Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 236–237

Synthesis of cinnamyl substituted dihydrofuranones by the Heck cross-coupling reaction

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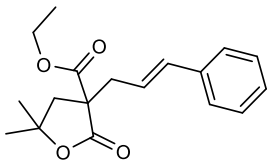
Experimental part

General remarks. ^{1}H NMR (250.13 MHz, 300.13 MHz) and ^{13}C NMR (62.9 MHz, 75.5 MHz) spectra were taken on Bruker AVANCE 250 I ARX 300 instruments in $CDCl_3$. The calibration of spectra was carried out according to the solvent signal ($CDCl_3$ δ, ^{1}H = 7.25, ^{13}C = 7.70 ppm). Mass spectrometry data were obtained on devices ADM MS40 <ADM 402, Varian MAT CH7, MAT 731, by direct inlet at an ionization energy of 70 eV. HRMS (EI) (ESI-TOF) analyses were performed on LTQ Therma Finigan and Agilent 1200/6210 Time-of-Flight spectrometers. The melting points were determined on a micro heating stage HMK 67/1825 Kuestner. IR spectra were taken on spectrophotometers Bruker IFS 66 (FT IR), Nicolet 205 (FT IR). Protégé 460, Smart Orbit (ATR). For preparative chromatography, silica gel 60 (0.063-0.2 mm, 70-230 mesh) was used. TLC was performed on Merck 60 F 254 plates, developed by UV light (λ = 254 nm). Heptane/ethyl acetate was used as an eluent in various volume ratios. X-ray structural analysis was performed on a Bruker Apex instrument with a Kappa II diffractometer. Synthesis of reactants **1a-d** was carried out as described [Kochikyan T.V., Samvelyan M.A., Arutyunyan V.S., Arutyunyan E.V., Avetisyan A.A., *Russ. J. Org. Chem.*, 2006, 42(8), 1183].

General method for arylation of 3-allyldihydrofuran-2(3*H*)-ones (2a-h). Palladium acetate (3.93 mg, 0.0175 mmol, 2.5 mol%), P(*o*-Tol)$_3$ (10.65 mg, 0.0355 mmol, 5 mol%), the corresponding furan-2-one **1** (0.7 mmol), aryl bromide (1.75 mmol), potassium carbonate (2.1 mmol) and dry DMF (3 ml) are placed in the "Pressure Tube" equipped with a magnetic stirrer. The mixture is heated for 24 hours at 100 °C (TLC control). After cooling, the product is extracted with ethyl acetate (3x10 ml), the extract is dried over anhydrous sodium sulfate. After removal of the solvent, the product is purified by column chromatography (hexane: ethyl acetate – 1:4).

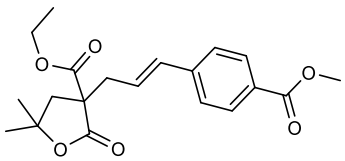
Ethyl 3-cinnamyl-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate (2a).



Yellowish liquid (93 mg, 67%)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.30 – 7.18 (m, 5H, CH_{Ph}), 6.44 (d, ^{3}J = 15.8 Hz, 1H, =CH), 6.01 (dt, ^{3}J = 15.7 Hz, ^{3}J = 7.5 Hz, 1H, =CH), 4.19 (q, ^{3}J = 7.1 Hz, 2H, CH_2-CH_3), 2.78 (dt, ^{2}J = 7.2 Hz, ^{3}J = 1.1 Hz, 2H, CH_2), 2.56 (d, ^{2}J = 13.6 Hz, 1H, CH_{2Lac}), 2.12 (d, ^{2}J = 13.7 Hz, 1H, CH_{2Lac}), 1.38 (s, 3H, CH_{3Lac}), 1.34 (s, 3H, CH_{3Lac}), 1.24 (t, ^{3}J = 7.1 Hz, 3H, CH_2-CH_3) ppm**. ^{13}C NMR** (63 MHz, $CDCl_3$) δ = 173.87 (C-O_{Lac}), 170.56 (C-O-$_{Et}$), 136.77 (C_{Ph}), 135.52 (CH_{Ph}), 128.75 (CH_{Ph}), 127.87 (CH), 126.43 (CH_{Ph}), 123.43 (CH), 82.71 (C_{Lac}), 62.51 (CH_2-CH_3), 56.98 (C_{Lac}-$_{EtOOC}$), 42.83 (CH_2), 39.25 (CH_{2Lac}), 30.01 (CH_{3Lac}), 28.73 (CH_{3Lac}), 14.18 (CH_2-CH_3) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2980 (w), 1762 (s), 1727 (s), 1449 (m), 1374 (m), 1269 (s), 1195 (s), 1140 (s), 1018 (m), 968 (s), 859 (m), 746 (s), 692 (s), 602 (m), 492 (m). **MS** (EI, 70^{o}eV): *m/z* (%) = 302 ($[M]^+$, 24), 247 (11), 246 (73), 229 (11), 228 (29), 201 (12), 200 (77), 199 (36), 172 (14), 155 (12), 143 (11), 142 (11), 141 (22), 129 (16), 128 (27), 118 (11), 117 (100), 116 (12), 115 (50), 91 (48), 43 (13). **HRMS** (ESI-TOF): calcd. for $C_{18}H_{22}O_4$ ($[M+Na]^+$) 325.1410, found 325.1417.

Ethyl (*E*)-3-[3-(4-methoxycarbonylphenyl)allyl]-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate (2b).

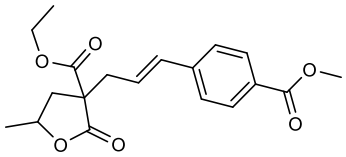


Yellowish liquid (163.2 mg, 68%)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 – 7.95 (m, 2H, CH_{Ph}), 7.42 – 7.36 (m, 2H, CH_{Ph}), 6.54 (d, ^{3}J = 15.8 Hz, 1H, =CH), 6.23 (dt, ^{3}J = 15.7 Hz, ^{3}J = 7.5 Hz, 1H, =CH), 4.26 (q, ^{3}J = 7.1 Hz, 2H, CH_2-CH_3), 3.91 (s, 3H, CH_3), 2.94 – 2.79 (m, 2H, CH_2), 2.65 (d, ^{2}J = 13.6 Hz, 1H, CH_{2Lac}), 2.16 (d, ^{2}J = 13.7 Hz, 1H, CH_{2Lac}), 1.45 (s, 3H, CH_{3Lac}), 1.41 (s, 3H, CH_{3Lac}), 1.30 (t, ^{3}J = 7.1 Hz, 3H, CH_2-CH_3) ppm. **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 173.72 (C-O_{Lac}), 170.44 (C-O-$_{Et}$), 166.93 (C-O), 141.13 ($C_{Ph\text{-}COOMe}$), 134.56 (CH_{Ph}), 130.13 (CH_{Ph}), 129.38 (C_{Ph}), 126.41 (CH), 126.30 (CH), 82.74 (C_{Lac}), 62.59 (CH_2-CH_3), 56.85 (C_{Lac}-$_{EtOOC}$), 52.22 (CH_3), 43.05 (CH_2), 39.28 (CH_{2Lac}), 30.12 (CH_{3Lac}), 28.68 (CH_{3Lac}), 14.17 (CH_2-CH_3) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2980 (w), 1764 (s), 1717 (s), 1605 (m), 1434 (m), 1374 (w), 1271 (s), 1177 (s), 1140 (s), 1107 (s), 1016 (m), 968 (m), 931 (m), 859 (m), 760 (s), 696 (m), 602 (w),

