Supporting Information

Synthesis of Cyclobutane-Fused Oxygen-Containing Tricyclic Framework via Thermally-Promoted Intramolecular Cycloaddition of Cyclohexadienone-Tethered Allenes

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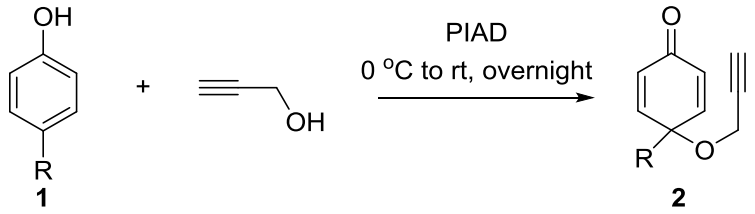
1. Materials and methods

All reactions were carried out under Argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed on Tsingdao silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 400 or 500 MHz) and reported relative to deuterated solvent signals or tetramethylsilane internal standard signals. Data for ^{1}H NMR spectra were reported as follows: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.), coupling constant (J/Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (100 or 125 MHz). Data for ^{13}C NMR spectra were reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was conducted on Bruker Apex IV RTMS. X-ray diffraction was performed on Bruker APEX-II CCD diffractometer using graphite monochromated Mo-Kα radiation at a temperature of 296 ±2 K.

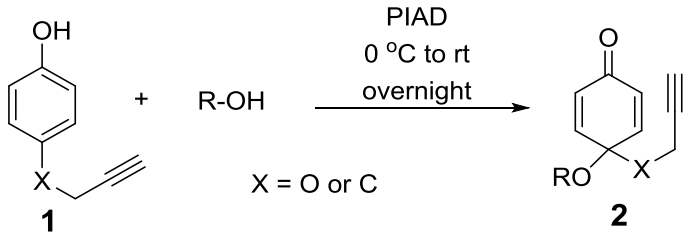
2. Preparation of substrates **2**[1]

Representative Method A：(**2h**, **2i**, **2o**, **2r**, **2u**)



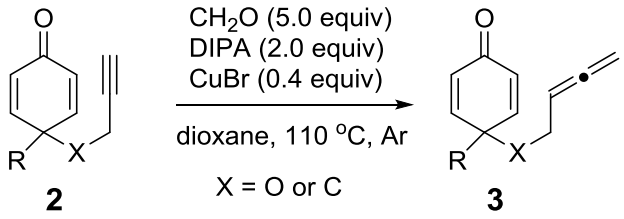
A well-stirred solution of 4-substituted phenol **1** (5 mmol, 1.0 equiv) in 6.0 mL of Propargyl alcohol was cooled to 0 °C and treated with (diacetoxyiodo)benzene (PIDA, 2.415 g, 7.5 mmol, 1.5 equiv) in several portions. The resulting mixture was warmed to room temperature and stirred overnight. Then the reaction mixture was diluted with water (20 mL) and extracted with ethyl acetate (20 mL×3). The combined organic phases were washed three time with brine (30 mL), the organic layer was dried over with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using PE/EA eluent to afford the cyclohexadienone-tethered terminal alkynes **2**.

Representative Method B: (**2j**, **2k**, **2m**, **2n**)



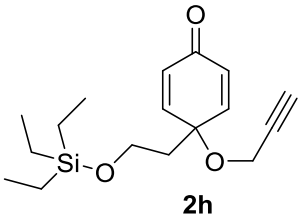
A well-stirred solution of 4-(prop-2-yn-1-yloxy)phenol **1** (5 mmol, 1.0 equiv) in 6.0 mL of alcohol was cooled to 0 °C and treated with (diacetoxyiodo)benzene (PIDA, 2.415 g, 7.5 mmol, 1.5 equiv) in several portions. The resulting mixture was warmed to room temperature and stirred overnight. Then the reaction mixture was diluted with water (20 mL) and extracted with ethyl acetate (20 mL×3). The combined organic phases were washed three time with brine (30 mL), the organic layer was dried over with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using PE/EA eluent to afford the cyclohexadienone-tethered terminal alkynes **2**.

3. Preparation of cyclohexadienone-tethered terminal allenes **3**[2]



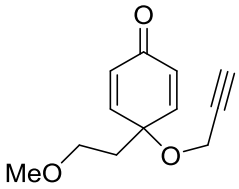
To a well-stirred solution of cyclohexadienone-tethered terminal alkynes **2** (2.0 mmol, 1.0 equiv) in dioxane (10 mL) was sequentially added paraformaldehyde (300 mg, 10.0 mmol, 5 equiv), CuBr (114.8 mg, 0.8 mmol, 0.4 equiv) and diisopropylamine (0.56 mL, 4.0 mmol, 2.0 equiv) under argon atmosphere. The resulting mixture was stirred at 110 ^{o}C for about 1 h (traced by TLC). After cooled to room temperature, the reaction mixture was filtered through a plug of celite and followed by washed with DCM (10 mL ×3). The organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography using PE/EA eluent to afford the cyclohexadienone-tethered terminal allenes **3**.

4. Characterization data for substrates **2** and **3**



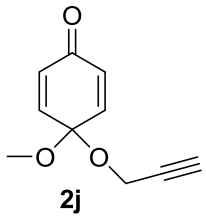
2h

4-(Prop-2-yn-1-yloxy)-4-(2-((triethylsilyl)oxy)ethyl)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure A, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **2h** (919 mg, 60% yield) as a sticky oil as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, *J* = 10.0 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 3.99 (d, *J* = 2.4 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 2.4 Hz, 1H), 2.00 (t, *J* = 6.4 Hz, 2H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 149.9, 130.8, 80.4, 75.2, 74.8, 57.5, 53.2, 42.8, 6.7, 4.3. HRMS calculated for $C_{17}H_{26}NaO_3Si$ $[M+Na]^+$, 329.1549, found 329.1543.



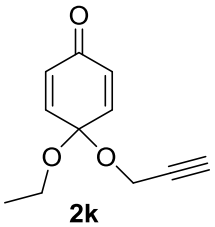
2i

4-(2-Methoxyethyl)-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure A, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **2i** (464 mg, 45% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (dd, *J* = 1.6, 8.0 Hz, 2H), 6.30 (d, *J* = 10.0 Hz, 2H), 3.96 (d, *J* = 2.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 3.21(s, 3H), 2.44 (t, *J* = 2.4 Hz, 1H), 2.01 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 149.6, 130.9, 80.2, 74.9, 74.9, 67.1, 58.4, 53.3, 39.4. HRMS calculated for $C_{12}H_{15}O_3$ $[M+H]^+$, 207.1021, found 207.1012.



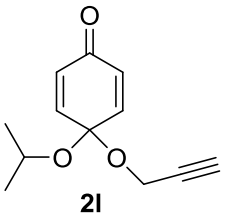
2j

4-Methoxy-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure B, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2j** (463 mg, 52% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 10.4 Hz, 2H), 6.27 (d, *J* = 10.4 Hz, 2H), 4.30 (d, *J* = 2.0 Hz, 2H), 3.41 (s, 3H), 2.47 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ184.9, 142.4, 129.9, 92.8, 79.7, 74.8, 50.7. HRMS calculated for $C_{10}H_{11}O_3$ $[M+H]^+$, 179.0708, found 179.0706.



2k

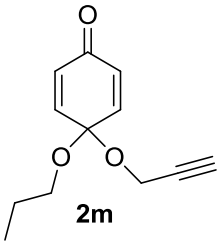
4-Ethoxy-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure B, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2k** (424 mg, 44% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* = 10.4 Hz, 2H), 6.28 (d, *J* = 10.4 Hz, 2H), 4.31 (d, *J* = 2.4 Hz, 2H), 3.69 (q, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 2.4 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 142.9, 129.6, 92.6, 79.8, 74.7, 58.9, 50.7, 15.5. HRMS calculated for $C_{11}H_{13}O_3$ $[M+H]^+$, 193.0865, found 193.0856.



2l

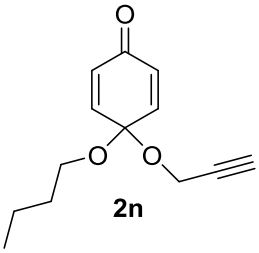
4-Isopropoxy-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure B, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2l** (413 mg, 40% yield)

as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 10.4 Hz, 2H), 6.26 (d, *J* = 10.4 Hz, 2H), 4.31 (d, *J* = 2.4 Hz, 2H), 4.16 (m, 1H), 2.46 (t, *J* = 2.4 Hz, 1H), 1.22 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 143.5, 129.2, 92.8, 80.0, 74.7, 66.4, 50.8, 24.3. HRMS calculated for $C_{12}H_{15}O_3$ $[M+H]^+$, 207.1021, found 207.1015.



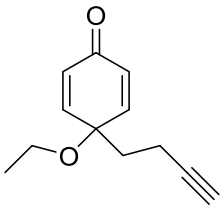
2m

4-(Prop-2-yn-1-yloxy)-4-propoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure B, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2m** (454 mg, 44% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, *J* = 10.0 Hz, 2H), 6.26 (d, *J* = 10.0 Hz, 2H), 4.31 (d, *J* = 2.4 Hz, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 2.4 Hz, 1H), 1.58-1.67 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 143.0, 129.6, 92.6, 79.8, 74.7, 64.9, 50.6, 23.2, 10.5. HRMS calculated for $C_{12}H_{15}O_3$ $[M+H]^+$, 207.1021, found 207.1016.



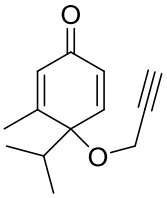
2n

4-Butoxy-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure B, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2n** (331 mg, 30% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, *J* = 10.4 Hz, 2H), 6.26 (d, *J* = 10.4 Hz, 2H), 4.31 (d, *J* = 2.4 Hz, 2H), 3.60 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 2.4 Hz, 1H), 1.55-1.62 (m, 2H), 1.34-1.44 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 143.0, 129.6, 92.6, 79.8, 74.7, 63.1, 50.6, 31.9, 19.2, 13.8. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1172.



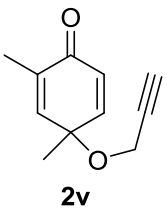
2p

4-(But-3-yn-1-yl)-4-ethoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure B, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2p** (523 mg, 55% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, *J* = 10.0 Hz, 2H), 6.34 (d, *J* = 10.0 Hz, 2H), 3.37 (q, *J* = 6.8 Hz, 2H), 2.24 (dt, *J* = 2.8, 8.0 Hz, 2H), 1.95-2.00 (m, 3H), 1.16 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 150.7, 131.3, 83.3, 74.4, 69.2, 60.9, 38.5, 15.9, 13.1. HRMS calculated for $C_{12}H_{14}O_2$ $[M+H]^+$, 191.1072, found 191.1074.



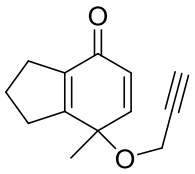
2s

4-Isopropyl-3-methyl-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure A, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2s** (253 mg, 25% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (d, *J* = 10.4 Hz, 1H), 6.41(dd, *J* = 2.0, 10.0 Hz, 1H), 6.25 (dd, *J* = 2.0, 2.5 Hz, 1H), 3.86 (m, 2H), 2.43 (t, *J* = 2.4 Hz, 1H), 2.17 (m, 1H), 1.95 (d, *J* = 1.2 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 185.1, 159.6, 147.1, 132.9, 130.9, 81.3, 79.9, 74.5, 53.2, 35.0, 17.9, 17.1, 16.5. HRMS calculated for $C_{13}H_{17}O_2$ $[M+H]^+$, 205.1229, found 205.1221.



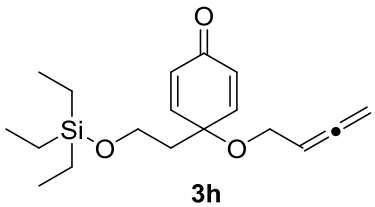
2v

2,4-Dimethyl-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure A, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 5:1) to afford the corresponding product **2v** (308 mg, 35% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (dd, *J* = 2.8, 10.0 Hz, 1H), 6.54 (m, 1H), 6.25 (d, *J* = 10.0 Hz, 1H), 3.92 (d, *J* = 2.4 Hz, 2H), 2.43 (t, *J* = 2.4 Hz, 1H), 1.87 (d, *J* = 1.6 Hz, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 150.2, 145.8, 137.1, 130.3, 80.5, 74.6, 73.5, 53.3, 26.3, 15.6. HRMS calculated for $C_{11}H_{13}O_2$ $[M+H]^+$, 177.0916, found 177.0909.



2x

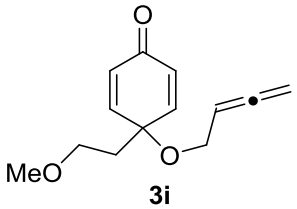
7-Methyl-7-(prop-2-yn-1-yloxy)-1,2,3,7-tetrahydro-4H-inden-4-one: Prepared according to the general procedure A, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **2x** (334 mg, 33% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (d, *J* = 10.0 Hz, 1H), 6.21(d, *J* = 10.0 Hz, 1H), 3.79 (m, 2H), 2.56-2.70 (m, 4H), 2.41 (t, *J* = 2.4 Hz, 1H), 1.86-2.01 (m, 2H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 161.8, 150.4, 140.5, 131.0, 79.9, 74.5, 73.9, 53.1, 32.6, 29.6, 24.9, 21.3. HRMS calculated for $C_{13}H_{15}O_2$ $[M+H]^+$, 203.1072, found 203.1066.



3h

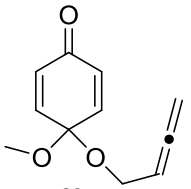
4-(Buta-2,3-dien-1-yloxy)-4-(2-((triethylsilyl)oxy)ethyl)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3h** (416 mg, 65% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 10.0 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 2H), 5.17-5.23 (m, 1H), 4.75-4.78 (m, 2H), 3.86-3.89 (m, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 1.98 (t, *J* = 6.4 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* =

8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 185.5, 151.1, 130.4, 88.6, 76.1, 74.4, 63.5, 57.6, 42.9, 6.8, 4.3. HRMS calculated for $C_{18}H_{28}NaO_3Si$ $[M+Na]^+$, 343.1705, found 343.1705.



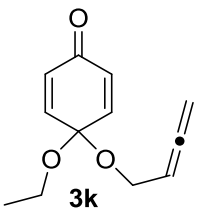
3i

4-(Buta-2,3-dien-1-yloxy)-4-(2-methoxyethyl)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3i** (247 mg, 56% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, *J* = 8.0 Hz, 2H), 6.29 (d, *J* = 10.4 Hz, 2H), 5.17 (m, 1H), 4.74 (td, *J* = 2.4, 6.8 Hz, 2H), 4.85 (td, *J* = 2.4, 6.8 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 3.23 (s, 3H), 1.99 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 185.3, 150.8, 130.4, 88.5, 76.1, 74.3, 67.2, 63.4, 58.4, 39.5. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1170.



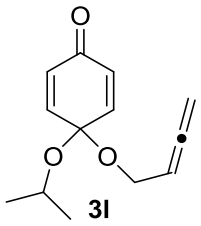
3j

4-(Buta-2,3-dien-1-yloxy)-4-methoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3j** (277 mg, 72% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 10.4 Hz, 2H), 6.26 (d, *J* = 10.4 Hz, 2H), 5.22-5.29 (m, 1H), 4.82 (td, *J* = 2.4, 6.8 Hz, 2H), 4.16 (td, *J* = 2.4, 6.8 Hz, 2H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 185.1, 143.2, 129.7, 92.6, 88.0, 76.4, 61.0, 50.5. HRMS calculated for $C_{11}H_{13}O_3$ $[M+H]^+$, 193.0865, found 193.0858.



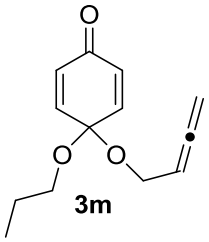
3k

4-(Buta-2,3-dien-1-yloxy)-4-ethoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3k** (276 mg, 67% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, *J* = 10.4 Hz, 2H), 6.25 (d, *J* = 10.4 Hz, 2H), 5.22-5.29 (m, 1H), 4.80-4.82 (m, 2H), 4.15-4.18 (m, 2H), 3.66 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 185.2, 143.8, 129.4, 92.4, 88.1, 76.4, 61.0, 58.6, 15.5. HRMS calculated for $C_{12}H_{15}O_3$ $[M+H]^+$, 207.1021, found 207.1015.



3l

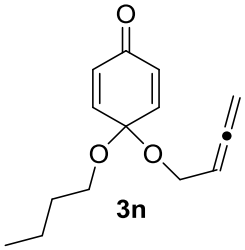
4-(Buta-2,3-dien-1-yloxy)-4-isopropoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3l** (264 mg, 60% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 10.4 Hz, 2H), 6.24 (d, *J* = 10.4 Hz, 2H), 5.21-5.27 (m, 1H), 4.81 (td, *J* = 2.4, 6.8 Hz, 2H), 4.11-4.18 (m, 3H), 1.21 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 185.4, 144.3, 128.9, 92.5, 88.2, 76.4, 66.0, 61.0, 24.3. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1168.



3m

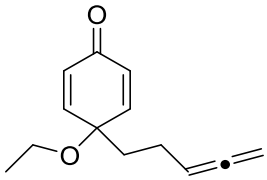
4-(Buta-2,3-dien-1-yloxy)-4-propoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3m** (255 mg, 58% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, *J* = 10.4 Hz, 2H), 6.25 (d, *J* = 10.4 Hz, 2H), 5.22-5.28 (m, 1H), 4.79-4.82 (m, 2H), 4.15-4.18 (m, 2H), 3.54 (t, *J* = 6.8 Hz, 2H), 1.57-1.66 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2,

185.2, 143.9, 129.4, 92.4, 88.1, 76.4, 64.7, 60.9, 23.2, 10.5. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1172.



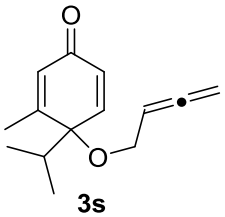
3n

4-(Buta-2,3-dien-1-yloxy)-4-butoxycyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3n** (258 mg, 55% yield) as a sticky oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 10.4 Hz, 2H), 6.25 (d, *J* = 10.4 Hz, 2H), 5.22-5.28 (m, 1H), 4.79-4.82 (m, 2H), 4.15-4.18 (m, 2H), 3.58 (t, *J* = 6.8 Hz, 2H), 1.54-1.61 (m, 2H), 1.34-1.43 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 185.2, 143.9, 129.4, 92.4, 88.1, 76.4, 62.8, 61.0, 32.0, 19.2, 13.8. HRMS calculated for $C_{14}H_{19}O_3$ $[M+H]^+$, 235.1334, found 235.1331.



3p

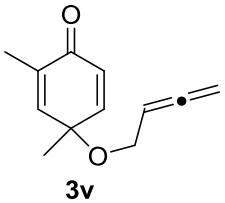
4-Ethoxy-4-(penta-3,4-dien-1-yl)cyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3p** (348 mg, 62% yield) as a sticky oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, *J* = 10.0 Hz, 2H), 6.33 (d, *J* = 10.0 Hz, 2H), 5.05-5.11 (m, 1H), 4.67-4.70 (m, 2H), 3.38 (q, *J* = 6.8 Hz, 2H), 1.94-2.021 (m, 2H), 1.83-1.88 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 185.5, 151.4, 131.1, 89.3, 75.9, 75.1, 60.9, 38.5, 22.1, 15.9. HRMS calculated for $C_{13}H_{16}O_2$ $[M+H]^+$, 205.1229, found 205.1227.



3s

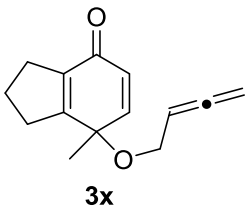
4-(Buta-2,3-dien-1-yloxy)-4-isopropyl-3-methylcyclohexa-2,5-dien-1-one:

Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3s** (257 mg, 59% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (td, *J* = 1.6, 10.4 Hz, 1H), 6.39 (dd, *J* = 2.4, 10.0 Hz, 1H), 6.23 (s, 1H), 5.21 (m, 1H), 4.76 (td, *J* = 2.4, 6.4 Hz, 2H), 3.65-3.79 (m, 2H), 2.14 (m, 1H), 1.93 (d, *J* = 1.6 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 185.4, 160.6, 148.3, 132.4, 130.5, 88.3, 80.7, 76.1, 63.2, 35.1, 17.8, 17.1, 16.5. HRMS calculated for $C_{14}H_{19}O_2$ $[M+H]^+$, 219.1385, found 219.1383.



3v

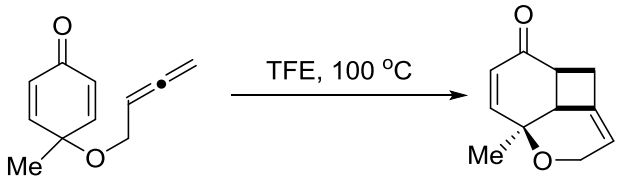
4-(Buta-2,3-dien-1-yloxy)-2,4-dimethylcyclohexa-2,5-dien-1-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3v** (266 mg, 70% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (dd, *J* = 3.2, 10.0 Hz, 1H), 6.56 (dd, *J* = 1.6, 3.2 Hz, 1H), 6.27 (d, *J* = 10.0 Hz, 1H), 5.20 (m, 1H), 4.75 (td, *J* = 2.4, 6.8 Hz, 2H), 3.82-3.85 (m, 2H), 1.90 (d, *J* = 1.2 Hz, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 185.9, 151.5, 146.9, 136.6, 129.8, 88.5, 75.9, 73.0, 63.7, 26.5, 15.7.HRMS calculated for $C_{12}H_{15}O_2$ $[M+H]^+$, 191.1072, found 191.1066.



3x

7-(Buta-2,3-dien-1-yloxy)-7-methyl-1,2,3,7-tetrahydro-4H-inden-4-one: Prepared according to the general procedure, purified by column chromatography on silica gel (PE/EtOAc = 15:1 to 10:1) to afford the corresponding product **3x** (208 mg, 48% yield) as a sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (dd, *J* = 0.4, 10.0 Hz, 1H), 6.25 (dd, *J* = 0.8, 10.0 Hz, 1H), 5.18 (m, 1H), 4.74-4.76 (m, 2H), 3.71-3.77 (m, 1H), 3.60-3.65 (m, 1H), 2.59-2.73 (m, 4H), 1.90-2.05 (m, 2H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 184.5, 163.0, 151.7, 140.1, 130.5, 88.1, 75.9, 73.5, 63.6, 32.7, 29.7, 25.2, 21.6. HRMS calculated for $C_{14}H_{17}O_2$ $[M+H]^+$, 217.1229, found 217.1225.

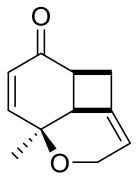
5. General procedure for cycloadditions



3a **4a**

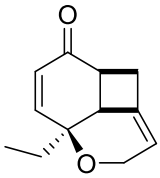
To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-methylcyclohexa-2,5-dien-1-one (**3a**, 100.2 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 4 h at 100 °C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4a** (86.4 mg, 86% yield) as a colorless sticky oil.

6. Characterization data for products



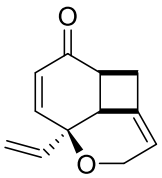
4a

(3a^1*R*,4a*R*,7a*R*)-7a-Methyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.99 (d, *J* = 10.4 Hz, 1H), 5.31 (t, *J* = 1.6 Hz, 1H), 4.29 (dd, *J* = 1.6, 16.4 Hz, 1H), 4.11 (dd, *J* = 1.6, 16.4 Hz, 1H), 3.32-3.38 (m, 1H), 3.26-3.29 (m, 1H), 3.07 (d, *J* = 8.4 Hz, 1H), 2.63 (dd, *J* = 0.8, 13.6 Hz, 1H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 151.9, 134.6, 130.8, 113.2, 67.5, 63.7, 46.5, 40.7, 39. 7, 27.0.



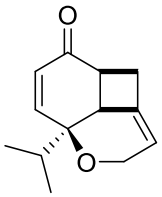
4b

(3a^1*R*,4a*R*,7a*R*)-7a-Ethyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-ethylcyclohexa-2,5-dien-1-one (**3b**, 100.9 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 5 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4b** (85.0 mg, 84% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (dd, *J* = 1.6, 10.4 Hz, 1H), 6.14 (d, *J* = 10.4 Hz, 1H), 5.35 (t, *J* = 1.6 Hz, 1H), 4.29-4.35 (m, 1H), 4.13-4.18 (m, 1H), 3.36-3.44 (m, 1H), 3.28-3.31 (m, 1H), 3.06 (t, *J* = 8.8 Hz, 1H), 2.67 (dd, *J* = 0.8, 13.6 Hz, 1H), 1.61-1.71 (m, 2H), 0.84 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 150.6, 134.8, 132.4, 113.4, 70.9, 63.7, 45.3, 41.6, 40.2, 33.2, 7.4. HRMS calculated for $C_{12}H_{15}O_2$ $[M+H]^+$, 191.1072, found 191.1070.



4c

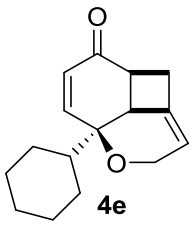
(3a^1*R*,4a*R*,7a*R*)-7a-Vinyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-vinylcyclohexa-2,5-dien-1-one (**3c**, 100.6 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 6h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4c** (85.8 mg, 85% yield) as a colorless sticky oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.55 (dd, *J* = 1.5, 10.5 Hz, 1H), 6.13 (d, *J* = 10.5 Hz, 1H), 5.88 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.37 (m, 1H), 5.22 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 4.39 (dd, *J* = 2.0, 16.5 Hz, 1H), 4.20 (d, *J* = 16.5 Hz, 1H), 3.38-3.44 (m, 2H), 3.11 (d, *J* = 9.0 Hz, 1H), 2.69 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 149.0, 139.6, 134.6, 131.5, 115.3, 113.4, 70.4, 63. 6, 45.4, 40.7, 39.7. HRMS calculated for $C_{12}H_{13}O_2$ $[M+H]^+$, 189.0916, found 189.0913.



4d

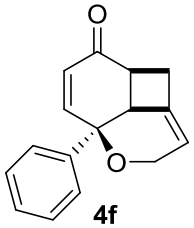
(3a^1*R*,4a*R*,7a*R*)-7a-Isopropyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-vinylcyclohexa-2,5-dien-1-one (**3d**, 102.5 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 12 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4d** (81.4 mg, 79% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.18 (d, *J* = 10.4 Hz, 1H), 5.33 (t, *J* = 1.6 Hz, 1H), 4.29-4.36 (m, 1H), 4.11-4.16 (m,

1H), 3.35-3.42 (m, 1H), 3.27-3.30 (m, 1H), 3.03 (t, *J* = 8.0 Hz, 1H), 2.66 (dd, *J* = 0.8, 13.6 Hz, 1H), 1.79-1.89 (m, 1H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.6, 149.1, 134.9, 133.1, 113.4, 72.8, 63.7, 44.4, 42.2, 40.2, 37.6, 16.5, 16.2. HRMS calculated for $C_{13}H_{17}O_2$ $[M+H]^+$, 205.1229, found 205.1223.



4e

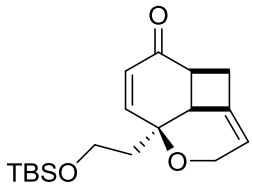
(3a^1*R*,4a*R*,7a*R*)-7a-Cyclohexyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 1-(buta-2,3-dien-1-yloxy)-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (**3e**, 109.6 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 6 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4e** (88.1 mg, 80% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 (dd, *J* = 1.6, 10.8 Hz, 1H), 6.14 (d, *J* = 10.8 Hz, 1H), 5.31 (t, *J* = 1.6 Hz, 1H), 4.28-4.34 (m, 1H), 4.13 (dd, *J* = 1.6, 16.8 Hz, 1H), 3.28-3.41 (m, 2H), 3.01 (t, *J* = 8.8 Hz, 1H), 2.64 (dd, *J* = 1.2, 13.6 Hz, 1H), 1.89 (d, *J* = 13.6 Hz, 1H), 1.63-1.77 (m, 4H), 1.51 (tt, *J* = 2.8, 12.0 Hz, 1H), 1.01-1.28 (m, 3H), 0.84-0.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199. 6, 149. 8, 135.0, 132. 7, 113.4, 72.5, 63.5, 47. 9, 44.7, 42.2, 40.2, 26.7, 26.4, 26.4, 26.3, 26.1. HRMS calculated for $C_{16}H_{21}O_2$ $[M+H]^+$, 245.1542, found 245.1537.



4f

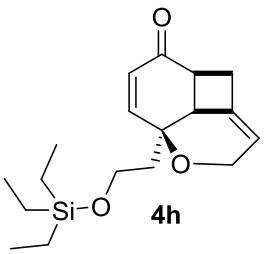
(3a^1*R*,4a*R*,7a*R*)-7a-Phenyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 1-(buta-2,3-dien-1-yloxy)-[1,1'-biphenyl]-4(1H)-one (**3f**, 118.8 mg) and TFE (2.0

mL), The container was sealed and the resulting mixture was stirred for 10 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4f** (98.5 mg, 83% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.40 (m, 4H), 7.26-7.30 (m, 1H), 6.64 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.15(d, *J* = 10.4 Hz, 1H), 5.45 (s, 1H), 4.52-4.59 (m, 1H), 4.35 (d, *J* = 16.8 Hz, 1H), 3.59-3.62 (m, 1H), 3.41-3.47 (m, 1H), 3.25 (t, *J* = 8.8 Hz, 1H), 2.77 (dd, *J* = 0.8, 13.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 150.2, 143.0, 134.7, 130.8, 128.6, 127.7, 124.8, 113.4, 71.2, 63.8, 47.5, 41.5, 39.9. HRMS calculated for $C_{16}H_{15}O_2$ $[M+H]^+$, 239.1072, found 239.1069.



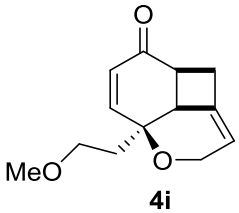
4g

(3a^1*R*,4a*R*,7a*R*)-7a-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-(2-((tert-butyldimethylsilyl) oxy)ethyl)cyclohexa-2,5-dien-1-one (**3g**, 101.9 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 5 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4f** (88.9 mg, 87% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (dd, *J* = 1.6, 10.4 Hz, 1H), 6.08 (d, *J* = 10.4 Hz, 1H), 5.34 (t, *J* = 1.6 Hz, 1H), 4.31 (dd, *J* = 1.2, 16.4 Hz, 1H), 4.13 (dd, *J* = 1.2, 18.0 Hz, 1H), 3.67-3.71 (m, 2H), 3.43-3.46 (m, 1H), 3.33-3.39 (m, 1H), 3.08 (t, *J* = 8.0 Hz, 1H), 2.65 (dd, *J* = 1.2, 13.6 Hz, 1H), 1.79-1.94 (m, 2H), 0.86 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 150.7, 134.7, 131.8, 113.2, 69.4, 63.3, 58.2, 45.8, 43.4, 41.3, 39.8, 25.9, 18.2, -5.4, -5.5. HRMS calculated for $C_{18}H_{28}NaO_3Si$ $[M+Na]^+$, 343.1705, found 343.1703.



4h

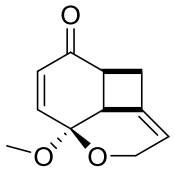
(3a^1*S*,4a*S*,7a*S*)-7a-(2-((Triethylsilyl)oxy)ethyl)-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-(2-((triethylsilyl)oxy)ethyl)cyclohexa -2,5-dien-1-one (**3h**, 115.1 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 5 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4h** (102.5 mg, 89% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 5.34 (m, 1H), 4.31 (dd, *J* = 1.6, 16.4 Hz, 1H), 4.14 (d, *J* = 16.4 Hz, 1H), 3.62-3.73 (m, 2H), 3.44-3.46 (m, 1H), 3.30-3.39 (m, 1H), 3.08 (t, *J* = 8.4 Hz, 1H), 2.65 (d, *J* = 13.2 Hz, 1H), 1.90-1.97 (m, 1H), 1.83 (td, *J* = 5.6, 14.0 Hz, 1H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 150.5, 134.7, 131.9, 113.2, 69.4, 63.2, 57.9, 46.0, 43.3, 41.4, 39.7, 6.7, 4.3. HRMS calculated for $C_{18}H_{29}O_3Si$ $[M+H]^+$, 321.1886, found 321.1880.



4i

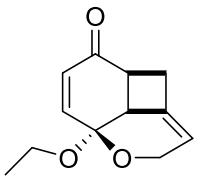
(3a^1*R*,4a*R*,7a*R*)-7a-(2-Methoxyethyl)-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4 -(2-methoxyethyl)cyclohexa-2,5-dien-1-one (**3i**, 121.5 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 5 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column

chromatography on silica gel (*n*-hexanes/EtOAc = 10:1 to 5:1) to give **4i** (96.2 mg, 79% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 5.33 (t, *J* = 1.6 Hz, 1H), 4.26-4.32 (m, 1H), 4.11-4.15 (m, 1H), 3.29-3.44 (m, 4H), 3.20 (s, 3H), 3.07 (t, *J* = 8.0 Hz, 1H), 2.61 (dd, *J* = 0.8, 13.6 Hz, 1H), 1.93-2.00 (m, 1H), 1.79-1.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 150.1, 134.8, 132.1, 113.2, 69.6, 67.8, 63.3, 58.6, 46.1, 41.4, 40.1, 39.4. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1173.



4j

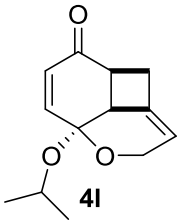
(3a^1*S*,4a*S*,7a*S*)-7a-Methoxy-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-methoxycyclohexa-2,5-dien-1-one (**3j**, 102.9 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4j** (96.2 mg, 93% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 5.36 (m, 1H), 4.48-4.54 (m, 1H), 4.20-4.24 (m, 1H), 3.50-3.53 (m, 1H), 3.36-3.44 (m, 4H), 3.16-3.21 (m, 1H), 2.65 (dd, *J* = 1.0, 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 144.5, 135.3, 133.6, 113.5, 91.9, 65.2, 49.8, 45.2, 41.0, 38.8. HRMS calculated for $C_{11}H_{13}O_3$ $[M+H]^+$, 193.0865, found 193.0858.



4k

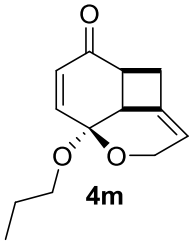
(3a^1*S*,4a*S*,7a*S*)-7a-Ethoxy-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the

4-(buta-2,3-dien-1-yloxy)-4-ethoxycyclohexa-2,5-dien-1-one (**3k**, 95.4 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 30 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4k** (93.2 mg, 98% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (dd, *J* = 2.0, 10.8 Hz, 1H), 6.20 (d, *J* = 10.8 Hz, 1H), 5.36 (m, 1H), 4.49-4.54 (m, 1H), 4.20-4.26 (m, 1H), 3.73-3.81 (m, 1H), 3.60-3.67 (m, 1H), 3.52-3.55 (m, 1H), 3.36-3.49 (m, 1H), 3.17-3.22 (m, 1H), 2.66 (dd, *J* = 1.2, 10.0 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 145.1, 135.3, 133.4, 113.5, 91.9, 65.2, 57.8, 45.7, 41.1, 38.9, 15.6. HRMS calculated for $C_{12}H_{15}O_3$ $[M+H]^+$, 207.1021, found 207.1015.



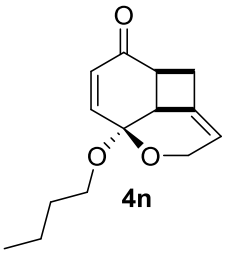
4l

(3a^{1}*S*,4a*S*,7a*R*)-7a-Isopropoxy-3a^{1},4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-isopropoxy cyclohexa-2,5-dien-1-one (**3l**, 89.3 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4l** (70.4 mg, 79% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (dd, *J* = 2.0, 10.8 Hz, 1H), 6.17 (d, *J* = 10.8 Hz, 1H), 5.36 (m, 1H), 4.47-4.52 (m, 1H), 4.19-4.27 (m, 2H), 3.51-3.53 (m, 1H), 3.36-3.53 (m, 1H), 3.18-3.23 (m, 1H), 2.65 (d, *J* = 13.6 Hz, 1H), 1.22 (d, *J* = 6.0 Hz, 3H), 1.18 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 145.7, 135.4, 132.7, 113.5, 92.0, 65.5, 65.0, 46.3, 41.1, 38.8, 24.6, 24.5. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1169.



4m

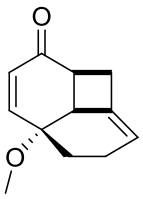
(3a^1*S*,4a*S*,7a*S*)-7a-Propoxy-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-propoxycy clohexa-2,5-dien-1-one (**3m**, 89.2 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4m** (79.0 mg, 89% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (dd, *J* = 2.0, 10.8 Hz, 1H), 6.20 (d, *J* = 10.8 Hz, 1H), 5.36 (m, 1H), 4.49-4.54 (m, 1H), 4.21-4.25 (m, 1H), 3.61-3.65 (m, 1H), 3.49-3.56 (m, 2H), 3.37-3.45 (m, 1H), 3.18-3.22 (m, 1H), 2.66 (dd, *J* = 1.0, 13.6 Hz, 1H), 1.56-1.63 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 145.3, 135.3, 133.3, 113.5, 91.9, 65.2, 64.0, 45.6, 41.2, 38.9, 23.3, 10.5. HRMS calculated for $C_{13}H_{17}O_3$ $[M+H]^+$, 221.1178, found 221.1170.



4n

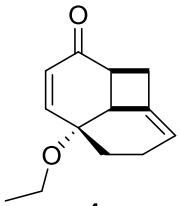
(3a^1*S*,4a*S*,7a*S*)-7a-Butoxy-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-butoxycyclohexa-2,5-dien-1-one (**3n**, 97.2 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4n** (86.0 mg, 88% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (dd, *J* = 2.0, 10.8 Hz, 1H),

6.19 (d, *J* = 10.8 Hz, 1H), 5.36 (m, 1H), 4.48-4.53 (m, 1H), 4.20-4.24 (m, 1H), 3.65-3.70 (m, 1H), 3.52-3.58 (m, 2H), 3.37-3.43 (m, 1H), 3.19 (t, *J* = 8.0 Hz, 1H), 2.65 (d, *J* = 13.6 Hz, 1H), 1.52-1.59 (m, 2H), 1.32-1.41 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 145.2, 135.3, 133.3, 113.5, 91.9, 65.2, 62.0, 45.6, 41.1, 38.9, 32.1, 19.2, 13.8. HRMS calculated for $C_{14}H_{19}O_3$ $[M+H]^+$, 235.1334, found 235.1329.



4o

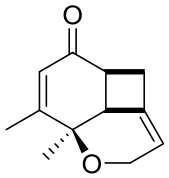
(1a*S*,1a^1*S*,4a*R*)-4a-Methoxy-1,1a,1a^1,4a,5,6-hexahydro-2*H*-cyclobuta[*de*]naphthalen-2-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-methoxy-4-(penta-3,4-dien-1-yl)cyclohexa-2,5-dien-1-one (**3o**, 96.5 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 150 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4o** (77.6 mg, 80% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.24 (d, *J* = 10.4 Hz, 1H), 5.23 (m, 1H), 3.26-3.34 (m, 2H), 3.14 (s, 3H), 2.98 (t, *J* = 8.8 Hz, 1H), 2.53 (d, *J* = 12.8 Hz, 1H), 2.23-2.27 (m, 1H), 1.94-2.02 (m, 1H), 1.80-1.84 (m, 1H), 1.67-1.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 146.3, 135.8, 133.8, 114.8, 70.7, 51.0, 47.3, 41.3, 39.3, 31.9, 24.2. HRMS calculated for $C_{12}H_{14}O_2$ $[M+H]^+$, 191.1072, found 191.1070.



4p

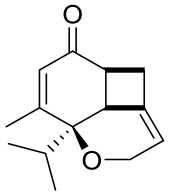
(1a*S*,1a^1*S*,4a*R*)-4a-Ethoxy-1,1a,1a^1,4a,5,6-hexahydro-2*H*-cyclobuta[*de*]naphthalen-2-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-ethoxy-4-(penta-3,4-dien-1-yl)cyclohexa-2,5-dien-1-one (**3p**, 100.2 mg) and TFE

(2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 150 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 5:1) to give **4p** (84.4 mg, 84% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.25 (d, *J* = 10.4 Hz, 1H), 5.36 (m, 1H), 3.26-3.42 (m, 4H), 3.01 (t, *J* = 8.4 Hz, 1H), 2.56 (d, *J* = 12.8 Hz, 1H), 2.26-2.31 (m, 1H), 1.97-2.04 (m, 1H), 1.85-1.90 (m, 1H), 1.74-1.81 (m, 1H), 1.17 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 147.1, 135.9, 133.4, 114.9, 70.3, 58.7, 47.9, 41.5, 39.3, 32.2, 24.2, 15.7. HRMS calculated for $C_{13}H_{16}O_2$ $[M+H]^+$, 205.1229, found 205.1231.



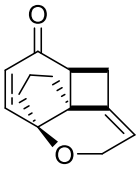
4r

(3a^{1}*R*,4a*R*,7a*S*)-7,7a-Dimethyl-3a^{1},4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-3,4-dimethylcyclo hexa-2,5-dien-1-one (**3r**, 95.0 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 10 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4r** (75.3 mg, 79% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (d, *J* = 0.8 Hz, 1H), 5.34 (s, 1H), 4.24-4.30 (m, 1H), 3.99 (d, *J* = 16.4 Hz, 1H), 3.30-3.38 (m, 1H), 3.24-3.28 (m, 1H), 3.11 (t, *J* = 10.4 Hz, 1H), 2.62 (dd, *J* = 0.8, 13.6 Hz, 1H), 1.96 (d, *J* = 1.2 Hz, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 162.0, 134.6, 129.4, 113.4, 69.71, 63.6, 47.10, 41.1, 39.4, 26.6, 17.7. HRMS calculated for $C_{12}H_{15}O_2$ $[M+H]^+$,191.1072, found 191.1067.



4s

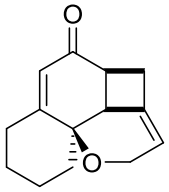
(3a^1*R*,4a*R*,7a*S*)-7a-Isopropyl-7-methyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-isopropyl-3-methylcyclohexa-2,5-dien-1-one (**3s**, 111.6 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 30 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4s** (78.3 mg, 70% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (d, *J* = 0.8 Hz, 1H), 5.34 (t, *J* = 1.6 Hz, 1H), 4.25-4.32 (m, 1H), 4.00 (dd, *J* = 1.6, 16.4 Hz, 1H), 3.33-3.43 (m, 2H), 3.01 (t, *J* = 8.0 Hz, 1H), 2.63 (dd, *J* = 0.8, 13.6 Hz, 1H), 1.97-2.04 (m, 1H), 1.93 (d, *J* = 1.2 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H) , 0.74 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.6, 160.7, 134.9, 131.7, 113.3, 75.1, 63.6, 42.4, 40.2, 33.8, 17.6, 17.2, 15.9. HRMS calculated for $C_{14}H_{19}O_2$ $[M+H]^+$, 219.1385, found 219.1378.



4t

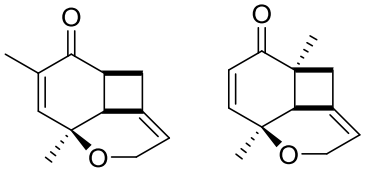
(2a*S*,5a*R*,8a*R*)-2,2a,7,8-Tetrahydro-3*H*,6*H*-5a,1-(epoxyethan[1]yl[2]ylidene)cyclobuta[*d*]inden-3-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 7*a*-(buta-2,3-dien-1-yloxy)-1,2,3,7*a*–tetrahydro-5H-inden-5-one (**3t**, 114.8 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4t** (81.4 mg,

71% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (d, *J* = 10.4 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 5.34 (d, *J* = 2.0 Hz, 1H), 4.28-4.34 (m, 1H), 4.07-4.12 (m, 1H), 3.44-3.51 (m, 1H), 2.72-2.77 (m, 2H), 2.16-2.24 (m, 1H), 2.07-2.13 (m, 1H), 1.88-2.03 (m, 2H), 1.79-1.85 (m, 1H), 1.64-1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.2, 150.2, 136.8, 130.5, 112.8, 76.7, 63.9, 55.2, 48.3, 40.0, 39.7, 35.6, 22.5. HRMS calculated for $C_{13}H_{15}O_2$ $[M+H]^+$, 203.1072, found 203.1069.



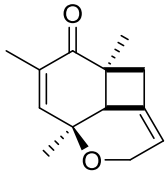
4u

(4a^1*R*,8a*R*)-1,2,3,4,4a^1,6,8,8a-Octahydro-9*H*-benzo[*i*]cyclobuta[*de*]chromen-9-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4a-(buta-2,3-dien-1-yloxy)-5,6,7,8-tetrahydro naphthalen-2(4aH)-one (**3u**, 130.8 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 36 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4u** (79.4 mg, 61% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (s, 1H), 5.35 (t, *J* = 1.6 Hz, 1H), 4.26 (dd, *J* = 2.0, 16.4 Hz, 1H), 3.96-4.01 (m, 1H), 3.24-3.30 (m, 1H), 3.15-3.17 (m, 1H), 3.05 (t, *J* = 8.8 Hz, 1H), 2.67 (d, *J* = 12.8 Hz, 1H), 2.48-2.56 (m, 1H), 2.15-2.19 (m, 1H), 1.96-2.02 (m, 2H), 1.88-1.93 (m, 1H), 1.55-1.70 (m, 2H), 1.38-1.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.2, 165.7, 134.1, 126.9, 113.1, 69.7, 62.5, 47.2, 41.3, 40.9, 39.8, 32.8, 29.9, 21.0. HRMS calculated for $C_{14}H_{17}O_2$ $[M+H]^+$, 217.1229, found 217.1220.



