Supporting Information

for

Assembly of 5*H*-dibenzo[*a,d*]cycloheptenes by a formal [5 + 2] annulation of *ortho*-aryl alkynyl benzyl alcohols with arenes

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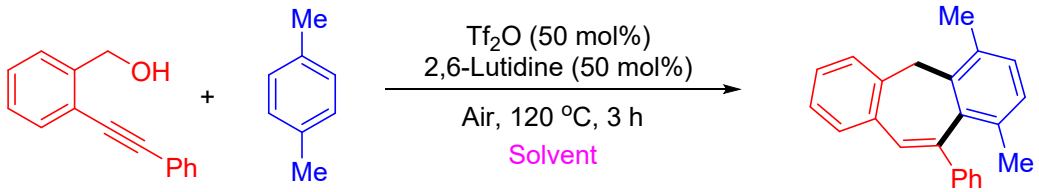
General information

All reactions were carried out under Air. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were measured on Bruker AVIII 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.16 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 7.26. Column chromatography was performed on silica gel 300-400 mesh. The X-ray crystallographic data collections were performed on an Oxford Gemini S Ultra using graphite-monochromated Cu Kα radiation (λ =1.54178 Å). The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares onF2 using the Bruker SHELXTL-97 and Olex 2.0 program. The unknown products were further characterized by HRMS-ESI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Optimization of the Solvent



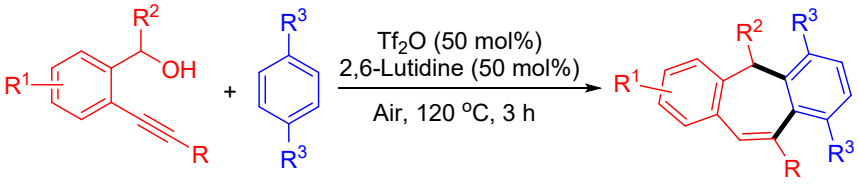
1a **2a** (10 equiv) **3a**

Entry	Solvent	Yield of **3a** (%)
1	DCE	12
2	DMF	0
3	DMSO	0
4	THF	0
5	1,4-dioxane	0
6	CH_3CN	0
7	$CHCl_3$	Trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2 mmol), Tf_2O (0.1 mmol), 2,6-lutidine (0.1 mmol) stirring in solvent (1 mL) under air in an oil bath at 120 °C for 3 h.

Having established Tf_2O as the most efficient catalyst and lutidine as the best base, we next turned our attention to the screening of different solvent systems, when a mixture of (2-(phenylethynyl)phenyl)methanol **1a** react with *p*-xylene **2a** in a 1:10 mole ratio was heated in different solvent systems, such as DCE, DMF, DMSO, THF, 1,4-dioxane, CH_3CN, as well as $CHCl_3$, with stirring at 120 °C in an oil bath for 3 hours, the results indicated that both of them were less effective than *p*-xylene.

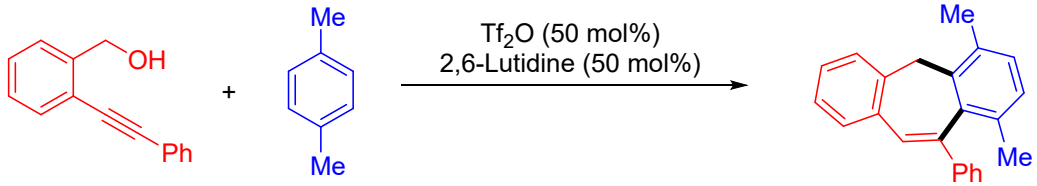
General procedure for the synthesis of the products 3



1 **2** (1 mL) **3**

In a Schlenk tube, a mixture of *ortho*-alkynyl benzyl alcohols **1** (0.2 mmol, 1.0 equiv.), arene compounds **2** (1 mL), Tf_2O (0.1 mmol, 0.5 equiv) and 2,6-lutidine (0.1 mmol, 0.5 equiv) was heated with stirring at 120 °C in an oil bath for 3 hours. Upon completion, the reaction mixture was added H_2O (5 mL) and extracted with Et_2OAc (2 x 5 mL). The combined organic solution was dried by Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with pure PE or PE/EA=100:1(*v*/*v*) as eluent to give the corresponding products **3**.

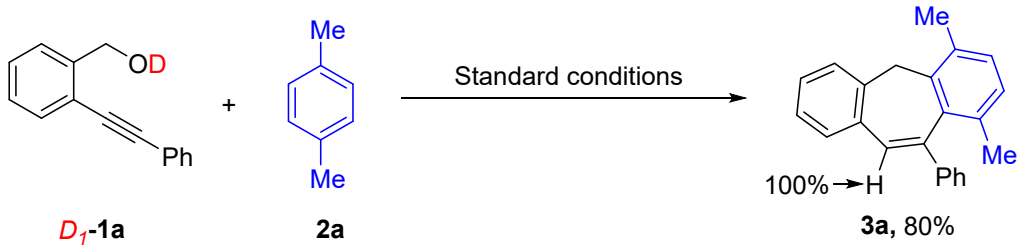
2 mmol scale synthesis of 3a



1a (416 mg, 2 mmol) **2a** (10 mL) **3a** (462 mg, 78% yield)

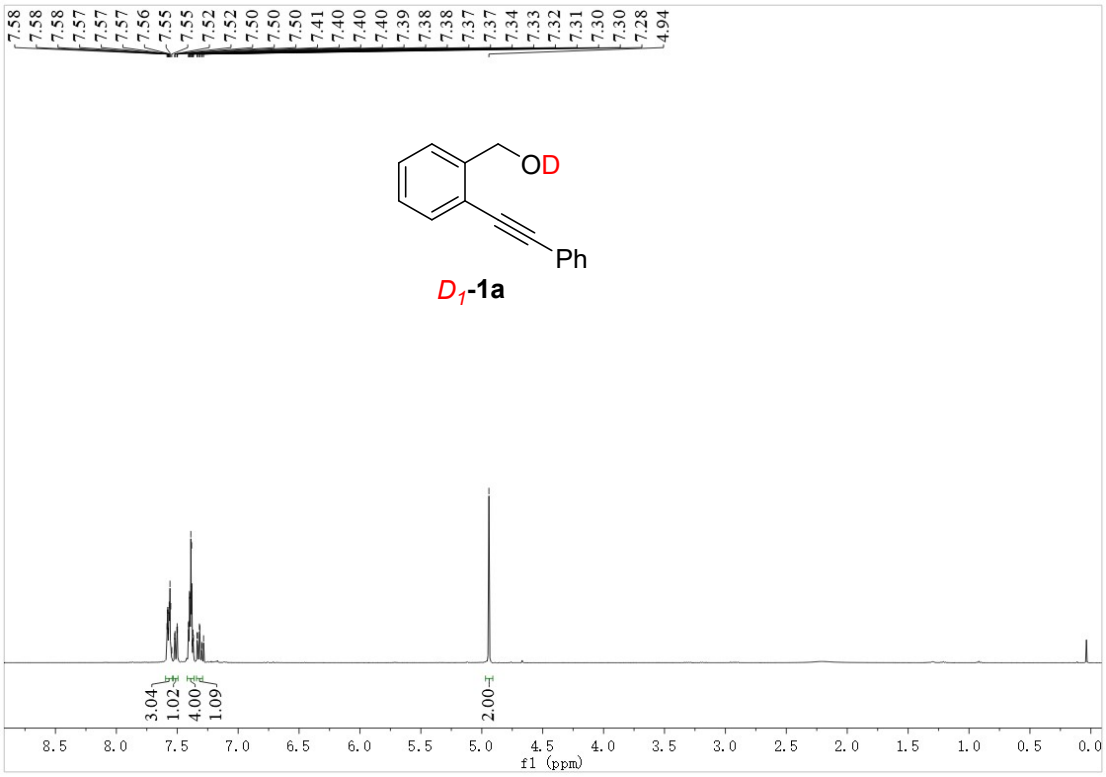
In a Schlenk tube, a mixture of (2-(phenylethynyl)phenyl)methanol **1a** (2 mmol, 1.0 equiv.), *p*-xylene **2** (10 mL), Tf_2O (1 mmol, 0.5 equiv) and 2,6-lutidine (1 mmol, 0.5 equiv) was heated with stirring at 120 °C in an oil bath for 3 hours. Upon completion, the reaction mixture was added H_2O (25 mL) and extracted with Et_2OAc (2 x 15 mL). The combined organic solution was dried by Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with pure PE as eluent to give the corresponding products **3a** (462 mg, 78% yield).

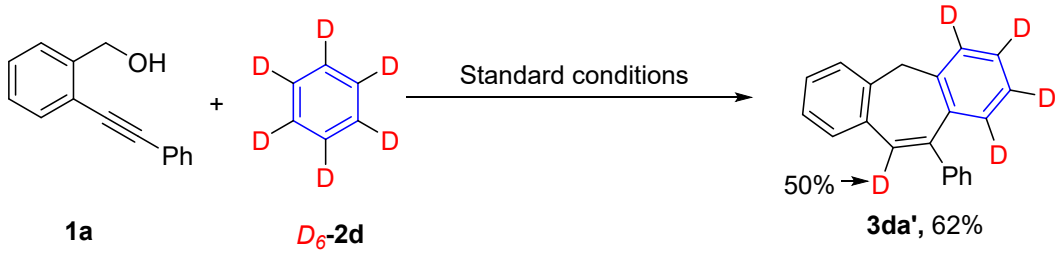
Deuterium labeling experiments



D$_1$-**1a** **2a** **3a**, 80%

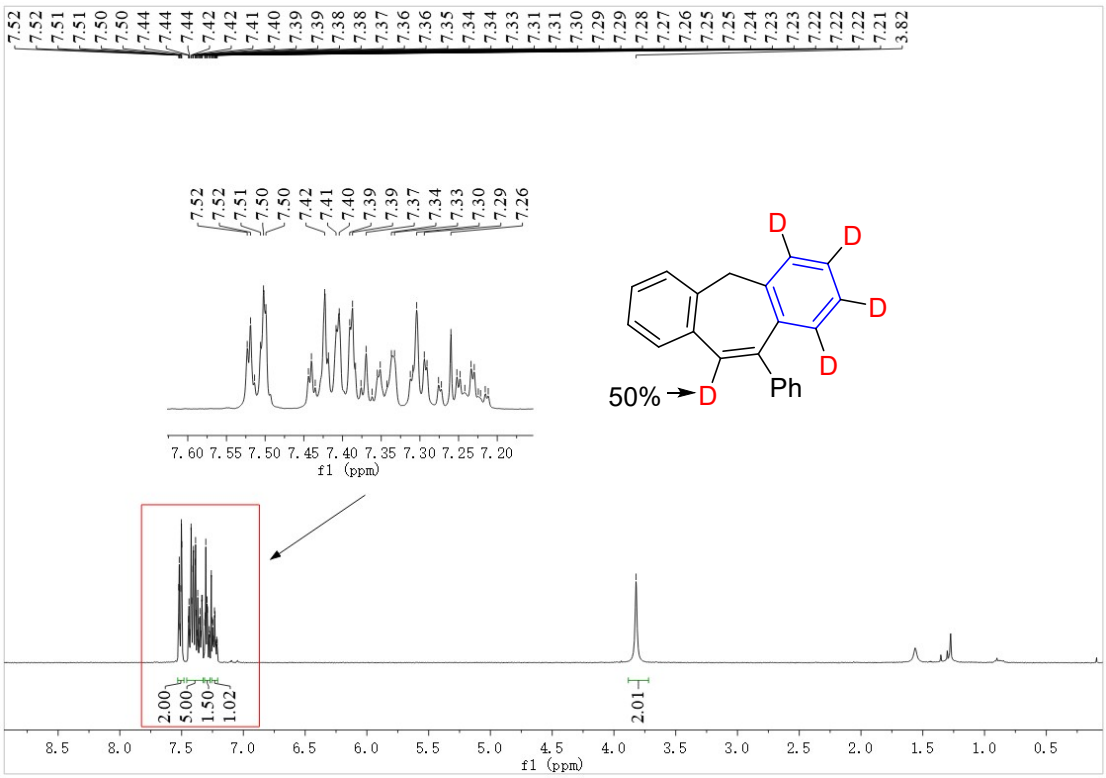
In a Schlenk tube, a mixture of deuterium labelled (2-(phenylethynyl)phenyl)methanol *D*$_1$-**1a** (0.2 mmol, 1.0 equiv.), *p*-xylene **2a** (1 mL), Tf_2O (0.1 mmol, 0.5 equiv) and 2,6-lutidine (0.1 mmol, 0.5 equiv) was heated with stirring at 120 °C in an oil bath for 3 hours. Upon completion, the reaction mixture was added H_2O (5 mL) and extracted with Et_2OAc (2 x 5 mL). The combined organic solution was dried by Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with pure PE as eluent to give the corresponding products **3a** (47.2 mg, 80% yield).



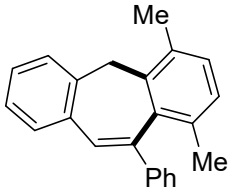


1a D_6**-2d** **3da'**, 62%

In a Schlenk tube, a mixture of (2-(phenylethynyl)phenyl)methanol **1a** (0.2 mmol, 1.0 equiv.), D_6-benzene D_6-**2d** (1 mL), Tf_2O (0.1 mmol, 0.5 equiv) and 2,6-lutidine (0.1 mmol, 0.5 equiv) was heated with stirring at 120 °C in an oil bath for 3 hours. Upon completion, the reaction mixture was added H_2O (5 mL) and extracted with Et_2OAc (2 x 5 mL). The combined organic solution was dried by Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with pure PE as eluent to give the corresponding products **3da'** in 62% yield.

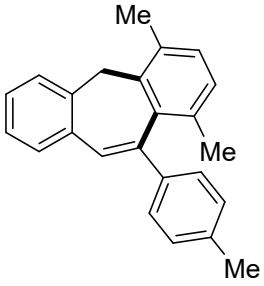


The spectra data of products



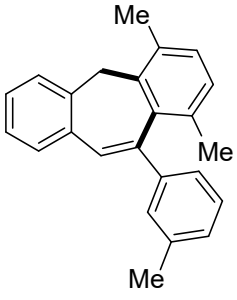
1,4-dimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3a)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (48.0mg, 81%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (s, 1H), 7.56 – 7.42 (m, 6H), 7.41 – 7.27 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 4.24 (d, *J* = 12.8 Hz, 1H), 3.48 (d, *J* = 12.8 Hz, 1H), 2.68 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.6, 144.5, 141.4, 141.3, 135.8, 134.8, 134.5, 130.9, 130.7, 129.9, 128.7, 128.6, 128.1, 127.7, 127.2, 127.0, 126.7, 125.9, 35.9, 22.6, 20.7; **HRMS** Calcd for $C_{23}H_{21}^+$ $[M+H]^+$ 297.1638, found 297.1629.



1,4-dimethyl-11-(*p*-tolyl)-5*H*-dibenzo[a,d][7]annulene (3b)

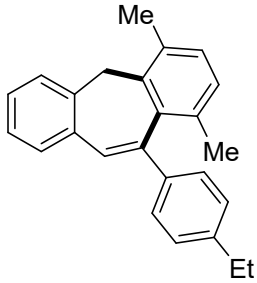
Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (46.5mg, 75%). mp 79-81 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (s, 1H), 7.46 – 7.33 (m, 4H), 7.29 – 7.20 (m, 4H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.41 (d, *J* = 12.8 Hz, 1H), 2.63 (s, 3H), 2.44 (s, 3H), 1.79 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.3, 141.5, 141.3, 141.2, 136.7, 135.8, 134.8, 134.5, 130.5, 130.1, 129.8, 129.3, 128.5, 128.0, 127.5, 126.9, 126.6, 125.8, 35.8, 22.5, 21.2, 20.6; **HRMS** Calcd for $C_{24}H_{23}^+$ $[M+H]^+$ 311.1794, found 311.1792.



1,4-dimethyl-11-(*m*-tolyl)-5*H*-dibenzo[a,d][7]annulene (3c)

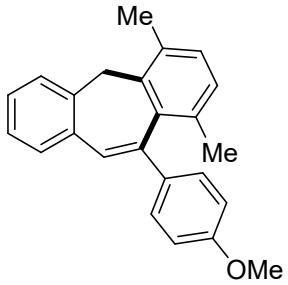
Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (47.1mg, 76%). mp 83-85 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (s, 1H), 7.45 (dd, *J* = 6.8, 2.3 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.35 – 7.23 (m, 5H), 7.19 – 7.15 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.19 (d, *J* = 12.8 Hz, 1H), 3.42 (d, *J* = 12.8 Hz, 1H), 2.65 (s, 3H), 2.44 (s, 3H), 1.81 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.6, 144.4, 141.3, 141.2, 138.2, 135.8, 134.8, 134.5,

130.8, 130.5, 129.8, 128.6, 128.5, 128.1, 127.7, 127.7, 127.6, 126.6, 125.9, 124.3, 35.8, 22.6, 21.6, 20.7; **HRMS** Calcd for $C_{24}H_{23}^+$ $[M+H]^+$ 311.1794, found 311.1791.



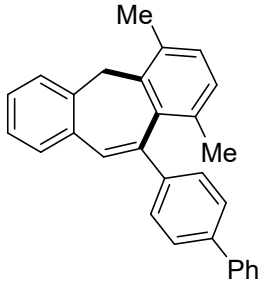
11-(4-ethylphenyl)-1,4-dimethyl-5*H*-dibenzo[a,d][7]annulene (3d)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (53.1mg, 82%). mp 84-86 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (s, 1H), 7.49 – 7.36 (m, 4H), 7.34 – 7.21 (m, 4H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 4.19 (d, *J* = 12.7 Hz, 1H), 3.43 (d, *J* = 12.7 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.65 (s, 3H), 1.80 (s, 3H), 1.34 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.4, 143.1, 141.8, 141.3, 141.2, 135.8, 134.9, 134.5, 130.5, 130.2, 129.8, 128.5, 128.1, 128.0, 127.5, 127.0, 126.6, 125.9, 35.8, 28.6, 22.6, 20.7, 15.7; **HRMS** Calcd for $C_{25}H_{25}^+$ $[M+H]^+$ 325.1951, found 325.1954.



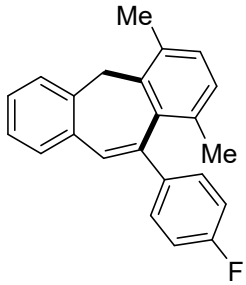
11-(4-methoxyphenyl)-1,4-dimethyl-5*H*-dibenzo[*a,d*][7]annulene (3e)

Flash chromatography of the crude reaction product (petroleum ether/EA=100:1) gave a white solid (45.6mg, 70%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (s, 1H), 7.43 – 7.32 (m, 4H), 7.29 – 7.18 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.90 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.16 (d, *J* = 12.7 Hz, 1H), 3.88 (s, 3H), 3.38 (d, *J* = 12.7 Hz, 1H), 2.62 (s, 3H), 1.78 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 143.9, 141.2, 141.1, 137.1, 135.8, 134.8, 134.5, 130.5, 129.7, 129.5, 128.5, 128.1, 127.9, 127.4, 126.6, 125.8, 113.9, 55.3, 35.8, 22.5, 20.6; **HRMS** Calcd for $C_{24}H_{23}O^+$ $[M+H]^+$ 327.1743, found 327.1739.



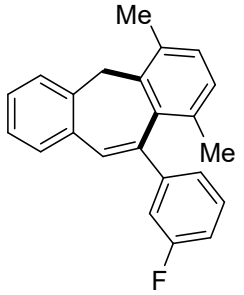
11-([1,1'-biphenyl]-4-yl)-1,4-dimethyl-5*H*-dibenzo[*a,d*][7]annulene (3f)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (63.2mg, 85%). mp 88-90 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.56 (m, 4H), 7.53 (s, 1H), 7.51 – 7.42 (m, 4H), 7.41 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 4.14 (d, *J* = 12.8 Hz, 1H), 3.37 (d, *J* = 12.8 Hz, 1H), 2.59 (s, 3H), 1.78 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.9, 143.3, 141.3, 141.2, 140.7, 139.7, 135.6, 134.6, 134.4, 130.7, 130.6, 129.9, 128.8, 128.6, 128.1, 127.6, 127.4, 127.3, 126.9, 126.7, 125.9, 35.8, 22.6, 20.6; **HRMS** Calcd for $C_{29}H_{25}^+$ $[M+H]^+$ 373.1951, found 373.1938.



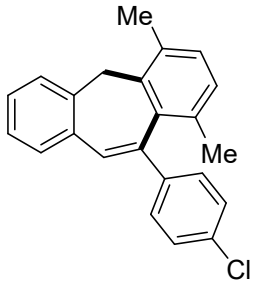
11-(4-fluorophenyl)-1,4-dimethyl-5*H*-dibenzo[*a,d*][7]annulene (3g)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (46.5mg, 74%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (s, 1H), 7.43 – 7.38 (m, 4H), 7.30 – 7.23 (m, 2H), 7.17 – 7.01 (m, 3H), 6.87 (d, *J* = 7.7 Hz, 1H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.38 (d, *J* = 12.8 Hz, 1H), 2.62 (s, 3H), 1.76 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.9 (d, ^1J = 245.8 Hz), 143.4, 141.3, 141.1, 140.5 (d, ^4J = 3.4 Hz), 135.5, 134.5, 134.3, 130.7, 130.6, 130.0, 128.7, 128.6 (d, ^3J = 7.8 Hz), 128.0, 127.7, 126.7, 125.9, 115.5 (d, ^2J = 21.3 Hz), 35.8, 22.5, 20.6; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.63; **HRMS** Calcd for $C_{23}H_{20}F^+$ $[M+H]^+$ 315.1544, found 315.1546.



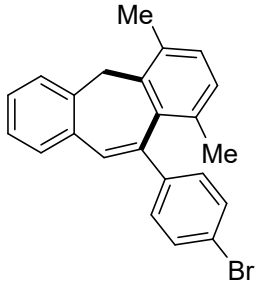
11-(3-fluorophenyl)-1,4-dimethyl-5*H*-dibenzo[*a,d*][7]annulene (3h)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (47.1mg, 75%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (s, 1H), 7.41 – 7.28 (m, 3H), 7.25 – 7.16 (m, 3H), 7.13 (dt, *J* = 8.6, 2.5 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.98 (td, *J* = 8.6, 2.5 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 3.34 (d, *J* = 12.8 Hz, 1H), 2.58 (s, 3H), 1.74 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2 (d, ^1J = 245.7 Hz), 146.7 (d, ^3J = 7.4 Hz), 143.3 (d, ^4J = 2.5 Hz), 141.4, 141.2, 135.3, 134.2 (d, *J* = 8.2 Hz), 131.5, 130.7, 130.1, 129.9, 128.6, 128.1, 127.8, 126.7, 125.9, 122.7 (d, ^4J = 2.8 Hz), 113.8 (d, ^2J = 22.0 Hz), 113.7 (d, ^2J = 21.4 Hz), 35.7, 22.4, 20.6 (one aryl carbon overlapped); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.42; **HRMS** Calcd for $C_{23}H_{20}F^+$ $[M+H]^+$ 315.1544, found 315.1550.



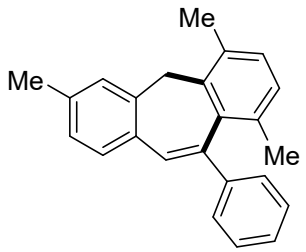
11-(4-chlorophenyl)-1,4-dimethyl-5*H*-dibenzo[*a,d*][7]annulene (3i)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (51.5mg, 78%). mp 91-93 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (s, 1H), 7.41 – 7.30 (m, 6H), 7.27 – 7.20 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.14 (d, *J* = 12.8 Hz, 1H), 3.34 (d, *J* = 12.8 Hz, 1H), 2.59 (s, 3H), 1.74 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.2, 142.8, 141.4, 141.2, 135.4, 134.3, 134.2, 132.7, 131.1, 130.7, 130.0, 128.8, 128.7, 128.3, 128.1, 127.8, 126.7, 125.9, 35.7, 22.6, 20.6; **HRMS** Calcd for $C_{23}H_{20}Cl^+$ $[M+H]^+$ 331.1248, found 331.1244.



11-(4-bromophenyl)-1,4-dimethyl-5*H*-dibenzo[*a,d*][7]annulene (3j)

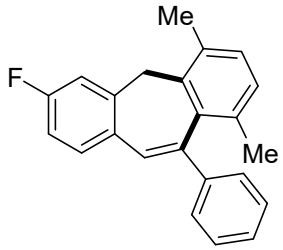
Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (53.8mg, 72%). mp 98-100 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.44 (s, 1H), 7.36 (ddd, *J* = 7.0, 5.2, 1.7 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 (ddd, *J* = 7.0, 5.2, 1.7 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 3.32 (d, *J* = 12.8 Hz, 1H), 2.57 (s, 3H), 1.73 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.3, 143.2, 141.4, 141.1, 135.4, 134.2, 134.1, 131.7, 131.1, 130.7, 130.0, 128.6, 128.0, 127.8, 126.7, 125.9, 120.8, 35.7, 22.6, 20.6 (one aryl carbon overlapped); **HRMS** Calcd for $C_{23}H_{20}Br^+$ $[M+H]^+$ 375.0743, found 375.0737.



1,4,7-trimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3k)

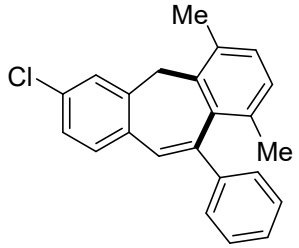
Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (43.4mg, 70%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (s, 1H), 7.42 – 7.31 (m, 4H), 7.30 – 7.23 (m, 2H), 7.15 (s, 1H), 7.08 – 6.99 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.33 (d, *J* = 12.8 Hz, 1H), 2.58 (s, 3H), 2.34 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.5, 143.7, 141.3, 141.1, 137.5, 134.8, 134.4, 132.9, 130.8, 130.5, 129.7, 128.6, 128.5, 127.9, 127.3,

127.0, 126.8, 126.7, 35.7, 22.5, 21.2, 20.6; **HRMS** Calcd for $C_{24}H_{23}^+$ $[M+H]^+$ 311.1794, found 311.1790.



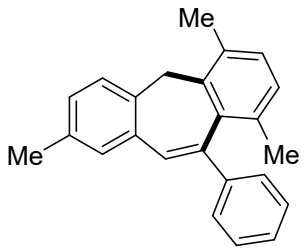
7-fluoro-1,4-dimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3l)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (40.8mg, 65%). mp 76-78 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.27 (m, 7H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.91 (td, *J* = 8.5, 2.6 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.09 (d, *J* = 12.8 Hz, 1H), 3.36 (d, *J* = 12.8 Hz, 1H), 2.57 (s, 3H), 1.72 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.6 (d, ^1J = 246.5 Hz), 144.2, 143.0 (d, ^3J = 7.3 Hz), 140.6, 134.6, 134.5, 131.7 (d, ^4J = 2.9 Hz), 130.6, 129.9, 129.8, 129.5 (d, ^3J = 8.8 Hz), 128.8, 128.6, 128.4, 127.1, 126.9, 113.4 (d, ^2J = 21.3 Hz), 112.9 (d, ^2J = 21.9 Hz), 35.7, 22.4, 20.6; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.16; **HRMS** Calcd for $C_{23}H_{20}F^+$ $[M+H]^+$ 315.1544, found 315.1545.



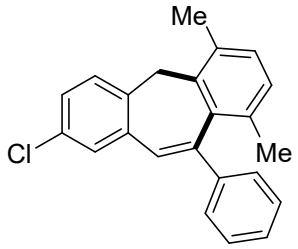
7-chloro-1,4-dimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3m)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (47.5mg, 72%). mp 88-90 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.33 (m, 6H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.19 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.09 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 2.59 (s, 3H), 1.73 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.0, 144.1, 142.5, 140.6, 134.6, 134.5, 134.1, 133.4, 130.6, 130.0, 129.6, 129.2, 128.9, 128.6, 127.1, 127.0, 126.5, 126.0, 35.5, 22.4, 20.6; **HRMS** Calcd for $C_{23}H_{20}Cl^+$ $[M+H]^+$ 331.1248, found 331.1251.



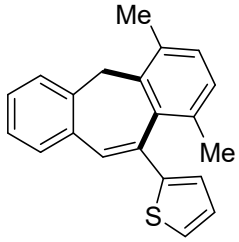
1,4,8-trimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3n)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (46.5mg, 75%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.42 (m, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.29 – 7.23 (m, 2H), 7.11 – 7.05 (m, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 3.36 (d, *J* = 12.8 Hz, 1H), 2.60 (s, 3H), 2.36 (s, 3H), 1.74 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.5, 144.3, 141.5, 138.4, 135.5, 135.3, 134.7, 134.4, 130.9, 130.4, 129.8, 128.6, 128.5, 128.48, 128.44, 127.0, 126.8, 126.5, 35.3, 22.5, 21.0, 20.6; **HRMS** Calcd for $C_{24}H_{23}^+$ $[M+H]^+$ 311.1794, found 311.1796.



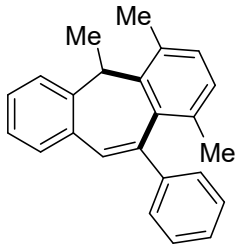
8-chloro-1,4-dimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3o)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (44.9mg, 68%). mp 88-90 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.32 (m, 6H), 7.31 – 7.26 (m, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.09 (d, *J* = 12.9 Hz, 1H), 3.30 (d, *J* = 12.9 Hz, 1H), 2.55 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.7, 143.9, 140.9, 139.5, 137.1, 134.5, 134.4, 131.4, 130.5, 130.0, 129.4, 128.7, 128.6, 127.7, 127.4, 127.2, 127.0, 35.1, 22.4, 20.6 (one aryl carbon overlapped); **HRMS** Calcd for $C_{23}H_{20}Cl^+$ $[M+H]^+$ 331.1248, found 285.1249.



