Supporting Information

Magnetically recoverable silica catalysed solvent-free domino Knoevenagel-hetero-Diels-Alder reaction to access divergent chromenones

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Experimental

Materials and apparatus

All the chemicals were purchased from Sigma Aldrich, Merck, SRL, and Spectrochem and used without further purification. The powder XRD measurements were carried out by using a 2-80° 2θ on a Rigaku Ultima IV X-ray diffractometer with CuKα source (λ = 1.54056 Å). In built program 'XG operation RINT 2200' associated with the XRD was used to process the data and 'Rigaku PDXL 1.2.0.1' library database was used for identification of the peaks. IR spectra (4000-400 cm^{-1}) were recorded in a Perkin Elmer Spectrum 100 machine using KBr pellet. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were recorded on a JEOL JEM-2011 electron microscope functioned at an accelerating voltage of 200 kV. All NMR spectra of the products were recorded by using Bruker AV500 Avance-III 500 MHz FTNMR spectrometer. Thermogravimetric analysis (TGA) was carried out on a SDT Q600 V20.9 Build 20 instrument at a heating rate of 10 °C/min under N_2 atmosphere. HRMS data were recorded in a Waters XEVO G2-Xs QTof apparatus.

General procedure for the synthesis of silica-supported iron oxide catalyst

Iron (III) chloride hexahydrate {$FeCl_3.6H_2O$} (1.2 g) and iron (II) chloride tetrahydrate {$FeCl_2.4H_2O$} (0.47 g) was dissolved in 100 mL of Milli-Q water under N_2 atmosphere to form a homogeneous solution. This was followed by the dropwise addition of 10 mL of 10 N NaOH solutions into the mixture under vigorous stirring and the resulting solution was heated at 80 °C for 1 h when a black precipitate of Fe_3O_4 appeared. Silicic acid (2 g) was also homogeneously dispersed separately in 40 mL of Milli-Q water under N_2 atmosphere in another flask. The silicic acid solution was then added dropwise into the iron oxide solution with stirring. The mixture was further allowed to stir at room temperature under N_2 atmosphere for 16 h. The precipitate obtained was separated by magnetic decantation and washed with Milli-Q water and ethanol until neutral and then dehydrated at 200 °C for 4 h in a vacuum oven. A brownish-black powder of $Fe_3O_4@SiO_2$ was obtained.

General procedure for the synthesis of chromenone / spirochromenone

To a mixture of 1,3-cyclohexanedione (0.9 mmol), benzaldehyde (0.9 mmol) and phenylacetylene (0.9 mmol), $Fe_3O_4@SiO_2$ (10 wt%) was added and the mixture was heated at 100 °C for 2 h under solvent-free condition. The progress of the reaction was followed using thin layer chromatography (TLC). After the completion of the reaction, 5 mL ethyl acetate was added to the reaction mixture and the catalyst was removed by magnetic filtration. Organics were extracted with ethyl acetate (2 x 20 mL) and the combined organic fraction was washed with water (2 x 10 mL) and brine (10 mL). Drying over Na_2SO_4 and removal of the solvent under reduced pressure, produced the crude mixture which was purified by column chromatography using ethyl acetate /hexane as eluent. For further recyclability experiments, the recovered catalyst was oven-dried (at 100 °C for 2 h) under vacuum before the next run.

Characterization of Fe_3O_4@SiO_2 nanoparticle

Initially, the crystalline structure of the synthesized material was monitored by powder XRD analysis (Figure S1). The diffraction peaks at 2θ = 35.7°, 53.2° and 65.8° could be ascribed to the (311), (422) and (440) planes of cubic spinel phase of Fe_3O_4 crystal. These values are in good agreement with the JCPDS card no. 19-629 for magnetite, respectively. The broad, low intensity diffraction peaks observed at 2θ from 20° to 27° can be ascribed to the silica surrounding the Fe_3O_4 core.[1,2] The crystallite size of the prepared material was calculated from XRD pattern at 2θ value of 35.7° by means of Scherer equation and found to be in the range of 3.5 nm.

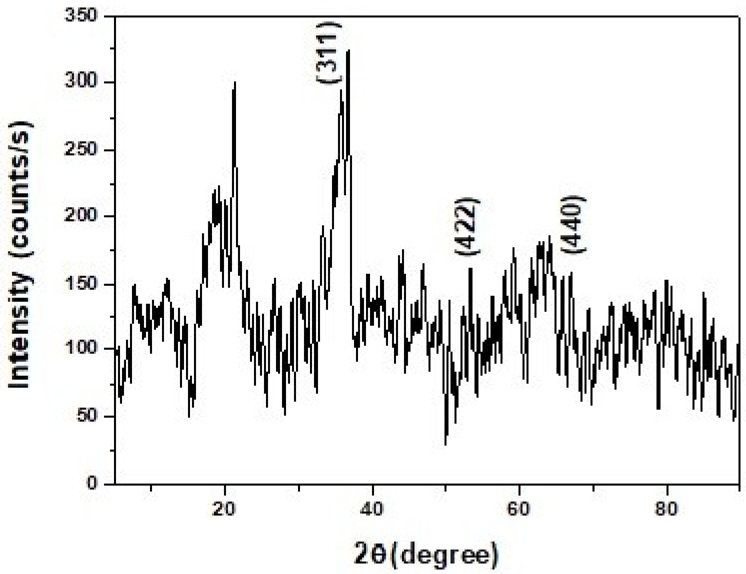


Figure S1. Powder XRD pattern of Fe_3O_4@SiO_2 nanoparticle

The functional groups present and the mode of bonding in the Fe_3O_4@SiO_2 nanoparticles were examined through FTIR spectroscopy recorded in the 4000-400 cm^{-1} range (Figure S2).

The bands observed in the regions of 3391 and 1631 cm^{-1} could be assigned to the –OH stretching and H-O-H bond vibrations of the surface adsorbed water molecules, respectively. The absorption peaks at 583 and 619 cm^{-1} is due to Fe-O stretching vibration. The absorption peaks at 795 and 1054 cm^{-1} may be attributed to stretching vibration of Si–O–Si (symmetrical), and Si–O–Si (asymmetrical), respectively.[3] These peaks confirm the coating of silica over Fe_3O_4.

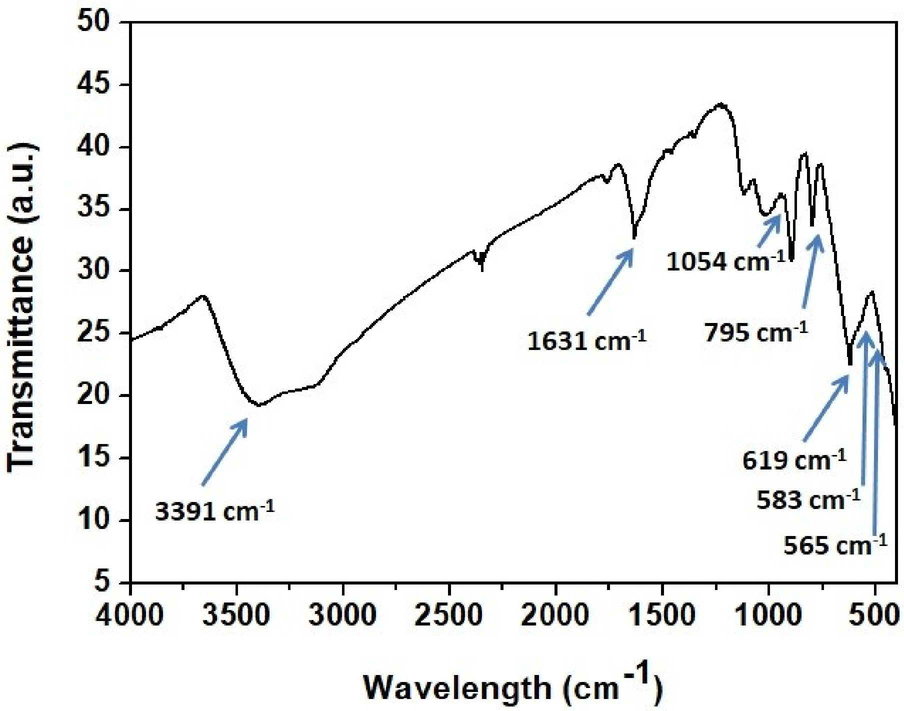


Figure S2. IR spectrum of Fe_3O_4@SiO_2 nanoparticle

The particle size and microstructure of the prepared Fe_3O_4@SiO_2 catalyst was characterized by TEM and HRTEM analysis (Figure S3). The low resolution TEM image revealed homogeneous distribution of the particles with nearly spherical shape. The particle size distribution was found to be in the range 2-3 nm with number-average diameter of 2.5 nm (standard deviation (SD) = 0.22). The close relation between surface-weighted diameter (Ds = 2.58 nm) and volume-weighted diameter (Dv = 2.59 nm) revealed narrow-size distribution of the prepared nanoparticle. The HRTEM image indicated that silica shell was successfully coated on the surface of Fe_3O_4 nanoparticle and the inter-planar lattice-fringe spacing of the Fe_3O_4 core was found to be 0.25 nm, corresponding to the (311) spinel phase of Fe_3O_4 crystal (Figure S3b). The selected area electron diffraction (SAED) pattern further confirmed the crystalline nature of the sample as indicated by the (311) and (422) crystalline planes (Figure S3c). Energy Dispersive X-ray (EDX) analysis of the prepared nanoparticle indicates the presence of Fe, Si and O signals, devoid of the presence of any other metal or impurity (Figure S3d).

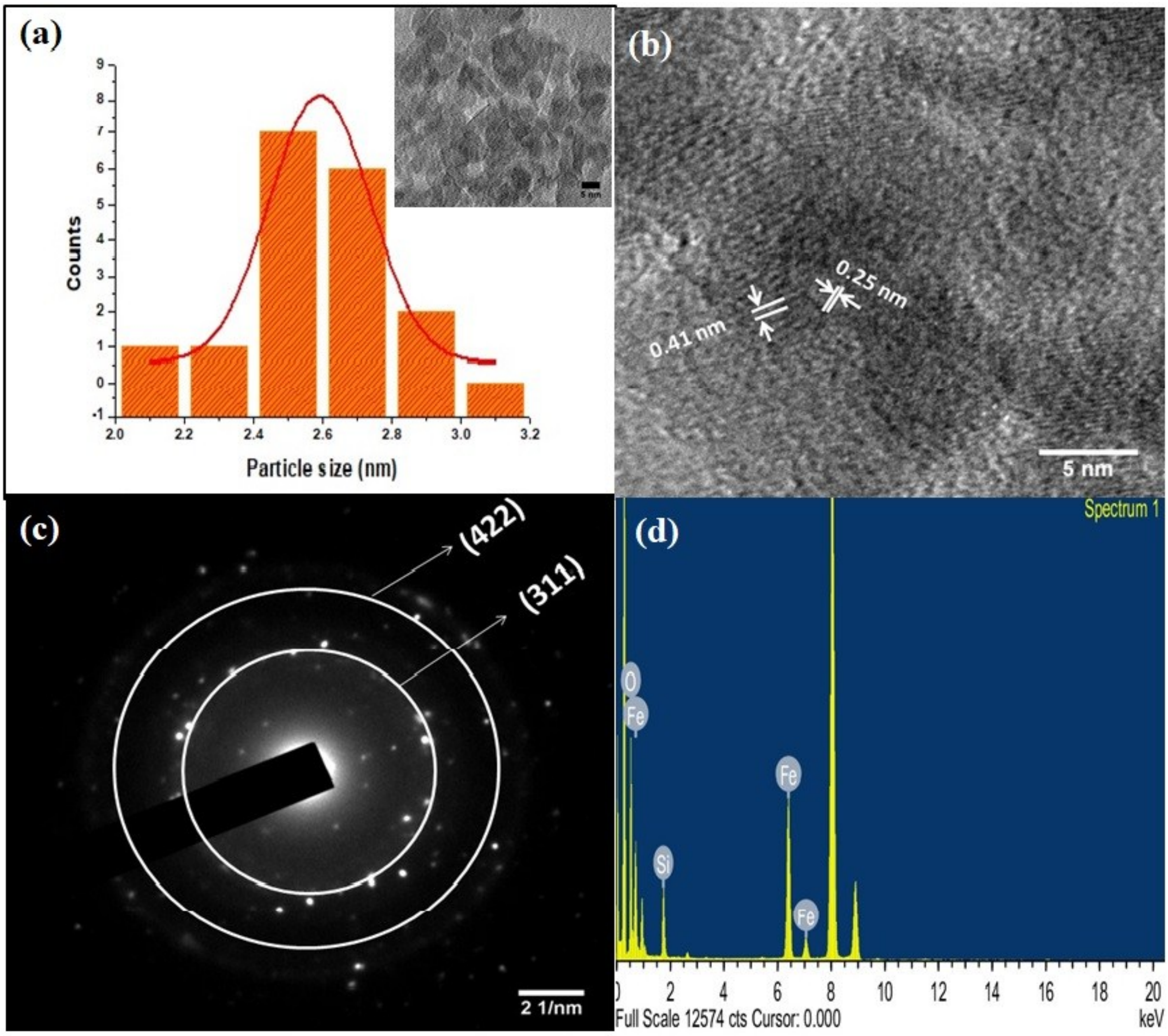


Figure S3. (a) Particle size distribution histogram, TEM image of $Fe_3O_4@SiO_2$ (inset a), (b) HRTEM image with fringe spacing (c) SAED pattern of $Fe_3O_4@SiO_2$ nanoparticles (d) and EDX spectra of $Fe_3O_4@SiO_2$ nanoparticles showing the presence of Fe, O and Si.

The magnetic properties of the synthesized $Fe_3O_4@SiO_2$ nanoparticles were studied by Vibrating Sample Magnetometer at room temperature (Figure S4). Saturation magnetization value of 13.24 emu/g was obtained for the synthesized nanoparticle, which was quite lower than that reported for bare Fe_3O_4 nanoparticle.[2] This reduction in saturation magnetization value can be attributed to the coating of Fe_3O_4 nanoparticles by an amorphous silica shell.[2]

However, the decrease in saturation magnetization value did not affect the magnetic properties of the nanoparticles and they could be magnetically separated by the application of an external magnetic field.

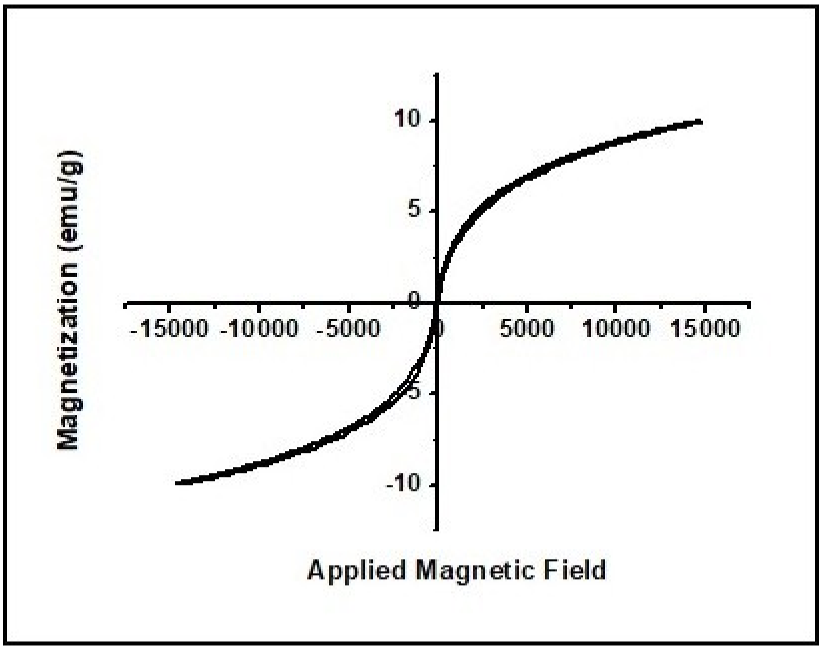


Figure S4. Magnetisation curve of Fe_3O_4@SiO_2 nanoparticles

The thermal stability of the magnetic Fe_3O_4@SiO_2 nanoparticles was analysed by thermogravimetric analysis (TGA) as shown in Figure S5. The TGA curve of Fe_3O_4@SiO_2 nanoparticles showed a weight loss of 12.49% at 800 °C. The initial weight loss of 9.73% below 200 °C can be attributed to the release of adsorbed water molecules from the catalyst surface. This confirms high thermal stability of the prepared Fe_3O_4@SiO_2 nanoparticle.

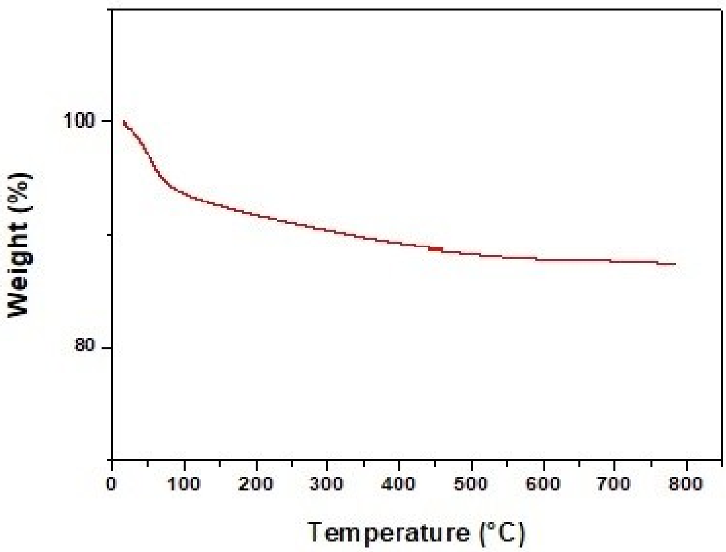


Figure S5. TGA curve of $Fe_3O_4@SiO_2$ nanoparticles

To study the recyclability of the catalyst, after the completion of the reaction, the solid catalyst was recovered by using an external magnet followed by washing with Milli-Q water and drying at 100 °C. It was observed that the catalyst could be reused up to five consecutive catalytic cycles without any significant loss in the activity (Figure S6). However, after the 5th run, the catalytic activity of the recovered catalyst decreased gradually.

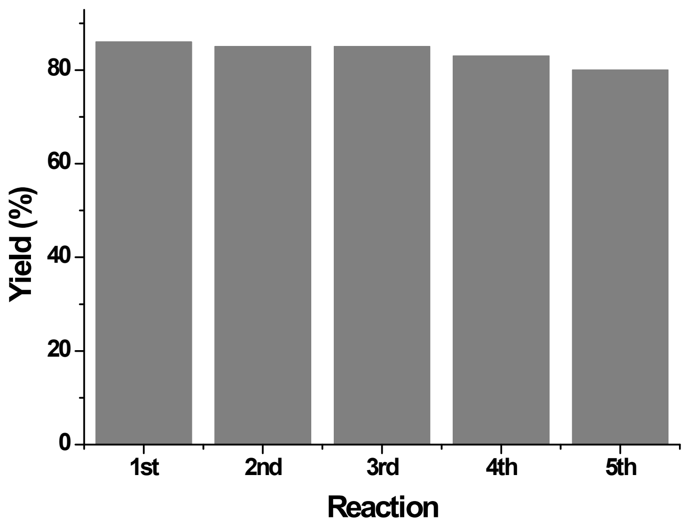
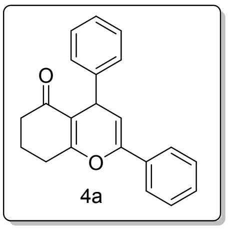


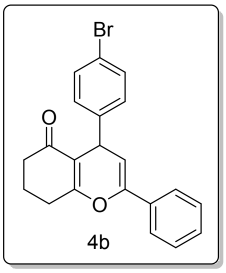
Figure S6. Study of recyclability of the catalyst

Characterization data of the product



2,4-diphenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4a)

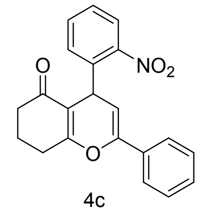
Orange solid compound. Mp: 169-171 °C (Lit.[4] 171-173 °C); Yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.38 – 7.31 (m, 5H), 7.30 -7.25 (m, 2H), 7.20 -7.15 (m, 1H), 5.71 (d, 1H, J = 5.0 Hz), 4.52 (d, 1H, J = 5.0 Hz), 2.75 – 2.64 (m, 2H), 2.40 – 2.35 (m, 2H), 2.08 – 2.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.7 (C), 166.6 (C), 147.0 (C), 145.4 (C), 133.1 (C), 128.9 (CH), 128.6 (CH), 128.6 (CH), 128.4 (CH), 126.8 (CH), 124.7 (CH), 114.0 (C), 104.7 (CH), 37.3 (CH2), 35.5 (CH), 27.9 (CH2), 20.6 (CH2); HRMS (ESI) *m*/*z* 303.1394 ($[M+H]^+$ $C_{21}H_{19}O_2$ requires 303.1385).



4-(4-bromophenyl)-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4b)[5]

White solid compound. Mp: 110-112 °C. Yield: 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 - 7.56 (m, 2H), 7.41 – 7.35 (m, 5H), 7.21 (d, 2H, J = 8.5 Hz), 5.66 (d, 1H, J = 5.0 Hz), 4.49 (d, 1H, J = 5.0 Hz), 2.71 – 2.64 (m, 2H), 2.41 – 2.35 (m, 2H), 2.09 – 2.01 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.3 (C), 166.4 (C), 147.0 (C), 144.1 (C), 132.6 (C), 131.3 (CH), 129.9 (CH), 128.8 (CH), 128.4 (CH), 124.4 (CH), 120.3 (C), 113.3 (C), 103.7 (CH), 36.9

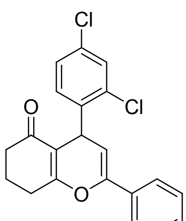
(CH2), 34.7 (CH), 27.6 (CH2), 20.3 (CH2); HRMS (ESI) *m/z* 381.0497 ($[M+H]^+$ $C_{21}H_{18}O_2Br$ requires 381.0490).



4c

4-(2-nitrophenyl)-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4c)

Yellow solid compound. Mp: 160-162 °C. Yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, 1H, J = 8.0 Hz), 7.62 – 7.58 (dd, 2H, J = 8.0 Hz, 1.5 Hz), 7.49 (t, 1H, J = 7.5 Hz), 7.40 – 7.33 (m, 4H), 7.29 (t, 1H, J = 7.5 Hz), 5.88 (d, 1H, J = 4.5 Hz), 5.09 (d, 1H, J = 4.5 Hz), 2.76 – 2.68 (m, 2H), 2.38 – 2.34 (m, 2H), 2.11 – 2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1 (C), 167.5 (C), 149.4 (C), 147.7 (C), 139.9 (C), 133.1 (CH), 132.8 (C), 130.7 (CH), 129.2 (CH), 128.7 (CH), 127.4 (CH), 124.7 (CH), 124.3 (CH), 112.9 (C), 102.9 (CH), 36.9 (CH2), 31.1 (CH), 27.8 (CH2), 20.7 (CH2); HRMS (ESI) *m/z* 348.1238 ($[M+H]^+$ $C_{21}H_{18}NO_4$ requires 348.1236).

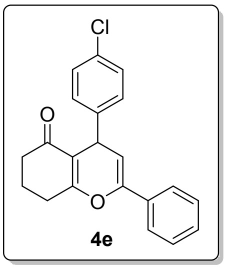


4d

4-(2,4-dichlorophenyl)-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4d)

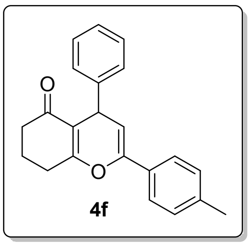
Pale yellow solid compound. Mp: 85-87 °C. Yield: 80 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 2H), 7.38 – 7.33 (m, 4H), 7.15 (dd, 1H, J = 8.5 Hz, 2.5 Hz), 7.09 (d, 1H, J = 8.5 Hz), 5.68 (d, 1H, J = 4.5 Hz), 4.93 (d, 1H, J = 4.5 Hz), 2.80 – 2.69 (m, 2H), 2.46 – 2.40

(m, 2H), 2.18 – 2.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.2 (C), 168.1 (C), 147.3 (C), 140.9 (C), 133.7 (C), 132.8 (CH), 130.4 (C), 129.6 (CH), 129.2 (CH), 128.8 (C), 128.6 (CH), 127.7 (CH), 124.7 (CH), 112.1 (C), 102.4 (CH), 37.2 (CH2), 32.5 (CH), 28.0 (CH2), 20.7 (CH2),; HRMS (ESI) *m*/*z* 371.0591 ($[M+H]^+$ $C_{21}H_{17}O_2Cl_2$ requires 371.0606).



4-(4-chlorophenyl)-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4e)

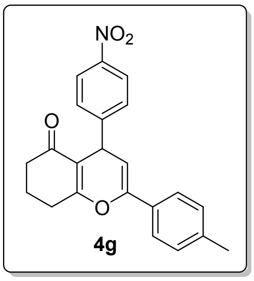
White solid compound. Mp: 117-119 °C (Lit.[4] 117-118 °C). Yield: 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.57 (m, 2H), 7.40 – 7.34 (m, 3H), 7.29 – 7.22 (m, 4H), 5.66 (d, 1H, J = 5.0 Hz), 4.50 (d, 1H, J = 5.0 Hz), 2.74 – 2.64 (m, 2H), 2.42 – 2.36 (m, 2H), 2.09 – 2.00 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.6 (C), 166.7 (C), 147.3 (C), 143.9 (C), 132.9 (C), 132.5 (C), 129.8 (CH), 129.1 (CH), 128.7 (CH), 128.7 (CH), 124.7 (CH), 113.7 (C), 104.1 (CH), 37.2 (CH2), 34.9 (CH), 27.9 (CH_2), 20.6 (CH_2); HRMS (ESI) *m*/*z* 337.0996 ($[M+H]^+$ $C_{21}H_{18}O_2Cl$ requires 337.0995).



4-phenyl-2-(p-tolyl)-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4f)

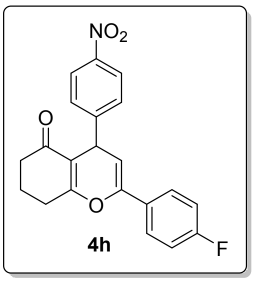
White solid compound. Mp: 130-132 °C (lit.[6] 130-131 °C). Yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, 2H, J = 8.0 Hz), 7.33 – 7.29 (m, 2H), 7.26 (d, 2H, J = 8.0 Hz), 7.17 – 7.13 (m, 3H), 5.64 (d, 1H, J = 5.0 Hz), 4.49 (d, 1H, J = 5.0 Hz), 2.72 – 2.61 (m, 2H), 2.39 - 2.35

(m, 2H), 2.34 (s, 2H), 2.07 – 1.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.7 (C), 166.6 (C), 147.1 (C), 145.6 (C), 138.9 (C), 130.2 (C), 129.3 (CH), 128.6 (CH), 128.4 (CH), 126.7 (CH), 124.6 (CH), 114.1 (C), 103.8 (CH), 37.3 (CH2), 35.4 (CH), 28.0 (CH_2), 21.4 (CH_2), 20.6 (CH_3); HRMS (ESI) *m/z* 317.1554 ($[M+H]^+$ $C_{22}H_{21}O_2$ requires 317.1542).



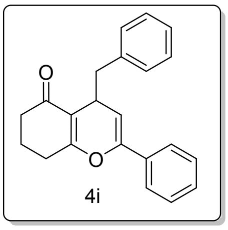
4-(4-nitrophenyl)-2-(p-tolyl)-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4g)

Pale yellow solid compound. Mp: 144-145 °C. Yield: 80%. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, 2H, J = 8.5 Hz), 7.49 - 7.43 (m, 4H), 7.17 (d, 2H, J = 8.5 Hz), 5.57 (d, 1H, J = 4.5 Hz), 4.60 (d, 1H, J = 4.5 Hz), 2.74 – 2.65 (m, 2H), 2.39 – 2.35 (m, 2H), 2.35 (s, 3H), 2.11 – 2.00 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.9 (C), 167.3 (C), 152.8 (C), 148.0 (C), 146.8 (C), 139.5 (C), 129.8 (C), 129.4 (CH), 129.3 (CH), 124.7 (CH), 123.9 (CH), 113.0 (C), 102.1 (CH), 37.1 (CH2), 35.7 (CH), 28.0 (CH2), 21.5 (CH2), 20.6 (CH3); HRMS (ESI) *m/z* 362.1390 ($[M+H]^+$ $C_{22}H_{20}NO_4$ requires 362.1392).



2-(4-fluorophenyl)-4-(4-nitrophenyl)-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4h)

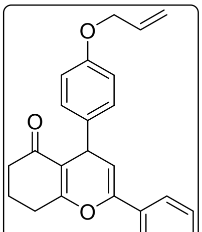
Yellow solid compound. Mp: 55-57 °C. Yield: 74%. ^1H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, 2H, J = 8.5 Hz), 7.57 - 7.52 (m, 2H), 7.47 (d, 2H, J = 8.5 Hz), 7.08 - 7.02 (m, 2H), 5.56 (d, 1H, J = 4.5 Hz), 4.61 (d, 1H, J = 4.5 Hz), 2.72 - 2.64 (m, 2H), 2.40 -2.36 (m, 2H), 2.12-1.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4 (C), 167.1 (C), 163.4 (C, d, J = 247.5 Hz), 152.5 (C), 147.1 (C), 146.9 (C), 129.3 (CH), 128.8 (C), 126.7 (CH, d, J = 8.7 Hz), 124.0 (CH), 115.8 (CH, d, J = 21.2 Hz), 113.0 (C), 102.7 (CH), 37.1 (CH2), 35.7 (CH), 27.9 (CH2), 20.5 (CH2); HRMS (ESI) m/z 366.1136 ($[M+H]^+$ $C_{21}H_{17}NO_4F$ requires 366.1142).



4i

4-benzyl-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4i)

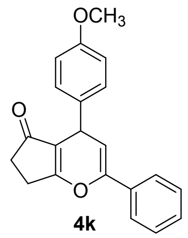
Yellow solid compound. Mp: 55-57 °C. Yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 - 7.45 (m, 2H), 7.35 – 7.30 (m, 4H), 7.28 – 7.23 (m, 4H), 5.47 (d, 1H, J = 5.0 Hz), 3.71 – 3.63 (m, 1H), 3.06 – 3.01 (m, 1H), 2.69 – 2.63 (m, 1H), 2.51 – 2.40 (m, 4H), 2.06 – 2.01 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4 (C), 167.9 (C), 147.9 (C), 139.1 (C), 133.4 (C), 129.9 (CH), 128.8 (CH), 128.6 (CH), 128.1 (CH), 126.3 (CH), 124.6 (CH), 113.4 (C), 103.9 (CH), 42.9 (CH2), 37.4 (CH2), 31.2 (CH), 27.8 (CH2), 20.7 (CH2); HRMS (ESI) m/z 317.1554 ($[M+H]^+$ $C_{22}H_{21}O_2$ requires 317.1542).



