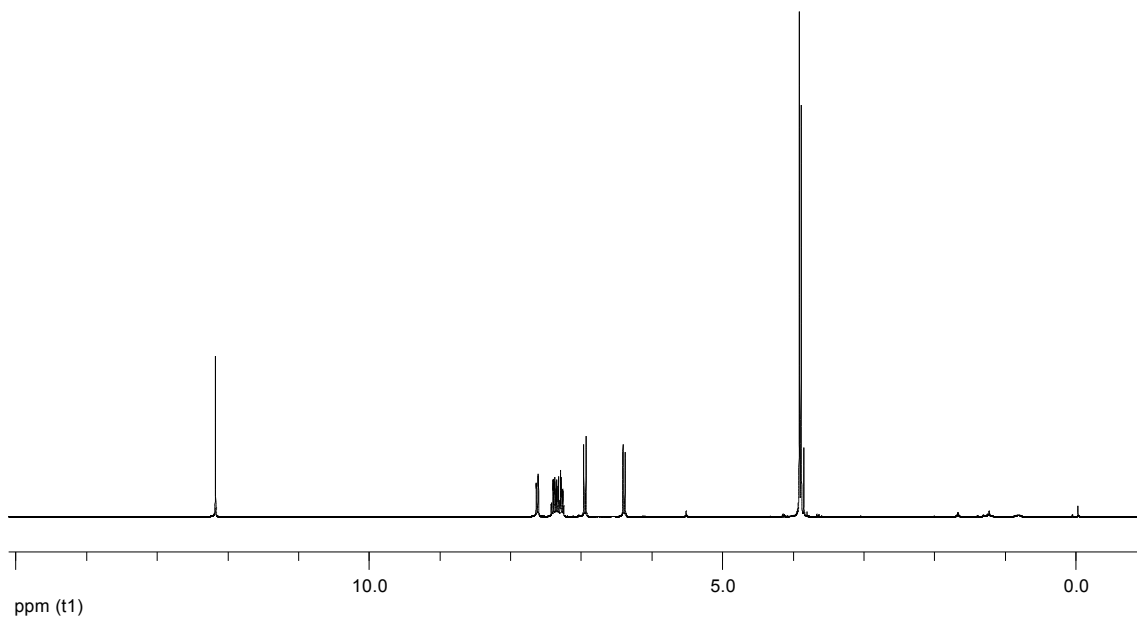


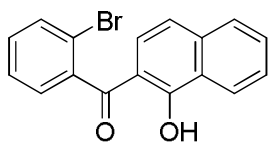
(2-Bromophenyl)(2-hydroxy-4,5-dimethylphenyl)
methanone (2b')