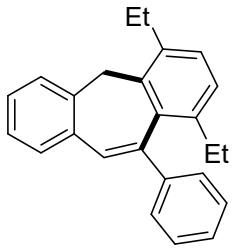
2-(6,9-dimethyl-5*H*-dibenzo[*a,d*][7]annulen-10-yl)thiophene (3p)

Flash chromatography of the crude reaction product (petroleum ether/EA=100:1) gave a white solid (48.3mg, 80%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (s, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.18 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 3.6, 1.1 Hz, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 3.39 (d, *J* = 12.8 Hz, 1H), 2.59 (s, 3H), 1.96 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.4, 141.3, 141.0, 137.6, 135.3, 134.7, 134.2, 130.5, 130.0, 129.5, 128.5, 128.1, 127.7, 127.5, 126.7, 125.9, 125.5, 124.1, 35.7, 21.9, 20.5; **HRMS** Calcd for $C_{21}H_{19}S^+$ $[M+H]^+$ 303.1202, found 303.1203.



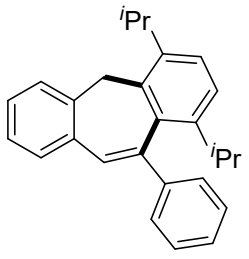
1,4,5-trimethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3q)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (32.2mg, 52%). mp 70-72 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.27 – 7.15 (m, 6H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.91 (s, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 1H), 2.50 (s, 3H), 1.84 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.7, 141.4, 138.6, 136.2, 134.4, 132.6, 131.3, 129.1, 128.6, 128.4, 128.3, 128.0, 126.9, 126.6, 126.4, 126.2, 123.4, 39.2, 21.5, 20.1, 19.0 (one aryl carbon overlapped); **HRMS** Calcd for $C_{24}H_{23}^+$ $[M+H]^+$ 311.1794, found 311.1799.



1,4-diethyl-11-phenyl-5*H*-dibenzo[*a,d*][7]annulene (3ba)

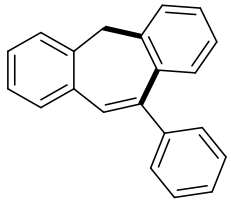
Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (45.4mg, 70%). mp 78-80 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.30 (m, 7H), 7.29 – 7.25 (m, 1H), 7.22 – 7.17 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.13 (d, *J* = 12.9 Hz, 1H), 3.38 (d, *J* = 12.9 Hz, 1H), 3.05 – 2.84 (m, 2H), 2.14 – 1.99 (m, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.7, 144.5, 141.6, 141.3, 140.3, 136.6, 135.9, 134.5, 130.9, 128.5, 128.3, 127.9, 127.5, 127.4, 126.9, 126.8, 125.8, 35.2, 27.7, 26.9, 15.7, 14.1 (one aryl carbon overlapped); **HRMS** Calcd for $C_{25}H_{25}^+$ $[M+H]^+$ 325.1951, found 325.1947.



1,4-diisopropyl-11-phenyl-5H-dibenzo[a,d][7]annulene (3ca)

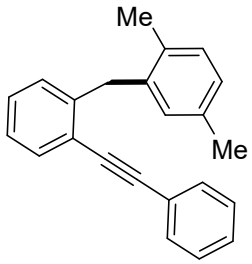
Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (50.7mg, 72%). mp 79-81 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (s, 1H), 7.40 – 7.30 (m, 6H), 7.28 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.23 (d, *J* = 13.1 Hz, 1H), 3.60 (p, *J* = 6.8 Hz, 1H), 3.38 (d, *J* = 13.1 Hz, 1H), 2.73 (p, *J* = 6.8 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.33 (d, *J* =

6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.9, 144.7, 142.1, 141.0, 140.6, 136.0, 134.1, 130.7, 128.4, 127.8, 127.3, 126.9, 126.8, 126.7, 125.8, 124.9, 123.9, 34.8, 30.7, 29.5, 25.6, 24.7, 23.6, 21.9; **HRMS** Calcd for $C_{27}H_{29}^+$ $[M+H]^+$ 353.2264, found 353.2254.



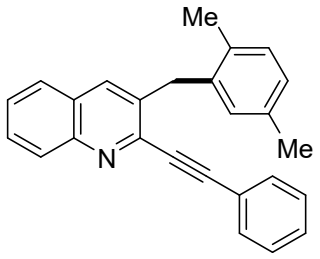
10-phenyl-5*H*-dibenzo[*a*,*d*][7]annulene (3da)

Flash chromatography of the crude reaction product (petroleum ether) gave a white solid (32.2mg, 60%). mp 70-72 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 – 7.52 (m, 2H), 7.49 – 7.41 (m, 4H), 7.39 – 7.30 (m, 5H), 7.28 – 7.23 (m, 1H), 7.16 – 7.05 (m, 2H), 3.85 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.1, 143.6, 140.2, 139.3, 136.4, 135.3, 129.9, 129.5, 129.2, 128.6, 128.3, 128.1, 127.4, 127.3, 127.1, 125.9, 125.6, 41.6 (one aryl carbon overlapped); **HRMS** Calcd for $C_{21}H_{17}^+$ $[M+H]^+$ 269.1325, found 269.1312.



1,4-dimethyl-2-(2-(phenylethynyl)benzyl)benzene (4a)

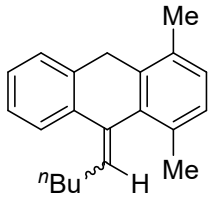
Flash chromatography of the crude reaction product (petroleum ether) gave a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 – 7.58 (m, 1H), 7.56 – 7.51 (m, 2H), 7.41 – 7.36 (m, 3H), 7.29 – 7.19 (m, 2H), 7.12 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.05 – 6.92 (m, 3H), 4.25 (s, 2H), 2.32 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 138.2, 135.4, 133.6, 132.0, 131.5, 130.9, 130.1, 128.6, 128.5, 128.4, 128.3, 127.1, 125.9, 123.4, 122.9, 93.8, 88.2, 37.7, 21.0, 19.2; **HRMS** $C_{23}H_{21}^+$ $[M+H]^+$ 297.1638, found297.1627.



3-(2,5-dimethylbenzyl)-2-(phenylethynyl)quinoline (4r)

Flash chromatography of the crude reaction product (petroleum ether/EA=100:1) gave a pale green oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.62 (m, 4H), 7.60 (s, 1H), 7.51 (ddd, *J* = 8.4, 6.7, 1.7 Hz, 1H), 7.41 (qd, *J* = 4.7, 1.7 Hz, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.08 (dd, *J*

= 7.6, 1.7 Hz, 1H), 7.01 (d, *J* = 1.7 Hz, 1H), 4.38 (s, 2H), 2.33 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 138.2, 135.4, 133.6, 132.0, 131.5, 130.9, 130.1, 128.6, 128.5, 128.4, 128.3, 127.1, 125.9, 123.4, 122.9, 93.8, 88.2, 37.7, 21.0, 19.2; **HRMS** $C_{26}H_{22}N^+$ $[M+H]^+$ 348.1747, found 348.1730.

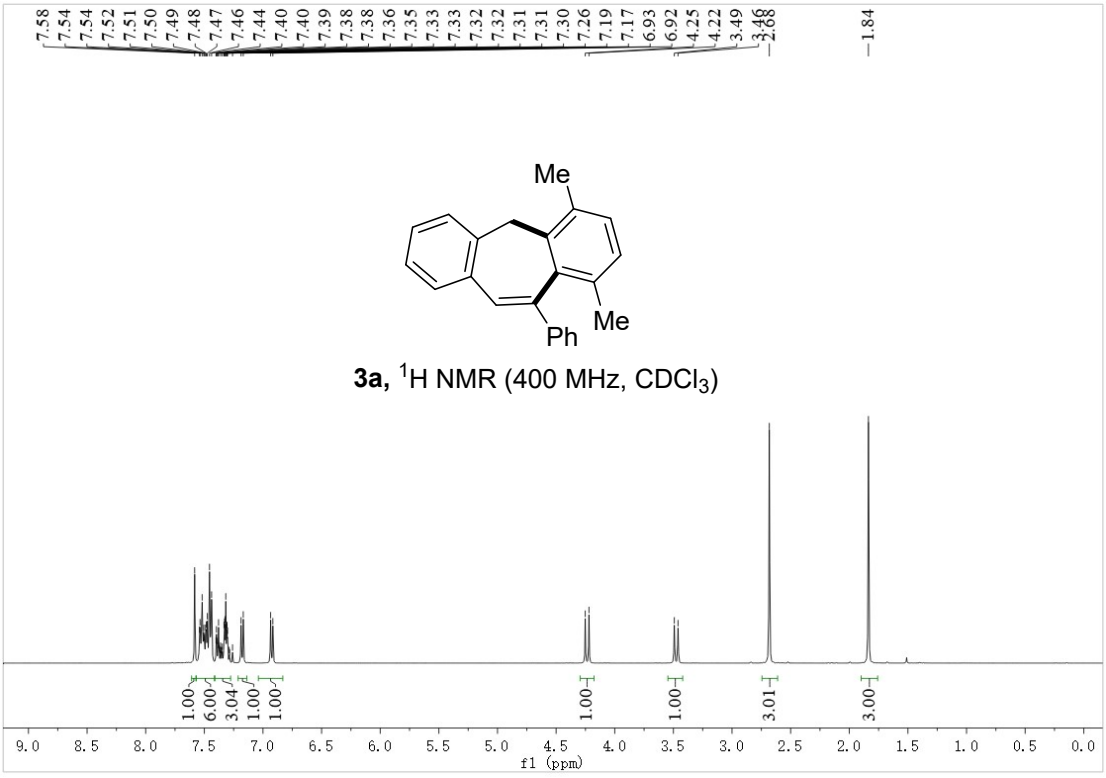


5

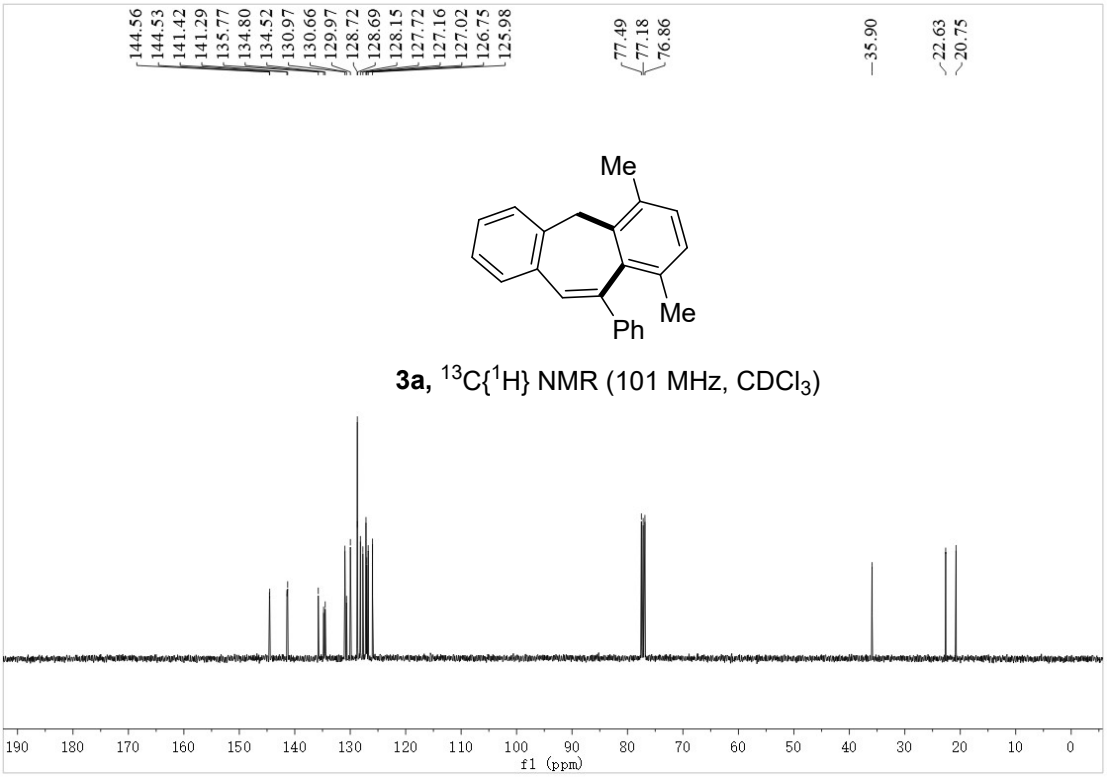
(*E*)- and (*Z*)-1,4-dimethyl-9-pentylidene-9,10-dihydroanthracene (5)

Flash chromatography of the crude reaction product (petroleum ether) gave a colorless oil (total: 41.4mg, 75%). The title compound was obtained as a mixture of (*E*)- and (*Z*)-isomers (major:minor =5:3). **^{1}H NMR (400 MHz, $CDCl_3$)** (mixture) δ 8.48 (s, 1H), 8.43 (s, 0.6H), 8.33 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 0.6H), 8.05 – 8.01 (m, 1.6H), 7.91 (s, 0.6H), 7.56 – 7.44 (m, 3.2H), 7.23 – 7.13 (m, 2.6H), 3.80 (t, *J* = 8.5 Hz, 2H), 3.59 (t, *J* = 8.5 Hz, 1.2H), 3.06 (s, 3H), 2.81 (s, 1.8H), 2.78 (s, 3H), 2.57 (s, 1.8H), 1.93 – 1.76 (m, 3.2H), 1.67 – 1.54 (m, 3.2H), 1.51 – 1.41 (m, 3.2H), 0.99 (t, *J* = 7.2 Hz, 4.8H); **^{13}C NMR (101 MHz, $CDCl_3$)** (mixture) δ 137.2, 134.8, 134.7, 134.4, 133.4, 132.8, 132.7, 130.9, 130.8, 130.7, 130.0, 129.9, 129.63, 129.61, 129.4, 129.3, 128.1, 125.5, 125.3, 125.0, 124.7, 124.6, 124.33, 124.30, 123.1, 121.6, 121.2, 32.9, 32.5, 32.4, 31.1, 30.4, 28.2, 27.0, 22.7, 22.5, 20.7, 20.0, 14.2, 14.2 (one aryl carbon and one alkyl carbon overlapped); **HRMS** Calcd for $C_{21}H_{25}^+$ $[M+H]^+$ 277.1951, found 277.1950.

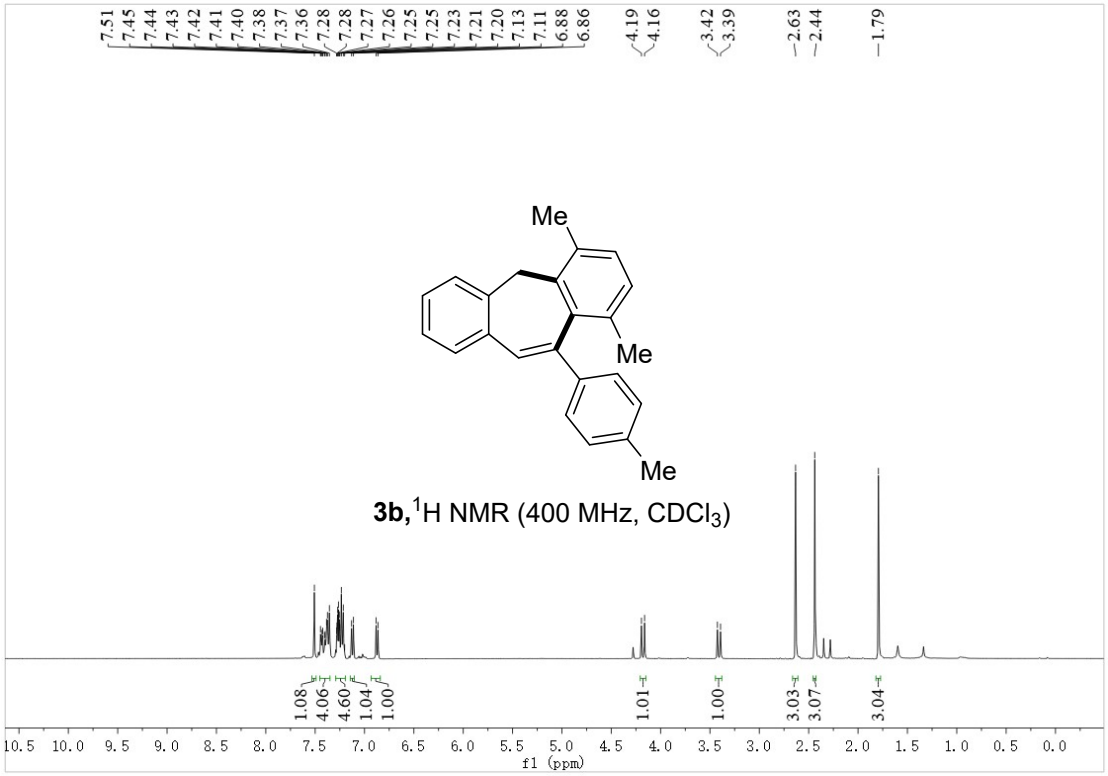
Copies of the NMR spectra



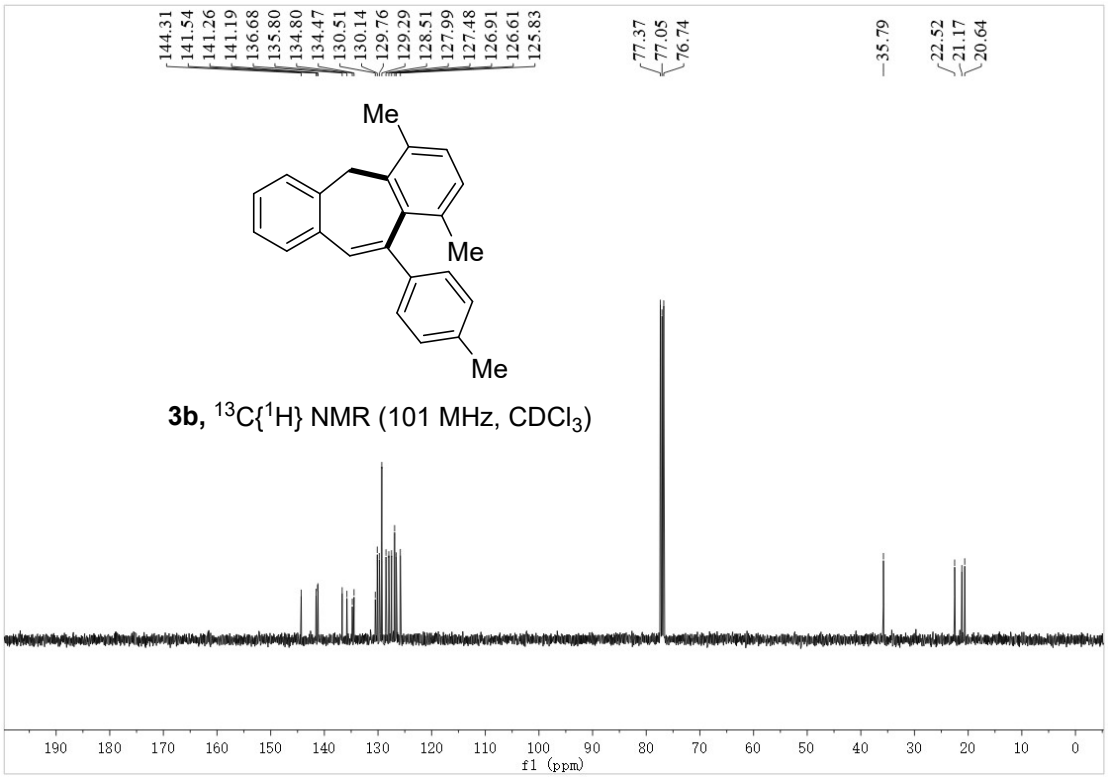
3a, ^{1}H NMR (400 MHz, $CDCl_3$)



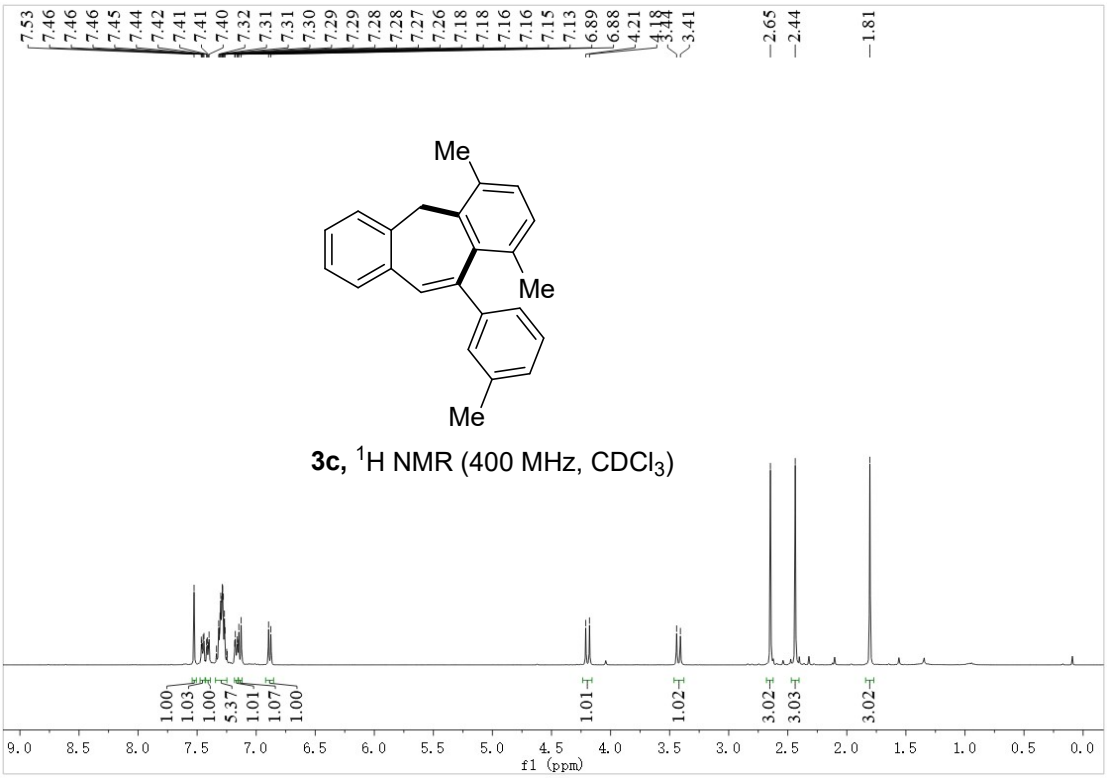
3a, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



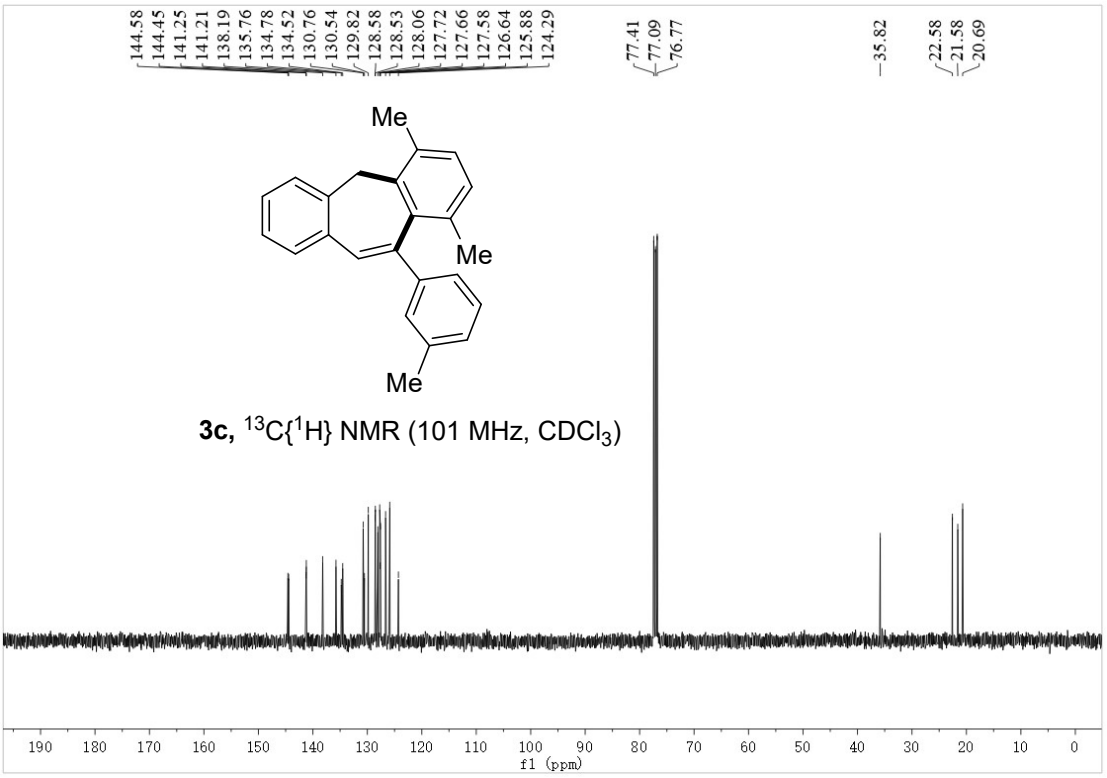
3b, ^{1}H NMR (400 MHz, $CDCl_3$)



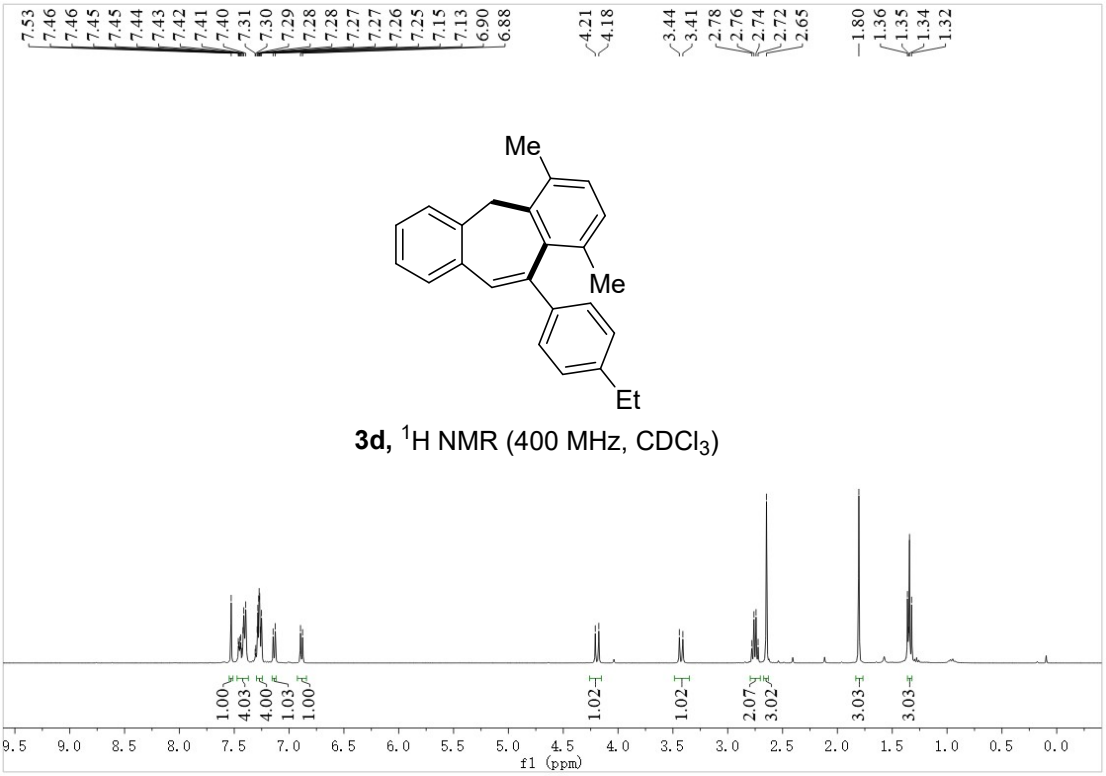
3b, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



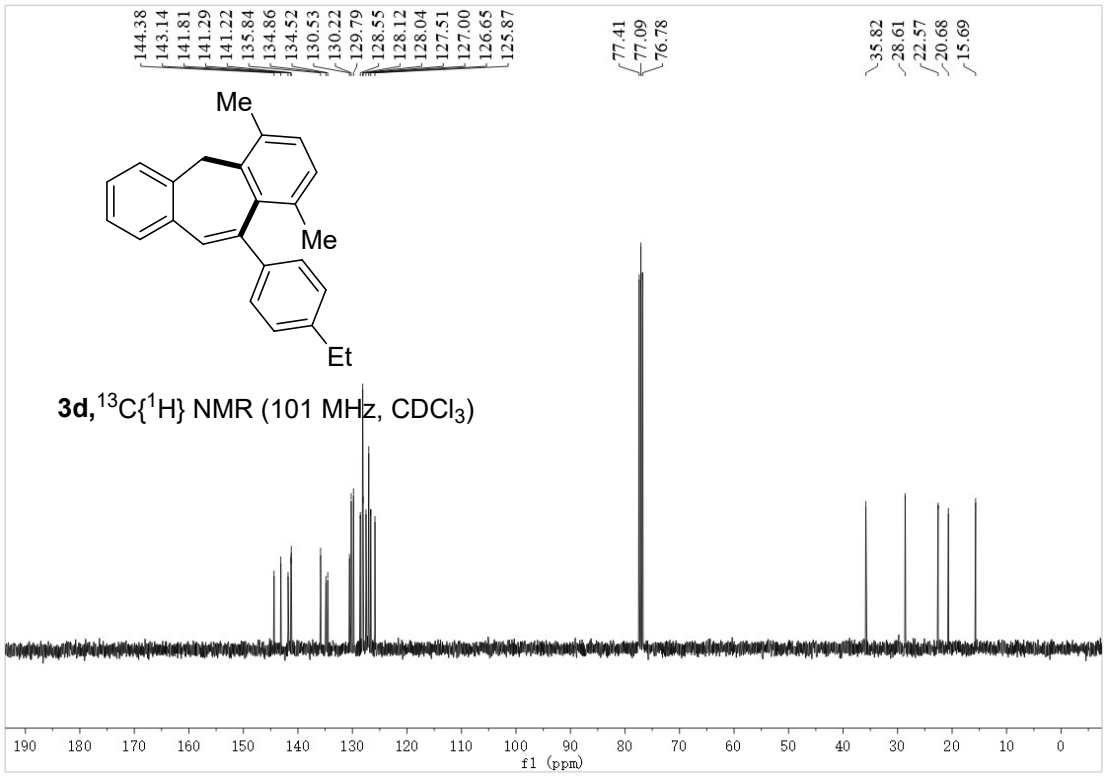
3c, ^{1}H NMR (400 MHz, $CDCl_3$)



