Supplementary data

Metal-free, Visible-Light-Mediated Phototransformations of *ortho*-Biaryl Appended Chalcones: Access to Oxathia[5]helicenes and 1,2,3,4-Tetrasubstituted Cyclobutanes

A. V. Zakharov, E. E. Evsikova, P. D. Grebennikova, M. A. Krylova, A. N. Fakhrutdinov, V. Z. Shirinian

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky prosp., 119991 Moscow, Russian Federation

Table of Contents

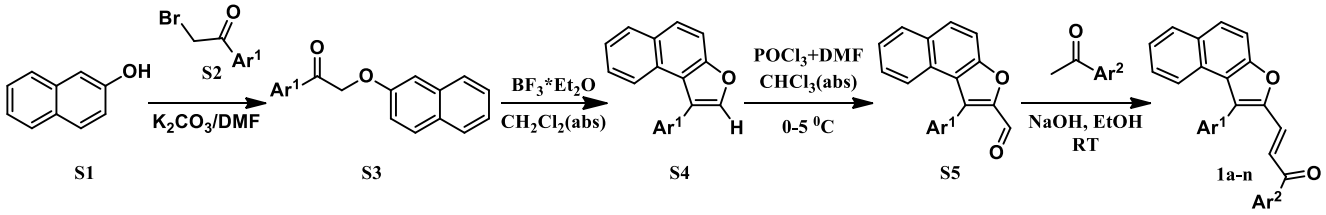
I. General information, synthesis and characterization of starting compounds

General information. Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C{^{1}H} NMR) were recorded in deuterated solvents using spectrometers working at 300 MHz for ^{1}H and 75 MHz for ^{13}C{^{1}H}. Both ^{1}H and ^{13}C{^{1}H} NMR are reported in parts per million (ppm) at 293 K. The data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; m, multiplet; br, broad; q, quartet), coupling constant in hertz (Hz). Melting points (m.p.) were recorded using an apparatus and not corrected. High-resolution mass spectra were obtained using a time-of-flight (TOF) mass spectrometer with an electrospray ionization (ESI) source. All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70-230 mesh); thin-layer chromatography (TLC) analysis was conducted on silica gel 60 F_{254} plates.

Photochemical Studies. UV-Vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed at 293 K in the presence of air in solutions of acetonitrile. The spectra of the studied compounds were recorded on an Agilent Cary 60 UV-Vis.

Photochemical Synthesis. Photochemical reactions were performed in the commercial 10 ml flat-bottomed glass vessels. The choice of vials from ordinary glass instead photochemical vessels is due to the desire to simplify the experiment and make it accessible to a wide range of experimenters. The irradiation was carried out by blue lamp with an absorption maximum of 415-420 nm. The distance between the lamp and the bottle was 10 cm.

Synthesis of starting compounds.



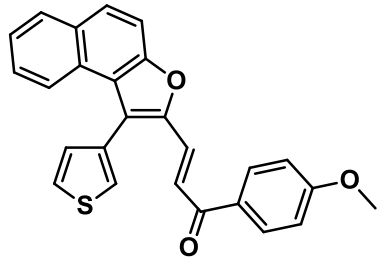
Scheme S1. Synthesis of *ortho*-bihetaryl chalcones **1a-n**.

The starting compounds **S3-S5** were prepared according to previously described protocols.[S1]

1a. Synthesis of bihetaryl chalcones 1a-n.

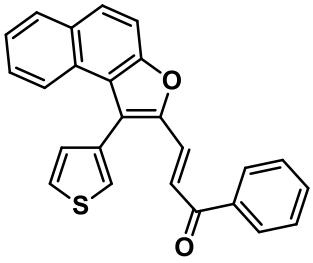
Sodium hydroxide (0.74 mmol) was added to a solution of aldehyde **S5** (0.57 mmol) and the corresponding ketone (0.57 mmol) in 10 ml of EtOH. The mixture was stirred at room temperature until the initial aldehyde completely disappeared (TLC control). After completion of the reaction, ethanol was evaporated to a quarter of the initial volume, the precipitate was filtered and washed with cold ethanol.

(*E*)-1-(4-methoxyphenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1a)



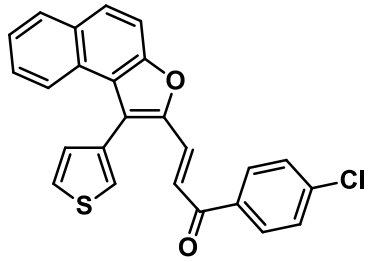
Dark yellow powder, 81 % yield (0.19 g); mp 198-200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.91 (s, 3H, OCH_3), 7.01 (d, *J*= 8.8 Hz, 2H, H^{arom}), 7.34 (d, *J*= 4.8 Hz, 1H, H^{arom}), 7.41-7.52 (m, 3H, H^{arom}), 7.60-7.62 (m, 1H, H^{arom}), 7.67-7.78 (m, 3H, H^{arom}), 7.83-7.97 (m, 3H, H^{arom}), 8.12 (d, *J*= 8.8 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.5, 112.2, 113.9 (2C),120.9, 122.8, 123.3, 123.5, 125.0, 125.8, 126.7, 126.8, 128.2, 128.8 (2C), 129.1, 129.4, 130.8 (2C), 130.9, 131.2, 131.8, 150.1, 153.0, 163.5, 187.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{18}O_3S$ 411.1049, found 411.1049.

(*E*)-1-phenyl-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1b)



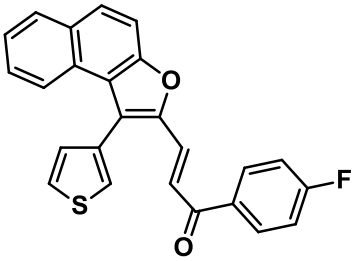
Yellow powder, 78 % yield (0.17 g); mp 168-170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34 (dd, *J*= 4.9, 1.3 Hz, 1H), 7.41-7.57 (m, 5H, H^{arom}), 7.59-7.65 (m, 2H, H^{arom}), 7.70-7.75 (m, 2H, H^{arom}), 7.82 (d, *J*= 15.2 Hz, 1H), 7.89 (d, *J*= 9.0 Hz, 1H), 7.92-7.98 (m, 2H, H^{arom}), 8.10-8.14 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.2, 120.8, 122.8, 123.3, 124.0, 125.0, 125.8, 126.8, 126.9, 128.2, 128.5(2C), 128.7(2C), 129.0, 129.2, 129.4, 129.5, 130.9, 131.7, 132.9, 138.2, 149.9, 153.2, 189.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{16}O_2S$ 381.0944, found 381.0932.

(*E*)-1-(4-chlorophenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1c)



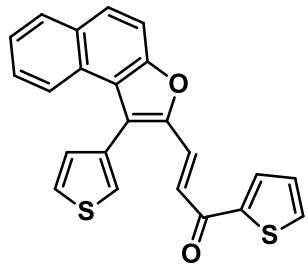
Yellow powder, 83 % yield (0.2 g); mp 196-198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34 (dd, *J*= 4.9, 1.3 Hz, 1H), 7.41-7.53 (m, 5H, H^{arom}), 7.61-7.63 (m, 1H, H^{arom}), 7.70-7.72 (m, 3H, H^{arom}), 7.88-7.97 (m, 3H, H^{arom}), 8.02-8.06 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.1, 120.1, 122.7, 123.3, 124.4, 125.1, 125.9, 126.8, 127.0, 128.1, 128.9(2C), 129.1, 129.2, 129.4, 129.9(3C), 130.9, 131.6, 136.5, 139.3, 149.8, 153.2, 187.93; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{15}ClO_2S$ 415.0554, found 415.0540.

(*E*)-1-(4-fluorophenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1d)



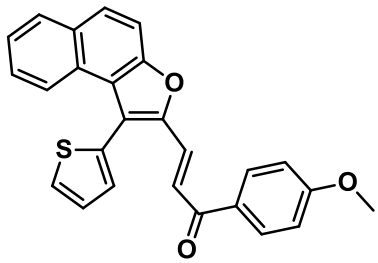
Yellow powder, 76 % yield (0.17 g); mp 149-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.17-7.24 (m, 2H, H^{arom}), 7.34 (dd, *J*= 4.9, 1.2 Hz, 1H), 7.41-7.53 (m, 3H, H^{arom}), 7.61-7.63 (m, 1H, H^{arom}), 7.68-7.73 (m, 2H, H^{arom}), 7.77 (d, *J*= 15.2 Hz, 1H), 7.89 (d, *J*=9.4 Hz, 1H), 7.92-7.98 (m, 2H, H^{arom}), 8.10-8.17 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.1, 115.6, 115.9, 120.3, 122.7, 123.3, 124.2, 125.1, 125.8, 126.8, 126.9, 128.1, 129.1, 129.2, 129.4, 129.7, 130.9, 131.0, 131.1, 131.7, 134.5 and 134.6, 149.9, 153.2, 164.0 and 167.4 (CF), 187.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{15}FO_2S$ 399.0850, found 399.0846.

(*E*)-1-(thiophen-2-yl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1e)



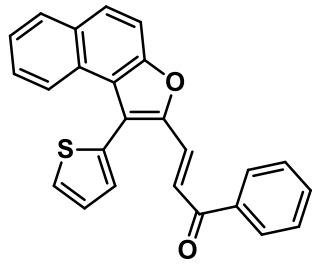
Yellow powder; 88% yield (0.19 g); mp 188-190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.21-7.24 (m, 1H, $H^{Thiophene}$), 7.33-7.35 (m, 1H, $H^{Thiophene}$), 7.41-7.53 (m, 3H, H^{arom}), 7.61-7.65 (m, 2H, H^{arom}), 7.69-7.74 (m, 3H, H^{arom}), 7.88-7.98 (m, 4H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.2, 120.9, 122.8, 123.3, 124.1, 125.1, 125.8, 126.8, 126.9, 128.2, 128.3, 128.9, 129.0, 129.1, 129.4, 130.9, 131.7, 131.8, 133.9, 145.9, 149.8, 153.2, 181.5; HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{23}H_{14}O_2S_2$ 387.0508, found 387.0507.

(*E*)-1-(4-methoxyphenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1f)



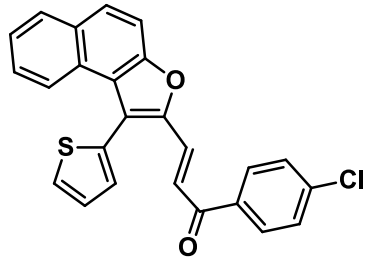
Yellow powder, 75 % yield (0.18 g); mp 176-178°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.91 (s, 3H, OCH_3) 7.01 (d, *J*= 8.9 Hz, 2H, H^{arom}), 7.29-7.31 (m, 2H, H^{arom}), 7.41-7.52 (m, 2H, H^{arom}), 7.62 (dd, *J*= 4.6, 1.7 Hz, 1H, H^{arom}), 7.71 (d, *J*= 8.8 Hz, 1H, H^{arom}), 7.75-7.84 (m, 2H, H^{arom}), 7.88 (d, *J*= 9.0 Hz, 1H, H^{arom}), 7.94-7.98 (m, 2H, H^{arom}), 8.11 (d, *J*= 8.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.5, 112.1, 113.9 (2C), 120.8, 121.5, 123.1, 123.2, 125.1, 136.9, 127.8, 127.9, 128.0, 128.4, 128.9, 129.1, 129.7, 130.8 (2C), 130.9, 131.1, 131.9, 151.2, 152.9, 163.5, 187.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{18}O_3S$ 411.1049, found 411.1051.

(*E*)-1-phenyl-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1g)



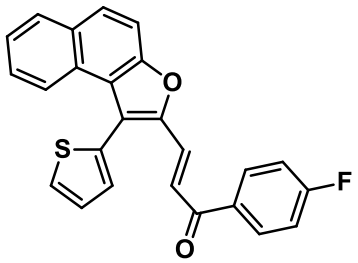
Brown-yellow powder, 53 % yield (0.11 g); mp 159-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.29-7.33 (m, 2H, H^{arom}), 7.42-7.57 (m, 4H, H^{arom}), 7.60-7.64 (m, 2H, H^{arom}), 7.70- 7.78 (m, 2H, H^{arom}), 7.83 (d, *J*= 15.3 Hz, 1H), 7.90 (d, *J*= 9.0 Hz, 1H), 7.95-7.99 (m, 2H, H^{arom}), 8.10-8.13 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.1, 121.3, 121.4, 125.2, 126.9, 127.8, 127.9, 128.0, 128.5(2C), 128.7 (2C), 129.1 (2C), 129.2, 129.7, 131.0, 131.7, 133.0, 138.1, 151.0, 153.0, 189.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{16}O_2S$ 381.0944, found 381.0949.

(*E*)-1-(4-chlorophenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1h)



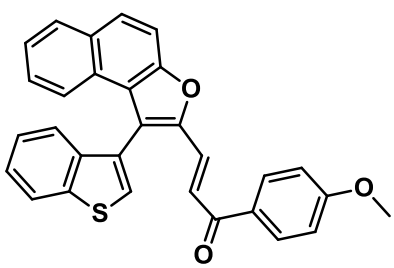
Brown powder, 54 % yield (0.13 g); mp 195-198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.30-7.32 (m, 2H, H^{arom}), 7.42-7.52 (m, 4H, H^{arom}), 7.63-7.64 (m, 1H, H^{arom}), 7.70-7.80 (m, 3H, H^{arom}), 7.90 (d, *J*=9.0 Hz, 1H, H^{arom}), 7.95-7.98 (m, 2H, H^{arom}), 8.04 (d, *J*=8.4 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.1, 120.7, 121.7, 123.0, 123.2, 125.2, 127.0, 127.8 (2C), 127.9, 128.0, 129.0, 129.2, 129.3, 129.5, 129.7, 129.9 (2C), 130.9, 131.6, 136.4, 139.4, 150.9, 153.1, 187.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{15}ClO_2S$ 415.0554, found 415.0547.

(*E*)-1-(4-fluorophenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1i)



Brown-yellow powder, 54% yield (0.12 g); mp 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.18-7.24 (m, 2H, H^{arom}), 7.29-7.32 (m, 2H, H^{arom}), 7.42- 7.53 (m, 2H, H^{arom}), 7.62-7.65 (m, 1H, H^{arom}), 7.70-7.76 (m, 3H, H^{arom}), 7.90 (d, *J*= 9.0 Hz, 1H), 7.95-7.99 9 (m, 2H, H^{arom}),8,10-8.17 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.1, 115.6, 115.9, 120.9, 121.6, 123.0, 123.2, 125.2, 127.0, 127.9 (2C), 128.0, 129.1, 129.2, 129.3, 129.7, 130.9, 131.1, 131.2, 131.7, 134.4 and 134.5, 150.9, 153.0, 164.0 and 167.4 (CF), 187.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{15}FO_2S$ 399.0850, found 399.0842.

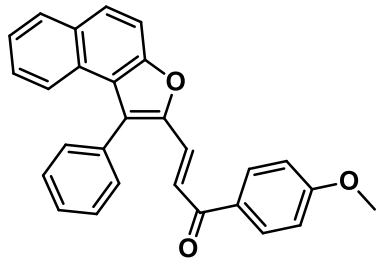
(*E*)-3-(1-(benzo[b]thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1j)



Yellow powder; 90 % yield (0.24 g); mp 244-246ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.91 (s, 3H, OCH_3), 7.00 (d, *J* = 8.9 Hz, 2H, H^{arom}), 7.21-7.31 (m, 2H, H^{arom}), 7.40-7.48 (m, 4H, H^{arom}), 7.61 (d, *J* = 15.2 Hz, 1H, vinyl), 7.66 (s, 1H, $H^{Thianaphthene}$), 7.77-7.80 (m, 1H, H^{arom}), 7.83 (d, *J* = 15.0 Hz, 1H, vinyl), 7.91-7.97 (m, 2H, H^{arom}), 8.03-8.06 (m, 1H, H^{arom}), 8.09 (d, *J* = 8.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.5, 112.2, 113.9 (2C),

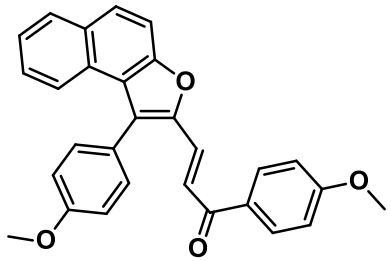
121.2, 121.6, 122.9, 123.2, 123.4, 123.7, 124.8, 125.0 (2C), 126.9, 127.2, 127.3, 127.9, 128.5, 128.8, 128.9, 130.8 (2C), 130.9, 131.1, 138.9, 140.1, 150.9, 153.3, 163.5, 187.6; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{30}H_{20}O_3S$ 461.1206, found 461.1199.

(*E*)-1-(4-methoxyphenyl)-3-(1-phenylnaphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1k)



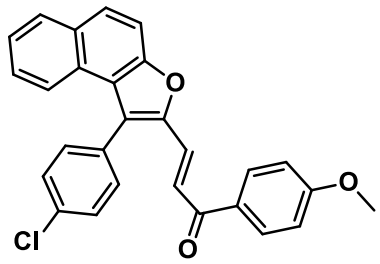
Orange powder, 54 % yield (0.12 g); mp 193-195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.91 (s, 3H, OCH_3), 7.01 (d, *J* = 8.9 Hz, 2H, H^{arom}), 7.35-7.40 (m, 1H, H^{arom}), 7.45-7.50 (m, 1H, H^{arom}), 7.56-7.59 (m, 5H, H^{arom}), 7.63 (d, *J* = 15.3 Hz, 1H, vinyl), 7.74 (d, *J* = 9.0 Hz, 1H, H^{arom}), 7.81 (d, *J* = 15.1 Hz, 1H, vinyl), 7.84 (d, *J* = 7.8 Hz, 1H, H^{arom}), 7.89 (d, *J* = 9.0 Hz, 1H, H^{arom}), 7.96 (d, *J* = 8.0 Hz, 1H, H^{arom}), 8.11 (d, *J* = 8.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.5, 112.2, 113.9 (2C), 120.9, 122.6, 123.3, 124.9, 126.7, 128.2, 128.6, 128.7, 128.9 (4C), 129.1, 130.4 (2C), 130.8 (2C), 130.9, 131.2, 132.2, 149.8, 153.0, 163.5, 187.7; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{28}H_{20}O_3$ 405.1485, found 405.1488.

(*E*)-1-(4-methoxyphenyl)-3-(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1l)



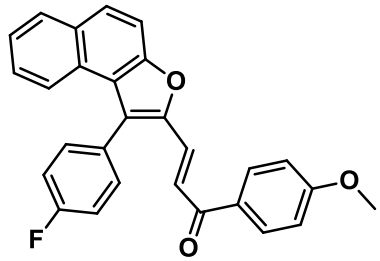
Yellow powder; 70% yield (0.17 g); mp 187-189ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.92 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.01 (d, *J*= 8.9 Hz, 2H, H^{arom}), 7.12 (d, *J*= 8.7 Hz, 2H, H^{arom}), 7.36-7.42 (m, 1H, H^{arom}), 7.44-7.51 (m, 3H, H^{arom}), 7.63 (d, *J*=15.2 Hz, 1H, H^{vinyl}), 7.72 (d, *J*=8.9 Hz, 1H, H^{arom}), 7.79 (d, *J*=15.2 Hz, 1H, H^{vinyl}), 7.86-7.97 (m, 3H, H^{arom}), 8.11 (d, *J*=8.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.4, 55.5, 112.2, 113.9 (2C), 114.4 (2C), 120.5, 122.8, 123.3, 124.2, 124.9, 126.7, 128.2, 128.6, 128.7, 129.0, 129.1, 130.8 (2C), 130.9, 131.2, 131.6 (2C), 149.9, 153.0, 159.9, 163.5, 187.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{29}H_{22}O_4$ 435.1591, found 435.1586.

(*E*)-3-(1-(4-chlorophenyl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1m)



Yellow powder; 83% yield (0.21 g); mp 189-191ºC; 1H NMR (300 MHz, CDCl3) δ = 3.92 (s, 3H, OCH3), 7.02 (d, *J*=8.9 Hz, 2H, H^{arom}), 7.38-7.44 (m, 1H, H^{arom}), 7.46-7.60 (m, 6H, H^{arom}), 7.73 (d, *J*= 9.0 Hz, 1H, H^{arom}), 7.79-7.84 (m, 2H, H^{arom}), 7.89 (d, *J*= 9.0 Hz, 1H, H^{arom}), 7.97 (d, *J*=7.9 Hz, 1H, H^{arom}), 8.11 (d, *J*= 8.9 Hz, 2H, H^{arom}); 13C NMR (75 MHz, CDCl3) δ = 55.5, 112.2, 113.9 (2C), 121.2, 122.4, 123.1, 125.0, 126.9, 127.2, 127.9, 128.4, 128.9, 129.2 (3C), 130.7, 130.8 (2C), 130.9, 131.1, 131.8 (2C), 134.9, 149.8, 153.0, 163.6, 187.6; HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{28}H_{19}ClO_3$ 439.1095, found 439.1091.

(*E*)-3-(1-(4-fluorophenyl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1n)

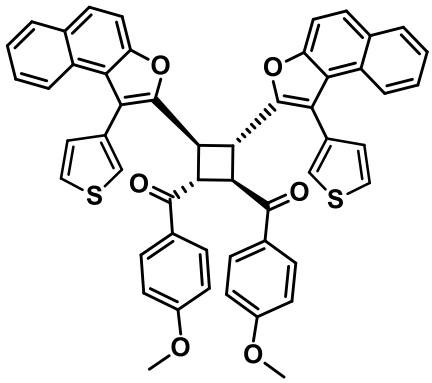


Yellow powder, 67 % yield (0.16 g); mp 181-183°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.92 (s, 3H, OCH_3), 7.02 (d, *J* = 8.9 Hz, 2H, H^{arom}), 7.27-7.34 (m, 2H, H^{arom}), 3.37-7.42 (m, 1H, H^{arom}), 7.46-7.51 (m, 1H, H^{arom}), 7.53-7.60 (m, 3H, H^{arom}), 7.70-7.83 (m, 3H, H^{arom}), 7.89 (d, *J*=9.0 Hz, 1H, H^{arom}), 7.97 (d, *J*=8.1 Hz, 1H, H^{arom}), 8.11 (d, *J*=8.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.5, 112.2, 113.9 (2C), 115.9, 116.2, 121.1, 122.6, 123.1, 124.9, 126.8, 127.5, 128.0, 128.1, 128.5, 128.9, 129.2, 130.8 (2C), 130.9, 131.1, 132.1, 132.2, 149.9, 153.0, 161.4 and 164.7 (CF), 163.5, 187.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{19}FO_3$ 423.1391, found 423.1391.

1b. Synthesis of cyclobutanes

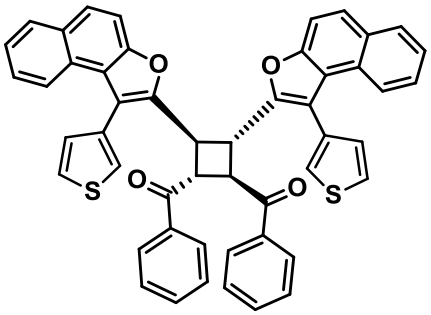
Bihetarylchalcones (0.24 mmol) were dissolved in 8 ml toluene with Et_3N (1.2 mmol) and the reaction mixture was irradiated (Blue lamp, λ = 420 nm) with stirring in 10 ml flat-bottomed glass vessel. After completion of the reaction (TLC control) the solution was evaporated under vacuum, the residue was purified by column chromatography eluting by light petroleum – ethyl acetate (6:1).

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2ahh-a)



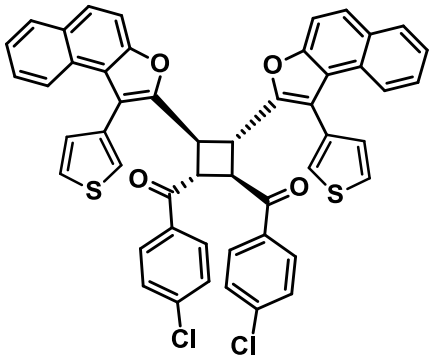
Yellow powder; 51% yield (0.05 g); mp 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.76 (s, 6H, OCH_3), 4.30 (d, *J* = 9.6 Hz, 2H, CH), 5.01 (d, *J* = 9.5 Hz, 2H, CH), 6.71-6.76 (m, 4H, H^{arom}), 6.78 (d, *J* = 8.9 Hz, 4H, H^{arom}), 7.23-7.25 (m, 2H, H^{arom}), 7.29-7.34 (m, 2H, H^{arom}), 7.41-7.46 (m, 2H, H^{arom}), 7.71 (d, *J* = 8.2 Hz, 2H, H^{arom}), 7.79 (d, *J* = 9.0 Hz, 2H, H^{arom}), 7.83 (d, *J* = 9.2 Hz, 2H, H^{arom}), 7.90 (d, *J* = 8.9 Hz, 4H, H^{arom}), 7.97 (d, *J* = 8.1 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.9 (2C), 44.5 (2C), 55.4 (2C), 112.5 (2C), 113.8 (4C), 116.7 (2C), 122.2 (2C), 123.2 (2C), 124.3 (2C), 124.4 (2C), 125.8 (2C), 125.9 (2C), 126.1 (2C), 128.1 (2C), 128.6 (2C), 128.8 (2C), 129.2 (2C), 130.8 (2C), 131.1 (4C), 132.0 (2C), 151.4 (2C), 152.0 (2C), 163.8 (2C), 196.2 (2C); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{52}H_{36}O_6S_2$ 821.2026, found 821.2004.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (2bhh-a)



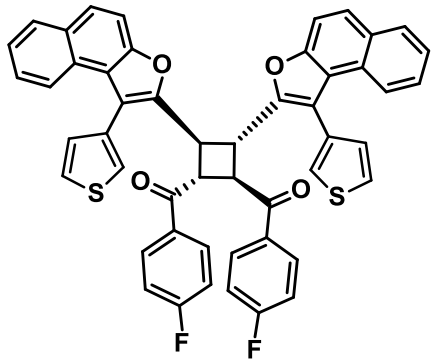
Yellow powder; 47% yield (0.04 g); mp 124-126ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.24 (d, *J* = 9.7 Hz, 2H, CH), 5.04 (d, *J* = 9.6 Hz, 2H, CH), 6.60-6.61 (m, 2H, H^{arom}), 6.64-6.66 (m, 2H, H^{arom}), 7.20-C7.22 (m, 2H, H^{arom}), 7.29-7.33 (m, 4H, H^{arom}), 7.40-7.43 (m, 2H, H^{arom}), 7.46-7.49 (m, 2H, H^{arom}), 7.65 (d, *J* = 8.3 Hz, 2H, H^{arom}), 7.76-7.81 (m, 5H, H^{arom}), 7.84-7.88 (m, 5H, H^{arom}), 7.96 (d, *J* = 8.0 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.0 (2C), 44.8 (2C), 112.5 (2C), 116.9 (2C), 122.2 (2C), 123.1 (2C), 124.3 (2C), 124.4 (2C), 125.9 (2C), 126.0 (2C), 126.1 (2C), 128.0 (2C), 128.6 (4C), 128.7 (4C), 128.8 (2C), 129.1 (2C), 130.8 (2C), 131.9 (2C), 133.5 (2C), 135.4 (2C), 141.4 (2C), 150.9 (2C), 197.7 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{50}H_{32}O_4S_2$ 783.1634, found 783.1614.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-chlorophenyl)methanone) (2chh-a)



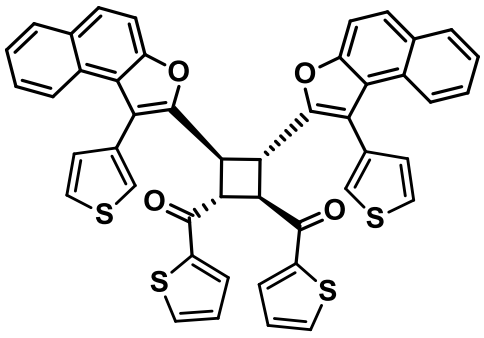
Yellow powder; 43 % yield (0.04 g); mp 128-130ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.24 (d, *J* = 9.7 Hz, 2H, CH), 4.97 (d, *J* = 9.7 Hz, 2H, CH), 6.68-6.72 (m, 4H, H^{arom}),7.22-7.27 (m, 2H, H^{arom}), 7.28 (d, *J* = 8.6 Hz, 4H, H^{arom}), 7.34-7.36 (m, 2H, H^{arom}), 7.42-7.47 (m, 2H, H^{arom}), 7.64-7.69 (m, 2H, H^{arom}), 7.77 (d, *J* = 9.1 Hz, 2H, H^{arom}), 7.80 (d, *J* = 8.8 Hz, 4H, H^{arom}), 7.83 (d, *J* = 8.7 Hz, 2H, H^{arom}), 7.97 (d, *J* = 8.1 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.1 (2C), 44.6 (2C), 112.3 (2C), 117.1 (2C), 122.1 (2C), 123.1 (2C), 123.2 (2C), 124.4 (2C), 124.5 (2C), 126.2 (4C), 128.0 (2C), 128.8 (2C), 128.9 (4C), 129.0 (2C), 130.2 (4C), 130.9 (2C), 131.8 (2C), 133.6 (2C), 140.2 (2C), 150.6 (2C), 152.0 (2C), 196.4 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{50}H_{30}Cl_2O_4S_2$ 851.0855, found 851.0853.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-fluorophenyl)methanone) (2dhh-a)



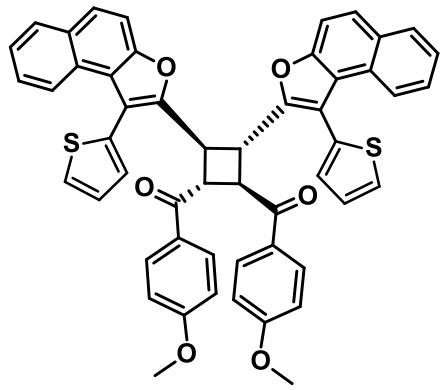
Yellow powder; 43% yield (0.04 g); mp 140-142°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.25 (d, *J* = 9.6 Hz, 2H, CH), 4.98 (d, *J* = 9.6 Hz, 2H, CH), 6.67-6.72 (m, 2H, H^{arom}), 6.95-7.01 (m, 4H, H^{arom}), 7.21-7.23 (m, 2H, H^{arom}), 7.32-7.35 (m, 2H, H^{arom}), 7.42-7.47 (m, 2H, H^{arom}), 7.64-7.69 (m, 4H, H^{arom}), 7.77 (d, *J* = 9.0 Hz, 2H, H^{arom}), 7.83 (d, *J* = 8.7 Hz, 2H, H^{arom}), 7.88-7.93 (m, 4H, H^{arom}), 7.96-7.98 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.1 (2C), 44.7 (2C), 112.4 (2C), 115.6 (2C), 115.9 (2C), 117.1 (2C), 122.1 (2C), 123.1 (2C), 124.4 (2C), 124.6 (2C), 126.1 (2C), 126.2 (2C), 126.3 (2C), 128.0 (2C), 128.9 (2C), 129.0 (2C), 130.9 (2C), 131.4 (2C), 131.6 (2C), 131.8 and 130.0 (2C), 131.9 (2C), 150.7 (2C), 152.0 (2C), 164.3 and 167.7 (2C, CF), 196.0 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{50}H_{30}F_2O4S_2$ 797.1626, found 797.1637.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(thiophen-2-ylmethanone) (2ehh-a)



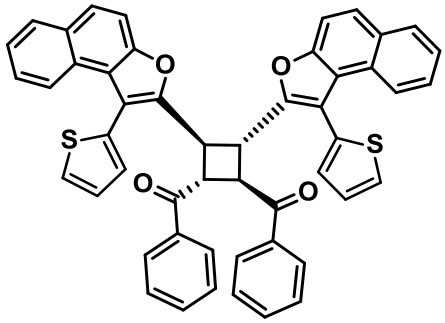
Yellow powder; 38% yield (0.04 g); mp 120-122°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.34 (d, *J* = 9.6 Hz, 2H, CH), 4.88 (d, *J* = 9.6 Hz, 2H, CH), 6.75-6.79 (m, 4H, H^{arom}), 6.95-6.98 (m, 2H, H^{arom}), 7.25-7.30 (m, 2H, H^{arom}), 7.32-7.35 (m, 2H, H^{arom}), 7.41-7.46 (m, 2H, H^{arom}), 7.54-7.56 (m, 2H, H^{arom}), 7.61-7.63 (m, 2H, H^{arom}), 7.70 (d, *J* = 8.3 Hz, 2H, H^{arom}), 7.78-7.84 (m, 4H, H^{arom}), 7.96 (d, *J* = 8.0 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.9 (2C), 45.5 (2C), 112.5 (2C), 116.9 (2C), 122.2 (2C), 123.2 (2C), 124.4 (2C), 124.5 (2C), 126.0 (2C), 126.1 (2C), 126.2 (2C), 128.1 (2C), 128.4 (2C), 128.9 (2C), 129.1 (2C), 130.9 (2C), 131.9 (2C), 133.4 (2C), 134.8 (2C), 142.8 (2C), 150.9 (2C), 151.9 (2C), 189.9 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{46}H_{28}O_4S_4$ 795.0763, found 795.0780.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2fhh-a)



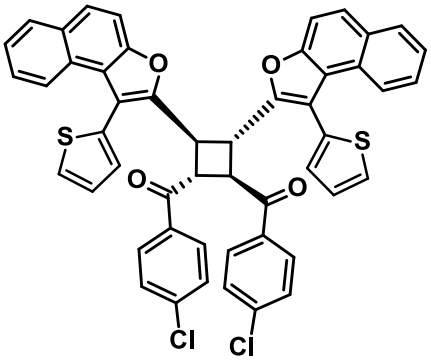
Yellow powder; 47% yield (0.05 g); mp 124-126ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.77 (s, 6H, OCH_3), 4.33 (d, *J* = 9.5 Hz, 2H, CH), 5.05 (d, *J* = 9.6 Hz, 2H, CH), 6.60-6.61 (m, 2H, H^{arom}), 6.79 (d, *J* = 8.9 Hz, 4H, H^{arom}), 6.88-6.91 (m, 2H, H^{arom}), 7.23-7.25 (m, 2H, H^{arom}), 7.28-7.35 (m, 3H, H^{arom}), 7.42-7.47 (m, 2H, H^{arom}), 7.74 (d, *J* = 9.0 Hz, 2H, H^{arom}), 7.80 (d, *J* = 6.7 Hz, 3H, H^{arom}), 7.90 (d, *J* = 8.8 Hz, 4H, H^{arom}), 7.97 (d, *J* = 8.1 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.4 (2C), 44.3 (2C), 55.5 (2C), 112.5 (2C), 113.8 (4C), 114.3 (2C), 122.5 (2C), 123.1 (2C), 124.5 (2C), 125.9 (2C), 126.1 (2C), 127.1 (2C), 124.3 (2C), 127.9 (2C), 128.6 (2C), 128.7 (2C), 128.8 (2C), 130.9 (2C), 131.1 (4C), 132.4 (2C), 151.9 (2C), 152.8 (2C), 163.9 (2C), 196.1 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{52}H_{36}O_6S_2$ 843.1846, found 843.1856.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (2ghh-a)



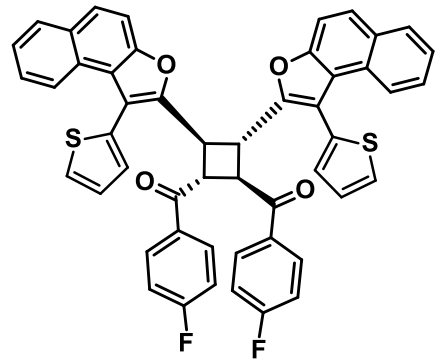
Yellow powder; 44% yield (0.04 g); mp 118-120ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.28 (d, *J* = 9.6 Hz, 2H, CH), 5.09 (d, *J* = 9.7 Hz, 2H, CH), 6.51-6.53 (m, 2H, H^{arom}), 6.85-6.88 (m, 2H, H^{arom}), 7.21-7.23 (m, 2H, H^{arom}), 7.30-7.33 (m, 4H, H^{arom}), 7.41-7.47 (m, 5H, H^{arom}), 7.70 (d, *J* = 8.3 Hz, 2H, H^{arom}), 7.76 (d, *J* = 9.0 Hz, 2H, H^{arom}), 7.82 (d, *J* = 9.0 Hz, 2H, H^{arom}), 7.85-7.89 (m, 5H, H^{arom}), 7.96 (d, *J* = 8.2 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.9 (2C), 44.5 (2C), 112.4 (2C), 114.5 (2C), 122.5 (2C), 123.1 (2C), 124.5 (2C), 126.0 (2C), 126.1 (2C), 127.1 (2C), 127.3 (2C), 127.9 (2C), 128.6 (4C), 128.7 (2C), 128.8 (4C), 128.9 (2C), 130.9, 132.3 (2C), 133.6 (2C), 135.4 (2C), 151.9 (2C), 152.5 (2C), 197.6 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{50}H_{32}O_4S_2$ 783.1634, found 783.1640.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-chlorophenyl)methanone) (2hhh-a)



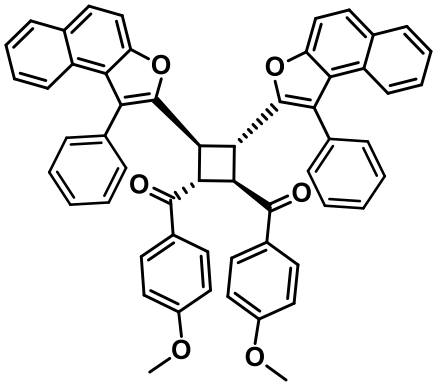
Yellow powder; 43% yield (0.04 g); mp 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.27 (d, *J* = 9.6 Hz, 2H, CH), 5.01 (d, *J* = 9.6 Hz, 2H, CH), 6.59 (m, 2H, H^{arom}), 6.88-6.90 (m, 2H, H^{arom}), 7.23-7.24 (m, 2H, H^{arom}), 7.28-7.32 (m, 4H, H^{arom}), 7.34-7.36 (m, 2H, H^{arom}), 7.43-7.48 (m, 2H, H^{arom}), 7.70-7.73 (m, 2H, H^{arom}), 7.75 (d, *J* = 8.9 Hz, 2H, H^{arom}),7.79-7.85 (m, 6H, H^{arom}), 7.97 (d, *J* = 8.2 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.0, 44.4, 112.3, 114.7, 122.4, 123.1, 124.7, 126.2, 126.3, 127.2, 127.4, 127.9, 128.7, 128.8, 128.9, 129.0, 129.8, 130.2, 130.9, 132.1, 133.6, 140.2, 151.9, 152.0, 196.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{50}H_{30}Cl_2O_4S_2$ 829.1035, found 829.1019.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-fluorophenyl)methanone) (2ihh-a)



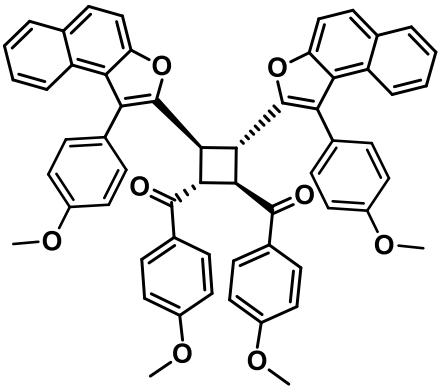
Yellow powder; 47% yield (0.04 g); mp 126-128°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.26 (d, *J* = 9.6 Hz, 2H, CH), 5.01 (d, *J* = 9.7 Hz, 2H, CH), 6.56-6.58 (m, 2H, H^{arom}), 6.87-6.89 (m, 2H, H^{arom}), 6.95-7.01 (m, 4H, H^{arom}), 7.22-7.24 (m, 2H, H^{arom}), 7.30-7.35 (m, 2H, H^{arom}), 7.42-7.48 (m, 2H, H^{arom}), 7.70 (d, *J* = 8.2 Hz, 2H, CH), 7.75 (d, *J* = 9.0 Hz, 2H, CH), 7.83 (d, *J* = 8.9 Hz, 2H, CH), 7.87-7.92 (m, 4H, H^{arom}), 7.97 (, *J* = 8.2 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.9 (2C), 44.4 (2C), 112.3 (2C), 114.6 (2C), 115.7 (2C), 115.9 (2C), 122.4 (2C), 123.1 (2C), 124.6 (2C), 126.3 (4C), 127.2 (2C), 127.3 (2C), 127.9 (2C), 128.8 (2C), 128.9 (2C), 130.9 (2C), 131.4 (2C), 131.6 (2C), 131.7 and 131.8 (2C), 132.1 (2C), 151.9 (2C), 152.1 (2C), 164.4 and 167.8 (2C, CF), 195.9 (2C); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{50}H_{30}F_2O4S_2$ 819.1446, found 819.1454.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-phenylnaphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2khh-a)



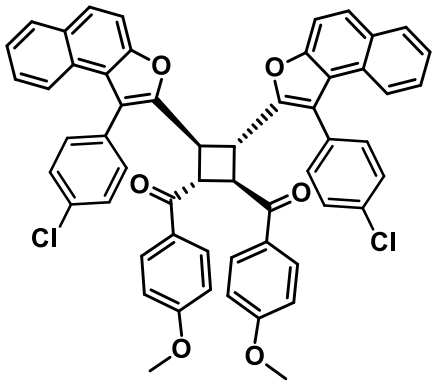
Yellow powder; 48% yield (0.05 g); mp 132-134ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.77 (s, 6H, OCH_3), 4.18 (d, *J* = 9.7 Hz, 2H, vinyl), 5.01 (d, *J* = 9.7 Hz, 2H, vinyl), 6.76-6.82 (m, 6H, H^{arom}), 6.88-6.97 (m, 4H, H^{arom}), 7.23-7.28 (m, 6H, H^{arom}), 7.39-7.44 (m, 3H, H^{arom}), 7.63 (d, *J* = 8.4 Hz, 2H, H^{arom}), 7.78 (d, *J* = 8.9 Hz, 2H, H^{arom}), 7.83 (d, *J* = 9.1 Hz, 2H, H^{arom}), 7.87 (d, *J* = 8.9 Hz, 4H, H^{arom}), 7.97 (d, *J* = 7.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.2 (2C), 44.4 (2C), 55.4 (2C), 112.5 (2C), 113.7 (2C), 122.0 (2C), 122.1 (2C), 123.2 (2C), 124.3 (2C), 125.7 (2C), 125.9 (2C), 127.7 (2C), 128.1 (2C), 128.4 (4C), 128.7 (2C), 128.8 (2C), 130.0 (4C), 130.8 (2C), 131.1 (4C), 132.4 (2C), 150.8 (2C), 151.9 (2C), 163.8 (2C), 196.3 (2C); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{56}H_{40}O_6$ 809.2898, found 809.2892.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2lhh-a)



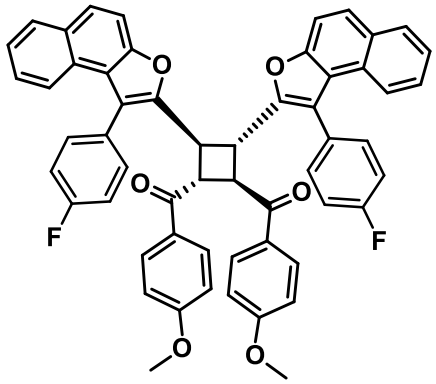
Light yellow powder; 53% yield (0.06 g); mp 210-212ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.75 (s, 6H, OCH_3), 3.77 (s, 6H, OCH_3), 4.16- 4.19 (m, 2H), 4.98-5.02 (m, 2H), 6.39-6.41 (m, 2H, H^{arom}), 6.71-6.87 (m, 10H, H^{arom}), 7.24-7.29 (m, 2H, H^{arom}), 7.39-7.44 (m, 2H, H^{arom}), 7.68 (d, *J* = 8.3 Hz, 2H, H^{arom}), 7.77 (d, *J* = 8.9 Hz, 2H, H^{arom}), 7.82 (d, *J* = 9.1 Hz, 2H, H^{arom}), 7.86-7.89 (m, 4H, H^{arom}), 7.96 (d, *J* = 8.1 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.2 (2C), 44.4 (2C), 55.1 (2C), 55.4 (2C), 112.5 (2C), 113.5 (2C), 113.7 (4C), 114.2 (2C), 121.6 (2C), 122.3 (2C), 123.2 (2C), 124.3 (2C), 124.4 (2C), 125.6 (2C), 125.9(2C), 128.2 (2C), 128.7 (2C), 128.8 (2C), 130.8 (2C), 131.1 (8C), 151.0 (2C), 151.9 (2C), 159.1 (2C), 163.8 (2C), 196.3 (2C).; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{58}H_{44}O_8$ 869.3109, found 869.3107.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-chlorophenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2mhh-a)



Yellow powder; 58% yield (0.06 g); mp 136-138ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.78 (s, 6H, OCH_3), 4.17 (d, *J* = 9.6 Hz, 2H, CH), 4.96 (d, *J* = 9.6 Hz, 2H, CH), 6.74-6.80 (m, 6H, H^{arom}), 6.85-6.91 (m, 4H, H^{arom}), 7.26-7.31 (m, 4H, H^{arom}), 7.41-7.46 (m, 2H, H^{arom}), 7.57 (d, *J* = 8.2 Hz, 2H, H^{arom}), 7.77 (d, *J* = 9.0 Hz, 2H, H^{arom}), 7.84-7.88 (m, 6H, H^{arom}), 7.98 (d, *J* = 8.1 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.8 (2C), 44.5 (2C), 55.5 (2C), 112.4 (2C), 113.8 (4C), 120.8 (2C), 121.7 (2C), 122.9 (2C), 124.5 (2C), 126.1 (2C), 126.2 (2C), 127.8 (2C), 128.5 (2C), 128.7 (2C), 128.8 (2C), 129.0 (2C), 130.8 (2C), 130.9 (2C), 131.1 (4C), 131.2 (2C), 131.4 (2C), 133.9 (2C), 150.9 (2C), 151.9 (2C), 163.9 (2C), 196.0 (2C); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{56}H_{38}Cl_2O$ 877.2118, found 877.2107.

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-fluorophenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2nhh-a)

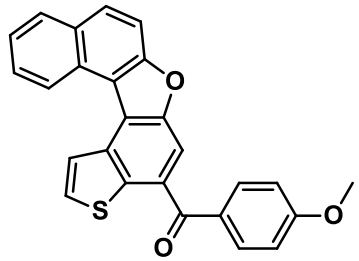


Yellow powder, 61% yield (0.06 g); mp 148-150°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.78 (s, 6H, OCH_3), 4.16 (d, *J* = 9.6 Hz, 2H, CH), 4.97 (d, *J* = 9.6 Hz, 2H, CH), 6.58-6.64 (m, 2H, $H^{Fluorobenzene}$), 6.73-6.80 (m, 6H, $H^{Methoxybenzene}$+$H^{Fluorobenzene}$), 6.88-6.92 (m, 2H, $H^{Fluorobenzene}$), 6.96-7.02 (m, 2H, $H^{Fluorobenzene}$), 7.24-7.29 (m, 2H, H^{arom}), 7.40-7.45 (m, 2H, H^{arom}), 7.56 (d, *J* = 8.1 Hz, 2H, H^{arom}), 7.75-7.78 (m, 2H, H^{arom}), 7.83-7.88 (m, 6H, H^{arom}), 7.97 (d, J = 7.9 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.9 (2C), 44.5 (2C), 55.5 (2C), 112.4 (2C), 113.8 (4C), 115.3 and 115.4 (4C), 115.6 and 115.7 (4C), 120.9 (2C), 121.8 (2C), 122.9 (2C), 124.4 (2C), 126.0 and 126.1 (4C), 127.9 (2C), 128.2 (2C), 128.3 (2C), 128.5 (2C), 129.0 (2C), 130.9 (2C), 131.1 (4C), 131.5 (2C), 131.6 (2C), 131.7 (2C), 150.9 (2C), 151.9 (2C), 160.8 and 164.4 (2C, CF), 163.9 (2C), 196.1 (2C); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{56}H_{38}F_2O_6$ 845.2709 found 845.2703.

1c. Synthesis of oxathia[5]helicenes

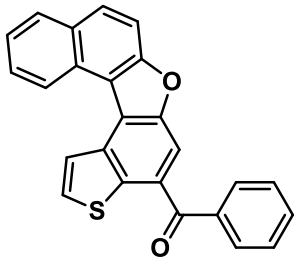
To *ortho*-bihetarylchalcones (0.24 mmol) in 8 ml chloroform was added MsOH (1.2 mmol) and the reaction mixture was irradiated (Blue lamp, λ = 420 nm) with stirring in 10 ml flat-bottomed glass vessel. After completion of the reaction (TLC control) the organic phase was washed with water and saturated $NaHCO_3$ solution and dried over anhydrous $CaCl_2$. The solvent was evaporated in a vacuum. The products were isolated using column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1).

(4-methoxyphenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3a)



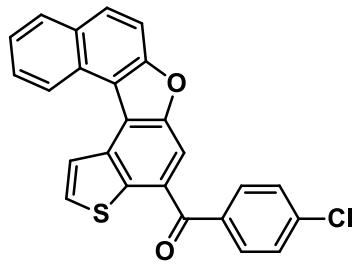
Yellow powder; 73% yield (0.07 g); mp 226-228°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.96 (s, 3H, OCH_3), 7.08 (d, *J* = 8.8 Hz, 2H, H^{arom}), 7.63-7.68 (m, 1H, H^{arom}), 7.83-7.88 (m, 2H, H^{arom}), 7.94 (d, *J* = 8.8 Hz, 2H, H^{arom}), 8.01-8.13 (m, 3H, H^{arom}), 8.20 (s, 1H, H^{arom}), 8.61 (d, *J* = 5.8 Hz, 1H, H^{arom}), 9.15 (d, *J* = 8.5 Hz, 1H, H^{arom});^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.7, 112.8, 113.8 (2C), 114.2, 118.2, 123.3, 123.5, 124.8, 125.1, 127.2, 128.1, 128.7, 129.8, 130.4, 130.7, 131.0, 131.1, 132.3 (2C), 133.8, 136.2, 153.0, 156.3, 163.0, 194.1 HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{16}O_3S$ 409.0893, found 409.0886.

Naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl(phenyl)methanone (3b)



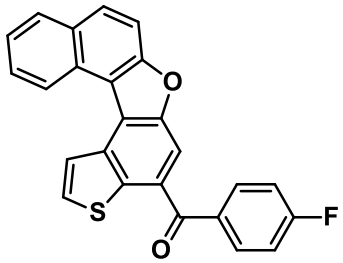
Yellow powder; 68% yield (0.06 g); mp 218-220°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56-7.68 (m, 4H, H^{arom}),7.80-7.87 (m, 2H, H^{arom}), 7.89-7.92 (m, 2H, H^{arom}), 7.80-7.87 (m, 2H, H^{arom}), 7.89-7.92 (m, 2H, H^{arom}), 8.02-8.06 (m, 2H, H^{arom}), 8.10 (d, *J* = 8.1 Hz, 1H, H^{arom}), 8.18 (s, 1H, H^{arom}), 8.60 (d, *J* = 5.8 Hz, 1H, H^{arom}), 9.12 (d, *J* = 8.4 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.7, 114.9, 118.1, 123.4, 123.8, 124.9, 125.1, 128.3, 127.4, 128.5 (2C), 128.7, 129.7, 129.8 (2C), 130.6, 130.9, 131.4, 132.0, 133.8, 136.0, 138.4, 152.9, 156.5, 195.3; HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{25}H_{14}O_2S$ 379.0787, found .79.0788.

(4-chlorophenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3c)



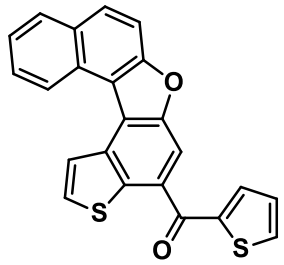
Yellow powder; 84% yield (0.08 g); mp 206-208°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.5 Hz, 2H, H^{arom}), 7.60-7.65 (m, H, H^{arom}), 7.77-7.79 (m, 2H, H^{arom}), 7.84 (d, *J* = 8.5 Hz, 2H, H^{arom}), 7.99-8.08 (m, 4H, H^{arom}), 8.55 (d, *J* = 5.7 Hz, 1H, H^{arom}), 9.06 (d, *J* = 8.4 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.7, 114.6, 118.0, 123.4, 124.0, 124.9, 125.0, 126.9, 127.3, 128.6, 128.8 (2C), 129.8, 130.7, 131.0, 131.2 (2C), 131.3, 133.8, 135.9, 136.6, 138.4, 152.8, 156.5, 193.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{13}ClO_2S$ 413.0398, found 413.0400.

(4-fluorophenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3d)



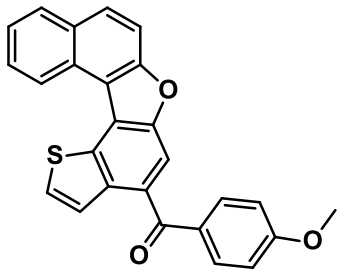
Yellow powder, 70% yield (0.07 g); mp 204-206°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.27-7.30 (m, 2H, H^{arom}), 7.64-7.67 (m, 1H, H^{arom}), 7.83-7.87 (m, 2H, H^{arom}), 7.93-7.96 (m, 2H, H^{arom}), 8.04 (d, *J* = 5.6 Hz, 1H, H^{arom}), 8.06 (d, *J* = 8.9 Hz, 1H, H^{arom}), 8.11 (d, *J* = 8.0 Hz, 1H, H^{arom}), 8.15 (s, 1H, H^{arom}), 8.61 (d, *J* = 5.6 Hz, 1H, H^{arom}), 9.13 (d, *J* = 8.4 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.8, 114.6, 115.6, 115.8, 118.1, 123.5, 123.9, 124.9, 125.1, 127.2, 127.3, 128.7, 129.8, 130.7, 131.0, 131.3, 132.3, 132.4, 133.8, 134.4 and 134.5, 136.1, 152.9, 156.5, 164.1 and 166.1 (CF), 193.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{13}FO_2S$ 397.0693, found 397.0694.

Naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl(thiophen-2-yl)methanone (3e)



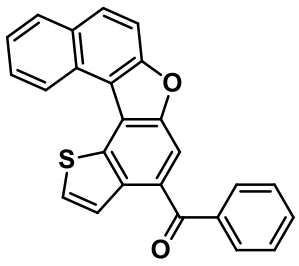
Yellow powder; 43% yield (0.04 g); mp 186-188°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.26-7.28 (m, 1H, H^{arom}), 7.62-7.67 (m, 1H, H^{arom}), 7.81-7.88 (m, 4H, H^{arom}), 7.99 (d, *J* = 5.7 Hz, 1H, $H^{Thiophene}$), 8.04-8.06 (d, 1H, H^{arom}), 8.09-8.11 (d, 1H, H^{arom}), 8.47 (s, 1H, H^{arom}), 8.58 (d, *J* = 5.7 Hz, 1H, $H^{Thiophene}$), 9.11 (d, *J* = 8.4 Hz, 1H, H^{arom}); ;^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.8, 113.1, 118.2, 123.5, 123.6, 124.9, 125.1, 127.3, 127.9, 128.0, 128.7, 128.9, 129.8, 130.5, 131.0, 131.1, 133.9, 134.3, 136.0, 143.2, 153.1, 156.3, 186.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{23}H_{12}O_2S_2$ 385.0351, found 385.0338.

(4-methoxyphenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3f)



Light green powder powder, 45 % yield (0.04 g); mp 198-200°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.98 (s, 3H, CH_3), 7.06 (d, *J*= 8.8 Hz, 2H), 7.67-7.70 (m, 2H, H^{arom}), 7.89-7.92 (m, 2H, H^{arom}), 7.99-8.01 (m, 4H, H^{arom}), 8.08-8.10 (m, 1H, H^{arom}), 8.13-8.15 (m, 1H, H^{arom}), 9.58 (d, *J*= 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.6, 112.5, 112.8, 113.8 (2C), 117.7, 121.9, 124.7, 124.8, 124.9, 125.4, 127.2, 128.5, 129.6, 130.2, 130.8, 131.0, 131.5, 132.9 (2C), 133.8, 135.3, 152.4, 155.6, 163.7, 195.1; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{16}O_3S$ 409.0893, found 409.0897.