4j

4-(4-(allyloxy)phenyl)-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4j)

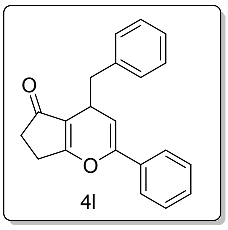
Yellow solid compound. Mp: 92-94 °C. Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 2H), 7.41 – 7.32 (m, 3H), 7.26 (d, 2H, J = 9.0 Hz), 6.85 (d, 2H, J = 9.0 Hz), 6.10 – 6.0 (m, 1H), 5.72 (d, 1H, J = 5.0 Hz), 5.42 (dd, 1H, J = 17.0, 1.5 Hz), 5.39 (dd, 1H, J = 11.0, 1.5 Hz), 4.52 – 4.48 (m, 3H), 2.75 – 2.65 (m, 2H), 2.43 – 2.37 (m, 2H), 2.09 – 2.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8 (C), 166.3 (C), 157.5 (C), 146.9 (C), 137.9 (C), 133.6 (CH), 133.2 (C), 129.4 (CH), 128.9 (CH), 128.6 (CH), 124.6 (CH), 117.8 (CH2), 114.8 (CH), 114.3 (C), 104.8 (CH), 69.0 (CH2), 37.3 (CH2), 34.5 (CH), 27.9 (CH2), 20.6 (CH2); HRMS (ESI) m/z 359.1665 ($[M+H]^+$ $C_{24}H_{23}O_3$ requires 359.1647).



4k

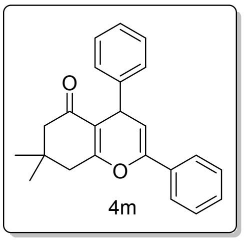
4-(4-methoxyphenyl)-2-phenyl-6,7-dihydrocyclopenta[b]pyran-5(4*H*)-one (4k)

Brown solid compound. Mp: 60-62 °C. Yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, 2H, J = 7.0 Hz), 7.44 – 7.38 (m, 3H), 7.29 – 7.27 (m, 2H), 6.87 (d, 2H, J = 8.5 Hz), 5.68 (d, 1H, J = 4.5 Hz), 4.44 (d, 1H, J = 3.5 Hz), 3.80 (s, 3H), 2.83 -2.78 (m, 2H), 2.52 – 2.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.4 (C), 178.7 (C), 158.7 (C), 148.5 (C), 135.6 (C), 133.0 (C), 129.4 (CH), 129.2 (CH), 128.7 (CH), 124.9 (CH), 117.5 (C), 114.1 (CH), 104.3 (CH), 55.5 (CH3), 35.0 (CH), 33.6 (CH2), 25.8 (CH2); HRMS (ESI) m/z 319.1346 ($[M+H]^+$ $C_{21}H_{19}O_3$ requires 319.1334).



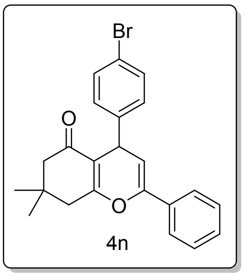
4-benzyl-2-phenyl-6,7-dihydrocyclopenta[b]pyran-5(4*H*)-one (4l)

Orange solid compound. Mp: 88-90 °C. Yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 2H), 7.41 – 7.33 (m, 3H), 7.30 – 7.16 (m, 5H), 5.42 (d, 1H, J = 4.0 Hz), 3.62 – 3.58 (m, 1H), 3.33 – 3.28 (m, 1H), 2.75 – 2.63 (m, 3H), 2.54 – 2.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.3 (C), 180.2 (C), 149.0 (C), 138.6 (C), 133.2 (C), 129.8 (CH), 129.1 (CH), 128.7 (CH), 128.4 (CH), 126.4 (CH), 124.9 (CH), 117.0 (C), 103.6 (CH), 41.2 (CH2), 33.6 (CH), 31.8 (CH2), 25.7 (CH2); HRMS (ESI) *m/z* 303.1394 ($[M+H]^+$ $C_{21}H_{19}O_2$ requires 303.1385).



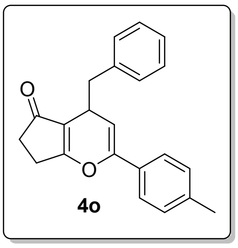
7,7-dimethyl-2,4-diphenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4m)

Yellow solid compound. Mp: 141-143 °C (lit.[6] 142-143 °C). Yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 2H), 7.40 – 7.27 (m, 7H), 7.19 (t, 1H, J = 7 Hz), 5.74 (d, 1H, J = 5.0 Hz), 4.52 (d, 1H, J = 5.0 Hz), 2.58 (s, 2H), 2.27 (ABq, 2H, J = 16.5 Hz), 1.16 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5 (C), 164.8 (C), 146.9 (C), 145.4 (C), 133.2 (C), 128.9 (CH), 128.6 (CH), 128.6 (CH), 128.4 (CH), 126.8 (CH), 124.7 (CH), 112.7 (C), 104.7 (CH), 51.1 (CH2), 41.7 (CH), 35.6 (CH2), 32.3 (C), 29.4 (CH3), 27.9 (CH3); HRMS (ESI) *m/z* 331.1716 ($[M+H]^+$ $C_{23}H_{23}O_2$ requires 331.1698).



4-(4-bromophenyl)-7,7-dimethyl-2-phenyl-4,6,7,8-tetrahydro-5*H*-chromen-5-one (4n)[3]

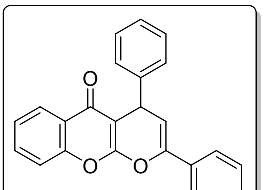
Pale yellow solid compound. Mp: 93-94 °C. Yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 2H), 7.43 – 7.35 (m, 5H), 7.23 (d, 2H, J = 8.5 Hz), 5.68 (d, 1H, J = 5.0 Hz), 4.49 (d, 1H, J = 5.0 Hz), 2.57 (s, 2H), 2.26 (ABq, 2H, J = 16.0 Hz), 1.15 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4 (C), 164.9 (C), 147.3 (C), 144.5 (C), 132.9 (C), 131.7 (CH), 130.2 (CH), 129.1 (CH), 128.7 (CH), 124.7 (CH), 120.6 (C), 112.4 (C), 103.9 (CH), 51.1 (CH2), 41.6 (CH2), 35.2 (CH), 32.4 (C), 29.4 (CH3), 27.8 (CH3); HRMS (ESI) *m*/*z* 425.0768 ($[M+H]^+$ $C_{23}H_{22}O_3Br$ requires 425.0752)



4-benzyl-2-(p-tolyl)-6,7-dihydrocyclopenta[*b*]pyran-5(4*H*)-one (4o)

Yellow solid compound. Mp: 125-126 °C. Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, J = 8.5 Hz), 7.30 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 7.20 – 7.15 (m, 4H), 5.37 (d, 1H, J = 4.0 Hz), 3.62 – 3.55 (m, 1H), 3.30 (dd, 1H, J = 13.0, 3.5 Hz), 2.71 (dd, 1H, J = 13.0, 9.0 Hz), 2.67 - 2.63 (m, 2H), 2.54 – 2.50 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.3 (C), 180.2 (C), 149.0 (C), 139.1 (C), 138.6 (C), 130.3 (C), 129.8 (CH), 129.3 (CH), 128.3 (CH), 126.4 (CH), 124.8 (CH), 117.0 (C), 102.7 (CH), 41.2 (CH_2), 33.6 (CH), 31.8

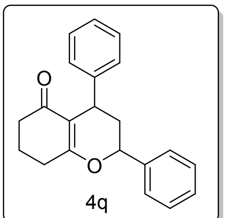
(CH_2), 25.7 (CH_2), 21.4 (CH_3); HRMS (ESI) *m/z* 317.1554 ($[M+H]^+$ $C_{22}H_{21}O_2$ requires 317.1542)



4p

2,4-diphenyl-4*H*,5*H*-pyrano[2,3-*b*]chromen-5-one (4p)

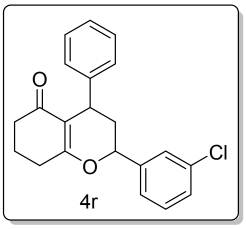
Yellow solid compound. Mp: 158-159 °C. Yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 – 8.03 (m, 1H), 7.79 – 7.74 (m, 2H), 7.62 – 7.57 (m, 1H), 7.50 – 7.41 (m, 5H), 7.40 -7.32 (m, 4H), 7.28 – 7.23 (m, 1H), 5.87 (d, 1H, J = 4.5 Hz), 4.74 (d, 1H, J = 4.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.7 (C), 156.0 (C), 153.0 (C), 147.1 (C), 143.7 (C), 132.8 (C), 132.2 (CH), 129.5 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.4 (CH), 124.9 (CH), 124.0 (CH), 123.0 (CH), 117.1 (CH), 114.8 (C), 104.0 (CH), 103.9 (C), 36.8 (CH); HRMS (ESI) *m/z* 353.1198 ($[M+H]^+$ $C_{24}H_{17}O_3$ requires 353.1178)



4q

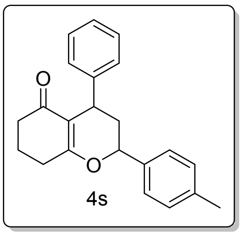
2,4-diphenyl-2,3,4,6,7,8-hexahydro-5*H*-chromen-5-one (4q)

White solid compound. Mp: 127-129 °C (lit.[7] 129-130 °C). Yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.36 (m, 4H), 7.34-7.31 (m, 1H), 7.26-7.23 (m, 2H), 7.19-7.13 (m, 3H), 4.97 (dd, 1H, J = 11.5, 1.5 Hz), 3.97-3.93 (m, 1H), 2.64-2.24 (m, 5H), 2.05-1.96 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8 (C), 173.1 (C), 145.0 (C), 139.3 (C), 128.6 (CH), 128.3 (CH), 128.3 (CH), 126.4 (CH), 126.0 (CH), 125.9 (CH), 115.6 (C), 79.0 (CH), 41.7 (CH_2), 37.1 (CH_2), 36.9 (CH), 29.2 (CH_2), 20.2 (CH_2); HRMS (ESI) *m*/*z* 305.1555 ($[M+H]^+$ $C_{21}H_{21}O_2$ requires 305.1542)



2-(3-chlorophenyl)-4-phenyl-2,3,4,6,7,8-hexahydro-5*H*-chromen-5-one (4r)

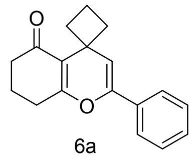
White solid compound. Mp: 150-151 °C. Yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.30-7.28 (m, 2H), 7.26-7.23 (m, 3H), 7.17-7.13 (m, 3H), 4.96 (dd, 1H, J = 11.5, 1.5 Hz), 3.96-3.92 (m, 1H), 2.67-2.36 (m, 5H), 2.07-1.91 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4 (C), 172.8 (C), 144.6 (C), 141.5 (C), 134.4 (C), 130.0 (CH), 128.5 (CH), 128.5 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 124.1 (CH), 115.6 (C), 78.1 (CH), 41.7 (CH_2), 37.7 (CH_2), 36.8 (CH), 29.0 (CH_2), 20.1 (CH_2); HRMS (ESI) *m*/*z* 339.1162 ($[M+H]^+$ $C_{21}H_{20}O_2Cl$ requires 339.1152).



4-phenyl-2-(p-tolyl)-2,3,4,6,7,8-hexahydro-5*H*-chromen-5-one (4s)

White solid compound. Mp: 121-123 °C. Yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 5H), 7.21 – 7.14 (m, 4H), 4.94 (d, 1H, J = 10.5 Hz), 3.96 – 3.91 (m, 1H), 2.64 –2.39 (m, 3H), 2.35 (s, 3H), 2.36 – 2.17 (m, 2H), 2.05-1.97 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.7 (C), 173.2 (C), 145.0 (C), 138.2 (C), 136.3 (C), 129.2 (CH), 128.3 (CH), 126.3 (CH), 126.1 (CH), 125.8 (CH), 115.5 (C), 79.0 (CH), 41.6 (CH_2), 38.0 (CH_2), 36.9 (CH), 29.1

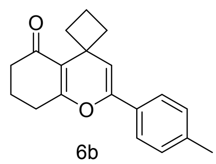
(CH_2), 21.1 (CH_2), 20.0 (CH_3); HRMS (ESI) *m/z* 319.1708 ($[M+H]^+$ $C_{22}H_{23}O_2$ requires 319.1698)



6a

2-phenyl-7,8-dihydrospiro[chromene-4,1'-cyclobutan]-5(6*H*)-one (6a)

Yellow solid compound. Mp: 77-78 °C. Yield: 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, 2H, J = 7.0 Hz), 7.40 (t, 1H, J = 7.0 Hz), 7.37 (d, 2H, J = 7.0 Hz), 5.87 (s, 1H), 3.16 – 3.07 (m, 2H), 2.56 (t, 2H, J = 6.5 Hz), 2.47 (t, 2H, J = 6.5 Hz), 2.14 – 2.0 (m, 4H), 1.88 – 1.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.2 (C), 166.3 (C), 143.8 (C), 133.3 (C), 128.6 (CH), 128.6 (CH), 124.4 (CH), 115.7 (C), 111.3 (CH), 39.0 (CH_2), 36.6 (CH_2), 35.9 (CH_2), 29.9 (C), 28.4 (CH_2), 20.7 (CH_2), 14.2 (CH_2); HRMS (ESI) *m/z* 267.1389 ($[M+H]^+$ $C_{18}H_{19}O_2$ requires 267.1385)

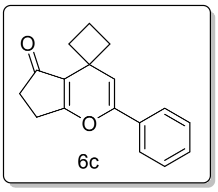


6b

2-(p-tolyl)-7,8-dihydrospiro[chromene-4,1'-cyclobutan]-5(6*H*)-one (6b)

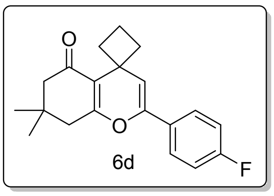
White solid compound. Mp: 128-129 °C. Yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 8.0 Hz), 5.79 (s, 1H), 3.11 - 3.05 (m, 2H), 2.53 (t, 2H, J = 6.0 Hz), 2.44 (t, 2H, J = 6.0 Hz), 2.36 (s, 3H), 2.10 – 1.95 (m, 4H), 1.85 – 1.78 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.9 (C), 166.1 (C), 143.5 (C), 138.3 (C), 130.2 (C), 129.0 (CH), 124.0 (CH), 115.4 (C), 110.2 (CH), 38.7 (CH_2), 36.3 (CH_2), 35.6 (CH_2), 29.6 (C), 28.1

(CH_2), 21.1 (CH_2), 20.4 (CH_3), 13.9 (CH_2); HRMS (ESI) *m/z* 281.1563 ($[M+H]^+$ $C_{19}H_{21}O_2$ requires 281.1542).



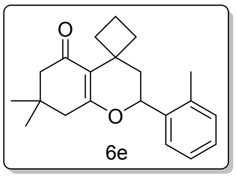
2'-phenyl-6',7'-dihydro-5'*H*-spiro[cyclobutane-1,4'-cyclopenta[b]pyran]-5'-one (6c)

White solid compound. Mp: 100-101 °C. Yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 – 7.53 (m, 2H), 7.35 – 7.27 (m, 3H), 5.79 (s, 1H), 2.85 – 2.77 (m, 2H), 2.61 – 2.57 (m, 2H), 2.45 – 2.41 (m, 2H), 2.09 - 1.82 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4 (C), 178.3 (C), 146.5 (C), 133.1 (C), 129.0 (CH), 128.7 (CH), 124.8 (CH), 119.7 (C), 110.5 (CH), 35.8 (CH_2), 35.6 (CH_2), 34.0 (CH_2), 29.9 (C), 25.2 (CH_2), 15.2 (CH_2); HRMS (ESI) *m/z* 253.1218 ($[M+H]^+$ $C_{17}H_{17}O_2$ requires 253.1229).



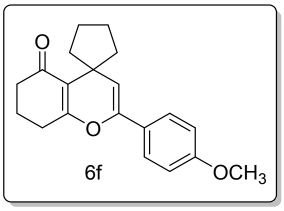
2-(4-fluorophenyl)-7,7-dimethyl-7,8-dihydrospiro[chromene-4,1'-cyclobutan]-5(6*H*)-one (6d)

White solid compound. Mp: 124-125 °C. Yield: 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 – 7.53 (m, 2H), 7.10-7.03 (m, 2H), 5.78 (s, 1H), 3.11 – 3.03 (m, 2H), 2.40 (s, 2H), 2.31 (s, 2H), 2.12 – 2.01 (m, 2H), 1.87 – 1.79 (m, 2H), 1.11 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.0 (C), 164.3 (C), 162.9 (d, C, J = 246.5 Hz), 143.1 (C), 129.4 (C), 126.3 (d, CH, J = 8.75 Hz), 115.5 (d, CH, J = 21.25 Hz), 114.5 (C), 111.0 (CH), 52.7 (CH_2), 42.0 (CH_2), 36.6 (CH_2), 35.7 (CH_2), 31.8 (C), 29.9 (C), 28.4 (CH_3), 28.4 (CH_3), 14.2 (CH_2); HRMS (ESI) *m/z* 313.1599 ($[M+H]^+$ $C_{20}H_{22}O_2F$ requires 313.1604).



7,7-dimethyl-2-(o-tolyl)-2,3,7,8-tetrahydrospiro[chromene-4,1'-cyclobutan]-5(6H)-one (6e)

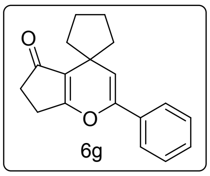
White solid compound. Mp: 110-111 °C. Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, 1H, J = 7.5 Hz), 7.16 – 7.02 (m, 3H), 4.83 (d, 1H, J = 10.5 Hz), 3.10 (q, 1H, J = 10.5 Hz), 2.6 (q, 1H, J = 10.5 Hz), 2.24 (s, 3H), 2.19-2.15 (m, 4H), 2.02 - 1.79 (m, 4H), 1.75 –1.51 (m, 2H), 0.95 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9 (C), 169.4 (C), 137.8 (C), 134.4 (C), 130.4 (CH), 127.8 (CH), 126.2 (CH), 125.4 (CH), 115.9 (C), 73.7 (CH), 51.9 (CH_2), 44.0 (CH_2), 42.6 (CH_2), 36.2 (CH_2), 33.4 (C), 31.2 (CH_2), 30.3 (C), 29.1 (CH_3), 27.1 (CH_3), 18.8 (CH_3), 14.3 (CH_2); HRMS (ESI) m/z 311.2017 ($[M+H]^+$ $C_{21}H_{27}O_2$ requires 311.2011).



2-(4-methoxyphenyl)-7,8-dihydrospiro[chromene-4,1'-cyclopentan]-5(6H)-one (6f)

Yellow semi-solid compound. Yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, 2H, J = 9.0 Hz), 6.82 (d, 2H, J = 9.0 Hz), 5.24 (s, 1H), 3.76 (s, 3H), 2.49 (t, 2H, J = 6.5 Hz), 2.34 (t, 2H, J = 6.5 Hz), 2.25 – 2.17 (m, 2H), 1.99 – 1.92 (m, 4H), 1.89 – 1.84 (m, 2H), 1.66 – 1.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4 (C), 166.4 (C), 159.6 (C), 141.8 (C), 135.1 (C), 125.5 (CH), 116.2 (C), 113.6 (CH), 109.6 (C), 55.2 (CH_3), 42.2 (CH_2), 38.8 (CH_2), 38.8

(CH_2), 32.1 (C), 28.3 (CH_2), 26.2 (CH_2), 20.5 (CH_2), 14.0 (CH_2); HRMS (ESI) *m/z* 311.2939 ($[M+H]^+$ $C_{21}H_{23}O_3$ requires 311.1647).



2'-phenyl-6',7'-dihydro-5'H-spiro[cyclopentane-1,4'-cyclopenta[b]pyran]-5'-one (6g)

Yellow solid compound. Mp: 191-192 °C. Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 2H), 7.41 – 7.33 (m, 3H), 5.49 (s, 1H), 2.70 – 2.66 (m, 2H), 2.50 – 2.46 (m, 2H), 2.25 – 2.13 (m, 2H), 1.94 – 1.88 (m, 2H), 1.78 – 1.73 (m, 2H), 1.58-1.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.7 (C), 178.4 (C), 145.1 (C), 133.0 (C), 128.5 (CH_2), 128.3 (CH_2), 124.5 (CH_2), 120.1 (C), 110.2 (CH), 40.8 (CH_2), 39.7 (CH_2), 33.6 (CH_2), 29.6 (C), 25.3 (CH_2), 25.0 (CH_2), 14.0 (CH_2); HRMS (ESI) *m/z* 267.1630 ($[M+H]^+$ $C_{18}H_{19}O_2$ requires 267.1385).

