Supporting Information for

Designing Naphthopyran Mechanophores with Tunable Mechanochromic Behavior

Brooke A. Versaw, Molly E. McFadden, Corey C. Husic, and Maxwell J. Robb*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

*E-mail: mrobb@caltech.edu

Table of Contents

I. General Experimental Details

Reagents from commercial sources were used without further purification unless otherwise stated. Dry tetrahydrofuran (THF) and dichloromethane (DCM) were obtained from a Pure Process Technology solvent purification system. All reactions were performed under a N_2 or argon atmosphere unless specified otherwise. Column chromatography was performed on a Biotage Isolera system using SiliCycle SiliaSep HP flash cartridges.

NMR spectra were recorded using a 400 MHz Bruker Avance III HD with Prodigy Cryoprobe, a 400 MHz Bruker Avance Neo, or Varian Inova 500 or 600 MHz spectrometers. All ^{1}H NMR spectra are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual acetone (2.05 ppm) or chloroform (7.26 ppm) in deuterated solvent. All ^{13}C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for acetone (206.26 ppm) or chloroform (77.16 ppm).

High resolution mass spectra (HRMS) were obtained from an Agilent 6200 series time-of-flight mass spectrometer equipped with an Agilent G1978A multimode source (ESI+ or ESI-) or a JEOL JMS-600H magnetic sector mass spectrometer equipped with a FAB+ probe.

UV-Vis absorption spectra were recorded on a Thermo Scientific Evolution 220 spectrometer. UV irradiation was performed using a Philips PL-S 9W/01/2P UVB bulb with a narrow emission of 305–315 nm and a peak at 311 nm under ambient conditions.

II. Supplementary Figures

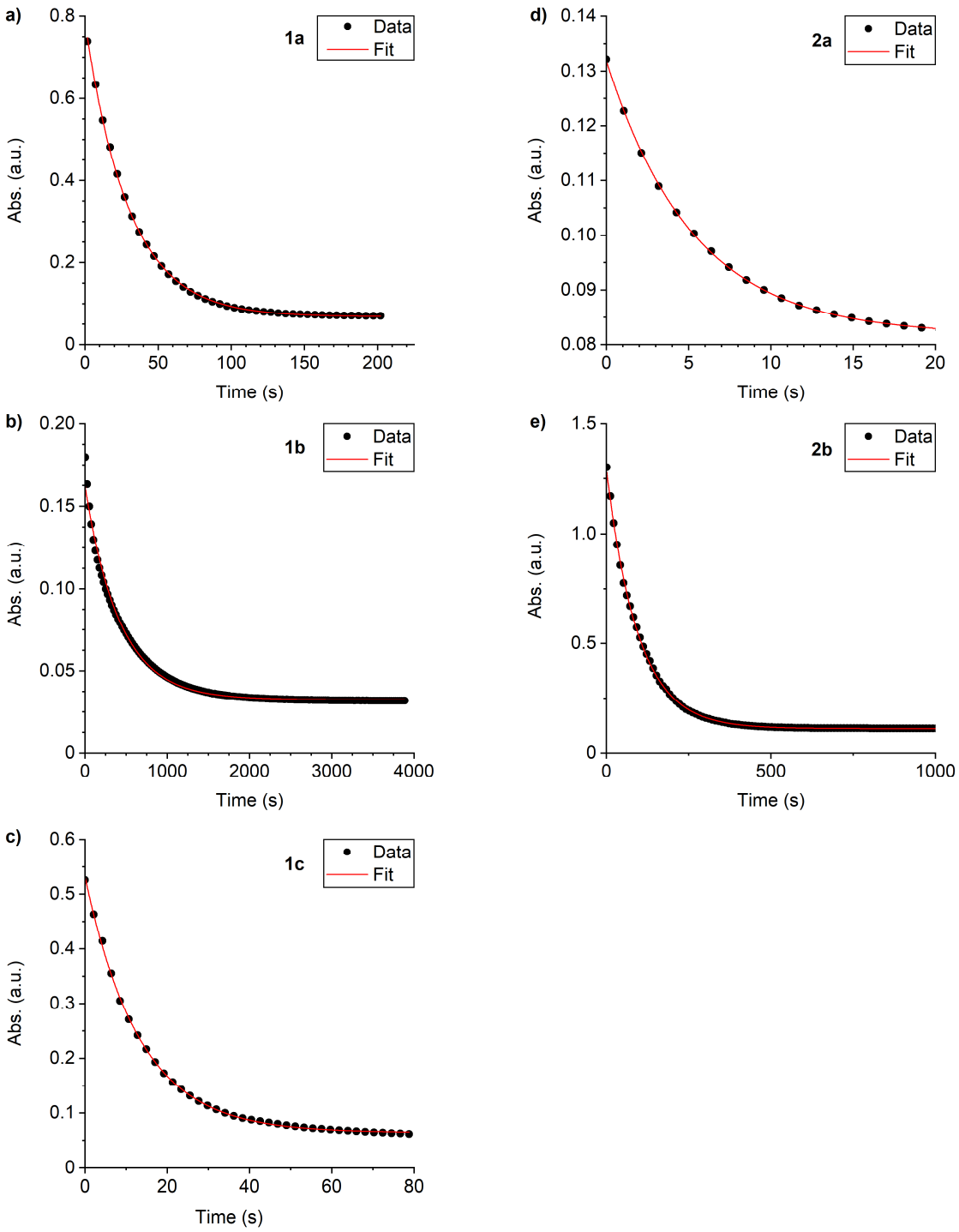


Figure S1. Representative plots for characterizing the kinetics of thermal reversion for the different merocyanines. Solutions of naphthopyrans in THF were irradiated with UV light (λ = 311 nm, 30 s) and absorbance was subsequently monitored at the λ_{max} corresponding to each merocyanine in the dark at room temperature. Data were fit to first-order exponential decay (eq S1) as described in Section VI to extract the rate constant for electrocyclization. The ring-closing reaction of the merocyanine generated from naphthopyran **2c** was too rapid to characterize effectively (see Section VI for additional details). Solution concentrations were 0.1 mM (**1a**, **1c**, **2b**), 0.01 mM (**1b**), and 0.25 mM (**2a**).

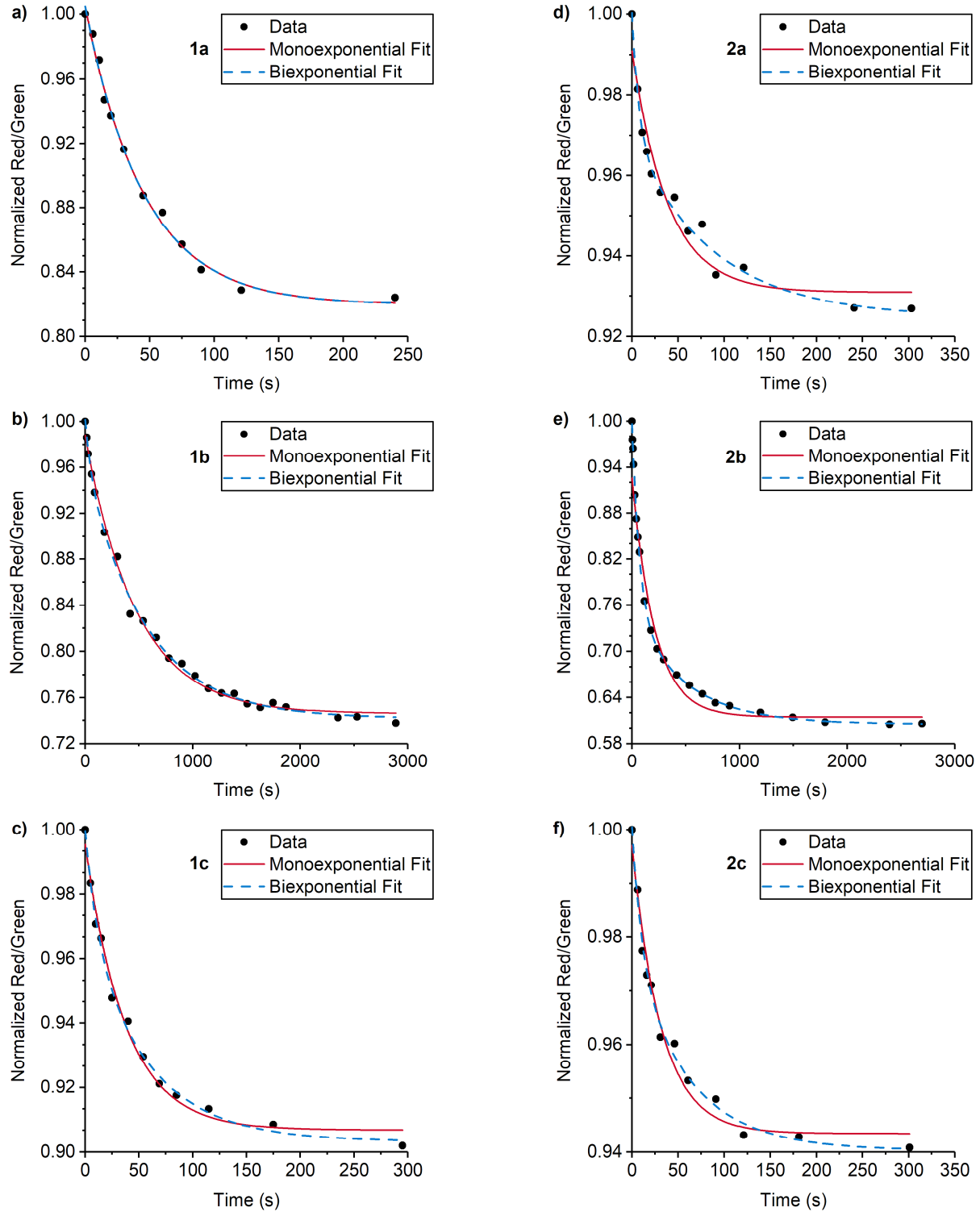
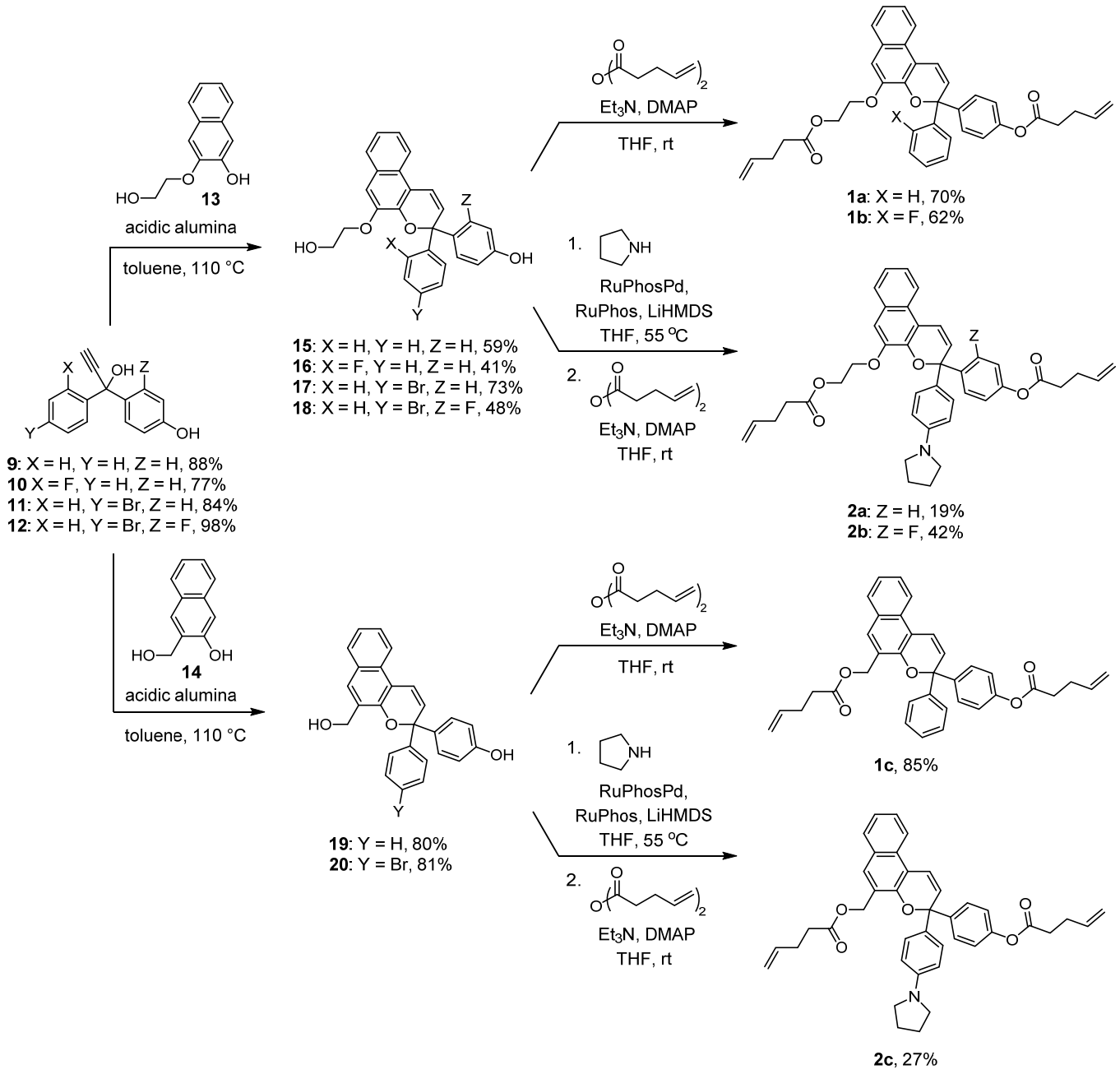


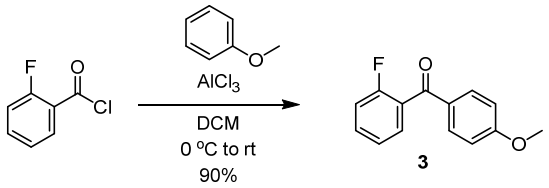
Figure S2. Characterization of thermal reversion kinetics for merocyanines in solid PDMS materials. Digital images of PDMS films containing 1.5 wt % naphthopyran were acquired after uniform irradiation with UV light (λ = 311 nm, 90 s). The intensities of the red and green color channels were extracted from each image and the ratio was plotted as a function of time. Data were fit to models of exponential decay to extract the rate constants for electrocyclization, as described in detail in Section VI. With the exception of **1a**, biexponential decay (eq S2) was required to accurately model the thermal fading behavior of the merocyanine dyes in the solid state.

III. Synthetic Details

The synthesis of naphthopyran crosslinker **1a**[1] and spiropyran crosslinker **SP**[2] has been described previously.

Scheme S1. Synthesis of naphthopyran crosslinkers





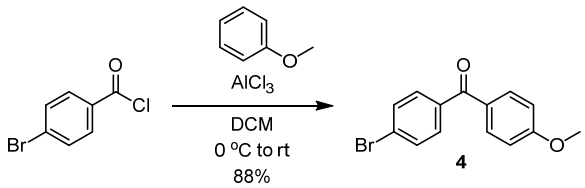
(2-fluorophenyl)(4-methoxyphenyl)methanone (3). A round bottom flask equipped with a stir bar and rubber septum was charged with $AlCl_3$ (4.63 g, 34.7 mmol) and dry DCM (80 mL). The flask was cooled to 0 °C in an ice bath, followed by the slow sequential addition of anisole (17.0 mL, 156 mmol) and 2-fluorobenzoyl chloride (3.8 mL, 32 mmol). The flask was allowed to warm to room temperature and stirred overnight. The mixture was then poured over ice and partitioned between water and ethyl acetate. The aqueous layer was discarded and the organic phase was washed with water (80 mL) and brine (80 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Trituration with hexanes afforded the title compound as an off-white crystalline solid (6.6 g, 90%).

TLC (3:7 EtOAc/hexanes): R_f = 0.70.

^{1}H NMR (400 MHz, acetone-d_6) δ: 7.83–7.77 (m, 2H), 7.63 (dddd, J_{HF} = 5.3, J_{HH} = 8.4, 7.3, 1.8 Hz, 1H), 7.55–7.50 (m, 1H), 7.36 (ddd, J_{HF} = 7.5 Hz, J_{HH} = 7.5, 1.0 Hz, 1H), 7.32–7.25 (m, 1H), 7.09–7.04 (m, 2H), 3.91 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 192.0, 164.0, 159.8 (d, J_{CF} = 251.1 Hz), 132.7 (d, J_{CF} = 8.1 Hz), 132.6, 130.5 (d, J_{CF} = 3.2 Hz), 130.3, 127.6 (d, J_{CF} = 15.5 Hz), 124.3 (d, J_{CF} = 3.6 Hz), 116.2 (d, J_{CF} = 21.8 Hz), 113.8, 55.6 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{14}H_{12}FO_2]^+$ $(M+H)^+$, 231.0816; found 231.0810.



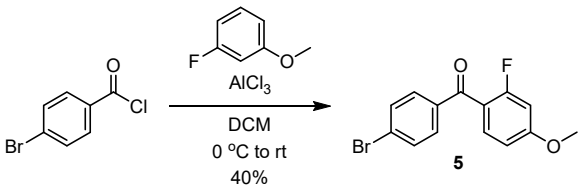
(4-bromophenyl)(4-methoxyphenyl)methanone (4). A round bottom flask equipped with a stir bar and rubber septum was charged with $AlCl_3$ (3.72 g, 27.9 mmol) and dry DCM (80 mL). The flask was cooled to 0 °C in an ice bath, followed by the slow sequential addition of anisole (14.2 mL, 131 mmol) and a solution of 4-bromobenzoyl chloride (6.025 g, 27.46 mmol) dissolved in dry DCM (10 mL). The flask was allowed to warm to room temperature and stirred for 26 h. The mixture was then cooled to 0 °C in an ice bath, quenched with water (40 mL), and diluted with DCM (80 mL). The aqueous layer was discarded and the organic phase was washed with water (2 x 70 mL), saturated aqueous $NaHCO_3$ (70 mL), and brine (70 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was dried under vacuum at 60 °C overnight to yield the title compound as a light pink crystalline solid (7.05 g, 88%).

TLC (5:95 EtOAc/hexanes): R_f = 0.34.

^{1}H NMR (400 MHz, acetone-d_6) δ: 7.83–7.78 (m, 2H), 7.77–7.72 (m, 2H), 7.70–7.66 (m, 2H), 7.11–7.06 (m, 2H), 3.92 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 194.6, 163.6, 137.2, 132.6, 131.6, 131.4, 129.9, 127.0, 113.8, 55.7 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{14}H_{12}BrO_2]^+$ $(M+H)^+$, 291.0015; found, 291.0012.



5

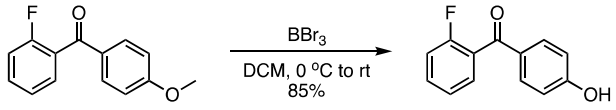
(4-bromophenyl)(2-fluoro-4-methoxyphenyl)methanone (5). A round bottom flask equipped with a stir bar and rubber septum was charged with $AlCl_3$ (6.32 g, 47.4 mmol) and dry DCM (100 mL). The flask was cooled to 0 °C in an ice bath, followed by the slow sequential addition of 3-fluoroanisole (8.0 mL, 70 mmol) and a solution of 4-bromobenzoyl chloride (10.195 g, 46.455 mmol) dissolved in dry DCM (35 mL). After warming to room temperature and stirring overnight, the mixture was cooled to 0 °C in an ice bath, quenched with water (200 mL), and diluted with ethyl acetate (100 mL). The aqueous layer was discarded and the organic phase washed with saturated aqueous $NaHCO_3$ (75 mL) and brine (75 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (0–20% EtOAc/hexanes) afforded the title compound as a white crystalline solid (5.7 g, 40%).

TLC (15:85 EtOAc/hexanes): R_f = 0.58.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71–7.63 (m, 2H), 7.61–7.54 (m, 3H), 6.79 (dd, J = 8.7, 2.4 Hz, 1H), 6.65 (dd, J_{HF} = 12.0 Hz, J_{HH} = 2.4 Hz, 1H), 3.87 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 191.8, 164.3 (d, J_{CF} = 11.4 Hz), 162.0 (d, J_{CF} = 254.0 Hz), 137.3, 132.8 (d, J_{CF} = 4.3 Hz), 131.7, 131.2, 128.0, 118.9 (d, J_{CF} = 13.7 Hz), 110.7 (d, J_{CF} = 2.9 Hz), 102.0 (d, J_{CF} = 25.7 Hz), 56.0 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{14}H_{11}FO_2Br]^+$ $(M+H)^+$, 308.9926; found, 308.9915.



