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β-Cyclodextrin in water: Highly facile biomimetic one pot deprotection of phenolic THP/MOM/Ac/Ts ethers and concomitant regioselective cyclization of chalcone epoxides and 2'-aminochalcones

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1. General methods

All the required chemicals were purchased from Merck and Aldrich Chemical Company. Pre-coated aluminium sheets (silica gel 60 F254, Merck) were used for thin-layer chromatography (TLC) and spots were visualized under UV light. Silica gel column chromatography was performed using silica gel 60–120 mesh size (RANKEM Limited). IR spectra were recorded with KBr on Thermo Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol ECX 400 MHz and Bruker Spectrospin DPX 500 MHz spectrometer using $CDCl_3$ as a solvent and trimethylsilane (TMS) as an internal standard. Spectra were processed using Bruker Topspin® 3.0.b.8. Splitting patterns are designated as follows; s = singlet, d = doublet, dd = doublets of doublet, m = multiplet, br = broad. Chemical shift (δ) values are given in ppm. Mass spectra were collected using a direct inlet system (70 eV) with a VL detector (ES, 4000 V) on Perkin Elmer GC-MS. High-resolution mass spectra (HRMS) were obtained on a Brüker micrOTOF™-Q II mass spectrometer (ESIMS).

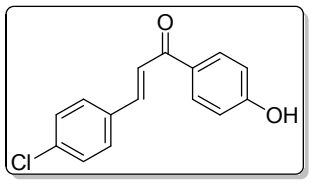
Microwave Irradiation Experiment. All microwave experiments were carried out in a dedicated Anton Paar Monowave 300 reactor®, operating at a frequency of 2.455 GHz with continuous irradiation power of 0 to 850 W. The reactions were performed in a G-30 Borosilicate glass vial sealed with Teflon septum and placed in a microwave cavity. Initially, microwave of required power was used and temperature was being ramped from room temperature to a desired temperature. Once this temperature was attained, the process vial was held at this temperature for required time. The reactions were continuously stirred. Temperature was measured by an IR sensor. After the experiments a cooling jet cooled the reaction vessel to ambient temperature.

2. General procedure for the microwave-assisted deprotection of THP, MOM, acetyl and tosyl ethers and concomitant cyclization of chalcone epoxides and 2'-aminochalcones: The substrate (1 mmol) dissolved in water (2 mL) was added to an aqueous solution of β-cyclodextrin (10 mol% in 10 mL of water) kept in a G-30 process vial and capped with Teflon septum. After a pre-stirring for one minute, the vial was subjected to microwave irradiation with the holding temperature of 60 °C for the prescribed time (Table 3 and 4). After completion of reaction, the mixture was cooled to room temperature and extracted with EtOAc (3 × 15 mL) and the catalyst was filtered off and washed with EtOAc (2×10 ml), filterate was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (8:2) as an eluent if required otherwise compounds were pure enough for the spectral elucidation.

3. Characterization data for representative compounds

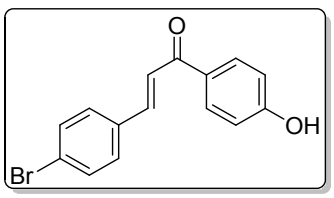
(a) Spectral data of THP, MOM, OAc and OTs deprotected products:

(E)-3-(4-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (5a)



^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.99 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.63 (t, *J* = 8Hz, 2H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 5.38 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 186.88, 162.05, 141.32, 131.41, 130.90, 130.83, 128.92, 121.85, 115.81, 115.21. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265, 1078, 862, 730. GC-MS (m/z): 302 [$M^{+\cdot}$, $C_{15}H_{11}BrO_2$], 304 [M+2].

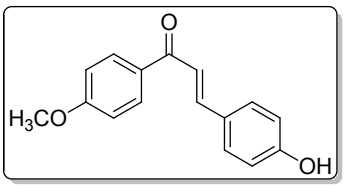
(E)-3-(4-bromophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (6a)



^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.99 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.63 (t, *J* = 8Hz, 2H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 5.48 (s, 1H,

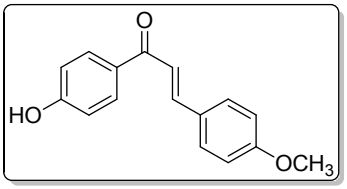
D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 186.88, 162.05, 141.32, 131.41, 130.90, 130.83, 128.92, 121.85, 115.81, 115.21. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265, 1078, 862, 730. GC-MS (m/z): 302 [$M^{+\cdot}$, $C_{15}H_{11}BrO_2$], 304 [M+2].

(E)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (7a)



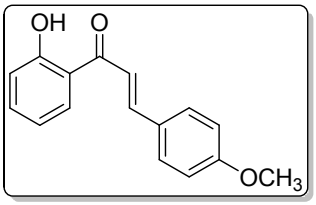
^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.03 (d, *J* = 8 Hz, 2H), 7.74 (d, *J* = 15.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 16 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 9 Hz, 2H), 5.48 (s, 1H, D_2O exchangeable), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 188.2, 163.9, 142.7, 131.4, 131.3, 130.1, 121.5, 116.8, 116.6, 114.2, 55.1. IR (KBr, ν_{max} = cm^{-1}): 3410, 2928, 2880, 1684, 1599, 1265. GC-MS (m/z): 254 [M^+, $C_{16}H_{14}O_3$].

(E)-1-(4-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (8a)



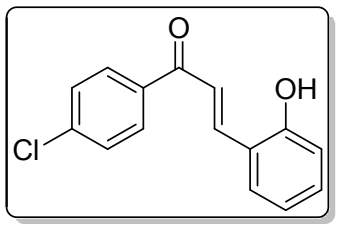
^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.03 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 16 Hz, 1H), 7.55 (d, *J* = 8Hz, 2H), 7.42 (d, *J* = 15.5 Hz, 1H), 6.98 (d, *J* = 8 Hz, 2H), 6.89 (d, *J* = 8 Hz, 2H), 5.82 (s, 1H, D_2O exchangeable), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 188.7, 163.6, 142.8, 131.2, 131.0, 130.4, 121.7, 116.3, 116.2, 114.0, 55.7. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265. GC-MS (m/z): 254 [M^+, $C_{16}H_{14}O_3$].

(E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (9a)



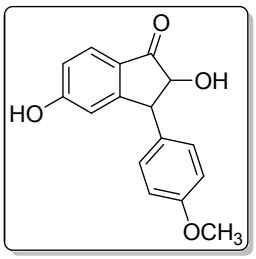
^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.91-7.86 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 15.6 Hz, 1H), 7.49-7.45 (m, 2H), 7.00 (dd, *J* = 1.2, 8.8 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 1.68 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 193.8, 163.7, 162.1, 145.5, 136.3, 130.7, 129.7, 127.4, 120.2, 118.9, 118.7, 117.7, 114.6, 55.6. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265. GC-MS (m/z): 254 [M^+, $C_{16}H_{14}O_3$].

(E)-1-(4-chlorophenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one (12a)



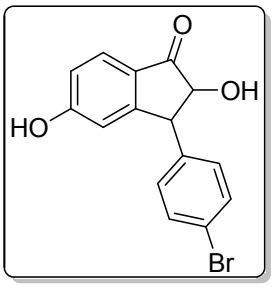
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.92-7.84 (m, 2H), 7.64-7.58 (m, 3H), 7.53-7.49 (m, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 4.84 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 193.6, 163.8, 144.1, 136.7, 133.2, 131.7, 130.0, 129.8, 129.5, 129.0, 120.7, 119.1, 118.9. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265. GC-MS (m/z): 258 [M^+, $C_{15}H_{11}ClO_2$], 260 [M+2]$^+$.

2,5-dihydroxy-3-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (16a)



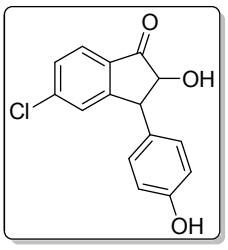
^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (dd, *J* = 1.5, 7 Hz, 2H), 7.55-7.52 (m, 2H), 7.07-7.01 (m, 3H), 5.31 (d, *J* = 2 Hz, 1H), 5.22 (d, *J* = 2 Hz, 1H), 4.19 (s, 1H, D_2O exchangeable), 3.91 (s, 3H), 1.61 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.9, 162.6, 162.2, 136.8, 134.8, 131.4, 129.3, 128.9, 125.6, 116.7, 115.8, 75.4, 63.6, 53.7. IR (KBr, ν_{max} = cm^{-1}): 3408, 2925, 2879, 1685, 1595, 1266, 1089, 858, 731. GC-MS (m/z): 270 [M^+, $C_{16}H_{14}O_4$].

3-(4-bromophenyl)-2,5-dihydroxy-2,3-dihydro-1H-inden-1-one (18a)



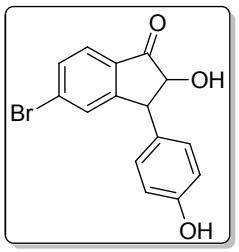
^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.93 (m, 2H), 7.70-7.67 (m, 1H), 7.58-7.53 (m, 2H), 7.08-7.04 (m, 2H), 6.10 (s, 1H, D_2O exchangeable), 5.37 (d, *J* = 2 Hz, 1H), 5.22 (d, *J* = 2.5 Hz, 1H), 4.15 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.6, 161.9, 137.4, 132.4, 131.9, 131.5, 130.0, 129.8, 126.0, 123.1, 116.3, 75.4, 63.6. IR (KBr, ν_{max} = cm^{-1}): 3433, 2935, 2877, 1687, 1585, 1266, 1088, 862, 733. GC-MS (m/z): 318 [M^+, $C_{15}H_{11}BrO_3$], 320 [M+2]$^+$.

5-chloro-2-hydroxy-3-(4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-one (20a)



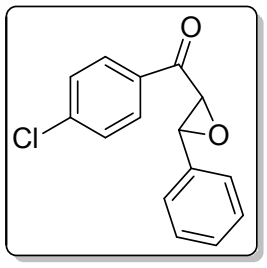
^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (m, 2H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.58-7.50 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.36 (d, *J* = 1.5 Hz, 1H), 5.19 (d, *J* = 2 Hz, 1H), 4.13 (s, 1H, D_2O exchangeable), 1.81 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.7, 162.4, 161.5, 136.7, 134.7, 131.4, 130.5, 129.4, 128.8, 125.3, 116.2, 75.4, 63.6. IR (KBr, ν_{max} = cm^{-1}): 3417, 2931, 2871, 1681, 1597, 1263, 1081, 860, 737. GC-MS (m/z): 274 [M^+, $C_{15}H_{11}ClO_3$], 276 $[M+2]^+$.

5-bromo-2-hydroxy-3-(4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-one (21a)



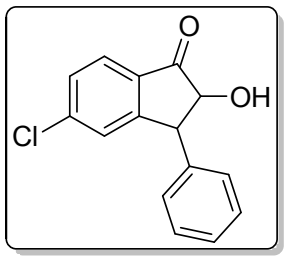
^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.91 (dd, *J* = 1, 8 Hz, 2H), 7.70-7.67 (m, 1H), 7.58-7.54 (m, 2H), 7.43 (t, *J* = 8.5 Hz, 2H), 6.10 (s, 1H, D_2O exchangeable), 5.38 (d, *J* = 2 Hz, 1H), 5.22 (d, *J* = 2.5 Hz, 1H), 4.15 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 197.7, 163.9, 161.9, 134.5, 134.2, 133.6, 130.1, 130.0, 129.3, 128.7, 115.7, 76.1, 63.1. IR (KBr, ν_{max} = cm-1): 3427, 2937, 2875, 1685, 1593, 1266, 1083, 864, 727. GC–MS (m/z): 318 [M^+, $C_{15}H_{11}BrO_3$], 320 $[M+2]^+$.

(4-chlorophenyl)(3-phenyloxiran-2-yl)methanone



^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.00 (d, *J* = 2.5 Hz, 2H), 7.63 (t, *J* = 7, 14 Hz, 1H), 7.54-7.48 (m, 4H), 7.24 (d, 2H), 4.25 (d, *J* = 2.5 Hz, 1H), 4.05 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.1, 137.2, 135.3, 131.9, 130.2, 128.7, 128.6, 127.8, 125.2, 70.1, 59.6. GC-MS (m/z): 258 [M^+, $C_{15}H_{11}ClO_2$], 260 $[M+2]^+$.

5-chloro-2-hydroxy-3-phenyl-2,3-dihydro-1H-inden-1-one

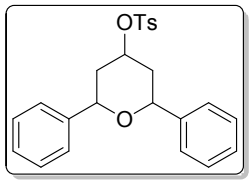


^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (d, *J* = 7 Hz, 2H), 7.68 (t, *J* = 7.5, 15 Hz, 1H), 7.58-7.54 (m, 3H), 7.08-7.04 (m, 2H), 5.37 (d, *J* =

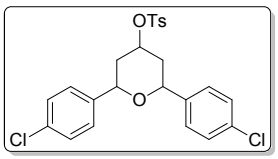
2 Hz, 1H), 5.22 (d, *J* = 2 Hz, 1H), 4.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 197.7, 163.9, 162.0, 134.5, 134.2, 133.6, 130.1, 130.0, 129.3, 128.7, 115.7, 76.1, 63.1. GC-MS (m/z): 258 [M^+, $C_{15}H_{11}ClO_2$], 260 $[M+2]^+$.

(b) Spectral data of OTs protected substrate:

2,6-diphenyltetrahydro-2H-pyran-4-yl 4-methylbenzenesulfonate (22)



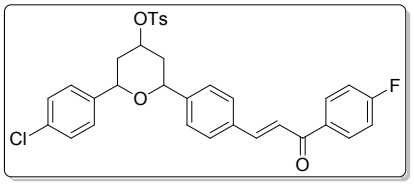
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.88 (d, *J* = 8Hz, 2H), 7.43-7.37 (m, 10H), 7.34-7.31 (m, 2H), 5.03 (tt, *J* = 4.5, 11.5Hz, 1H), 4.59 (d, *J* = 11.5Hz, 2H), 2.48 (s, 3H), 2.34 (dd, *J* = 4.5, 12.5Hz, 2H), 1.88 (q, *J* = 12.5Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 144.7, 140.9, 134.2, 129.8, 128.3, 127.7, 127.5, 125.7, 78.1, 77.4, 61.2, 39.9, 21.5. IR (KBr, cm^{-1}): 3056, 3039, 2923, 2852, 2373, 1717, 1629, 1454, 1379, 1178, 1065, 945, 903, 757, 699.



2,6-bis(4-chlorophenyl)tetrahydro-2H-pyran-4-yl 4-methylbenzenesulfonate (23)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.80 (d, *J* = 8Hz, 2H), 7.35-7.27 (m, 10H), 4.93 (tt, *J* = 4.5, 11Hz, 1H), 4.50 (dd, *J* = 1.5, 11.5 Hz, 2H), 2.44 (s, 3H), 2.26 (dd, *J* = 4.5, 11.5Hz, 2H,), 1.75 (q, *J* = 11.5Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 145.0, 139.3, 134.2, 133.7, 130.0, 128.7, 127.6, 127.2, 77.6, 76.8, 39.9, 21.7.

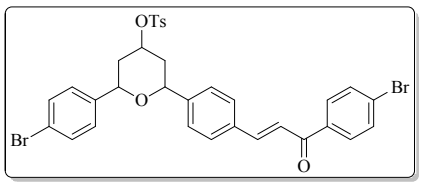
(E)-2-(4-chlorophenyl)-6-(4-(3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)phenyl)tetrahydro-2H-pyran-4-yl 4-methylbenzenesulfonate (24)



^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.02-8.05 (m, 4H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 5 Hz, 1H), 7.75 (d, *J* = 5 Hz, 1H), 7.60 (dd, *J* = 8, 2.5 Hz, 4H), 7.47 (d, *J* = 15.5 Hz, 2H), 7.39 (dd, *J* = 8.5, 3 Hz, 3H), 7.33 (d, *J* = 8 Hz, 2H), 4.96 (tt, *J* = 11, 4.5 Hz, 1H), 4.56-4.49 (m, 2H), 2.43 (s, 3H), 2.25-2.33 (m, 2H), 1.76-1.83 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 188.8, 164.6, 146.9, 144.8, 143.4, 139.3, 134.3, 134.1, 133.8, 133.6, 131.7,

131.1, 130.0, 128.6, 128.6, 127.6, 127.2, 126.4, 121.2, 77.6, 77.3, 76.9, 39.8, 39.8, 21.7. IR (KBr, cm^{-1}): 3000, 2945, 1678, 1614, 1350, 1200, 1121, 861. HRMS (ESIMS) for $C_{33}H_{28}ClFNaO_5S$ $(M+Na)^+$ Anal. calcd. 613.1228; found 613.1220.

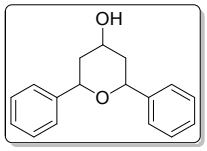
(E)-2-(4-bromophenyl)-6-(4-(3-(4-bromophenyl)-3-oxoprop-1-en-1yl)phenyl)tetrahydro-2H-pyran-4-yl 4-methylbenzenesulfonate (25)



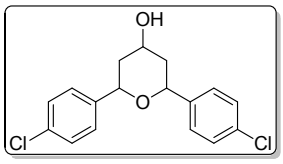
^{1}H NMR (500MHz, $CDCl_3$, ppm): δ 7.86 (dd, *J* = 8.5, 2Hz, 4H), 7.60 (dd, *J* = 10.5, 8.5 Hz, 6H), 7.39-7.46 (m, 6H), 7.33 (d, *J* = 8 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 4.95 (tt, *J* = 6.5, 3Hz, 1H), 4.52 (dd, *J* = 28, 10 Hz, 2H), 2.43 (s, 3H), 2.29 (dd, *J* = 24, 12.5Hz, 2H), 1.77 (q, *J* = 11 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 189.18, 146.84, 143.35, 139.67, 136.75, 133.91, 133.67, 131.78, 131.46, 129.90, 128.50, 127.46, 127.42, 126.33, 121.03, 118.61, 77.43, 76.73, 72.70, 39.65, 21.55. IR (KBr, cm^{-1}): 3000, 2945, 1678, 1614, 1350, 1200, 1121, 861. HRMS (ESIMS) for $C_{33}H_{28}Br_2NaO_5S$ $(M+Na)^+$ Anal. calcd. 716.9922; found 716.9900.