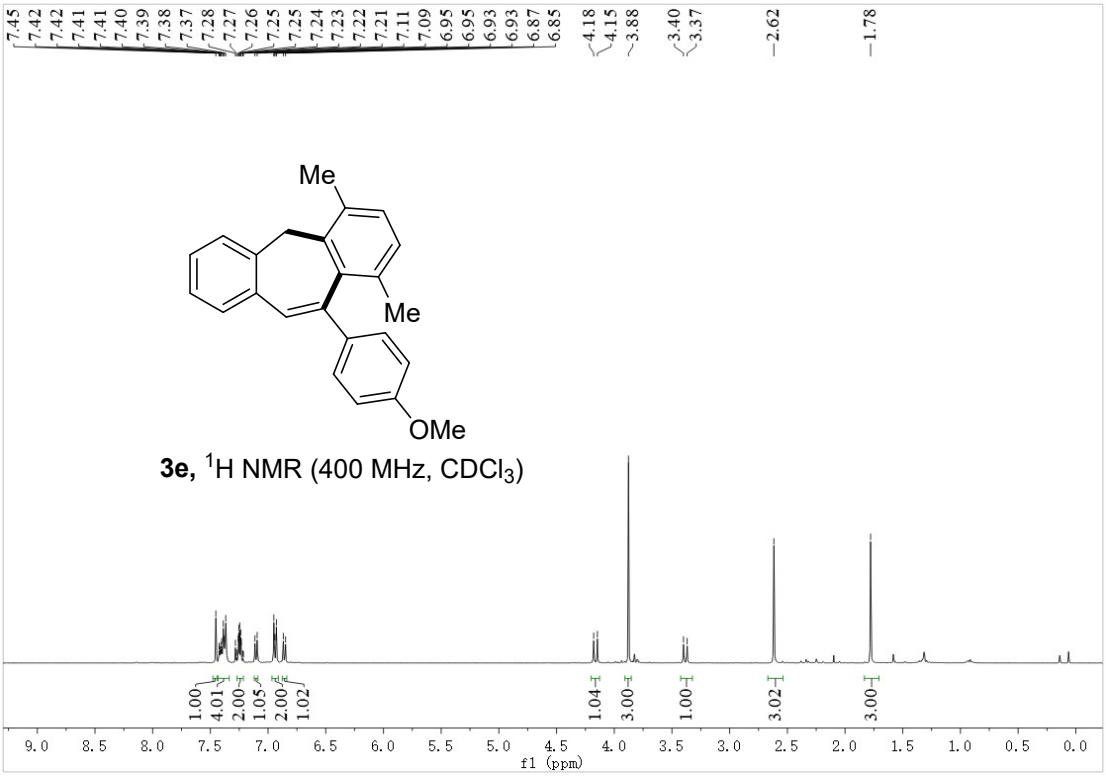
3c, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



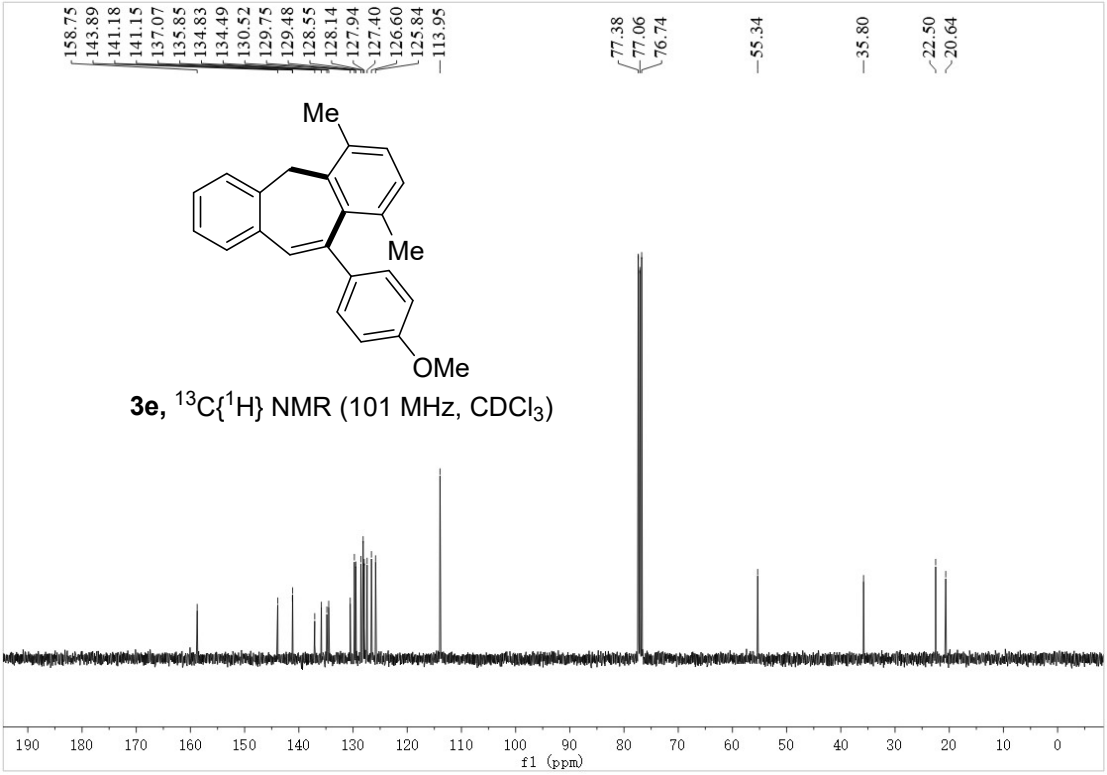
3d, ^{1}H NMR (400 MHz, $CDCl_3$)



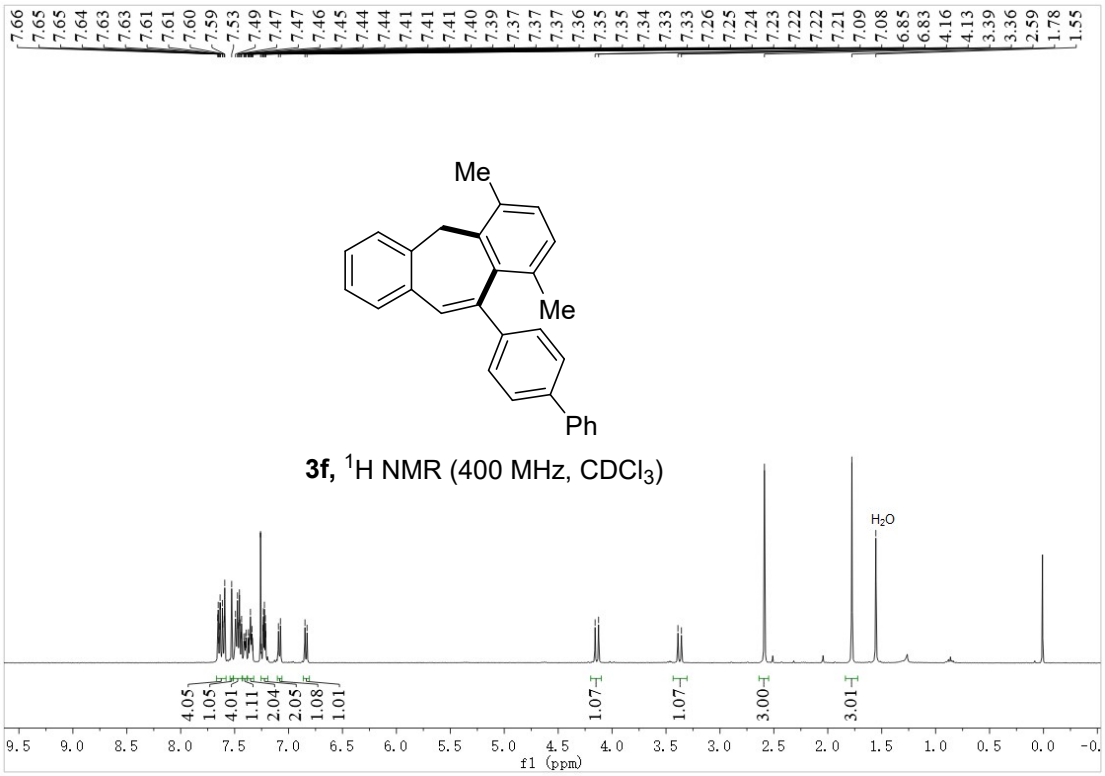
3d, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



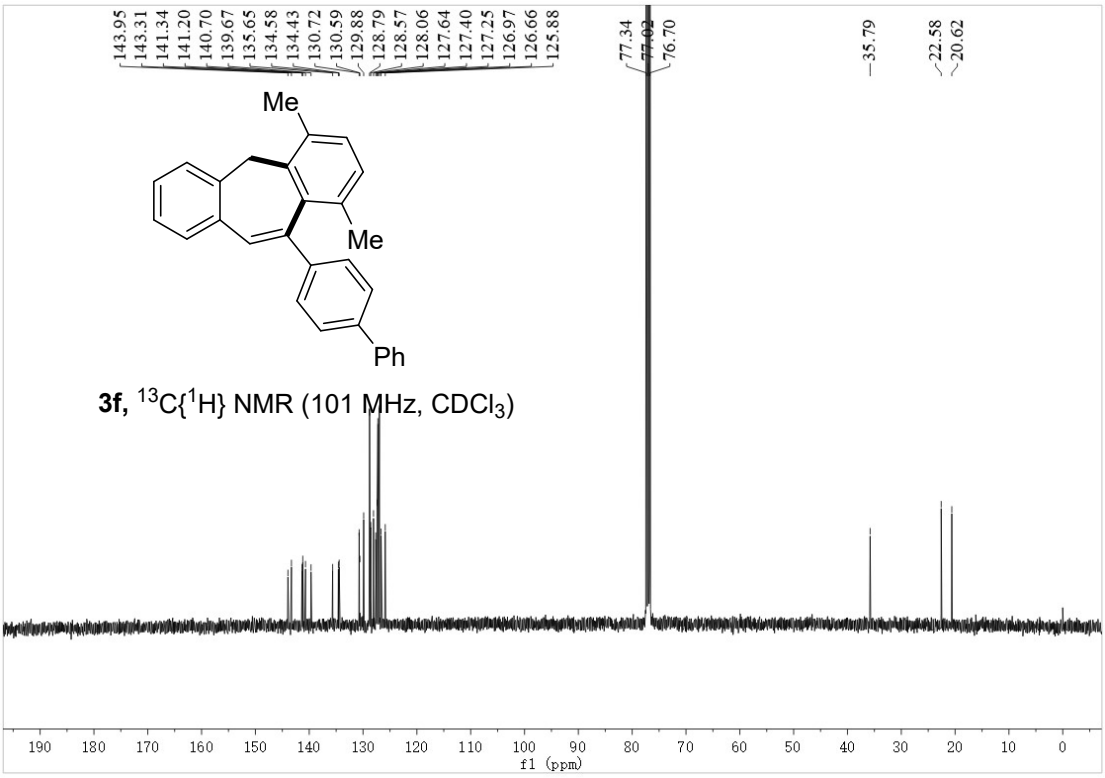
3e, ^{1}H NMR (400 MHz, $CDCl_3$)



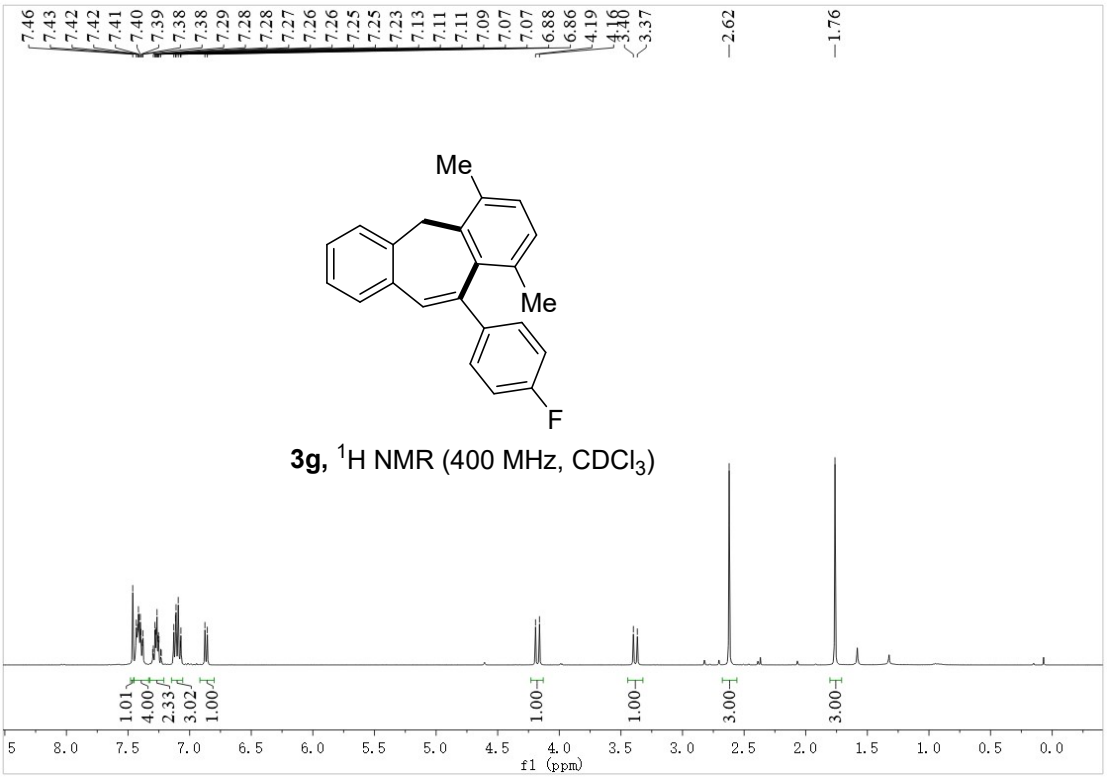
3e, ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



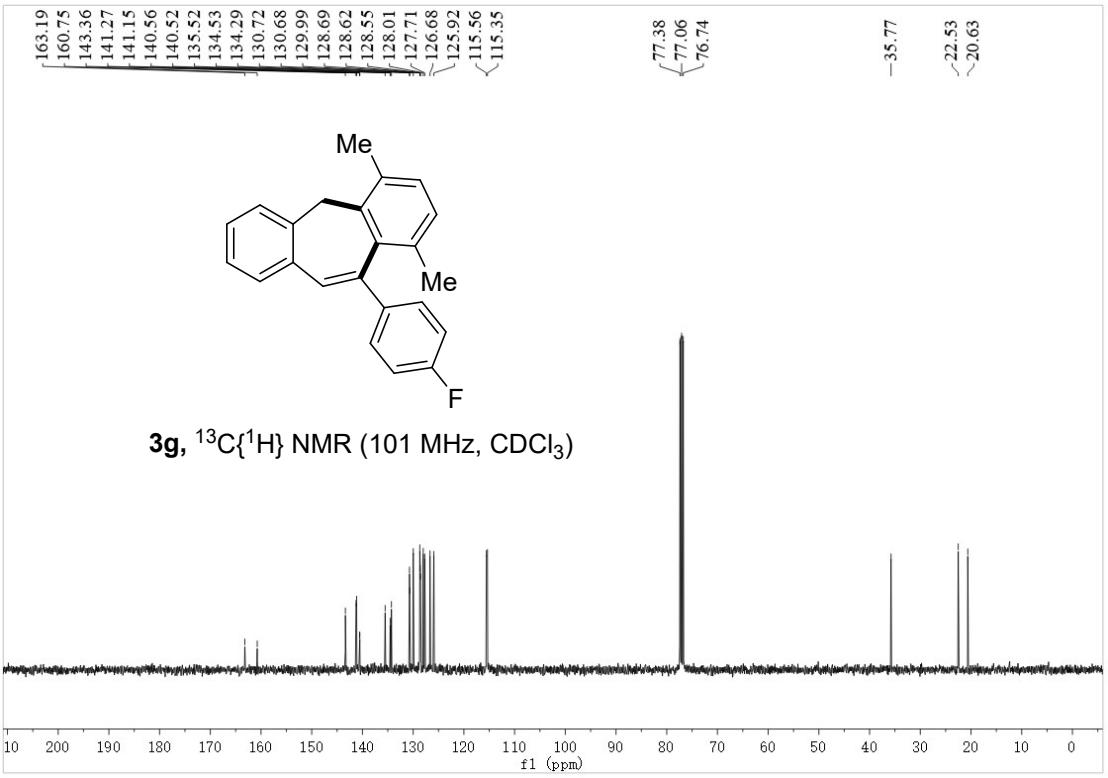
3f, ^{1}H NMR (400 MHz, $CDCl_3$)



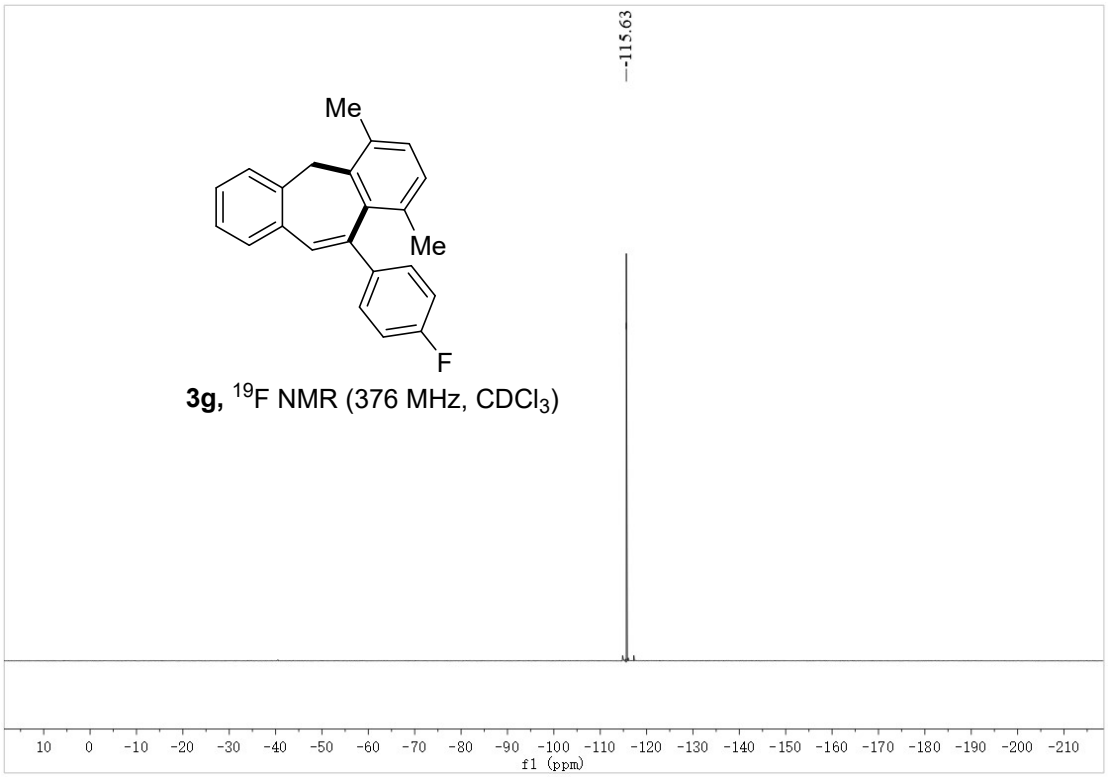
3f, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



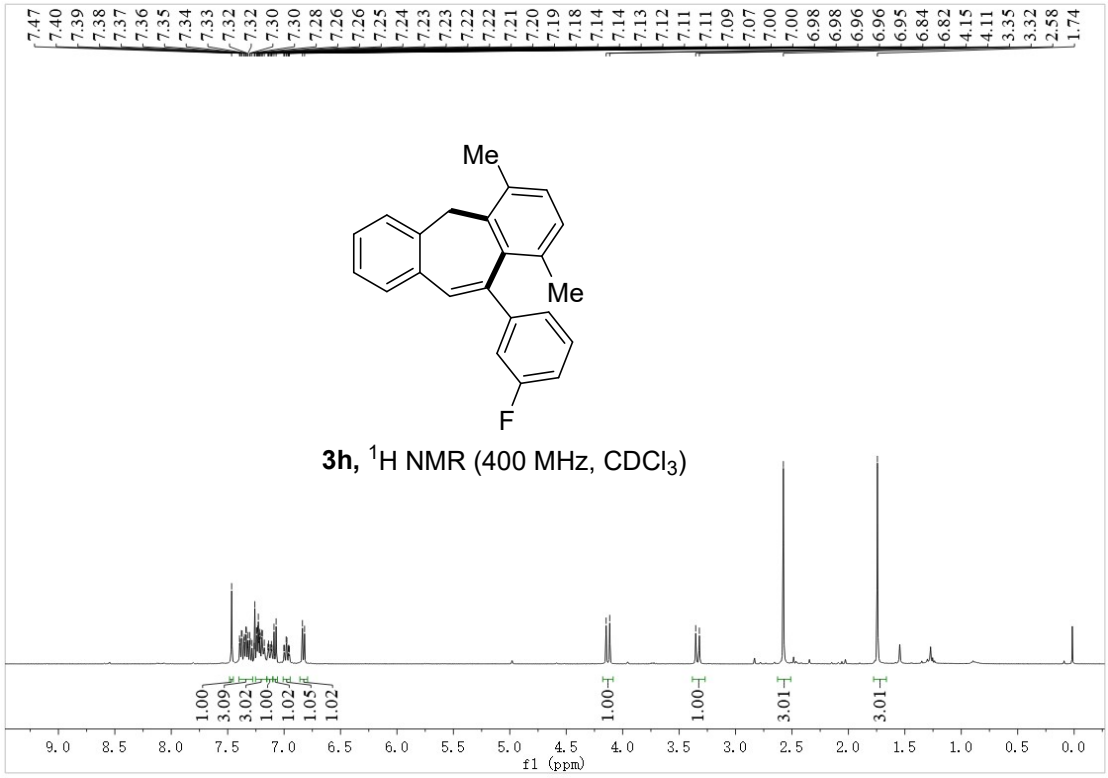
3g, ^{1}H NMR (400 MHz, $CDCl_3$)



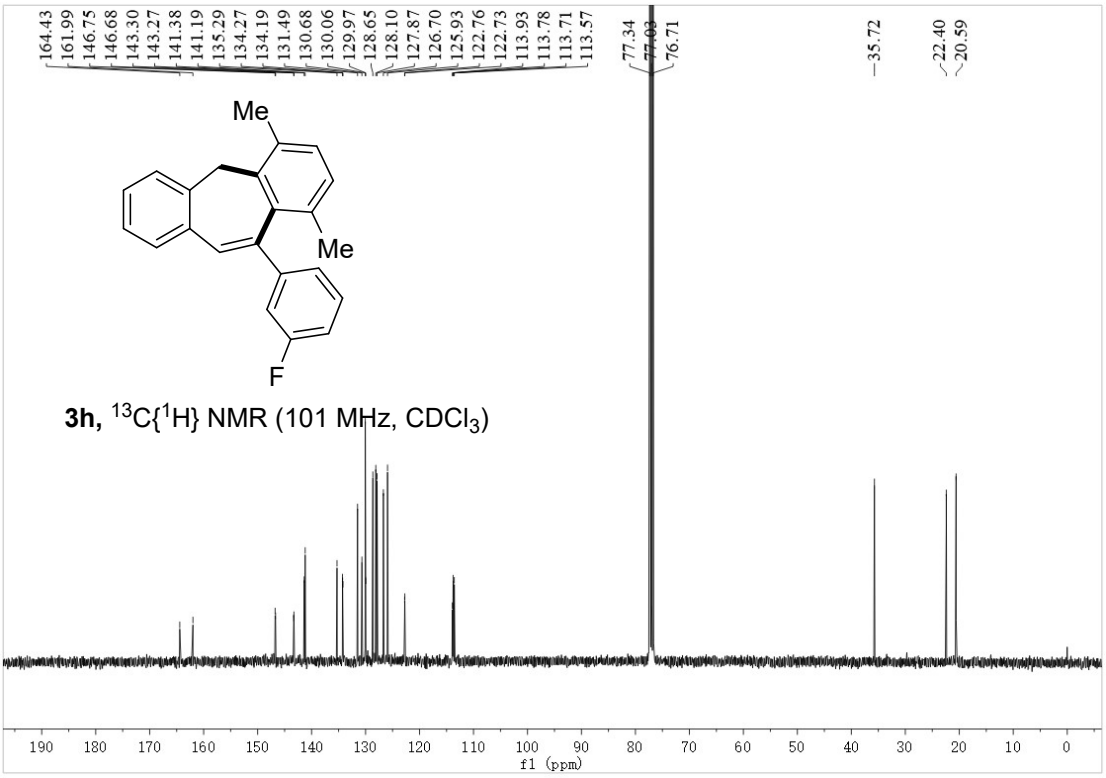
3g, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



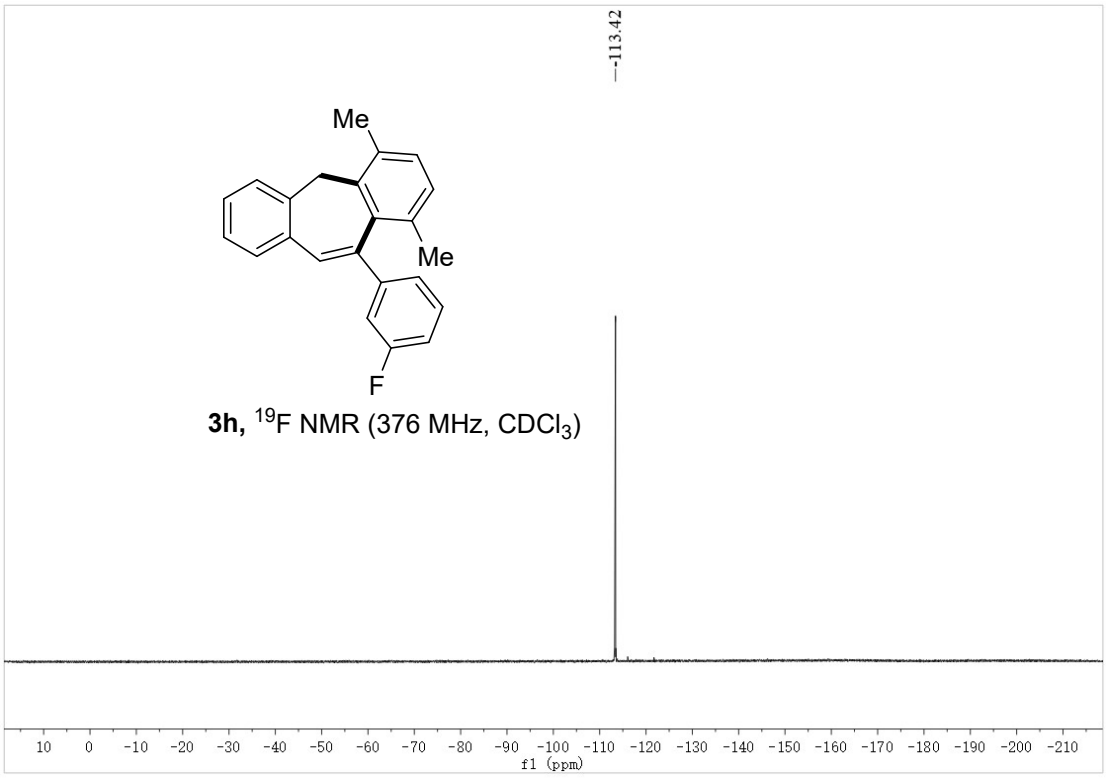
3g, ^{19}F NMR (376 MHz, $CDCl_3$)



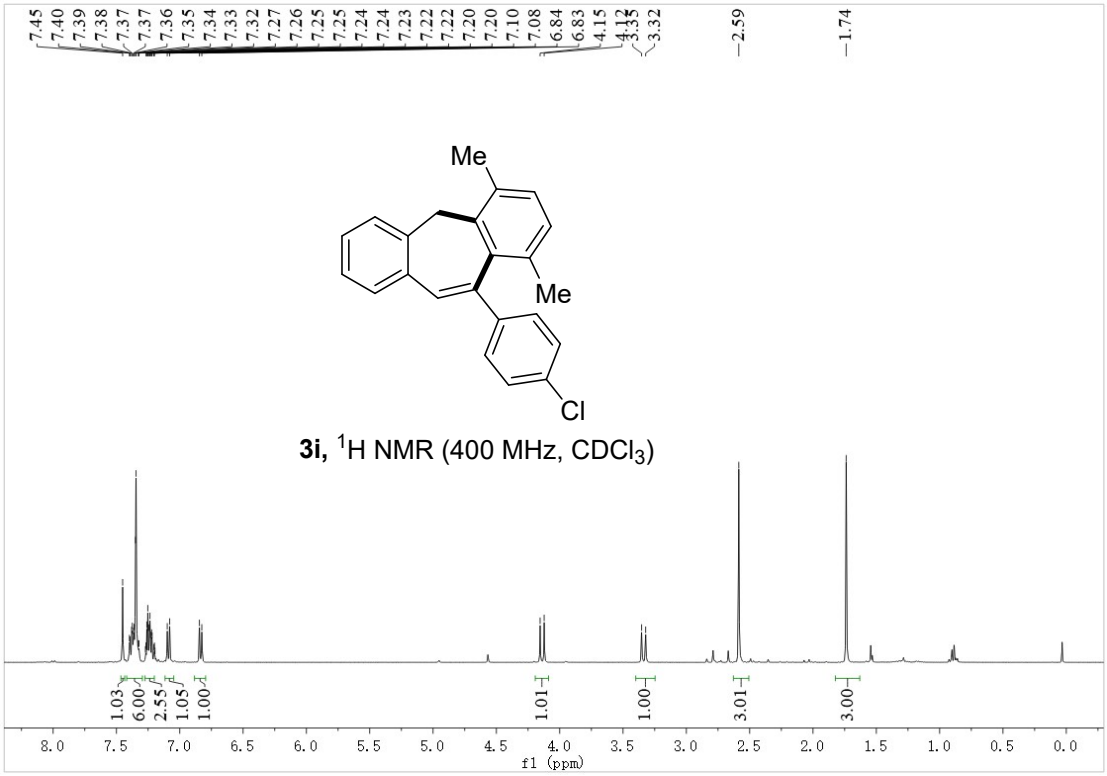
3h, ^{1}H NMR (400 MHz, $CDCl_3$)