466 (w). **MS** (EI, 70°eV): *m/z* (%) = 360 ([M]$^+$, 25), 329 (17), 305 (17), 304 (100), 287 (15), 286 (30), 258 (79), 257 (55), 255 (15), 199 (17), 175 (30), 149 (19), 141 (23), 131 (21), 116 (25), 115 (48), 91 (19), 59 (23). **HRMS** (ESI-TOF): calcd. for $C_{20}H_{24}O_6$ ([M+H]$^+$) 361.1651, found 361.1652. Calcd. for $C_{20}H_{24}O_6$ ([M+Na]$^+$) 383.1465, found 383.1470.

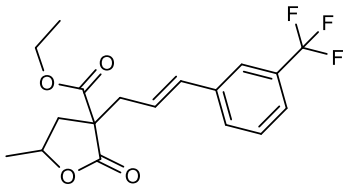
Ethyl (*E*)-3-[3-(4-methoxycarbonylphenyl)allyl]-5-methyl-2-oxotetrahydrofuran-3-carboxylate (2c).



Yellow solid (223.6 mg, 93%) mp 97-98°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 – 7.94 (m, 2H, CH_{Ph}), 7.41 – 7.36 (m, 2H, CH_{Ph}), 6.55 (dd, ^3J = 15.8 Hz, ^3J = 7.8 Hz, 1H, =CH), 6.31 – 6.15 (m, 1H, =CH), 4.76 – 4.53 (m, 1H, CH_{Lac}), 4.31 – 4.19 (m, 2H, CH_2-CH_3), 3.90 (s, 3H, CH_3), 2.94 (dddd, ^2J = 14.0 Hz, ^3J = 10.9 Hz, ^4J = 7.7 Hz, ^4J = 1.2 Hz, 1H, CH_2), 2.86 – 2.67 (m, 2H, CH_{2Lac}), 2.52 – 2.38 (m, 1H, CH_2), 1.42 (dd, ^3J = 11.4 Hz, ^3J = 6.2 Hz, 3H, CH_{3Lac}), 1.30 (td, ^3J = 7.1 Hz, ^3J = 5.1 Hz, 3H, CH_2-CH_3) ppm. **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 174.39, 173.86 (C-O_{Lac}), 169.98, 169.46 (*C*-*O*-$_{Et}$), 166.92, 166.90 (C-O), 141.21, 141.08 ($C_{Ph\text{-}COOMe}$), 134.46, 134.28 (CH), 130.08 (CH_{Ph}), 129.30 (C_{Ph}), 126.41, 126.33 (CH), 126.30, 126.12 (CH_{Ph}), 75.42, 74.75 (CH_{Lac}), 62.56, 62.50 (CH_2-CH_3), 56.55, 55.72 (C_{Lac}-$_{EtOOC}$), 52.20 (CH_3), 39.57 (CH_2), 38.24, 37.88, 37.79 (CH_{2Lac}), 21.56, 21.04 (CH_{3Lac}), 14.22, 14.16 (CH_2-CH_3) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2980 (w), 2957 (w), 1768 (s), 1727 (s), 1712 (s), 1605 (m), 1436 (m), 1389 (m), 1280 (s), 1189 (s), 1179 (s), 1113 (s), 983 (s), 859 (m), 756 (s), 699 (m), 480 (m). **MS** (EI, 70°eV): *m/z* (%) = 346 ([M]$^+$, 58), 315 (27), 304 (22), 274 (39), 273 (100), 272 (32), 258 (34), 257 (33), 241 (75), 199 (33), 175 (21), 169 (20), 149 (21), 143 (23), 141 (38), 131 (23), 128 (22), 116 (32), 115 (68), 91 (25), 59 (28). **HRMS** (ESI-TOF): calcd. for $C_{19}H_{22}O_6$ ([M+H]$^+$) 347.1494, found 347.1494. Calcd. for $C_{19}H_{22}O_6$ ([M+Na]$^+$) 369.1308, found 369.1313.

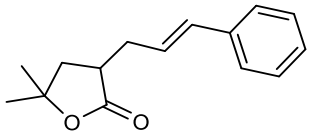
Ethyl (*E*)-5-methyl-2-oxo-3-[3-(3-trifluoromethylphenyl)allyl]tetrahydrofuran-3-carboxylate (2d).



Yellow liquid (202 mg, 81%)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.57 – 7.38 (m, 4H, CH_{Ph}), 6.55 (dd, ^{3}J = 15.8 Hz, ^{3}J = 7.7 Hz, 1H, =CH), 6.32 – 6.11 (m, 1H, , =CH), 4.75 – 4.56 (m, 1H, CH_{Lac}), 4.32 – 4.20 (m, 2H, CH_2-CH_3), 2.94 (dddd, ^{2}J = 14.0 Hz, ^{3}J = 11.3 Hz, ^{4}J = 7.8 Hz, ^{4}J = 1.2 Hz, 1H, CH_2), 2.84 – 2.69 (m, 2H, CH_{2Lac}), 2.52 – 2.39 (m, 1H, CH_2), 1.43 (dd, ^{3}J = 11.1 Hz, ^{3}J = 6.2 Hz, 3H, CH_{3Lac}), 1.30 (td, ^{3}J = 7.1 Hz, ^{3}J = 4.7 Hz, 3H, CH_2-CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -62.79(s, 3F, CF_3) ppm. **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 174.39, 173.87 (C-O_{Lac}), 169.98, 169.46 (*C*-*O*-$_{Et}$), 137.58, 137.46 (C_{Ph}), 133.81 (CH), 131.18 (q, $^{2}J_{C,F}$ = 32.2 Hz, C_{Ph}), 129.19 (CH_{Ph}), 128.50 (q, $^{1}J_{C,F}$ = 270.8 Hz, CF_3), 125.64 (CH), 124.37 (q, $^{3}J_{C,F}$ = 4.8 Hz, CH_{Ph}), 123.15 (q, $^{4}J_{C,F}$ = 1.8 Hz, CH_{Ph}), 75.43, 74.76 (CH_{Lac}), 62.57, 62.50 (CH_2-CH_3), 56.54, 55.72 (C_{Lac}-EtOOC), 39.57 (CH_2), 38.24, 37.77, 37.65 (CH_{2Lac}), 21.54, 21.02 (CH_{3Lac}), 14.21, 14.14 (CH_2-CH_3) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2982 (w), 2936 (w), 1770 (s), 1729 (s), 1447 (w), 1387 (w), 1327 (s), 1162 (s), 1117 (v), 1094 (s), 1072 (s), 971 (m), 944 (m), 793 (m), 696 (m), 661 (m), 451 (w). **MS** (EI, 70^{o}eV): *m/z* (%) = 356 ($[M]^+$, 29), 337 (17), 284 (34), 283 (100), 282 (31), 268 (19), 267 (30), 237 (25), 210 (22), 209 (18), 185 (45), 165 (25), 159 (54), 141 (16), 115 (19). **HRMS** (EI, 70^{o}eV): calcd. for $C_{18}H_{19}O_4F_3$ ($[M]^+$) 356.12300, found 356.12311.