(c) Spectral data of OTs deprotected product:

2,6-diphenyltetrahydro-2H-pyran-4-ol (22a)



^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.19-7.41 (m, 8H), 4.51-4.43 (m, 2H), 4.07 (tt, *J* = 4.5, 11.5 Hz, 1H), 2.28 (s, br, D_2O exchangeable, 1H, OH), 2.21 (dd, *J* = 4, 11.5Hz, 2H), 1.53 (q, *J* = 11.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 131.4, 128.3, 127.5, 125.8, 77.8, 68.6, 42.9. IR (KBr, cm^{-1}): 3433, 2965, 2921, 2852, 1634, 1452, 1382, 1265, 1156, 1065, 900, 760, 700. GC-MS (m/z): 410 [M^+, $C_{17}H_{18}O_2$].

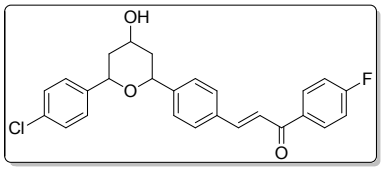


2,6-bis(4-chlorophenyl)tetrahydro-2H-pyran-4-ol (23a)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.29-7.24 (m, 8H), 4.47 (d, *J* = 11.5 Hz, 2H), 4.06 (tt, *J* = 4.5, 11.5 Hz, 1H), 2.19 (dd, *J* = 4, 11.5 Hz,

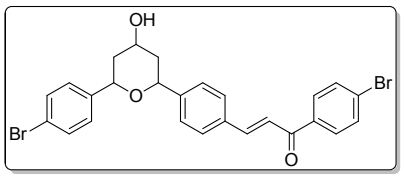
2H), 1.48 (q, J = 11.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 139.2, 132.3, 127.5, 126.2, 77.8, 67.4, 41.9. IR (KBr, cm^{-1}): 3447, 2960, 2886, 1652, 1543, 1088, 804. GC-MS (m/z): 323 [M^+, $C_{17}H_{16}Cl_2O_2$].

(E)-3-(4-(6-(4-chlorophenyl)-4-hydroxytetrahydro-2H-pyran-2-yl)phenyl)-1-(4-fluorophenyl)prop-2-en-1-one (24a)



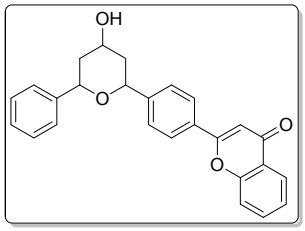
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.18 (d, J = 8 Hz, 1H), 7.95 (d, J = 8 Hz, 2H), 7.59 (d, J = 9 Hz, 3H), 7.48 (d, J = 8 Hz, 2H), 7.41 (d, J = 9 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 9 Hz, 2H), 4.66 (t, J = 3 Hz, 2H), 4.14 (tt, J = 11, 3 Hz, 1H), 2.22-2.85 (m, 2H), 2.04 (s, br, D_2O exchangeable, 1H), 1.73-1.84 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 188.8, 166.7, 164.6, 144.6, 143.7, 140.8, 134.5, 134.3, 131.2, 130.0, 128.7, 127.7, 126.5, 125.9, 121.6, 115.9, 78.0, 77.7, 69.4, 40.0. IR (KBr, cm^{-1}): 3434, 3010, 2922, 2843, 1734, 1626, 1456, 1256, 1069, 808.8. HRMS (ESIMS): for $C_{26}H_{22}ClFNaO_3$ $(M+Na)^+$ Anal. calcd. 459.1139; found 459.1150.

(E)-1-(4-bromophenyl)-3-(4-(6-(4-bromophenyl)-4-hydroxytetrahydro-2H-pyran-2-yl)phenyl)prop-2-en-1-one (25a)



^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.88 (d, J = 8 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.78 (s, 1H), 7.61-7.66 (m, 4H), 7.47 (s, 1H), 7.35 (d, J = 8 Hz, 2H), 7.31-7.32 (m, 2H), 4.45 (d, J = 32, 11.5 Hz, 2H), 4.07 (tt, J = 10.5, 3 Hz, 1H), 2.30-2.35 (m, 2H), 2.20 (s, br, D_2O exchangeable, 1H), 1.77-1.86 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 189.8, 143.7, 140.7, 135.4, 134.4, 134.1, 129.8, 129.2, 128.5, 128.4, 127.8, 127.5, 126.2, 125.7, 122.0, 77.8, 77.4, 67.2, 39.8. IR (KBr, cm^{-1}): 3454, 2961, 2878, 1651, 1541, 1091, 801. HRMS (ESIMS): for $C_{26}H_{22}Br_2NaO_3$ $(M+Na)^+$ Anal. calcd. 562.9833; found 562.9853.

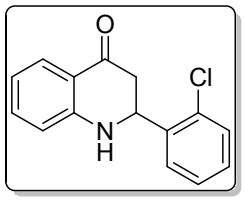
2-(4-(4-hydroxy-6-phenyltetrahydro-2H-pyran-2-yl)phenyl)-4H-chromen-4-one (26a)



^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.74 (d, *J* = 8 Hz, 2H), 7.37 (dd, *J* = 6, 3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.17-7.21 (m, 3H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.92 (s, 1H), 6.79 (dd, *J* = 6.5, 3 Hz, 2H), 4.40 (t, *J* = 11.5 Hz, 2H), 3.90 (tt, *J* = 11, 3 Hz, 1H), 2.15-2.22 (m, 2H), 1.68-1.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 190.0, 163.0, 156.0, 139.8, 135.5, 134.1, 131.6, 129.9, 129.3, 128.6, 128.6, 127.6, 127.5, 126.3, 122.2, 121.8, 77.1, 76.9, 65.0, 39.8, 39.7. IR (KBr, cm^{-1}): 3446, 2971, 2880, 1652, 1513, 1208, 799. HRMS (ESIMS): for $C_{26}H_{21}NaO_4$ $(M+Na)^+$ Anal. calcd. 421.1416; found 421.1441.

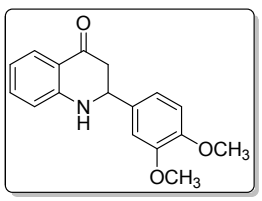
(d) Spectral data of synthesized flavanones:

2-(2-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one (29a)



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 11.34 (s, 1H, D_2O exchangeable), 8.58 (d, *J* = 6 Hz, 1H), 7.87 (dd, *J* = 10, 2.5 Hz, 1H), 7.75-7.79 (m, 1H), 7.59 (d, *J* = 10 Hz, 1H), 7.44-7.48 (m, 1H), 7.26-7.29 (m, 1H), 6.98-7.03 (m, 2H), 5.60 (dd, *J* = 13.5, 6.5 Hz, 1H), 3.06-3.16 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 191.2, 160.8, 157.1, 148.4, 138.3, 136.2, 127.1, 123.8, 121.9, 121.4, 121.2, 118.1, 79.1, 42.8. IR (KBr, cm^{-1}): 3164, 2926, 1693, 1606, 1462, 1305, 763. GC-MS (m/z): 257 [M^+, $C_{15}H_{12}ClNO$], 259 $[M+2]^+$.

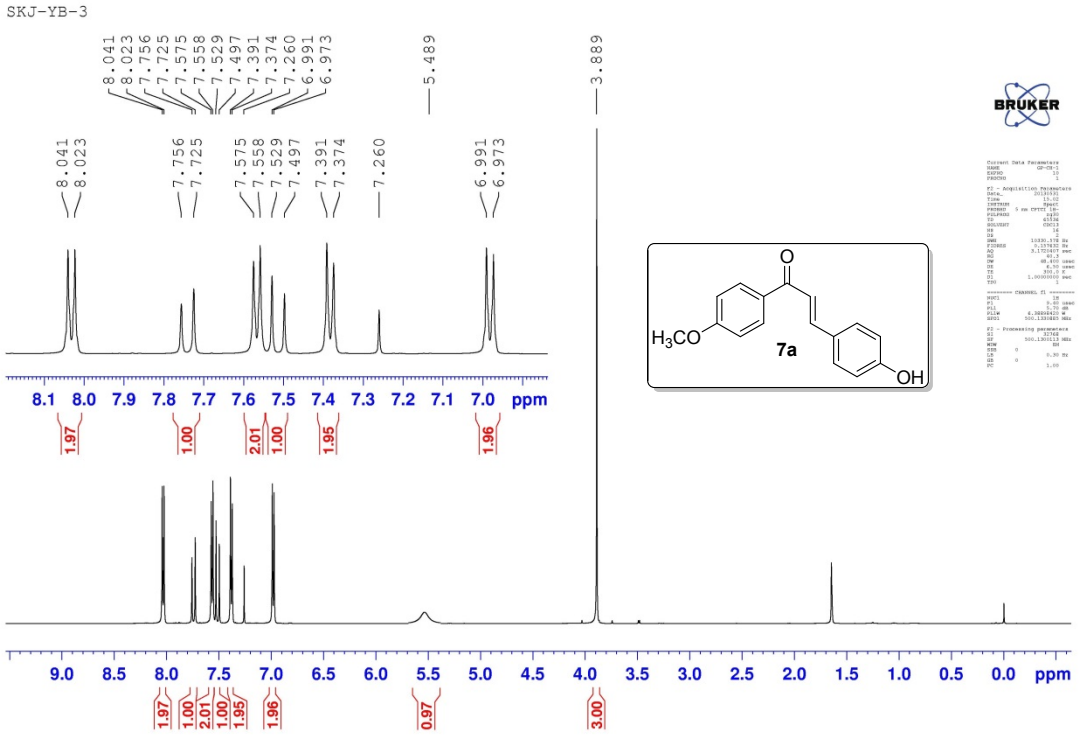
2-(3,4-dimethoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (33a)

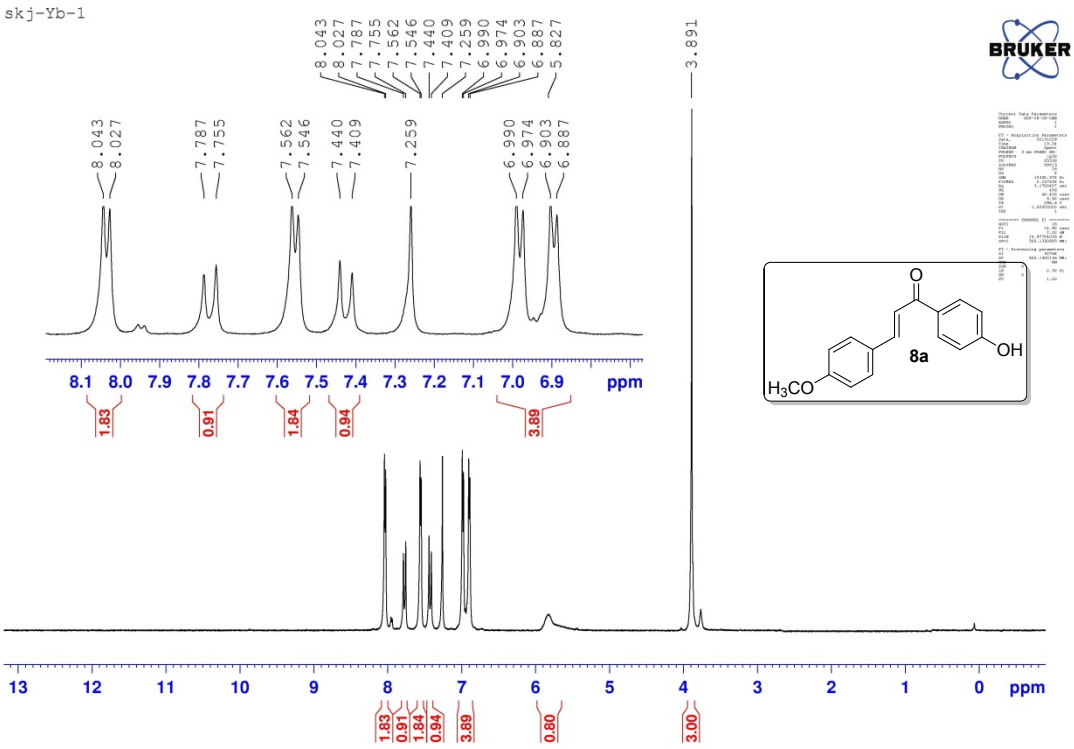


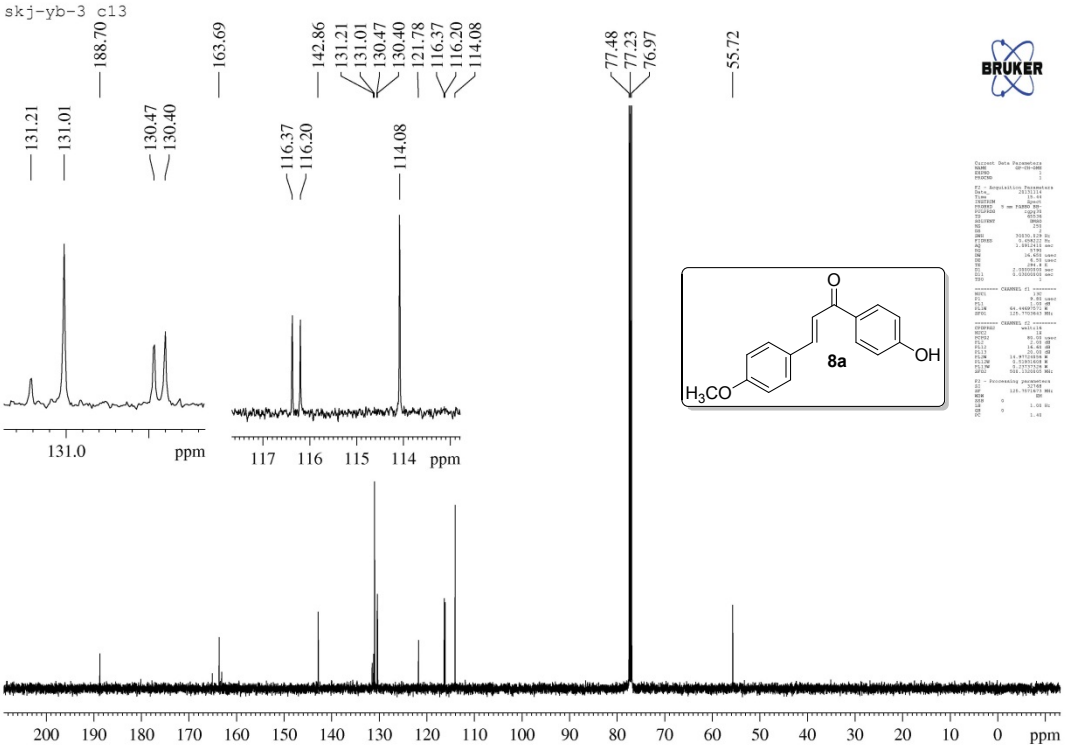
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 12.17 (s, 1H, D_2O exchangeable), 7.93 (d, *J* = 10 Hz, 1H), 7.51 (t, *J* = 10.5 Hz, 1H), 7.01-7.08 (m, 4H), 6.91 (d, *J* = 10 Hz, 1H), 5.43 (dd, *J* = 16.5, 2.5 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.13 (dd, *J* = 21, 17 Hz, 1H), 2.88 (dd, *J* = 21, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 192.2, 161.6, 149.4, 149.3, 136.2, 131.2, 127.1, 120.9, 121.6, 118.8,

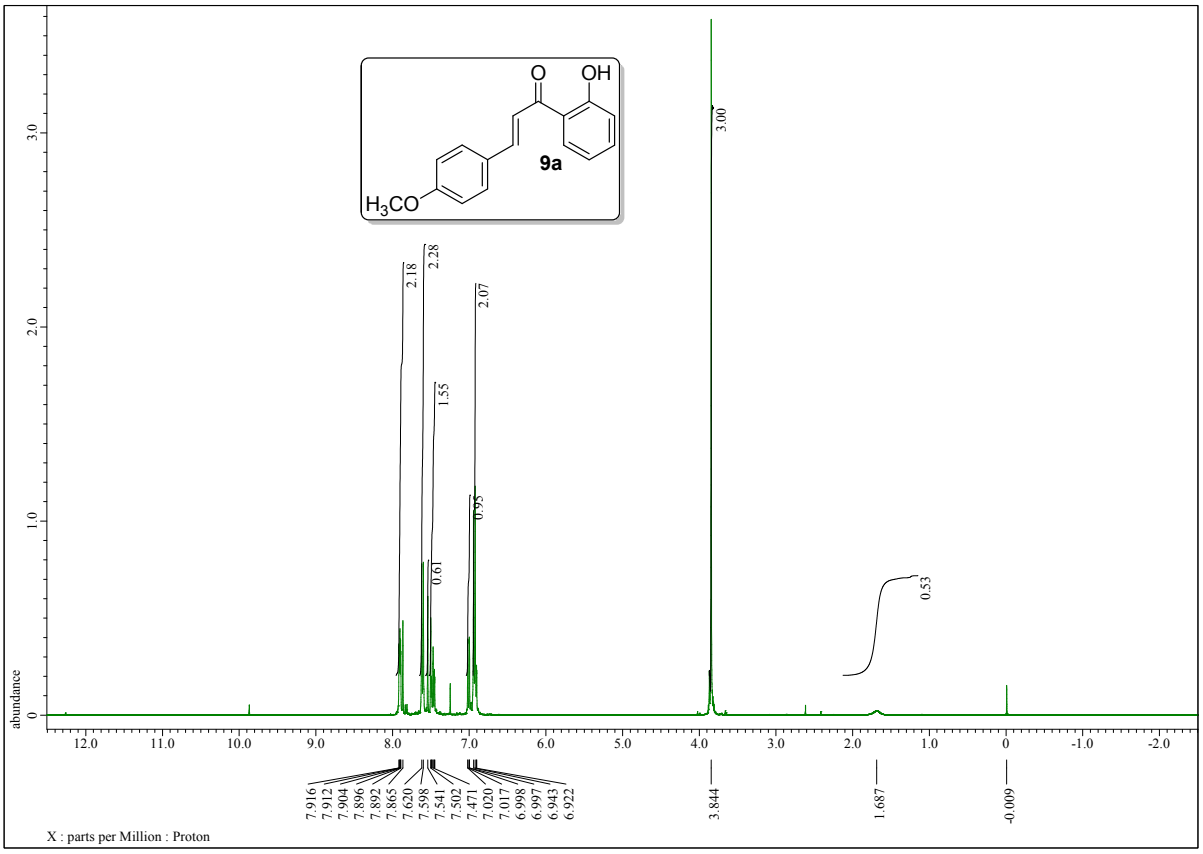
118.2, 111.1, 109.4, 79.6, 56.0, 55.9, 44.6. IR (KBr, cm^{-1}): 3110, 2837, 1687, 1598, 1026. GC-MS (m/z): 283 [M+, $C_{17}H_{17}NO_3$].

