Supplementary Material (ESI) for Chemical Communications

Rhodium-Catalyzed Tandem Nucleophilic Addition/Bicyclization of Diyne-enones with Alcohols: A Modular Entry to 2,3-Fused Bicyclic Furans.

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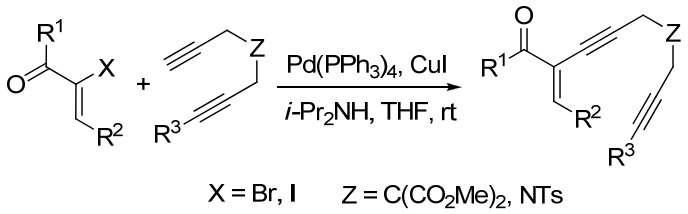
General information

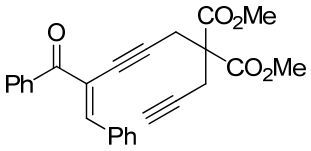
All reactions were carried out in oven-dried glassware under a positive pressure of nitrogen or a mixture of gas. Reactions were monitored using thin-layer chromatography (TLC) Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. 1,4-Dioxane and toluene were distilled from sodium and benzophenone prior to use. 1.2-Dichloroethane was distilled from CaH_2 prior to use. $[RhCl(CO)_2]_2$ were purchased from Alfa Aesar. Purification of products was accomplished by flash chromatography on silica gel. NMR spectra were recorded on a NMR spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm).

General procedure for the preparation of substrates.

Method A: *A typical procedure for the preparation of* **1a-i**: Under a N_2 atmosphere, to a stirred solution of the 2-bromo (iodo)-2-en-1-one and 1, 6-diynes (2.5 equiv) was added $Pd(PPh_3)_4$ (0.02 equiv), CuI (0.04 equiv) and diisopropylamine (3.0 equiv). The mixture was stirred until complete consumption of the starting material as determined by TLC. The crude reaction mixture was then diluted with ethyl acetate and successively washed with brine. The organic layer was dried over anhydrous $MgSO_4$. After filtration and concentration under reduced pressure, the product was isolated by flash column chromatography on silica gel.



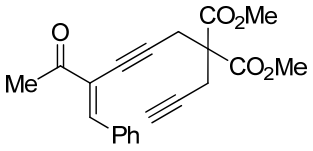
1. **Dimethyl 2-(4-benzoyl-5-phenylpent-4-en-2-ynyl)-2-(prop-2-ynyl) malonate (1a)**:.



1a

The reaction of 2-bromo-1,3-diphenylprop-2-en-1-one (5.0 mmol, 1.435 g) and dimethyl 2,2-di(prop-2-ynyl)malonate (12.5 mmol, 2.600 g) gave the product **1a** (1.449 g, 70%) after flash column chromatography (hexanes: ethyl acetate = 10:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.5 Hz, 2 H), 7.89 (d, *J* = 7.5 Hz, 2 H), 7.60-7.40 (m, 7 H), 3.70 (s, 6 H), 3.29 (s, 2 H), 2.94 (s, 2 H), 2.05 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.56, 168.94, 145.43, 137.02, 134.50, 132.36, 130.50, 130.09, 129.54, 128.55, 128.13, 120.73, 96.22, 80.79, 78.31, 71.85, 56.43, 53.09, 24.27, 22.96 ppm. MS (70 ev) *m/z* (%): 414 (M^+, 0.41), 105 (100), HRMS calcd for $C_{26}H_{22}O_5$: 414.1467, found: 414.1464.

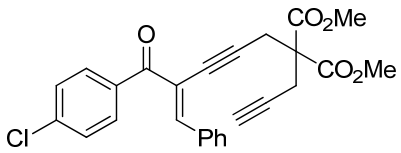
2. Dimethyl 2-(4-benzylidene-5-oxohex-2-ynyl)-2-(prop-2-ynyl)malonate (**1b**):



1b

The reaction of 3-bromo-4-phenylbut-3-en-2-one (5.0 mmol, 1.125 g) with dimethyl 2,2-di(prop-2-ynyl)malonate (12.5 mmol, 2.600 g) gave the product **1b** (1.092 g, 62%) after flash column chromatography (hexanes: ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00-7.90 (m, 2 H), 7.74 (s, 1 H), 7.45-7.38 (m, 2 H), 3.77 (s, 6 H), 3.38 (s, 2 H), 3.07 (d, *J* = 2.4 Hz, 2 H), 2.48 (s, 3 H), 2.10 (t, *J* = 2.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.99, 168.89, 143.17, 134.06, 130.58, 130.37, 128.43, 119.48, 94.23, 80.84, 78.03, 72.02, 56.28, 53.08, 27.82, 24.11, 23.00 ppm. MS (70 ev) *m/z* (%): 352 (M^+, 1.06), 43(100), HRMS calcd for $C_{21}H_{20}O_5$: 352.1311, found: 352.1312.

3. Dimethyl 2-(4-(4-chlorobenzoyl)-5-phenylpent-4-en-2-ynyl)-2-(prop-2-ynyl) malonate (**1c)**:

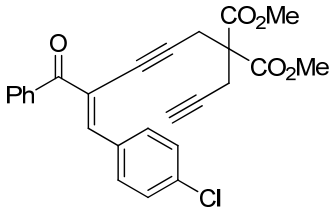


1c

The reaction of 1-(4-chlorophenyl)-2-iodo-3-phenylprop-2-en-1-one (5.0 mmol, 1.843 g) with 4-methyl-N,N-di(prop-2-ynyl)benzenesulfonamide (12.5 mmol, 3.091 g) gave the product **1c** (0.806 g, 36%) after flash column chromatography (hexanes: ethyl acetate = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02-7.94 (m, 2 H), 7.85 (d, *J* = 8.1 Hz, 2 H), 7.52 (s, 1 H), 7.50-7.38 (m, 5 H), 3.71 (s, 6 H), 3.28 (s, 2 H), 2.93 (s, 2 H), 2.06 (s, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.21, 168.91, 145.67, 138.73, 135.32, 134.36, 130.98, 130.70, 130.18, 128.60, 128.45, 120.18, 96.63, 80.79, 78.19, 71.94, 56.34, 53.11, 24.26, 22.98 ppm. MS (70 ev) *m/z* (%): 470 (M^+, 1.21), 139 (100),

HRMS calcd for $C_{21}H_{20}O_5Cl$: 448.1078, found: 448.1074.

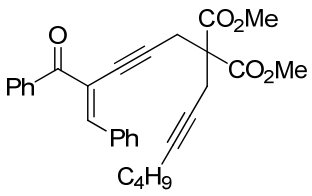
4. Dimethyl 2-(4-benzoyl-5-(4-chlorophenyl)pent-4-en-2-ynyl)-2-(prop-2-ynyl)-malonate (1d):



1d

The reaction of 3-(4-chlorophenyl)-2-iodo-1-phenylprop-2-en-1-one (5.0 mmol, 1.843 g) with 4-methyl-*N*,*N*-di(prop-2-ynyl)benzenesulfonamide (12.5 mmol, 3.091 g) gave the product **1d** (0.941 g, 42%) after flash column chromatography (hexanes: ethyl acetate = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98-7.85 (m, 4 H), 7.60-7.52 (m, 1 H), 7.50-7.37 (m, 5 H), 3.71 (s, 6 H), 3.27 (s, 2 H), 2.92 (d, *J* = 2.4 Hz, 2 H), 2.06 (t, *J* = 2.4 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.24, 168.92, 143.75, 136.83, 136.27, 133.00, 132.51, 131.28, 129.56, 128.86, 128.19, 121.21, 97.08, 80.64, 78.22, 71.97, 56.34, 53.15, 24.31, 23.01 ppm. MS (70 ev) *m/z* (%): 448 (M^+, 5.59), 105 (100), HRMS calcd for $C_{26}H_{21}O_5Cl$: 448.1078, found: 448.1075.

5. Dimethyl 2-(4-benzoyl-5-phenylpent-4-en-2-ynyl)-2-(hept-2-ynyl)malonate (1e):

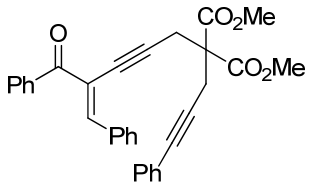


1e

The reaction of 2-bromo-1,3-diphenylprop-2-en-1-one (8.4mmol, 2.411g) with dimethyl 2-(hept-2-ynyl)-2-(prop-2-ynyl)malonate (5.6 mmol, 1.477 g) gave the product **1e** (1.105 g, 42%) after flash column chromatography (hexanes: ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.5 Hz, 2 H), 7.89 (d, *J* = 7.5

Hz, 2 H), 7.60-7.52 (m, 1 H), 7.50-7.38 (m, 6 H), 3.69 (s, 6 H), 3.25 (s, 2 H), 2.89 (s, 2 H), 2.12 (t, *J* = 6.6 Hz, 2 H), 1.47-1.30 (m, 4 H), 0.88 (t, *J* = 6.6 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.65, 169.34, 145.23, 137.07, 134.61, 132.37, 130.46, 130.15, 129.62, 128.55, 128.13, 120.91, 96.82, 84.09, 80.56, 73.76, 56.93, 52.95, 30.89, 24.34, 23.44, 21.78, 18.30, 13.53 ppm. MS (70 ev) *m/z* (%): 470 (M^+, 1.48), 105 (100), HRMS calcd for $C_{30}H_{30}O_5$: 470.2093, found: 470.2094.

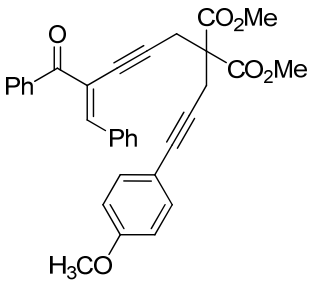
6. Dimethyl2-(4-benzoyl-5-phenylpent-4-en-2-ynyl)-2-(3-phenylprop-2-ynyl)malonate (1f):



1f

The title compound was prepared according to method A from 2-bromo-1,3-diphenylprop-2-en-1-one (7.500 mmol, 2.152 g) and dimethyl 2-(3-phenylprop-2-ynyl)-2-(prop-2-ynyl)malonate (5.000 mmol, 1.420 g) to yield the product **1f** (1.152 g, 47%) after flash column chromatography (hexanes: ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.5 Hz, 2 H), 7.90 (d, *J* = 7.8 Hz, 2 H), 7.53-7.51 (m, 2 H), 7.47-7.40 (m, 5 H), 7.35-7.34 (m, 2 H), 7.28-7.25 (m, 3 H), 3.72 (s, 2 H), 3.34 (s, 2 H), 3.15 (s, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.56, 169.12, 145.37, 137.01, 134.53, 132.36, 131.63, 130.49, 130.10, 129.55, 128.55, 128.18, 128.11, 128.08, 122.94, 120.77, 96.48, 83.95, 83.67, 80.81, 56.81, 53.07, 24.48, 23.94 ppm. MS (70 ev) *m/z* (%): 490 (M^+, 1.18), 105 (100), HRMS calcd for $C_{32}H_{26}O_5$: 490.1780, found: 490.1780.

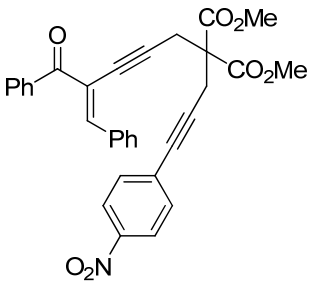
7. Dimethyl2-(4-benzoyl-5-phenylpent-4-en-2-ynyl)-2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (1g):



1g

The compound was prepared by Sonogashira coupling of **1a** (1 g, 2.42 mmol) with 1-iodo-4-methoxybenzene(1.13 g, 4.83 mmol) to yield the product **1g** (0.8 g, 1.54 mmol, 64%)after flash column chromatography (hexanes: ethyl acetate = 5:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05-7.95 (m, 2 H), 7.90 (d, *J* = 7.2 Hz, 2 H), 7.60-7.35 (m, 7 H), 7.29 (d, *J* = 8.7 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 3.80 (s, 3 H), 3.72 (s, 6 H), 3.33 (s, 2 H), 3.13 (s, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.50, 169.05, 159.27, 145.33, 136.82, 134.35, 132.90, 132.20, 130.44, 130.01, 129.45, 128.46, 128.02, 120.57, 114.85, 113.66, 96.45, 83.66, 81.89, 80.64, 56.67, 55.07, 52.99, 24.32, 23.82, MS (70 ev) *m/z* (%): 520 (M^+, 1.98), 105 (100), HRMS calcd for $C_{33}H_{28}O_6$: 520.1624, found: 520.1624.

8. dimethyl2-(4-benzoyl-5-phenylpent-4-en-2-ynyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (1h):

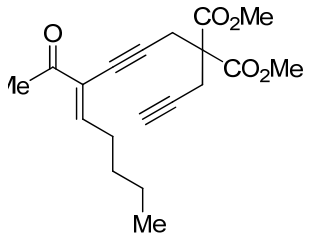


1h

The compound was prepared by Sonogashira coupling of **1a** (1 g, 2.42 mmol) with 1-iodo-4-nitrobenzene (1.20 g, 4.83 mmol) to yield the product **1h** (1.01 g, 1.89 mmol, 78%)after flash column chromatography (hexanes: ethyl acetate = 5:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.4 Hz, 2 H), 7.96-7.87 (m, 2 H), 7.84 (d, *J* = 7.2 Hz, 2 H), 7.55-7.30 (m, 9 H), 3.70 (s, 6 H), 3.23 (s, 2 H), 3.20 (s, 2 H), ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 193.02, 168.55, 146.62, 145.17, 136.65, 134.15, 132.09, 130.27, 129.77, 129.38, 129.21, 128.25, 127.85, 123.11, 120.35, 95.76, 89.49, 82.02, 80.72, 56.29, 52.88, 24.29, 23.75, MS (70 ev) *m/z* (%): 535 (M^+, 1.98), 105 (100), HRMS calcd for $C_{32}H_{25}NO_7$: 535.1624, found: 535.1624.

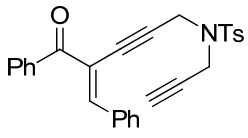
9. Dimethyl 2-(4-acetylnon-4-en-2-ynyl)-2-(prop-2-ynyl)malonate (1i):



1i

The title compound was prepared according to method A from 3-iodooct-3-en-2-one (3.600 mmol, 0.9083 g) and dimethyl 2,2-di(prop-2-ynyl)malonate (10.8 mmol, 2.250 g) to yield the product **1i** (0.5135 g, 45%) after flash column chromatography (hexanes: ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (t, *J* = 7.5 Hz, 1 H), 3.76 (s, 6 H), 3.23 (s, 2 H), 3.00 (d, *J* = 2.1 Hz, 2 H), 2.42-2.29 (m, 5 H), 2.04 (t, *J* = 2.1 Hz, 1 H), 1.50-1.25 (m, 4 H), 0.90 (t, *J* = 7.2 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.48, 169.03, 151.40, 124.52, 91.56, 78.63, 78.18, 71.80, 56.53, 53.07, 30.43, 30.20, 27.77, 23.84, 22.90, 22.39, 13.78. MS (70 ev) *m/z* (%): 332 (M^+, 1.98), 43 (100), HRMS calcd for $C_{19}H_{24}O_5$: 332.1624, found: 332.1624.

10. *N*-(4-benzoyl-5-phenylpent-4-en-2-ynyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (1j):

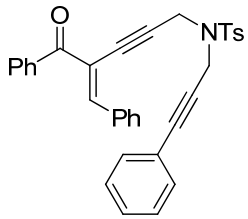


1j

The reaction of 2-bromo-1,3-diphenylprop-2-en-1-one(5.0 mmol, 1.430 g) with 4-methyl-*N*,*N*- di(prop-2-ynyl)benzenesulfonamide (12.5 mmol, 3.091 g) gave the product **1j** (0.930 g, 41%) after flash column chromatography (hexanes: ethyl acetate = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95-7.85 (m, 2 H), 7.77 (d, *J* = 7.5 Hz, 2 H),

7.61 (d, *J* = 8.1 Hz, 2 H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.48-7.36 (m, 6 H), 7.13 (d, *J* = 8.1Hz, 2 H), 4.43 (s, 2 H), 3.95 (s, 2 H), 2.28(s, 3H), 2.20 (s, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): 192.90, 146.01, 143.90, 136.62, 134.67, 134.03, 132.47, 130.72, 129.91, 129.43, 129.29, 128.52, 128.10, 127.58, 119.88, 93.29, 82.81, 76.13, 74.17, 37.17, 36.33, 21.27. ppm. MS (70 ev) *m/z* (%): 453(M^+, 1.33), 105 (100), HRMS calcd for $C_{28}H_{23}NO_3S$: 453.1399, found: 453.1402.

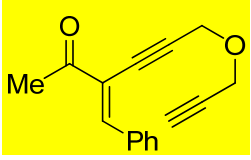
11. *N*-(4-Benzoyl-5-phenylpent-4-en-2-ynyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (1k):



1k

The title compound was prepared according to method A from 2-bromo-1,3-diphenylprop-2-en-1-one (20.00 mmol, 5.74 g) and 4-methyl-*N*-(3-phenylprop-2-ynyl)-*N*-(prop-2-ynyl)benzenesulfonamide (22.00 mmol, 5.214 g) to yield the product **1k** (4.761 g, 45%) after flash column chromatography (hexanes: ethyl acetate = 5:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05-7.92 (m, 2 H), 7.85 (d, *J* = 7.2 Hz, 2 H), 7.71 (d, *J* = 8.1 Hz, 2 H), 7.65-7.38 (m, 7 H), 7.35-7.12 (m, 7 H), 4.50 (s, 2 H), 4.23 (s, 2 H), 2.29 (s, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.01, 146.11, 143.88, 136.68, 134.71, 134.08, 132.49, 131.49, 130.75, 129.96, 129.48, 129.33, 128.55, 128.46, 128.11, 128.08, 127.68, 121.91, 119.94, 93.56, 85.90, 82.81, 81.17, 37.48, 37.24, 21.26. MS (70 ev) *m/z* (%): 529 (M^+, 3.94), 105 (100), HRMS calcd for $C_{34}H_{27}NO_3S$: 529.1712, found: 529.1710.

12. 3-benzylidene-6-(prop-2-ynyloxy)hex-4-yn-2-one (1l)

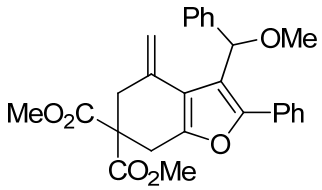


1l

The title compound was prepared according to method A from 3-bromo-4-phenylbut-3-en-2-one (6.35 g, 28.00 mmol) and 3-(prop-2-ynyloxy) prop-1-yne (5.30 g, 56.00 mmol) to yield the product **1l** (3.33 g, 45%) after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10-7.94 (m, 2 H), 7.79 (s, 1 H), 7.48-7.32 (m, 3 H), 4.59 (s, 2 H), 4.34 (d, *J* = 2.1 Hz, 2 H), 2.53 (d, *J* = 2.1 Hz, 1 H), 2.51 (s, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.66, 144.10, 133.88, 130.75, 130.39, 128.43, 119.20, 94.29, 83.78, 78.53, 75.30, 57.04, 56.44, 27.70. MS (70 ev) *m/z* (%): 238 (M^+, 3.94), 105 (100), HRMS calcd for $C_{16}H_{14}O_2$: 238.0975, found: 238.0978.

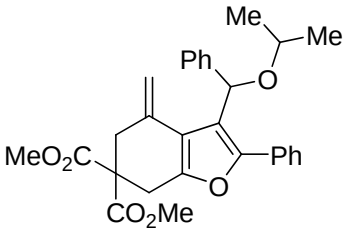
13. Synthesis of 2aa.

$[RhCl(cod)]_2$ (7.4 mg, 0.015 mmol) was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of the mixed CO (0.2 atm CO + 0.8 atm N_2), and then a solution of **1a** (124.2 mg, 0.3 mmol) in degassed TCE (3 mL) and methanol (0.3 mL) was added. The reaction mixture was stirred at 60 °C under the mixed CO atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was directly purified by flash column chromatography with silica gel (hexanes/ethyl acetate = 10:1) to afford **2aa** in 83% yield.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.2 Hz, 2 H), 7.41-7.19 (m, 8 H), 5.69 (s, 1 H), 5.22 (s, 1 H), 4.81 (s, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.43 (d, *J* = 16.8 Hz, 1 H), 3.32 (d, *J* = 16.8 Hz, 1 H), 2.97 (d, *J* = 14.7 Hz, 1 H), 2.91 (d, *J* = 14.7 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.71, 170.61, 152.81, 150.57, 140.56, 131.54, 130.44, 128.42, 128.17, 128.12, 127.60, 127.35, 126.92, 119.37, 116.82, 113.77, 76.23, 56.41, 54.74, 52.86, 39.03, 29.96, MS (70 ev) *m/z* (%): 446 (M^+, 71.72), 105 (100), HRMS calcd for $C_{27}H_{26}O_6$: 446.1729, found: 446.1730.

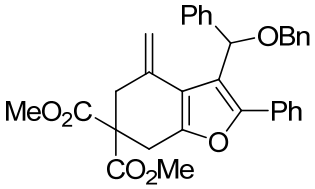
14. 2ab.



The title compound was prepared from **1a**(0.2 mmol, 82.8 mg) and i-PrOH under the optimized conditions to afford **2ab** (75.3 mg) in 79% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52-7.18 (m, 10 H), 5.86 (s, 1 H), 5.30 (s, 1 H), 4.81 (s, 1 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 3.45-3.60 (m, 1 H), 3.45 (d, *J* = 16.5 Hz, 1 H), 3.29 (d, *J* = 16.5 Hz, 1 H), 2.96 (d, *J* = 14.4 Hz, 1 H), 2.90 (d, *J* = 14.4 Hz, 1 H), 1.03 (d, *J* = 5.7 Hz, 3 H), 0.97 (d, *J* = 5.7 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.85, 170.62, 152.33, 150.45, 141.22, 131.35, 130.56, 128.43, 128.13, 128.04, 127.48, 127.15, 127.04, 119.65, 117.96, 114.33, 72.00, 68.93, 54.82, 52.90, 52.82, 39.09, 30.05, 22.94, 21.10. MS (70 ev) *m/z* (%): 474 (M^+, 37.69), 105 (100), HRMS calcd for $C_{29}H_{30}O_6$: 474.2042, found: 474.2043

.

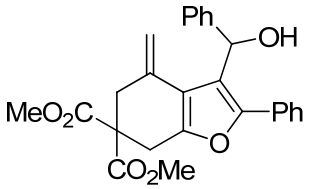
15. 2ac.



The title compound was prepared from **1a** (0.2 mmol, 82.8 mg) and BnOH under the optimized conditions to afford **2ac** (66.6 mg) in 51% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.11 (m, 15 H), 5.83 (s, 1 H), 5.27 (s, 1 H), 4.81 (s, 1 H), 4.51 (d, *J* = 11.7 Hz, 1 H), 4.23 (d, *J* = 11.7 Hz, 1 H), 3.72 (s, 3 H), 3.70 (s, 3 H), 3.45 (d, *J* = 16.5 Hz, 1 H), 3.33 (d, *J* = 16.5 Hz, 1 H), 2.97 (d, *J* = 14.7 Hz, 1 H), 2.91 (d, *J* = 14.7 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.75, 170.64, 152.99, 150.70, 140.60, 138.07, 131.34,

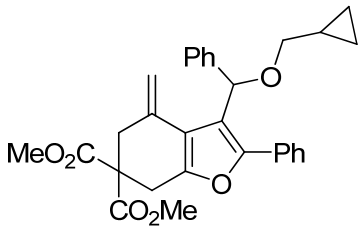
130.38, 128.43, 128.14, 128.05, 127.51, 127.31, 126.95, 119.42, 116.78, 114.17, 73.68, 70.37, 54.75, 52.90, 39.01, 30.02. MS (70 ev) *m/z* (%): 522 (M^+, 3.80), 105 (100), HRMS calcd for $C_{33}H_{30}O_6$: 522.2042, found: 522.2041.

16. 2ad.



The title compound was prepared from **1a**(0.2 mmol, 82.8 mg) and H_2O under the optimized conditions to afford **2ad**(49.0 mg) in 45% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.20 (m, 10 H), 6.19 (s, 1 H), 4.97 (s, 1 H), 4.81 (s, 1 H), 3.76 (brs, 4 H), 3.73 (s, 3 H), 3.43 (d, *J* = 16.8 Hz, 1 H), 3.35 (d, *J* = 16.8 Hz, 1 H), 2.94 (s, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.65, 170.51, 151.76, 150.85, 141.95, 132.52, 130.26, 128.54, 128.29, 127.46, 127.22, 126.34, 119.30, 118.69, 113.02, 67.86, 54.65, 53.02, 52.94, 38.89, 29.73, MS (70 ev) *m/z* (%): 432 (M^+, 10.09), 57 (100), HRMS calcd for $C_{26}H_{24}O_6$: 432.1573, found: 432.1570.

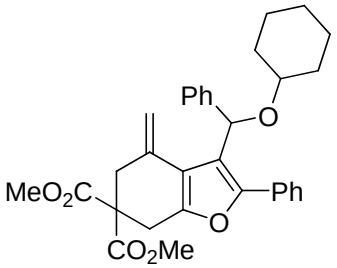
17. 2ae.



The title compound was prepared from **1a**(0.2 mmol, 82.8 mg) and cyclopropylmethanol under the optimized conditions to afford **2ae**(73.0 mg) in 60% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.21 (m, 10 H), 5.85 (s, 1 H), 5.37 (s, 1 H), 4.86 (s, 1 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.46 (d, *J* = 16.8 Hz, 1 H), 3.32 (d, *J* = 16.8 Hz, 1 H), 3.20-3.28 (m, 1 H), 3.05-3.15 (m, 1 H), 2.99 (d, *J* = 14.4 Hz, 1 H), 2.92 (d, *J* = 14.4 Hz, 1 H),

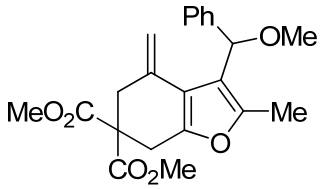
1.08-0.85 (m, 1 H), 0.39 (d, *J* = 7.8 Hz, 1 H), 0.04 (d, *J* = 4.8 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.78, 170.57, 152.37, 150.42, 140.75, 131.36, 130.46, 128.37, 128.15, 128.03, 127.49, 127.26, 127.09, 119.48, 117.31, 114.12, 74.46, 73.08, 54.72, 52.88, 52.82, 39.02, 29.95, 10.43, 3.01, MS (70 ev) *m/z* (%): 486 (M^+, 13.57), 57 (100), HRMS calcd for $C_{30}H_{30}O_6$: 486.2042, found: 486.2043.

18. 2af.



The title compound was prepared from **1a** (0.2 mmol, 82.8 mg) and cyclohexanol under the optimized conditions to afford **2ae** (80.5 mg) in 63% yield after flash column chromatography (hexanes: ethyl acetate = 10:1),^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.5 Hz, 1 H), 7.42-7.20 (m, 8 H), 5.76 (s, 1 H), 5.28 (s, 1 H), 4.80 (s, 1 H), 3.71 (s, 6 H), 3.50-3.20 (m, 3 H), 2.95 (d, *J* = 14.7 Hz, 1 H), 2.89 (d, *J* = 14.7 Hz, 1 H), 1.51-1.38 (m, 2 H), 1.31-1.11 (m, 6 H), 0.91-0.80 (m, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.77, 170.61, 152.42, 150.38, 140.94, 131.35, 130.53, 128.37, 128.08, 128.01, 127.55, 127.16, 126.89, 119.46, 117.54, 113.95, 77.00, 74.85, 68.83, 54.74, 52.87, 52.82, 39.02, 31.57, 29.96, 29.64, 25.94, 22.51, 13.98. MS (70 ev) *m/z* (%): 514 (M^+, 7.80), 105 (100), HRMS calcd for $C_{32}H_{34}O_6$: 514.2378, found: 514.2378.

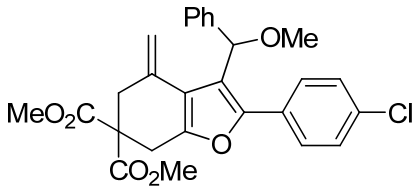
19. 2ba.



The title compound was prepared from **1b** (0.3 mmol, 105.6 mg) and methanol under the optimized conditions to afford **2ba** (71.0 mg) in 62% yield after flash column

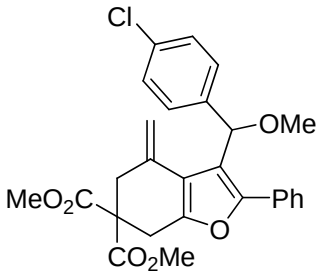
chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.18 (m, 5 H), 5.41 (s, 1 H), 5.11 (s, 1 H), 4.78 (s, 1 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 3.35 (s, 3 H), 3.29 (d, *J* = 16.5 Hz, 1 H), 3.23 (d, *J* = 16.5 Hz, 1 H), 2.88 (s, 2 H), 2.21 (s, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.81, 170.62, 150.36, 148.56, 140.75, 132.62, 128.05, 127.21, 126.76, 118.21, 115.85, 111.54, 77.23, 56.48, 54.83, 52.86, 52.83, 38.89, 29.66, 12.33. MS (70 ev) *m/z* (%): 384 (M^+, 59.50), 293 (100), HRMS calcd for $C_{22}H_{24}O_6$: 384.1573, found: 384.1572.

20. 2ca.



The title compound was prepared from **1c** (0.25 mmol, 112 mg) and methanol under the optimized conditions to afford **2ca** (87.8 mg) in 73% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45- 7.20 (m, 9 H), 5.64 (s, 1 H), 5.19 (s, 1 H), 4.83 (s, 1 H), 3.72 (s, 6 H), 3.42 (d, *J* = 16.8 Hz, 1 H), 3.31 (d, *J* = 16.8 Hz, 1 H), 3.23 (s, 3 H), 2.97 (d, *J* = 14.4 Hz, 1 H), 2.91 (d, *J* = 14.4 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.68, 170.55, 151.42, 150.74, 140.20, 134.01, 131.53, 128.90, 128.73, 128.62, 128.27, 127.52, 126.94, 119.56, 117.42, 113.78, 76.80, 56.53, 54.70, 52.92, 39.02, 29.92. MS (70 ev) *m/z* (%): 480 (M^+, 87.89), 139 (100), HRMS calcd for $C_{27}H_{25}O_6Cl$: 480.1340, found: 480.1341.

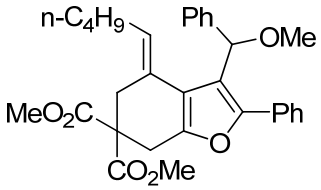
21. 2da.



The title compound was prepared from **1d** (0.25 mmol, 112 mg) and methanol under the optimized conditions to afford **2da** (84.2 mg) in 70% yield after flash column

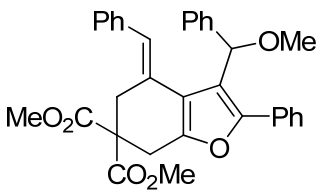
chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.5 Hz, 2 H), 7.41-7.20 (m, 7 H), 5.63 (s, 1 H), 5.18 (s, 1 H), 4.81 (s, 1 H), 3.72 (s, 6 H), 3.42 (d, *J* = 16.8 Hz, 1 H), 3.32 (d, *J* = 16.8 Hz, 1 H), 3.23 (s, 3 H), 2.97 (d, *J* = 14.4 Hz, 1 H), 2.90 (d, *J* = 14.4 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.65, 170.55, 152.97, 150.73, 139.13, 133.13, 131.50, 130.23, 128.48, 128.30, 127.57, 119.16, 116.31, 113.74, 76.04, 56.37, 54.67, 52.91, 38.94, 29.91. MS (70 ev) *m/z* (%): 480 (M^+, 57.82), 105 (100), HRMS calcd for $C_{27}H_{25}O_6Cl$: 480.1362, found: 480.1343.