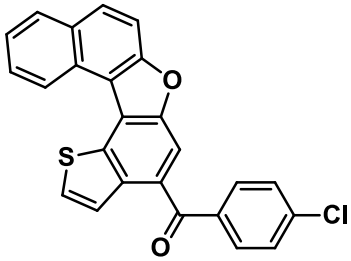
Naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl(phenyl)methanone (3g)



Yellow powder; 55% yield (0.05 g); mp 176-178ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53-7.71 (m, 5H, H^{arom}), 7.79-7.88 (m, 2H, H^{arom}), 7.94-7.97 (m, 2H, H^{arom}), 7.98 (s, 1H, H^{arom}), 8.03 (d, *J*= 8.9 Hz, 1H, H^{arom}), 8.07 (d, *J*= 8.1 Hz, 1H, H^{arom}), 8.11 (d, *J*= 5.6 Hz, 1H, H^{arom}), 9.51 (d, *J*= 8.0 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.7, 113.4, 117.5, 122.4, 124.8, 124.9, 125.0, 125.3, 127.2, 128.4, 128.5(2C), 129.6, 130.4(2C), 130.5, 130.9,

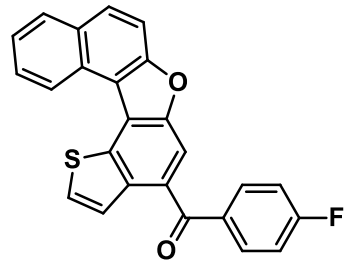
132.9(2C), 133.9, 135.4, 138.4, 152.2, 155.7, 196.4; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{14}O_2S$ 379.0787, found 379.0793.

(4-chlorophenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3h)



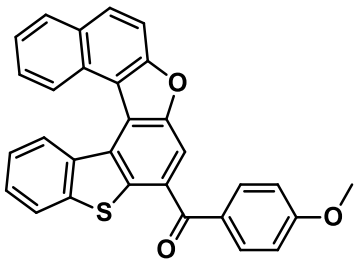
Yellow powder; 62% yield (0.06 g); mp 188-190ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ =7.53 (d, *J*= 8.5 Hz, 2H, H^{arom}), 7.63-7.70 (m, 2H, H^{arom}), 7.82-7.87 (m, 2H, H^{arom}), 7.90 (d, *J*= 8.5 Hz, 2H, H^{arom}), 7.96 (s, 1H, H^{arom}), 8.04-8.11 (m, 3H, H^{arom}), 9.52 (d, *J*= 8.4 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.7, 113.3, 117.5, 122.7, 124.7, 125.0, 125.2, 125.3, 127.3, 128.4, 128.8(2C), 129.6, 130.0, 130.6, 131.0, 131.7(2C), 134.0, 135.4, 136.7, 139.4, 152.1, 155.8, 195.0; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{13}ClO_2S$ 413.0398, found 413.0387.

(4-fluorophenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3i)



Yellow powder; 43% yield (0.04 g); mp 176-179ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19-7.25 (m, 2H, H^{arom}), 7.57-7.65 (m, 1H, H^{arom}), 7.64 (d, *J* = 5.7 Hz, 1H, H^{arom}), 7.75 (d, *J* = 8.9 Hz, 1H, H^{arom}), 7.78-7.83 (m, 1H, H^{arom}), 7.89 (s, 1H, H^{arom}), 7.96-8.04 (m, 5H, H^{arom}), 9.42 (d, *J* = 8.4 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ =112.6, 113.1, 115.5, 115.8, 117.4, 122.4, 124.6, 124.9, 125.1, 125.2, 127.1, 128.3, 129.5, 130.2, 130.4, 130.9, 132.9, 133.0, 133.9, 134.5 and 134.6, 135.3, 152.0, 155.7, 163.9 and 167.3 (CF), 194.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{13}FO_2S$ 397.0693, found 397.0704.

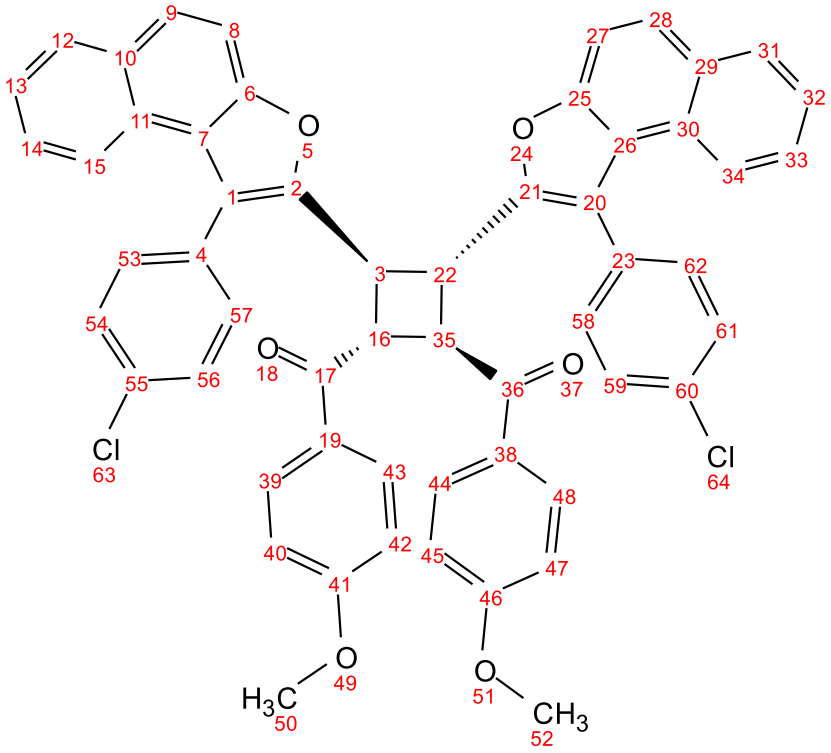
Benzo[4,5]thieno[3,2-*e*]naphtho[2,1-*b*]benzofuran-6-yl(4-methoxyphenyl)methanone (3j)



Yellow powder; 82% yield (0.09 g); mp 186-188ºC. Due to the very poor solubility of **3j** in organic solvents, only the ^{1}H NMR spectrum of this compound could be recorded in benzene-d6; a copy of the spectrum is given in the NMR spectra section. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{30}H_{18}O_3S$ 459.1049, found 459.1047.

II. 2D NMR characterization of compounds

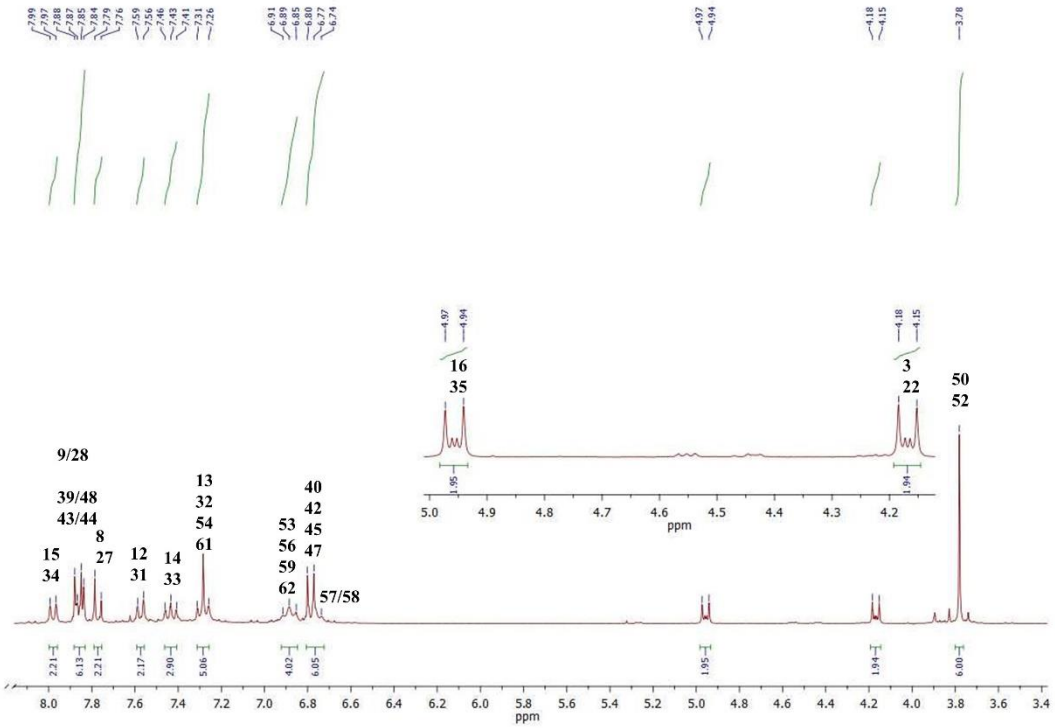
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-chlorophenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2mhh-a)



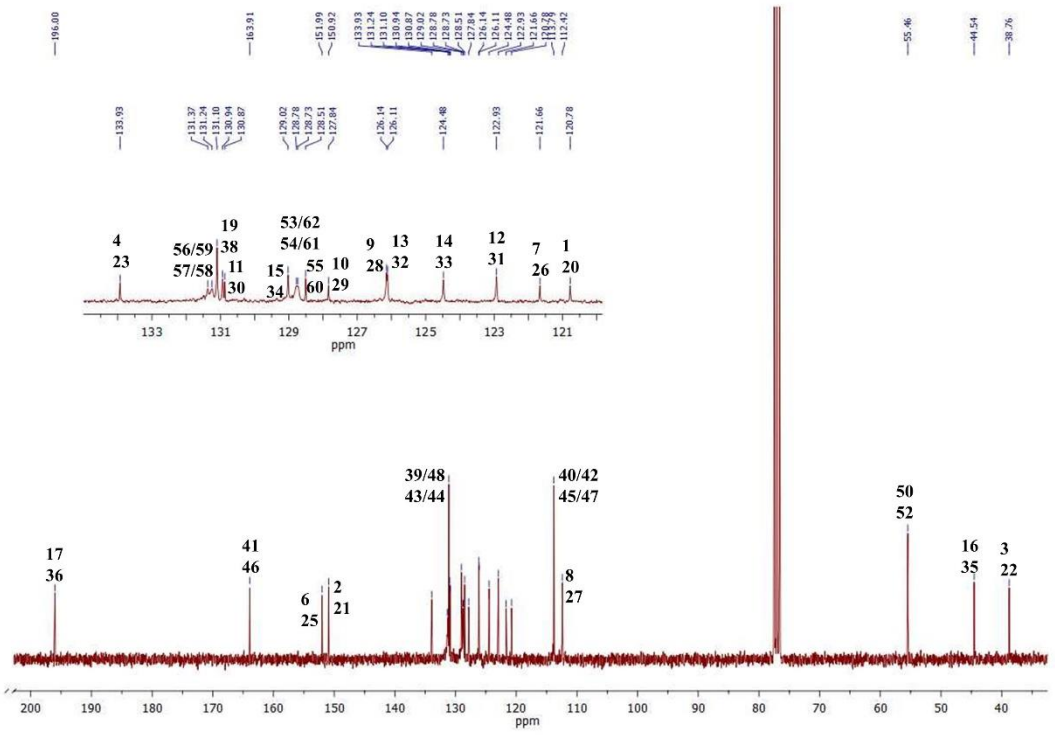
№/№	^{1}H	^{13}C	COSY	NOESY	HMBC
1	-	120.8	-	-	8
2	-	150.9	-	-	16
3	4.17 (m)	38.8	16	16, 35, 53, 57,	16, 17, 35, 36
4	-	133.9	-	-	-
5					
6	-	151.9	-	-	8, 9
7	-	121.7	-	-	12
8	7.77 (d, *J* = 9.0 Hz)	112.4	9	-	1, 6, 11
9	7.85 (d, *J* = 9.0 Hz)	126.2	8	40, 42	6
10	-	127.8	-	-	-
11	-	130.8	-	-	8, 14
12	7.57 (d, *J* = 8.2 Hz)	122.9	13	13	7, 11, 14
13	7.26-7.32 (m)	126.1	12 14	12	15
14	7.41-7.46 (m)	124.5	13 15	15	11, 12
15	7.98 (d, *J* = 8.1 Hz)	129.0	14	14	13
16	4.96 (m)	44.5	3	3, 22, 39, 43	2, 3, 17, 21, 22, 36
17	-	196.0	-	-	3, 16, 39, 43, 22, 35
18					
19	-	130.9	-	-	-
20	-	120.8	-	-	27
21	-	150.9	-	-	35

22	4.17 (m)	38.8	35	16, 35, 58, 62	16, 17, 35, 36
23	-	133.9	-	-	-
24					
25	-	151.9	-	-	27, 28
26	-	120.8	-	-	31
27	7.77 (d, *J* = 9.0 Hz)	112.4	28	-	20, 25, 30
28	7.85 (d, *J* = 9.0 Hz)	126.2	27	45, 47	25
29	-	127.8	-	-	-
30	-	130.8	-	-	27, 33
31	7.57 (d, *J* = 8.2 Hz)	122.9	61	61	26, 30, 33
32	7.26-7.32 (m)	126.1	31 33	31	34
33	7.41-7.46 (m)	124.5	32 34	34	30, 31
34	7.98 (d, *J* = 8.1 Hz)	129.0	33	33	61
35	4.96 (m)	44.5	22	3, 22, 48, 44	2, 3, 17, 21, 22, 36
36	-	196.0	-	-	3, 16, 22, 35, 48, 44
37					
38	-	130.9	-	-	-
39	7.86 (d, *J* = 9.0 Hz)	131.1	40	16, 40	17, 41
40	6.79 (d, *J* = 9.0 Hz)	113.8	39	50, 39	41
41	-	163.9	-	-	39, 40, 42, 43, 50
42	6.79 (d, *J* = 9.0 Hz)	113.8	43	50, 43	41
43	7.86 (d, *J* = 9.0 Hz)	131.1	42	16, 42	17, 41
44	7.86 (d, *J* = 9.0 Hz)	131.1	45	35, 47	36, 46
45	6.79 (d, *J* = 9.0 Hz)	113.8	48	52, 48	46
46	-	163.9	-	-	48, 45, 47, 44, 52
47	6.79 (d, *J* = 9.0 Hz)	113.8	44	52, 44	46
48	7.86 (d, *J* = 9.0 Hz)	131.1	47	35, 45	36, 46
49					
50	3.78 (s)	55.5		40, 42	41
51					
52	3.78 (s)	55.5	-	45, 47	46
53	6.85-6.91 (m)	128.7	54	3, 54	-
54	7.26-7.31 (m)	128.8	53	53	-
55	-	128.5	-	-	57
56	6.85-6.91 (m)	131.2	57	-	-
57	6.74-6.80 (m)	131.4	56	3	55
58	6.74-6.80 (m)	131.4	59	-	60
59	6.85-6.91 (m)	131.2	58	-	-
60	-	128.5	-	-	58
61	7.26-7.31 (m)	128.8	62	62	-
62	6.85-6.91 (m)	128.7	61	61	-
63					
64					

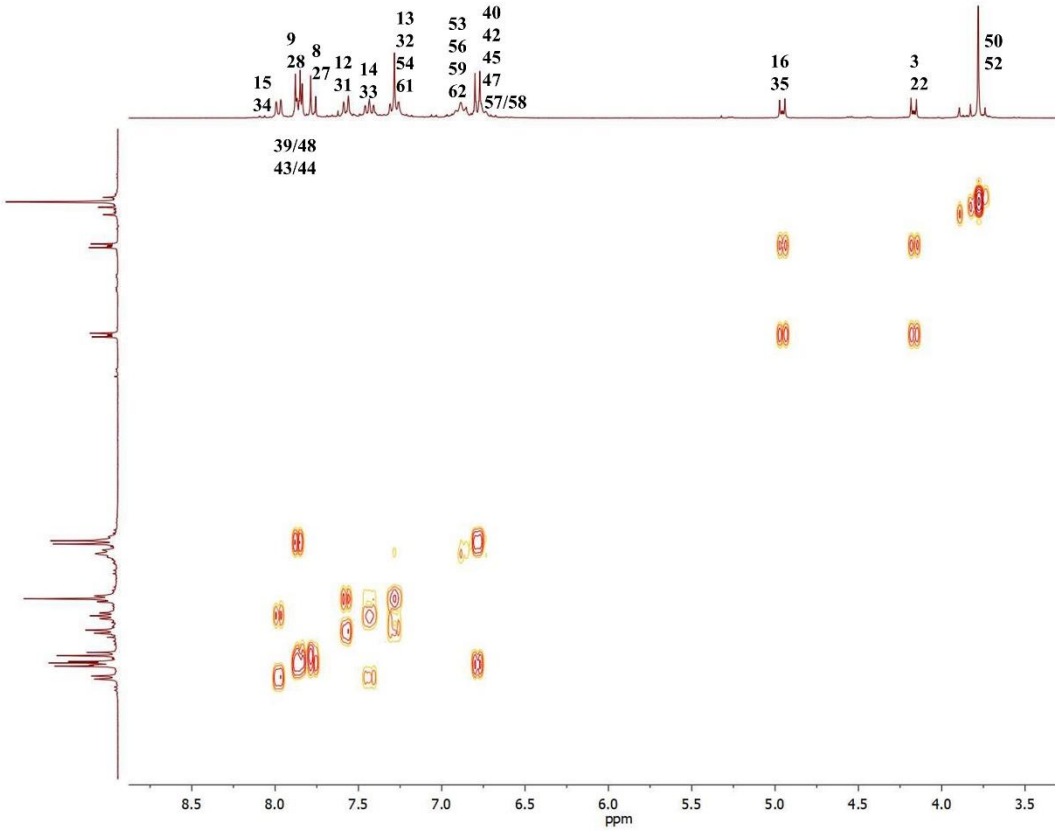
^{1}H NMR (300 MHz, $CDCl_3$)

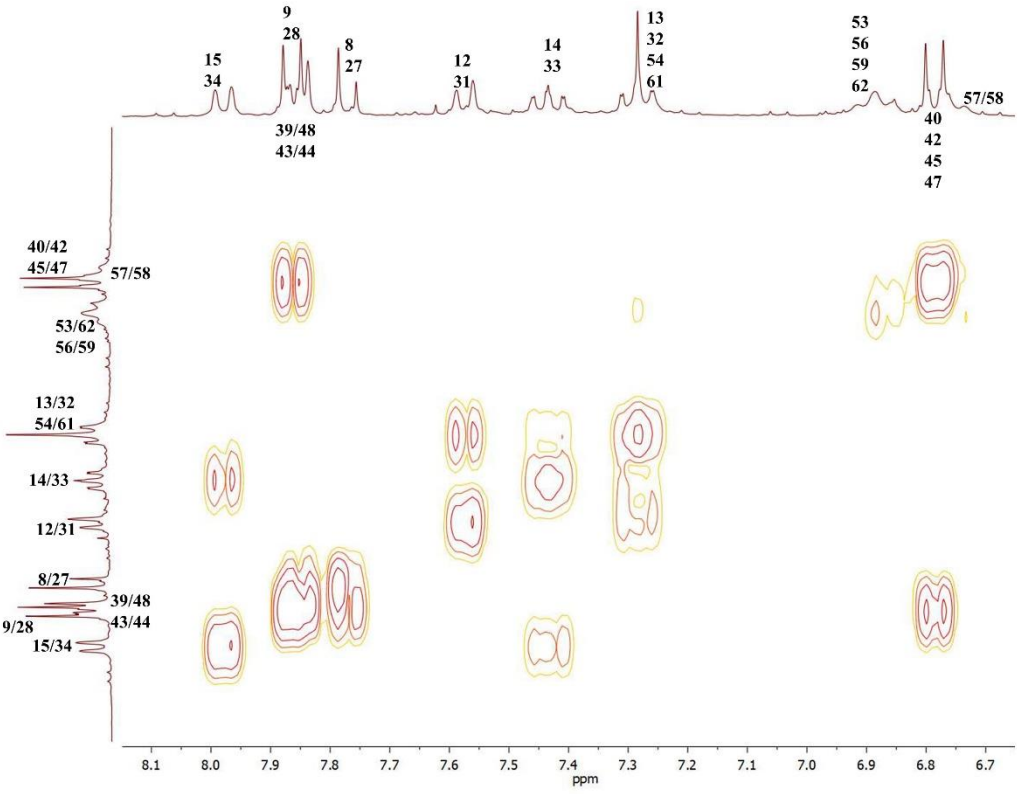


^{13}C NMR (75 MHz, $CDCl_3$)

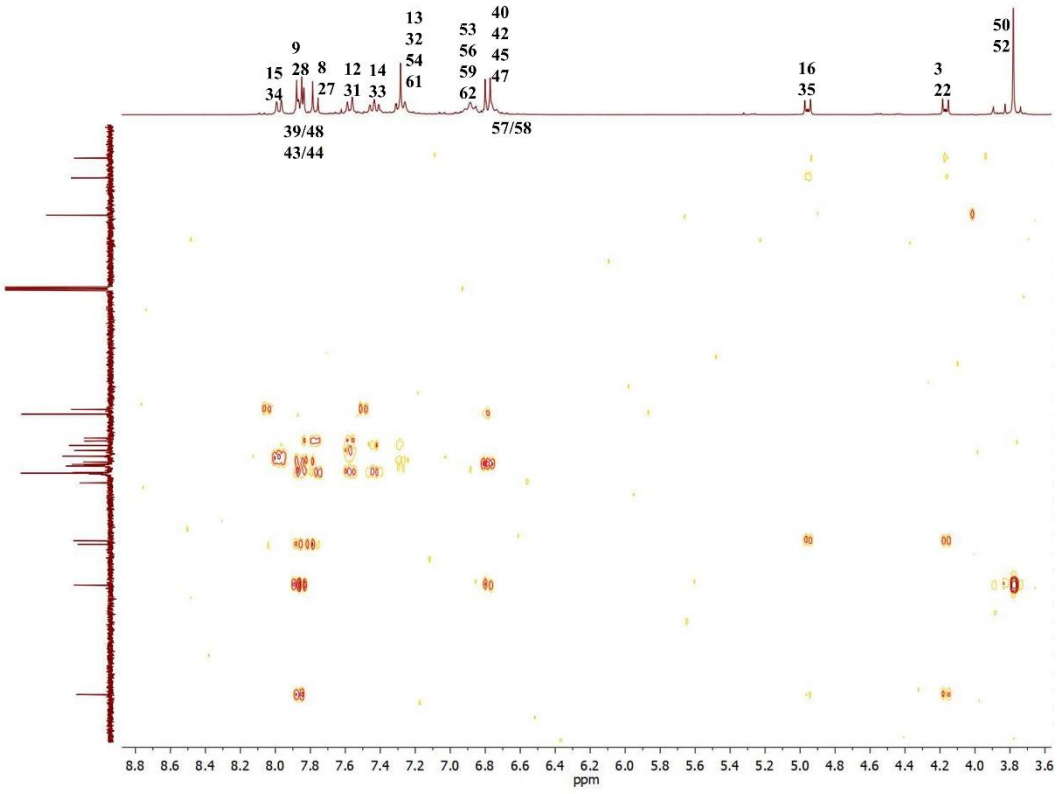


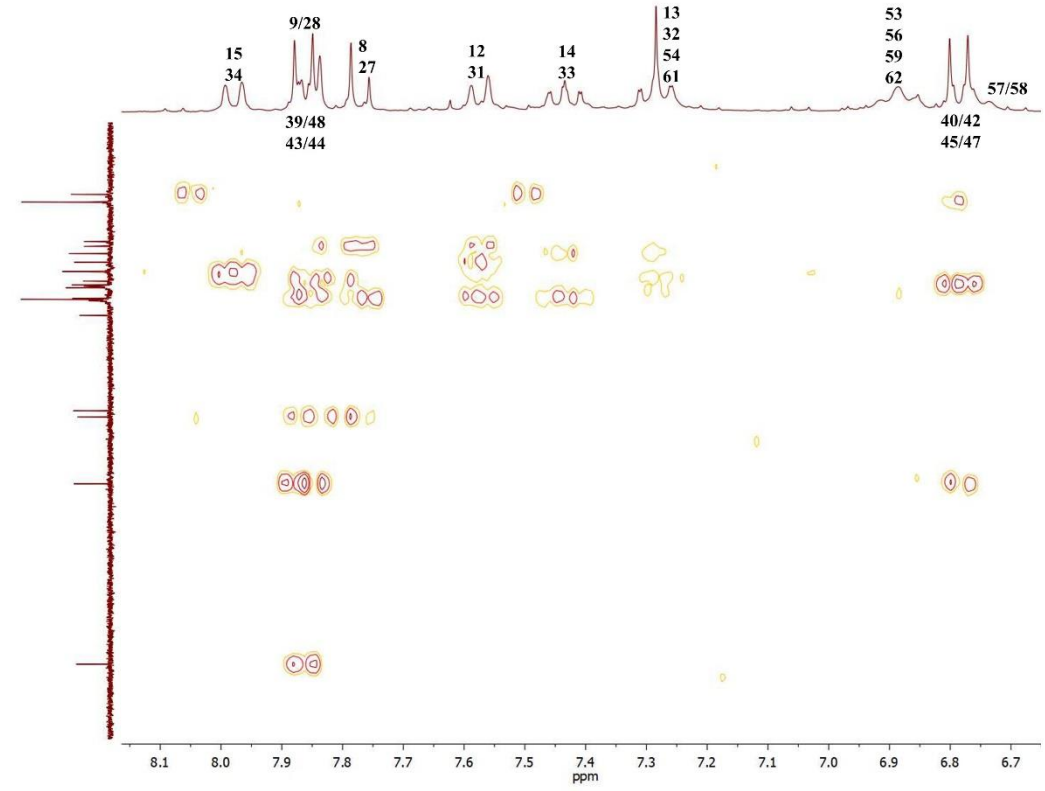
{^{1}H-^{1}H}COSY spectra



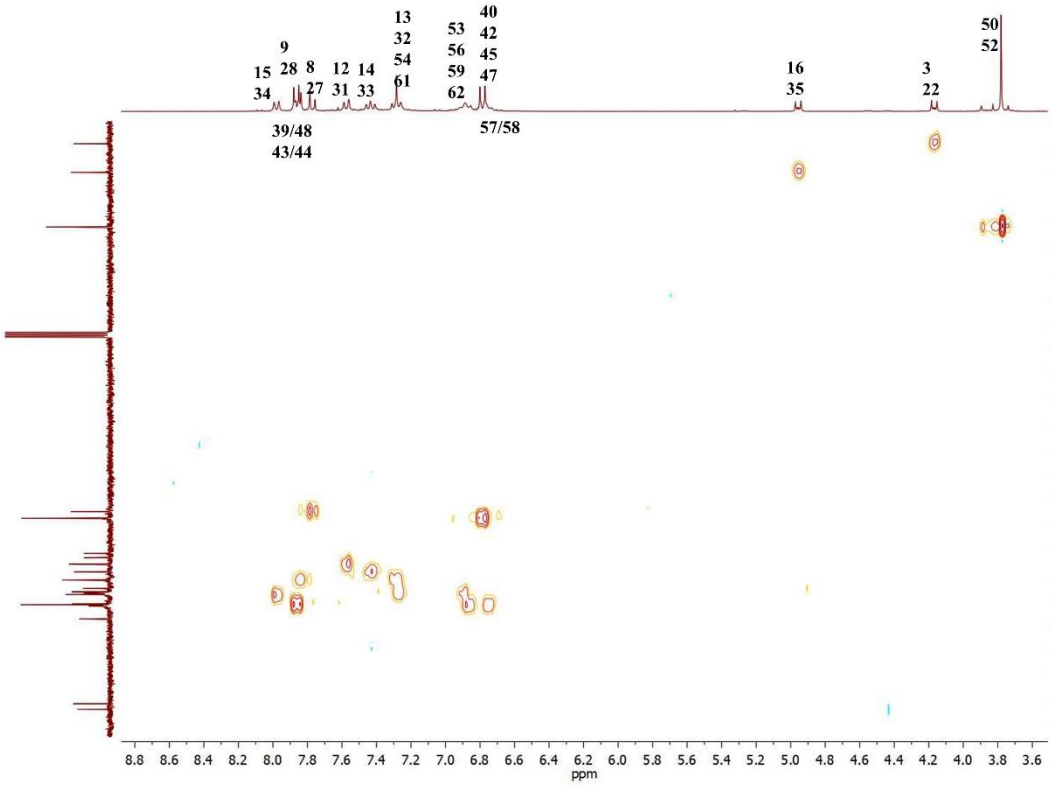


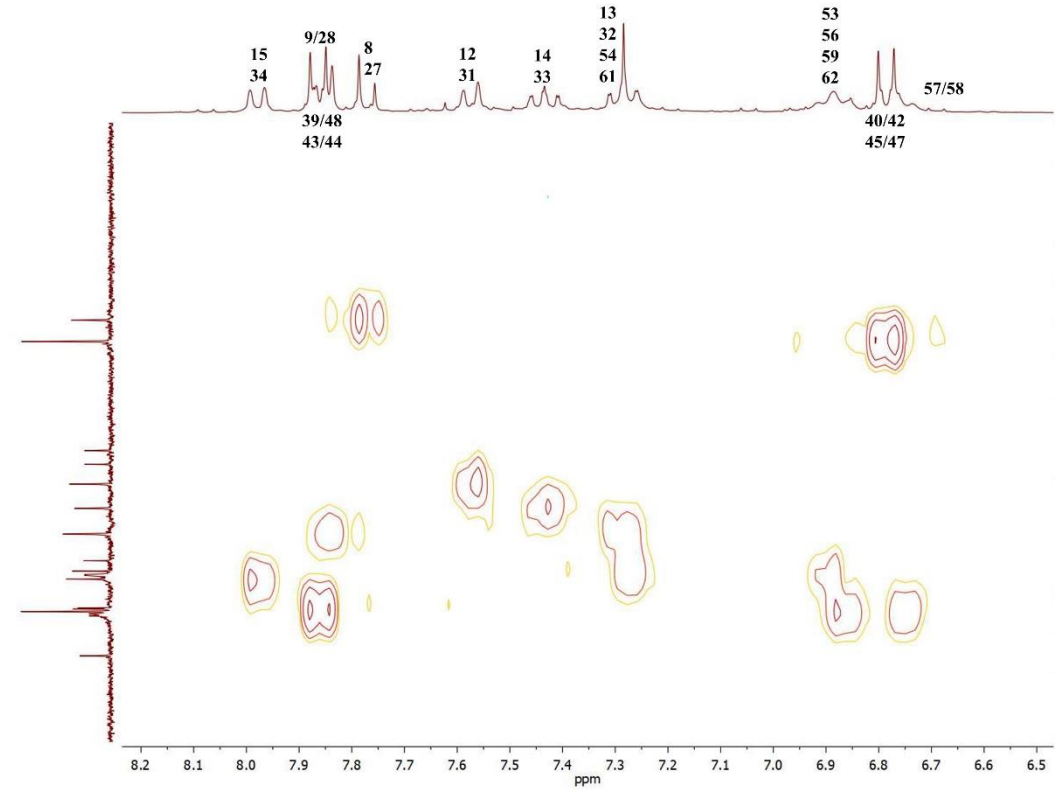
{^{1}H-^{13}C} HMBC spectra



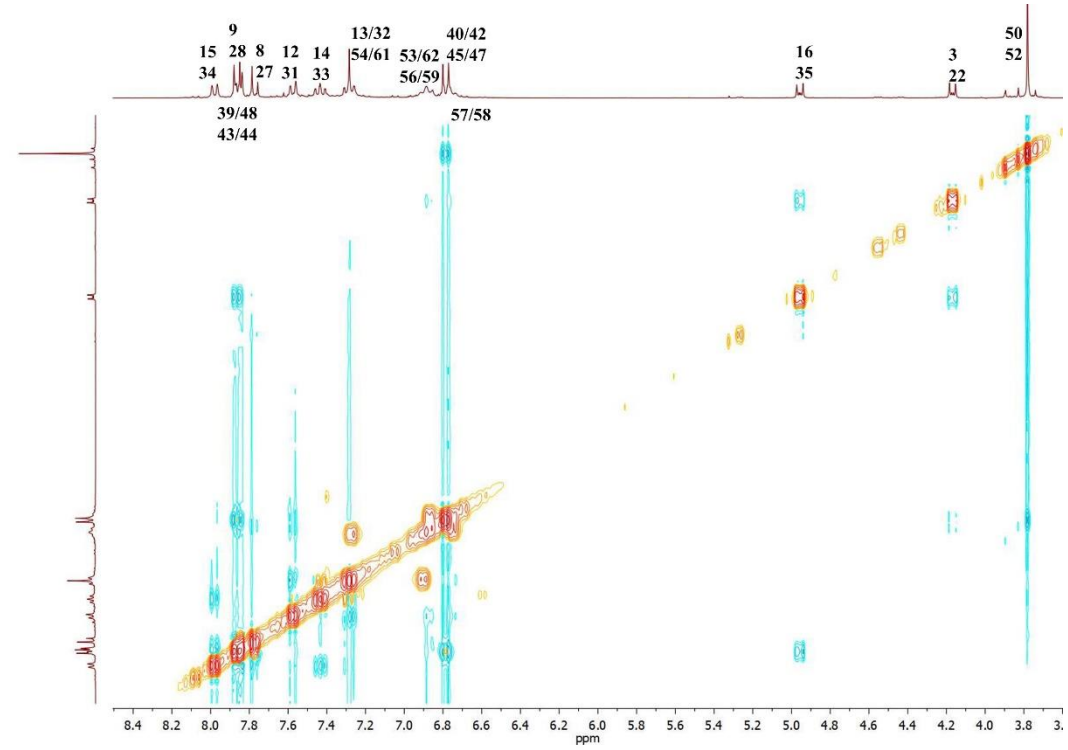


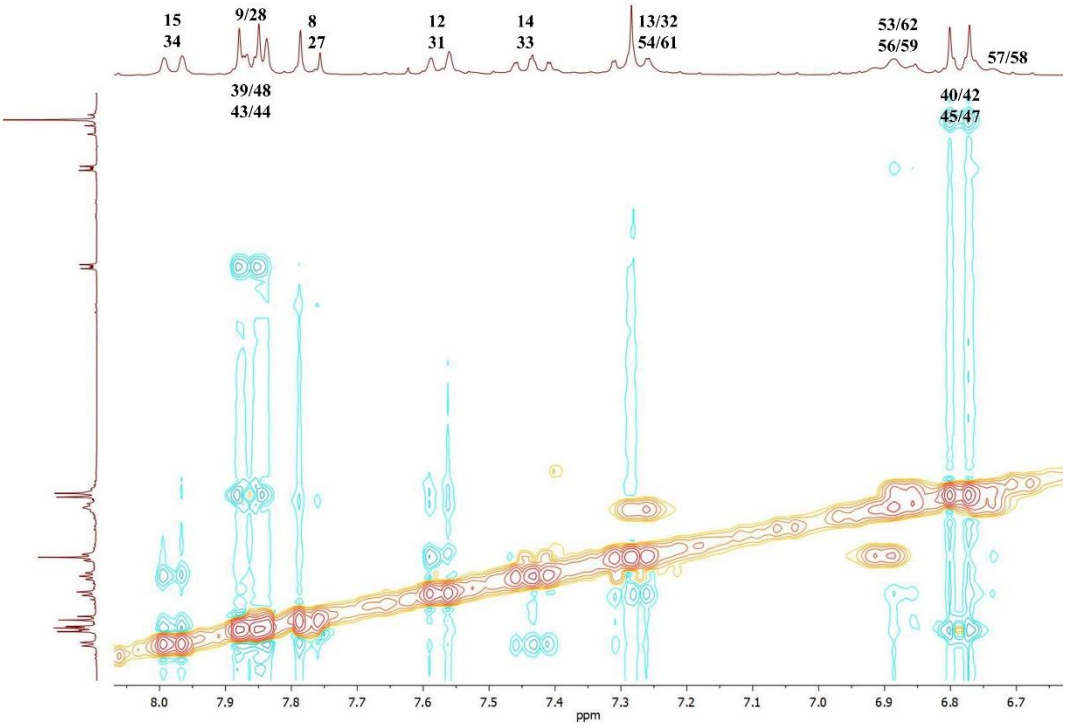
{^{1}H-^{13}C} HSQC spectra





{^{1}H-^{1}H} NOESY spectra





III. NMR monitoring

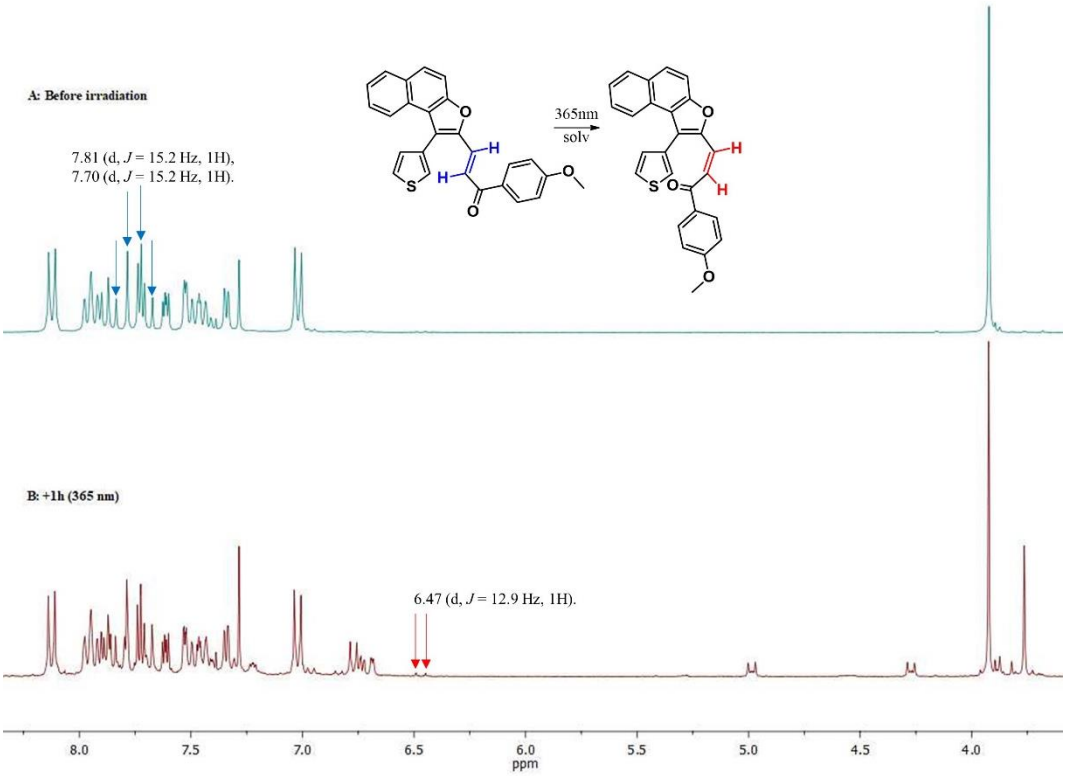


Figure S1. ^{1}H NMR monitoring of the photoreaction of **1a** in $CDCl_3$ induced by UV light (365 nm, C = 10^{-2} M).

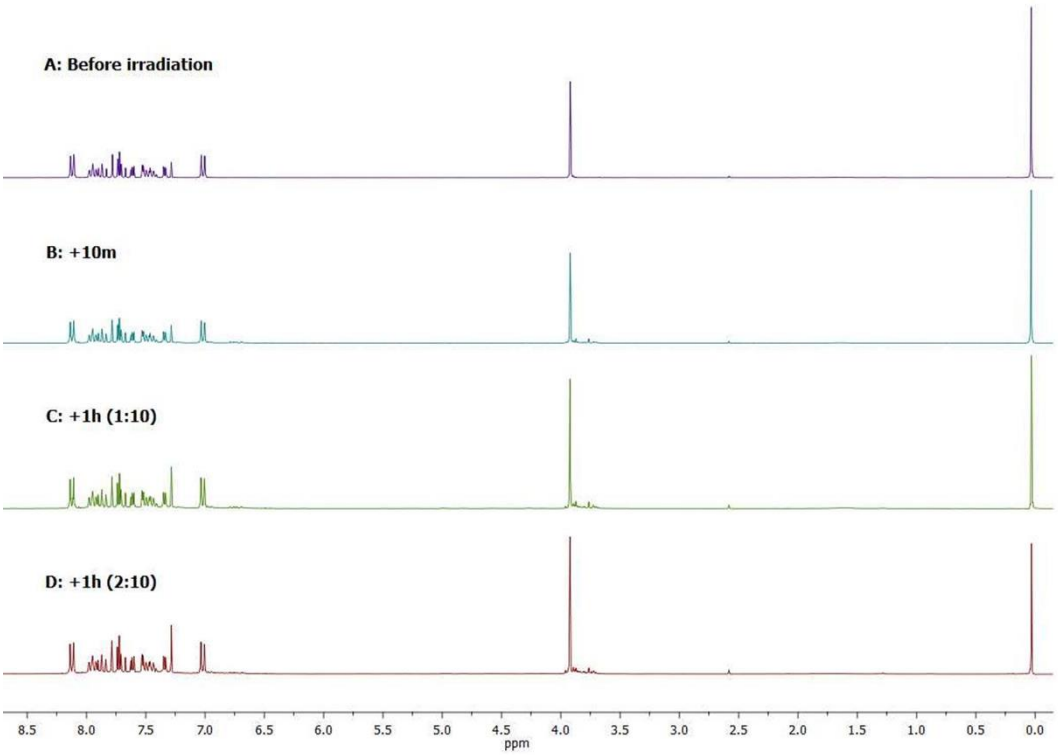


Figure S2. ^{1}H-NMR monitoring of photolysis of **1a** in $CDCl_3$ under UV light (λ = 254 nm, C = 10^{-2} M) in a quartz cuvette.

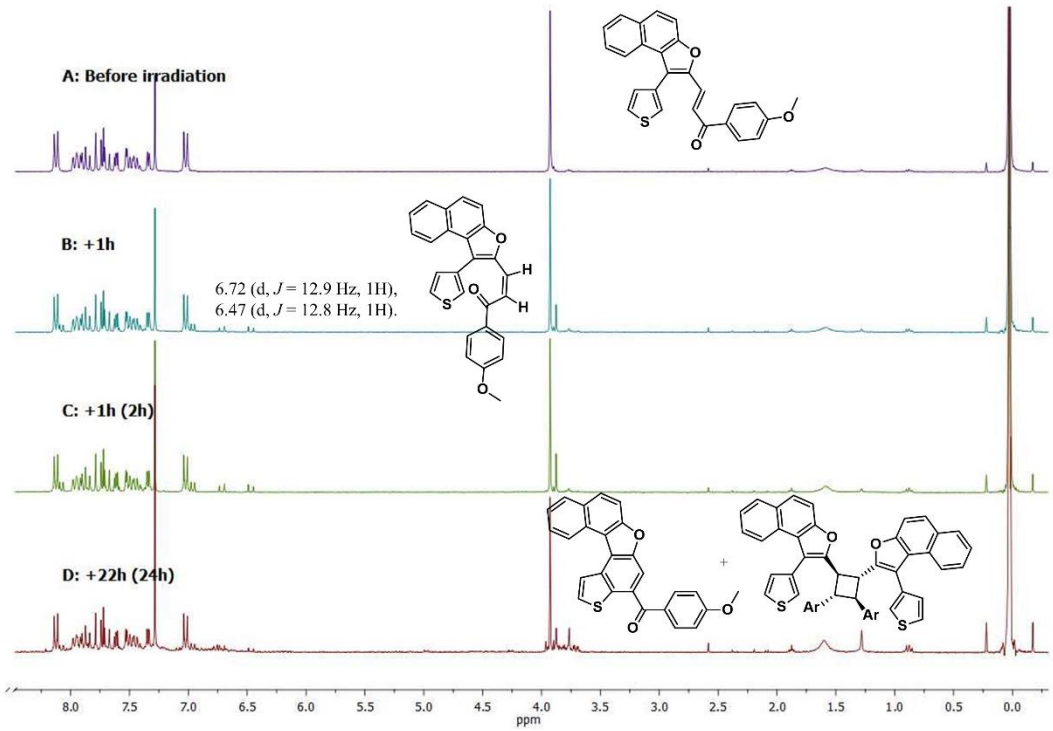


Figure S3. ^{1}H-NMR monitoring of photolysis of **1a** in $CDCl_3$ under sunlight irradiation (C = 10^{-2} M).

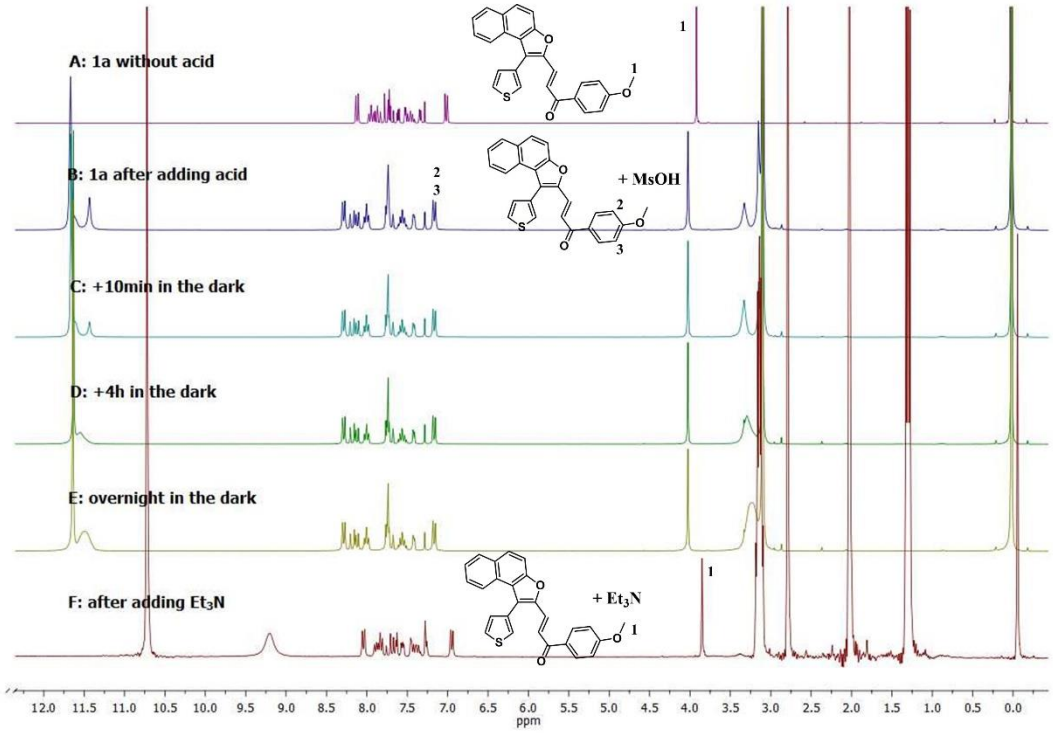


Figure S4. ^{1}H-NMR monitoring of photolysis of **1a** (C = 10^{-2} M) in $CDCl_3$ in the presence of MsOH (10 equiv) without irradiation (in the dark).

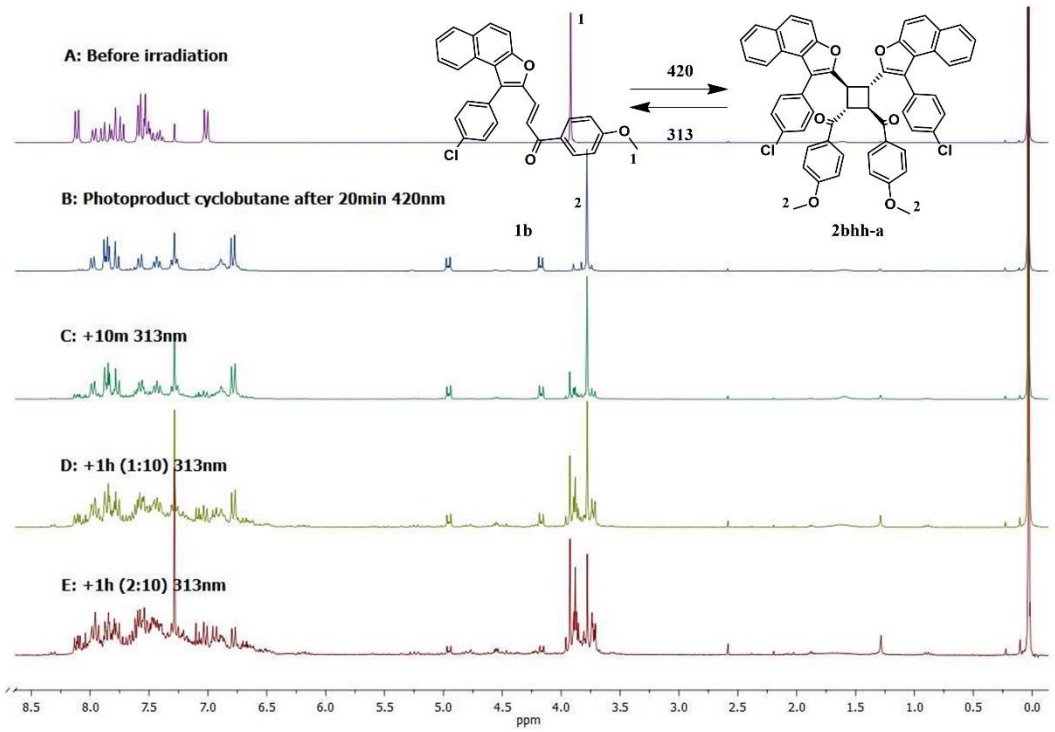


Figure S5. ^{1}H NMR-monitoring of the reversible reaction of **2bhh-a** under UV-irradiation (313 nm, C = 10^{-2} M).

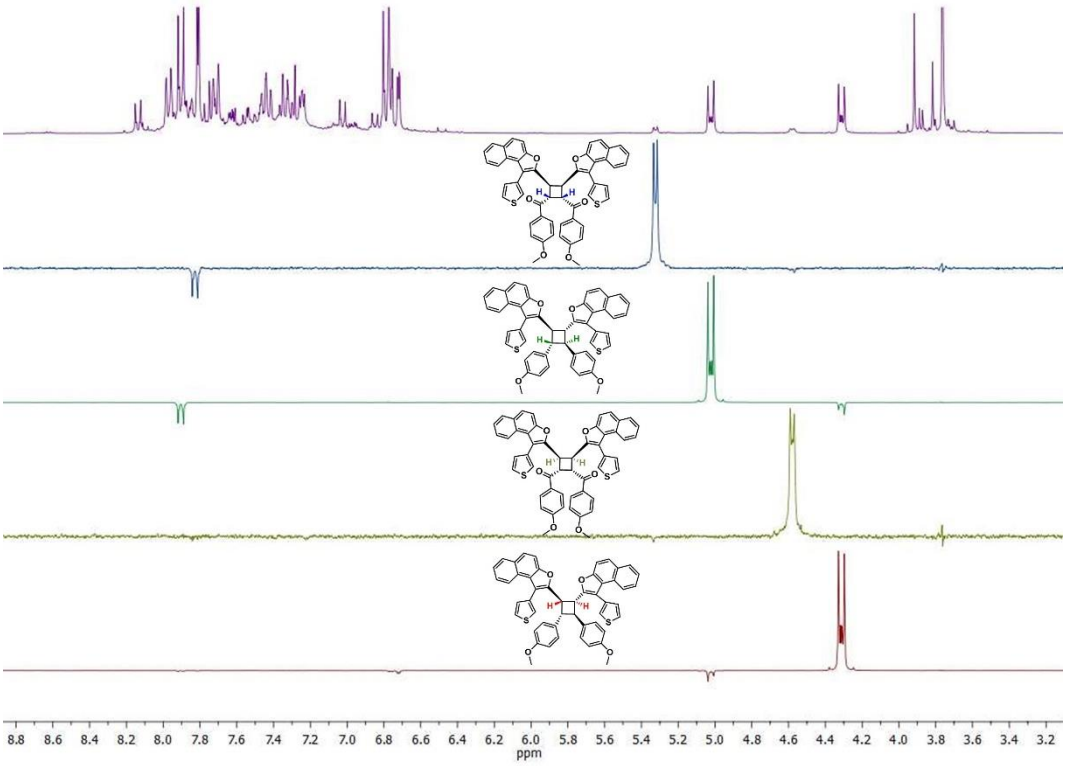


Figure S6. 1D NOE spectra of **2ahh-a** and **2ahh-s** photoproducts.

IV. Photochemical studies

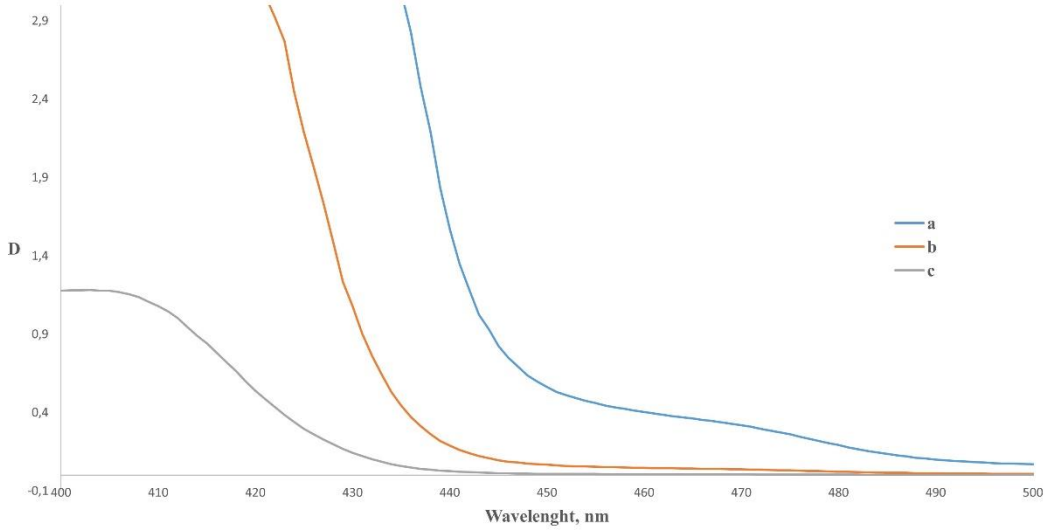


Figure S7. UV-vis spectra of **1a** at different concentrations (a = 2.5 × 10^{-4} M; b = 2.5 × 10^{-5} M; c = 2.5 × 10^{-6} M).