4v **4v'**

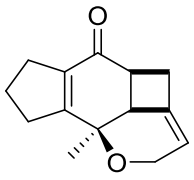
(4a*S*,7a*R*)-6,7a-Dimethyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-2,4-dimethylcyclohexa-2,5-dien-1-one (**3v**, 124.3 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 12 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4v** and **4v'** (inseparatable mixture 104.7 mg, 84% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (dd, *J* = 2.0, 10.4 Hz, 0.21H), 6.37 (m, 1H), 5.97 (d, *J* = 10.4 Hz, 0.21H), 5.28-5.32 (m, 1.21H), 4.26-4.33 (m, 1.21H), 4.07-4.16 (m, 1.21H), 3.31-3.39 (m, 1H), 3.25-3.28 (m, 1H), 3.10 (dt, *J* = 0.8, 8.8 Hz, 1H), 2.97-2.98 (m, 0.21H), 2.90-2.94 (m, 0.21H), 2.79 (d, *J* = 13.2 Hz, 0.21H), 2.62 (dd, *J* = 0.8, 13.2 Hz, 1H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.41 (s, 0.63H), 1.33 (s, 0.63H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.9, 199.3, 151.3, 147.3, 137.0, 134.9, 131.9, 130.2, 113.3, 112.7, 67.8, 67.5, 63.6, 63.5, 53.3, 46.9, 46.5, 46.4, 40.8, 39.9, 27.8, 27.5, 23.9, 16.7. HRMS calculated for $C_{12}H_{15}O_2$ $[M+H]^+$, 191.1072, found 191.1069.



4w

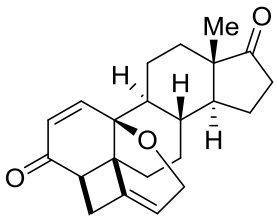
(3a^1*S*,4a*R*,7a*R*)-4a,6,7a-Trimethyl-3a^1,4,4a,7a-tetrahydrocyclobuta[*de*]chromen-5(2*H*)-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-2,4,6-trimethyl cyclohexa-2,5-dien-1-one (**3w**, 97.4 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 12 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4w** (55.7 mg, 57% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36 (s, 1H), 5.26 (m, 1H), 4.23-4.29 (m, 1H), 4.06-4.13 (m, 1H), 2.87-2.96 (m, 2H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.79 (d, *J* = 1.2 Hz, 3H), 1.41 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 202.1, 146.7, 136.3, 132.1, 112.7, 67.4, 63.4, 53.6, 46.7, 46.3, 28.3, 24.3, 16.8. HRMS calculated for $C_{13}H_{17}O_2$ $[M+H]^+$, 205.1229, found 205.1222.



4x

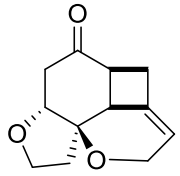
(3a^1*R*,4a*R*,8b*S*)-8b-Methyl-2,3a^1,4,4a,6,7,8,8b-octahydro-5*H*-cyclobuta[*de*]cyclopenta[*H*]chromen-5-one: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the 7-(buta-2,3-dien-1-yloxy)-7-methyl-1,2,3,7-tetrahydro-4H-inden-4-one (**3x**, 127.1 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 12 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 15:1 to 10:1) to give **4x** (107.4 mg, 85% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (s, 1H), 4.28 (d, *J* = 16.4 Hz, 1H), 4.00 (dd, *J* = 1.2, 16.4 Hz, 1H), 3.29-3.36 (m, 2H), 3.16 (t, *J* = 8.8 Hz, 1H), 2.51-2.66 (m, 5H), 1.84-1.98 (m, 2H), 1.36 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.6, 164.7, 140.1, 134.6, 113.3, 68.6, 63.7, 48.6, 42.6, 39.4, 32.7, 30.3, 26.5, 22.0. HRMS calculated for $C_{14}H_{17}O_2$ $[M+H]^+$, 217.1229, found 217.1222.



4y

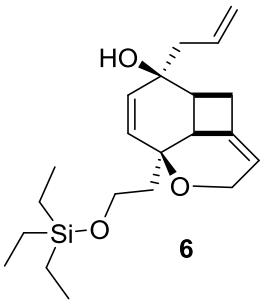
(2a*R*,5a*S*,5b*S*,7a*S*,10a*S*,10b*S*,12a*R*)-7a-Methyl-2,2a,5b,6,7,7a,9,10,10a,10b,11,12-dodecahydro-3*H*,8*H*-5a,1-(epoxyethan[1]yl[2]ylidene)cyclobuta[*j*]cyclopenta[*a*]phenanthrene-3,8-dione: To a 25 mL schlenk tube equipped with magnetic stirring bar were added the (8S,9S,10S,13S,14S)-10-(buta-2,3-dien-1-yloxy)-13-methyl-5,6,7,8,9,10,11,12,13,14,15,16-dodecahydro-3H-cyclopenta[*a*]phenanthrene-3,17(*4H*

)-dione (**3y**, 121.6 mg) and TFE (2.0 mL), The container was sealed and the resulting mixture was stirred for 50 h at 100 ^{o}C, before being cooled down to rt, and the mixture was concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel (*n*-hexanes/EtOAc = 10:1 to 2:1) to give **4y** (52.8 mg, 43% yield) as a foam solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 10.4 Hz, 1H), 6.04(d, *J* = 10.4 Hz, 1H), 5.30 (m, 1H), 4.39-4.44 (m, 1H), 4.20 (d, *J* = 16.4 Hz, 1H), 3.53-3.59 (m, 1H), 2.87-2.90 (d, *J* = 10.0 Hz, 1H), 2.56 (d, *J* = 14.8 Hz, 1H), 2.40-2.47 (m, 1H), 1.92-2.01 (m, 3H), 1.77-1.89 (m, 3H), 1.69-1.74 (m, 2H), 1.49-1.62 (m, 2H), 1.15-1.25 (m, 2H), 1.15-1.25 (m, 2H), 0.95-0.99 (m, 2H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 199.0, 155.1, 140.8, 129.2, 113.8, 71.6, 64.6, 52.3, 50.3, 47.6, 47.4, 46.69, 37.7, 35.6, 35.2, 31.2, 30.8, 25.7, 21.7, 19.9, 13.7.HRMS calculated for $C_{22}H_{27}O_3$ $[M+H]^+$, 339.1960, found 339.1952.



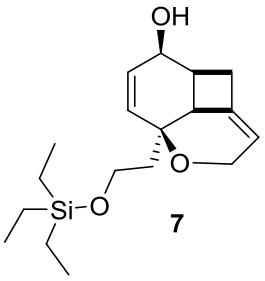
5

(3a*R*,3a^1*S*,7a*S*,9a*R*)-2,3,3a^1,5,7,7a,9,9a-Octahydro-8*H*-cyclobuta[*de*]furo[2,3-*i*]chromen-8-one: To a solution of **4h** (100.2 mg, 0.3129 mmol) in dry THF (5 mL) was added 1 M HCl (2.0 mL) dropwise at 0 ^{o}C for 5 minutes. The resulting mixture was stirred for 4 h at room temperature, then the mixture was diluted by DCM, followed by sequentially washed with $NaHCO_3$ and brine, the organic layer was dried over with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using PE/EA eluent to afford the foam solid **5** (59.2 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (m, 1H), 4.34-4.39 (m, 1H), 4.15-4.24 (m, 2H), 3.96-3.99 (m, 2H), 3.53-3.56 (m, 1H), 3.17-3.23 (m, 1H), 3.02 (t, *J* = 8.8 Hz, 1H), 2.79-2.84 (m, 2H), 2.43-2.49 (m, 1H), 2.15-2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 136.1, 113.0, 78.0, 77.6, 65.9, 62.2, 46.6, 45.0, 44.1, 38.3, 36.7. HRMS calculated for $C_{12}H_{15}O_3$ $[M+H]^+$, 207.1021, found 207.1014.



6

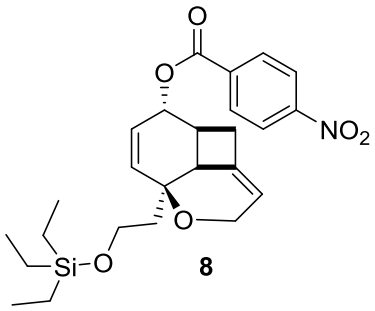
(3a^1*S*,4a*S*,5*R*,7a*S*)-5-Allyl-7a-(2-((triethylsilyl)oxy)ethyl)-2,3a^1,4,4a,5,7a-hexahydrocyclobuta[*de*]chromen-5-ol: To a solution of **4h** (64.1 mg, 0.2002 mmol) in dry THF (5 mL) was added allylmagnesium bromide (1 M) (1.0 mL, 5.0 equiv) dropwise at 0 ^{o}C for about 10 minutes. The resulting mixture was stirred for another 1 h at this temperature, then The reaction mixture was quenched by addition of NH_4Cl, and then diluted by 20 mL ethyl acetate. The phases were separated, the aqueous phase was extracted with ethyl acetate, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting sticky oil was purified by flash column chromatography using PE/EA eluent to afford the desired product **6** (45.2mg, 62% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79-5.90 (m, 1H), 5.66 (d, *J* = 10.8 Hz, 1H), 5.90 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.13-5.22 (m, 3H), 4.20 (d, *J* = 1.6, 16.4 Hz, 1H), 4.04 (d, *J* = 16.4 Hz, 1H), 3.79-3.85 (m, 1H), 3.68-3.74 (m, 1H), 3.21 (d, *J* = 8.4 Hz, 1H), 2.95-3.01 (m, 1H), 2.75-2.79 (m, 2H), 2.33 (dd, *J* = 7.2, 13.6 Hz, 1H), 2.18 (dd, *J* = 7.6, 13.6 Hz, 1H), 1.73-1.87 (m, 3H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.5, 132.7, 129.7, 120.0, 112.7, 69.3, 69.0, 62.8, 58.4, 49.5, 44.4, 43.6, 39.2, 33.6, 6.8, 4.4. HRMS calculated for $C_{21}H_{34}NaO_3Si$ $[M+Na]^+$, 385.2175, found 385.2167



7

(3a^1*S*,4a*S*,5*S*,7a*S*)-7a-(2-((Triethylsilyl)oxy)ethyl)-2,3a^1,4,4a,5,7a-hexahydrocyclobuta[*de*]chromen-5-ol: To a solution of **4h** (151.8 mg, 0.474 mmol) in dry MeOH (5

mL) was added $NaBH_4$ (36.05 mg, 2.0 equiv). The reaction mixture was stirred for another 1 h at room temperature, then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography using PE/EA eluent to afford the alcohol **7** (110.7 mg, 73% yield) as a colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (d, *J* = 10.4 Hz, 1H), 5.60 (d, *J* = 10.4 Hz, 1H), 5.19 (m, 1H), 4.46 (m, 1H), 4.23 (d, *J* = 16.4 Hz, 1H), 4.04 (d, *J* = 16.4 Hz, 1H), 3.67-3.73 (m, 1H), 3.57-3.64 (m, 1H), 3.16(m, 1H), 2.93-3.01 (m, 2H), 2.69-2.72 (m, 1H), 1.99 (br, 1H), 1.74-1.83 (m, 2H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ13C NMR (101 MHz, CDCl3) δ 137.6, 133.3, 130.5, 113.3, 70.1, 64.7, 63.0, 58.5, 44.4, 42.9, 34.8, 31.7, 6.7, 4.4. HRMS calculated for $C_{18}H_{30}NaO_3Si$ $[M+Na]^+$, 345.1862, found 345.1856.



8

(3a^1*S*,4a*S*,5*R*,7a*S*)-7a-(2-((Triethylsilyl)oxy)ethyl)-2,3a^1,4,4a,5,7a-hexahydrocyclobuta[*de*]chromen-5-yl-4-nitrobenzoate: To a stirred solution of alcohol **7** (54 mg, 0.17 mmol), *p*-nitrobenzoic acid (142.05 mg, 0.85 mmol), and PPh_3 (248.2 mg, 0.85 mmol) in THF (5.0 mL) was added DEAD (148.02 mg, 0.13 mL, 0.85 mmol) at 0 ℃. The resulting mixture was stirred at room temperature overnight before it was quenched with saturated aq. $NaHCO_3$ solution (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue so obtained was purified by flash column chromatography with petroleum ether/EtOAc (15:1 to 10:1) to give the ester **8** (55.5 mg, 70%) as a foam solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H), 6.08 (dd, *J* = 5.2, 10.4 Hz, 1H), 5.99 (d, *J* = 10.4 Hz, 1H), 5.44 (d, *J* = 5.2 Hz, 1H), 5.30 (m, 1H), 4.29 (d, *J* = 16.4 Hz, 1H), 4.10 (d, *J* = 16.4 Hz, 1H), 3.71-3.84 (m, 2H), 3.29-3.35 (m, 2H),

2.86 (d, *J* = 8.4 Hz, 1H), 2.50 (d, *J* = 14.4 Hz, 1H), 1.85-2.00 (m, 2H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 150.5, 137.2, 135.7, 135.5, 130.7, 126.1, 123.5, 113.8, 71.0, 69.6, 63.1, 58.3, 45.0, 43.6, 38.2, 36.0, 6.8, 4.5. HRMS calculated for $C_{25}H_{33}NNaO_6Si$ $[M+Na]^+$, 494.1975, found 494.1968.

7. Refences

1. (a) Xu, G.; Liu, K.; Sun, J. Divergent Synthesis of Fused Tricyclic Compounds via a Tandem Reaction from Alkynyl-cyclohexadienones and Diazoesters. *Org. Lett.* **2017**, *19*, 6440−6443. (b) Gollapelli, K. K.; Donikela, S.; Manjula, N.; Chegondi, R. Rhodium-Catalyzed Highly Regio- and Enantioselective Reductive Cyclization of Alkyne-Tethered Cyclohexadienones. *ACS Catal*. **2018**, *8*, 1440−1447. (c) Chen, J.; Han, X.; Lu, X. Enantioselective Synthesis of Tetrahydropyrano[3,4-b]indoles: Palladium(II)-Catalyzed Aminopalladation /1,4-Addition Sequence. *Angew. Chem. Int. Ed.* **2017**, *56*, 14698 –14701. (d) Yao, W.; Dou, X.; Wen, S.; Wu, J.; Vittal, J. J.; Lu, Y. Enantioselective desymmetrization of cyclohexadienones via an intramolecular Rauhut-Currier reaction of allenoates. *Nat. Commun.* **2016**, *7*, 13024-13031.
2. (a) Tan, Y.-X.; Tang, X.-Q.; Liu, P.; Kong, D.-S.; Chen, Y.-L.; Tian, P.; Lin, G.-Q. CuH-Catalyzed Asymmetric Intramolecular Reductive Coupling of Allenes to Enones. *Org. Lett.* **2018**, *20*, 248−251. (b) He, Z.-T.; Tang, X.-Q.; Xie, L.-B.; Cheng, M.; Tian, P.; Lin, G.-Q. Efficient Access to Bicyclo[4.3.0]nonanes: Copper-Catalyzed Asymmetric Silylative Cyclization of Cyclohexadienone-Tethered Allene. *Angew. Chem. Int. Ed.* **2015**, *54*, 14815 –14818.

8. Copies of ^{1}H NMR and ^{13}C NMR Spectras

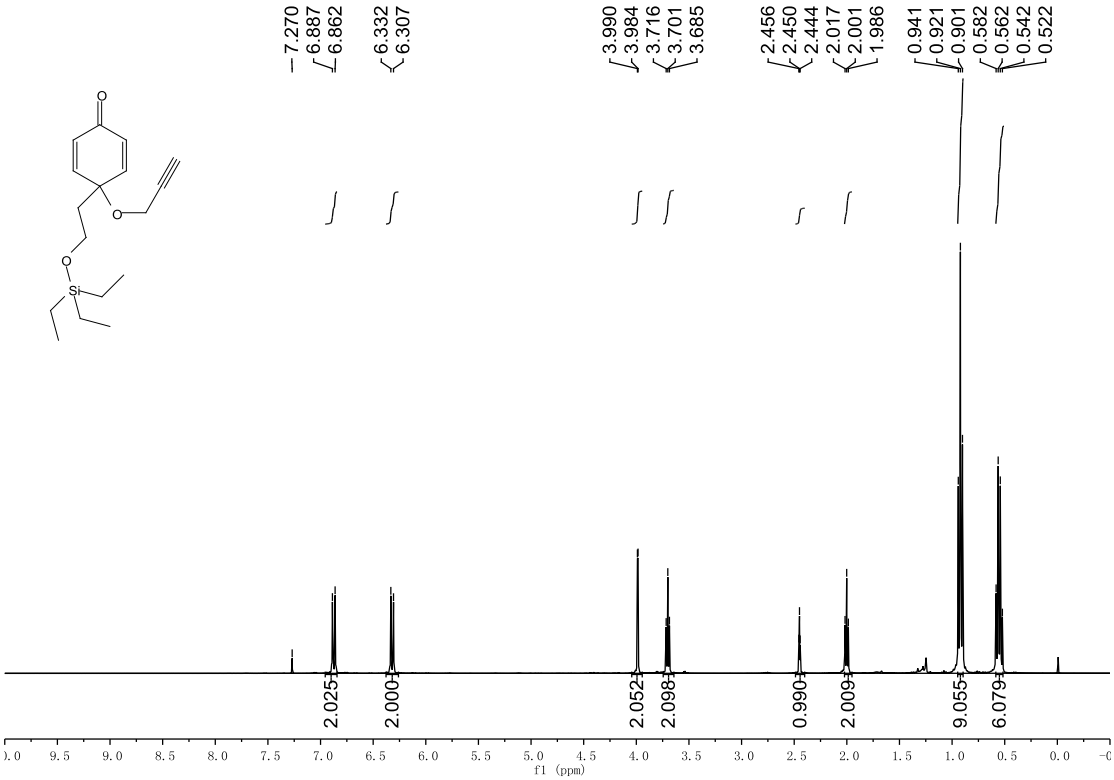


Fig. S1. ^{1}H NMR Spectrum of **2h** (400 MHz, $CDCl_3$).

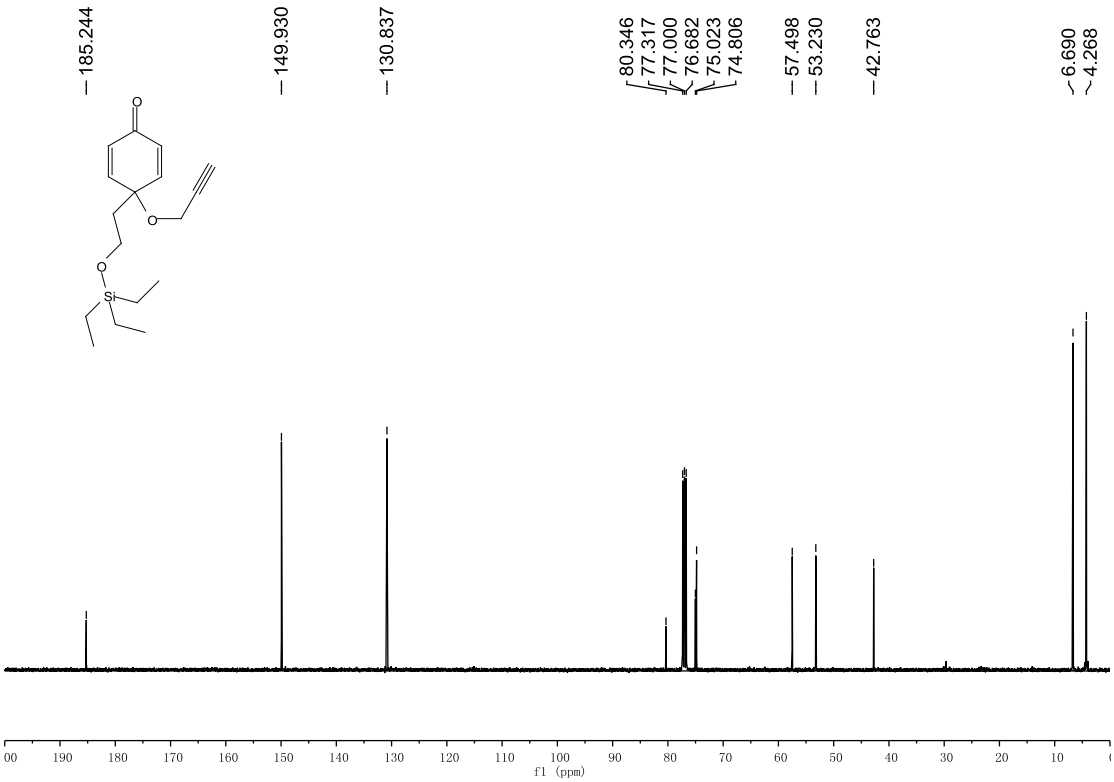


Fig. S2. ^{13}C NMR Spectrum of **2h** (100 MHz, $CDCl_3$).

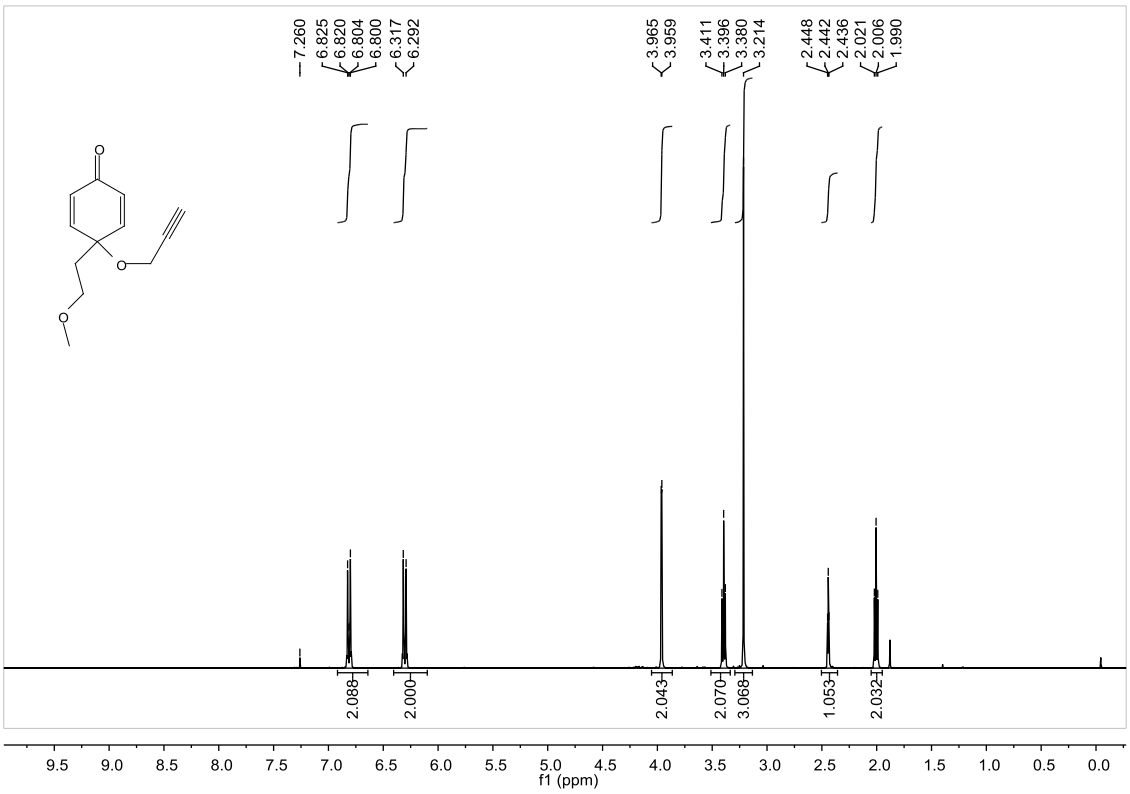


Fig. S3. ^{1}H NMR Spectrum of **2i** (400 MHz, $CDCl_3$).

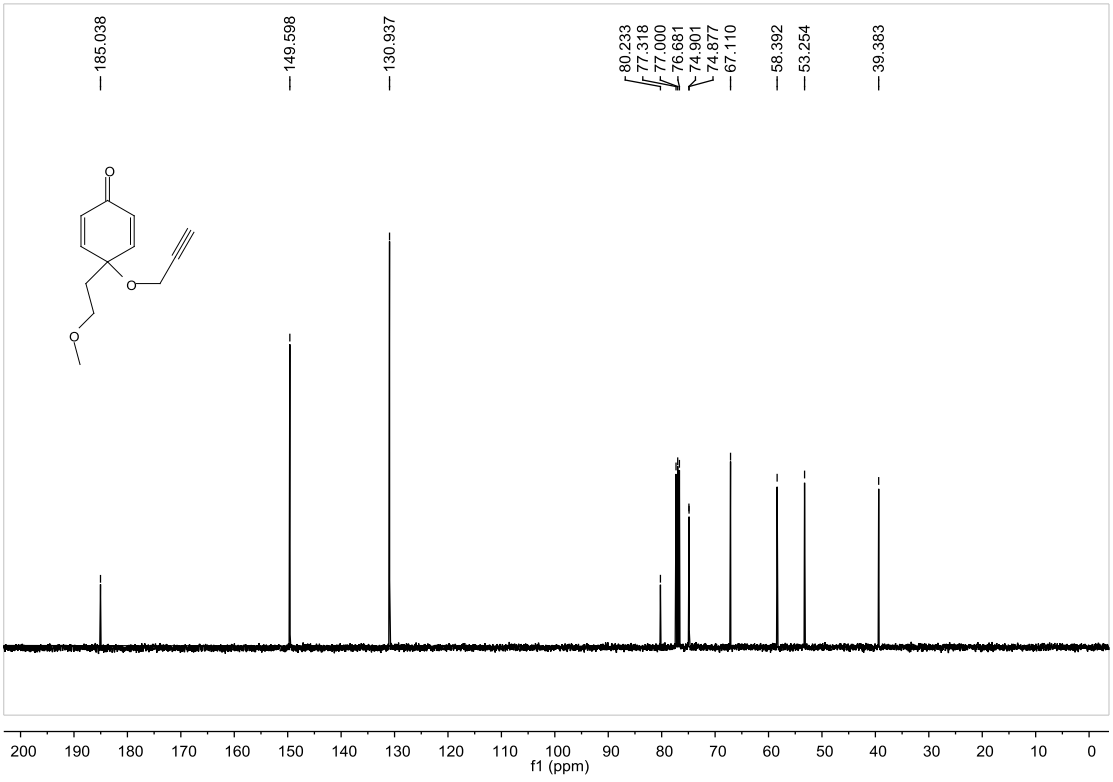


Fig. S4. ^{13}C NMR Spectrum of **2i** (100 MHz, $CDCl_3$).

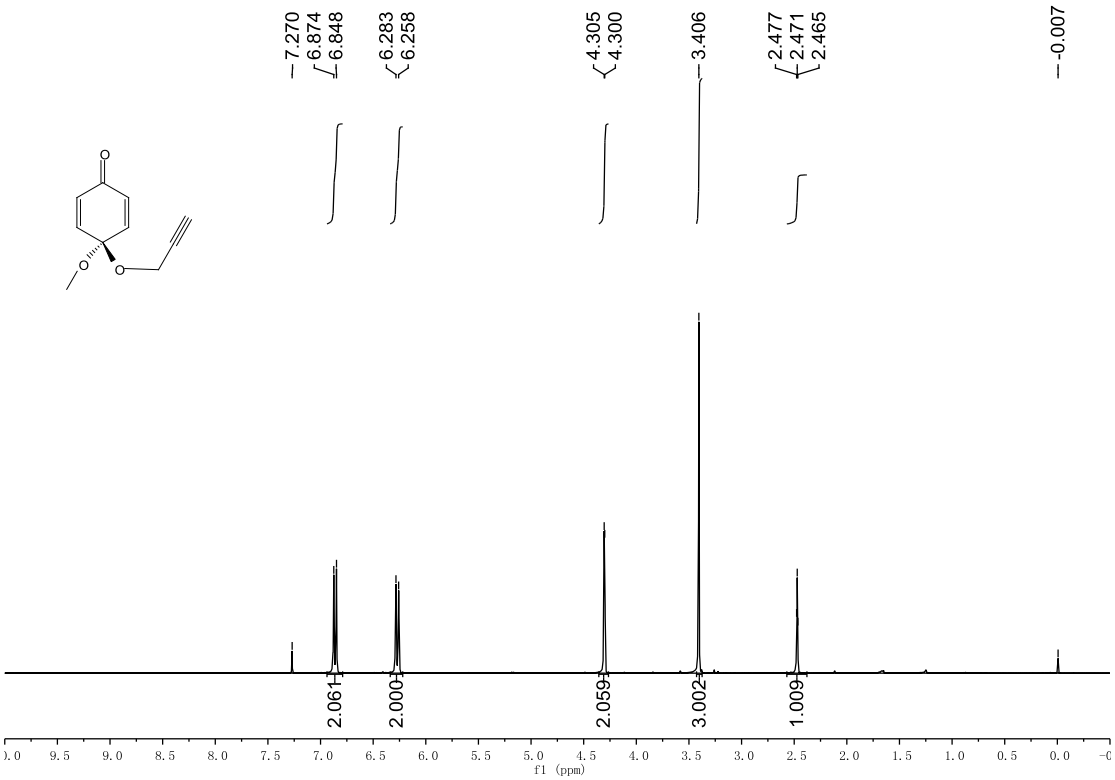


Fig. S5. ^{1}H NMR Spectrum of **2j** (400 MHz, $CDCl_3$).

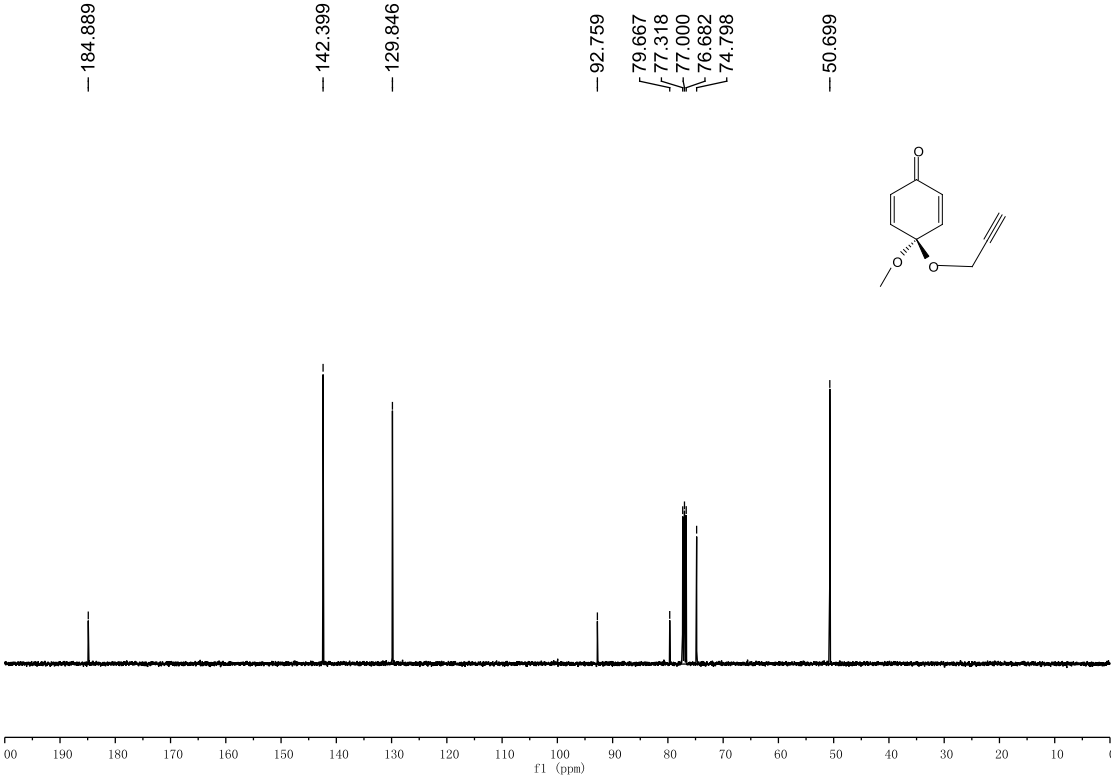


Fig. S6. ^{13}C NMR Spectrum of **2j** (100 MHz, $CDCl_3$).

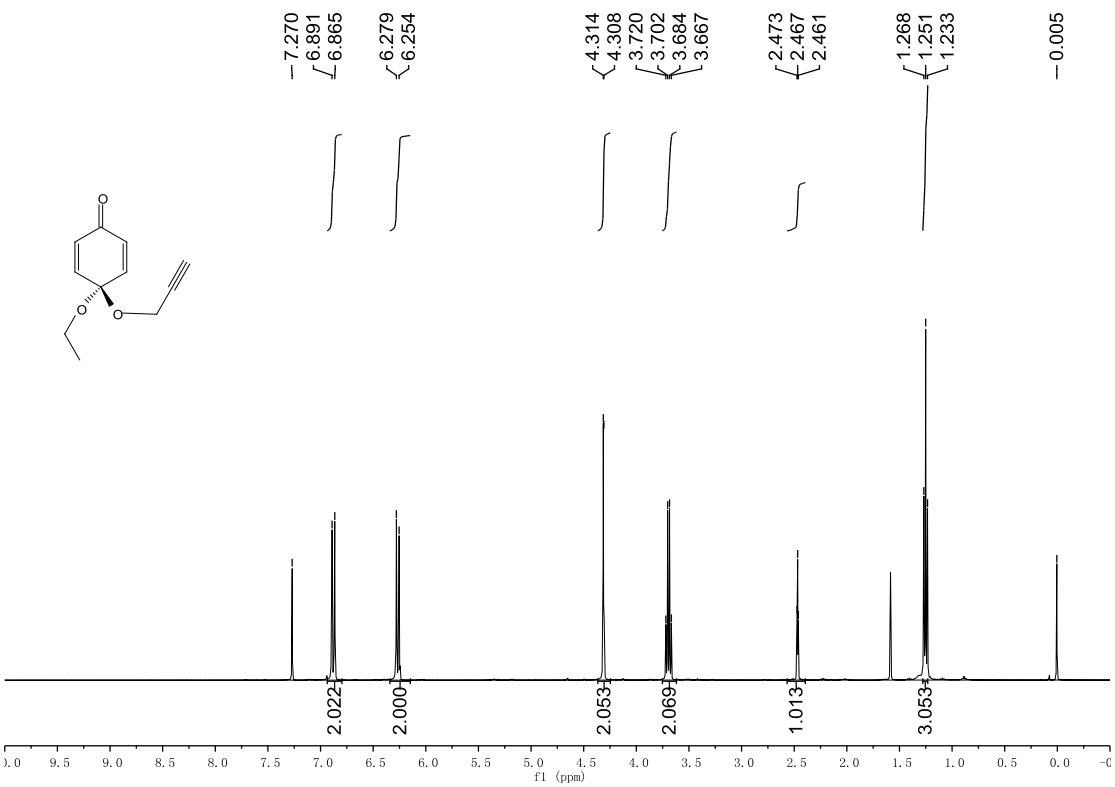


Fig. S7. ^{1}H NMR Spectrum of **2k** (400 MHz, $CDCl_3$).

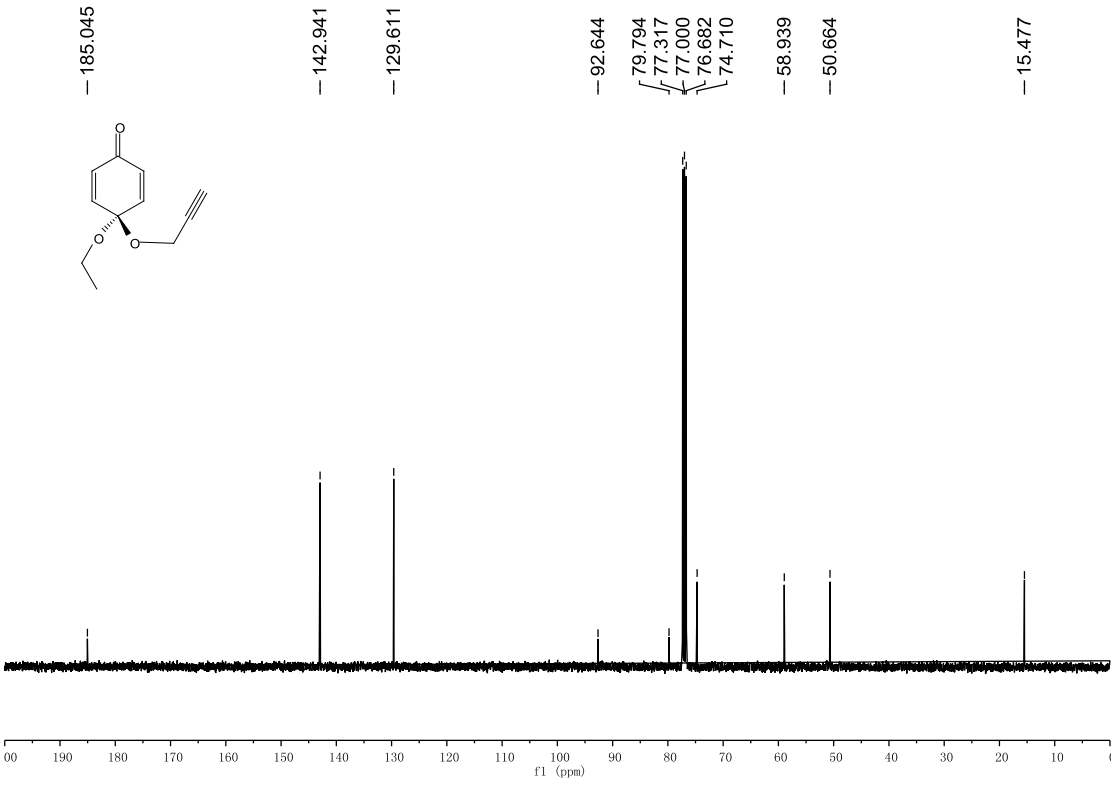


Fig. S8. ^{13}C NMR Spectrum of **2k** (100 MHz, $CDCl_3$).

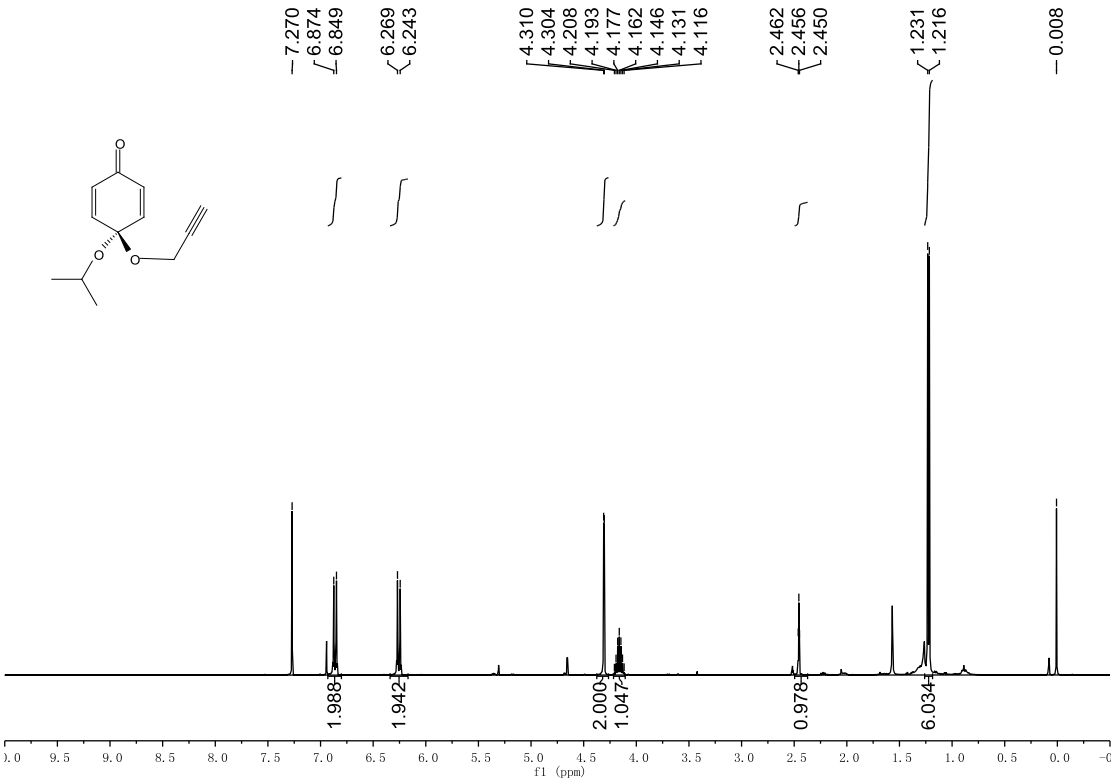


Fig. S9. ^{1}H NMR Spectrum of **2l** (400 MHz, $CDCl_3$).

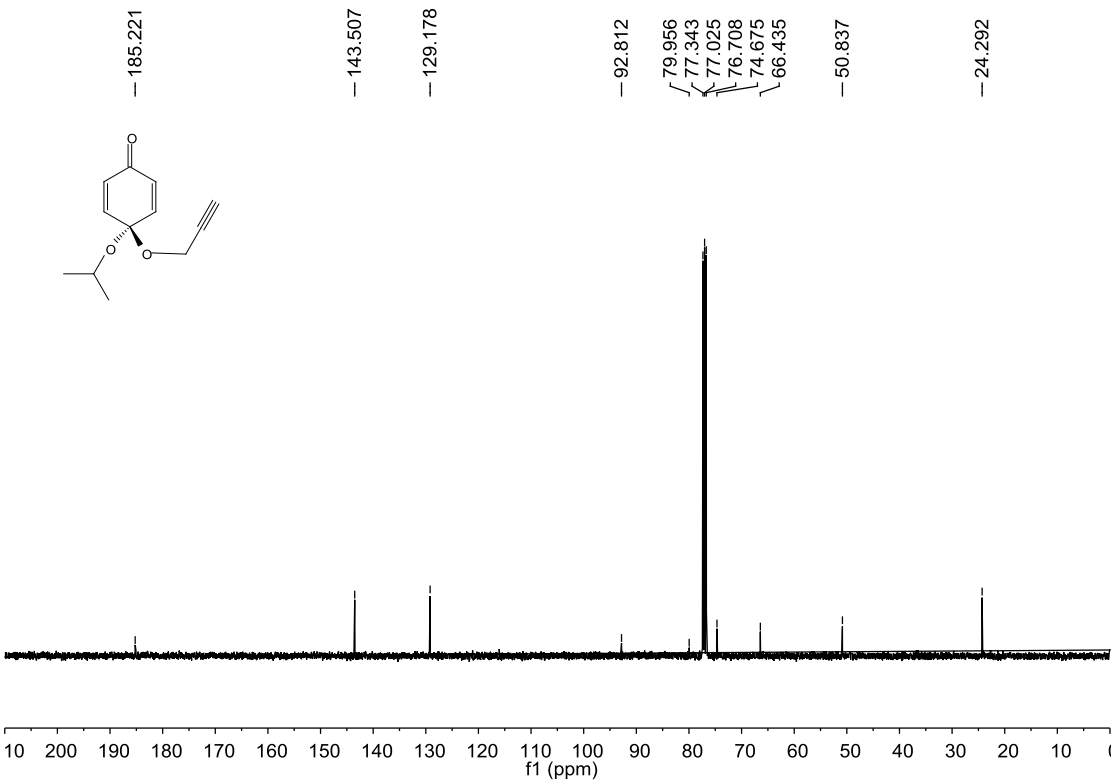


Fig. S10. ^{13}C NMR Spectrum of **2l** (100 MHz, $CDCl_3$).

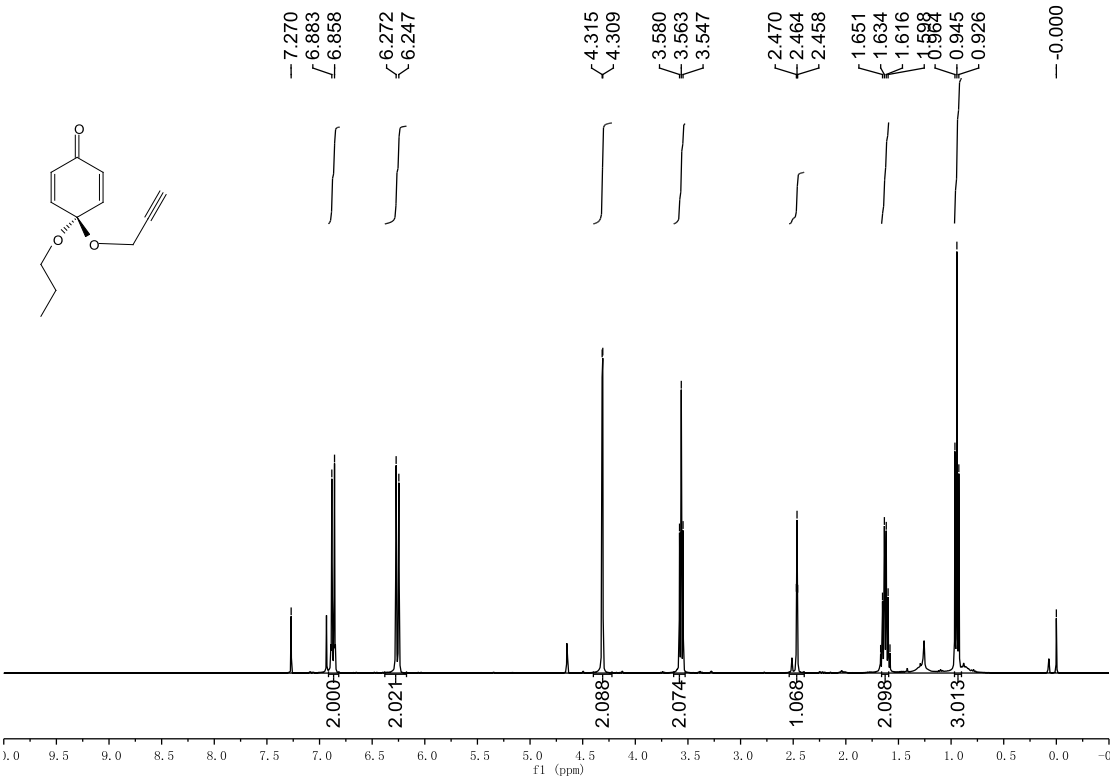


Fig. S11. ^{1}H NMR Spectrum of **2m** (400 MHz, $CDCl_3$).