3 6

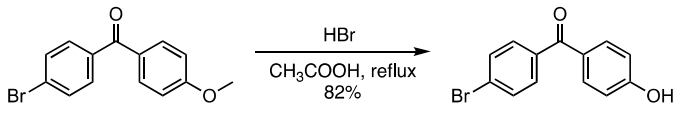
(2-fluorophenyl)(4-hydroxyphenyl)methanone (6). A flame-dried round bottom flask equipped with a stir bar was charged with **3** (1.027 g, 4.459 mmol) and dry DCM (6.5 mL). The flask was cooled in a bath of ice and salt, followed by the slow addition of BBr_3 (1 M in DCM, 22.0 mL, 22.0 mmol). The flask was allowed to warm to room temperature and stirred overnight, after which the crude mixture was poured over ice and partitioned between water and ethyl acetate. The organic layer was washed with water (40 mL) and brine (40 mL), then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography (7–60% EtOAc/hexanes) afforded the title compound as a white solid (821 mg, 85%).

TLC (3:7 EtOAc/hexanes): R_f = 0.42.

^{1}H NMR (400 MHz, acetone-d_6) δ: 9.41 (s, 1H), 7.77–7.71 (m, 2H), 7.61 (dddd, J_{HF} = 5.3, J_{HH} = 8.3, 7.3, 1.8 Hz, 1H), 7.51 (ddd, J_{HF} = 7.3 Hz, J_{HH} = 7.3, 1.8 Hz, 1H), 7.35 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.27 (ddd, J_{HF} = 9.6 Hz, J_{HH} = 8.3, 1.0 Hz, 1H), 7.01–6.92 (m, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 192.7, 161.2, 159.9 (d, J_{CF} = 251.3 Hz), 132.90, 132.88 (d, J_{CF} = 8.2 Hz), 130.6 (d, J_{CF} =3.0 Hz), 130.2, 127.4 (d, J_{CF} = 15.4 Hz), 124.4 (d, J_{CF} = 3.6 Hz), 116.4 (d, J_{CF} = 21.8 Hz), 115.6 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{13}H_{10}FO_2]^+$ $(M+H)^+$, 217.0659; found, 217.0667.



4 **7**

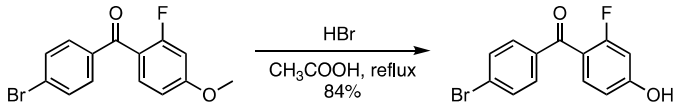
(4-bromophenyl)(4-hydroxyphenyl)methanone (7). A flame-dried round bottom flask equipped with a stir bar and reflux condenser was charged with **4** (5.012 g, 17.22 mmol), concentrated HBr (48% aqueous solution, 30.0 mL, 265 mmol), and glacial acetic acid (60.0 mL). After refluxing for 16 h, the reaction mixture was diluted with water (75 mL) and extracted with DCM (3 x 25 mL). The combined organic fractions were washed with water (25 mL) and brine (25 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the title compound as a peach solid (3.92 g, 82%).

TLC (3:7 EtOAc/hexanes): R_f = 0.40.

^{1}H NMR (400 MHz, acetone-d_6) δ: 9.26 (br s, 1H), 7.73 (d, *J* = 8.8 Hz, 4H), 7.67 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-d_6) δ: 194.2, 162.9, 138.6, 133.5, 132.4, 132.2, 129.7, 126.8, 116.2 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{13}H_{10}BrO_2]^+$ $(M+H)^+$, 276.9859; found, 276.9860.



5 **8**

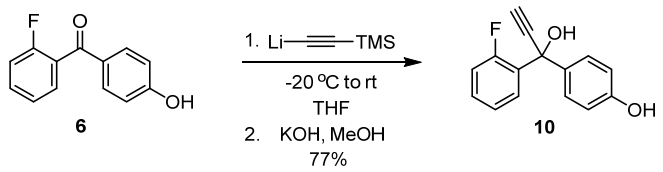
(4-bromophenyl)(2-fluoro-4-hydroxyphenyl)methanone (8). A round bottom flask equipped with a stir bar and reflux condenser was charged with **5** (579 mg, 1.87 mmol) and glacial acetic acid (8.5 mL). The flask was cooled to 0 °C in an ice bath, followed by the addition of HBr (48% aqueous solution, 3.6 mL, 32 mmol). The flask was then heated to reflux for 16 h, after which the reaction mixture was diluted with water (30 mL) and extracted with DCM (3 x 50 mL). The combined organic fractions were then washed with H_2O (60 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography (6–50% EtOAc/hexanes) afforded the title compound as a white solid (465 mg, 84%).

TLC (1:4 EtOAc/hexanes): R_f = 0.38.

^{1}H NMR (400 MHz, acetone-d_6) δ: 9.64 (br s, 1H), 7.76–7.68 (m, 4H), 7.53 (ddd, J_{HF} = 8.5 Hz, J_{HH} = 8.5, 1.5 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.70 (dd, J_{HF} = 12.2 Hz, J_{HH} = 1.4 Hz, 1H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-d_6) δ: 191.7, 163.6 (d, J_{CF} = 12.1 Hz), 162.9 (d, J_{CF} = 251.7 Hz), 138.6, 133.7 (d, J_{CF} = 4.5 Hz), 132.5, 131.9, 127.9, 118.7 (d, J_{CF} = 13.6 Hz), 112.9 (d, J_{CF} = 2.7 Hz), 104.0 (d, J_{CF} = 24.7 Hz) ppm.

HRMS (FAB, *m/z*): calcd for $[C_{13}H_9FO_2Br]^+$ $(M+H)^+$, 294.9770; found, 294.9779.



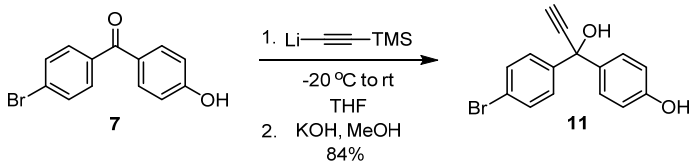
4-(1-(2-fluorophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (10). A flame-dried round bottom flask equipped with a stir bar and rubber septum was charged with dry THF (30 mL) and trimethylsilylacetylene (1.55 mL, 11.2 mmol). The flask was cooled to −20 °C in a bath of ice and salt, followed by the slow addition of n-butyllithium (2.5 M in hexanes, 5.0 mL, 13 mmol). After stirring for 1 h, a solution of benzophenone **6** (1.025 g, 4.742 mmol) dissolved in dry THF (2 mL) was added dropwise to the cold lithium TMS-acetylide mixture. After complete addition, the reaction mixture was allowed to warm to room temperature. After stirring for 18 h, the flask was cooled to 0 °C in an ice bath and a solution of KOH (1.261 g, 22.47 mmol) in methanol (10 mL) was added via syringe. The mixture was warmed to room temperature and stirred for approximately 1 h. The flask was subsequently cooled to 0 °C in an ice bath and neutralized by the slow addition of acetic acid (1.5 mL). The crude mixture was concentrated under reduced pressure and partitioned between water and ethyl acetate. The aqueous layer was discarded and the organic phase was washed with water (40 mL) and brine (40 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (10–60% EtOAc/hexanes) to yield the title compound as an off-white solid (0.88 g, 77%).

TLC (1:1 EtOAc/hexanes): R_f = 0.69.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.37 (s, 1H), 7.92 (ddd, J_{HF} = 8.0 Hz, J_{HH} = 8.0, 1.8 Hz, 1H), 7.43–7.38 (m, 2H), 7.34 (dddd, J_{HF} = 4.8 Hz, J_{HH} = 7.9, 7.9, 1.8 Hz, 1H), 7.22 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 6.99 (ddd, J_{HF} = 11.5 Hz, J_{HH} = 8.1, 1.3 Hz, 1H), 6.80–6.73 (m, 2H), 5.57 (s, 1H), 3.27 (s, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 160.2 (d, J_{CF} = 249.4 Hz), 157.4, 136.0, 133.7 (d, J_{CF} = 10.5 Hz), 130.0 (d, J_{CF} = 8.2 Hz), 128.1, 127.4 (d, J_{CF} = 2.9 Hz), 124.1 (d, J_{CF} = 3.7 Hz), 116.4 (d, J_{CF} = 21.7 Hz), 115.0, 86.2, 75.1 (d, J_{CF} = 2.5 Hz), 70.8 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{15}H_{10}FO]^+$ $(M-OH)^+$, 225.0710; found, 225.0707.



4-(1-(4-bromophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (11). A flame-dried round bottom flask equipped with a stir bar and rubber septum was charged with dry THF (90 mL) and trimethylsilylacetylene (4.3 mL, 31.0 mmol). The flask was cooled to −20 °C in a bath of ice and salt, followed by the slow addition of n-butyllithium (2.5 M in hexanes, 13.0 mL, 32.5 mmol). After stirring for 1 h, a solution of benzophenone **7** (3.753 g, 13.54 mmol) in dry THF (12 mL) was added dropwise to the cold lithium TMS-acetylide mixture. After complete addition, the reaction mixture was allowed to warm to room temperature. After stirring overnight, the flask was cooled to 0 °C in an ice bath and a solution of KOH (3.86 g, 68.8 mmol) in methanol

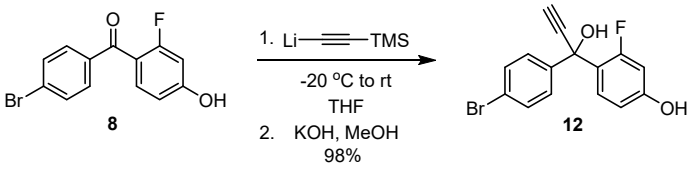
(20 mL) was added via syringe. The mixture was warmed to room temperature and stirred for approximately 1 h. The flask was subsequently cooled to 0 °C in an ice bath and neutralized by the slow addition of acetic acid (~ 6 mL). The crude mixture was concentrated under reduced pressure and partitioned between water and ethyl acetate. The aqueous layer was discarded and the organic phase was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (7–60% EtOAc/hexanes) afforded the title compound as an off-white solid (3.5 g, 84%).

TLC (1:5 EtOAc/hexanes): R_f = 0.27.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.34 (s, 1H), 7.57–7.46 (m, 4H), 7.44–7.38 (m, 2H), 6.82–6.73 (m, 2H), 5.63 (s, 1H), 3.35 (s, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 157.4, 146.6, 137.0, 131.5, 128.6, 127.9, 121.2, 115.3, 87.5, 76.0, 73.4 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{15}H_{10}BrO]^+$ $(M-OH)^+$, 284.9910; found, 284.9910.



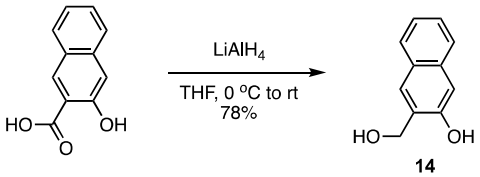
4-(1-(4-bromophenyl)-1-hydroxyprop-2-yn-1-yl)-3-fluorophenol (12). A flame-dried round bottom flask equipped with a stir bar and rubber septum was charged with dry THF (12 mL) and trimethylsilylacetylene (1.0 mL, 7.2 mmol). The flask was cooled to 0 °C in an ice bath, followed by the slow addition of n-butyllithium (2.5 M in hexanes, 2.8 mL, 7.0 mmol). After stirring for 1 h, a solution of **8** (865 mg, 2.93 mmol) in dry THF (13 mL) was added dropwise to the cold lithium TMS-acetylide mixture. After complete addition, the reaction mixture was allowed to warm to room temperature. After stirring for 18 h, the flask was cooled to 0 °C in an ice bath and a solution of KOH (850 mg, 15 mmol) in methanol (4 mL) was added via syringe. The mixture was warmed to room temperature and stirred for 3.5 h, then neutralized by the slow addition of hydrochloric acid (6 M). The crude material was then diluted in ethyl acetate (50 mL) and washed with water (2 x 50 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield the title compound as a sticky brown solid (920 mg, 98%).

TLC (1:1 EtOAc/hexanes): R_f = 0.68.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.81 (d, J_{HF} = 0.9 Hz, 1H), 7.73 (dd, J_{HF} = 9.4 Hz, J_{HH} = 8.6 Hz, 1H), 7.54–7.47 (m, 4H), 6.70 (ddd, J_{HF} = 0.8 Hz, J_{HH} = 8.6, 2.4 Hz, 1H), 6.48 (dd, J_{HF} = 12.8 Hz, J_{HH} = 2.4 Hz, 1H), 5.75 (s, 1H), 3.35 (s, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 161.1 (d, J_{CF} = 248.8 Hz), 159.7 (d, J_{CF} = 11.4 Hz), 145.4, 131.6, 129.0, 128.9 (d, J_{CF} = 4.7 Hz), 124.0 (d, J_{CF} = 11.3 Hz), 121.7, 111.2 (d, J_{CF} = 2.9 Hz), 104.3 (d, J_{CF} = 24.1 Hz), 86.2, 76.2 (d, J_{CF} = 2.1 Hz), 71.1 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{15}H_{10}FO_2Br]^+$ $(M)^+$, 319.9848; found, 319.9835.



14

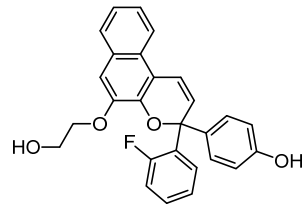
3-(hydroxymethyl)naphthalen-2-ol (14). A flame-dried round bottom flask equipped with a stir bar and rubber septum was cooled to 0 °C in an ice bath and charged with lithium aluminum hydride (3.5 M in THF, 34.5 mL, 121 mmol). A solution of 3-hydroxy-2-naphthoic acid (4.495 g, 23.89 mmol) in dry THF (20 mL) was added dropwise to the cold solution of LAH over 45 minutes. The flask was allowed to warm to room temperature and stirred for 16 h, after which the mixture was cooled to 0 °C in an ice bath and quenched by the slow, dropwise addition of ethyl acetate (40 mL), followed by a saturated aqueous solution of Rochelle's salt (150 mL). The crude mixture was stirred for 1 h, then warmed to room temperature and diluted with ethyl acetate (100 mL) and saturated Rochelle's salt (100 mL). Concentrated hydrochloric acid (6 M) was added to reach pH 5 and the solution was extracted with 1:1 DCM/ethyl acetate (900 mL). The organic phase was washed with water, saturated $NaHCO_3$, and brine, then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography (12–100% EtOAc/hexanes) afforded the title compound as a beige powder (3.25 g, 78%).

TLC (1:1 EtOAc/hexanes): R_f = 0.50.

^{1}H NMR (400 MHz, acetone-d_6) δ: 7.83 (d, J = 1.1 Hz, 1H), 7.76 (dd, J = 8.2, 1.2 Hz, 1H), 7.65 (dd, J = 8.4, 1.2 Hz, 1H), 7.35 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.26 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.19 (s, 1H), 4.89 (d, J = 1.2 Hz, 2H), 3.05 (br s, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 154.4, 134.9, 131.5, 129.3, 128.3, 126.8, 126.5, 126.4, 123.7, 109.6, 61.5 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{11}H_9O_2]^-$ $(M-H)^-$, 173.0608; found 173.0605.



16

5-(2-hydroxyethoxy)-3-(4-hydroxyphenyl)-3-(2-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (16). A two-neck round bottom flask equipped with a stir bar and reflux condenser was charged with **13**[1] (285 mg, 1.40 mmol), **10** (440 mg, 1.82 mmol), acidic alumina (1.095 g), and dry toluene (16.5 mL). After refluxing for 18 h, the mixture was removed from heat and filtered through a plug of silica, eluting with ethyl acetate, and the filtrate was concentrated under reduced pressure. Purification by column chromatography (52–67% EtOAc/hexanes) provided the title compound as a red foamy solid (246 mg, 41%).

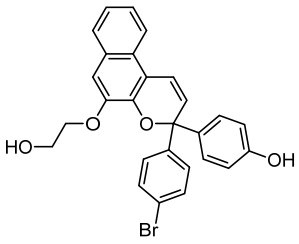
TLC (1:1 EtOAc/hexanes): R_f = 0.38.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.01–7.95 (m, 1H), 7.86 (ddd, J_{HF} = 8.0 Hz, J_{HH} = 8.0, 1.8 Hz, 1H), 7.73–7.68 (m, 1H), 7.43 (d, J = 10.1 Hz, 1H), 7.40–7.28 (m, 6H), 7.16 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.08 (ddd,

J_{HF} = 11.8 Hz, J_{HH} = 8.2, 1.2 Hz, 1H), 6.83–6.77 (m, 2H), 6.59 (dd, J_{HF} = 5.5 Hz, J_{HH} = 10.0 Hz, 1H), 4.32–4.22 (m, 2H), 4.02–3.95 (m, 2H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6) δ: 160.1 (d, J_{CF} = 246.4 Hz), 158.1, 149.1, 143.0, 135.3, 132.4 (d, J_{CF} = 11.3 Hz), 130.7, 130.5 (d, J_{CF} = 8.4 Hz), 129.3, 129.0 (d, J_{CF} = 3.6 Hz), 128.5 (d, J_{CF} = 4.7 Hz), 128.1, 125.9, 125.3, 125.1, 124.8 (d, J_{CF} = 3.4 Hz), 122.1, 120.4, 117.0 (d, J_{CF} = 22.3 Hz), 116.2, 115.6, 110.2, 81.6 (d, J_{CF} = 2.8 Hz), 71.5, 61.3 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{27}H_{21}FO_4Na]^+$ $(M+Na)^+$, 451.1316; found, 451.1324.



17

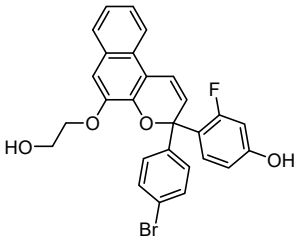
5-(2-hydroxyethoxy)-3-(4-hydroxyphenyl)-3-(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran (17). A two-neck round bottom flask equipped with a stir bar and reflux condenser was charged with **13**[1] (313 mg, 1.53 mmol), **11** (603 mg, 1.99 mmol), acidic alumina (1.200 g), and toluene (18 mL). After refluxing overnight, the mixture was removed from heat and filtered through a plug of celite, eluting with ethyl acetate, and the filtrate was concentrated under reduced pressure. Purification by column chromatography (20–100% EtOAc/hexanes) provided the title compound as a red foamy solid (548 mg, 73%).

TLC (1:1 EtOAc/hexanes): R_f = 0.40.

^1H NMR (400 MHz, acetone-d_6) δ: 8.41 (s, 1H), 7.97 (dd, J = 8.0, 1.3 Hz, 1H), 7.71–7.66 (m, 1H), 7.59–7.53 (m, 2H), 7.50–7.46 (m, 2H), 7.45 (d, J = 9.9 Hz, 1H), 7.42–7.26 (m, 5H), 6.81–6.76 (m, 2H), 6.53 (d, J = 9.9 Hz, 1H), 4.26 (dd, J = 5.9, 3.4 Hz, 2H), 4.05–3.97 (m, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6) δ: 157.9, 149.3, 145.8, 143.4, 136.3, 131.9, 130.8, 129.9, 129.7, 129.2, 128.1, 126.0, 125.3, 125.2, 122.1, 121.8, 120.9, 116.7, 115.8, 110.3, 82.7, 71.6, 61.4 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{27}H_{22}BrO_4]^+$ $(M+H)^+$, 489.0696; found, 489.0688.



18

5-(2-hydroxymethyl)-3-(2-fluoro-4-hydroxyphenyl)-3-(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran (18). A two-neck round bottom flask equipped with a stir bar and reflux condenser was charged with **12** (579 mg, 1.80 mmol), **13**[1] (582 mg, 2.85 mmol), acidic alumina (2.343 g), and toluene (18 mL). After refluxing overnight, the mixture was filtered through a plug of celite, eluting with ethyl acetate, and the filtrate was

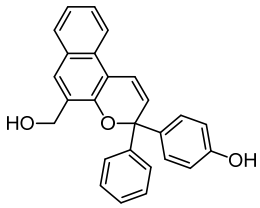
concentrated under reduced pressure. Purification by column chromatography (20–100% EtOAc/hexanes) afforded the title product as a foamy red-orange solid (437 mg, 48%).

TLC (1:1 EtOAc/hexanes): R_f = 0.25.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.86 (s, 1H), 8.02–7.95 (m, 1H), 7.73–7.67 (m, 1H), 7.59–7.48 (m, 5H), 7.44 (d, J = 10.0 Hz, 1H), 7.38–7.28 (m, 3H), 6.64 (ddd, J_{HF} = 0.6 Hz, J_{HH} = 8.6, 2.4 Hz, 1H), 6.57 (dd, J_{HF} = 13.2 Hz, J_{HH} = 2.4 Hz, 1H), 6.52 (dd, J_{HF} = 4.5 Hz, J_{HH} = 10.0 Hz, 1H), 4.31–4.22 (m, 2H), 4.02–3.93 (m, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 161.0 (d, J_{CF} = 246.7 Hz), 159.8 (d, J_{CF} = 12.2 Hz), 149.0, 144.4, 142.8, 131.9, 130.7, 129.8 (d, J_{CF} = 5.3 Hz), 129.7, 128.2 (d, J_{CF} = 3.7 Hz), 128.1, 125.8, 125.3, 125.2, 122.4 (d, J_{CF} = 11.5 Hz), 122.1, 120.6, 120.5, 116.4, 111.7 (d, J_{CF} = 2.9 Hz), 110.3, 104.5 (d, J_{CF} = 24.7 Hz), 81.1 (d, J_{CF} = 2.5 Hz), 71.5, 61.3 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{27}H_{20}FO_4Br]^+$ $(M)^+$, 506.0529; found, 506.0540.



