

## Electronic Supplementary Information

# **Construction of polycyclic bridged indene derivatives by a tandem 1,3-rearrangement/intramolecular Friedel-Crafts cyclization of propargyl acetates**

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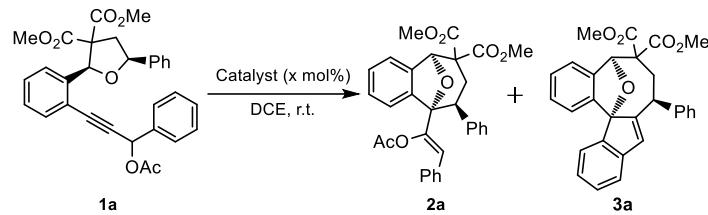
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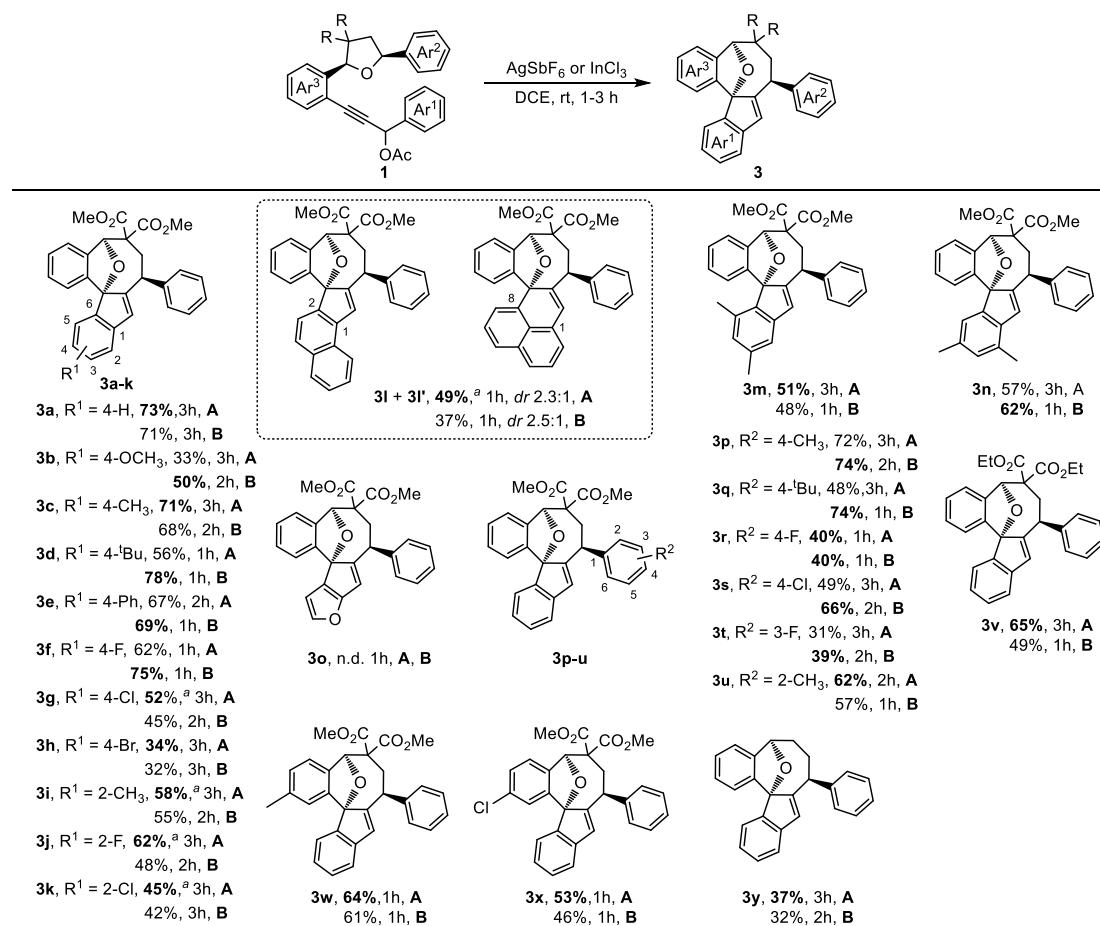
**I. Table S1 Optimization of the reaction condition for **3a****



Entry	Catalyst (x mol%)	2a/%	3a/%
1	IPrAuCl (5 %) + AgSbF <sub>6</sub> (5 %)	24	13
2	SIPrAuCl (5 %) + AgSbF <sub>6</sub> (5 %)	10	30
3	IMesAuCl (5 %) + AgSbF <sub>6</sub> (5 %)	10	54
4	SIMesAuCl (5 %) + AgSbF <sub>6</sub> (5 %)	3	61
5	PPh <sub>3</sub> AuCl (5 %) + AgSbF <sub>6</sub> (5 %)	-	52
<b>6</b>	<b>AgSbF<sub>6</sub> (5 %)</b>	-	<b>73<sup>b</sup></b>
7	Cu(OTf) <sub>2</sub> (20 %)	-	36
8	Zn(OTf) <sub>2</sub> (20 %)	-	19
9	Sn(OTf) <sub>2</sub> (20 %)	-	28
10	Sc(OTf) <sub>3</sub> (20 %)	-	41
11	Yb(OTf) <sub>3</sub> (20 %)	-	31
12	Fe(OTf) <sub>3</sub> (20 %)	-	20
<b>13</b>	<b>InCl<sub>3</sub> (20 %)</b>	-	<b>71<sup>b</sup></b>
14	AgSbF <sub>6</sub> (2 %)	-	64
15	AgSbF <sub>6</sub> (10 %)	-	65
16	AgBF <sub>4</sub> (5 %)	-	56
17	AgNTf <sub>2</sub> (5 %)	-	69
18	TfOH (20 %)	-	30

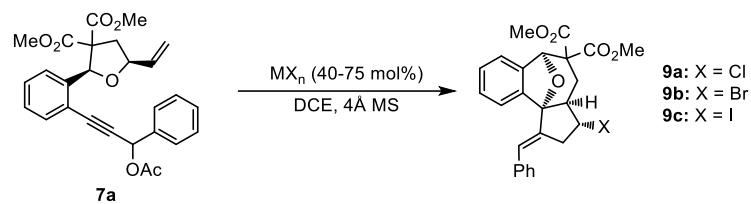
<sup>a</sup> Unless other noted, the reaction was performed in air by using 20 mol% catalysts at r.t. for 1-3 h, **1a** (0.1 mmol), [1a] = 0.1 M. <sup>b</sup> Isolated yield.

**II. Table S2 Substrate scope for the synthesis of 3**



Condition A:  $\text{AgSbF}_6$  (5 mol%); Condition B:  $\text{InCl}_3$  (20 mol%). The reaction was performed at r.t. for 1-3 h; **1** (0.1 mmol), **[1]** = 0.1 M; isolated yield. <sup>a</sup> 2 mol%  $\text{AgSbF}_6$  was used.

### III. Table S3 Optimization of the reaction condition for 9



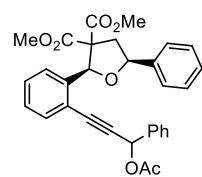
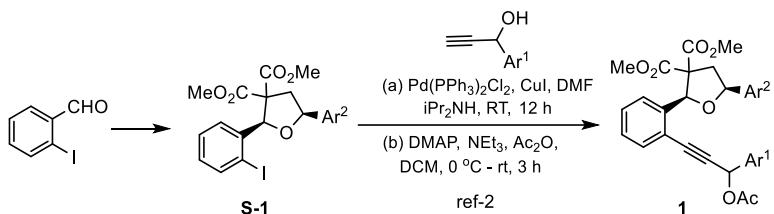
Entry	MX <sub>n</sub> /%	T/°C	t/h	9/%
1	InCl <sub>3</sub> (50 %)	r.t.	12	29 ( <b>9a</b> )
2	FeCl <sub>2</sub> (75 %)	r.t.	12	n.r.
3	NiCl <sub>2</sub> (75 %)	r.t.	12	n.r.
4	CuCl (150 %)	r.t.	12	n.r.
5	CrCl <sub>2</sub> (75 %)	50	12	n.r.
6	PdCl <sub>2</sub> (75 %)	50	12	n.r.
7	ZrCl <sub>4</sub> (40 %)	r.t.	0.5	n.d.
8	CdCl <sub>2</sub> (75 %)	50	12	n.r.
9	CoCl <sub>2</sub> (75 %)	50	12	trace ( <b>9a</b> )
10	ZnCl <sub>2</sub> (75 %)	50	24	18 ( <b>9a</b> )
11	InCl <sub>3</sub> (50 %)	0	12	n.r.
12	MgBr <sub>2</sub> (75 %)	r.t.	12	trace ( <b>9b</b> )
13	MnBr <sub>2</sub> (75 %)	50	12	5 ( <b>9b</b> )
14	ZnBr <sub>2</sub> (75 %)	r.t.	12	34 ( <b>9b</b> )
15 <sup>a</sup>	ZnBr <sub>2</sub> (20 %)	r.t.	12	n.r.
16 <sup>a</sup>	ZnBr <sub>2</sub> (20 %)	40	12	n.r.
17	ZnI <sub>2</sub> (75 %)	r.t.	12	35 ( <b>9c</b> )

Unless other noted, the reaction was performed under N<sub>2</sub> at r.t. by adding 100 mg 4 Å MS, **7a** (0.1 mmol), [7a] = 0.1 M; isolated yield. <sup>a</sup>1.5 equiv. of KBr was used as additive.

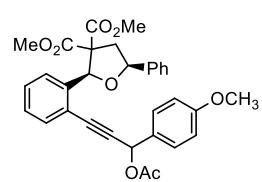
## IV. Supplemental experimental procedures

### 1. General information

The substrates **S-1**<sup>1</sup> were synthesized according to the literature. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz or 500 MHz for <sup>1</sup>H; 100 MHz for <sup>13</sup>C; 376 MHz for <sup>19</sup>F), <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts were determined relative to internal standard TMS at  $\delta$  0.0. Chemical shifts ( $\delta$ ) are reported in ppm, and coupling constants ( $J$ ) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra were obtained using ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

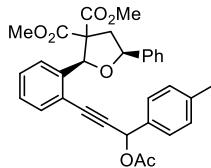


Compound **1a** (1:0.83 diasteromer):  $R_f$  = 0.35 (EtOAc/petroleum ether = 1/5), The following data are for a mixture of two diastereomers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d,  $J$  = 6.9 Hz, 2H), 7.54 – 7.47 (m, 3H), 7.42 (dd,  $J$  = 19.1, 8.1 Hz, 6H), 7.32 (t,  $J$  = 7.2 Hz, 2H), 7.21 (d,  $J$  = 7.3 Hz, 1H), 6.81 and 6.79 (d,  $J$  = 9.2 Hz, 1H), 6.52 and 6.45 (d,  $J$  = 28.1 Hz, 1H), 5.02 (d,  $J$  = 11.1 Hz, 1H), 3.77 and 3.69 (d,  $J$  = 32.4 Hz, 3H), 3.12 and 3.09 (d,  $J$  = 8.5 Hz, 3H), 3.02 (t,  $J$  = 12.5 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.17 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.94 and 170.91, 169.88 and 169.86, 168.81 and 168.79, 140.92 and 140.80, 139.38 and 139.35, 137.29 and 137.25, 132.14 and 132.05, 128.90, 128.69, 128.64, 128.59, 128.12 and 128.11, 128.01, 127.96, 127.51 and 127.49, 126.27, 121.75 and 121.68, 90.6 and 90.51, 84.73 and 84.69, 81.77 and 81.70, 79.62, 66.28 and 66.25, 66.13 and 66.12, 53.15 and 53.13, 53.06 and 53.03, 52.09 and 52.05, 42.93 and 42.85, 21.21. IR (KBr)  $\nu_{max}$  3816, 3704, 3520, 3498, 2952, 1735, 1451, 1226, 1052, 760, 699 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>31</sub>H<sub>28</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 473.1571; Found: 535.1729.

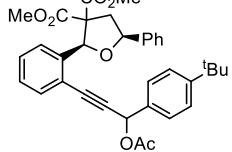


Compound **1b** (1:0.77 diasteromer):  $R_f$  = 0.30 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (d,  $J$  = 8.6 Hz, 2H), 7.52 (dd,  $J$  = 12.8, 5.9 Hz, 3H), 7.44 (d,  $J$  = 7.6 Hz, 1H), 7.39 (t,  $J$  = 7.3 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.22 (t,  $J$  = 7.5 Hz, 1H), 6.93 (d,  $J$  = 8.6 Hz, 2H), 6.76 and 6.74 (d,  $J$  = 6.3 Hz, 1H), 6.51 and 6.44 (d,  $J$  = 27.6 Hz, 1H), 5.02 (m, 1H), 3.81 (s, 3H), 3.79 and 3.71 (d,  $J$  = 31.9 Hz, 3H), 3.13 and 3.11 (d,  $J$  = 7.5 Hz, 3H), 3.05 – 2.98 (m, 1H), 2.64 (dt,  $J$  = 13.3, 5.1 Hz, 1H), 2.14 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.95 and 170.91, 169.93 and 169.90, 168.79 and 168.77, 160.10, 140.88 and 140.76, 139.40 and 139.37, 132.13 and 132.06, 129.58, 129.54 and 129.49, 128.62 and 128.56, 128.09 and 128.07, 127.91, 127.51 and 127.49, 126.25 and 126.24, 121.84 and 121.77, 113.97,

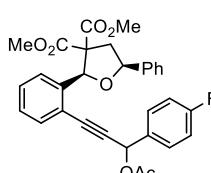
90.82 and 90.74, 84.53 and 84.47, 81.80 and 81.74, 79.62, 66.30 and 66.27, 65.87, 55.36 and 55.34, 53.13 and 53.10, 53.03 and 53.01, 52.07 and 52.03, 42.93 and 42.85, 21.22 and 21.21. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 2952, 1736, 1513, 1453, 1369, 1256, 1227, 1174, 1093, 1053, 1015, 948, 834, 759, 702, 568 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>32</sub>H<sub>30</sub>NaO<sub>8</sub> [M + Na]<sup>+</sup>: 565.1833; Found: 565.1837.



Compound **1c** (1:0.88 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.55 (m, 5H), 7.51 (d, J = 7.3 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 7.29 – 7.25 (m, 3H), 6.85 and 6.83 (d, J = 8.1 Hz, 1H), 6.60 and 6.52 (d, J = 28.5 Hz, 1H), 5.12 – 5.06 (m, 1H), 3.85 and 3.77 (d, J = 33.9 Hz, 3H), 3.19 and 3.17 (d, J = 8.8 Hz, 3H), 3.13 – 3.05 (m, 1H), 2.71 (dt, J = 13.3, 5.2 Hz, 1H), 2.42 (s, 3H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.96 and 170.93, 169.87 and 169.84, 168.82 and 168.78, 140.95 and 140.82, 139.46 and 139.42, 138.80, 134.46 and 134.40, 132.12 and 132.07, 129.33 and 129.31, 128.64, 128.59, 128.12 and 128.10, 128.04 and 127.99, 127.93, 127.53 and 127.51, 126.28 and 126.26, 121.87 and 121.80, 90.85 and 90.77, 84.58 and 84.52, 81.83 and 81.77, 79.63, 66.31 and 66.29, 66.06 and 66.03, 53.12 and 53.11, 53.02 and 53.01, 52.07 and 52.03, 42.98 and 42.91, 21.28 and 21.21. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 3464, 2952, 1741, 1489, 1451, 1368, 1273, 1093, 1053, 1016, 949, 909, 847, 816, 758, 567, 503 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>32</sub>H<sub>30</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 549.1884; Found: 549.1888.

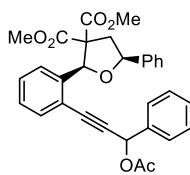


Compound **1d** (1:0.85 diasteromer): R<sub>f</sub> = 0.37 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, J = 8.3 Hz, 2H), 7.51 (td, J = 9.0, 3.5 Hz, 3H), 7.46 – 7.41 (m, 3H), 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 6.79 and 6.72 (d, J = 5.8 Hz, 1H), 6.53 and 6.45 (d, J = 29.4 Hz, 1H), 5.02 (dt, J = 11.5, 4.4 Hz, 1H), 3.78 and 3.70 (d, J = 33.2 Hz, 3H), 3.12 and 3.10 (d, J = 9.5 Hz, 3H), 3.05 – 2.98 (m, 1H), 2.64 (m, 1H), 2.16 and 2.15 (d, J = 1.0 Hz, 3H), 1.33 and 1.32 (d, J = 1.2 Hz, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.95 and 170.91, 169.90 and 169.86, 168.83 and 168.79, 151.97 and 151.94, 140.91 and 140.79, 139.45 and 139.41, 134.31 and 134.27, 132.14 and 132.06, 128.61, 128.57, 128.09 and 128.08, 127.90, 127.82 and 127.76, 127.51 and 127.48, 126.27 and 126.25, 125.58, 121.88 and 121.81, 90.83 and 90.74, 84.57 and 84.50, 81.83 and 81.76, 79.62, 66.30 and 66.28, 65.96, 53.10 and 53.09, 53.02 and 53.00, 52.06 and 52.02, 42.96 and 42.89, 34.70, 31.36, 21.22. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 2952, 1737, 1452, 1368, 1272, 1227, 1093, 1054, 1016, 949, 759, 701, 579 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>35</sub>H<sub>36</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 591.2353; Found: 591.2349.

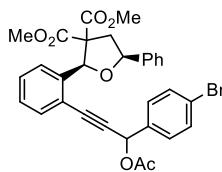


Compound **1e** (1:0.9 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (dd, J = 8.4, 5.5 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.44 (d, J = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 (tt, J = 5.5, 2.1 Hz, 2H), 7.21 (dd, J = 7.5, 1.0 Hz, 1H), 7.09 (t, J = 8.6 Hz, 2H), 6.78 and 6.76 (d, J = 7.5 Hz, 1H), 6.50 and 6.44 (d, J = 25.6 Hz, 1H), 5.01 (dt, J = 11.6, 4.2 Hz, 1H), 3.759 and 3.71 (d, J = 30.7 Hz, 3H), 3.11 and 3.10 (d, J = 4.5 Hz, 3H), 3.02 (t, J = 12.5 Hz, 1H), 2.63 (dt, J = 13.3, 4.4 Hz, 1H), 2.15 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.93 and 170.89, 169.77 and 169.74, 168.71 and 168.69, 162.99 (d, J = 247.7 Hz), 140.94 and 140.85, 139.34 and 139.31, 133.29 (d, J = 3.0 Hz) and 133.26 (d, J = 3.3 Hz),

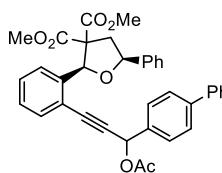
132.15 and 132.06, 130.03 (d,  $J = 5.0$  Hz) and 129.94 (d,  $J = 5.0$  Hz), 128.77 and 128.74, 128.58, 128.12 and 128.11, 127.96, 127.59 and 127.57, 126.25 and 126.23, 121.59 and 121.54, 115.63 and 115.42, 90.33 and 90.25, 84.91 and 84.87, 81.75 and 81.69, 79.63, 66.30 and 66.28, 65.46, 53.11 and 53.08, 53.01 and 52.99, 52.07 and 52.04, 42.89 and 42.81, 21.13 and 21.12.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.71, -112.74. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 2953, 1736, 1511, 1369, 1272, 1224, 1094, 1054, 1016, 760, 702  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{31}\text{H}_{27}\text{FNaO}_7$  [ $\text{M} + \text{Na}$ ] $^+$ : 553.1633; Found: 553.1639.



Compound **1f** (1:0.87 diasteromer):  $R_f$  = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 8.1$  Hz, 2H), 7.51 (dd,  $J = 14.0, 5.3$  Hz, 3H), 7.44 (d,  $J = 7.6$  Hz, 1H), 7.38 (t,  $J = 6.5$  Hz, 4H), 7.33 (t,  $J = 5.7$  Hz, 2H), 7.20 (d,  $J = 7.5$  Hz, 1H), 6.77 and 6.75 (d,  $J = 8.9$  Hz, 1H), 6.50 and 6.43 (d,  $J = 24.8$  Hz, 1H), 5.01 (dd,  $J = 11.7, 4.1$  Hz, 1H), 3.78 and 3.70 (d,  $J = 31.4$  Hz, 3H), 3.11 and 3.10 (d,  $J = 4.4$  Hz, 3H), 3.02 (t,  $J = 12.5$  Hz, 1H), 2.63 (dt,  $J = 13.3, 4.6$  Hz, 1H), 2.15 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.92 and 170.89, 169.74 and 169.72, 168.70 and 168.68, 140.97 and 140.88, 139.33 and 139.30, 135.90 and 135.87, 134.79 and 134.78, 132.15 and 132.06, 129.47, 129.40, 128.83 and 128.81, 128.59, 128.14 and 128.13, 127.99, 127.60 and 127.58, 126.26 and 126.24, 121.52 and 121.47, 90.11 and 90.04, 85.04 and 85.00, 81.74 and 81.67, 79.64, 66.30 and 66.28, 65.44, 53.14 and 53.12, 53.04 and 53.02, 52.09 and 52.06, 42.89 and 42.82, 21.12 and 21.11  $\text{cm}^{-1}$ . **IR (KBr)**  $\nu_{\text{max}}$  3744, 3522, 3497, 3464, 2952, 1736, 1490, 1435, 1369, 1271, 1225, 1171, 1092, 950, 825, 758, 605, 547  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{31}\text{H}_{27}\text{ClNaO}_7$  [ $\text{M} + \text{Na}$ ] $^+$ : 569.1338; Found: 569.1343.

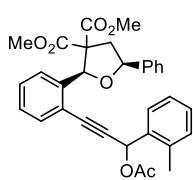


Compound **1g** (1:0.92 diasteromer):  $R_f$  = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.48 (m, 7H), 7.43 (d,  $J = 7.6$  Hz, 1H), 7.38 (t,  $J = 7.5$  Hz, 2H), 7.32 (m, 2H), 7.21 (d,  $J = 7.1$  Hz, 1H), 6.75 and 6.73 (d,  $J = 9.2$  Hz, 1H), 6.49 and 6.42 (d,  $J = 24.8$  Hz, 1H), 5.00 (dd,  $J = 11.6, 4.2$  Hz, 1H), 3.78 and 3.71 (d,  $J = 31.2$  Hz, 3H), 3.11 and 3.10 (d,  $J = 4.5$  Hz, 3H), 3.06 – 2.98 (m, 1H), 2.63 (dt,  $J = 13.3, 4.7$  Hz, 1H), 2.16 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.90 and 170.88, 169.71 and 169.69, 168.69 and 168.67, 140.97 and 140.88, 139.33 and 139.29, 136.40 and 136.38, 132.15 and 132.05, 131.79 and 131.77, 129.75 and 129.68, 128.82 and 128.79, 128.58, 128.12 and 128.11, 127.97, 127.60 and 127.58, 126.25 and 126.24, 123.01, 121.51 and 121.46, 90.02 and 89.95, 85.05 and 85.02, 81.73 and 81.66, 79.63, 66.29 and 66.27, 65.48, 53.13 and 53.11, 53.03 and, 53.02, 52.09 and 52.05, 42.89 and 42.81, 21.11. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3494, 2952, 1736, 1487, 1453, 1370, 1270, 1226, 1172, 1094, 1052, 1014, 950, 841, 758, 701, 571, 545  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{31}\text{H}_{27}\text{BrNaO}_7$  [ $\text{M} + \text{Na}$ ] $^+$ : 613.0832; Found: 613.0836.

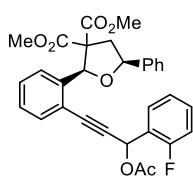


Compound **1h** (1:0.86 diasteromer):  $R_f$  = 0.40 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 7.7$  Hz, 2H), 7.63 (d,  $J = 7.8$  Hz, 2H), 7.59 (d,  $J = 7.5$  Hz, 2H), 7.52 (dd,  $J = 17.4, 7.0$  Hz, 3H), 7.47 – 7.41 (m, 3H), 7.35 (dd,  $J = 16.8, 7.5$  Hz, 5H), 7.21 (d,  $J = 5.4$  Hz, 1H), 6.86 and 6.84 (d,  $J = 7.9$  Hz, 1H), 6.55 and 6.48 (d,  $J = 27.4$  Hz, 1H), 5.06 – 4.98 (m, 1H), 3.79 and 3.70 (d,  $J = 35.2$  Hz, 3H), 3.13 and 3.11 (d,  $J = 7.4$  Hz, 3H), 3.03 (t,  $J = 12.5$  Hz, 1H), 2.64 (dt,  $J = 11.7, 4.9$  Hz, 1H), 2.18 (s, 3H).  **$^{13}\text{C}$  NMR**

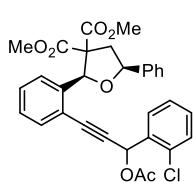
(100 MHz, CDCl<sub>3</sub>) δ 170.98 and 170.95, 169.93 and 169.91, 168.84 and 168.81, 141.89, 140.97 and 140.86, 140.62 and 140.57, 139.41 and 139.37, 136.29 and 136.25, 132.17 and 132.10, 128.90, 128.74 and 128.71, 128.61, 128.55 and 128.47, 128.15 and 128.13, 127.98, 127.64 and 127.62, 127.56 and 127.55, 127.43 and 127.41, 127.21 and 127.19, 126.30 and 126.29, 121.77 and 121.71, 90.60 and 90.51, 84.88 and 84.82, 81.83 and 81.76, 79.66, 66.33 and 66.30, 65.96, 53.18 and 53.16, 53.07 and 53.06, 52.14 and 52.10, 42.98 and 42.90, 21.25. **IR (KBr)** ν<sub>max</sub> 3744, 3521, 3497, 3031, 2952, 1735, 1487, 1453, 1368, 1271, 1225, 1093, 1053, 1015, 949, 846, 760, 700, 625, 573, 521 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>37</sub>H<sub>32</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup> : 611.2040; Found: 611.2046.



Compound **1i** (1:0.9 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 – 7.78 (m, 1H), 7.57 (dd, J = 11.7, 4.4 Hz, 3H), 7.49 – 7.41 (m, 3H), 7.34 (dtd, J = 19.9, 7.2, 2.8 Hz, 4H), 7.26 (dd, J = 8.8, 5.3 Hz, 2H), 6.97 and 6.95 (d, J = 6.9 Hz, 1H), 6.57 and 6.48 (d, J = 33.5 Hz, 1H), 5.07 (dt, J = 10.9, 5.1 Hz, 1H), 3.84 and 3.75 (d, J = 37.3 Hz, 3H), 3.17 and 3.14 (d, J = 11.9 Hz, 3H), 3.11 – 3.03 (m, 1H), 2.68 (m, 1H), 2.56 and 2.55 (d, J = 1.6 Hz, 3H), 2.23 and 2.22 (d, J = 2.0 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.90 and 170.86, 169.73 and 169.72, 168.82 and 168.77, 140.89 and 140.75, 139.43 and 139.41, 136.42 and 136.41, 135.32 and 135.30, 132.11 and 132.06, 130.77 and 130.72, 128.94 and 128.91, 128.60, 128.57, 128.50 and 128.47, 128.09 and 128.08, 127.90, 127.51, 126.26, 126.23, 121.90 and 121.82, 90.58 and 90.50, 84.61 and 84.55, 81.78 and 81.69, 79.60, 66.28 and 66.26, 64.18, 53.09 and 53.07, 52.98 and 52.95, 52.03 and 52.00, 42.87, 21.07 and 21.06, 19.13. **IR (KBr)** ν<sub>max</sub> 3744, 3522, 3497, 2952, 1741, 1490, 1453, 1369, 1273, 1229, 1093, 1053, 1016, 950, 758, 701, 571 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>32</sub>H<sub>30</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup> : 549.1884; Found: 549.1887.

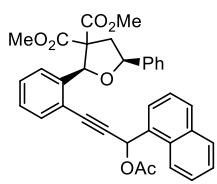


Compound **1j** (0.92:1 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (t, J = 7.5 Hz, 1H), 7.56 (m, 3H), 7.52 – 7.47 (m, 1H), 7.45 – 7.34 (m, 5H), 7.25 (d, J = 7.5 Hz, 2H), 7.17 – 7.11 (m, 1H), 7.08 and 7.07 (d, J = 6.8 Hz, 1H), 6.56 and 6.47 (d, J = 35.1 Hz, 1H), 5.06 (m, 1H), 3.80 (d, J = 25.4 Hz, 3H), 3.16 (d, J = 7.2 Hz, 3H), 3.06 (t, J = 13.6 Hz, 1H), 2.68 (dd, J = 13.3, 4.8 Hz, 1H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.88 and 170.86, 169.44, 168.77 and 168.75, 160.29 (d, J = 254.7 Hz), 140.97 and 140.85, 139.38 and 139.36, 132.24 and 132.13, 130.89 (d, J = 2.6 Hz) and 130.80 (d, J = 2.6 Hz), 130.06 and 130.03, 128.77 and 128.74, 128.57, 128.10 and 128.08, 127.95 and 127.94, 127.53 and 127.51, 126.25 and 126.23, 124.56, 124.39 (d, J = 6.3 Hz) and 124.30 (d, J = 4.4 Hz), 121.59 and 121.53, 115.75 (d, J = 1.8 Hz) and 115.54 (d, J = 1.9 Hz), 89.54 and 89.42, 84.83 and 84.77, 81.74 and 81.66, 79.61, 66.27, 60.39 and 60.33, 60.31 and 60.26, 53.11 and 53.09, 53.03 and 53.02, 52.06 and 52.03, 42.85 and 42.77, 20.98. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -117.37, -117.40. **IR (KBr)** ν<sub>max</sub> 3743, 3521, 3497, 3464, 2953, 1736, 1589, 1492, 1454, 1272, 1234, 1172, 1094, 1052, 956, 912, 759, 605, 531 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>27</sub>FNaO<sub>7</sub> [M + Na]<sup>+</sup> : 553.1633; Found: 553.1639.

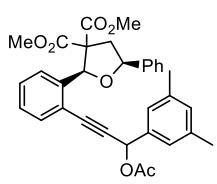


Compound **1k** (1:0.81 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, J = 7.3 Hz, 1H), 7.56 (dt, J = 11.8, 5.7 Hz, 3H), 7.52 – 7.48 (m, 1H), 7.41 (m, 7H), 7.26 (d, J = 7.5 Hz, 1H), 7.13 and 7.11 (d, J = 7.7 Hz,

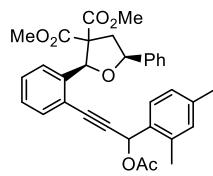
1H), 6.57 and 6.49 (d,  $J = 32.7$  Hz, 1H), 5.07 (m, 1H), 3.83 and 3.77 (d,  $J = 25.7$  Hz, 3H), 3.17 (s, 3H), 3.06 (td,  $J = 12.6, 4.0$  Hz, 1H), 2.68 (dd,  $J = 13.3, 4.5$  Hz, 1H), 2.22 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.87, 169.44, 168.75 and 168.74, 140.96 and 140.85, 139.39 and 139.36, 134.62 and 134.57, 133.61 and 133.57, 132.30 and 132.19, 130.28 and 130.13, 129.75, 128.78 and 128.76, 128.58, 128.11 and 128.09, 127.97, 127.56 and 127.53, 127.17 and 127.11, 126.25, 126.23, 121.62 and 121.56, 89.59 and 89.49, 85.11 and 85.04, 81.73 and 81.67, 79.62, 66.30, 63.45 and 63.39, 53.15 and 53.13, 53.06 and 53.03, 52.08, 42.83 and 42.74, 20.92. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 1497, 3464, 1953, 1738, 1480, 1440, 1369, 1335, 1272, 1222, 1170, 1093, 1052, 1017, 956, 912, 758, 625, 570  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{31}\text{H}_{27}\text{ClNaO}_7$  [M + Na]<sup>+</sup>: 569.1338; Found: 569.1340.



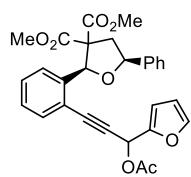
Compound **1l** (1:0.88 diasteromer):  $R_f = 0.37$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 and 8.33 (d,  $J = 8.4$  Hz, 1H), 7.96 and 7.95 (d,  $J = 7.1$  Hz, 1H), 7.87 and 7.85 (d,  $J = 7.8$  Hz, 2H), 7.59 – 7.47 (m, 6H), 7.45 – 7.34 (m, 4H), 7.29 (t,  $J = 7.5$  Hz, 2H), 7.17 and 7.15 (d,  $J = 7.4$  Hz, 1H), 6.57 and 6.46 (d,  $J = 47.2$  Hz, 1H), 5.00 (m, 1H), 3.74 and 3.65 (d,  $J = 39.0$  Hz, 3H), 3.08 and 3.02 (d,  $J = 8.8$  Hz, 3H), 3.02 (d,  $J = 24.8$  Hz, 1H), 2.63 (d,  $J = 13.1$  Hz, 1H), 2.15 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.97 and 170.95, 169.96, 168.93 and 168.84, 140.96 and 140.76, 139.47 and 139.44, 134.13 and 134.08, 132.65 and 132.61, 132.17 and 132.13, 130.84 and 130.79, 130.00 and 129.95, 128.91 and 128.89, 128.73, 128.64, 128.17 and 128.16, 128.00, 127.56, 127.05 and 126.97, 126.70 and 126.67, 126.32, 126.06 and 126.04, 125.35 and 125.33, 124.00 and 123.98, 121.92 and 121.81, 90.77 and 90.64, 85.36 and 85.26, 81.87 and 81.78, 79.66, 66.35 and 66.33, 64.64 and 64.52, 53.18 and 53.16, 53.08 and 53.06, 52.15 and 52.07, 42.98, 21.19. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 2952, 1736, 1512, 1435, 1368, 1270, 1223, 1170, 1092, 1052, 1017, 947, 804, 779, 760, 701, 570  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{35}\text{H}_{30}\text{NaO}_7$  [M + Na]<sup>+</sup>: 585.1884; Found: 585.1883.



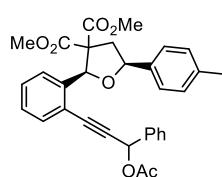
Compound **1m** (0.92:1 diasteromer):  $R_f = 0.37$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.48 (m, 3H), 7.44 (d,  $J = 7.6$  Hz, 1H), 7.38 (t,  $J = 7.3$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.22 (d,  $J = 4.7$  Hz, 3H), 7.00 (s, 1H), 6.75 and 6.72 (d,  $J = 13.9$  Hz, 1H), 6.52 and 6.45 (d,  $J = 27.9$  Hz, 1H), 5.02 (d,  $J = 11.3$  Hz, 1H), 3.78 and 3.69 (d,  $J = 35.2$  Hz, 3H), 3.13 and 3.11 (d,  $J = 9.8$  Hz, 3H), 3.02 (t,  $J = 12.5$  Hz, 1H), 2.63 (dt,  $J = 12.9, 6.2$  Hz, 1H), 2.34 (s, 6H), 2.17 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.93 and 170.90, 169.93 and 169.90, 168.89 and 168.87, 140.87 and 140.75, 139.43 and 139.39, 138.26 and 138.24, 137.10 and 137.07, 132.06 and 132.03, 130.63 and 130.56, 128.59, 128.52, 128.12 and 128.11, 127.93, 127.48 and 127.47, 126.27, 125.77 and 125.75, 121.93 and 121.88, 90.85 and 90.80, 84.53 and 84.45, 81.84 and 81.77, 79.64, 66.30 and 66.26, 66.22 and 66.14, 53.12 and 53.10, 52.99 and 52.96, 52.06, 43.06 and 43.01, 21.32 and 21.27. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 3465, 2952, 1737, 1606, 1486, 1436, 1369, 1331, 1270, 1169, 1093, 1053, 1016, 946, 851, 817, 701, 606, 571, 537  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{33}\text{H}_{32}\text{NaO}_7$  [M + Na]<sup>+</sup>: 563.2040; Found: 563.2042.



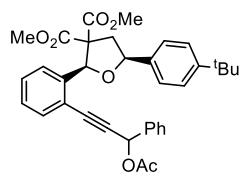
Compound **1n** (1:0.92 diasteromer):  $R_f = 0.37$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 and 7.63 (d,  $J = 7.8$  Hz, 1H), 7.51 (t,  $J = 7.1$  Hz, 3H), 7.39 (q,  $J = 7.8, 7.3$  Hz, 3H), 7.34 – 7.27 (m, 2H), 7.19 (d,  $J = 7.5$  Hz, 1H), 7.05 (dd,  $J = 15.6, 5.6$  Hz, 2H), 6.88 and 6.86 (d,  $J = 6.3$  Hz, 1H), 6.51 and 6.42 (d,  $J = 34.1$  Hz, 1H), 5.01 (dt,  $J = 11.3, 5.5$  Hz, 1H), 3.74 (d,  $J = 37.4$  Hz, 3H), 3.10 (d,  $J = 12.8$  Hz, 3H), 3.01 (t,  $J = 12.5$  Hz, 1H), 2.62 (dt,  $J = 13.3, 3.9$  Hz, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.15 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.93 and 170.88, 169.80 and 169.79, 168.86 and 168.80, 140.86 and 140.71, 139.45 and 139.42, 138.81 and 138.77, 136.31 and 136.28, 132.42 and 132.38, 132.07, 131.58 and 131.52, 128.64 and 128.62, 128.58, 128.51, 128.10 and 128.08, 127.90, 127.48, 126.92 and 126.89, 126.27 and 126.26, 121.98 and 121.90, 90.79 and 90.74, 84.46 and 84.38, 81.80 and 81.71, 79.60, 66.27 and 66.26, 64.12 and 64.09, 53.10 and 53.08, 52.97, 52.05 and 52.02, 42.91, 21.14 and 21.11, 19.05. **IR (KBr)**  $\nu_{max}$  3744, 3522, 3497, 2952, 1736, 1490, 1436, 1271, 1225, 1170, 1093, 1053, 1016, 950, 908, 822, 760, 701, 609, 572, 531 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>33</sub>H<sub>32</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 563.2040; Found: 563.2043.



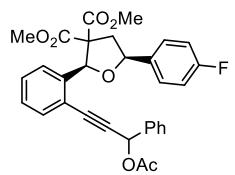
Compound **1o** (1:0.88 diasteromer):  $R_f = 0.36$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 – 7.45 (m, 5H), 7.39 (t,  $J = 7.5$  Hz, 2H), 7.33 (q,  $J = 6.6$  Hz, 2H), 7.22 (d,  $J = 7.5$  Hz, 1H), 6.85 and 6.84 (d,  $J = 3.1$  Hz, 1H), 6.68 (dd,  $J = 8.1, 3.2$  Hz, 1H), 6.49 and 6.43 (d,  $J = 22.9$  Hz, 1H), 6.42 – 6.38 (m, 1H), 5.05 – 4.99 (m, 1H), 3.78 and 3.74 (d,  $J = 22.2$  Hz, 3H), 3.14 and 3.12 (d,  $J = 8.8$  Hz, 3H), 3.02 (t,  $J = 12.5$  Hz, 1H), 2.64 (dt,  $J = 13.3, 5.1$  Hz, 1H), 2.17 and 2.16 (d,  $J = 3.2$  Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.93 and 170.91, 169.68 and 169.63, 168.81 and 168.79, 149.71 and 149.66, 143.55 and 143.49, 141.05 and 140.95, 139.36 and 139.33, 132.27 and 132.15, 128.84 and 128.82, 128.56, 128.10 and 128.09, 127.94, 127.52 and 127.48, 126.26 and 126.25, 121.44 and 121.39, 110.62, 110.31, 88.05 and 87.96, 83.87 and 83.83, 81.78 and 81.73, 79.64, 66.30 and 66.28, 59.13 and 59.08, 53.15 and 53.12, 53.07 and 53.05, 52.09 and 52.05, 42.98 and 42.89, 20.99.



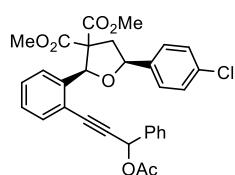
Compound **1p** (1:0.8 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d,  $J = 7.7$  Hz, 2H), 7.52 (dd,  $J = 7.4, 5.1$  Hz, 1H), 7.41 (dt,  $J = 16.2, 8.1$  Hz, 6H), 7.31 (t,  $J = 7.7$  Hz, 1H), 7.21 (t,  $J = 8.3$  Hz, 3H), 6.80 and 6.78 (d,  $J = 8.6$  Hz, 1H), 6.50 and 6.43 (d,  $J = 27.8$  Hz, 1H), 4.98 (dt,  $J = 11.5, 4.0$  Hz, 1H), 3.77 and 3.69 (d,  $J = 32.2$  Hz, 3H), 3.12 and 3.10 (d,  $J = 8.7$  Hz, 3H), 3.05 – 2.97 (m, 1H), 2.60 (dt,  $J = 13.3, 5.0$  Hz, 1H), 2.36 (s, 3H), 2.17 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.97 and 170.94, 169.87 and 169.84, 168.84 and 168.82, 141.00 and 140.88, 137.83 and 137.81, 137.31 and 137.27, 136.32 and 136.29, 132.10 and 132.02, 129.24, 128.86, 128.66, 128.62, 127.99 and 127.95, 127.87, 127.55 and 127.53, 126.28 and 126.27, 121.73 and 121.67, 90.56 and 90.47, 84.76 and 84.72, 81.70 and 81.63, 79.55, 66.30 and 66.27, 66.13, 53.09 and 53.06, 53.00 and 52.98, 52.04 and 52.00, 42.83 and 42.75, 21.18.



Compound **1q** (1:0.77 diasteromer):  $R_f = 0.37$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d,  $J = 7.7$  Hz, 2H), 7.54 (dd,  $J = 7.5, 4.9$  Hz, 1H), 7.42 (p,  $J = 7.5, 6.9$  Hz, 7H), 7.37 – 7.35 (m, 1H), 7.31 (t,  $J = 8.0$  Hz, 1H), 7.19 (d,  $J = 7.4$  Hz, 1H), 6.81 and 6.79 (d,  $J = 9.4$  Hz, 1H), 6.51 and 6.44 (d,  $J = 27.7$  Hz, 1H), 4.99 (dt,  $J = 11.6, 3.9$  Hz, 1H), 3.77 and 3.68 (d,  $J = 34.2$  Hz, 3H), 3.11 and 3.09 (d,  $J = 8.5$  Hz, 3H), 3.08 – 3.01 (m, 1H), 2.60 (dt,  $J = 13.3, 5.0$  Hz, 1H), 2.16 (s, 3H), 1.33 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.01 and 170.98, 169.84 and 169.81, 168.85 and 168.82, 151.11 and 151.09, 141.06 and 140.95, 137.34 and 137.31, 136.29 and 136.26, 132.10 and 132.01, 128.88, 128.64 and 128.63, 128.01, 127.97, 127.88, 127.61 and 127.58, 126.16 and 126.14, 125.50, 121.74 and 121.67, 90.61 and 90.51, 84.80 and 84.76, 81.75 and 81.67, 79.54, 66.33 and 66.31, 66.14, 53.11 and 53.09, 53.02 and 52.99, 52.03 and 51.99, 42.77 and 42.69, 34.62, 31.41, 21.19. **IR (KBr)**  $\nu_{\text{max}}$  3725, 3521, 1497, 2957, 1736, 1488, 1453, 1368, 1271, 1225, 1171, 1061, 949, 834, 762, 737, 699, 577 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>35</sub>H<sub>36</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 591.2353; Found: 591.2357.

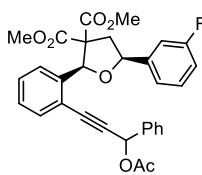


Compound **1r** (1:0.8 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 and 7.68 (d,  $J = 7.6$  Hz, 2H), 7.51 (dt,  $J = 12.6, 5.4$  Hz, 4H), 7.44 (q,  $J = 9.4, 8.5$  Hz, 3H), 7.36 (t,  $J = 7.8$  Hz, 1H), 7.25 (d,  $J = 7.5$  Hz, 1H), 7.11 (t,  $J = 8.5$  Hz, 2H), 6.85 and 6.83 (d,  $J = 9.4$  Hz, 1H), 6.53 and 6.46 (d,  $J = 29.4$  Hz, 1H), 5.02 (dt,  $J = 11.3, 4.1$  Hz, 1H), 3.77 (d,  $J = 34.1$  Hz, 3H), 3.15 (d,  $J = 9.4$  Hz, 3H), 3.06 – 2.98 (m, 1H), 2.65 (dt,  $J = 13.3, 5.0$  Hz, 1H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.84 and 170.81, 169.83 and 169.81, 168.78 and 168.74, 162.56 (d,  $J = 246.5$  Hz), 140.71 and 140.57, 137.27 and 137.24, 135.16 (d,  $J = 3.6$  Hz) and 135.12 (d,  $J = 3.2$  Hz), 132.19 and 132.11, 128.88, 128.66, 128.62 (d,  $J = 1.4$  Hz), 128.07, 127.99, 127.97, 127.93, 127.39 and 127.36, 121.80 and 121.73, 115.45 (d,  $J = 21.5$  Hz), 90.66 and 90.56, 84.68 and 84.63, 81.83 and 81.75, 78.99, 66.20 and 66.18, 66.09, 53.12 and 53.10, 53.03 and 53.01, 52.10 and 52.05, 42.98 and 42.90, 21.17 and 21.16. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -114.14, -114.17. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 3464, 2953, 1737, 1604, 1512, 1436, 1272, 1054, 1016, 941, 836, 762, 737, 700, 630, 569, 518 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>27</sub>FN<sub>7</sub> [M + Na]<sup>+</sup>: 553.1633; Found: 553.1635.

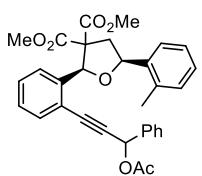


Compound **1s** (1:1 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 and 7.63 (d,  $J = 7.2$  Hz, 2H), 7.45 (dd,  $J = 17.1, 8.5$  Hz, 4H), 7.40 (d,  $J = 7.6$  Hz, 2H), 7.38 – 7.29 (m, 4H), 7.21 (d,  $J = 7.5$  Hz, 1H), 6.81 and 6.78 (d,  $J = 8.9$  Hz, 1H), 6.50 and 6.43 (d,  $J = 29.0$  Hz, 1H), 5.02 – 4.95 (m, 1H), 3.78 and 3.69 (d,  $J = 33.8$  Hz, 3H), 3.11 (d,  $J = 9.1$  Hz, 3H), 2.96 (t,  $J = 12.4$  Hz, 1H), 2.63 (dt,  $J = 13.1, 4.8$  Hz, 1H), 2.16 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.79 and 170.77, 169.83 and 169.81, 168.69 and 168.65, 140.67 and 140.53, 138.03 and 137.99, 137.26 and 137.22, 133.79 and 133.77, 132.21 and 132.13, 128.90, 128.75, 128.69, 128.65 and 128.63, 128.03, 127.97 and 127.93, 127.62, 127.39 and 127.37, 121.79 and 121.72, 90.71 and 90.61, 84.67 and 84.62, 81.89 and 81.82, 78.89, 66.19 and 66.18, 66.10, 53.17 and 53.14, 53.08 and 53.06, 52.13 and 52.09, 42.86 and 42.78, 21.18 and 21.16. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 3033, 2952, 1735, 1594, 1491, 1369, 1273, 1226, 1171, 1089, 1055, 1015, 949, 907, 824, 762, 699, 636, 568 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>27</sub>ClNaO<sub>7</sub> [M + Na]<sup>+</sup>:

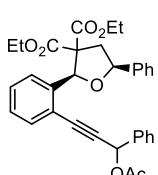
569.1338; Found: 569.1342.



Compound **1t** (1:0.79 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (d,  $J = 7.6$  Hz, 2H), 7.51 (dd,  $J = 13.3, 7.9$  Hz, 2H), 7.41 (dq,  $J = 21.4, 7.1$  Hz, 5H), 7.26 (d,  $J = 6.4$  Hz, 3H), 7.05 (t,  $J = 8.3$  Hz, 1H), 6.85 and 6.82 (d,  $J = 9.7$  Hz, 1H), 6.55 and 6.48 (d,  $J = 28.9$  Hz, 1H), 5.04 (dt,  $J = 11.3, 4.0$  Hz, 1H), 3.82 and 3.74 (d,  $J = 33.0$  Hz, 3H), 3.16 and 3.14 (d,  $J = 9.1$  Hz, 3H), 3.04 – 2.96 (m, 1H), 2.68 (dt,  $J = 13.2, 4.9$  Hz, 1H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.78 and 170.76, 169.84 and 169.82, 168.63 and 168.60, 162.97 (d,  $J = 246.1$  Hz), 142.17 (d,  $J = 3.8$  Hz) and 142.10 (d,  $J = 3.6$  Hz), 140.64 and 140.51, 137.26 and 137.23, 132.19 and 132.11, 130.17 and 130.09, 128.88, 128.72 and 128.68, 128.63 and 128.62, 128.03 and 128.02, 127.96 and 127.93, 127.41 and 127.38, 121.78 (d,  $J = 1.8$  Hz) and 121.74 (d,  $J = 1.3$  Hz), 114.99 and 114.98, 114.79 and 114.77, 113.23 and 113.02, 90.68 and 90.59, 84.66 and 84.62, 81.88 and 81.80, 78.86, 66.17 and 66.15, 66.12 and 66.10, 53.16 and 53.14, 53.07 and 53.05, 52.11 and 52.07, 42.86 and 42.78, 21.15. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.61. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 3464, 2953, 1736, 1615, 1489, 1451, 1272, 1226, 1196, 1093, 1055, 1018, 953, 891, 786, 762, 698, 631, 604, 522 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>27</sub>FNaO<sub>7</sub> [M + Na]<sup>+</sup>: 553.1633; Found: 553.1630.

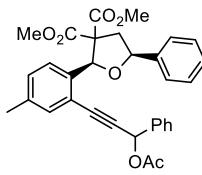


Compound **1u** (1:0.86 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 and 7.76 (d,  $J = 7.5$  Hz, 1H), 7.70 and 7.68 (d,  $J = 7.5$  Hz, 2H), 7.60 (dd,  $J = 7.7, 3.5$  Hz, 1H), 7.51 and 7.49 (d,  $J = 7.6$  Hz, 1H), 7.42 (dt,  $J = 28.9, 7.3$  Hz, 4H), 7.32 (d,  $J = 7.3$  Hz, 1H), 7.26 (d,  $J = 7.7$  Hz, 2H), 7.20 (d,  $J = 7.3$  Hz, 1H), 6.86 and 6.84 (d,  $J = 7.4$  Hz, 1H), 6.52 and 6.45 (d,  $J = 28.8$  Hz, 1H), 5.21 (dt,  $J = 10.8, 4.3$  Hz, 1H), 3.82 and 3.73 (d,  $J = 37.4$  Hz, 3H), 3.17 and 3.14 (d,  $J = 9.5$  Hz, 3H), 3.01 – 2.93 (m, 1H), 2.70 (dt,  $J = 12.8, 5.7$  Hz, 1H), 2.39 (s, 3H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.98 and 170.96, 169.87 and 169.84, 168.88 and 168.86, 140.90 and 140.79, 137.44 and 137.38, 137.31 and 137.28, 135.19 and 135.13, 132.20 and 132.11, 130.36, 128.87, 128.67, 128.62 and 128.61, 127.99 and 127.94, 127.91 and 127.90, 127.78 and 127.75, 127.61 and 127.58, 126.33, 125.14, 121.81 and 121.74, 90.55 and 90.46, 84.81 and 84.77, 81.43 and 81.37, 66.32 and 66.29, 66.14, 53.11 and 53.08, 53.00 and 52.98, 52.06 and 52.02, 41.53 and 41.44, 21.19, 19.24. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 2952, 1736, 1490, 1453, 1370, 1272, 1225, 1122, 1052, 1017, 949, 758, 699 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>32</sub>H<sub>30</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 549.1884; Found: 549.1889.

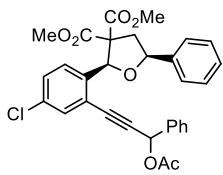


Compound **1v** (1:0.92 diasteromer):  $R_f = 0.36$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (d,  $J = 7.3$  Hz, 2H), 7.60 (d,  $J = 7.8$  Hz, 1H), 7.56 (d,  $J = 7.3$  Hz, 2H), 7.46 (dt,  $J = 13.7, 7.2$  Hz, 6H), 7.37 (t,  $J = 7.4$  Hz, 2H), 7.26 (d,  $J = 7.4$  Hz, 1H), 6.89 and 6.86 (d,  $J = 13.5$  Hz, 1H), 6.60 and 6.54 (d,  $J = 23.3$  Hz, 1H), 5.10 – 5.04 (m, 1H), 4.42 – 4.33 (m, 0.5H), 4.31 – 4.15 (m, 1.5H), 3.84 – 3.73 (m, 1H), 3.46 – 3.35 (m, 1H), 3.08 (t,  $J = 12.5$  Hz, 1H), 2.67 (dt,  $J = 12.9, 4.6$  Hz, 1H), 2.21 (s, 3H), 1.31 (t,  $J = 7.0$  Hz, 1.5H), 1.25 (t,  $J = 7.0$  Hz, 1.5H), 0.88 (q,  $J = 8.2, 7.5$  Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.48 and 170.46, 169.81, 168.41, 141.18 and 141.07, 139.47 and 139.44, 137.37 and 137.32, 132.05 and 131.99, 128.84, 128.69 and 128.66,

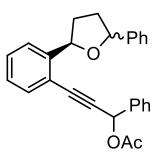
128.62 and 128.60, 128.57, 128.09 and 128.07, 128.03 and 127.97, 127.91, 127.71 and 127.68, 126.29 and 126.26, 122.11 and 122.06, 90.69 and 90.60, 84.88 and 84.84, 81.51 and 81.47, 79.51, 66.19 and 66.14, 61.90 and 61.80, 61.42 and 61.40, 43.09 and 43.01, 21.17, 14.09 and 14.04, 13.39. **IR (KBr)**  $\nu_{\text{max}}$  3743, 3521, 3497, 3034, 2983, 1736, 1490, 1451, 1369, 1265, 1225, 1180, 1094, 1053, 953, 905, 759, 699, 605, 546 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>33</sub>H<sub>32</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup> : 563.2040; Found: 563.2044.



