

Supporting Information for

**Catalytic Asymmetric Multiple Dearomatizations of Phenols
Enabled by a Cascade 1,8-Addition and Diels-Alder Reaction**

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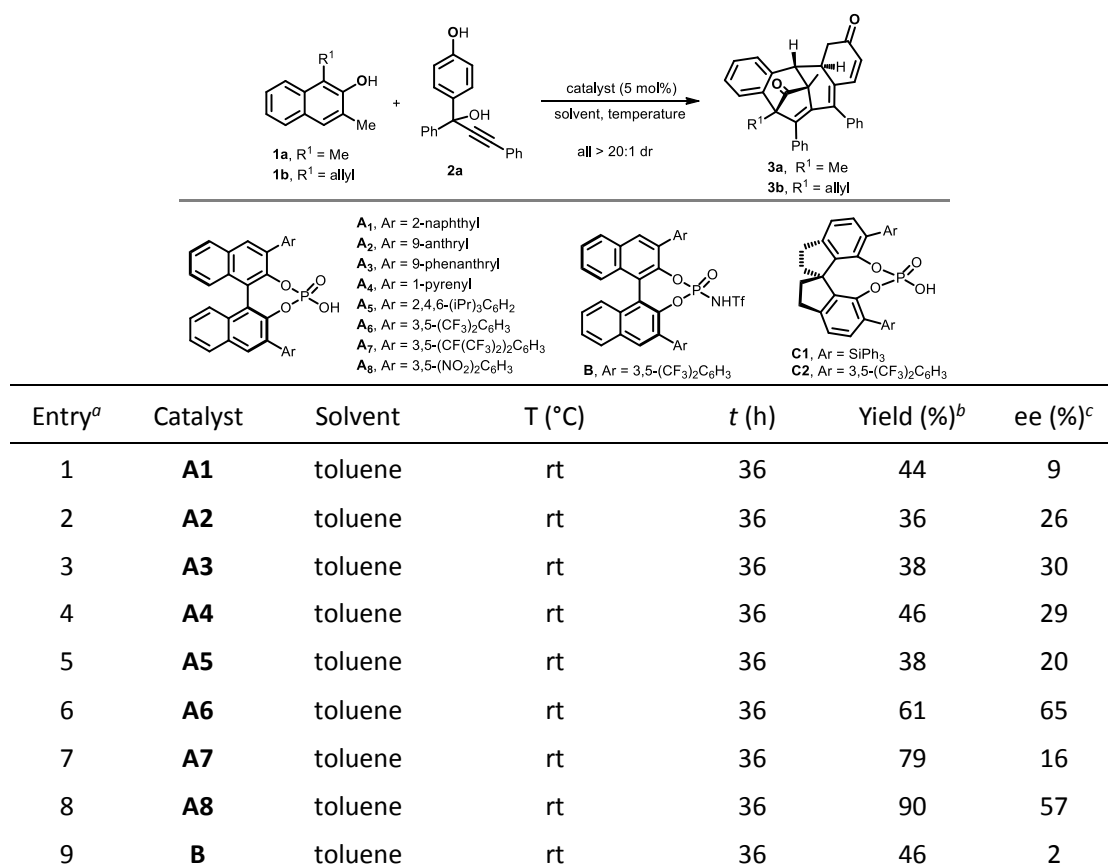
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(A) General information

Unless stated otherwise, all reactions were carried out in flame dried glassware. All solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. ^1H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^1H NMR are recorded as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet) and coupling constant in Hertz (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm). Optical rotations were reported as follows: $[\alpha]_{\text{D}}^{\text{T}}$ (c: g/100mL, in CHCl_3). The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel column on Waters with a 996 UV-detector. β -Naphthols^[1-3] and propargylic alcohols^[4] were synthesized according to the previous reported procedures.

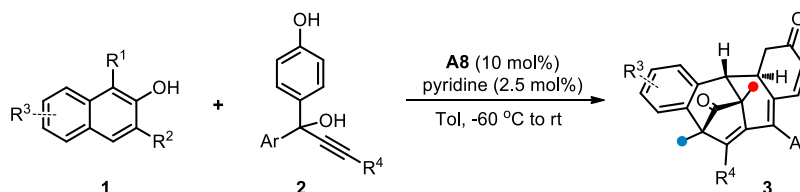
(B) Optimization of the reaction conditions



10	C1	toluene	rt	36	trace	n.d.
11	C2	toluene	rt	36	48	30
12	A8	benzene	rt	36	trace	n.d.
13	A8	CH ₂ Cl ₂	rt	36	81	34
14	A8	THF	rt	36	trace	n.d.
15	A8	Et ₂ O	rt	36	trace	n.d.
16	A8	EtOAc	rt	36	trace	n.d.
17	A8	CH ₃ CN	rt	36	trace	n.d.
18	A8	MeOH	rt	36	trace	n.d.
19 ^d	A8	toluene	-20 °C to rt	1, 24	91	60
20 ^d	A8	toluene	-40 °C to rt	1.5, 24	92	62
21 ^d	A8	toluene	-60 °C to rt	24, 24	92	65
22 ^{d,e}	A8	toluene	-60 °C to rt	48, 48	92	83
23 ^{d,e,f}	A8	toluene	-60 °C to rt	72, 72	80	98
24 ^{d,f,g}	A8	toluene	-60 °C to rt	72, 72	80	94
25 ^{d,f,h}	A8	toluene	rt	72	0	-

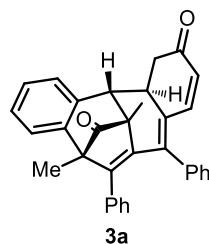
^aReaction conditions: β -naphthol **1a** (0.12 mmol, 1.2 equiv), propargylic alcohol **2a** (0.1 mmol, 1 equiv), catalyst (5 mol%) in 1.0 mL of solvent. ^bIsolated yield. ^cEnantiomeric excess was determined by chiral HPLC. ^dWith 10 mol% **A8**. ^e2.5 mol% pyridine was added. ^fConducted with **1b**. ^g2.0 mol% pyridine was added. ^h10 mol% pyridine was added.

(C) General procedure for the catalytic asymmetric multiple dearomatizations of phenols

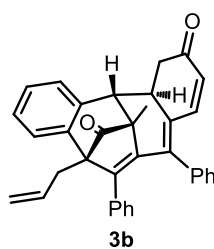


To a solution of catalyst **A8** (0.01 mmol, 10 mol%) and β -naphthol **1** (0.12 mmol, 1.2 equiv) in dry toluene (1.0 mL) was added pyridine (2.5 mol%), and the mixture was stirred at room temperature for 10 min. Then, the solution was cooled to -60 °C (-45 °C for **3f**, **3g**, **3l** and **3p**; -50 °C for **3i-3k**, **3ac** and **3ae**; -70 °C for **3w**) and stirred for another 10 min. Finally, propargylic alcohol **2** (0.1 mmol, 1.0 equiv) was added and the reaction mixture was stirred at this temperature until the complete consumption of starting material (monitored by TLC). After which the reaction mixture was warmed to room temperature and stirred for further 72 h. Upon completion, the residue was directly purified by silica gel chromatography (eluting with petroleum ether/ethyl acetate = 20:1 to 10:1) to afford the desired products **3**. (For the cases of **3c-3g**, 2.0 mol% pyridine was added)

(D) Characterization data of compounds 3

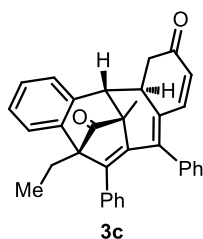


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 198 – 199 °C, 41.8 mg, 92% yield; 83% ee determined by HPLC on a Chiralpak IA-H column (hexane / *i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.3$ min, $t_{\text{minor}} = 7.8$ min); $[\alpha]_{\text{D}}^{23.2} = 907$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.38 – 6.94 (m, 9H), 6.93 – 6.70 (m, 4H), 6.34 (dd, $J = 5.1, 3.3$ Hz, 2H), 5.86 (d, $J = 10.1$ Hz, 1H), 3.58 – 3.35 (m, 1H), 3.30 (s, 1H), 3.07 – 2.89 (m, 2H), 1.61 (s, 3H), 1.34 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.67, 198.07, 150.42, 143.59, 141.68, 141.27, 141.12, 140.15, 137.52, 133.45, 132.92, 129.45, 129.19, 128.30, 128.06, 128.01, 127.62, 127.26, 127.09, 126.25, 124.31, 57.74, 53.97, 52.33, 46.86, 44.82, 15.26, 11.40 ppm; **HRMS** (ESI): $\text{C}_{33}\text{H}_{26}\text{NaO}_2$ [$\text{M} + \text{Na}$] $^+$ calcd: 477.1825, found: 477.1829.

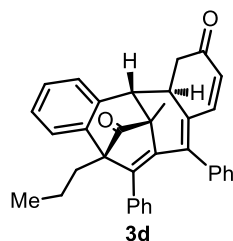


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 92 – 93 °C, 38.4 mg, 80% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.1$ min, $t_{\text{minor}} = 9.3$ min); $[\alpha]_{\text{D}}^{23.2} = 740$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 – 7.30 (m, 1H), 7.30 – 7.06 (m, 7H), 6.99 (t, $J = 7.4$ Hz, 1H), 6.90 – 6.70 (m, 4H), 6.38 – 6.23 (m, 2H), 5.84 (d, $J = 10.1$ Hz, 1H), 5.73 (ddt, $J = 17.0, 10.2, 6.8$ Hz, 1H), 4.97 (d, $J = 10.3$ Hz, 1H), 4.84 (dd, $J = 17.1, 1.5$ Hz, 1H), 3.40 (t, $J = 10.1$ Hz, 1H), 3.28 (s, 1H), 2.99 – 2.86 (m, 2H), 2.76 (dd, $J = 14.4, 6.3$ Hz, 1H), 2.59 (dd, $J = 14.4, 7.3$ Hz, 1H), 1.61 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz,

CDCl₃) δ 212.98, 198.09, 149.73, 143.65, 142.11, 141.76, 140.92, 140.33, 138.16, 133.72, 132.90, 132.81, 129.70, 129.17, 128.39, 128.14, 127.61, 127.16, 127.03, 126.28, 124.60, 118.57, 60.88, 54.27, 52.59, 46.85, 44.68, 29.91, 15.21 ppm; **HRMS** (ESI): C₃₅H₂₈NaO₂ [M + Na]⁺ calcd: 503.1982, found: 503.2001.

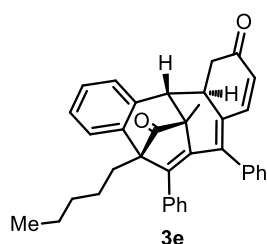


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 131 – 132 °C, 40.7 mg, 87% yield; 91% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.0 min, t_{minor} = 8.4 min); $[\alpha]_{\text{D}}^{23.2}$ = 874 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃) δ 7.39 – 7.28 (m, 1H), 7.28 – 7.05 (m, 7H), 6.99 (t, J = 7.4 Hz, 1H), 6.91 – 6.73 (m, 4H), 6.45 – 6.24 (m, 2H), 5.83 (d, J = 10.1 Hz, 1H), 3.40 (t, J = 10.1 Hz, 1H), 3.27 (s, 1H), 3.05 – 2.87 (m, 2H), 2.01 (dq, J = 14.4, 7.2 Hz, 1H), 1.82 (tt, J = 16.4, 8.2 Hz, 1H), 1.62 (s, 3H), 0.84 (t, J = 7.3 Hz, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 213.68, 198.21, 149.87, 143.75, 142.65, 141.93, 141.72, 140.39, 138.51, 134.04, 132.80, 129.63, 129.25, 128.25, 128.18, 127.68, 127.24, 126.32, 124.66, 62.43, 54.47, 52.86, 46.94, 44.71, 18.22, 15.33, 8.84 ppm; **HRMS** (ESI): C₃₄H₂₈NaO₂ [M + Na]⁺ calcd: 491.1982, found: 491.1983.

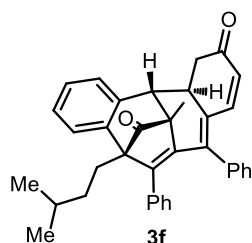


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 113 – 114 °C, 43.4 mg, 90% yield; 88% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.8 min, t_{minor} = 6.1 min); $[\alpha]_{\text{D}}^{23.2}$ = 696 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃) δ 7.37 – 7.29 (m, 1H), 7.29 – 7.10 (m, 7H), 6.99 (t, J = 7.4 Hz, 1H), 6.89 – 6.74 (m,

4H), 6.36 – 6.25 (m, 2H), 3.40 (t, $J = 10.1$ Hz, 1H), 3.26 (s, 1H), 2.93 (d, $J = 10.7$ Hz, 2H), 2.03 – 1.83 (m, 1H), 1.78 – 1.63 (m, 1H), 1.61 (s, 3H), 1.57 – 1.37 (m, 1H), 1.20 – 0.97 (m, 1H), 0.79 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.85, 198.13, 150.08, 143.68, 142.28, 141.87, 141.66, 140.27, 138.34, 133.91, 132.69, 129.57, 129.17, 128.15, 128.07, 127.59, 127.16, 127.09, 126.22, 124.62, 62.04, 54.43, 52.79, 46.86, 44.64, 27.65, 17.60, 15.24, 14.70 ppm; **HRMS** (ESI): $\text{C}_{35}\text{H}_{30}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 505.2138, found: 505.2141.

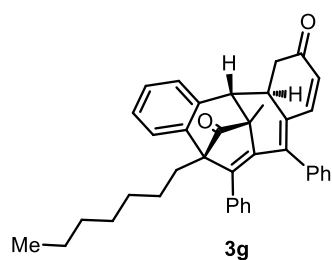


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 80 – 81 °C, 39.8 mg, 78% yield; 88% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.6$ min, $t_{\text{minor}} = 6.3$ min); $[\alpha]_{\text{D}}^{23.2} = 972$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.40 – 7.29 (m, 1H), 7.29 – 7.07 (m, 7H), 6.99 (t, $J = 7.4$ Hz, 1H), 6.93 – 6.73 (m, 4H), 6.30 (d, $J = 7.5$ Hz, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 3.40 (t, $J = 10.1$ Hz, 1H), 3.26 (s, 1H), 2.94 (d, $J = 10.1$ Hz, 2H), 1.94 (dd, $J = 16.8, 8.5$ Hz, 1H), 1.72 (t, $J = 11.4$ Hz, 1H), 1.61 (s, 3H), 1.55 – 1.38 (m, 1H), 1.22 – 0.92 (m, 5H), 0.75 (t, $J = 6.8$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.89, 198.19, 150.19, 143.75, 142.30, 141.97, 141.83, 140.37, 138.45, 134.00, 132.80, 129.63, 129.25, 128.22, 128.18, 127.65, 127.21, 127.16, 126.30, 124.72, 62.08, 54.52, 52.86, 46.95, 44.74, 32.37, 25.40, 23.73, 22.20, 15.32, 13.93 ppm; **HRMS** (ESI): $\text{C}_{37}\text{H}_{34}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 533.2451, found: 533.2464.

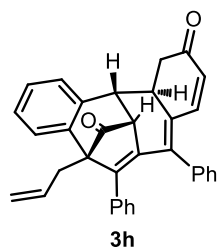


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 51 – 52 °C, 46.3

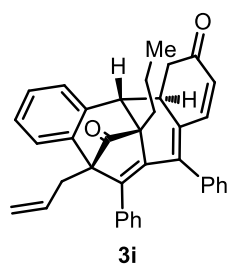
mg, 91% yield; 74% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.4$ min, $t_{\text{minor}} = 5.5$ min); $[\alpha]_{\text{D}}^{23.2} = 522$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 – 7.29 (m, 1H), 7.29 – 7.08 (m, 7H), 6.98 (dd, $J = 10.6, 4.3$ Hz, 1H), 6.82 (dd, $J = 11.0, 4.7$ Hz, 4H), 6.42 – 6.25 (m, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 3.40 (t, $J = 10.1$ Hz, 1H), 3.27 (s, 1H), 2.94 (d, $J = 10.6$ Hz, 2H), 1.96 (ddd, $J = 17.3, 11.2, 3.1$ Hz, 1H), 1.84 – 1.66 (m, 1H), 1.61 (s, 3H), 1.52 – 1.25 (m, 2H), 0.94 – 0.81 (m, 1H), 0.79 (d, $J = 6.4$ Hz, 3H), 0.61 (d, $J = 6.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.80, 198.16, 150.10, 143.72, 142.17, 141.91, 141.83, 140.30, 138.44, 133.85, 132.72, 129.56, 129.19, 128.18, 127.59, 127.09, 126.21, 124.65, 61.90, 54.42, 52.77, 46.87, 44.65, 32.75, 28.49, 23.18, 22.41, 22.00, 15.25 ppm; **HRMS** (ESI): $\text{C}_{37}\text{H}_{34}\text{NaO}_2$ $[\text{M} + \text{H}]^+$ calcd: 511.2632, found: 511.2628.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 96 – 97 °C, 42.0 mg, 78% yield; 74% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.3$ min, $t_{\text{minor}} = 6.8$ min); $[\alpha]_{\text{D}}^{23.2} = 666$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.41 – 7.28 (m, 1H), 7.28 – 7.10 (m, 7H), 6.99 (t, $J = 7.4$ Hz, 1H), 6.92 – 6.78 (m, 4H), 6.30 (d, $J = 7.4$ Hz, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 3.39 (t, $J = 10.1$ Hz, 1H), 3.26 (s, 1H), 2.93 (d, $J = 10.1$ Hz, 2H), 2.00 – 1.84 (m, 1H), 1.84 – 1.65 (m, 1H), 1.61 (s, 3H), 1.55 – 1.37 (m, 1H), 1.37 – 0.92 (m, 9H), 0.81 (t, $J = 6.9$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.84, 198.13, 150.19, 143.70, 142.29, 141.95, 141.85, 140.38, 138.47, 134.01, 132.82, 129.62, 129.25, 128.22, 128.19, 127.64, 127.21, 127.16, 126.30, 124.72, 62.08, 54.54, 52.86, 46.95, 44.76, 31.62, 30.10, 28.80, 25.42, 24.02, 22.56, 15.32, 14.05 ppm; **HRMS** (ESI): $\text{C}_{39}\text{H}_{38}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 561.22764, found: 561.22763.

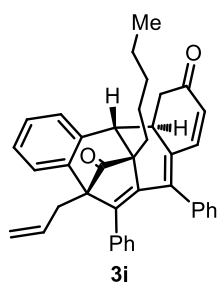


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 194 – 195 °C, 33.6 mg, 72% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.7 min, t_{minor} = 6.8 min); $[\alpha]_{\text{D}}^{23.2}$ = 1041 (c = 1.0 in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.42 – 7.31 (m, 1H), 7.24 (dd, J = 16.1, 8.3 Hz, 3H), 7.17 – 7.03 (m, 4H), 6.97 (t, J = 7.3 Hz, 1H), 6.91 – 6.76 (m, 4H), 6.31 (d, J = 7.4 Hz, 2H), 5.84 (d, J = 10.1 Hz, 1H), 5.82 – 5.69 (m, 1H), 5.01 (d, J = 10.2 Hz, 1H), 4.87 (d, J = 17.1 Hz, 1H), 3.63 – 3.50 (m, 2H), 3.50 – 3.36 (m, 1H), 2.94 – 2.82 (m, 2H), 2.75 (dd, J = 14.4, 6.0 Hz, 1H), 2.59 (dd, J = 14.3, 7.0 Hz, 1H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 211.91, 198.27, 151.67, 144.61, 143.06, 141.73, 138.47, 137.65, 137.12, 133.56, 133.29, 132.99, 130.21, 129.30, 128.54, 128.43, 128.13, 127.69, 127.34, 127.27, 127.06, 126.75, 124.86, 118.67, 62.16, 52.51, 48.21, 45.84, 44.75, 29.86 ppm; **HRMS** (ESI): $\text{C}_{34}\text{H}_{26}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 489.1825, found: 489.1819.

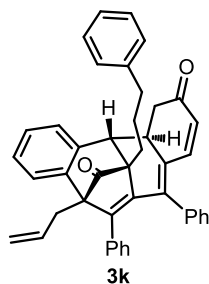


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 63 – 64 °C, 14.4 mg, 28% yield; 95% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.6 min, t_{minor} = 8.1 min); $[\alpha]_{\text{D}}^{23.2}$ = 992 (c = 1.0 in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.33 (t, J = 7.3 Hz, 1H), 7.28 – 7.02 (m, 7H), 6.98 (t, J = 7.4 Hz, 1H), 6.81 (dd, J = 18.0, 7.5 Hz, 4H), 6.31 (d, J = 7.4 Hz, 2H), 5.83 (d, J = 10.1 Hz, 1H), 5.73 (td, J = 17.0, 6.9 Hz, 1H), 5.02 (d, J = 10.1 Hz, 1H), 4.90 (d, J = 17.1 Hz, 1H), 3.41 (dd, J = 12.1, 8.2 Hz, 1H), 3.29 (s, 1H), 3.03 – 2.87 (m,

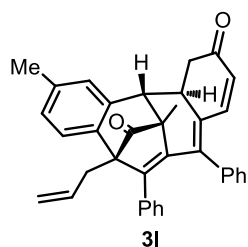
2H), 2.77 (dd, $J = 14.3, 6.0$ Hz, 1H), 2.54 (dd, $J = 14.4, 7.5$ Hz, 1H), 2.15 – 1.90 (m, 2H), 1.57 (dd, $J = 15.7, 7.7$ Hz, 2H), 1.06 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.61, 198.21, 151.31, 144.01, 141.73, 141.60, 140.90, 140.40, 137.82, 133.97, 133.23, 132.97, 129.86, 129.61, 128.62, 128.39, 128.08, 127.65, 127.15, 127.06, 126.27, 124.56, 118.64, 61.73, 57.27, 53.74, 47.02, 45.13, 31.06, 29.81, 18.37, 14.91 ppm; **HRMS** (ESI): $\text{C}_{37}\text{H}_{32}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 531.2295, found: 531.2293.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 92 – 93 °C, 17.6 mg, 33% yield; 85% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.5$ min, $t_{\text{minor}} = 8.7$ min); $[\alpha]_{\text{D}}^{23.2} = 764$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.32 (t, $J = 7.3$ Hz, 1H), 7.28 – 7.02 (m, 7H), 6.98 (t, $J = 7.3$ Hz, 1H), 6.81 (dd, $J = 17.1, 7.6$ Hz, 4H), 6.32 (d, $J = 7.5$ Hz, 2H), 5.83 (d, $J = 10.2$ Hz, 1H), 5.72 (dt, $J = 16.8, 8.2$ Hz, 1H), 5.03 (d, $J = 10.1$ Hz, 1H), 4.91 (d, $J = 17.2$ Hz, 1H), 3.51 – 3.33 (m, 1H), 3.29 (s, 1H), 3.02 – 2.87 (m, 2H), 2.77 (dd, $J = 14.7, 5.8$ Hz, 1H), 2.54 (dd, $J = 14.5, 7.2$ Hz, 1H), 2.20 – 1.89 (m, 2H), 1.58 – 1.33 (m, 6H), 0.95 (t, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.55, 198.21, 151.30, 143.99, 141.73, 141.57, 140.92, 140.43, 137.81, 133.97, 133.26, 132.99, 129.84, 129.61, 128.63, 128.37, 128.07, 127.64, 127.13, 127.06, 126.26, 124.58, 118.61, 61.69, 57.22, 53.73, 47.04, 45.14, 32.57, 29.82, 28.77, 24.59, 22.60, 14.13 ppm; **HRMS** (ESI): $\text{C}_{39}\text{H}_{36}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 559.2608, found: 559.2600.

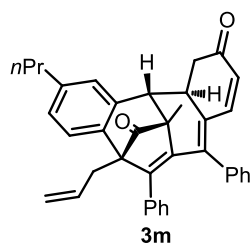


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 77 – 78 °C, 20.0 mg, 34% yield; 94% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.2$ min, $t_{\text{minor}} = 10.0$ min); $[\alpha]_{\text{D}}^{23.2} = 859$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.38 – 7.01 (m, 13H), 6.97 (t, $J = 7.4$ Hz, 1H), 6.82 (t, $J = 7.6$ Hz, 2H), 6.73 (d, $J = 7.2$ Hz, 2H), 6.29 (d, $J = 7.4$ Hz, 2H), 5.81 (d, $J = 10.2$ Hz, 1H), 5.70 (dt, $J = 16.9, 8.6$ Hz, 1H), 5.01 (d, $J = 10.1$ Hz, 1H), 4.89 (d, $J = 17.1$ Hz, 1H), 3.38 (dd, $J = 13.2, 6.8$ Hz, 1H), 3.27 (s, 1H), 2.92 – 2.63 (m, 5H), 2.53 (dd, $J = 14.5, 7.3$ Hz, 1H), 2.21 – 2.02 (m, 2H), 2.02 – 1.75 (m, 2H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 213.40, 198.14, 151.47, 143.92, 141.93, 141.56, 141.39, 140.70, 140.32, 137.67, 133.88, 133.31, 132.94, 129.82, 129.61, 128.61, 128.56, 128.41, 128.07, 127.66, 127.20, 127.08, 126.21, 125.94, 124.63, 118.73, 61.61, 57.03, 53.68, 46.94, 45.09, 36.53, 29.85, 28.46, 26.60 ppm; **HRMS** (ESI): $\text{C}_{43}\text{H}_{36}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 607.2608, found: 607.2594.

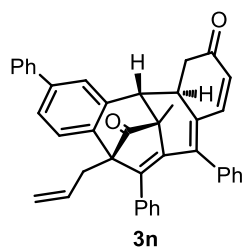


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 97 – 98 °C, 39.0 mg, 79% yield; 97% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.3$ min, $t_{\text{minor}} = 9.1$ min); $[\alpha]_{\text{D}}^{23.2} = 978$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.24 (d, $J = 8.9$ Hz, 1H), 7.20 – 7.07 (m, 3H), 7.09 – 6.94 (m, 4H), 6.90 – 6.75 (m, 4H), 6.32 (d, $J = 7.3$ Hz, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 5.72 (td, $J = 17.0, 6.9$ Hz, 1H), 4.96 (d, $J = 10.1$ Hz, 1H), 4.82 (d, $J = 17.1$ Hz, 1H), 3.49 – 3.30 (m, 1H), 3.23 (s, 1H), 3.08 – 2.85 (m, 2H), 2.74 (dd, $J =$

14.3, 6.2 Hz, 1H), 2.56 (dd, $J = 14.4, 7.3$ Hz, 1H), 2.35 (s, 3H), 1.60 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.06, 198.31, 149.94, 143.77, 142.05, 141.96, 140.21, 138.33, 138.22, 137.93, 133.91, 133.11, 132.86, 130.34, 129.25, 128.48, 128.19, 127.94, 127.64, 127.17, 127.06, 126.28, 124.54, 118.46, 60.69, 54.32, 52.58, 47.00, 44.71, 30.00, 21.13, 15.30 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{30}\text{NaO}_2$ [$\text{M} + \text{Na}$] $^+$ calcd: 517.2138, found: 517.2130.

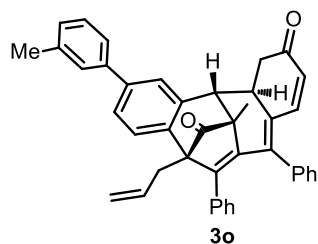


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 80 – 81 °C, 38.6 mg, 74% yield; 95% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.0$ min, $t_{\text{minor}} = 8.6$ min); $[\alpha]_{\text{D}}^{23.2} = 894$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.24 (dd, $J = 12.0, 5.0$ Hz, 1H), 7.21 – 7.08 (m, 3H), 7.07 – 6.91 (m, 4H), 6.82 (t, $J = 8.2$ Hz, 4H), 6.31 (d, $J = 7.4$ Hz, 2H), 5.84 (d, $J = 10.1$ Hz, 1H), 5.72 (dq, $J = 10.1, 6.8$ Hz, 1H), 4.96 (d, $J = 10.1$ Hz, 1H), 4.82 (d, $J = 17.2$ Hz, 1H), 3.39 (dd, $J = 11.9, 8.2$ Hz, 1H), 3.24 (s, 1H), 3.04 – 2.85 (m, 2H), 2.75 (dd, $J = 14.4, 6.1$ Hz, 1H), 2.67 – 2.45 (m, 3H), 1.66 (dd, $J = 15.4, 7.9$ Hz, 2H), 1.60 (s, 3H), 0.96 (t, $J = 7.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.08, 198.32, 149.90, 143.80, 143.11, 142.04, 141.98, 140.17, 138.37, 138.11, 133.94, 133.11, 132.87, 129.72, 129.26, 128.47, 128.19, 127.64, 127.30, 127.17, 127.06, 126.28, 124.49, 118.45, 60.73, 54.40, 52.61, 47.03, 44.74, 37.66, 30.01, 24.63, 15.31, 13.88 ppm; **HRMS** (ESI): $\text{C}_{38}\text{H}_{34}\text{NaO}_2$ [$\text{M} + \text{Na}$] $^+$ calcd: 545.2451, found: 545.2446.

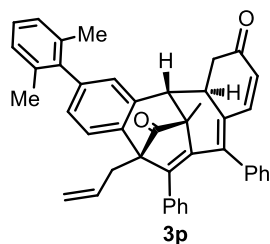


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash

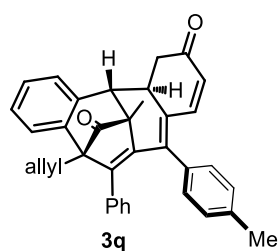
chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 114 – 115 °C, 39.8 mg, 72% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.0 min, t_{minor} = 20.1 min); $[\alpha]_{\text{D}}^{23.2}$ = 927 (c = 1.0 in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.58 (d, J = 7.3 Hz, 2H), 7.52 – 7.32 (m, 5H), 7.32 – 7.05 (m, 5H), 7.00 (t, J = 7.1 Hz, 1H), 6.83 (dd, J = 14.4, 7.0 Hz, 4H), 6.36 (d, J = 7.3 Hz, 2H), 5.84 (d, J = 10.1 Hz, 1H), 5.74 (dt, J = 16.3, 8.2 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.86 (d, J = 17.1 Hz, 1H), 3.49 (dd, J = 12.6, 7.2 Hz, 1H), 3.34 (s, 1H), 3.13 – 2.91 (m, 2H), 2.80 (dd, J = 14.1, 5.9 Hz, 1H), 2.63 (dd, J = 14.2, 7.3 Hz, 1H), 1.63 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.81, 198.06, 149.81, 143.74, 142.24, 141.90, 141.40, 140.83, 140.00, 139.90, 138.24, 133.82, 132.97, 132.90, 129.26, 128.98, 128.51, 128.36, 128.23, 127.81, 127.70, 127.30, 127.15, 127.02, 126.42, 125.91, 125.17, 118.66, 60.86, 54.51, 52.66, 46.99, 44.80, 30.06, 15.33 ppm; **HRMS** (ESI): $\text{C}_{41}\text{H}_{32}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 579.2295, found: 579.2282.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 117 – 118 °C, 44.4 mg, 78% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.7 min, t_{minor} = 19.4 min); $[\alpha]_{\text{D}}^{23.2}$ = 931 (c = 1.0 in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.53 – 7.30 (m, 5H), 7.30 – 7.06 (m, 6H), 6.99 (d, J = 7.0 Hz, 1H), 6.93 – 6.75 (m, 4H), 6.36 (d, J = 7.1 Hz, 2H), 5.84 (d, J = 10.1 Hz, 1H), 5.81 – 5.61 (m, 1H), 4.99 (d, J = 9.9 Hz, 1H), 4.85 (d, J = 16.9 Hz, 1H), 3.49 (dd, J = 12.8, 6.8 Hz, 1H), 3.34 (s, 1H), 2.98 (d, J = 13.8 Hz, 2H), 2.79 (dd, J = 14.2, 6.0 Hz, 1H), 2.62 (dd, J = 14.0, 7.1 Hz, 1H), 2.45 (s, 3H), 1.63 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.86, 198.13, 149.86, 143.82, 142.22, 141.92, 141.62, 140.73, 139.89, 138.62, 138.25, 133.83, 133.00, 132.88, 129.26, 128.90, 128.52, 128.38, 128.23, 127.76, 127.69, 127.28, 127.14, 126.41, 126.02, 125.10, 124.20, 118.65, 60.88, 54.51, 52.65, 46.97, 44.76, 30.06, 21.61, 15.34 ppm; **HRMS** (ESI): $\text{C}_{42}\text{H}_{34}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 593.2451, found: 593.2443.

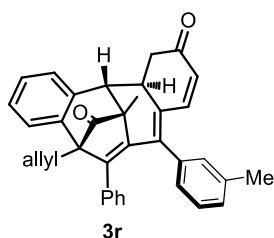


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 121 – 122 °C, 33.4 mg, 57% yield; 88% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 3.9$ min, $t_{\text{minor}} = 4.5$ min); $[\alpha]_{\text{D}}^{23.2} = 791$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.27 (d, $J = 11.2$ Hz, 1H), 7.24 – 7.07 (m, 7H), 7.02 (s, 3H), 6.95 – 6.79 (m, 4H), 6.34 (d, $J = 7.4$ Hz, 2H), 5.82 (d, $J = 10.1$ Hz, 1H), 5.80 – 5.69 (m, 1H), 5.02 (d, $J = 10.1$ Hz, 1H), 4.90 (d, $J = 17.1$ Hz, 1H), 3.43 – 3.23 (m, 2H), 3.02 – 2.73 (m, 3H), 2.62 (dd, $J = 14.4, 7.3$ Hz, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 1.63 (s, 3H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 213.15, 197.80, 149.67, 143.52, 142.45, 141.76, 141.46, 140.70, 139.26, 138.14, 135.90, 135.64, 133.97, 133.05, 132.89, 130.23, 129.28, 128.44, 128.19, 127.94, 127.71, 127.57, 127.43, 127.31, 127.22, 126.42, 124.79, 118.64, 60.92, 54.57, 52.87, 46.88, 45.11, 30.00, 21.06, 20.93, 15.22 ppm; **HRMS** (ESI): $\text{C}_{43}\text{H}_{36}\text{NaO}_2$ [$\text{M} + \text{Na}$] $^+$ calcd: 607.2608, found: 607.2593.

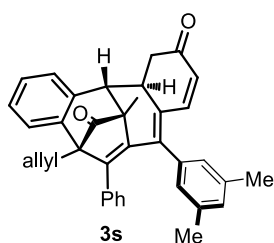


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 94 – 95 °C, 36.0 mg, 73% yield; 89% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.9$ min, $t_{\text{minor}} = 7.8$ min); $[\alpha]_{\text{D}}^{23.2} = 785$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.39 – 7.18 (m, 4H), 7.14 (d, $J = 7.5$ Hz, 1H), 6.98 (dd, $J = 16.8, 7.7$ Hz, 3H), 6.83 (t, $J = 7.5$ Hz, 2H), 6.68 (d, $J = 7.7$ Hz, 2H), 6.32 (d, $J = 7.4$ Hz, 2H), 5.82 (d, $J = 10.1$ Hz, 1H), 5.71 (dt, $J = 16.8, 8.3$ Hz, 1H), 4.97 (d, $J = 10.0$ Hz, 1H), 4.84 (d, $J = 17.1$ Hz, 1H), 3.38 (t, $J = 10.0$ Hz, 1H), 3.26 (s, 1H), 2.93 (d, $J = 9.9$ Hz, 2H), 2.77 (dd, $J = 14.5, 6.0$ Hz, 1H), 2.59 (dd, $J = 14.4, 7.2$ Hz, 1H), 2.30 (s,

3H), 1.60 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.11, 198.23, 149.56, 143.92, 142.35, 142.03, 141.01, 140.48, 137.59, 135.29, 133.89, 133.03, 132.69, 129.73, 129.16, 128.86, 128.50, 128.39, 127.20, 127.05, 126.08, 124.65, 118.57, 60.93, 54.44, 52.72, 46.96, 44.78, 29.98, 29.72, 21.20, 15.27 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{30}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 517.2138, found: 517.2143.

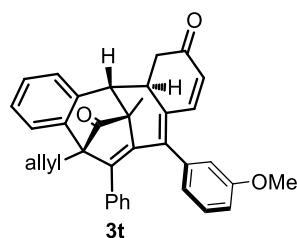


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 193 – 194 °C, 40.5 mg, 82% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.6 min, t_{minor} = 7.3 min); $[\alpha]_{\text{D}}^{23.2}$ = 1034 (c = 1.0 in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.33 (t, J = 7.1 Hz, 1H), 7.28 – 7.10 (m, 4H), 7.10 – 6.95 (m, 3H), 6.84 (t, J = 7.6 Hz, 2H), 6.62 (d, J = 7.2 Hz, 1H), 6.47 (s, 1H), 6.30 (d, J = 7.3 Hz, 2H), 5.82 (d, J = 10.1 Hz, 1H), 5.79 – 5.62 (m, 1H), 4.97 (d, J = 10.0 Hz, 1H), 4.84 (d, J = 17.1 Hz, 1H), 3.39 (t, J = 10.1 Hz, 1H), 3.27 (s, 1H), 2.94 (d, J = 10.2 Hz, 2H), 2.76 (dd, J = 14.3, 6.2 Hz, 1H), 2.60 (dd, J = 14.4, 7.3 Hz, 1H), 2.16 (s, 3H), 1.61 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.06, 198.22, 149.62, 143.97, 142.19, 142.07, 141.06, 140.44, 138.13, 137.80, 133.91, 133.03, 132.75, 129.76, 128.55, 128.39, 128.33, 128.12, 127.17, 127.02, 126.25, 126.17, 124.67, 118.59, 60.94, 54.28, 52.63, 46.92, 44.81, 30.02, 21.22, 15.32 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{30}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 517.2138, found: 517.2144.

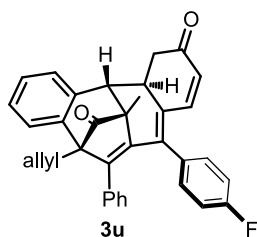


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 102 – 103 °C, 37.6 mg, 74% yield; 97% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.4 min, t_{minor} = 6.4 min); $[\alpha]_{\text{D}}^{23.2}$ = 848 (c = 1.0 in CHCl_3); $^1\text{H NMR}$

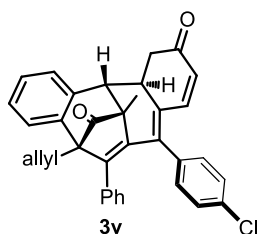
(300 MHz, CDCl₃) δ 7.40 – 7.29 (m, 1H), 7.29 – 7.12 (m, 4H), 7.02 (t, J = 7.5 Hz, 1H), 6.84 (dd, J = 15.3, 7.8 Hz, 3H), 6.35 – 6.27 (m, 4H), 5.81 (d, J = 10.1 Hz, 1H), 5.78 – 5.62 (m, 1H), 4.97 (dd, J = 10.3, 1.7 Hz, 1H), 4.85 (dd, J = 17.1, 1.7 Hz, 1H), 3.37 (t, J = 10.1 Hz, 1H), 3.26 (s, 1H), 2.93 (d, J = 10.6 Hz, 2H), 2.76 (dd, J = 14.4, 6.4 Hz, 1H), 2.61 (dd, J = 14.4, 7.2 Hz, 1H), 2.14 (s, 6H), 1.61 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 213.06, 198.27, 149.34, 144.17, 142.21, 142.08, 141.04, 140.38, 137.97, 137.62, 133.90, 132.99, 132.53, 129.73, 129.06, 128.54, 128.30, 127.12, 127.05, 126.87, 126.73, 125.92, 124.58, 118.50, 60.82, 54.13, 52.54, 46.84, 44.74, 29.98, 21.06, 15.30 ppm; HRMS (ESI): C₃₇H₃₂NaO₂ [M + Na]⁺ calcd: 531.2295, found: 531.2298.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 93 – 94 °C, 40.0 mg, 78% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.3 min, t_{minor} = 10.9 min); $[\alpha]_{\text{D}}^{23.2}$ = 908 (c = 1.0 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.29 (m, 1H), 7.25 (d, J = 10.3 Hz, 3H), 7.19 – 6.98 (m, 3H), 6.87 (t, J = 7.6 Hz, 2H), 6.74 (d, J = 8.2 Hz, 1H), 6.44 (d, J = 7.5 Hz, 1H), 6.34 (d, J = 7.4 Hz, 2H), 6.21 (s, 1H), 5.83 (d, J = 10.1 Hz, 1H), 5.72 (td, J = 16.9, 6.8 Hz, 1H), 4.97 (d, J = 10.2 Hz, 1H), 4.84 (d, J = 17.2 Hz, 1H), 3.60 (s, 3H), 3.39 (t, J = 10.1 Hz, 1H), 3.27 (s, 1H), 2.94 (d, J = 10.2 Hz, 2H), 2.77 (dd, J = 14.4, 6.1 Hz, 1H), 2.60 (dd, J = 14.4, 7.2 Hz, 1H), 1.60 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 212.94, 198.14, 159.29, 149.68, 143.73, 141.95, 141.58, 141.04, 140.39, 139.54, 133.96, 132.95, 129.79, 129.34, 128.52, 128.41, 127.27, 127.23, 127.12, 126.37, 124.66, 121.68, 118.62, 114.39, 113.55, 60.95, 55.18, 54.28, 52.62, 46.90, 44.78, 29.98, 15.29 ppm; HRMS (ESI): C₃₆H₃₀NaO₃ [M + Na]⁺ calcd: 533.2087, found: 533.2093.

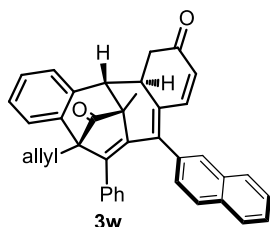


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 95 – 96 °C, 37.7 mg, 76% yield; 97% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.2$ min, $t_{\text{minor}} = 8.2$ min); $[\alpha]_{\text{D}}^{23.2} = 968$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.42 – 7.29 (m, 1H), 7.29 – 7.08 (m, 4H), 7.02 (t, $J = 7.2$ Hz, 1H), 6.95 – 6.63 (m, 6H), 6.30 (d, $J = 7.4$ Hz, 2H), 5.85 (d, $J = 10.1$ Hz, 1H), 5.73 (dt, $J = 16.8, 8.5$ Hz, 1H), 5.00 (d, $J = 10.2$ Hz, 1H), 4.86 (d, $J = 17.0$ Hz, 1H), 3.40 (t, $J = 10.1$ Hz, 1H), 3.28 (s, 1H), 2.94 (d, $J = 9.9$ Hz, 2H), 2.76 (dd, $J = 14.3, 5.8$ Hz, 1H), 2.58 (dd, $J = 14.3, 7.2$ Hz, 1H), 1.60 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.91, 198.01, 162.23 ($J_{\text{C-F}} = 246.0$ Hz), 150.23, 143.25, 142.12, 140.91, 140.60, 140.29, 134.05 ($J_{\text{C-F}} = 3.8$ Hz), 133.74, 133.24, 132.95, 131.03, 130.92, 129.78, 128.44, 127.41, 127.27, 127.20, 126.60, 124.72, 118.71, 115.38, 115.09, 61.07, 54.27, 52.57, 46.85, 44.82, 29.98, 15.22 ppm; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -113.68 ppm; **HRMS** (ESI): $\text{C}_{35}\text{H}_{27}\text{FNaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 521.1887, found: 521.1893.

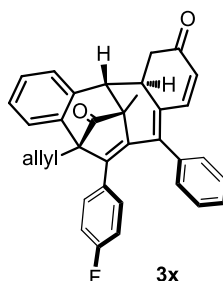


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 103 – 104 °C, 34.4 mg, 67% yield; 96% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.4$ min, $t_{\text{minor}} = 8.3$ min); $[\alpha]_{\text{D}}^{23.2} = 893$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.34 (t, $J = 7.2$ Hz, 1H), 7.29 – 6.98 (m, 7H), 6.88 (t, $J = 7.6$ Hz, 2H), 6.71 (d, $J = 8.3$ Hz, 2H), 6.30 (d, $J = 7.4$ Hz, 2H), 5.85 (d, $J = 10.1$ Hz, 1H), 5.74 (td, $J = 16.9, 7.0$ Hz, 1H), 4.99 (d, $J = 10.2$ Hz, 1H), 4.85 (d, $J = 17.1$ Hz, 1H), 3.48 – 3.32 (m, 1H), 3.28 (s, 1H), 2.94 (d, $J = 9.6$ Hz, 2H), 2.76 (dd, $J = 14.4, 6.1$ Hz, 1H), 2.58 (dd, $J = 14.4, 7.3$ Hz, 1H), 1.60 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.81, 197.92, 150.35, 143.05, 141.95, 140.87, 140.35, 140.24, 136.51, 133.72, 133.69,

133.40, 132.92, 130.56, 129.78, 128.46, 128.41, 127.48, 127.29, 127.23, 126.77, 124.73, 118.74, 61.07, 54.25, 52.56, 46.83, 44.83, 29.98, 15.24 ppm; **HRMS** (ESI): C₃₅H₂₇ClNaO₂ [M + Na]⁺ calcd: 537.1592, found: 537.1595.

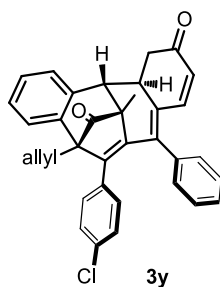


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 111 – 112 °C, 26.8 mg, 51% yield; 97% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, *t*_{major} = 5.7 min, *t*_{minor} = 9.0 min); [α]_D^{23.2} = 828 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.38 – 7.30 (m, 1H), 7.30 – 7.19 (m, 3H), 7.15 (s, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 2H), 6.26 (d, *J* = 7.4 Hz, 2H), 5.83 (d, *J* = 10.1 Hz, 1H), 5.71 (dt, *J* = 16.8, 8.4 Hz, 1H), 4.95 (d, *J* = 10.1 Hz, 1H), 4.82 (d, *J* = 17.2 Hz, 1H), 3.45 (t, *J* = 10.0 Hz, 1H), 3.31 (s, 1H), 2.97 (d, *J* = 10.1 Hz, 2H), 2.77 (dd, *J* = 14.3, 6.0 Hz, 1H), 2.59 (dd, *J* = 14.3, 7.4 Hz, 1H), 1.68 (s, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 198.14, 150.06, 143.80, 141.99, 141.81, 141.01, 140.43, 135.62, 133.71, 133.30, 132.97, 132.87, 132.47, 129.79, 128.42, 127.93, 127.55, 127.30, 127.00, 126.90, 126.46, 126.37, 126.30, 124.71, 118.63, 61.00, 54.38, 52.73, 46.95, 44.91, 30.00, 15.38 ppm; **HRMS** (ESI): C₃₉H₃₀NaO₂ [M + Na]⁺ calcd: 553.2138, found: 553.2147.

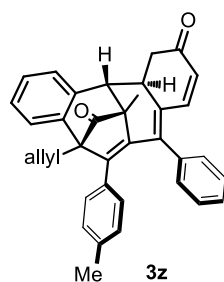


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 75 – 76 °C, 39.1 mg, 79% yield; 96% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow

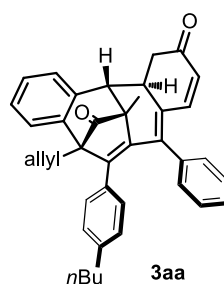
rate = 1.0 mL/min, $t_{\text{major}} = 5.2$ min, $t_{\text{minor}} = 15.2$ min); $[\alpha]_{\text{D}}^{23.2} = 904$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.35 (t, $J = 7.1$ Hz, 1H), 7.30 – 7.04 (m, 7H), 6.81 (d, $J = 6.1$ Hz, 2H), 6.53 (t, $J = 8.7$ Hz, 2H), 6.27 (dd, $J = 8.5, 5.6$ Hz, 2H), 5.85 (d, $J = 10.1$ Hz, 1H), 5.79 – 5.61 (m, 1H), 4.97 (d, $J = 10.0$ Hz, 1H), 4.81 (d, $J = 17.1$ Hz, 1H), 3.40 (t, $J = 10.1$ Hz, 1H), 3.28 (s, 1H), 2.94 (d, $J = 10.4$ Hz, 2H), 2.77 (dd, $J = 14.4, 5.9$ Hz, 1H), 2.55 (dd, $J = 14.4, 7.6$ Hz, 1H), 1.61 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.76, 198.01, 161.83 ($J_{\text{C-F}} = 245.2$ Hz), 148.76, 143.53, 142.88, 141.44, 140.86, 140.35, 138.19, 132.99, 132.86, 130.28, 130.18, 129.88, 129.74 ($J_{\text{C-F}} = 3.38$ Hz), 129.21, 128.52, 128.33, 127.82, 127.30, 126.55, 124.52, 118.71, 114.28, 113.99, 60.88, 54.28, 52.66, 46.89, 44.78, 29.92, 15.23 ppm; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -114.13 ppm; **HRMS** (ESI): $\text{C}_{35}\text{H}_{27}\text{FNaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 521.1887, found: 521.1888.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 97 – 98 °C, 39.2 mg, 76% yield; 97% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.6$ min, $t_{\text{minor}} = 17.5$ min); $[\alpha]_{\text{D}}^{23.2} = 935$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.35 (t, $J = 7.2$ Hz, 1H), 7.29 – 7.04 (m, 7H), 6.94 – 6.69 (m, 4H), 6.23 (d, $J = 8.3$ Hz, 2H), 5.85 (d, $J = 10.1$ Hz, 1H), 5.70 (td, $J = 16.9, 7.3$ Hz, 1H), 4.97 (d, $J = 10.1$ Hz, 1H), 4.81 (d, $J = 17.2$ Hz, 1H), 3.39 (t, $J = 10.1$ Hz, 1H), 3.28 (s, 1H), 2.94 (d, $J = 10.5$ Hz, 2H), 2.77 (dd, $J = 14.3, 5.7$ Hz, 1H), 2.55 (dd, $J = 14.3, 7.6$ Hz, 1H), 1.61 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.59, 197.98, 148.47, 143.48, 143.03, 141.29, 140.78, 140.31, 138.15, 133.20, 133.08, 132.77, 132.33, 129.89, 129.81, 129.23, 128.58, 128.38, 127.91, 127.34, 126.63, 124.51, 118.82, 60.86, 54.26, 52.69, 46.87, 44.77, 29.90, 15.24 ppm; **HRMS** (ESI): $\text{C}_{35}\text{H}_{27}\text{ClNaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 537.1592, found: 537.1599.

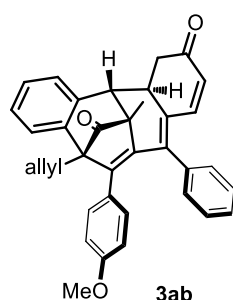


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 104 – 105 °C, 40.3 mg, 82% yield; 94% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.9$ min, $t_{\text{minor}} = 10.7$ min); $[\alpha]_{\text{D}}^{23.2} = 1037$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 – 7.05 (m, 8H), 6.81 (d, $J = 6.5$ Hz, 2H), 6.63 (d, $J = 7.9$ Hz, 2H), 6.20 (d, $J = 8.0$ Hz, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 5.71 (dq, $J = 10.2, 6.8$ Hz, 1H), 4.97 (d, $J = 10.0$ Hz, 1H), 4.86 (d, $J = 17.2$ Hz, 1H), 3.39 (t, $J = 10.1$ Hz, 1H), 3.27 (s, 1H), 2.93 (d, $J = 9.7$ Hz, 2H), 2.76 (dd, $J = 14.4, 6.3$ Hz, 1H), 2.60 (dd, $J = 14.4, 7.1$ Hz, 1H), 2.16 (s, 3H), 1.60 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.15, 198.19, 149.87, 143.77, 142.06, 141.95, 141.05, 140.46, 138.38, 136.94, 133.06, 132.83, 130.81, 129.71, 129.27, 128.31, 128.16, 127.81, 127.64, 127.17, 126.26, 124.65, 118.54, 60.92, 54.45, 52.69, 46.95, 44.75, 29.94, 21.15, 15.29 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{30}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 517.2138, found: 517.2149.

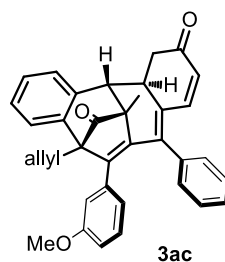


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 62 – 63 °C, 41.0 mg, 76% yield; 91% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.5$ min, $t_{\text{minor}} = 7.6$ min); $[\alpha]_{\text{D}}^{23.2} = 880$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.33 (t, $J = 7.1$ Hz, 1H), 7.29 – 7.09 (m, 7H), 6.79 (d, $J = 6.9$ Hz, 2H), 6.63 (d, $J = 7.9$ Hz, 2H), 6.21 (d, $J = 7.9$ Hz, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 5.79 – 5.58 (m, 1H), 4.98 (d, $J = 10.0$ Hz, 1H), 4.86 (d, $J = 17.1$ Hz, 1H), 3.39 (t, $J = 10.1$ Hz, 1H), 3.27 (s, 1H), 2.93 (d, $J = 10.2$ Hz, 2H), 2.76

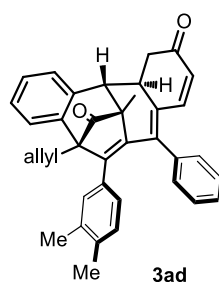
(dd, $J = 14.4, 6.3$ Hz, 1H), 2.61 (dd, $J = 14.4, 7.1$ Hz, 1H), 2.41 (t, $J = 7.4$ Hz, 2H), 1.60 (s, 3H), 1.52 – 1.36 (m, 2H), 1.30 – 1.11 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.21, 198.22, 150.11, 143.83, 142.09, 141.99, 141.89, 141.08, 140.44, 138.33, 133.10, 132.76, 130.99, 129.72, 129.29, 128.31, 128.12, 127.59, 127.21, 126.22, 124.69, 118.53, 60.95, 54.38, 52.64, 46.93, 44.78, 35.14, 33.41, 29.98, 22.00, 15.28, 13.96 ppm; **HRMS** (ESI): $\text{C}_{39}\text{H}_{36}\text{NaO}_2$ [$\text{M} + \text{Na}$] $^+$ calcd: 559.2608, found: 559.2628.



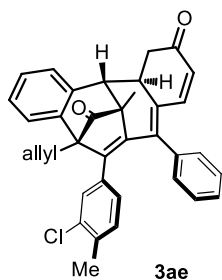
Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 79 – 80 °C, 38.0 mg, 75% yield; 87% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.4$ min, $t_{\text{minor}} = 14.7$ min); $[\alpha]_{\text{D}}^{23.2} = 929$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 – 7.10 (m, 8H), 6.83 (d, $J = 5.6$ Hz, 2H), 6.37 (d, $J = 8.5$ Hz, 2H), 6.25 (d, $J = 8.5$ Hz, 2H), 5.83 (d, $J = 10.1$ Hz, 1H), 5.70 (td, $J = 17.0, 6.9$ Hz, 1H), 4.96 (d, $J = 10.2$ Hz, 1H), 4.84 (d, $J = 17.1$ Hz, 1H), 3.66 (s, 3H), 3.39 (t, $J = 10.0$ Hz, 1H), 3.26 (s, 1H), 2.93 (d, $J = 10.2$ Hz, 2H), 2.76 (dd, $J = 14.2, 6.1$ Hz, 1H), 2.61 (dd, $J = 14.3, 7.2$ Hz, 1H), 1.60 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.11, 198.18, 158.63, 149.57, 143.76, 142.07, 141.93, 141.07, 140.46, 138.55, 133.04, 132.81, 129.74, 129.68, 129.28, 128.34, 128.26, 127.69, 127.19, 126.26, 126.13, 124.57, 118.53, 112.59, 60.89, 55.08, 54.44, 52.68, 46.95, 44.73, 29.93, 15.29 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{30}\text{NaO}_3$ [$\text{M} + \text{Na}$] $^+$ calcd: 533.2087, found: 533.2104.



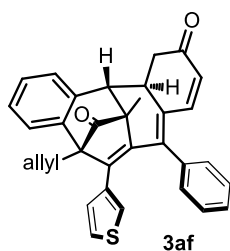
Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 91 – 92 °C, 45.4 mg, 89% yield; 95% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.2 min, t_{minor} = 11.7 min); $[\alpha]_{\text{D}}^{23.2}$ = 961 (c = 1.0 in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 – 7.29 (m, 1H), 7.29 – 7.03 (m, 7H), 6.94 – 6.68 (m, 3H), 6.55 (d, J = 7.6 Hz, 1H), 5.85 (t, J = 10.1 Hz, 3H), 5.72 (dt, J = 16.8, 8.4 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.87 (d, J = 17.1 Hz, 1H), 3.53 – 3.33 (m, 4H), 3.27 (s, 1H), 2.94 (d, J = 10.4 Hz, 2H), 2.77 (dd, J = 14.3, 6.1 Hz, 1H), 2.60 (dd, J = 14.3, 7.3 Hz, 1H), 1.61 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.94, 198.09, 158.28, 149.63, 143.66, 142.13, 141.72, 141.01, 140.39, 138.23, 135.09, 133.08, 132.99, 129.78, 129.20, 128.46, 128.20, 127.70, 127.18, 126.41, 124.69, 120.83, 118.65, 113.58, 60.94, 54.81, 54.36, 52.68, 46.92, 44.77, 30.03, 15.28 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{30}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ calcd: 533.2087, found: 533.2107.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 94 – 95 °C, 42.6 mg, 84% yield; 93% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.7 min, t_{minor} = 12.8 min); $[\alpha]_{\text{D}}^{23.2}$ = 924 (c = 1.0 in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.40 – 7.29 (m, 2H), 7.29 – 7.13 (m, 6H), 6.83 (d, J = 6.1 Hz, 2H), 6.64 (d, J = 7.7 Hz, 1H), 6.13 (d, J = 7.7 Hz, 1H), 6.02 (s, 1H), 5.82 (d, J = 10.1 Hz, 1H), 5.78 – 5.59 (m, 1H), 4.96 (d, J = 10.0 Hz, 1H), 4.86 (d, J = 17.1 Hz, 1H), 3.50 – 3.31 (m, 1H), 3.25 (s, 1H), 3.02 – 2.88 (m, 1H), 2.70 (ddd, J = 34.4, 14.3, 6.8 Hz, 2H), 2.07 (s, 3H), 1.80 (s, 3H), 1.59 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 213.10, 198.25, 149.95, 143.82, 142.21, 141.52, 141.10, 140.49, 138.67, 135.67, 135.15, 133.08, 132.84, 131.25, 130.23, 129.69, 129.30, 128.34, 128.11, 127.67, 127.12, 126.19, 125.17, 124.67, 118.48, 60.80, 54.48, 52.69, 46.97, 44.66, 29.95, 19.44, 15.35 ppm; **HRMS** (ESI): $\text{C}_{37}\text{H}_{32}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 531.2295, found: 531.2311.

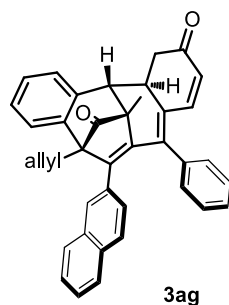


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 100 – 101 °C, 42.1 mg, 80% yield; 99% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.9 min, t_{minor} = 11.8 min); $[\alpha]_{\text{D}}^{23.2} = 1013$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.64 – 7.06 (m, 8H), 6.84 (d, $J = 6.5$ Hz, 2H), 6.70 (d, $J = 7.7$ Hz, 1H), 6.26 (s, 1H), 6.13 (d, $J = 7.6$ Hz, 1H), 5.85 (d, $J = 10.1$ Hz, 1H), 5.67 (dt, $J = 16.7, 8.2$ Hz, 1H), 4.98 (d, $J = 10.0$ Hz, 1H), 4.84 (d, $J = 17.1$ Hz, 1H), 3.54 – 3.31 (m, 1H), 3.27 (s, 1H), 2.94 (d, $J = 9.5$ Hz, 2H), 2.77 (dd, $J = 14.1, 5.7$ Hz, 1H), 2.59 (dd, $J = 14.2, 7.2$ Hz, 1H), 2.18 (s, 3H), 1.60 (s, 3H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 212.61, 198.01, 148.12, 143.54, 142.84, 141.45, 140.80, 140.30, 138.10, 135.06, 133.09, 132.90, 132.80, 129.85, 129.57, 129.18, 128.56, 128.32, 128.09, 127.32, 126.56, 126.43, 124.52, 118.80, 60.81, 54.30, 52.71, 46.89, 44.71, 29.90, 19.73, 15.26 ppm; **HRMS** (ESI): $\text{C}_{36}\text{H}_{29}\text{ClNaO}_2$ [$\text{M} + \text{Na}$] $^+$ calcd: 551.1748, found: 551.1767.

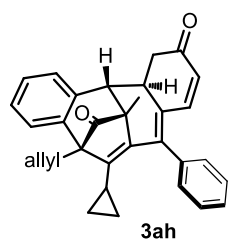


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 101 – 102 °C, 44.6 mg, 92% yield; 97% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.3 min, t_{minor} = 12.6 min); $[\alpha]_{\text{D}}^{23.2} = 1050$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.41 – 7.15 (m, 8H), 6.95 (dd, $J = 6.4, 2.8$ Hz, 1H), 6.86 (dd, $J = 4.9, 3.0$ Hz, 1H), 6.24 – 6.03 (m, 1H), 5.86 (d, $J = 10.1$ Hz, 1H), 5.65 (dq, $J = 10.1, 6.9$ Hz, 1H), 4.93 (d, $J = 9.9$ Hz, 1H), 4.79 (d, $J = 17.1$ Hz, 1H), 3.46 – 3.30 (m, 1H), 3.26 (s, 1H), 3.05 – 2.88 (m, 2H), 2.73 (ddd, $J = 21.6,$

14.2, 6.9 Hz, 2H), 1.59 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.78, 198.09, 145.02, 143.60, 141.70, 140.90, 140.45, 138.78, 133.49, 132.96, 132.88, 129.75, 129.35, 128.53, 128.45, 128.03, 127.35, 127.25, 126.48, 124.38, 123.98, 123.90, 118.51, 60.67, 54.54, 52.86, 46.94, 44.66, 29.83, 15.22 ppm; **HRMS** (ESI): $\text{C}_{33}\text{H}_{26}\text{NaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ calcd: 509.1546, found: 509.1561.

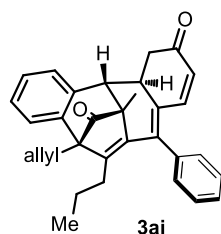


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 108 – 109 °C, 45.1 mg, 85% yield; 99% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.8 min, t_{minor} = 17.8 min); $[\alpha]_{\text{D}}^{23.2}$ = 680 (c = 1.0 in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.63 (d, J = 7.9 Hz, 1H), 7.45 – 7.19 (m, 9H), 7.19 – 6.99 (m, 3H), 6.78 (dd, J = 8.6, 7.1 Hz, 3H), 6.53 (dd, J = 8.5, 1.7 Hz, 1H), 5.82 (d, J = 10.1 Hz, 1H), 5.71 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 4.93 (dd, J = 10.2, 1.7 Hz, 1H), 4.75 (dd, J = 17.1, 1.6 Hz, 1H), 3.43 (dd, J = 12.1, 8.2 Hz, 1H), 3.30 (s, 1H), 3.03 – 2.89 (m, 2H), 2.84 – 2.73 (m, 1H), 2.65 (dd, J = 14.4, 7.3 Hz, 1H), 1.64 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 212.76, 198.08, 149.47, 143.56, 142.31, 141.75, 140.96, 140.41, 138.78, 132.95, 132.81, 132.19, 131.30, 129.77, 129.17, 128.46, 128.21, 127.98, 127.76, 127.25, 126.51, 126.34, 125.95, 125.76, 125.61, 124.64, 118.66, 60.95, 54.38, 52.76, 46.89, 44.61, 29.97, 15.31 ppm; **HRMS** (ESI): $\text{C}_{39}\text{H}_{30}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 553.2138, found: 553.2148.

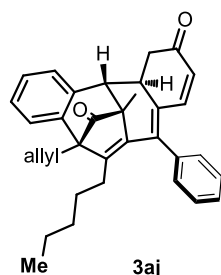


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 93 – 94 °C, 43.9

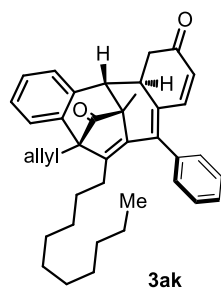
mg, 99% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 6.8 min, t_{minor} = 13.3 min); $[\alpha]_{\text{D}}^{23.2}$ = 1009 (c = 1.0 in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.52 (d, J = 10.2 Hz, 1H), 7.38 – 6.86 (m, 9H), 5.82 (d, J = 10.2 Hz, 1H), 5.71 (dt, J = 16.7, 8.4 Hz, 1H), 5.13 (d, J = 17.2 Hz, 1H), 5.00 (d, J = 10.2 Hz, 1H), 3.16 (dd, J = 13.3, 6.5 Hz, 1H), 3.01 (s, 1H), 2.97 – 2.64 (m, 4H), 1.33 (s, 3H), 0.92 – 0.64 (m, 1H), 0.23 – 0.81 (m, 1H), 0.08 – -0.09 (m, 2H), -0.09 – -0.31 (m, 1H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 213.50, 198.11, 148.54, 143.45, 142.15, 141.27, 141.16, 140.50, 137.78, 133.95, 132.59, 129.82, 129.40, 128.49, 128.21, 128.09, 126.92, 126.34, 124.08, 118.12, 60.83, 54.94, 52.97, 47.08, 44.61, 30.03, 14.82, 9.45, 6.82, 3.92 ppm; **HRMS** (ESI): $\text{C}_{32}\text{H}_{28}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 467.1982, found: 467.1991.



Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 66 – 67 °C, 26.8 mg, 60% yield; >99% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.7 min, t_{minor} = 7.5 min); $[\alpha]_{\text{D}}^{23.2}$ = 937 (c = 1.0 in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.52 (d, J = 10.2 Hz, 1H), 7.38 (t, J = 7.9 Hz, 3H), 7.24 (d, J = 7.1 Hz, 3H), 7.14 (d, J = 4.4 Hz, 3H), 5.91 (d, J = 10.1 Hz, 1H), 5.76 (dd, J = 16.8, 10.0 Hz, 1H), 5.20 (d, J = 17.2 Hz, 1H), 5.09 (d, J = 10.1 Hz, 1H), 3.33 (t, J = 10.1 Hz, 1H), 3.17 (s, 1H), 3.01 – 2.70 (m, 4H), 1.90 – 1.63 (m, 1H), 1.48 (s, 4H), 1.02 – 0.63 (m, 2H), 0.29 (t, J = 7.1 Hz, 3H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 213.72, 198.11, 150.59, 143.50, 141.92, 141.24, 140.66, 140.23, 137.27, 133.59, 132.64, 129.49, 128.73, 128.35, 128.07, 126.94, 126.24, 124.18, 118.09, 59.99, 54.61, 52.15, 47.01, 44.74, 29.61, 28.95, 22.03, 14.90, 13.64 ppm; **HRMS** (ESI): $\text{C}_{32}\text{H}_{30}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 469.2138, found: 469.2127.

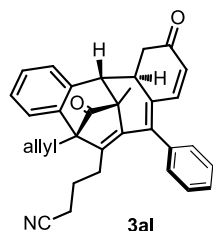


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 57 – 58 °C, 39.0 mg, 82% yield; >99% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.7$ min, $t_{\text{minor}} = 7.3$ min); $[\alpha]_{\text{D}}^{23.2} = 1066$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.53 (d, $J = 10.1$ Hz, 1H), 7.47 – 7.31 (m, 3H), 7.30 – 7.19 (m, 3H), 7.15 (d, $J = 4.6$ Hz, 3H), 5.91 (d, $J = 10.1$ Hz, 1H), 5.85 – 5.65 (m, 1H), 5.20 (d, $J = 17.2$ Hz, 1H), 5.10 (d, $J = 10.3$ Hz, 1H), 3.32 (t, $J = 10.1$ Hz, 1H), 3.17 (s, 1H), 3.01 – 2.70 (m, 4H), 1.85 – 1.70 (m, 1H), 1.60 – 1.40 (m, 4H), 1.02 – 0.41 (m, 9H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 213.79, 198.18, 150.75, 143.54, 141.96, 141.23, 140.64, 140.06, 137.34, 133.65, 132.61, 129.52, 129.48, 128.73, 128.36, 128.07, 126.93, 126.21, 124.22, 118.09, 59.98, 54.63, 52.17, 47.03, 44.73, 31.51, 29.69, 28.17, 27.01, 22.08, 14.91, 13.87 ppm; **HRMS** (ESI): $\text{C}_{34}\text{H}_{34}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 497.2451, found: 497.2464.

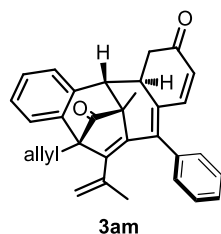


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow oil, 35.6 mg, 65% yield; >99% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.0$ min, $t_{\text{minor}} = 6.0$ min); $[\alpha]_{\text{D}}^{23.2} = 952$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.53 (d, $J = 10.1$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 3H), 7.24 (d, $J = 6.7$ Hz, 3H), 7.14 (d, $J = 4.2$ Hz, 3H), 5.91 (d, $J = 10.1$ Hz, 1H), 5.77 (td, $J = 16.7, 6.5$ Hz, 1H), 5.20 (d, $J = 17.0$ Hz, 1H), 5.10 (d, $J = 10.0$ Hz, 1H), 3.46 – 3.23 (m, 1H), 3.17 (s, 1H), 3.01 – 2.70 (m, 4H), 1.76 (dd, $J = 12.5, 7.7$ Hz, 1H), 1.61 – 1.50 (m, 1H), 1.47 (s, 3H), 1.37 – 1.02 (m, 9H), 1.02 – 0.54 (m, 10H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 213.72,

198.09, 150.73, 143.48, 141.95, 141.25, 140.65, 140.08, 137.35, 133.65, 132.64, 129.54, 129.47, 128.72, 128.35, 128.07, 126.91, 126.23, 124.23, 118.06, 59.98, 54.66, 52.17, 47.04, 44.74, 31.88, 29.69, 29.44, 29.33, 29.24, 29.01, 28.50, 27.05, 22.67, 14.91, 14.13 ppm; **HRMS** (ESI): C₃₉H₄₄NaO₂ [M + Na]⁺ calcd: 567.3234, found: 567.3219.

