

Supporting Information

Metal-free dearomative [5+2]/[2+2] cycloaddition of 1*H*-indoles with *ortho*-(trimethylsilyl)aryl triflates

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1. General Considerations

All ^1H NMR and ^{13}C NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (600 MHz and 150 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) and a Thermo Fisher Scientific LTQ FTICR-MS instrument. Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

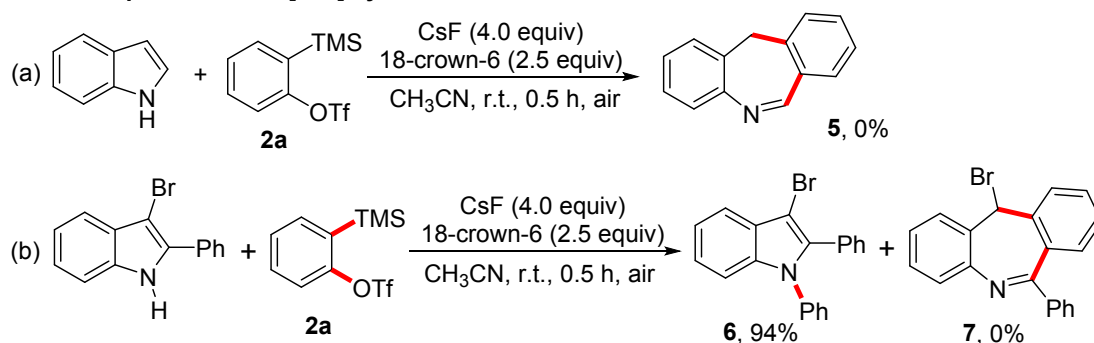
The starting materials, such as 1*H*-indoles and 2-(trimethylsilyl)aryltrifluoromethanesulfonates, were prepared according to the reported methods ^[1-2]. All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on silica gels, eluting with petroleum ether/ethyl acetate (20:1 to 100:1).

2. Typical Procedure for the Synthesis of 3a

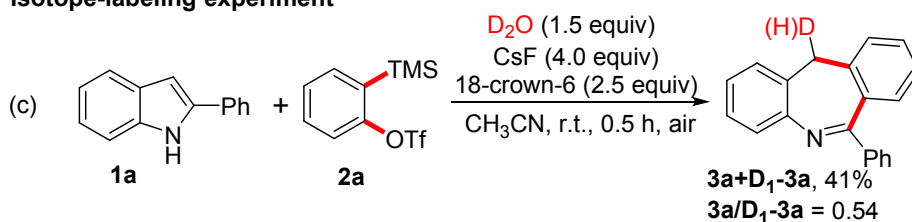
In a 10 mL oven-dried quartz equipped with a magnetic stirrer bar was charged with 2-phenyl-1*H*-indole (**1a**, 36.4 mg, 0.20 mmol), CsF (121.5 mg, 0.80 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (**2a**, 149.0 mg, 0.50 mmol) and 18-crown-6 (132.16 mg, 0.50 mmol). Then freshly distilled acetonitrile (1.0 mL) was added to the resulted mixture. The reaction was stirred at room temperature for 0.5 h. After that, the mixture in reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 100:1), affording the desired product **3a** as a pale green solid (40.9 mg, 76% yield).

3. Mechanistic Experiments

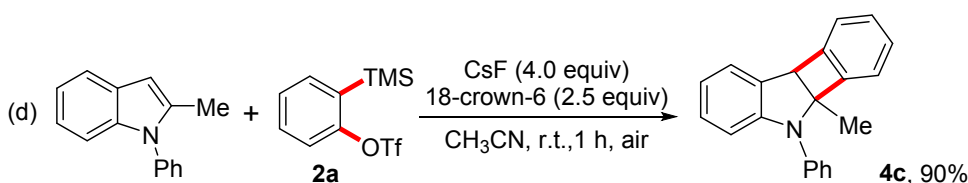
Control experiments for [5+2] cycloaddition



Isotope-labeling experiment

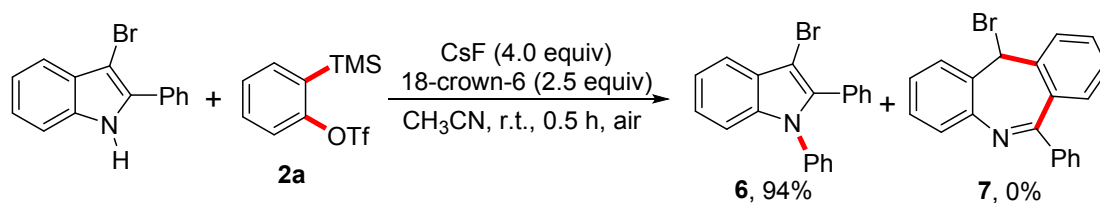


Control experiments for [2+2] cycloaddition

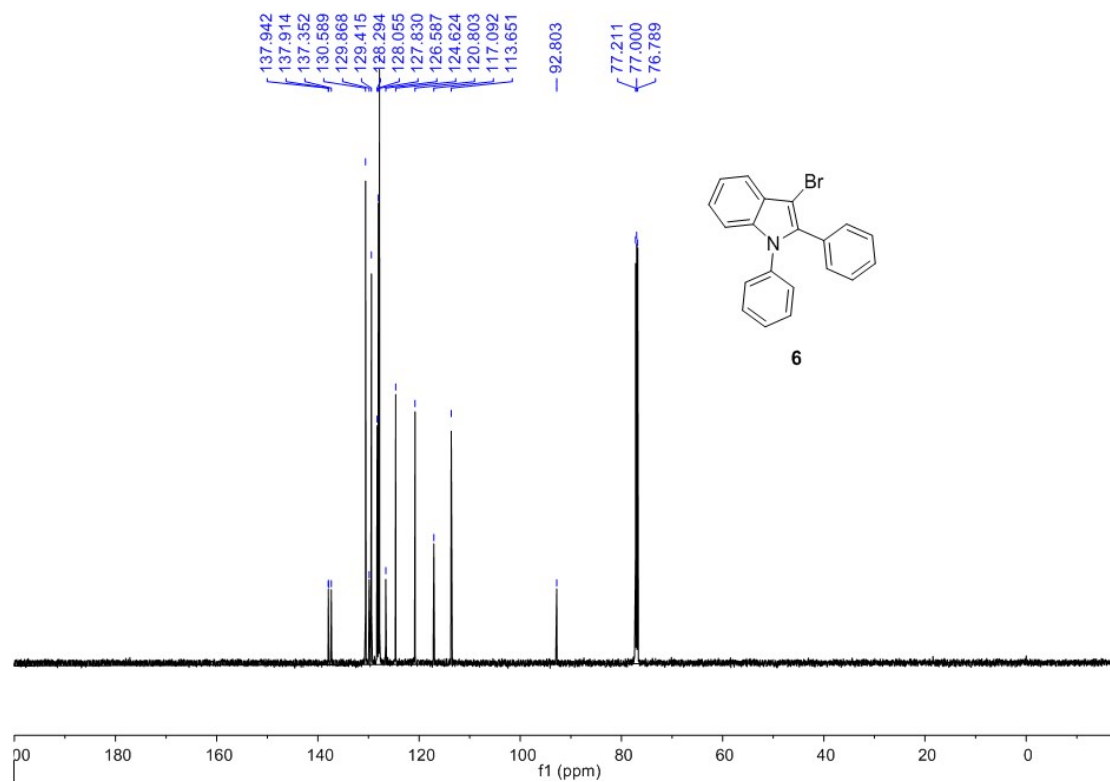
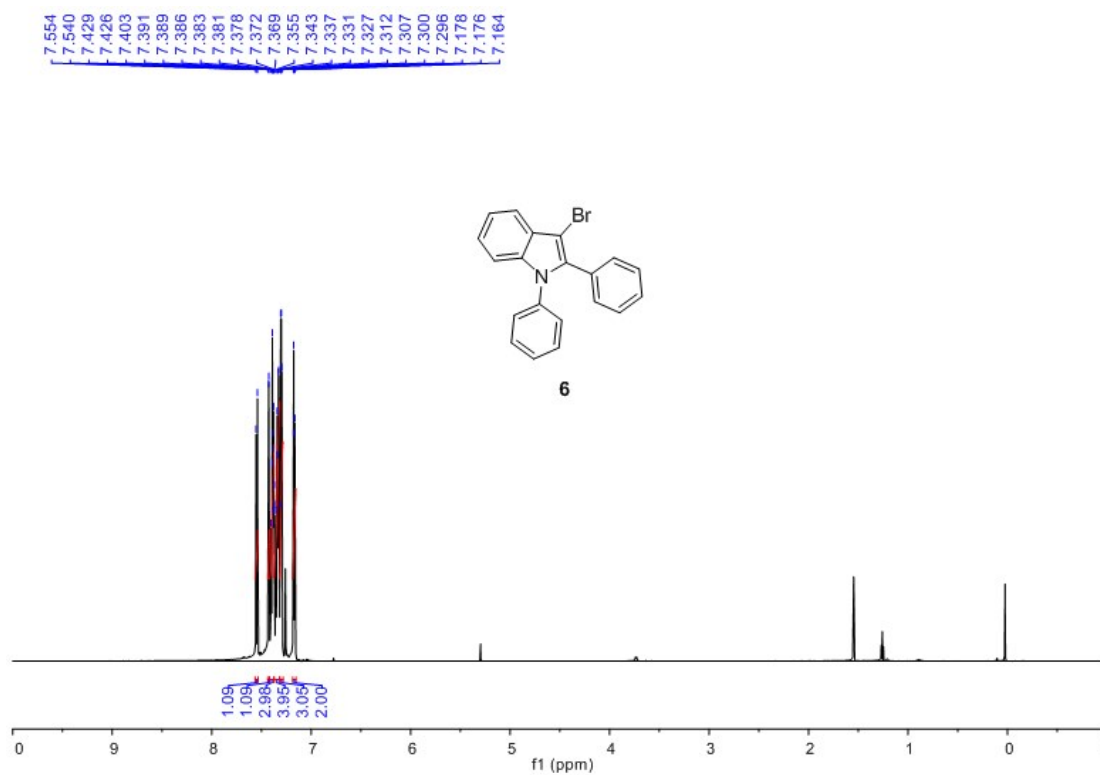


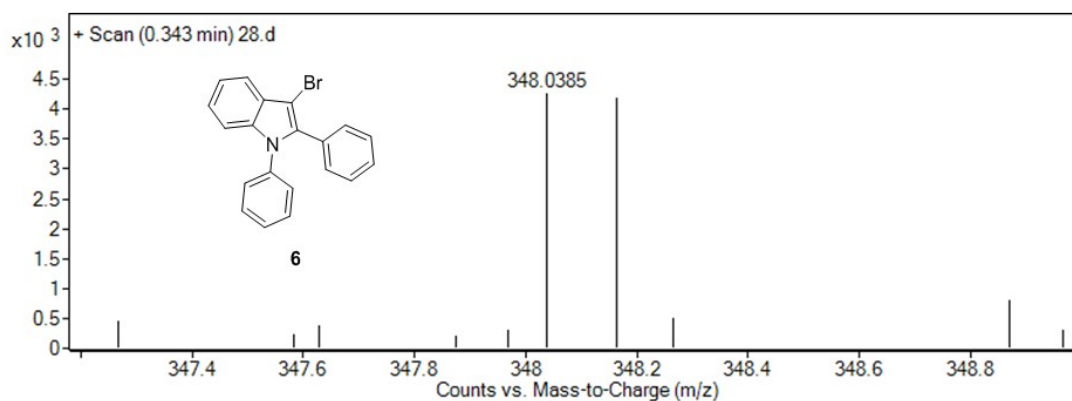
Scheme S1 Mechanistic experiments.

3.1 Control Experiments for [5+2] Cycloaddition



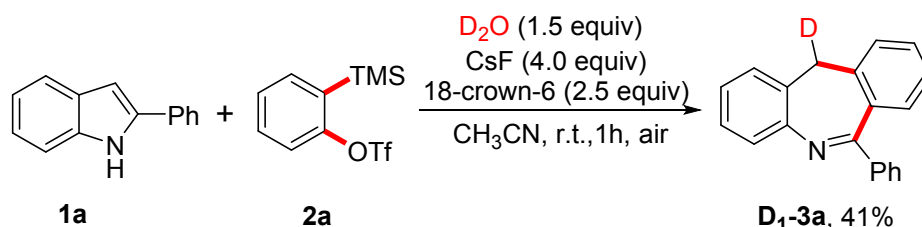
In a 10 mL oven-dried quartz equipped with a magnetic stirrer bar was charged with 3-bromo-2-phenyl-1*H*-indole (54.2 mg, 0.2 mmol), CsF (121.5 mg, 0.8 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (**2a**, 149.0 mg, 0.5 mmol) and 18-crown-6 (132.1 mg, 0.5 mmol). Then freshly distilled acetonitrile (1.0 mL) was added to the resulted mixture. The reaction was stirred at room temperature for 0.5 h. After that, the mixture in reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1), affording the desired product **6** as a white solid (65.2 mg, 94% yield).



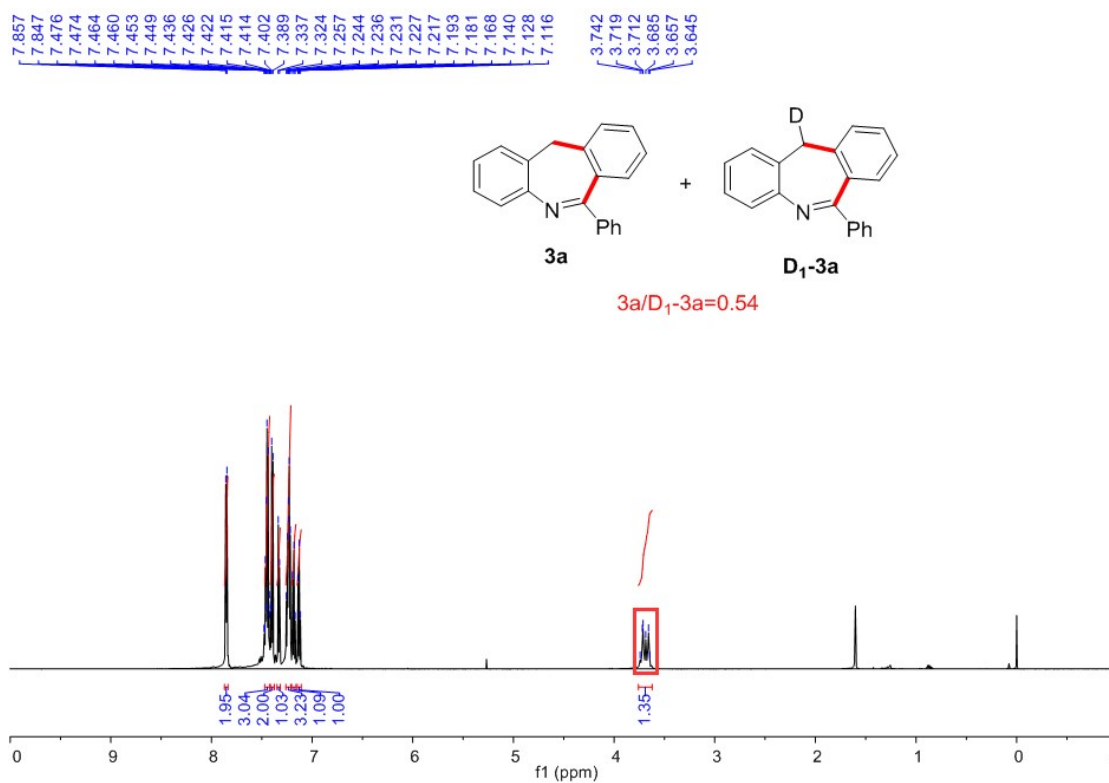
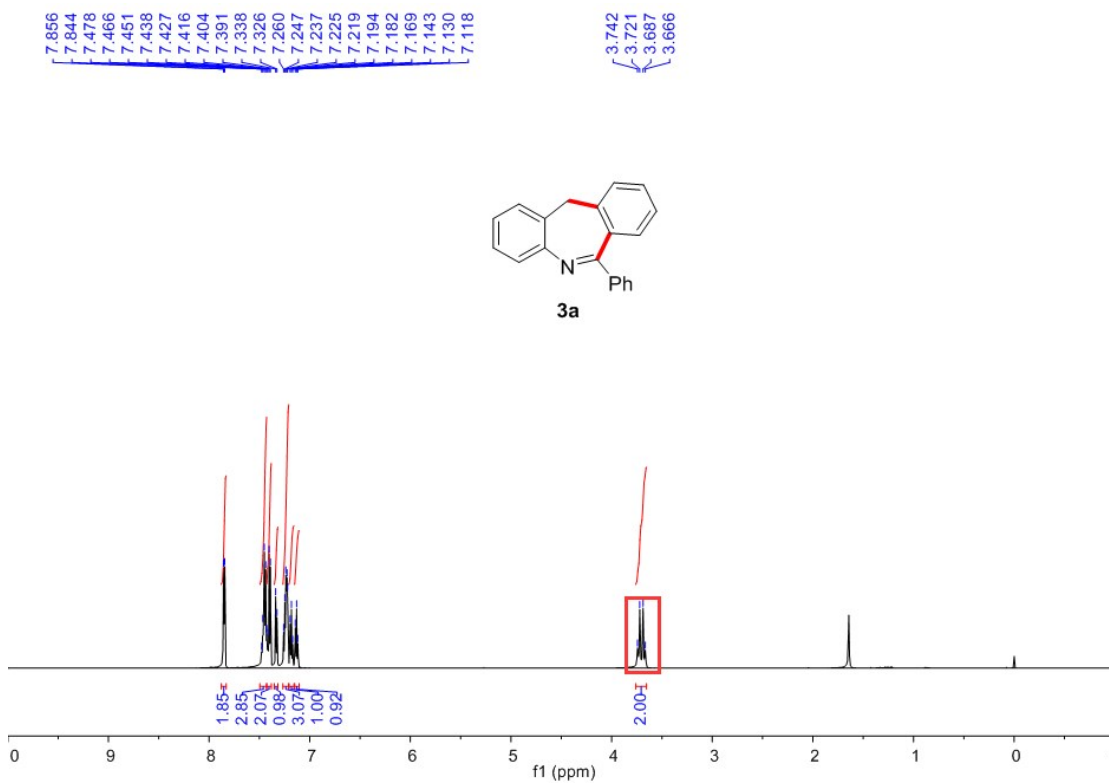


3-Bromo-1,2-diphenyl-1H-indole (6): White solid; 65.2 mg, 94% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.42–7.37 (m, 3H), 7.37–7.32 (m, 4H), 7.31–7.30 (m, 3H), 7.19–7.15 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 137.94, 137.91, 137.35, 130.59, 129.87, 129.42, 128.29, 128.06, 127.83, 126.59, 124.62, 120.80, 117.09, 113.65, 92.80, 77.21, 77.00, 76.79. HRMS (ESI) calcd for C₂₀H₁₅BrN [M+H]⁺ 348.0382, found 348.0385.

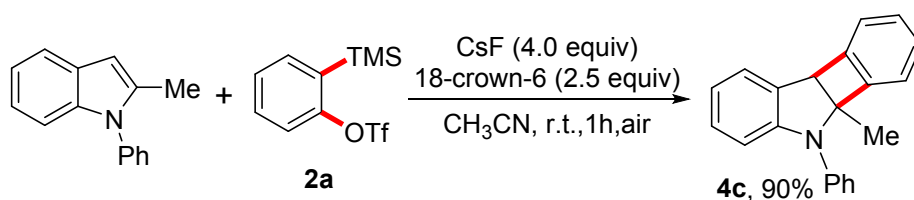
3.2 Isotope-labeling Experiment



In a 10 mL oven-dried quartz equipped with a magnetic stirrer bar was charged with 2-phenyl-1H-indole (**1a**, 36.4 mg, 0.20 mmol), CsF (121.5 mg, 0.80 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (**2a**, 149.0 mg, 0.50 mmol), D₂O (5.5 μL, 0.30 mmol) and 18-crown-6 (132.1 mg, 0.50 mmol). Then freshly distilled acetonitrile (1.0 mL) was added to the resulted mixture. The reaction was stirred at room temperature for 0.5 h. After that, the mixture in reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50:1), affording the desired product **3a** and **D₁-3a** as a Pale green solid (22.2 mg, 41% yield). The ratio of **3a**/**D₁-3a** was determined as 0.54 by ¹H NMR analysis.



3.3 Control Experiments for [2+2] Cycloaddition



In a 10 mL oven-dried quartz equipped with a magnetic stirrer bar was charged with 2-methyl-1-phenyl-1*H*-indole (41.4 mg, 0.20 mmol), CsF (121.5 mg, 0.80 mmol), 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (**2a**, 149.0 mg, 0.50 mmol) and 18-crown-6 (132.1 mg, 0.50 mmol). Then freshly distilled acetonitrile (1.0 mL) was added to the resulted mixture. The reaction was stirred at room temperature for 1 h. After that, the mixture in reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 100:1), affording the desired product **4c** as a Pale green liquid. (51.0 mg, 90% yield).

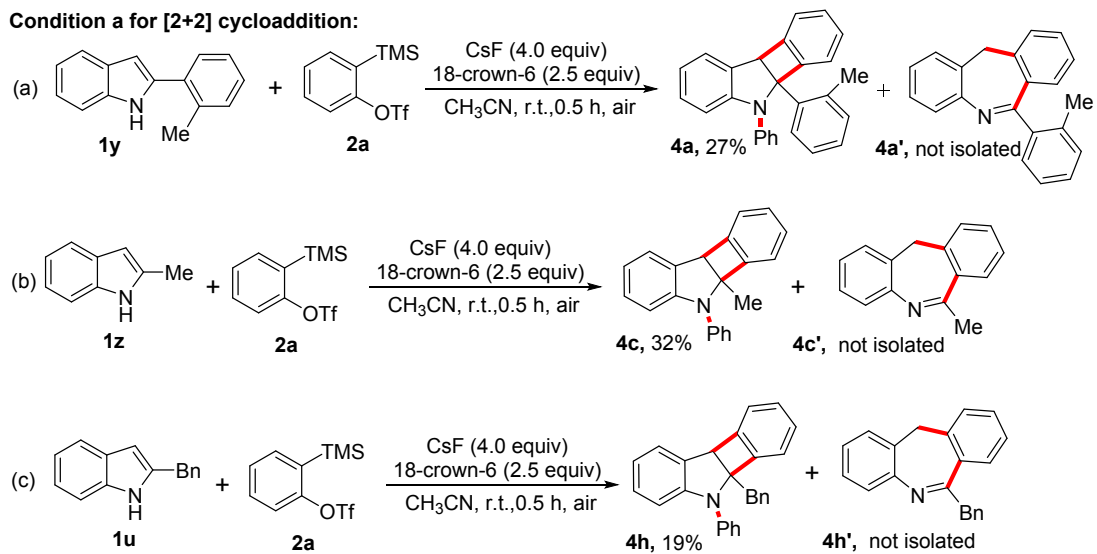
3.4 Conditional controlled experiments for the [5+2]/[2+2] cycloaddition

To get a deeper understanding of the reaction mechanism, some representative 2-substitued indoles with steric group, such as **1y**, **1z** and **1u**, were tested their reactions with **2a** under the conditions a in table 2, indicating that only [2+2] cycloaddition products were achieved in lower yields and [5+2] products were not observed (Scheme 1a-c). Similarly, we tested the reaction of 2-arylindoles, such as **1a**, **1g** and **1s**, with **2a** under the conditions b in table 3, and found that only according [5+2] products were observed, and no [2+2] products were isolated (Scheme 1d-f).

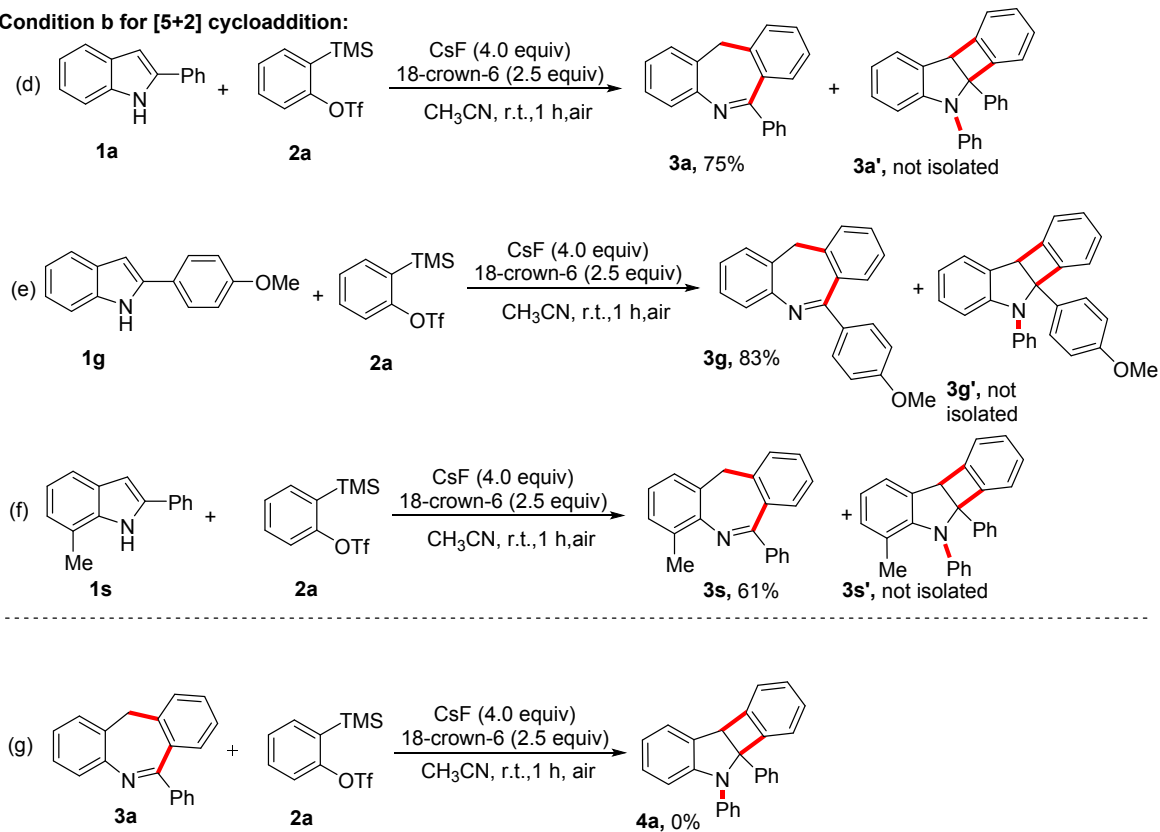
In addition, we performed the pure [5+2] product **3a** under the conditions b for exploring the possible transformation into [2+2] cycloaddition product, but no desired product was observed (Scheme 1g).

Finally, the results from the above control experiments further support the mechanism proposal for the [5+2] and [2+2] cycloaddition that listed in the main text of the manuscript.

Condition a for [2+2] cycloaddition:

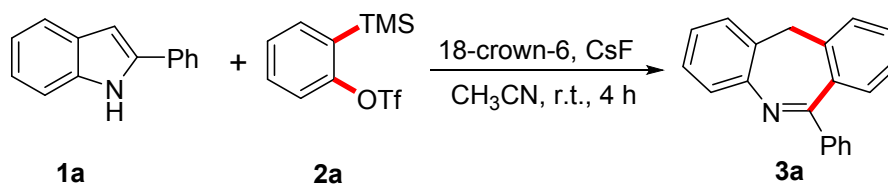


Condition b for [5+2] cycloaddition:



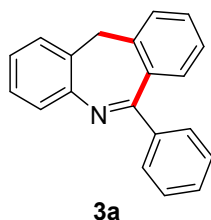
Scheme S2 Conditional controlled experiments.

4. Gram-scale Synthesis of 3a

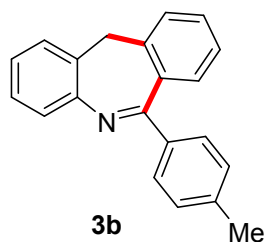


In a 50 mL oven-dried quartz equipped with a magnetic stirrer bar was charged with 2-phenyl-1*H*-indole (**1a**, 1.16 g, 6.0 mmol), CsF (3.64 g, 24.0 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (**2a**, 4.47 g, 15.0 mmol) and 18-crown-6 (3.96 g, 15.0 mmol). Then freshly distilled acetonitrile (20 mL) was added to the resulted mixture. The reaction was stirred under room temperature for 4 h. After that, the mixture in reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 100:1), affording the desired product **3a** as a pale green solid (1.02 g, 63% yield).

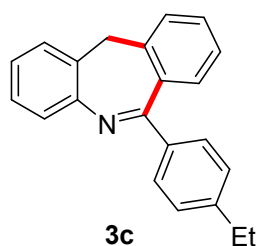
5. Characterization Data for the Products



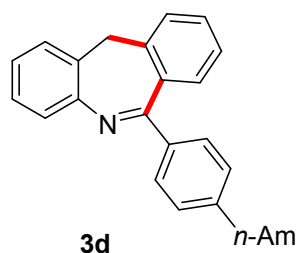
6-Phenyl-11*H*-dibenzo[*b,e*]azepine (3a**)**^[3]: Pale green solid; 40.9 mg, 76% yield; m.p.: 150~152 °C; ¹H NMR (600 MHz, CDCl₃) δ: 7.85 (d, *J* = 7.2 Hz, 2H), 7.48–7.42 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.26–7.22 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 3.70 (dd, *J* = 33.0, 12.6 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 166.96, 145.66, 143.61, 141.08, 132.86, 131.56, 131.05, 130.11, 129.84, 129.78, 128.10, 126.94, 126.92, 126.37, 126.03, 125.66, 125.53, 39.20. HRMS (ESI) calcd for C₂₀H₁₆N [M+H]⁺ 270.1277, found 270.1275.



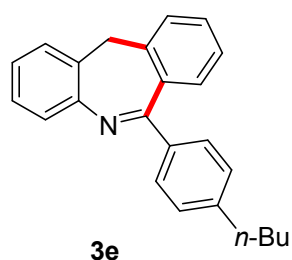
6-(*p*-Tolyl)-11*H*-dibenzo[*b,e*]azepine (3b): Pale green solid; 41.9 mg, 74% yield; m.p.: 132~134 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.41-7.37 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.25 (s, 2H), 7.24 (s, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 (td, *J* = 7.2, 1.2 Hz, 1H), 3.69 (dd, *J* = 36.0, 13.2 Hz, 2H), 2.42 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.79, 145.84, 143.65, 140.36, 138.36, 132.92, 131.66, 130.94, 129.89, 129.78, 128.82, 126.90, 126.32, 125.82, 125.62, 125.49, 39.25, 21.40. HRMS (ESI) calcd for C₂₁H₁₈N [M+H]⁺ 284.1434, found 284.1434.



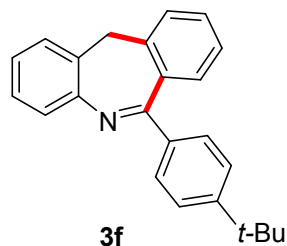
6-(4-Ethylphenyl)-11*H*-dibenzo[*b,e*]azepine (3c): Pale green liquid; 46.9 mg, 79% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.69 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 3H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 3.60 (dd, *J* = 36.6, 13.2 Hz, 2H), 2.63 (q, *J* = 7.2 Hz, 2H), 1.19 (td, *J* = 7.8, 1.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.77, 146.65, 145.85, 143.62, 138.58, 132.88, 131.64, 130.92, 129.89, 129.84, 127.62, 126.88, 126.30, 125.80, 125.60, 125.49, 39.23, 28.76, 15.41. HRMS (ESI) calcd for C₂₂H₂₀N [M+H]⁺ 298.1590, found 298.1589.



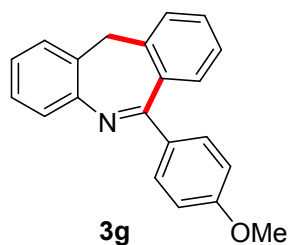
6-(4-Pentylphenyl)-11H-dibenzo[*b,e*]azepine (3d): Pale green liquid; 48.8 mg, 72% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 7.8$ Hz, 2H), 7.42–7.38 (m, 2H), 7.33 (d, $J = 7.8$ Hz, 1H), 7.27 (s, 1H), 7.25 (d, $J = 7.8$ Hz, 3H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.12 (t, $J = 7.4$ Hz, 1H), 3.70 (q, $J = 12.6$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 1.69–1.64 (m, 2H), 1.35 (d, $J = 3.6$ Hz, 4H), 0.91 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.86, 145.81, 145.42, 143.60, 138.52, 132.89, 131.62, 130.94, 129.93, 129.74, 128.20, 126.88, 126.31, 125.81, 125.61, 125.48, 39.22, 35.79, 31.45, 31.01, 22.53, 14.03. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 340.2060, found 340.2061.



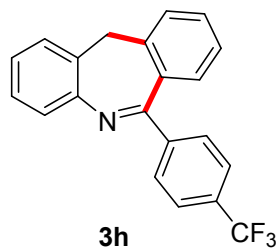
6-(4-Butylphenyl)-11H-dibenzo[*b,e*]azepine (3e): Pale green liquid; 48.1 mg, 74% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 7.8$ Hz, 2H), 7.41–7.37 (m, 2H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.25 (t, $J = 7.2$ Hz, 4H), 7.21 (d, $J = 7.8$ Hz, 1H), 7.18 (t, $J = 7.8$ Hz, 1H), 7.11 (t, $J = 7.2$ Hz, 1H), 3.69 (dd, $J = 36.0, 12.6$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H), 1.66–1.61 (m, 2H), 1.38 (dd, $J = 15.0, 7.8$ Hz, 2H), 0.94 (t, $J = 7.8$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 166.90, 145.88, 145.44, 143.66, 138.58, 132.94, 131.68, 131.00, 129.98, 129.81, 128.26, 126.94, 126.37, 125.87, 125.67, 125.54, 39.28, 35.58, 33.53, 22.39, 14.01. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 326.1903, found 326.1900.



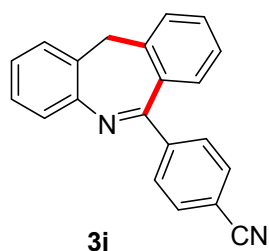
6-(4-(*tert*-Butyl)phenyl)-11*H*-dibenzo[*b,e*]azepine (3f): Pale green liquid; 50.1 mg, 77% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, $J = 7.8$ Hz, 2H), 7.39 (d, $J = 7.8$ Hz, 2H), 7.33 (dd, $J = 15.0, 7.2$ Hz, 2H), 7.26 (d, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 7.17 (d, $J = 7.8$ Hz, 1H), 7.13 (dd, $J = 18.6, 7.8$ Hz, 2H), 7.05 (t, $J = 7.2$ Hz, 1H), 3.62 (q, $J = 30.0, 12.6$ Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.73, 153.47, 148.76, 147.99, 145.85, 143.60, 142.90, 139.47, 138.39, 132.86, 130.94, 130.24, 130.20, 130.17, 129.94, 129.89, 129.53, 129.30, 128.91, 128.86, 128.81, 128.66, 128.43, 128.26, 128.24, 127.29, 126.88, 126.32, 125.81, 125.67, 125.61, 125.51, 125.06, 122.83, 39.22, 34.81, 31.25. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 326.1903, found 326.1907.



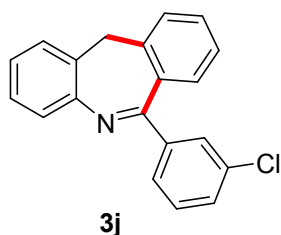
6-(4-Methoxyphenyl)-11*H*-dibenzo[*b,e*]azepine (3g): Pale green liquid; 48.5 mg, 81% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 7.8$ Hz, 2H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 1H), 7.27 (s, 1H), 7.25–7.18 (m, 3H), 7.11 (t, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 2H), 3.88 (s, 3H), 3.70 (dd, $J = 37.2, 13.2$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.20, 161.33, 145.84, 143.62, 133.62, 132.89, 131.50, 131.37, 130.94, 129.88, 126.89, 126.87, 126.33, 125.65, 125.61, 125.36, 113.42, 55.38, 39.22. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$ 300.1383, found 300.1382.



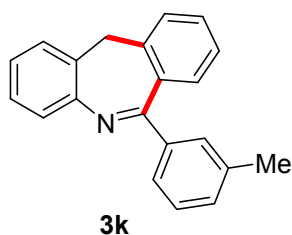
6-(4-(Trifluoromethyl)phenyl)-11H-dibenzo[*b,e*]azepine (3h): Pale green liquid; 47.2 mg, 70% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.45–7.41 (m, 2H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.27 (td, $J = 7.8, 1.2$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.22–7.15 (m, 3H), 3.71 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 165.53, 145.34, 144.35, 143.67, 132.69, 131.73 (q, $J = 32.1$ Hz), 131.43, 131.10, 130.07, 129.46, 127.12, 127.09, 126.76, 126.66, 126.62, 125.87, 125.73, 125.08 (q, $J = 3.3$ Hz), 124.05 (q, $J = 270.4$ Hz), 39.18. ^{19}F NMR (600 MHz, CDCl_3) δ -62.61. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 338.1151, found 338.1151.