Compound **1w** (1:0.64 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, J = 7.0 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.43 – 7.35 (m, 6H), 7.32 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 13.2 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 6.80 and 6.78 (d, J = 8.2 Hz, 1H), 6.48 and 6.41 (d, J = 26.2 Hz, 1H), 5.00 (d, J = 9.1 Hz, 1H), 3.77 and 3.70 (d, J = 30.7 Hz, 3H), 3.15 and 3.13 (d, J = 7.9 Hz, 3H), 2.99 (t, J = 12.4 Hz, 1H), 2.62 (dd, J = 12.4, 4.9 Hz, 1H), 2.28 (s, 3H), 2.16 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.98 and 170.96, 169.88, 168.86 and 168.84, 139.53 and 139.49, 137.95 and 137.83, 137.73 and 137.72, 137.34 and 137.31, 132.59 and 132.49, 129.63 and 129.61, 128.87, 128.63 and 128.55, 128.05, 128.00, 127.97, 127.48 and 127.45, 126.25 and 126.23, 121.51 and 121.44, 90.10 and 89.99, 84.97 and 84.93, 81.68 and 81.62, 79.51, 66.23 and 66.20, 66.16, 53.10 and 53.01, 52.09 and 52.06, 42.83 and 42.74, 21.20 and 20.90. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3522, 3497, 2952, 1735, 1540, 1454, 1368, 1271, 1226, 1054, 1017, 953, 757, 699 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>32</sub>H<sub>30</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup> : 549.1884; Found: 549.1882.

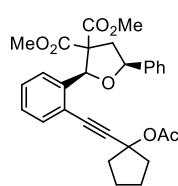


Compound **1x** (1:0.43 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, J = 7.0 Hz, 2H), 7.41 (dt, J = 15.9, 9.5 Hz, 9H), 7.31 (dd, J = 18.0, 7.8 Hz, 2H), 6.78 and 6.76 (d, J = 12.1 Hz, 1H), 6.45 and 6.38 (d, J = 29.8 Hz, 1H), 4.99 (d, J = 11.4 Hz, 1H), 3.79 and 3.69 (d, J = 38.5 Hz, 3H), 3.19 and 3.16 (d, J = 11.1 Hz, 3H), 2.98 (t, J = 12.5 Hz, 1H), 2.63 (dd, J = 13.0, 5.0 Hz, 1H), 2.17 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.74 and 170.71, 169.79, 168.66 and 168.63, 139.46 and 139.33, 139.14 and 139.11, 136.95 and 136.93, 133.68, 131.63 and 131.57, 129.00 and 128.96, 128.92 and 128.88, 128.71 and 128.69, 128.62, 128.21, 127.95, 127.89, 126.22, 123.32 and 123.25, 91.89 and 91.81, 83.30 and 83.26, 81.29 and 81.22, 79.66, 66.11, 65.95 and 65.92, 53.19 and 53.09, 52.25 and 52.20, 42.80 and 42.73, 21.15. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3497, 3464, 2952, 1736, 1560, 1489, 1454, 1435, 1369, 1274, 1172, 1091, 1019, 952, 755, 699, 594, 533, 502 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>27</sub>ClNaO<sub>7</sub> [M + Na]<sup>+</sup> : 569.1338; Found: 569.1343.

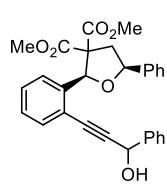


Compound **1y** (1:0.83 diasteromer): R<sub>f</sub> = 0.4 (EtOAc/petroleum ether = 1/10), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.5 Hz, 3H), 7.47 (d, J = 6.2 Hz, 2H), 7.37 (p, J = 8.9, 8.2 Hz, 7H), 7.27 (q, J = 7.7 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 6.9 Hz, 1H), 5.57 (t, J = 7.0 Hz, 1H), 5.38 (t, J = 6.8 Hz, 1H), 5.28 (q, J = 6.7 Hz, 1H), 5.00 (t, J = 7.1 Hz, 1H), 2.44 (m, 2H), 2.12 (d, J = 12.0 Hz, 3H), 1.87 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.87, 169.85, 169.85, 169.83, 146.74, 146.64, 146.12, 146.04, 143.65, 142.60, 142.58, 137.26, 137.11, 132.54, 132.49, 132.43, 132.38, 129.28, 129.25, 129.22, 129.06, 129.03, 128.78, 128.44, 128.40, 127.78, 127.74, 127.70, 127.43, 127.24, 126.80, 126.12, 125.59, 125.58, 125.04, 124.99, 124.74, 124.71, 119.31,

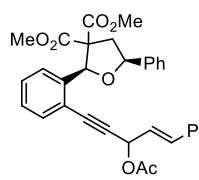
119.27, 119.13, 119.09, 90.80, 90.71, 90.64, 90.60, 85.39, 85.33, 81.72, 81.30, 81.27, 79.90, 79.20, 66.30, 35.57, 34.65, 34.58, 33.93, 33.89, 33.83, 21.15, 21.12. **IR (KBr)**  $\nu_{\text{max}}$  3839, 3818, 3744, 3675, 3652, 3522, 3498, 3465, 2928, 1739, 1540, 1453, 1368, 1223, 1018, 953, 756, 698  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{27}\text{H}_{24}\text{NaO}_3$  [M + Na]<sup>+</sup>: 419.1618; Found: 419.1621.



Compound **1aa**  $R_f = 0.4$  (EtOAc/petroleum ether = 1/8), yellow oil. **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (t,  $J = 8.7$  Hz, 3H), 7.39 (t,  $J = 7.7$  Hz, 3H), 7.35 – 7.26 (m, 2H), 7.18 (t,  $J = 7.5$  Hz, 1H), 6.45 (s, 1H), 5.03 (dd,  $J = 11.7, 4.5$  Hz, 1H), 3.83 (s, 3H), 3.16 (s, 3H), 2.99 (t,  $J = 12.5$  Hz, 1H), 2.62 (dd,  $J = 13.3, 4.6$  Hz, 1H), 2.39 – 2.27 (m, 4H), 2.07 (s, 3H), 1.88 – 1.75 (m, 4H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 169.5, 168.7, 140.4, 139.5, 132.1, 128.5, 128.1, 128.0, 127.8, 127.4, 126.2, 122.5, 94.5, 82.2, 81.6, 81.1, 79.5, 66.2, 53.1, 52.1, 42.5, 40.4, 40.3, 23.6, 23.5, 21.8. **IR (KBr)**  $\nu_{\text{max}}$  3464, 2953, 2906, 1736, 1635, 1442, 1344, 1269, 1177, 1053, 1015, 754, 701, 613  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{30}\text{NaO}_7$  [M + Na]<sup>+</sup>: 513.1884; Found: 513.1882.

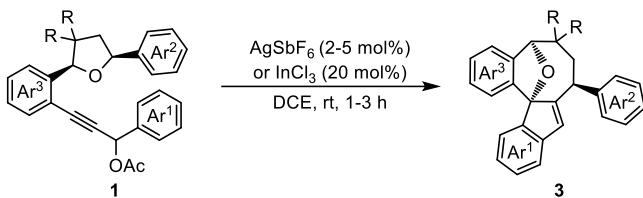


Compound **1ab** (1:0.69 diasteromer):  $R_f = 0.3$  (EtOAc/petroleum ether = 1/3), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (dd,  $J = 10.6, 8.1$  Hz, 2H), 7.63 (t,  $J = 7.4$  Hz, 1H), 7.58 (d,  $J = 7.5$  Hz, 2H), 7.46 (t,  $J = 7.0$  Hz, 5H), 7.39 (dt,  $J = 11.1, 5.3$  Hz, 3H), 7.27 (s, 1H), 6.65 (d,  $J = 10.0$  Hz, 1H), 5.78 – 5.74 (m, 1H), 5.03 (dd,  $J = 11.6, 4.6$  Hz, 1H), 3.97 – 3.89 (m, 1H), 3.79 (d,  $J = 47.6$  Hz, 3H), 3.16 (t,  $J = 6.4$  Hz, 4H), 2.70 (m, 1H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.30 and 172.19, 168.77 and 168.73, 141.27 and 141.06, 140.57 and 140.53, 139.23 and 139.18, 131.36 and 131.19, 128.64, 128.60, 128.49, 128.38, 128.26, 128.18 and 128.15, 128.01, 127.38, 126.85, 126.38 and 126.37, 122.03, 94.49, 84.52, 84.36, 82.04, 81.96, 79.70, 66.30, 66.23, 64.96, 53.50, 52.26, 52.17, 43.48, 43.38. **IR (KBr)**  $\nu_{\text{max}}$  3524, 3035, 2952, 2878, 2226, 1961, 1891, 1814, 1729, 1489, 1444, 1382, 1276, 1183, 1019, 814, 757, 703, 636, 503  $\text{cm}^{-1}$ .

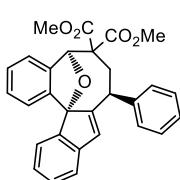


Compound **1ac** (1:0.83 diasteromer):  $R_f = 0.4$  (EtOAc/petroleum ether = 1/6), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (td,  $J = 13.1, 11.9, 5.9$  Hz, 6H), 7.44 (t,  $J = 7.4$  Hz, 3H), 7.38 (t,  $J = 7.3$  Hz, 4H), 7.33 – 7.30 (m, 1H), 7.02 (d,  $J = 15.5$  Hz, 1H), 6.58 (s, 1H), 6.52 – 6.42 (m, 2H), 5.08 (dd,  $J = 11.7, 4.6$  Hz, 1H), 3.81 – 3.77 (m, 3H), 3.19 (d,  $J = 3.0$  Hz, 3H), 3.15 – 3.09 (m, 1H), 2.73 – 2.67 (m, 1H), 2.22 (d,  $J = 3.8$  Hz, 3H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.97 and 170.93, 169.82, 168.83 and 168.81, 140.98, 140.95, 139.39, 139.36, 136.05, 136.01, 134.52, 134.45, 132.24, 132.06, 128.72, 128.68, 128.64, 128.59, 128.41, 128.39, 128.13, 127.98, 127.96, 127.57, 127.52, 127.03, 126.97, 126.30, 126.28, 124.26, 124.24, 121.74, 121.71, 89.75, 89.69, 84.69, 84.58, 81.80, 79.65, 66.32, 66.29, 64.93, 53.17 and 53.14, 53.12 and 53.09, 52.12, 43.08, 42.94, 21.21. **IR (KBr)**  $\nu_{\text{max}}$  3818, 3744, 3521, 3497, 2920, 1733, 1539, 1367, 1270, 1014, 753  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{33}\text{H}_{30}\text{NaO}_7$  [M + Na]<sup>+</sup>: 561.1884; Found: 561.1888.

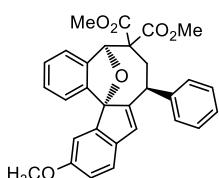
## 2. General procedure for synthesis of 3



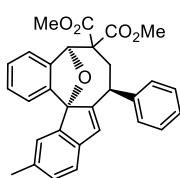
To a solution of **1** in DCE was added the catalyst (2-5 mol% AgSbF<sub>6</sub> or 20 mol% InCl<sub>3</sub>) at room temperature. Then the solution mixture was stirred at the same temperature, after completion of the reaction, the solvent was removed under reduced pressure and the crude product was subjected to silica gel column chromatography to afford **3**.



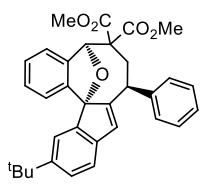
**Compound 3a:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 73%, yellow solid (m.p. 157–158 °C).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.23 (m, 5H), 7.21 – 7.16 (m, 2H), 7.04 (m, 5H), 6.79 – 6.75 (m, 1H), 6.51 (s, 1H), 5.83 (d,  $J = 2.6$  Hz, 1H), 4.35 (dt,  $J = 12.5, 2.8$  Hz, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 2.35 – 2.30 (m, 1H), 1.69 (dd,  $J = 15.0, 12.6$  Hz, 1H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 168.5, 159.0, 146.7, 13, 129.0, 128.9, 128.5, 128.1, 128.0, 127.1, 127.1, 126.6, 125.5, 123.3, 122.5, 121.3, 65.7, 53.10, 52.88, 43.1, 34.5. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3522, 3497, 2953, 1736, 1492, 1042, 1108, 969, 887, 751, 702, 638, 526  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{24}\text{NaO}_5$  516; Found: 475.1519.



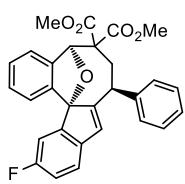
**Compound 3b:**  $R_f = 0.48$  (EtOAc/petroleum ether = 1/5), Yield: 50%, yellow solid (m.p. 206–207 °C).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 7.6$  Hz, 3H), 7.26 (d,  $J = 7.2$  Hz, 2H), 7.24 – 7.19 (m, 1H), 7.07 (d,  $J = 7.1$  Hz, 2H), 6.96 (d,  $J = 8.1$  Hz, 1H), 6.81 (d,  $J = 7.1$  Hz, 1H), 6.75 (d,  $J = 8.2$  Hz, 1H), 6.71 (s, 1H), 6.53 (s, 1H), 5.80 (s, 1H), 4.34 (d,  $J = 12.5$  Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 2.37 – 2.31 (m, 1H), 1.70 (s, 1H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 168.5, 158.4, 156.8, 148.5, 145.6, 144.1, 140.6, 136.4, 129.0, 128.5, 128.1, 128.0, 126.7, 126.5, 122.3, 121.4, 121.0, 114.2, 110.1, 97.3, 85.4, 65.7, 55.5, 53.1, 52.9, 43.0, 34.5. **IR (KBr)**  $\nu_{\text{max}}$  3743, 3522, 3497, 3464, 2952, 1735, 1593, 1271, 1041, 750, 704  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{30}\text{H}_{26}\text{NaO}_6$  [ $\text{M} + \text{Na}^+$ ] : 505.1622; Found: 505.1625.



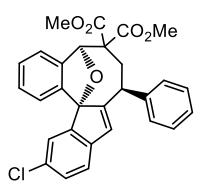
**Compound 3c:**  $R_f = 0.57$  (EtOAc/petroleum ether = 1/5), Yield: 71%, yellow solid (m.p. 214–215 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (d,  $J = 7.5$  Hz, 2H), 7.26 – 7.21 (m, 3H), 7.20 – 7.16 (m, 1H), 7.04 (d,  $J = 7.3$  Hz, 2H), 6.99 (d,  $J = 7.6$  Hz, 1H), 6.91 (d,  $J = 6.6$  Hz, 2H), 6.79 (d,  $J = 7.5$  Hz, 1H), 6.50 (s, 1H), 5.80 (s, 1H), 4.35 (d,  $J = 12.5$  Hz, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 2.34 – 2.29 (m, 1H), 2.24 (s, 3H), 1.71 – 1.63 (m, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.6, 157.9, 146.9, 145.6, 144.0, 141.0, 140.8, 135.3, 129.4, 128.9, 128.5, 128.1, 128.0, 127.1, 126.5, 124.3, 122.4, 121.4, 120.2, 97.4, 85.4, 65.7, 53.11, 52.88, 43.0, 34.5, 21.3. **IR (KBr)**  $\nu_{max}$  3744, 3522, 3498, 2952, 1737, 1540, 1270, 1130, 1043, 969, 843, 750 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>30</sub>H<sub>26</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup>: 489.1672; Found: 489.1671.



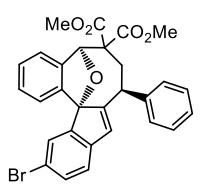
**Compound 3d:**  $R_f = 0.58$  (EtOAc/petroleum ether = 1/5), Yield: 78%, yellow solid (m.p. 145–146 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.25 (m, 3H), 7.21 (dd,  $J$  = 16.4, 7.3 Hz, 4H), 7.10 (s, 1H), 7.03 (d,  $J$  = 7.1 Hz, 2H), 6.94 (d,  $J$  = 7.8 Hz, 1H), 6.77 (d,  $J$  = 7.4 Hz, 1H), 6.51 (s, 1H), 5.80 (d,  $J$  = 2.1 Hz, 1H), 4.31 (d,  $J$  = 12.5 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 2.35 – 2.28 (m, 1H), 1.71 – 1.63 (m, 1H), 1.22 (s, 9H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.6, 158.4, 148.9, 146.6, 145.6, 144.2, 141.0, 140.8, 128.9, 128.5, 128.1, 127.9, 126.9, 126.5, 125.7, 122.3, 121.4, 120.6, 119.9, 97.6, 85.3, 65.7, 53.11, 52.89, 43.1, 34.8, 34.5, 31.5. **IR (KBr)**  $\nu_{\text{max}}$  3839, 3744, 3522, 3497, 3464, 2954, 1540, 1367, 1274, 1060, 751, 523 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>33</sub>H<sub>32</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> : 531.2142; Found: 531.2146.



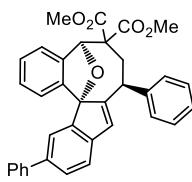
**Compound 3e:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 75%, yellow solid (m.p. 238–239 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (dd,  $J$  = 14.7, 5.9 Hz, 3H), 7.22 (dd,  $J$  = 15.3, 7.3 Hz, 3H), 7.03 (d,  $J$  = 7.2 Hz, 2H), 6.95 (dd,  $J$  = 8.0, 5.0 Hz, 1H), 6.88 (td,  $J$  = 9.3, 2.2 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.50 (s, 1H), 5.79 (d,  $J$  = 2.3 Hz, 1H), 4.32 (d,  $J$  = 12.4 Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 2.35 – 2.29 (m, 1H), 1.67 (dd,  $J$  = 14.8, 12.8 Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.80, 168.40, 162.89, 160.45, 159.01, 158.97, 148.96, 148.89, 145.25, 143.21, 140.70, 139.46, 139.43, 129.05, 128.56, 128.26, 128.03, 126.61, 126.21, 122.55, 121.22, 121.12, 121.04, 115.49, 115.26, 111.83, 111.59, 97.11, 97.09, 85.52, 65.61, 53.16, 53.13, 52.94, 52.91, 43.05, 34.42. **19F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -116.89. **IR (KBr)**  $\nu_{\text{max}}$  3838, 3744, 3693, 3522, 3497, 3464, 3442, 2953, 1733, 1540, 1522, 1472, 1369, 1272, 1033, 751 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>FNaO<sub>5</sub> [M + Na]<sup>+</sup> : 493.1422; Found: 493.1424.



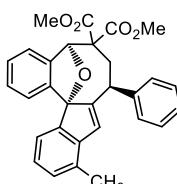
**Compound 3f:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 52%, yellow solid (m.p. 256–257 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (dd,  $J$  = 15.9, 8.2 Hz, 3H), 7.24 (d,  $J$  = 8.6 Hz, 2H), 7.18 (dd,  $J$  = 14.4, 7.4 Hz, 2H), 7.08 – 7.00 (m, 3H), 6.94 (d,  $J$  = 7.9 Hz, 1H), 6.79 (d,  $J$  = 7.1 Hz, 1H), 6.50 (s, 1H), 5.80 (s, 1H), 4.34 (d,  $J$  = 12.4 Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 2.36 – 2.29 (m, 1H), 1.66 (s, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.78, 168.4, 159.7, 148.5, 145.1, 142.8, 142.2, 140.7, 131.5, 129.1, 129.0, 128.6, 128.3, 128.0, 126.7, 126.3, 124.1, 122.6, 121.30, 121.26, 97.1, 85.5, 77.4, 77., 76.7, 65.6, 53.18, 52.96, 43.1, 34.4. **IR (KBr)**  $\nu_{\text{max}}$  3837, 3819, 3745, 3621, 3522, 3498, 3464, 3434, 2952, 1731, 1651, 1540, 1522, 1456, 1432, 1367, 1261, 1211, 1032, 750, 701, 525 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>ClNaO<sub>5</sub> [M + Na]<sup>+</sup> : 509.1126; Found: 509.1121.



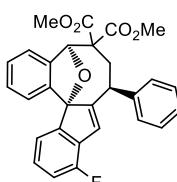
**Compound 3g:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 34%, yellow solid (m.p. 268–369 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (q,  $J$  = 9.1, 7.7 Hz, 4H), 7.26 – 7.16 (m, 4H), 7.02 (d,  $J$  = 7.2 Hz, 2H), 6.89 (d,  $J$  = 7.9 Hz, 1H), 6.79 (d,  $J$  = 7.1 Hz, 1H), 6.50 (s, 1H), 5.79 (s, 1H), 4.33 (d,  $J$  = 12.0 Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 2.32 (d,  $J$  = 14.7 Hz, 1H), 1.66 (t,  $J$  = 13.7 Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.8, 168.4, 159.7, 148.7, 145.1, 142.8, 142.6, 140.7, 132.0, 129.1, 128.6, 128.4, 128.0, 126.8, 126.7, 126.3, 122.7, 121.8, 121.3, 119.4, 97.2, 85.6, 65.6, 53.19, 52.98, 43.1, 34.4. **IR (KBr)**  $\nu_{\text{max}}$  3745, 3522, 3497, 2926, 1725, 1540, 1545, 1208, 1122, 1053, 1032, 998, 781, 741, 587, 526 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>BrNaO<sub>5</sub> [M + Na]<sup>+</sup> : 553.0621; Found: 553.0619.



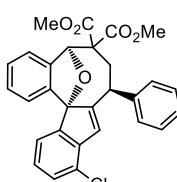
**Compound 3h:**  $R_f = 0.58$  (EtOAc/petroleum ether = 1/5), Yield: 69%, yellow solid (m.p. 210-211 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d,  $J = 7.5$  Hz, 2H), 7.37 (d,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 7.5$  Hz, 2H), 7.16 (dd,  $J = 21.8, 7.1$  Hz, 8H), 7.02 (d,  $J = 7.7$  Hz, 1H), 6.98 (d,  $J = 7.1$  Hz, 2H), 6.75 (d,  $J = 7.1$  Hz, 1H), 6.46 (s, 1H), 5.80 (s, 1H), 4.29 (d,  $J = 11.9$  Hz, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 2.27 (d,  $J = 14.7$  Hz, 1H), 1.63 (t,  $J = 13.7$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.5, 159.4, 147.5, 145.4, 143.6, 143.0, 141.1, 140.8, 138.6, 129.0, 128.62, 128.58, 128.1, 127.9, 127.0, 126.92, 126.88, 126.6, 122.5, 122.4, 121.5, 120.8, 97.4, 85.5, 65.7, 53.18, 52.95, 43.20, 34.48. **IR (KBr)**  $\nu_{max}$  3838, 3818, 3693, 3653, 3497, 3464, 2956, 1737, 1540, 1522, 1457, 1368, 1273, 751 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>35</sub>H<sub>28</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup>: 551.1829; Found: 551.1826.



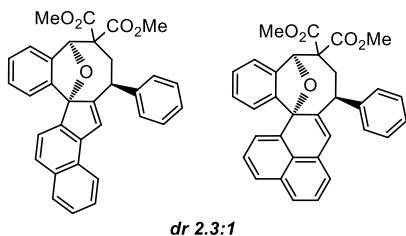
**Compound 3i:**  $R_f = 0.57$  (EtOAc/petroleum ether = 1/5), Yield: 58%, yellow solid (m.p. 205-206 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.27 (m, 2H), 7.25 (d,  $J = 5.9$  Hz, 3H), 7.22 – 7.18 (m, 1H), 7.06 (d,  $J = 7.3$  Hz, 2H), 6.97 (dt,  $J = 14.7, 7.4$  Hz, 2H), 6.89 (d,  $J = 7.0$  Hz, 1H), 6.79 (d,  $J = 7.6$  Hz, 1H), 6.50 (s, 1H), 5.94 (s, 1H), 4.38 (d,  $J = 12.4$  Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 2.34 – 2.28 (m, 1H), 2.22 (s, 3H), 1.71 – 1.64 (m, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.6, 158.2, 146.6, 145.7, 143.8, 142.2, 140.9, 130.3, 129.7, 128.9, 128.6, 128.1, 128.0, 126.5, 125.7, 125.5, 122.5, 121.4, 120.9, 97.7, 85.4, 65.7, 53.1, 52.9, 43.2, 34.7, 18.1. **IR (KBr)**  $\nu_{max}$  3818, 3746, 3521, 3497, 2953, 1735, 1600, 1491, 1455, 1436, 1333, 1268, 1130, 1056, 1010, 968, 924, 870, 845, 817, 746, 702, 644, 623, 531, 501 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>30</sub>H<sub>26</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup>: 489.1672; Found: 489.1675.



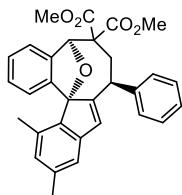
**Compound 3j:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 62%, yellow solid (m.p. 148-149 °C). **1H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 – 7.26 (m, 4H), 7.24 (s, 1H), 7.22 – 7.19 (m, 1H), 7.03 (m, 3H), 6.89 (dd,  $J = 20.4, 8.1$  Hz, 2H), 6.79 (d,  $J = 7.3$  Hz, 1H), 6.51 (s, 1H), 5.96 (s, 1H), 4.34 (d,  $J = 12.4$  Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 2.33 (d,  $J = 14.9$  Hz, 1H), 1.70 – 1.65 (m, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.78, 168.40, 159.26, 156.48, 154.01, 149.55, 149.49, 145.01, 143.03, 140.71, 130.09, 129.93, 129.08, 128.63, 128.29, 128.18, 128.03, 127.27, 127.21, 126.71, 122.56, 121.51, 121.27, 119.42, 119.39, 116.30, 116.10, 97.52, 85.56, 65.60, 53.18, 53.16, 52.96, 52.95, 43.12, 34.37. **19F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -123.31. **IR (KBr)**  $\nu_{max}$  3744, 3522, 3497, 2954, 1735, 1540, 1472, 1269, 1008, 701 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>FNaO<sub>5</sub> [M + Na]<sup>+</sup>: 493.1422; Found: 493.1421.



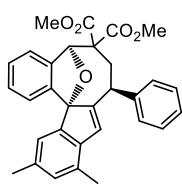
**Compound 3k:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 45%, yellow solid (m.p. 178-179 °C). **1H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.30 (m, 1H), 7.27 (d,  $J = 9.5$  Hz, 3H), 7.25 (s, 1H), 7.23 – 7.20 (m, 1H), 7.17 (m, 1H), 7.05 – 7.02 (m, 2H), 7.01 – 6.95 (m, 2H), 6.82 (d,  $J = 7.2$  Hz, 1H), 6.50 (s, 1H), 5.98 (d,  $J = 2.6$  Hz, 1H), 4.36 (dt,  $J = 12.5, 2.9$  Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 2.33 (m, 1H), 1.66 (d,  $J = 2.5$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.8, 168.4, 160.3, 148.4, 145.0, 142.7, 141.7, 140.8, 129.3, 129.1, 128.7, 128.4, 128.1, 126.9, 126.7, 125.9, 124.4, 122.6, 121.7, 121.3, 97.9, 85.6, 65.6, 53.18, 52.96, 43.2, 34.5. **IR (KBr)**  $\nu_{max}$  3819, 3746, 3691, 3498, 3440, 2953, 1733, 1539, 1454, 1434, 1296, 1133, 1054, 1003, 749, 703, 530 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>ClNaO<sub>5</sub> [M + Na]<sup>+</sup>: 509.1126; Found: 509.1127.



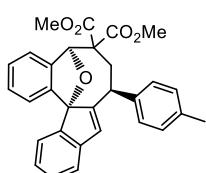
**Compound 3l and 3l':**  $R_f = 0.57$  (EtOAc/petroleum ether = 1/5), Yield: 49%, yellow solid (m.p. 257–258 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (t,  $J = 8.0$  Hz, 1.33H), 7.71 (d,  $J = 7.9$  Hz, 0.33H), 7.66 (d,  $J = 8.5$  Hz, 0.33H), 7.59 (t,  $J = 9.1$  Hz, 1H), 7.48 – 7.35 (m, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.17 (m, 2H), 7.11 (d,  $J = 7.1$  Hz, 2H), 7.05 (dd,  $J = 16.3, 7.3$  Hz, 1H), 6.69 (d,  $J = 6.1$  Hz, 1H), 6.58 (s, 1H), 6.54 (d,  $J = 7.5$  Hz, 0.33H), 6.37 (s, 0.69H), 5.81 (s, 0.33H), 4.45 (d,  $J = 12.5$  Hz, 0.67H), 4.08 (d,  $J = 11.7$  Hz, 0.33H), 3.89 (s, 3H), 3.80 (s, 1H), 3.77 (s, 2H), 2.53 (d,  $J = 15.1$  Hz, 0.33H), 2.38 (d,  $J = 14.7$  Hz, 0.67H), 1.90 – 1.81 (m, 0.33H), 1.75 (t,  $J = 13.7$  Hz, 0.67H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.91, 168.51, 160.05, 145.46, 143.48, 142.94, 141.12, 140.19, 134.37, 130.36, 128.97, 128.69, 128.64, 128.51, 128.19, 127.07, 127.00, 125.88, 125.77, 125.23, 124.08, 122.59, 121.21, 121.14, 98.28, 85.74, 65.72, 53.17, 52.96, 43.39, 34.66. **IR (KBr)**  $\nu_{\text{max}}$  3834, 3798, 3747, 3712, 3692, 3670, 3584, 3565, 3438, 2918, 2355, 1732, 1538, 1455, 1342, 1269, 1009, 748, 511 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>33</sub>H<sub>26</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup>: 525.1672; Found: 525.1670.



**Compound 3m:**  $R_f = 0.58$  (EtOAc/petroleum ether = 1/5), Yield: 51%, yellow solid (m.p. 103–104 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d,  $J = 7.0$  Hz, 1H), 7.24 (d,  $J = 9.2$  Hz, 4H), 7.19 (d,  $J = 8.0$  Hz, 1H), 7.04 (d,  $J = 7.2$  Hz, 2H), 6.81 (d,  $J = 7.1$  Hz, 1H), 6.66 (s, 1H), 6.60 (s, 1H), 6.49 (s, 1H), 5.74 (s, 1H), 4.30 (d,  $J = 12.1$  Hz, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 2.31 (d,  $J = 14.9$  Hz, 1H), 2.24 (s, 3H), 1.81 (s, 3H), 1.70 (t,  $J = 13.8$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.5, 158.6, 145.6, 144.1, 142.8, 140.8, 140.4, 138.9, 134.3, 128.9, 128.5, 128.2, 128.1, 127.9, 127.3, 126.5, 122.4, 120.9, 119.1, 97.8, 85.1, 65.8, 53.12, 52.86, 43.2, 34.4, 21.4, 16.8. **IR (KBr)**  $\nu_{\text{max}}$  3836, 3817, 3744, 3692, 3522, 3497, 3464, 2954, 1735, 1539, 1522, 1456, 1434, 1367, 1271, 1012, 966, 750, 703, 524 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>28</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup>: 503.1829; Found: 503.1832.

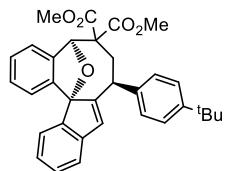


**Compound 3n:**  $R_f = 0.58$  (EtOAc/petroleum ether = 1/5), Yield: 62%, yellow solid (m.p. 236–237 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (d,  $J = 7.0$  Hz, 2H), 7.24 (t,  $J = 3.7$  Hz, 3H), 7.19 (t,  $J = 7.1$  Hz, 1H), 7.05 (d,  $J = 7.1$  Hz, 2H), 6.82 (d,  $J = 4.6$  Hz, 2H), 6.73 (s, 1H), 6.49 (s, 1H), 5.90 (d,  $J = 2.2$  Hz, 1H), 4.38 (d,  $J = 12.4$  Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 2.34 – 2.28 (m, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 1.66 (dd,  $J = 14.7, 12.8$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.6, 157.1, 146.8, 145.8, 144.1, 140.8, 139.6, 135.4, 130.9, 129.4, 128.9, 128.6, 128.2, 127.9, 126.5, 125.4, 122.5, 121.8, 121.5, 97.6, 85.3, 65.7, 53.08, 52.88, 43.1, 34.8, 21.2, 18.0. **IR (KBr)**  $\nu_{\text{max}}$  3849, 3814, 3733, 3709, 3646, 3567, 3529, 3458, 3377, 2955, 2350, 1734, 1436, 1268, 1133, 1057, 1010, 968, 899, 864, 746, 702, 636, 601, 526 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>28</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup>: 503.1829; Found: 503.1827.

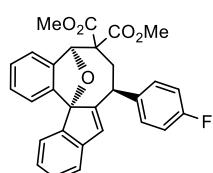


**Compound 3p:**  $R_f = 0.57$  (EtOAc/petroleum ether = 1/5), Yield: 74%, yellow solid (m.p. 185–186 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.26 (m, 2H), 7.23 (s, 1H), 7.18 (td,  $J = 7.2, 1.7$  Hz, 1H), 7.08 – 7.01 (m, 5H), 6.93 (d,  $J = 7.9$  Hz, 2H), 6.76 (d,  $J = 7.0$  Hz, 1H), 6.50 (s, 1H), 5.84 (d,  $J = 2.5$  Hz, 1H), 4.35 – 4.29 (m, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 2.30 (s, 4H), 1.67 (dd,  $J = 14.9, 12.7$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 168.6, 159.2, 146.8, 143.78, 143.76, 142.5, 140.9, 136.1, 129.2, 129.0, 128.9,

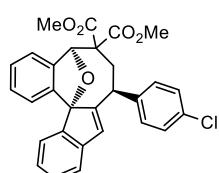
128.0, 127.9, 127.0, 125.5, 123.3, 122.5, 121.3, 120.5, 97.4, 85.4, 65.6, 53.09, 52.86, 42.7, 34.6, 21.1 (d,  $J = 1.8$  Hz). **IR (KBr)**  $\nu_{\text{max}}$  3744, 3522, 3497, 2952, 1736, 1512, 1457, 1436, 1266, 1121, 1042, 1010, 969, 888, 752, 633, 520  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{30}\text{H}_{26}\text{NaO}_5$  [ $\text{M} + \text{Na}^+$ ] : 489.1672; Found: 489.1676.



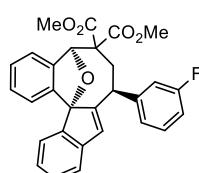
**Compound 3q:**  $R_f = 0.58$  (EtOAc/petroleum ether = 1/5), Yield: 74%, yellow solid (m.p. 206–207 °C). **1H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J = 5.4$  Hz, 5H), 7.18 (t,  $J = 7.1$  Hz, 1H), 7.05 (q,  $J = 7.2$  Hz, 3H), 6.96 (d,  $J = 8.0$  Hz, 2H), 6.77 (d,  $J = 7.0$  Hz, 1H), 6.50 (s, 1H), 5.89 – 5.85 (m, 1H), 4.34 (d,  $J = 12.3$  Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 2.35 – 2.29 (m, 1H), 1.70 – 1.63 (m, 1H), 1.29 (s, 9H). **13C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 168.6, 159.1, 149.3, 146.8, 143.82, 143.75, 142.4, 140.9, 129.0, 128.9, 128.0, 127.6, 127.1, 125.5, 125.4, 123.3, 122.5, 121.3, 120.5, 97.4, 85.4, 65.6, 53.08, 52.86, 42.5, 34.6, 34.4, 31.4. **IR (KBr)**  $\nu_{\text{max}}$  3834, 3742, 3521, 3497, 3464, 2956, 1736, 1511, 1458, 1364, 1266, 1042, 1011, 969, 751  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{33}\text{H}_{32}\text{NaO}_5$  [ $\text{M} + \text{Na}^+$ ] : 531.2142; Found: 531.2146.



**Compound 3r:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 40%, yellow solid (m.p. 181–182 °C). **1H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 13.9, 6.7$  Hz, 2H), 7.25 (s, 1H), 7.20 (td,  $J = 7.3, 2.6$  Hz, 1H), 7.08 – 7.03 (m, 3H), 7.02 – 6.97 (m, 2H), 6.93 (t,  $J = 8.6$  Hz, 2H), 6.75 (d,  $J = 7.8$  Hz, 1H), 6.51 (s, 1H), 5.82 (d,  $J = 2.3$  Hz, 1H), 4.35 (d,  $J = 12.5$  Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 2.32 – 2.26 (m, 1H), 1.62 (d,  $J = 14.6$  Hz, 1H). **13C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.82, 168.43, 162.75, 160.32, 158.87, 146.68, 143.63, 143.55, 141.19, 141.16, 140.75, 129.55, 129.47, 129.06, 128.98, 128.10, 127.19, 125.65, 123.36, 122.47, 121.25, 120.59, 115.42, 115.21, 97.36, 85.39, 65.60, 53.17, 53.15, 52.96, 52.94, 42.32, 34.60. **19F NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.42. **IR (KBr)**  $\nu_{\text{max}}$  3745, 3651, 3567, 3522, 3464, 3442, 2953, 1736, 1651, 1558, 1540, 1457, 1453, 1335, 1265, 1220, 1042, 969, 842, 751, 523  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{23}\text{FNaO}_5$  [ $\text{M} + \text{Na}^+$ ] : 493.1422; Found: 493.1424.

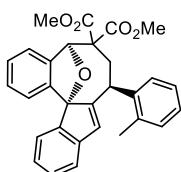


**Compound 3s:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 66%, yellow solid (m.p. 178–179 °C). **1H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 15.0, 8.0$  Hz, 2H), 7.21 (t,  $J = 8.1$  Hz, 4H), 7.08 – 7.03 (m, 3H), 6.98 (d,  $J = 8.1$  Hz, 2H), 6.75 (d,  $J = 7.8$  Hz, 1H), 6.51 (s, 1H), 5.83 (d,  $J = 2.2$  Hz, 1H), 4.35 (d,  $J = 12.5$  Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 2.28 (dd,  $J = 14.9, 2.5$  Hz, 1H), 1.63 (s, 1H). **13C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 168.4, 158.5, 146.6, 143.9, 143.6, 143.5, 140.8, 132.3, 129.5, 129.1, 129.0, 128.7, 128.1, 127.3, 125.7, 123.4, 122.5, 121.3, 120.6, 97.4, 85.4, 65.6, 53.16, 52.96, 42.4, 34.4. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3521, 3498, 2953, 1736, 1539, 1263, 1013, 751  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{23}\text{ClNaO}_5$  [ $\text{M} + \text{Na}^+$ ] : 509.1126; Found: 509.1125.

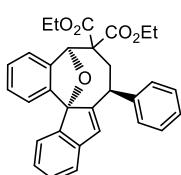


**Compound 3t:**  $R_f = 0.56$  (EtOAc/petroleum ether = 1/5), Yield: 39%, yellow solid (m.p. 137–138 °C). **1H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.29 (m, 1H), 7.27 (d,  $J = 7.5$  Hz, 1H), 7.26 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 7.08 – 7.04 (m, 3H), 6.91 – 6.85 (m, 2H), 6.77 (d,  $J = 7.3$  Hz, 1H), 6.72 (m, 1H), 6.51 (s, 1H), 5.86 (d,  $J = 2.6$  Hz, 1H), 4.37 (dt,  $J = 12.5, 2.8$  Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.31 (m, 1H), 1.65 (d,  $J = 2.4$  Hz, 1H). **13C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.77, 168.38, 164.06, 161.61, 158.15, 147.92, 147.85, 146.63, 143.52, 143.51, 140.71, 130.04, 129.96, 129.09, 129.06, 128.16, 127.38, 125.72, 123.84,

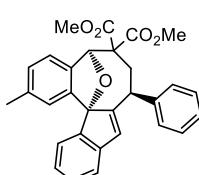
123.81, 123.37, 122.47, 121.30, 120.65, 115.01, 114.80, 113.61, 113.40, 97.38, 85.39, 65.62, 53.20, 53.18, 52.98, 52.97, 42.81, 34.28. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -113.01. **IR (KBr)** ν<sub>max</sub> 3744, 3522, 3497, 2954, 1736, 1588, 1486, 1438, 1334, 1265, 1130, 1043, 1012, 969, 914, 885, 790, 752, 639, 521 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>FNaO<sub>5</sub> [M + Na]<sup>+</sup> : 493.1422; Found: 493.1426.



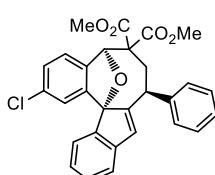
Compound **3u**: R<sub>f</sub> = 0.57 (EtOAc/petroleum ether = 1/5), Yield: 62%, yellow solid (m.p. 192–193 °C). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.30 (d, J = 7.3 Hz, 1H), 7.25 (s, 1H), 7.21 – 7.13 (m, 3H), 7.09 – 7.01 (m, 5H), 6.79 (d, J = 7.1 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.53 (s, 1H), 5.76 (d, J = 2.4 Hz, 1H), 4.65 (d, J = 12.3 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 2.44 (s, 3H), 2.23 (dd, J = 15.0, 2.8 Hz, 1H), 1.66 – 1.62 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.9, 168.5, 159.5, 146.7, 144.0, 143.8, 143.7, 140.8, 135.4, 130.1, 129.02, 128.99, 128.1, 128.0, 126.6, 126.4, 126.3, 125.5, 123.3, 122.5, 121.4, 120.5, 97.6, 85.5, 65.6, 53.1, 52.9, 38.0, 33.6, 19.5. **IR (KBr)** ν<sub>max</sub> 3745, 3521, 3497, 2953, 1736, 1458, 1436, 1334, 1267, 1131, 1043, 1010, 969, 748, 638 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>30</sub>H<sub>26</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> : 489.1672; Found: 489.1674.



Compound **3v**: R<sub>f</sub> = 0.58 (EtOAc/petroleum ether = 1/5), Yield: 65%, yellow solid (m.p. 168–169 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.26 (dd, J = 13.9, 7.2 Hz, 6H), 7.21 – 7.15 (m, 2H), 7.04 (q, J = 8.0, 7.4 Hz, 5H), 6.76 (d, J = 7.2 Hz, 1H), 6.50 (s, 1H), 5.82 (s, 1H), 4.43 (dd, J = 10.7, 7.1 Hz, 1H), 4.35 (d, J = 12.4 Hz, 1H), 4.23 (ddt, J = 18.0, 10.8, 5.4 Hz, 3H), 2.31 (d, J = 14.7 Hz, 1H), 1.72 – 1.65 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.0, 168.1, 159.2, 146.9, 145.6, 143.8, 143.8, 141.0, 128.9, 128.9, 128.5, 128.1, 128.0, 127.1, 126.5, 125.5, 123.4, 122.5, 121.3, 120.5, 97.4, 85.4, 65.7, 62.0, 61.9, 43.1, 34.3, 14.2, 14.1. **IR (KBr)** ν<sub>max</sub> 3743, 3522, 3498, 3464, 2929, 1733, 1593, 1457, 1367, 1264, 1019, 750, 701, 525 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>28</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> : 503.1829; Found: 503.1827.

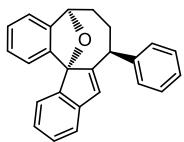


Compound **3w**: R<sub>f</sub> = 0.57 (EtOAc/petroleum ether = 1/5), Yield: 64%, yellow solid (m.p. 179–180 °C). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.26 (m, 1H), 7.24 (s, 1H), 7.21 – 7.17 (m, 2H), 7.10 (m, 2H), 7.04 (m, 5H), 6.56 (s, 1H), 6.46 (s, 1H), 5.82 (d, J = 2.4 Hz, 1H), 4.32 – 4.28 (m, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 2.33 – 2.30 (m, 1H), 2.29 (s, 3H), 1.71 (dd, J = 14.9, 12.6 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.0, 168.5, 159.3, 146.8, 145.4, 143.9, 143.8, 139.0, 138.0, 129.0, 128.9, 128.5, 128.1, 127.0, 126.6, 125.5, 123.4, 122.1, 121.6, 120.5, 97.4, 85.3, 65.7, 53.10, 52.88, 43.1, 34.4, 21.4. **IR (KBr)** ν<sub>max</sub> 3744, 3521, 3497, 3464, 2952, 1736, 1539, 1456, 1266, 1043, 751, 703 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>30</sub>H<sub>26</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> : 489.1672; Found: 489.1673.

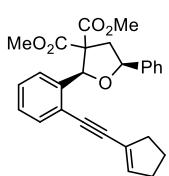


Compound **3x**: R<sub>f</sub> = 0.56 (EtOAc/petroleum ether = 1/5), Yield: 53%, yellow solid (m.p. 201–202 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.28 (s, 2H), 7.25 – 7.18 (m, 4H), 7.05 (d, J = 19.4 Hz, 5H), 6.74 (s, 1H), 6.46 (s, 1H), 5.85 (s, 1H), 4.38 (d, J = 12.2 Hz, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 2.35 (d, J = 14.9 Hz, 1H), 1.71 (t, J = 13.8 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.7, 168.5, 158.5, 146.2, 146.1, 145.1, 143.6, 139.4, 134.8, 129.3, 128.7, 128.4, 128.1, 127.7, 126.7, 125.8, 123.9, 123.4, 121.5, 120.8, 97.2, 85.1, 65.5, 53.20, 53.01, 43.1, 34.5. **IR (KBr)** ν<sub>max</sub> 3744, 3522, 3497, 2954, 1735, 1492, 1457, 1436,

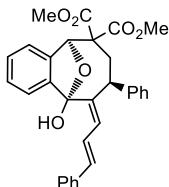
1262, 1131, 1045, 1008, 823, 750, 702, 641, 540, 518 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>23</sub>ClNaO<sub>5</sub> [M + Na]<sup>+</sup> : 509.1126; Found: 509.1125.



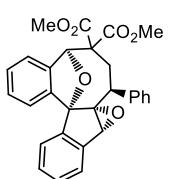
**Compound 3y:** R<sub>f</sub> = 0.48 (EtOAc/petroleum ether = 1/10), Yield: 37%, yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 8.3 Hz, 3H), 7.20 – 7.17 (m, 2H), 7.08 (dd, J = 13.4, 7.4 Hz, 2H), 7.01 (d, J = 7.1 Hz, 3H), 6.72 (d, J = 7.5 Hz, 1H), 5.80 (s, 1H), 5.75 (s, 1H), 3.88 (d, J = 12.3 Hz, 1H), 2.43 (t, J = 13.4 Hz, 1H), 2.06 – 2.00 (m, 1H), 1.51 – 1.45 (m, 1H), 1.34 (d, J = 12.0 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.8, 147.4, 146.1, 143.8, 143.7, 143.2, 128.8, 128.4, 128.0, 127.9, 127.9, 127.0, 126.3, 125.4, 123.1, 120.9, 120.4, 120.4, 97.3, 83.7, 48.3, 38.6, 30.0. **IR (KBr)** ν<sub>max</sub> 3744, 3521, 3497, 2928, 1739, 1540, 1457, 1265, 1033, 750, 701 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>25</sub>H<sub>21</sub>O<sub>5</sub> [M + H]<sup>+</sup> : 337.1587; Found: 337.1591.



**Compound 3aa:** R<sub>f</sub> = 0.45 (EtOAc/petroleum ether = 1/8), Yield: 37%, yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d, J = 6.9 Hz, 3H), 7.43 (t, J = 7.9 Hz, 3H), 7.39 – 7.30 (m, 2H), 7.24 (t, J = 7.4 Hz, 1H), 6.53 (s, 1H), 6.28 (s, 1H), 5.06 (dd, J = 11.5, 4.5 Hz, 1H), 3.86 (s, 3H), 3.17 (s, 3H), 3.07 (t, J = 12.5 Hz, 1H), 2.67 (dd, J = 13.5, 4.5 Hz, 3H), 2.54 (s, 2H), 2.00 (q, J = 7.5 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 171.2, 167.0, 140.2, 139.4, 138.3, 131.6, 128.5, 128.1, 127.9, 127.8, 127.4, 126.3, 124.9, 123.2, 91.7, 88.2, 82.0, 79.6, 66.2, 53.1, 52.1, 43.2, 36.3, 33.5, 23.4. **IR (KBr)** ν<sub>max</sub> 3682, 3065, 2956, 2200, 1734, 1500, 1441, 1370, 1272, 1094, 1042, 937, 756, 705, 562 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>27</sub>H<sub>26</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> : 453.1672; Found: 453.1674.

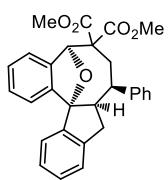


**Compound 4ac:** R<sub>f</sub> = 0.2 (EtOAc/petroleum ether = 1/3), Yield: 21%, yellow solid (m.p. 168–169 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, J = 15.5, 11.4 Hz, 1H), 7.59 (d, J = 7.3 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.28 (d, J = 8.2 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.06 (d, J = 7.4 Hz, 2H), 7.01 (d, J = 7.3 Hz, 1H), 6.35 (s, 1H), 6.22 (d, J = 15.6 Hz, 1H), 5.35 (d, J = 11.4 Hz, 1H), 4.04 (d, J = 10.7 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.60 (s, 1H), 2.60 (d, J = 15.0 Hz, 1H), 1.86 (dd, J = 14.9, 10.9 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.5, 168.0, 147.8, 144.9, 144.7, 137.5, 137.4, 134.7, 130.0, 129.2, 129.0, 128.71, 128.65, 128.6, 127.6, 126.7, 126.6, 125.8, 122.3, 122.1, 109.9, 83.3, 64.7, 53.18, 53.15, 53.12, 52.80, 46.2, 34.7. **IR (KBr)** ν<sub>max</sub> 3672, 3146, 3067, 2954, 1735, 1493, 1442, 1266, 1026, 978, 894, 754, 701, 541 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>28</sub>NaO<sub>6</sub> [M + Na]<sup>+</sup> : 519.1778; Found: 519.1770.



**Compound 5a:** To a solution of **3a** in DCM was added the *m*-CPBA (2.0 eq) and NaHCO<sub>3</sub> (1.5 eq) at room temperature. Then the solution mixture was stirred at the same temperature for 3 h, after completion of the reaction, the solvent was removed under reduced pressure and the crude product was subjected to silica gel column chromatography to afford **5**. R<sub>f</sub> = 0.52 (EtOAc/petroleum ether = 1/5), Yield: 75%, yellow solid (m.p. 117–118 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31 (dd, J = 12.7, 6.8 Hz, 3H), 7.25 (d, J = 5.3 Hz, 5H), 7.07 (t, J = 7.7 Hz, 4H), 6.90 (d, J = 7.3 Hz, 1H), 6.52 (s, 1H), 3.95 (d, J = 11.5 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.57 (s, 1H), 2.51 (d, J = 15.0 Hz, 1H), 2.28 – 2.20 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.3, 167.9, 147.7, 145.1, 140.93, 140.0, 138.5, 129.2, 129.0, 128.9, 128.8, 128.3, 128.1,

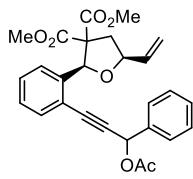
127.0, 126.5, 125.1, 124.7, 120.9, 92.3, 85.8, 75.8, 65.4, 60.8, 53.21, 52.95, 40.8, 31.9. **IR (KBr)**  $\nu_{\text{max}}$  3838, 3818, 3745, 3693, 3522, 3497, 3464, 3442, 2926, 1736, 1540, 1522, 1367, 1275, 1072, 751  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{24}\text{NaO}_6$  [ $\text{M} + \text{Na}]^+$  : 491.1465; Found: 491.1463.



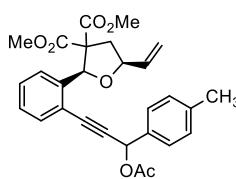
**Compound 6a:**  $R_f = 0.54$  (EtOAc/petroleum ether = 1/5), Yield: 86%, yellow solid (m.p. 205–206  $^\circ\text{C}$ ). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.25 (m, 1H), 7.22 – 7.15 (m, 4H), 7.14 – 7.11 (m, 1H), 7.08 (d,  $J = 7.3$  Hz, 3H), 7.02 (d,  $J = 7.3$  Hz, 1H), 6.95 – 6.89 (m, 2H), 6.85 (d,  $J = 7.5$  Hz, 1H), 6.28 (s, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 2.99 (t,  $J = 10.6$  Hz, 1H), 2.83 (q,  $J = 8.9$  Hz, 1H), 2.69 (d,  $J = 8.1$  Hz, 2H), 2.31 (d,  $J = 15.0$  Hz, 1H), 1.96 – 1.85 (m, 1H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 168.1, 149.0, 146.2, 144.5, 143.6, 138.7, 129.5, 129.1, 128.7, 127.7, 127.2, 127.2, 126.4, 126.1, 124.2, 122.1, 121.4, 96.9, 84.3, 65.0, 57.9, 53.1, 52.8, 46.4, 38.5, 34.9. **IR (KBr)**  $\nu_{\text{max}}$  3744, 3522, 3497, 2952, 1739, 1456, 1436, 1340, 1260, 1153, 1016, 961, 868, 756, 702, 531  $\text{cm}^{-1}$ . **HRMS (ESI)** calcd for  $\text{C}_{29}\text{H}_{26}\text{NaO}_5$  [ $\text{M} + \text{Na}]^+$  : 477.1672; Found: 477.1673.

### 3. General procedure for synthesis of 7

7 were synthesized according to 1

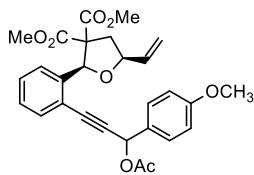


**Compound 7a** (1:0.87 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 7.3$  Hz, 2H), 7.39 (q,  $J = 7.3$  Hz, 5H), 7.31 (t,  $J = 7.5$  Hz, 1H), 7.20 (t,  $J = 7.4$  Hz, 1H), 6.77 and 6.76 (d,  $J = 5.1$  Hz, 1H), 6.40 and 6.34 (d,  $J = 25.7$  Hz, 1H), 6.05 (dt,  $J = 16.8, 8.2$  Hz, 1H), 5.42 (d,  $J = 17.2$  Hz, 1H), 5.27 (d,  $J = 10.4$  Hz, 1H), 4.48 – 4.40 (m, 1H), 3.75 and 3.69 (d,  $J = 24.4$  Hz, 3H), 3.12 and 3.10 (d,  $J = 7.4$  Hz, 3H), 2.78 (t,  $J = 12.4$  Hz, 1H), 2.46 – 2.38 (m, 1H), 2.16 (s, 3H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.77 and 170.76, 169.85 and 169.83, 168.57 and 168.56, 140.97 and 140.86, 137.23 and 137.19, 136.01 and 135.99, 132.09 and 131.97, 128.86, 128.66, 128.61, 127.97 and 127.93, 127.87, 127.48 and 127.44, 121.50 and 121.44, 117.90, 90.48 and 90.35, 84.66 and 84.62, 81.55 and 81.49, 79.23, 66.16 and 66.09, 53.08 and 53.06, 53.01 and 52.98, 52.05 and 52.02, 40.74 and 40.64, 21.16.