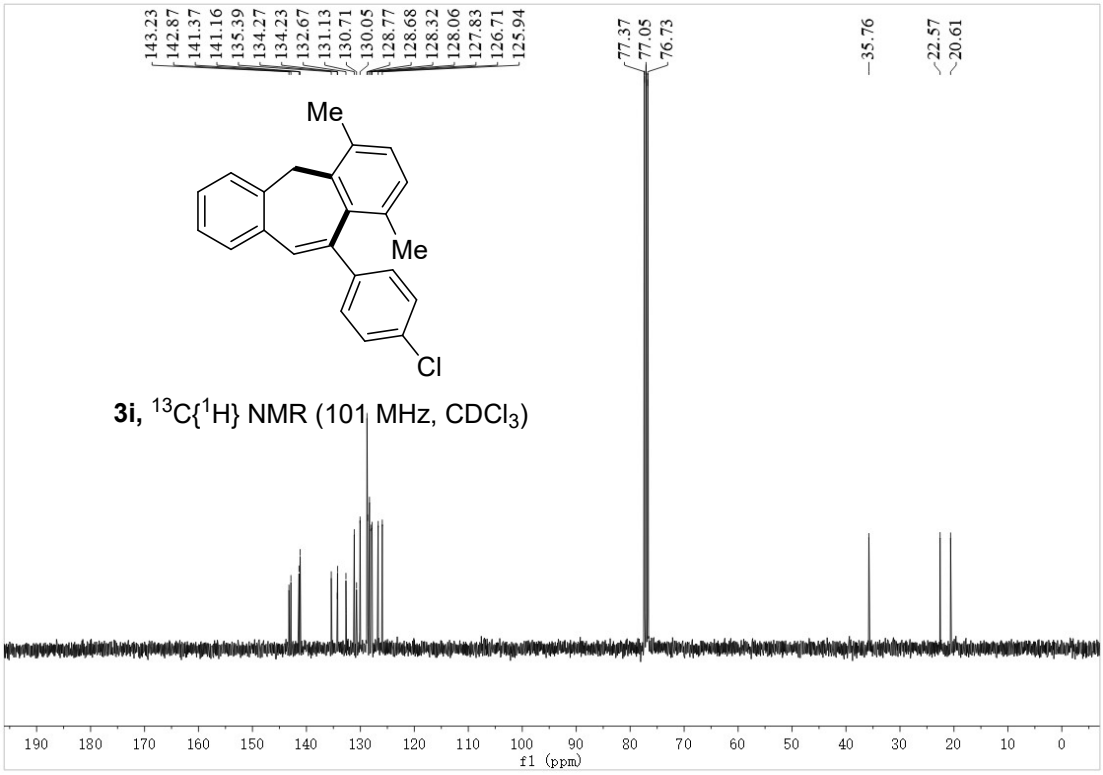


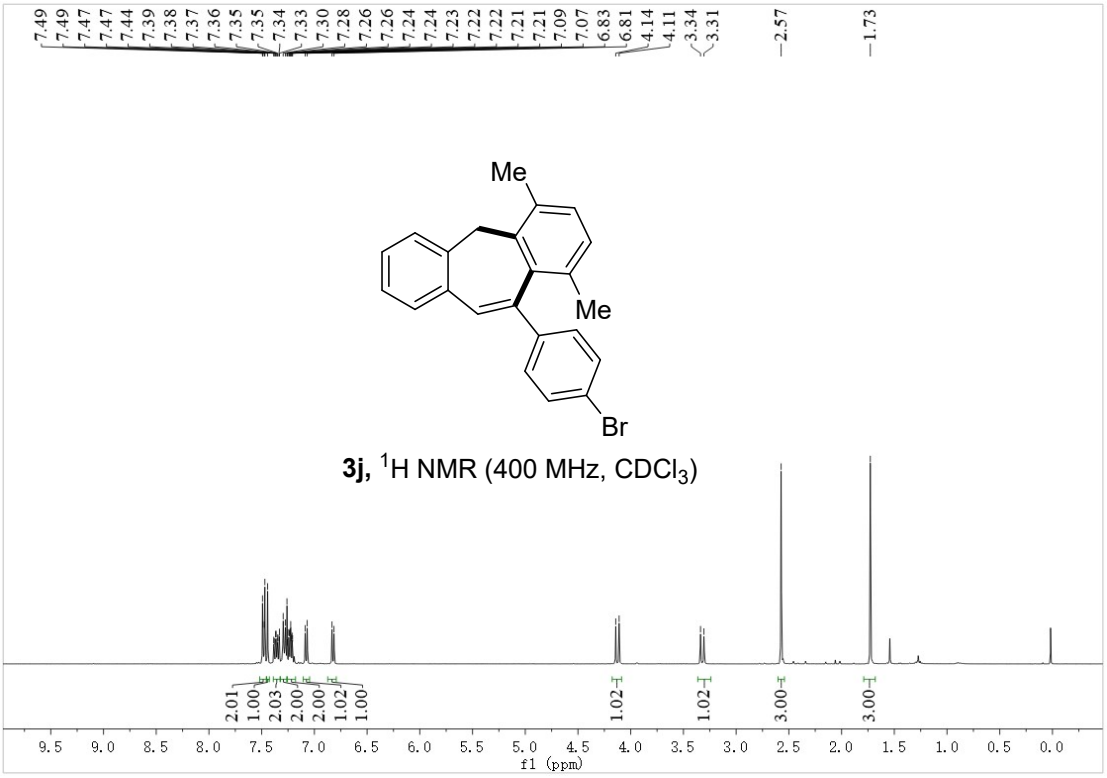
3h, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



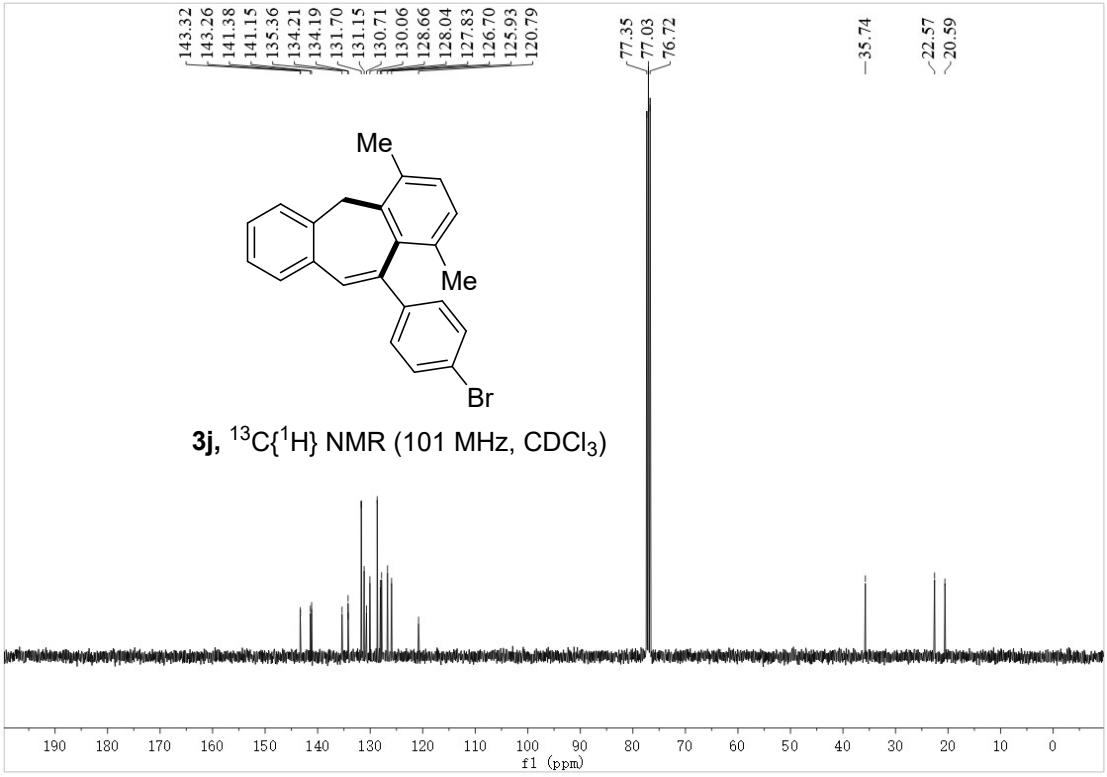
3h, ^{19}F NMR (376 MHz, $CDCl_3$)


Me
Me
Cl
3i, 1H NMR (400 MHz, CDCl3)
f1 (ppm)

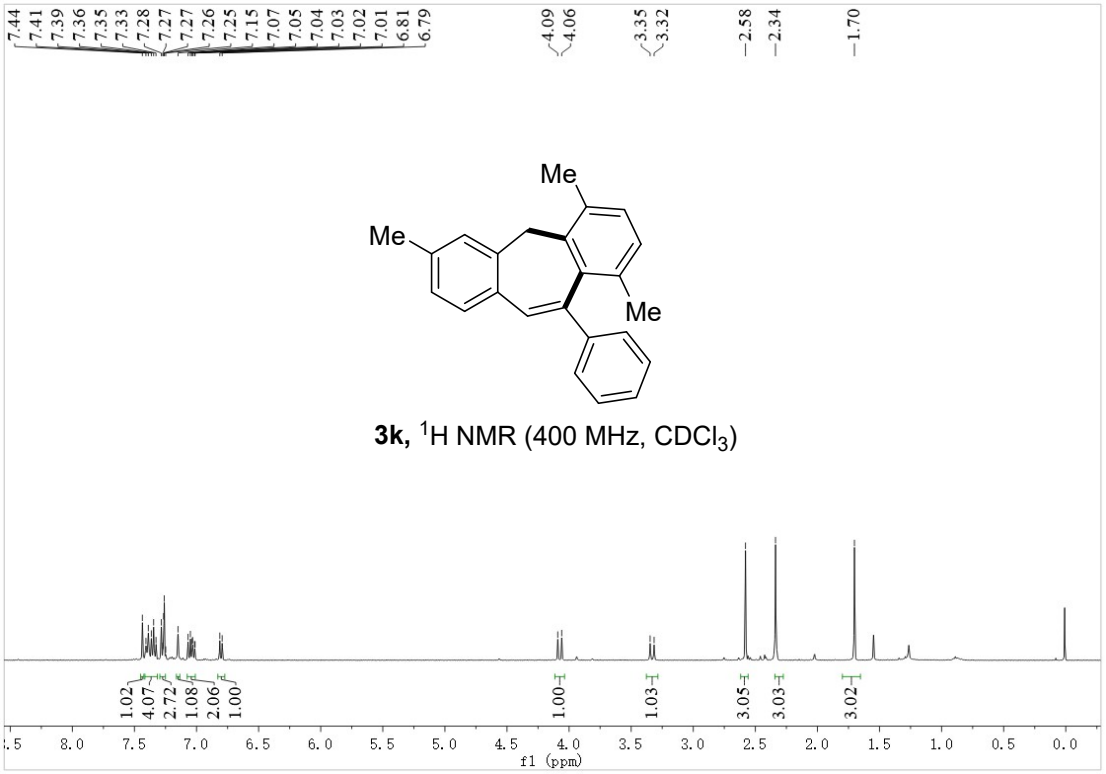

Me
Me
Cl
3i, 13C{1H} NMR (101 MHz, CDCl3)
f1 (ppm)



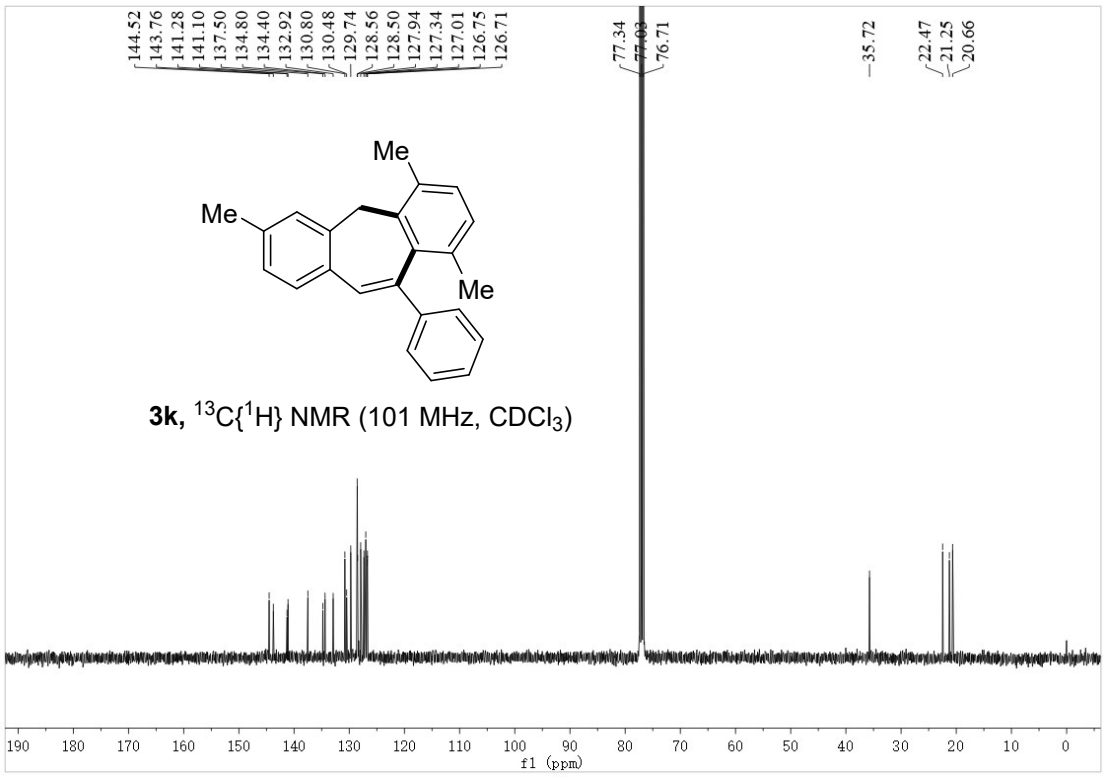
3j, ^{1}H NMR (400 MHz, $CDCl_3$)



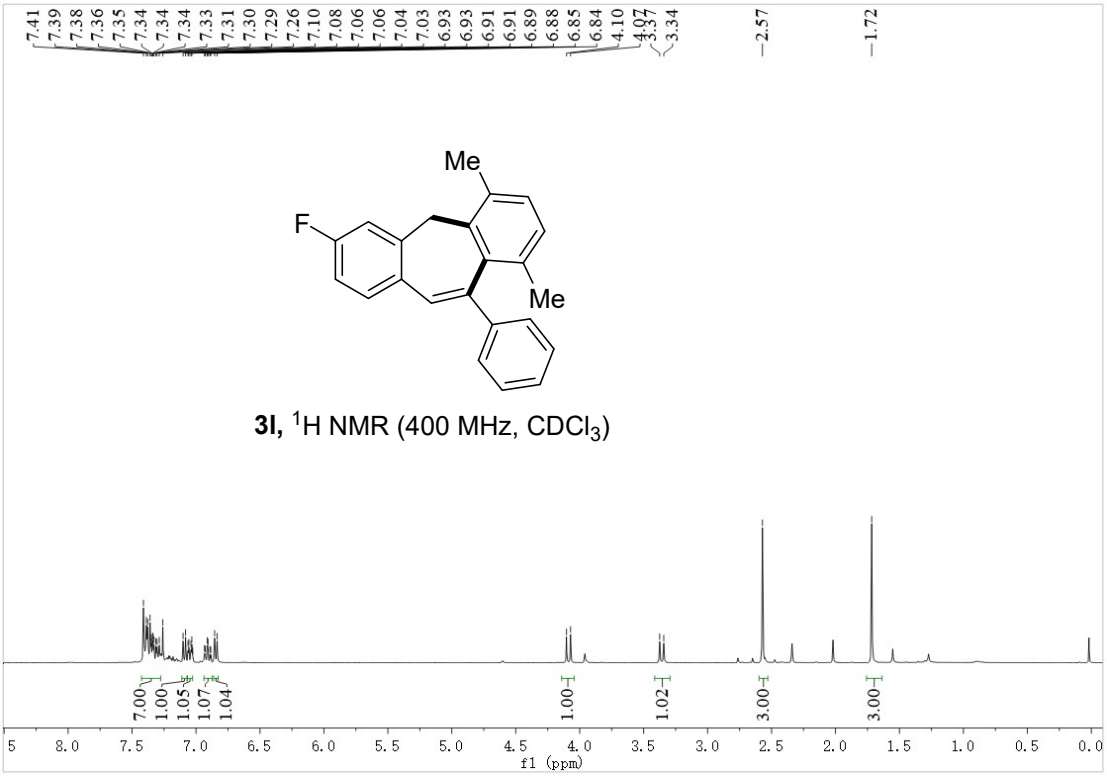
3j, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



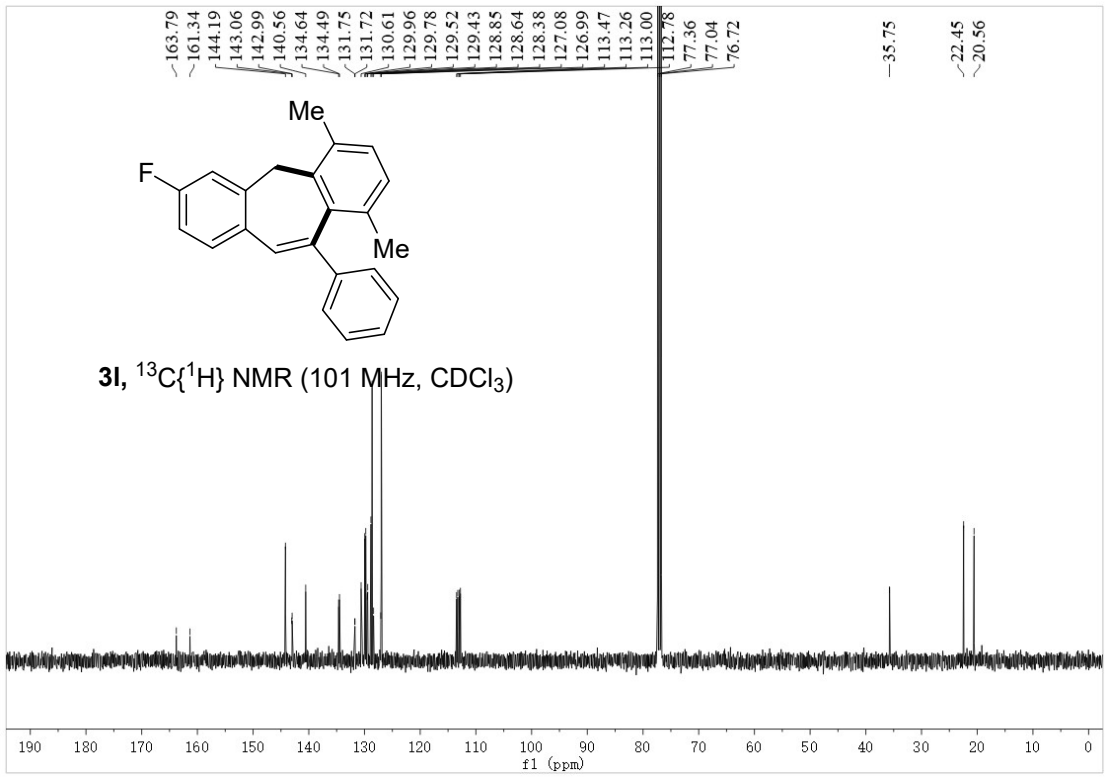
3k, ^{1}H NMR (400 MHz, $CDCl_3$)



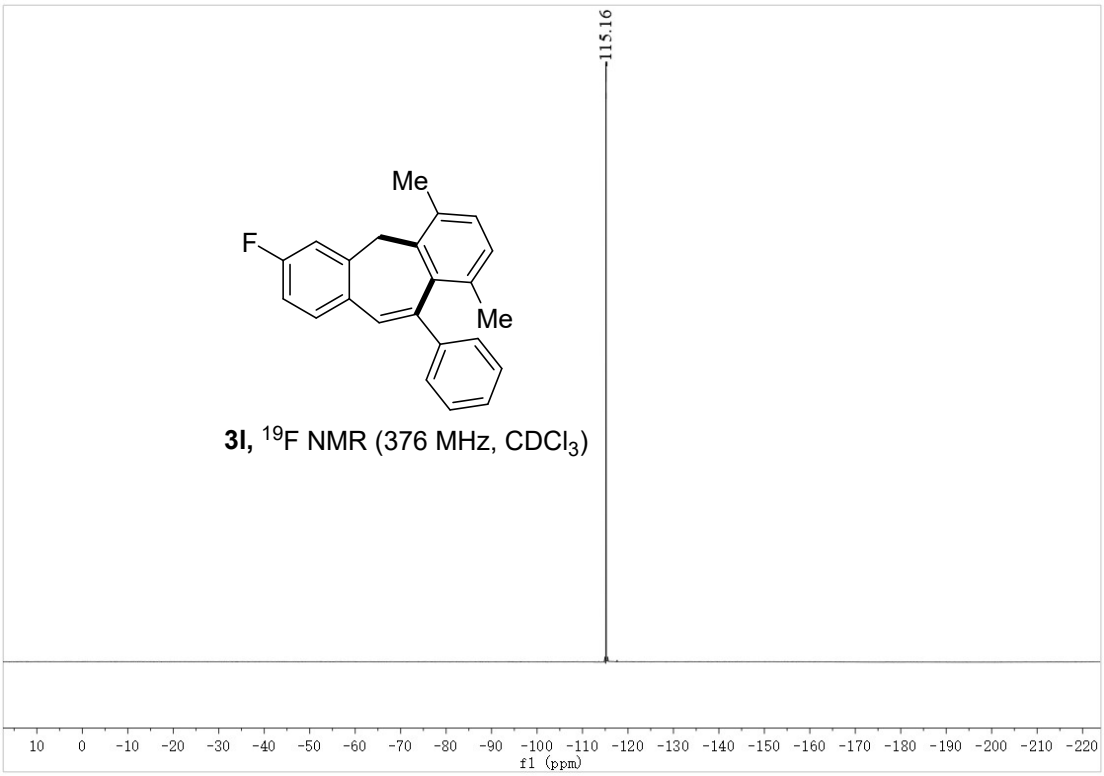
3k, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



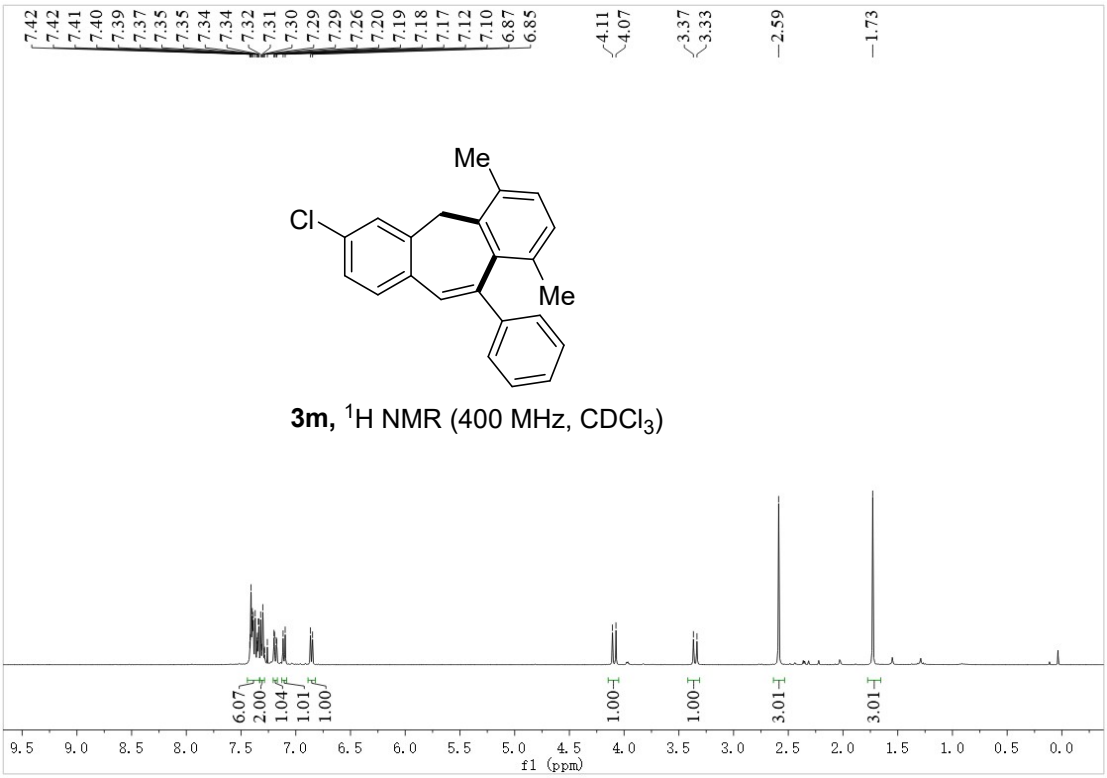
3l, ^{1}H NMR (400 MHz, $CDCl_3$)



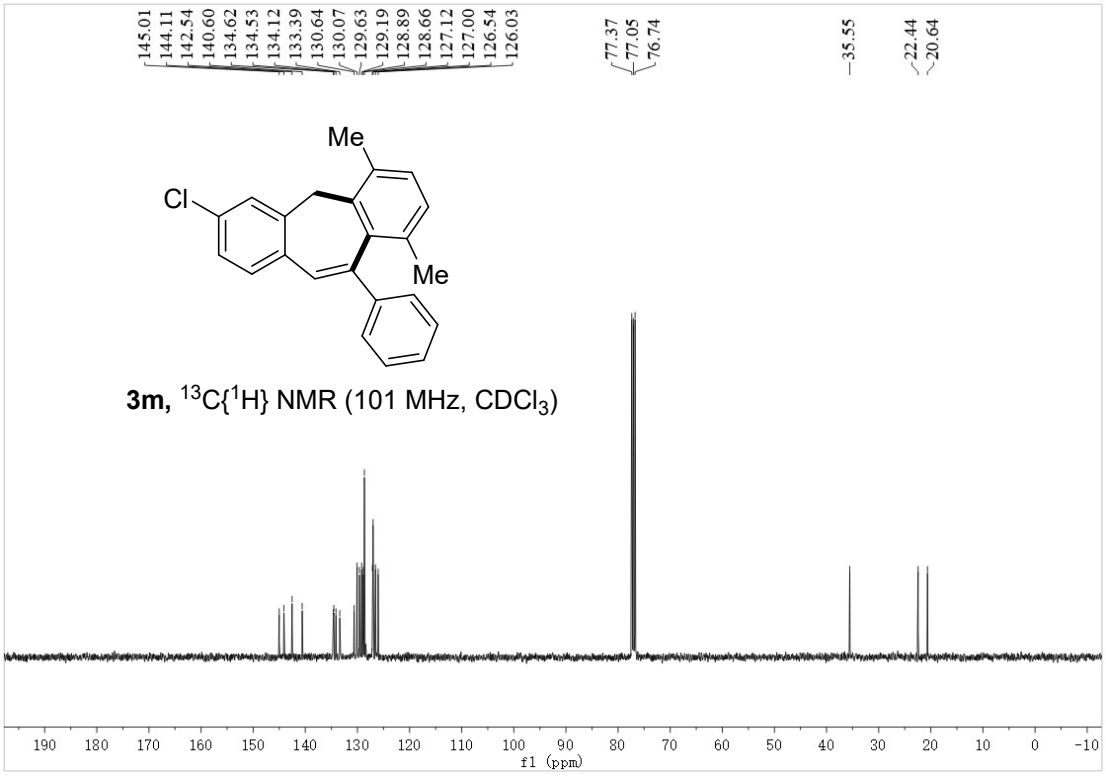
3l, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



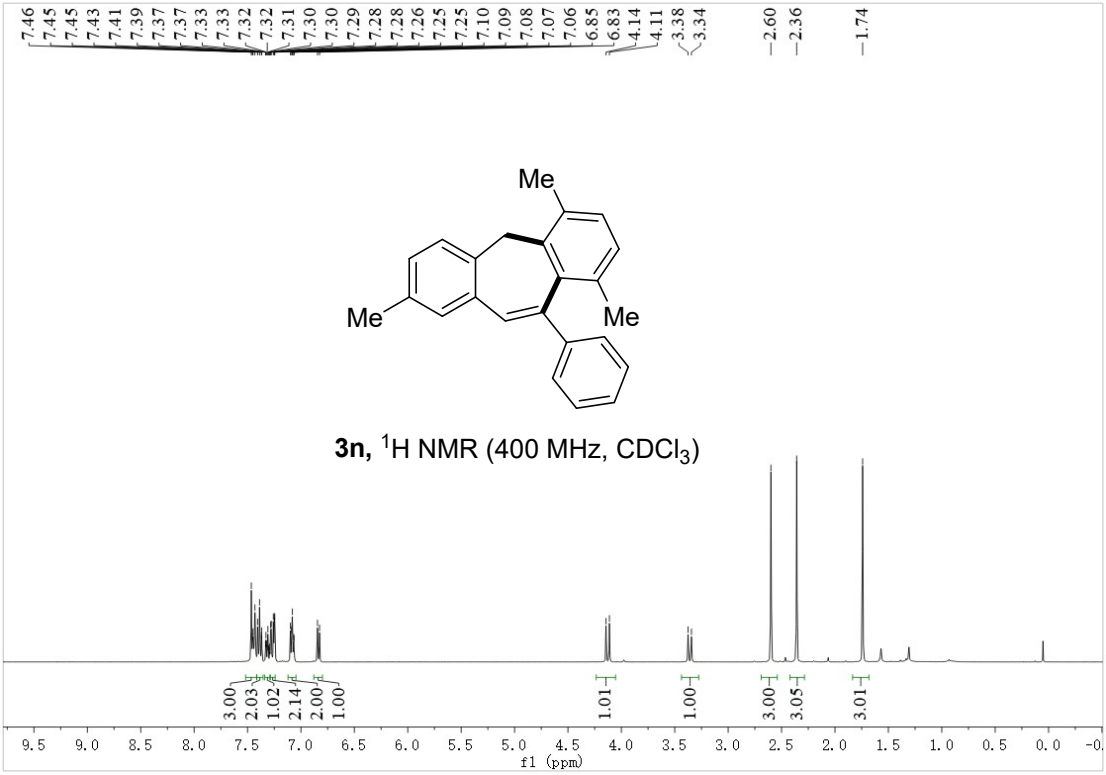
3l, ^{19}F NMR (376 MHz, $CDCl_3$)