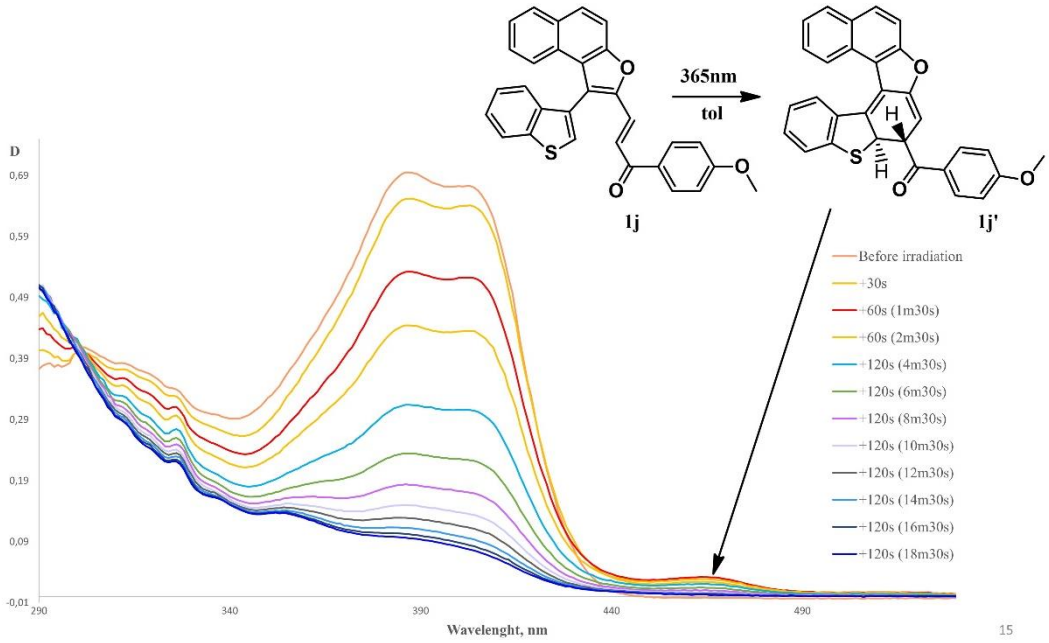
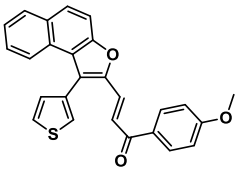
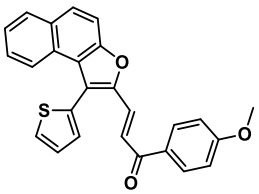
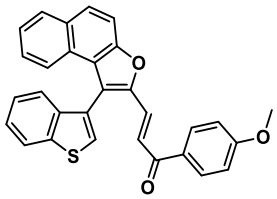
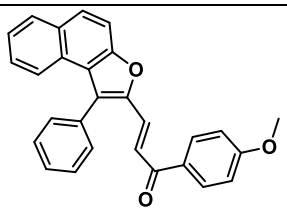
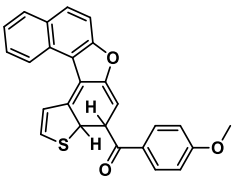
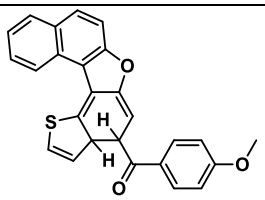
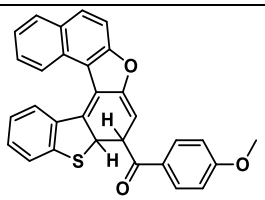
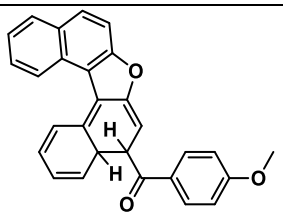


Figure S8. UV-vis spectra of **1j** with UV light (λ = 365 nm) in toluene (C = 2.5 × 10^{-5} M) and intermediate **1j'** observed at 465 nm.

V. DFT calculations

Table S1. Calculated Values of Ground State's Energy Differences of Model Structures*

№/№	**1**	**2**	**3**	**4**
Structure I				
Structure II				
ΔE_{II-I}, kJ/mol	38.54	54.57	42.77	112.01

*Calculated at the PBE1PBE/6-31G (d,p) level of theory.

VI. Structures of possible photoproducts

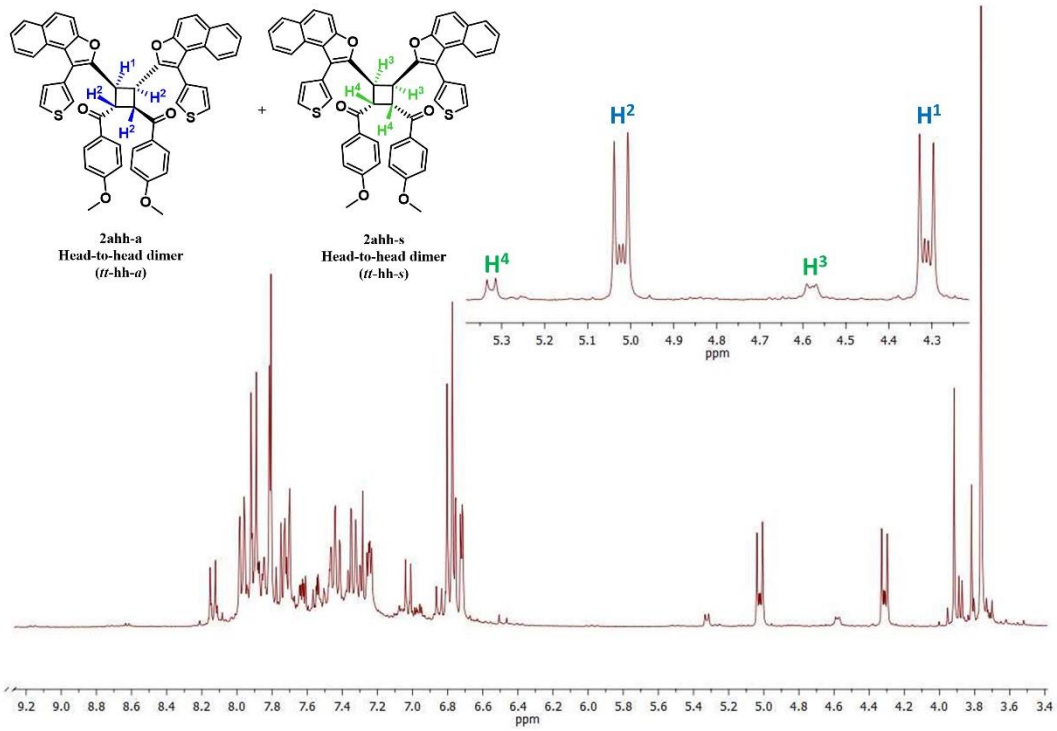
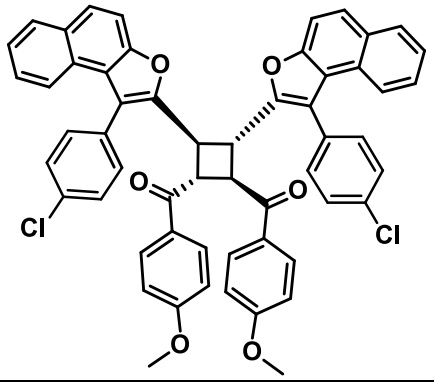
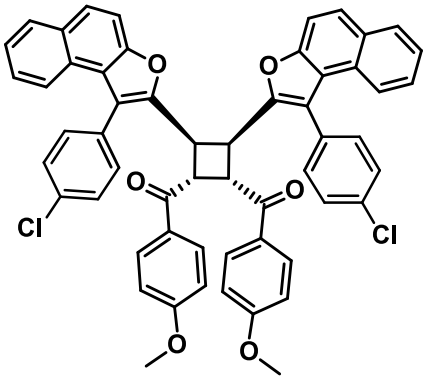
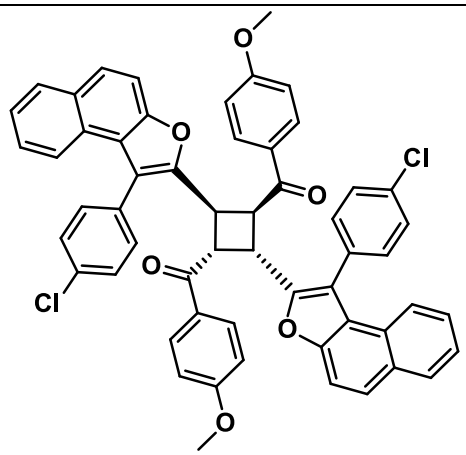
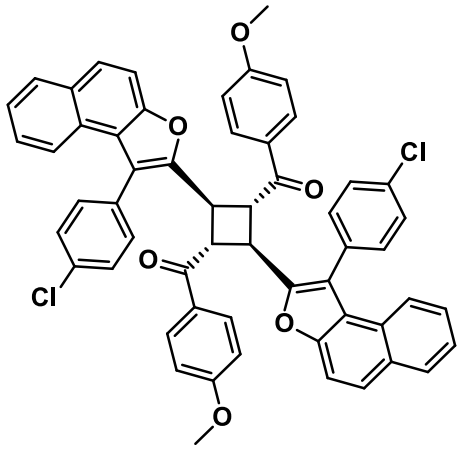


Figure S9. ^{1}H NMR of photoproducts **2ahh-a** and **2ahh-s**.

Table S2. Structures of possible photoproducts including the characteristics determining their nomenclature and abbreviations.

	Molecules	Characteristics	Abbreviation
1		trans + trans head-to-head anti	*tt*-hh-a
2		trans + trans head-to-head syn	*tt*-hh-s

3		trans + trans head-to-tail syn	*tt*-ht-s
4		trans + trans head-to-tail anti	*tt*-ht-a

VII. X-ray crystallography

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K□-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[S2] The structure was solved by direct methods using SHELXT[S3] and refined on F^2 using SHELXL-2018[S4] in the OLEX2 program.[S5] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups.

Acknowledgment

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

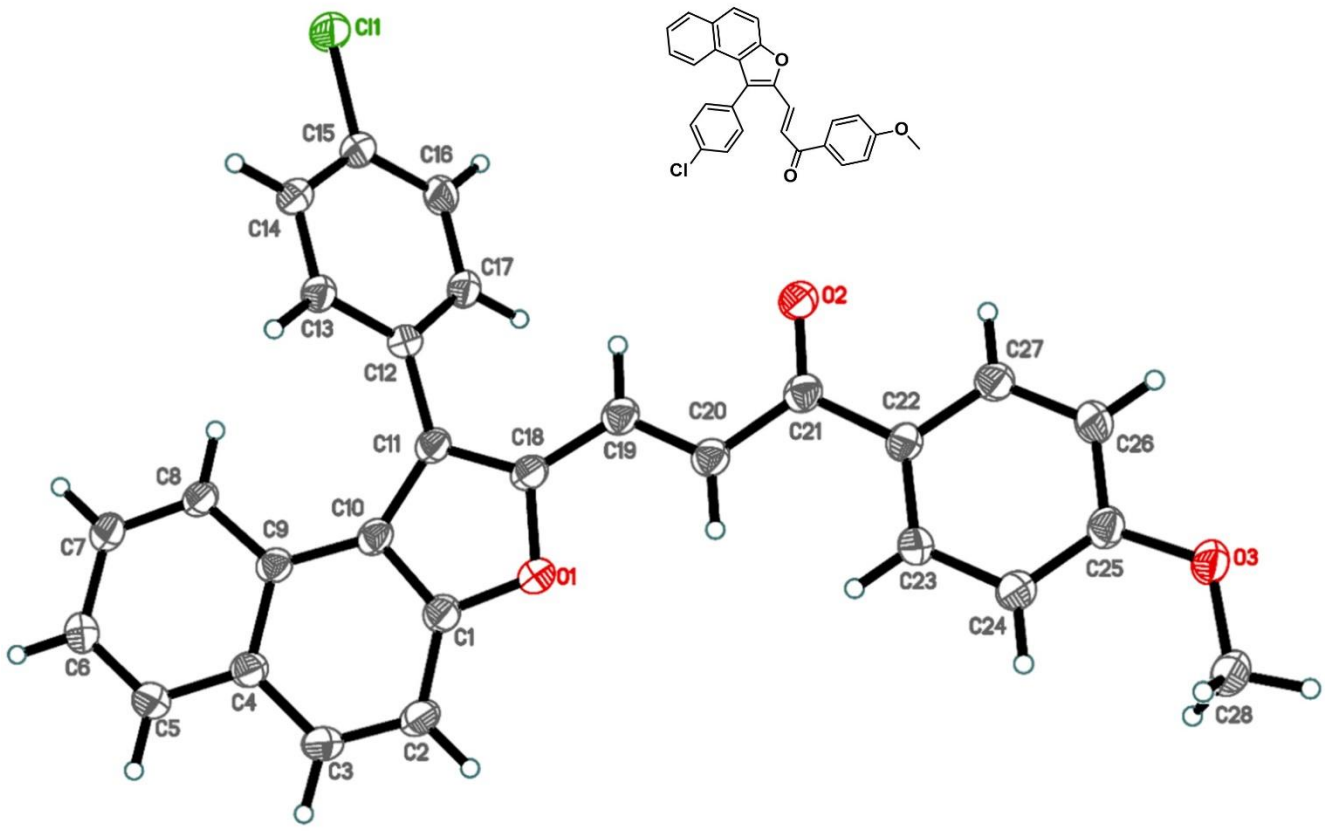


Figure S10. Molecular structure of photoproduct **1m** determined by X-ray analysis.

Table S3. Crystal data and structure refinement for **1m**.

Identification code	**1m**	
Empirical formula	C28 H19 Cl O3	
Formula weight	438.88	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 4.43650(10) Å	a= 90°.
	b = 11.7816(2) Å	b= 90°.
	c = 40.0556(6) Å	g = 90°.
Volume	2093.67(7) $Å^3$	
Z	4	
Density (calculated)	1.392 g/cm^3	
Absorption coefficient	1.850 mm^{-1}	
F(000)	912	
Crystal size	0.042 x 0.033 x 0.031 mm^3	
Theta range for data collection	2.206 to 80.761°.	
Index ranges	-5<=h<=5, -14<=k<=15, -51<=l<=50	
Reflections collected	8900	
Independent reflections	8900 [R(int) = 0.0317]	
Observed reflections	8349	
Completeness to theta = 67.684°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63770	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8900 / 0 / 291	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1384	
R indices (all data)	R1 = 0.0540, wR2 = 0.1450	
Absolute structure parameter	0.005(11)	
Largest diff. peak and hole	0.257 and -0.227 $e.Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1m**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	9336(3)	9400(1)	5297(1)	44(1)
O(1)	7070(6)	4000(2)	6544(1)	27(1)
O(2)	987(6)	7396(2)	6869(1)	30(1)
O(3)	-5524(7)	5554(2)	8153(1)	32(1)
C(1)	8952(8)	3385(3)	6346(1)	26(1)
C(2)	9769(9)	2263(3)	6419(1)	29(1)
C(3)	11637(9)	1749(3)	6197(1)	29(1)
C(4)	12746(8)	2322(3)	5907(1)	26(1)
C(5)	14673(9)	1742(3)	5684(1)	30(1)
C(6)	15827(9)	2272(3)	5407(1)	30(1)
C(7)	15101(8)	3413(3)	5346(1)	27(1)
C(8)	13215(8)	4001(3)	5556(1)	25(1)
C(9)	11944(8)	3473(3)	5842(1)	24(1)
C(10)	9922(8)	4017(3)	6073(1)	24(1)
C(11)	8550(8)	5118(3)	6112(1)	23(1)
C(12)	8797(8)	6166(3)	5907(1)	23(1)
C(13)	8375(8)	6152(3)	5560(1)	25(1)
C(14)	8551(9)	7137(3)	5372(1)	28(1)
C(15)	9155(10)	8154(3)	5532(1)	31(1)
C(16)	9581(10)	8204(3)	5874(1)	32(1)
C(17)	9398(9)	7209(3)	6060(1)	28(1)
C(18)	6826(8)	5053(3)	6398(1)	25(1)
C(19)	4837(8)	5835(3)	6560(1)	26(1)
C(20)	3244(8)	5593(3)	6838(1)	26(1)
C(21)	1234(8)	6441(3)	6990(1)	26(1)
C(22)	-496(8)	6139(3)	7295(1)	25(1)
C(23)	-717(9)	5039(3)	7419(1)	28(1)
C(24)	-2401(9)	4796(3)	7705(1)	29(1)
C(25)	-3859(8)	5681(3)	7870(1)	27(1)
C(26)	-3689(9)	6787(3)	7748(1)	30(1)
C(27)	-2042(9)	7008(3)	7463(1)	28(1)
C(28)	-5735(10)	4452(3)	8297(1)	36(1)

Table S5. Bond lengths [Å] and angles [°] for **1m**.

Cl(1)-C(15)	1.746(4)
O(1)-C(1)	1.363(4)
O(1)-C(18)	1.377(4)
O(2)-C(21)	1.231(4)
O(3)-C(25)	1.359(4)
O(3)-C(28)	1.425(4)
C(1)-C(2)	1.403(5)
C(1)-C(10)	1.391(5)
C(2)-H(2)	0.9500
C(2)-C(3)	1.358(5)
C(3)-H(3)	0.9500
C(3)-C(4)	1.430(5)
C(4)-C(5)	1.413(5)
C(4)-C(9)	1.427(5)
C(5)-H(5)	0.9500
C(5)-C(6)	1.373(5)
C(6)-H(6)	0.9500
C(6)-C(7)	1.404(5)
C(7)-H(7)	0.9500
C(7)-C(8)	1.373(5)
C(8)-H(8)	0.9500
C(8)-C(9)	1.419(5)
C(9)-C(10)	1.439(5)
C(10)-C(11)	1.442(5)
C(11)-C(12)	1.487(4)
C(11)-C(18)	1.380(5)
C(12)-C(13)	1.402(4)
C(12)-C(17)	1.399(5)
C(13)-H(13)	0.9500
C(13)-C(14)	1.385(5)
C(14)-H(14)	0.9500
C(14)-C(15)	1.385(5)
C(15)-C(16)	1.385(5)
C(16)-H(16)	0.9500
C(16)-C(17)	1.390(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.431(5)
C(19)-H(19)	0.9500

C(19)-C(20)	1.347(5)
C(20)-H(20)	0.9500
C(20)-C(21)	1.472(5)
C(21)-C(22)	1.486(5)
C(22)-C(23)	1.392(5)
C(22)-C(27)	1.404(5)
C(23)-H(23)	0.9500
C(23)-C(24)	1.397(5)
C(24)-H(24)	0.9500
C(24)-C(25)	1.395(5)
C(25)-C(26)	1.395(5)
C(26)-H(26)	0.9500
C(26)-C(27)	1.379(5)
C(27)-H(27)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800

C(1)-O(1)-C(18)	106.1(3)
C(25)-O(3)-C(28)	118.3(3)
O(1)-C(1)-C(2)	122.5(3)
O(1)-C(1)-C(10)	111.4(3)
C(10)-C(1)-C(2)	126.1(3)
C(1)-C(2)-H(2)	121.9
C(3)-C(2)-C(1)	116.1(3)
C(3)-C(2)-H(2)	121.9
C(2)-C(3)-H(3)	119.0
C(2)-C(3)-C(4)	122.1(3)
C(4)-C(3)-H(3)	119.0
C(5)-C(4)-C(3)	119.5(3)
C(5)-C(4)-C(9)	119.6(3)
C(9)-C(4)-C(3)	120.8(3)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-C(4)	121.1(3)
C(6)-C(5)-H(5)	119.4
C(5)-C(6)-H(6)	120.3
C(5)-C(6)-C(7)	119.4(3)
C(7)-C(6)-H(6)	120.3
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-C(6)	121.1(3)

C(8)-C(7)-H(7)	119.5
C(7)-C(8)-H(8)	119.5
C(7)-C(8)-C(9)	120.9(3)
C(9)-C(8)-H(8)	119.5
C(4)-C(9)-C(10)	117.4(3)
C(8)-C(9)-C(4)	117.8(3)
C(8)-C(9)-C(10)	124.8(3)
C(1)-C(10)-C(9)	117.4(3)
C(1)-C(10)-C(11)	105.3(3)
C(9)-C(10)-C(11)	137.2(3)
C(10)-C(11)-C(12)	131.0(3)
C(18)-C(11)-C(10)	106.0(3)
C(18)-C(11)-C(12)	123.1(3)
C(13)-C(12)-C(11)	121.9(3)
C(17)-C(12)-C(11)	120.1(3)
C(17)-C(12)-C(13)	118.0(3)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-C(12)	121.4(3)
C(14)-C(13)-H(13)	119.3
C(13)-C(14)-H(14)	120.5
C(15)-C(14)-C(13)	119.0(3)
C(15)-C(14)-H(14)	120.5
C(14)-C(15)-Cl(1)	119.2(3)
C(14)-C(15)-C(16)	121.4(3)
C(16)-C(15)-Cl(1)	119.5(3)
C(15)-C(16)-H(16)	120.5
C(15)-C(16)-C(17)	119.1(3)
C(17)-C(16)-H(16)	120.5
C(12)-C(17)-H(17)	119.4
C(16)-C(17)-C(12)	121.2(3)
C(16)-C(17)-H(17)	119.4
O(1)-C(18)-C(11)	111.1(3)
O(1)-C(18)-C(19)	115.8(3)
C(11)-C(18)-C(19)	133.1(3)
C(18)-C(19)-H(19)	117.9
C(20)-C(19)-C(18)	124.2(3)
C(20)-C(19)-H(19)	117.9
C(19)-C(20)-H(20)	119.5
C(19)-C(20)-C(21)	121.1(3)
C(21)-C(20)-H(20)	119.5

O(2)-C(21)-C(20)	120.7(3)
O(2)-C(21)-C(22)	119.9(3)
C(20)-C(21)-C(22)	119.4(3)
C(23)-C(22)-C(21)	123.6(3)
C(23)-C(22)-C(27)	118.2(3)
C(27)-C(22)-C(21)	118.2(3)
C(22)-C(23)-H(23)	119.3
C(22)-C(23)-C(24)	121.5(3)
C(24)-C(23)-H(23)	119.3
C(23)-C(24)-H(24)	120.5
C(25)-C(24)-C(23)	118.9(3)
C(25)-C(24)-H(24)	120.5
O(3)-C(25)-C(24)	124.5(3)
O(3)-C(25)-C(26)	115.1(3)
C(24)-C(25)-C(26)	120.4(3)
C(25)-C(26)-H(26)	120.1
C(27)-C(26)-C(25)	119.7(3)
C(27)-C(26)-H(26)	120.1
C(22)-C(27)-H(27)	119.4
C(26)-C(27)-C(22)	121.2(3)
C(26)-C(27)-H(27)	119.4
O(3)-C(28)-H(28A)	109.5
O(3)-C(28)-H(28B)	109.5
O(3)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1m**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	75(1)	23(1)	33(1)	7(1)	14(1)	4(1)
O(1)	32(1)	26(1)	23(1)	5(1)	3(1)	2(1)
O(2)	43(2)	24(1)	24(1)	1(1)	3(1)	1(1)
O(3)	43(1)	28(1)	26(1)	-2(1)	10(1)	-1(1)
C(1)	28(2)	27(2)	24(1)	1(1)	0(1)	-1(1)
C(2)	34(2)	28(2)	24(2)	6(1)	1(1)	-2(2)
C(3)	35(2)	23(2)	29(2)	4(1)	-1(2)	1(1)
C(4)	29(2)	24(2)	24(1)	2(1)	-2(1)	0(1)
C(5)	37(2)	24(2)	28(2)	-1(1)	-1(1)	2(2)
C(6)	36(2)	29(2)	25(2)	-3(1)	4(1)	1(2)
C(7)	30(2)	30(2)	21(1)	1(1)	0(1)	-1(1)
C(8)	30(2)	25(2)	20(1)	3(1)	-1(1)	-2(1)
C(9)	28(2)	23(2)	21(1)	1(1)	-3(1)	-1(1)
C(10)	29(2)	26(2)	18(1)	1(1)	-3(1)	-3(1)
C(11)	27(2)	23(1)	19(1)	1(1)	-1(1)	-2(1)
C(12)	26(2)	22(2)	22(1)	2(1)	1(1)	2(1)
C(13)	29(2)	24(2)	21(1)	-1(1)	0(1)	-1(1)
C(14)	35(2)	27(2)	22(1)	2(1)	0(1)	1(1)
C(15)	41(2)	25(2)	26(2)	4(1)	7(2)	4(2)
C(16)	44(2)	23(2)	28(2)	-4(1)	7(2)	-1(2)
C(17)	35(2)	26(2)	22(1)	-1(1)	3(1)	0(2)
C(18)	30(2)	24(2)	21(1)	3(1)	-1(1)	-2(1)
C(19)	32(2)	25(2)	21(1)	0(1)	-2(1)	-1(1)
C(20)	30(2)	25(2)	22(1)	0(1)	-1(1)	-1(1)
C(21)	30(2)	26(2)	21(1)	-1(1)	-2(1)	-2(1)
C(22)	30(2)	26(2)	19(1)	0(1)	-1(1)	1(1)
C(23)	35(2)	26(2)	22(1)	-1(1)	3(1)	5(2)
C(24)	37(2)	25(2)	25(2)	1(1)	3(1)	0(2)
C(25)	30(2)	29(2)	21(1)	-1(1)	2(1)	-1(2)
C(26)	37(2)	26(2)	27(2)	-5(1)	4(2)	1(2)
C(27)	35(2)	22(2)	25(2)	-1(1)	1(1)	-1(1)
C(28)	48(2)	30(2)	29(2)	0(1)	12(2)	-4(2)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1m**.

	x	y	z	U(eq)
H(2)	9056	1883	6613	35
H(3)	12226	985	6235	35
H(5)	15178	971	5727	35
H(6)	17106	1871	5258	36
H(7)	15927	3785	5157	32
H(8)	12756	4773	5509	30
H(13)	7961	5452	5451	30
H(14)	8262	7115	5137	33
H(16)	9991	8907	5981	38
H(17)	9687	7238	6295	33
H(19)	4627	6571	6466	31
H(20)	3420	4863	6936	31
H(23)	300	4441	7307	33
H(24)	-2551	4039	7785	35
H(26)	-4705	7386	7860	36
H(27)	-1951	7761	7379	33
H(28A)	-6745	3938	8141	53
H(28B)	-6899	4494	8505	53
H(28C)	-3708	4166	8346	53

Table S8. Torsion angles [°] for **1m**.

Cl(1)-C(15)-C(16)-C(17)	179.3(3)
O(1)-C(1)-C(2)-C(3)	179.4(3)
O(1)-C(1)-C(10)-C(9)	179.6(3)
O(1)-C(1)-C(10)-C(11)	1.0(4)
O(1)-C(18)-C(19)-C(20)	-0.4(5)
O(2)-C(21)-C(22)-C(23)	169.8(4)
O(2)-C(21)-C(22)-C(27)	-8.9(5)
O(3)-C(25)-C(26)-C(27)	179.7(3)
C(1)-O(1)-C(18)-C(11)	-0.7(4)
C(1)-O(1)-C(18)-C(19)	177.7(3)
C(1)-C(2)-C(3)-C(4)	0.8(5)
C(1)-C(10)-C(11)-C(12)	178.0(4)
C(1)-C(10)-C(11)-C(18)	-1.4(4)
C(2)-C(1)-C(10)-C(9)	0.2(6)
C(2)-C(1)-C(10)-C(11)	-178.4(4)
C(2)-C(3)-C(4)-C(5)	-179.7(4)
C(2)-C(3)-C(4)-C(9)	0.7(6)
C(3)-C(4)-C(5)-C(6)	-178.7(4)
C(3)-C(4)-C(9)-C(8)	177.7(3)
C(3)-C(4)-C(9)-C(10)	-1.7(5)
C(4)-C(5)-C(6)-C(7)	0.6(6)
C(4)-C(9)-C(10)-C(1)	1.3(5)
C(4)-C(9)-C(10)-C(11)	179.3(4)
C(5)-C(4)-C(9)-C(8)	-1.9(5)
C(5)-C(4)-C(9)-C(10)	178.6(3)
C(5)-C(6)-C(7)-C(8)	-1.1(6)
C(6)-C(7)-C(8)-C(9)	0.1(5)
C(7)-C(8)-C(9)-C(4)	1.4(5)
C(7)-C(8)-C(9)-C(10)	-179.2(3)
C(8)-C(9)-C(10)-C(1)	-178.1(3)
C(8)-C(9)-C(10)-C(11)	-0.1(7)
C(9)-C(4)-C(5)-C(6)	0.9(6)
C(9)-C(10)-C(11)-C(12)	-0.1(7)
C(9)-C(10)-C(11)-C(18)	-179.5(4)
C(10)-C(1)-C(2)-C(3)	-1.3(6)
C(10)-C(11)-C(12)-C(13)	50.4(6)
C(10)-C(11)-C(12)-C(17)	-131.1(4)
C(10)-C(11)-C(18)-O(1)	1.3(4)

C(10)-C(11)-C(18)-C(19)	-176.6(4)
C(11)-C(12)-C(13)-C(14)	178.7(3)
C(11)-C(12)-C(17)-C(16)	-178.7(4)
C(11)-C(18)-C(19)-C(20)	177.5(4)
C(12)-C(11)-C(18)-O(1)	-178.2(3)
C(12)-C(11)-C(18)-C(19)	3.9(6)
C(12)-C(13)-C(14)-C(15)	0.0(6)
C(13)-C(12)-C(17)-C(16)	-0.1(6)
C(13)-C(14)-C(15)-Cl(1)	-179.3(3)
C(13)-C(14)-C(15)-C(16)	0.0(6)
C(14)-C(15)-C(16)-C(17)	0.0(6)
C(15)-C(16)-C(17)-C(12)	0.0(6)
C(17)-C(12)-C(13)-C(14)	0.1(5)
C(18)-O(1)-C(1)-C(2)	179.1(3)
C(18)-O(1)-C(1)-C(10)	-0.3(4)
C(18)-C(11)-C(12)-C(13)	-130.3(4)
C(18)-C(11)-C(12)-C(17)	48.2(5)
C(18)-C(19)-C(20)-C(21)	-179.9(3)
C(19)-C(20)-C(21)-O(2)	-0.7(5)
C(19)-C(20)-C(21)-C(22)	179.7(3)
C(20)-C(21)-C(22)-C(23)	-10.6(5)
C(20)-C(21)-C(22)-C(27)	170.7(3)
C(21)-C(22)-C(23)-C(24)	-179.3(3)
C(21)-C(22)-C(27)-C(26)	-180.0(3)
C(22)-C(23)-C(24)-C(25)	-0.8(6)
C(23)-C(22)-C(27)-C(26)	1.3(6)
C(23)-C(24)-C(25)-O(3)	-179.0(3)
C(23)-C(24)-C(25)-C(26)	1.4(6)
C(24)-C(25)-C(26)-C(27)	-0.7(6)
C(25)-C(26)-C(27)-C(22)	-0.6(6)
C(27)-C(22)-C(23)-C(24)	-0.6(6)
C(28)-O(3)-C(25)-C(24)	2.0(5)
C(28)-O(3)-C(25)-C(26)	-178.4(3)

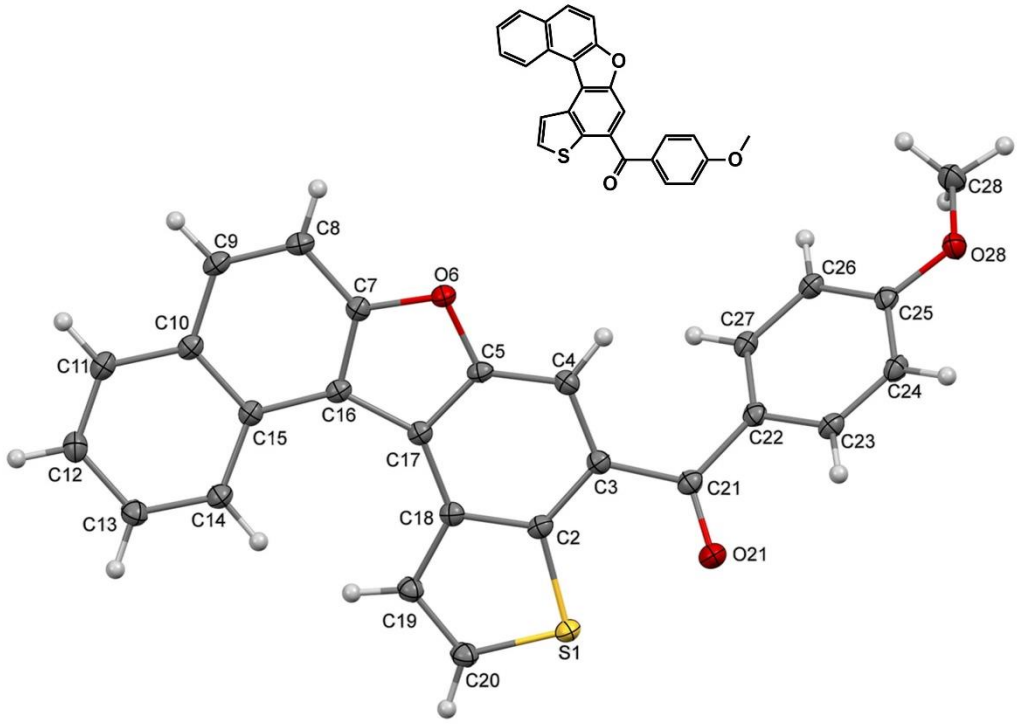


Figure S11. Molecular structure of photoproduct **3a** determined by X-ray analysis.

Table S9. Crystal data and structure refinement for **3a**.

Identification code	**3a**	
Empirical formula	C26 H16 O3 S	
Formula weight	408.45	
Temperature	99.97(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 7.74314(5) Å	a= 90°.
	b = 7.47998(5) Å	b= 94.3152(5)°.
	c = 31.73273(18) Å	g = 90°.
Volume	1832.703(19) $Å^3$	
Z	4	
Density (calculated)	1.480 g/cm^3	
Absorption coefficient	1.796 mm^{-1}	
F(000)	848	
Crystal size	0.31 x 0.16 x 0.07 mm^3	
Theta range for data collection	2.793 to 79.671°.	

Index ranges	-9<=h<=8, -9<=k<=9, -38<=l<=40
Reflections collected	25432
Independent reflections	3976 [R(int) = 0.0315]
Observed reflections	3855
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.462
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3976 / 0 / 272
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0896
R indices (all data)	R1 = 0.0347, wR2 = 0.0905
Largest diff. peak and hole	0.242 and -0.381 e.Å^{-3}

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	8944(1)	8104(1)	6130(1)	17(1)
O(6)	2270(1)	6239(1)	5292(1)	16(1)
O(21)	7424(1)	6401(1)	6774(1)	22(1)
O(28)	910(1)	6166(1)	7826(1)	19(1)
C(2)	6865(2)	7549(2)	5926(1)	15(1)
C(3)	5542(2)	6885(2)	6170(1)	15(1)
C(4)	3952(2)	6457(2)	5960(1)	15(1)
C(5)	3774(2)	6694(2)	5526(1)	14(1)
C(7)	2562(2)	6629(2)	4881(1)	15(1)
C(8)	1282(2)	6358(2)	4550(1)	17(1)
C(9)	1716(2)	6798(2)	4155(1)	17(1)
C(10)	3408(2)	7423(2)	4080(1)	16(1)
C(11)	3831(2)	7757(2)	3660(1)	18(1)
C(12)	5487(2)	8195(2)	3572(1)	20(1)
C(13)	6794(2)	8308(2)	3904(1)	20(1)
C(14)	6413(2)	8037(2)	4316(1)	17(1)
C(15)	4715(2)	7625(2)	4420(1)	14(1)
C(16)	4223(2)	7286(2)	4841(1)	14(1)
C(17)	5030(2)	7363(2)	5272(1)	14(1)
C(18)	6637(2)	7878(2)	5486(1)	14(1)
C(19)	8160(2)	8687(2)	5336(1)	17(1)
C(20)	9454(2)	8876(2)	5644(1)	19(1)
C(21)	5916(2)	6561(2)	6629(1)	16(1)
C(22)	4486(2)	6449(2)	6916(1)	15(1)
C(23)	4746(2)	5370(2)	7278(1)	17(1)
C(24)	3522(2)	5305(2)	7571(1)	17(1)
C(25)	2022(2)	6346(2)	7516(1)	15(1)
C(26)	1741(2)	7444(2)	7162(1)	16(1)
C(27)	2978(2)	7470(2)	6864(1)	15(1)
C(28)	-558(2)	7337(2)	7811(1)	24(1)

Table S11. Bond lengths [Å] and angles [°] for **3a**.

S(1)-C(2)	1.7386(12)
S(1)-C(20)	1.7204(13)
O(6)-C(5)	1.3767(14)
O(6)-C(7)	1.3709(14)
O(21)-C(21)	1.2284(16)
O(28)-C(25)	1.3620(15)
O(28)-C(28)	1.4325(16)
C(2)-C(3)	1.4181(17)
C(2)-C(18)	1.4167(17)
C(3)-C(4)	1.3922(17)
C(3)-C(21)	1.4850(16)
C(4)-H(4)	0.9500
C(4)-C(5)	1.3830(17)
C(5)-C(17)	1.4012(16)
C(7)-C(8)	1.4034(17)
C(7)-C(16)	1.3913(17)
C(8)-H(8)	0.9500
C(8)-C(9)	1.3639(18)
C(9)-H(9)	0.9500
C(9)-C(10)	1.4281(17)
C(10)-C(11)	1.4178(17)
C(10)-C(15)	1.4315(16)
C(11)-H(11)	0.9500
C(11)-C(12)	1.3723(19)
C(12)-H(12)	0.9500
C(12)-C(13)	1.4078(18)
C(13)-H(13)	0.9500
C(13)-C(14)	1.3771(18)
C(14)-H(14)	0.9500
C(14)-C(15)	1.4137(17)
C(15)-C(16)	1.4371(16)
C(16)-C(17)	1.4624(16)
C(17)-C(18)	1.4252(16)

C(18)-C(19)	1.4380(17)
C(19)-H(19)	0.9500
C(19)-C(20)	1.3527(17)
C(20)-H(20)	0.9500
C(21)-C(22)	1.4888(17)
C(22)-C(23)	1.4054(17)
C(22)-C(27)	1.3949(17)
C(23)-H(23)	0.9500
C(23)-C(24)	1.3776(17)
C(24)-H(24)	0.9500
C(24)-C(25)	1.3982(17)
C(25)-C(26)	1.3954(17)
C(26)-H(26)	0.9500
C(26)-C(27)	1.3962(17)
C(27)-H(27)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800

C(20)-S(1)-C(2)	90.91(6)
C(7)-O(6)-C(5)	105.51(9)
C(25)-O(28)-C(28)	117.32(10)
C(3)-C(2)-S(1)	124.61(9)
C(18)-C(2)-S(1)	111.59(9)
C(18)-C(2)-C(3)	123.78(11)
C(2)-C(3)-C(21)	119.75(11)
C(4)-C(3)-C(2)	117.96(11)
C(4)-C(3)-C(21)	122.18(11)
C(3)-C(4)-H(4)	121.1
C(5)-C(4)-C(3)	117.72(11)
C(5)-C(4)-H(4)	121.1
O(6)-C(5)-C(4)	121.51(11)
O(6)-C(5)-C(17)	111.90(10)
C(4)-C(5)-C(17)	126.59(11)
O(6)-C(7)-C(8)	121.53(11)

O(6)-C(7)-C(16)	112.48(10)
C(16)-C(7)-C(8)	125.98(11)
C(7)-C(8)-H(8)	121.8
C(9)-C(8)-C(7)	116.44(11)
C(9)-C(8)-H(8)	121.8
C(8)-C(9)-H(9)	119.2
C(8)-C(9)-C(10)	121.61(11)
C(10)-C(9)-H(9)	119.2
C(9)-C(10)-C(15)	120.97(11)
C(11)-C(10)-C(9)	119.55(11)
C(11)-C(10)-C(15)	119.40(11)
C(10)-C(11)-H(11)	119.4
C(12)-C(11)-C(10)	121.22(12)
C(12)-C(11)-H(11)	119.4
C(11)-C(12)-H(12)	120.3
C(11)-C(12)-C(13)	119.48(12)
C(13)-C(12)-H(12)	120.3
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-C(12)	120.59(12)
C(14)-C(13)-H(13)	119.7
C(13)-C(14)-H(14)	119.2
C(13)-C(14)-C(15)	121.55(12)
C(15)-C(14)-H(14)	119.2
C(10)-C(15)-C(16)	117.41(11)
C(14)-C(15)-C(10)	117.62(11)
C(14)-C(15)-C(16)	124.85(11)
C(7)-C(16)-C(15)	117.33(11)
C(7)-C(16)-C(17)	105.11(10)
C(15)-C(16)-C(17)	137.50(11)
C(5)-C(17)-C(16)	104.97(10)
C(5)-C(17)-C(18)	116.20(11)
C(18)-C(17)-C(16)	138.83(11)
C(2)-C(18)-C(17)	117.54(11)
C(2)-C(18)-C(19)	110.79(11)
C(17)-C(18)-C(19)	131.67(11)

C(18)-C(19)-H(19)	123.6
C(20)-C(19)-C(18)	112.73(11)
C(20)-C(19)-H(19)	123.6
S(1)-C(20)-H(20)	123.1
C(19)-C(20)-S(1)	113.86(9)
C(19)-C(20)-H(20)	123.1
O(21)-C(21)-C(3)	119.56(11)
O(21)-C(21)-C(22)	119.67(11)
C(3)-C(21)-C(22)	120.76(11)
C(23)-C(22)-C(21)	117.71(11)
C(27)-C(22)-C(21)	123.42(11)
C(27)-C(22)-C(23)	118.63(11)
C(22)-C(23)-H(23)	119.7
C(24)-C(23)-C(22)	120.54(11)
C(24)-C(23)-H(23)	119.7
C(23)-C(24)-H(24)	119.9
C(23)-C(24)-C(25)	120.19(11)
C(25)-C(24)-H(24)	119.9
O(28)-C(25)-C(24)	114.79(11)
O(28)-C(25)-C(26)	124.77(11)
C(26)-C(25)-C(24)	120.44(11)
C(25)-C(26)-H(26)	120.7
C(25)-C(26)-C(27)	118.70(11)
C(27)-C(26)-H(26)	120.7
C(22)-C(27)-C(26)	121.48(11)
C(22)-C(27)-H(27)	119.3
C(26)-C(27)-H(27)	119.3
O(28)-C(28)-H(28A)	109.5
O(28)-C(28)-H(28B)	109.5
O(28)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	13(1)	21(1)	16(1)	-1(1)	-1(1)	-2(1)
O(6)	13(1)	19(1)	15(1)	-1(1)	0(1)	-2(1)
O(21)	16(1)	32(1)	18(1)	1(1)	-1(1)	0(1)
O(28)	18(1)	22(1)	16(1)	4(1)	3(1)	1(1)
C(2)	14(1)	14(1)	16(1)	-2(1)	-1(1)	1(1)
C(3)	15(1)	14(1)	15(1)	-1(1)	1(1)	1(1)
C(4)	15(1)	15(1)	16(1)	-1(1)	3(1)	-1(1)
C(5)	12(1)	14(1)	17(1)	-2(1)	-1(1)	0(1)
C(7)	16(1)	14(1)	15(1)	-1(1)	1(1)	1(1)
C(8)	13(1)	18(1)	20(1)	-1(1)	-1(1)	-1(1)
C(9)	16(1)	18(1)	18(1)	-2(1)	-4(1)	0(1)
C(10)	17(1)	14(1)	16(1)	-1(1)	-1(1)	2(1)
C(11)	21(1)	19(1)	15(1)	0(1)	-2(1)	1(1)
C(12)	25(1)	20(1)	15(1)	1(1)	2(1)	-1(1)
C(13)	18(1)	22(1)	19(1)	-1(1)	2(1)	-3(1)
C(14)	17(1)	19(1)	16(1)	-1(1)	-1(1)	-2(1)
C(15)	16(1)	12(1)	15(1)	-1(1)	0(1)	1(1)
C(16)	14(1)	12(1)	16(1)	-1(1)	-1(1)	1(1)
C(17)	14(1)	12(1)	15(1)	-1(1)	1(1)	1(1)
C(18)	14(1)	13(1)	16(1)	-2(1)	1(1)	1(1)
C(19)	17(1)	18(1)	17(1)	-1(1)	2(1)	-2(1)
C(20)	16(1)	21(1)	20(1)	-2(1)	2(1)	-4(1)
C(21)	17(1)	15(1)	17(1)	-2(1)	0(1)	-1(1)
C(22)	16(1)	16(1)	13(1)	-2(1)	0(1)	-2(1)
C(23)	17(1)	16(1)	17(1)	0(1)	-2(1)	1(1)
C(24)	19(1)	17(1)	15(1)	3(1)	-2(1)	0(1)
C(25)	16(1)	16(1)	14(1)	-1(1)	0(1)	-3(1)
C(26)	16(1)	16(1)	15(1)	0(1)	-2(1)	1(1)
C(27)	18(1)	15(1)	14(1)	1(1)	-2(1)	-1(1)
C(28)	21(1)	32(1)	21(1)	3(1)	5(1)	6(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3a**.

	x	y	z	U(eq)
H(4)	3022	6018	6109	18
H(8)	173	5894	4599	20
H(9)	871	6686	3923	21
H(11)	2952	7676	3435	22
H(12)	5749	8421	3289	24
H(13)	7949	8572	3844	23
H(14)	7312	8129	4536	21
H(19)	8248	9050	5052	21
H(20)	10545	9388	5596	23
H(23)	5774	4680	7321	20
H(24)	3697	4551	7812	21
H(26)	727	8160	7125	19
H(27)	2788	8200	6620	19
H(28A)	-1272	7144	7547	36
H(28B)	-161	8581	7825	36
H(28C)	-1246	7086	8051	36

Table S14. Torsion angles [°] for **3a**.

S(1)-C(2)-C(3)-C(4)	-178.42(9)
S(1)-C(2)-C(3)-C(21)	-2.24(16)
S(1)-C(2)-C(18)-C(17)	175.64(9)
S(1)-C(2)-C(18)-C(19)	-3.66(13)
O(6)-C(5)-C(17)-C(16)	-0.84(13)
O(6)-C(5)-C(17)-C(18)	179.82(10)
O(6)-C(7)-C(8)-C(9)	179.83(11)
O(6)-C(7)-C(16)-C(15)	175.85(10)
O(6)-C(7)-C(16)-C(17)	-1.83(13)
O(21)-C(21)-C(22)-C(23)	-30.02(17)
O(21)-C(21)-C(22)-C(27)	144.30(13)
O(28)-C(25)-C(26)-C(27)	-178.62(11)
C(2)-S(1)-C(20)-C(19)	-1.83(11)
C(2)-C(3)-C(4)-C(5)	0.56(17)
C(2)-C(3)-C(21)-O(21)	-19.42(18)
C(2)-C(3)-C(21)-C(22)	159.84(11)
C(2)-C(18)-C(19)-C(20)	2.35(15)
C(3)-C(2)-C(18)-C(17)	-5.63(18)
C(3)-C(2)-C(18)-C(19)	175.07(11)
C(3)-C(4)-C(5)-O(6)	177.45(10)
C(3)-C(4)-C(5)-C(17)	-1.41(19)
C(3)-C(21)-C(22)-C(23)	150.72(12)
C(3)-C(21)-C(22)-C(27)	-34.95(18)
C(4)-C(3)-C(21)-O(21)	156.60(12)
C(4)-C(3)-C(21)-C(22)	-24.15(18)
C(4)-C(5)-C(17)-C(16)	178.11(12)
C(4)-C(5)-C(17)-C(18)	-1.23(18)
C(5)-O(6)-C(7)-C(8)	-179.04(11)
C(5)-O(6)-C(7)-C(16)	1.33(13)
C(5)-C(17)-C(18)-C(2)	4.51(16)
C(5)-C(17)-C(18)-C(19)	-176.37(12)
C(7)-O(6)-C(5)-C(4)	-179.25(11)
C(7)-O(6)-C(5)-C(17)	-0.24(13)

C(7)-C(8)-C(9)-C(10)	2.75(19)
C(7)-C(16)-C(17)-C(5)	1.56(13)
C(7)-C(16)-C(17)-C(18)	-179.35(14)
C(8)-C(7)-C(16)-C(15)	-3.76(19)
C(8)-C(7)-C(16)-C(17)	178.55(12)
C(8)-C(9)-C(10)-C(11)	176.07(12)
C(8)-C(9)-C(10)-C(15)	-0.50(19)
C(9)-C(10)-C(11)-C(12)	-173.78(12)
C(9)-C(10)-C(15)-C(14)	172.37(11)
C(9)-C(10)-C(15)-C(16)	-3.89(17)
C(10)-C(11)-C(12)-C(13)	0.3(2)
C(10)-C(15)-C(16)-C(7)	5.75(17)
C(10)-C(15)-C(16)-C(17)	-177.56(13)
C(11)-C(10)-C(15)-C(14)	-4.20(17)
C(11)-C(10)-C(15)-C(16)	179.54(11)
C(11)-C(12)-C(13)-C(14)	-2.1(2)
C(12)-C(13)-C(14)-C(15)	0.6(2)
C(13)-C(14)-C(15)-C(10)	2.57(18)
C(13)-C(14)-C(15)-C(16)	178.52(12)
C(14)-C(15)-C(16)-C(7)	-170.21(11)
C(14)-C(15)-C(16)-C(17)	6.5(2)
C(15)-C(10)-C(11)-C(12)	2.84(19)
C(15)-C(16)-C(17)-C(5)	-175.39(14)
C(15)-C(16)-C(17)-C(18)	3.7(3)
C(16)-C(7)-C(8)-C(9)	-0.59(19)
C(16)-C(17)-C(18)-C(2)	-174.52(13)
C(16)-C(17)-C(18)-C(19)	4.6(2)
C(17)-C(18)-C(19)-C(20)	-176.81(12)
C(18)-C(2)-C(3)-C(4)	3.01(18)
C(18)-C(2)-C(3)-C(21)	179.19(11)
C(18)-C(19)-C(20)-S(1)	0.03(15)
C(20)-S(1)-C(2)-C(3)	-175.58(11)
C(20)-S(1)-C(2)-C(18)	3.14(10)
C(21)-C(3)-C(4)-C(5)	-175.52(11)
C(21)-C(22)-C(23)-C(24)	175.59(11)

C(21)-C(22)-C(27)-C(26)	-174.03(11)
C(22)-C(23)-C(24)-C(25)	-1.47(19)
C(23)-C(22)-C(27)-C(26)	0.25(18)
C(23)-C(24)-C(25)-O(28)	179.91(11)
C(23)-C(24)-C(25)-C(26)	0.73(19)
C(24)-C(25)-C(26)-C(27)	0.47(18)
C(25)-C(26)-C(27)-C(22)	-0.96(18)
C(27)-C(22)-C(23)-C(24)	0.98(18)
C(28)-O(28)-C(25)-C(24)	173.53(11)
C(28)-O(28)-C(25)-C(26)	-7.33(18)

VIII. References

[S1]. I. S. Mekeda, R. Yu. Balakhonov and V. Z. Shirinian, *Org. Biomol. Chem.*, **2024**, *22*, 7715-7724;

[S2]. CrysAlisPro. Version 1.171.41. *Rigaku Oxford Diffraction*, **2021**;

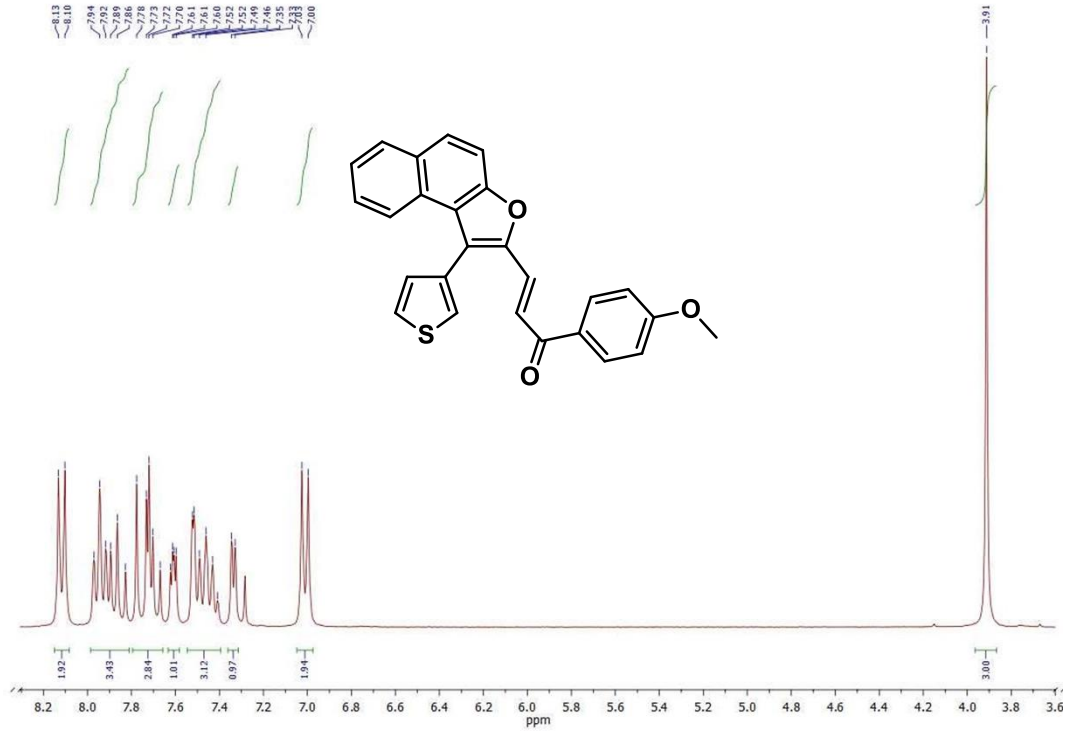
[S3]. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71(1), 3-8. http://doi.org/10.1107/S2053273314026370;

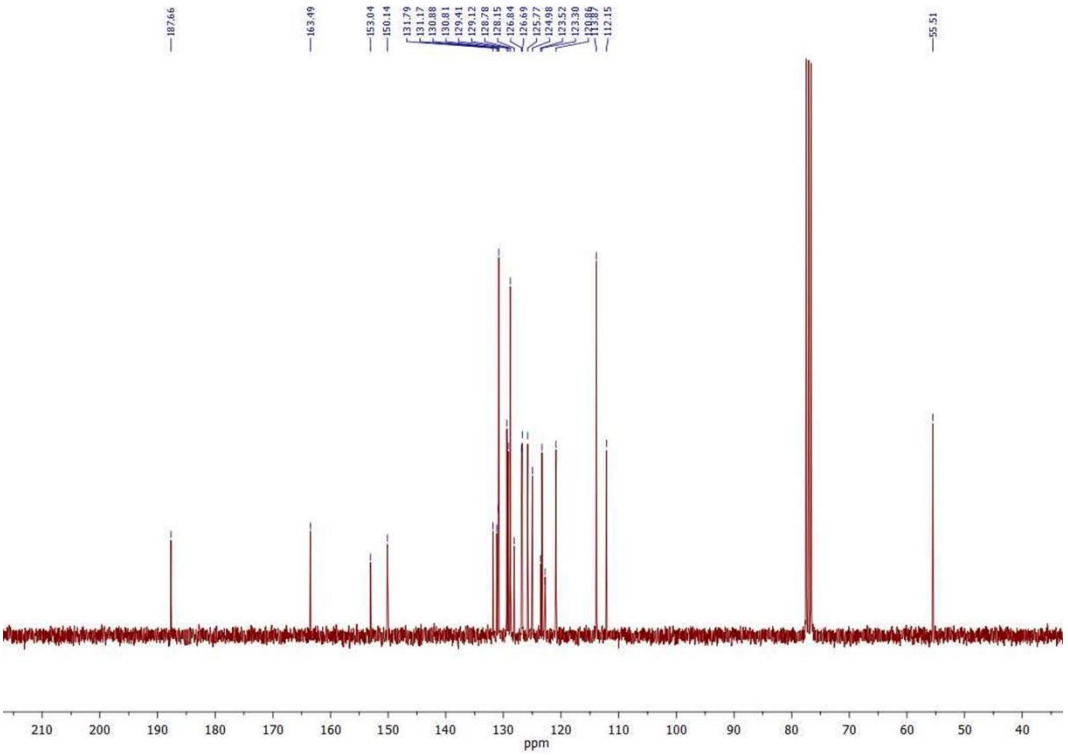
[S4]. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71(1), 3-8. http://doi.org/10.1107/S2053229614024218;

[S5]. Dolomanov O.V.; Bourhis L.J.; Gildea R.J.; Howard J.A.K.; Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42(2), 229-341. http://doi.org/10.1107/S0021889808042726.