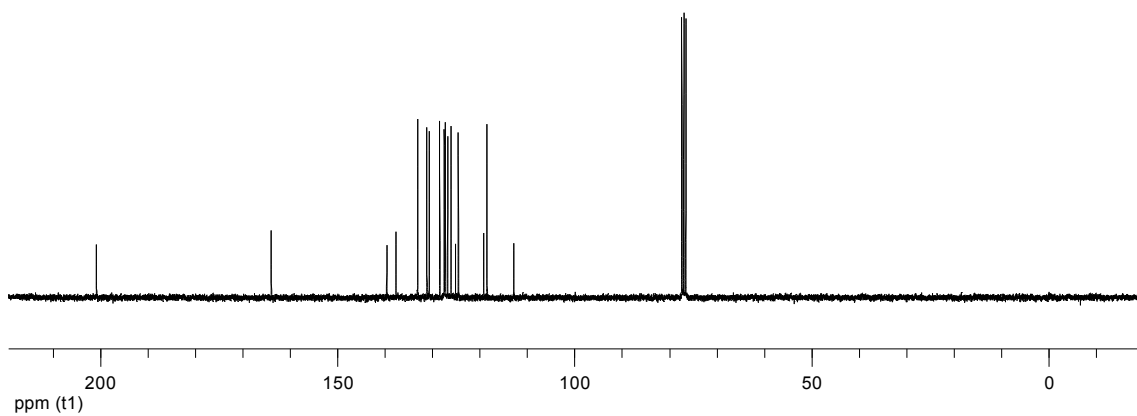
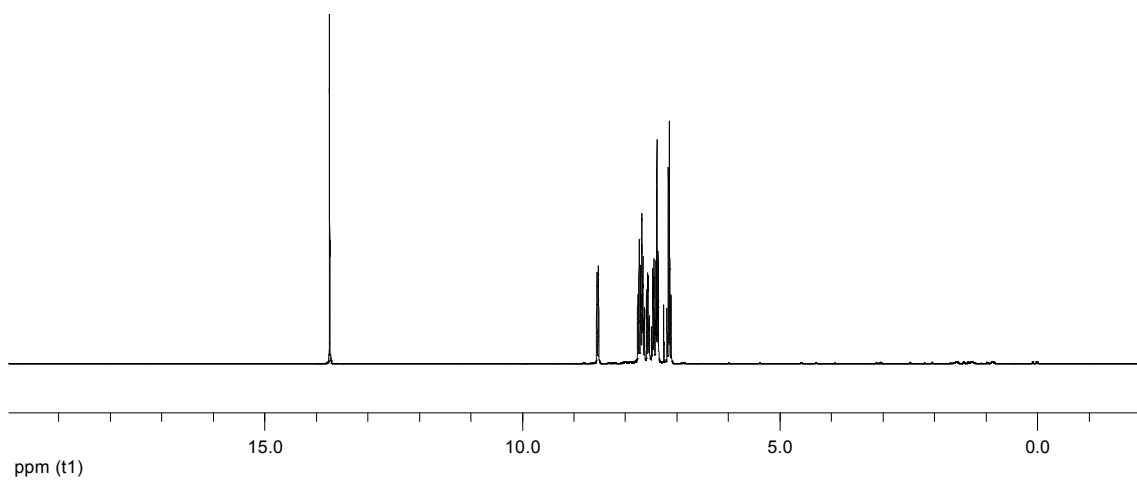


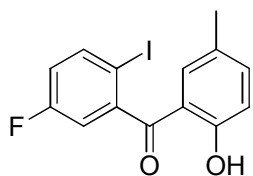
(2-Bromophenyl) (2-hydroxy-3,4-dimethoxyphenyl)methanone (2c)