22. 2ea.



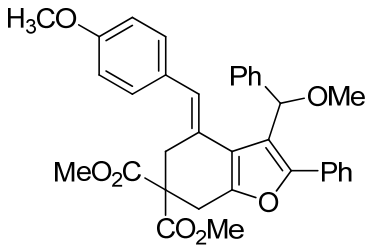
The title compound was prepared from **1e** (0.25 mmol, 117.5 mg) and methanol under the optimized conditions to afford **2ea** (78 mg) in 62% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 2 H), 7.41-7.18 (m, 8 H), 5.77 (t, *J* = 7.5 Hz, 1 H), 5.69 (s, 1 H), 3.71 (s, 6 H), 3.41 (d, *J* = 16.5 Hz, 1 H), 3.30 (d, *J* = 16.5 Hz, 1 H), 3.23 (s, 3 H), 2.99 (d, *J* = 14.7 Hz, 1 H), 2.82 (d, *J* = 14.7 Hz, 1 H), 2.10-1.90 (m, 2 H), 1.12-0.91 (m, 4 H), 0.76 (t, *J* = 6.9 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.02, 170.86, 152.81, 148.70, 140.76, 130.69, 129.86, 128.36, 128.01, 127.74, 127.09, 126.79, 122.57, 120.37, 116.50, 76.63, 56.29, 54.58, 52.78, 31.92, 31.45, 30.13, 27.31, 21.92, 13.96. MS (70 ev) *m/z* (%): 502 (M^+, 39.20), 105 (100), HRMS calcd for $C_{31}H_{34}O_6$: 502.2355, found: 502.2356.

23. 2fa.



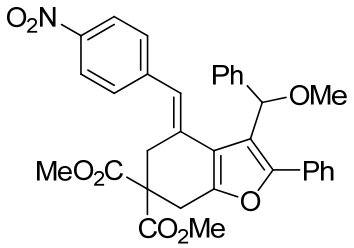
The title compound was prepared from **1f** (0.25 mmol, 122 mg) and methanol under the optimized conditions to afford **2fa** (96.9 mg) in 81% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 6.6 Hz, 2 H), 7.51-7.10 (m, 10 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.99 (d, *J* = 7.8 Hz, 2 H), 6.90 (s,1 H), 5.80 (s, 1 H), 3.70 (s, 3 H), 3.67 (s, 3 H), 3.51 (d, *J* = 16.5 Hz, 1 H), 3.41 (d, *J* = 16.5 Hz, 1 H), 3.34 (s, 3 H), 3.28 (d, *J* = 14.7 Hz, 1 H), 3.09 (d, *J* = 14.7 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.73, 170.68, 153.20, 150.27, 140.68, 137.87, 130.45, 128.67, 128.44, 128.20, 128.12, 127.87, 127.80, 127.27, 126.77, 125.98, 125.05, 120.33, 116.64, 77.00, 56.44, 54.80, 52.77, 32.57, 30.29. MS (70 ev) *m/z* (%): 522 (M^+, 9.39), 105 (100), HRMS calcd for $C_{33}H_{30}O_6$: 522.2042 found: 522.2040.

24. 2ga



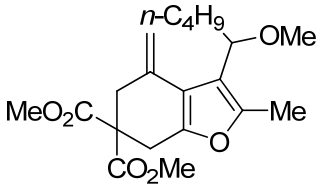
The title compound was prepared from **1g** (0.2 mmol, 104 mg) and methanol under the optimized conditions to afford **2ga** (108 mg) in 98% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 6.6 Hz, 2 H), 7.51-7.25 (m, 8 H), 6.95 (d, *J* = 8.7 Hz, 2 H), 6.90-6.78 (m, 3 H), 5.81 (s, 1 H), 3.83 (s, 3 H), 3.72 (s, 3 H), 3.68 (s, 3 H), 3.61-3.38 (m, 2 H), 3.35 (s, 3 H), 3.29 (d, *J* = 14.7 Hz, 1 H), 3.11 (d, *J* = 14.7 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.73, 170.68, 157.75, 153.08, 149.87, 140.70, 130.44, 130.35, 129.82, 128.40, 128.13, 128.07, 127.73, 127.22, 126.74, 123.83, 120.41, 116.53, 113.29, 76.58, 56.41, 55.07, 54.73, 52.75, 32.54, 30.23, MS (70 ev) *m/z* (%): 552 (M^+, 33.77), 105 (100), HRMS calcd for $C_{34}H_{32}O_7$: 552.1974, found: 552.1974.

25. 2ha



The title compound was prepared from **1h** (0.2 mmol, 107 mg) and methanol under the optimized conditions to afford **2ha** (77.8 mg) in 69% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.7 Hz, 2 H), 7.61-7.25 (m, 10 H), 7.09 (d, *J* = 8.7 Hz, 2 H), 6.91 (s, 1 H), 5.80 (s, 1 H), 3.73 (s, 3 H), 3.68 (s, 3 H), 3.53 (d, *J* = 16.8 Hz, 1 H), 3.45 (d, *J* = 16.8 Hz, 1 H), 3.34 (s, 3 H), 3.23 (d, *J* = 14.7 Hz, 1 H), 3.06 (d, *J* = 14.4 Hz, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.28, 153.80, 151.49, 145.61, 144.82, 140.45, 129.99, 129.21, 128.54, 128.47, 128.19, 127.76, 127.43, 126.56, 126.46, 123.30, 119.80, 116.33, 76.34, 56.50, 54.75, 52.97, 52.94, 32.54, 30.16, MS (70 ev) *m/z* (%): 567 (M^+, 33.77), 105 (100), HRMS calcd for $C_{33}H_{29}NO_8$: 567.1974, found: 567.1974.

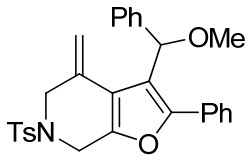
26. 2ia.



The title compound was prepared from **1i** (0.25 mmol, 83 mg) and methanol under the optimized conditions to afford **2ia** (55 mg) in 60% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.46 (s, 1 H), 4.93 (s, 1 H), 4.19 (t, *J* = 6.9 Hz, 1 H), 3.72 (s, 3 H), 3.68 (s, 3 H), 3.30 (d, *J* = 16.5 Hz, 1 H), 3.15 (s, 3 H), 3.01 (d, *J* = 16.5 Hz, 1 H), 2.95 (d, *J* = 14.4 Hz, 1 H), 2.88 (d, *J* = 14.4 Hz, 1 H), 2.23 (s, 3 H), 1.85-1.60 (m, 2 H), 1.38-1.09 (m, 4 H), 1.23 (d, *J* = 6.3 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.98, 170.52, 149.13, 148.34, 133.27, 117.97, 116.84, 111.53, 76.54, 55.86, 54.83, 52.86, 52.80, 39.04, 34.67, 29.58,

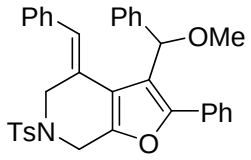
28.25, 22.50, 13.99, 12.16. MS (70 ev) *m/z* (%): 364 (M^+, 43.50), 307 (100), HRMS calcd for $C_{20}H_{28}O_6$: 364.1886, found: 364.1886.

27. 2ja.



The title compound was prepared from **1j**(0.25 mmol, 113 mg) and methanol under the optimized conditions to afford **2ja** (74.2 mg) in 61% yield after flash column chromatography (hexanes: ethyl acetate = 6:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.1 Hz, 2 H), 7.45-7.20 (m, 12 H), 5.60 (s, 1 H), 5.20 (s, 1 H), 4.85 (s, 1 H), 4.55 (d, *J* = 16.2 Hz, 1 H), 4.43 (d, *J* = 16.2 Hz, 1 H), 4.03 (d, *J* = 14.1 Hz, 1 H), 3.83 (d, *J* = 14.1 Hz, 1 H), 3.14 (s, 3 H), 2.39 (s, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.05, 147.68, 143.60, 140.16, 133.98, 130.31, 129.90, 129.56, 128.56, 128.49, 128.23, 127.68, 127.51, 126.72, 118.66, 116.92, 113.30, 76.57, 56.46, 50.96, 43.84, 21.48. MS (70 ev) *m/z* (%): 485 (M^+, 13.57), 57 (100), HRMS calcd for $C_{29}H_{27}NO_4S$: 485.1661, found: 485.1660.

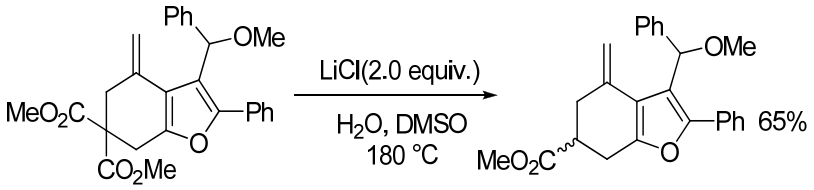
28. 2ka.



The title compound was prepared from **1k** (0.3 mmol, 158 mg) and methanol under the optimized conditions to afford **2ka** (126.2 mg) in 75% yield after flash column chromatography (hexanes: ethyl acetate = 10:1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.4 Hz, 2 H), 7.58-7.18 (m, 15 H), 6.99 (d, *J* = 7.5 Hz, 2 H), 6.80 (s, 1 H), 5.73 (s, 1 H), 4.71 (d, *J* = 16.8 Hz, 1 H), 4.55 (d, *J* = 16.8 Hz, 1 H), 4.51 (d, *J* = 14.4 Hz, 1 H), 4.11 (d, *J* = 14.4 Hz, 1 H), 3.24 (s, 3 H), 2.43 (s, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.32, 147.32, 143.43, 140.27, 136.65, 134.22, 129.90, 129.43, 128.62, 128.54, 128.17, 127.62, 127.48, 127.39, 126.65, 126.55, 123.63, 119.58, 116.62,

76.37, 56.38, 45.43, 43.88, 21.45 ppm. MS (70 ev) *m/z* (%): 561 (M^+, 33.77), 121 (100), HRMS calcd for $C_{35}H_{31}NO_4S$: 561.1974, found: 561.1974.

29. Synthesis of methyl 3-(methoxy(phenyl)methyl)-4-methylene-2-phenyl-4,5,6,7- tetrahydrobenzofuran-6-carboxylate 3



2aa **3**

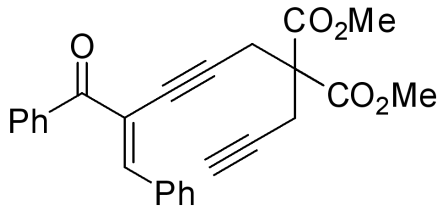
LiCl (0.4 mmol, 17.0 mg) was charged in a base-washed, oven-dried Schlenk flask, and then a solution of **2aa** (89.2 mg, 0.2 mmol) in DMSO (1.0 mL) and water (0.1 mL) was added. The reaction mixture was stirred at 180 °C under the nitrogen atmosphere for 30 mins. After being cooled to room temperature, the mixture was extracted with EtOAc and dried with $MgSO_4$. After filtration and concentration under reduced pressure, the residue was purified by flash column chromatography with silica gel (hexanes/ethyl acetate = 20:1) to afford **3** as a 46/54 mixture of diastereoisomers in 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (m, 10 H), 5.75 (s, 1 H), [5.31 (s, 0.46 H), 5.09 (s, 0.54 H)], 4.82 (s, 1 H), 3.78 (s, 3 H), [3.34 (s, 1.38 H), 3.31 (s, 1.62 H)], 3.15-2.87 (m, 3 H), 2.75-2.45 (m, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.49, 152.51, 152.42, 151.95, 151.88, 140.82, 140.46, 134.04, 133.75, 130.56, 130.47, 128.43, 128.40, 128.27, 128.13, 128.08, 128.05, 127.66, 127.50, 127.37, 127.28, 126.89, 126.84, 119.72, 119.43, 117.03, 116.86, 112.26, 112.19, 76.91, 76.81, 56.64, 56.59, 51.96, 40.18, 39.88, 36.17, 36.06, 31.54, 26.33, 26.24, ppm. MS (70 ev) *m/z* (%): 388 (M^+, 57.38), 105 (100), HRMS calcd for $C_{25}H_{24}O_4$: 388.1675, found: 388.1675.

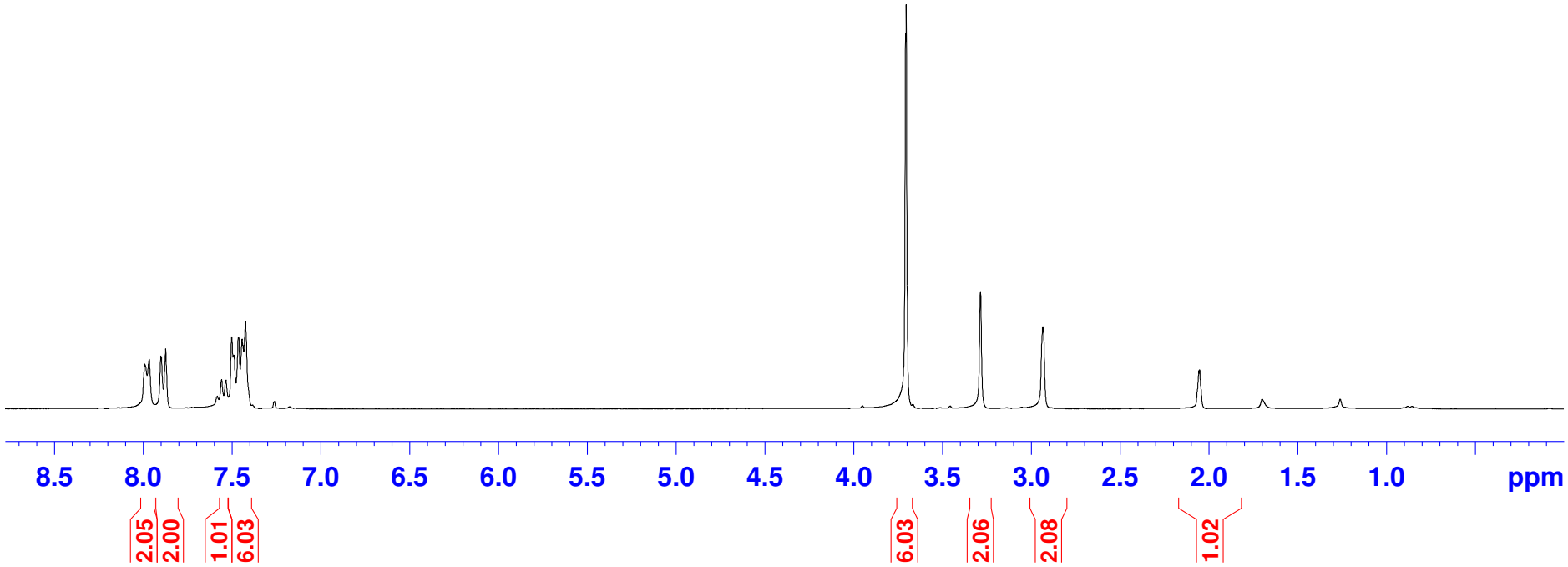
.

7.991
7.966
7.900
7.873
7.558
7.537
7.501
7.490
7.465
7.462
7.442
7.438
7.423

3.706
3.280
2.935
2.052

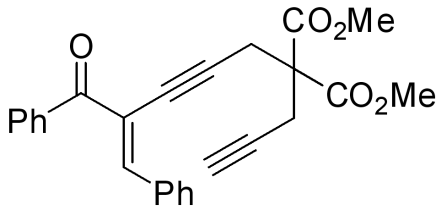
zwx-285

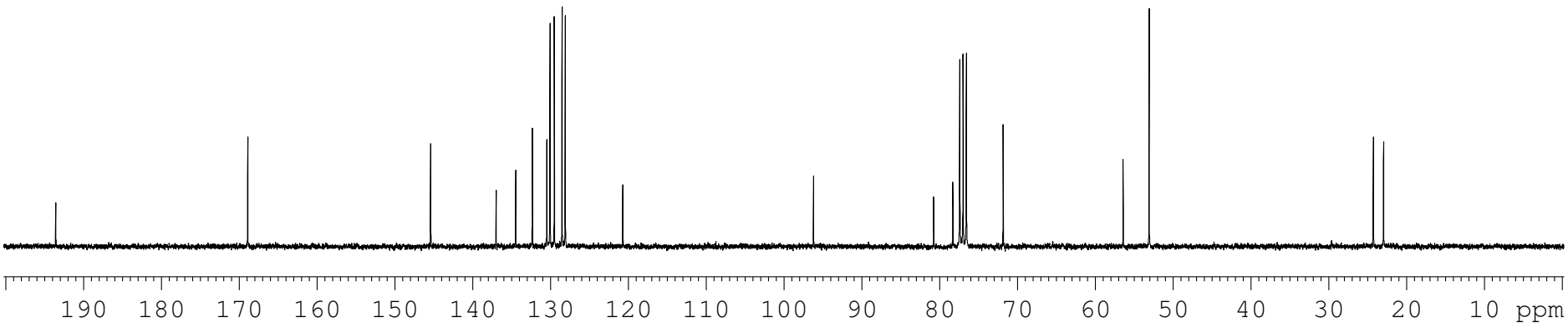




193.56
168.94
145.43
137.02
134.50
132.36
130.50
130.09
129.54
128.53
128.14
120.77
96.22
80.79
78.31
77.43
77.00
76.58
71.85
56.43
53.09
24.27
22.96

zwx-285



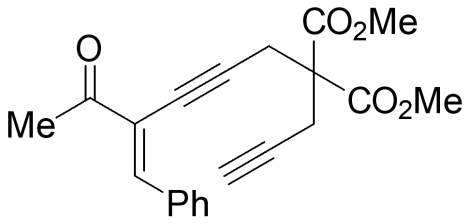


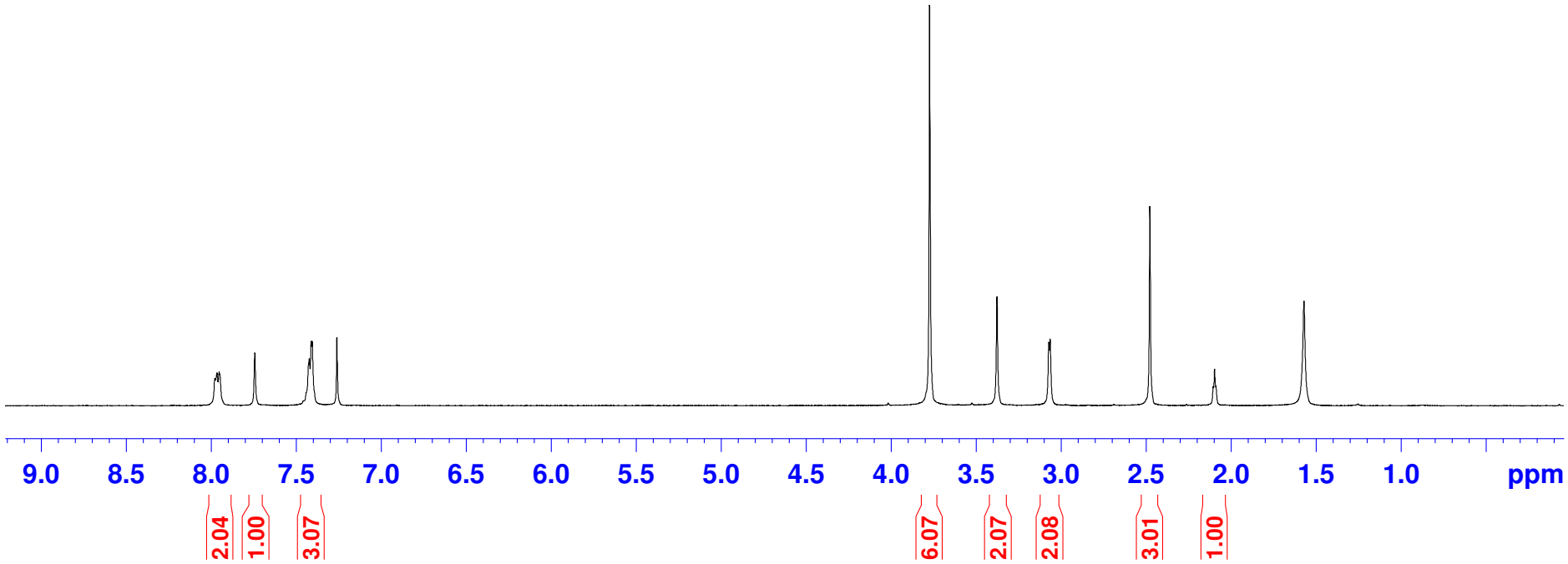
7.978
7.965
7.953
7.743
7.423
7.411
7.405
7.260

3.774
3.377
3.072
3.064

2.478
2.106
2.097
2.088

zwx-271





195.99
168.89
143.17
134.06
130.58
130.33
128.47
119.48
94.23
80.84
78.03
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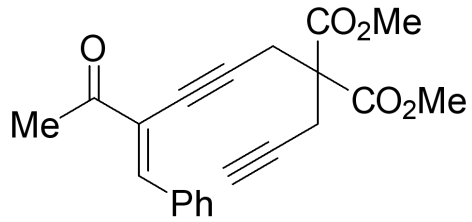
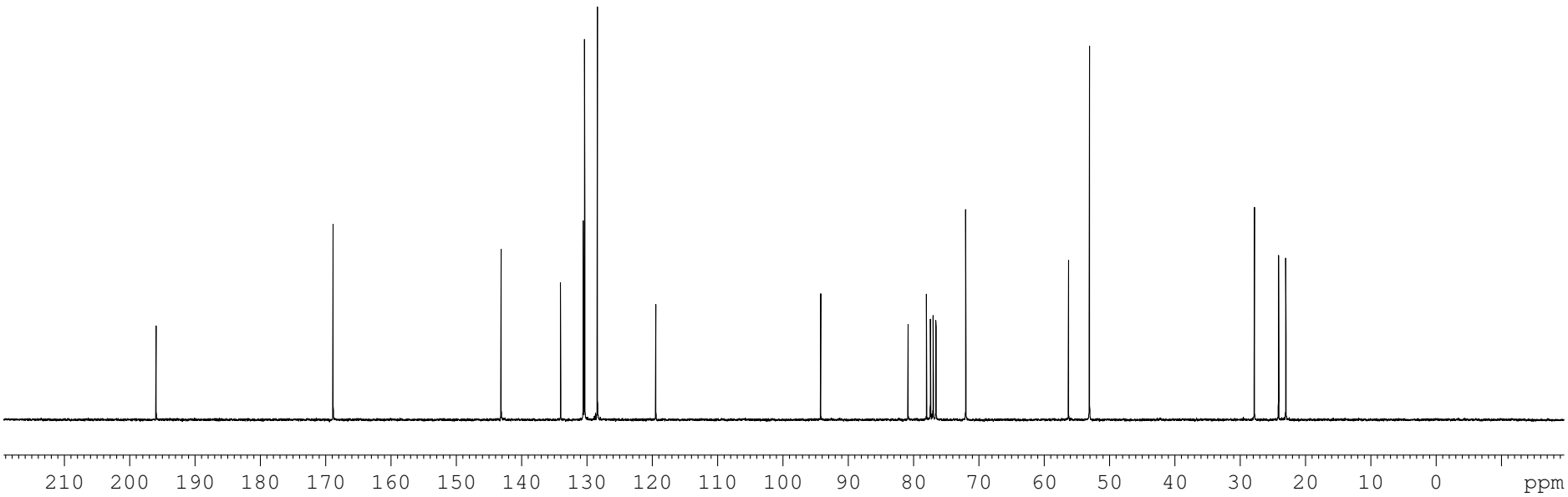
77.00
76.58
72.02
56.28
53.08
27.82
24.11
23.00

zwx-271-C





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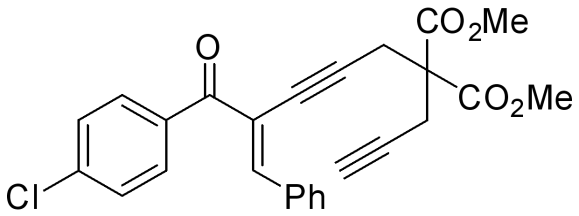
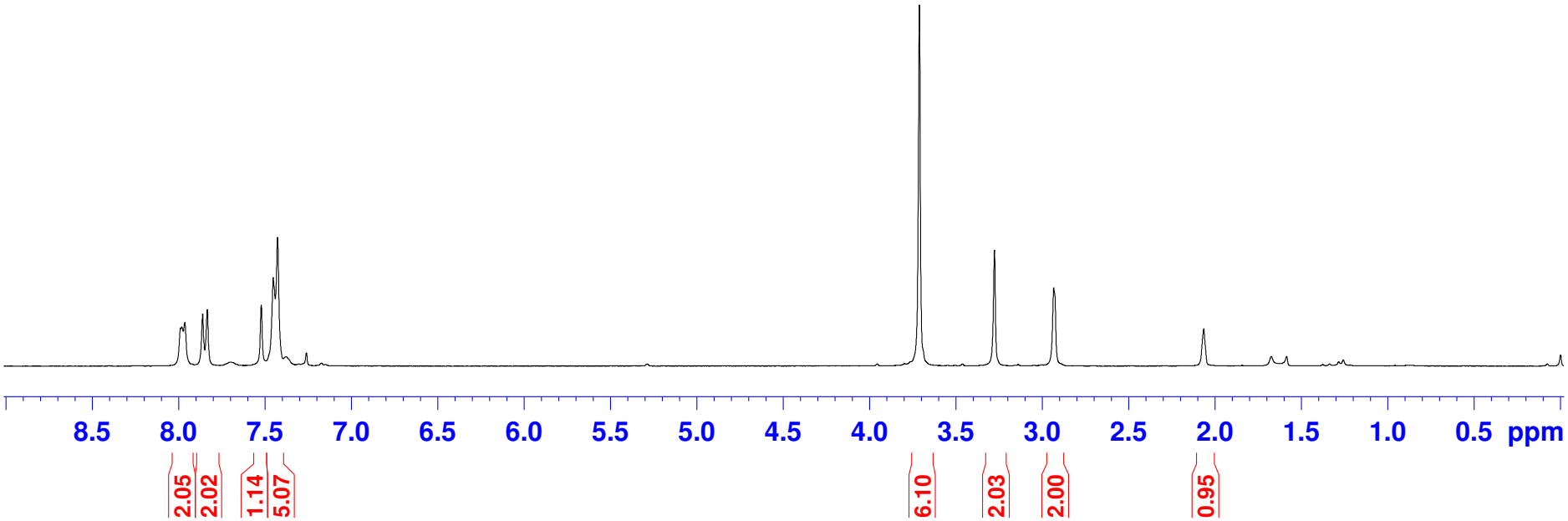
7.981
7.964
7.861
7.834
7.521
7.452
7.427

3.711
3.271
2.933
2.064

zwx-0722-1





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138.73
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134.36
130.98
130.70
130.18
128.65
128.40
120.13
96.63
80.79
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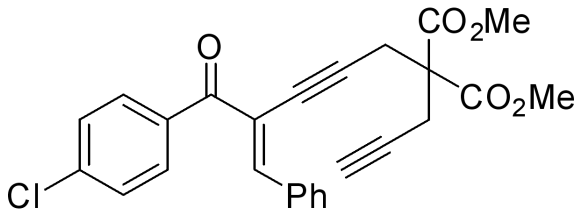
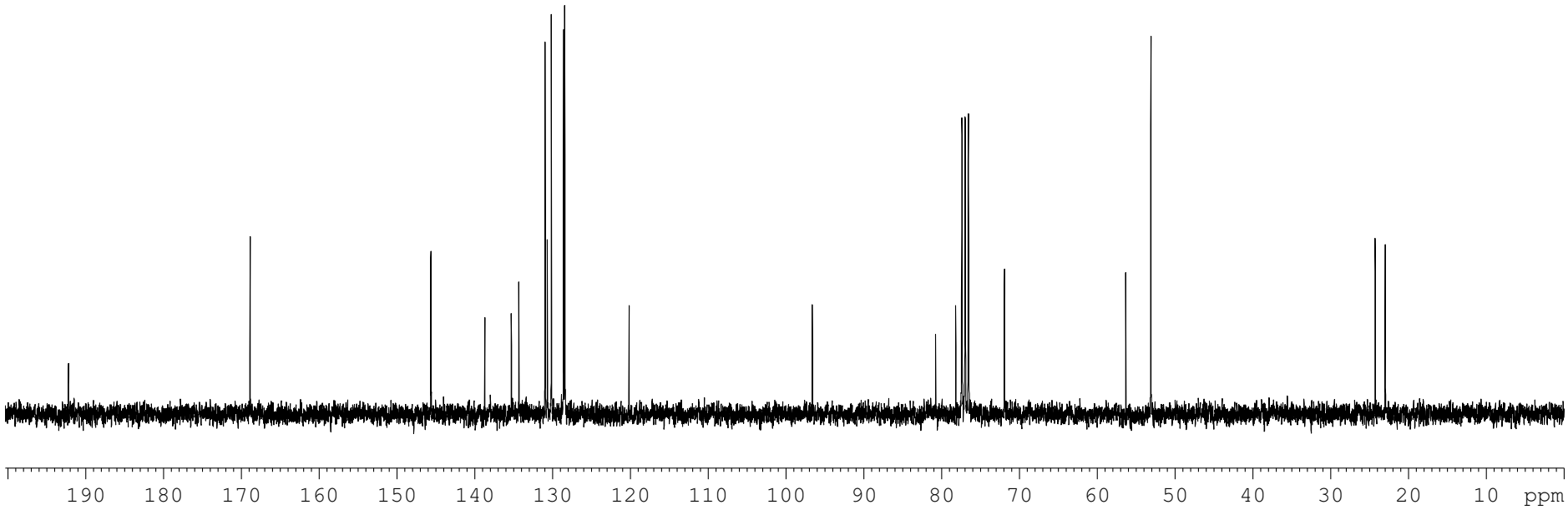
77.42
77.00
76.58
71.94
56.34
53.11
24.26
22.98

zwx-0722-1





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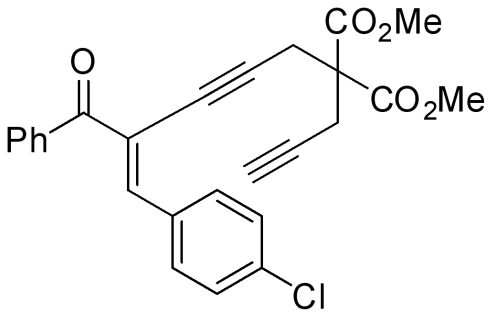
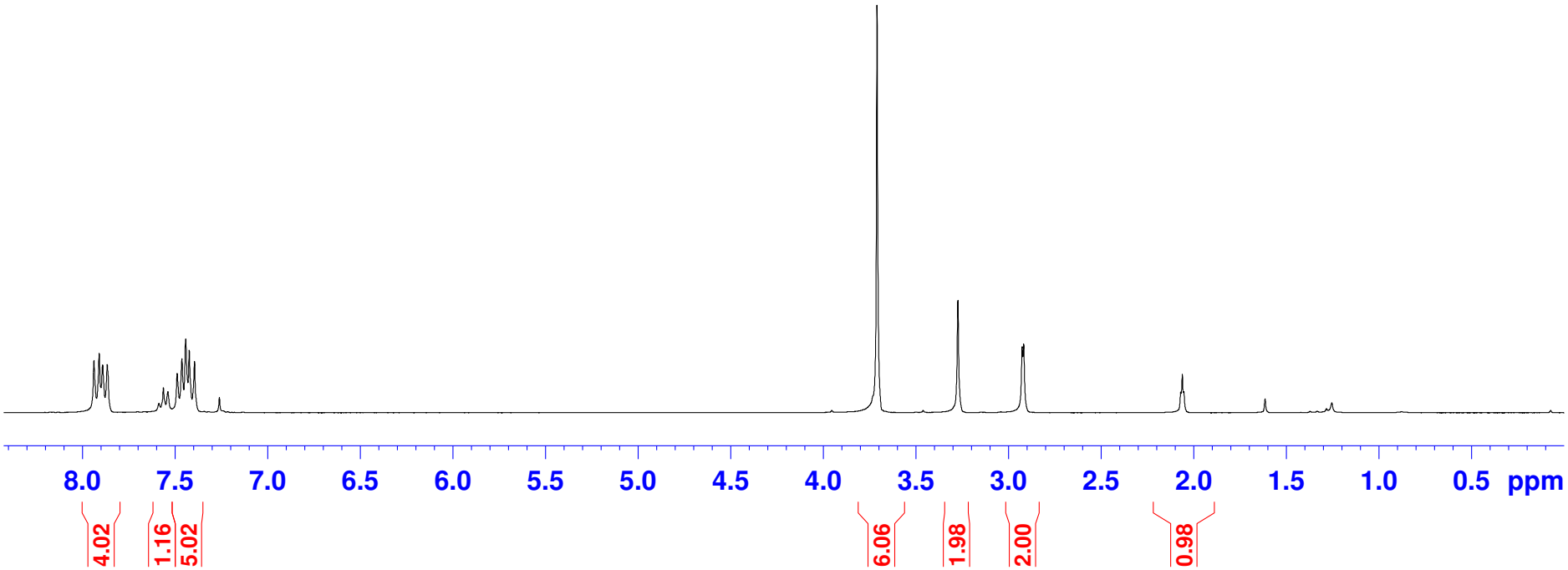
7.890
7.866
7.563
7.538
7.488
7.462
7.442
7.423
7.394
7.260