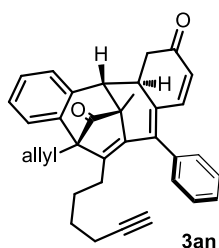


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 10/1 to 4/1). Yellow solid, m.p. 186 – 187 °C, 36.7 mg, 78% yield; 98% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 9.3 min, t_{minor} = 11.8 min); $[\alpha]_{\text{D}}^{23.2}$ = 792 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃) δ 7.53 (d, J = 10.1 Hz, 1H), 7.49 – 7.33 (m, 3H), 7.26 (d, J = 4.4 Hz, 3H), 7.23 – 6.99 (m, 3H), 5.95 (d, J = 10.2 Hz, 1H), 5.87 – 5.61 (m, 1H), 5.22 (d, J = 17.0 Hz, 1H), 5.12 (d, J = 10.1 Hz, 1H), 3.43 – 3.26 (m, 1H), 3.20 (s, 1H), 2.87 (dq, J = 34.9, 7.4 Hz, 4H), 2.04 – 1.85 (m, 1H), 1.85 – 1.53 (m, 3H), 1.50 (s, 3H), 1.13 – 0.96 (m, 1H), 0.96 – 0.67 (m, 1H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 212.94, 197.75, 147.57, 143.00, 141.89, 140.88, 140.71, 140.42, 137.01, 133.25, 129.83, 129.37, 129.08, 128.71, 128.55, 127.40, 126.91, 123.97, 118.54, 59.98, 54.43, 52.40, 46.89, 44.85, 29.57, 25.88, 24.20, 16.42, 14.79 ppm; **HRMS** (ESI): C₃₃H₂₉NNaO₂ [M + Na]⁺ calcd: 494.2091, found: 494.2080.



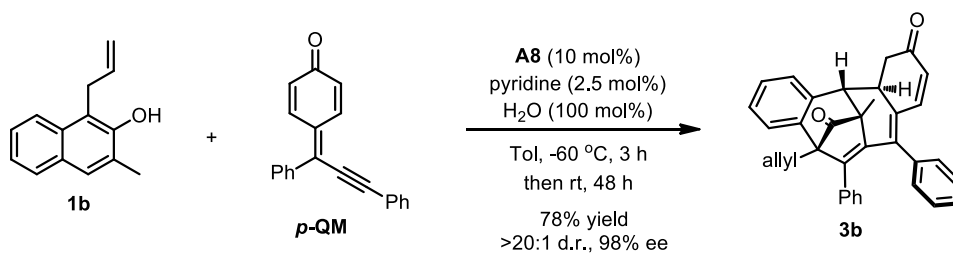
Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 65 – 66 °C, 22.2 mg, 50% yield; 93% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 4.7 min, t_{minor} = 7.9 min); $[\alpha]_{\text{D}}^{23.2}$ = 970 (c = 1.0 in CHCl₃); **¹H NMR** (300

MHz, CDCl₃) δ 7.40 (d, J = 10.1 Hz, 1H), 7.36 – 7.21 (m, 4H), 7.21 – 7.01 (m, 5H), 5.89 (d, J = 10.2 Hz, 1H), 5.80 (ddd, J = 16.8, 8.5, 4.7 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 5.09 (d, J = 10.2 Hz, 1H), 4.54 (s, 1H), 3.96 (s, 1H), 3.35 (t, J = 10.1 Hz, 1H), 3.20 (s, 1H), 2.91 (d, J = 10.8 Hz, 2H), 2.88 – 2.67 (m, 2H), 1.53 (s, 3H), 1.15 (s, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 213.18, 198.08, 151.70, 143.68, 141.86, 140.92, 140.30, 140.03, 137.97, 137.87, 133.69, 132.72, 129.64, 129.52, 128.31, 128.19, 128.05, 126.88, 126.37, 124.81, 118.28, 117.14, 60.36, 54.38, 52.40, 46.91, 44.74, 30.19, 22.94, 15.11 ppm; **HRMS** (ESI): C₃₂H₂₈NaO₂ [M + Na]⁺ calcd: 467.1982, found: 467.1970.

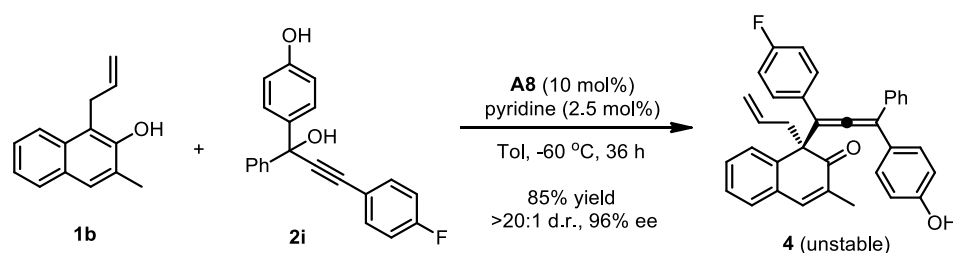


Prepared according to the general procedure on a 0.1 mmol scale and purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1). Yellow solid, m.p. 54 – 55 °C, 30.0 mg, 62% yield; >99% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 5.2 min, t_{minor} = 9.0 min); $[\alpha]_{\text{D}}^{23.2}$ = 1013 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃) δ 7.53 (d, J = 10.1 Hz, 1H), 7.47 – 7.30 (m, 3H), 7.26 (d, J = 6.2 Hz, 3H), 7.15 (d, J = 4.0 Hz, 3H), 5.92 (d, J = 10.1 Hz, 1H), 5.76 (td, J = 16.8, 6.6 Hz, 1H), 5.21 (d, J = 17.0 Hz, 1H), 5.10 (d, J = 10.2 Hz, 1H), 3.46 – 3.23 (m, 1H), 3.18 (s, 1H), 2.98 – 2.75 (m, 4H), 1.80 – 1.75 (m, 2H), 1.75 – 1.60 (m, 2H), 1.60 – 1.50 (m, 1H), 1.48 (s, 3H), 1.12 – 0.68 (m, 4H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 213.54, 198.06, 150.03, 143.38, 141.64, 141.15, 140.59, 137.28, 133.56, 132.80, 129.56, 129.49, 128.81, 128.44, 128.17, 127.00, 126.36, 124.19, 118.16, 84.02, 68.30, 59.97, 54.61, 52.22, 47.00, 44.73, 29.66, 27.93, 27.45, 26.39, 17.76, 14.88 ppm; **HRMS** (ESI): C₃₅H₃₂NaO₂ [M + Na]⁺ calcd: 507.2295, found: 507.2278.

(E) Control experiments



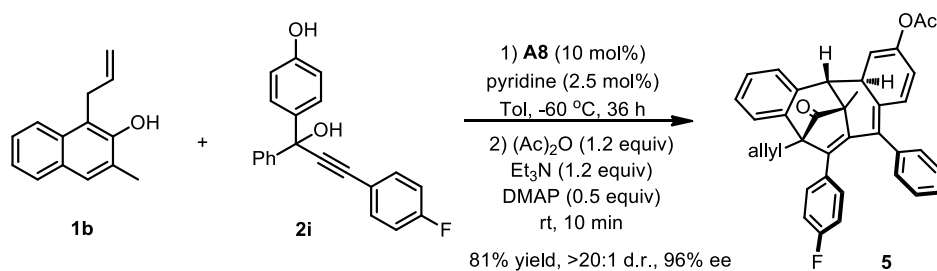
To a solution of catalyst **A8** (0.01 mmol, 10 mol%), β -naphthol **1b** (0.12 mmol, 1.2 equiv), H₂O (0.1 mmol, 1.0 equiv) and pyridine (0.0025 mmol, 2.5 mol%) in dry toluene (1.0 mL) was added *para*-quinone methide (0.1 mmol, 1.0 equiv) at -60 °C. The reaction mixture was stirred at this temperature until the complete consumption of **p-QM**. After which the reaction mixture was warmed to room temperature and stirred for further 48 h. Upon completion, the residue was directly purified by silica gel chromatography to afford the desired products **3b** as a yellow solid (37.4 mg, 78% yield, 98% ee).



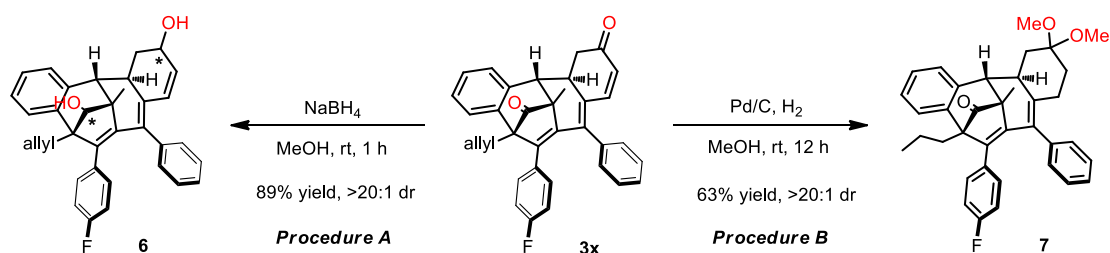
To a solution of catalyst **A8** (0.01 mmol, 10 mol%), β -naphthol **1b** (0.12 mmol, 1.2 equiv) and pyridine (0.0025 mmol, 2.5 mol%) in dry toluene (1.0 mL) was added propargylic alcohol **2i** (0.1 mmol, 1.0 equiv) at -60 °C. The reaction mixture was stirred at this temperature until the complete consumption of the substrate **2i**, the progress of which was monitored by TLC analysis. Then the reaction mixture was directly purified by silica gel chromatography (eluting with hexane/ethyl acetate = 10:1 to 7:1) to afford the desired chiral allene **4** as a yellow solid (42.3 mg, 85% yield, >20:1 dr). 96% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 9/1, flow rate = 0.7 mL/min, t_{minor} = 7.6 min, t_{major} = 21.2 min); ¹H NMR (300 MHz, MeOD) δ 7.60 – 7.31 (m, 8H), 7.31 – 7.05 (m, 4H), 6.89 (t, J = 7.5 Hz, 4H), 6.76 (t, J = 8.6 Hz, 2H), 5.19 (dt, J = 17.2, 7.6 Hz, 1H), 4.76 – 4.60 (m, 2H), 3.33 (s, 1H), 2.95 (dd, J = 12.2, 8.5 Hz, 1H), 2.68 (dd, J = 12.6, 6.6 Hz, 1H), 1.96 (s, 3H) ppm; ¹³C NMR (75 MHz, MeOD) δ 208.43, 203.33, 163.13 ($J_{\text{C-F}}$ = 244.5 Hz), 158.66, 144.58, 144.01, 138.38, 135.37, 132.89, 132.46, 130.59, 130.37, 130.05, 129.91, 129.78, 129.73,

129.67, 129.06, 128.65, 128.43, 127.46, 118.92, 116.61, 116.35, 116.17, 115.89, 113.86, 60.80, 51.06, 15.79 ppm; **HRMS** (ESI): C₃₅H₂₇FNao₂ [M + Na]⁺ calcd: 521.1887, found: 521.1875.

(F) Versatile transformations of the dearomatized products



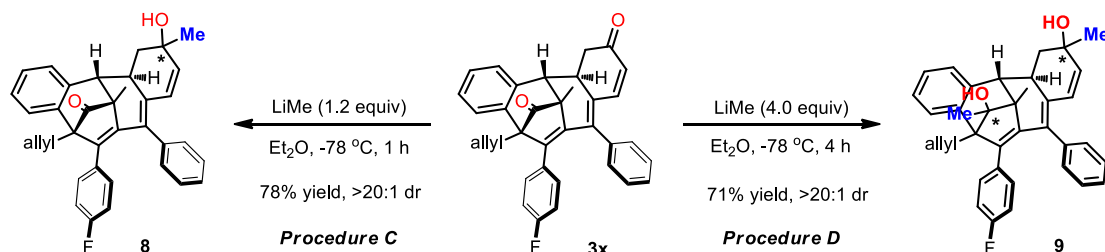
To a solution of catalyst **A8** (0.01 mmol, 10 mol%), β-naphthol **1b** (0.12 mmol, 1.2 equiv) and pyridine (0.0025 mmol, 2.5 mol%) in dry toluene (1.0 mL) was added propargylic alcohol **2i** (0.1 mmol, 1.0 equiv) at -60 °C. After stirring at -60 °C for indicated time, the reaction mixture was warmed to room temperature. Then, acetic anhydride (0.15 mmol, 1.5 equiv), triethylamine (0.15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (0.02 mmol, 0.2 equiv) were successively added to the stirred solution. The resulting reaction mixture was stirred at room temperature for 30 min and directly purified by silica gel chromatography (eluting with hexane/ethyl acetate = 20:1 to 10:1) to afford compound **5** as a white solid (43.9 mg, 81% yield, 96% ee). 96% ee determined by HPLC on a Chiralpak IA-H column (hexane/*i*PrOH = 97/3, flow rate = 1.0 mL/min, *t*_{minor} = 5.9 min, *t*_{major} = 7.6 min); ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.37 (s, 1H), 7.32 – 7.10 (m, 8H), 7.10 – 6.80 (m, 6H), 5.79 (td, *J* = 16.9, 7.3 Hz, 1H), 5.05 (d, *J* = 10.1 Hz, 1H), 4.91 (d, *J* = 17.0 Hz, 1H), 4.81 (s, 1H), 4.11 (s, 1H), 2.88 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.65 (dd, *J* = 14.2, 7.7 Hz, 1H), 2.36 (s, 3H), 1.05 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 213.90, 169.47, 162.43 (*J*_{C-F} = 246.0 Hz), 149.15, 145.22, 141.99, 141.48, 140.05, 139.89, 137.45, 134.98, 133.31, 132.49, 130.37, 129.83, 128.50, 128.35, 127.76, 126.60, 124.02, 123.83, 120.22, 118.54, 115.40, 115.12, 59.49, 55.61, 51.18, 43.96, 30.11, 21.30, 16.00 ppm; ¹⁹F NMR (282 MHz, CDCl₃) δ -113.48 ppm; **HRMS** (ESI): C₃₇H₂₉FNao₃ [M + Na]⁺ calcd: 563.1993, found: 563.2016.



Procedure A: To a solution of **3x** (0.061 mmol, 31.5 mg) in methanol (0.5 mL) was added NaBH₄ (0.3 mmol, 5 equiv) at room temperature. The mixture was stirred for 1 h until the complete consumption of the start material. Then the mixture was quenched by water and the aqueous layer was extracted with EtOAc for three times, and the combined organic layers were washed with brine, dried, and concentrated. The residue was then purified by flash chromatography (eluting with hexane/ethyl acetate = 4:1 to 2:1) to give **6** in 89% yield. White solid, m.p. 117-118 °C.; [α]_D^{23.2} = 678 (c = 1.0 in CHCl₃); ¹H NMR (300 MHz, MeOD) δ 7.40 – 7.21 (m, 2H), 7.20 – 7.02 (m, 5H), 6.78 (s, 2H), 6.49 (t, *J* = 8.8 Hz, 2H), 6.38 – 6.21 (m, 2H), 6.17 (d, *J* = 10.3 Hz, 1H), 5.74 (dt, *J* = 15.9, 9.0 Hz, 1H), 5.62 (d, *J* = 10.2 Hz, 1H), 5.04 (t, *J* = 13.4 Hz, 2H), 4.91 (s, 1H), 4.54 (s, 1H), 4.26 (s, 1H), 2.89 (s, 1H), 2.74 – 2.38 (m, 4H), 1.86 (dd, *J* = 25.0, 11.4 Hz, 1H), 1.39 (s, 3H) ppm; ¹³C NMR (75 MHz, MeOD) δ 162.82 (*J*_{C-F} = 243.0 Hz), 146.78, 146.39, 145.24, 141.33, 140.37, 135.81, 135.45, 135.04, 134.49, 133.12 (*J*_{C-F} = 3.0 Hz), 131.76, 131.65, 130.71, 130.39, 128.90, 128.24, 127.66, 126.93, 126.69, 126.07, 118.47, 114.84, 114.55, 80.14, 69.52, 57.84, 47.42, 44.30, 44.05, 33.86, 21.78 ppm; ¹⁹F NMR (282 MHz, MeOD) δ -117.87 ppm; HRMS (ESI): C₃₅H₃₁FNaO₂ [M + Na]⁺ calcd: 525.2200, found: 525.2221.

Procedure B: To a solution of **3x** (0.067 mmol, 33.4 mg) in methanol (1.0 mL) was added 10% palladium on carbon catalyst (0.0067 mmol, 0.1 equiv). The mixture was stirred with a hydrogen balloon at room temperature until the complete consumption of the start material (monitored by TLC). Then the mixture was filtrated with celite and evaporated to give a residue, which was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to afford the desired product **7** in 63% yield. White solid, m.p. 100-101 °C; [α]_D^{23.2} = 463 (c = 1.0 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.14 (m, 3H), 7.14 – 7.00 (m, 4H), 6.70 (d, *J* = 3.6 Hz, 2H), 6.48 (t, *J* = 8.7 Hz, 2H), 6.29 – 6.11 (m, 2H), 3.26 (s, 6H), 3.13 (s, 1H), 2.80 (dd, *J* = 13.5, 4.6 Hz, 1H), 2.44 (t, *J* = 14.5 Hz, 1H), 2.14 – 1.76 (m, 4H), 1.70 – 1.38 (m, 5H), 1.35 – 1.13 (m, 1H), 1.13 – 0.92 (m, 1H), 0.78 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 214.55, 160.39 (*J*_{C-F} = 244.5 Hz),

143.18, 142.12, 141.62, 139.78, 139.04, 135.80, 129.84 ($J_{C-F} = 3.75$ Hz), 129.11, 129.03, 129.00, 128.95, 128.55, 126.74, 126.60, 125.73, 125.30, 123.21, 113.04, 112.75, 98.54, 60.72, 54.01, 50.55, 46.85, 46.78, 42.17, 41.23, 30.63, 26.58, 24.82, 16.60, 14.32, 13.72 ppm; ^{19}F NMR (282 MHz, CDCl_3) δ -115.59 ppm; HRMS (ESI): $\text{C}_{37}\text{H}_{37}\text{FNaO}_3$ $[\text{M} + \text{Na}]^+$ calcd: 571.2619, found: 571.2639.

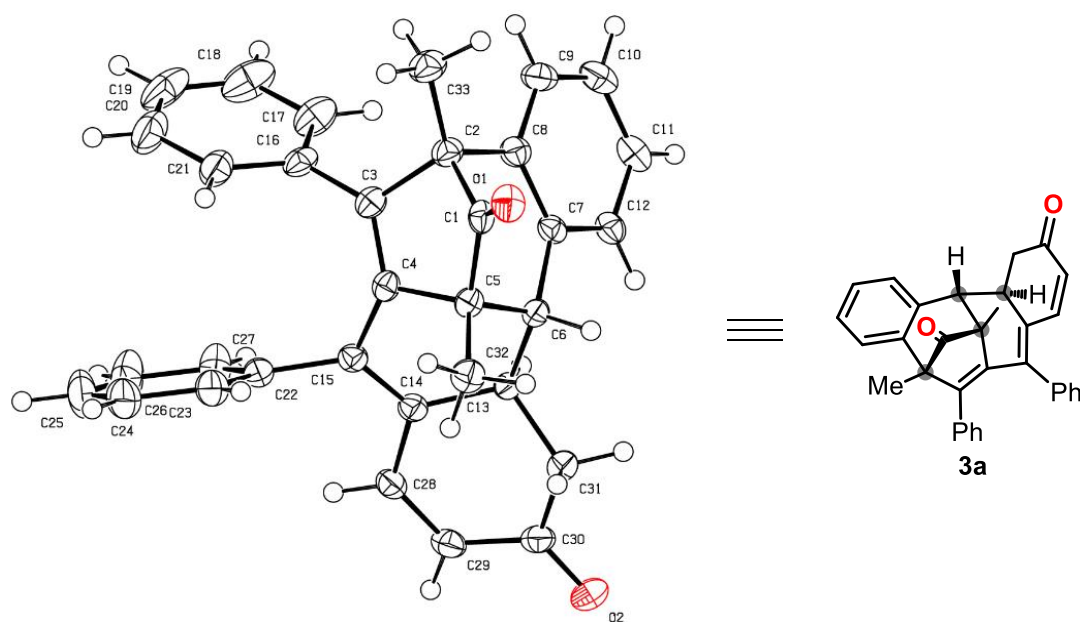


Procedure C: A solution of 1.6 M MeLi (0.06 mmol, 37.5 μL) in ether was added dropwise to a stirred solution of **3x** (0.05 mmol, 25 mg) in ether (1.0 mL) at -78 $^{\circ}\text{C}$ under Ar. After being stirred for 1 h, the reaction mixture was quenched by saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EtOAc for three times, and the combined organic layers were washed with brine, dried, and concentrated. The residue was then purified by flash chromatography (eluting with hexane/ethyl acetate = 7:1 to 4:1) to give **8** in 78% yield. White solid, m.p. 92 – 93 $^{\circ}\text{C}$.; $[\alpha]_{\text{D}}^{23.2} = 578$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.42 – 7.28 (m, 1H), 7.28 – 7.05 (m, 6H), 6.82 (d, $J = 3.2$ Hz, 2H), 6.52 (t, $J = 8.6$ Hz, 2H), 6.40 – 6.24 (m, 2H), 6.18 (d, $J = 10.2$ Hz, 1H), 5.79 – 5.62 (m, 1H), 5.60 (d, $J = 10.2$ Hz, 1H), 4.94 (d, $J = 10.1$ Hz, 1H), 4.79 (d, $J = 17.0$ Hz, 1H), 3.20 (s, 1H), 2.79 (dd, $J = 25.2, 10.4$ Hz, 2H), 2.58 (dd, $J = 14.2, 7.4$ Hz, 1H), 2.31 (d, $J = 9.9$ Hz, 1H), 2.10 (t, $J = 13.4$ Hz, 1H), 1.47 (s, 6H) ppm; ^{19}F NMR (282 MHz, CDCl_3) δ -114.79 ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 213.64, 161.7 ($J_{C-F} = 244.5$ Hz), 145.10, 143.68, 141.70, 141.19, 139.49, 136.82, 134.64, 133.14, 132.97, 130.42, 130.31, 129.45, 128.26, 128.06, 126.99, 126.94, 124.51, 124.33, 118.37, 114.13, 113.85, 71.12, 60.35, 55.08, 52.72, 48.81, 44.25, 29.97, 26.92, 15.20 ppm; HRMS (ESI): $\text{C}_{36}\text{H}_{31}\text{FNaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 537.2200, found: 537.2185.

Procedure D: A solution of 1.6 M MeLi (0.06 mmol, 37.5 μL) in ether was added dropwise to a stirred solution of **3x** (0.05 mmol, 25 mg) in ether (1.0 mL) at -78 $^{\circ}\text{C}$ under Ar. After being stirred for 1 h, 0.14 mmol of MeLi was added again and the reaction mixture was stirred for another 3 h. Then the reaction mixture was quenched by saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EtOAc for three times, and the combined organic layers were washed with brine, dried, and concentrated. The residue was then purified by flash chromatography (eluting with

hexane/ethyl acetate = 4:1 to 2:1) to give **9** in 71% yield. White solid, m.p. 108-109 °C.; $[\alpha]_D^{23.2} = 657$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.40 – 7.22 (m, 2H), 7.15 (d, $J = 2.7$ Hz, 2H), 7.05 (d, $J = 2.5$ Hz, 3H), 6.73 (d, $J = 3.4$ Hz, 2H), 6.53 (t, $J = 8.7$ Hz, 2H), 6.37 – 6.19 (m, 2H), 6.15 (d, $J = 10.1$ Hz, 1H), 6.02 (dt, $J = 17.1, 7.7$ Hz, 1H), 5.55 (d, $J = 10.1$ Hz, 1H), 5.12 (dd, $J = 25.3, 13.6$ Hz, 2H), 2.97 (s, 1H), 2.67 (dd, $J = 19.0, 8.2$ Hz, 2H), 2.53 – 2.29 (m, 2H), 2.13 (t, $J = 13.4$ Hz, 1H), 1.62 (d, $J = 10.9$ Hz, 6H), 1.47 (s, 3H), 1.28 (s, 3H) ppm; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -115.79 ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 161.5 ($J_{\text{C-F}} = 243.8$ Hz), 146.51, 144.37, 143.72, 139.04, 138.00, 135.94, 134.70, 133.81, 133.42, 131.12, 130.29, 130.19, 129.43, 129.31, 127.69, 126.51, 125.81, 124.61, 117.77, 114.11, 113.83, 82.21, 71.25, 59.09, 51.10, 49.21, 47.19, 43.88, 33.10, 27.11, 18.73, 16.41 ppm; **HRMS** (ESI): $\text{C}_{37}\text{H}_{35}\text{FNaO}_2$ $[\text{M} + \text{Na}]^+$ calcd: 553.2513, found: 553.2501.

(G) X-ray structure of **3a**



Displacement ellipsoids are drawn at the 50% probability level.

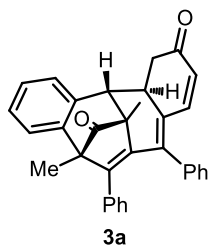
Bond precision:	C-C = 0.0029 Å	Wavelength=1.54178
Cell:	a = 11.3659(4)	b = 11.9259(4)
	alpha = 90	beta = 90
		gamma = 90
Temperature: 153 K		

	Calculated	Reported
Volume	2430.58(14)	2430.58(14)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C33 H26 O2	C33 H26 O2
Sum formula	C33 H26 O2	C33 H26 O2
Mr	454.54	454.54
Dx, g cm-3	1.242	1.242
Z	4	4
Mu (mm-1)	0.591	0.591
F000	960.0	960.0
F000'	962.67	
h, k, lmax	13,13,20	13,13,20
Nref	3891[2222]	3865
Tmin, Tmax	0.899, 0.932	0.698, 0.752
Tmin'	0.899	
Correction method = # Reported T Limits: Tmin=0.698 Tmax=0.752 AbsCorr = MULTI-SCAN		
Data completeness=	1.74/0.99	Theta(max)= 62.730
R(reflections)=	0.0265(3784)	wR2(reflections)= 0.0663(3865)
S =	1.080	Npar= 318

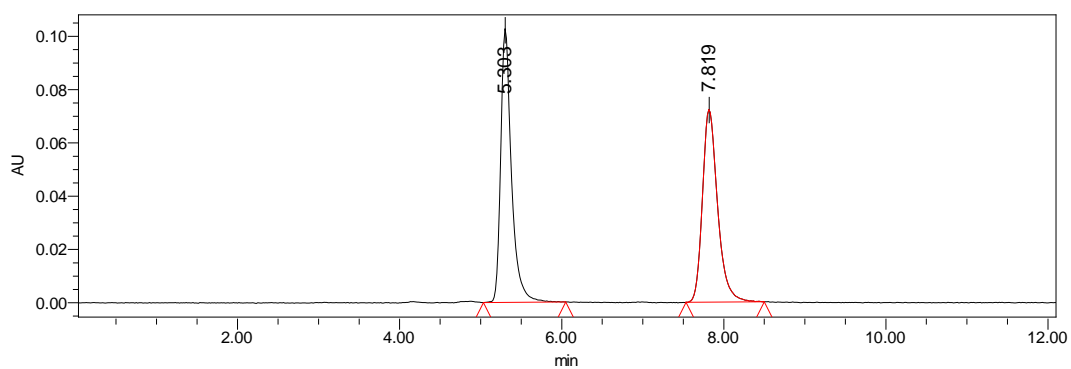
(H) Reference

- [1] T. Oguma and T. Katsuki, *J. Am. Chem. Soc.*, 2012, **134**, 20017–20020.
- [2] J. Nan, J. Liu, H. Zheng, Z. Zuo, L. Hou, H. Hu, Y. Wang and X. Luan, *Angew. Chem. Int. Ed.*, 2015, **54**, 2356–2360.
- [3] L. Wang, D. Yang, D. Li, H. Zhu, P. Wang, X. Liu, L. Bai and R. Wang, *Adv. Synth. Catal.*, 2018, **360**, 4491–4496.
- [4] D. Qian, L. Wu, Z. Lin and J. Sun, *Nat. Commun.*, 2017, **8**, 567–575.

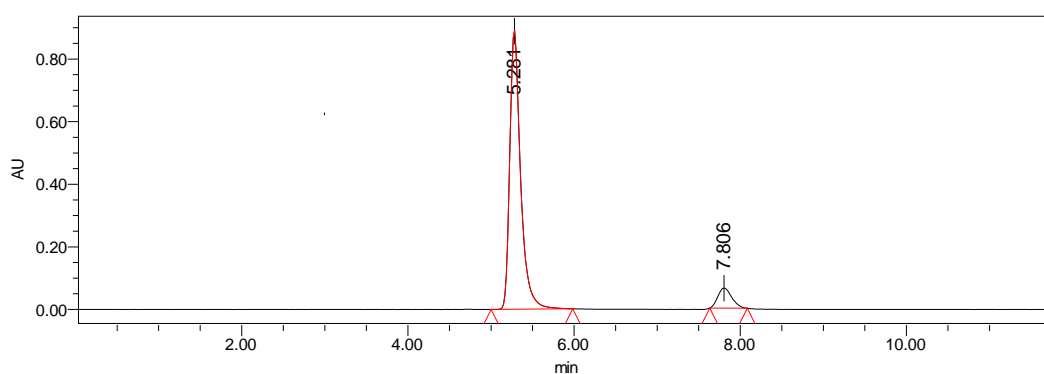
HPLC results



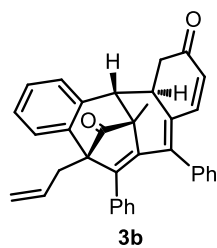
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



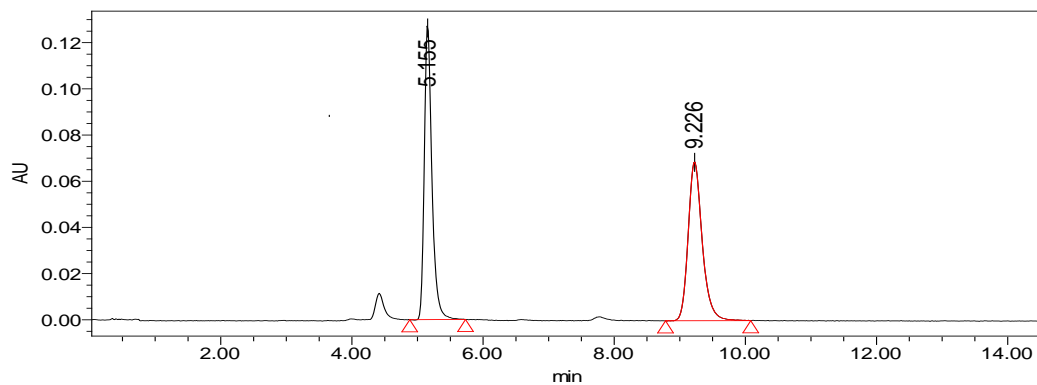
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.303	952851	50.34	102687	bb
2	7.819	940117	49.66	72370	bb



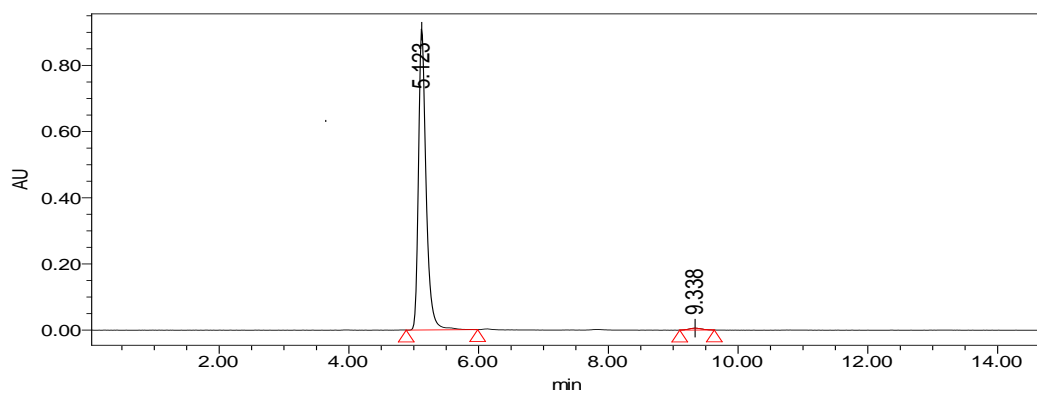
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1	5.281	8051815	91.46	889845	bb
2	7.806	752132	8.54	64573	bb



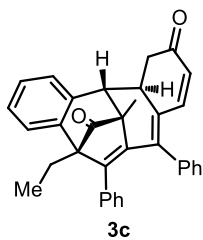
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



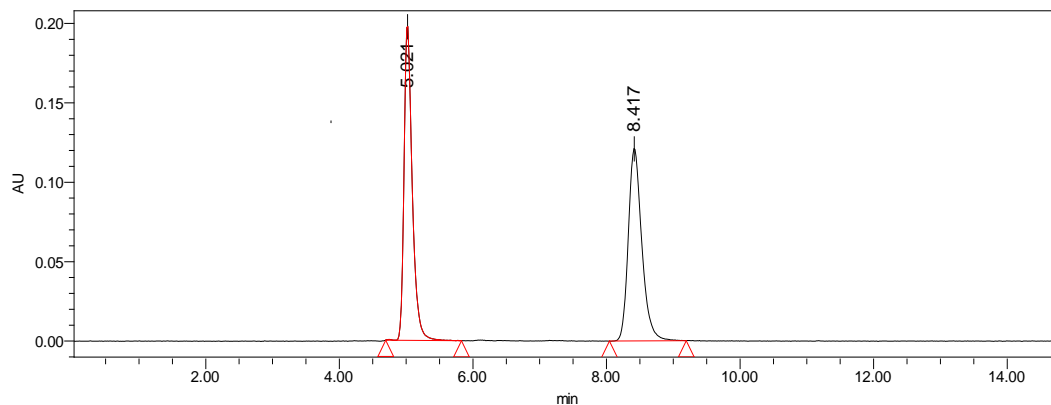
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.155	1028872	50.05	127774	bb
2	9.226	1026637	49.95	68814	bb



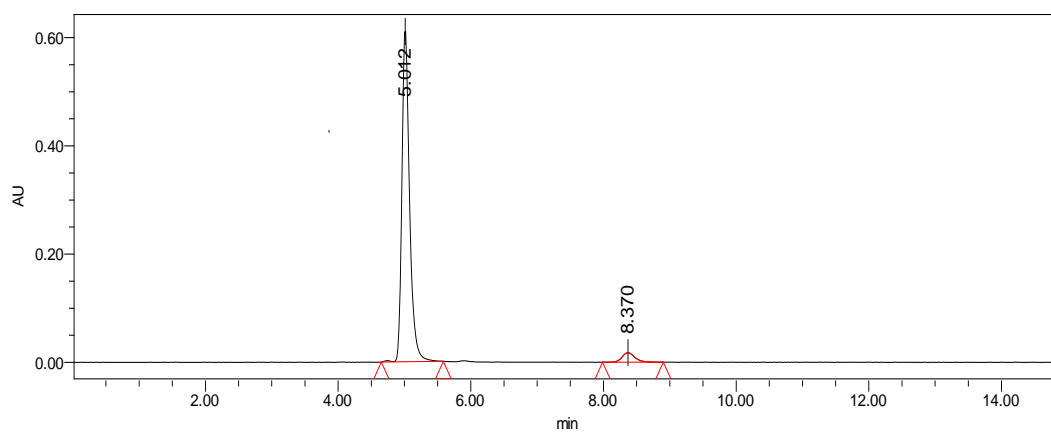
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.123	7469027	98.97	913088	bb
2	9.338	77852	1.03	5749	bb



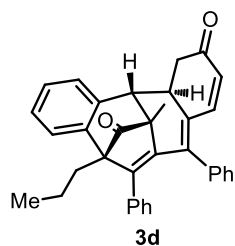
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



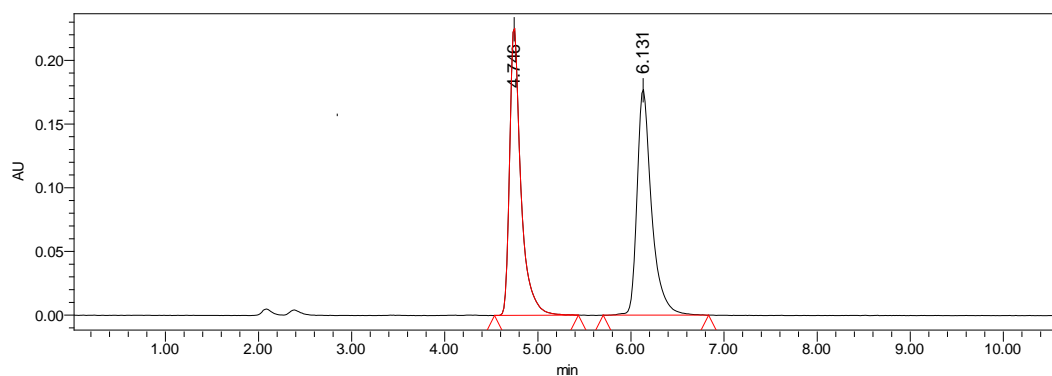
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1	5.021	1693019	49.86	198266	bb
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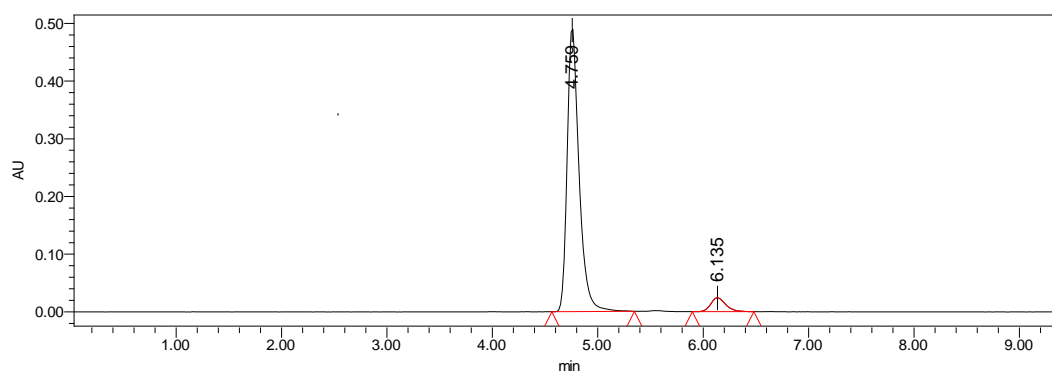
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.012	4943935	95.50	613290	bb
2	8.370	232916	4.50	17537	bb



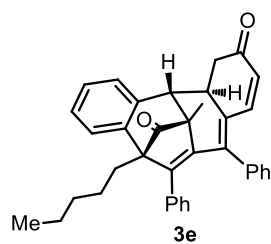
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



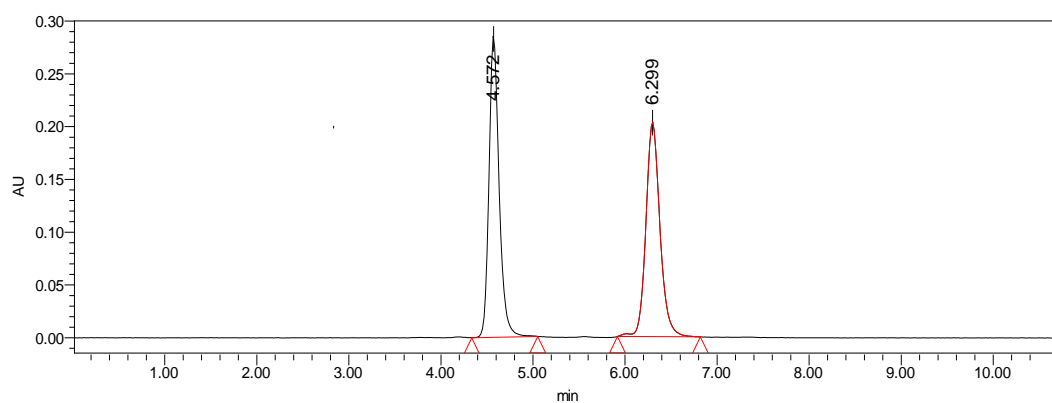
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.746	1889100	49.65	225444	bb
2	6.131	1916023	50.35	177058	bb



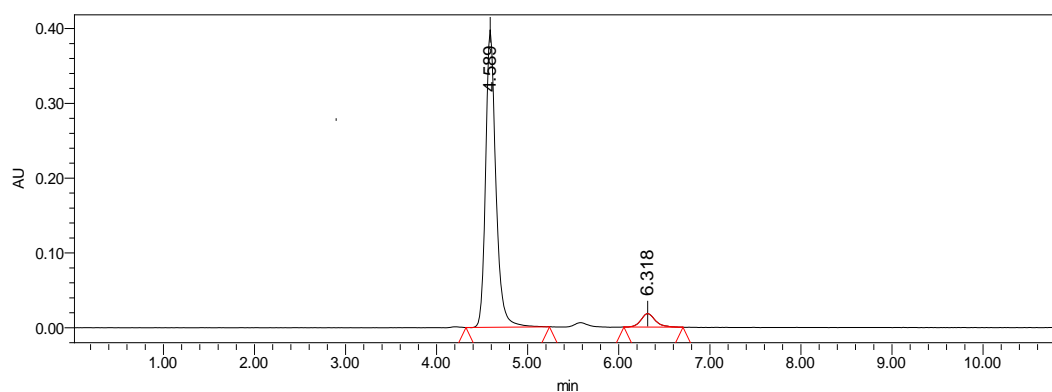
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.759	3851512	94.25	490297	bb
2	6.135	235064	5.75	24042	bb



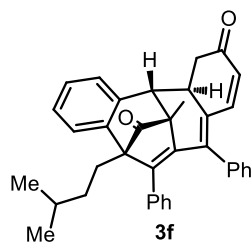
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



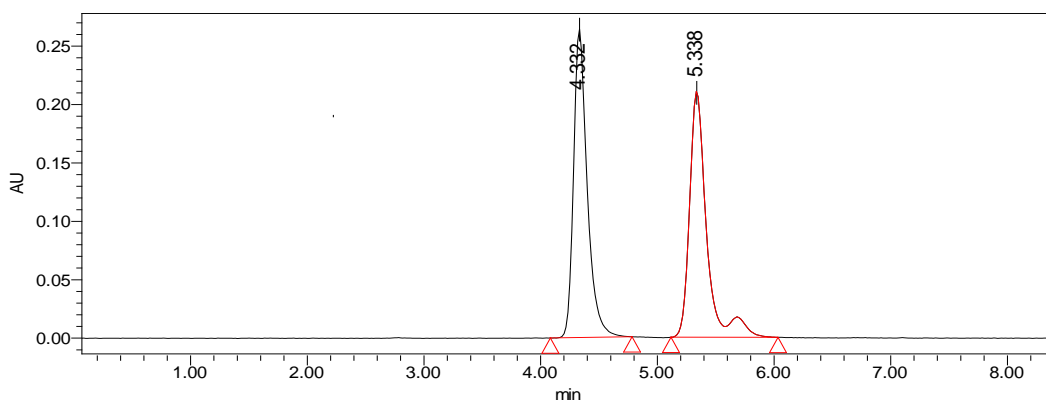
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1	4.572	2179963	50.25	284742	bb
2	6.299	2158006	49.75	203185	bb



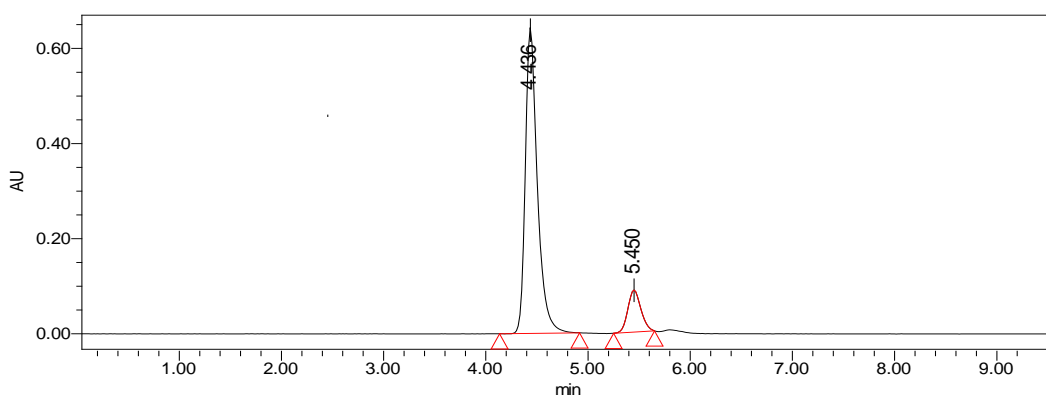
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.589	3096911	93.99	396109	bb
2	6.318	197927	6.01	18084	bb



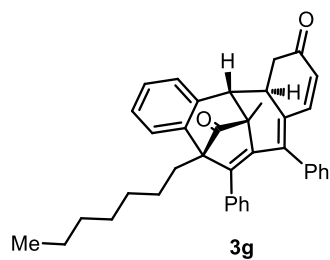
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



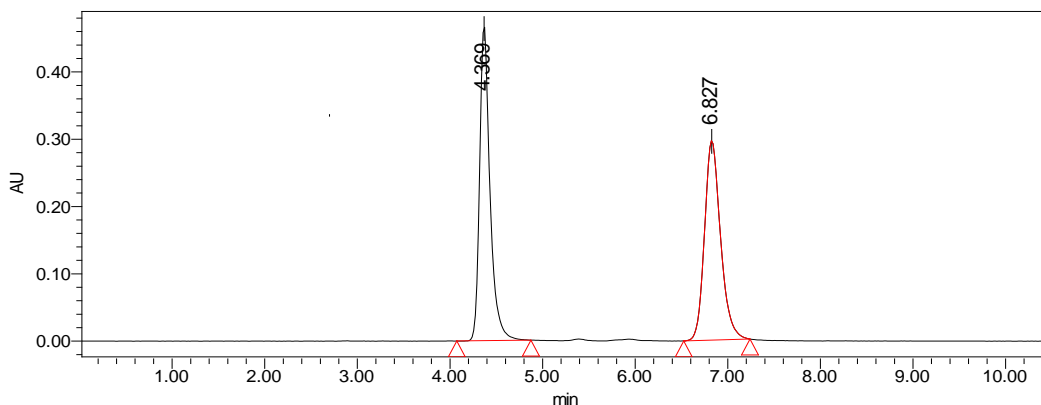
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1	4.332	2147715	49.96	263368	bb
2	5.338	2150796	50.04	210732	bb



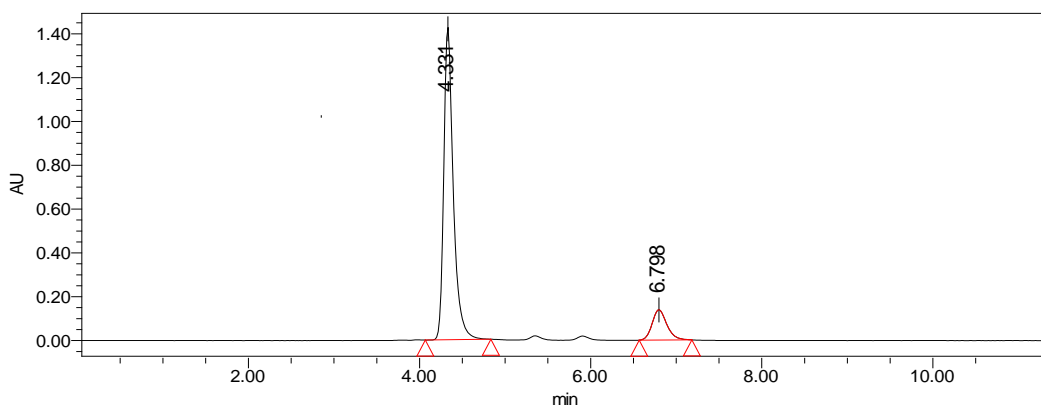
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.436	5245473	86.99	640984	bb
2	5.450	784673	13.01	88396	bb



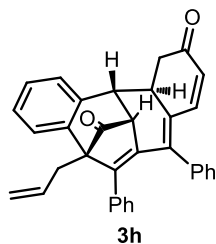
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



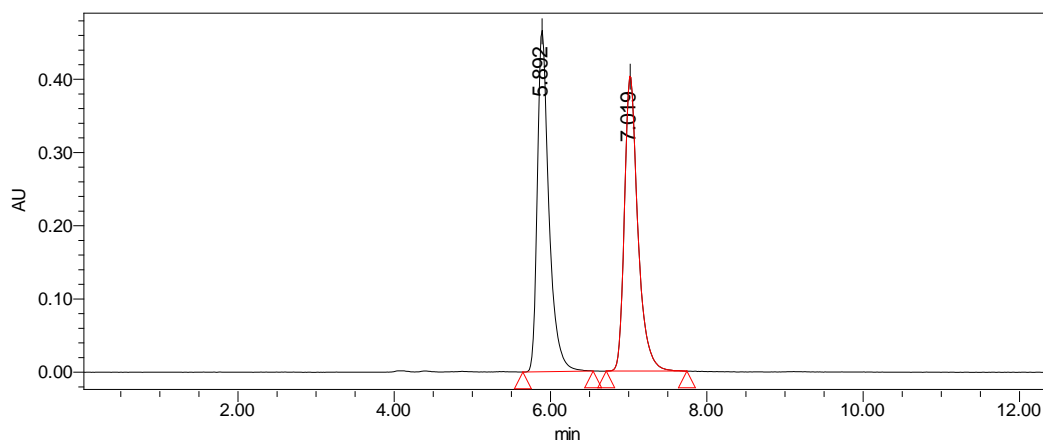
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.369	3629162	50.42	465609	bb
2	6.827	3568890	49.58	296598	bb



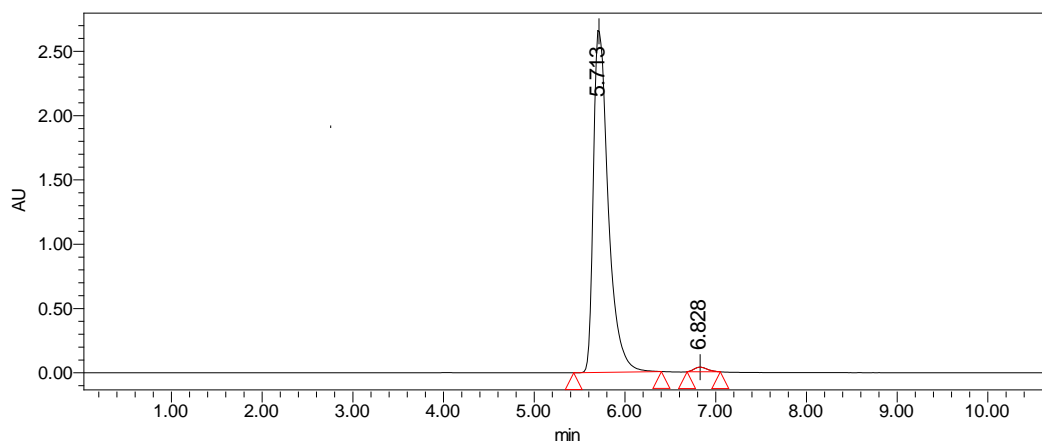
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.331	11022314	86.98	1422030	bb
2	6.798	1649350	13.02	138582	bb



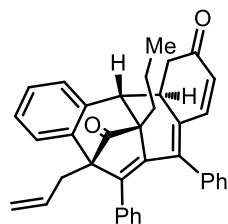
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



Entry	Retention time	Area	Area (%)	Height	Int type
1	5.892	4795231	49.98	465956	bb
2	7.019	4799667	50.02	404534	bb

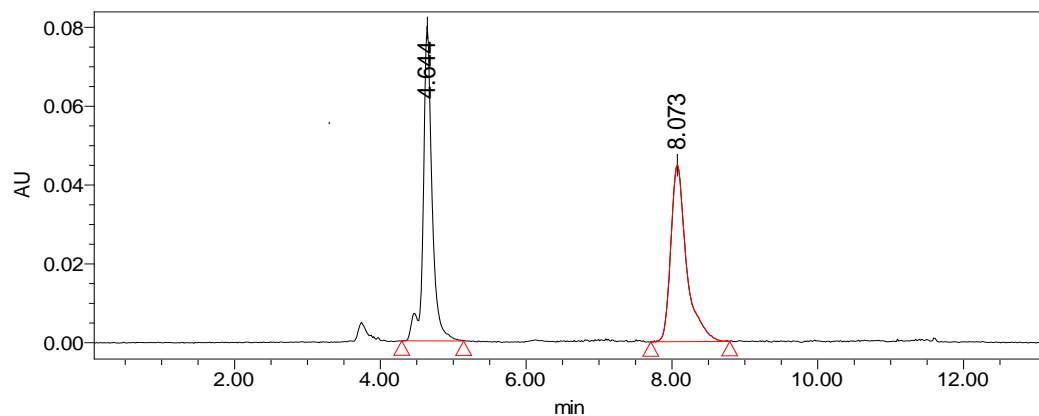


Entry	Retention time	Area	Area (%)	Height	Int type
1	5.713	30326901	98.81	2681253	bb
2	6.828	363727	1.19	35876	bb

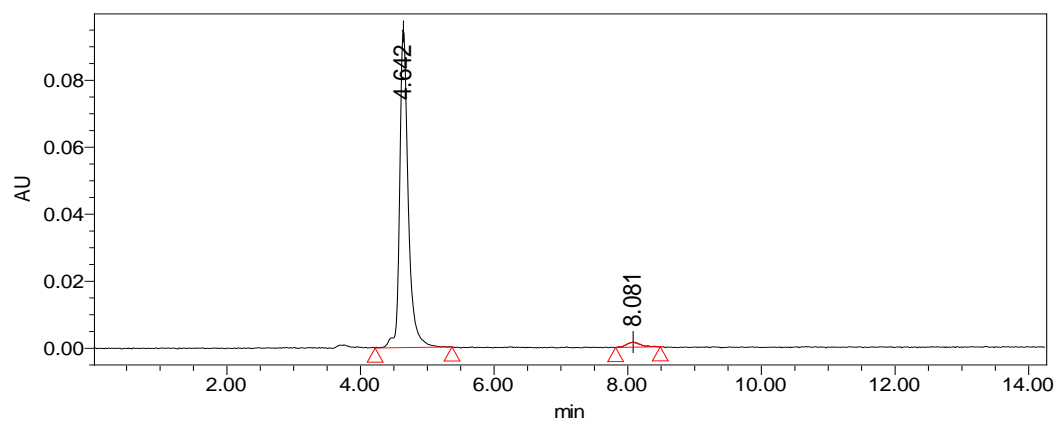


3i

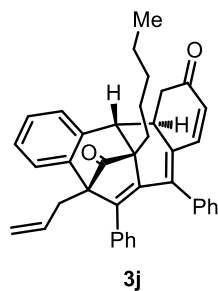
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



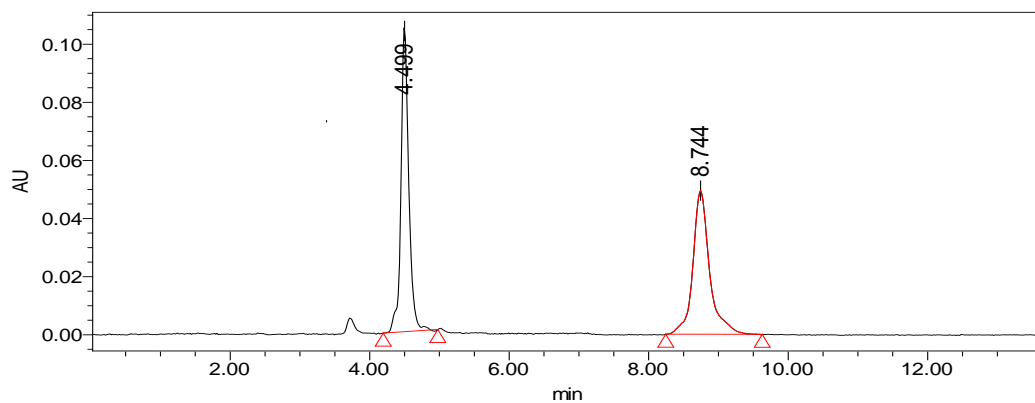
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.644	674434	50.11	79503	bb
2	8.073	671548	49.89	44864	bb



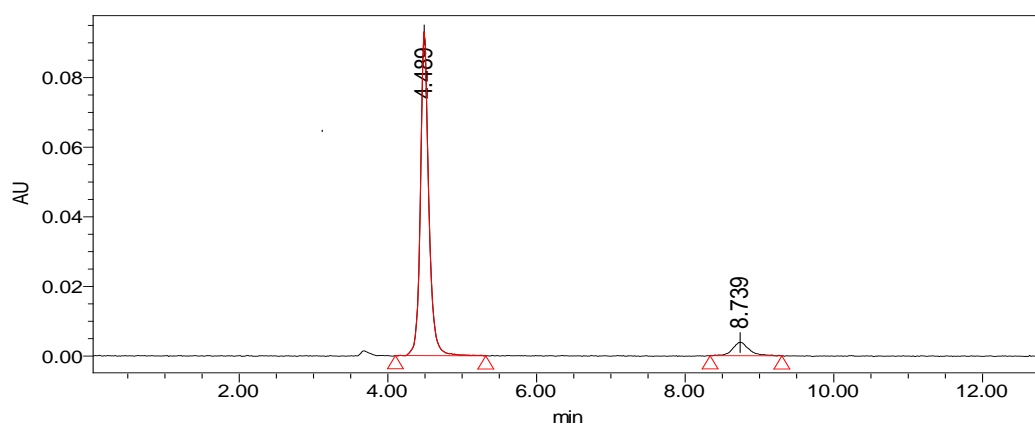
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.642	843669	97.48	95494	bb
2	8.081	21766	2.52	1534	bb



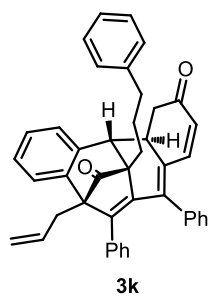
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



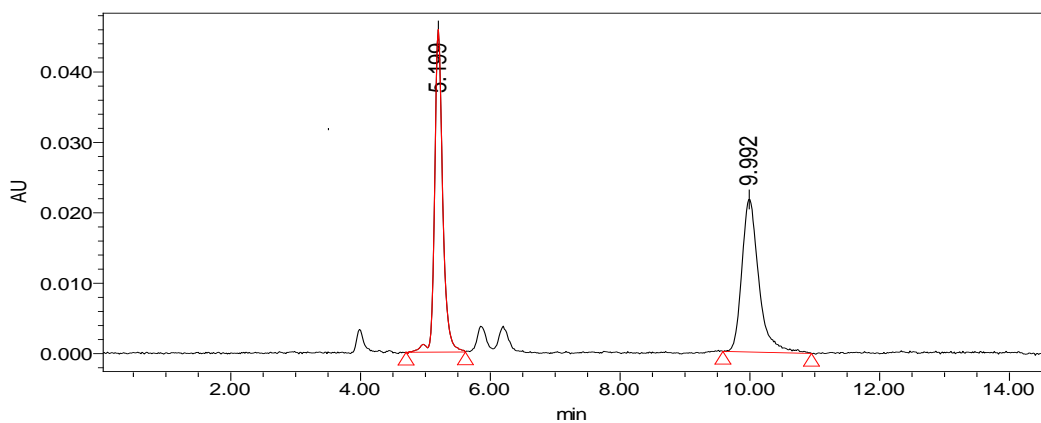
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.499	813149	49.85	104650	bb
2	8.744	818077	50.15	49368	bb



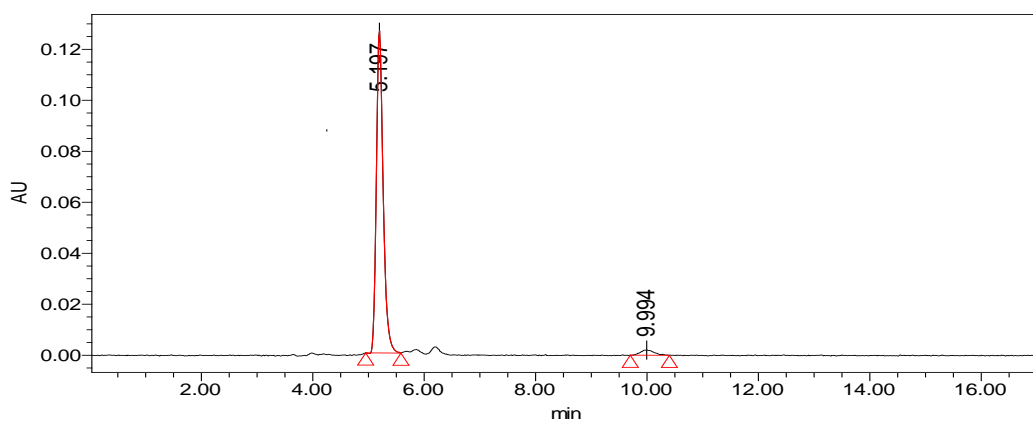
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.489	731995	92.47	93138	bb
2	8.739	59578	7.53	3842	bb



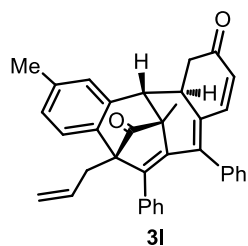
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



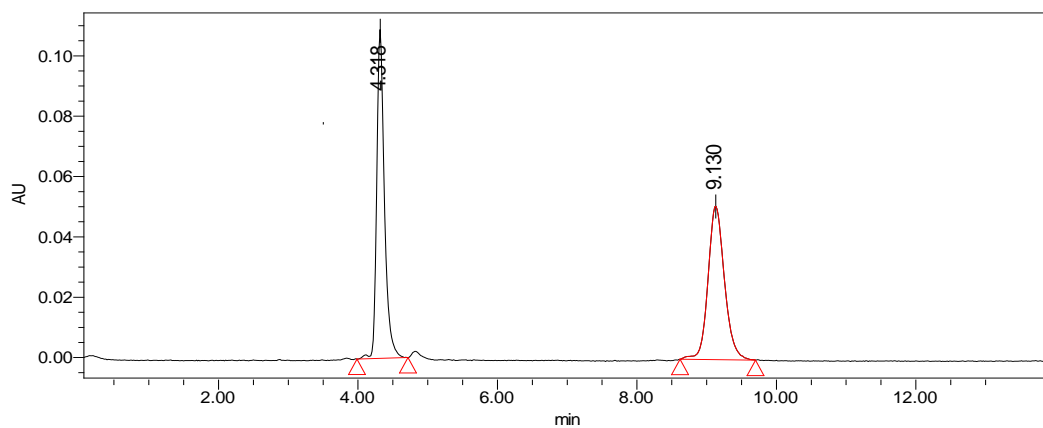
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.199	397813	50.21	45621	bb
2	9.992	394466	49.79	21741	bb



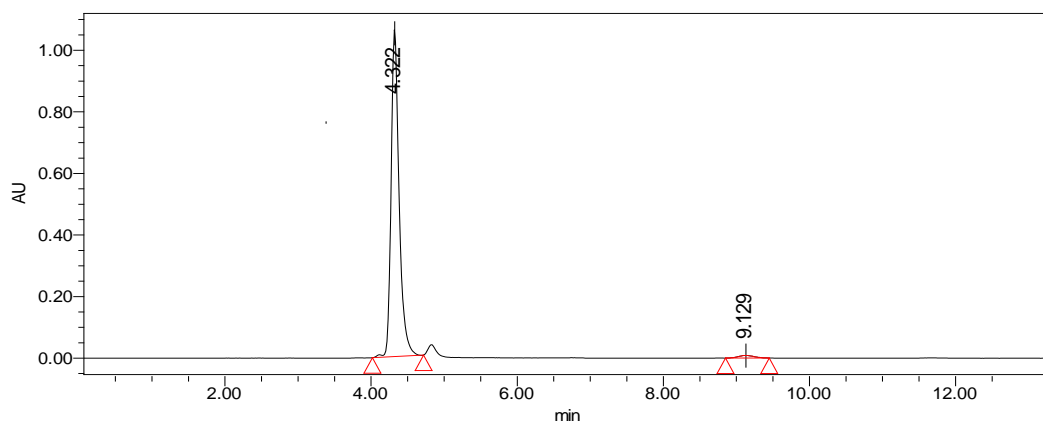
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.197	1076338	96.76	126206	bb
2	9.994	36088	3.24	2043	bb



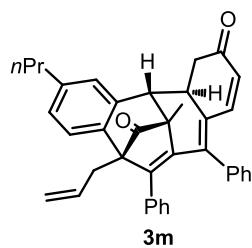
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



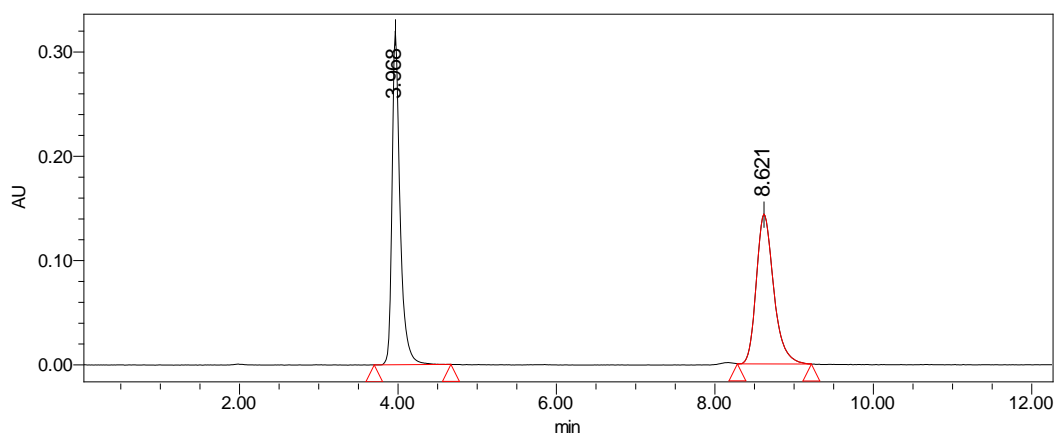
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.318	828226	49.83	108459	bb
2	9.130	833870	50.17	50873	bb



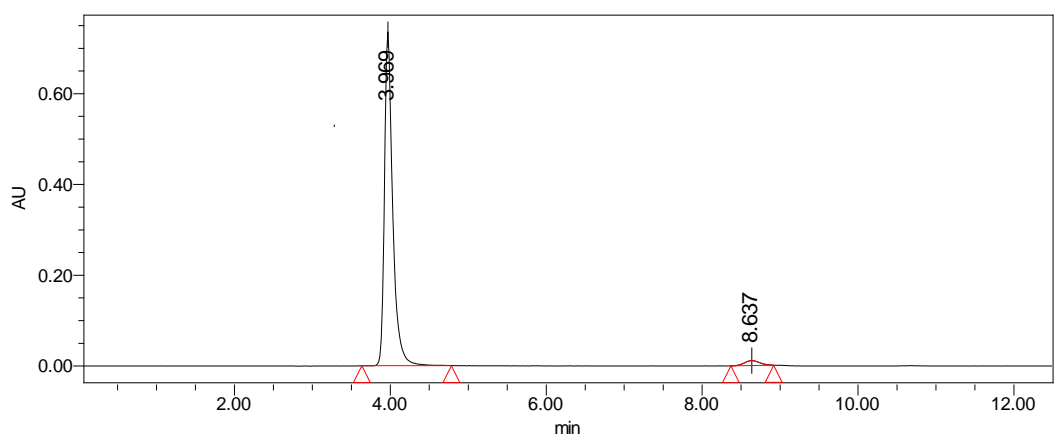
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.322	8081797	98.45	1061034	bb
2	9.129	127124	1.55	8363	bb



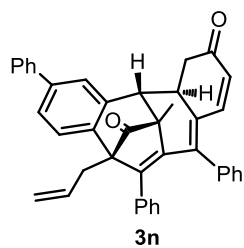
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



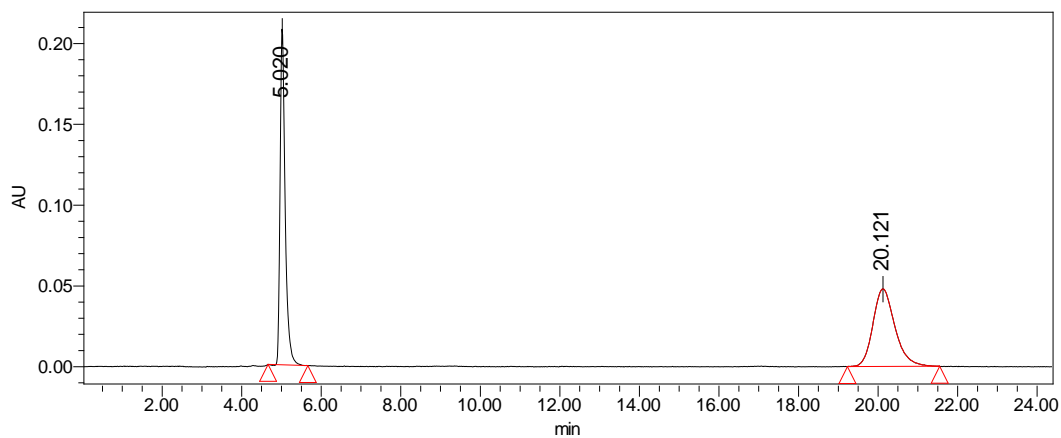
Entry	Retention time	Area	Area (%)	Height	Int type
1	3.968	2245698	50.70	317810	bb
2	8.621	2183610	49.30	143658	bb