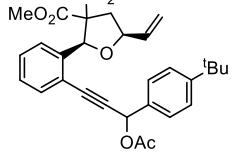


**Compound 7d** (1:0.87 diasteromer):  $R_f = 0.35$  (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.1$  Hz, 2H), 7.43 – 7.40 (m, 2H), 7.33 – 7.29 (m, 1H), 7.20 (t,  $J = 6.9$  Hz, 3H), 6.73 and 6.72 (d,  $J = 5.4$  Hz, 1H), 6.40 and 6.33 (d,  $J = 32.9$  Hz, 1H), 6.05 (m, 1H), 5.42 (m, 1H), 5.29 – 5.25 (m, 1H), 4.47 – 4.42 (m, 1H), 3.76 and 3.70 (d,  $J = 30.6$  Hz, 3H), 3.13 and 3.11 (d,  $J = 10.3$  Hz, 3H), 2.80 – 2.75 (m, 1H), 2.42 (m, 1H), 2.37 (s, 3H), 2.15 and 2.14 (d,  $J = 2.5$  Hz, 3H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.79 and 170.77, 169.86 and 169.83, 168.57 and 168.55, 140.96 and 140.84, 138.77, 136.06 and 136.03, 134.36 and 134.30, 132.06 and 131.98, 129.27, 128.59 and 128.56, 127.98 and 127.93, 127.85 and 127.84, 127.47 and 127.43, 121.60 and 121.54, 117.82 and 117.79, 90.67 and 90.56, 84.48 and 84.42, 81.59 and 81.53, 79.21, 66.19 and 66.17, 65.99, 53.05 and 53.04, 52.98 and 52.95, 52.02 and 51.99, 40.76 and 40.68, 21.24 and 21.16. **IR (KBr)**  $\nu_{\text{max}}$  3918, 3744, 3520, 2952, 1737, 1513, 1434, 1369, 1271,

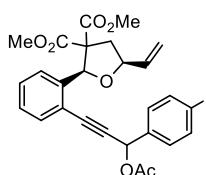
1226, 1094, 1014, 950, 764, 548 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>28</sub>H<sub>28</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 499.1727; Found: 499.1731.



Compound **7e** (1:0.88 diasteromer): R<sub>f</sub> = 0.30 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.93 and 6.91 (d, J = 8.3 Hz, 2H), 6.72 and 6.71 (d, J = 2.4 Hz, 1H), 6.40 and 6.33 (d, J = 25.2 Hz, 1H), 6.05 (m, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.27 (d, J = 10.4 Hz, 1H), 4.49 – 4.41 (m, 1H), 3.81 (s, 3H), 3.76 and 3.70 (d, J = 23.5 Hz, 3H), 3.13 and 3.12 (d, J = 6.0 Hz, 3H), 2.78 (t, J = 12.4 Hz, 1H), 2.42 (dt, J = 13.2, 4.2 Hz, 1H), 2.13 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.79 and 170.76, 169.90 and 169.87, 168.55 and 168.53, 160.07, 140.94 and 140.83, 136.04 and 136.02, 132.08 and 131.98, 129.54 and 129.50, 129.43, 128.59 and 128.56, 127.85 and 127.84, 127.48 and 127.44, 121.59 and 121.53, 117.81, 113.95, 90.71 and 90.59, 84.46 and 84.40, 81.58 and 81.53, 79.21, 66.19, 66 and 17, 65.83, 55.35 and 55.33, 53.06 and 53.04, 52.99 and 52.97, 52.03 and 52.01, 40.75 and 40.65, 21.17. **IR (KBr)** ν<sub>max</sub> 3743, 3521, 3497, 2953, 1736, 1610, 1584, 1613, 1485, 1435, 1369, 1341, 1226, 1177, 1040, 946, 832, 763, 608, 556 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>28</sub>H<sub>28</sub>NaO<sub>8</sub> [M + Na]<sup>+</sup>: 515.1676; Found: 515.1679.

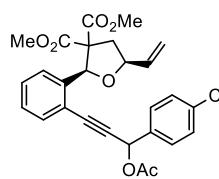


Compound **7f** (1:1 diasteromer): R<sub>f</sub> = 0.38 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 8.1 Hz, 4H), 7.30 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.74 (s, 1H), 6.41 and 6.34 (d, J = 27.9 Hz, 1H), 6.05 (m, 1H), 5.45 – 5.38 (m, 1H), 5.26 (d, J = 10.4 Hz, 1H), 4.49 – 4.41 (m, 1H), 3.75 and 3.70 (d, J = 23.4 Hz, 3H), 3.13 and 3.11 (d, J = 8.7 Hz, 3H), 2.78 (t, J = 12.4 Hz, 1H), 2.43 (dt, J = 13.1, 4.2 Hz, 1H), 2.14 (s, 3H), 1.33 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.79 and 170.77, 169.88 and 169.84, 168.58 and 168.55, 151.94 and 151.91, 140.96 and 140.85, 136.08 and 136.05, 134.24 and 134.19, 132.08 and 131.98, 128.58 and 128.55, 127.84, 127.78 and 127.72, 127.47 and 127.43, 125.55, 121.62 and 121.56, 117.81 and 117.79, 90.72 and 90.59, 84.49 and 84.43, 81.61 and 81.55, 79.21, 66.19 and 66.17, 65.92, 53.04 and 53.03, 52.98 and 52.96, 52.02 and 51.99, 40.77 and 40.68, 34.67, 31.33, 21.18. **IR (KBr)** ν<sub>max</sub> 3743, 3521, 3497, 3465, 2957, 2870, 2231, 1738, 1512, 1483, 1434, 1368, 1336, 1271, 1226, 1156, 1095, 1048, 950, 835, 762, 702, 607, 518 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>31</sub>H<sub>34</sub>NaO<sub>7</sub> [M + Na]<sup>+</sup>: 541.2197; Found: 541.2194.



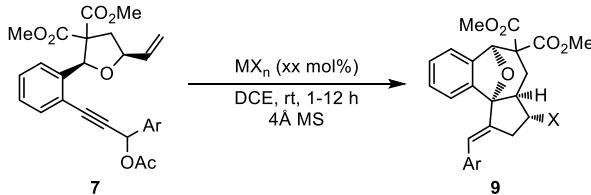
Compound **7g** (1:0.92 diasteromer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.60 (m, 2H), 7.44 – 7.40 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 8.6 Hz, 2H), 6.74 and 6.73 (d, J = 3.9 Hz, 1H), 6.38 and 6.33 (d, J = 22.5 Hz, 1H), 6.05 (m, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.27 (d, J = 10.4 Hz, 1H), 4.44 (dt, J = 10.5, 4.6 Hz, 1H), 3.76 and 3.70 (d, J = 23.1 Hz, 3H), 3.12 and 3.11 (d, J = 2.4 Hz, 3H), 2.78 (t, J = 12.4 Hz, 1H), 2.42 (dt, J = 13.2, 3.7 Hz, 1H), 2.15 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.76 and 170.74, 169.75 and 169.73, 168.46 and 168.45, 162.95 (d, J = 247.6 Hz), 140.98 and 140.90, 135.97 and 135.95, 133.21 (d, J = 3.8 Hz) and 133.18 (d, J = 3.5 Hz), 132.09 and 131.97, 129.98 (d, J = 5.2 Hz) and 129.90 (d, J = 5.2 Hz), 128.74 and 128.72, 127.90, 127.52 (d, J = 2.9 Hz), 121.34 and 121.28, 117.85 and 117.84, 115.50 (d, J = 21.8 Hz), 90.19 and 90.09, 84.83

and 84.79, 81.52 and 81.47, 79.21, 66.17 and 66.16, 65.42, 53.03 and 53.02, 52.97 and 52.95, 52.02 and 52.01, 40.71 and 40.61, 21.09. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -112.75, -112.80. **IR (KBr)** ν<sub>max</sub> 3744, 3522, 3497, 3464, 2953, 1737, 1604, 1511, 1486, 1434, 1369, 1224, 1158, 1095, 1047, 951, 837, 763, 608, 550 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>27</sub>H<sub>25</sub>FNaO<sub>7</sub> [M + Na]<sup>+</sup> : 503.1477; Found: 503.1481.



Compound **7h** (1:0.94 diastereomer): R<sub>f</sub> = 0.35 (EtOAc/petroleum ether = 1/5), yellow oil. The following data are for a mixture of two diastereomers. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, J = 7.3 Hz, 2H), 7.39 (dd, J = 14.4, 7.4 Hz, 4H), 7.32 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.73 and 6.72 (d, J = 5.3 Hz, 1H), 6.37 and 6.32 (d, J = 21.8 Hz, 1H), 6.04 (m, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.27 (d, J = 10.4 Hz, 1H), 4.43 (dt, J = 11.2, 5.4 Hz, 1H), 3.76 and 3.70 (d, J = 23.8 Hz, 3H), 3.12 and 3.11 (d, J = 2.8 Hz, 3H), 2.81 – 2.74 (m, 1H), 2.42 (dt, J = 13.2, 4.0 Hz, 1H), 2.15 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.74 and 170.73, 169.71 and 169.69, 168.46, 140.99 and 140.92, 135.95 and, 135.93, 135.82 and 135.79, 134.78 and 134.76, 132.09 and 131.97, 129.41, 129.34, 128.78, 127.89, 127.54 and 127.51, 121.27 and 121.23, 117.88 and 117.86, 89.94 and 89.84, 84.95 and 84.92, 81.51, 81.46 and 79.21, 66.17 and 66.16, 65.39, 53.06 and 53.05, 52.98 and 52.96, 52.04 and 52.02, 40.72 and 40.62, 21.08. **IR (KBr)** ν<sub>max</sub> 3743, 3522, 3497, 3464, 2952, 2231, 1736, 1489, 1434, 1369, 1333, 1270, 1156, 1092, 1047, 953, 824, 737, 606, 546 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>27</sub>H<sub>25</sub>ClNaO<sub>7</sub> [M + Na]<sup>+</sup> : 519.1181; Found: 519.1186.

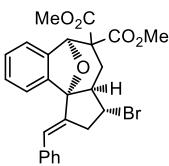
#### 4. General procedure for synthesis of **9**



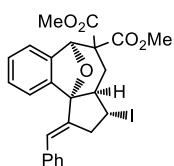
To a solution of **7** in DCE was added the catalyst (50–75 mol% MX<sub>n</sub>) at room temperature. Then the solution mixture was stirred at the same temperature, after completion of the reaction, the solvent was removed under reduced pressure and the crude product was subjected to silica gel column chromatography to afford **9**.



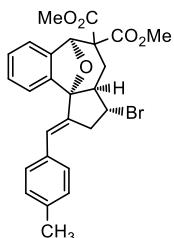
Compound **9a**: R<sub>f</sub> = 0.36 (EtOAc/petroleum ether = 1/8), Yield: 29%, yellow solid (m.p. 158–159 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39 (d, J = 6.2 Hz, 1H), 7.34 (s, 4H), 7.30 (s, 1H), 7.26 (s, 2H), 6.92 (d, J = 5.5 Hz, 1H), 6.48 (s, 1H), 6.00 (s, 1H), 3.88 (s, 3H), 3.81 – 3.75 (m, 1H), 3.73 (s, 3H), 3.62 (dd, J = 17.9, 7.8 Hz, 1H), 3.18 (dd, J = 17.9, 8.4 Hz, 1H), 2.79 (d, J = 13.2 Hz, 1H), 2.61 (dt, J = 11.6, 6.2 Hz, 1H), 1.07 (t, J = 12.8 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.7, 168.6, 143.9, 140.7, 136.5, 136.5, 128.6, 128.5, 128.4, 128.0, 127.3, 125.0, 122.7, 121.0, 90.4, 82.2, 55.7, 55.3, 53.4, 52.8, 48.2, 41.7, 26.9. **IR (KBr)** ν<sub>max</sub> 3744, 3521, 1497, 2953, 1735, 1540, 1262, 992, 751 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>25</sub>H<sub>23</sub>ClNaO<sub>5</sub> [M + Na]<sup>+</sup> : 461.1126; Found: 461.1121.



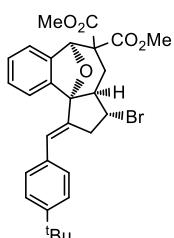
**Compound 9b:**  $R_f = 0.36$  (EtOAc/petroleum ether = 1/8), Yield: 34%, yellow solid (m.p. 134–135 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d,  $J = 6.6$  Hz, 1H), 7.34 (d,  $J = 3.8$  Hz, 4H), 7.28 (d,  $J = 7.7$  Hz, 1H), 7.24 (d,  $J = 8.3$  Hz, 2H), 6.92 (d,  $J = 6.5$  Hz, 1H), 6.48 (s, 1H), 5.99 (s, 1H), 3.88 (s, 3H), 3.81 – 3.74 (m, 1H), 3.73 (s, 3H), 3.66 (dd,  $J = 17.6, 7.7$  Hz, 1H), 3.32 (dd,  $J = 17.7, 8.1$  Hz, 1H), 2.77 (dd,  $J = 13.3, 3.9$  Hz, 1H), 2.68 (td,  $J = 11.8, 4.1$  Hz, 1H), 1.03 (t,  $J = 12.7$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.7, 168.6, 143.8, 140.7, 137.1, 136.4, 128.6, 128.5, 128.4, 128.0, 127.3, 124.8, 122.7, 121.1, 90.3, 82.2, 55.4, 53.4, 52.8, 48.8, 44.9, 42.2, 27.2. **IR (KBr)**  $\nu_{max}$  3745, 3522, 3497, 2954, 1736, 1492, 1435, 1265, 1219, 1123, 1064, 991, 913, 865, 762, 697, 644, 518 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>25</sub>H<sub>23</sub>BrNaO<sub>5</sub> [M + Na]<sup>+</sup>: 505.0621; Found: 505.0623.



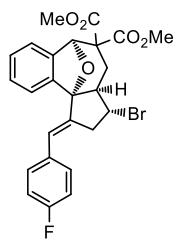
**Compound 9c:**  $R_f = 0.36$  (EtOAc/petroleum ether = 1/8), Yield: 35%, yellow solid (m.p. 125–126 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d,  $J = 6.5$  Hz, 1H), 7.34 (s, 4H), 7.28 (d,  $J = 7.6$  Hz, 2H), 7.23 (s, 1H), 6.92 (d,  $J = 6.6$  Hz, 1H), 6.46 (s, 1H), 5.96 (s, 1H), 3.87 (s, 3H), 3.77 – 3.69 (m, 4H), 3.65 (t,  $J = 7.7$  Hz, 1H), 3.46 – 3.38 (m, 1H), 2.73 – 2.68 (m, 1H), 2.63 (td,  $J = 12.0, 4.2$  Hz, 1H), 0.96 (t,  $J = 12.6$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.7, 168.6, 143.8, 140.7, 138.3, 136.5, 128.6, 128.5, 128.4, 128.0, 127.3, 124.5, 122.7, 121.3, 89.7, 82.1, 55.7, 53.4, 52.8, 50.1, 44.0, 27.8, 18.3. **IR (KBr)**  $\nu_{max}$  3744, 3522, 3498, 2952, 1735, 1540, 1434, 1266, 1218, 990, 864, 762, 697, 519 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>25</sub>H<sub>23</sub>InaO<sub>5</sub> [M + Na]<sup>+</sup>: 553.0482; Found: 553.0480.



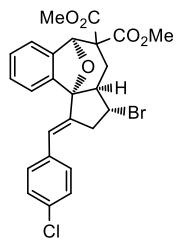
**Compound 9d:**  $R_f = 0.36$  (EtOAc/petroleum ether = 1/8), Yield: 45%, yellow solid (m.p. 118–119 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d,  $J = 6.5$  Hz, 1H), 7.27 (d,  $J = 13.3$  Hz, 2H), 7.23 (s, 2H), 7.15 (d,  $J = 7.7$  Hz, 2H), 6.91 (d,  $J = 6.5$  Hz, 1H), 6.44 (s, 1H), 5.98 (s, 1H), 3.87 (s, 3H), 3.74 (d,  $J = 7.4$  Hz, 4H), 3.64 (dd,  $J = 17.8, 7.8$  Hz, 1H), 3.31 (dd,  $J = 17.7, 8.2$  Hz, 1H), 2.77 (d,  $J = 13.4$  Hz, 1H), 2.68 (dt,  $J = 12.1, 6.0$  Hz, 1H), 2.34 (s, 3H), 1.03 (t,  $J = 12.7$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.7, 168.6, 143.9, 140.7, 137.2, 136.0, 133.7, 129.2, 128.5, 128.3, 128.0, 124.7, 122.7, 121.1, 90.3, 82.1, 55.4, 53.39, 52.75, 48.8, 45.1, 42.3, 27.2, 21.2. **IR (KBr)**  $\nu_{max}$  3468, 3423, 3023, 3005, 2953, 1739, 1585, 1513, 1443, 1343, 1116, 994, 810, 763, 637, 518 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>26</sub>H<sub>25</sub>BrNaO<sub>5</sub> [M + Na]<sup>+</sup>: 519.0778; Found: 519.0780.



**Compound 9f:**  $R_f = 0.36$  (EtOAc/petroleum ether = 1/8), Yield: 37%, yellow solid (m.p. 142–143 °C). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d,  $J = 7.9$  Hz, 3H), 7.29 (d,  $J = 8.4$  Hz, 2H), 7.25 (d,  $J = 6.0$  Hz, 2H), 6.90 (d,  $J = 6.6$  Hz, 1H), 6.46 (s, 1H), 5.98 (s, 1H), 3.87 (s, 3H), 3.73 (s, 4H), 3.65 (dd,  $J = 17.9, 7.6$  Hz, 1H), 3.32 (dd,  $J = 17.4, 8.1$  Hz, 1H), 2.77 (dd,  $J = 13.4, 3.3$  Hz, 1H), 2.67 (td,  $J = 11.8, 4.1$  Hz, 1H), 1.32 (s, 9H), 1.03 (t,  $J = 12.7$  Hz, 1H). **13C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.7, 168.6, 150.4, 143.9, 140.7, 136.2, 133.7, 128.38, 128.35, 128.0, 1255, 124.6, 122.7, 121.1, 90.3, 82.1, 55.4, 53.42, 52.77, 48.8, 45.1, 42.3, 34.6, 31.3, 27.2. **IR (KBr)**  $\nu_{max}$  3675, 3275, 3074, 2959, 2322, 1739, 1509, 1443, 1366, 1263, 1218, 1114, 1058, 985, 868, 818, 764, 636, 559 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>29</sub>H<sub>31</sub>BrNaO<sub>5</sub> [M + Na]<sup>+</sup>: 561.1247; Found: 561.1245.



**Compound 9g:**  $R_f = 0.36$  (EtOAc/petroleum ether = 1/8), Yield: 41%, yellow solid (m.p. 127-128 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d,  $J = 6.4$  Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 (s, 1H), 7.04 (t,  $J = 8.4$  Hz, 2H), 6.92 (d,  $J = 6.5$  Hz, 1H), 6.44 (s, 1H), 5.98 (s, 1H), 3.87 (s, 3H), 3.73 (s, 4H), 3.62 (dd,  $J = 17.8, 7.6$  Hz, 1H), 3.27 (dd,  $J = 17.8, 8.6$  Hz, 1H), 2.80 – 2.74 (m, 1H), 2.67 (td,  $J = 11.9, 3.9$  Hz, 1H), 1.03 (t,  $J = 12.7$  Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.65, 168.53, 163.08, 160.61, 143.68, 140.65, 136.70, 136.68, 132.64, 132.61, 130.22, 130.14, 128.38, 128.04, 123.67, 122.76, 121.02, 115.61, 115.39, 90.24, 82.15, 55.40, 53.41, 53.39, 52.77, 52.75, 48.77, 44.75, 27.15. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -113.99. **IR (KBr)**  $\nu_{\text{max}}$  3733, 3473, 3415, 3279, 2954, 2840, 1793, 1605, 1545, 1441, 1366, 1264, 1224, 1164, 1112, 1060, 997, 868, 821, 766, 739, 636, 522 cm<sup>-1</sup>. **HRMS (ESI)** calcd for C<sub>25</sub>H<sub>22</sub>BrFNaO<sub>5</sub> [M + Na]<sup>+</sup>: 523.0527; Found: 523.0526.



**Compound 9h:**  $R_f = 0.36$  (EtOAc/petroleum ether = 1/8), Yield: 44%, yellow solid (m.p. 120-121 °C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d,  $J = 6.3$  Hz, 1H), 7.31 (d,  $J = 8.4$  Hz, 3H), 7.26 (d,  $J = 4.2$  Hz, 3H), 6.91 (d,  $J = 6.7$  Hz, 1H), 6.43 (s, 1H), 5.98 (s, 1H), 3.87 (s, 3H), 3.73 (s, 4H), 3.62 (dd,  $J = 18.0, 7.6$  Hz, 1H), 3.27 (dd,  $J = 18.1, 8.3$  Hz, 1H), 2.77 (dd,  $J = 13.3, 3.8$  Hz, 1H), 2.67 (td,  $J = 11.9, 4.2$  Hz, 1H), 1.03 (t,  $J = 12.7$  Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 168.5, 143.6, 140.6, 137.9, 134.9, 133.1, 129.8, 128.7, 128.4, 128.1, 123.6, 122.8, 121.0, 90.2, 82.2, 55.4, 53.44, 52.80, 48.7, 44.7, 42.1, 27.1. **IR (KBr)**  $\nu_{\text{max}}$  3674, 3289, 3037, 2953, 1739, 1492, 1441, 1264, 1221, 1096, 1059, 997, 868, 816, 740, 662, 522 cm<sup>-1</sup>.

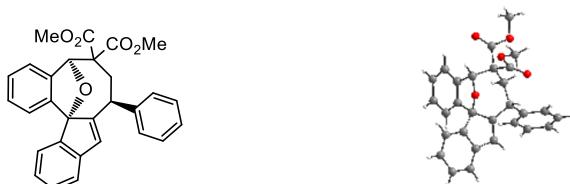
## V. Supplemental References

- (1). P. D. Pohlhaus, S. D. Sanders, A. T. Parsons, W. Li, J. S. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 8642-8650.
- (2) J. Zhang, Z. Liao, L. Chen, and S. Zhu, *Chem. Eur. J.* **2019**, *25*, DOI: 10.1002/chem.201900807.

## VI. Supplemental Figures

### 1. Crystal data and structure refinement for 3a

The crystal structure of has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1896147.



Identification code	3a
Empirical formula	$\text{C}_{29}\text{H}_{24}\text{O}_5$
Formula weight	452.48
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	10.1019(10)
$b/\text{\AA}$	10.2418(11)
$c/\text{\AA}$	11.6590(11)
$\alpha/^\circ$	68.442(10)
$\beta/^\circ$	84.392(8)
$\gamma/^\circ$	87.479(8)
Volume/ $\text{\AA}^3$	1116.5(2)
Z	2
$\rho_{\text{calcd}}/\text{cm}^3$	1.346
$\mu/\text{mm}^{-1}$	0.092
F(000)	476.0
Crystal size/ $\text{mm}^3$	0.15 $\times$ 0.13 $\times$ 0.12
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.276 to 50
Index ranges	-12 $\leq$ h $\leq$ 9, -11 $\leq$ k $\leq$ 12, -13 $\leq$ l $\leq$ 13
Reflections collected	7816
Independent reflections	3939 [ $R_{\text{int}} = 0.0547$ , $R_{\text{sigma}} = 0.0776$ ]
Data/restraints/parameters	3939/0/309
Goodness-of-fit on $F^2$	1.029
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0721$ , $wR_2 = 0.1811$
Final R indexes [all data]	$R_1 = 0.0923$ , $wR_2 = 0.2026$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.40/-0.37

## 2. Crystal data and structure refinement for 4ac

The crystal structure of has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1905661.



Identification code	4ac
Empirical formula	C <sub>31</sub> H <sub>28</sub> O <sub>6</sub>
Formula weight	496.53
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	10.6945(8)
b/Å	24.562(2)
c/Å	9.9544(9)
$\alpha/^\circ$	90
$\beta/^\circ$	98.892(7)
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	2583.4(4)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.277
$\mu/\text{mm}^{-1}$	0.088
F(000)	1048.0
Crystal size/mm <sup>3</sup>	0.12 × 0.11 × 0.1
Radiation	MoKα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	4.196 to 49.99
Index ranges	-12 ≤ h ≤ 12, -25 ≤ k ≤ 29, -9 ≤ l ≤ 11
Reflections collected	11688
Independent reflections	4545 [ $R_{\text{int}} = 0.0569$ , $R_{\text{sigma}} = 0.0780$ ]
Data/restraints/parameters	4545/0/337
Goodness-of-fit on F <sup>2</sup>	1.056
Final R indexes [I>=2σ (I)]	$R_1 = 0.0576$ , $wR_2 = 0.1177$
Final R indexes [all data]	$R_1 = 0.0895$ , $wR_2 = 0.1321$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.23/-0.23

### 3. Crystal data and structure refinement for 9a

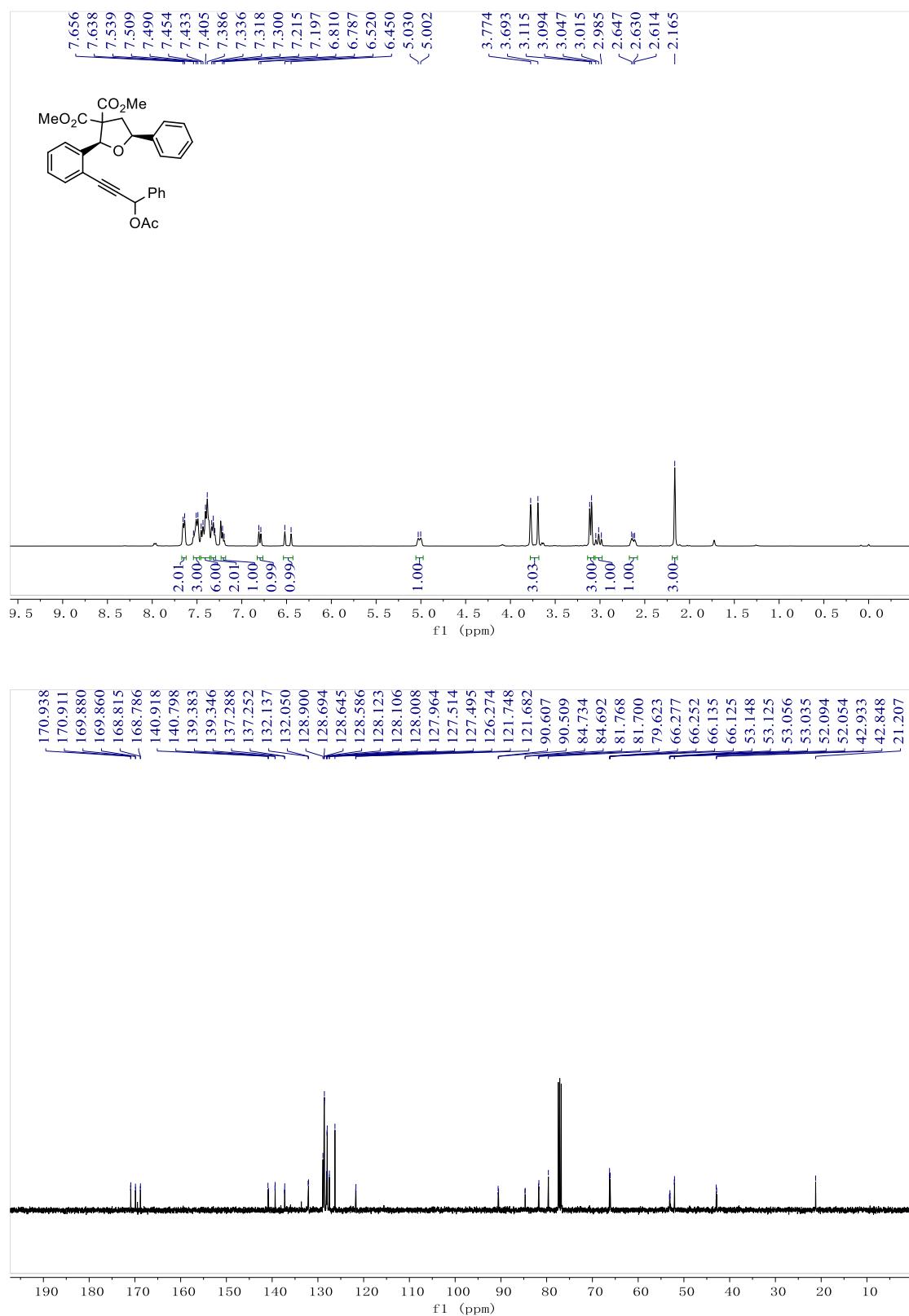
The crystal structure of has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1896148.

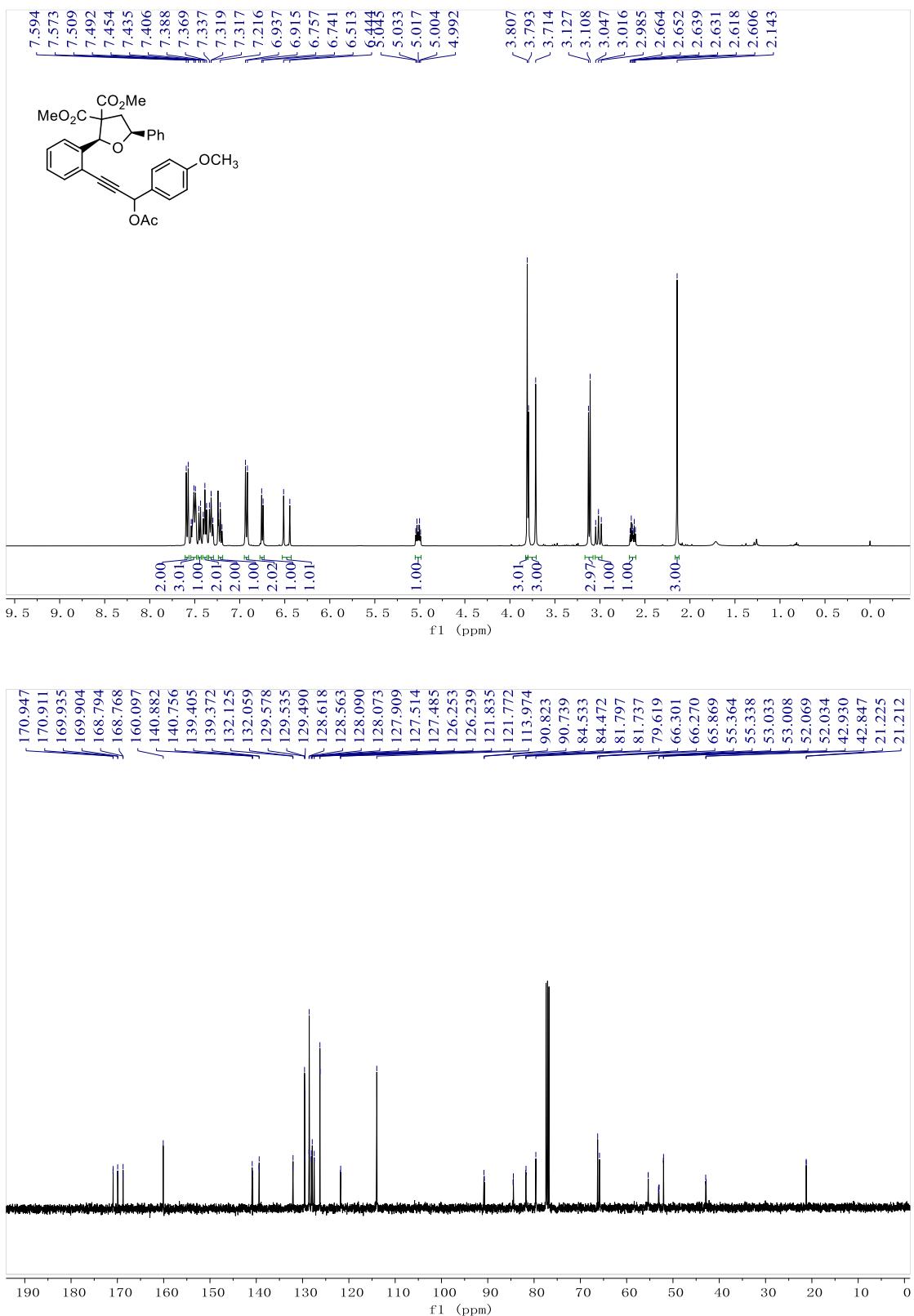


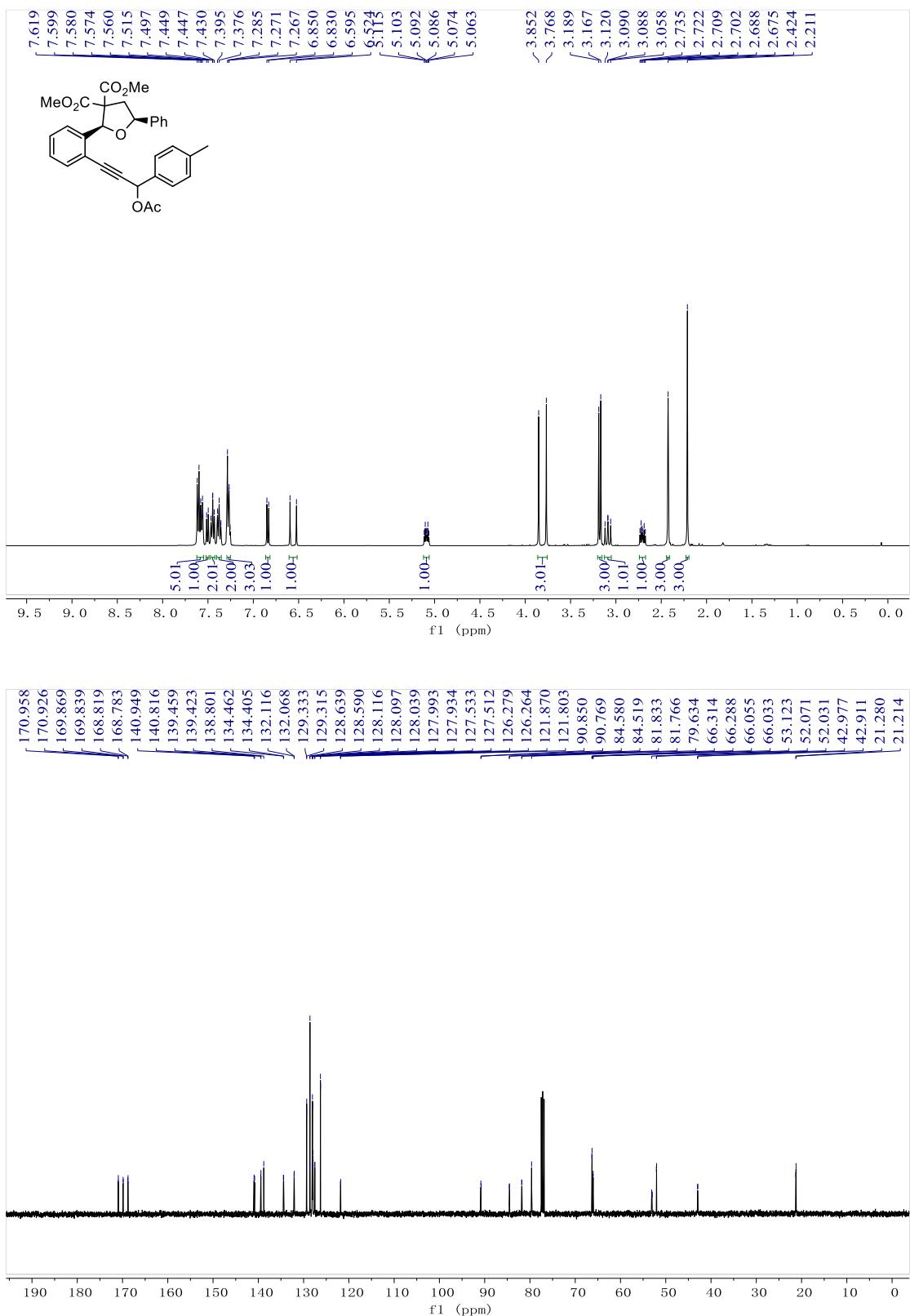
Identification code	9a
Empirical formula	$\text{C}_{25}\text{H}_{23}\text{ClO}_5$
Formula weight	438.88
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/ $\text{\AA}$	10.7102(14)
b/ $\text{\AA}$	11.1405(13)
c/ $\text{\AA}$	11.3689(13)
$\alpha/^\circ$	69.694(11)
$\beta/^\circ$	76.371(11)
$\gamma/^\circ$	62.034(13)
Volume/ $\text{\AA}^3$	1119.3(3)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.302
$\mu/\text{mm}^{-1}$	1.791
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.12 $\times$ 0.11 $\times$ 0.1
Radiation	$\text{CuK}\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^\circ$	8.324 to 148.87
Index ranges	-10 $\leq$ h $\leq$ 12, -10 $\leq$ k $\leq$ 13, -14 $\leq$ l $\leq$ 13
Reflections collected	7321
Independent reflections	4371 [ $\text{R}_{\text{int}} = 0.0614$ , $\text{R}_{\text{sigma}} = 0.0653$ ]
Data/restraints/parameters	4371/0/282
Goodness-of-fit on $\text{F}^2$	1.092
Final R indexes [ $\text{I} \geq 2\sigma(\text{I})$ ]	$\text{R}_1 = 0.0971$ , $\text{wR}_2 = 0.2885$
Final R indexes [all data]	$\text{R}_1 = 0.1089$ , $\text{wR}_2 = 0.3048$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.92/-0.76

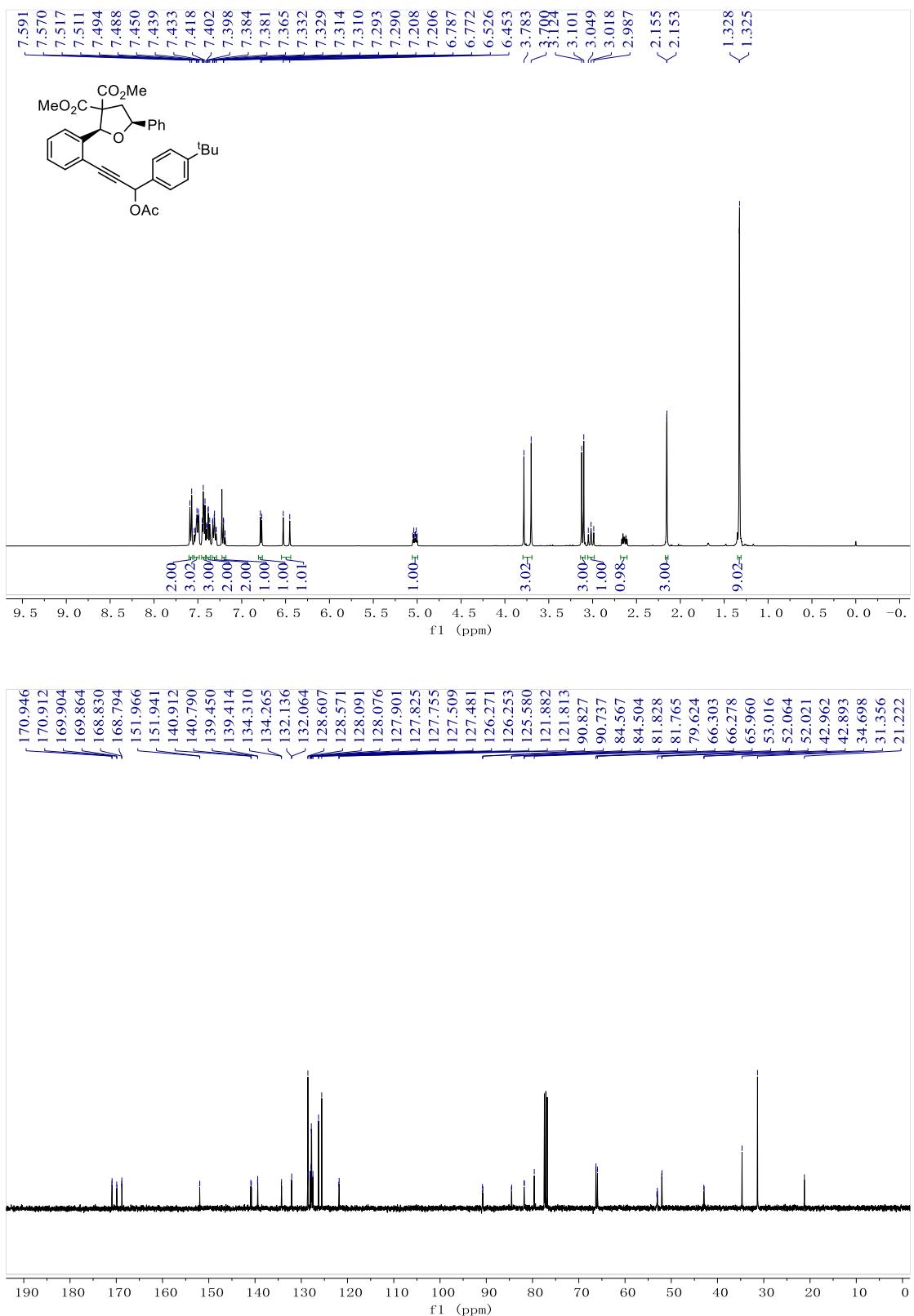
#### 4. Copies of NMR spectra

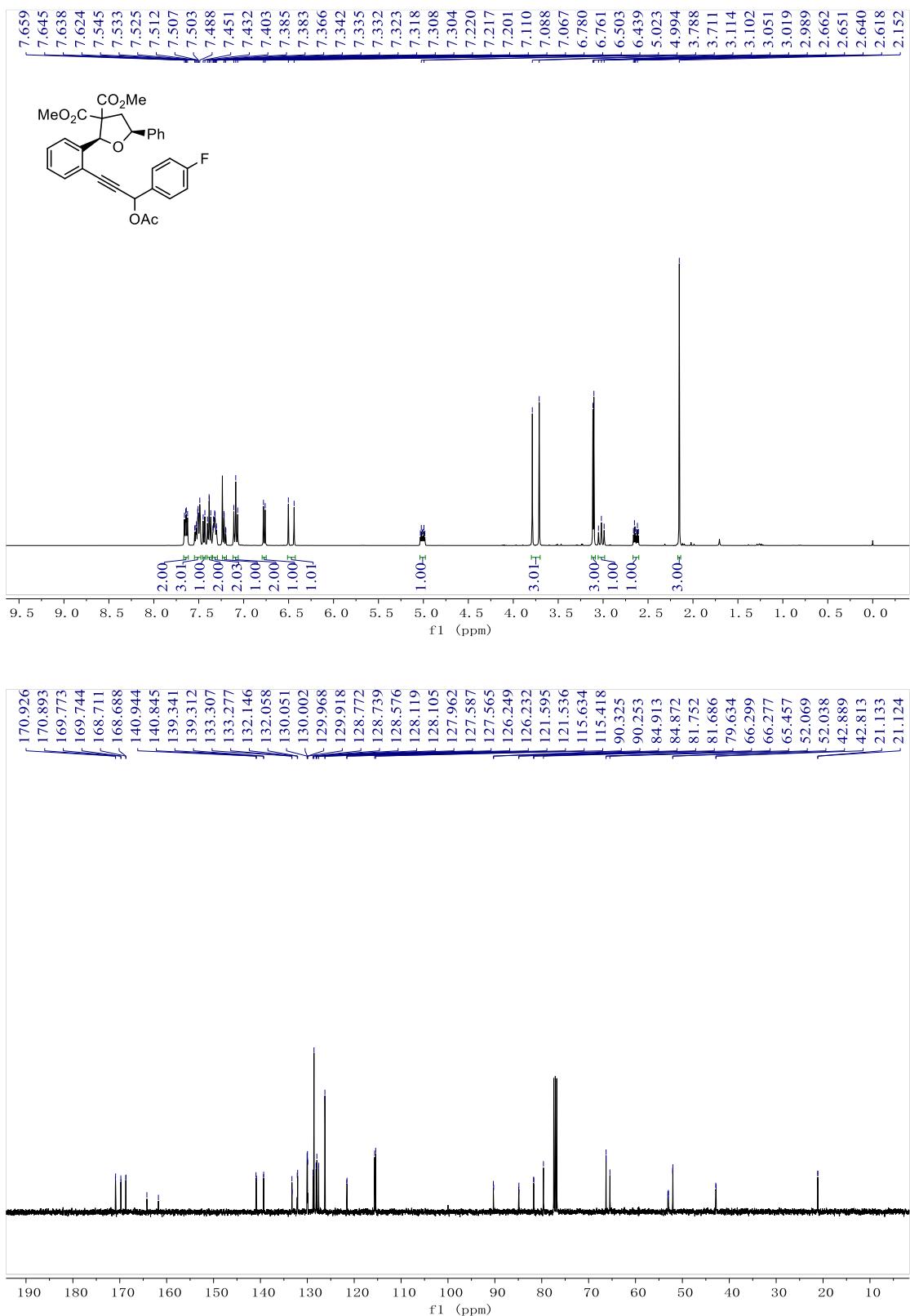
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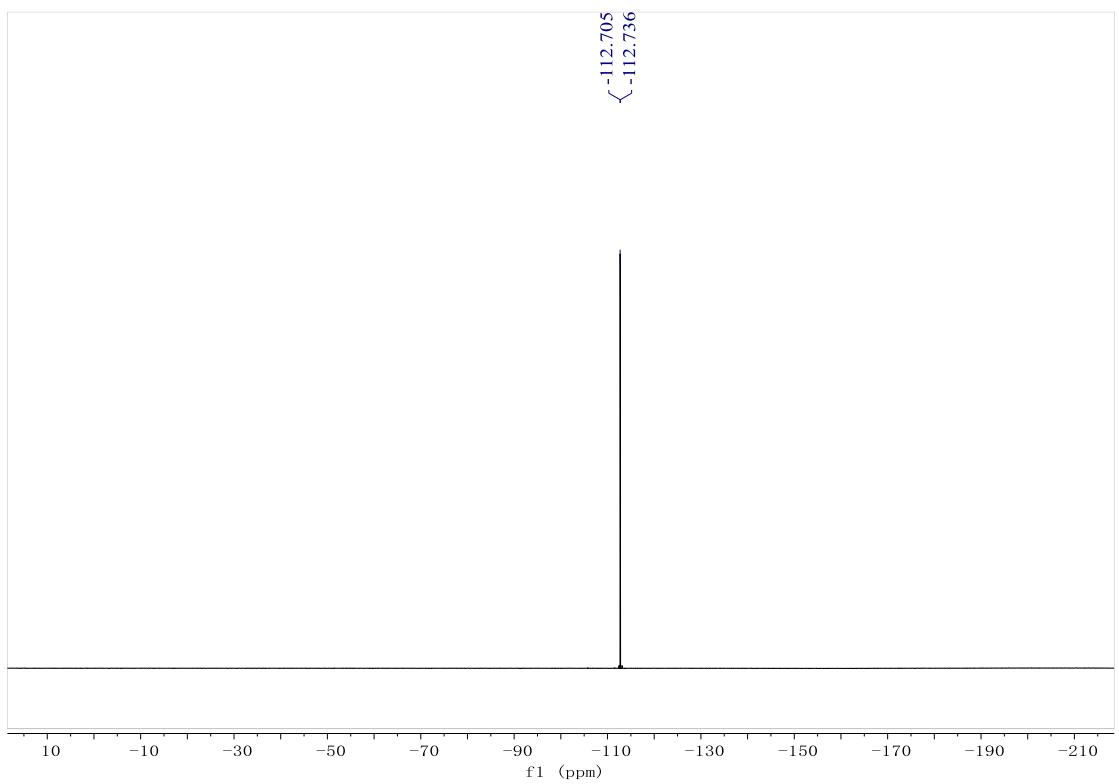