3.707
3.277
2.928
2.918

2.069
2.061
2.053

zwx-3-68-1





193.24
168.92
143.75
136.83
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132.51
131.28
129.56
128.89
128.19
121.21
97.08
80.64
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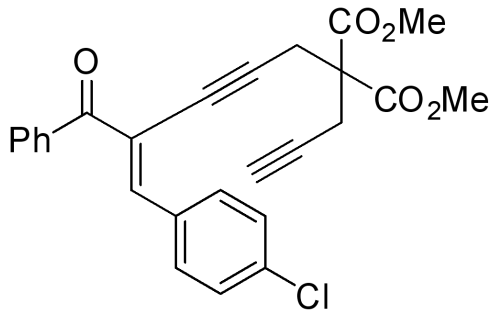
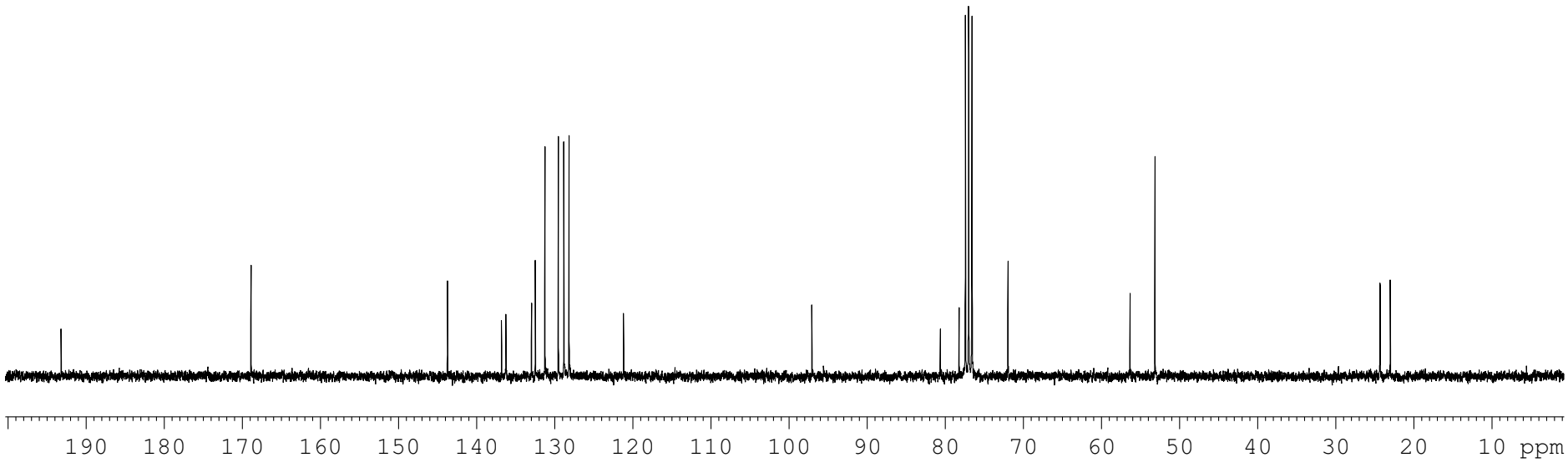
77.42
77.00
76.58
71.97
56.34
53.15
24.31
23.01

zwx-3-68-1





7.997
7.972
7.907
7.882
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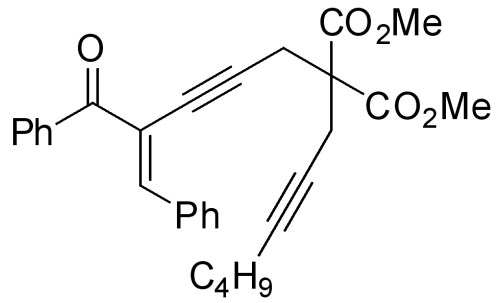
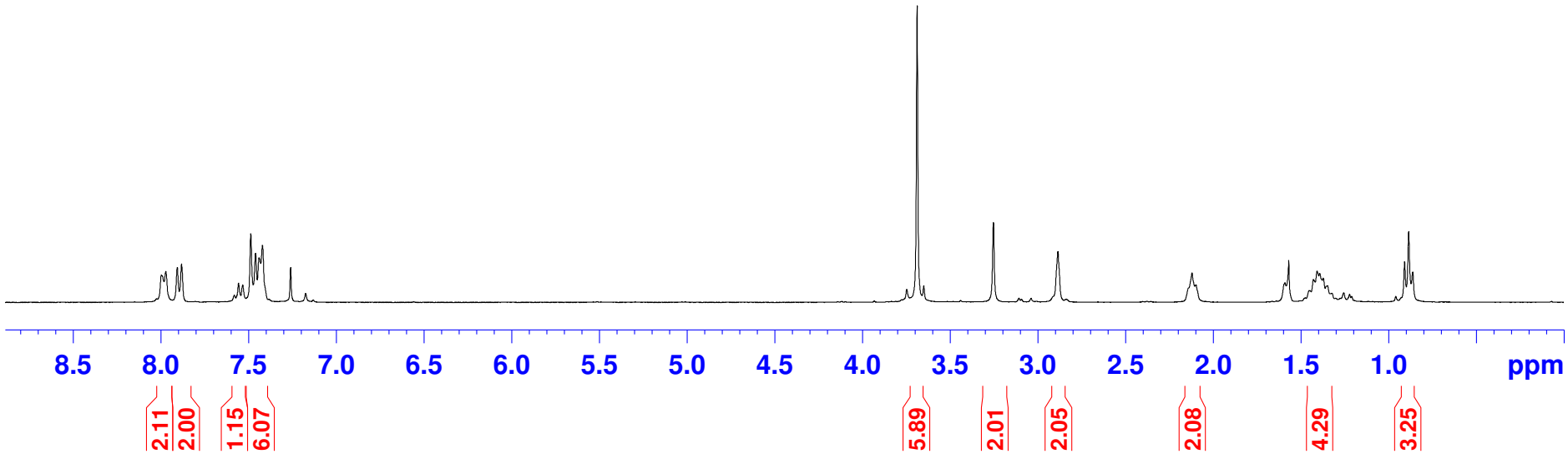
7.533
7.488
7.460
7.440
7.421
7.260

3.68
3.25
2.886

2.121
2.099
1.591
1.570
1.429
1.408
1.393
1.373
1.348
0.909
0.885
0.863

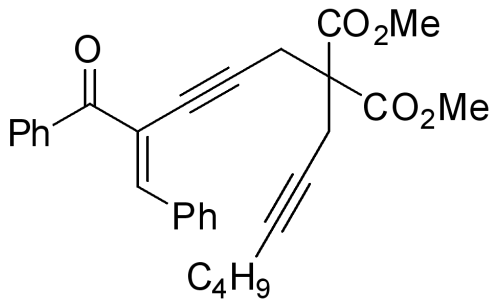
zwx-0615

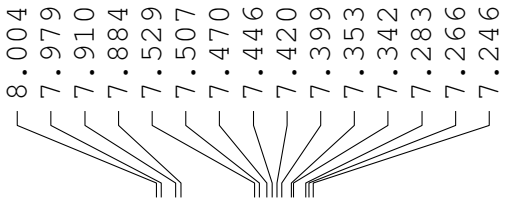




193.65
169.34
145.23
137.07
134.61
132.37
130.46
130.15
129.65
128.52
128.11
120.90
96.82
84.09
80.56
77.42
77.00
76.58
73.76
56.93
52.95
30.89
24.34
23.44
21.78
18.30
13.53

zwx-0615

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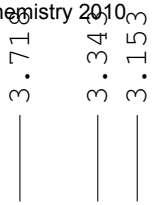
7.399
7.353
7.342
7.283
7.266
7.246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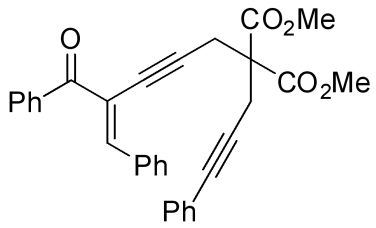
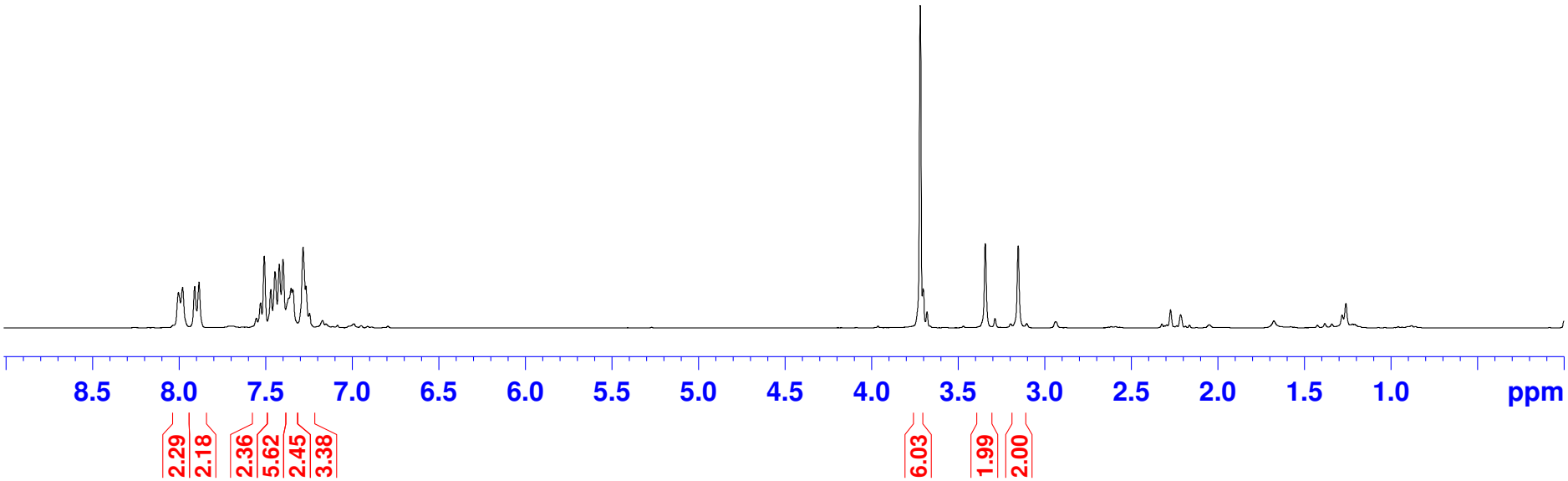

O
Ph
CO2Me
CO2Me
Ph
Ph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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.29
2.18
2.36
5.62
2.45
3.38
6.03
1.99
2.00

193.56
169.12
145.37
137.01
134.53
132.36
131.63
130.49
130.10
129.55
128.55
128.14
128.10
128.04
122.94
120.72
96.48
83.95
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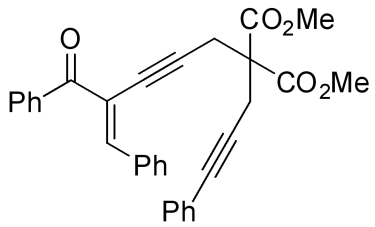
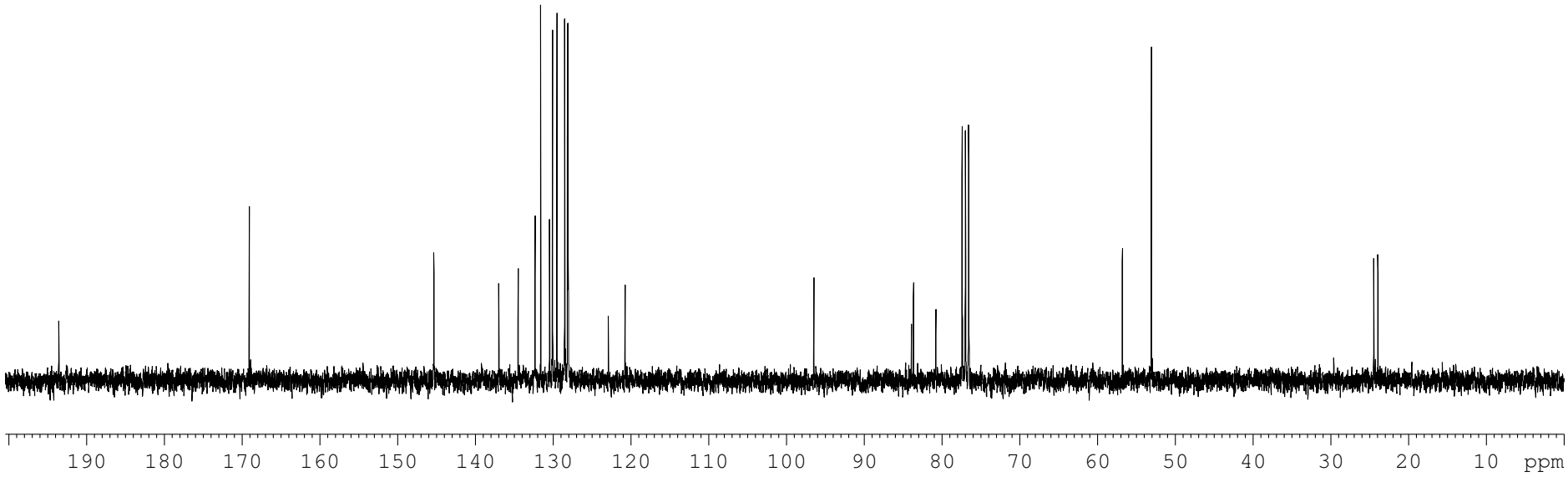
77.00
76.58
56.81
53.07
24.48
23.94

zwx-3-77-1





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7.261
6.821
6.792

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3.723
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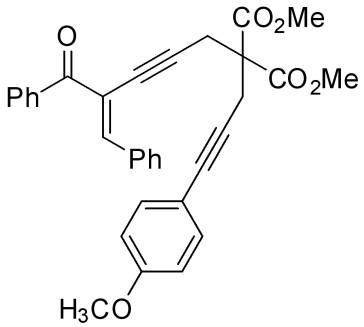
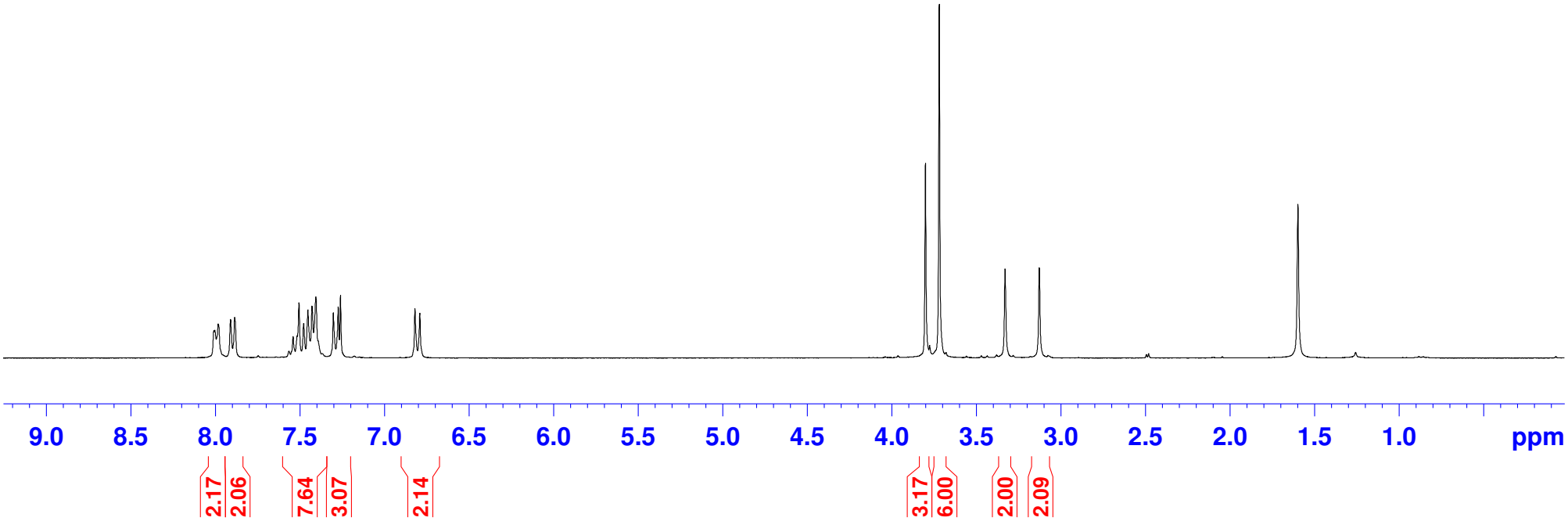
3.128

1.598

lrr25701H





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129.45
128.41
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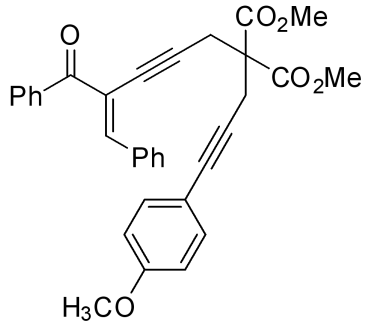
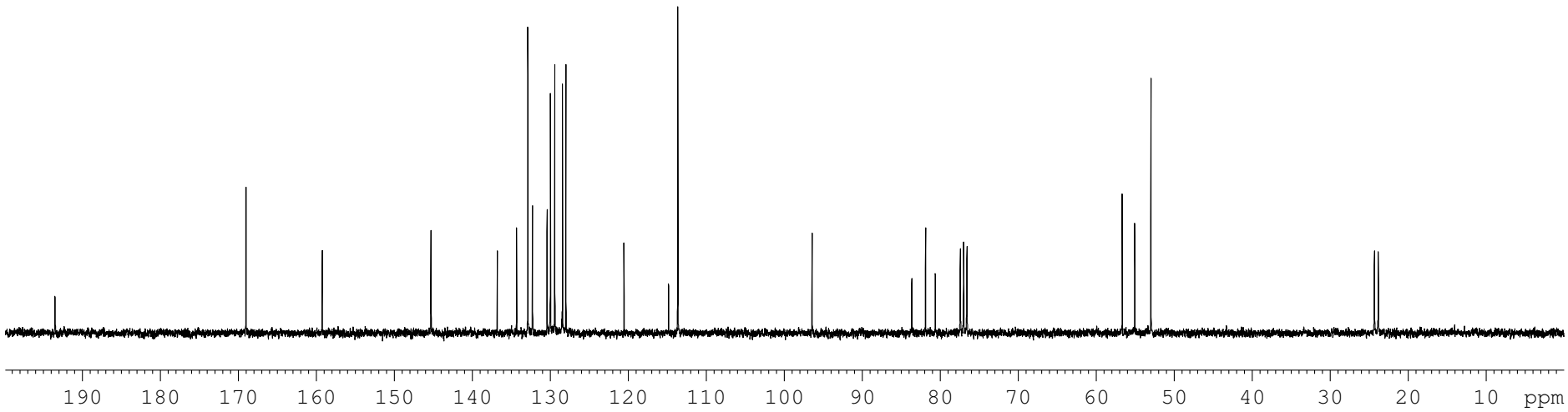
114.85
113.66
96.45
83.66
81.89
80.64
77.43
77.00
76.58
56.67
55.07
52.99
24.32
23.82

zwx-5-13





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7.370
7.348

3.697
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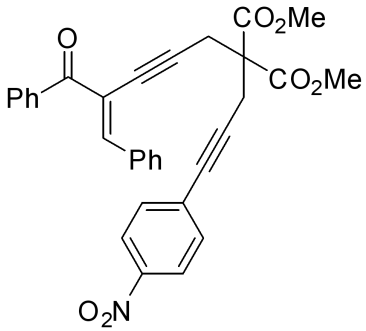
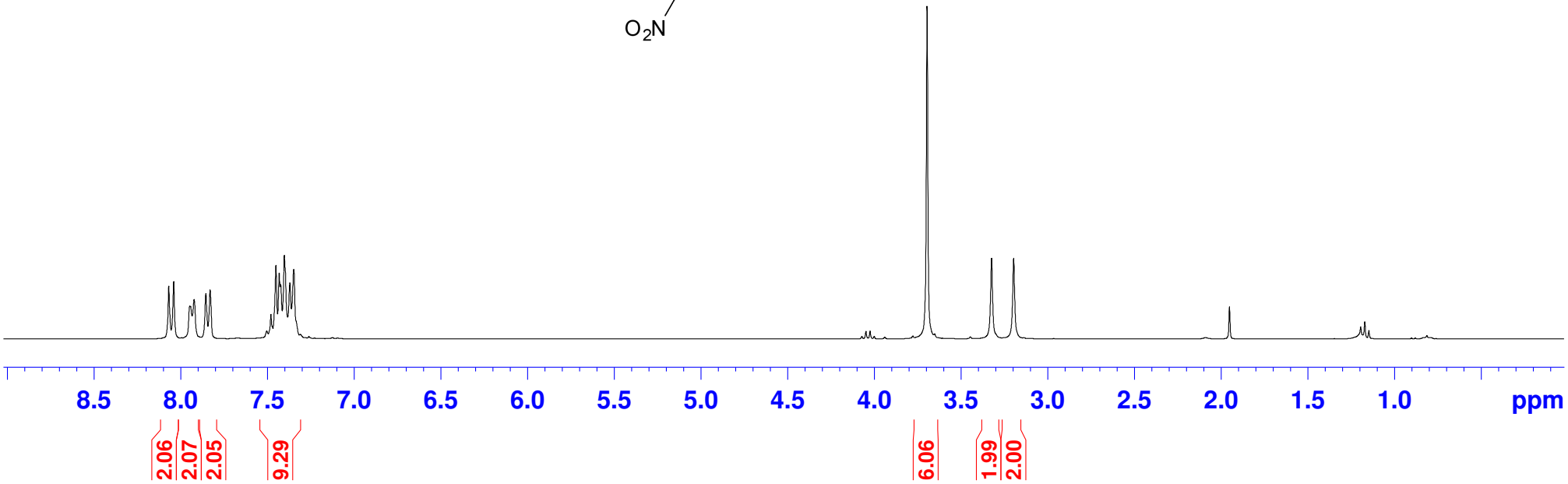
3.196

lrr28502H





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128.27
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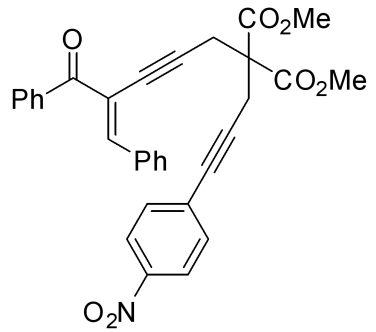

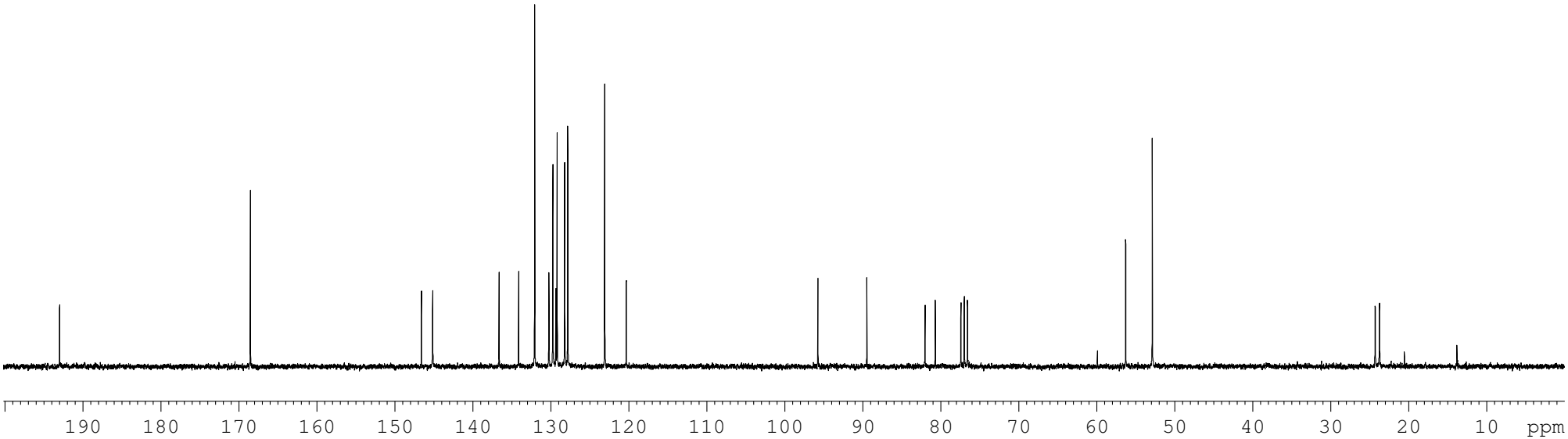

zwx-3-63

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7.008

3.75
3.23
3.00
3.00
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2.330
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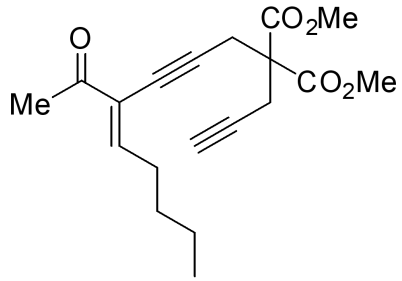
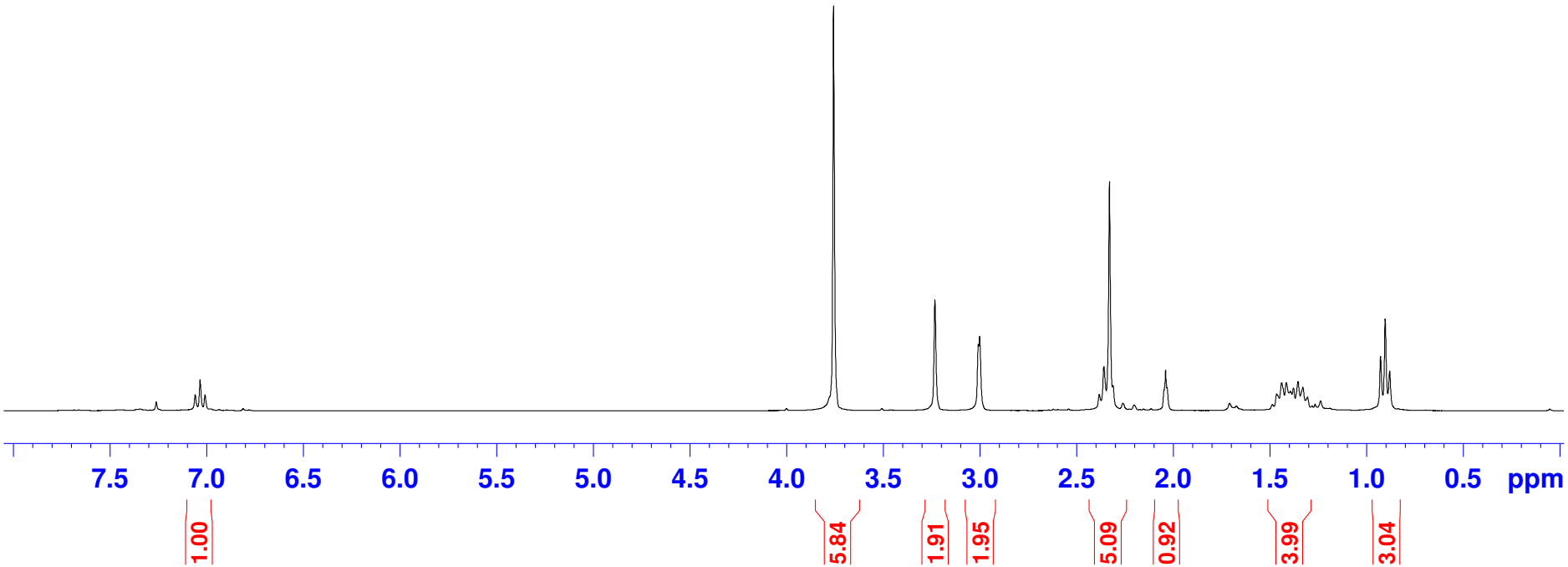
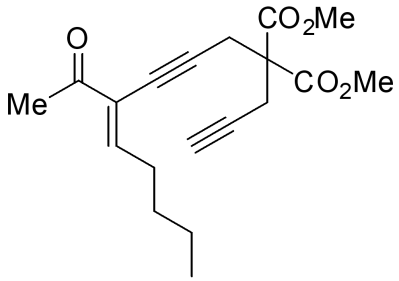
0.904
0.880