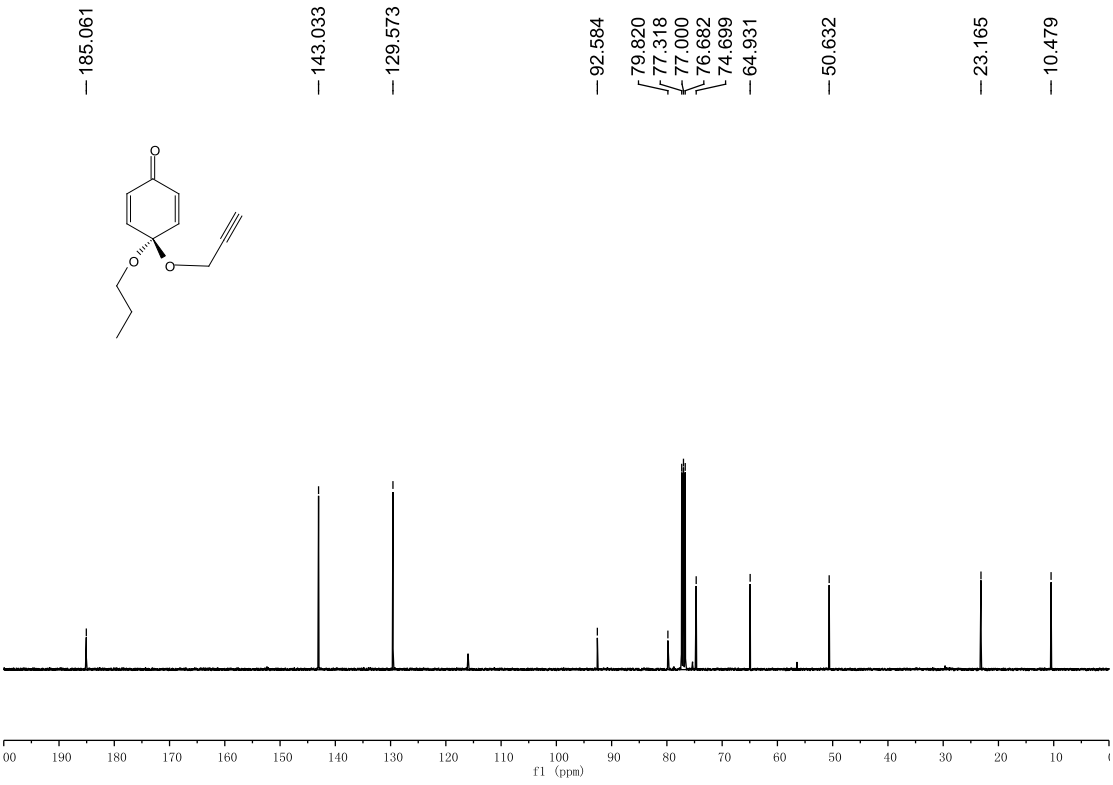


Fig. S12. ^{13}C NMR Spectrum of **2m** (100 MHz, $CDCl_3$).

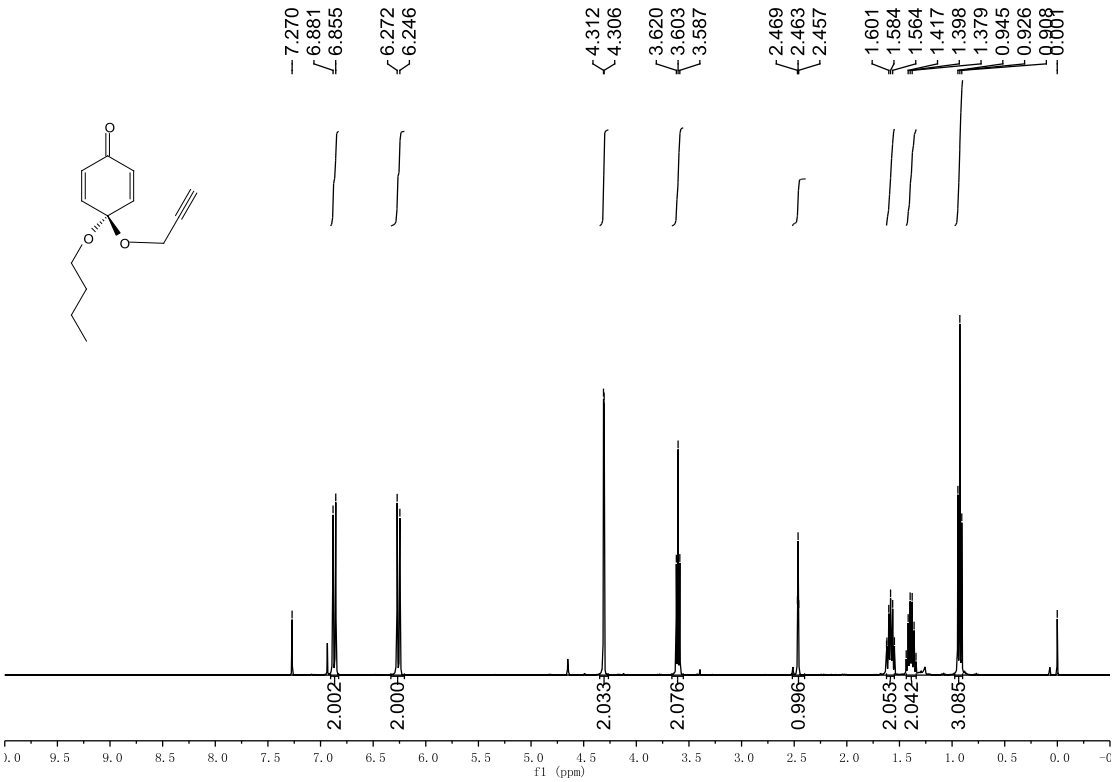


Fig. S13. ^{1}H NMR Spectrum of **2n** (400 MHz, $CDCl_3$).

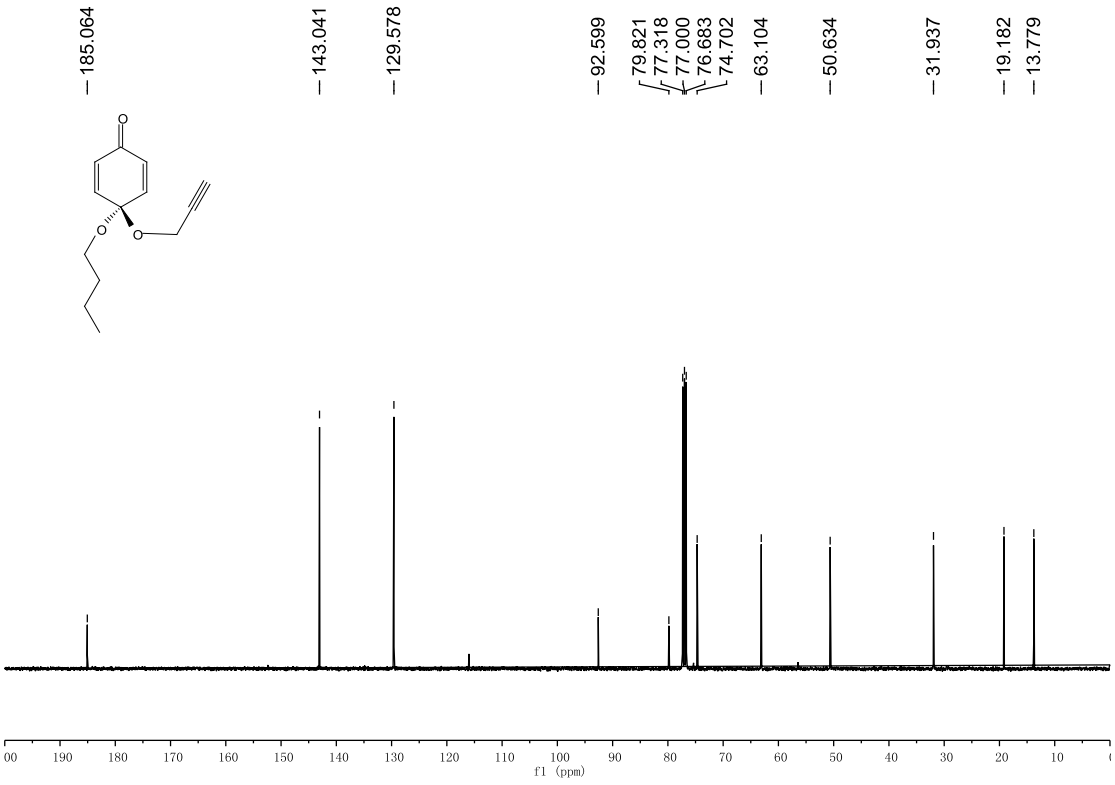


Fig. S14. ^{13}C NMR Spectrum of **2n** (100 MHz, $CDCl_3$).

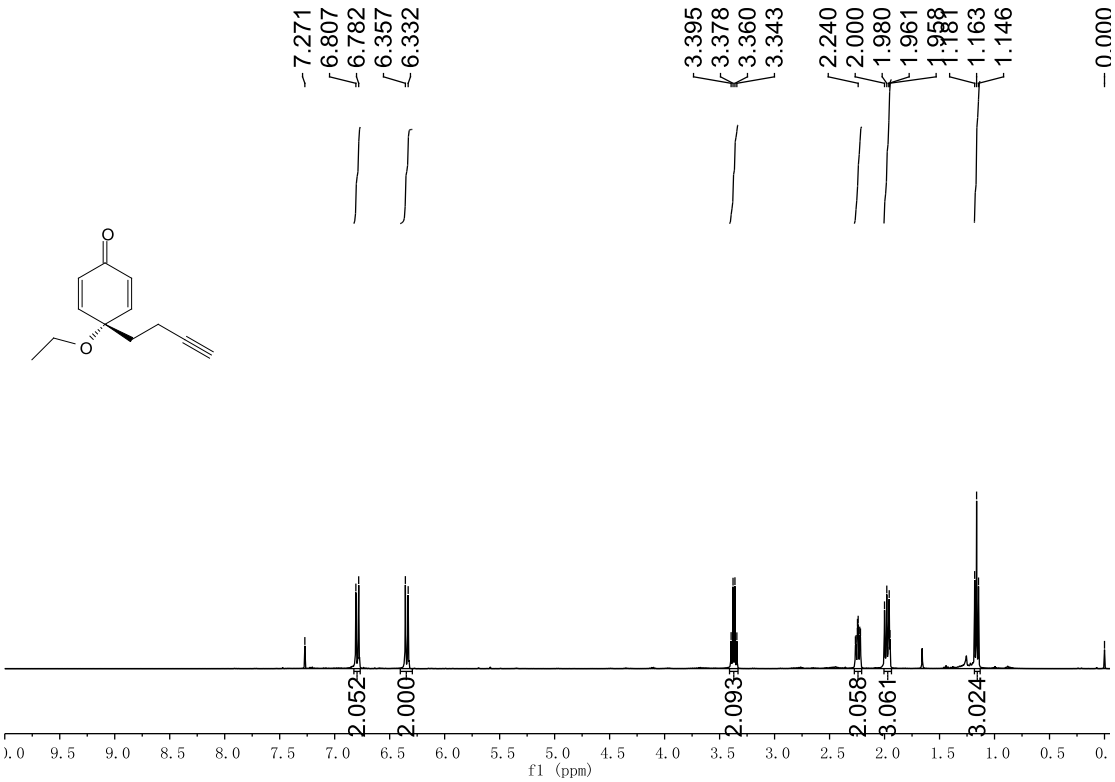


Fig. S15. ^{1}H NMR Spectrum of **2p** (400 MHz, $CDCl_3$).

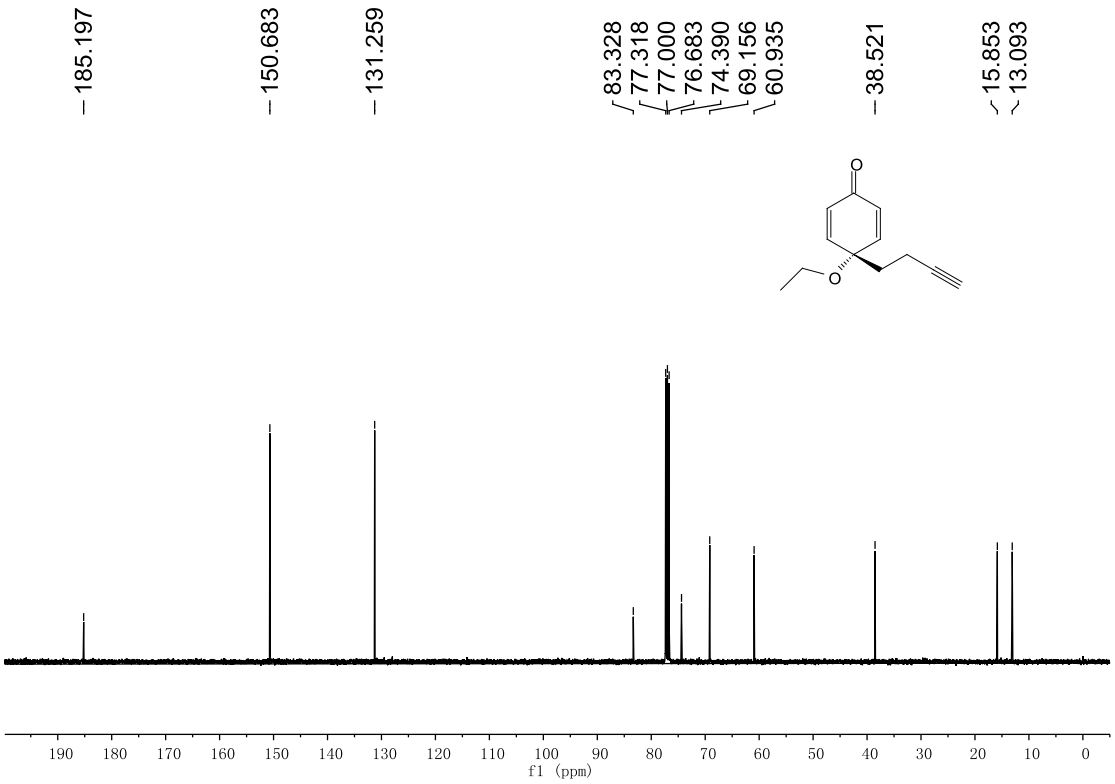


Fig. S16. ^{13}C NMR Spectrum of **2p** (100 MHz, $CDCl_3$).

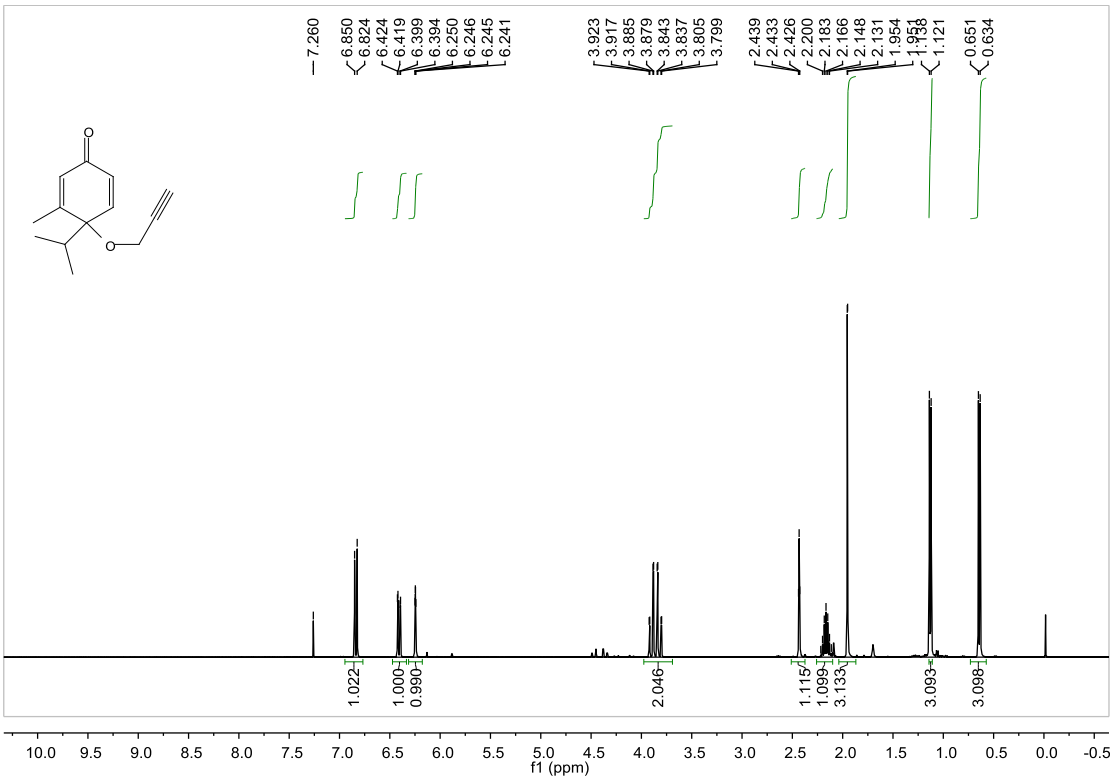


Fig. S17. ^{1}H NMR Spectrum of **2s** (400 MHz, $CDCl_3$).

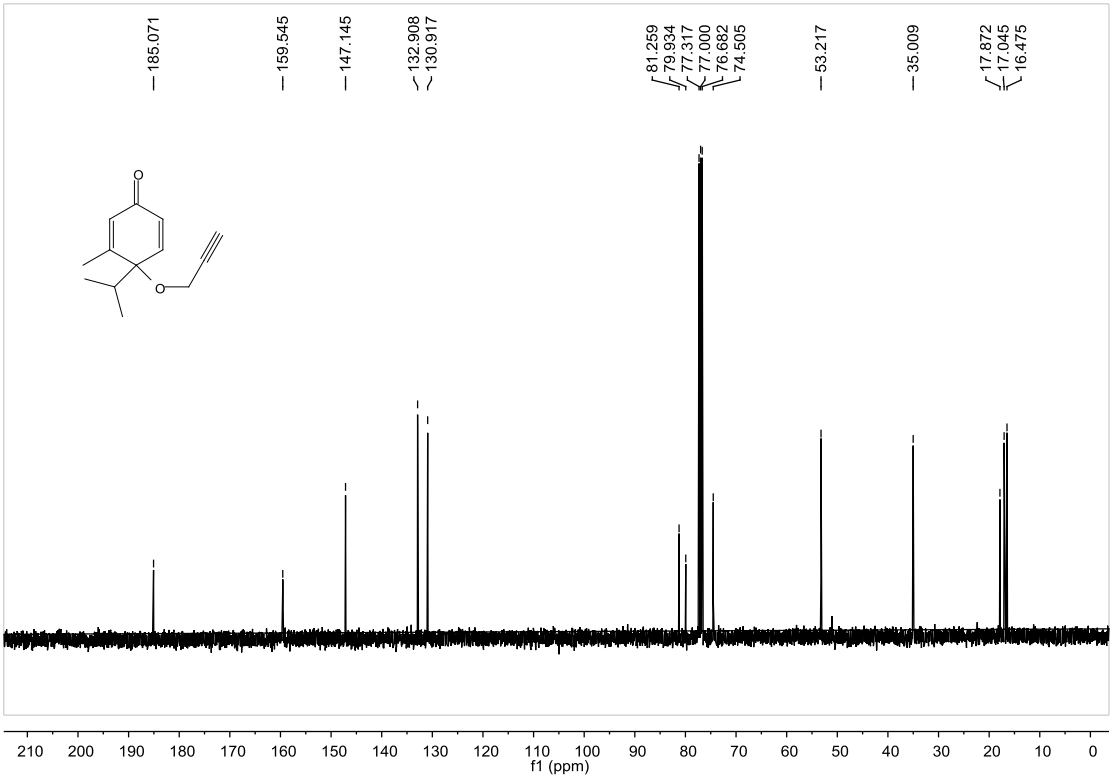


Fig. S18. ^{13}C NMR Spectrum of **2s** (100 MHz, $CDCl_3$).

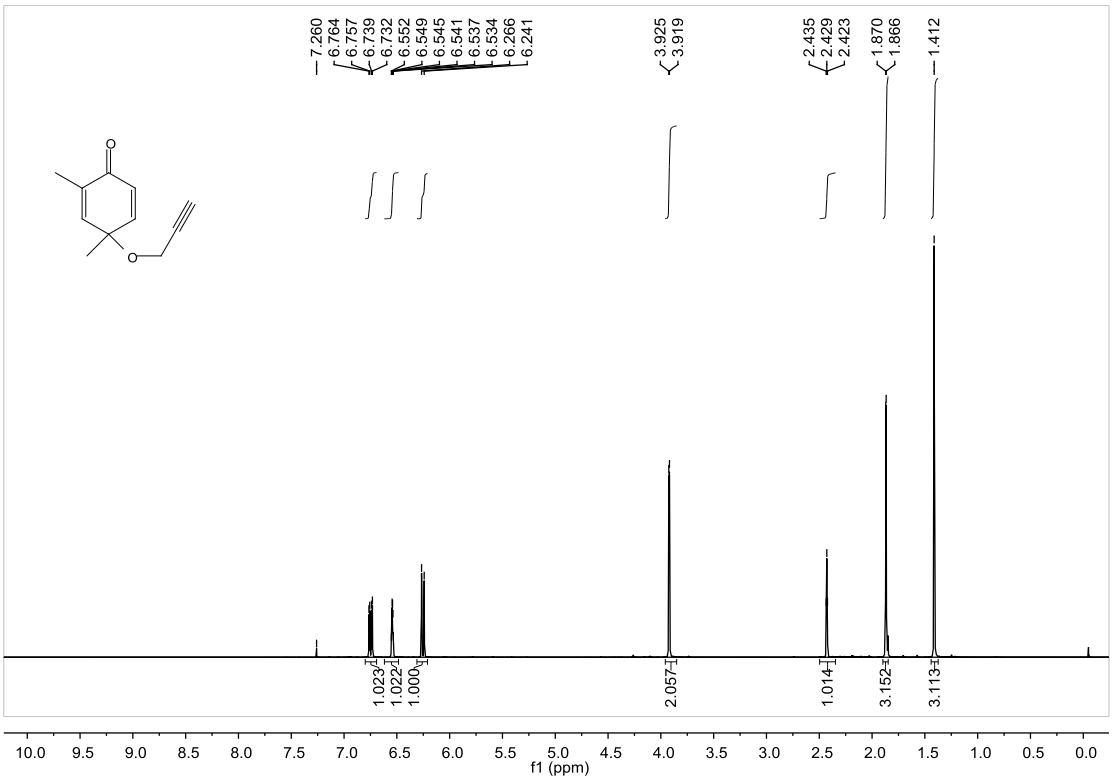


Fig. S19. ^{1}H NMR Spectrum of **2v** (400 MHz, $CDCl_3$).

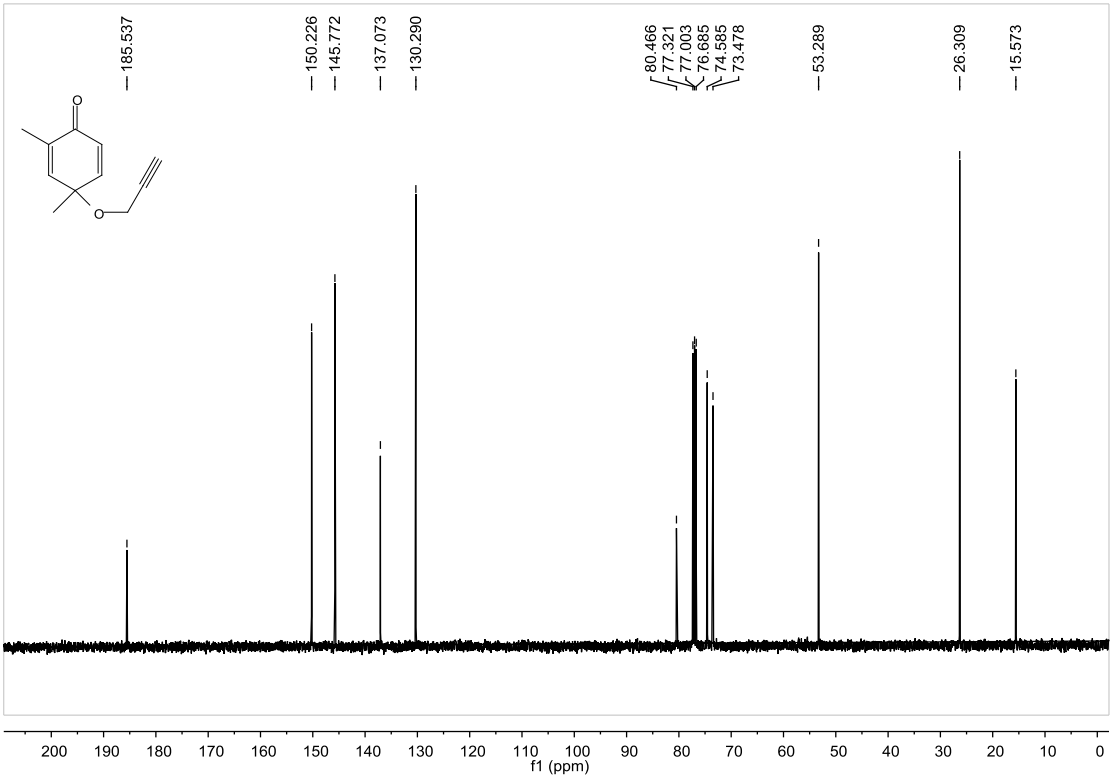


Fig. S20. ^{13}C NMR Spectrum of **2v** (100 MHz, $CDCl_3$).

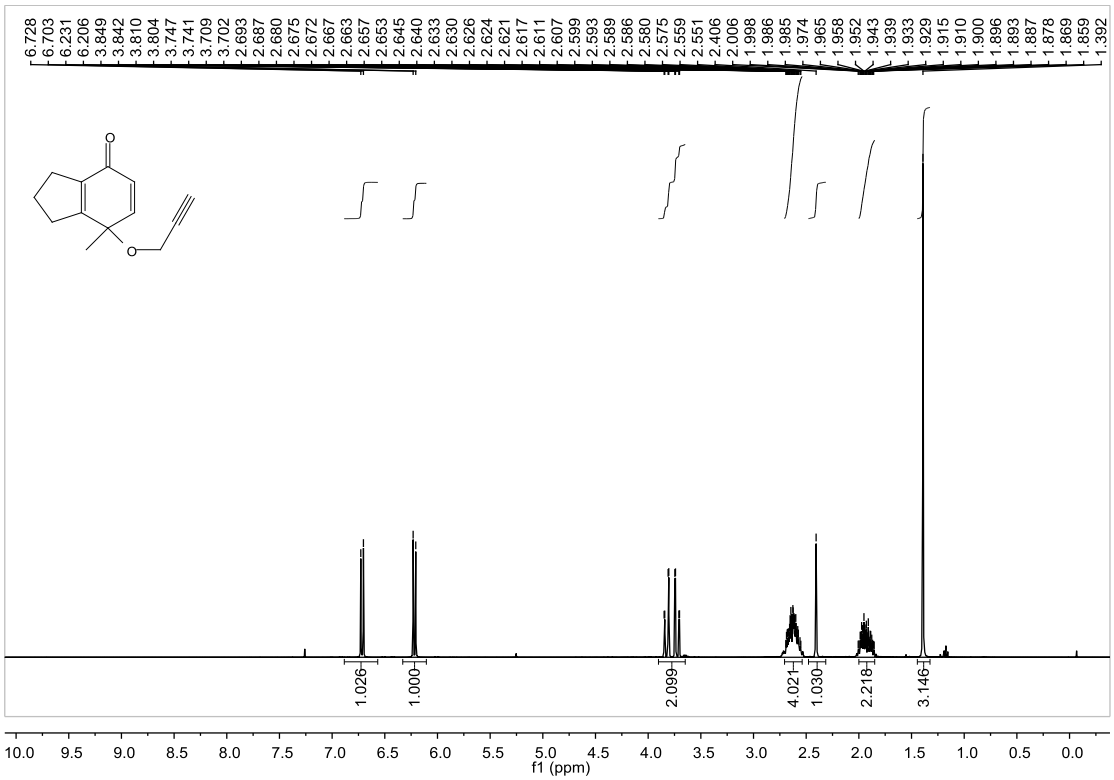


Fig. S21. ^{1}H NMR Spectrum of **2x** (400 MHz, $CDCl_3$).

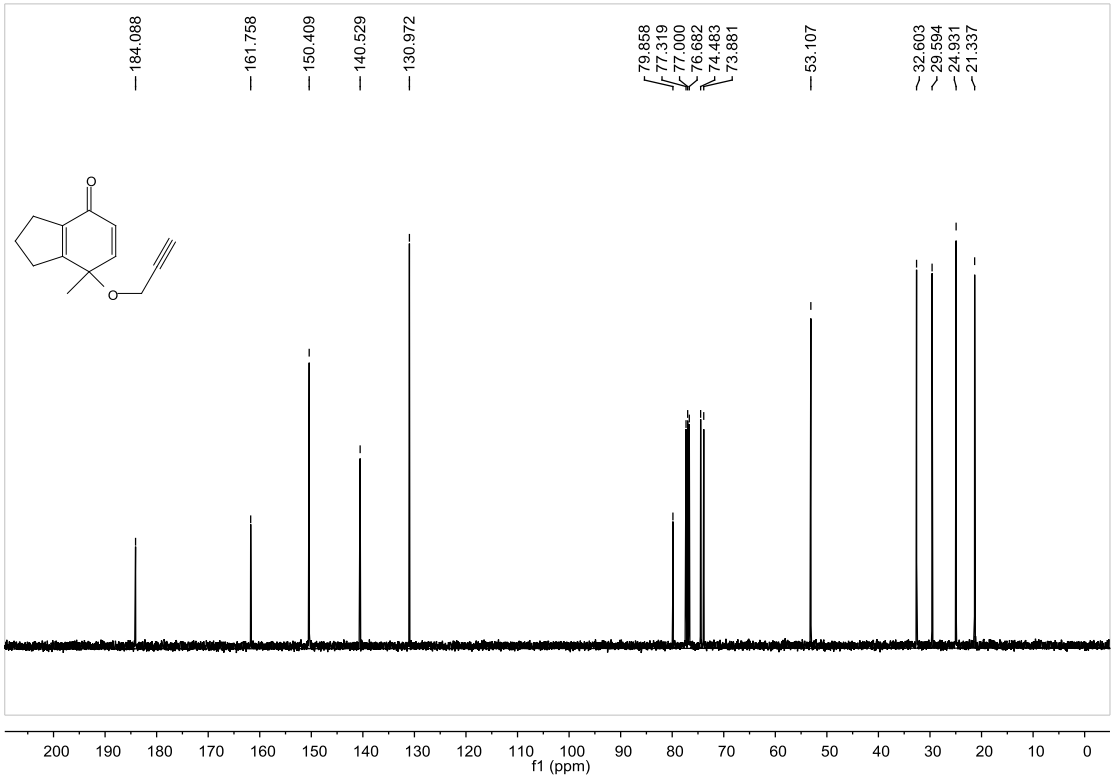


Fig. S22. ^{13}C NMR Spectrum of **2x** (100 MHz, $CDCl_3$).

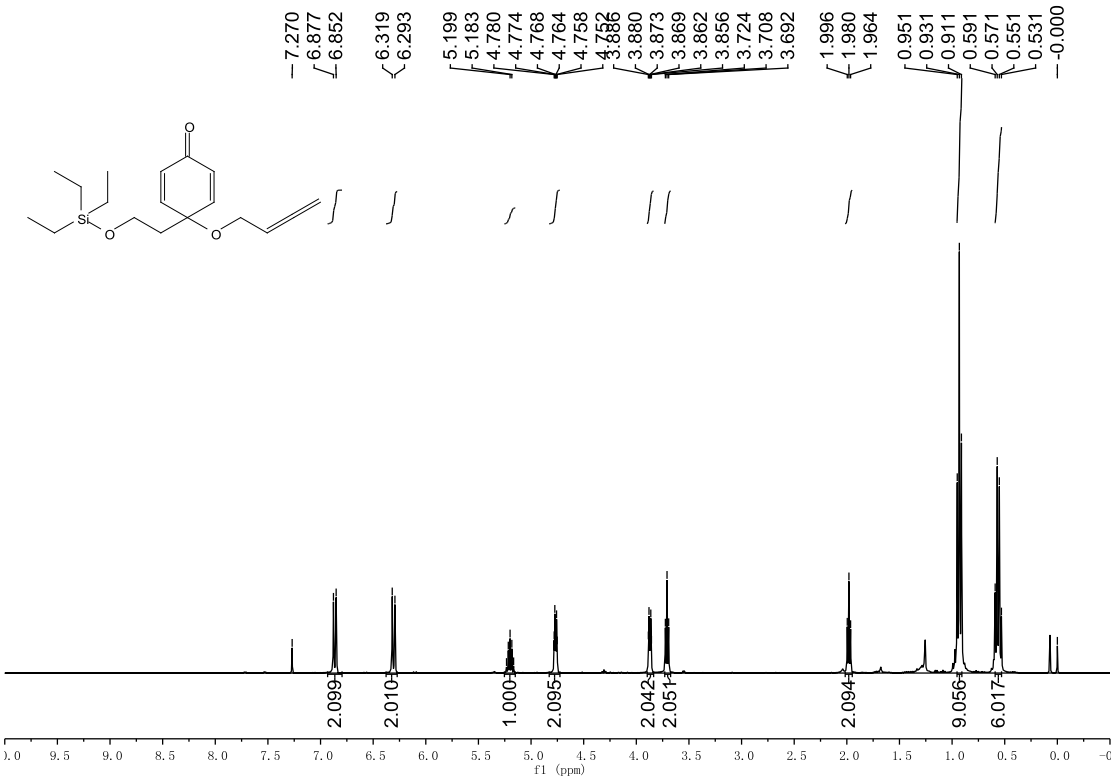


Fig. S23. ^{1}H NMR Spectrum of **3h** (400 MHz, $CDCl_3$).

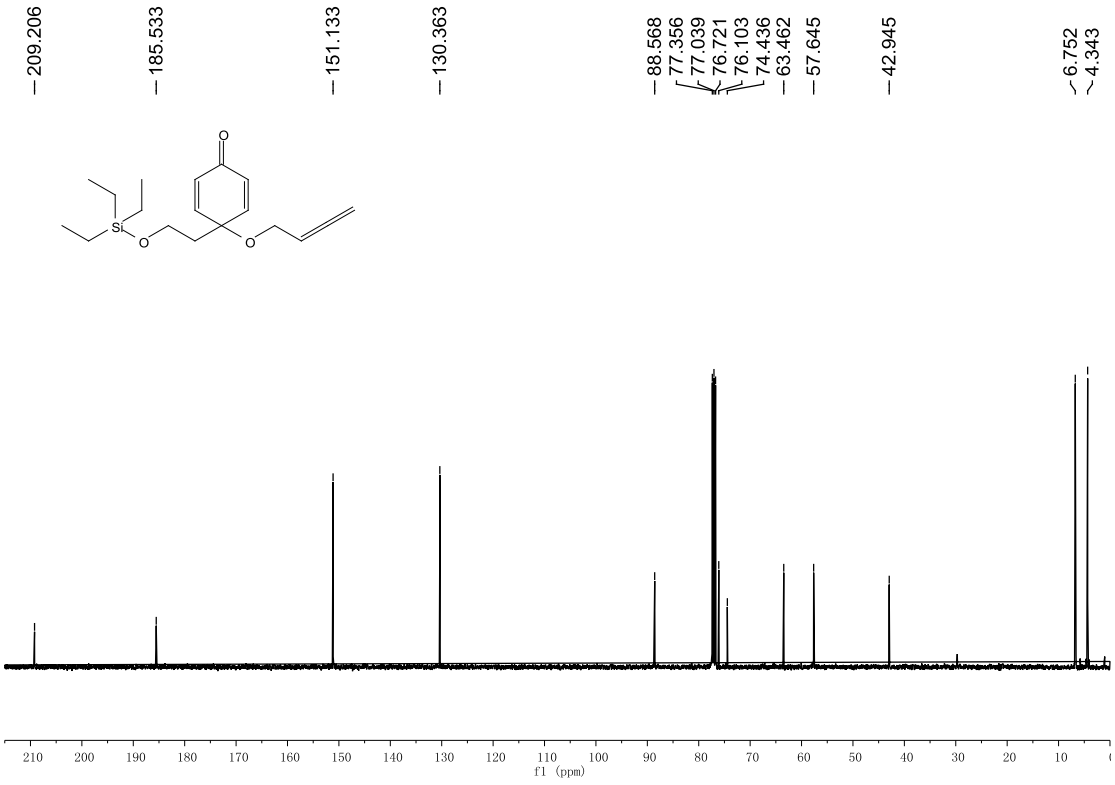


Fig. S24. ^{13}C NMR Spectrum of **3h** (100 MHz, $CDCl_3$).

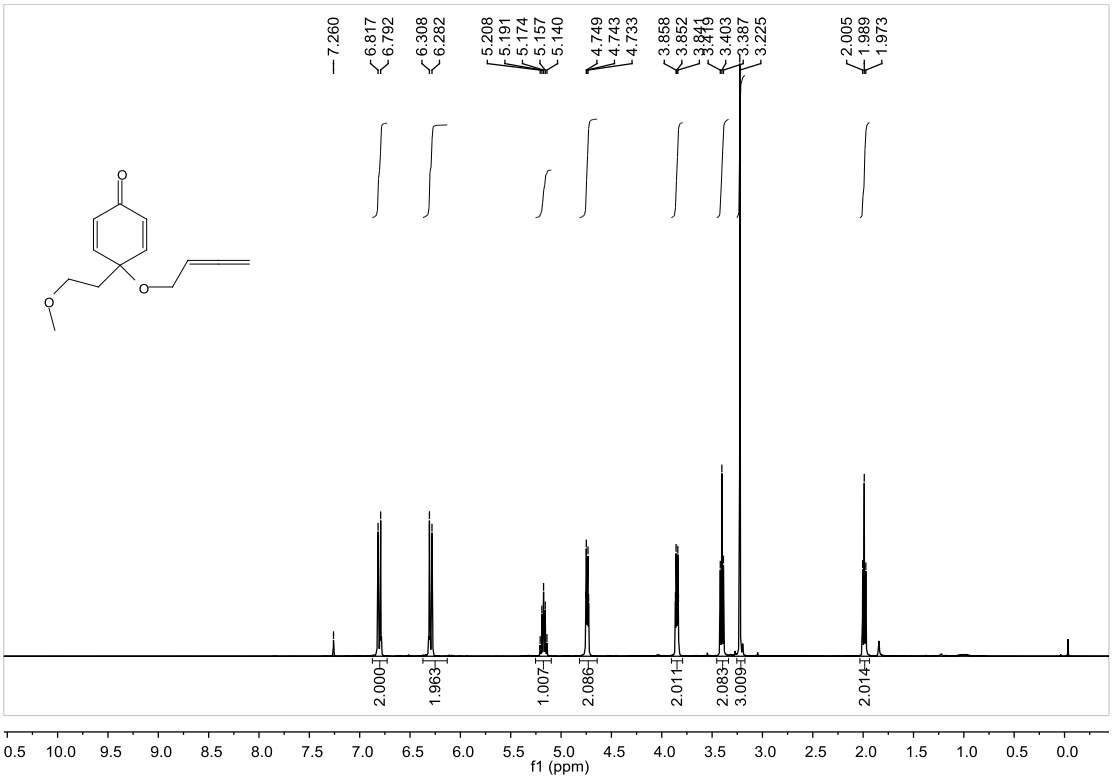


Fig. S25. ^{1}H NMR Spectrum of **3i** (400 MHz, $CDCl_3$).

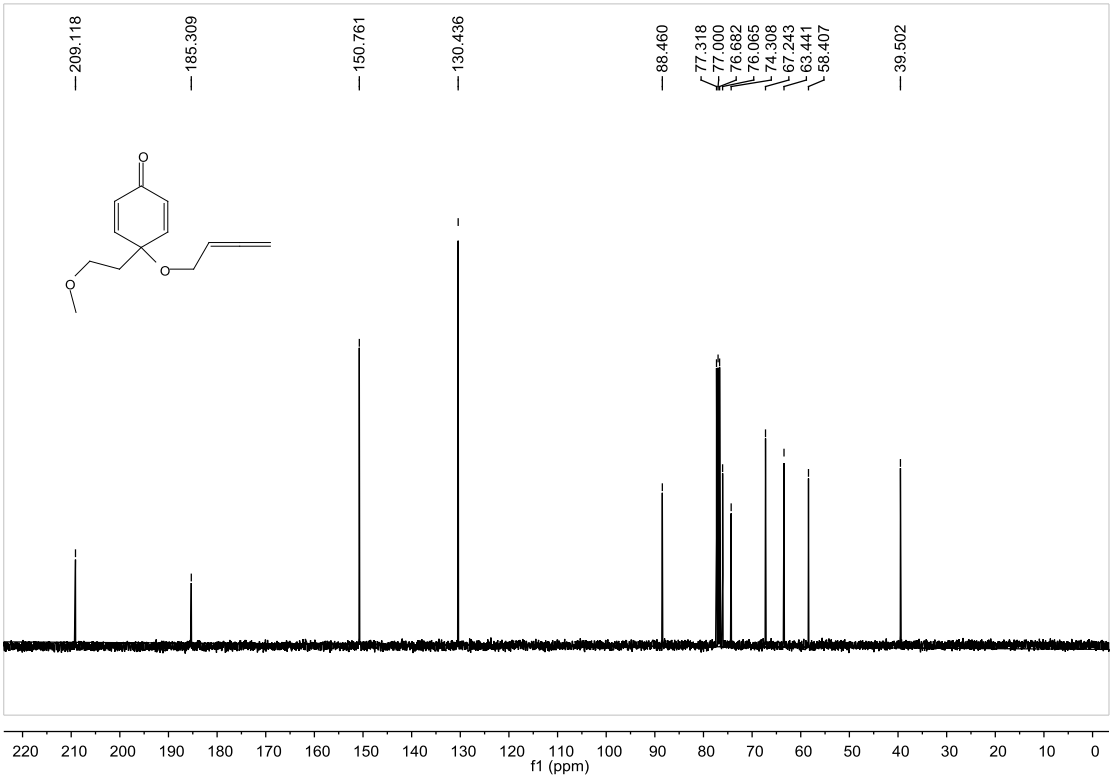


Fig. S26. ^{13}C NMR Spectrum of **3i** (100 MHz, $CDCl_3$).

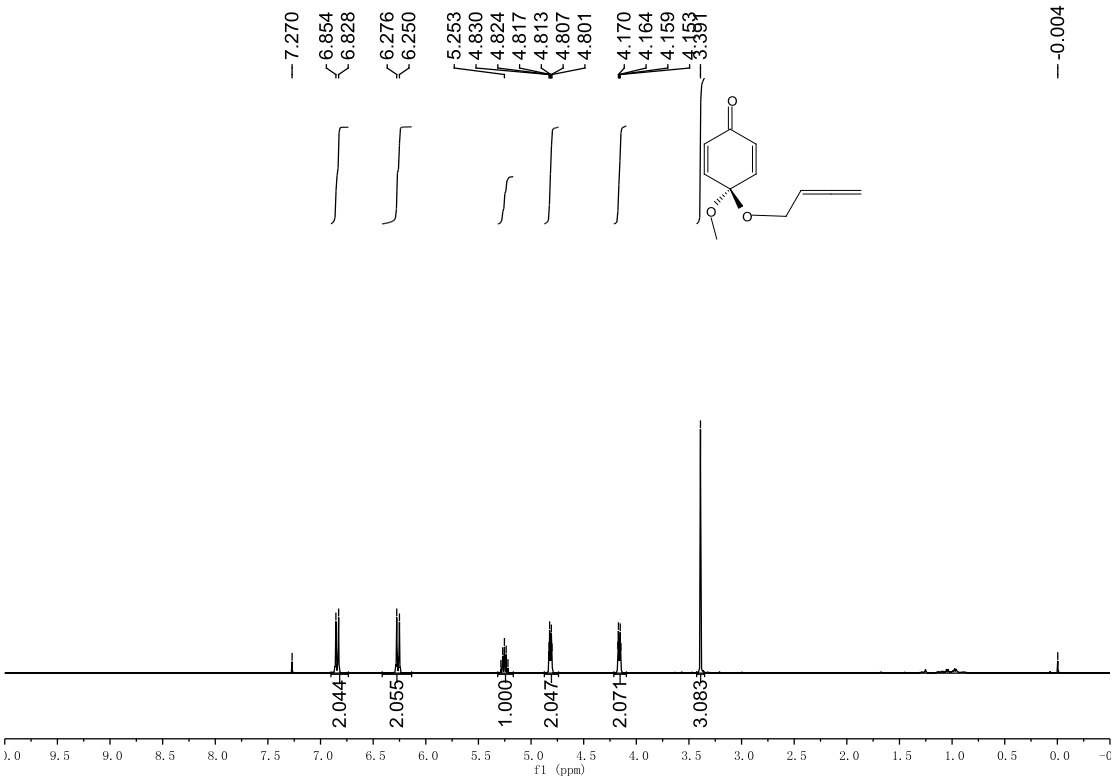


Fig. S27. ^{1}H NMR Spectrum of **3j** (400 MHz, $CDCl_3$).