19

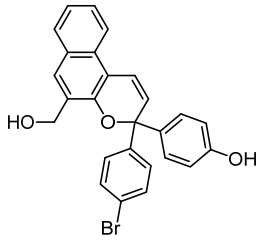
5-(2-hydroxymethyl)-3-(4-hydroxyphenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (19). A two-neck round bottom flask equipped with a stir bar and reflux condenser was charged with **14** (0.503 g, 2.89 mmol), **9**[1] (0.843 g, 3.76 mmol), acidic alumina (1.932 g), and dry toluene (34 mL). After refluxing 13 h, the mixture was removed from heat and filtered through a plug of silica, eluting with ethyl acetate, and the filtrate was concentrated under reduced pressure. Purification by column chromatography (7–60% EtOAc/hexanes) afforded the title product as a foamy red-orange solid (882 mg, 80%).

TLC (1:1 EtOAc/hexanes): R_f = 0.54.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.06 (dd, J = 8.5, 1.0 Hz, 1H), 7.86 (d, J = 1.3 Hz, 1H), 7.80–7.75 (m, 1H), 7.57–7.51 (m, 2H), 7.49–7.43 (m, 2H), 7.38–7.30 (m, 5H), 7.27–7.21 (m, 1H), 6.81–6.75 (m, 2H), 6.37 (d, J = 10.0 Hz, 1H), 5.00–4.90 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 157.7, 149.0, 146.6, 136.8, 132.1, 130.0, 129.9, 129.13, 129.07, 128.9, 128.0, 127.3, 127.1, 127.0, 124.6, 122.1, 120.4, 115.6, 114.6, 83.1, 60.1 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{26}H_{21}O_3]^+$ $(M+H)^+$, 381.1485; found, 381.1488.



20

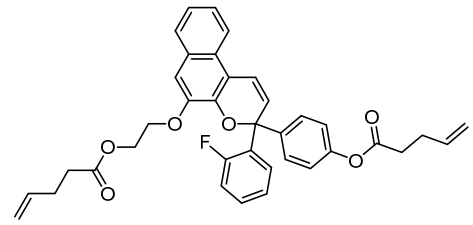
5-(2-hydroxymethyl)-3-(4-hydroxyphenyl)-3-(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran (20). A two-neck round bottom flask equipped with a stir bar and reflux condenser was charged with **14** (0.507 g, 2.91 mmol), **11** (1.148 g, 3.79 mmol), acidic alumina (1.947 g), and dry toluene (35 mL). After refluxing overnight, the mixture was removed from heat, filtered through a plug of celite, eluting with ethyl acetate, and the filtrate was concentrated under reduced pressure. Purification by column chromatography (7–60% EtOAc/hexanes) afforded the title product as a foamy red-orange solid (1.09 g, 81%).

TLC (1:1 EtOAc/hexanes): R_f = 0.50.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.42 (s, 1H), 8.06 (dd, J = 8.6, 1.1 Hz, 1H), 7.87 (d, J = 1.2 Hz, 1H), 7.80–7.76 (m, 1H), 7.54–7.43 (m, 6H), 7.38–7.31 (m, 3H), 6.82–6.77 (m, 2H), 6.36 (d, J = 10.0 Hz, 1H), 5.01–4.87 (m, 2H), 4.29 (t, J = 5.7 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 157.8, 148.8, 145.9, 136.2, 131.92, 131.90, 130.0, 129.8, 129.5, 129.1, 129.0, 128.3, 127.4, 127.1, 124.7, 122.1, 121.7, 120.8, 115.8, 114.5, 82.7, 60.1 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{26}H_{20}BrO_3]^+$ $(M+H)^+$,459.0590; found, 459.0578.



1b

5-(2-(pent-4-enoyloxy)ethoxy)-3-(4-(pent-4-enoyloxy)phenyl)-3-(2-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (1b). A flame-dried round bottom flask equipped with a stir bar and rubber septum was charged with **16** (142 mg, 0.331 mmol) and DMAP (11 mg, 0.090 mmol). Dry THF (3.2 mL), triethylamine (105 µL, 0.753 mmol), and 4-pentenoic anhydride (155 µL, 0.848 mmol) were then added sequentially. After stirring overnight, THF was removed under reduced pressure and the crude reaction mixture was partitioned between ethyl acetate (12 mL) and water (6 mL). The aqueous layer was discarded and the organic layer was washed with 10% aqueous $NaHSO_4$ (6 mL), 10% aqueous $NaHCO_3$ (6 mL), and brine (6 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (5–30% EtOAc/hexanes) to afford the title compound as a red oil (127 mg, 62%).

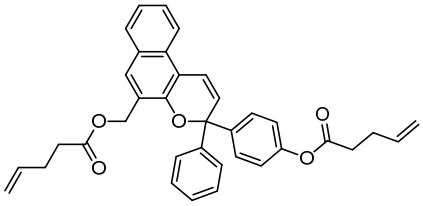
TLC (3:7 EtOAc/hexanes): R_f = 0.62.

^{1}H NMR (400 MHz, acetone-d_6) δ: 7.99 (dd, J_{HF} = 1.4 Hz, J_{HH} = 8.2 Hz, 1H), 7.86 (ddd, J_{HF} = 8.0 Hz, J_{HH} = 8.0, 1.8 Hz, 1H), 7.75–7.68 (m, 1H), 7.67–7.59 (m, 2H), 7.48 (d, J = 10.1 Hz, 1H), 7.40–7.29 (m, 4H), 7.20 (ddd, J_{HF} = 1.2 Hz, J_{HH} = 7.6, 7.6 Hz, 1H), 7.15–7.06 (m, 3H), 6.65 (dd, J_{HF} = 5.0 Hz, J_{HH} = 10.0 Hz, 1H),

5.96–5.76 (m, 2H), 5.14–4.89 (m, 4H), 4.56 (t, J = 4.6 Hz, 2H), 4.49–4.36 (m, 2H), 2.65 (t, J = 7.3 Hz, 2H), 2.49–2.39 (m, 4H), 2.38–2.30 (m, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-d_6) δ: 173.1, 171.7, 160.1 (d, J_{CF} = 246.9 Hz), 151.6, 148.5, 142.7, 141.8, 137.9, 137.7, 132.1 (d, J_{CF} = 11.0 Hz), 130.9 (d, J_{CF} = 8.5 Hz), 130.7, 128.8, 128.7 (d, J_{CF} = 3.4 Hz), 128.2, 127.7 (d, J_{CF} = 4.8 Hz), 126.0, 125.6, 125.4, 125.0 (d, J_{CF} = 3.4 Hz), 122.3, 122.2, 120.9, 117.3 (d, J_{CF} = 22.1 Hz), 116.4, 116.0, 115.8, 110.5, 81.3 (d, J_{CF} = 2.7 Hz), 67.8, 63.3, 34.0, 29.63, 29.55 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{37}H_{37}FO_6N]^+$ $(M+NH_4)^+$, 610.2599; found, 610.2599.



1c

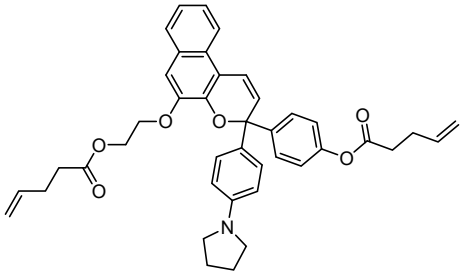
5-(2-(pent-4-enoyloxy)methyl)-3-(4-(pent-4-enoyloxy)phenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (1c). A flame-dried round bottom flask equipped with a stir bar was charged with **19** (401 mg, 1.06 mmol) and DMAP (36 mg, 0.28 mmol). THF (10.2 mL), triethylamine (0.34 mL, 2.4 mmol), and 4-pentenoic anhydride (0.49 mL, 2.7 mmol) were added sequentially. After stirring at room temperature 10 h, THF was removed under reduced pressure. The crude reaction mixture was then partitioned between ethyl acetate (10 mL) and water (5 mL). The aqueous layer was discarded, and the organic layer washed with 10% aqueous $NaHSO_4$ (2 x 5 mL), 10% aqueous $NaHCO_3$ (5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by column chromatography (5–30% EtOAc/hexanes) afforded the title compound as an orange oil (0.49 g, 85%).

TLC (3:7 EtOAc/hexanes): R_f = 0.70.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.10 (dd, J = 8.7, 1.1 Hz, 1H), 7.86–7.79 (m, 2H), 7.62–7.48 (m, 6H), 7.41–7.33 (m, 3H), 7.30–7.24 (m, 1H), 7.13–7.08 (m, 2H), 6.49 (d, J = 10.0 Hz, 1H), 5.96–5.82 (m, 2H), 5.42 (d, J = 0.8 Hz, 2H), 5.15–4.94 (m, 4H), 2.65 (t, J = 7.3 Hz, 2H), 2.55–2.47 (m, 2H), 2.47–2.34 (m, 4H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-d_6) δ: 172.0, 170.8, 150.4, 148.5, 144.9, 142.4, 137.1, 136.8, 129.79, 129.77, 128.8, 128.5, 128.2, 127.8, 127.8, 127.6, 127.1, 126.6, 125.0, 124.2, 121.5, 121.4, 119.7, 115.1, 114.9, 114.2, 82.4, 61.3, 33.2, 33.1, 28.74, 28.66 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{36}H_{36}O_5N]^+$ $(M+NH_4)^+$, 562.2588; found 562.2589.



2a

5-(2-(pent-4-enoyloxy)ethoxy)-3-(4-(pent-4-enoyloxy)phenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (2a). A scintillation vial equipped with a stir bar was charged with **17** (256 mg, 0.524 mmol), RuPhosPd G2 (33 mg, 0.043 mmol), and RuPhos (19 mg, 0.043 mmol) under nitrogen and sealed with a rubber septum. Pyrrolidine (62 µL, 0.75 mmol), LHMDS (1.5 M in THF, 1.4 mL, 2.1 mmol), and THF (2 mL) were then added sequentially under nitrogen and the mixture was stirred at 55 °C. After 14 h, THF was removed under reduced pressure and the reaction mixture was resuspended in a mixture of ethyl acetate (3 mL) and DMF (3 mL). After stirring at room temperature 5 minutes, the mixture was diluted with ethyl acetate (150 mL) and methanol (5 mL) and washed with saturated aqueous ammonium chloride (60 mL), water (3 x 50 mL), and brine (50 mL). The aqueous layers were extracted with ethyl acetate (2 x 50 mL) and the combined organic fractions were dried over Na_2SO_4, eluted through a plug of celite with ethyl acetate, and the filtrate was concentrated under reduced pressure to afford the crude diol, which was carried forward in the next step without further purification.

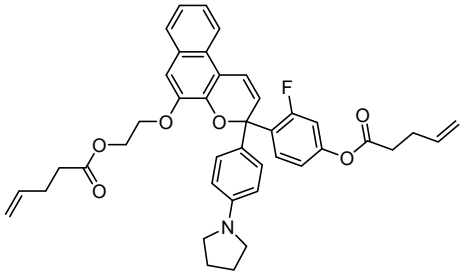
A flame-dried round-bottom flask equipped with a stir bar and rubber septum was charged with the crude diol and DMAP (32 mg, 0.26 mmol). Dry THF (5.1 mL), triethylamine (0.35 mL, 2.5 mmol, and 4-pentenoic anhydride (0.45 mL, 2.5 mmol) were then added sequentially and the mixture was stirred at room temperature. After 15 h, THF was removed under reduced pressure and the crude reaction mixture was dissolved in ethyl acetate (30 mL) and washed with water (2 x 30 mL), dried over Na_2SO_4, filtered through a plug of basic alumina, and concentrated under reduced pressure. Purification by column chromatography (5–30% EtOAc/hexanes) afforded the title compound as a blue oil (65 mg, 19% over 2 steps).

TLC (1:5 EtOAc/hexanes): R_f = 0.44.

^{1}H NMR (400 MHz, acetone-d_6) δ: 7.97 (d, J = 8.1 Hz, 1H), 7.70–7.66 (m, 1H), 7.62–7.58 (m, 2H), 7.42 (d, J = 10.0 Hz, 1H), 7.38–7.27 (m, 5H), 7.09–7.03 (m, 2H), 6.53 (d, J = 9.9 Hz, 1H), 6.48–6.43 (m, 2H), 5.97–5.75 (m, 2H), 5.15–4.89 (m, 4H), 4.57–4.52 (m, 2H), 4.43–4.38 (m, 2H), 3.23–3.17 (m, 4H), 2.64 (t, J = 7.2 Hz, 2H), 2.49–2.39 (m, 4H), 2.37–2.30 (m, 2H), 1.98–1.92 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 173.0, 171.7, 150.8, 148.8, 148.2, 144.2, 143.5, 137.8, 137.6, 131.6, 130.4, 130.2, 128.5, 128.3, 128.0, 126.1, 125.3, 125.0, 122.0, 121.9, 120.2, 116.7, 115.9, 115.7, 111.8, 110.2, 82.9, 67.7, 63.3, 48.0, 33.9, 29.64, 29.59, 25.9 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{41}H_{42}NO_6]^+$ $(M+H)^+$, 644.3007; found, 644.2987.



2b

5-(2-(pent-4-enoyloxy)ethoxy)-3-(2-fluoro-4-(pent-4-enoyloxy)phenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (2b). A scintillation vial equipped with a stir bar was charged with **18** (449 mg, 0.885 mmol), RuPhosPd G2 (44.8 mg, 0.0577 mmol), and RuPhos (31.0 mg, 0.0664 mmol) under nitrogen and sealed with a rubber septum. Pyrrolidine (110 µL, 1.3 mmol) and LHMDS (1.5 M in THF, 2.5 mL, 3.8 mmol) were then added sequentially under nitrogen and the mixture was stirred at 65 °C. After 22 h, the reaction was diluted with a mixture of ethyl acetate, DCM, and methanol. The organic phase was washed with saturated aqueous NH_4Cl (2 x 100 mL) and concentrated under reduced pressure. The crude product was then taken up in a mixture of DMF (3 mL) and DCM (10 mL). After stirring for 10 min, the solution was diluted with ethyl acetate (50 mL), washed with H_2O (2 x 50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude diol, which was carried forward in the next step without further purification.

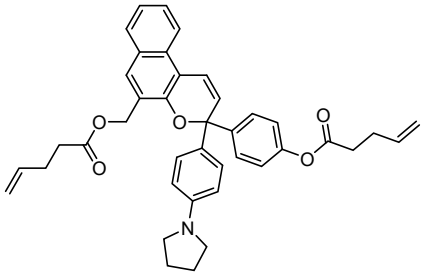
A round-bottom flask equipped with a stir bar and rubber septum was charged with the crude diol and DMAP (60.1 mg, 0.492 mmol). Dry THF (20 mL), triethylamine (0.60 mL, 4.3 mmol), and 4-pentenoic anhydride (0.75 mL, 4.1 mmol) were then added sequentially and the mixture was stirred at room temperature. After 15 h, the crude reaction mixture was diluted with ethyl acetate (100 mL) and washed with saturated aqueous NH_4Cl (150 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered through a plug of basic alumina, and concentrated under reduced pressure. Purification by column chromatography (3–30% EtOAc/hexanes) afforded the title compound as a blue oil (245 mg, 42% over 2 steps).

TLC (1:5 EtOAc/hexanes): R_f = 0.34.

^{1}H NMR (400 MHz, acetone-d_6) δ: 7.99 (d, J = 8.2 Hz, 1H), 7.84 (t, J = 8.9 Hz, 1H), 7.72–7.68 (m, 1H), 7.44 (d, J = 10.1 Hz, 1H), 7.39–7.28 (m, 5H), 6.99–6.92 (m, 2H), 6.59 (dd, J_{HF} = 5.1 Hz, J_{HH} = 10.0 Hz, 1H), 6.50–6.44 (m, 2H), 5.96–5.77 (m, 2H), 5.15–4.89 (m, 4H), 4.59–4.49 (m, 2H), 4.47–4.36 (m, 2H), 3.26–3.16 (m, 4H), 2.66 (t, J = 7.3 Hz, 2H), 2.48–2.39 (m, 4H), 2.38–2.29 (m, 2H), 2.00–1.92 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 173.1, 171.6, 159.9 (d, J_{CF} = 248.3 Hz), 152.3 (d, J_{CF} = 11.0 Hz), 148.7, 143.1, 138.0, 137.7, 130.7, 130.5 (d, J_{CF} = 11.3 Hz), 130.2, 129.2 (d, J_{CF} = 4.8 Hz), 128.9, 128.5 (d, J_{CF} = 4.6 Hz), 128.2, 126.2, 125.5, 125.3, 122.2, 120.6, 118.1 (d, J_{CF} = 3.4 Hz), 116.6, 116.2, 115.9, 111.9, 111.4 (d, J_{CF} = 25.4 Hz), 110.4, 81.7 (d, J_{CF} = 3.0 Hz), 67.9, 63.4, 48.2, 34.1, 34.0, 29.7, 29.6, 26.1 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{41}H_{41}FNO_6]^+$ $(M+H)^+$, 662.2912; found, 662.2902.



2c

5-(2-(pent-4-enoyloxy)methyl)-3-(4-(pent-4-enoyloxy)phenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (2c). A scintillation vial equipped with a stir bar was charged with **20** (298 mg, 0.649 mmol), RuPhosPd G2 (39 mg, 0.050 mmol). and RuPhos (23 mg, 0.049 mmol) under nitrogen and sealed with a rubber septum. Pyrrolidine (75 µL, 0.91 mmol), LHMDS (1.5 M in THF, 1.8 mL, 2.7 mmol), and THF (2 mL) were then added sequentially. After stirring at 55 °C overnight, THF was removed under reduced pressure and the reaction mixture was resuspended in a mixture of ethyl acetate (5 mL) and DMF (3 mL). After stirring for 5 minutes, the mixture was diluted with ethyl acetate (150 mL) and methanol (5 mL) and washed with saturated aqueous ammonium chloride (2 x 50 mL), water (2 x 50 mL), and brine (50 mL). The organic phase was dried over Na_2SO_4 and passed through a plug of celite, eluting with ethyl acetate, and then concentrated under reduced pressure to afford the crude diol, which was carried forward in the next step without further purification.

A flame-dried round-bottom flask equipped with a stir bar and rubber septum was charged with the crude diol and DMAP (42 mg, 0.36 mmol). Dry THF (6.3 mL), triethylamine (0.40 mL, 2.9 mmol), and 4-pentenoic anhydride (0.56 mL, 3.1 mmol) were then added sequentially and the mixture was stirred at room temperature. After 15 h, THF was removed under reduced pressure and the crude reaction mixture was dissolved in ethyl acetate (30 mL) and washed with water (2 x 30 mL), dried over Na_2SO_4, filtered through a plug of basic alumina, and concentrated under reduced pressure. Purification by column chromatography (5–30% EtOAc/hexanes) yielded the title compound as a blue oil (110 mg, 27% over 2 steps).

TLC (1:5 EtOAc/hexanes): R_f = 0.33.

^{1}H NMR (400 MHz, acetone-d_6) δ: 8.09 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.82–7.77 (m, 2H), 7.58–7.53 (m, 2H), 7.50 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.46 (d, *J* = 10.1 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.33–7.28 (m, 2H), 7.12–7.07 (m, 2H), 6.49–6.45 (m, 2H), 6.37 (d, *J* = 9.9 Hz, 1H), 5.97–5.82 (m, 2H), 5.43–5.33 (m, 2H), 5.16–4.94 (m, 4H), 3.24–3.15 (m, 4H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.54–2.33 (m, 6H), 1.99–1.91 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 173.0, 171.9, 151.1, 149.7, 148.5, 144.4, 138.1, 137.8, 131.6, 130.8, 130.4, 129.8, 129.49, 129.46, 129.0, 128.6, 127.9, 126.1, 125.0, 122.34, 122.26, 120.1, 116.1, 115.8, 115.3, 112.0, 83.8, 62.4, 48.2, 34.13, 34.11, 29.74, 29.69, 26.1 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{40}H_{40}NO_5]^+$ $(M+H)^+$, 614.2901; found 614.2910.