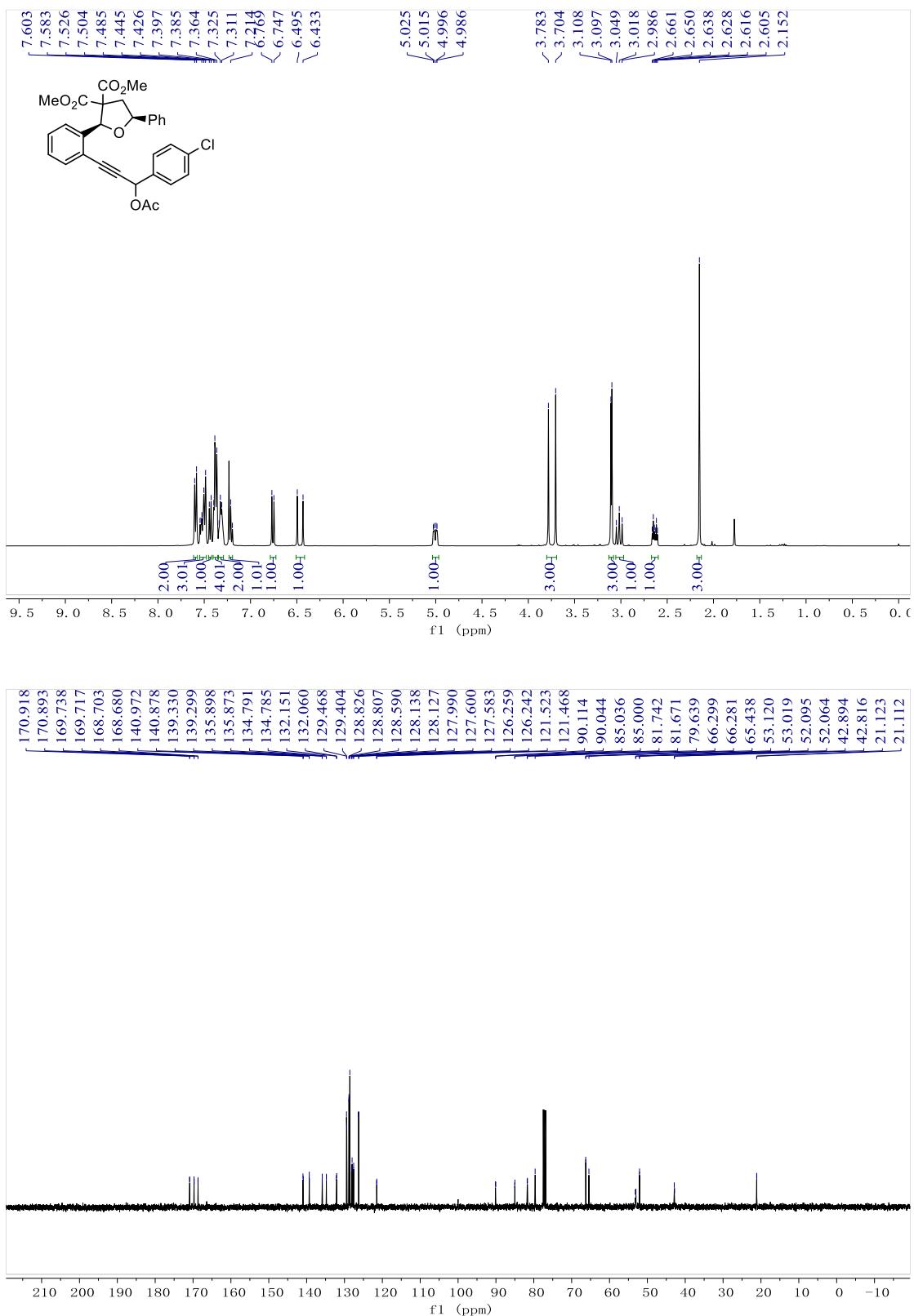
**1b**

**1c**

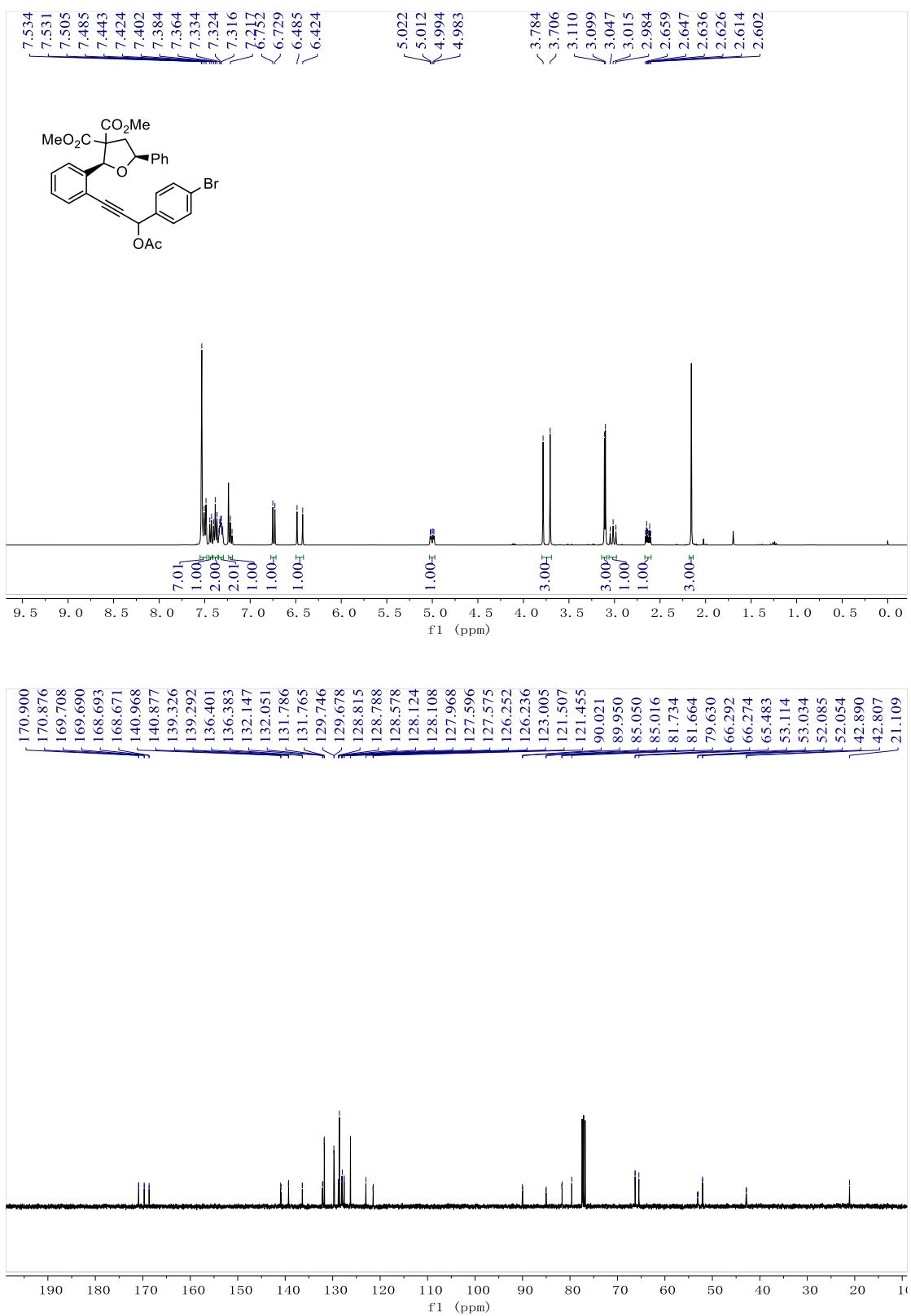
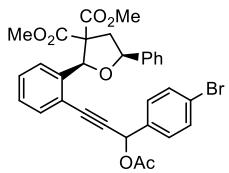
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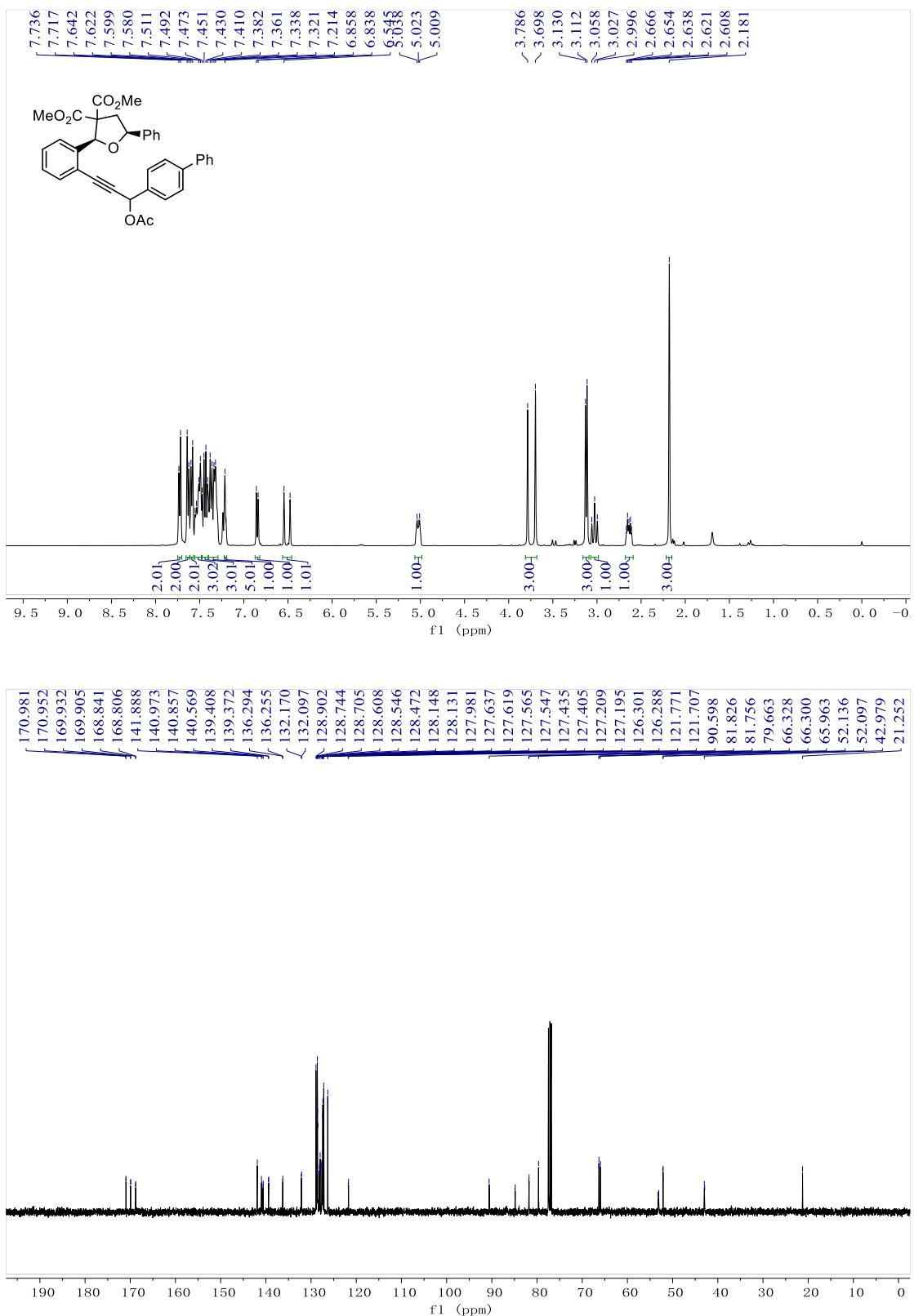
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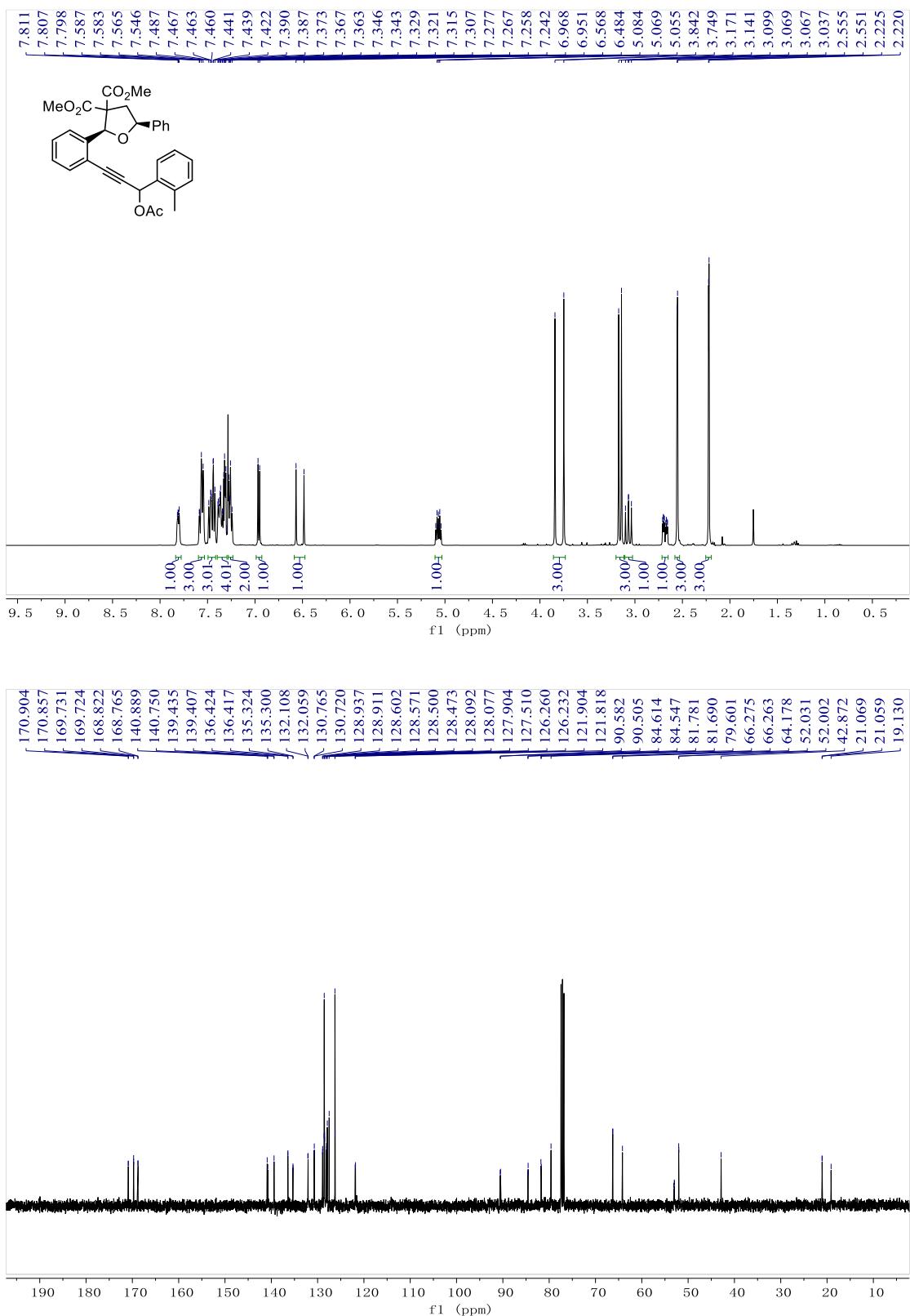
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1g

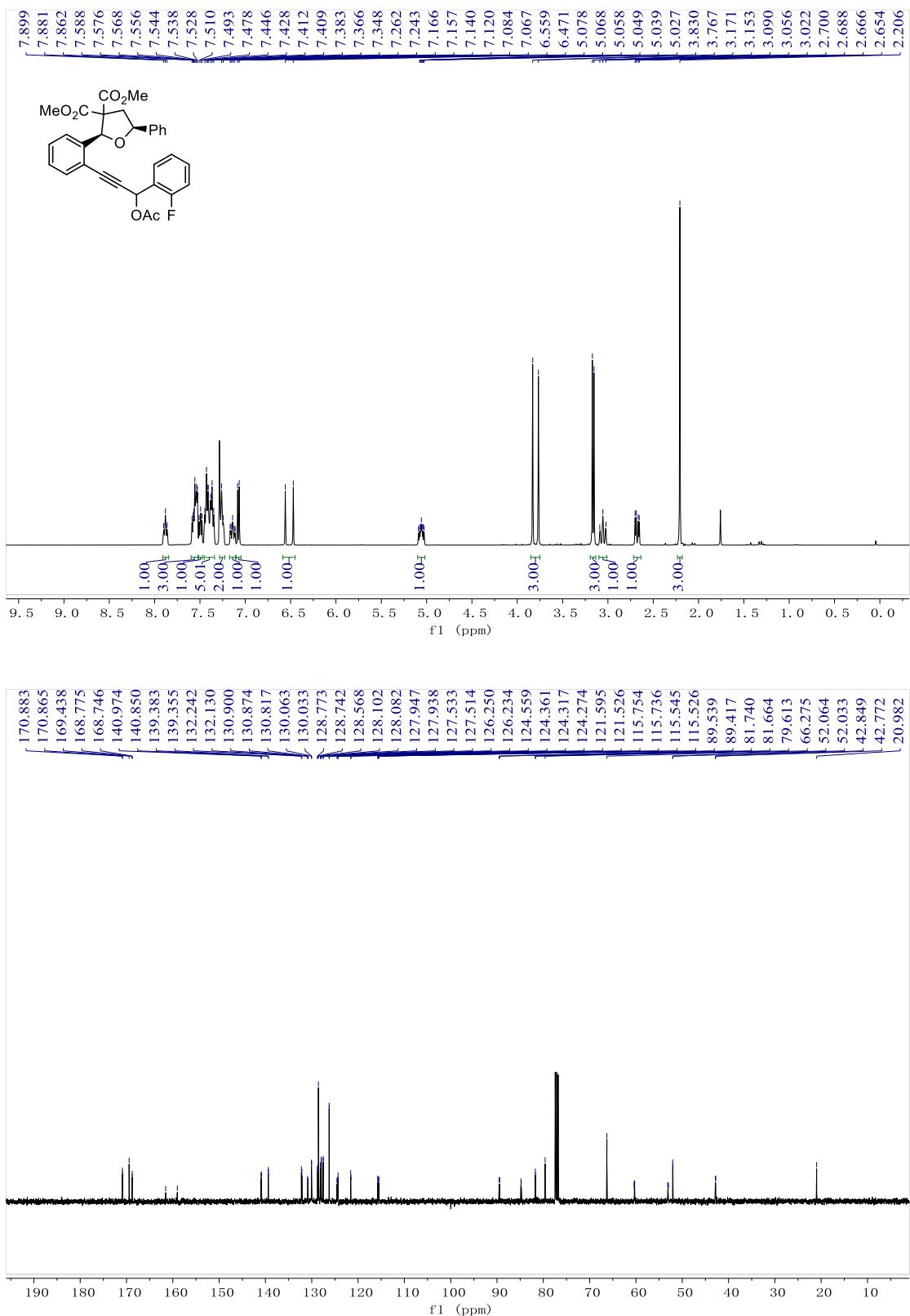


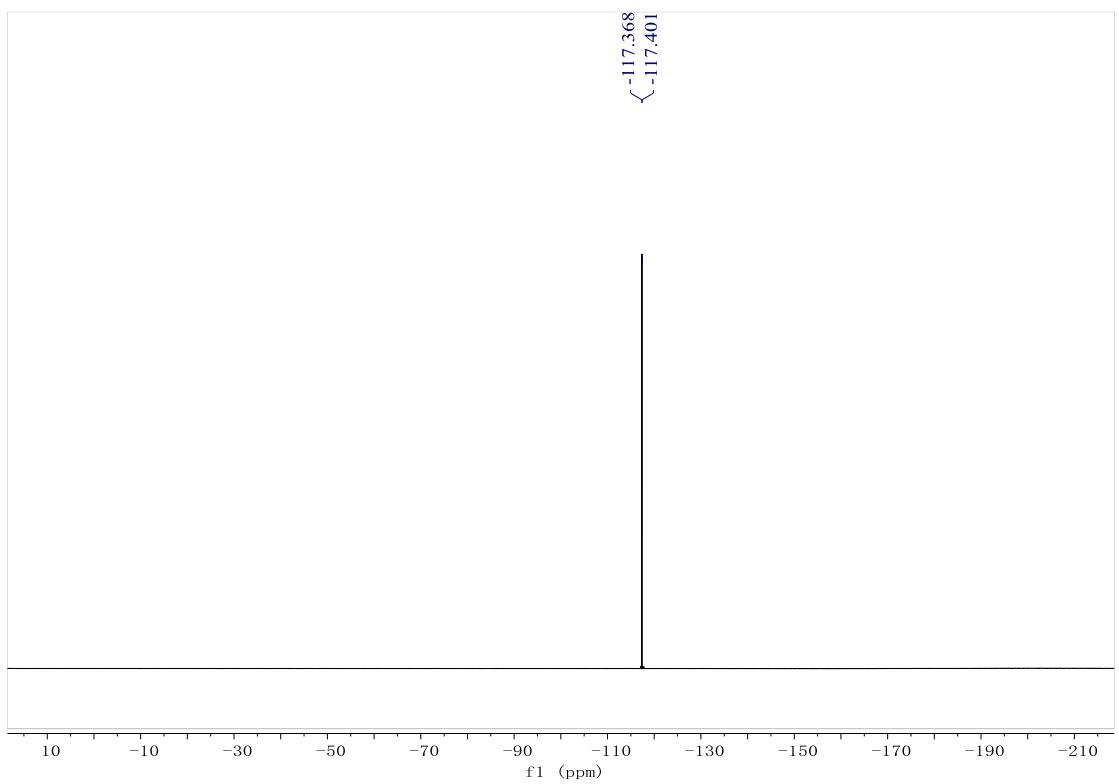
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**1i**

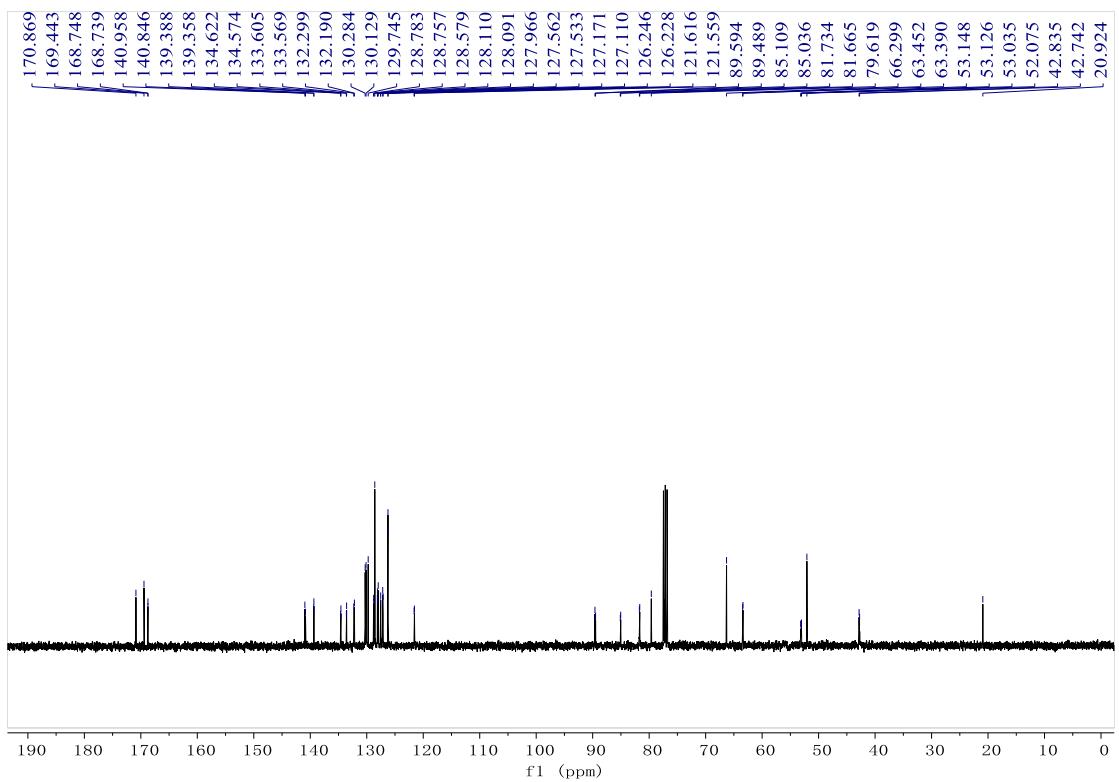
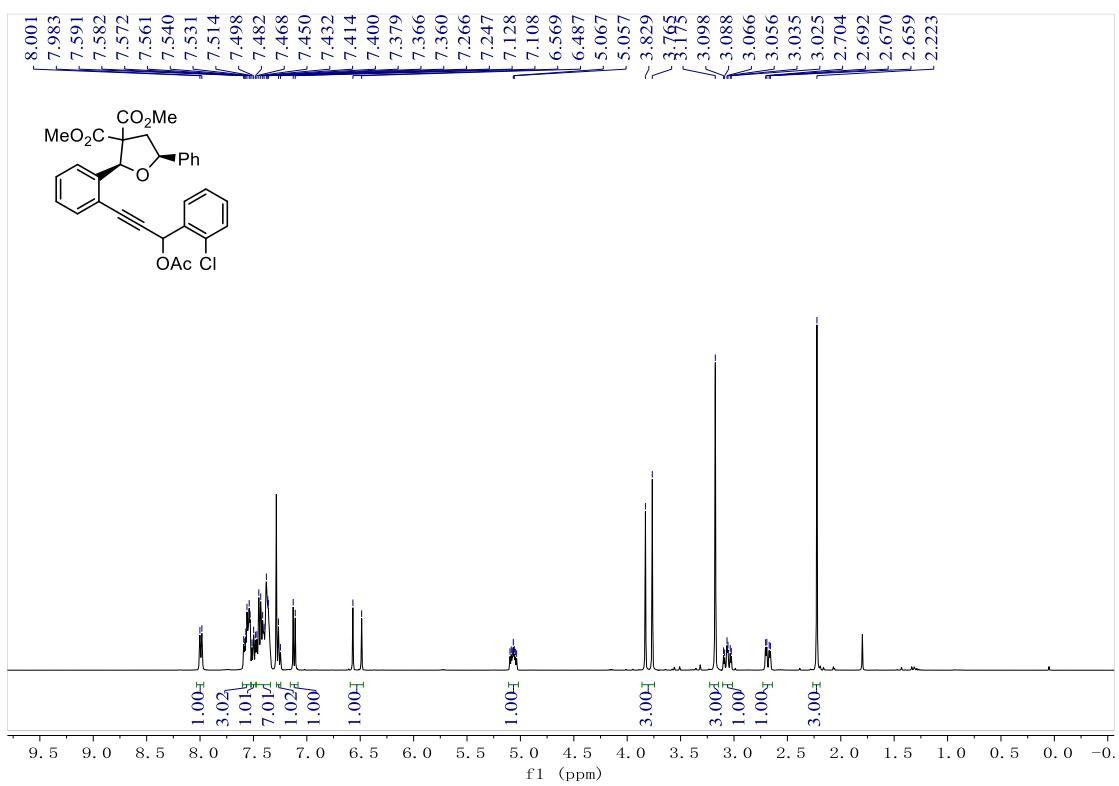
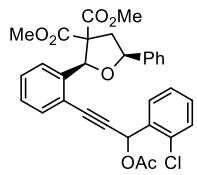


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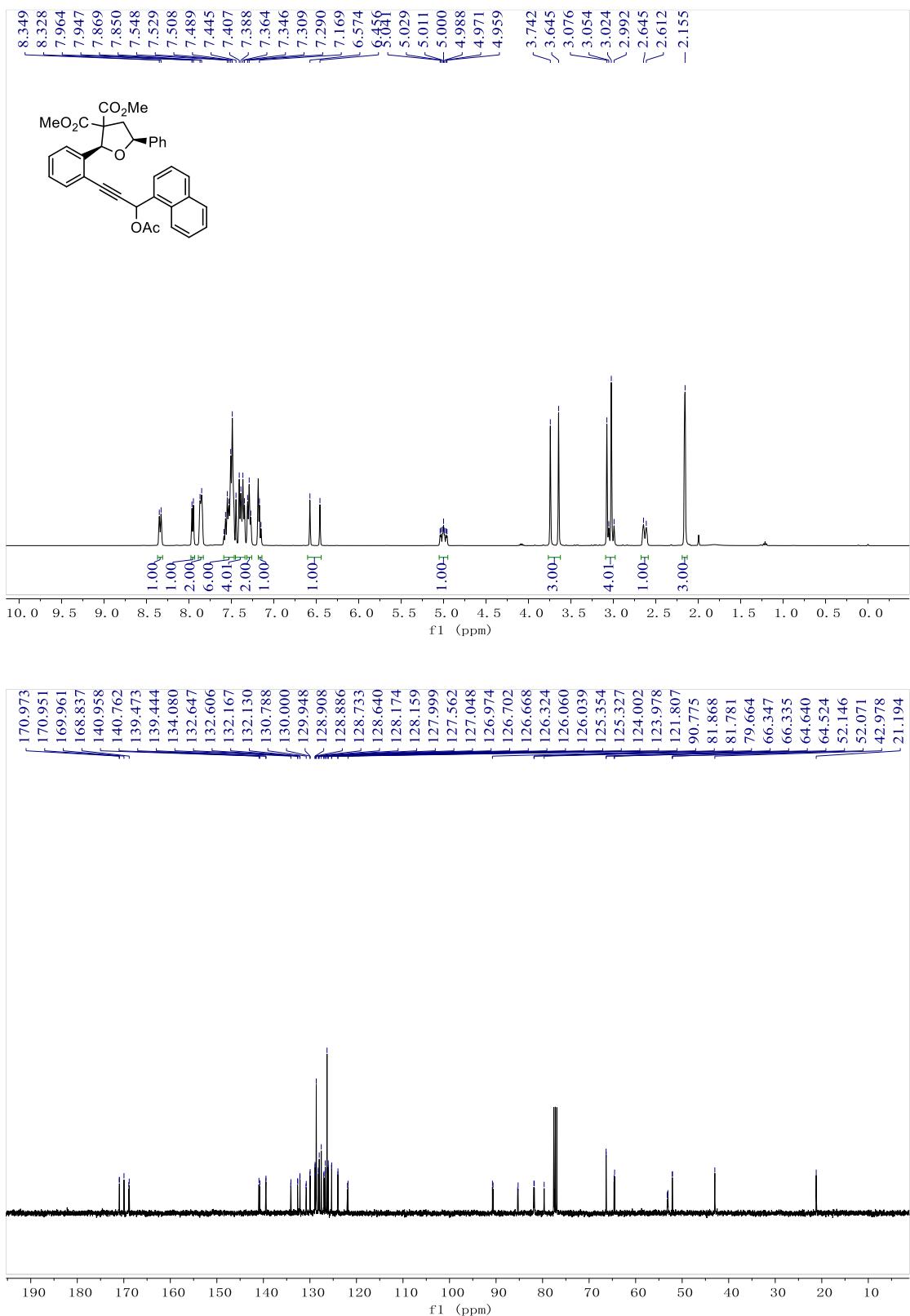


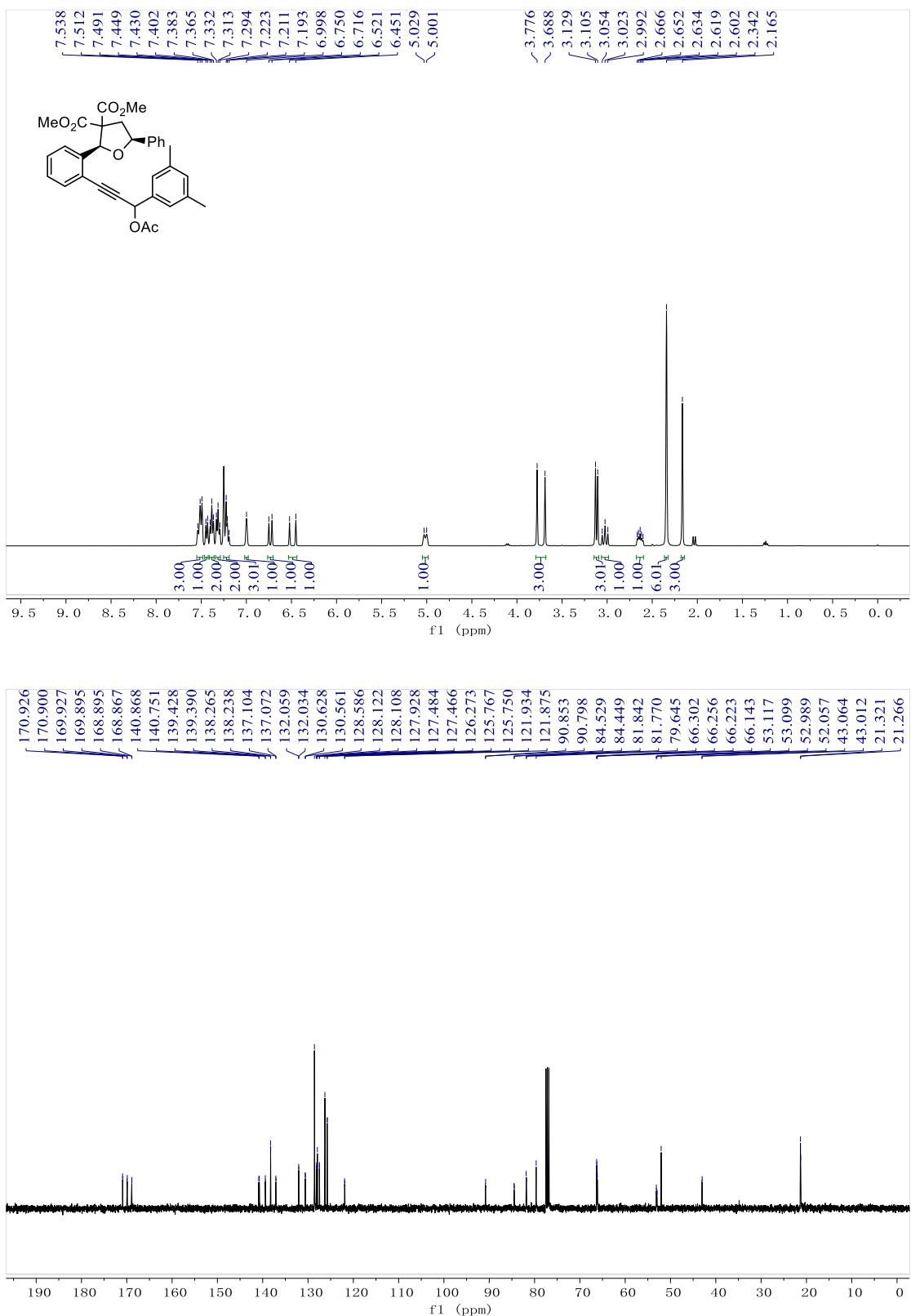


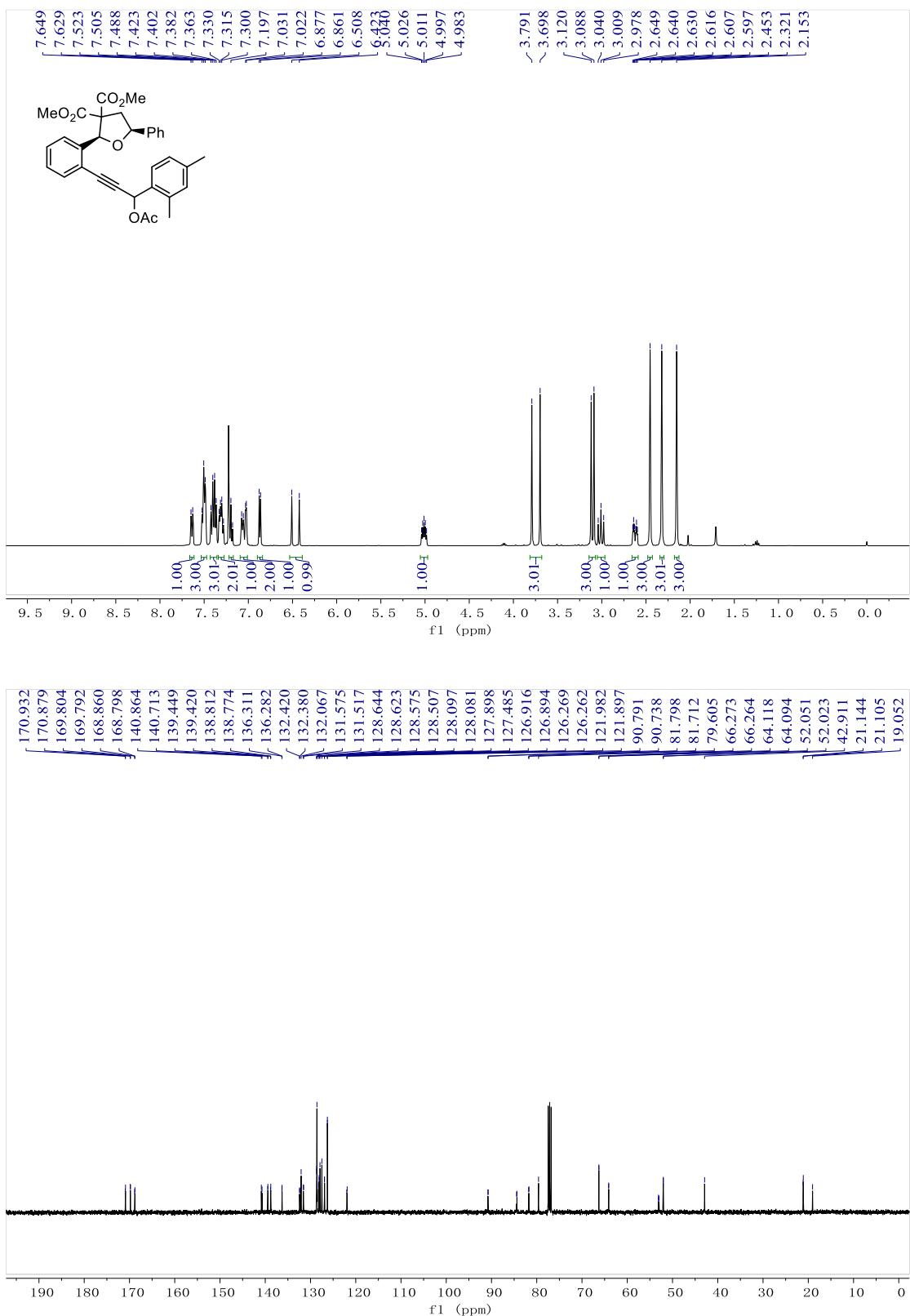
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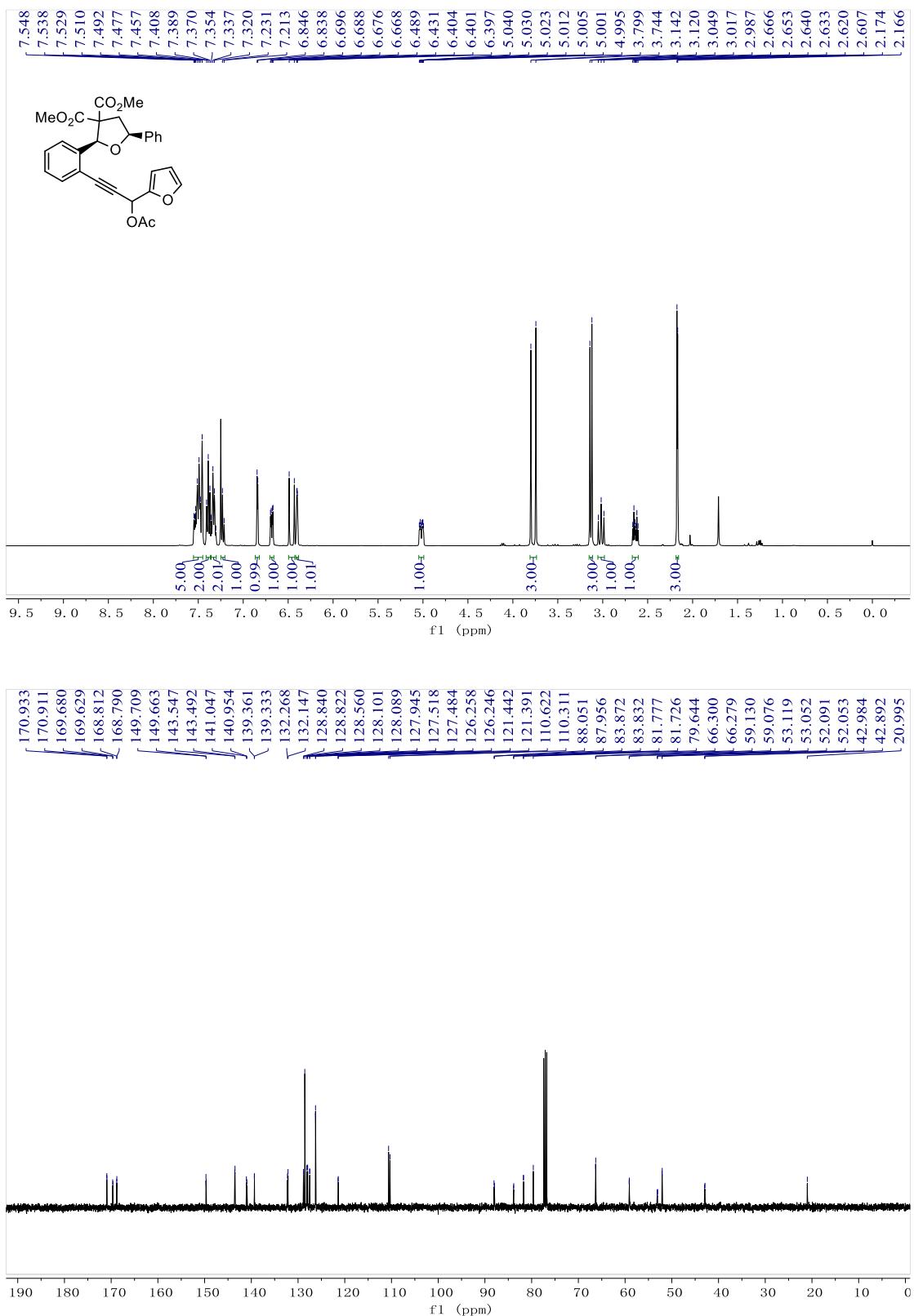
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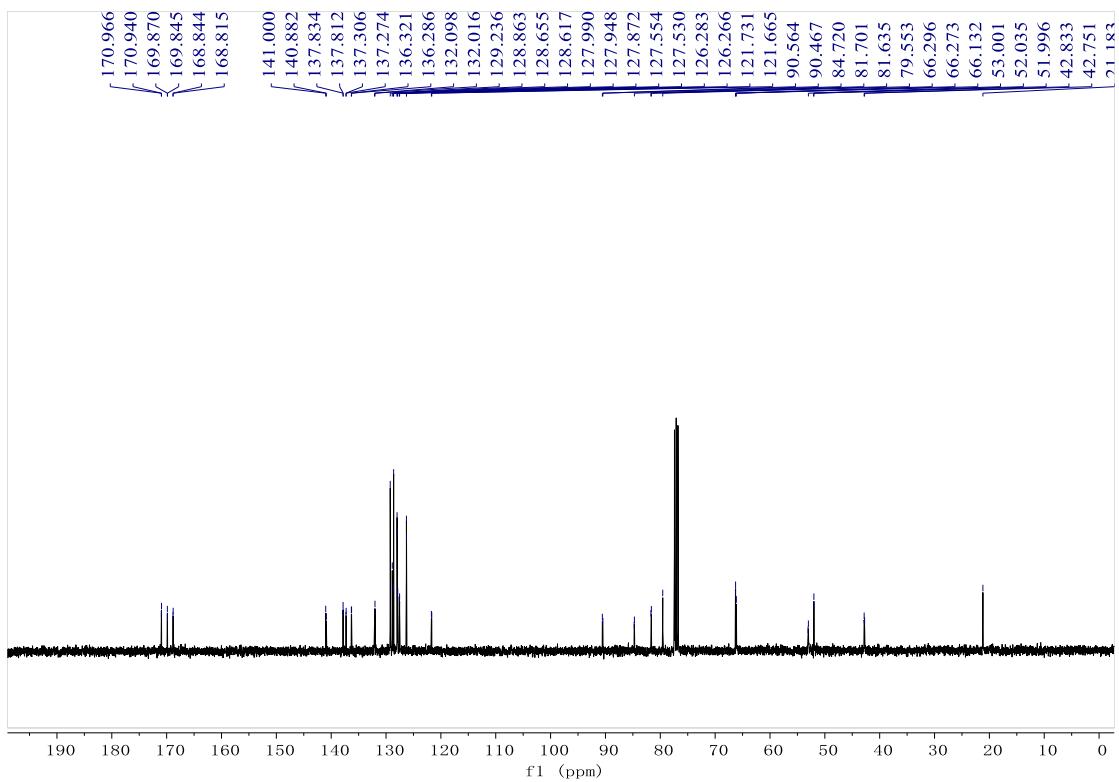
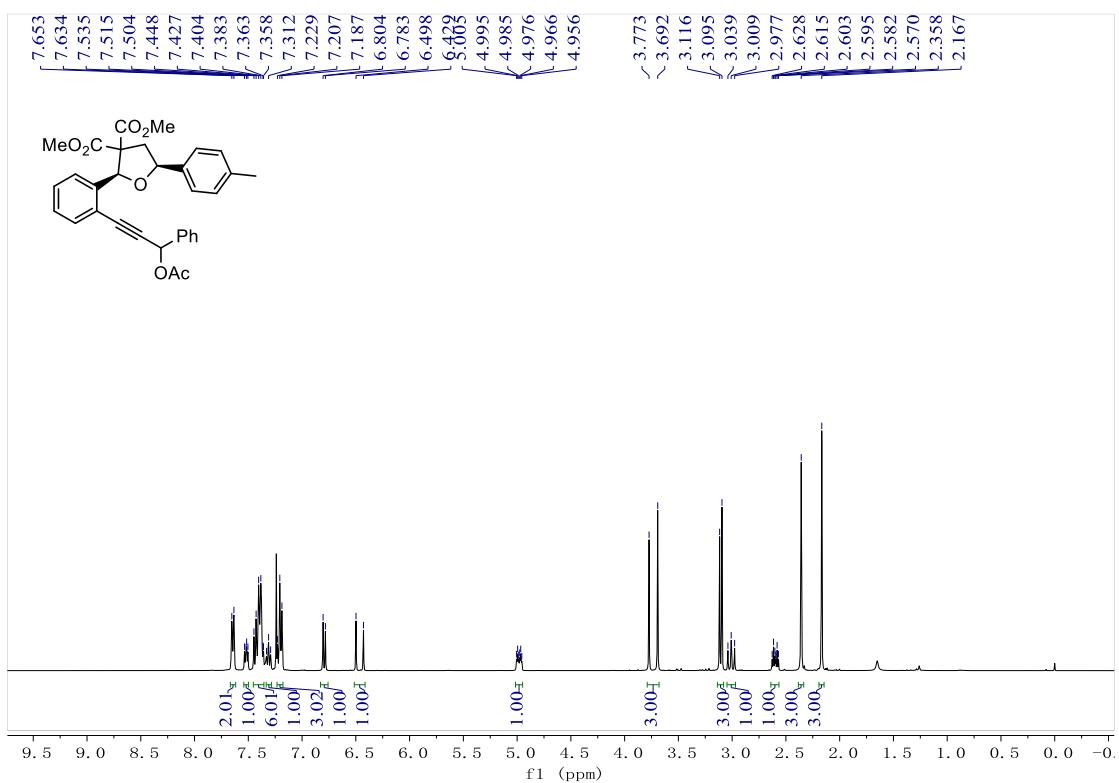
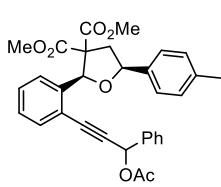
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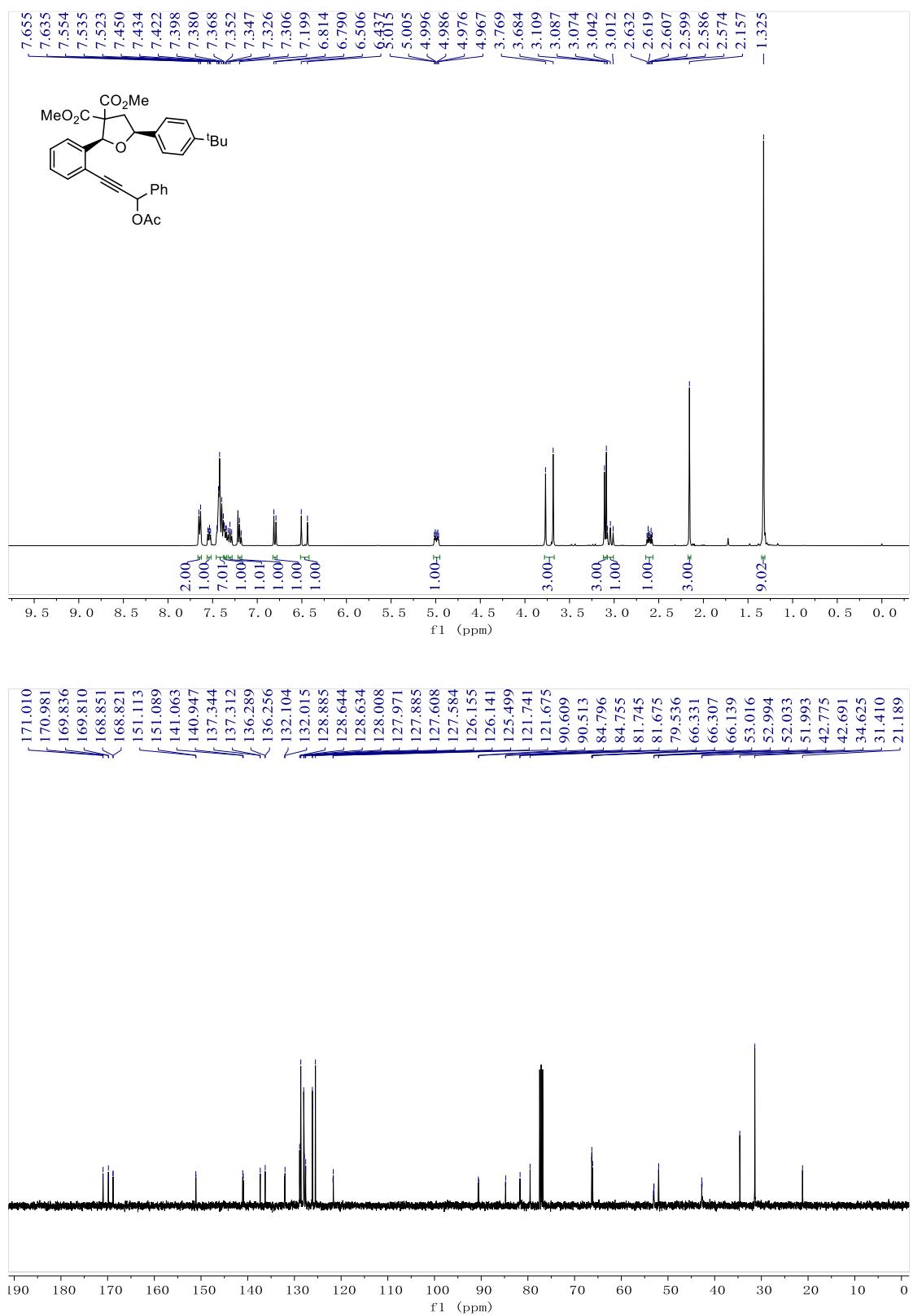
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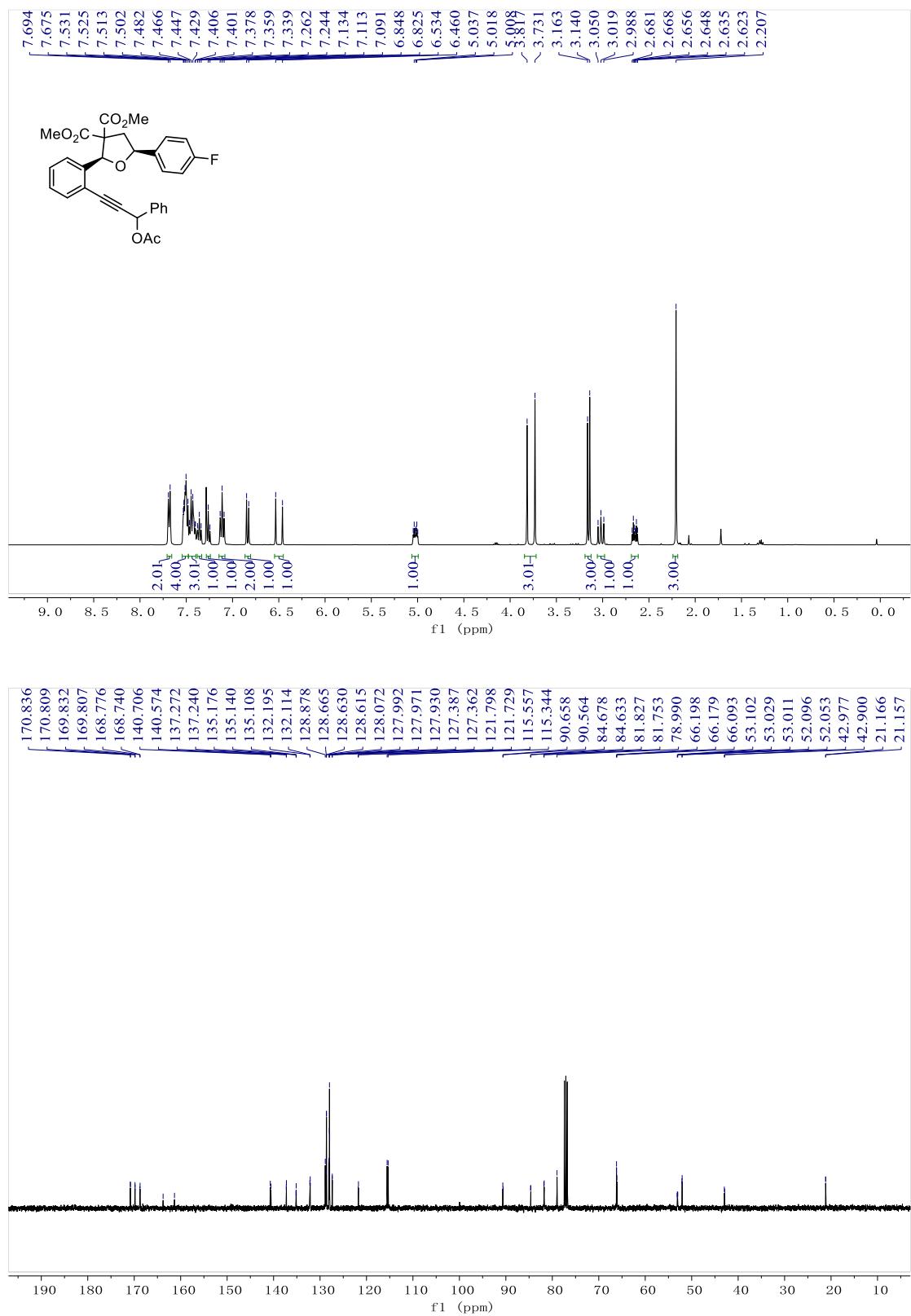
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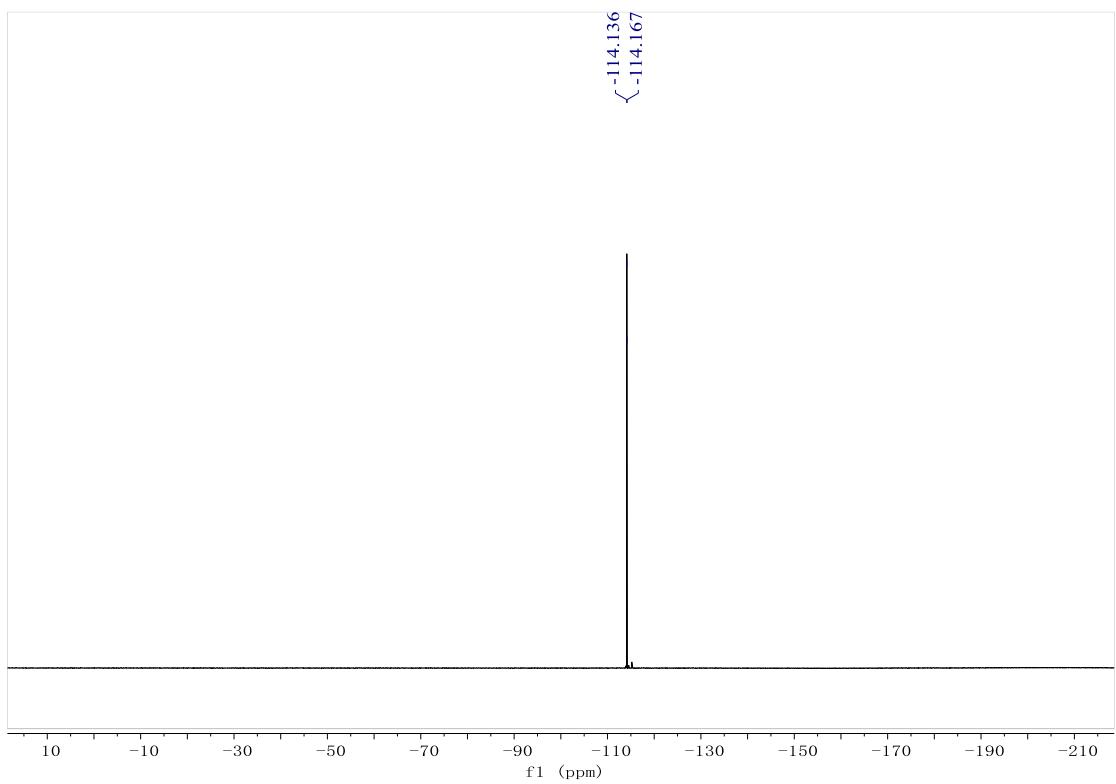


