

Copper-catalyzed intramolecular aryl-bicyclization of diynes with diaryliodonium salts via vinyl cations

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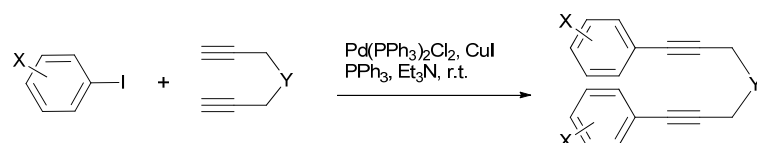
1. General information

All the reactions were carried out in oven dried screw capped tube with a Teflon lined septum under N₂ atmosphere. Diynes reagents were prepared according to the literature.¹ Diaryliodonium triflate reagents were synthesized according to the literatures.² All of the solvents were fresh distilled according to standard method. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ¹H NMR and ¹³C NMR spectras were recorded on an AL -300MHz, AL -400MHz or AL-600MHz spectrometer at ambient temperature with CDCl₃ as the solvent. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl₃ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants (Hz). ¹³C NMR spectra are reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77.16 ppm. Two dimensional NMR spectras were recorded on an AL-600MHz spectrometer at ambient temperature with CDCl₃ as the solvent. The reaction progress was monitored by GC-MS if applicable.

2. Synthesis of starting material **1**

2.1 General procedure

To a solution of the respective diyne (10 mmol) and 1-iodo-4-methylbenzene (30 mmol) in NEt₃ (60 mL), Pd(PPh₃)₂Cl₂ (421 mg), CuI (191 mg) and PPh₃ (185 mg) were added at ambient temperature. The reaction mixture was stirred at room temperature (60 °C for **1j**) under nitrogen for 12-24 h. Then the suspension was filtered through a 3 cm thick layer of Celite, and the Celite was rinsed well with ethyl acetate (50 mL). The solvents of the filtrate were removed under reduced pressure, and the residue was subjected to chromatography on silica gel. Elution with hexane/ethyl acetate afforded the coupling product.

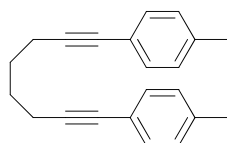


X	Y	Time (h)	Product	Yield
4-CH ₃	(CH ₂) ₂	18	1a	80%
4-CH ₃	CH ₂	12	1b	75%
4-F	(CH ₂) ₂	24	1c	80%
4-F	CH ₂	24	1d	75%
4-Cl	(CH ₂) ₂	24	1e	71%
4-Cl	CH ₂	24	1f	75%
4-Br	(CH ₂) ₂	24	1g	63%
4-Br	CH ₂	24	1h	60%
4-COOMe	CH ₂	24	1i	30%
2-F	CH ₂	24	1j	35%
3-Br	CH ₂	24	1k	81%
4-CH ₃	O	20	1l	99%
4-CH ₃	C(COOMe) ₂	24	1m	93%
4-Meo	CH ₂	24	1n	67%

2.2 Synthesis of unsymmetrical diyne **1o**.

A mixture of methyl 4-iodobenzoate (2.62 g, 10 mmol), CuI (98 mg, 0.5 mmol), PdCl₂(PPh₃)₂ (420 mg, 0.6 mmol), 1,6-heptadiyne (1.8 mL, 15.67 mmol) and 40 mL of triethylamine was stirred at 60 °C for 24 h. After filtration and solvent removal, the crude product was purified on a silica gel column using PE/EA as an eluent to give **1p** as a colorless oil (985 mg, 4.4 mmol, 44%). A mixture of **1p** (452 mg, 2 mmol), 1-iodo-4-methylbenzene (654 mg, 3 mmol), CuI (38 mg, 0.2 mmol), PdCl₂(PPh₃)₂ (84.2 mg, 0.12 mmol) and PPh₃ (37 mg, 0.14 mmol) in 5 mL triethylamine was stirred for 24 h at RT. After removal of the volatile components under reduced pressure, the residue was subjected to silica gel column chromatography (PE/EA) to afford **1o** as white solid (452 mg, 72%).

3. Characterization data of starting materials 1



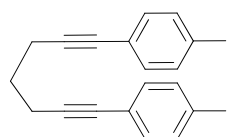
1,8-di-*p*-tolyl-octa-1,7-diyne 1a: white solid, melting point: 89 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 4H), 2.46 (t, *J* = 5.8 Hz, 4H), 2.32 (s, 6H), 1.81 - 1.74 (m, 4H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 137.6(2×C), 131.6(4×CH), 129.1(4×CH), 121.0(2×C), 89.2(2×C≡C), 81.1(2×C≡C), 28.1(2×CH₂), 21.5(2×CH₂), 19.2(2×CH₃).