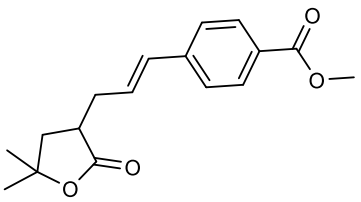
3-Cinnamyl-5,5-dimethyldihydrofuran-2(3*H*)-one (2e).



Yellow liquid (108.6 mg, 67%)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34 – 7.20 (m, 5H, CH_{Ph}), 6.42 (br.d, ^{3}J = 15.8 Hz, 1H, =CH), 6.11 (dt, ^{3}J = 15.8 Hz, ^{3}J = 7.2 Hz, 1H, =CH), 2.90 (dtd, ^{2}J = 11.2 Hz, ^{2}J = 8.9 Hz, ^{3}J = 4.5 Hz, 1H, CH_2), 2.74 (dddd, ^{3}J = 14.3 Hz, ^{3}J = 7.0 Hz, ^{3}J = 4.5 Hz, ^{3}J = 1.4 Hz, 1H, CH_{Lac}), 2.44 – 2.33 (dddd, ^{3}J = 16.1 Hz, ^{3}J = 8.8 Hz, ^{3}J = 7.3 Hz, ^{3}J = 1.3 Hz, 1H, CH_2), 2.20 (dd, ^{2}J = 12.7 Hz, ^{3}J = 9.0 Hz, 1H, CH_{2Lac}), 1.78 (dd, ^{2}J = 12.5 Hz, ^{3}J = 11.5 Hz, 1H, CH_{2Lac}), 1.41 (s, 3H, CH_{3Lac}), 1.34 (s, 3H, CH_{3Lac}) ppm. **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 177.85 (C-O_{Lac}), 137.11 (C_{Ph}), 132.87 (CH), 128.66 (CH_{Ph}), 127.51 (CH), 126.29 (CH_{Ph}), 126.24 (CH_{Ph}), 82.52 (C_{Lac}), 40.89 (CH_{Lac}), 40.70 (CH_2), 34.03 (CH_{2Lac}), 29.07 (CH_{3Lac}), 27.31 (CH_{3Lac}) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2976 (w), 2932 (w), 1754 (s), 1496 (w), 1451 (w), 1387 (w), 1374 (m), 1317 (w), 1265 (s), 1212 (w), 1181 (m), 1133 (s), 1102 (m), 1072 (m), 1024 (w), 950 (s), 929 (m), 744 (s), 694 (s), 620 (m), 579 (w), 501 (m), 468 (w). **MS** (EI, 70^{o}eV): *m/z* (%) = 230 ($[M]^+$, 6), 175 (6), 174 (51), 130 (13), 129 (100), 128 (26), 117 (38), 115 (27), 91 (18), 43 (11), 41 (6), 39 (6). **HRMS** (ESI-TOF): calcd. for $C_{15}H_{18}O_2$ ($[M+H]^+$) 231.1385, found 231.1388. Calcd. for $C_{15}H_{18}O_2$ ($[M+Na]^+$) 253.1199, found 253.1204.

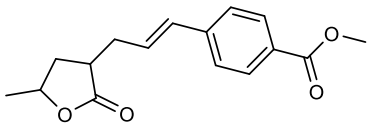
Methyl (*E*)-4-[3-(5,5-dimethyl-2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl]benzoate (2f).



Yellowish solid (200.3 mg, 99%), mp 78-79 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 – 7.95 (m, 2H, CH_{Ph}), 7.42 – 7.37 (m, 2H, CH_{Ph}), 6.50 (br.d, ^{3}J = 15.8 Hz, 1H, =CH), 6.29 (dt, ^{3}J = 15.8 Hz, ^{3}J = 7.1 Hz, 1H, =CH), 3.90 (s, 3H, CH_3), 2.96 (dtd, ^{2}J = 11.3 Hz, ^{2}J = 8.8 Hz, ^{3}J = 4.6 Hz, 1H, CH_2), 2.80 (dddd, ^{3}J = 14.3 Hz, ^{3}J = 6.6 Hz, ^{3}J = 4.7 Hz, ^{3}J = 1.3 Hz, 1H, CH_{Lac}), 2.45 (dddd, ^{3}J = 16.0 Hz, ^{3}J = 8.7 Hz, ^{3}J = 7.4 Hz, ^{3}J = 1.2 Hz 1H, CH_2), 2.26 (dd, ^{2}J = 12.7 Hz, ^{3}J = 9.0 Hz, 1H, CH_{2Lac}), 1.82 (dd, ^{2}J = 12.4 Hz, ^{3}J = 11.7 Hz, 1H, CH_{2Lac}), 1.46 (s, 3H, CH_{3Lac}), 1.39 (s, 3H, CH_{3Lac}) ppm. **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 177.69 (C-O_{Lac}), 166.98 (C-O), 141.57 (C_{Ph}), 132.09 (CH), 130.08 (CH_{Ph}), 129.28 (CH), 129.05 (C_{Ph}) 126.15 (CH_{Ph}), 82.60 (C_{Lac}), 52.18 (CH_3), 40.84 (CH_2), 40.79 (CH_{Lac}), 34.16 (CH_{2Lac}), 29.11 (CH_{3Lac}), 27.32 (CH_{3Lac}) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2976 (w), 2951 (w), 1758 (s), 1714 (s), 1605 (m), 1434 (m), 1412 (w), 1374 (w), 1269 (s), 1177 (s), 1135 (s), 1105 (s), 1016 (m), 952 (s), 929 (m), 865 (m), 758 (s), 699 (m), 606 (m), 579 (w), 515 (w). **MS** (EI, 70°eV): *m/z* (%) = 288 ($[M]^+$, 9), 257 (12), 233 (14), 232 (100), 201 (12), 187 (70), 186 (11), 155 (28), 143 (41), 131 (12), 129 (33), 128 (41), 127 (11), 116 (21), 115 (45), 91 (15), 59 (20), 43 (16), 41 (11). **HRMS** (ESI-TOF): calcd. for $C_{17}H_{20}O_4$ ($[M+H]^+$) 289.1440, found 289.1436. Calcd. for $C_{17}H_{20}O_4$ ($[M+Na]^+$) 311.1254, found 311.1255.