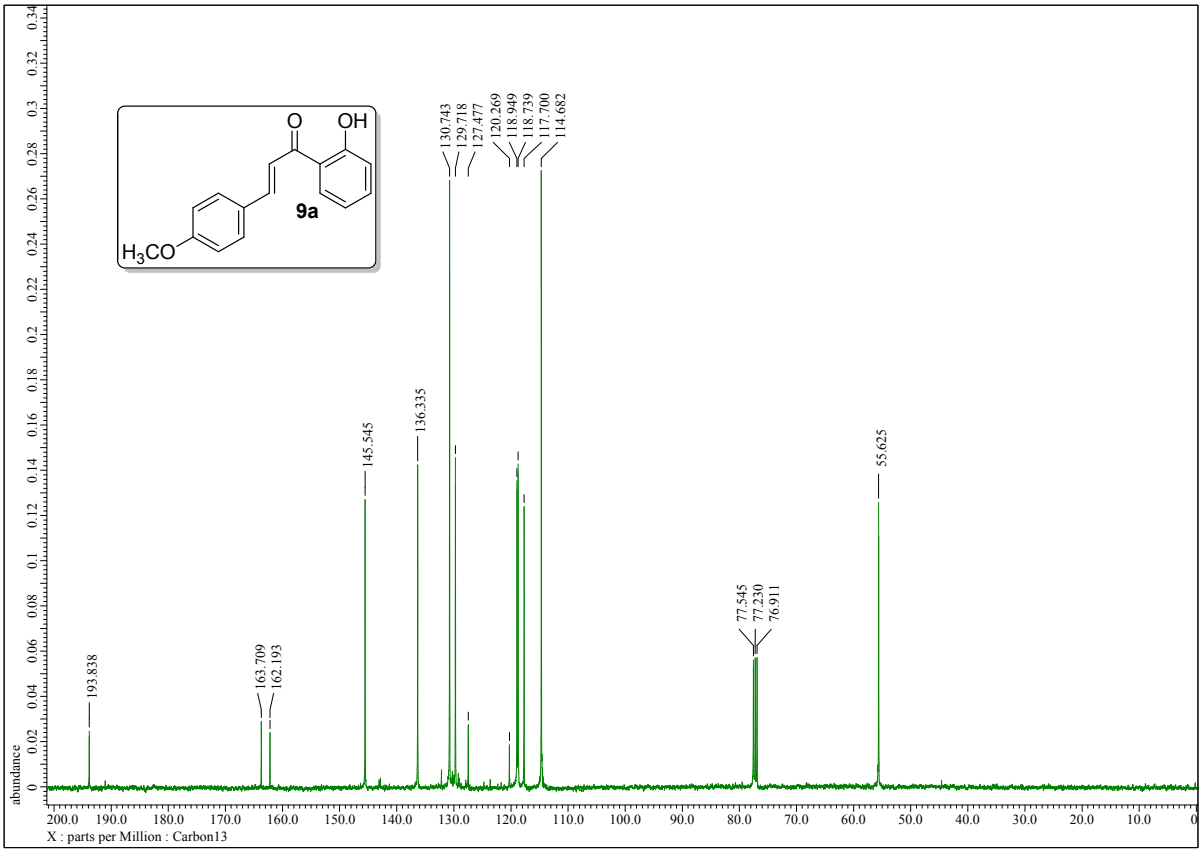
4. ^{1}H and ^{13}C NMR Spectra

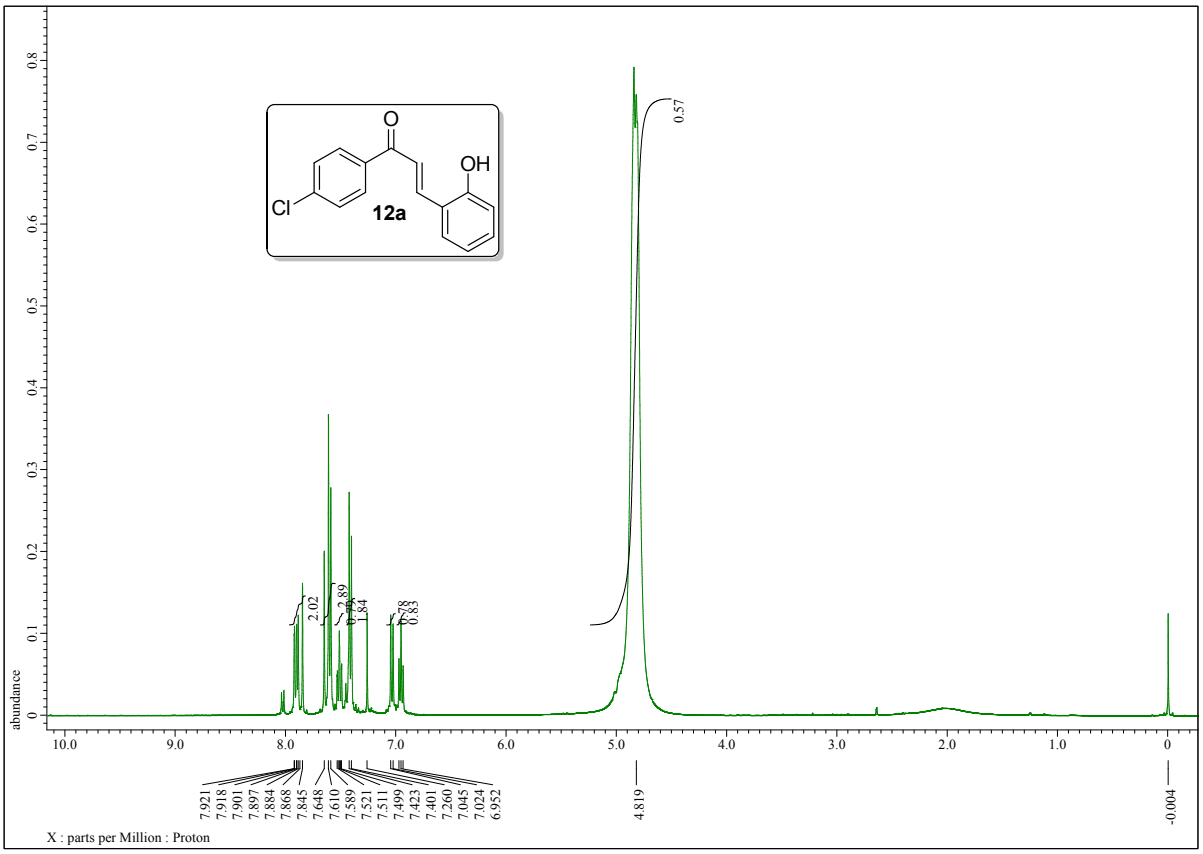


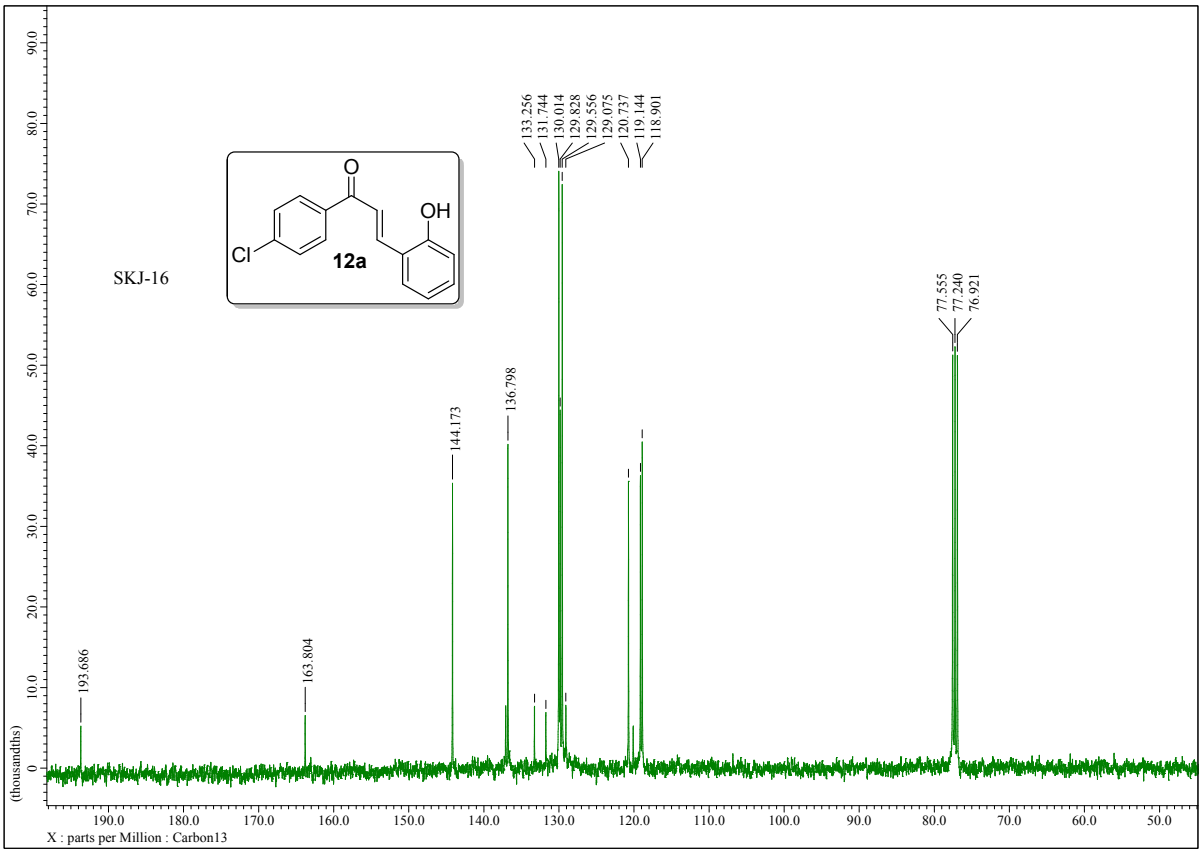

skj-Yb-1
8.043
8.027
7.787
7.755
7.562
7.546
7.440
7.409
7.259
6.990
6.974
6.903
6.887
5.827
3.891
BRUKER
8a
OH
H3CO
ppm


skj-yb-3 c13
188.70
163.69
142.86
131.21
131.01
130.47
130.40
121.78
116.37
116.20
114.08
77.48
77.23
76.97
55.72
BRUKER
8a
OH
H3CO
ppm

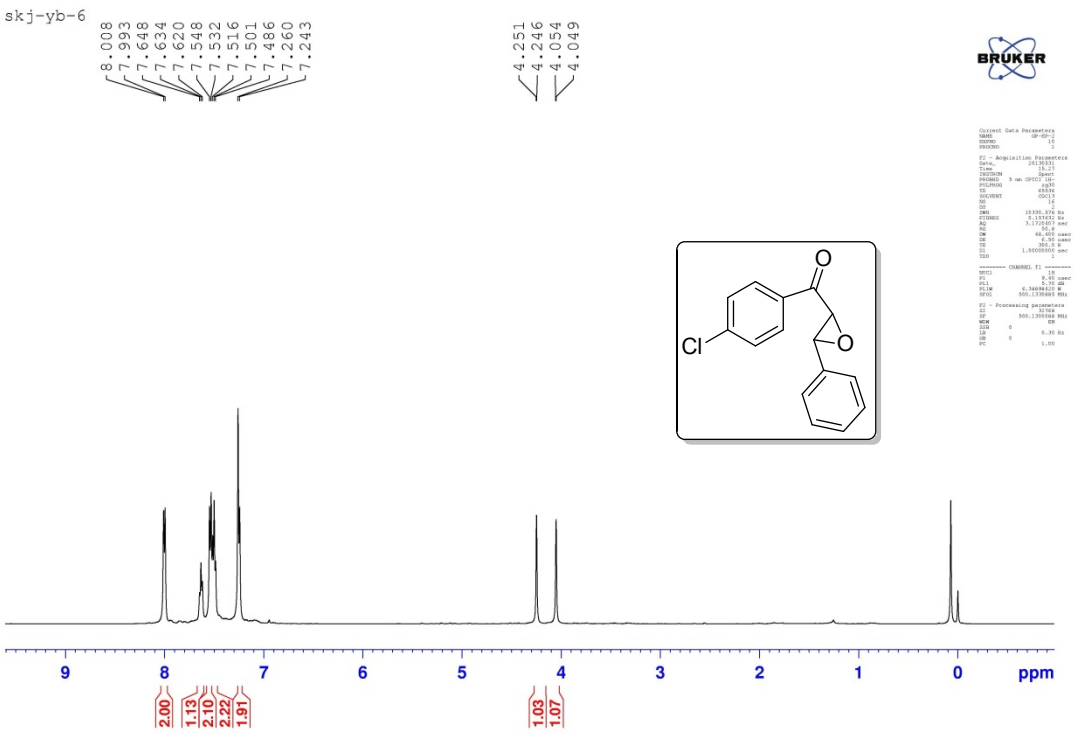

O
OH
9a
H3CO
3.00
2.18
2.28
2.07
1.55
0.95
0.61
0.53
abundance
7.916
7.912
7.904
7.896
7.892
7.865
7.620
7.598
7.541
7.502
7.471
7.020
7.017
6.998
6.997
6.943
6.922
3.844
1.687
-0.009
X : parts per Million : Proton


O
OH
9a
H3CO
130.743
129.718
127.477
120.269
118.949
118.739
117.700
114.682
145.545
136.335
55.625
77.545
77.230
76.911
193.838
163.709
162.193
abundance
X : parts per Million : Carbon13

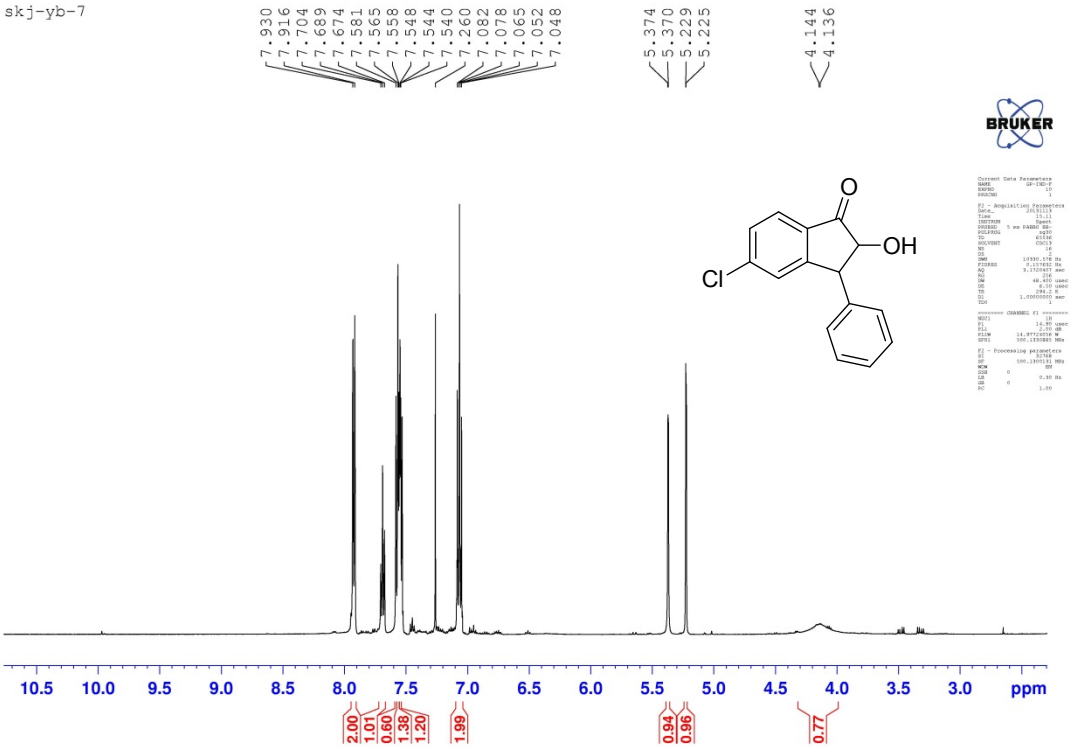

O
OH
Cl
12a
0.57
2.02
2.89
1.84
0.83
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.921
7.918
7.901
7.897
7.884
7.868
7.845
7.648
7.610
7.589
7.521
7.511
7.499
7.423
7.401
7.260
7.045
7.024
6.952
4.819
-0.004
X : parts per Million : Proton