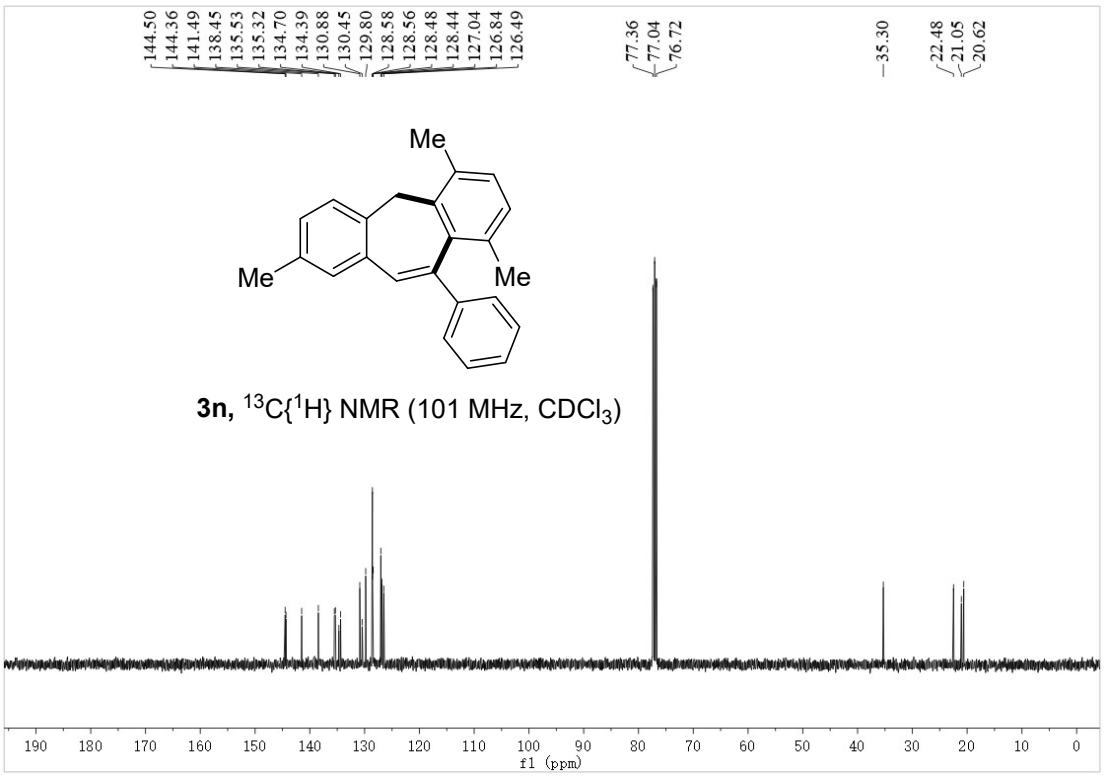
3m, ^{1}H NMR (400 MHz, $CDCl_3$)



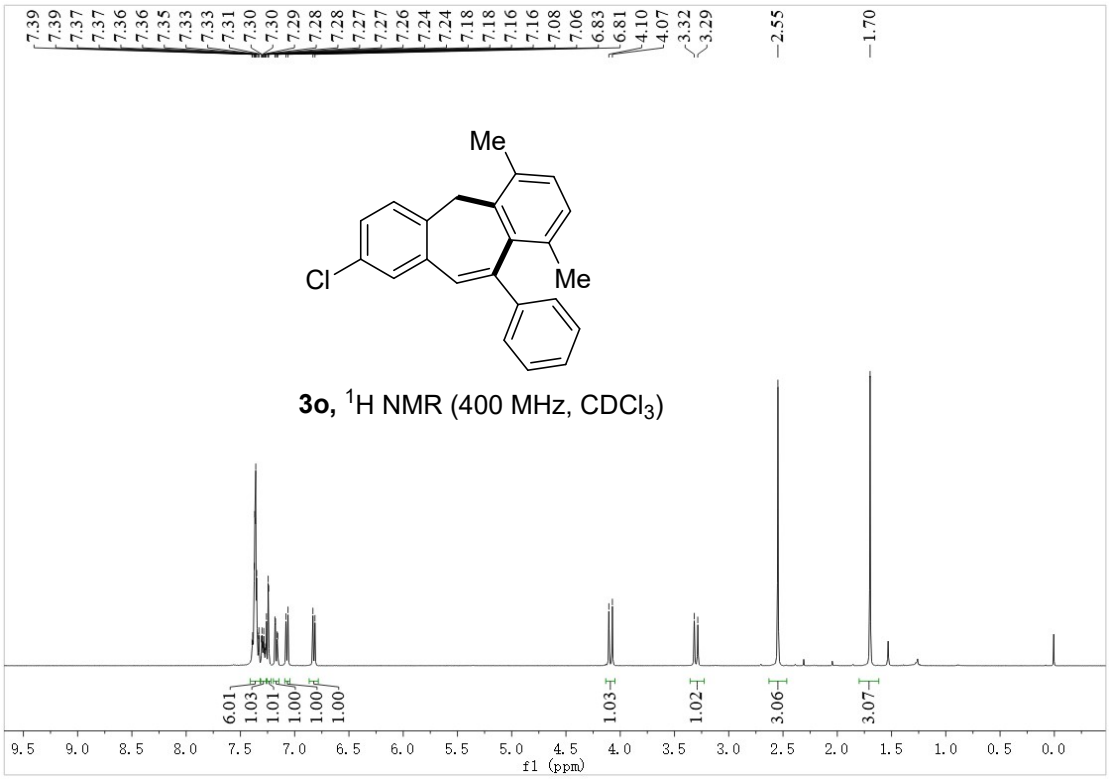
3m, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



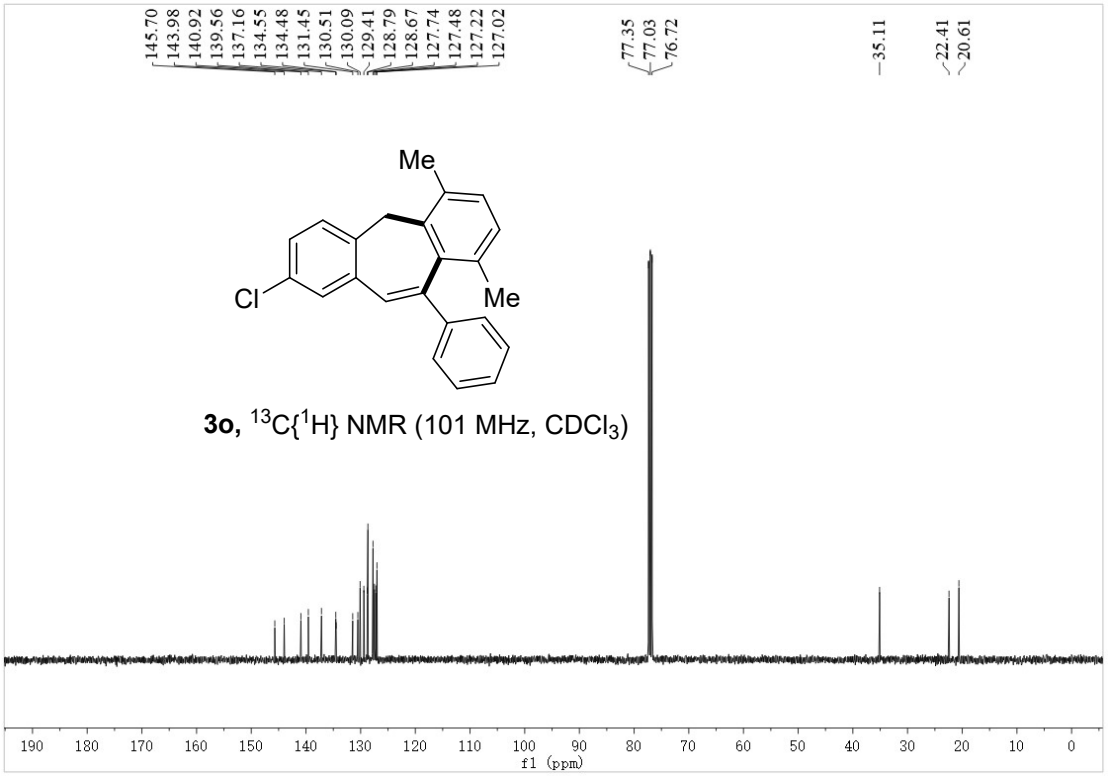
3n, ^{1}H NMR (400 MHz, $CDCl_3$)



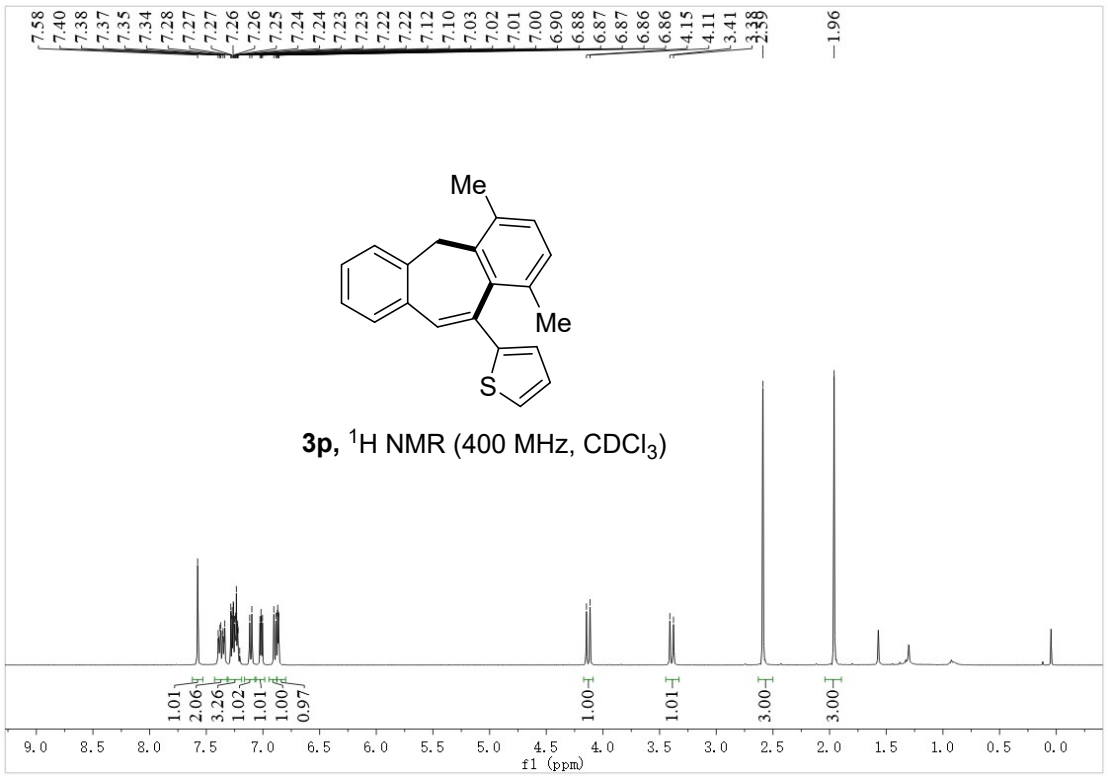
3n, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



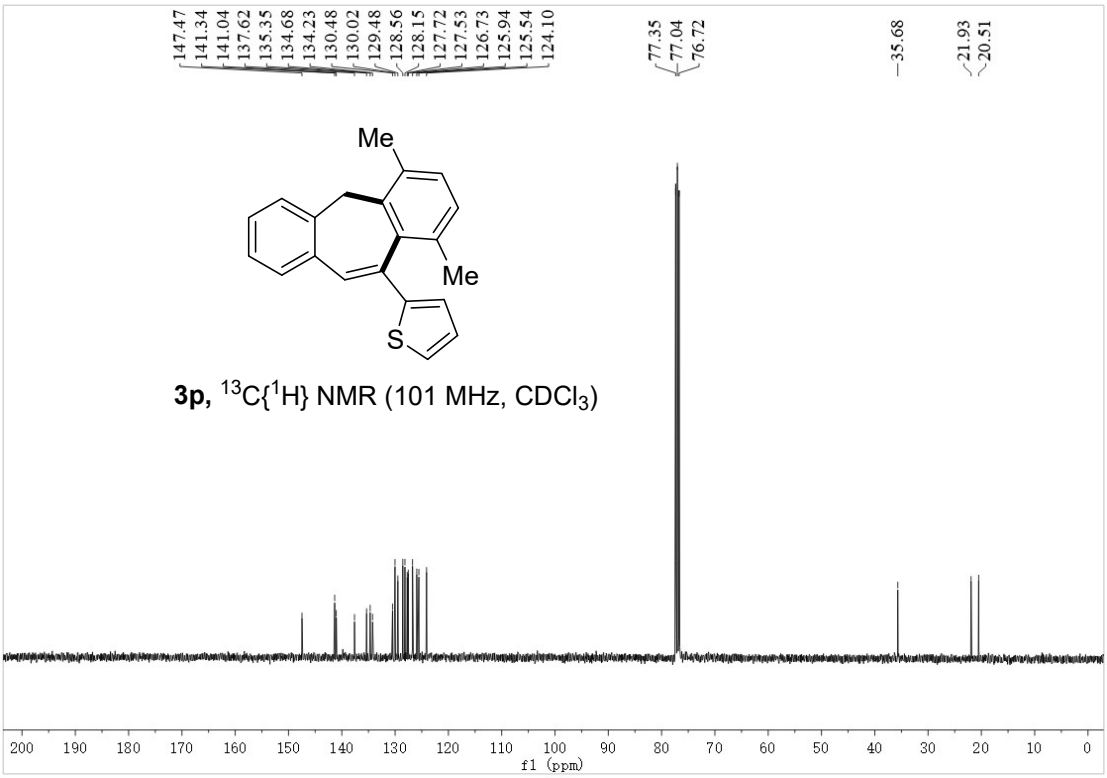
3o, ^{1}H NMR (400 MHz, $CDCl_3$)



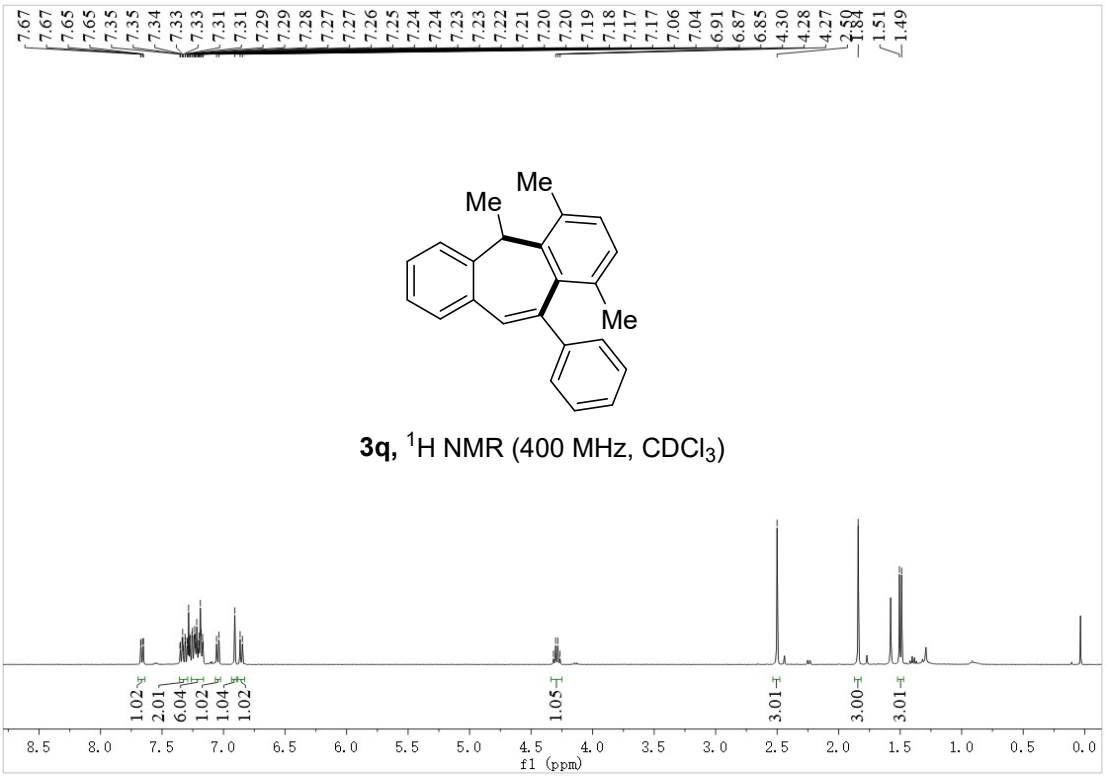
3o, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



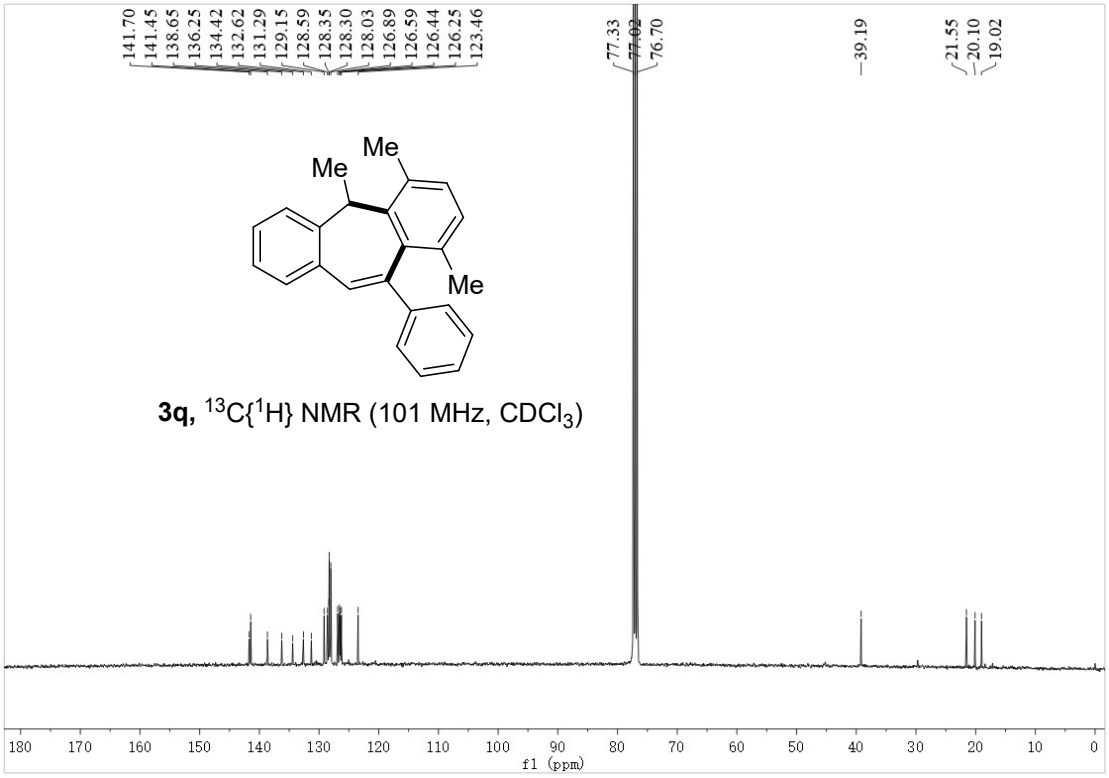
3p, ^{1}H NMR (400 MHz, $CDCl_3$)



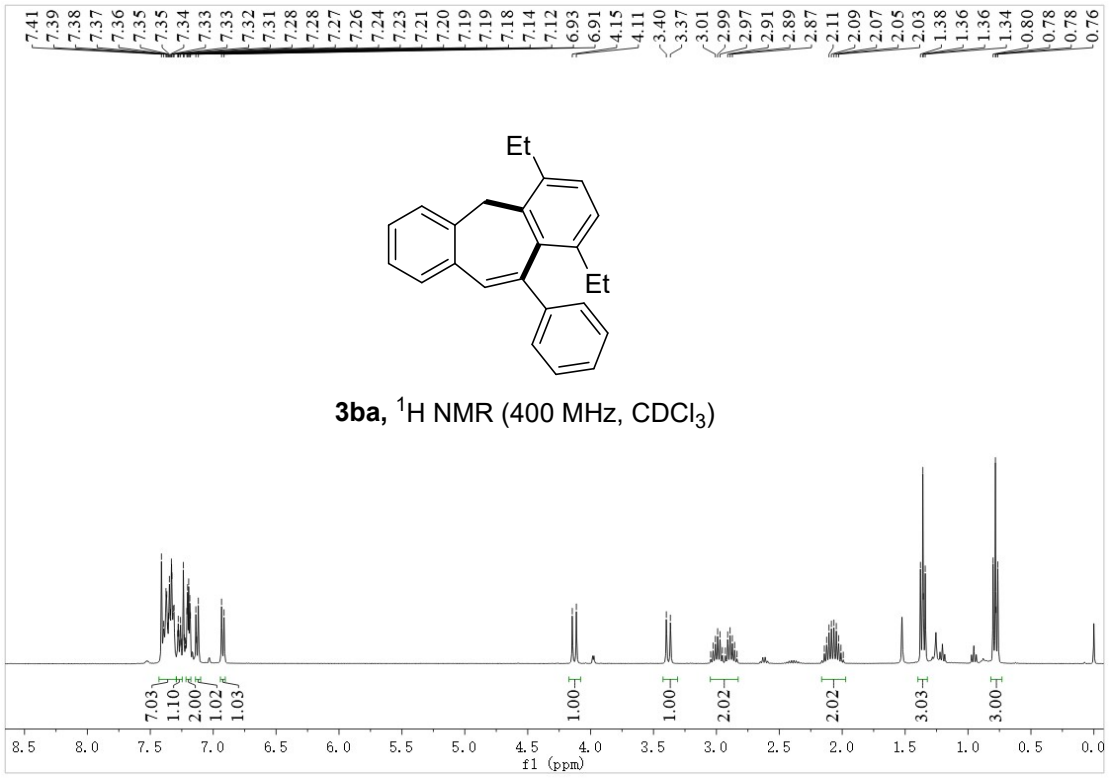
3p, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



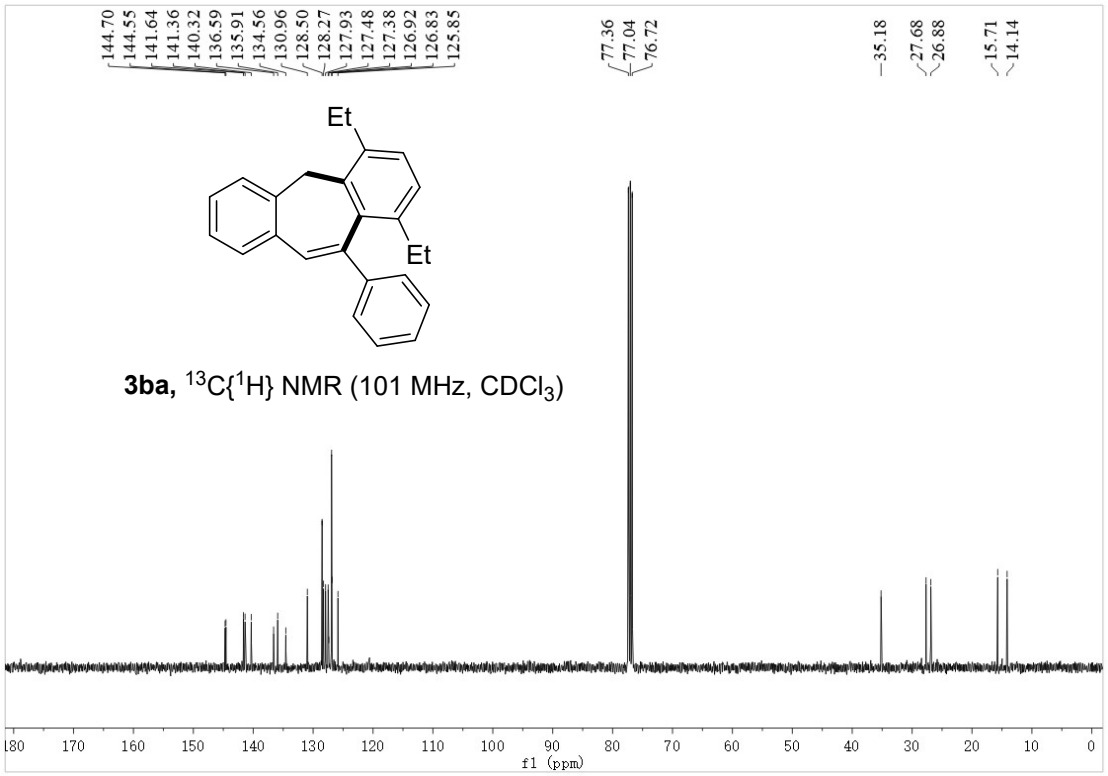
3q, ^{1}H NMR (400 MHz, $CDCl_3$)



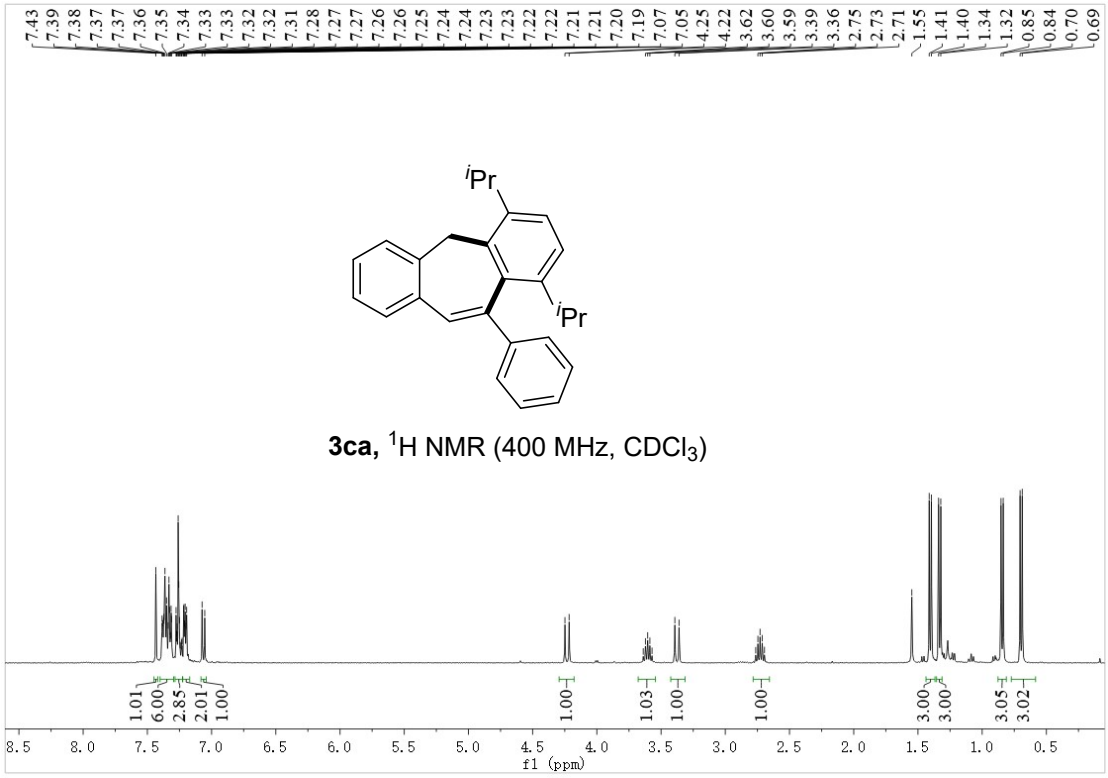
3q, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



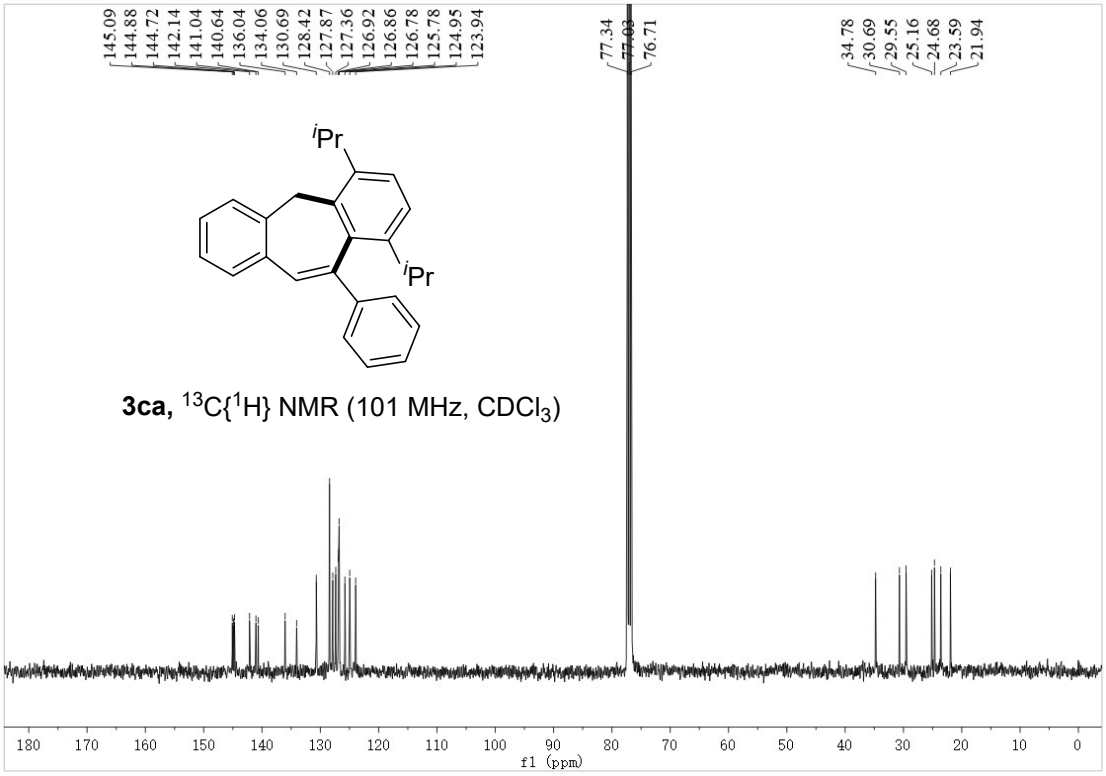
3ba, ^{1}H NMR (400 MHz, $CDCl_3$)