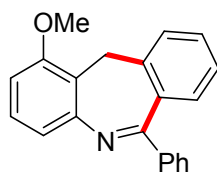
4-(11H-Dibenzo[*b,e*]azepin-6-yl)benzonitrile (3i): Pale green liquid; 38.2 mg, 65% yield; ^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.30–7.27 (m, 2H), 7.25–7.22 (m, 1H), 7.20 (d, $J = 7.8$ Hz, 1H), 3.75 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 165.02, 145.26, 145.12, 143.78, 132.64, 131.98, 131.62, 130.78, 130.33, 129.25, 127.22, 127.19, 126.93, 126.83, 125.97, 125.83, 118.66, 113.50, 39.20. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$ 295.1230, found 295.1231.



6-(3-Chlorophenyl)-11H-dibenzo[*b,e*]azepine (3j): Pale green liquid; 41.2 mg, 68% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.90 (t, *J* = 1.8 Hz, 1H), 7.69 (dt, dd, *J* = 7.8, 1.2 Hz, 1H), 7.45–7.42 (m, 2H), 7.39 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.36 (q, *J* = 7.8 Hz, 2H), 7.28–7.26 (m, 1H), 7.24–7.21 (m, 3H), 7.15 (td, *J* = 7.2, 1.2 Hz, 1H), 3.70 (s, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 165.45, 145.42, 143.65, 142.92, 134.33, 132.74, 131.33, 131.11, 130.08, 129.65, 129.55, 129.33, 128.06, 127.05, 126.58, 126.42, 125.86, 125.67, 39.20. HRMS (ESI) calcd for C₂₀H₁₅ClN [M+H]⁺ 304.0888, found 304.0886.

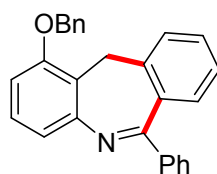


6-(*m*-Tolyl)-11H-dibenzo[*b,e*]azepine (3k): Pale solid; 41.9 mg, 74% yield; m.p.: 138~140 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.73 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 18.0, 8.4 Hz, 3H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 3.70 (dd, *J* = 35.4, 13.2 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 167.17, 145.82, 143.65, 141.19, 137.88, 132.93, 131.77, 131.04, 130.97, 130.19, 129.94, 128.00, 127.29, 126.97, 126.37, 126.02, 125.70, 125.62, 39.29, 21.50. HRMS (ESI) calcd for C₂₁H₁₈N [M+H]⁺ 284.1434, found 284.1436.



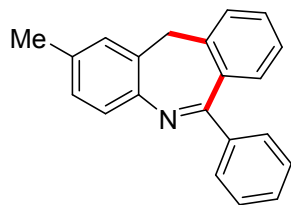
3l

1-Methoxy-6-phenyl-11H-dibenzo[*b,e*]azepine (3l): White solid; 31.1 mg, 52% yield; m.p.: 151~153 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.49–7.42 (m, 3H), 7.41–7.37 (m, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.20–7.15 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 13.2 Hz, 1H), 3.89 (s, 3H), 3.20 (d, *J* = 13.2 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.18, 155.29, 147.11, 144.06, 141.14, 132.13, 130.92, 130.12, 129.87, 129.70, 128.11, 126.65, 126.43, 125.51, 121.57, 118.02, 107.75, 56.04, 29.46. HRMS (ESI) calcd for C₂₁H₁₈NO [M+H]⁺ 300.1383, found 300.1382.



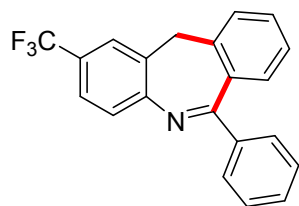
3m

1-(Benzyloxy)-6-phenyl-11H-dibenzo[*b,e*]azepine (3m): White solid; 42.0 mg, 56% yield; m.p.: 151~153 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.47–7.43 (m, 5H), 7.41–7.35 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 3.0 Hz, 2H), 4.47 (d, *J* = 13.2 Hz, 1H), 3.20 (d, *J* = 13.2 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.21, 154.40, 147.22, 143.98, 141.08, 137.44, 132.10, 130.93, 130.13, 129.86, 129.72, 128.60, 128.09, 127.88, 127.31, 126.60, 126.45, 125.53, 121.99, 118.30, 109.24, 70.74, 29.69. HRMS (ESI) calcd for C₂₇H₂₂NO [M+H]⁺ 376.1696, found 376.1699.



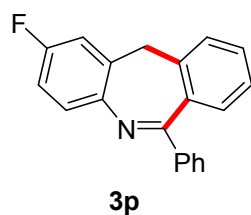
3n

2-Methyl-6-phenyl-11H-dibenzo[*b,e*]azepine (3n): White solid; 39.6 mg, 70% yield; m.p.: 147~149 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.42–7.39 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 2H), 3.67 (dd, *J* = 45.6, 12.6 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.44, 143.57, 143.43, 141.32, 135.95, 132.62, 131.75, 131.02, 129.99, 129.89, 129.78, 128.13, 127.76, 127.61, 126.39, 125.65, 125.61, 39.31, 20.97. HRMS (ESI) calcd for C₂₁H₁₈N [M+H]⁺ 284.1434, found 284.1433.

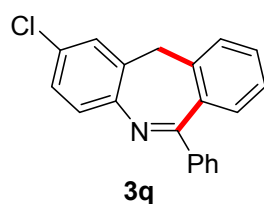


3o

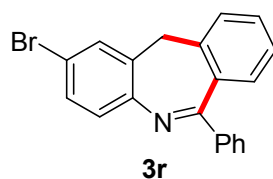
6-Phenyl-2-(trifluoromethyl)-11H-dibenzo[*b,e*]azepine (3o): White solid; 42.5 mg, 63% yield; m.p.: 141~143 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.51-7.48 (m, 7H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.26-7.23 (m, 2H), 3.74 (q, *J* = 13.2 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 168.61, 148.45, 143.06, 140.50, 133.17, 131.51, 131.37, 130.69, 129.96, 129.92, 128.23, 127.55 (q, *J* = 32.2 Hz), 126.57, 126.14, 125.61, 124.34 (q, *J* = 270 Hz), 123.98 (q, *J* = 3.6 Hz), 38.90. ¹⁹F NMR (565 MHz, CDCl₃) δ -61.74. HRMS (ESI) calcd for C₂₁H₁₅F₃N [M+H]⁺ 338.1151, found 338.1149.



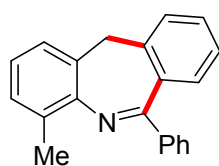
2-Fluoro-6-phenyl-11H-dibenzo[*b,e*]azepine (3p): White solid; 35.0 mg, 61% yield; m.p.: 153~155 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.87–7.81 (m, 2H), 7.50–7.42 (m, 4H), 7.38–7.32 (m, 2H), 7.26–7.21 (m, 2H), 6.98–6.92 (m, 2H), 3.68 (dd, $J = 52.2$, 12.0 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 166.78, 162.12, 160.49, 142.12, 141.89 (d, $J = 269.0$ Hz), 134.27 (d, $J = 7.65$ Hz), 131.59, 131.20, 130.19, 129.90, 129.75, 128.16, 127.11 (d, $J = 8.7$ Hz), 126.49, 125.99, 113.78 (d, $J = 22.1$ Hz), 113.45 (d, $J = 22.1$ Hz), 39.13. ^{19}F NMR (565 MHz, CDCl_3) δ -117.80. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{FN}$ $[\text{M}+\text{H}]^+$ 288.1183, found 288.1184.



2-Chloro-6-phenyl-11H-dibenzo[*b,e*]azepine (3q): White solid; 38.8 mg, 64% yield; m.p.: 145~147 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.87–7.79 (m, 2H), 7.51–7.40 (m, 4H), 7.32 (dd, $J = 10.8$, 7.8 Hz, 2H), 7.25–7.18 (m, 4H), 3.66 (dd, $J = 48.6$, 12.6 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.42, 144.36, 142.90, 140.82, 134.13, 131.53, 131.40, 131.28, 130.34, 129.90, 129.80, 128.17, 127.01, 126.80, 126.50, 126.01, 38.90. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}$ $[\text{M}+\text{H}]^+$ 304.0888, found 304.0887.

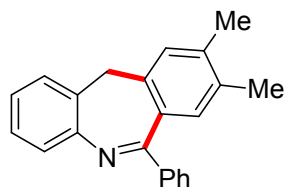


2-Bromo-6-phenyl-11H-dibenzo[*b,e*]azepine (3r): White solid; 46.5 mg, 67% yield; m.p.: 158~160 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 3H), 7.39–7.32 (m, 3H), 7.24 (t, *J* = 5.4 Hz, 3H), 3.67 (dd, *J* = 48.0, 13.2 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 167.53, 144.82, 142.96, 140.82, 134.55, 131.54, 131.32, 130.39, 129.97, 129.93, 129.83, 129.71, 128.19, 127.13, 126.54, 126.05, 119.39, 38.85. HRMS (ESI) calcd for C₂₀H₁₅BrN [M+H]⁺ 348.0382, found 348.0380.



3s

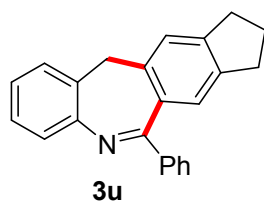
4-Methyl-6-phenyl-11H-dibenzo[*b,e*]azepine (3s): White solid; 35.7 mg, 63% yield; m.p.: 155~157 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.47–7.42 (m, 3H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 13.8, 7.2 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 3.65 (dd, *J* = 19.8, 13.2 Hz, 2H), 2.53 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.38, 144.01, 143.88, 141.39, 133.56, 133.00, 131.57, 130.98, 130.16, 129.79, 129.65, 128.62, 128.19, 126.41, 125.97, 125.69, 124.69, 39.30, 18.73. HRMS (ESI) calcd for C₂₁H₁₈N [M+H]⁺ 284.1434, found 284.1435.



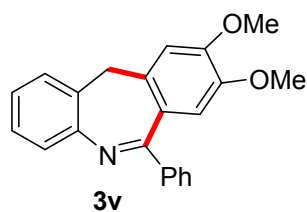
3t

8,9-Dimethyl-6-phenyl-11H-dibenzo[*b,e*]azepine (3t): White solid; 42.8 mg, 72% yield; m.p.: 161~162 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 6.6 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.14–7.11 (m, 2H), 7.04–7.00 (m, 2H), 6.90 (s, 1H), 3.55 (dd, *J* = 51.6, 12.0 Hz, 2H), 2.18 (s, 3H), 2.04 (s, 3H). ¹³C NMR

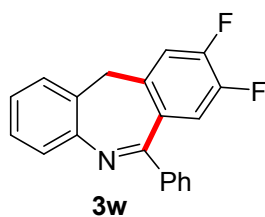
(150 MHz, CDCl₃) δ 167.06, 145.86, 141.35, 140.10, 133.88, 133.19, 130.73, 129.94, 129.82, 129.35, 128.04, 127.55, 126.79, 126.76, 125.87, 125.53, 38.75, 19.64, 19.23. HRMS (ESI) calcd for C₂₂H₂₀N [M+H]⁺ 298.1590, found 298.1590.



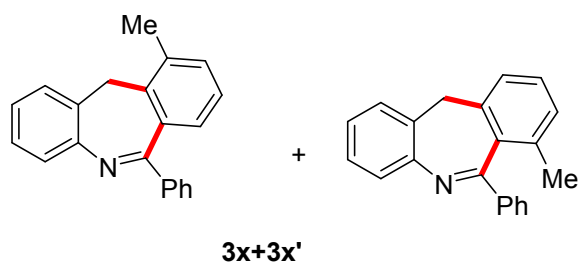
6-Phenyl-8,9,10,12-tetrahydrobenzo[*b*]indeno[5,6-*e*]azepine (3u): White solid; 46.4 mg, 75% yield; m.p.: 157~159 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.94 (d, *J* = 6.6 Hz, 2H), 7.52 (d, *J* = 6.0 Hz, 3H), 7.47–7.43 (m, 1H), 7.33–7.27 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 3.0 Hz, 1H), 3.74 (dd, *J* = 46.2, 12.6 Hz, 2H), 3.05–2.89 (m, 3H), 2.79–2.76 (m, 1H), 2.18–2.04 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 167.37, 147.95, 145.86, 141.97, 141.66, 141.57, 133.24, 129.90, 129.84, 128.03, 126.78, 126.73, 125.85, 125.46, 125.43, 122.20, 77.21, 77.00, 76.79, 39.18, 32.84, 32.31, 25.39. HRMS (ESI) calcd for C₂₃H₂₀N [M+H]⁺ 310.1590, found 310.1593.



8,9-Dimethoxy-6-phenyl-11H-dibenzo[*b,e*]azepine (3v): White solid; 49.4 mg, 75% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.50–7.43 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 6.72 (s, 1H), 3.95 (s, 3H), 3.71 (d, *J* = 12.6 Hz, 1H), 3.67 (s, 3H), 3.59 (d, *J* = 13.2 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 166.40, 151.50, 146.61, 145.77, 141.13, 137.29, 132.97, 130.12, 129.82, 128.12, 126.89, 126.74, 125.93, 125.46, 123.86, 112.80, 109.06, 56.06, 55.94, 38.83. HRMS (ESI) calcd for C₂₂H₂₀NO₂⁺ [M+H]⁺ 330.1489, found 330.1491.

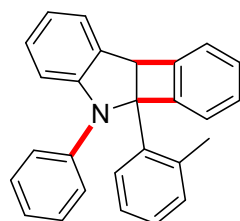


8,9-Difluoro-6-phenyl-11H-dibenzo[*b,e*]azepine (3w): White solid; 37.2 mg, 61% yield; m.p.: 153~155 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, *J* = 6.6 Hz, 2H), 7.53–7.45 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.20–7.13 (m, 2H), 7.06 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.66 (dd, *J* = 45.6, 13.2 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 164.68, 151.98 (dd, *J* = 252.2, 12.5 Hz), 148.28 (dd, *J* = 244.1, 14.5 Hz), 145.36, 140.50 (dd, *J* = 5.6, 3.8 Hz), 140.27, 131.96, 130.56, 129.62, 128.35, 127.94, 127.37, 126.96, 126.44, 125.65, 118.58 (d, *J* = 17.8 Hz), 115.15 (d, *J* = 17.3 Hz), 38.33. ¹⁹F NMR (565 MHz, CDCl₃) δ -129.95 (d, *J* = 22.0 Hz), -133.77 (d, *J* = 22.0 Hz), -139.93 (d, *J* = 20.9 Hz), -140.64 (d, *J* = 21.5 Hz). HRMS (ESI) calcd for C₂₀H₁₄F₂N [M+H]⁺ 306.1089, found 306.1087.



10-Methyl-6-phenyl-11H-dibenzo[*b,e*]azepine (3x) and 7-Methyl-6-phenyl-11H-dibenzo[*b,e*]azepine (3x'): Pale green liquid; 39.6 mg, 70% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.88–7.86 (m, 0.5H), 7.73 (d, *J* = 5.4 Hz, 1.8H), 7.46–7.43 (m, 0.9H), 7.43–7.39 (m, 3.1H), 7.32 (dd, *J* = 7.8, 0.6 Hz, 1.0H), 7.27 (d, *J* = 7.8 Hz, 1.4H), 7.24 (d, *J* = 6.0 Hz, 1.1H), 7.22 (dd, *J* = 7.2, 1.2 Hz, 0.76H), 7.17 (dd, *J* = 13.8, 6.0 Hz, 2H), 7.13 (td, *J* = 7.2, 1.2 Hz, 0.38H), 7.07–7.05 (m, 1.0 H), 7.04 (d, *J* = 1.2 Hz, 0.37H), 7.01 (d, *J* = 7.8 Hz, 1.0 H), 4.01 (d, *J* = 13.2 Hz, 0.25H), 3.62 (d, *J* = 13.2 Hz, 1.0H), 3.56 (d, *J* = 13.2 Hz, 1.0 H), 3.35 (d, *J* = 13.2 Hz, 0.26H), 2.56 (s, 0.77H), 1.87 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 167.89, 167.39, 146.03, 145.99, 145.53, 141.63, 141.56, 141.26, 136.71, 133.33, 133.16, 132.64, 132.44, 131.98, 130.36, 130.08, 130.04, 129.95, 129.77, 129.23, 128.48, 128.10, 128.06, 127.63, 126.93,

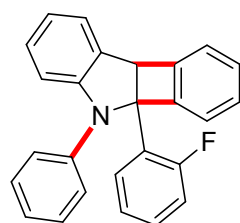
126.88, 126.74, 126.61, 125.78, 125.40, 125.33, 125.15, 124.30, 123.47, 39.08, 33.84, 21.89, 20.01. HRMS (ESI) calcd for C₂₁H₁₈N [M+H]⁺ 284.1434, found 284.1433.



4a

5-Phenyl-4b-(*o*-tolyl)-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-*b*]indole (4a):

White solid; 51.0 mg, m.p.: 143~145 °C, 71% yield; ¹H NMR (600 MHz, CDCl₃) δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 2H), 7.22–7.15 (m, 4H), 7.08 (t, *J* = 7.8 Hz, 3H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.8, 2.4 Hz, 2H), 6.80 (td, *J* = 7.2, 2.4 Hz, 1H), 6.75 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.00 (s, 1H), 2.32 (d, *J* = 2.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 148.99, 146.01, 143.54, 141.97, 138.46, 138.28, 131.65, 129.84, 129.42, 128.75, 128.03, 127.92, 127.49, 125.13, 124.22, 124.20, 124.17, 123.88, 122.28, 118.89, 110.43, 80.55, 58.96, 20.40. HRMS (ESI) calcd for C₂₇H₂₂N [M+H]⁺ 360.1747, found 360.1746.

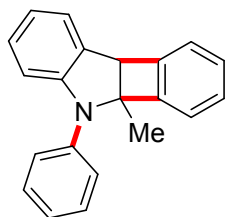


4b

4b-(2-Fluorophenyl)-5-phenyl-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-

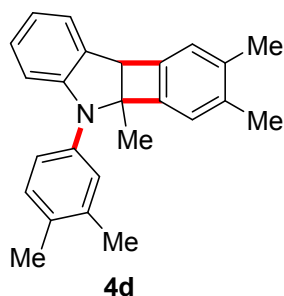
***b*]indole (4b):** Pale green solid; 55.9 mg, 77% yield; m.p.: 149~151 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.47 (td, *J* = 7.8, 1.8 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.31 (m, 2H), 7.27 (m, 1H), 7.26–7.21 (m, 3H), 7.14–7.11 (m, 2H), 7.10–7.08 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.05–7.02 (m, 1H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.19 (s, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 161.67 (d,

$J = 249.15$ Hz), 149.33, 146.23, 143.37, 141.90, 130.61 (d, $J = 3.45$ Hz), 129.73 (d, $J = 8.1$ Hz), 129.67, 128.83, 128.75, 127.90, 127.83, 127.70, 124.66, 124.33(d, $J = 5.25$ Hz), 123.44, 123.32(d, $J = 3.3$ Hz), 122.41, 118.74, 116.03, 115.89, 110.05, 77.45, 60.01. ^{19}F NMR (565 MHz, CDCl_3) $\delta -112.07$. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{19}\text{FN}$ $[\text{M}+\text{H}]^+$ 364.1496, found 364.1493.



4c

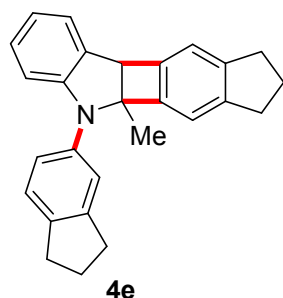
4b-Methyl-5-phenyl-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-*b*]indole (4c): Pale green liquid; 46.4 mg, 82% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.25 (d, $J = 7.2$ Hz, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.19–7.06 (m, 5H), 6.93 (d, $J = 6.6$ Hz, 1H), 6.90 (t, $J = 7.8$ Hz, 1H), 6.61 (t, $J = 7.2$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 4.67 (s, 1H), 1.67 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 149.90, 147.47, 145.99, 141.58, 129.23, 128.96, 128.66, 127.88, 127.68, 125.64, 124.69, 124.56, 122.07, 121.54, 118.11, 109.02, 74.39, 58.04, 22.35. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 284.1434, found 284.1436.



4d

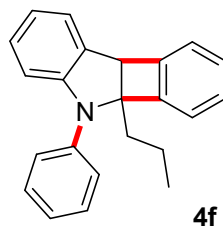
5-(3,4-Dimethylphenyl)-2,3,4b-trimethyl-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-*b*]indole (4d): Pale green liquid; 50.2 mg, 74% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.26 (d, $J = 7.2$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 7.15 (s, 1H), 7.09 (d, $J = 8.4$ Hz, 1H), 7.02 (s, 1H), 6.96 (t, $J = 7.8$ Hz, 1H), 6.87 (s, 1H), 6.66 (t, $J = 7.8$ Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 1H), 4.70 (s, 1H), 2.30 (d, $J = 3.0$ Hz, 6H),

2.24 (s, 6H), 1.72 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.19, 145.49, 143.70, 139.12, 137.49, 137.39, 136.13, 133.04, 130.33, 128.85, 127.80, 127.09, 124.39, 123.30, 122.97, 122.60, 117.54, 108.75, 74.14, 57.60, 22.45, 20.52, 20.46, 20.03, 19.37. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 340.2060, found 340.2058.



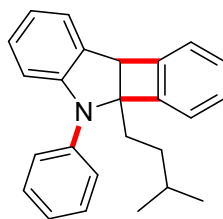
5-(2,3-Dihydro-1H-inden-5-yl)-4b-methyl-1,2,3,4b,5,9b-

hexahydroindeno[5',6':3,4]cyclobuta[1,2-*b*]indole (4e): Pale green liquid; 50.1 mg, 69% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.30 (t, $J = 9.0$ Hz, 3H), 7.15 (d, $J = 13.2$ Hz, 2H), 7.03–6.98 (m, 2H), 6.69 (t, $J = 7.2$ Hz, 1H), 6.52 (d, $J = 7.8$ Hz, 1H), 4.71 (s, 1H), 2.99 (t, $J = 7.2$ Hz, 4H), 2.94–2.89 (m, 2H), 2.19 (dd, $J = 15.0, 7.2$ Hz, 2H), 2.06 (dd, $J = 14.4, 7.2$ Hz, 2H), 1.77 (s, 3H), 1.31 (s, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.46, 145.58, 145.31, 144.61, 143.76, 143.22, 140.81, 139.67, 128.91, 127.77, 124.77, 124.36, 124.09, 122.25, 118.25, 117.83, 117.48, 108.78, 73.42, 56.87, 33.25, 33.19, 33.06, 32.53, 25.65, 25.30, 22.50. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 364.2060, found 364.2063.



5-Phenyl-4b-propyl-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-*b*]indole (4f): Pale green liquid; 53.5 mg, 86% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.43 (t, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 7.2$ Hz, 1H), 7.22 (dd, $J = 14.4, 7.2$ Hz, 3H), 7.05 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H), 6.75–6.70 (m, 1H), 6.62

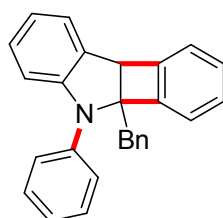
(d, $J = 7.8$ Hz, 1H), 4.88 (s, 1H), 2.24–2.19 (m, 1H), 1.97–1.92 (m, 1H), 1.56–1.52 (m, 1H), 1.41–1.34 (m, 1H), 0.90 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 146.91, 146.38, 129.18, 128.85, 128.66, 127.81, 127.57, 125.50, 124.54, 124.47, 121.83, 121.80, 118.04, 108.87, 78.00, 55.39, 36.72, 18.34, 14.28. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 312.1747, found 312.1748.



4g

4b-iso-Pentyl-5-phenyl-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-b]indole (4g):

Pale green liquid; 56.3 mg, 83% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.39 (t, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.23 (d, $J = 9.0$ Hz, 1H), 7.20–7.16 (m, 3H), 7.02 (d, $J = 7.8$ Hz, 1H), 6.98 (t, $J = 7.2$ Hz, 1H), 6.69 (t, $J = 7.2$ Hz, 1H), 6.59 (d, $J = 7.8$ Hz, 1H), 4.82 (s, 1H), 2.23–2.17 (m, 1H), 1.92–1.85 (m, 1H), 1.46–1.42 (m, 1H), 1.40–1.34 (m, 1H), 1.24–1.18 (m, 1H), 0.79 (d, $J = 6.6$ Hz, 3H), 0.76 (d, $J = 6.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.44, 147.10, 146.35, 141.58, 129.15, 128.85, 128.73, 127.81, 127.60, 125.40, 124.51, 124.49, 121.89, 121.72, 118.04, 108.92, 77.97, 55.23, 33.77, 32.16, 28.16, 22.61, 22.38. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 340.2060, found 340.2063.



4h

4b-Benzyl-5-phenyl-4b,9b-dihydro-5H-benzo[3,4]cyclobuta[1,2-b]indole (4h):

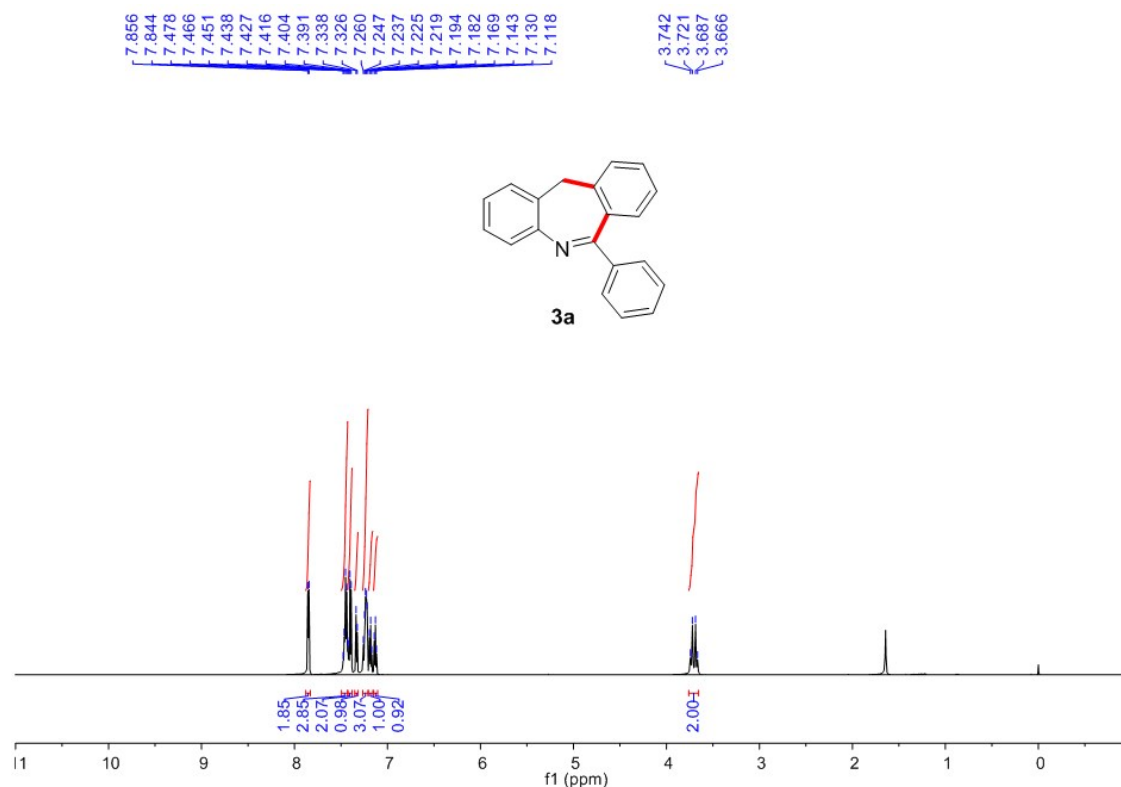
Pale green liquid; 38.1 mg, 53% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.41 (t, $J = 7.2$ Hz, 3H), 7.35 (d, $J = 7.8$ Hz, 2H), 7.25–7.19 (m, 4H), 7.17–7.08 (m, 6H), 7.03 (d, $J =$

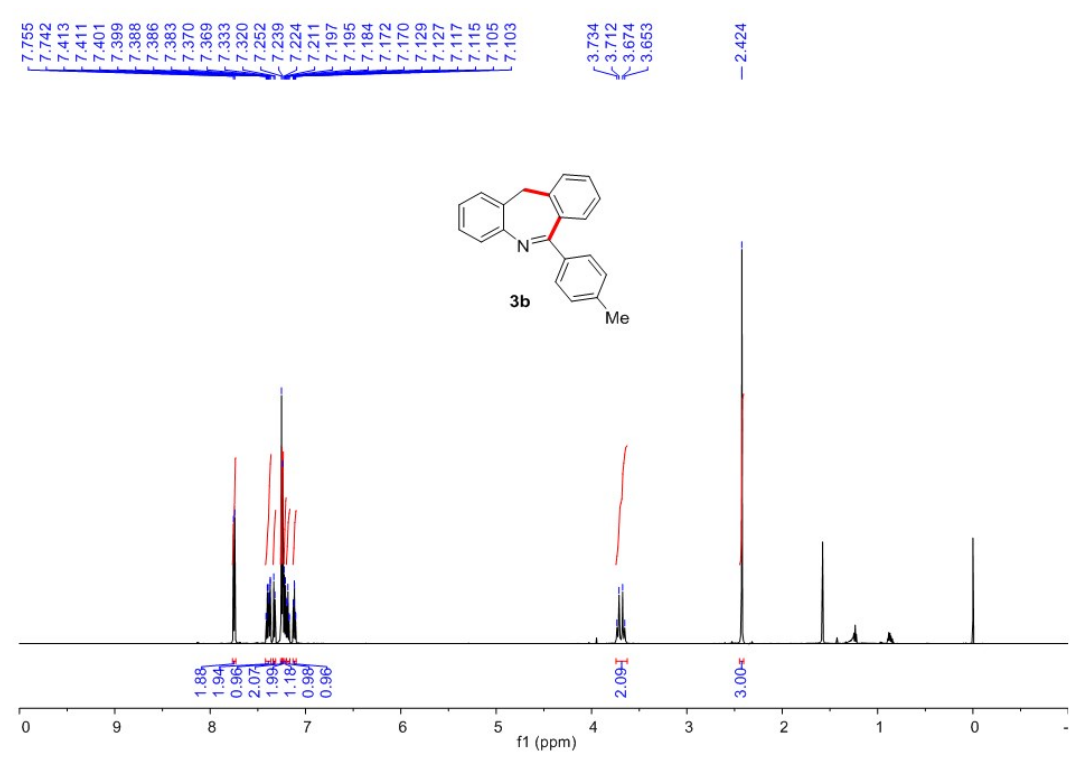
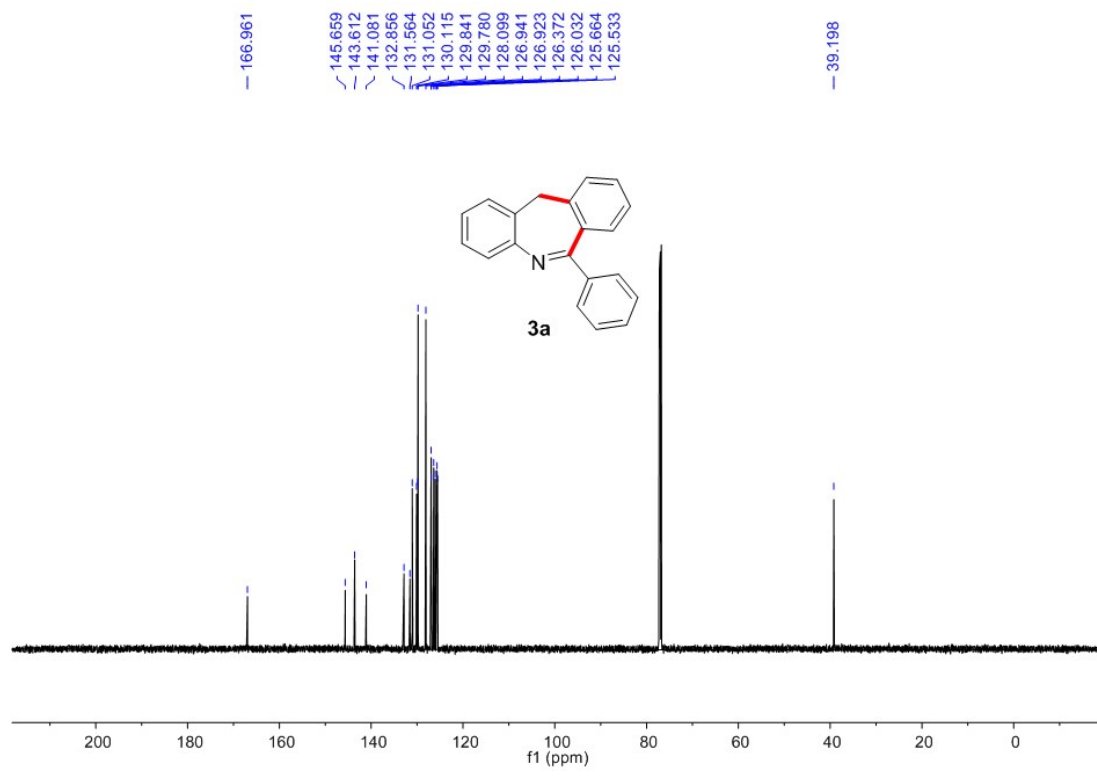
6.6 Hz, 2H), 6.97 (t, $J = 7.8$ Hz, 1H), 6.68 (t, $J = 7.2$ Hz, 1H), 6.58 (d, $J = 7.8$ Hz, 1H), 4.88 (s, 1H), 3.50 (d, $J = 14.4$ Hz, 1H), 3.37 (d, $J = 14.4$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.08, 146.27, 146.00, 141.48, 137.14, 129.75, 129.26, 129.07, 128.45, 127.92, 127.80, 127.60, 126.16, 125.62, 124.66, 124.48, 122.01, 121.79, 118.21, 108.89, 77.68, 54.87, 40.55. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 360.1747, found 360.1748.