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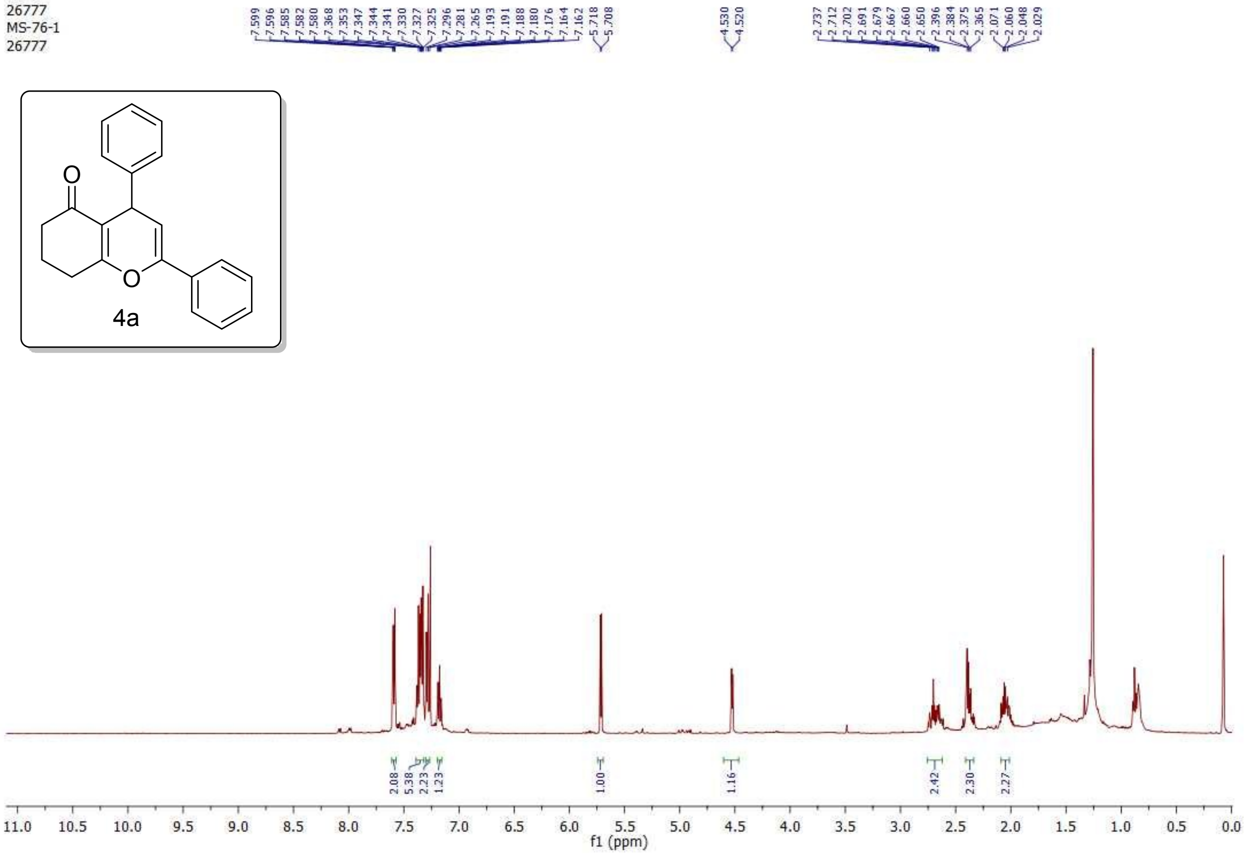
Spectra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26777
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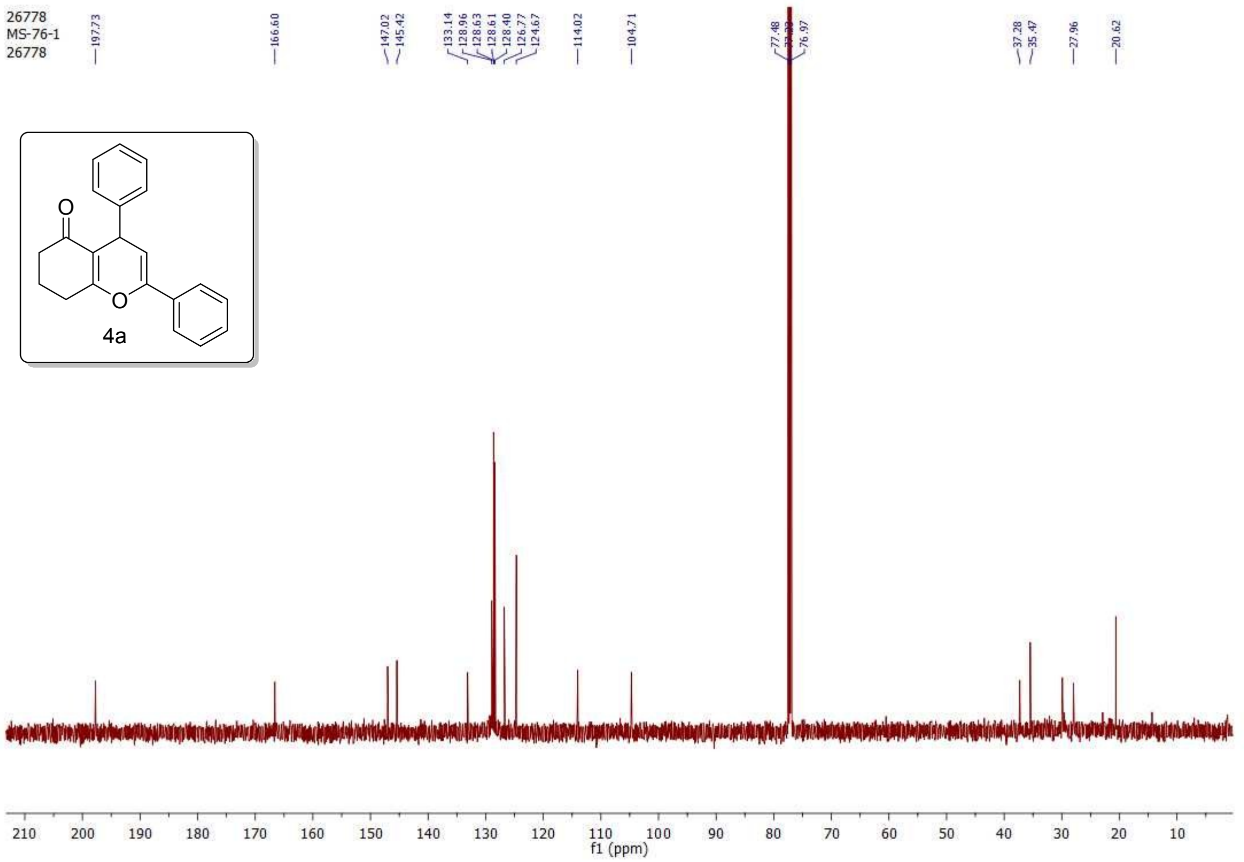
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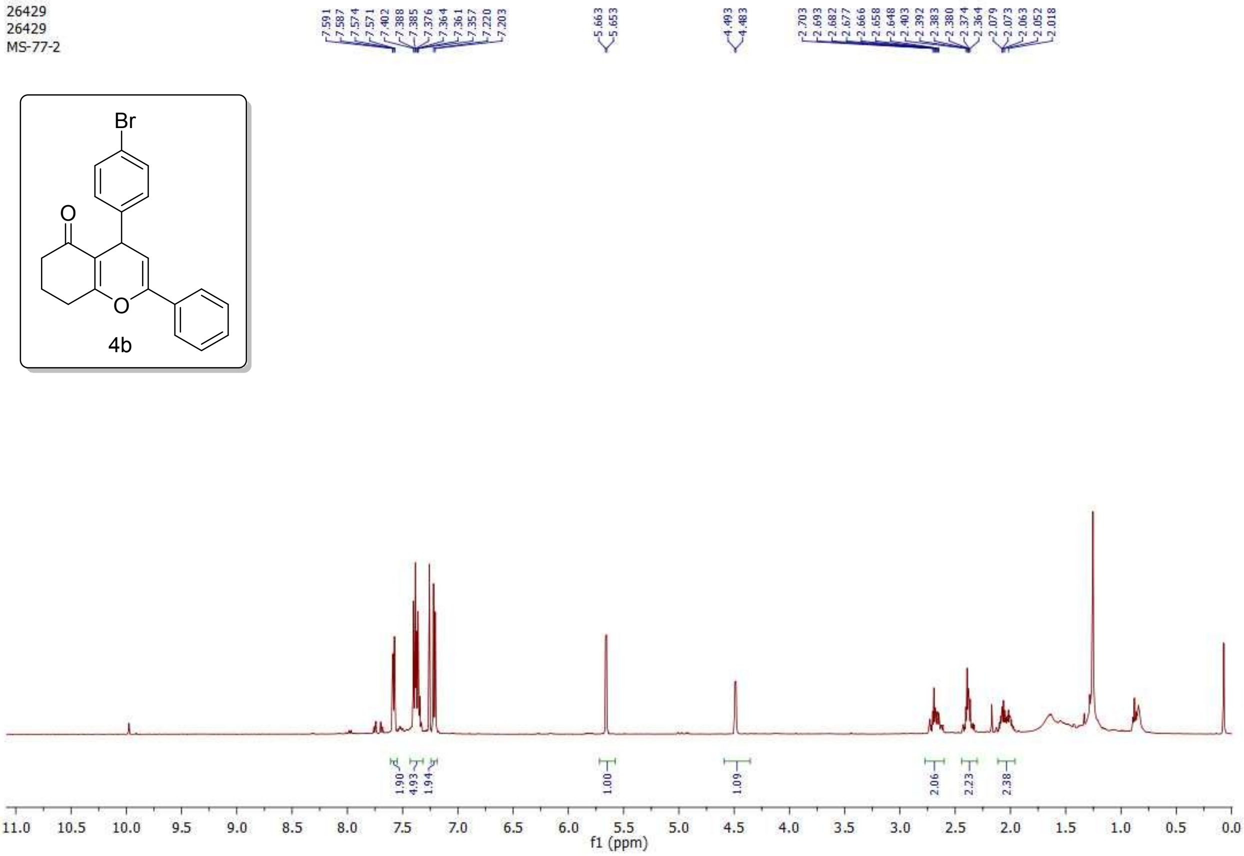
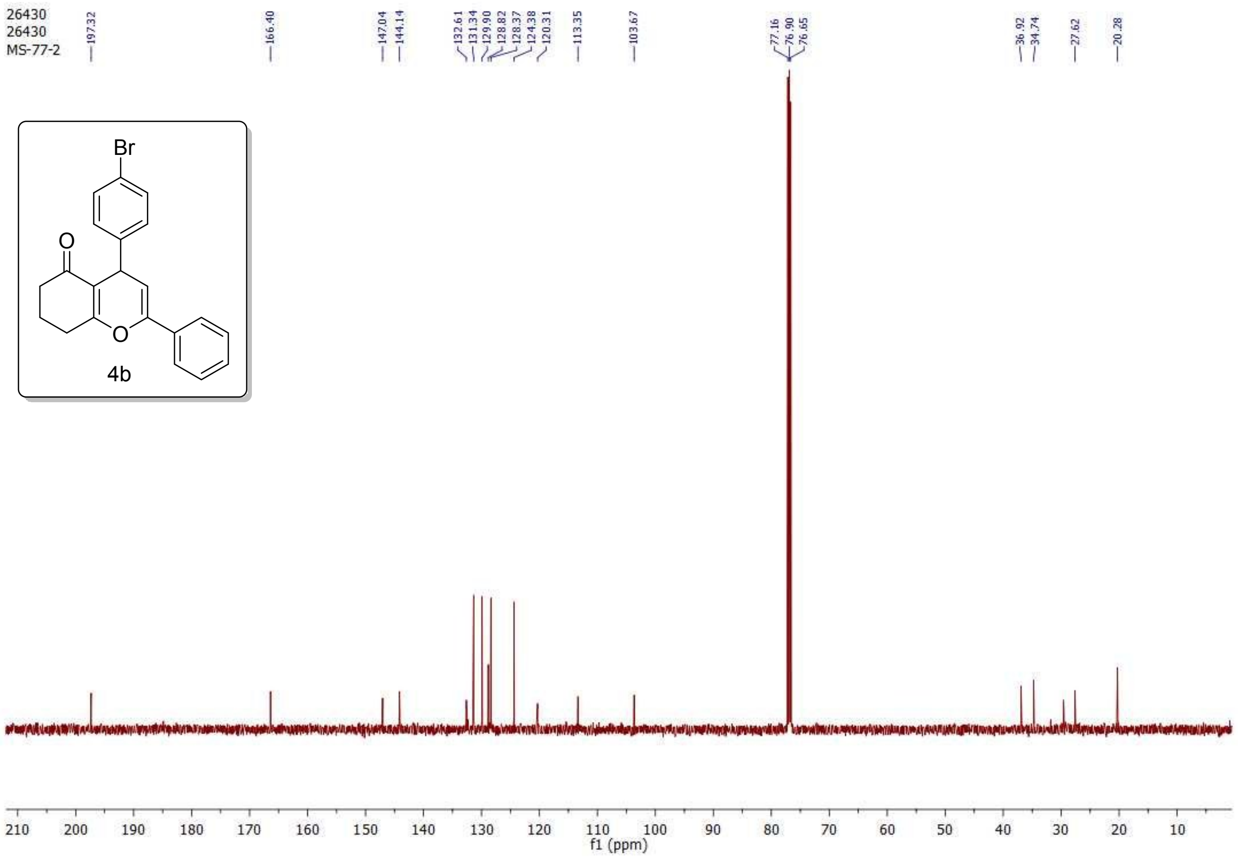
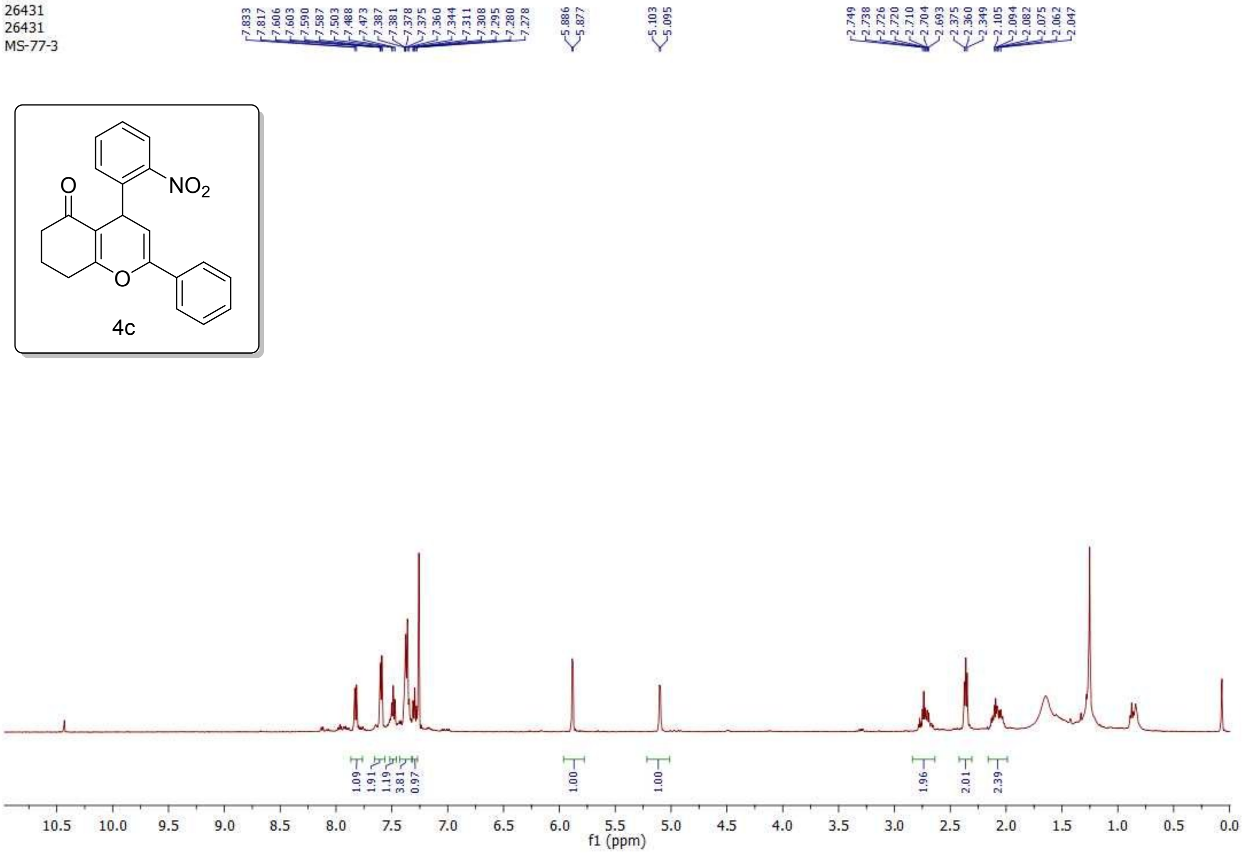
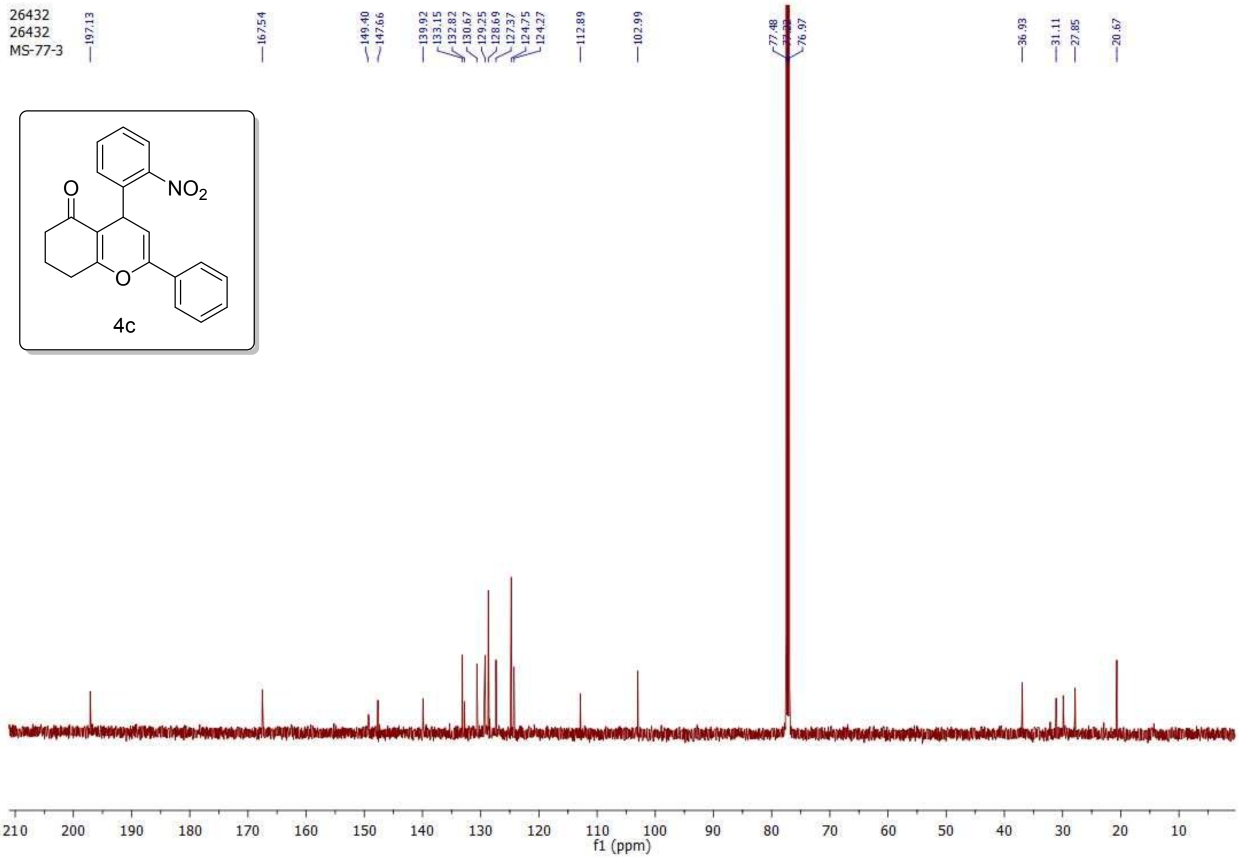
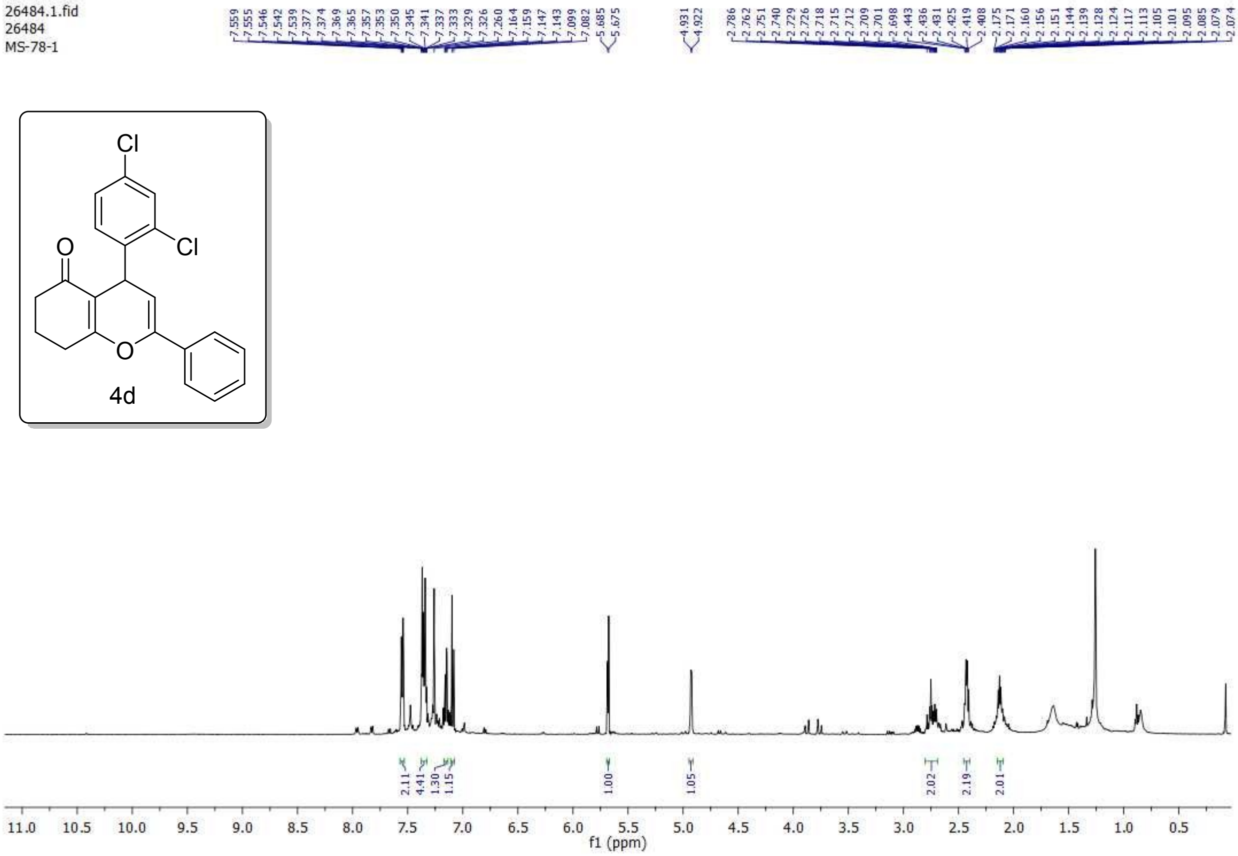
MS-76-1
26778
197.73 166.60 147.02 145.42 133.14 128.96 128.63 128.61 128.40 126.77 124.67 114.02 104.71 77.48 76.97 37.28 35.47 27.96 20.62
4a
f1 (ppm)

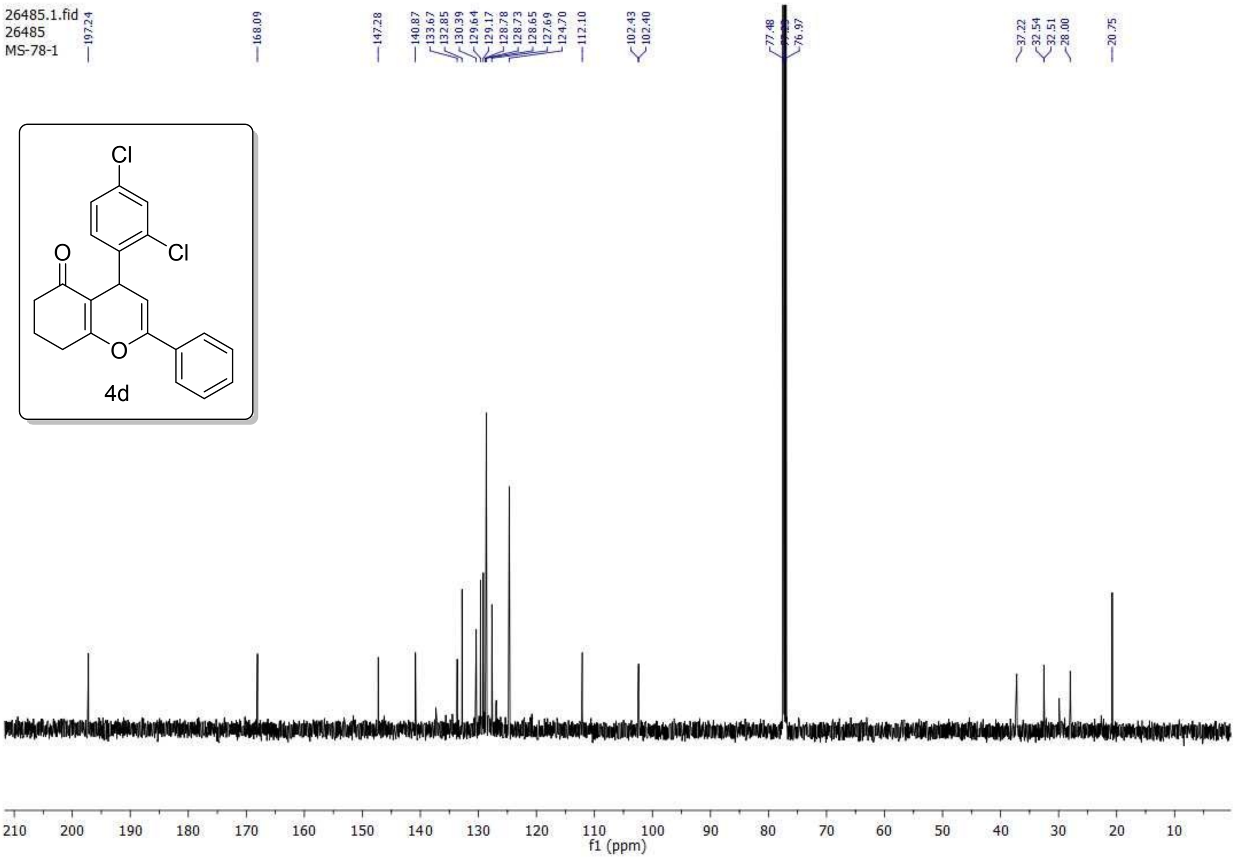

26429
26429
MS-77-2
7.591 7.587 7.574 7.571 7.402 7.388 7.385 7.376 7.364 7.361 7.357 7.220 7.203
5.663 5.653
4.493 4.483
2.703 2.693 2.682 2.677 2.666 2.658 2.648 2.403 2.392 2.383 2.380 2.374 2.364 2.079 2.073 2.063 2.052 2.018
Br
O
O
4b
1.90 4.93 1.94
1.00
1.09
2.06 2.23 2.38
11.0 10.5 10.0 9.5 9.0 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 0.5 0.0
f1 (ppm)

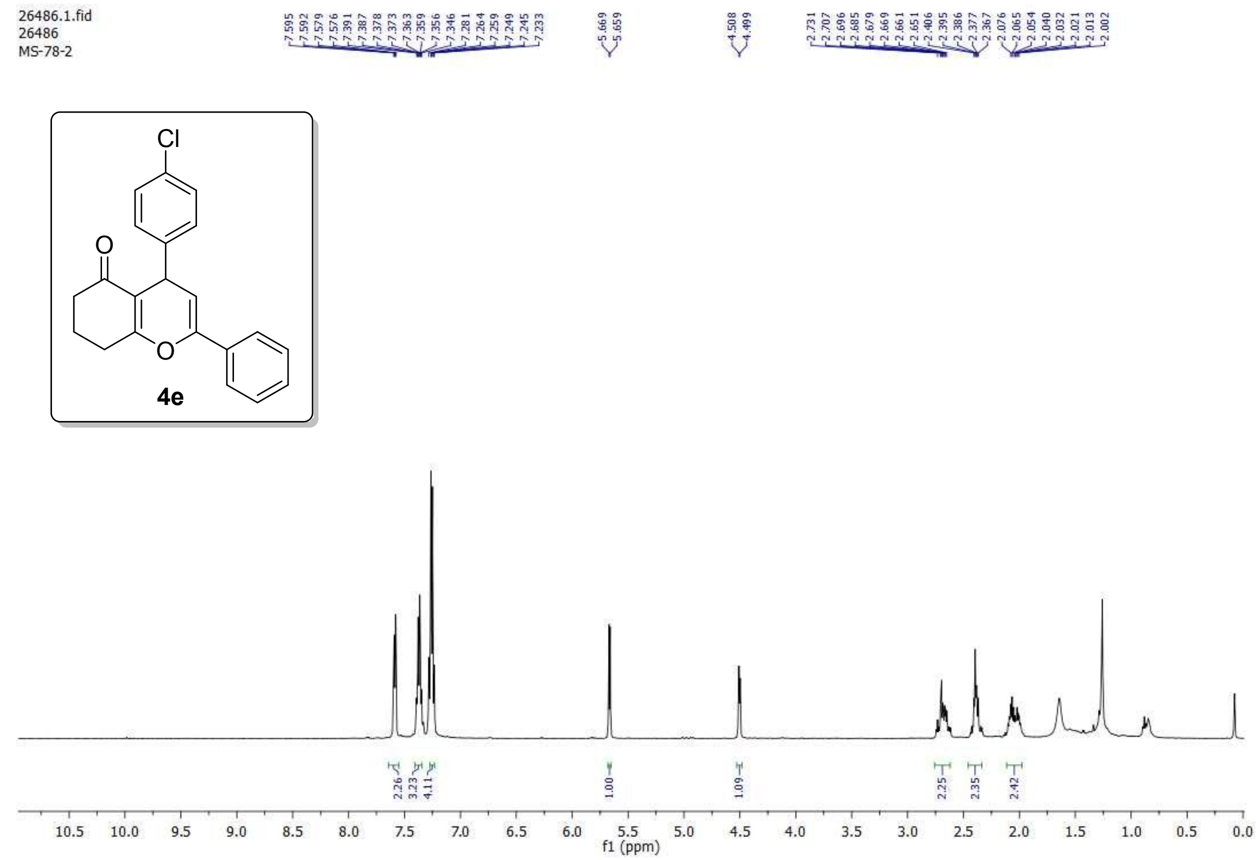

26430
26430
MS-77-2
197.32
166.40
147.04 144.14
132.61 131.34 129.90 128.82 128.37 124.38 120.31
113.35
103.67
77.16 76.90 76.65
36.92 34.74
27.62
20.28
Br
O
O
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


26431
26431
MS-77-3
7.833 7.817 7.606 7.603 7.590 7.587 7.503 7.488 7.473 7.387 7.381 7.378 7.375 7.360 7.344 7.311 7.308 7.295 7.280 7.278
5.886 5.877
5.103 5.095
2.749 2.738 2.726 2.720 2.710 2.704 2.693 2.375 2.360 2.349 2.105 2.094 2.082 2.075 2.062 2.047
NO2
O
O
4c
1.09 1.91 1.19 3.81 0.97
1.00
1.00
1.96 2.01 2.39
10.5 10.0 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 0.5 0.0
f1 (ppm)

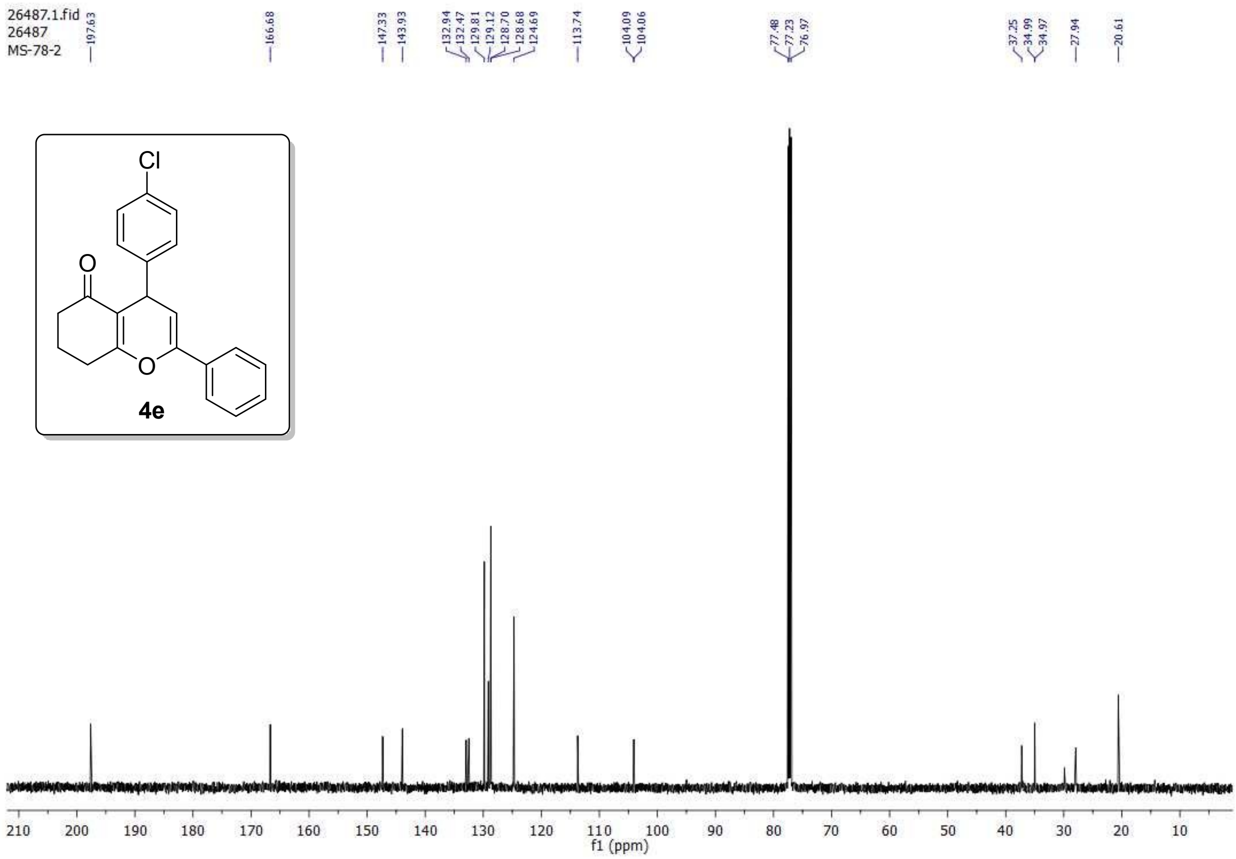

26432
26432
MS-77-3
197.13
167.54
149.40 147.66
139.92 133.15 132.82 130.67 129.25 128.69 127.37 124.75 124.27
112.89
102.99
77.48 76.97
36.93
31.11 27.85
20.67
NO2
O
O
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


26484.1.fid
26484
MS-78-1
7.559 7.555 7.546 7.542 7.539 7.377 7.374 7.369 7.365 7.357 7.353 7.350 7.345 7.341 7.337 7.333 7.329 7.326 7.260 7.164 7.159 7.147 7.143 7.099 7.082 5.685 5.675
4.931 4.922
2.786 2.762 2.751 2.740 2.729 2.726 2.718 2.715 2.712 2.709 2.701 2.698 2.443 2.436 2.431 2.425 2.419 2.408 2.175 2.171 2.160 2.156 2.151 2.144 2.139 2.128 2.124 2.117 2.113 2.105 2.101 2.095 2.085 2.079 2.074
Cl
Cl
O
O
4d
2.11 4.41 1.30 1.15 1.00 1.05 2.02 2.19 2.01
11.0 10.5 10.0 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 0.5
f1 (ppm)

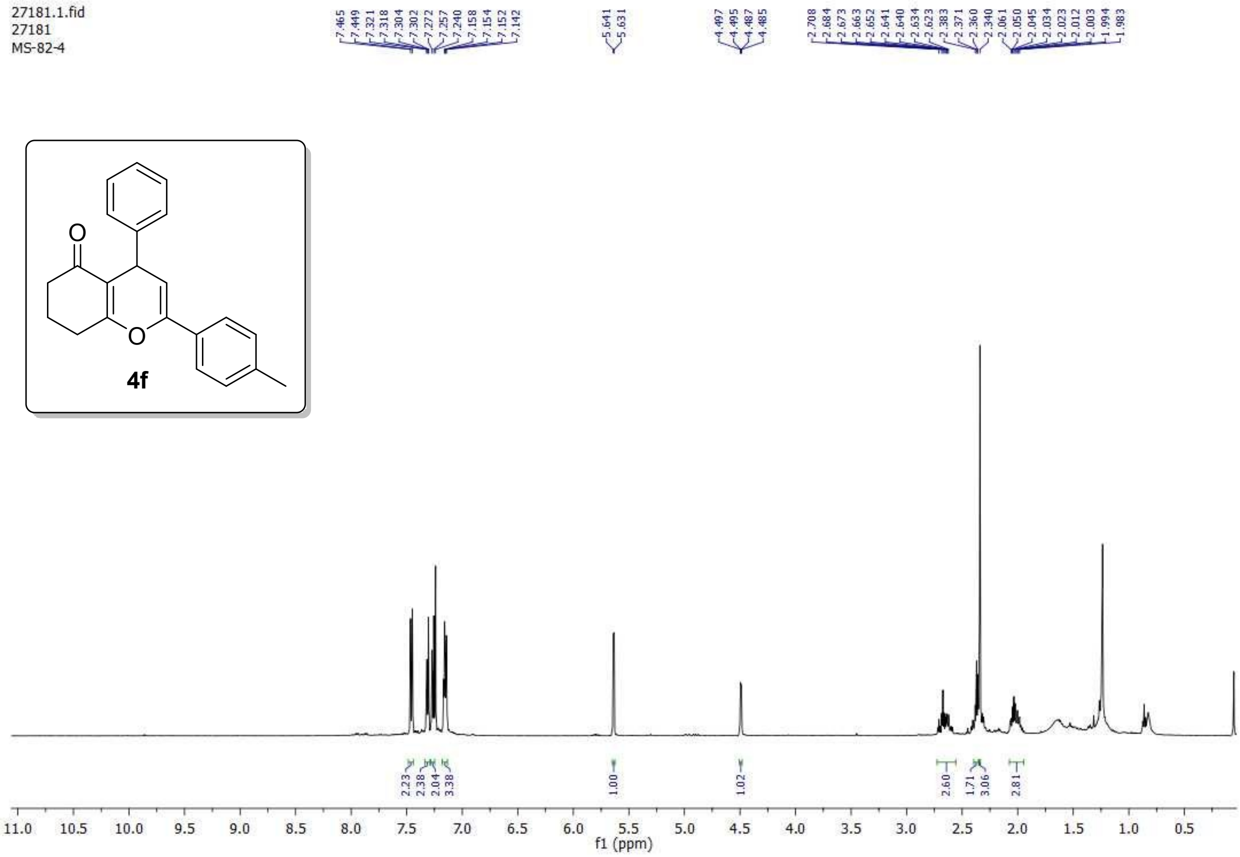

26485.1.fid
26485
MS-78-1
197.24
168.09
147.28
140.87 133.67 132.85 130.39 129.64 129.17 128.78 128.73 128.65 127.69 124.70
112.10
102.43 102.40
77.48 76.97
37.22 32.54 32.51 28.00
20.75
Cl
Cl
O
O
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