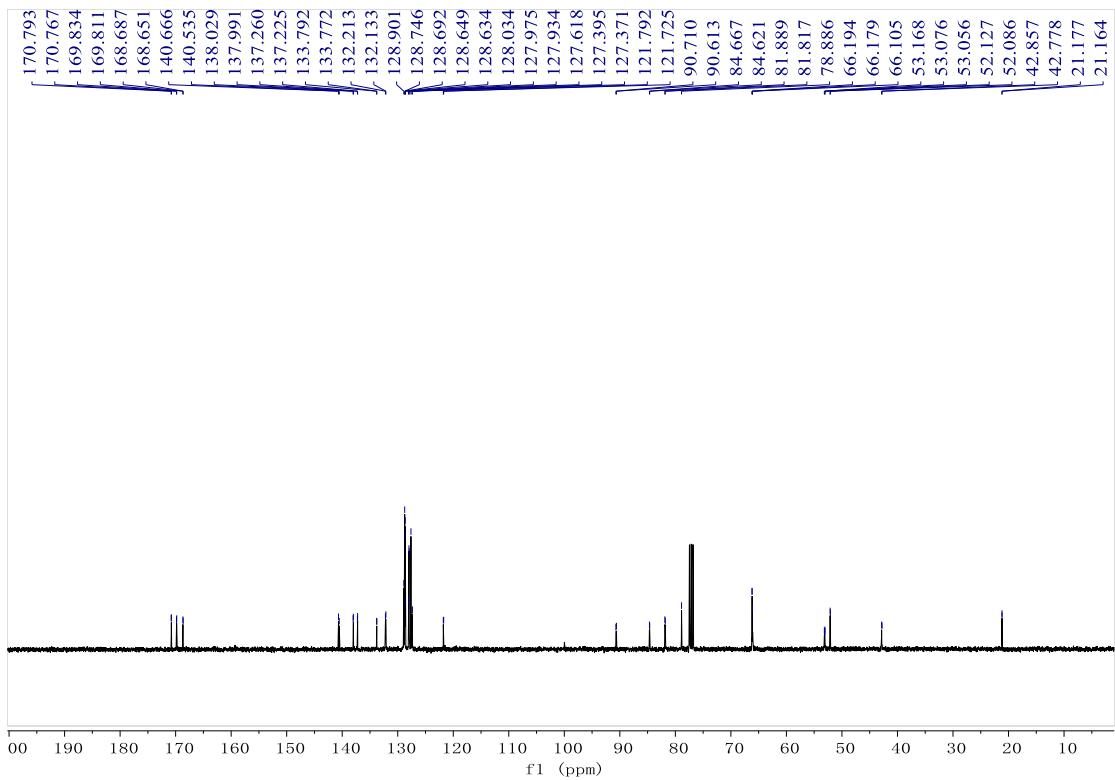
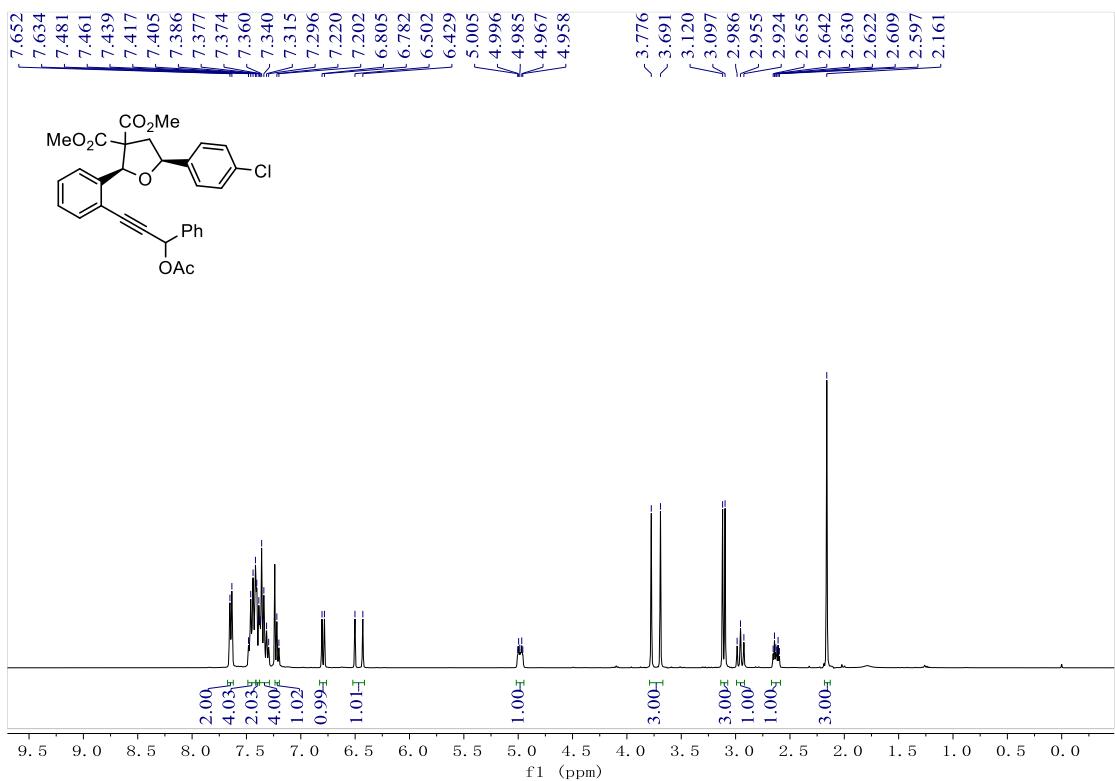
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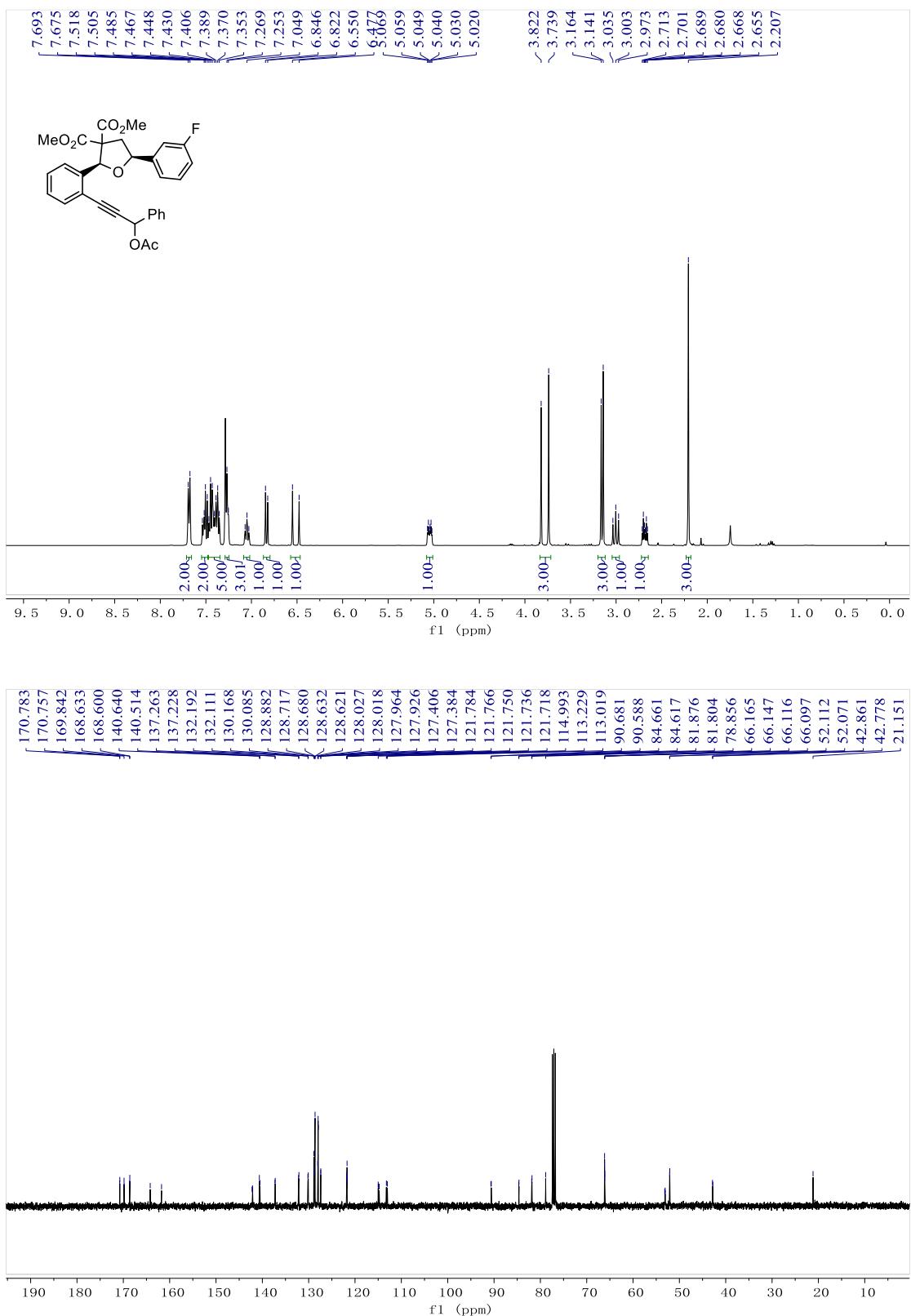
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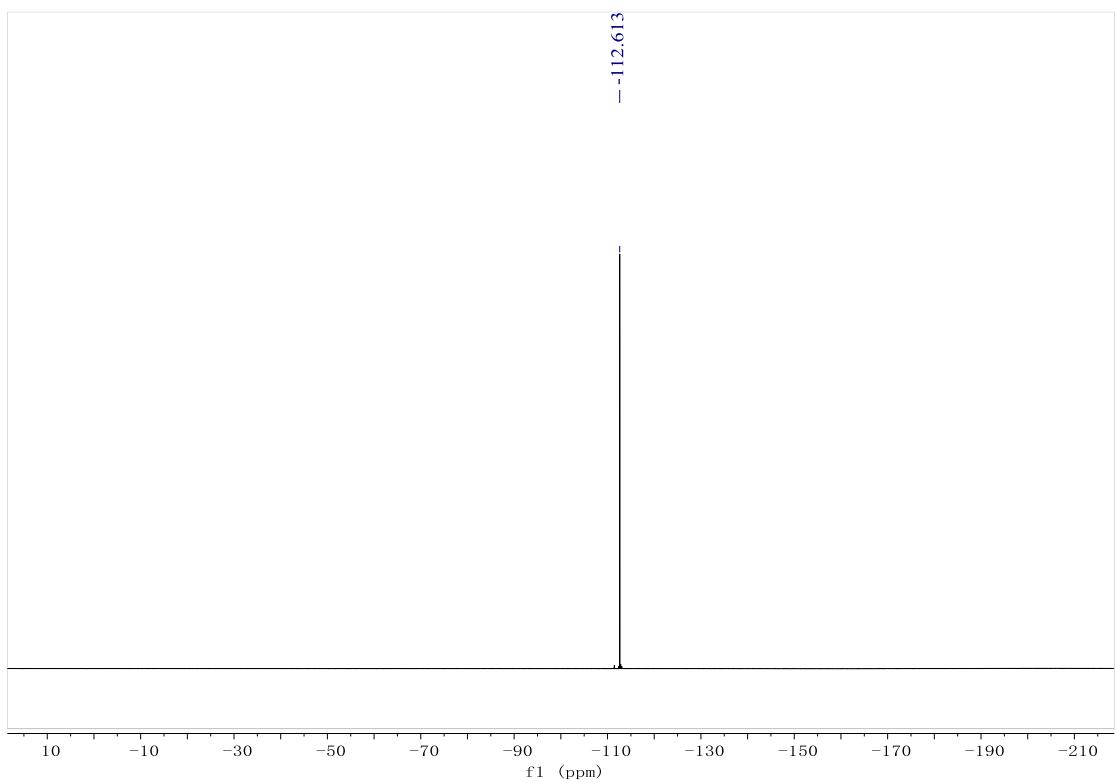


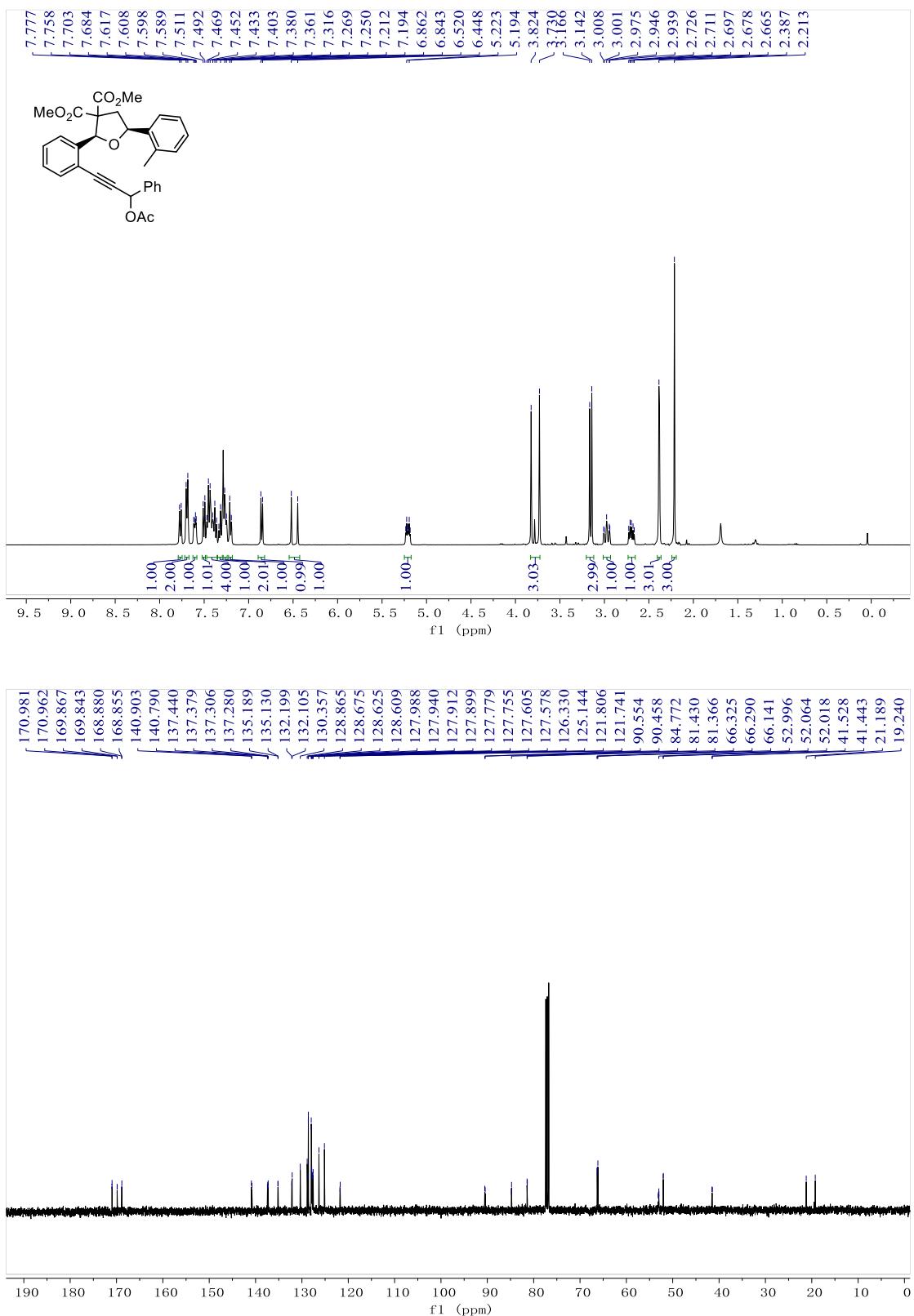


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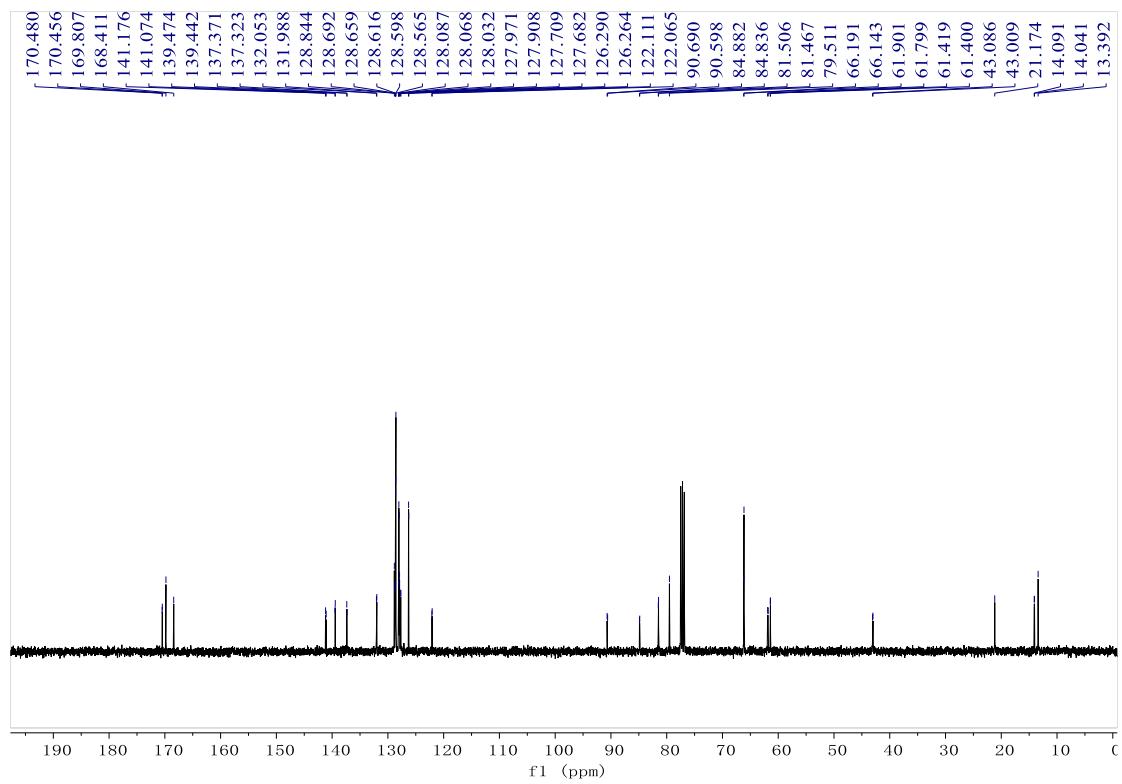
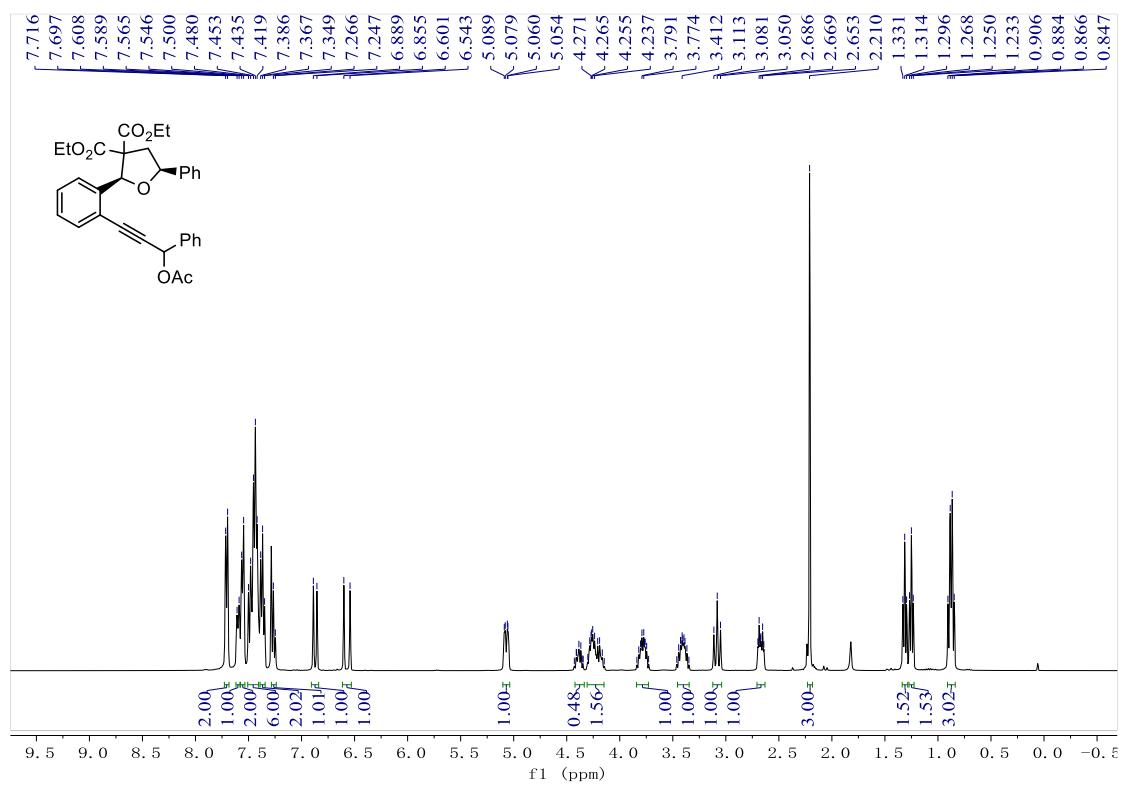
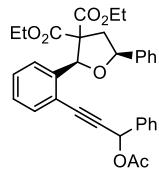
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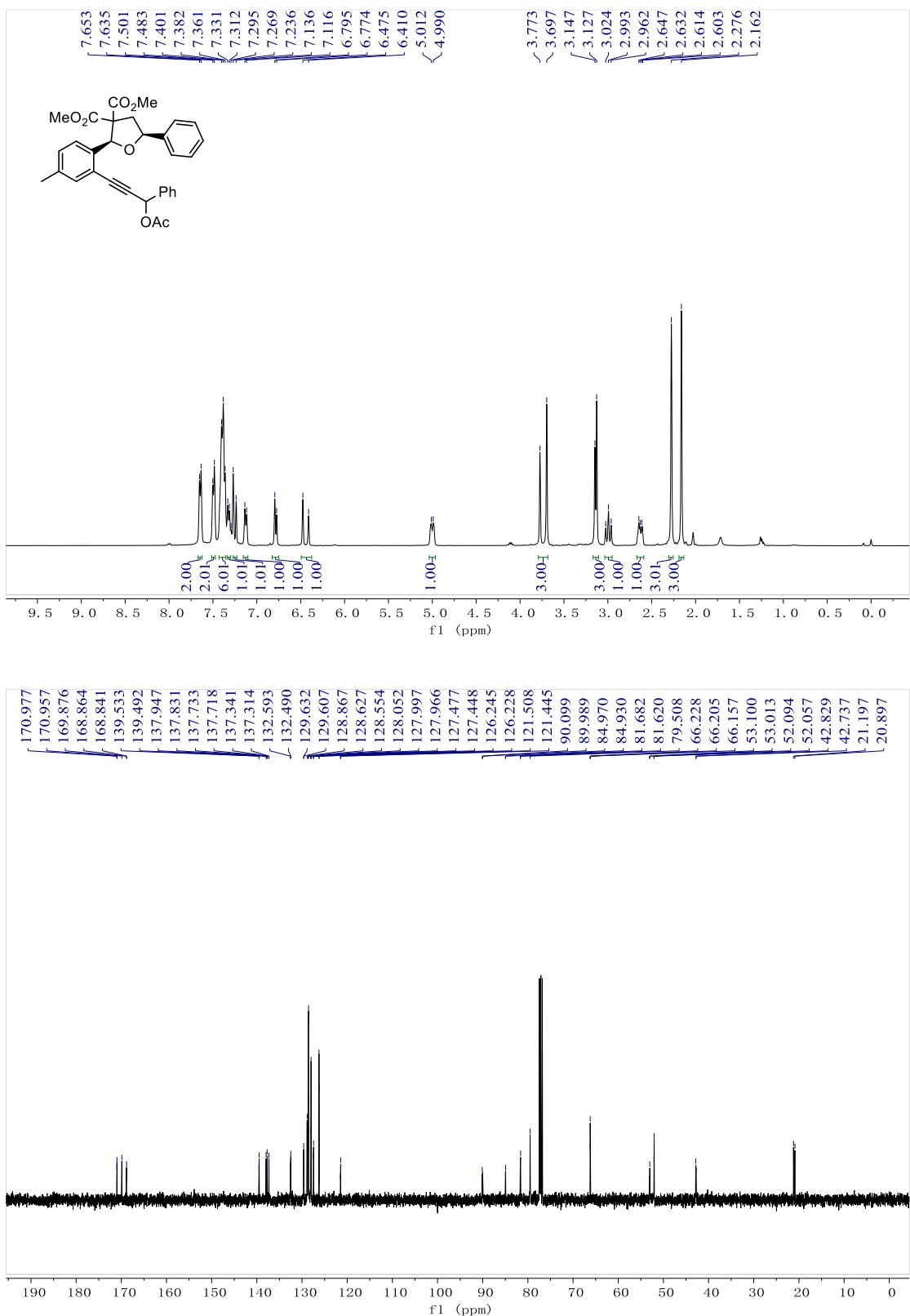




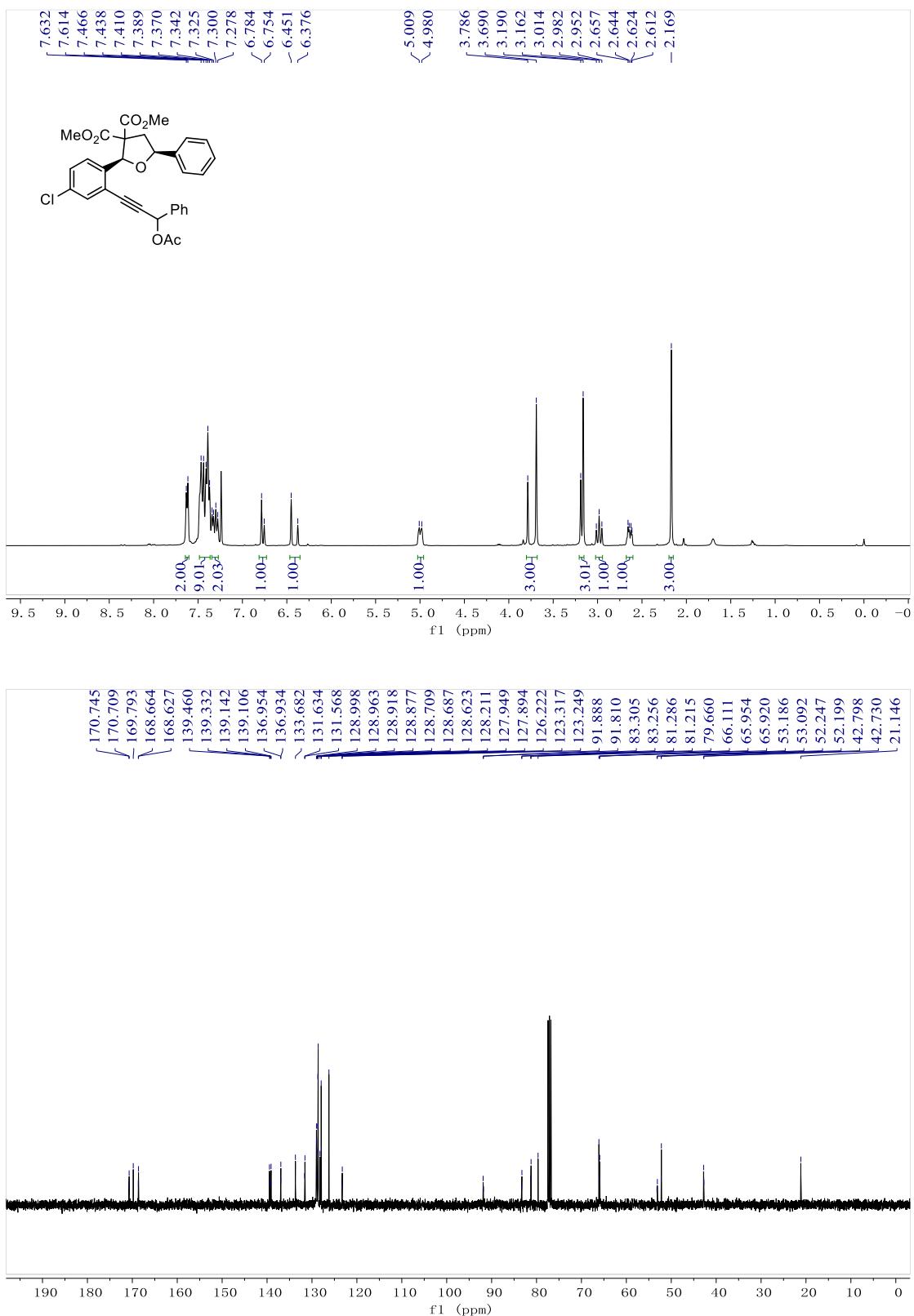
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1v

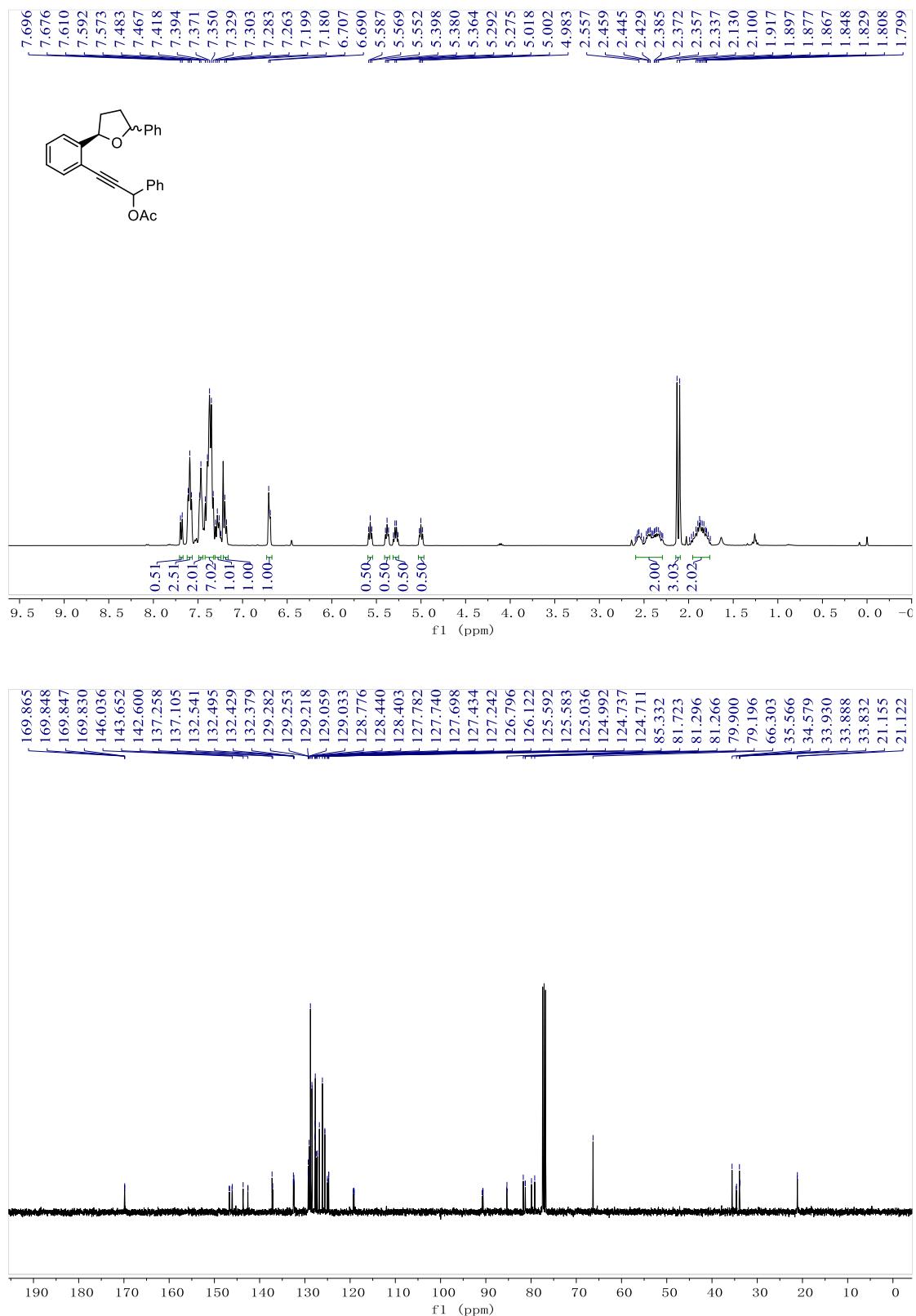


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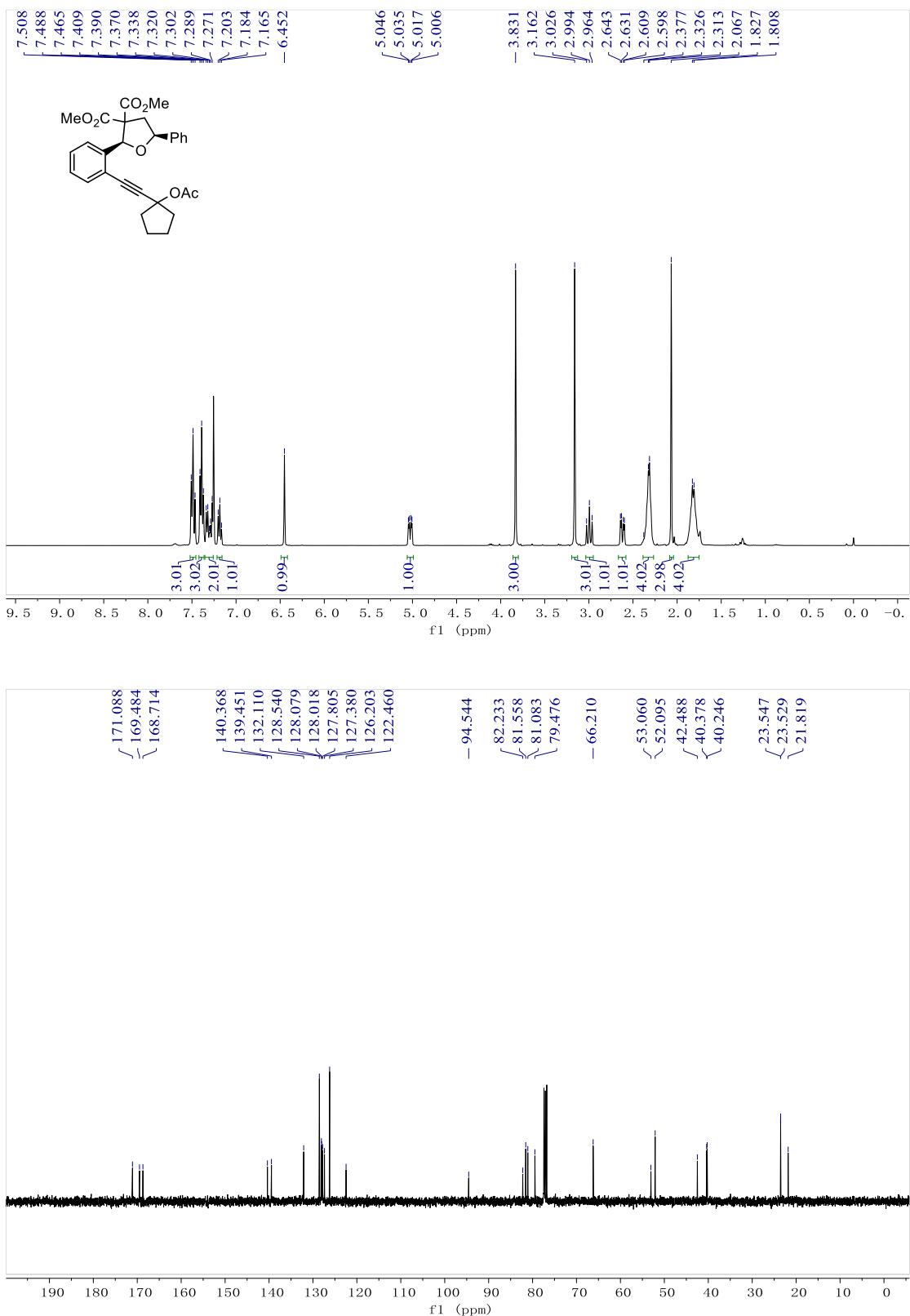
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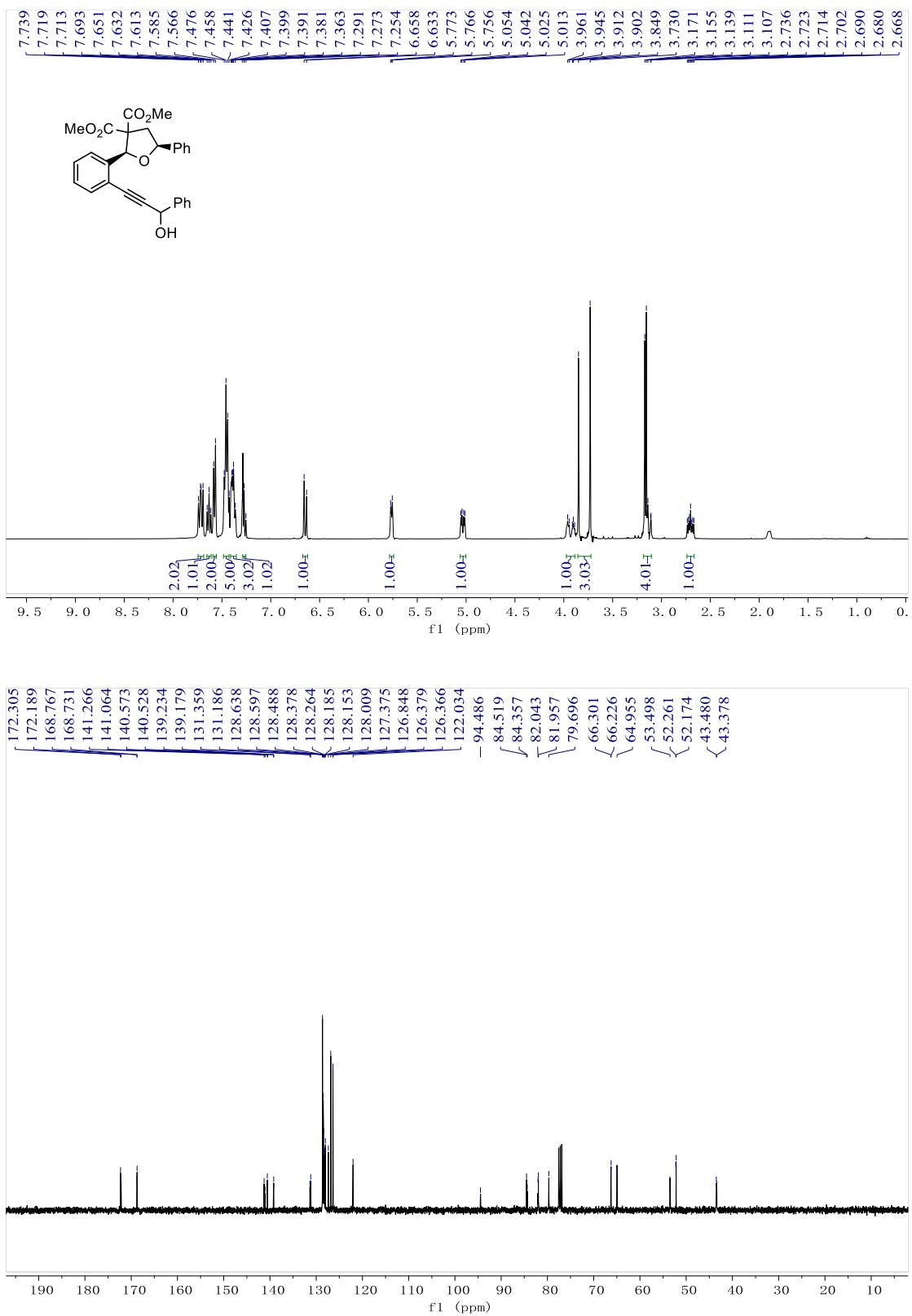
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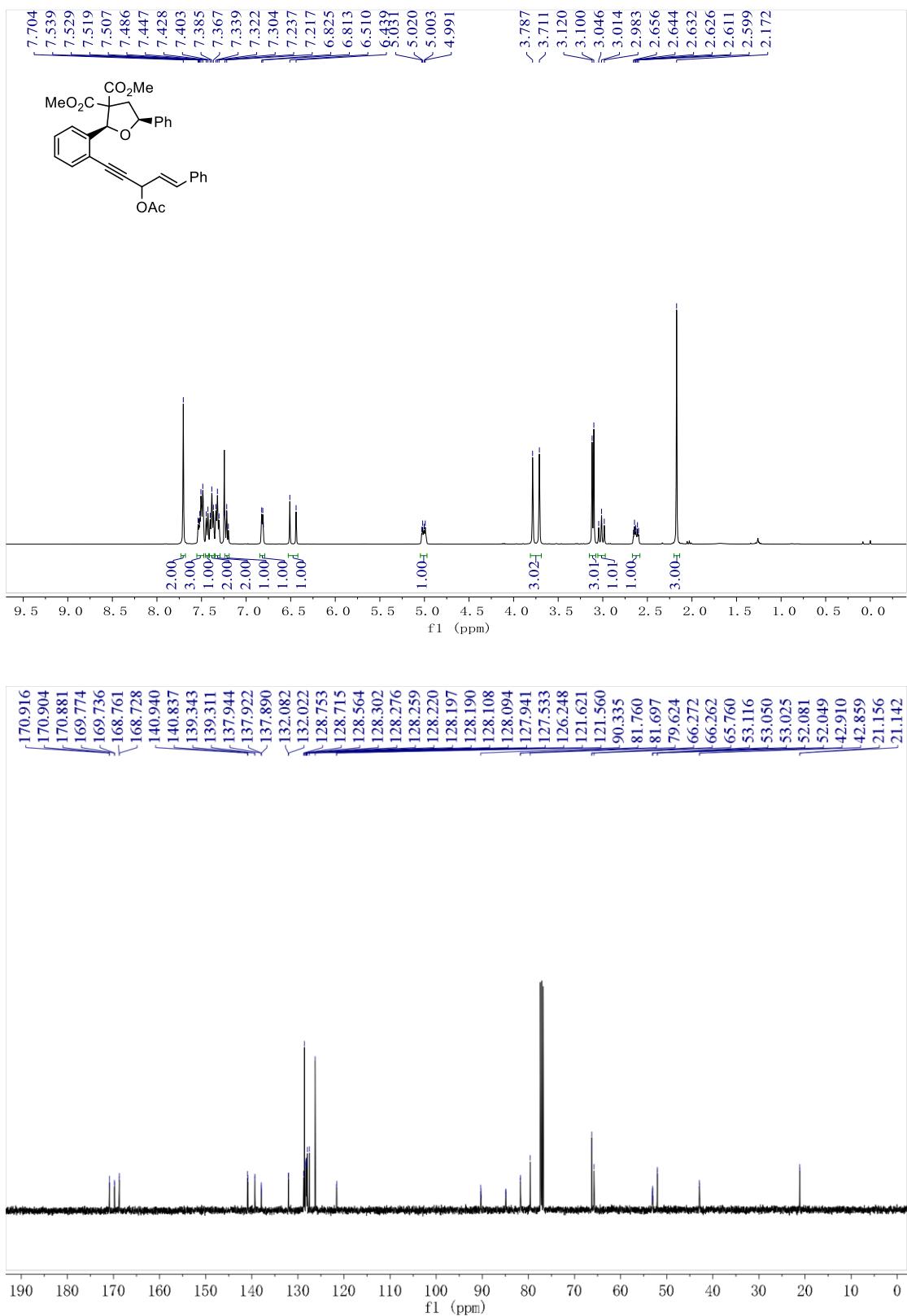
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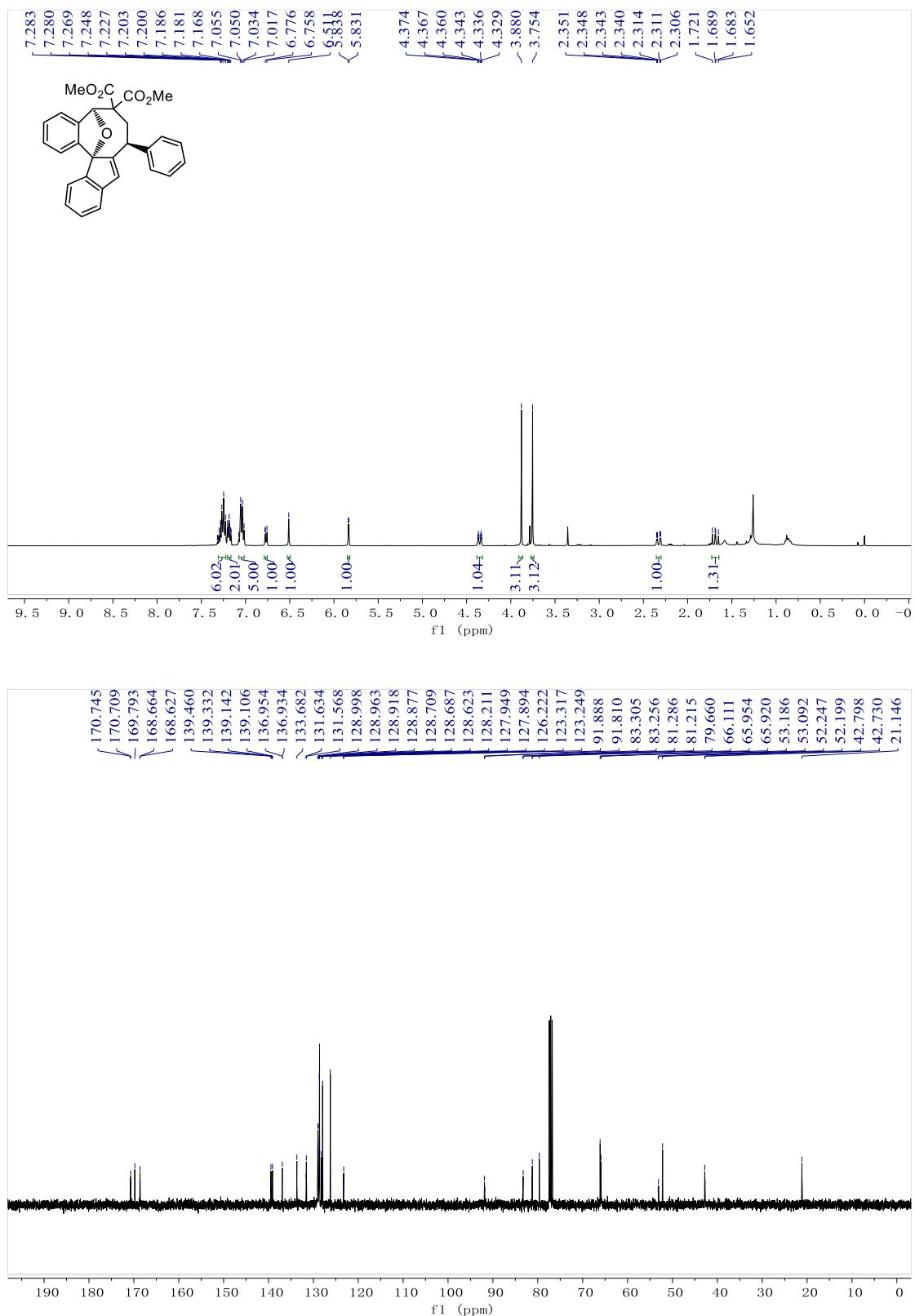
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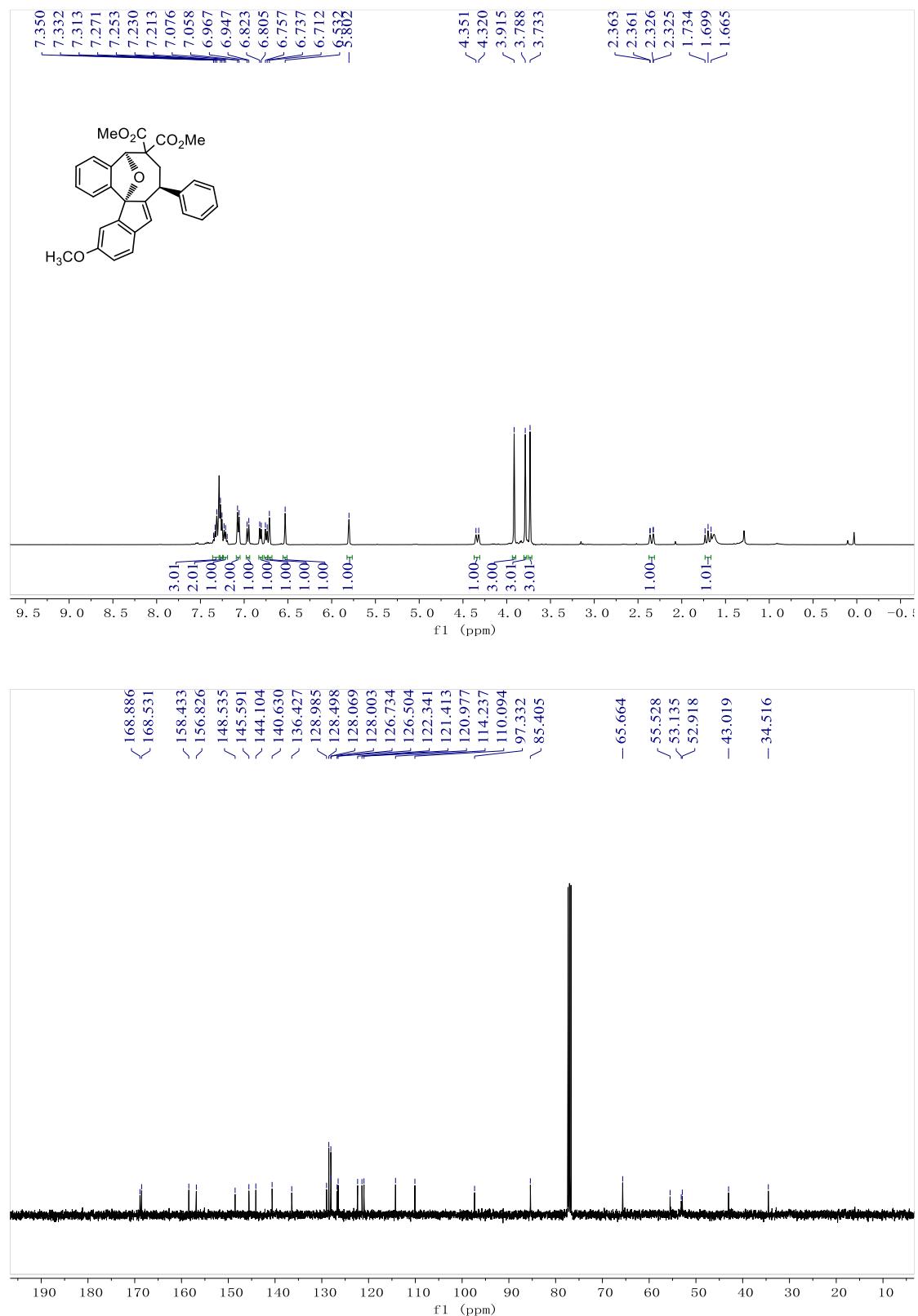