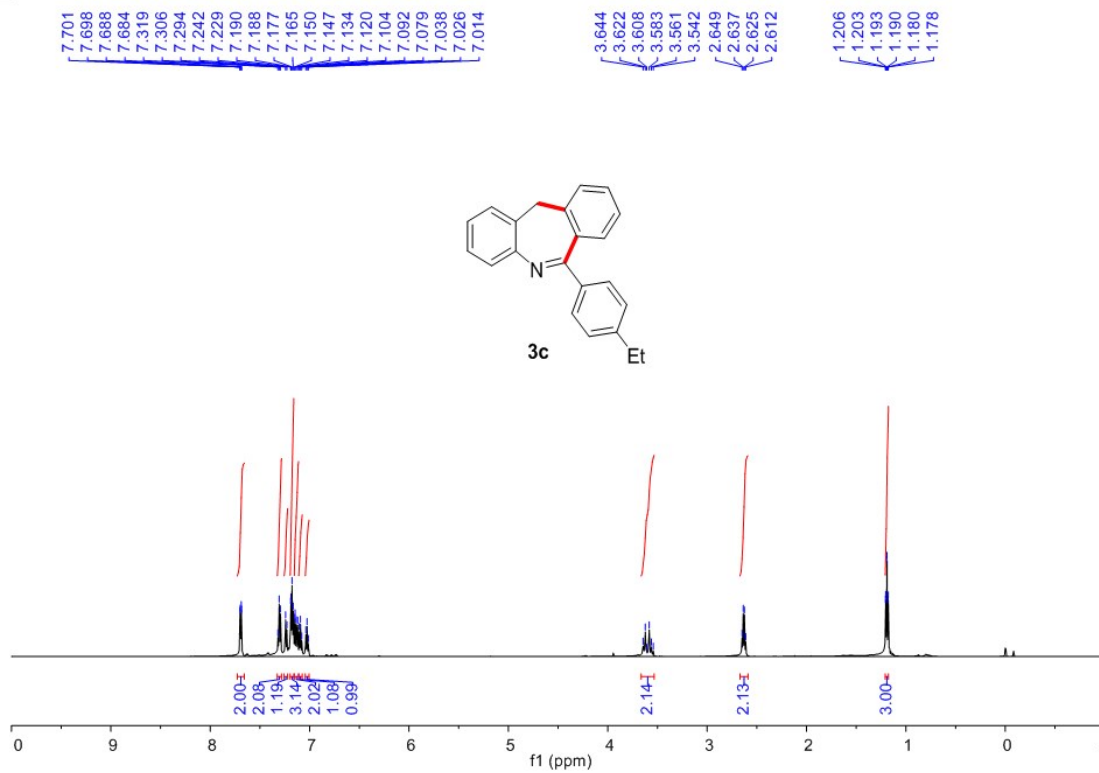
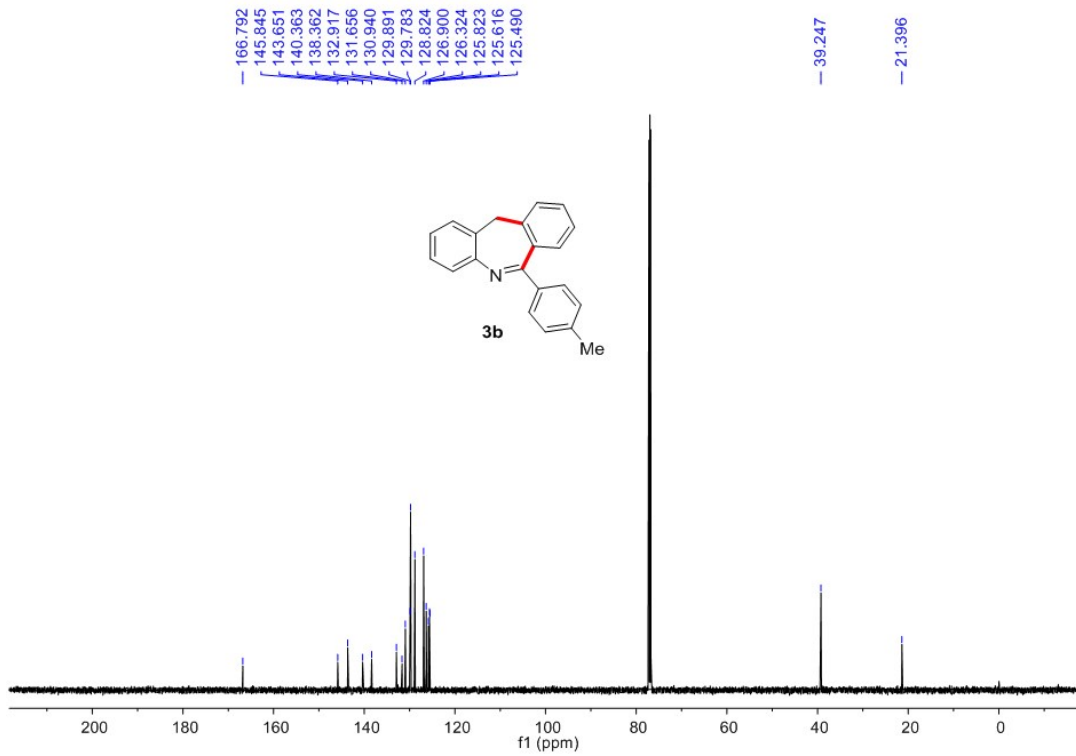
6. References

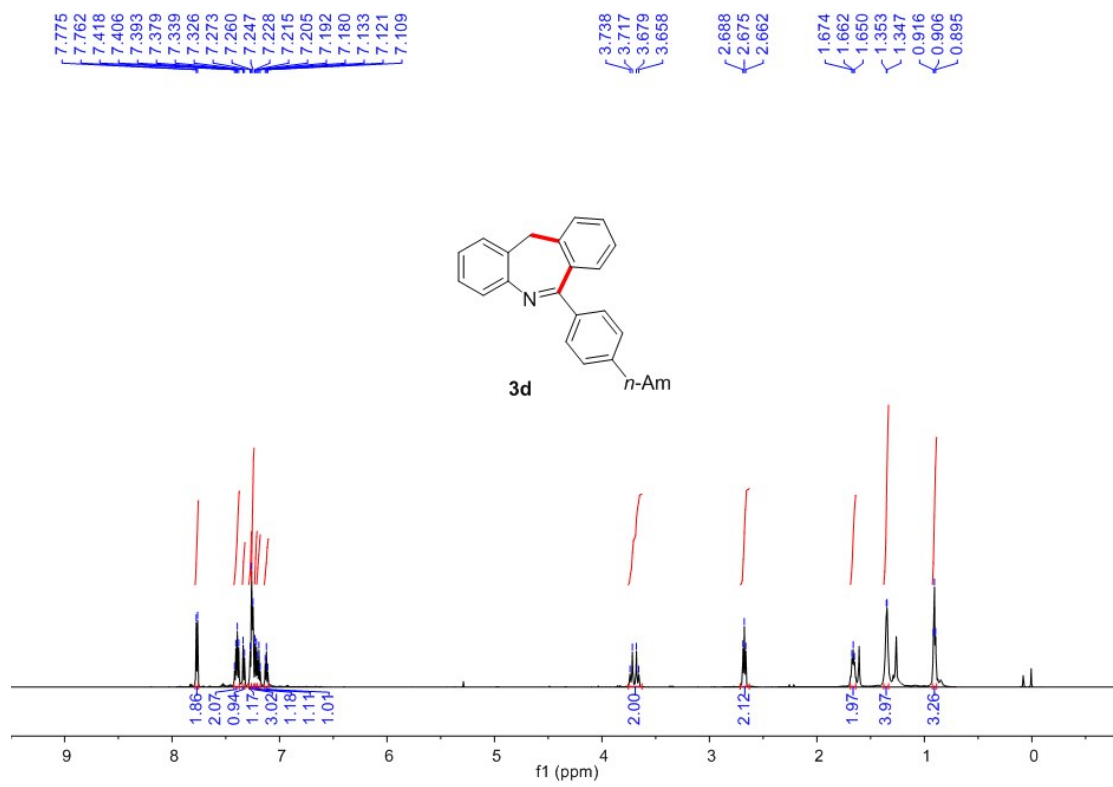
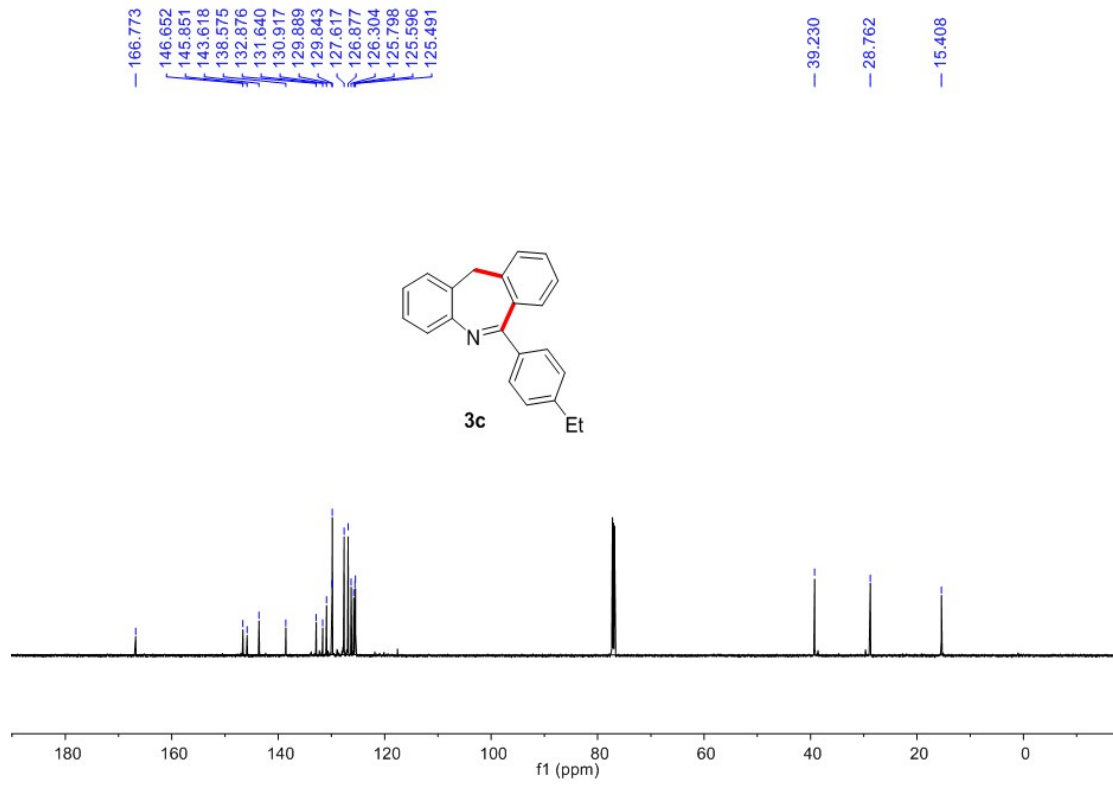
- [1] Y. Yin, W. Ma, Z. Chai and G. Zhao, *J. Org. Chem.*, 2007, **72**, 5731.
- [2] A.-T. Biju and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 9761.
- [3] B. Balakrishna, A. Bauzá, A. Frontera and A. Vidal-Ferran, *Chem.–Eur. J.*, 2016, **22**, 10607.

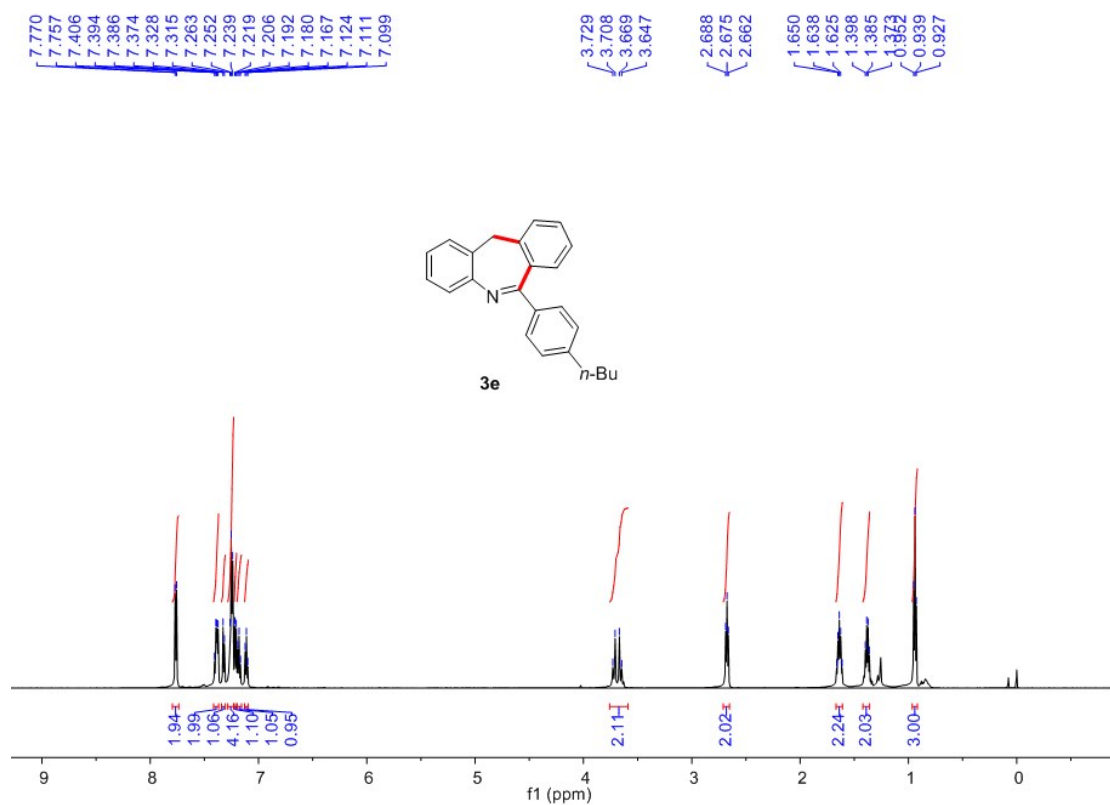
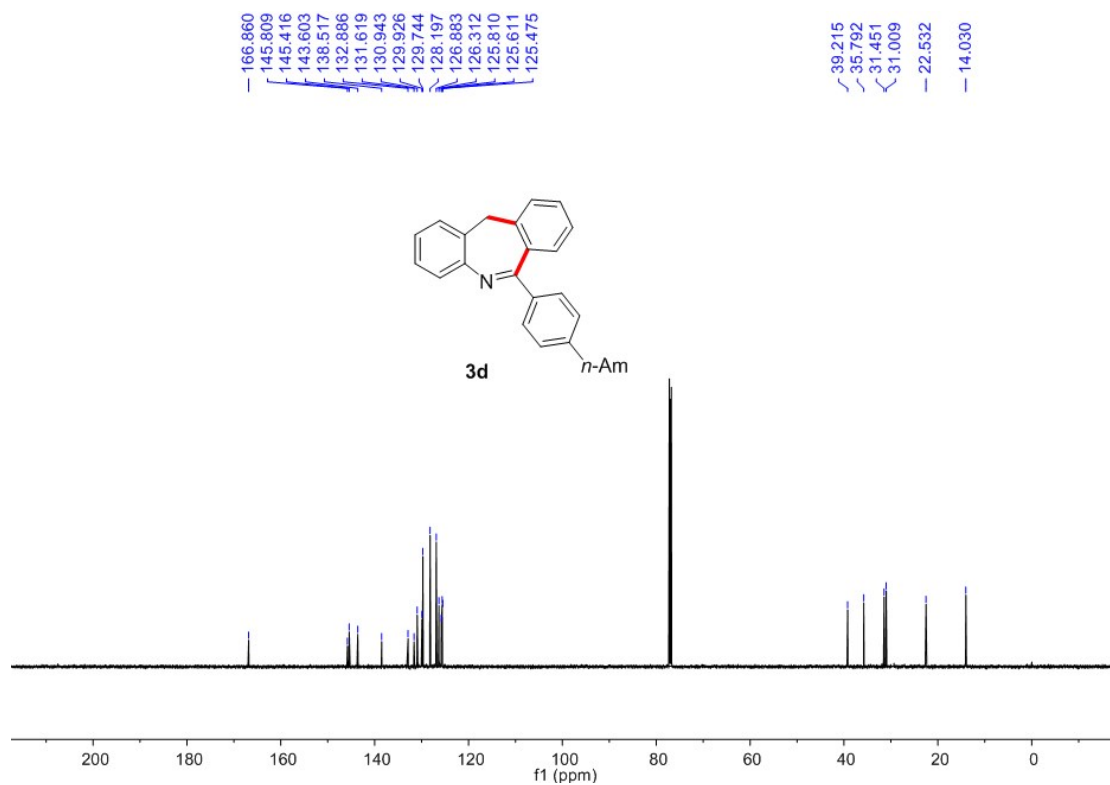
7. ^1H and ^{13}C NMR Spectra of the Products

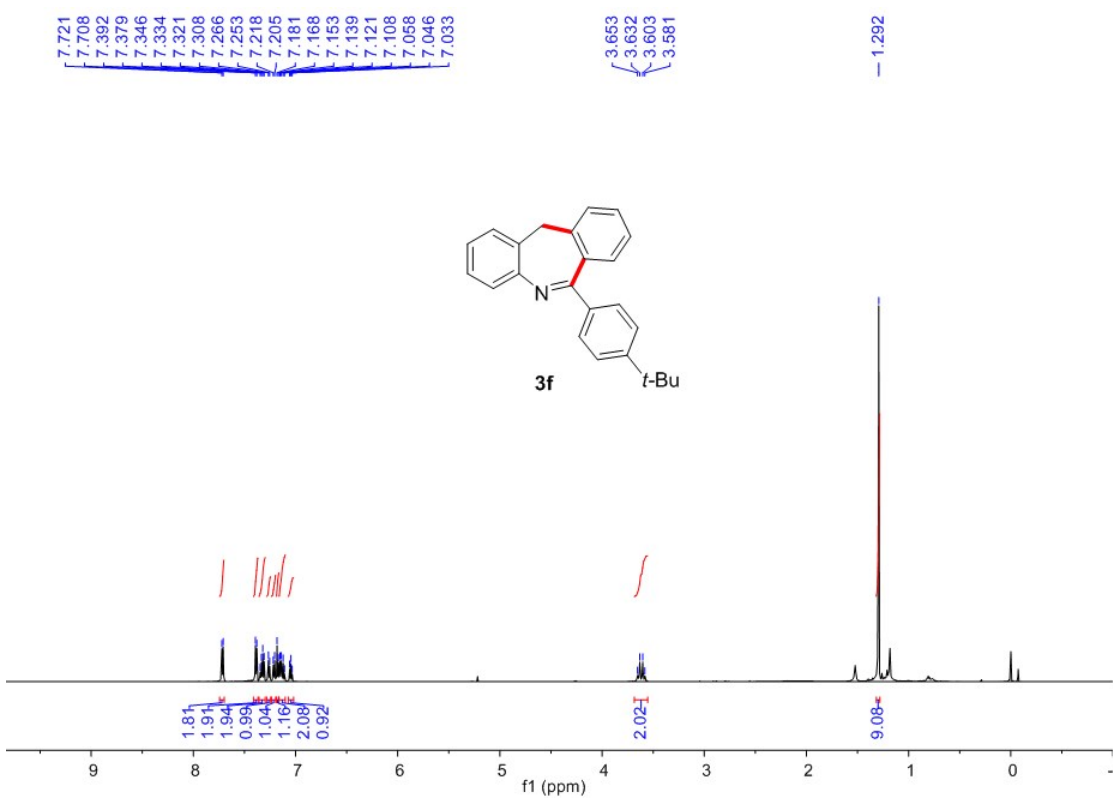
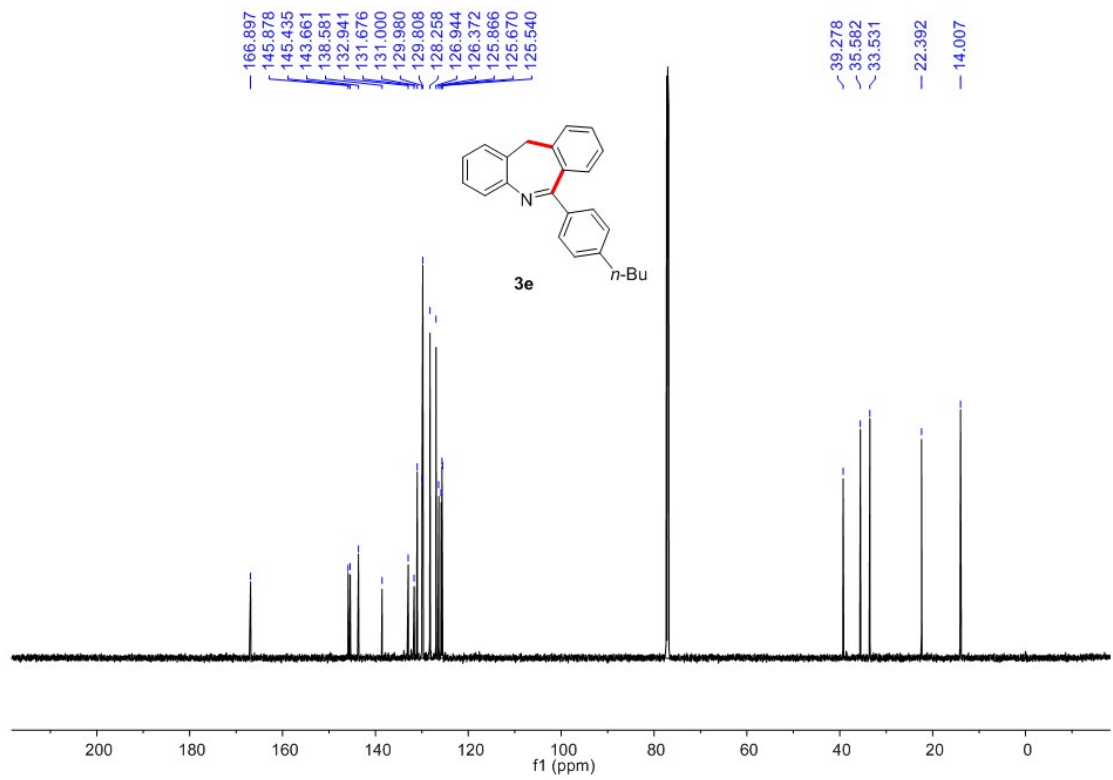


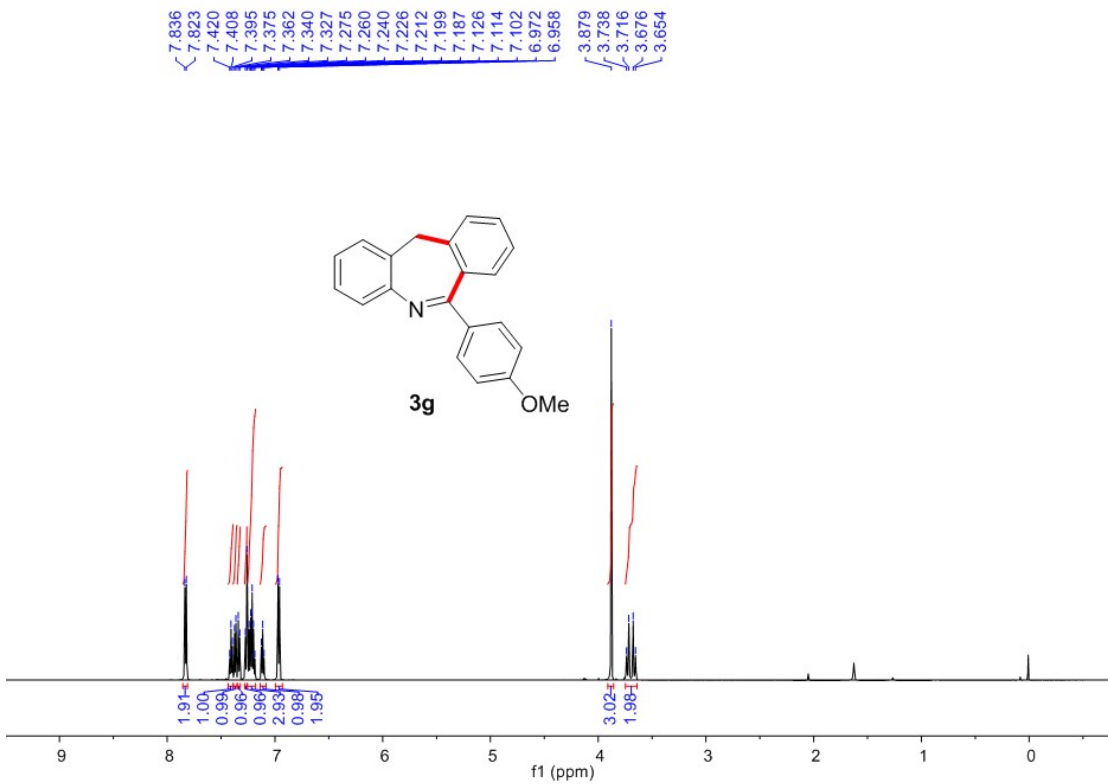
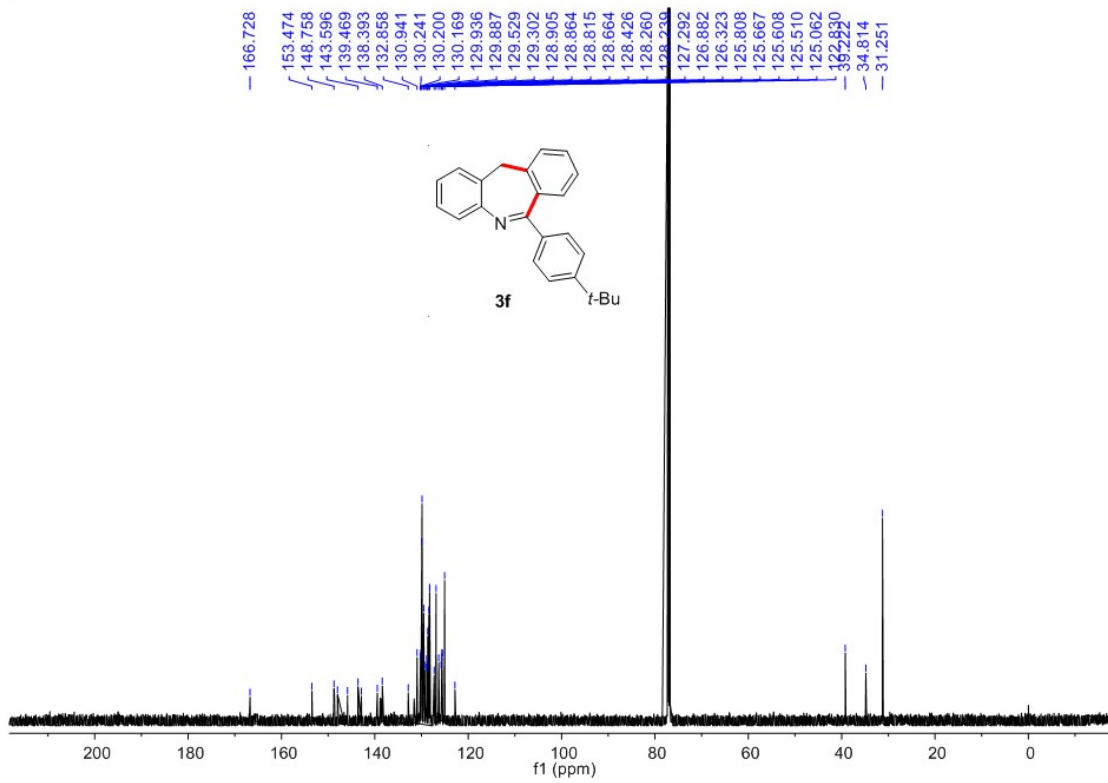


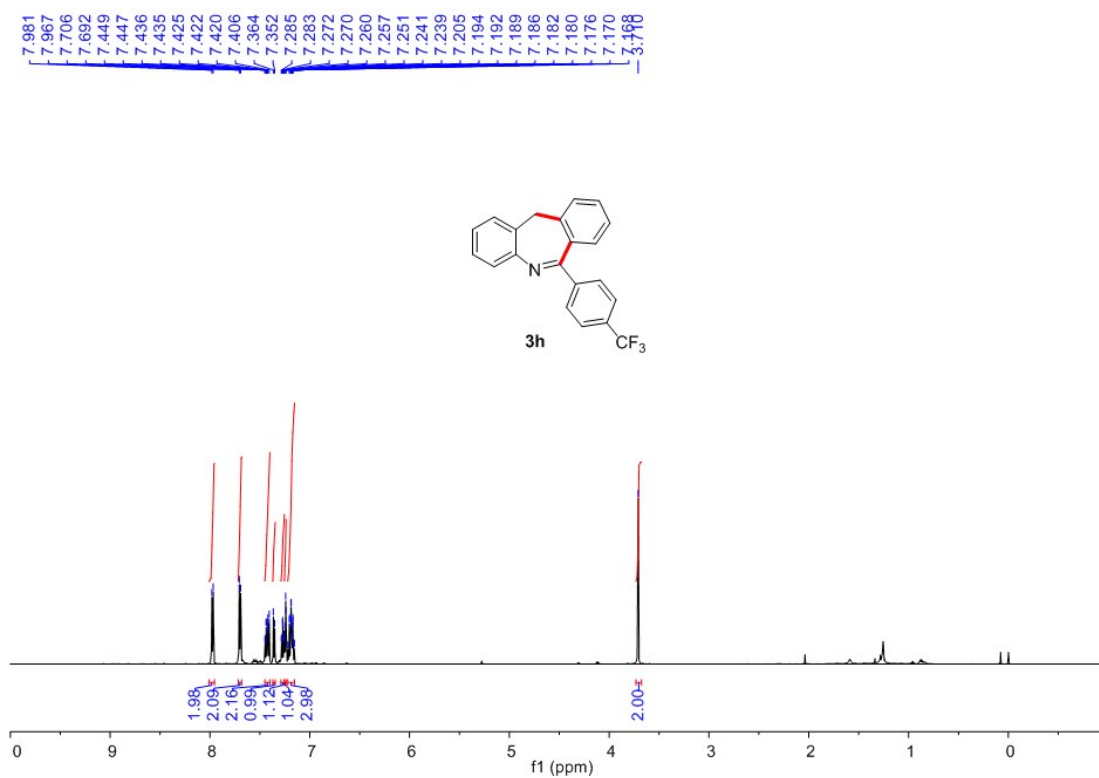
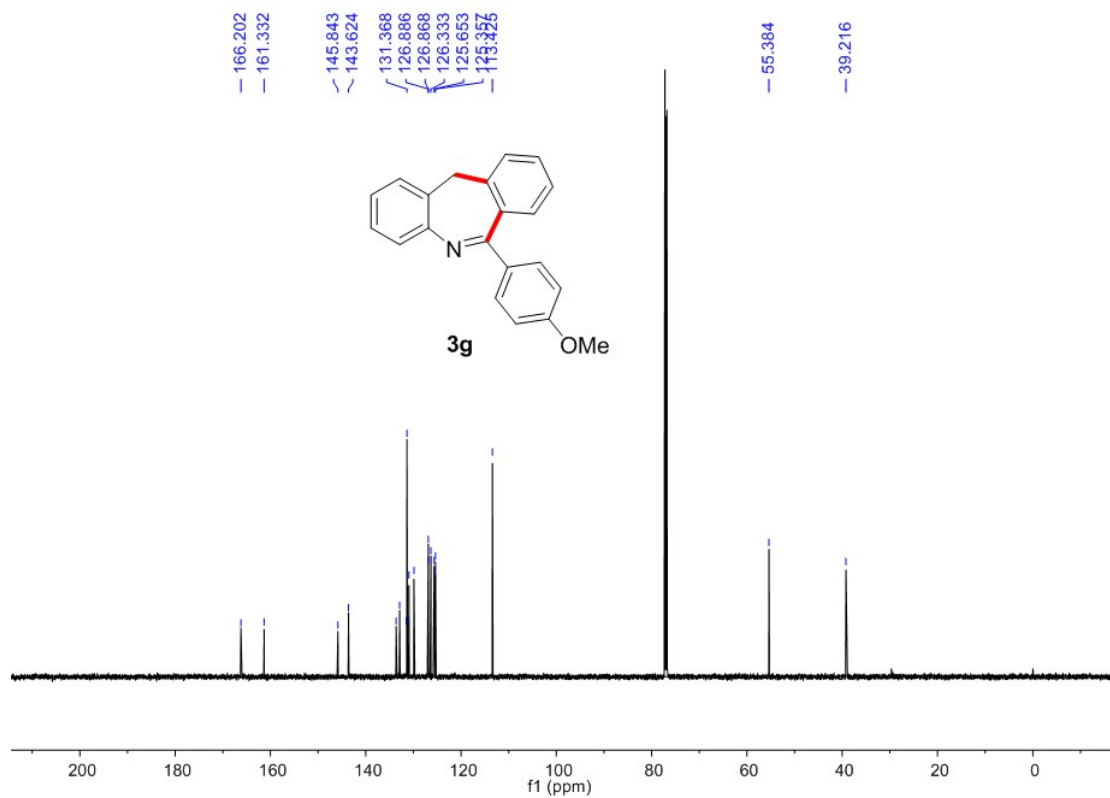


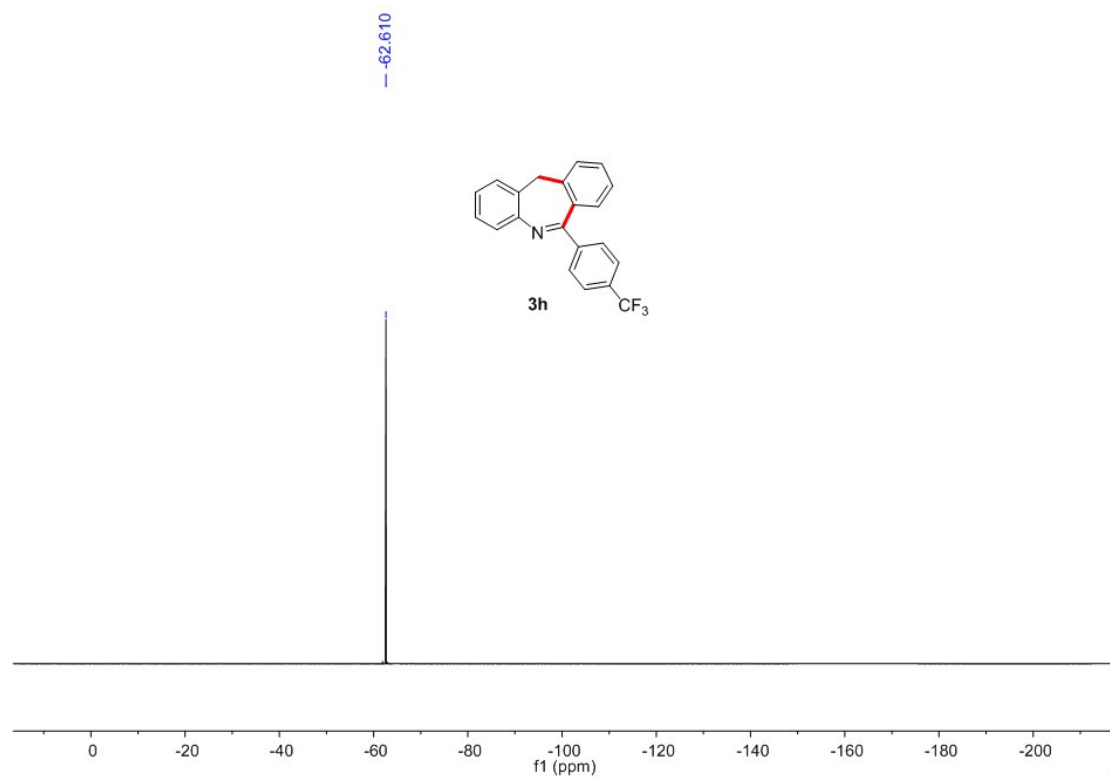
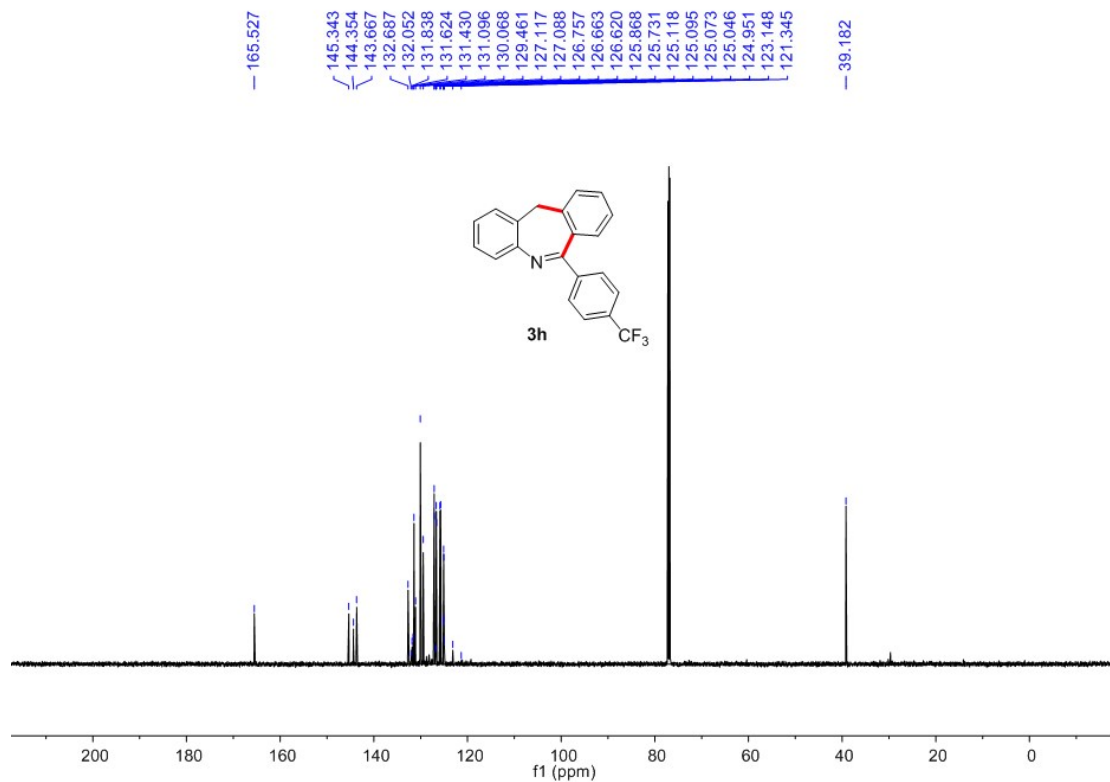