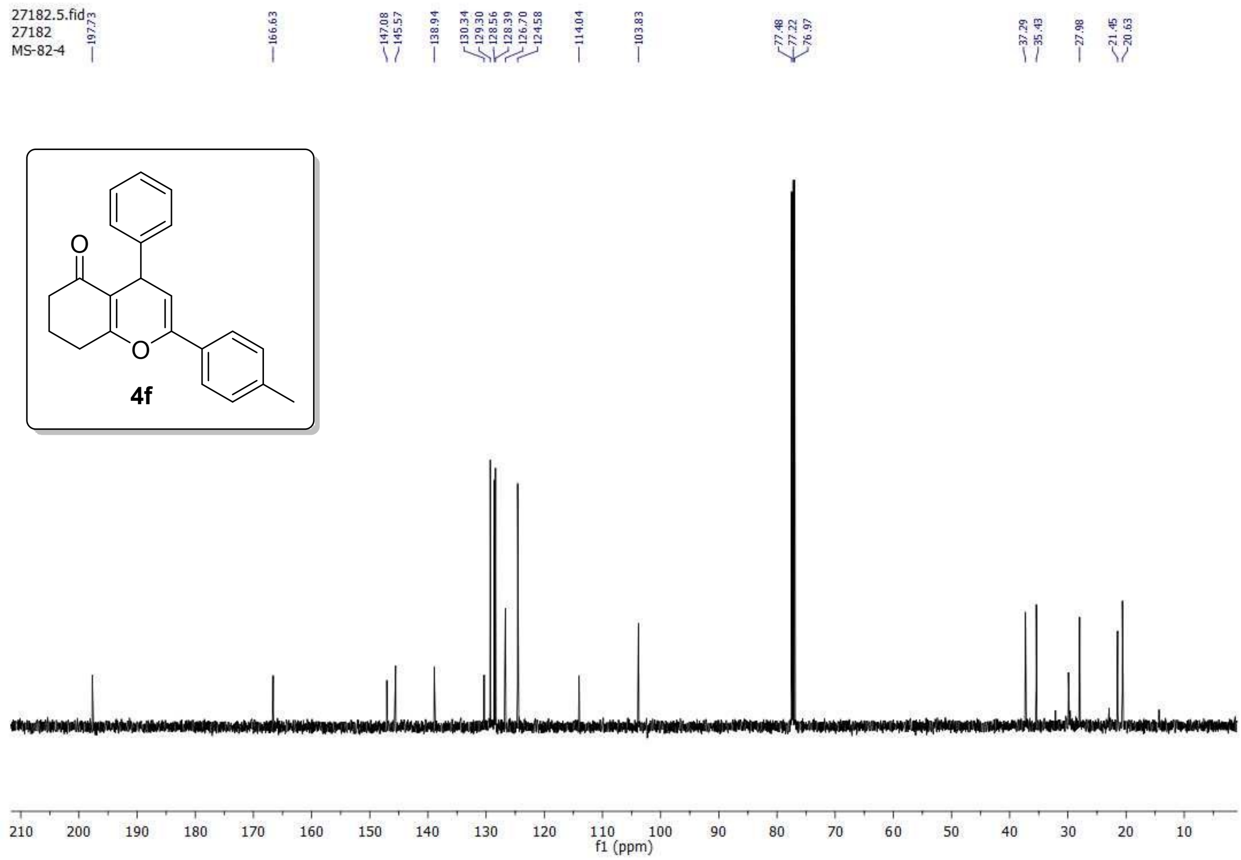


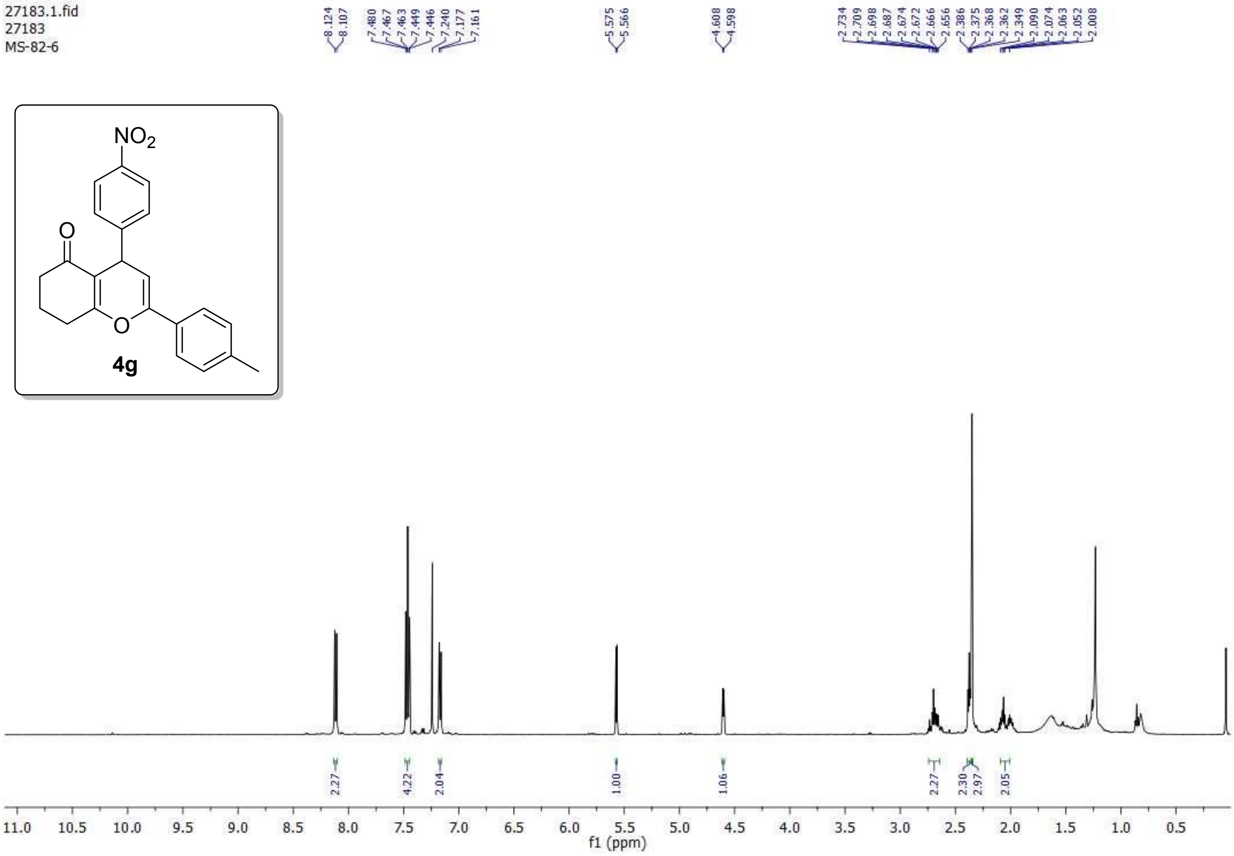
26486.1.fid
26486
MS-78-2
7.595 7.592 7.579 7.576 7.391 7.387 7.378 7.373 7.363 7.359 7.356 7.346 7.281 7.264 7.259 7.249 7.245 7.233
5.669 5.659
4.508 4.499
2.731 2.707 2.696 2.685 2.679 2.669 2.661 2.651 2.406 2.395 2.386 2.377 2.367 2.076 2.065 2.054 2.040 2.032 2.021 2.013 2.002
Cl
O
O
4e
2.26 3.23 4.11 1.00 1.09 2.25 2.35 2.42
10.5 10.0 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 0.5 0.0
f1 (ppm)

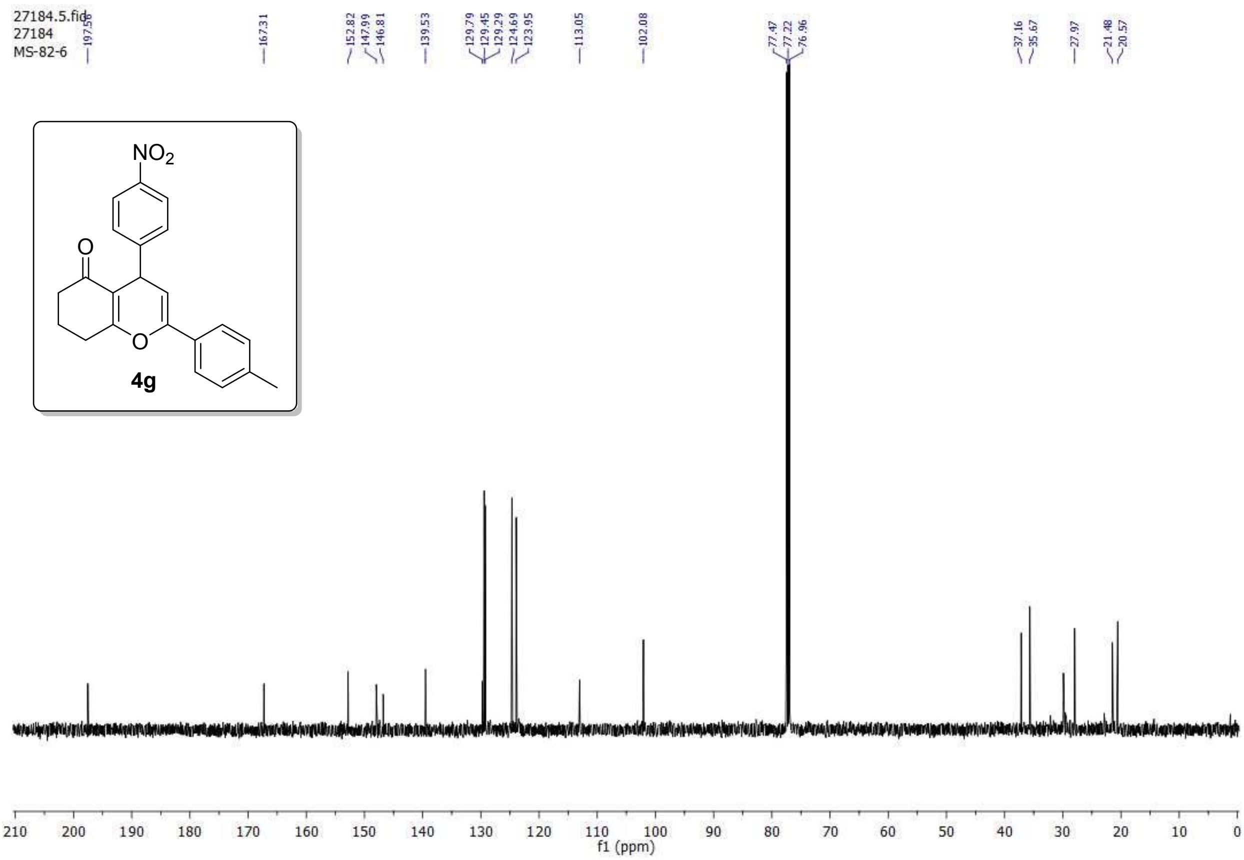


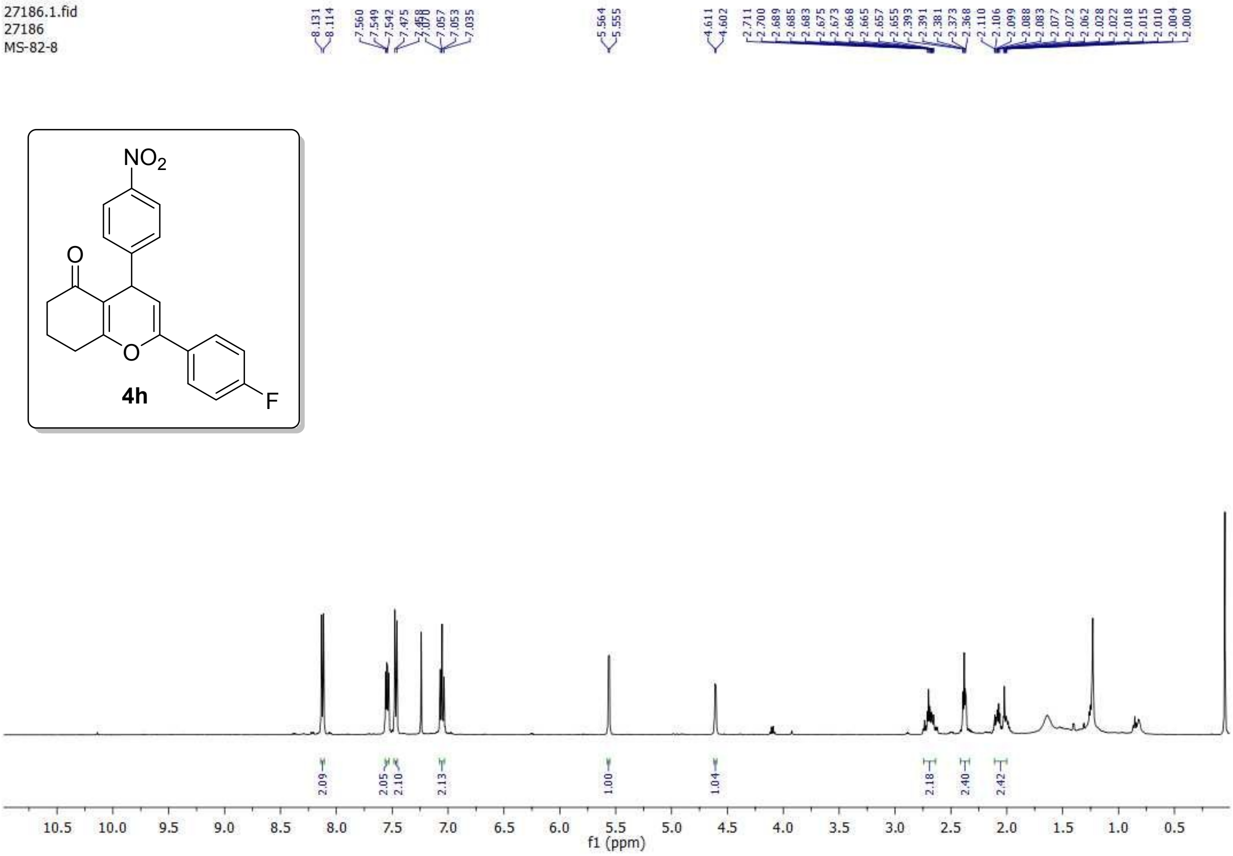
26487.1.fid
26487
MS-78-2
197.63
166.68
147.33 143.93
132.94 132.47 129.81 129.12 128.70 128.68 124.69
113.74
104.09 104.06
77.48 77.23 76.97
37.25 34.99 34.97 27.94 20.61
Cl
O
O
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

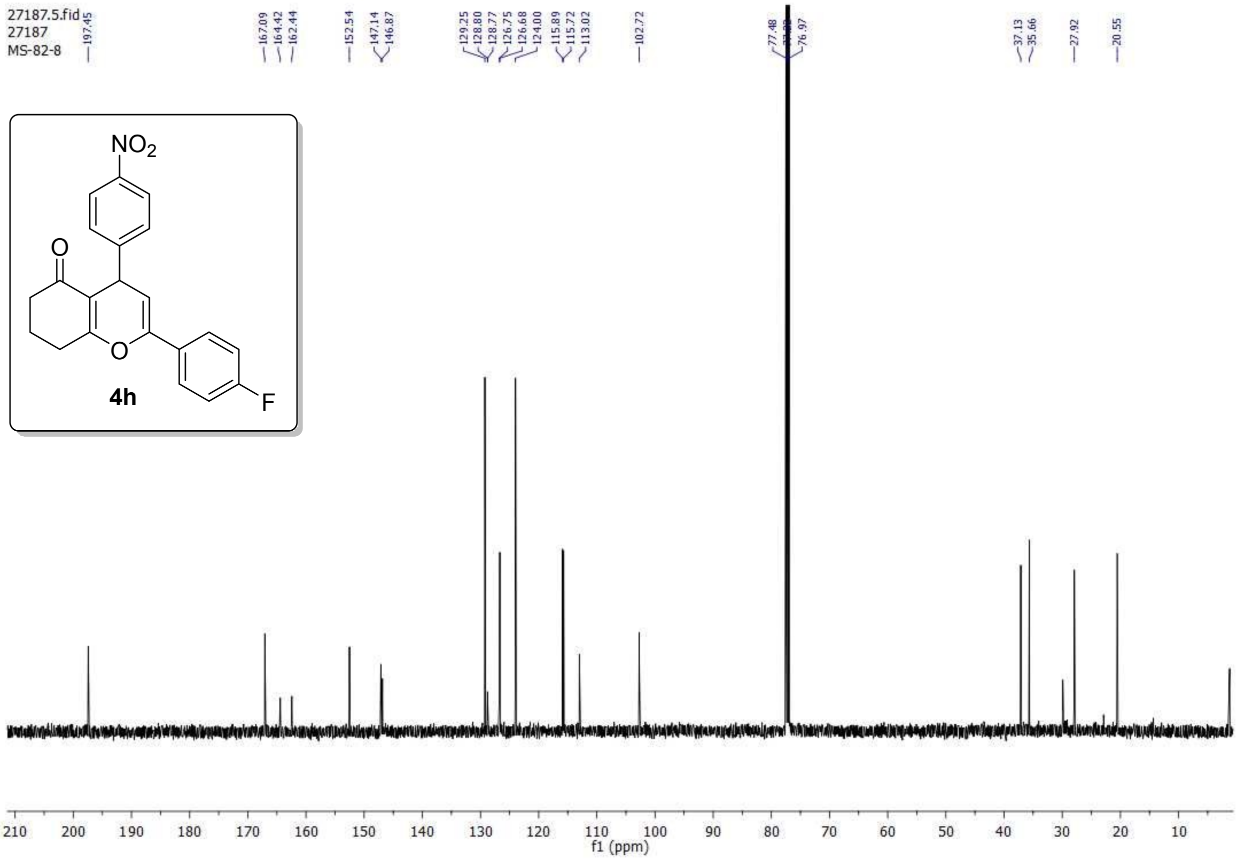

27181.1.fid
27181
MS-82-4
7.465
7.449
7.321
7.318
7.304
7.302
7.272
7.257
7.240
7.158
7.154
7.152
7.142
5.641
5.631
4.497
4.495
4.487
4.485
2.708
2.684
2.673
2.663
2.652
2.641
2.640
2.634
2.623
2.383
2.371
2.360
2.340
2.061
2.050
2.045
2.034
2.023
2.012
2.003
1.994
1.983
O
O
4f
2.23
2.38
2.04
3.38
1.00
1.02
2.60
1.71
3.06
2.81
11.0 10.5 10.0 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 0.5
f1 (ppm)

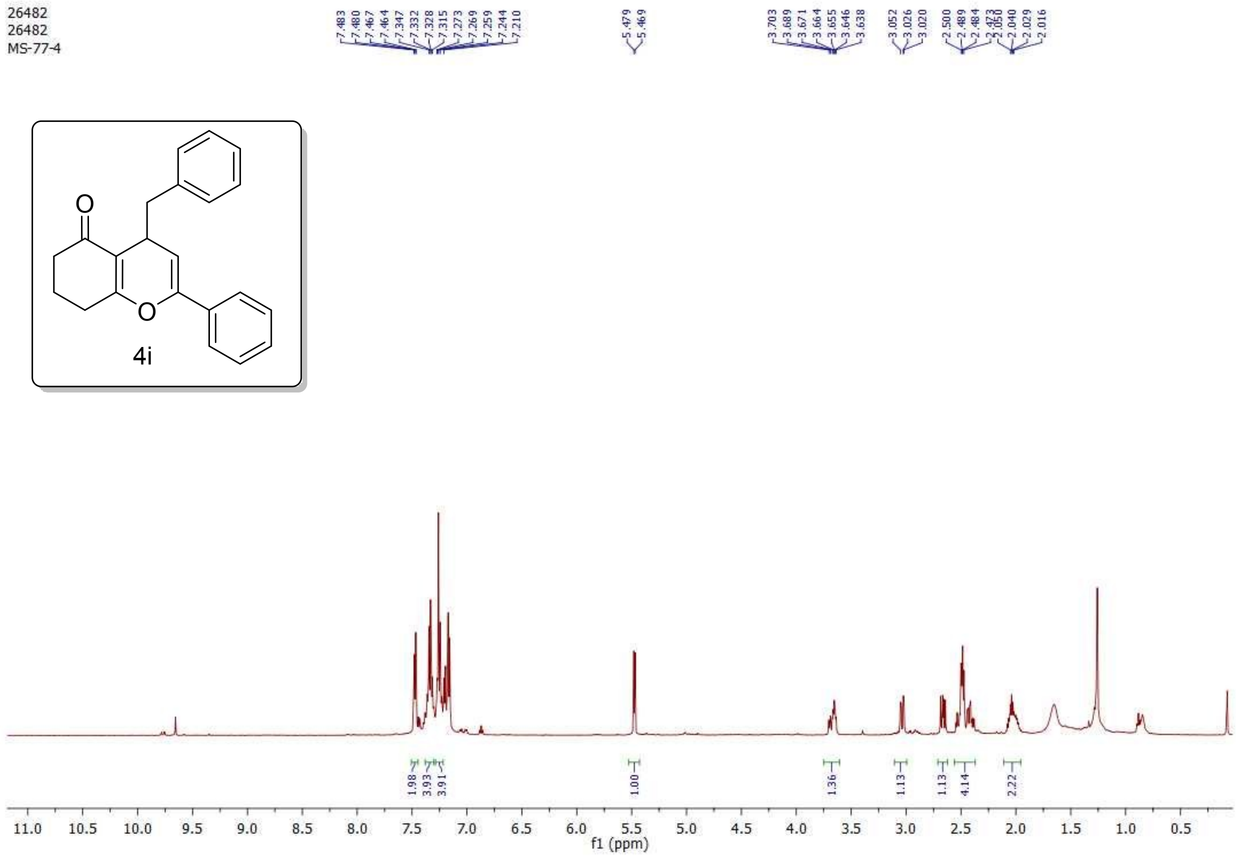

27182.5.fid
27182
MS-82-4
197.73
166.63
147.08
145.57
138.94
130.34
129.30
128.56
128.39
126.70
124.58
114.04
103.83
77.48
77.22
76.97
37.29
35.43
27.98
21.45
20.63
O
O
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

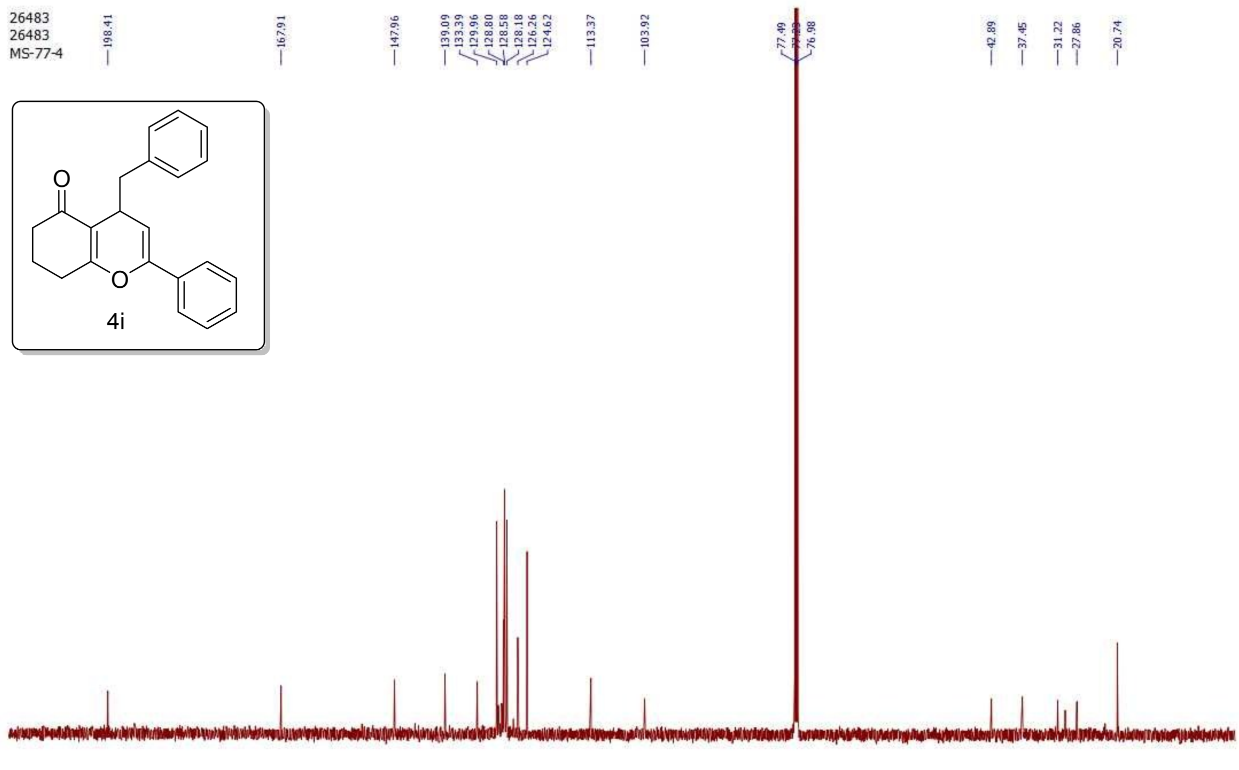

27183.1.fid
27183
MS-82-6
8.124
8.107
7.480
7.467
7.463
7.449
7.446
7.240
7.177
7.161
5.575
5.566
4.608
4.598
2.734
2.709
2.698
2.687
2.674
2.672
2.666
2.656
2.386
2.375
2.368
2.362
2.349
2.090
2.074
2.063
2.052
2.008
NO_2
O
O
4g
2.27
4.22
2.04
1.00
1.06
2.27
2.30
2.97
2.05
f1 (ppm)

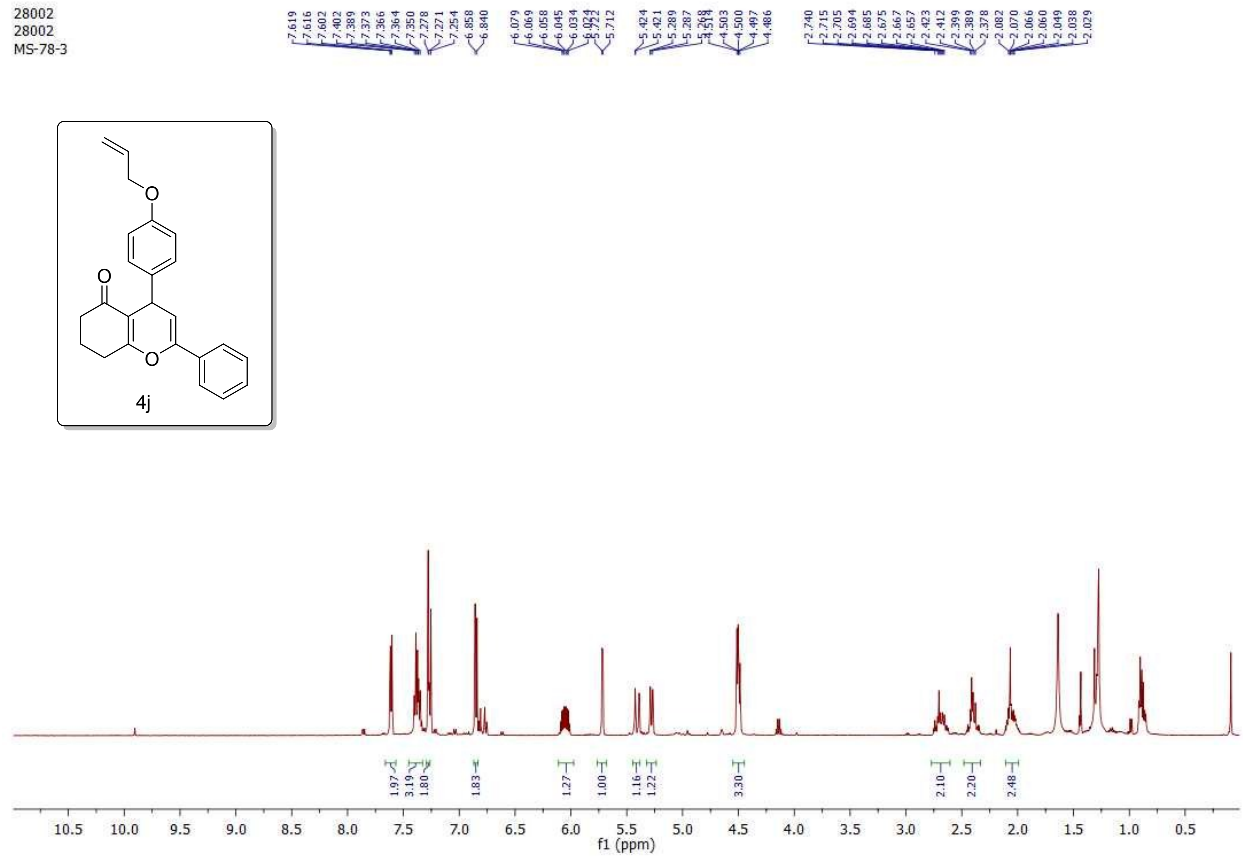

27184.5.fid
27184
MS-82-6
197.56
167.31
152.82
147.99
146.81
139.53
129.79
129.45
129.29
124.69
123.95
113.05
102.08
77.47
77.22
76.96
37.16
35.67
27.97
21.48
20.57
NO_2
O
O
4g
f1 (ppm)

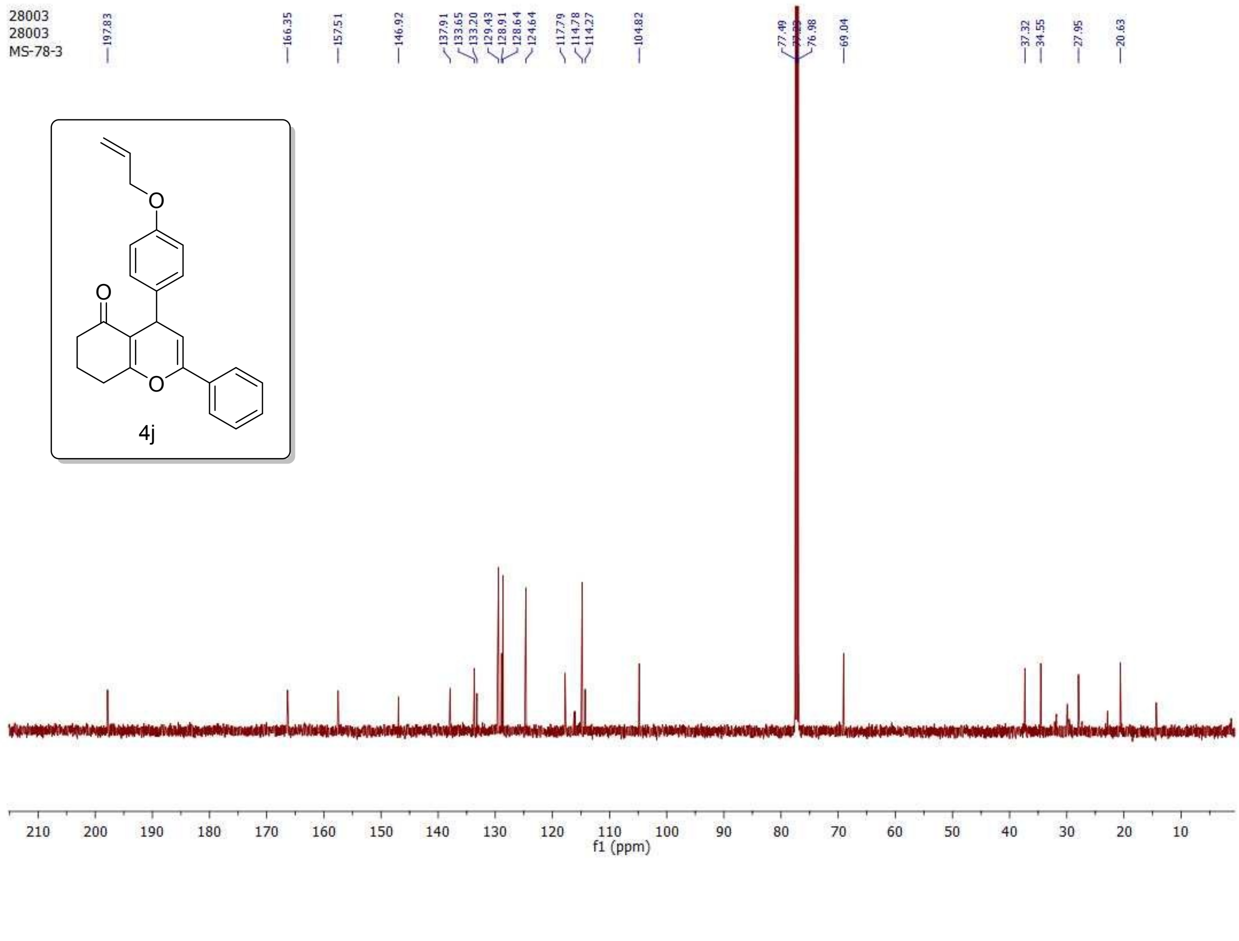

27186.1.fid
27186
MS-82-8
NO2
O
O
F
4h
2.09
2.05
2.10
2.13
1.00
1.04
2.18
2.40
2.42
f1 (ppm)