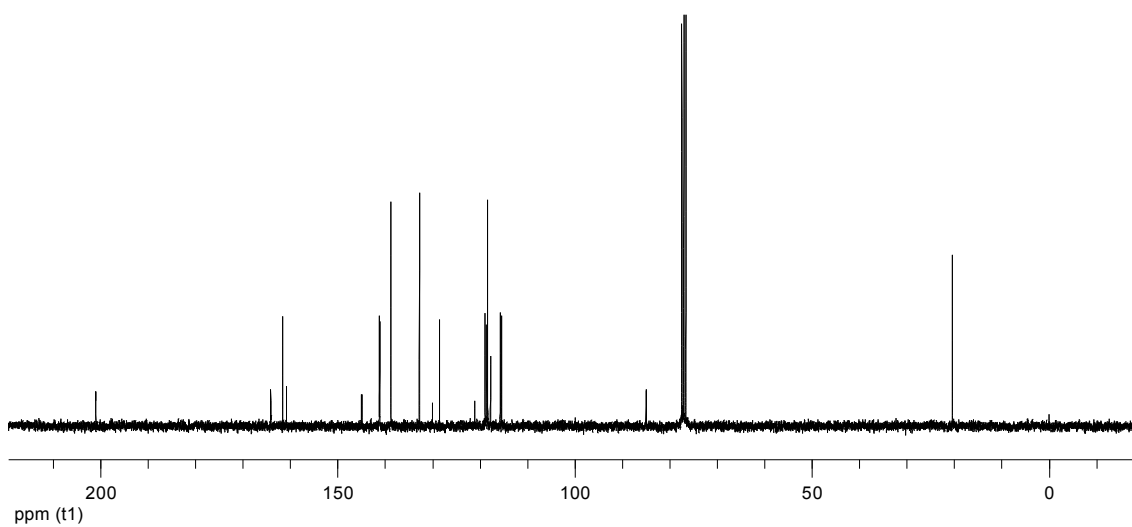
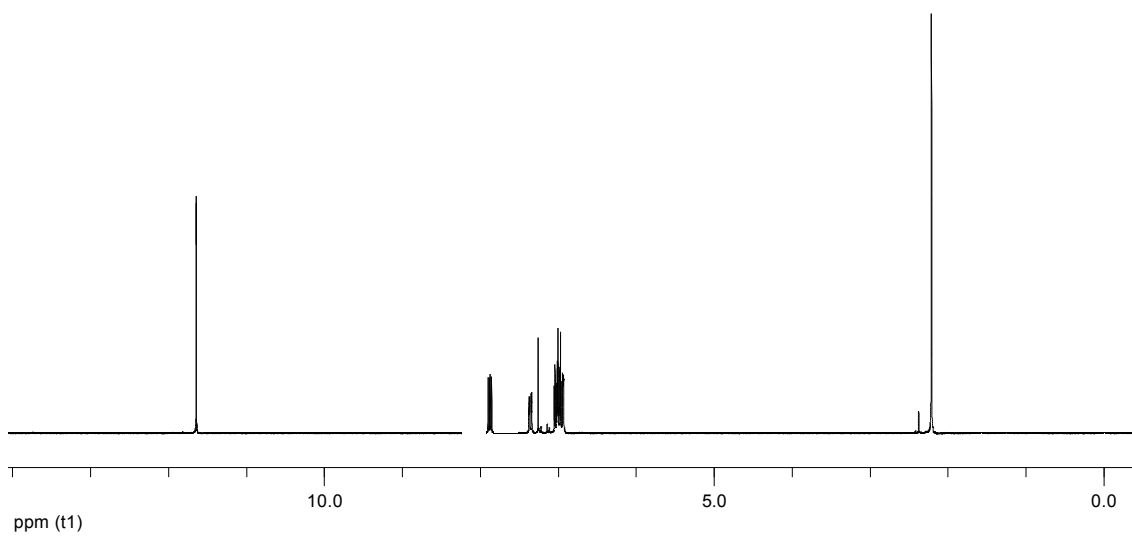


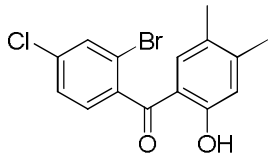
**(2-Bromophenyl)(1-hydroxynaphthalen-2-yl)
methanone (2d')**