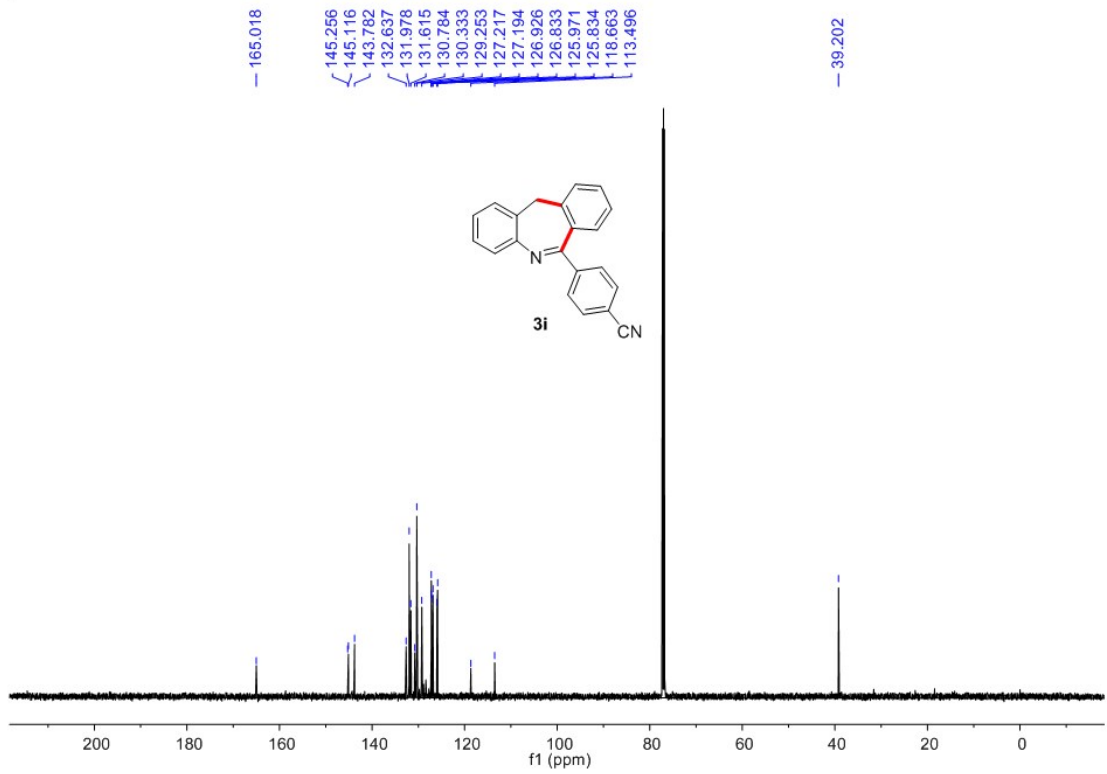
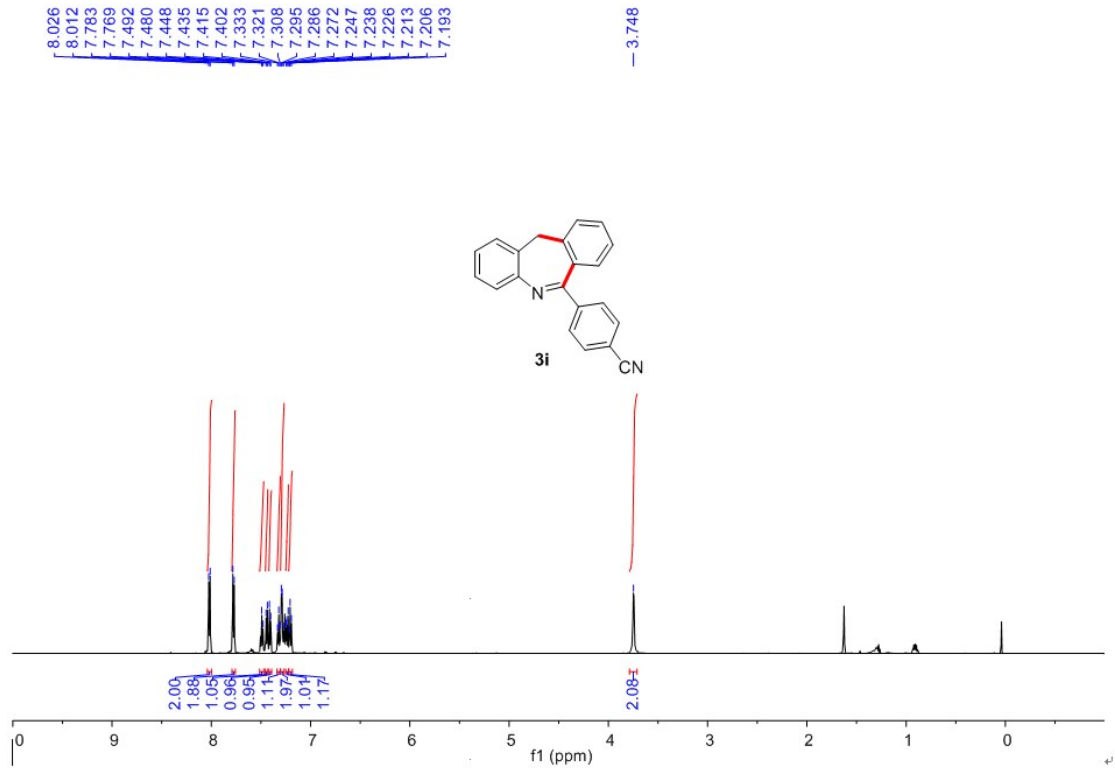


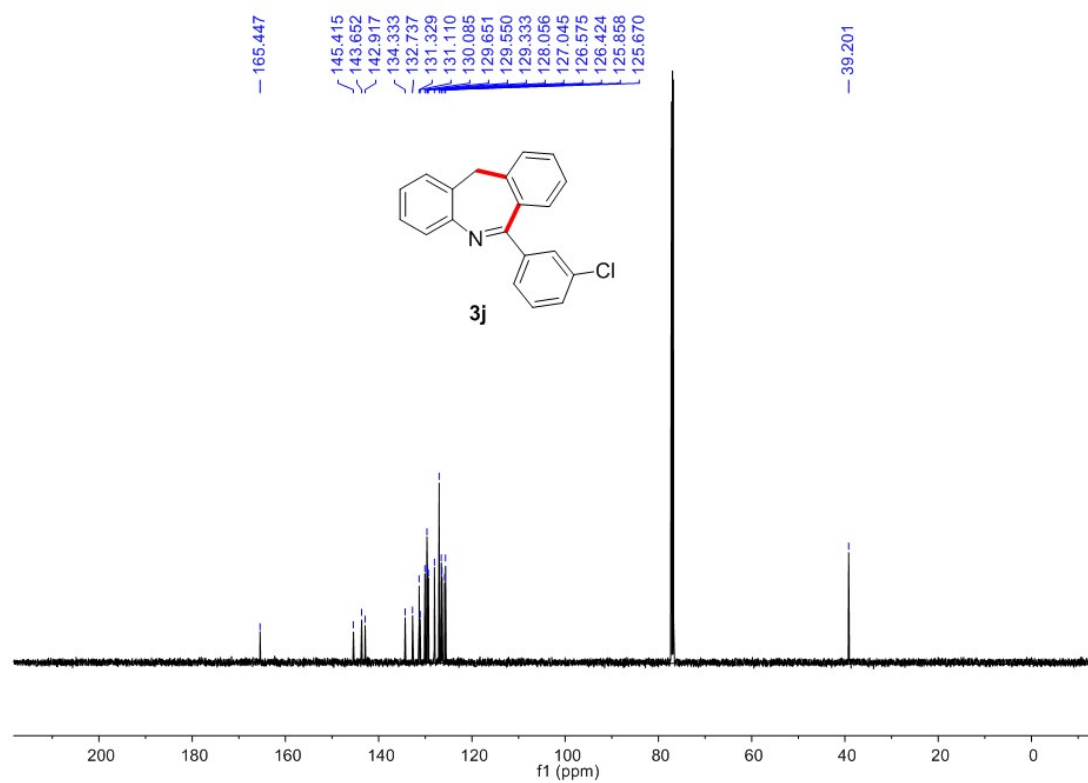
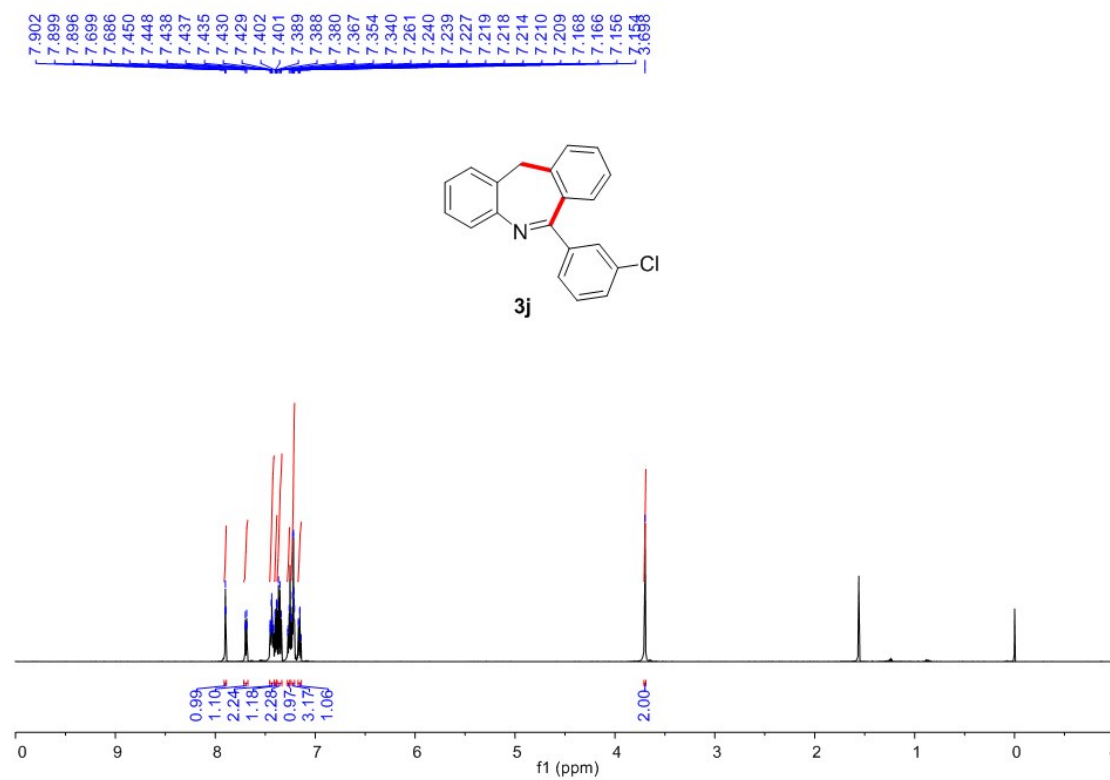


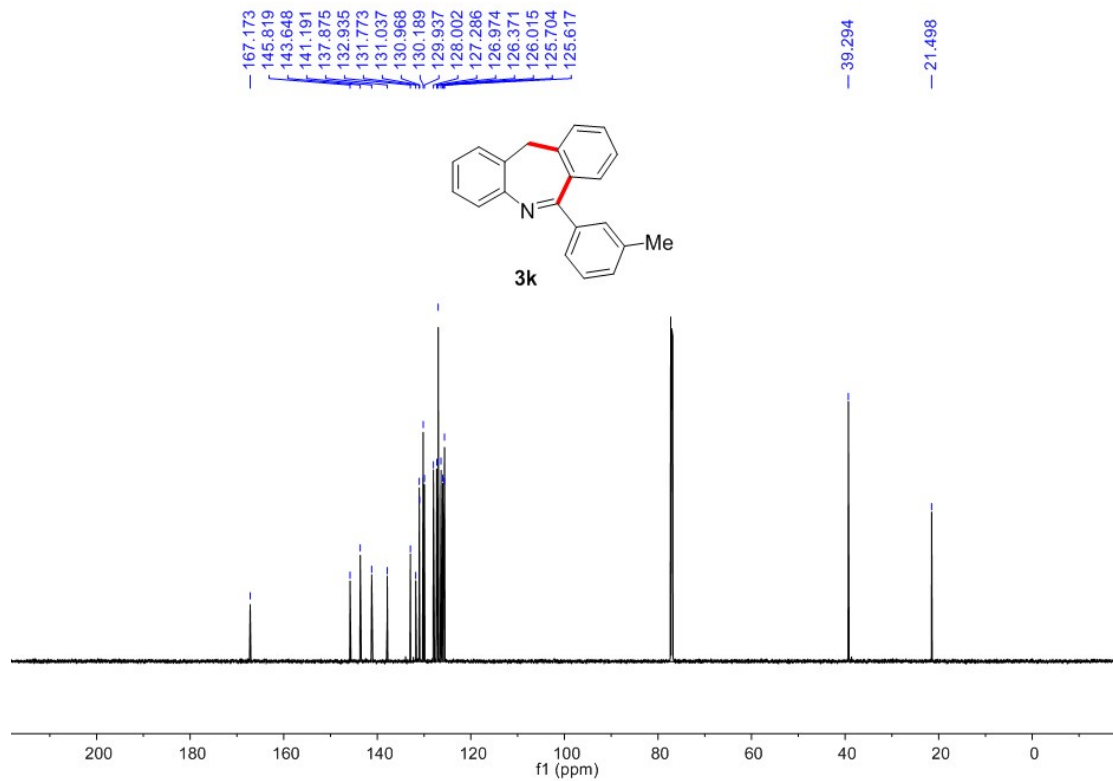
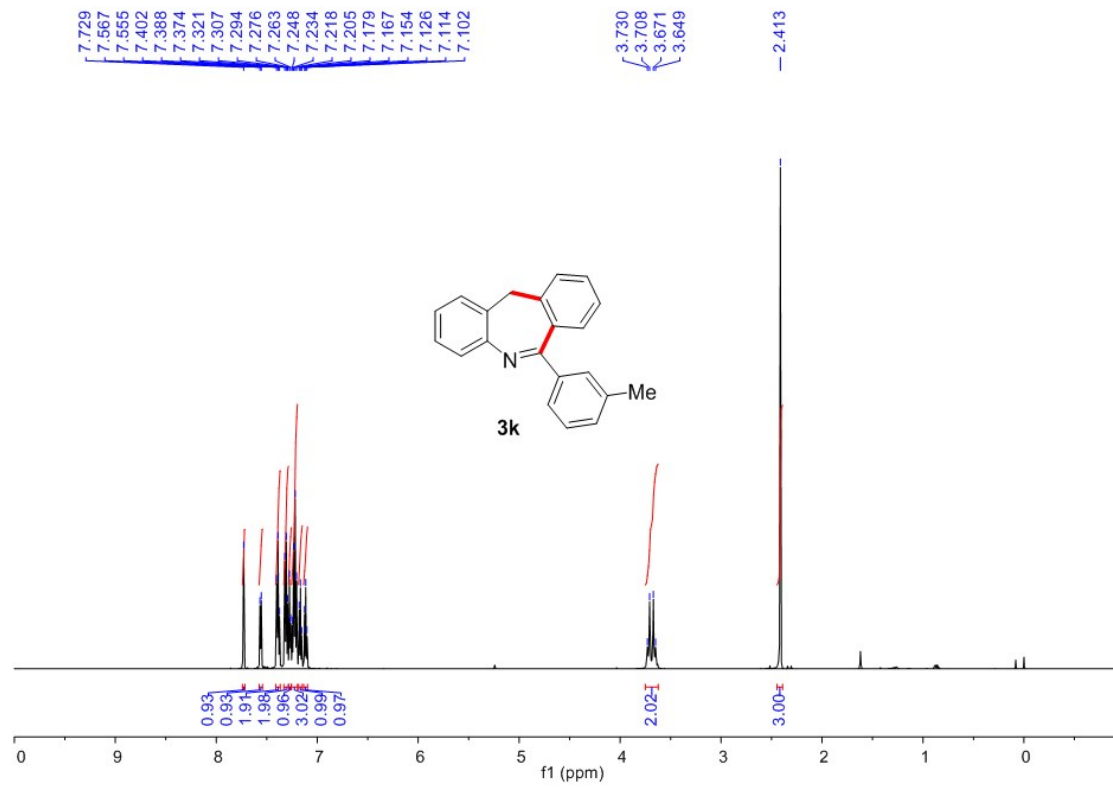


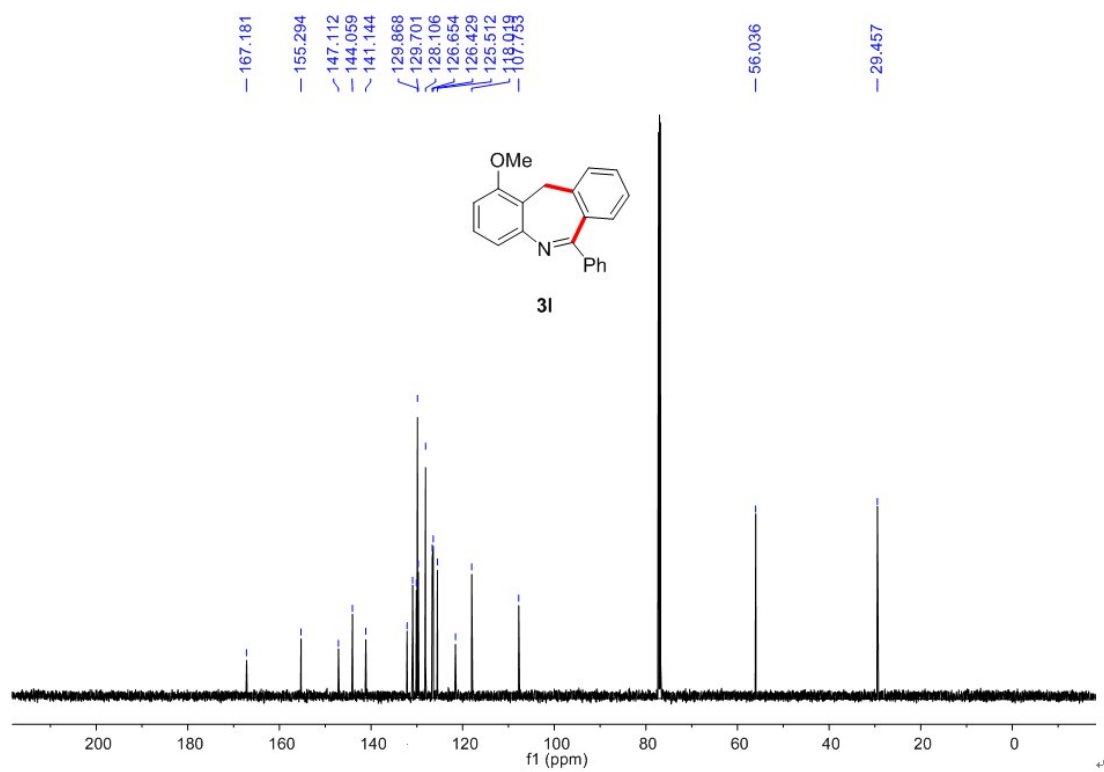
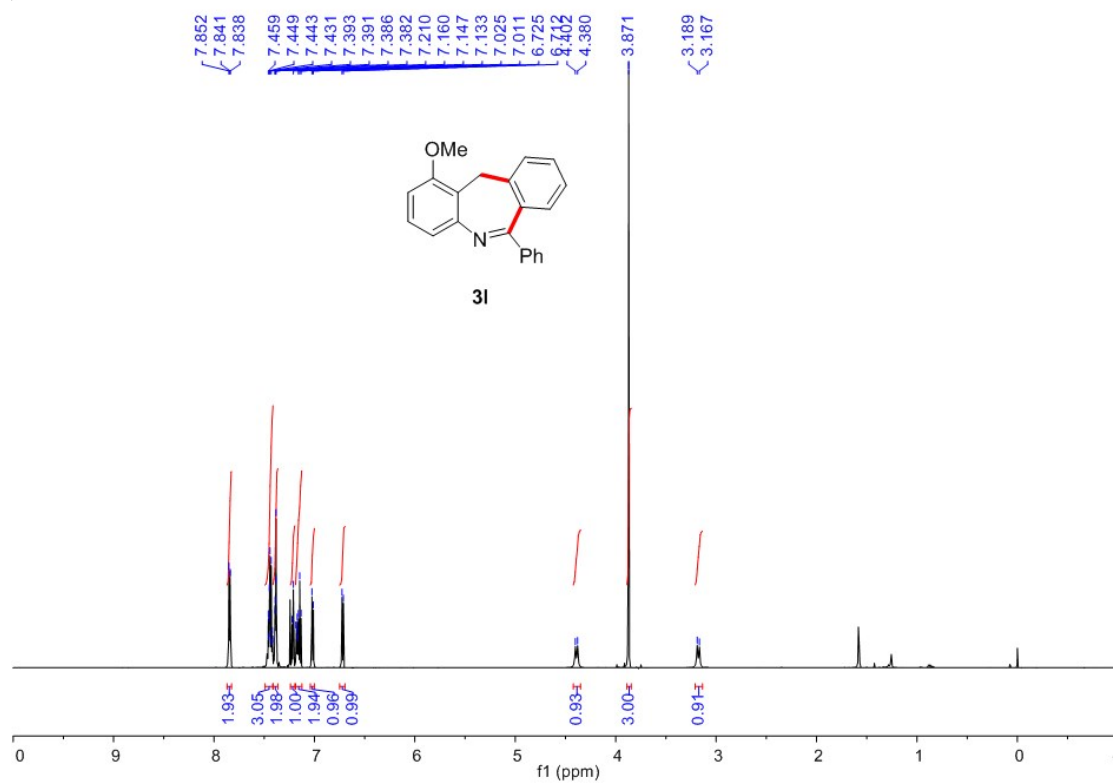


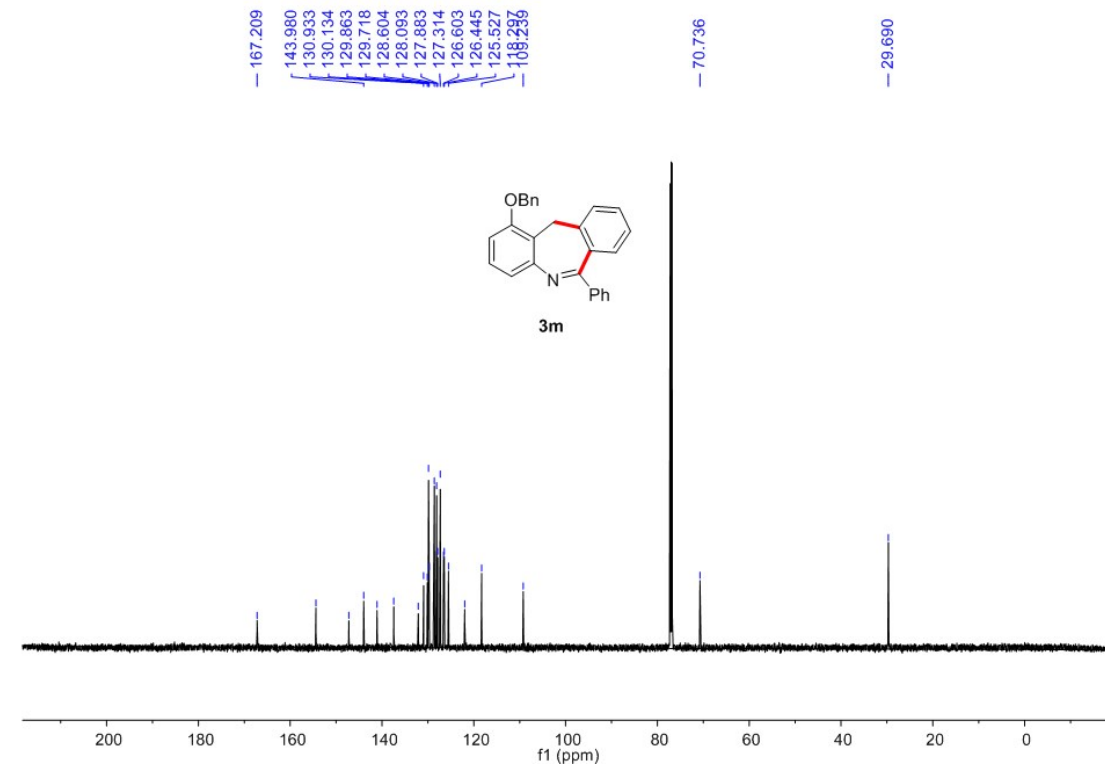
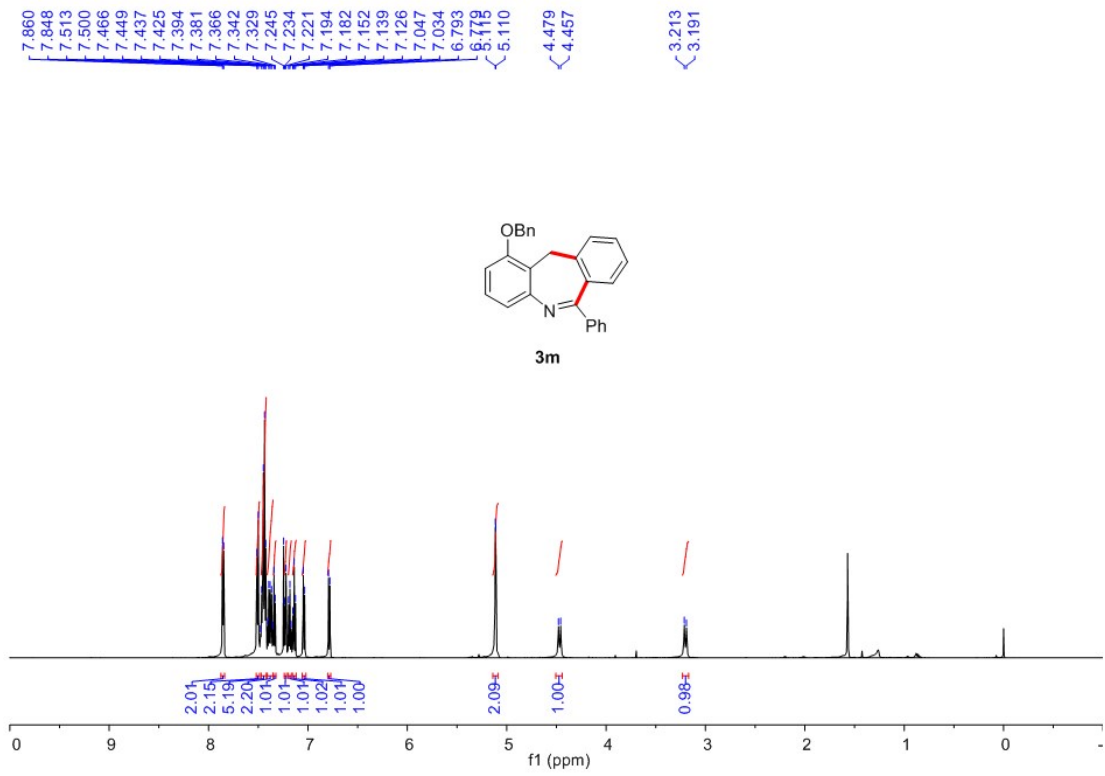


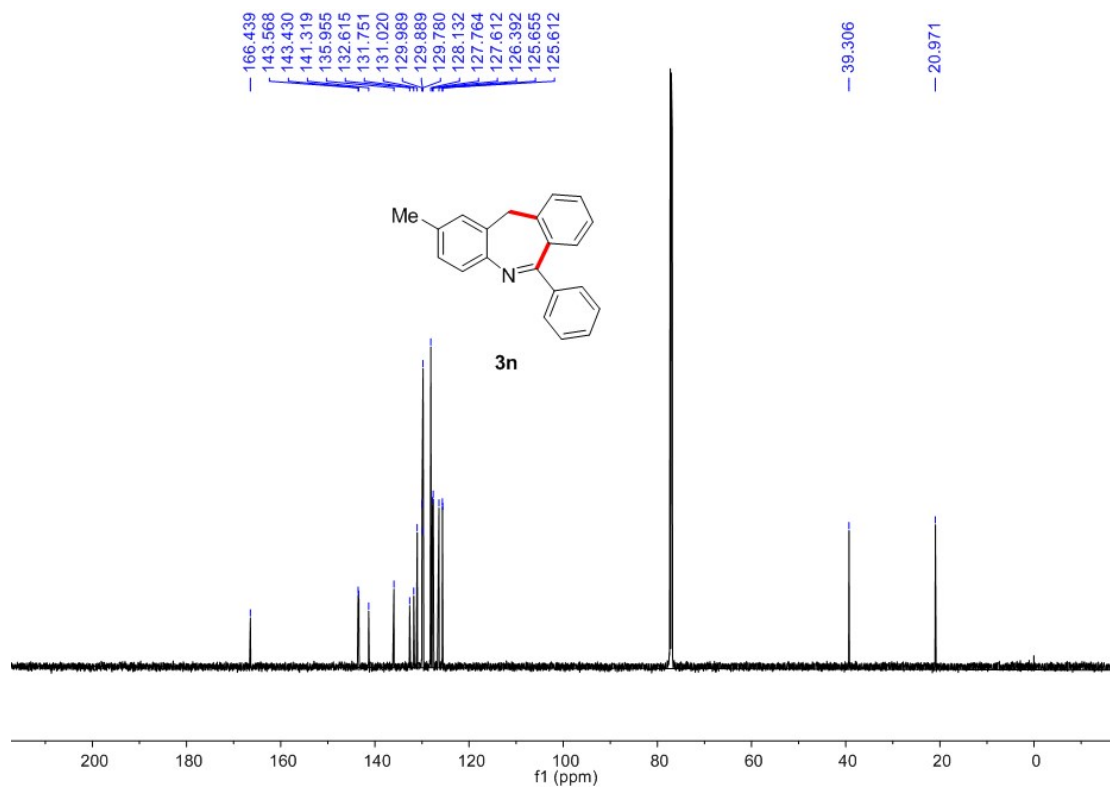
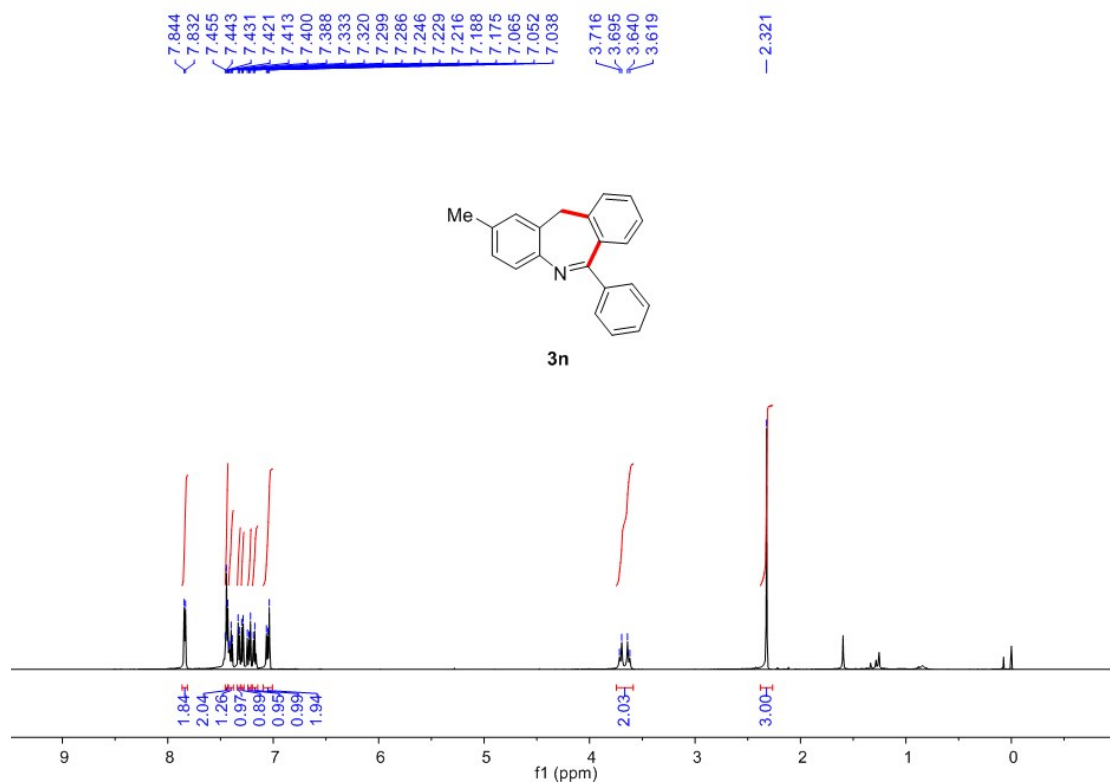






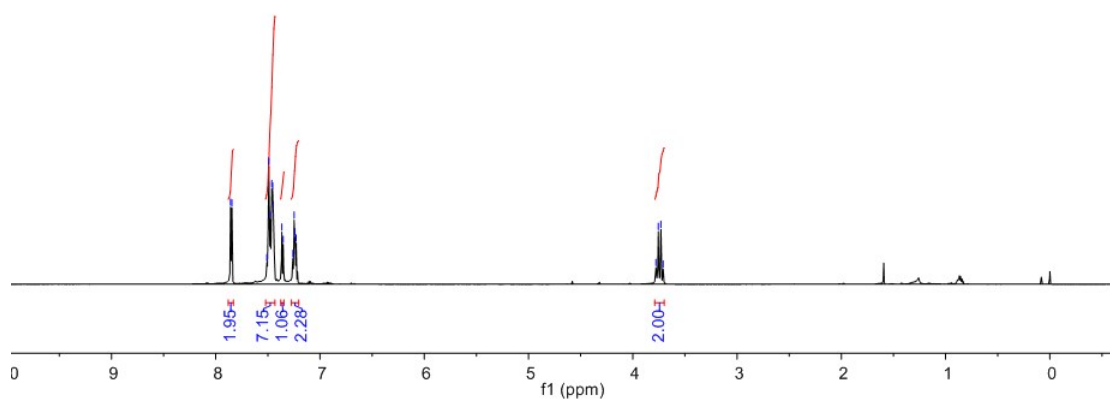
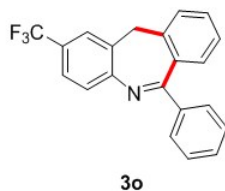