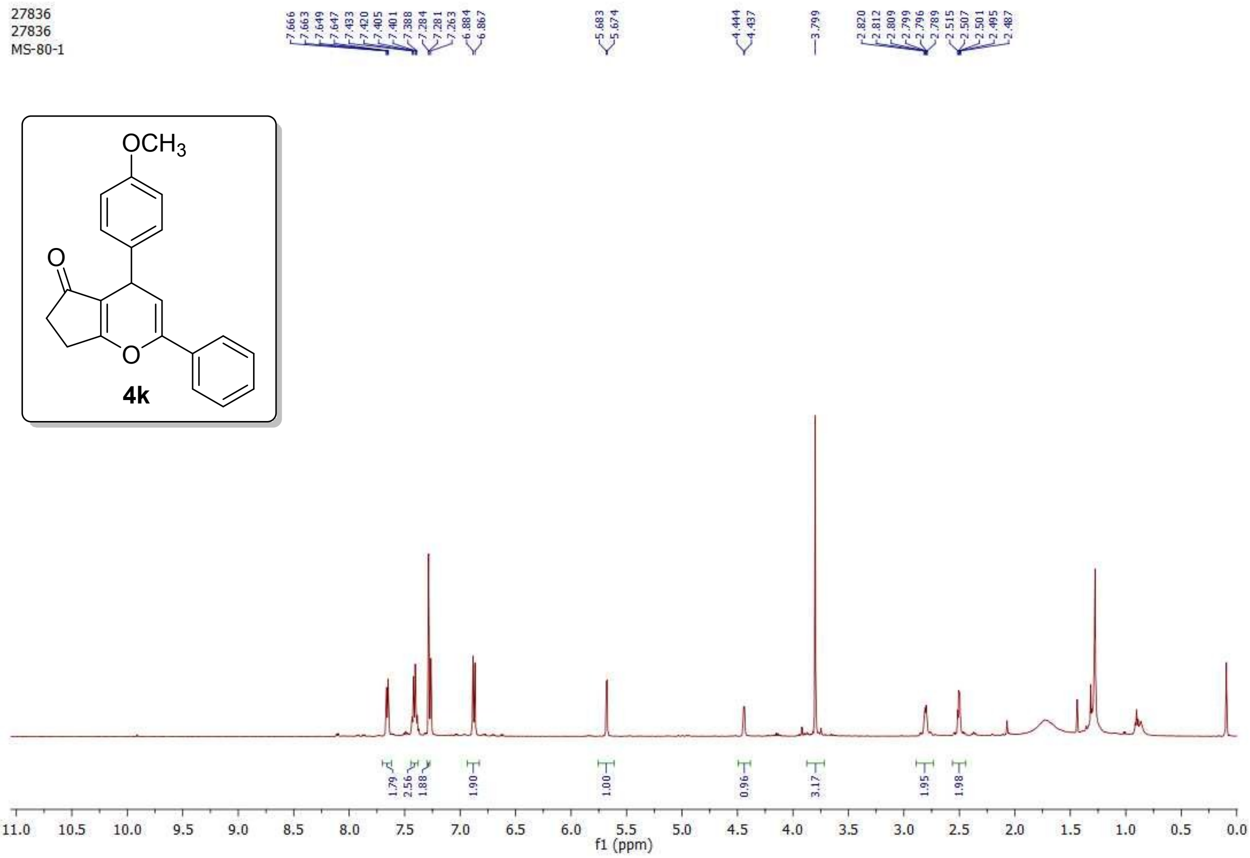

27187.5.fid
27187
MS-82-8
197.45
167.09
164.42
162.44
152.54
147.14
146.87
129.25
128.80
128.77
126.75
126.68
124.00
115.89
115.72
113.02
102.72
77.48
76.97
37.13
35.66
27.92
20.55
NO2
O
O
F
4h
f1 (ppm)

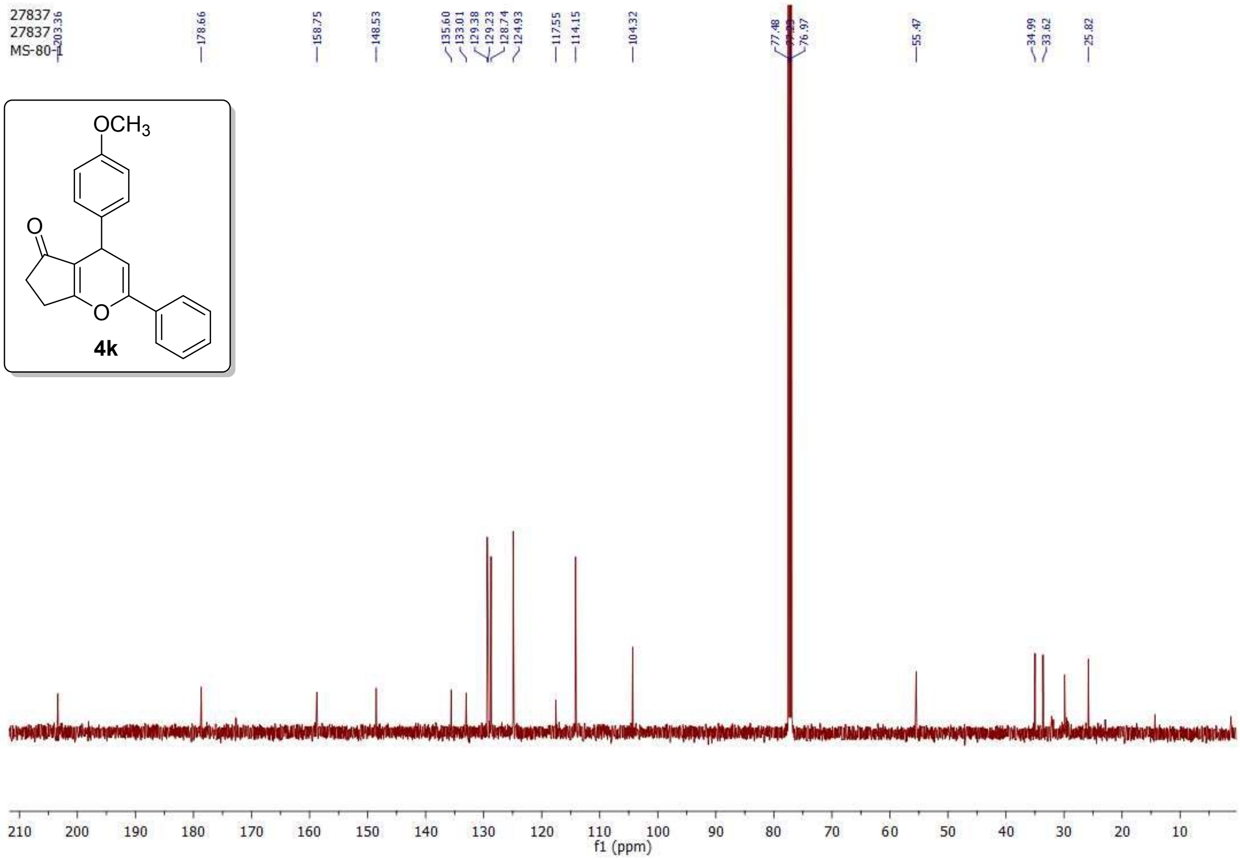

26482
26482
MS-77-4
7.483
7.480
7.467
7.464
7.347
7.332
7.328
7.315
7.273
7.269
7.259
7.244
7.210
5.479
5.469
3.703
3.689
3.671
3.664
3.655
3.646
3.638
3.052
3.026
3.020
2.500
2.489
2.484
2.040
2.029
2.016
O
O
4i
1.98
3.93
3.91
1.00
1.36
1.13
1.13
4.14
2.22
f1 (ppm)

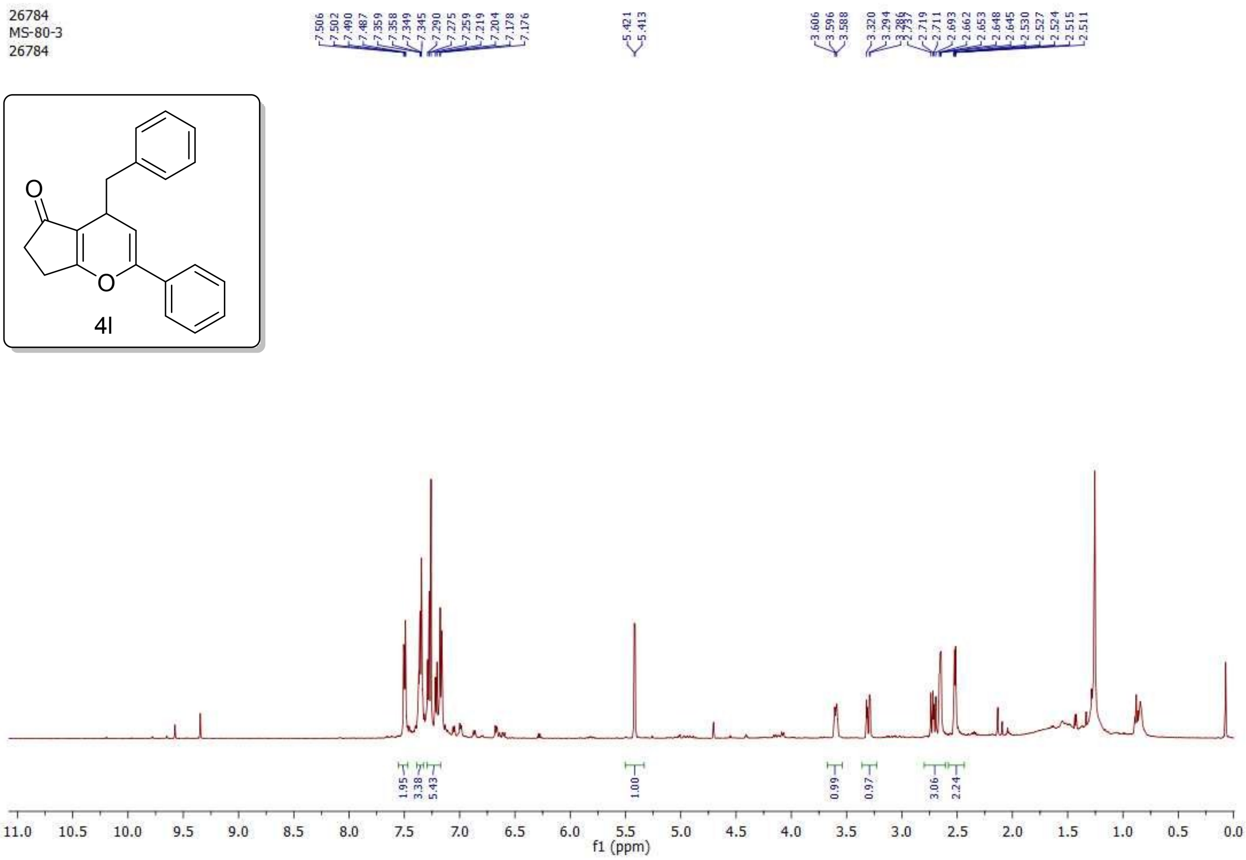

26483
26483
MS-77-4
198.41
167.91
147.96
139.09
133.39
129.96
128.80
128.58
128.18
126.26
124.62
113.37
103.92
77.49
76.98
42.89
37.45
31.22
27.86
20.74
O
O
4i
f1 (ppm)


28002
28002
MS-78-3
4j
f1 (ppm)

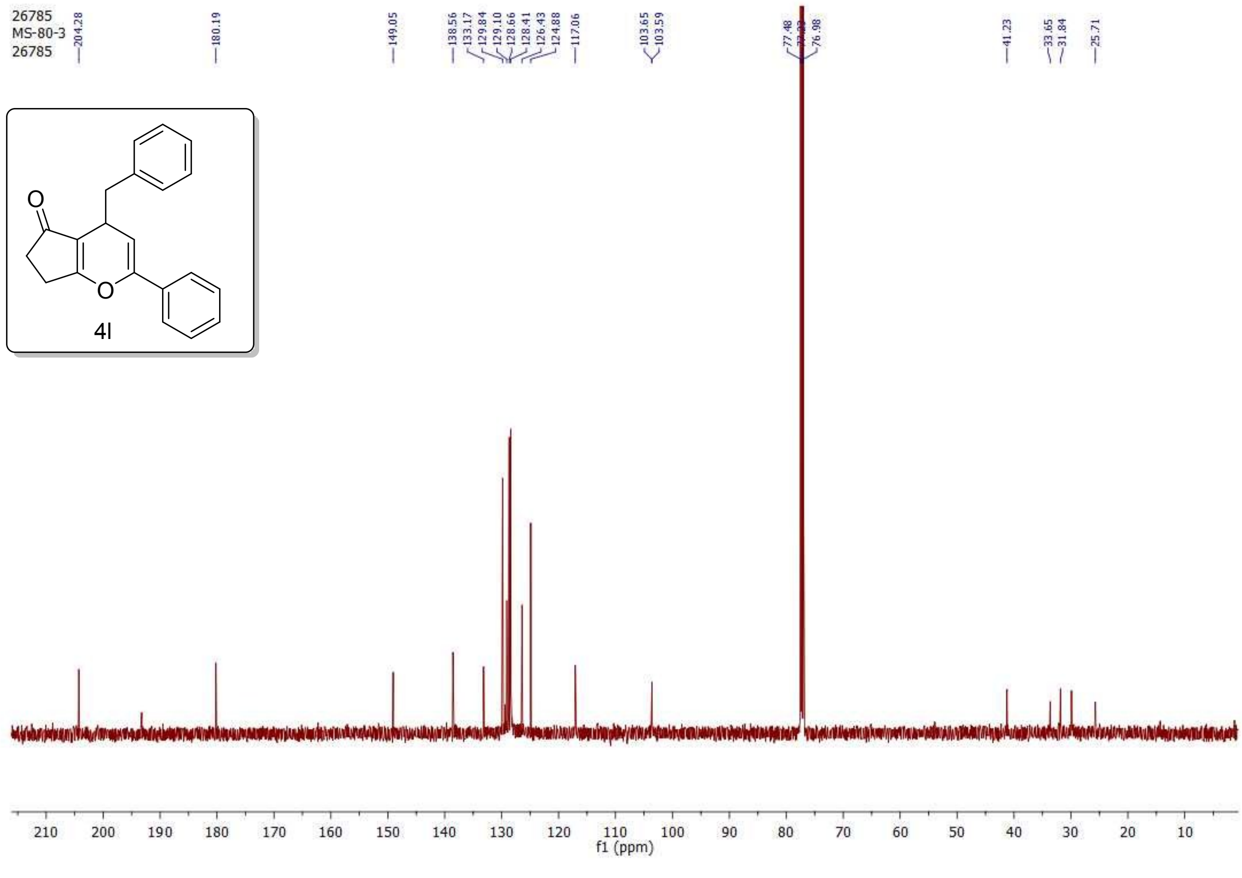

28003
28003
MS-78-3
4j
f1 (ppm)


27836
27836
MS-80-1
7.666 7.663 7.649 7.647 7.433 7.420 7.405 7.401 7.388 7.284 7.281 7.263 6.884 6.867
5.683 5.674
4.444 4.437
3.799
2.820 2.812 2.809 2.796 2.789 2.515 2.507 2.501 2.495 2.487
OCH3
O
O
4k
1.79 2.56 1.88 1.90 1.00 0.96 3.17 1.95 1.98
f1 (ppm)

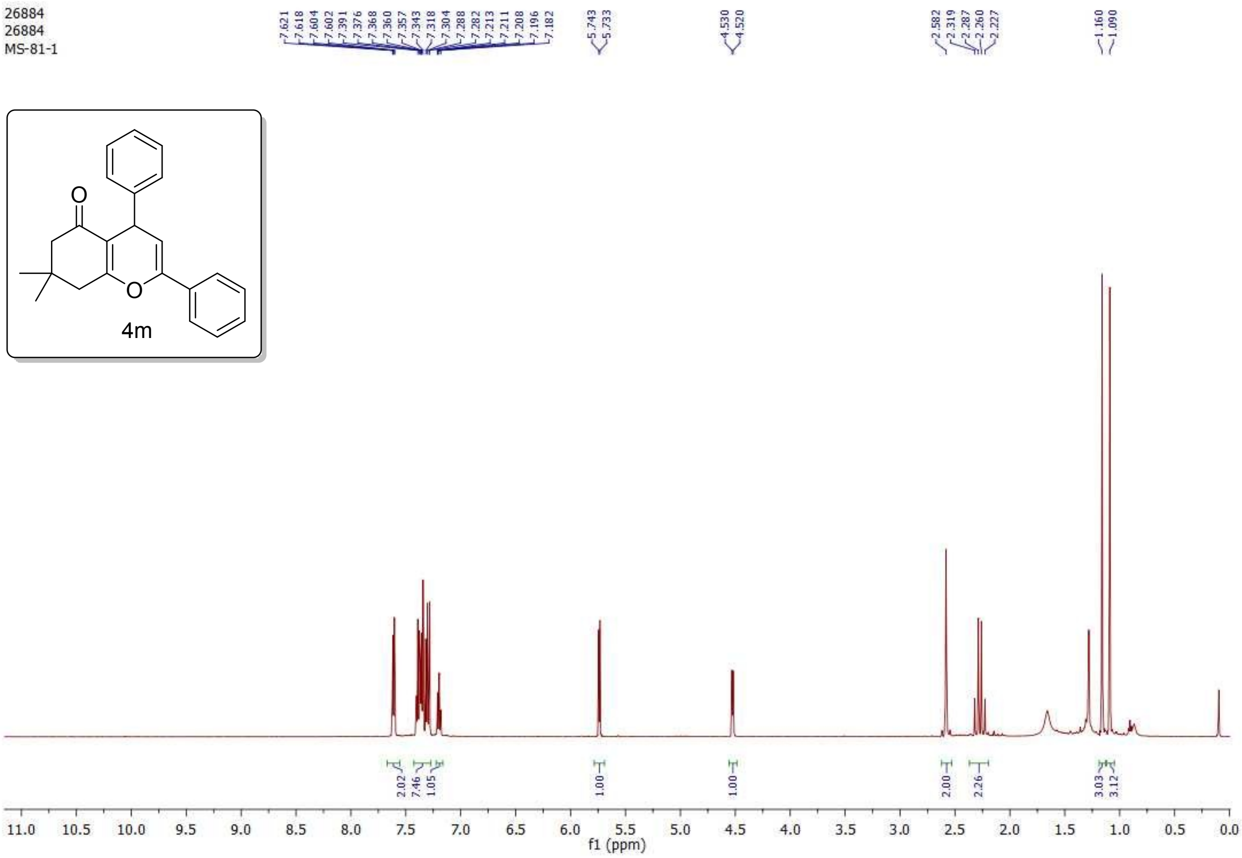

27837
27837
MS-80-1
203.36
178.66
158.75
148.53
135.60 133.01 129.38 129.23 128.74 124.93
117.55 114.15
104.32
77.48 76.97
55.47
34.99 33.62
25.82
OCH3
O
O
4k
f1 (ppm)

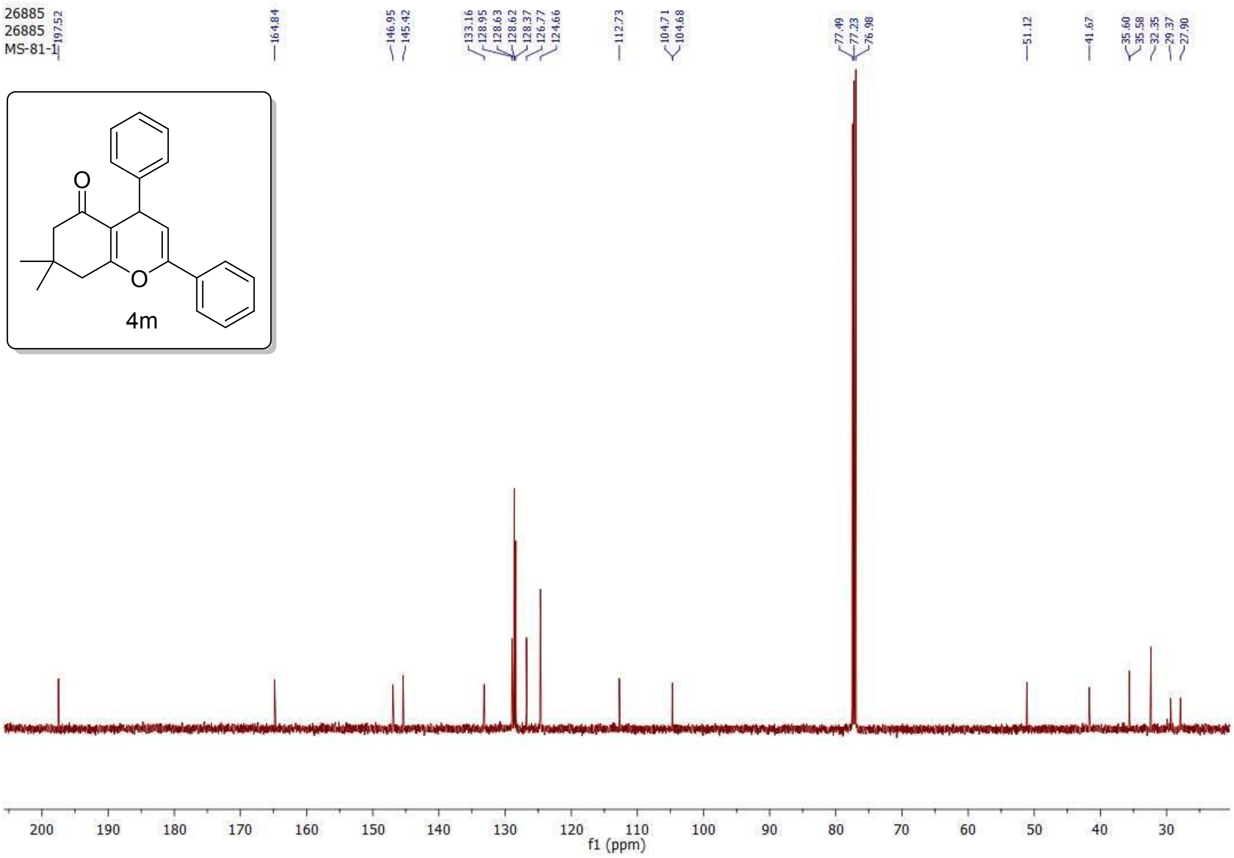


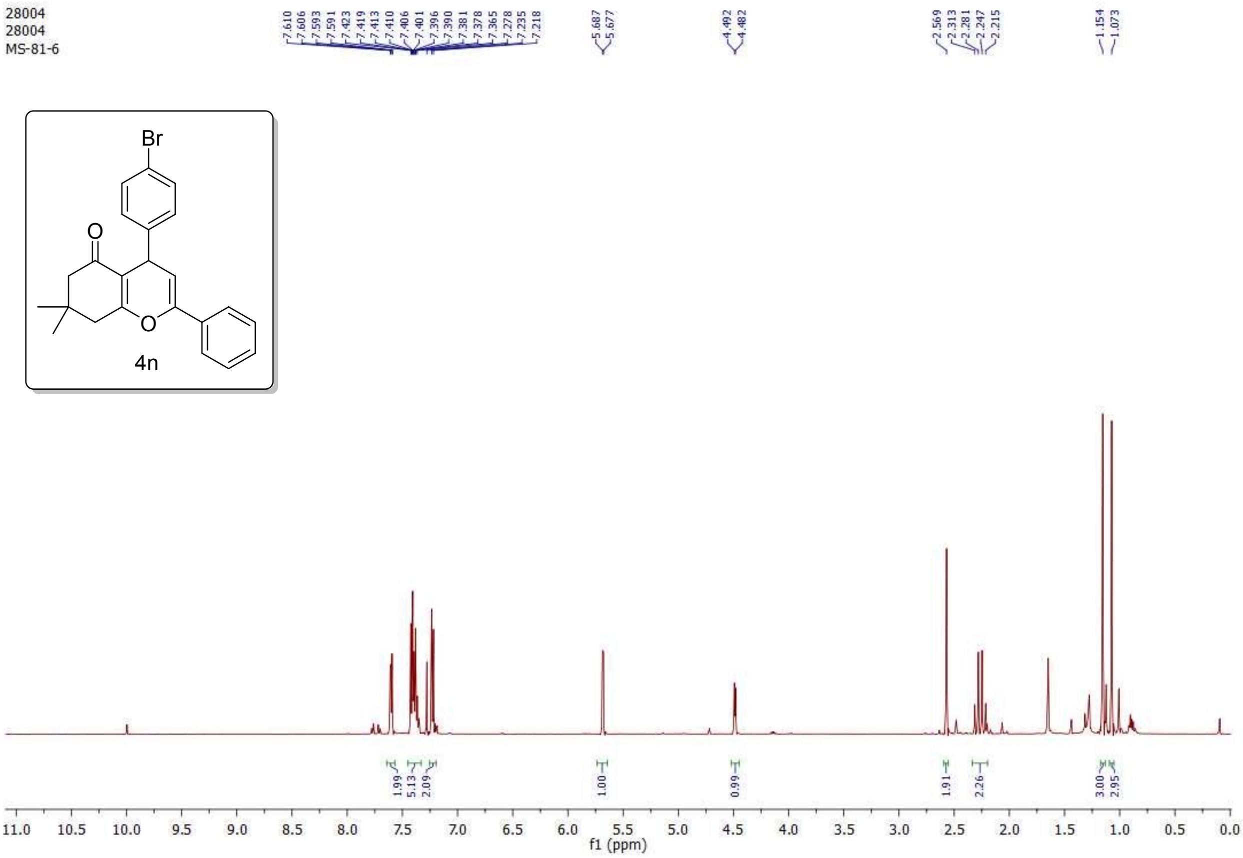
26784
MS-80-3
26784
7.506
7.502
7.490
7.487
7.359
7.358
7.349
7.345
7.290
7.275
7.259
7.219
7.204
7.178
7.176
5.421
5.413
3.606
3.596
3.588
3.320
3.294
2.719
2.711
2.693
2.662
2.653
2.648
2.645
2.530
2.527
2.524
2.515
2.511
O
O
4l
1.95
3.38
5.43
1.00
0.99
0.97
3.06
2.24
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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
0.5
0.0
f1 (ppm)