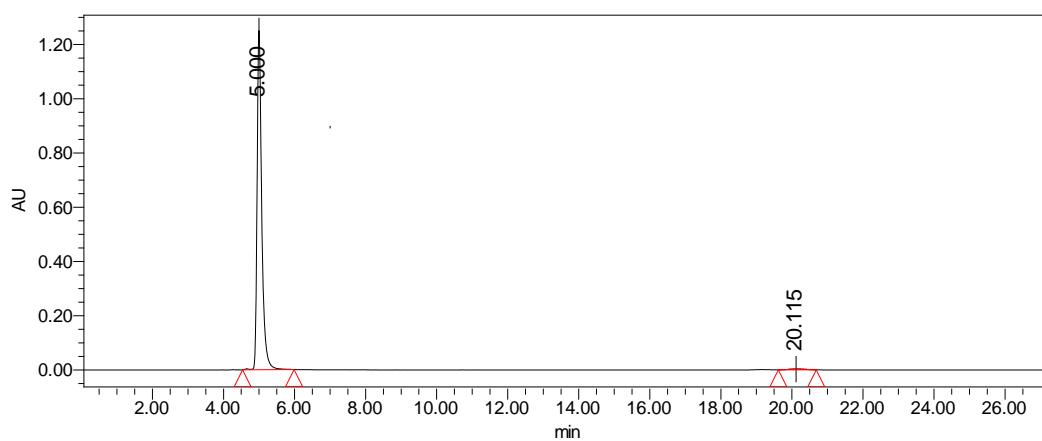
Entry	Retention time	Area	Area (%)	Height	Int type
1	3.969	5397906	97.32	731681	bb
2	8.637	148899	2.68	10942	bb



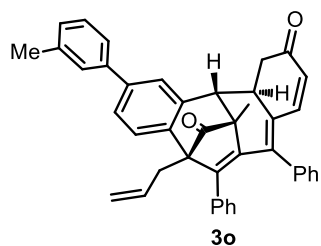
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



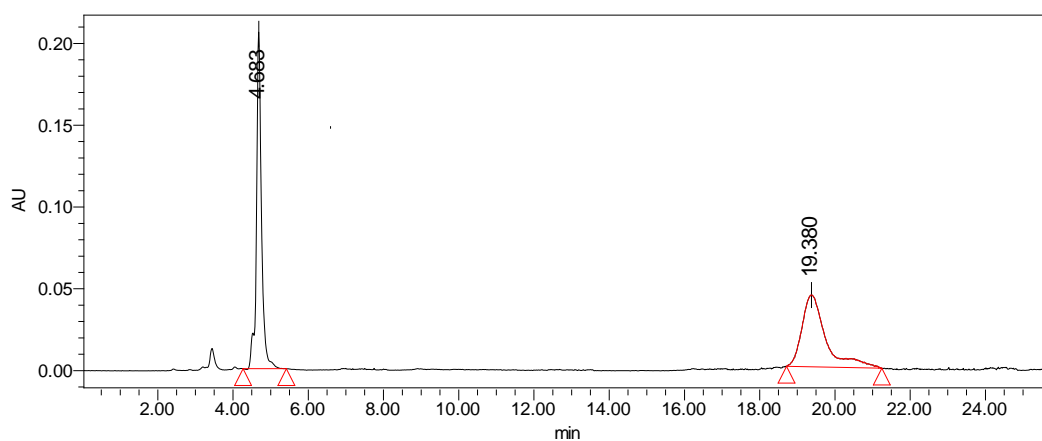
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.020	1827657	49.89	208606	bb
2	20.121	1835440	50.11	47934	bb



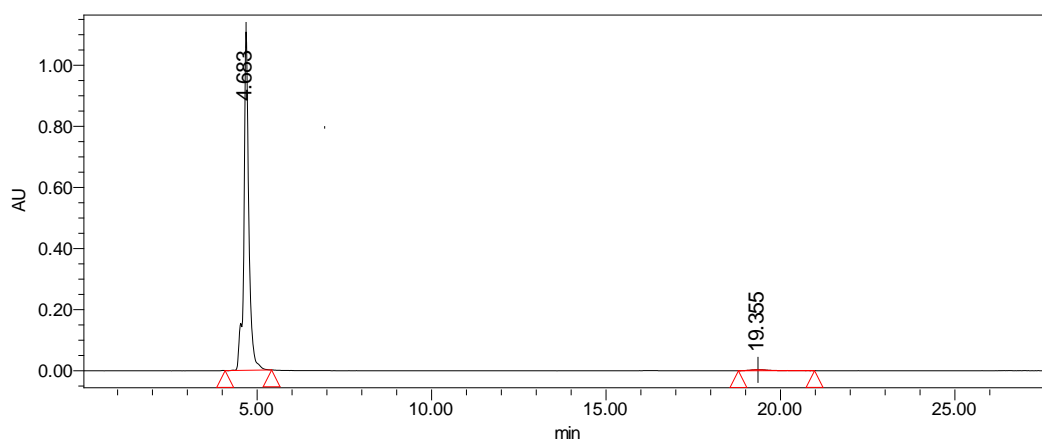
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.000	11339023	99.11	1248605	bb
2	20.115	101664	0.89	3222	bb



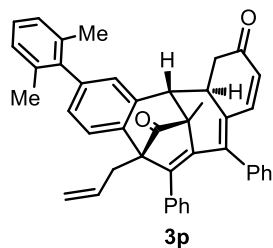
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



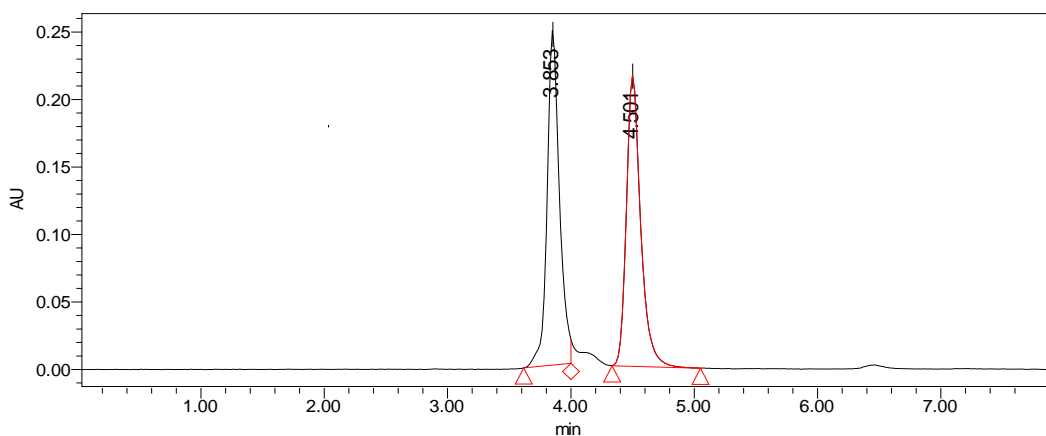
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.683	1918381	49.93	205147	bb
2	19.380	1923824	50.07	43955	bb



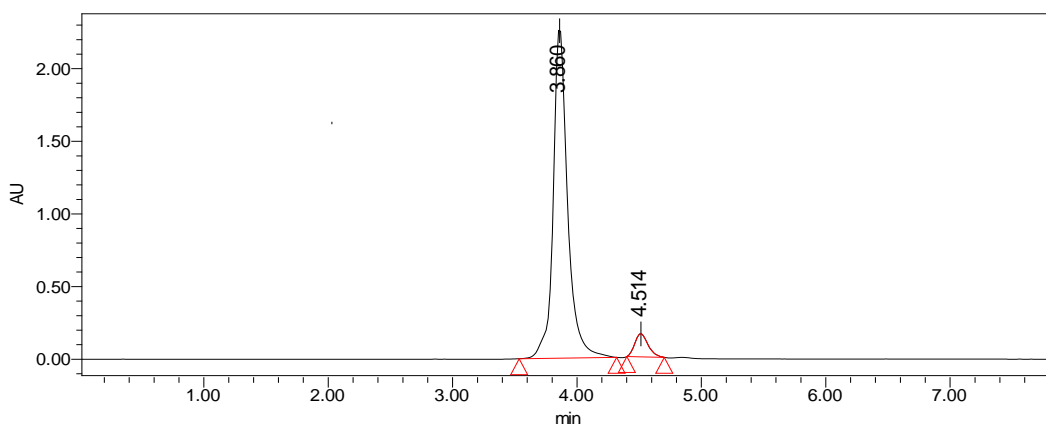
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.683	10986670	98.87	1106660	bb
2	19.355	125674	1.13	3154	bb



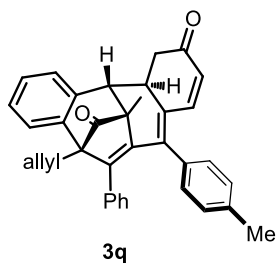
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



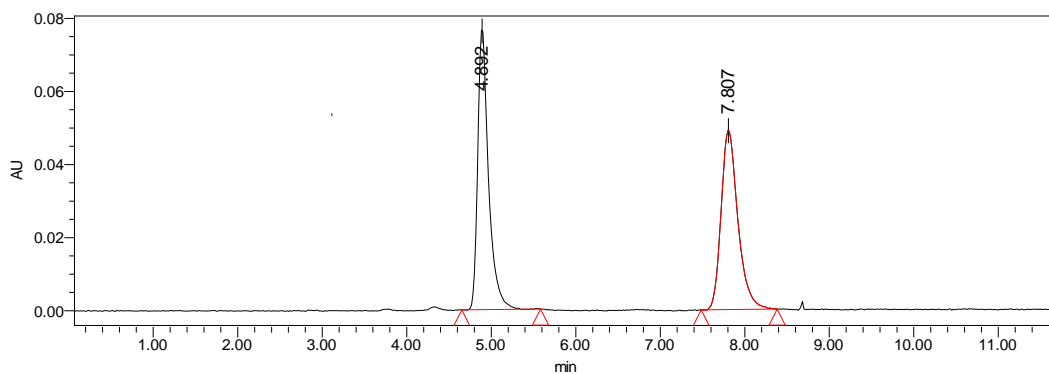
Entry	Retention time	Area	Area (%)	Height	Int type
1	3.853	1721681	49.85	246560	bv
2	4.501	1731761	50.15	214895	bb



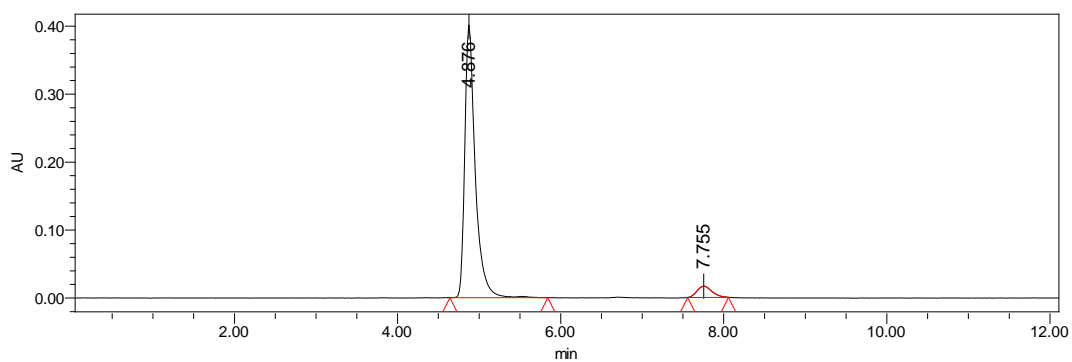
Entry	Retention time	Area	Area (%)	Height	Int type
1	3.860	18352219	93.91	2289046	bb
2	4.514	1189301	6.09	159975	bb



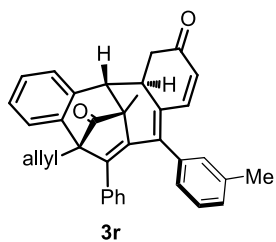
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



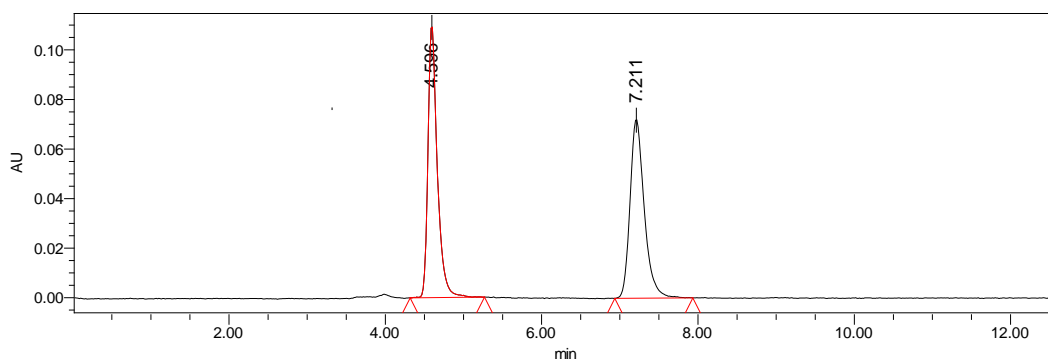
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.892	681987	50.15	77182	bb
2	7.807	677879	49.85	49190	bb



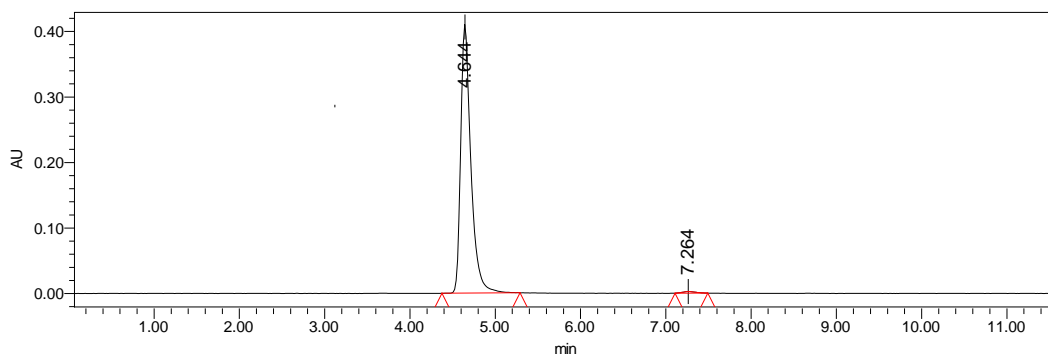
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.876	3582738	94.48	400528	bb
2	7.755	209445	5.52	16634	bb



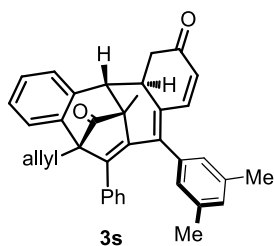
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



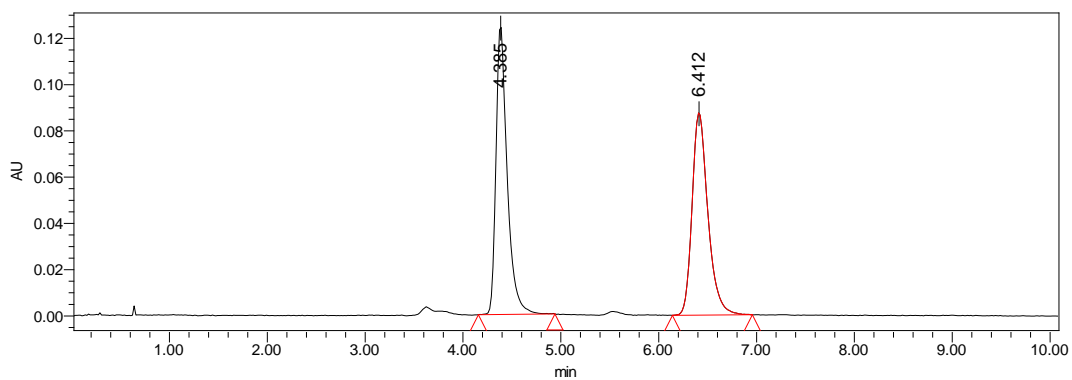
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.596	911563	49.95	109547	bb
2	7.211	913310	50.05	72195	bb



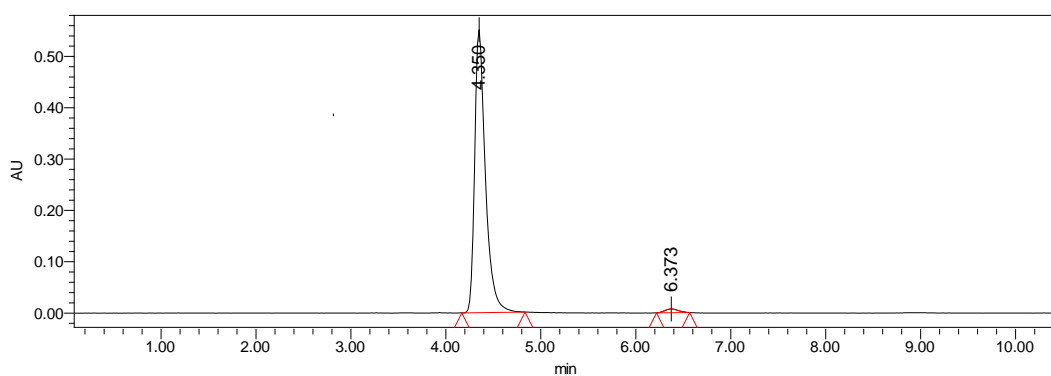
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.644	3395232	99.17	409151	bb
2	7.264	28575	0.83	2604	bb



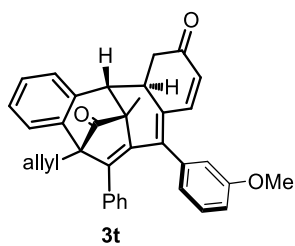
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



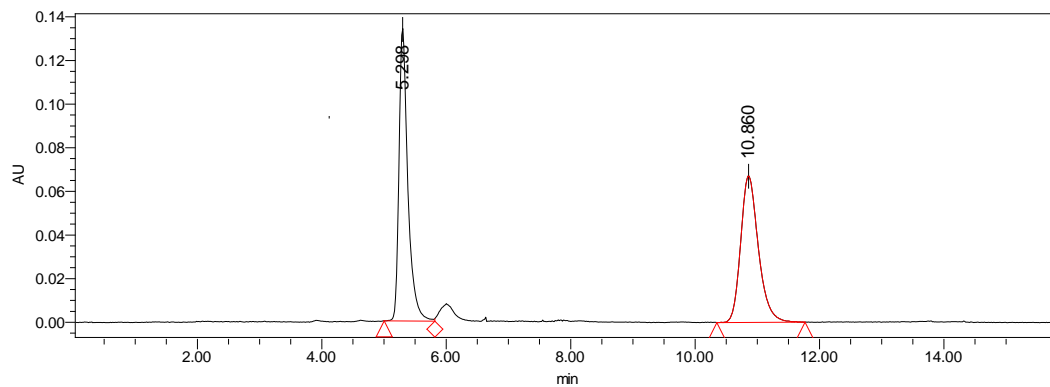
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.385	992454	50.25	124265	bb
2	6.412	982703	49.75	87655	bb



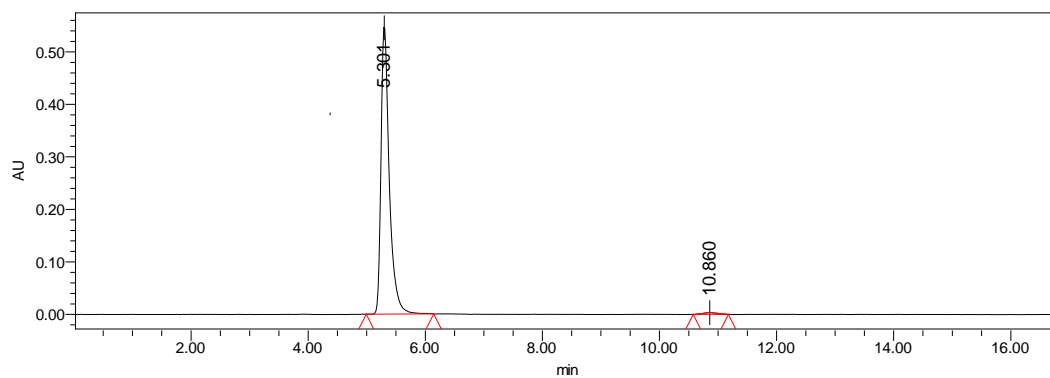
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.350	4309993	98.35	549417	bb
2	6.373	72461	1.65	7424	bb



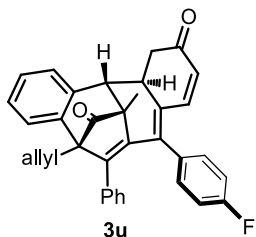
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



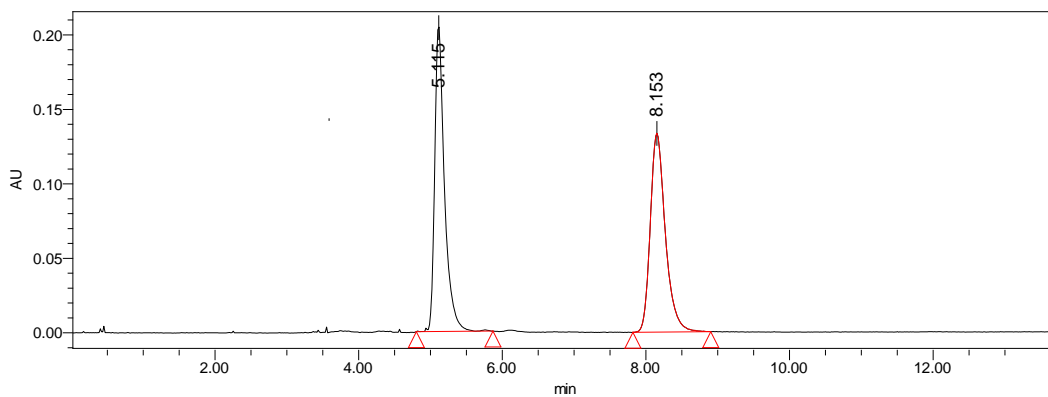
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.298	1327573	50.00	133953	bv
2	10.860	1327678	50.00	67159	bb



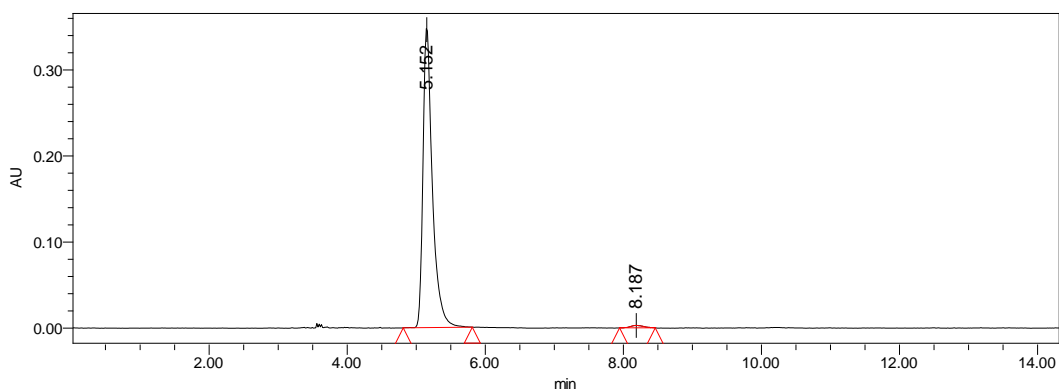
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.301	5381719	98.96	550799	bb
2	10.860	56728	1.04	3275	bb



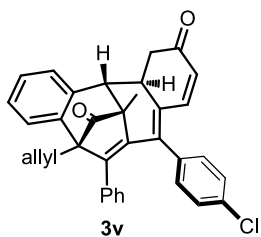
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



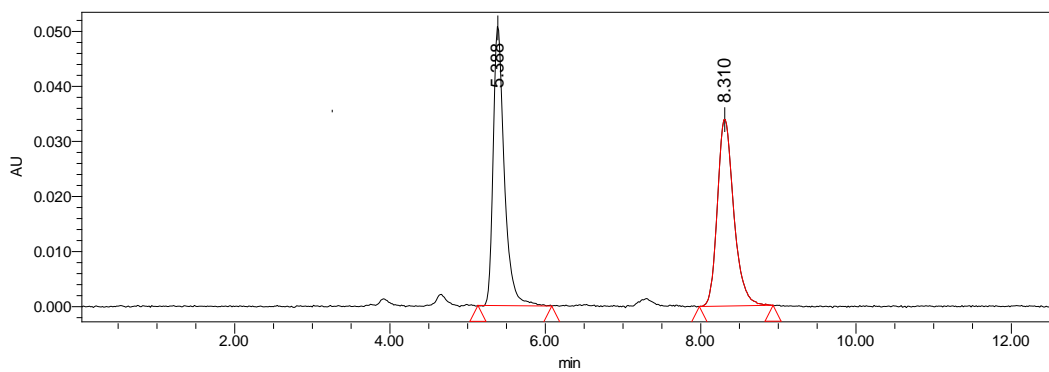
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.115	1937219	49.97	204748	bb
2	8.153	1939367	50.03	133479	bb



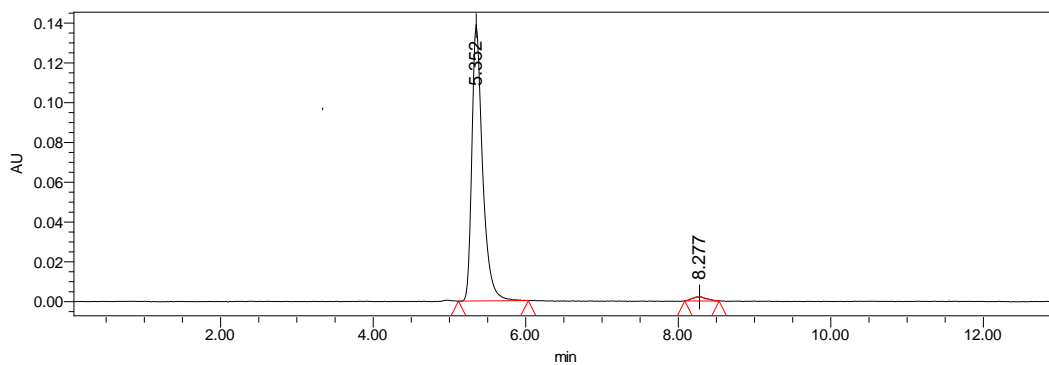
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.152	3313364	98.89	350406	bb
2	8.187	37352	1.11	2823	bb



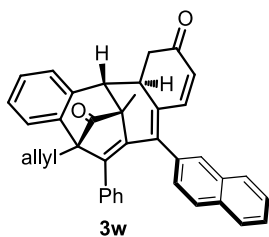
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



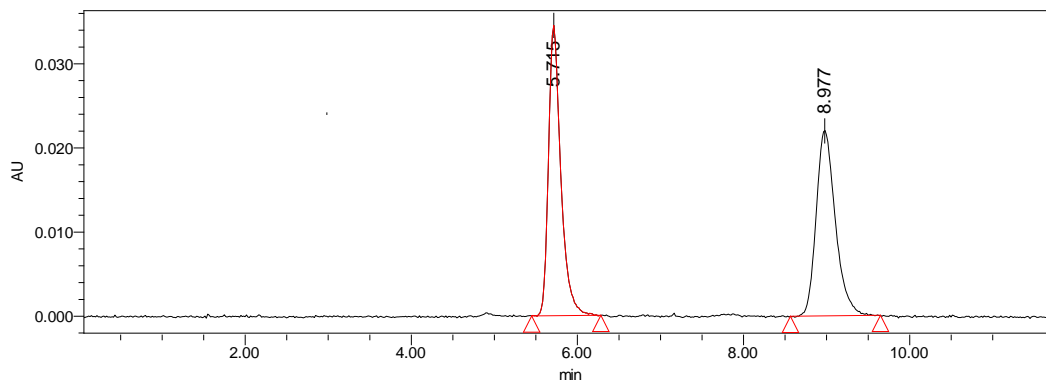
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.388	503170	50.32	50908	bb
2	8.310	496869	49.68	33981	bb



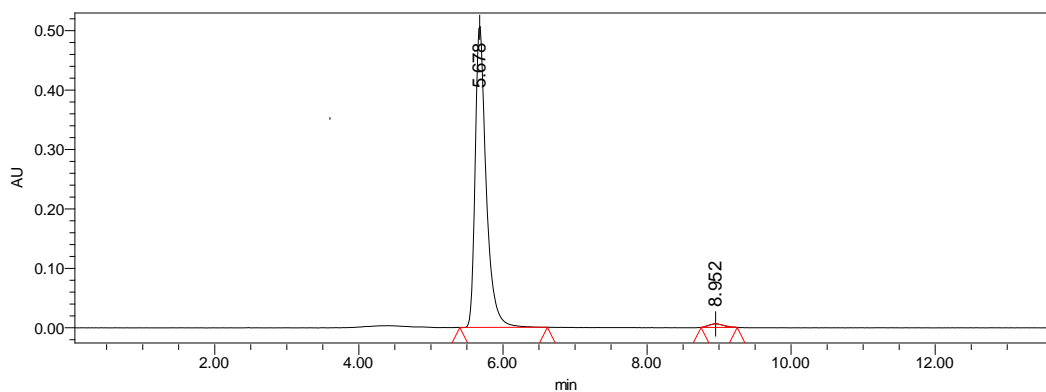
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.352	1353544	98.00	138605	bb
2	8.277	27602	2.00	2039	bb



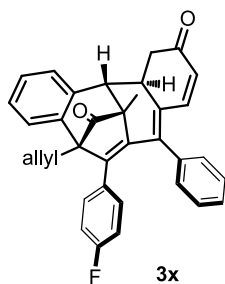
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



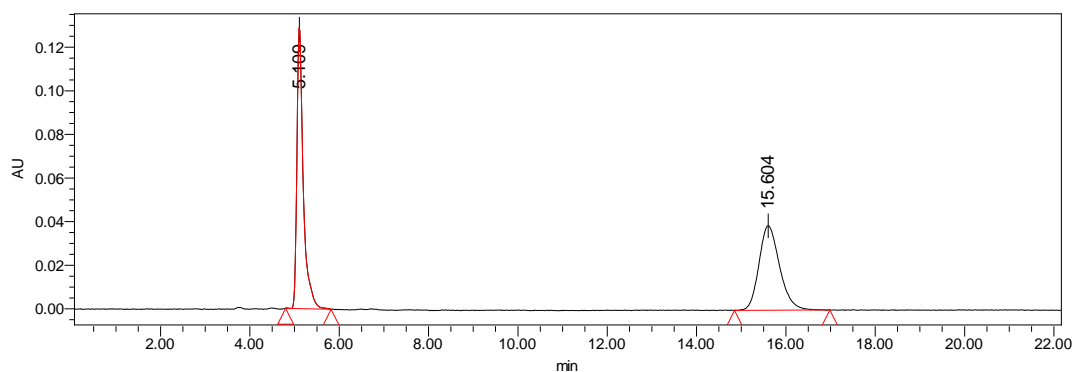
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.715	355927	50.13	34350	bb
2	8.977	354012	49.87	22026	bb



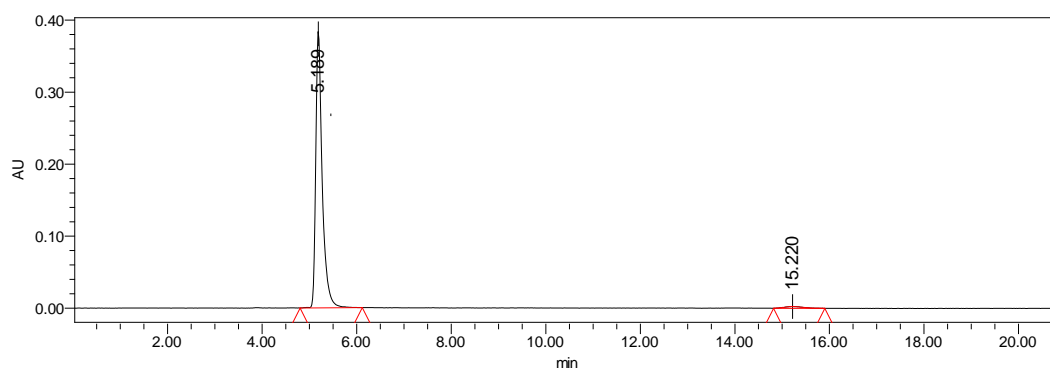
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.678	5373604	98.43	507181	bb
2	8.952	85891	1.57	6121	bb



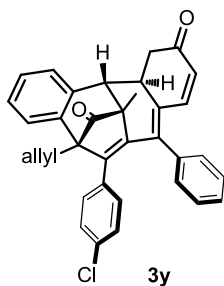
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



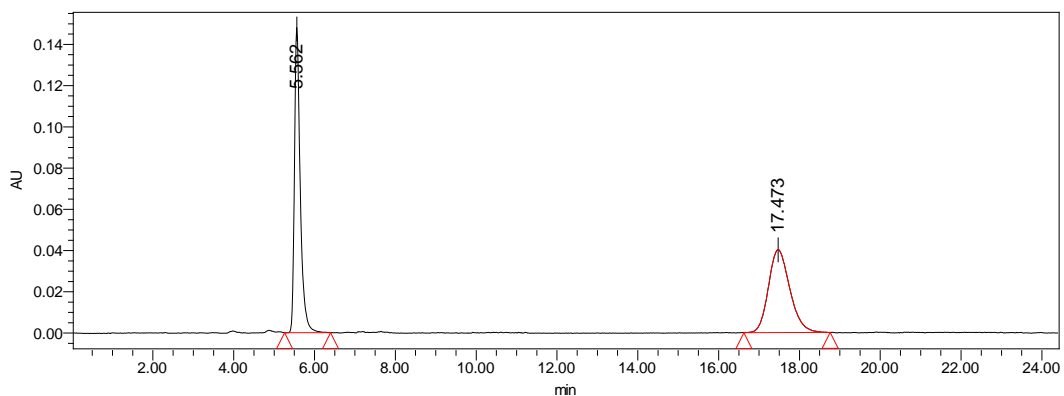
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.109	1277773	50.70	129537	bb
2	15.604	1242654	49.30	38743	bb



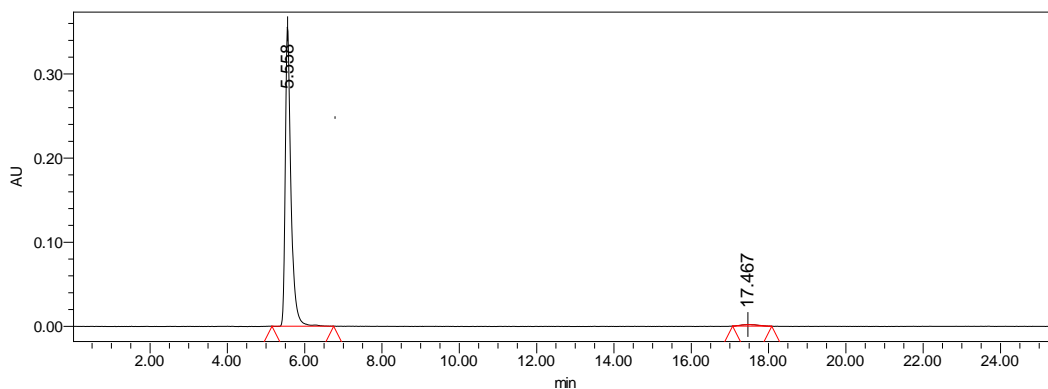
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.189	3631344	98.01	384123	bb
2	15.220	73561	1.99	2575	bb



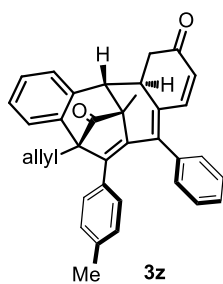
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



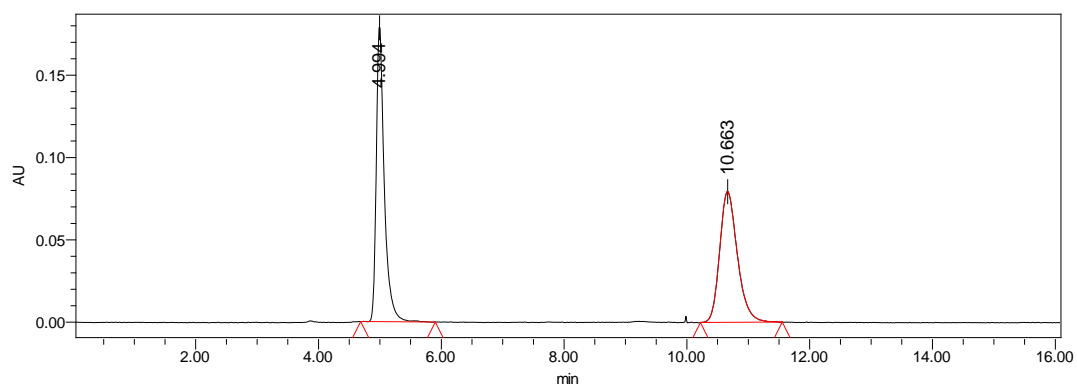
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.562	1475931	50.00	147828	bb
2	17.473	1475841	50.00	40169	bb



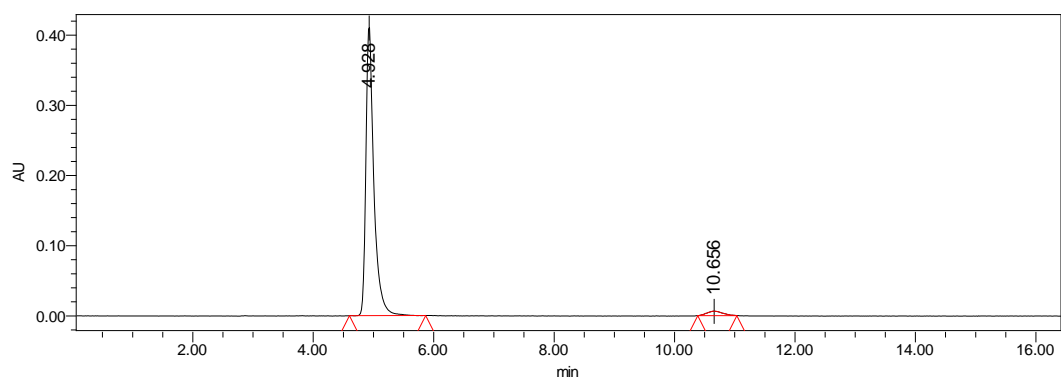
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.558	3608782	98.49	356834	bb
2	17.467	55214	1.51	1899	bb



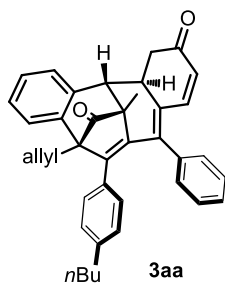
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



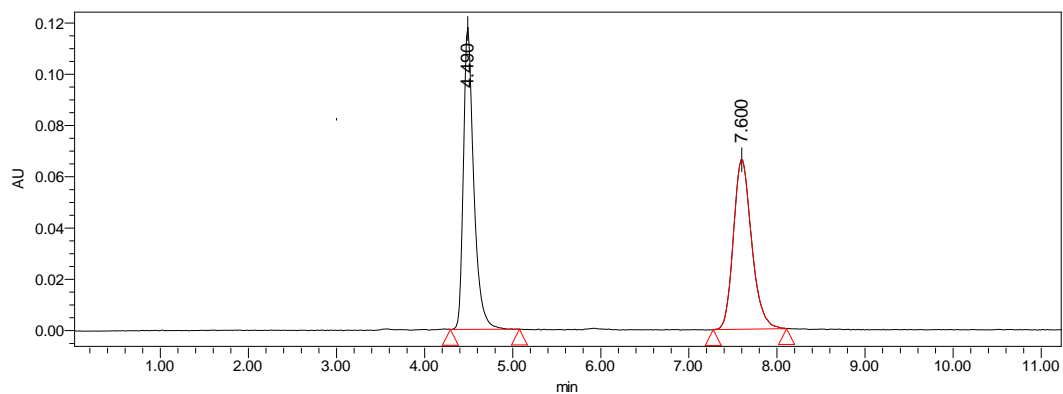
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.994	1622877	50.46	180118	bb
2	10.663	1593436	49.54	79544	bb



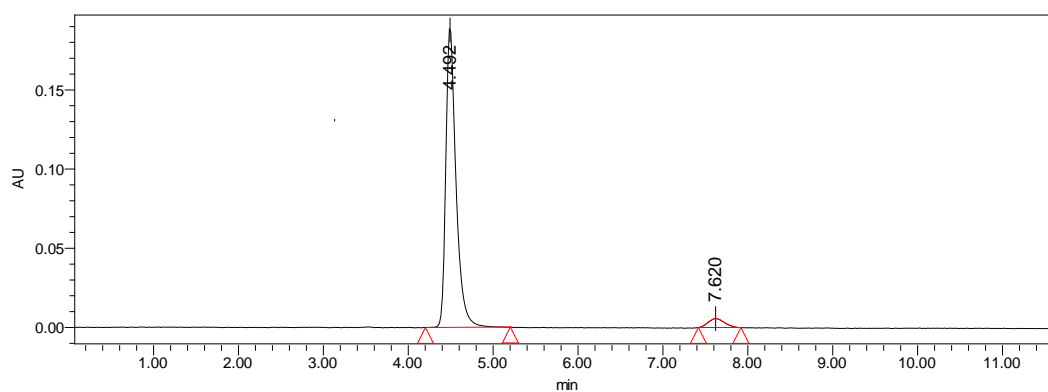
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.928	3769915	96.97	411387	bb
2	10.656	117743	3.03	6336	bb



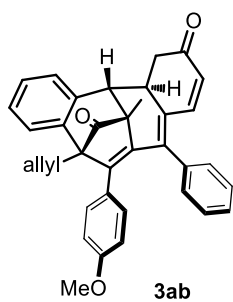
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



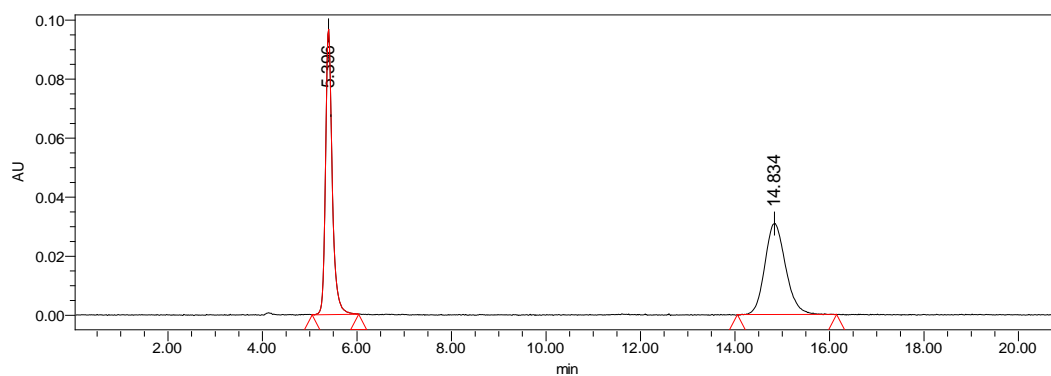
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.490	961438	50.28	117533	bb
2	7.600	950646	49.72	66402	bb



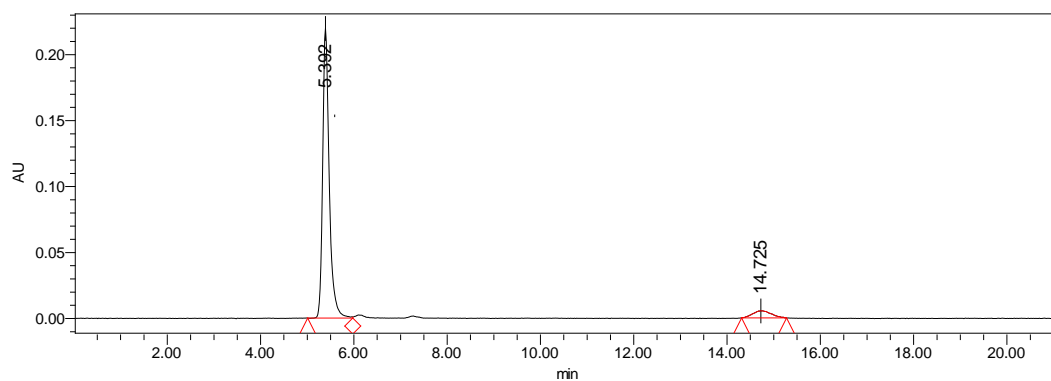
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.492	1571237	95.52	190137	bb
2	7.620	73715	4.48	5639	bb



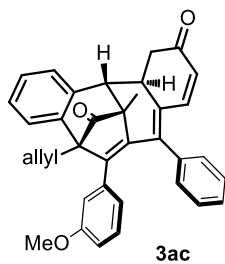
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



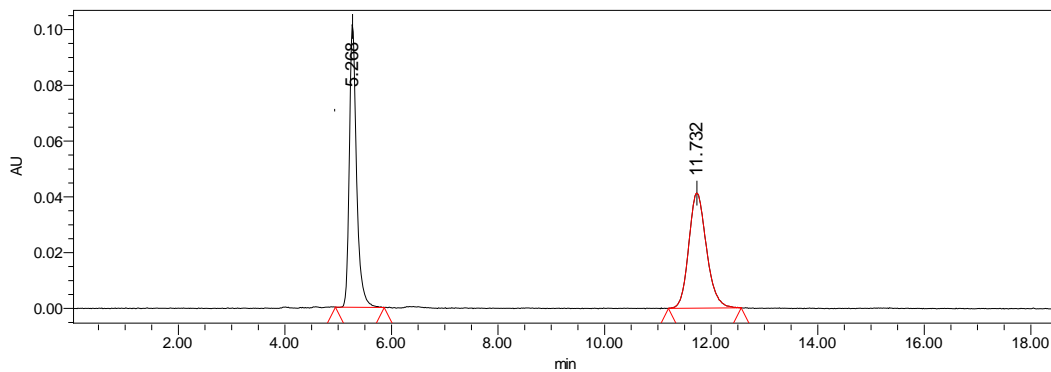
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.396	950915	50.32	96666	bb
2	14.834	938977	49.68	30842	bb



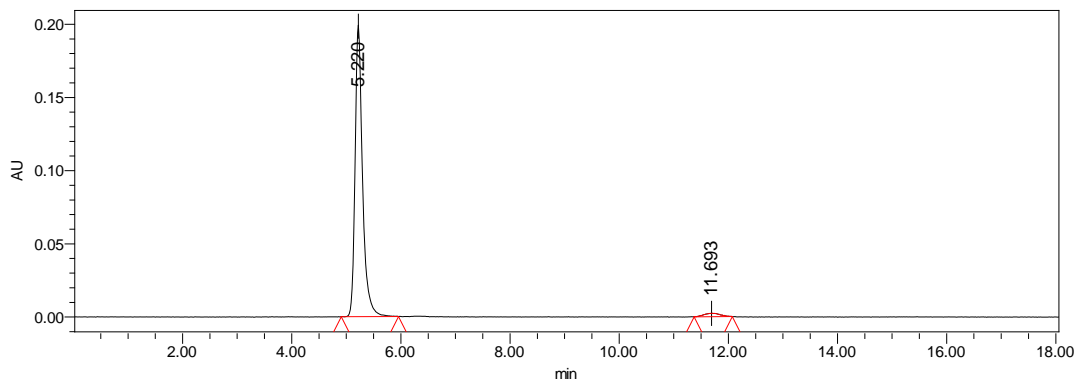
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.392	2145170	93.58	219043	bv
2	14.725	147184	6.42	5273	bb



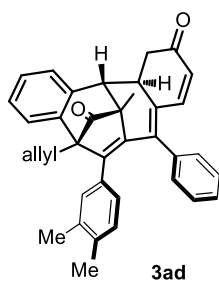
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



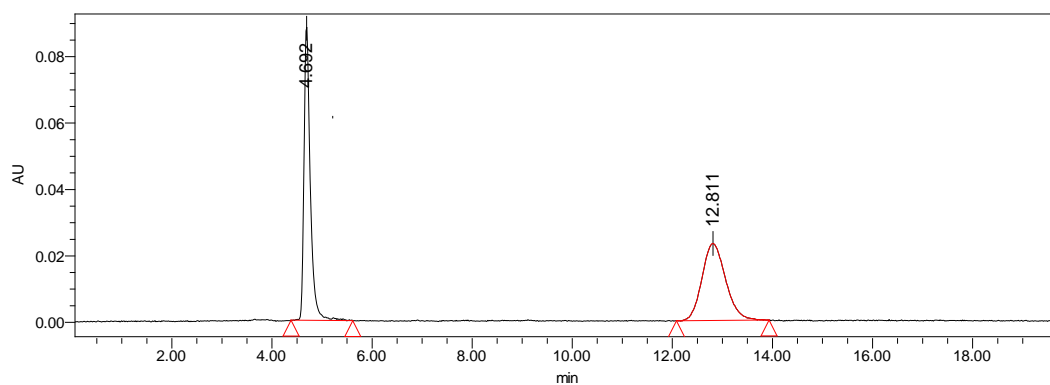
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.268	948563	49.86	101364	bb
2	11.732	953731	50.14	41268	bb



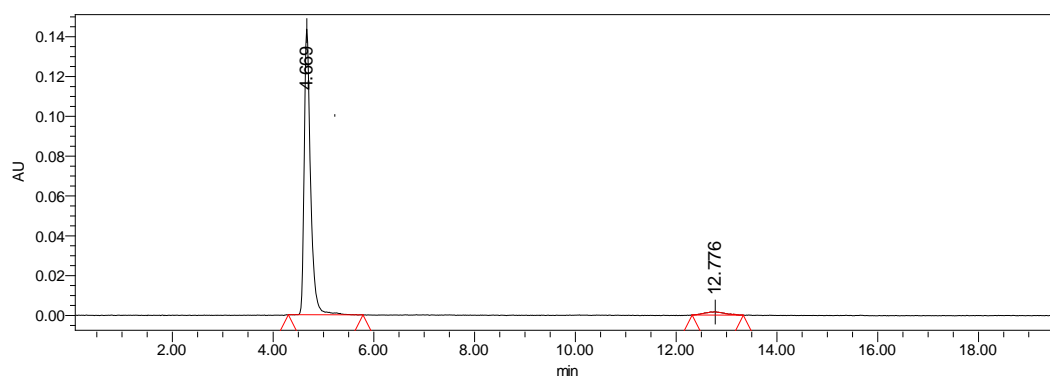
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.220	1886777	97.47	198859	bb
2	11.693	48929	2.53	2346	bb



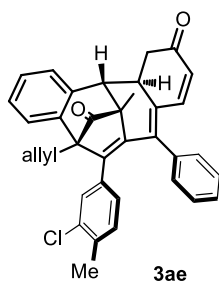
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



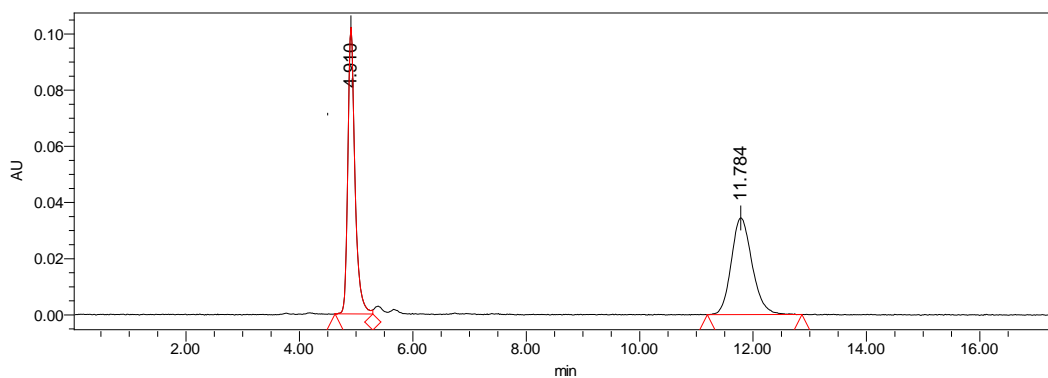
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.692	774184	50.55	88345	bb
2	12.811	757383	49.45	23180	bb



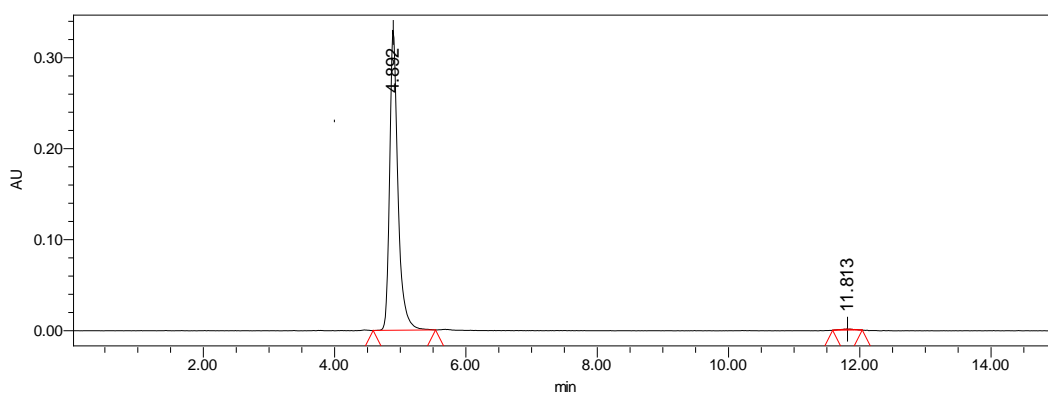
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.669	1256762	96.53	143328	bb
2	12.776	45165	3.47	1589	bb



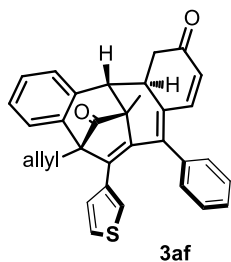
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



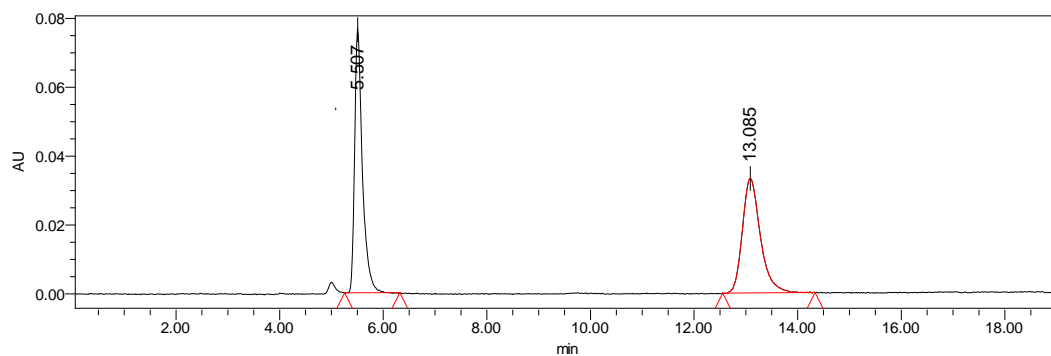
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.910	891243	50.35	101896	bv
2	11.784	879022	49.65	34484	bb



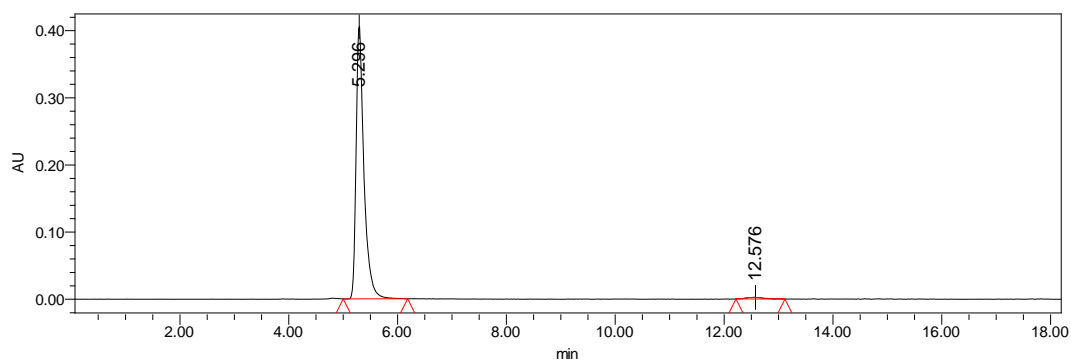
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.892	2891429	99.44	330284	bb
2	11.813	16201	0.56	1062	bb



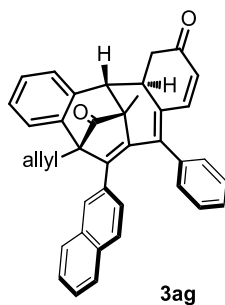
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



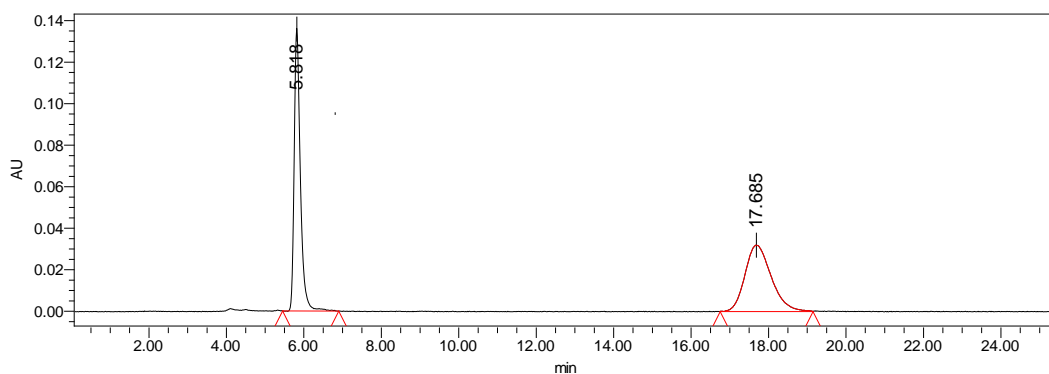
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.507	797752	49.93	76868	bb
2	13.085	799960	50.07	33264	bb



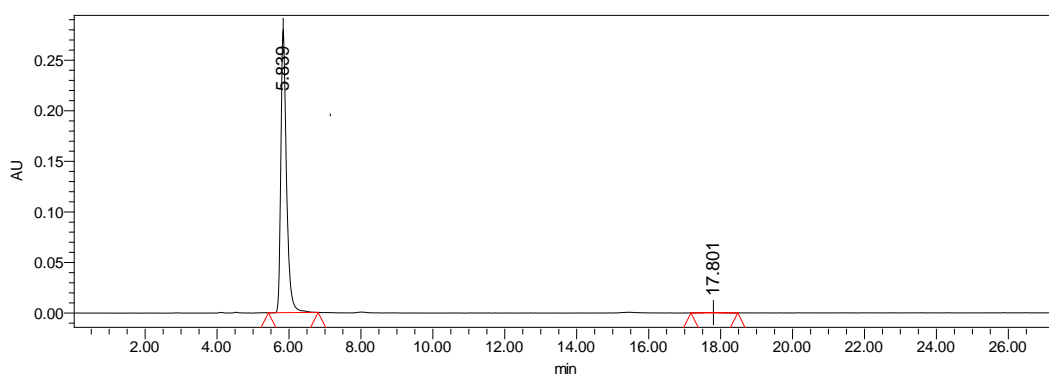
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.296	4068516	98.53	406703	bb
2	12.576	60748	1.47	2584	bb



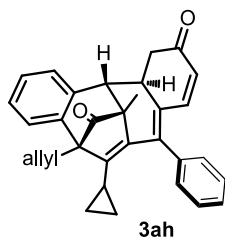
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



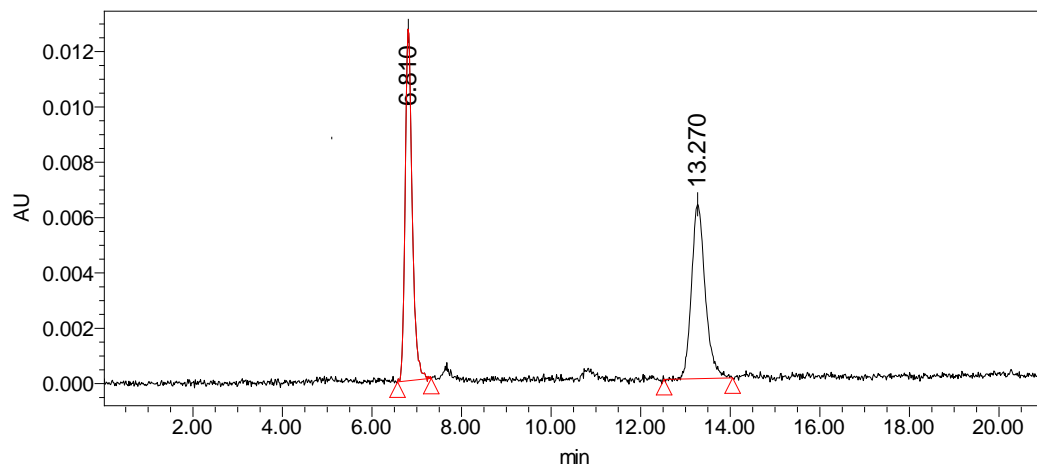
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.818	1512614	50.16	135979	bb
2	17.685	1503164	49.84	32001	bb



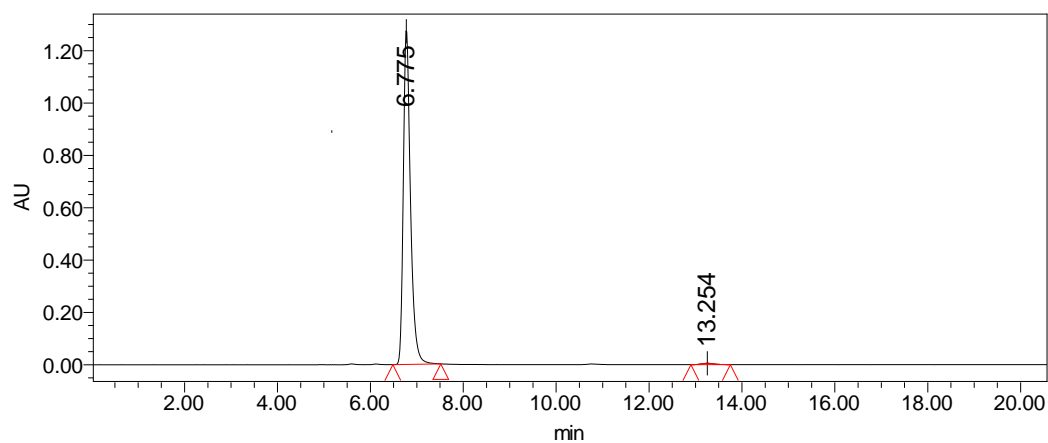
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.839	3054852	99.46	279867	bb
2	17.801	16457	0.54	442	bb



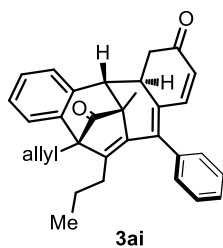
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



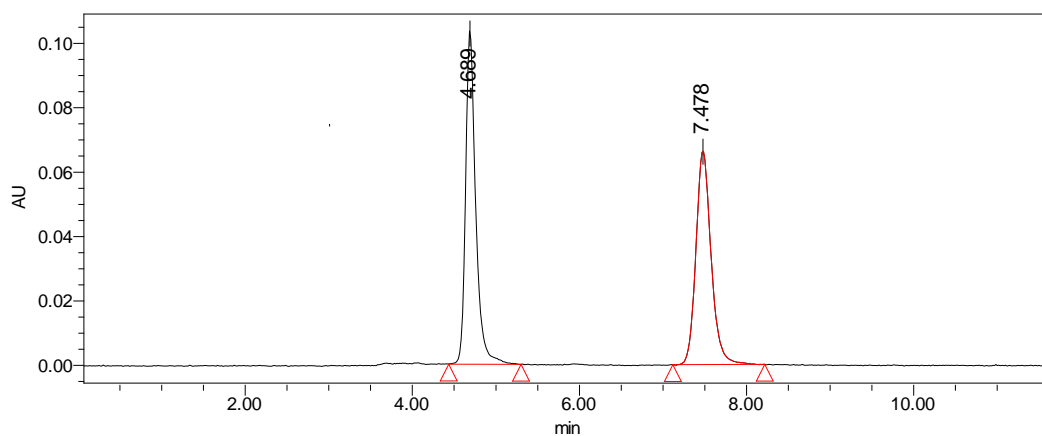
Entry	Retention time	Area	Area (%)	Height	Int type
1	6.810	138480	50.68	12692	bb
2	13.270	134761	49.32	6283	bb



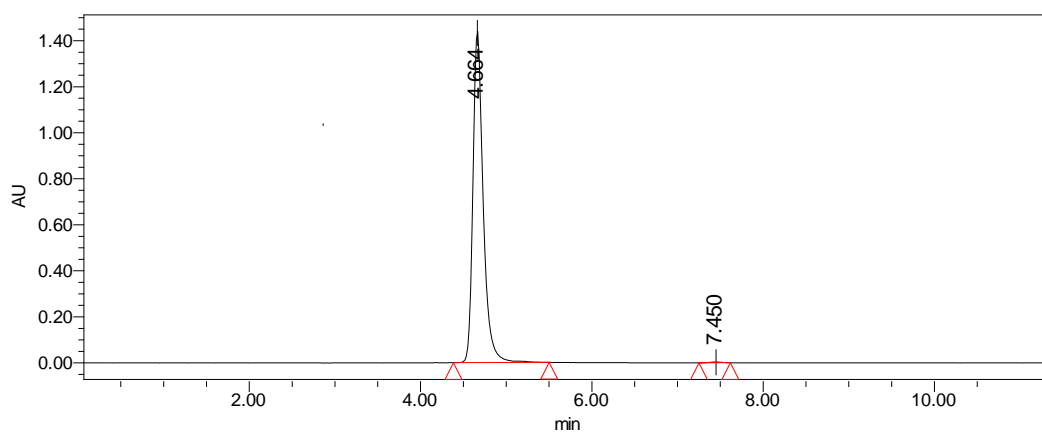
Entry	Retention time	Area	Area (%)	Height	Int type
1	6.775	13661837	99.24	1283138	bb
2	13.254	104254	0.76	5198	bb



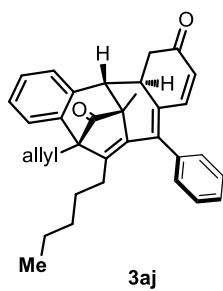
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



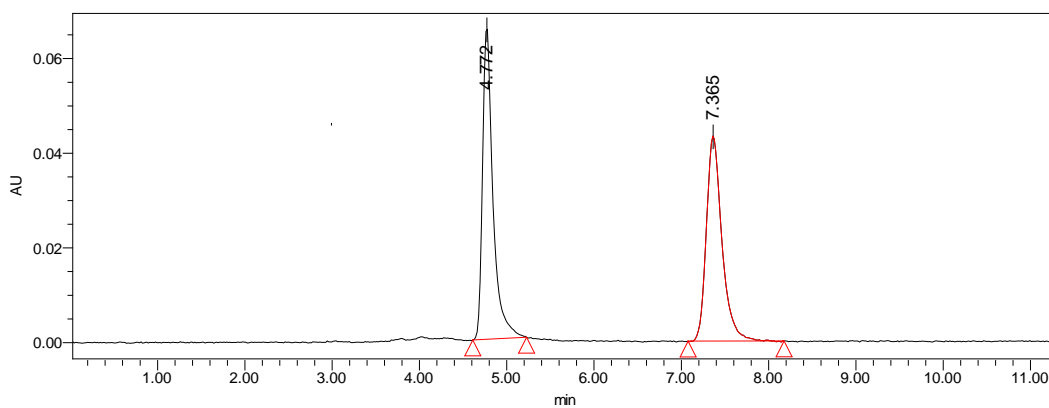
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.689	867934	50.84	103711	bb
2	7.478	839119	49.16	66390	bb



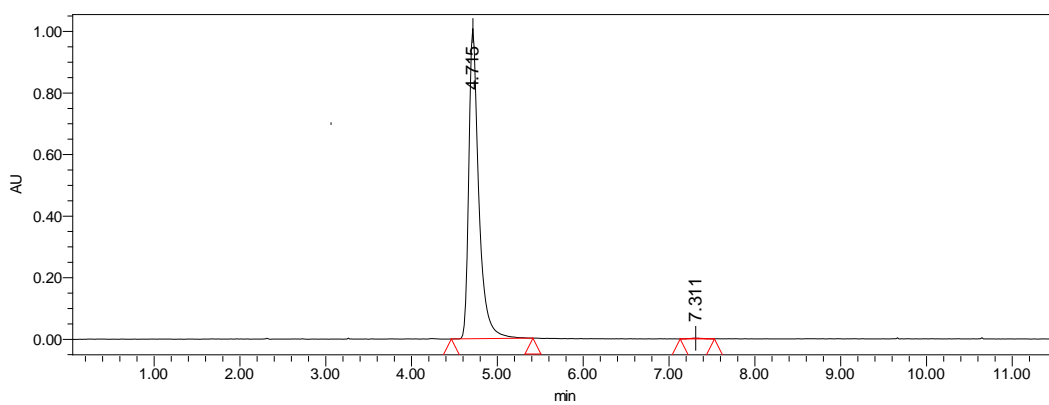
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.664	12002151	99.77	1437185	bb
2	7.450	27534	0.23	2553	bb