IV. Preparation of PDMS Materials

PDMS materials incorporating mechanophore crosslinkers (1.5 wt %) were prepared following previously reported procedures using the two-part Sylgard® 184 elastomer kit (Dow Corning).[1,3] PDMS films were cut into 25 mm x 3 mm strips for testing.

General procedure for preparation of PDMS strips. A representative procedure is provided for the preparation of PDMS containing a 1:1 mixture of mechanophores **1c** and **SP**. Naphthopyran **1c** (22 mg) and spiropyran crosslinker **SP**[2] (17 mg) were dissolved in 0.1 mL xylene in a 20 mL scintillation vial. Sylgard® 184 prepolymer base (2.083 g) and 0.1 mL xylene were added and the contents were thoroughly mixed in a vortex mixer with intermittent gentle heating to form a homogeneous, pale orange dispersion. Sylgard® 184 curing agent (0.208 g) was added and the contents were mixed thoroughly using a vortex mixer. The mixture was pipetted onto a clean 5 cm x 5 cm delrin plate, which was placed inside a vacuum chamber and evacuated under high vacuum (~30 mTorr) for 3 h. The delrin plate was then transferred to an oven and cured at 80 °C overnight. After curing, the plate was removed from the oven and the PDMS film was peeled off and cut into strips with a razor blade.

V. DFT Calculations

CoGEF calculations were performed using Spartan ′18 according to previously reported methods.[4] Ground state energies were calculated using DFT at the B3LYP/6-31G* level of theory. Starting from the equilibrium geometry of the unconstrained molecule (relative energy = 0 kJ/mol), the distance between the terminal methyl groups of the truncated structure was increased in increments of 0.05 Å and the energy was minimized at each step. The maximum force associated with the transformation was calculated from the slope of the energy–displacement curve immediately prior to bond cleavage. All naphthopyrans examined in this study are predicted to undergo cleavage of the C–O pyran bond, resulting in generation of the merocyanine product *via* a 6π electrocyclic ring-opening reaction. The CoGEF results for each naphthopyran mechanophore are illustrated below in Figures S3–S8.

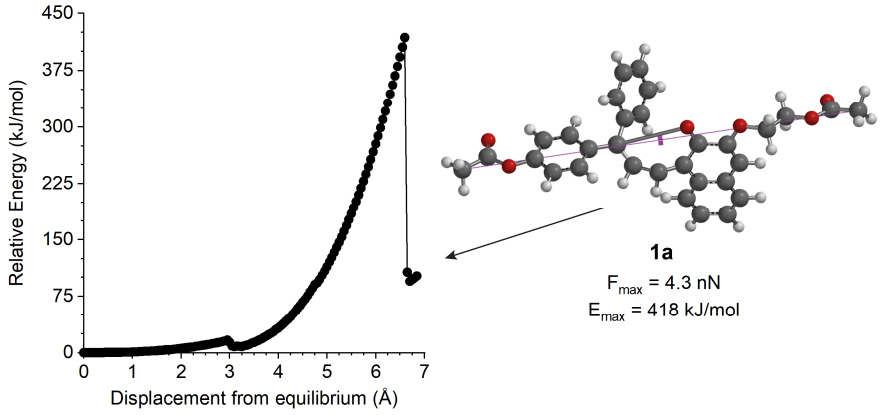


Figure S3. CoGEF plot of relative energy vs. displacement and the calculated structure immediately after the ring-opening reaction for naphthopyran **1a**.

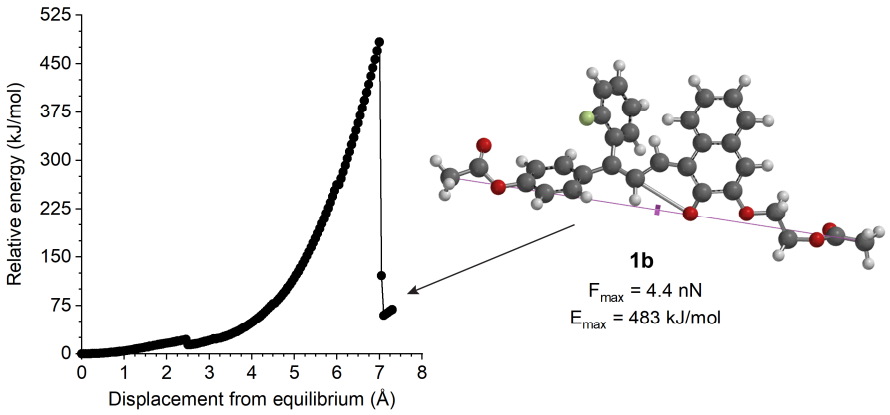


Figure S4. CoGEF plot of relative energy vs. displacement and the calculated structure immediately after the ring-opening reaction for naphthopyran **1b**.

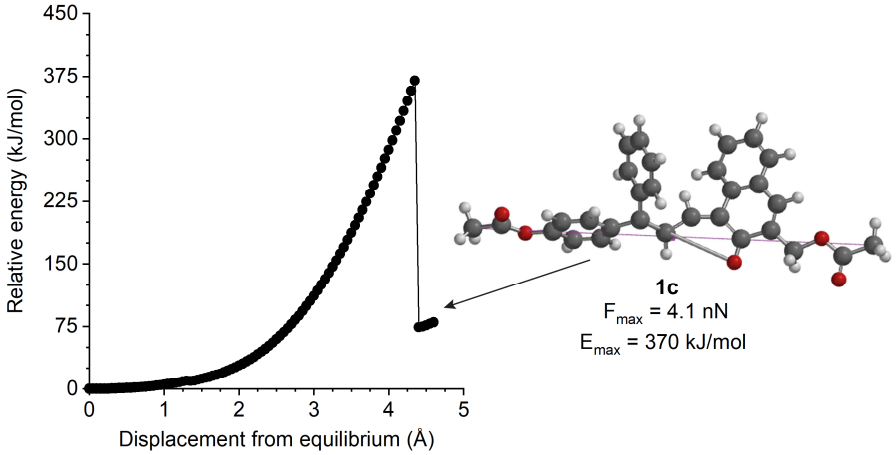


Figure S5. CoGEF plot of relative energy vs. displacement and the calculated structure immediately after the ring-opening reaction for naphthopyran **1c**.

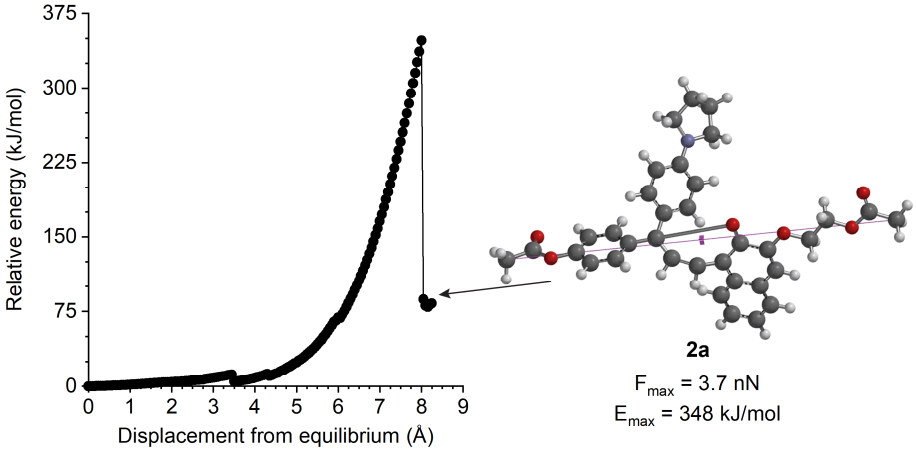


Figure S6. CoGEF plot of relative energy vs. displacement and the calculated structure immediately after the ring-opening reaction for naphthopyran **2a**.

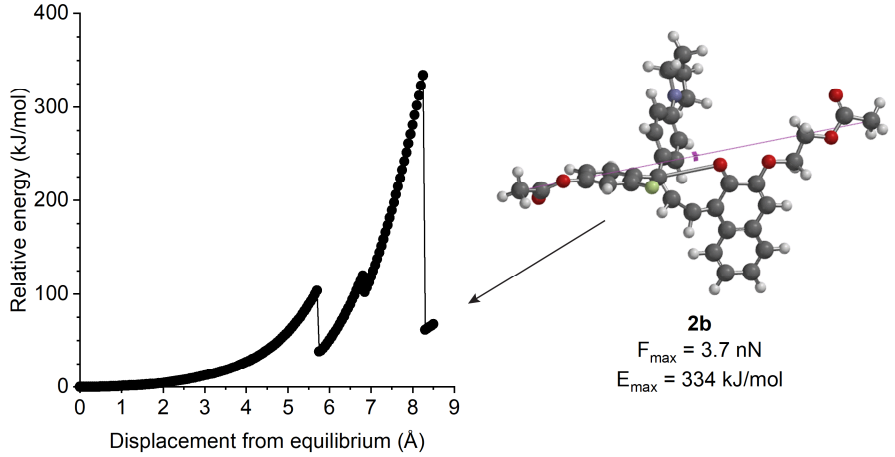


Figure S7. CoGEF plot of relative energy vs. displacement and the calculated structure immediately after the ring-opening reaction for naphthopyran **2b**. The energetic relaxation at ~5.5 Å corresponds to a conformational rotation.

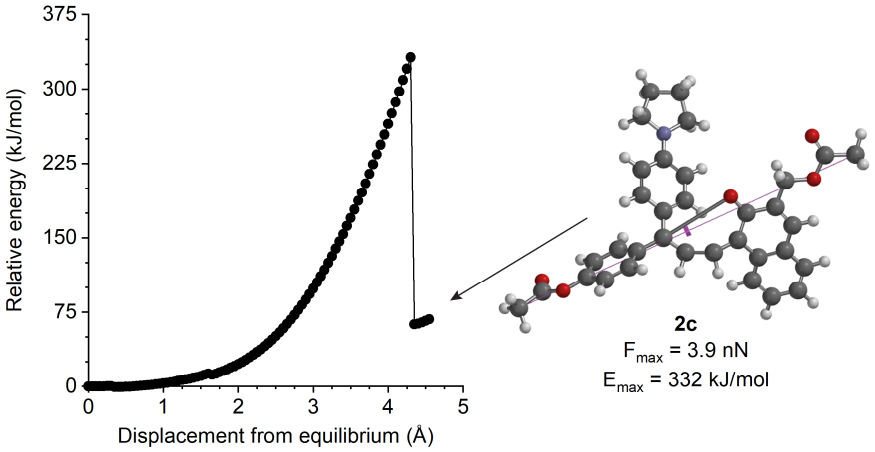


Figure S8. CoGEF plot of relative energy vs. displacement and the calculated structure immediately after the ring-opening reaction for naphthopyran **2c**.

VI. Characterization of Thermal Reversion Kinetics

Characterization of merocyanine electrocyclization in solution. The kinetics of thermal ring-closure for each merocyanine was evaluated in solution after photoirradiation of the naphthopyran at room temperature in the dark. Solutions of each naphthopyran (**1a**–**2b**) in THF (non-stabilized) were irradiated with UV light (λ = 311 nm, 30 s) in a quartz cuvette and immediately transferred to a spectrophotometer. Concentrations were 0.1 mM (**1a**, **1c**, **2b**), 0.01 mM (**1b**), and 0.25 mM (**2a**). The time-dependent absorbance was monitored at the λ_{max} corresponding to each merocyanine and the data were fit to first-order exponential decay using OriginPro 2020, given by eq S1:

$$A(t) = Ae^{-k_r t} + c \quad (S1)$$

where A(*t*) is the absorbance at λ_{max} at time *t*, c is the residual absorbance, *A* is the pre-exponential factor, and k_r is the rate constant for the thermal ring-closing reaction. Rate constants are reported in s^{-1} as an average of three separate trials (error is reported as standard deviation). Representative plots are displayed

in Figure S1 and a summary of the determined parameters and fit statistics for all trials are reported below in Table S1. Electrocyclization of the merocyanine derived from **2c** was too rapid for the initial fading rate to be measured under these conditions, although a persistent merocyanine isomer fraction remains after an extended period of time post-irradiation enabling characterization of the absorption spectrum of the merocyanine species. The persistent color observed after photoactivation of some naphthopyrans has been attributed to the relative thermal stability of the merocyanine isomer with *trans* configuration of the exocyclic double bond, which isomerizes slowly in the dark to the *cis* isomer prior to ring-closure.[5–7] The isomerization is promoted efficiently, however, with visible light. Irradiation of the solution containing **2c** and the persistent merocyanine isomer with a fluorescent white light source for 1 min results in complete attenuation of the visible absorption peak and recovery of the original absorption spectrum (prior to UV irradiation), indicating full conversion of the merocyanine back to the ring-closed naphthopyran (Figure S9).

Table S1. Fit parameters and statistics for the thermal reversion of merocyanine dyes in solution.[a]

	Trial	*A*	$k_{r,soln}$ (s^{-1})	*c*	Reduced χ^2	R^2 (COD)
	1	0.72	0.033	0.068	8.13E-06	1.00
1a	2	0.51	0.033	0.053	2.07E-06	1.00
	3	0.48	0.033	0.058	9.37E-07	1.00
	Average	*0.57 ± 0.1*	*0.033*	*0.060 ± 0.008*		
	1	0.12	0.0022	0.028	3.44E-06	0.995
1b	2	0.13	0.0024	0.032	3.57E-06	0.995
	3	0.13	0.0024	0.030	4.05E-06	0.994
	Average	*0.13 ± 0.006*	*0.0023 ± 0.0001*	*0.030 ± 0.002*		
	1	0.39	0.073	0.051	6.84E-06	0.999
1c	2	0.47	0.075	0.064	7.89E-06	0.999
	3	0.37	0.076	0.052	5.29E-06	0.999
	Average	*0.41 ± 0.05*	*0.075 ± 0.002*	*0.056 ± 0.007*		
	1	0.040	0.21	0.070	9.18E-08	0.999
2a	2	0.057	0.17	0.072	9.63E-08	1.00
	3	0.050	0.19	0.082	2.33E-08	1.00
	Average	*0.049 ± 0.009*	*0.19 ± 0.02*	*0.075 ± 0.006*		
	1	1.19	0.010	0.11	1.22E-05	1.00
2b	2	1.08	0.010	0.10	1.33E-05	1.00
	3	1.31	0.010	0.12	2.54E-05	0.999
	Average	*1.19 ± 0.1*	*0.010*	*0.11 ± 0.01*		

[a]Error is reported as standard deviation.

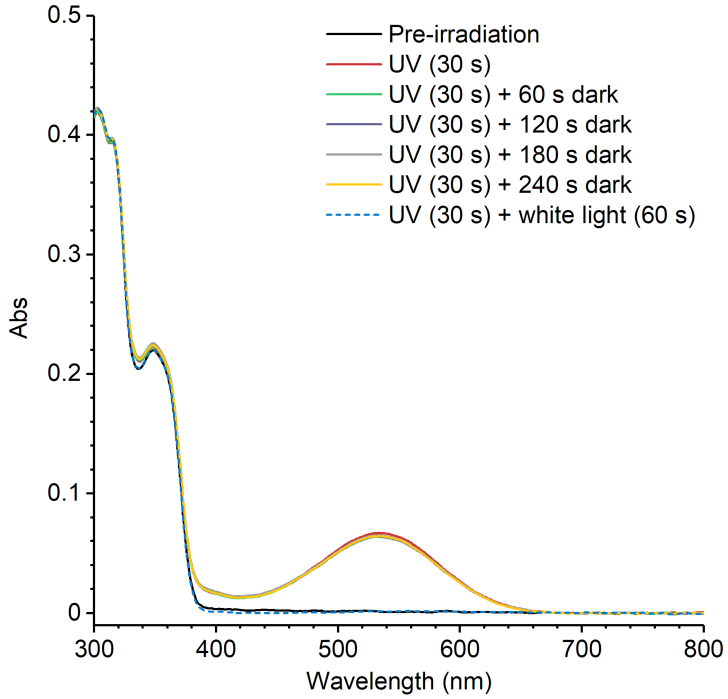


Figure S9. Photochemical activation of naphthopyran **2c** results in a persistent merocyanine species that can be efficiently reverted upon irradiation with visible light. A solution of **2c** in THF (0.1 mM) was irradiated with UV light (λ = 311 nm, 30 s) and absorbance spectra were subsequently collected over 240 s, demonstrating negligible changes over that time period in the dark. After irradiating the solution with fluorescent white light for 60 s, the visible absorption peak is completely attenuated and the original absorption spectrum is returned, indicating full conversion of the merocyanine species back to the naphthopyran.

Characterization of merocyanine electrocyclization in PDMS materials. PDMS strips were activated mechanically by hand in tension or photochemically by irradiation with UV light (λ = 311 nm, 90 s). Digital images were acquired with a Canon EOS 5D Mark IV DSLR camera equipped with a Canon 24-70 f/4 lens and a Canon Speedlite flash. Images were standardized to a white balance of 6500 K in Adobe Lightroom, then straightened and cropped in Adobe Photoshop. For Figure 2 and Figure 3 in the main text, images were also individually adjusted to achieve equal exposure levels using the exposure adjustment tool in Adobe Photoshop.

To determine approximate rates of thermal reversion of the merocyanine dyes in PDMS materials, samples were uniformly irradiated with UV light (λ = 311 nm, 90 s) and photographs were subsequently acquired at regular time intervals. After correcting white balance, straightening, and cropping, average intensity values of the red and green channels over a 1000 x 80 pixel area at the center of each film were extracted from the RGB histogram in Adobe Photoshop. Ratios of the red and green channel intensities were then plotted as a function of time for each PDMS sample and the data were fit to a model of biexponential decay in OriginPro 2020, given by eq S2:

$$A(t) = A_1 e^{-k_{r1}t} + A_2 e^{-k_{r2}t} + c \qquad (S2)$$

where A(t) is the absorbance at λ_{max} at time t, c is the residual ratio, A_1 and A_2 are pre-exponential factors, and k_{r1} and k_{r2} are the rate constants that describe the thermal electrocyclization reaction. Terms A_1 and A_2

express the relative contributions of $k_{1,solid}$ and $k_{2,solid}$ to the observed fading behavior, respectively. The data are displayed in Figure S2 and a summary of the determined parameters and fit statistics are reported below in Table S2. For the PDMS material incorporating naphthopyran **1a**, the fit-determined values of k_{r1} and k_{r2} are equivalent, as are the values of A_1 and A_2 (0.09). Thus, the thermal reversion data for sample **1a** were fit to the simpler monoexponential eq S1.

Table S2. Fit parameters and statistics for the thermal reversion of merocyanine dyes in solid materials.

	$A_{1,solid}$	$A_{2,solid}$	$k_{1,solid}$ (s^{-1})	$k_{2,solid}$ (s^{-1})	c	Reduced χ^2	R^2 (COD)
1a[a]	0.2	-	0.02	-	0.8	2.71E-05	0.994
1b	0.2	0.04	0.002	0.02	0.7	1.63E-05	0.998
1c	0.07	0.03	0.02	0.09	0.9	5.89E-06	0.996
2a	0.04	0.03	0.01	0.1	0.9	8.11E-06	0.988
2b	0.2	0.1	0.01	0.002	0.6	1.55E-05	0.999
2c	0.04	0.02	0.02	0.1	0.9	3.99E-06	0.993

[a]Thermal reversion data were fit to monoexponential eq. S1.