**1ac**

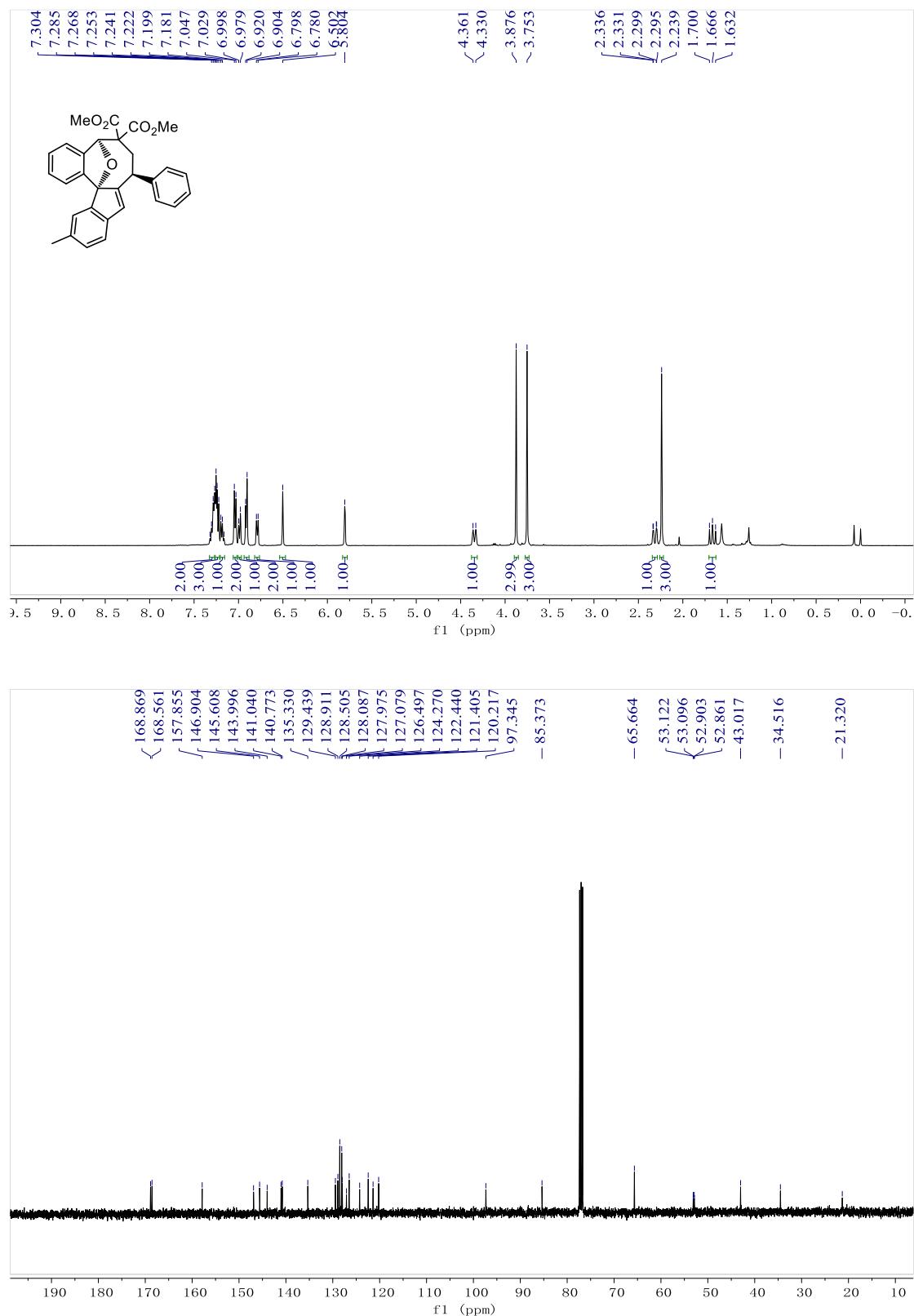


**3a**

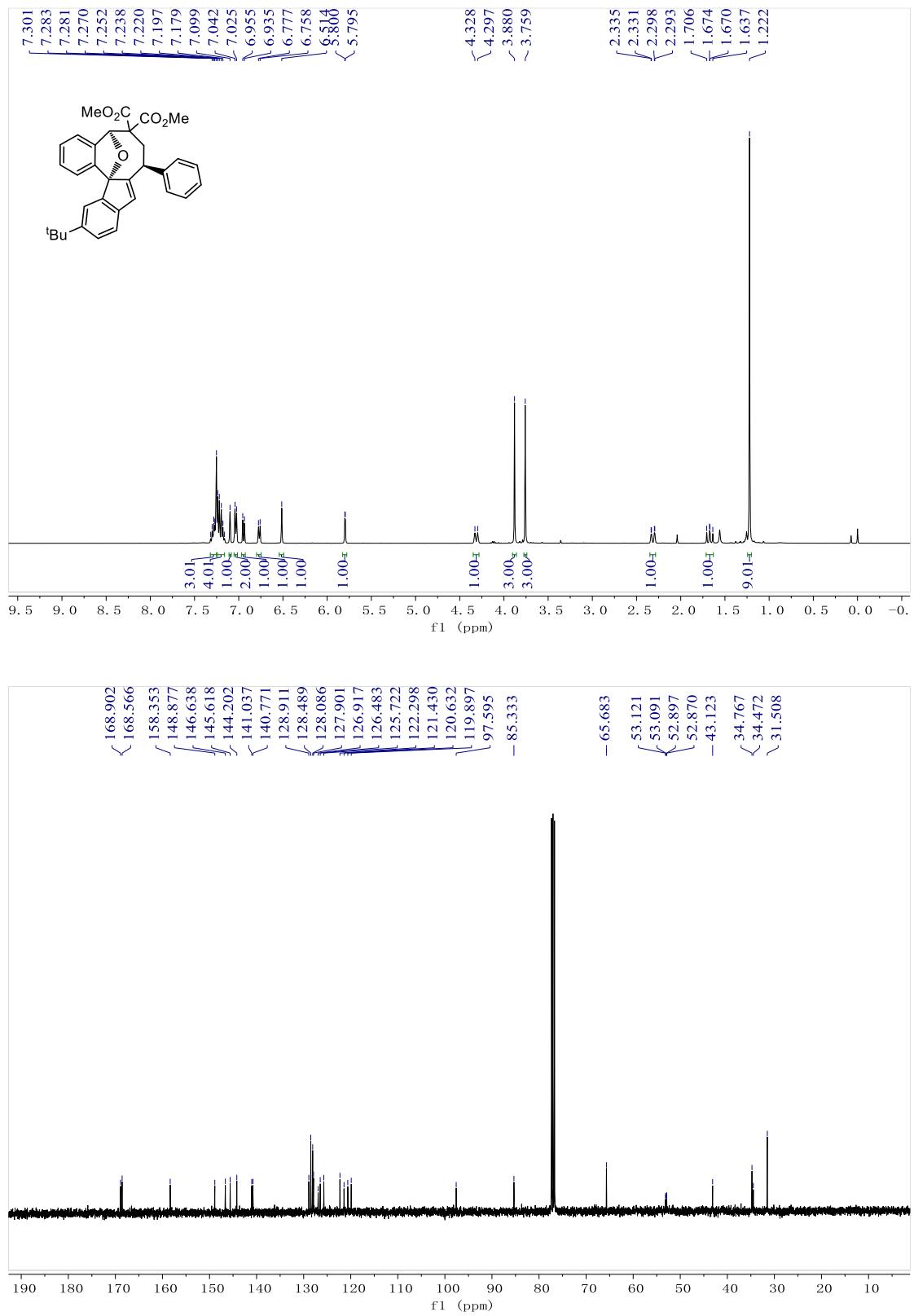


**3b**

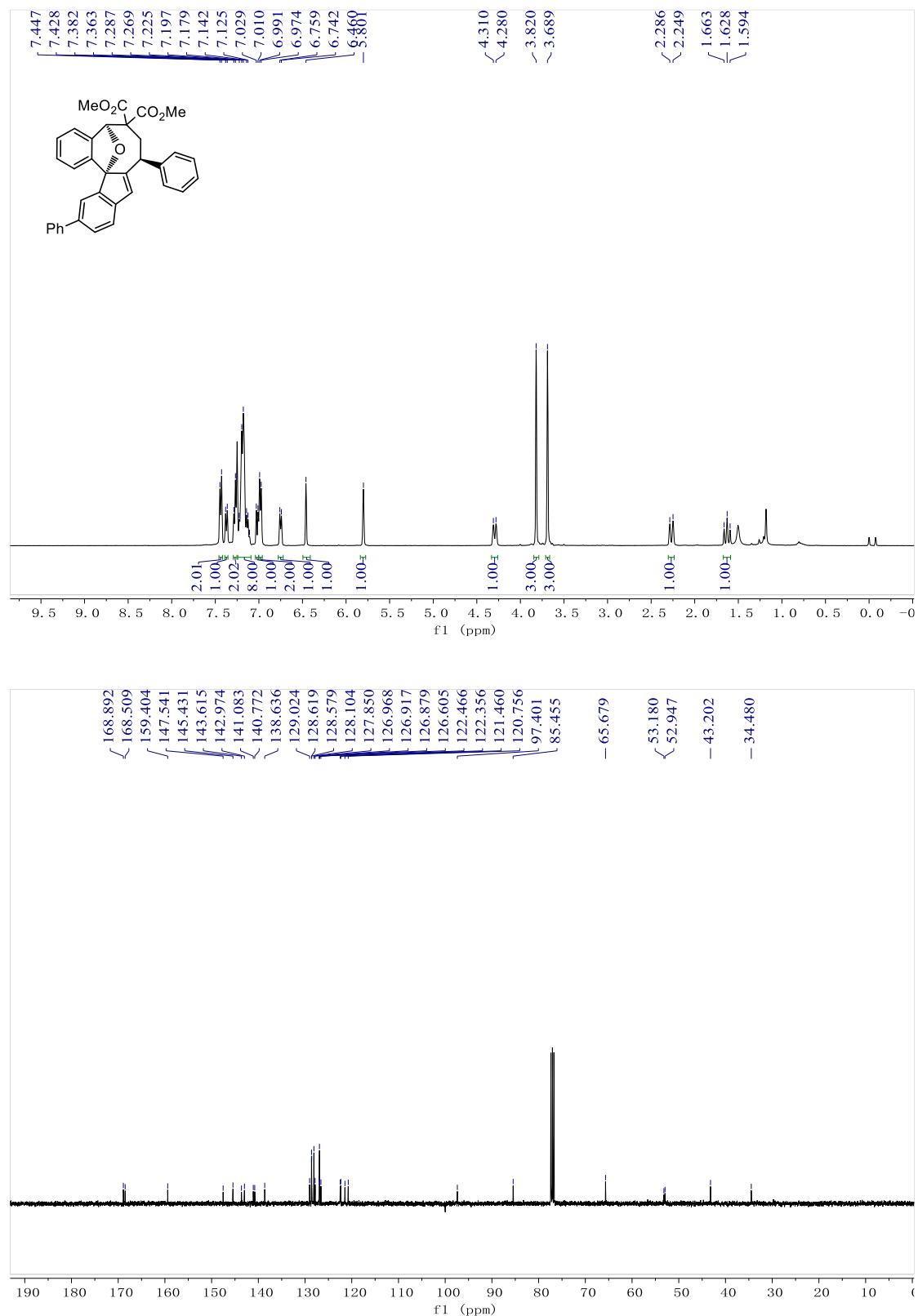
**3c**



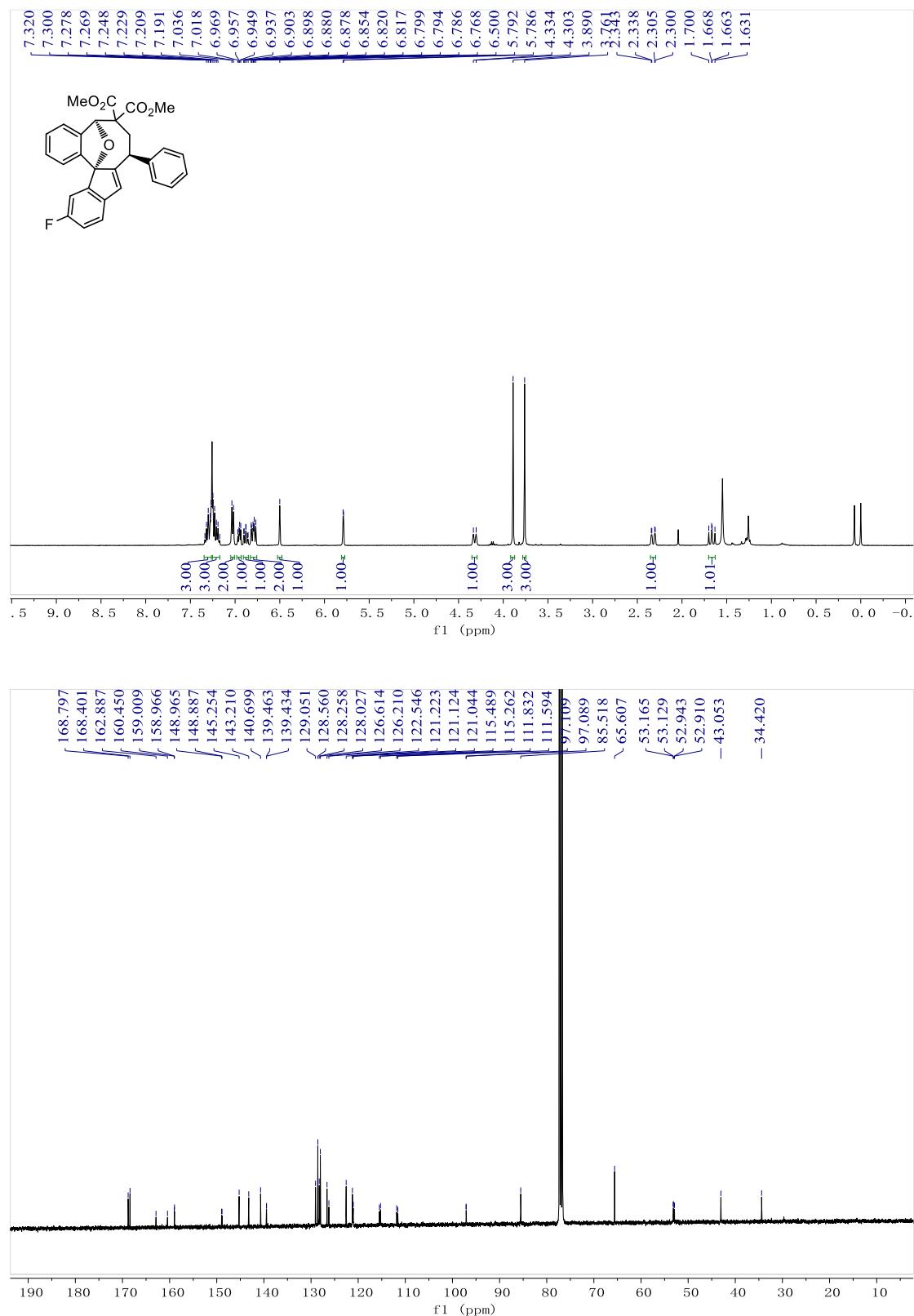
3d

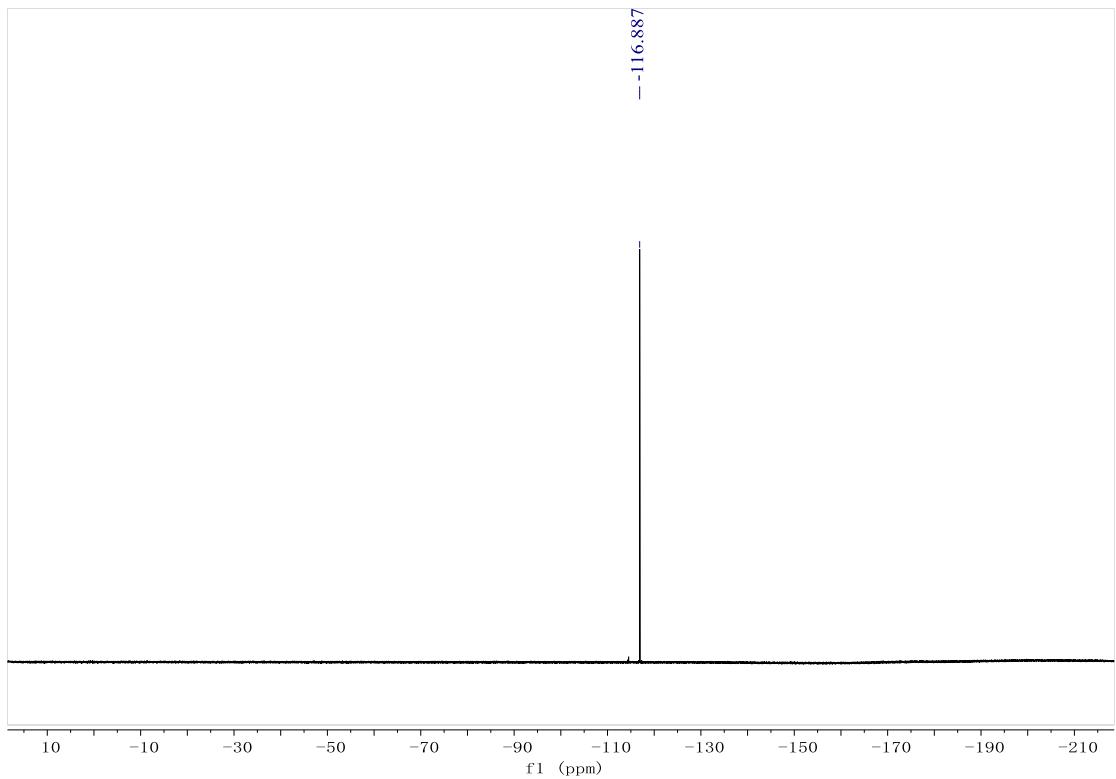


**3e**

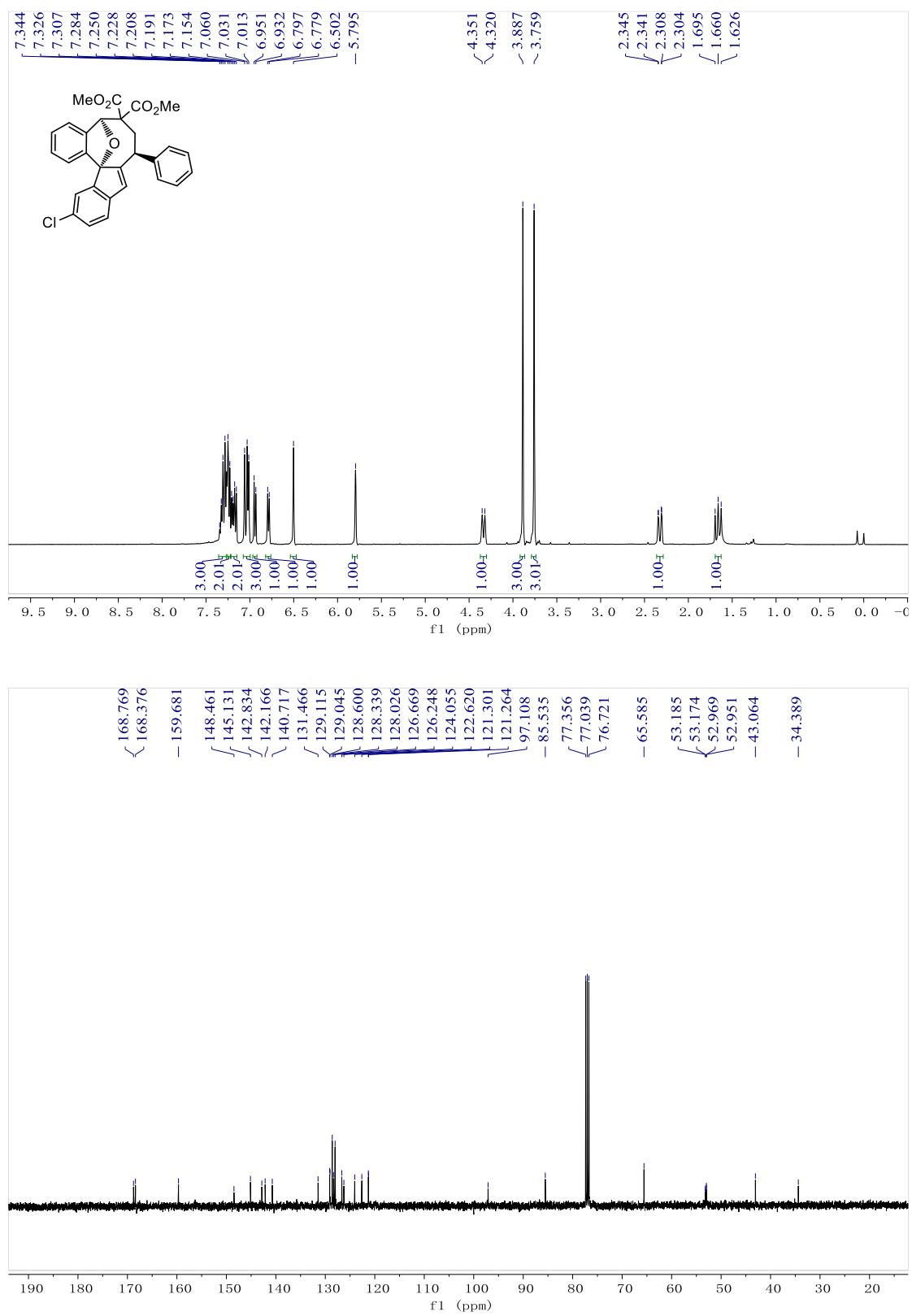


**3f**

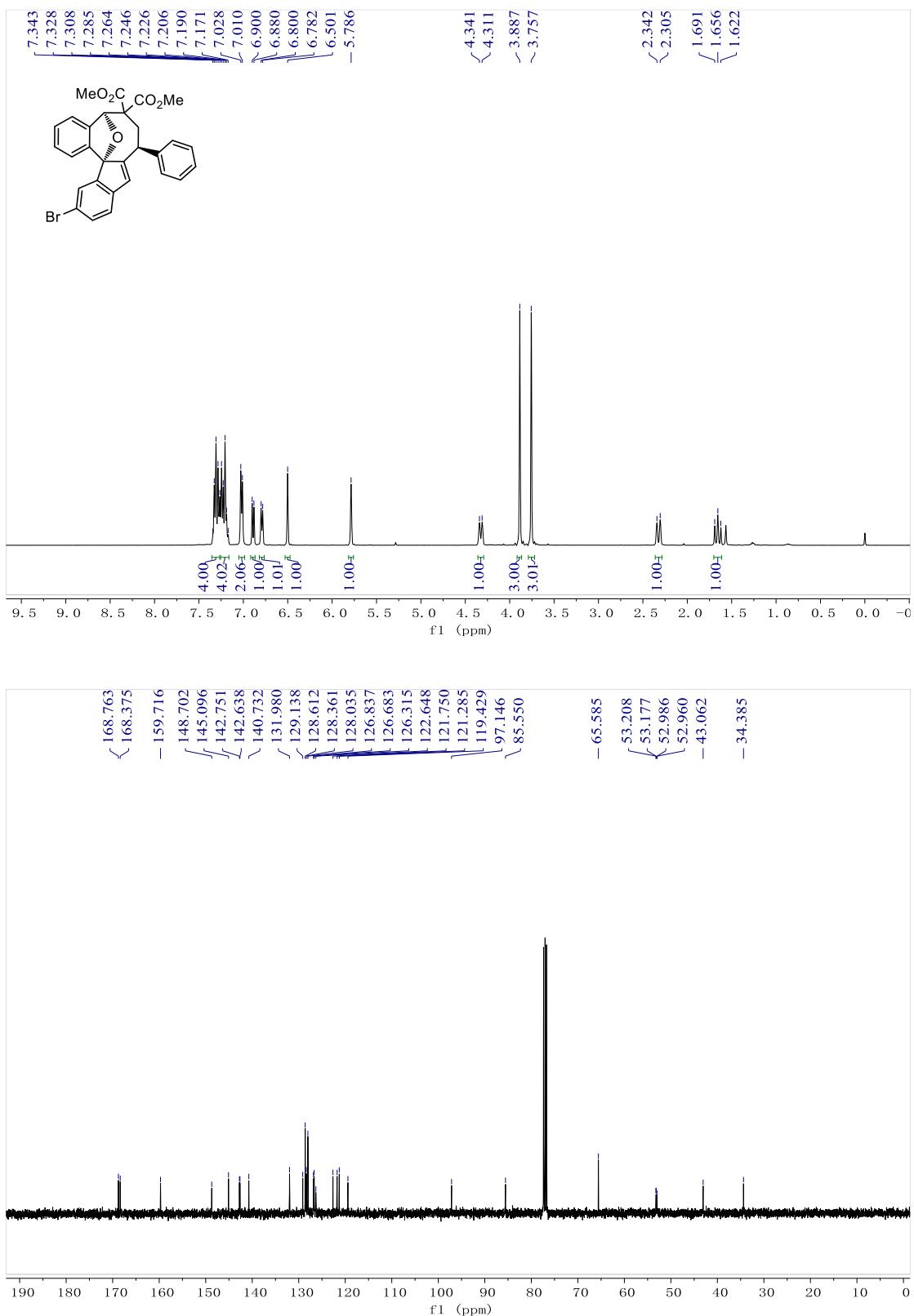


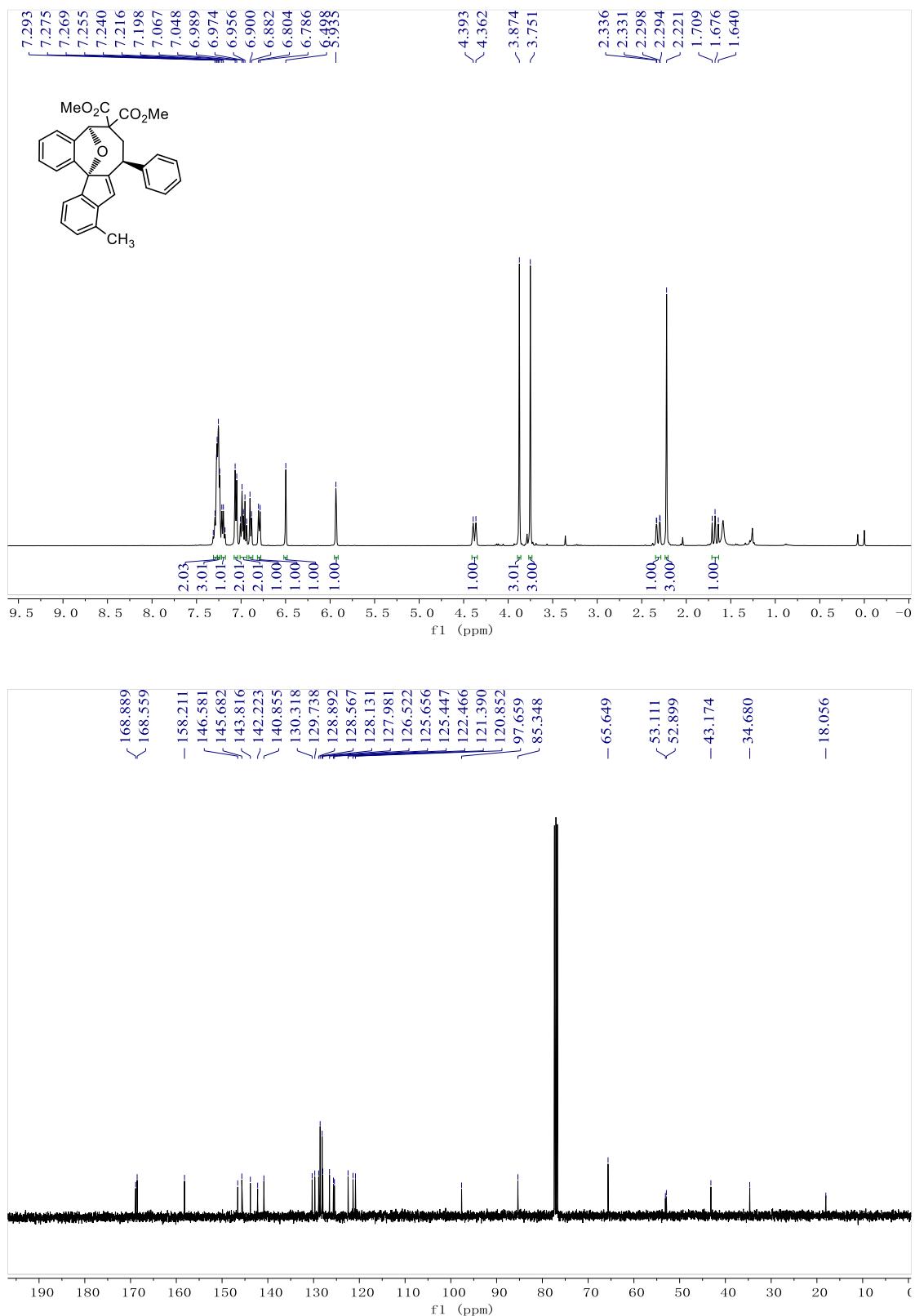


3g

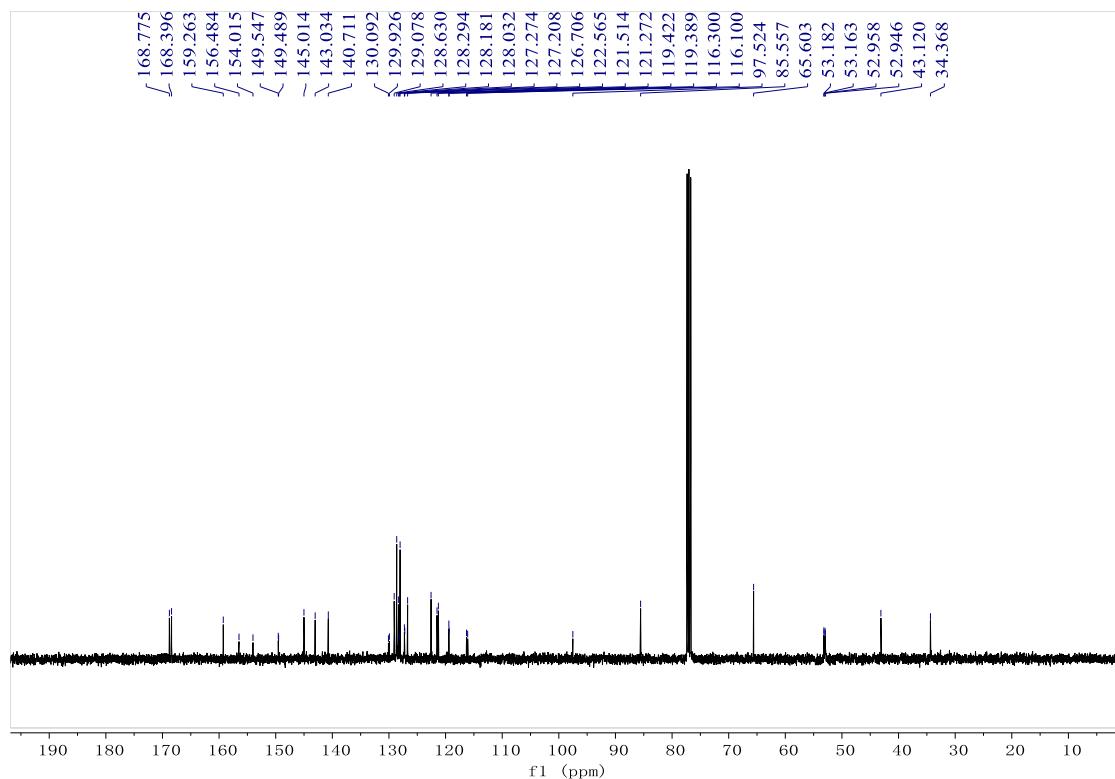
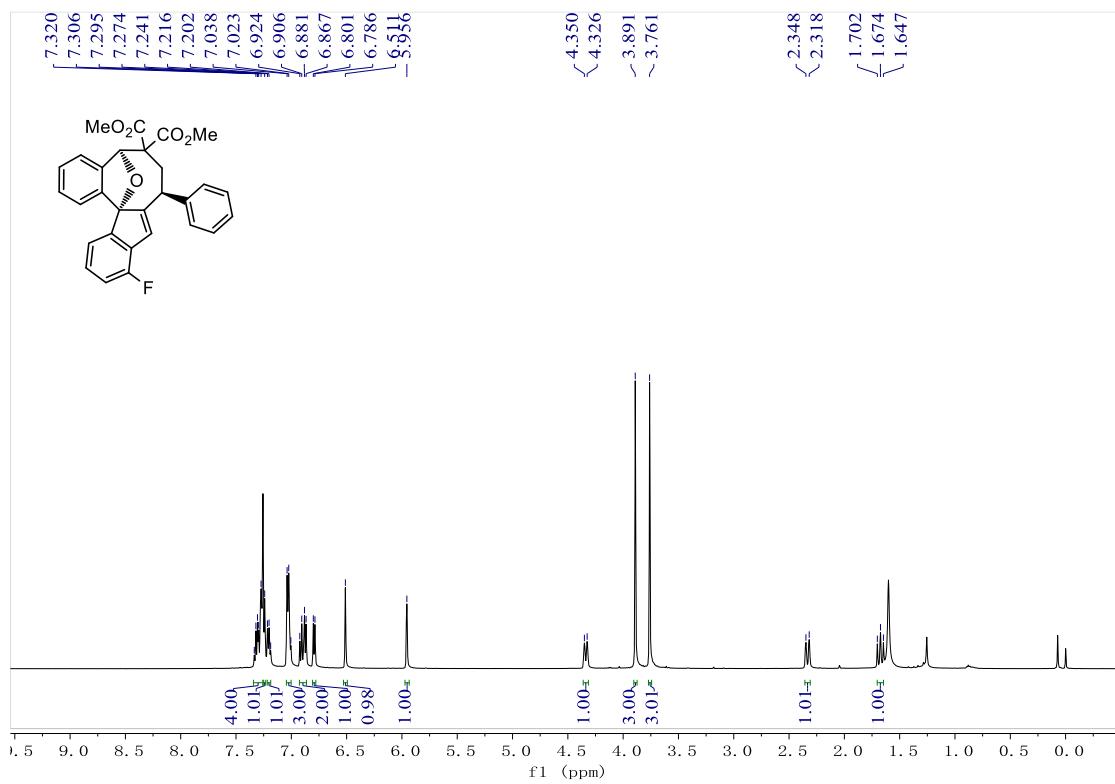


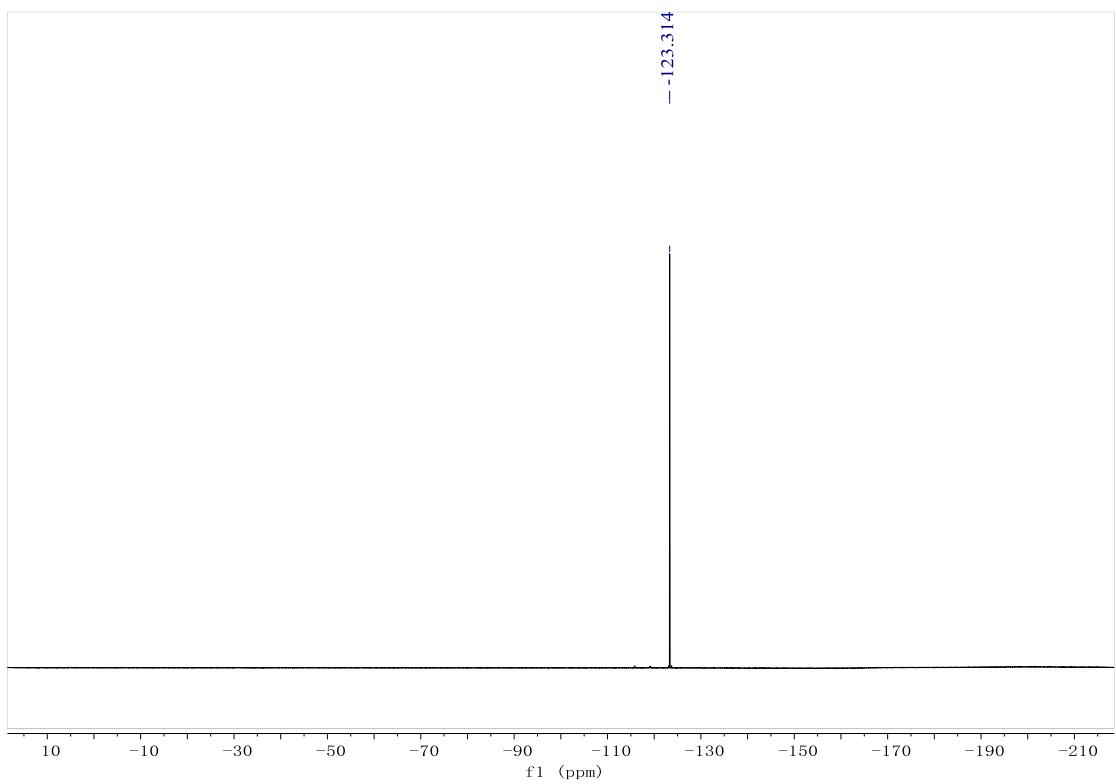
**3h**



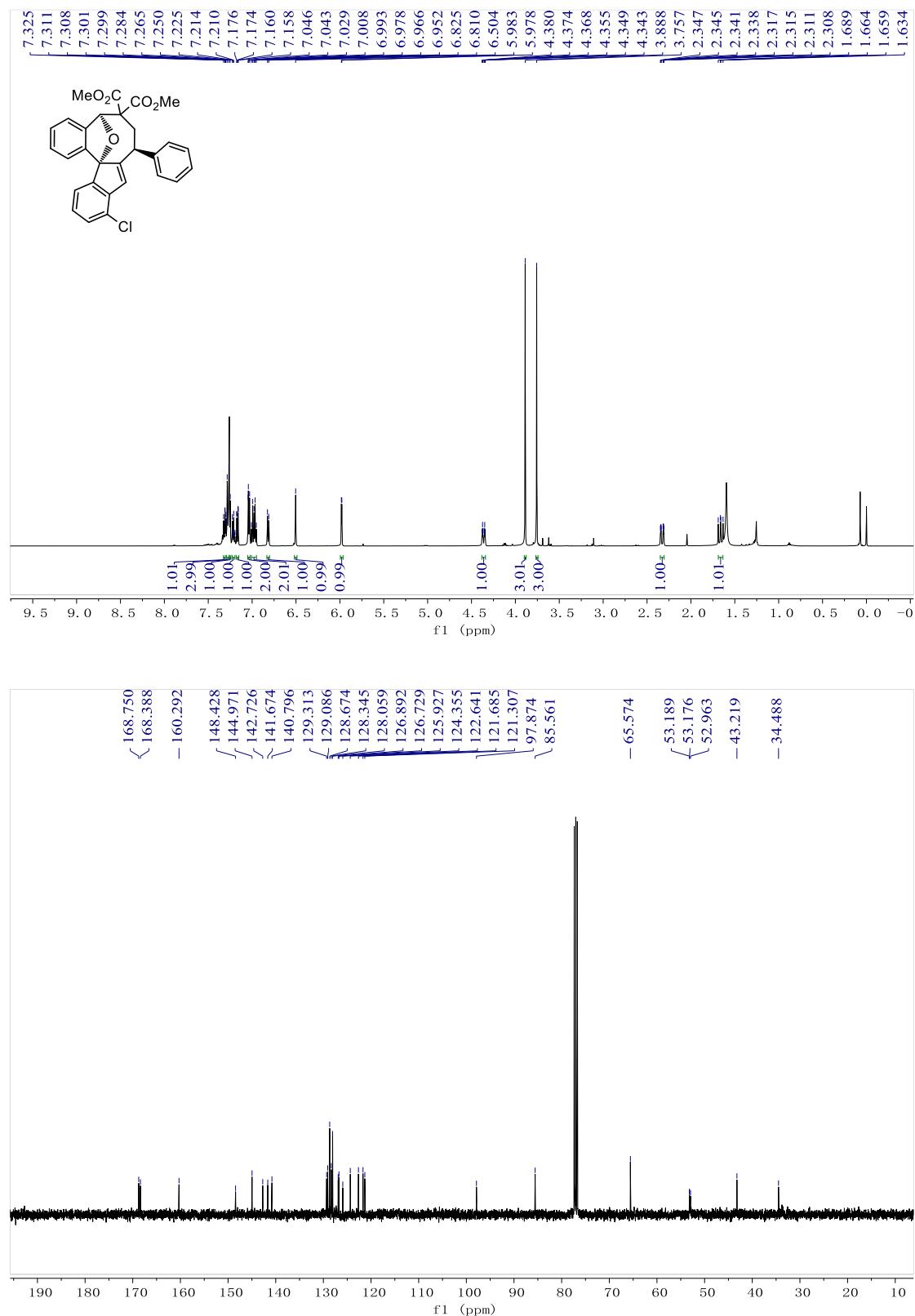
**3i**

3j

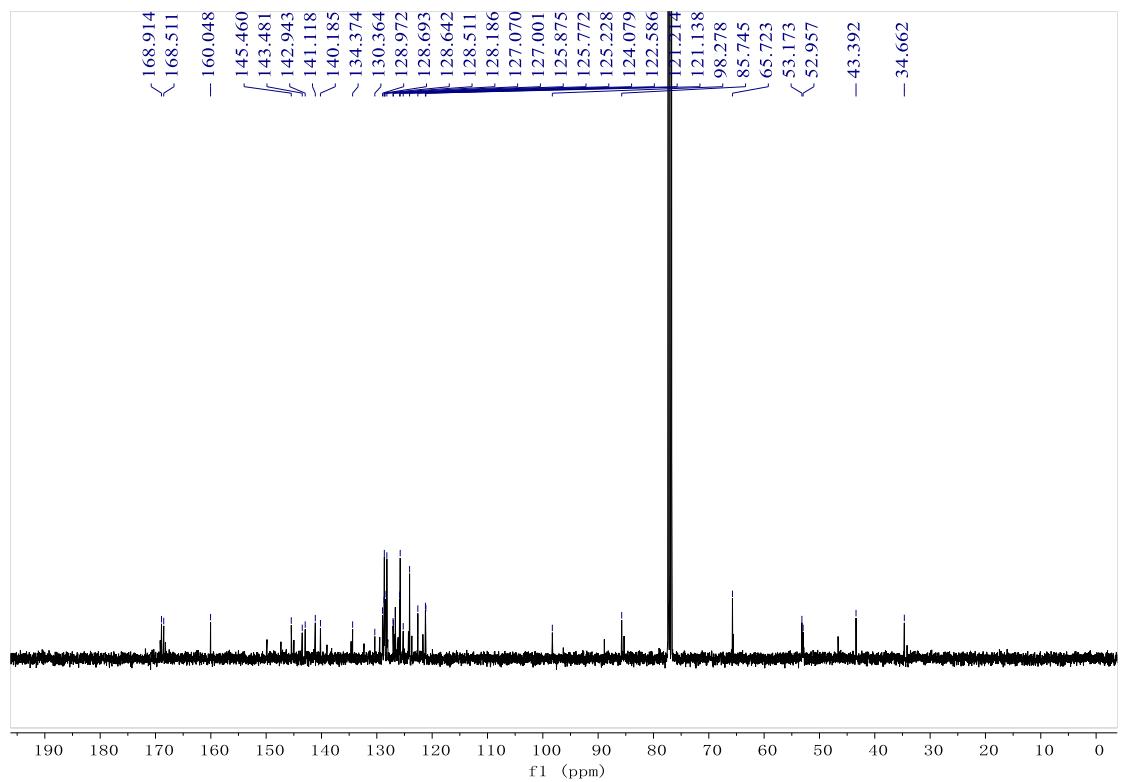
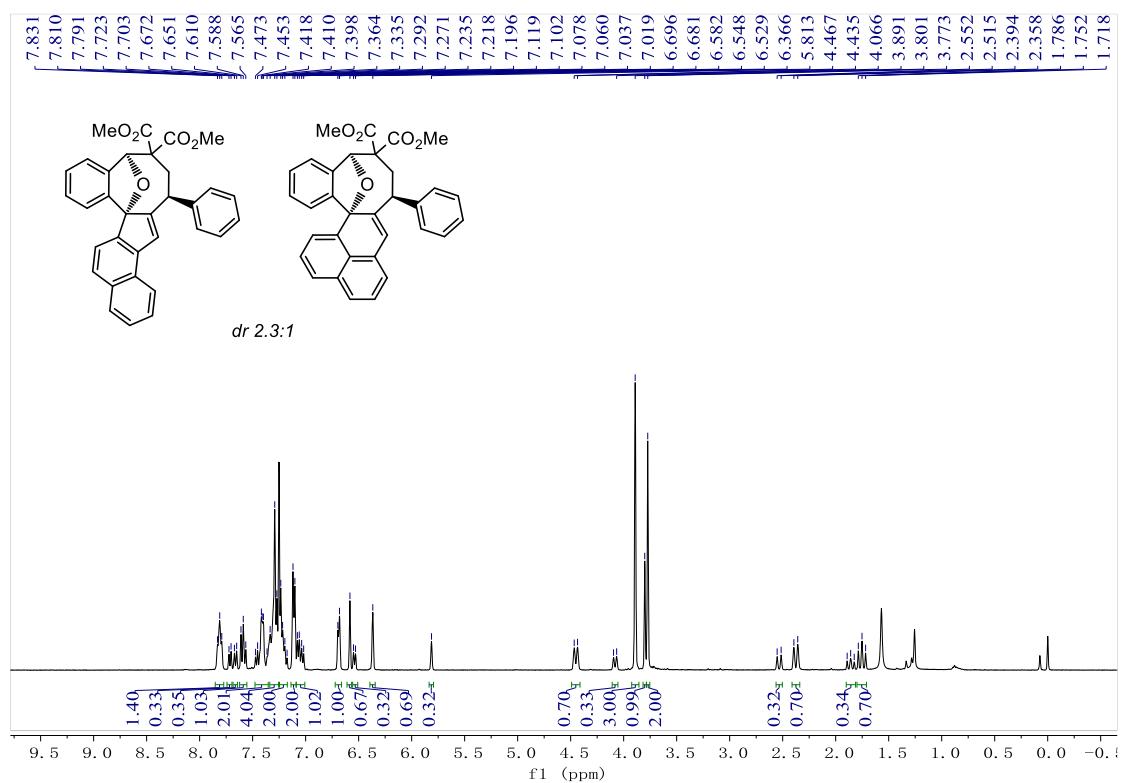




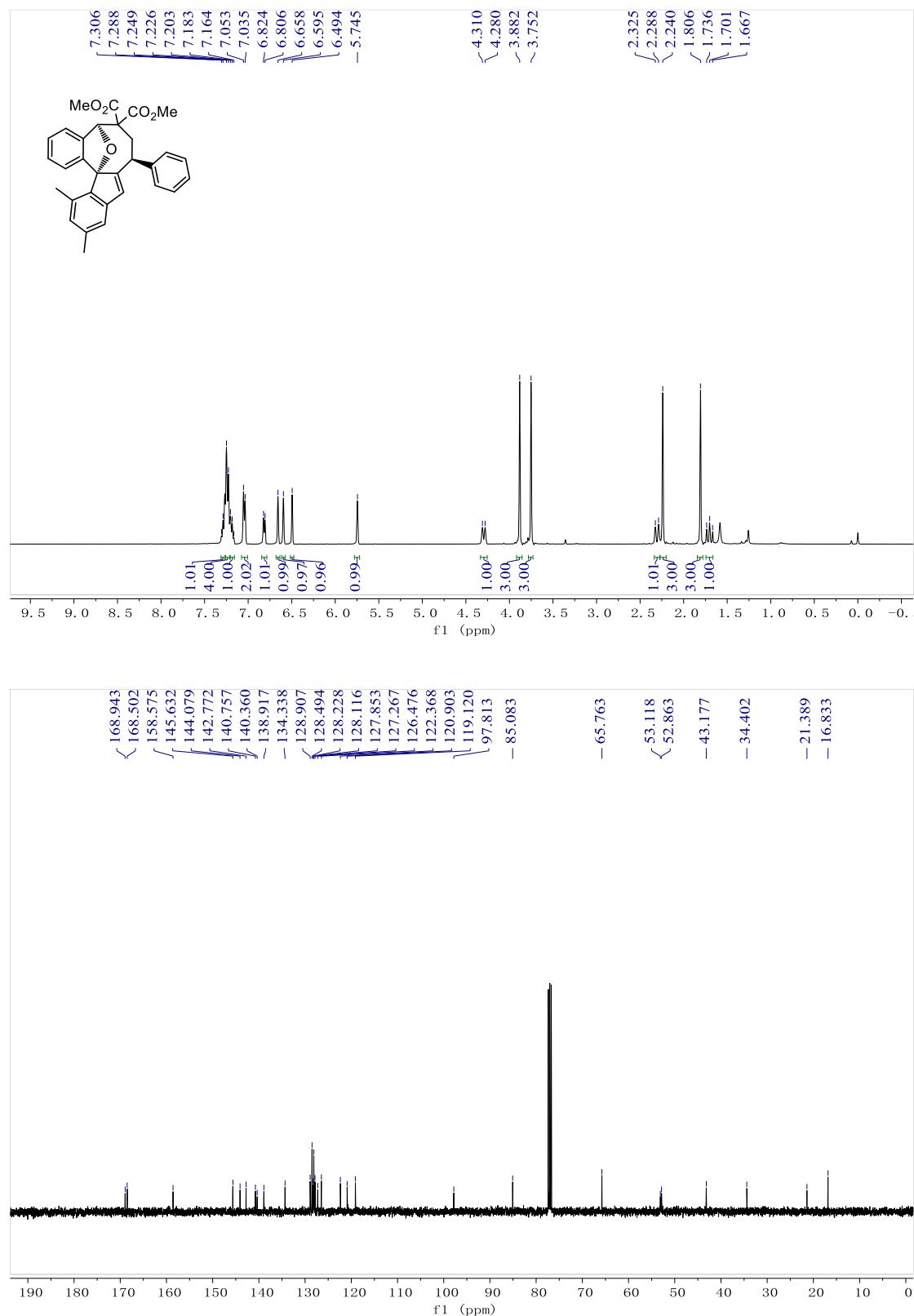
**3k**



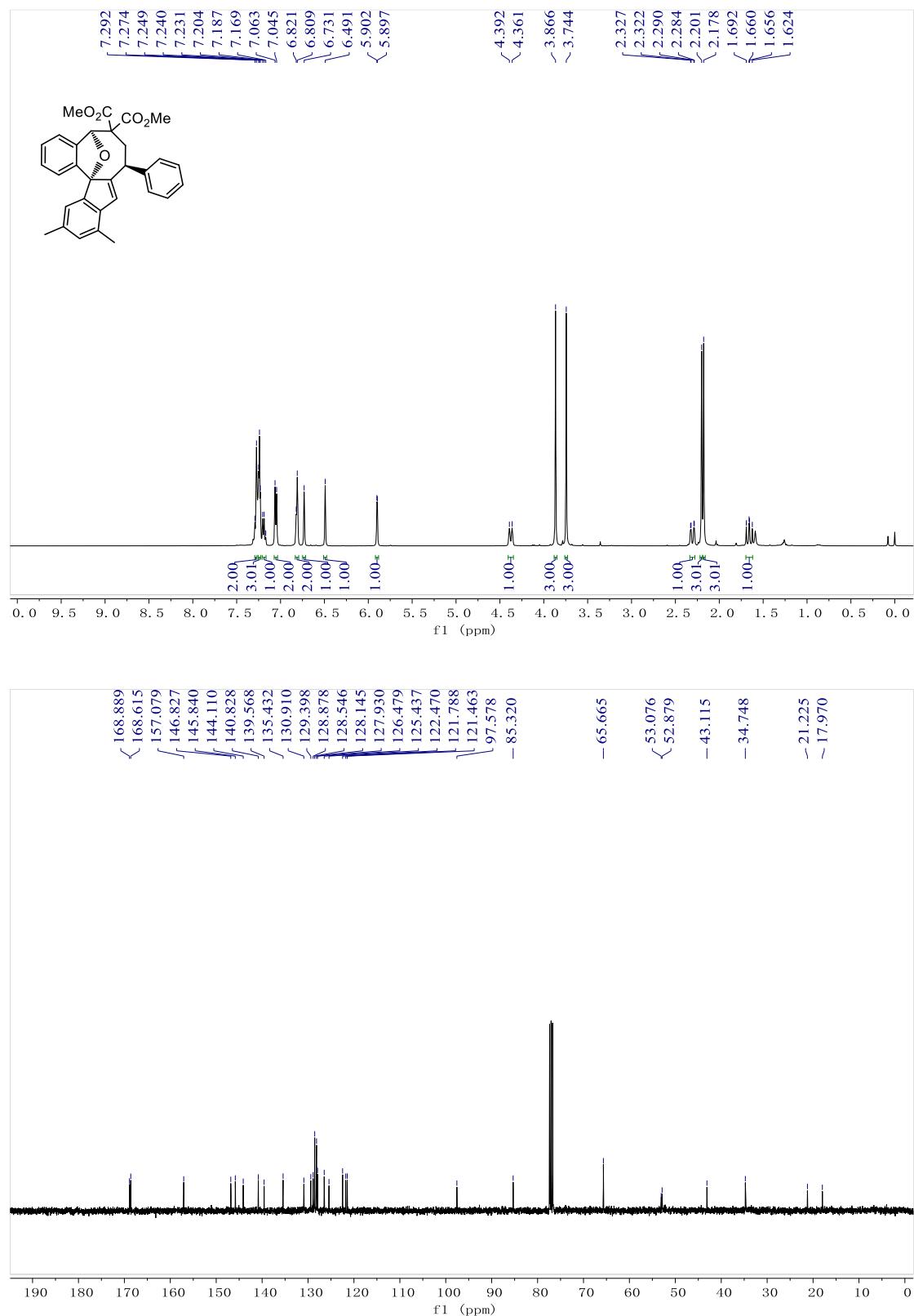
31 and 31'