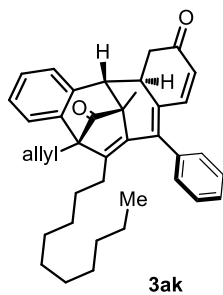
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



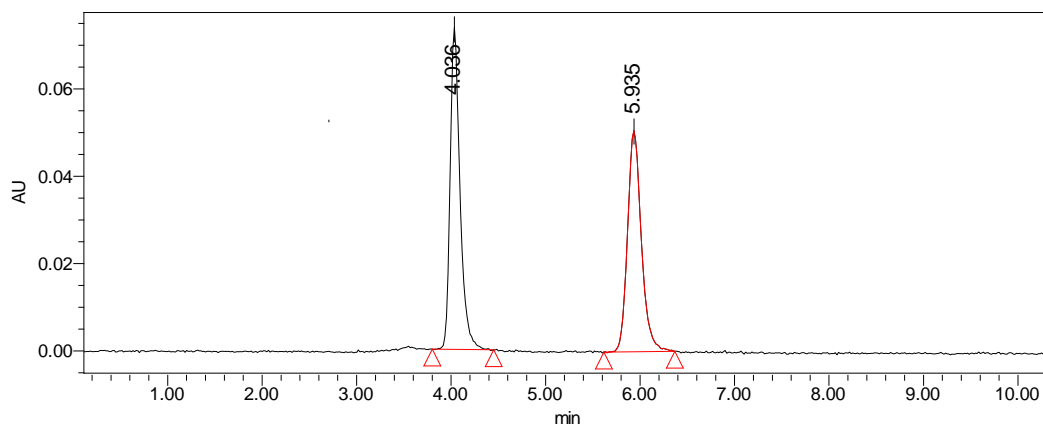
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.772	546383	50.41	65613	bb
2	7.365	537461	49.59	43337	bb



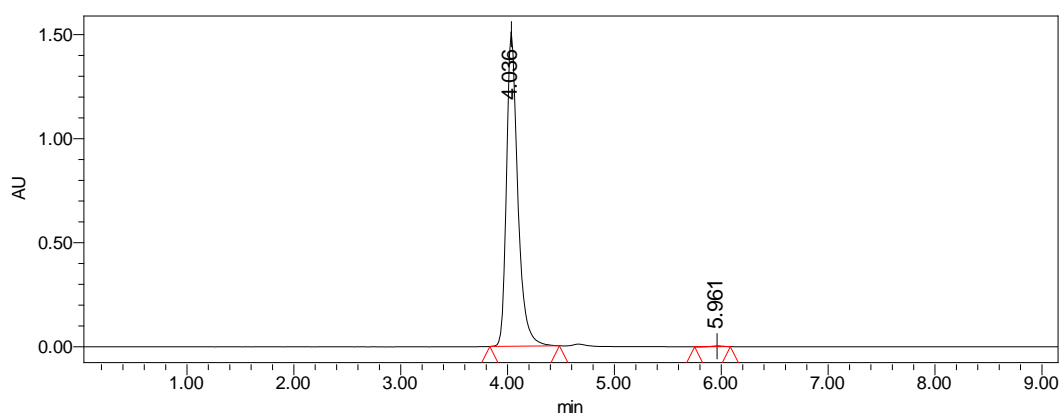
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.715	8144008	99.72	1003087	bb
2	7.311	22855	0.28	1987	bb



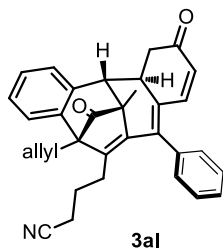
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



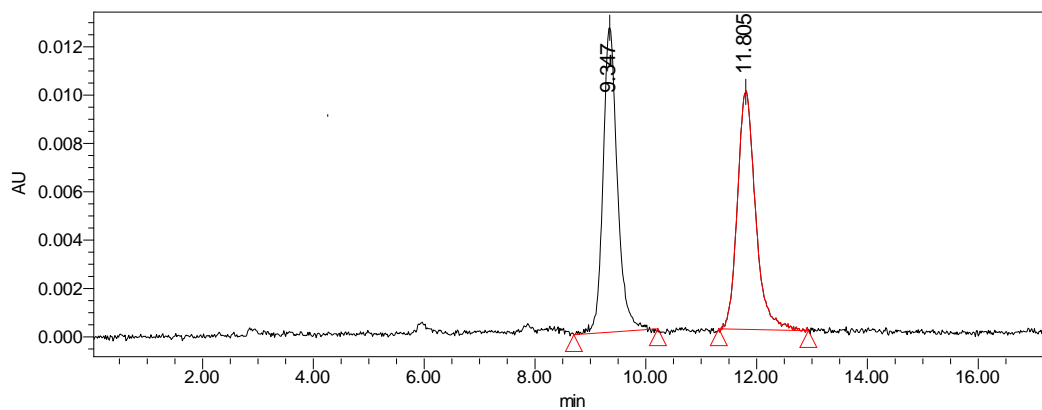
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.036	535226	50.94	73378	bb
2	5.935	515492	49.06	50556	bb



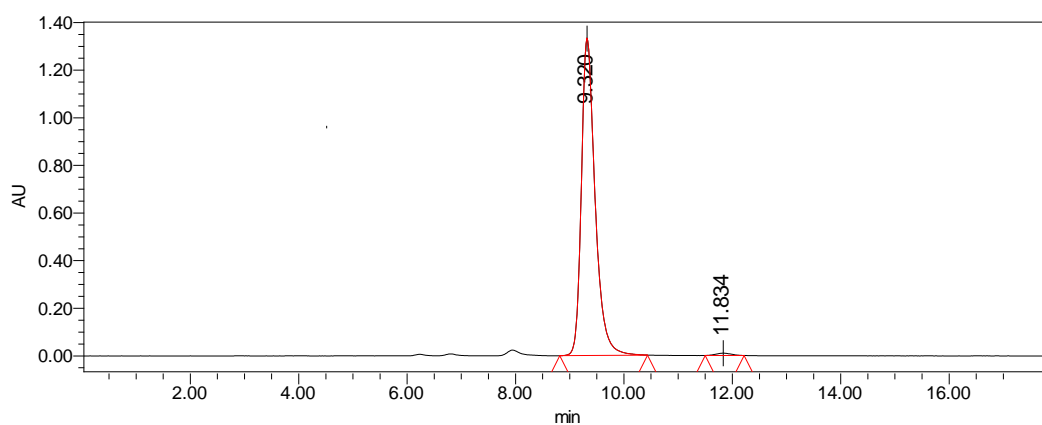
Entry	Retention time	Area	Area (%)	Height	Int type
1	4.036	11062568	99.81	1503602	bb
2	5.961	20536	0.19	2512	bb



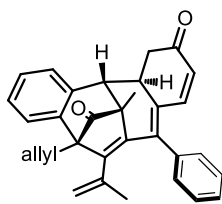
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



Entry	Retention time	Area	Area (%)	Height	Int type
1	9.347	227172	50.32	12636	bb
2	11.805	224281	49.68	9858	bb

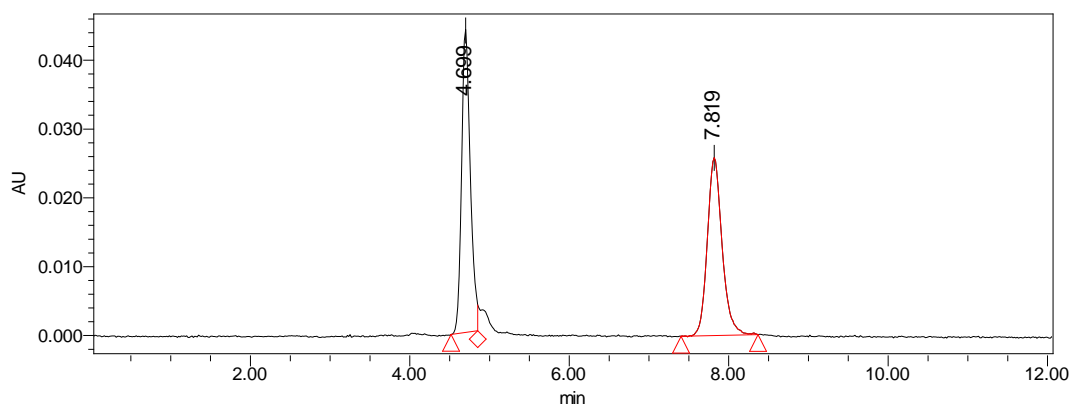


Entry	Retention time	Area	Area (%)	Height	Int type
1	9.320	23450328	99.19	1332992	bb
2	11.834	191484	0.81	9701	bb

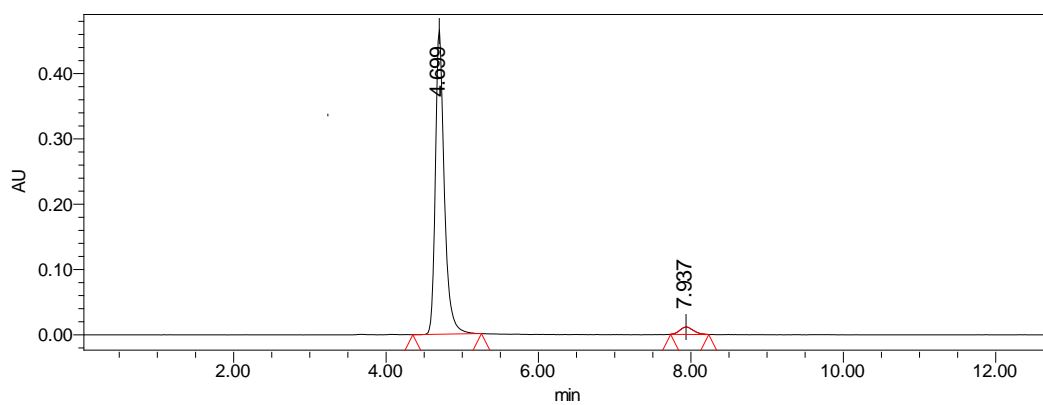


3am

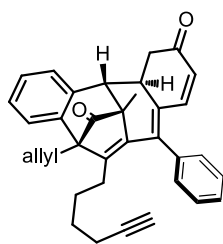
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



Entry	Retention time	Area	Area (%)	Height	Int type
1	4.699	335697	50.14	43904	bv
2	7.819	333853	49.86	25847	bb

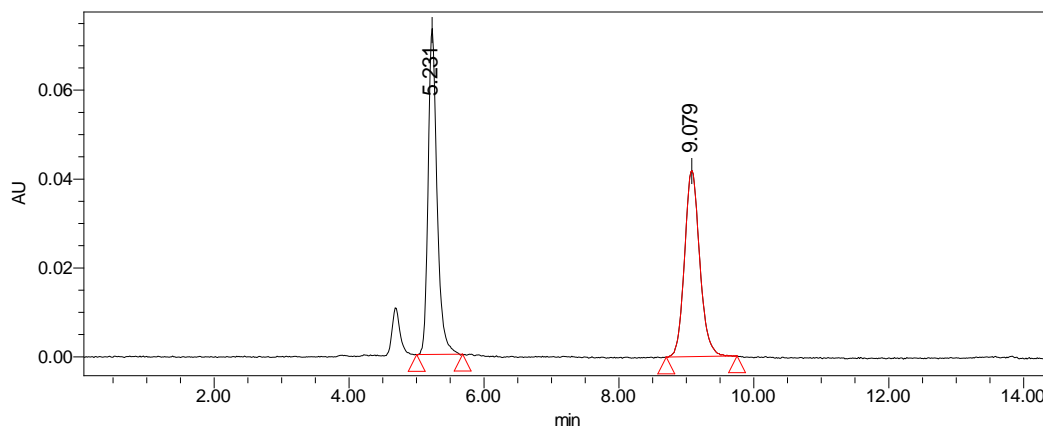


Entry	Retention time	Area	Area (%)	Height	Int type
1	4.699	3782208	96.45	464788	bb
2	7.937	139134	3.55	11332	bb

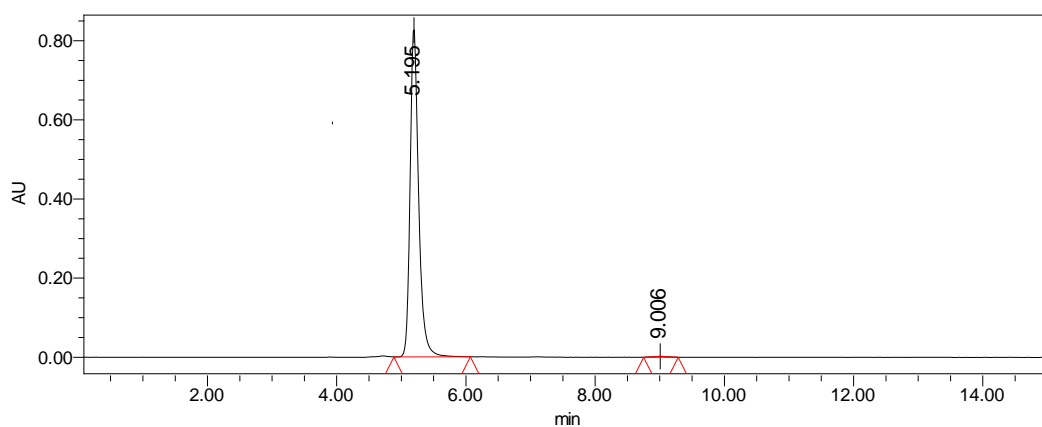


3an

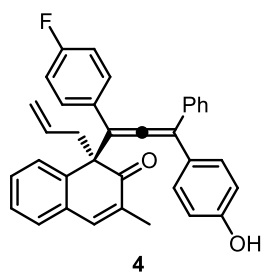
HPLC using an IA-H column (hexane/*i*PrOH = 8/2, flow rate 1.0 mL/min)



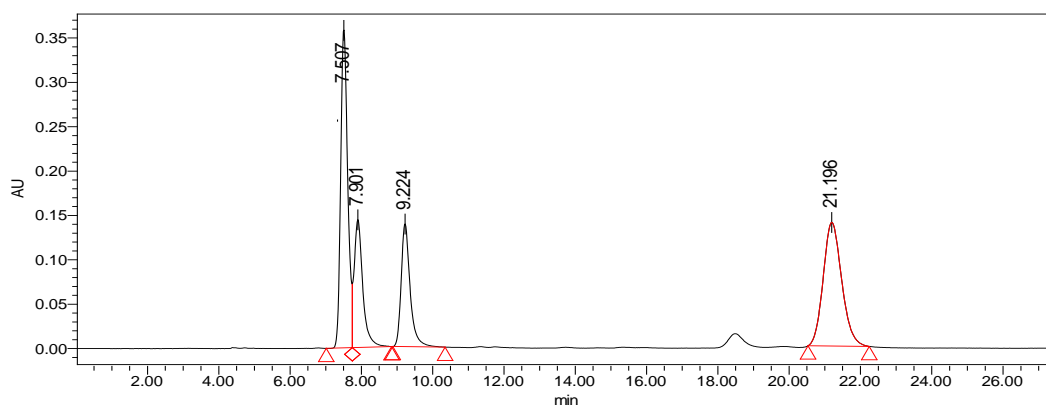
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.231	672140	50.74	73193	bb
2	9.079	652463	49.26	41915	bb



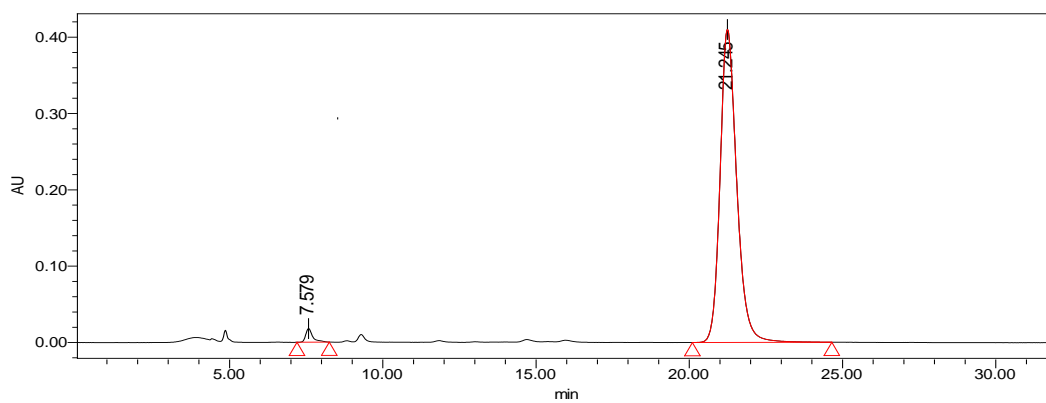
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.195	7619481	99.60	829791	bb
2	9.006	30333	0.40	2153	bb



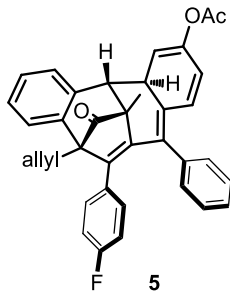
HPLC using an IA-H column (hexane/*i*PrOH = 9/1, flow rate 0.7 mL/min)



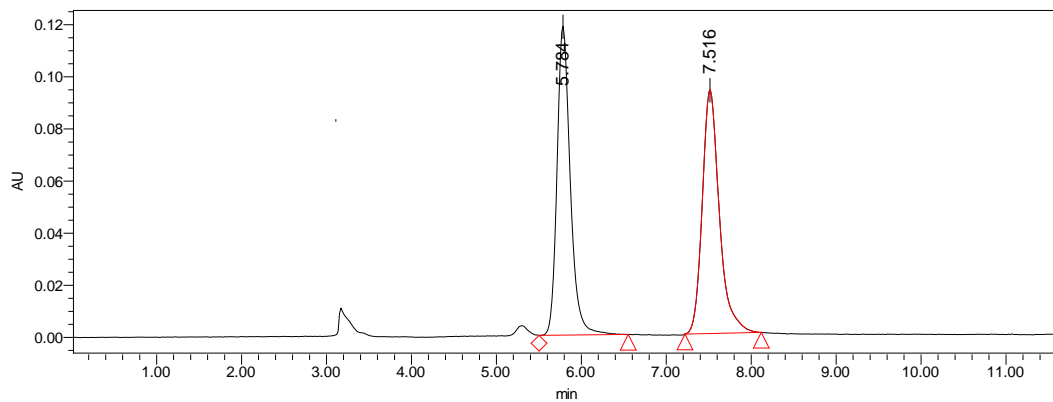
Entry	Retention time	Area	Area (%)	Height	Int type
1	7.507	4933728	33.36	358763	bv
2	7.901	2425974	16.40	144307	vb
3	9.224	2405862	16.27	138474	bb
4	21.196	5026002	33.98	139270	bb



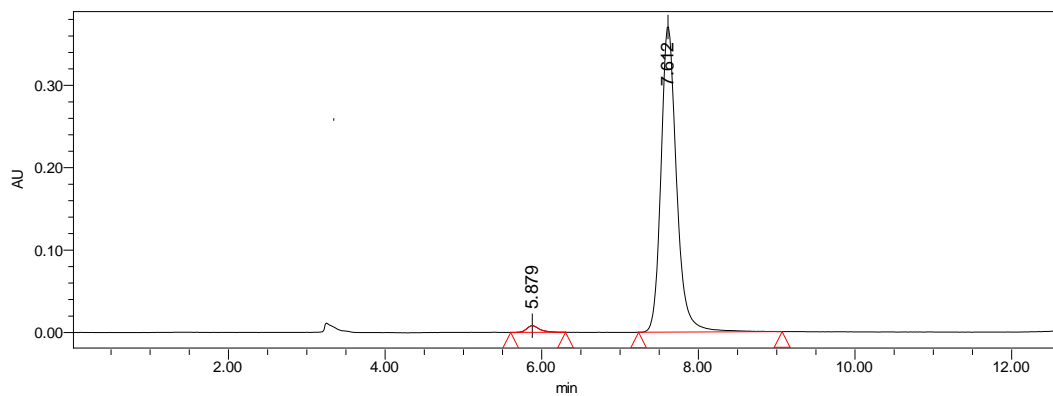
Entry	Retention time	Area	Area (%)	Height	Int type
1	7.579	284040	1.80	17954	bb
2	21.245	15489334	98.20	409991	bb



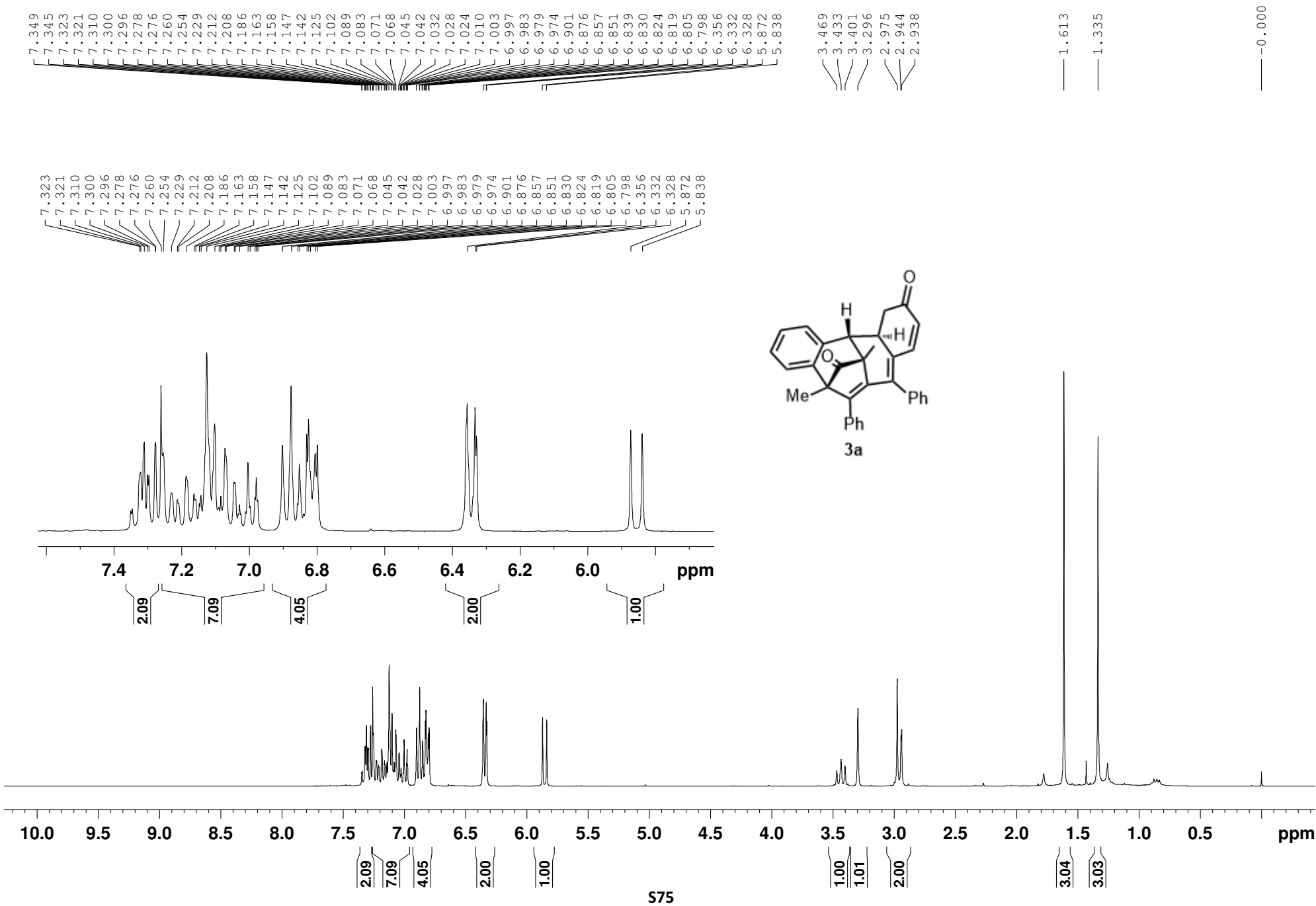
HPLC using an IA-H column (hexane/*i*PrOH = 97/3, flow rate 1.0 mL/min)

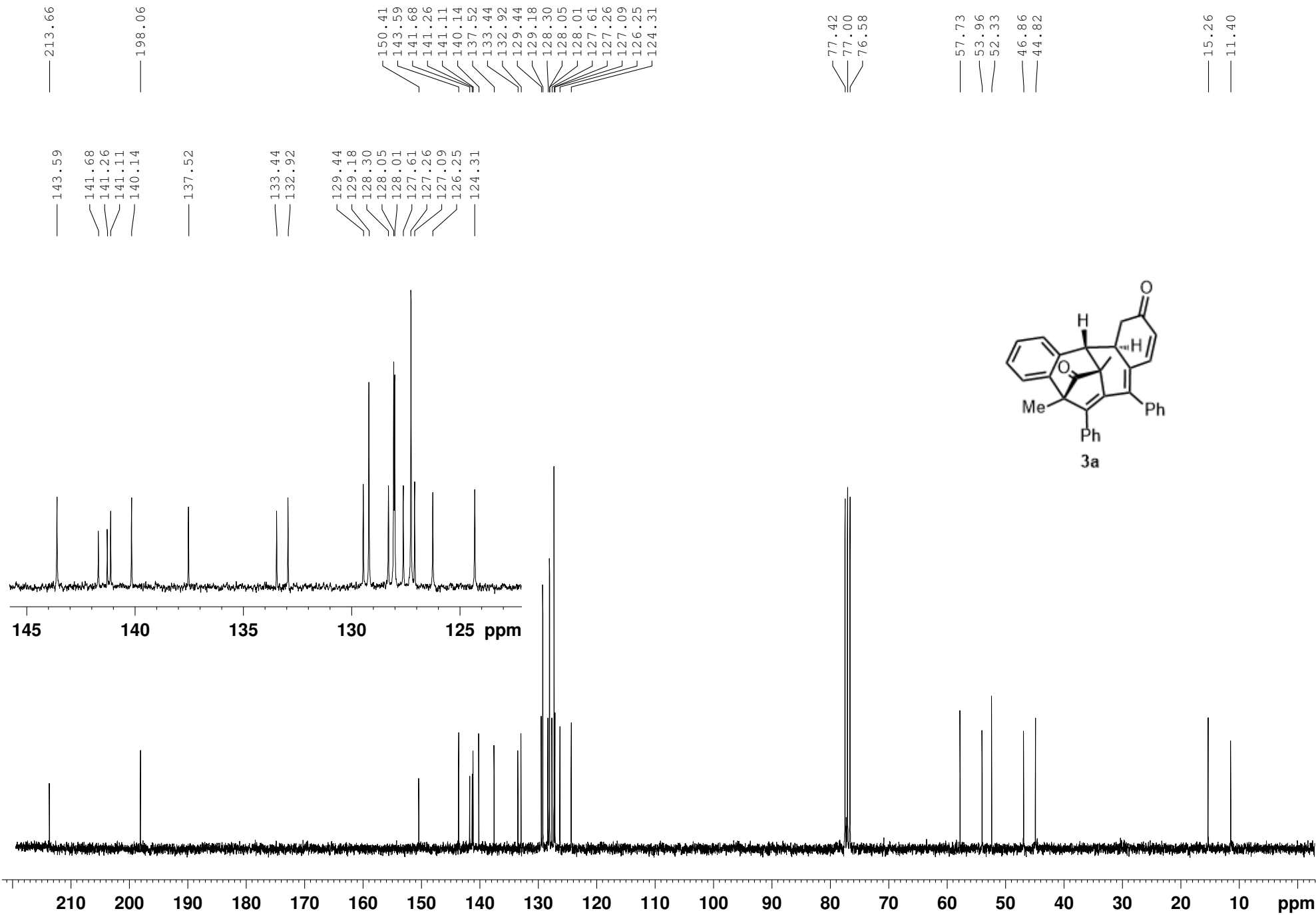


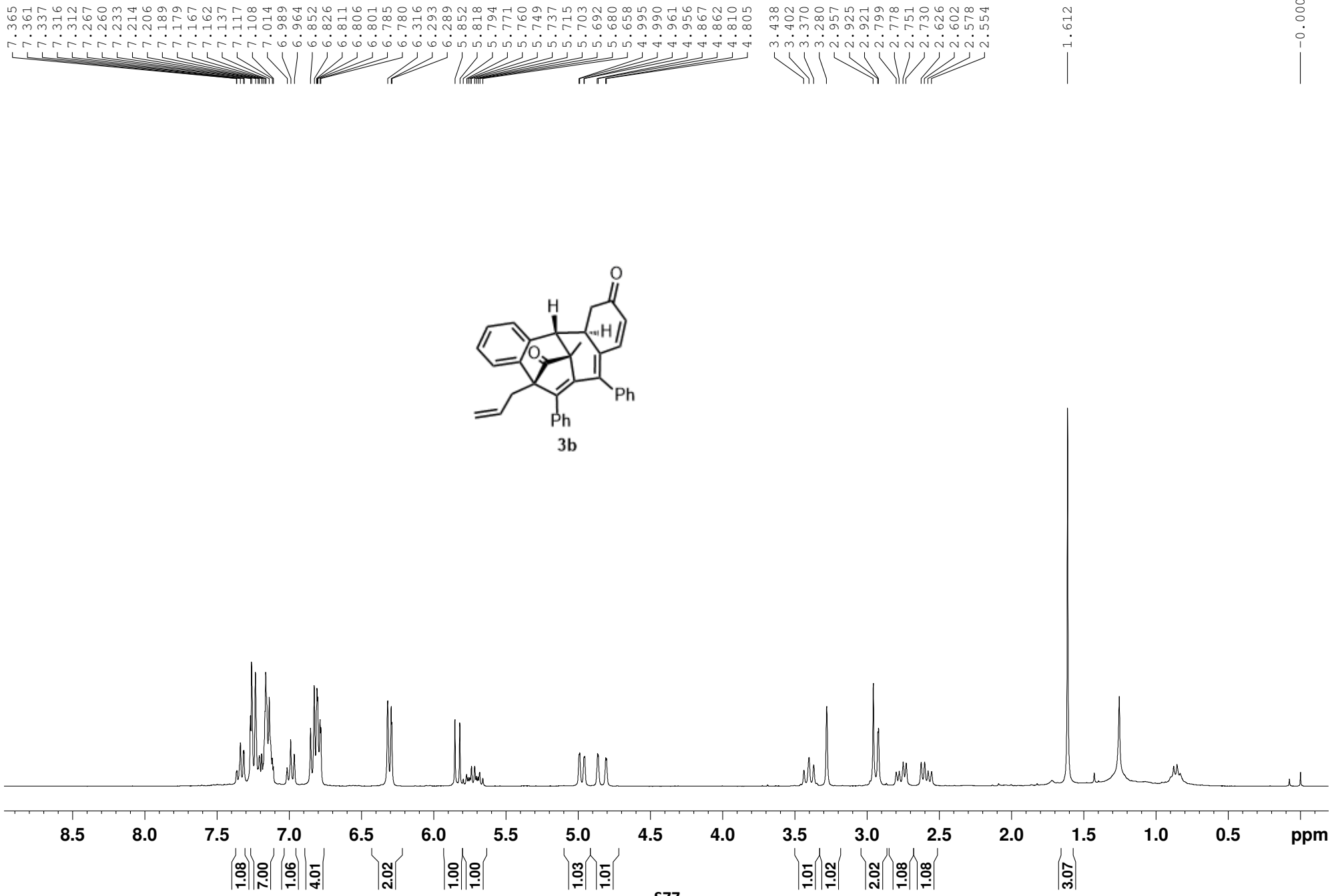
Entry	Retention time	Area	Area (%)	Height	Int type
1	5.784	1292135	49.71	118643	vb
2	7.516	1307167	50.29	93645	bb

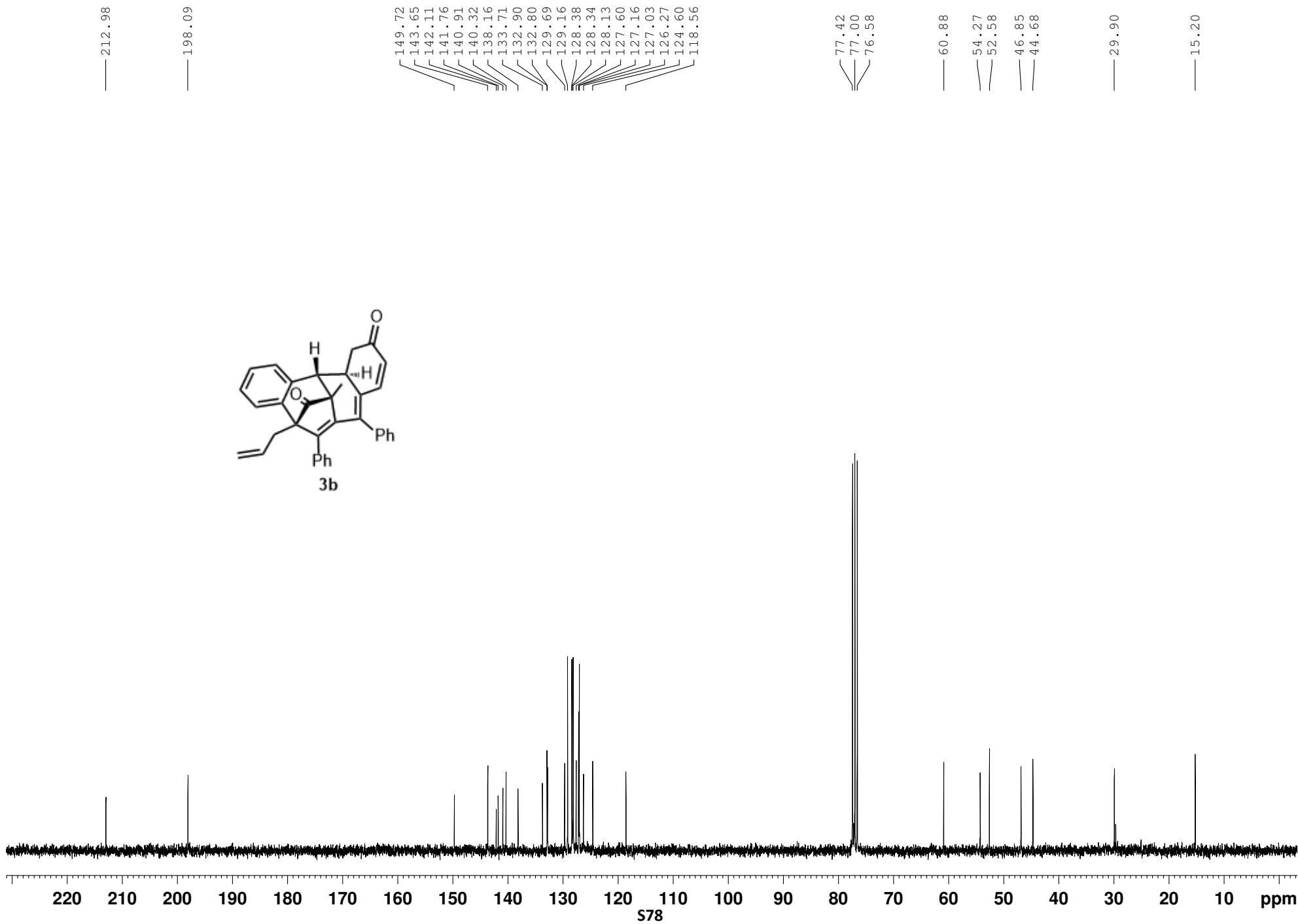
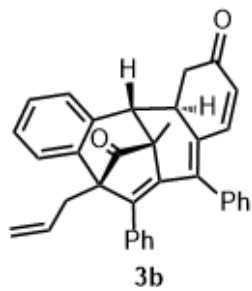


Entry	Retention time	Area	Area (%)	Height	Int type
1	5.879	92170	1.76	8067	bb
2	7.612	5143130	98.24	371482	bb









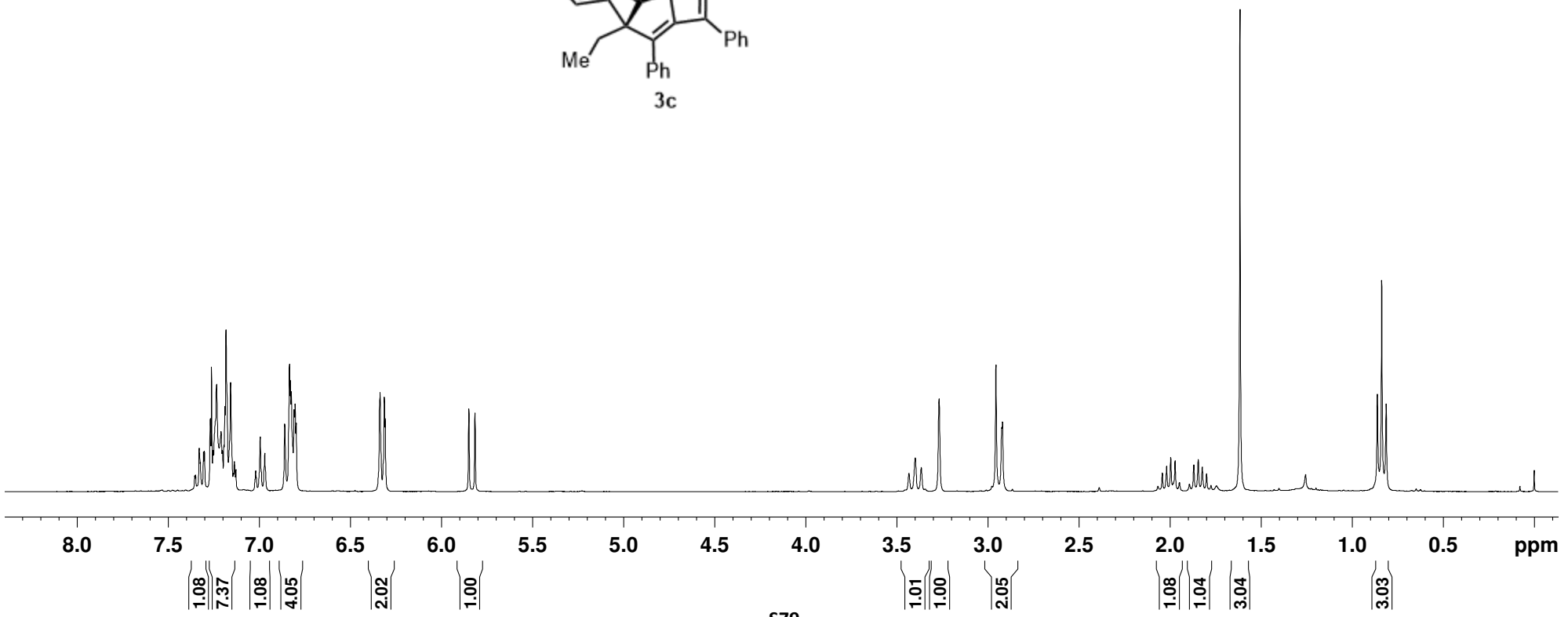
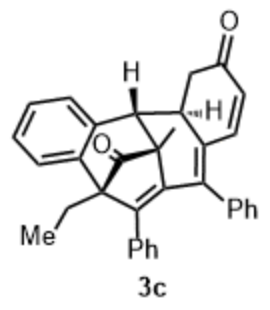
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— 213.68

— 198.20

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— 62.43

54.47

52.85

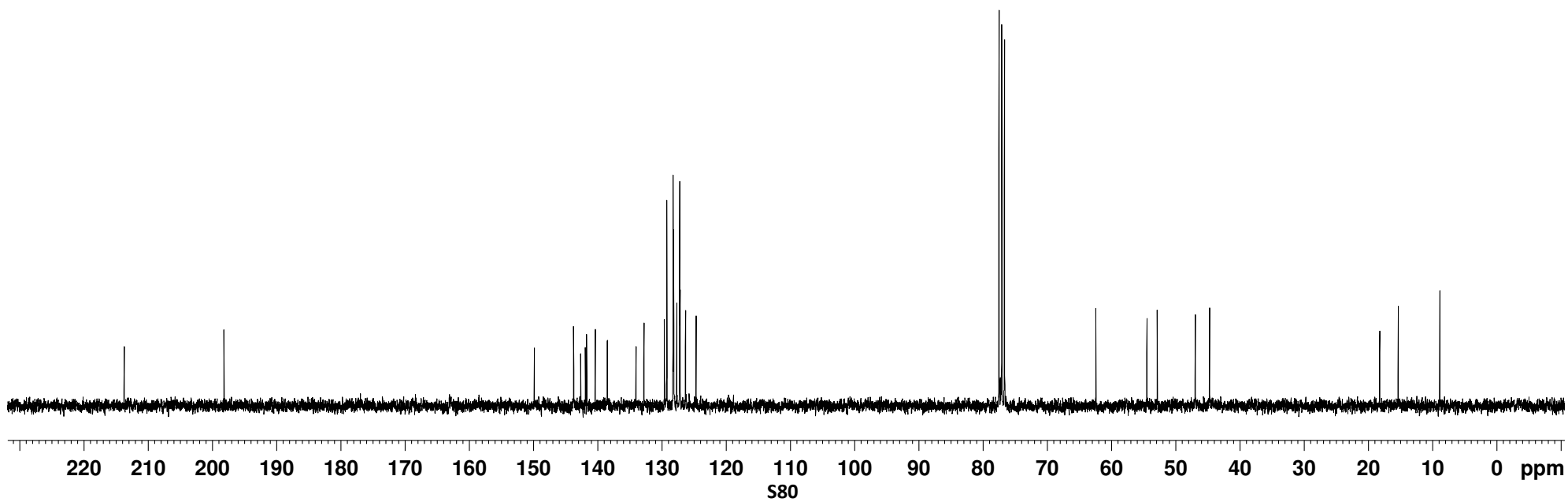
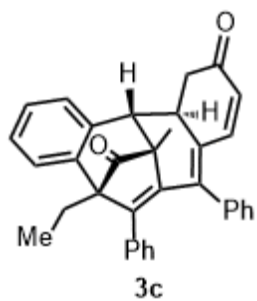
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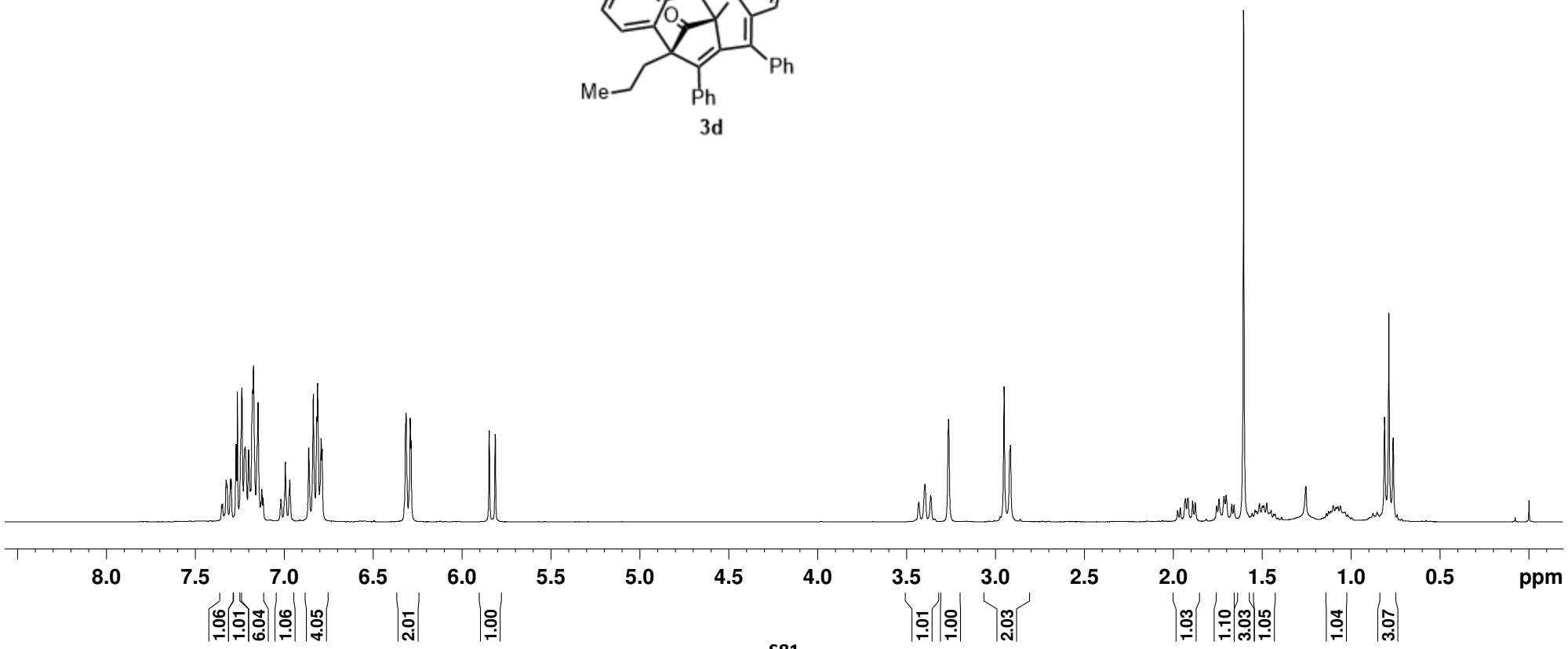
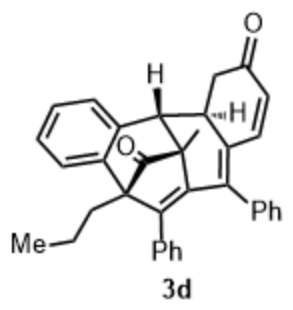
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— 8.83



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— 213.85

— 198.13

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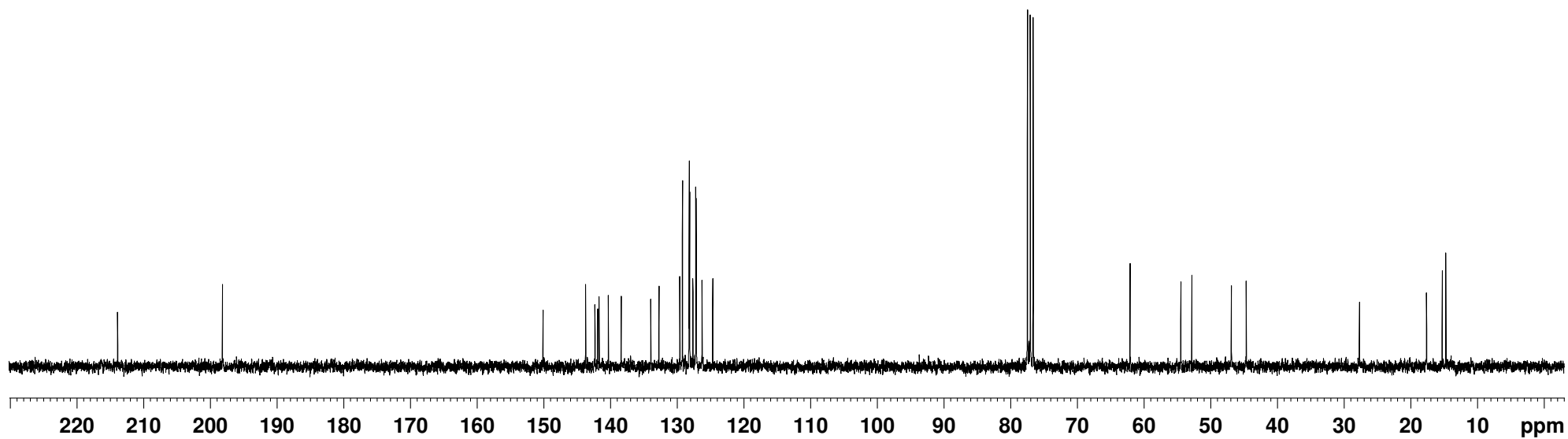
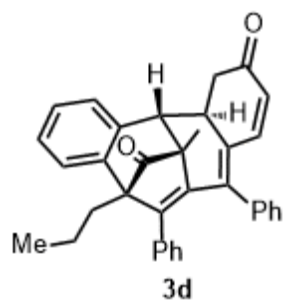
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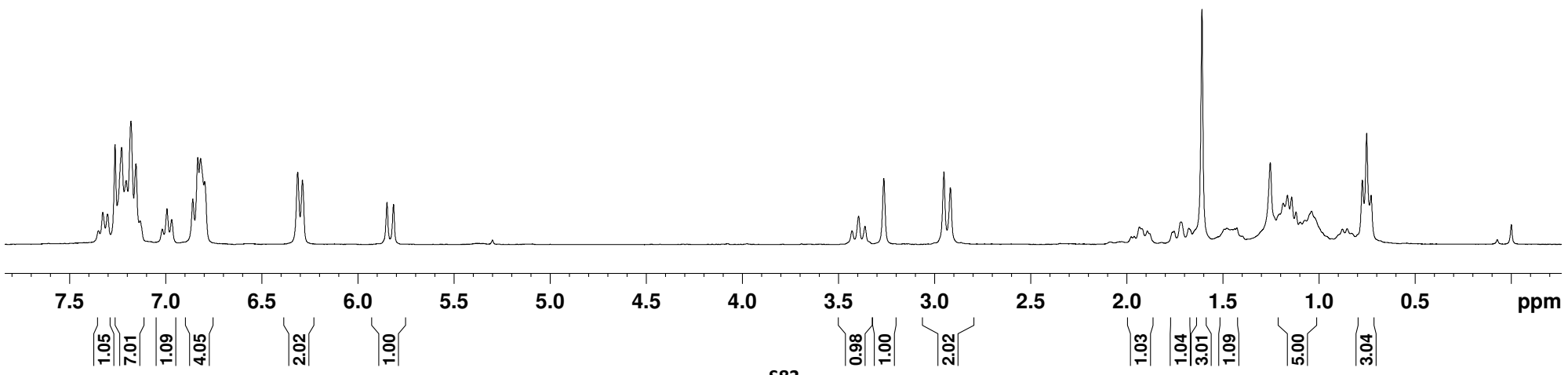
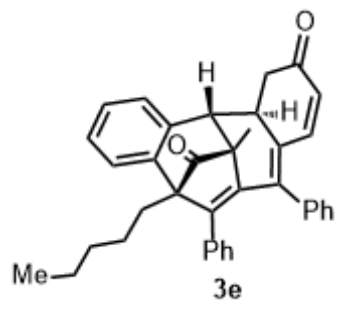
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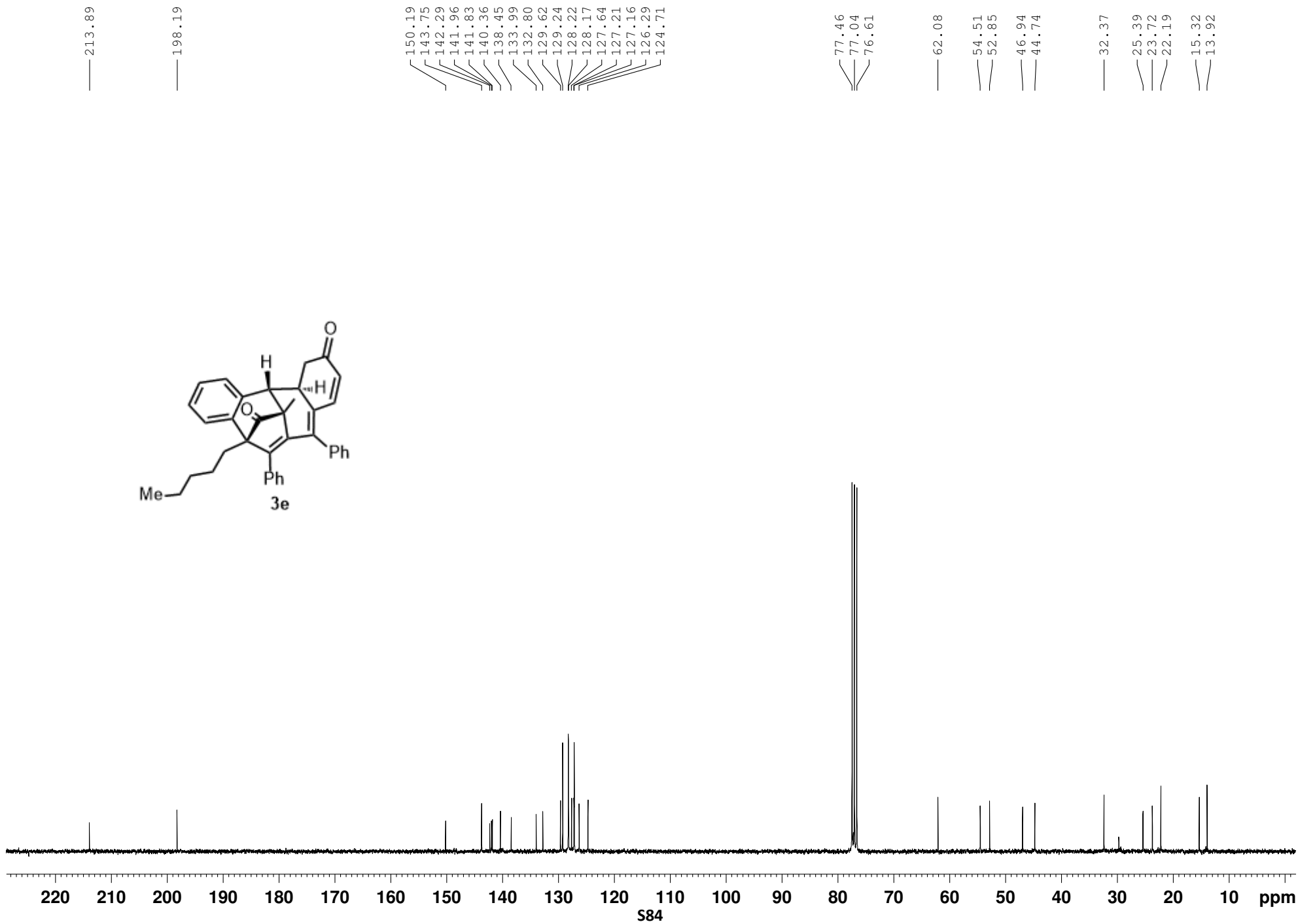
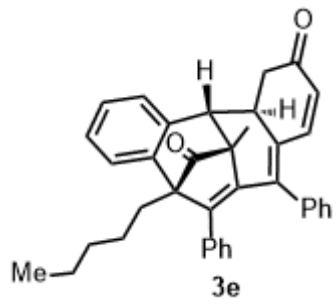
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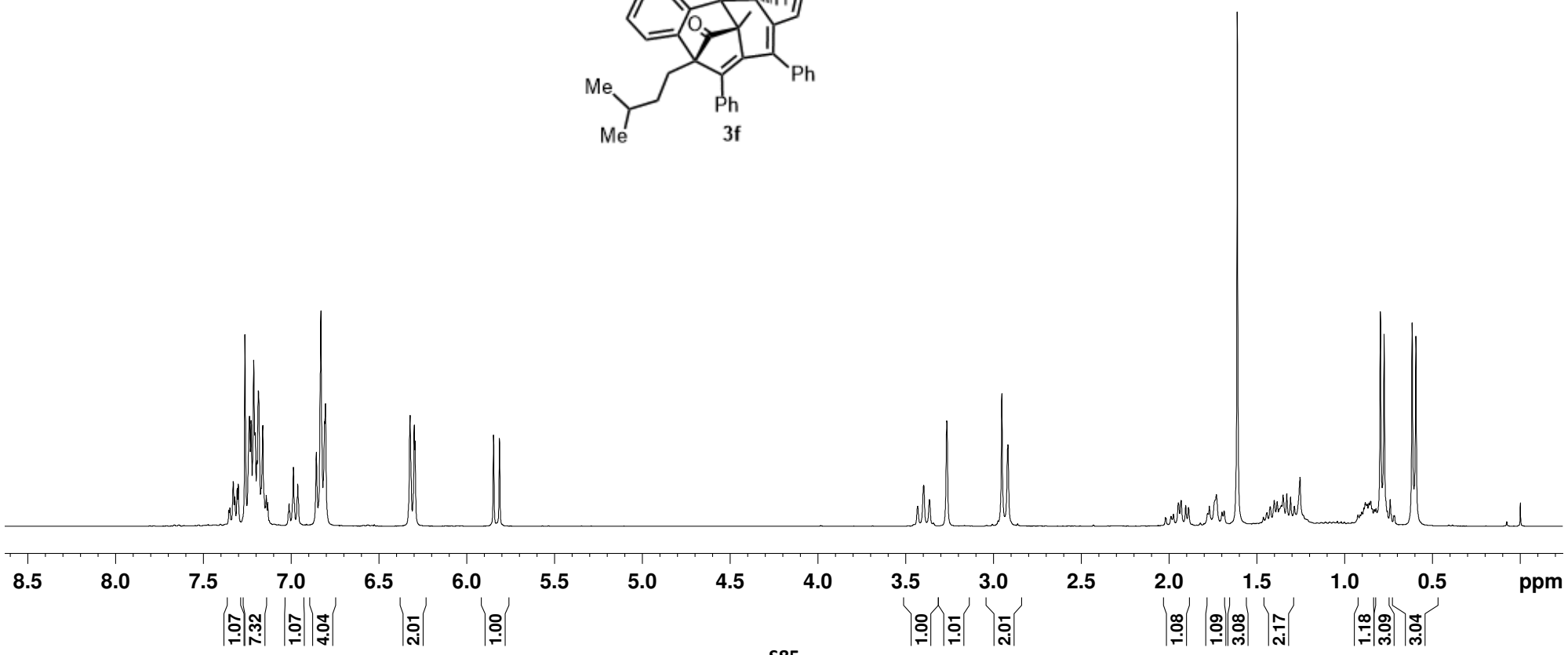
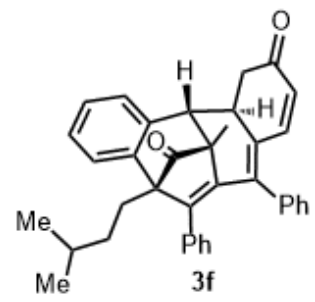
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— 213.80

— 198.16

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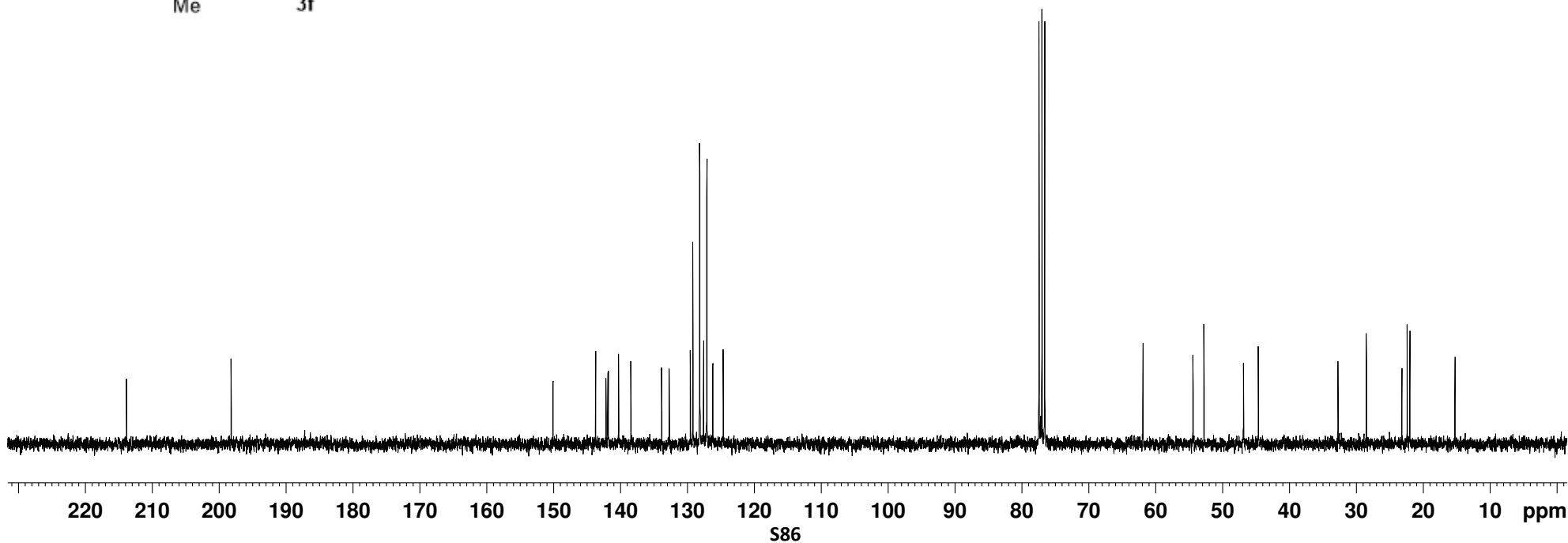
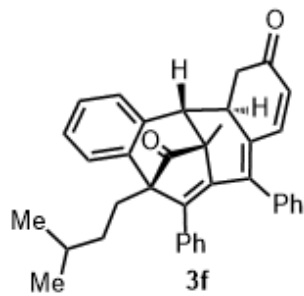
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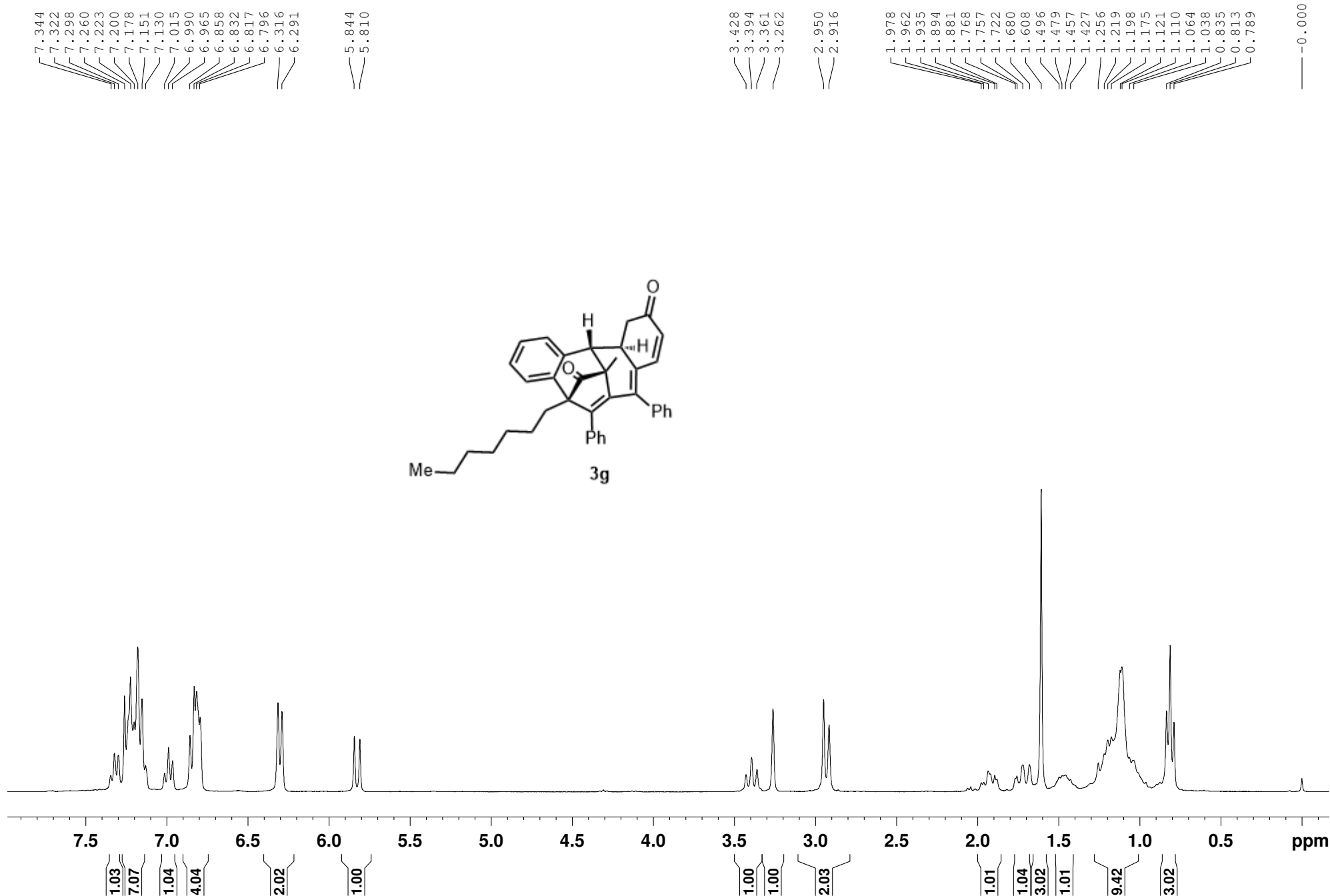
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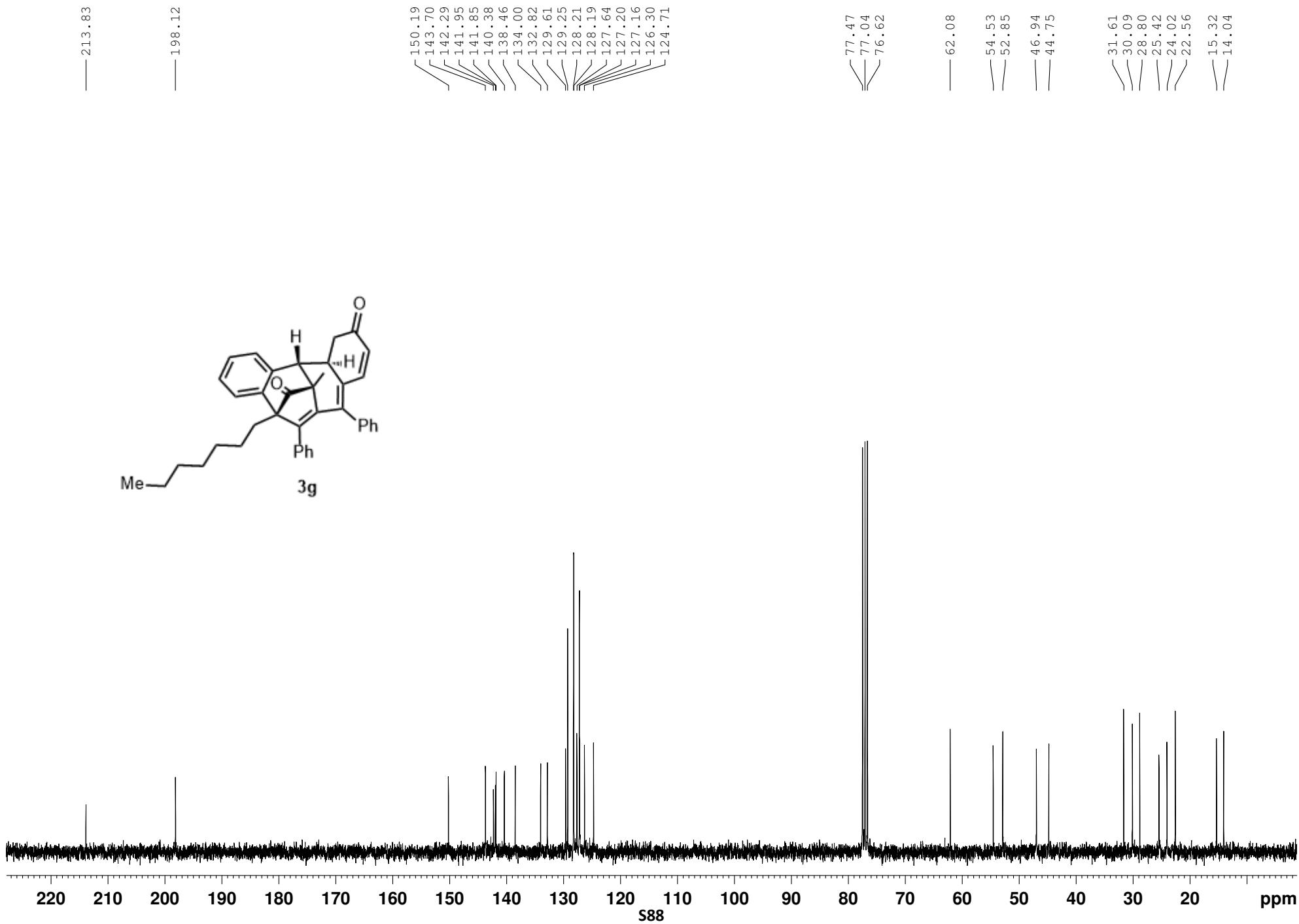
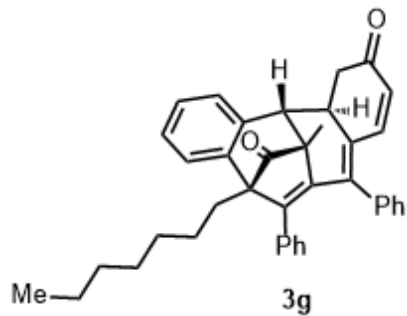
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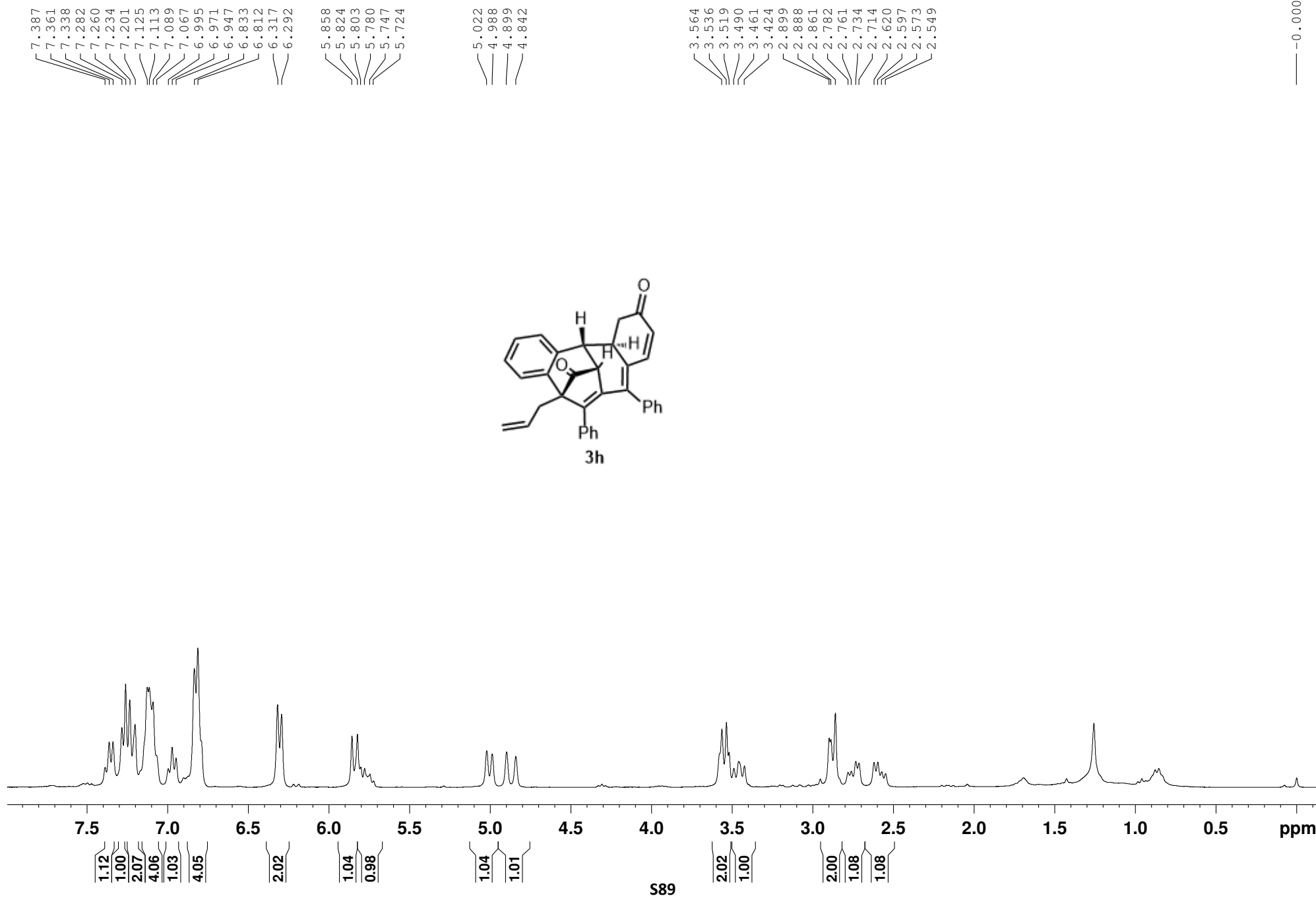
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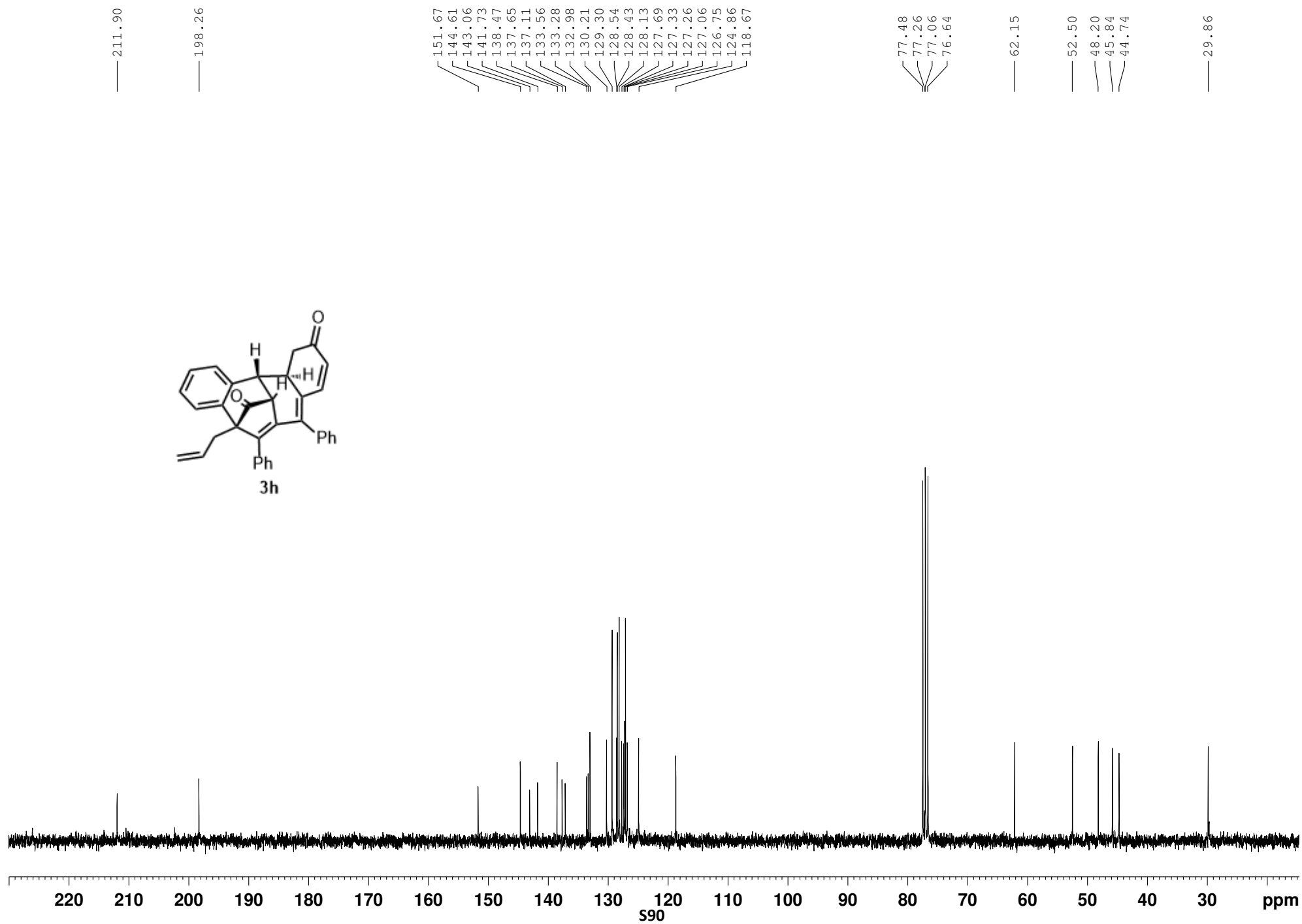
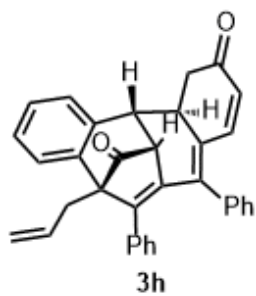
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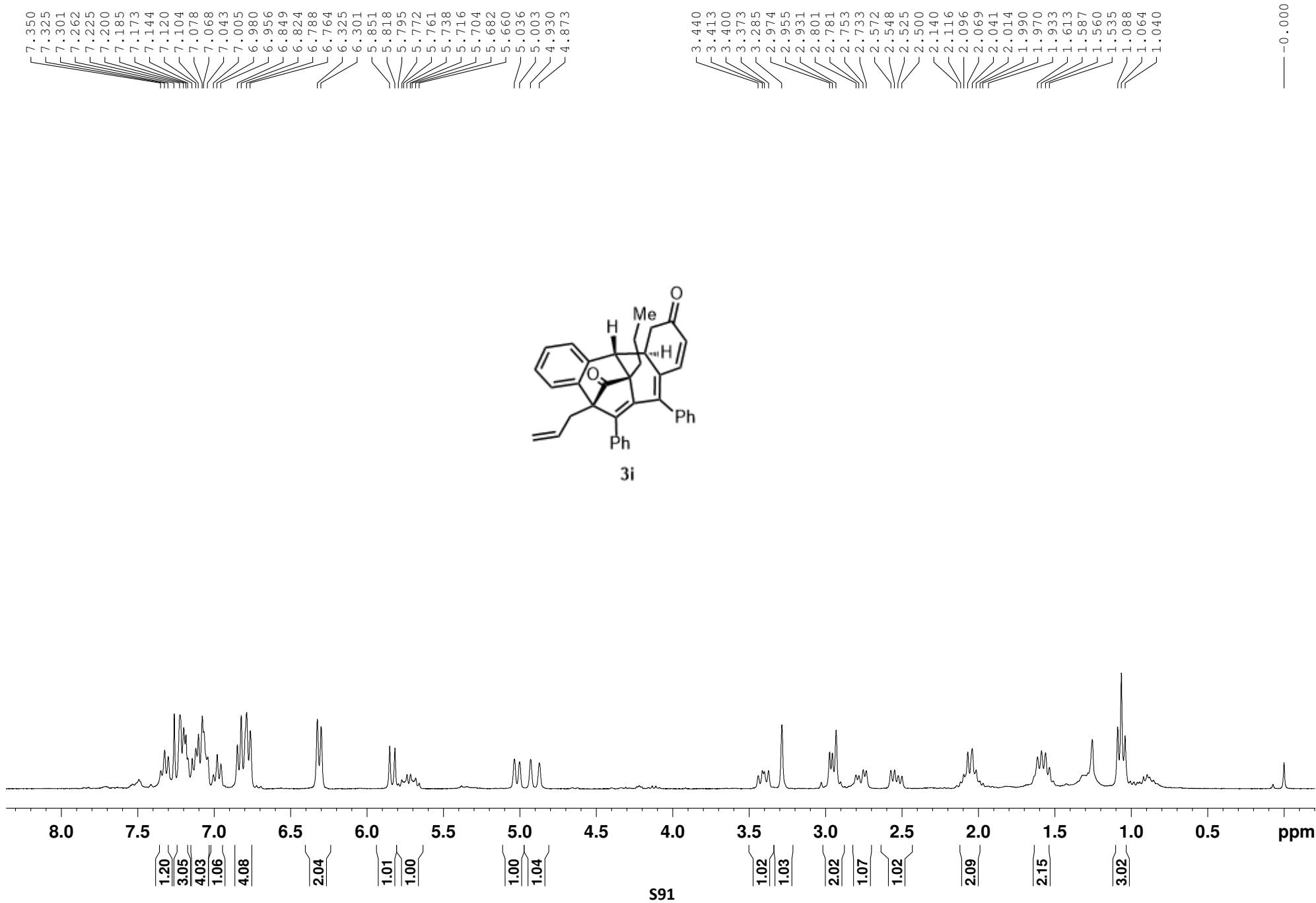