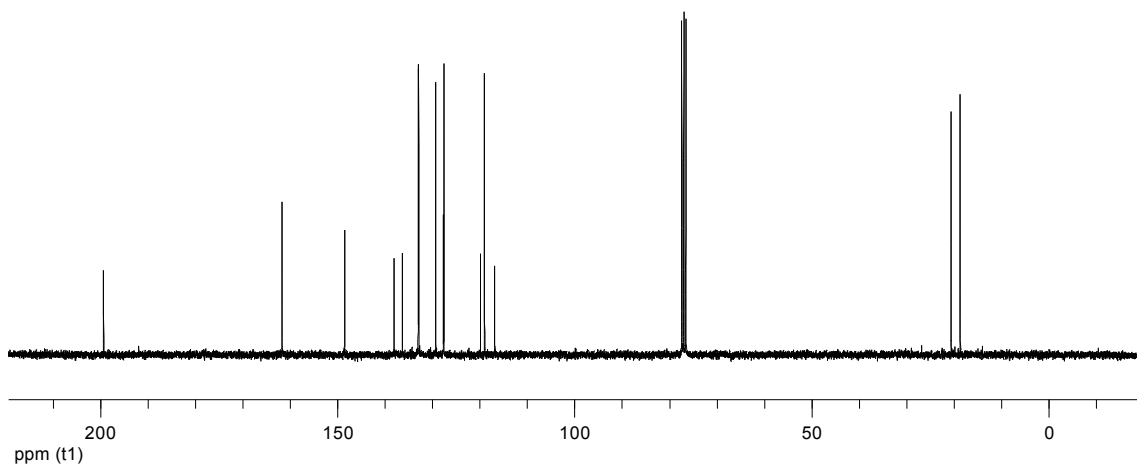
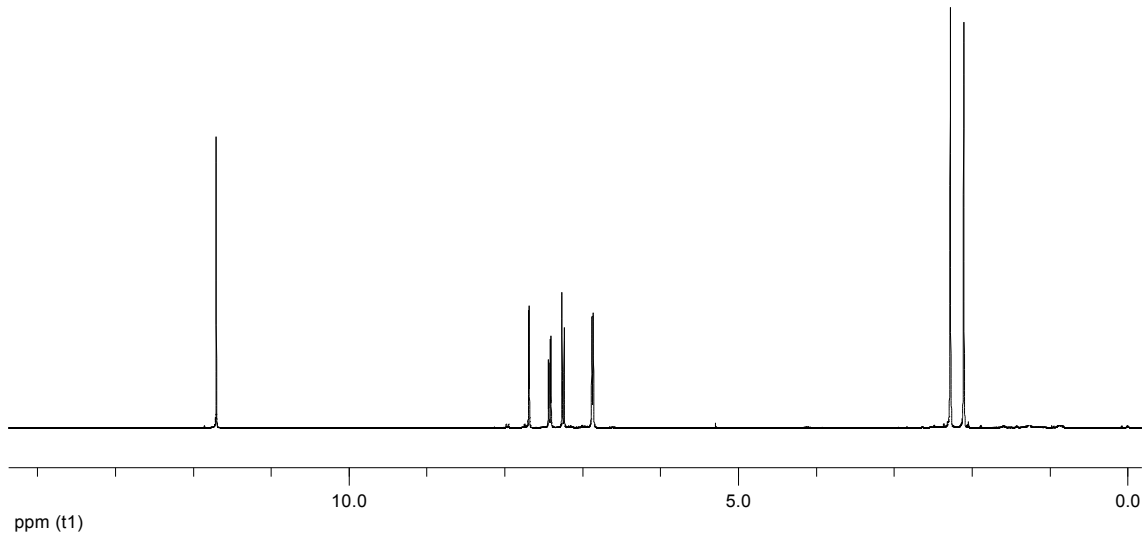


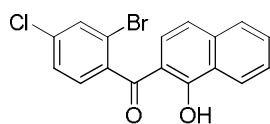
(5-Fluoro-2-iodophenyl)(2-hydroxy-5-methylphenyl)methanone (2e)



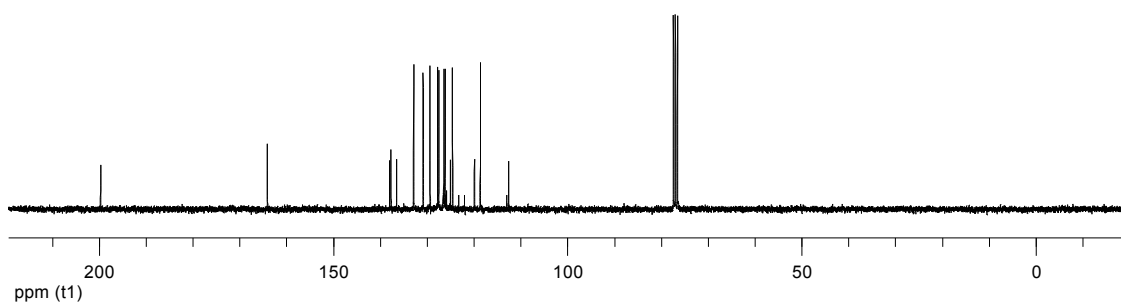
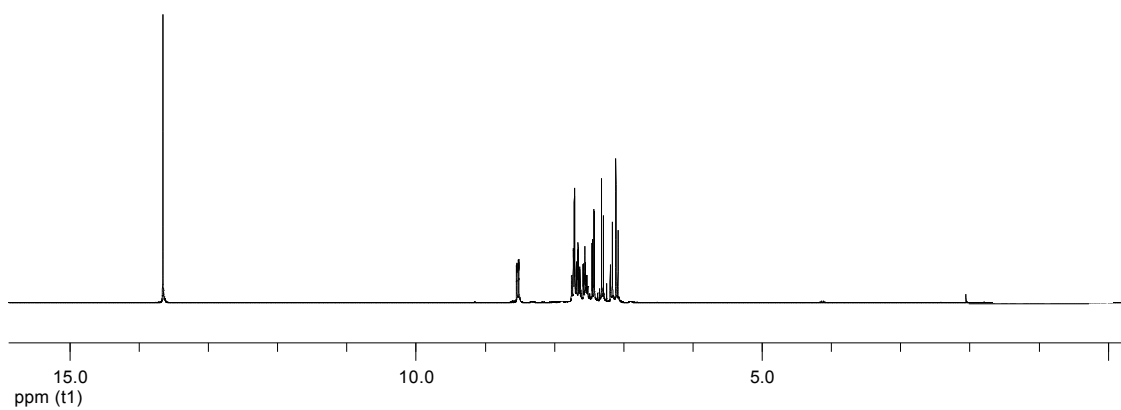