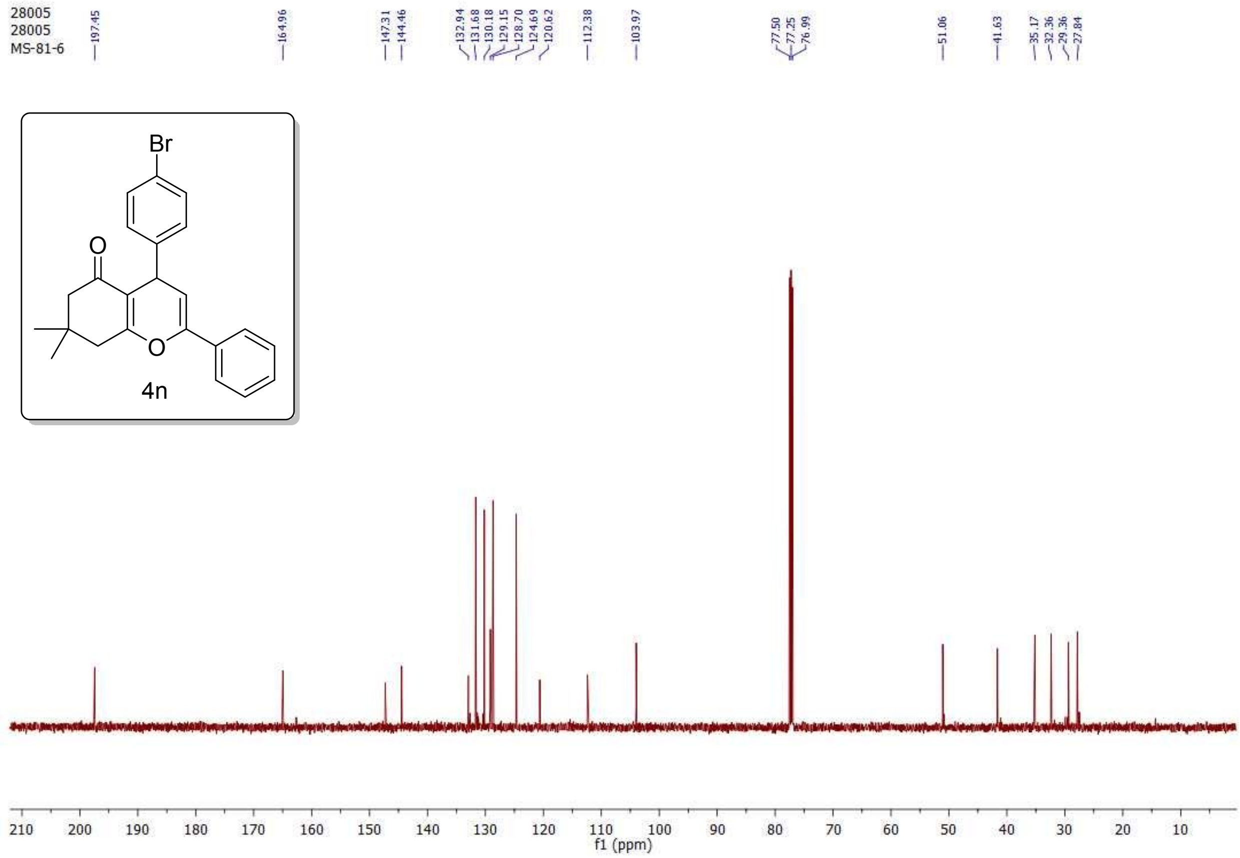


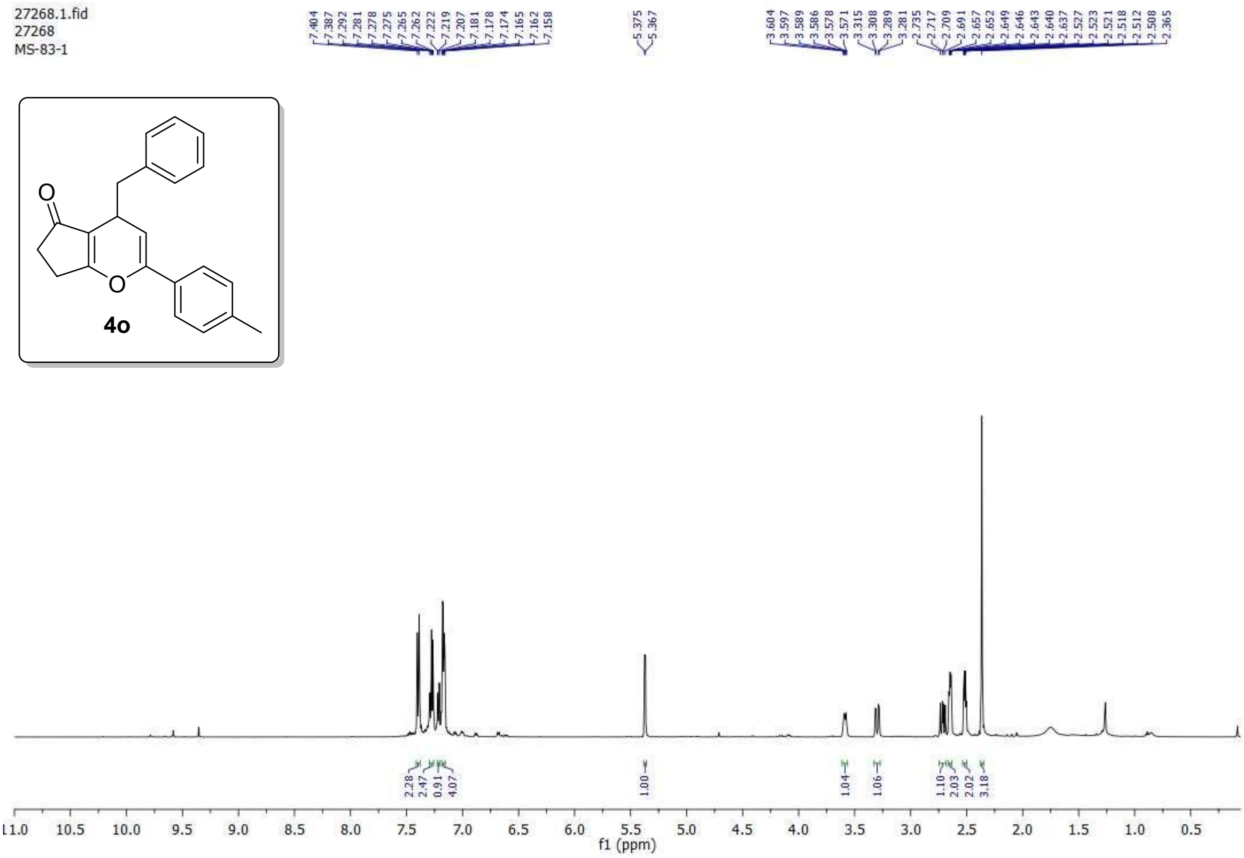
26785
MS-80-3
26785
204.28
180.19
149.05
138.56
133.17
129.84
129.10
128.66
128.41
126.43
124.88
117.06
103.65
103.59
77.48
76.98
41.23
33.65
31.84
25.71
O
O
4l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

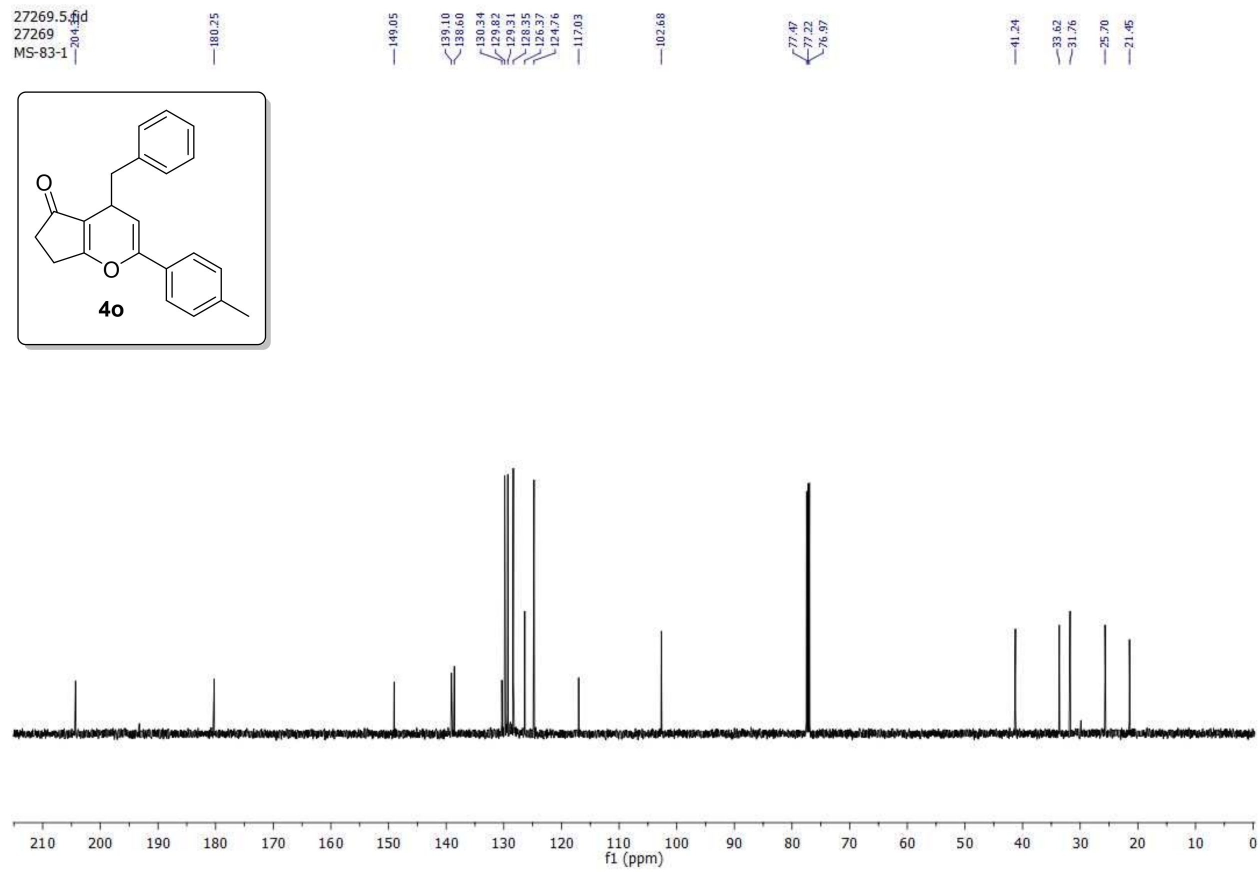

26884
26884
MS-81-1
4m
O
O
7.621
7.618
7.604
7.602
7.391
7.376
7.368
7.360
7.357
7.343
7.318
7.304
7.288
7.282
7.213
7.211
7.208
7.196
7.182
5.743
5.733
4.530
4.520
2.582
2.319
2.287
2.260
2.227
1.160
1.090
2.02
7.46
1.05
1.00
1.00
2.00
2.26
3.03
3.12
f1 (ppm)

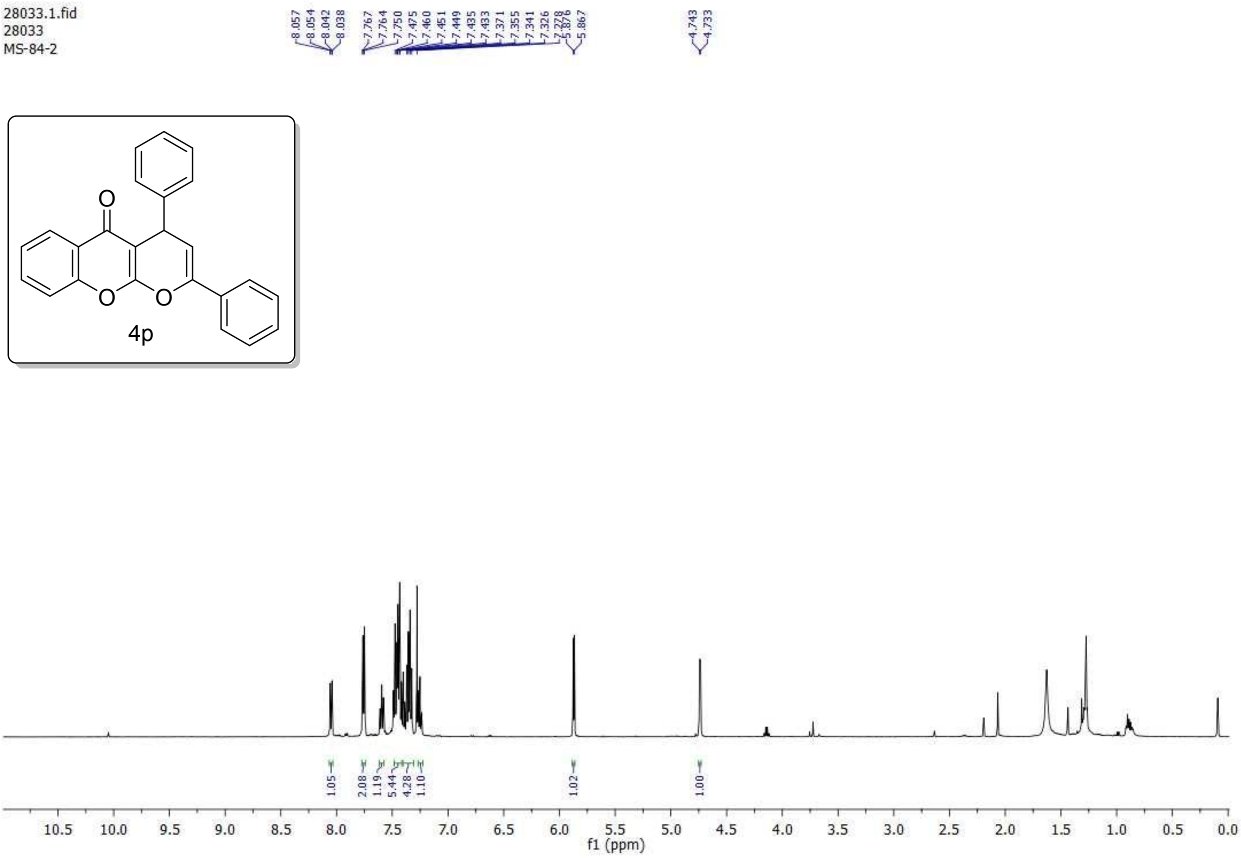

26885
26885
MS-81-1
4m
O
O
197.52
164.84
146.95
145.42
133.16
128.95
128.63
128.62
128.37
126.77
124.66
112.73
104.71
104.68
77.49
77.23
76.98
51.12
41.67
35.60
35.58
32.35
29.37
27.90
f1 (ppm)

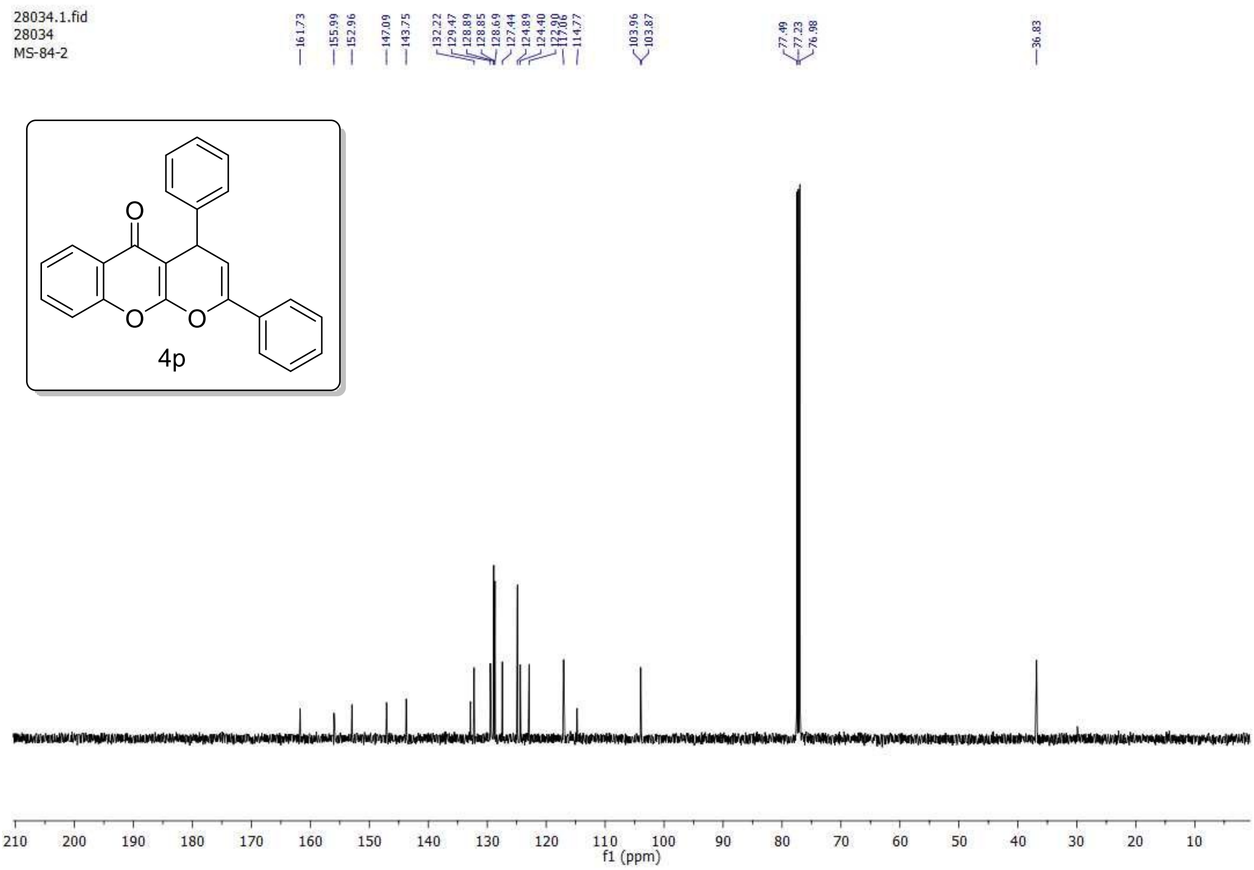

28004
28004
MS-81-6
7.610 7.606 7.593 7.591 7.423 7.419 7.413 7.410 7.406 7.401 7.396 7.390 7.381 7.378 7.365 7.278 7.235 7.218
5.687 5.677
4.492 4.482
2.569 2.313 2.281 2.247 2.215
1.154 1.073
Br
O
O
4n
1.99 5.13 2.09
1.00
0.99
1.91
2.26
3.00 2.95
f1 (ppm)

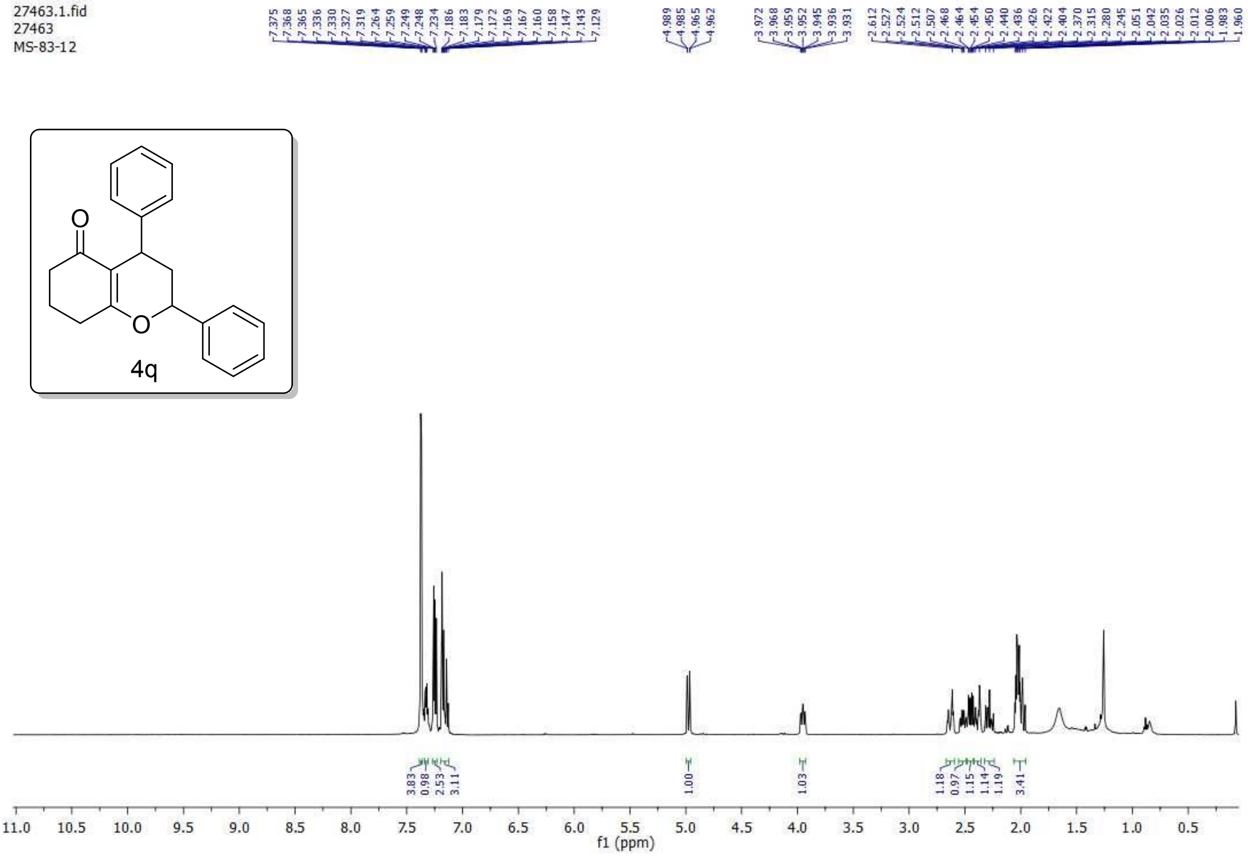

28005
28005
MS-81-6
197.45
164.96
147.31 144.46
132.94 131.68 130.18 129.15 128.70 124.69 120.62
112.38
103.97
77.50 77.25 76.99
51.06
41.63
35.17 32.36 29.36 27.84
Br
O
O
4n
f1 (ppm)

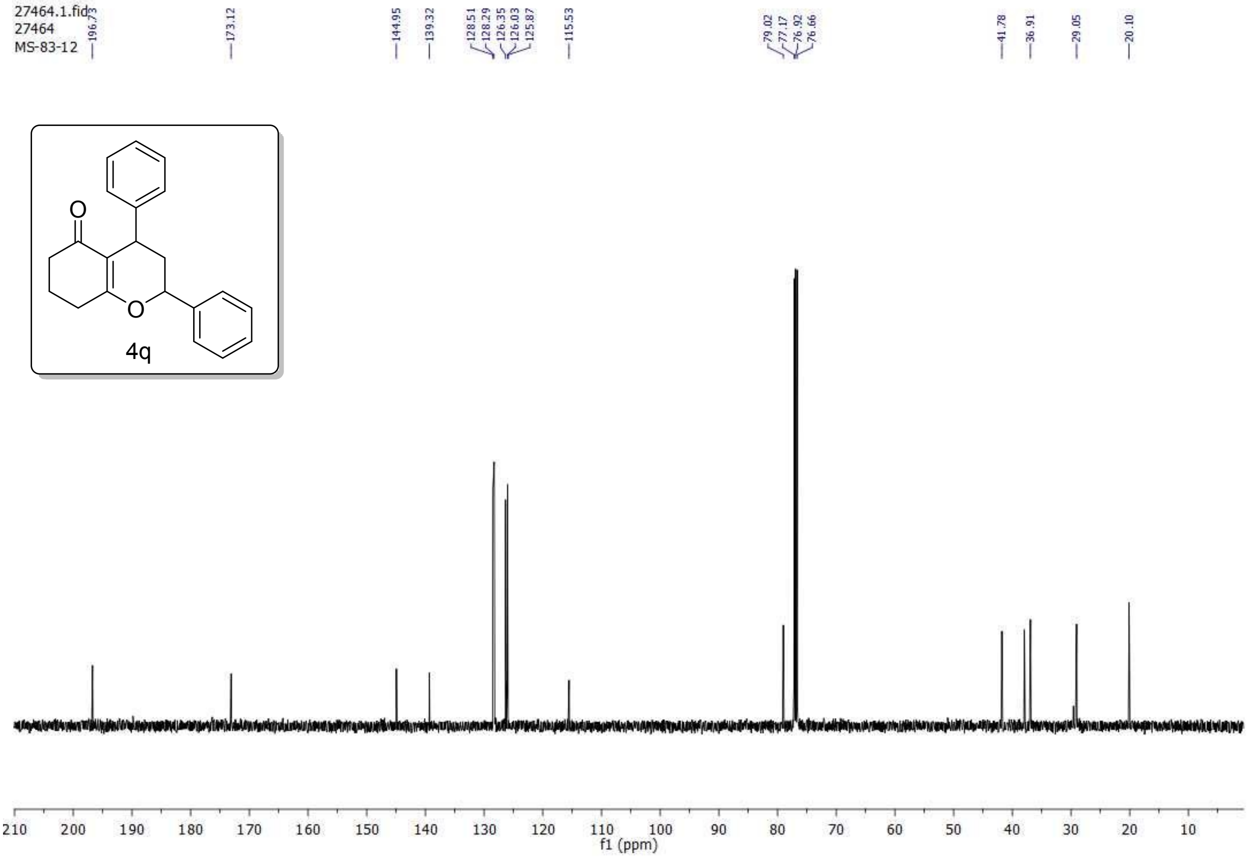

27268.1.fid
27268
MS-83-1
7.404
7.387
7.292
7.281
7.278
7.275
7.265
7.262
7.222
7.219
7.207
7.181
7.178
7.174
7.165
7.162
7.158
5.375
5.367
3.604
3.597
3.589
3.586
3.578
3.571
3.315
3.308
3.289
3.281
2.735
2.717
2.709
2.691
2.657
2.652
2.649
2.646
2.643
2.640
2.637
2.527
2.523
2.521
2.518
2.512
2.508
2.365
O
O
4o
2.28
2.47
0.91
4.07
1.00
1.04
1.06
1.10
2.03
2.02
3.18
11.0 10.5 10.0 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 0.5
f1 (ppm)

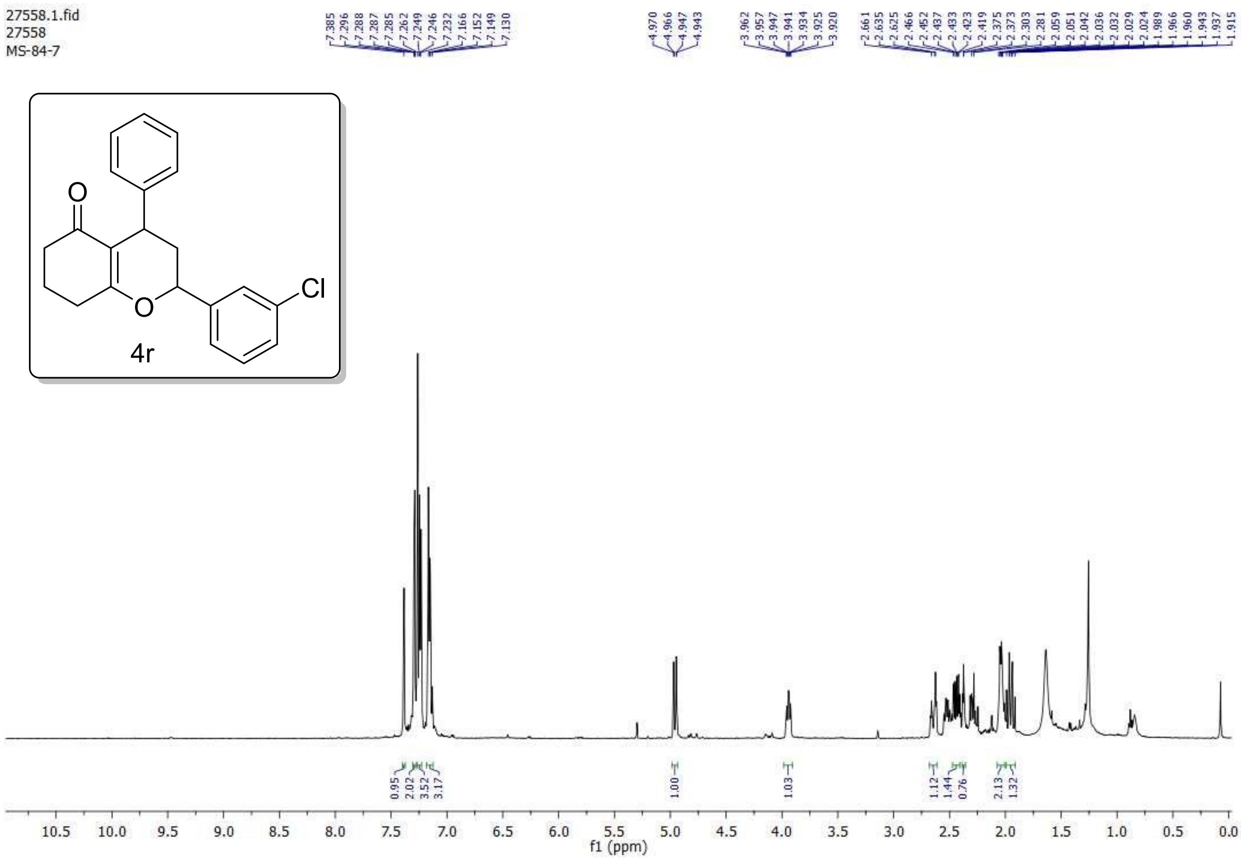

27269.5.fid
27269
MS-83-1
204.3
180.25
149.05
139.10
138.60
130.34
129.82
129.31
128.35
126.37
124.76
117.03
102.68
77.47
77.22
76.97
41.24
33.62
31.76
25.70
21.45
O
O
4o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

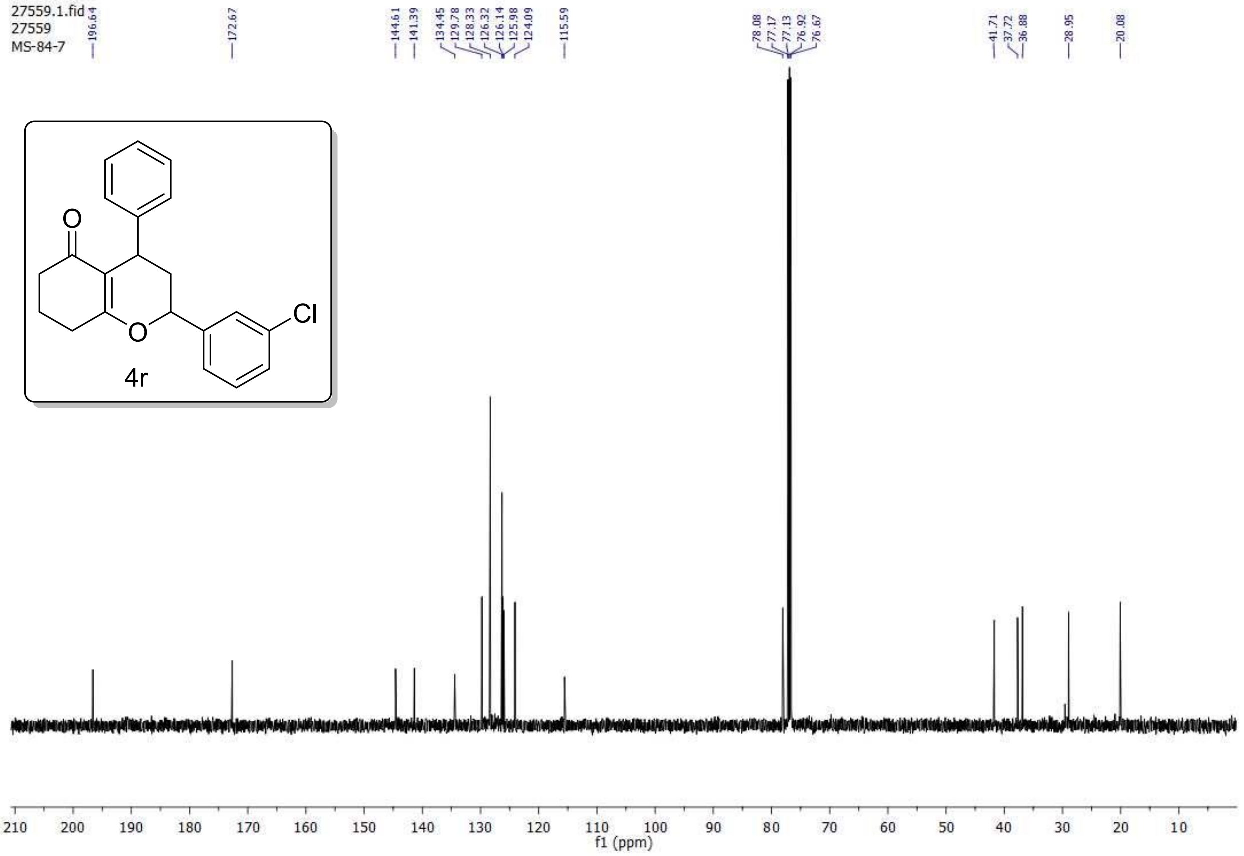

28033.1.fid
28033
MS-84-2
8.057
8.054
8.042
8.038
7.767
7.764
7.750
7.475
7.460
7.451
7.449
7.435
7.433
7.371
7.355
7.341
7.326
7.278
5.876
5.867
4.743
4.733
4p
O
O
O
1.05
2.08
1.19
5.44
4.28
1.10
1.02
1.00
f1 (ppm)