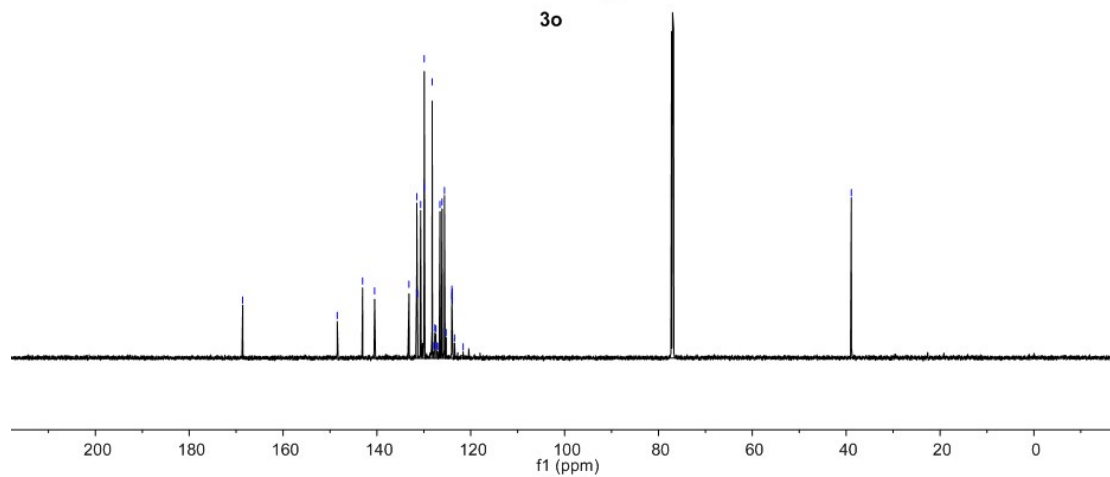
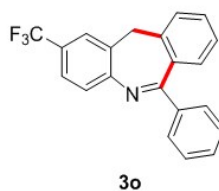
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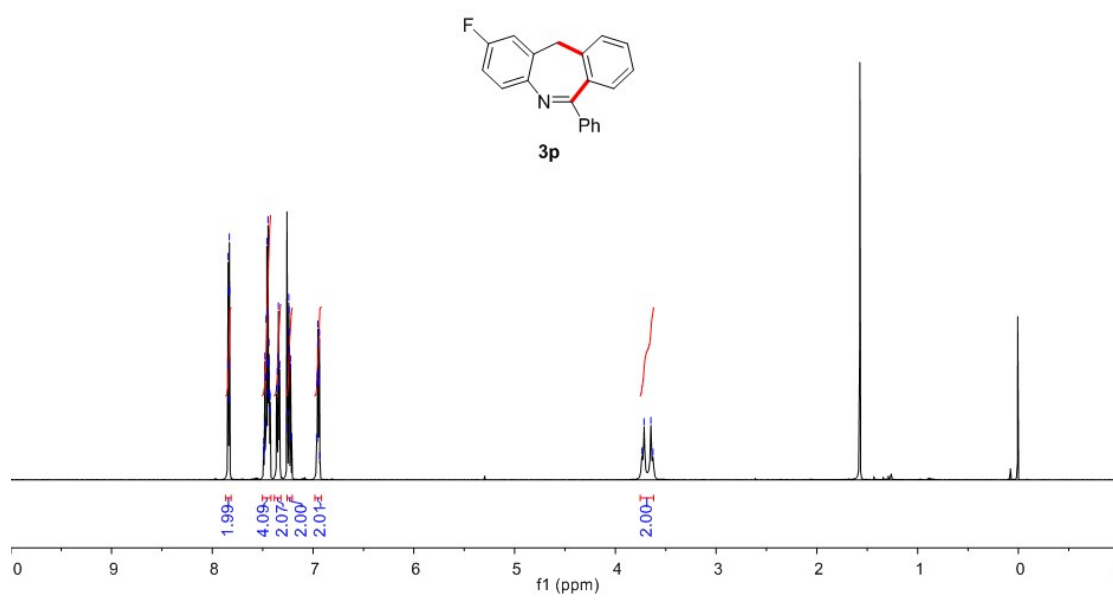
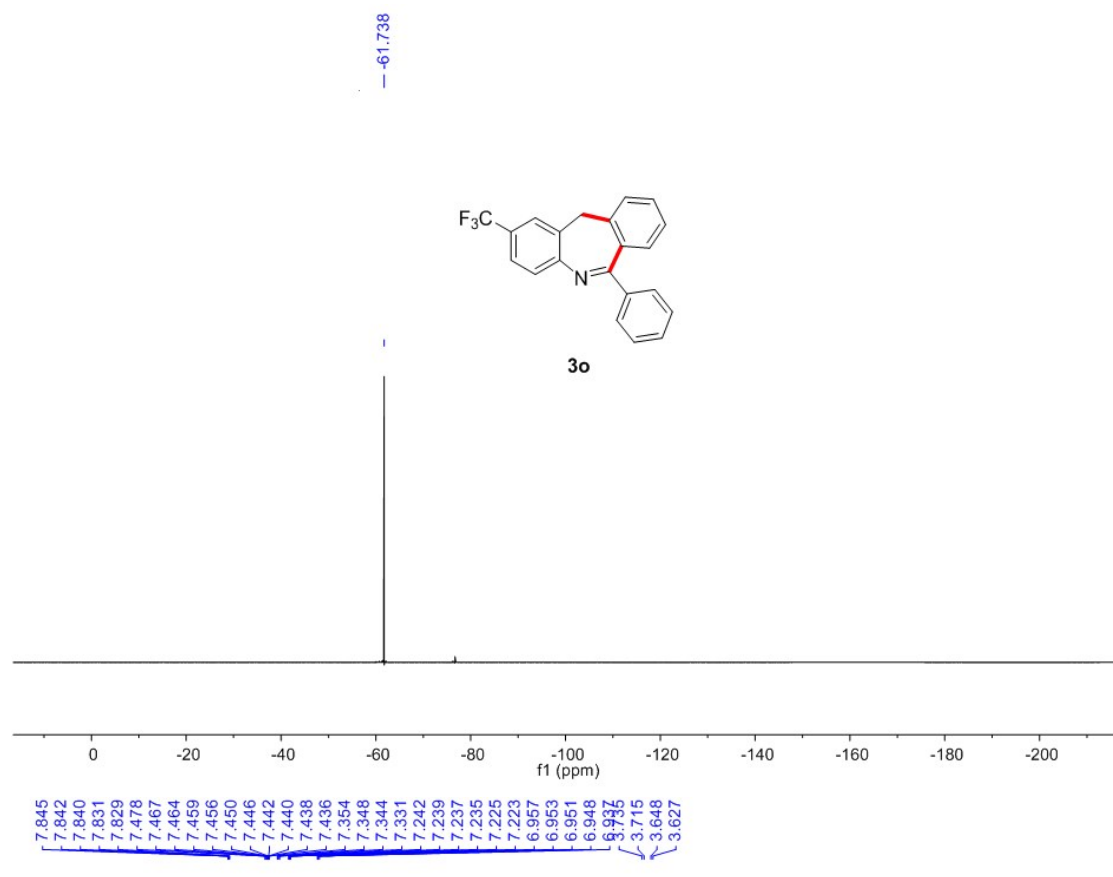
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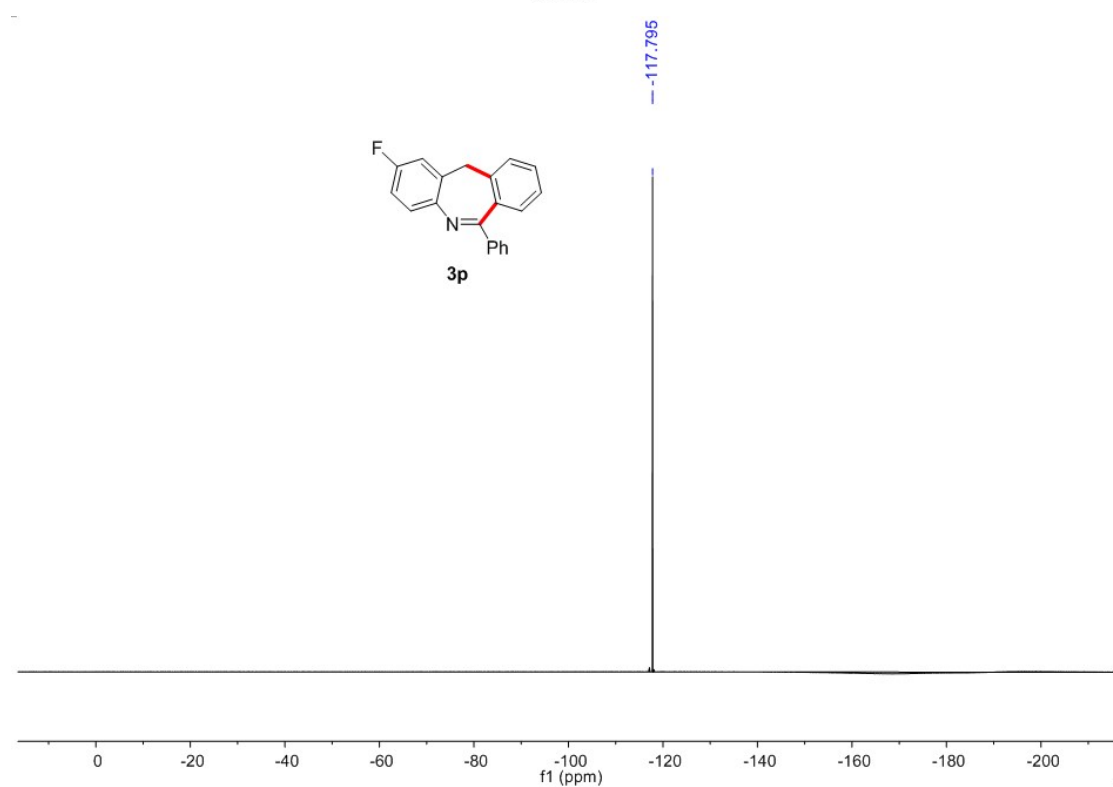
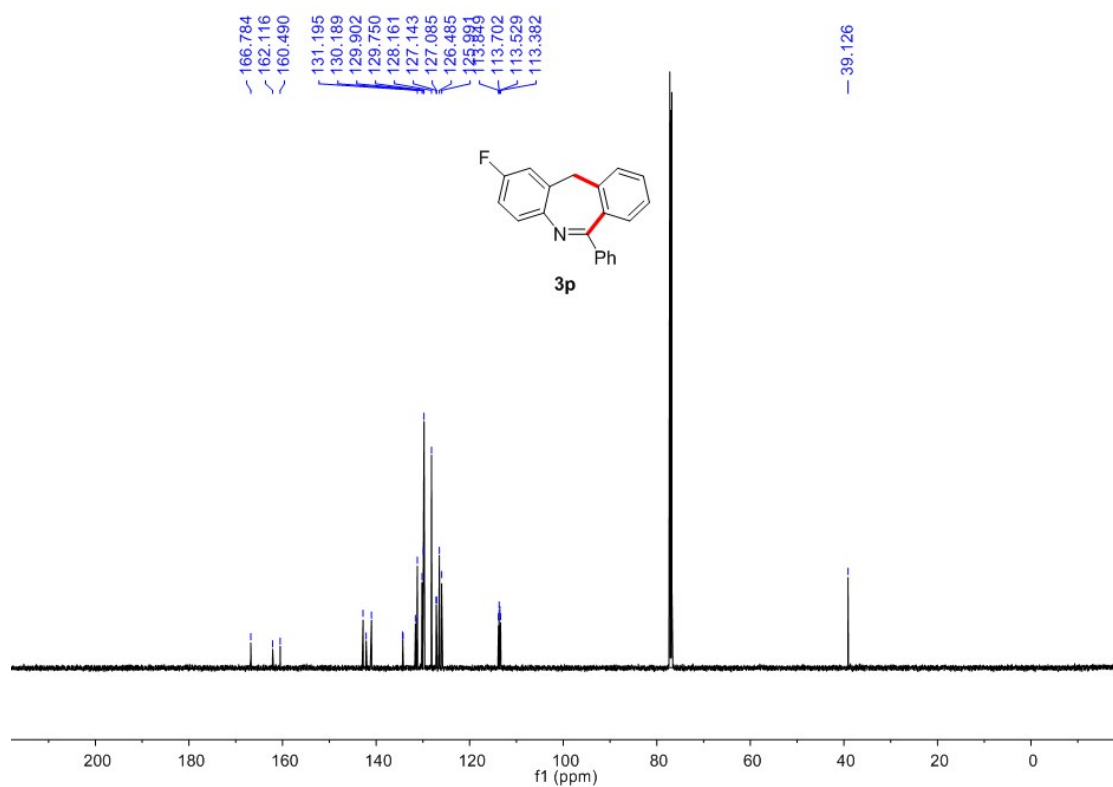


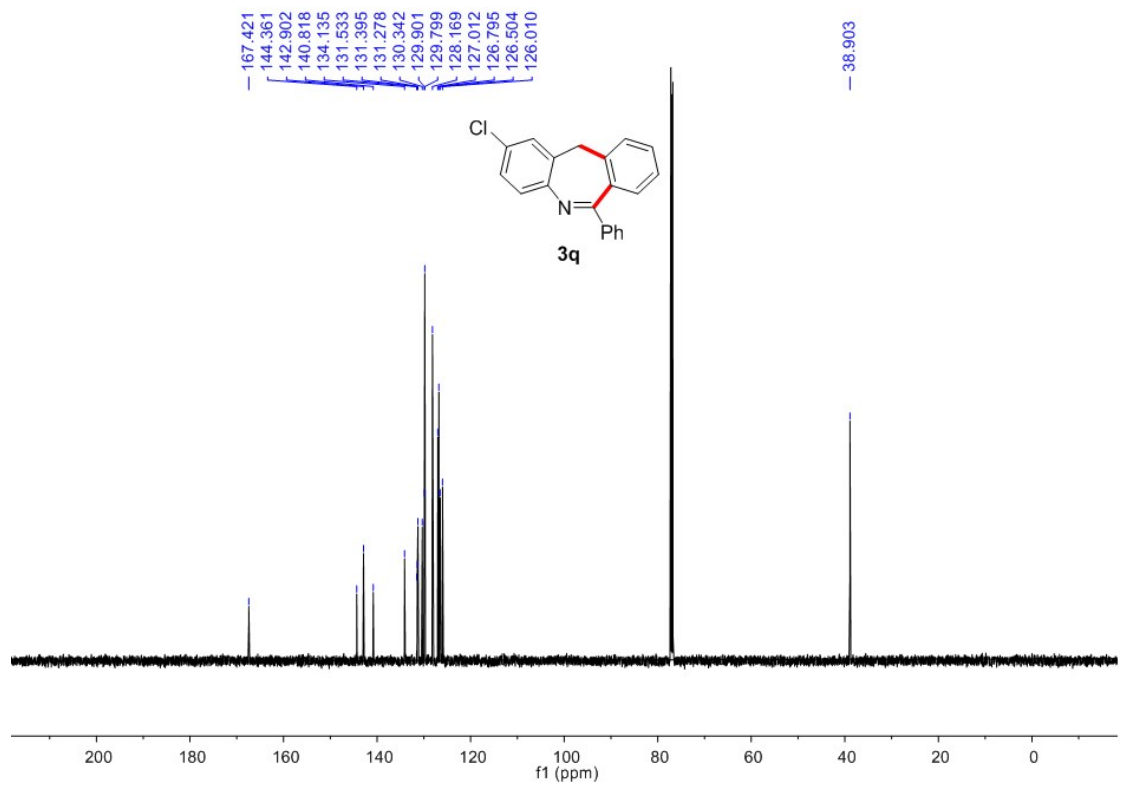
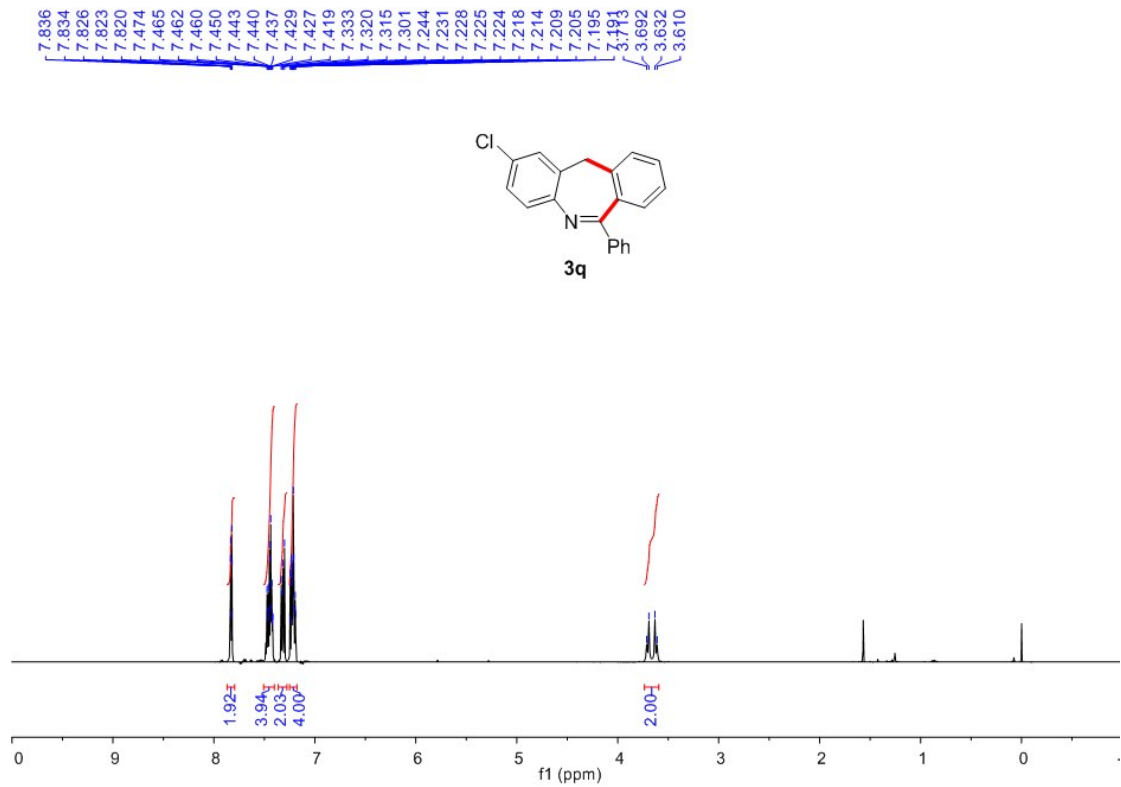
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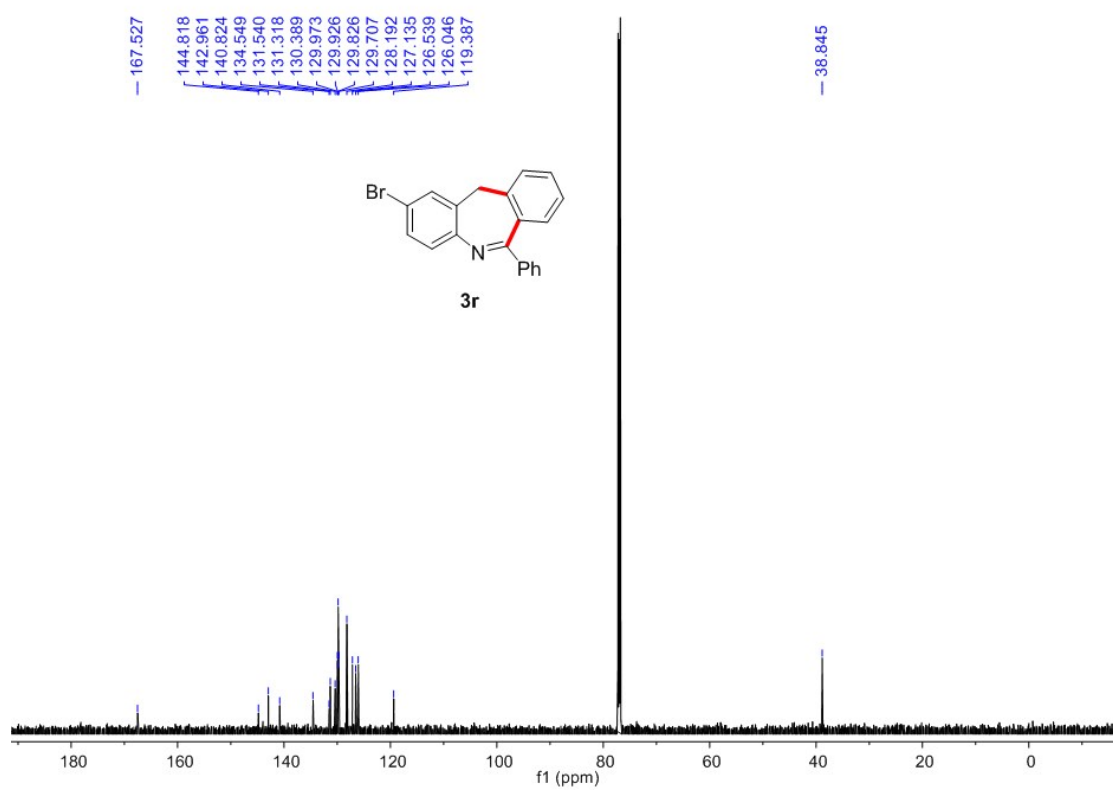
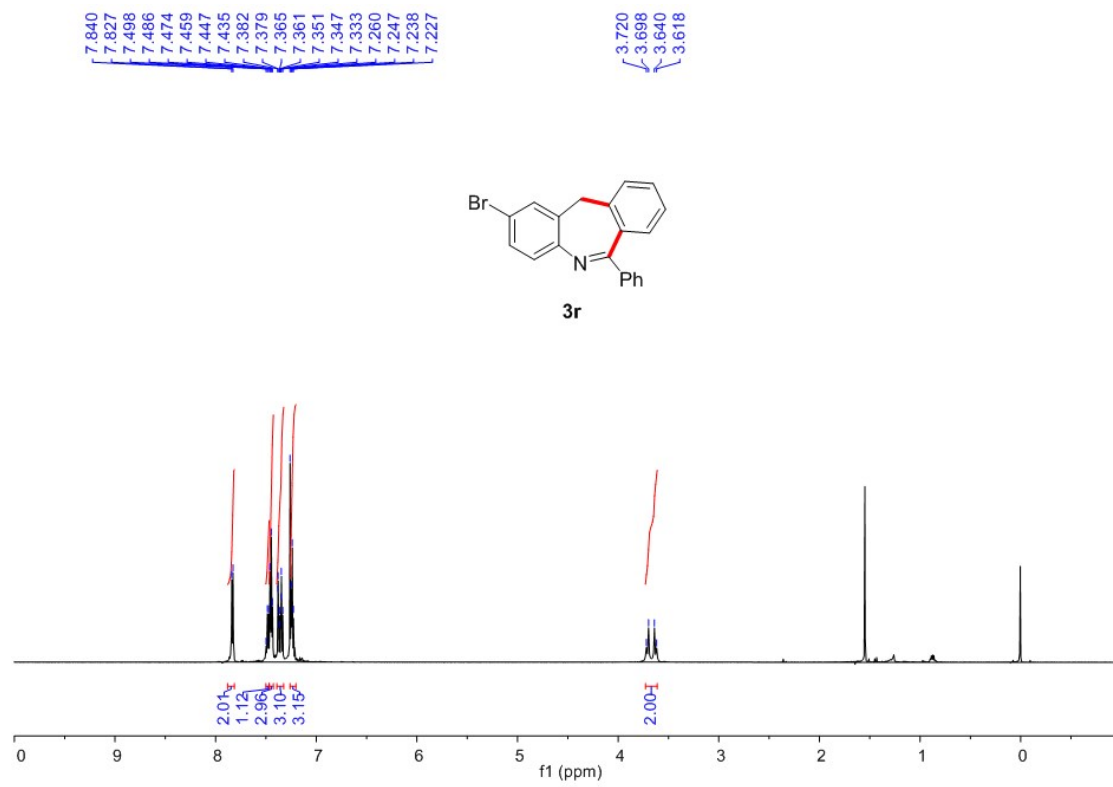
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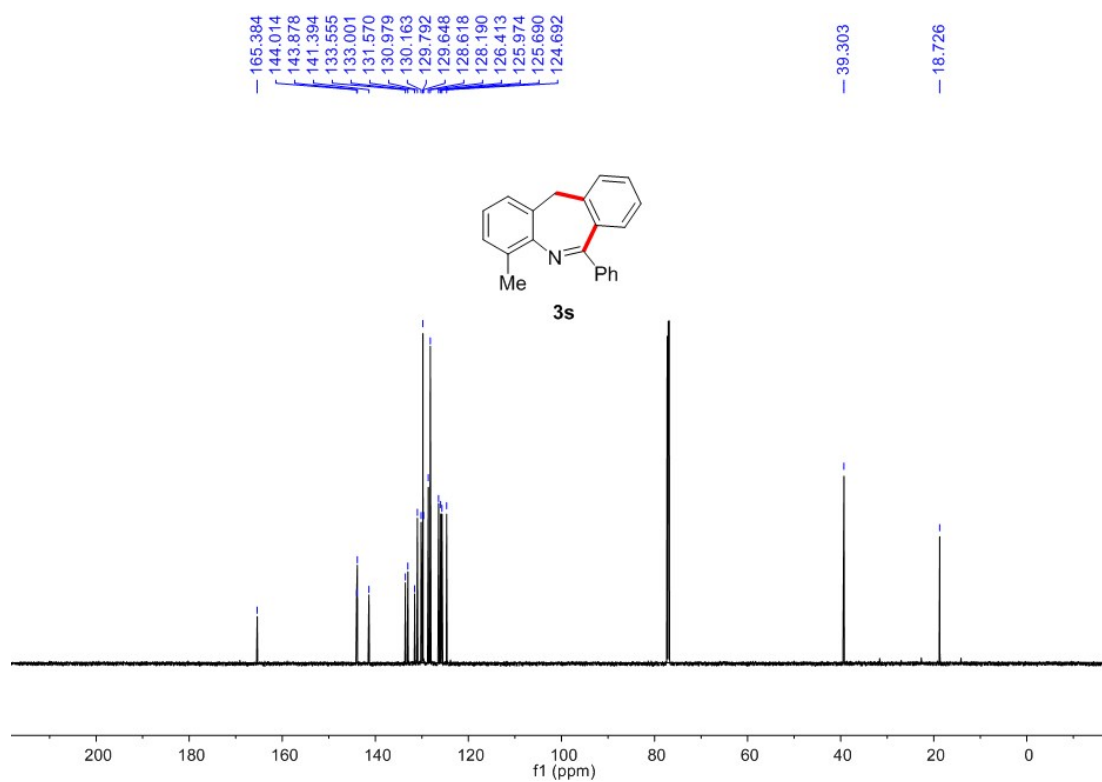
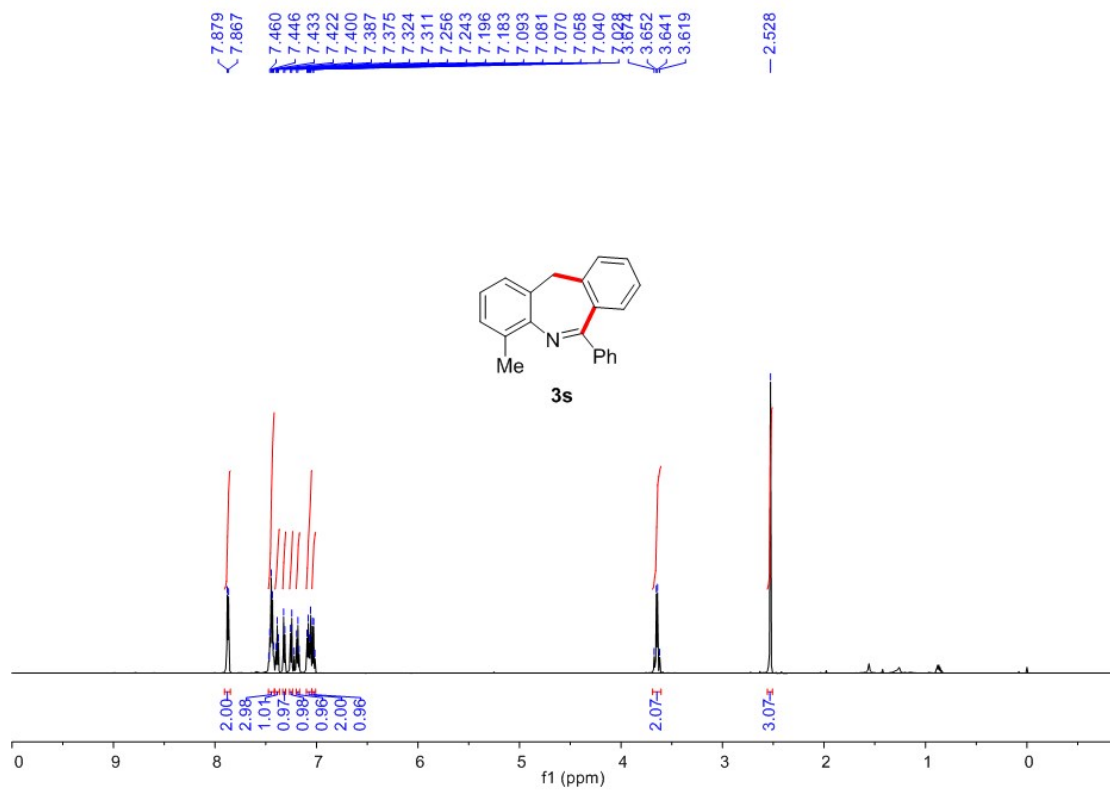


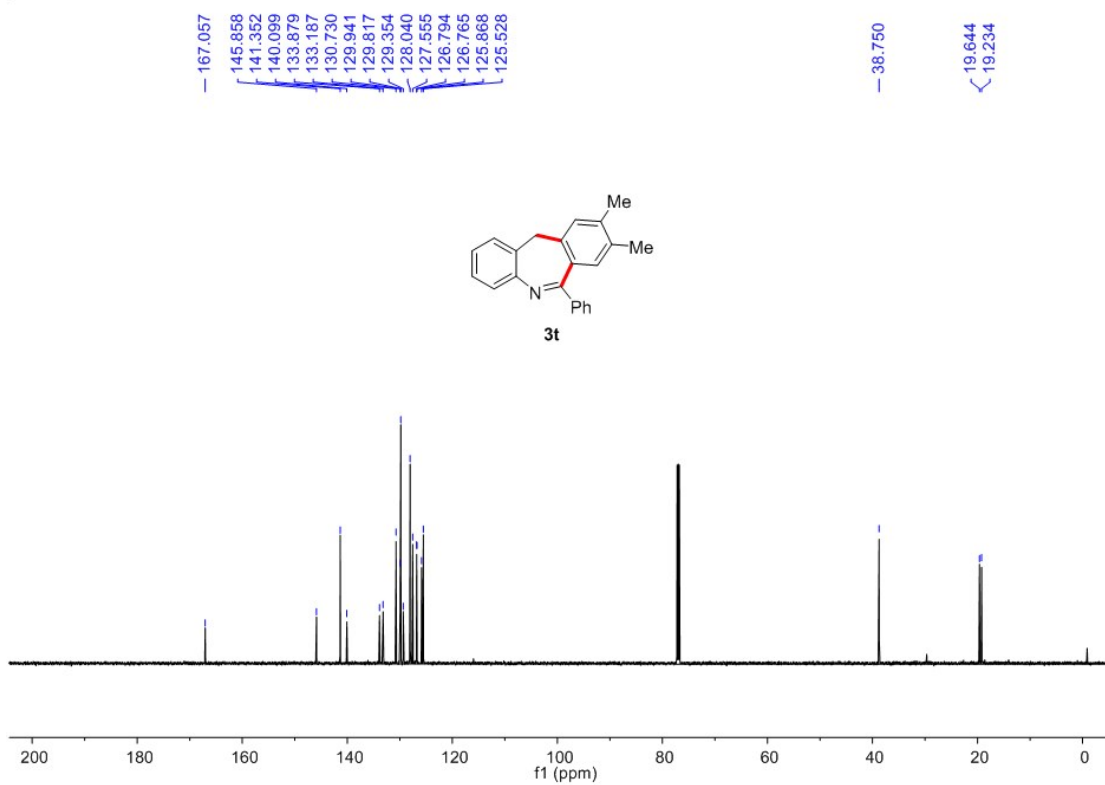
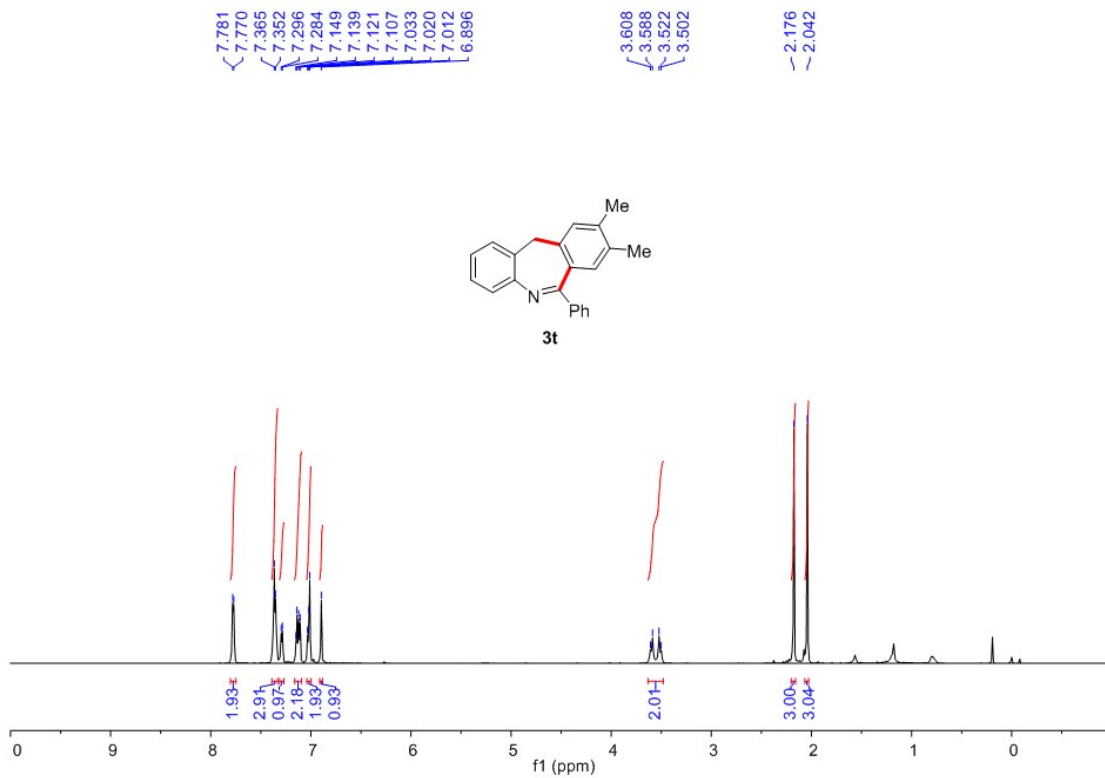


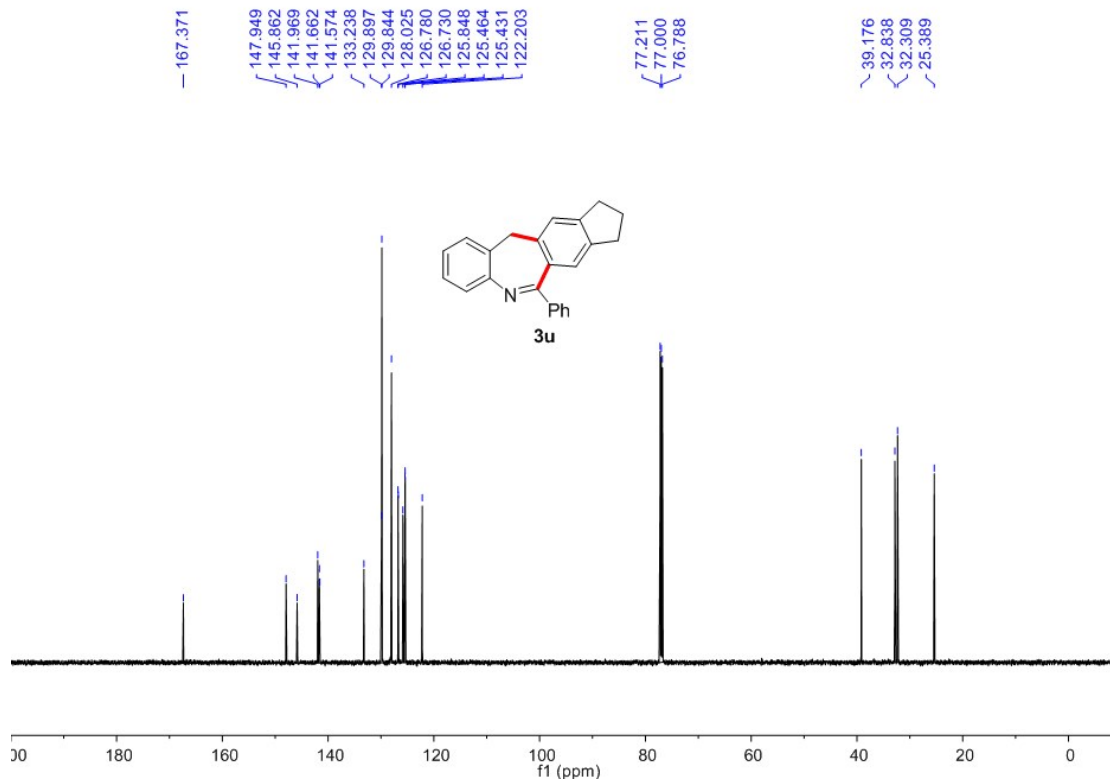
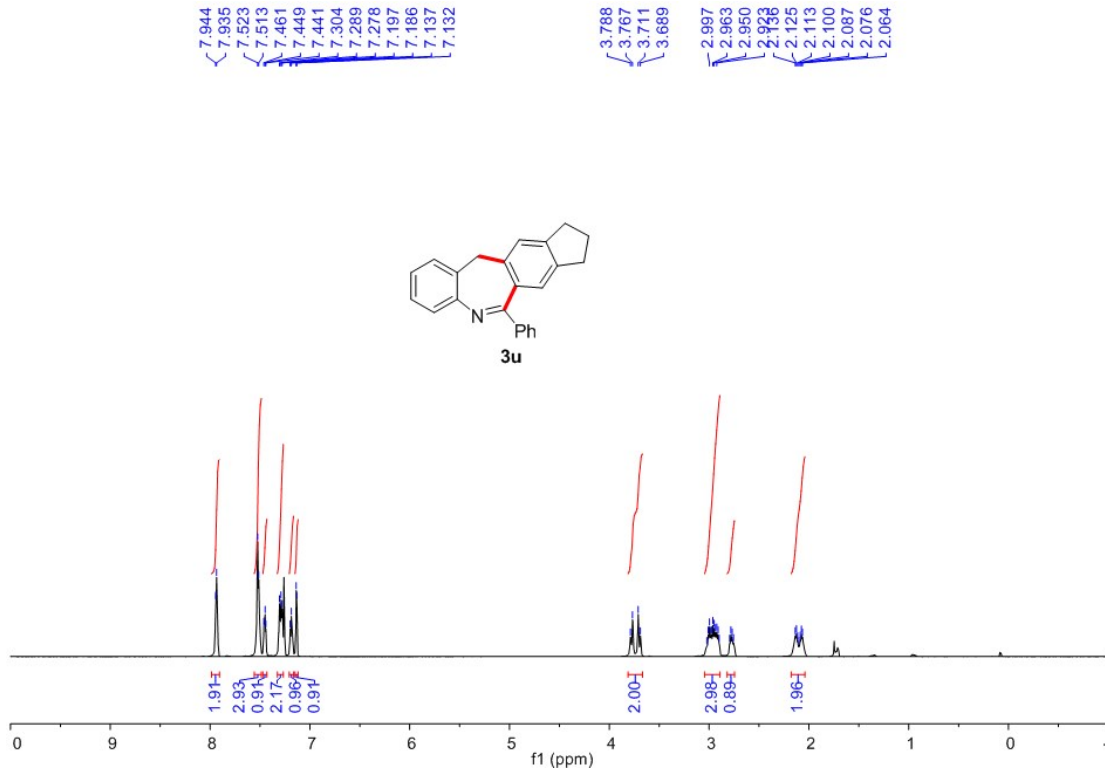