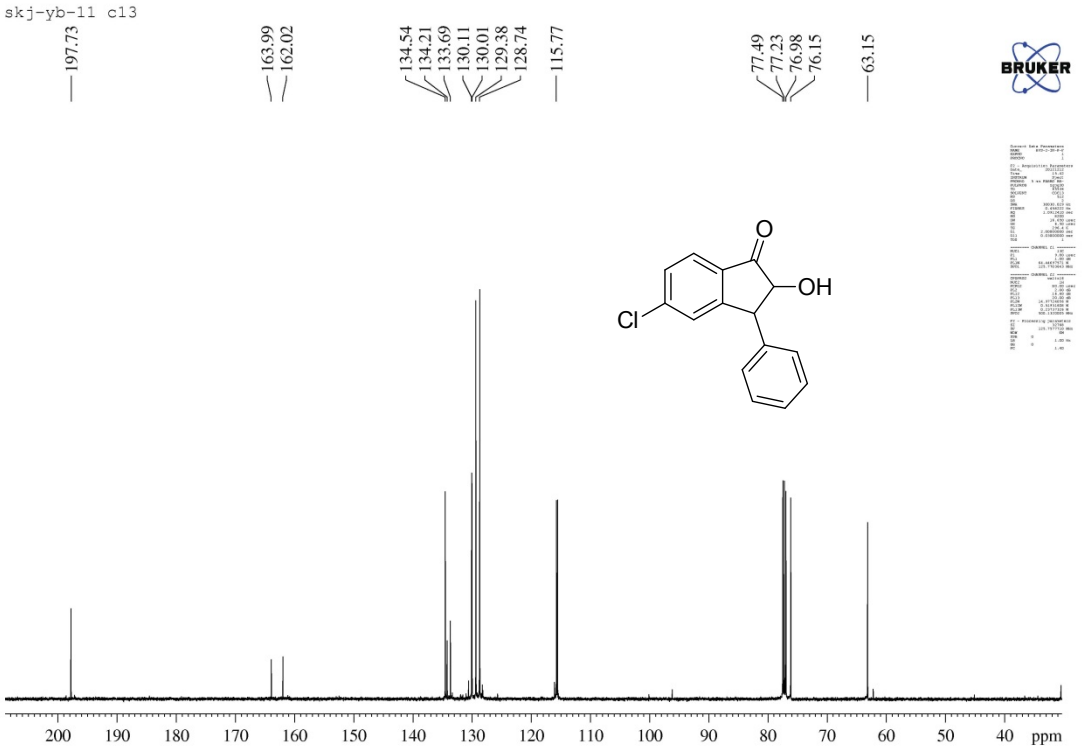

SKJ-16
O
OH
Cl
12a
133.256
131.744
130.014
129.828
129.556
129.075
120.737
119.144
118.901
77.555
77.240
76.921
144.173
136.798
193.686
163.804
(thousandths)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
X : parts per Million : Carbon13

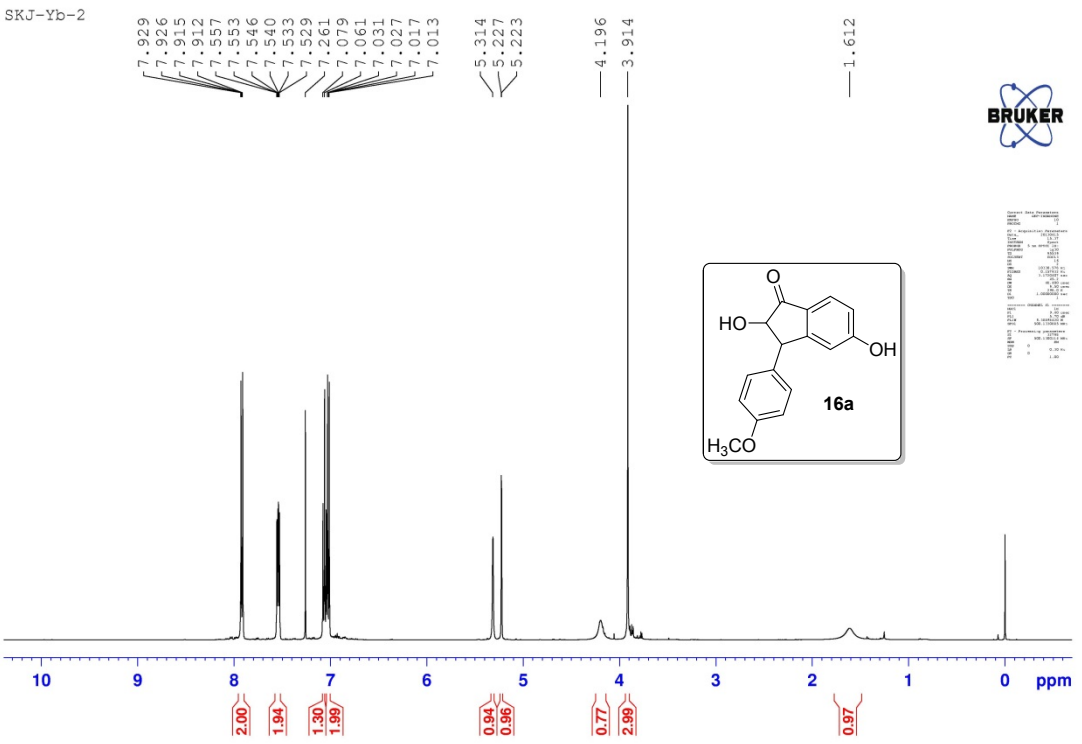
skj-yb-6



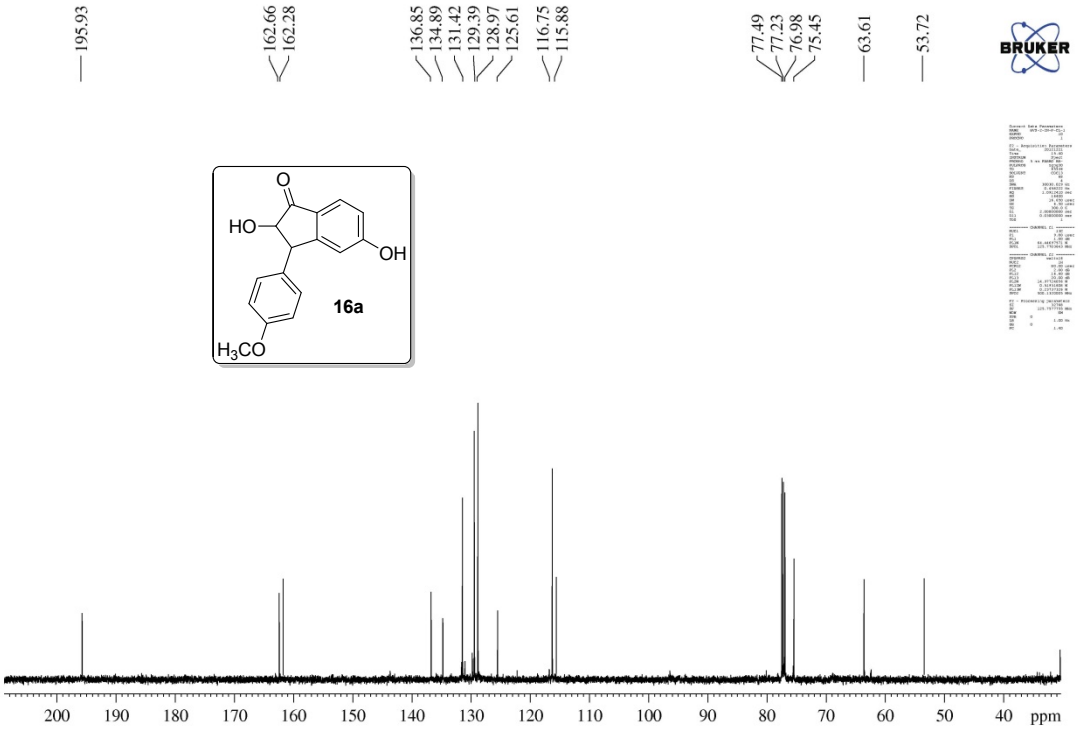
skj-yb-7



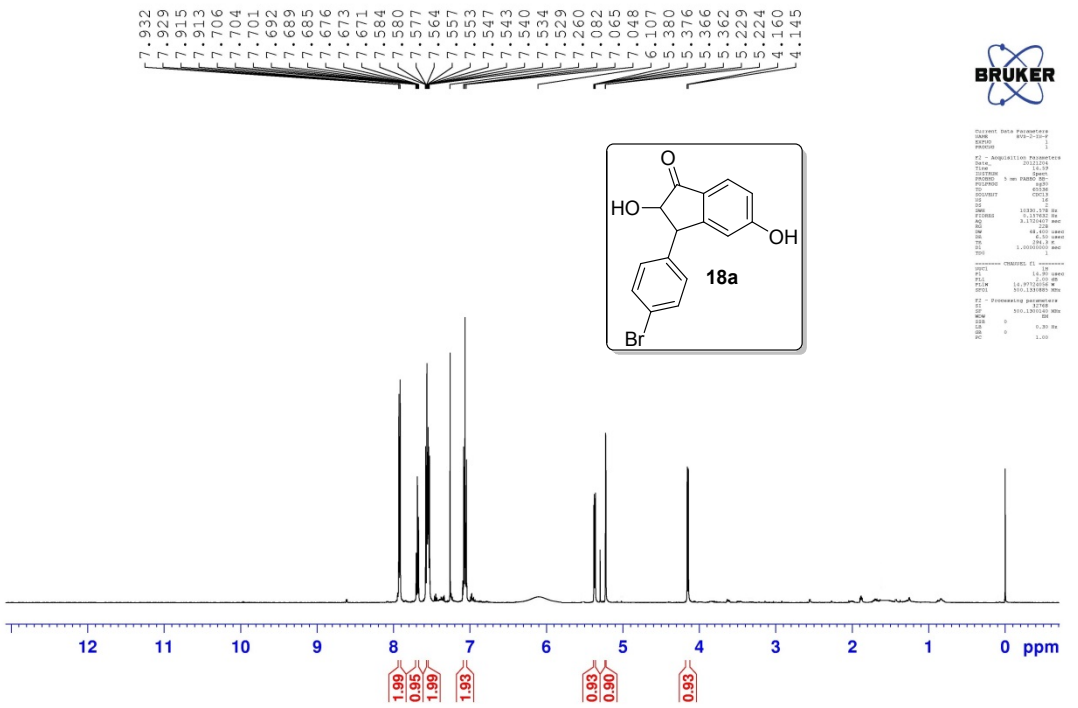

skj-yb-11 c13
197.73
163.99
162.02
134.54
134.21
133.69
130.11
130.01
129.38
128.74
115.77
77.49
77.23
76.98
76.15
63.15
BRUKER
O
OH
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm


SKJ-Yb-2
7.929
7.926
7.915
7.912
7.557
7.553
7.546
7.540
7.533
7.529
7.261
7.079
7.061
7.031
7.027
7.017
7.013
5.314
5.227
5.223
4.196
3.914
1.612
BRUKER
O
HO
OH
16a
H3CO
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.94
1.30
1.99
0.94
0.96
0.77
2.99
0.97