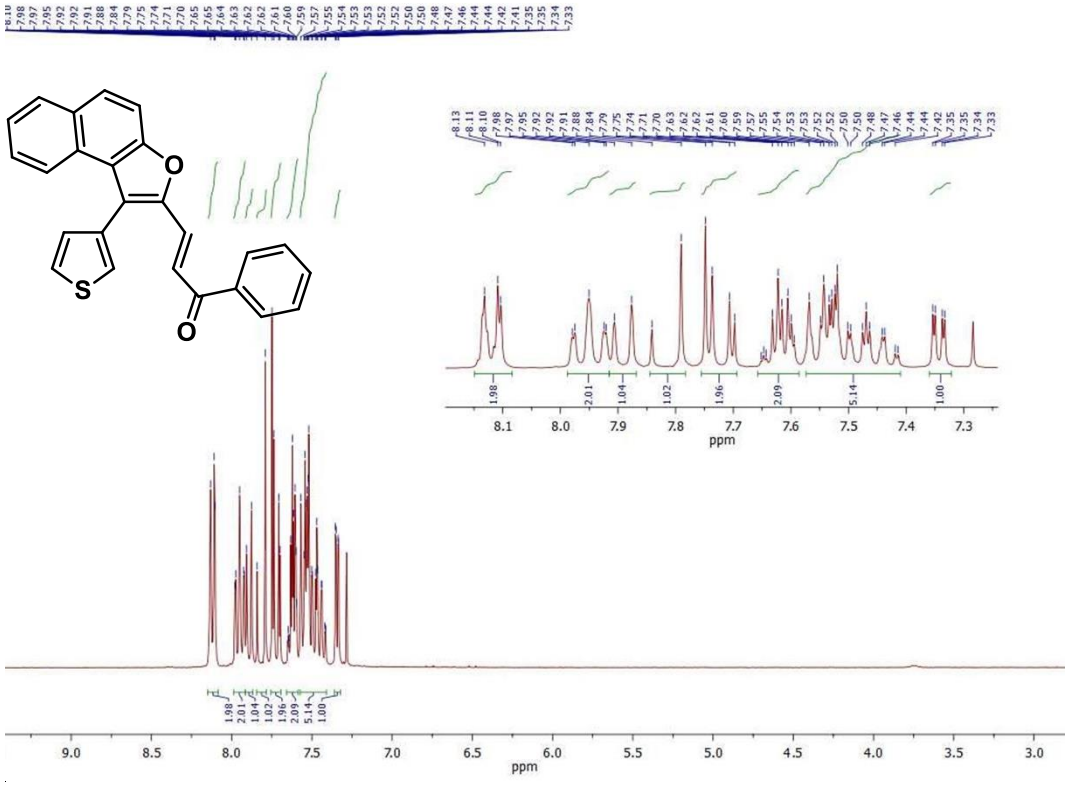
IX. Copies of ^{1}H and ^{13}C NMR spectra of starting compounds

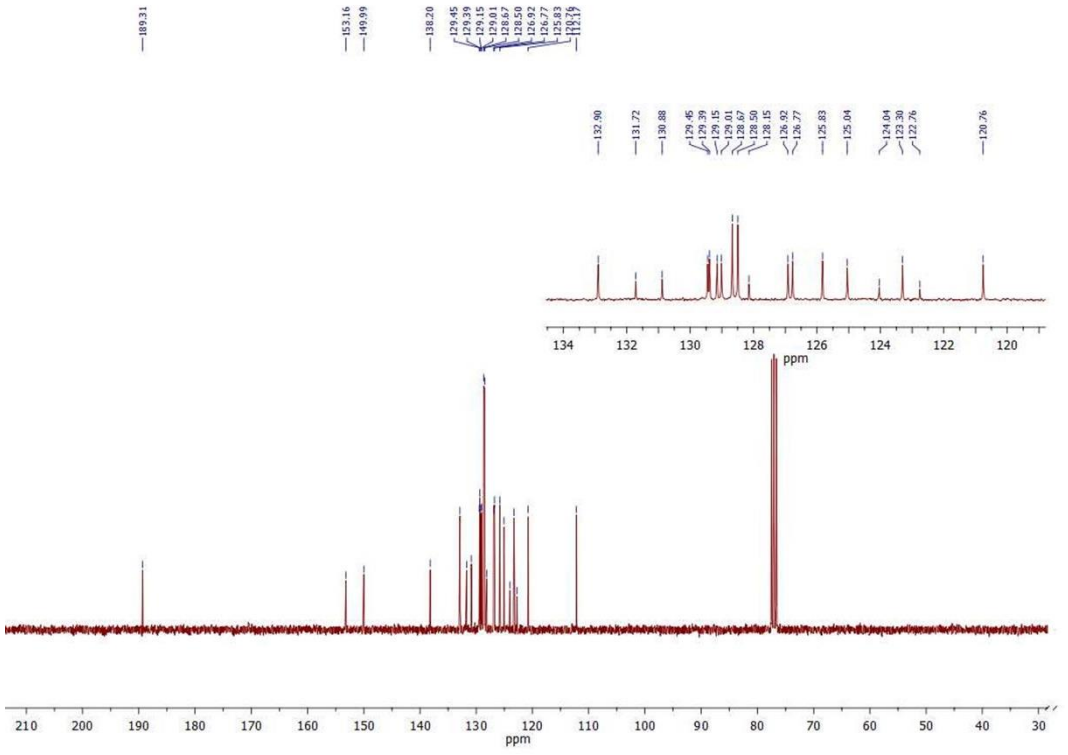
(*E*)-1-(4-methoxyphenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1a)



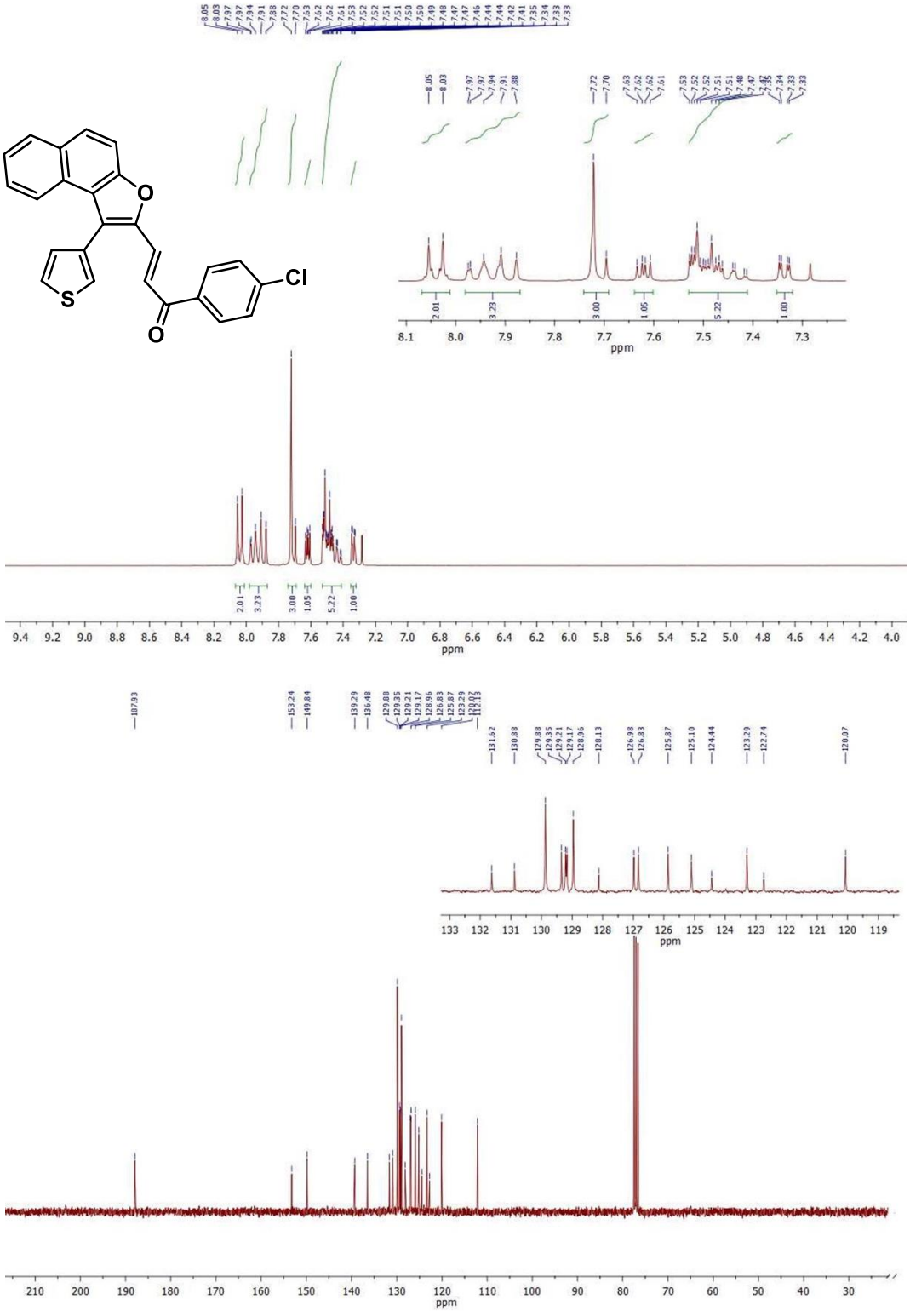


(*E*)-1-phenyl-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1b)

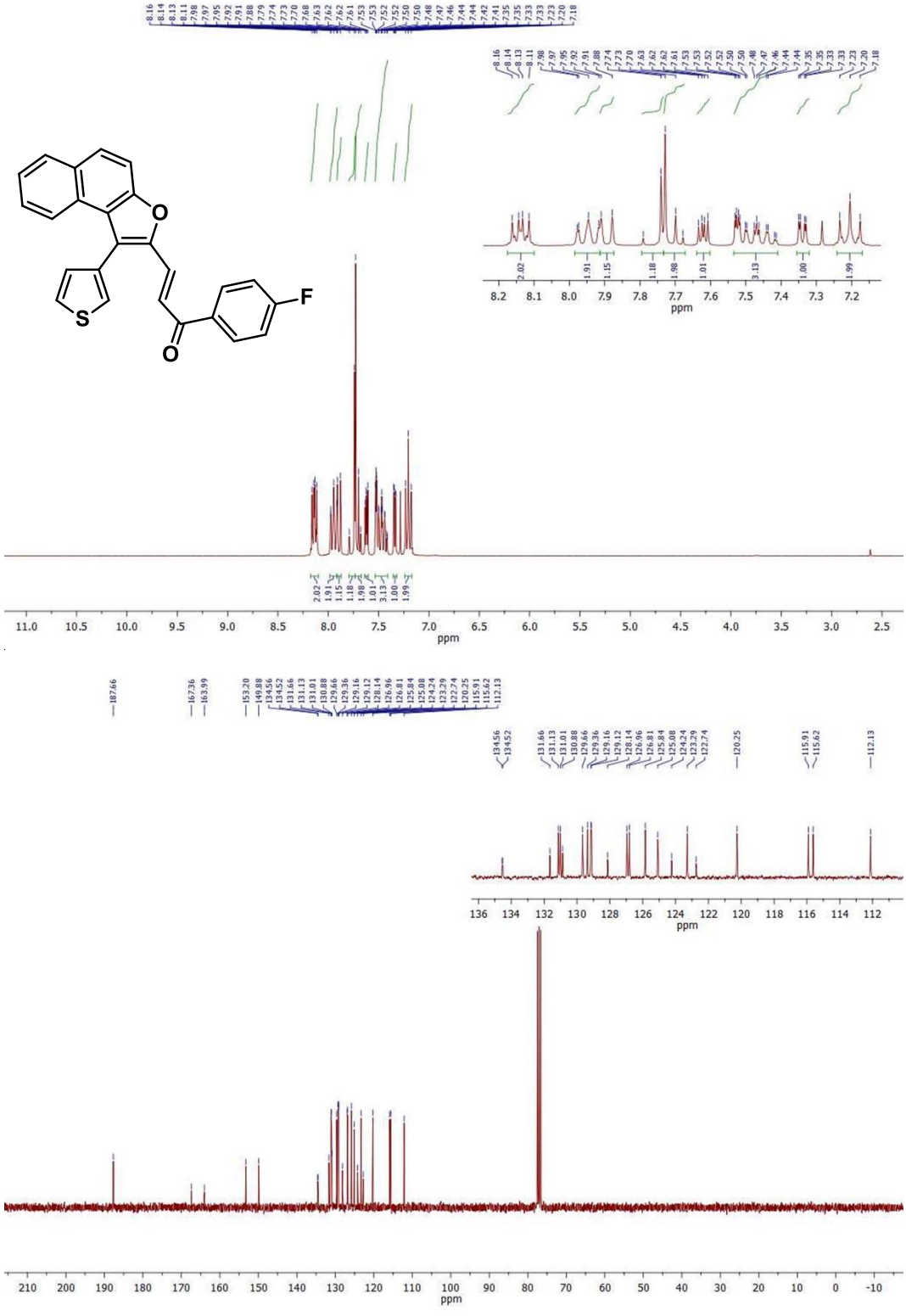




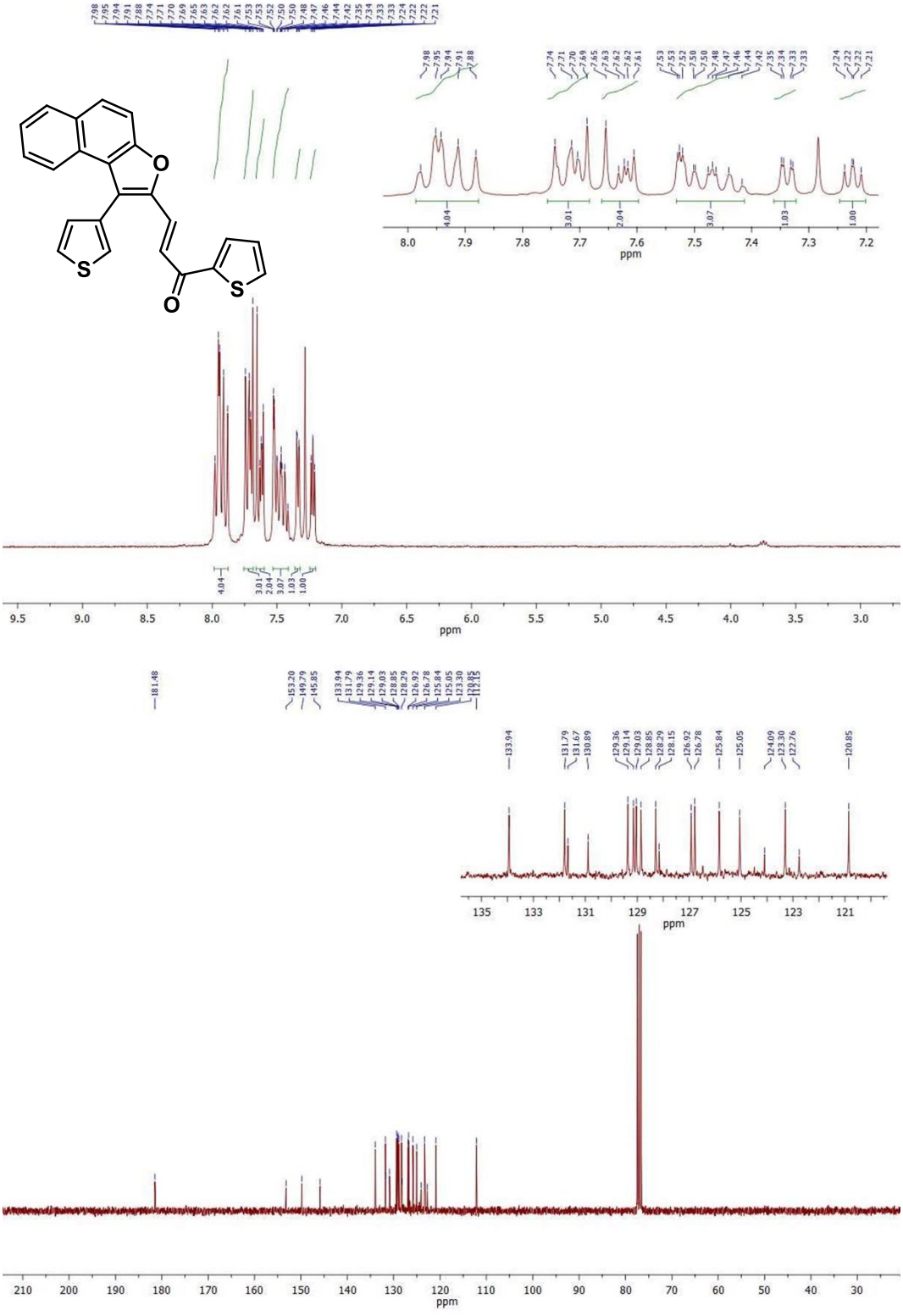
(*E*)-1-(4-chlorophenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1c)



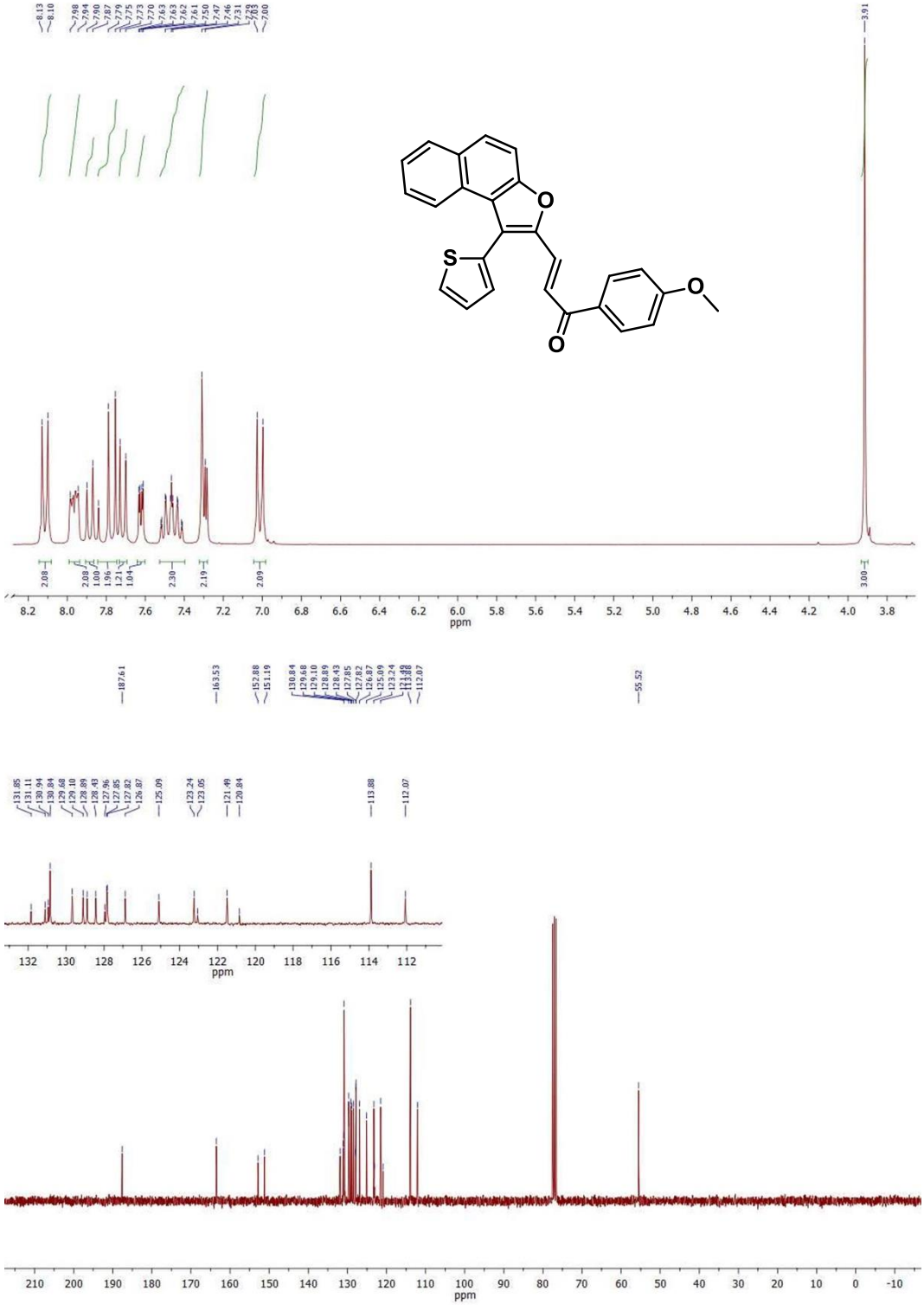
(*E*)-1-(4-fluorophenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1d)



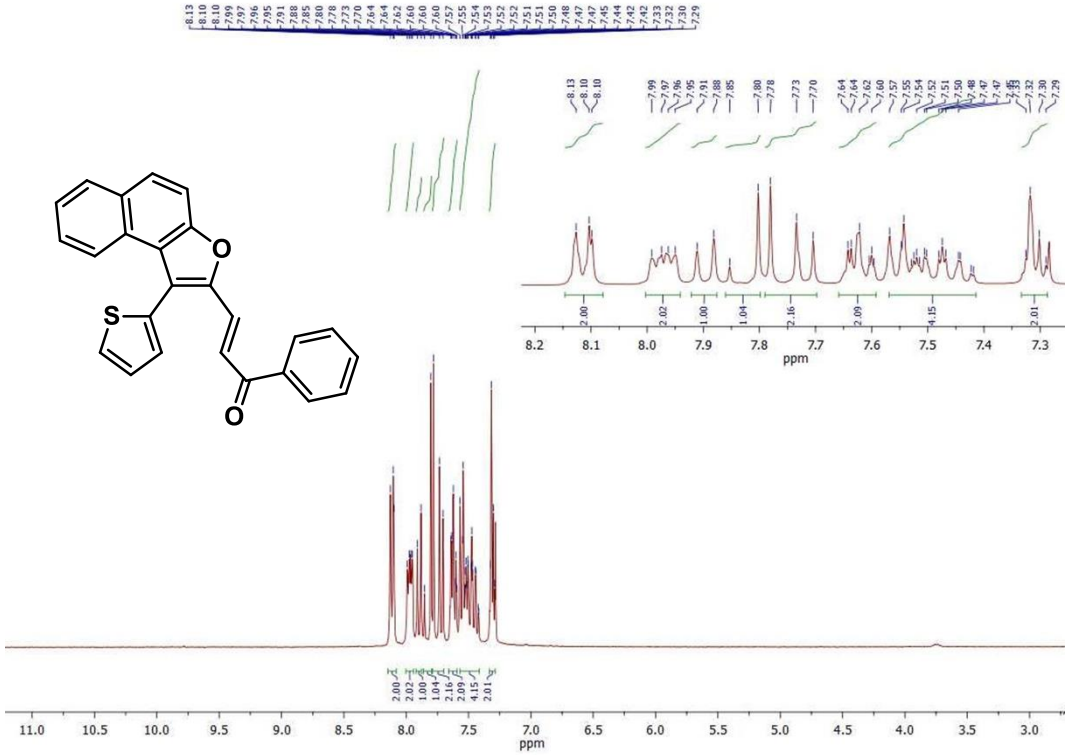
(*E*)-1-(thiophen-2-yl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1e)

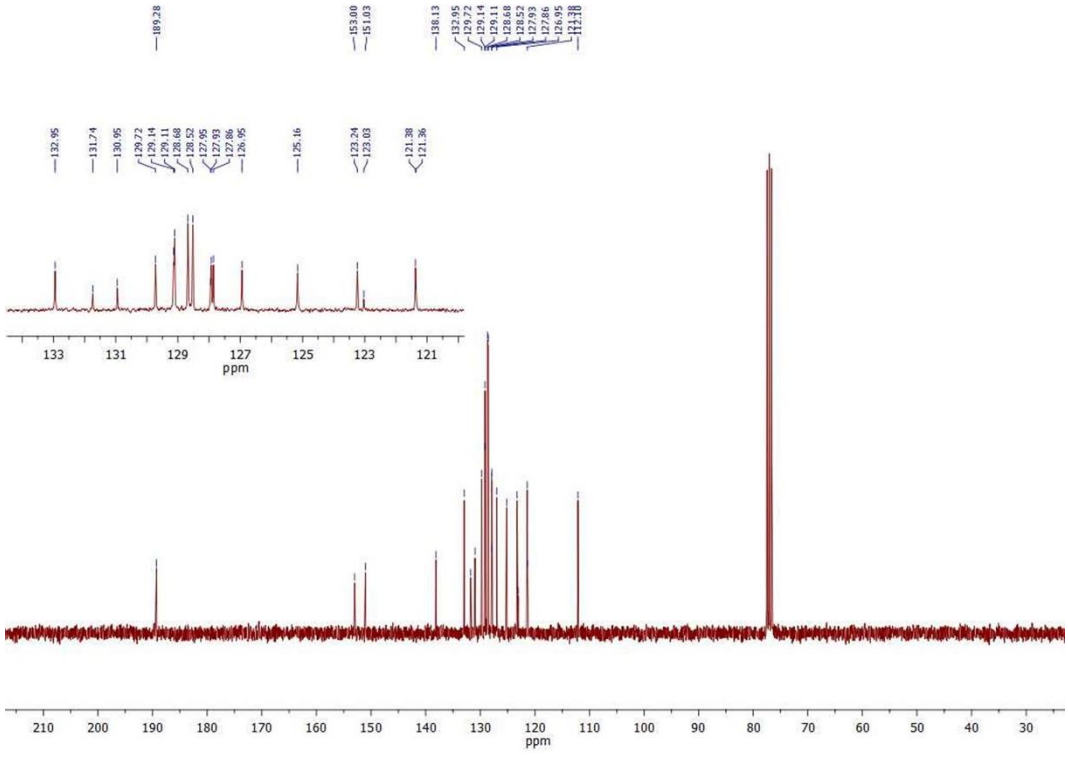


(*E*)-1-(4-methoxyphenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1f)

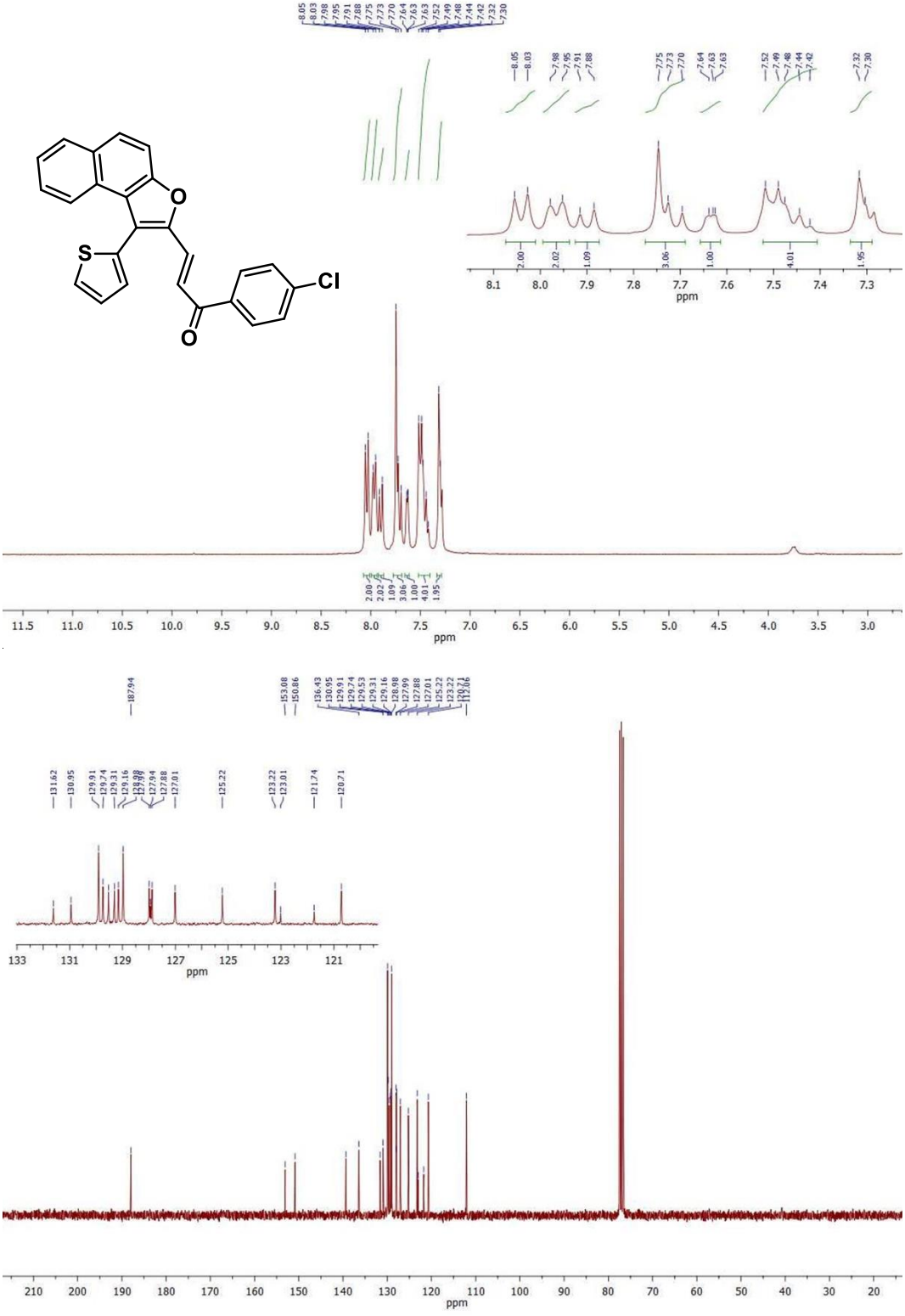


(*E*)-1-phenyl-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1g)

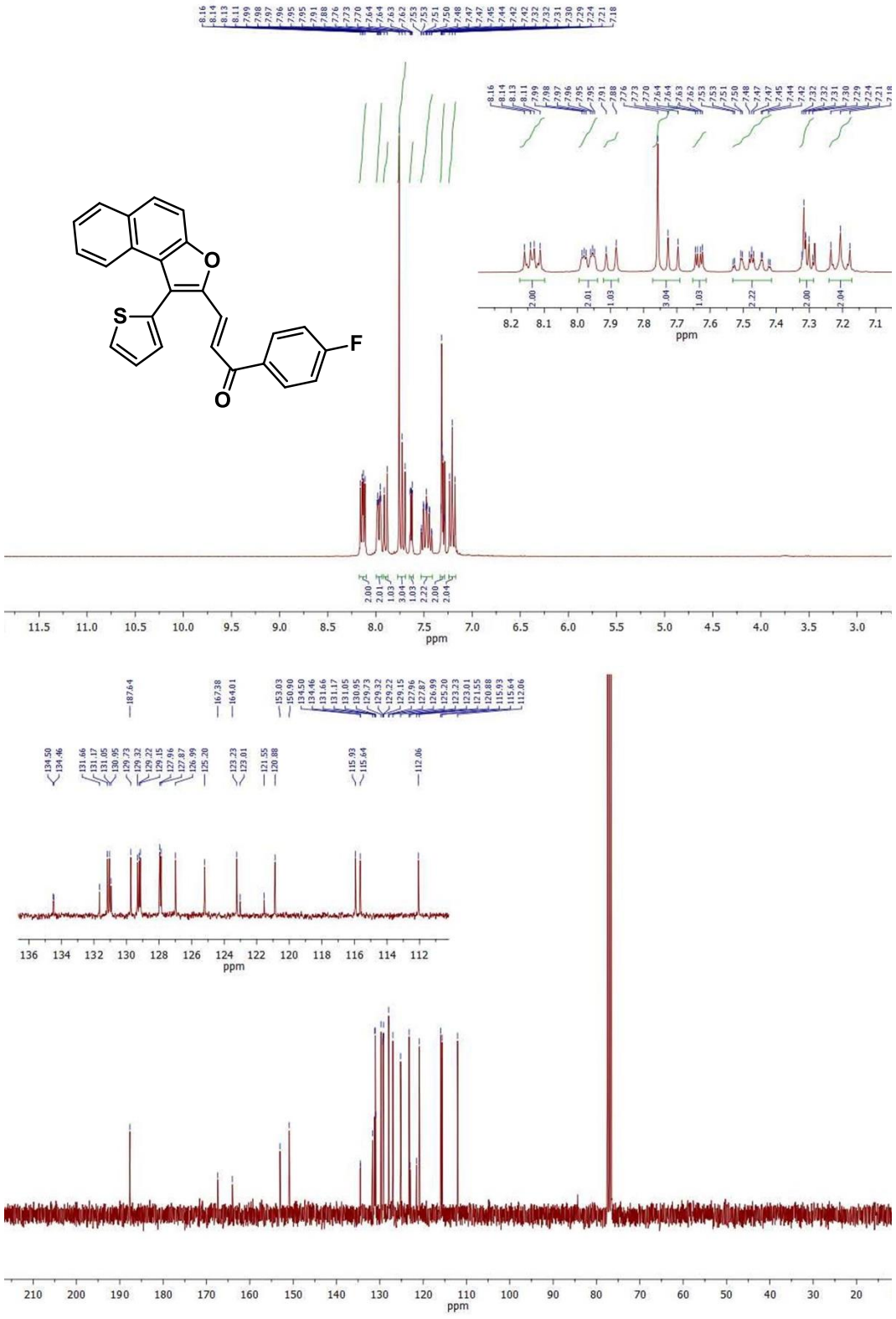




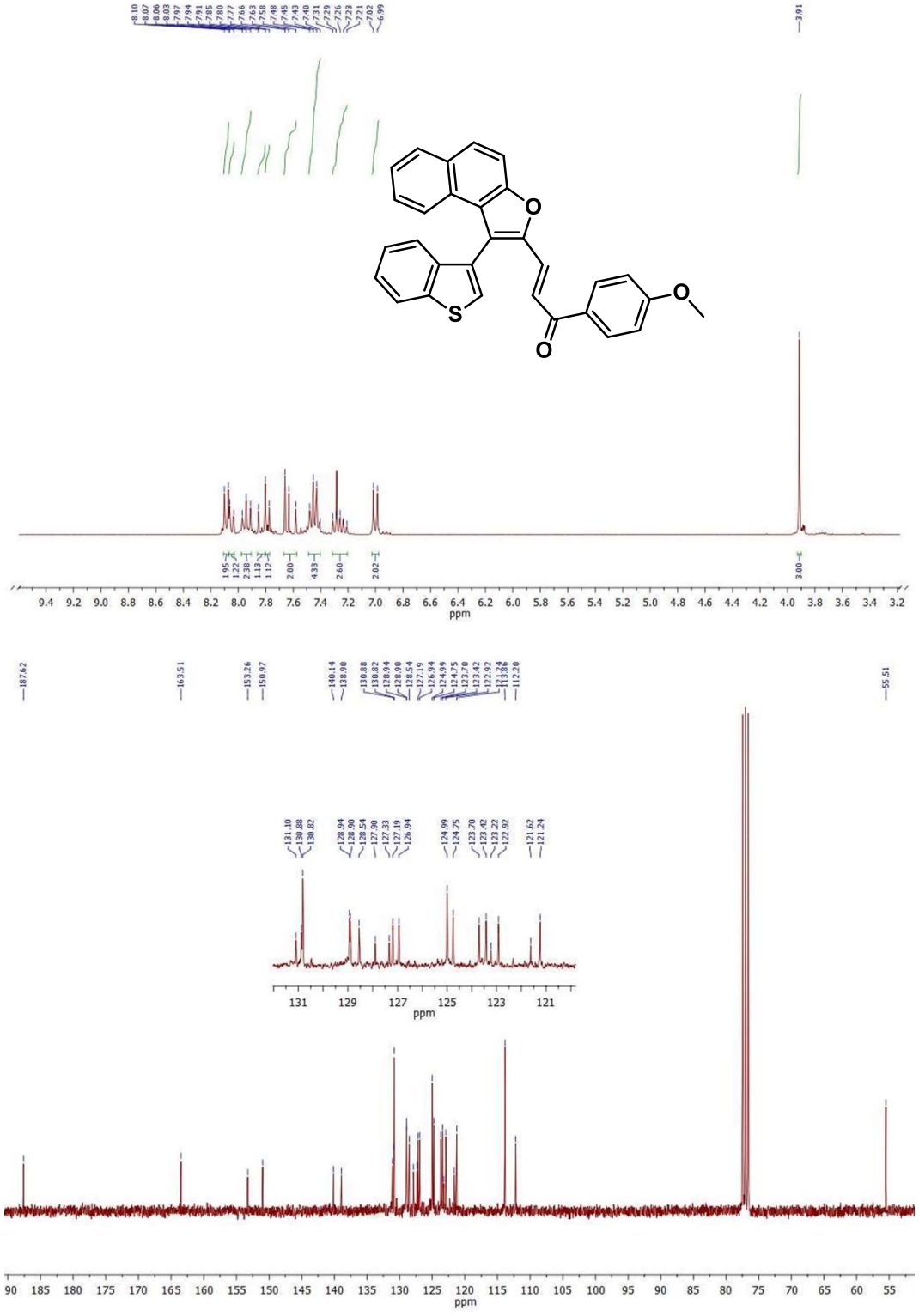
(*E*)-1-(4-chlorophenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1h)



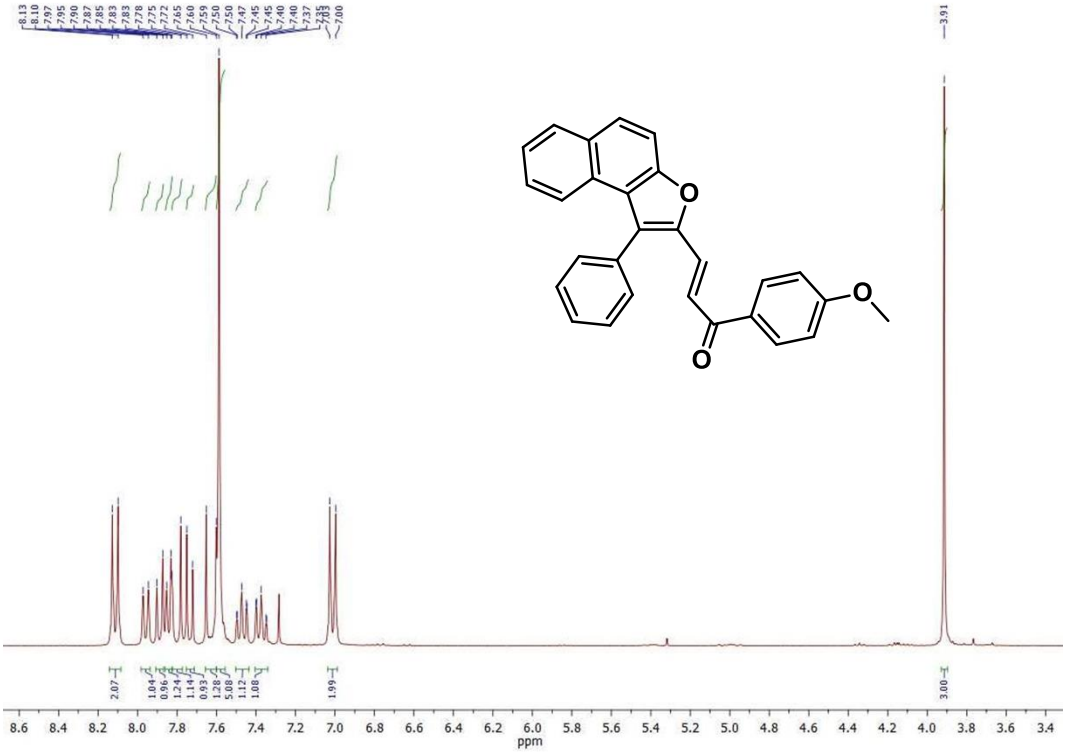
(*E*)-1-(4-fluorophenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1i)

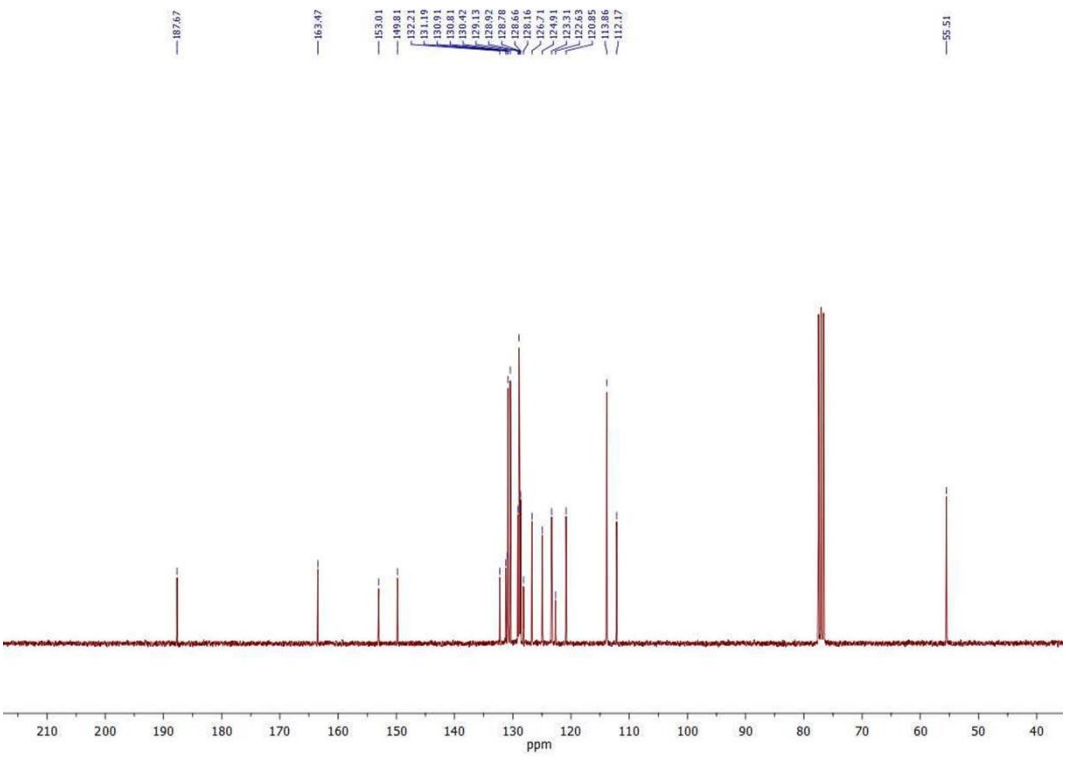


(*E*)-3-(1-(benzo[b]thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1j)

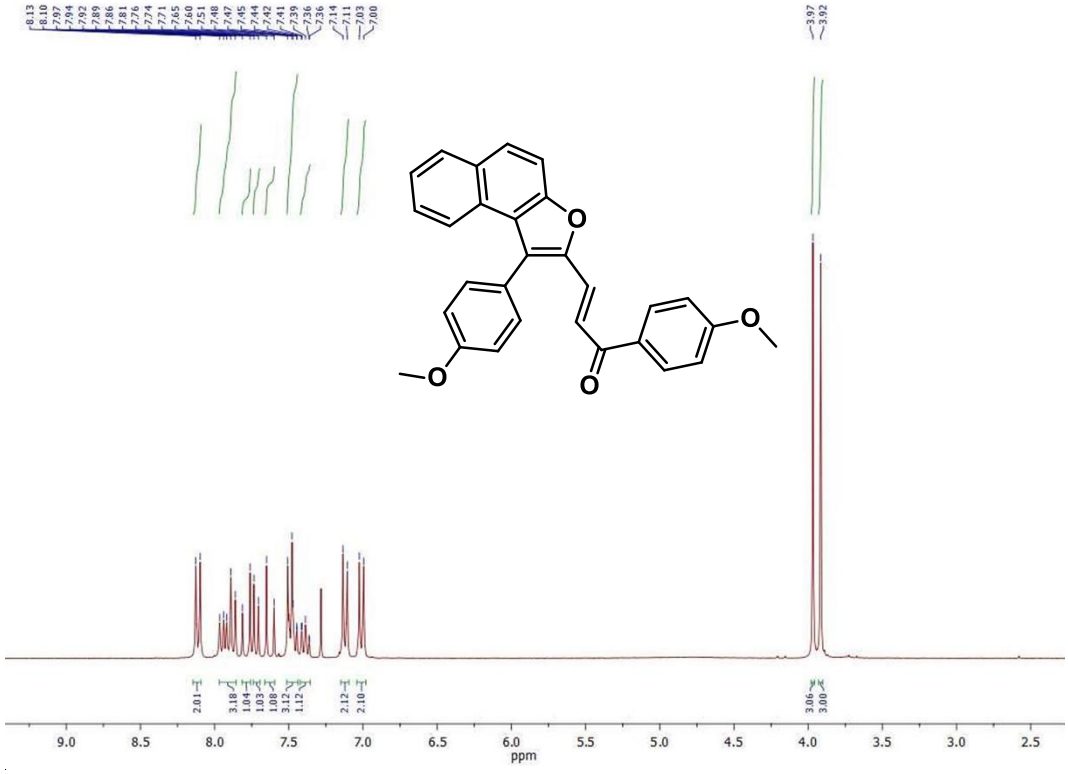


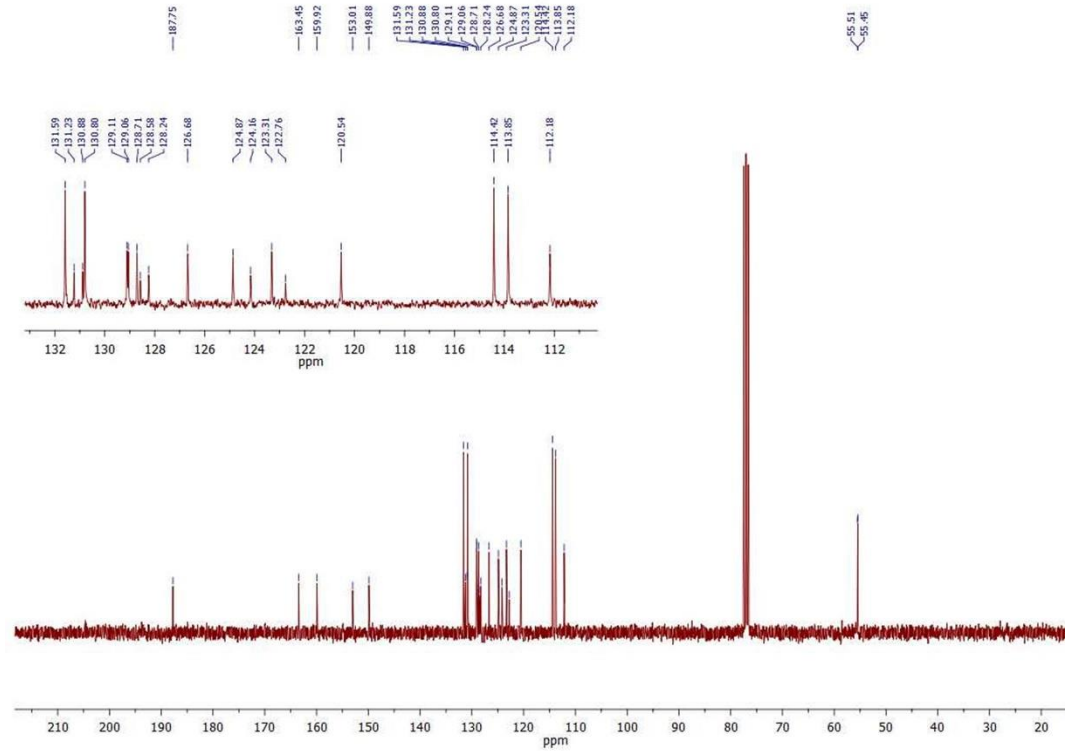
(*E*)-1-(4-methoxyphenyl)-3-(1-phenylnaphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1k)



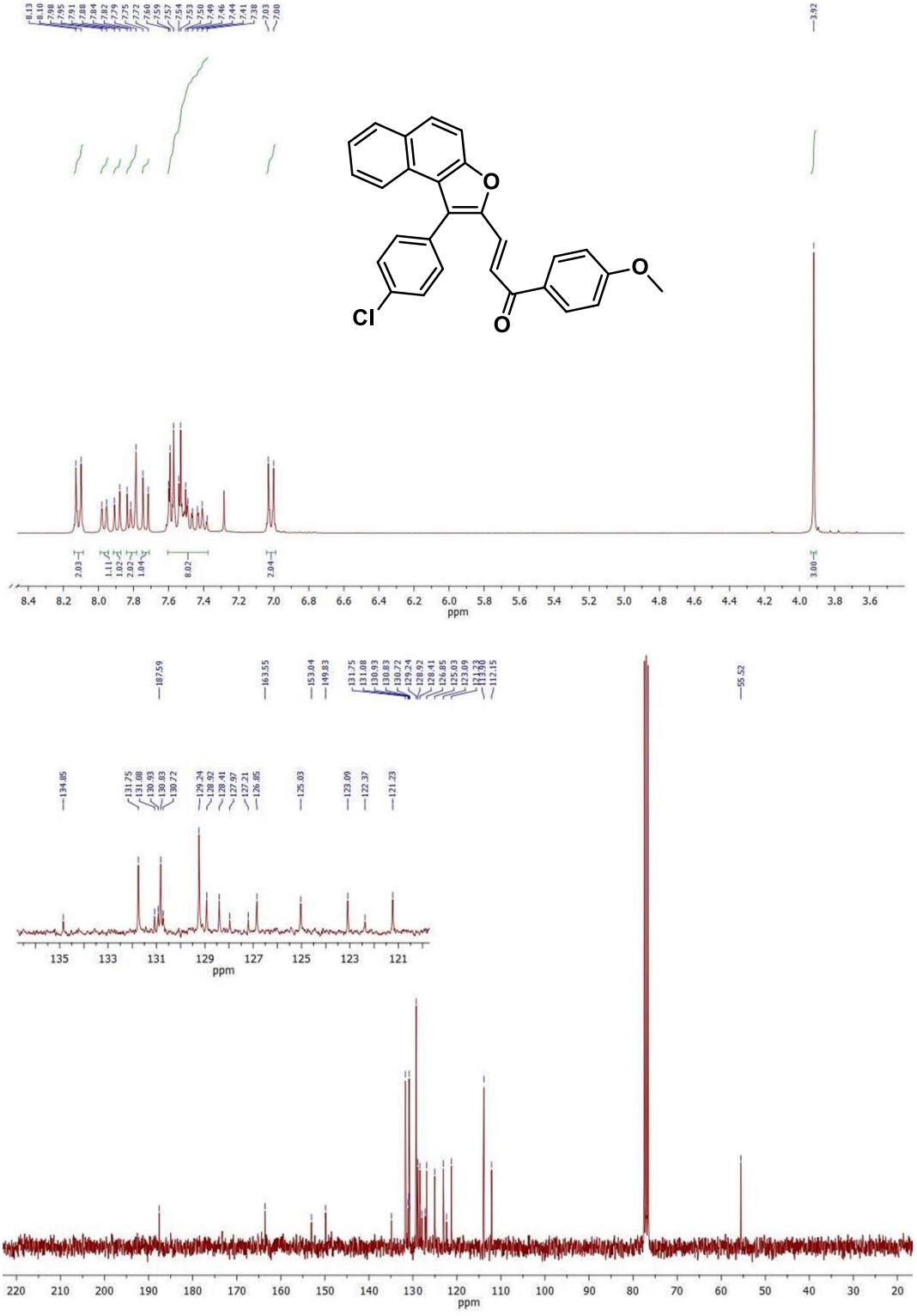


(*E*)-1-(4-methoxyphenyl)-3-(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one(1l)

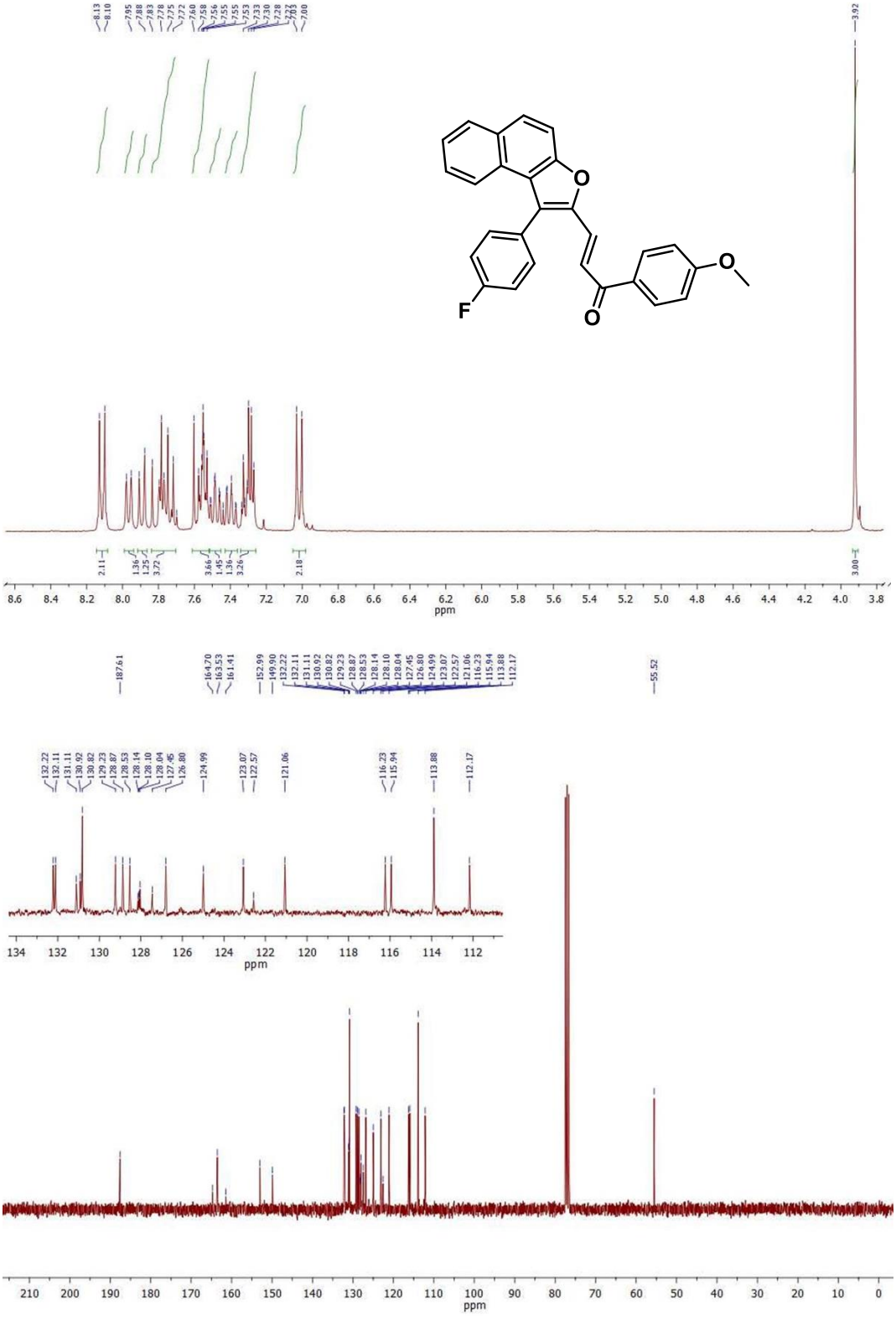




(*E*)-3-(1-(4-chlorophenyl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one(1m)

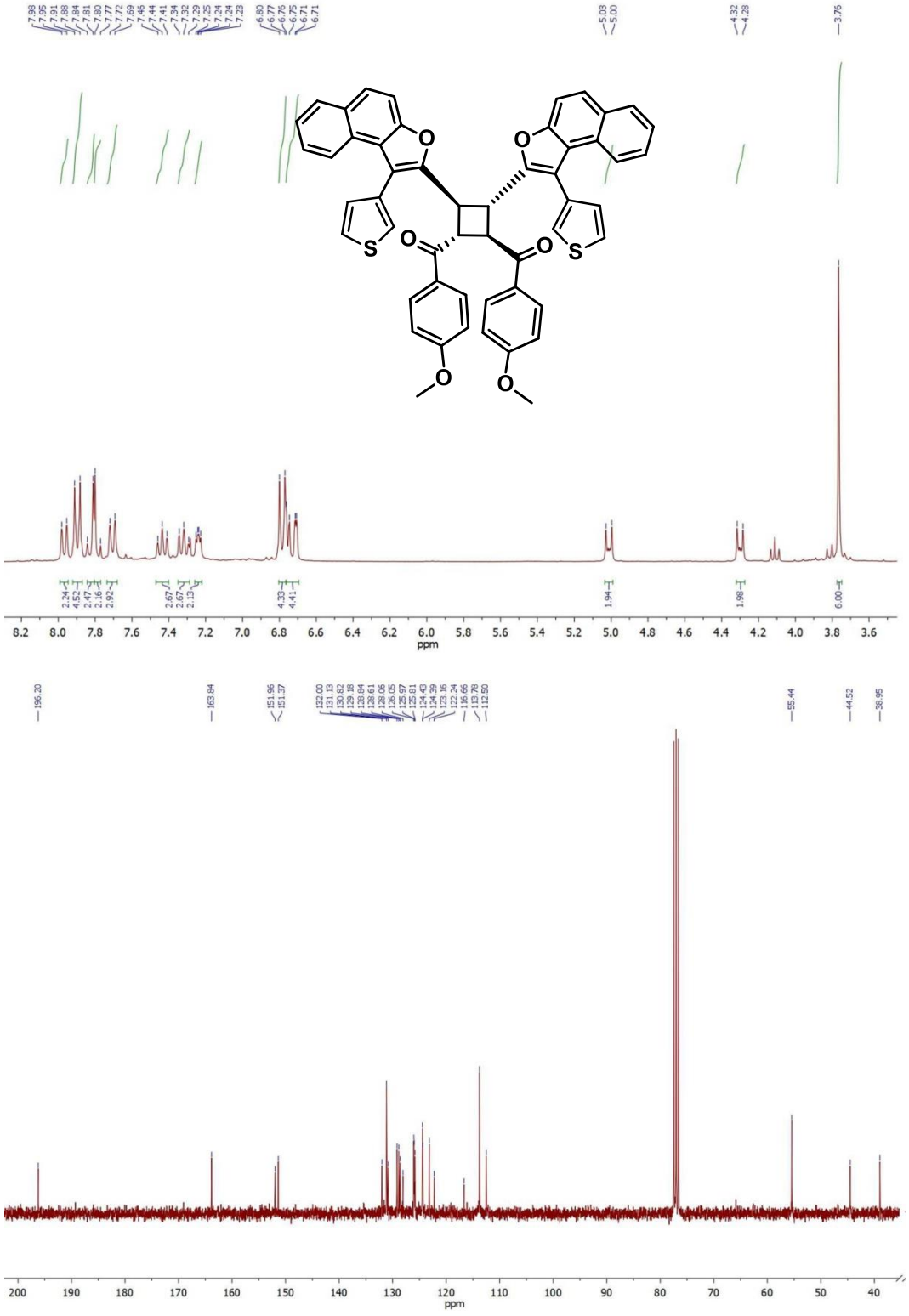


(*E*)-3-(1-(4-fluorophenyl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1n)