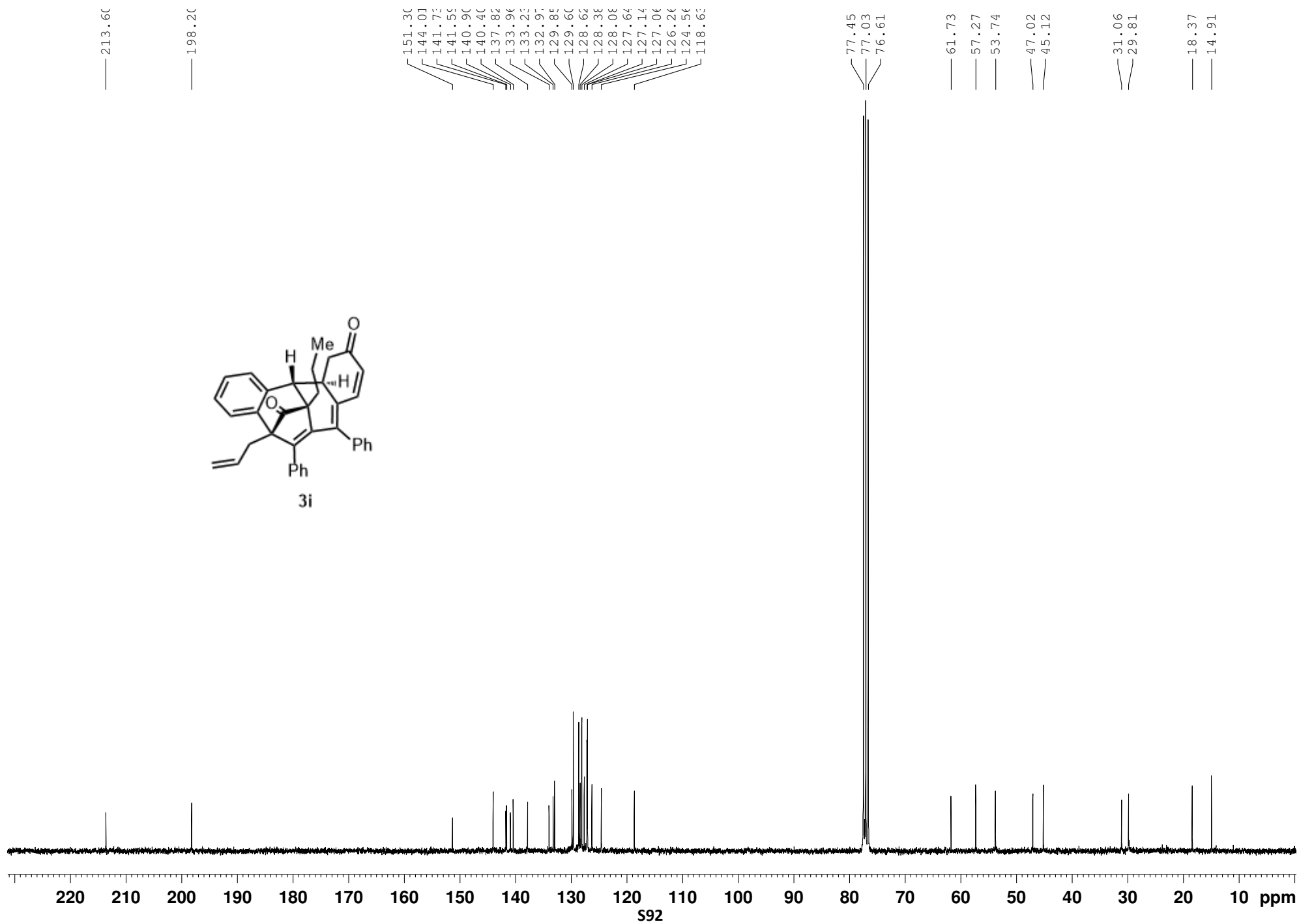
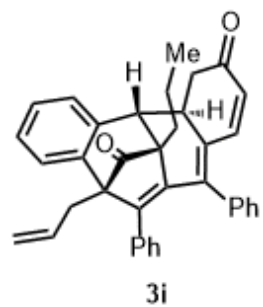






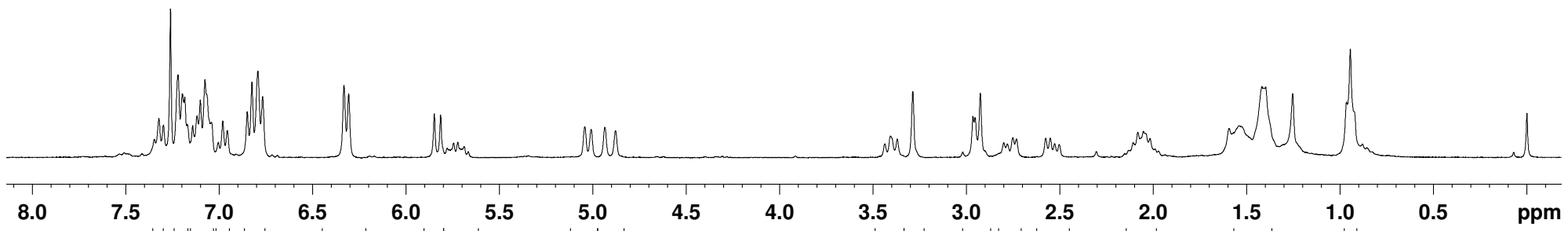
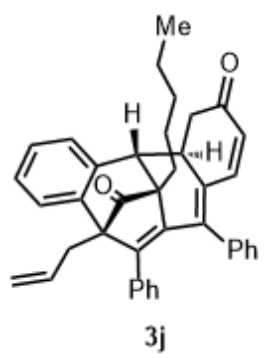






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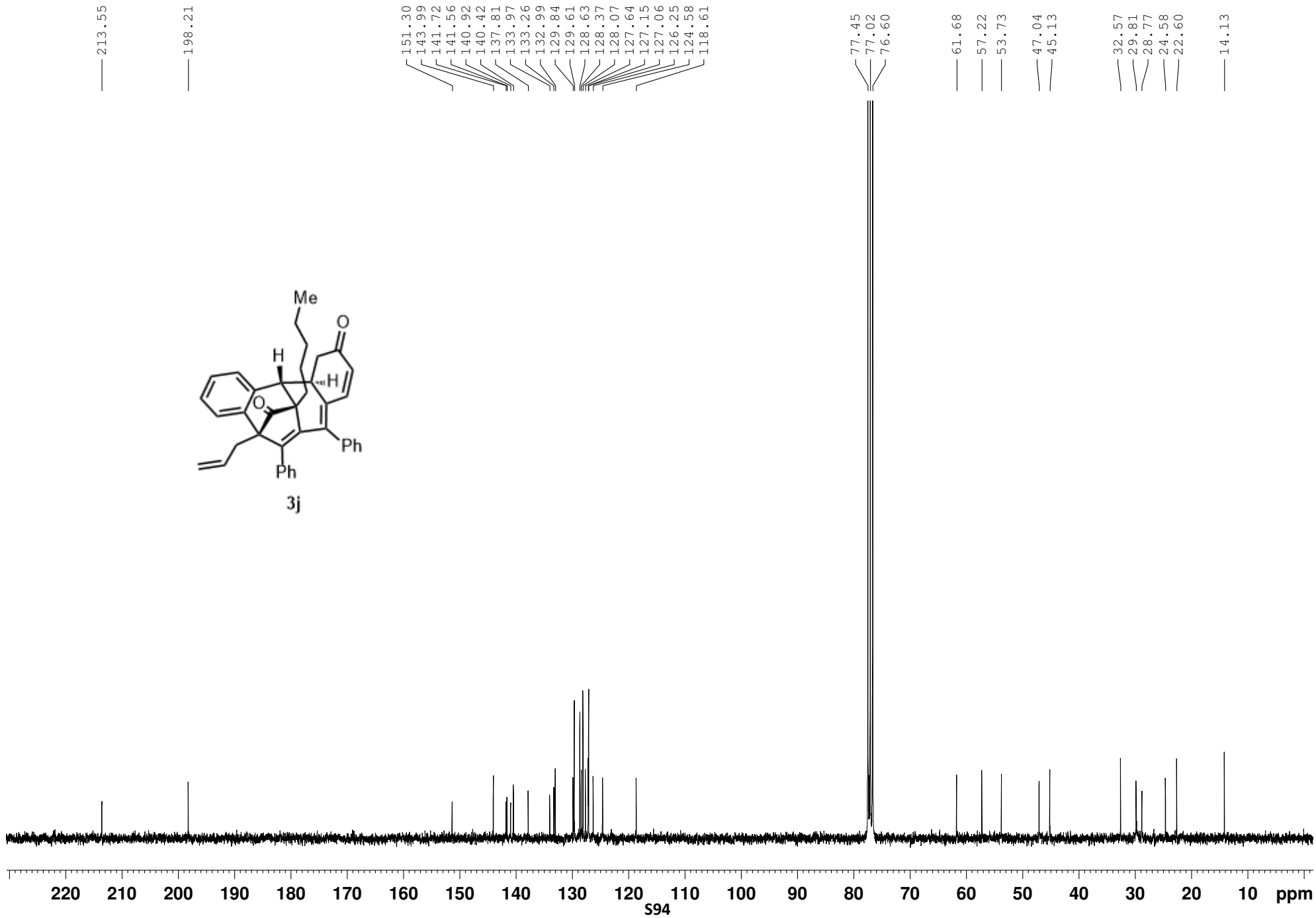
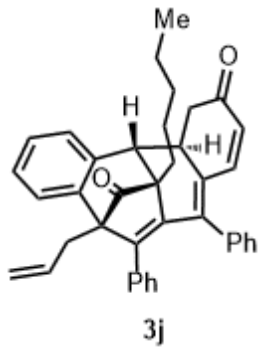
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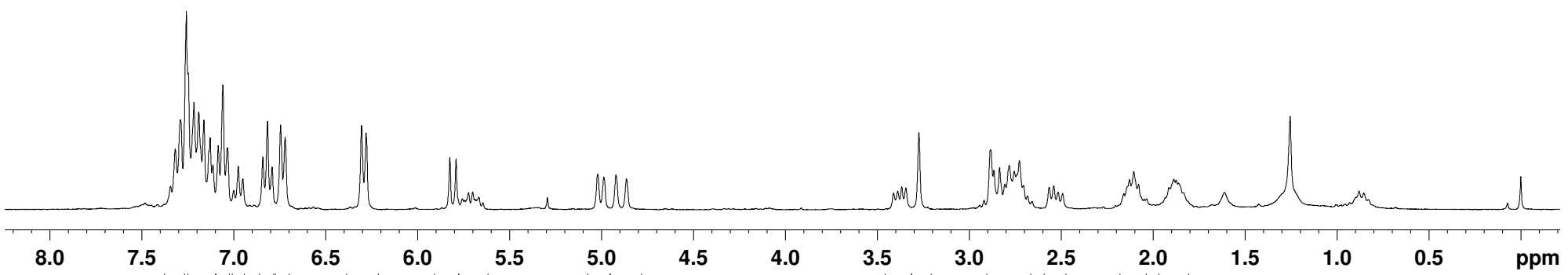
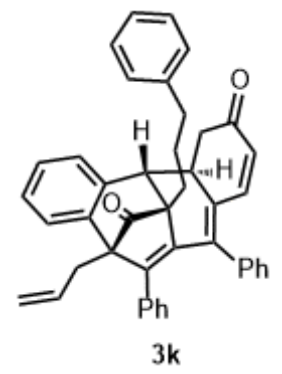
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S95

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5.04

1.07

2.03

2.08

— 213.39

— 198.13

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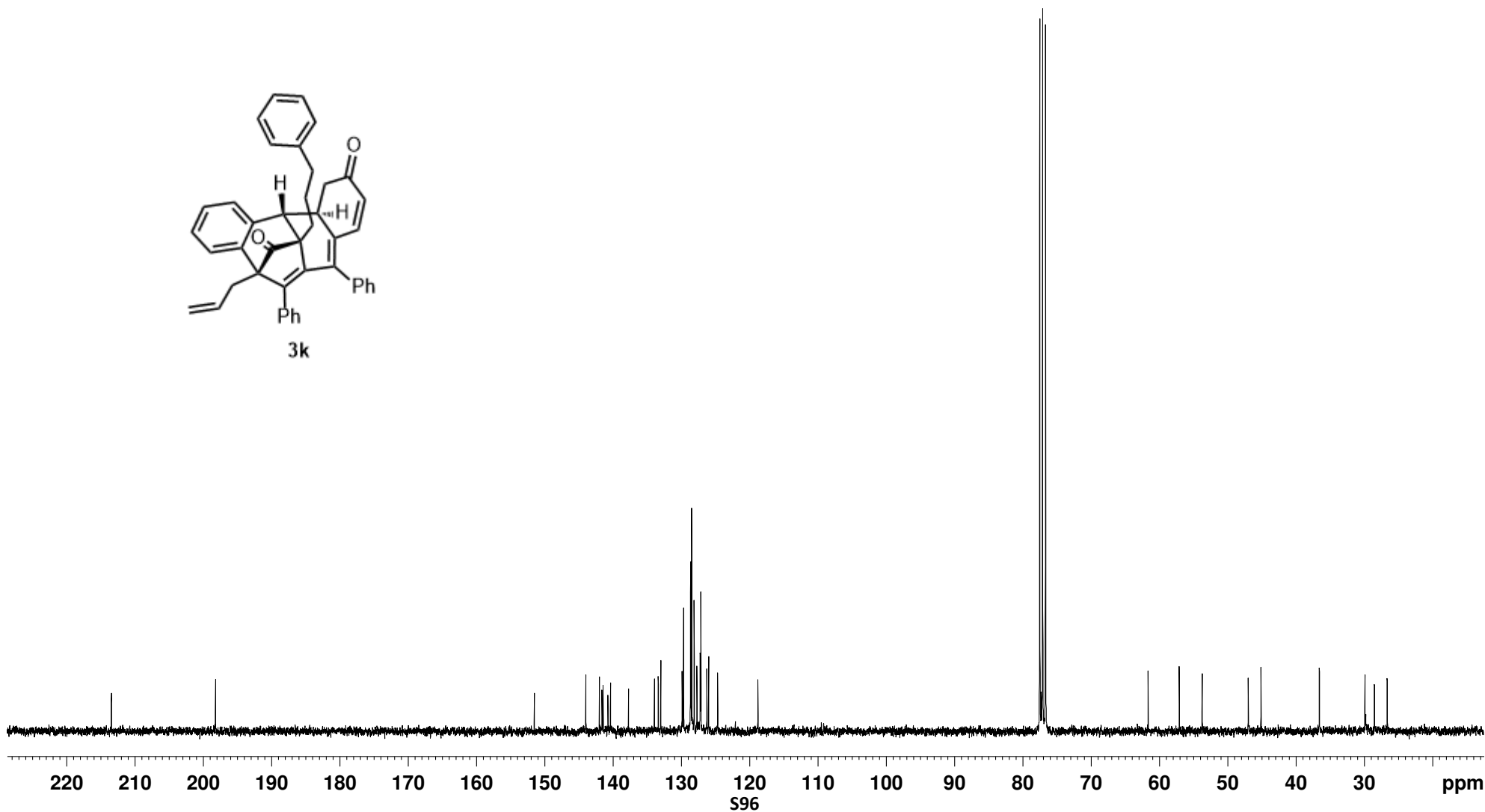
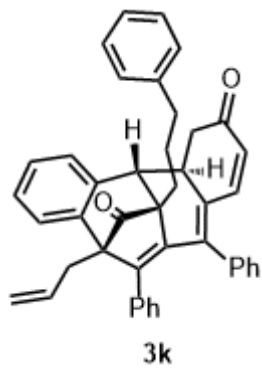
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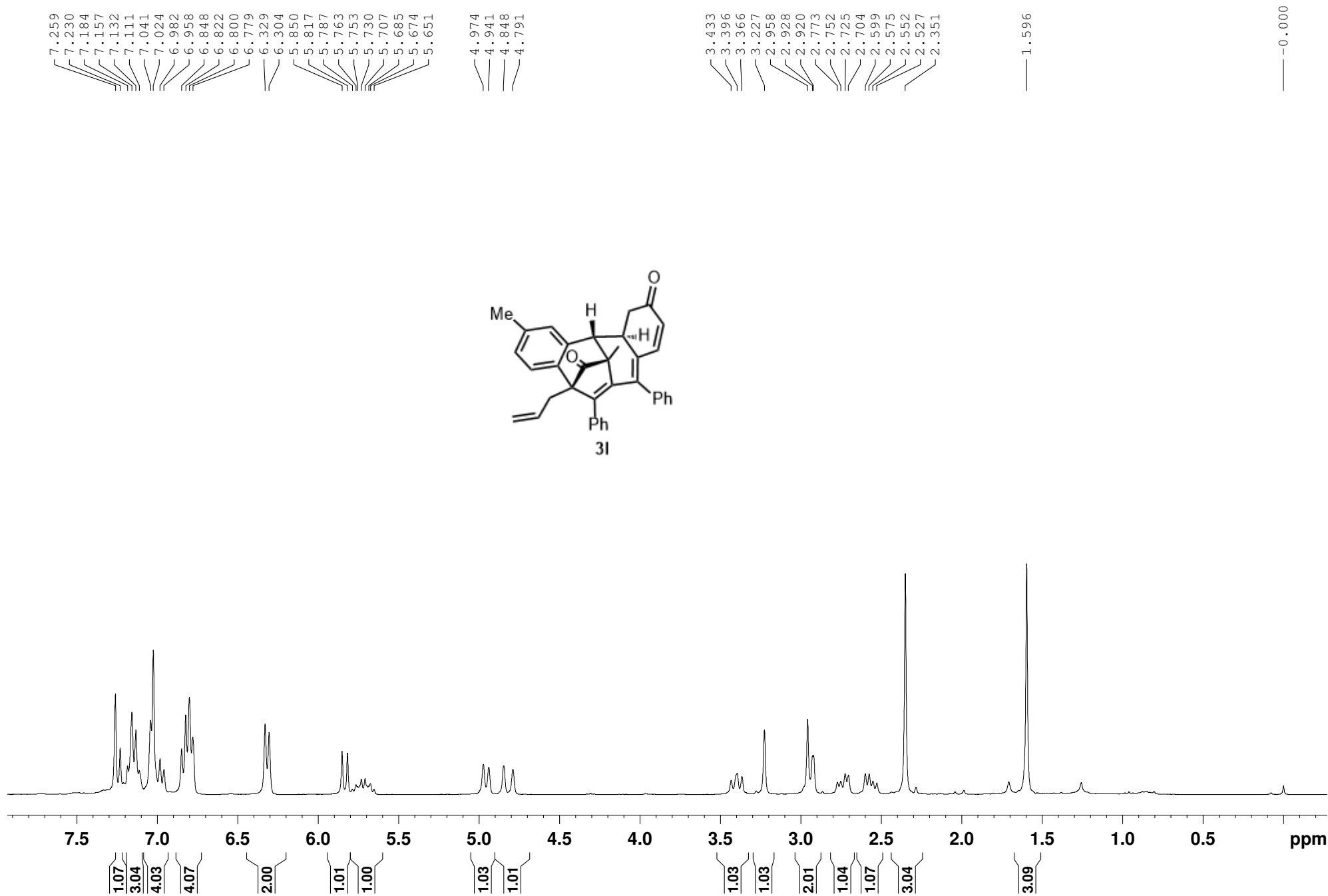
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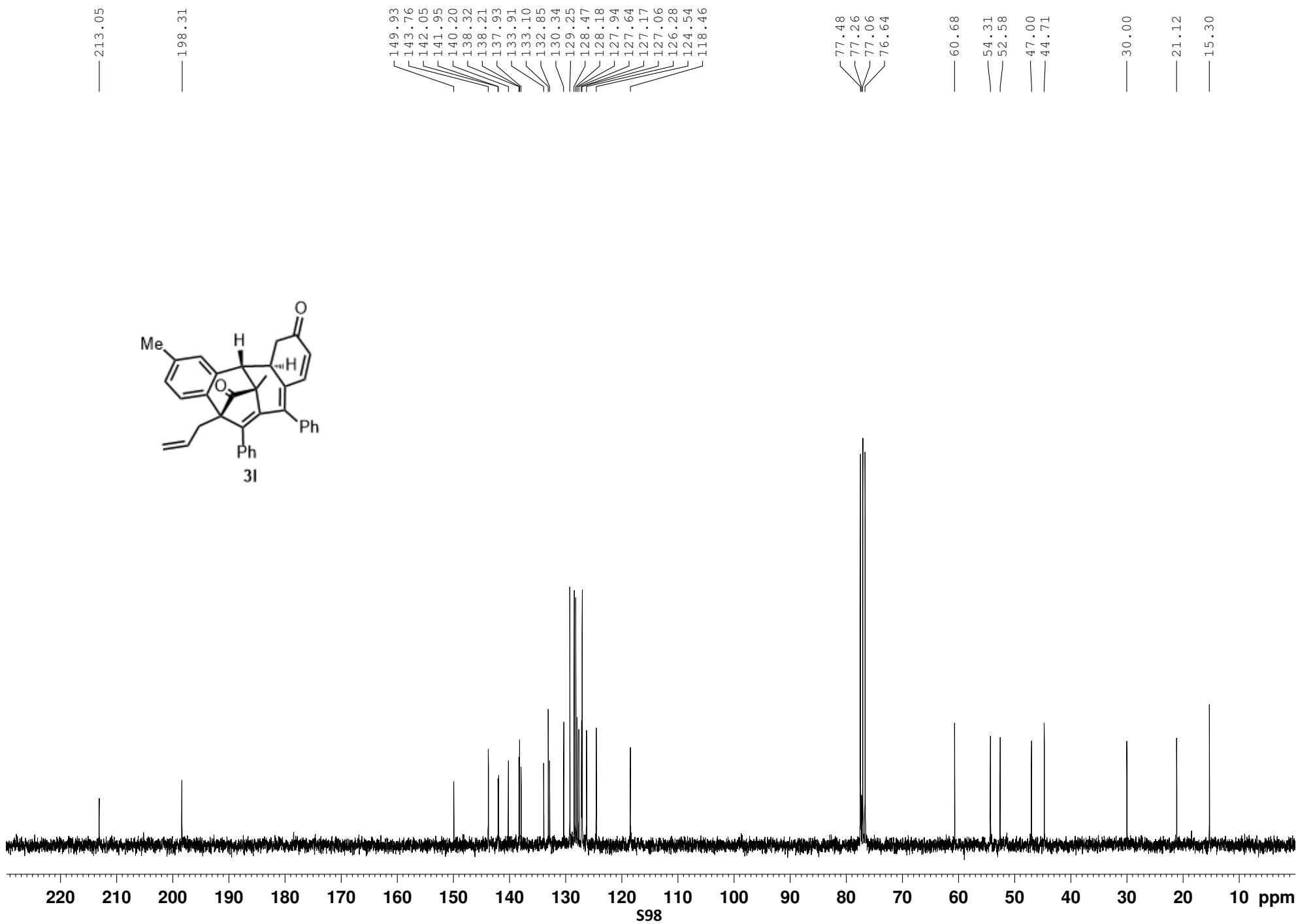
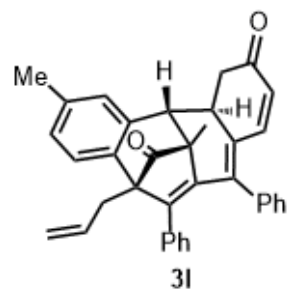
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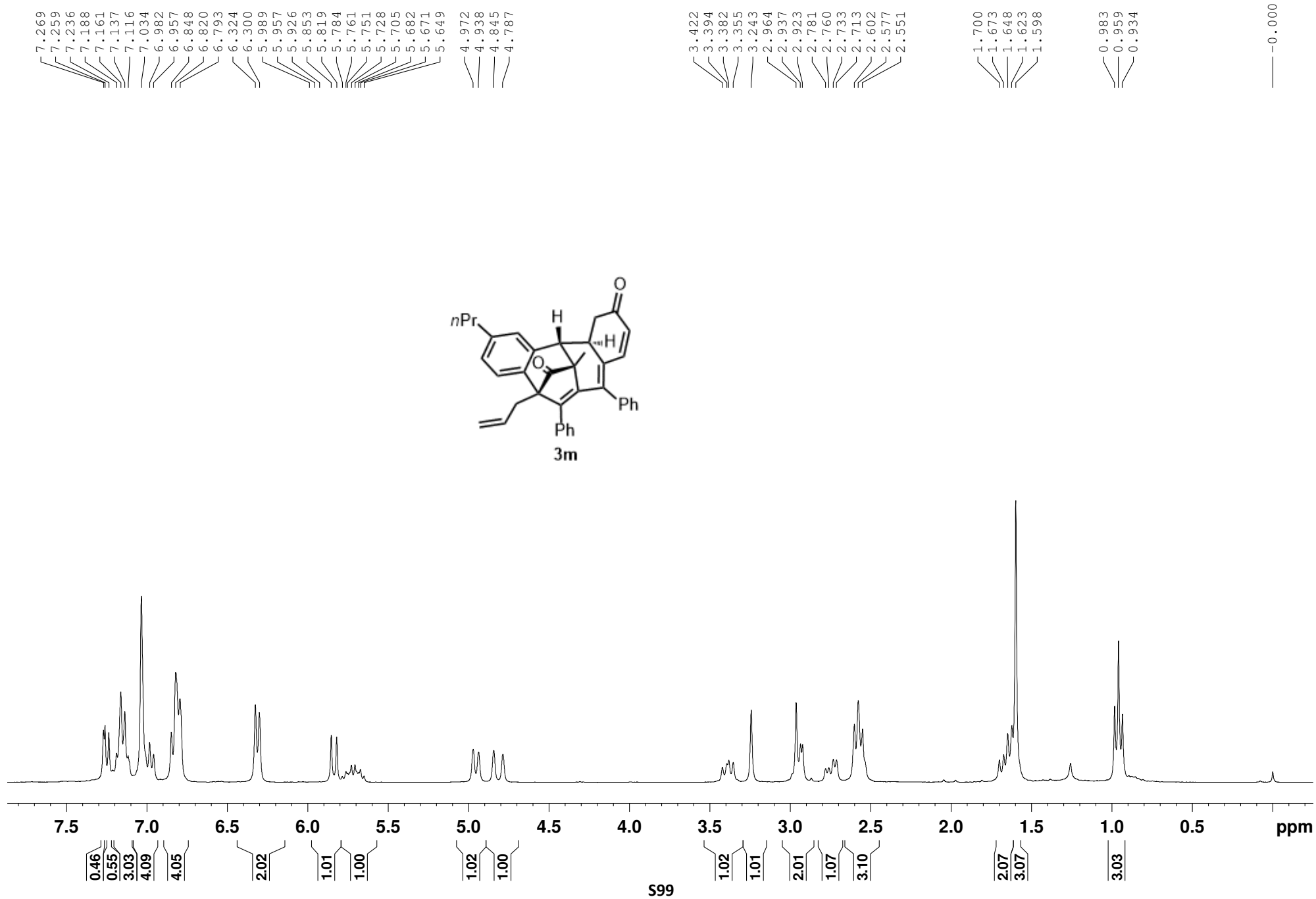
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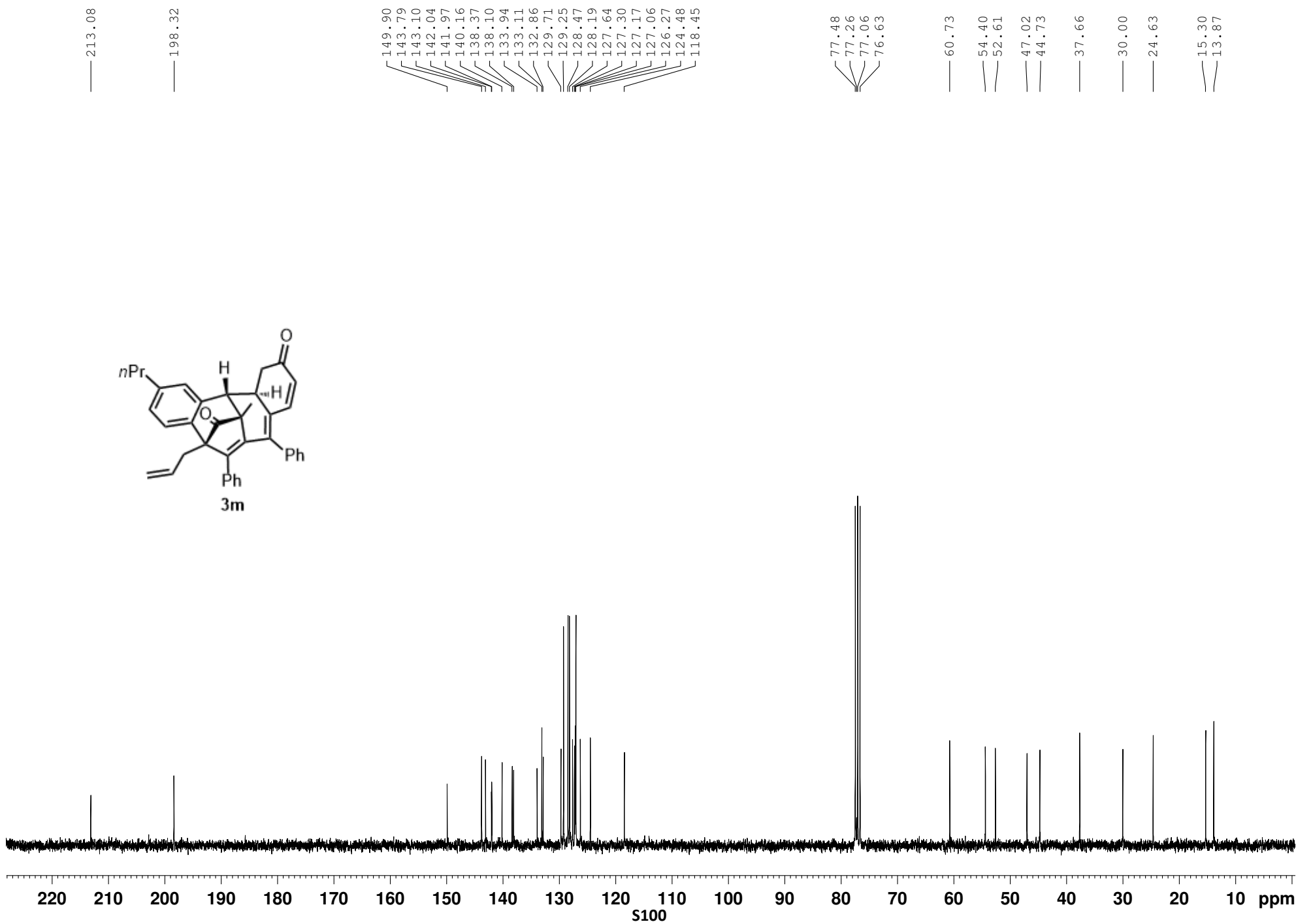
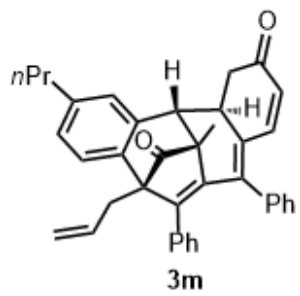
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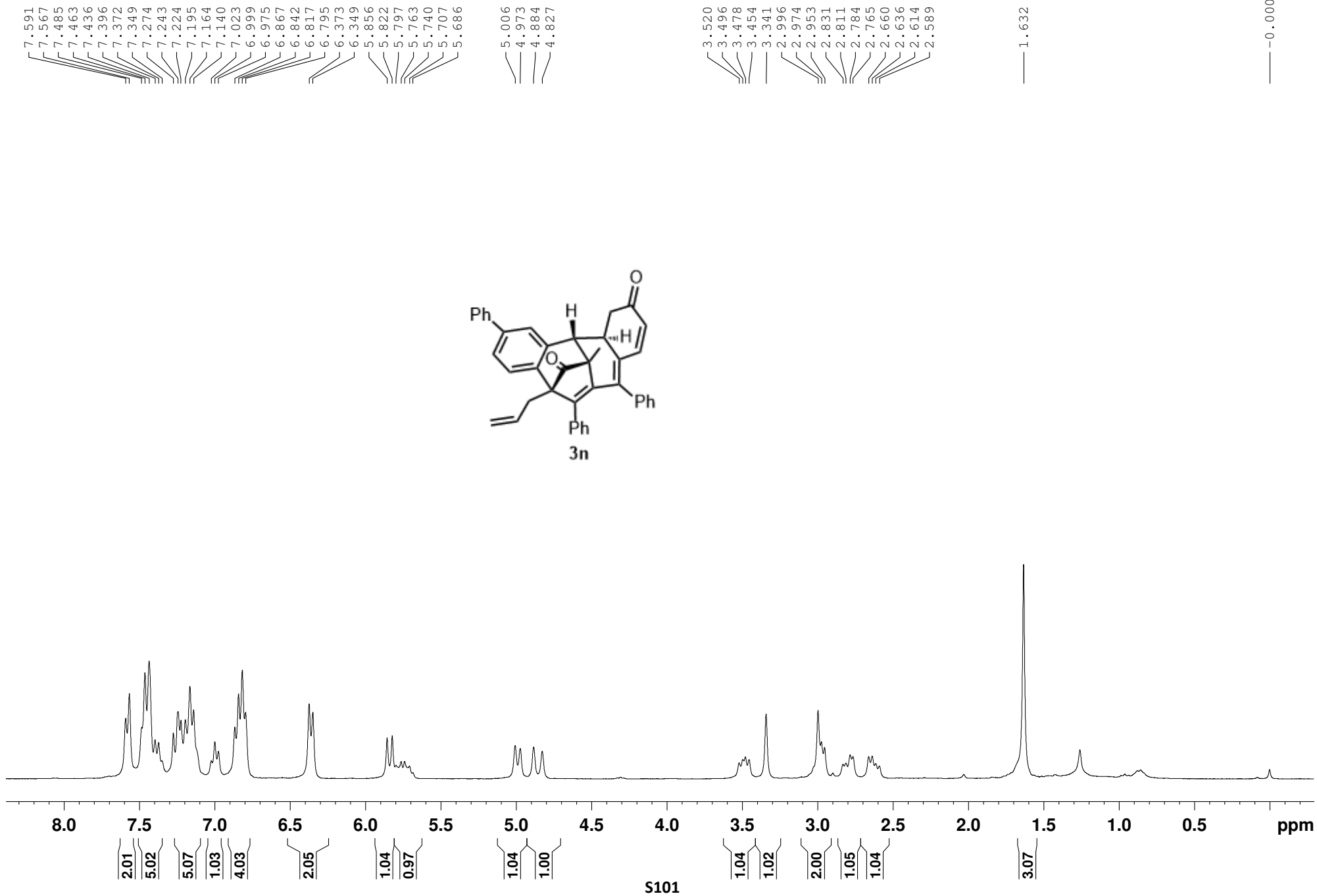




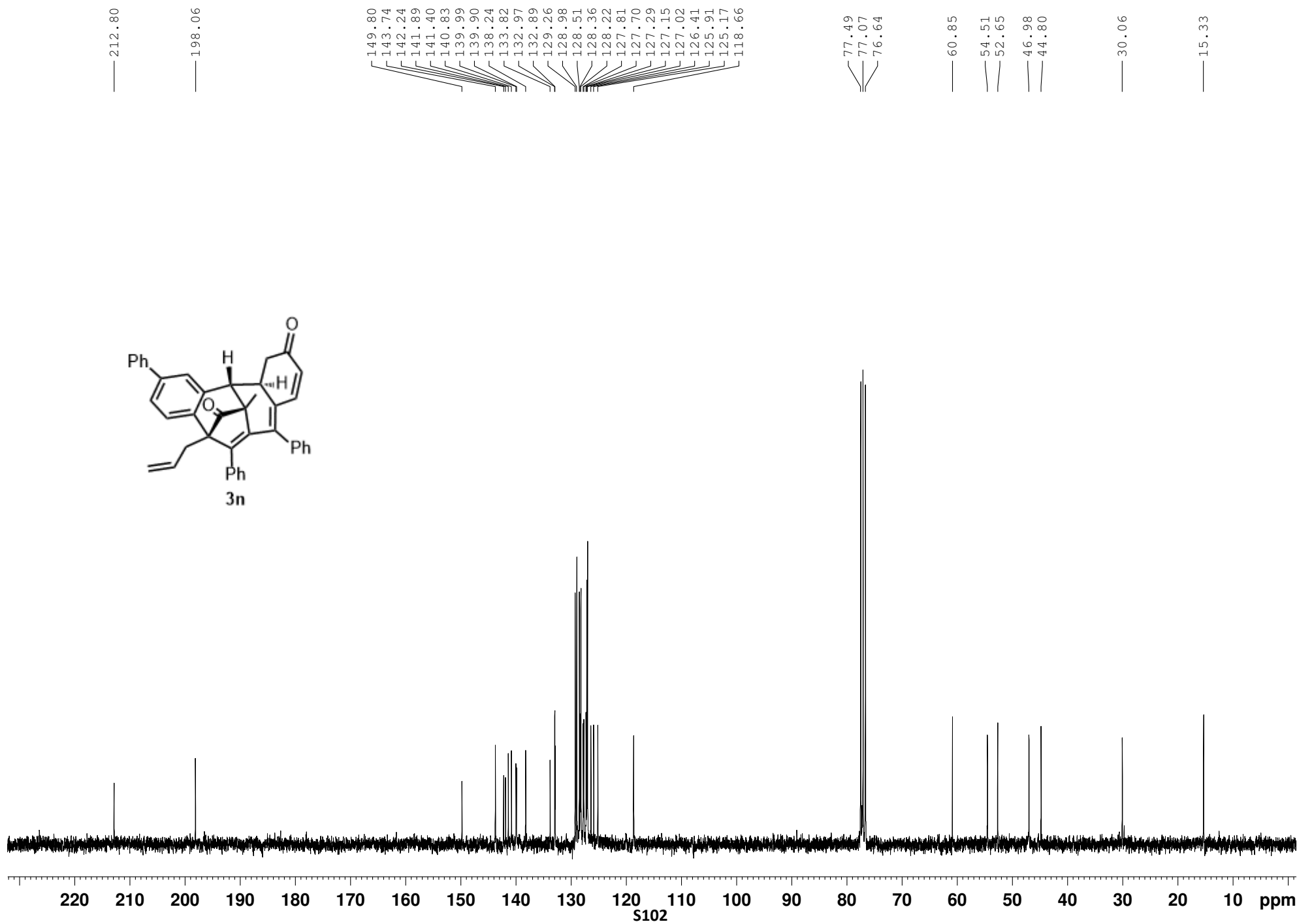
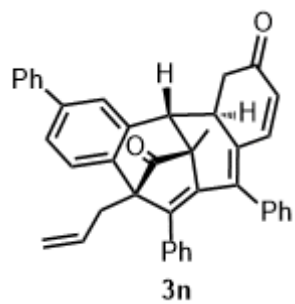








S101



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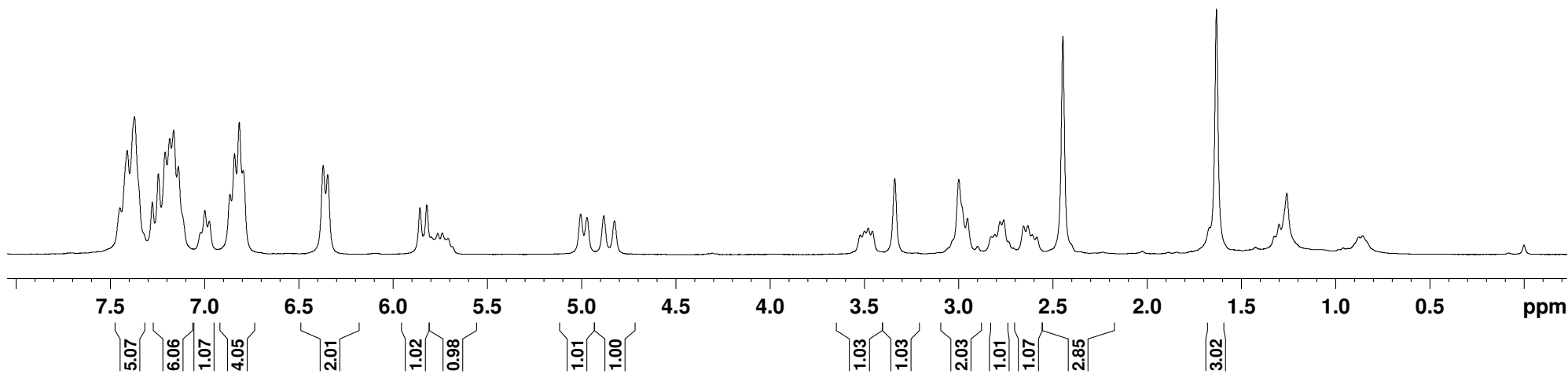
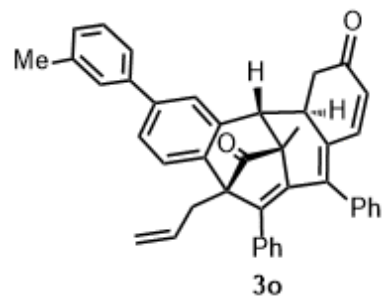
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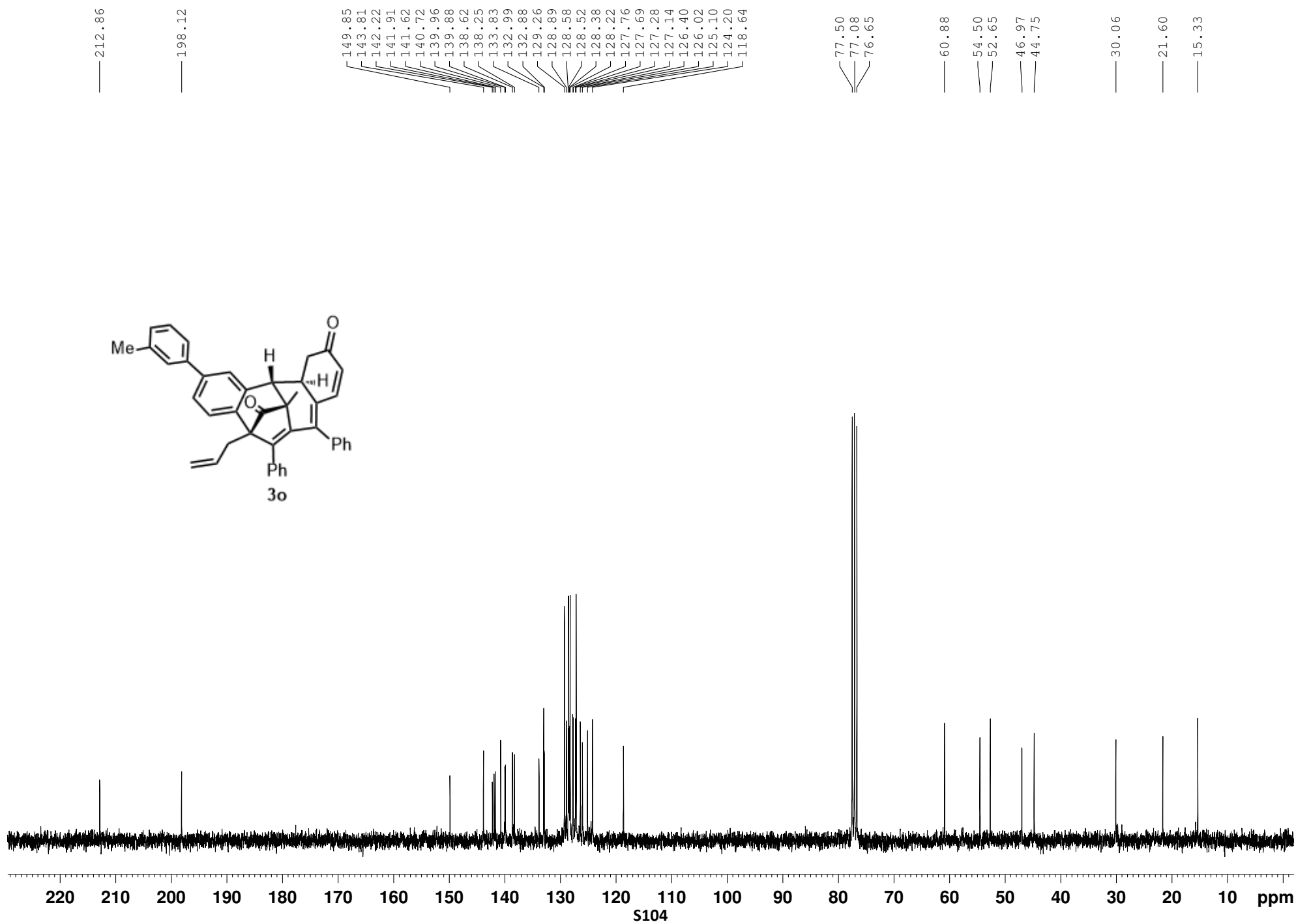
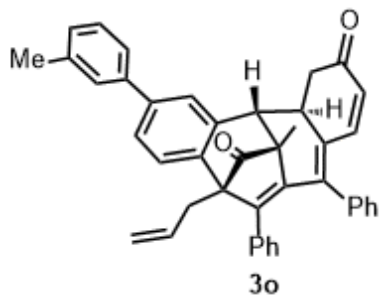
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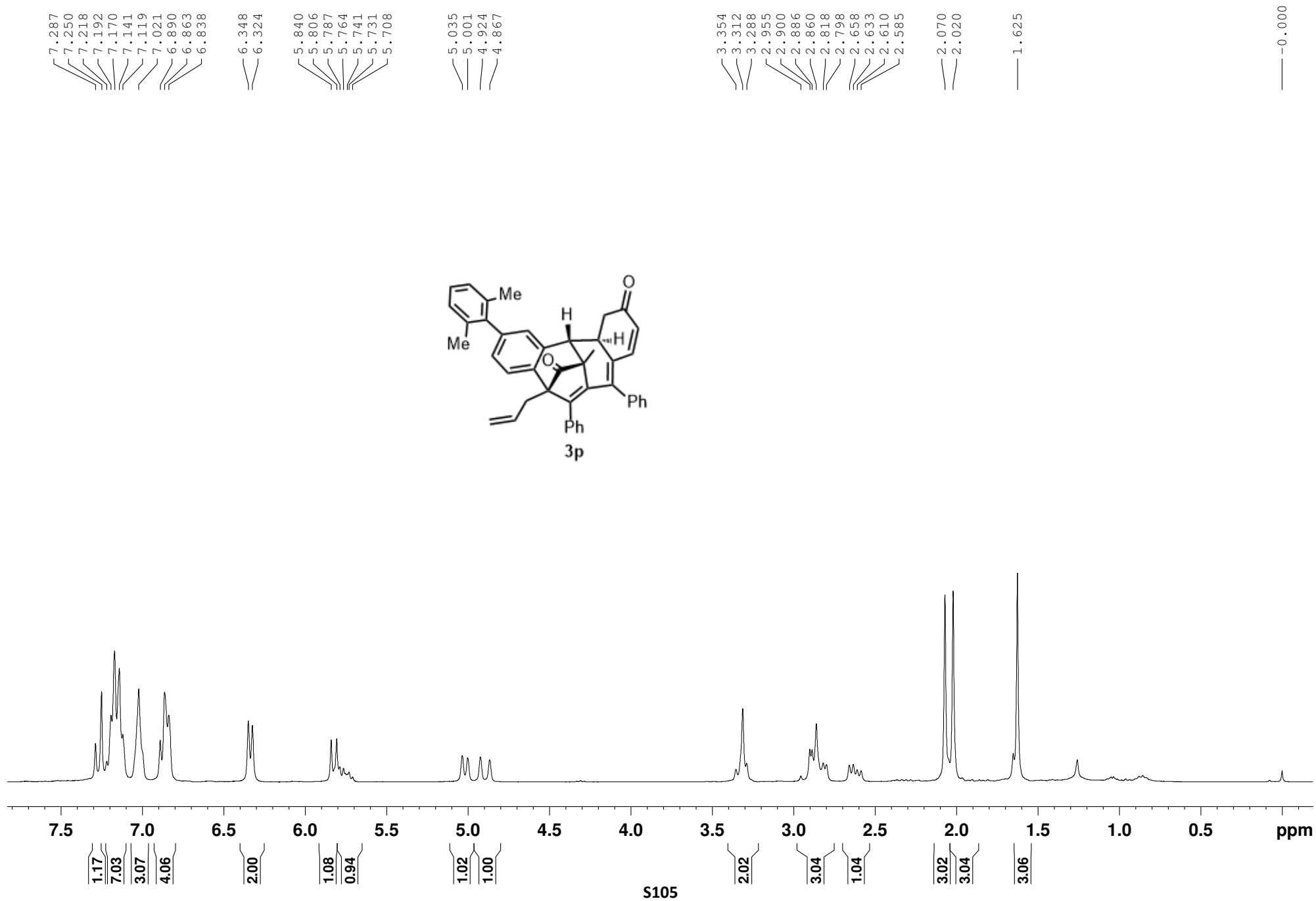
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S103





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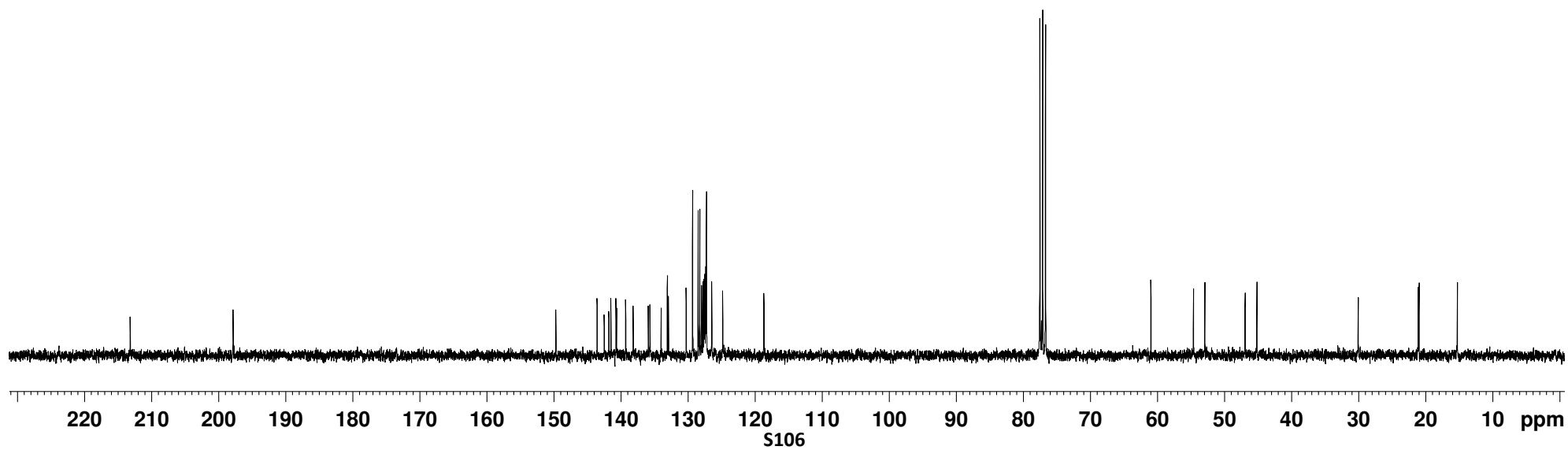
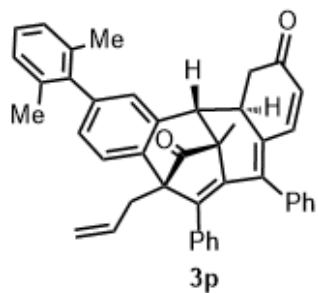
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— 15.21



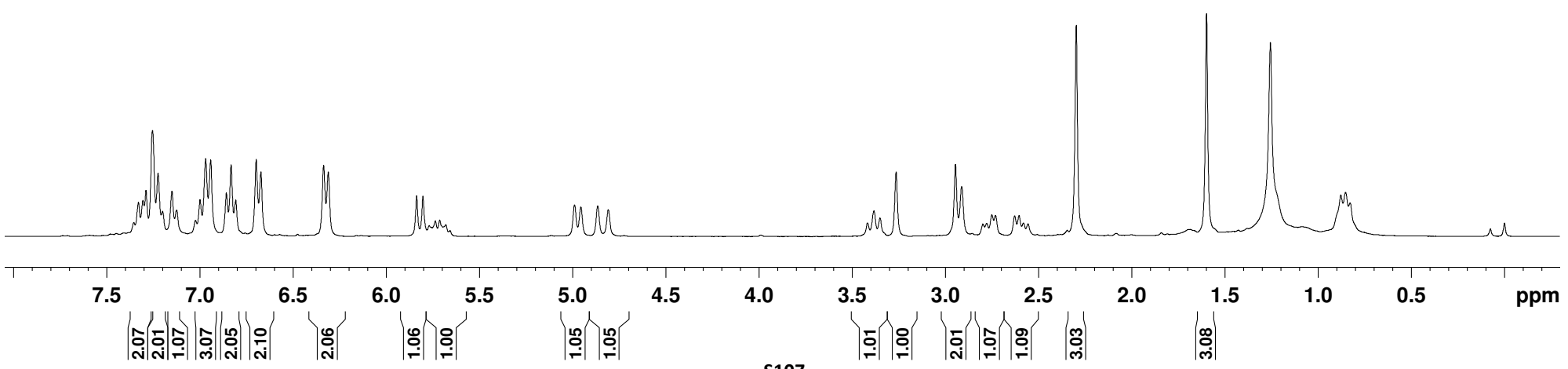
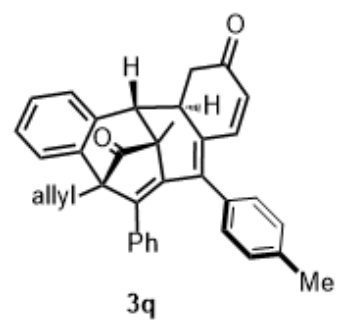
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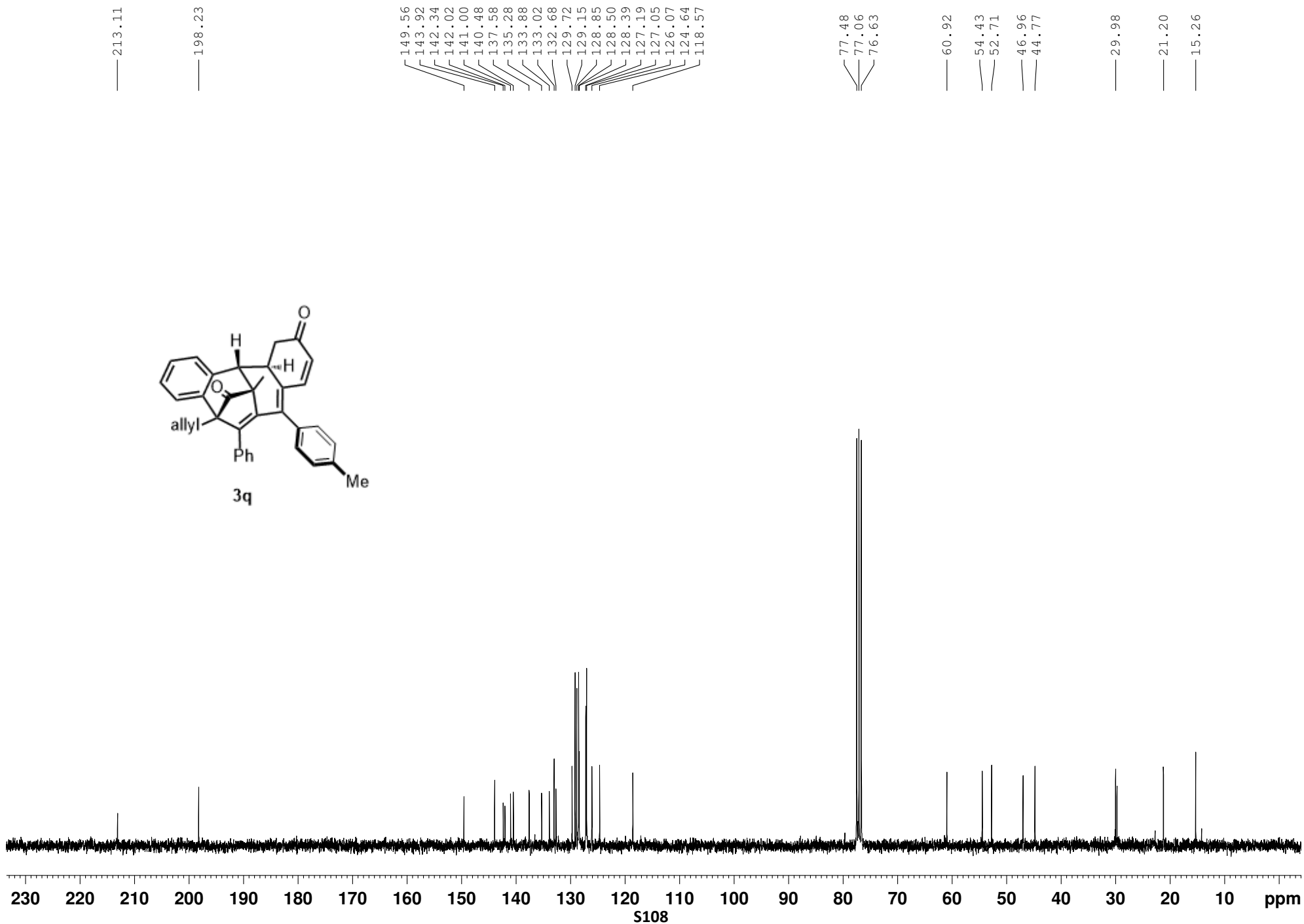
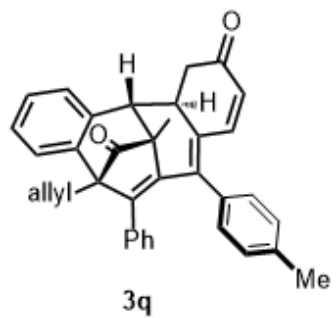
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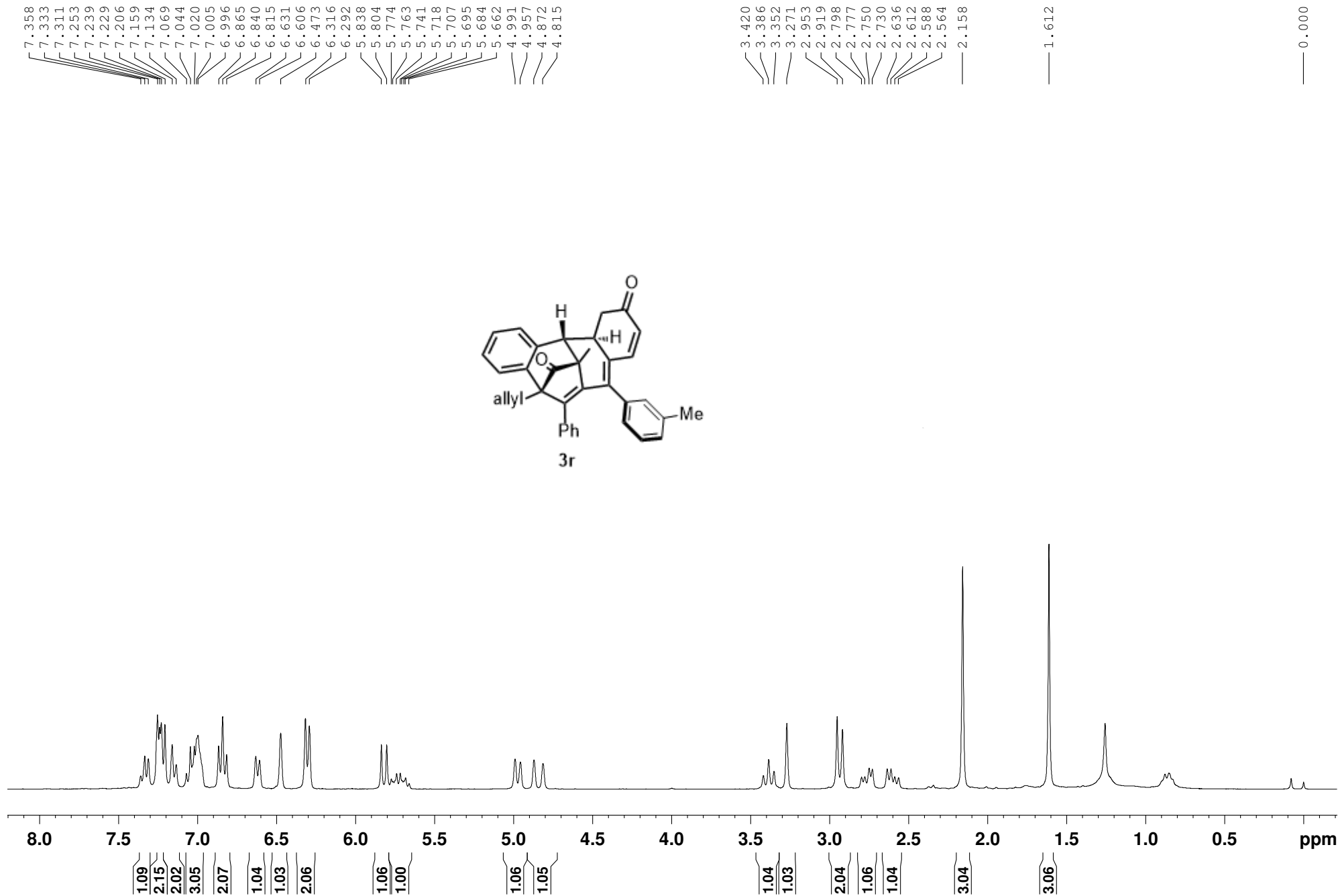
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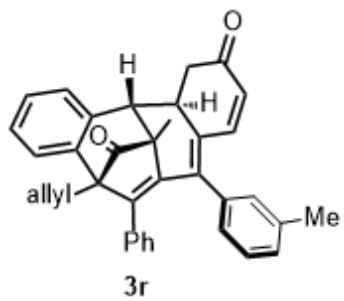
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— 213.06