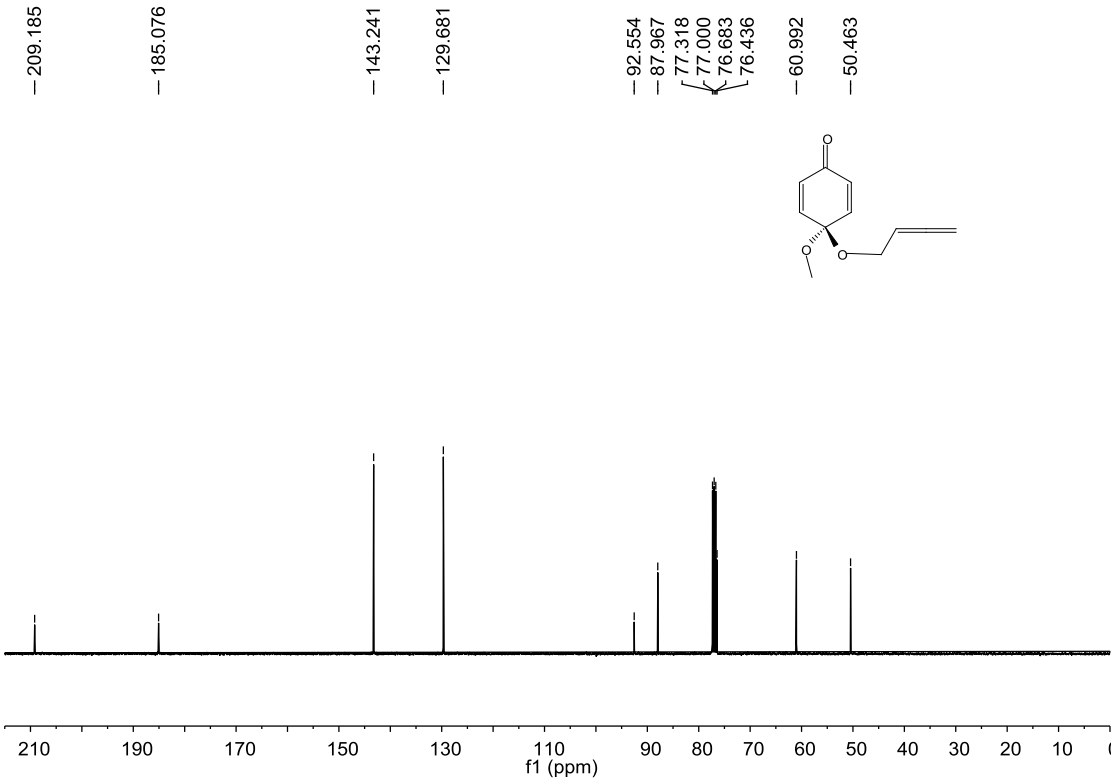


Fig. S28. ^{13}C NMR Spectrum of **3j** (100 MHz, $CDCl_3$).

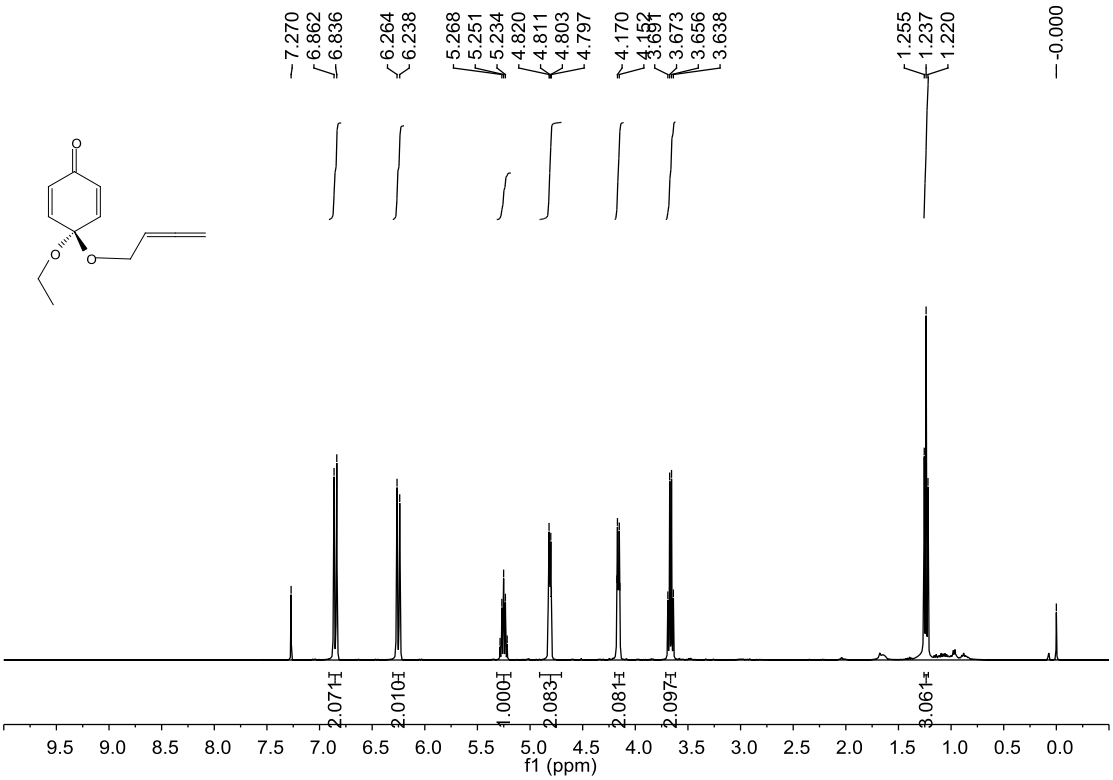


Fig. S29. ^{1}H NMR Spectrum of **3k** (400 MHz, $CDCl_3$).

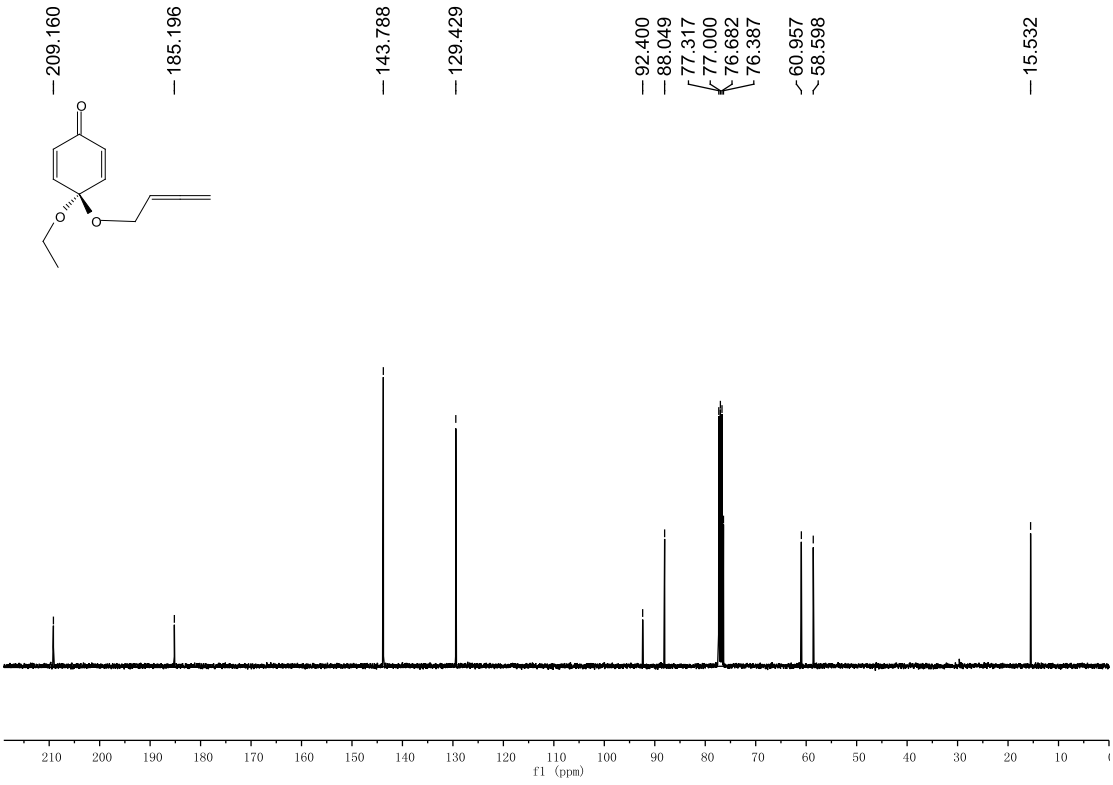


Fig. S30. ^{13}C NMR Spectrum of **3k** (100 MHz, $CDCl_3$).

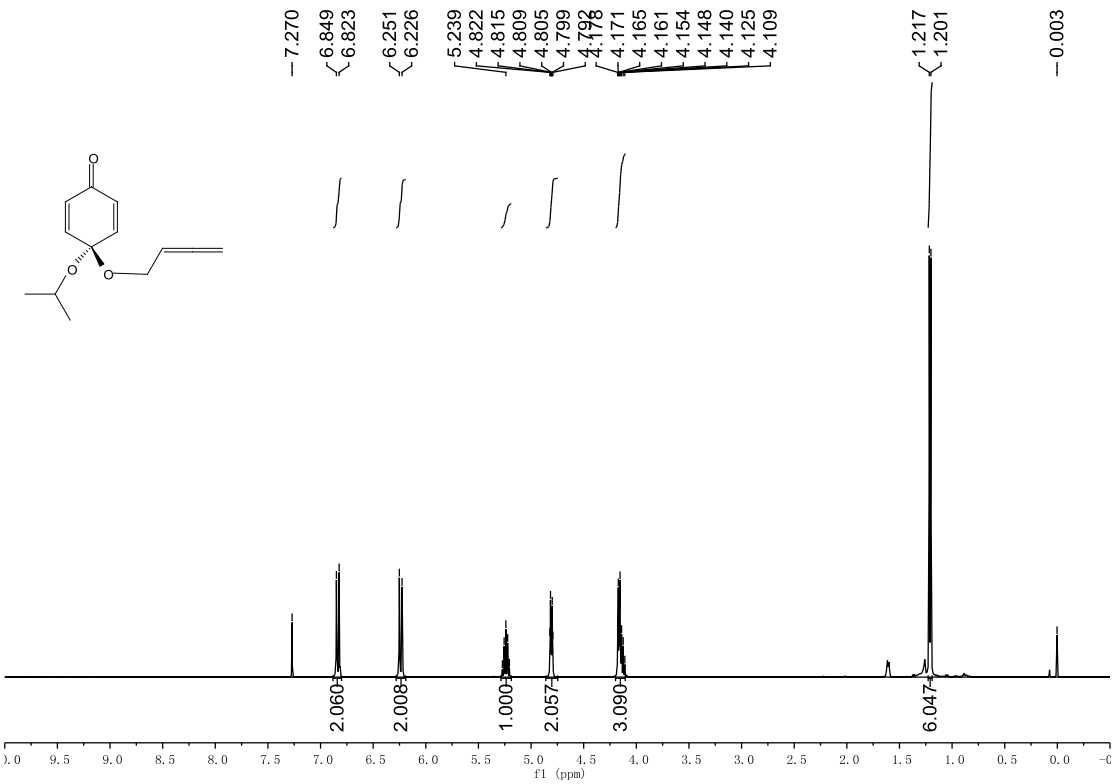


Fig. S31. ^{1}H NMR Spectrum of **3l** (400 MHz, $CDCl_3$).

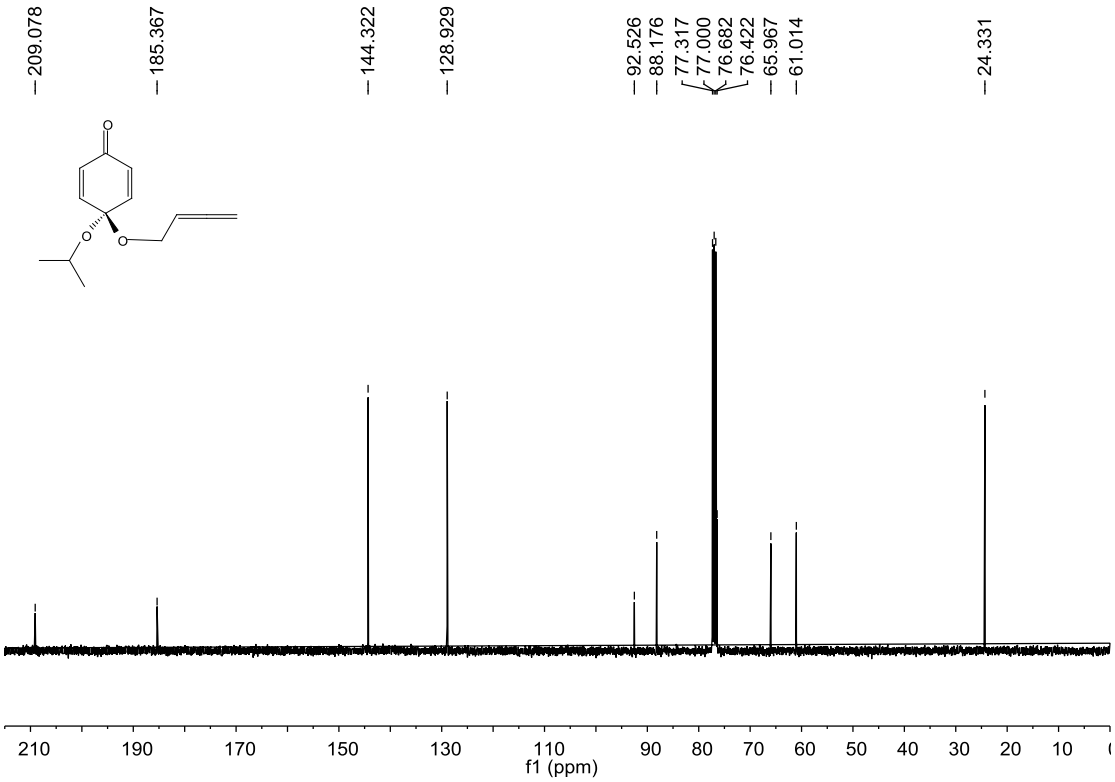


Fig. S32. ^{13}C NMR Spectrum of **3l** (100 MHz, $CDCl_3$).

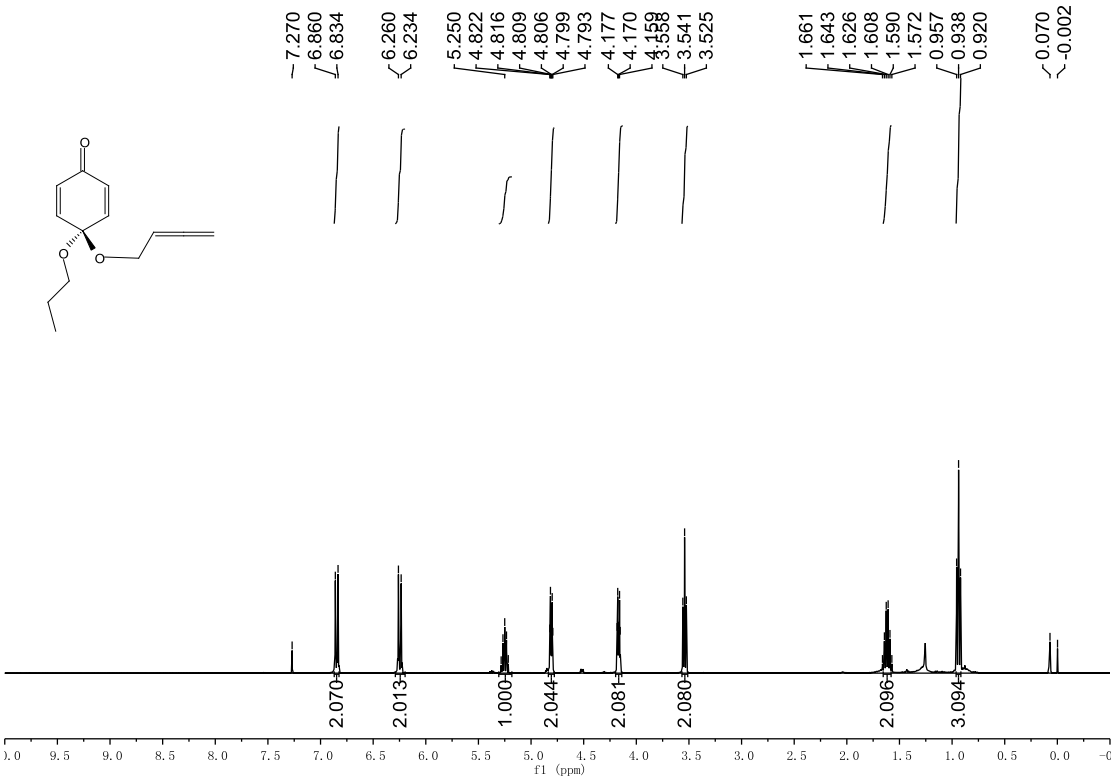


Fig. S33. ^{1}H NMR Spectrum of **3m** (400 MHz, $CDCl_3$).

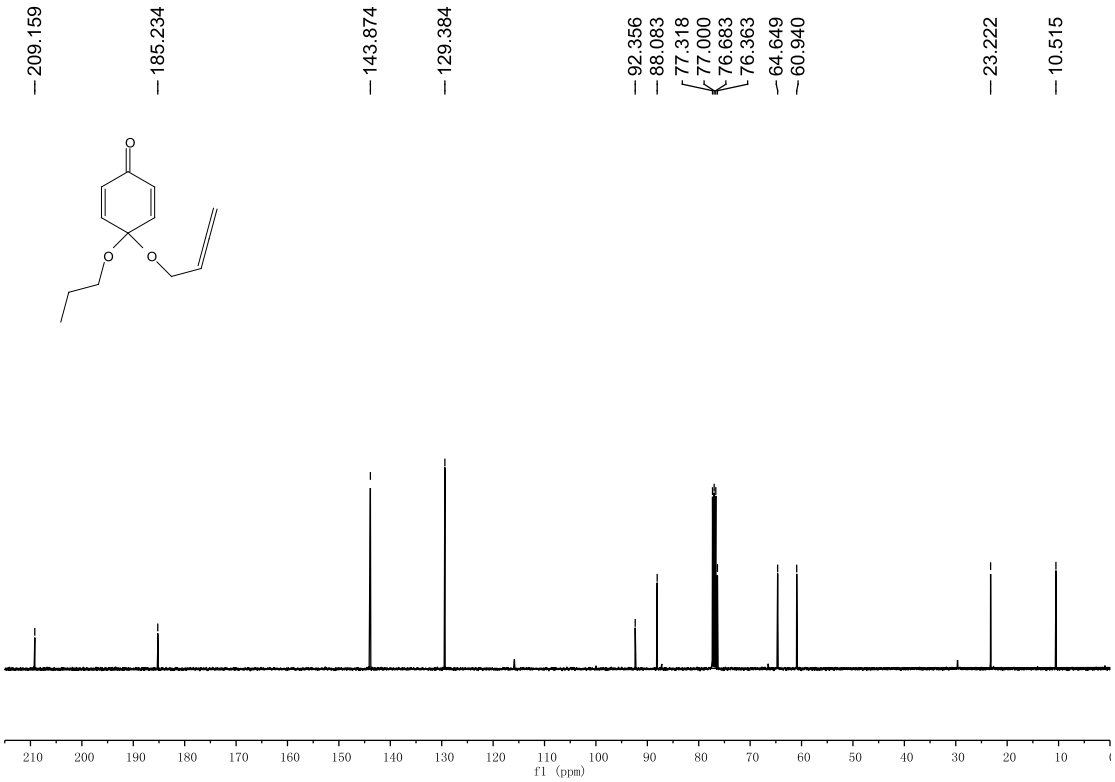


Fig. S34. ^{13}C NMR Spectrum of **3m** (100 MHz, $CDCl_3$).

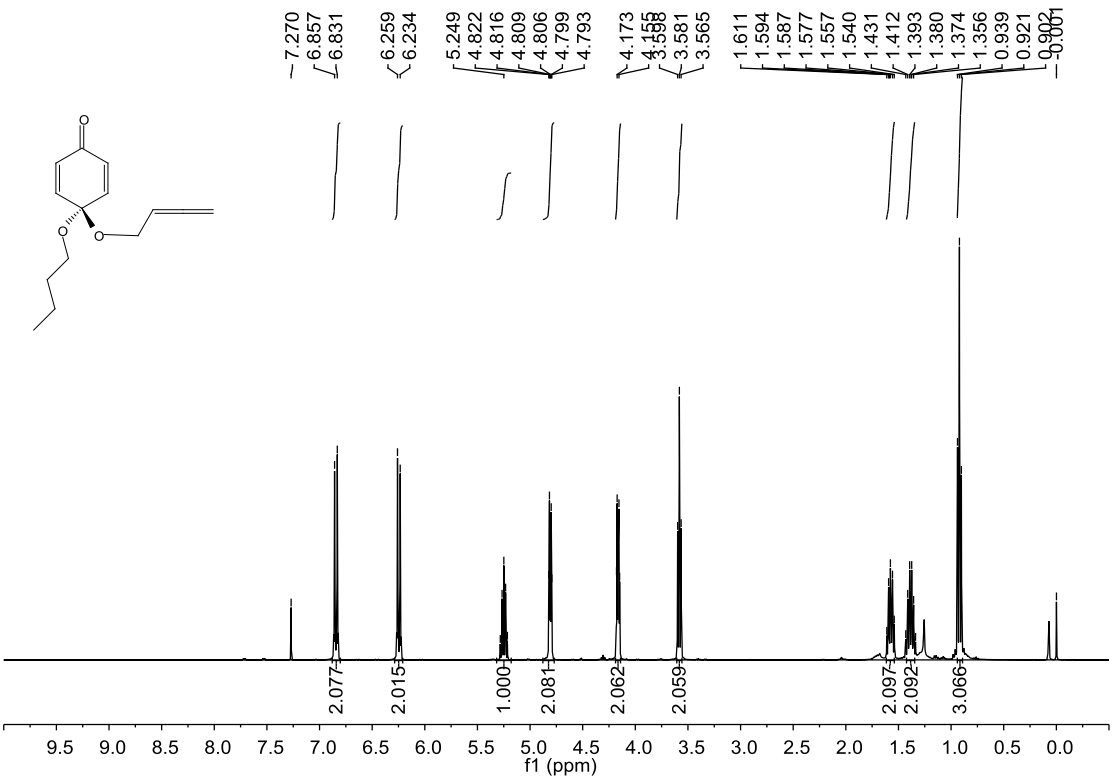


Fig. S35. ^{1}H NMR Spectrum of **3n** (400 MHz, $CDCl_3$).

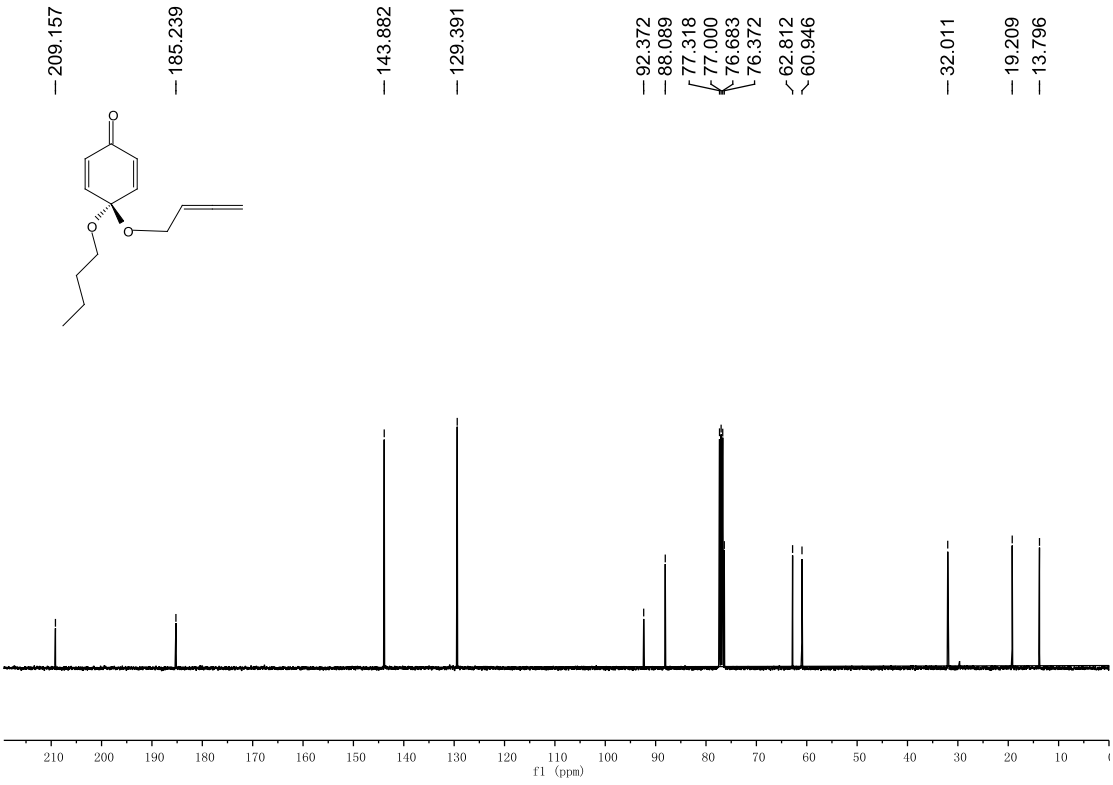


Fig. S36. ^{13}C NMR Spectrum of **3n** (100 MHz, $CDCl_3$).

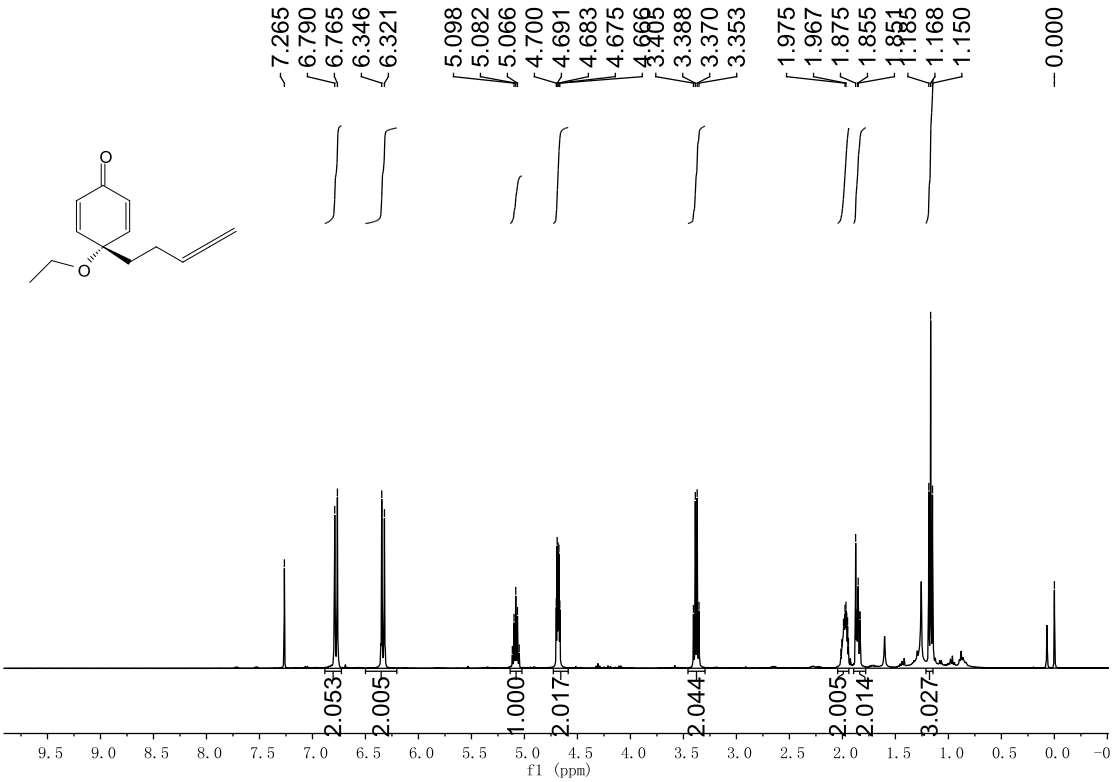


Fig. S37. ^{1}H NMR Spectrum of **3p** (400 MHz, $CDCl_3$).

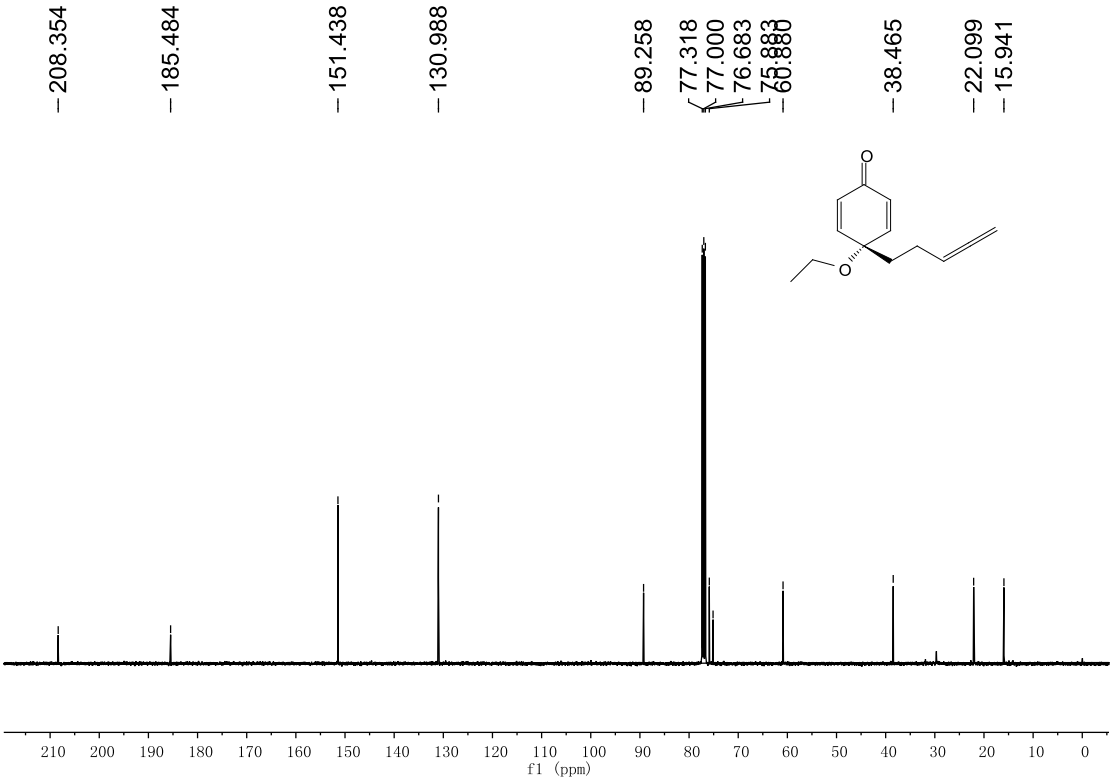


Fig. S38. ^{13}C NMR Spectrum of **3p** (100 MHz, $CDCl_3$).

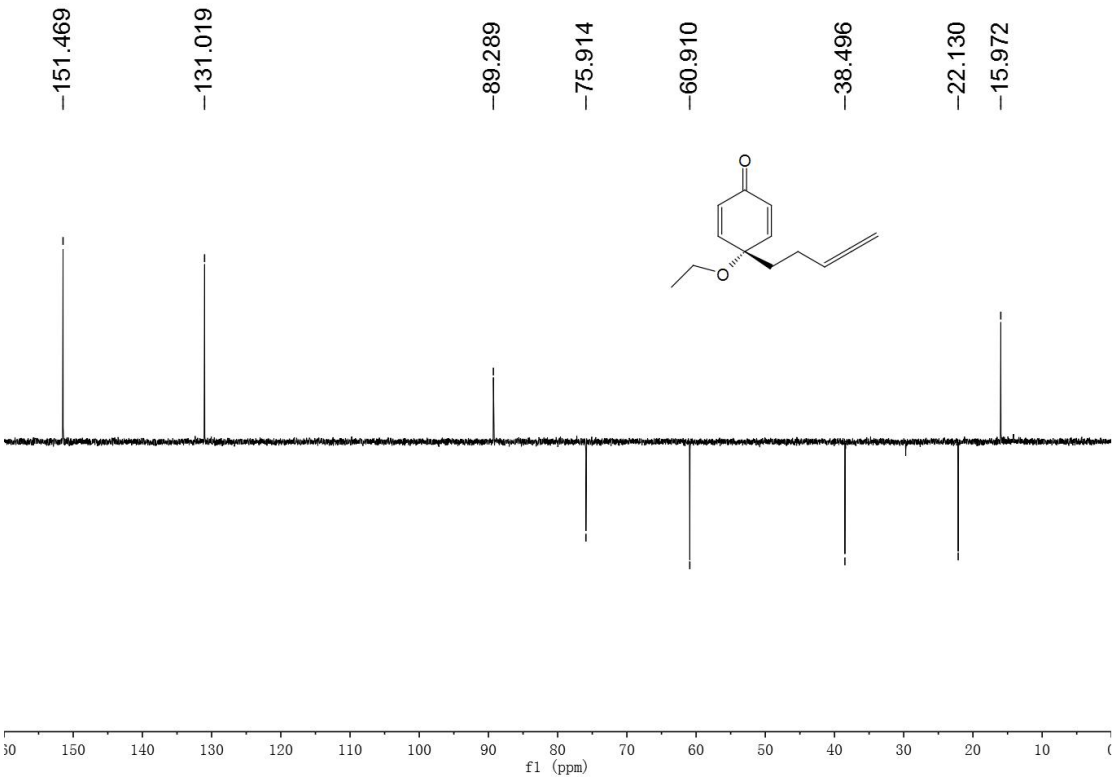


Fig. S39. DEPT 135 Spectrum of **3p** (100 MHz, $CDCl_3$).

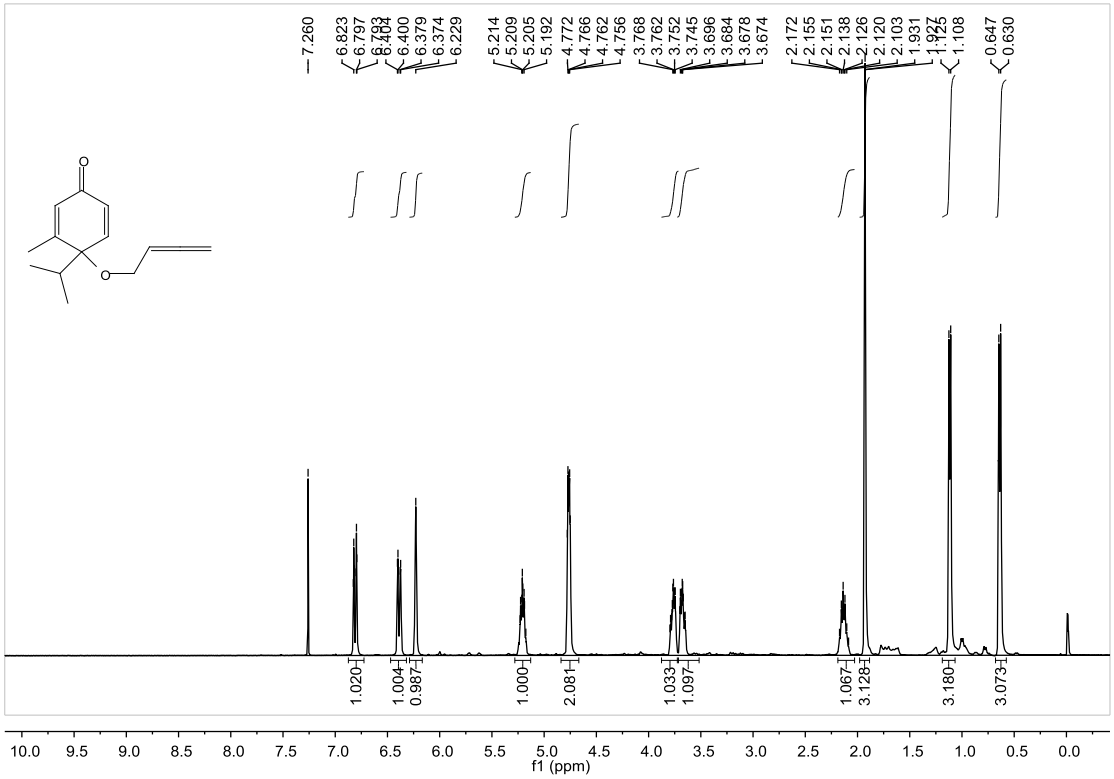


Fig. S40. ^{1}H NMR Spectrum of **3s** (400 MHz, $CDCl_3$).

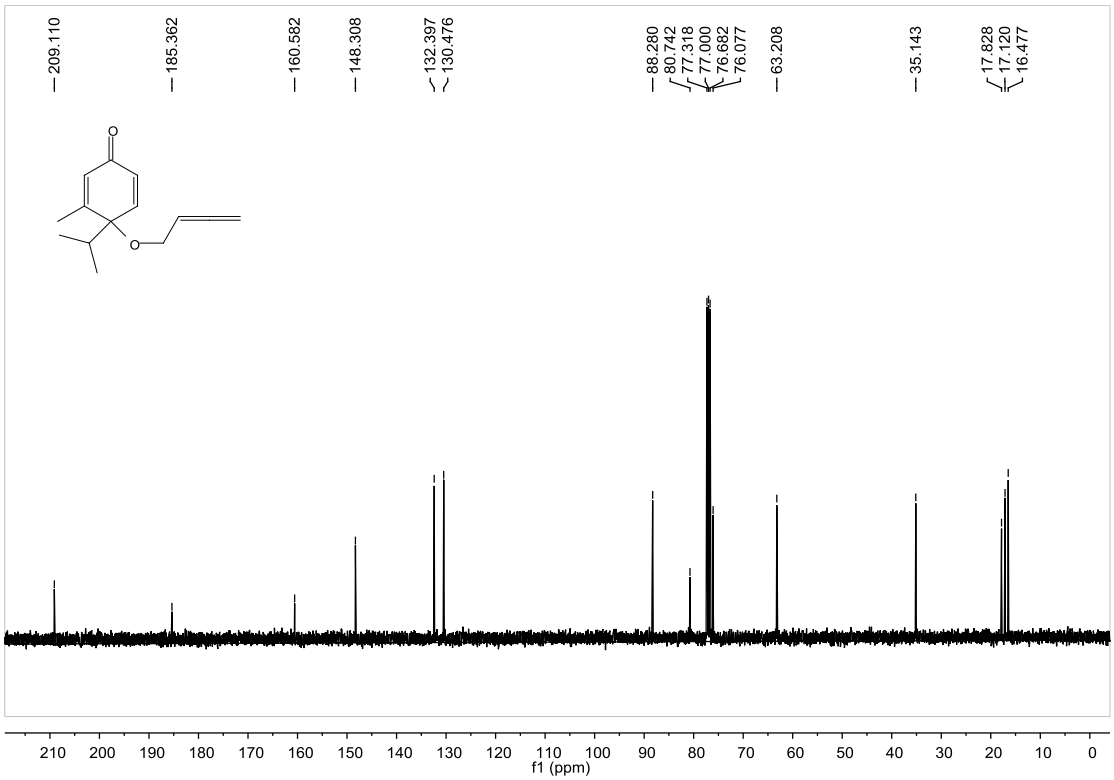


Fig. S41. ^{13}C NMR Spectrum of **3s** (100 MHz, $CDCl_3$).

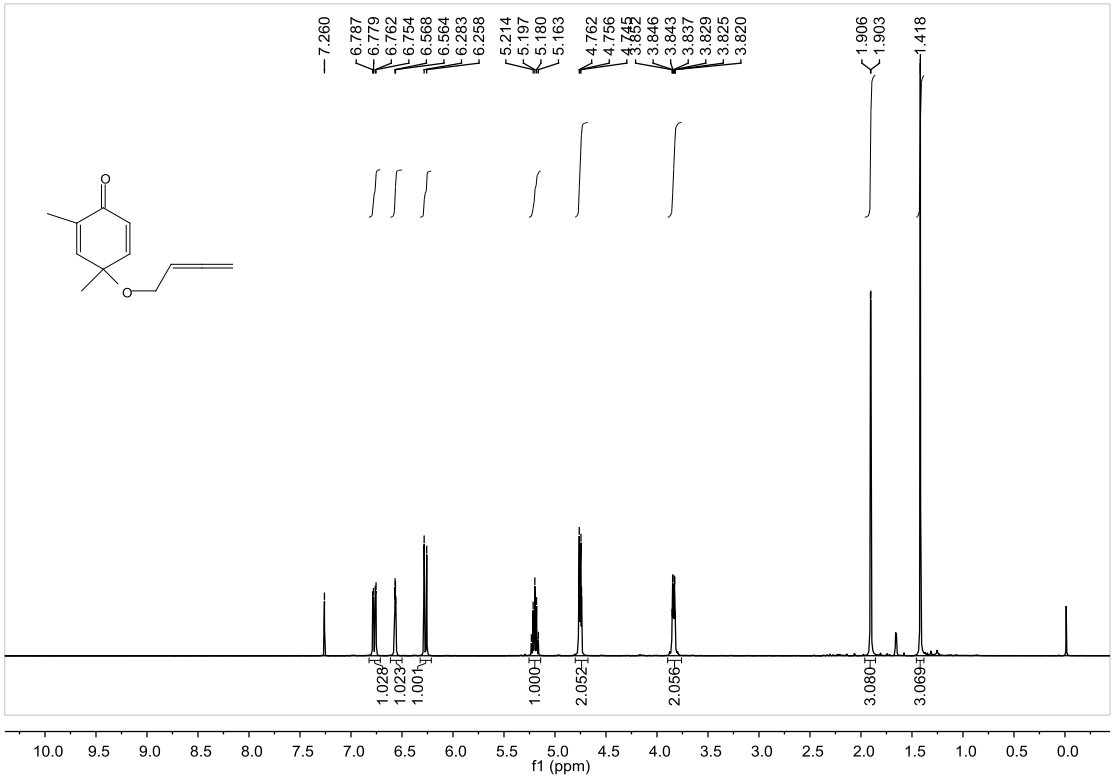


Fig. S42. ^{1}H NMR Spectrum of **3v** (400 MHz, $CDCl_3$).

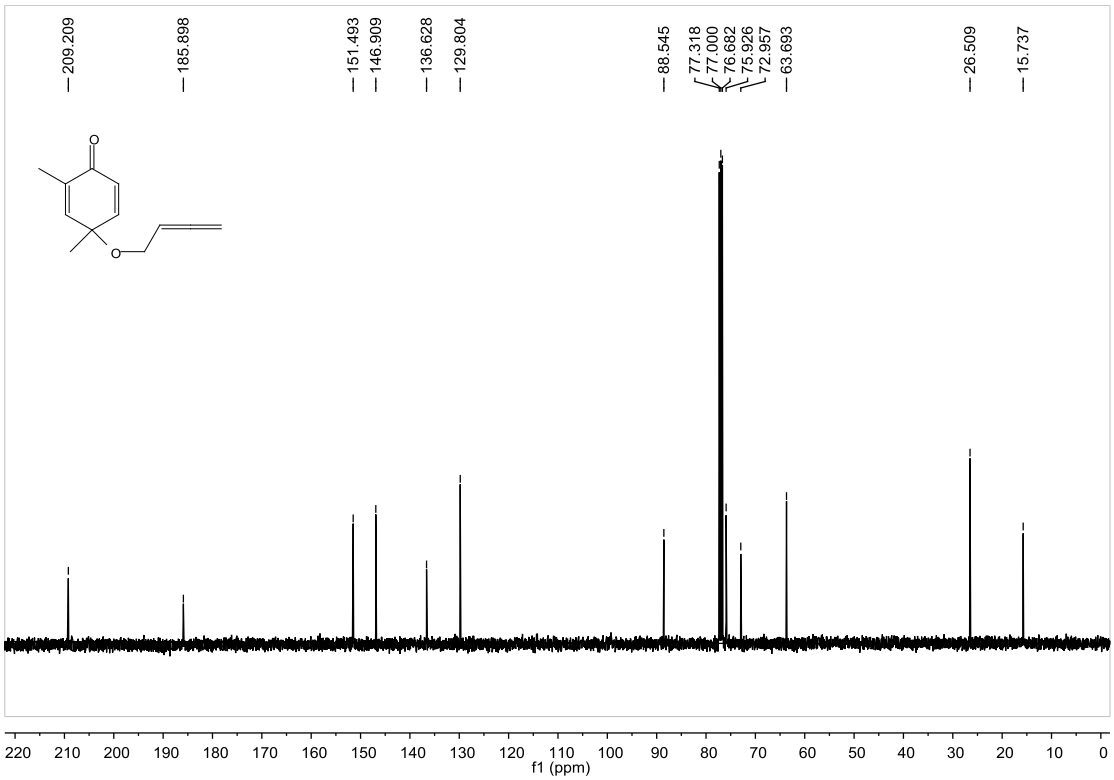


Fig. S43. ^{13}C NMR Spectrum of **3v** (100 MHz, $CDCl_3$).