VII. References

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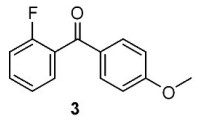
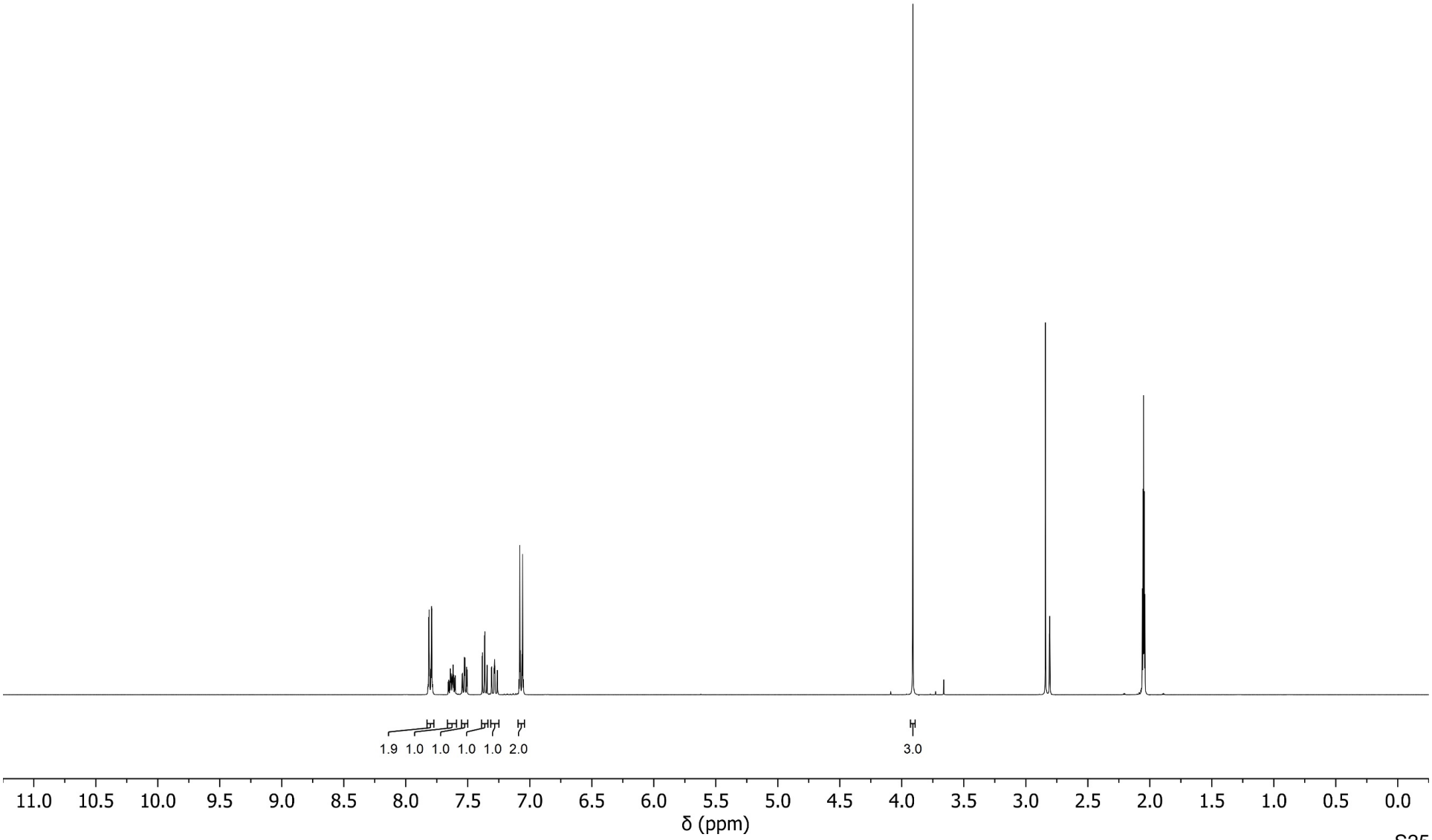
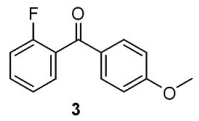


3

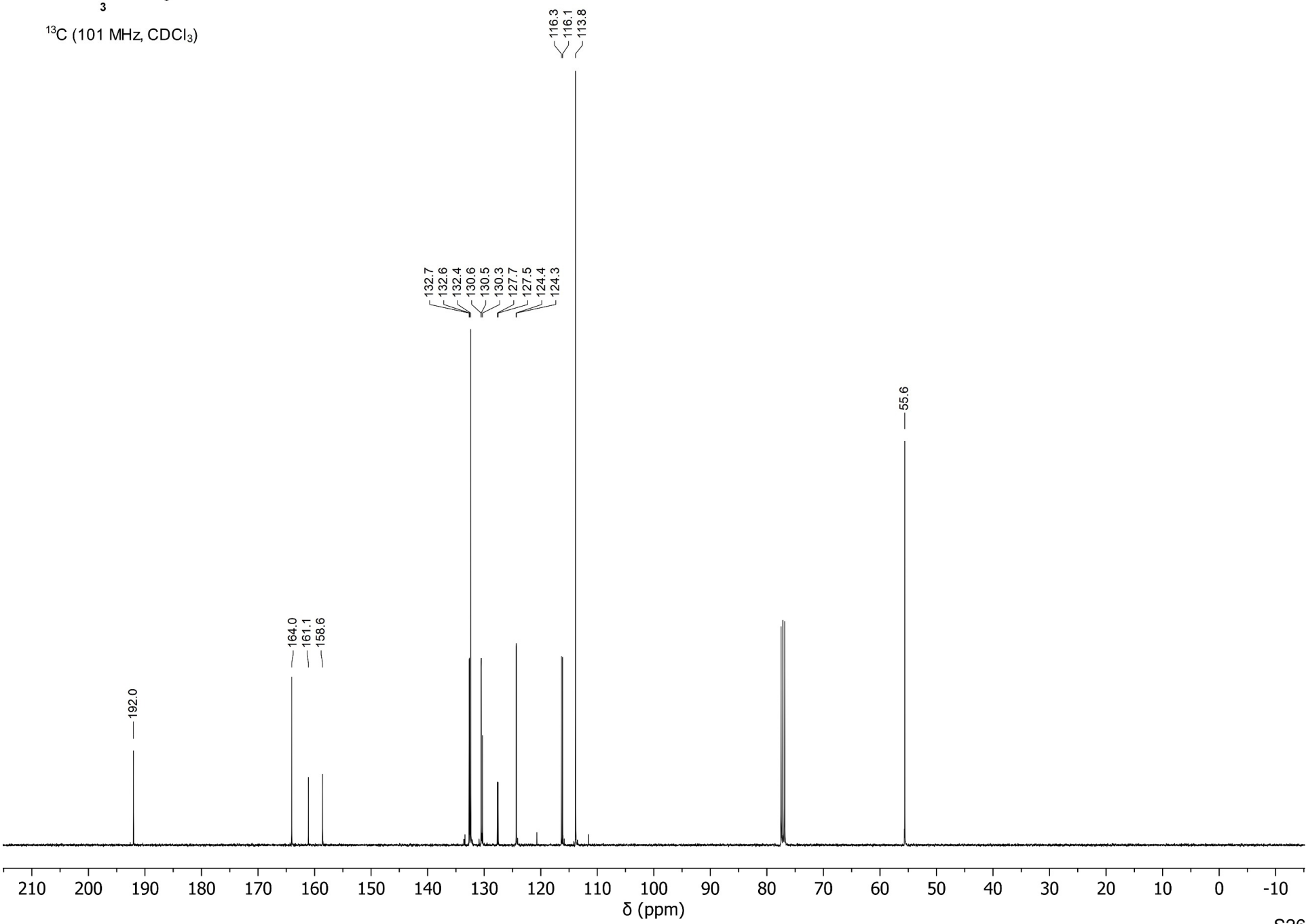
^{1}H (400 MHz, acetone-d_6)

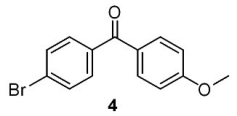




3

^{13}C (101 MHz, $CDCl_3$)





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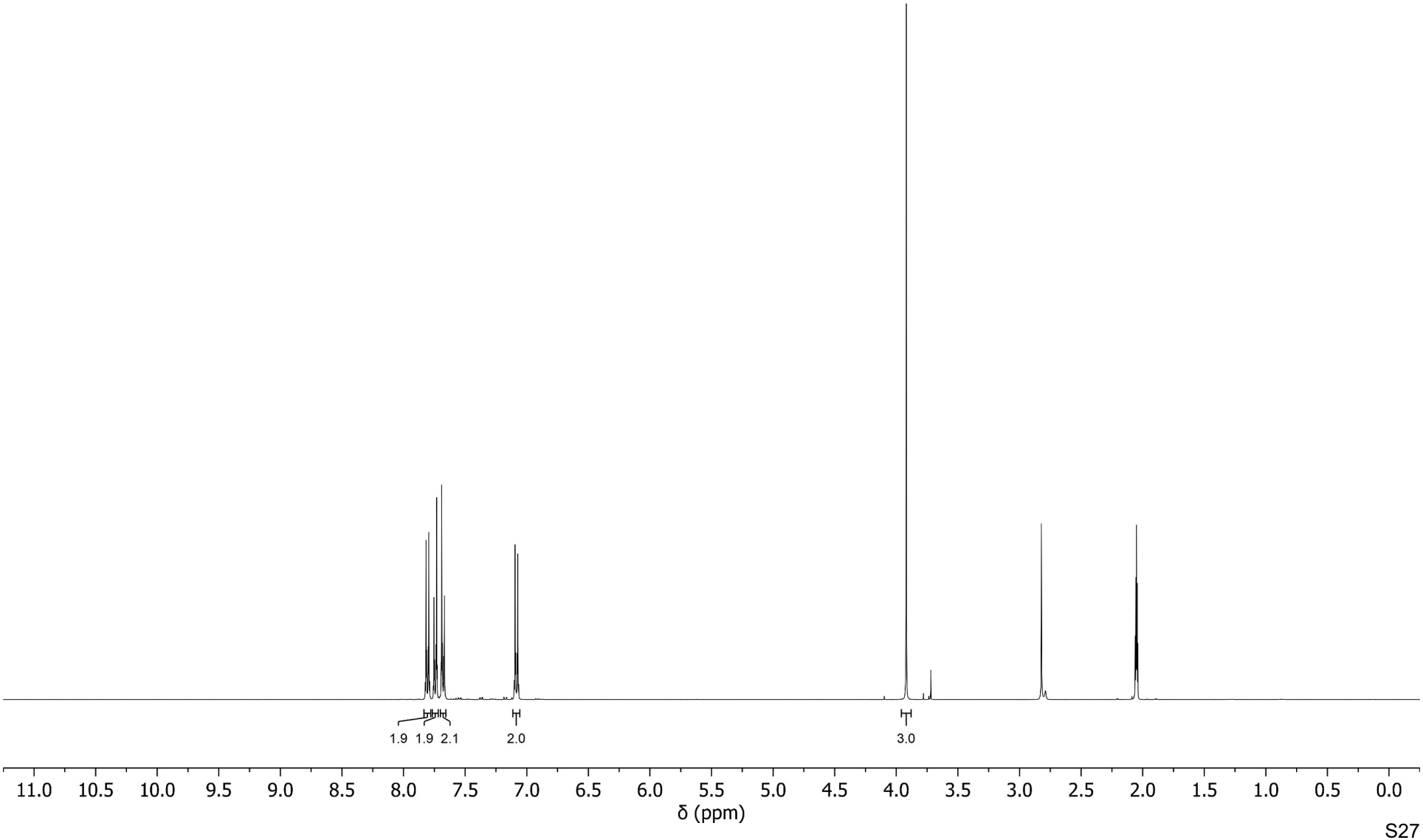

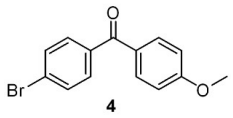

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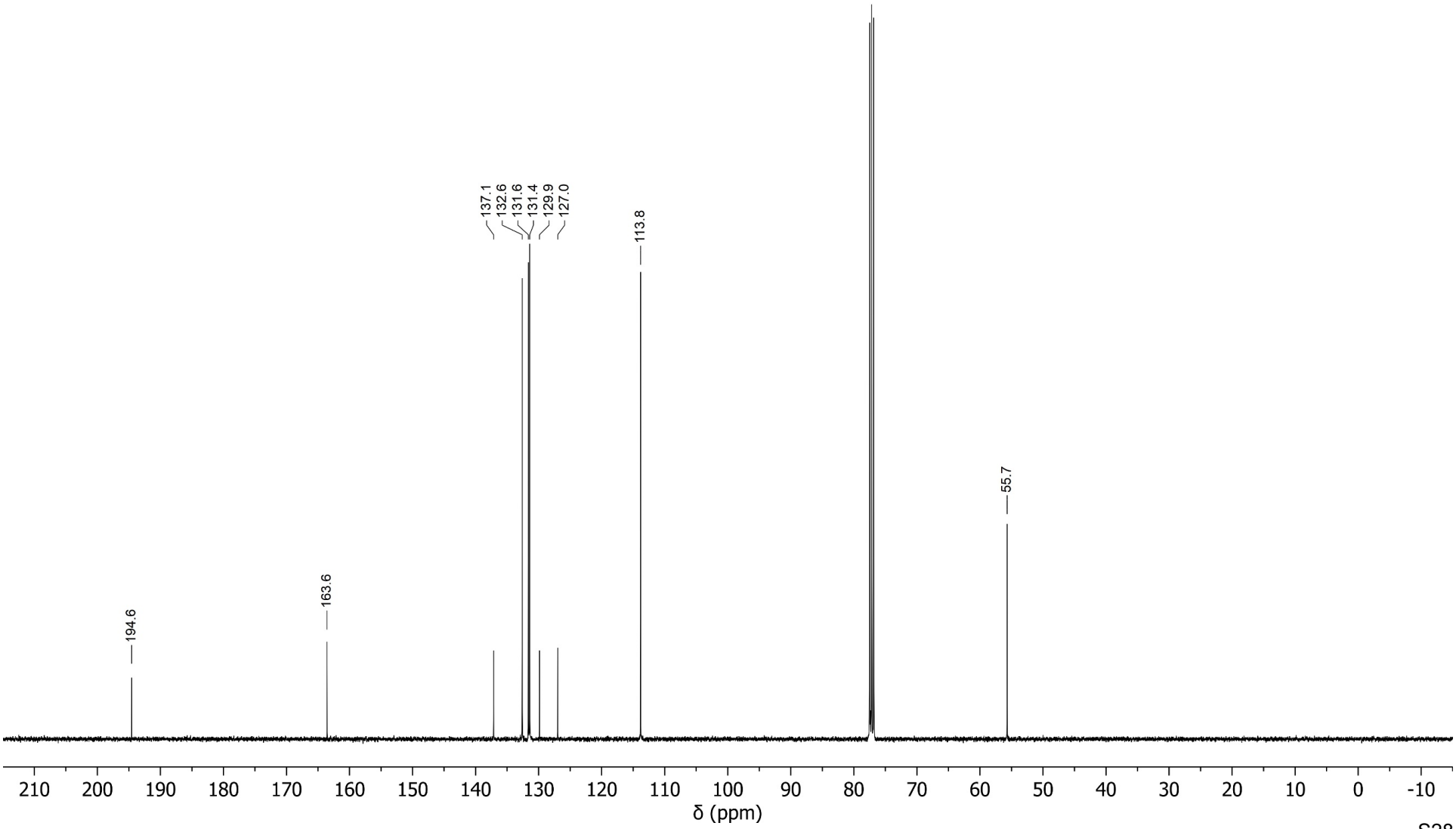

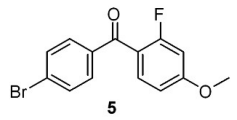

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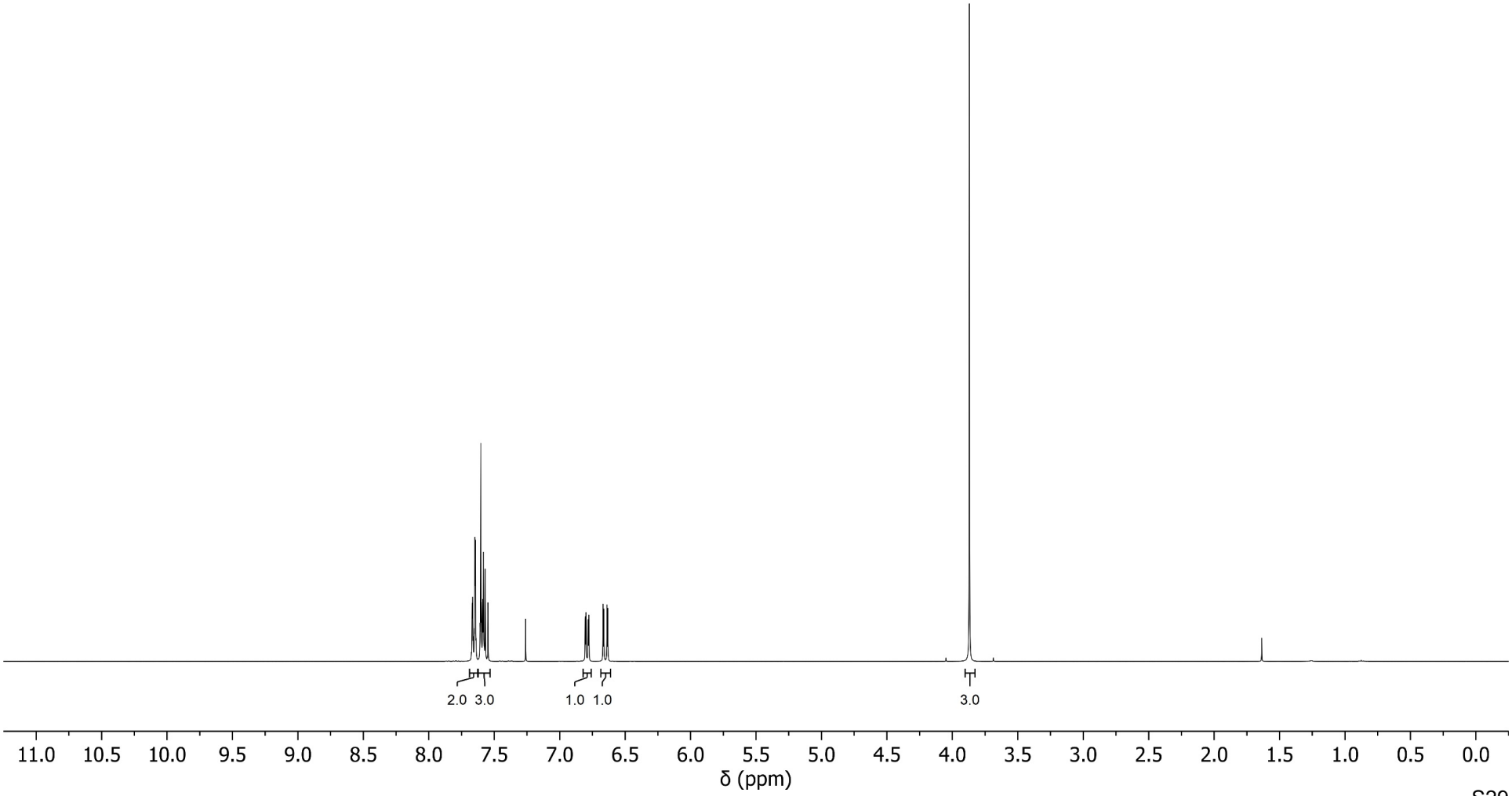
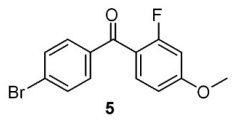
^{1}H (400 MHz, $CDCl_3$)