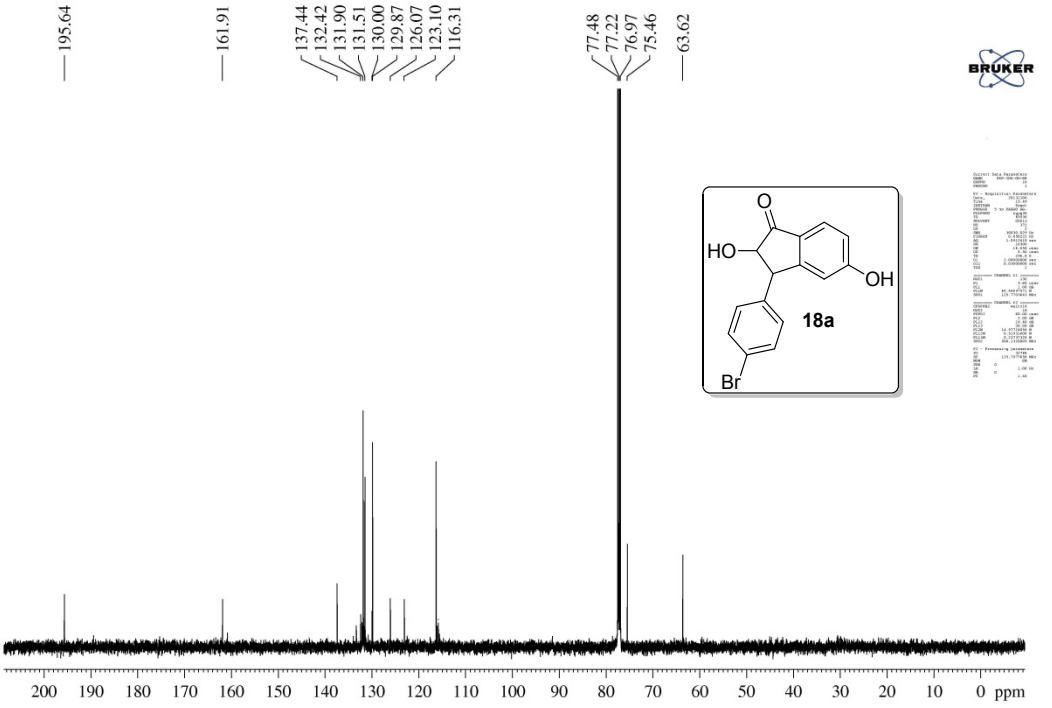
skj-yb-2 c13



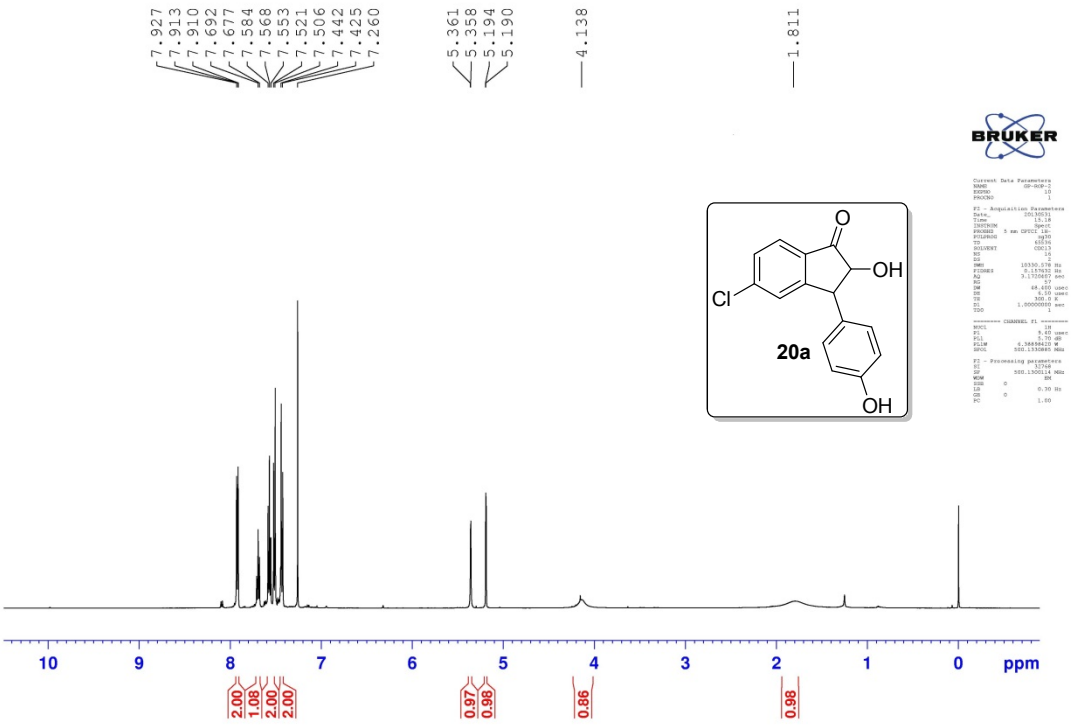
skj-yb-br



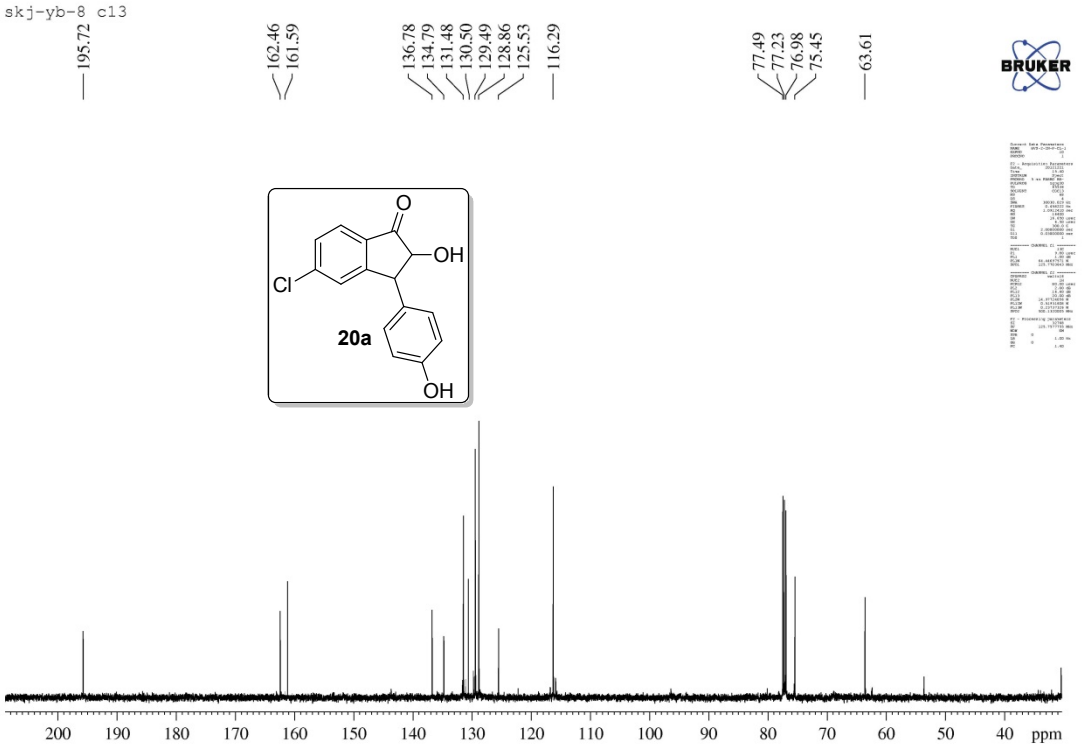
skj-yb-10 c13



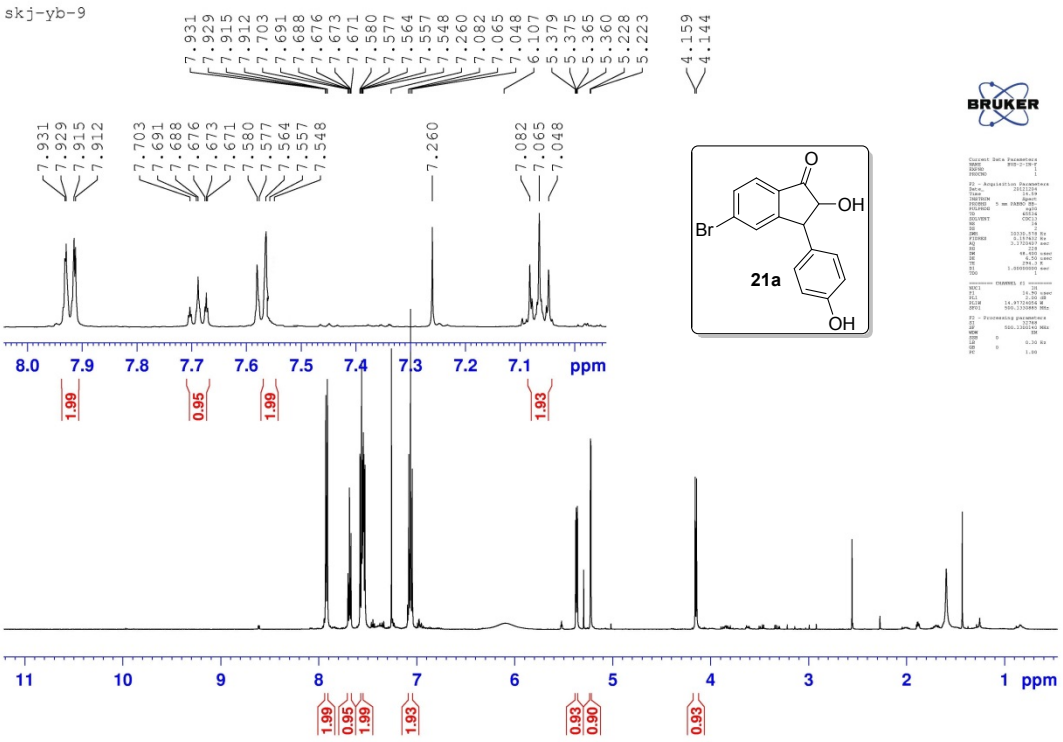
skj-yb-8

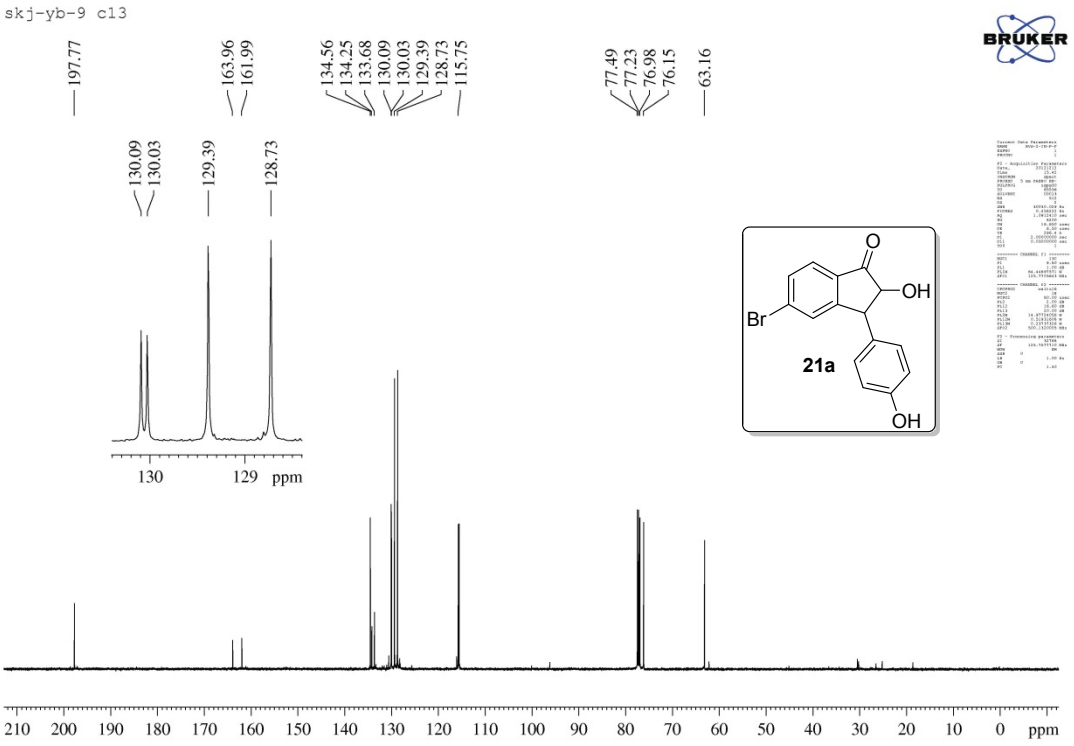


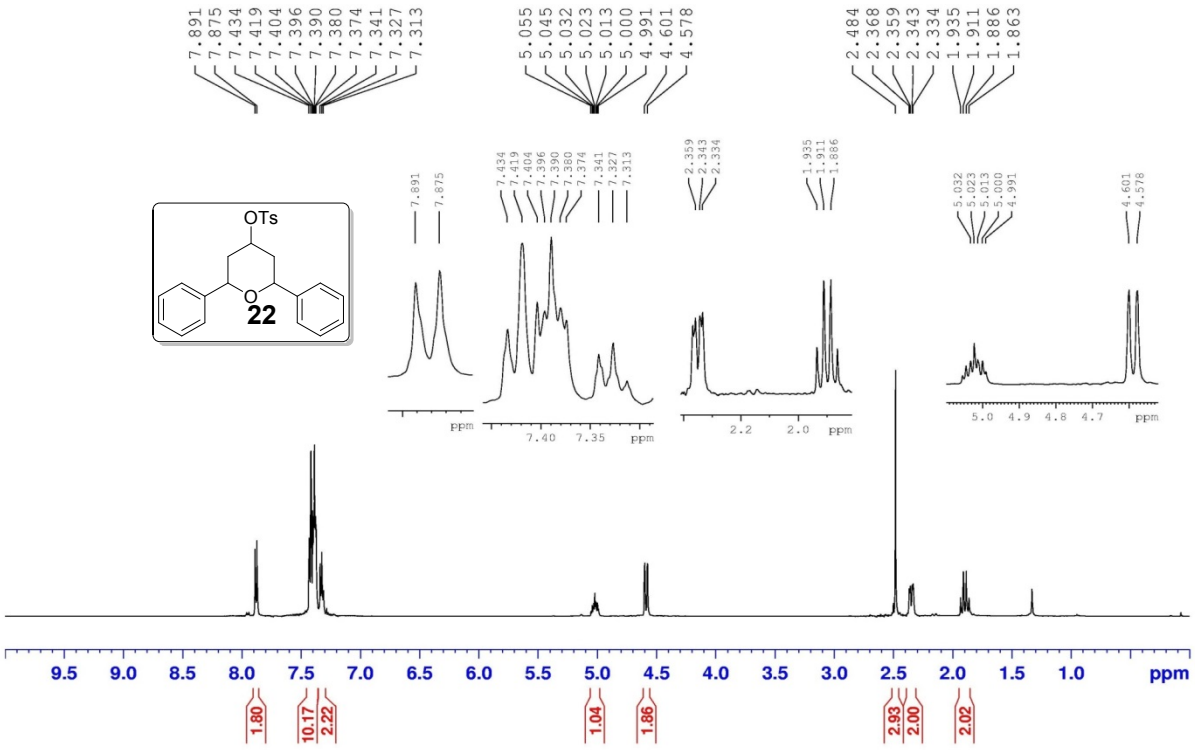
skj-yb-8 c13

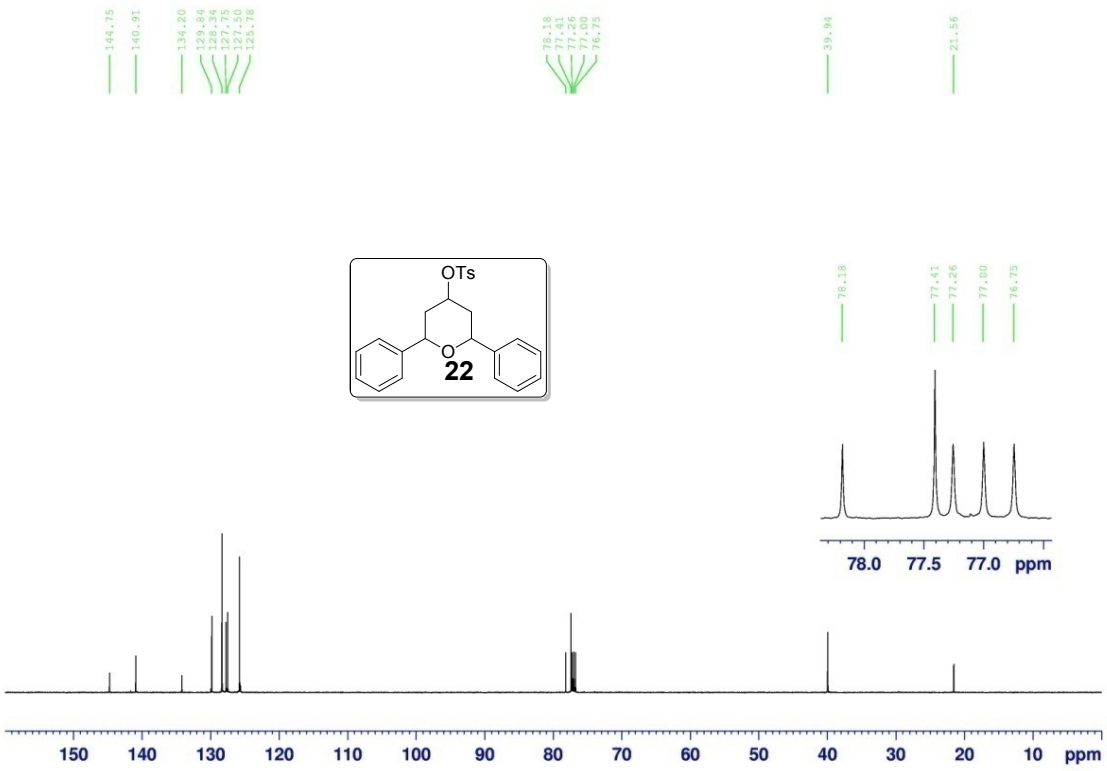


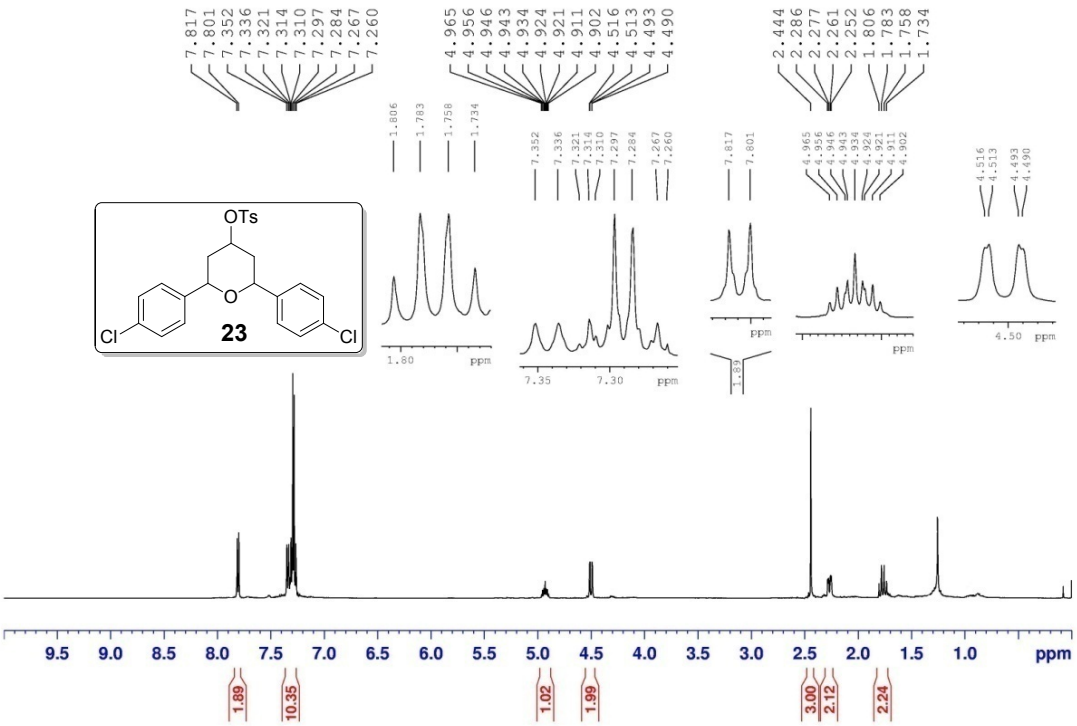
skj-yb-9




skj-yb-9 c13
197.77
163.96
161.99
134.56
134.25
133.68
130.09
130.03
129.39
128.73
115.75
77.49
77.23
76.98
76.15
63.16
130.09
130.03
129.39
128.73
130
129
ppm
O
OH
Br
21a
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.891
7.875
7.434
7.419
7.404
7.396
7.390
7.380
7.374
7.341
7.327
7.313
5.055
5.045
5.032
5.023
5.013
5.000
4.991
4.601
4.578
2.484
2.368
2.359
2.343
2.334
1.935
1.911
1.886
1.863
OTs
O
22
ppm
7.40
7.35
ppm
2.2
2.0
ppm
5.0
4.9
4.8
4.7
ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.80
10.17
2.22
1.04
1.86
2.93
2.00
2.02