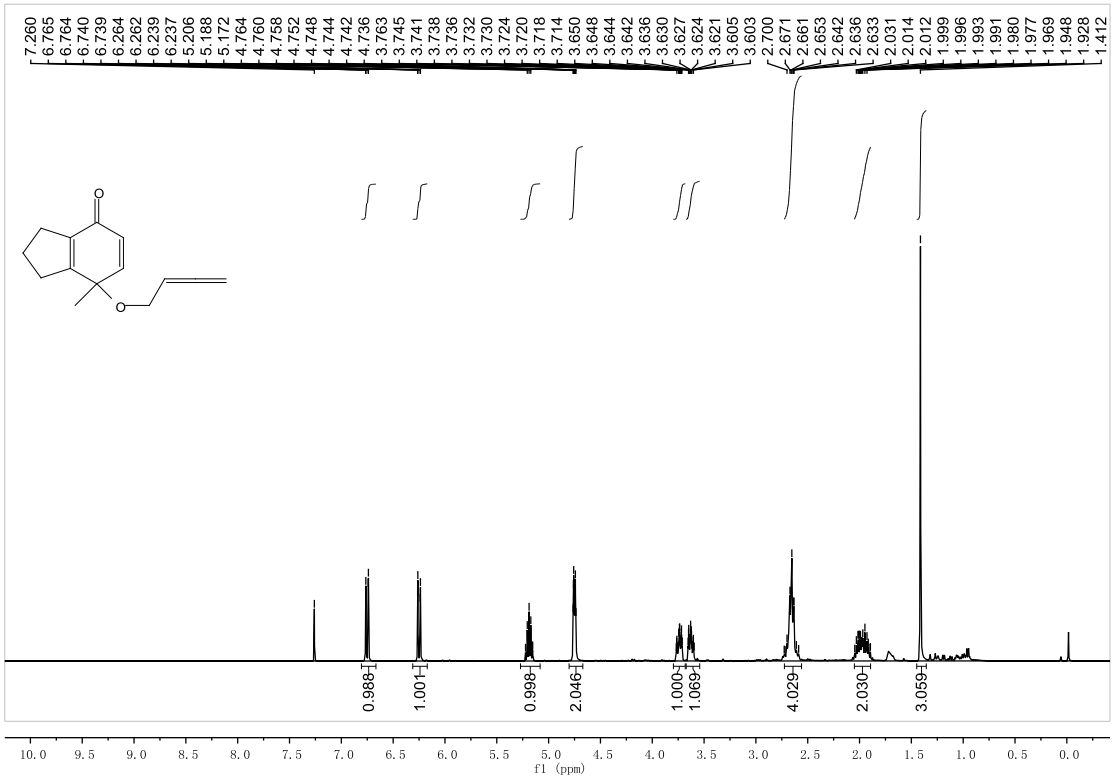


Fig. S44. ^{1}H NMR Spectrum of **3x** (400 MHz, $CDCl_3$).

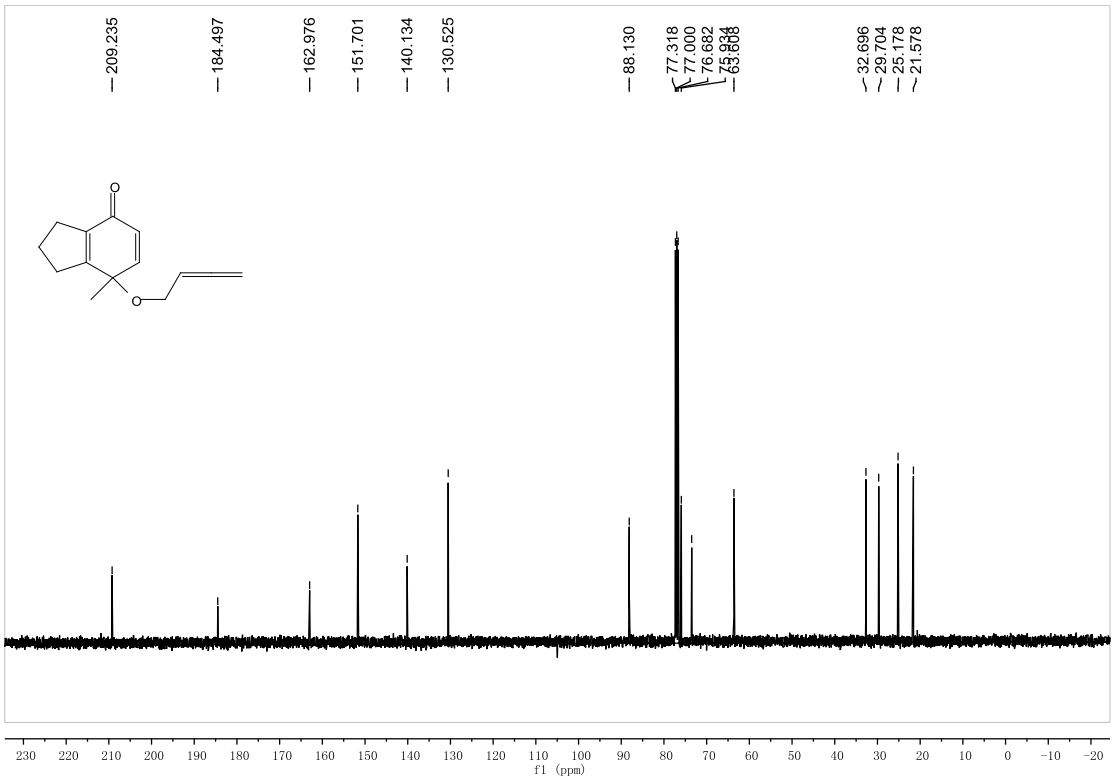


Fig. S45. ^{13}C NMR Spectrum of **3x** (100 MHz, $CDCl_3$).

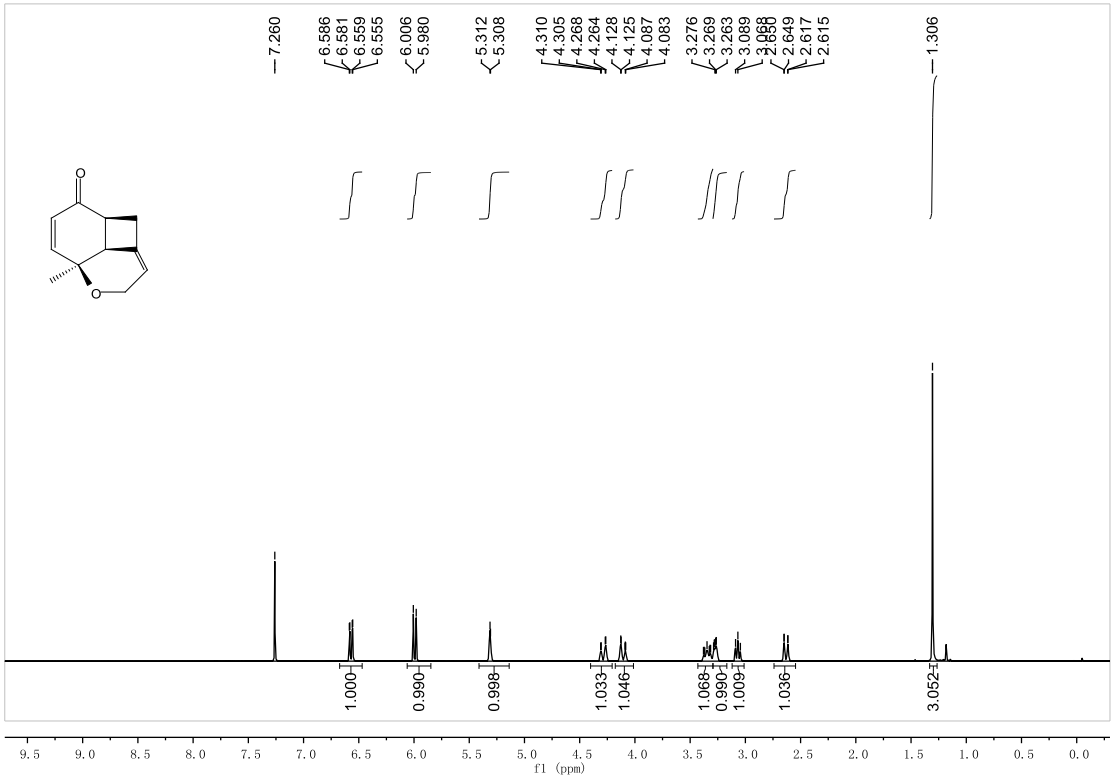


Fig. S46. ^{1}H NMR Spectrum of **4a** (400 MHz, $CDCl_3$).

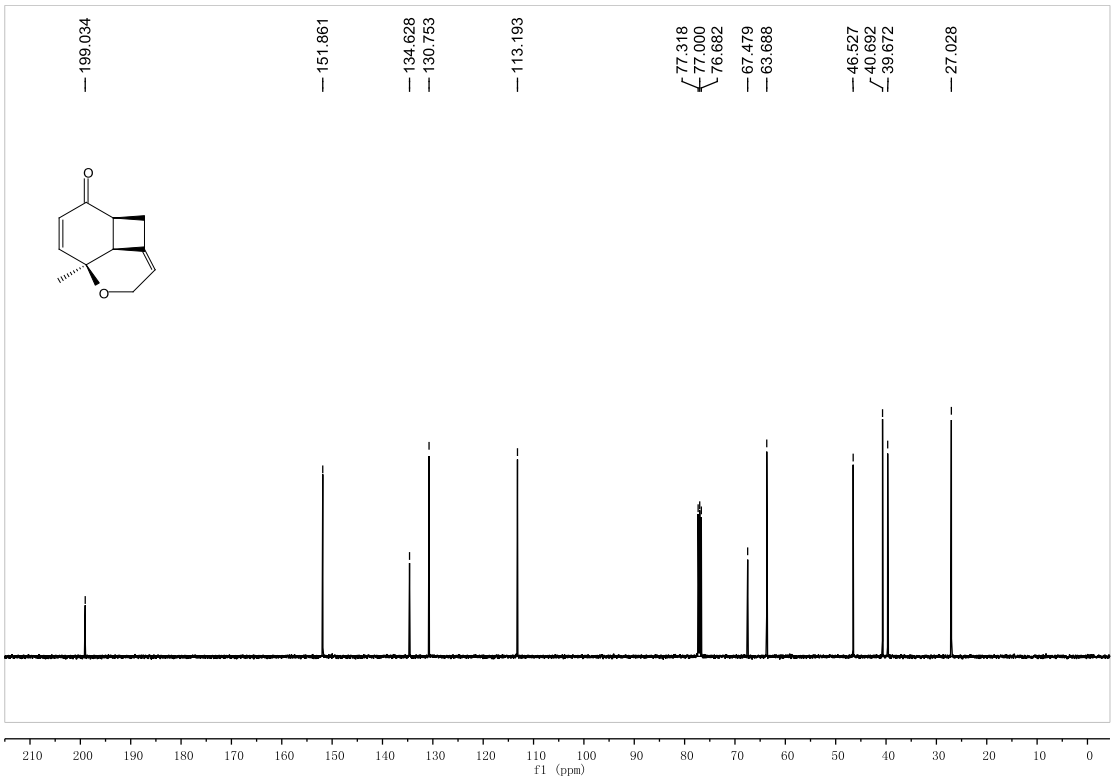


Fig. S47. ^{13}C NMR Spectrum of **4a** (100 MHz, $CDCl_3$).

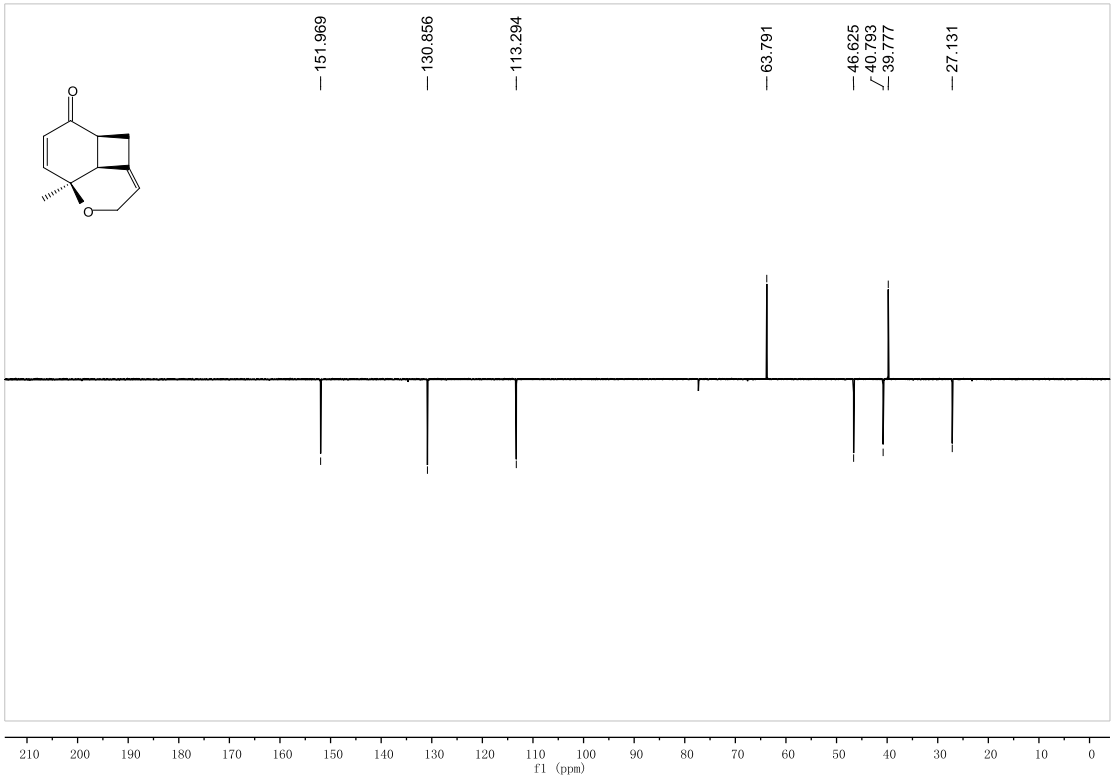


Fig. S48. DEPT 135 Spectrum of **4a** (100 MHz, $CDCl_3$).

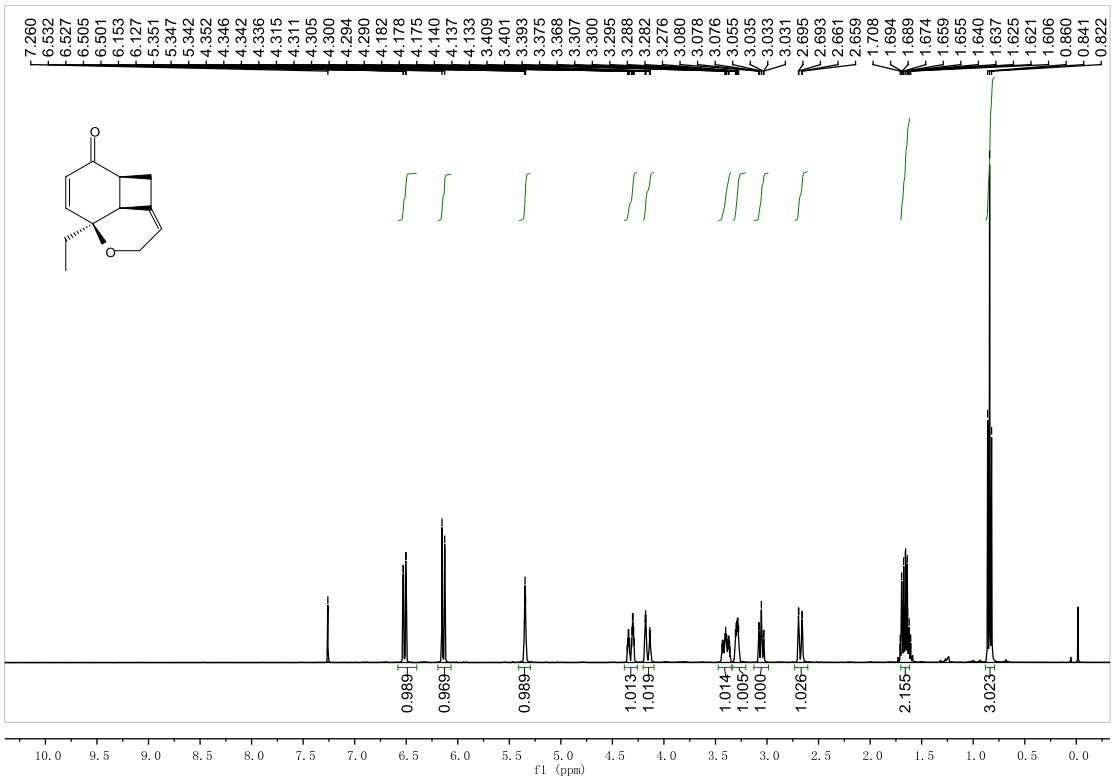


Fig. S49. ^{1}H NMR Spectrum of **4b** (400 MHz, $CDCl_3$).

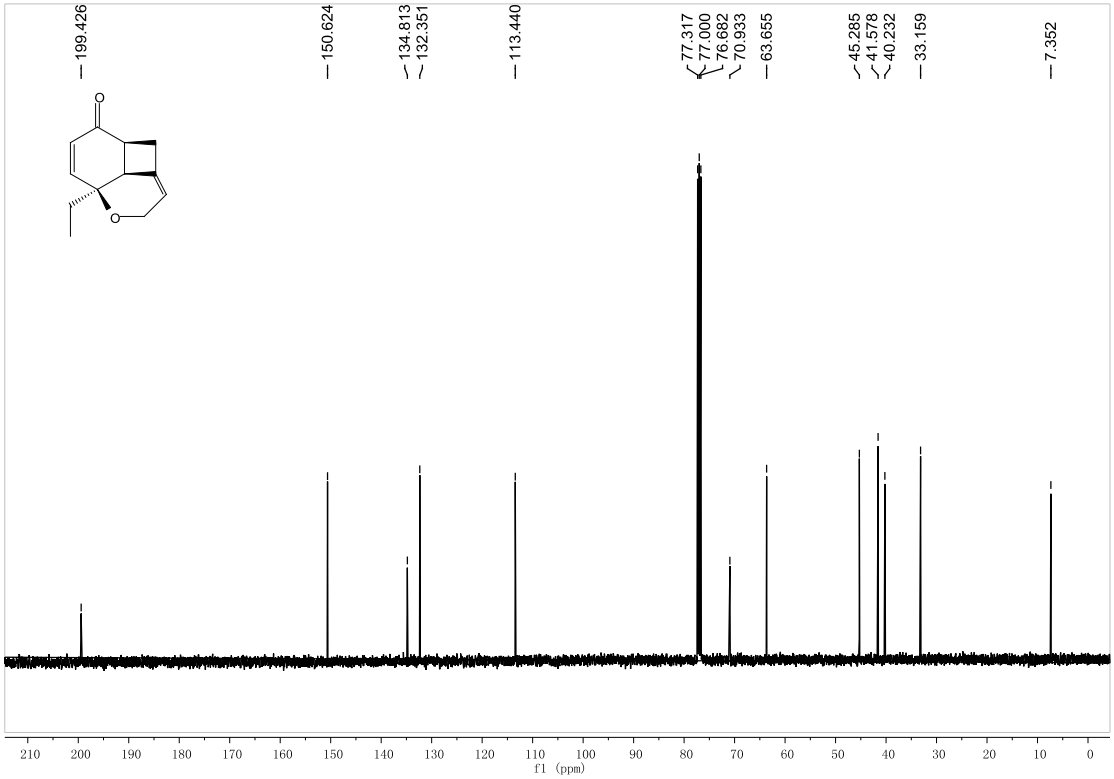


Fig. S50. ^{13}C NMR Spectrum of **4b** (100 MHz, $CDCl_3$).

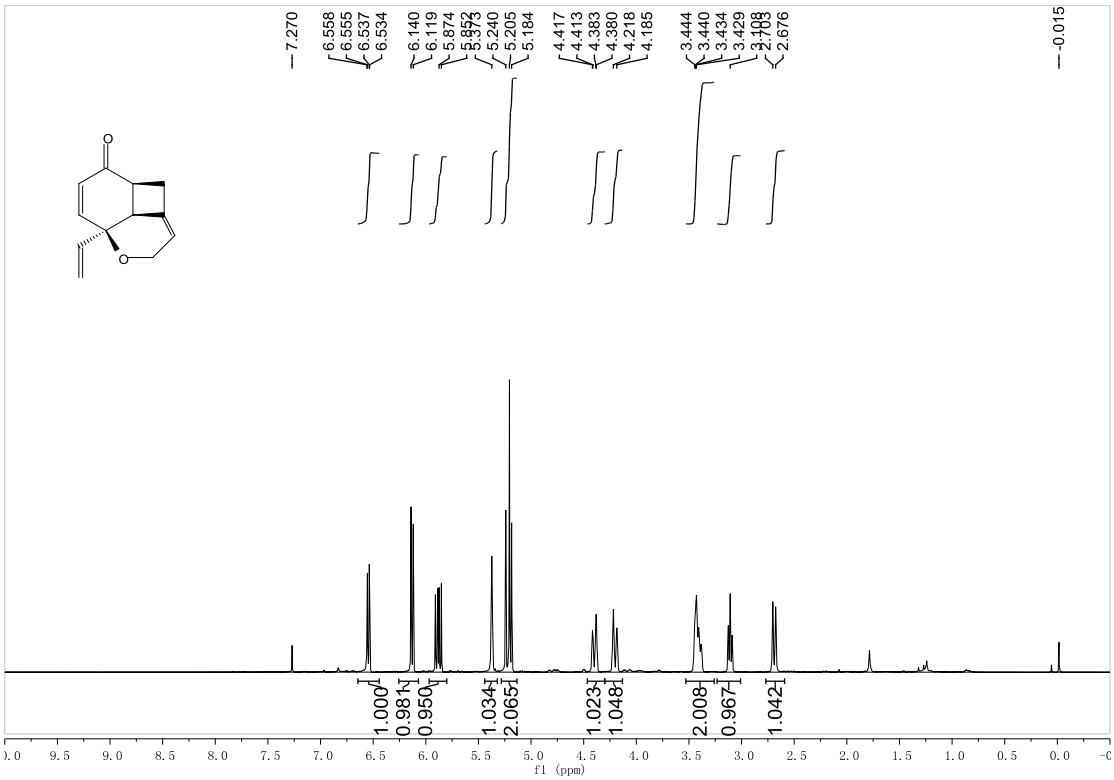


Fig. S51. ^{1}H NMR Spectrum of **4c** (400 MHz, $CDCl_3$).

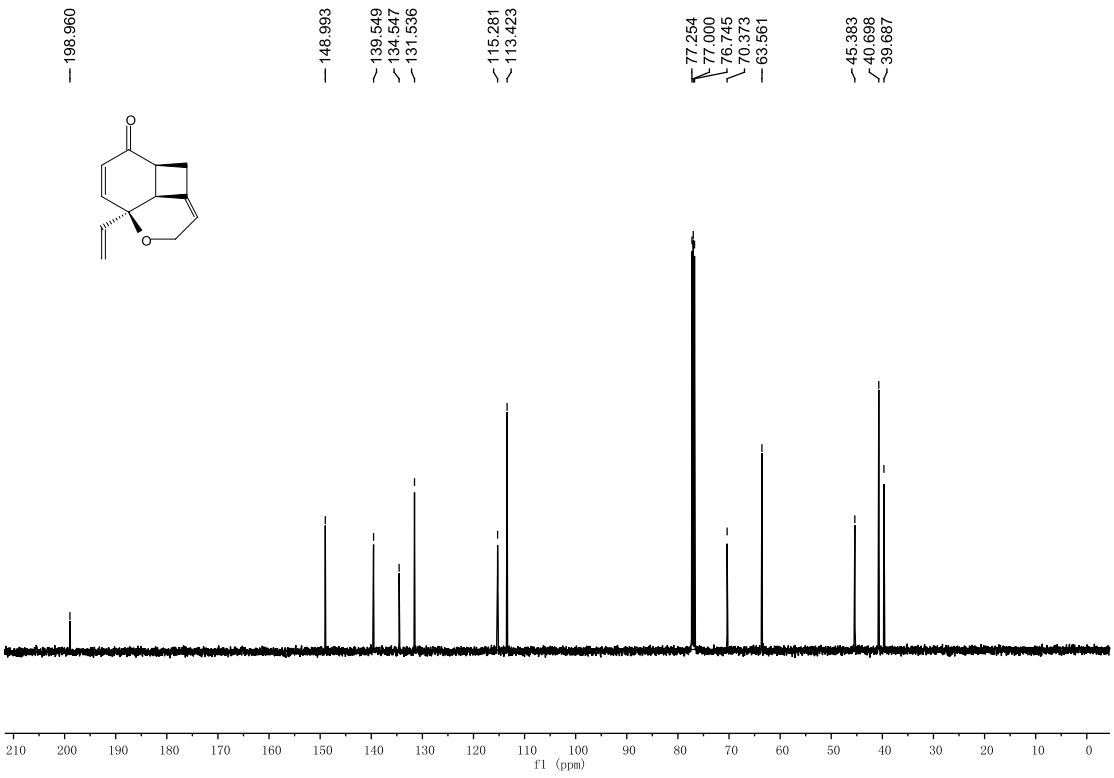


Fig. S52. ^{13}C NMR Spectrum of **4c** (100 MHz, $CDCl_3$).

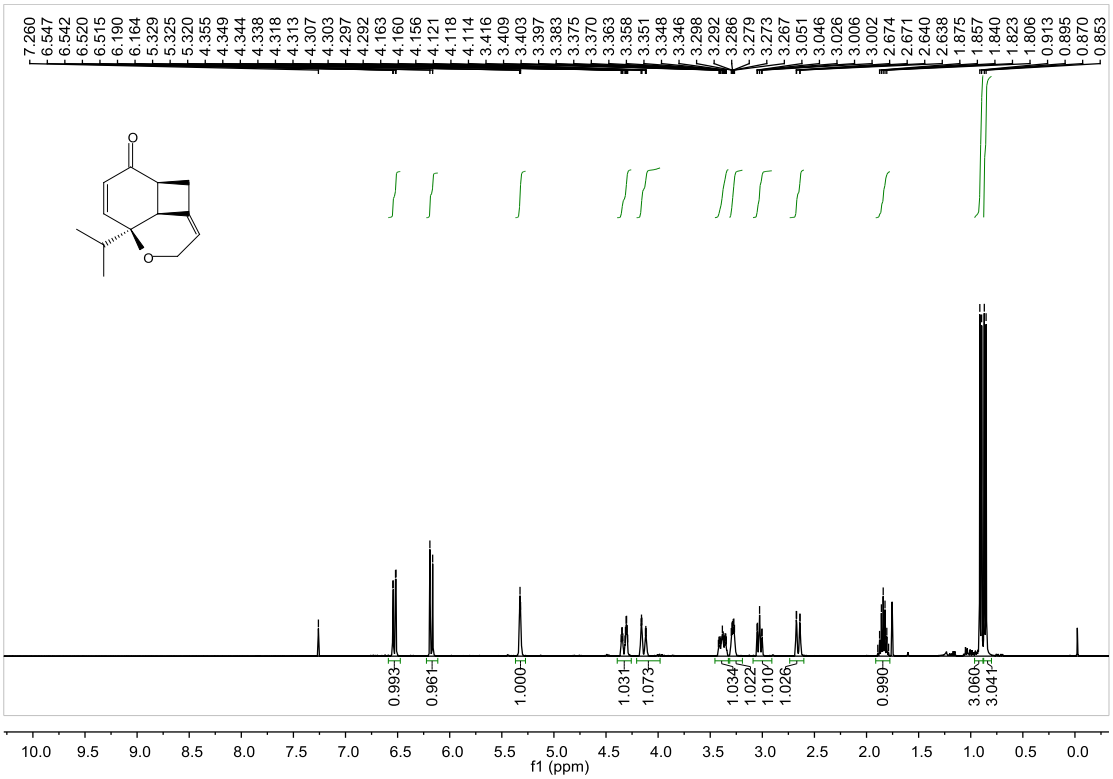


Fig. S53. ^{1}H NMR Spectrum of **4d** (400 MHz, $CDCl_3$).

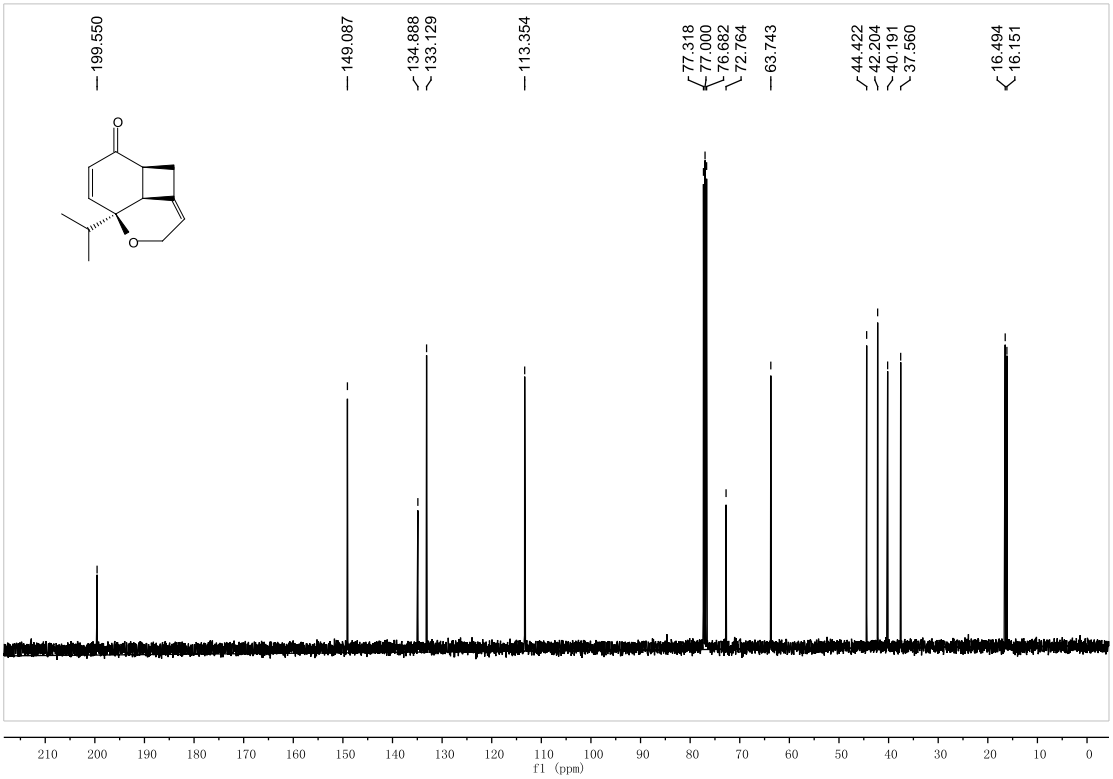


Fig. S54. ^{13}C NMR Spectrum of **4d** (100 MHz, $CDCl_3$).

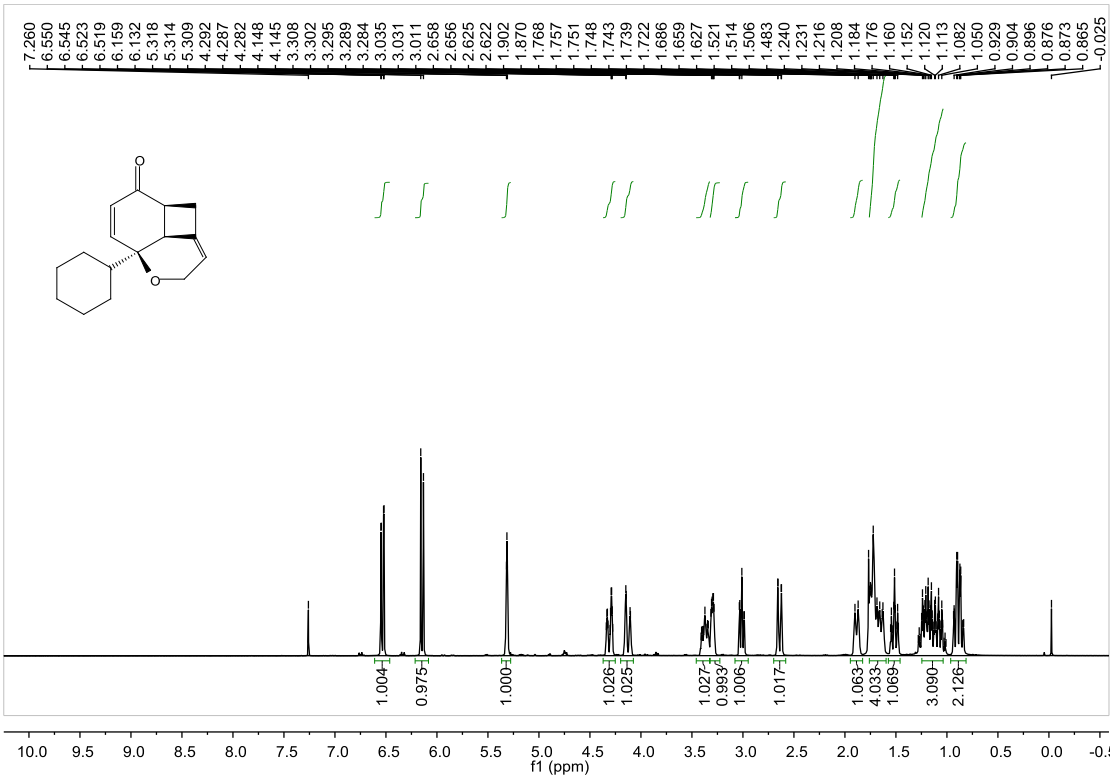


Fig. S55. ^{1}H NMR Spectrum of **4e** (400 MHz, $CDCl_3$).

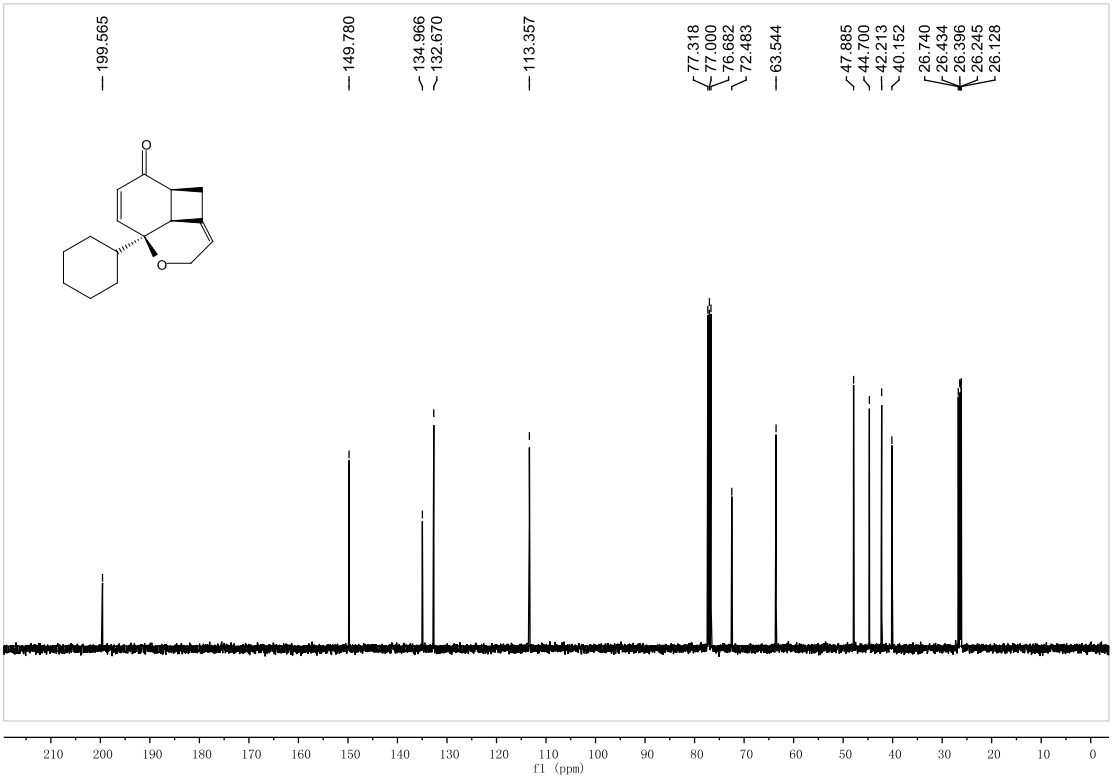


Fig. S56. ^{13}C NMR Spectrum of **4e** (100 MHz, $CDCl_3$).

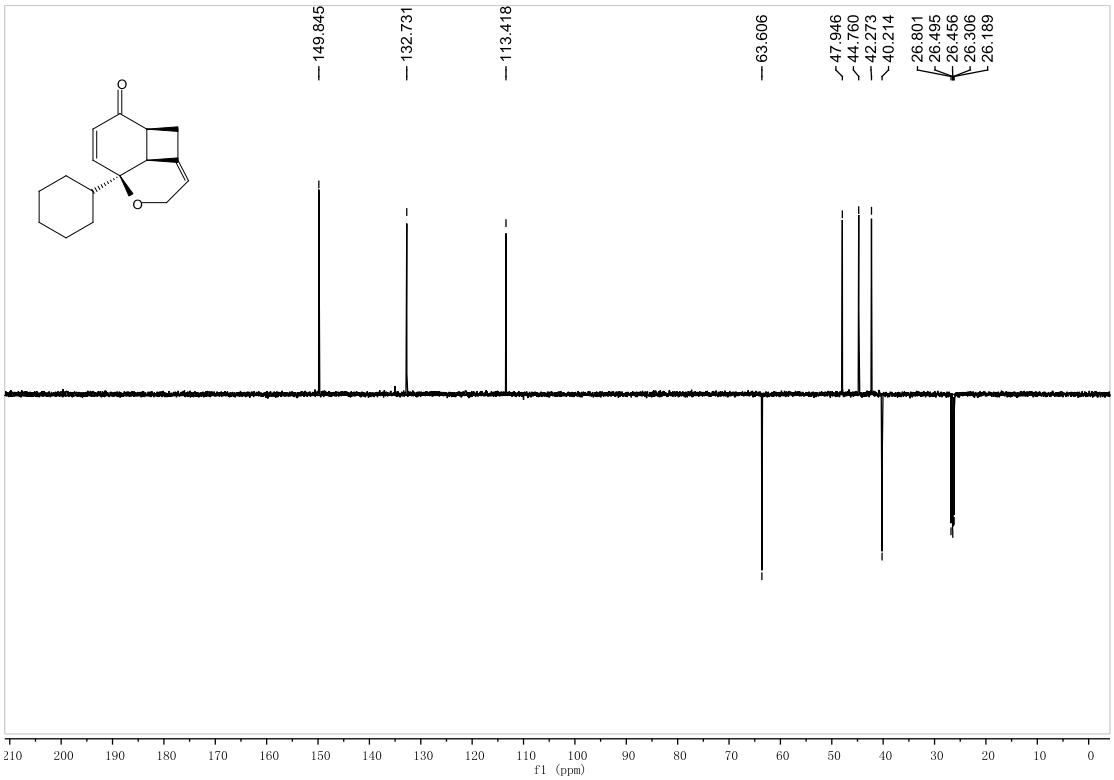


Fig. S57. DEPT 135 Spectrum of **4e** (100 MHz, $CDCl_3$).

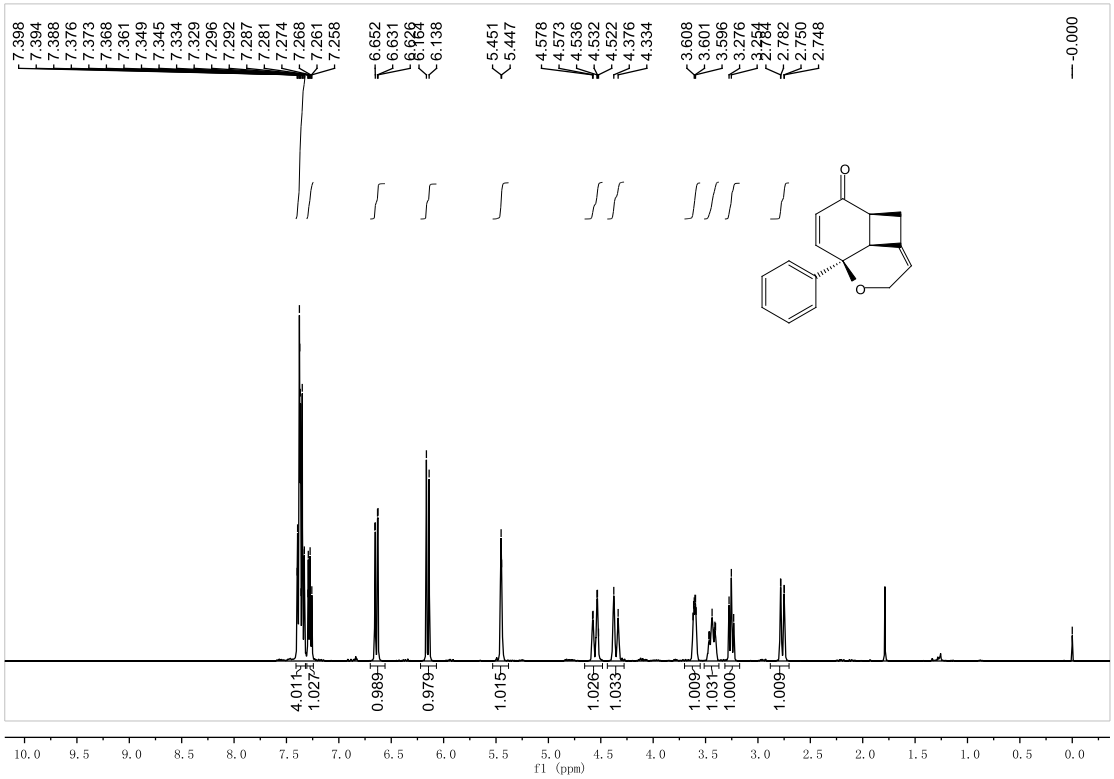


Fig. S58. ^{1}H NMR Spectrum of **4f** (400 MHz, $CDCl_3$).

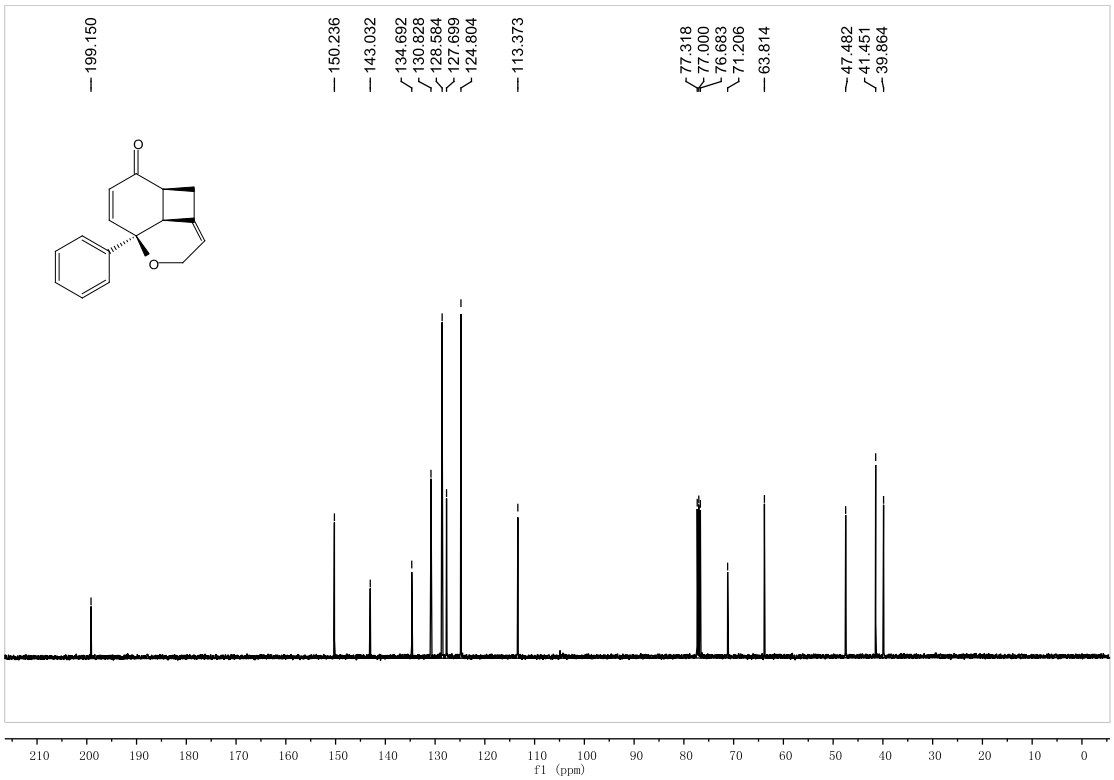


Fig. S59. ^{13}C NMR Spectrum of **4f** (100 MHz, $CDCl_3$).

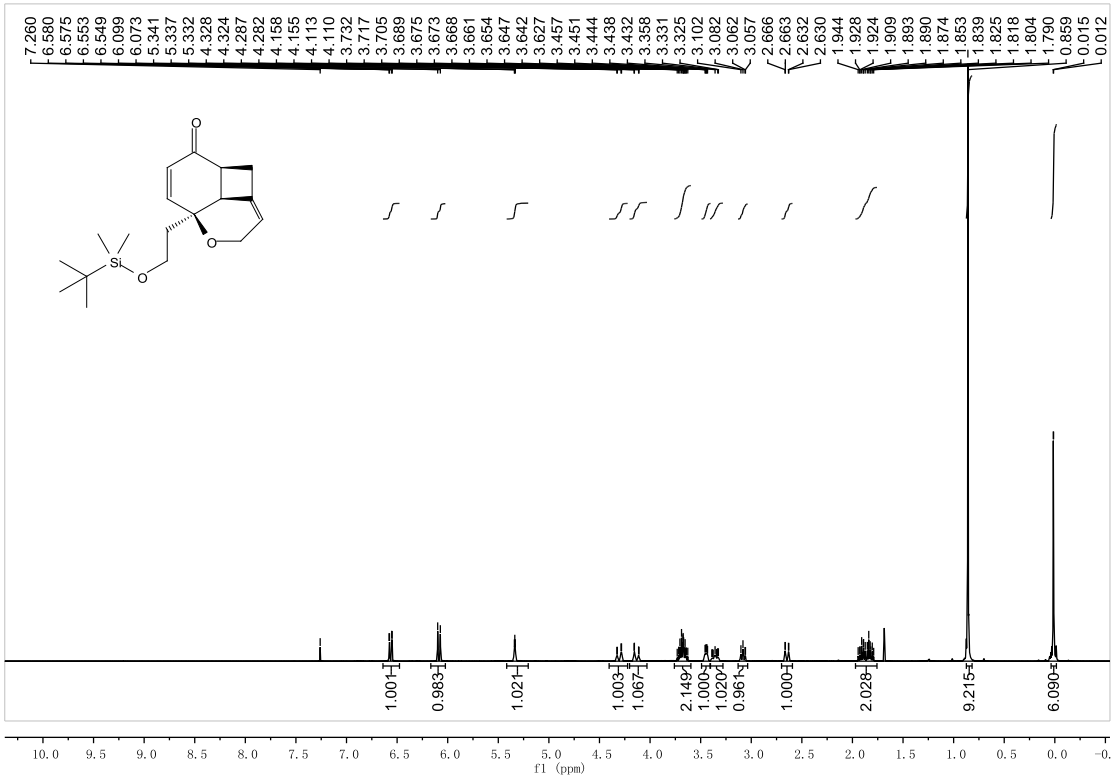


Fig. S60. ^{1}H NMR Spectrum of **4g** (400 MHz, $CDCl_3$).