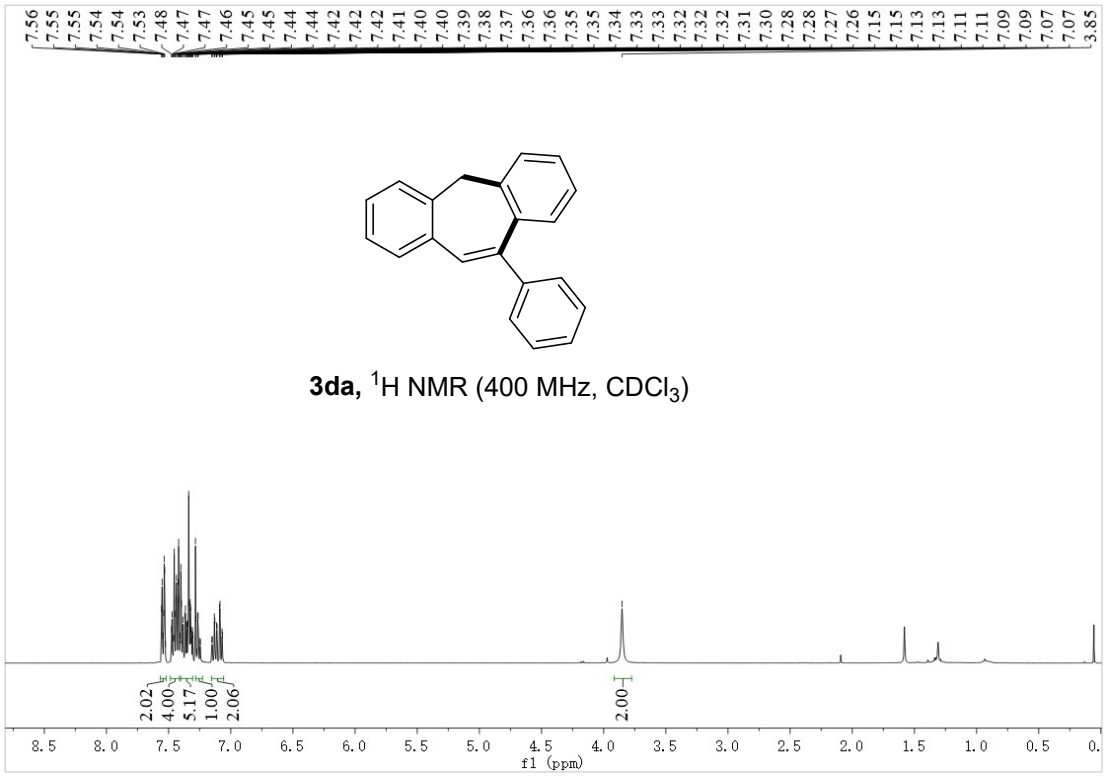
3ba, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



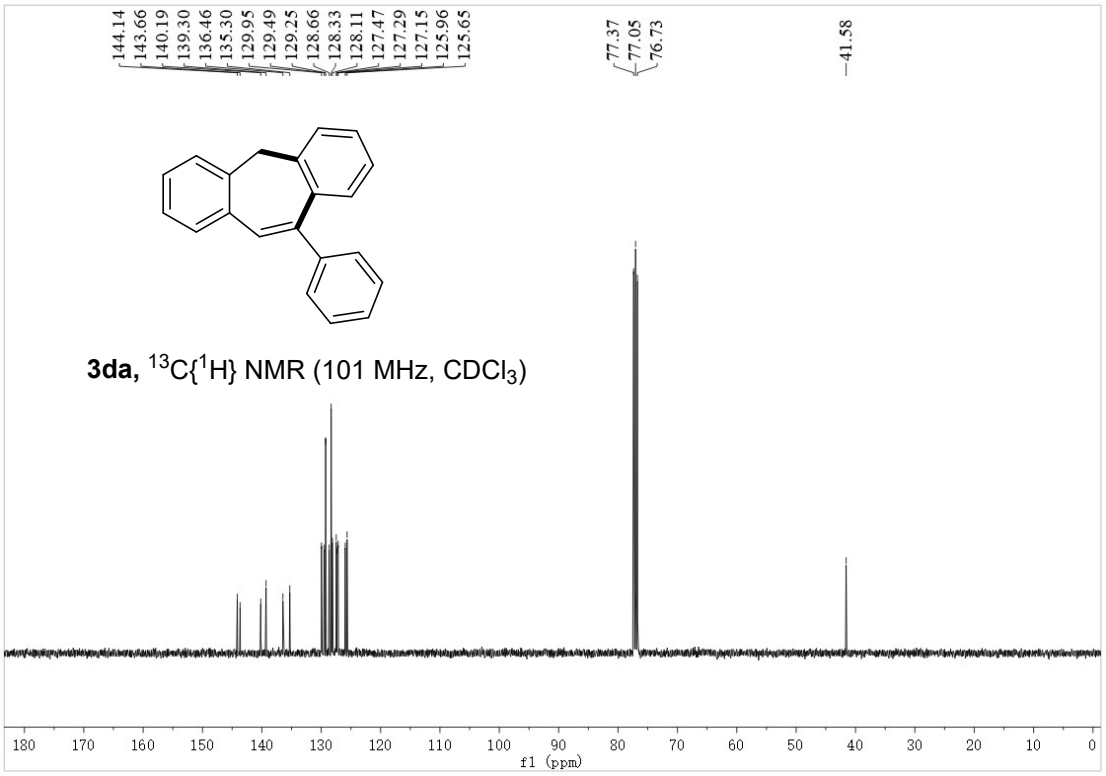
3ca, ^{1}H NMR (400 MHz, $CDCl_3$)



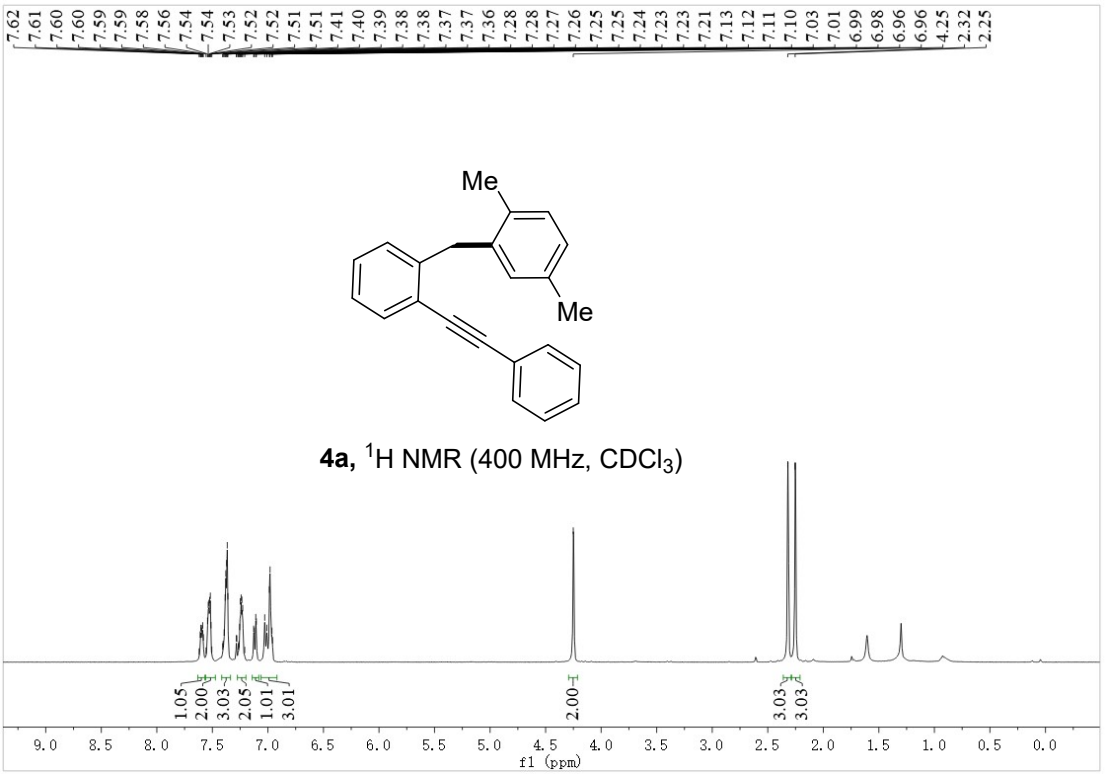
3ca, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



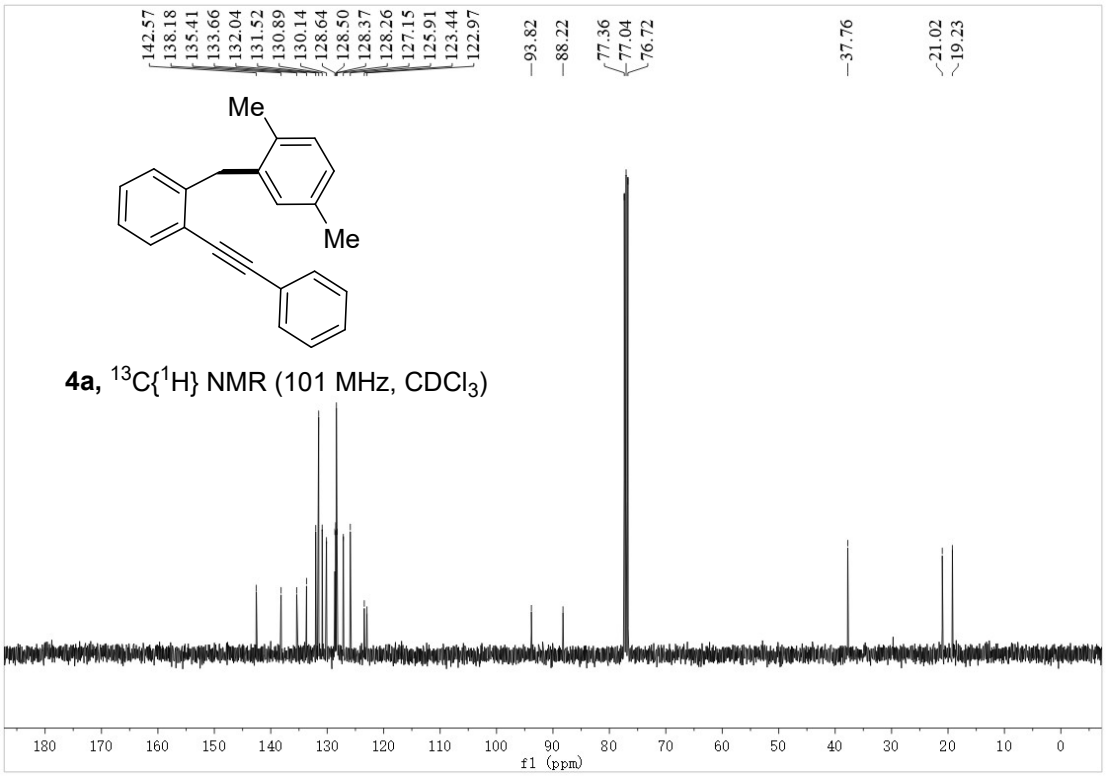
3da, ^{1}H NMR (400 MHz, $CDCl_3$)



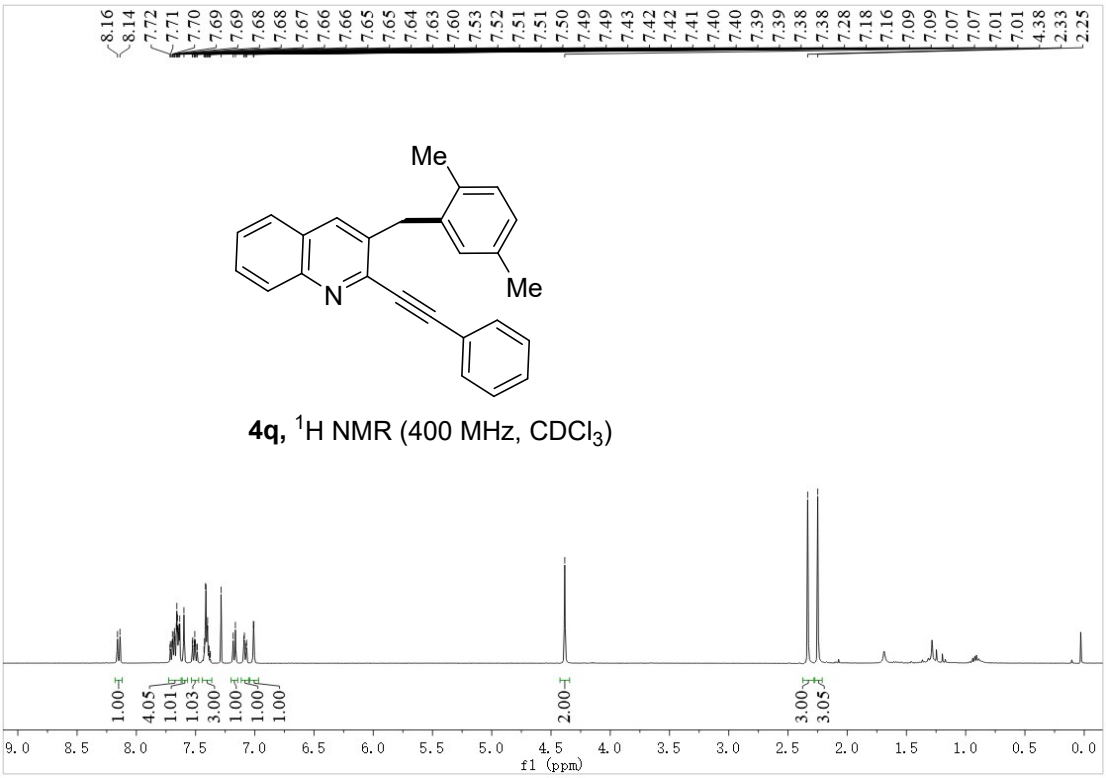
3da, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



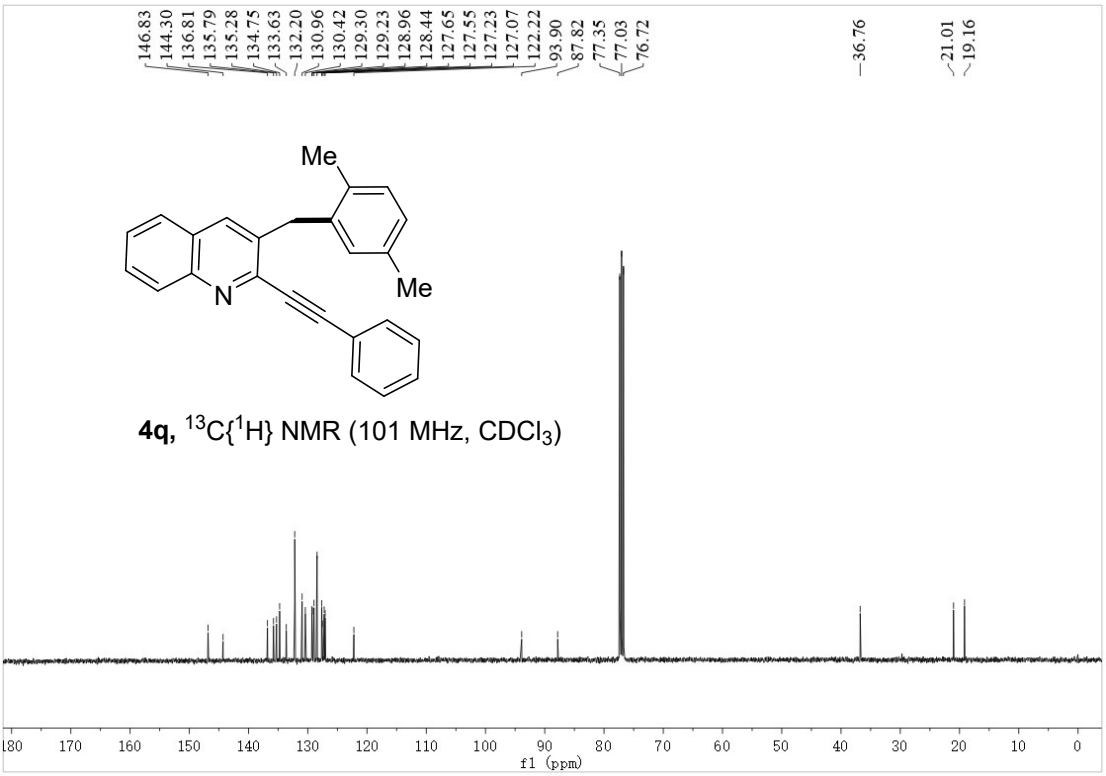
4a, ^{1}H NMR (400 MHz, $CDCl_3$)



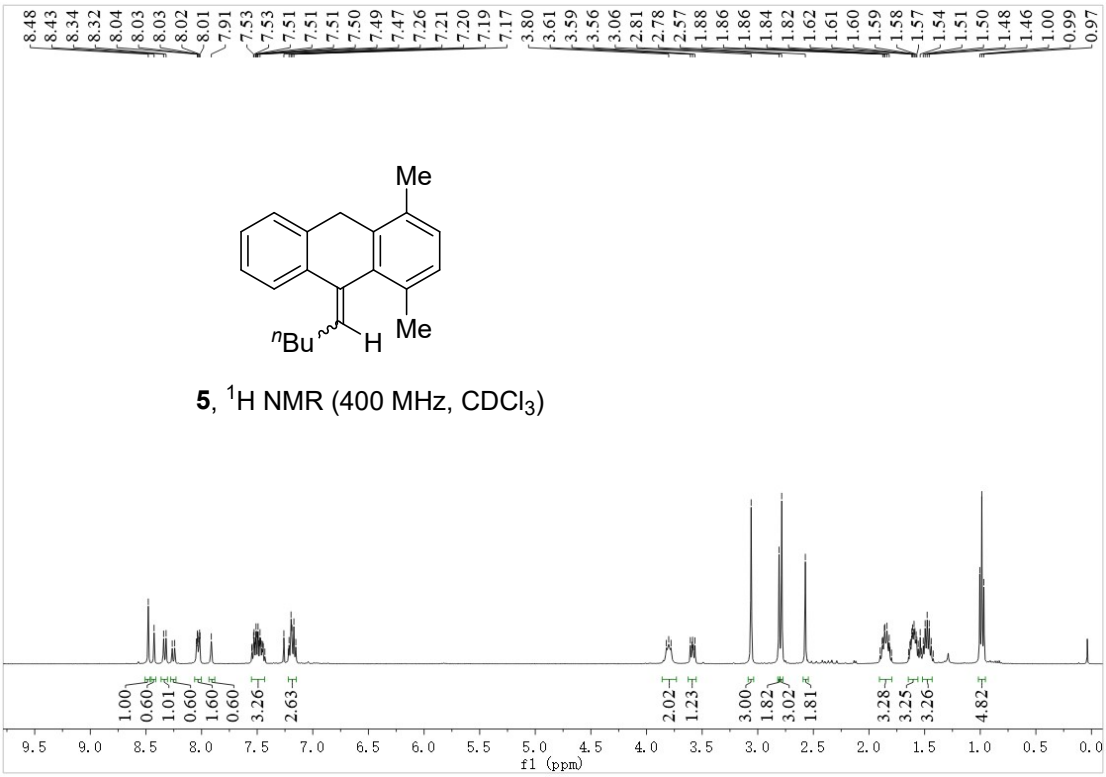
4a, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



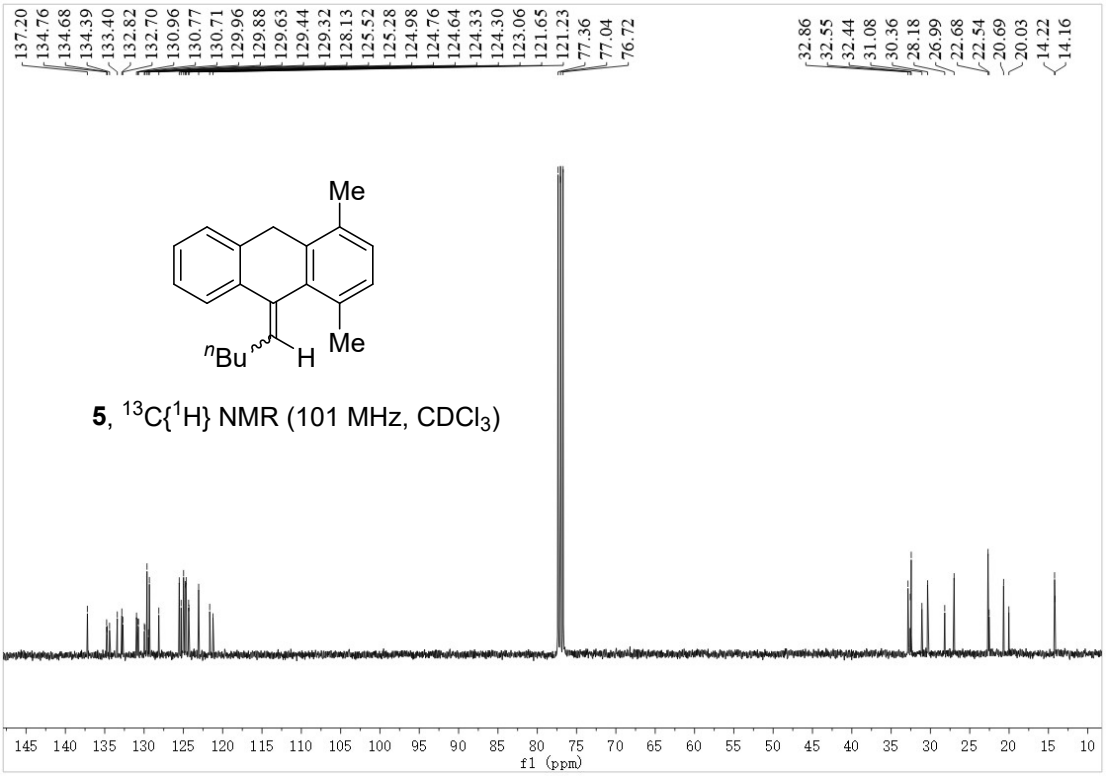
4q, ^{1}H NMR (400 MHz, $CDCl_3$)



4q, $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



5, ^{1}H NMR (400 MHz, $CDCl_3$)



Crystallographic spectrum of 3a

Qualified crystals of **3a** suitable for the X-ray crystallographic study were readily obtained by slow diffusion of n-hexane into $CHCl_3$ solution of **3a**. Crystal data Crystallographic data for compound **3a** (CCDC 2163866) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

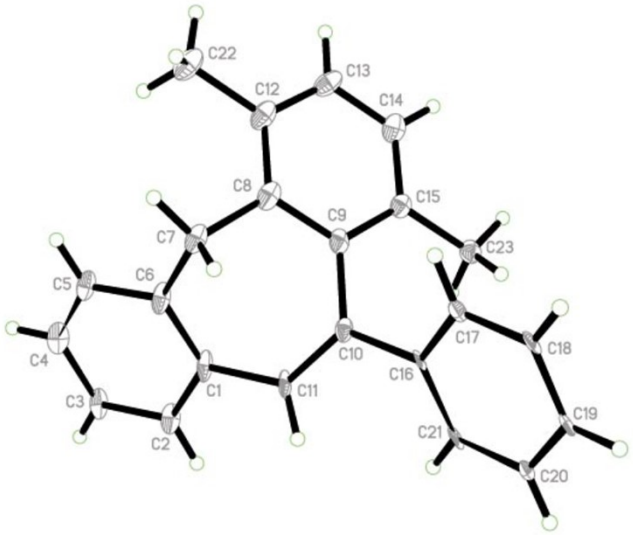


Figure S1: Ortep view of the complex **3a (**The ellipsoid contour percent probability level is 30%).

Table 1. Crystal data and structure refinement for **3a**.

Identification code	2	
Empirical formula	C23 H20	
Formula weight	296.39	
Temperature	153(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 5.66890(10) Å	α= 90°.
	b = 10.27550(10) Å	β= 90°.
	c = 27.4770(4) Å	γ = 90°.
Volume	1600.56(4) $Å^3$	
Z	4	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.520 mm^{-1}	
F(000)	632	
Crystal size	0.80 x 0.30 x 0.30 mm^3	
Theta range for data collection	3.22 to 74.14°.	
Index ranges	-6<=h<=2, -12<=k<=12, -32<=l<=34	
Reflections collected	6090	
Independent reflections	2973 [R(int) = 0.0213]	
Completeness to theta = 74.14°	96.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.35460	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2973 / 0 / 210	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0908	
R indices (all data)	R1 = 0.0365, wR2 = 0.0919	
Absolute structure parameter	-0.7(18)	
Extinction coefficient	0.0059(5)	
Largest diff. peak and hole	0.186 and -0.185 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(8)	5774(2)	1340(1)	3553(1)	24(1)
C(12)	4960(3)	531(1)	3177(1)	28(1)
C(9)	7610(3)	2236(1)	3471(1)	24(1)
C(10)	8466(3)	3086(1)	3873(1)	27(1)
C(15)	8689(3)	2298(1)	3006(1)	27(1)
C(2)	6592(3)	626(2)	4392(1)	29(1)
C(11)	9028(3)	2640(2)	4318(1)	30(1)
C(7)	4789(3)	1244(1)	4062(1)	28(1)
C(16)	8612(3)	4518(1)	3773(1)	29(1)
C(1A)	8634(3)	1326(2)	4513(1)	30(1)
C(17B)	6802(3)	5116(1)	3514(1)	32(1)
C(13C)	6004(3)	631(1)	2724(1)	32(1)
C(23D)	10777(3)	3159(1)	2901(1)	34(1)
C(14E)	7850(3)	1489(1)	2643(1)	31(1)
C(18F)	6778(3)	6456(2)	3443(1)	37(1)
C(6G)	10206(3)	799(2)	4852(1)	37(1)
C(3H)	6271(3)	-614(2)	4585(1)	36(1)
C(21I)	10434(3)	5291(2)	3954(1)	37(1)
C(19J)	8581(3)	7216(2)	3629(1)	40(1)
C(22K)	2955(3)	-417(2)	3256(1)	36(1)
C(20L)	10402(3)	6634(2)	3881(1)	42(1)
C(4M)	7903(3)	-1140(2)	4905(1)	46(1)
C(5N)	9870(3)	-432(2)	5043(1)	46(1)

Table 3. Bond lengths [Å] and angles [°] for 2.