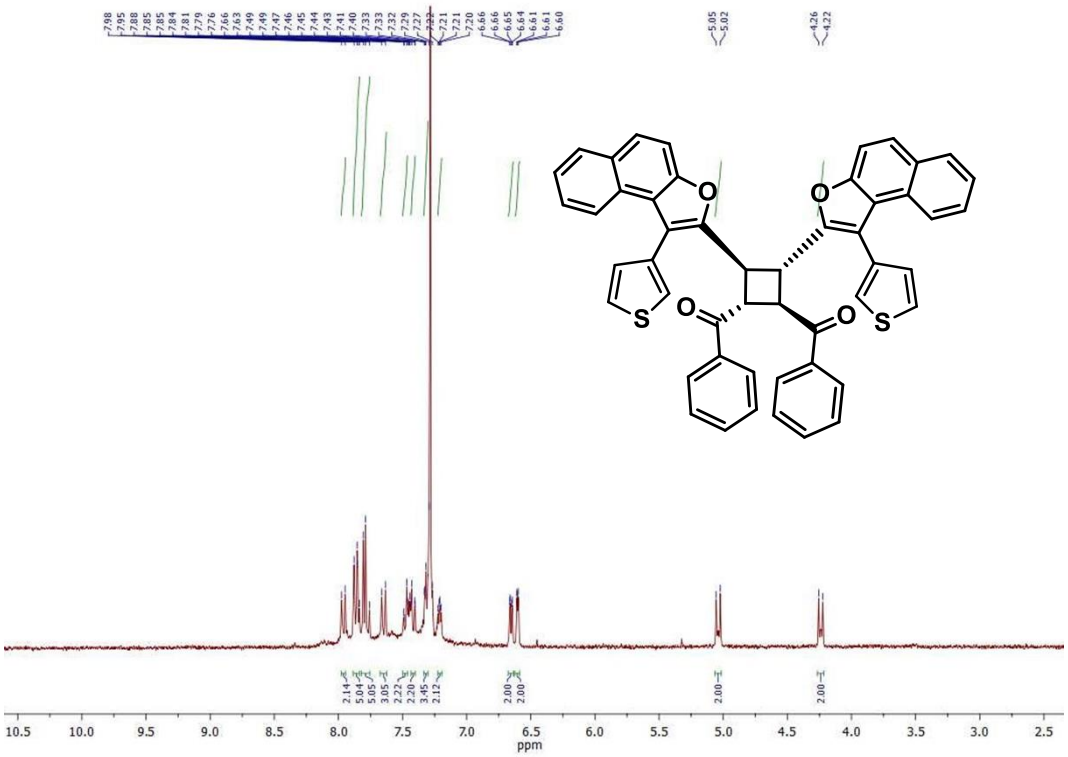


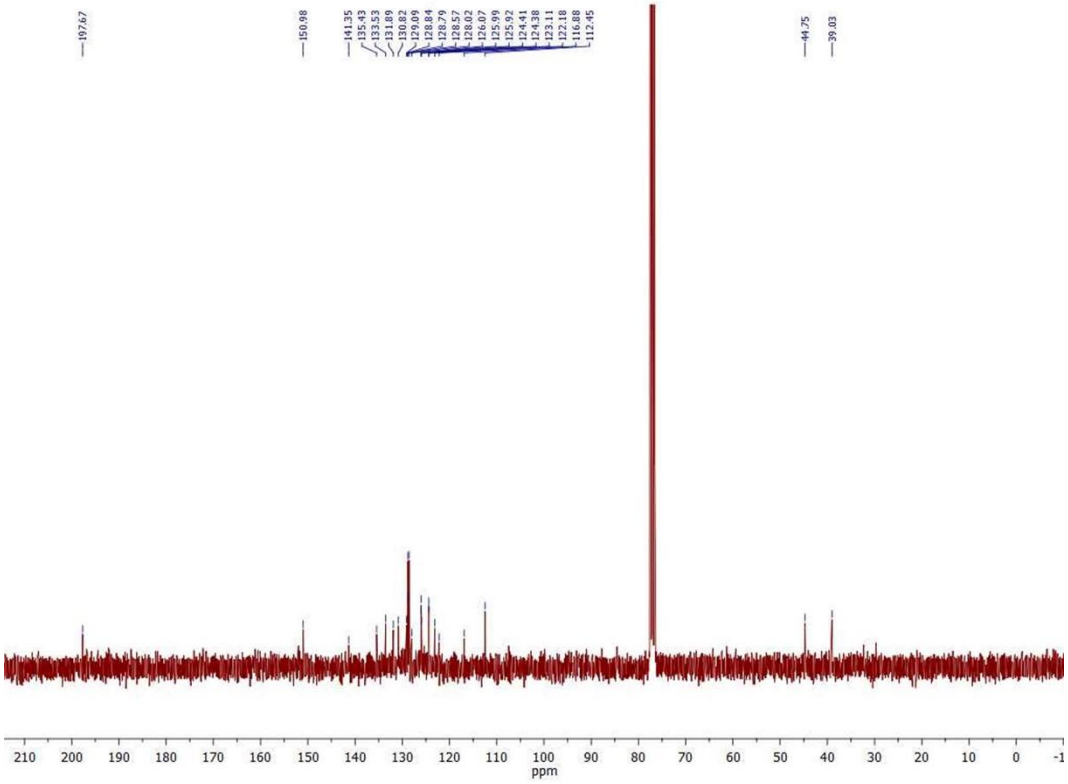
X. Copies of ^{1}H and ^{13}C NMR spectra of photoproducts

((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2ahh-a)

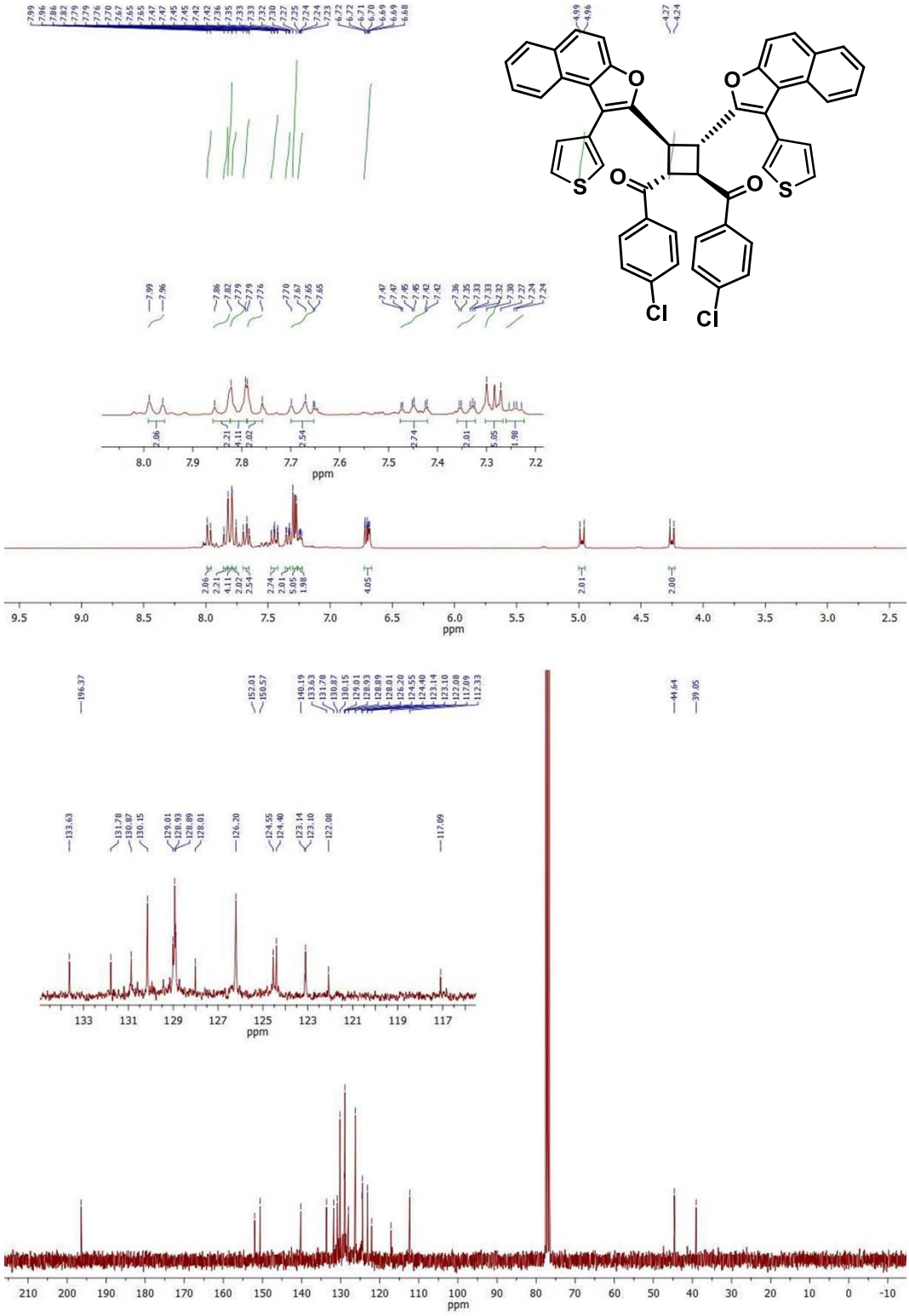


((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (2bhh-a)

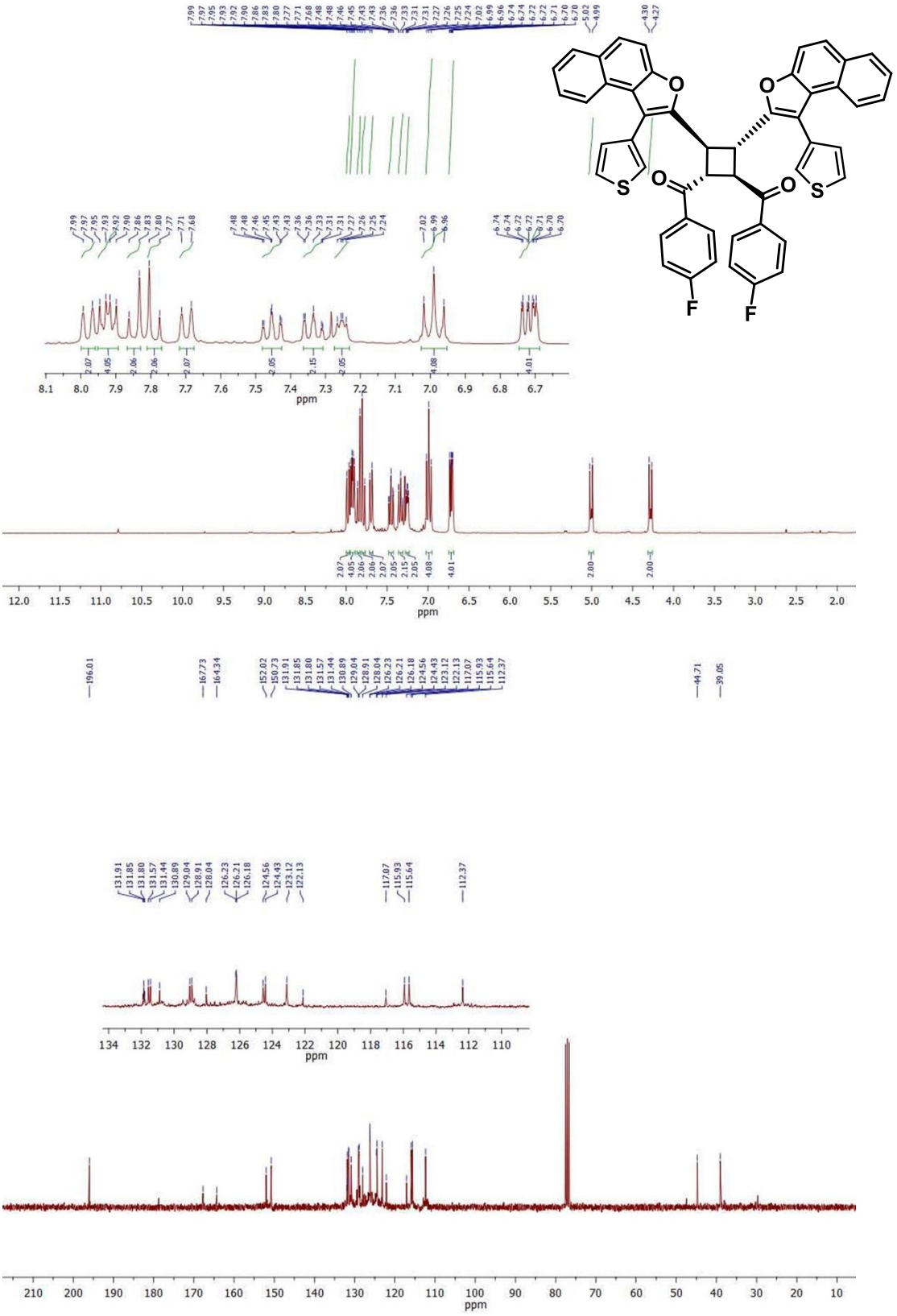




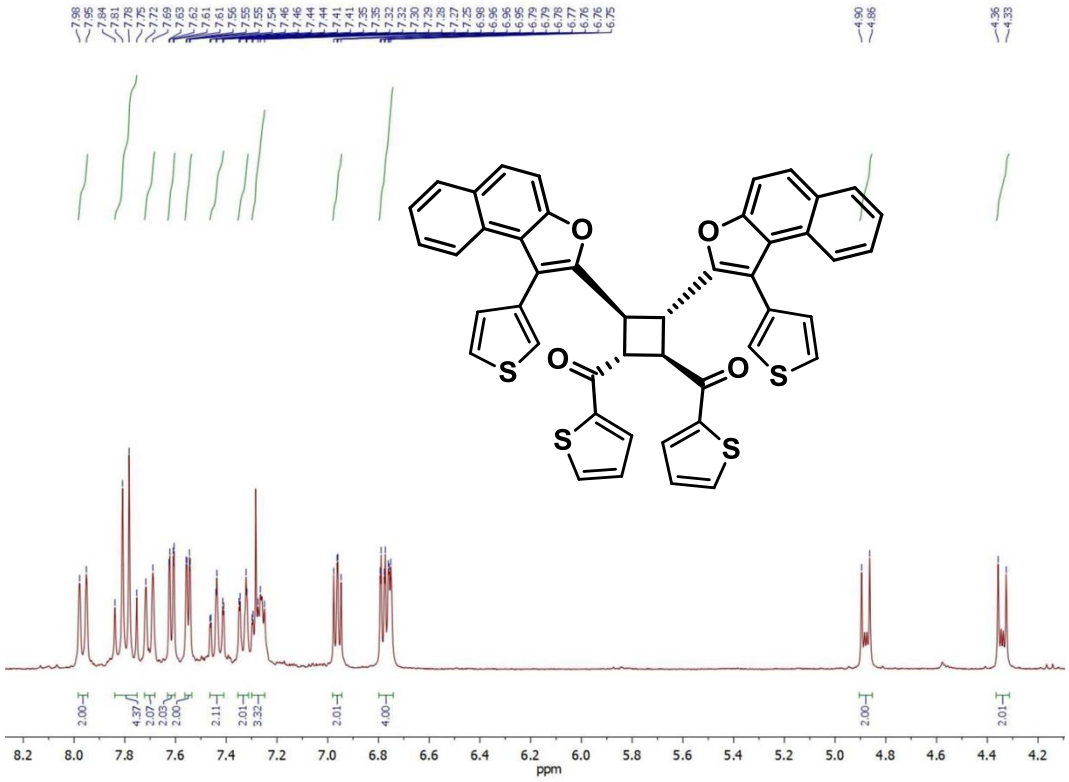
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-chlorophenyl)methanone) (2chh-a)

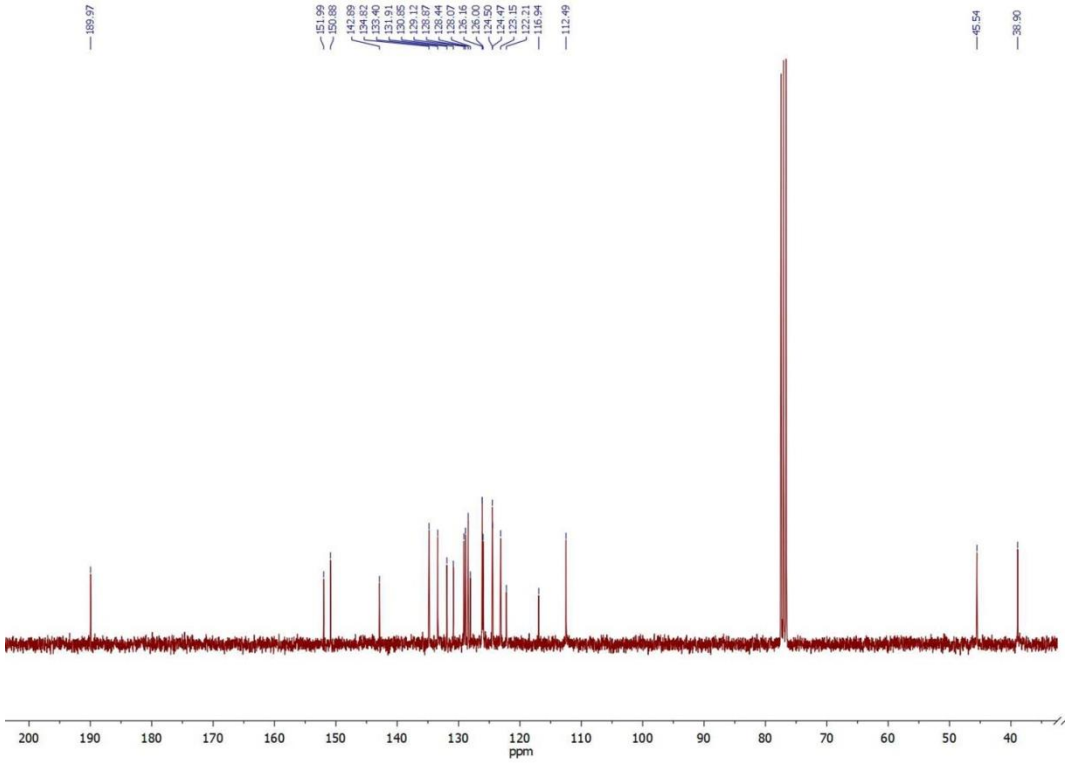


((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-fluorophenyl)methanone) (2dhh-a)

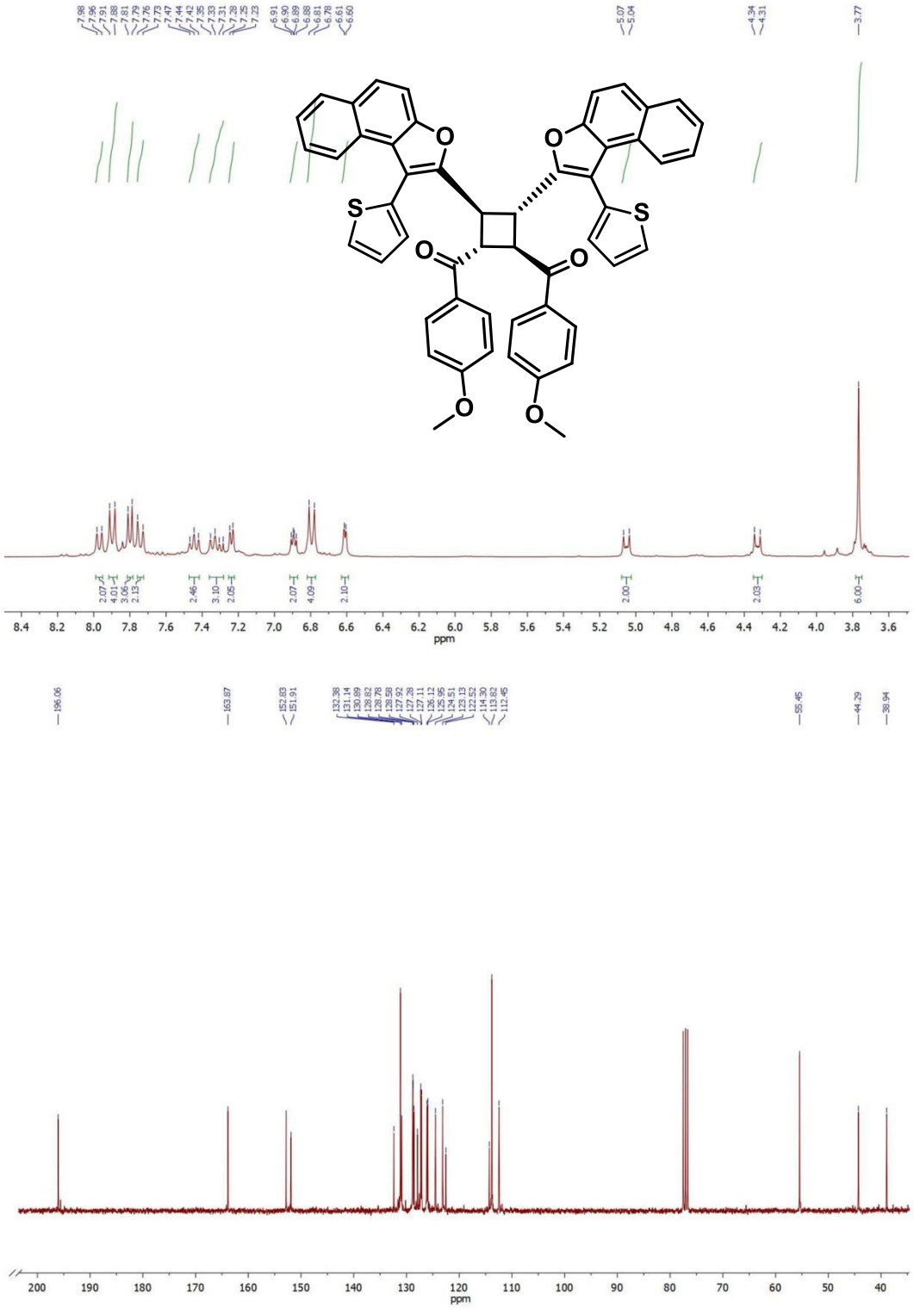


((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(thiophen-2-ylmethanone) (2ehh-a)

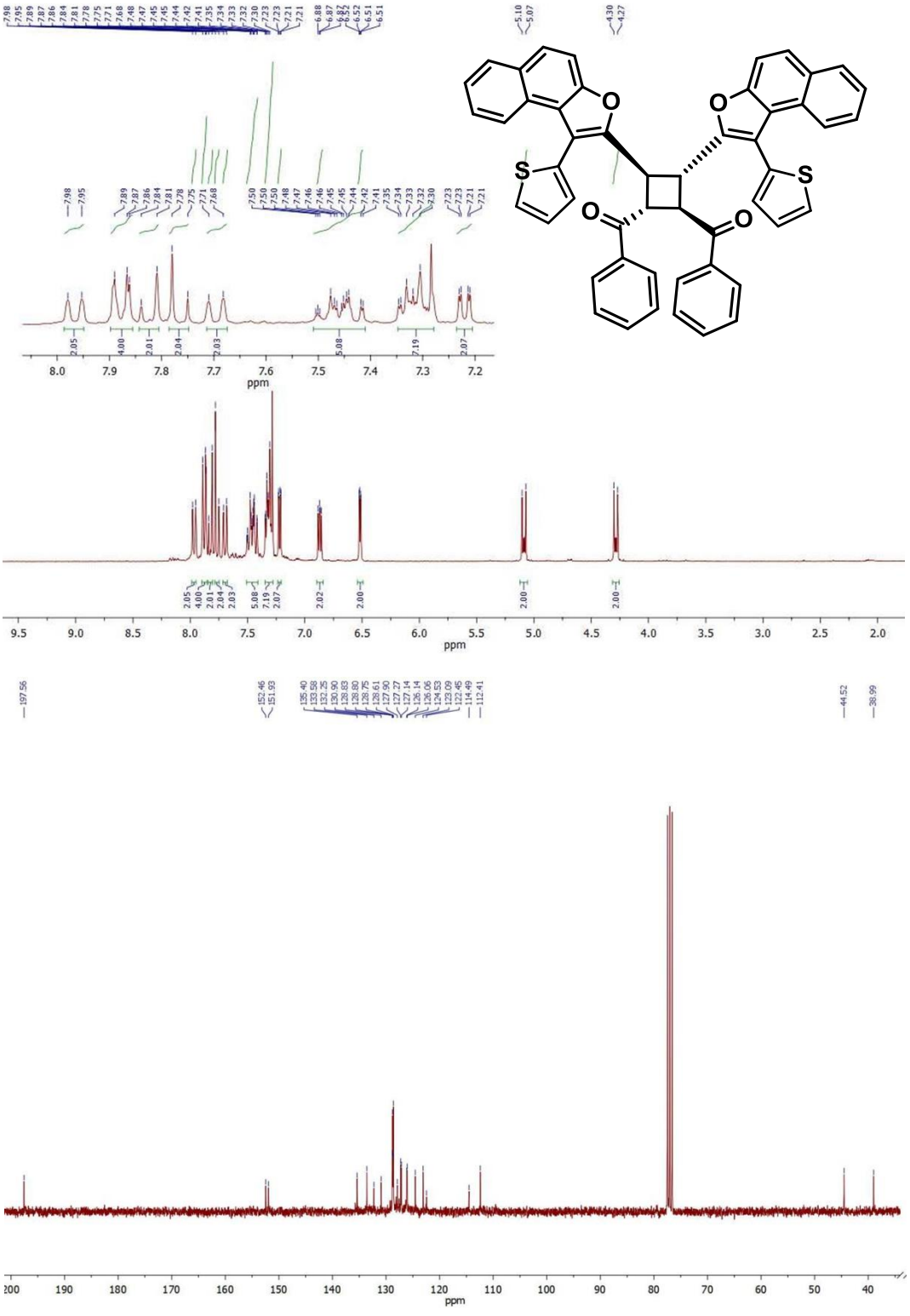




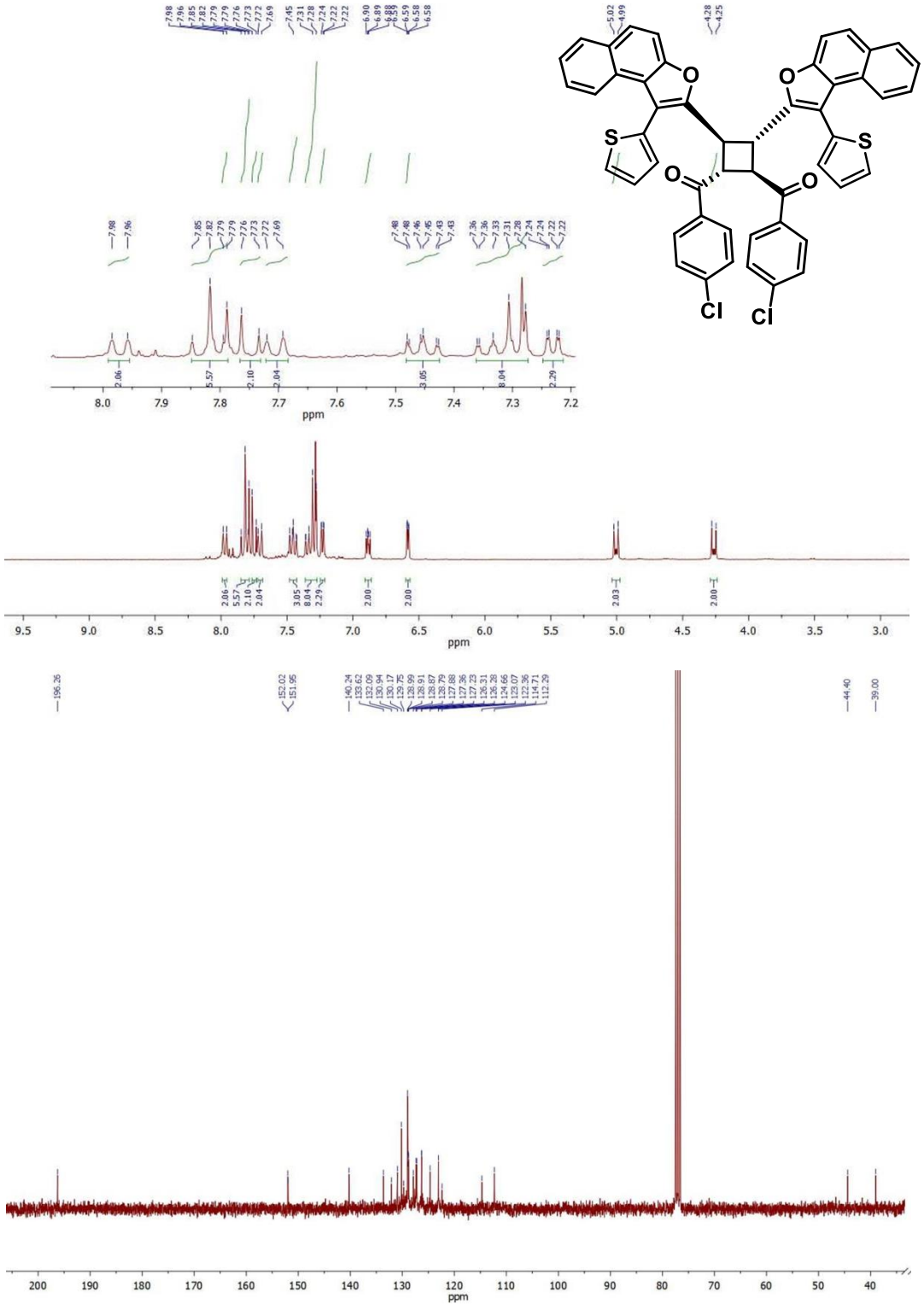
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2fhh-a)



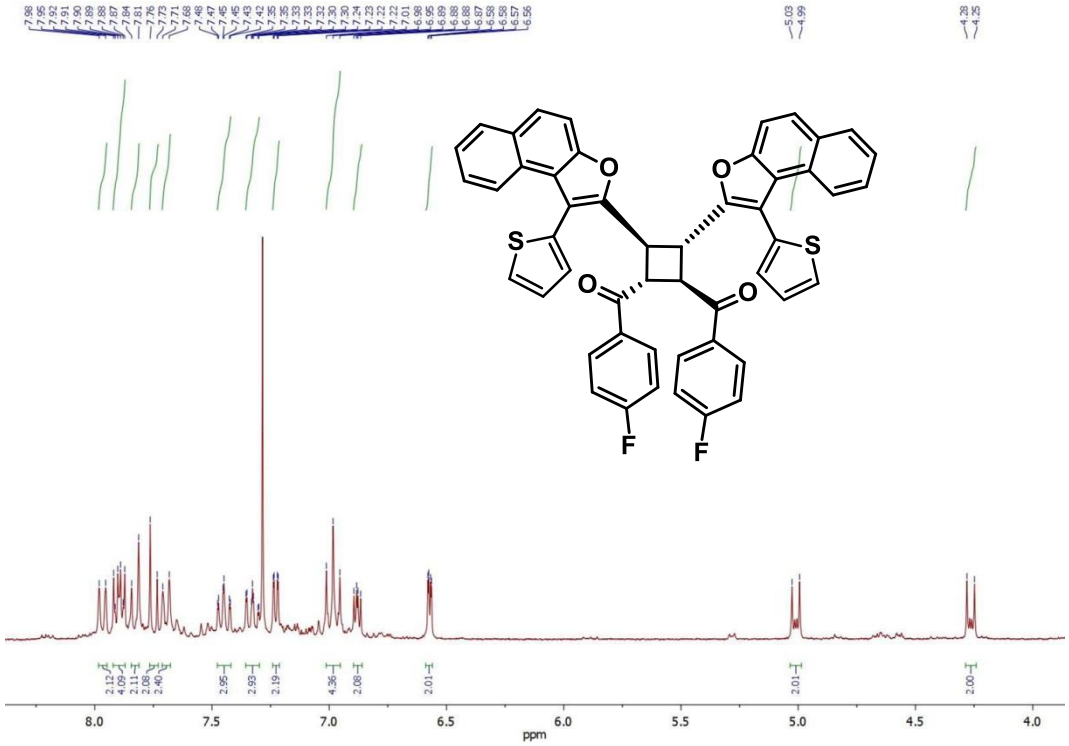
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (2ghh-a)

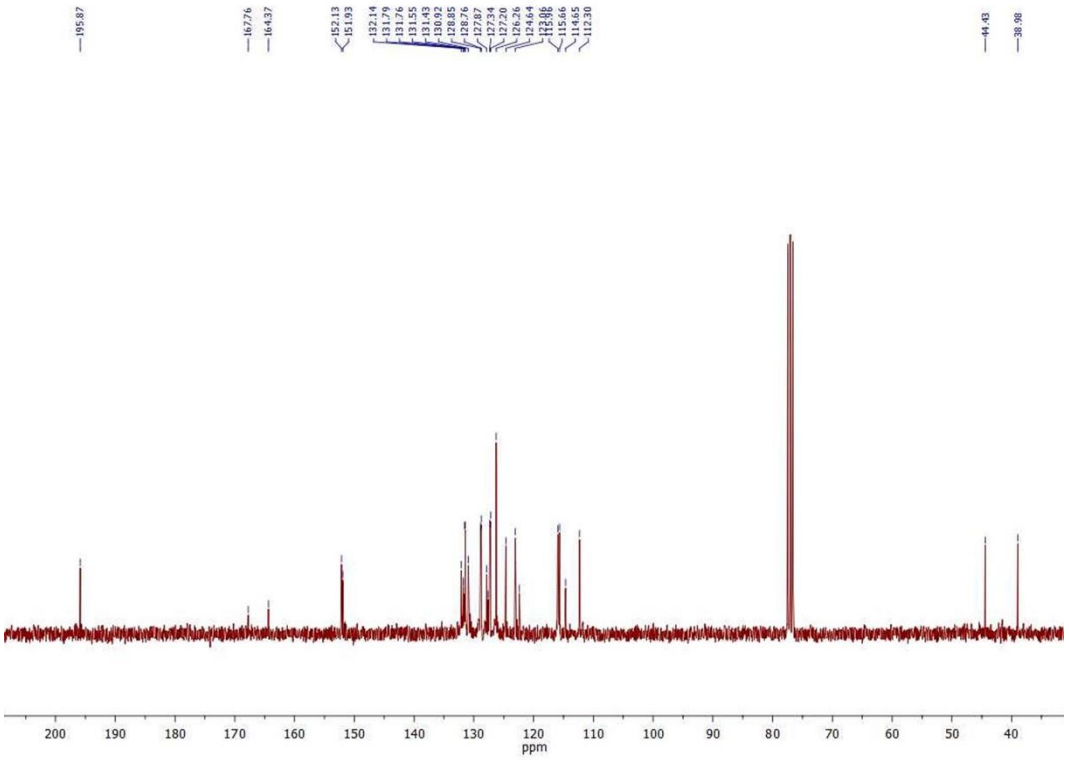


((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-chlorophenyl)methanone) (2hhh-a)

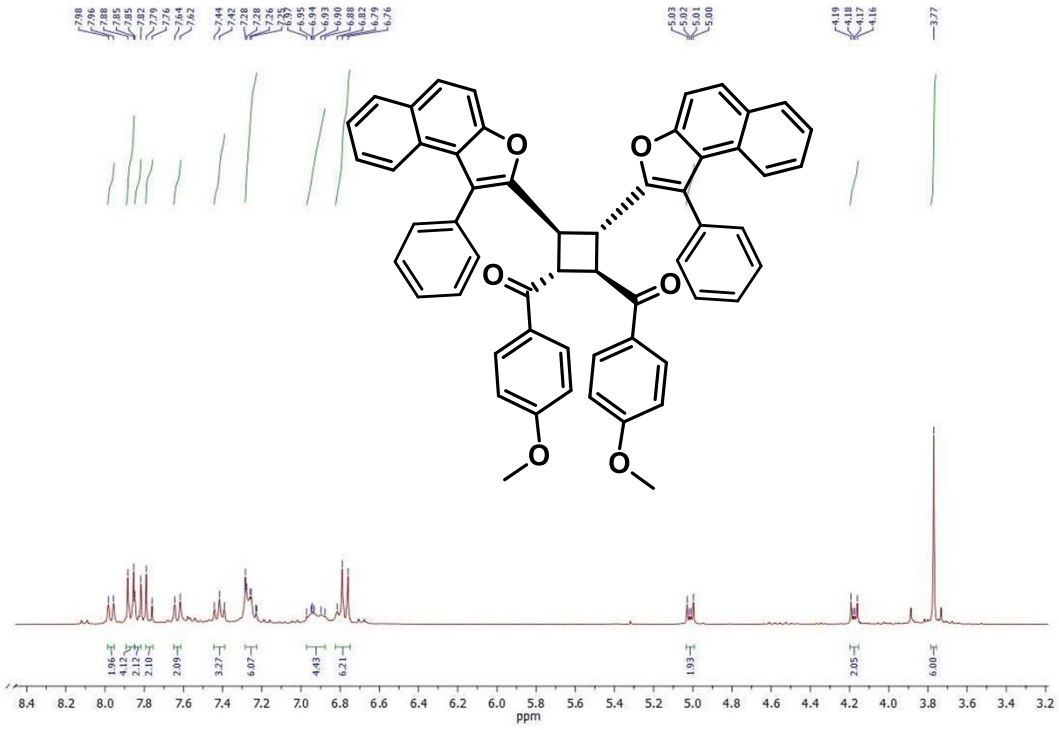


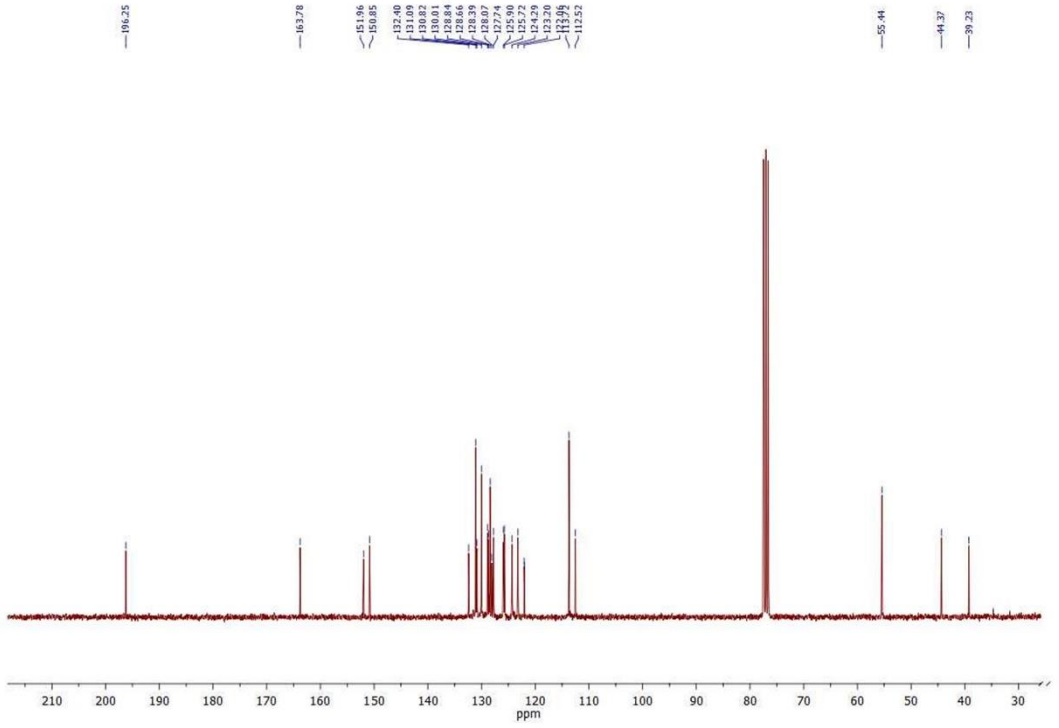
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-fluorophenyl)methanone) (2ihh-a)



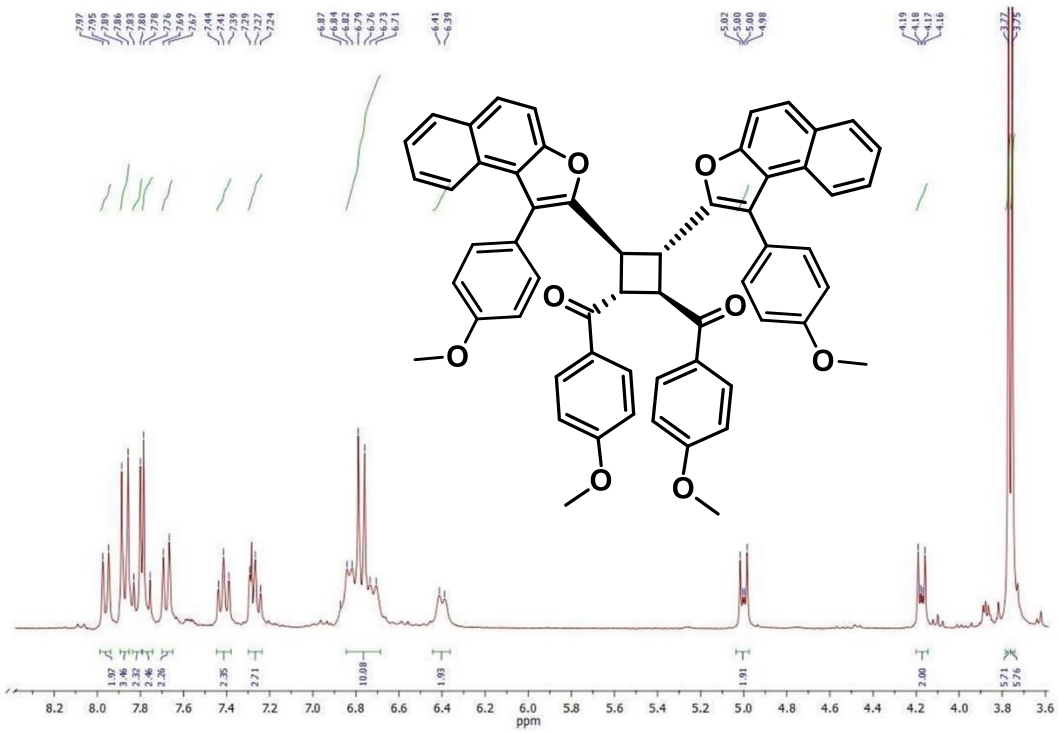


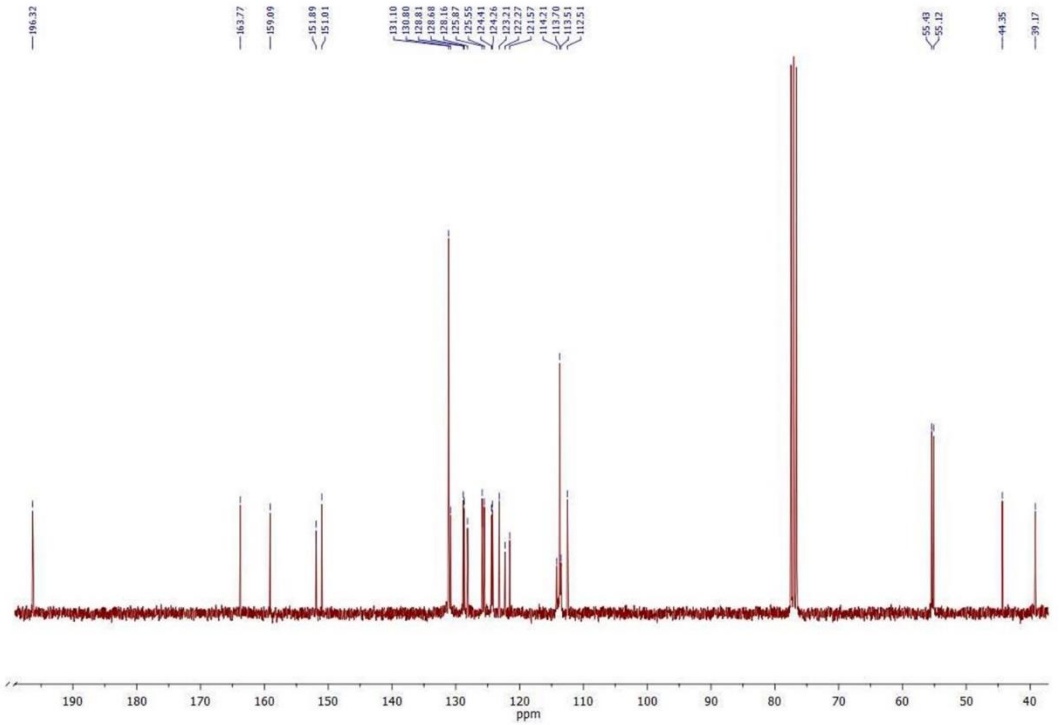
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-phenylnaphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2khh-a)



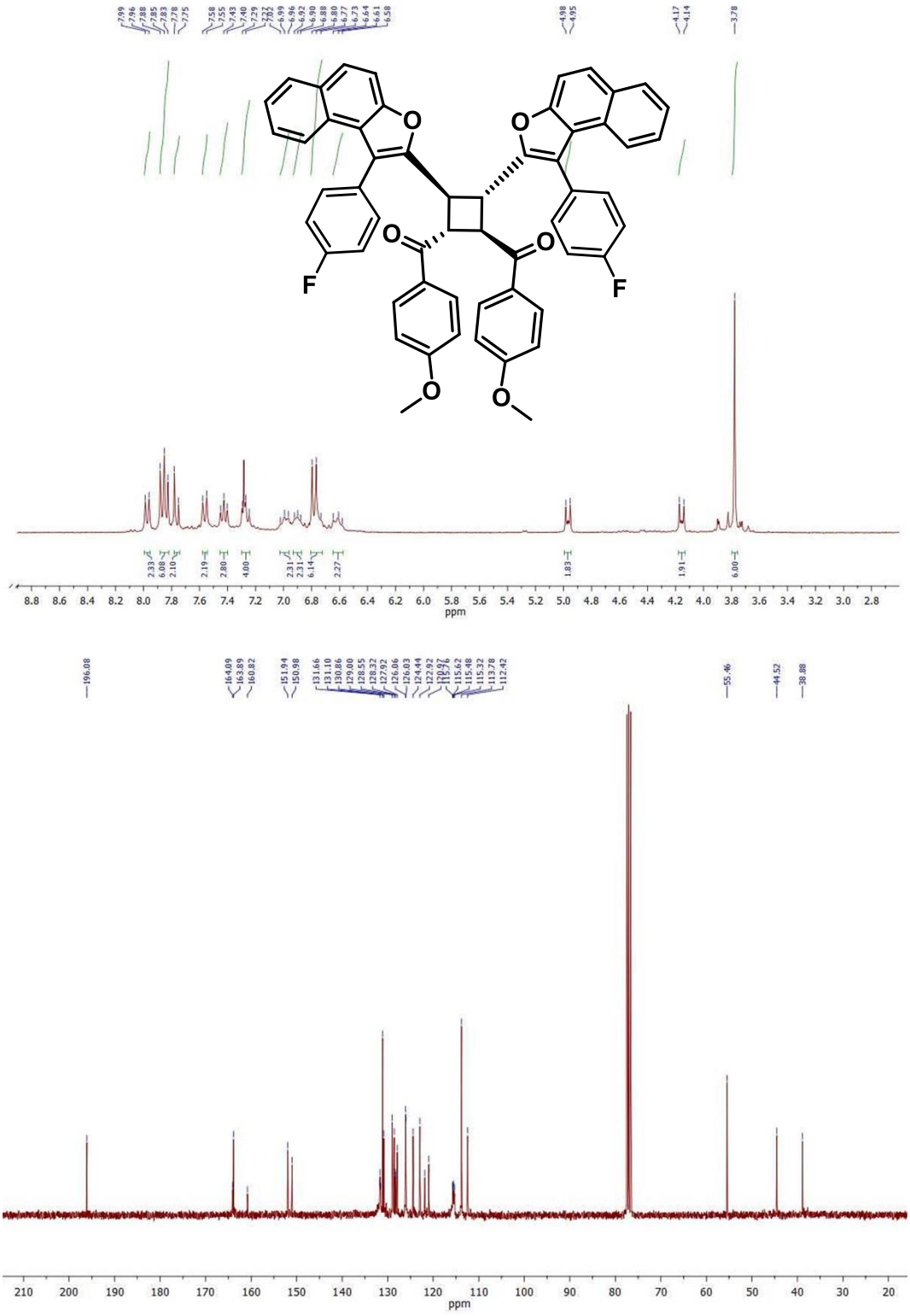


((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2lhh-a)

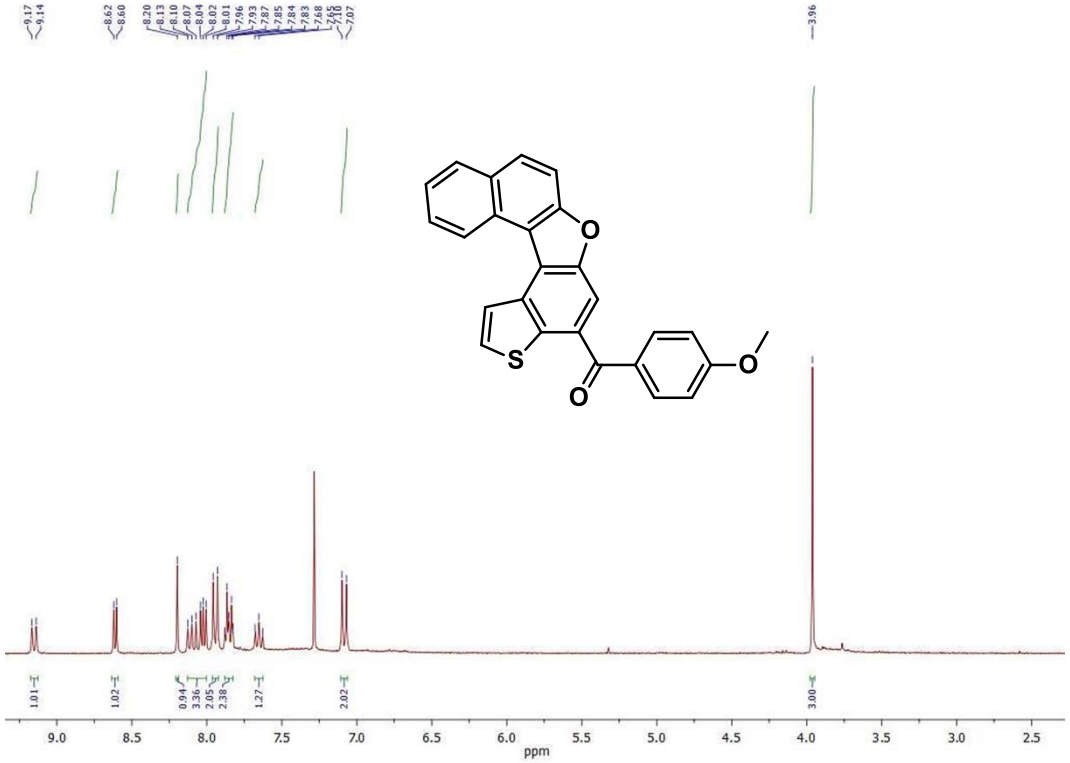


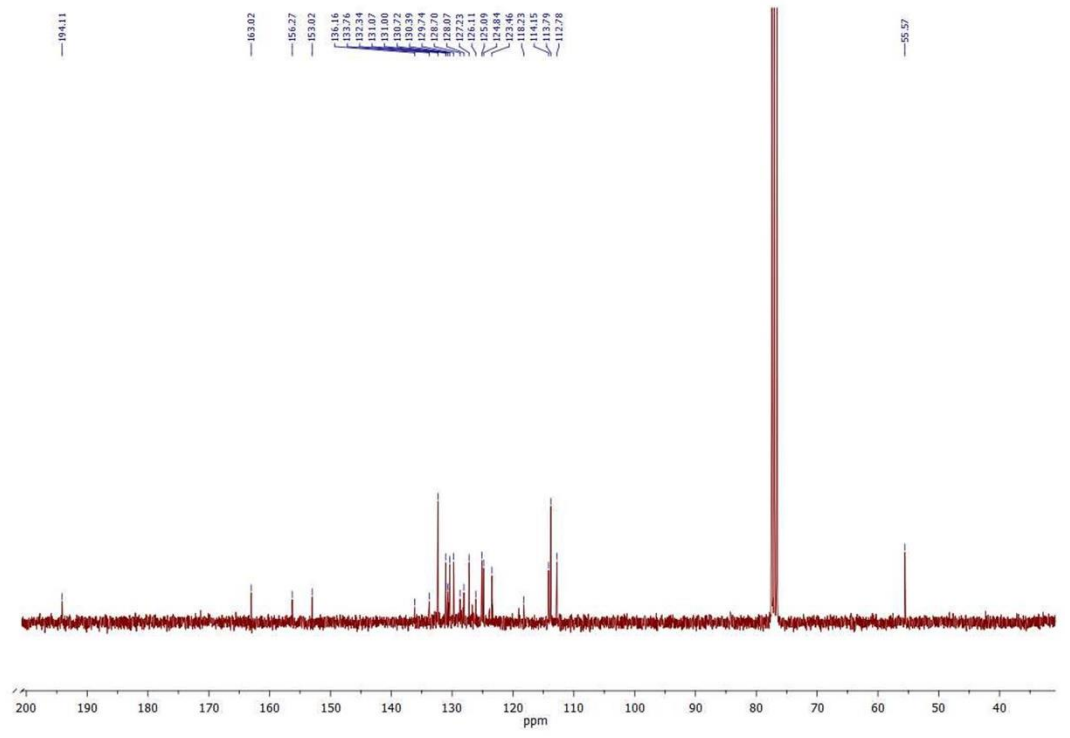


((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-fluorophenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2nhh-a)