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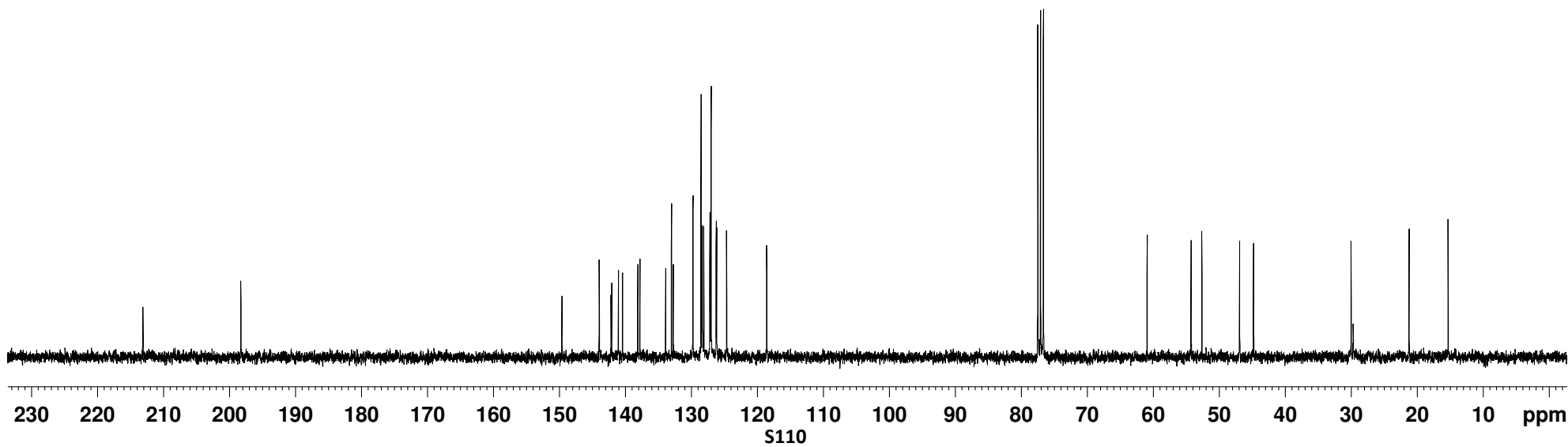
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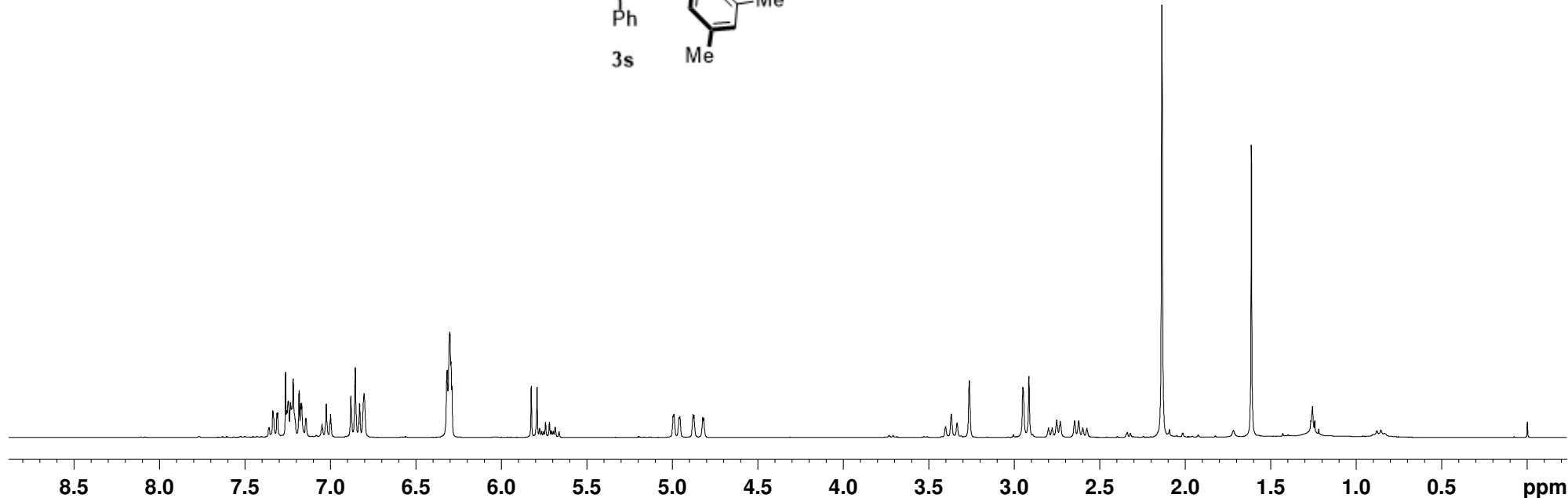
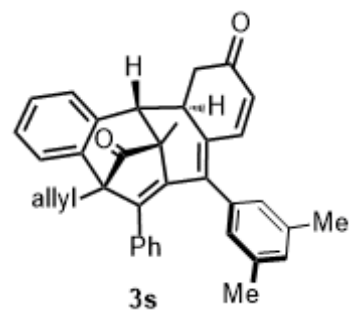


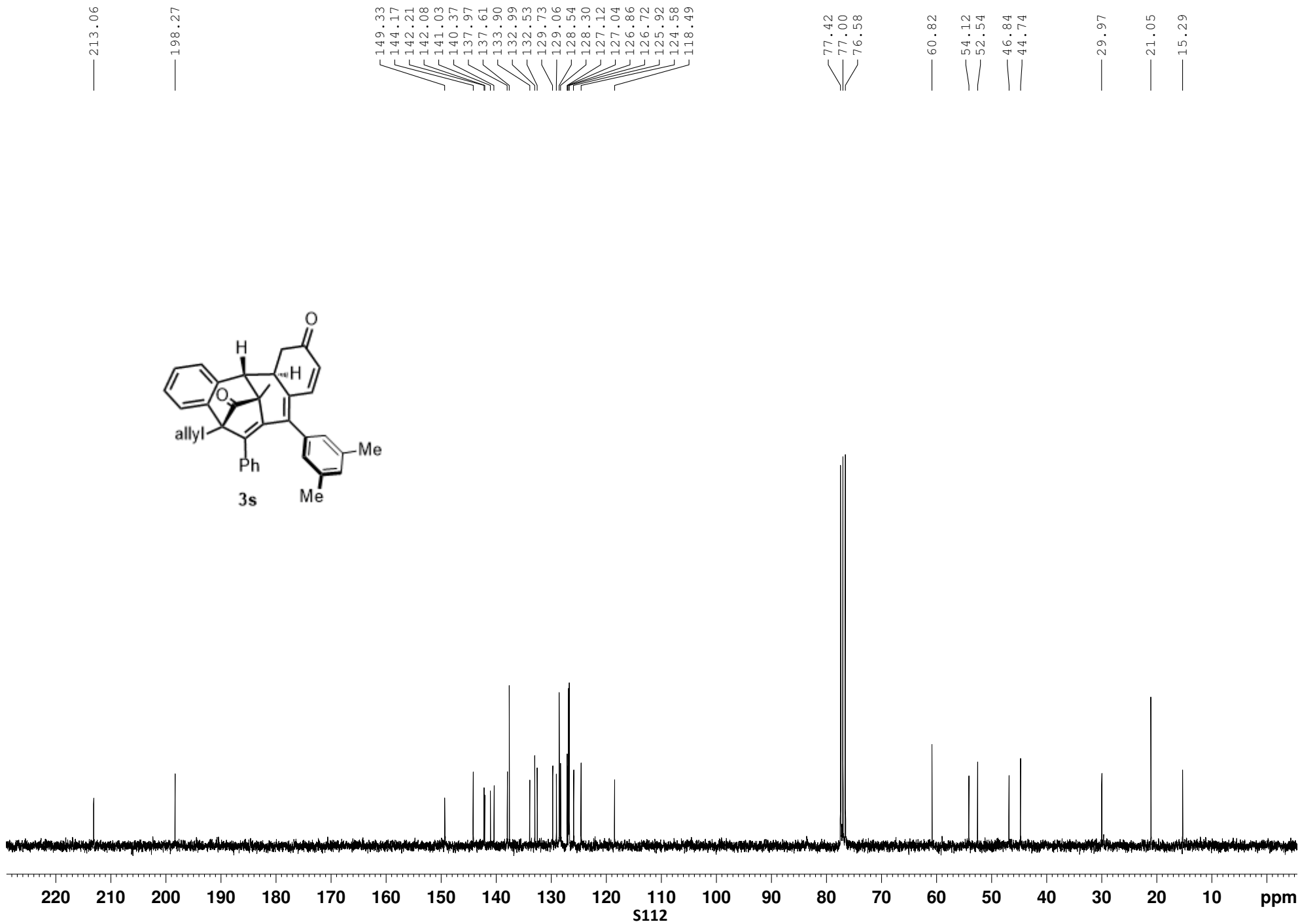
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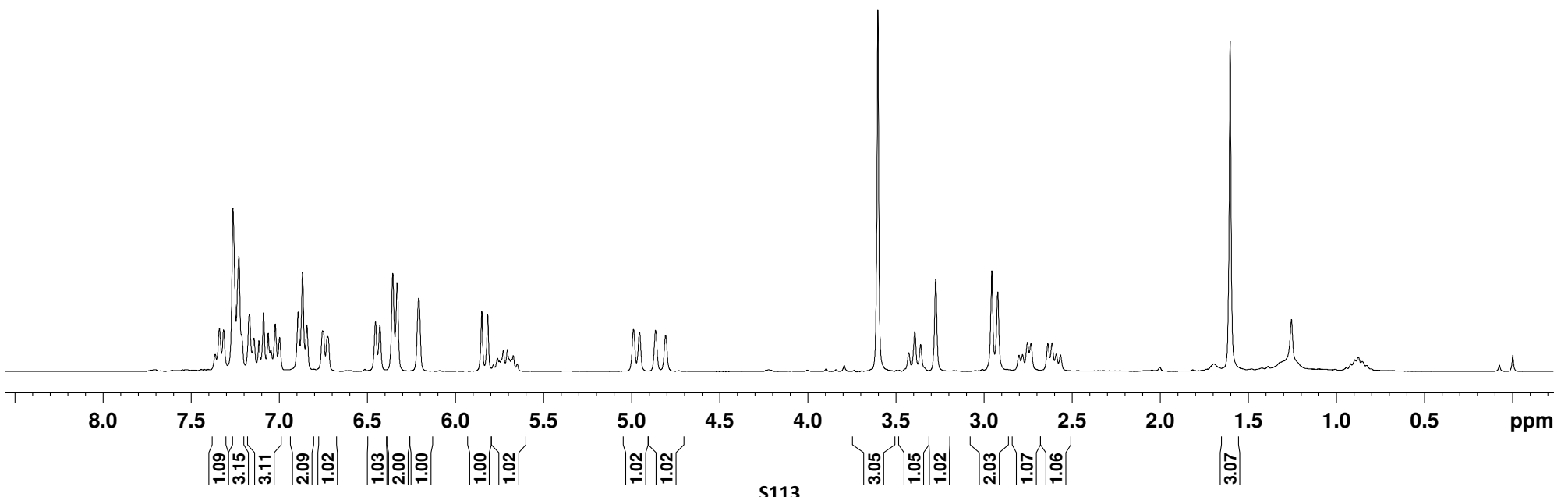
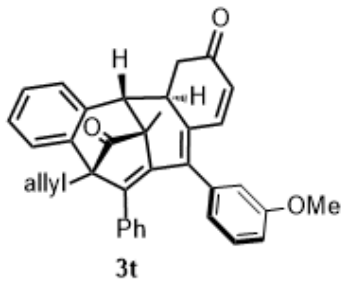


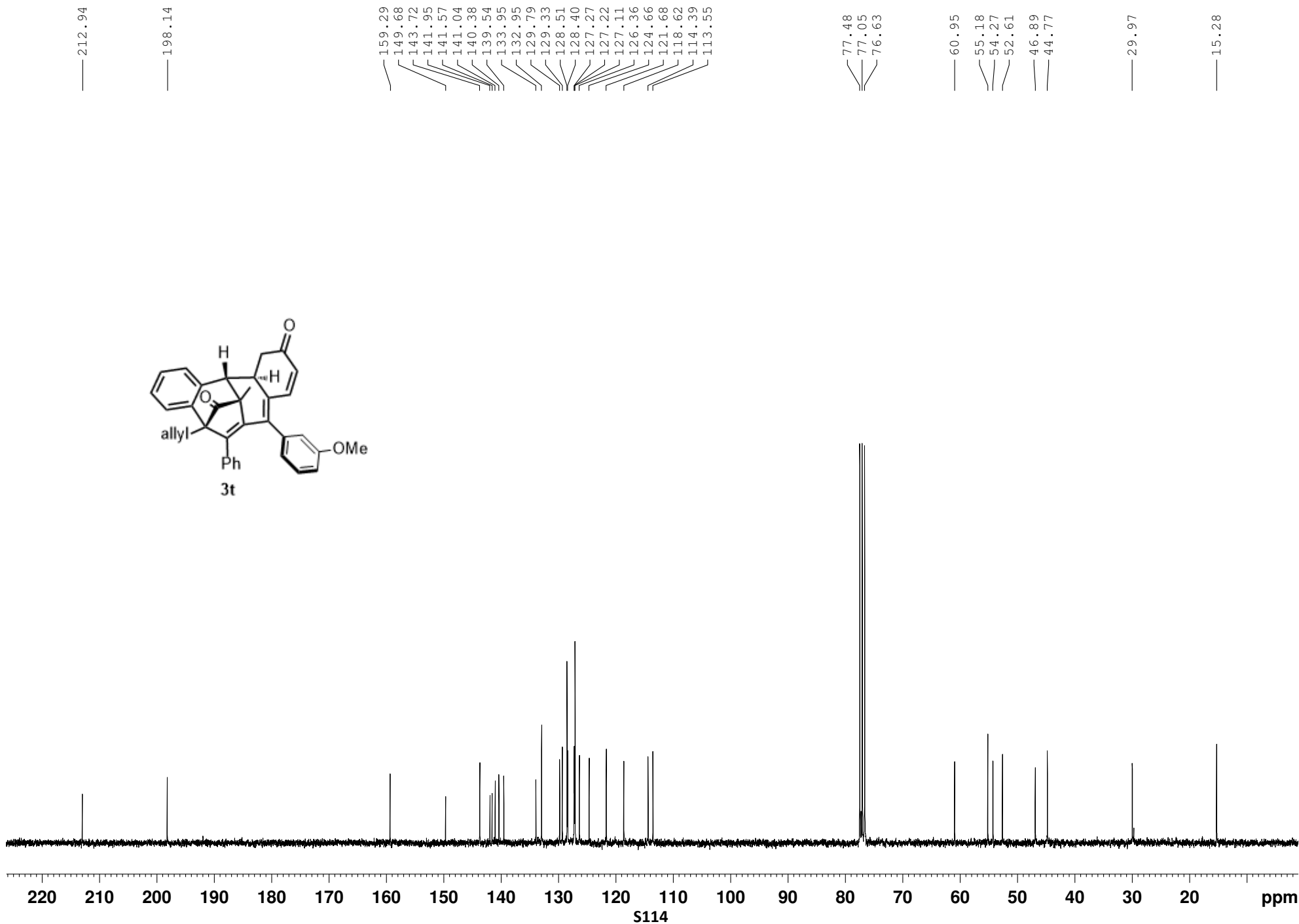
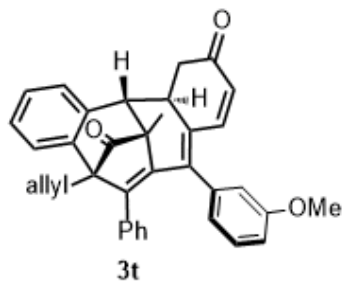
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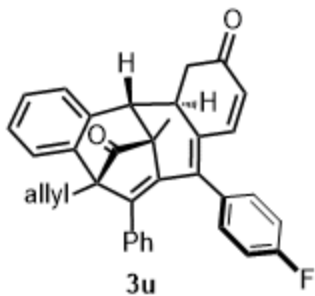
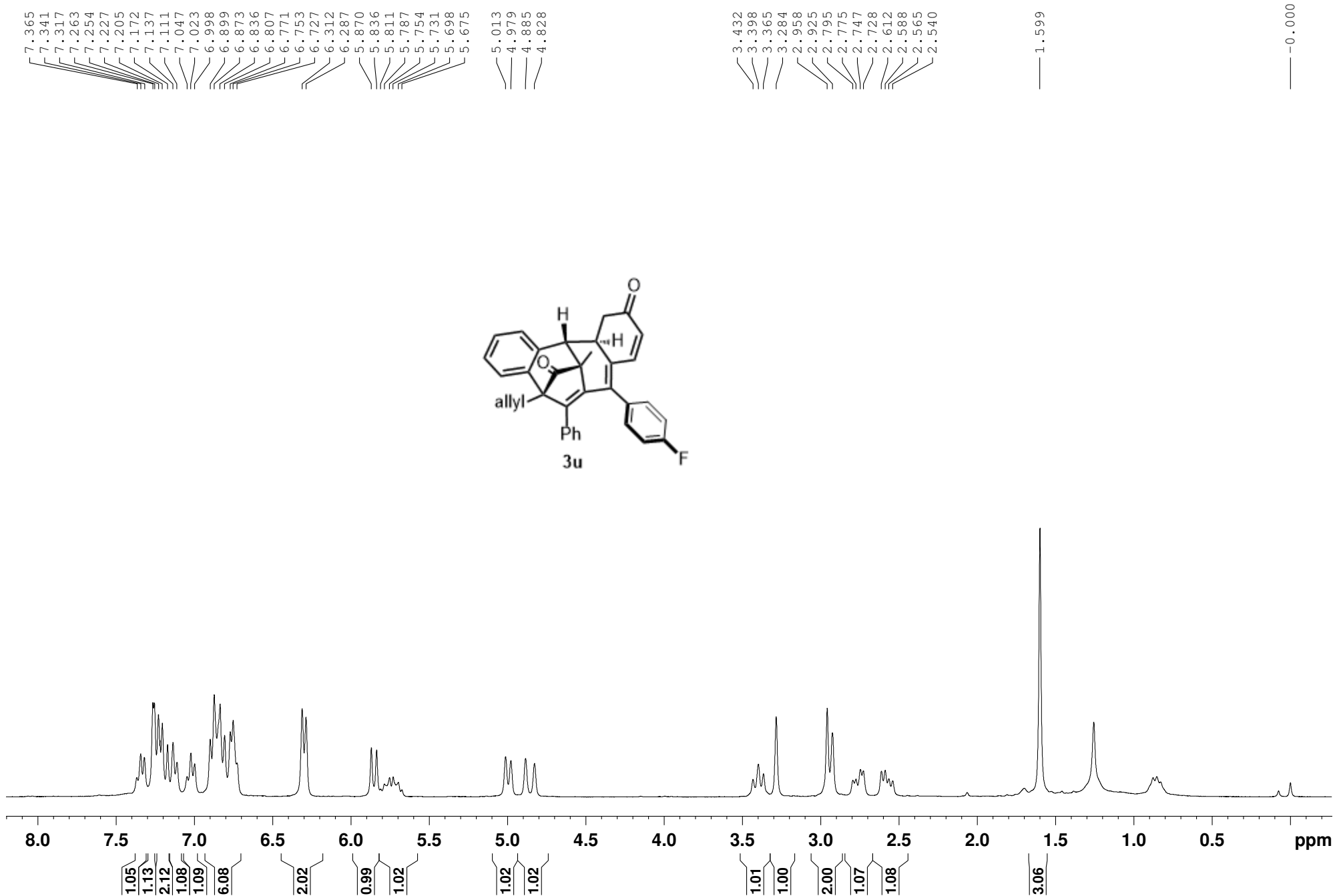
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1.604

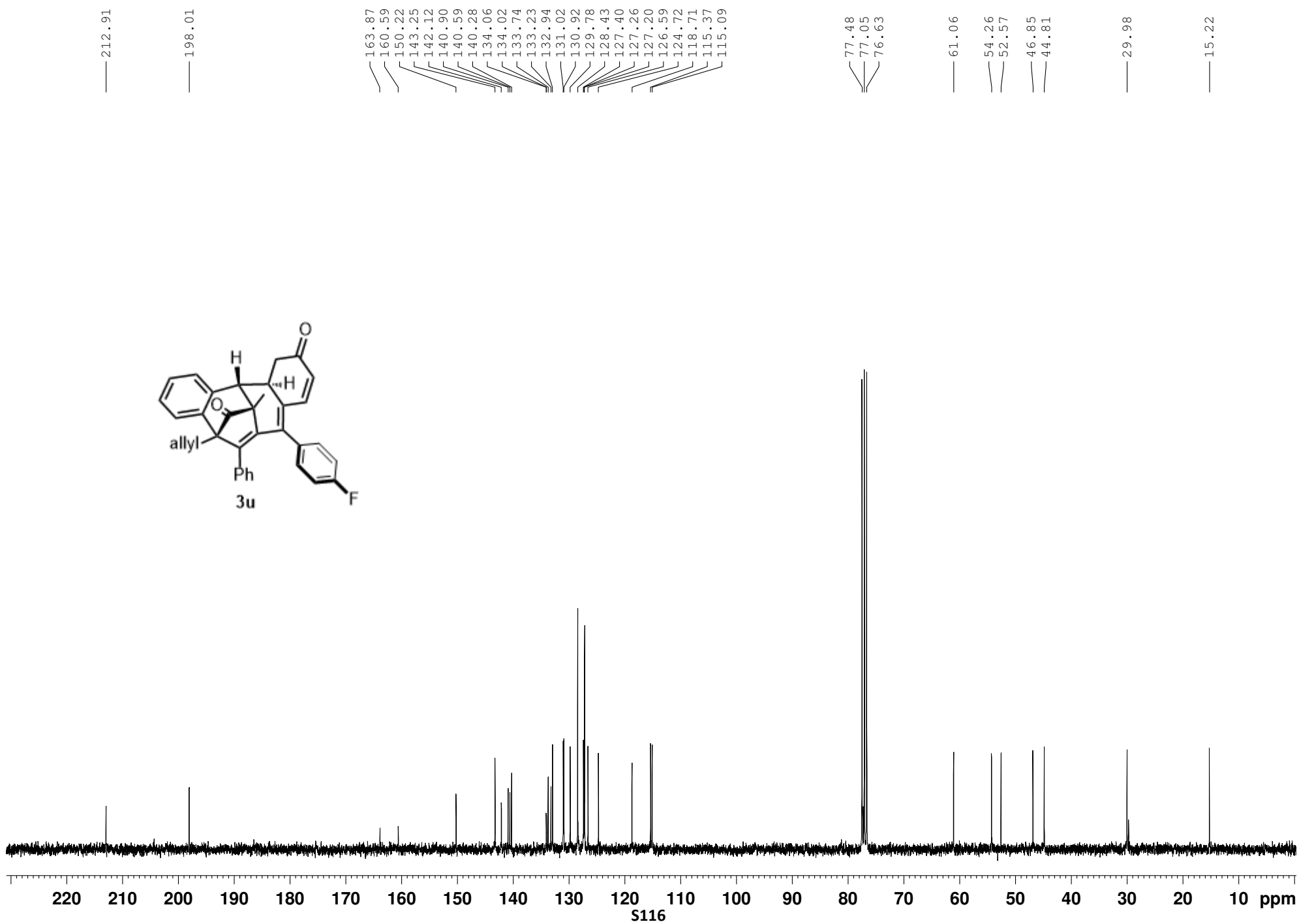
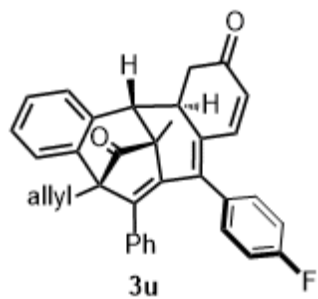
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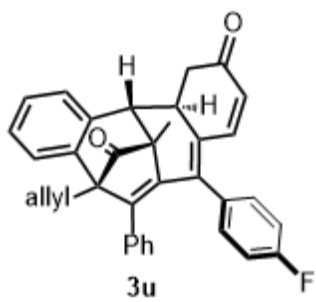




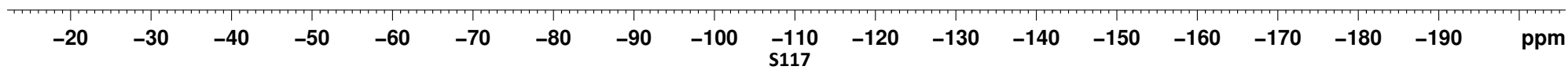


S115





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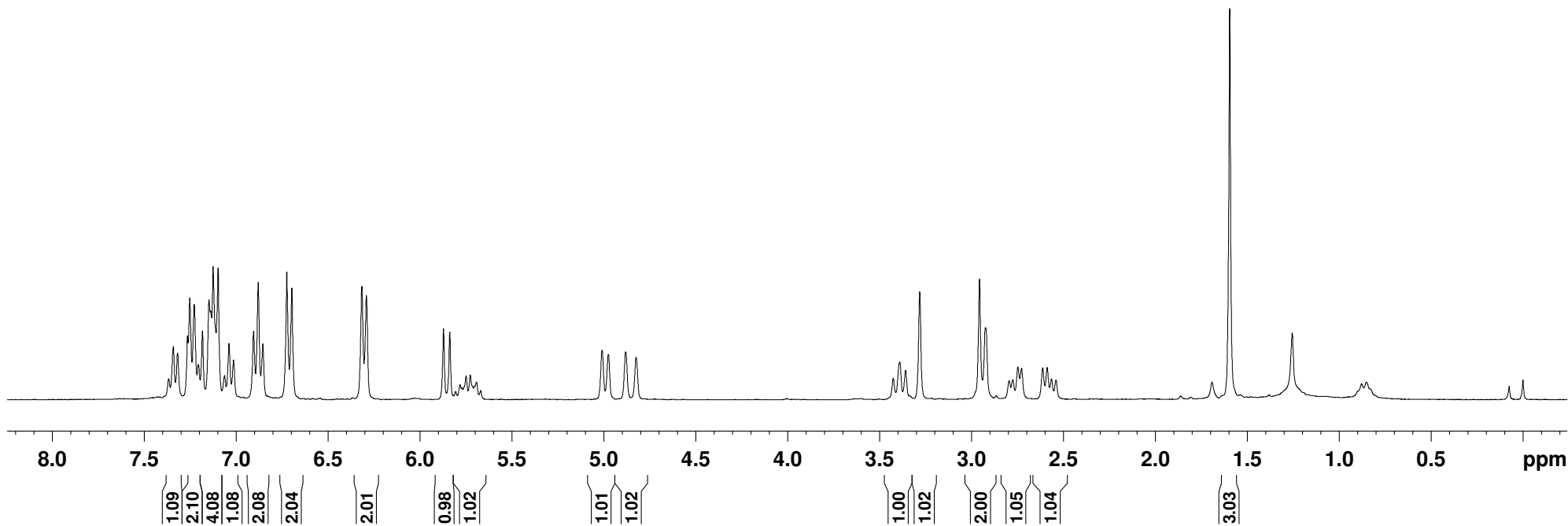
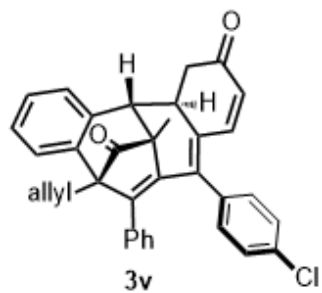


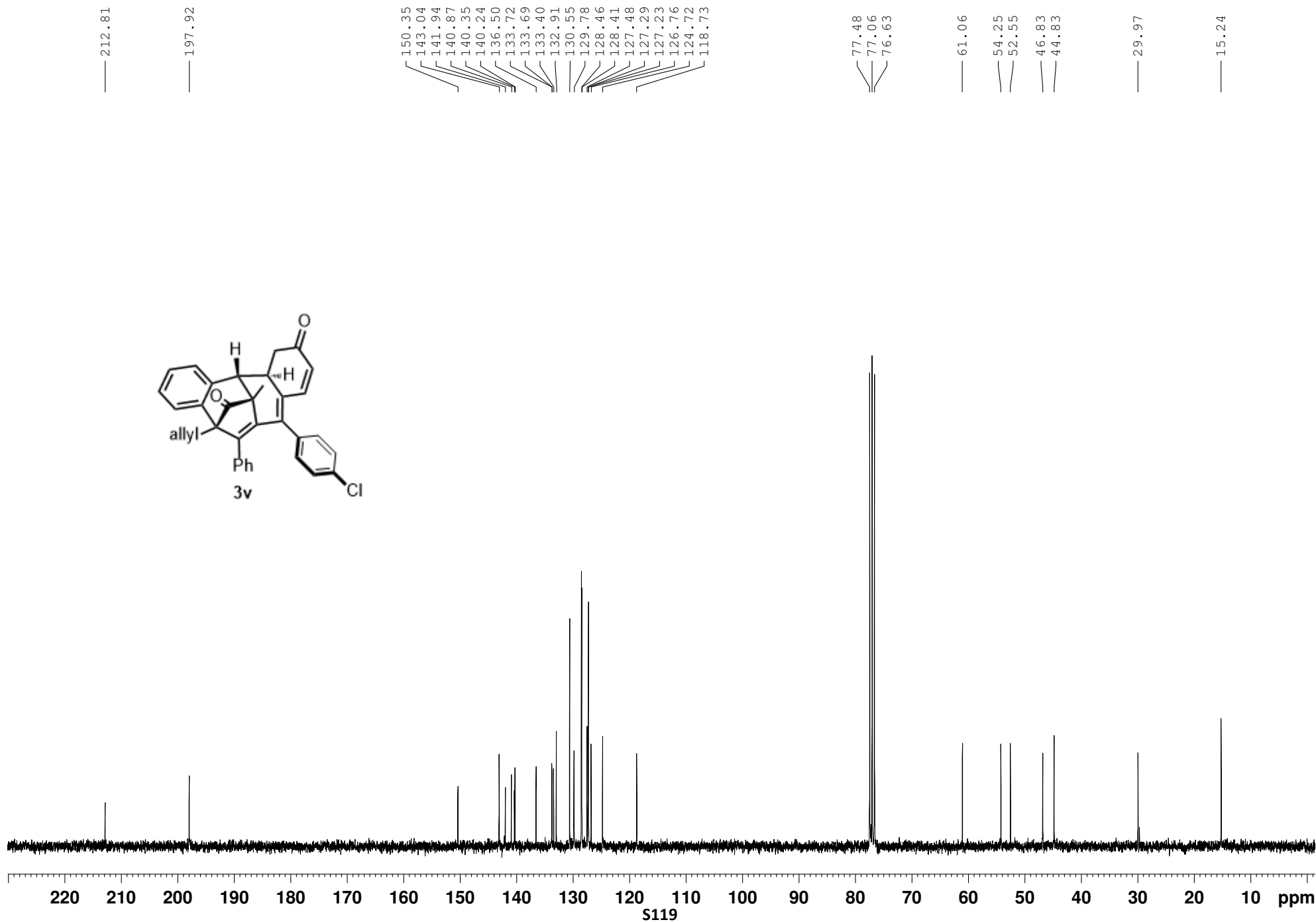
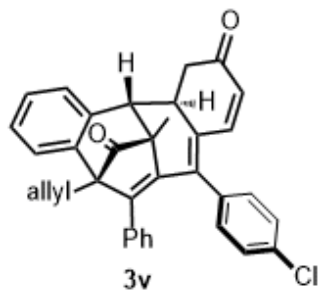
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7.062
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7.013
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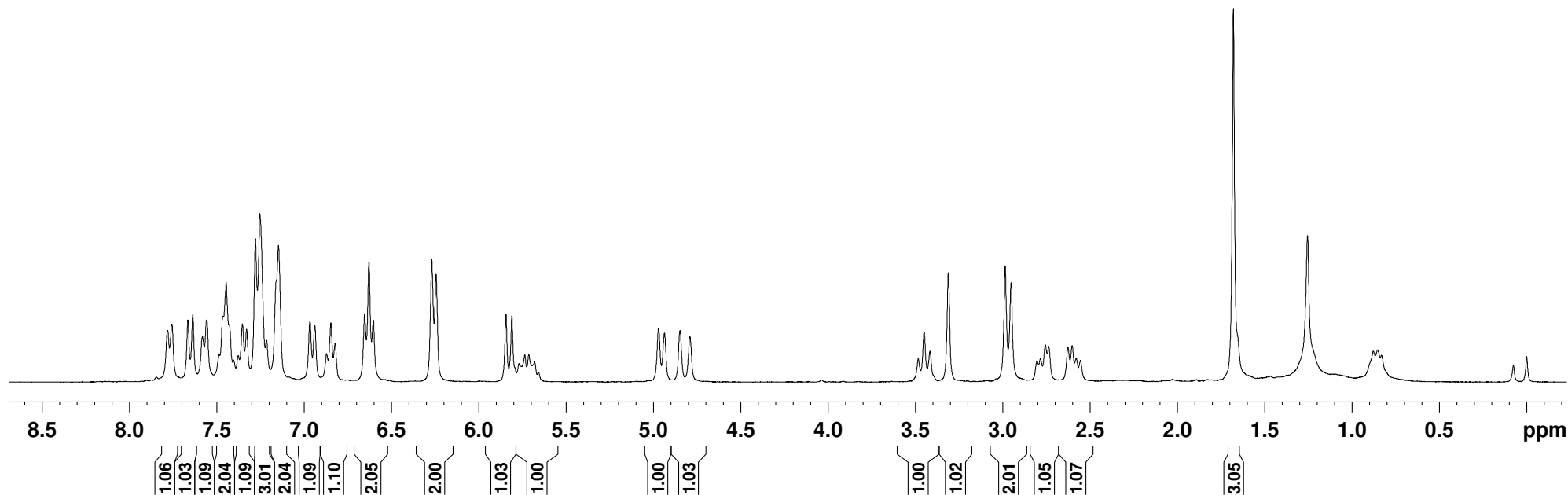
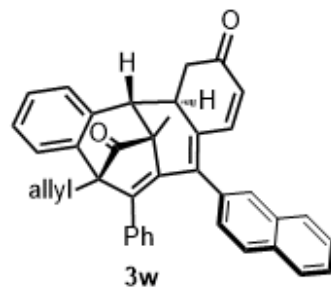


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-0.000



S120

— 213.01

— 198.14

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141.80
141.00
140.42
135.62
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132.97
132.87
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129.79
128.41
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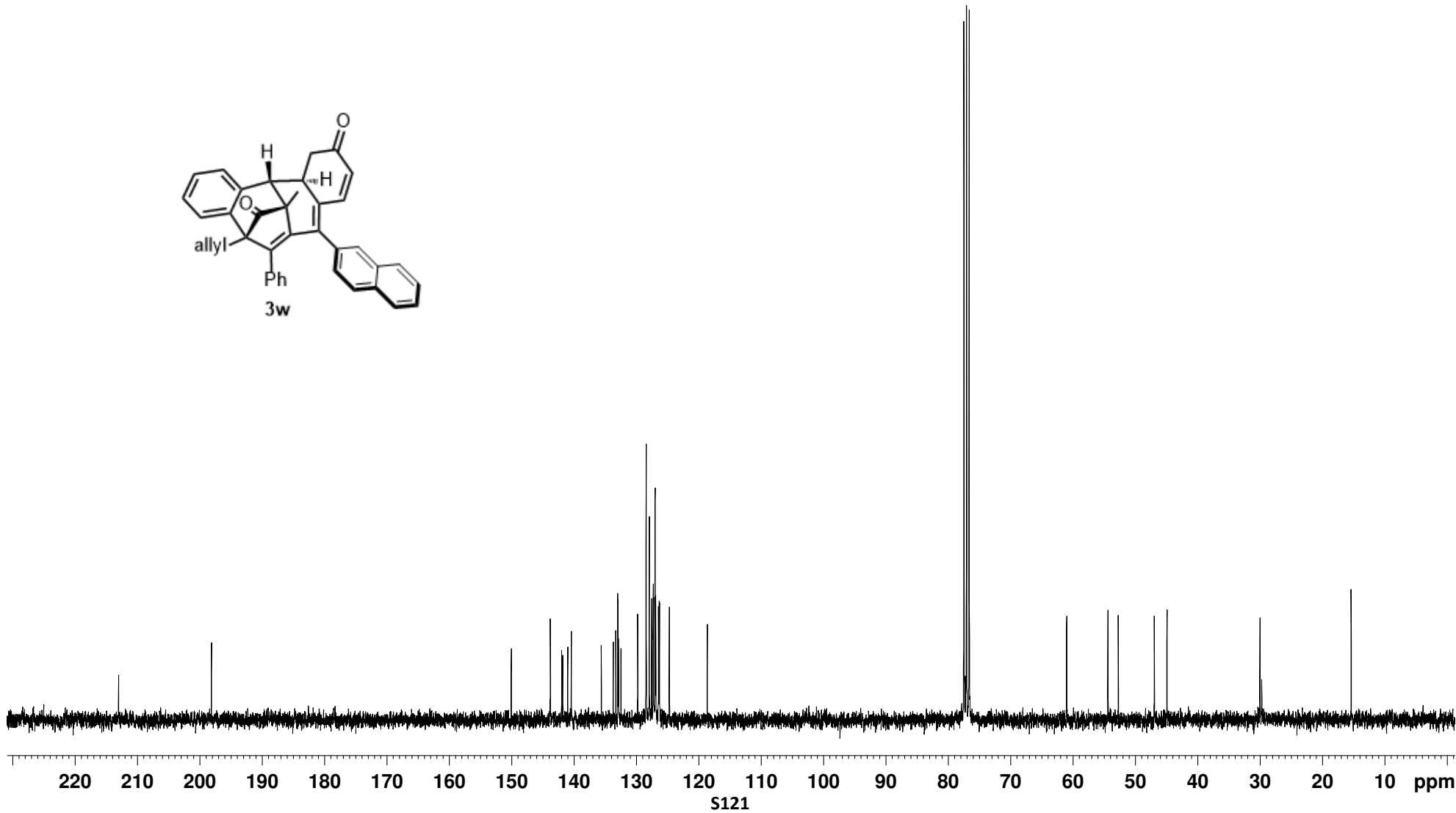
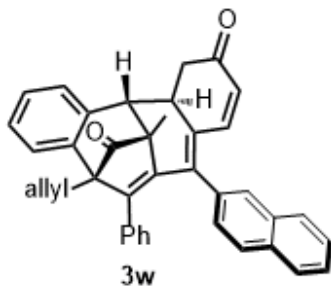
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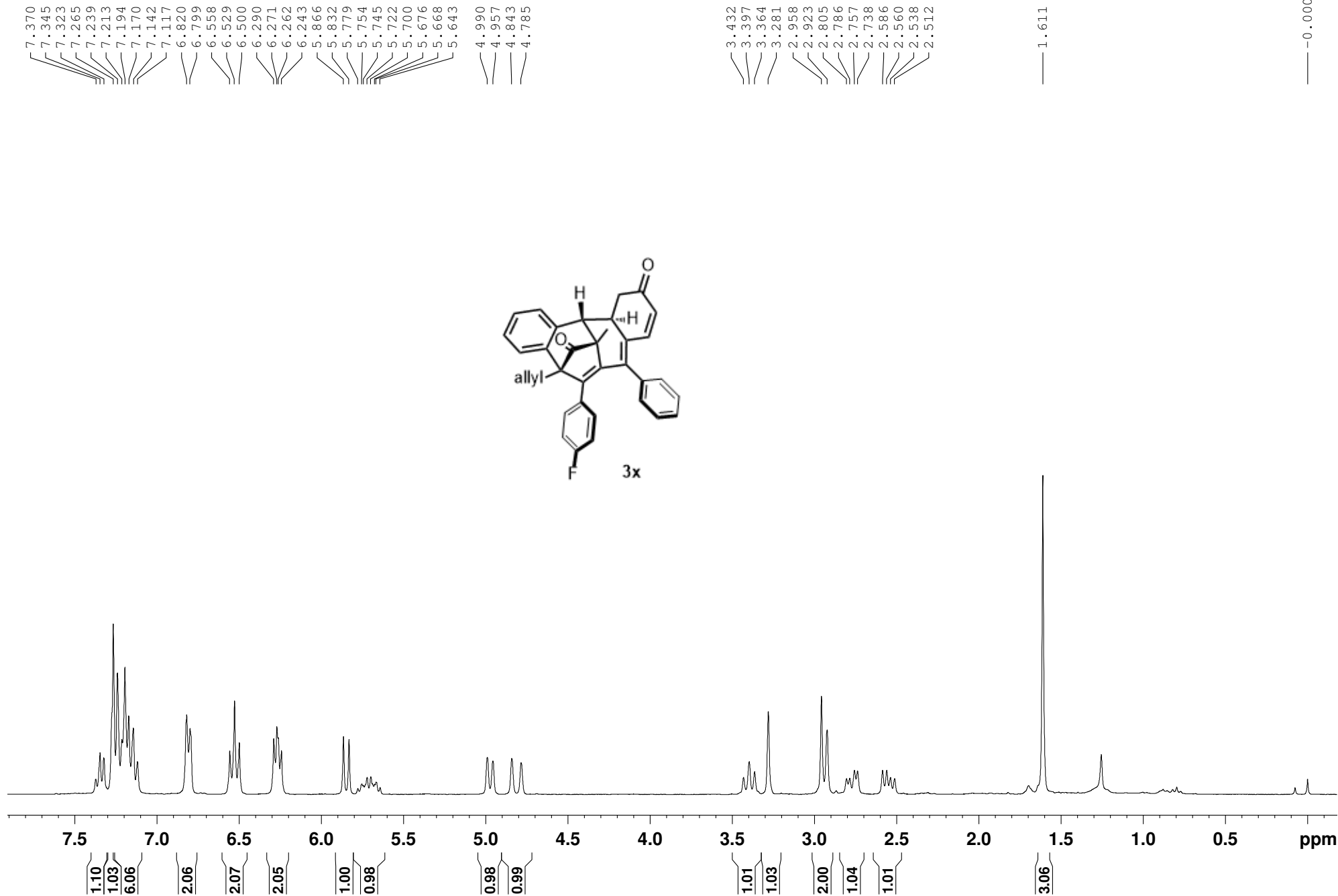
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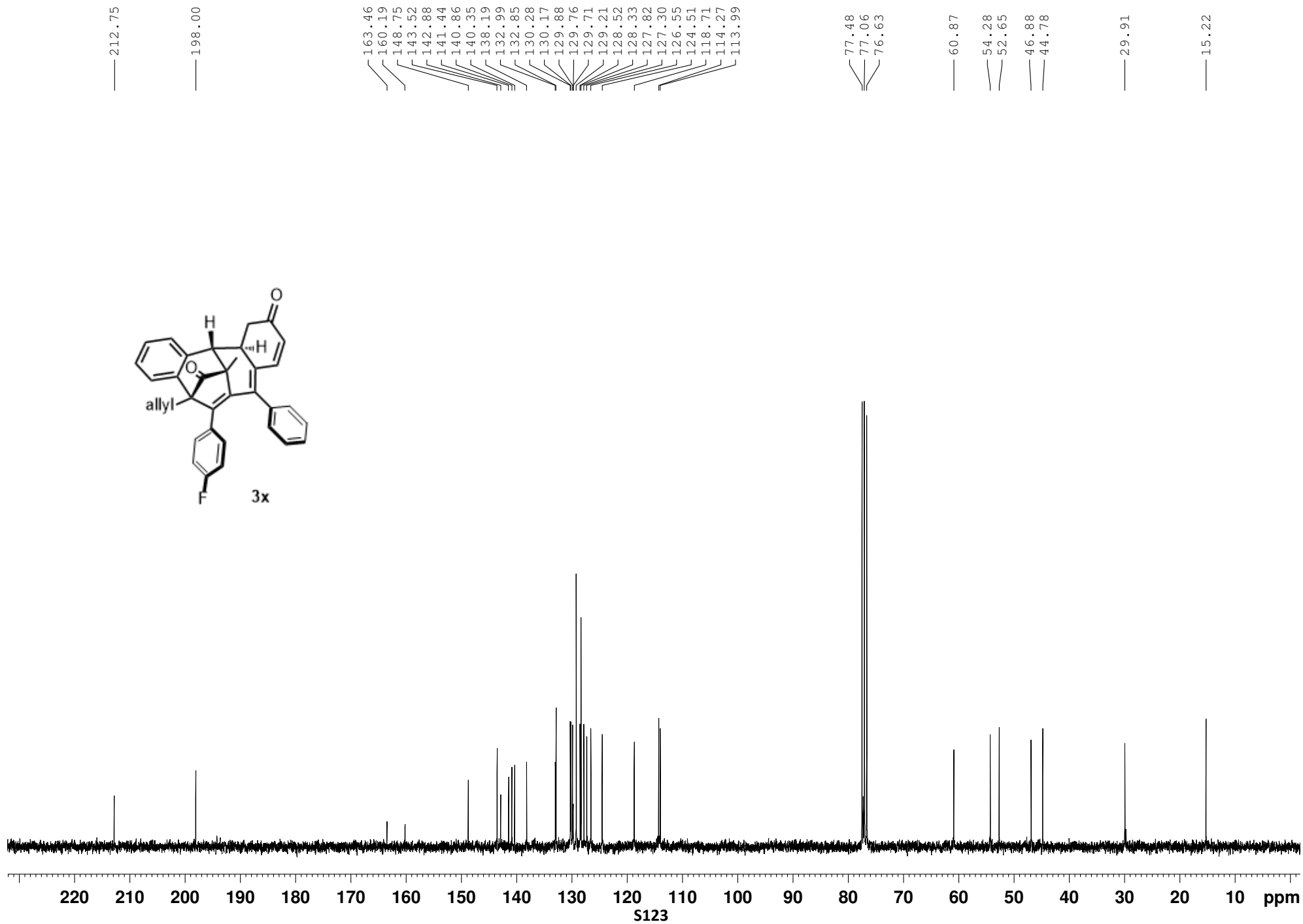
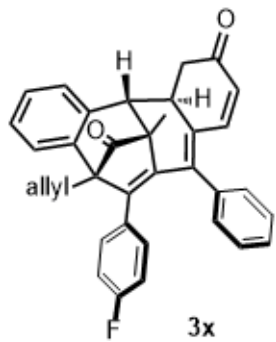
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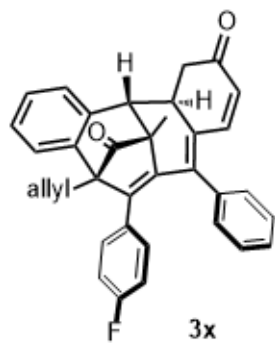
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— 15.37

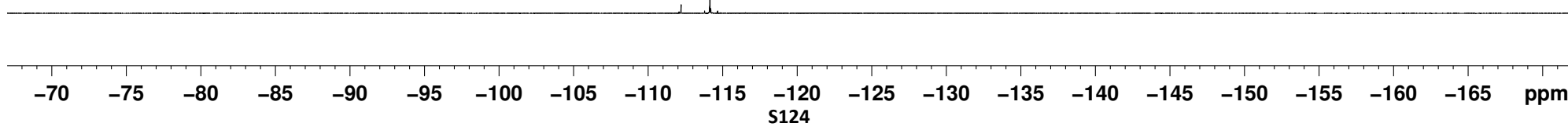


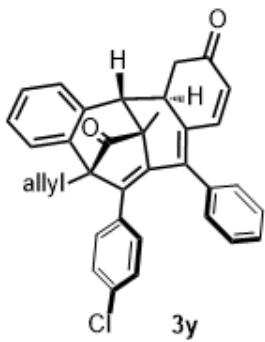
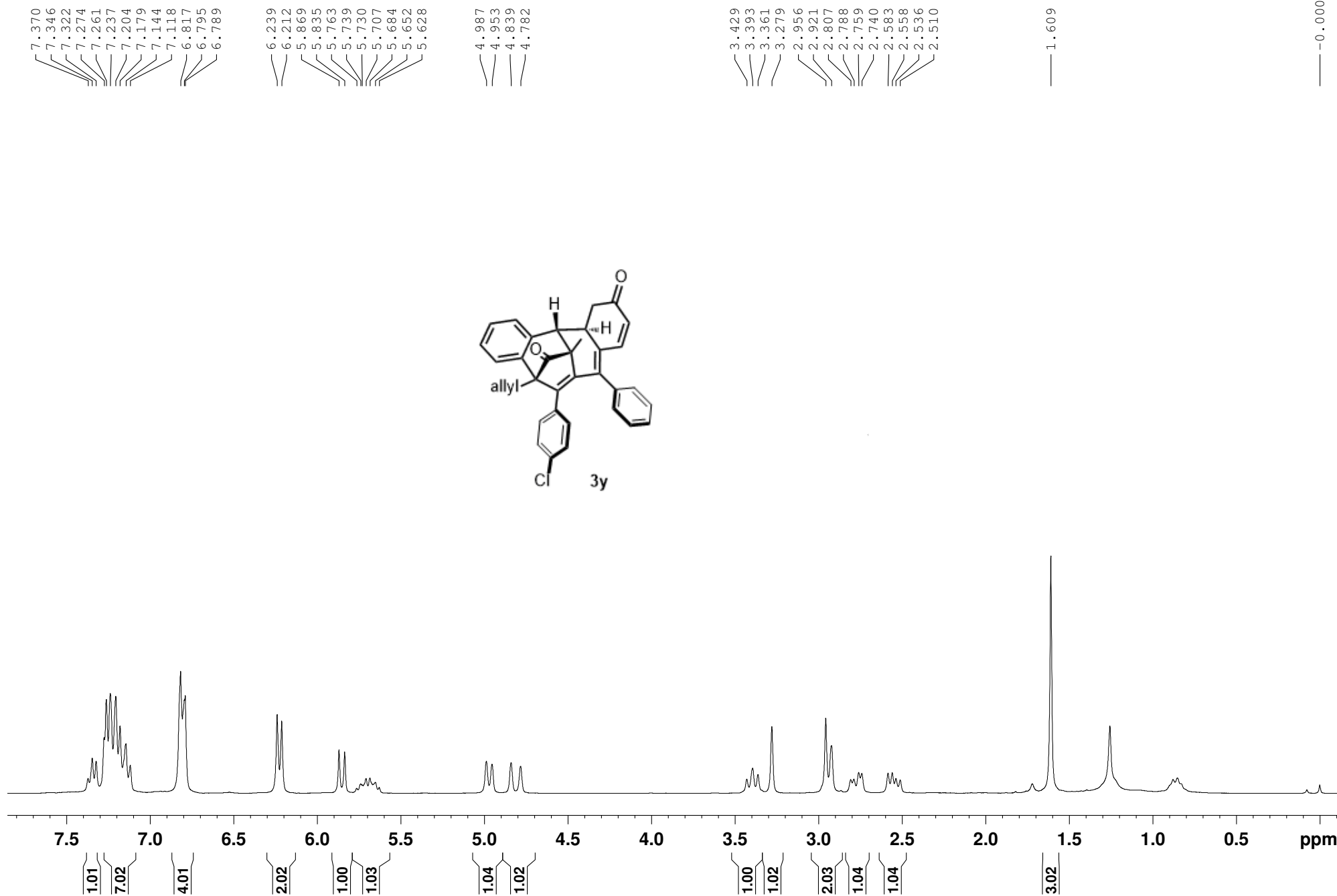


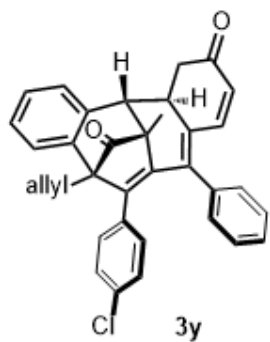




— -114.130







— 212.58

— 197.97

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133.07
132.77
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76.65

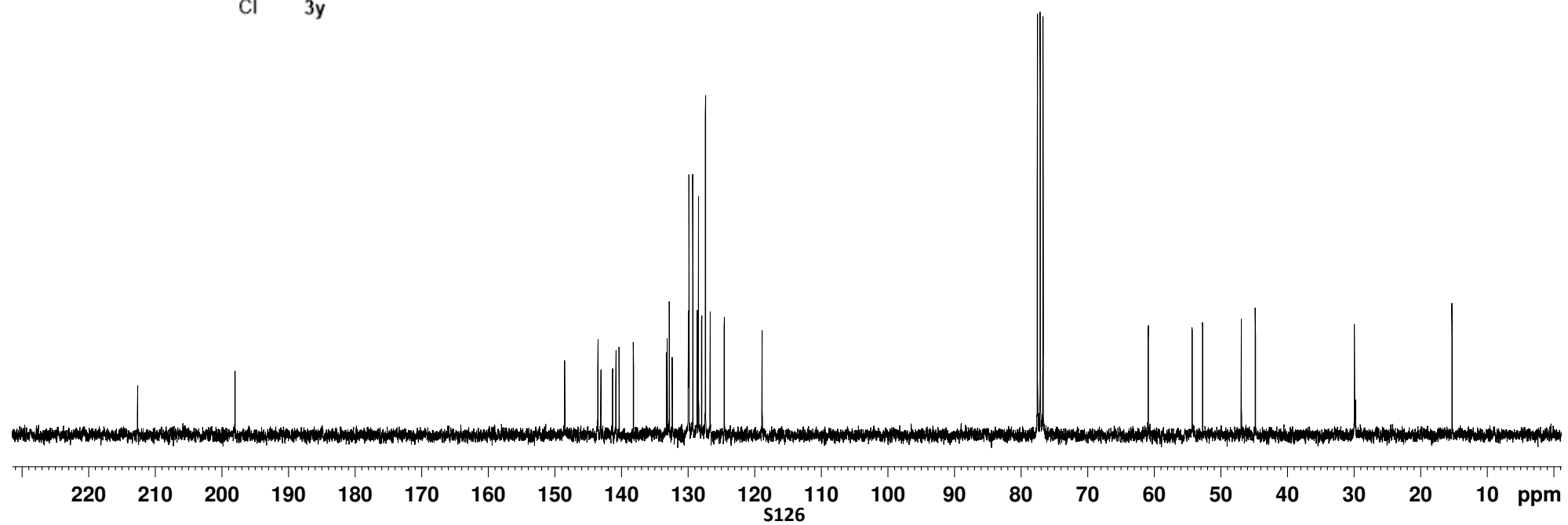
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— 29.89

— 15.23

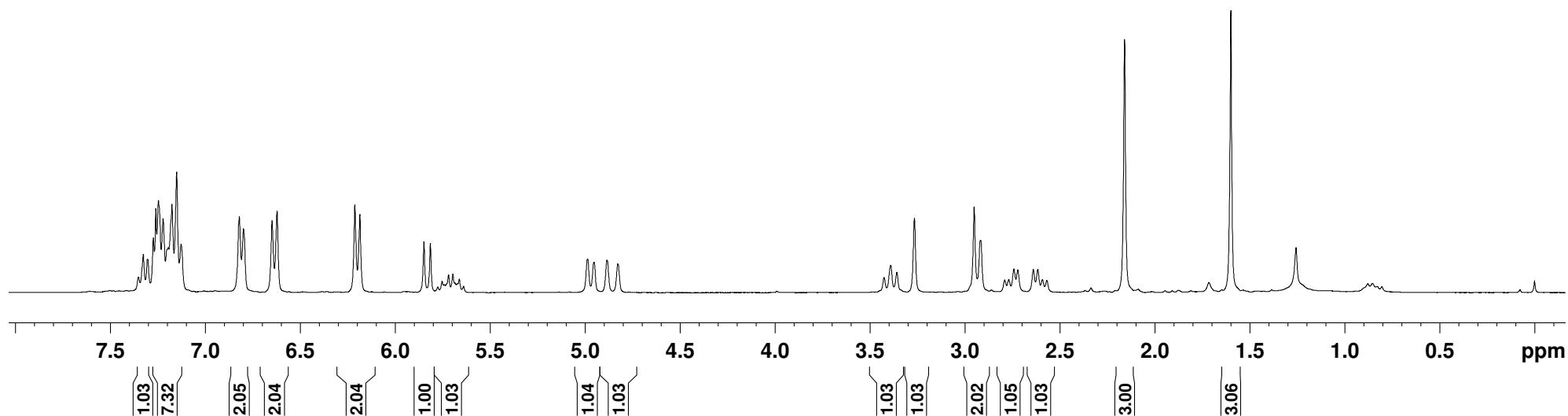
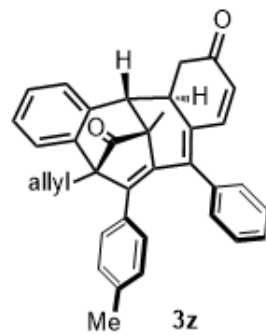


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7.304
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7.201
7.193
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7.149
7.127
6.820
6.798
6.647
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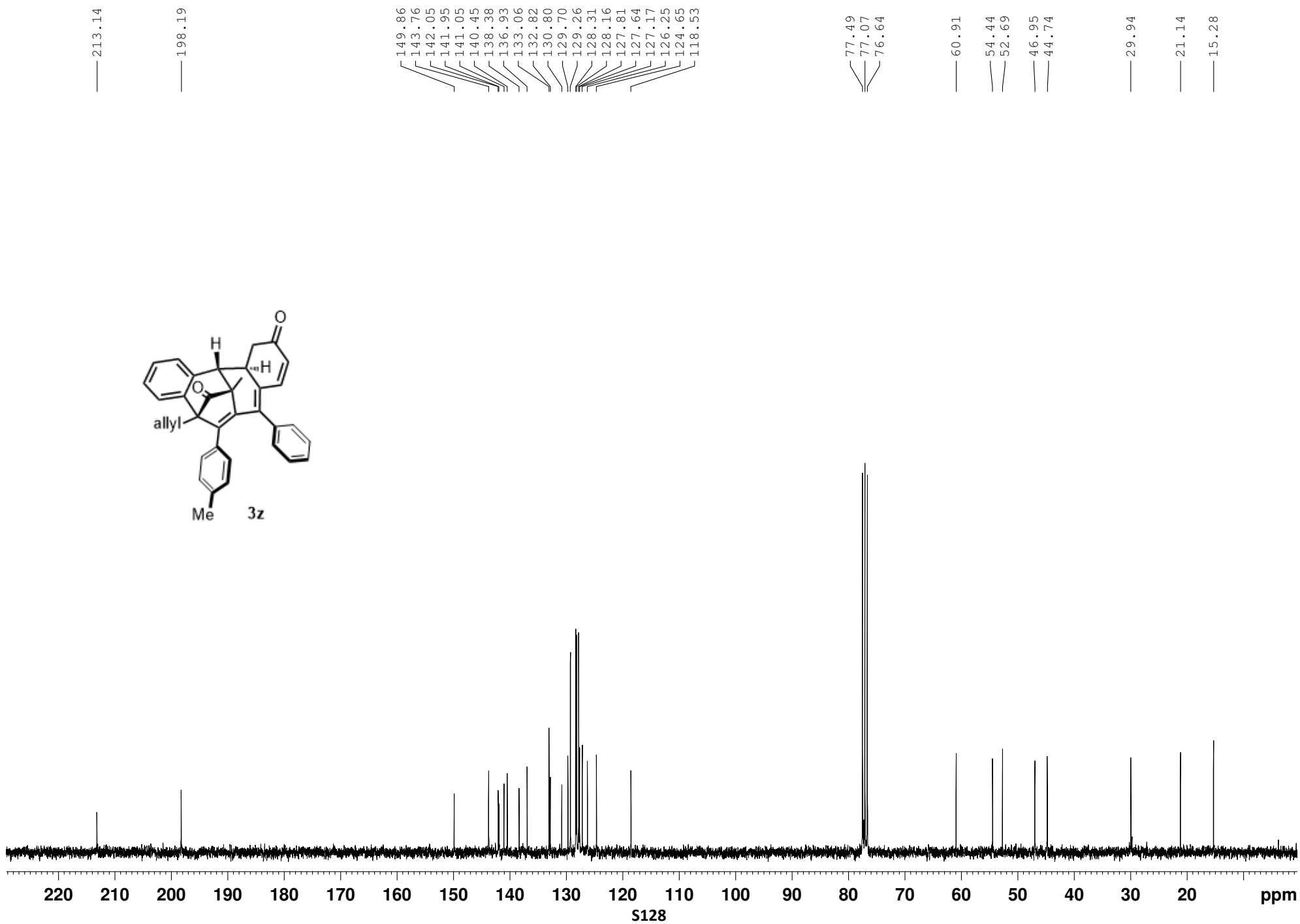
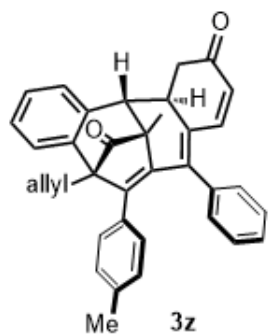
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2.568
2.159

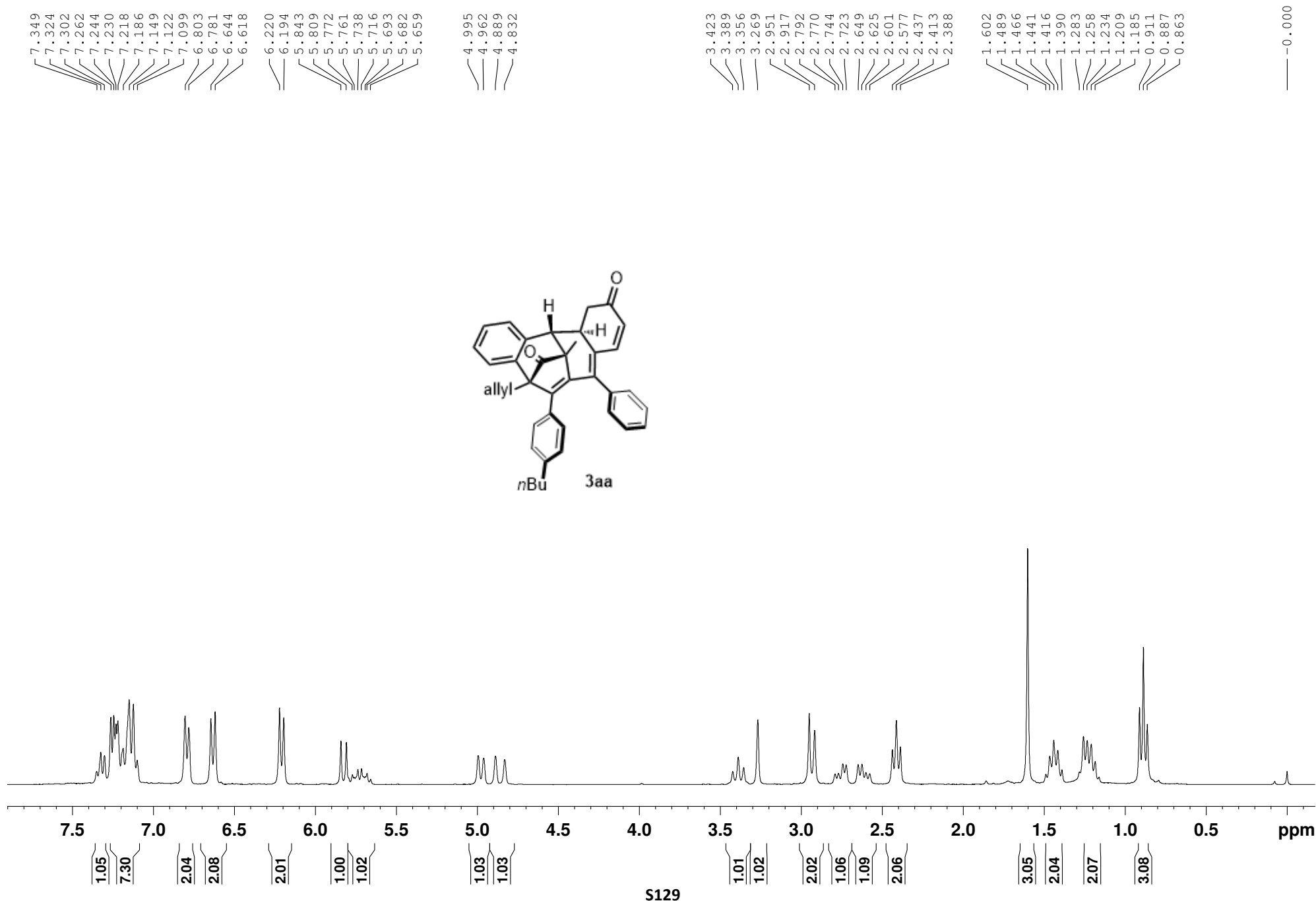
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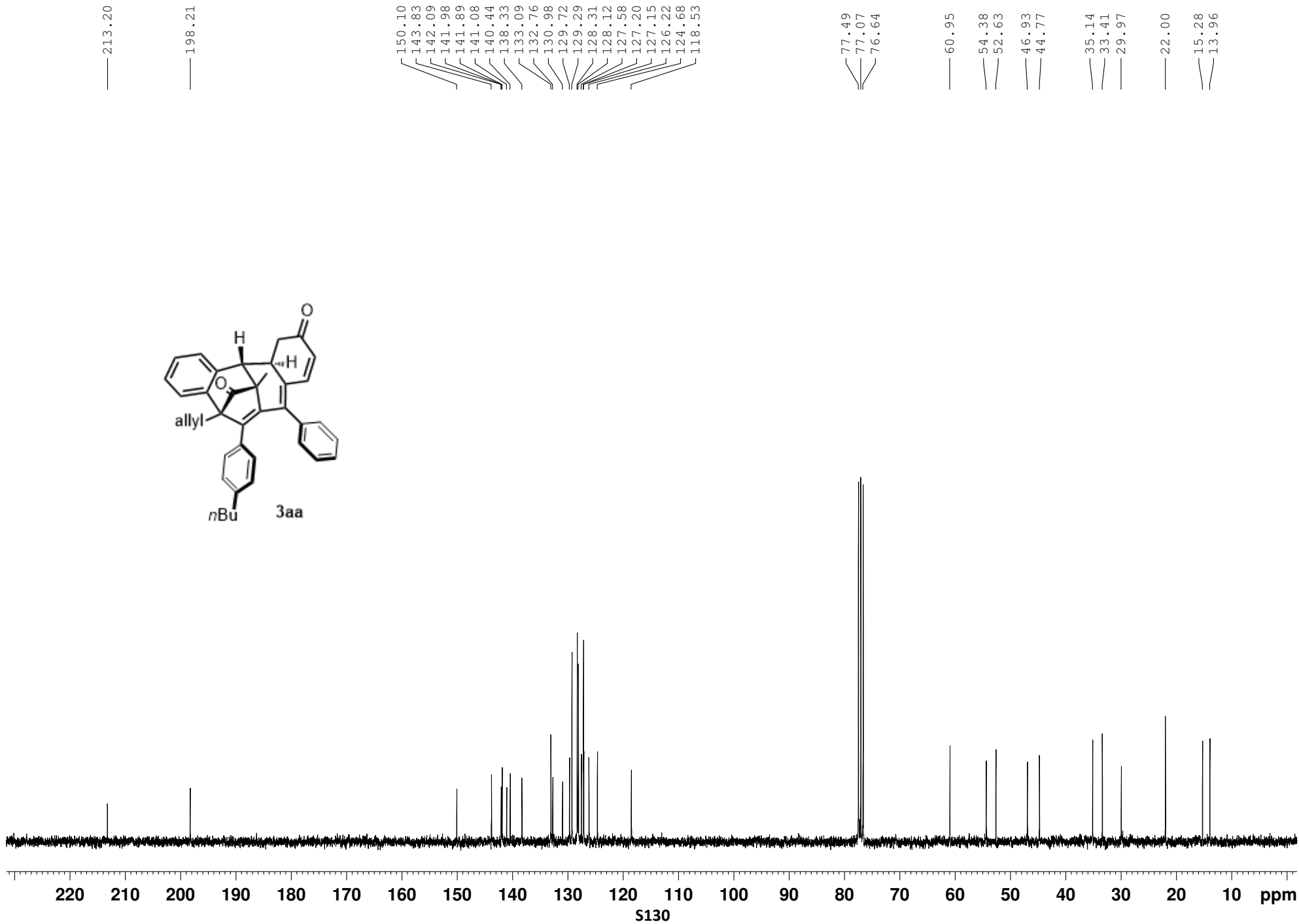
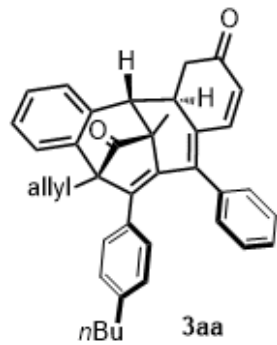
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S127