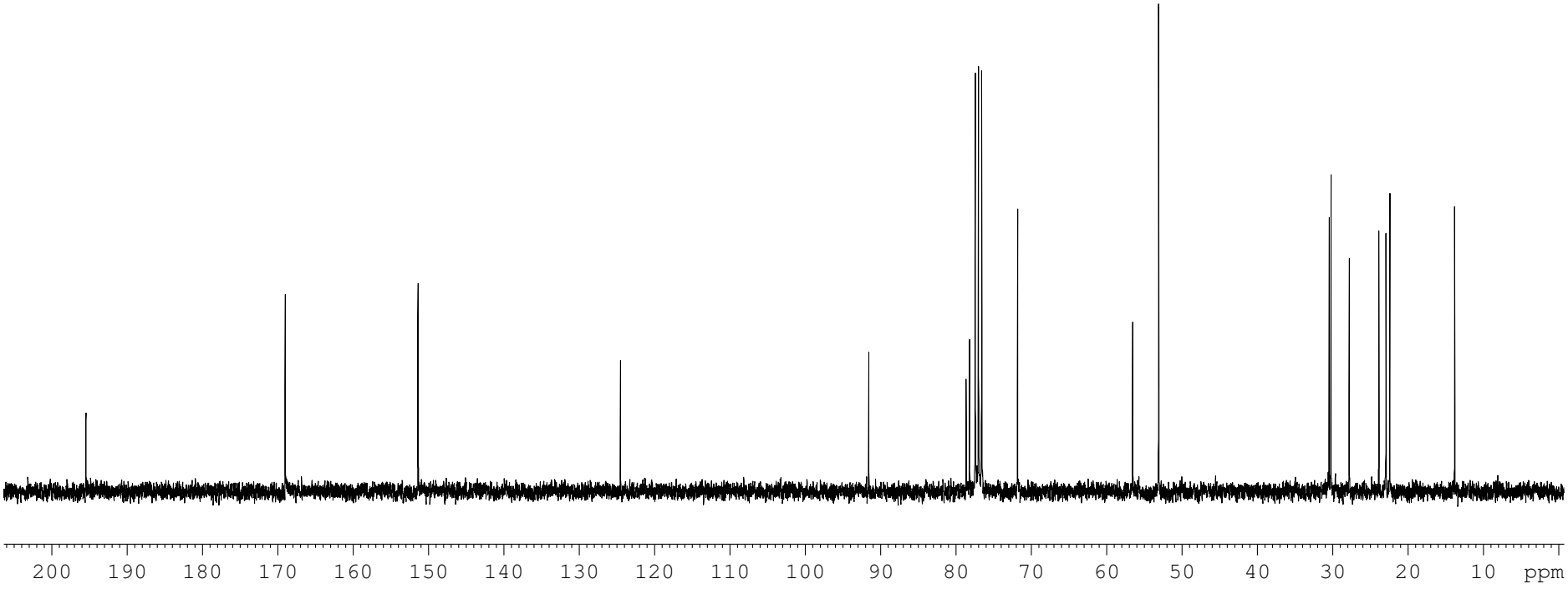


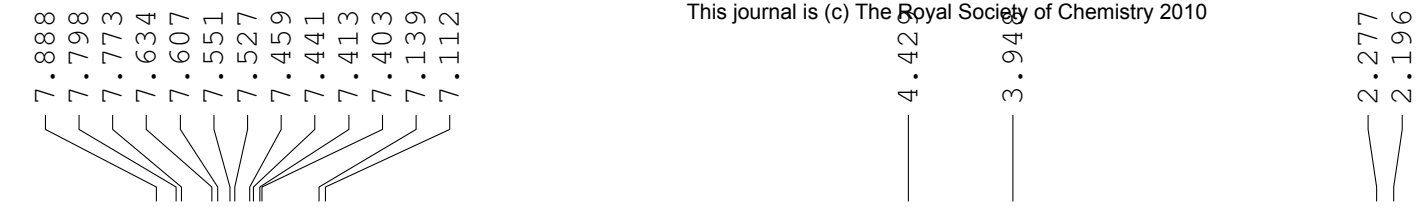


195.48
169.03
151.40
124.57
91.56
78.63
78.18
77.42
77.00
76.57
71.80
56.53
53.07
30.43
30.20
27.77
23.84
22.90
22.39
13.78

zwx-3-63C



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7.413
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7.139
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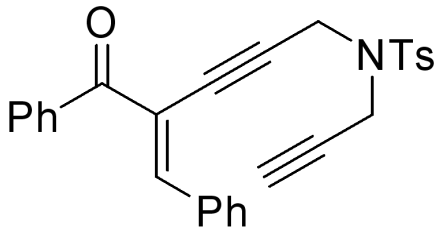
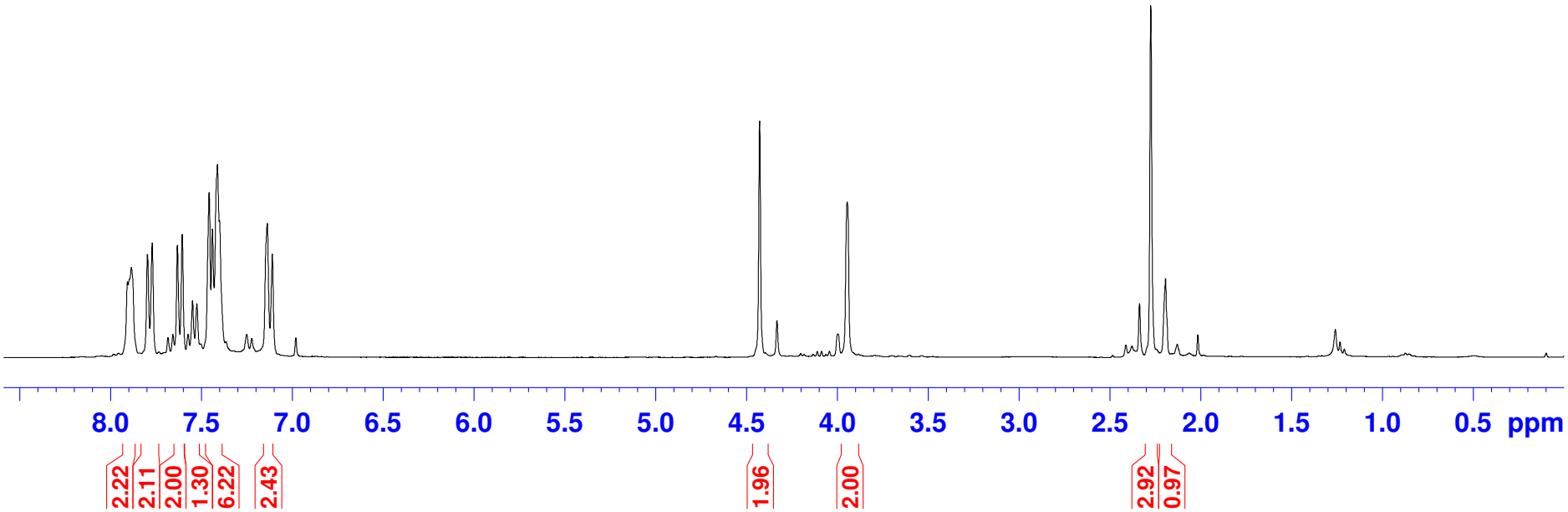
3.940
2.277
2.196

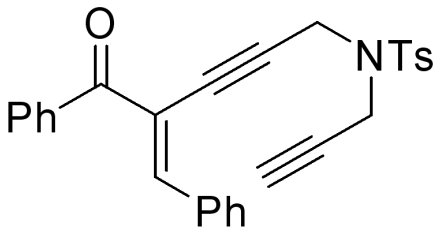
zwx-0717

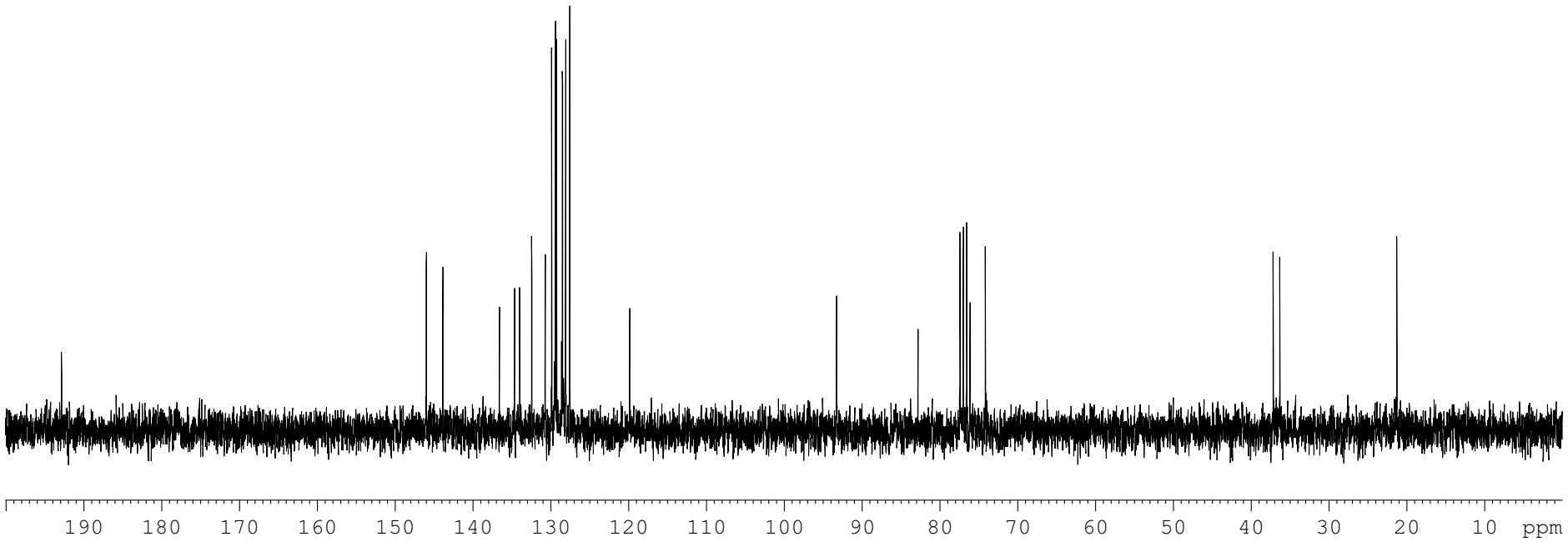

O
Ph
NTs
Ph


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.22
2.11
2.00
1.30
6.22
2.43
1.96
2.00
2.92
0.97

192.90
146.01
143.90
136.62
134.67
134.03
132.47
130.72
129.91
129.43
129.21
128.50
128.13
127.58
119.80
93.29
82.81
77.43
77.00
76.58
76.13
74.17
37.17
36.33
21.27

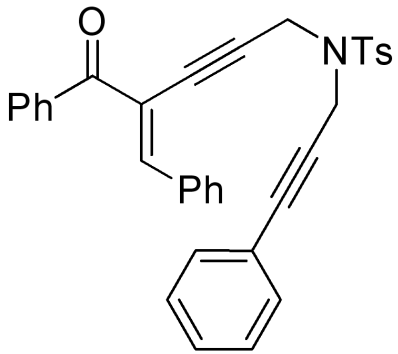
zwx-0717

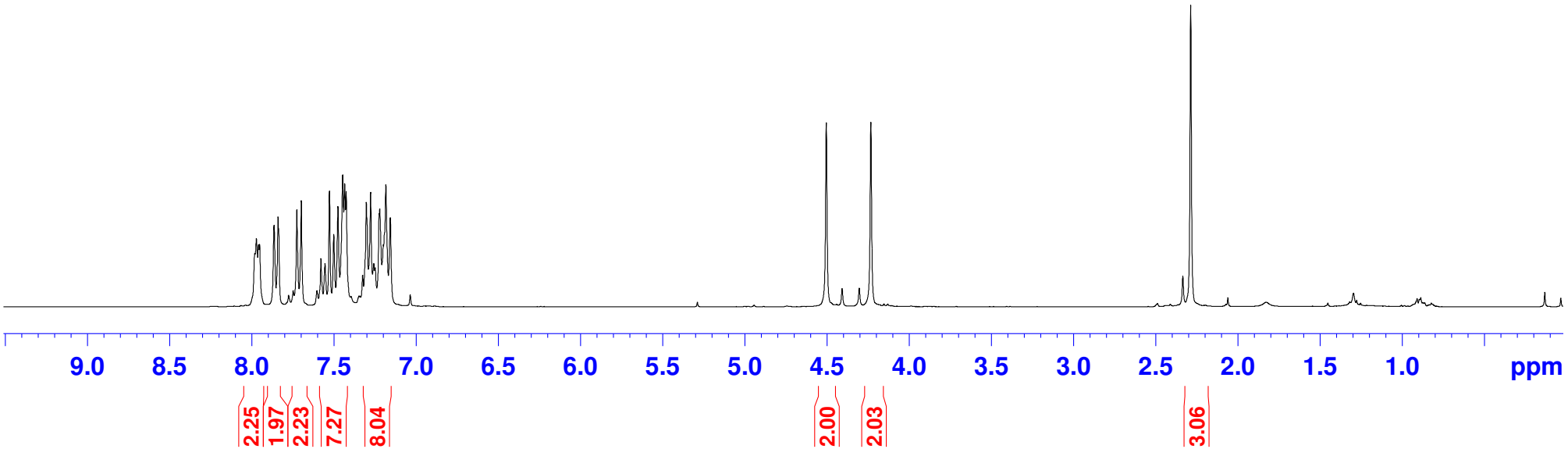




7.972
7.959
7.952
7.864
7.840
7.726
7.699
7.579
7.554
7.527
7.501
7.475
7.447
7.435
7.426
7.325
7.303
7.277
7.257
7.249
7.225
7.221
7.194
7.187
7.151
4.504
4.232
2.286

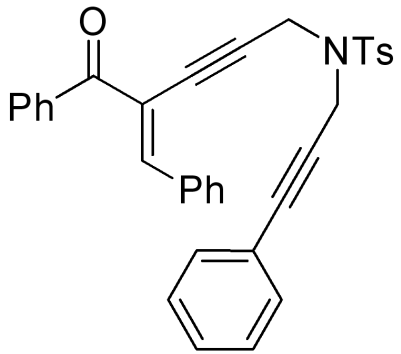
zwx-4-97

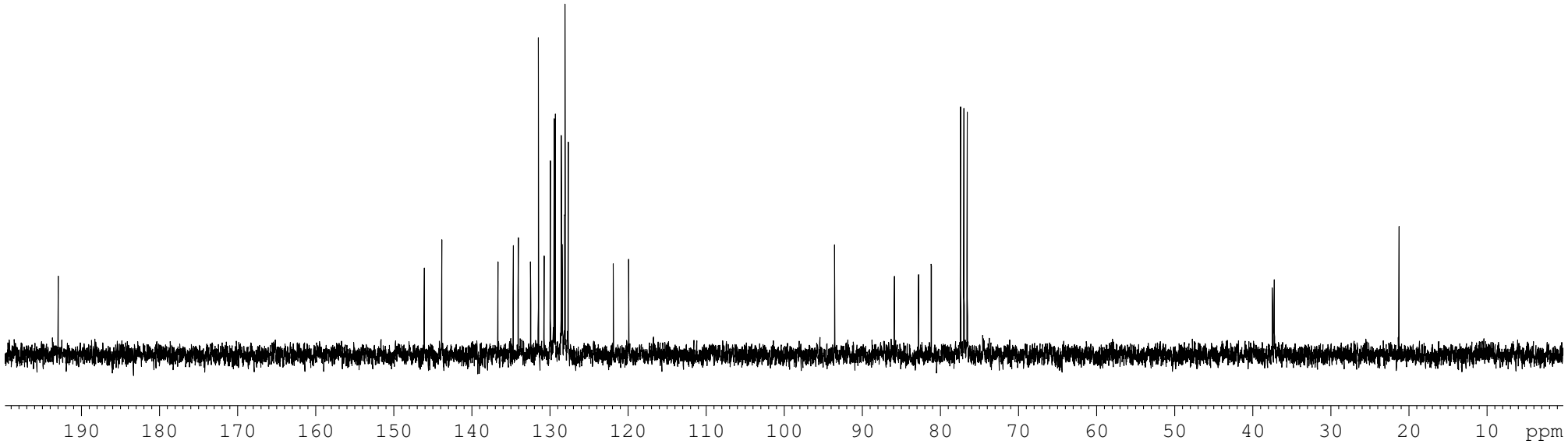




193.01
146.11
143.88
136.68
134.71
134.08
132.49
131.49
130.75
129.96
129.48
129.33
128.55
128.41
128.14
128.08
127.66
121.90
119.94
93.56
85.90
82.81
81.17
77.42
77.00
76.57
37.48
37.24
21.26

zwx-4-97



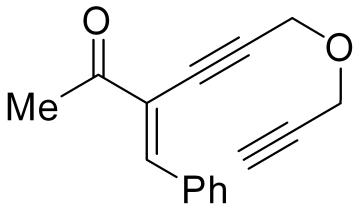


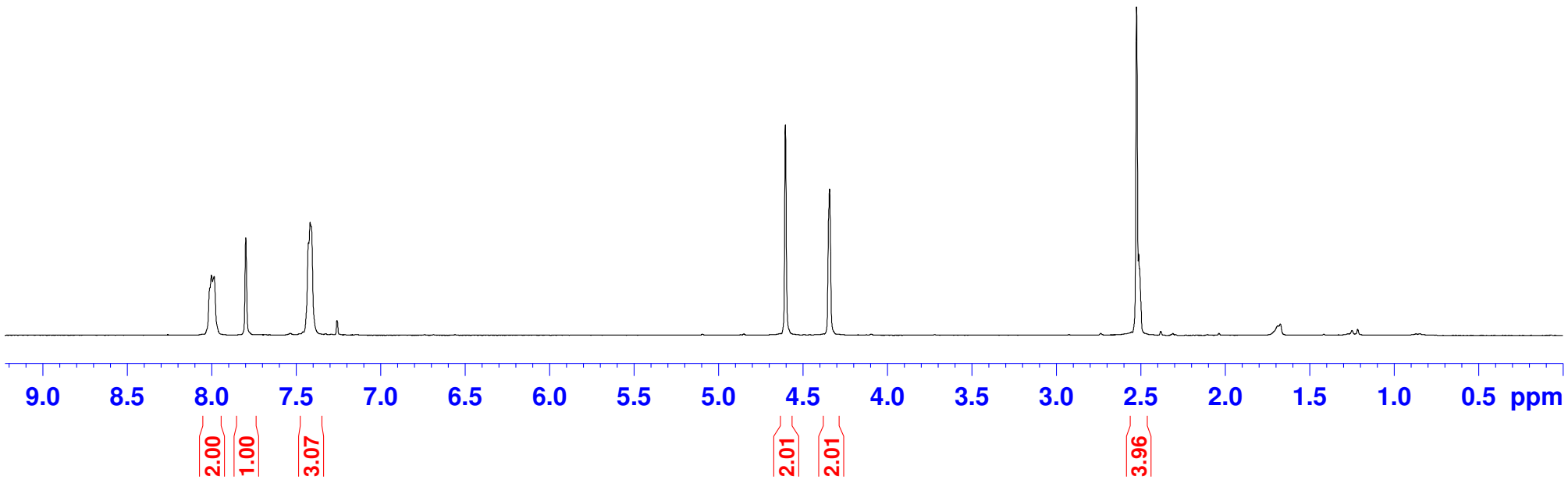
8.003
7.987
7.800
7.428
7.419
7.414
7.261

4.60
4.34

2.526
2.513
2.507

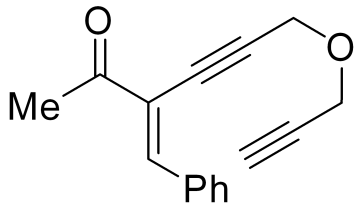
zwx-336A

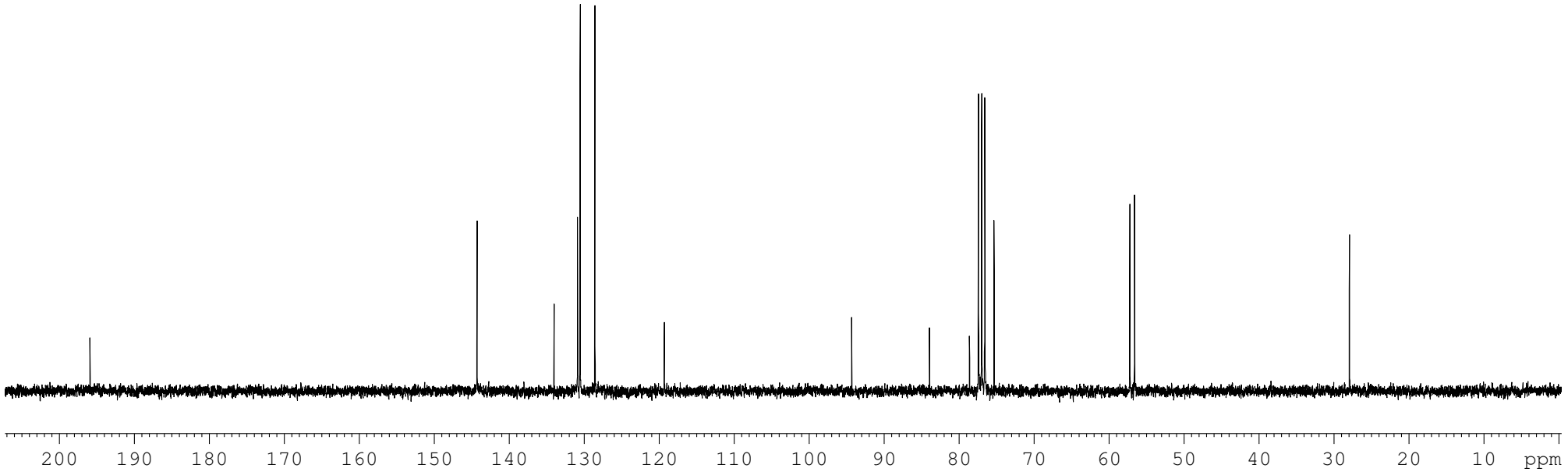




195.90
144.31
134.04
130.91
130.56
128.57
119.34
94.34
83.97
78.62
77.42
77.00
76.58
75.35
57.23
56.61
27.93

zwx-336A C



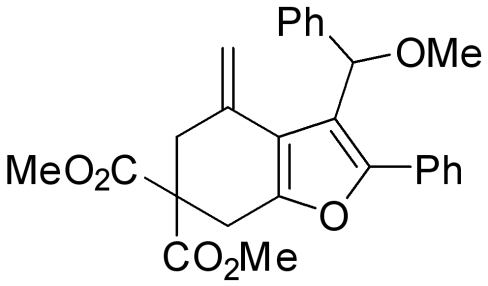


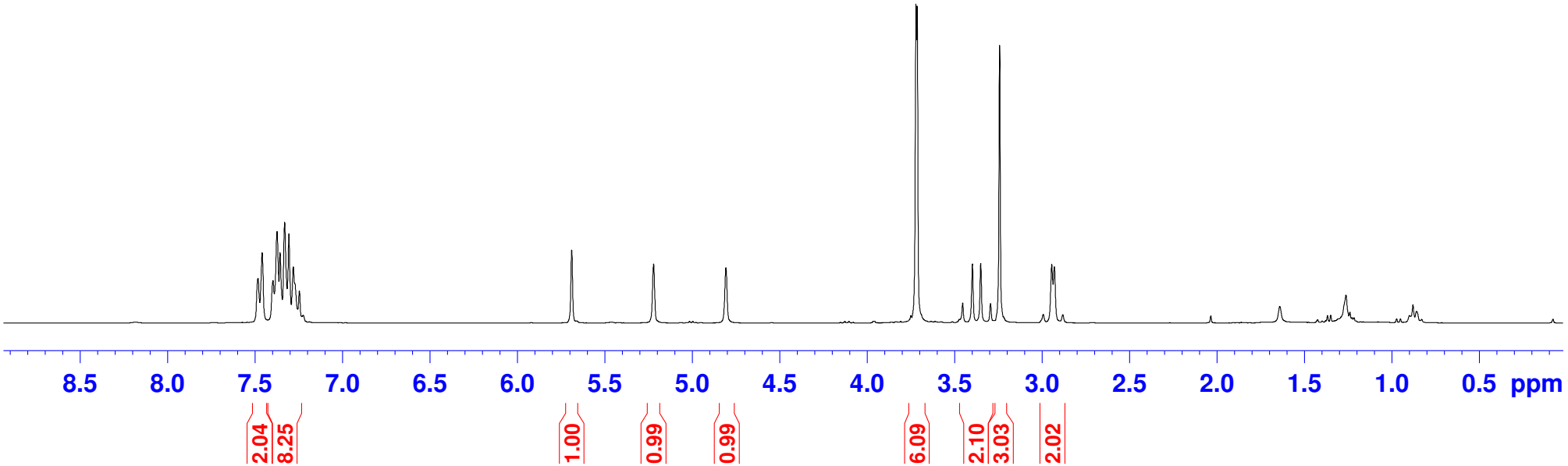
7.483
7.459
7.397
7.374
7.357
7.330
7.306
7.281
7.272
7.246

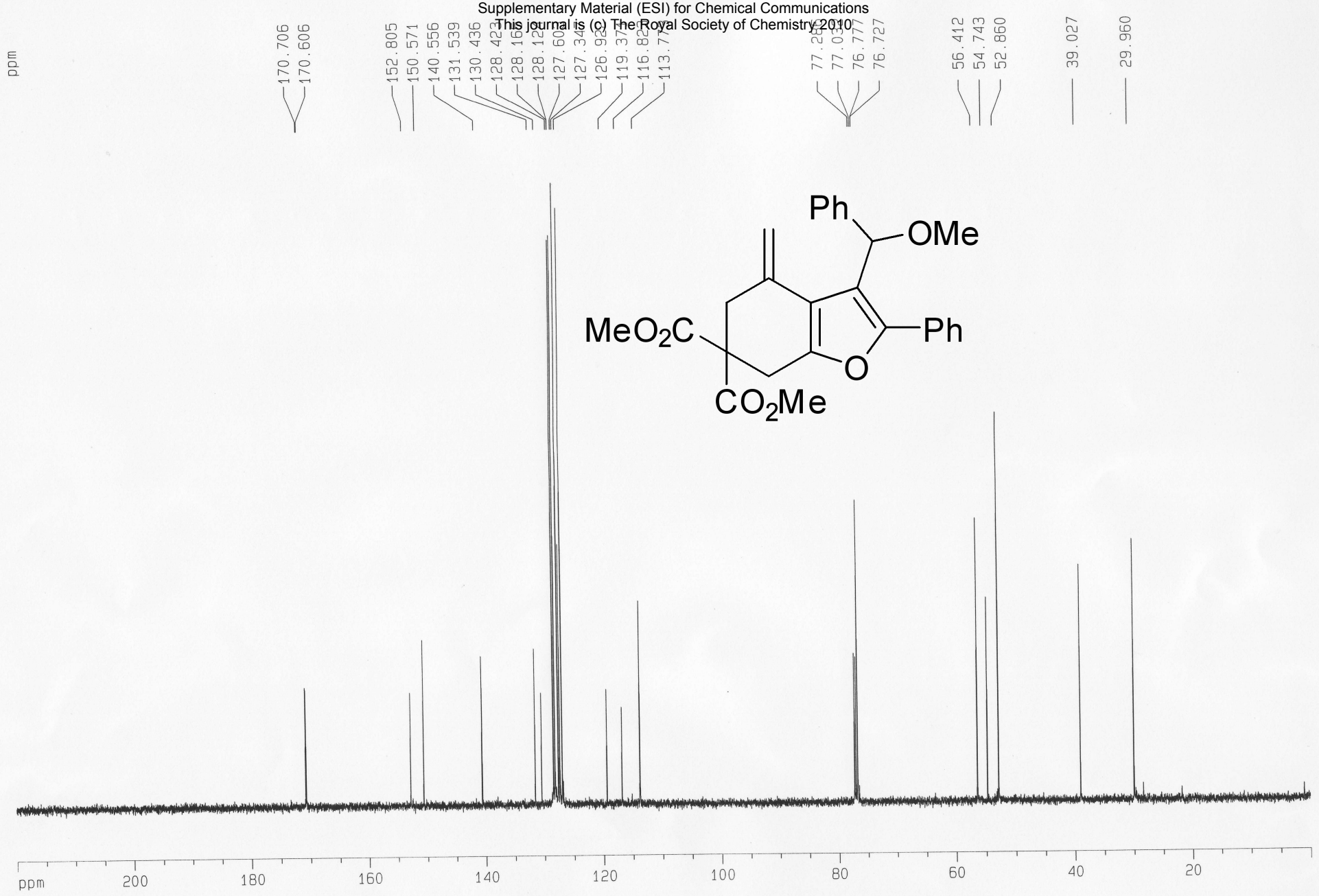
5.689
5.224
4.807

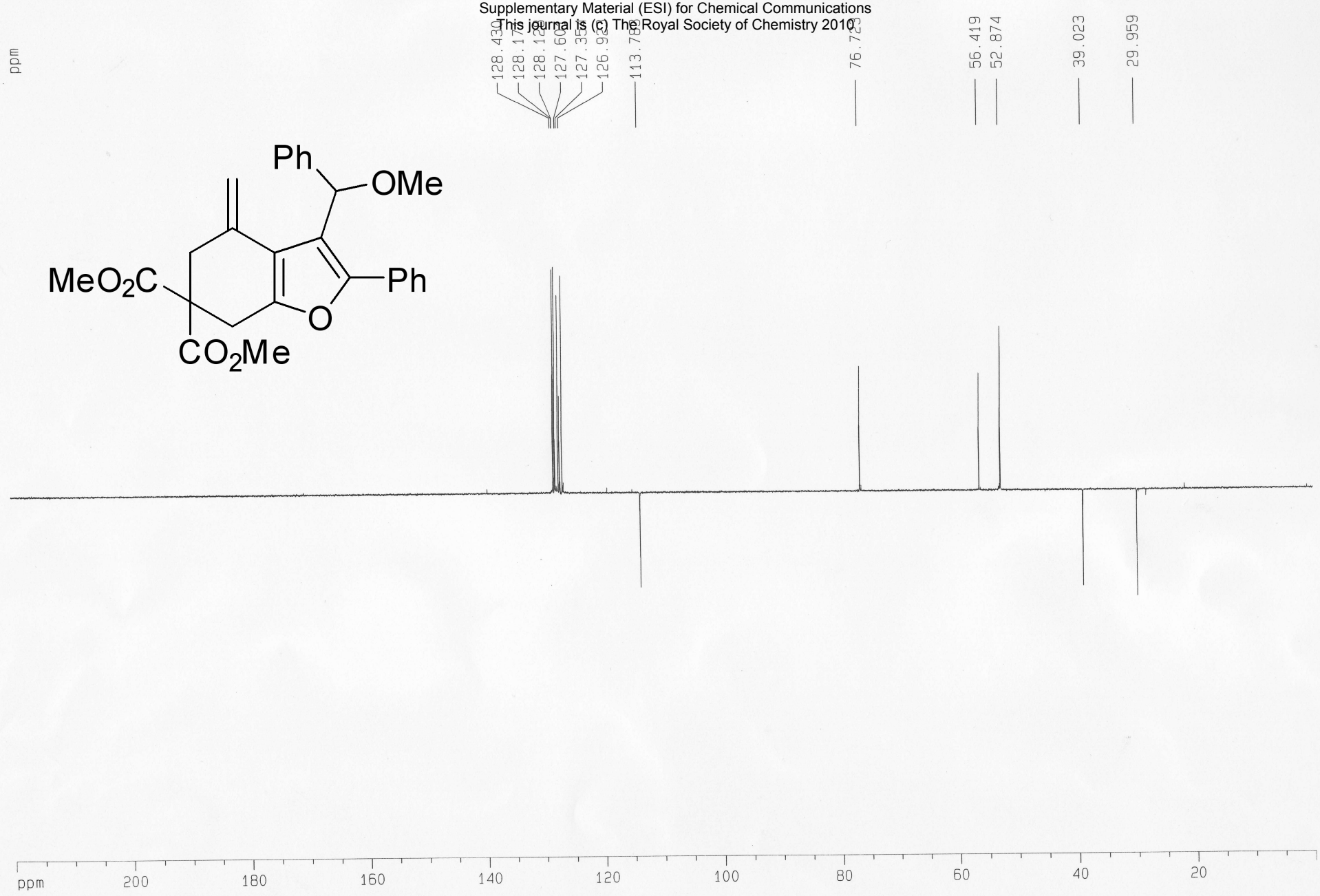
3.726
3.711
3.450
3.399
3.354
3.294
3.242
2.993
2.944
2.929
2.881