Methyl (*E*)-4-[3-(5-methyl-2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl]benzoate (2g)

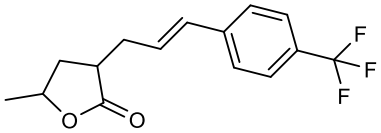


White solid (146.4 mg, 76%) mp 68-69°C

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 – 7.93 (m, 2H, CH_{Ph}), 7.39 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.6 Hz, 2H, CH_{Ph}), 6.49 (d, ^{3}J = 15.8 Hz, 1H, =CH), 6.35 – 6.22 (m, 1H, =CH), 4.72 – 4.43 (m, 1H, CH_{Lac}), 3.89 (s, 3H, CH_3), 2.88 – 2.69 (m, 2H, CH_2), 2.54 – 2.37 (m, 2H, CH_{2Lac}), 2.23 – 1.97 (m, 1H, CH_{Lac}), 1.39 (dd, ^{2}J = 11.5 Hz, ^{3}J = 6.3 Hz, 3H, CH_{3Lac}) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 178.45, 178.05 (C-O_{Lac}), 166.92, 166.90 (C-O), 141.53, 141.42($C_{Ph\text{-}COOMe}$), 132.26, 132.00 (CH), 130.01 (CH_{Ph}), 129.96, 129.18 (C_{Ph}), 128.96, 128.90 (CH), 126.14, 126.10 (CH_{Ph}), 75.38, 75.16 (CH_{Lac}), 52.13 (CH_3), 41.44, 39.26 (CH_{Lac}), 36.48 (CH_2), 34.35, 34.10, 33.71 (CH_{2Lac}), 21.35, 21.04 (CH_{3Lac}) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2982

(w), 2934 (w), 1758 (s), 1704 (s), 1607 (m), 1438 (m), 1387 (m), 1278 (s), 1173 (s), 1111 (s), 1065 (m), 1018 (m), 956 (s), 863 (m), 758 (s), 699 (s), 620 (m), 495 (m). **MS** (EI, 70^{o}eV): *m/z* (%) = 274 ([M]$^{+}$, 50), 243 (29), 242 (15), 232 (96), 202 (18), 201 (16), 187 (100), 186 (17), 155 (46), 143 (69), 141 (17), 131 (18), 129 (51), 128 (63), 127 (19), 116 (37), 115 (77), 91 (27), 59 (33). **HRMS** (ESI-TOF): calcd. for $C_{16}H_{18}O_4$ ([M+H]$^{+}$) 275.1283, found 275.1280. Calcd. for $C_{16}H_{18}O_4$ ([M+Na]$^{+}$) 297.1097, found 297.1100.

(*E*)-5-Methyl-3-[3-(4-trifluoromethylphenyl)allyl]dihydrofuran-2(3*H*)-one (2h).

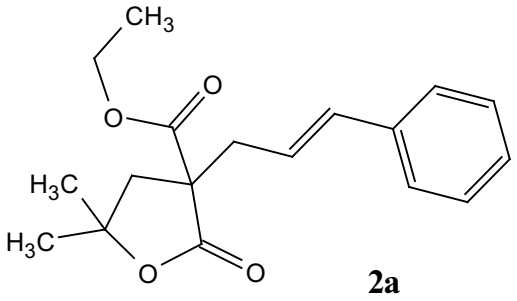


Yellow liquid (147.9 mg, 74%)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, ^{3}J = 8.2 Hz, 2H, CH_{Ph}), 7.44 (d, ^{3}J = 8.2 Hz, 2H, CH_{Ph}), 6.51 (d, ^{3}J = 15.8 Hz, 1H, =CH), 6.36 – 6.20 (m, 1H, =CH), 4.74 – 4.46 (m, 1H, CH_{Lac}), 2.91 – 2.69 (m, 2H, CH_2), 2.56 – 2.42 (m, 2H, CH_{2Lac}), 2.25 – 1.99 (m, 1H, CH_{Lac}), 1.41 (dd, ^{2}J = 11.2 Hz, ^{3}J = 6.3 Hz, 3H, CH_{3Lac}) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -62.51(s, 3F, CF_3) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 178.46, 178.06 (C-O_{Lac}), 140.58 (C_{Ph}), 132.22 (CH), 130.41 (q, $^{2}J_{C,F}$ = 19.2 Hz, C_{Ph}), 129.13 (CH), 127.90 (q, $^{1}J_{C,F}$ = 271.1 Hz, CF_3), 126.44 (CH_{Ph}), 125.68 (q, $^{3}J_{C,F}$ = 7.6 Hz, CH_{Ph}), 75.43, 75.21 (CH_{Lac}), 41.50, 39.32 (CH_{Lac}), 36.51 (CH_2), 34.41, 34.10 33.68 (CH_{2Lac}), 21.43, 21.12 (CH_{3Lac}) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2980 (w), 2934 (w), 1764 (s), 1616 (w), 1387 (w), 1323 (s), 1162 (s), 1115 (s), 1065 (s), 1016 (m), 952 (m), 837 (m), 600 (m), 507 (w). **MS** (EI, 70^{o}eV): *m/z* (%) = 284 ([M]$^{+}$, 19), 265 (10), 242 (60), 198 (13), 197 (100), 196 (26), 185 (21), 177 (33), 165 (22), 159 (15), 129 (15), 128 (14), 116 (12). 115 (20). **HRMS** (ESI-TOF): calcd. for $C_{15}H_{15}F_3O_2$ ([M+H]$^{+}$) 285.1102, found 285.1097. Calcd. for $C_{15}H_{15}F_3O_2$ ([M+Na]$^{+}$) 307.0916, found 307.0922.

The counter synthesis of 3-cinnamyl-5,5-dimethyldihydrofuran-2(3*H*)-one **(2e)**. Sodium hydroxide solution (40%, 20 mg of NaOH) is added to compound **2a** (60.4 mg, 0.2 mmol), and this is stirred at 80–85 °C for 2 hours. After cooling, the mixture is diluted with hydrochloric acid to adjust pH to 1-2. The product is extracted with ether (3x10 ml) and, after the distillation of the solvent; the residue is heated in vacuum (13-15 Torr) at 200–250 °C for 0.5 hours. After cooling, the product is purified by column chromatography. The yield of product **2e** is 41.4 mg (90%), its MNR data are identical to those of alternative synthesis.

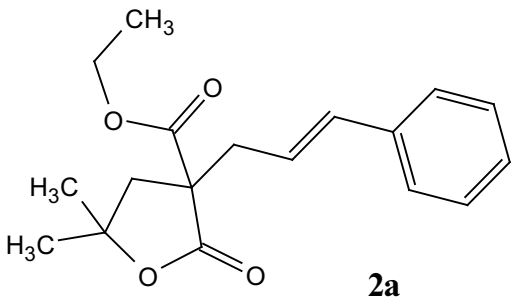
Molecular Formula: $C_{18}H_{22}O_4$



2a

^{1}H NMR (300 MHz, $CDCl_3$)

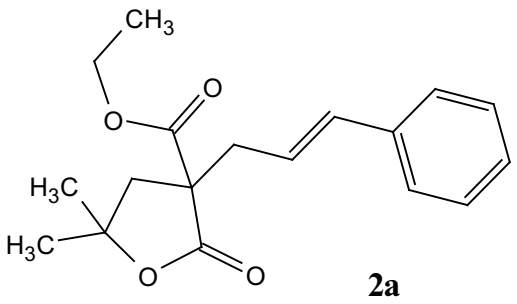
Molecular Formula: $C_{18}H_{22}O_4$



2a

^{13}C NMR (63 MHz, $CDCl_3$)