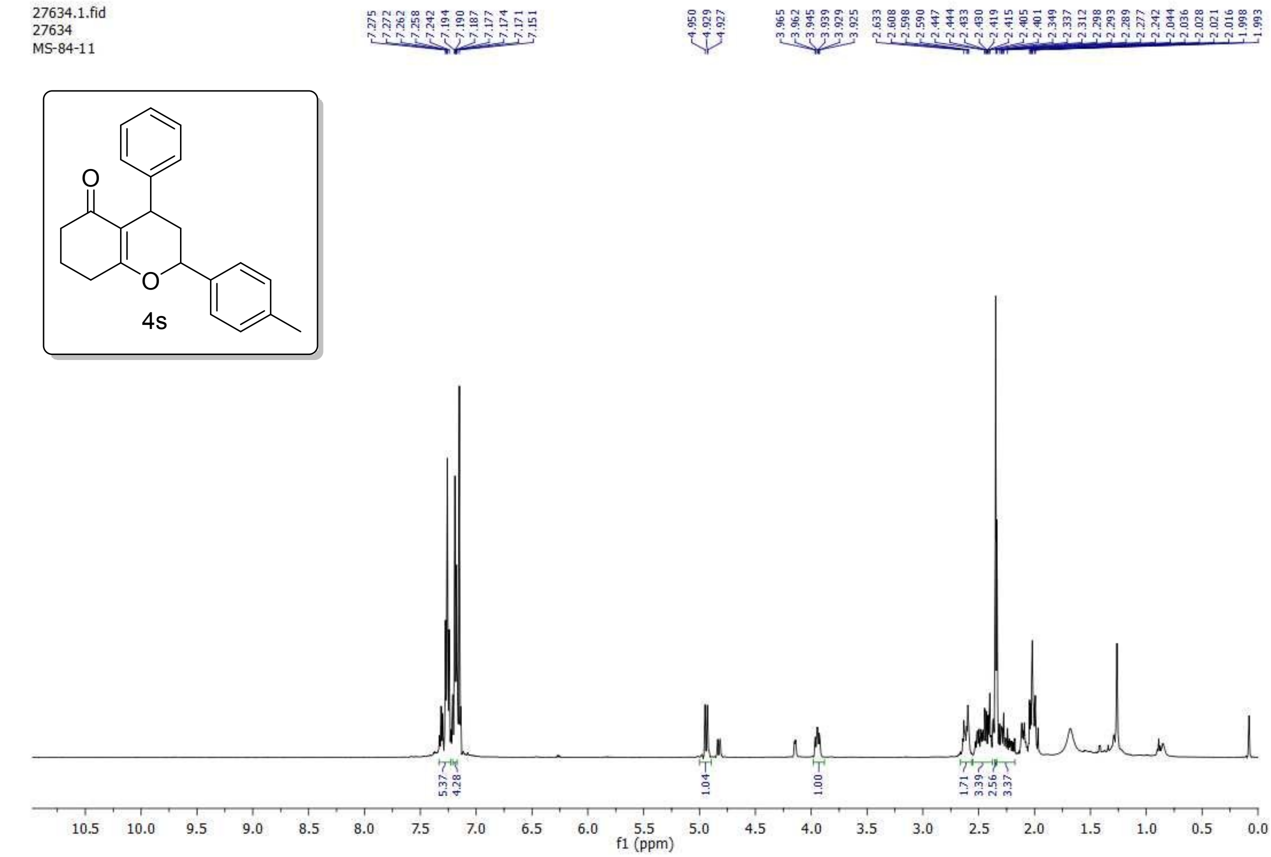

28034.1.fid
28034
MS-84-2
161.73
155.99
152.96
147.09
143.75
132.22
129.47
128.89
128.85
128.69
127.44
124.89
124.40
122.90
117.06
114.77
103.96
103.87
77.49
77.23
76.98
36.83
4p
O
O
O
f1 (ppm)

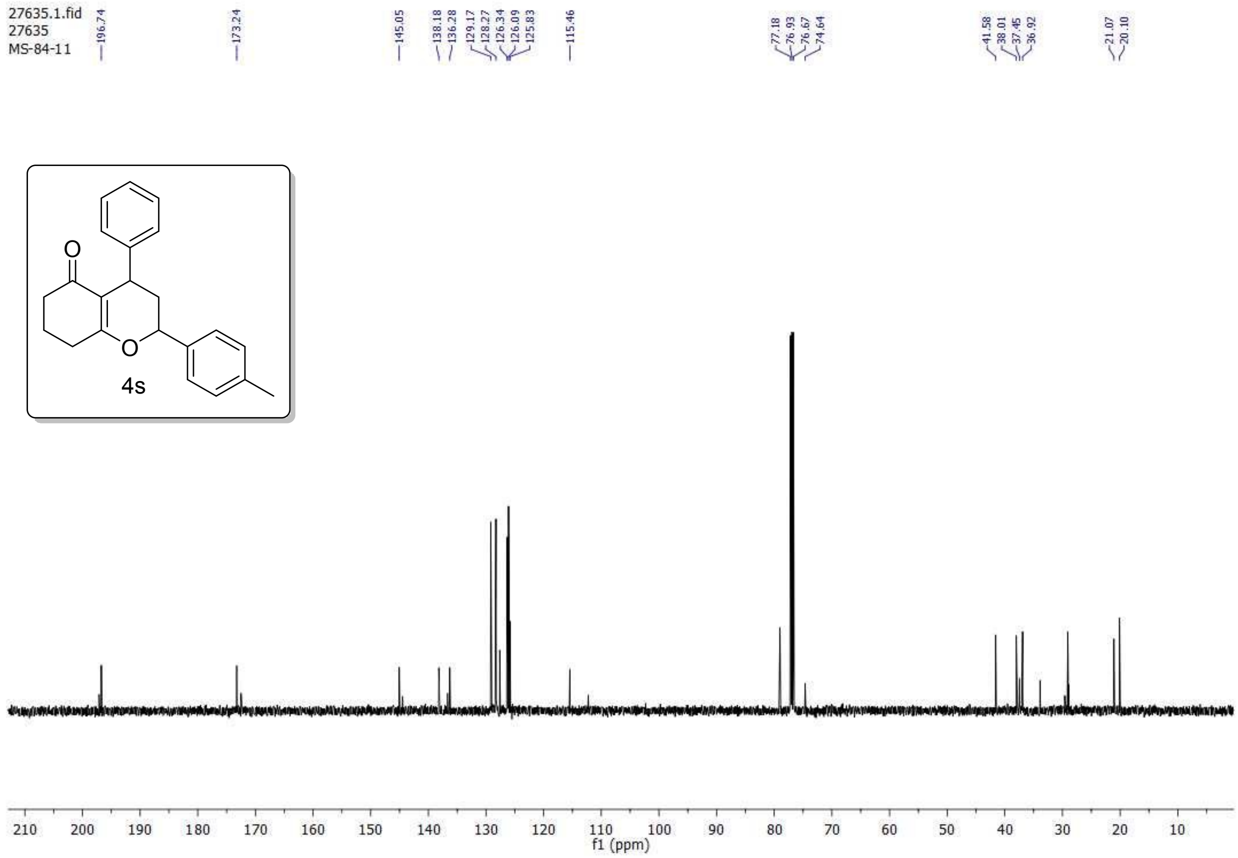

27463.1.fid
27463
MS-83-12
7.375 7.368 7.365 7.336 7.330 7.327 7.319 7.264 7.259 7.249 7.248 7.234 7.186 7.183 7.179 7.172 7.169 7.167 7.160 7.158 7.147 7.143 7.129
4.989 4.985 4.965 4.962
3.972 3.968 3.959 3.952 3.945 3.936 3.931
2.612 2.527 2.524 2.512 2.507 2.468 2.464 2.454 2.450 2.440 2.436 2.426 2.422 2.404 2.370 2.315 2.280 2.245 2.051 2.042 2.035 2.026 2.012 2.006 1.983 1.960
O
O
4q
3.83 0.98 2.53 3.11
1.00
1.03
1.18 0.97 1.15 1.14 1.19
3.41
11.0 10.5 10.0 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 0.5
f1 (ppm)

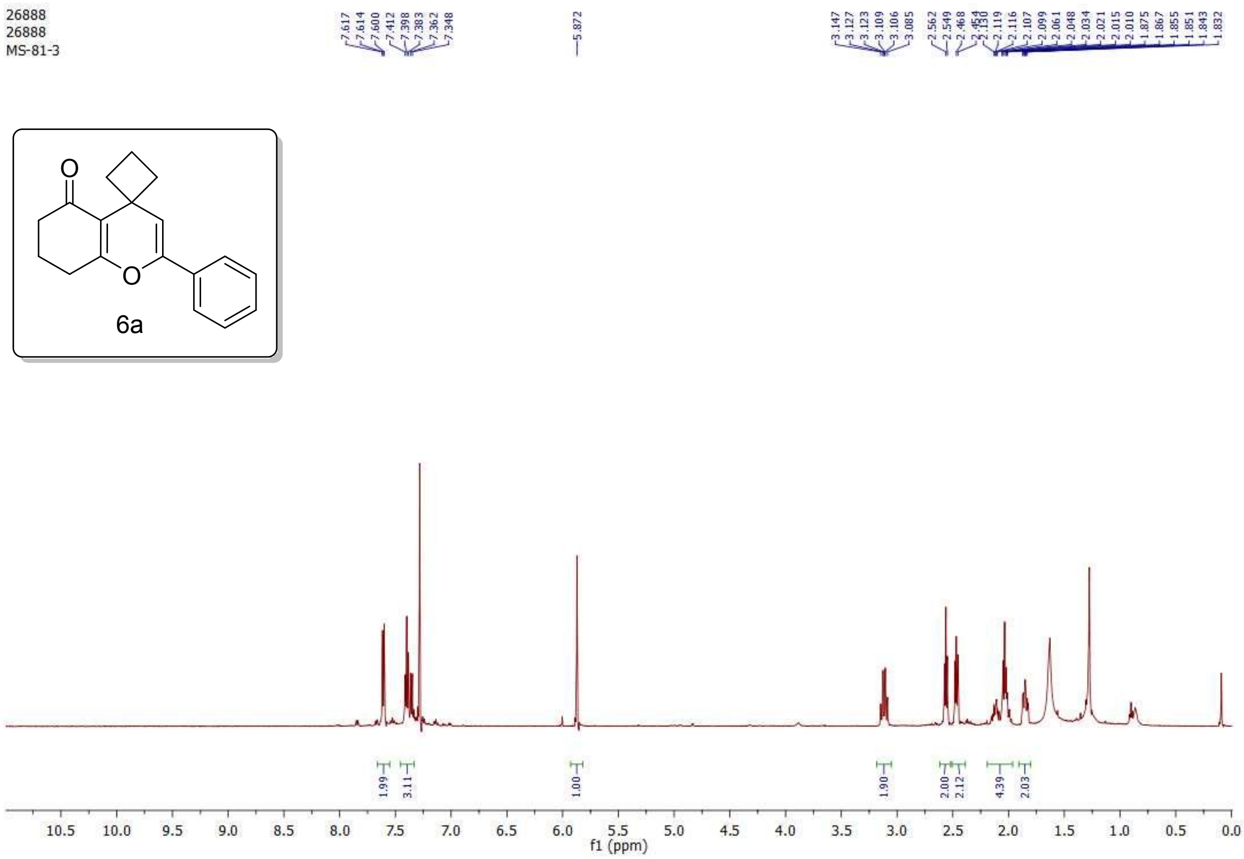

27464.1.fid
27464
MS-83-12
196.73
173.12
144.95
139.32
128.51 128.29 126.35 126.03 125.87
115.53
79.02 77.17 76.92 76.66
41.78
36.91
29.05
20.10
O
O
4q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

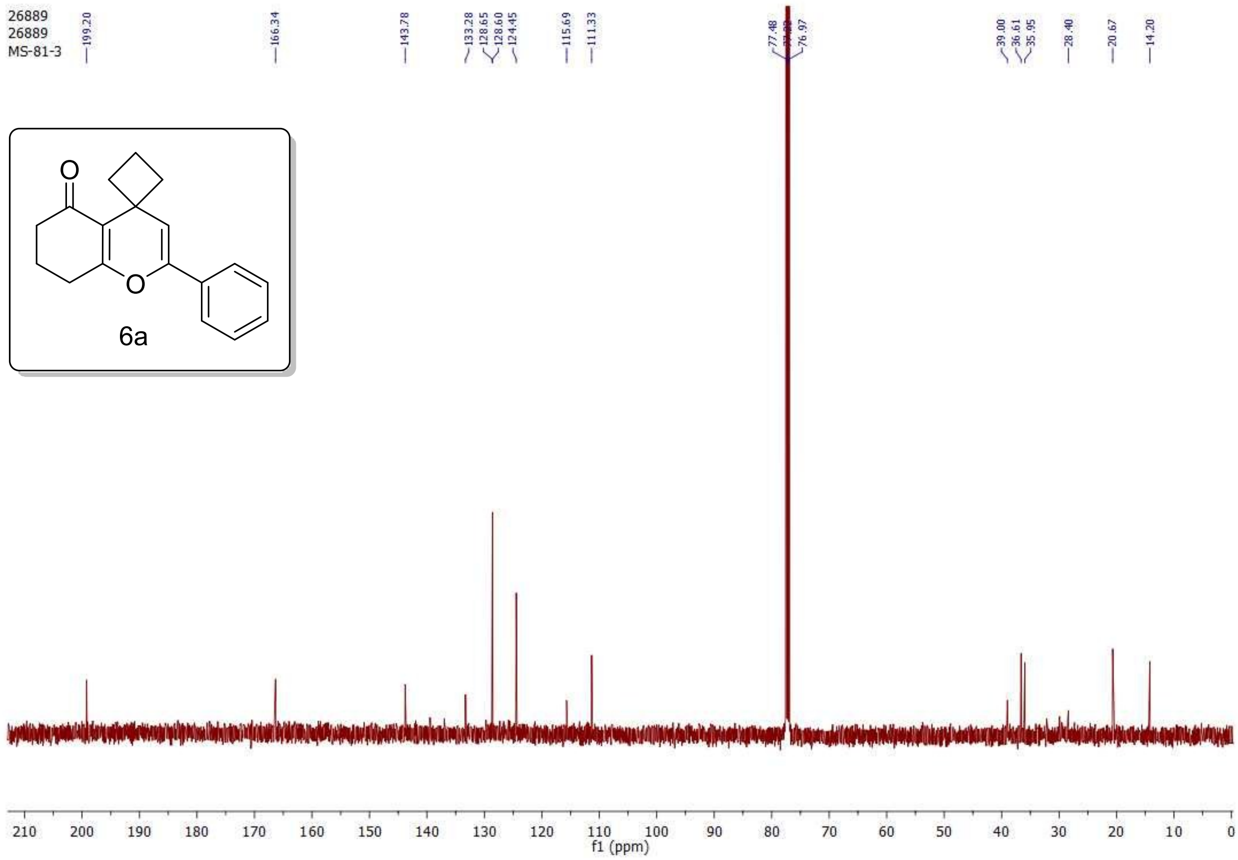

27558.1.fid
27558
MS-84-7
7.385 7.296 7.288 7.287 7.285 7.262 7.249 7.246 7.232 7.166 7.152 7.149 7.130
4.970 4.966 4.947 4.943
3.962 3.957 3.947 3.941 3.934 3.925 3.920
2.661 2.635 2.625 2.466 2.452 2.437 2.433 2.423 2.419 2.375 2.373 2.303 2.281 2.059 2.051 2.042 2.036 2.032 2.029 2.024 1.989 1.966 1.960 1.943 1.937 1.915
O
O
Cl
4r
0.95 2.02 3.52 3.17
1.00
1.03
1.12 1.44 0.76
2.13 1.32
10.5 10.0 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 0.5 0.0
f1 (ppm)

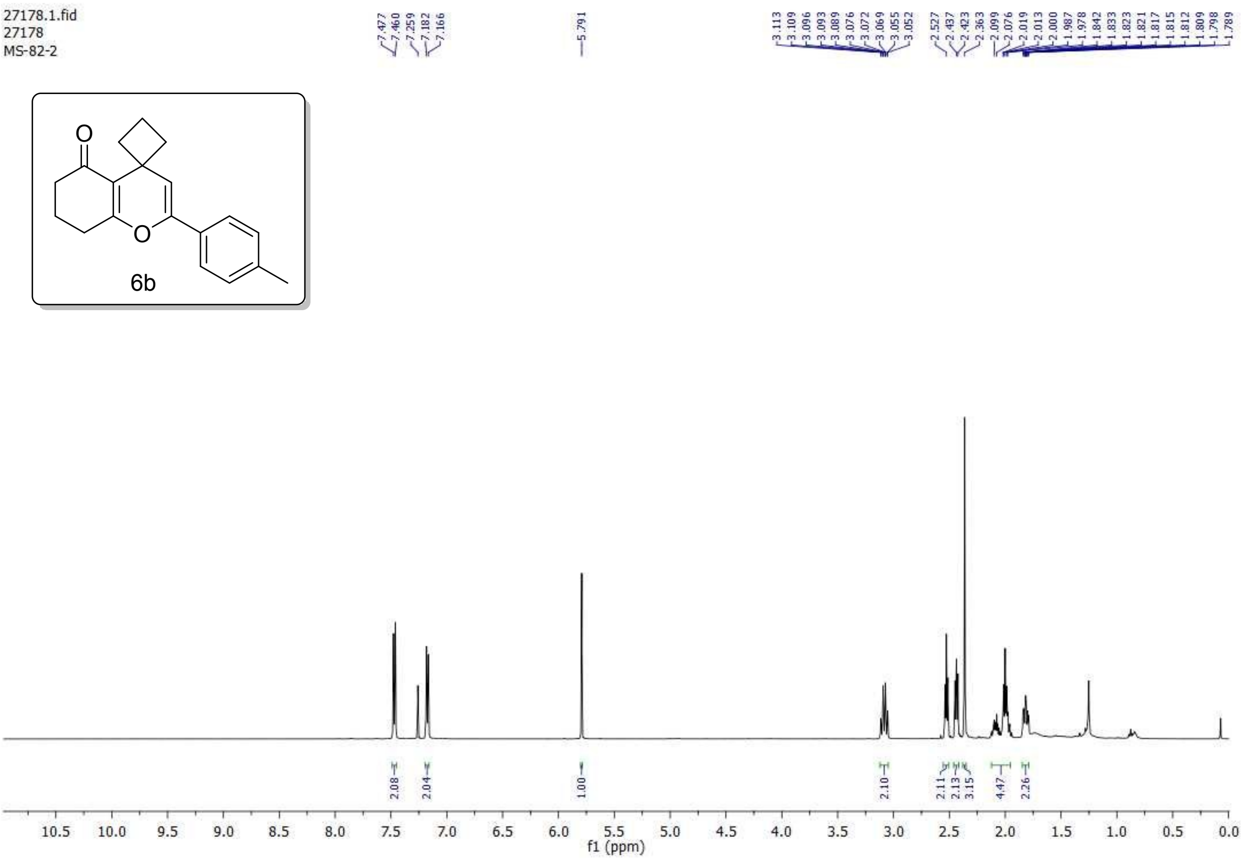

27559.1.fid
27559
MS-84-7
196.64
172.67
144.61 141.39 134.45 129.78 128.33 126.32 126.14 125.98 124.09
115.59
78.08 77.17 77.13 76.92 76.67
41.71 37.72 36.88
28.95
20.08
O
O
Cl
4r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

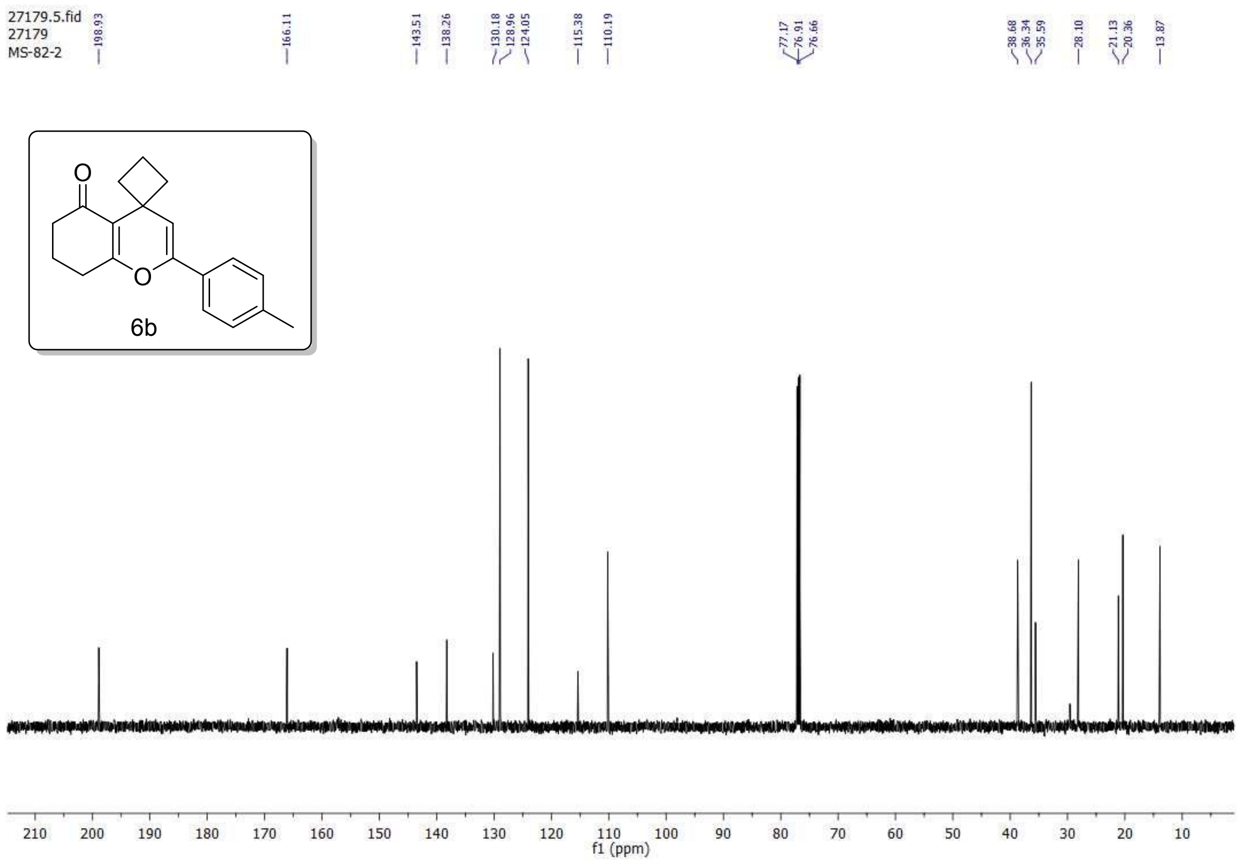

27634.1.fid
27634
MS-84-11
7.275
7.272
7.262
7.258
7.242
7.194
7.190
7.187
7.177
7.174
7.171
7.151
4.950
4.929
4.927
3.965
3.962
3.945
3.939
3.929
3.925
2.633
2.608
2.598
2.590
2.447
2.444
2.433
2.430
2.419
2.415
2.405
2.401
2.349
2.337
2.312
2.298
2.293
2.289
2.277
2.242
2.044
2.036
2.028
2.021
2.016
1.998
1.993
O
O
4s
5.37
4.28
1.04
1.00
1.71
3.39
2.56
3.37
10.5
10.0
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
0.5
0.0
f1 (ppm)

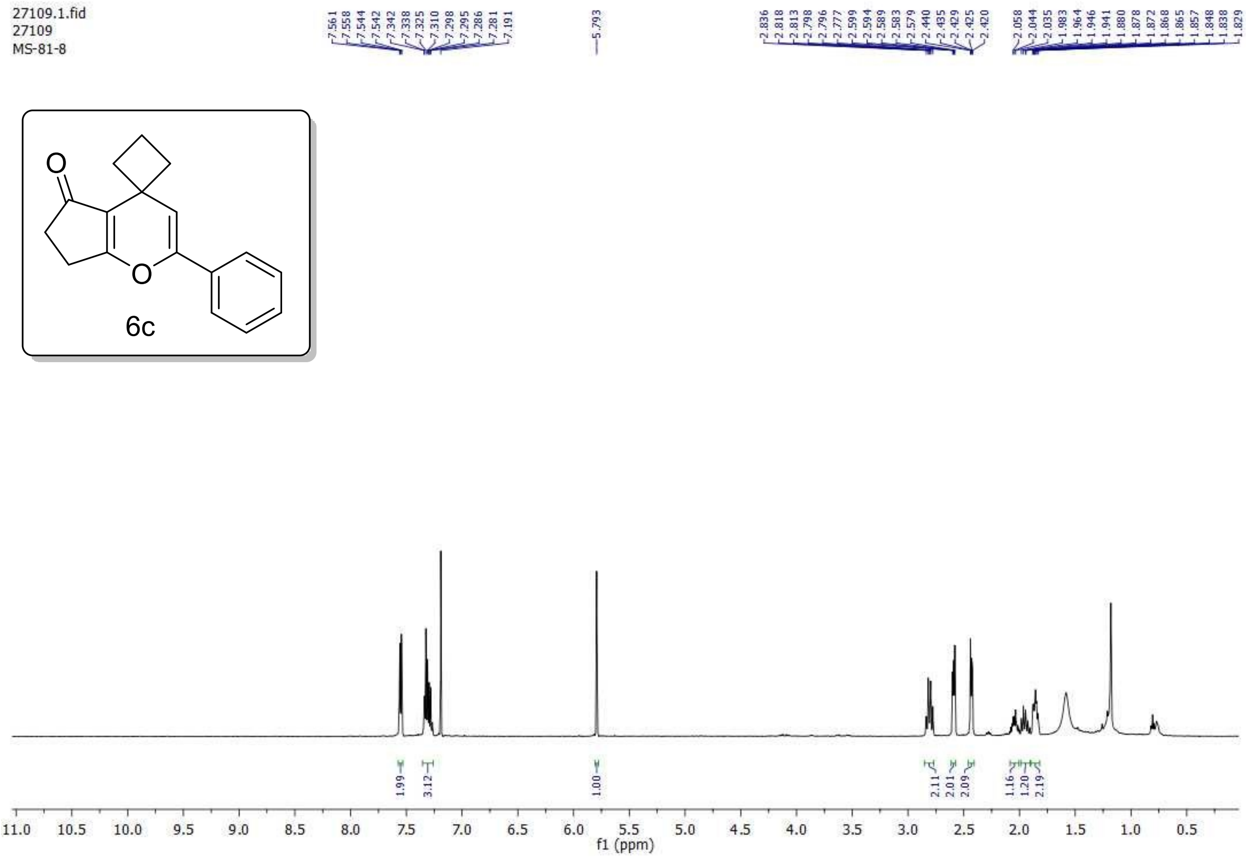

27635.1.fid
27635
MS-84-11
196.74
173.24
145.05
138.18
136.28
129.17
128.27
126.34
126.09
125.83
115.46
77.18
76.93
76.67
74.64
41.58
38.01
37.45
36.92
21.07
20.10
O
O
4s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


26888
26888
MS-81-3
7.617
7.614
7.600
7.412
7.398
7.383
7.362
7.348
5.872
3.147
3.127
3.123
3.109
3.106
3.085
2.562
2.549
2.468
2.119
2.116
2.107
2.099
2.061
2.048
2.034
2.021
2.015
2.010
1.875
1.867
1.855
1.851
1.843
1.832
6a
1.99
3.11
1.00
1.90
2.00
2.12
4.39
2.03
f1 (ppm)

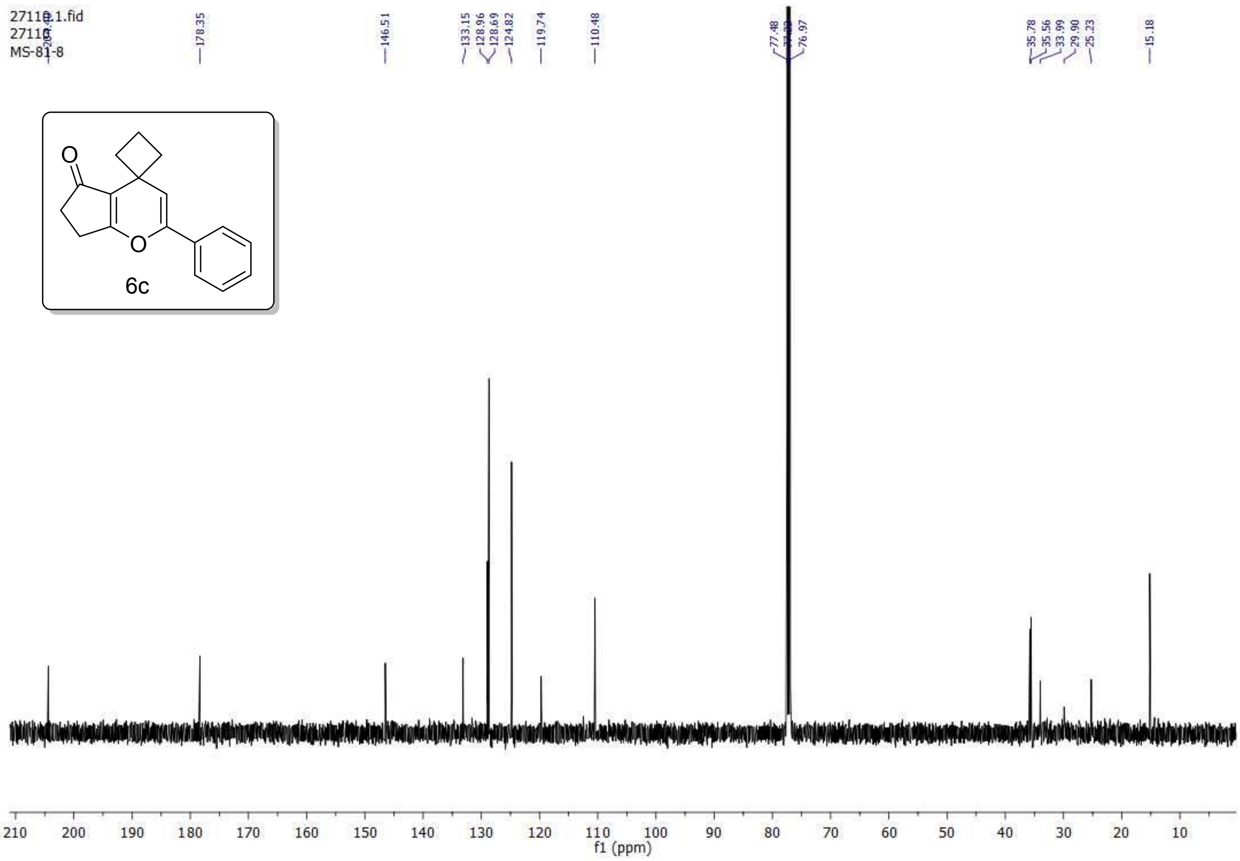

26889
26889
MS-81-3
199.20
166.34
143.78
133.28
128.65
128.60
124.45
115.69
111.33
77.48
76.97
39.00
36.61
35.95
28.40
20.67
14.20
6a
f1 (ppm)