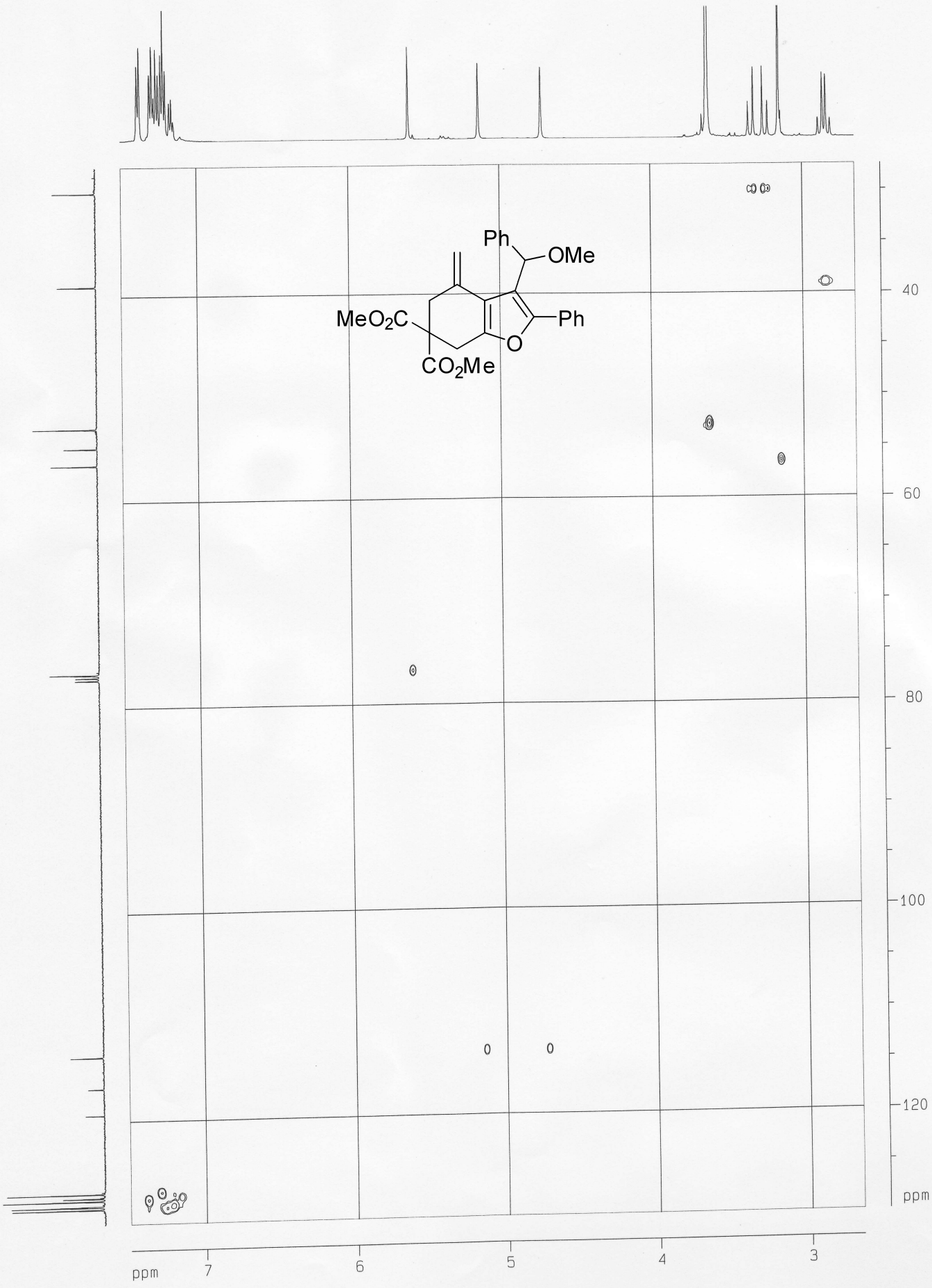
zwx-4-28-2

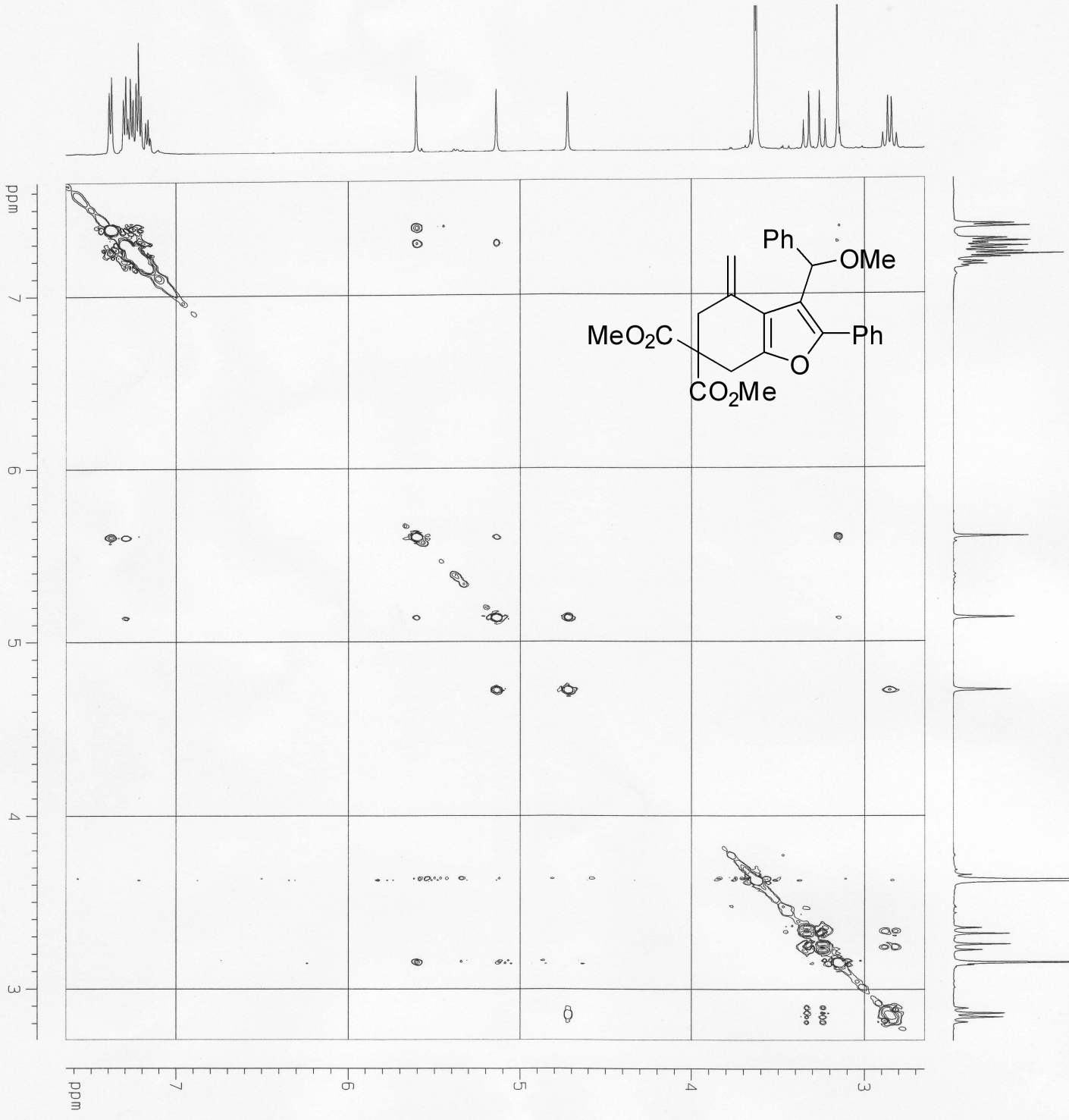


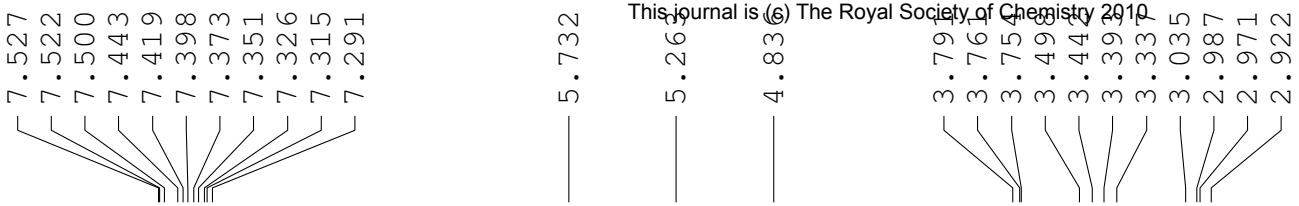




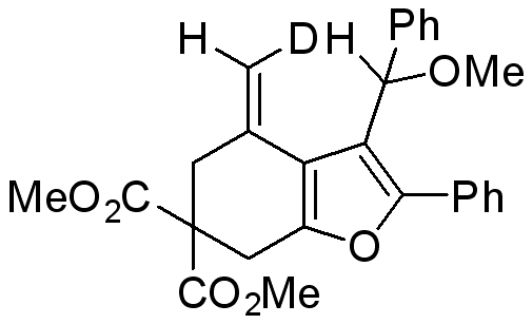


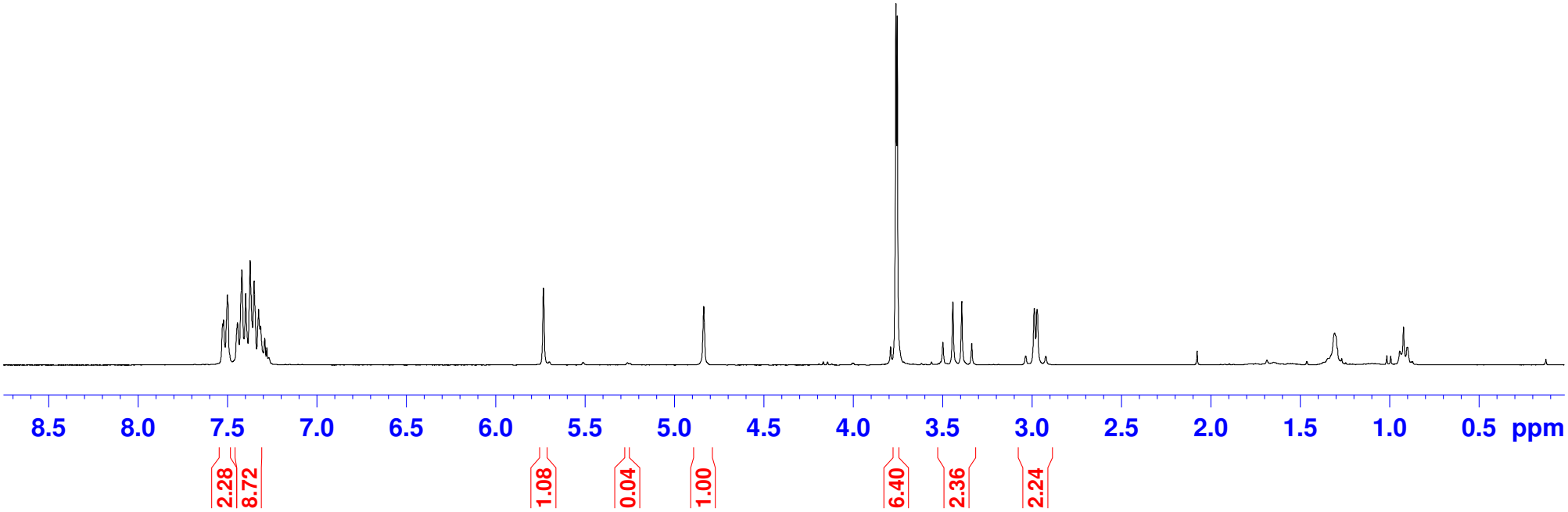

Ph
OMe
MeO2C
Ph
O
CO2Me
40
60
80
100
120
ppm
ppm
7
6
5
4
3


Ph
OMe
MeO2C
Ph
O
CO2Me
ppm
7
6
5
4
3

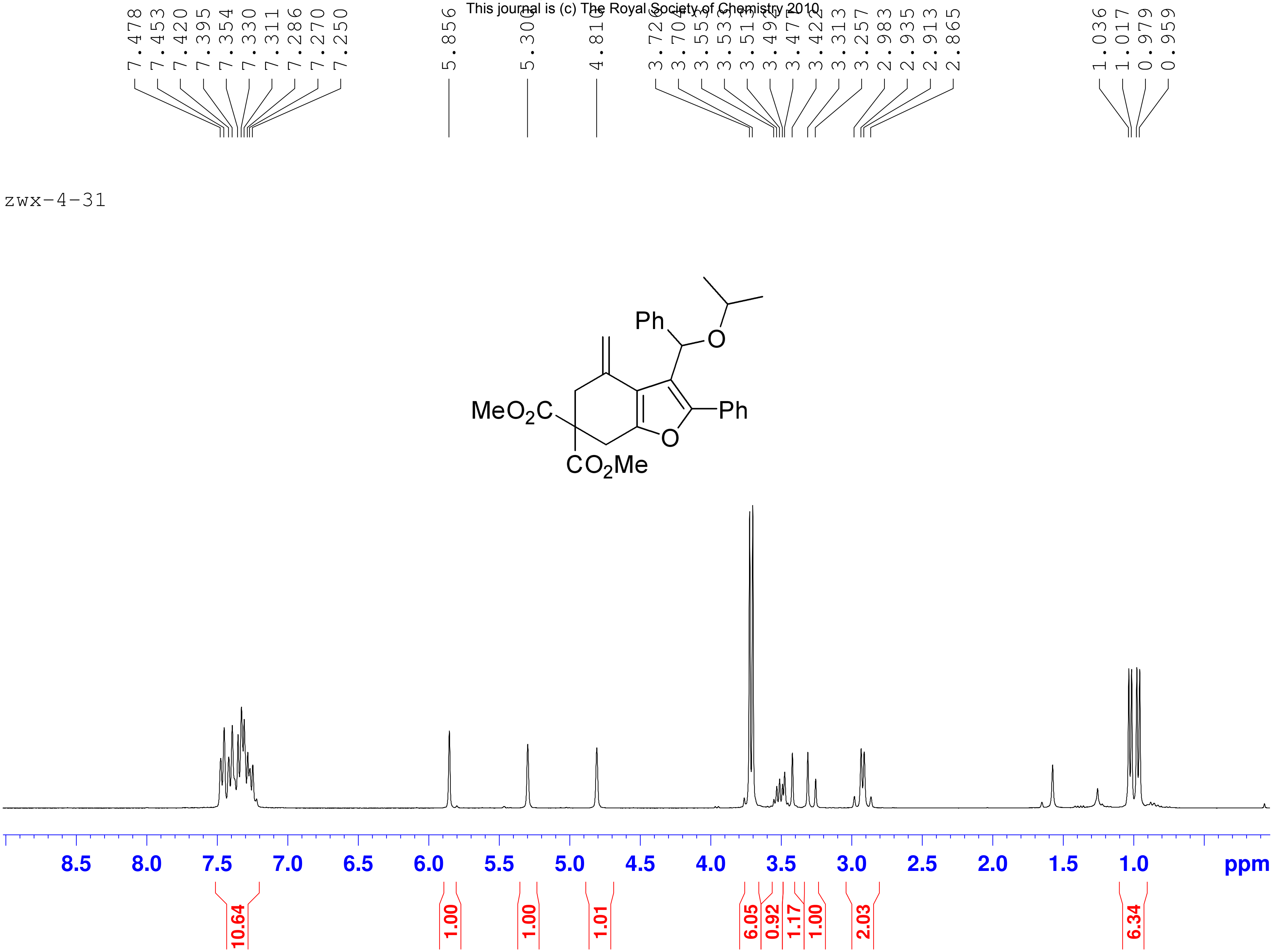

7.527
7.522
7.500
7.443
7.419
7.398
7.373
7.351
7.326
7.315
7.291
5.732
5.26
4.83
3.79
3.76
3.75
3.49
3.44
3.39
3.33
3.035
2.987
2.971
2.922

zwx-5-12


H
DH
Ph
OMe
MeO2C
Ph
O
CO2Me


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.28
8.72
1.08
0.04
1.00
6.40
2.36
2.24

zwx-4-31


7.478
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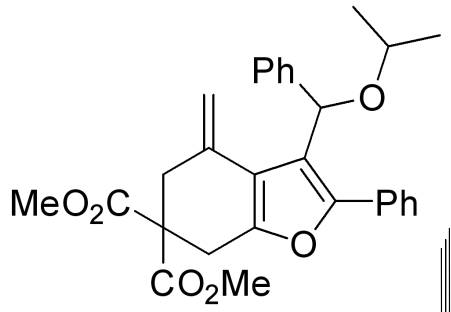
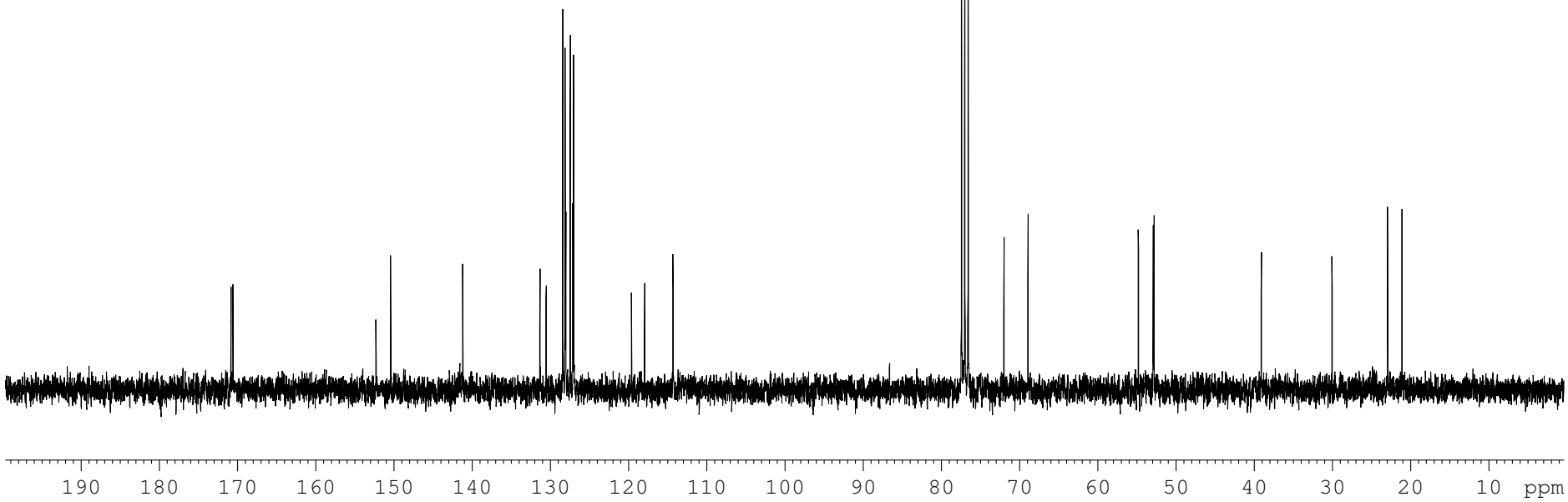
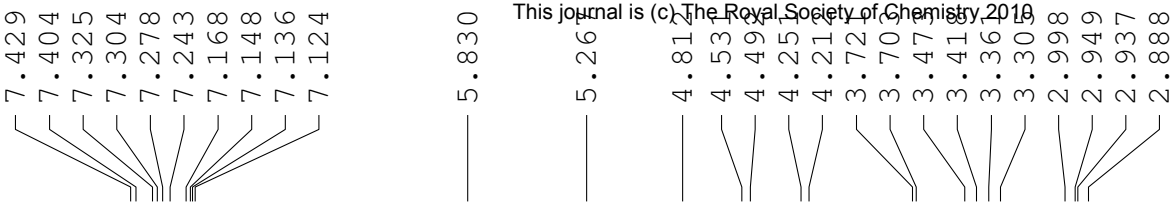
7.420
7.395
7.354
7.330
7.311
7.286
7.270
7.250
5.856
3.422
3.313
3.257
2.983
2.935
2.913
2.865
1.036
1.017
0.979
0.959
Ph
O
MeO2C
Ph
O
CO2Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10.64
1.00
1.00
1.01
6.05
0.92
1.17
1.00
2.03
6.34

170.85
170.62
152.33
150.45
141.22
131.35
130.56
128.43
128.13
128.04
127.41
127.14
127.05
119.69
117.96
114.37
77.43
77.01
76.59
72.00
68.93
54.82
52.90
52.82
39.09
30.05
22.94
21.10

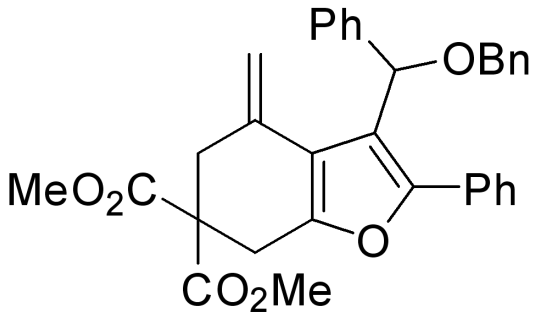
zwx-4-31

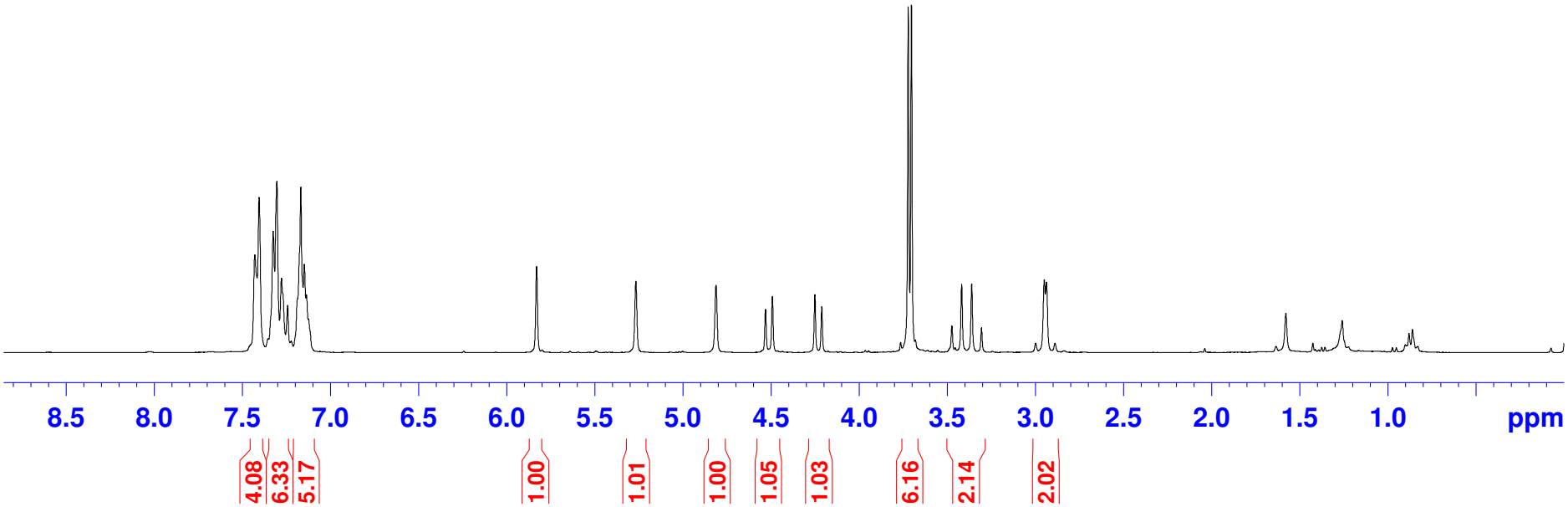





7.429
7.404
7.325
7.304
7.278
7.243
7.168
7.148
7.136
7.124
5.830
5.26
4.81
4.53
4.49
4.25
4.21
3.72
3.70
3.47
3.41
3.36
3.30
2.998
2.949
2.937
2.888

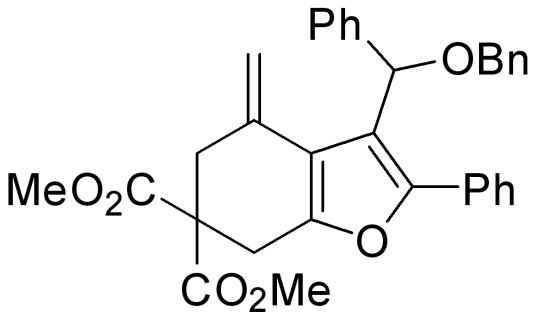
zwx-4-35

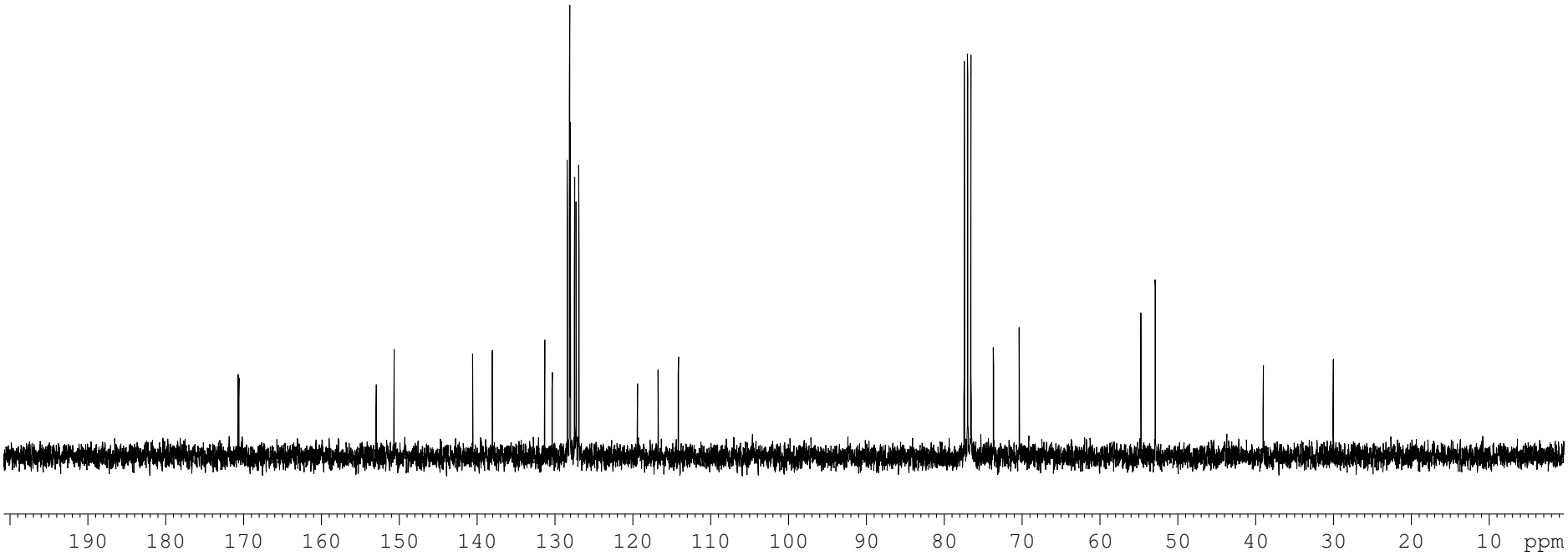

Ph
OBn
MeO2C
Ph
O
CO2Me


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.08
6.33
5.17
1.00
1.01
1.00
1.05
1.03
6.16
2.14
2.02

170.75
170.64
152.99
150.70
140.60
138.07
131.34
130.38
128.43
128.14
128.05
127.53
127.31
126.99
119.44
116.71
114.11
77.42
77.00
76.57
73.68
70.37
54.75
52.90
39.01
30.02

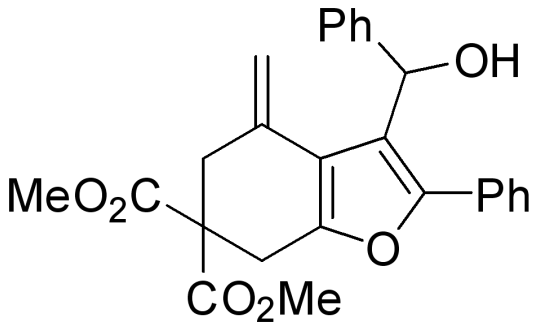
zwx-4-35

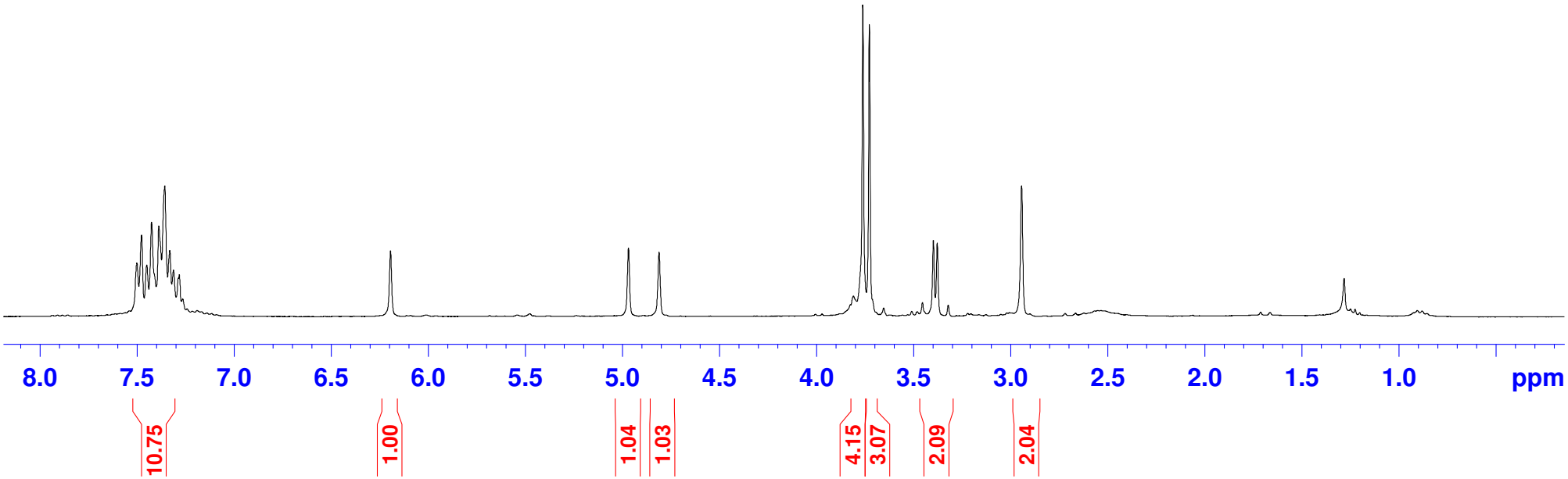




7.501
7.476
7.450
7.425
7.387
7.357
7.331
7.312
7.282
6.194
4.961
4.811
3.763
3.724
3.454
3.390
3.377
3.322
2.943
2.568
2.554