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6.825

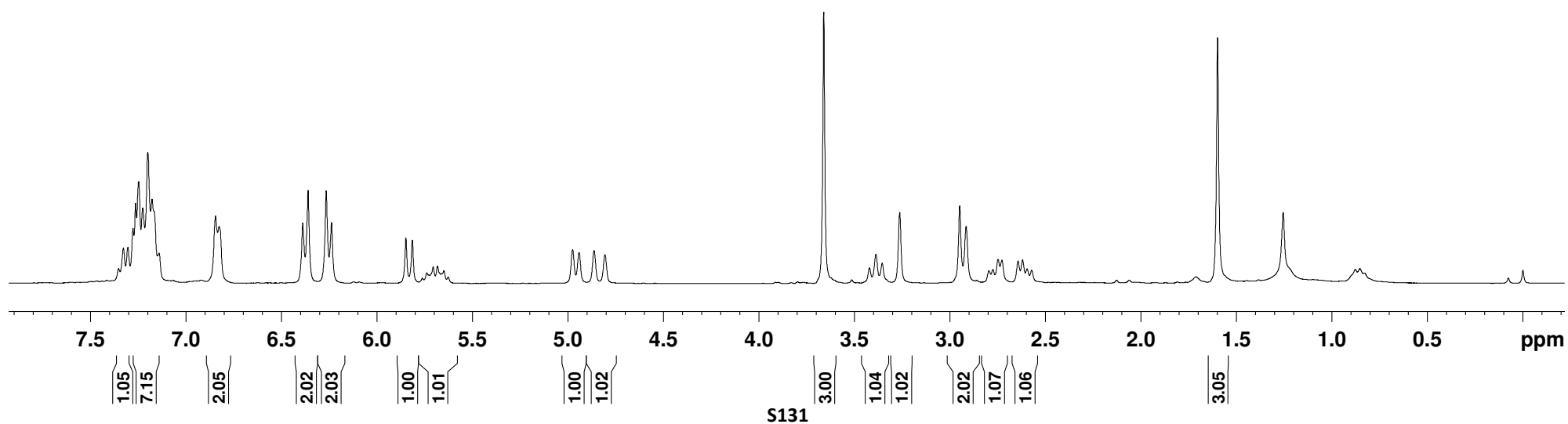
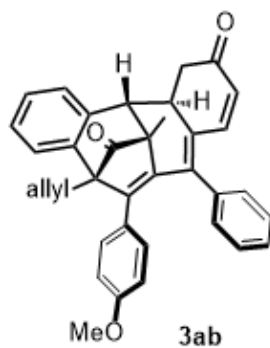
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5.628

4.976
4.942
4.864
4.806

3.661
3.422
3.388
3.355
3.263
2.949
2.915
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2.572

1.599

-0.000



— 213.10

— 198.18

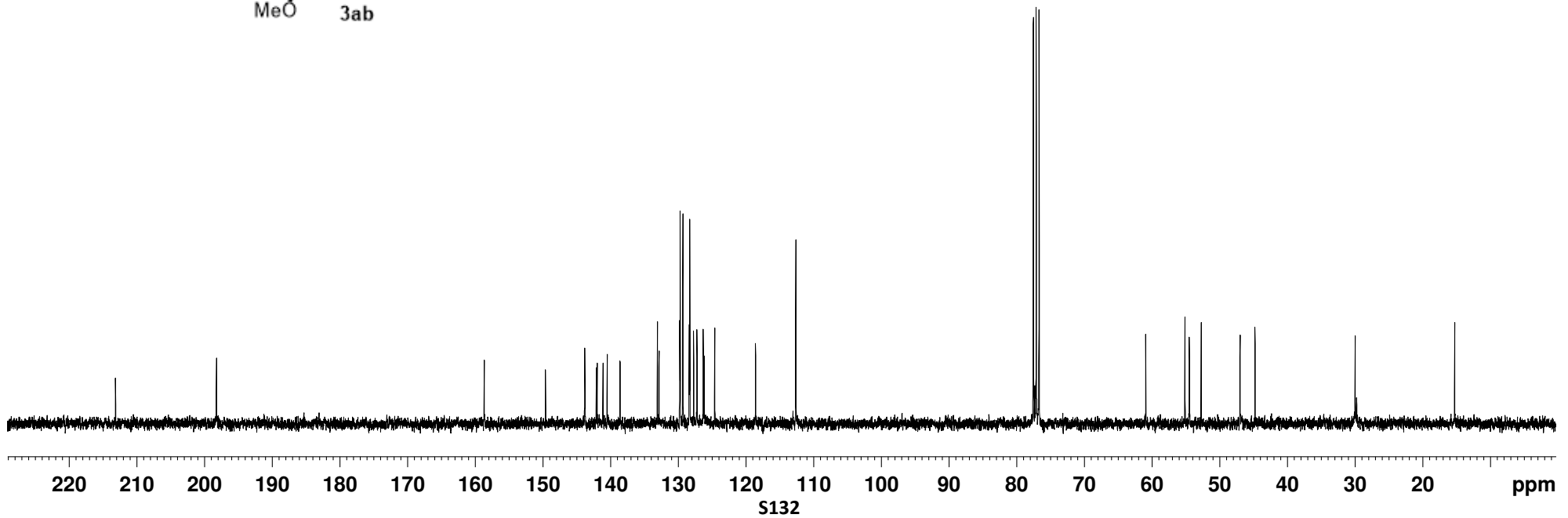
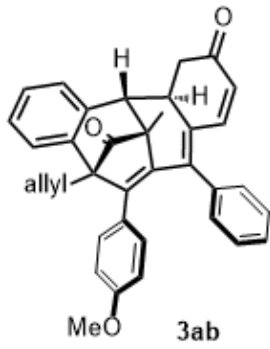
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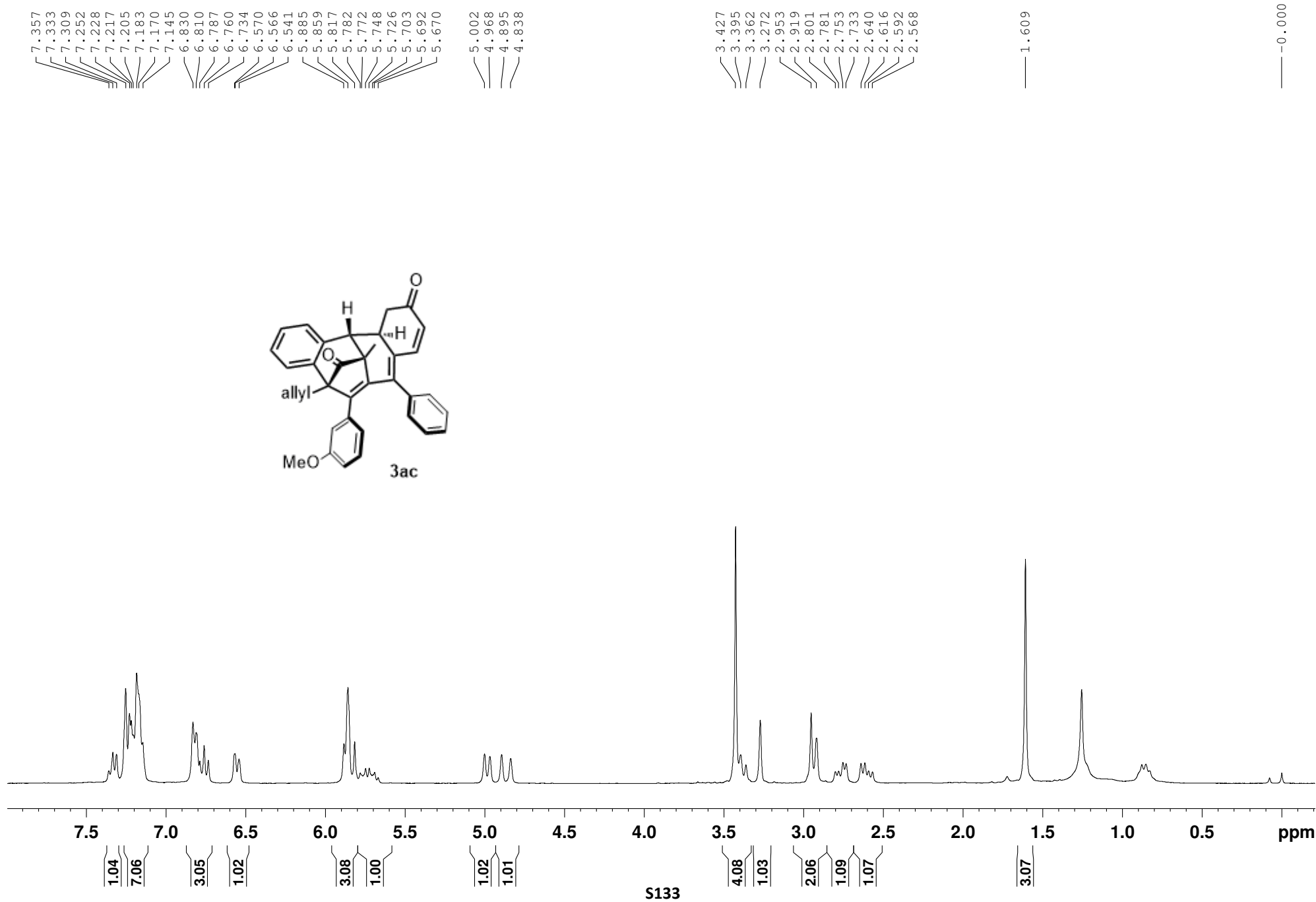
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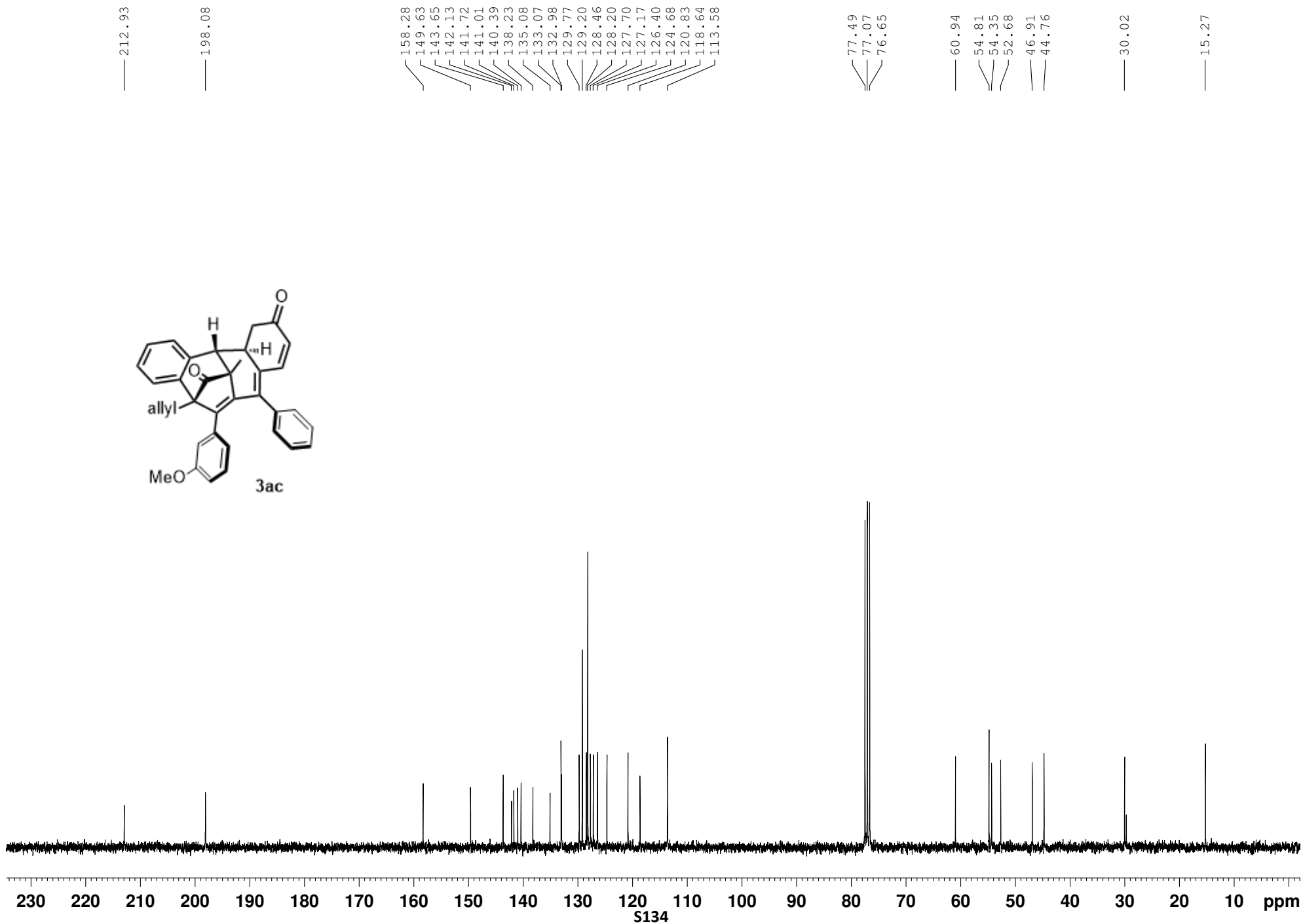
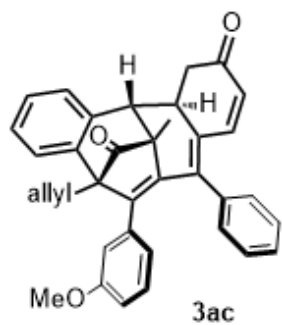
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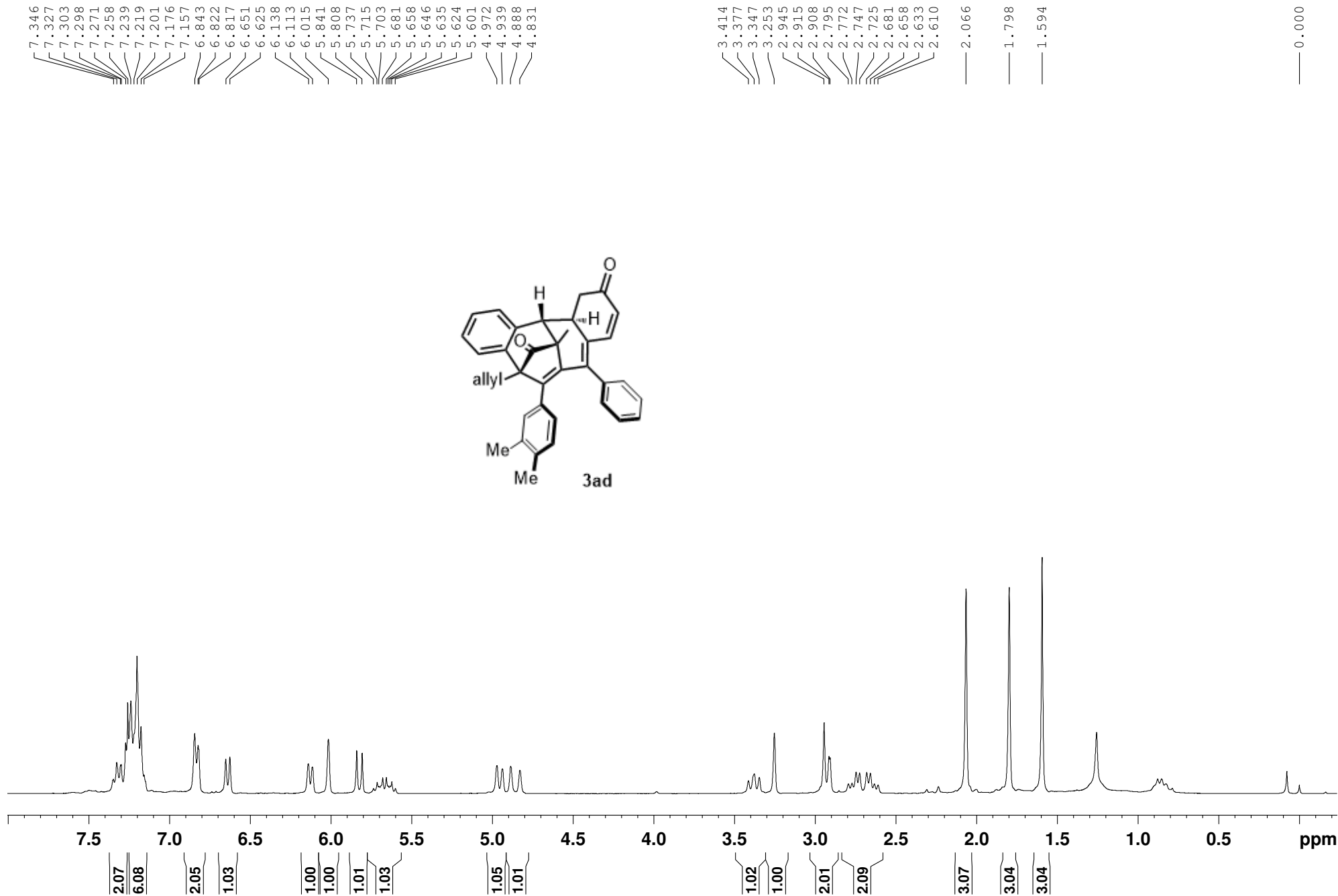
— 29.92

— 15.29









— 213.10

— 198.25

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129.68
129.30
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118.47

77.49
77.07
76.65

— 60.79

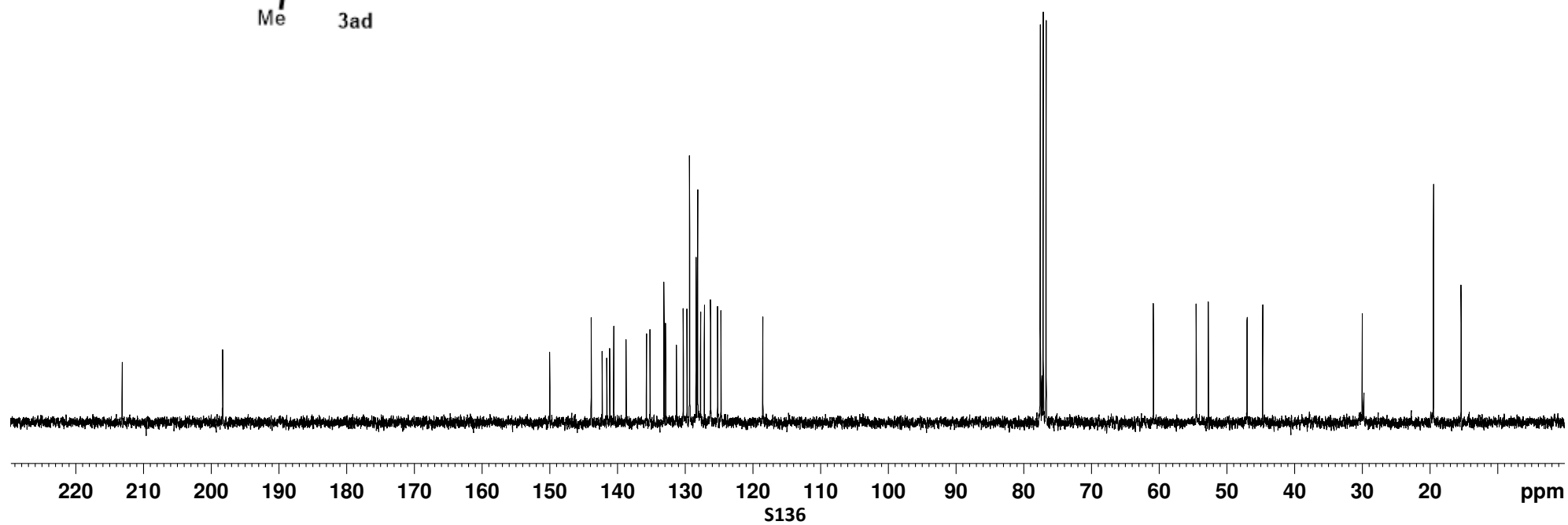
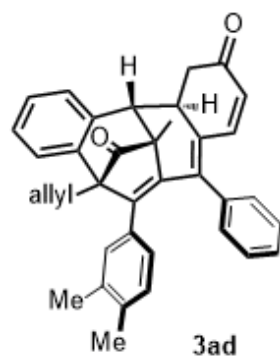
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— 52.69

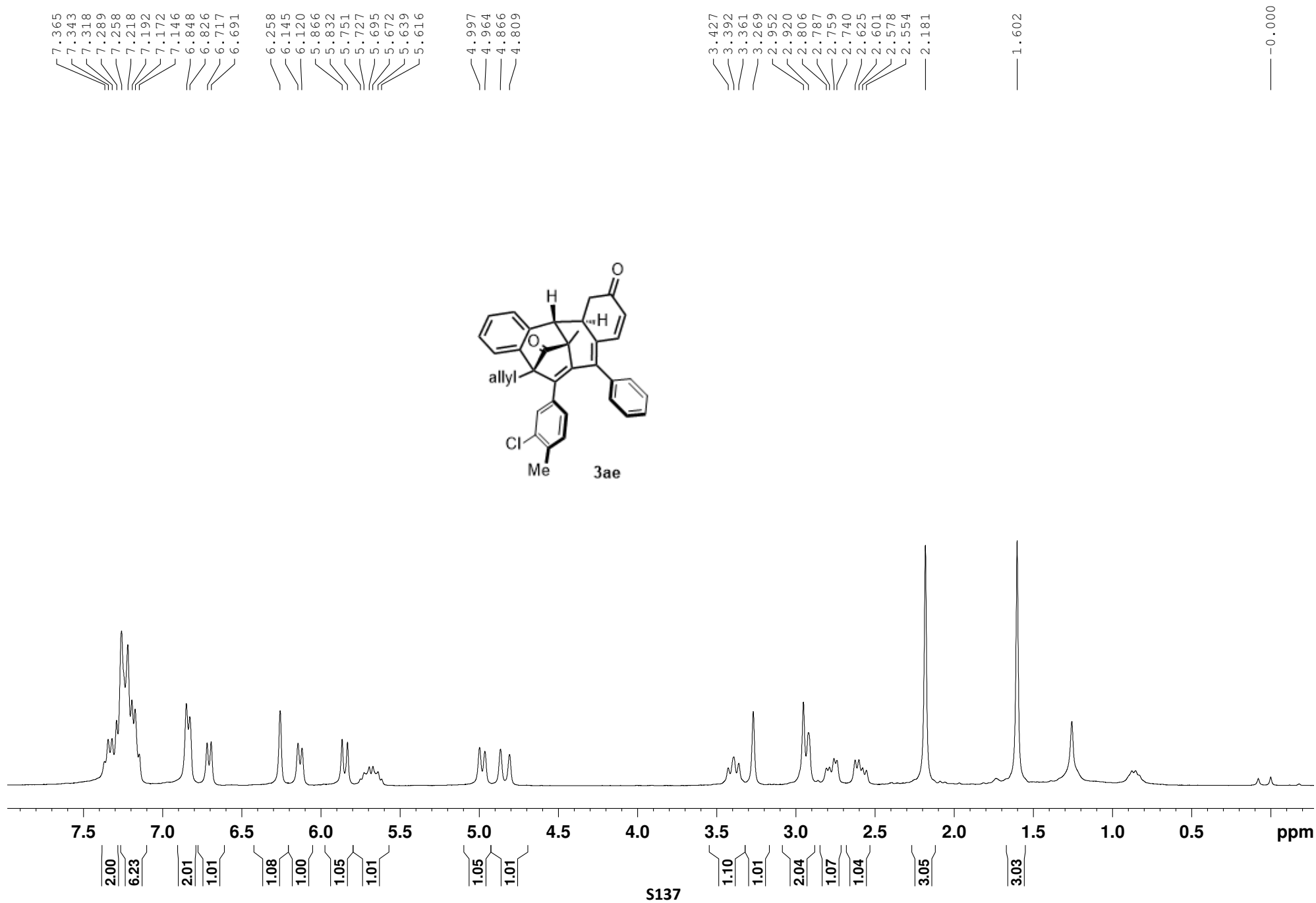
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— 44.66

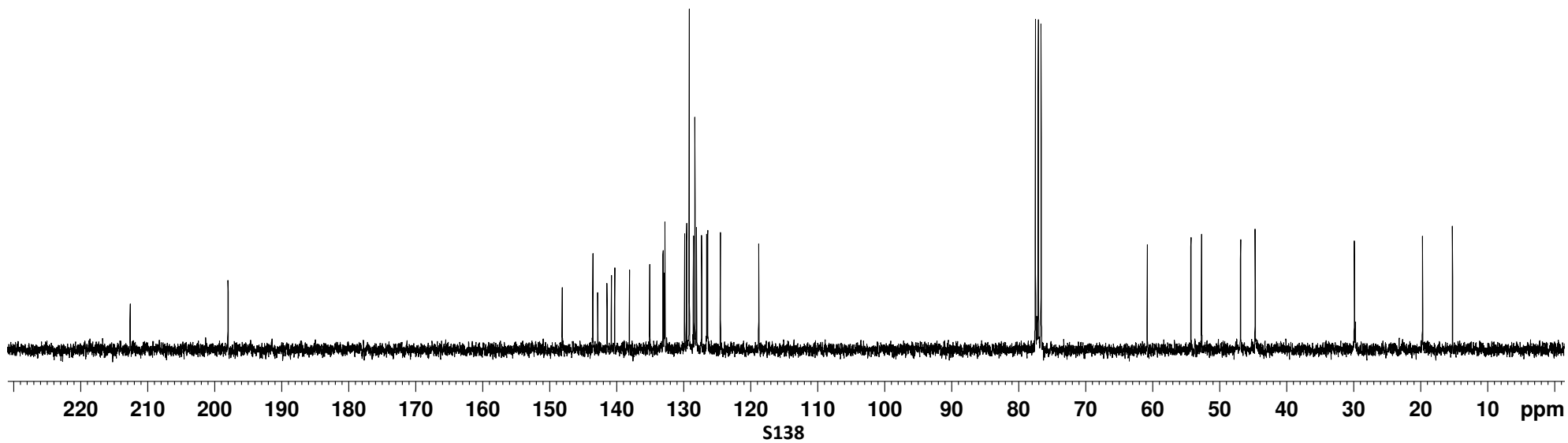
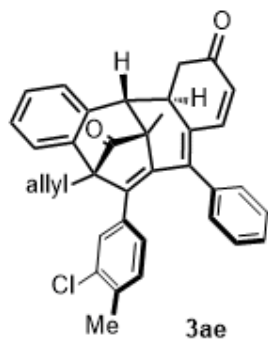
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— 19.44

— 15.34







— 212.61

— 198.00

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128.56
128.32
128.09
127.32
126.55
126.42
124.52
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— 60.81

— 54.30

— 52.70

— 46.89

— 44.71

— 29.89

— 19.72

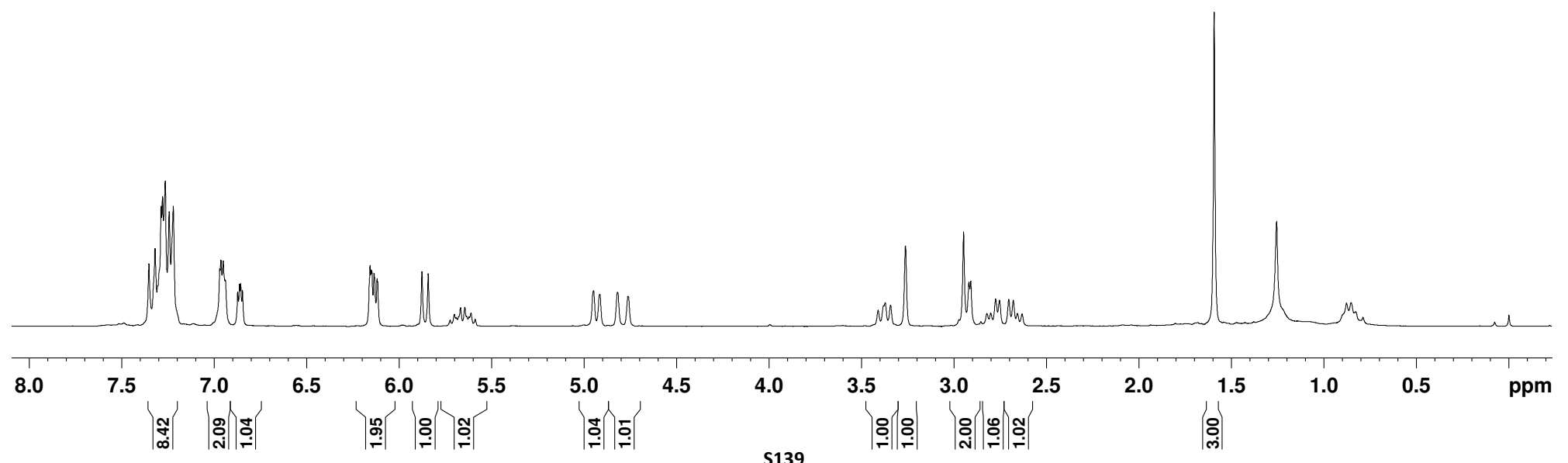
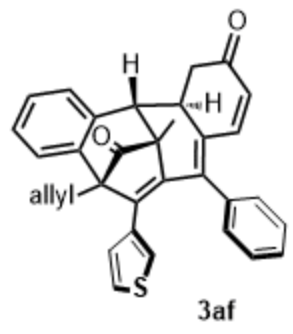
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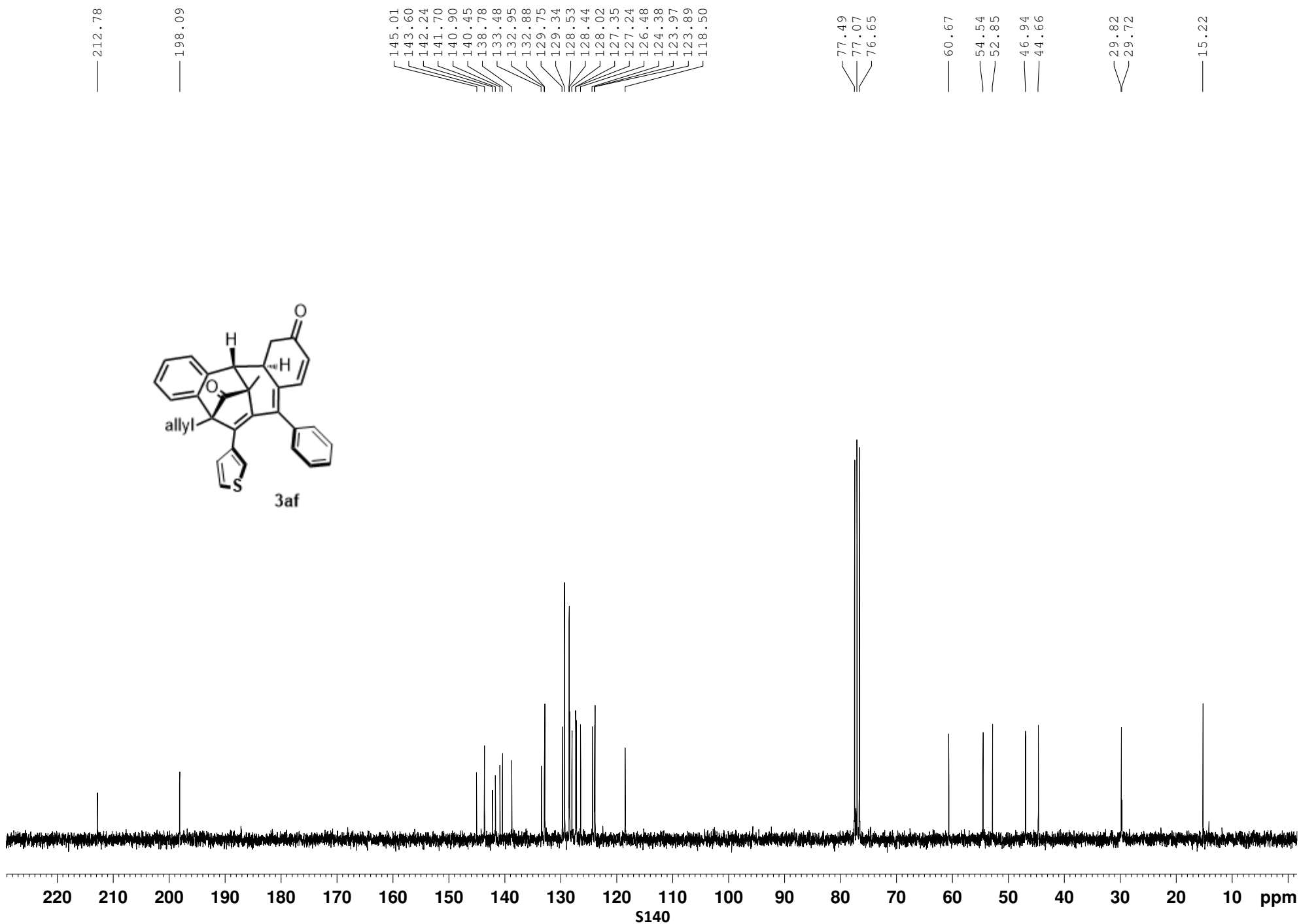
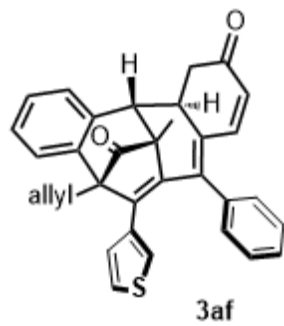
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6.961
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6.845
6.155
6.149
6.146
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6.131
6.117
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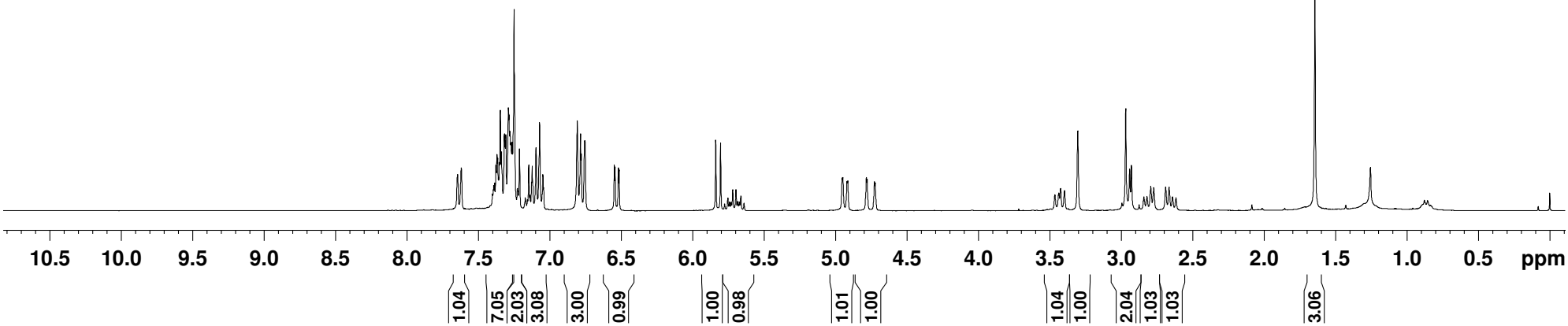
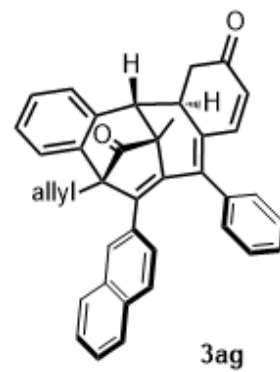
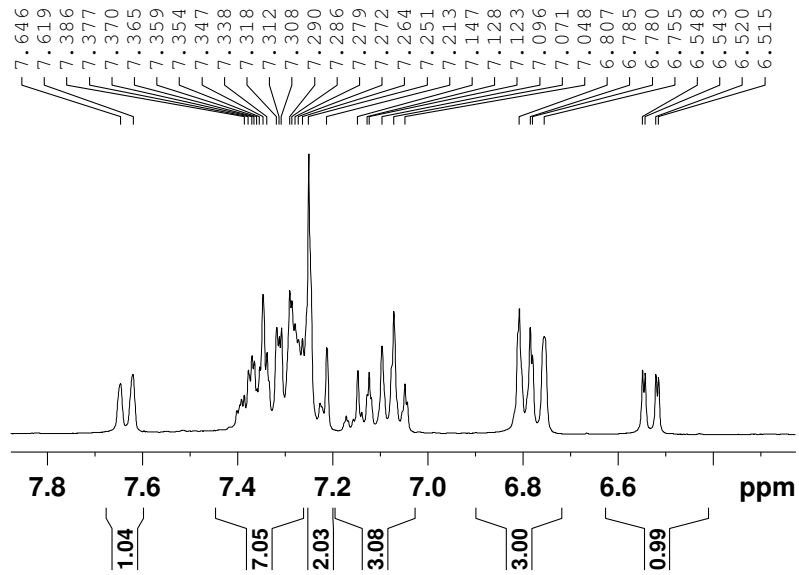
— 1.593

— -0.000





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S141

— 0.000

— 212.76

— 198.07

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138.78
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131.30
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76.58

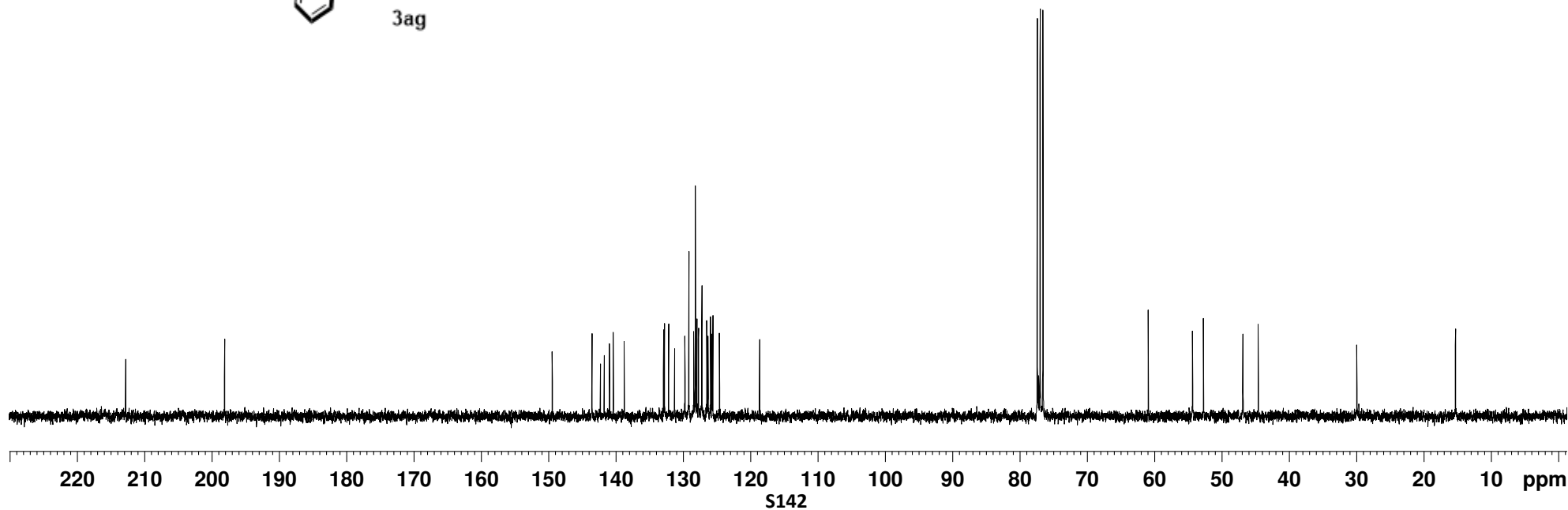
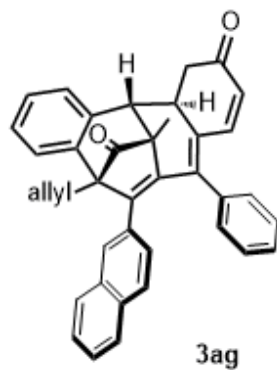
— 60.95

54.37
52.75

46.88
44.60

— 29.96

— 15.31



7.532
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7.241
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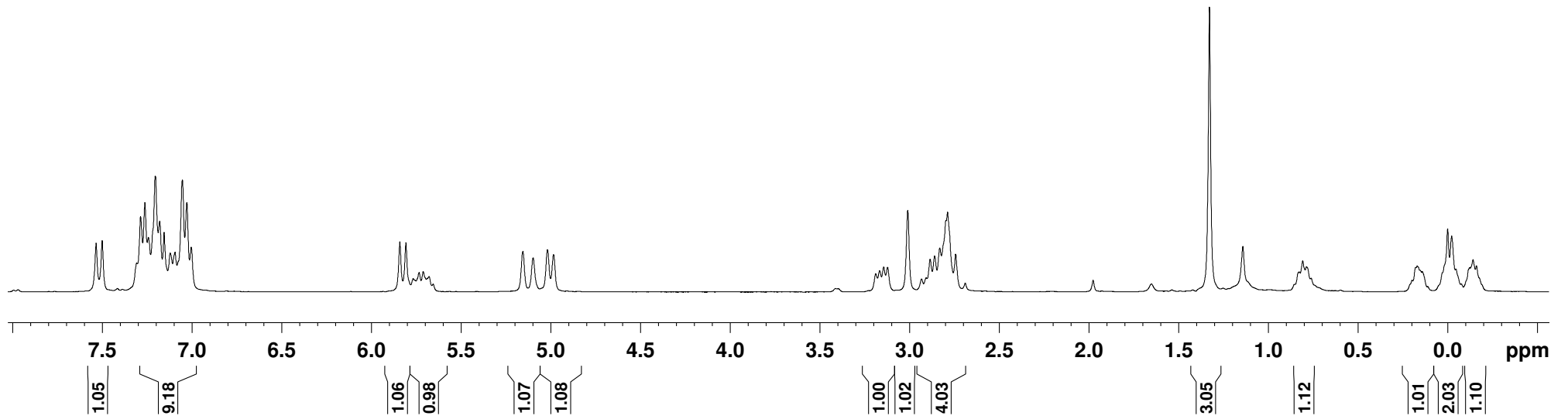
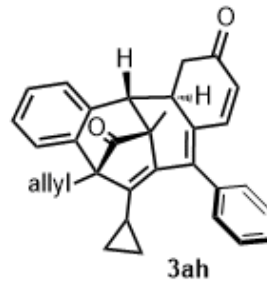
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3.122
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2.689

1.327

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S143

— 213.49

— 198.11

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118.11

77.50
77.07
76.65

— 60.83

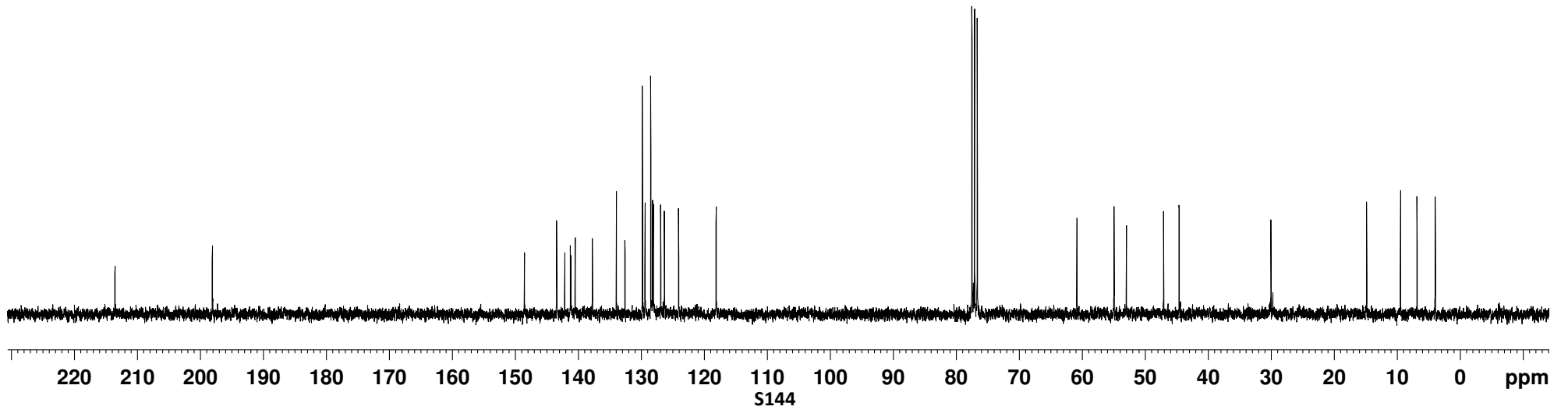
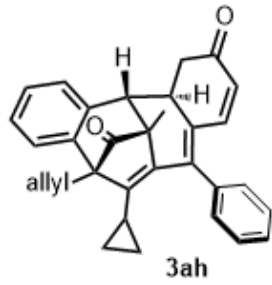
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— 52.97

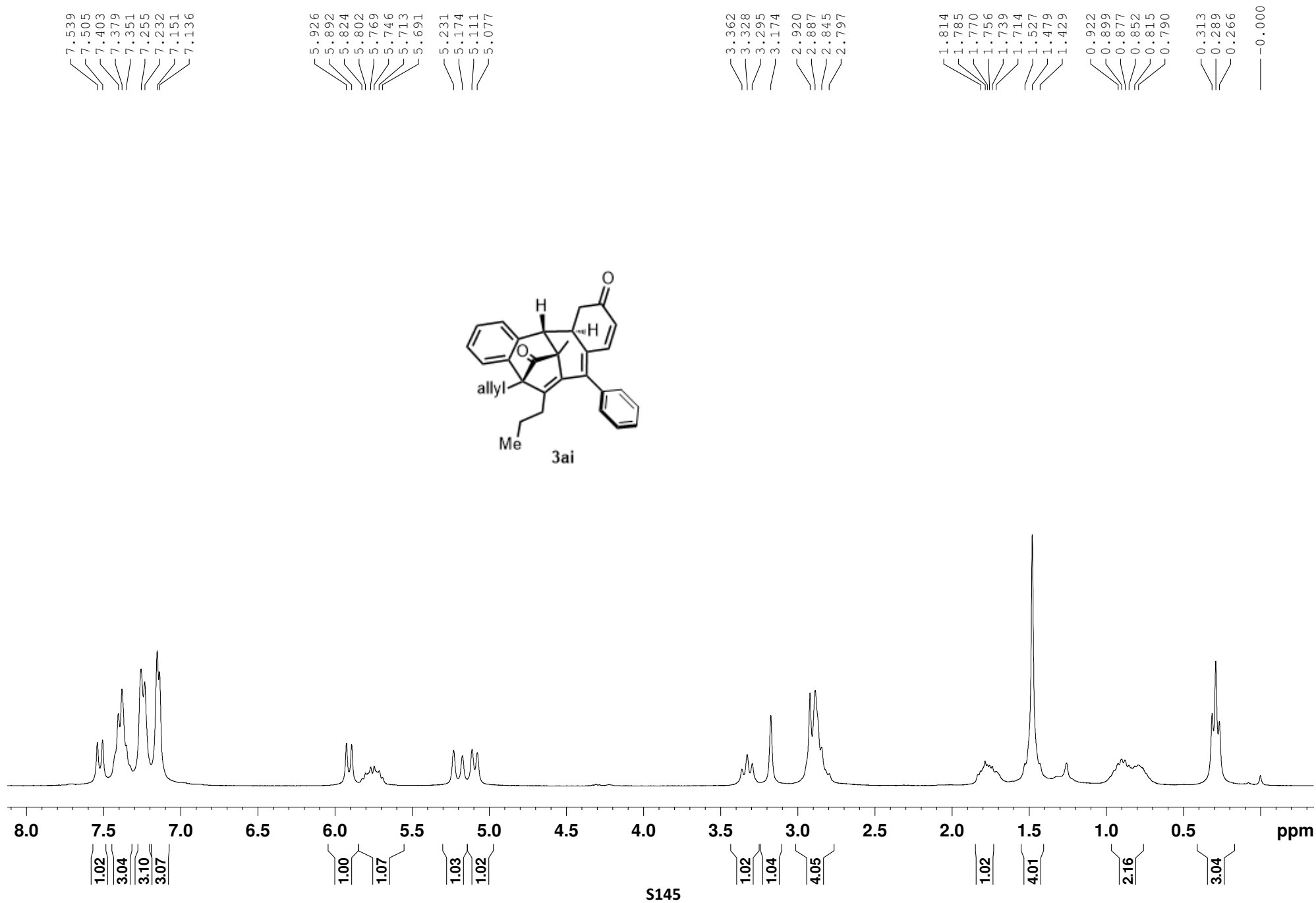
— 47.07
— 44.60

— 30.03

— 14.82

— 9.44
— 6.82
— 3.92





— 213.72

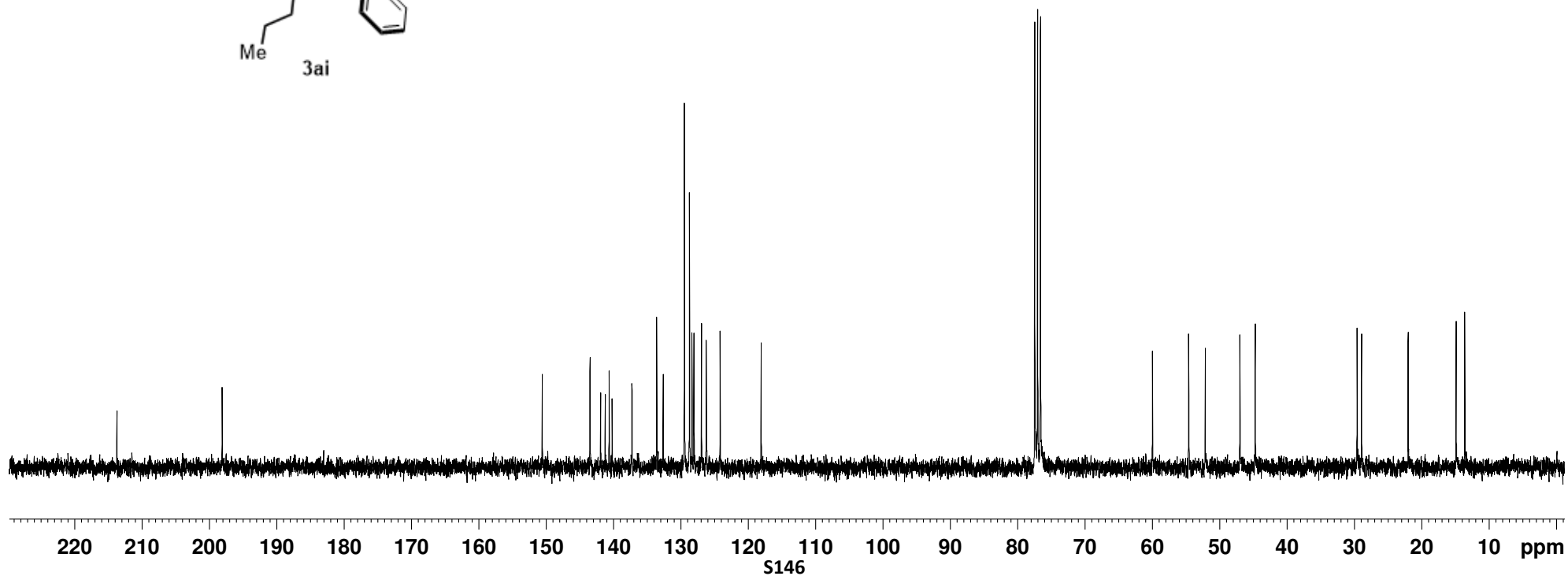
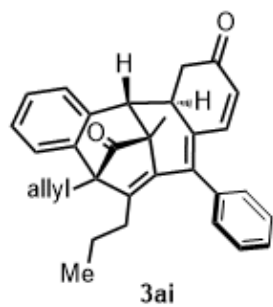
— 198.10

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143.50
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140.22
137.26
133.59
132.63
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128.35
128.06
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124.18
118.08

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77.04
76.62

59.99
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52.14
47.00
44.73

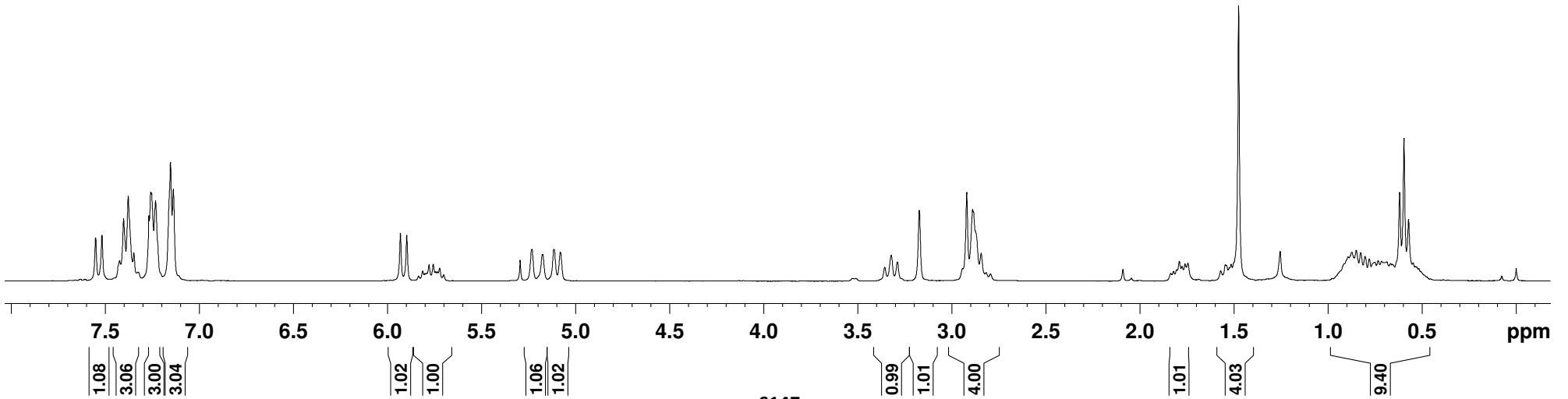
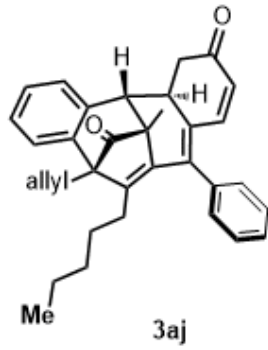
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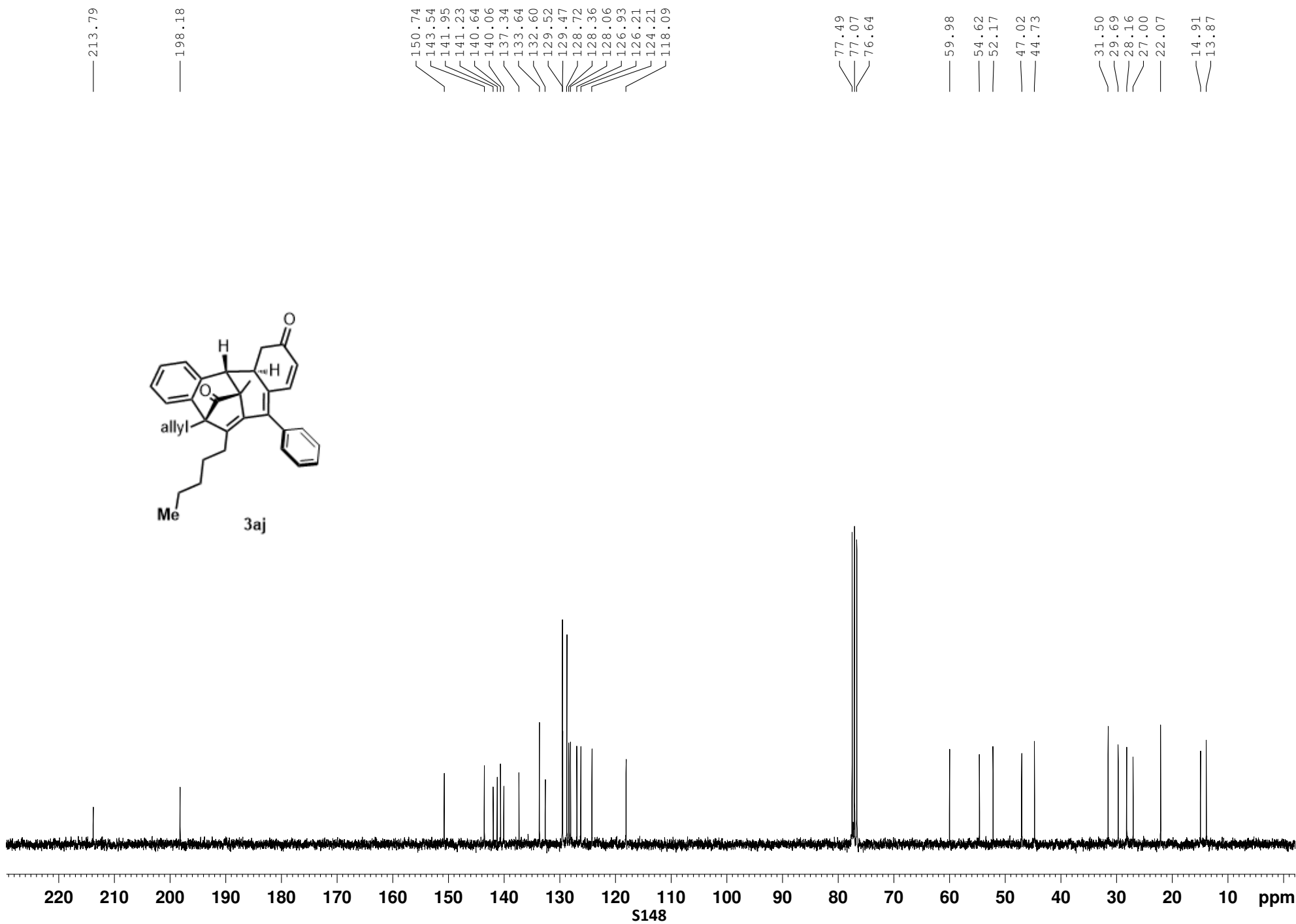
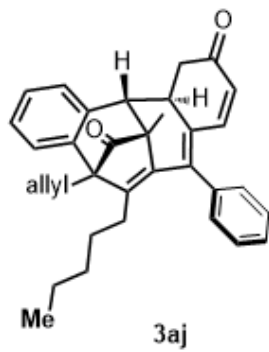
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7.231
7.152
7.137

5.930
5.896
5.834
5.812
5.800
5.790
5.777
5.755
5.743
5.734
5.721
5.700
5.232
5.175
5.116
5.082

3.357
3.322
3.290
3.173
2.944
2.921
2.890
2.885
2.844
2.818
2.795
1.837
1.822
1.805
1.791
1.777
1.760
1.745
1.571
1.547
1.540
1.525
1.516
1.476
0.894
0.873
0.850
0.827
0.803
0.780
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0.596
0.572



S147

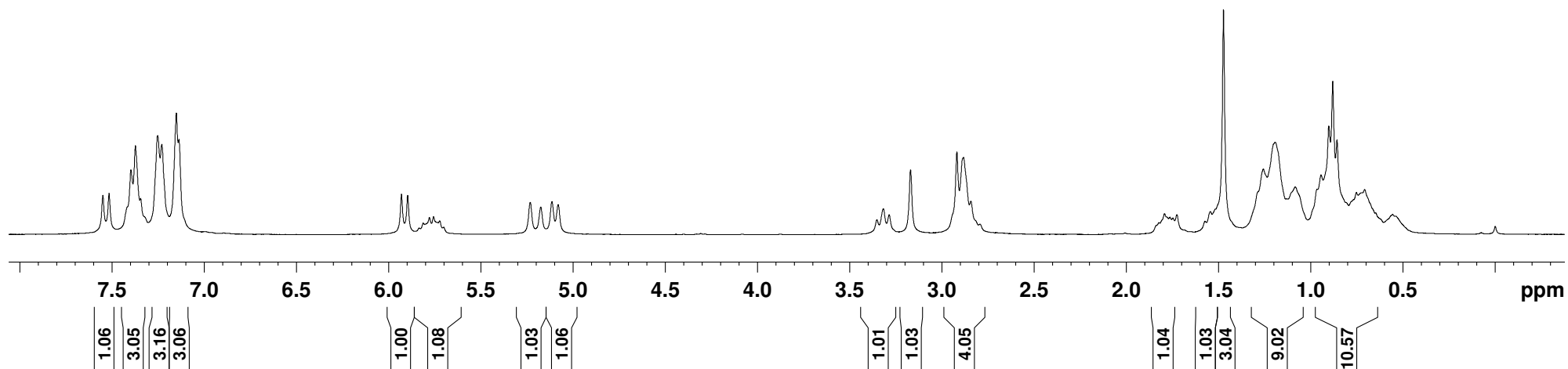
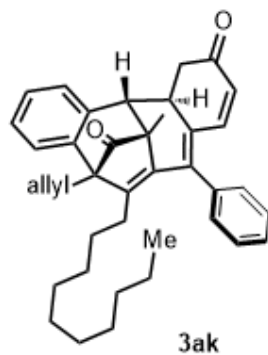


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5.777
5.755
5.734
5.721
5.700
5.231
5.174
5.113
5.080

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3.318
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3.171
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S149

— 213.71

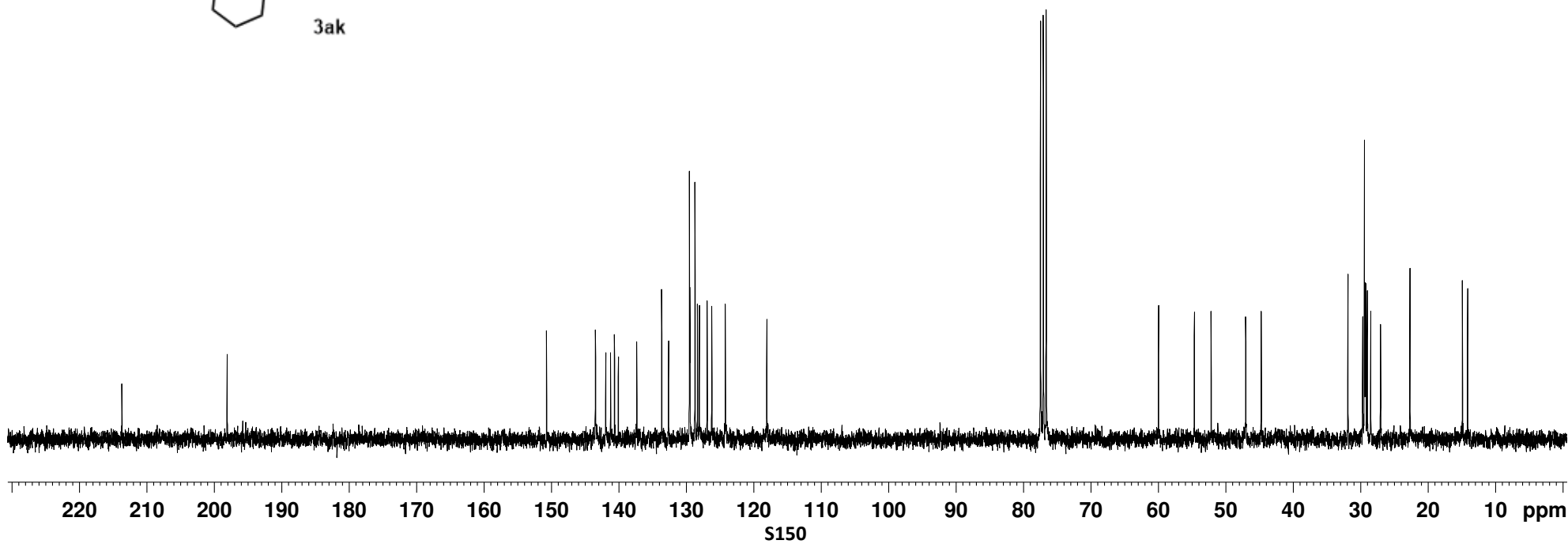
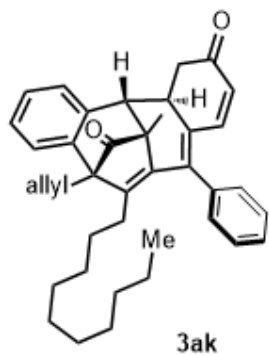
— 198.09

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118.06

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76.63

59.97
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52.17
47.03
44.74

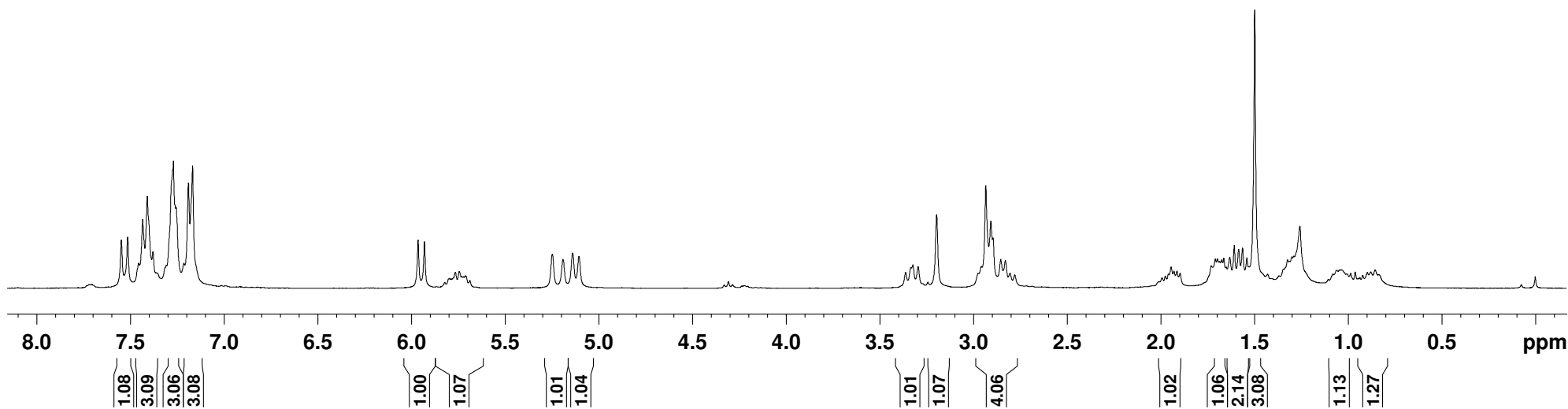
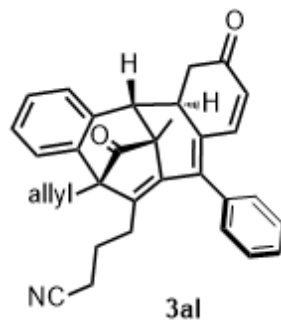
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29.01
28.49
27.04
22.67
14.91
14.13