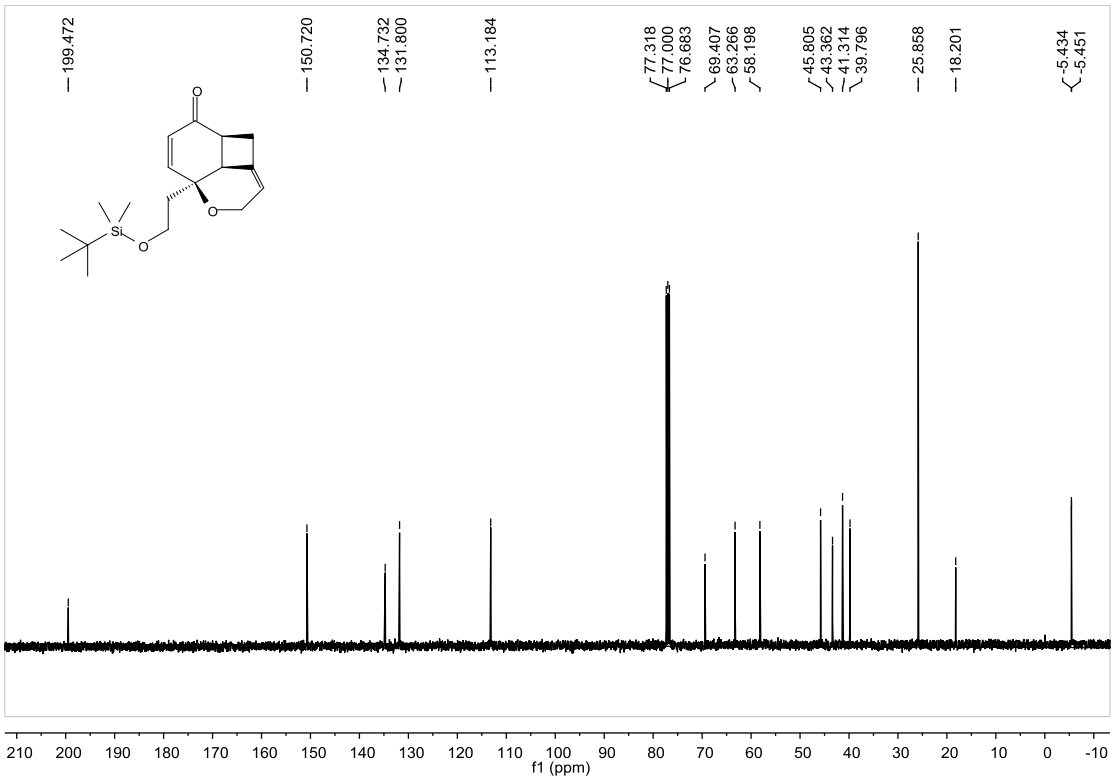


Fig. S61. ^{13}C NMR Spectrum of **4g** (100 MHz, $CDCl_3$).

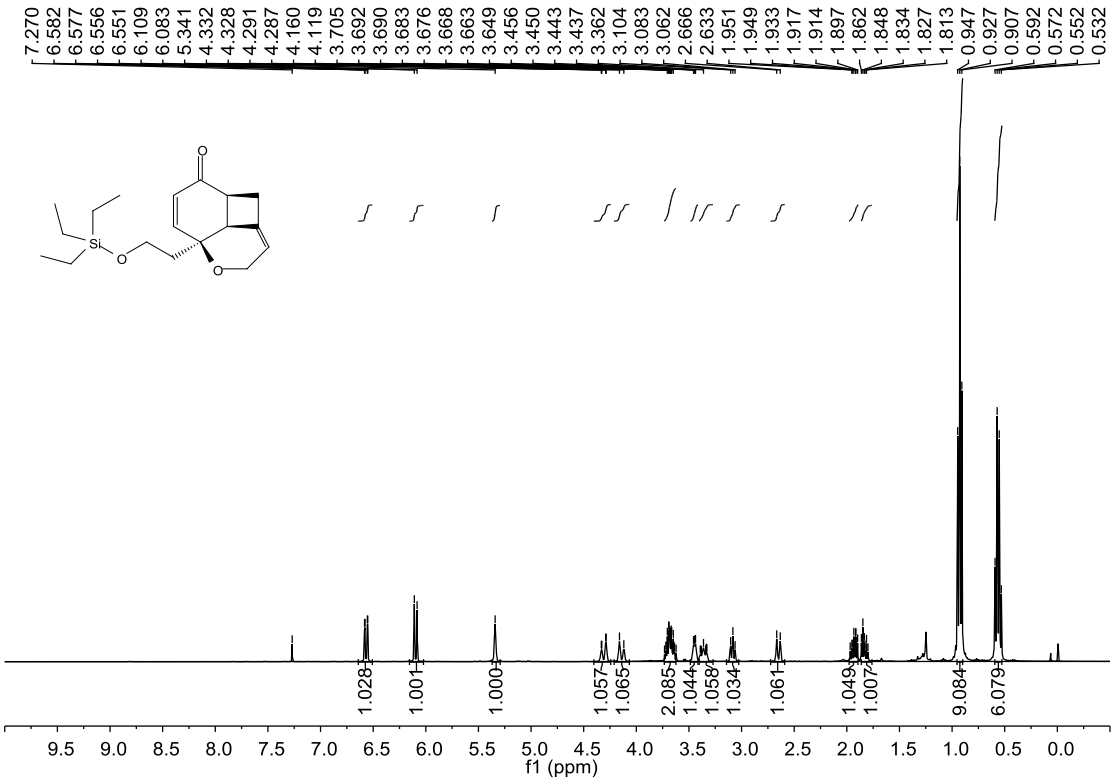


Fig. S62. ^{1}H NMR Spectrum of **4h** (400 MHz, $CDCl_3$).

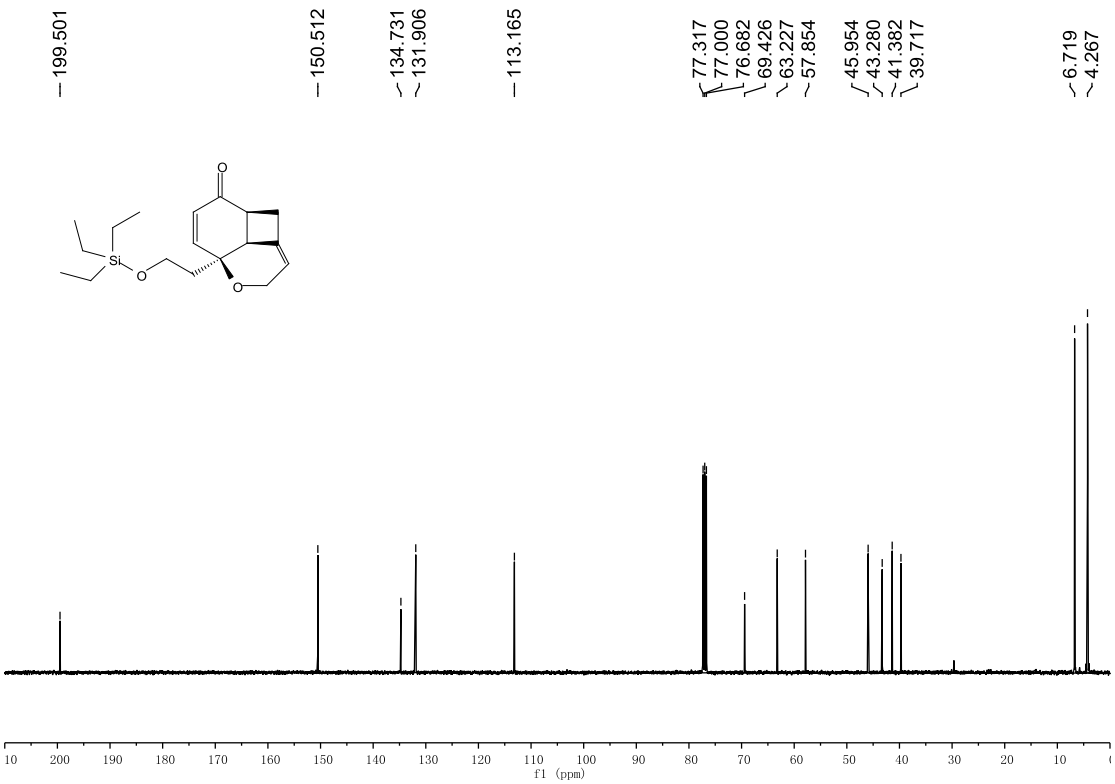


Fig. S63. ^{13}C NMR Spectrum of **4h** (100 MHz, $CDCl_3$).

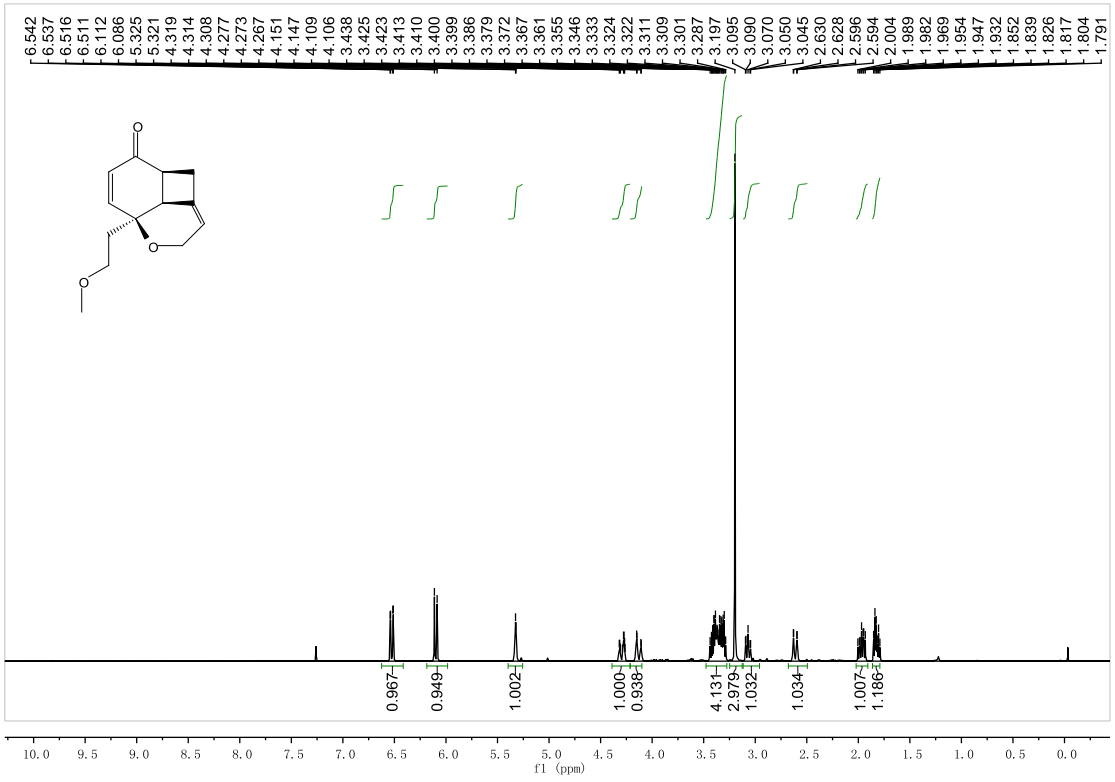


Fig. S64. ^{1}H NMR Spectrum of **4i** (400 MHz, $CDCl_3$).

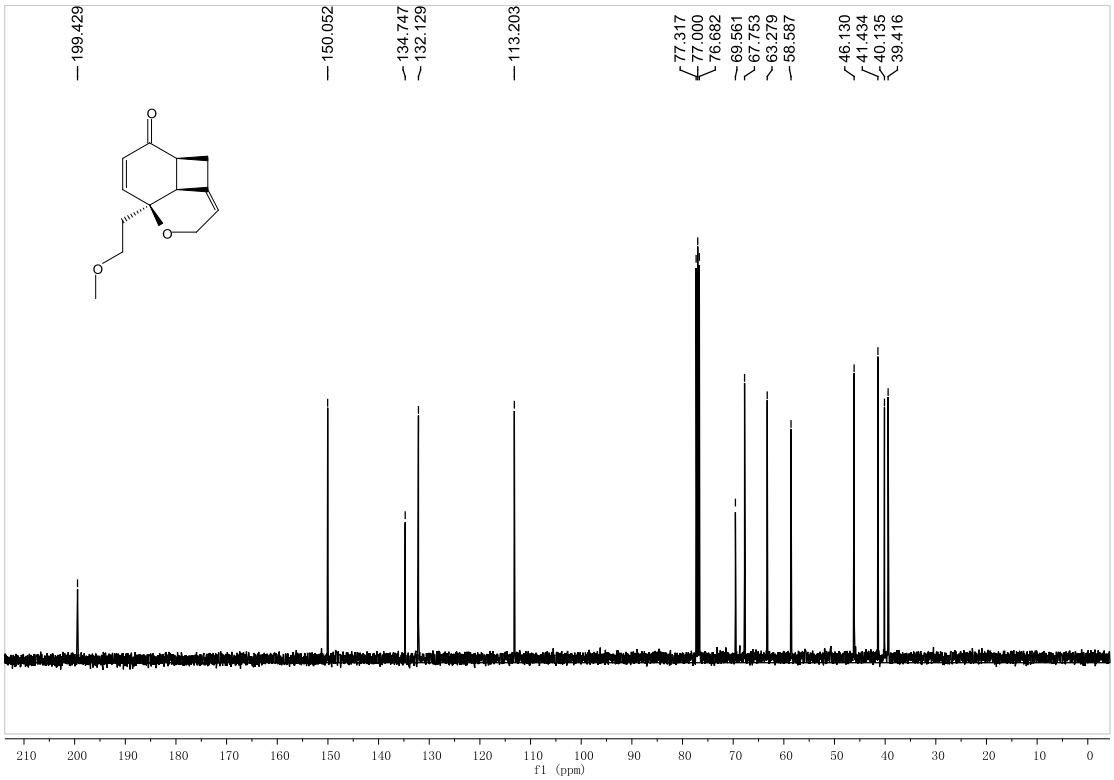


Fig. S65. ^{13}C NMR Spectrum of **4i** (100 MHz, $CDCl_3$).

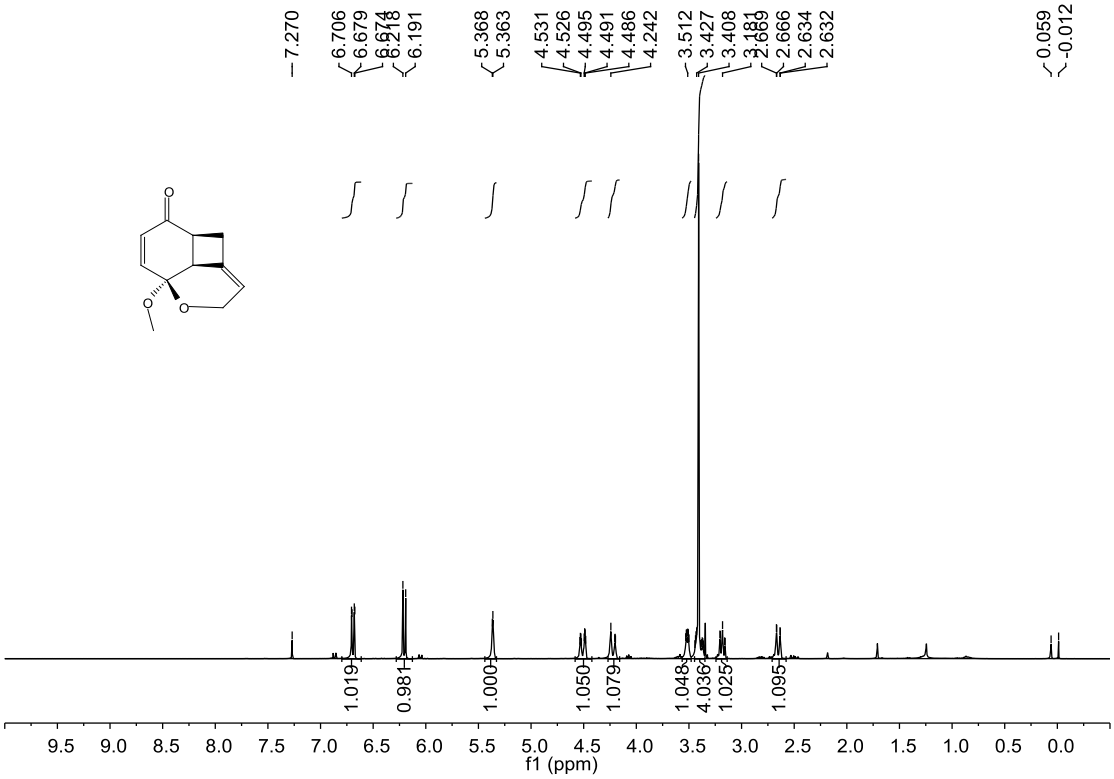


Fig. S66. ^{1}H NMR Spectrum of **4j** (400 MHz, $CDCl_3$).

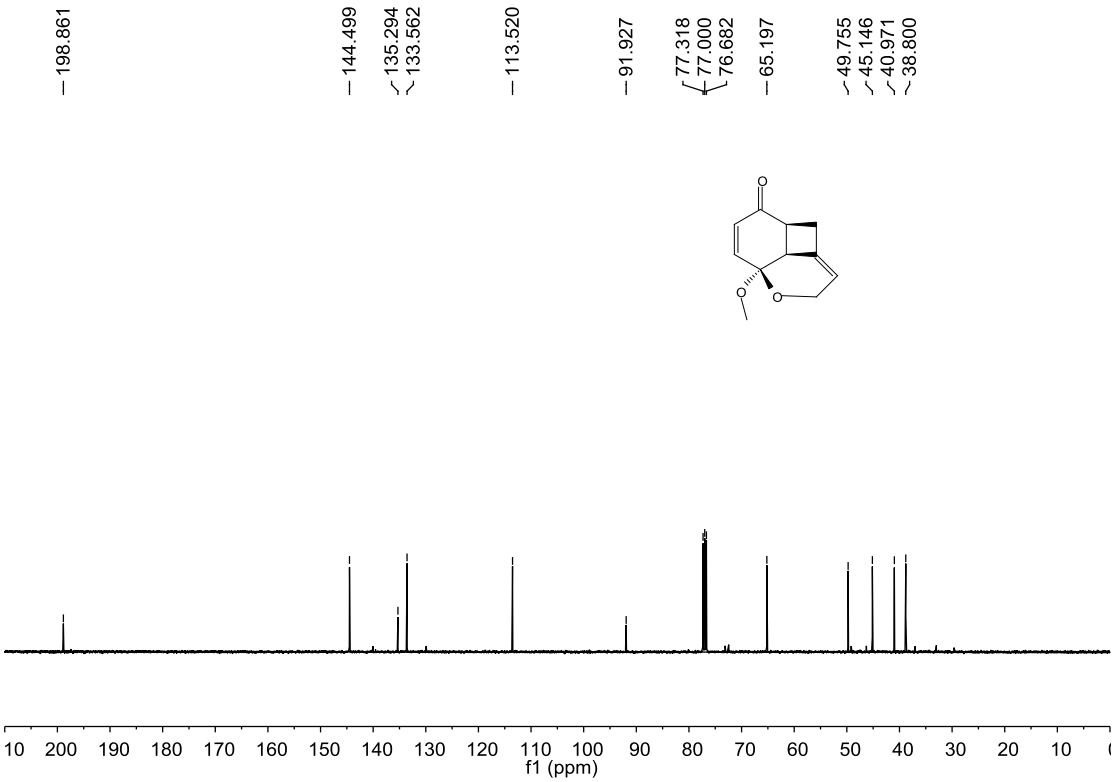


Fig. S67. ^{13}C NMR Spectrum of **4j** (100 MHz, $CDCl_3$).

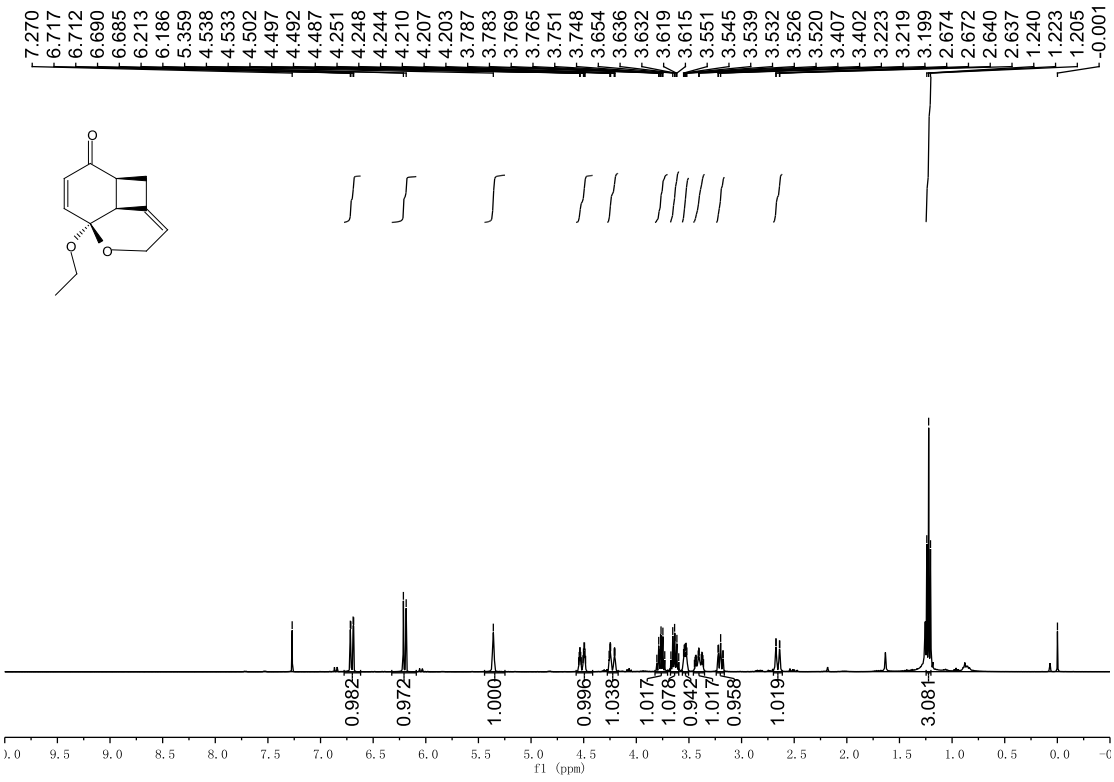


Fig. S68. ^{1}H NMR Spectrum of **4k** (400 MHz, $CDCl_3$).

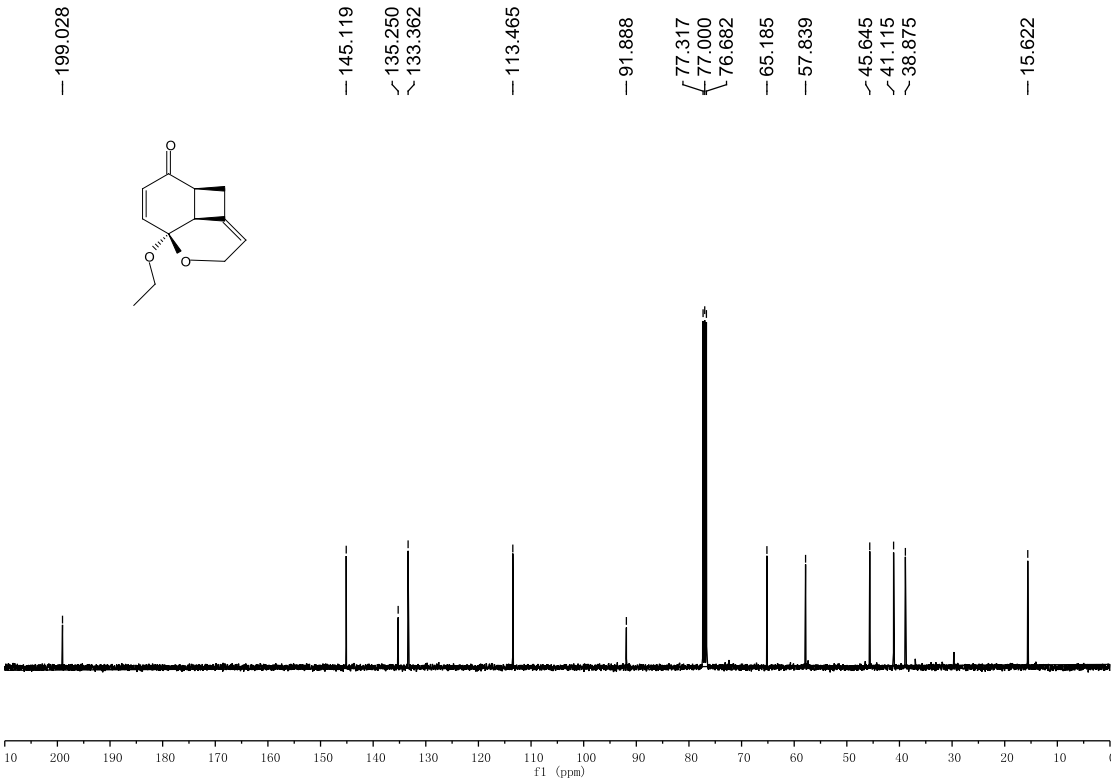


Fig. S69. ^{13}C NMR Spectrum of **4k** (100 MHz, $CDCl_3$).

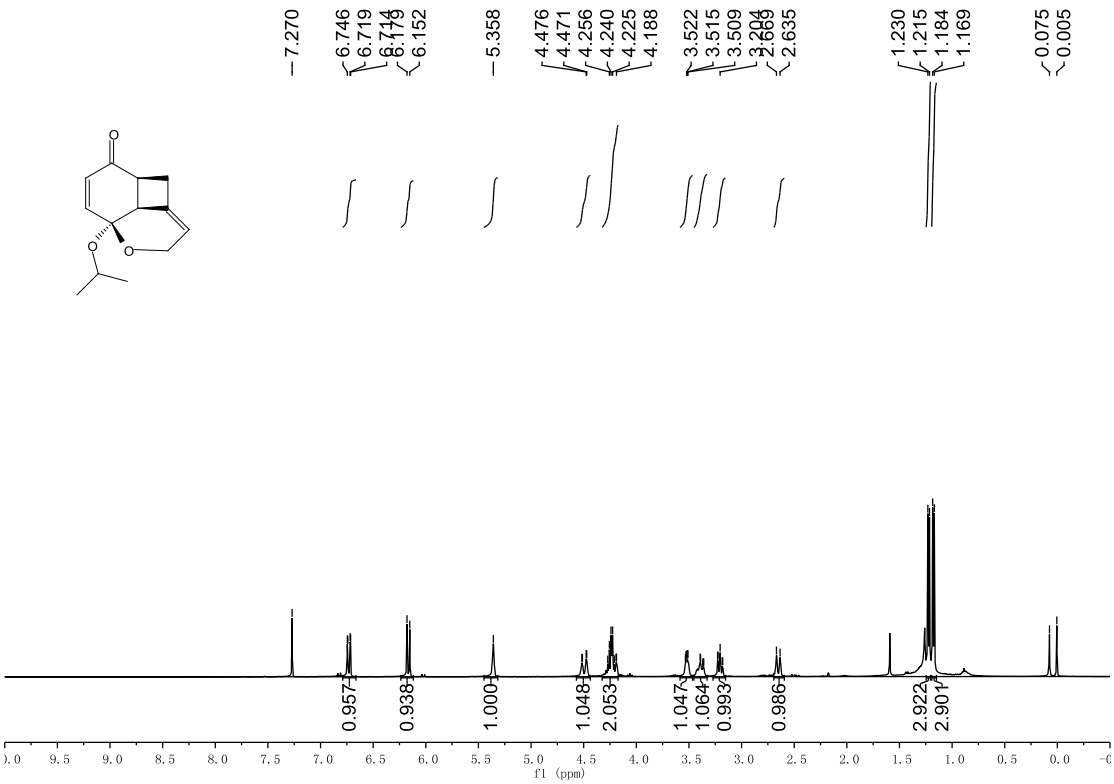


Fig. S70. ^{1}H NMR Spectrum of **4l** (400 MHz, $CDCl_3$).

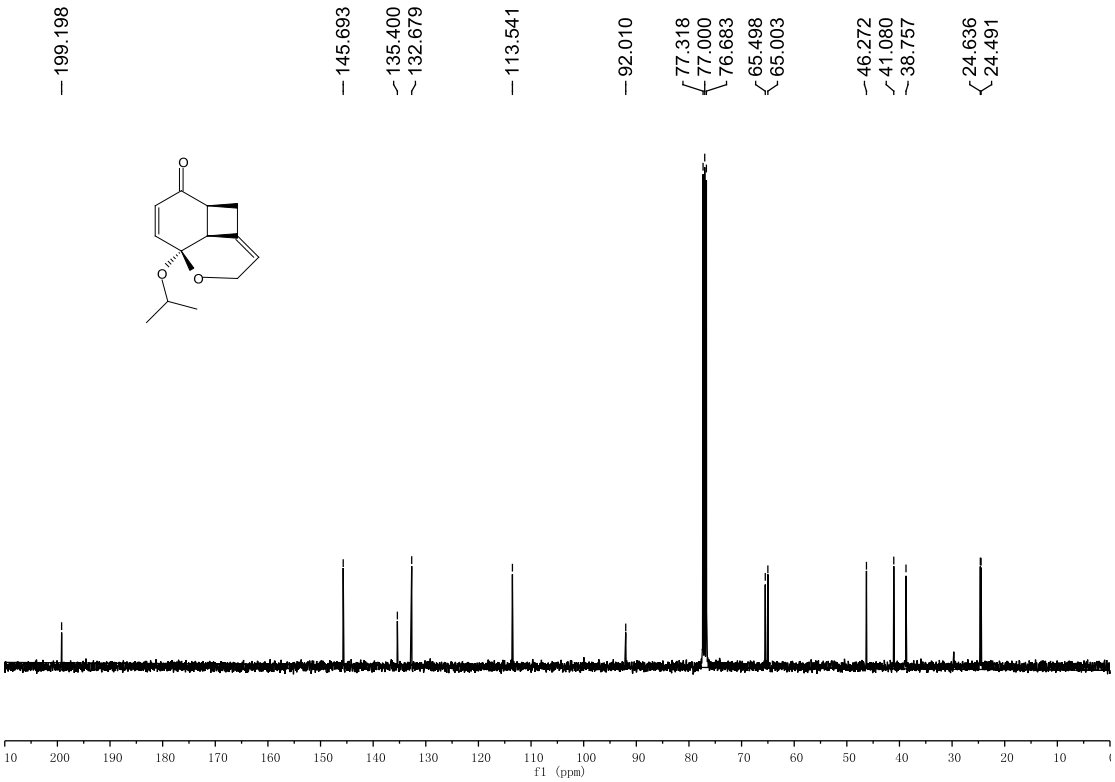


Fig. S71. ^{13}C NMR Spectrum of **4l** (100 MHz, $CDCl_3$).

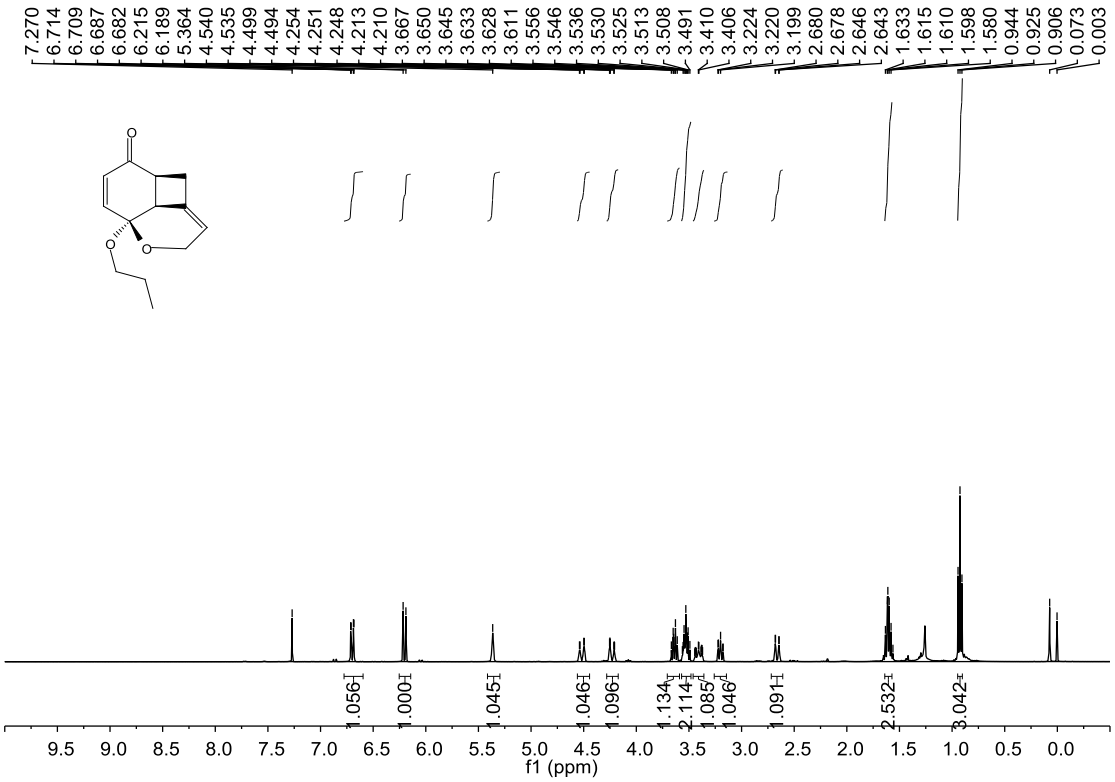


Fig. S72. ^{1}H NMR Spectrum of **4m** (400 MHz, $CDCl_3$).

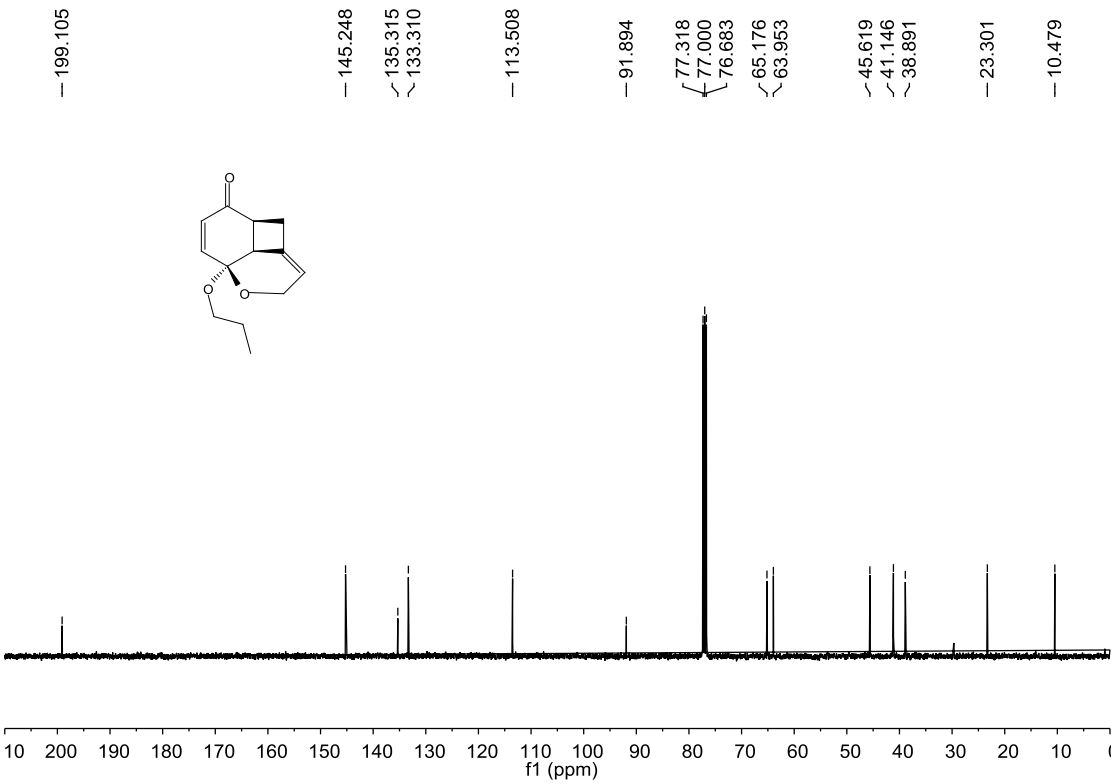


Fig. S73. ^{13}C NMR Spectrum of **4m** (100 MHz, $CDCl_3$).

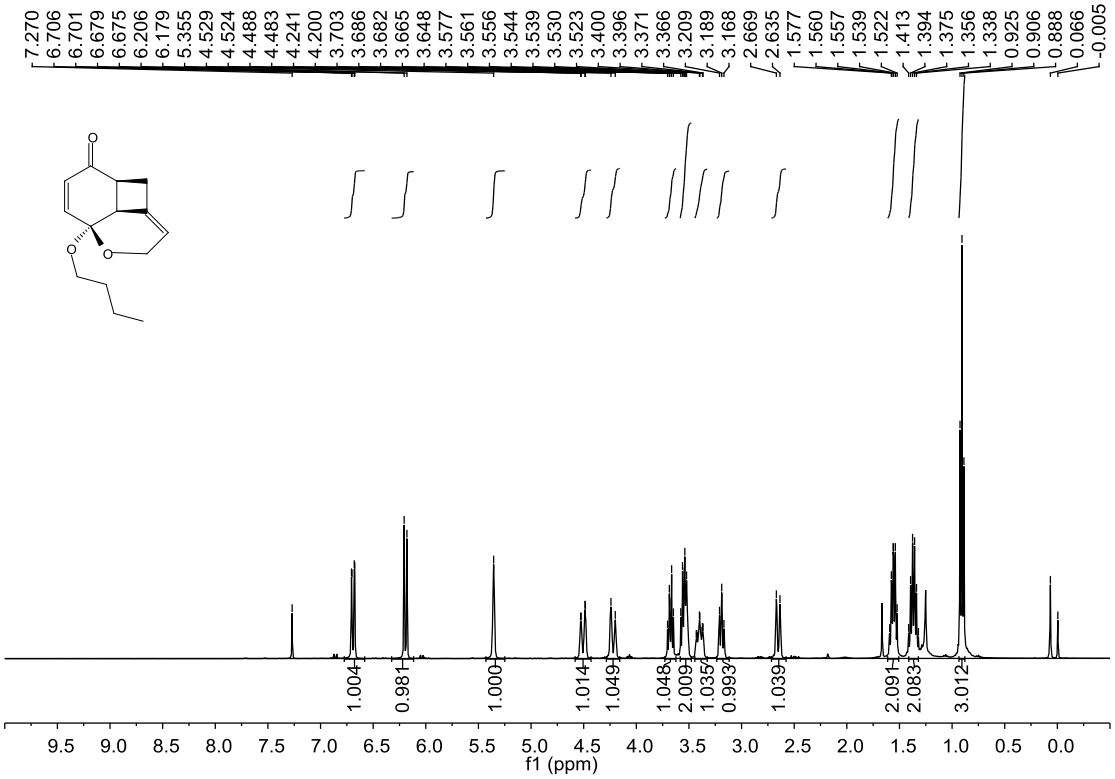


Fig. S74. ^{1}H NMR Spectrum of **4n** (400 MHz, $CDCl_3$).

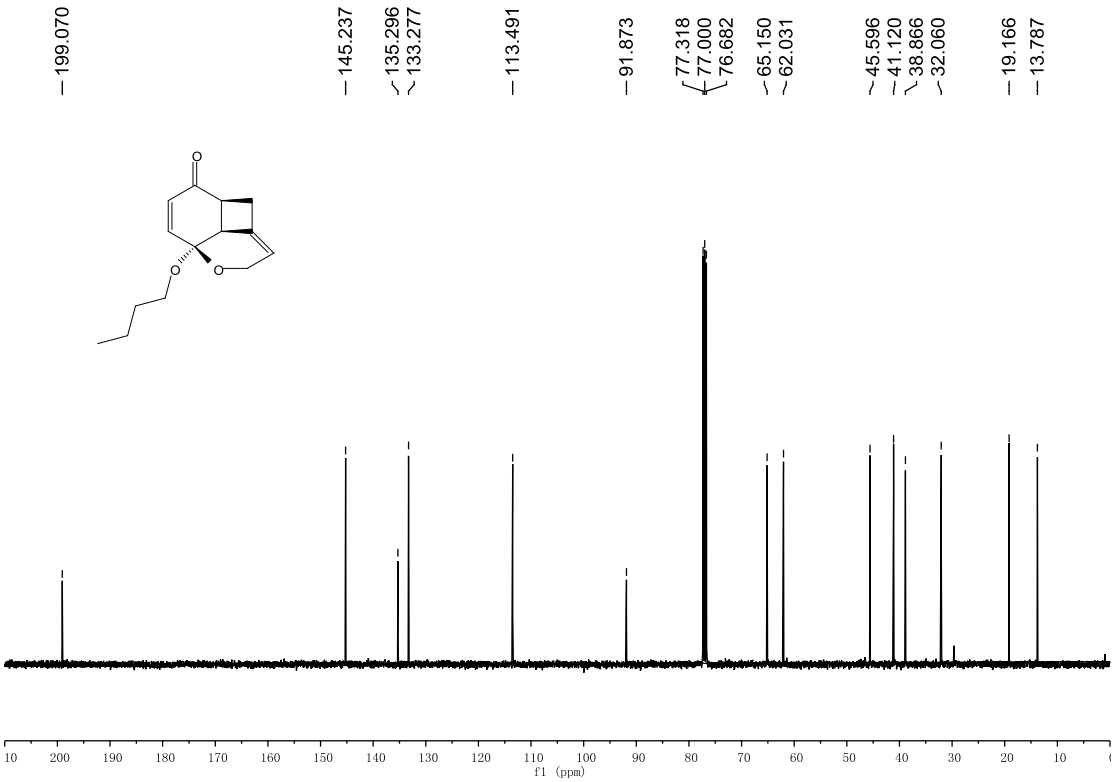


Fig. S75. ^{13}C NMR Spectrum of **4n** (100 MHz, $CDCl_3$).

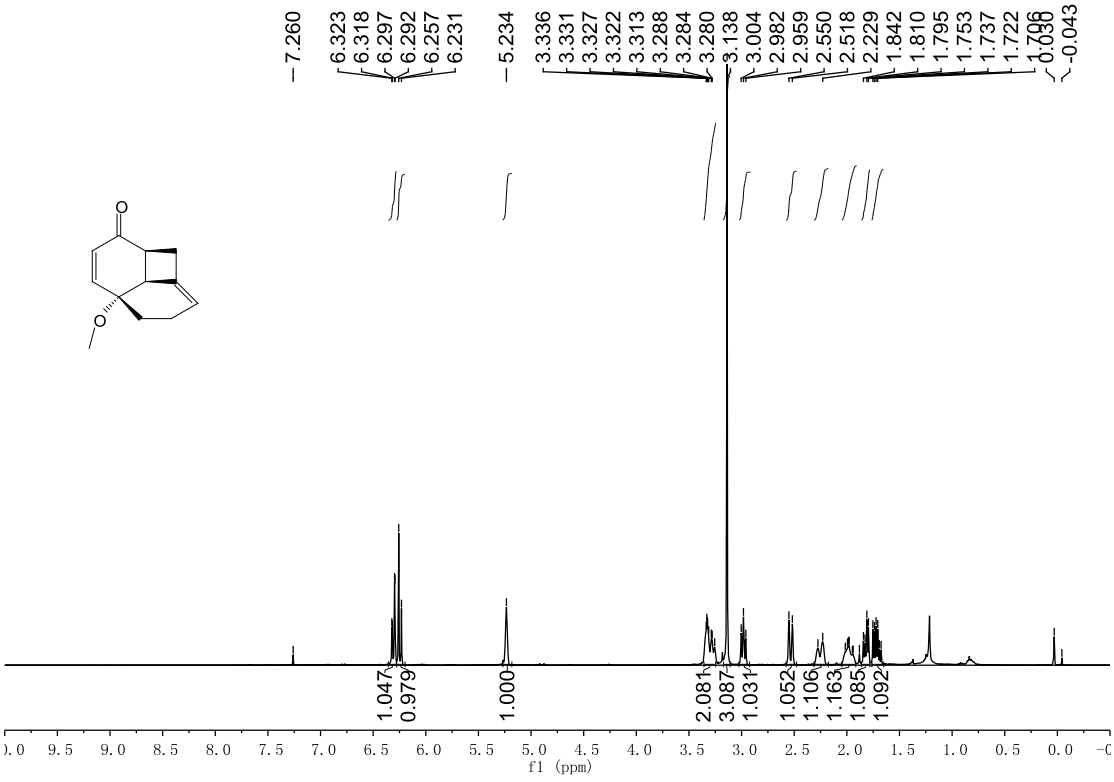


Fig. S76. ^{1}H NMR Spectrum of **4o** (400 MHz, $CDCl_3$).