OTs
O
22
144.75
140.91
134.20
129.84
128.34
127.75
127.50
125.78
78.18
77.41
77.26
77.00
76.75
39.94
21.56
78.0
77.5
77.0
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OTs
O
Cl
Cl
23
7.817
7.801
7.352
7.336
7.321
7.314
7.310
7.297
7.284
7.267
7.260
4.965
4.956
4.946
4.943
4.934
4.924
4.921
4.911
4.902
4.516
4.513
4.493
4.490
2.444
2.286
2.277
2.261
2.252
1.806
1.783
1.758
1.734
1.80
ppm
7.35
7.30
ppm
4.50
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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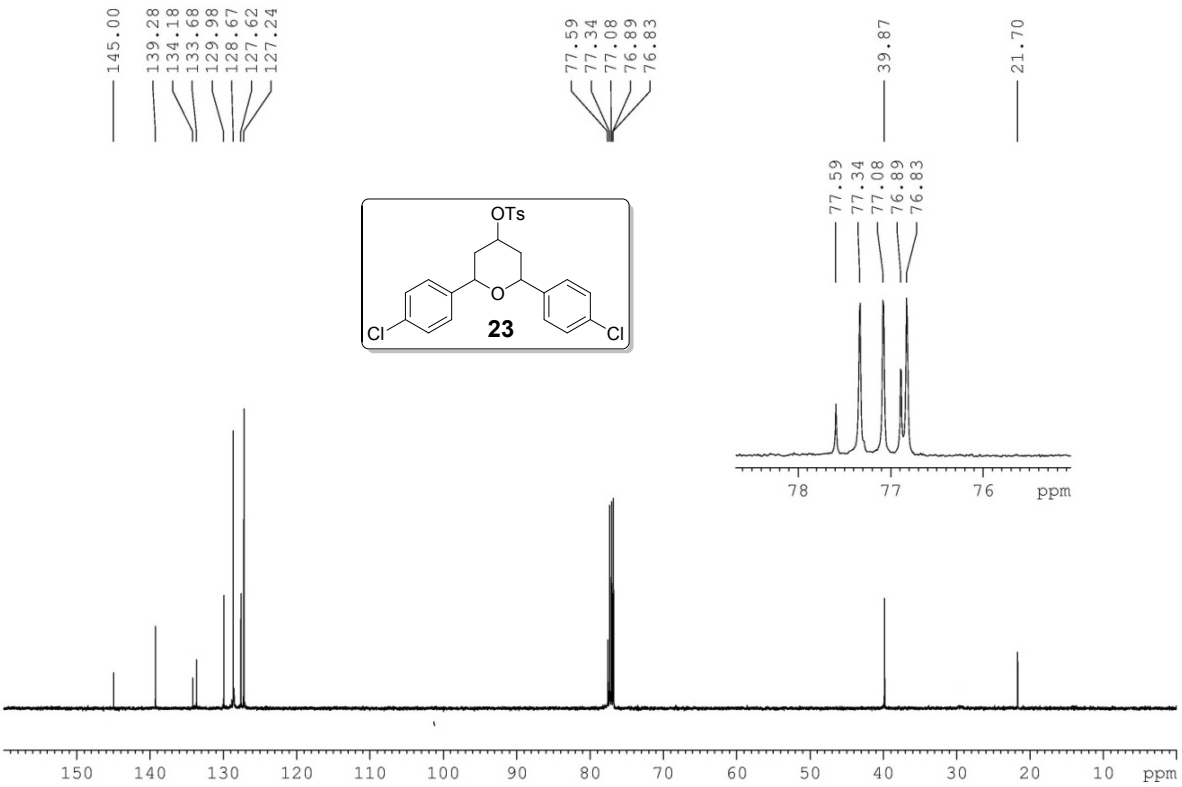
10.35
1.02
1.99
3.00
2.12
2.24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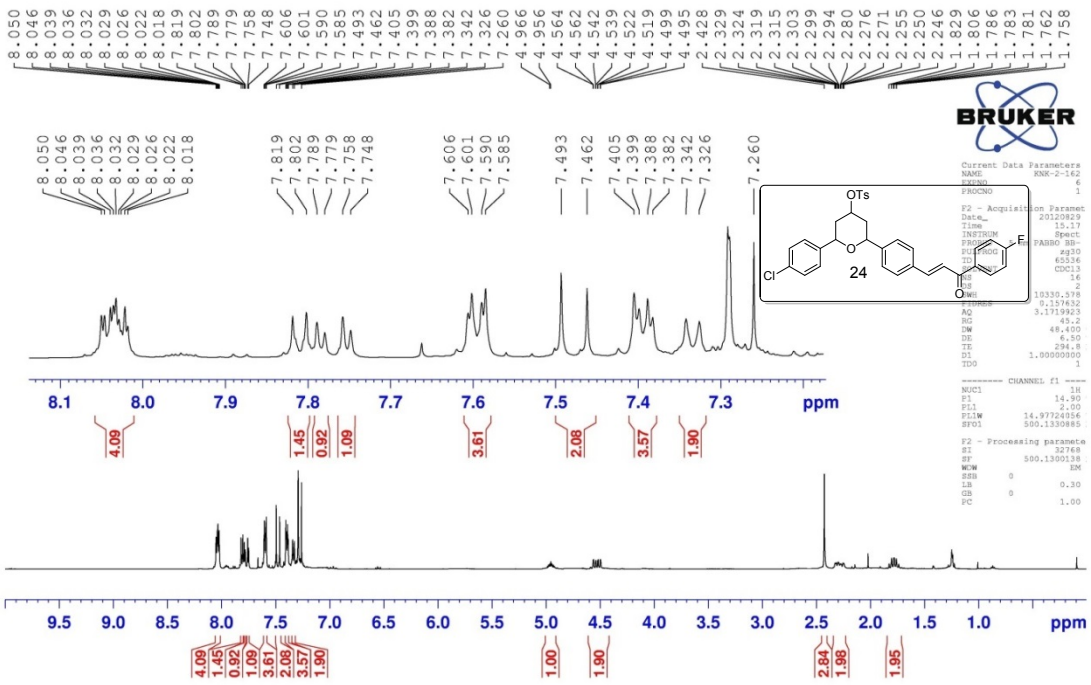
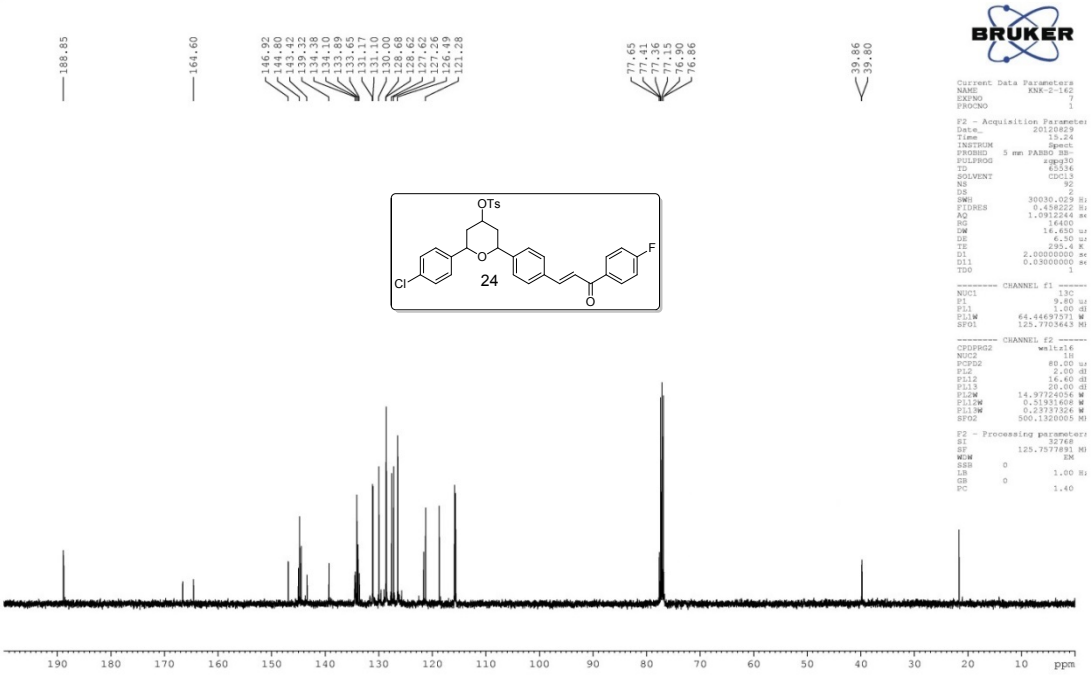
139.28
134.18
133.68
129.98
128.67
127.62
127.24
77.59
77.34
77.08
76.89
76.83
39.87
21.70
OTs
O
Cl
Cl
23
78
77
76
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BRUKER
OTs
O
Cl
F
O
24
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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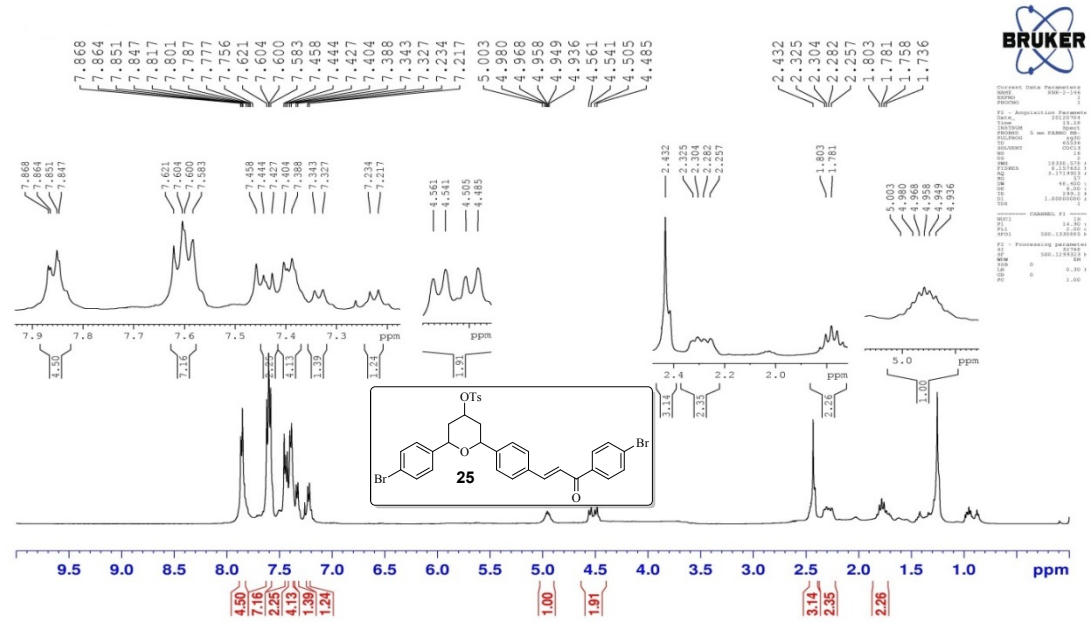
164.60
146.92
144.80
143.42
139.32
134.38
134.10
133.89
133.65
131.17
131.10
130.00
128.68
128.62
127.26
126.49
121.28
77.65
77.41
77.36
77.15
76.90
76.86
39.86
39.80
OTs
O
Cl
F
O
24
BRUKER
Current Data Parameters
NAME KNK-2-162
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120829
Time 15.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 92
DS 2
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 16400
DW 16.650 usec
DE 6.50 usec
TE 295.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.80 usec
PL1 1.00 dB
PL1W 64.44697571 W
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 16.60 dB
PL13 20.00 dB
PL2W 14.97724056 W
PL12W 0.51931608 W
PL13W 0.23737326 W
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577891 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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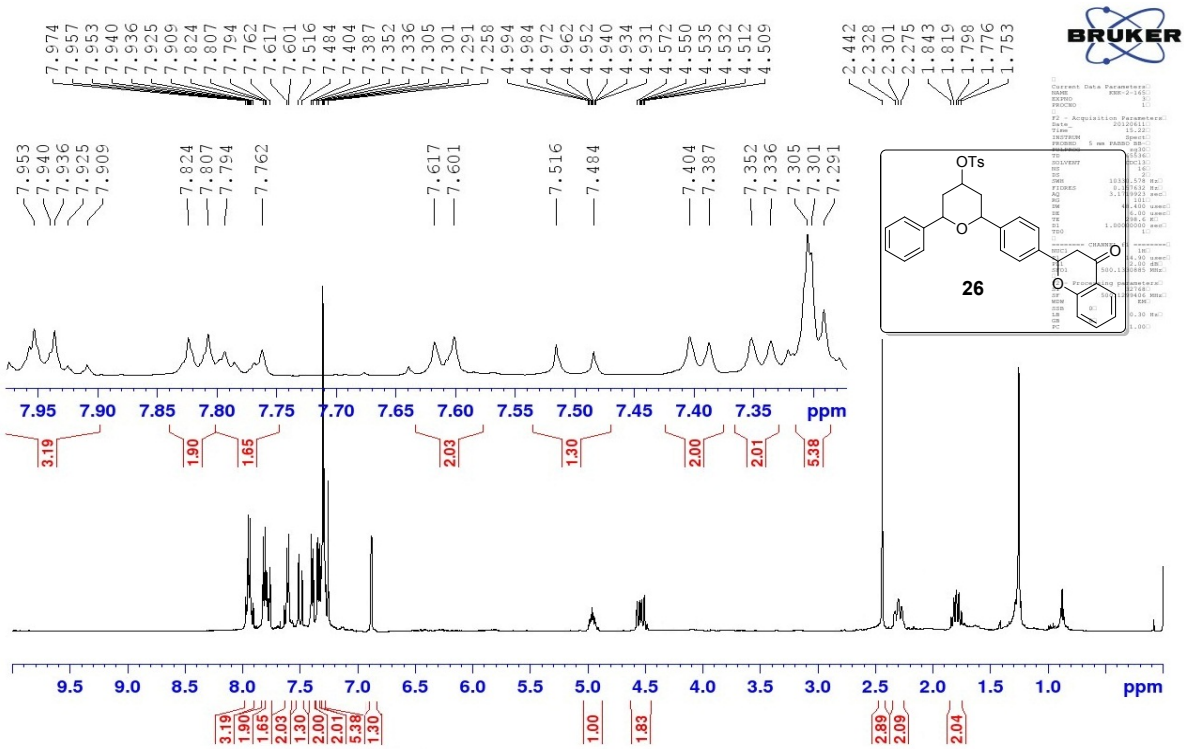
7.847
7.817
7.801
7.787
7.777
7.756
7.621
7.604
7.600
7.583
7.458
7.444
7.427
7.404
7.388
7.343
7.327
7.234
7.217
5.003
4.980
4.968
4.958
4.949
4.936
4.561
4.541
4.505
4.485
2.432
2.325
2.304
2.282
2.257
1.803
1.781
1.758
1.736
BRUKER
OTs
O
Br
Br
O
25
4.50
7.16
2.25
4.13
1.39
1.24
1.00
1.91
3.14
2.35
2.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm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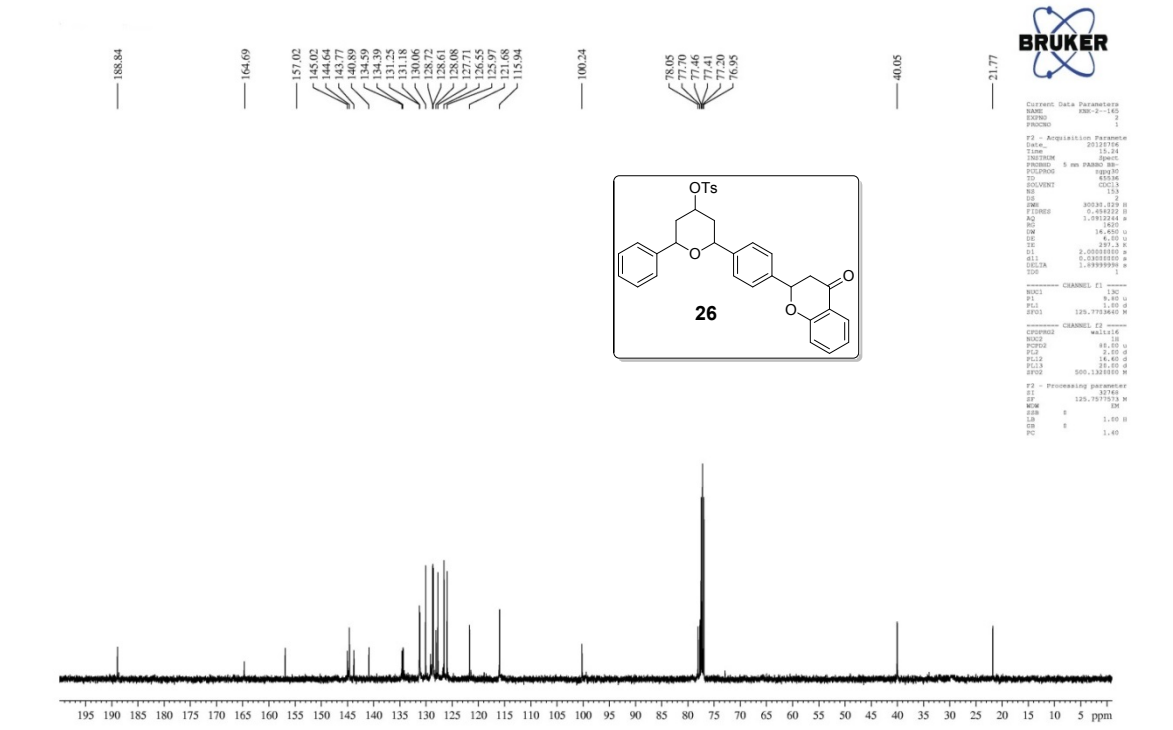
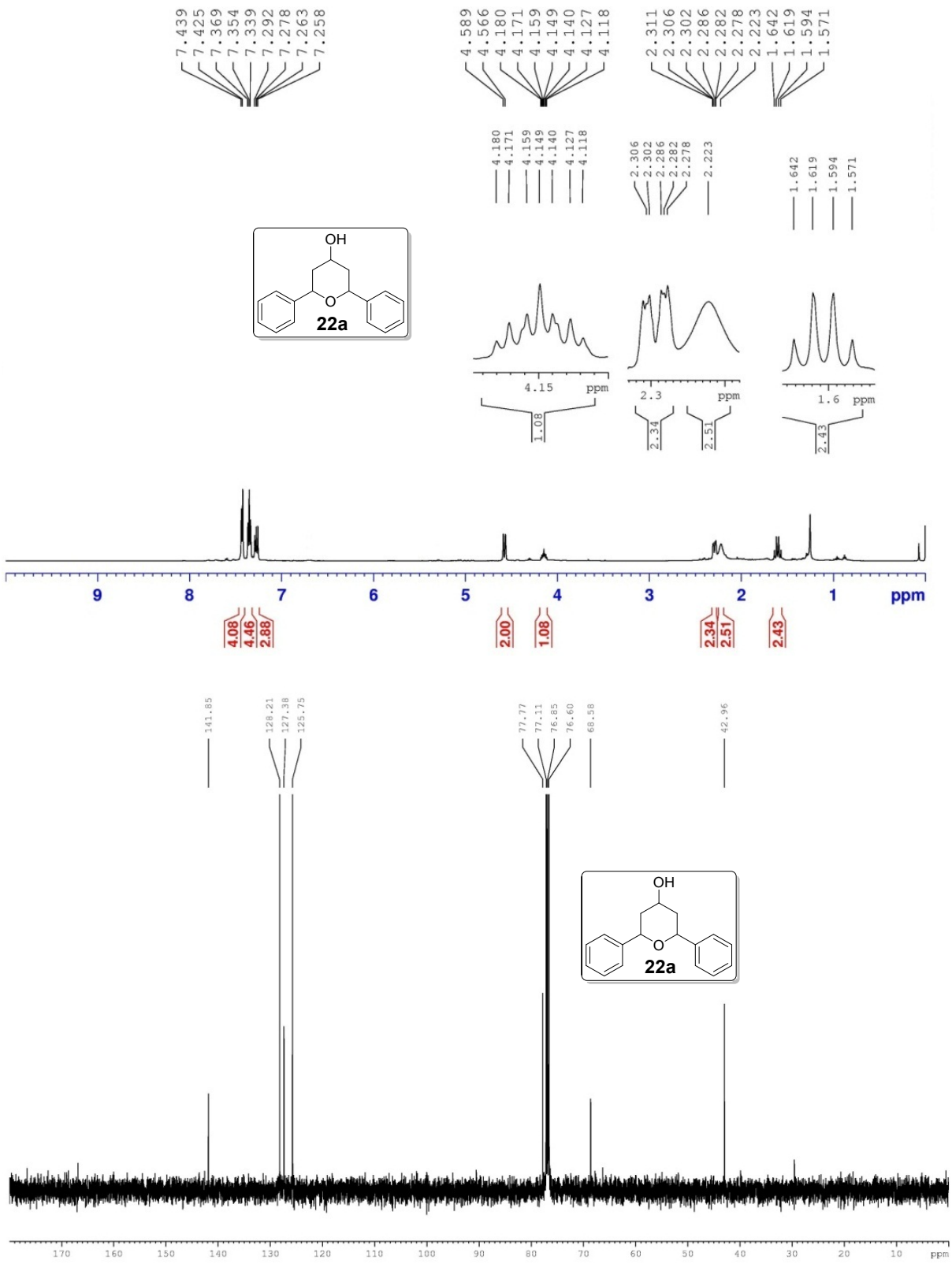
7.953
7.940
7.936
7.925
7.909
7.824
7.807
7.794
7.762
7.617
7.601
7.516
7.484
7.404
7.387
7.352
7.336
7.305
7.301
7.291
7.258
4.994
4.984
4.972
4.962
4.952
4.940
4.934
4.931
4.572
4.550
4.535
4.532
4.512
4.509
2.442
2.328
2.301
2.275
1.843
1.819
1.798
1.776
1.753
BRUKER
OTs
O
O
O
26
7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 ppm
3.19 1.90 1.65 2.03 1.30 2.00 2.01 5.38
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.19 1.90 1.65 2.03 1.30 2.00 2.01 5.38 1.30
1.00 1.83 2.89 2.09 2.04