27178.1.fid
27178
MS-82-2
7.477
7.460
7.259
7.182
7.166
5.791
3.113
3.109
3.096
3.093
3.089
3.076
3.072
3.069
3.055
3.052
2.527
2.437
2.423
2.363
2.099
2.076
2.019
2.013
2.000
1.987
1.978
1.842
1.833
1.823
1.821
1.817
1.815
1.812
1.809
1.798
1.789
6b
2.08
2.04
1.00
2.10
2.11
2.13
3.15
4.47
2.26
f1 (ppm)

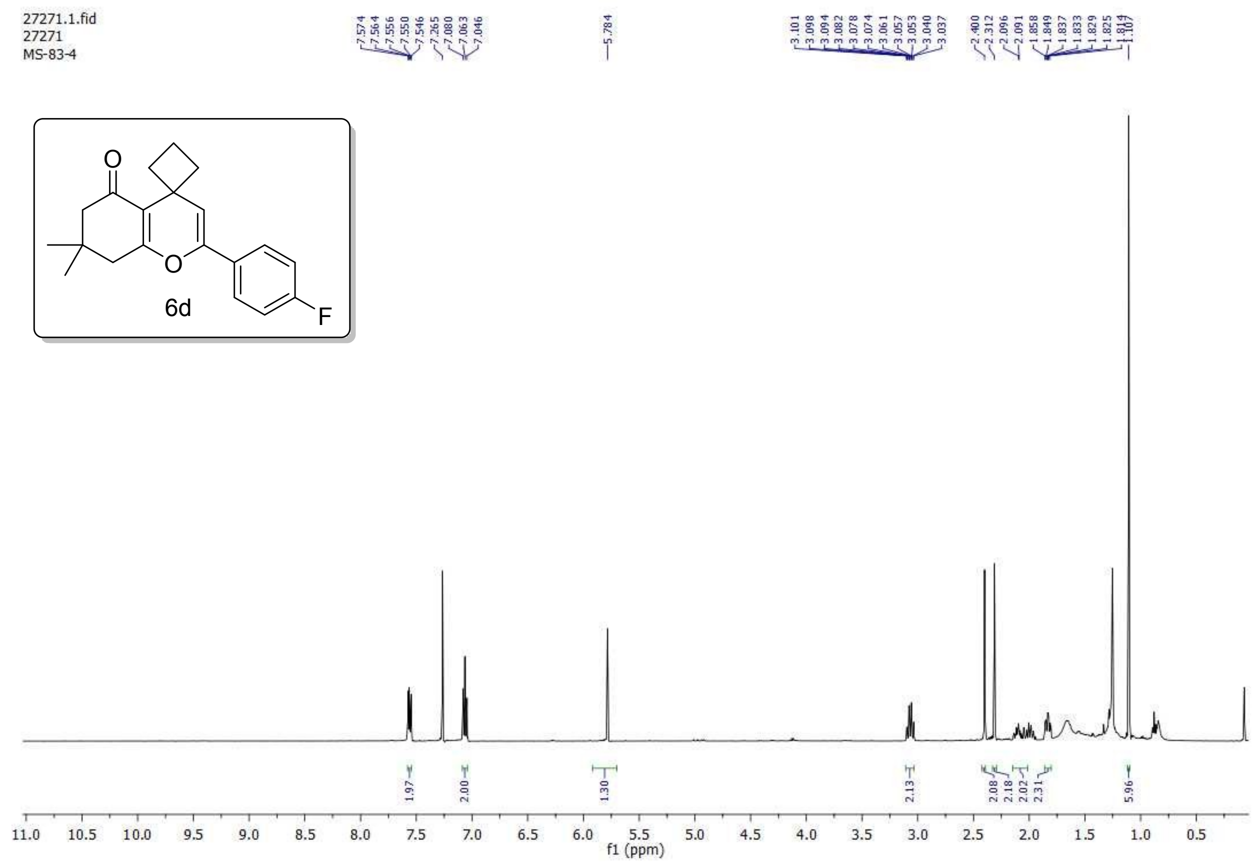

27179.5.fid
27179
MS-82-2
198.93
166.11
143.51
138.26
130.18
128.96
124.05
115.38
110.19
77.17
76.91
76.66
38.68
36.34
35.59
28.10
21.13
20.36
13.87
6b
f1 (ppm)

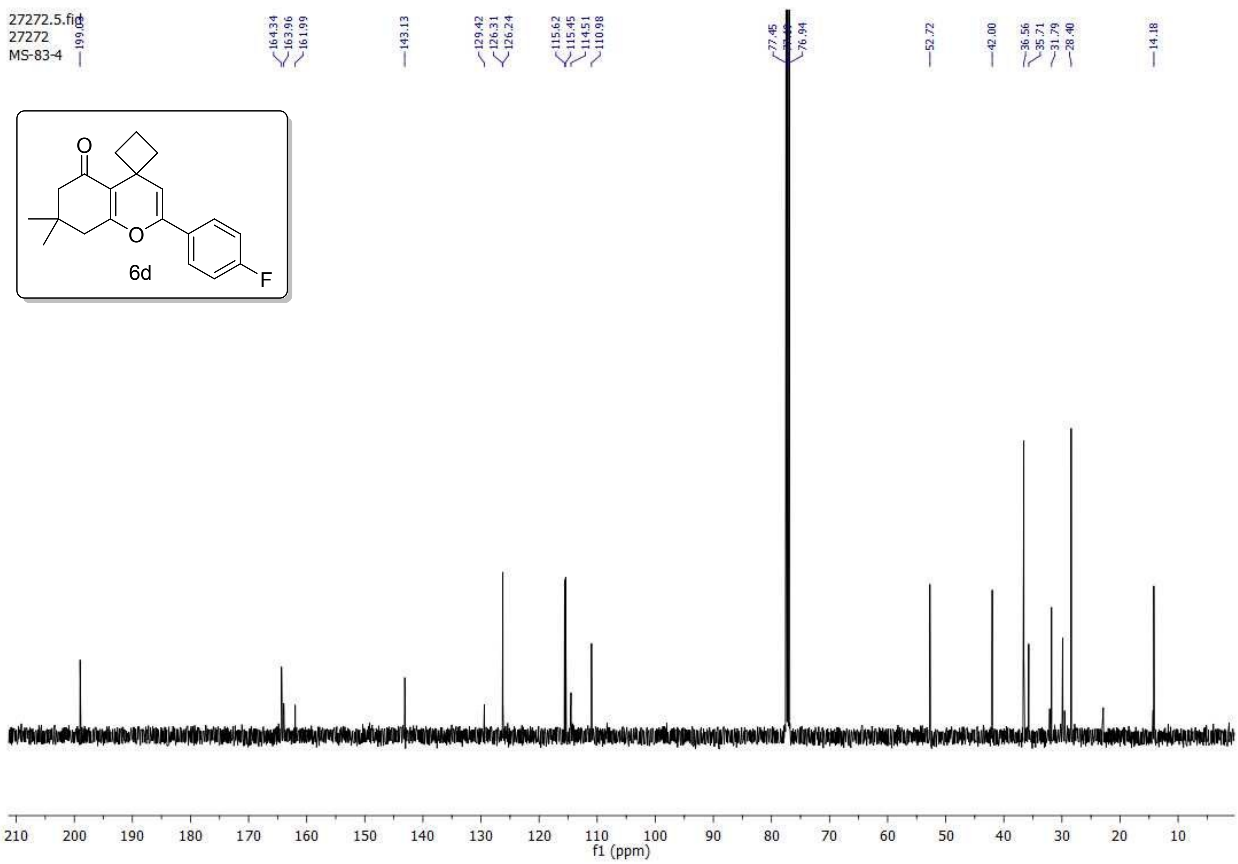


27109.1.fid
27109
MS-81-8
7.561 7.558 7.544 7.542 7.342 7.338 7.325 7.310 7.298 7.295 7.286 7.281 7.191
5.793
2.836 2.818 2.813 2.798 2.796 2.777 2.599 2.594 2.589 2.583 2.579 2.440 2.435 2.429 2.425 2.420
2.058 2.044 2.035 1.983 1.964 1.946 1.941 1.880 1.878 1.872 1.868 1.865 1.857 1.848 1.838 1.829
6c
1.99
3.12
1.00
2.11
2.01
2.09
1.16
1.20
2.19
11.0 10.5 10.0 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 0.5
f1 (ppm)

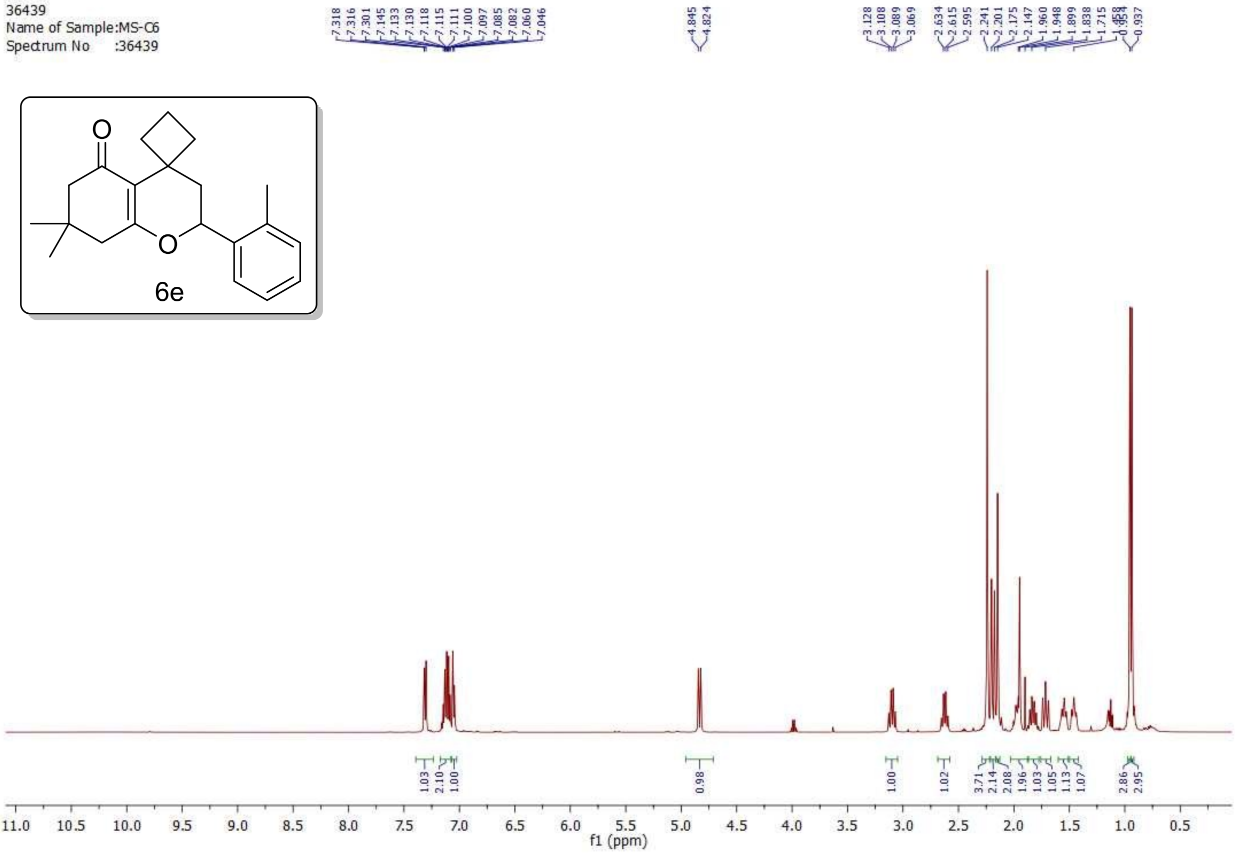


MS-81-8
178.35
146.51
133.15 128.96 128.69 124.82
119.74
110.48
77.48 76.97
35.78 35.56 33.99 29.90 25.23
15.18
6c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

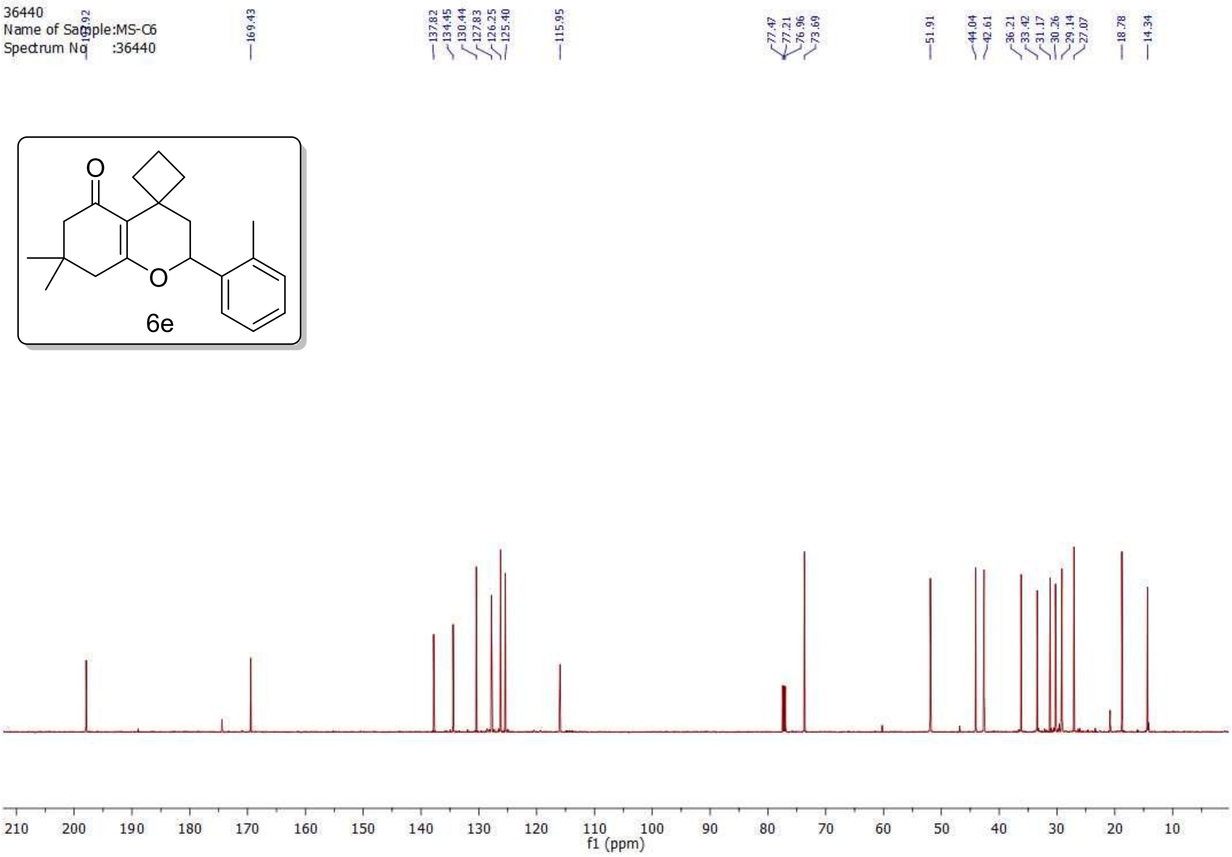

27271.1.fid
27271
MS-83-4
O
O
6d
F
f1 (ppm)

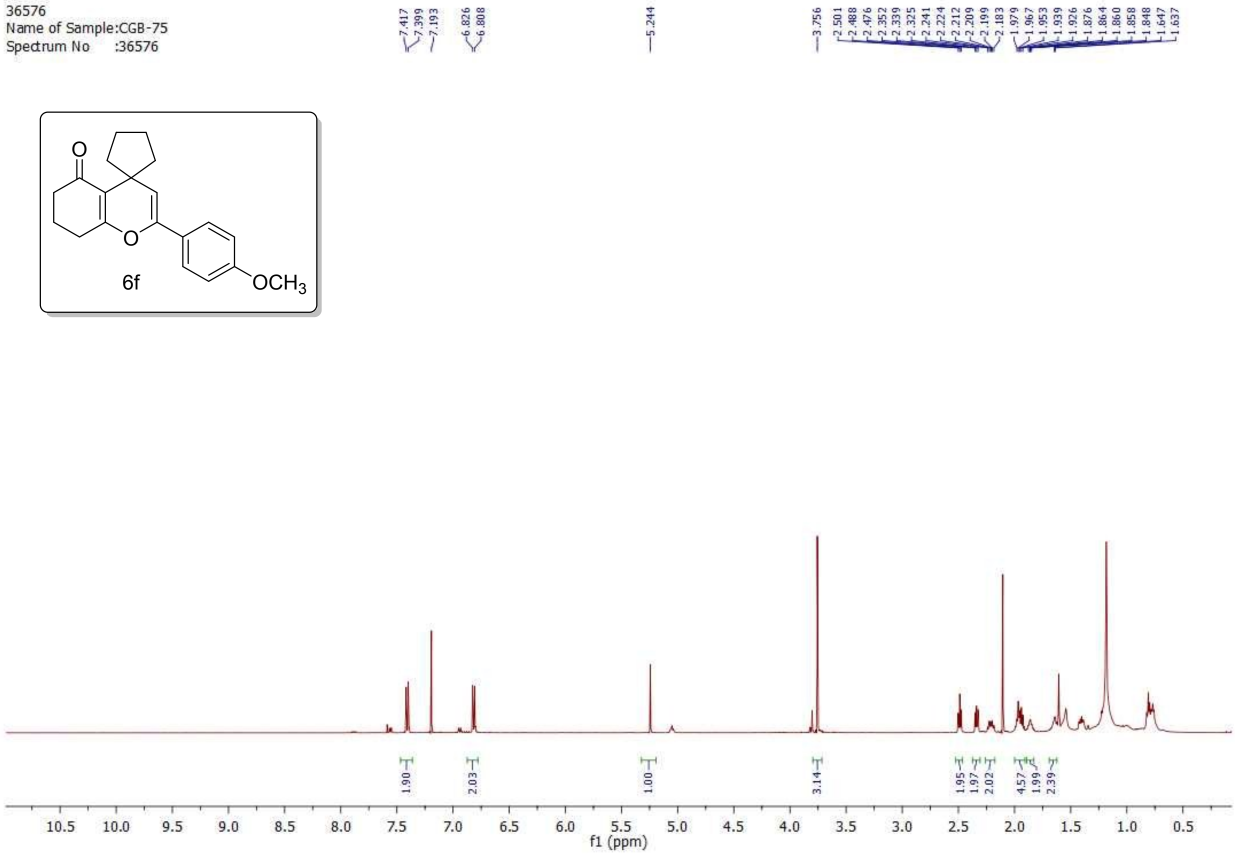

27272.5.fid
27272
MS-83-4
O
O
6d
F
f1 (ppm)

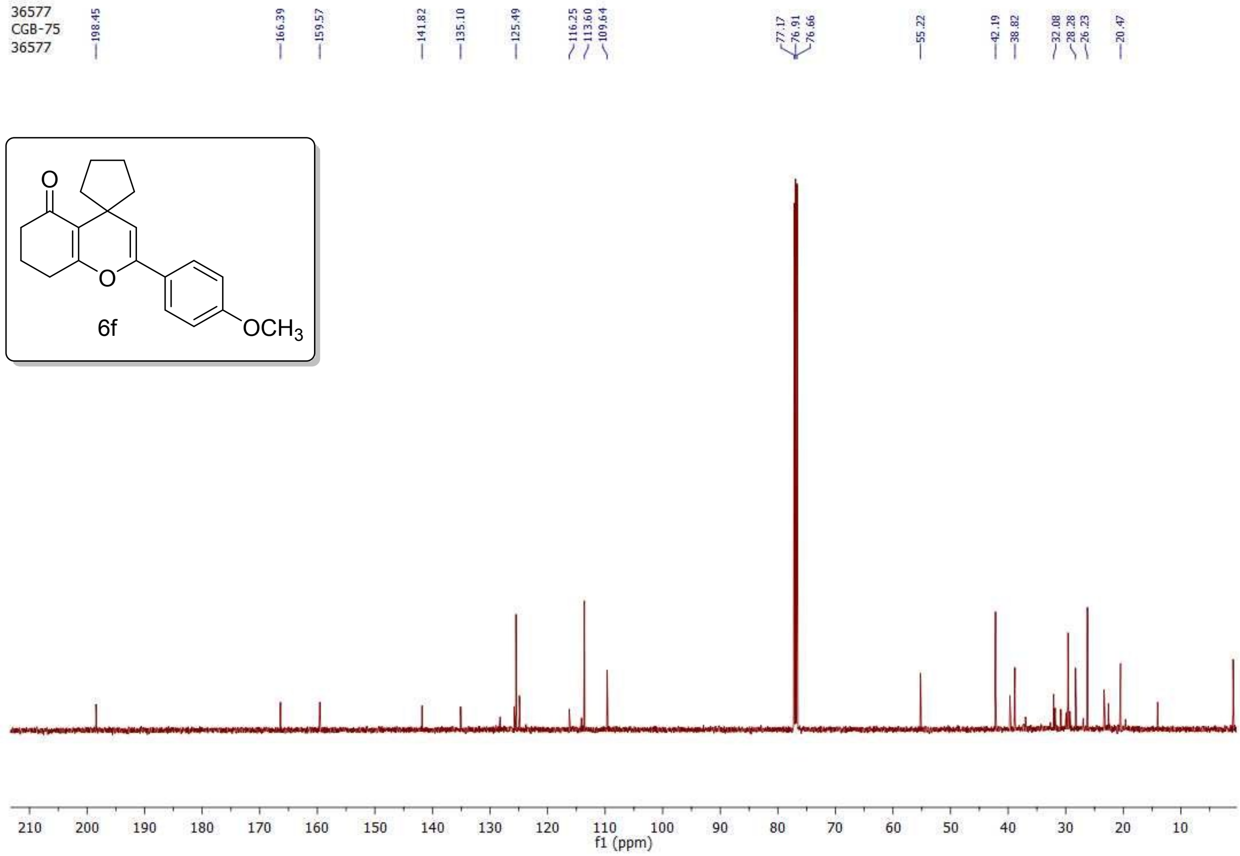
36439
Name of Sample:MS-C6
Spectrum No :36439

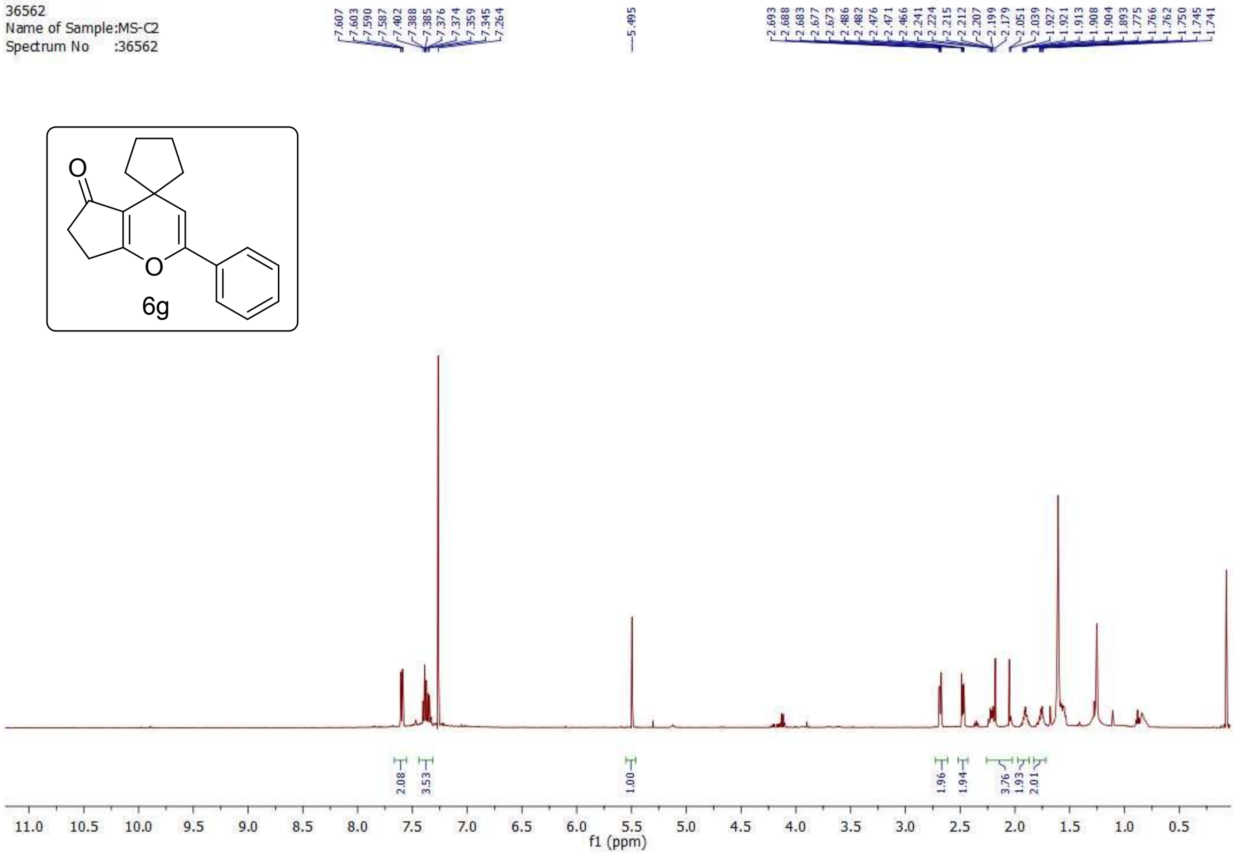


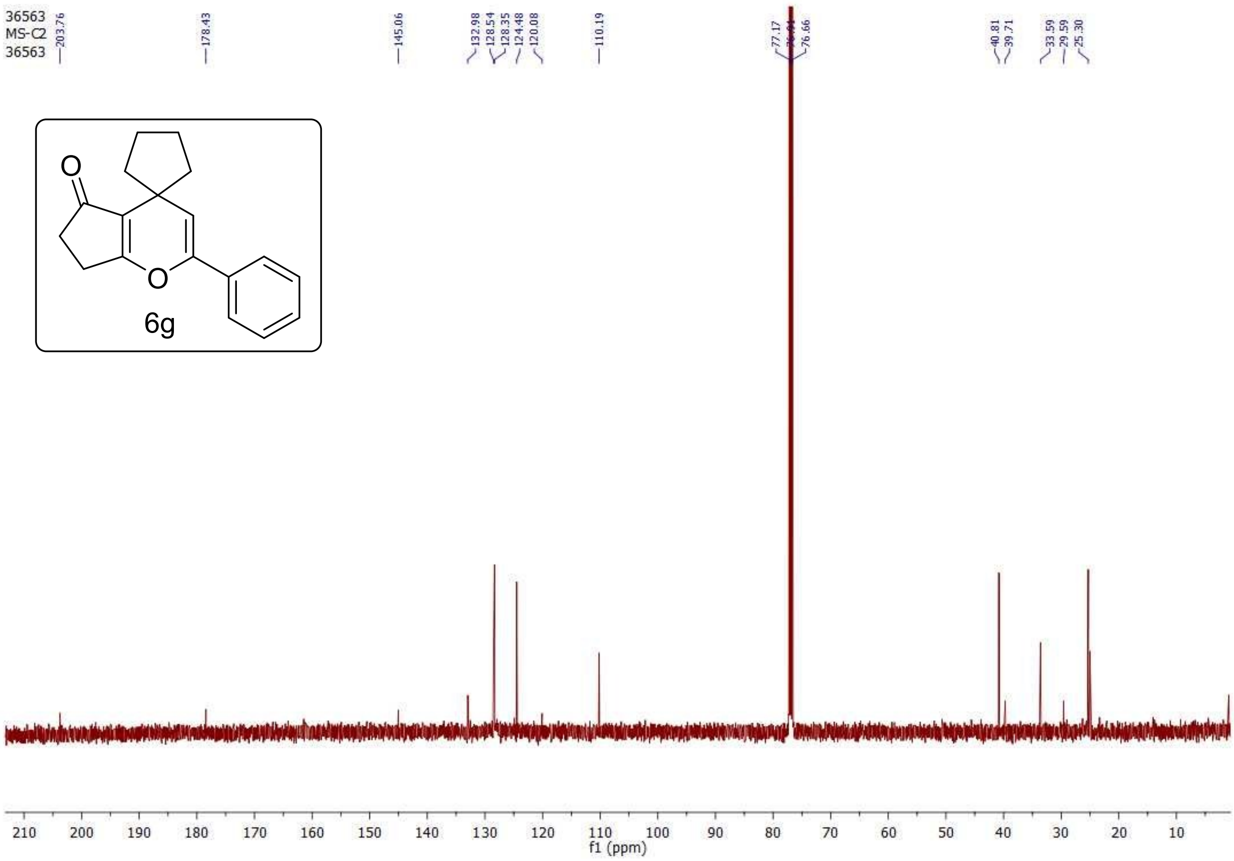
36440
Name of Sample:MS-C6
Spectrum No :36440




36576
Name of Sample:CGB-75
Spectrum No :36576
7.417
7.399
7.193
6.826
6.808
5.244
3.756
2.501
2.488
2.476
2.352
2.339
2.325
2.241
2.224
2.212
2.209
2.199
2.183
1.979
1.967
1.953
1.939
1.926
1.876
1.864
1.860
1.858
1.848
1.647
1.637
O
O
OCH3
6f
1.90
2.03
1.00
3.14
1.95
1.97
2.02
4.57
1.99
2.39
10.5
10.0
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
0.5
f1 (ppm)


36577
CGB-75
36577
198.45
166.39
159.57
141.82
135.10
125.49
116.25
113.60
109.64
77.17
76.91
76.66
55.22
42.19
38.82
32.08
28.28
26.23
20.47
O
O
OCH3
6f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


36562
Name of Sample:MS-C2
Spectrum No :36562
7.607
7.603
7.590
7.587
7.402
7.388
7.385
7.376
7.374
7.359
7.345
7.264
5.495
2.693
2.688
2.683
2.677
2.673
2.486
2.482
2.476
2.471
2.466
2.241
2.224
2.215
2.212
2.207
2.199
2.179
2.051
2.039
1.927
1.921
1.913
1.908
1.904
1.893
1.775
1.766
1.762
1.750
1.745
1.741
O
O
6g
2.08
3.53
1.00
1.96
1.94
3.76
1.93
2.01
f1 (ppm)


36563
MS-C2
36563
203.76
178.43
145.06
132.98
128.54
128.35
124.48
120.08
110.19
77.17
76.66
40.81
39.71
33.59
29.59
25.30
O
O
6g
f1 (ppm)