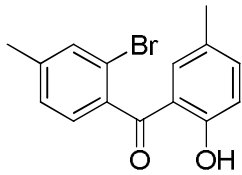
(2-Bromo-4-chlorophenyl)(2-hydroxy-4,5-dimethylphenyl)methanone (2g)



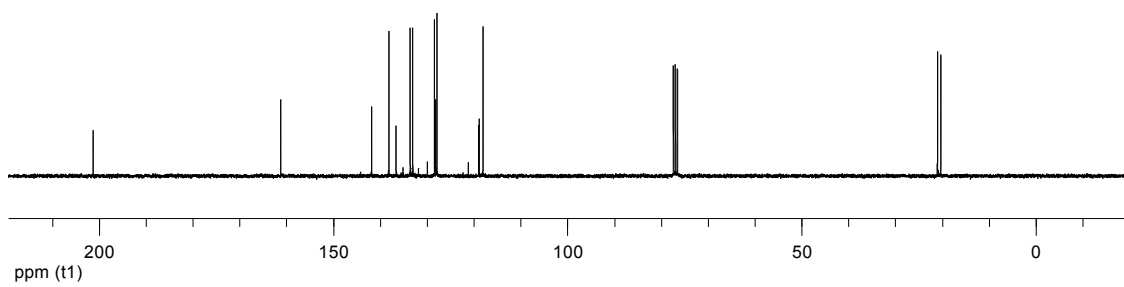
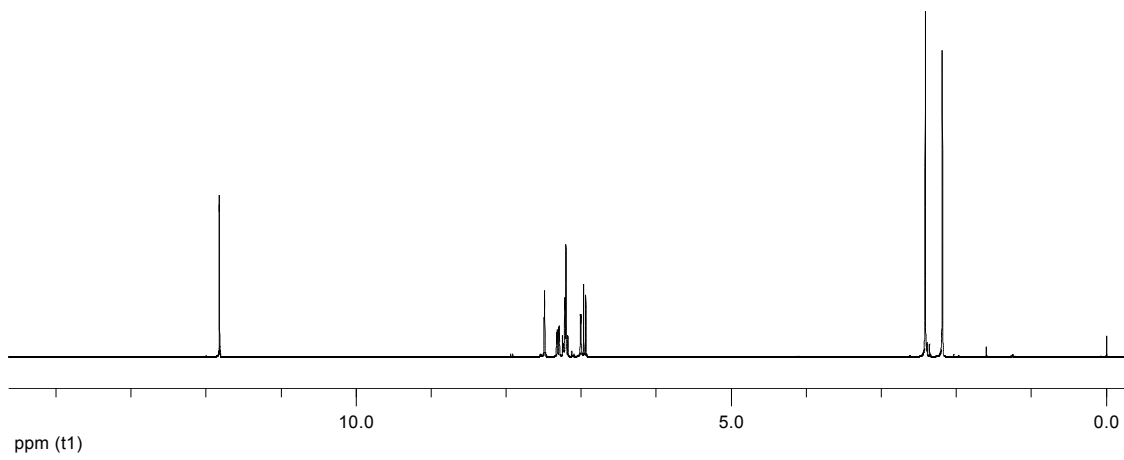