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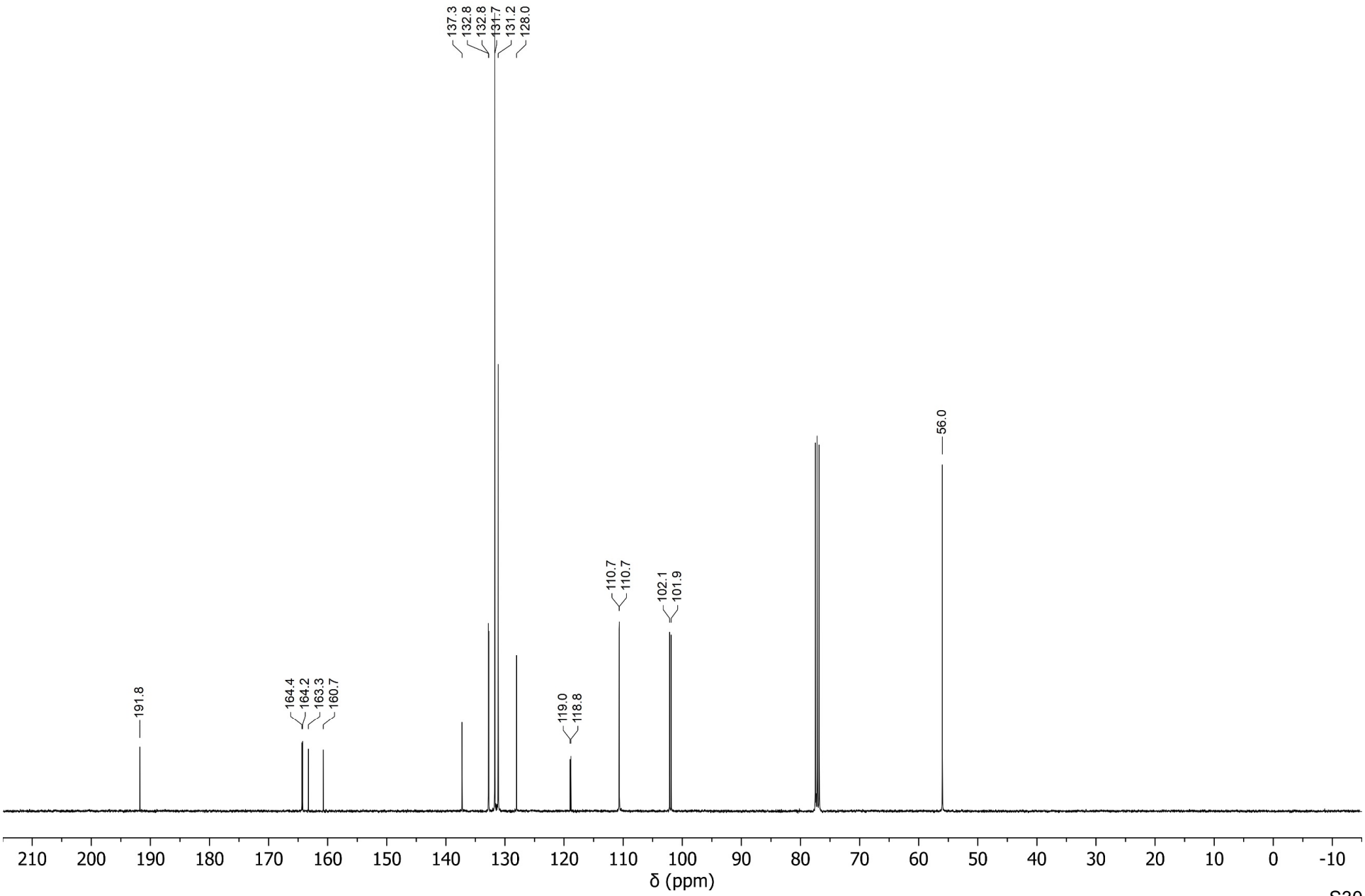
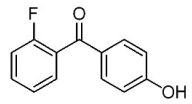
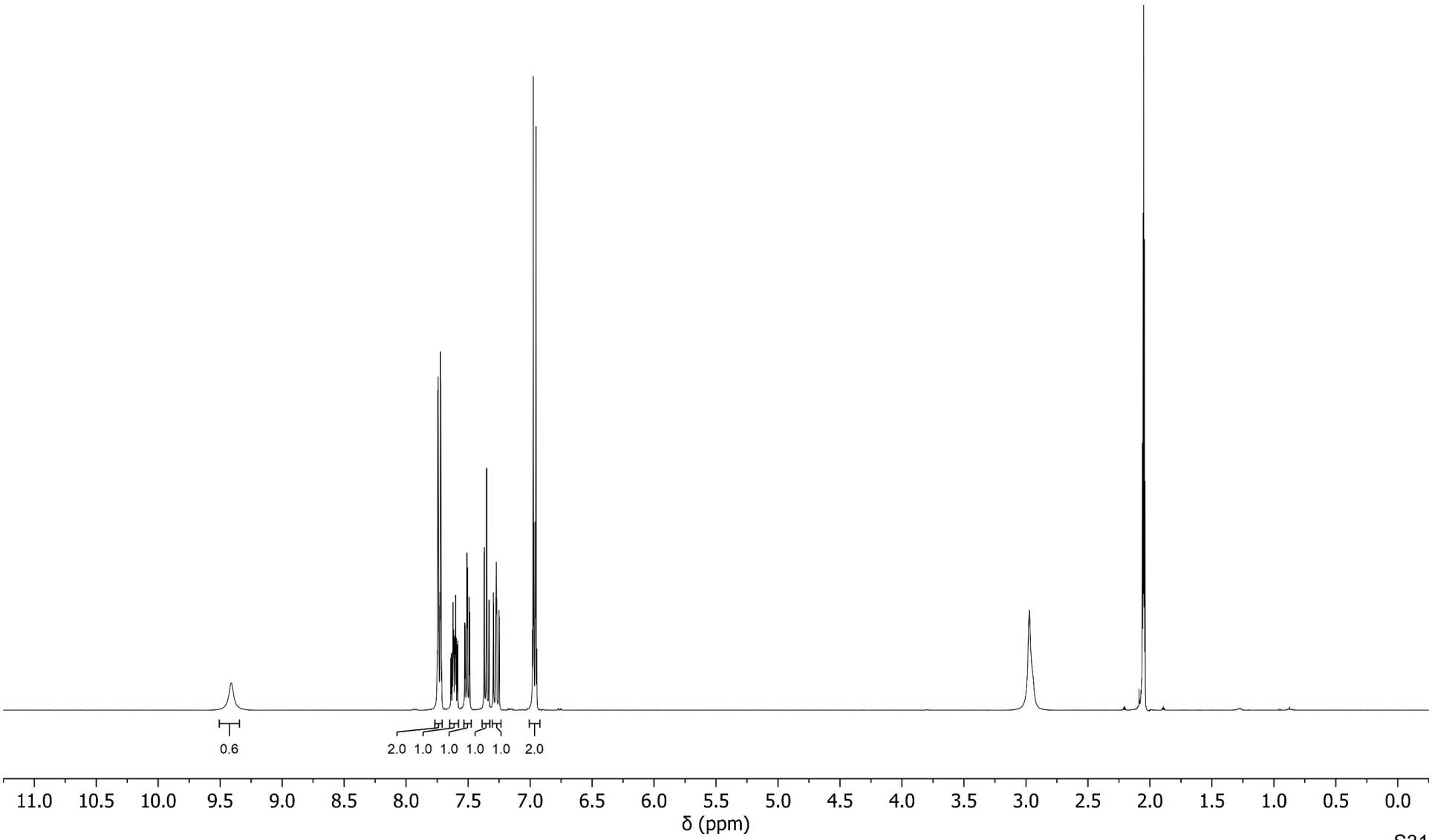
^{13}C (101 MHz, $CDCl_3$)

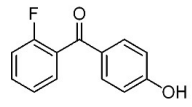




6

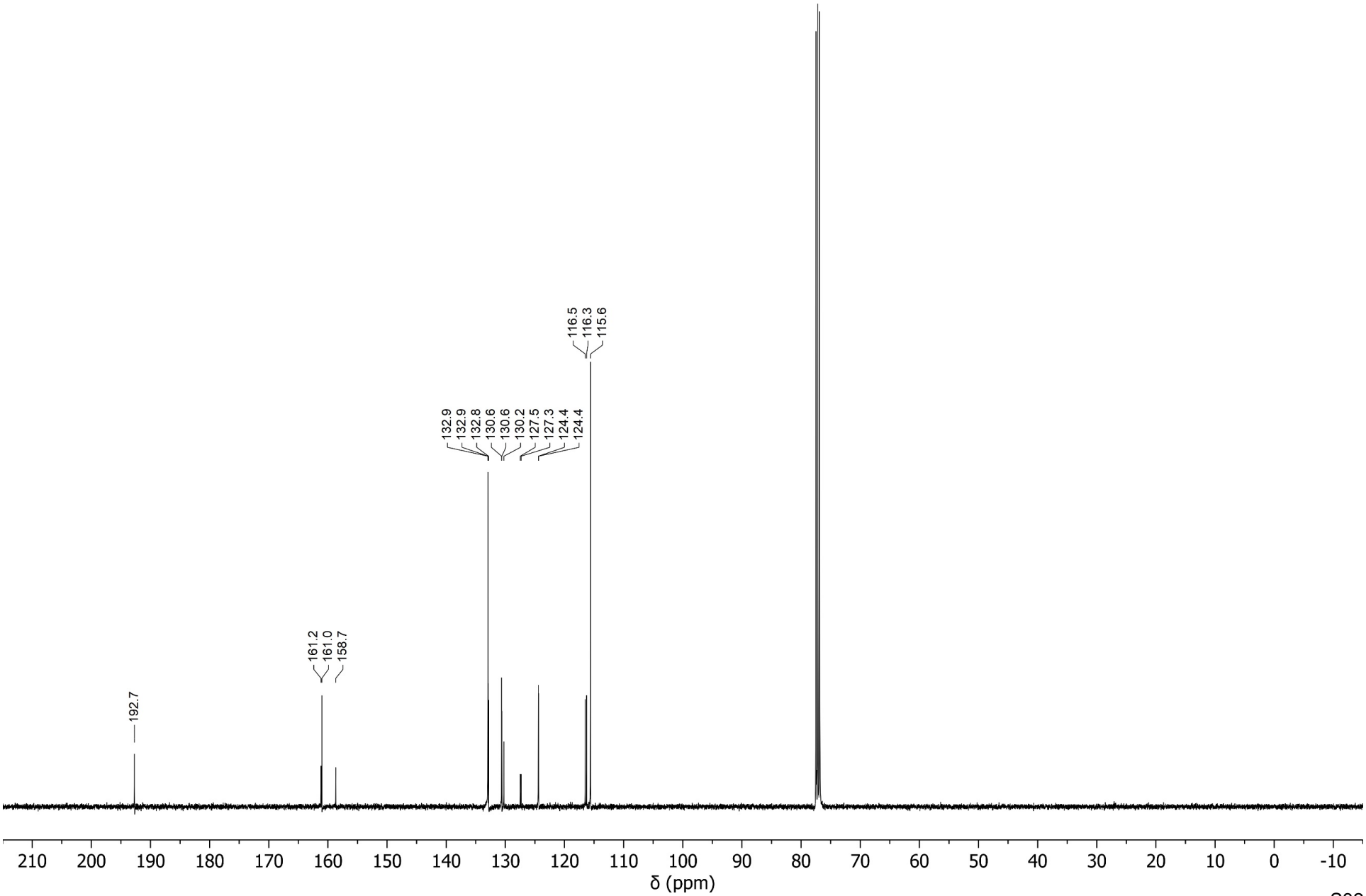
^{1}H (400 MHz, acetone-d_6)

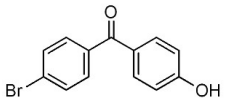




6

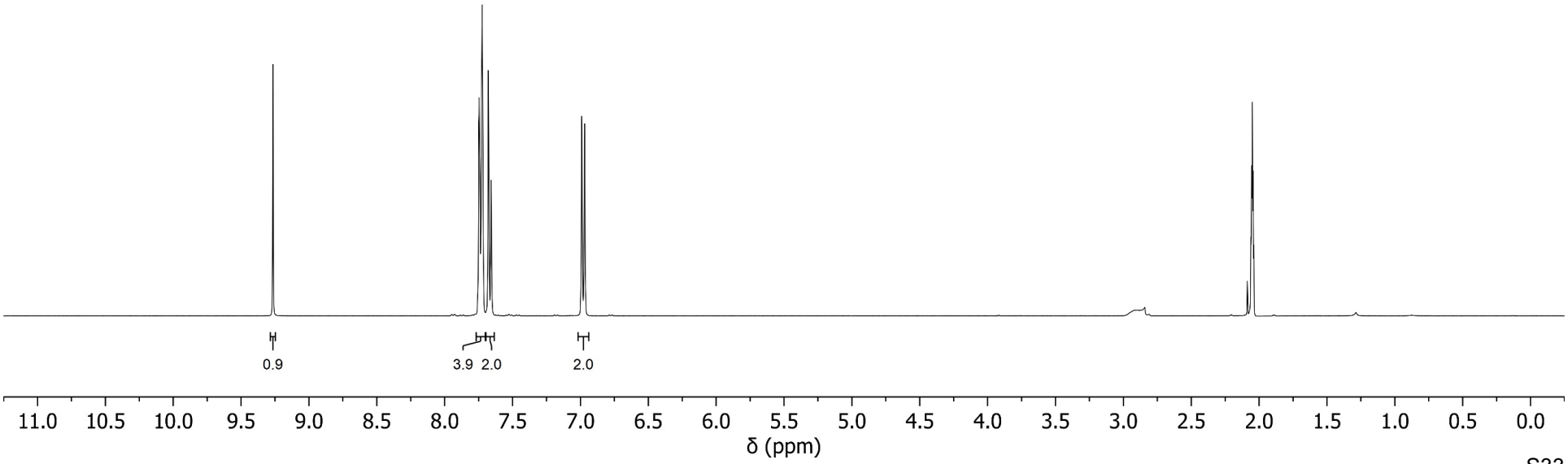
^{13}C (101 MHz, $CDCl_3$)

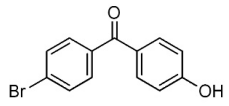




7

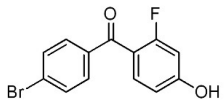
^{1}H (400 MHz, acetone-d_6)





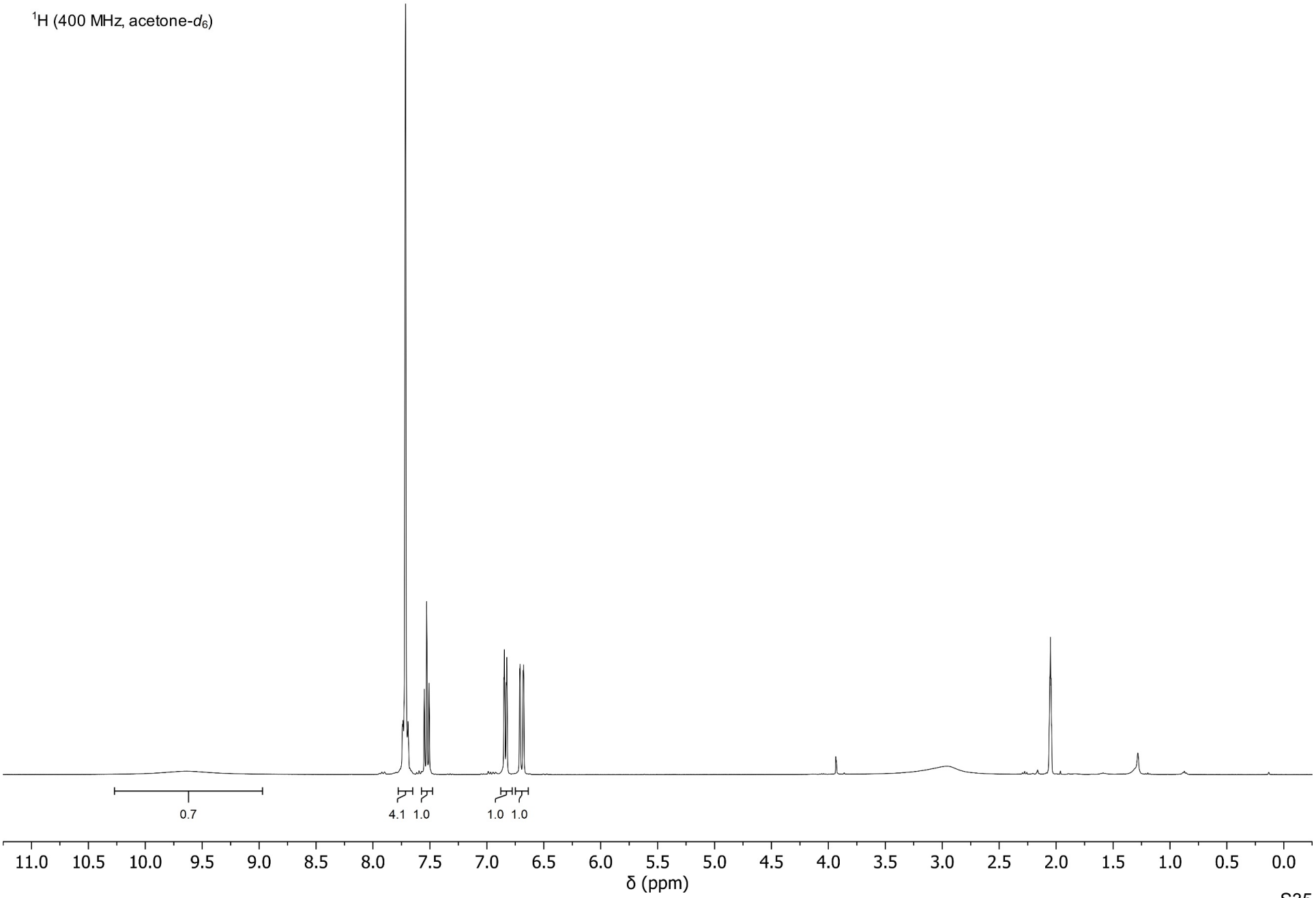
7

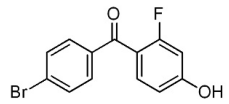
^{13}C (101 MHz, acetone-d_6)



8

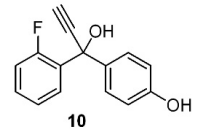
^{1}H (400 MHz, acetone-d_6)





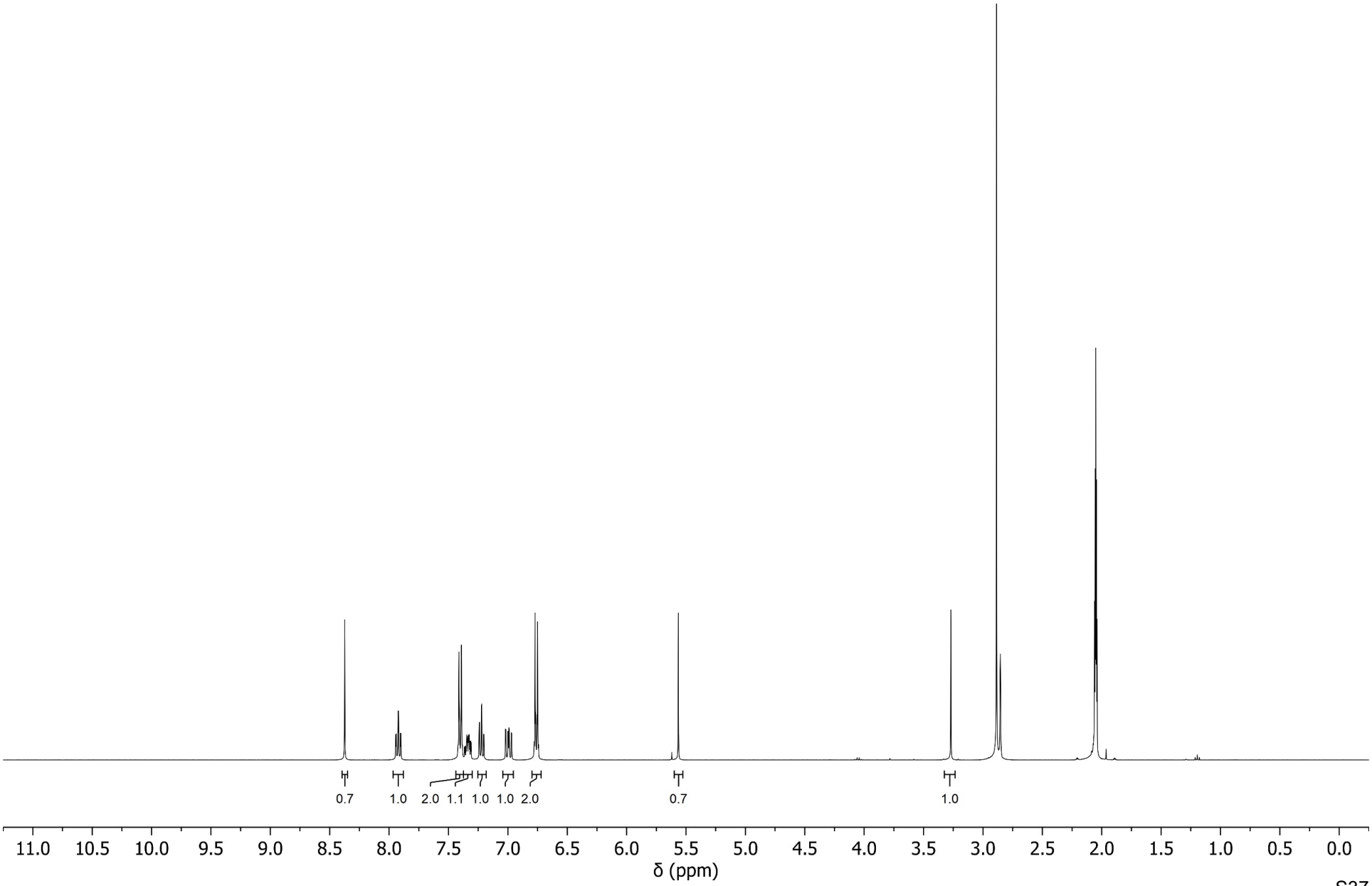
8

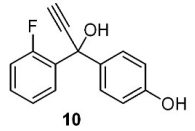
^{13}C (101 MHz, acetone-d_6)