188.84
164.69
157.02
145.02
144.64
143.77
140.89
134.59
134.39
131.25
131.18
130.06
128.72
128.61
128.08
127.71
126.55
125.97
121.68
115.94
100.24
78.05
77.70
77.46
77.41
77.20
76.95
40.05
21.77
BRUKER
OTs
O
O
O
26
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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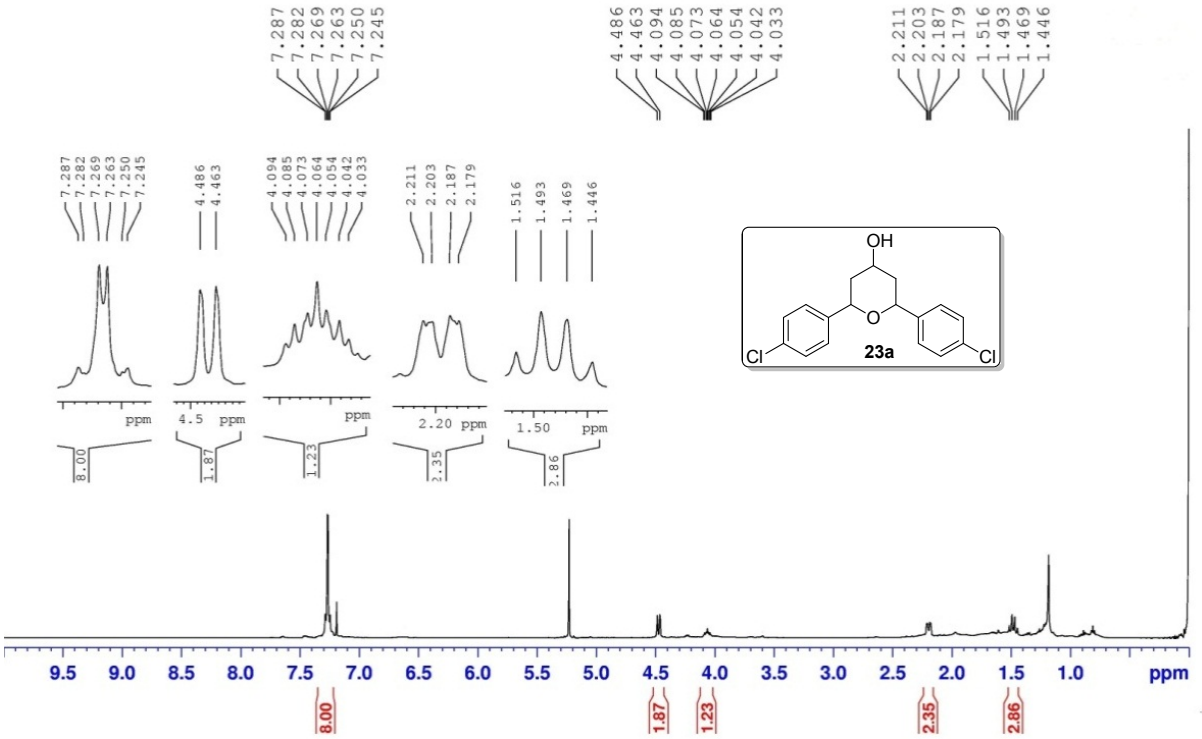
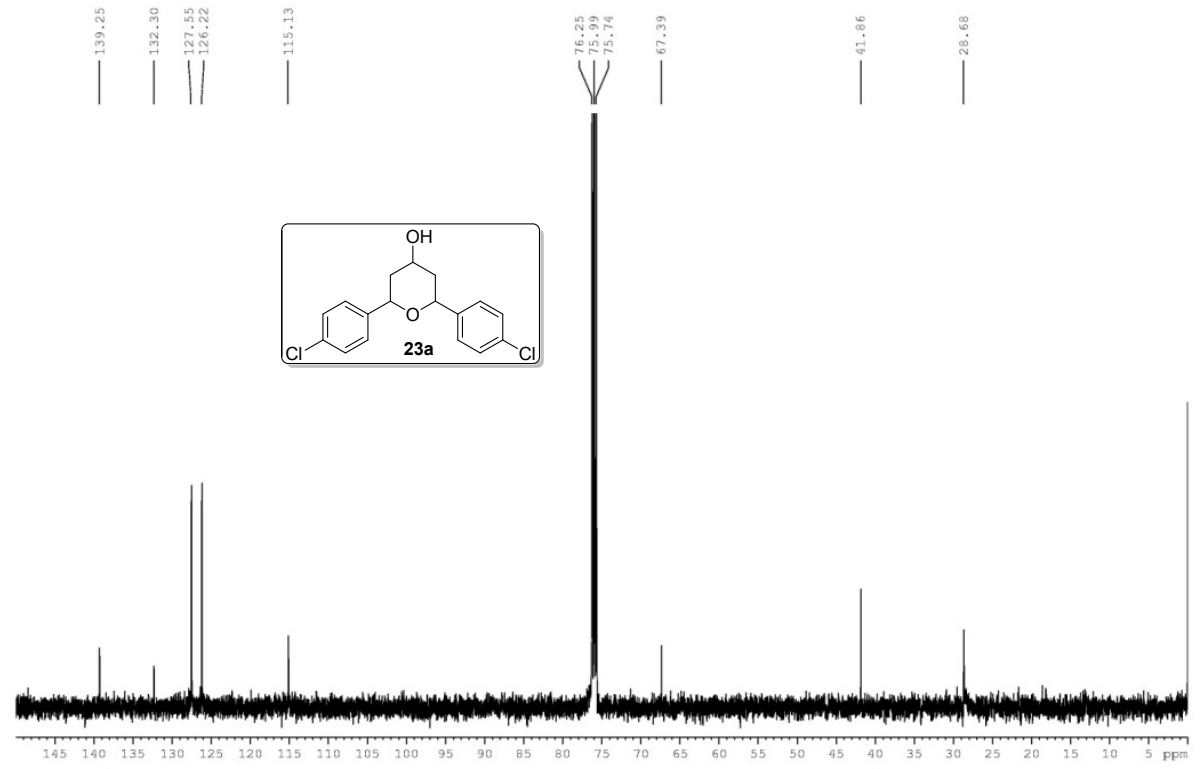
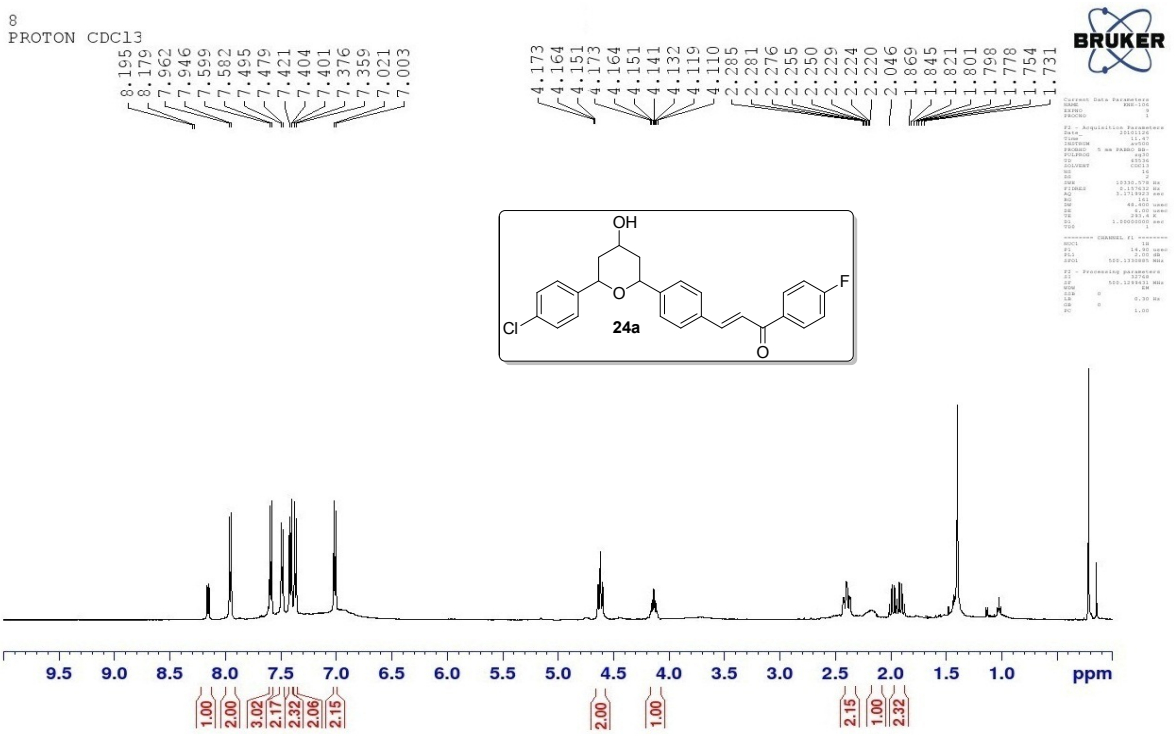
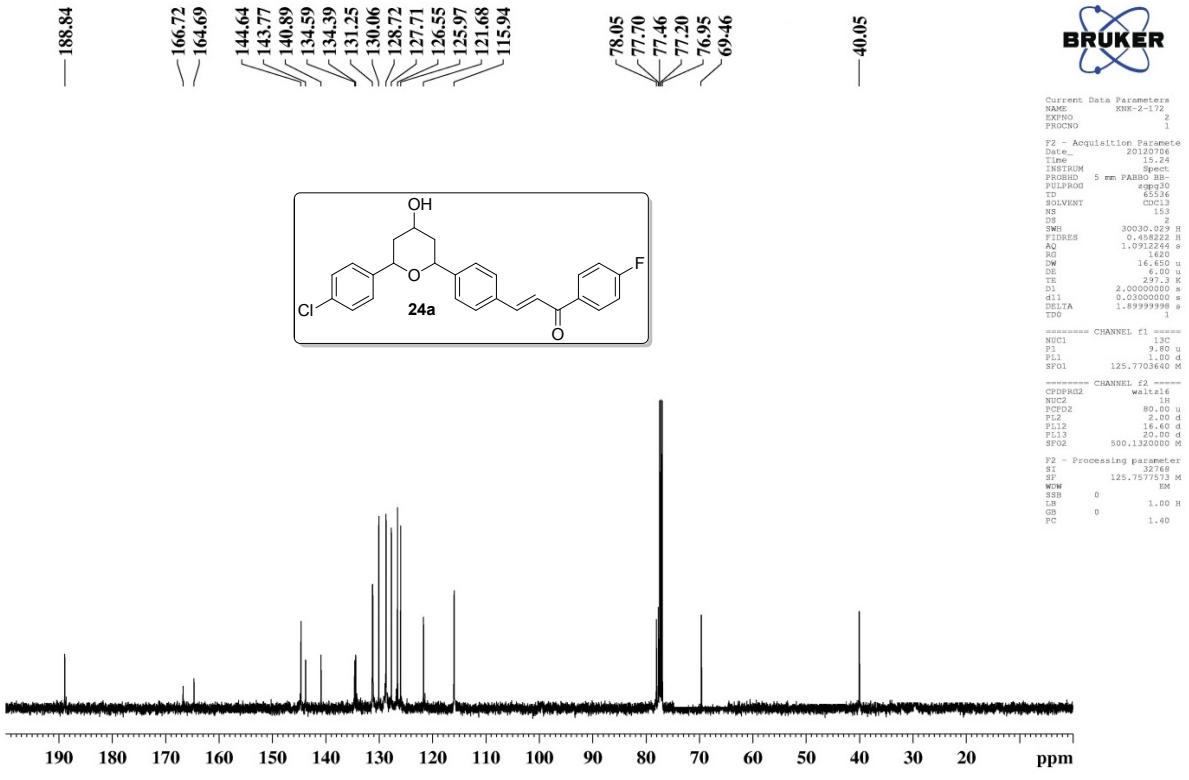
7.425
7.369
7.354
7.339
7.292
7.278
7.263
7.258
4.589
4.566
4.180
4.171
4.159
4.149
4.140
4.127
4.118
2.311
2.306
2.302
2.286
2.282
2.278
2.223
1.642
1.619
1.594
1.571
OH
O
22a
4.15 ppm
2.3 ppm
1.6 ppm
1.08
2.34
2.51
2.43
9 8 7 6 5 4 3 2 1 ppm
4.08
4.46
2.88
2.00
1.08
2.34
2.51
2.43
141.85
128.21
127.38
125.75
77.77
77.11
76.85
76.60
68.58
42.96
OH
O
22a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.287
7.282
7.269
7.263
7.250
7.245
4.486
4.463
4.094
4.085
4.073
4.064
4.054
4.042
4.033
2.211
2.203
2.187
2.179
1.516
1.493
1.469
1.446
OH
O
Cl
Cl
23a
ppm
4.5 ppm
ppm
2.20 ppm
1.50 ppm
8.00
1.87
1.23
2.35
2.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


139.25
132.30
127.55
126.22
115.13
76.25
75.99
75.74
67.39
41.86
28.68
OH
O
Cl
Cl
23a
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