C(8)-C(12)	1.404(2)
C(8)-C(9)	1.4078(19)
C(8)-C(7)	1.509(2)
C(12)-C(13C)	1.383(2)
C(12)-C(22K)	1.512(2)
C(9)-C(15)	1.417(2)
C(9)-C(10)	1.489(2)
C(10)-C(11)	1.345(2)
C(10)-C(16)	1.498(2)
C(15)-C(14E)	1.384(2)
C(15)-C(23D)	1.506(2)
C(2)-C(3H)	1.392(2)
C(2)-C(1A)	1.402(2)
C(2)-C(7)	1.507(2)
C(11)-C(1A)	1.469(2)
C(11)-H(11A)	0.9500
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(16)-C(17B)	1.392(2)
C(16)-C(21I)	1.395(2)
C(1A)-C(6G)	1.398(2)
C(17B)-C(18F)	1.391(2)
C(17B)-H(17A)	0.9500
C(13C)-C(14E)	1.386(2)
C(13C)-H(13A)	0.9500
C(23D)-H(23A)	0.9800
C(23D)-H(23B)	0.9800
C(23D)-H(23C)	0.9800
C(14E)-H(14A)	0.9500
C(18F)-C(19J)	1.384(2)
C(18F)-H(18A)	0.9500
C(6G)-C(5N)	1.382(3)
C(6G)-H(6GA)	0.9500
C(3H)-C(4M)	1.386(2)
C(3H)-H(3HA)	0.9500
C(21I)-C(20L)	1.395(2)

C(21I)-H(21A)	0.9500
C(19J)-C(20L)	1.379(3)
C(19J)-H(19A)	0.9500
C(22K)-H(22A)	0.9800
C(22K)-H(22B)	0.9800
C(22K)-H(22C)	0.9800
C(20L)-H(20A)	0.9500
C(4M)-C(5N)	1.384(3)
C(4M)-H(4MA)	0.9500
C(5N)-H(5NA)	0.9500

C(12)-C(8)-C(9)	120.80(13)
C(12)-C(8)-C(7)	121.41(12)
C(9)-C(8)-C(7)	117.74(13)
C(13C)-C(12)-C(8)	118.54(13)
C(13C)-C(12)-C(22K)	119.87(14)
C(8)-C(12)-C(22K)	121.58(14)
C(8)-C(9)-C(15)	119.54(13)
C(8)-C(9)-C(10)	120.38(13)
C(15)-C(9)-C(10)	120.06(13)
C(11)-C(10)-C(9)	123.44(14)
C(11)-C(10)-C(16)	119.19(13)
C(9)-C(10)-C(16)	117.33(13)
C(14E)-C(15)-C(9)	118.39(13)
C(14E)-C(15)-C(23D)	118.98(14)
C(9)-C(15)-C(23D)	122.57(14)
C(3H)-C(2)-C(1A)	119.16(15)
C(3H)-C(2)-C(7)	121.74(14)
C(1A)-C(2)-C(7)	119.09(13)
C(10)-C(11)-C(1A)	127.52(14)
C(10)-C(11)-H(11A)	116.2
C(1A)-C(11)-H(11A)	116.2
C(2)-C(7)-C(8)	109.54(12)
C(2)-C(7)-H(7A)	109.8
C(8)-C(7)-H(7A)	109.8
C(2)-C(7)-H(7B)	109.8
C(8)-C(7)-H(7B)	109.8
H(7A)-C(7)-H(7B)	108.2

C(17B)-C(16)-C(21I)	118.49(14)
C(17B)-C(16)-C(10)	119.06(13)
C(21I)-C(16)-C(10)	122.34(15)
C(6G)-C(1A)-C(2)	119.03(15)
C(6G)-C(1A)-C(11)	120.10(15)
C(2)-C(1A)-C(11)	120.68(14)
C(18F)-C(17B)-C(16)	121.07(15)
C(18F)-C(17B)-H(17A)	119.5
C(16)-C(17B)-H(17A)	119.5
C(12)-C(13C)-C(14E)	121.02(14)
C(12)-C(13C)-H(13A)	119.5
C(14E)-C(13C)-H(13A)	119.5
C(15)-C(23D)-H(23A)	109.5
C(15)-C(23D)-H(23B)	109.5
H(23A)-C(23D)-H(23B)	109.5
C(15)-C(23D)-H(23C)	109.5
H(23A)-C(23D)-H(23C)	109.5
H(23B)-C(23D)-H(23C)	109.5
C(15)-C(14E)-C(13C)	121.67(14)
C(15)-C(14E)-H(14A)	119.2
C(13C)-C(14E)-H(14A)	119.2
C(19J)-C(18F)-C(17B)	120.00(16)
C(19J)-C(18F)-H(18A)	120.0
C(17B)-C(18F)-H(18A)	120.0
C(5N)-C(6G)-C(1A)	121.27(16)
C(5N)-C(6G)-H(6GA)	119.4
C(1A)-C(6G)-H(6GA)	119.4
C(4M)-C(3H)-C(2)	120.72(16)
C(4M)-C(3H)-H(3HA)	119.6
C(2)-C(3H)-H(3HA)	119.6
C(20L)-C(21I)-C(16)	120.13(17)
C(20L)-C(21I)-H(21A)	119.9
C(16)-C(21I)-H(21A)	119.9
C(20L)-C(19J)-C(18F)	119.51(15)
C(20L)-C(19J)-H(19A)	120.2
C(18F)-C(19J)-H(19A)	120.2
C(12)-C(22K)-H(22A)	109.5
C(12)-C(22K)-H(22B)	109.5

H(22A)-C(22K)-H(22B)	109.5
C(12)-C(22K)-H(22C)	109.5
H(22A)-C(22K)-H(22C)	109.5
H(22B)-C(22K)-H(22C)	109.5
C(19J)-C(20L)-C(21I)	120.79(16)
C(19J)-C(20L)-H(20A)	119.6
C(21I)-C(20L)-H(20A)	119.6
C(5N)-C(4M)-C(3H)	120.41(17)
C(5N)-C(4M)-H(4MA)	119.8
C(3H)-C(4M)-H(4MA)	119.8
C(6G)-C(5N)-C(4M)	119.23(16)
C(6G)-C(5N)-H(5NA)	120.4
C(4M)-C(5N)-H(5NA)	120.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

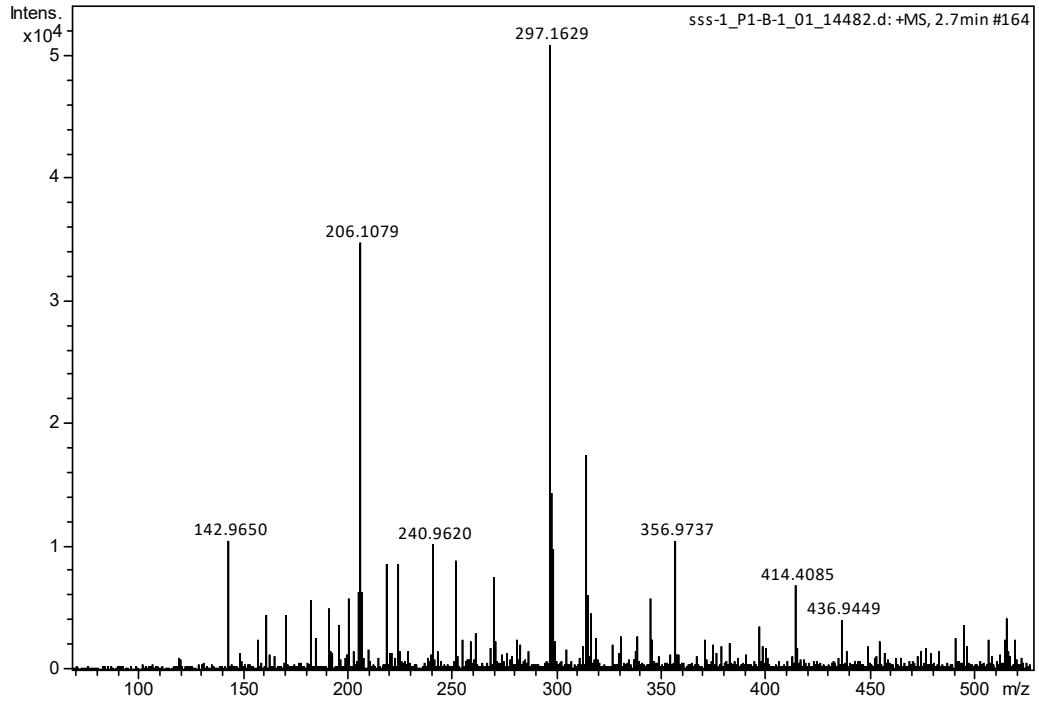
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(8)	22(1)	18(1)	33(1)	3(1)	0(1)	3(1)
C(12)	29(1)	15(1)	39(1)	1(1)	-2(1)	1(1)
C(9)	22(1)	18(1)	32(1)	3(1)	2(1)	2(1)
C(10)	18(1)	26(1)	38(1)	-3(1)	5(1)	-3(1)
C(15)	27(1)	17(1)	37(1)	3(1)	6(1)	4(1)
C(2)	23(1)	36(1)	28(1)	4(1)	6(1)	-1(1)
C(11)	19(1)	34(1)	36(1)	-5(1)	2(1)	-4(1)
C(7)	21(1)	29(1)	34(1)	2(1)	2(1)	-3(1)
C(16)	25(1)	23(1)	39(1)	-6(1)	5(1)	-2(1)
C(1A)	24(1)	40(1)	26(1)	2(1)	6(1)	-1(1)
C(17B)	24(1)	24(1)	48(1)	-7(1)	2(1)	-4(1)
C(13C)	41(1)	20(1)	36(1)	-5(1)	-2(1)	3(1)
C(23D)	32(1)	24(1)	47(1)	5(1)	13(1)	2(1)
C(14E)	40(1)	21(1)	33(1)	2(1)	8(1)	7(1)
C(18F)	31(1)	24(1)	55(1)	-4(1)	2(1)	1(1)
C(6G)	25(1)	58(1)	27(1)	6(1)	3(1)	-1(1)
C(3H)	31(1)	44(1)	35(1)	13(1)	6(1)	-6(1)
C(21I)	28(1)	31(1)	52(1)	-4(1)	0(1)	-7(1)
C(19J)	39(1)	22(1)	60(1)	-7(1)	9(1)	-5(1)
C(22K)	36(1)	21(1)	51(1)	0(1)	-4(1)	-5(1)
C(20L)	37(1)	31(1)	59(1)	-9(1)	0(1)	-14(1)
C(4M)	40(1)	57(1)	41(1)	27(1)	5(1)	-4(1)
C(5N)	33(1)	74(1)	31(1)	22(1)	3(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 2.

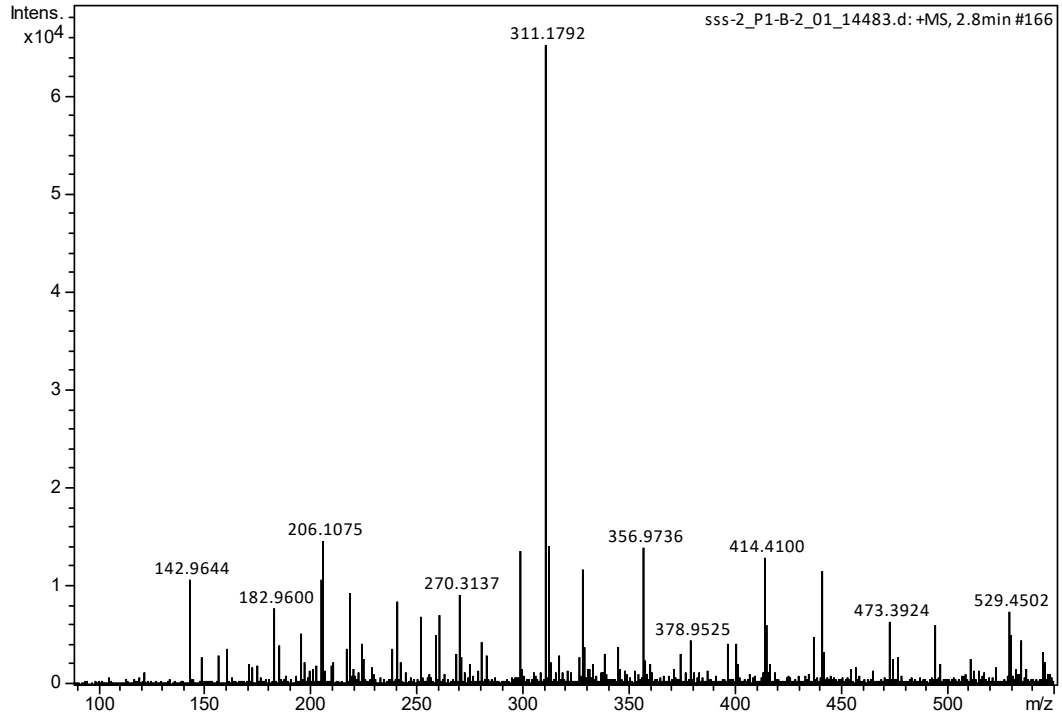
	x	y	z	U(eq)
H(11A)	9764	3243	4531	36
H(7A)	4386	2123	4184	33
H(7B)	3332	713	4059	33
H(17A)	5563	4600	3384	38
H(13A)	5448	104	2464	39
H(23A)	11245	3057	2560	51
H(23B)	12095	2912	3113	51
H(23C)	10350	4069	2962	51
H(14A)	8558	1523	2329	38
H(18A)	5525	6849	3267	44
H(6GA)	11531	1296	4953	44
H(3HA)	4918	-1106	4496	43
H(21A)	11700	4902	4128	44
H(19A)	8564	8133	3584	48
H(22A)	2646	-891	2953	54
H(22B)	1535	61	3353	54
H(22C)	3384	-1036	3512	54
H(20A)	11648	7154	4006	51
H(4MA)	7670	-1992	5031	55
H(5NA)	10977	-787	5266	55