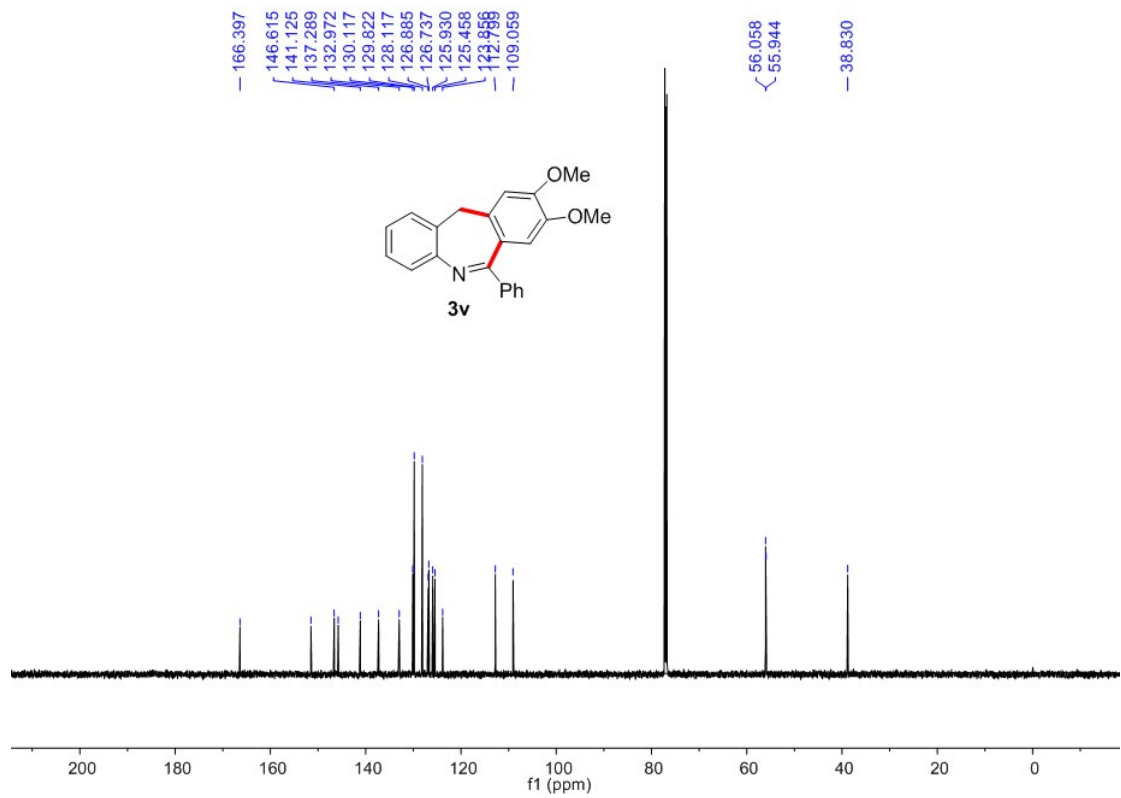
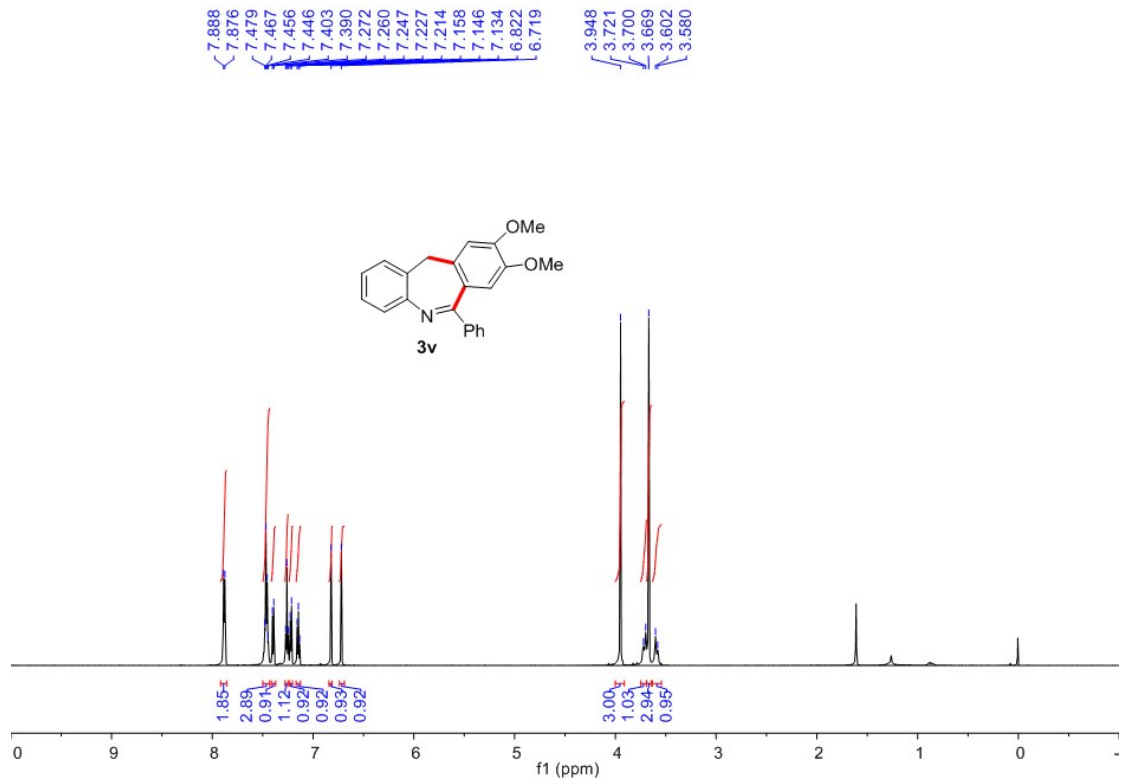


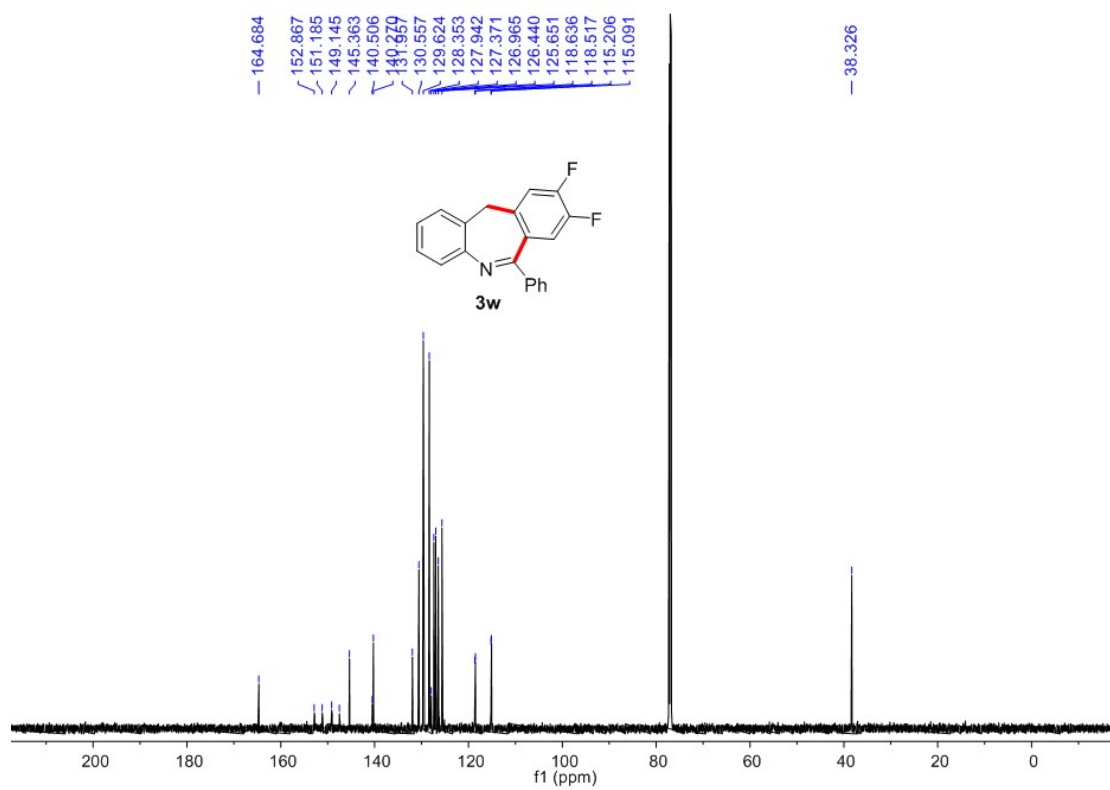
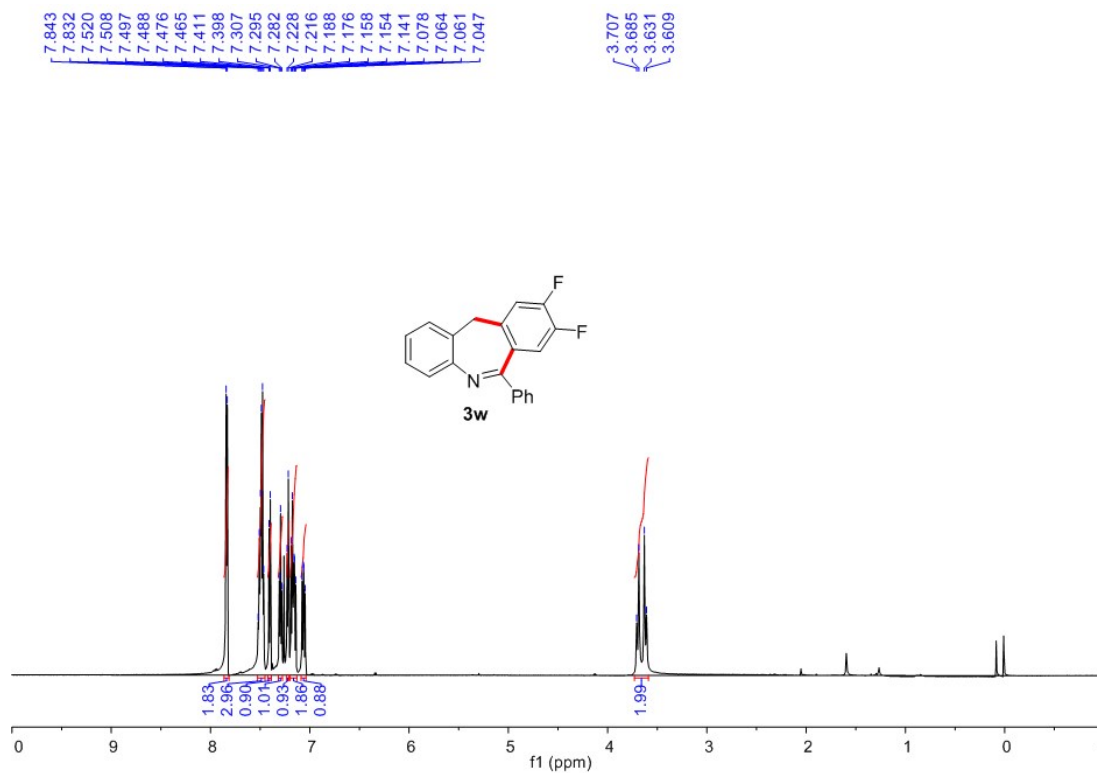


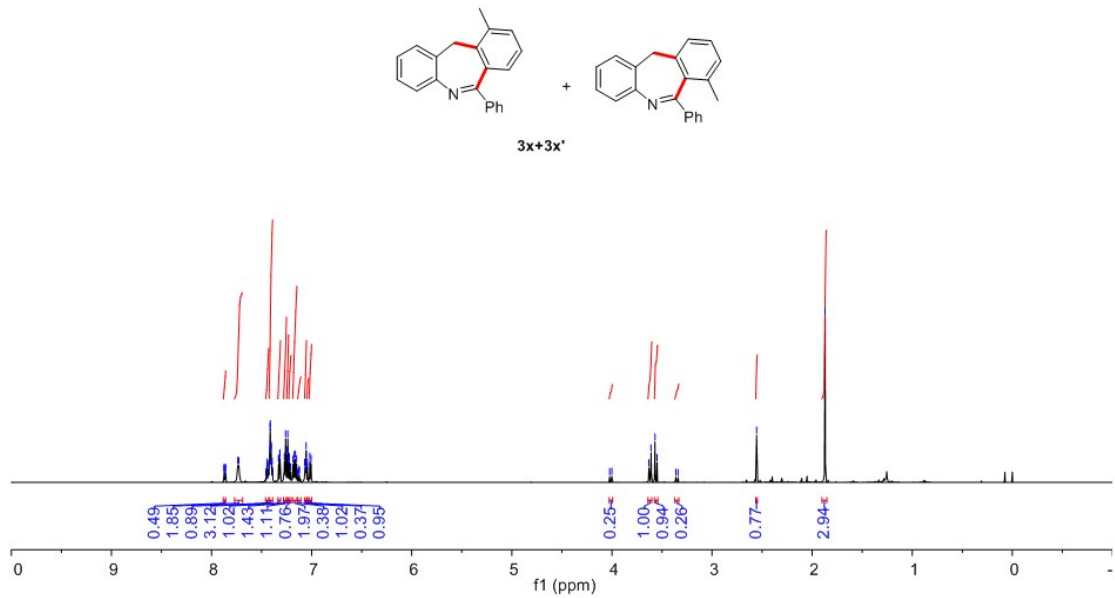
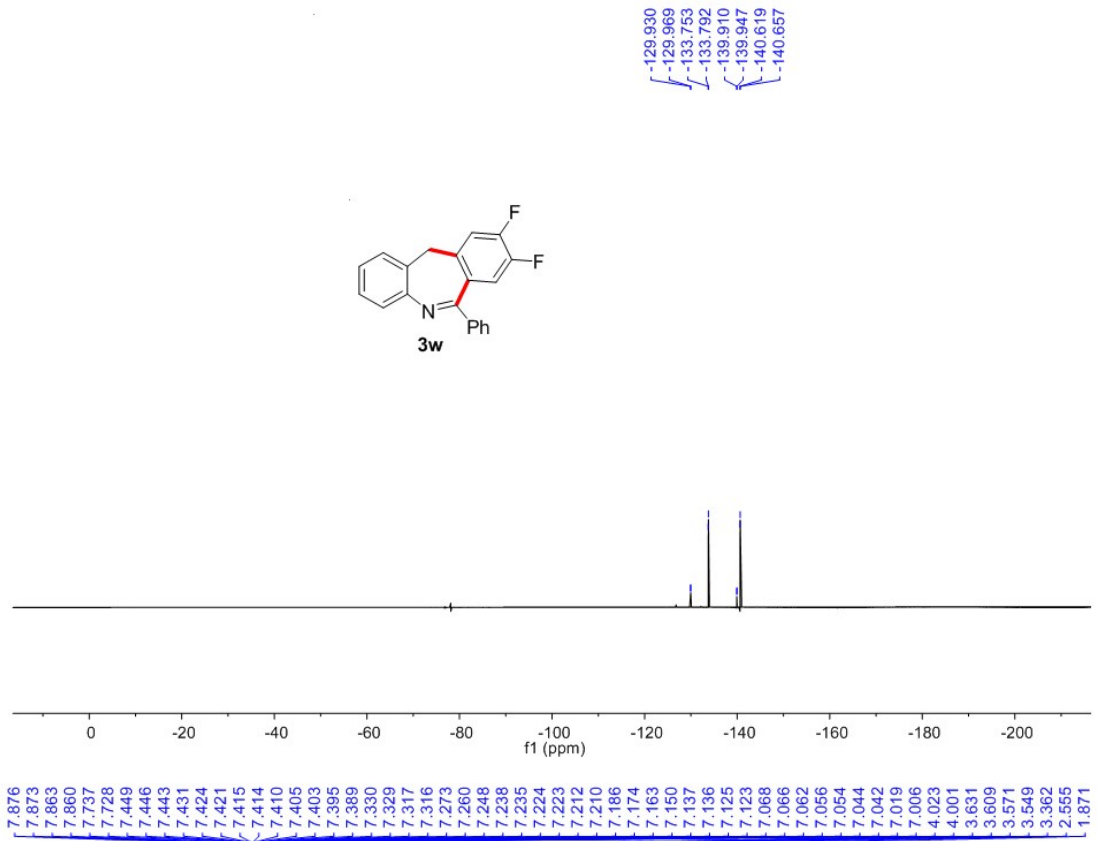


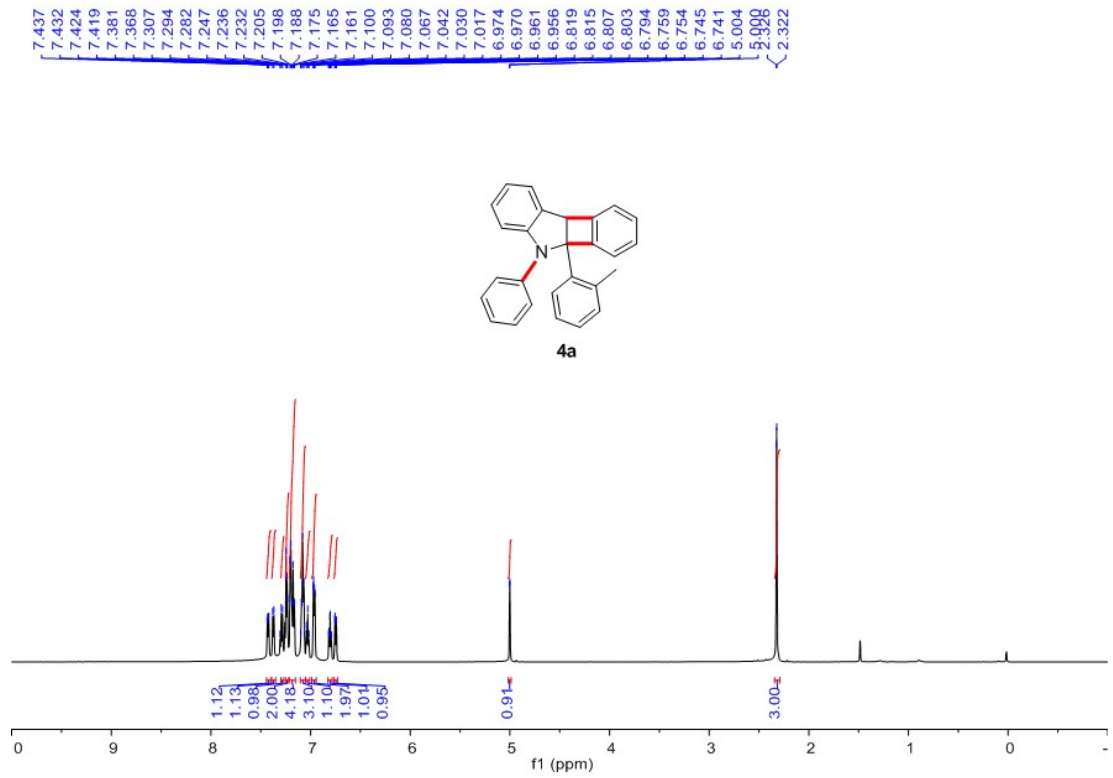
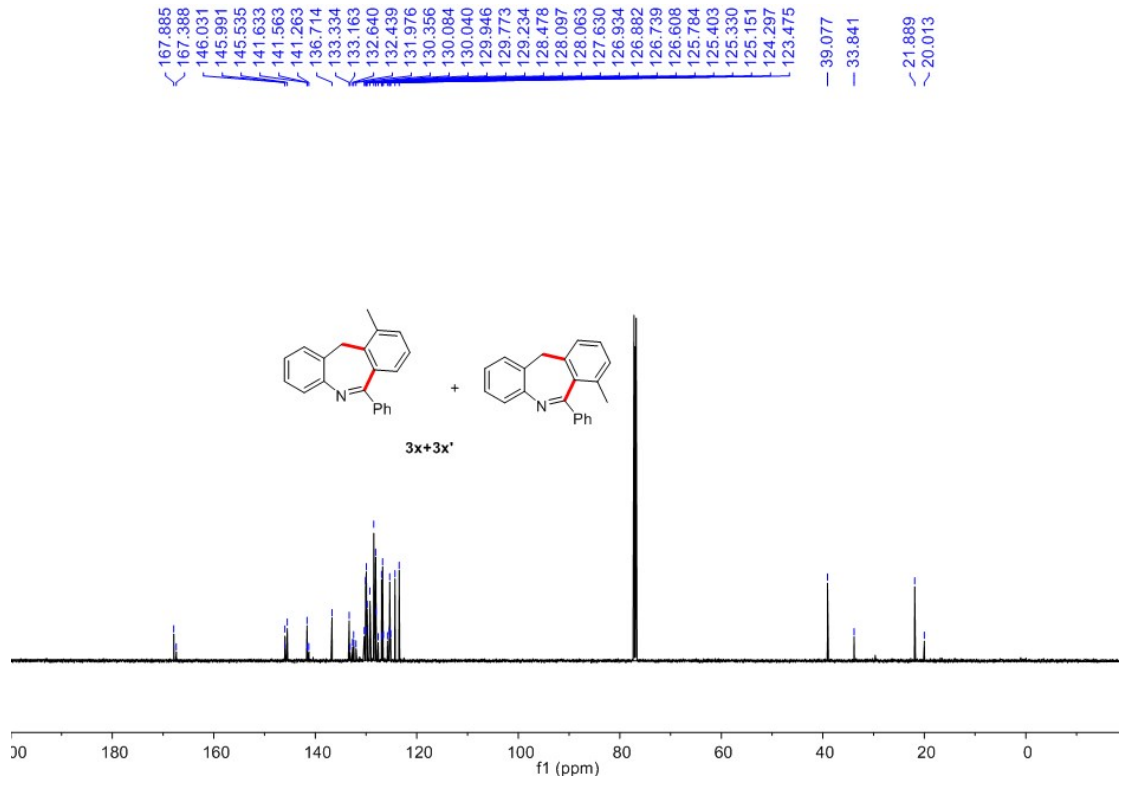


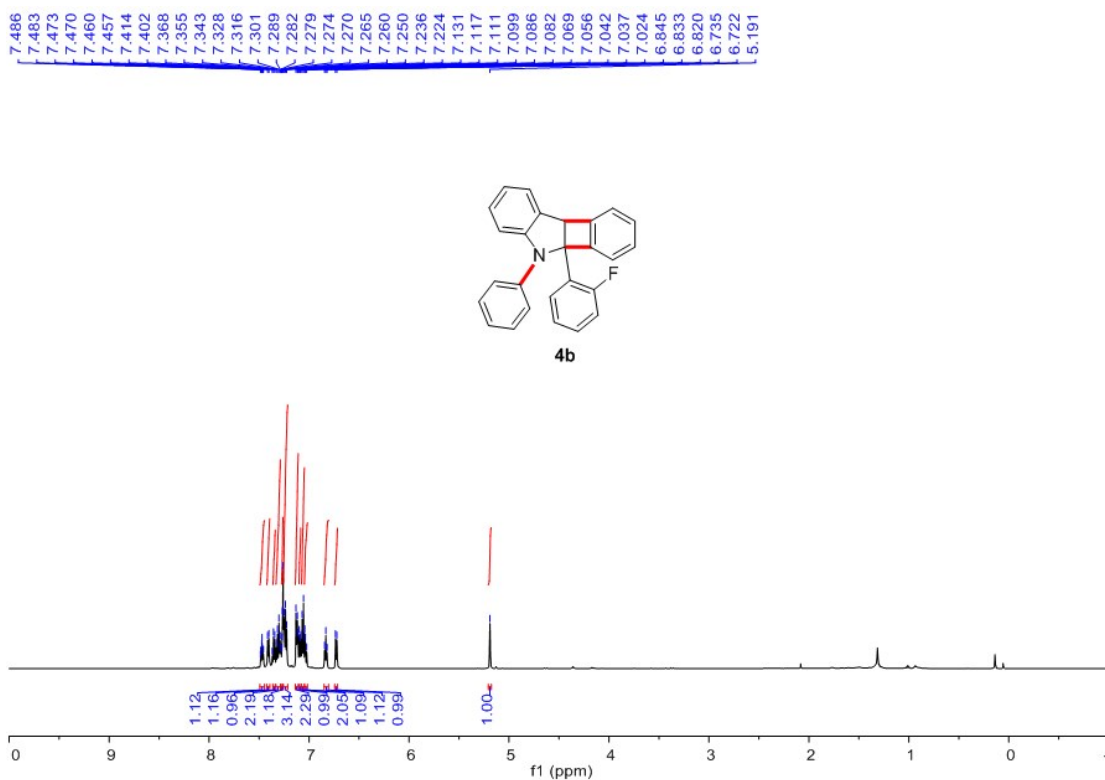
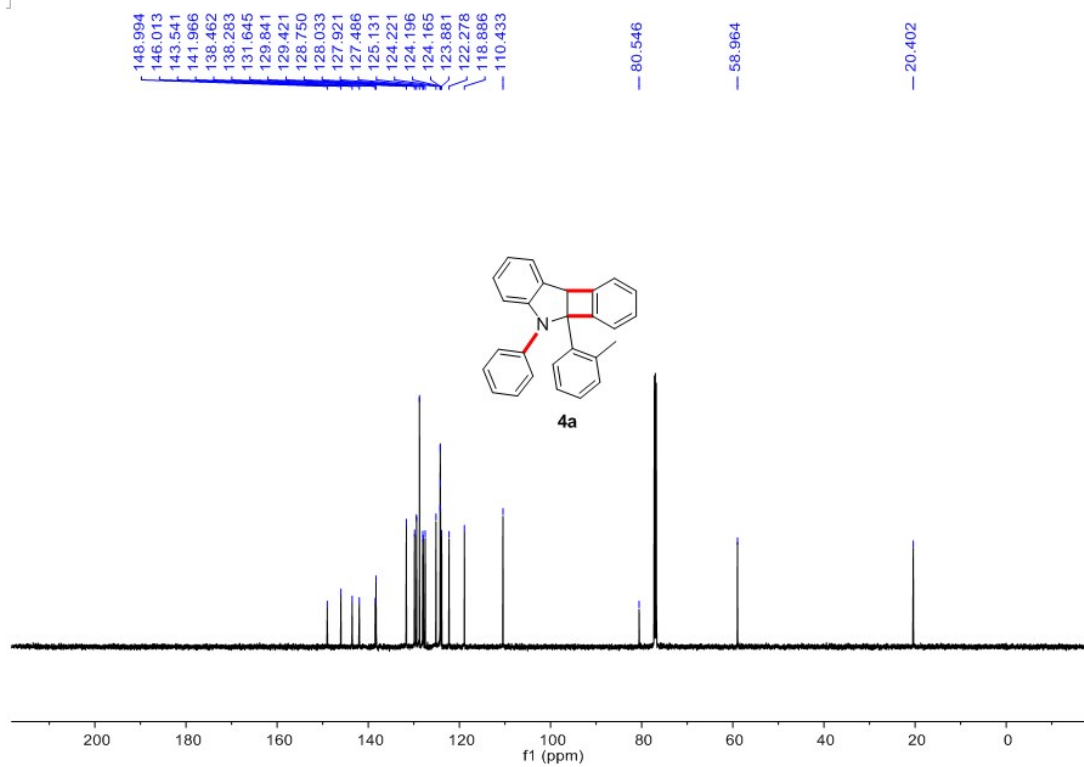




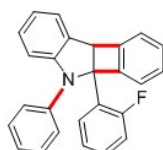




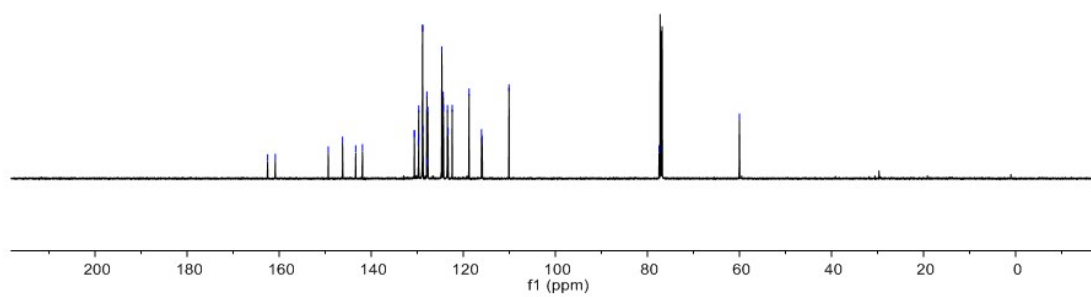




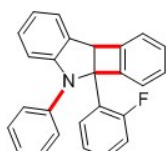
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127.902
127.833
127.702
124.657
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60.010



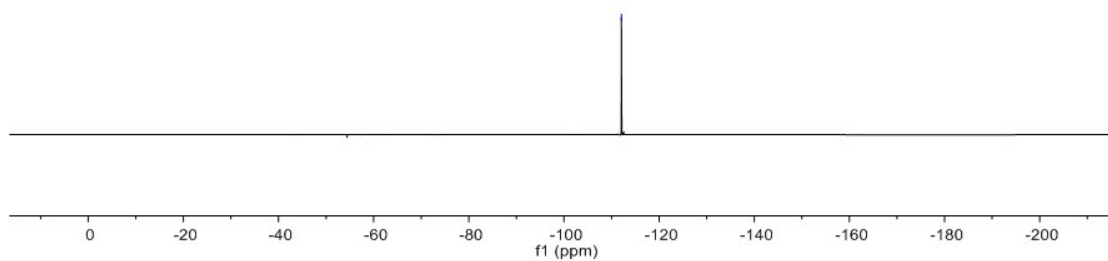
4b

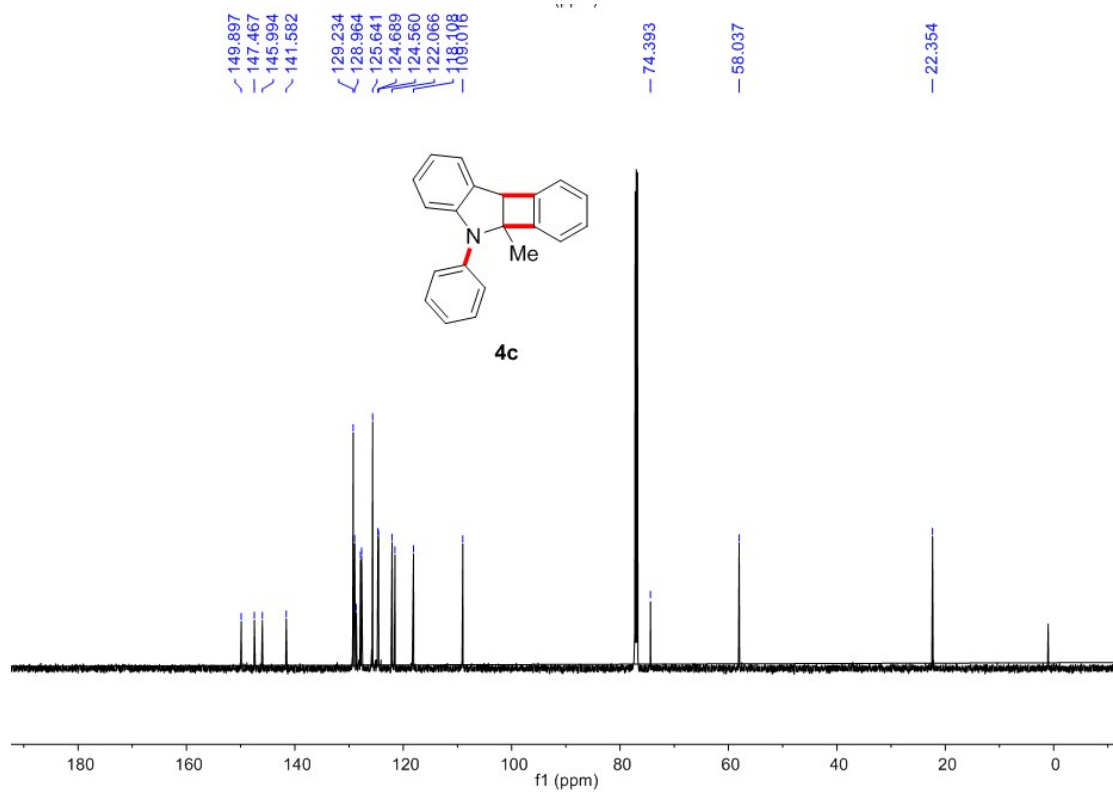
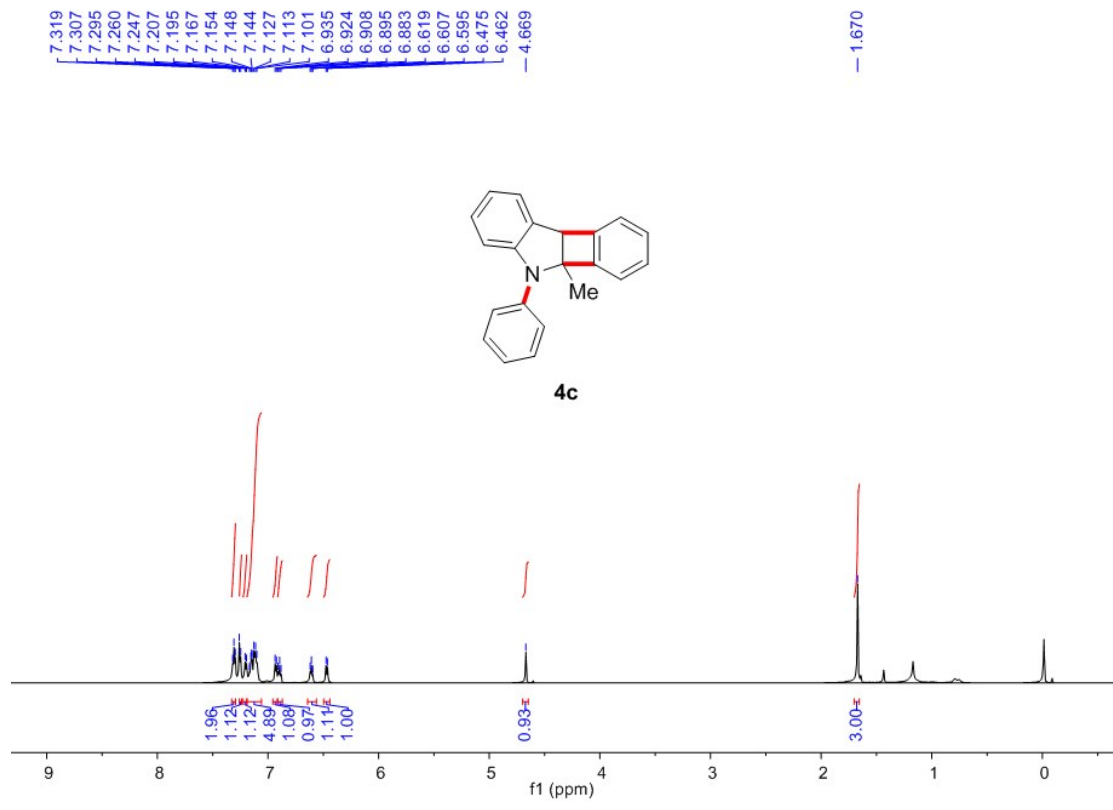