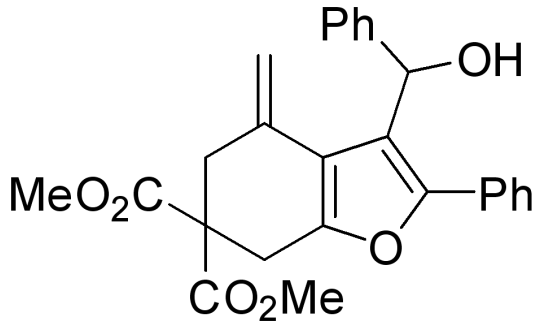
zwx-4-51

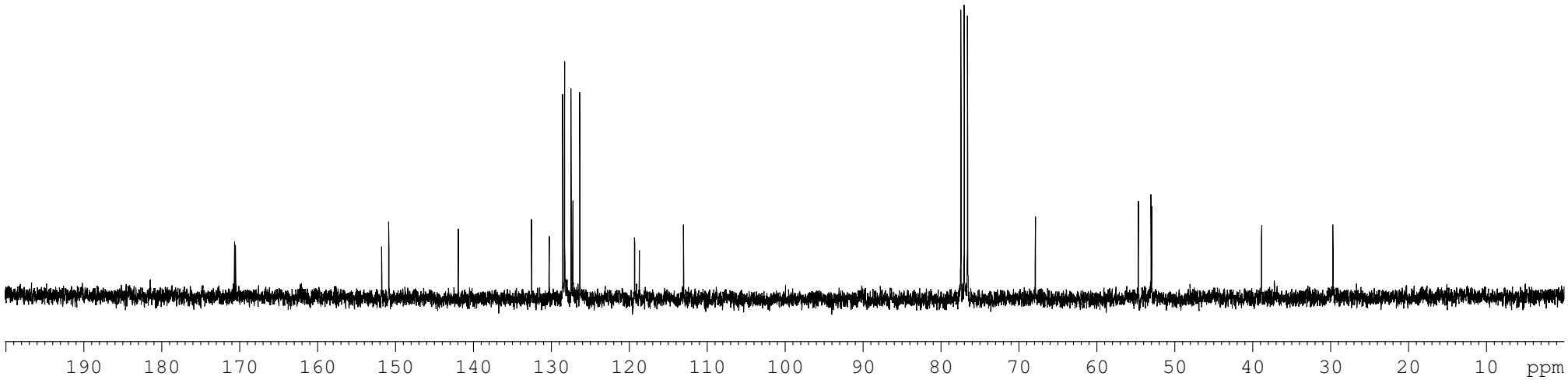




170.65
170.51
151.76
150.85
141.91
132.52
130.26
128.54
128.29
127.46
127.24
126.34
119.36
118.60
113.02
77.42
77.00
76.57
67.86
54.65
53.02
52.94
38.89
29.73

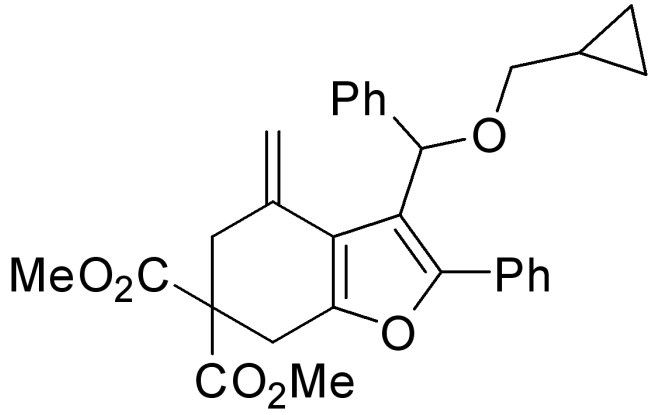
zwx-4-51

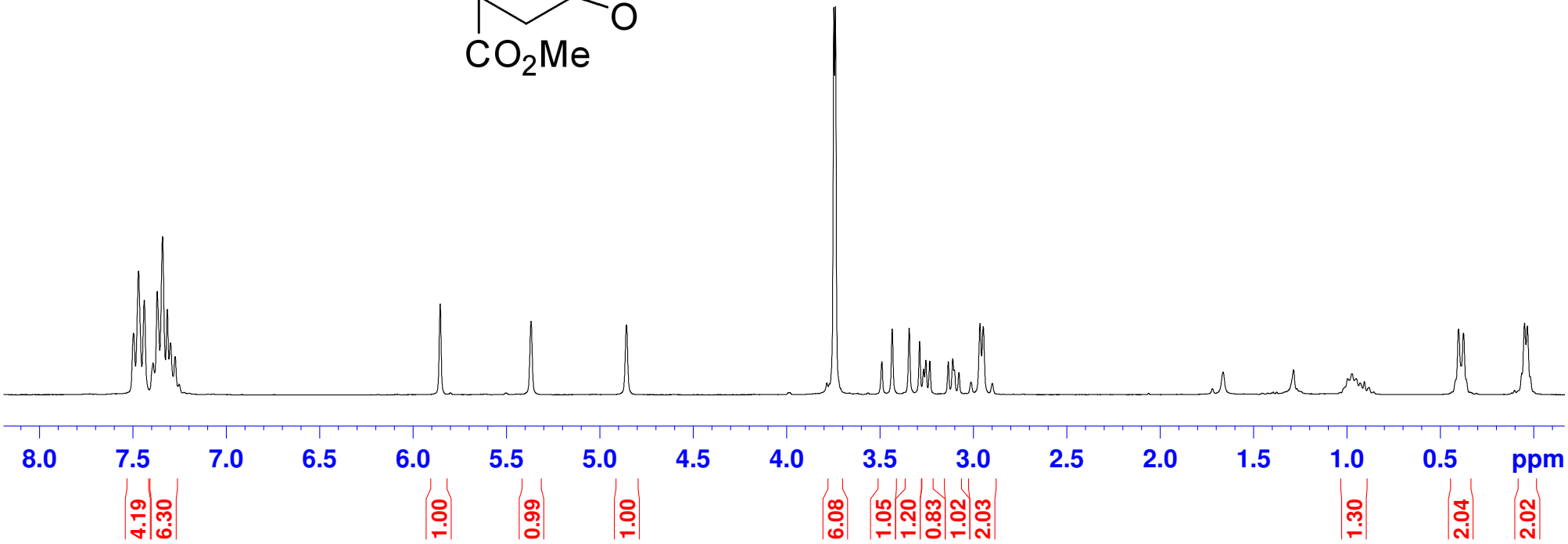


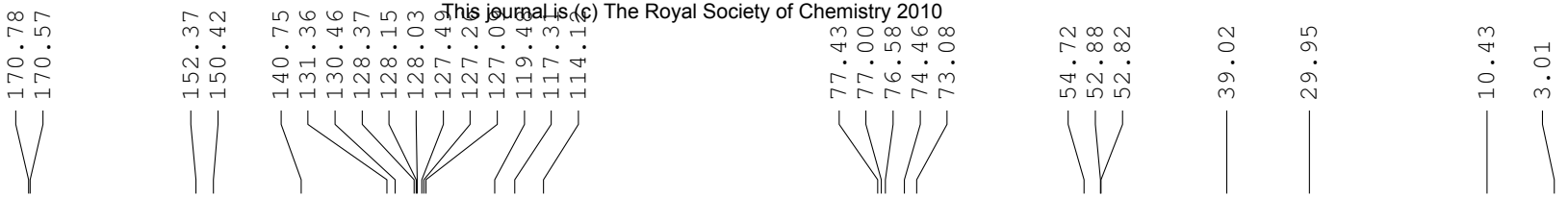


7.496 7.469 7.439 7.392 7.369 7.341 7.316 7.298 7.274 7.252 5.854 5.368 4.851 3.743 3.733 3.494 3.434 3.341 3.285 3.264 3.254 3.233 3.130 3.110 3.101 3.077 3.012 2.964 2.946 2.898 0.996 0.972 0.949 0.906 0.401 0.375 0.051 0.035

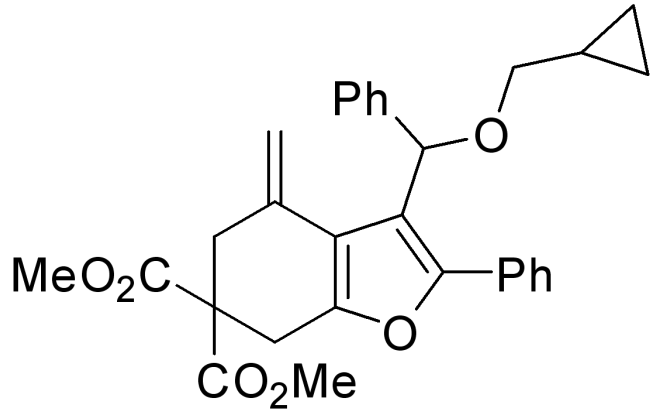
zwx-4-57

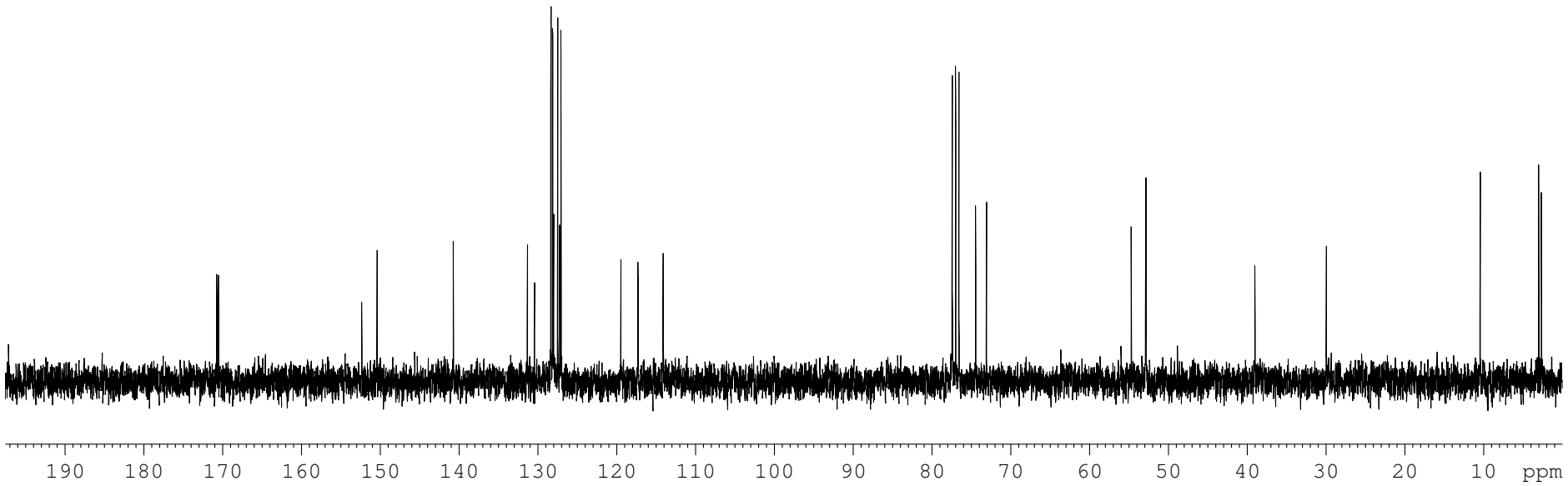


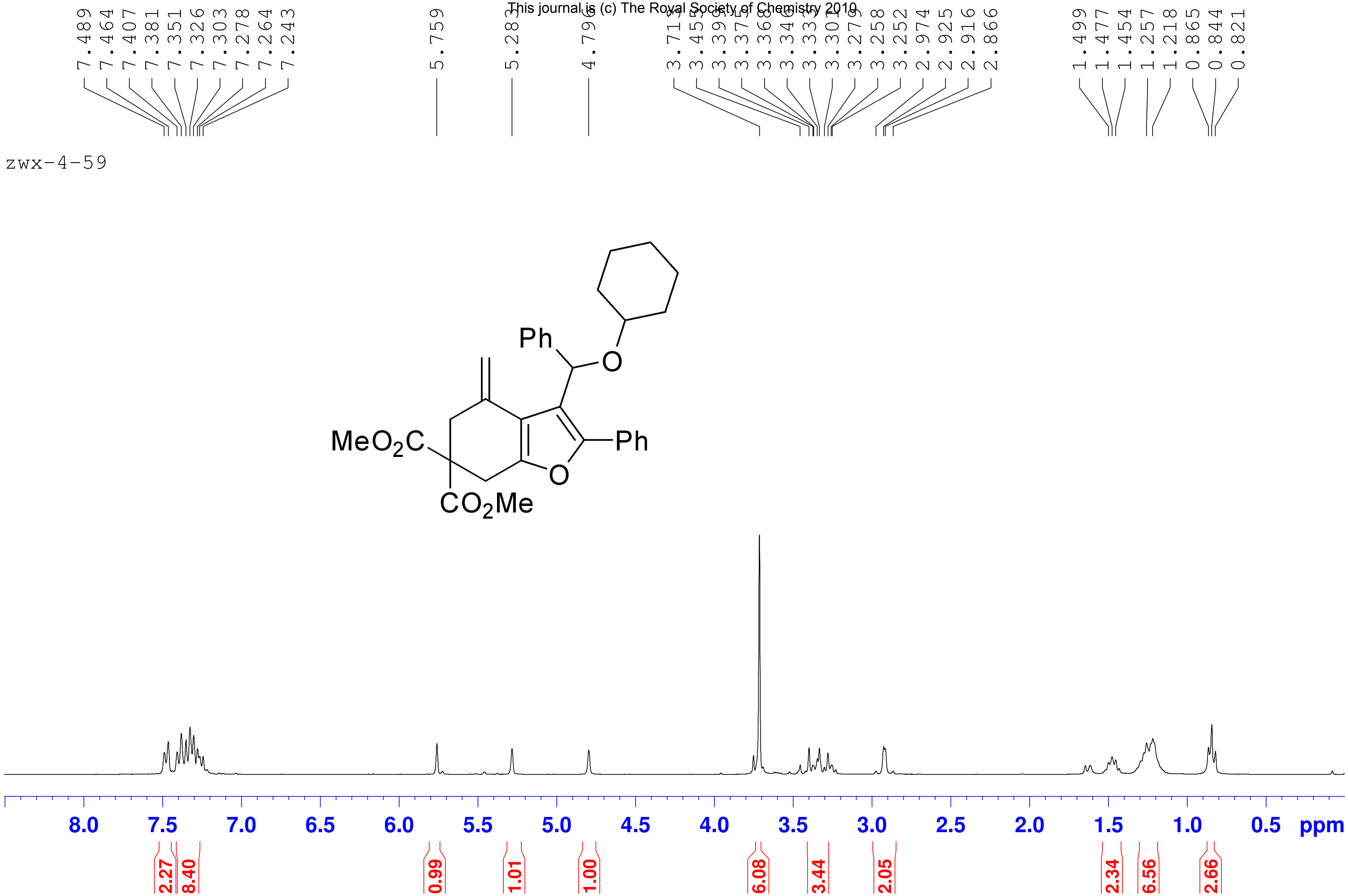



170.78
170.57
152.37
150.42
140.75
131.36
130.46
128.37
128.15
128.03
127.49
127.22
127.00
119.41
117.31
114.11
77.43
77.00
76.58
74.46
73.08
54.72
52.88
52.82
39.02
29.95
10.43
3.01

zwx-4-57


Ph
O
MeO2C
Ph
O
CO2Me


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.489
7.464
7.407
7.381
7.351
7.326
7.303
7.278
7.264
7.243
5.759
2.974
2.925
2.916
2.866
1.499
1.477
1.454
1.257
1.218
0.865
0.844
0.821
zwx-4-59
Ph
O
MeO2C
Ph
O
CO2Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.27
8.40
0.99
1.01
1.00
6.08
3.44
2.05
2.34
6.56
2.66

170.77
170.61
152.42
150.38
140.94
131.35
130.53
128.37
128.08
128.01
127.53
127.13
126.83
119.43
117.53
113.90
77.42
77.00
76.58
74.85
68.83
54.74
52.87
52.82
39.02
31.57
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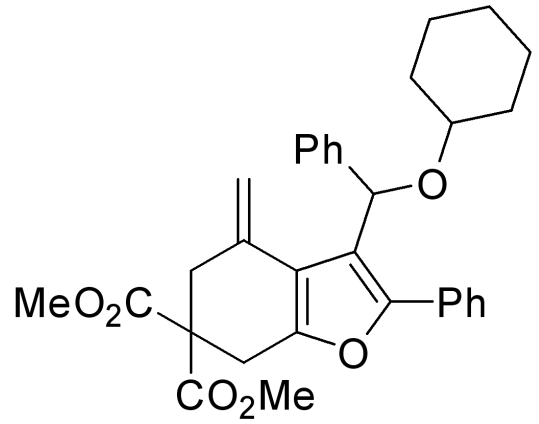
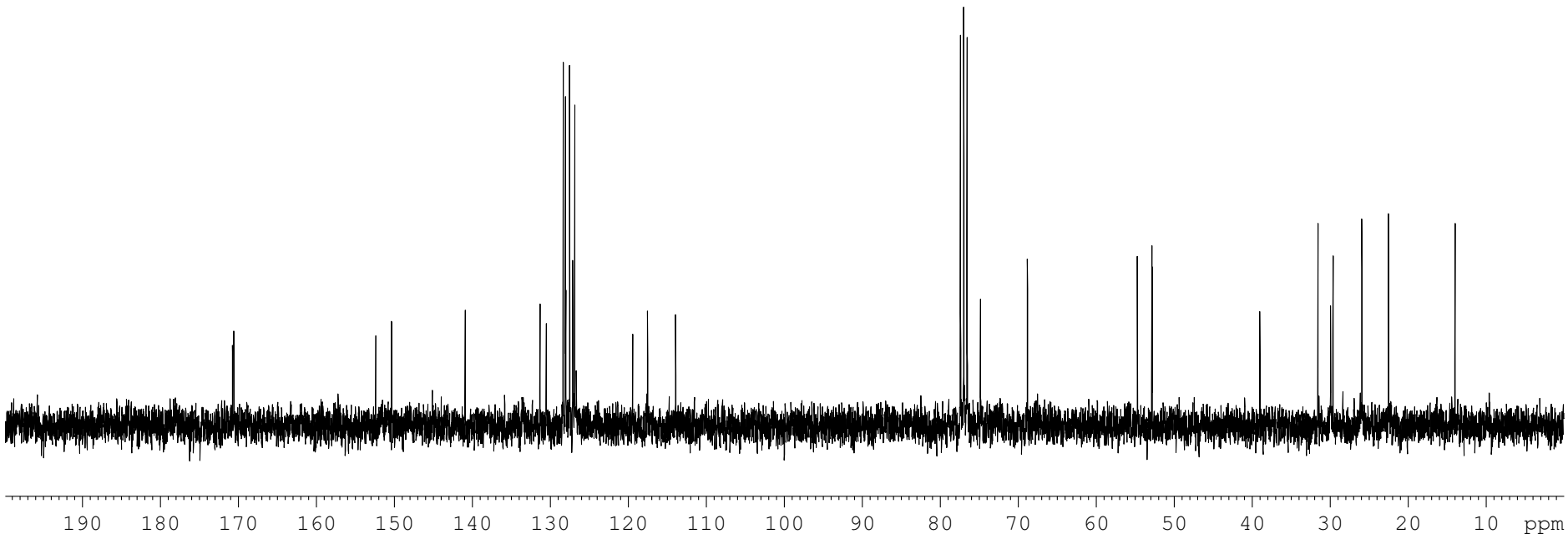
25.94
22.51
13.98

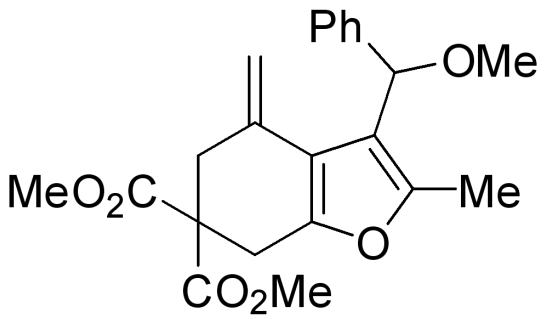
zwx-4-59

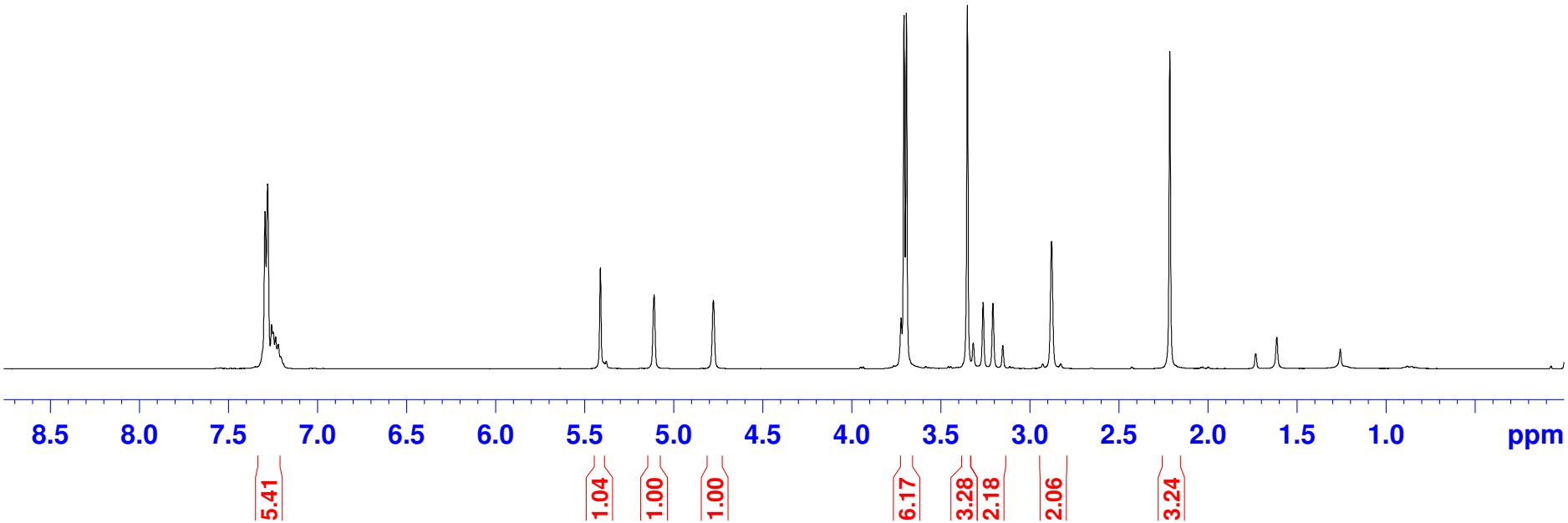




7.294
7.279
7.257
7.248
7.235
7.219
5.411
5.118
4.777
3.706
3.695
3.351
3.311
3.261
3.207
3.152
2.877
2.214

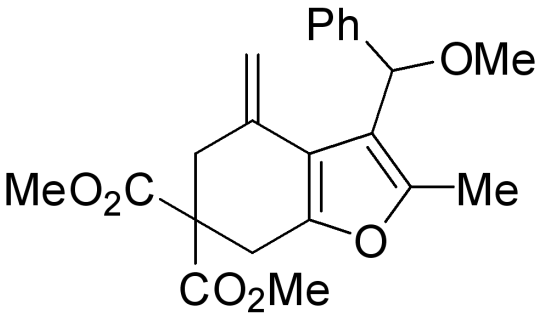
zwx-4-46

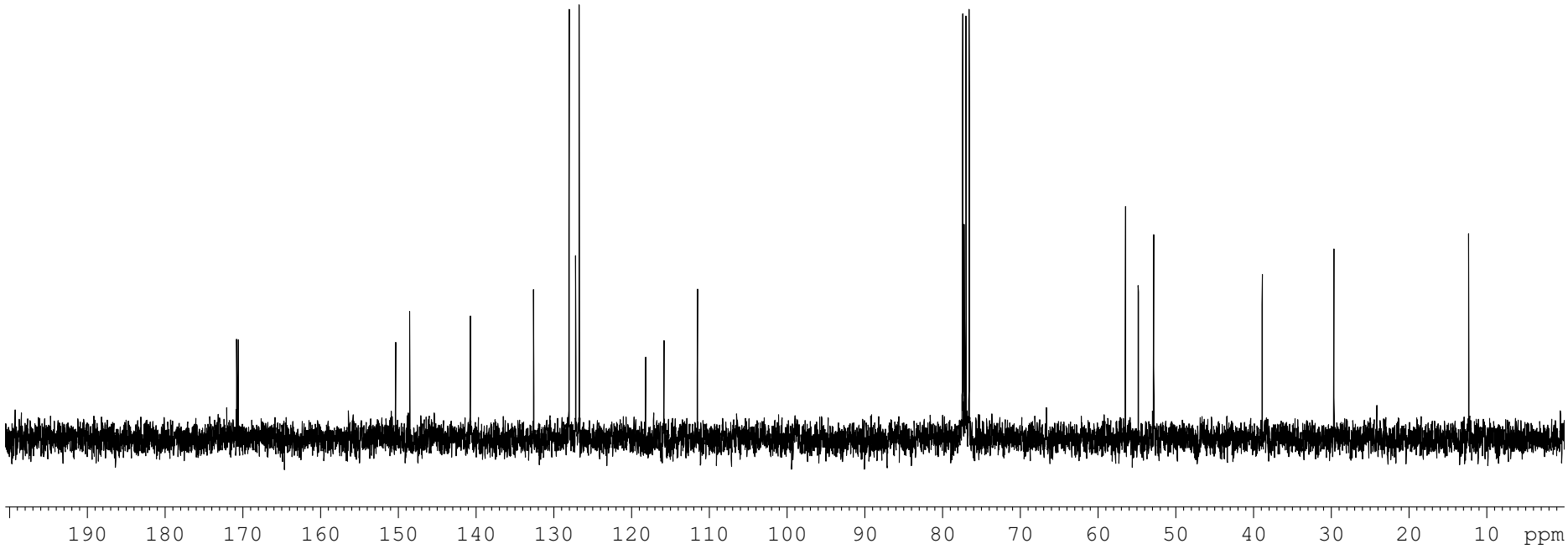




170.81
170.62
150.36
148.56
140.75
132.62
128.05
127.21
126.7
118.21
115.8
111.54
77.43
77.23
77.00
76.58
56.48
54.83
52.86
52.83
38.89
29.66
12.33

zwx-4-46



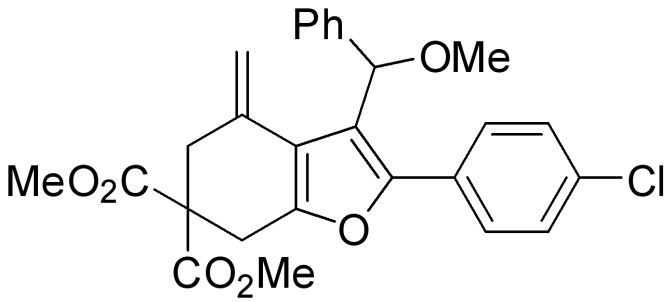


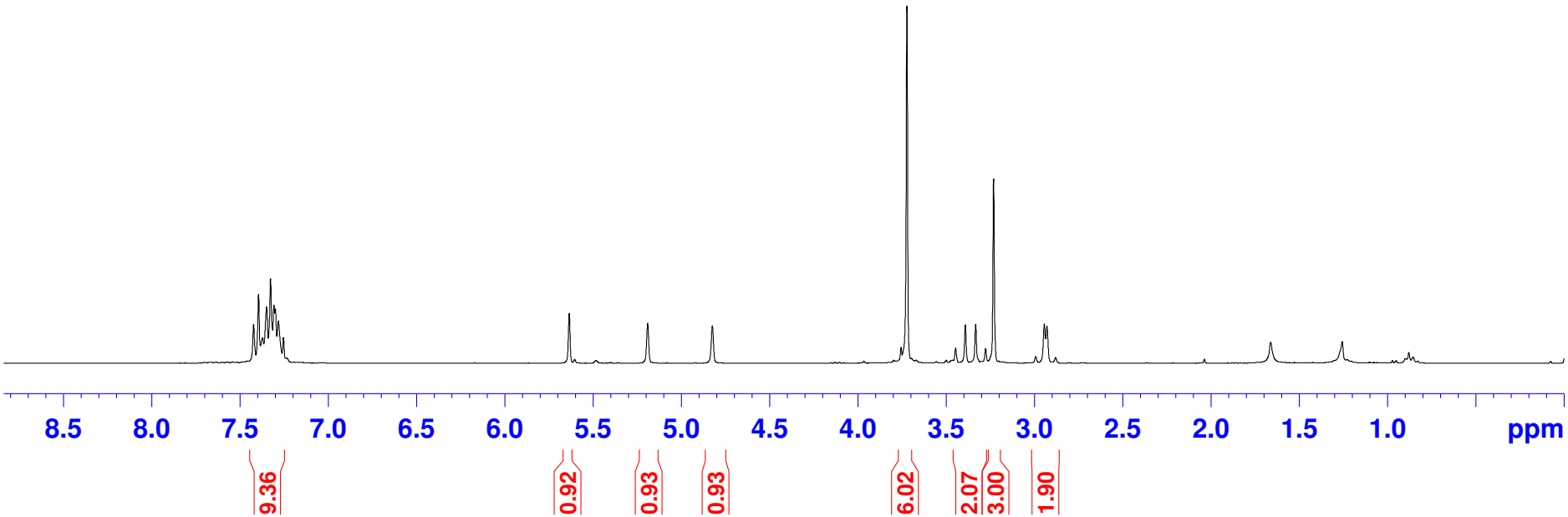
7.425
7.397
7.375
7.351
7.329
7.309
7.301
7.284
7.256