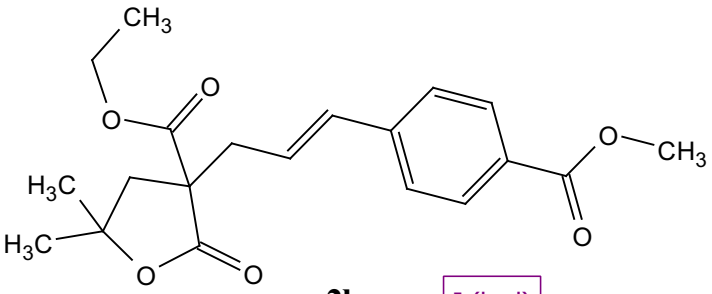
Molecular Formula: $C_{18}H_{22}O_4$



2a

^{13}C NMR (63 MHz, $CDCl_3$) DEPT

Molecular Formula: $C_{20}H_{24}O_6$



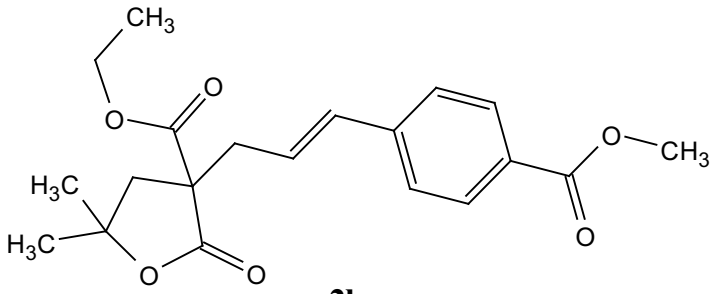
2b

^{1}H NMR (300 MHz, $CDCl_3$)

E (m) 7.97 | J (m) 7.39 | I (br.d) 6.54 | H (dt) 6.23 | G (q) 4.26 | F (s) 3.91 | K (m) 2.87 | D (d) 2.65 | C (d) 2.16 | B (s) 1.41 | A (t) 1.30 | L (s) 1.45

f1 (ppm)

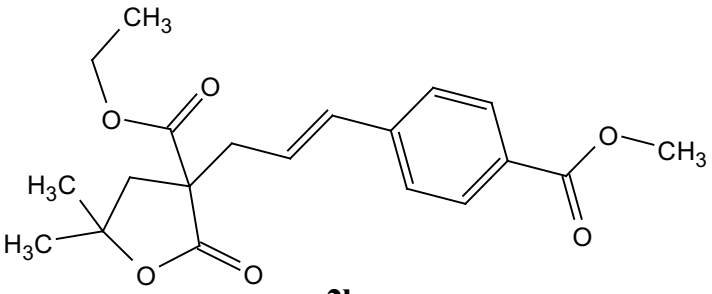
Molecular Formula: $C_{20}H_{24}O_6$



2b

^{13}C NMR (63 MHz, $CDCl_3$)

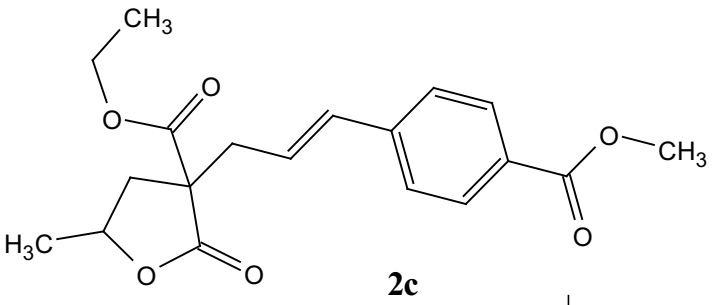
Molecular Formula: $C_{20}H_{24}O_6$



2b

^{13}C NMR (63 MHz, $CDCl_3$) DEPT

Molecular Formula: $C_{19}H_{22}O_6$



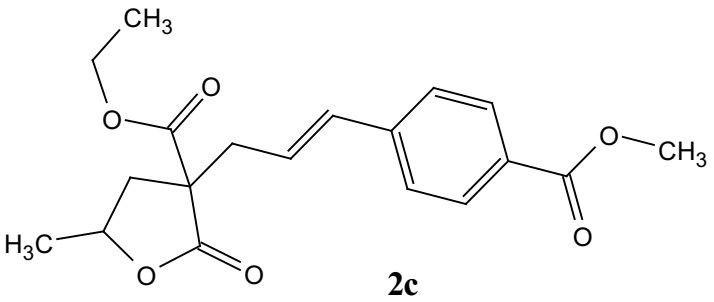
2c

^{1}H NMR (300 MHz, $CDCl_3$)

K (m) 7.97 | L (m) 7.39 | J (dd) 6.55 | I (m) 6.23 | H (m) 4.65 | G (m) 4.26 | F (s) 3.90 | E (dddd) 2.94 | D (m) 2.78 | C (m) 2.45 | B (dd) 1.42 | A (td) 1.30

f1 (ppm)

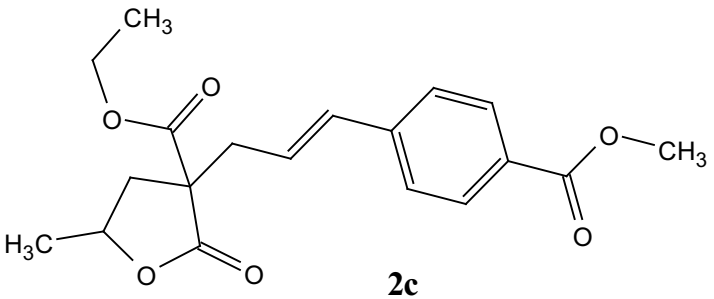
Molecular Formula: $C_{19}H_{22}O_6$



2c

^{13}C NMR (63 MHz, $CDCl_3$)

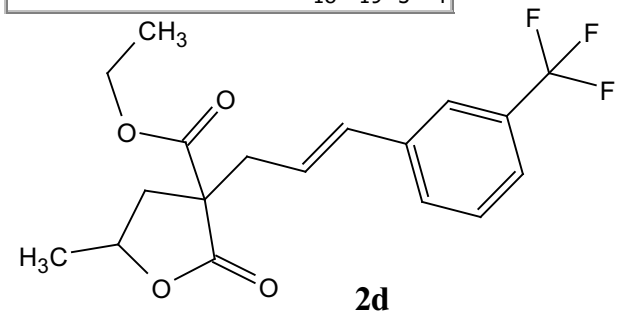
Molecular Formula: $C_{19}H_{22}O_6$



2c

^{13}C NMR (63 MHz, $CDCl_3$) DEPT

Molecular Formula: $C_{18}H_{19}F_3O_4$



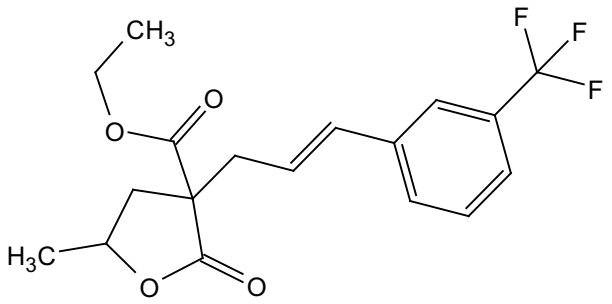
2d

^{1}H NMR (300 MHz, $CDCl_3$)