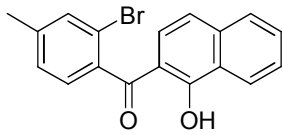
(2-Bromo-4-chlorophenyl)(1-hydroxynaphthalen-2-yl)methanone (2h)



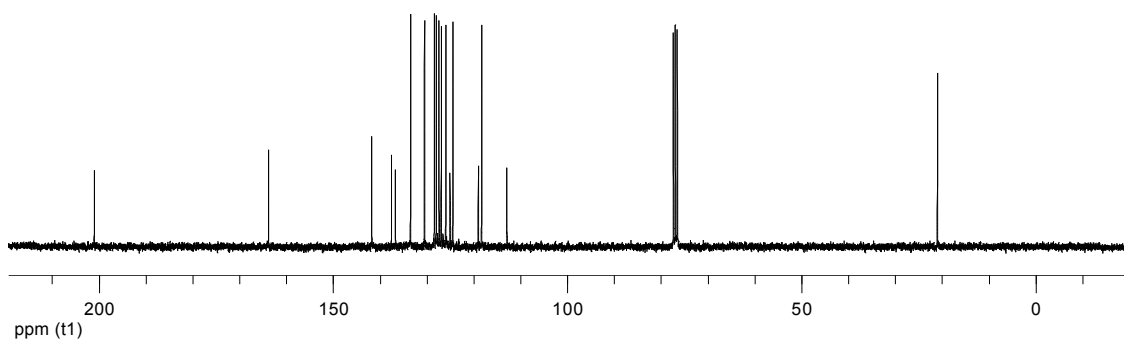
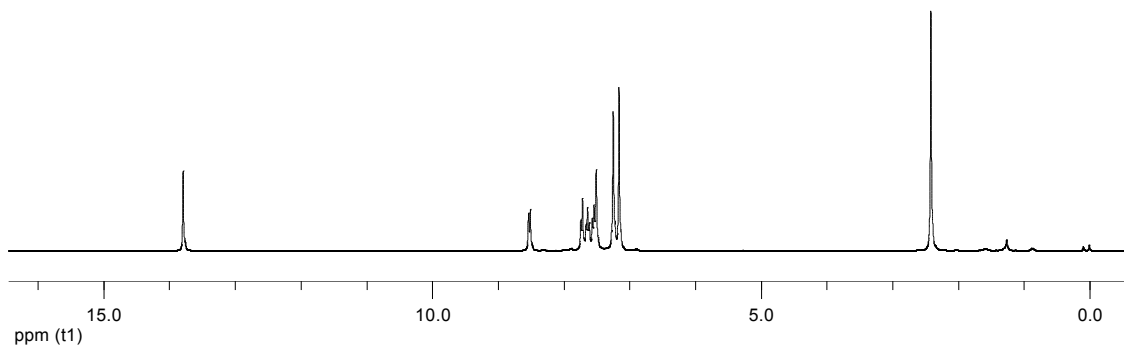


(2-Bromo-4-methylphenyl)(2-hydroxy-5-methylphenyl)methanone (2i)





(2-Bromo-4-methylphenyl)(1-hydroxynaphthalen-2-yl)methanone (2j)



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- ¹ H. Shargi, M. Hosseini-Sarvari and R. Eskandari, *Synthesis* 2006, 2047.
² G. Qabaja and G. B. Jones, *J. Org. Chem.* 2000, **65**, 7187.
³ R. Olivera, R. SanMartin, F. Churruca and E. Domínguez, *J. Org. Chem.* 2002, **67**, 7215.