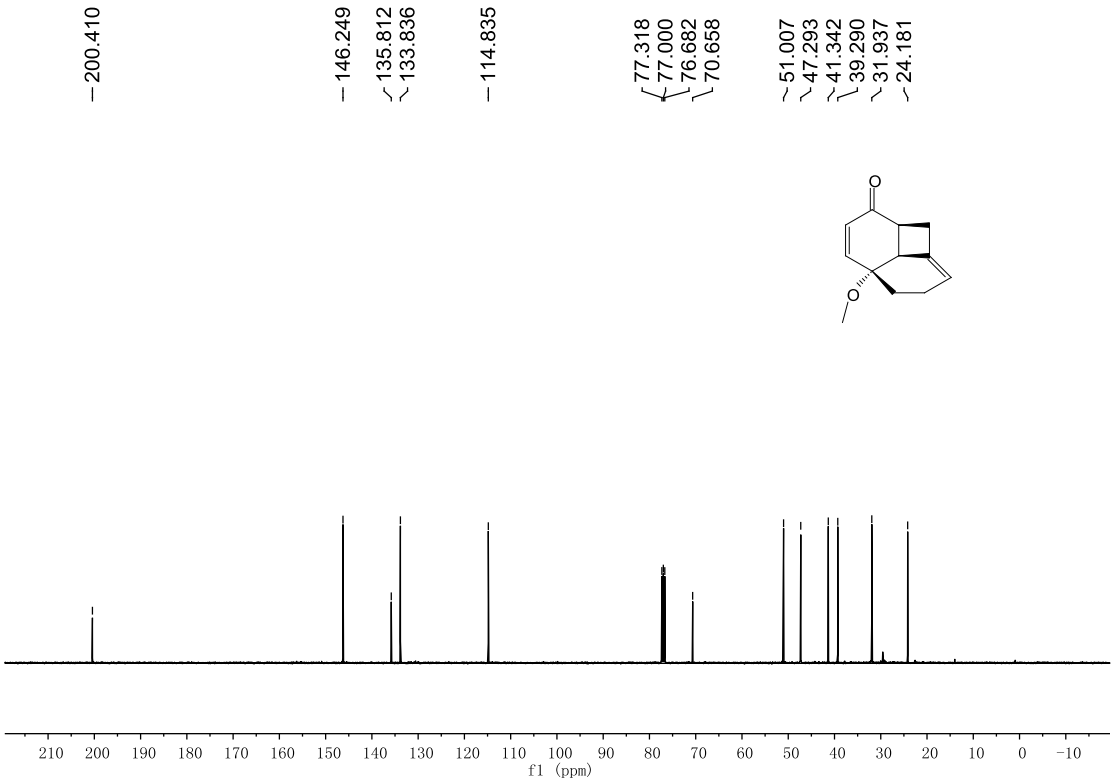


Fig. S77. ^{13}C NMR Spectrum of **4o** (100 MHz, $CDCl_3$).

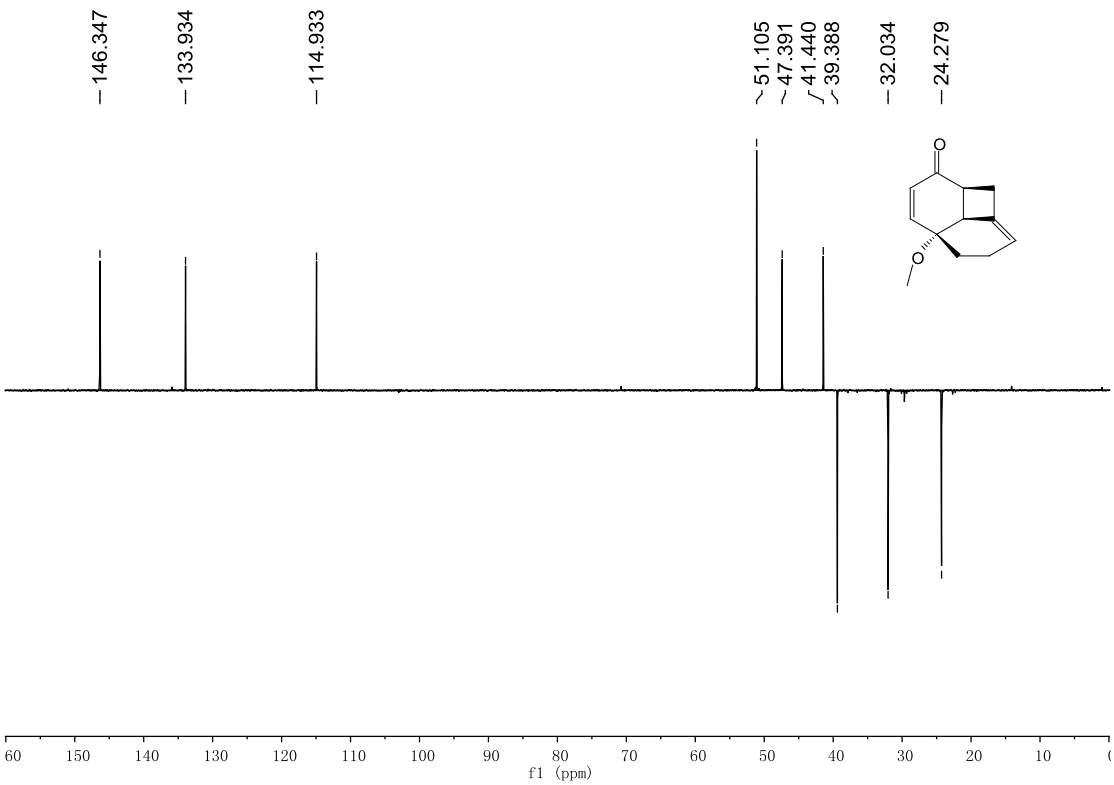


Fig. S78. DEPT 135 Spectrum of **4o** (100 MHz, $CDCl_3$).

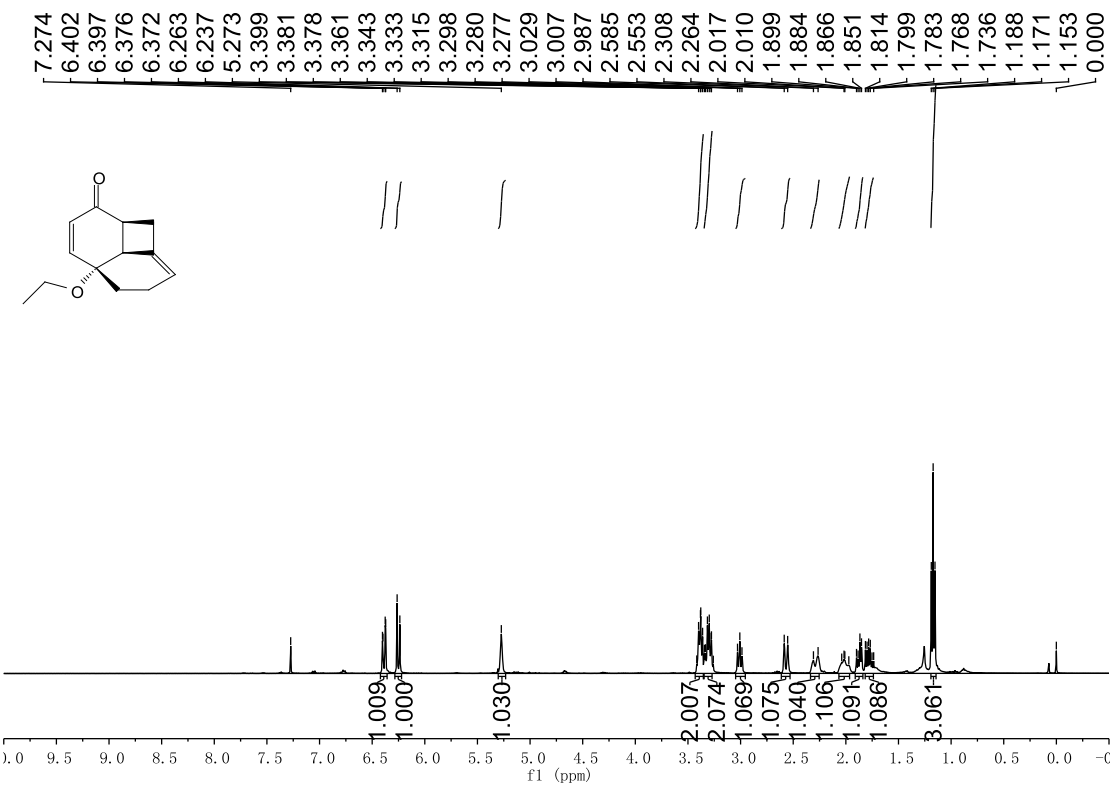


Fig. S79. ^{1}H NMR Spectrum of **4p** (400 MHz, $CDCl_3$).

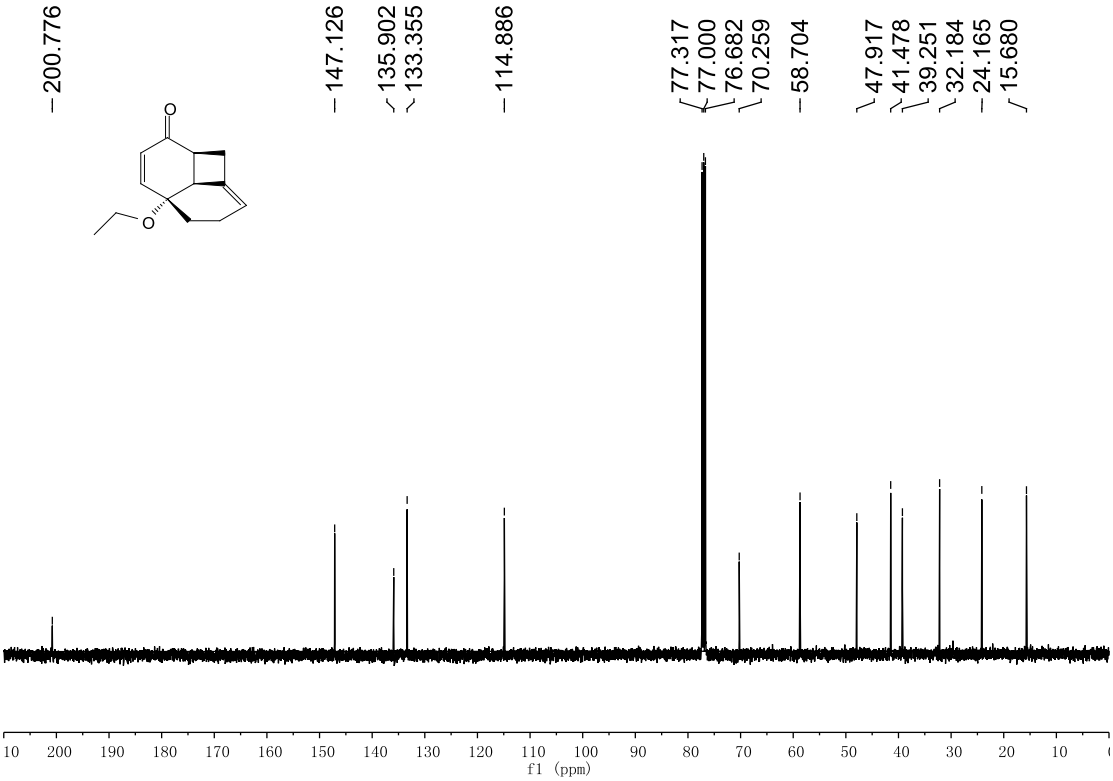


Fig. S80. ^{13}C NMR Spectrum of **4p** (100 MHz, $CDCl_3$).

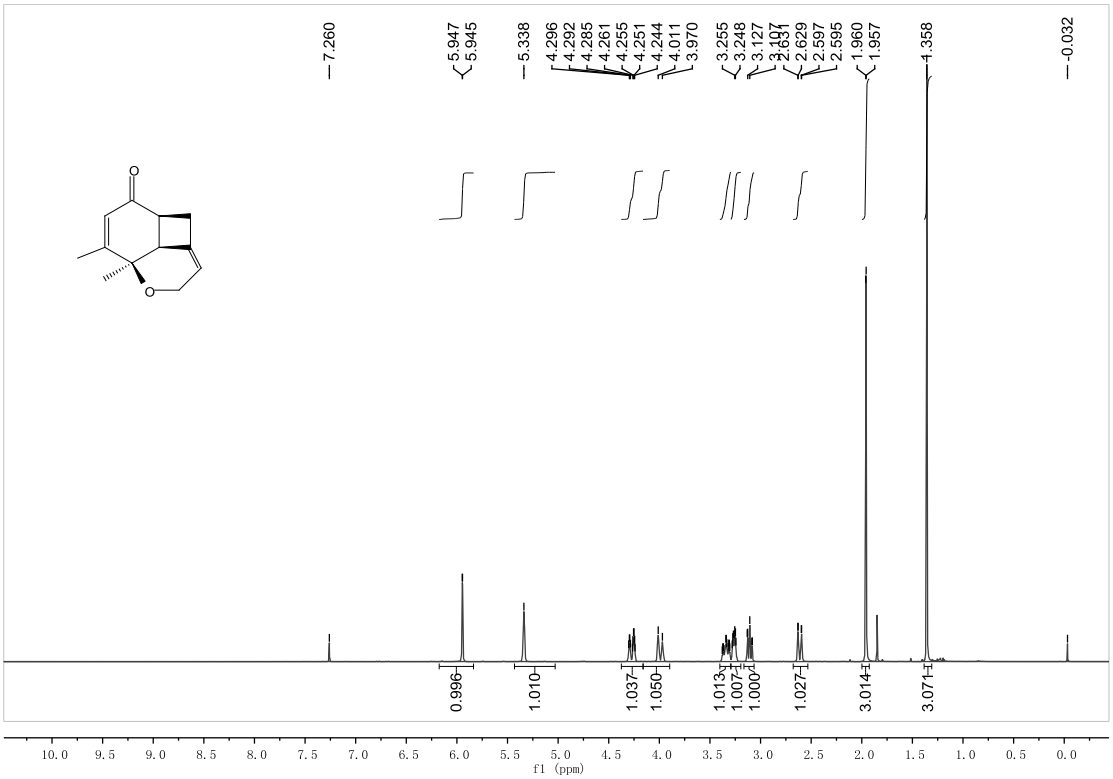


Fig. S81. ^{1}H NMR Spectrum of **4r** (400 MHz, $CDCl_3$).

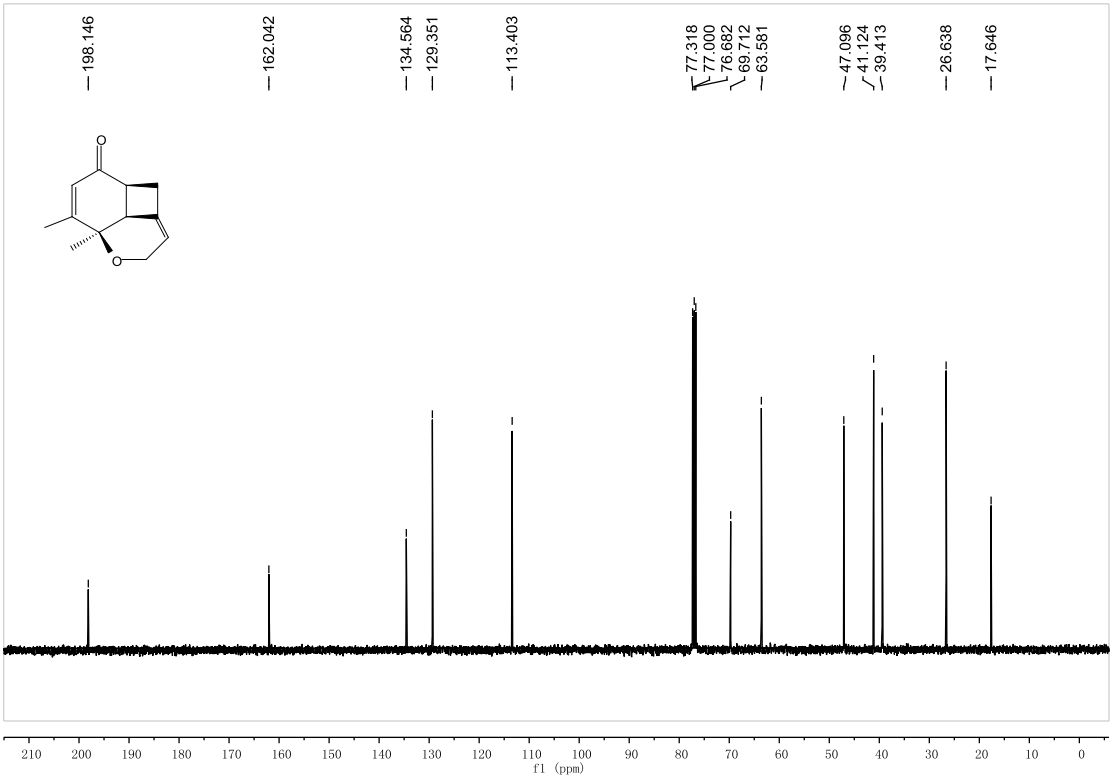


Fig. S82. ^{13}C NMR Spectrum of **4r** (100 MHz, $CDCl_3$).

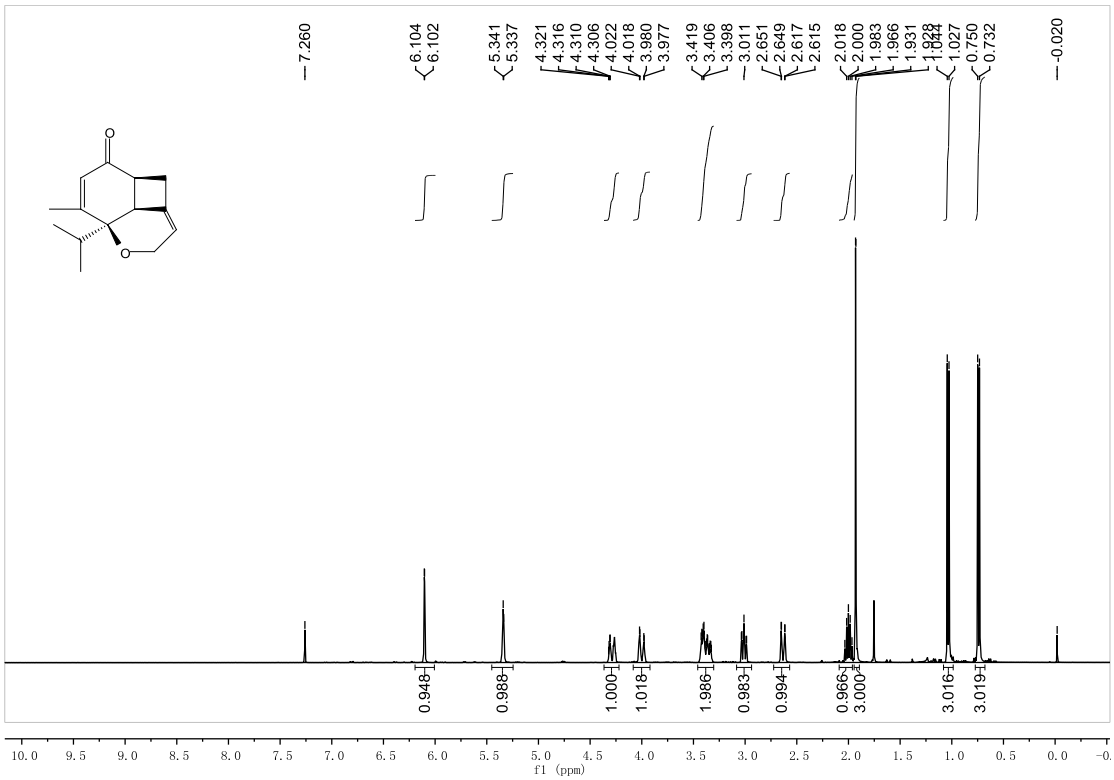


Fig. S83. ^{1}H NMR Spectrum of **4s** (400 MHz, $CDCl_3$).

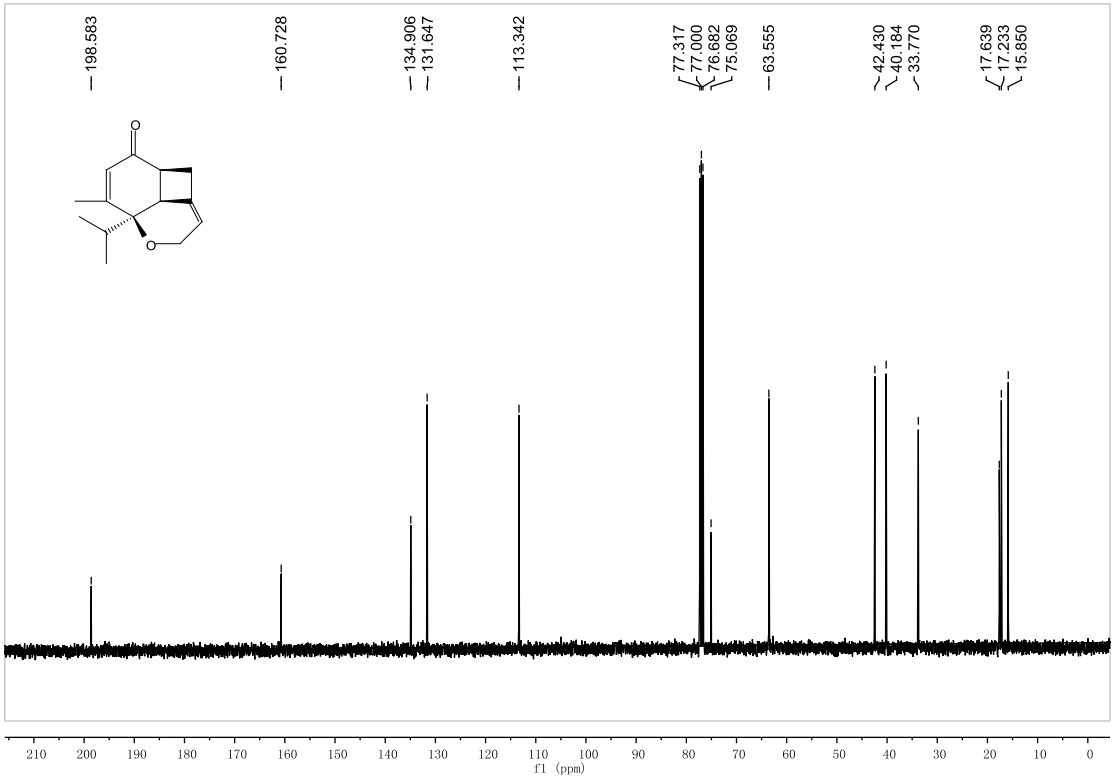


Fig. S84. ^{13}C NMR Spectrum of **4s** (100 MHz, $CDCl_3$).

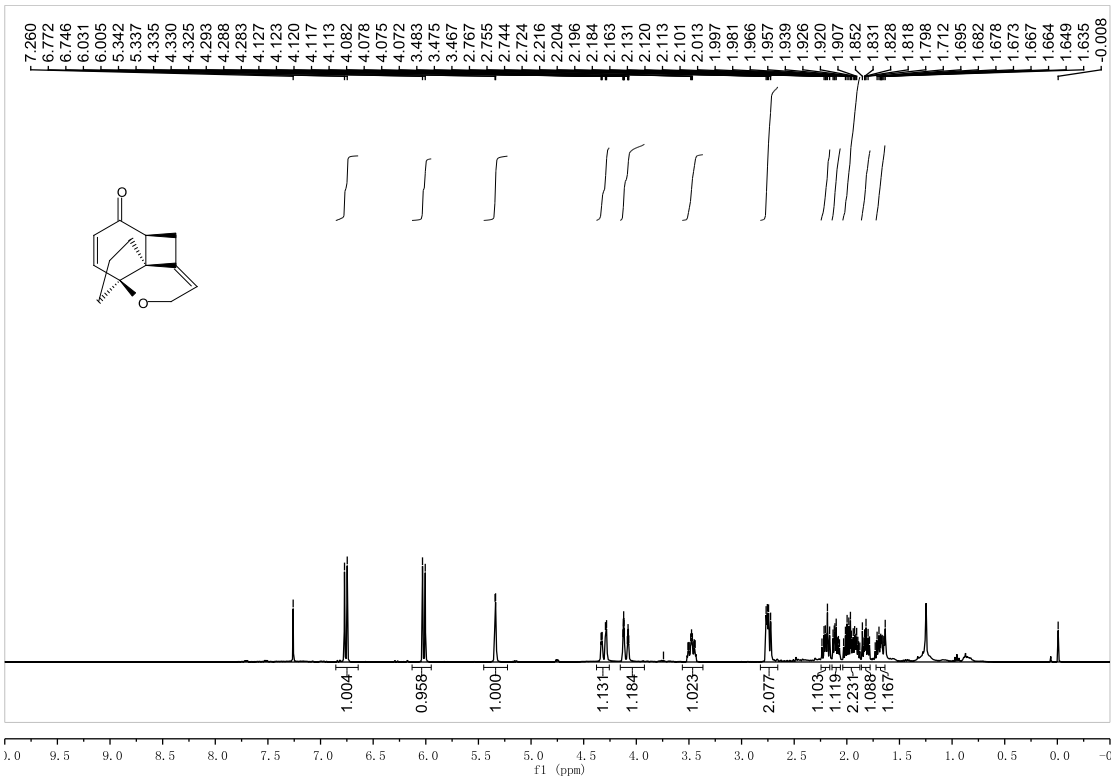


Fig. S85. ^{1}H NMR Spectrum of **4t** (400 MHz, $CDCl_3$).

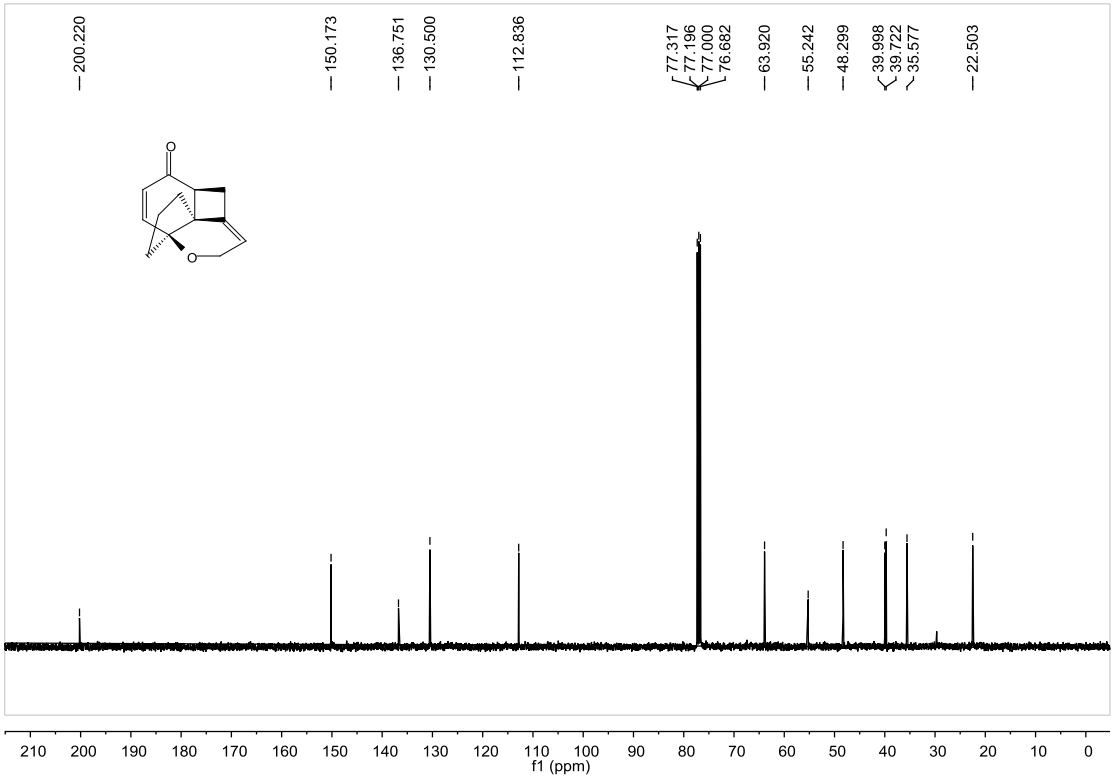


Fig. S86. ^{13}C NMR Spectrum of **4t** (100 MHz, $CDCl_3$).

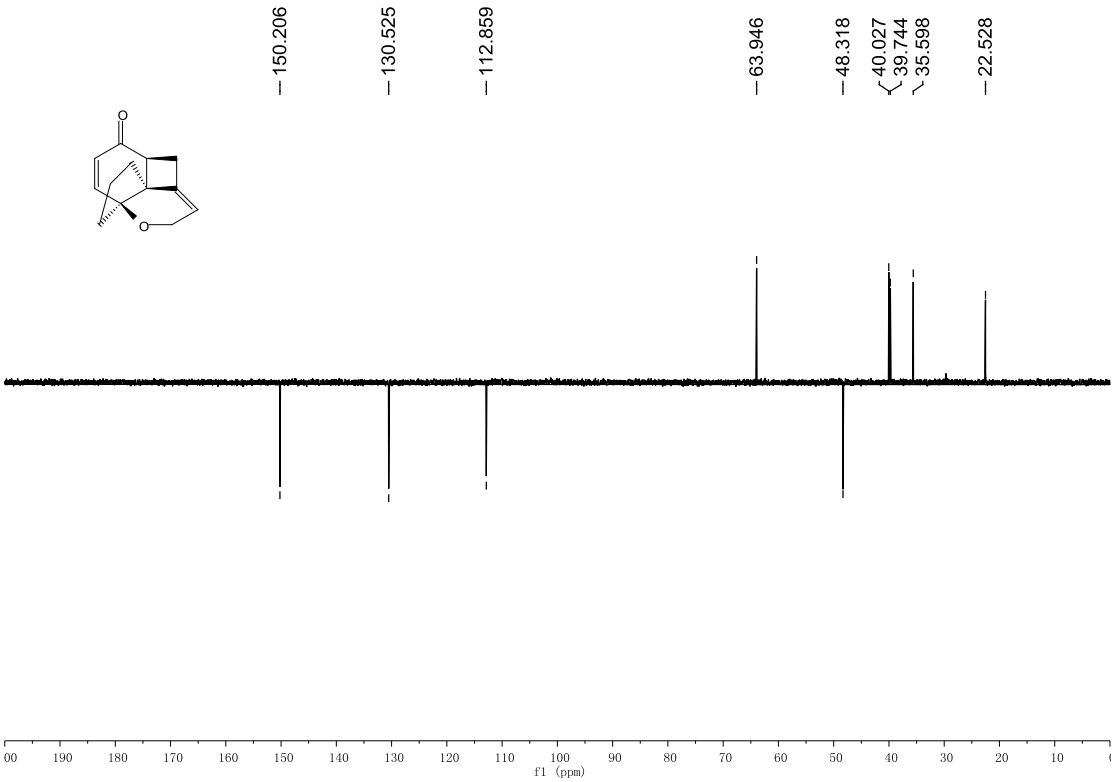


Fig. S87. DEPT 135 Spectrum of **4t** (100 MHz, $CDCl_3$).

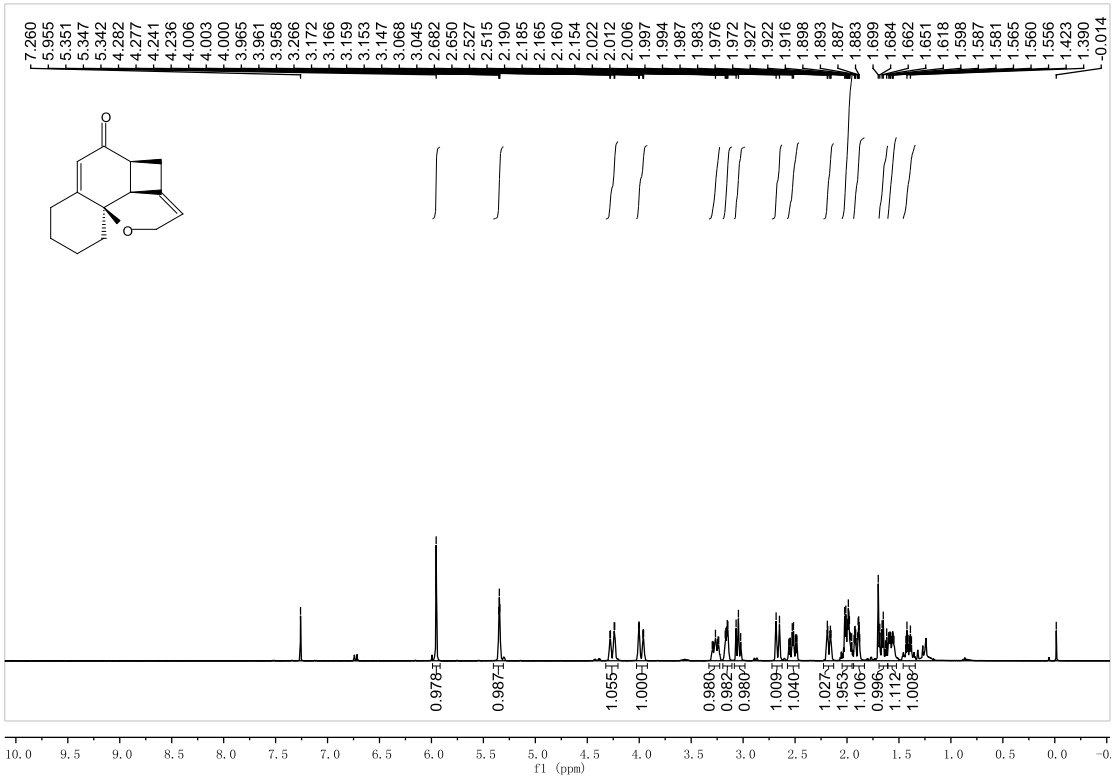


Fig. S88. ^{1}H NMR Spectrum of **4u** (400 MHz, $CDCl_3$).

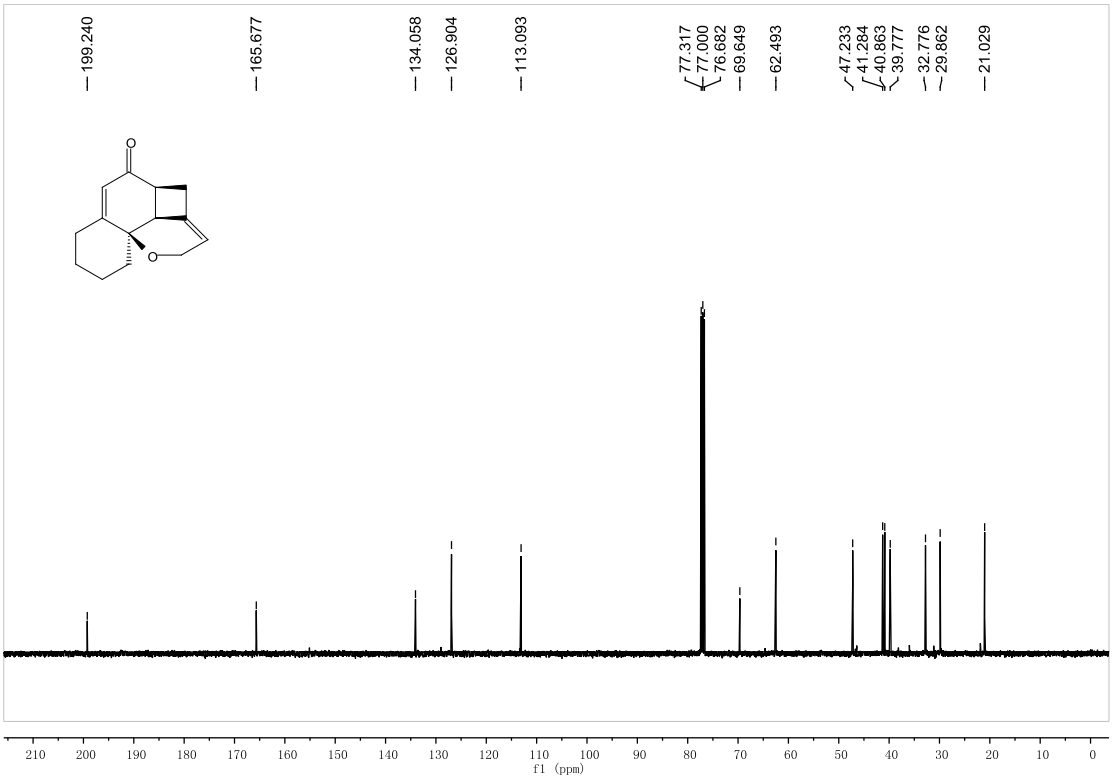


Fig. S89. ^{13}C NMR Spectrum of **4u** (100 MHz, $CDCl_3$).

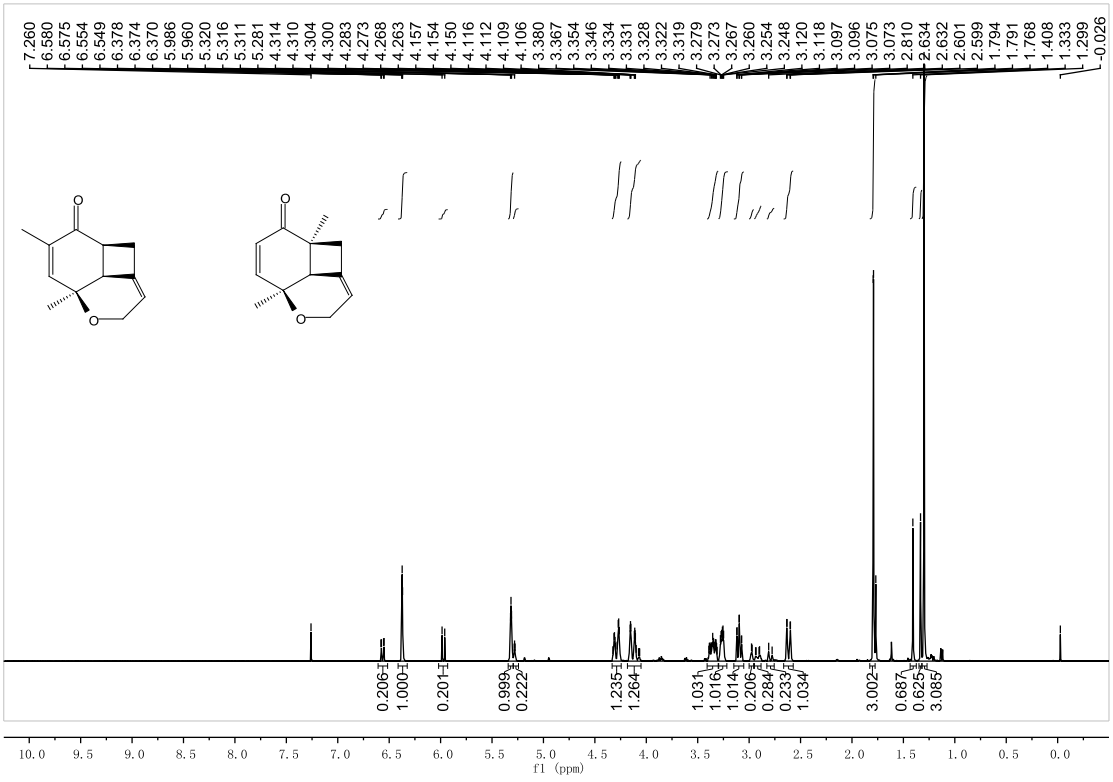


Fig. S90. ^{1}H NMR Spectrum of **4v** (400 MHz, $CDCl_3$).

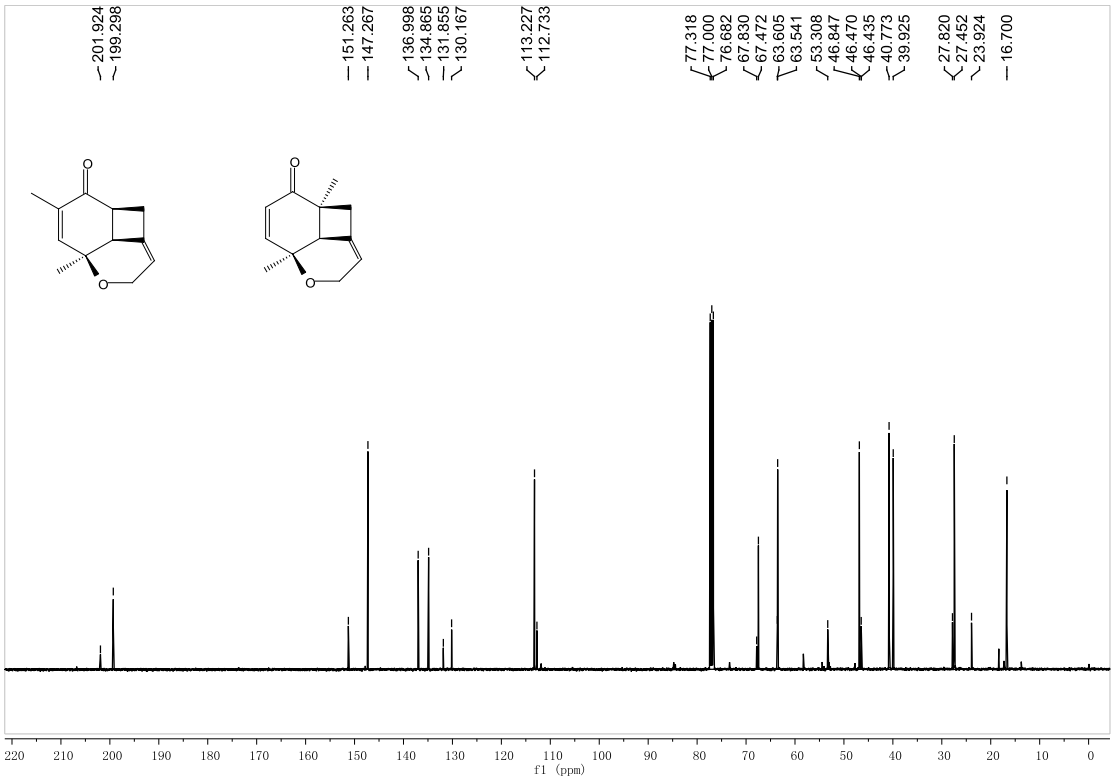


Fig. S91. ^{13}C NMR Spectrum of **4v** (100 MHz, $CDCl_3$).

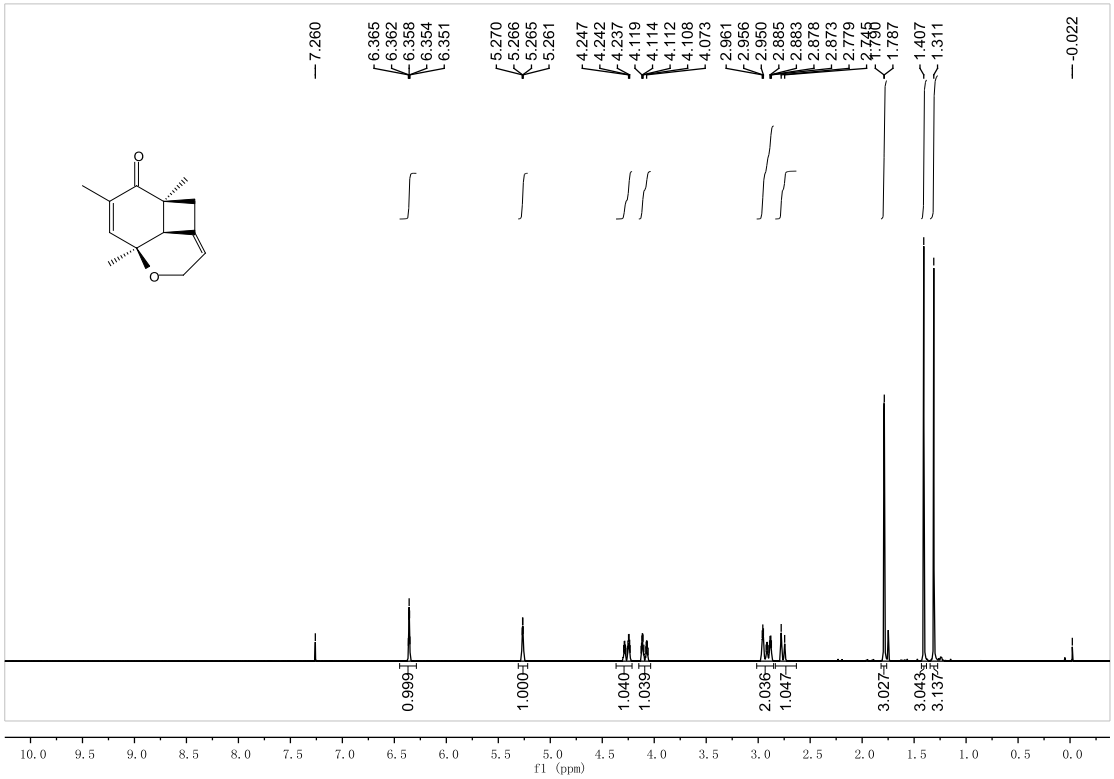


Fig. S92. ^{1}H NMR Spectrum of **4w** (400 MHz, $CDCl_3$).