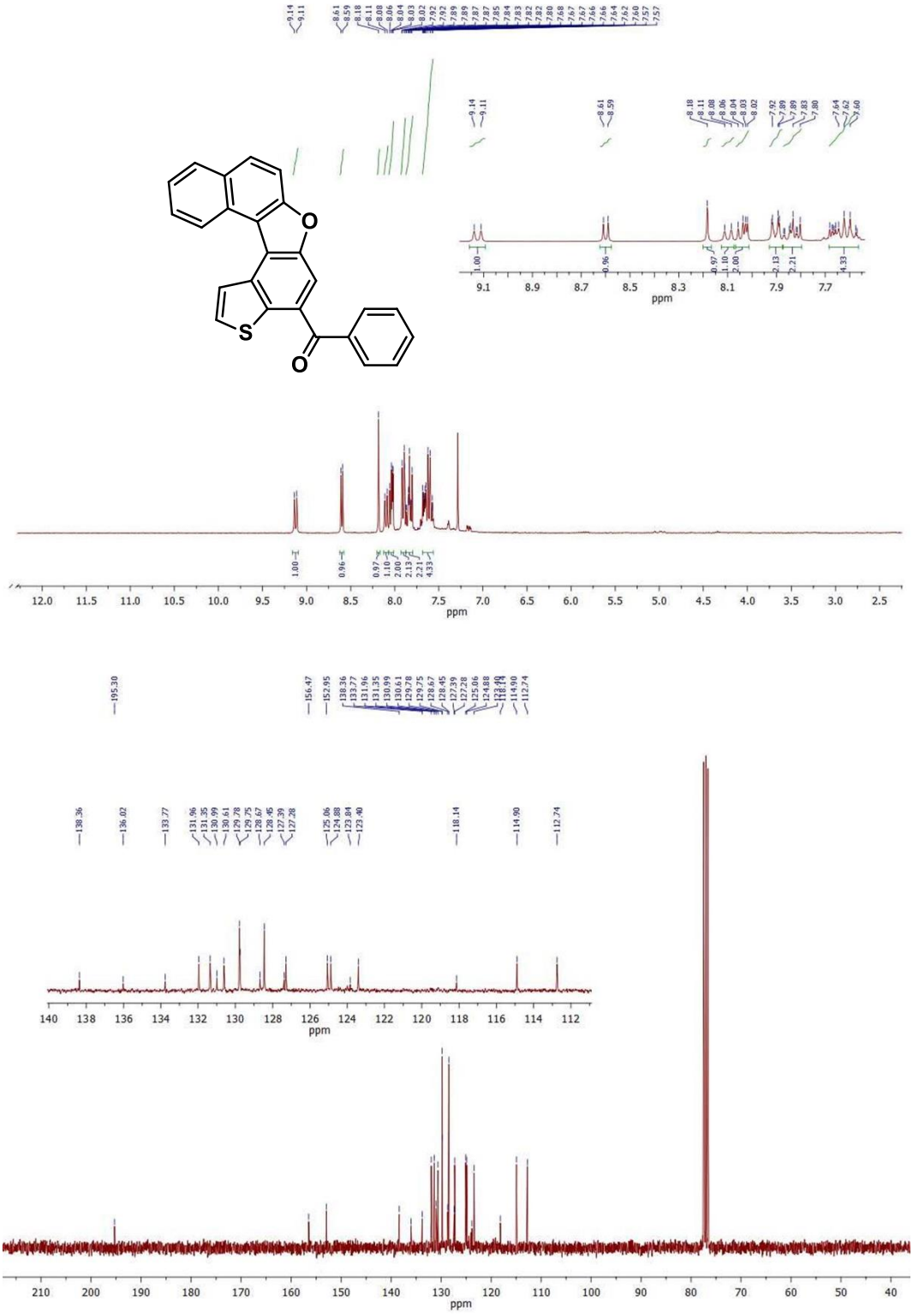


(4-methoxyphenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3a)

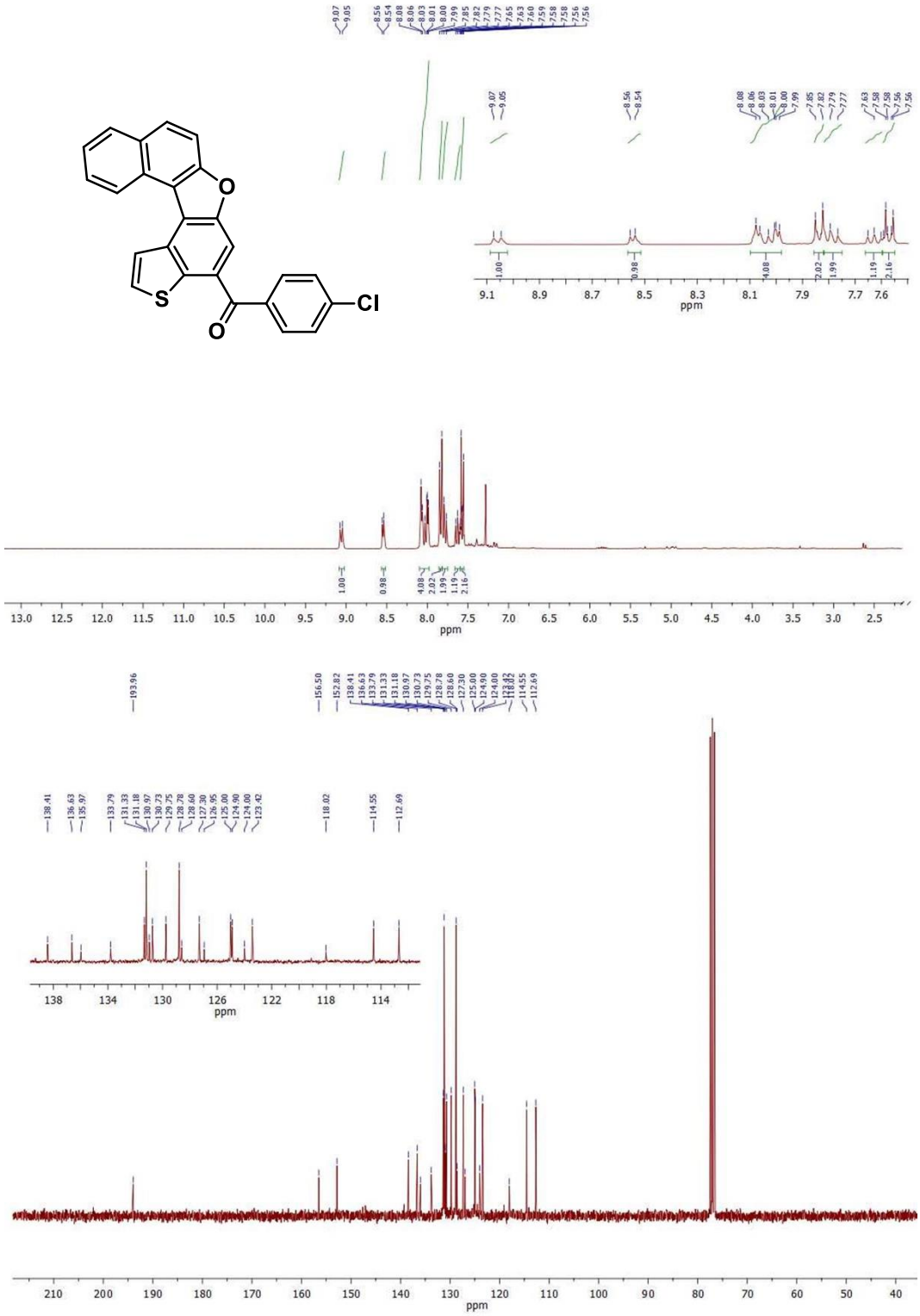




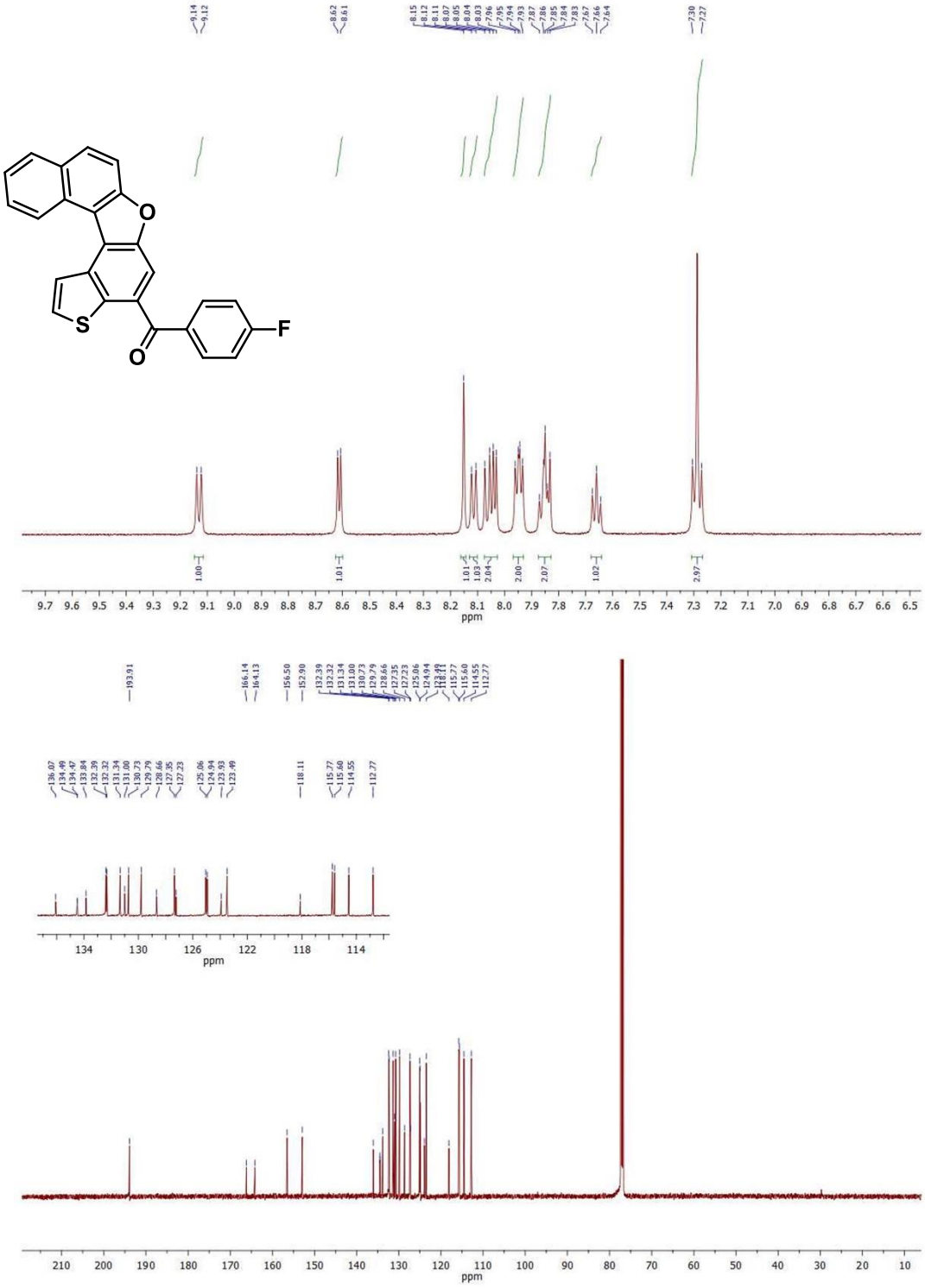
Naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl(phenyl)methanone (3b)



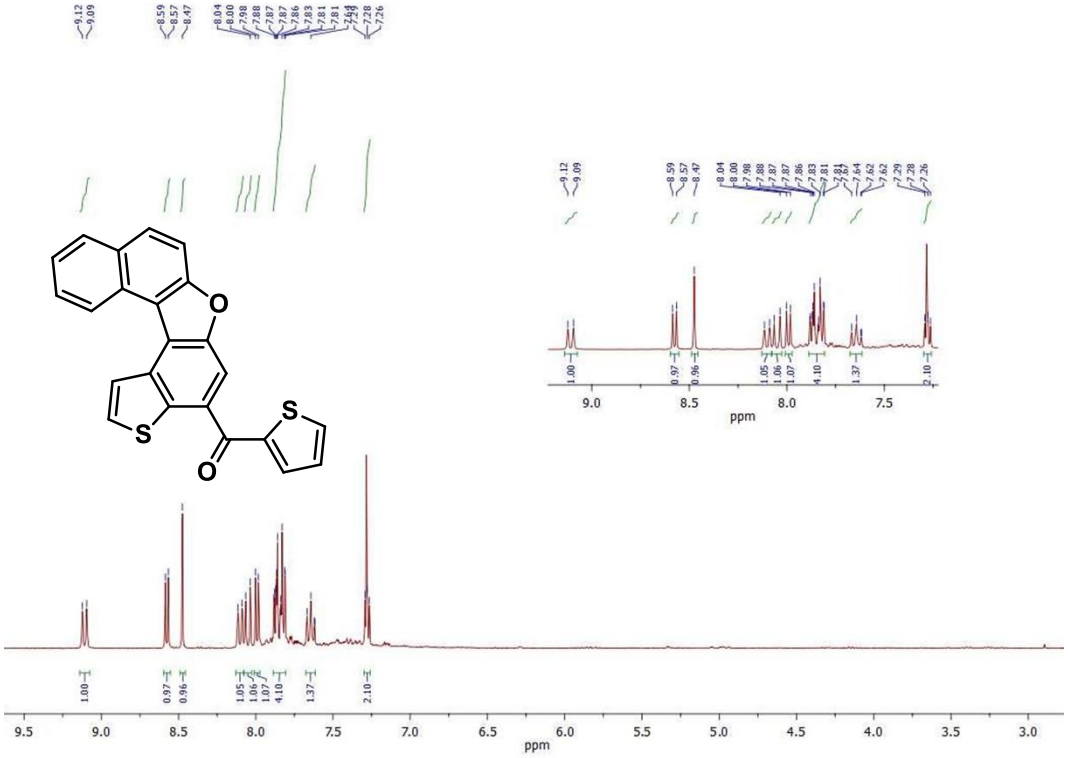
(4-chlorophenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3c)

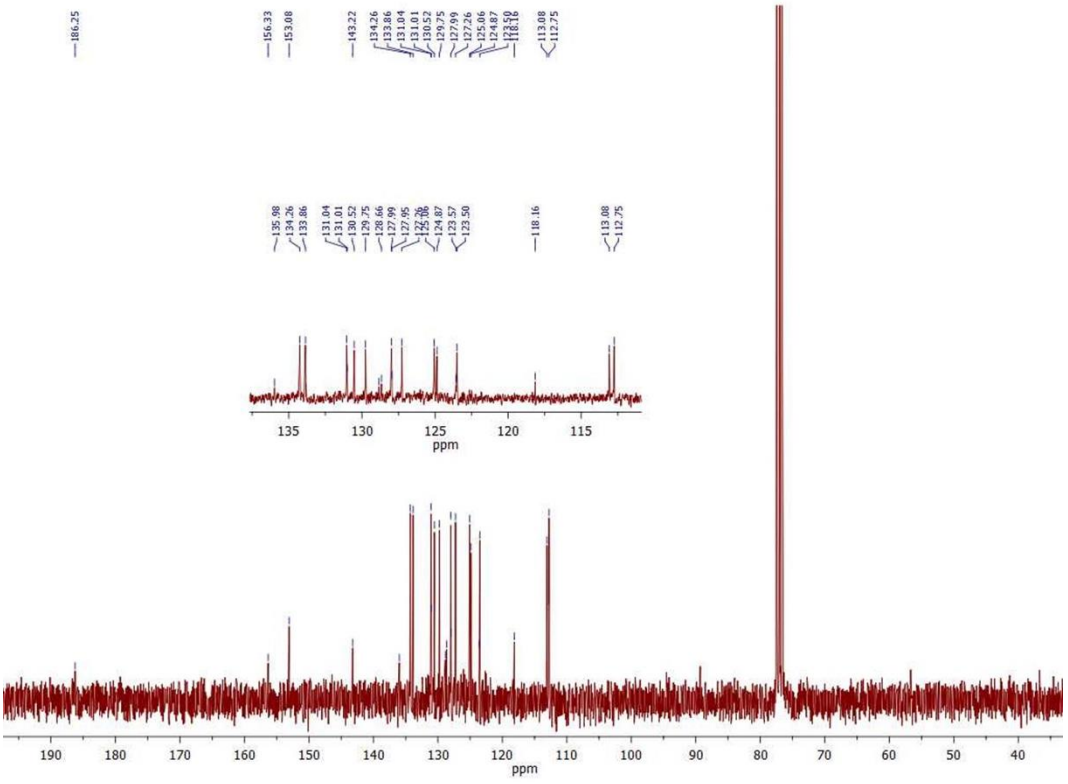


(4-fluorophenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3d)

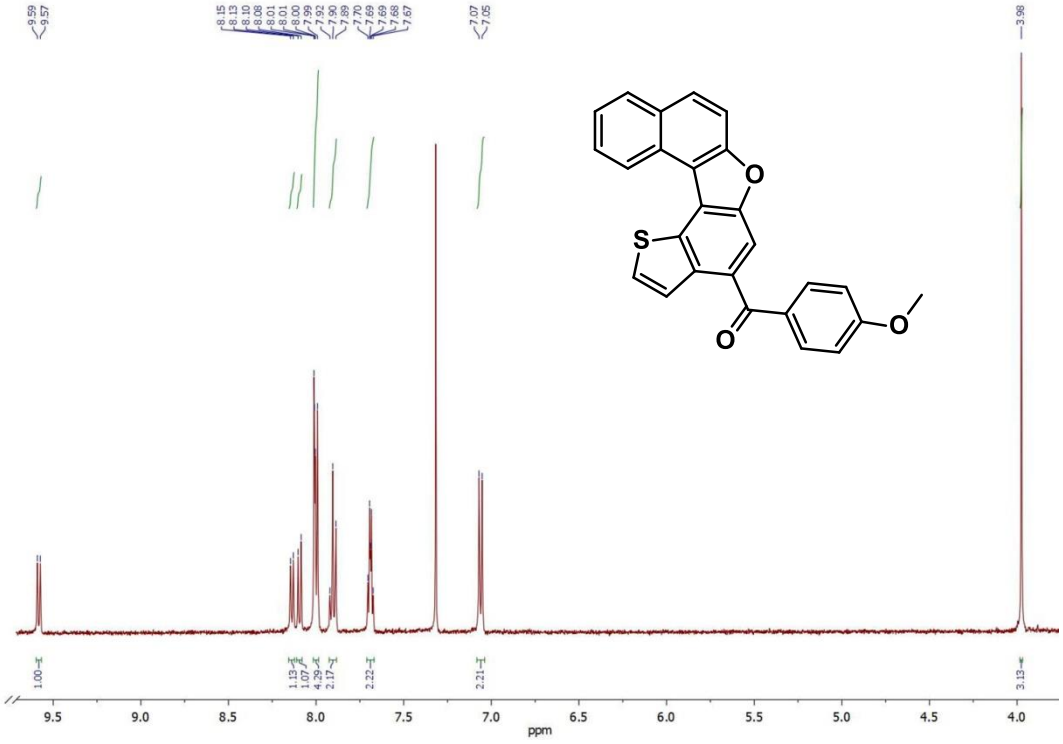


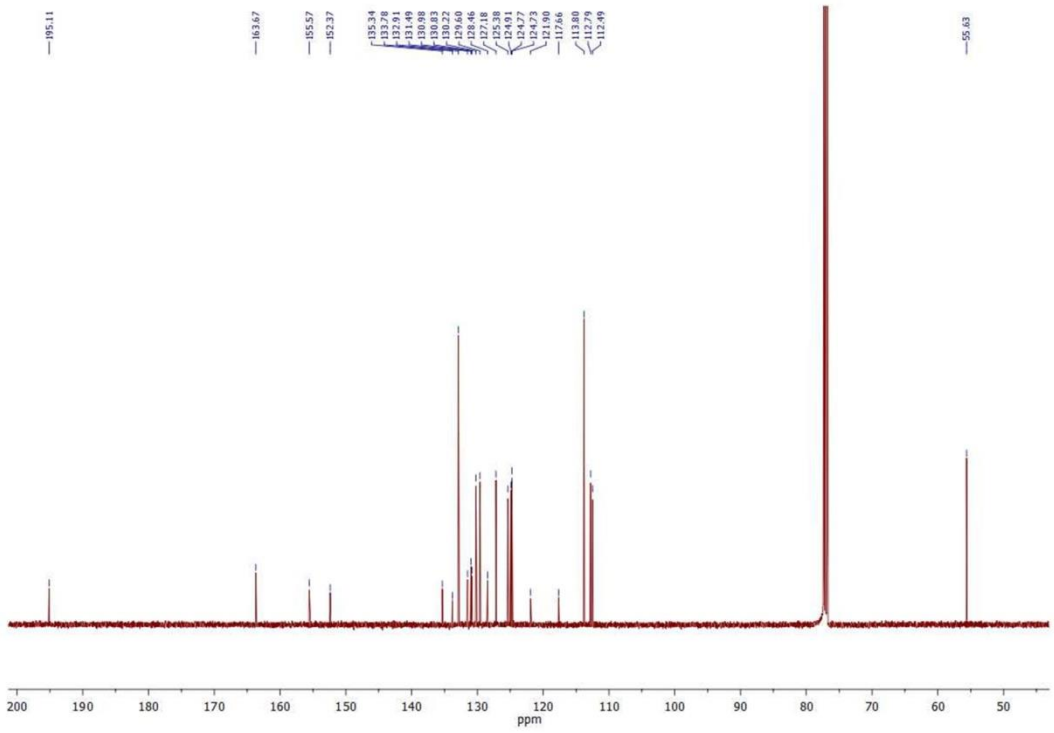
Naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl(thiophen-2-yl)methanone (3e)



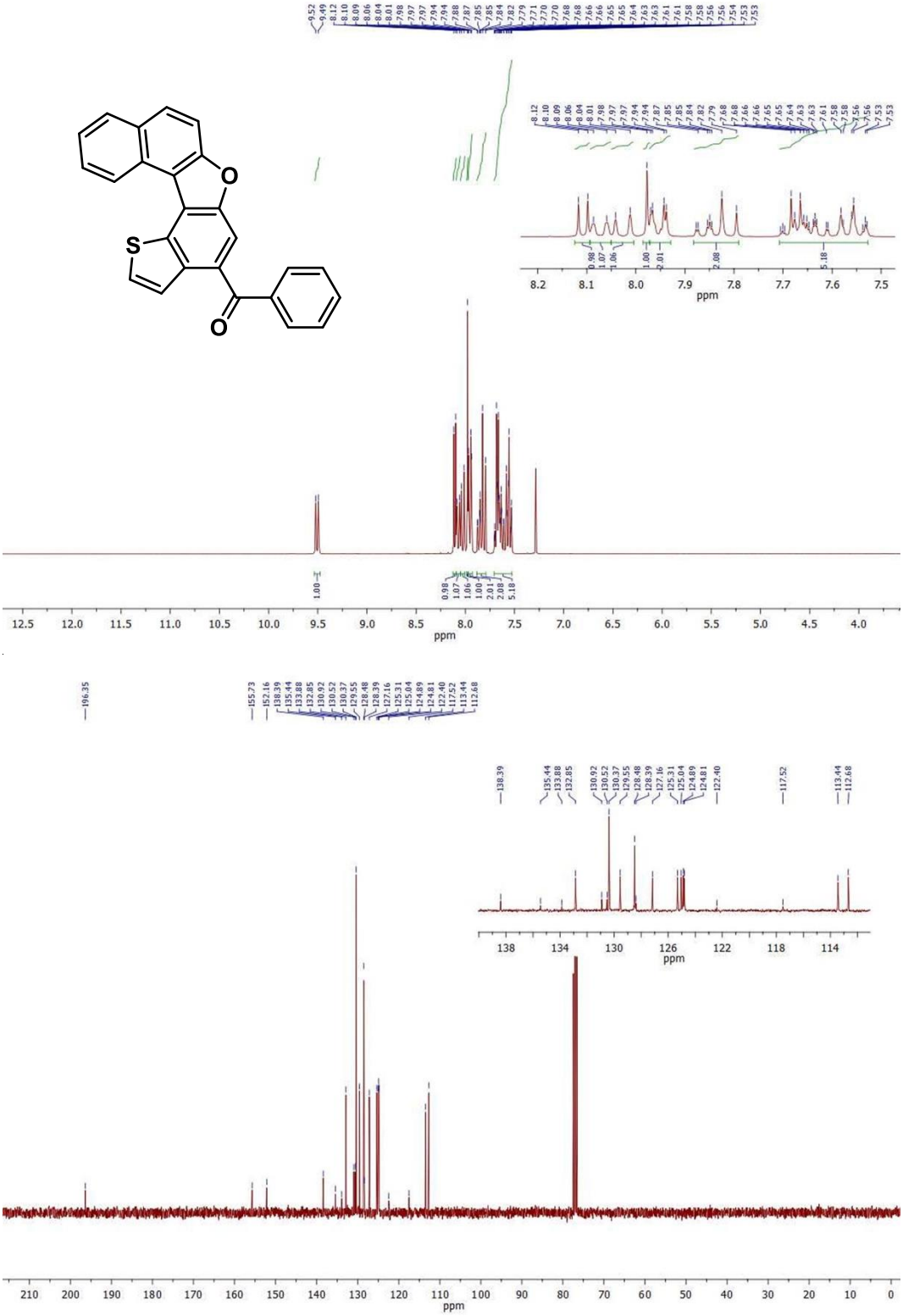


(4-methoxyphenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3f)

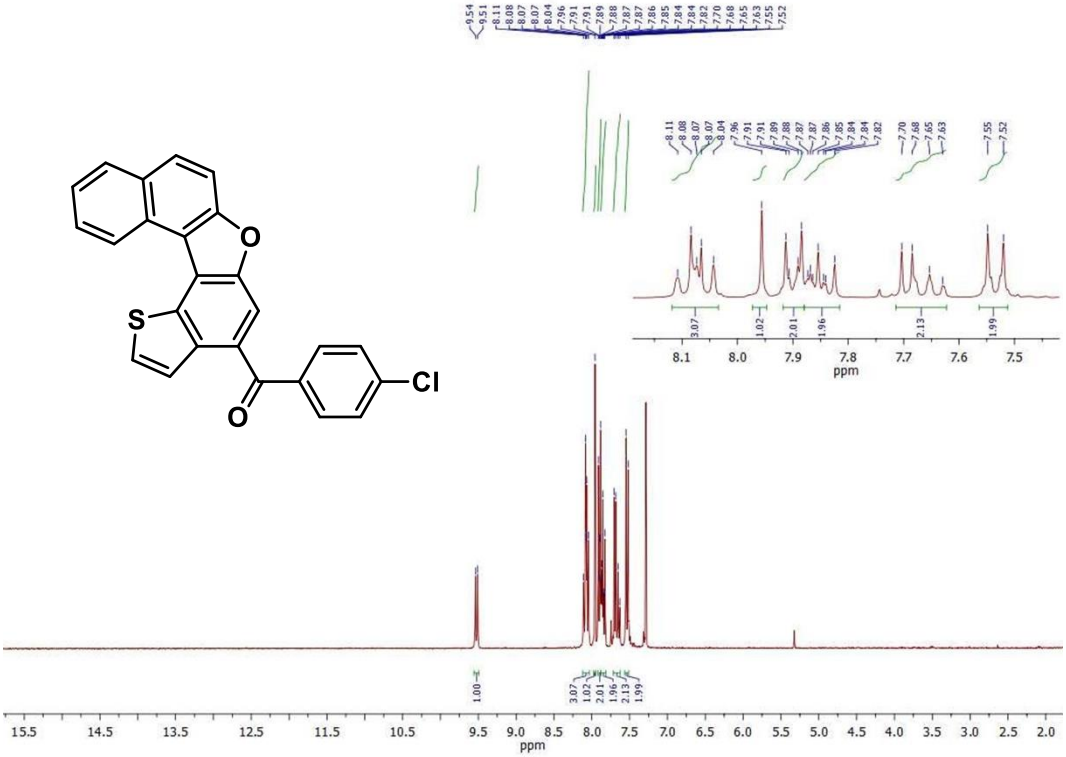


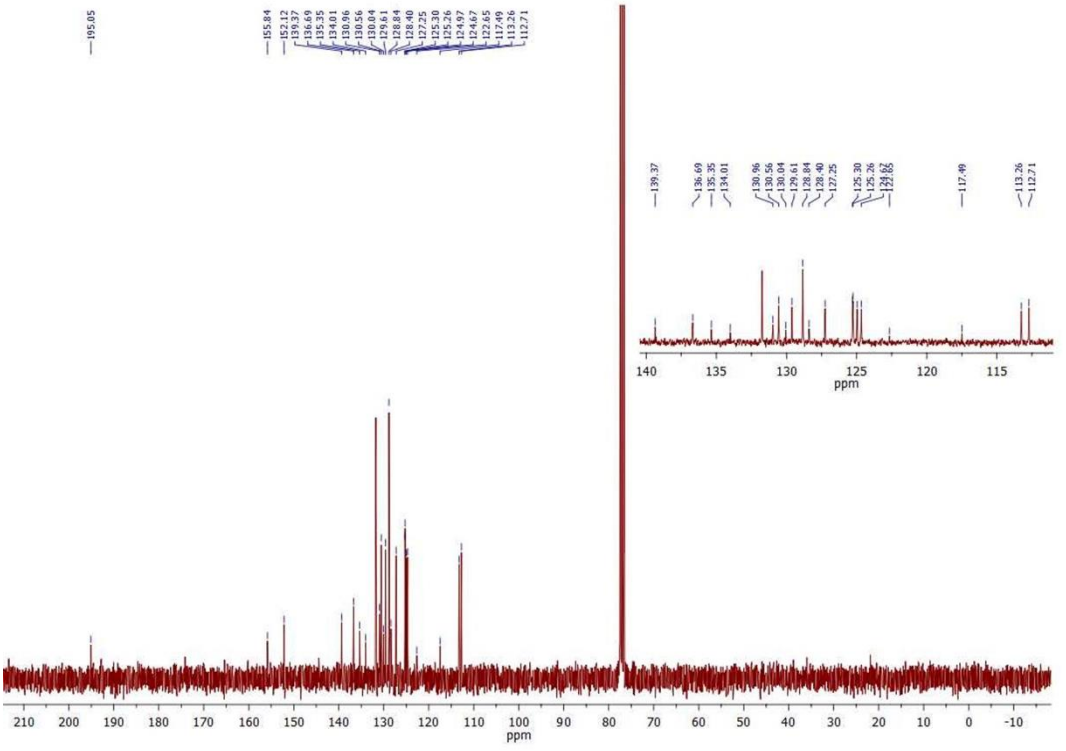


Naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl(phenyl)methanone (3g)

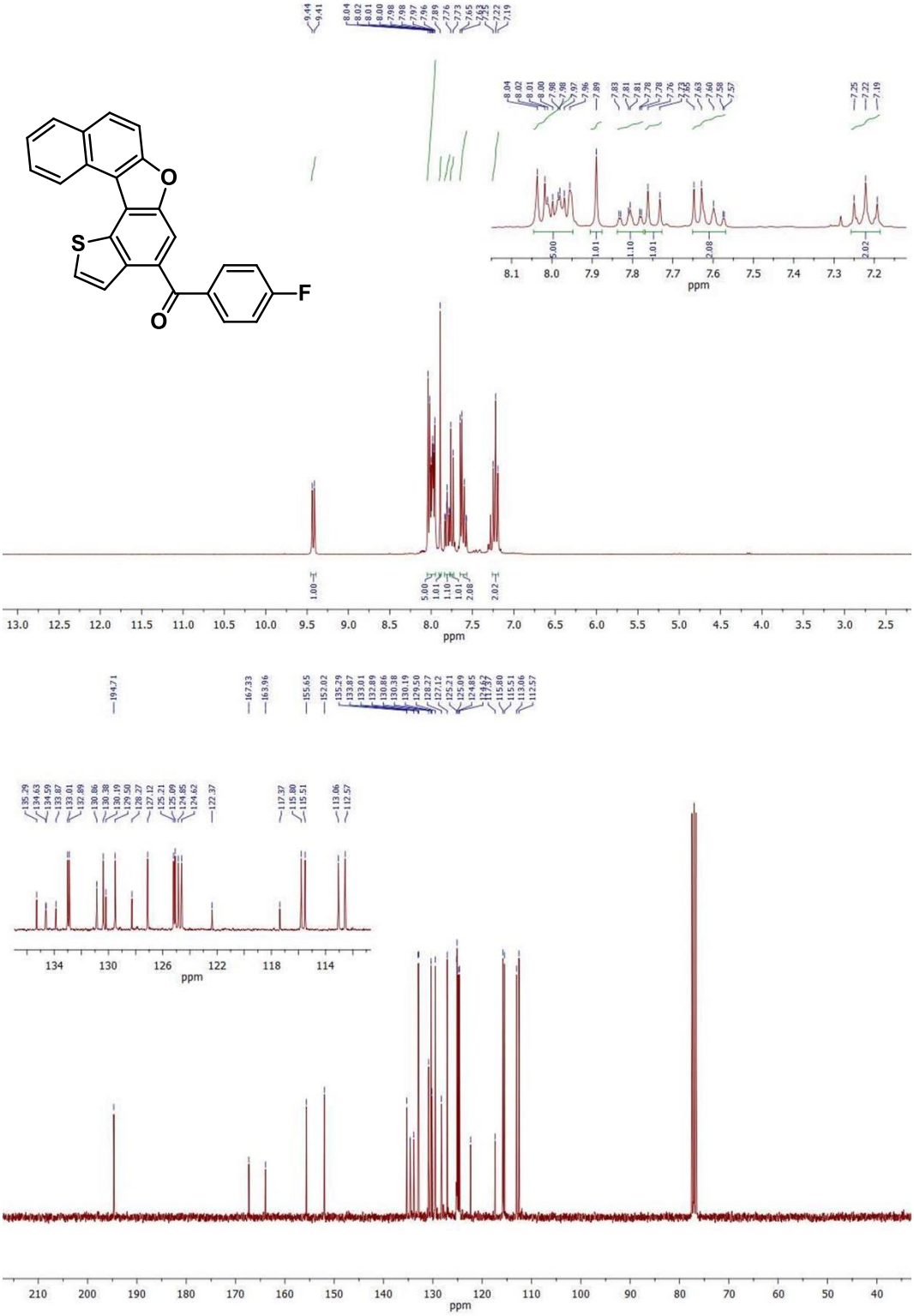


(4-chlorophenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3h)

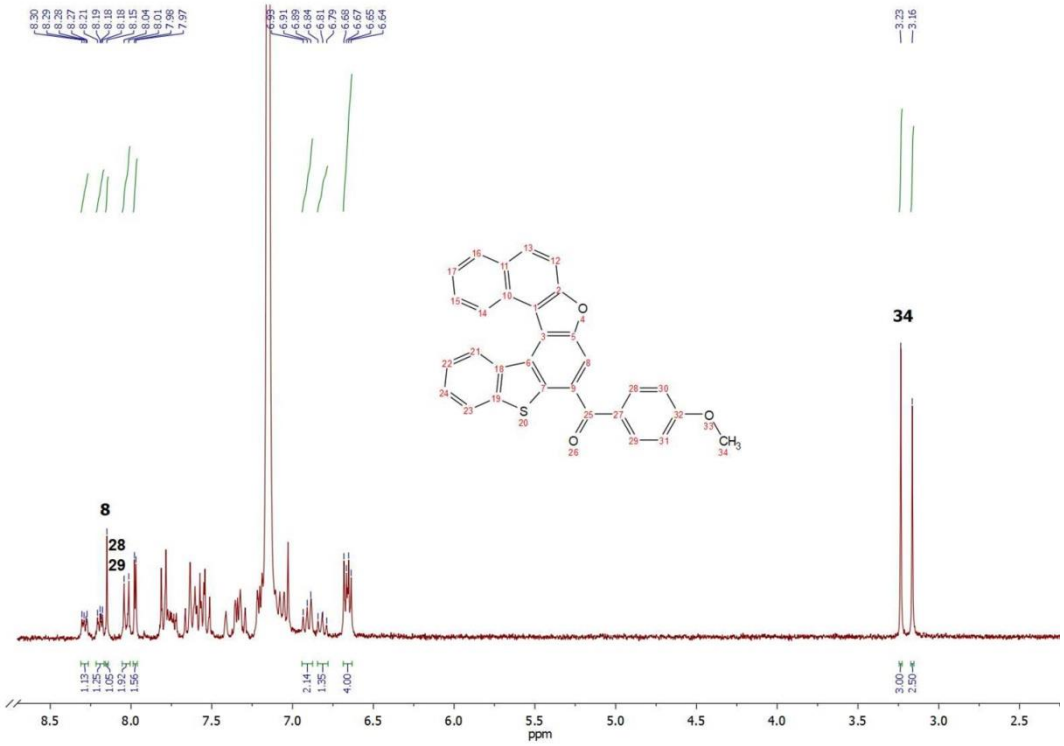




(4-fluorophenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3i)



Benzo[4,5]thieno[3,2-*e*]naphtho[2,1-*b*]benzofuran-6-yl(4-methoxyphenyl)methanone (3j)

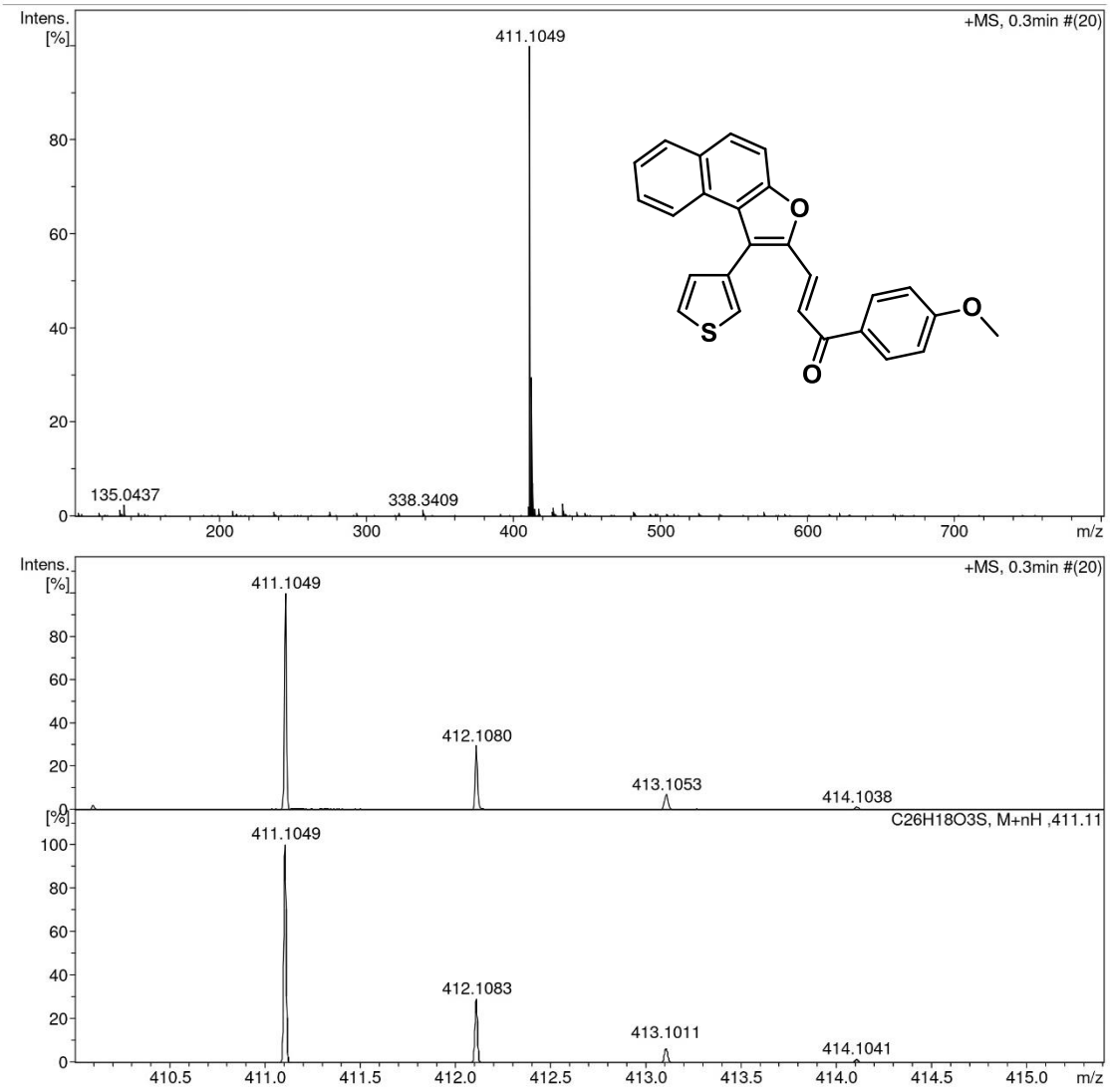


XI. Copies of HRMS spectra

(*E*)-1-(4-methoxyphenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1a)

Acquisition Parameter

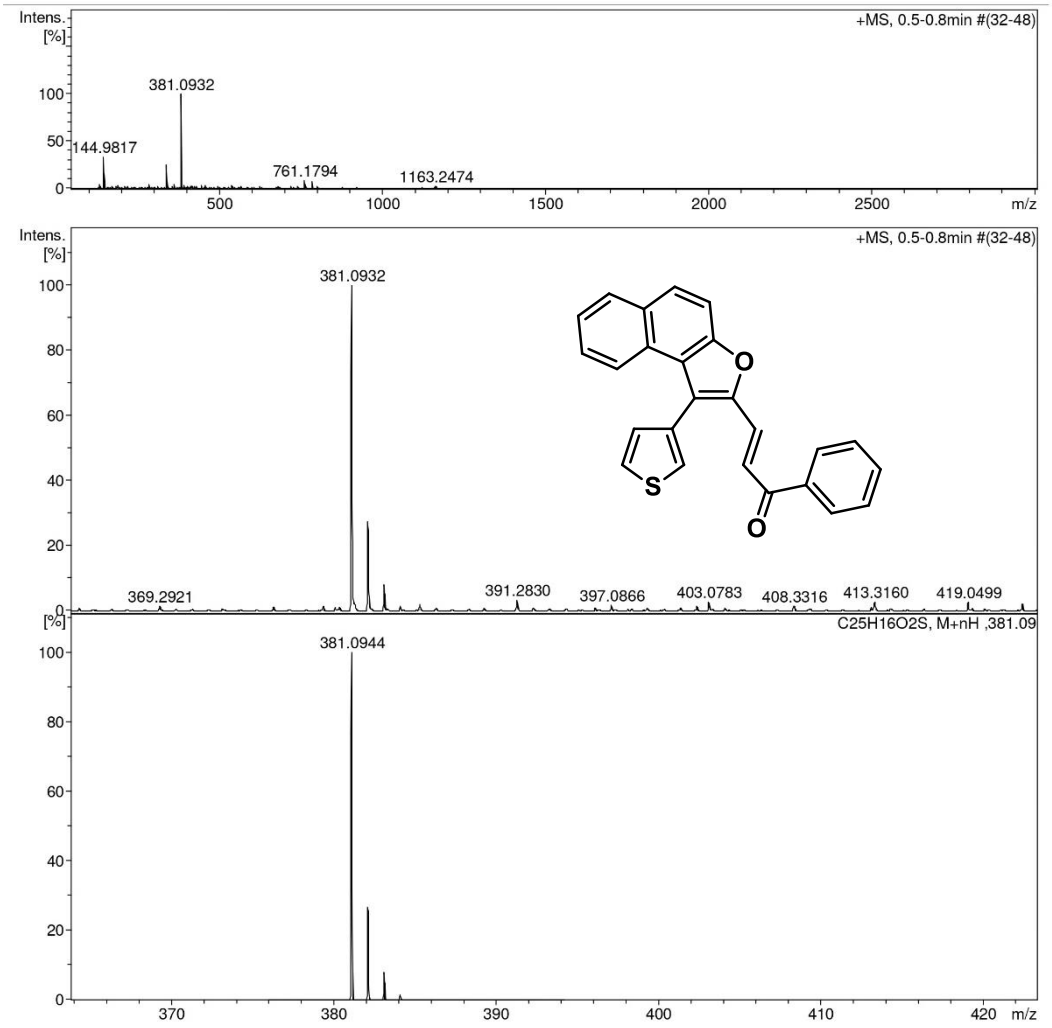
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(*E*)-1-phenyl-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1b)

Acquisition Parameter

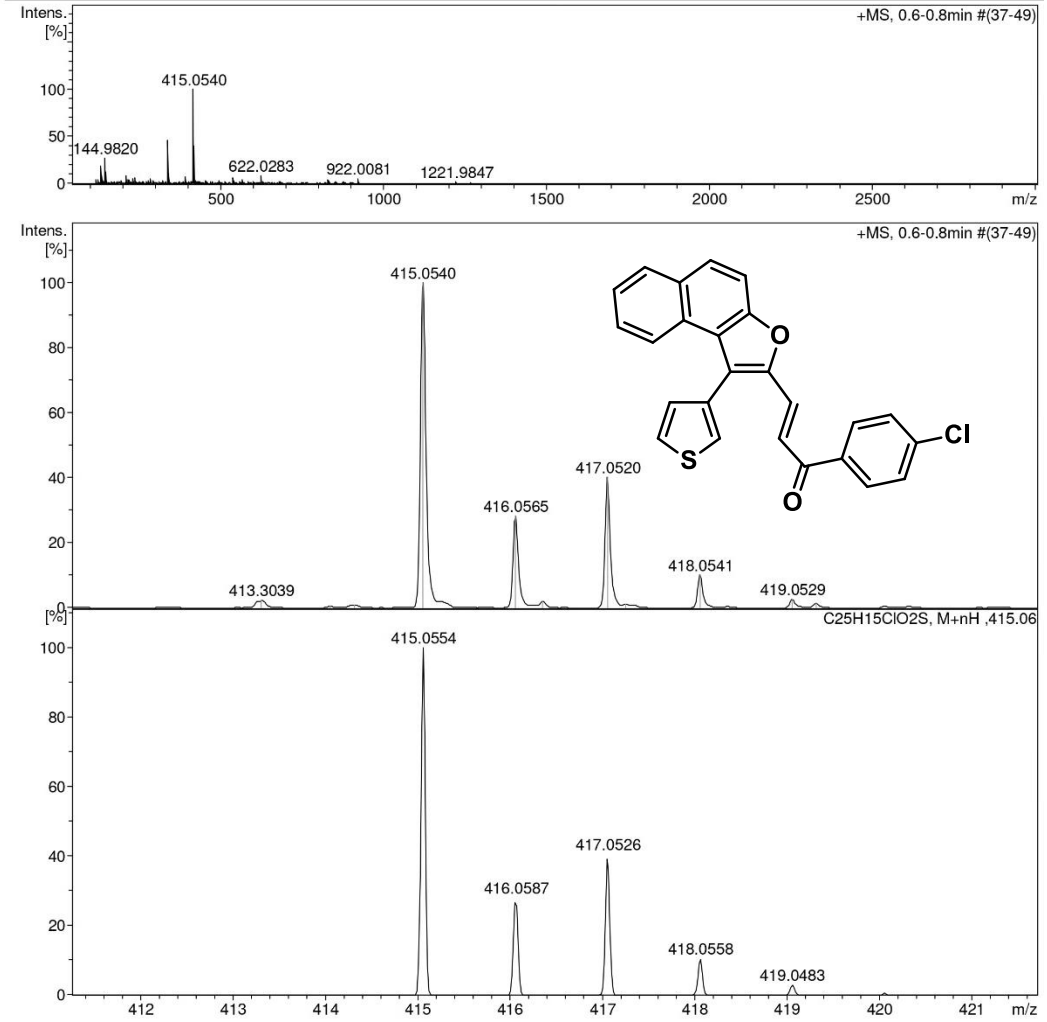
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(*E*)-1-(4-chlorophenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1c)

Acquisition Parameter

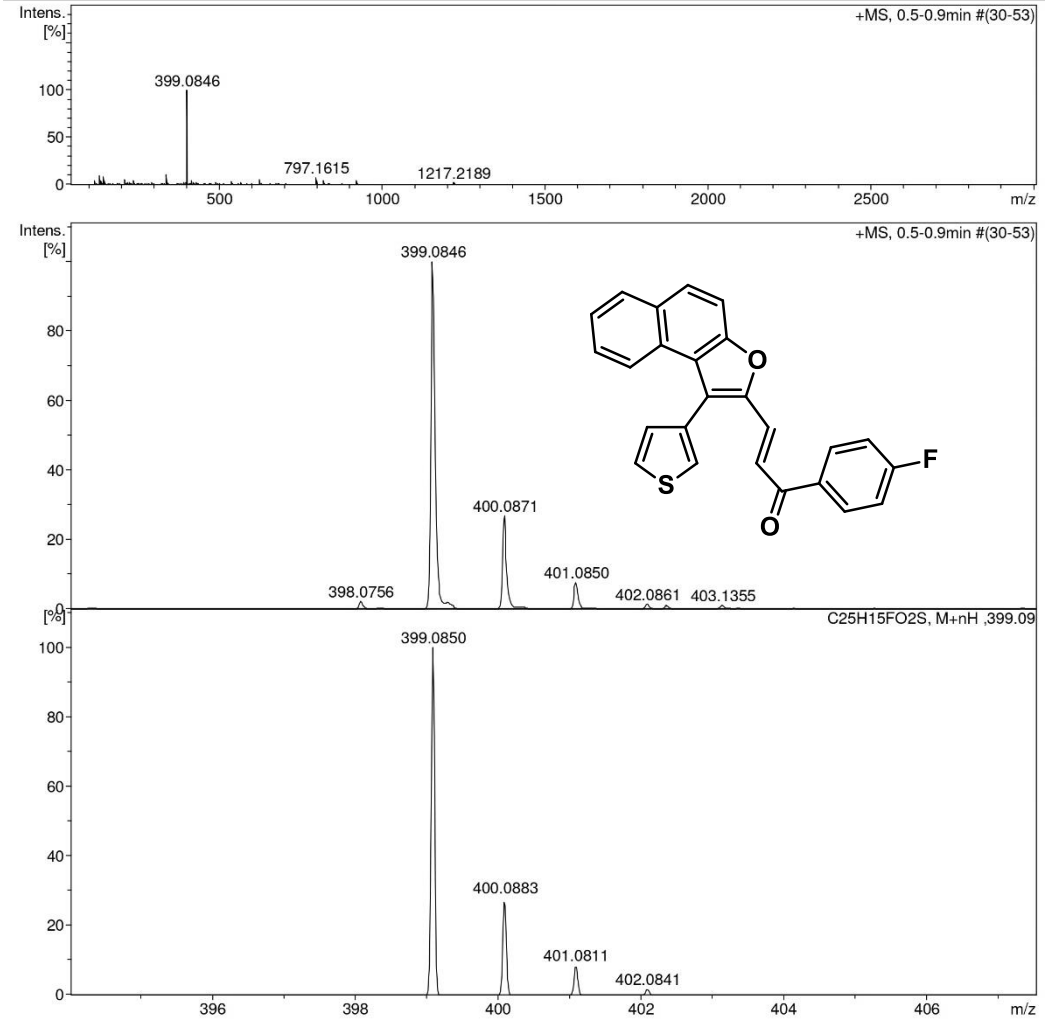
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(*E*)-1-(4-fluorophenyl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1d)

Acquisition Parameter

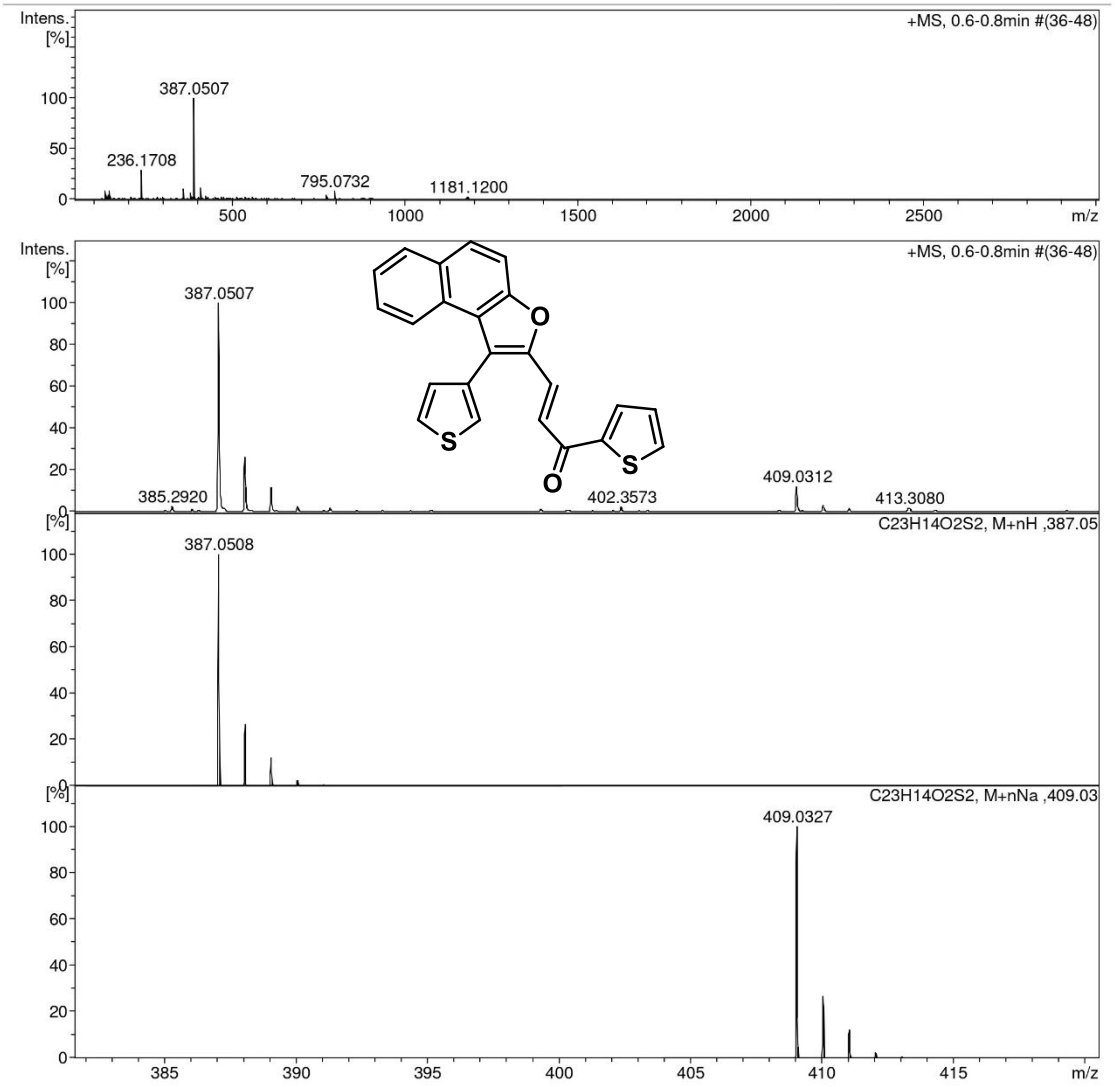
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(*E*)-1-(thiophen-2-yl)-3-(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1e)

Acquisition Parameter

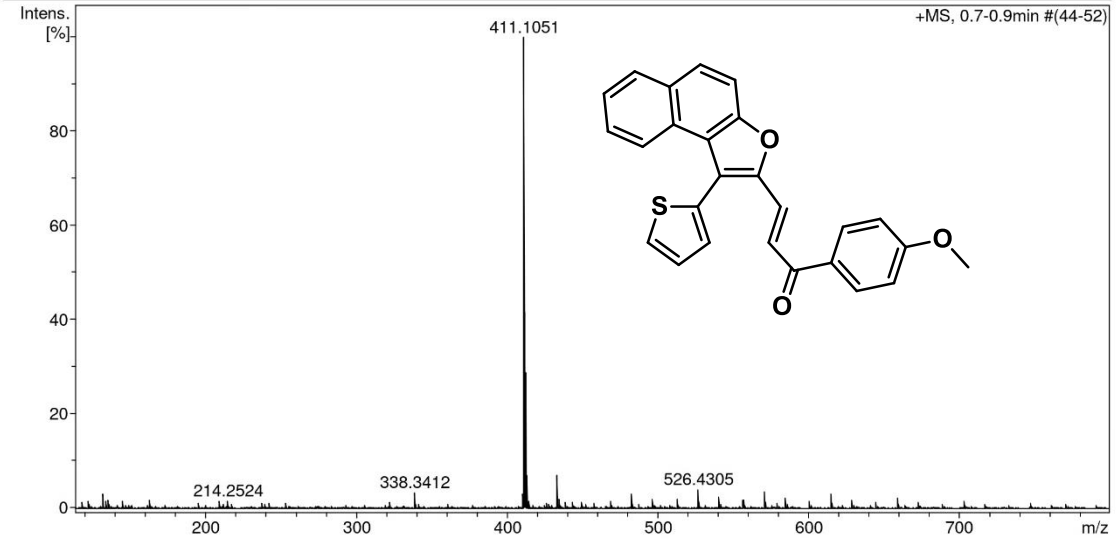
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