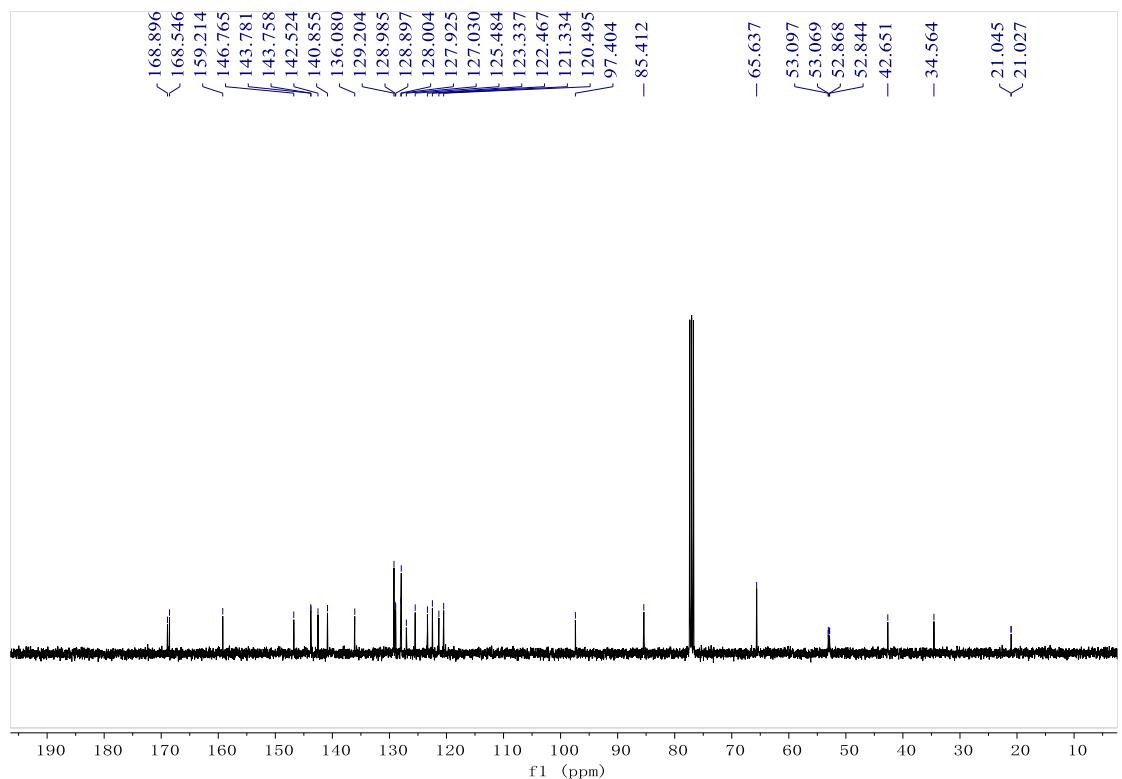
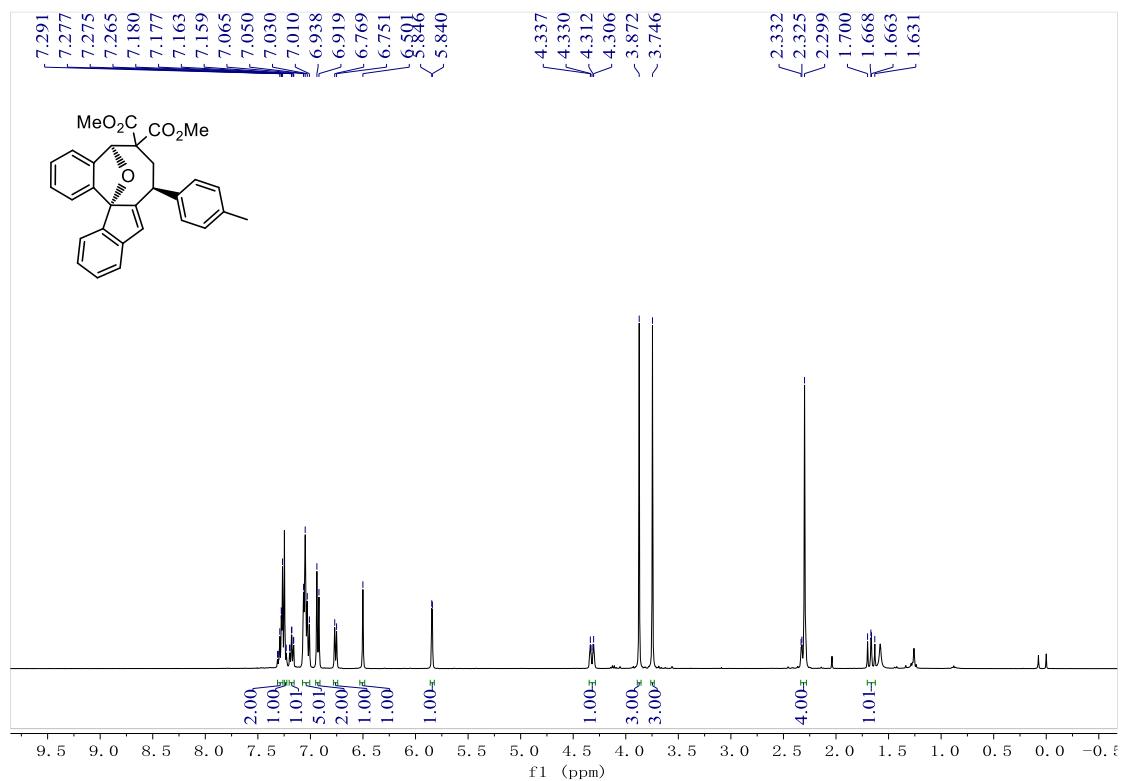
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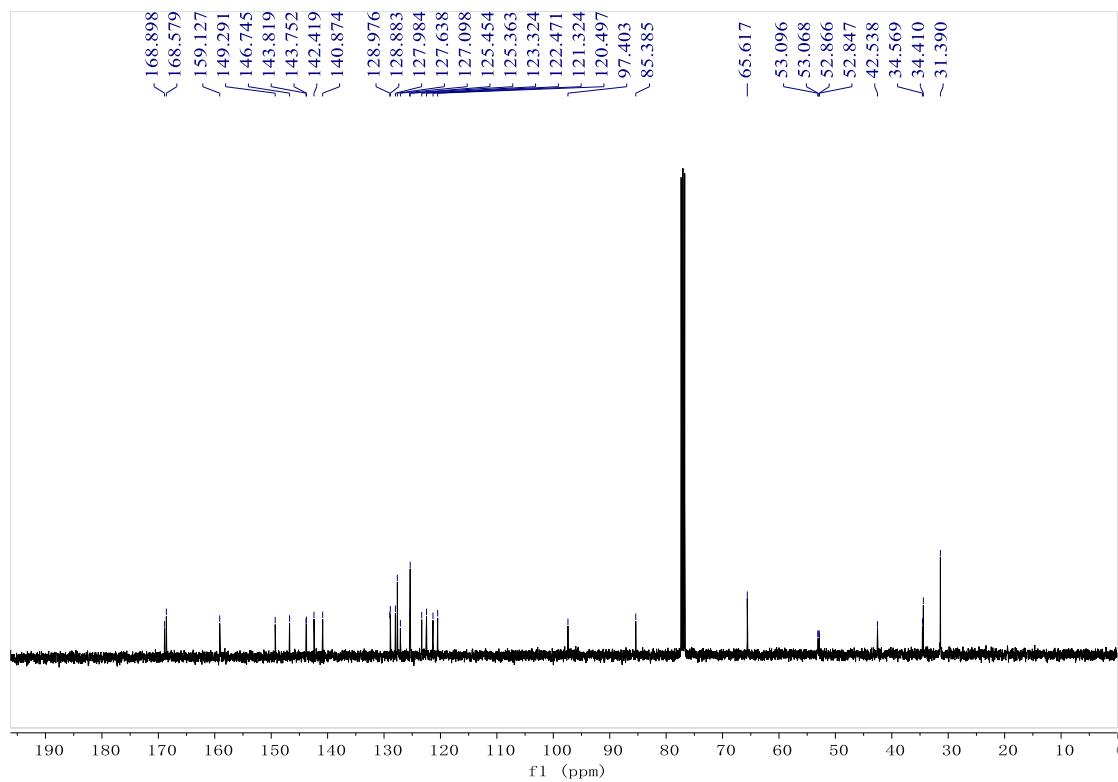
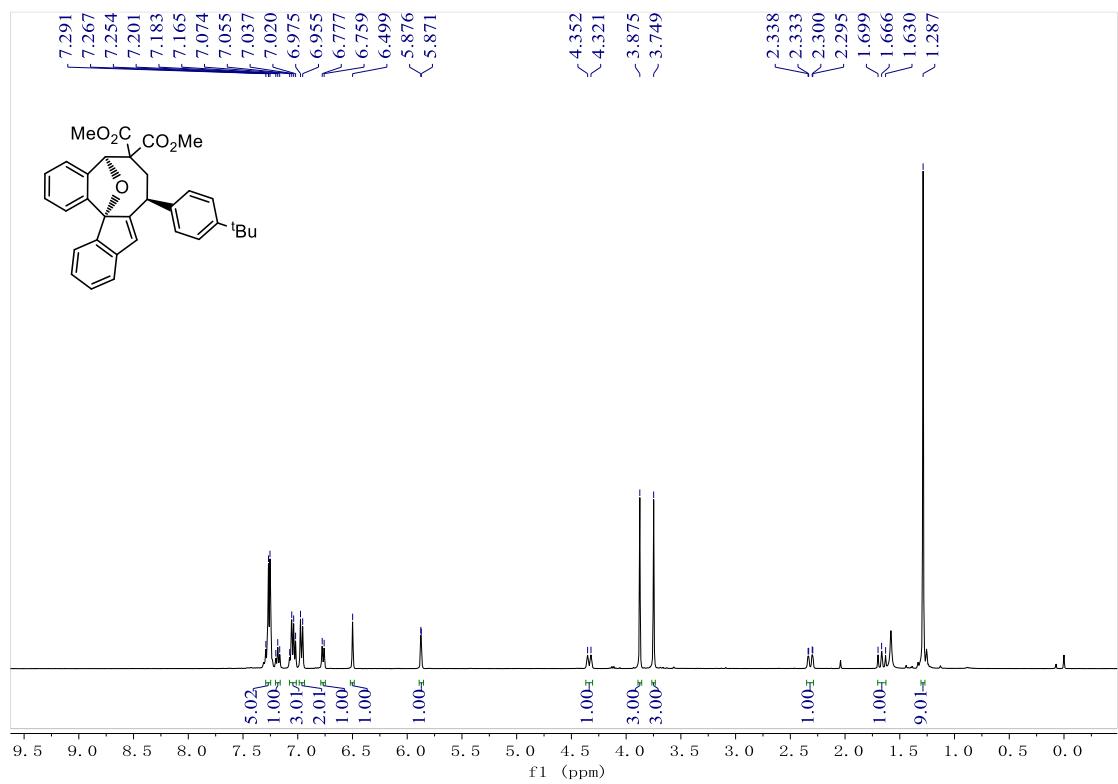
**3n**