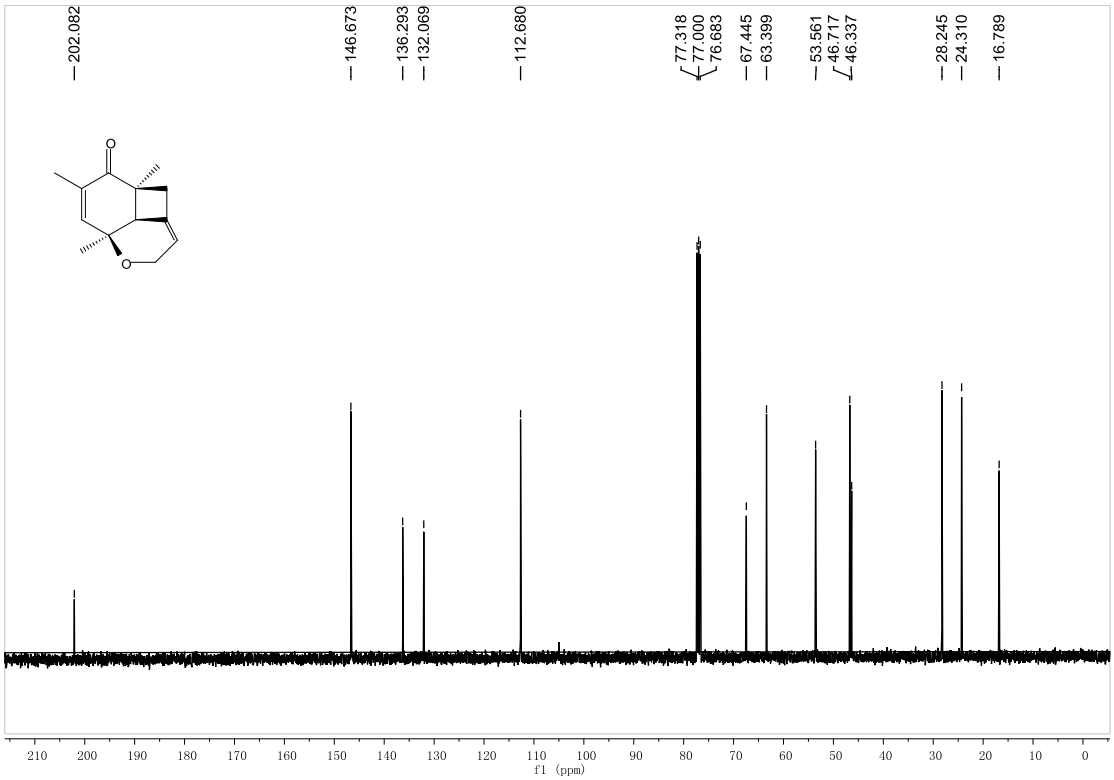


Fig. S93. ^{13}C NMR Spectrum of **4w** (100 MHz, $CDCl_3$).

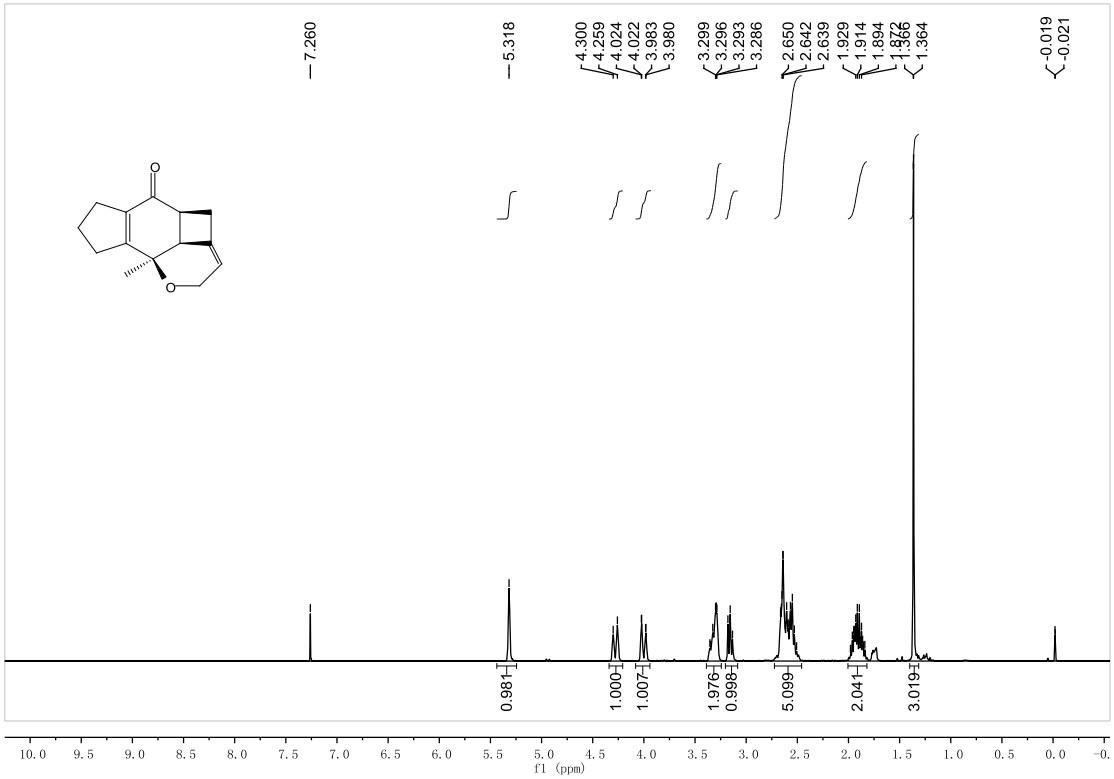


Fig. S94. ^{1}H NMR Spectrum of **4x** (400 MHz, $CDCl_3$).

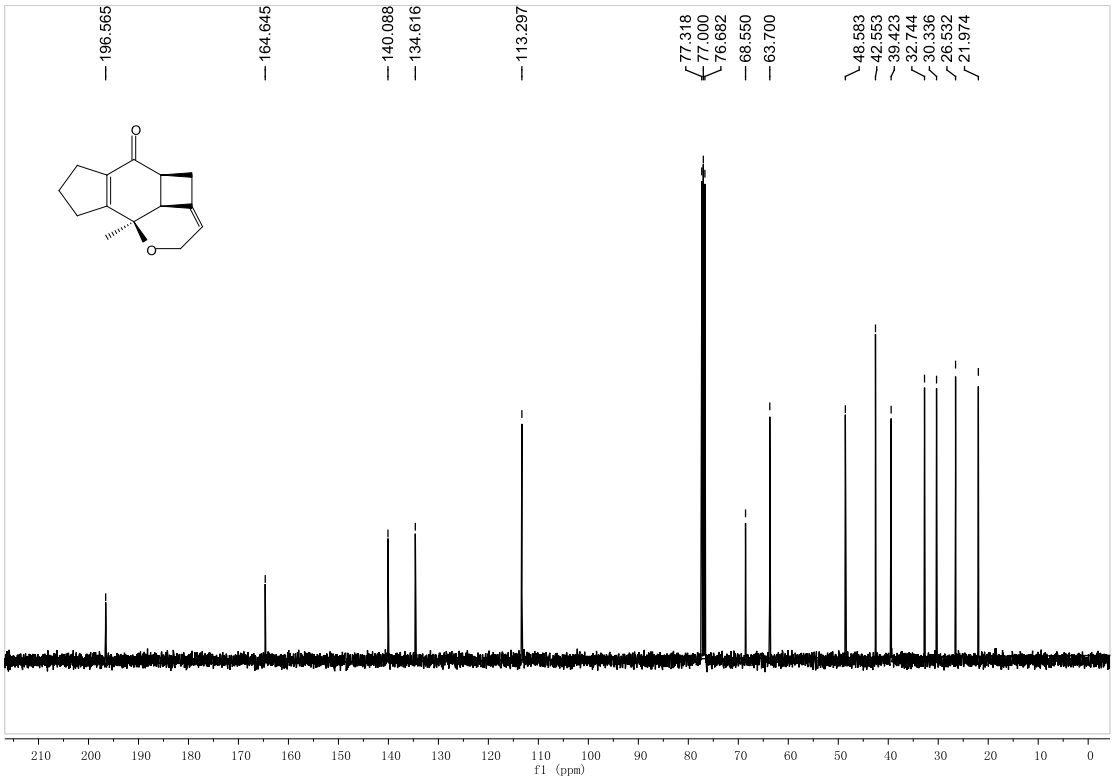


Fig. S95. ^{13}C NMR Spectrum of **4x** (100 MHz, $CDCl_3$).

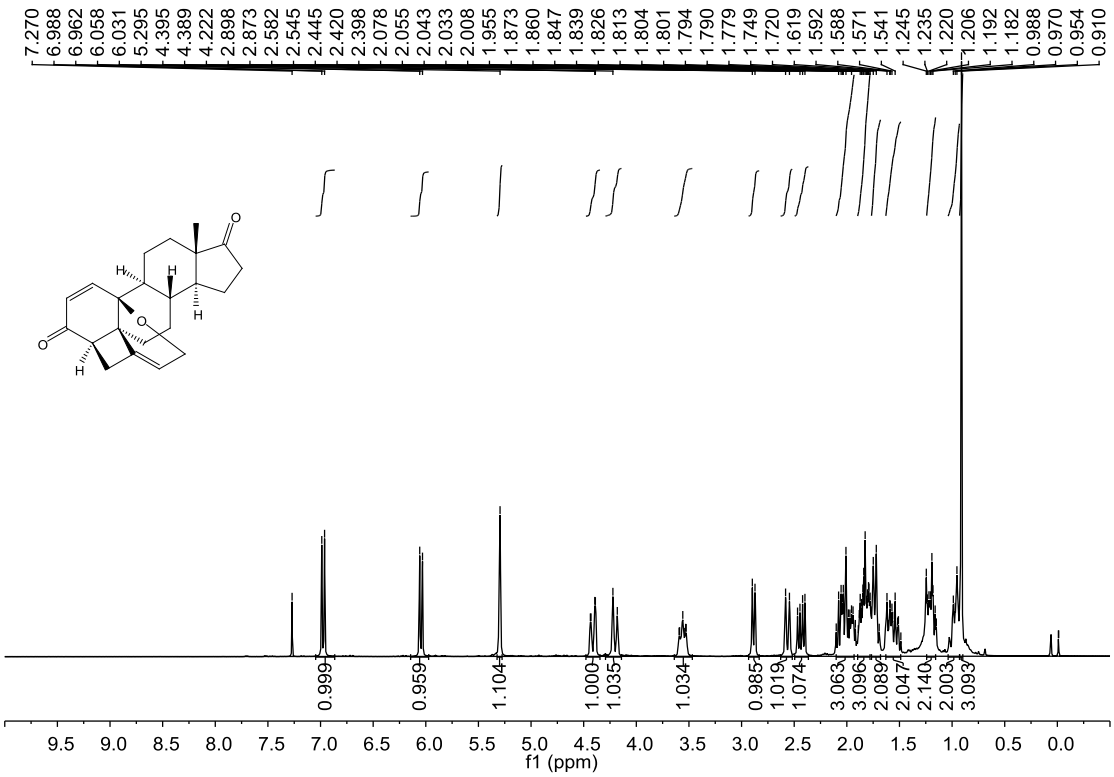


Fig. S96. ^{1}H NMR Spectrum of **4y** (400 MHz, $CDCl_3$).

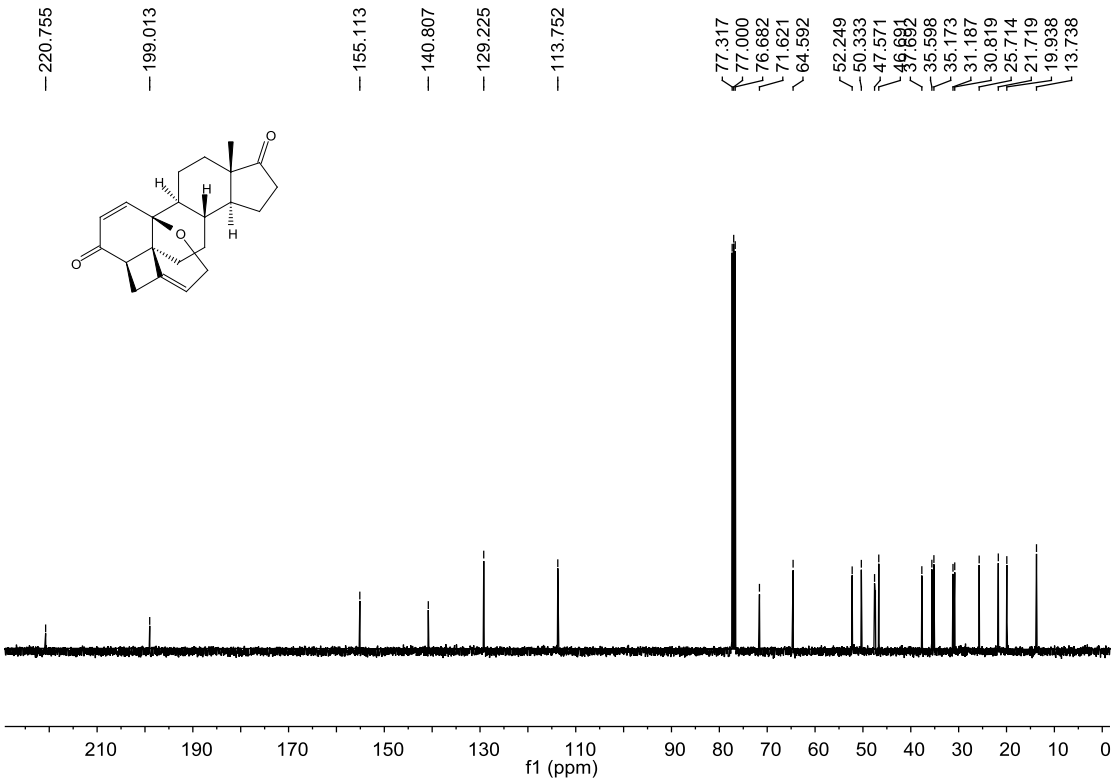


Fig. S97. ^{13}C NMR Spectrum of **4y** (100 MHz, $CDCl_3$).

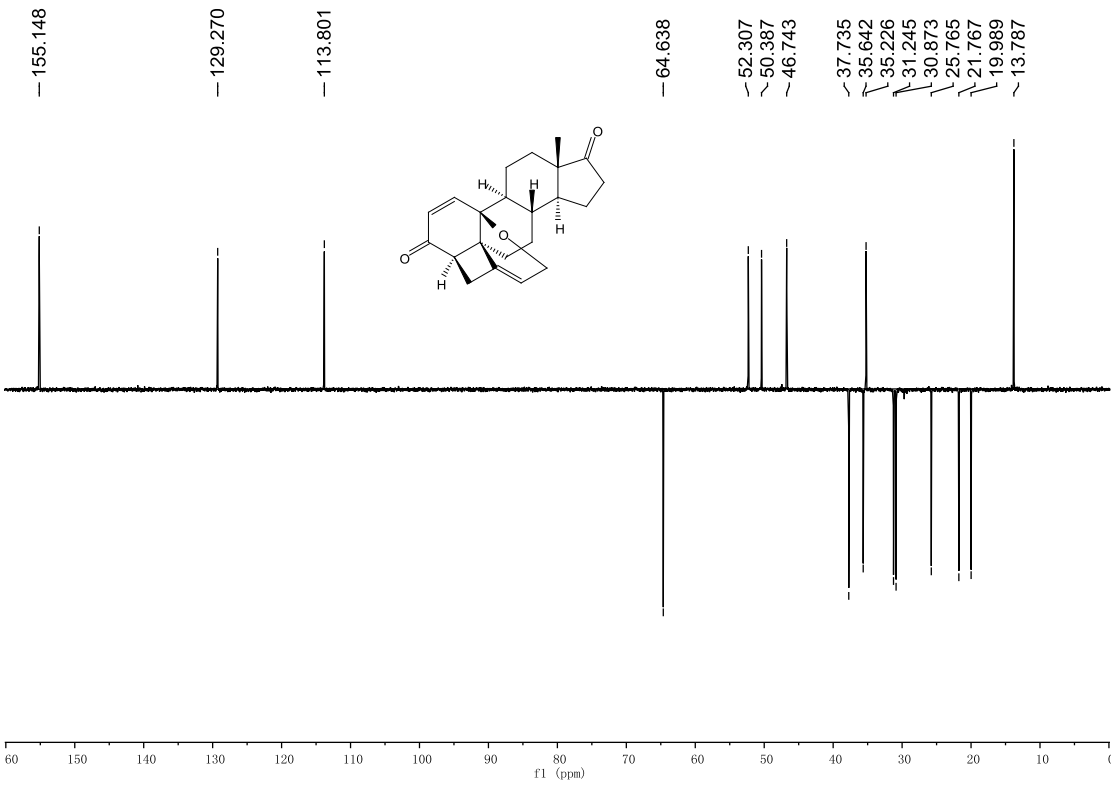


Fig. S98. DEPT 135 Spectrum of **4y** (100 MHz, $CDCl_3$).

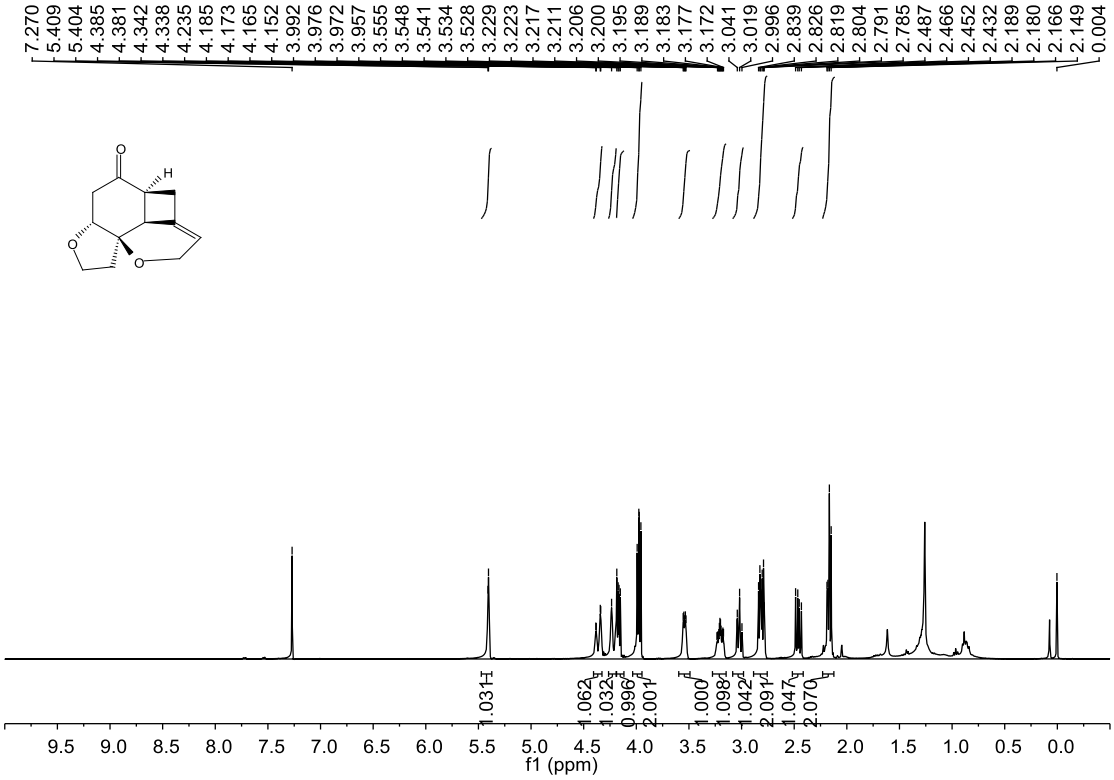


Fig. S99. ^{1}H NMR Spectrum of **5** (400 MHz, $CDCl_3$).

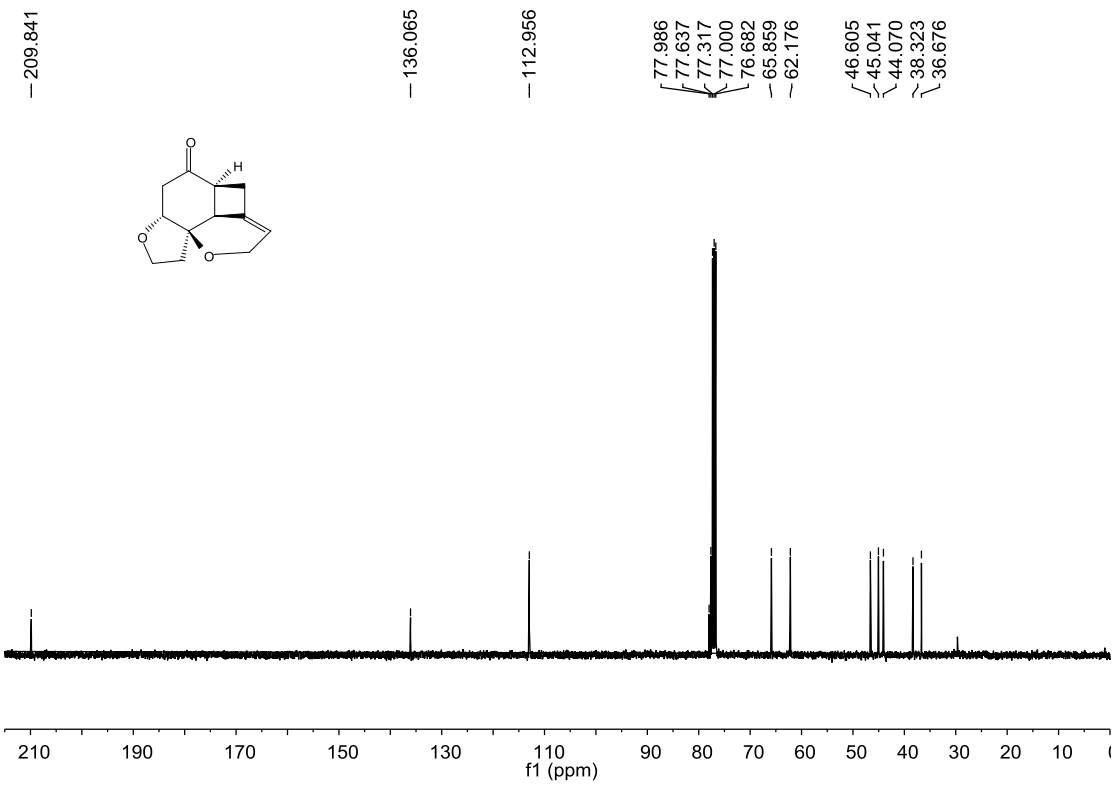


Fig. S100. ^{13}C NMR Spectrum of **5** (100 MHz, $CDCl_3$).

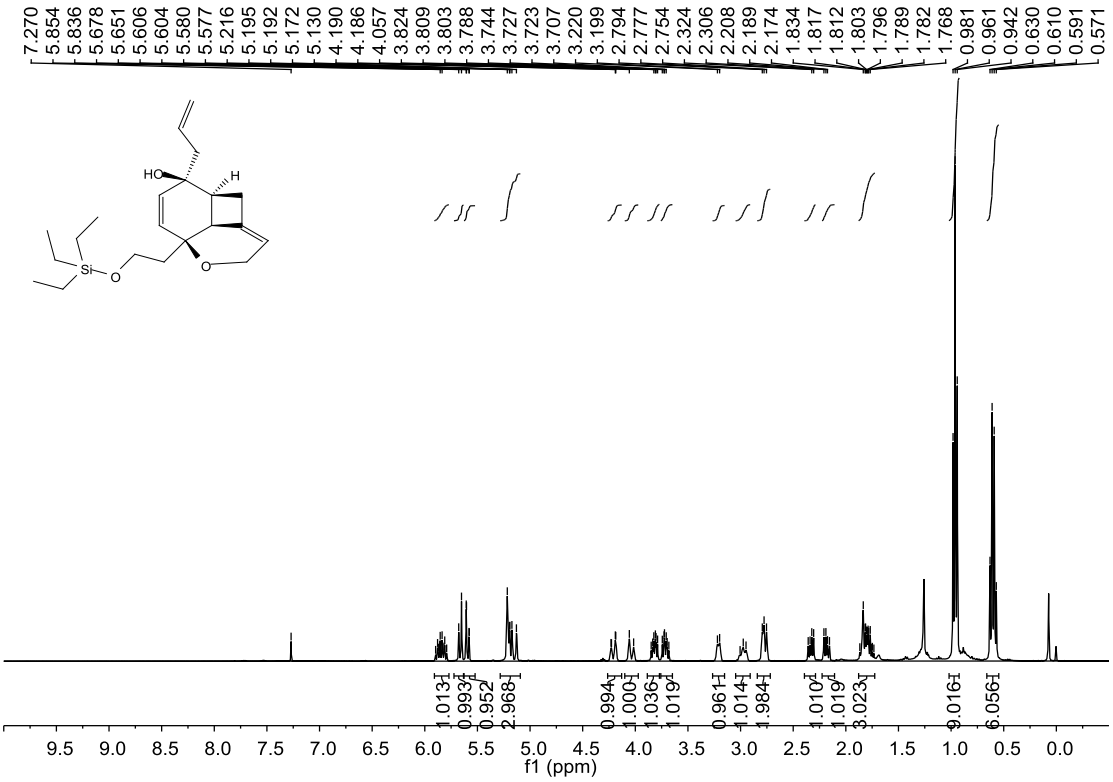


Fig. S101. ^{1}H NMR Spectrum of **6** (400 MHz, $CDCl_3$).

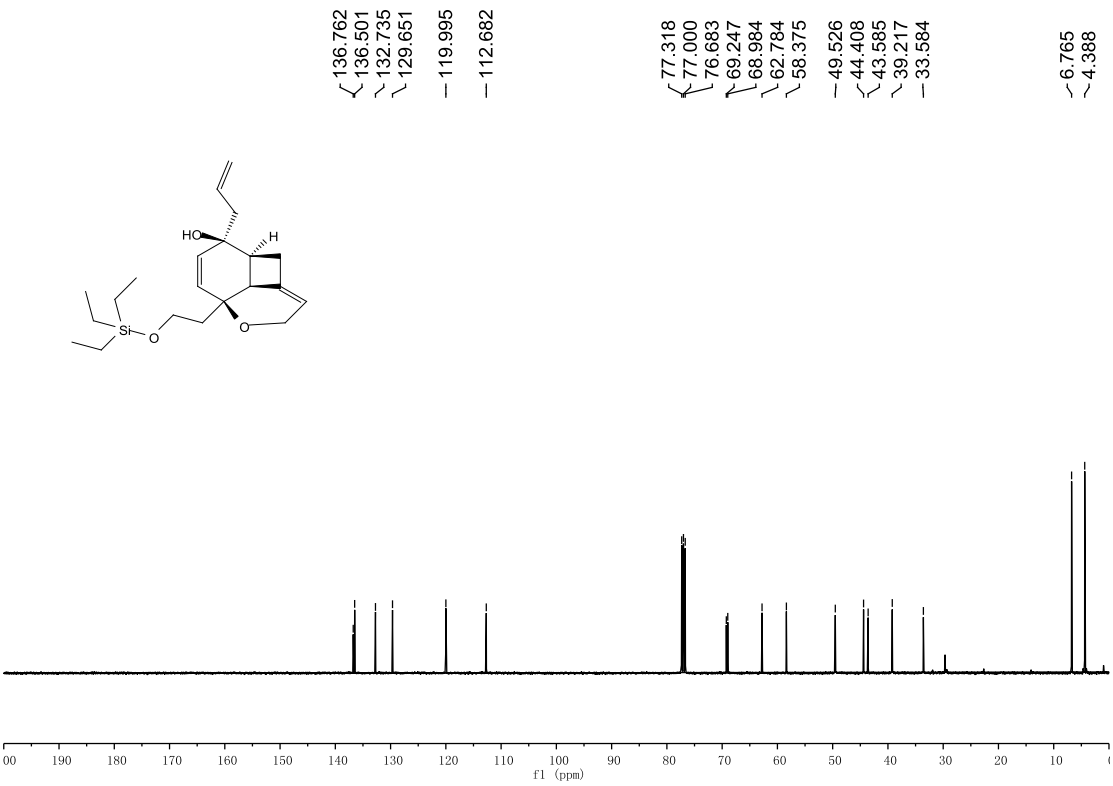


Fig. S102. ^{13}C NMR Spectrum of **6** (100 MHz, $CDCl_3$).

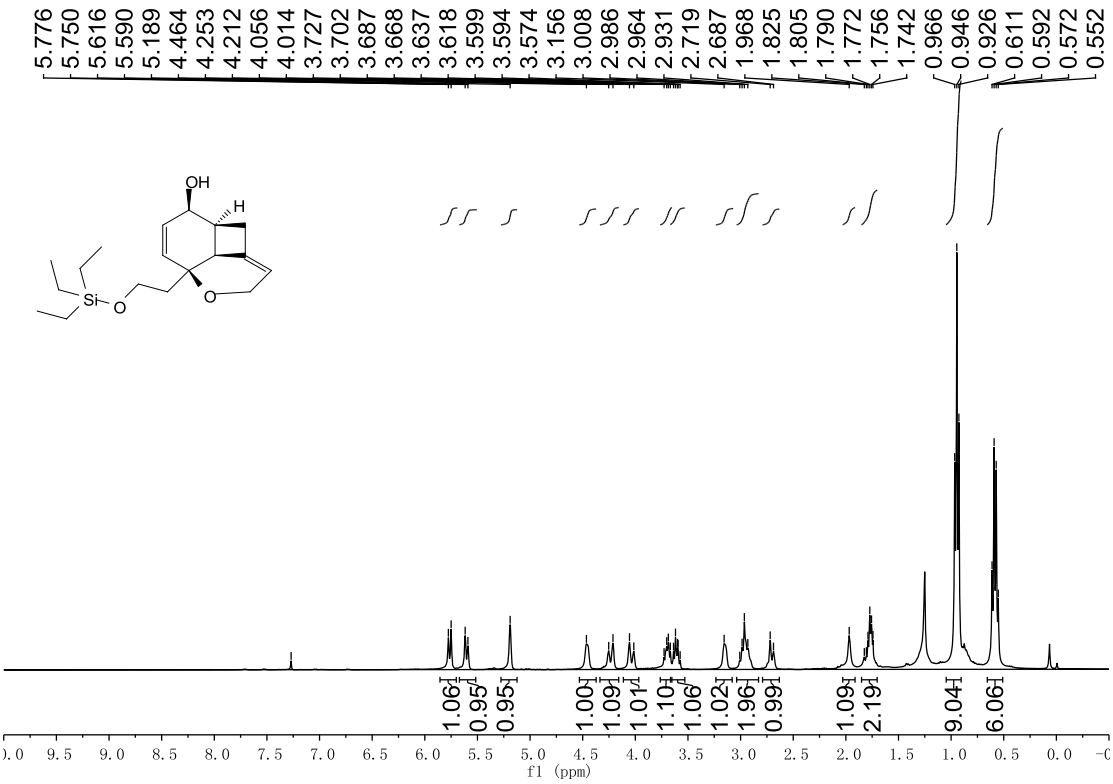


Fig. S103. ^{1}H NMR Spectrum of **7** (400 MHz, $CDCl_3$).

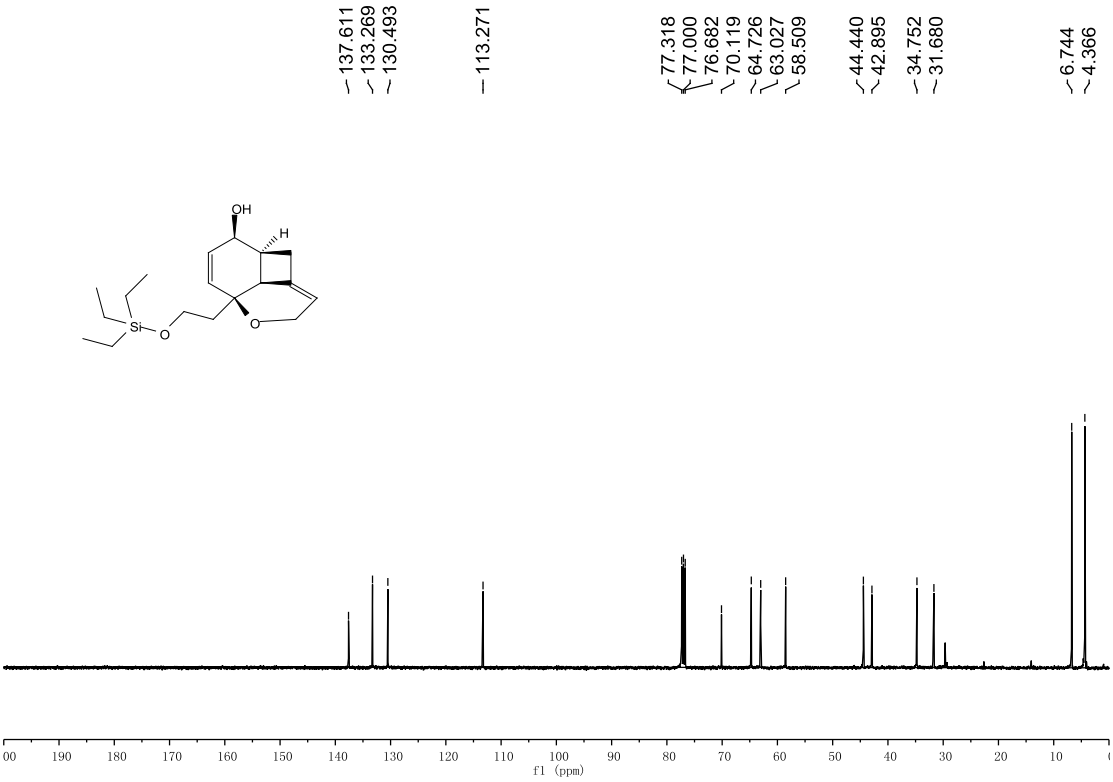


Fig. S104. ^{13}C NMR Spectrum of **7** (100 MHz, $CDCl_3$).

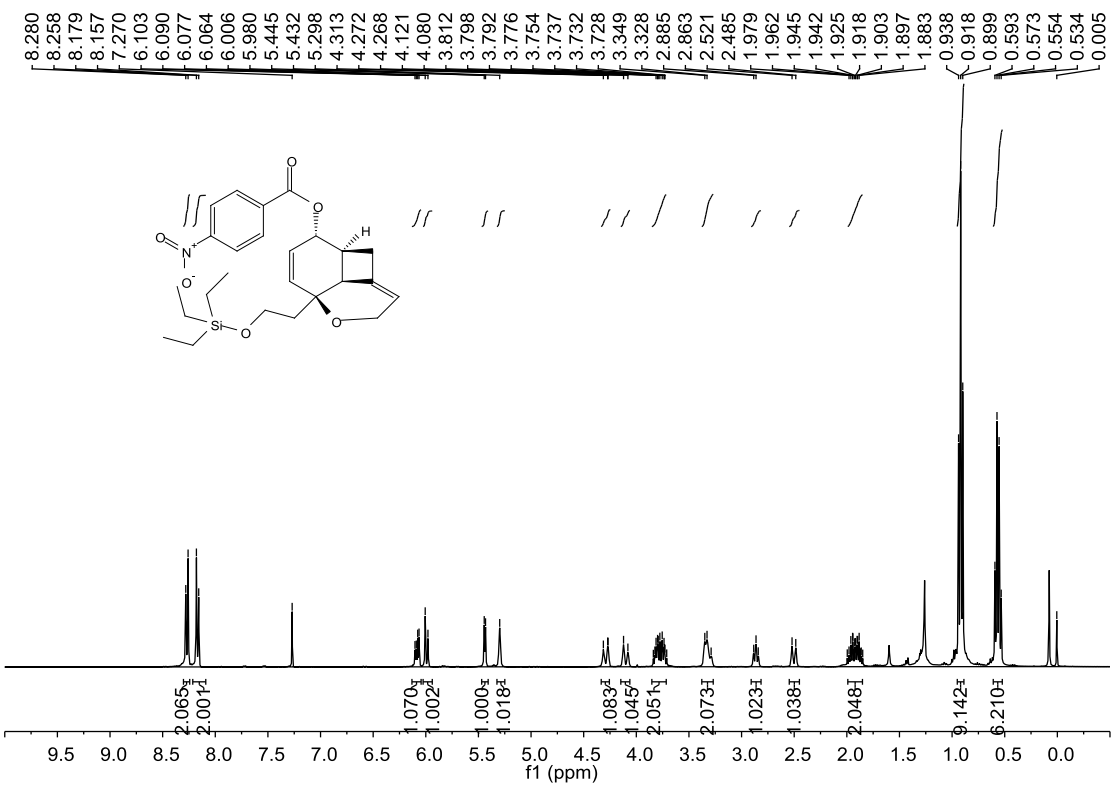


Fig. S105. ^{1}H NMR Spectrum of **8** (400 MHz, $CDCl_3$).

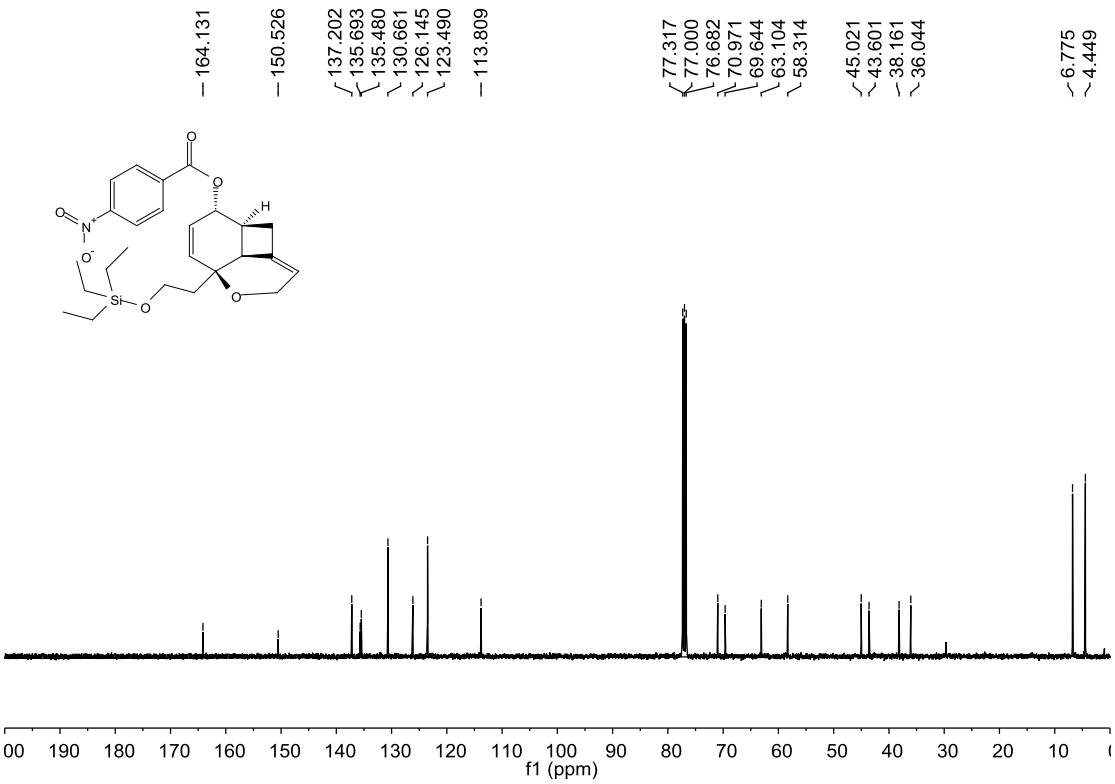
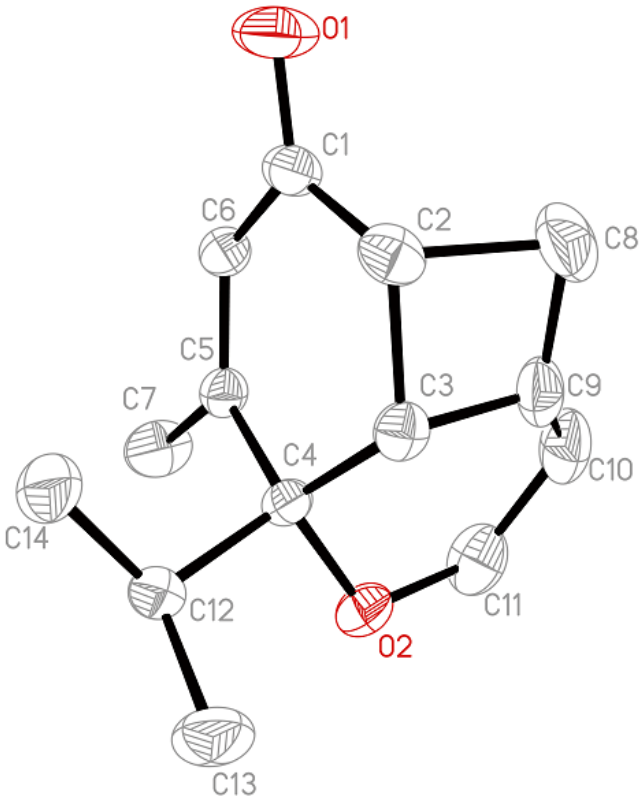
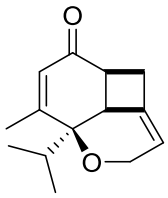


Fig. S106. ^{13}C NMR Spectrum of **8** (100 MHz, $CDCl_3$).

9. X-ray Crystallographic Data of Compound **4s**





4s

Crystal data and structure refinement for 123_a.

Identification code	123_a	
Empirical formula	C14 H19 N0 O2	
Formula weight	219.29	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 9.026(2) Å	α= 90 °.
	b = 11.173(2) Å	β= 90 °.
	c = 23.919(5) Å	γ = 90 °.

Volume	2412.3(9) $Å^3$
Z	8
Density (calculated)	1.208 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	952
Crystal size	0.100 x 0.060 x 0.040 mm^3
Theta range for data collection	2.827 to 25.020 °.
Index ranges	-10<=h<=10, -13<=k<=13, -27<=l<=28
Reflections collected	19432
Independent reflections	2128 [R(int) = 0.0518]
Completeness to theta = 25.020 °	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2128 / 0 / 148
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.1162
R indices (all data)	R1 = 0.0493, wR2 = 0.1237
Extinction coefficient	n/a
Largest diff. peak and hole	0.191 and -0.230 $e.Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for 123_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4224(2)	6886(1)	3611(1)	79(1)
C(1)	4537(2)	5829(1)	3672(1)	46(1)
C(2)	3367(2)	4890(2)	3610(1)	50(1)
O(2)	5800(1)	2311(1)	4079(1)	48(1)
C(3)	3934(2)	3590(1)	3708(1)	41(1)
C(4)	5564(2)	3281(1)	3684(1)	36(1)
C(5)	6532(2)	4343(1)	3838(1)	38(1)
C(8)	2412(2)	4753(2)	4155(1)	75(1)
C(7)	8116(2)	4091(2)	3992(1)	65(1)
C(6)	6037(2)	5470(1)	3814(1)	41(1)
C(9)	3409(2)	3720(2)	4301(1)	55(1)
C(10)	4130(2)	3312(2)	4736(1)	65(1)
C(11)	5439(2)	2539(2)	4651(1)	66(1)
C(12)	6068(2)	2763(1)	3116(1)	49(1)
C(13)	5270(3)	1604(2)	2966(1)	77(1)
C(14)	5877(3)	3670(2)	2647(1)	72(1)

Bond lengths [Å] and angles [°] for 123_a.

O(1)-C(1)	1.224(2)
C(1)-C(6)	1.453(2)
C(1)-C(2)	1.496(2)
C(2)-C(3)	1.558(2)

C(2)-C(8)	1.571(3)
C(2)-H(2)	0.9800
O(2)-C(11)	1.430(2)
O(2)-C(4)	1.4520(17)
C(3)-C(9)	1.502(2)
C(3)-C(4)	1.512(2)
C(3)-H(3)	0.9800
C(4)-C(5)	1.5186(19)
C(4)-C(12)	1.546(2)
C(5)-C(6)	1.337(2)
C(5)-C(7)	1.504(2)
C(8)-C(9)	1.504(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(6)-H(6)	0.9300
C(9)-C(10)	1.310(3)
C(10)-C(11)	1.477(3)
C(10)-H(10)	0.9300
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(14)	1.522(2)
C(12)-C(13)	1.525(2)
C(12)-H(12)	0.9800
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600

C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600

O(1)-C(1)-C(6)	120.64(15)
O(1)-C(1)-C(2)	120.15(15)
C(6)-C(1)-C(2)	119.21(13)
C(1)-C(2)-C(3)	114.02(13)
C(1)-C(2)-C(8)	111.91(15)
C(3)-C(2)-C(8)	87.91(13)
C(1)-C(2)-H(2)	113.5
C(3)-C(2)-H(2)	113.5
C(8)-C(2)-H(2)	113.5
C(11)-O(2)-C(4)	117.06(13)
C(9)-C(3)-C(4)	111.41(13)
C(9)-C(3)-C(2)	87.05(12)
C(4)-C(3)-C(2)	121.76(13)
C(9)-C(3)-H(3)	111.4
C(4)-C(3)-H(3)	111.4
C(2)-C(3)-H(3)	111.4
O(2)-C(4)-C(3)	106.76(11)
O(2)-C(4)-C(5)	110.01(11)
C(3)-C(4)-C(5)	111.86(12)
O(2)-C(4)-C(12)	104.38(11)
C(3)-C(4)-C(12)	113.89(13)
C(5)-C(4)-C(12)	109.60(12)
C(6)-C(5)-C(7)	120.26(14)
C(6)-C(5)-C(4)	122.27(13)
C(7)-C(5)-C(4)	117.40(13)
C(9)-C(8)-C(2)	86.50(13)
C(9)-C(8)-H(8A)	114.2

C(2)-C(8)-H(8A)	114.2
C(9)-C(8)-H(8B)	114.2
C(2)-C(8)-H(8B)	114.2
H(8A)-C(8)-H(8B)	111.4
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(5)-C(6)-C(1)	125.48(14)
C(5)-C(6)-H(6)	117.3
C(1)-C(6)-H(6)	117.3
C(10)-C(9)-C(3)	124.00(17)
C(10)-C(9)-C(8)	138.51(19)
C(3)-C(9)-C(8)	92.56(15)
C(9)-C(10)-C(11)	119.44(17)
C(9)-C(10)-H(10)	120.3
C(11)-C(10)-H(10)	120.3
O(2)-C(11)-C(10)	114.73(15)
O(2)-C(11)-H(11A)	108.6
C(10)-C(11)-H(11A)	108.6
O(2)-C(11)-H(11B)	108.6
C(10)-C(11)-H(11B)	108.6
H(11A)-C(11)-H(11B)	107.6
C(14)-C(12)-C(13)	109.76(16)
C(14)-C(12)-C(4)	111.48(13)
C(13)-C(12)-C(4)	112.74(14)
C(14)-C(12)-H(12)	107.5
C(13)-C(12)-H(12)	107.5

C(4)-C(12)-H(12)	107.5
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5