J (m) 7.47 | I (dd) 6.55 | H (m) 6.19 | G (m) 4.66 | F (m) 4.27 | E (m) 2.94 | D (m) 2.78 | C (m) 2.46 | B (dd) 1.43 | A (td) 1.30

f1 (ppm)

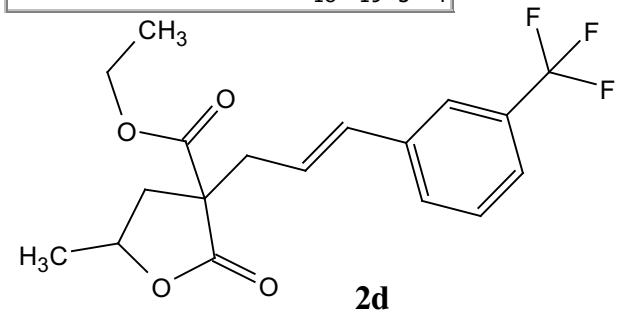
Molecular Formula: $C_{18}H_{19}F_3O_4$



2d

^{19}F NMR (282 MHz, $CDCl_3$)

Molecular Formula: $C_{18}H_{19}F_3O_4$



2d

^{13}C NMR (63 MHz, $CDCl_3$)

D (q)
131.18
J(32.16, 64.40)

B (q)
123.15
J(1.83, 3.78)

A (q)
124.37
J(4.77, 8.61)

C (t)
127.78
J(407.02)

137.6 137.5 135.0 134.0 133.8 131.9 131.4 130.9 130.7 130.4 129.5 129.5 129.2 129.2 126.4 125.6 125.4 124.5 124.4 124.3 124.3 123.2 123.2 123.1 123.1 122.0

174.4 173.9 170.0 169.5

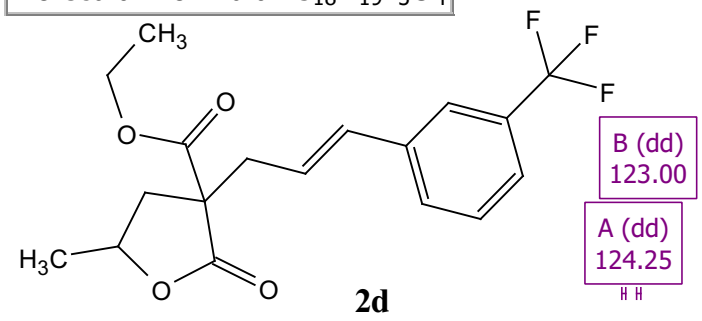
75.4 74.8 62.6 62.5 56.5 55.7 39.6 38.2 37.8 37.7 21.5 21.0 14.2 14.1

40000 35000 30000 25000 20000 15000 10000 5000 0

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

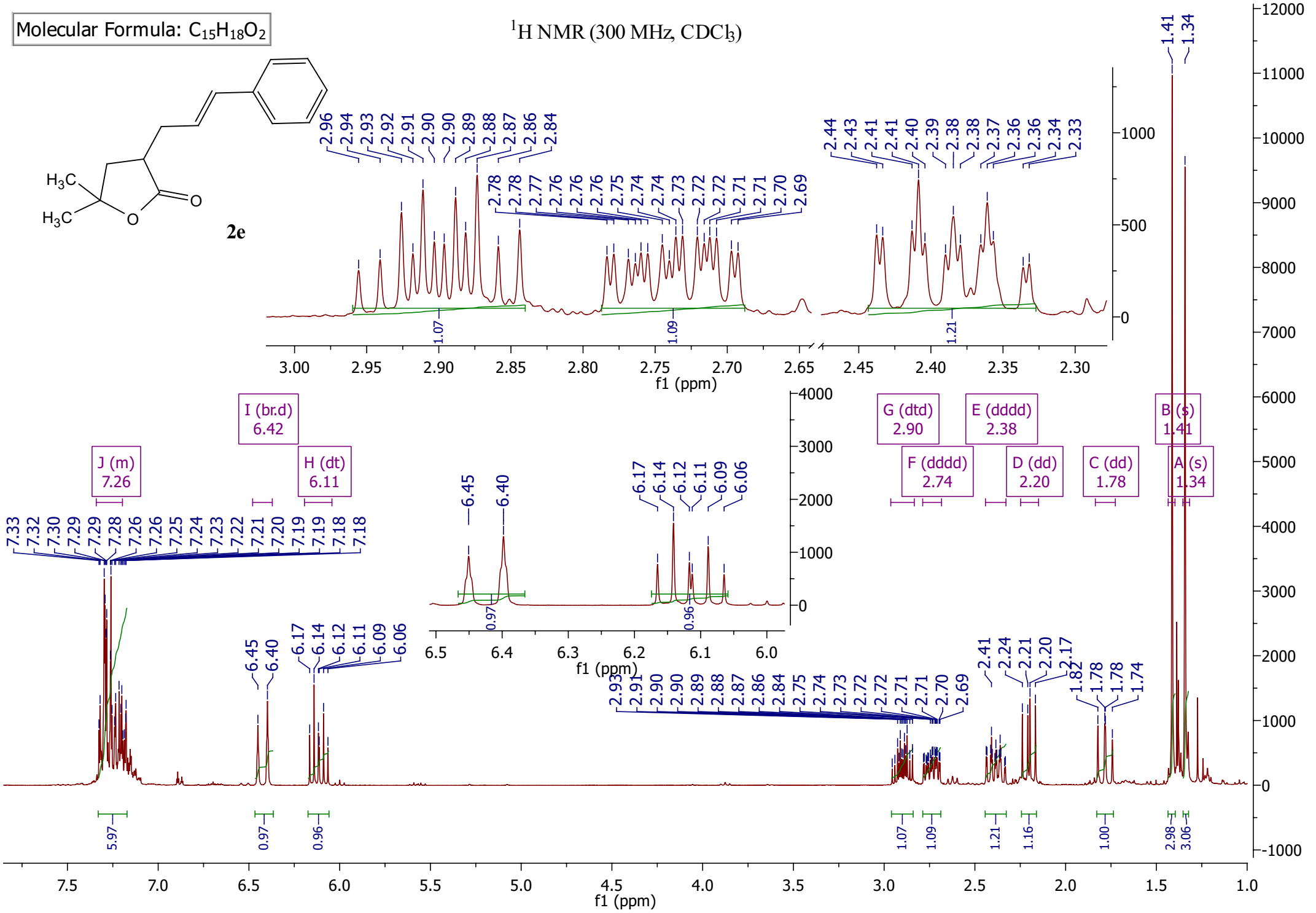
f1 (ppm)