The HRMS spectra of the new products

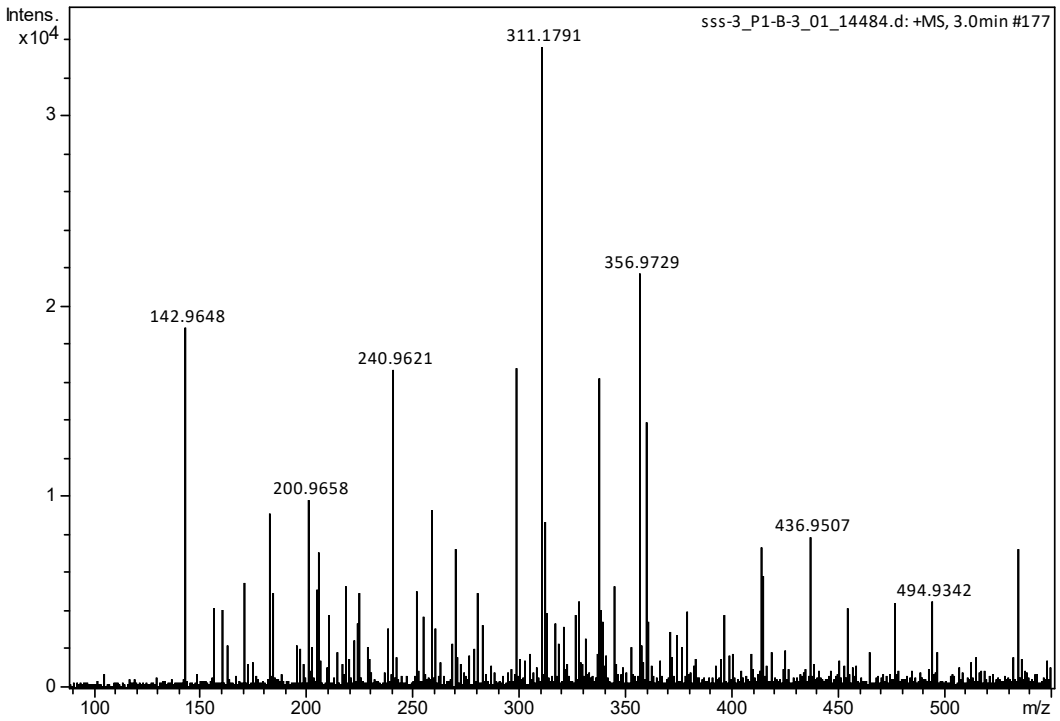
1. The HRMS Spectra of **3a**



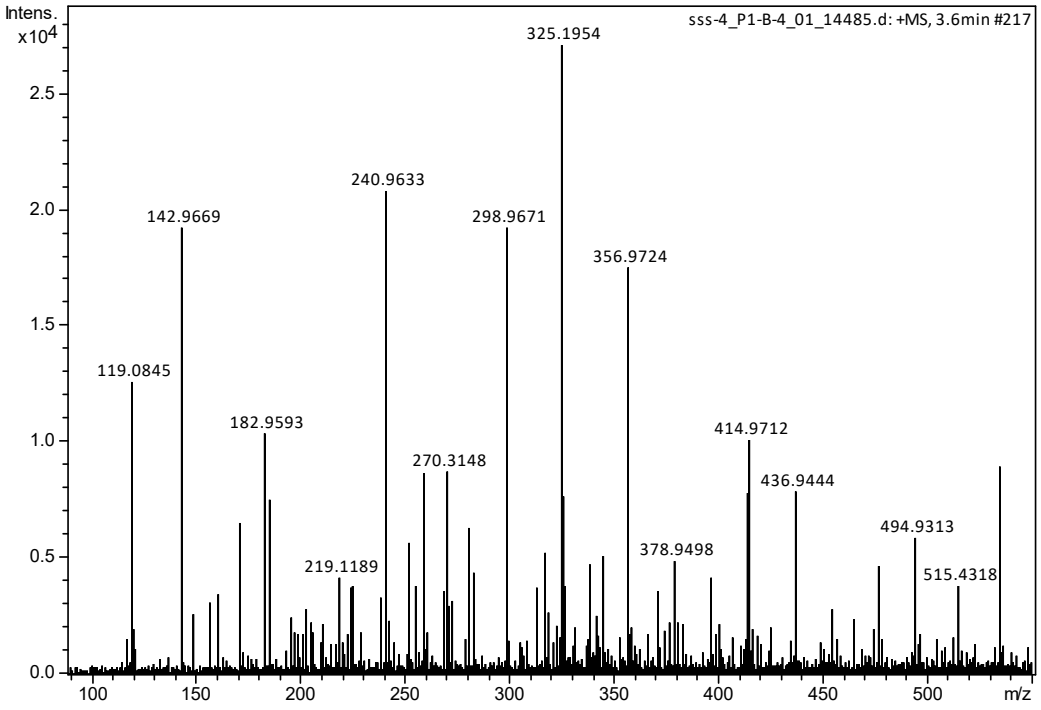
2. The HRMS Spectra of **3b**



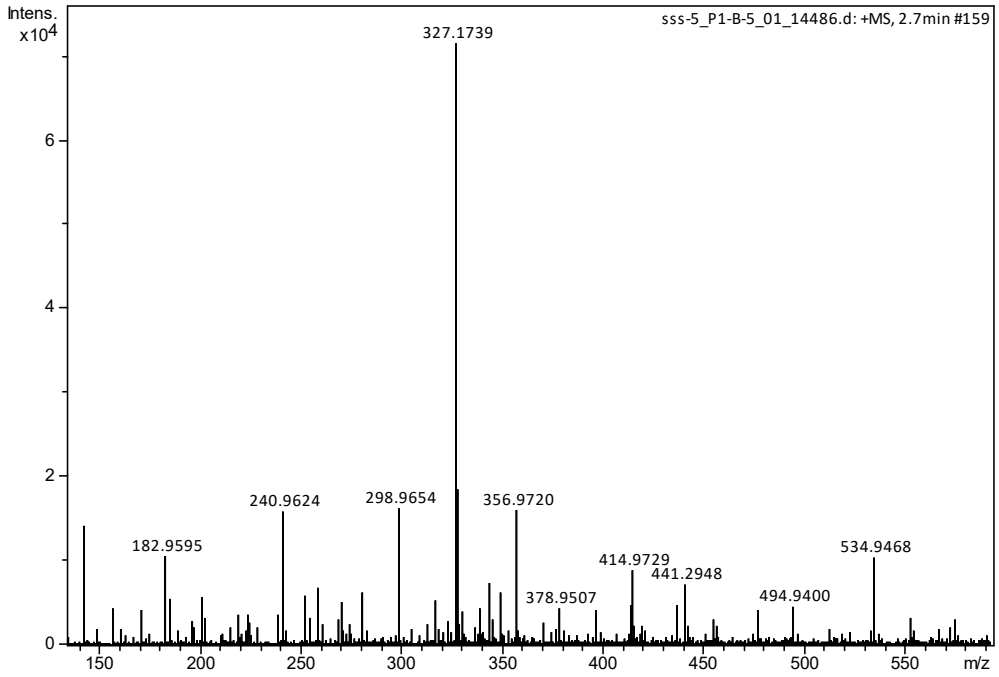
3. The HRMS Spectra of **3c**



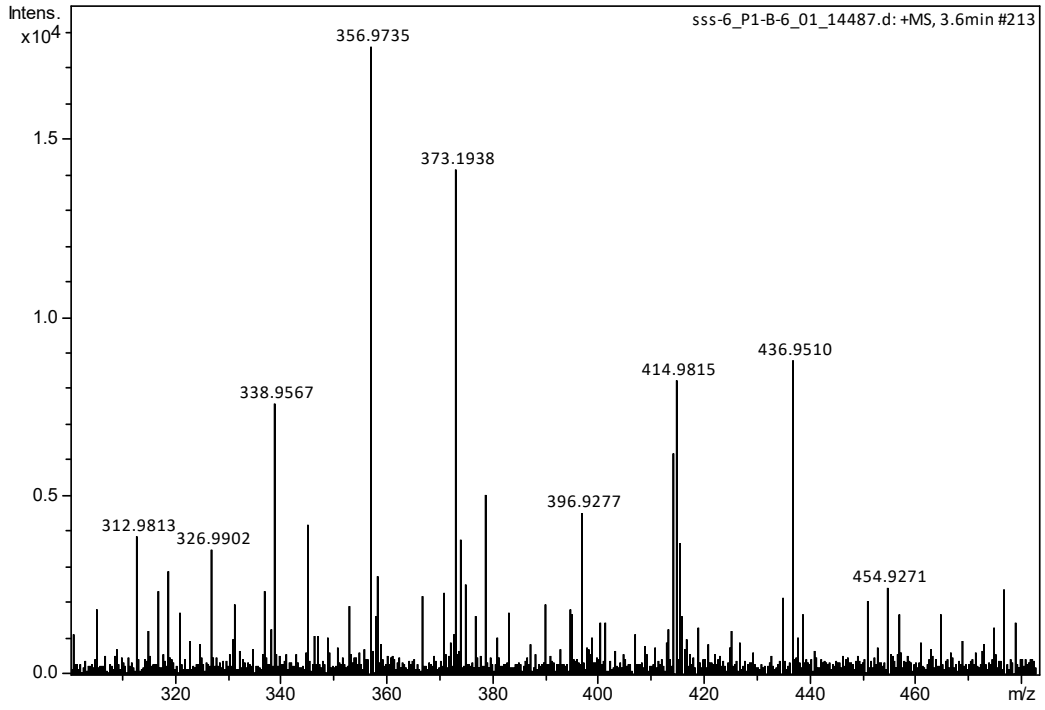
4. The HRMS Spectra of **3d**



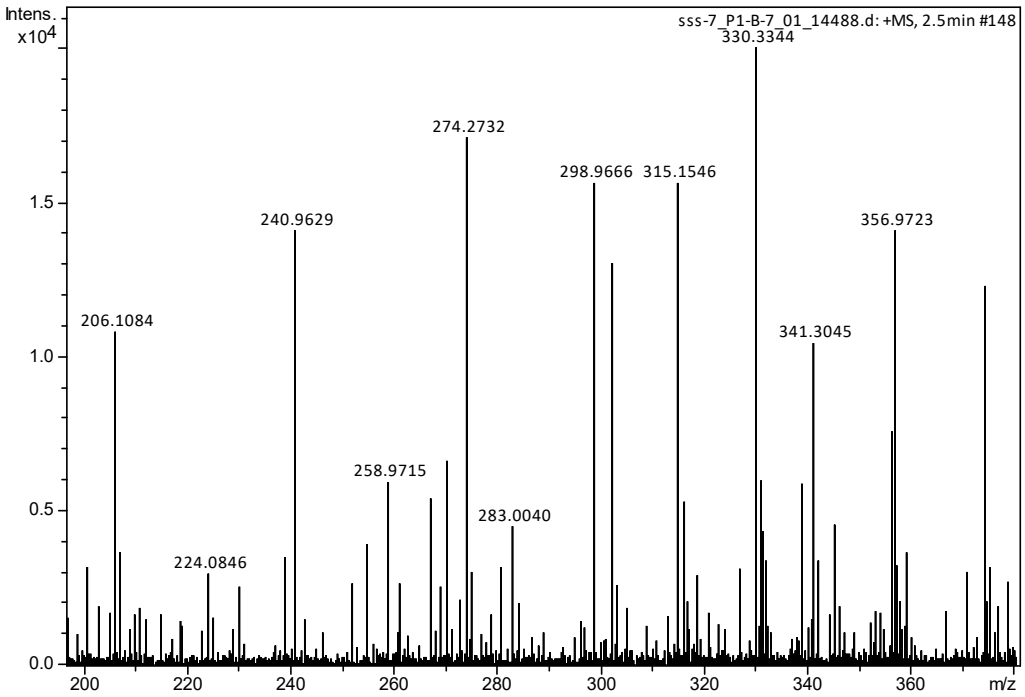
5. The HRMS Spectra of **3e**



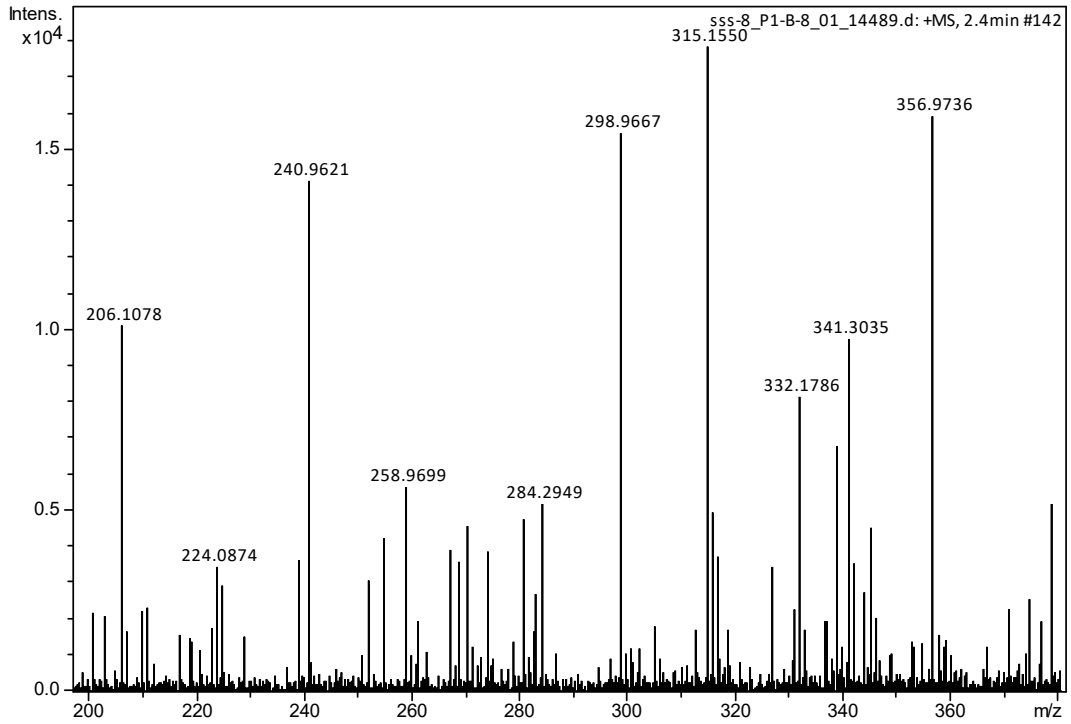
6. The HRMS Spectra of **3f**



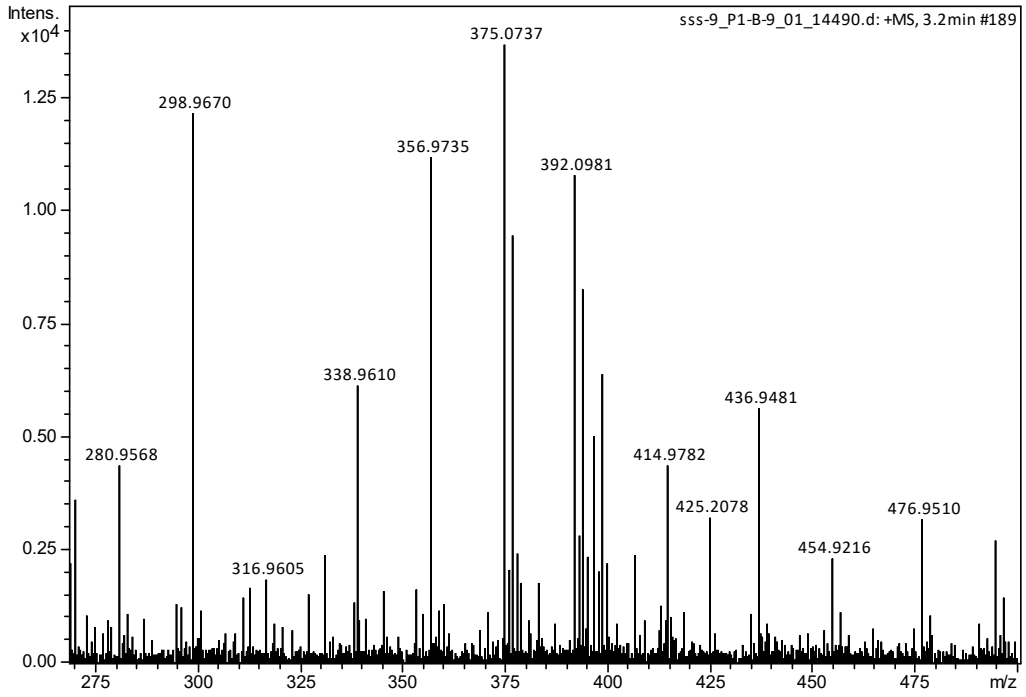
7. The HRMS Spectra of **3g**



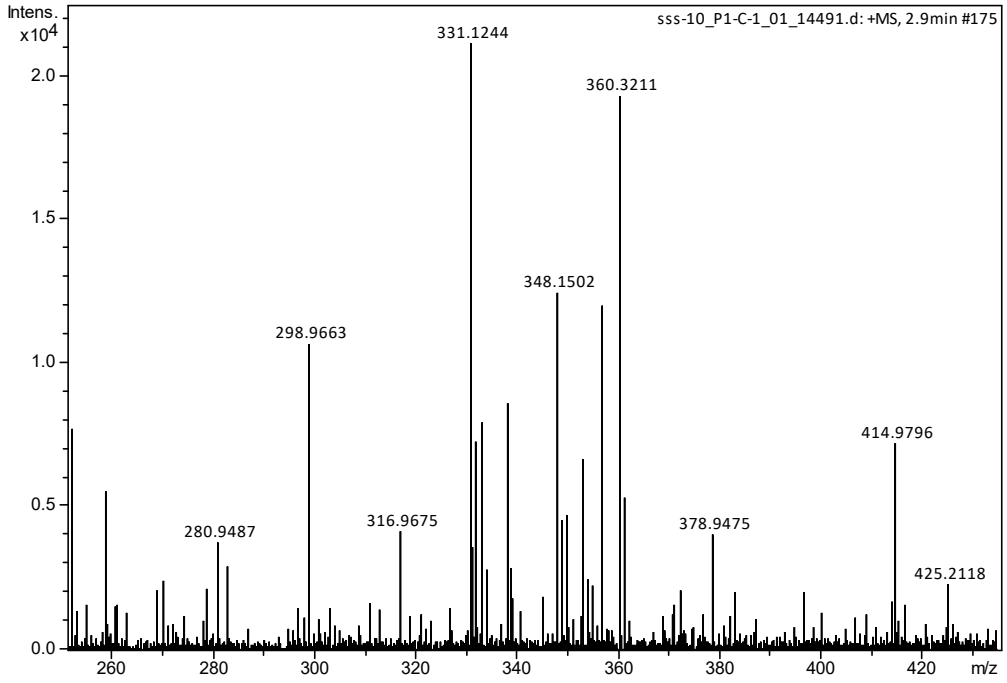
8. The HRMS Spectra of **3h**



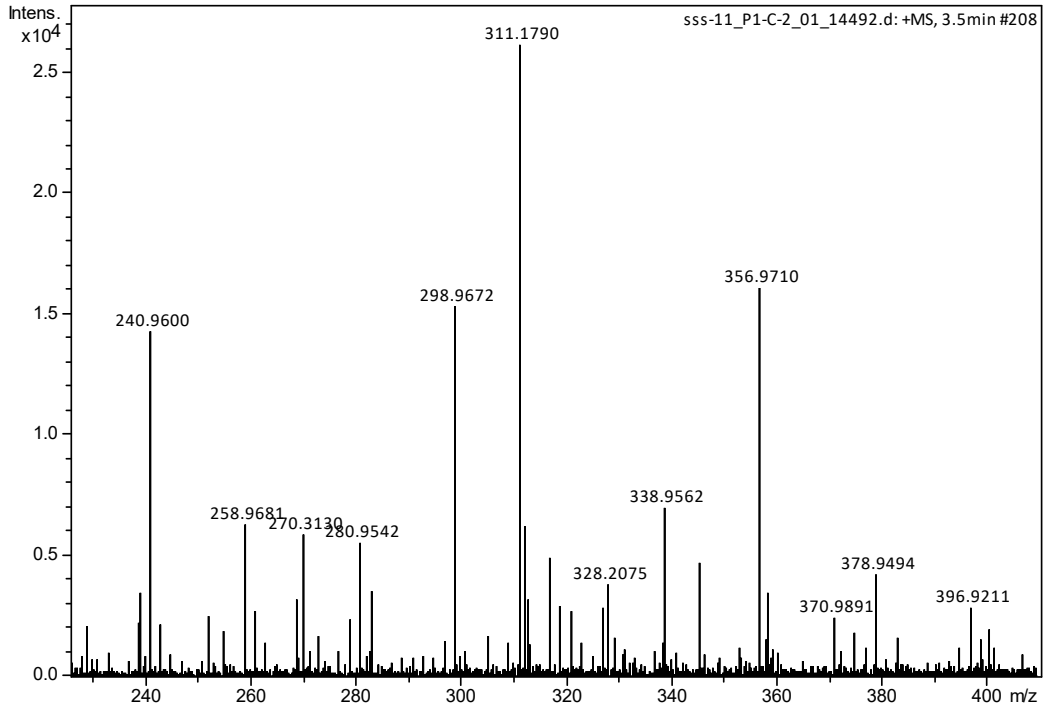
9. The HRMS Spectra of **3j**



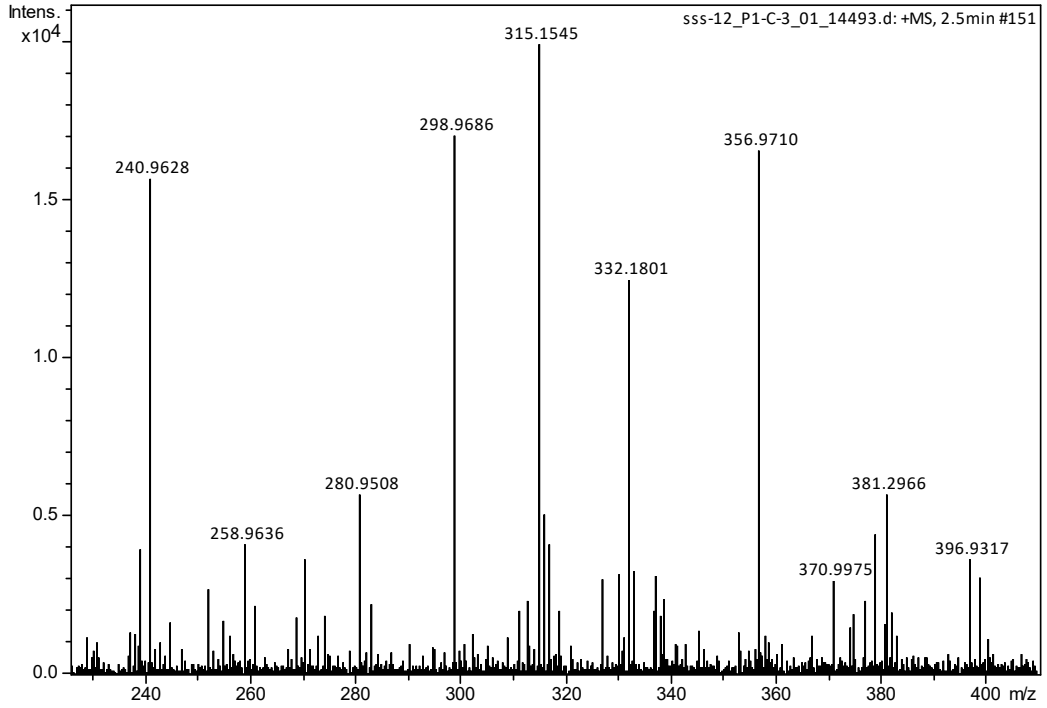
10. The HRMS Spectra of **3i**



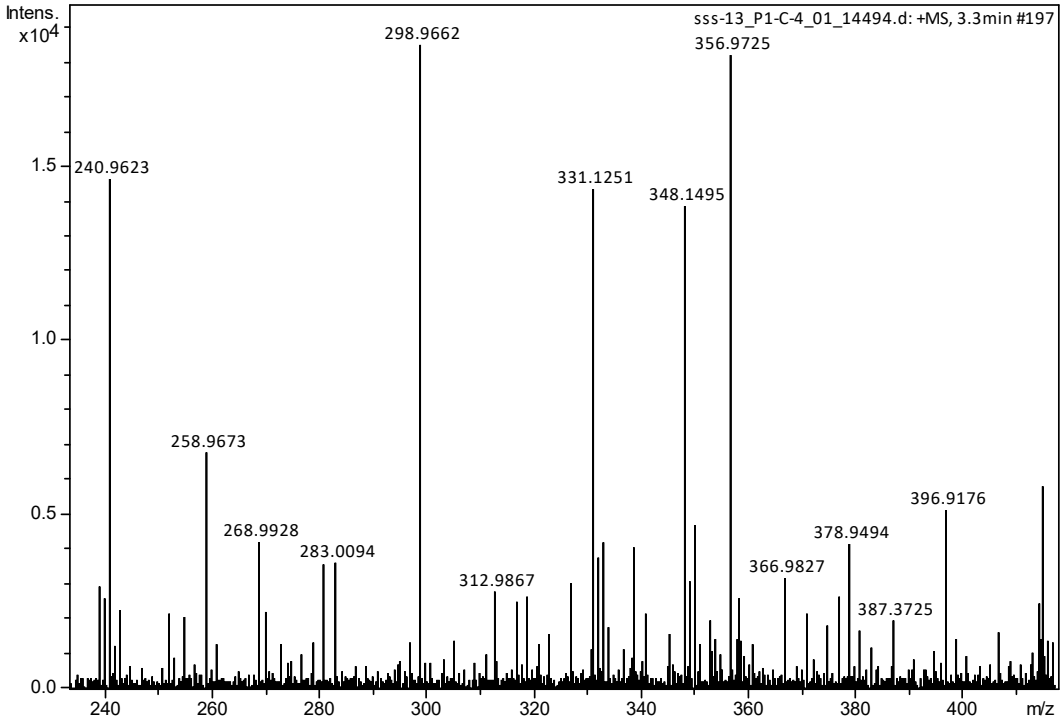
11. The HRMS Spectra of **3k**



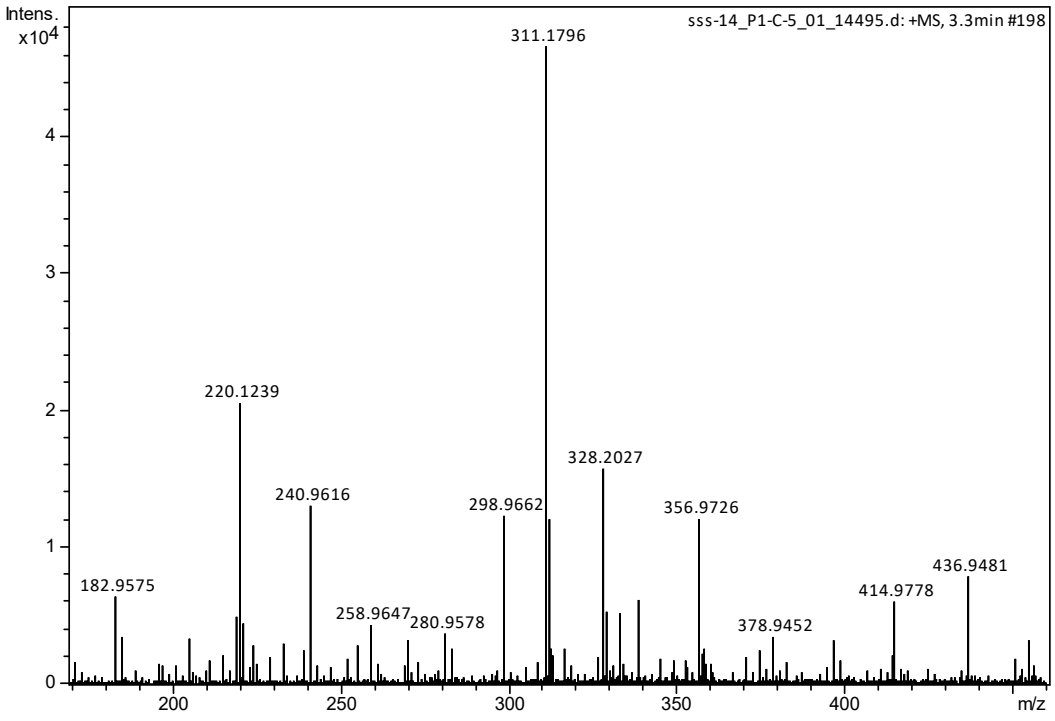
12. The HRMS Spectra of **3l**



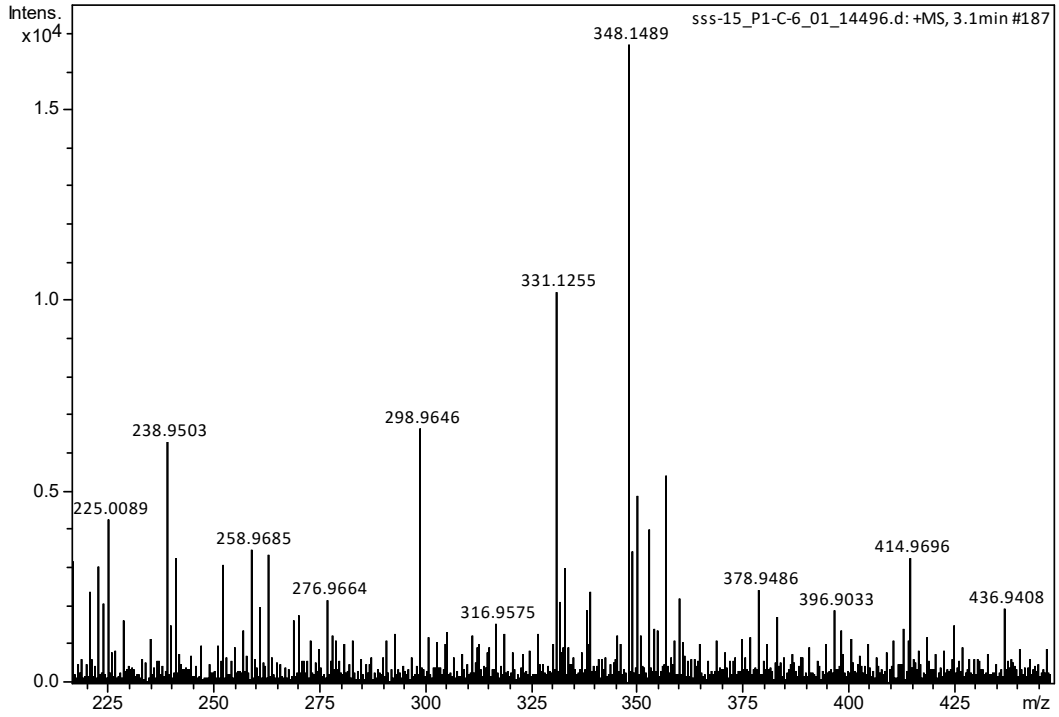
13. The HRMS Spectra of **3m**



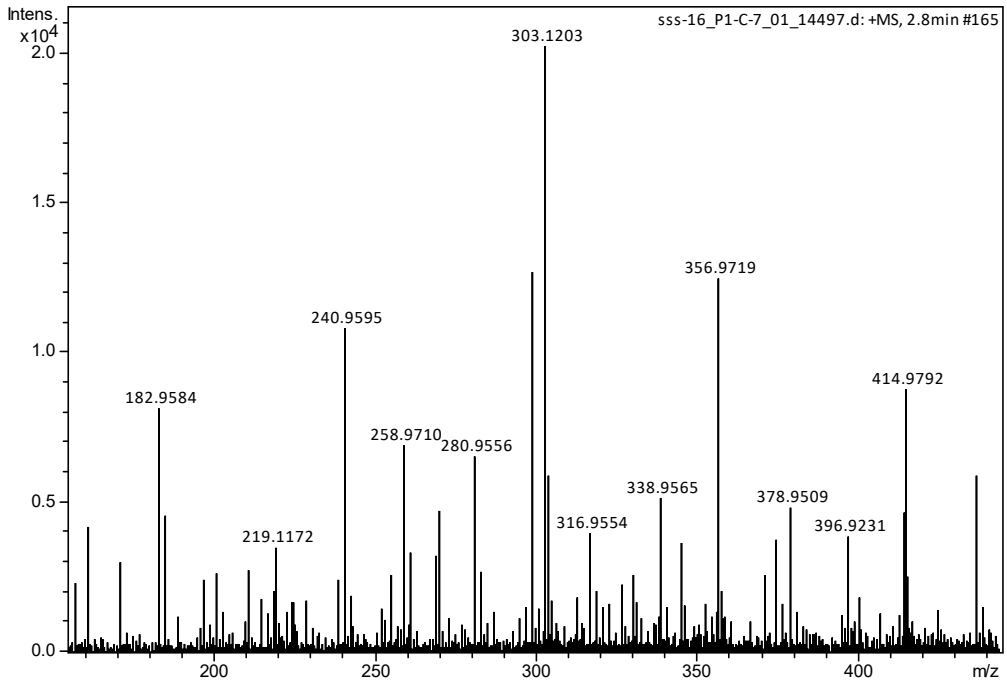
14. The HRMS Spectra of **3n**



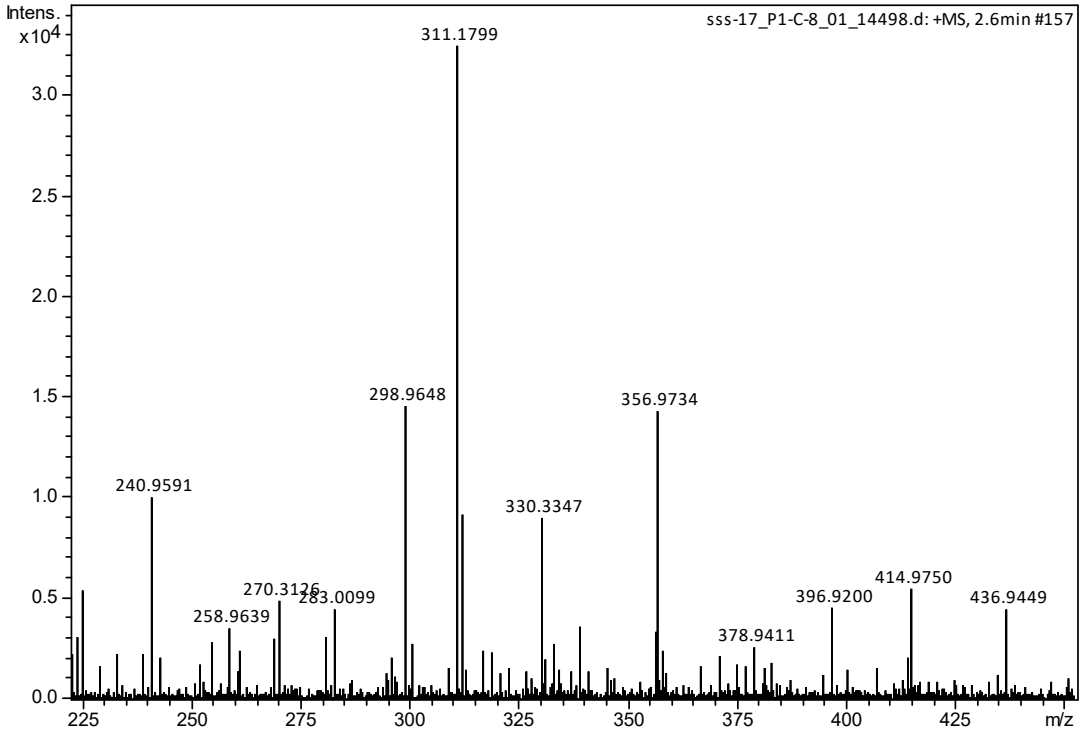
15. The HRMS Spectra of **3o**



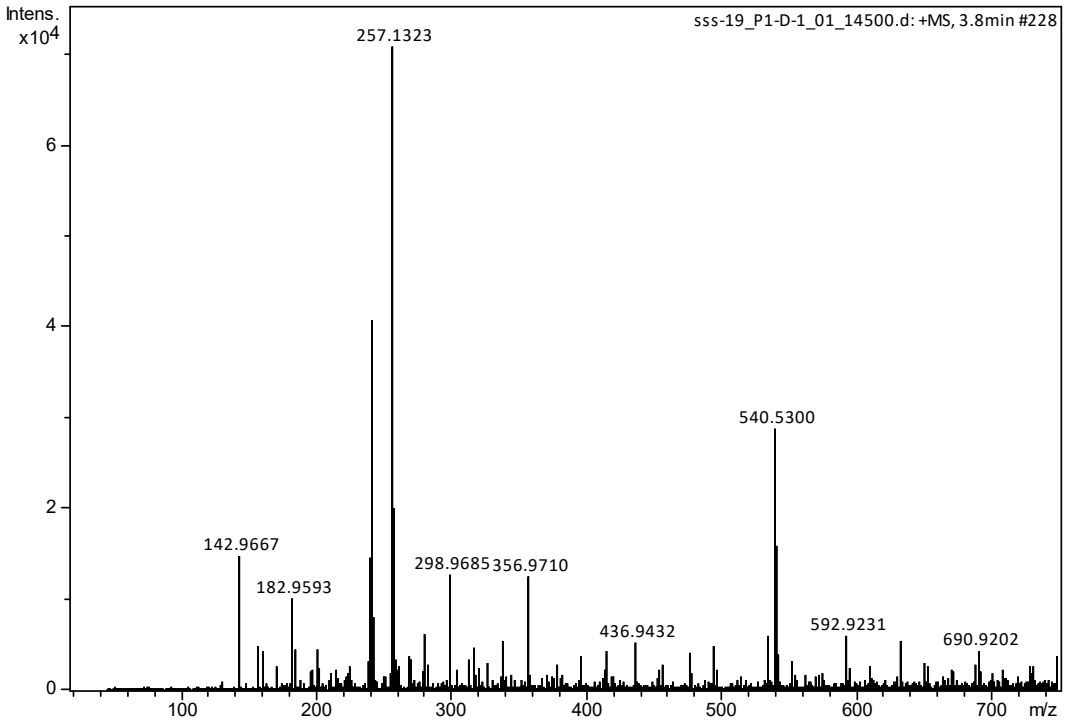
16. The HRMS Spectra of **3p**



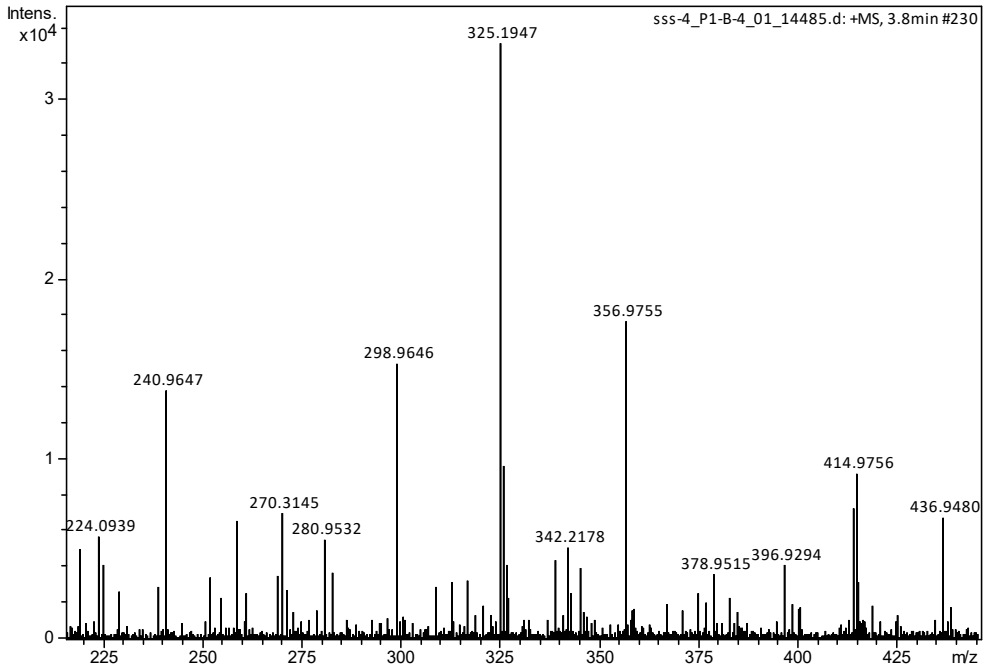
17. The HRMS Spectra of **3s**



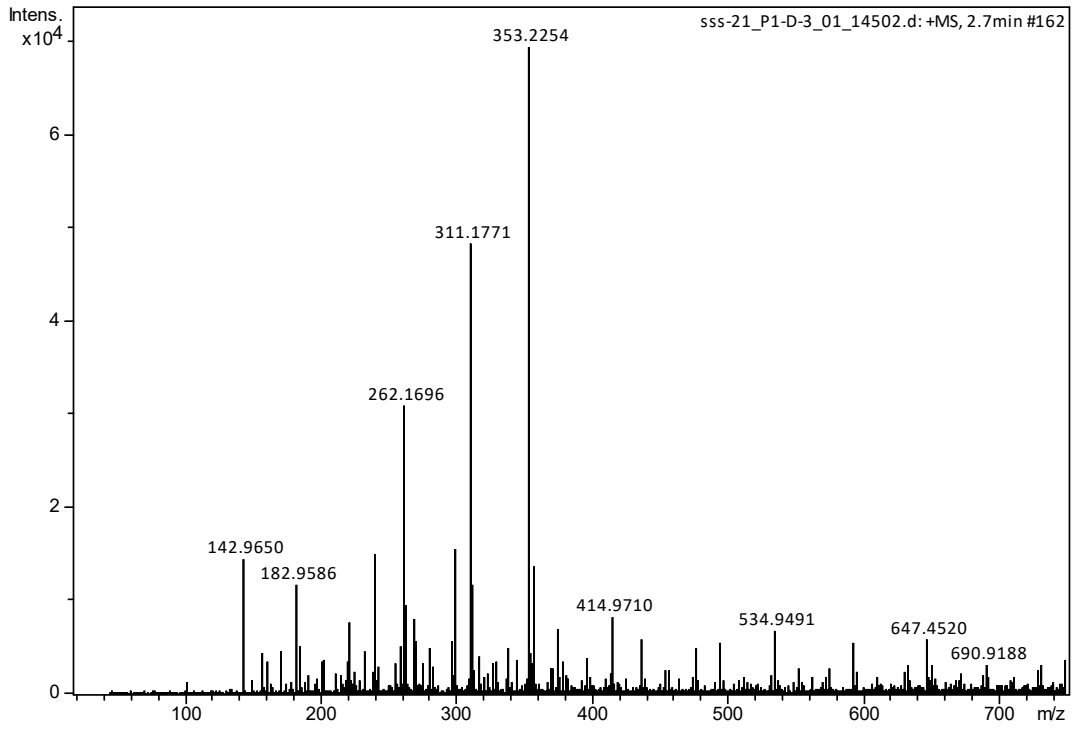
18. The HRMS Spectra of **5**



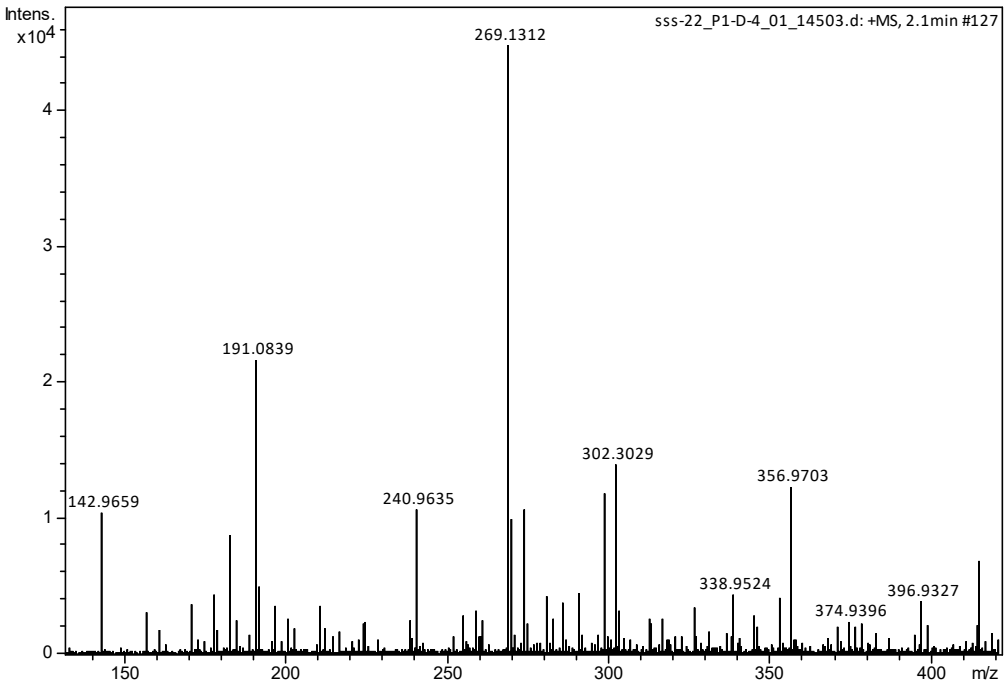
20. The HRMS Spectra of **3ba**



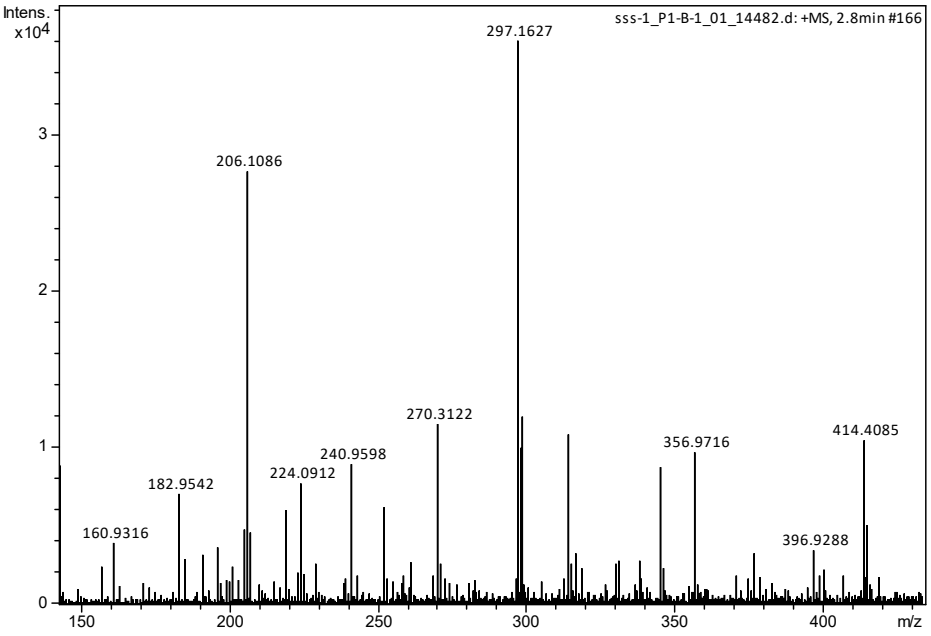
21. The HRMS Spectra of **3ca**



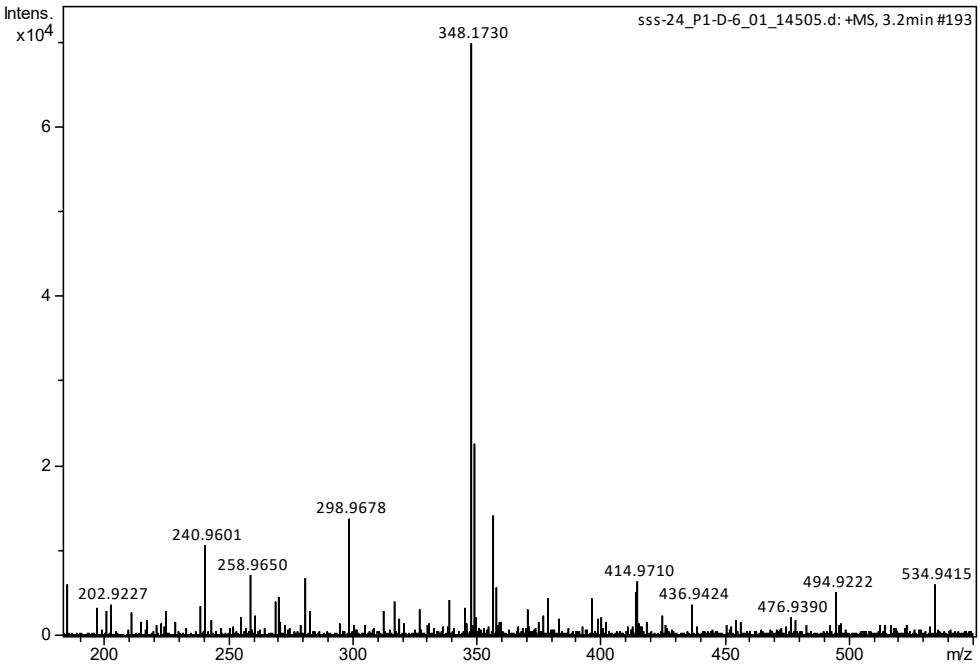
22. The HRMS Spectra of **3da**



23. The HRMS Spectra of **4a**



24. The HRMS Spectra of **4q**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