8
PROTON CDCl3
8.195
8.179
7.962
7.946
7.599
7.582
7.495
7.479
7.421
7.404
7.401
7.376
7.359
7.021
7.003
4.173
4.164
4.151
4.141
4.132
4.119
4.110
2.285
2.281
2.276
2.255
2.250
2.229
2.224
2.220
2.046
1.869
1.845
1.821
1.801
1.798
1.778
1.754
1.731
BRUKER
OH
O
F
Cl
24a
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.00
3.02
2.17
2.32
2.06
2.15
2.00
1.00
2.15
1.00
2.32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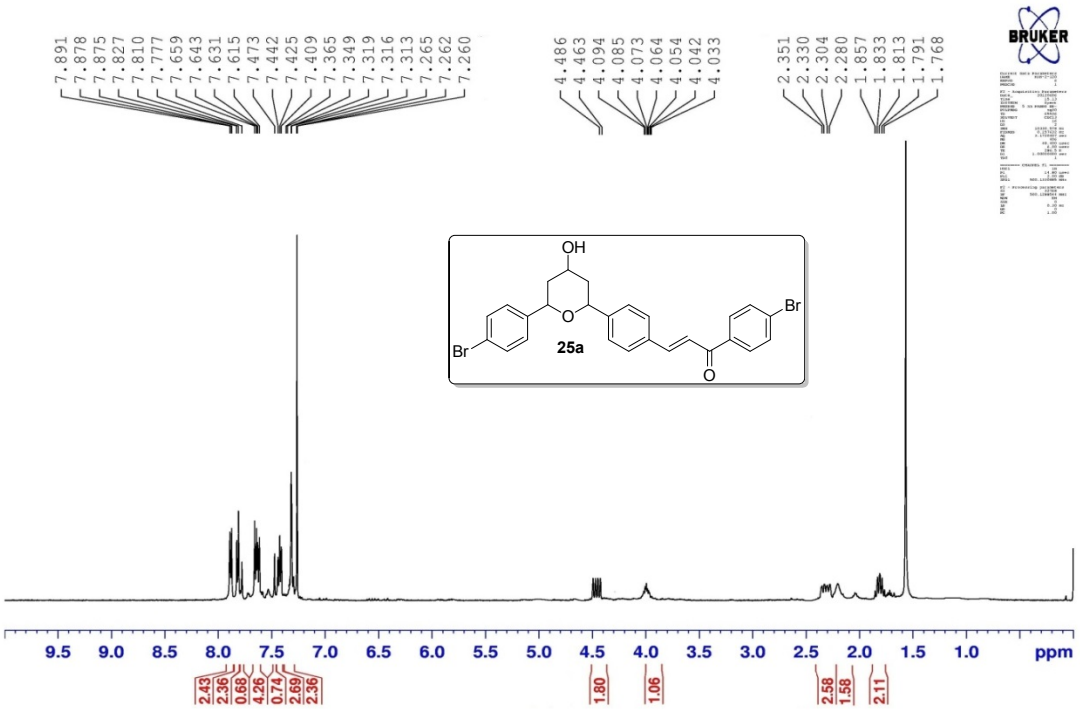
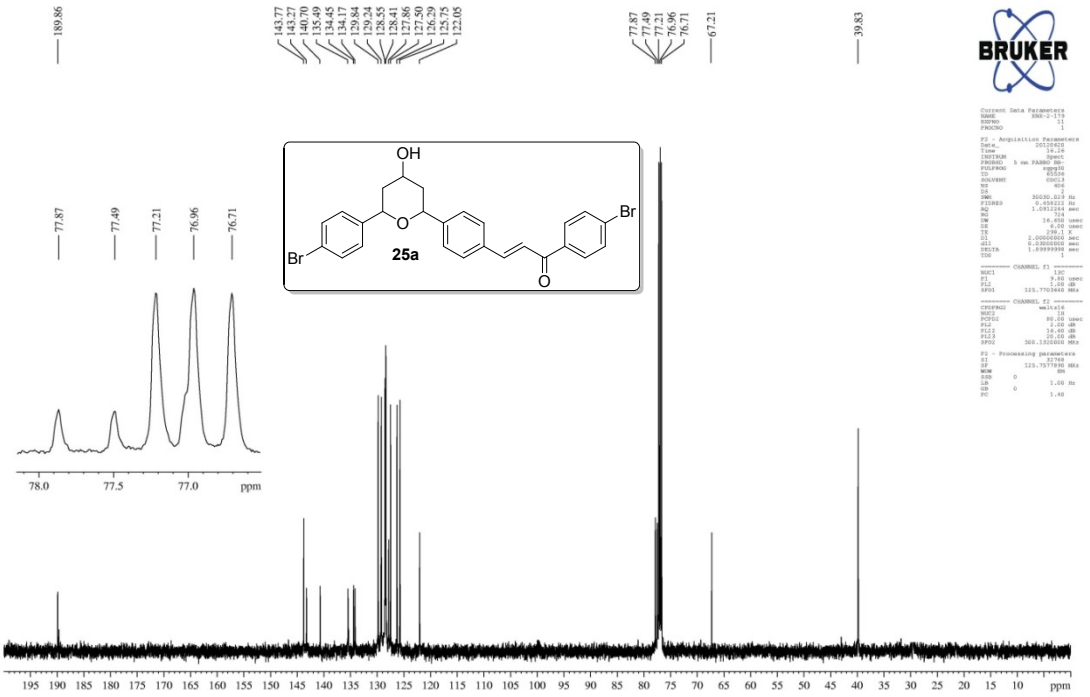
166.72
164.69
144.64
143.77
140.89
134.59
134.39
131.25
130.06
128.72
127.71
126.55
125.97
121.68
115.94
78.05
77.70
77.46
77.20
76.95
69.46
40.05
BRUKER
OH
O
F
Cl
24a
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.891
7.878
7.875
7.827
7.810
7.777
7.659
7.643
7.631
7.615
7.473
7.442
7.425
7.409
7.365
7.349
7.319
7.316
7.313
7.265
7.262
7.260
4.486
4.463
4.094
4.085
4.073
4.064
4.054
4.042
4.033
2.351
2.330
2.304
2.280
1.857
1.833
1.813
1.791
1.768
BRUKER
OH
O
Br
Br
25a
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.43
2.36
0.68
4.26
0.74
2.69
2.36
1.80
1.06
2.58
1.58
2.11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140.70
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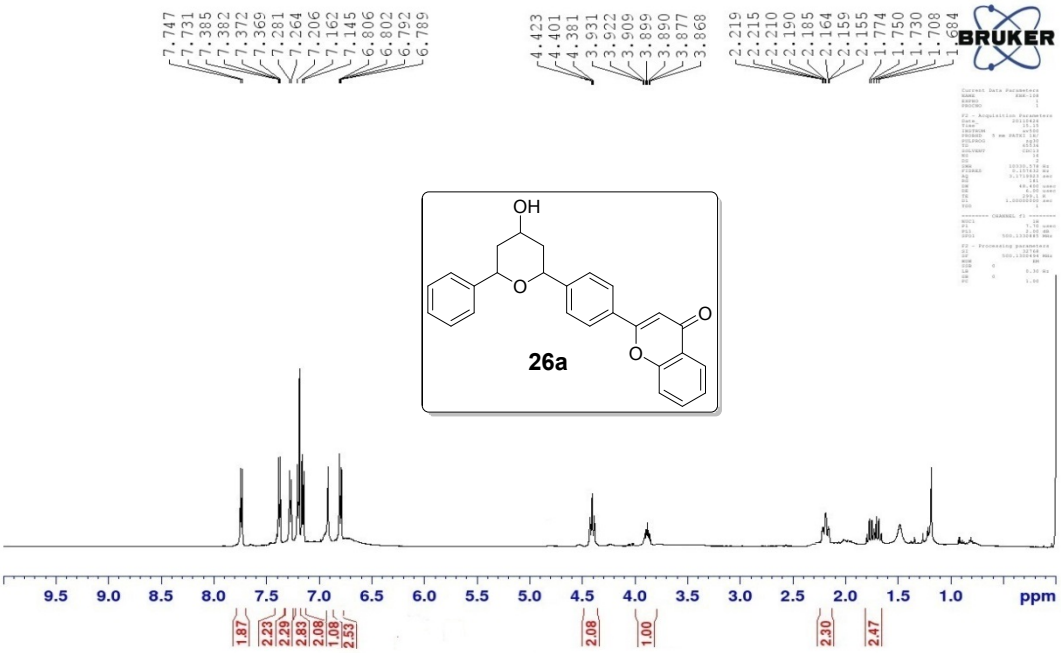
134.45
134.17
129.84
129.24
128.55
128.41
127.86
127.50
126.29
125.75
122.05
77.87
77.49
77.21
76.96
76.71
67.21
39.83
BRUKER
OH
O
Br
Br
25a
77.87
77.49
77.21
76.96
76.71
78.0
77.5
77.0
ppm
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 ppm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7.385
7.382
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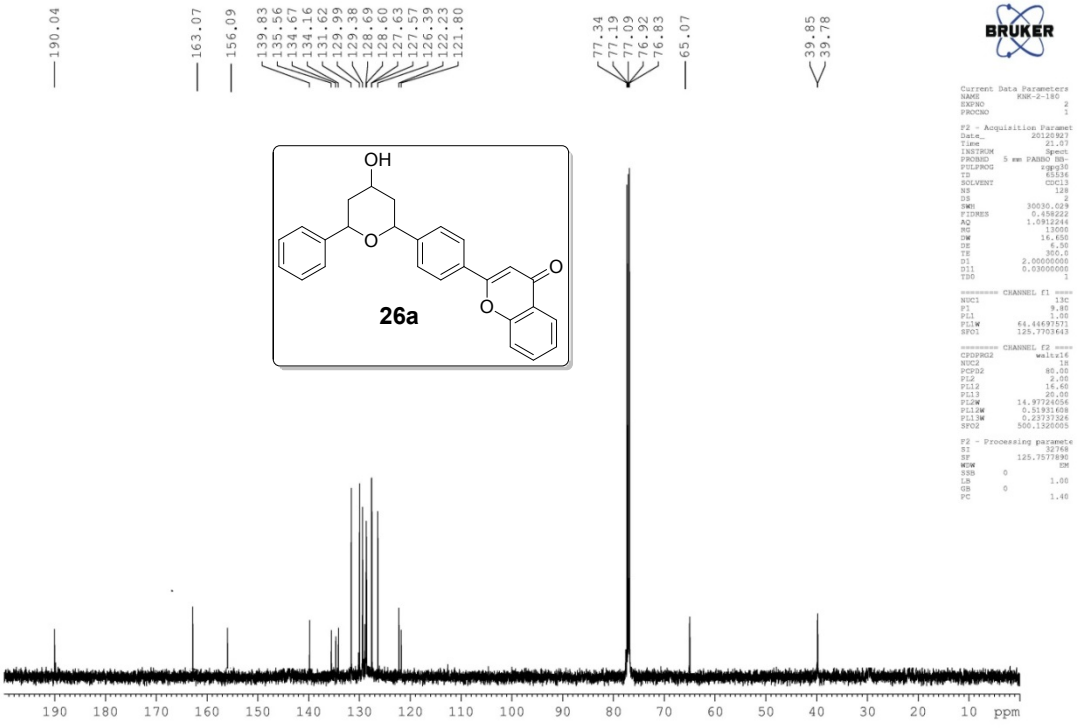
7.369
7.281
7.264
7.206
7.162
7.145
6.806
6.802
6.792
6.789
4.423
4.401
4.381
3.931
3.922
3.909
3.899
3.890
3.877
3.868
2.219
2.215
2.210
2.190
2.185
2.164
2.159
2.155
1.774
1.750
1.730
1.708
1.684
BRUKER
OH
O
O
O
26a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.87
2.23
2.29
2.83
2.08
1.08
2.53
2.08
1.00
2.30
2.47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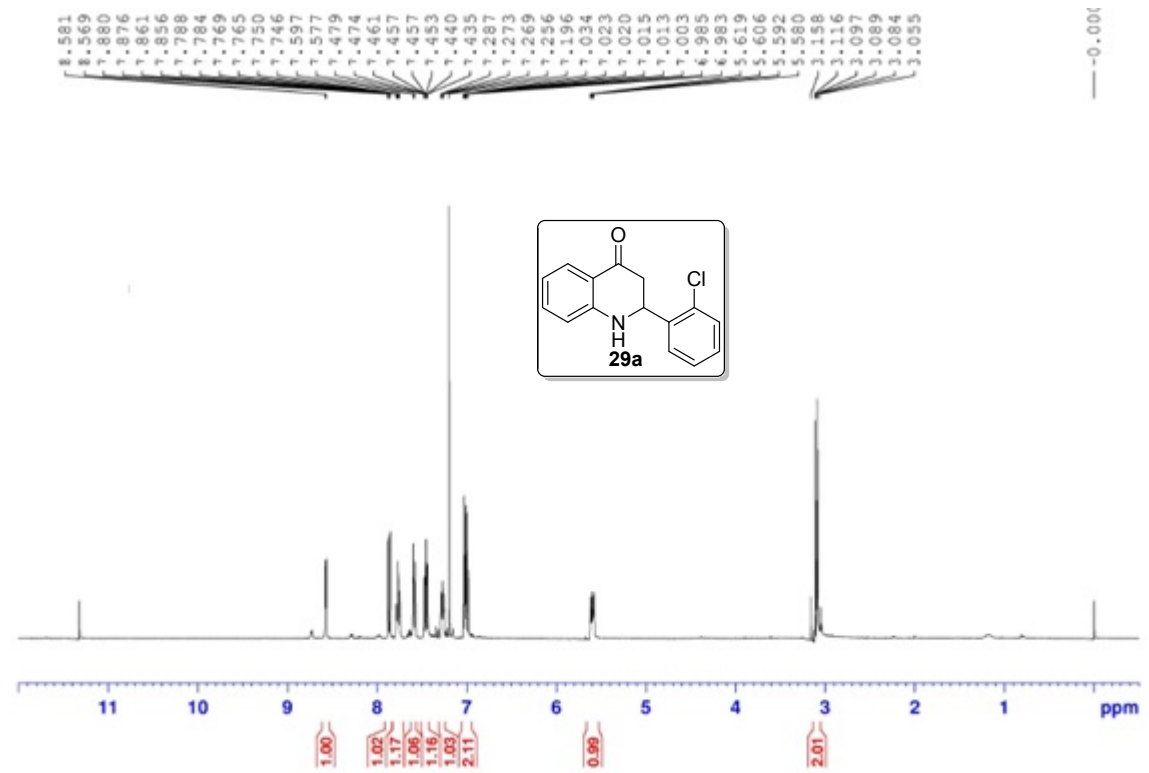
163.07
156.09
139.83
135.56
134.67
134.16
131.62
129.99
129.38
128.69
128.60
127.63
127.57
126.39
122.23
121.80
77.34
77.19
77.09
76.92
76.83
65.07
39.85
39.78
BRUKER
OH
O
O
O
26a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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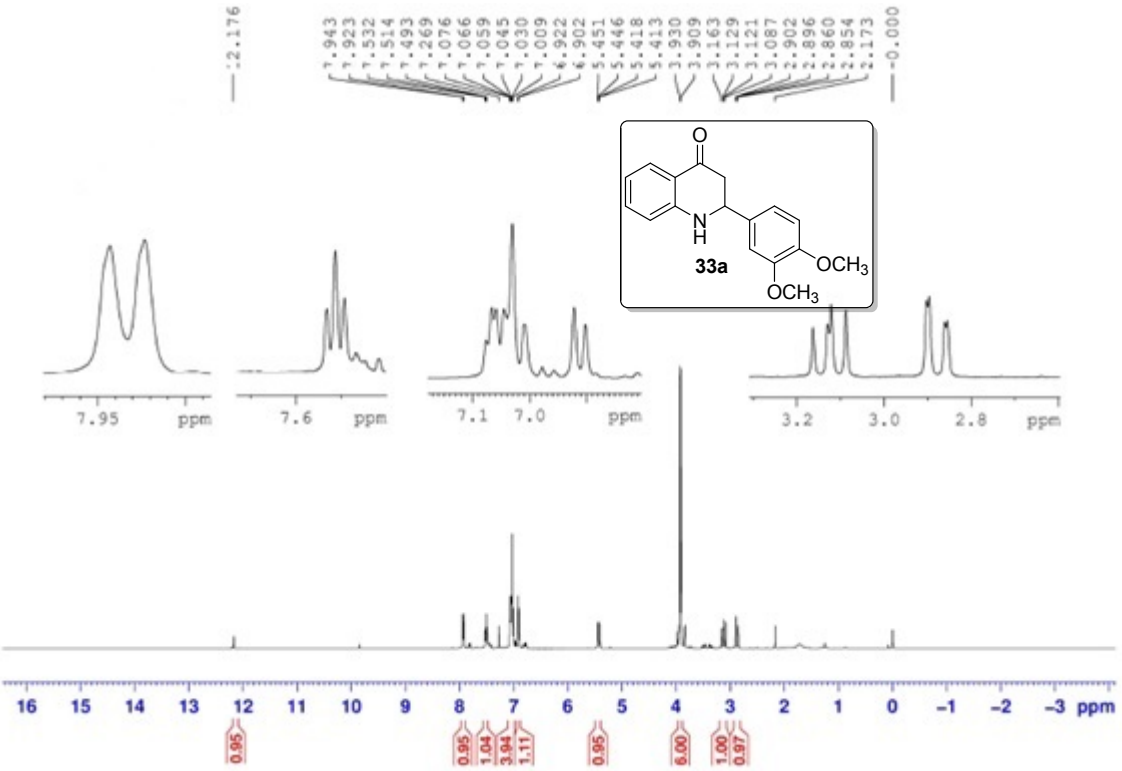
7.880
7.876
7.861
7.856
7.788
7.784
7.769
7.765
7.750
7.746
7.597
7.577
7.479
7.474
7.461
7.457
7.457
7.453
7.440
7.435
7.287
7.273
7.269
7.256
7.196
7.034
7.023
7.020
7.015
7.013
7.003
6.985
6.983
5.619
5.606
5.592
5.580
3.158
3.116
3.097
3.089
3.084
3.055
O
Cl
N
H
29a
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.02 1.17 1.06 1.16 1.03 2.11 0.99 2.01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7.514
7.493
7.269
7.076
7.066
7.059
7.045
7.030
7.009
6.922
6.902
5.451
5.446
5.418
5.413
3.930
3.909
3.163
3.129
3.121
3.087
2.902
2.896
2.860
2.854
2.173
0.000
O
N
H
33a
OCH3
OCH3
7.95 ppm
7.6 ppm
7.1 7.0 ppm
3.2 3.0 2.8 ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 ppm
0.95 0.95 1.04 3.94 1.11 0.95 6.00 1.00 0.97