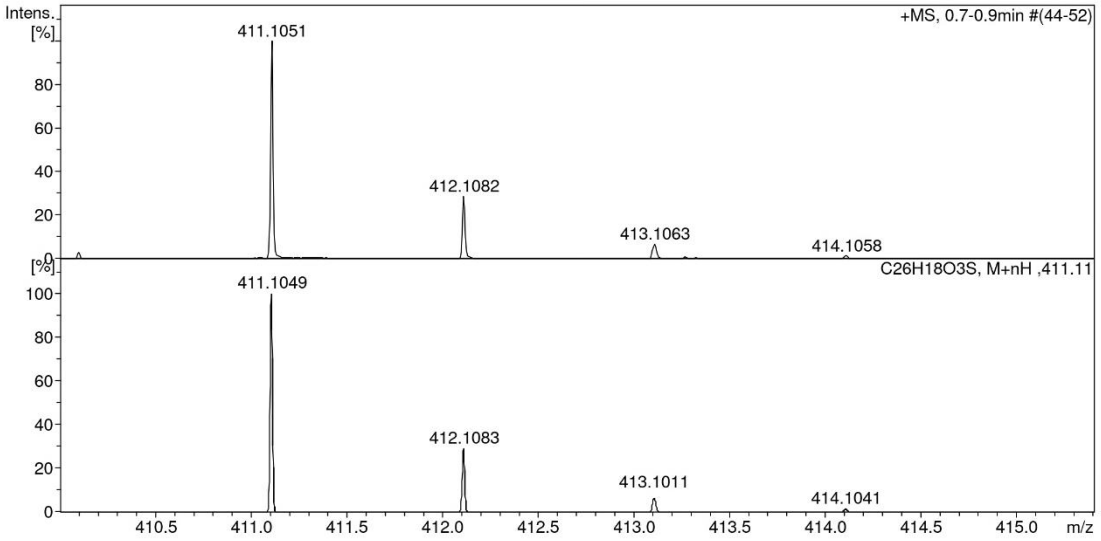


(*E*)-1-(4-methoxyphenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1f)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

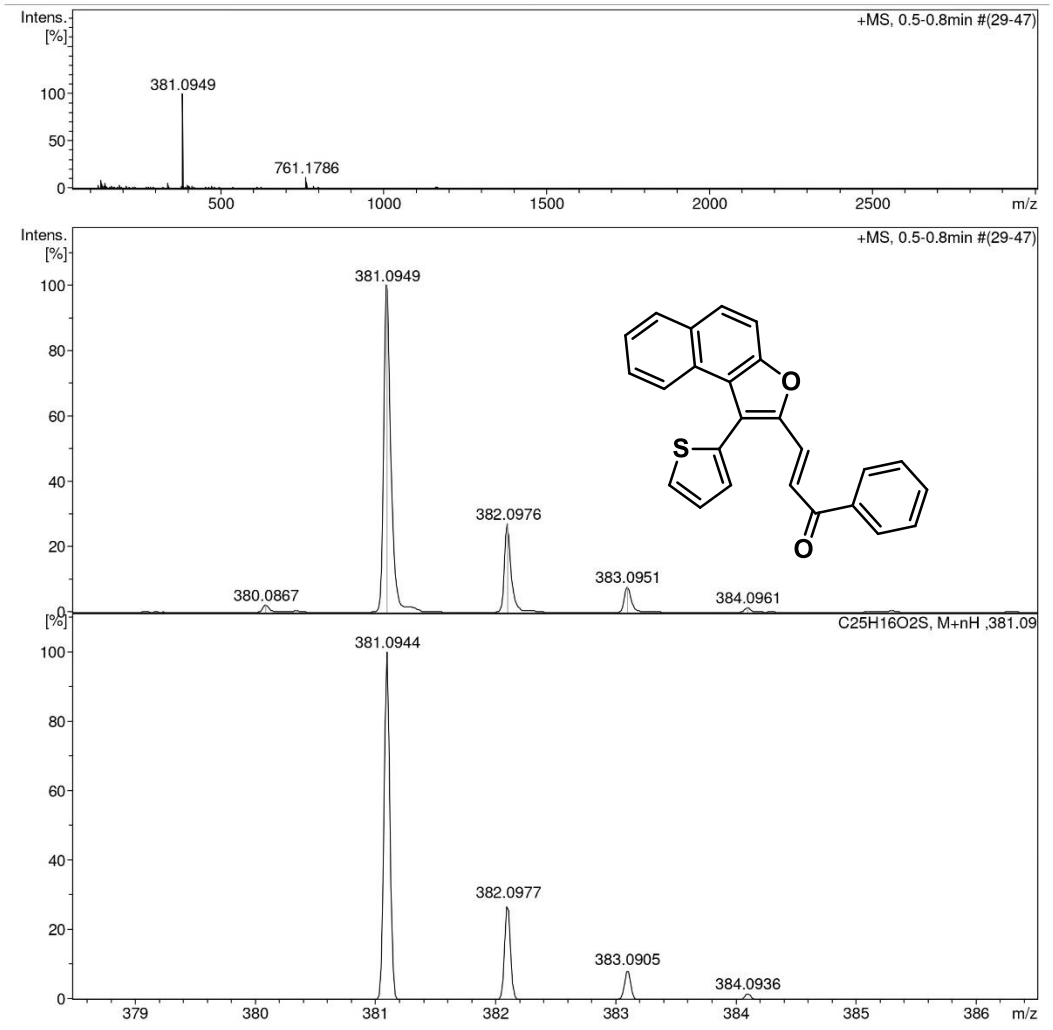




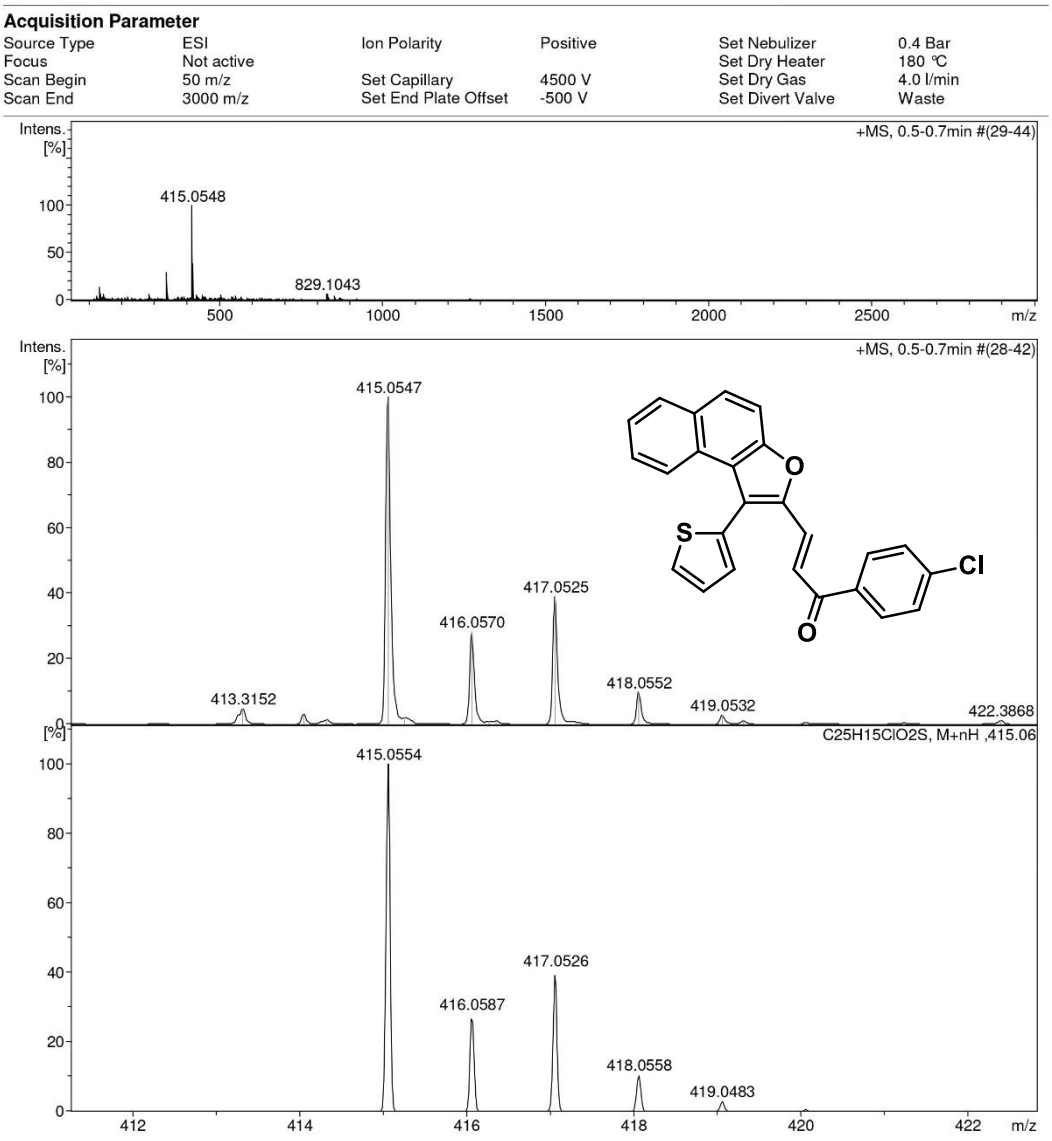
(*E*)-1-phenyl-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1g)

Acquisition Parameter

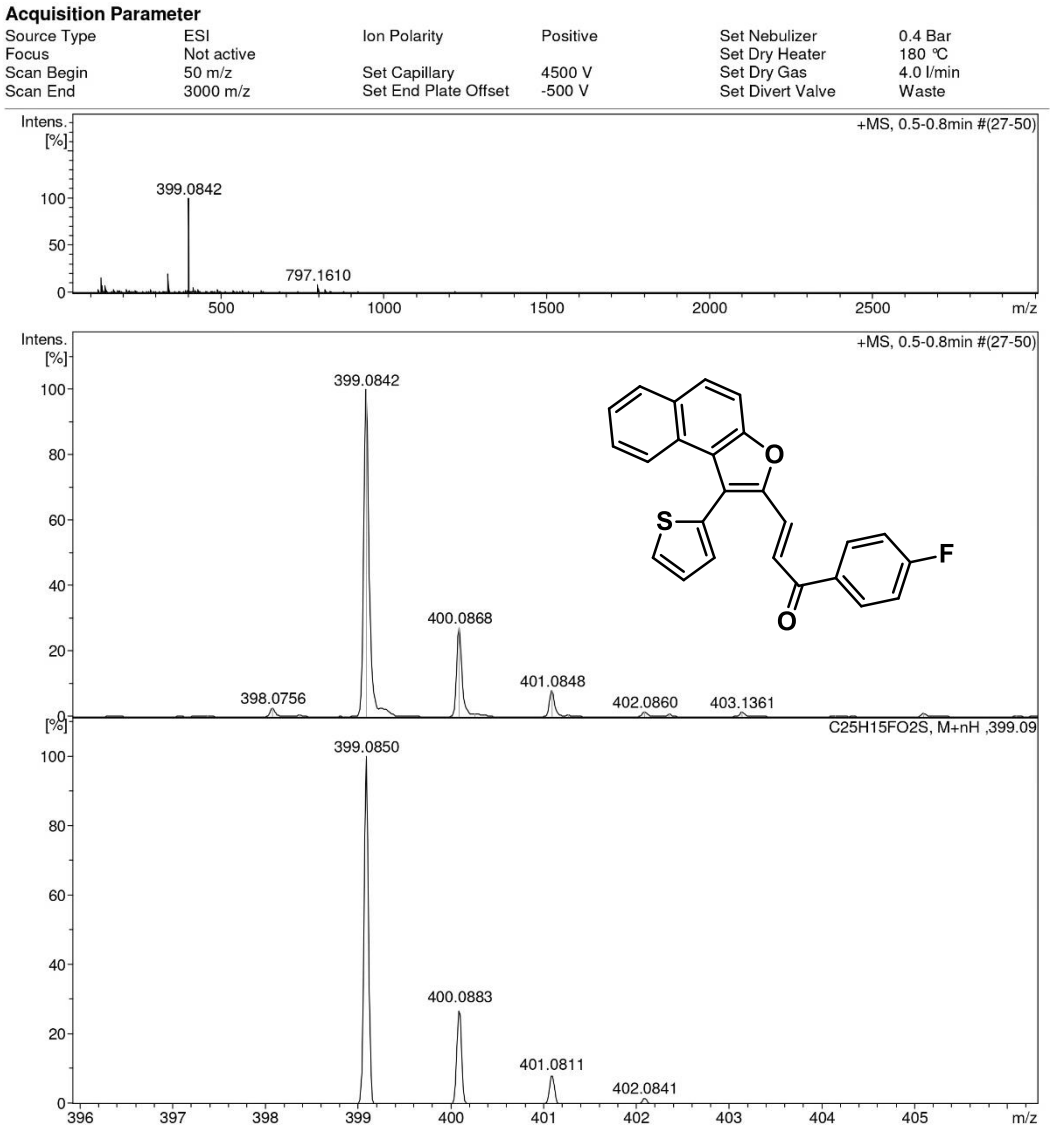
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



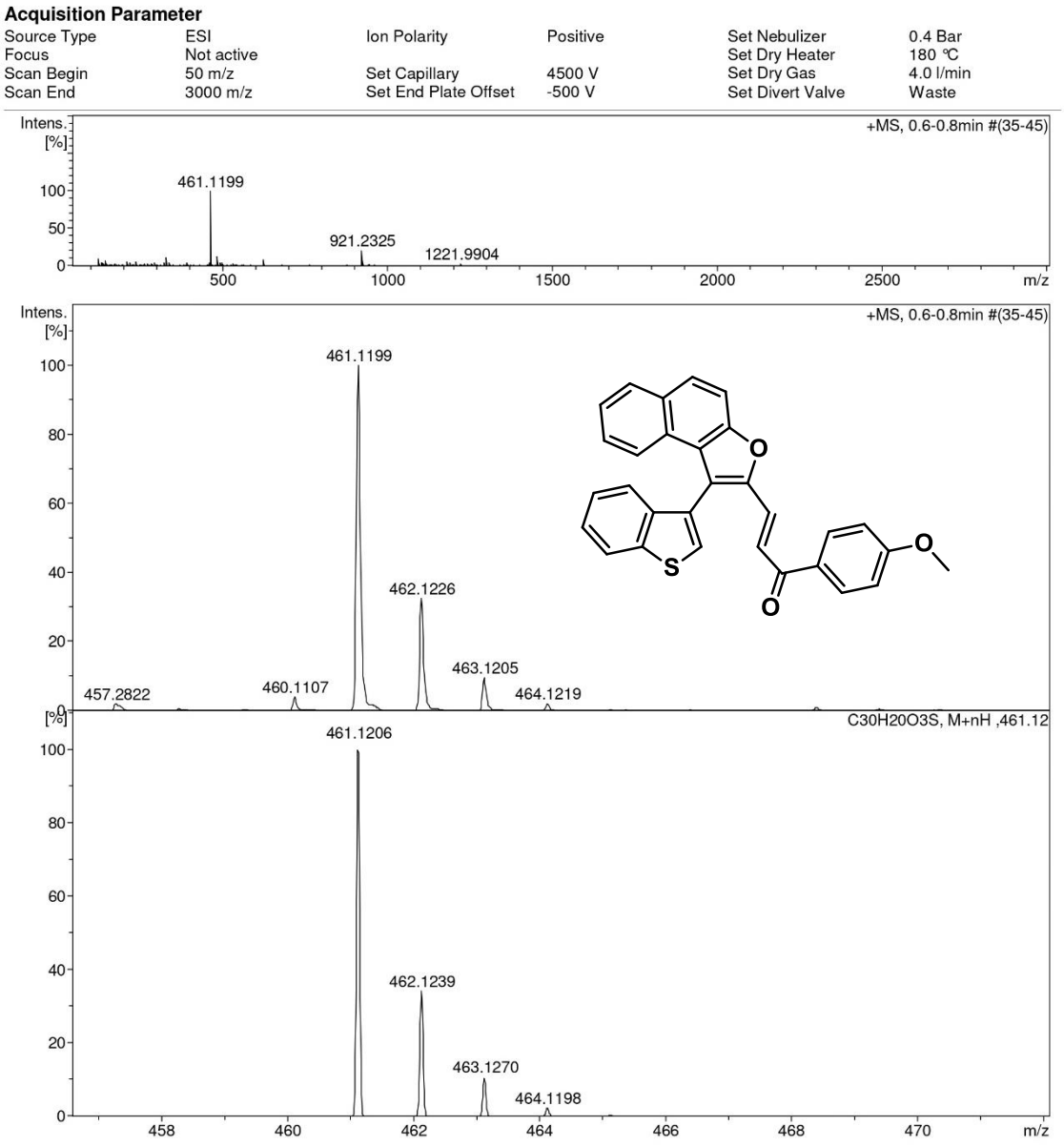
(*E*)-1-(4-chlorophenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1h)



(*E*)-1-(4-fluorophenyl)-3-(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1i)



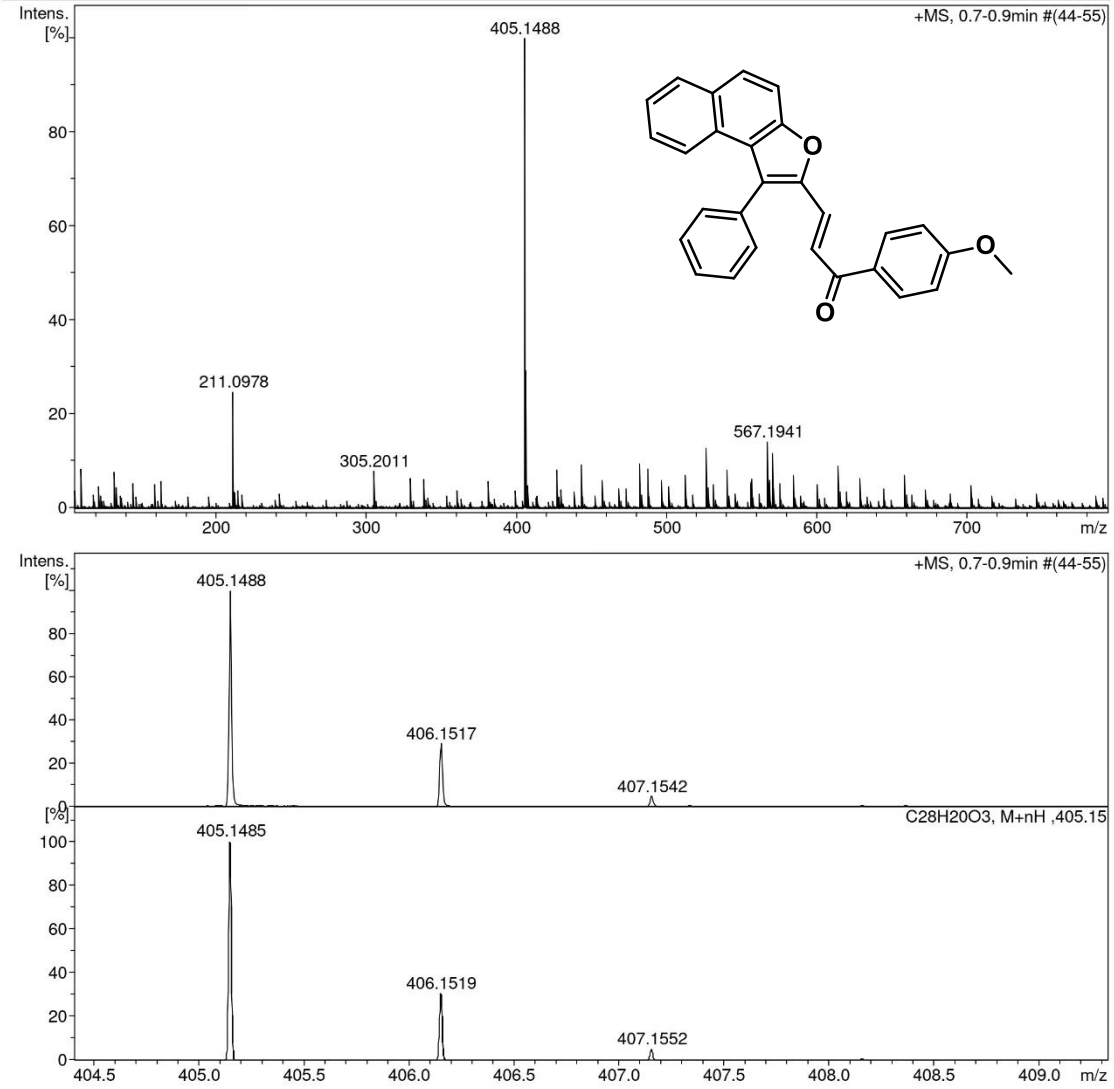
(*E*)-3-(1-(benzo[b]thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1j)



(*E*)-1-(4-methoxyphenyl)-3-(1-phenylnaphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one (1k)

Acquisition Parameter

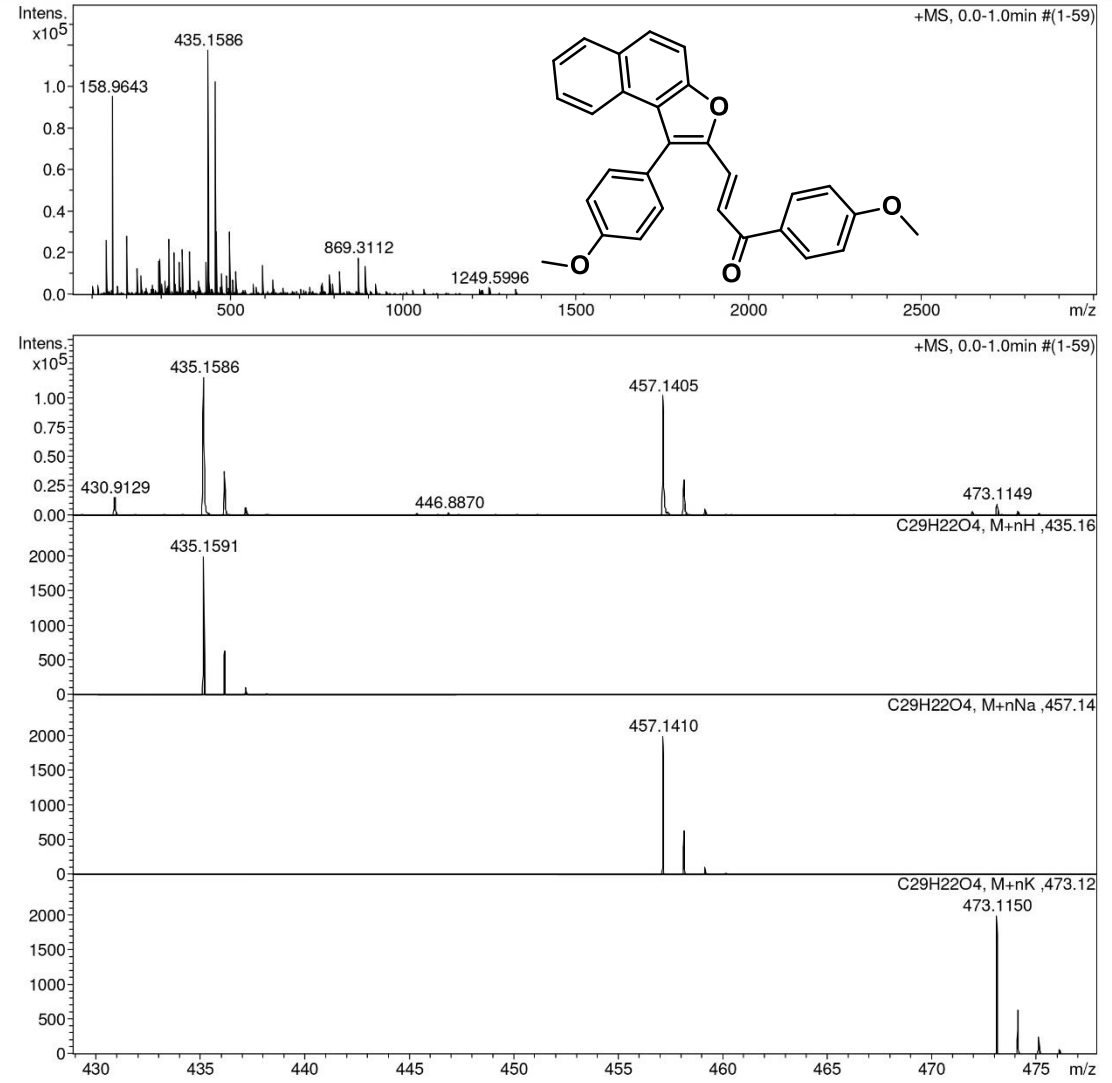
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(*E*)-1-(4-methoxyphenyl)-3-(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)prop-2-en-1-one(1l)

Acquisition Parameter

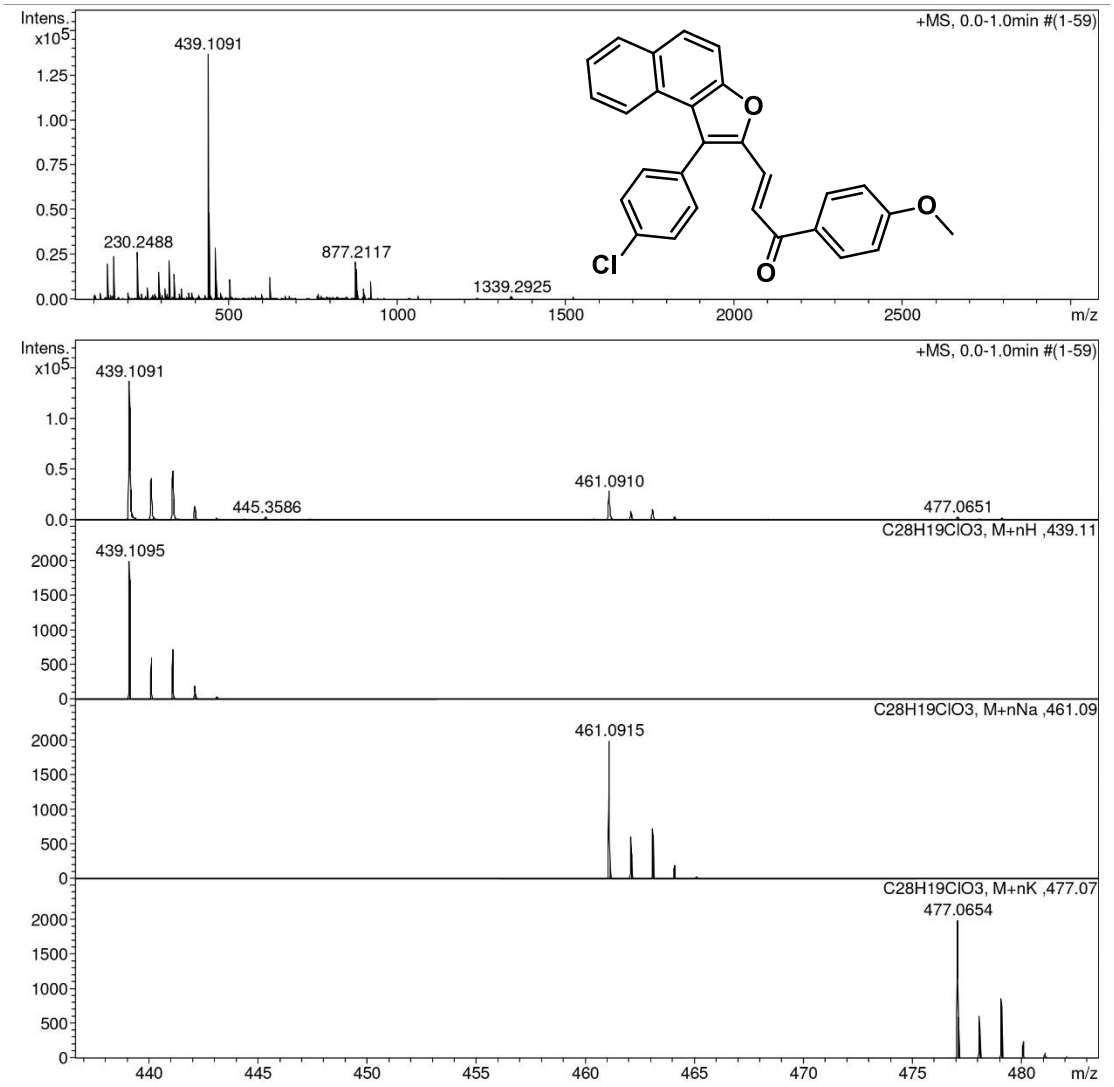
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(*E*)-3-(1-(4-chlorophenyl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one(1m)

Acquisition Parameter

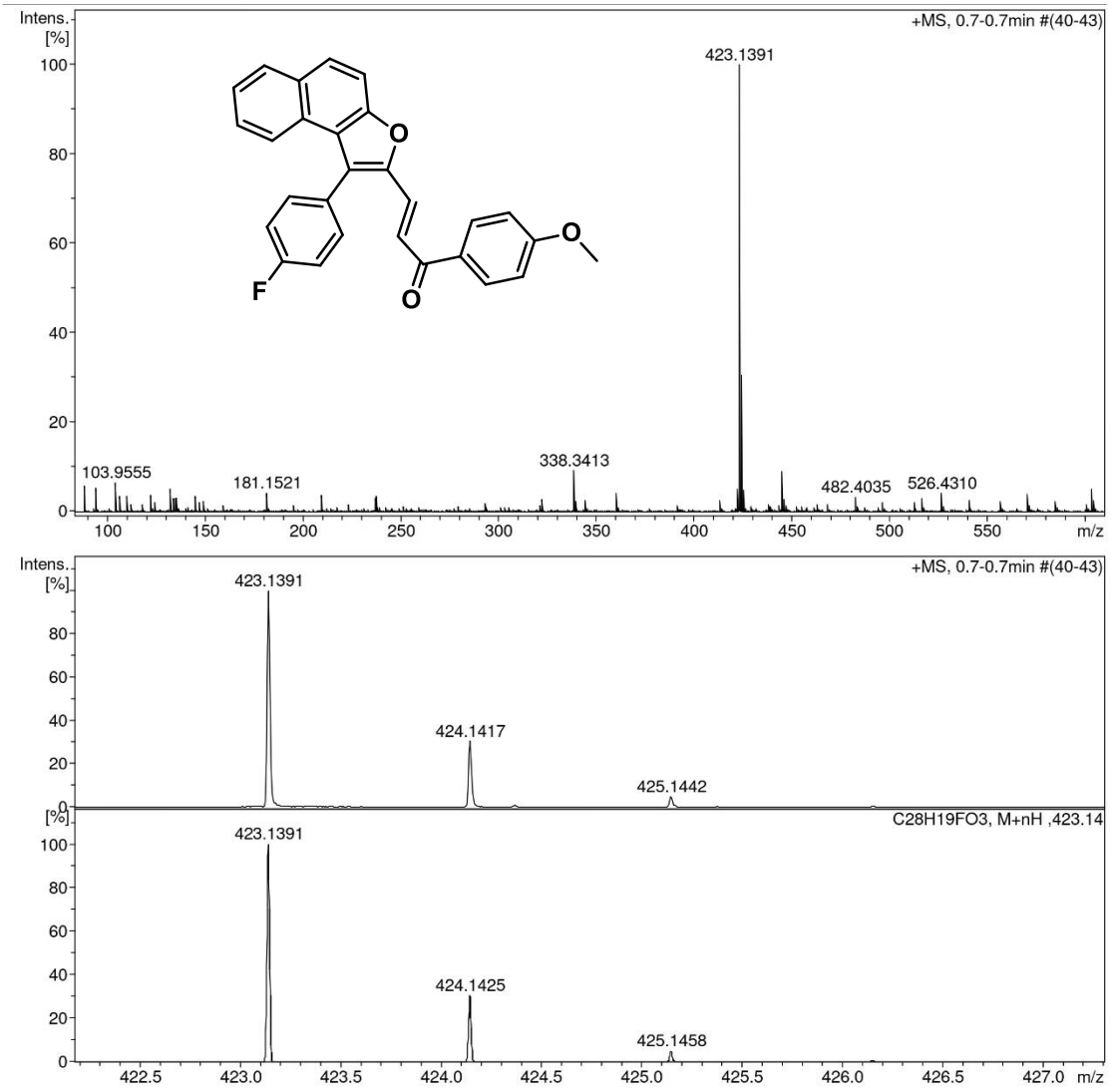
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



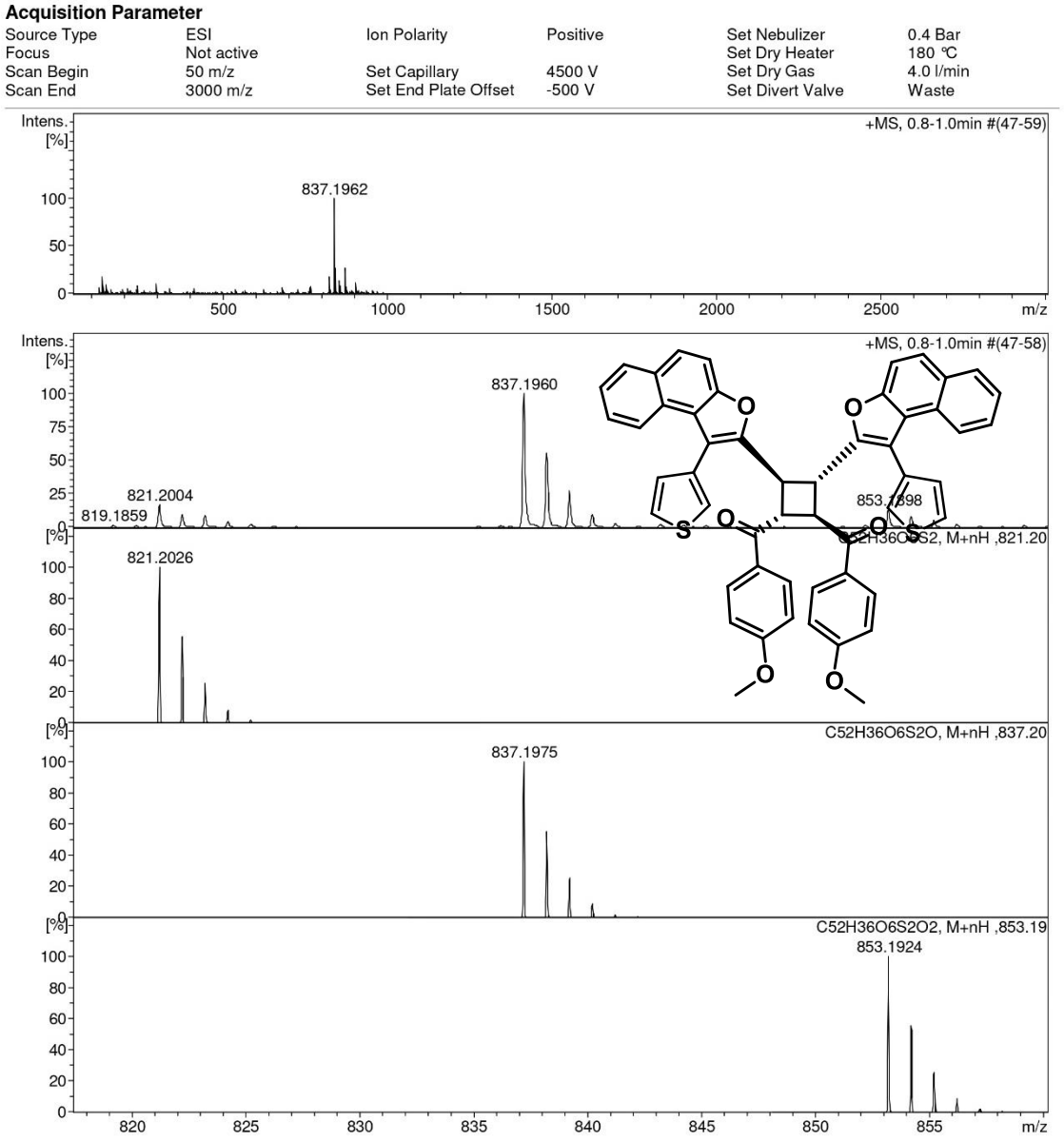
(*E*)-3-(1-(4-fluorophenyl)naphtho[2,1-*b*]furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1n)

Acquisition Parameter

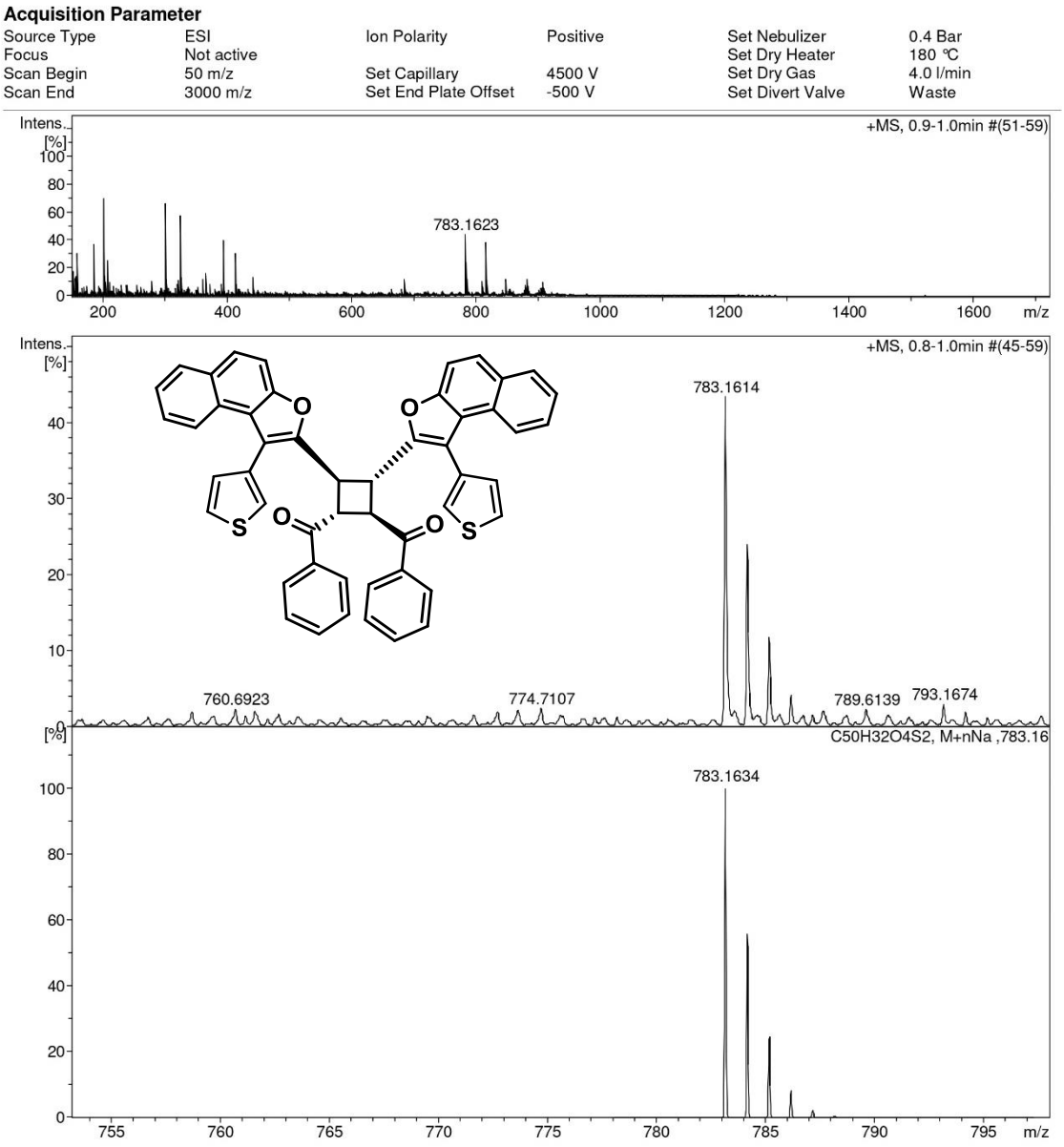
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



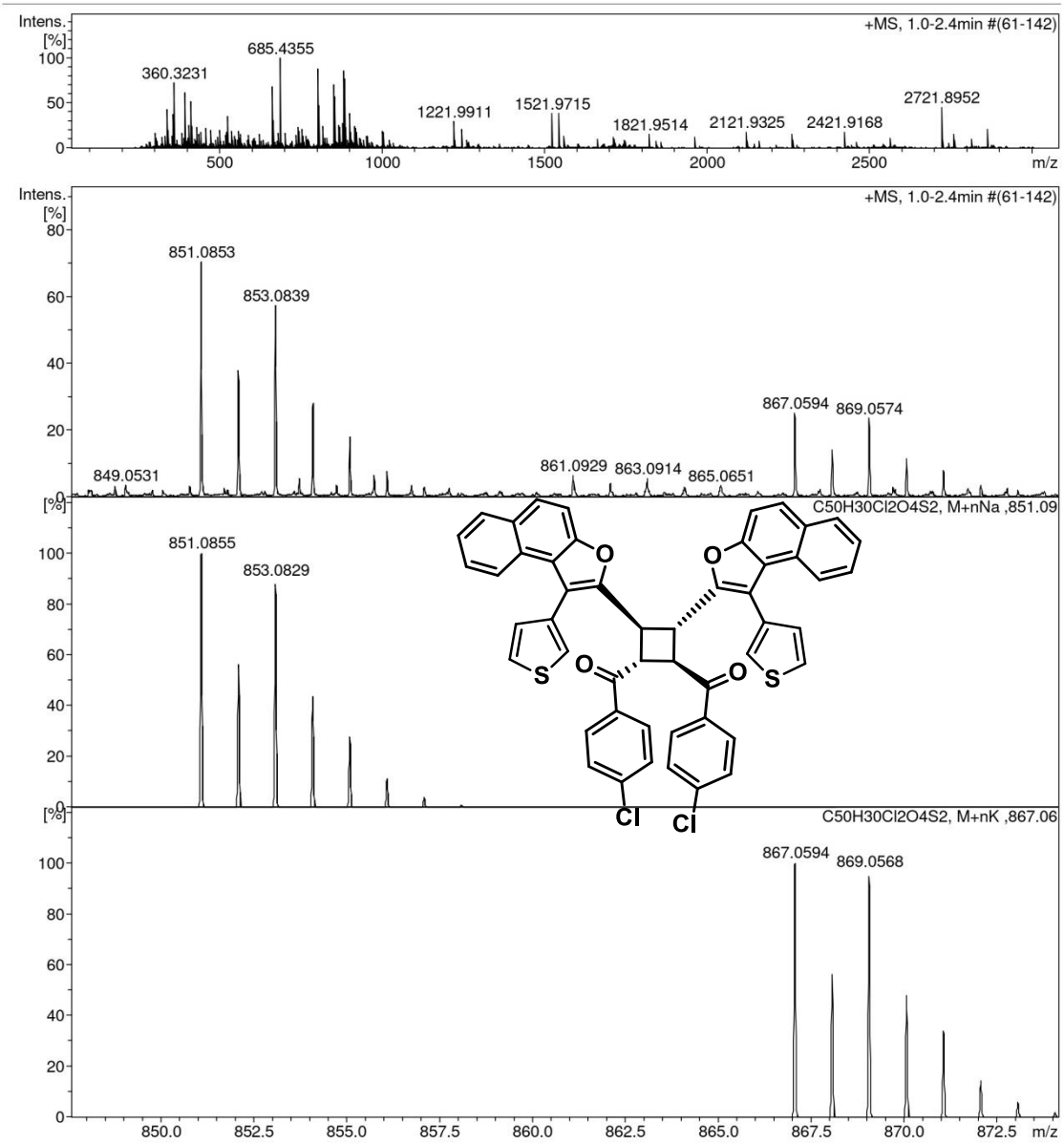
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2ahh-a)



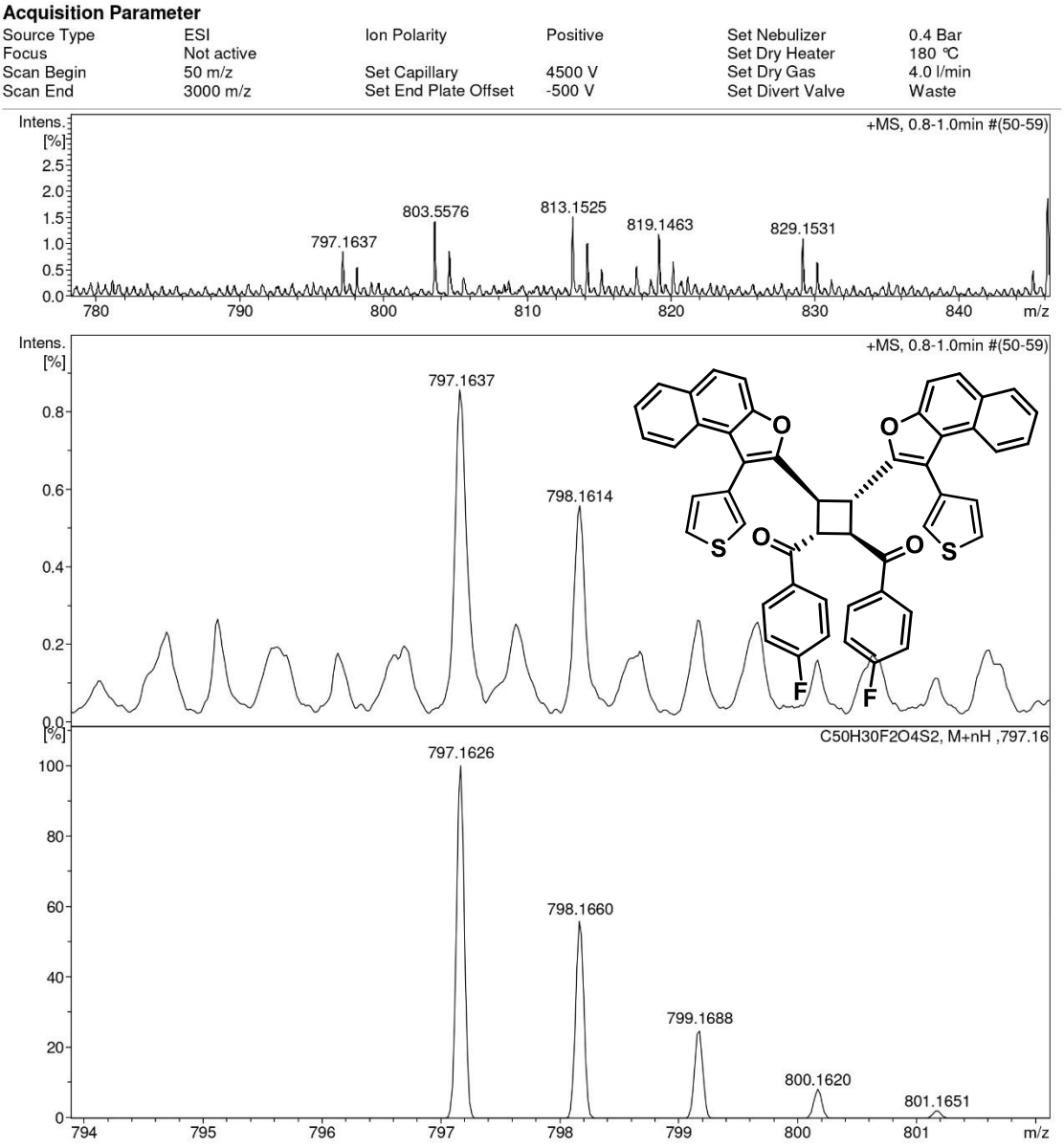
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (2bhh-a)



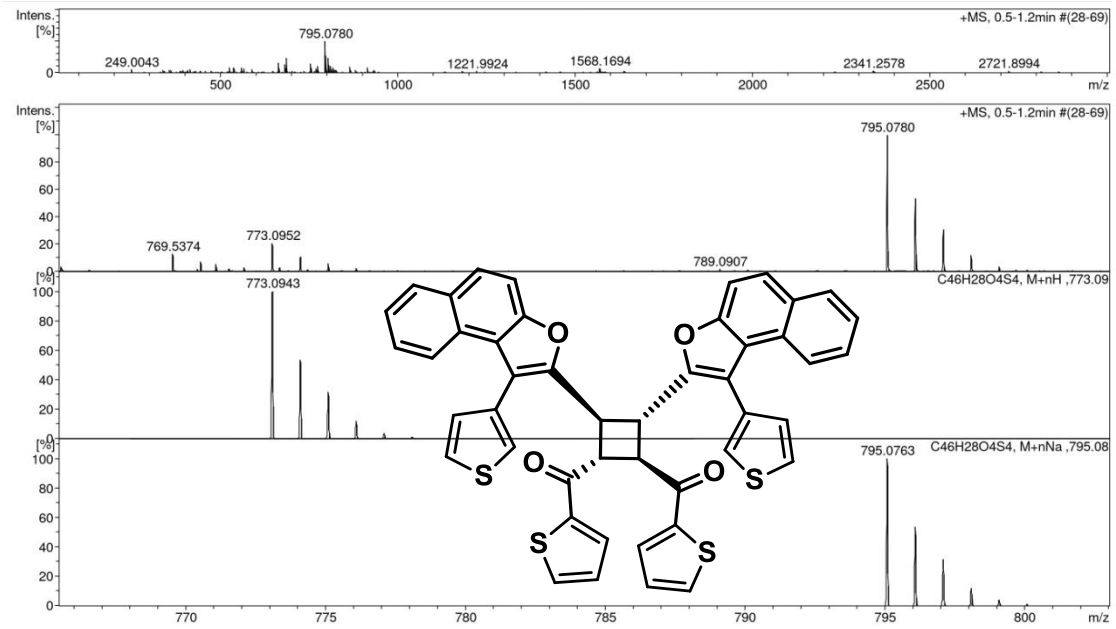
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-chlorophenyl)methanone) (2chh-a)



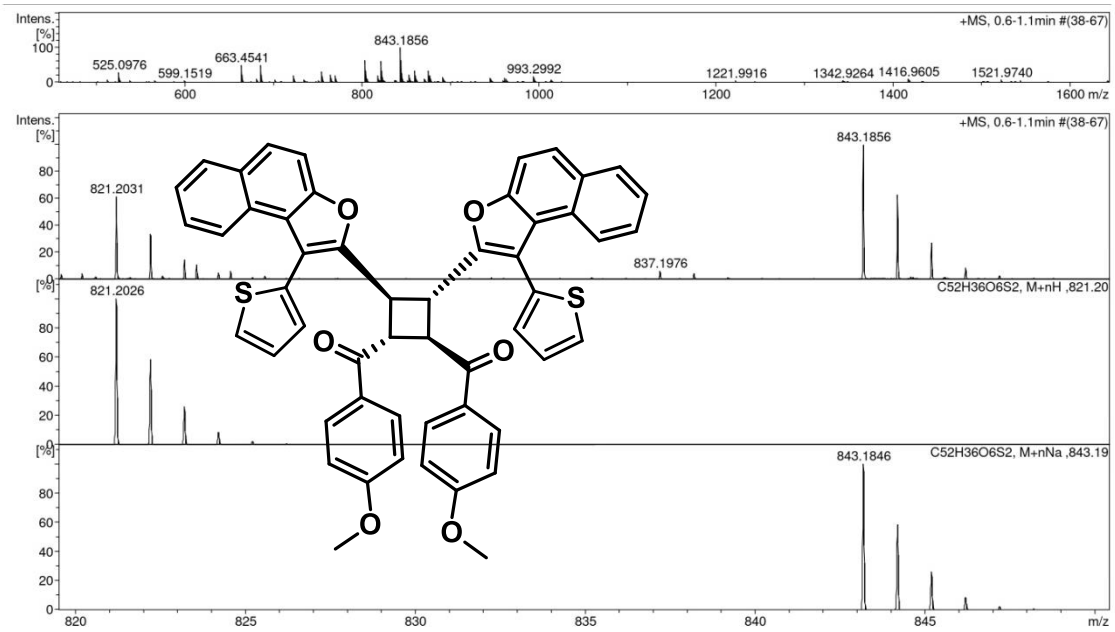
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-fluorophenyl)methanone) (2dhh-a)



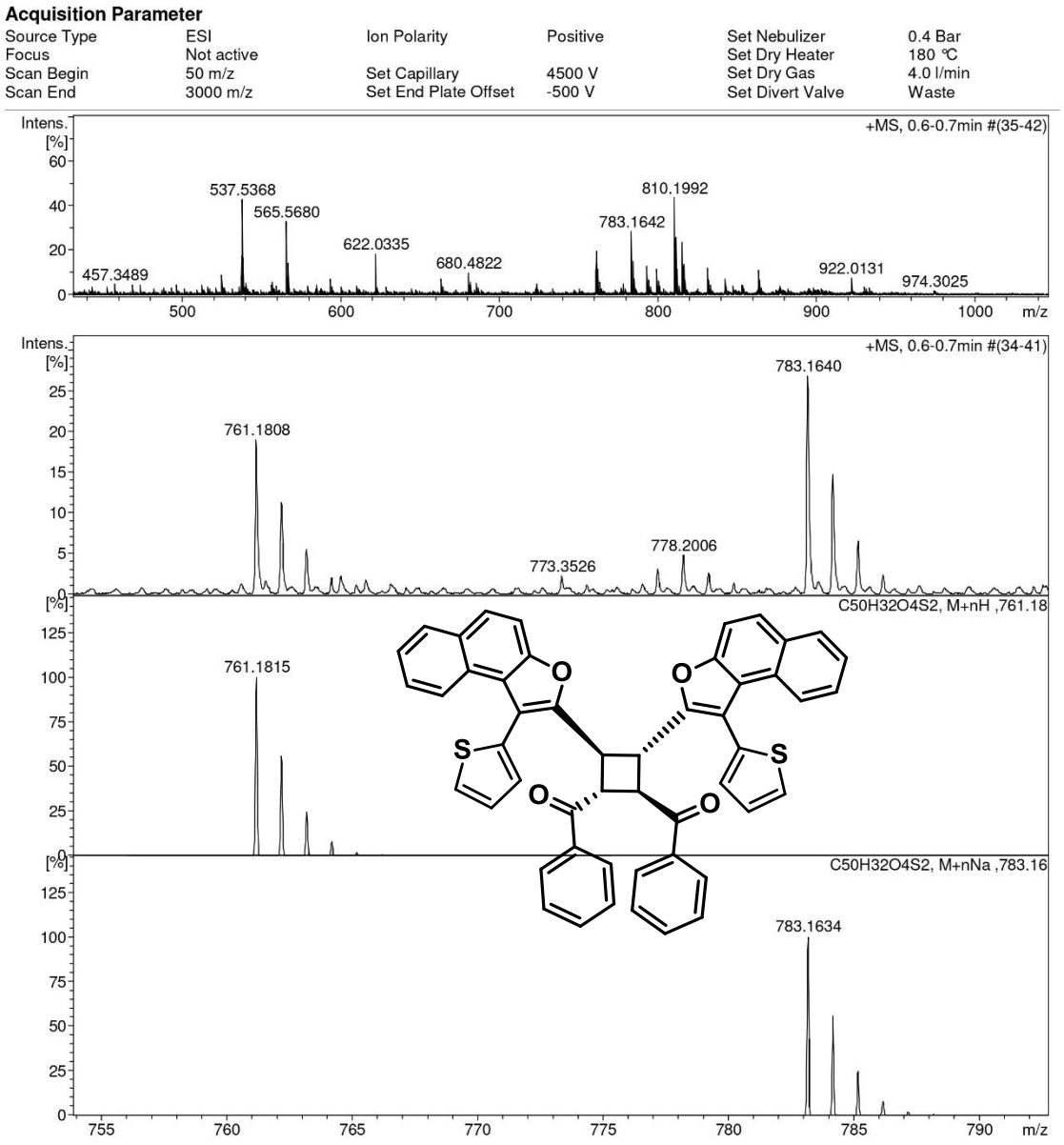
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-3-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(thiophen-2-ylmethanone) (2ehh-a)