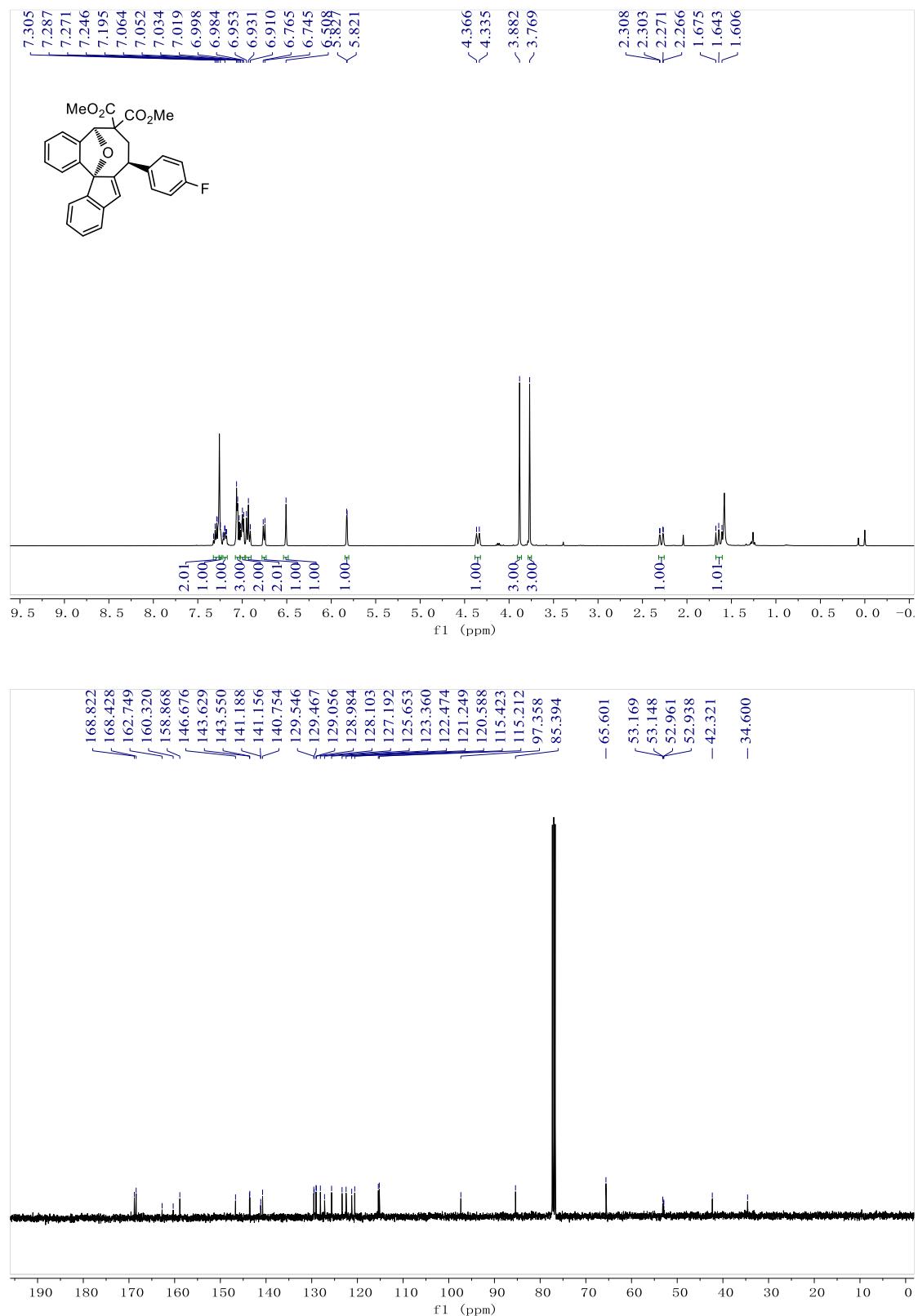
3p

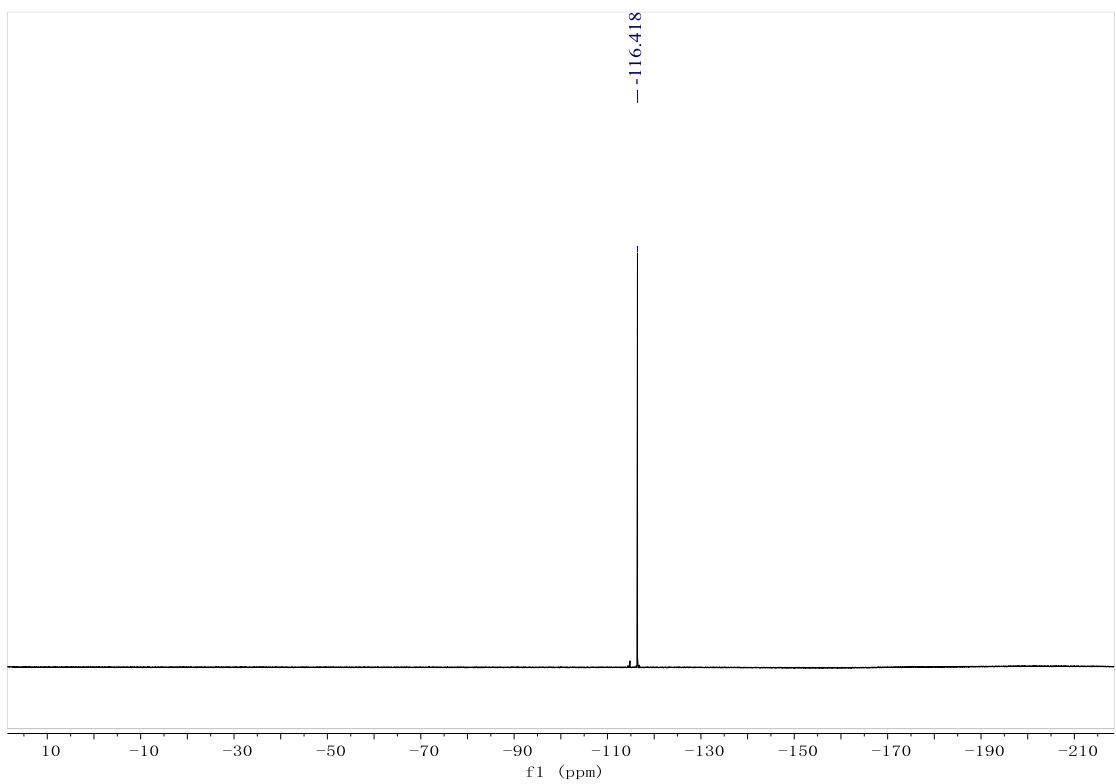


3q

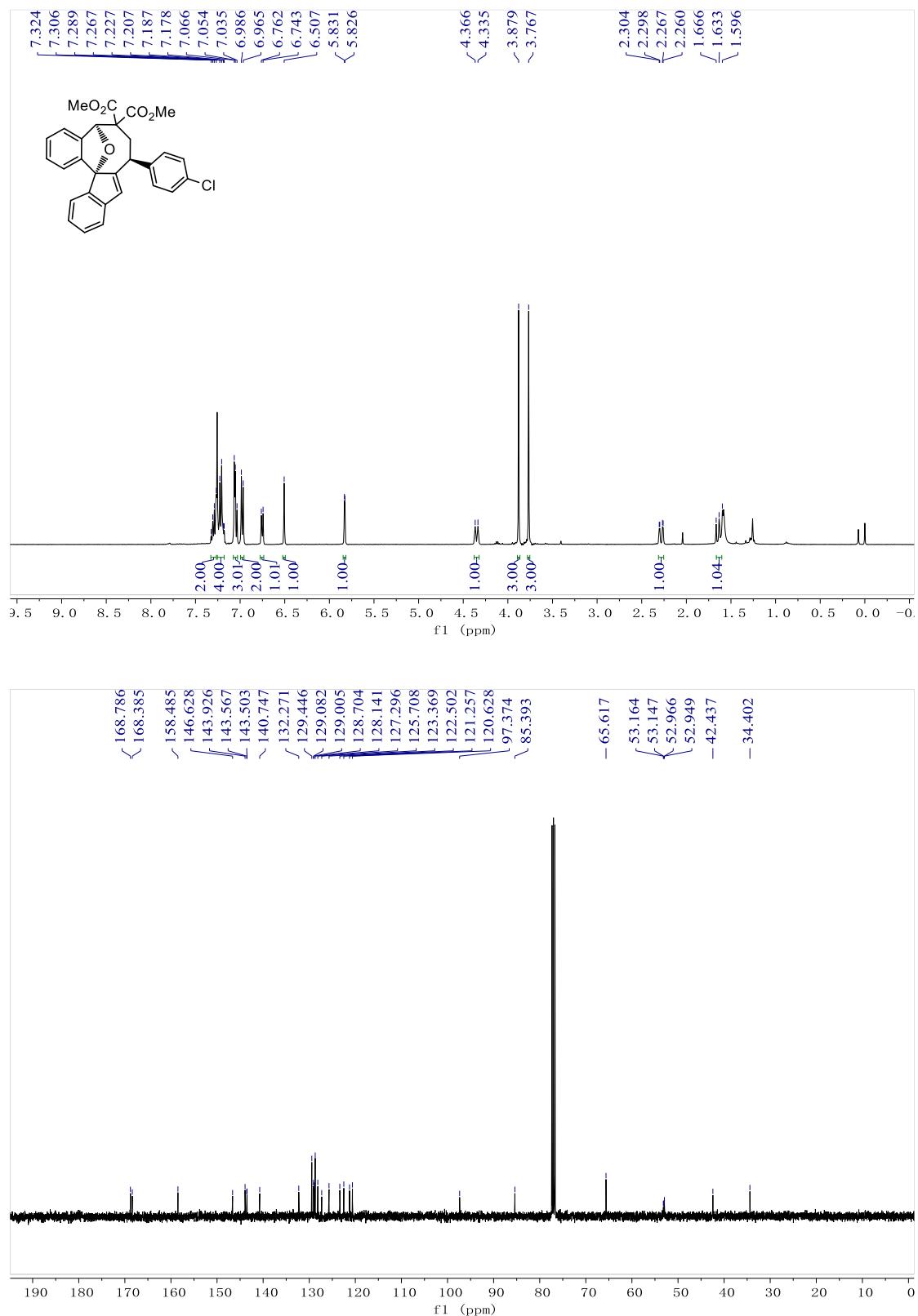


**3r**

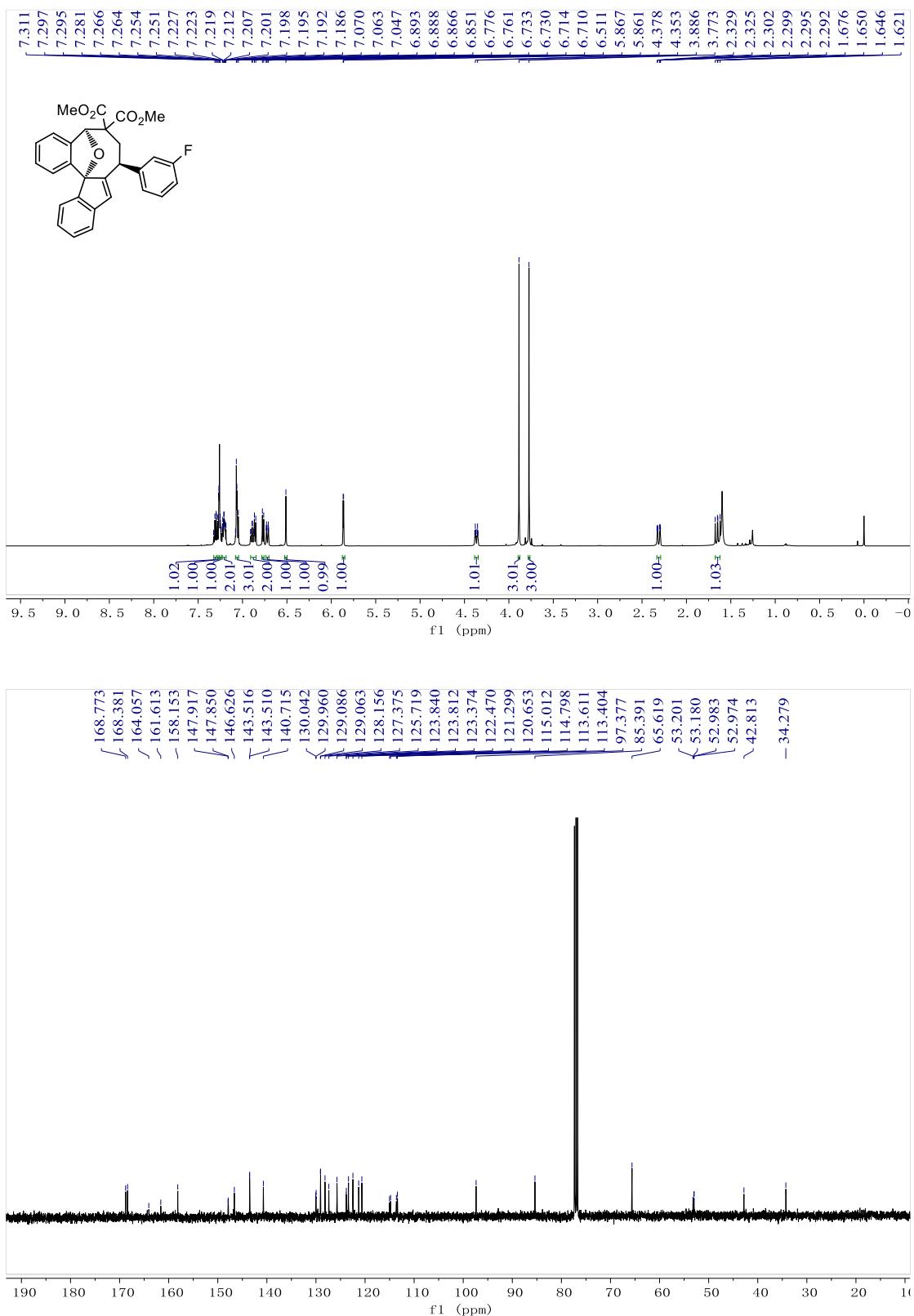


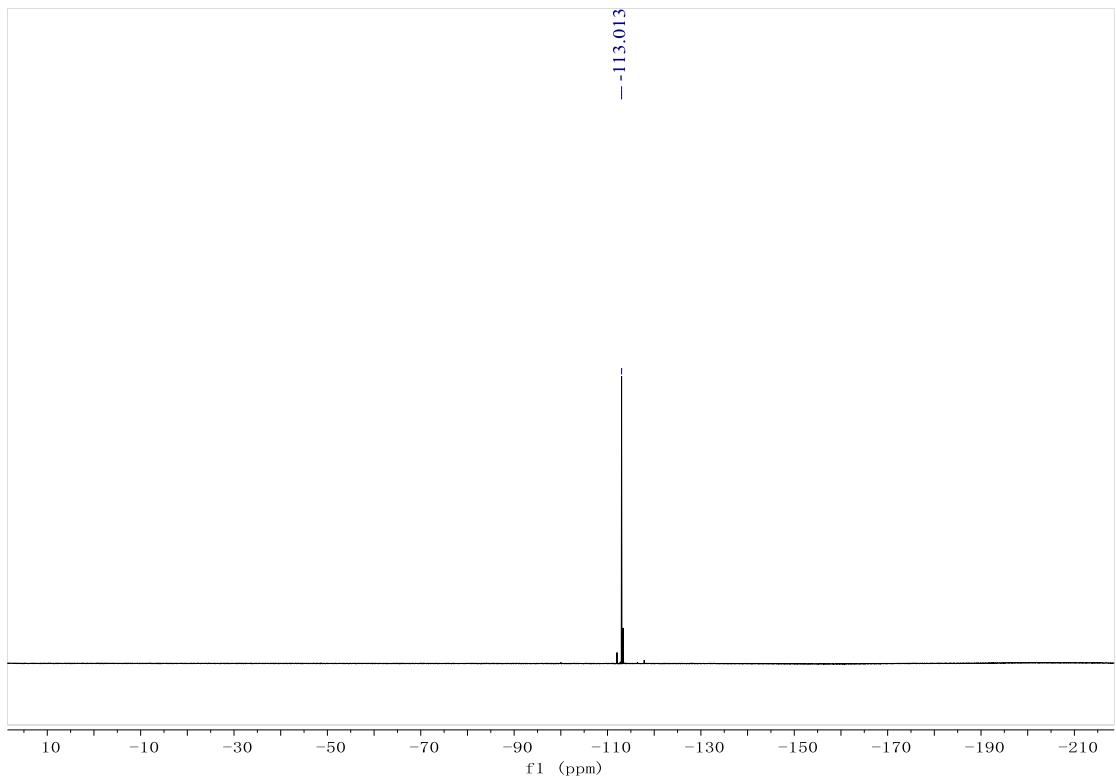


**3s**

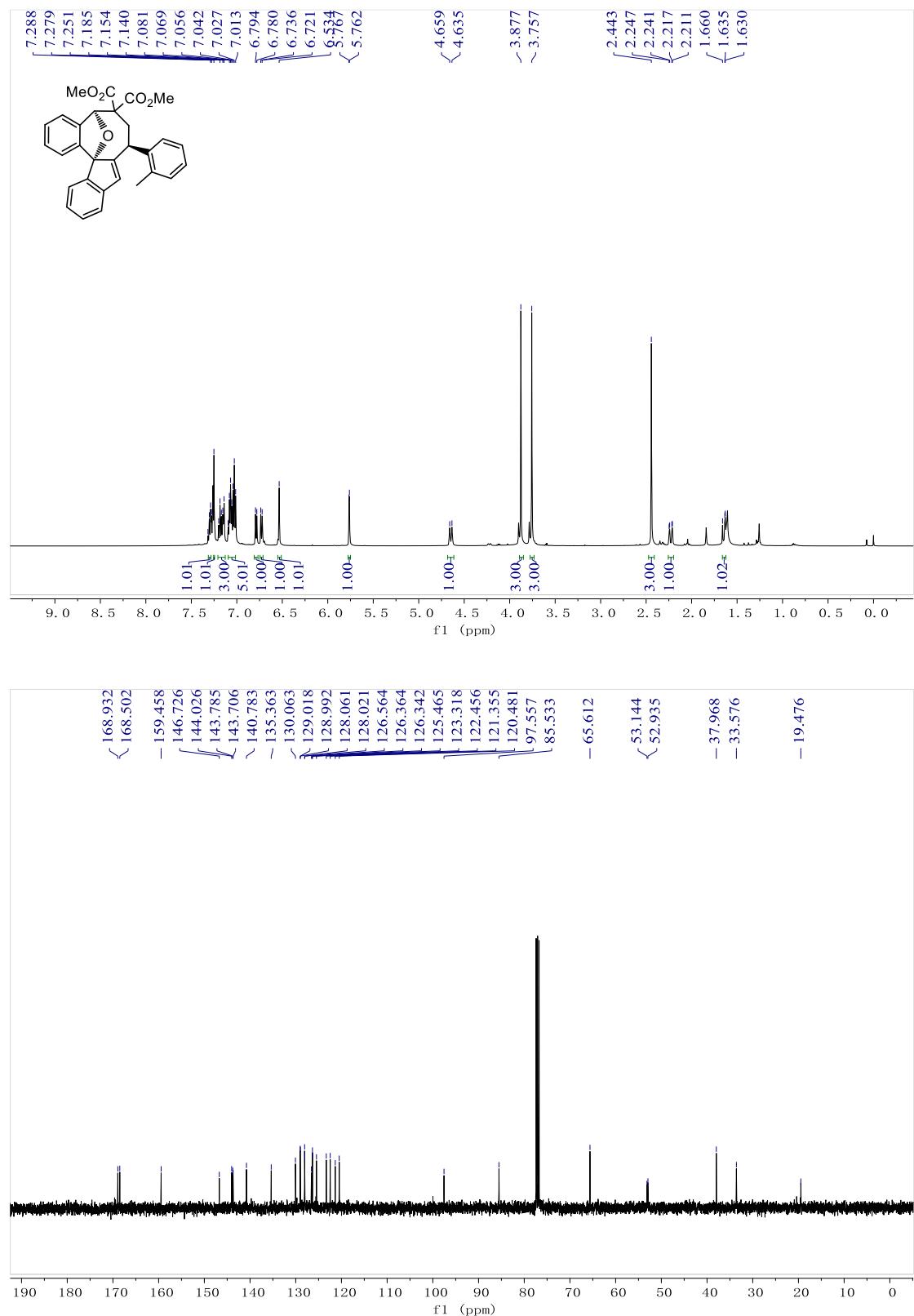


**3t**

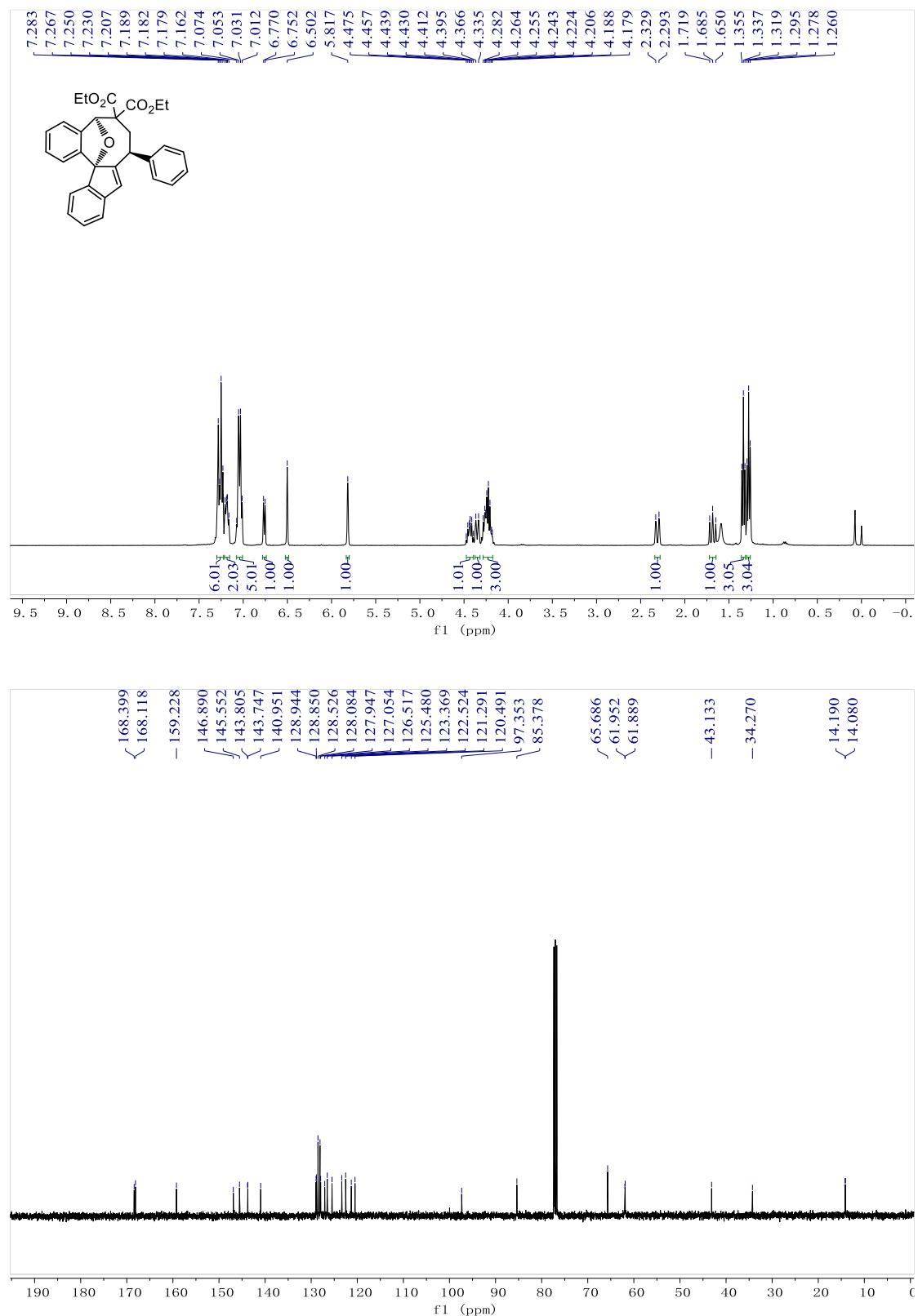




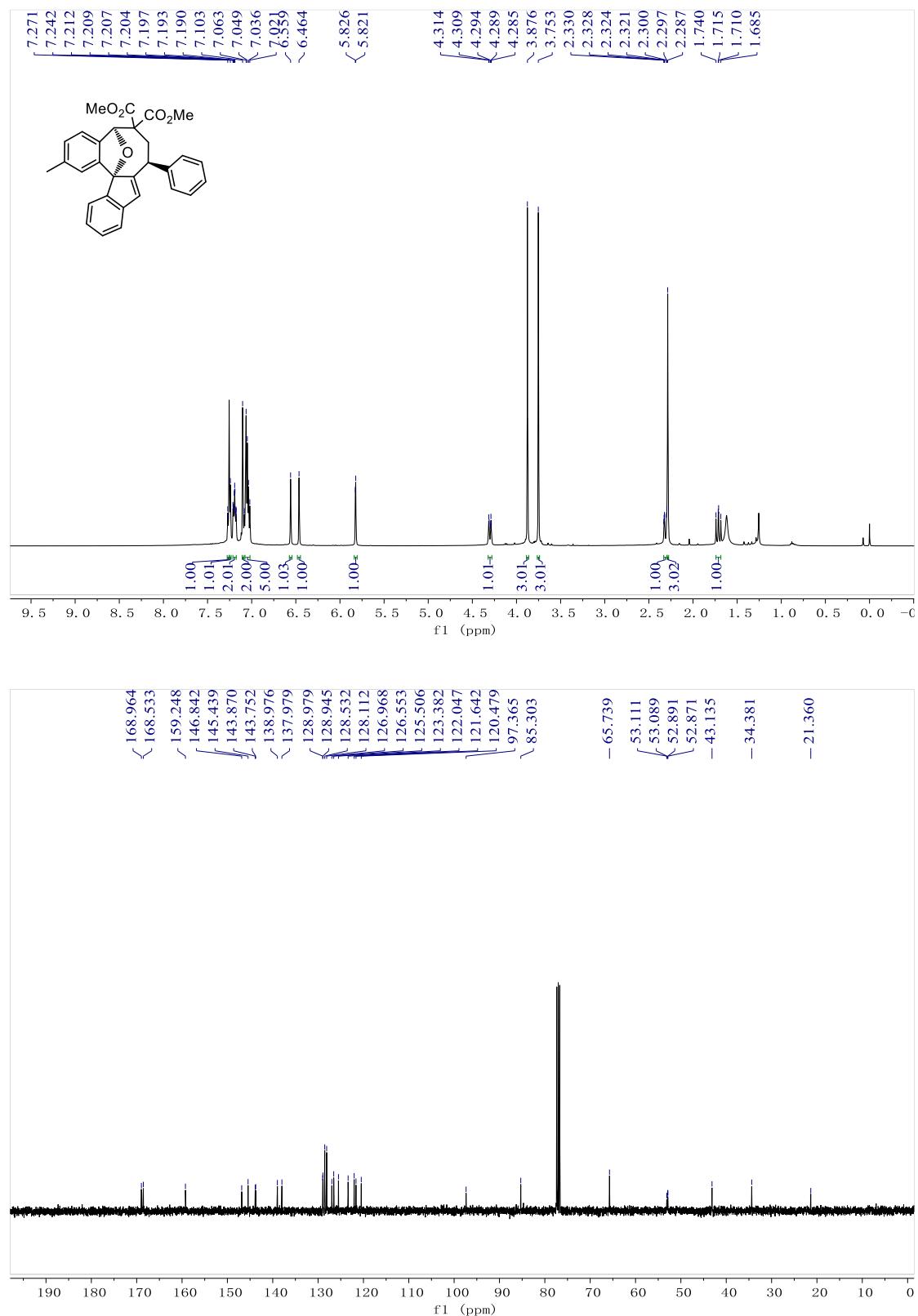
**3u**



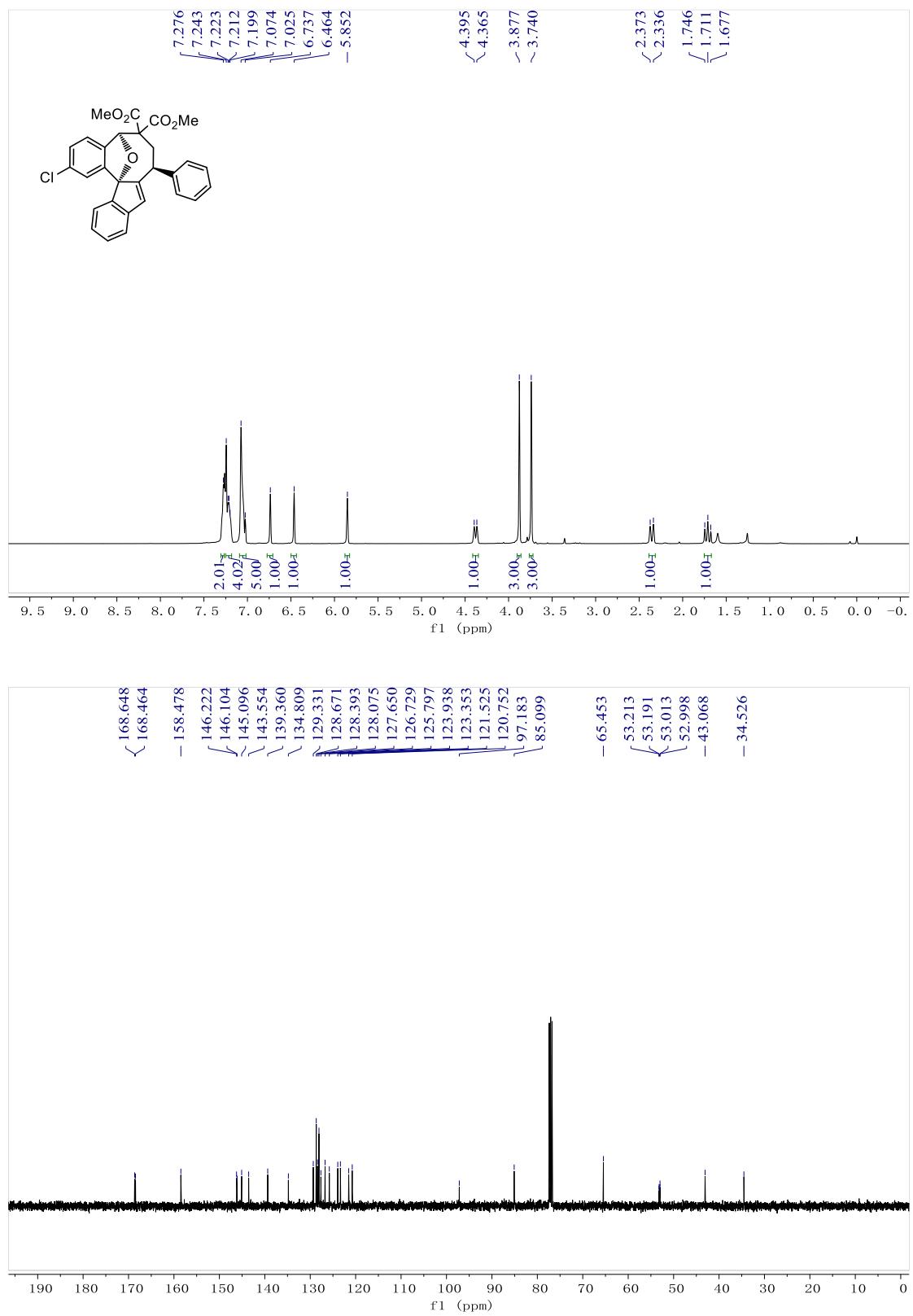
**3v**



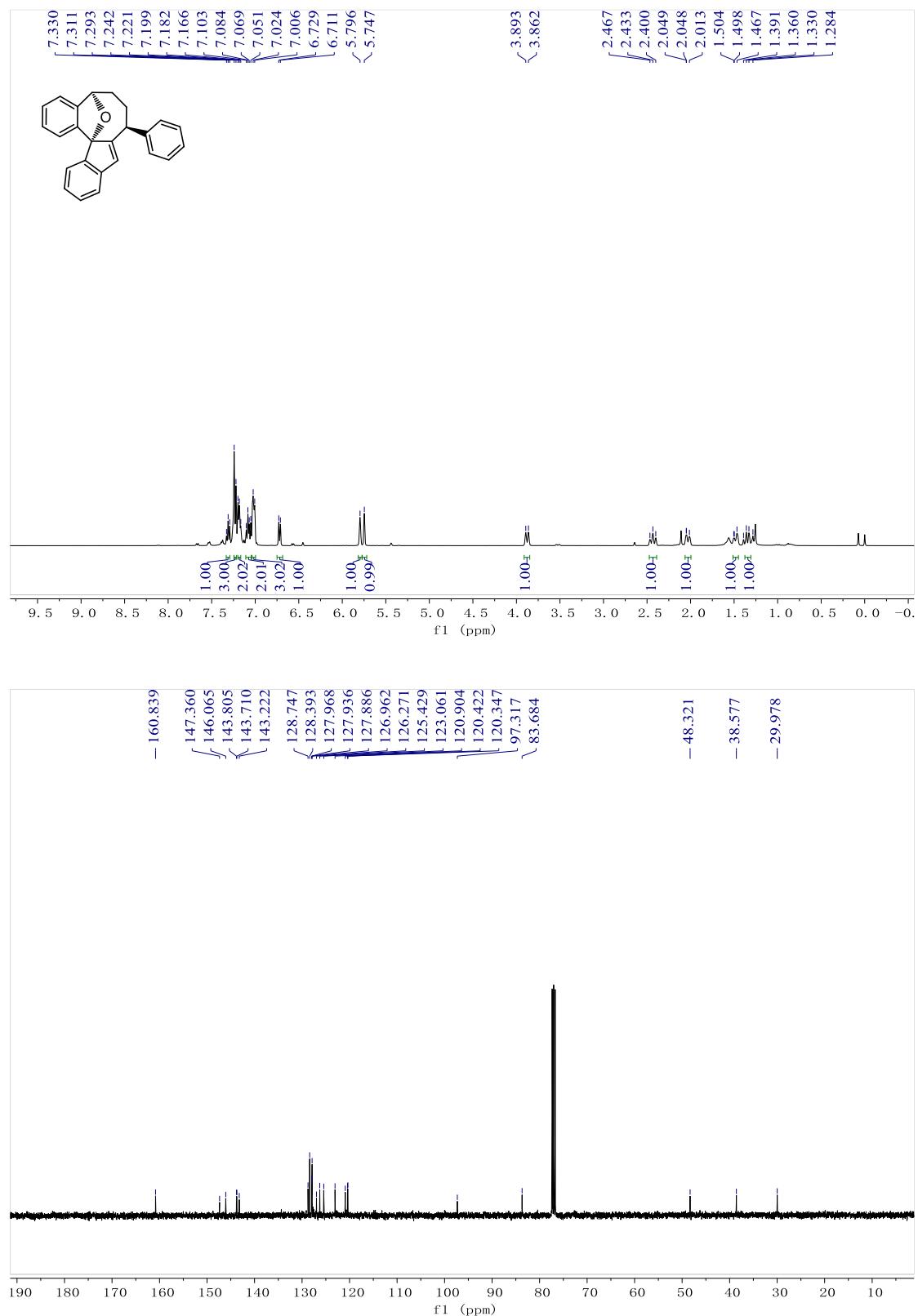
**3w**



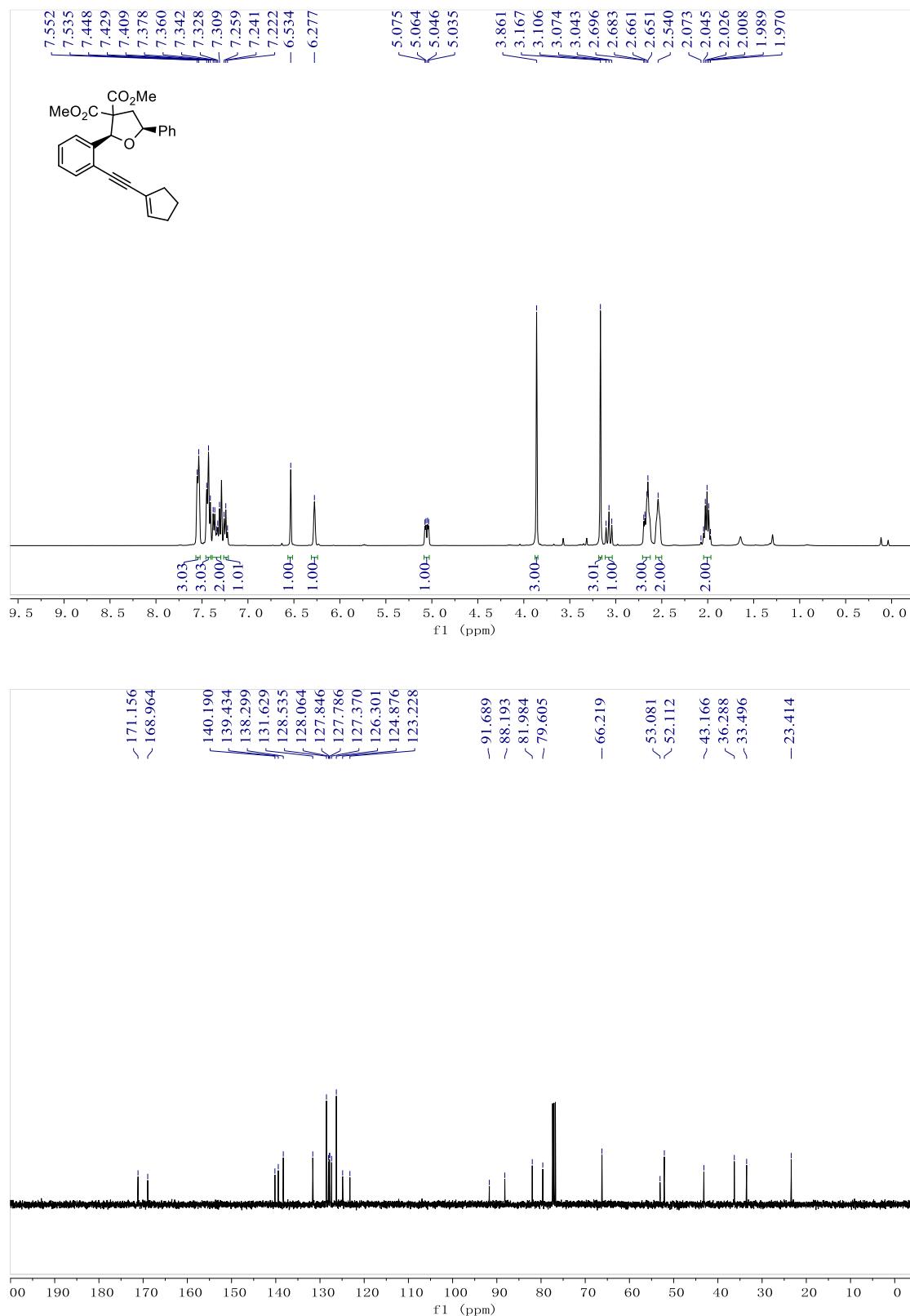
3x



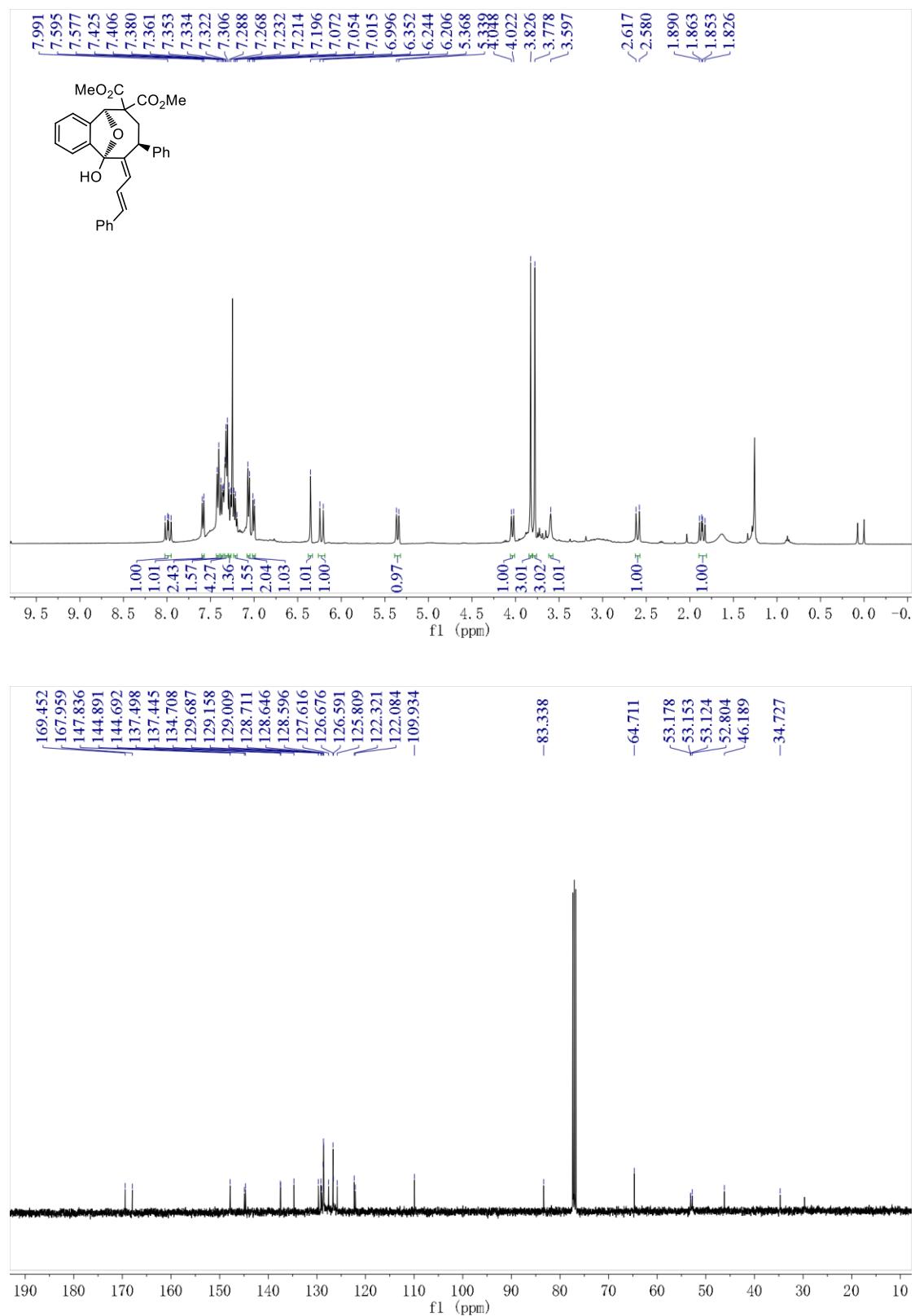
**3y**



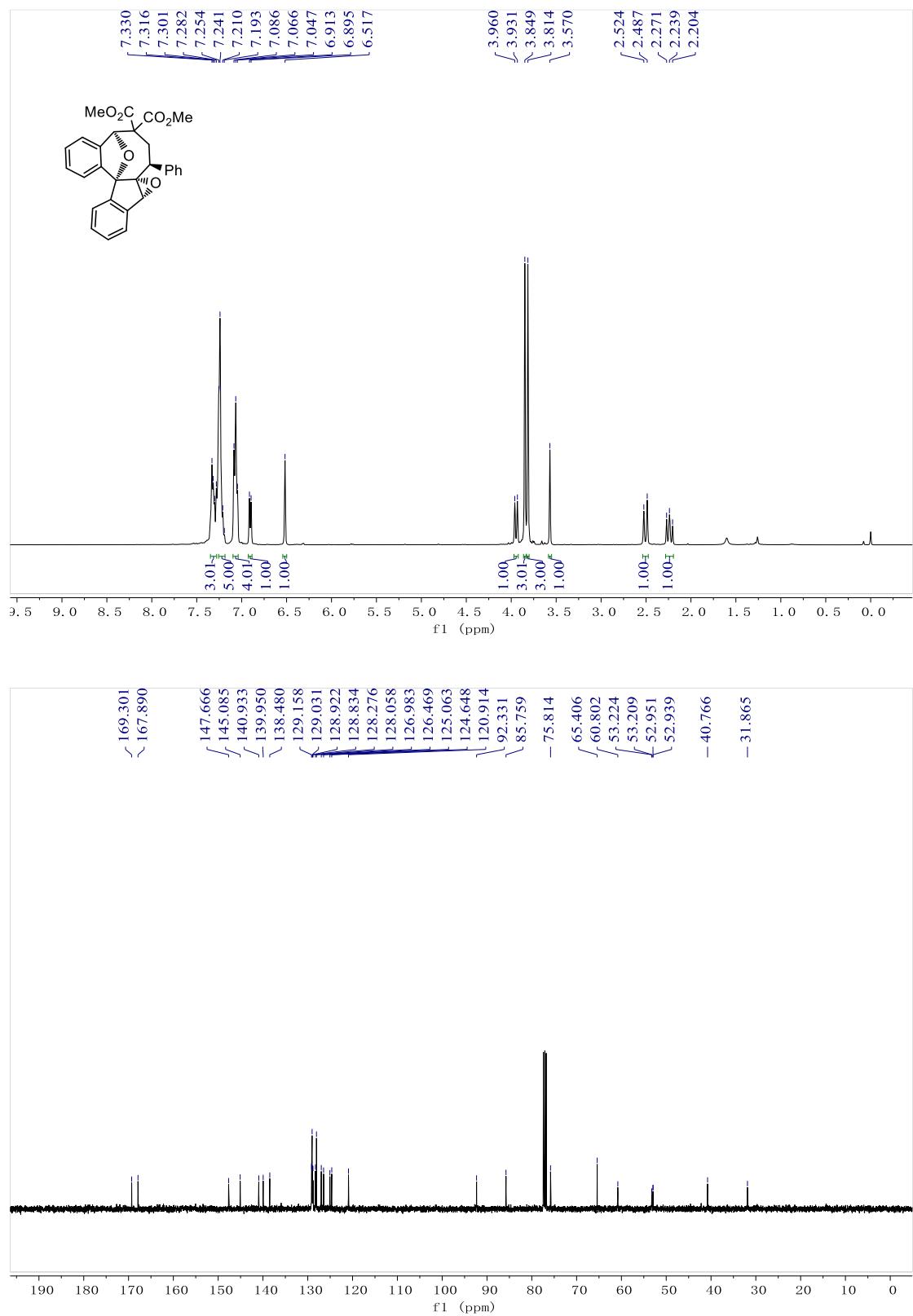
**3aa**



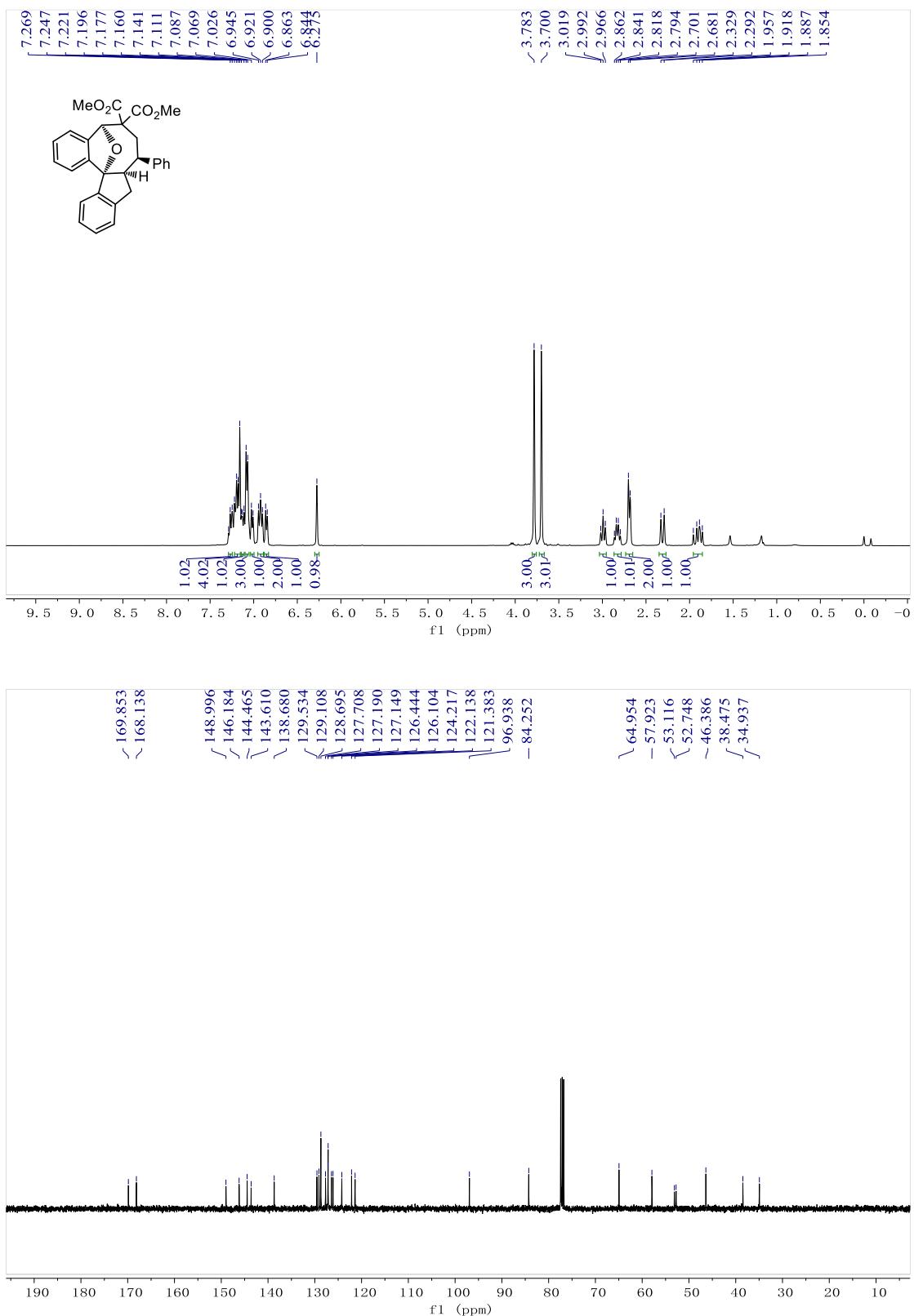
**4ac**



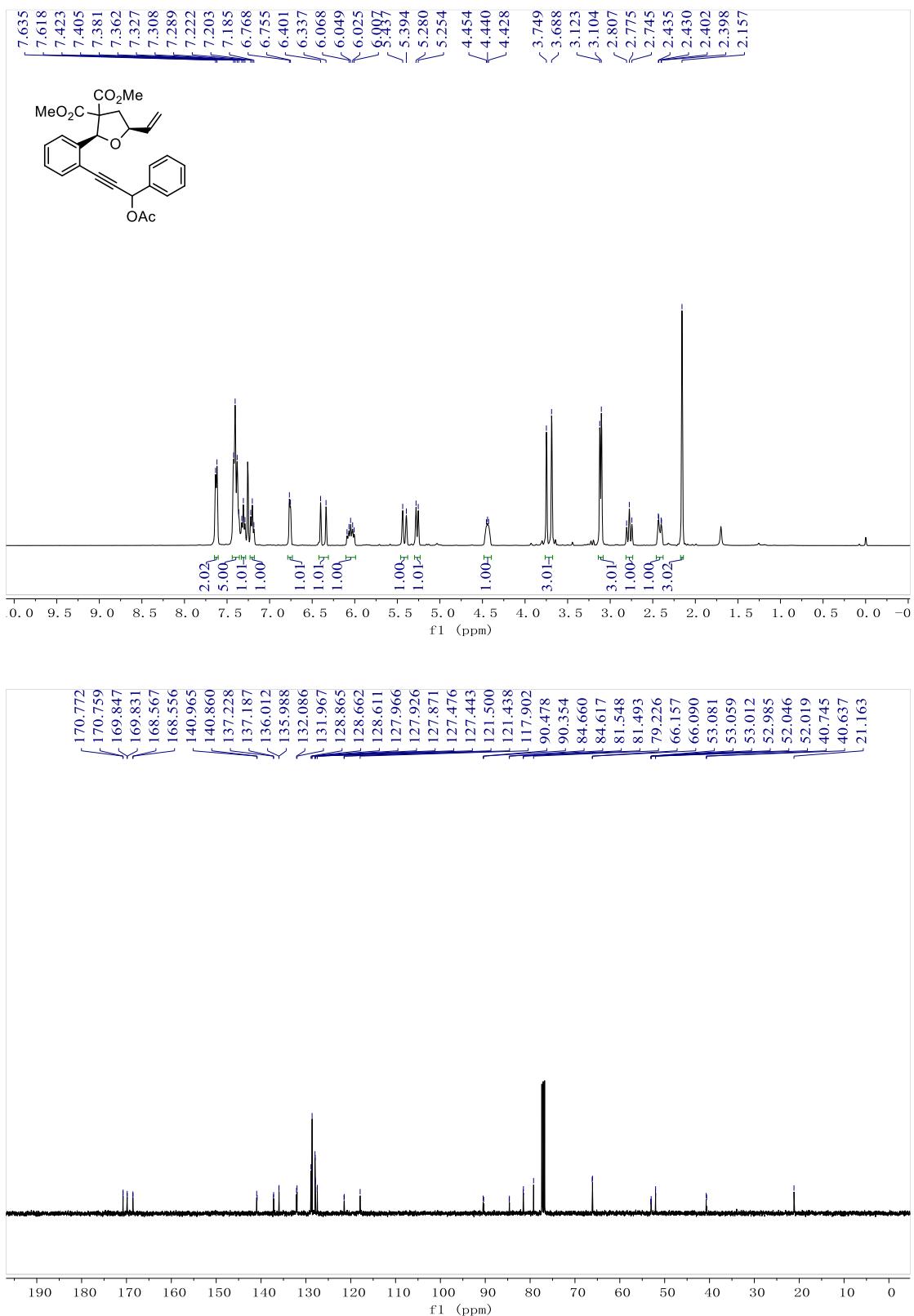
**5a**



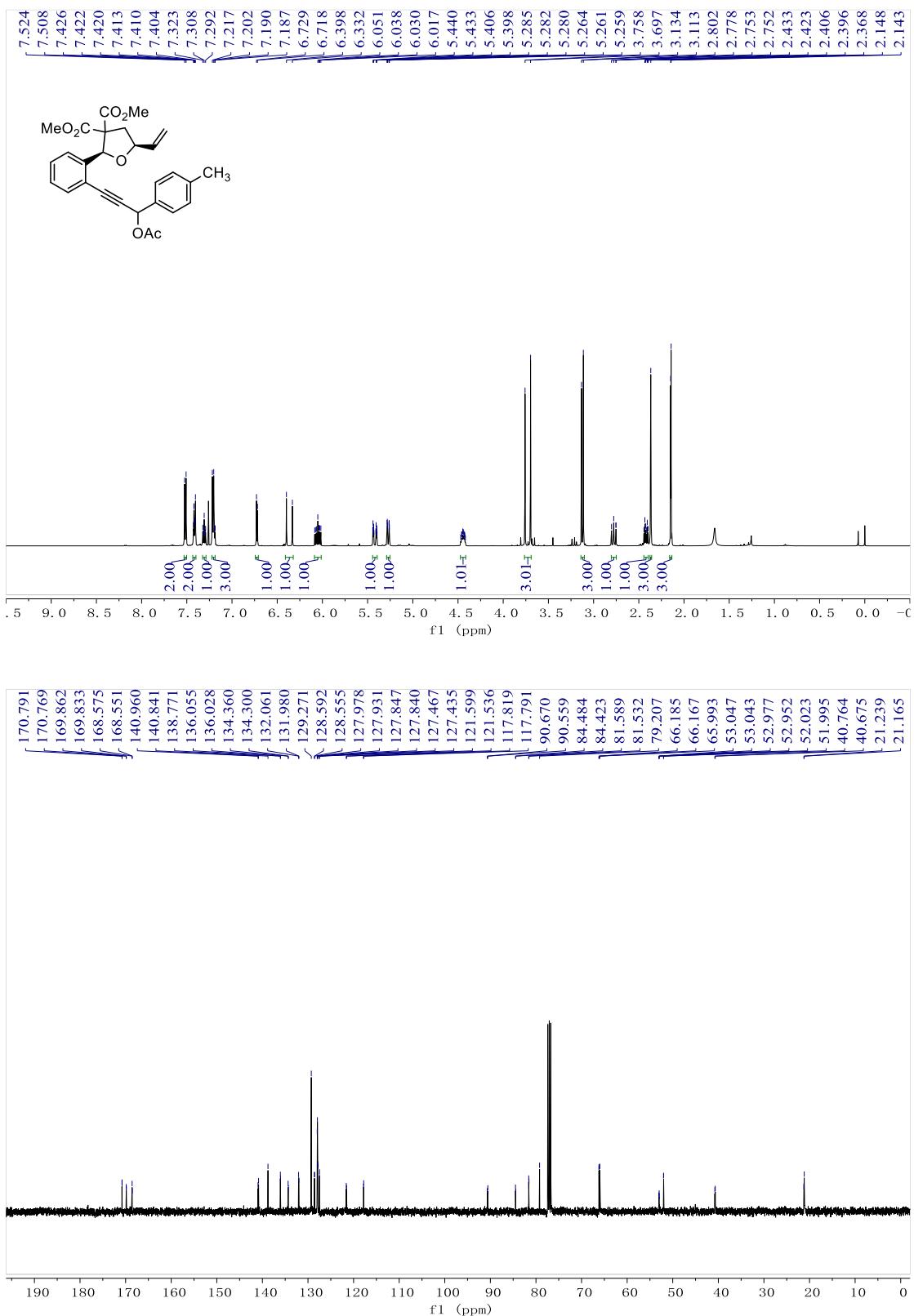
**6a**



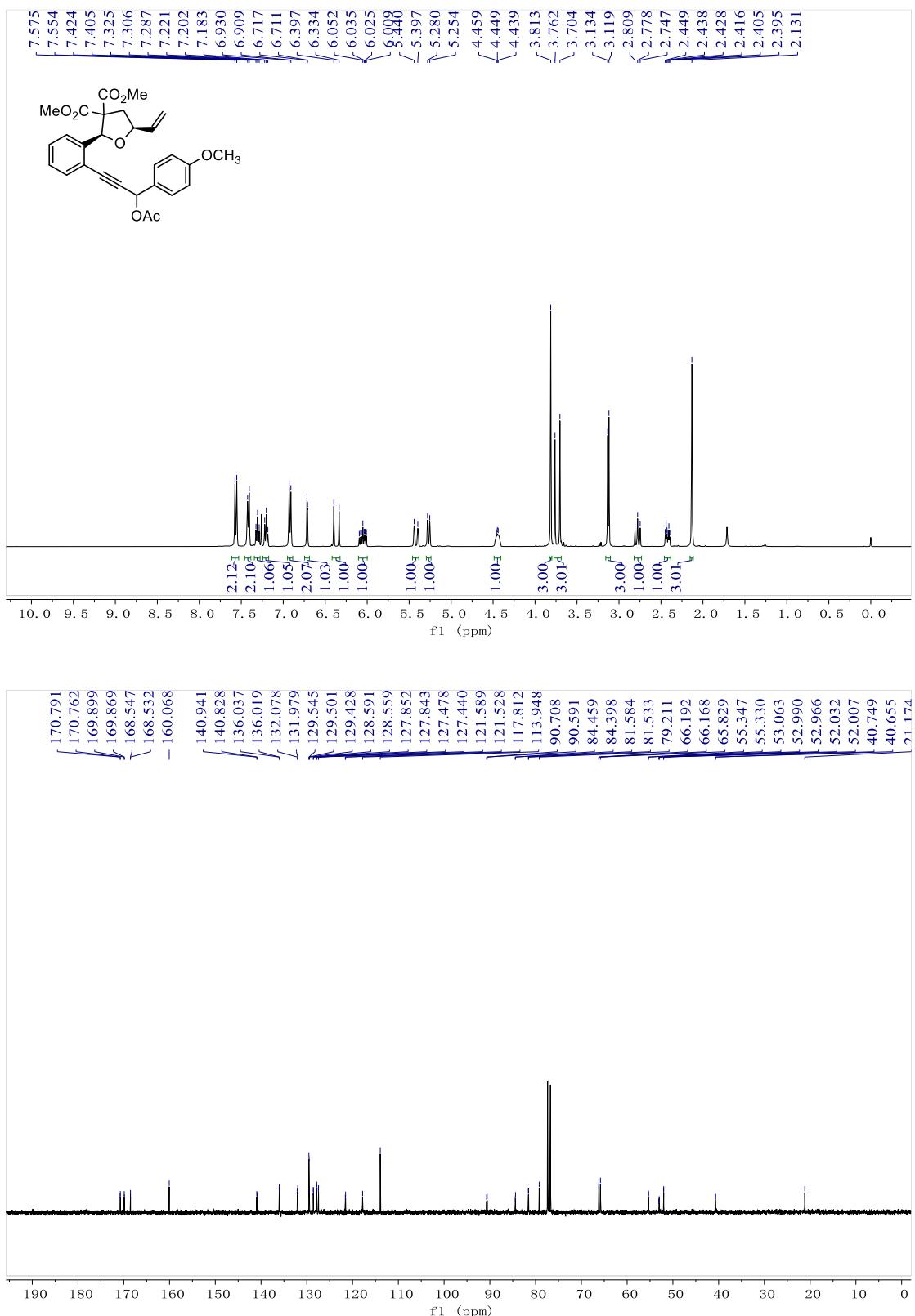
7a



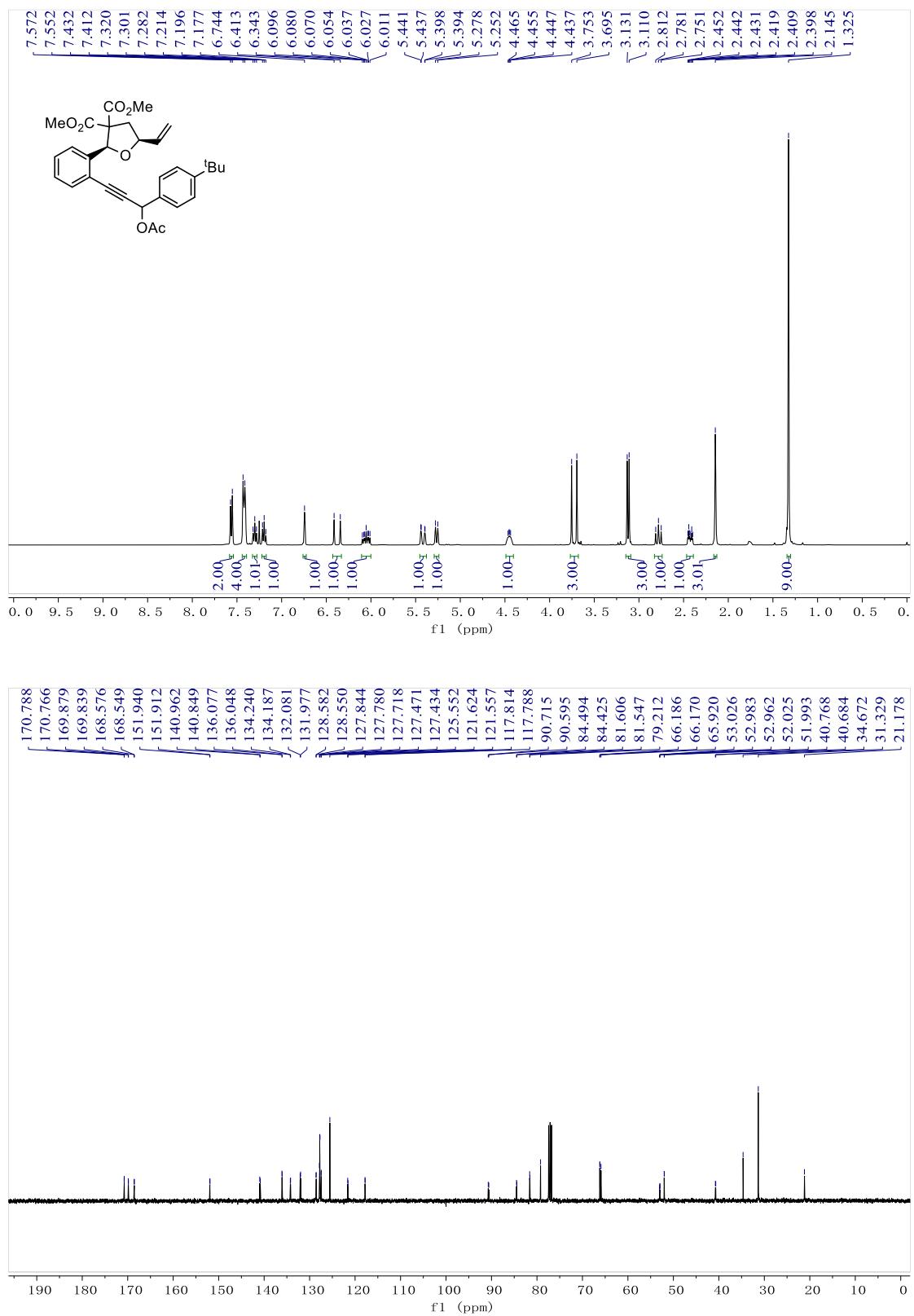
**7d**



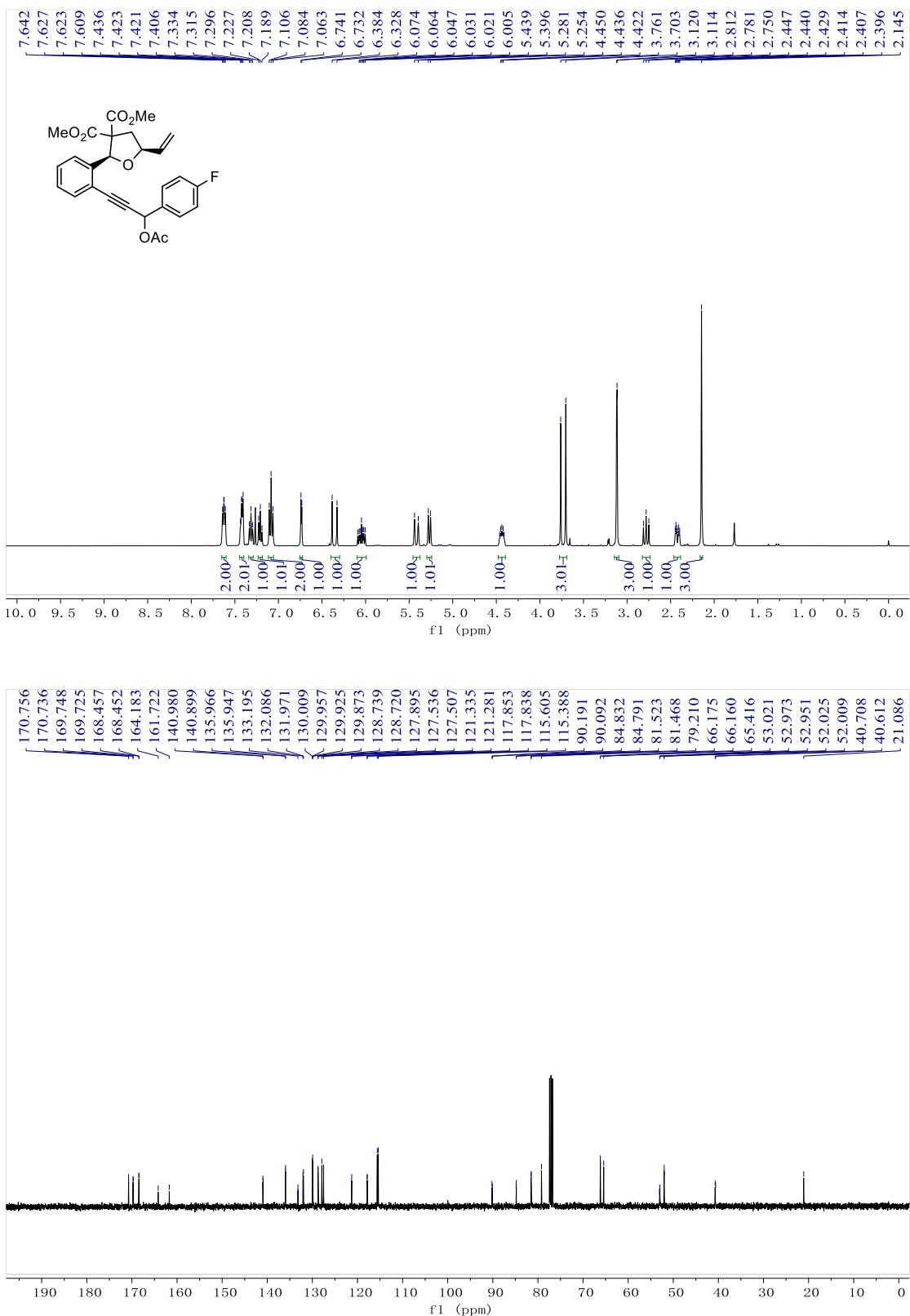
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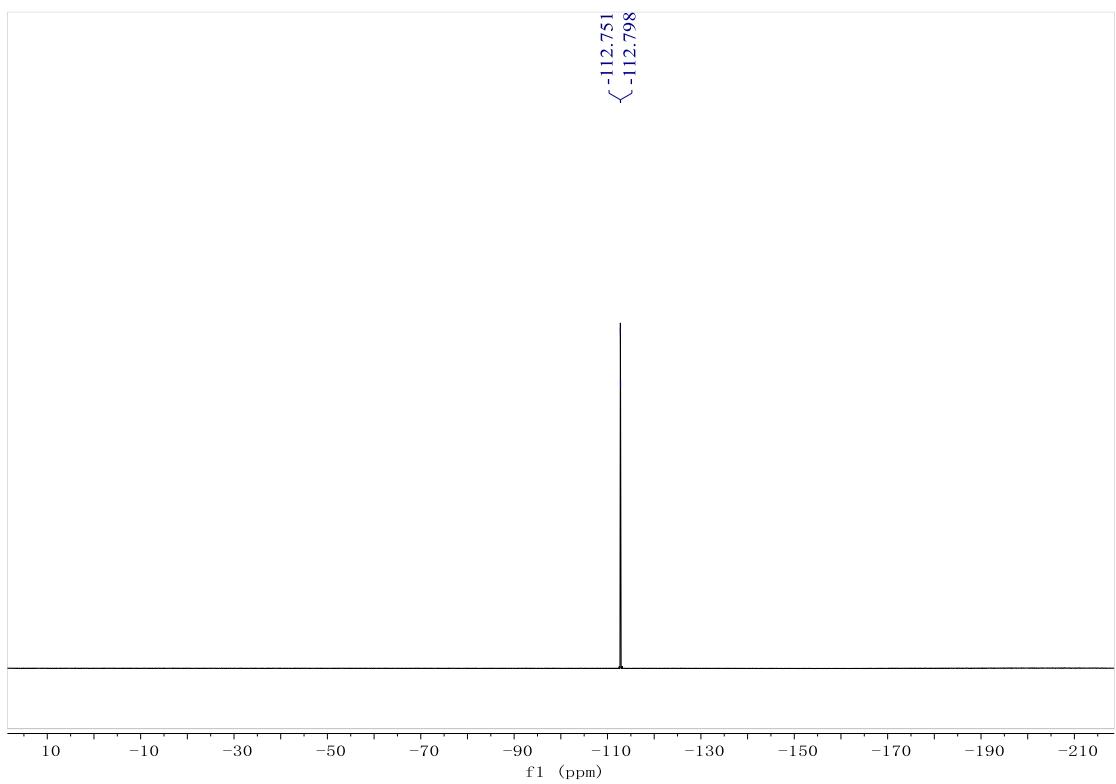


7f

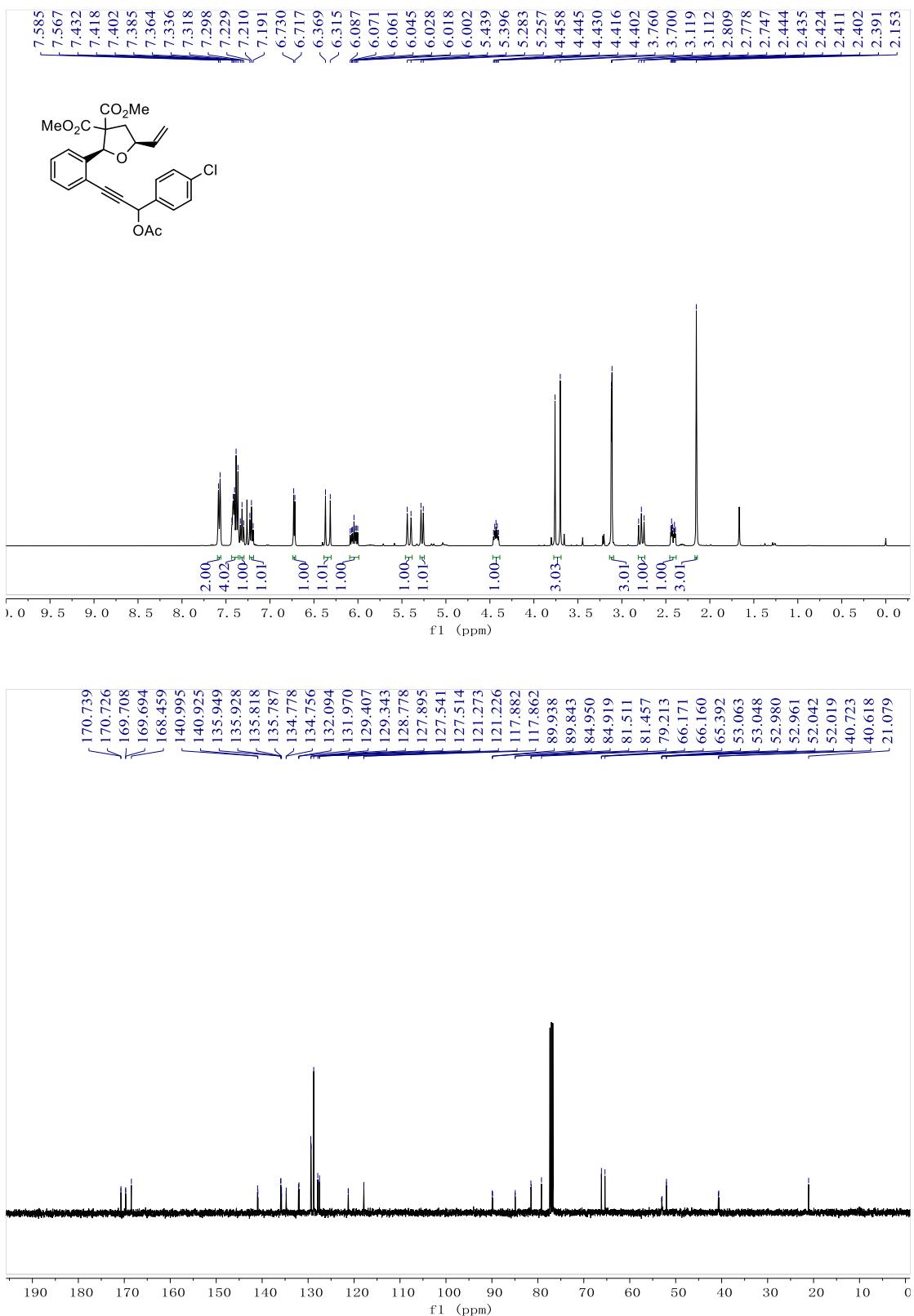


**7g**

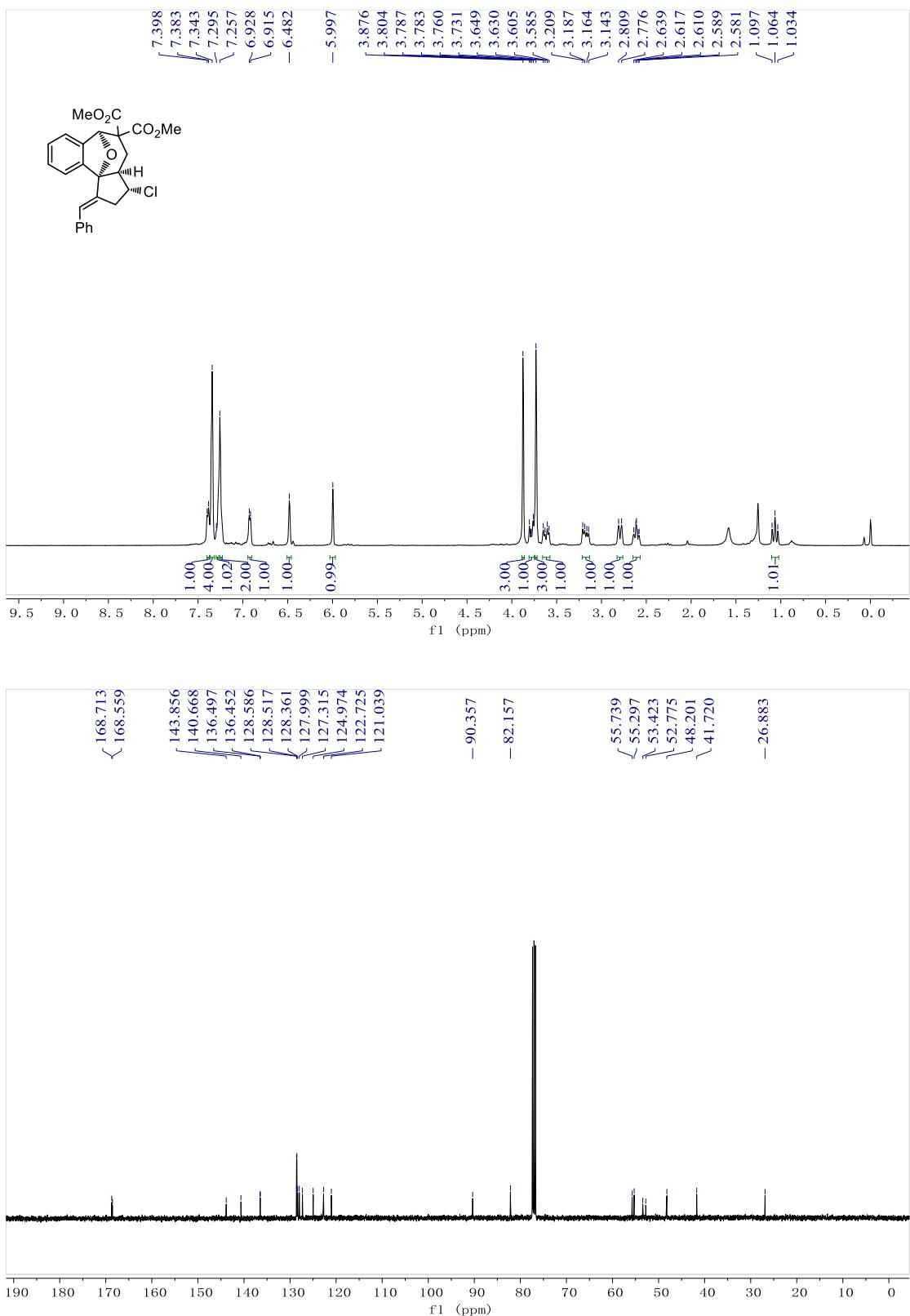




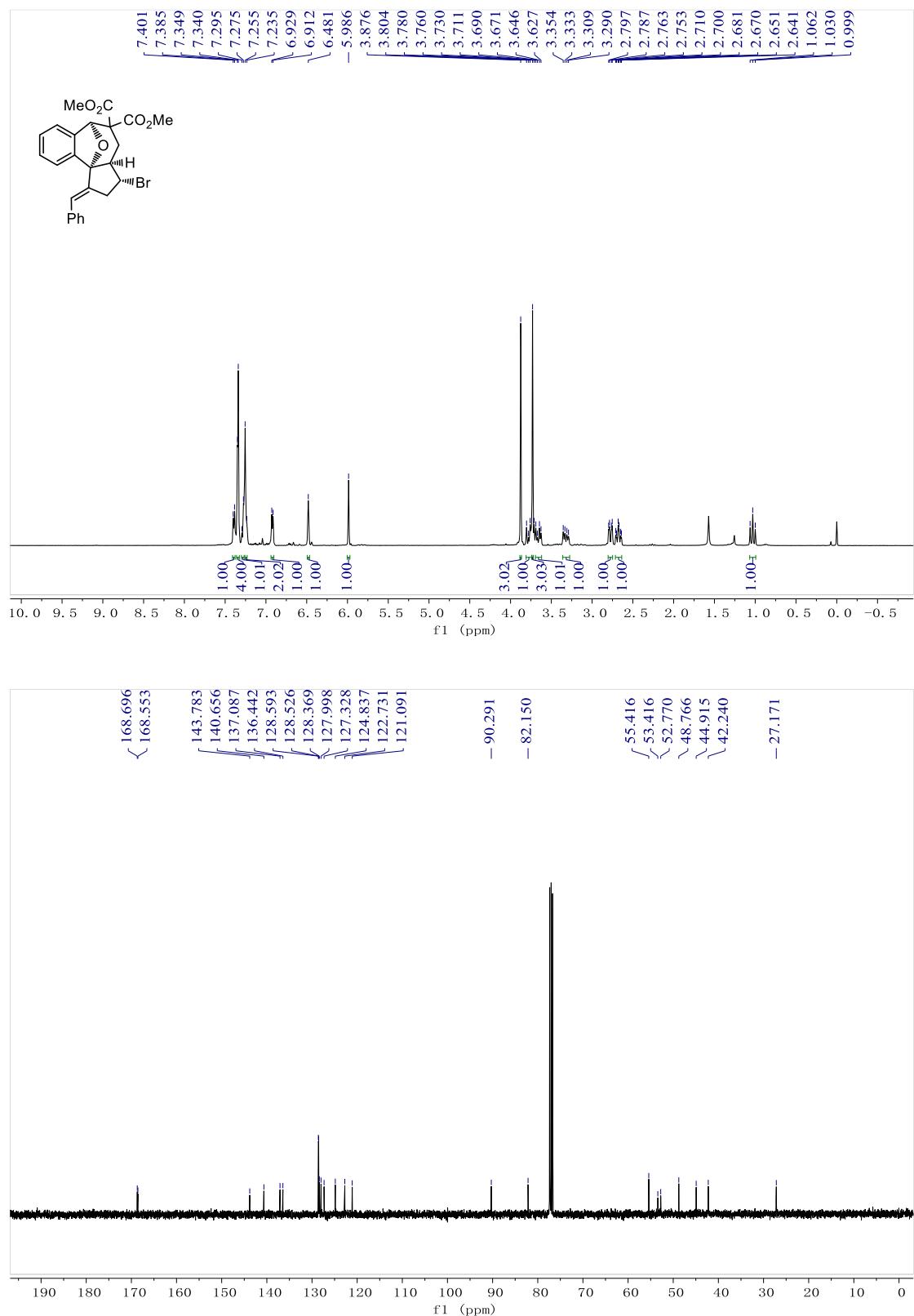
**7h**



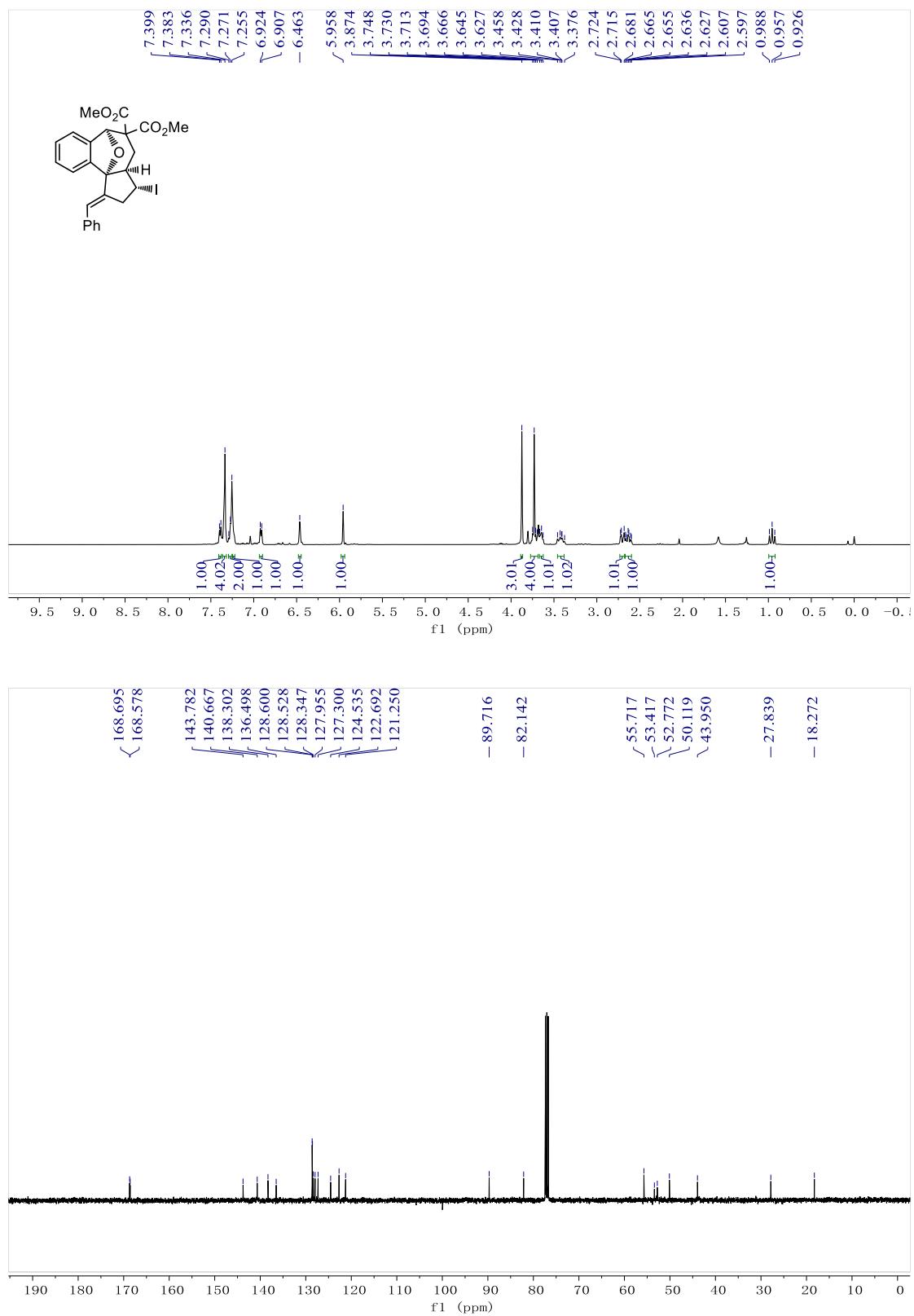
**9a**



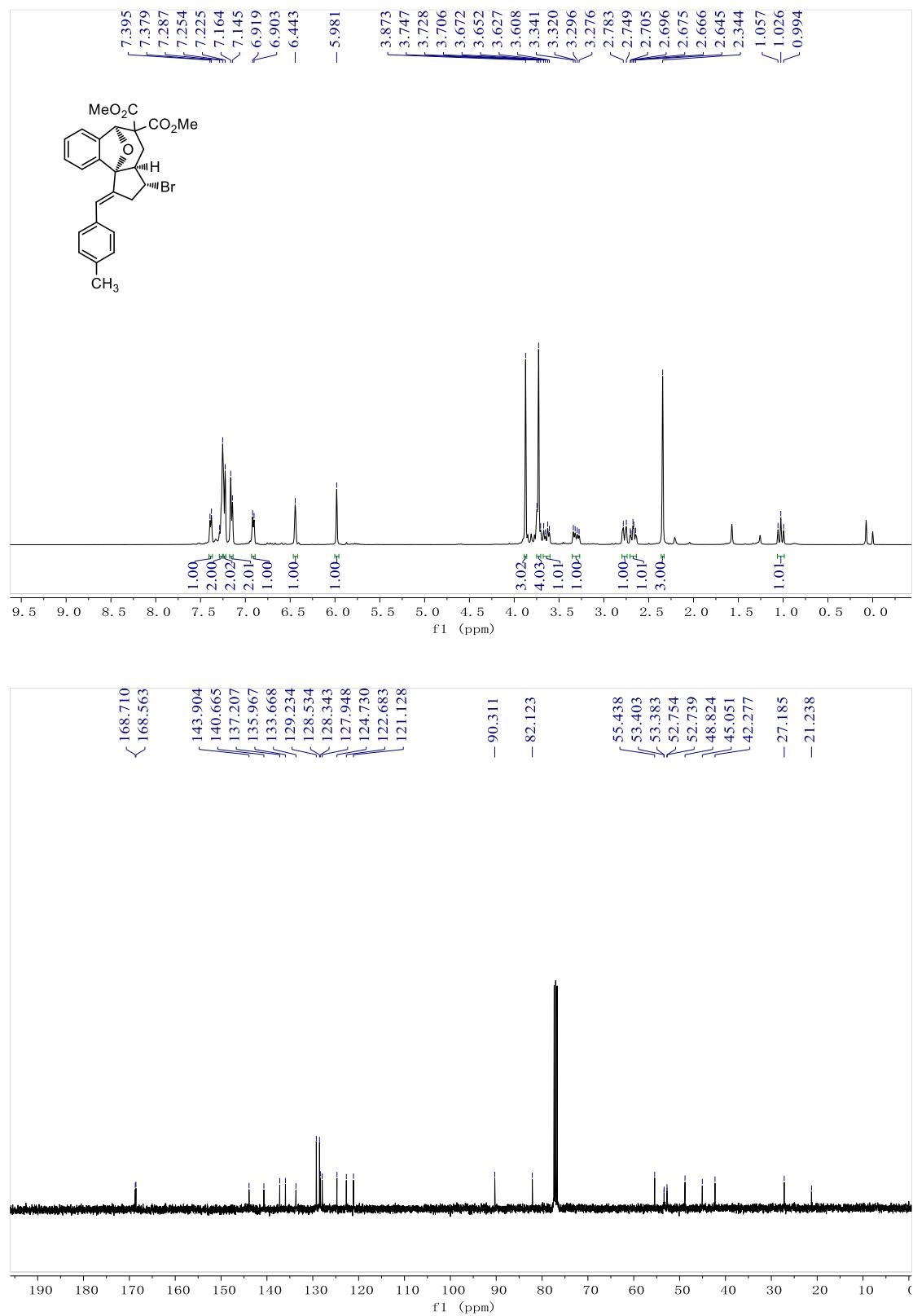
**9b**



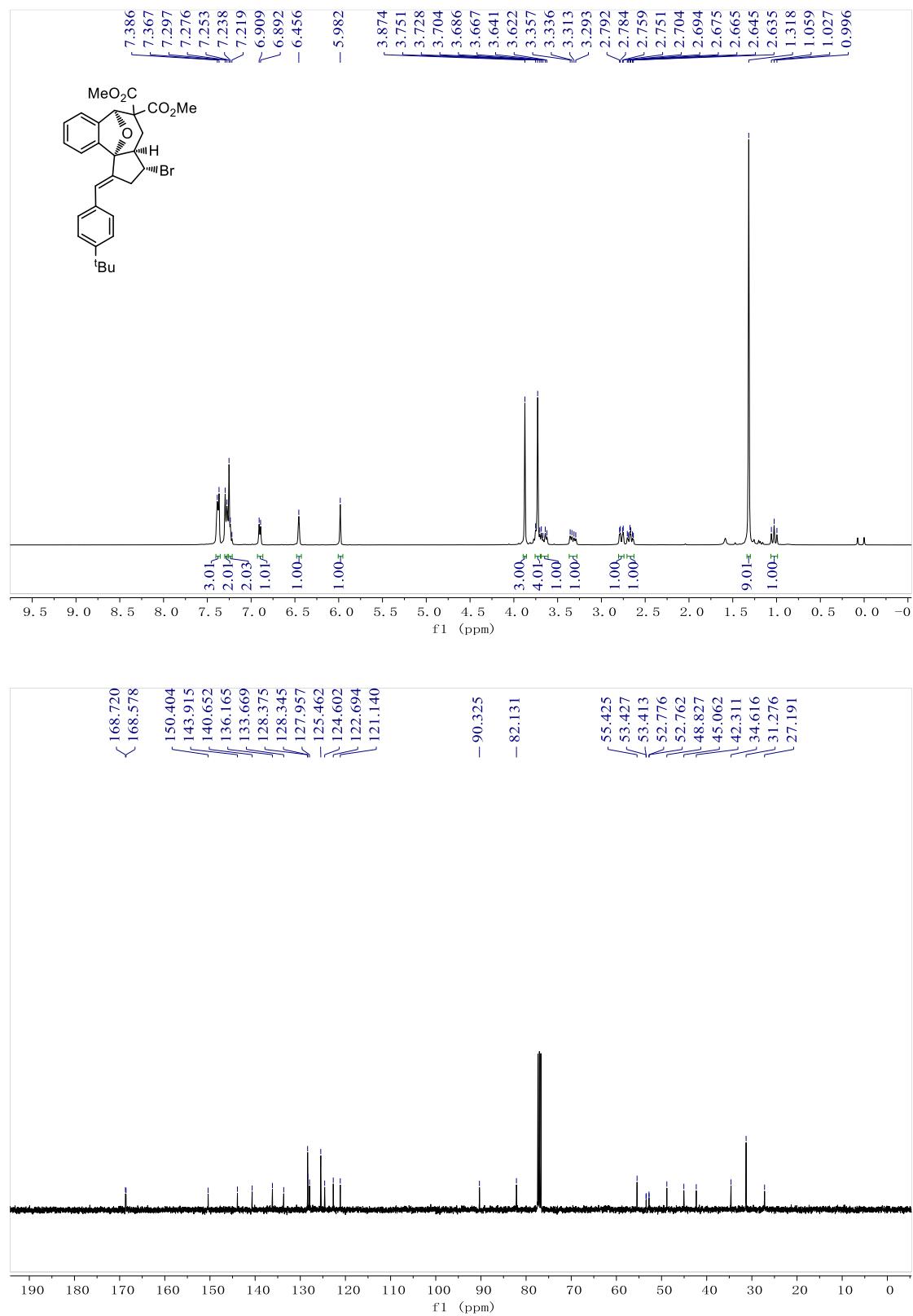
9c



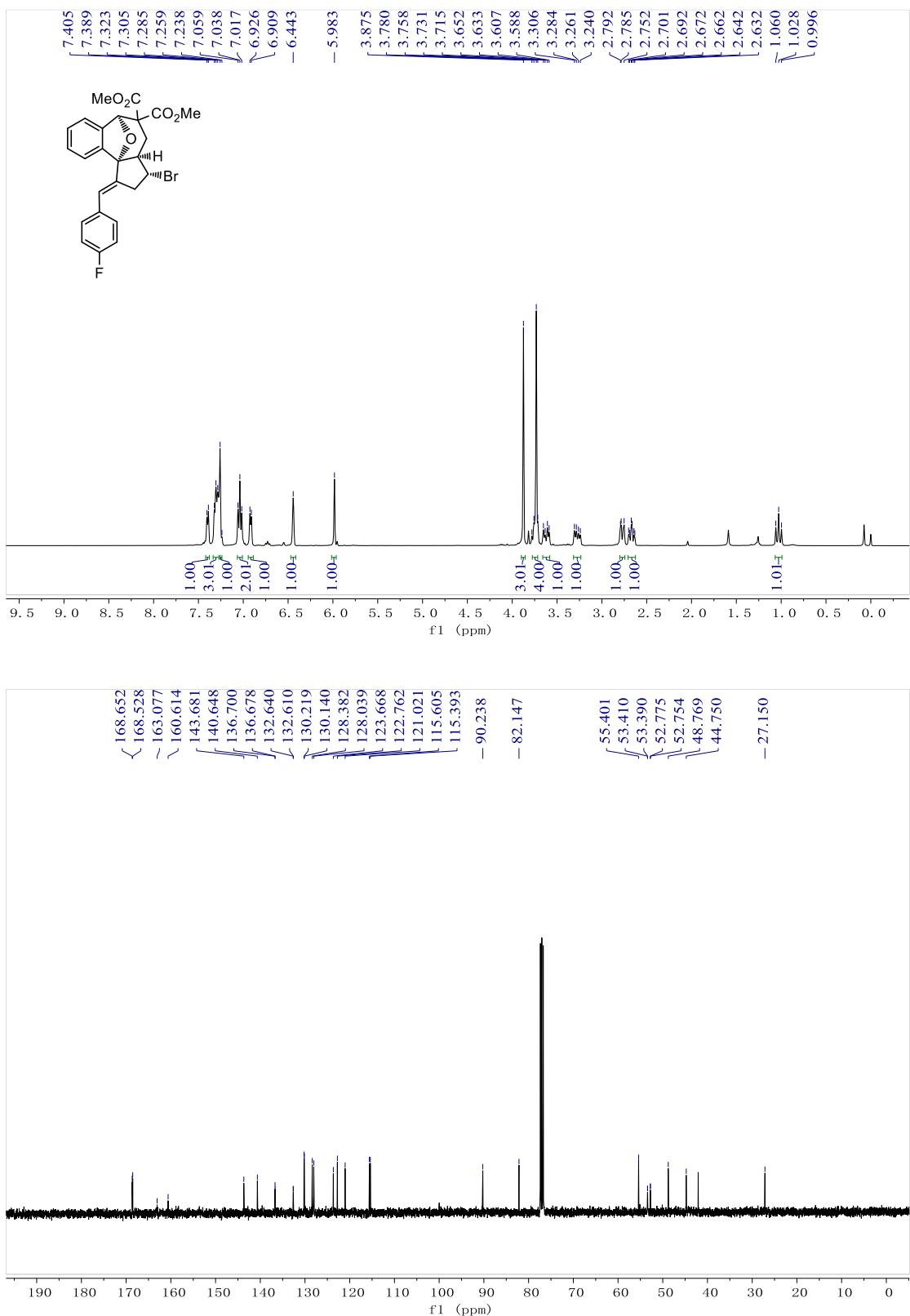
**9d**

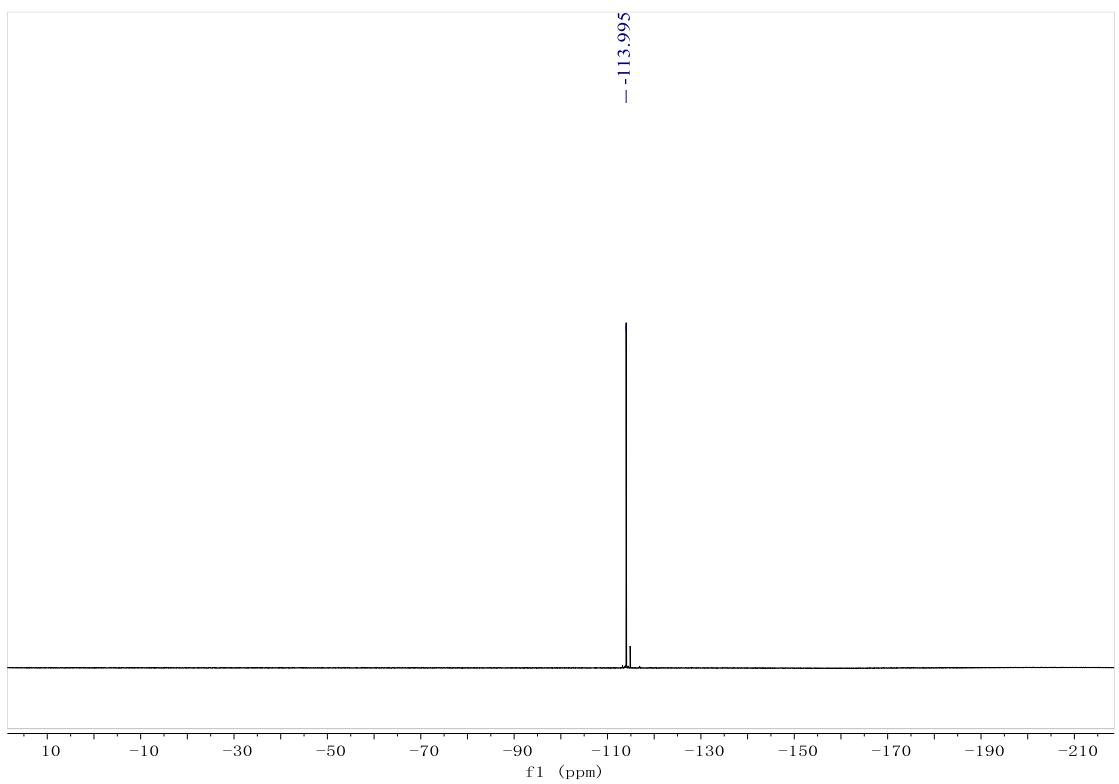


**9f**



**9g**





9h