5.637
5.194
4.824

3.722
3.445
3.399
3.333
3.270
3.233
2.994
2.946
2.931
2.882

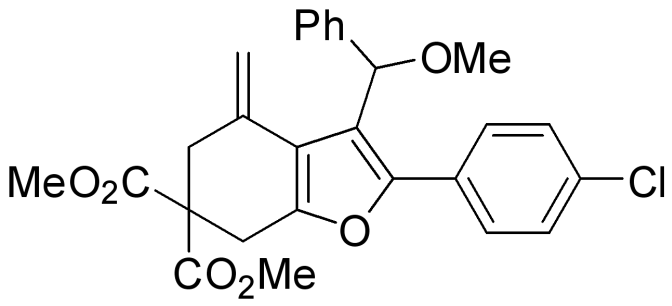
zwx-4-50

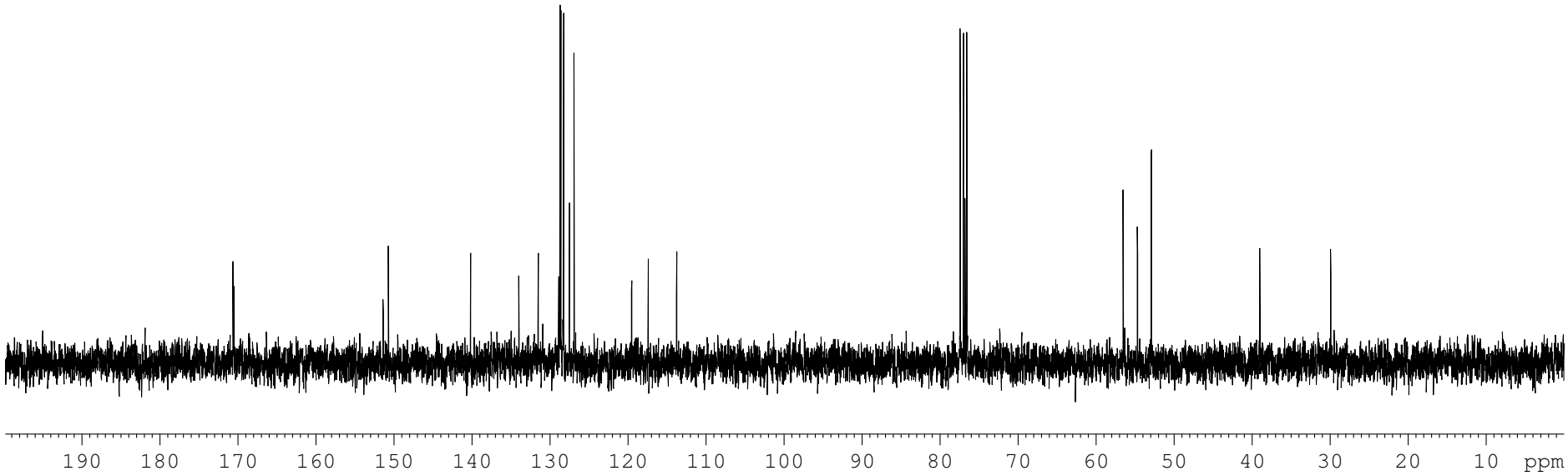




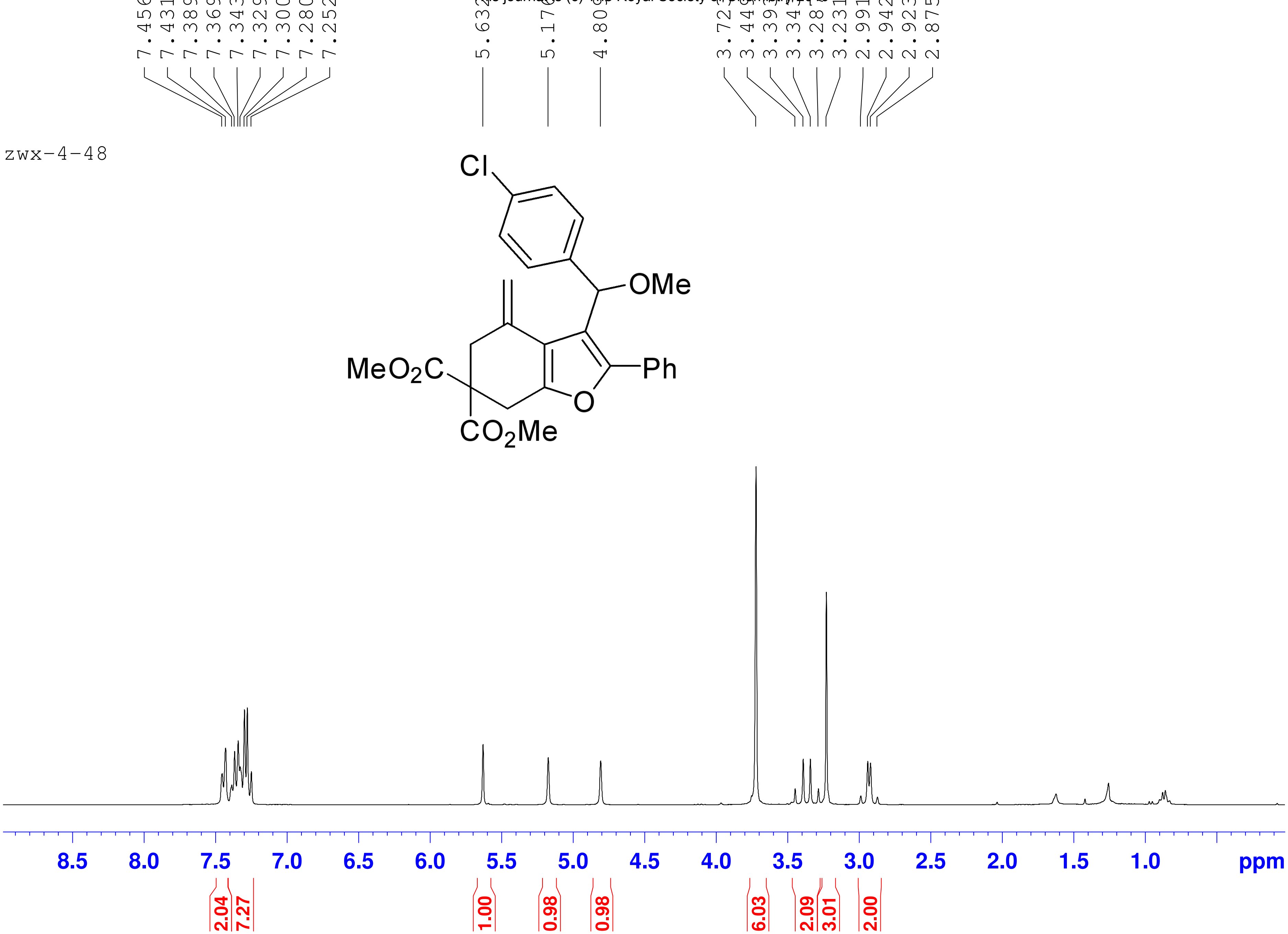
170.68
170.55
151.42
150.74
140.20
134.01
131.53
128.90
128.73
128.62
128.27
127.53
126.95
119.58
117.42
113.78
77.43
77.00
76.80
76.58
56.53
54.70
52.92
39.02
29.92

zwx-4-50





Supplementary Material (ESI) for Chemical Communications



zwx-4-49

170.65
170.55
152.97
150.73
139.13
133.13
131.50
130.23
128.48
128.30
127.50
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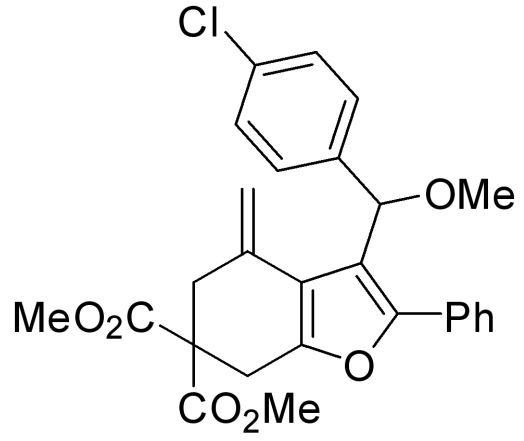
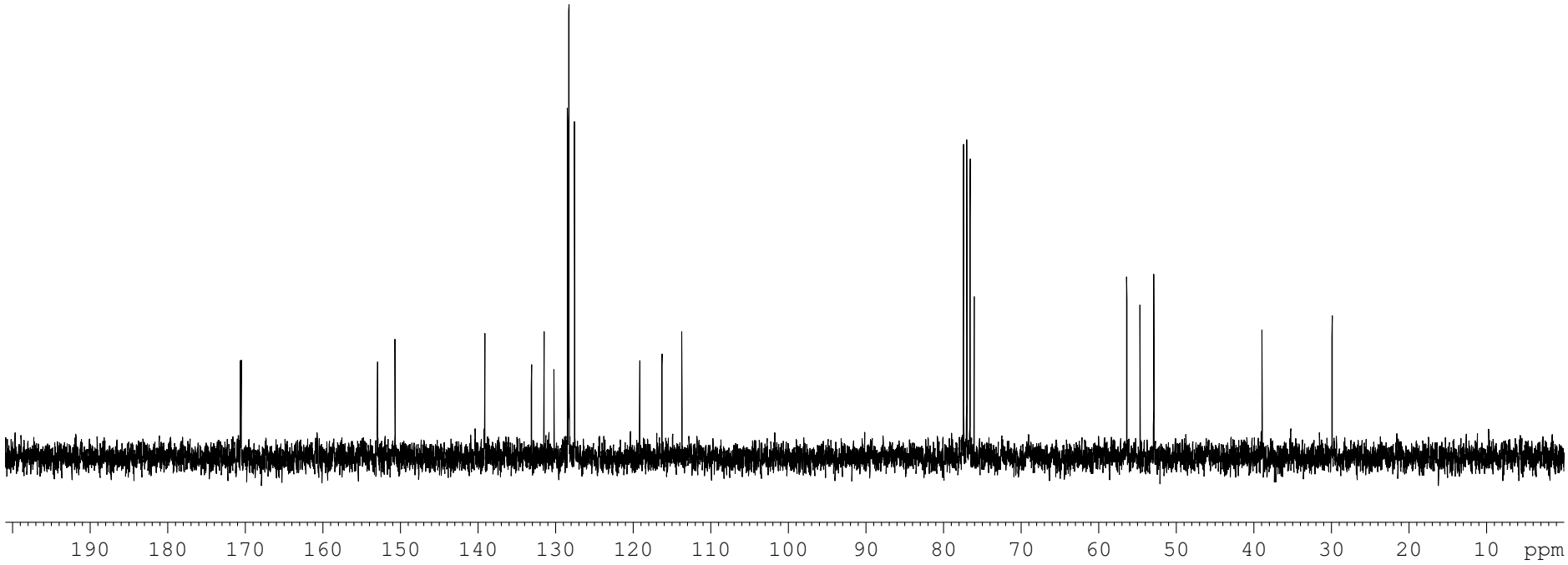
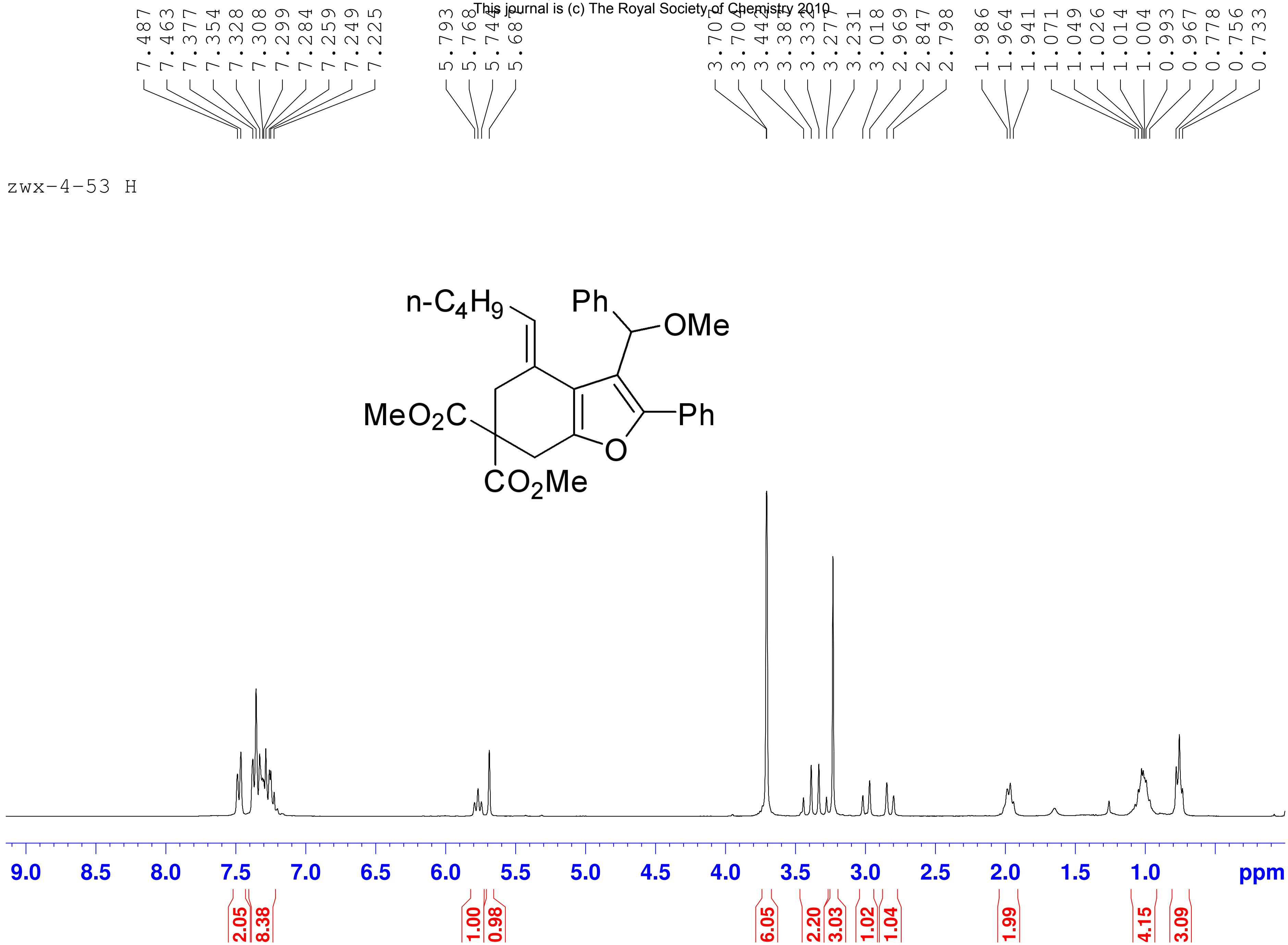
76.04
56.37
54.67
52.91
38.94
29.91

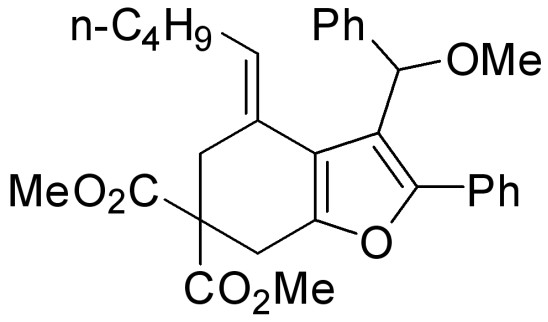


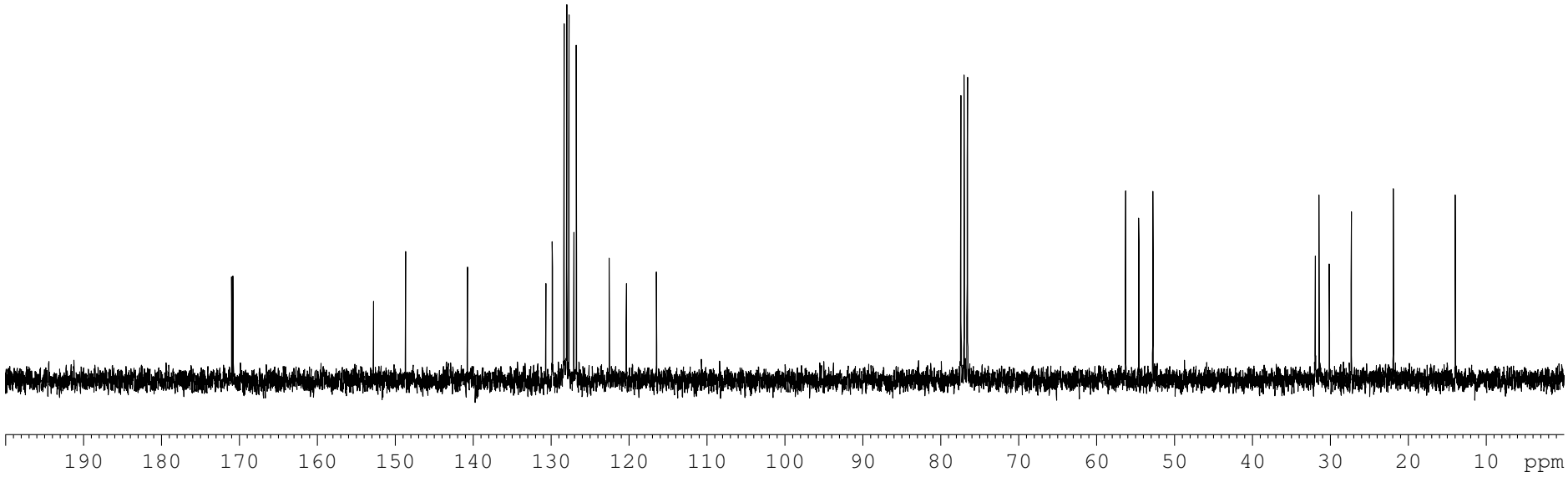


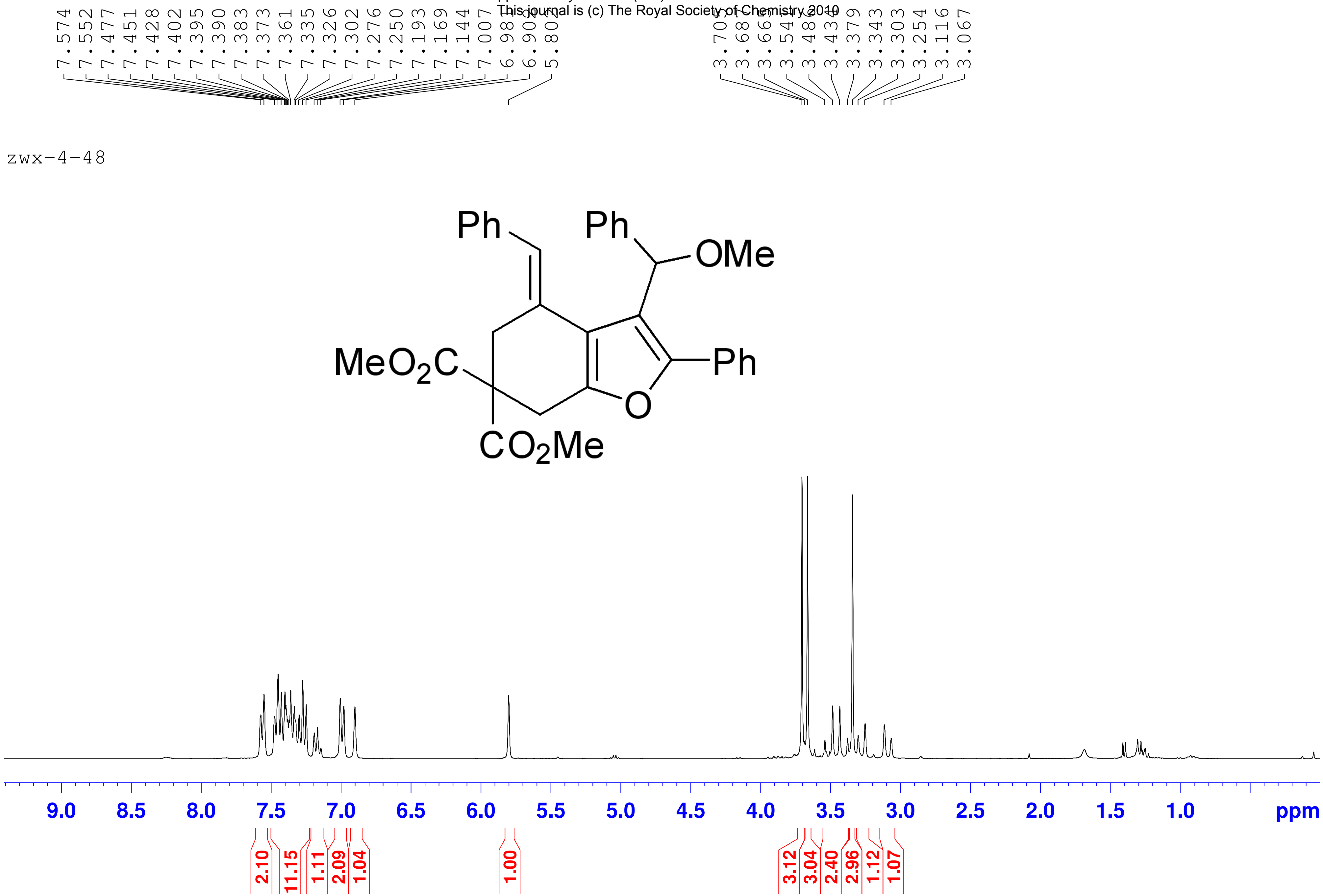


171.02
170.86
152.81
148.70
140.76
130.69
129.86
128.36
128.01
127.74
127.08
126.77
122.51
120.35
116.50
77.43
77.00
76.63
76.58
56.29
54.58
52.78
31.92
31.45
30.13
27.31
21.92
13.96

zwx-4-53 C



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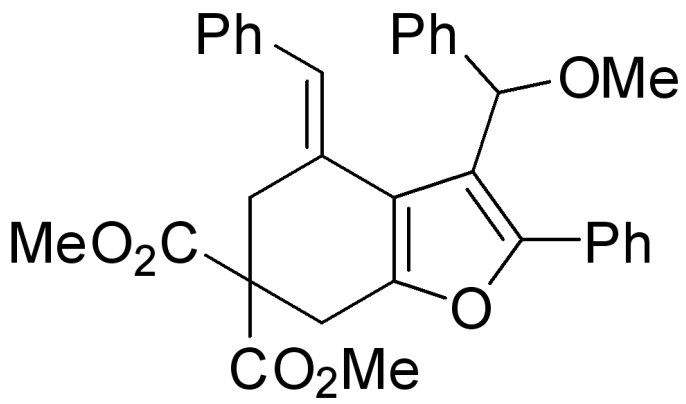
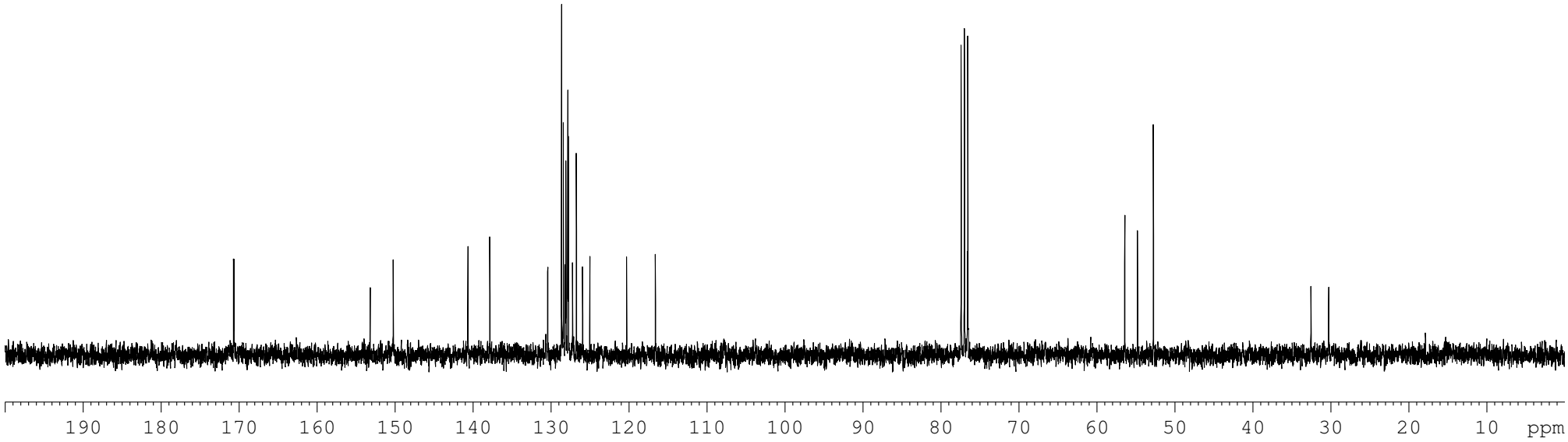
7.477
7.451
7.428
7.402
7.395
7.390
7.383
7.373
7.361
7.335
7.326
7.302
7.276
7.250
7.193
7.169
7.144
7.007
6.98
6.90
5.80
3.70
3.68
3.66
3.54
3.48
3.43
3.379
3.343
3.303
3.254
3.116
3.067
zwx-4-48
Ph
Ph
OMe
MeO2C
Ph
O
CO2Me
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.10
11.15
1.11
2.09
1.04
1.00
3.12
3.04
2.40
2.96
1.12
1.07

170.73
170.68
153.20
150.27
140.68
137.87
130.45
128.67
128.44
128.20
128.12
127.87
127.80
127.27
126.77
125.98
125.05
120.33
116.64
77.42
77.00
76.58
56.44
54.80
52.77
32.57
30.29

zwx-4-48

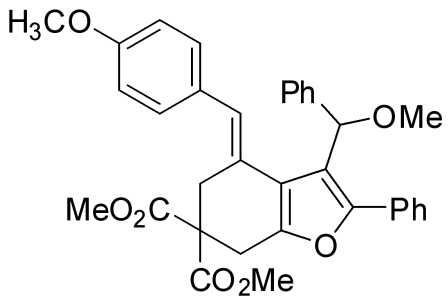


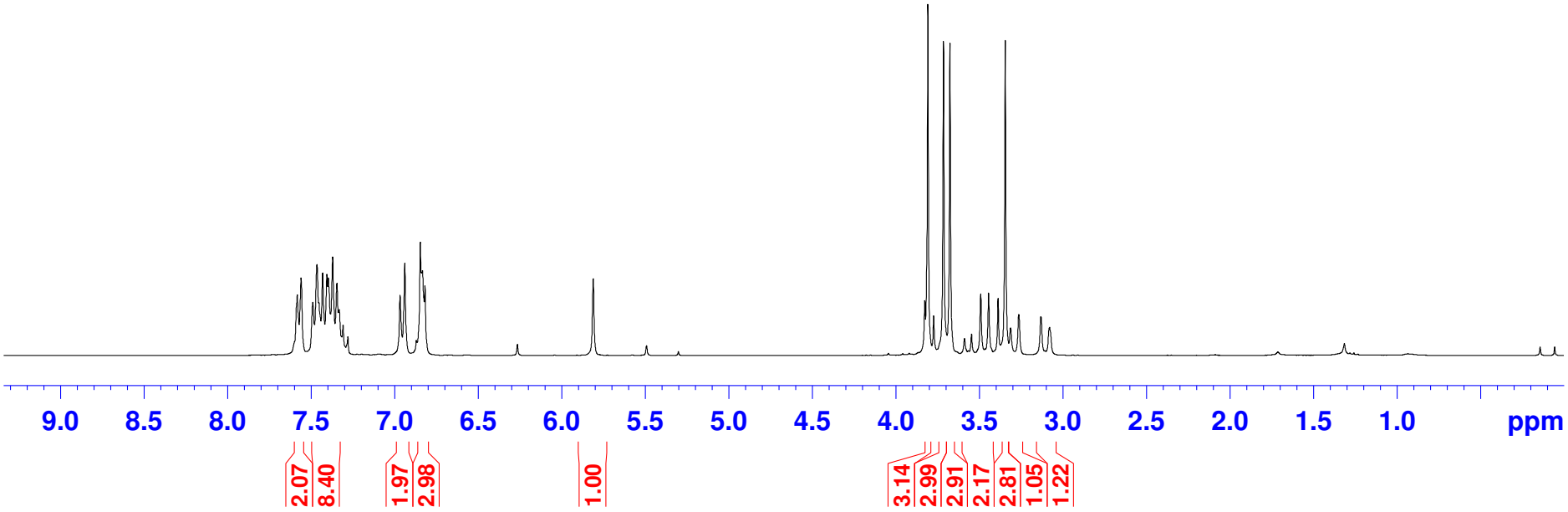


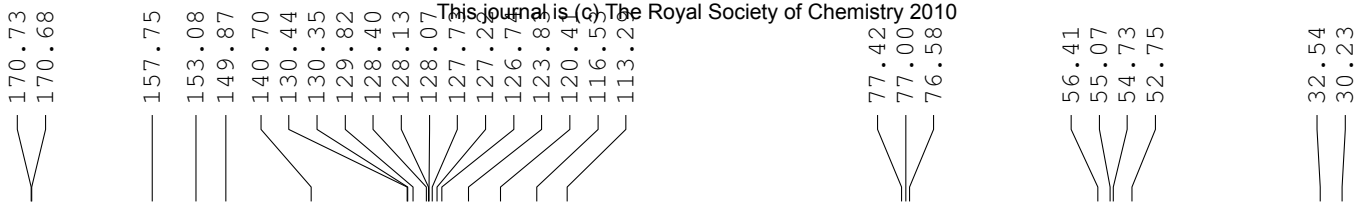
7.583 7.561 7.490 7.465 7.454 7.431 7.406 7.397 7.371 7.345 7.332 7.309 6.968 6.939 6.846 6.840 6.834 6.811 5.811

3.820 3.800 3.771 3.710 3.671 3.581 3.541 3.495 3.445 3.388 3.345 3.313 3.264 3.132 3.080

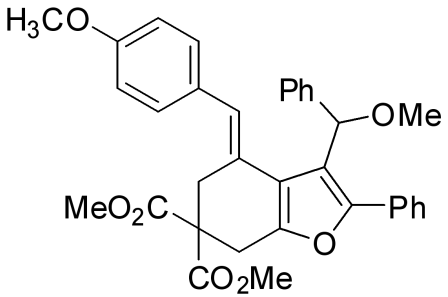
zwx-5-18

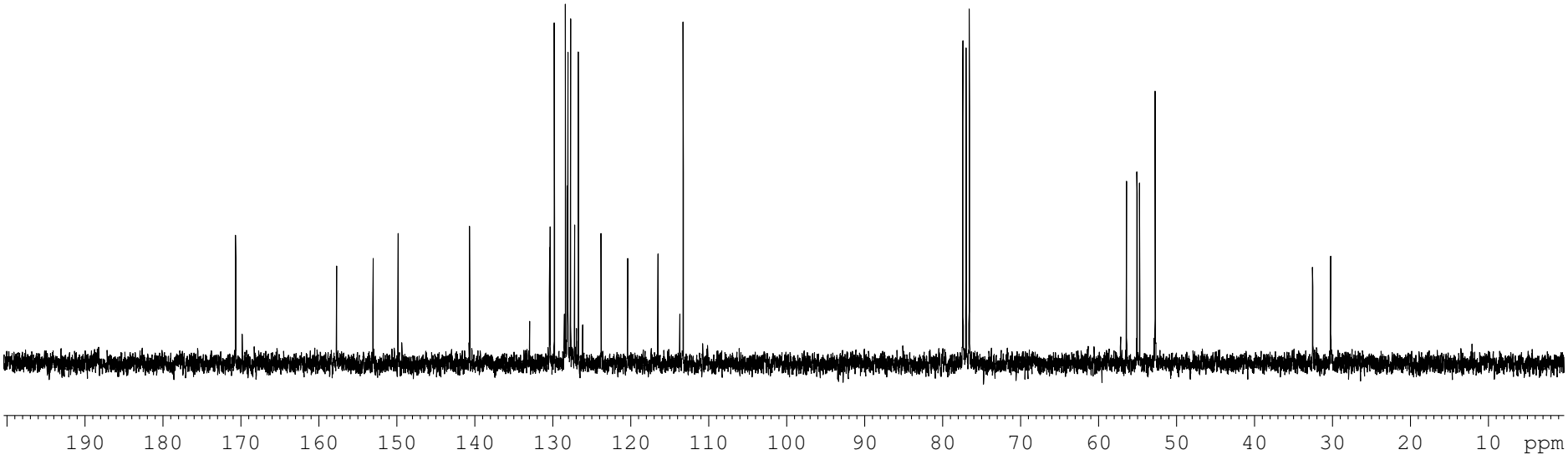





170.73
170.68
157.75
153.08
149.87
140.70
130.44
130.35
129.82
128.40
128.13
128.07
127.72
127.22
126.77
123.81
120.41
116.50
113.21
77.42
77.00
76.58
56.41
55.07
54.73
52.75
32.54
30.23

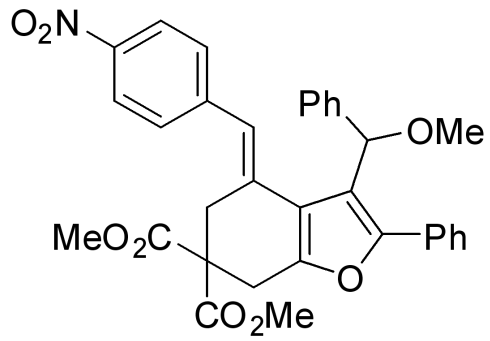
zwx-5-18

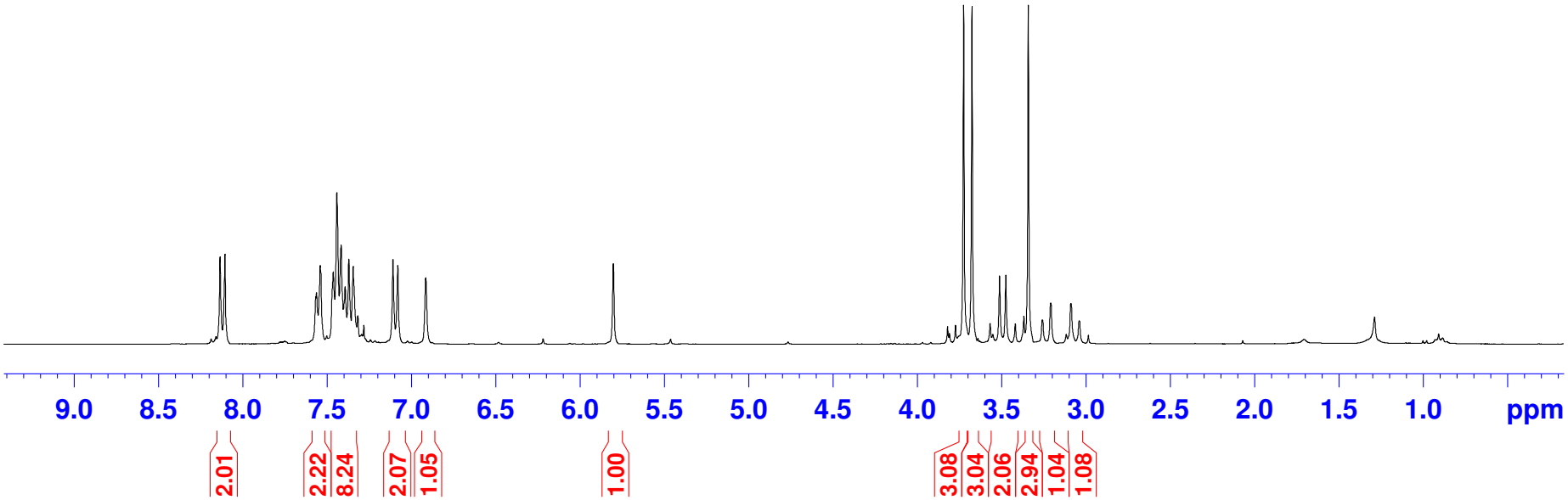

H3CO
Ph
OMe
MeO2C
Ph
O
CO2Me


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8.133
8.104
7.565
7.560
7.539
7.461
7.440
7.415
7.390
7.369
7.343
7.107
7.079
6.912
5.805
3.726
3.676
3.554
3.514
3.474
3.419
3.342
3.259
3.208
3.089
3.040

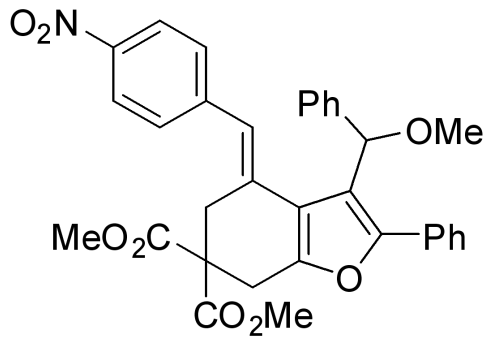
zwx-5-17

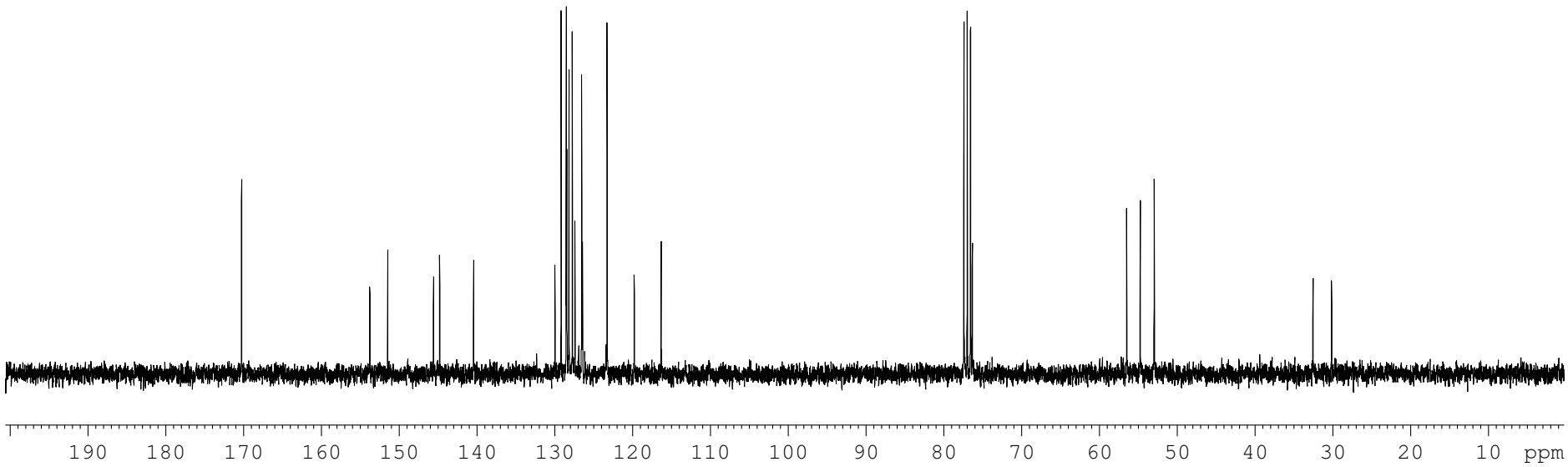




170.28
153.80
151.49
145.61
144.82
140.45
129.99
129.21
128.54
128.47
128.19
127.74
127.42
126.55
126.42
123.36
119.80
116.33
77.42
77.00
76.57
76.34
56.50
54.75
52.97
52.94
32.54
30.16

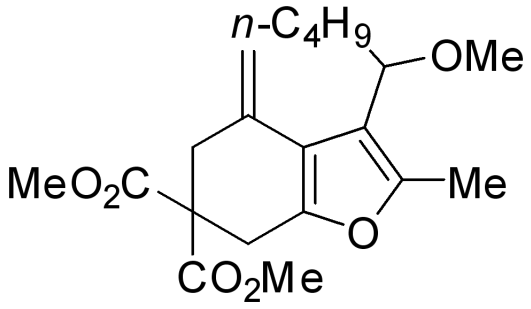
zwx-5-17

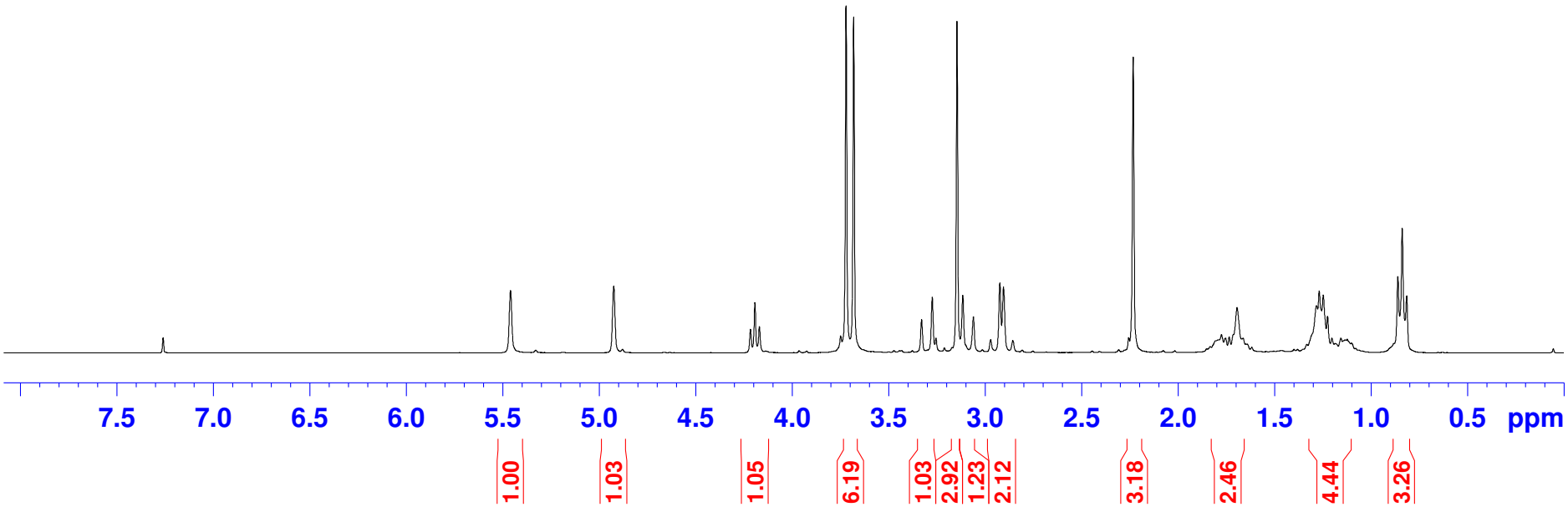




7.260
5.460
4.92
4.21
4.19
4.17
3.72
3.68
3.32
3.27
3.14
3.11
3.06
2.97
2.92
2.904
2.857
2.232
1.775
1.754
1.735
1.694
1.663
1.335
1.284
1.271
1.249
1.227
1.204
1.188
1.158
1.136
1.125
1.104

zwx-4-55





170.98
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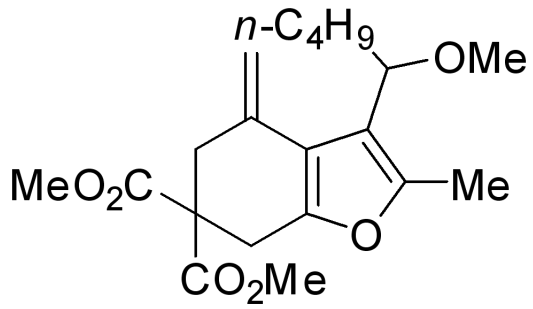
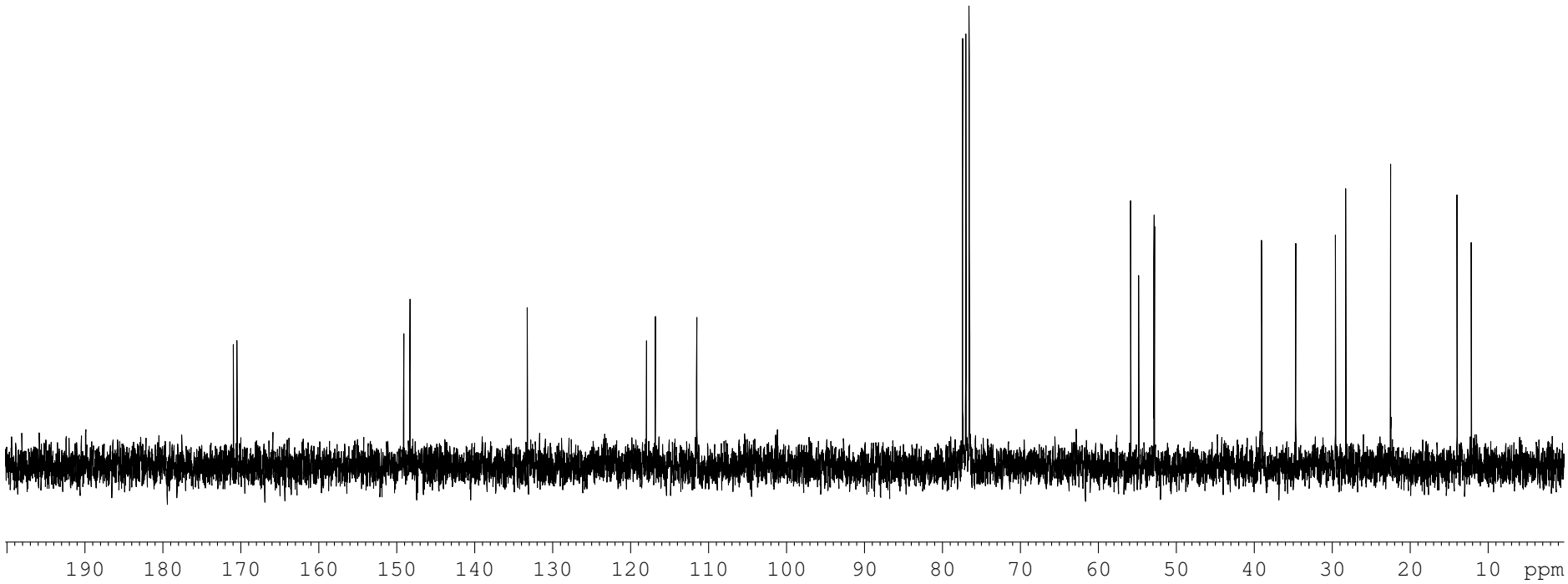
149.13
148.34
133.27
117.94
116.84
111.56
77.42
77.00
76.58
76.54
55.86
54.83
52.86
52.80
39.04
34.67
29.58
28.25
22.50
13.99
12.16

zwx-4-55





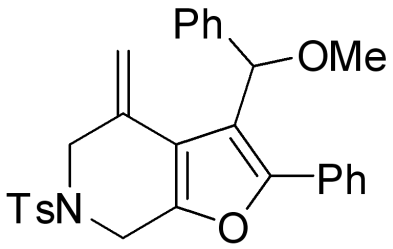
7.699
7.672
7.418
7.397
7.368
7.346
7.332
7.293
7.270
7.244

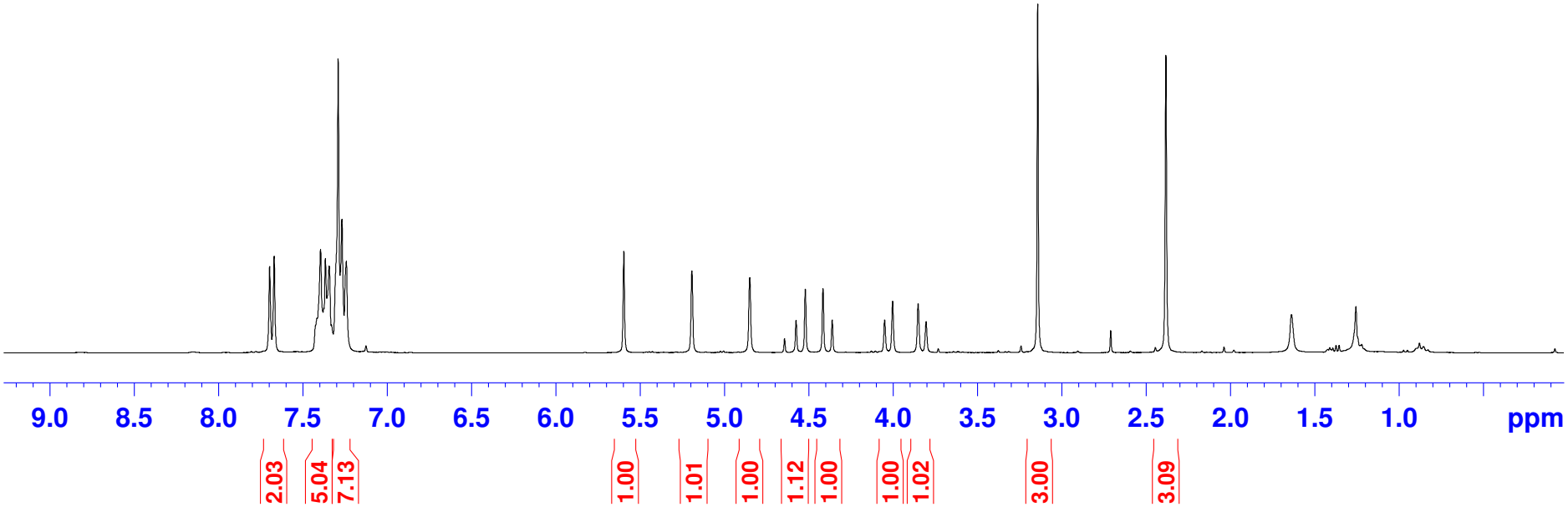
5.59
5.19
4.85
4.64
4.57
4.52
4.41
4.36
4.05
4.00
3.85
3.80

3.145

2.385

zwx-4-52





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130.31
129.90
129.56
128.56
128.49
128.22
127.61
127.51
126.77
118.66
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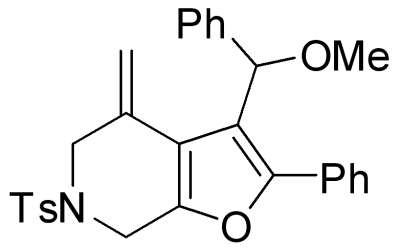
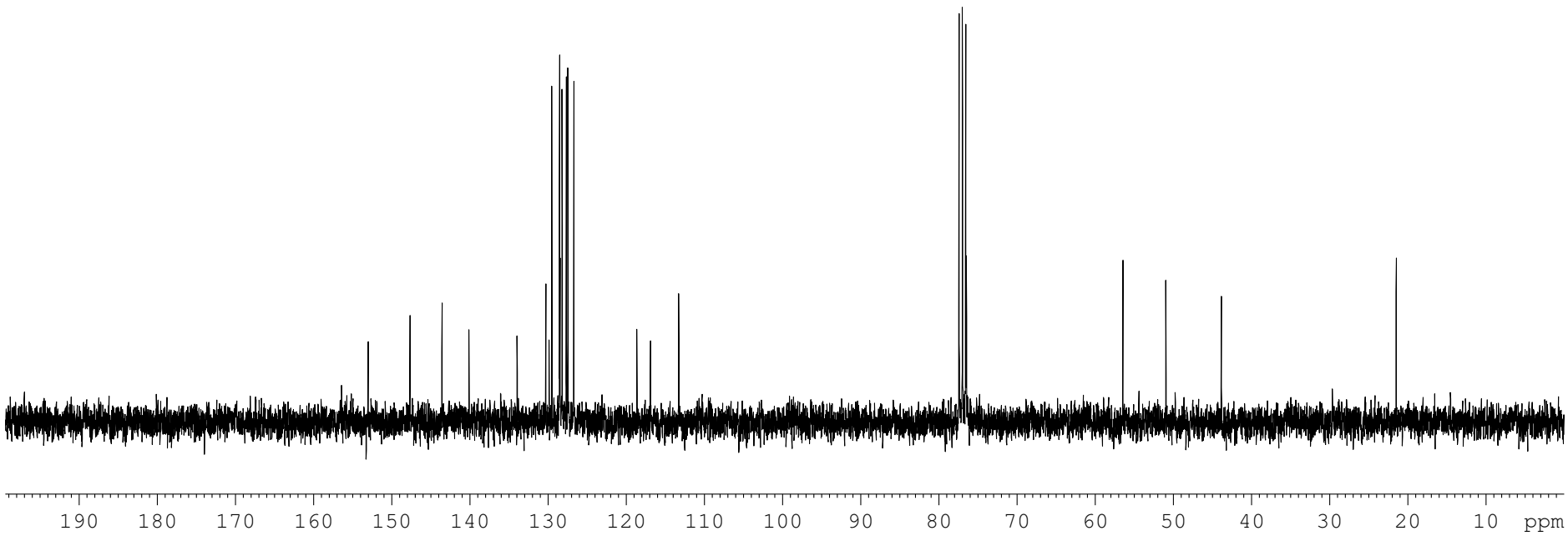
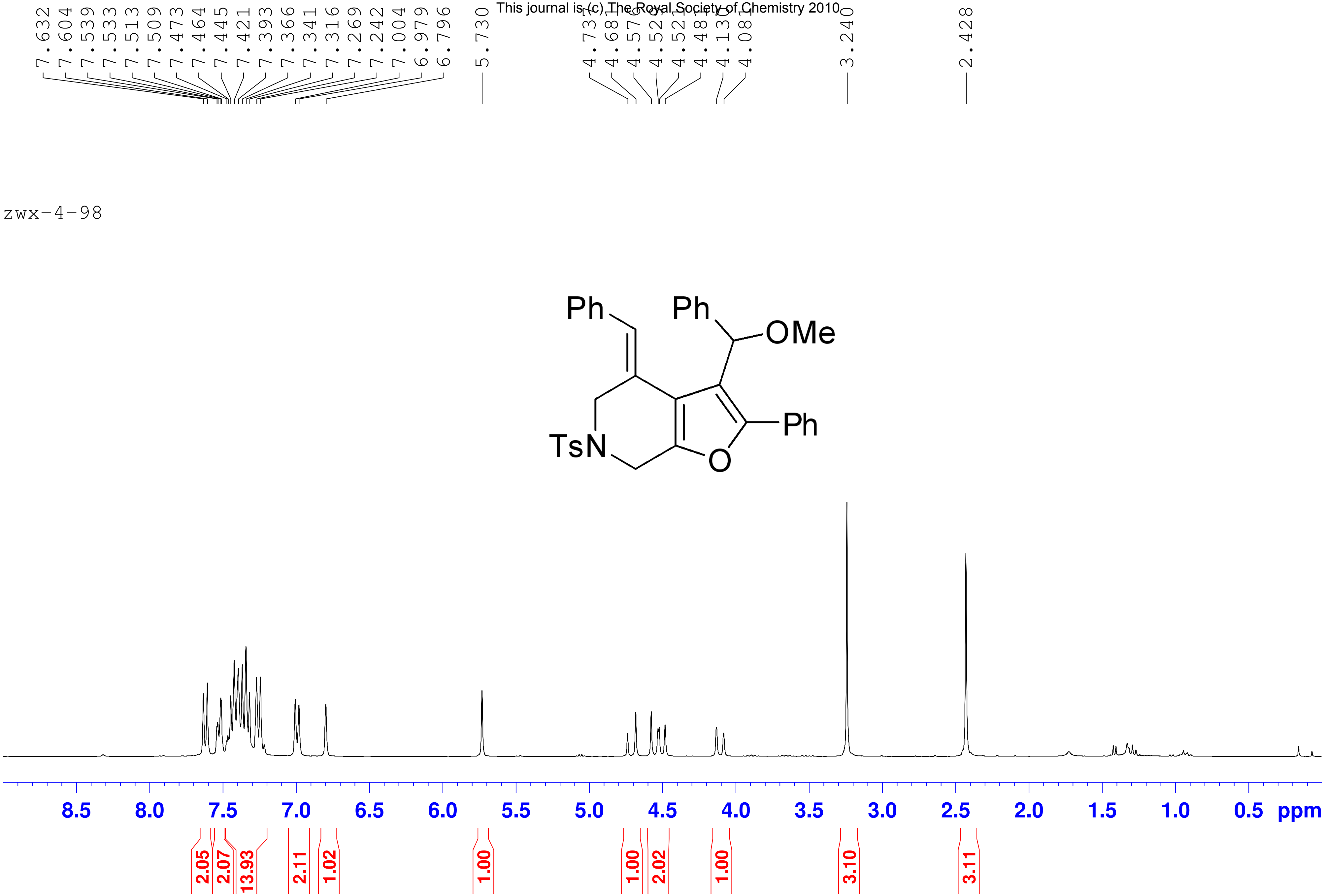
76.48
56.46
50.96
43.84
21.48

zwx-4-52







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143.43
140.27
136.65
134.22
129.90
129.43
128.62
128.54
128.17
127.62
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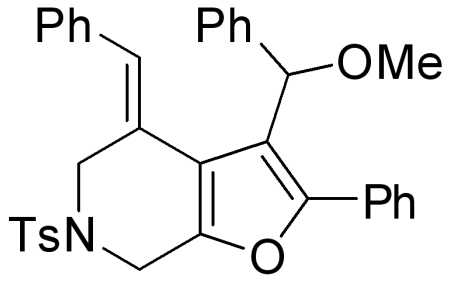
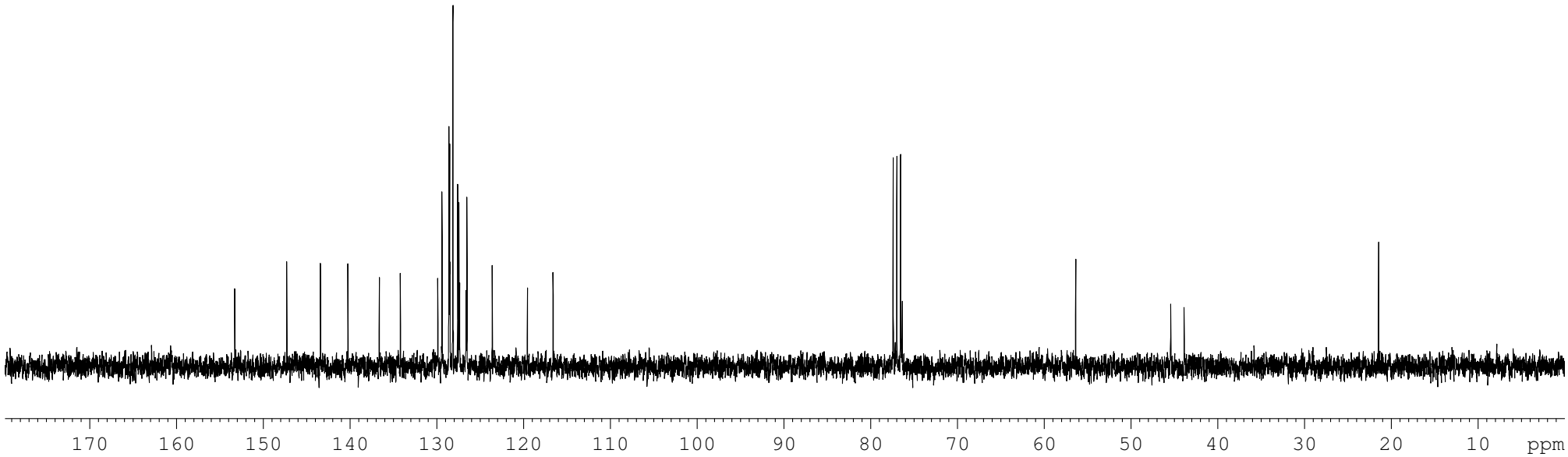
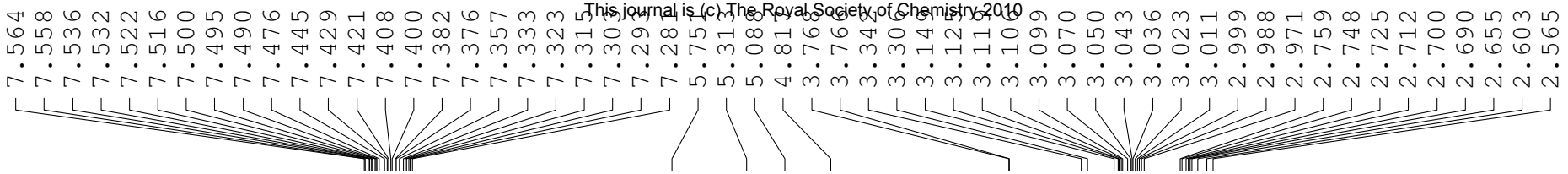
127.39
126.65
126.55
123.63
119.52
116.62
77.42
77.00
76.57
76.37
56.38
45.43
43.88
21.45

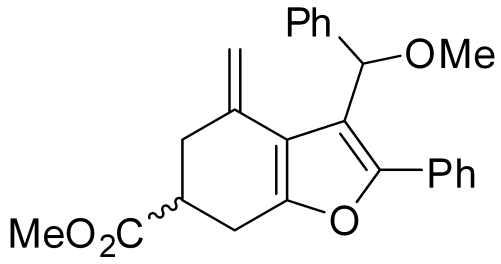
zwx-4-98

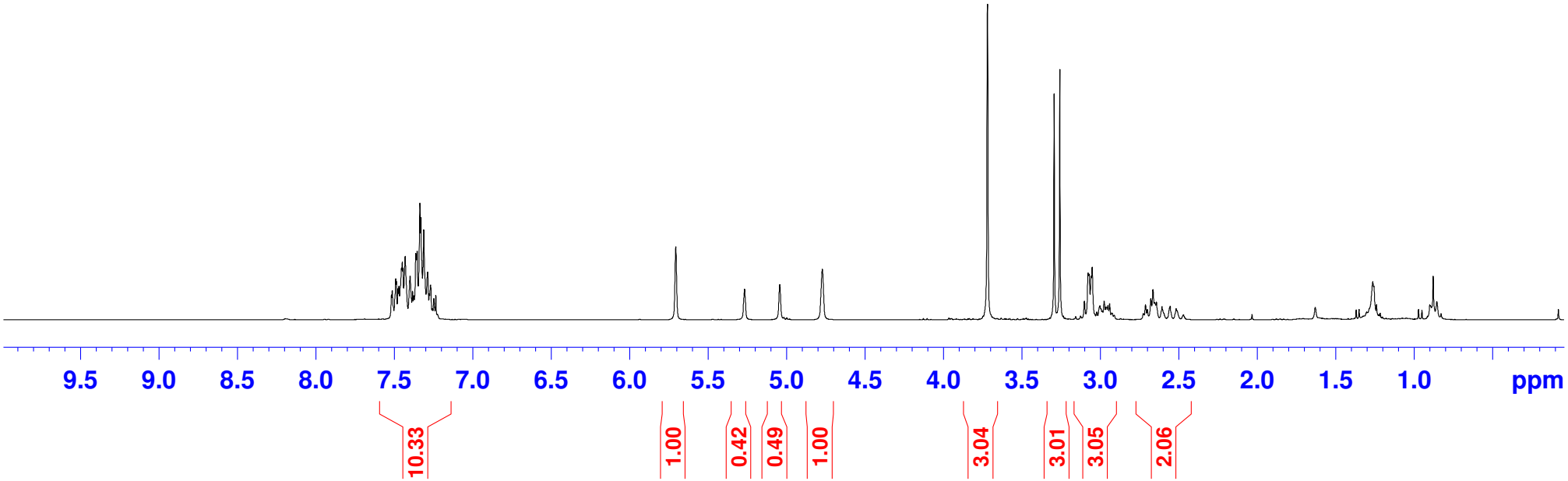






zwx-5-52





174.49
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134.04
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130.56
130.47
128.43
128.40
128.27
128.13
128.08
128.05
127.66
127.51
127.37
127.28
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126.84
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112.29
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76.91
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76.58
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56.59
51.96
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31.54
26.33
26.24
22.61
14.08

zwx-5-52