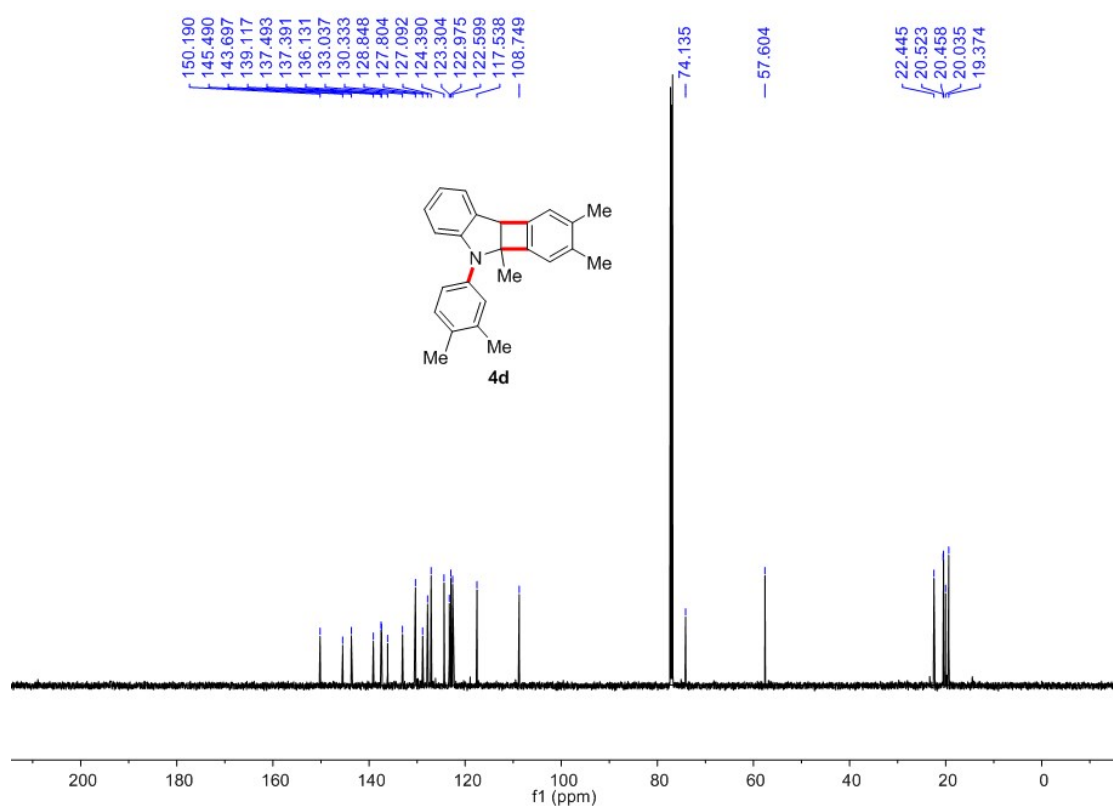
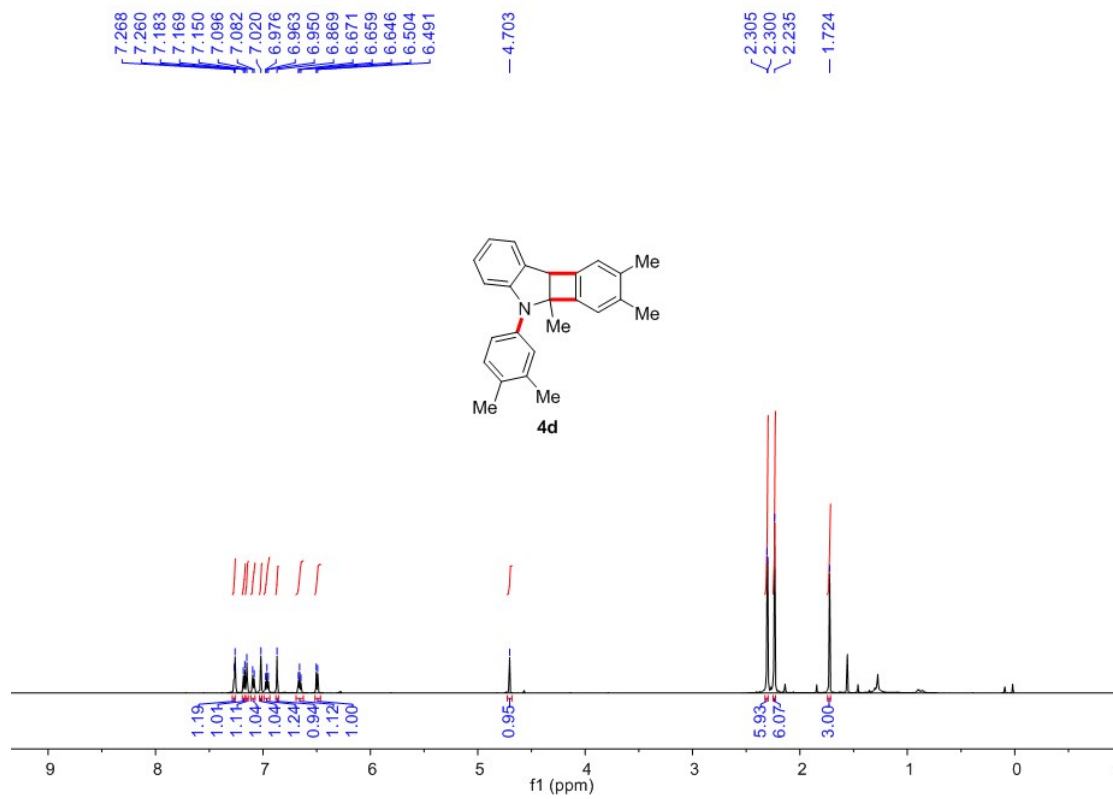
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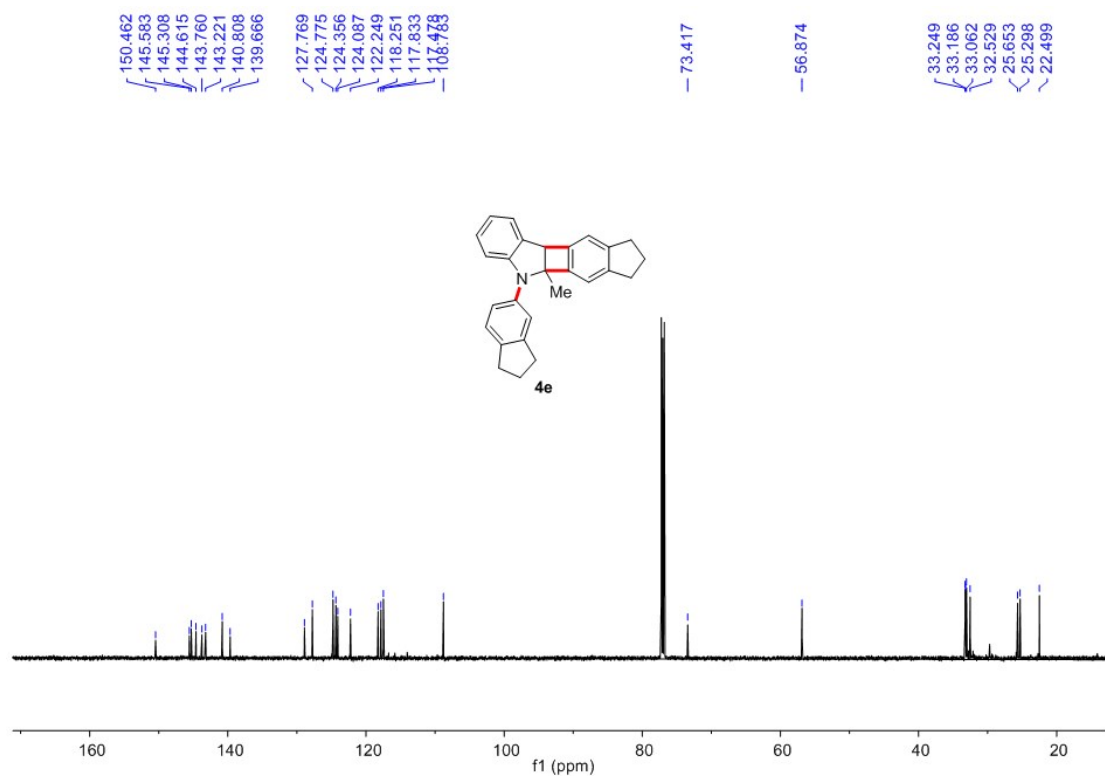
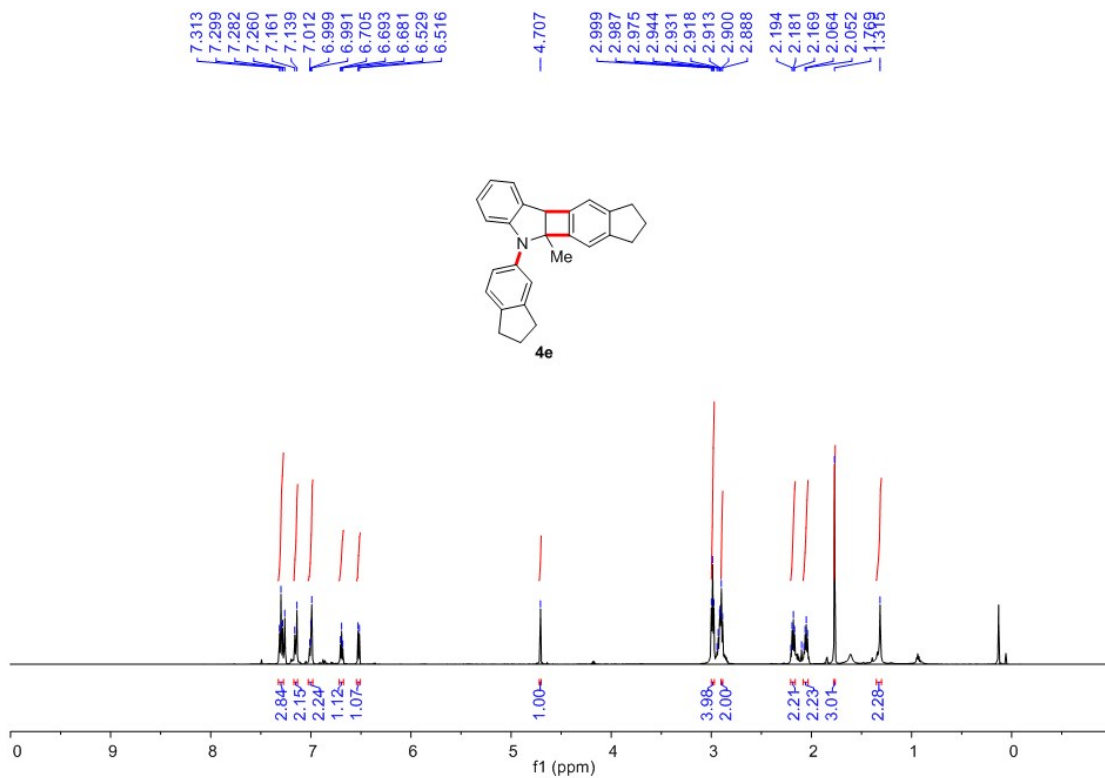


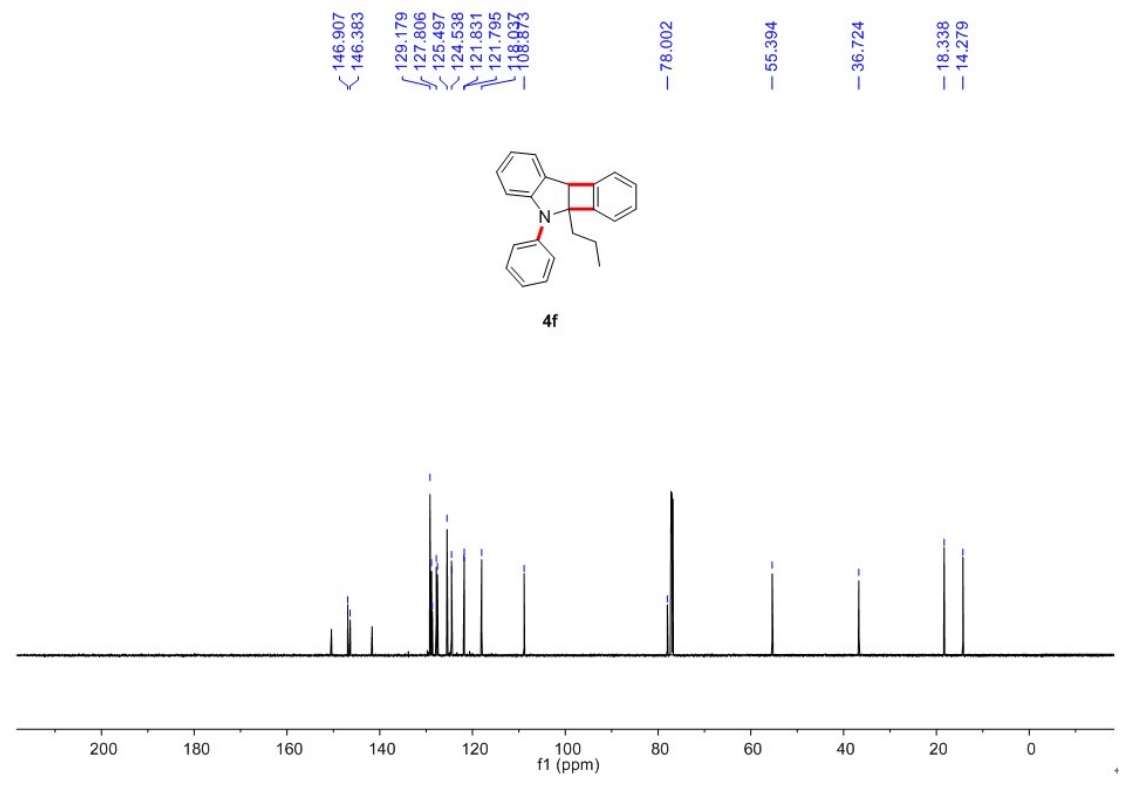
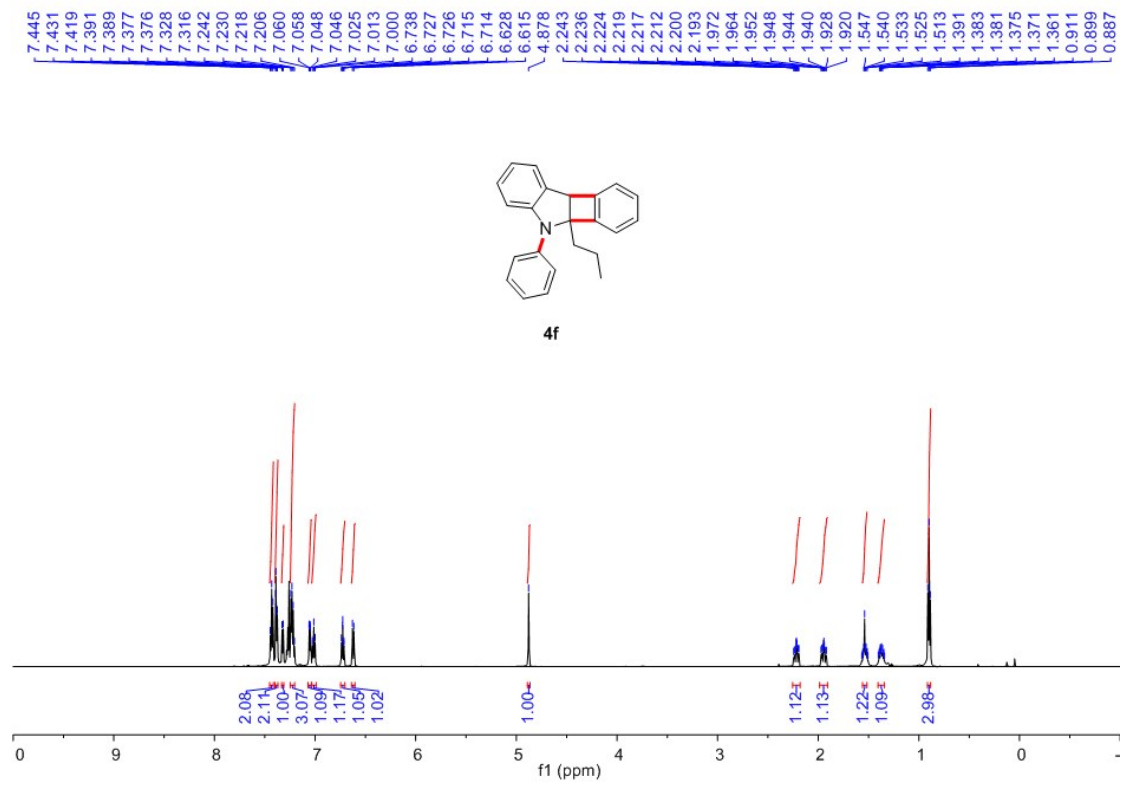
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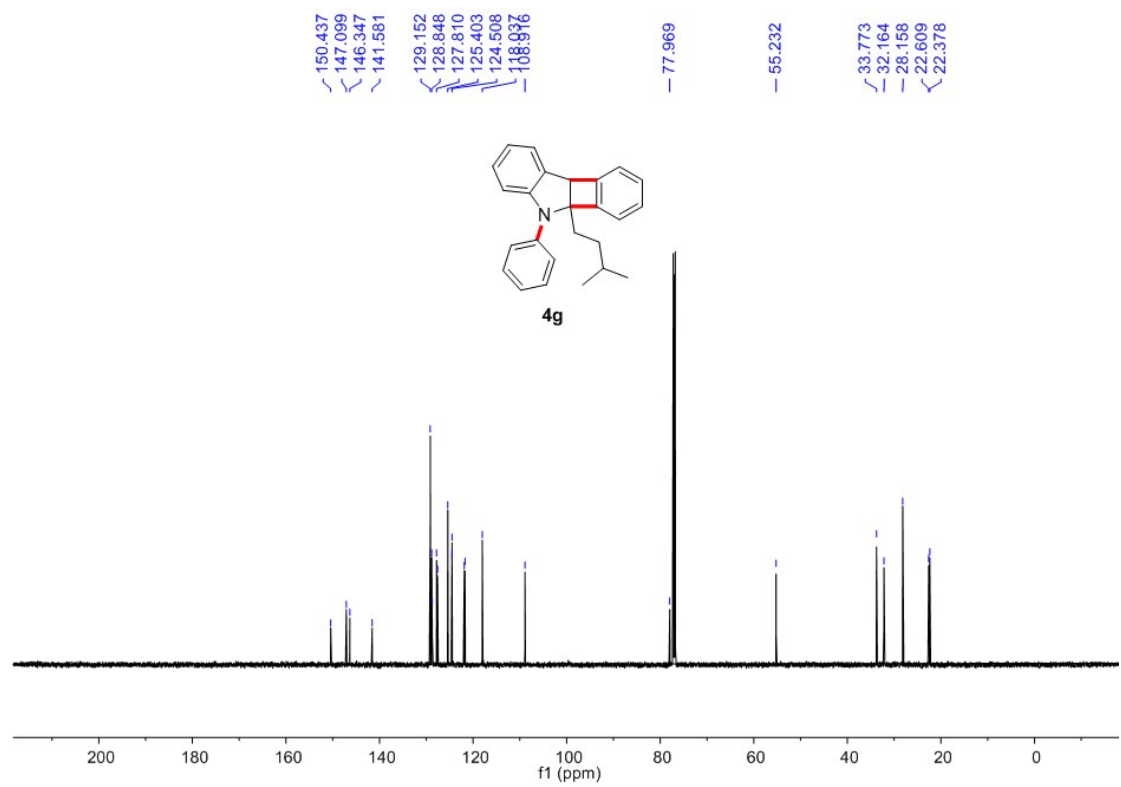
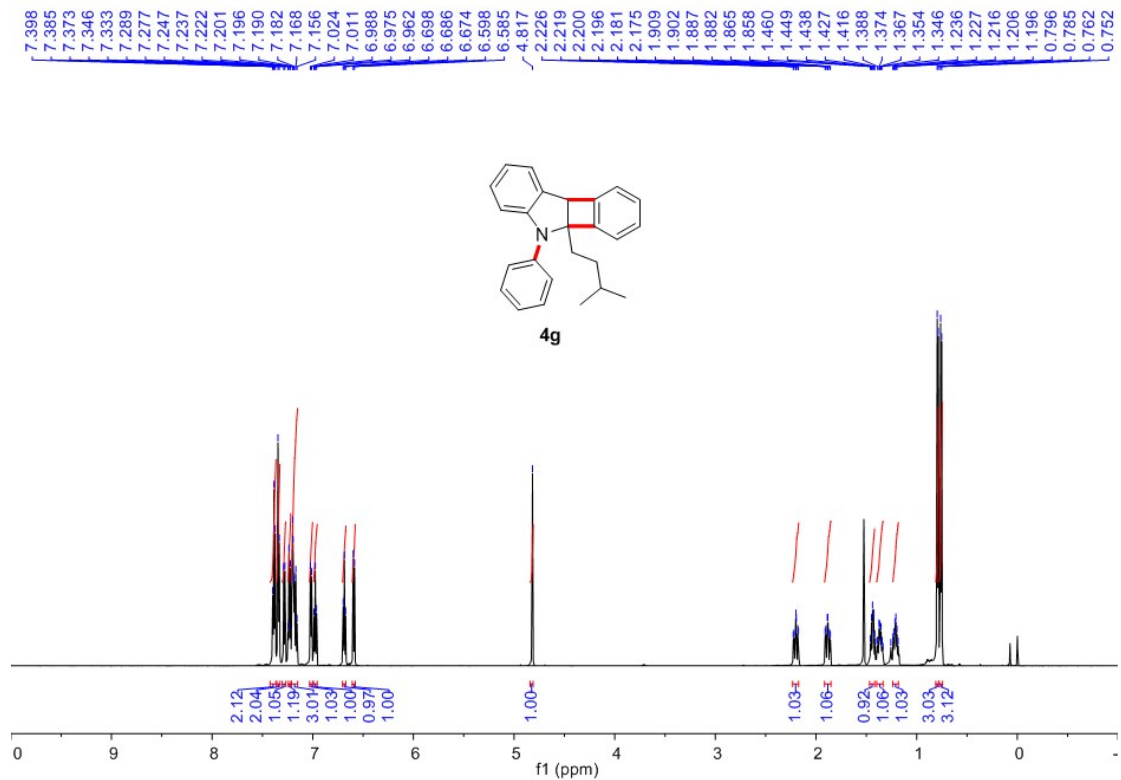


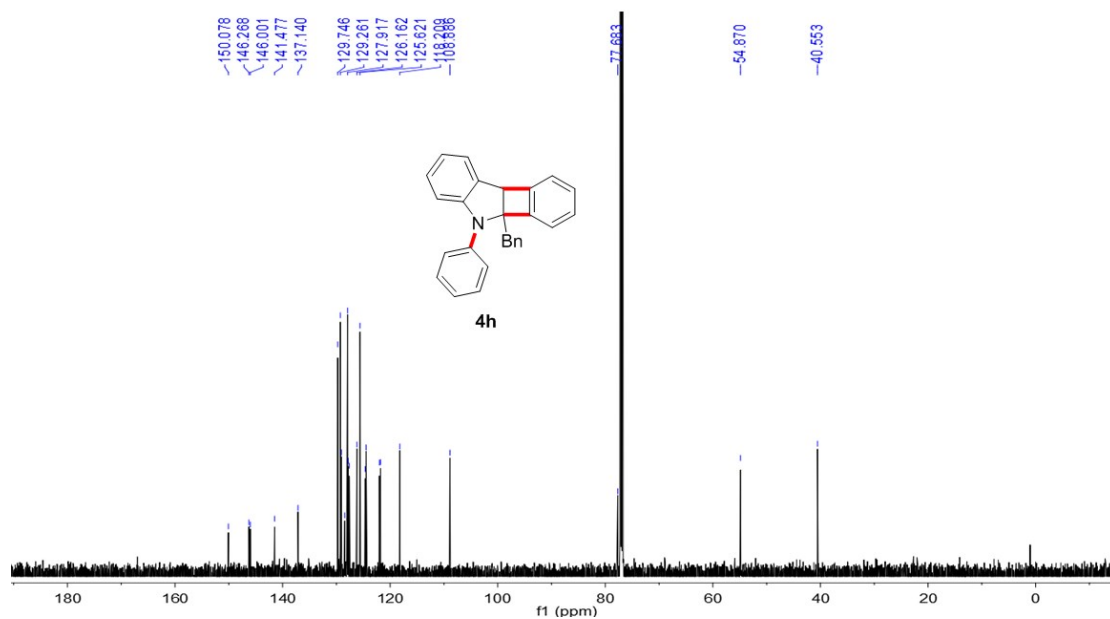
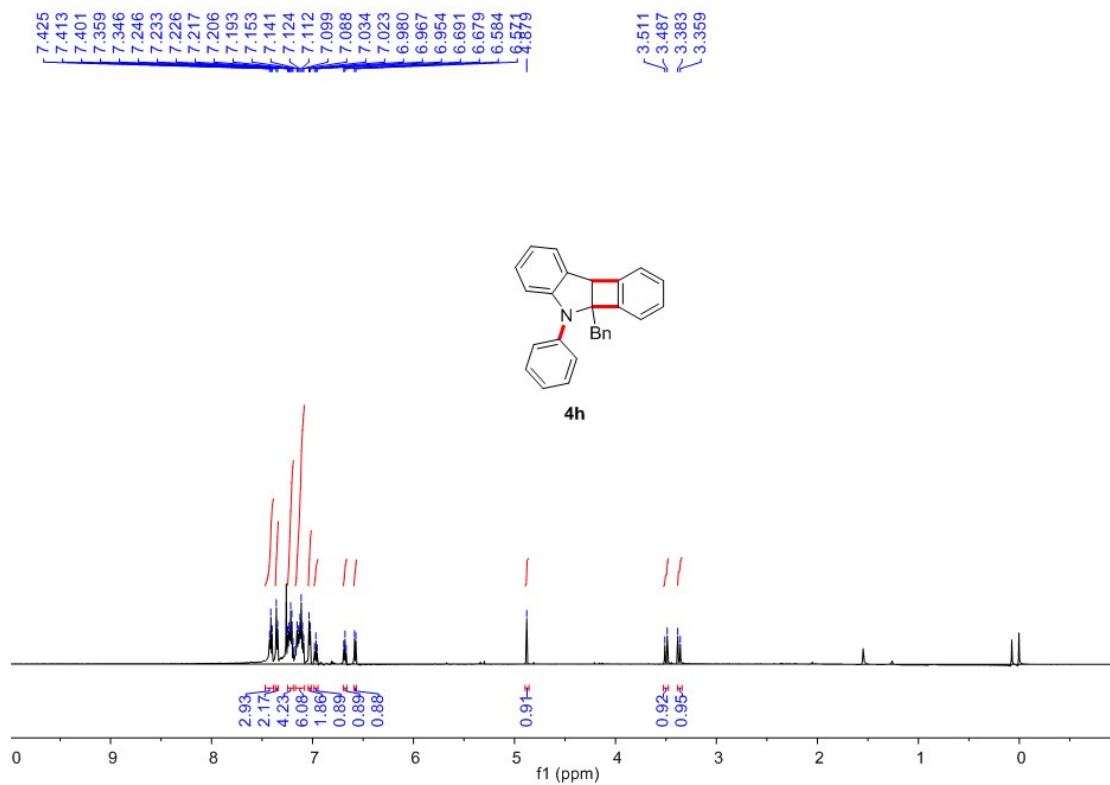




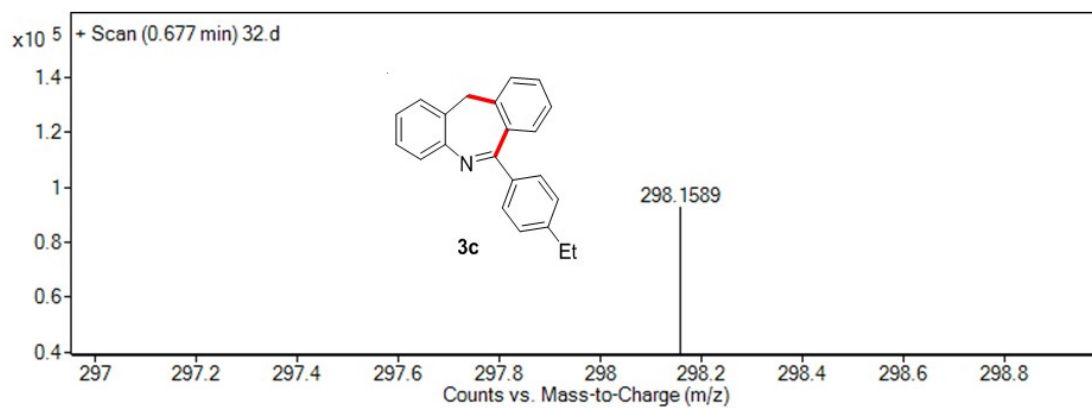
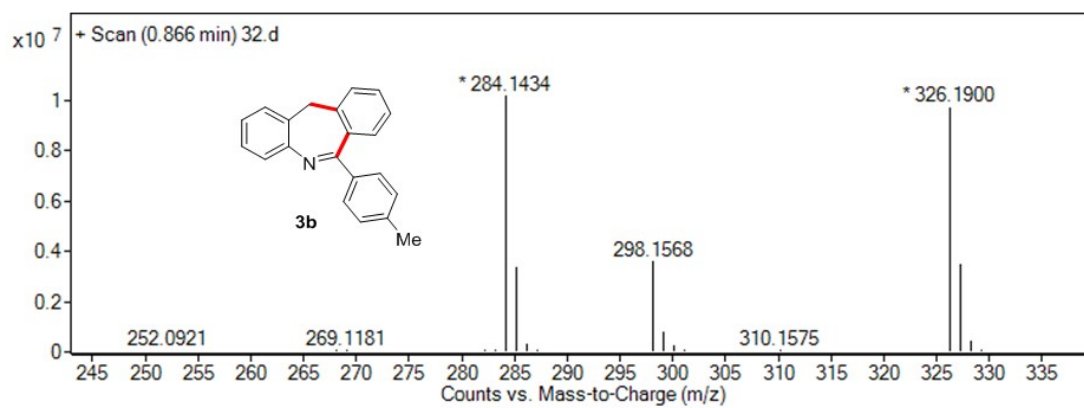
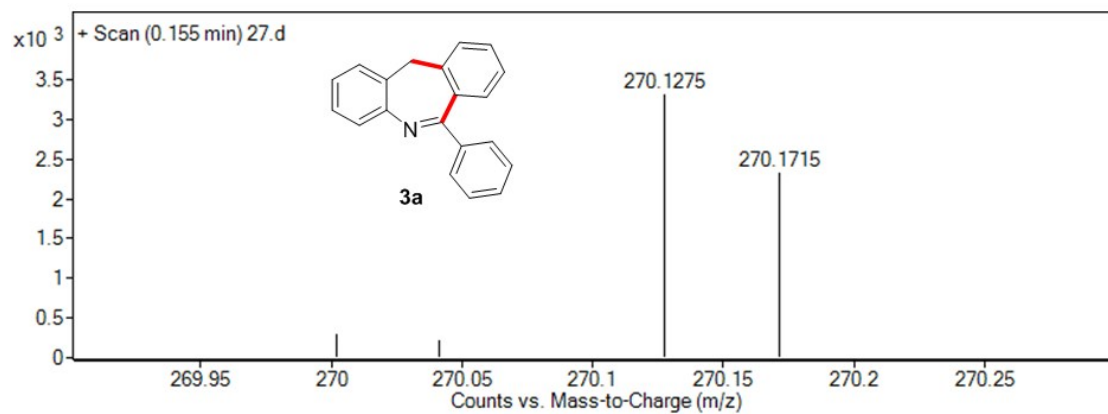


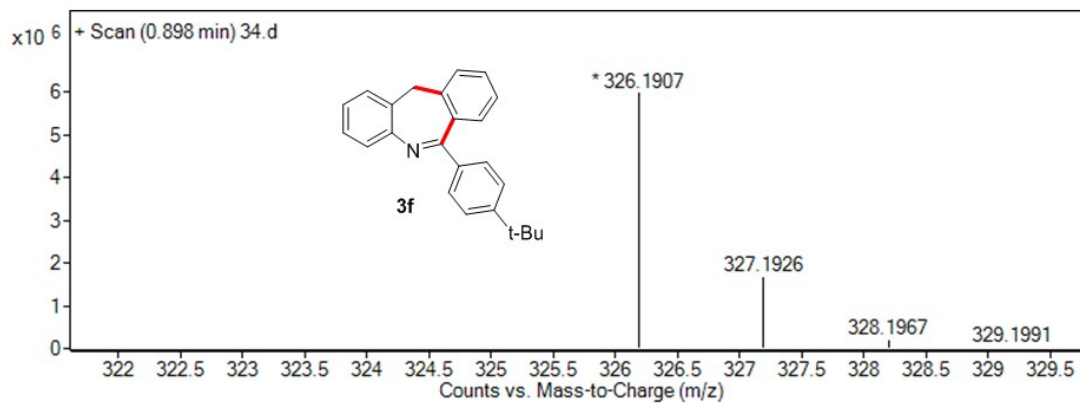
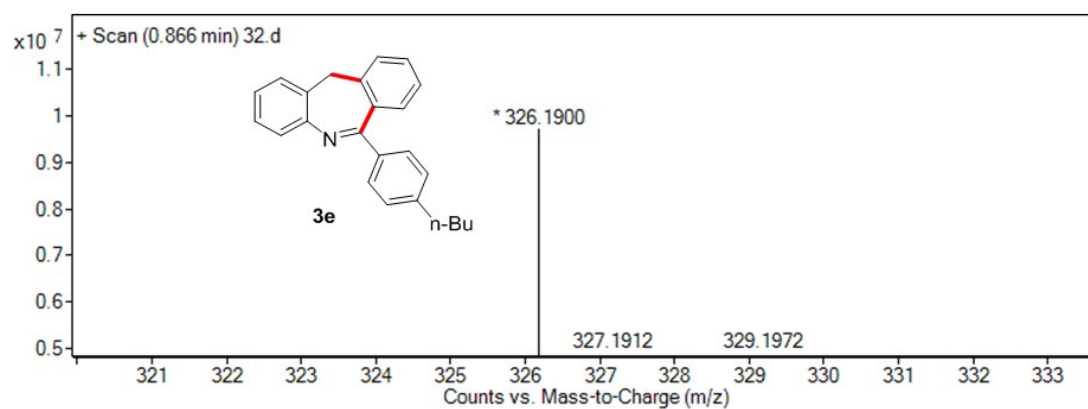
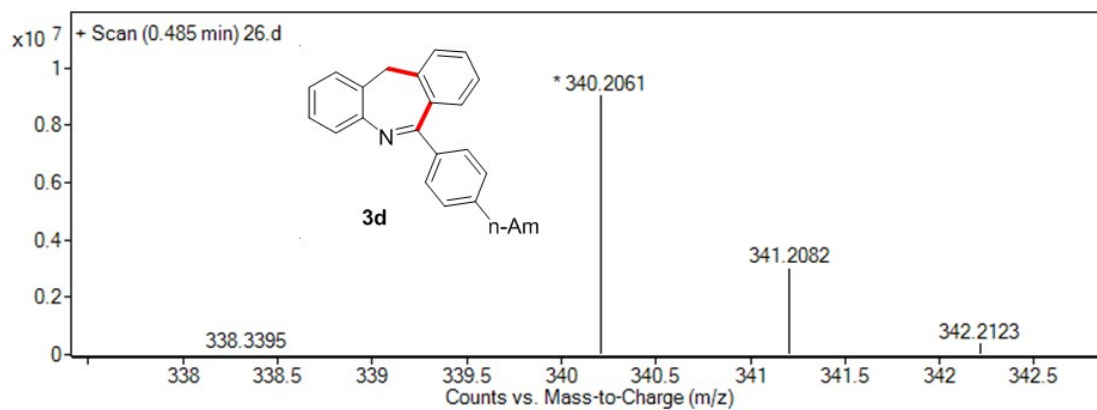


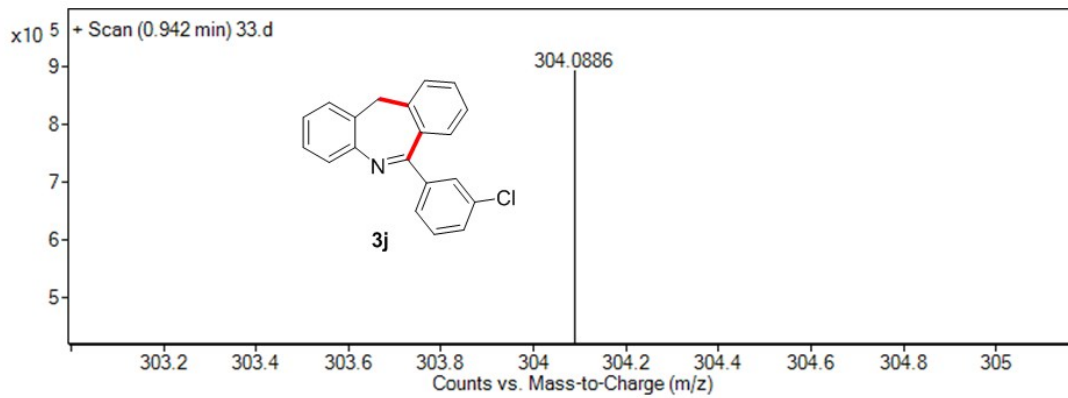
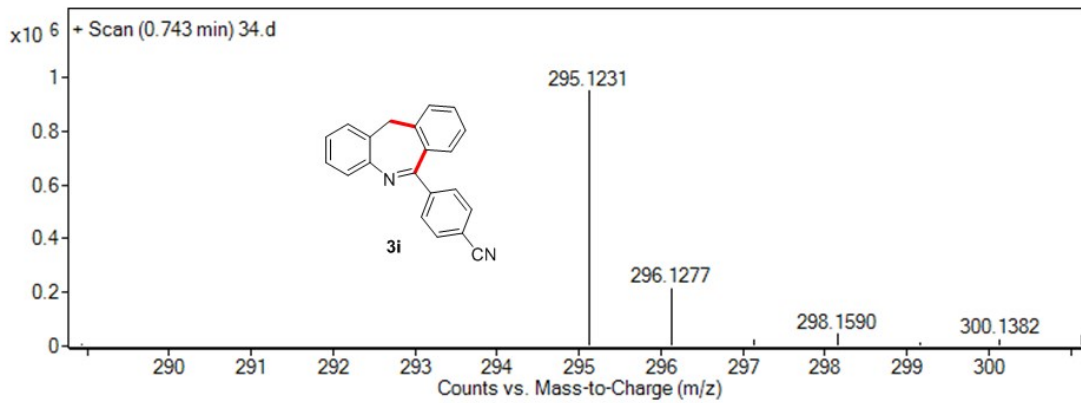
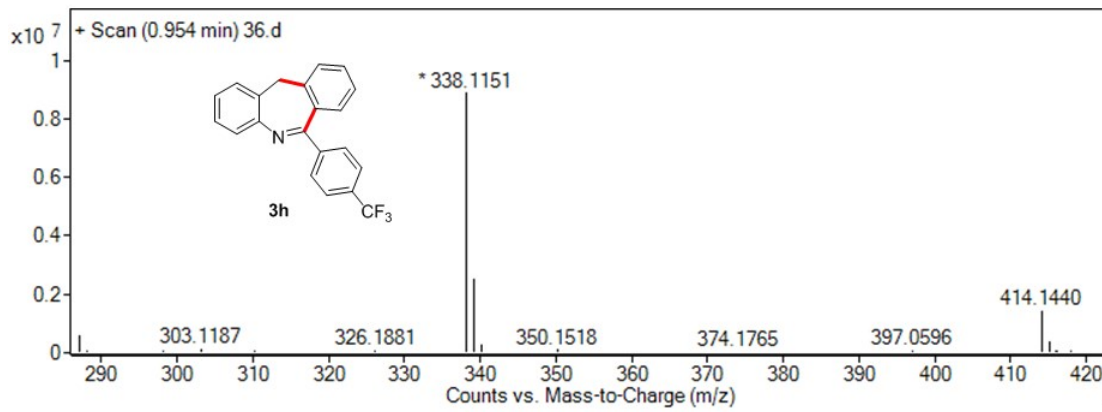
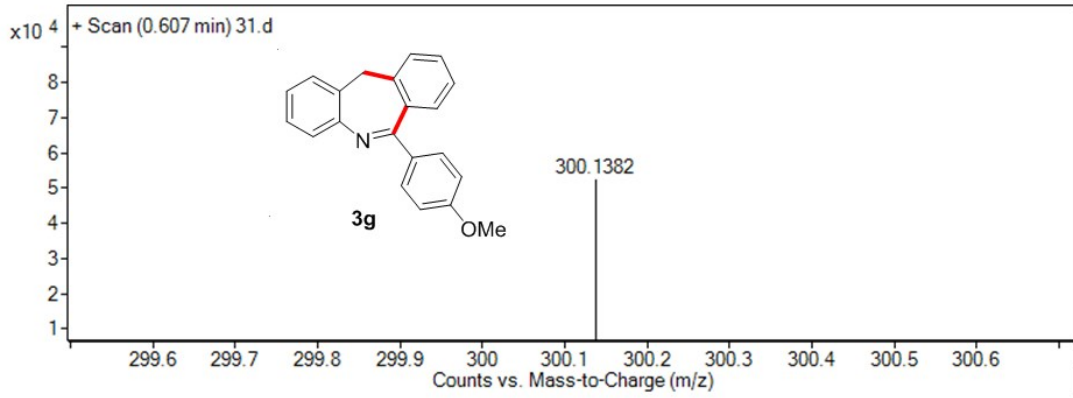