Molecular Formula: $C_{18}H_{19}F_3O_4$

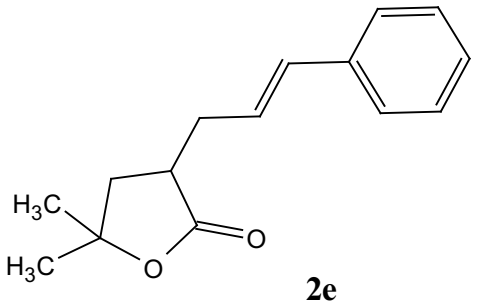


2d

^{13}C NMR (63 MHz, $CDCl_3$) DEPT


Molecular Formula: $C_{15}H_{18}O_2$
^{1}H NMR (300 MHz, $CDCl_3$)
2e
I (br.d) 6.42
H (dt) 6.11
J (m) 7.26
G (dtd) 2.90
E (dddd) 2.38
F (dddd) 2.74
D (dd) 2.20
C (dd) 1.78
B (s) 1.41
A (s) 1.34
f1 (ppm)

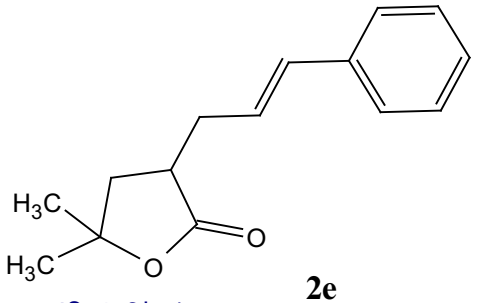
Molecular Formula: $C_{15}H_{18}O_2$



2e

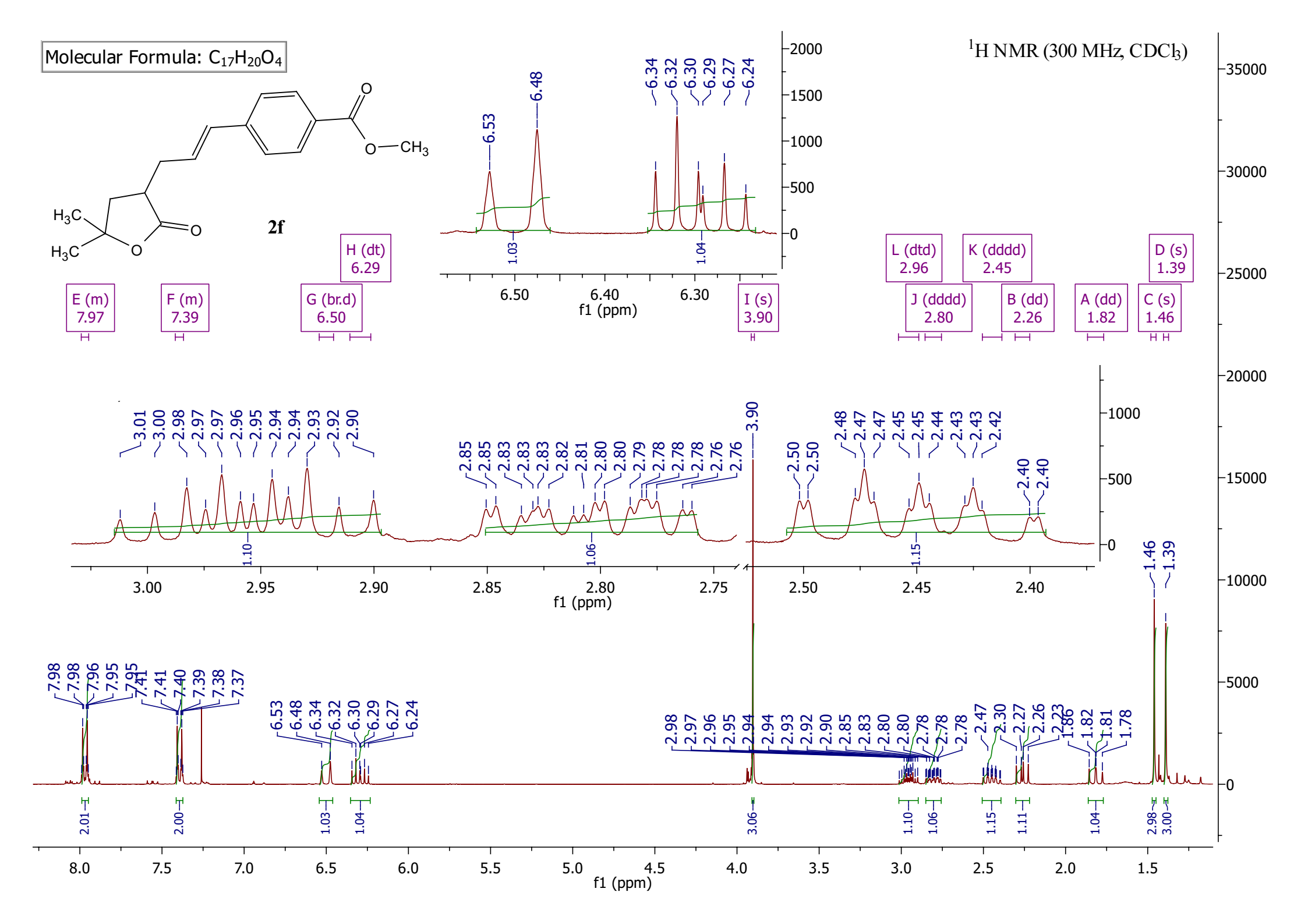
^{13}C NMR (63 MHz, $CDCl_3$)

Molecular Formula: $C_{15}H_{18}O_2$

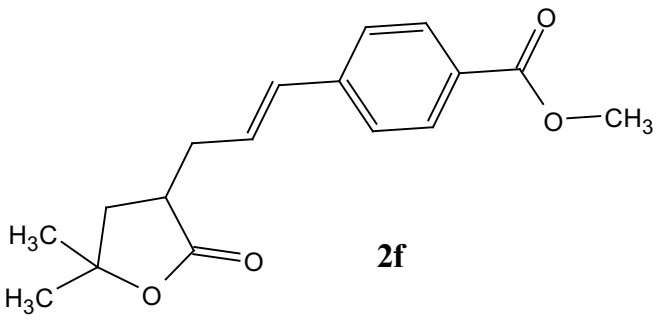


2e

^{13}C NMR (63 MHz, $CDCl_3$) DEPT


Molecular Formula: $C_{17}H_{20}O_4$
2f
^{1}H NMR (300 MHz, $CDCl_3$)
E (m) 7.97
F (m) 7.39
G (br.d) 6.50
H (dt) 6.29
I (s) 3.90
J (dddd) 2.80
L (dtd) 2.96
K (dddd) 2.45
B (dd) 2.26
A (dd) 1.82
C (s) 1.46
D (s) 1.39
f1 (ppm)

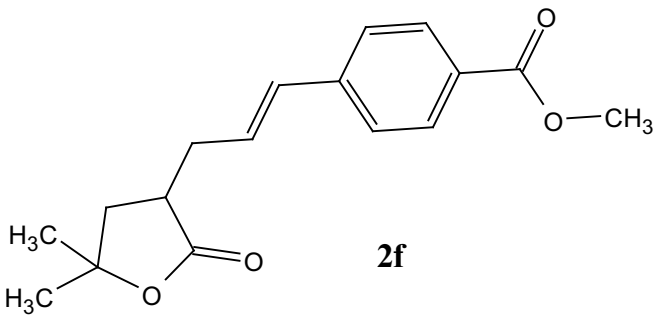
Molecular Formula: $C_{17}H_{20}O_4$



2f

^{13}C NMR (63 MHz, $CDCl_3$)