10

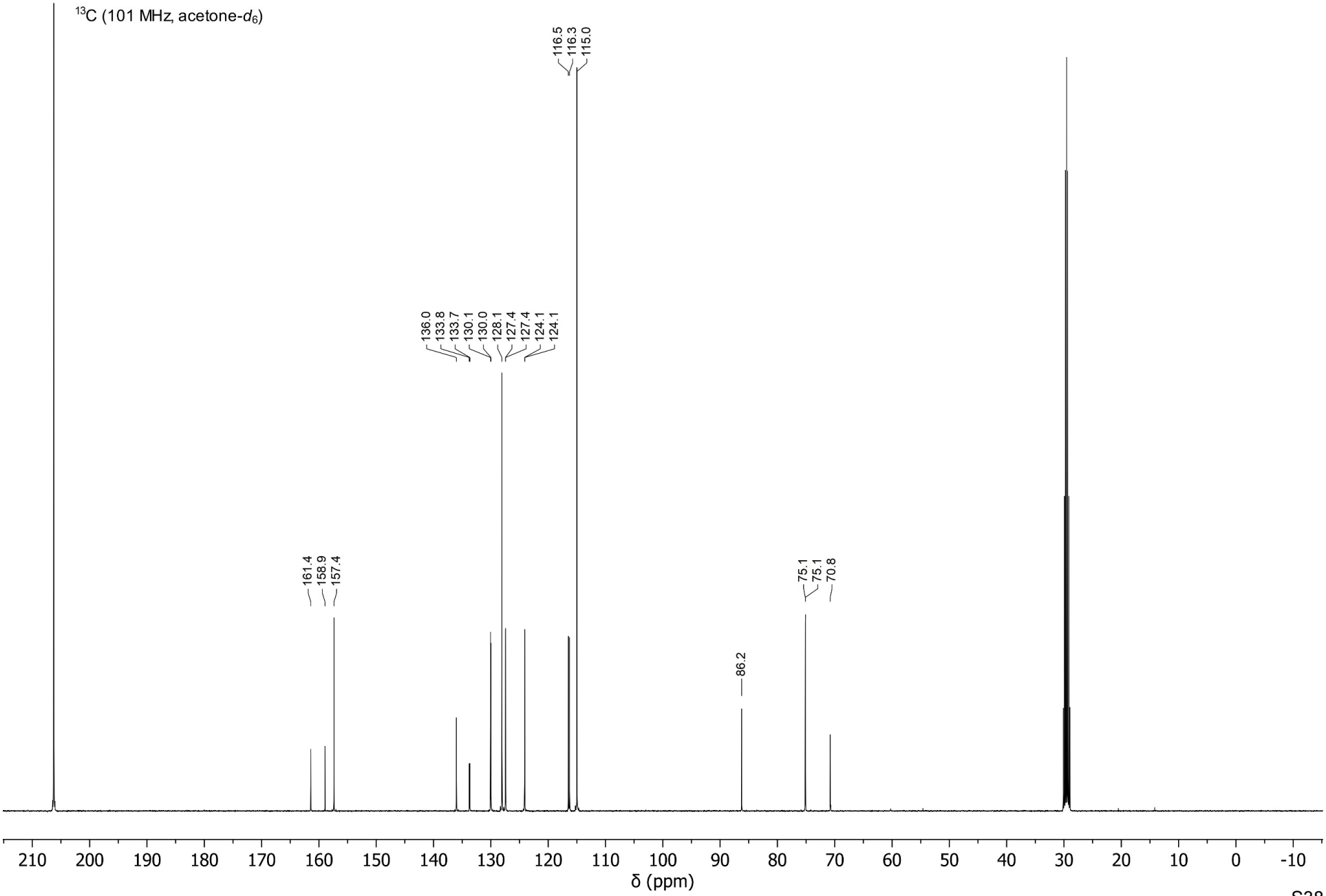
^{1}H (400 MHz, acetone-d_6)

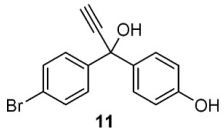




10

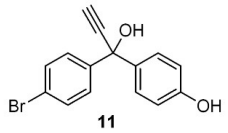
^{13}C (101 MHz, acetone-d_6)





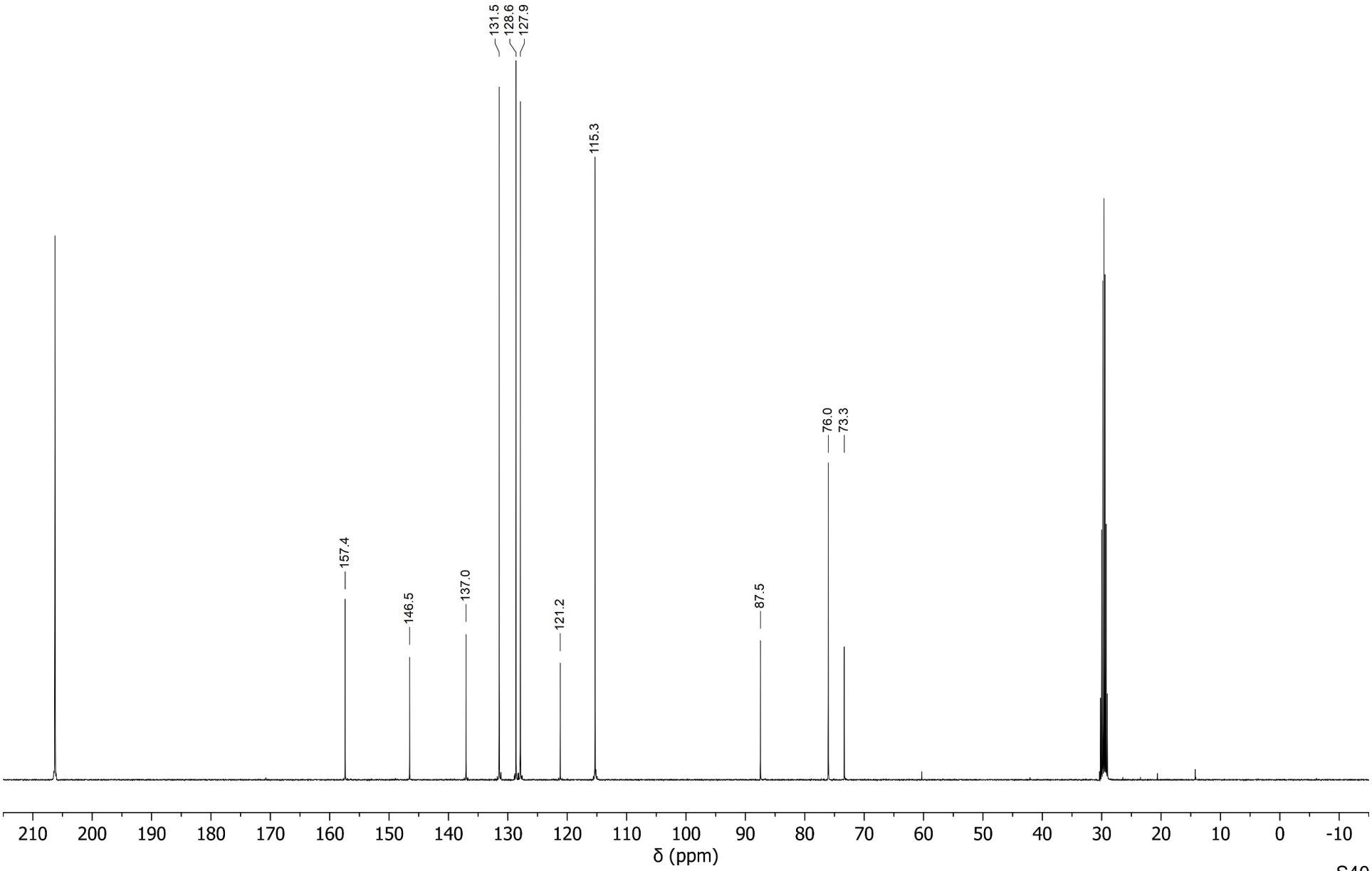
11

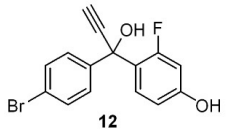
^{1}H (400 MHz, acetone-d_6)



11

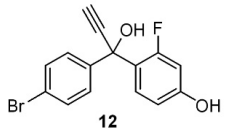
^{13}C (101 MHz, acetone-d_6)





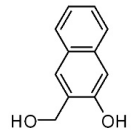
12

^{1}H (400 MHz, acetone-d_6)



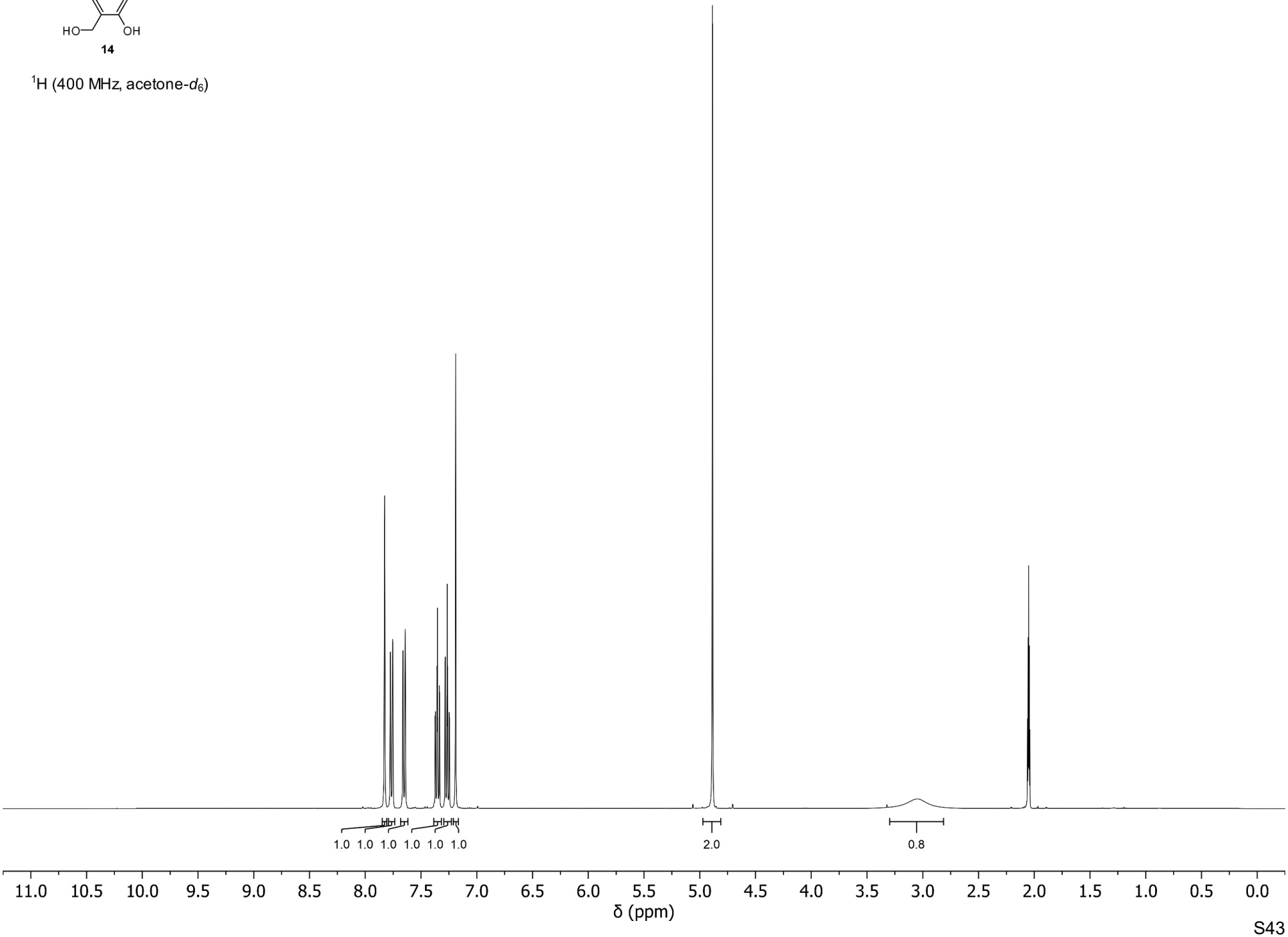
12

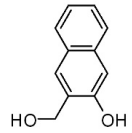
^{13}C (101 MHz, acetone-d_6)



14

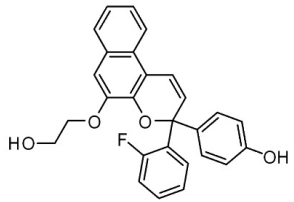
^{1}H (400 MHz, acetone-d_6)





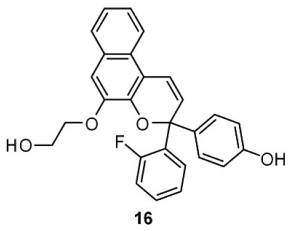
14

^{13}C (101 MHz, acetone-d_6)



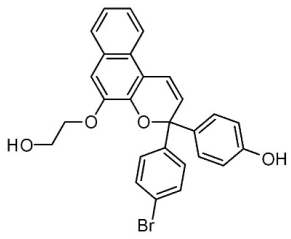
16

^{1}H (400 MHz, acetone-d_6)



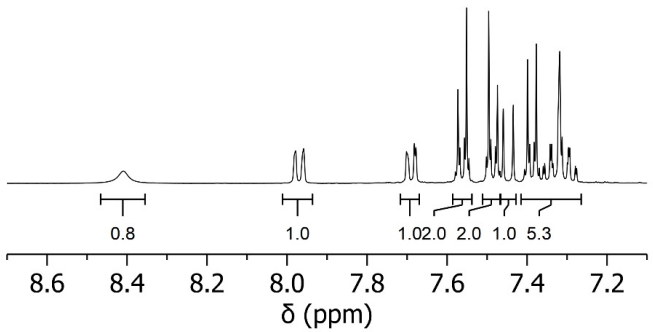
16

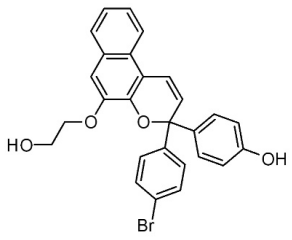
^{13}C (101 MHz, acetone-d_6)



17

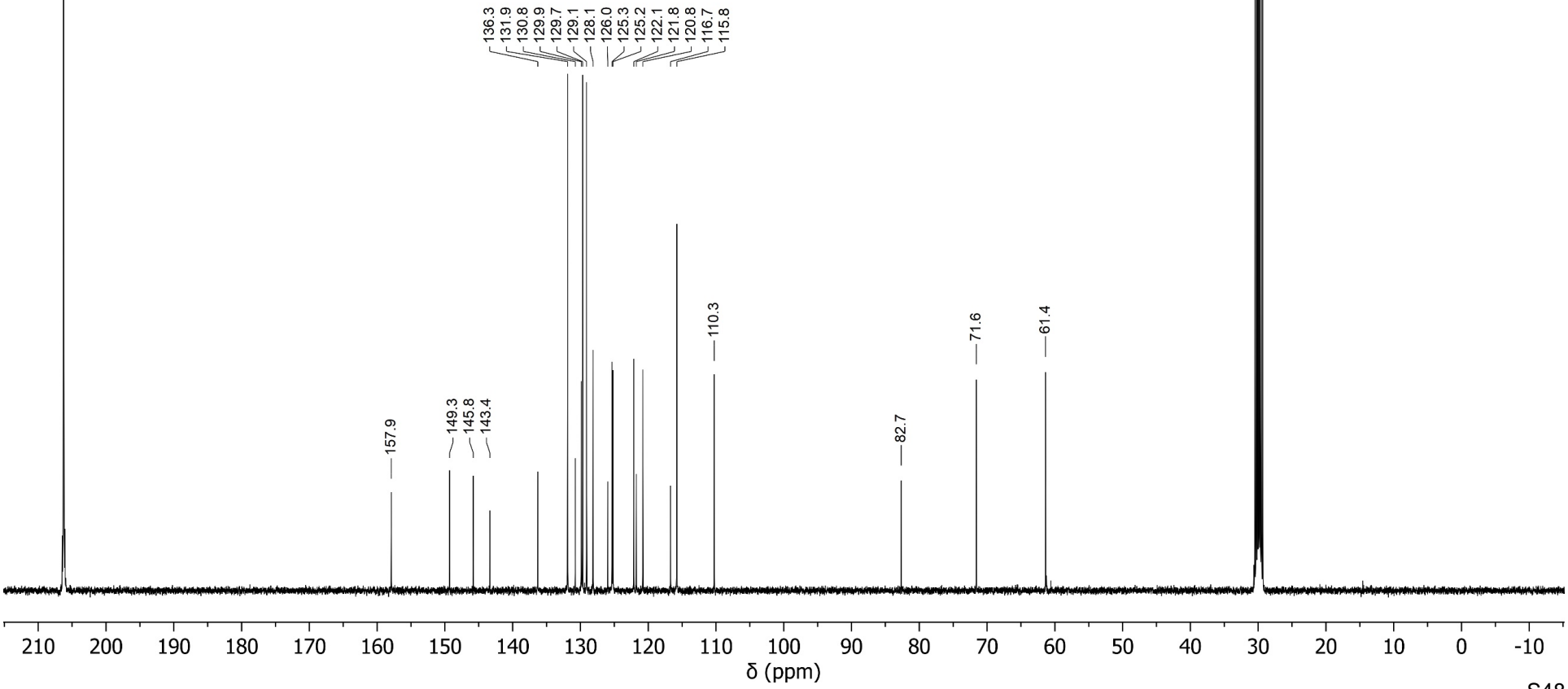
^{1}H (400 MHz, acetone-d_6)

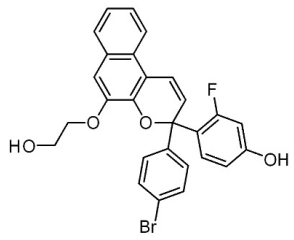




17

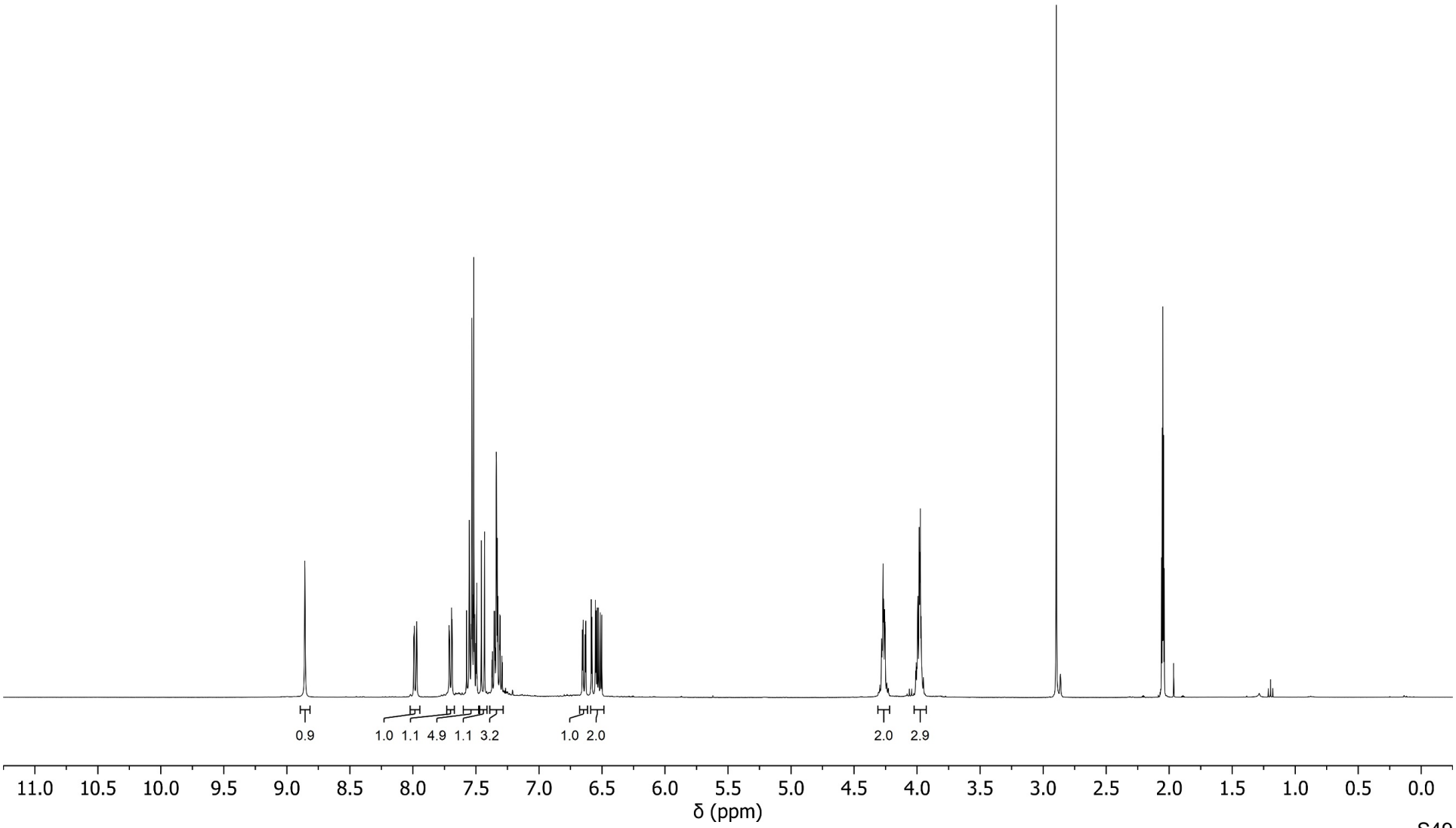
^{13}C (101 MHz, acetone-d_6)