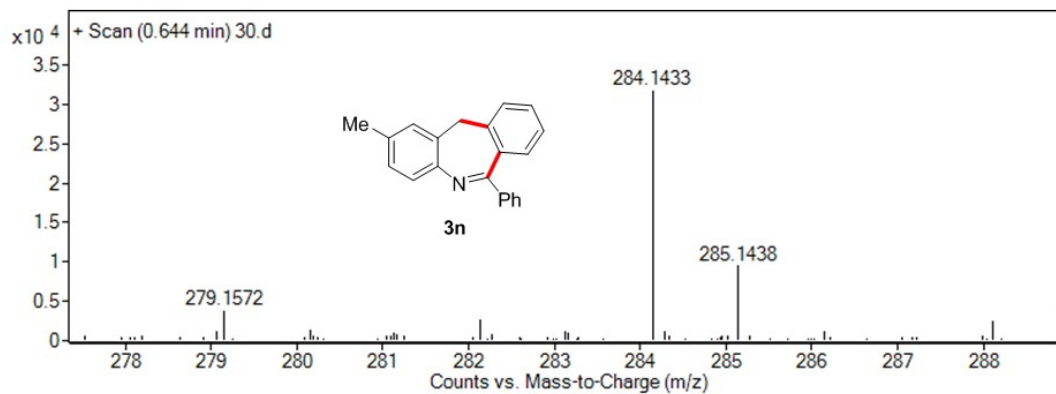
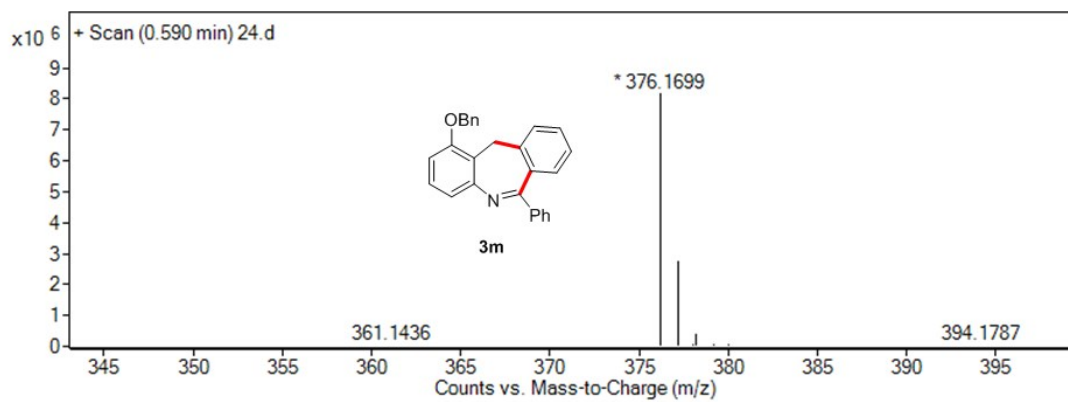
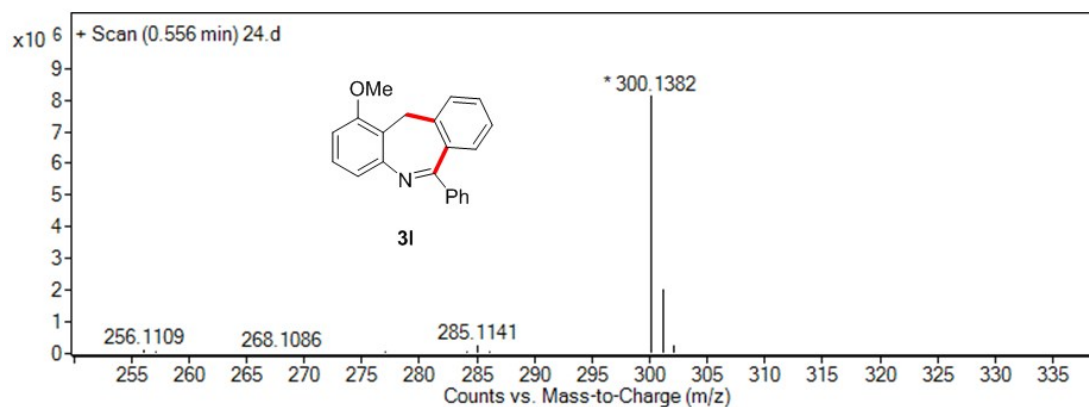
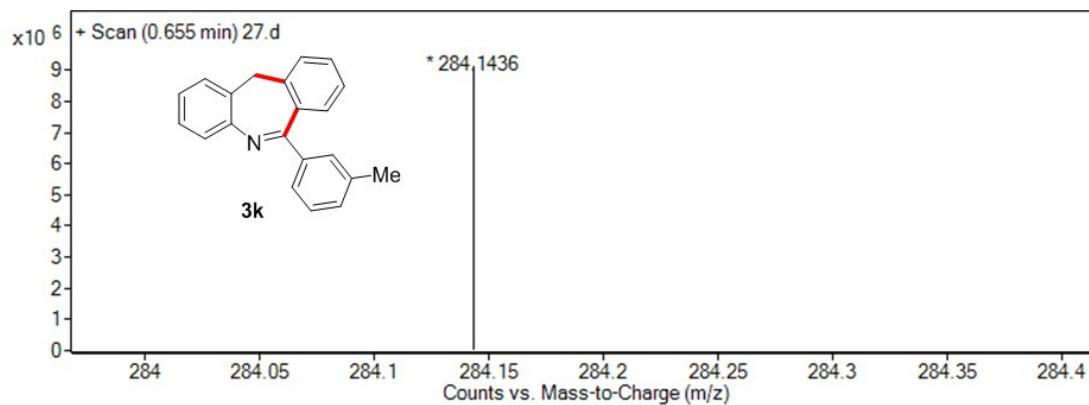


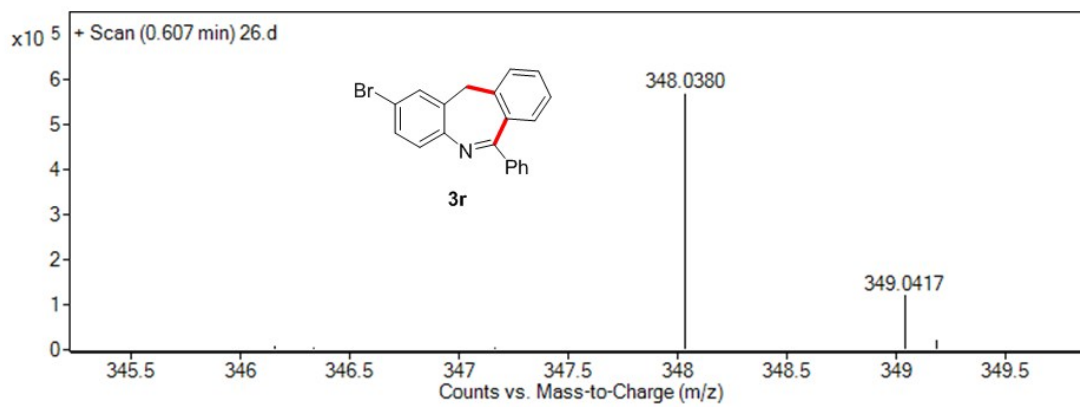
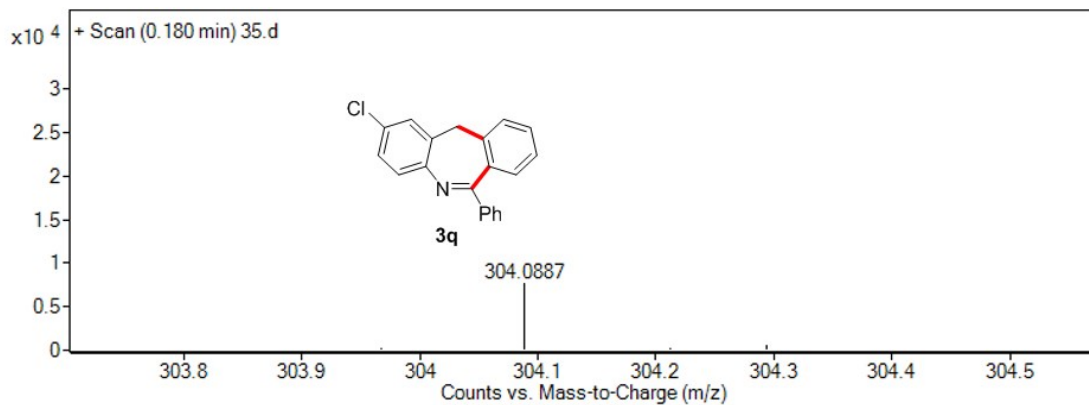
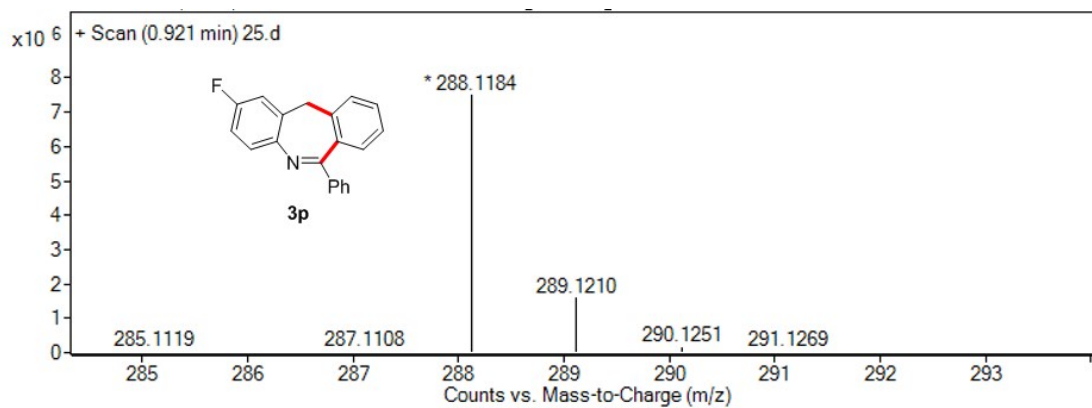
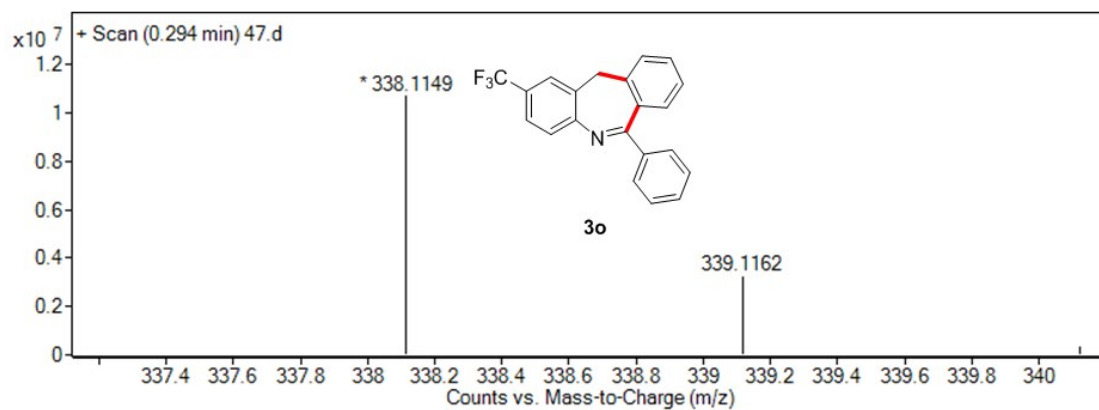
8. HRMS Analysis Reports for All Compounds

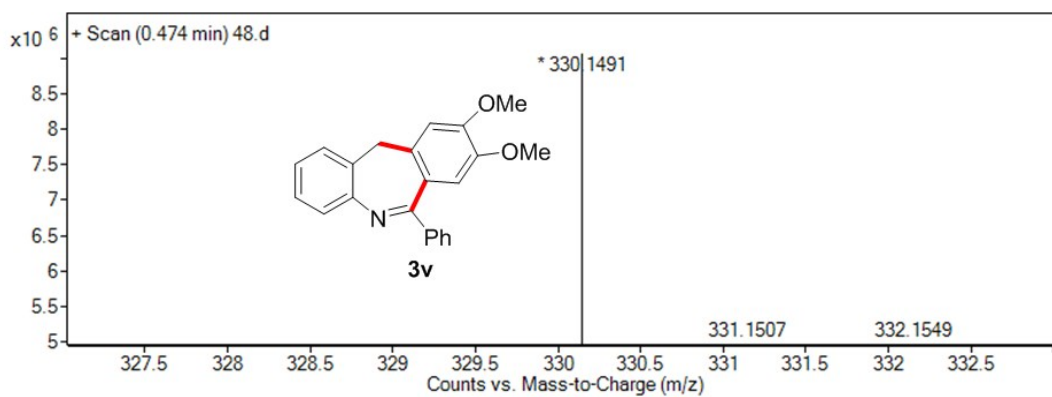
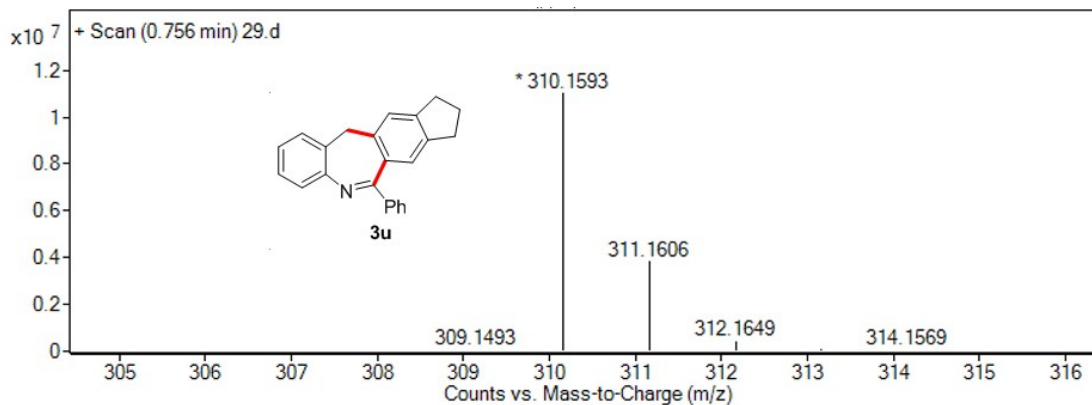
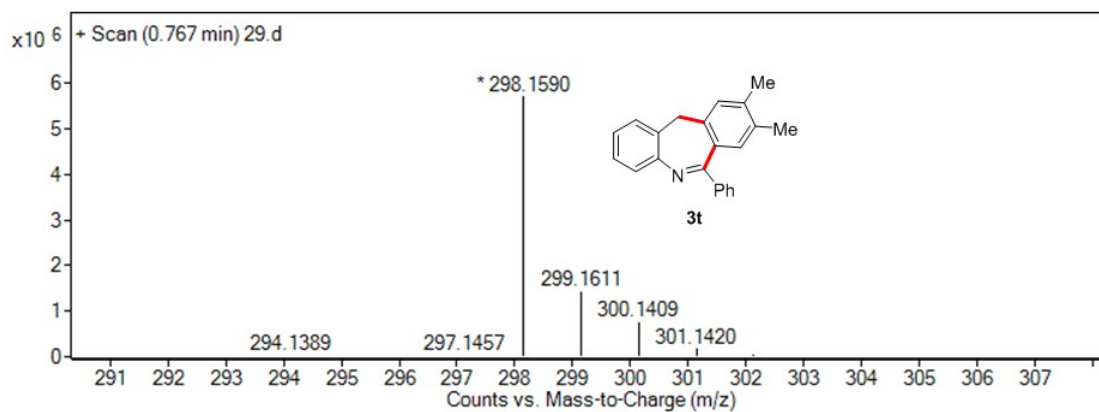
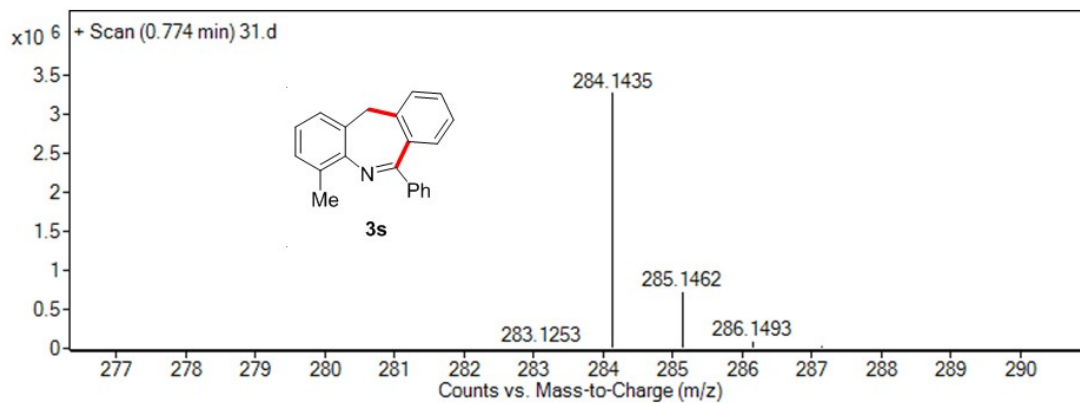


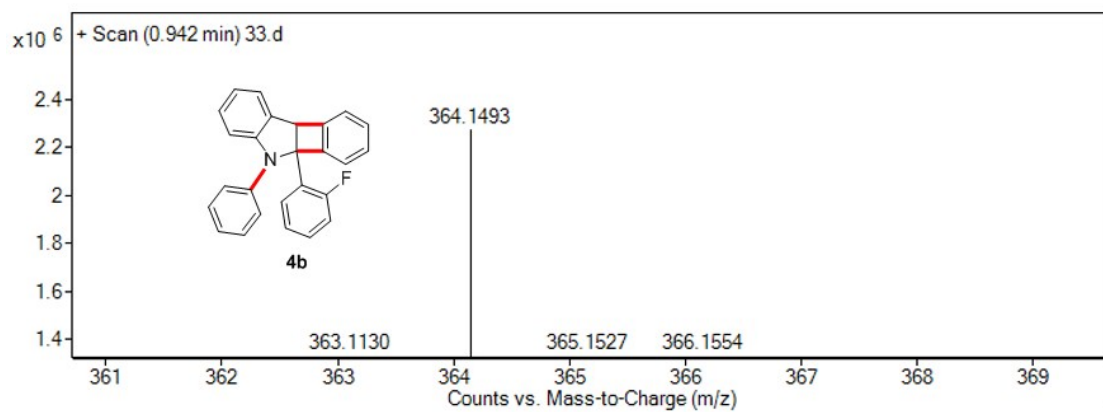
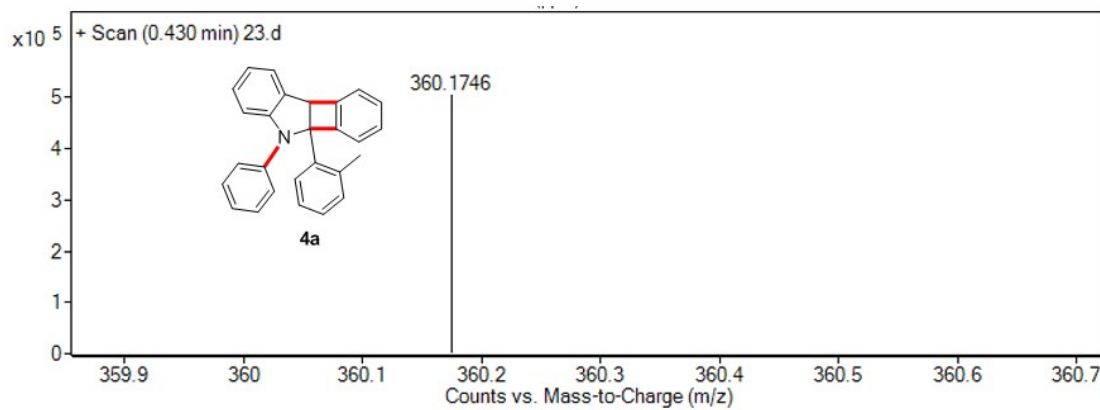
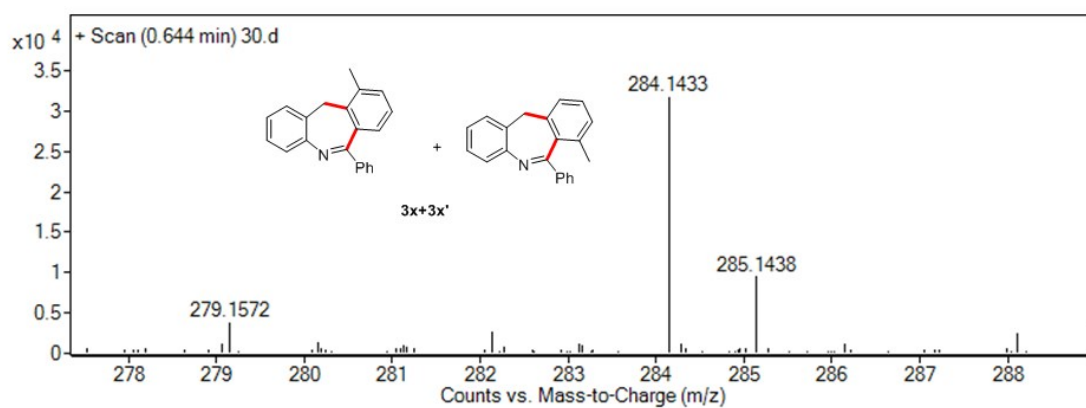
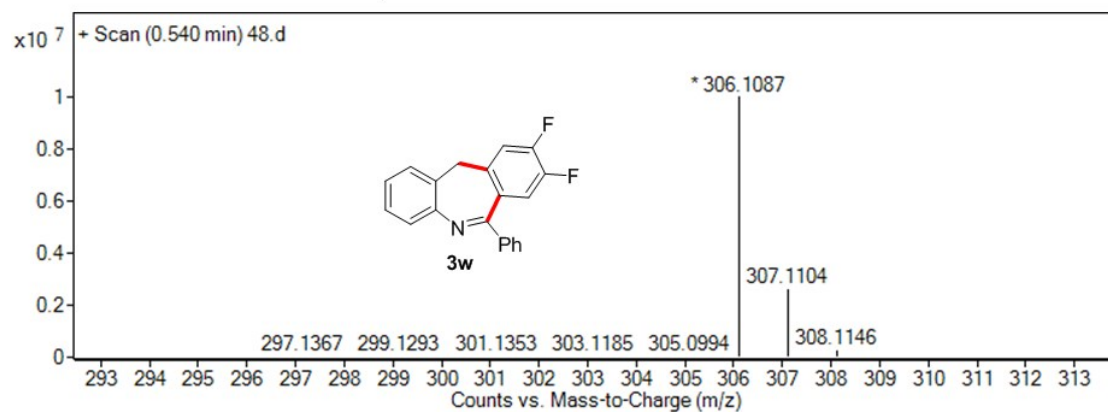


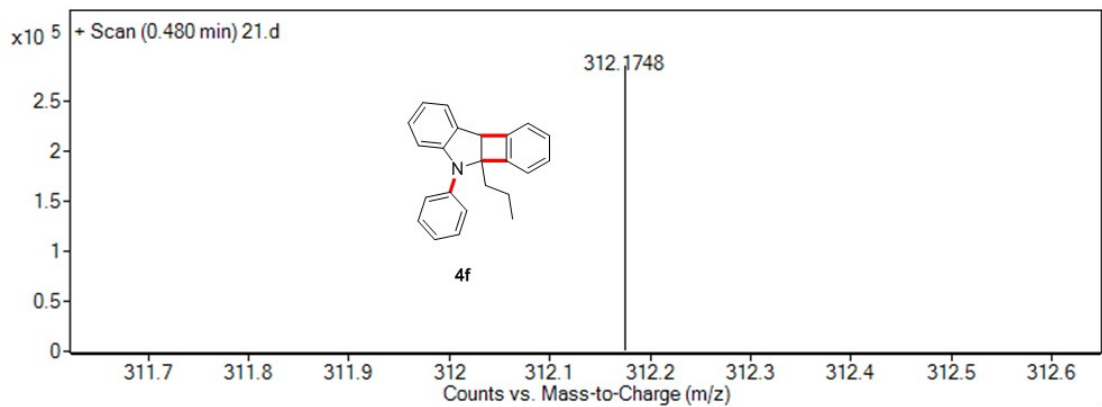
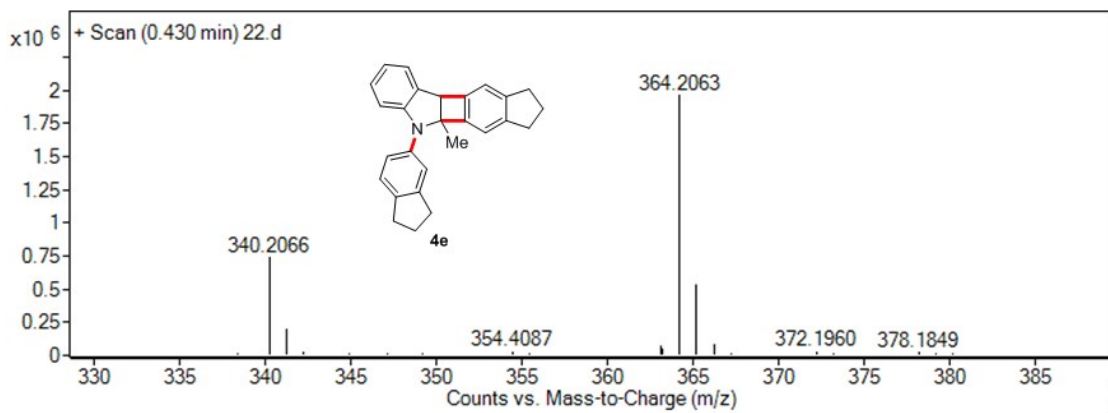
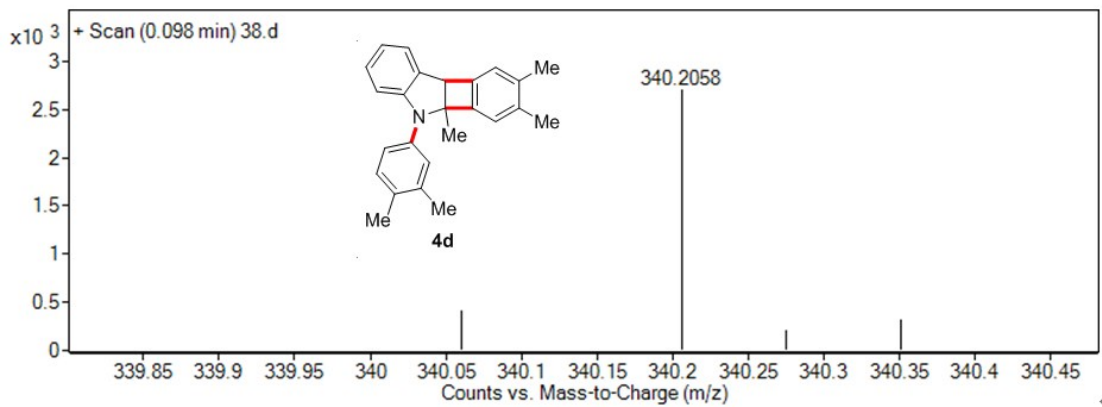
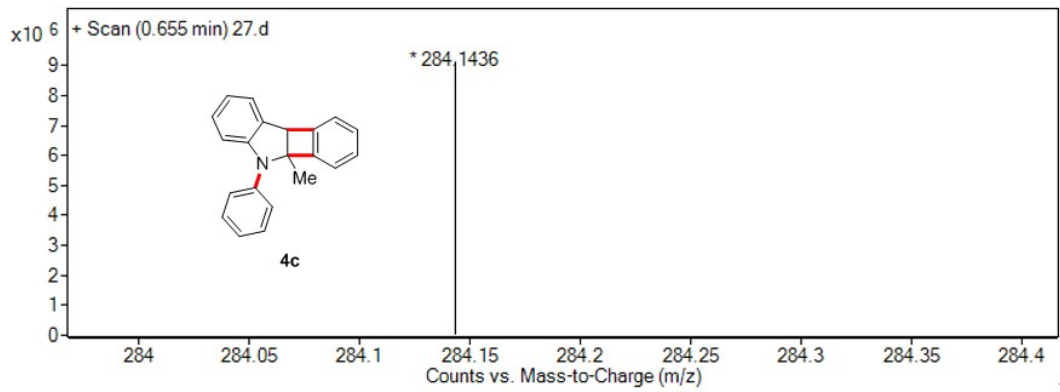


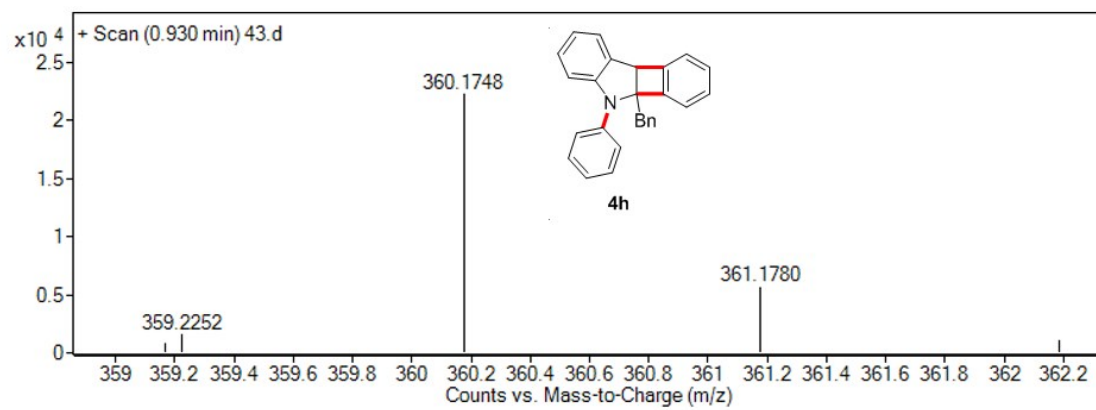
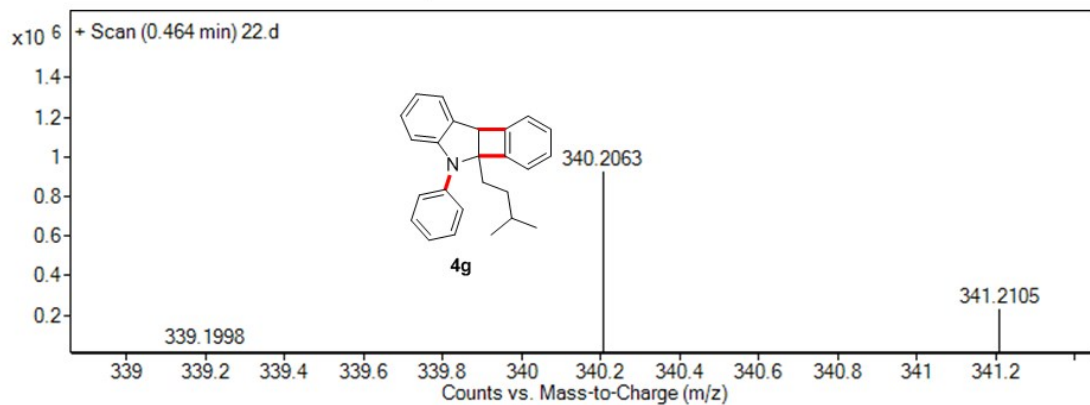












9. Crystallographic Data for 3a and 4a

9.1 Crystallographic Data for 3a

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1

Bond precision: C-C = 0.0052 Å Wavelength=0.71073

Cell: a=18.566 (2) b=5.4612 (7) c=14.391 (2)
 alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1459.1 (3)	1459.1 (3)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C20 H15 N	C20 H15 N
Sum formula	C20 H15 N	C20 H15 N
Mr	269.33	269.33
Dx, g cm-3	1.226	1.226
Z	4	4
Mu (mm-1)	0.071	0.071
F000	568.0	568.0
F000'	568.20	
h,k,lmax	22, 6, 17	22, 6, 17
Nref	2571 [1344]	2555
Tmin, Tmax	0.980, 0.985	0.628, 0.746
Tmin'	0.980	

Correction method= # Reported T Limits: Tmin=0.628 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.90/0.99 Theta(max) = 25.000

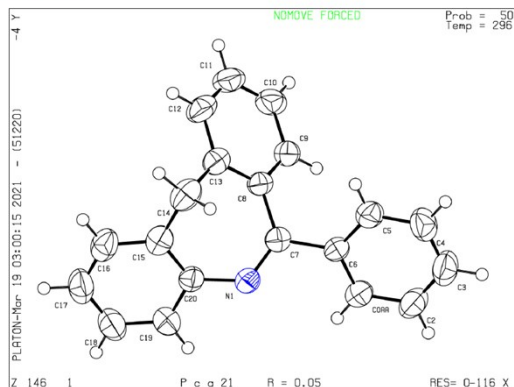
R(reflections)= 0.0503 (1786) wR2(reflections)= 0.0915 (2555)

S = 1.025 Npar= 191

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

PLATON version of 05/12/2020; check.def file version of 05/12/2020

Datablock 1 - clipped plot



9.2 Crystallographic Data for 4a

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: t

Bond precision: C-C = 0.0036 A Wavelength=0.71073

Cell: a=9.0099(13) b=10.3660(15) c=11.4985(16)
 alpha=67.411(2) beta=86.553(2) gamma=87.881(2)

Temperature: 296 K

	Calculated	Reported
Volume	989.6(2)	989.6(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C27 H21 N	C27 H21 N
Sum formula	C27 H21 N	C27 H21 N
Mr	359.45	359.45
Dx, g cm-3	1.206	1.206
Z	2	2
Mu (mm-1)	0.069	0.069
F000	380.0	380.0
F000'	380.13	
h,k,lmax	11,13,15	11,13,15
Nref	4650	4351
Tmin,Tmax	0.987,0.990	0.656,0.746
Tmin'	0.987	

Correction method= # Reported T Limits: Tmin=0.656 Tmax=0.746
AbsCorr = NONE

Data completeness= 0.936 Theta(max)= 27.735

R(reflections)= 0.0582(2652) wR2(reflections)= 0.1679(4351)

S = 1.007 Npar= 254

The following ALERTS were generated. Each ALERT has the format
test-name ALERT_alert-type alert-level.
Click on the hyperlinks for more details of the test.

Datablock: t - r0ipped plot