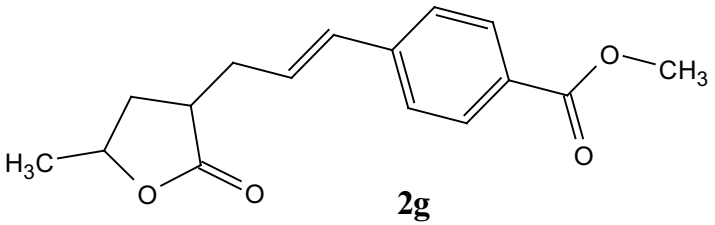
Molecular Formula: $C_{17}H_{20}O_4$



2f

^{13}C NMR (63 MHz, $CDCl_3$) DEPT

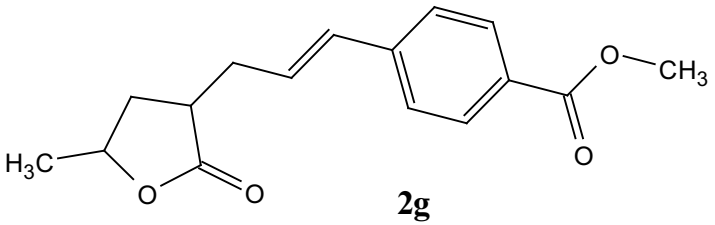
Molecular Formula: $C_{16}H_{18}O_4$



2g

^{1}H NMR (300 MHz, $CDCl_3$)

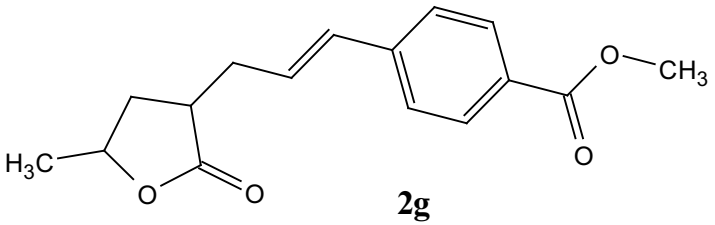
Molecular Formula: $C_{16}H_{18}O_4$



2g

^{13}C NMR (75 MHz, $CDCl_3$)

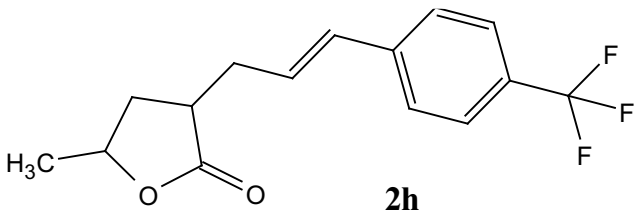
Molecular Formula: $C_{16}H_{18}O_4$



2g

^{13}C NMR (75 MHz, $CDCl_3$) DEPT

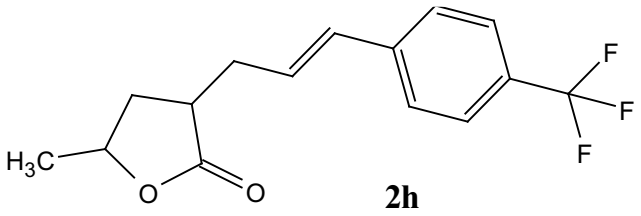
Molecular Formula: $C_{15}H_{15}F_3O_2$



2h

^{1}H NMR (300 MHz, $CDCl_3$)

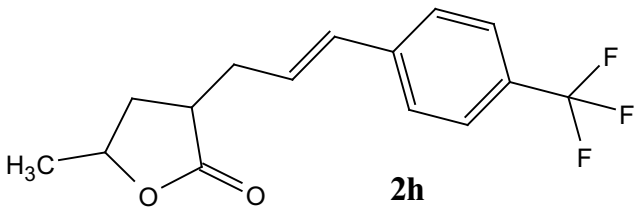
Molecular Formula: $C_{15}H_{15}F_3O_2$



2h

^{19}F NMR (282 MHz, $CDCl_3$)

Molecular Formula: $C_{15}H_{15}F_3O_2$



2h

^{13}C NMR (75 MHz, $CDCl_3$)

B (q)
127.90
J(271.07, 541.53)

A (q)
125.68
J(3.75, 7.60)

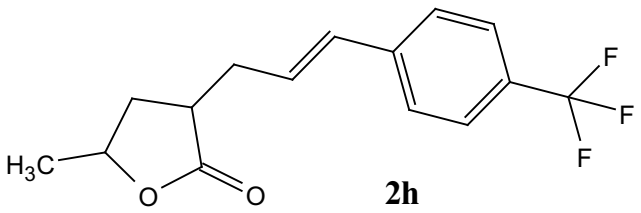
C (q)
130.41
J(19.16, 212.67)

133.3 131.9 131.7 129.7 129.1 128.9 126.5 126.4 126.1 125.8 125.7 125.7 125.6 122.5

178.5 178.1 140.6 75.4 75.2 41.5 39.3 36.5 34.4 34.1 33.7 21.4 21.1

f1 (ppm)

Molecular Formula: $C_{15}H_{15}F_3O_2$



2h

^{13}C NMR (75 MHz, $CDCl_3$) DEPT

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) is_av50

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: is_av50

```
Bond precision:  O- C = 0.0040 A         Wavelength=0.71073

Cell:            a=5.0081(14)     b=29.157(8)         c=9.843(3)
                 alpha=90         beta=98.930(8)      gamma=90
Temperature:     123 K

                Calculated                Reported
Volume          1419.9(7)                 1419.9(7)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C16 H18 O4                C16 H18 O4
Sum formula     C16 H18 O4                C16 H18 O4
Mr              274.30                    274.30
Dx,g cm-3       1.283                     1.283
Z               4                         4
Mu (mm-1)       0.092                     0.092
F000            584.0                     584.0
F000'           584.32
h,k,lmax        6,35,12                   6,35,12
Nref            2787                      2782
Tmin,Tmax       0.990,0.996               0.526,0.746
Tmin'           0.963

Correction method= # Reported T Limits: Tmin=0.526 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.996

R(reflections)= 0.0584( 1475)     wR2(reflections)= 0.1784( 2782)

S = 1.020                 Npar= 236
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.2 Note
PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ... -2.206 Report
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 3 Report

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 32 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 32 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 2 Report
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 80% Note
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O1A 109.8 Degree
PLAT793_ALERT_4_G Model has Chirality at C2A (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C4A (Centro SPGR) R Verify
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 345 Note
PLAT883_ALERT_1_G No Info for _atom_sites_solution_primary ..... Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 2 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 5 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
14 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/02/2019; check.def file version of 18/02/2019

Datablock is_av50 - ellipsoid plot