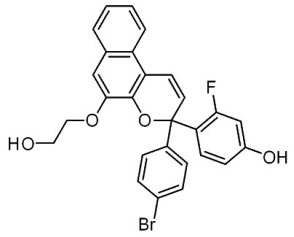




18

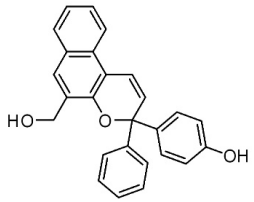
^{1}H (400 MHz, acetone-d_6)





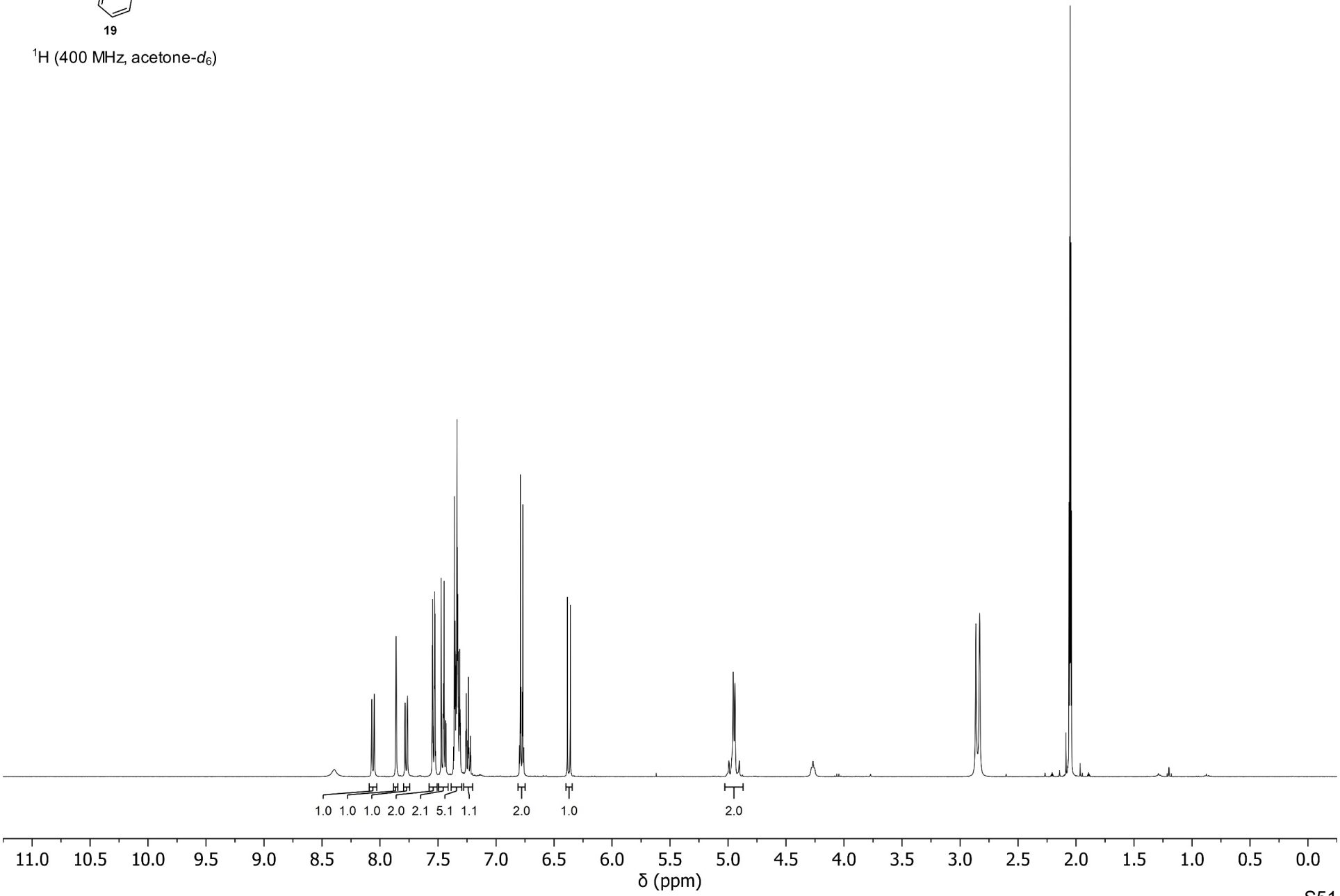
18

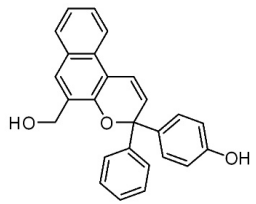
^{13}C (101 MHz, acetone-d_6)



19

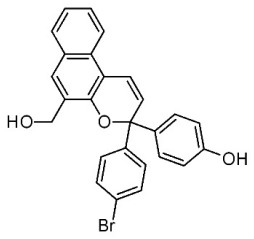
^{1}H (400 MHz, acetone-d_6)





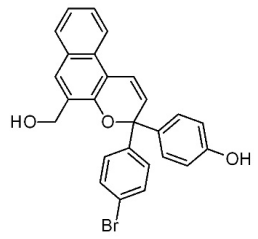
19

^{13}C (101 MHz, acetone-d_6)



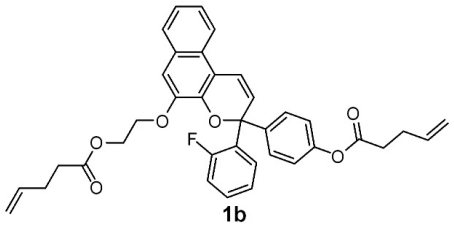
20

^{1}H (400 MHz, acetone-d_6)



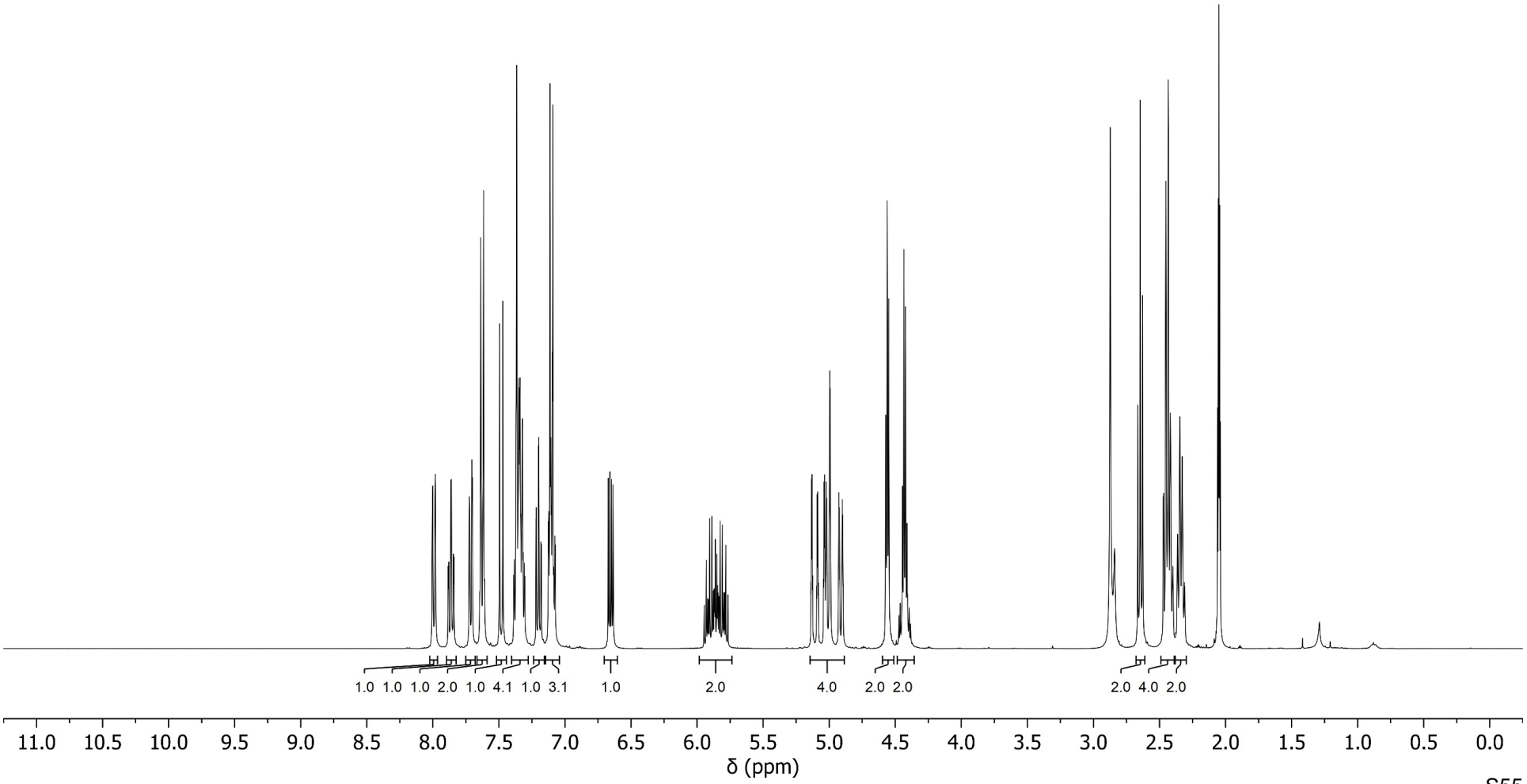
20

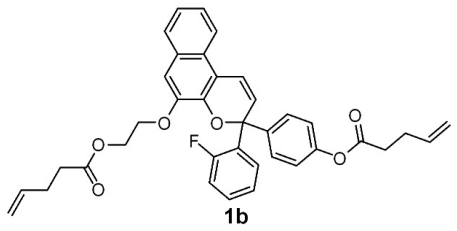
^{13}C (101 MHz, acetone-d_6)



1b

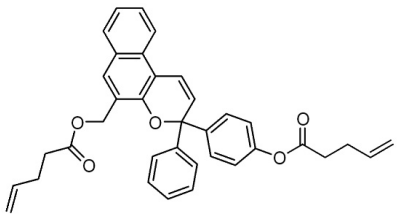
^{1}H (400 MHz, acetone-d_6)





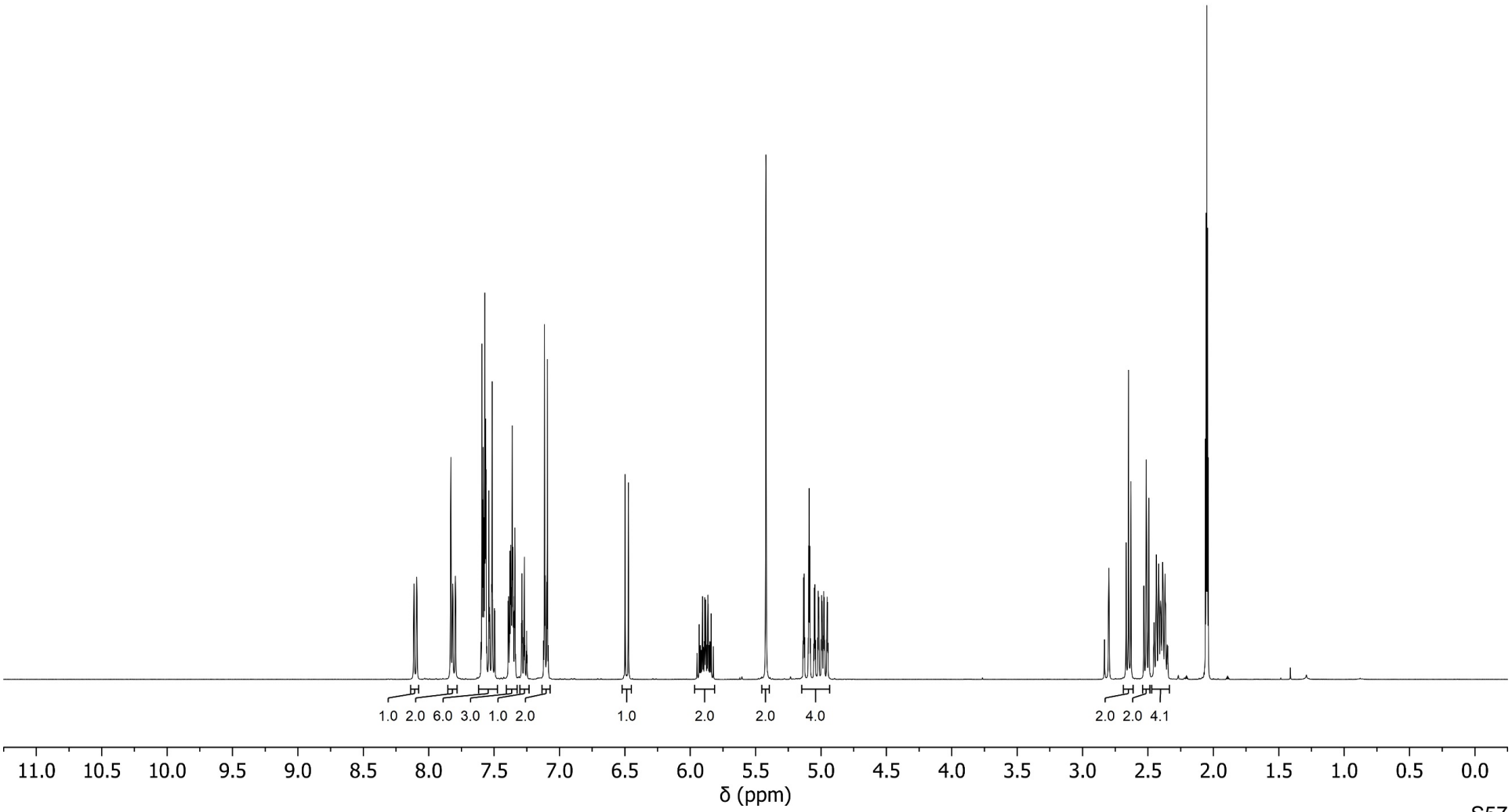
1b

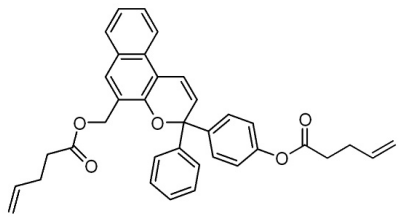
^{13}C (101 MHz, acetone-d_6)



1c

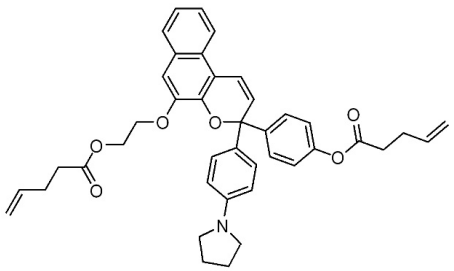
^{1}H (400 MHz, acetone-d_6)





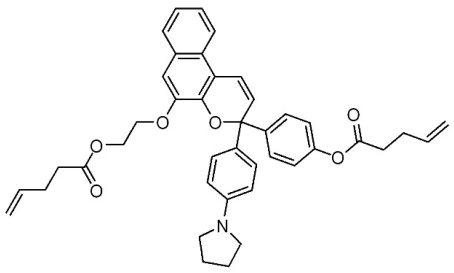
1c

^{13}C (101 MHz, acetone-d_6)



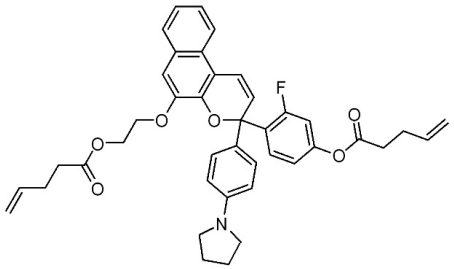
2a

^{1}H (400 MHz, acetone-d_6)



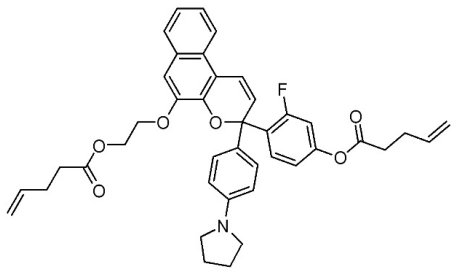
2a

^{13}C (101 MHz, acetone-d_6)



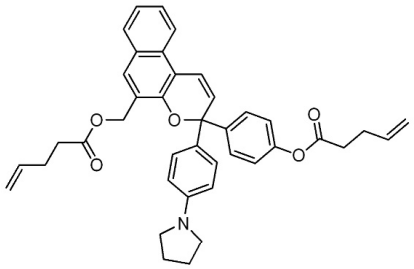
2b

^{1}H (400 MHz, acetone-d_6)



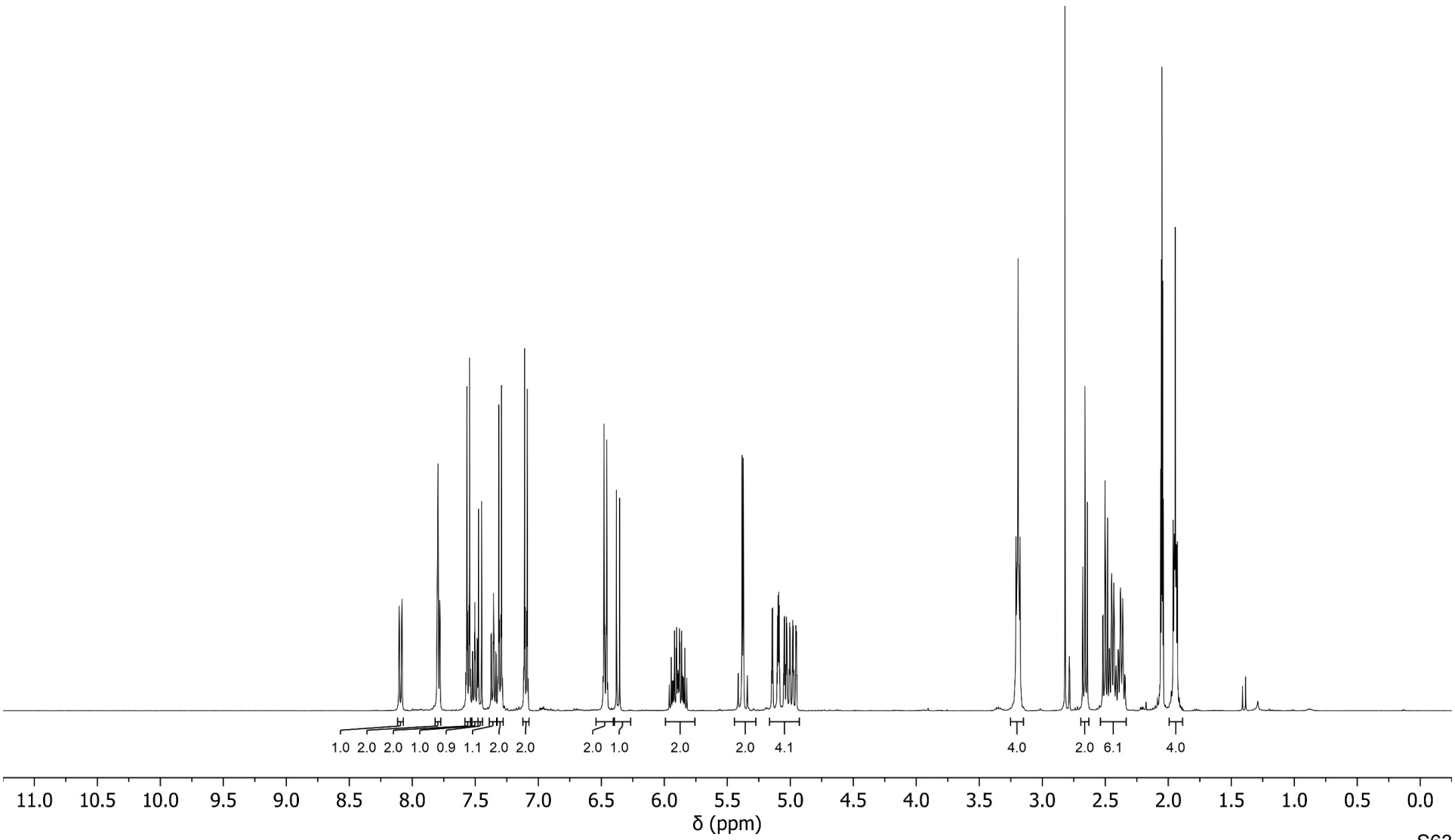
2b

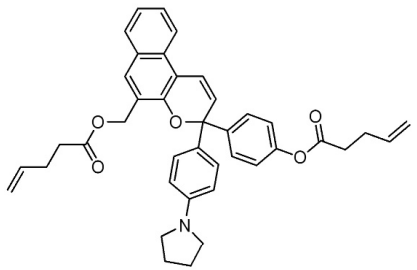
^{13}C (101 MHz, acetone-d_6)



2c

^{1}H (400 MHz, acetone-d_6)





2c

^{13}C (101 MHz, acetone-d_6)