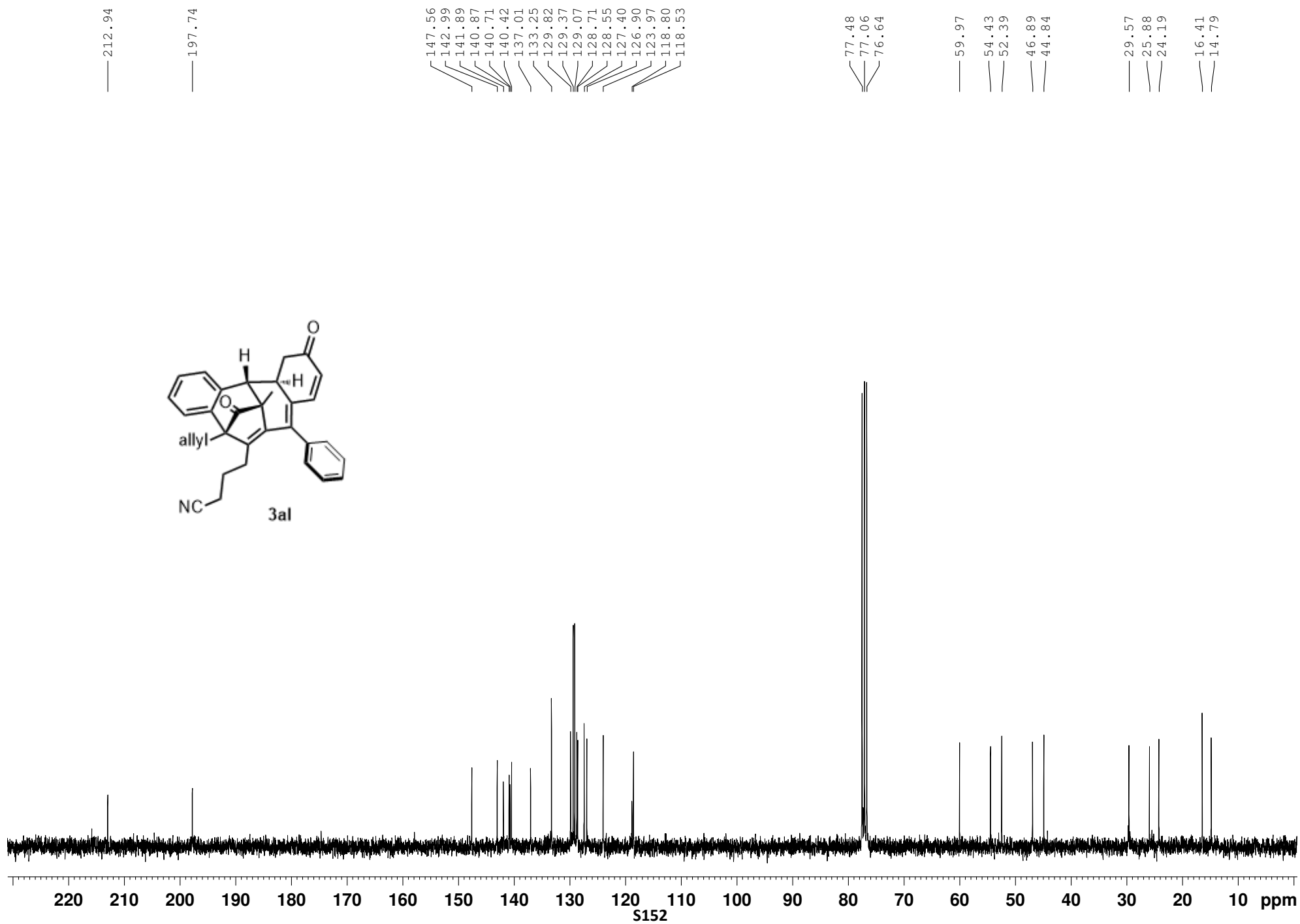
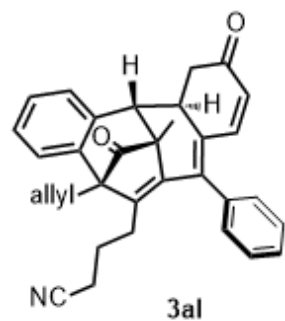
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7.166

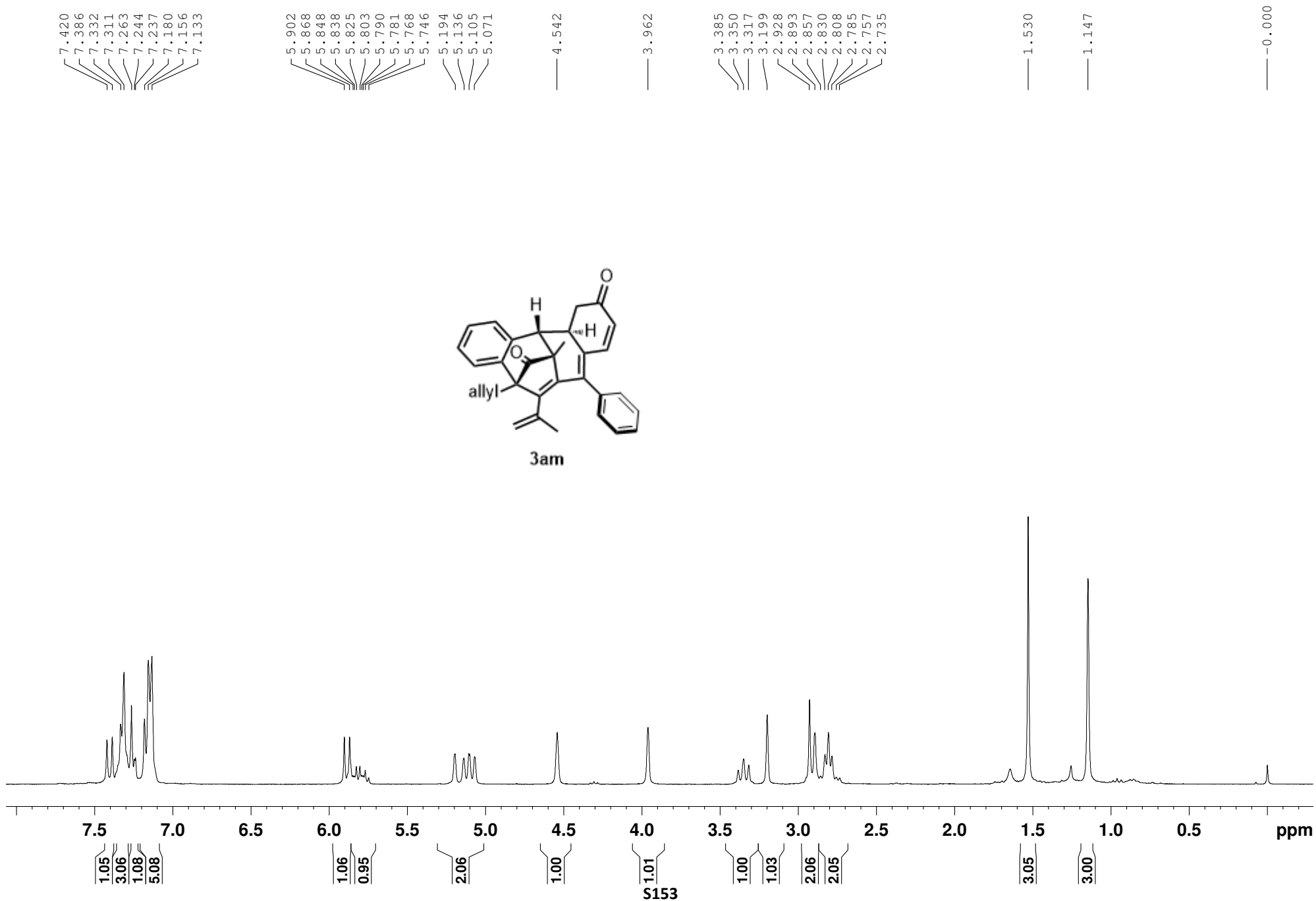
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5.246
5.189
5.138
5.104

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3.321
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0.878



S151





— 213.17

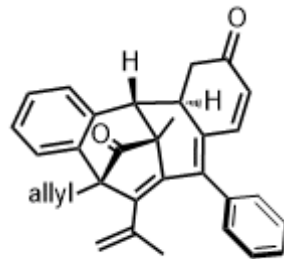
— 198.07

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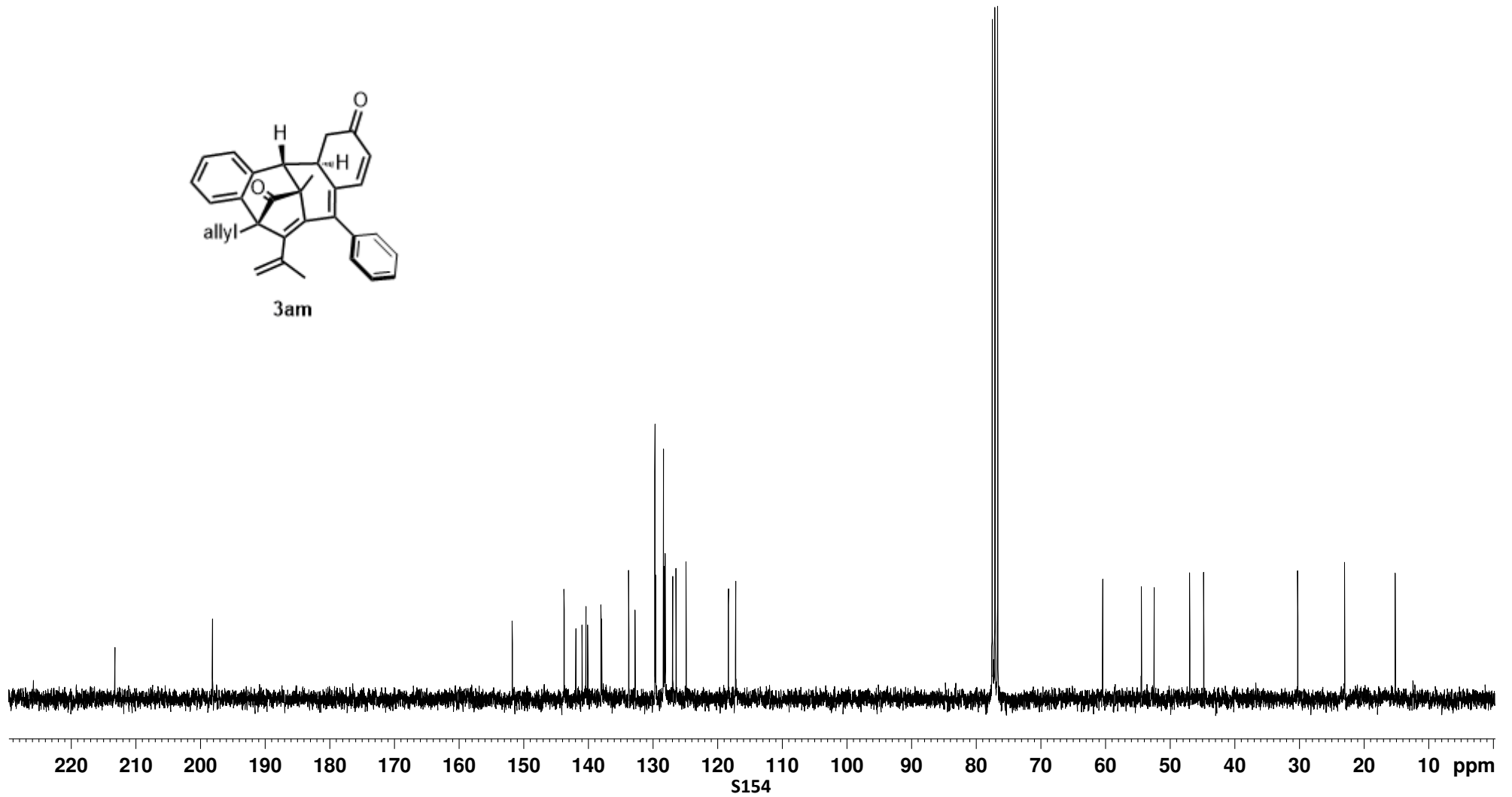
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22.93
15.10



3am



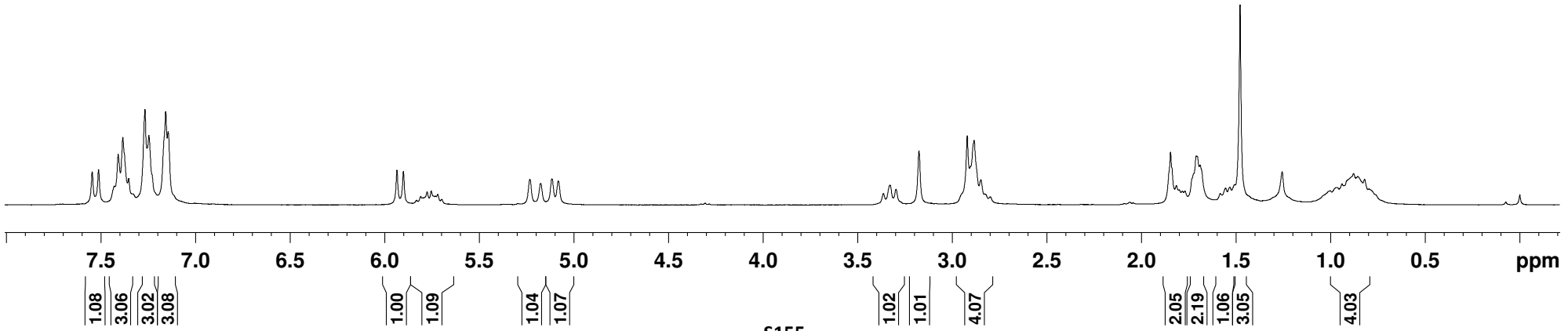
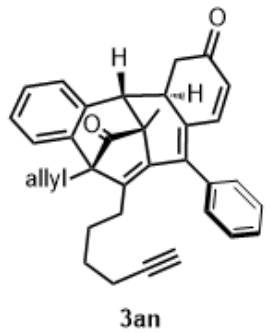
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5.719
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5.117
5.083

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2.885
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2.829
2.799

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1.584
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0.858
0.820
0.798

— 0.000



S155

— 213.54

— 198.06

150.03
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141.14
140.59
140.48
137.27
133.55
132.80
129.56
129.49
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124.18
118.16

— 84.02

77.46
77.04
76.62

— 68.30

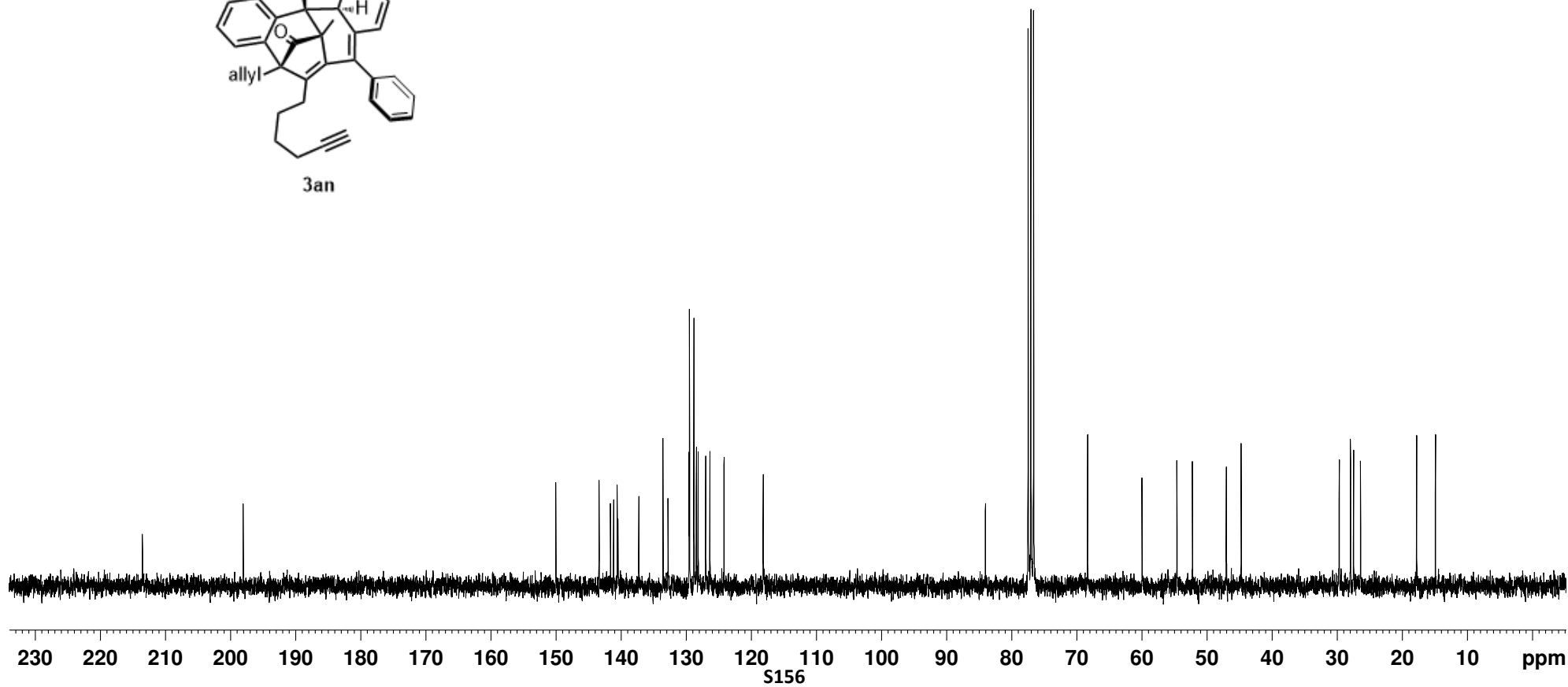
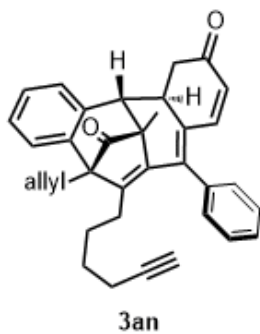
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— 54.60
— 52.22

— 47.00
— 44.73

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27.93
27.45
26.38

— 17.75
— 14.88

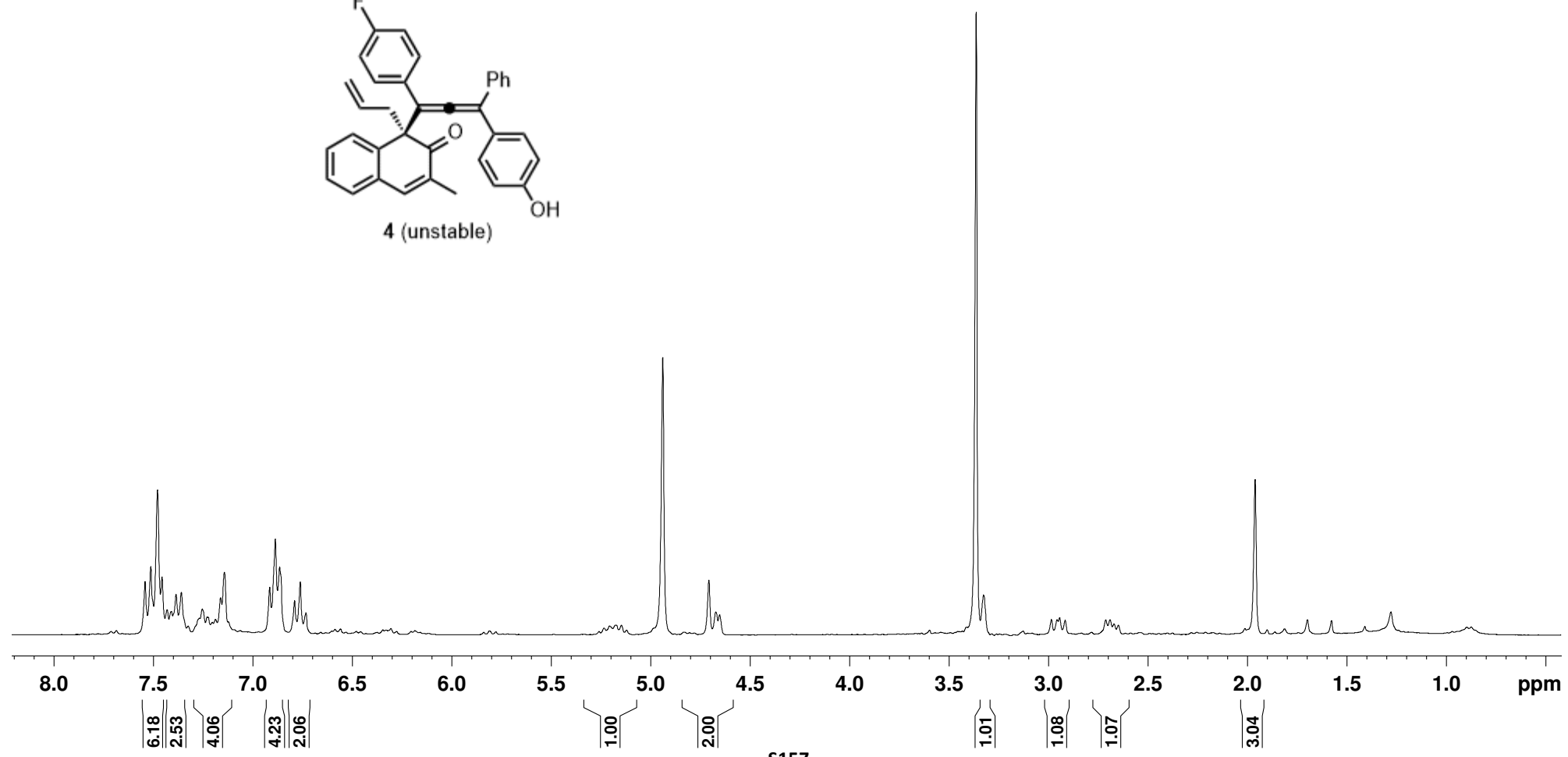
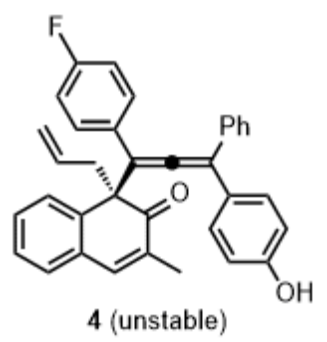


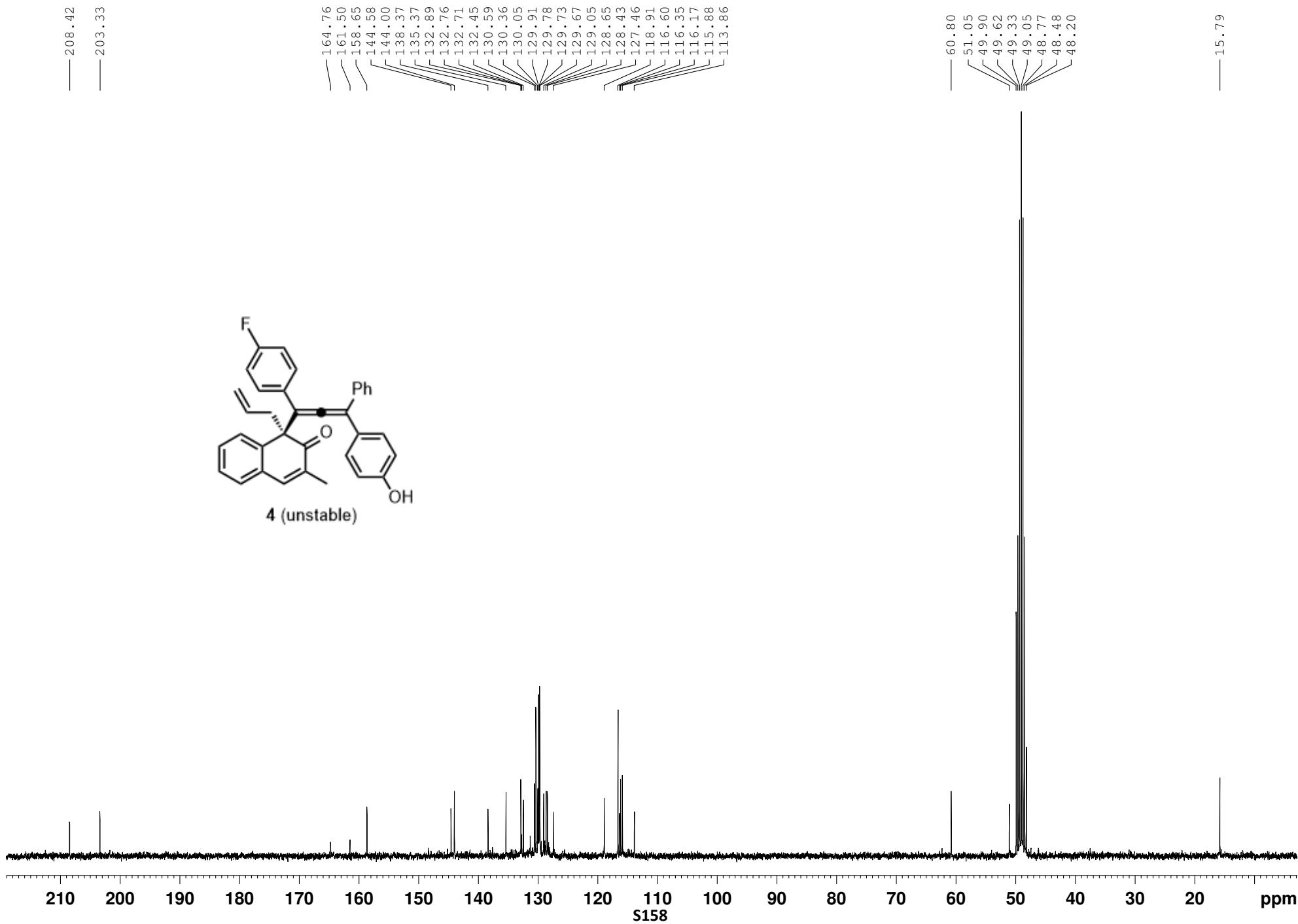
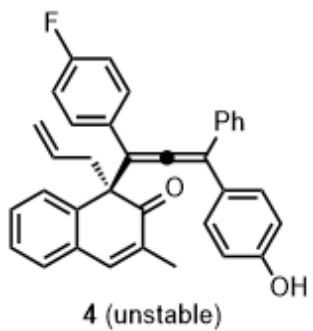
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6.731

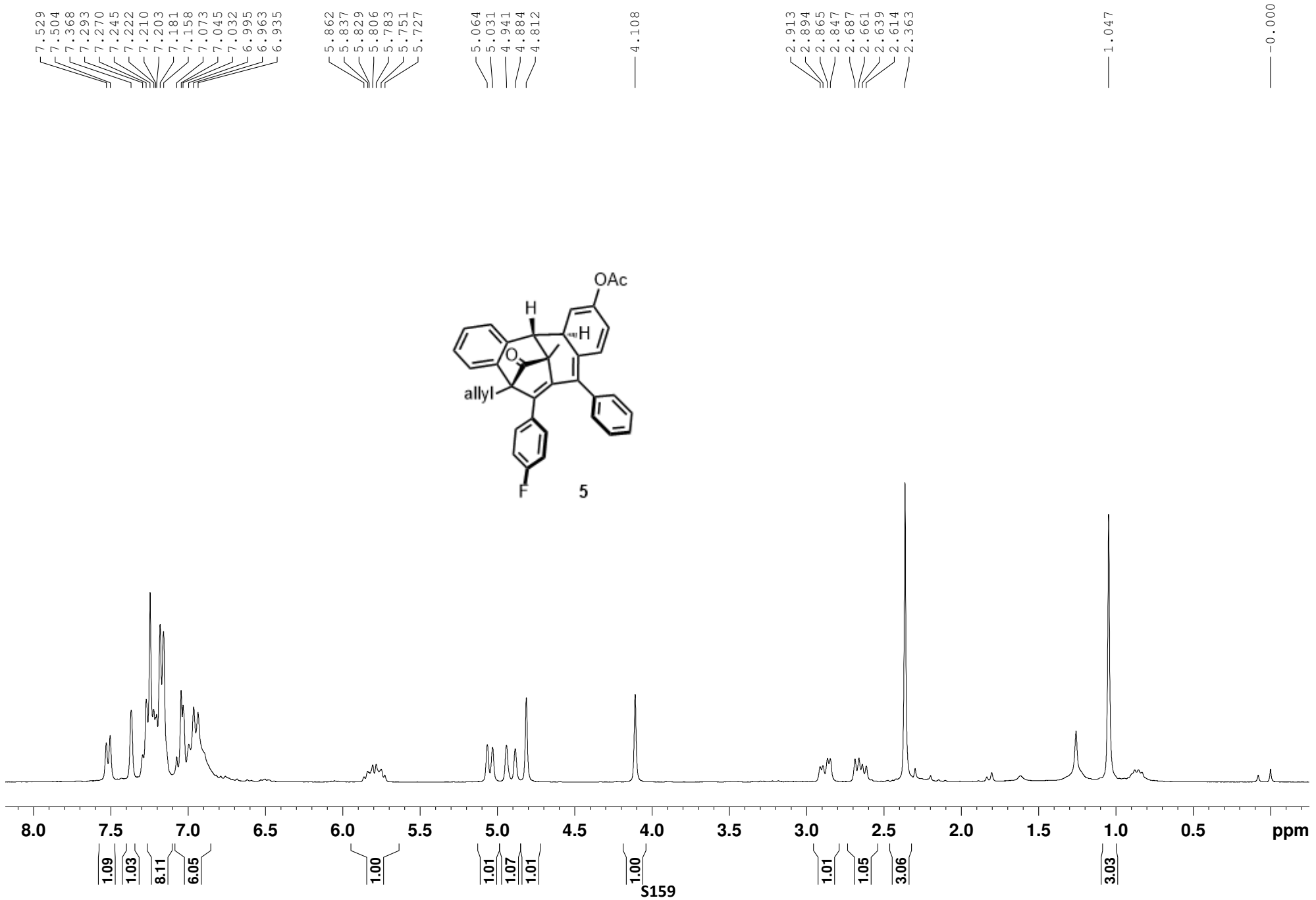
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4.671
4.652

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2.957
2.944
2.917
2.713
2.691
2.671
2.649

1.961







S159

— 213.89

— 169.46
— 164.07
— 160.79
— 149.14
— 145.21
— 141.99
— 141.48
— 140.05
— 139.88
— 137.45
— 134.98
— 133.30
— 132.49
— 130.36
— 130.32
— 129.83
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— 127.75
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— 124.01
— 123.83
— 120.21
— 118.53
— 115.40
— 115.12

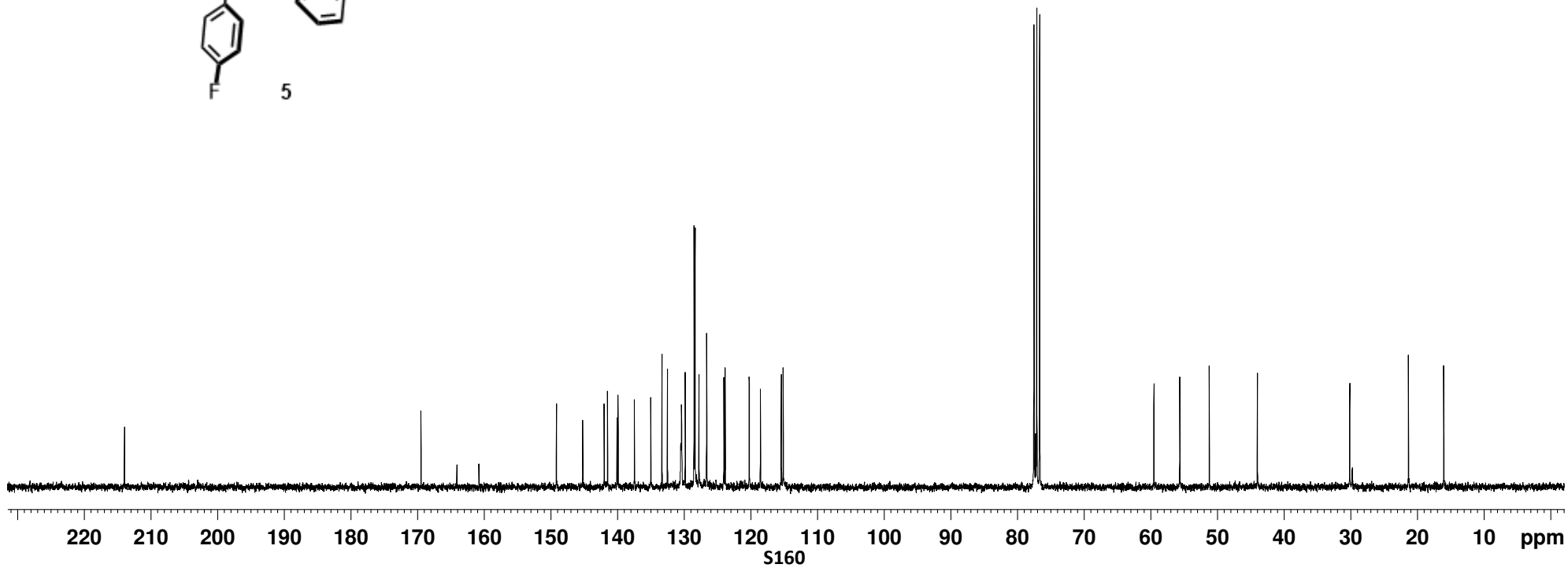
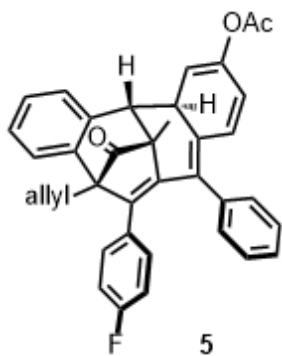
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— 77.06
— 76.64

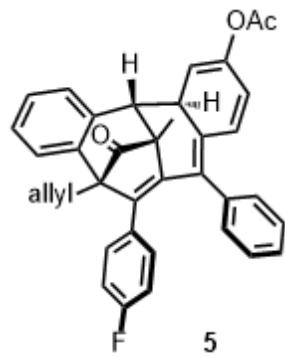
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— 55.61
— 51.18
— 43.95

— 30.10

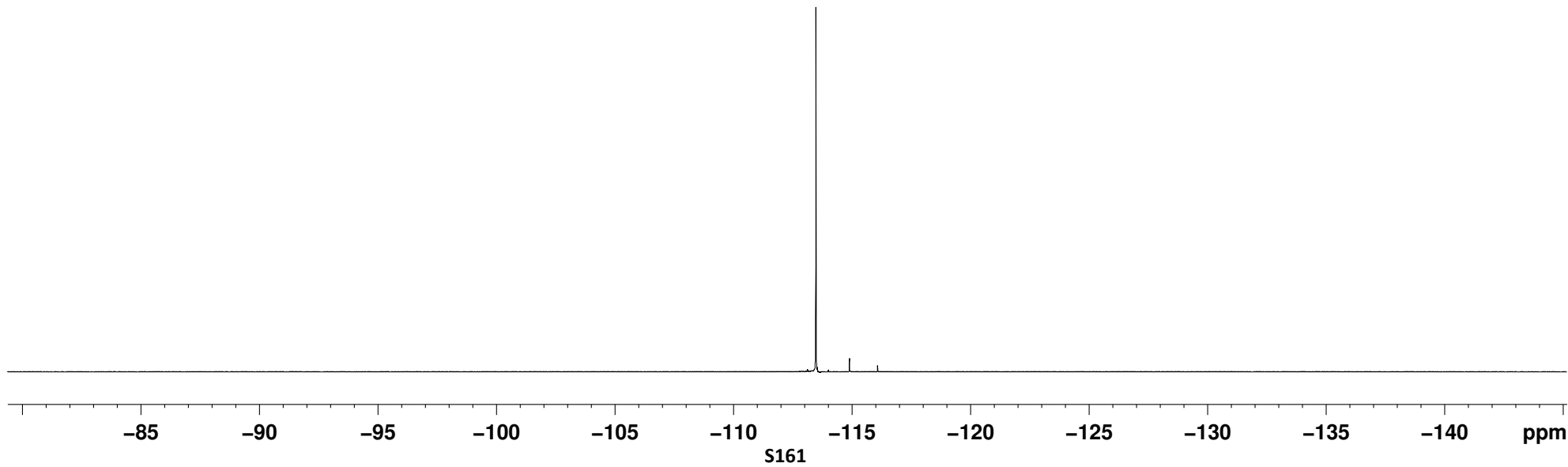
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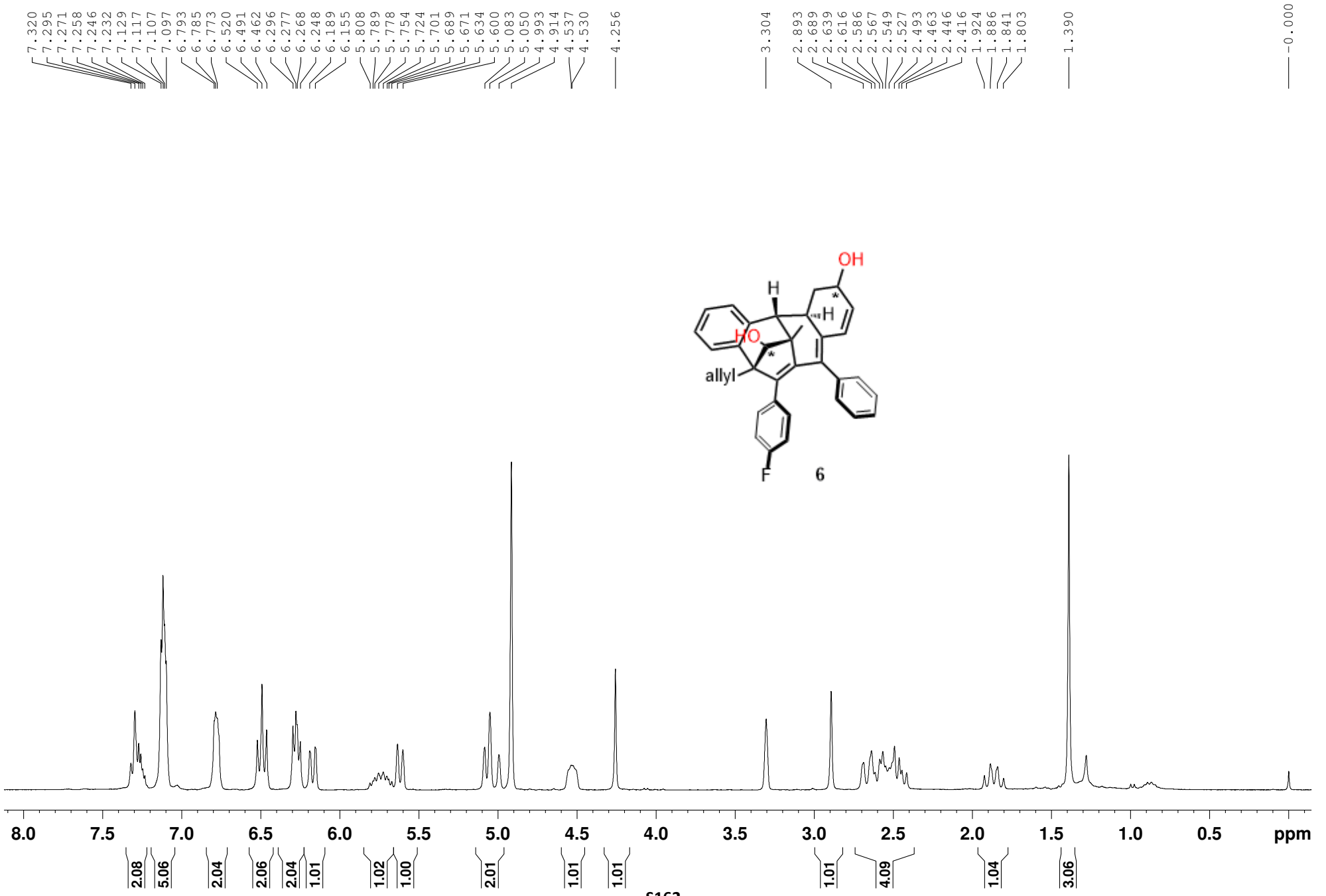
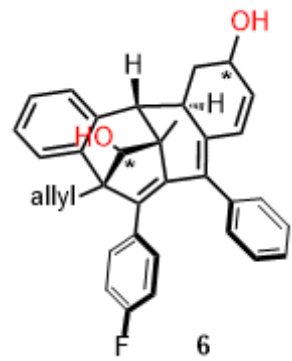
— 16.00

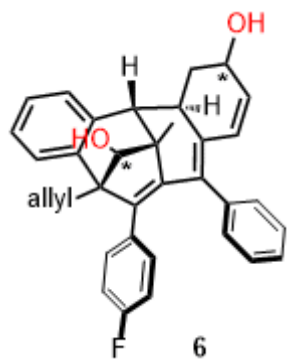
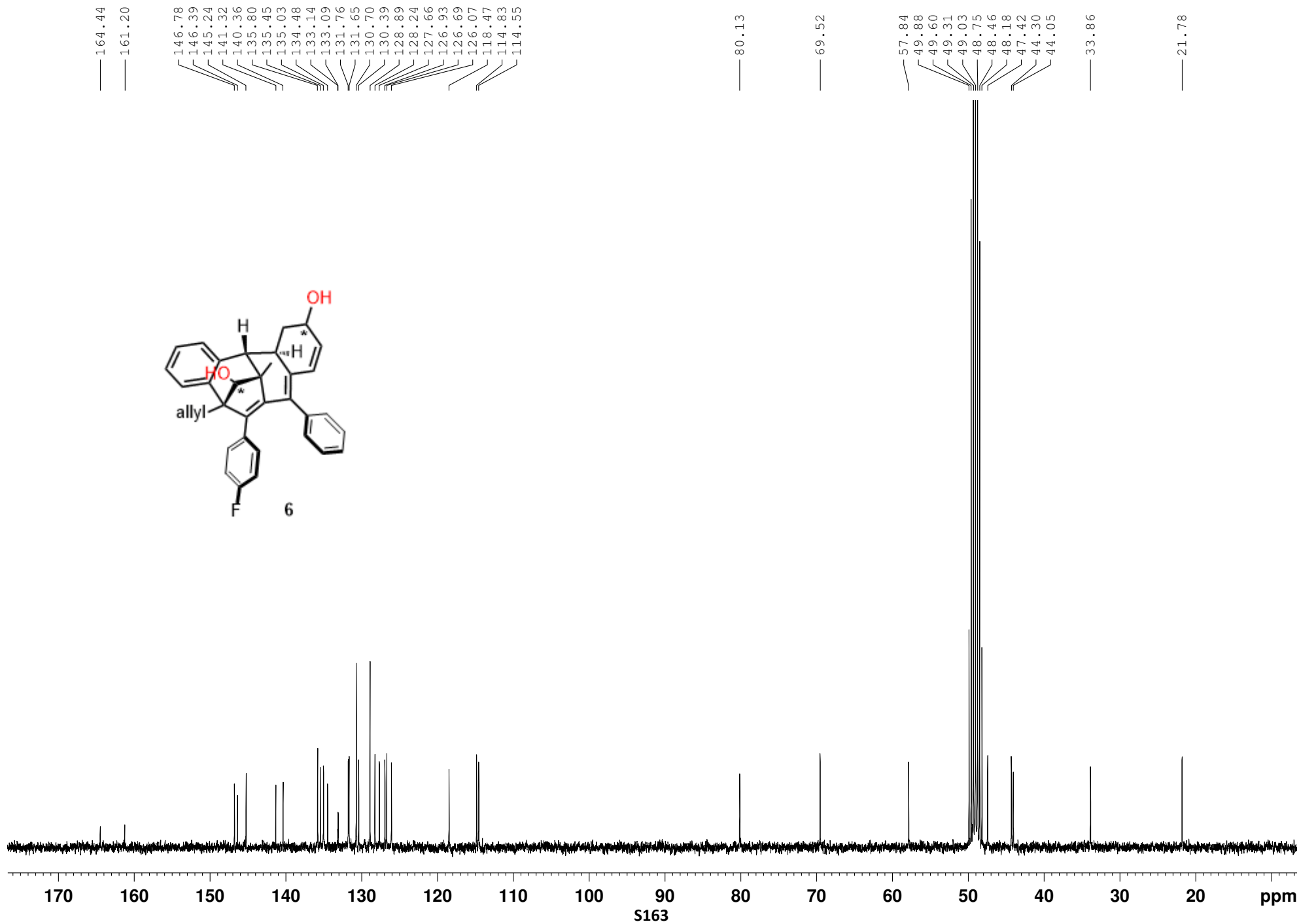


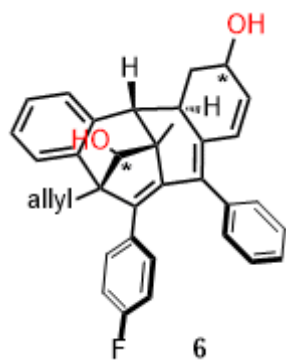


-113.4

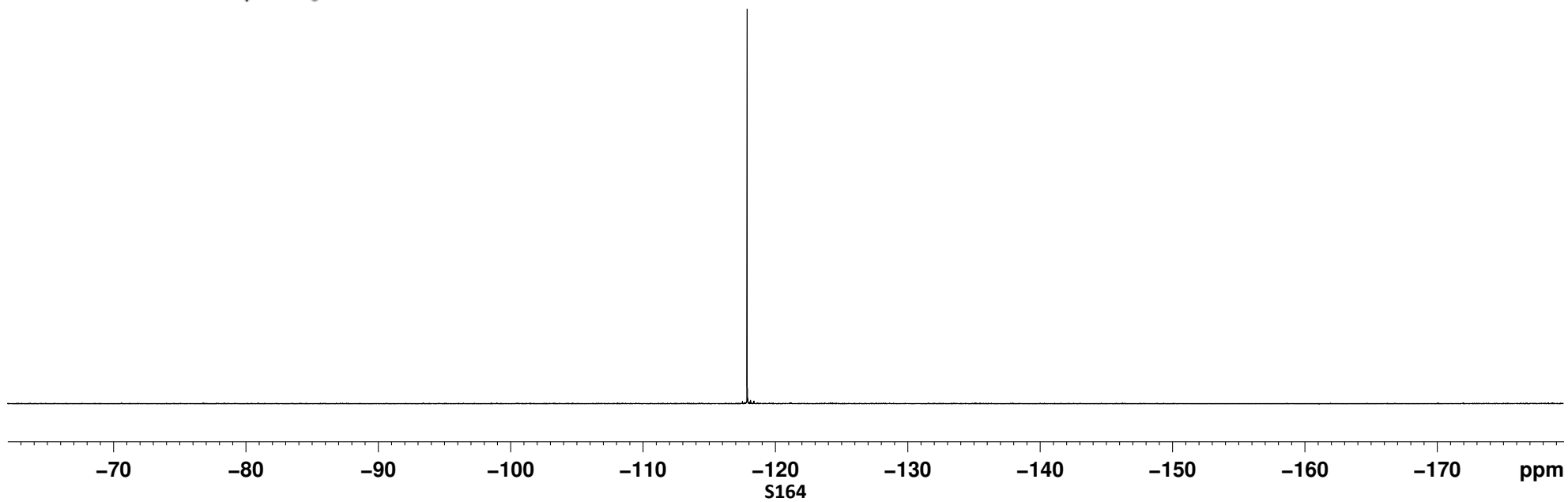




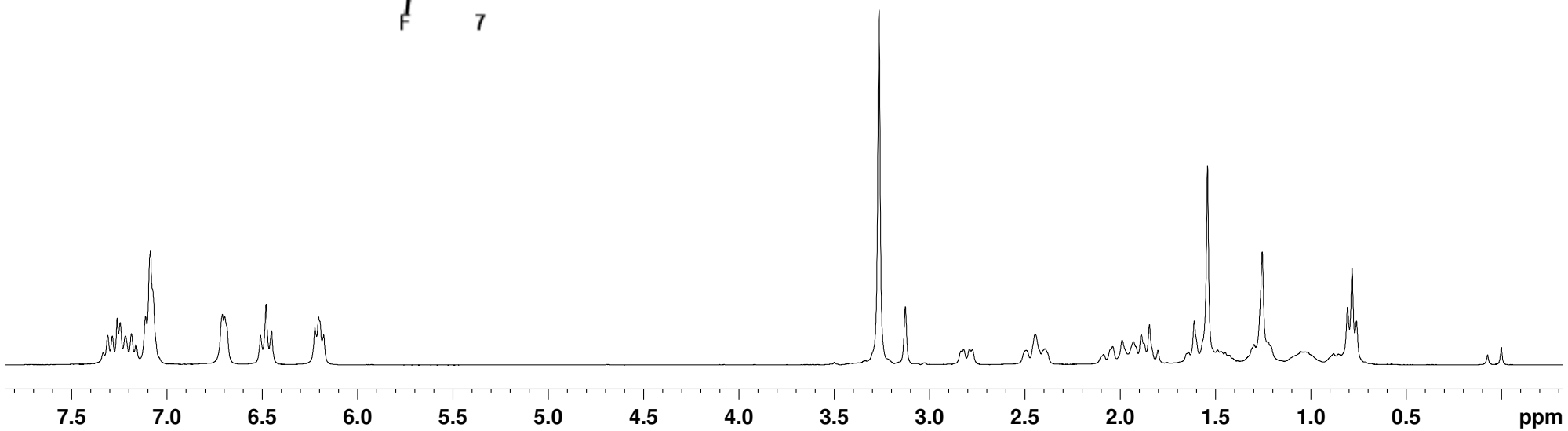
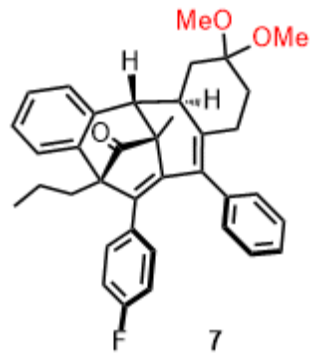




— -117.87

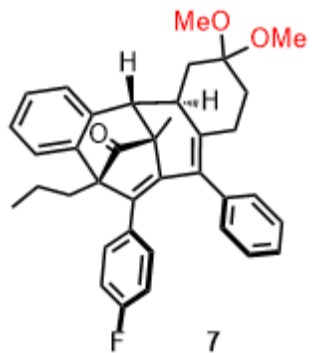


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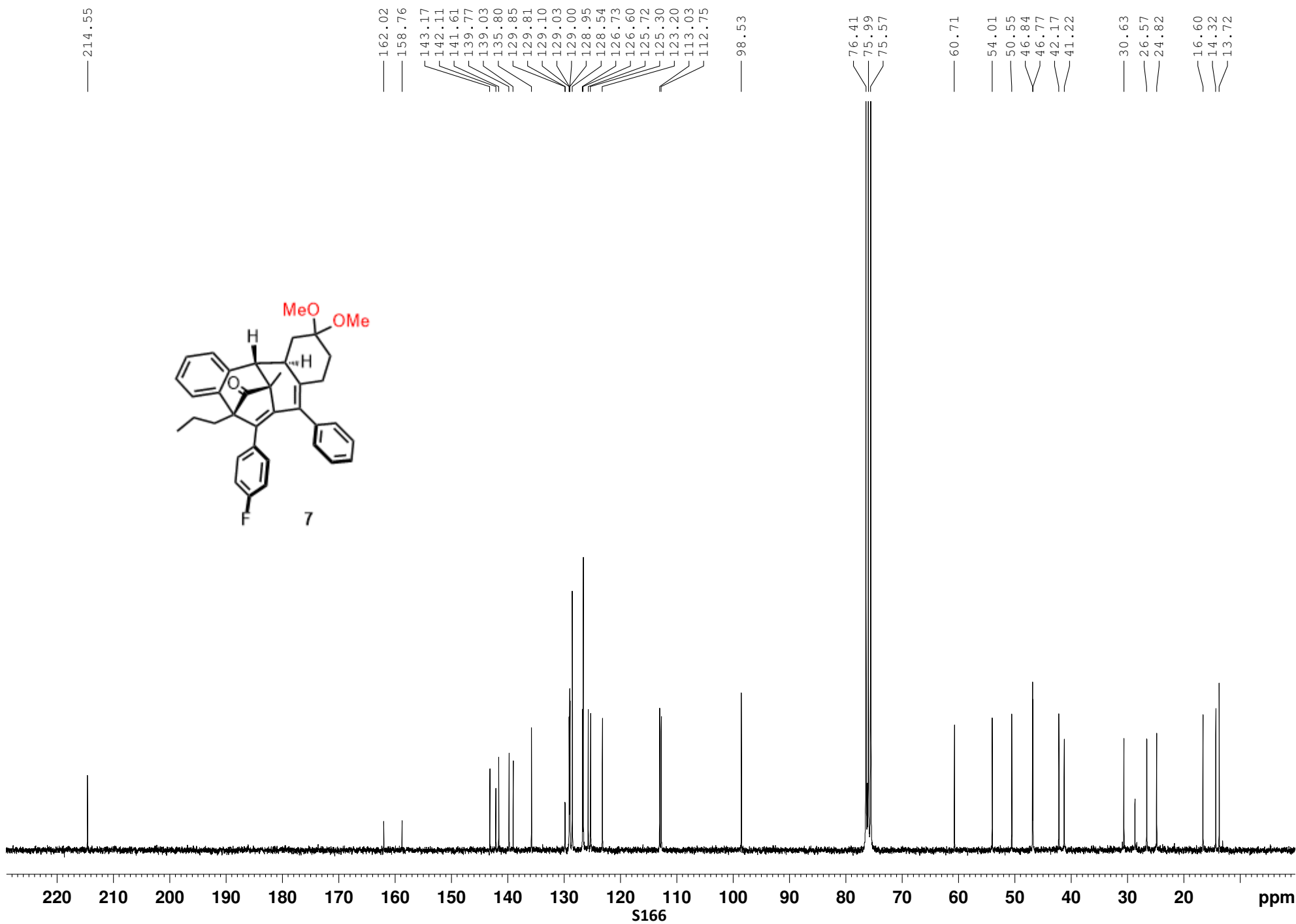


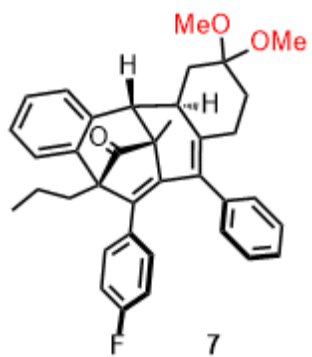
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2.01
2.04
6.06
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1.00
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4.07
5.13
0.50
0.56
1.13
3.06

S165



7





— -115.5



-85

-90

-95

-100

-105

-110

-115

-120

-125

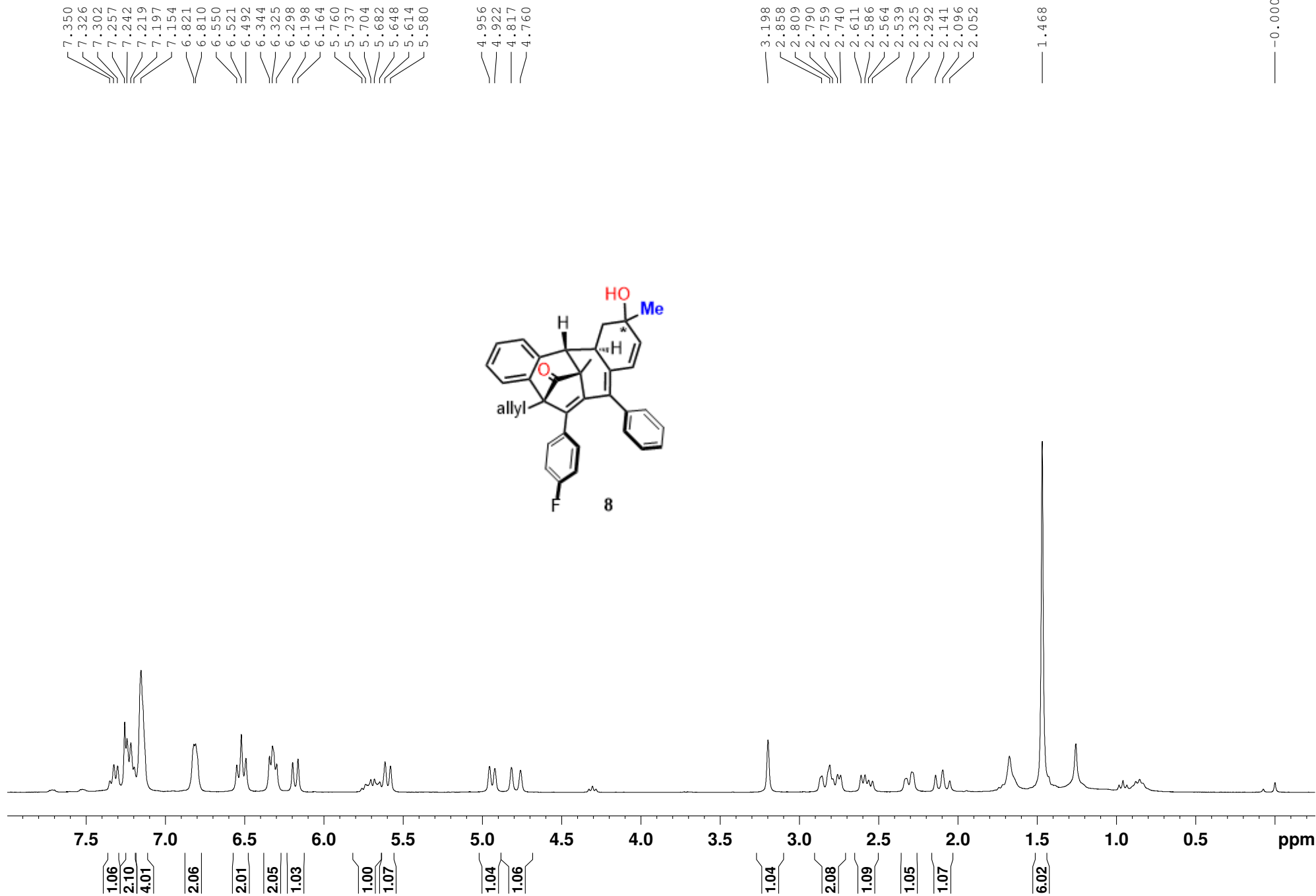
-130

-135

-140

ppm

S167



— 213.64



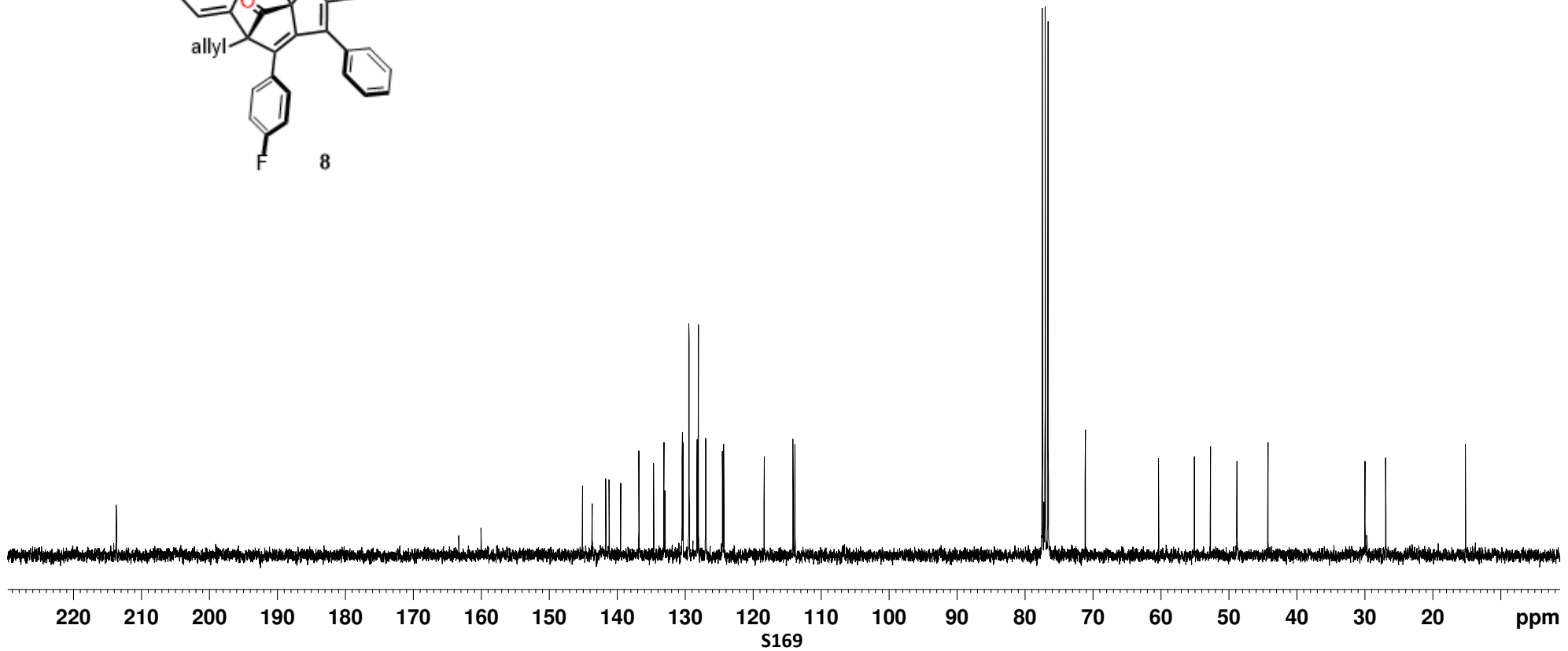
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— 134.64
— 133.13
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— 130.41
— 130.31
— 129.44
— 129.39
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— 128.06
— 126.99
— 126.94
— 124.50
— 124.32
— 118.37
— 114.13
— 113.85

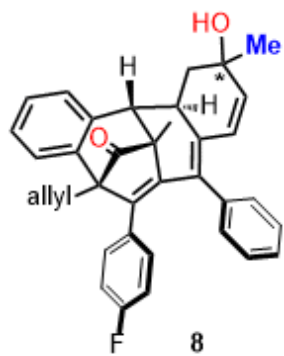
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— 77.03
— 76.61
— 71.12

— 60.34
— 55.07
— 52.71
— 48.80
— 44.25

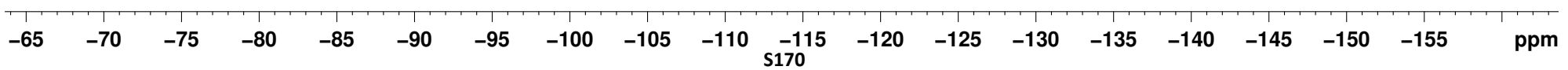
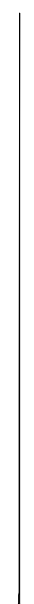
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— 26.92

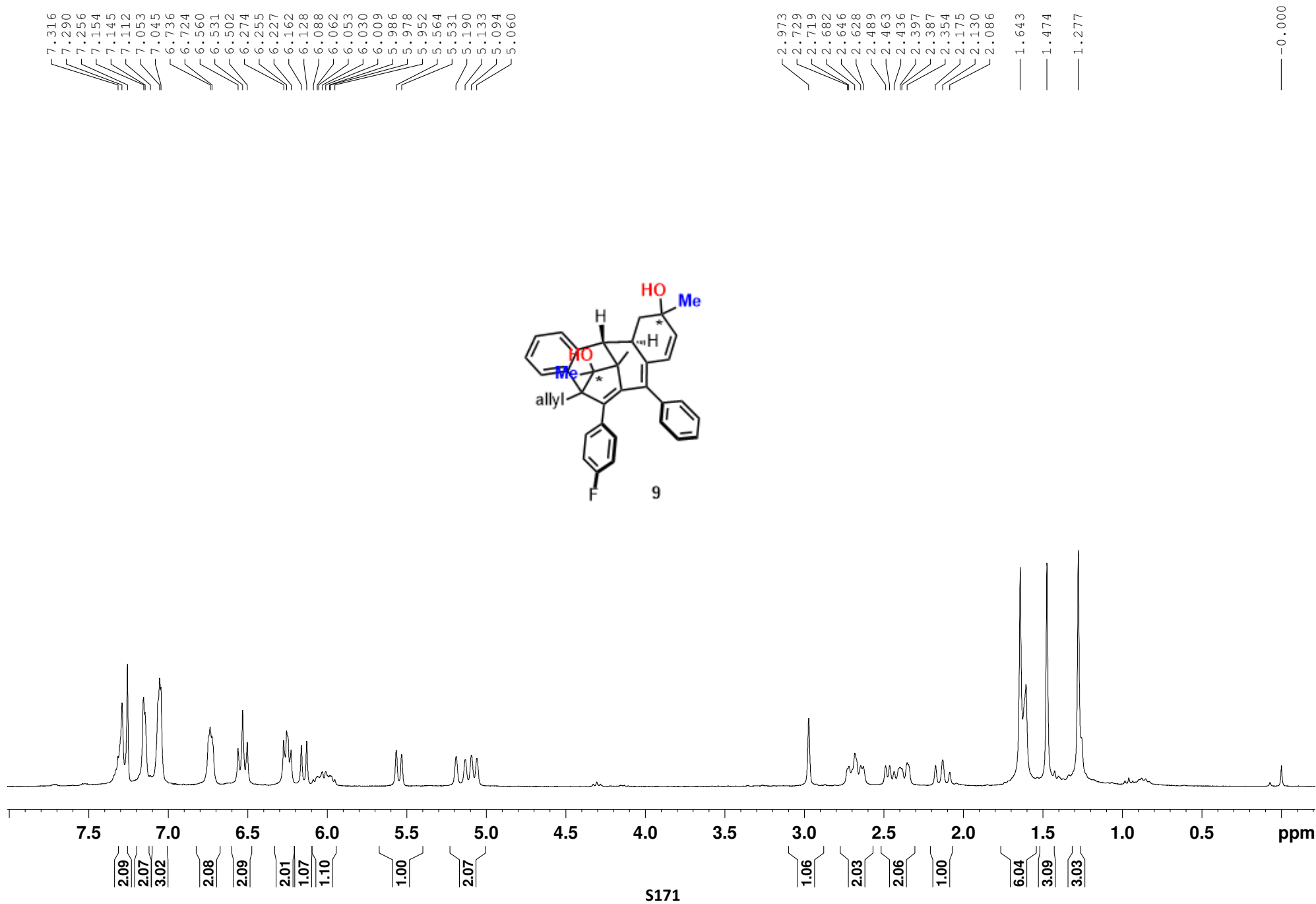
— 15.19





— -114.796

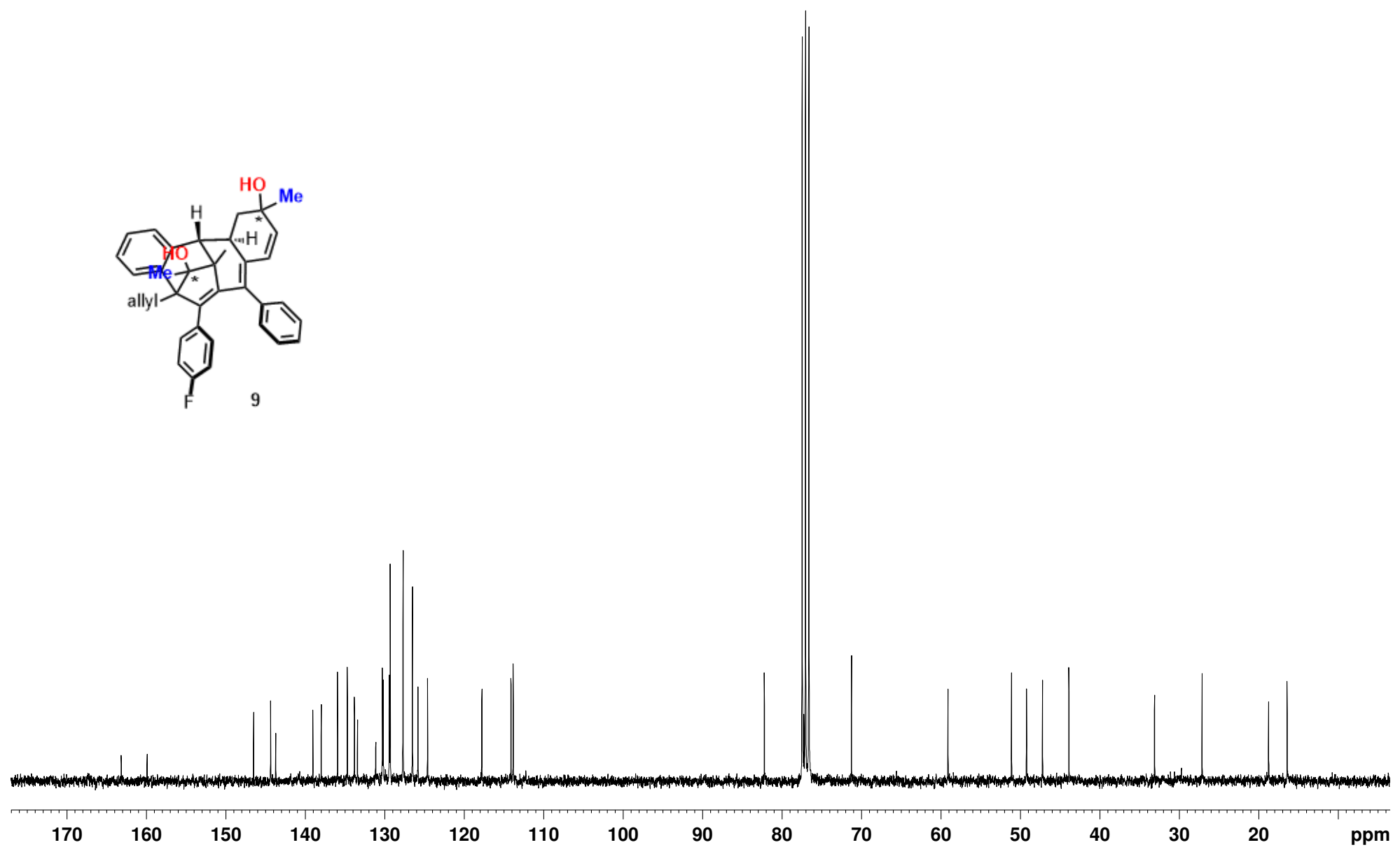
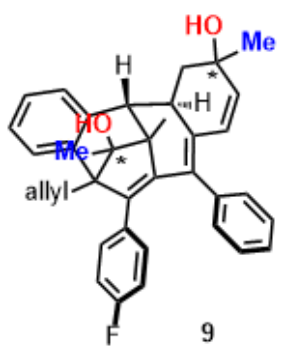


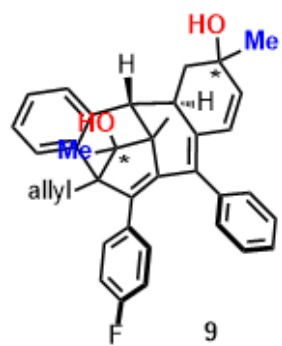


S171

— 163.16
 — 159.91
 — 146.50
 — 144.37
 — 143.71
 — 139.04
 — 137.99
 — 135.93
 — 134.70
 — 133.81
 — 133.42
 — 131.16
 — 131.12
 — 130.29
 — 130.18
 — 129.43
 — 129.31
 — 127.68
 — 126.51
 — 125.81
 — 124.60
 — 117.77
 — 114.10
 — 113.82

— 82.20
 — 77.45
 — 77.23
 — 77.02
 — 76.60
 — 71.24
 — 59.08
 — 51.09
 — 49.20
 — 47.19
 — 43.87
 — 33.09
 — 27.11
 — 18.73
 — 16.40





— -115.7