((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2fhh-a)



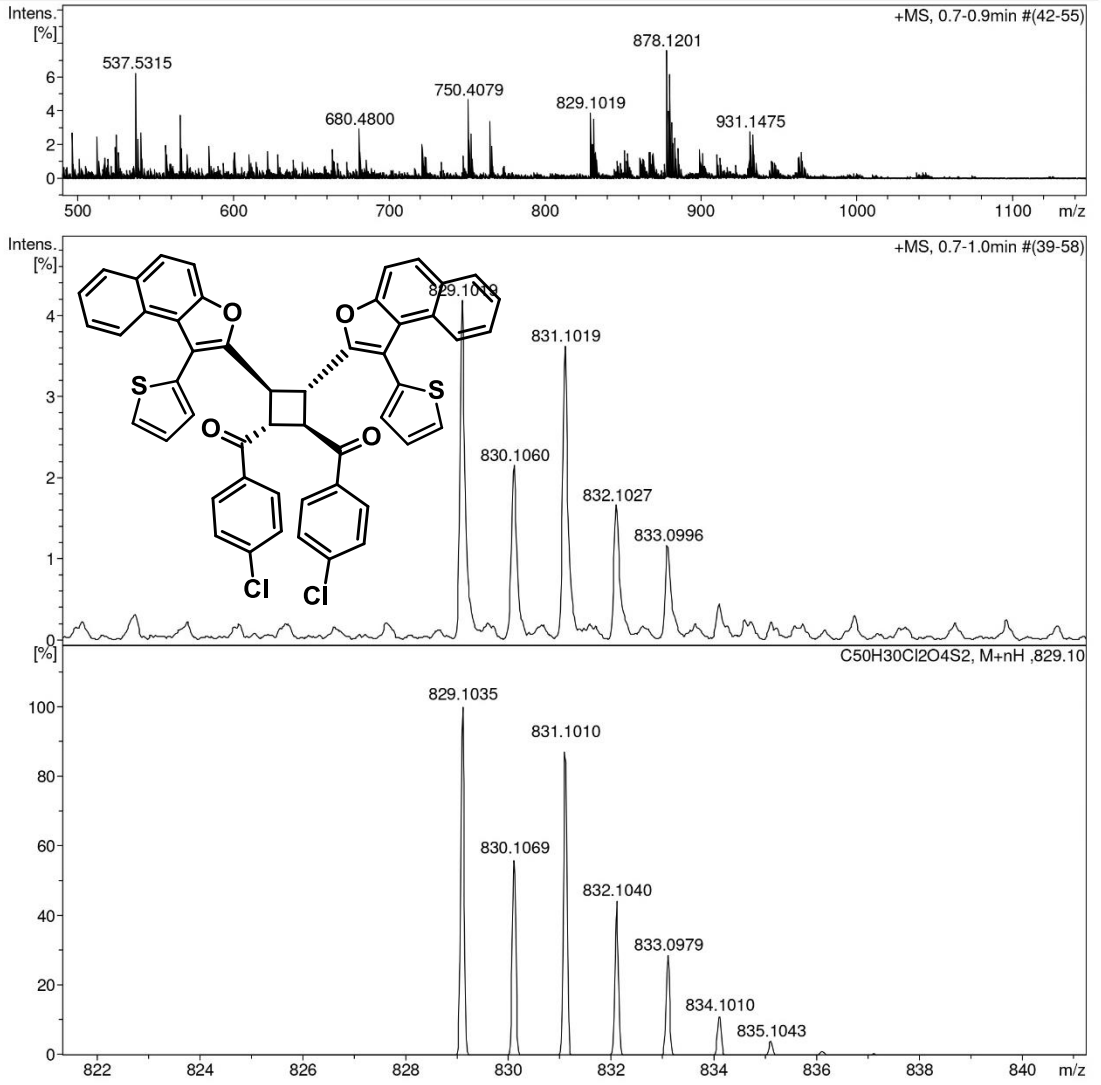
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis(phenylmethanone) (2ghh-a)



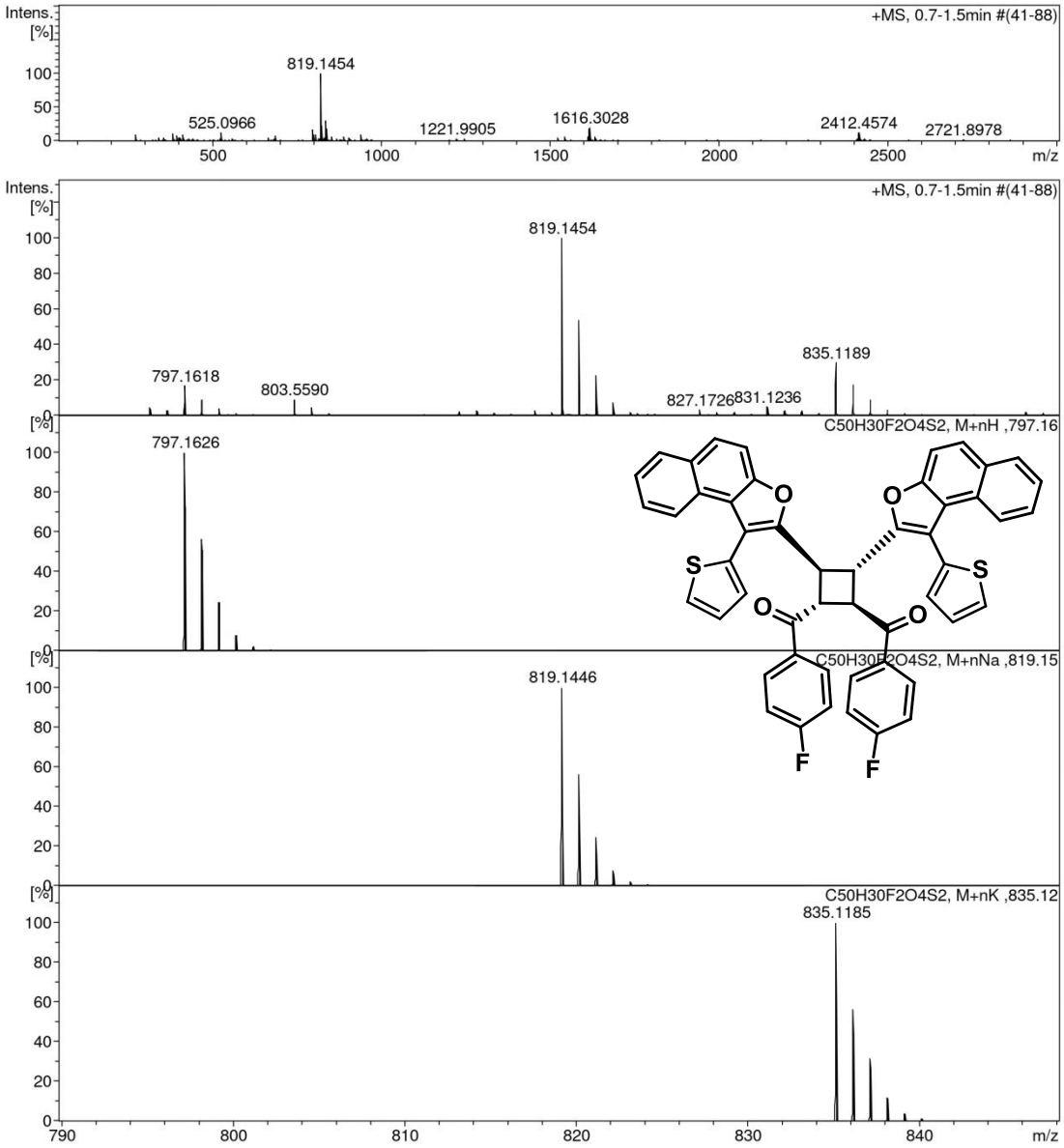
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-chlorophenyl)methanone) (2hhh-a)

Acquisition Parameter

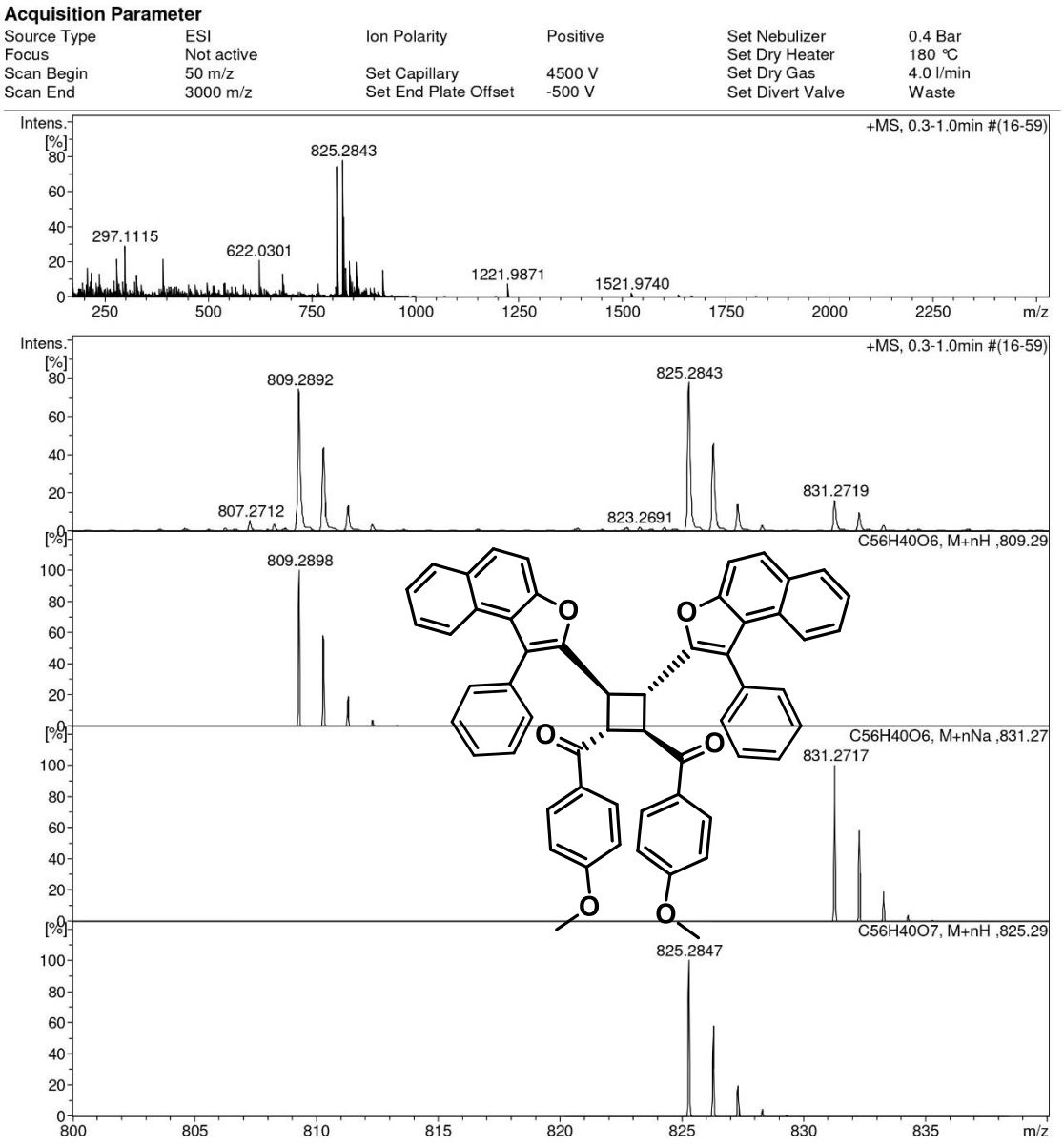
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



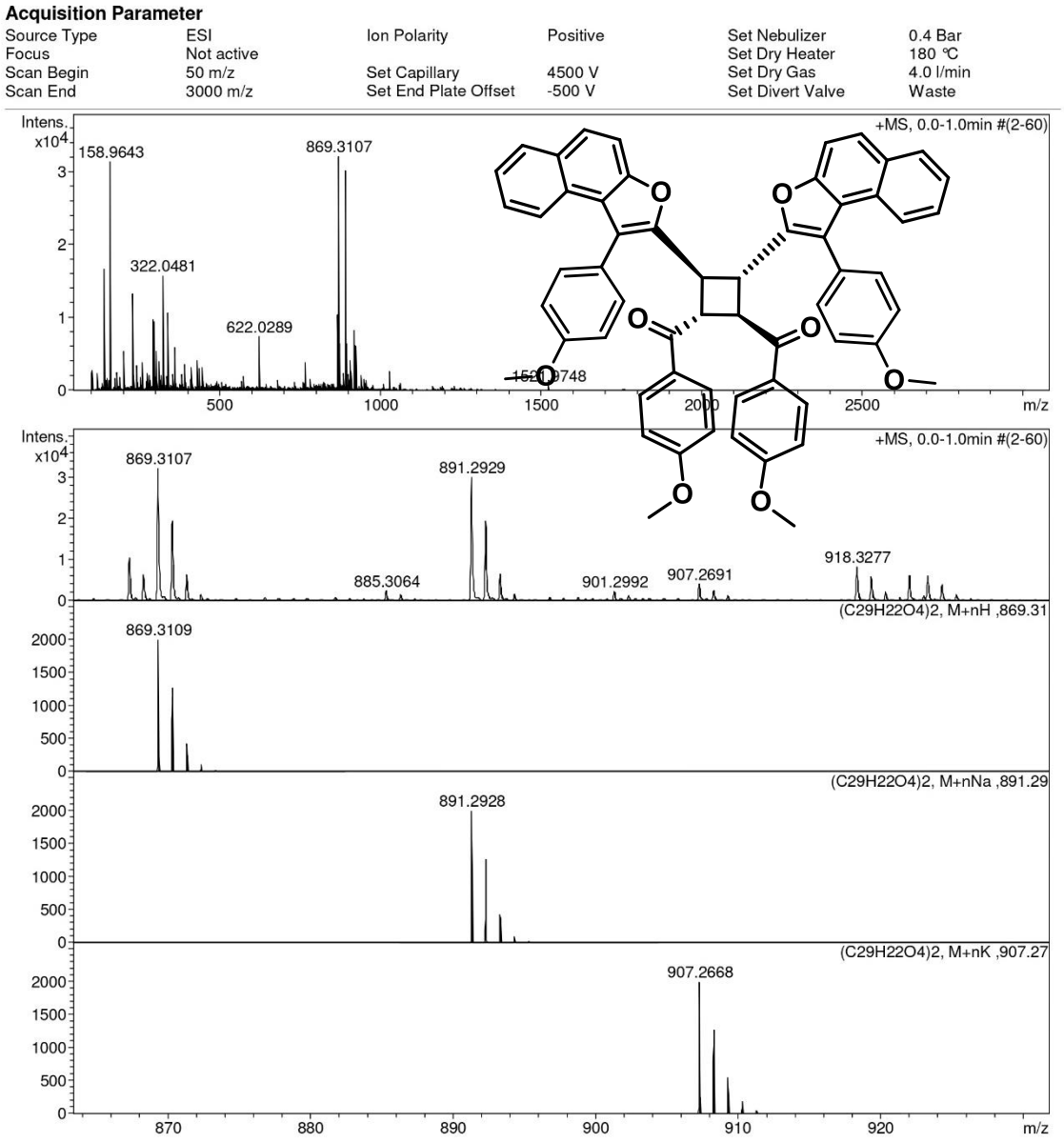
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(thiophen-2-yl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-fluorophenyl)methanone) (2ihh-a)



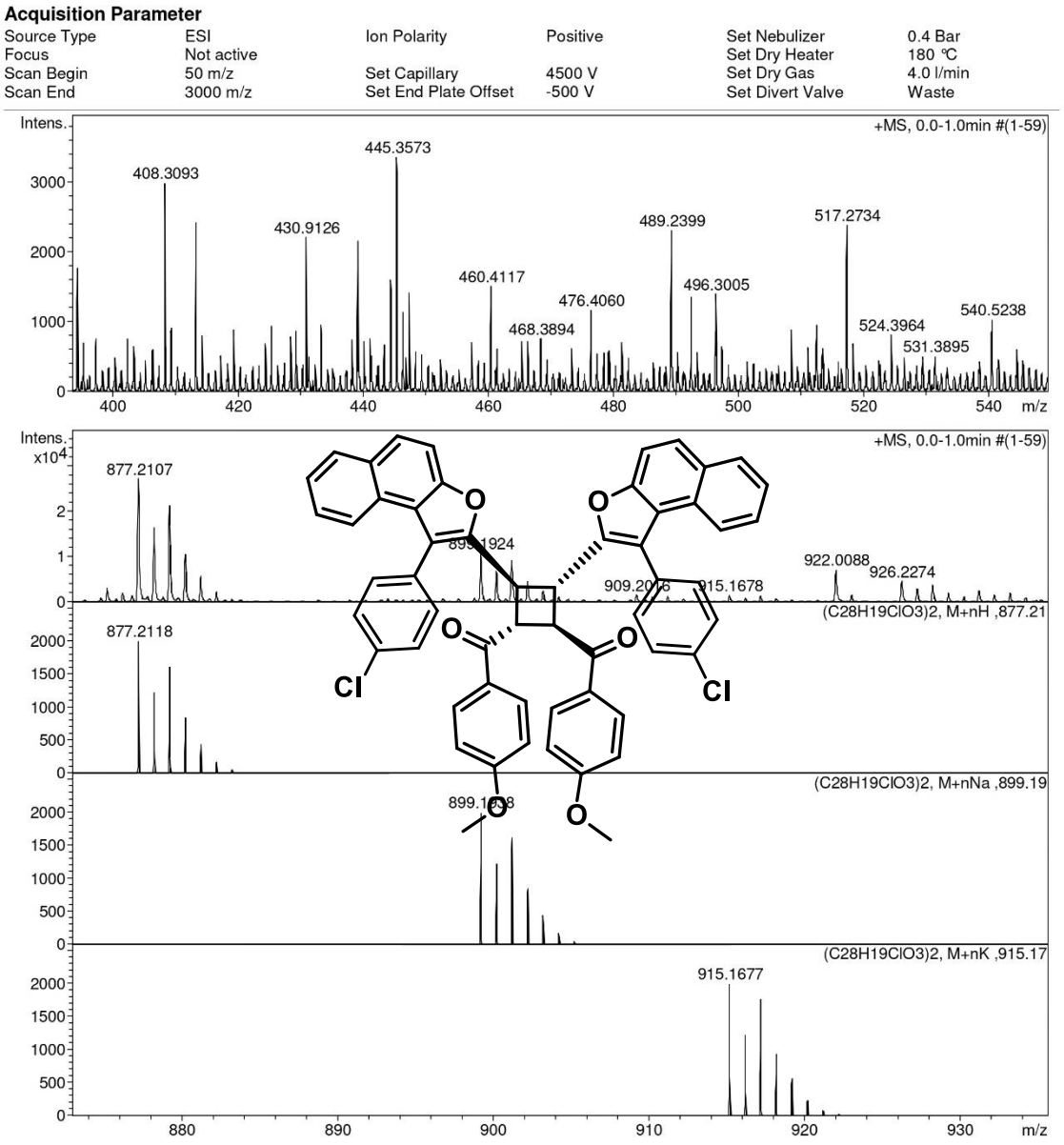
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-phenylnaphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2khh-a)



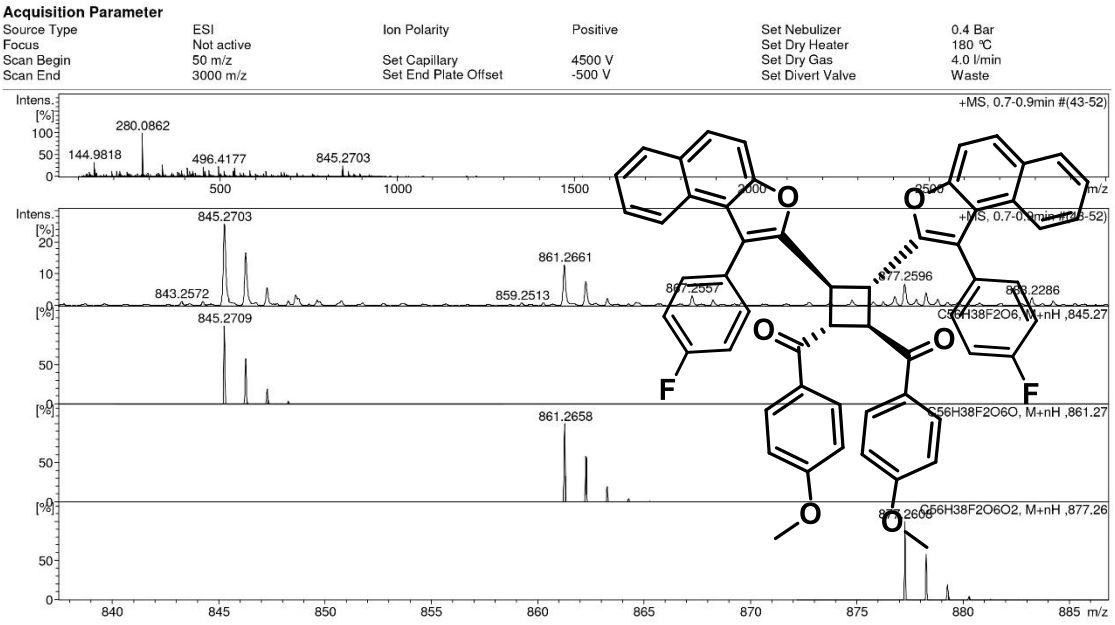
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2lhh-a)



((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-chlorophenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2mhh-a)



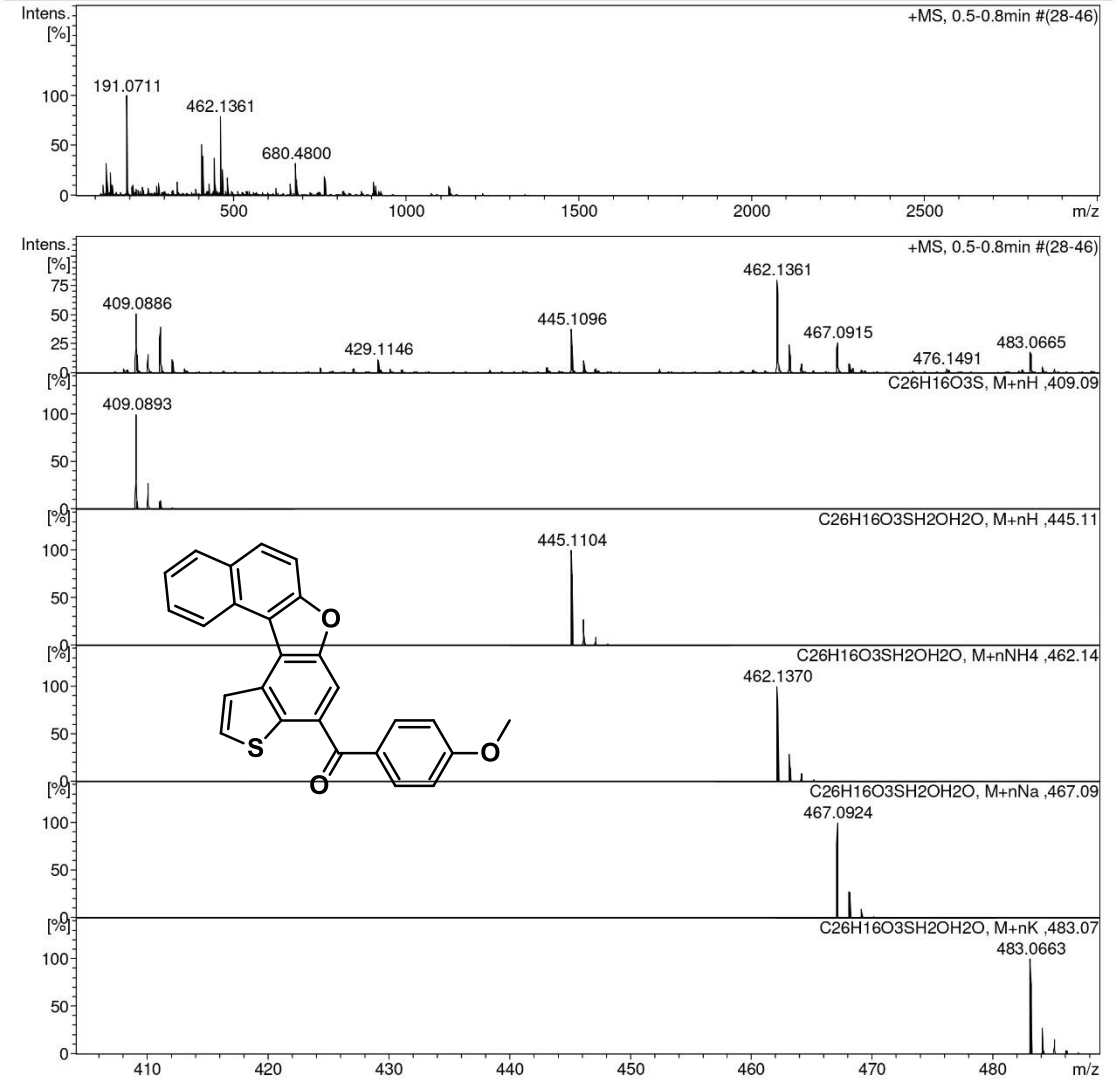
((*1RS,2RS,3SR,4SR*)-3,4-bis(1-(4-fluorophenyl)naphtho[2,1-*b*]furan-2-yl)cyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone) (2nhh-a)



(4-methoxyphenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3a)

Acquisition Parameter

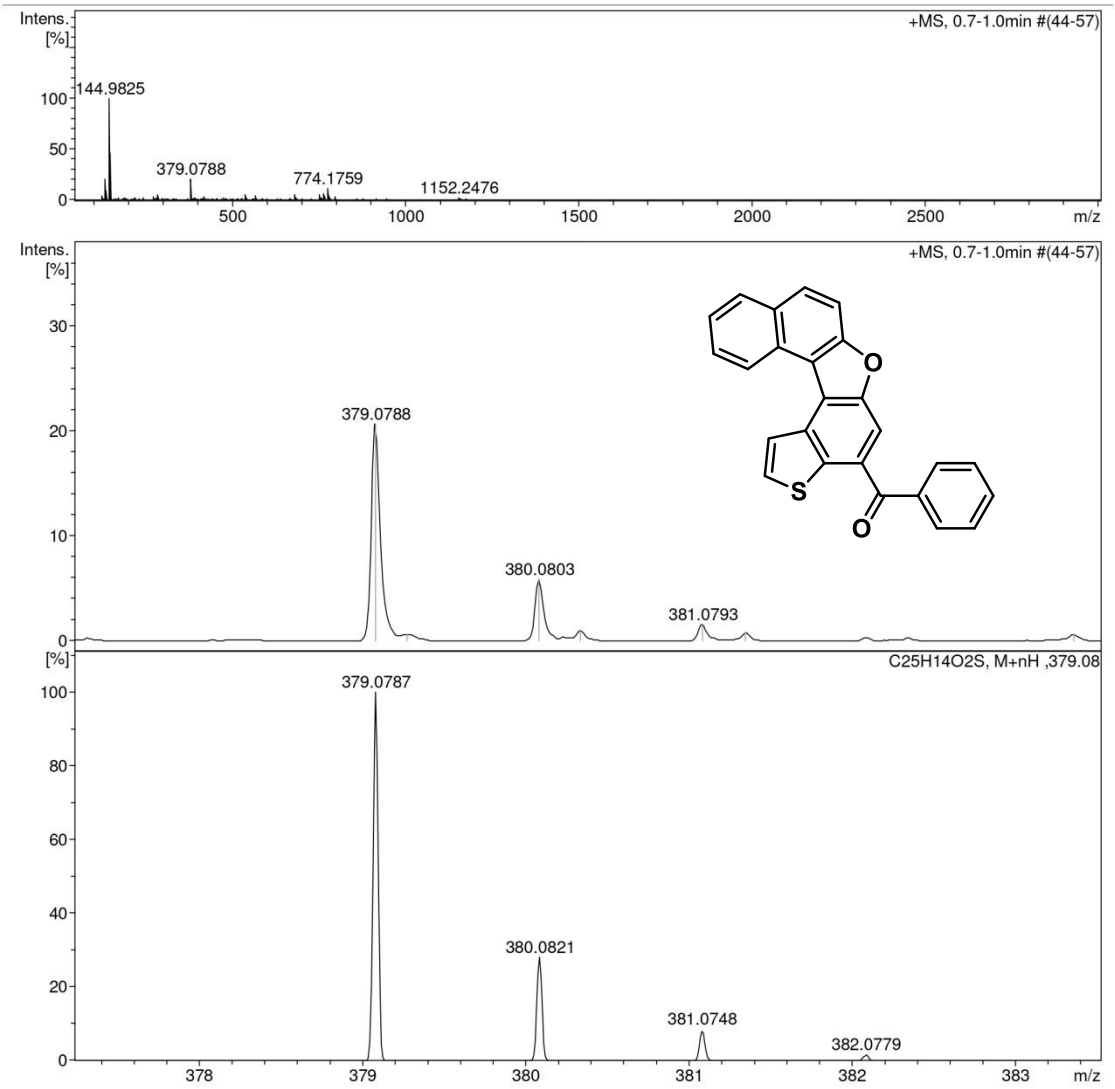
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl(phenyl)methanone (3b)

Acquisition Parameter

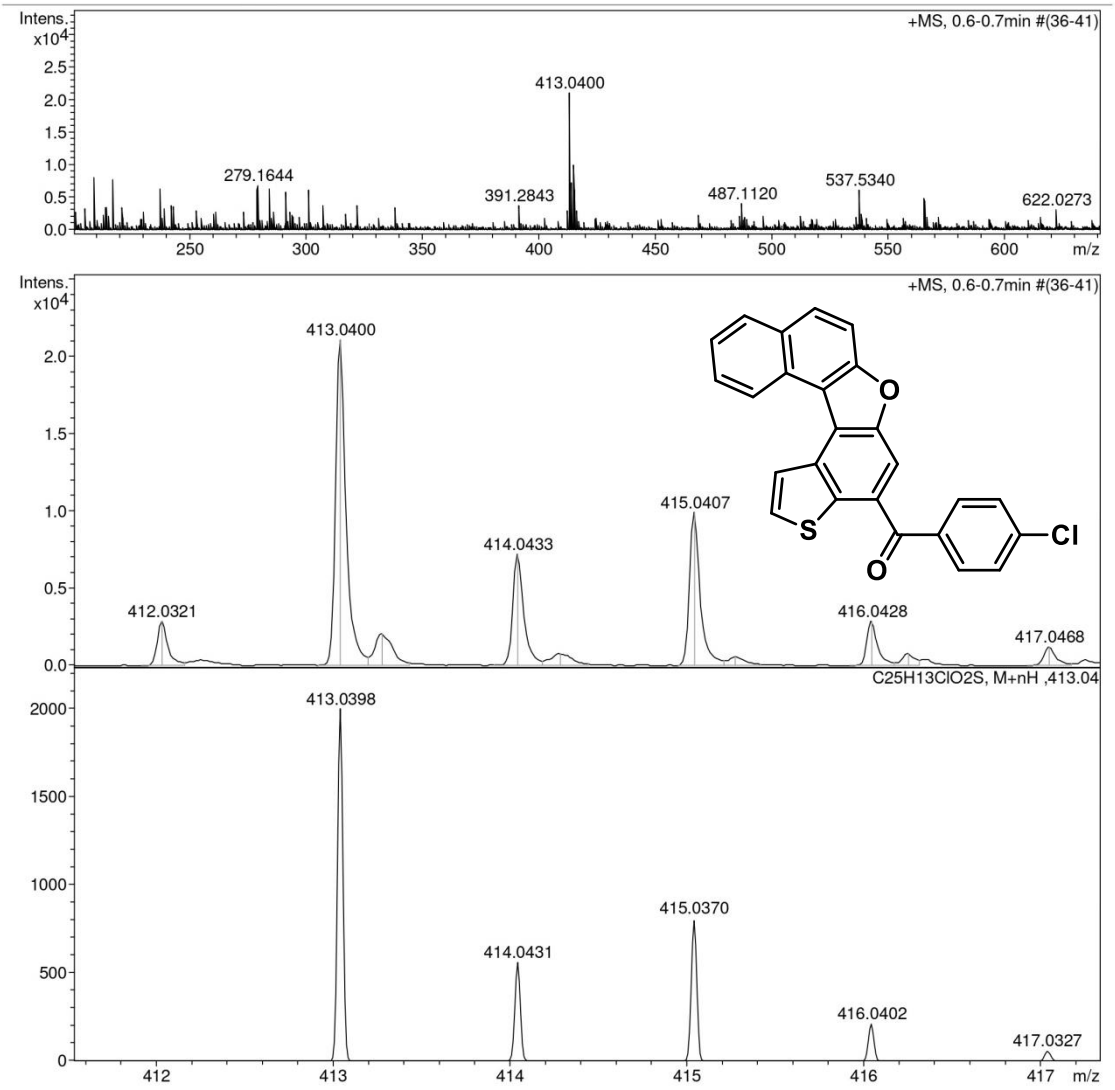
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(4-chlorophenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3c)

Acquisition Parameter

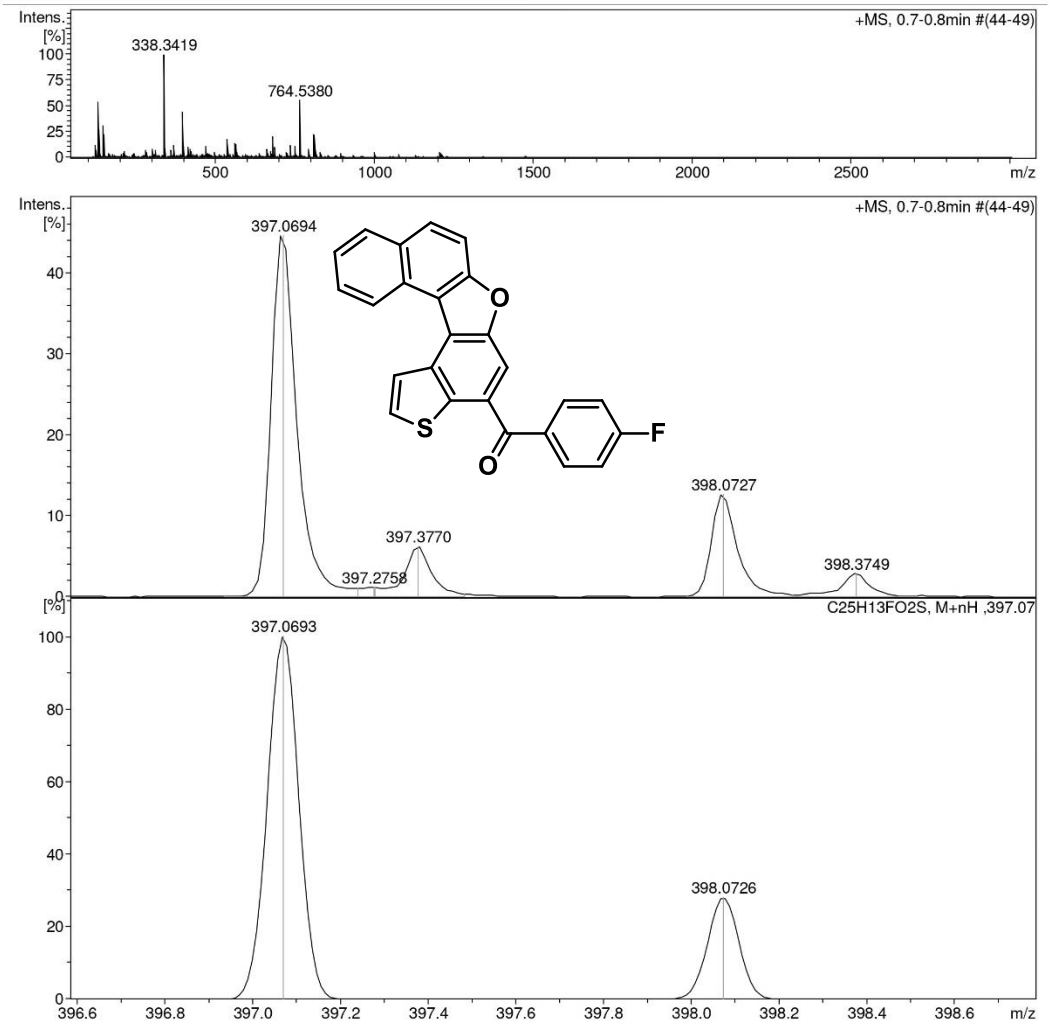
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(4-fluorophenyl)(naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl)methanone (3d)

Acquisition Parameter

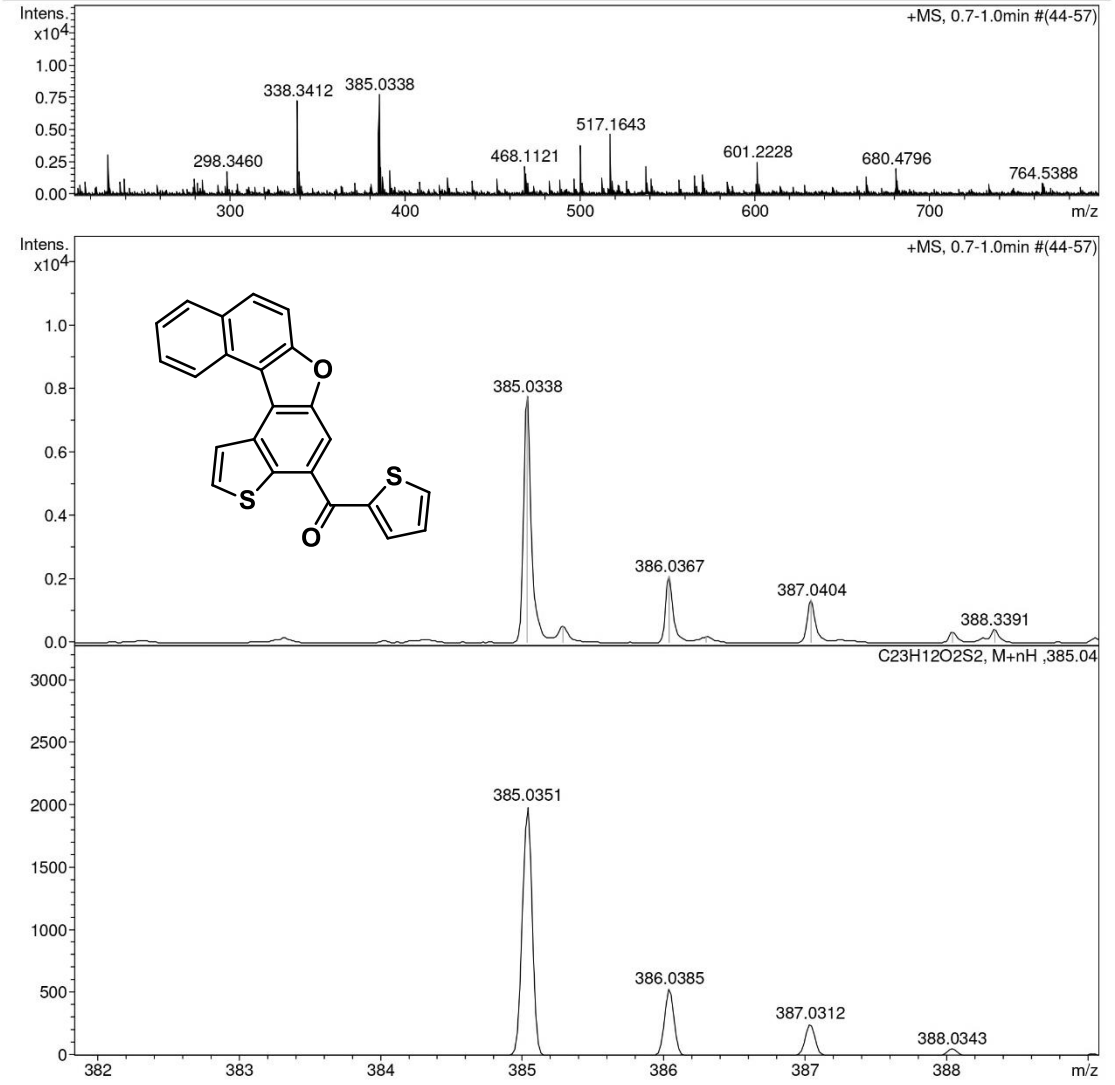
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Naphtho[2,1-*b*]thieno[3,2-*e*]benzofuran-4-yl(thiophen-2-yl)methanone (3e)

Acquisition Parameter

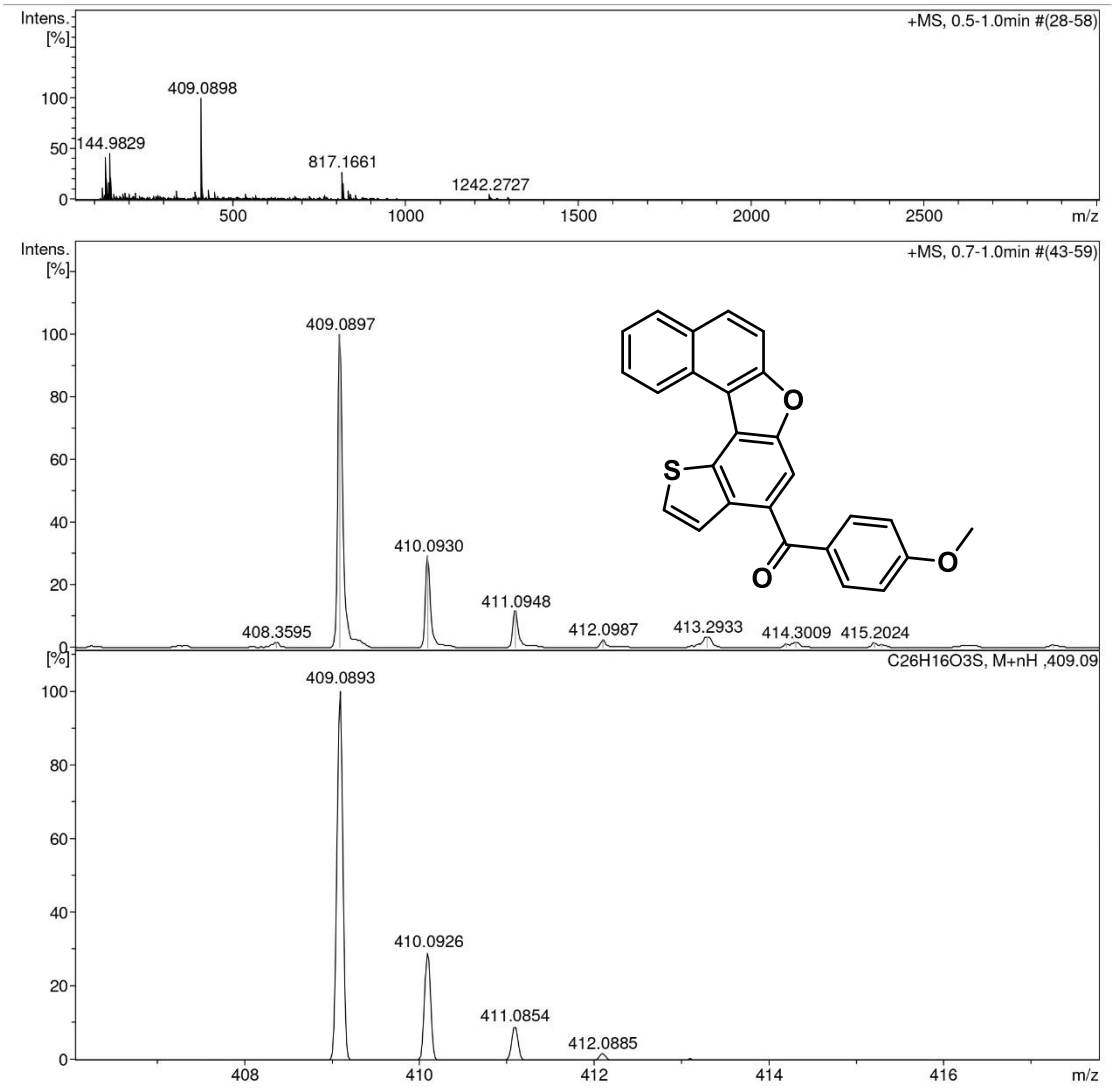
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(4-methoxyphenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3f)

Acquisition Parameter

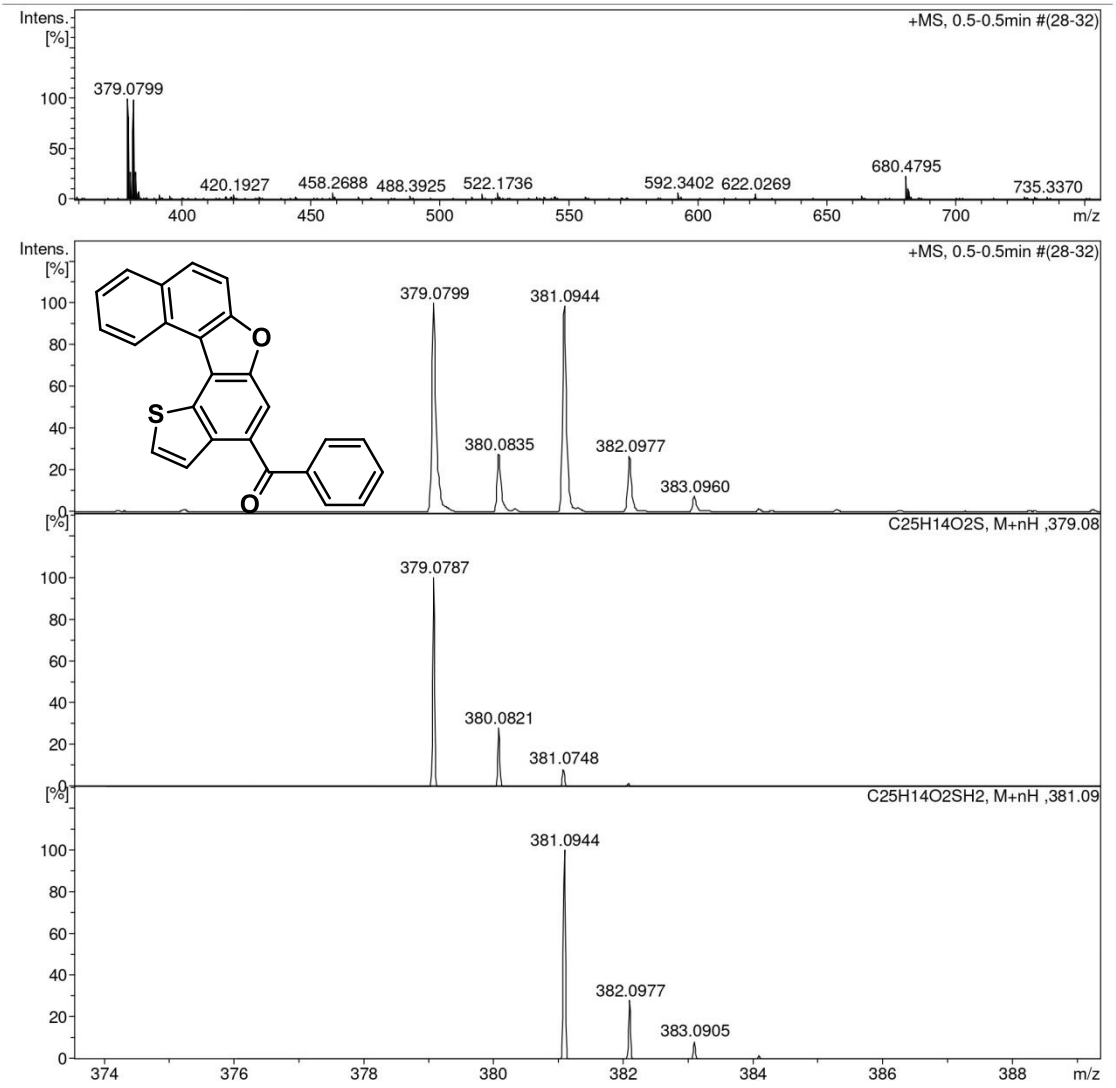
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



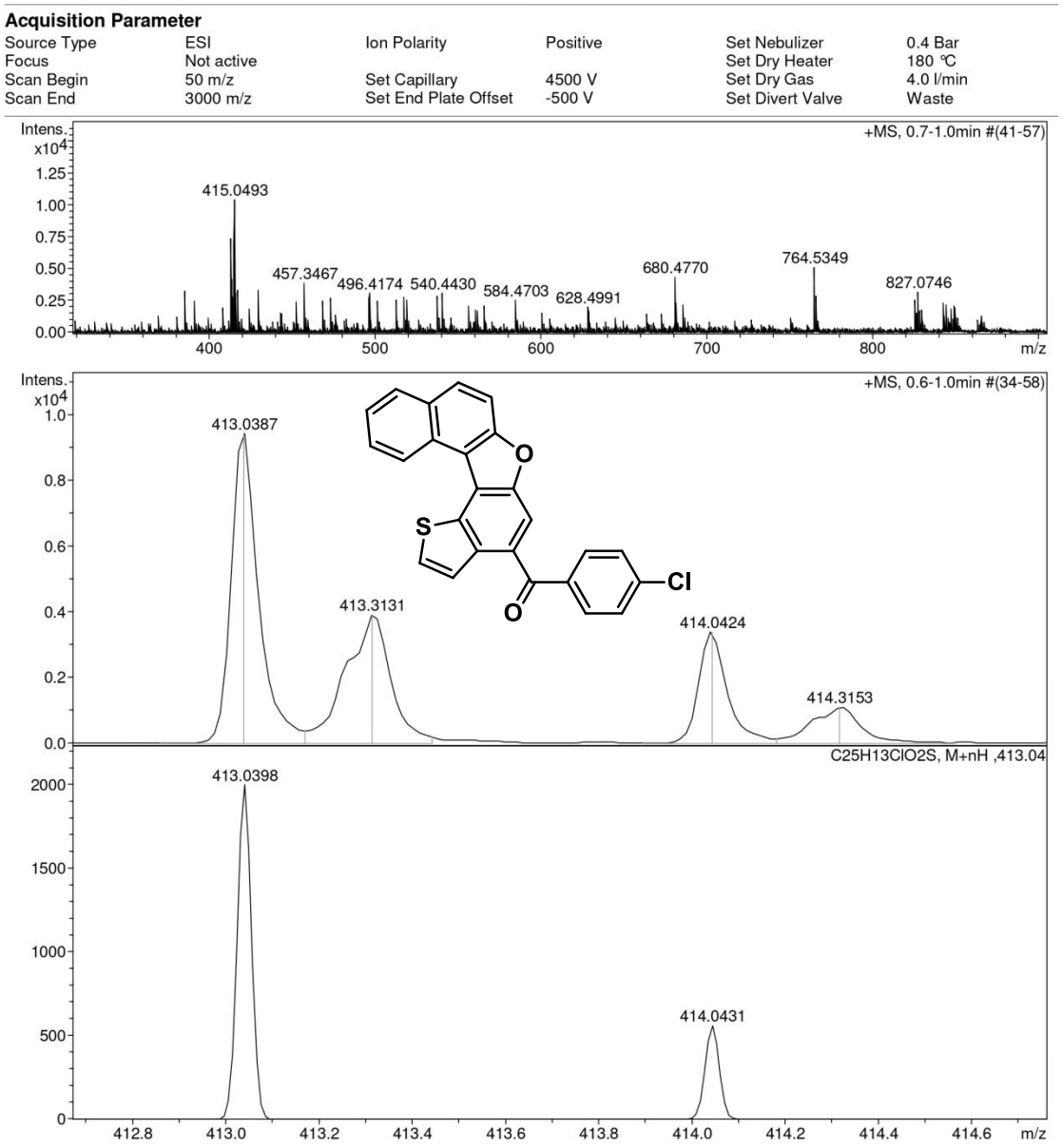
Naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl(phenyl)methanone (3g)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



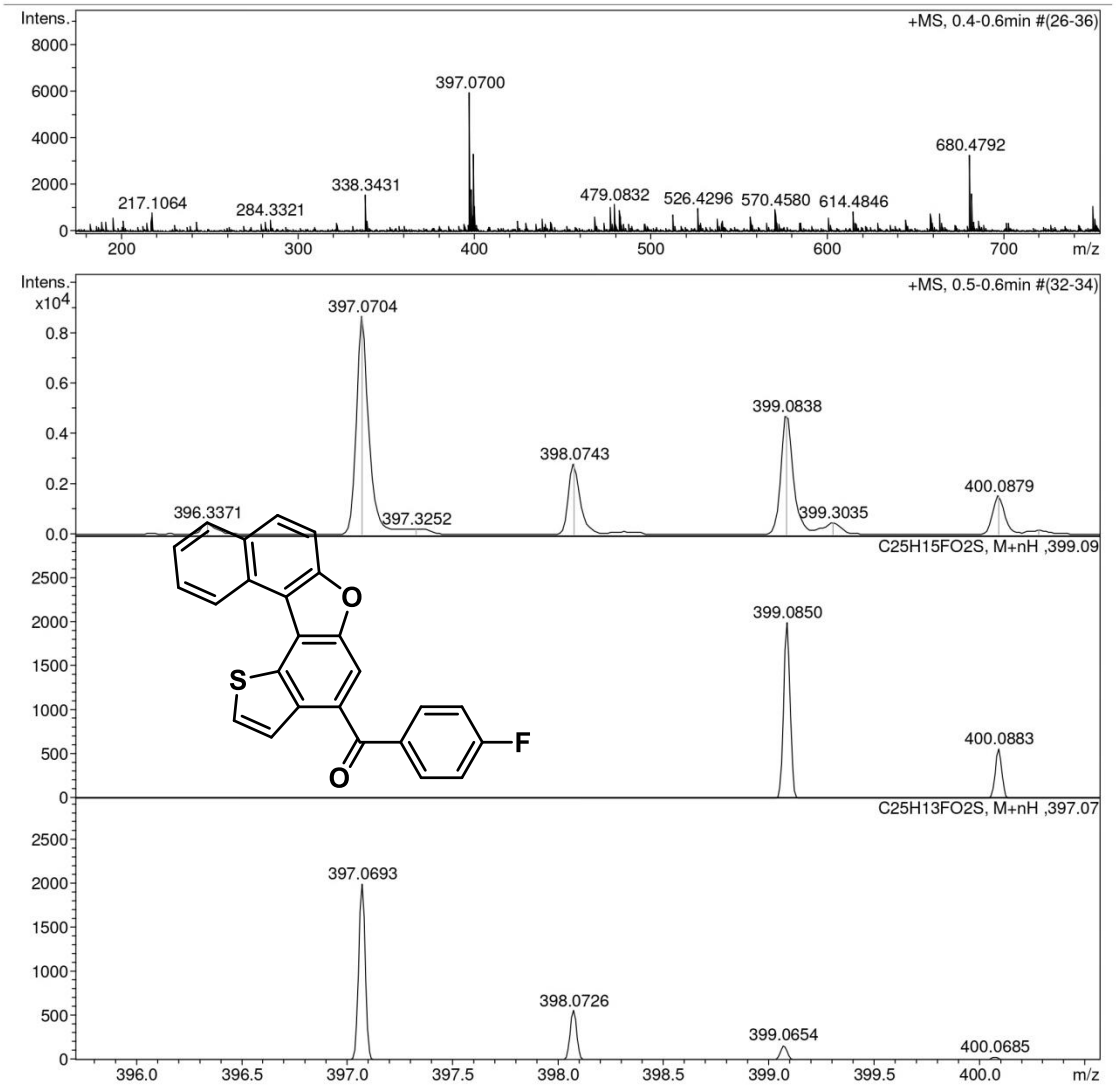
(4-chlorophenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3h)



(4-fluorophenyl)(naphtho[2,1-*b*]thieno[2,3-*e*]benzofuran-4-yl)methanone (3i)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Benzo[4,5]thieno[3,2-*e*]naphtho[2,1-*b*]benzofuran-6-yl(4-methoxyphenyl)methanone (3j)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste