

**Rhodium-Catalyzed Domino Heterocyclization and [(3+2)+2] Cycloaddition:
Construction of Fused Tricycloheptadienes.**

Wanxiang Zhao and Junliang Zhang*

*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department
of Chemistry, East China Normal University, 3663 N. Zhongshan Road, Shanghai
200062 ,People's Republic of China*

Fax:(+86)-021-6223-5039; e-mail :jlzhang@chem.ecnu.edu.cn

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 KMnO₄ stain. 1,4-Dioxane and toluene were distilled from sodium and benzophenone prior to use. 1,2-Dichloroethane was distilled from CaH₂ 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 ¹³C. Data for ¹³C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl₃: 77.0 ppm).

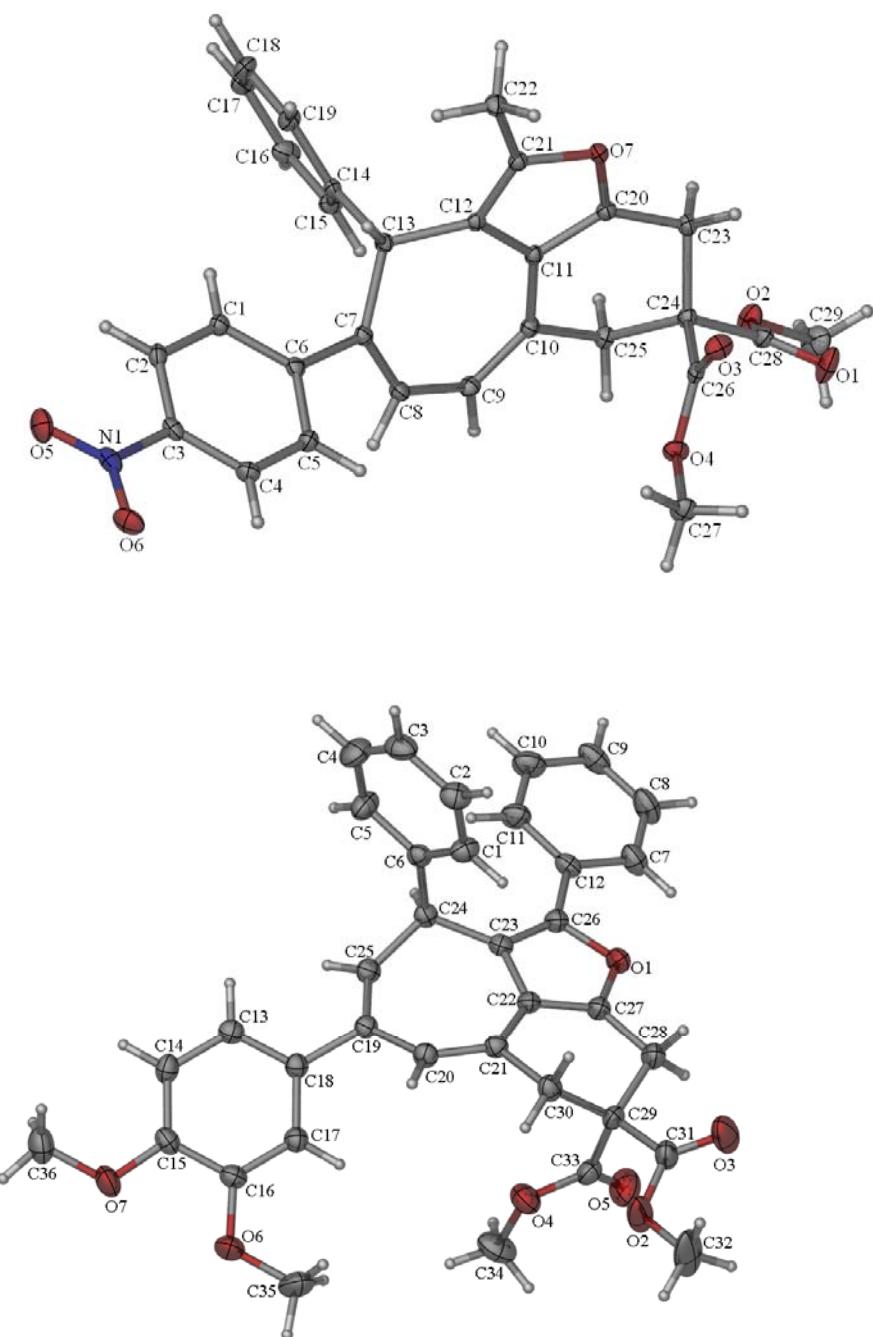
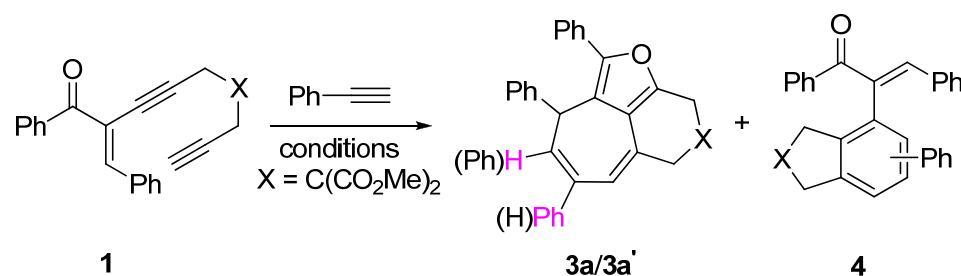


Figure 1. X-ray structures of compounds **3bf'** (upper) and **3ad**

Table 1 Optimization of the rhodium-catalyzed tandem heterocyclization and [(3+2)+2] cycloaddition.



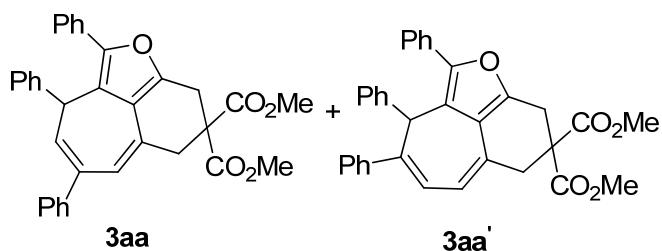
Entry	Conditions ^a	Yield (%) ^b	
		(3a/3a') ^c	4
1	[RhCl(CO) ₂] ₂ , DCE, 60 °C/2 h	57 (2.0/1)	38
2	[RhCl(CO) ₂] ₂ , dioxane, 80 °C/1 h	35 (1.4/1)	33
3	[RhCl(CO) ₂] ₂ , toluene, 80 °C/1 h	34 (1.4/1)	31
4	[RhCl(CO) ₂] ₂ , DCE, 80 °C/1 h	46 (1.8/1)	40
5	[RhCl(CO) ₂] ₂ , DCE, 40 °C/20 h	53 (2.0/1)	14
6	[RhCl(CO) ₂] ₂ , 10 mol % PPh ₃ , DCE, 60 °C/16 h	43 (2.0/1)	21
7 ^[d]	[RhCl(CO) ₂] ₂ , 10 mol % PCy ₃ , DCE, 60 °C/18 h	44 (2.2/1)	34
8	RhCl(CO)(PPh ₃) ₂ , DCE, 60 °C/20 h	0	0
9	[RhCl(CO) ₂] ₂ , 10 mol% AgOTf, DCE, 60 °C/2 h	0	87
10 ^[e]	[RhCl(CO) ₂] ₂ , DCE, 60 °C/2 h	45 (2.2/1)	trace
11 ^[f]	[RhCl(CO) ₂] ₂ , DCE, 60 °C/3 h	57 (2.2/1)	trace
12 ^[f,g]	[RhCl(CO) ₂] ₂ , DCE, 60 °C/3 h	65 (2.2/1)	trace
13 ^[f,h]	[RhCl(CO) ₂] ₂ , DCE, 60 °C/3 h	70 (2.2/1)	trace
14 ^[f]	[RhCl(COD)] ₂ , DCE, 60 °C/3 h	70 (1.6/1)	trace
15 ^[f,g,i]	[RhCl(CO) ₂] ₂ , DCE, 60 °C/3 h	61 (2.2/1)	trace
16 ^[f,h,i]	[RhCl(CO) ₂] ₂ , DCE, 60 °C/3 h	70 (2.2/1)	trace

[a] Conditions (unless otherwise noted): Rhodium (5 mol %), **1a** (1.0 equiv, 0.1 M), phenylacetylene (2.0 equiv). [b] Isolated yield. [c] The ratio of **3aa/3aa'** was determined by ¹H NMR. [d] 28% of **1a** was recovered. [e] The reaction was run under a carbon monoxide atmosphere (balloon 1 atm). [f] The reaction was run with 0.2 atm CO + 0.8 atm N₂. [g] 3.0 equiv of phenylacetylene. [h] 5.0 equiv of phenylacetylene. [i] **8a** (0.05 M) was used.

General Procedure for the Rh-catalyzed tandem heterocyclization and [(3+2)+2] cycloaddition.

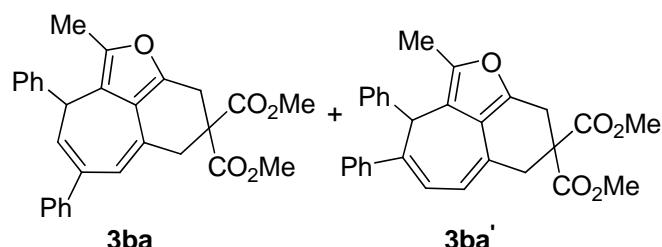
[Rh(CO)₂Cl]₂ (5 mol % to the substrate) was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of the mixed gas (0.2 atm CO + 0.8 atm N₂), and then a solution of **1** (0.1 M) and **2** in degassed DCE was added. The reaction mixture was stirred at 60 °C under the mixed CO/N₂ atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to afford the cycloaddition products.

1. Synthesis of fused 5,6,7-tricyclic **3aa/3aa'**:



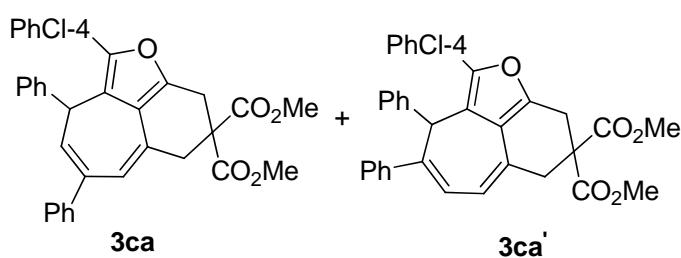
¹H NMR (300 MHz, CDCl₃) **3aa**: δ = 7.50 (d, *J* = 7.8 Hz, 2 H), 7.41-7.10 (m, 13 H), 6.19 (d, *J* = 8.7 Hz, 1 H), 5.96 (s, 1 H), 5.18 (d, *J* = 8.7 Hz, 1 H), 3.74 (s, 6 H), 3.59 (d, *J* = 16.2 Hz, 1 H), 3.30 (d, *J* = 16.2 Hz, 1 H), 3.12 (s, 2 H), **3aa'**: δ = 7.56 (d, *J* = 7.8 Hz, 2 H), 7.41-7.10 (m, 13 H), 6.35 (d, *J* = 7.5 Hz, 1 H), 5.83 (d, *J* = 7.5 Hz, 1 H), 5.64 (s, 1 H), 3.69 (s, 6 H), 3.59 (d, *J* = 16.2 Hz, 1 H), 3.30 (d, *J* = 16.2 Hz, 1 H), 3.04 (s, 2 H), ¹³C NMR (75 MHz, CDCl₃) (**3aa + 3aa'**): δ = 170.75, 170.16, 148.96, 148.29, 147.82, 145.11, 145.07, 143.88, 142.75, 140.74, 138.95, 130.92, 130.82, 130.07, 129.55, 128.85, 128.69, 128.54, 128.44, 128.39, 128.17, 128.05, 127.36, 127.29, 127.07, 127.00, 126.86, 126.66, 126.28, 126.24, 126.09, 125.93, 122.89, 121.23, 120.95, 120.61, 120.51, 120.06, 56.22, 56.19, 53.04, 53.00, 52.97, 45.21, 40.93, 37.92, 37.18, 29.59, 29.48 ppm. MS (70 ev) *m/z* (%): 516 (M⁺, 100), HRMS calcd for C₃₄H₂₈O₅: 516.1937, found: 516.1941.

2. Synthesis of fused 5,6,7-tricyclic **3ba/3ba':**



¹H NMR (300 MHz, CDCl₃) **3ba**: δ = 7.41-7.12(m, 10 H), 6.02 (d, *J* = 7.8 Hz, 1 H), 5.92 (s, 1 H), 4.71 (d, *J* = 7.8 Hz, 1 H), 3.71-3.68 (m, 6 H), 3.46 (s, 1 H), 3.23 (s, 1 H), 3.01(s, 2 H), 2.07 (s, 3 H), **3ba'**: δ = 7.41-7.12(m, 10 H), 6.31 (d, *J* = 7.5 Hz, 1 H), 5.80 (d, *J* = 7.5 Hz, 1 H), 5.03 (s, 1 H), 3.74 (s, 6 H), 3.40-3.38 (m, 1 H), 3.16 (d, *J* = 11.4 Hz, 1 H), 3.08 (s, 2 H), 2.30 (s, 3H), ¹³C NMR (75 MHz, CDCl₃) (**3ba + 3ba'**): δ = 170.92, 170.83, 170.42, 170.36, 147.43, 146.72, 146.41, 145.90, 145.76, 145.52, 144.84, 144.29, 140.37, 138.34, 130.11, 129.83, 129.19, 128.52, 128.41, 128.20, 128.06, 127.32, 127.15, 126.89, 126.79, 126.73, 126.65, 126.28, 121.88, 119.68, 119.50, 119.44, 119.23, 119.02, 56.29, 53.03, 52.98, 46.23, 42.08, 37.86, 37.10, 29.67, 29.49, 29.40, 11.66, 11.55. MS (70 ev) *m/z* (%): 454 (M⁺, 100), HRMS calcd for C₂₉H₂₆O₅: 454.1780, found: 454.1782.

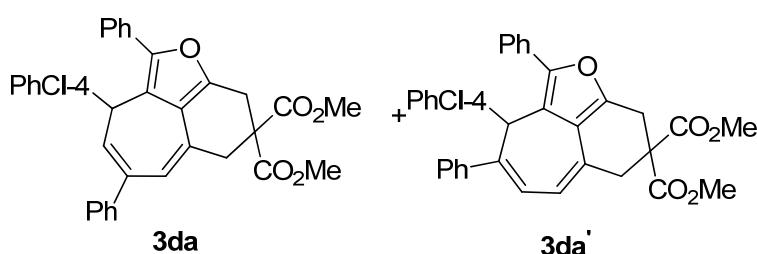
3. Synthesis of fused 5,6,7-tricyclic **3ca/3ca':**



¹H NMR (300 MHz, CDCl₃) **3ca**: δ = 7.51-7.07 (m, 14 H), 6.17 (d, *J* = 8.7 Hz, 1 H), 5.97 (s, 1 H), 5.12 (d, *J* = 8.7 Hz, 1 H), 3.85-3.70 (m, 6 H), 3.68-3.55 (m, 1 H), 3.29 (d, *J* = 16.2 Hz, 1 H), 3.12 (s, 2 H), **3ca'**: δ = 7.51-7.07 (m, 14 H), 6.34 (d, *J* = 7.5 Hz, 1 H), 5.84 (d, *J* = 7.5 Hz, 1 H), 5.55 (s, 1 H), 3.78-3.70 (m, 6 H), 3.68-3.55 (m, 1 H), 3.24 (d, *J* = 16.2 Hz, 1 H), 3.04 (s, 2 H), ¹³C NMR (75 MHz, CDCl₃) (**3ca + 3ca'**): δ = 170.77, 170.19, 149.31, 148.63, 146.76, 145.04, 143.69, 142.56, 140.70, 138.99,

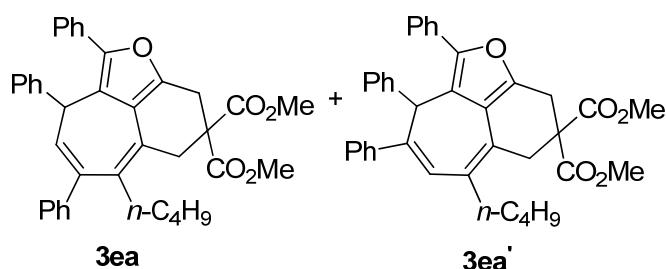
133.17, 133.10, 129.92, 129.42, 129.33, 128.99, 128.82, 128.72, 128.59, 128.49, 128.30, 128.12, 127.94, 127.30, 127.14, 127.11, 127.04, 126.99, 126.84, 126.70, 126.43, 126.26, 123.13, 121.35, 121.16, 121.07, 121.04, 120.29, 56.21, 53.15, 53.10, 45.36, 41.09, 37.96, 37.21, 29.63, 29.52 ppm. MS (70 ev) m/z (%): 550 (M^+ , 14.98), 488 (100), HRMS calcd for $C_{34}H_{27}O_5Cl$: 550.1547, found: 550.1551.

4. Synthesis of fused 5,6,7-tricyclic **3da/3da'**:



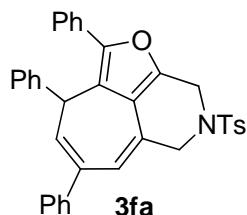
¹H NMR (300 MHz, CDCl₃) **3da**: δ = 7.48 (d, J = 8.1 Hz, 2 H), 7.38-7.10 (m, 12 H), 6.15 (d, J = 8.7 Hz, 1 H), 5.96 (s, 1 H), 5.15 (d, J = 8.7 Hz, 1 H), 3.82-3.75 (m, 6 H), 3.64 (d, J = 17.1 Hz, 1 H), 3.31 (d, J = 17.1 Hz, 1 H), 3.12 (s, 2 H), **3da'**: δ = 7.53 (d, J = 7.8 Hz, 2 H), 7.38-7.10 (m, 12 H), 6.35 (d, J = 7.5 Hz, 1 H), 5.83 (d, J = 7.5 Hz, 1 H), 5.58 (s, 1 H), 3.72-3.70 (m, 6 H), 3.62-3.55 (m, 1 H), 3.59 (d, J = 15 Hz, 1 H), 3.26 (d, J = 15 Hz, 2 H), 3.04 (s, 2 H), ¹³C NMR (75 MHz, CDCl₃) (**3da + 3da'**): δ = 170.71, 170.13, 149.19, 148.53, 147.91, 144.86, 142.31, 141.27, 140.32, 139.44, 132.08, 132.01, 130.73, 130.67, 130.28, 129.73, 128.78, 128.63, 128.55, 128.49, 128.36, 128.29, 128.12, 127.53, 127.48, 127.06, 127.00, 126.60, 126.42, 126.10, 125.93, 122.84, 121.07, 120.77, 120.21, 120.07, 119.98, 56.20, 53.10, 53.04, 44.68, 40.24, 37.87, 37.15, 29.59 ppm. MS (70 ev) m/z (%): 550 (M^+ , 6.84), 488 (100), HRMS calcd for $C_{34}H_{27}O_5Cl$: 550.1547, found: 550.1544.

5. Synthesis of fused 5,6,7-tricyclic 3ea/3ea[’]:



¹H NMR (300 MHz, CDCl₃) **3ea**: δ = 7.49 (d, *J* = 7.5 Hz, 2 H), 7.40-7.10 (m, 13 H), 6.31 (d, *J* = 9.6 Hz, 1 H), 5.09 (d, *J* = 9.6 Hz, 1 H), 3.79 (s, 6 H), 3.74-3.62 (m, 1 H), 3.44 (d, *J* = 13.8 Hz, 1 H), 3.26 (d, *J* = 17.1 Hz, 1 H), 2.70 (d, *J* = 13.8 Hz, 1 H), 2.33-2.20 (m, 1 H), 1.78-1.65 (m, 1 H), 0.95-0.45 (m, 7 H), **3ea'**: δ = 7.54 (d, *J* = 7.5 Hz, 2 H), 7.40-7.10 (m, 13 H), 6.24 (s, 1 H), 5.55 (s, 1 H), 3.72-3.65 (m, 6 H), 3.75-3.62 (m, 6 H), 3.74-3.62 (m, 1 H), 3.56 (d, *J* = 17.1 Hz, 1 H), 3.27 (d, *J* = 17.1 Hz, 1 H), 2.83 (d, *J* = 15 Hz, 1 H), 2.55-2.42 (m, 1 H), 2.12-2.00 (m, 1 H), 0.95-0.45 (m, 7 H), ¹³C NMR (75 MHz, CDCl₃) (**3ea + 3ea'**): δ = 171.36, 171.04, 170.43, 147.74, 147.41, 147.22, 144.96, 144.55, 144.28, 142.42, 142.31, 141.37, 135.11, 132.37, 131.62, 131.12, 128.70, 128.59, 128.47, 128.22, 128.13, 127.84, 127.79, 127.28, 127.17, 127.06, 127.04, 126.95, 126.61, 126.58, 126.10, 126.06, 125.90, 125.74, 125.62, 123.69, 123.21, 121.87, 121.62, 121.49, 56.19, 55.97, 53.11, 52.93, 52.87, 43.83, 39.02, 33.56, 33.30, 31.74, 31.32, 30.81, 29.76, 21.76, 13.94 ppm, MS (70 ev) *m/z* (%): 572 (M⁺, 2.37), 205 (100), HRMS calcd for C₃₈H₃₆O₅: 572.2563, found: 572.2568.

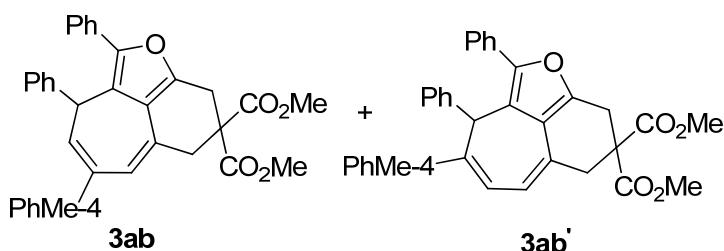
6. Synthesis of fused 5,6,7-tricyclic 3fa:



¹H NMR (300 MHz, CDCl₃): δ = 7.72 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 7.5 Hz, 2 H), 7.41-7.12 (m, 15 H), 6.19 (d, *J* = 8.4 Hz, 1 H), 6.03 (s, 1 H), 5.15 (d, *J* = 8.4 Hz, 1 H), 4.84 (d, *J* = 16.8 Hz, 1 H), 4.47 (d, *J* = 14.1 Hz, 1 H), 4.34 (d, *J* = 16.8 Hz, 1 H), 3.86

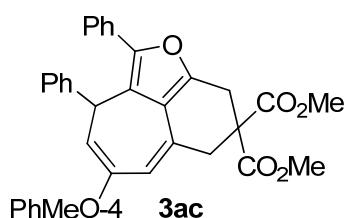
(d, $J = 13.8$ Hz, 1 H), 2.38 (s, 3 H), (d, $J = 8.1$ Hz, 1 H), ^{13}C NMR (75 MHz, CDCl_3): $\delta = 148.23, 145.98, 144.74, 143.74$ (2 C), 138.34, 134.12, 130.41, 129.95, 129.54, 128.68, 128.62, 128.24, 128.05, 127.71, 127.49, 127.10, 127.04, 126.93, 126.46, 125.98, 122.23, 120.62, 120.33, 50.02, 43.84, 41.31, 21.50 ppm. MS (70 ev) m/z (%): 555 (M^+ , 6.87), 105 (100), HRMS calcd for $\text{C}_{36}\text{H}_{29}\text{NO}_3\text{S}$: 555.1868, found: 555.1867.

7. Synthesis of fused 5,6,7-tricyclic **3ab/3ab'**:



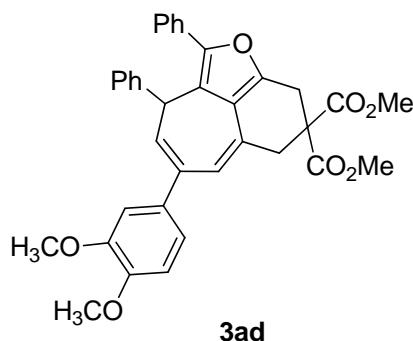
^1H NMR (300 MHz, CDCl_3) **3ab**: $\delta = 7.50$ (d, $J = 7.8$ Hz, 2 H), 7.40-7.07 (m, 12 H), 6.17 (d, $J = 8.7$ Hz, 1 H), 5.95 (s, 1H), 5.17 (d, $J = 8.7$ Hz, 1 H), 3.80-3.72 (m, 6 H), 3.64 (d, $J = 17.1$ Hz, 1 H), 3.30 (d, $J = 17.1$ Hz, 1 H), 3.11 (s, 2 H), 2.32 (s, 3 H), **3ab'**: $\delta = 7.56$ (d, $J = 7.8$ Hz, 2 H), 7.40-7.07 (m, 12 H), 6.34 (d, $J = 7.5$ Hz, 1 H), 5.82 (d, $J = 7.5$ Hz, 1 H), 5.62 (s, 1 H), 3.70 (s, 6 H), 3.59 (d, $J = 16.5$ Hz, 1 H), 3.30-3.20 (m, 1 H), 3.03 (s, 2 H), 2.32 (s, 3 H), ^{13}C NMR (75 MHz, CDCl_3) (**3ab + 3ab'**): $\delta = 170.83, 170.22, 148.91, 148.17, 147.80, 143.97, 142.83, 142.27, 140.64, 138.81, 136.53, 130.90, 129.90, 129.12, 128.76, 128.71, 128.56, 128.44, 128.27, 128.16, 127.29, 127.04, 126.98, 126.92, 126.57, 126.22, 126.13, 125.96, 125.57, 123.10, 121.29, 121.01, 120.74, 120.55, 120.20, 56.26, 53.08, 53.04, 45.12, 40.90, 37.96, 37.20, 29.63, 21.00$ ppm. MS (70 ev) m/z (%): 530 (M^+ , 51.57), 468 (100), HRMS calcd for $\text{C}_{35}\text{H}_{30}\text{O}_5$: 530.2093, found: 530.2096.

8. Synthesis of fused 5,6,7-tricyclic **3ac**:



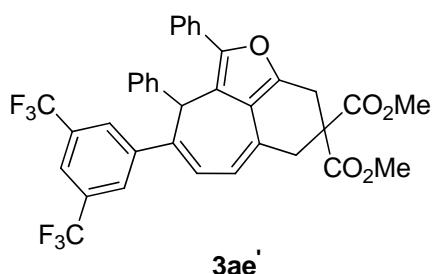
¹H NMR (300 MHz, CDCl₃): δ = 7.51 (d, *J* = 8.1 Hz, 2 H), 7.38-7.29 (m, 2 H), 7.27-7.10 (m, 8 H), 6.82 (d, *J* = 8.1 Hz, 2 H), 6.15 (d, *J* = 8.7 Hz, 1 H), 5.95 (s, 1 H), 5.17 (d, *J* = 8.7 Hz, 1 H), 3.75 (s, 9 H), 3.65 (d, *J* = 17.1 Hz, 1 H), 3.30 (d, *J* = 17.1 Hz, 1 H), 3.11 (s, 2 H), ¹³C NMR (75 MHz, CDCl₃): δ = 170.76, 170.16, 158.67, 148.86, 147.72, 143.92, 138.40, 137.62, 130.83, 129.89, 128.52, 128.39, 128.13, 127.68, 127.25, 126.97, 126.18, 125.89, 123.14, 120.97, 120.76, 113.40, 56.21, 55.15, 53.04, 53.00, 40.76, 37.91, 29.56 ppm. MS (70 ev) *m/z* (%): 546 (M⁺, 1.85), 484 (100), HRMS calcd for C₃₅H₃₀O₆: 546.2042, found: 546.2047.

9. Synthesis of fused 5,6,7-tricyclic 3ad:



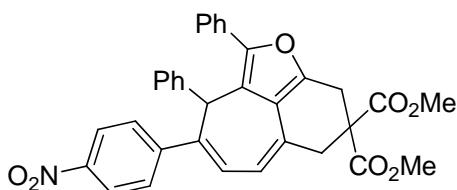
¹H NMR (300 MHz, CDCl₃): δ = 7.51 (d, *J* = 7.5 Hz, 2 H), δ = 7.39-7.31 (m, 2 H), 7.30-7.21 (m, 5 H), 7.20-7.12 (m, 1 H), 6.90-6.77 (m, 3 H), 6.17 (d, *J* = 9.0 Hz, 1H), 5.96 (s, 1 H), 5.18 (d, *J* = 9.0 Hz, 1 H), 3.91-3.85 (m, 6 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.64 (d, *J* = 17.1 Hz, 1 H), 3.32 (d, *J* = 17.1 Hz, 1 H), 3.12 (s, 1 H), ¹³C NMR (75 MHz, CDCl₃): δ = 170.83, 170.21, 148.92, 148.48, 148.23, 147.80, 143.89, 138.85, 138.19, 130.88, 129.97, 128.58, 128.45, 127.87, 127.33, 127.05, 126.25, 125.98, 123.17, 120.98, 120.80, 119.38, 110.79, 56.29, 55.89, 53.12, 53.00, 40.81, 37.98, 29.60 ppm. MS (70 ev) *m/z* (%): 576 (M⁺, 100), HRMS calcd for C₃₆H₃₂O₇: 576.2148, found: 576.2150.

10. Synthesis of fused 5,6,7-tricyclic 3ae':



¹H NMR (300 MHz, CDCl₃): δ = 7.87 (s, 2 H), 7.80 (s, 1 H), 7.59 (d, *J* = 7.5 Hz, 2 H), 7.48-7.39 (m, 2 H), 7.38-7.30 (m, 1 H), 7.29-7.19 (m, 3 H), 7.18-7.10 (m, 2 H), 6.48 (d, *J* = 7.2 Hz, 1 H), 5.93 (d, *J* = 7.2 Hz, 1 H), 5.57 (s, 1 H), 3.78 (s, 6 H), 3.67 (d, *J* = 17.1 Hz, 1 H), 3.33 (d, *J* = 17.1 Hz, 1 H), 3.12 (s, 2 H), ¹³C NMR (75 MHz, CDCl₃): δ = 170.63, 170.08, 149.18, 148.26, 147.17, 142.02, 137.83, 131.94, 131.78 (q, *J* = 22 Hz), 130.53, 129.01, 128.84, 128.54, 127.85, 126.83, 126.68, 126.25, 123.29 (q, *J* = 272 Hz), 120.89, 120.47, 119.90, 119.29, 56.23, 53.09, 45.25, 37.23, 29.47 ppm. MS (70 ev) *m/z* (%): 652 (M⁺, 5.82), 105 (100), HRMS calcd for C₃₆H₂₆O₅F₆: 652.1684, found: 652.1682.

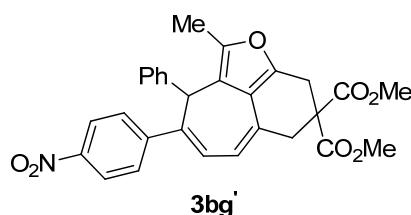
11. Synthesis of fused 5,6,7-tricyclic 3af':



3af'

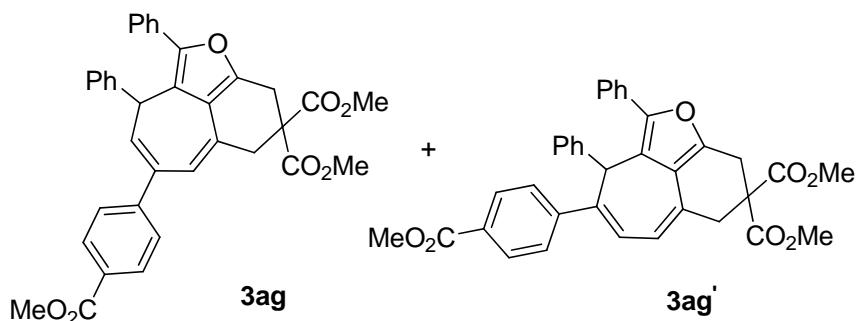
¹H NMR (300 MHz, CDCl₃): δ = 8.17 (d, *J* = 8.7 Hz, 2 H), 7.59- 7.49 (m, 4 H), 7.45-7.28 (m, 3 H), 7.22-7.15 (m, 3 H), 7.12-7.05 (m, 2 H), 6.48 (d, *J* = 7.5 Hz, 1 H), 5.89 (d, *J* = 7.5 Hz, 1 H), 5.57 (s, 1 H), 3.74 (s, 6 H), 3.62 (d, *J* = 17.1 Hz, 1 H), 3.28 (d, *J* = 17.1 Hz, 1 H), 3.08 (s, 2 H), ¹³C NMR (75 MHz, CDCl₃): δ = 170.53, 170.04, 151.50, 149.12, 148.13, 146.41, 142.02, 138.49, 131.87, 130.52, 129.22, 128.79, 128.43, 127.68, 127.21, 126.67, 126.62, 126.12, 123.79, 120.93, 119.84, 119.42, 56.12, 53.06, 45.01, 37.15, 29.40 ppm. MS (70 ev) *m/z* (%): 561 (M⁺, 3.46), 469 (100), HRMS calcd for C₃₄H₂₇NO₇: 561.1788, found: 561.1785.

12. Synthesis of fused 5,6,7-tricyclic **3bg':**



¹H NMR (300 MHz, CDCl₃): δ = 8.12 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.25-7.15 (m, 4 H), 6.42 (d, *J* = 7.8 Hz, 1 H), 5.84 (d, *J* = 7.8 Hz, 1H), 4.98 (s, 1 H), 3.72 (s, 6 H), 3.45 (d, *J* = 16.8 Hz, 1 H), 3.13 (d, *J* = 16.8 Hz, 1 H), 3.04 (s, 2 H), 2.31 (s, 3 H), ¹³C NMR (75 MHz, CDCl₃): δ = 170.71, 170.21, 151.95, 147.74, 146.40, 146.36, 143.61, 138.25, 132.17, 129.14, 128.71, 127.92, 127.25, 126.70, 123.64, 119.29, 119.17, 118.39, 56.28, 53.06, 46.08, 37.14, 29.37, 11.70 ppm. MS (70 ev) *m/z* (%): 499 (M⁺, 9.91), 105 (100), HRMS calcd for C₂₉H₂₅NO₇: 499.1631, found: 499.1633.

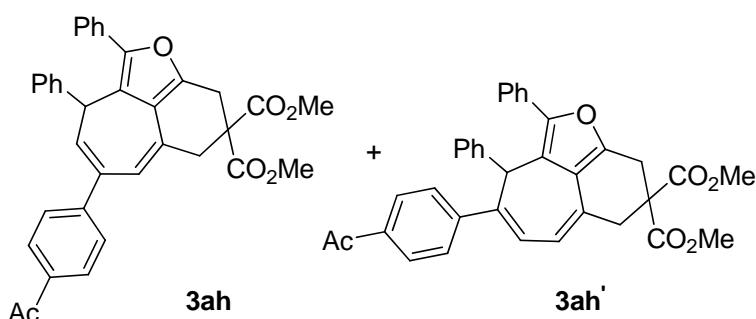
13. Synthesis of fused 5,6,7-tricyclic **3ag/3ag':**



¹H NMR (300 MHz, CDCl₃) **3ag**: δ = 8.00 (d, *J* = 8.1 Hz, 2 H), 7.62-7.11 (m, 12 H), 6.29 (d, *J* = 8.7 Hz, 1 H), 5.97 (s, 1 H), 5.24 (d, *J* = 8.7 Hz, 1 H), 3.92 (s, 3 H), 3.82-3.75 (m, 6 H), 3.70-3.60 (m, 1 H), 3.36 (d, *J* = 17.1 Hz, 2 H), 3.18 (s, 2 H), **3ag'**: δ = 8.00 (d, *J* = 8.1 Hz, 2 H), 7.62-7.11 (m, 12 H), 6.47 (d, *J* = 7.5 Hz, 1 H), 5.89 (d, *J* = 7.5 Hz, 1 H), 5.66 (s, 1 H), 3.92 (s, 3 H), 3.75 (s, 6 H), 3.64 (d, *J* = 17.1 Hz, 1 H), 3.31 (d, *J* = 17.1 Hz, 1 H), 3.09 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) (**3ag + 3ag'**): δ = 170.64, 170.09, 166.78, 149.60, 149.55, 149.19, 148.69, 148.00, 143.56, 142.39, 139.68, 138.17, 130.79, 130.73, 130.70, 130.66, 130.21, 130.16, 129.76, 129.46, 128.73, 128.53, 128.39, 128.27, 127.74, 127.51, 127.38, 127.00, 126.97, 126.74,

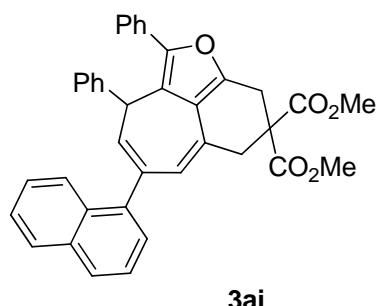
126.55, 126.44, 126.38, 126.09, 125.93, 121.93, 121.10, 120.80, 120.25, 120.15, 119.75, 56.16, 53.08, 53.00, 51.93, 44.99, 41.00, 37.88, 37.16, 29.56, 29.44 ppm. MS (70 ev) m/z (%): 574 (M^+ , 100), HRMS calcd for $C_{36}H_{30}O_7$: 574.1992, found: 574.1990.

14. Synthesis of fused 5,6,7-tricyclic **3ah/3ah'**:



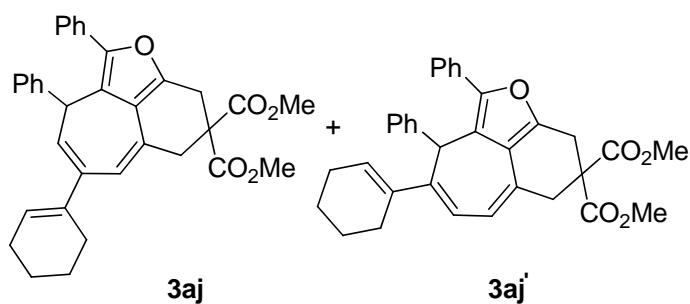
1H NMR (300 MHz, $CDCl_3$) **3ah**: δ = 7.90 (d, J = 7.8 Hz, 2 H), 7.58-7.05 (m, 12 H), 6.26 (d, J = 8.7 Hz, 1 H), 5.93 (s, 1 H), 5.20 (d, J = 8.7 Hz, 1 H), 3.82-3.75 (m, 6 H), 3.66 (d, J = 17.1 Hz, 1 H), 3.33 (d, J = 17.1 Hz, 1 H), 3.14 (s, 2 H), 2.58 (s, 3 H), **3ah'**: δ = 7.90 (d, J = 7.8 Hz, 2 H), 7.58-7.05 (m, 12 H), 6.44 (d, J = 7.5 Hz, 1 H), 5.86 (d, J = 7.5 Hz, 1 H), 5.62 (s, 1 H), 3.72 (s, 6 H), 3.60 (d, J = 17.1 Hz, 1 H), 3.27 (d, J = 17.1 Hz, 1 H), 3.06 (s, 2 H), 2.58 (s, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$) (**3ah + 3ah'**): δ = 197.48, 170.68, 170.14, 149.72, 148.76, 148.05, 142.40, 139.64, 135.46, 130.91, 130.74, 128.78, 128.64, 128.58, 128.32, 127.94, 127.57, 127.23, 127.01, 126.76, 126.74, 126.51, 126.14, 125.98, 121.12, 120.15, 119.76, 56.20, 53.06, 44.96, 37.02, 29.47, 26.50 ppm. MS (70 ev) m/z (%): 558 (M^+ , 2.31), 105 (100), HRMS calcd for $C_{36}H_{30}O_6$: 558.2042, found: 558.2065.

15. Synthesis of fused 5,6,7-tricyclic **3ai**:



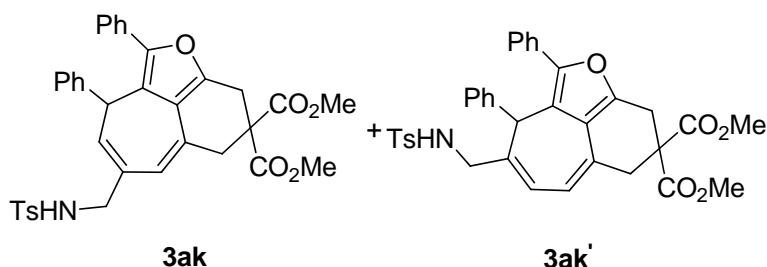
¹H NMR (300 MHz, CDCl₃): δ = 7.85-7.76 (m, 1 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.60-7.46 (m, 2 H), 7.43-7.26 (m, 9 H), 7.25-7.15 (m, 4 H), 6.09 (d, *J* = 7.8 Hz, 1 H), 5.79 (s, 1 H), 5.17 (d, *J* = 7.8 Hz, 1 H), 3.80-3.62 (m, 7 H), 3.37-3.20 (m, 1 H), 3.19-3.08 (m, 1 H), 3.00 (d, *J* = 14.7 Hz, 1 H), 170.79, 170.20, 149.09, 148.71, 147.87, 144.42, 143.40, 137.73, 133.54, 131.41, 130.94, 130.80, 128.74, 128.60, 128.53, 128.16, 128.03, 127.31, 127.10, 127.03, 126.32, 125.97, 125.71, 125.58, 125.33, 124.27, 121.08, 120.69, 56.06, 53.01, 41.53, 37.71, 29.62 ppm. MS (70 ev) *m/z* (%): 566 (M⁺, 88.48), 504 (100), HRMS calcd for C₃₈H₃₀O₅: 566.2093, found: 566.2095.

16. Synthesis of fused 5,6,7-tricyclic 3aj/3aj':



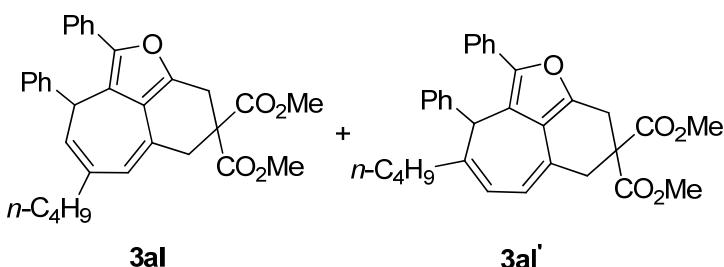
¹H NMR (300 MHz, CDCl₃) **3aj**: δ = 7.50 (d, *J* = 7.8 Hz, 2 H), 7.45-7.00 (m, 8 H), 6.07 (d, *J* = 9 Hz, 1 H), 5.80 (s, 1 H), 5.72-5.68 (m, 1 H), 5.07 (d, *J* = 9 Hz, 1 H), 3.85-3.67 (m, 6 H), 3.62 (d, *J* = 17.1 Hz, 1 H), 3.24 (d, *J* = 17.1 Hz, 1 H), 3.04 (s, 2 H), 2.35-1.98 (m, 4 H), 1.80-1.48 (m, 4 H); **3aj'**: δ = 7.59 (d, *J* = 7.8 Hz, 2 H), 7.45-7.00 (m, 8 H), 6.16 (d, *J* = 7.5 Hz, 1 H), 5.75-5.65 (m, 1 H), 5.61-5.45 (m, 2 H), 3.85-3.67 (m, 6 H), 3.55-3.35 (m, 1 H), 3.14 (d, *J* = 7.5 Hz, 1 H), 3.00 (m, 2 H), 2.35-1.98 (m, 4 H), 1.80-1.48 (m, 4 H), ¹³C NMR (75 MHz, CDCl₃) (**3aj+3aj'**): δ = 170.89, 170.17, 148.43, 147.51, 143.85, 140.61, 140.41, 131.00, 128.92, 128.67, 128.52, 128.24, 127.89, 127.77, 127.24, 127.14, 126.99, 126.85, 126.21, 126.03, 125.84, 125.55, 125.04, 124.73, 124.17, 122.27, 121.79, 121.25, 121.09, 56.28, 53.03, 52.94, 40.30, 37.95, 29.57, 27.95, 25.62, 23.05, 22.06 ppm. MS (70 ev) *m/z* (%): 520 (M⁺, 100), HRMS calcd for C₃₄H₃₂O₅: 520.2250, found: 520.2251.

17. Synthesis of fused 5,6,7-tricyclic 3ak/3ak':



^1H NMR (300 MHz, CDCl_3) **3ak**: δ = 7.64 (d, J = 7.8 Hz, 2 H), 7.54 (d, J = 7.8 Hz, 2 H), 7.42-7.08 (m, 10 H), 5.79 (d, J = 8.7 Hz, 1 H), 5.53 (s, 1 H), 4.84 (d, J = 8.7 Hz, 1 H), 4.65-4.55 (m, 1 H), 3.90 (d, J = 3.6 Hz, 2 H), 3.75-3.65 (m, 6 H), 3.58-3.50 (m, 1 H), 3.26 (d, J = 14.1 Hz, 1 H), 3.07-3.00 (m, 2 H), 2.32 (s, 3 H), **3ak'**: δ = 7.64 (d, J = 7.8 Hz, 2 H), 7.54 (d, J = 7.8 Hz, 2 H), 7.42-7.08 (m, 10 H), 5.87 (d, J = 7.5 Hz, 1 H), 5.62 (d, J = 7.2 Hz, 1 H), 5.03 (s, 1 H), 4.80-4.72 (m, 1 H), 3.77 (d, J = 3.6 Hz, 2 H), 3.75-3.65 (m, 6 H), 3.58-3.50 (m, 1 H), 3.20 (d, J = 17.1 Hz, 1 H), 3.07-3.00 (m, 2 H), 2.37 (s, 3 H), ^{13}C NMR (75 MHz, CDCl_3) (**3ak + 3ak'**): δ = 170.70, 170.19, 148.78, 147.86, 143.62, 143.26, 136.99, 136.17, 130.58, 129.59, 129.54, 128.58, 128.47, 127.45, 126.99, 126.88, 126.58, 126.26, 125.88, 125.58, 120.79, 119.83, 118.49, 55.91, 53.07, 53.04, 51.47, 42.81, 37.32, 29.44, 21.39 ppm. MS (70 ev) m/z (%): 623 (M^+ , 2.63), 392 (100), HRMS calcd for $\text{C}_{36}\text{H}_{33}\text{NO}_7\text{S}$: 623.1978, found: 623.1979.

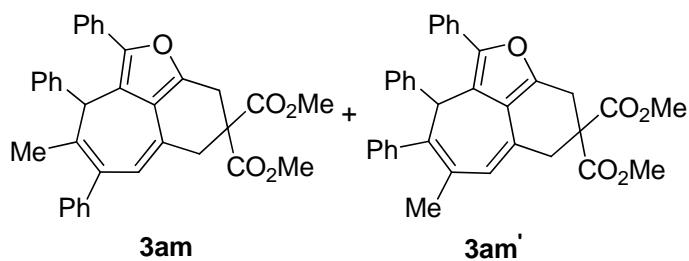
18. Synthesis of fused 5,6,7-tricyclic 3al/3al':



^1H NMR (300 MHz, CDCl_3) **3al**: δ = 7.48 (d, J = 7.8 Hz, 2 H), 7.42-7.09 (m, 8 H), 5.81 (d, J = 7.8 Hz, 1 H), 5.59 (s, 1 H), 4.94 (d, J = 7.8 Hz, 1 H), 3.80-3.65 (m, 6 H), 3.61 (d, J = 17.4 Hz, 1 H), 3.28-3.22 (m, 1 H), 3.10-3.00 (m, 2 H), 2.40-2.16 (m, 4 H), 1.48-1.16 (m, 3 H), 0.85 (t, J = 7.2 Hz, 3 H), **3al'**: δ = 7.56 (d, J = 7.8 Hz, 2 H), 7.42-7.09 (m, 8 H), 5.81 (d, J = 7.8 Hz, 1 H), 5.67 (d, J = 7.8 Hz, 1 H), 4.89 (s, 1 H),

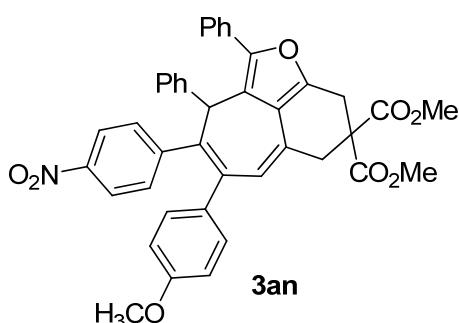
3.80-3.65 (m, 6 H), 3.55 (d, J = 18 Hz, 1 H), 3.20-3.15 (m, 1 H), 3.10-3.00 (m, 2 H), 2.40-2.16 (m, 4 H), 1.48-1.16 (m, 3 H), 0.85 (t, J = 7.2 Hz, 3 H), ^{13}C NMR (75 MHz, CDCl_3) (**3al** + **3al'**): δ = 170.90, 170.33, 170.18, 148.45, 147.95, 147.46, 147.32, 144.74, 143.97, 142.81, 137.58, 131.13, 131.00, 128.75, 128.56, 128.47, 128.34, 128.24, 127.68, 127.23, 127.12, 126.96, 126.26, 126.20, 126.02, 125.90, 123.58, 121.96, 121.09, 120.92, 120.77, 119.97, 56.14, 56.05, 53.02, 52.98, 52.93, 52.90, 45.89, 40.95, 40.72, 40.56, 37.87, 37.27, 31.90, 30.60, 29.57, 29.53, 22.38, 22.01, 13.90 ppm. MS (70 ev) m/z (%): 496 (M^+ , 57.41), 439 (100), HRMS calcd for $\text{C}_{32}\text{H}_{32}\text{O}_5$: 496.2250, found: 496.2249.

19. Synthesis of fused 5,6,7-tricyclic **3am**/**3am'**:



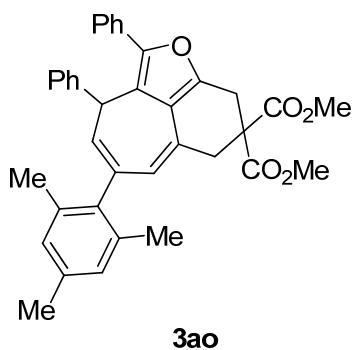
^1H NMR (300 MHz, CDCl_3) **3am**: 7.49 (d, J = 7.8 Hz, 2 H), 7.41-7.08 (m, 13 H), 5.73 (s, 1 H), 5.26 (s, 1 H), 3.81-3.58 (m, 7 H), 3.27 (s, 1 H), 3.00 (s, 2 H), 1.75 (s, 3 H), **3am'**: δ = 7.59 (d, J = 7.8 Hz, 2 H), 7.41-7.08 (m, 13 H), 5.63 (s, 1 H), 5.03 (s, 1 H), 3.81-3.58 (m, 7 H), 3.21 (s, 1 H), 2.95 (s, 2 H), 1.97 (s, 3 H), ^{13}C NMR (75 MHz, CDCl_3) (**3am** + **3am'**): δ = 170.87, 170.35, 148.09, 147.79, 147.34, 146.33, 145.36, 142.79, 142.69, 136.59, 135.65, 134.57, 131.03, 130.67, 128.72, 128.65, 128.25, 128.16, 127.98, 127.79, 127.28, 127.22, 127.13, 126.85, 126.59, 126.22, 126.08, 126.00, 125.74, 125.59, 125.02, 121.64, 121.02, 120.80, 56.48, 56.39, 53.04, 52.95, 52.91, 47.94, 47.08, 37.43, 29.60, 26.36, 24.24 ppm. MS (70 ev) m/z (%): 530 (M^+ , 15.83), 105 (100), HRMS calcd for $\text{C}_{35}\text{H}_{30}\text{O}_5$ 530.2093, found: 530.2092.

26. Synthesis of fused 5, 6, 7-tricyclic 3an:



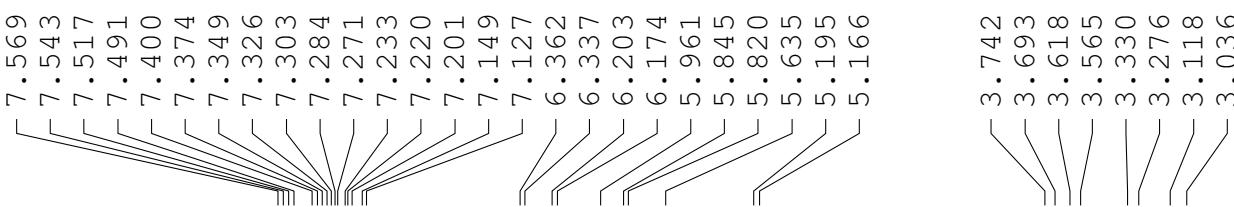
^1H NMR (300 MHz, CDCl_3): δ = 7.93 (d, J = 8.1 Hz, 2 H), 7.44 (d, J = 7.8 Hz, 2 H), 7.36-7.17 (m, 10 H), 6.93 (d, J = 8.1 Hz, 2 H), 6.67 (d, J = 8.1 Hz, 2 H), 5.86 (s, 1 H), 5.46 (s, 1 H), 3.78 (s, 3 H), 3.74 (s, 6 H), 3.68 (d, J = 17.1 Hz, 1 H), 3.31 (d, J = 17.1 Hz, 1 H), 3.00 (q, J = 14.1 Hz, 2 H), ^{13}C NMR (75 MHz, CDCl_3): δ = 170.66, 170.18, 158.47, 152.67, 149.01, 148.18, 145.56, 141.66, 140.19, 136.18, 134.37, 131.17, 130.62, 128.83, 128.33, 127.60, 126.92, 126.64, 125.73, 125.40, 123.10, 120.73, 113.45, 56.58, 55.13, 53.14, 53.08, 47.15, 37.37, 29.54 ppm. MS (70 ev) m/z (%): 667 (M^+ , 18.10), 81 (100), HRMS calcd for $\text{C}_{41}\text{H}_{33}\text{NO}_8$: 667.2206, found: 667.2191.

27. Synthesis of fused 5, 6, 7-tricyclic 3ao:

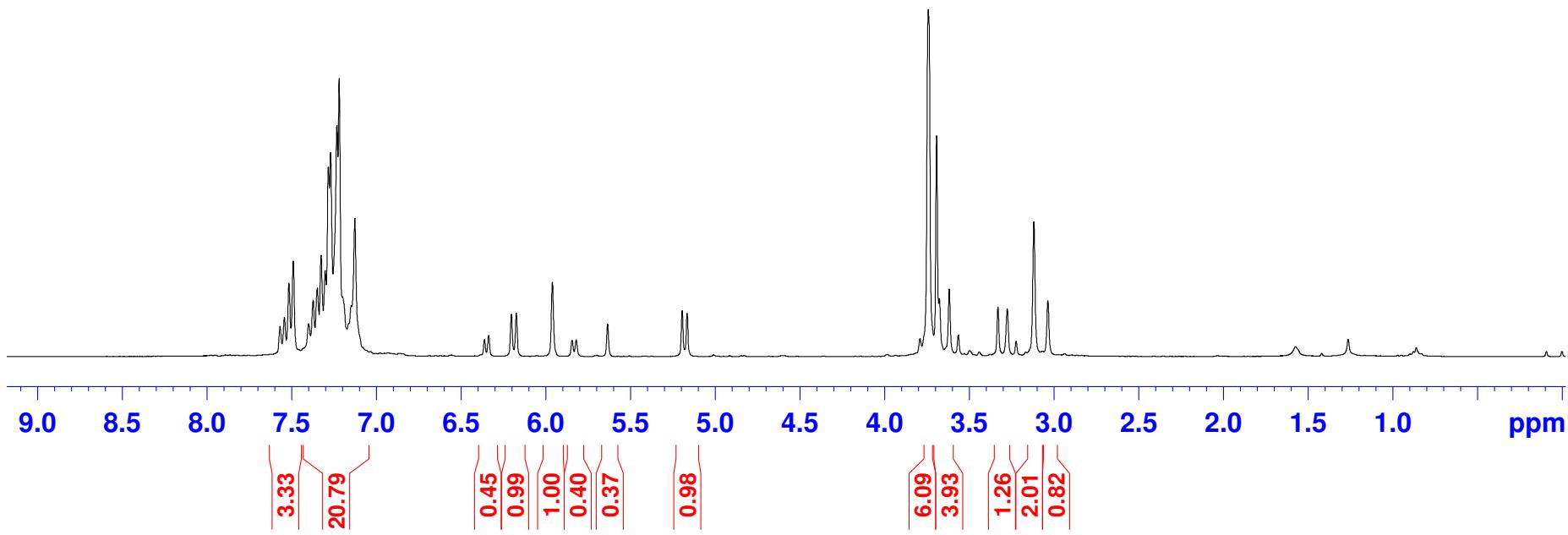
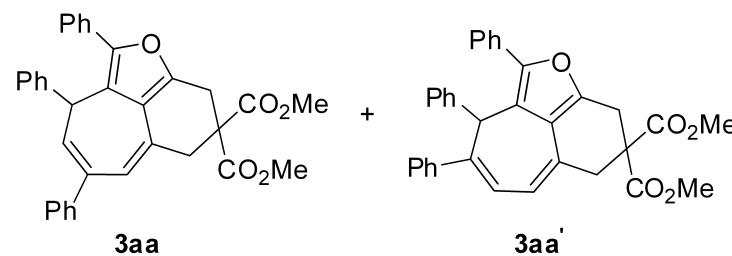


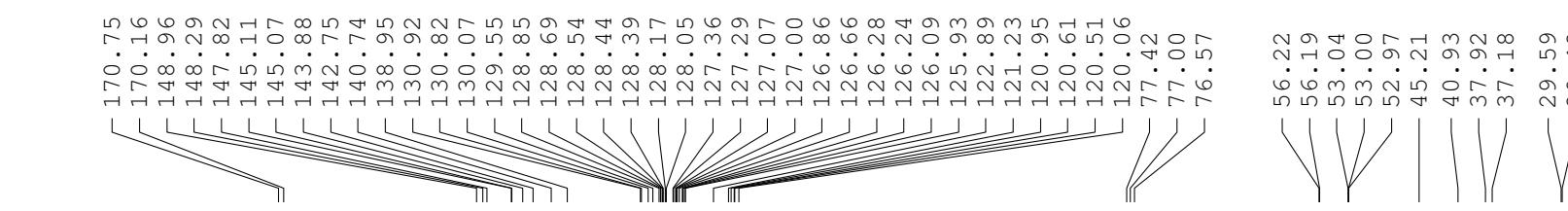
^1H NMR (400 MHz, CDCl_3): δ = 7.48 (d, J = 7.6 Hz, 2 H), 7.40-7.10 (m, 8 H), 6.79 (d, J = 9.2 Hz, 2 H), 5.71 (d, J = 8.4 Hz, 1 H), 5.48 (s, 1 H), 5.01 (d, J = 8.4 Hz, 1 H), 3.80 (s, 3 H), 3.73 (d, J = 17.2 Hz, 1 H), 3.67 (s, 3 H), 3.22 (d, J = 17.2 Hz, 1 H), 3.14 (d, J = 14.4 Hz, 1 H), 3.00 (d, J = 14.4 Hz, 1 H), 2.24 (s, 3 H), 2.07 (s, 3 H), 1.79 (s, 3 H), ^{13}C NMR (75 MHz, CDCl_3): δ = 170.93, 170.17, 148.90, 147.73, 144.40, 141.36, 136.61, 135.94, 135.63, 135.59, 130.79, 129.87, 129.36, 128.00, 127.72, 127.22, 126.97, 126.16, 125.87, 123.22, 121.14, 120.47, 55.96, 53.09, 52.95, 41.77, 37.70,

29.59, 20.89, 19.72, 19.50 ppm. MS (70 ev) *m/z* (%): 558 (M^+ , 13.06), 43 (100), HRMS calcd for $C_{37}H_{34}NO_5$: 558.2406, found: 558.2410.

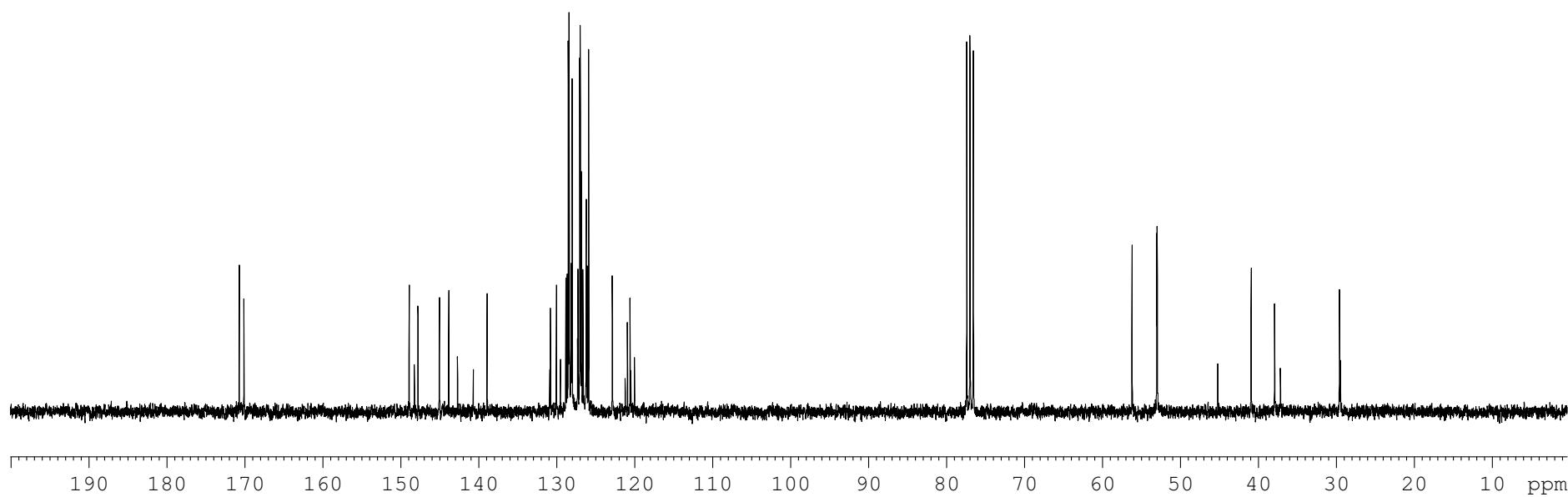
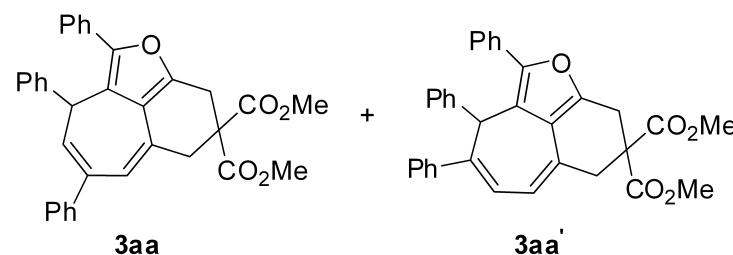


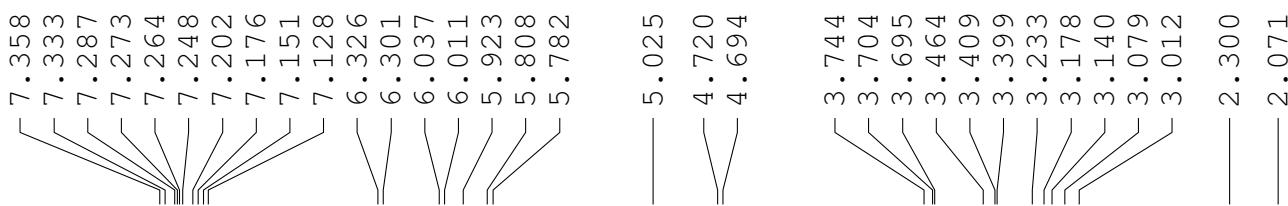
zwx-3-001



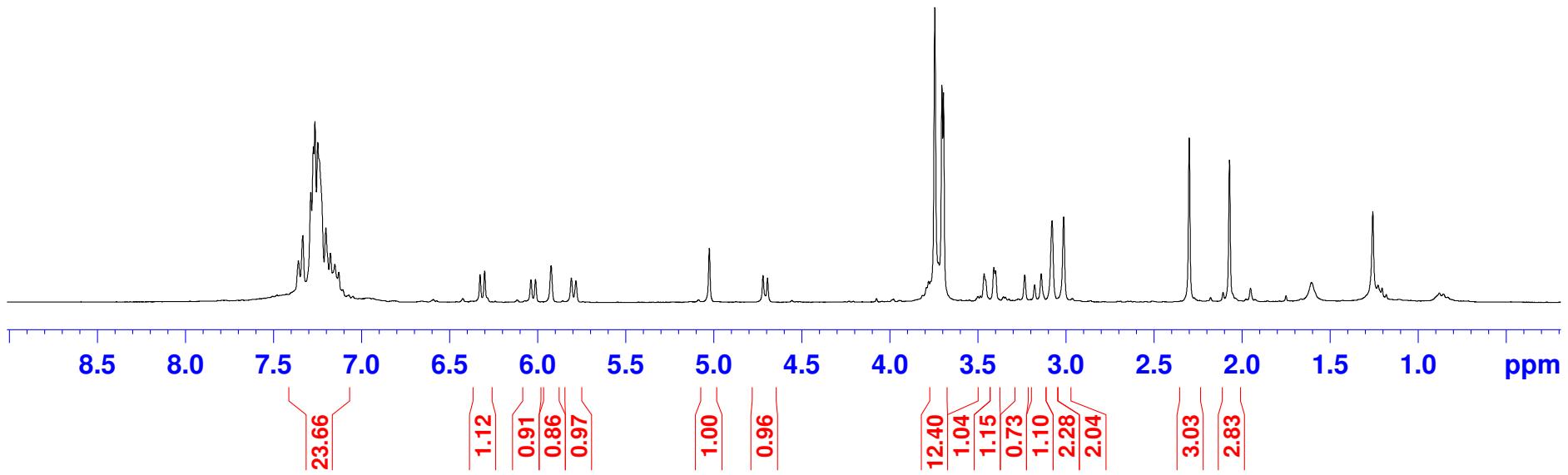
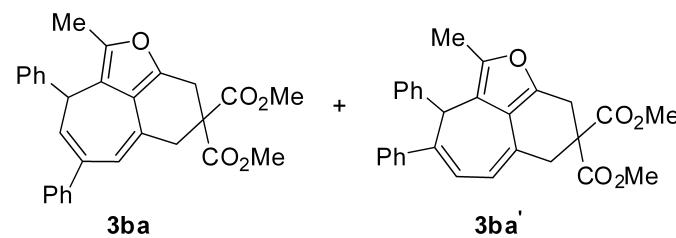


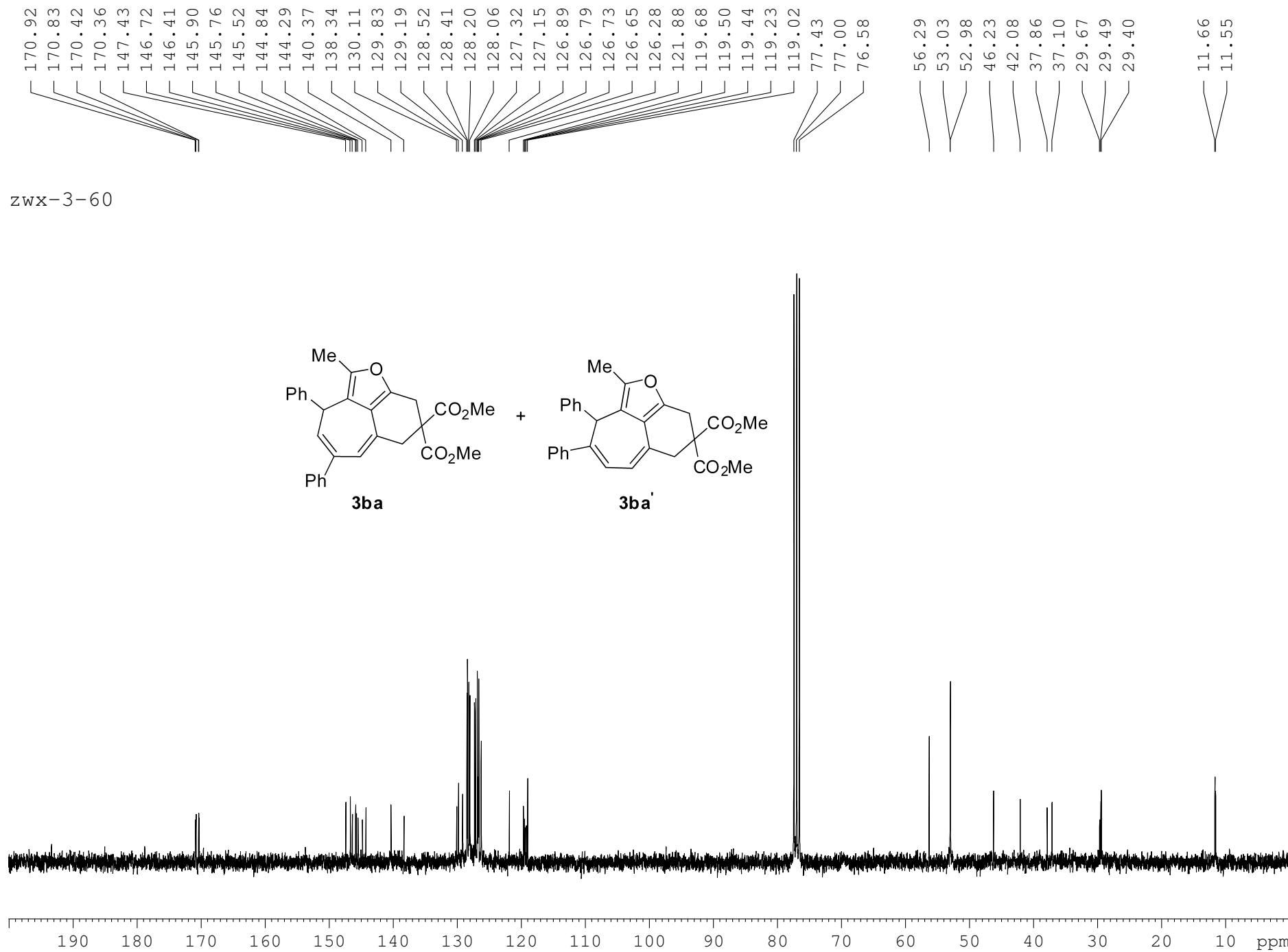
zwx-3-001

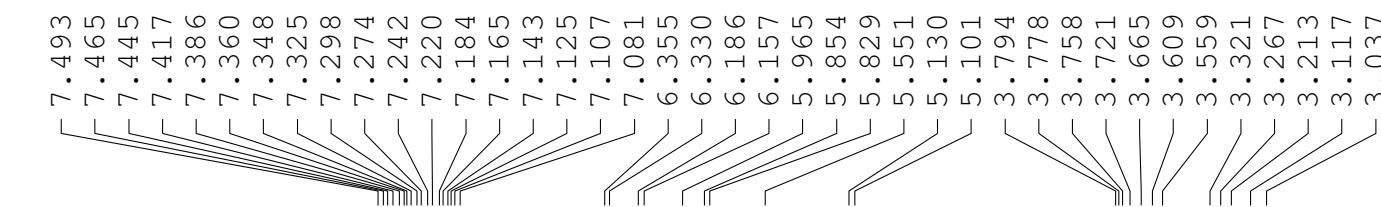




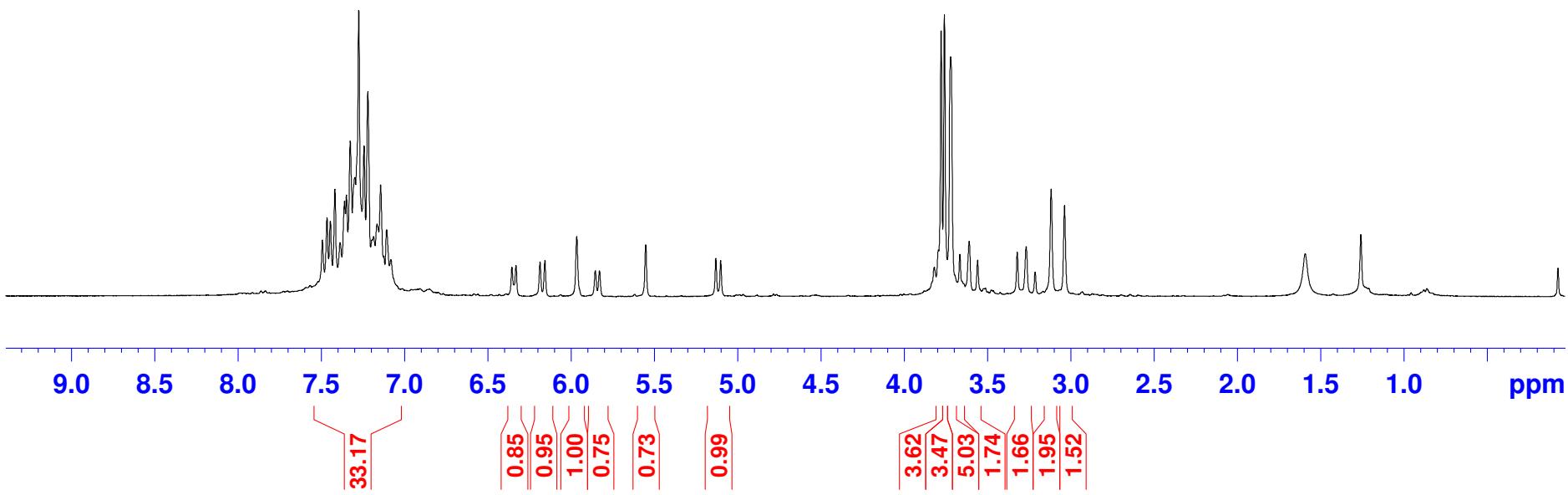
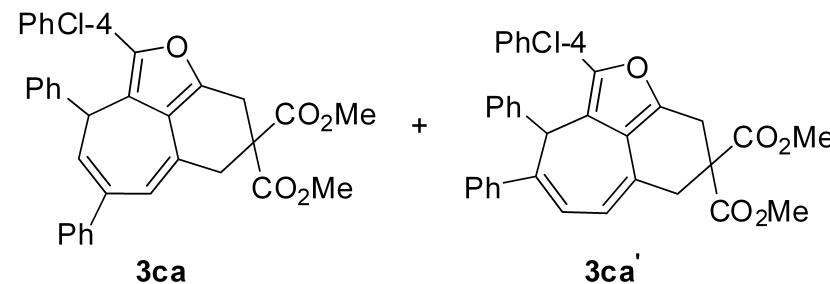
zwx-3-60

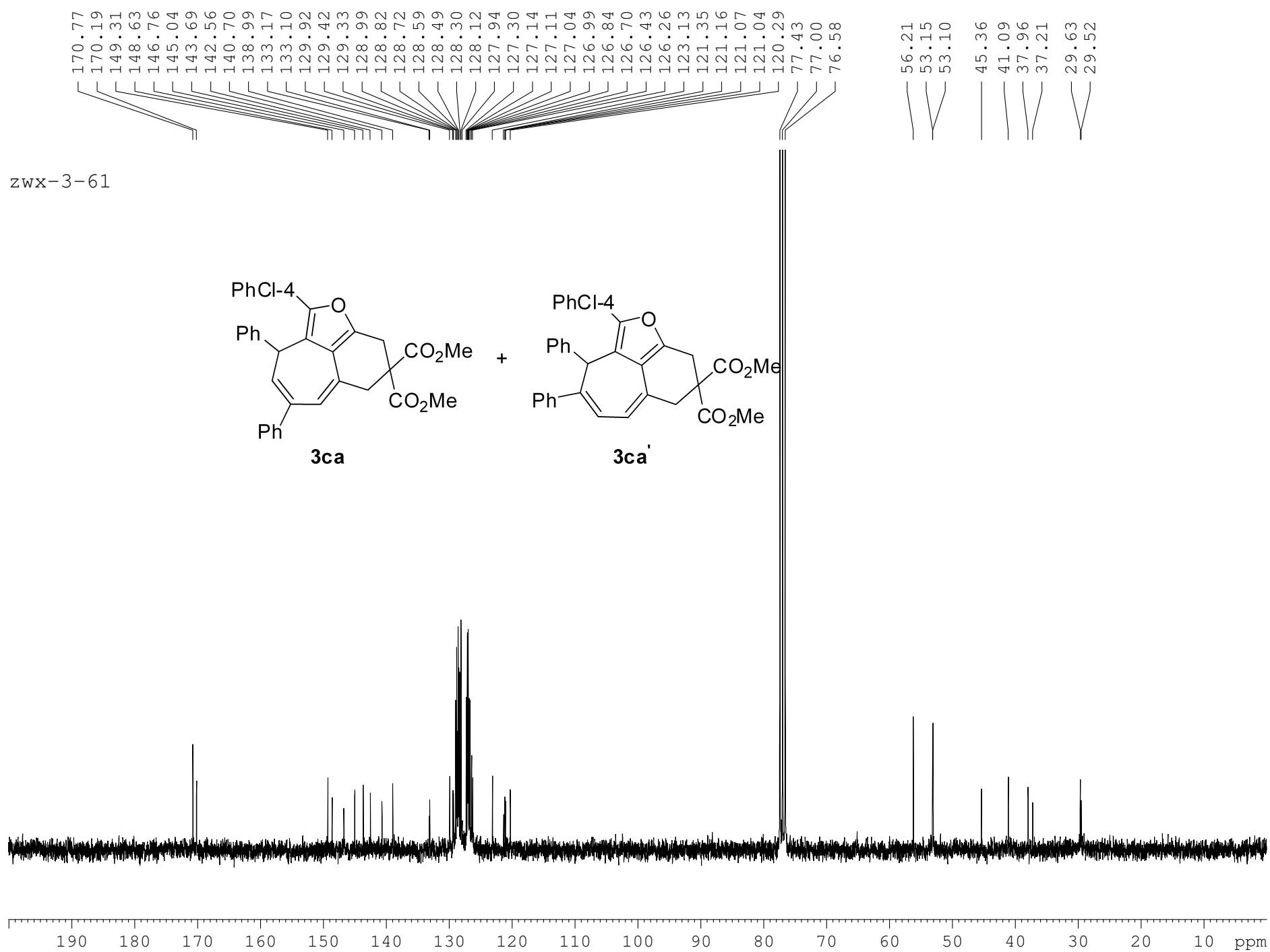


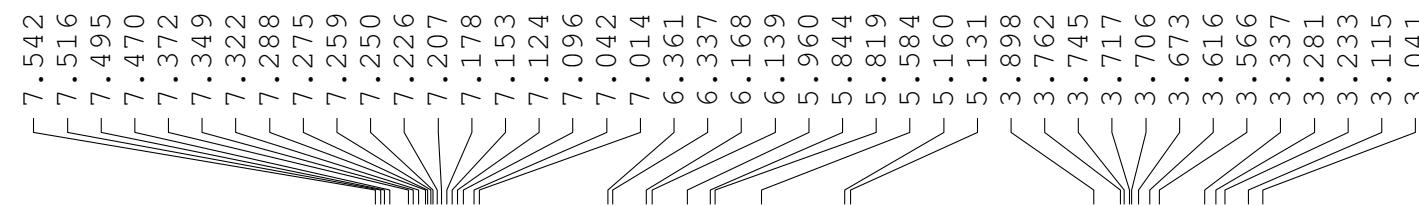




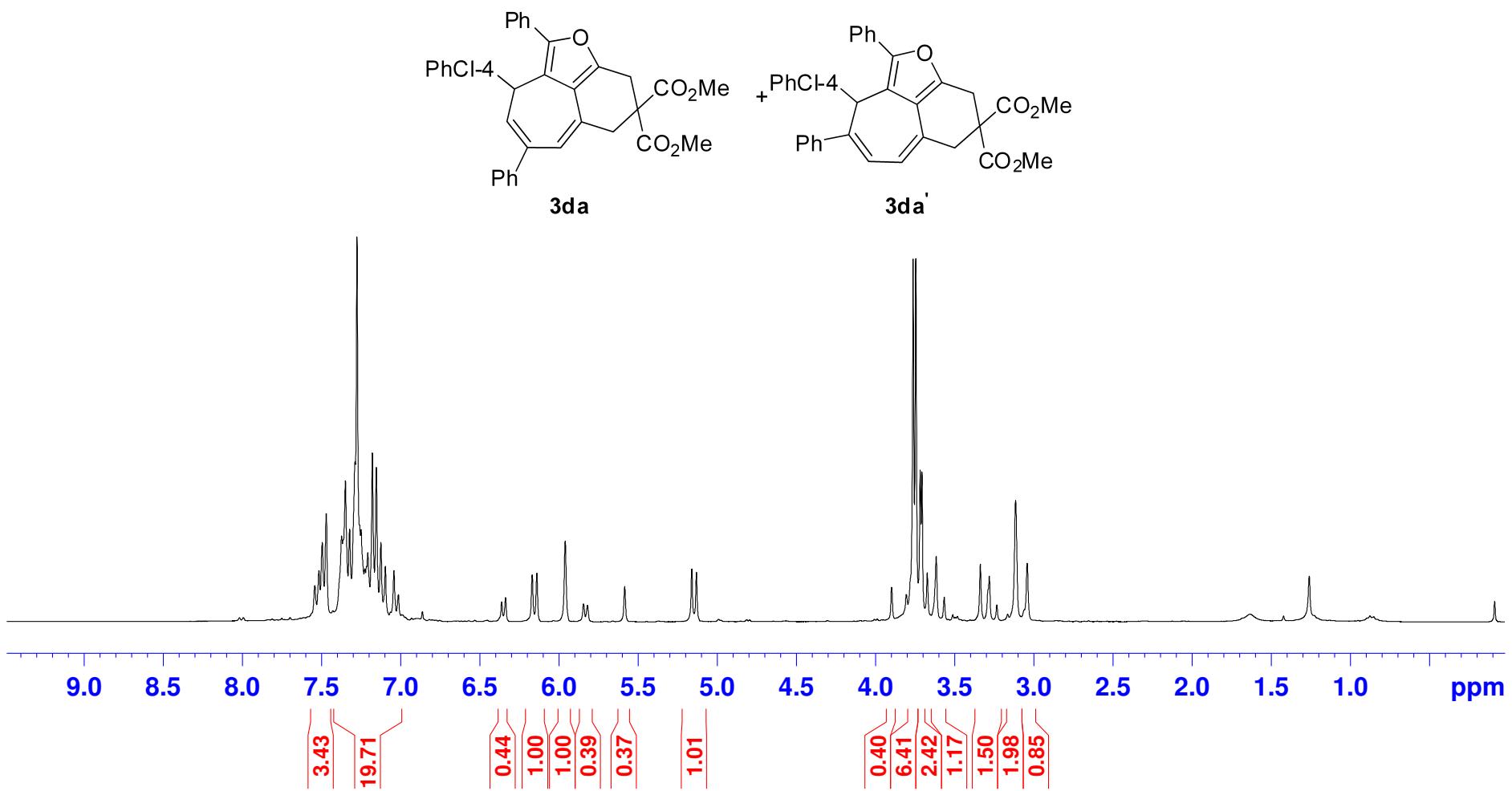
zwx-3-61

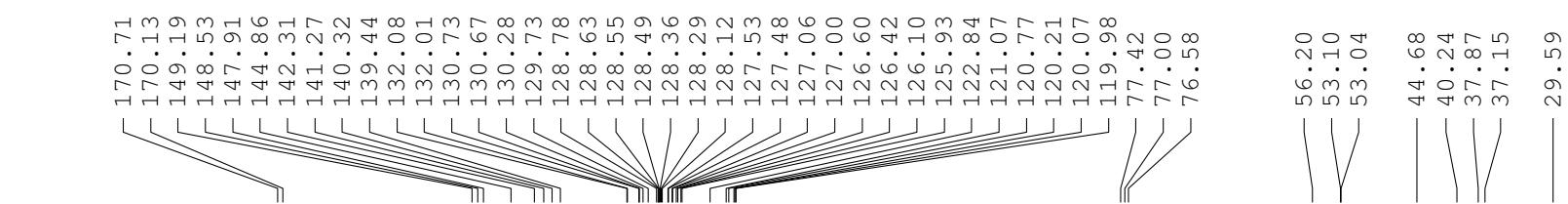




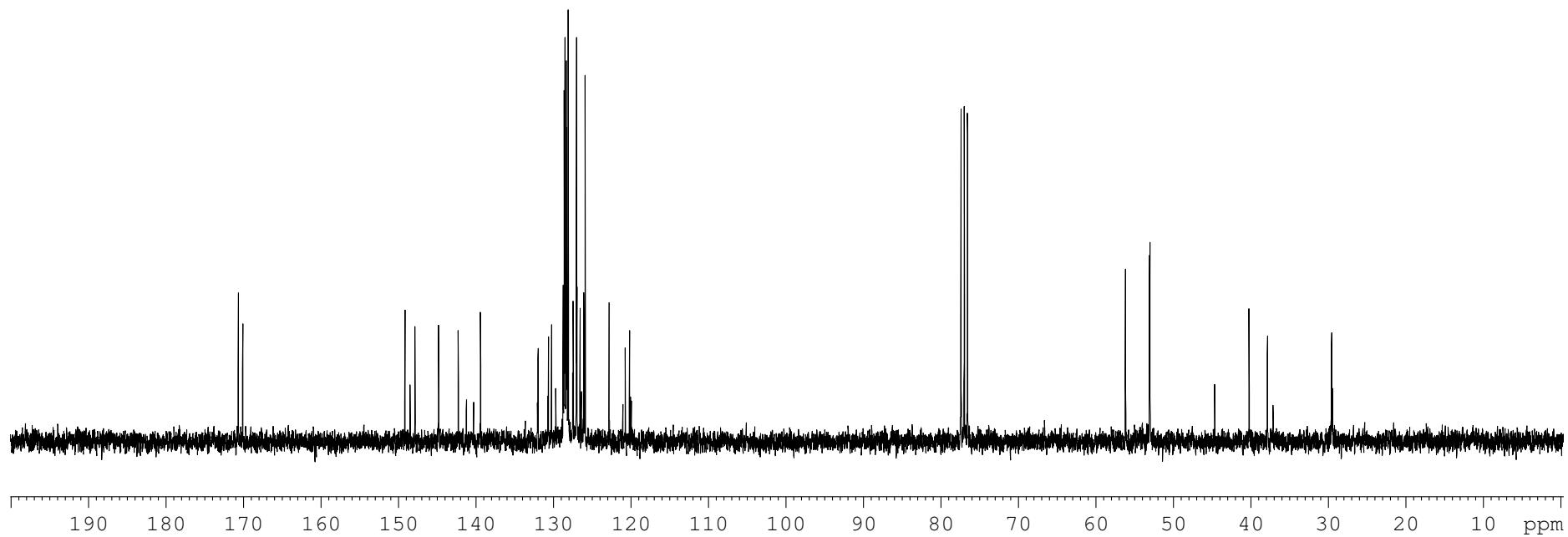
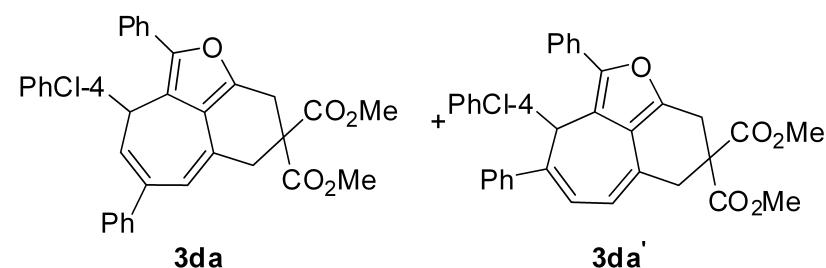


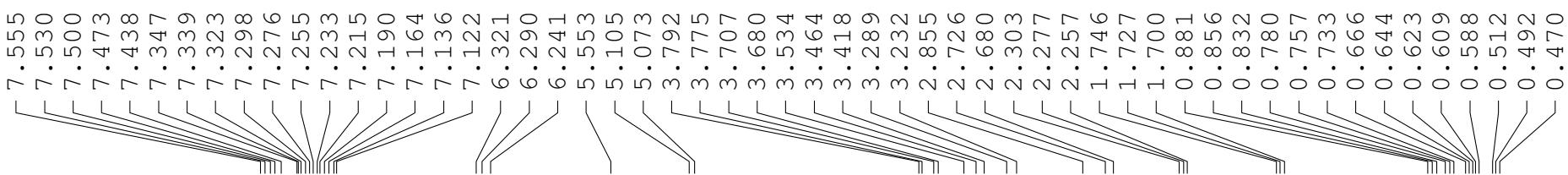
zwx-3-70



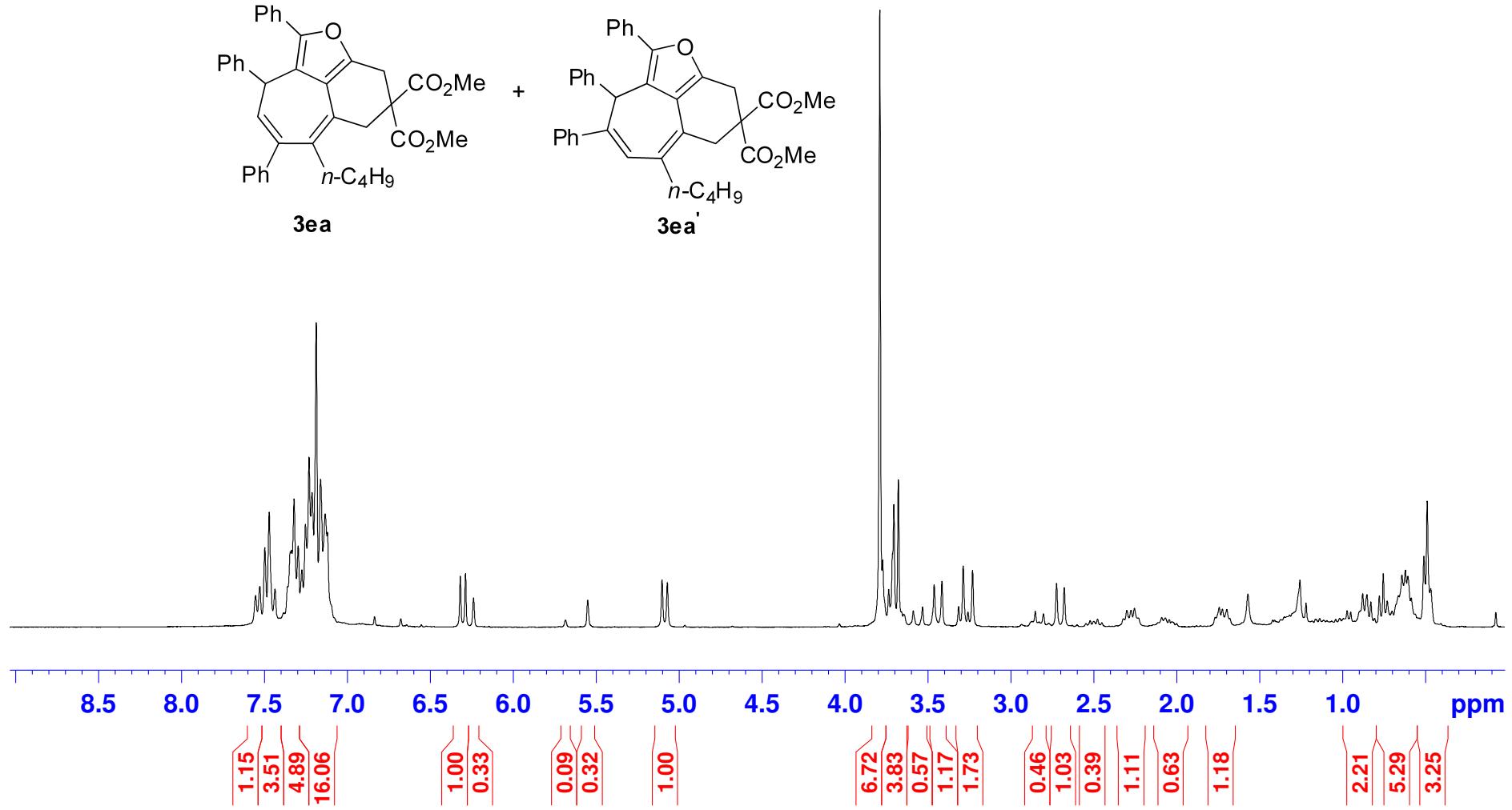
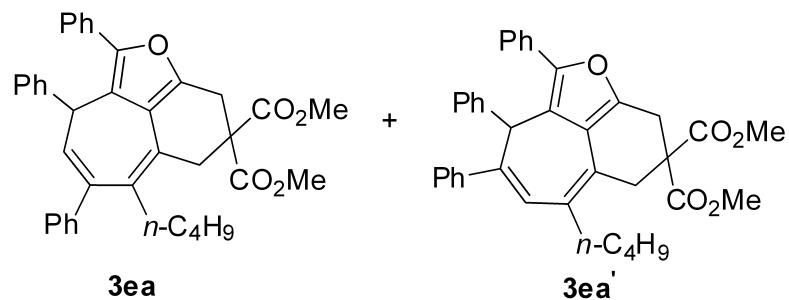


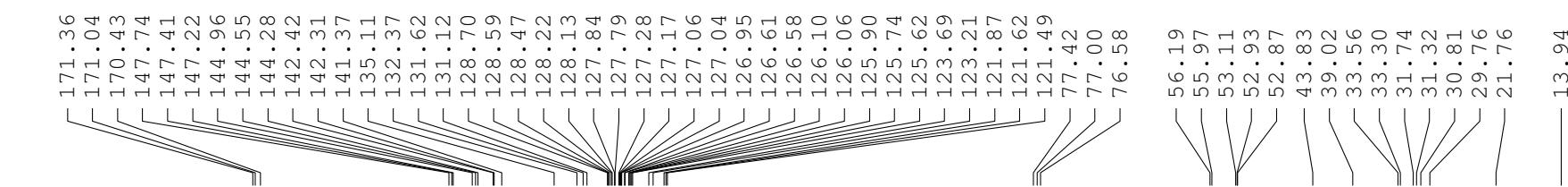
zwx-3-70



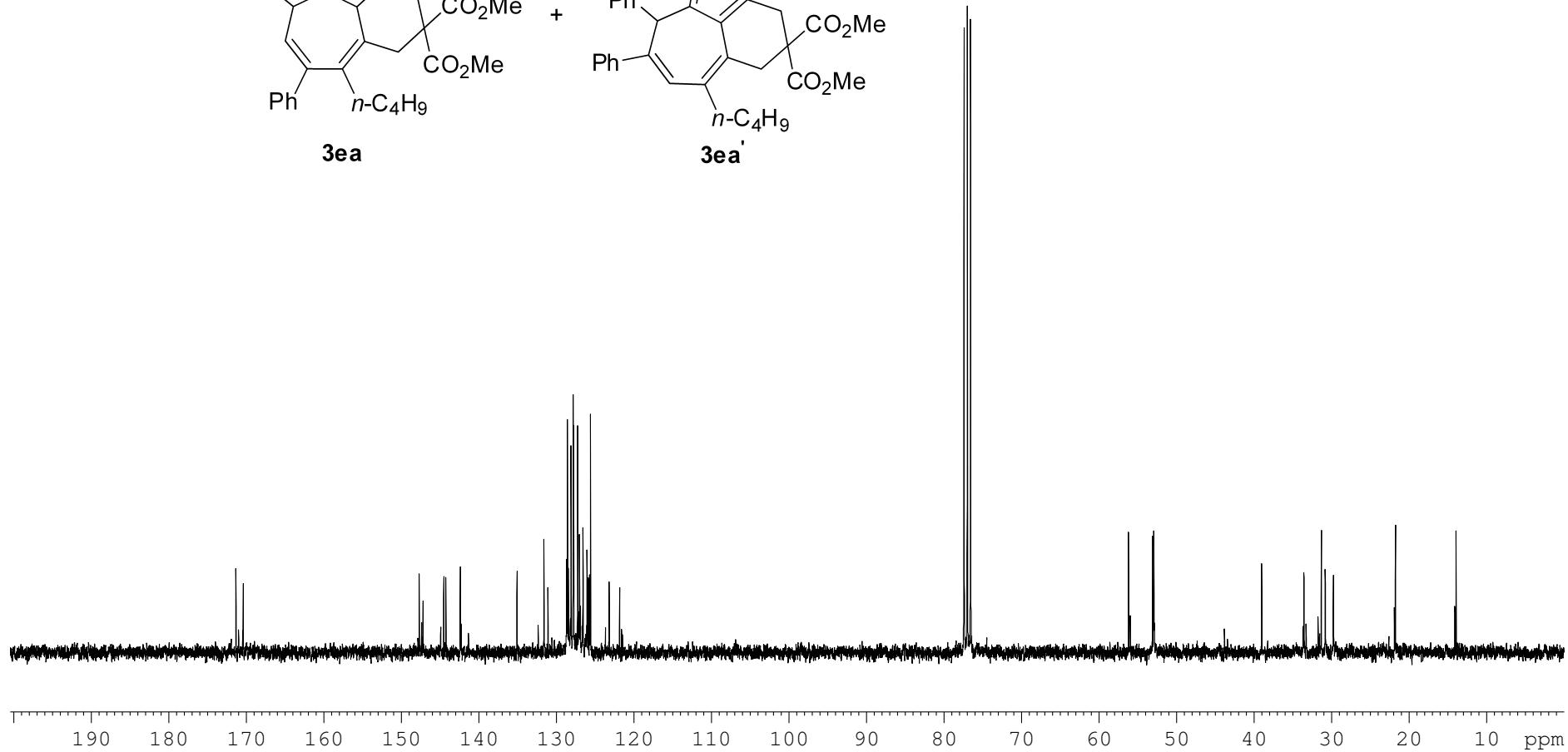
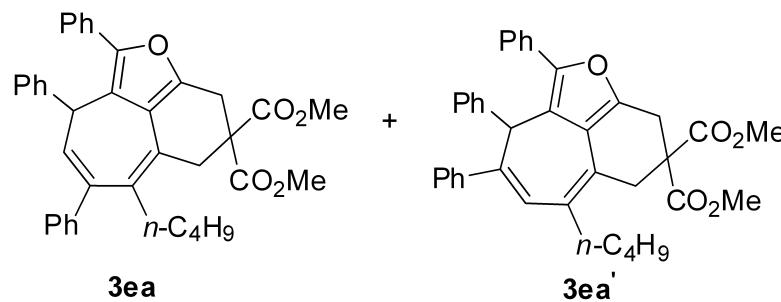


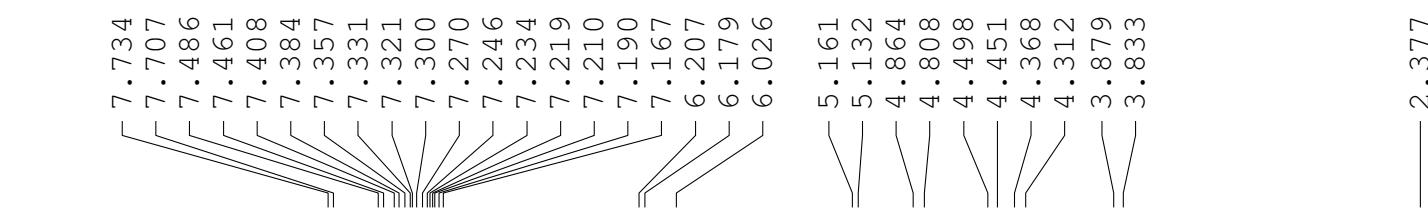
zwx-3-87



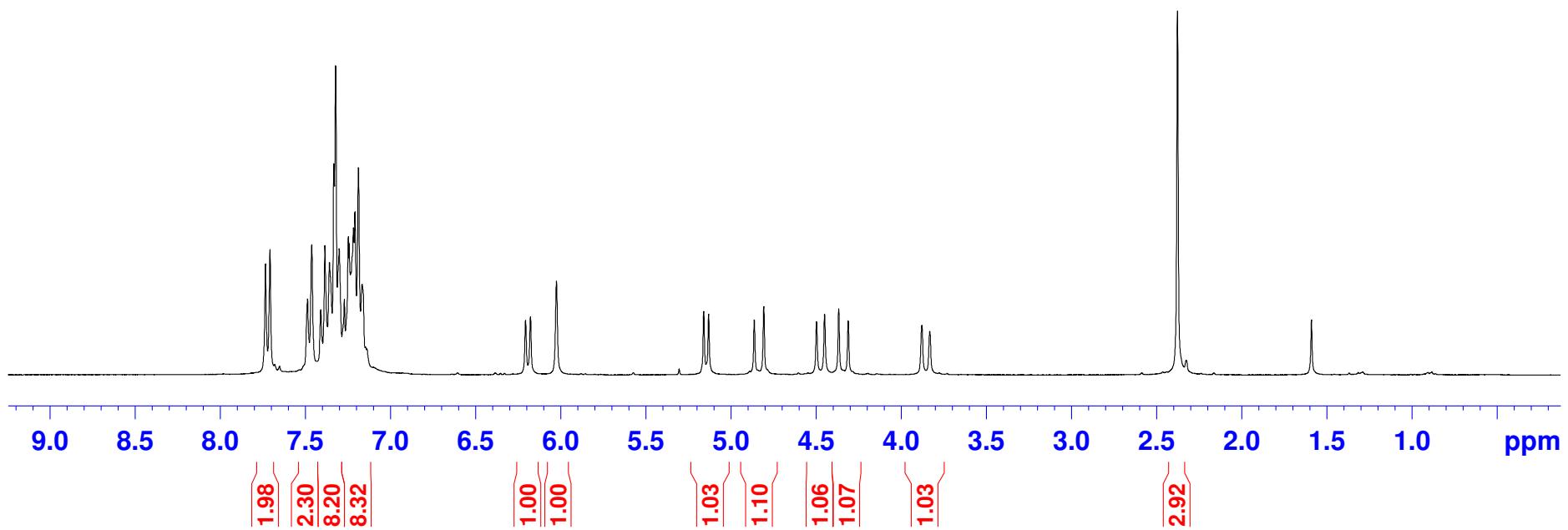
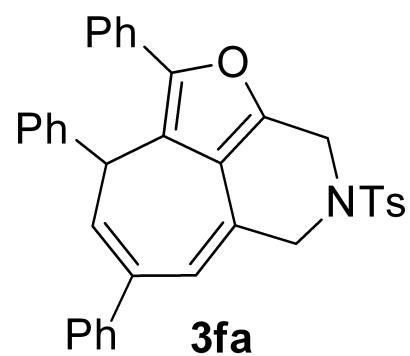


zwx-3-87

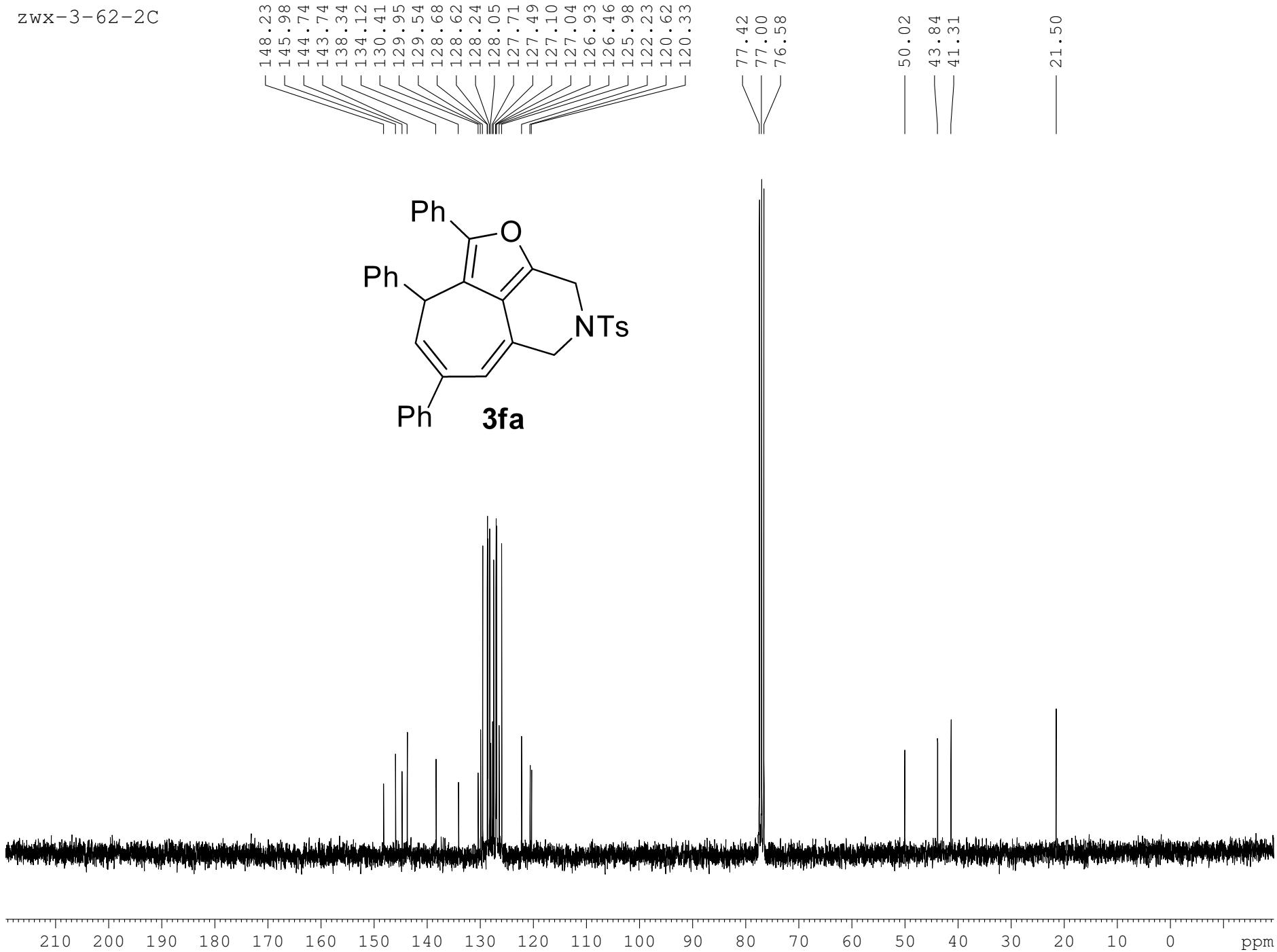


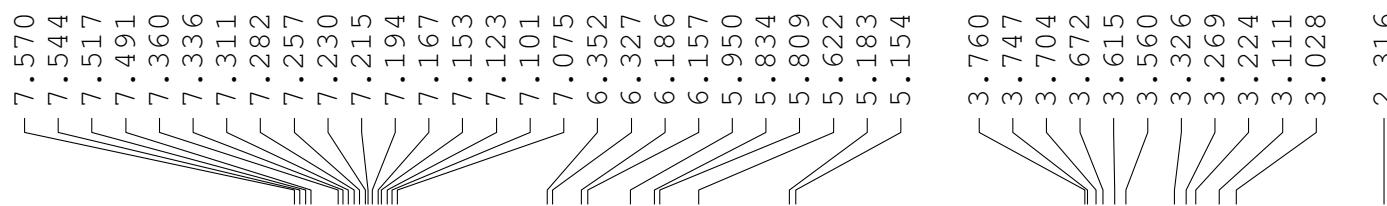


zwx-3-62-2

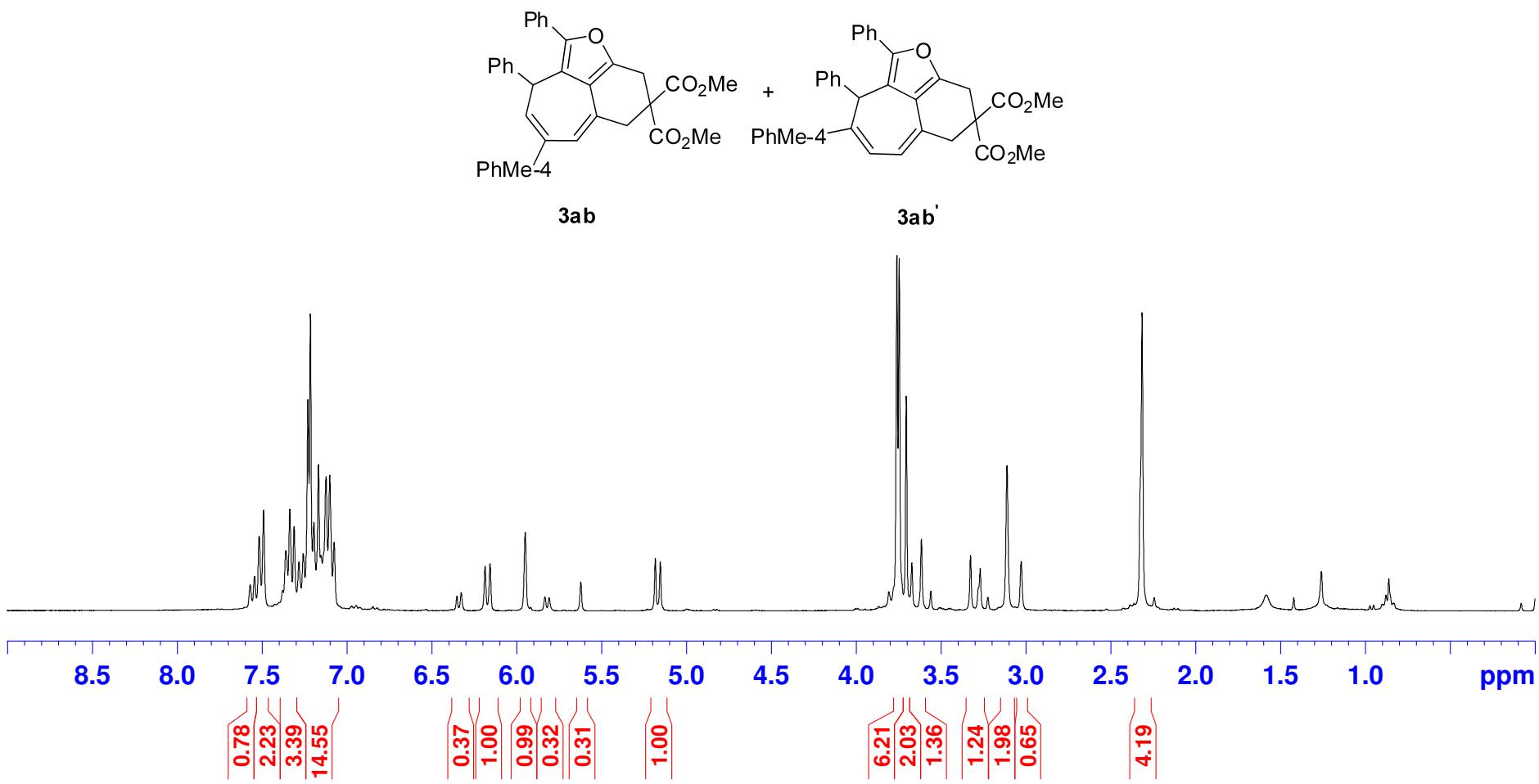


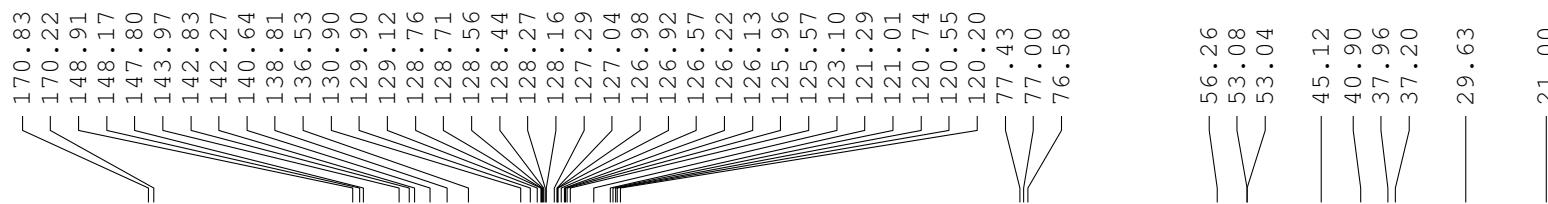
zwx-3-62-2C



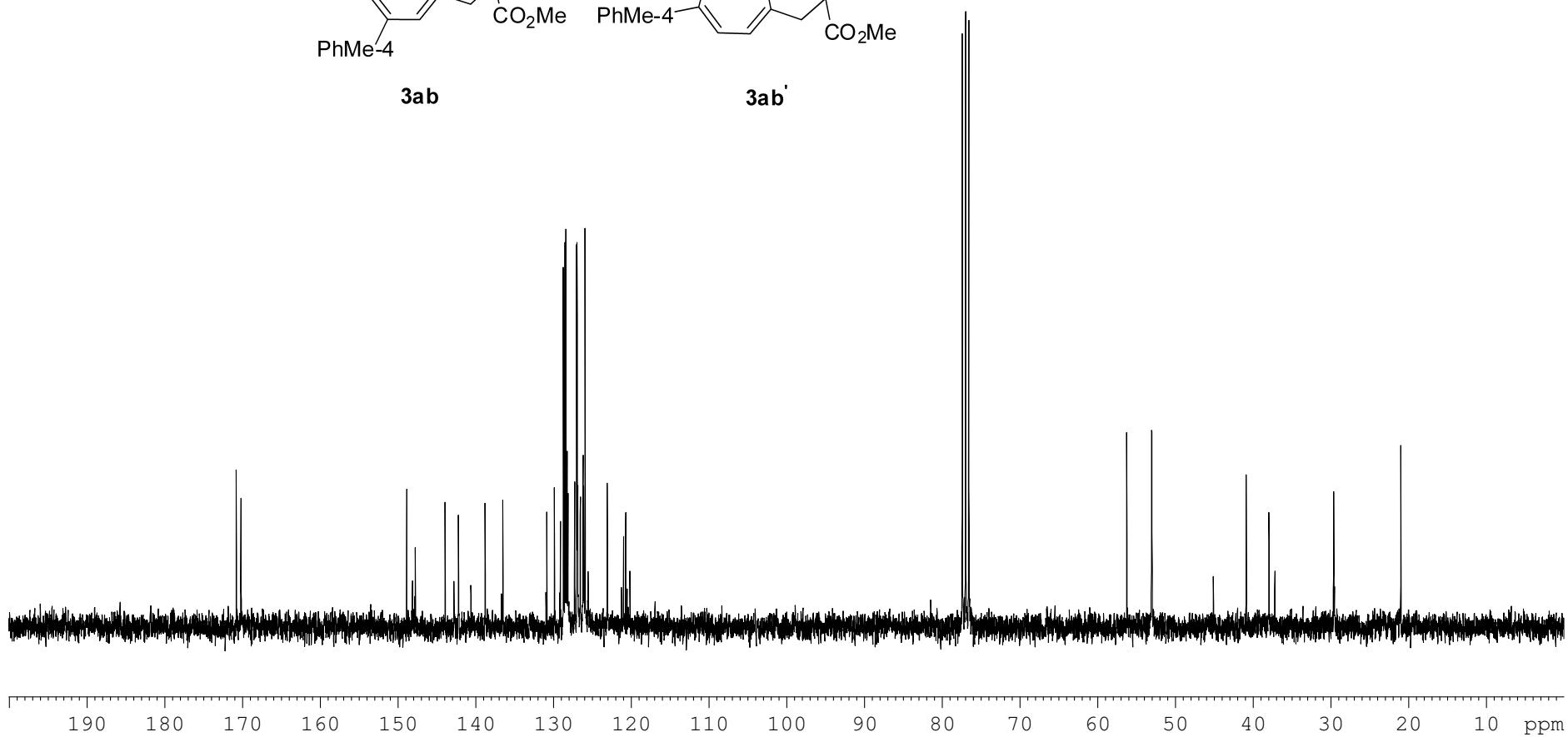
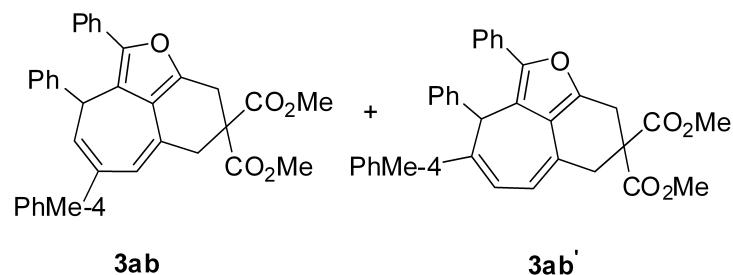


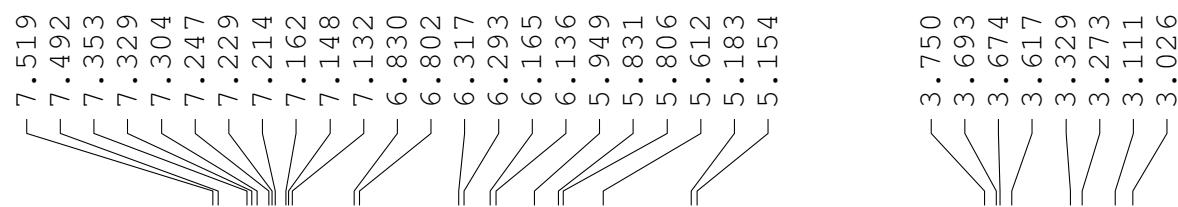
zwx-3-54



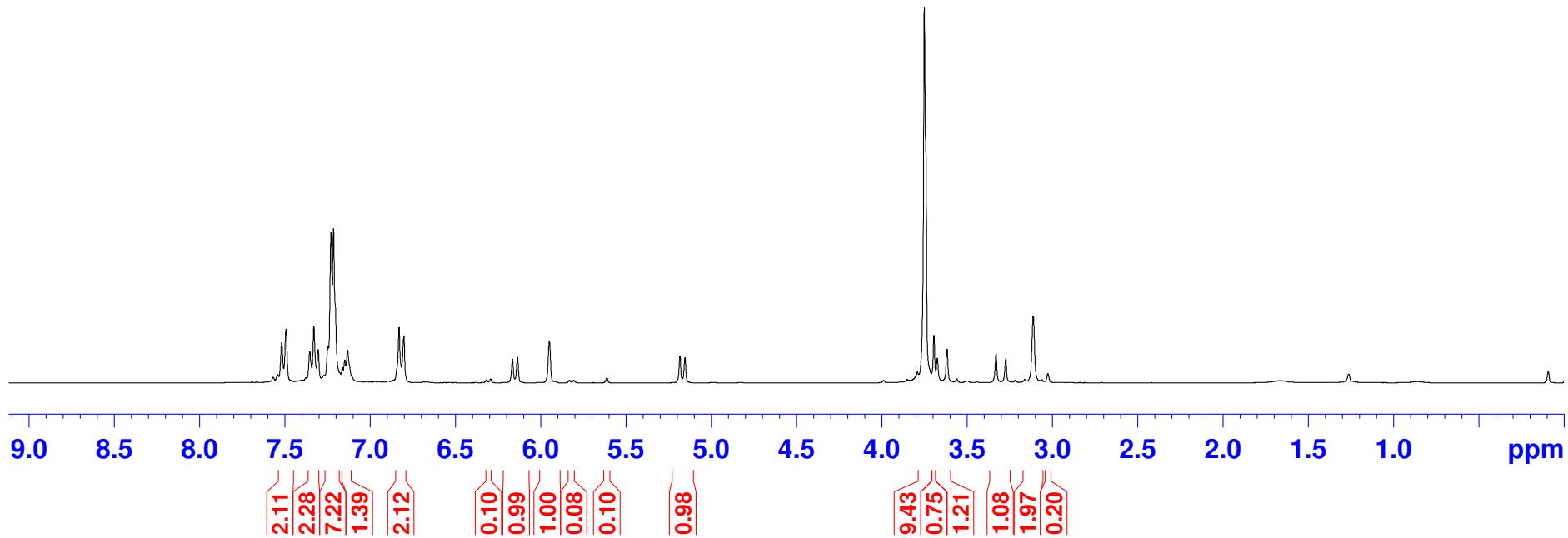
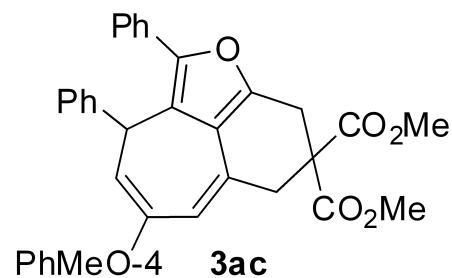


zwx-3-54

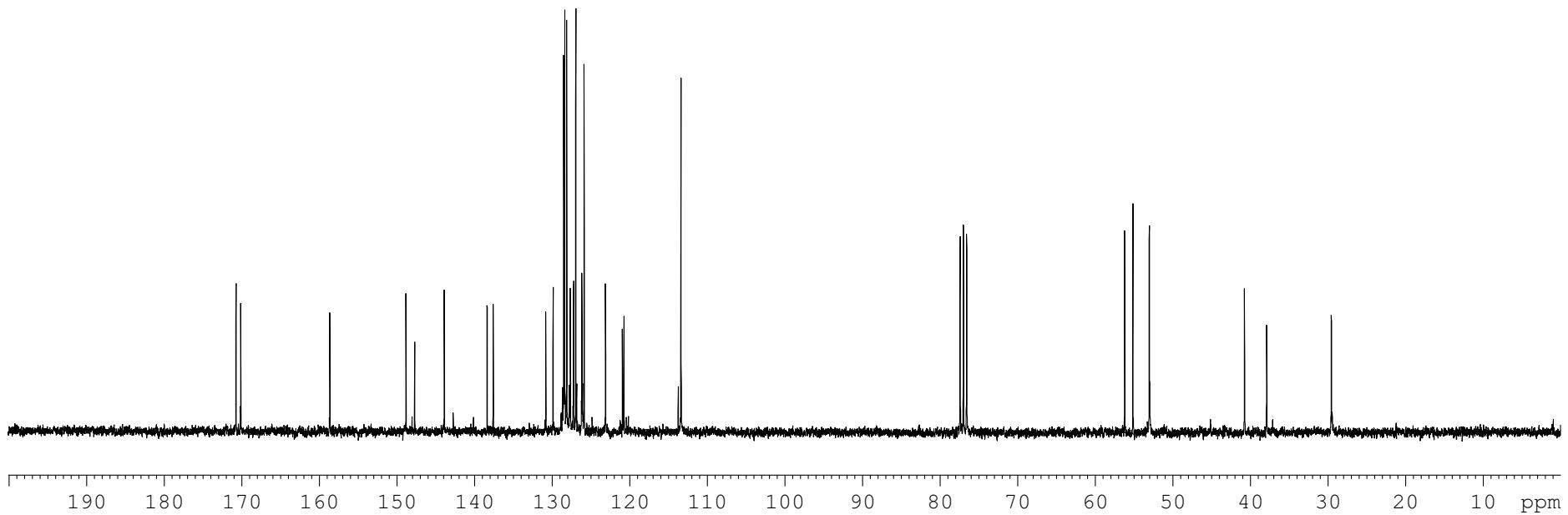
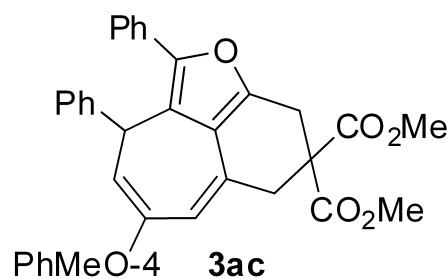
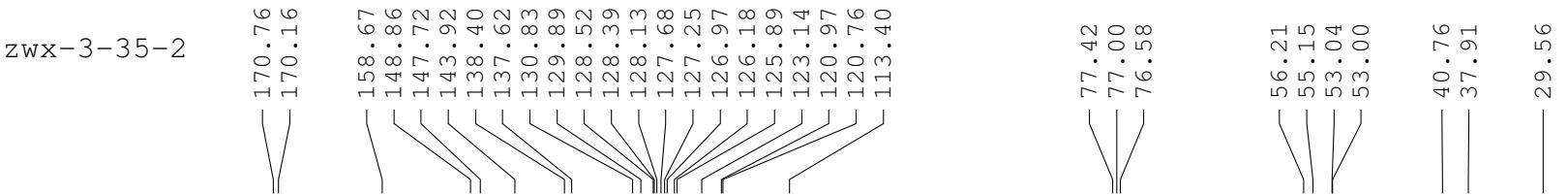


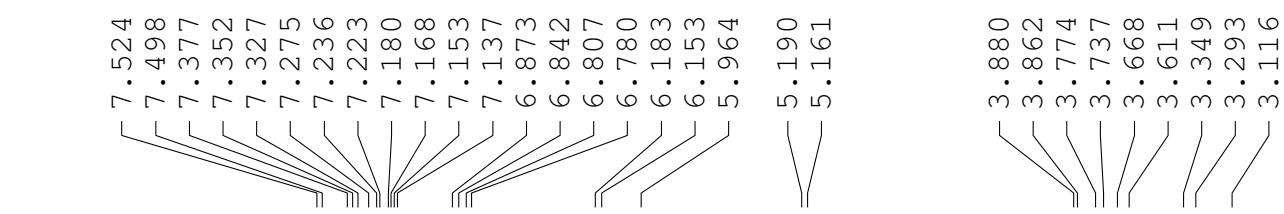


zwx-3-35-2

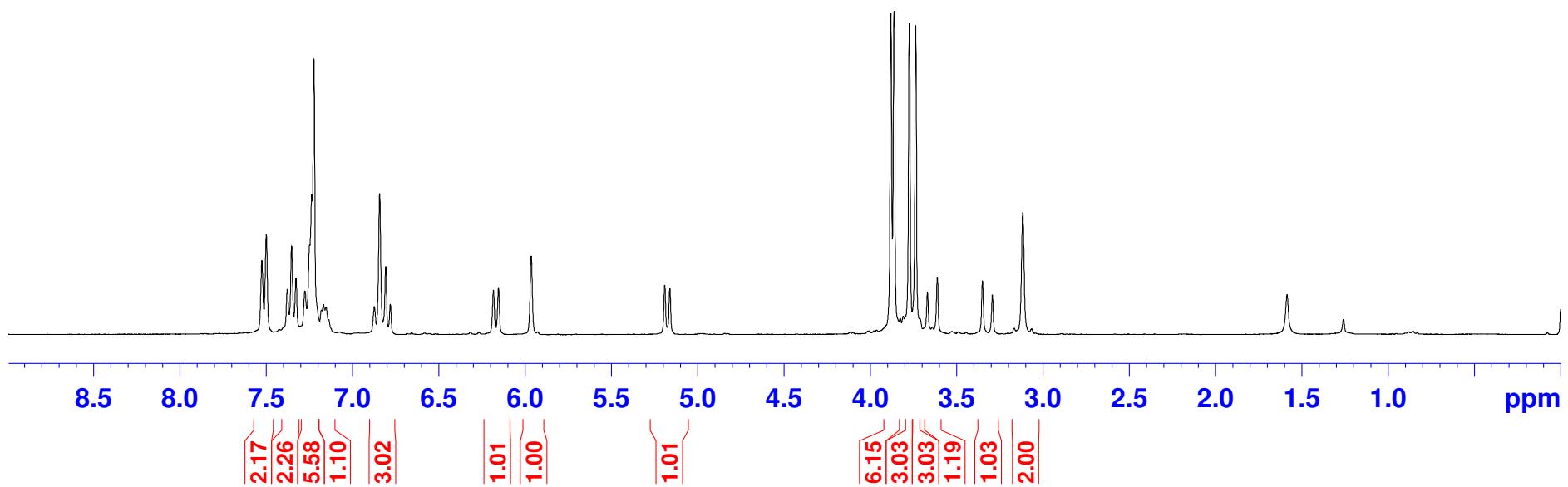
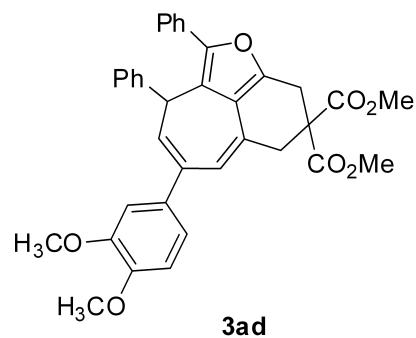


zwx-3-35-2

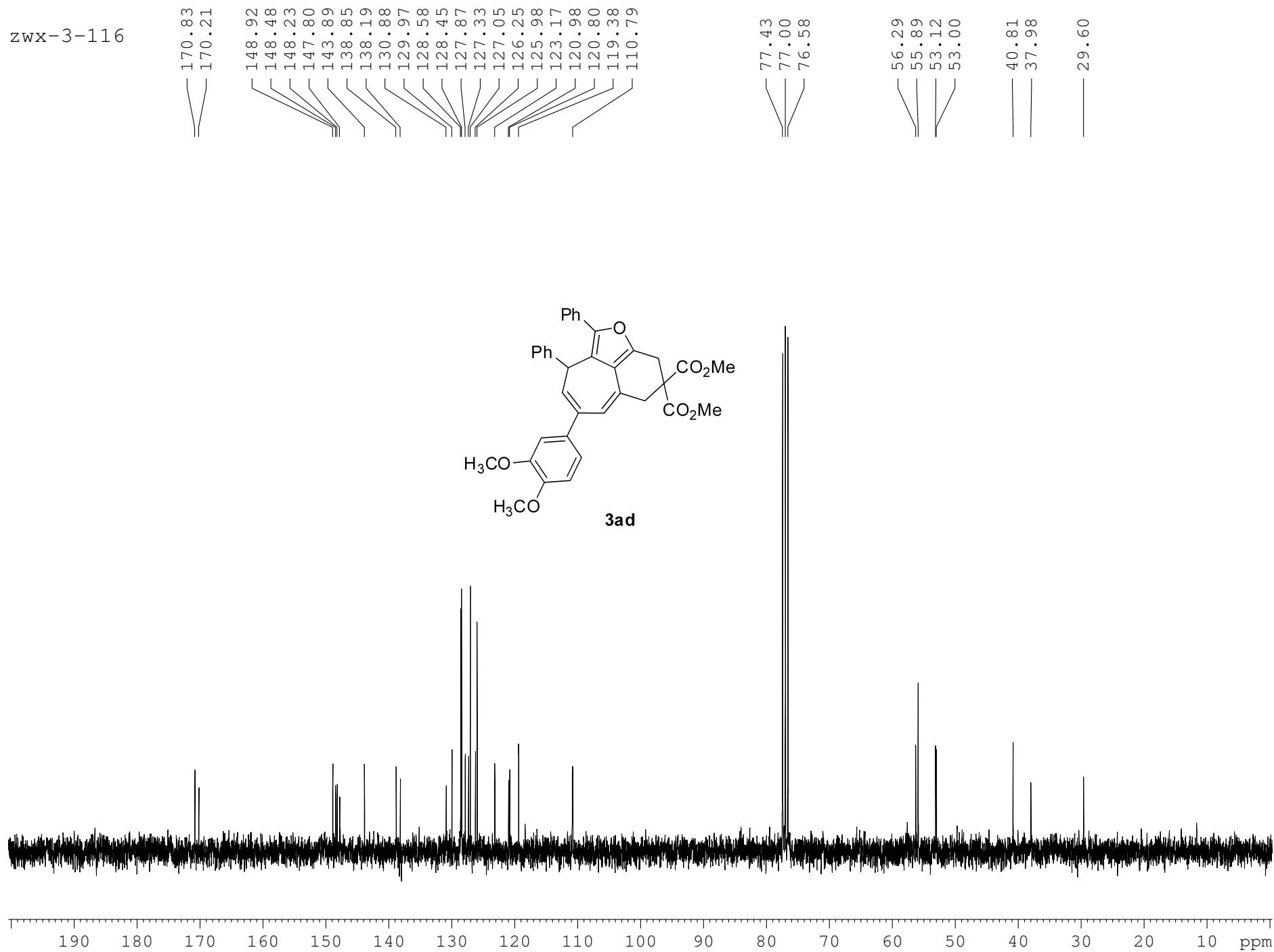


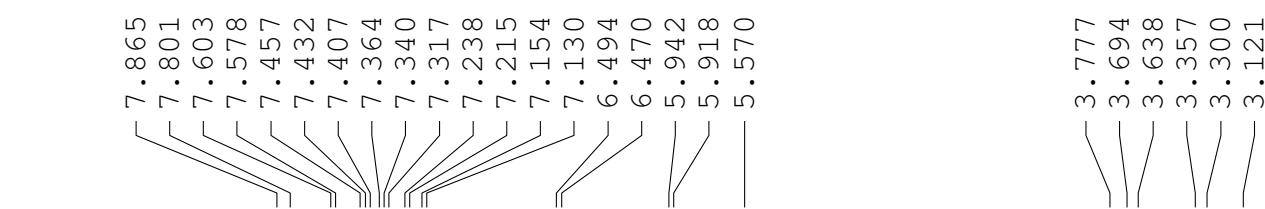


zwx-3-116

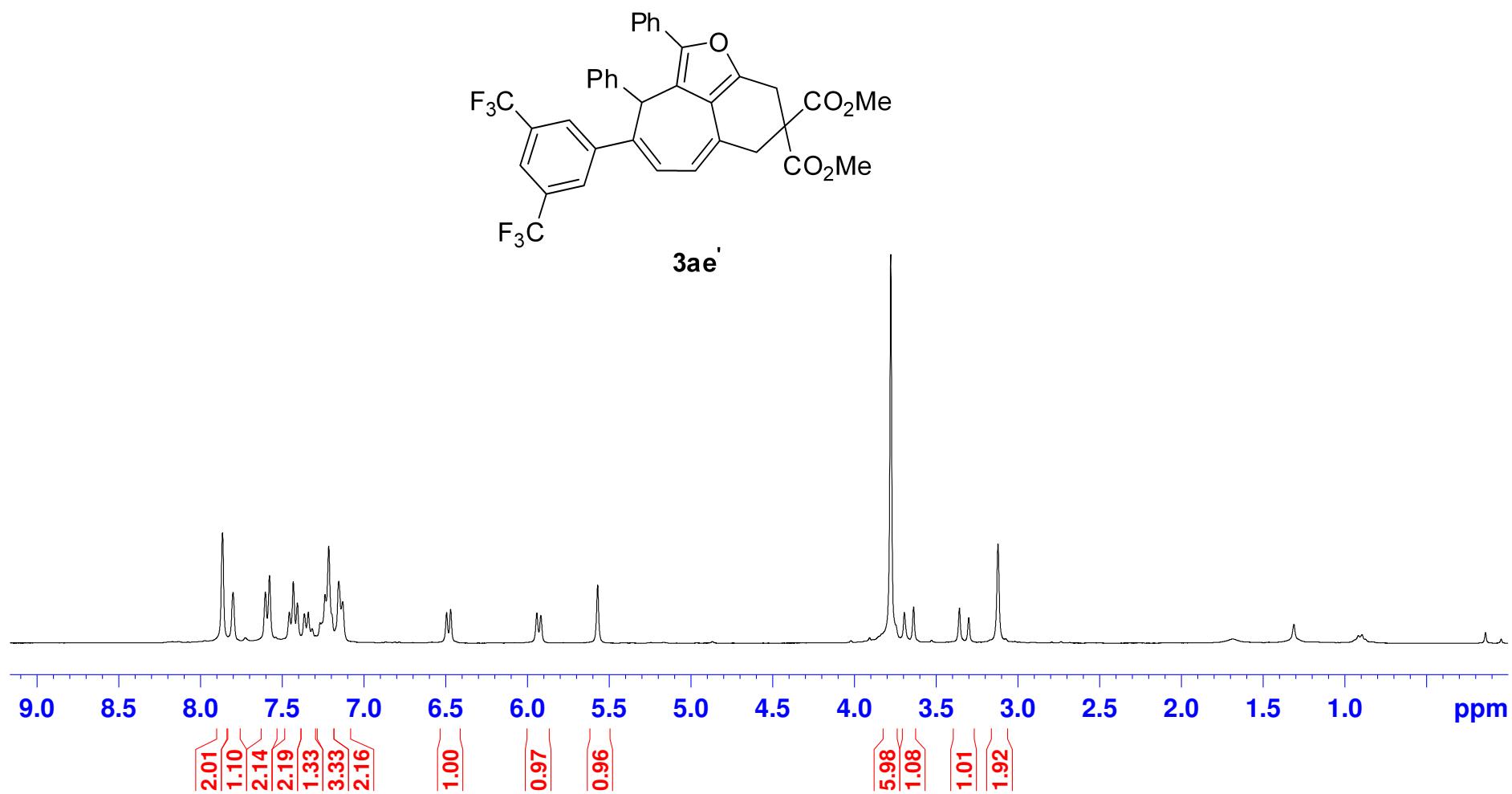


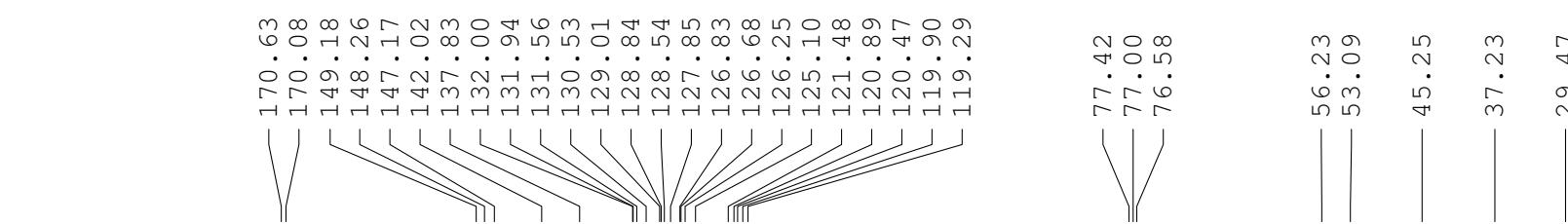
zwx-3-116



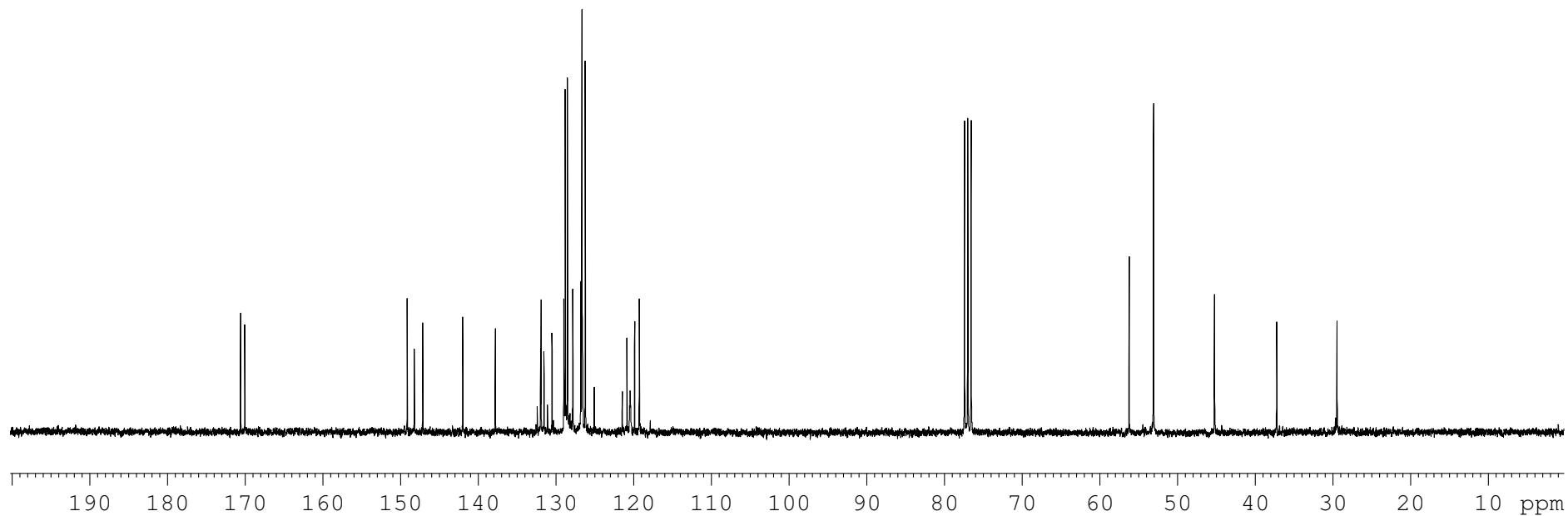
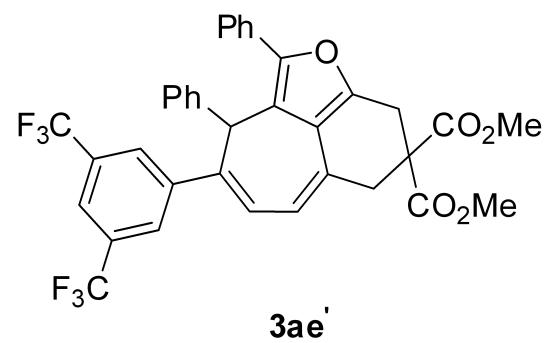


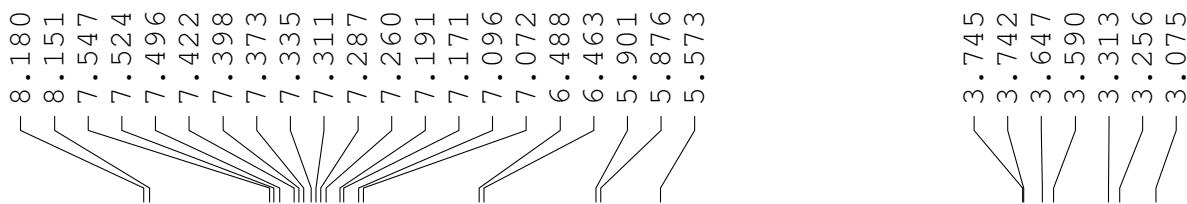
zwx-3-106



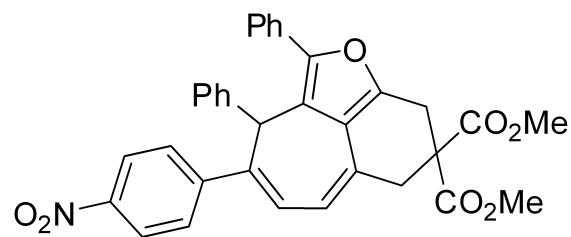


zwx-3-106

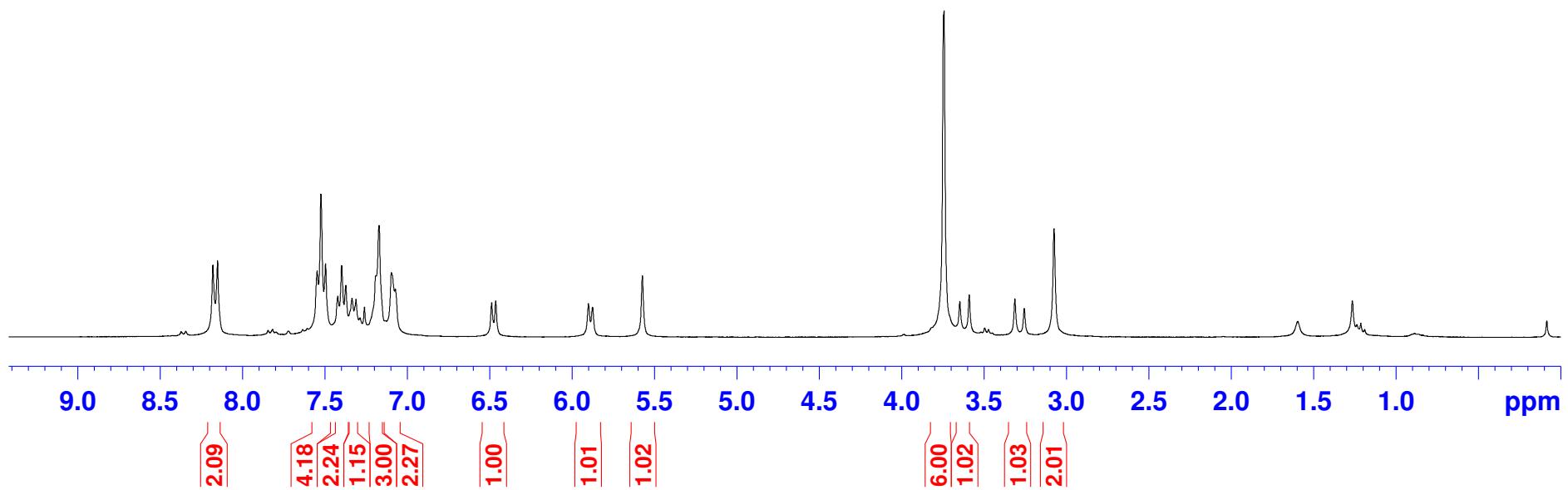


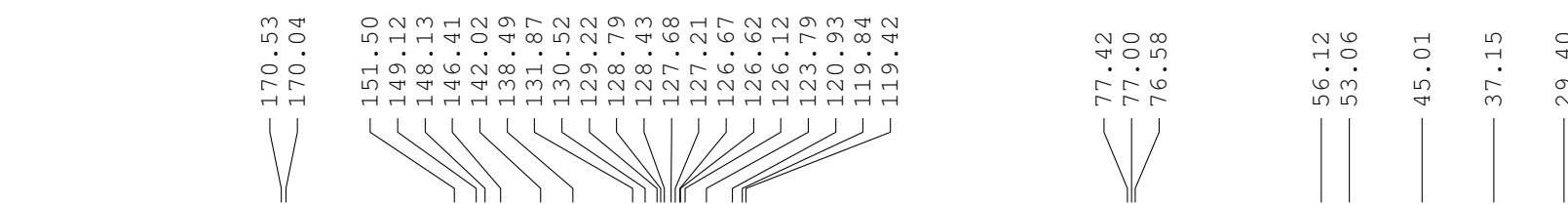


zwx-3-43-2

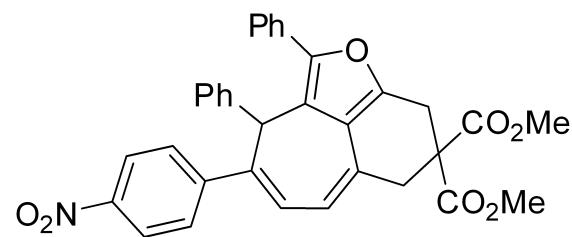


3af'

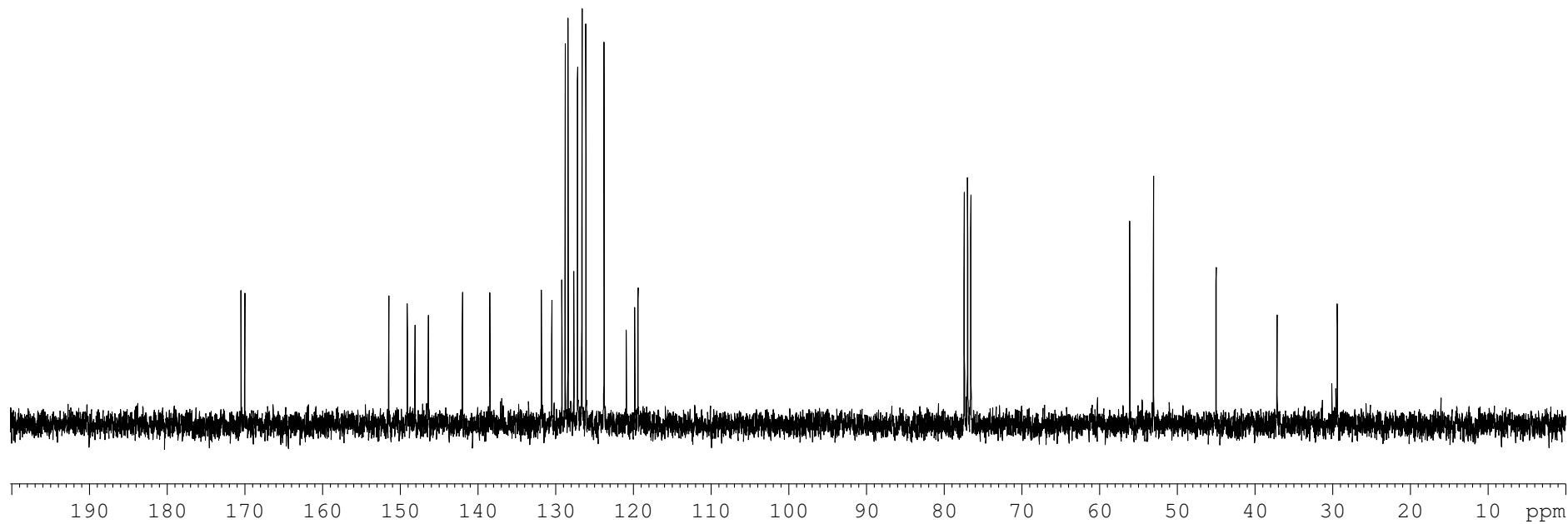


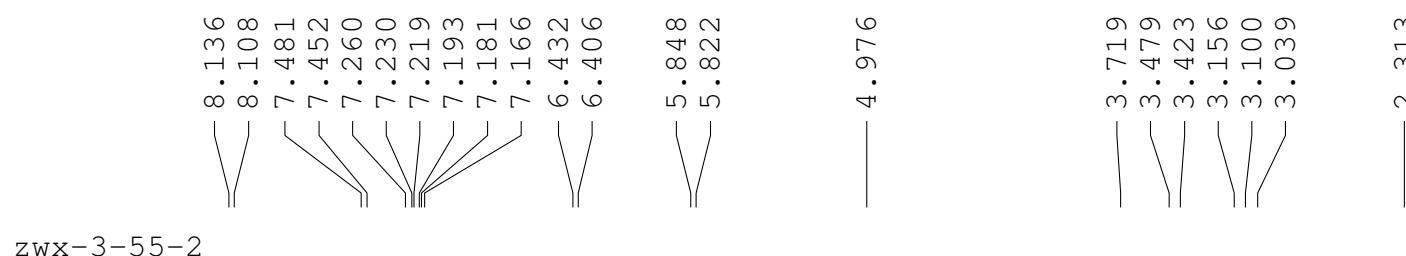


zwx-3-43-2

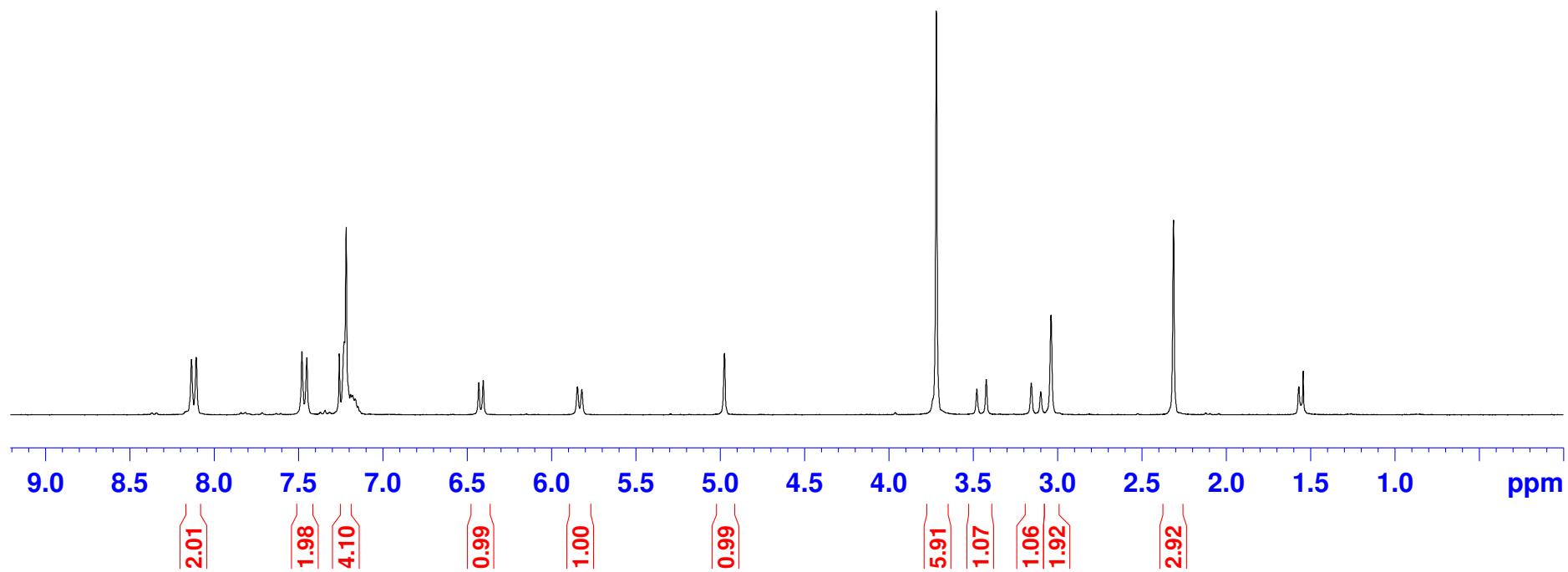
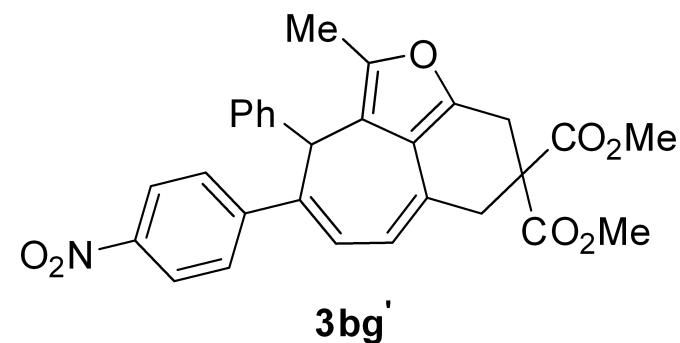


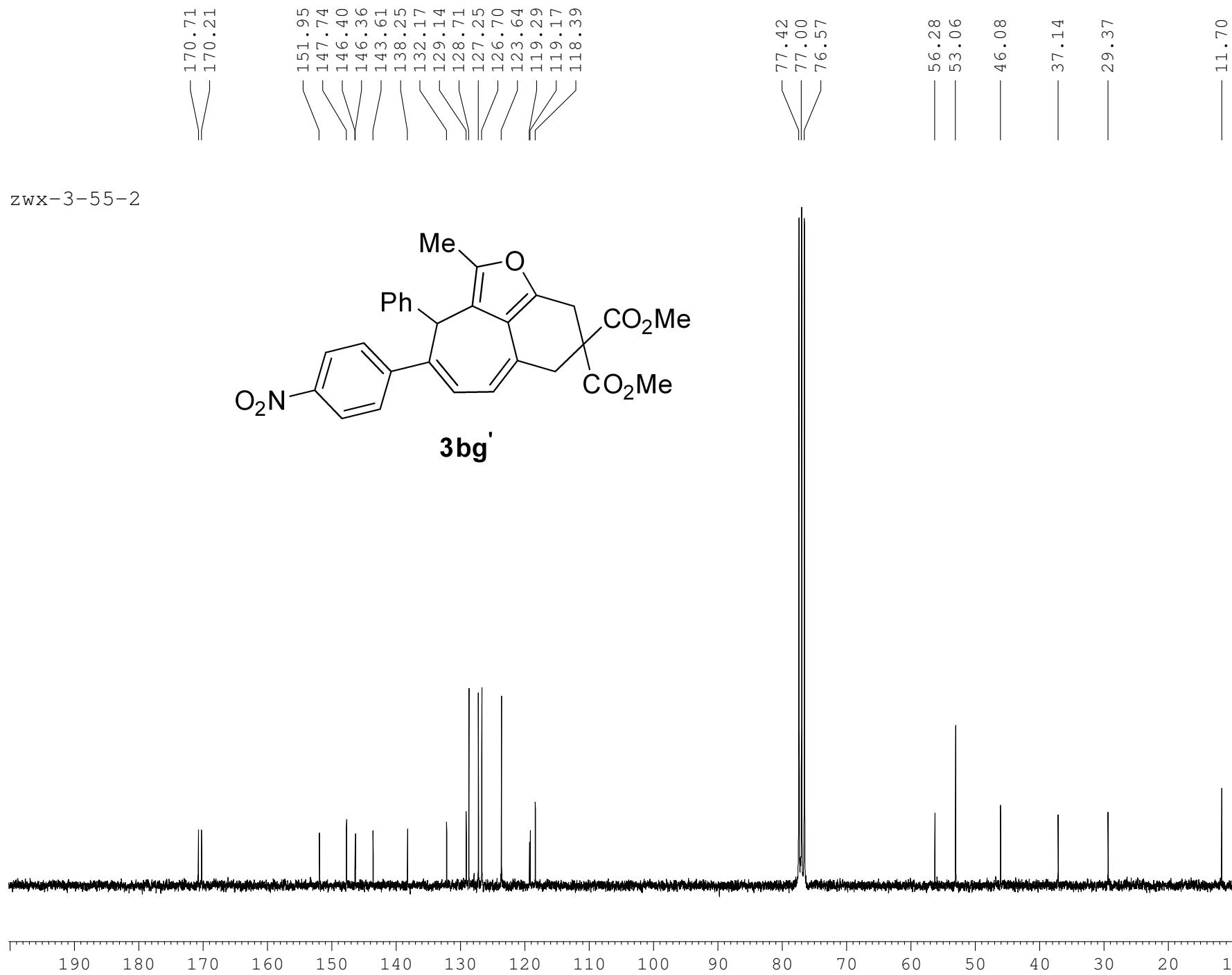
3af'

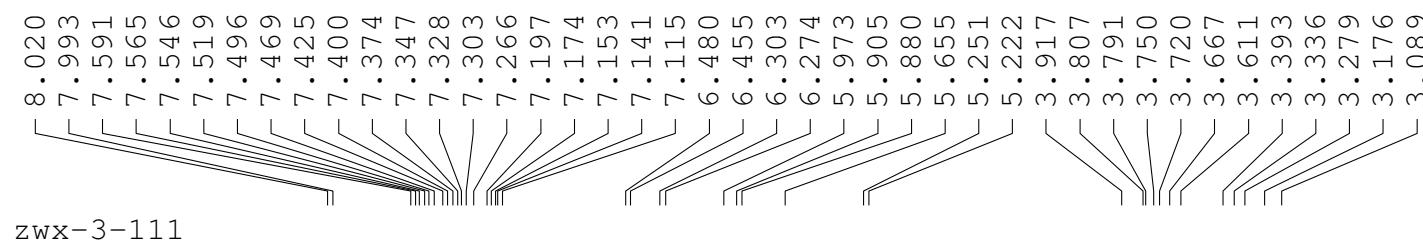




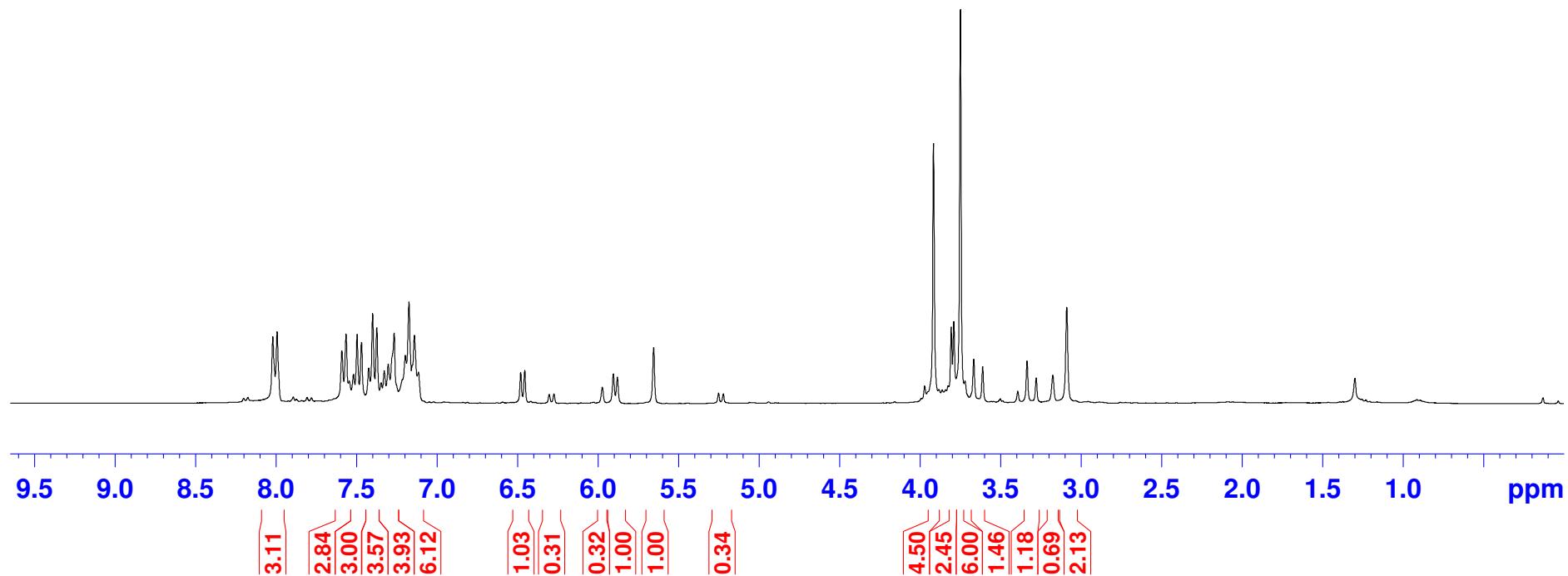
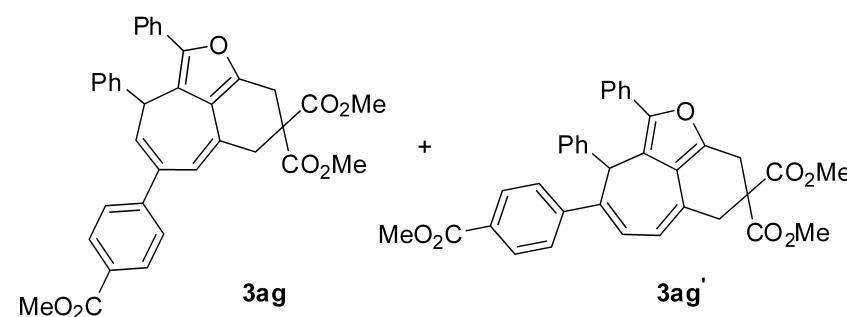
zwx-3-55-2

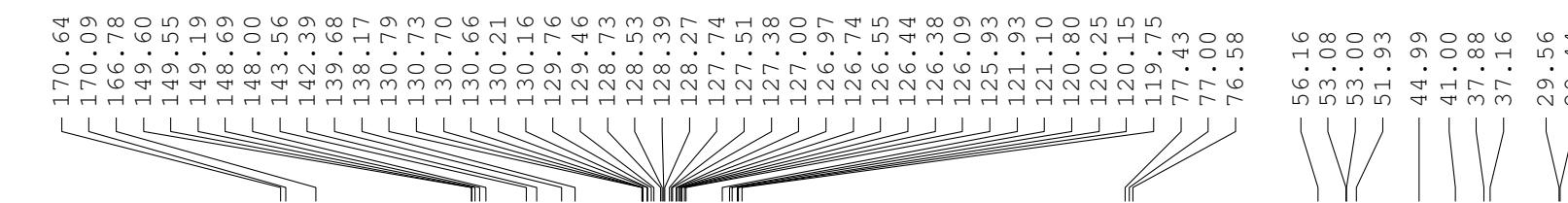




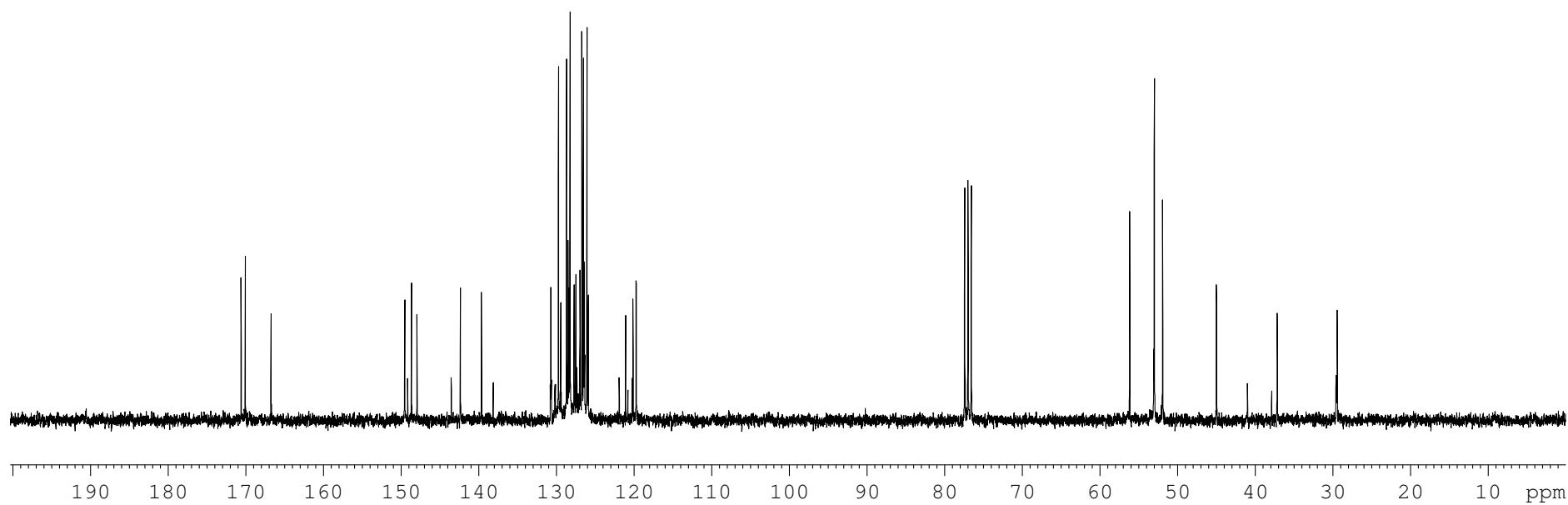
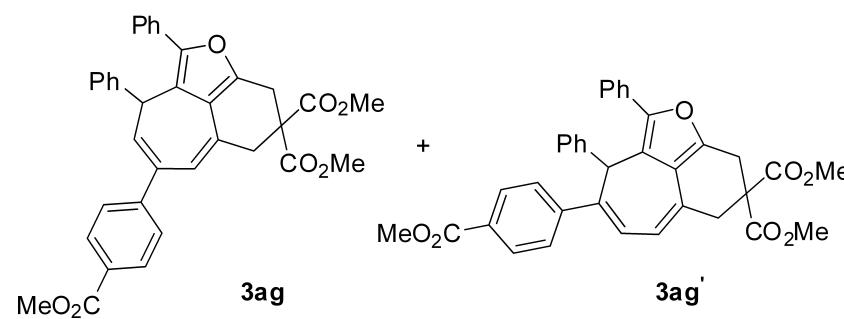


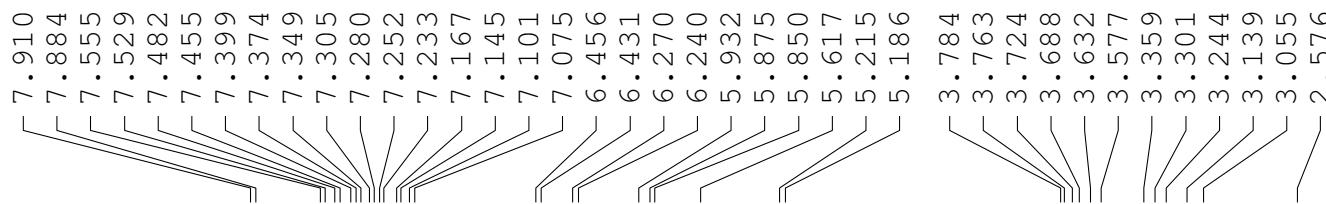
zwx-3-111



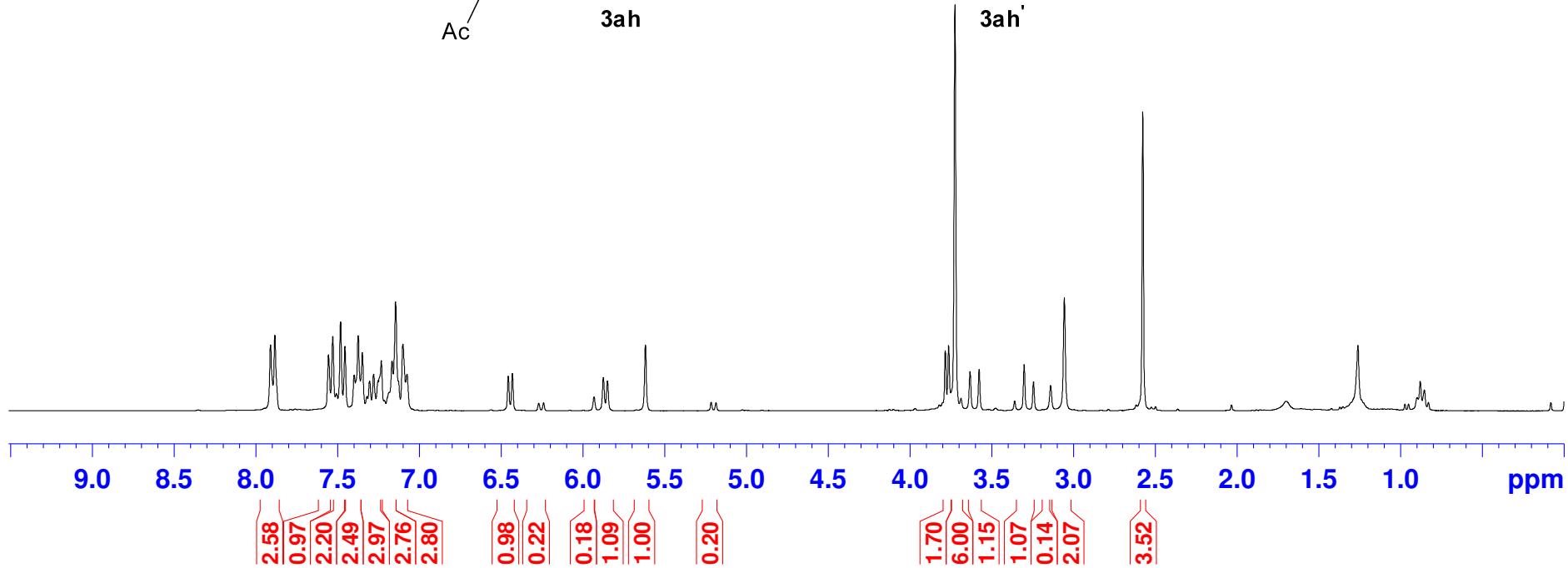
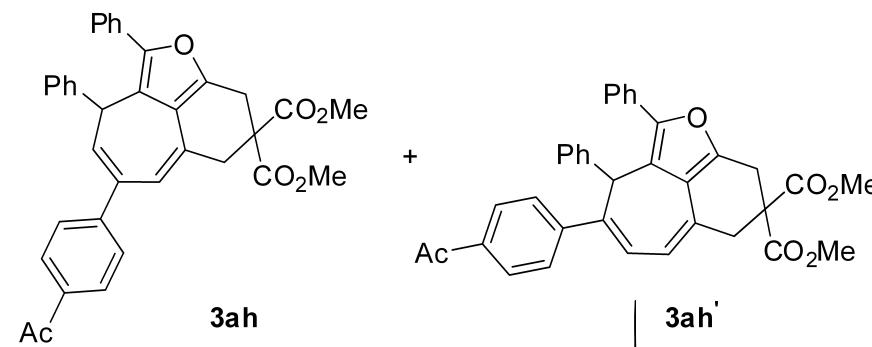


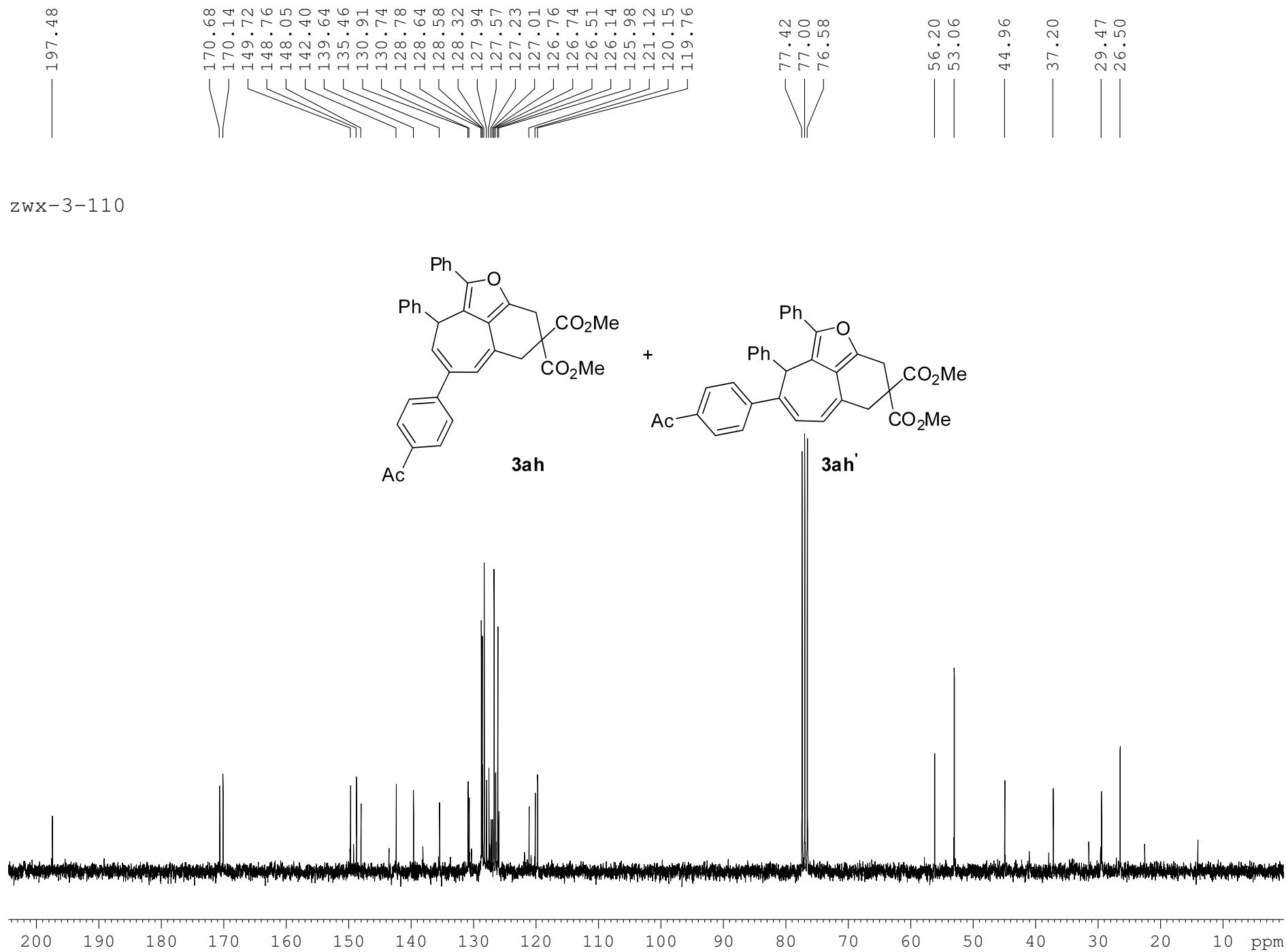
zwx-3-111

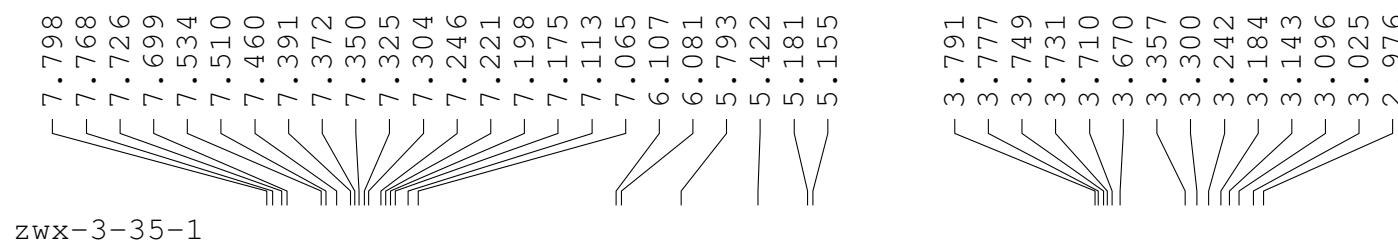




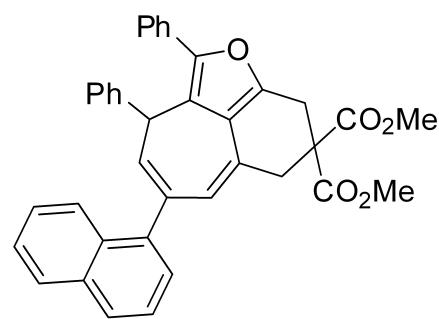
zwx-3-110



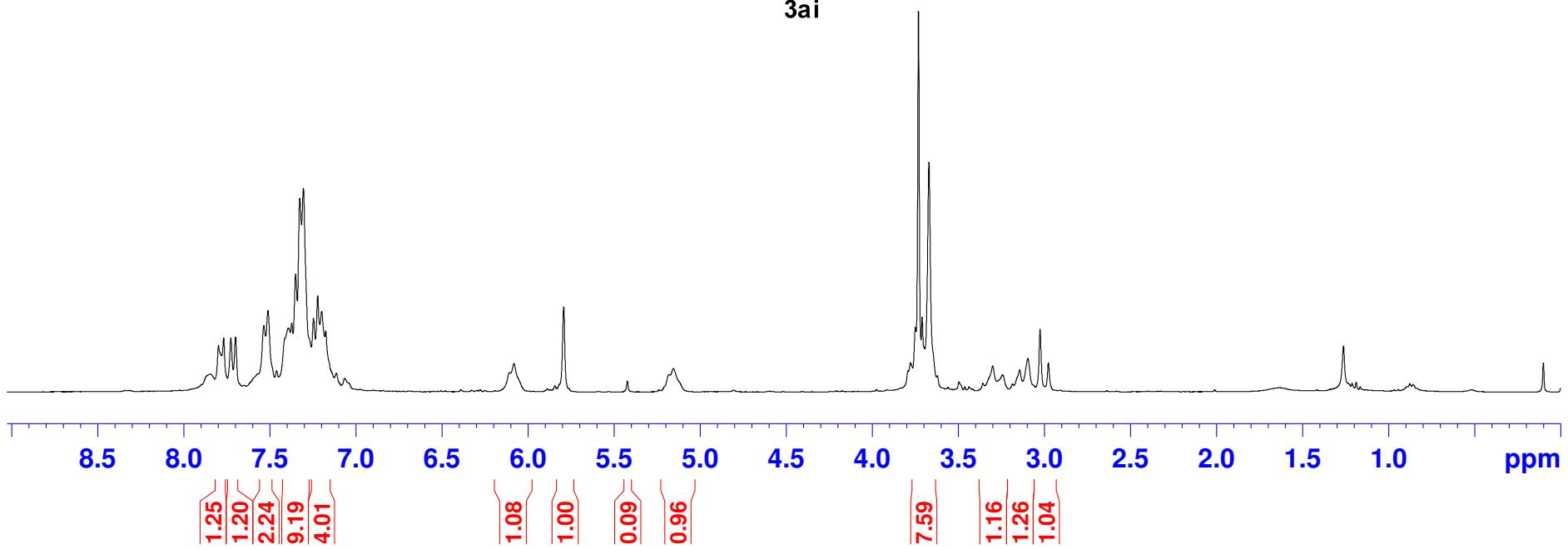


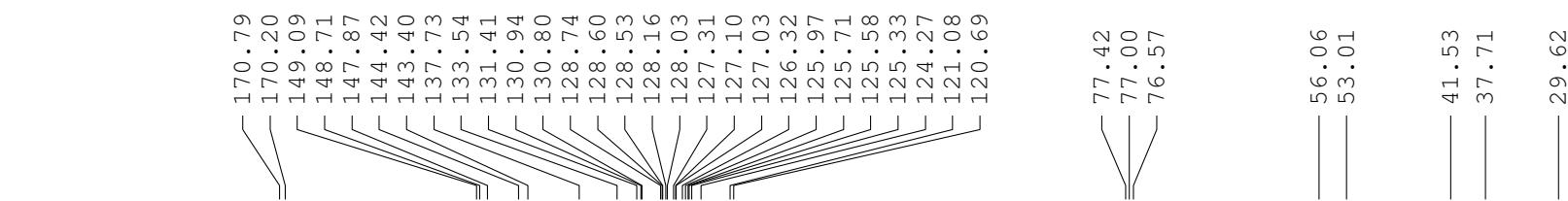


zwx-3-35-1

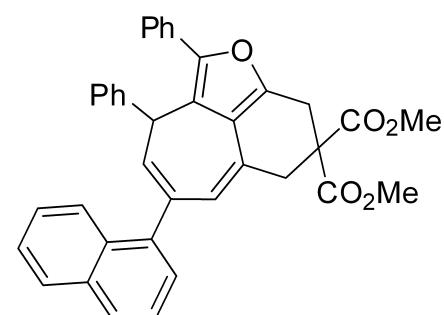


3ai

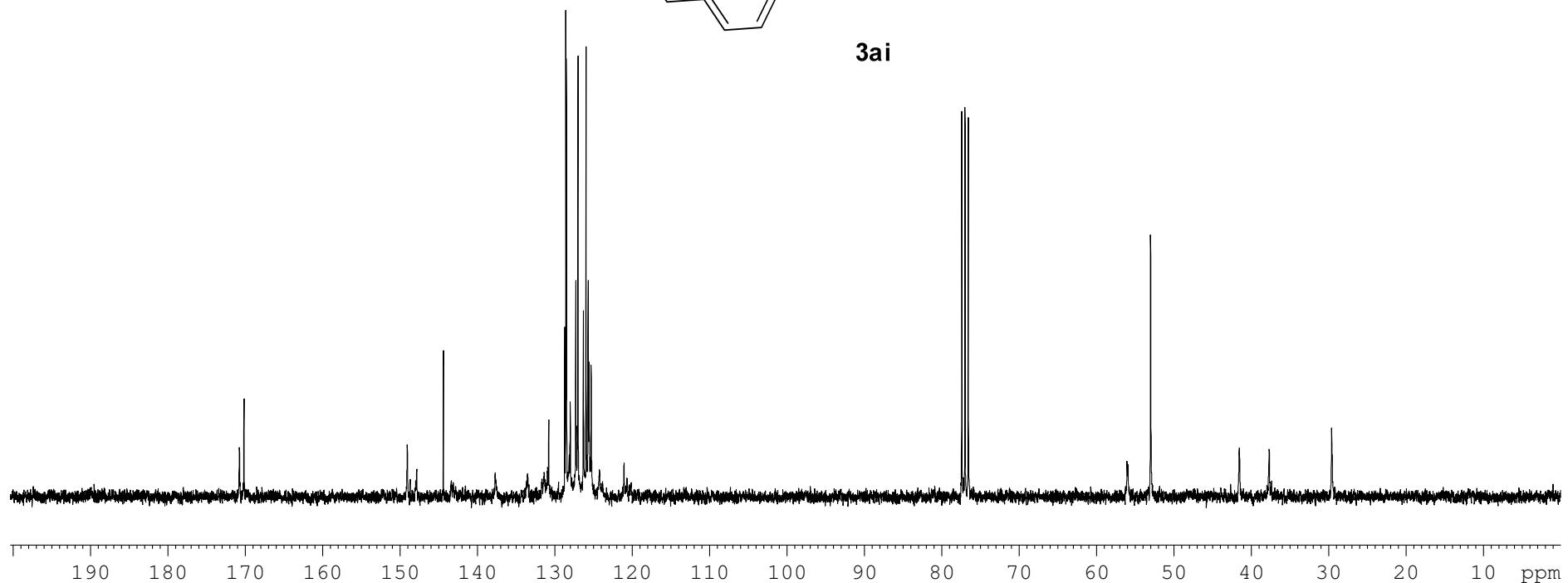


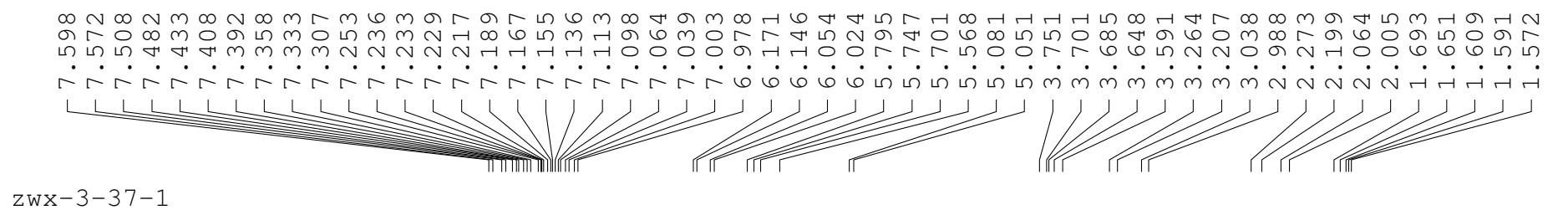


zwx-3-35-1

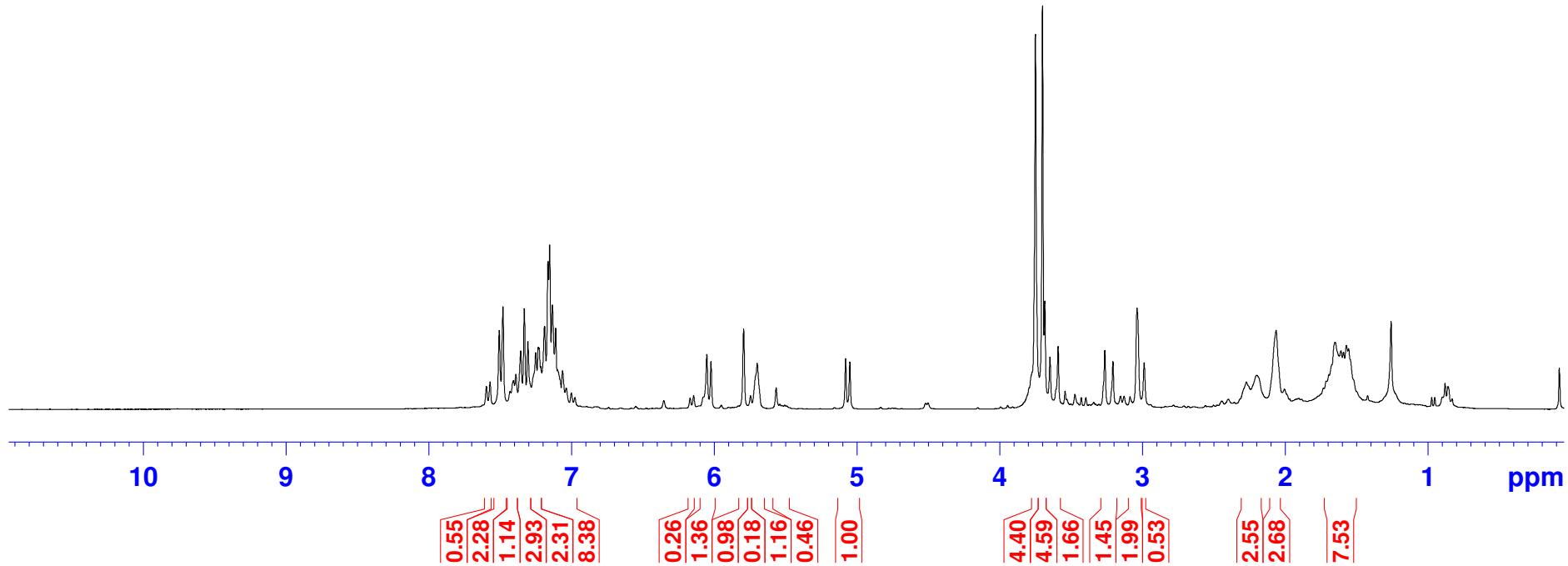
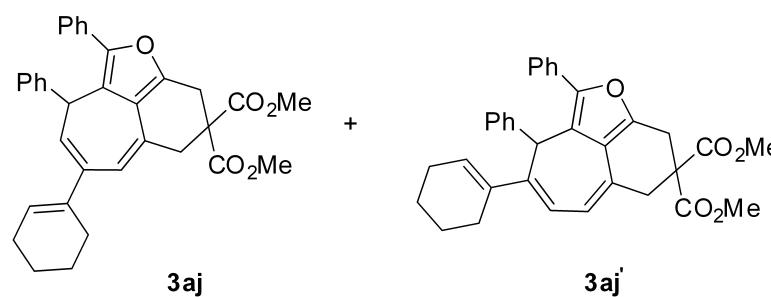


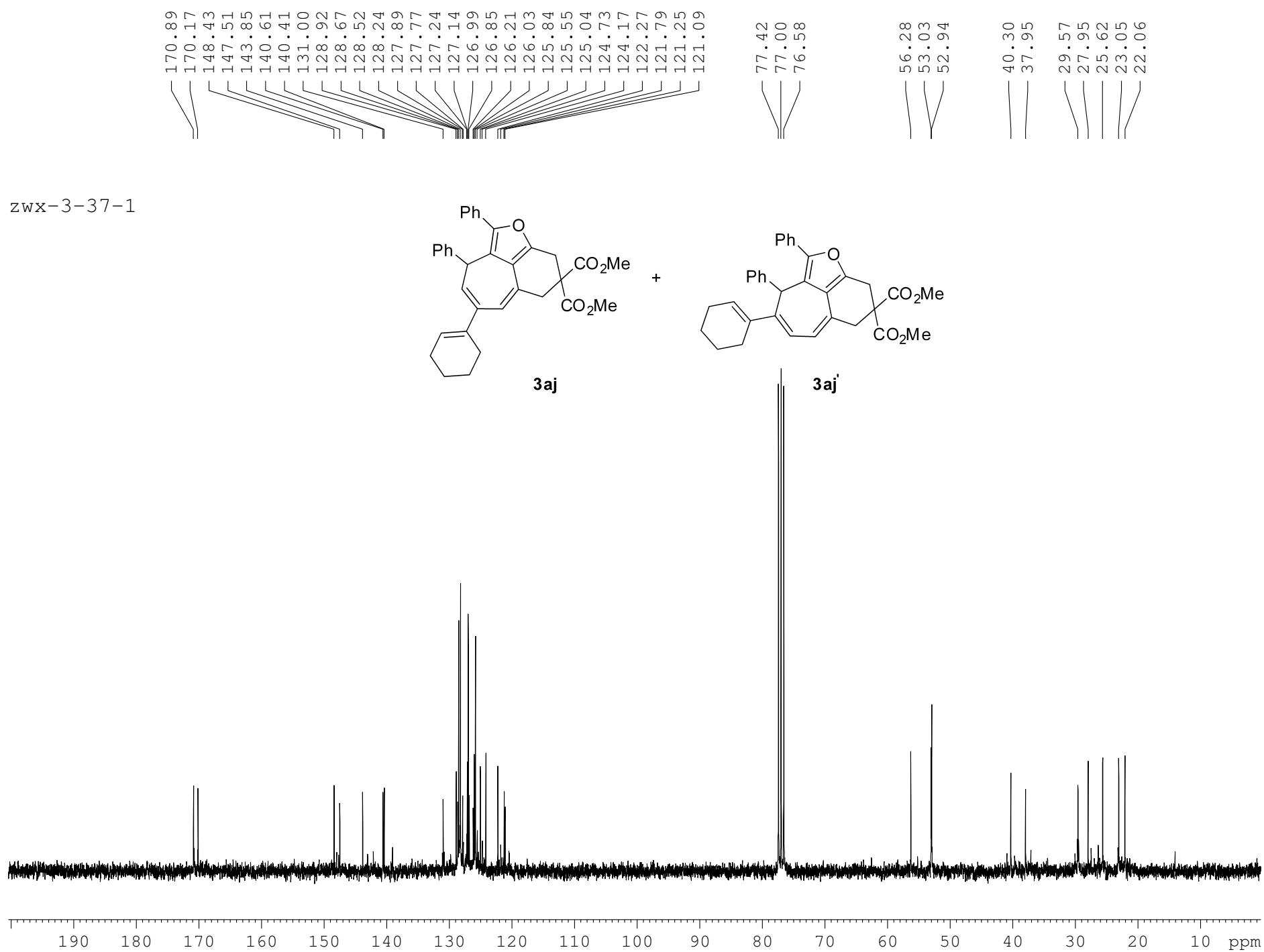
3ai

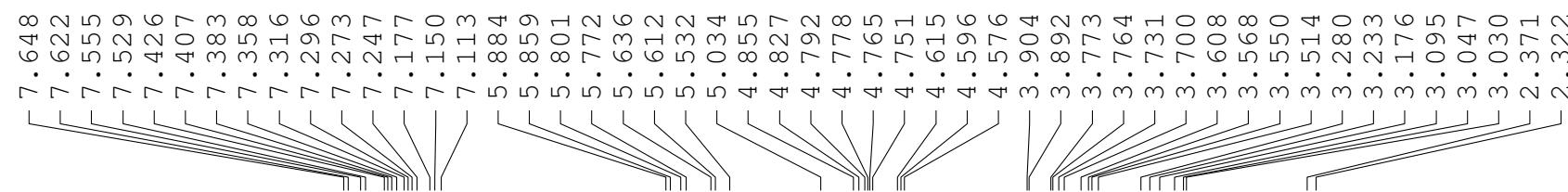




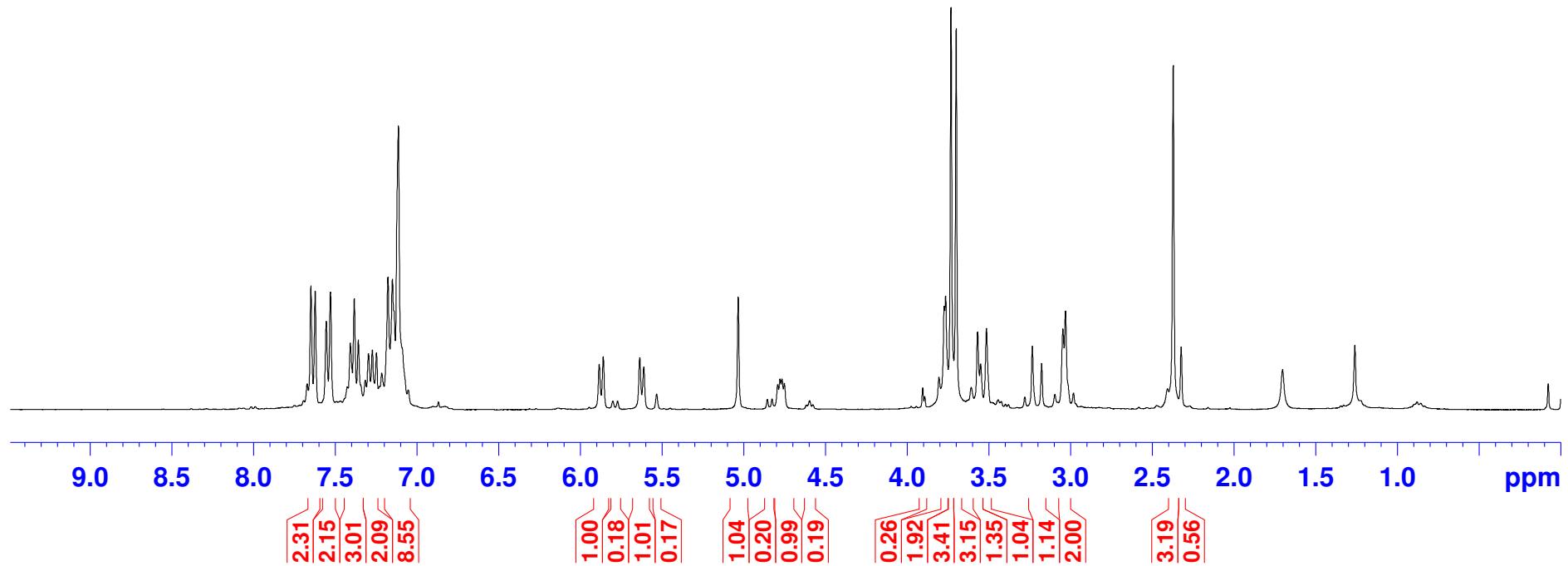
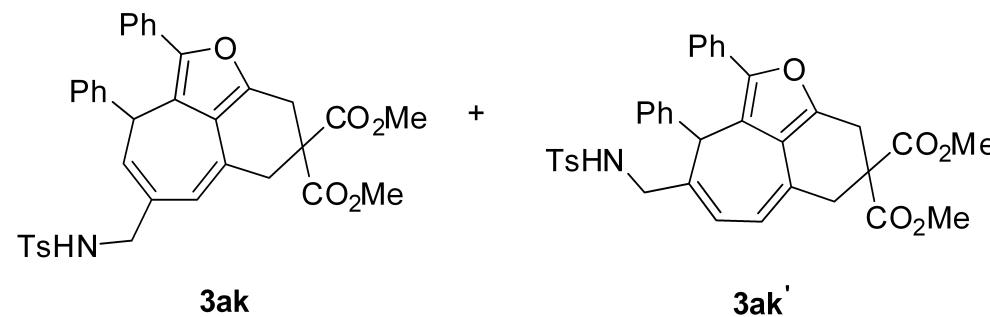
zwx-3-37-1



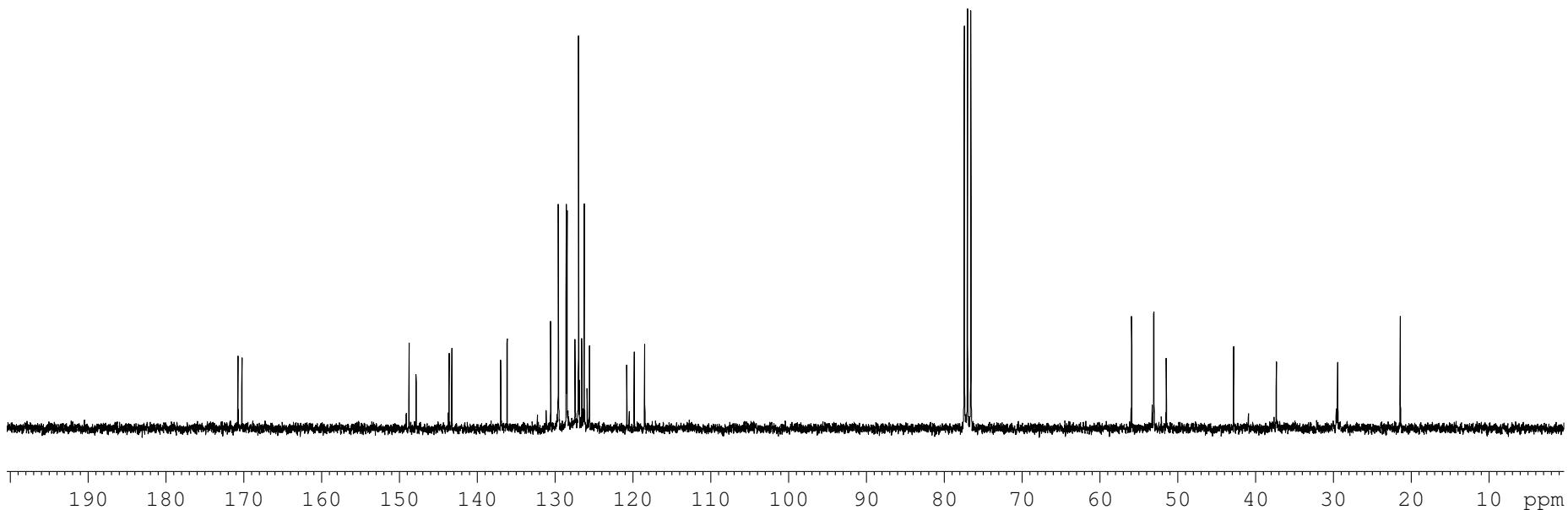
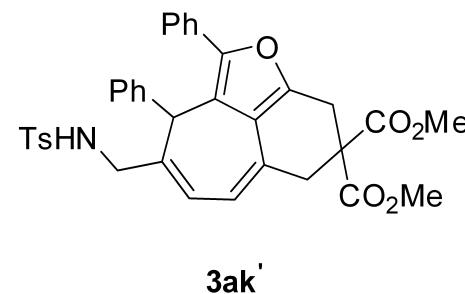
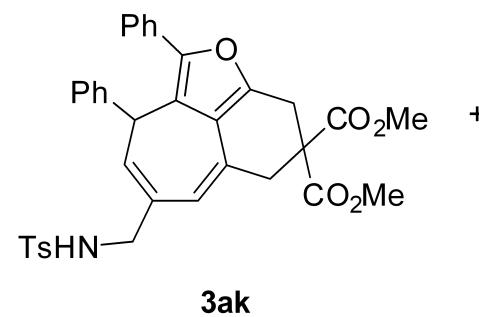
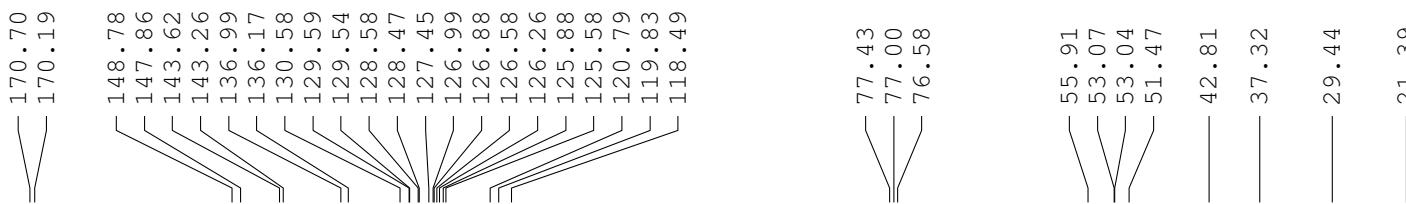


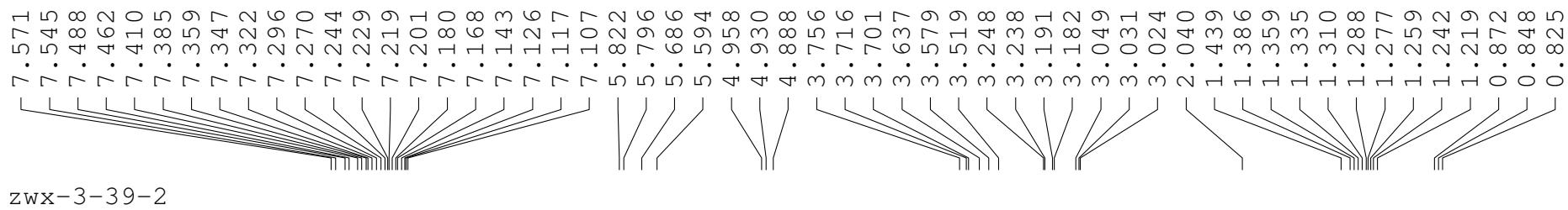


zwx-3-39-1

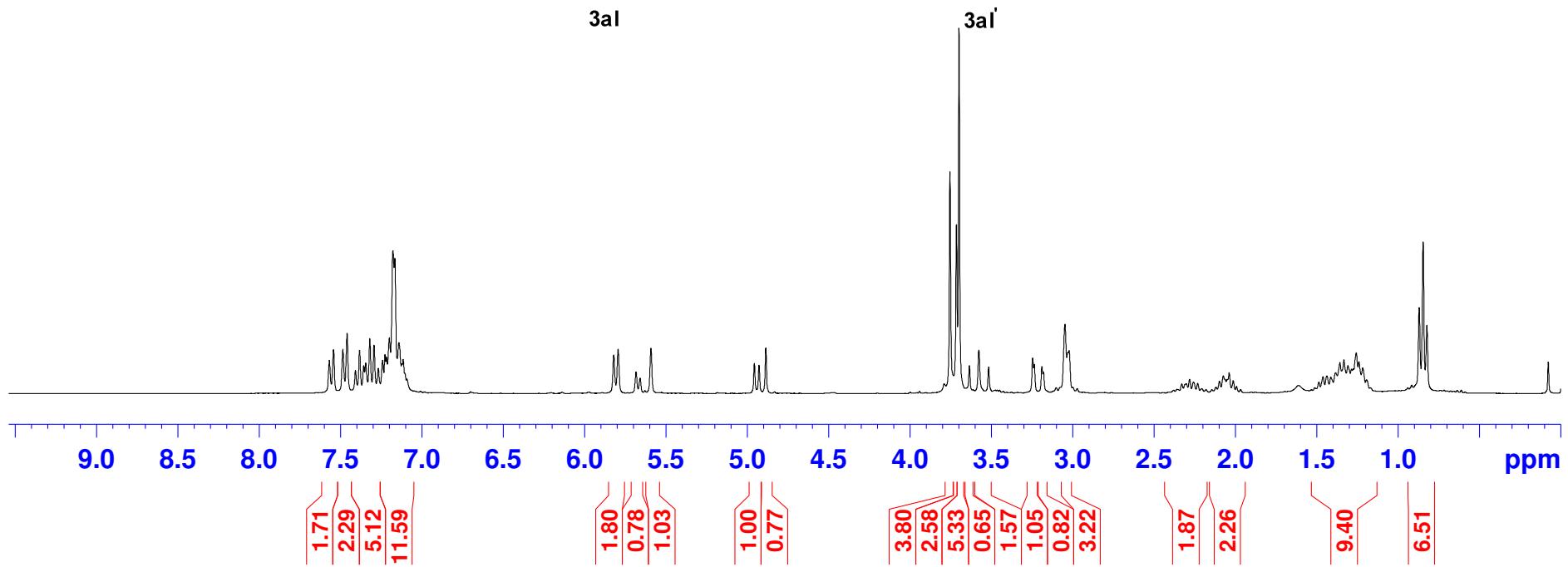
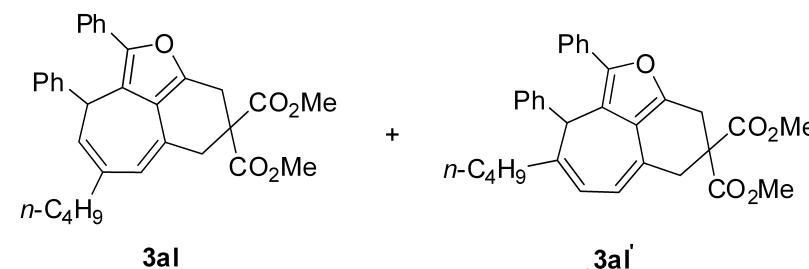


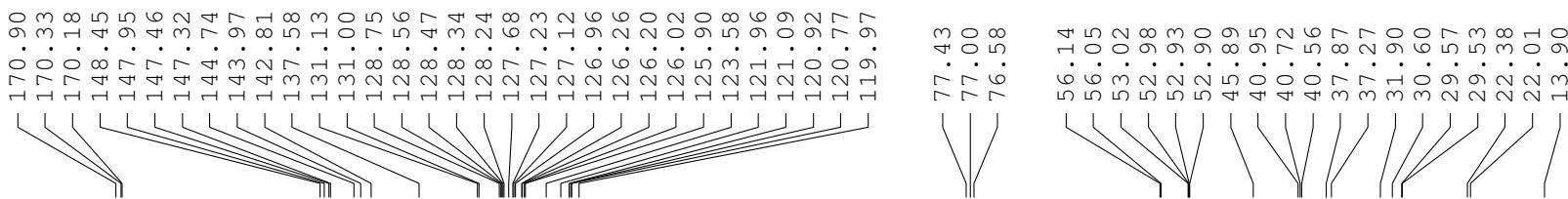
zwx-3-39-1



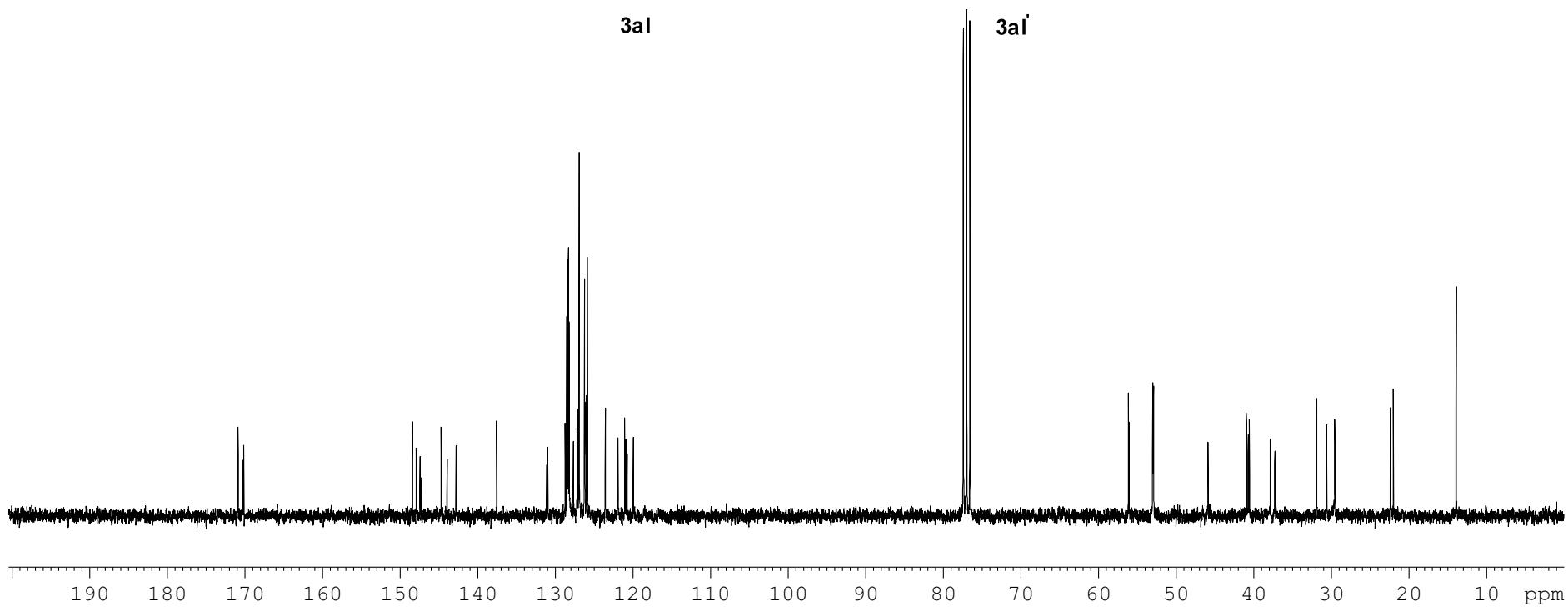
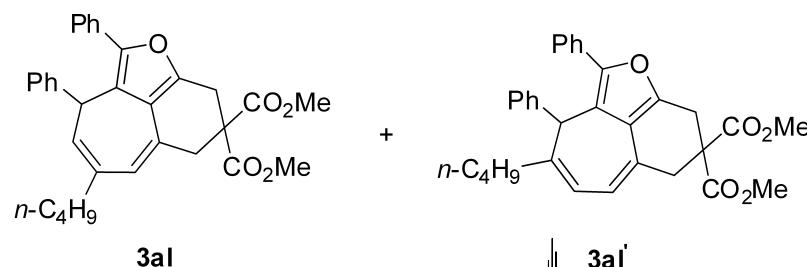


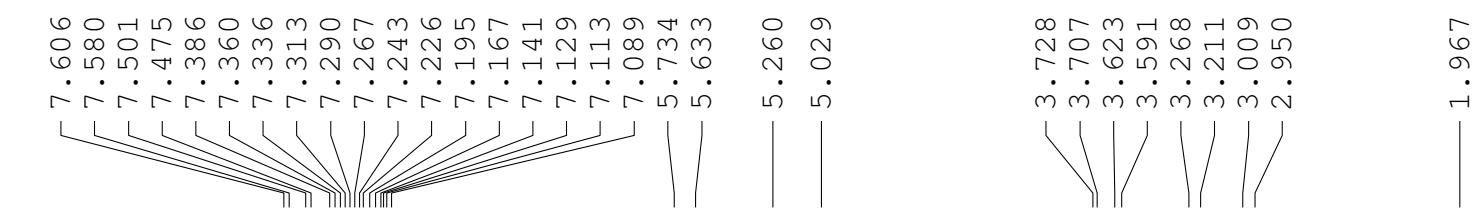
zwx-3-39-2



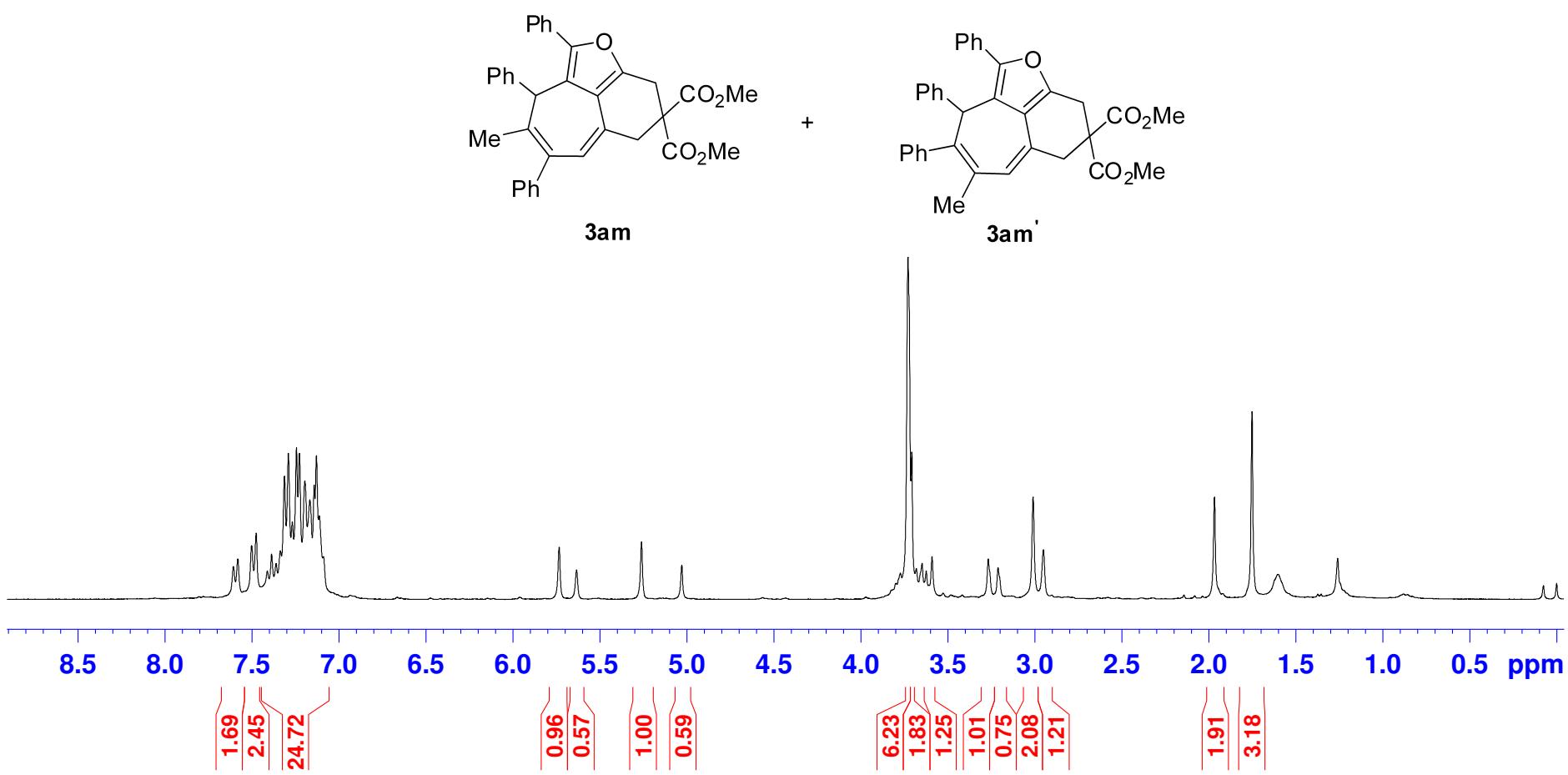


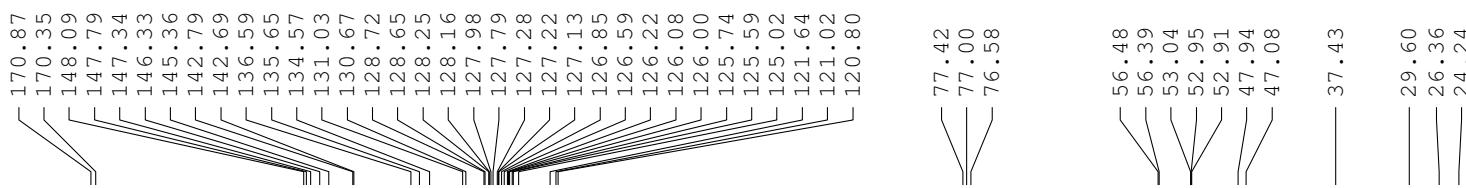
zwx-3-39-2





zwx-3-79





zwx-3-79