ESI-HRMS: *m/z* calcd for C₂₂H₂₂ [M+H]⁺: 287.1794; found: 287.1796.

GC-MS *m/z*: 286



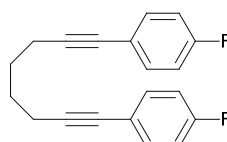
1,7-di-*p*-tolyl-hepta-1,6-diyne 1b: white solid, melting point: 47 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 4H), 2.57 (t, *J* = 7.0 Hz, 4H), 2.32 (s, 6H), 1.94 - 1.84 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 137.7(2×C), 131.6(4×CH), 129.1(4×CH), 120.9(2×C), 88.6(2×C≡C), 81.4(2×C≡C), 28.3, 21.6(2×CH₂), 18.9(2×CH₃).

ESI-HRMS: *m/z* calcd for C₂₁H₂₀ [M+H]⁺: 273.1638; found: 273.1637.

GC-MS *m/z*: 272

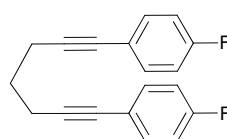


1,8-bis(4-fluorophenyl)octa-1,7-diyne 1c: white solid, melting point: 72 °C.

¹H NMR (301 MHz, CHLOROFORM-D) δ 7.41 - 7.34 (m, 2H), 7.02 - 6.92 (m, 2H), 2.46 (t, *J* = 6.2 Hz, 4H), 1.83 - 1.73 (m, 4H).

¹³C NMR (76 MHz, CHLOROFORM-D) δ 162.2 (d, *J* = 248.2 Hz, 2×C), 133.5 (d, *J* = 8.3 Hz, 4×CH), 120.1 (d, *J* = 3.4 Hz, 2×C), 115.5 (d, *J* = 22.0 Hz, 4×CH) 89.5(2×C≡C), 80.0(2×C≡C), 28.0(2×CH₂), 19.1(2×CH₂).

ESI-HRMS: *m/z* calcd for C₂₀H₁₆F₂ [M+H]⁺: 295.1293; found: 295.1292.

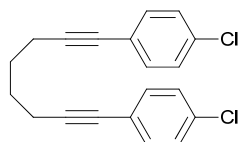


1,7-bis(4-fluorophenyl)hepta-1,6-diyne 1d: oil.

^1H NMR (301 MHz, CHLOROFORM-D) δ 7.50 - 7.30 (m, 4H), 7.13 - 6.85 (m, 4H), 2.58 (t, J = 7.0 Hz, 4H), 1.96 - 1.83 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 162.2 (d, J = 248.4 Hz, $2\times\text{C}$), 133.5 (d, J = 8.2 Hz, $4\times\text{CH}$), 119.9 (d, J = 3.4 Hz, $2\times\text{C}$), 115.5 (d, J = 21.9 Hz, $4\times\text{CH}$), 88.8($2\times\text{C}\equiv\text{C}$), 80.3($2\times\text{C}\equiv\text{C}$), 28.0, 18.7($2\times\text{CH}_2$).

ESI-HRMS: m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_2$ $[\text{M}+\text{H}]^+$: 281.1136; found: 281.1134.

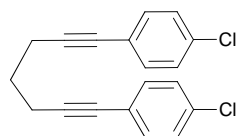


1,8-bis(4-chlorophenyl)octa-1,7-diyne 1e: white solid, melting point: 90 °C.

^1H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, J = 8.5 Hz, 4H), 7.24 (d, J = 8.5 Hz, 4H), 2.45 (t, J = 5.7 Hz, 4H), 1.81 - 1.73 (m, 4H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 133.7($2\times\text{C}$), 132.9($4\times\text{CH}$), 128.7($4\times\text{CH}$), 122.5($2\times\text{C}$), 91.0($2\times\text{C}\equiv\text{C}$), 80.1($2\times\text{C}\equiv\text{C}$), 27.9($2\times\text{CH}_2$), 19.2($2\times\text{CH}_2$).

ESI-HRMS: m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_2$ $[\text{M}+\text{H}]^+$: 327.0702; found: 327.0703.

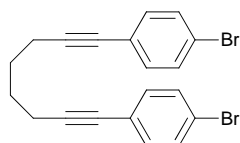


1,7-bis(4-chlorophenyl)hepta-1,6-diyne 1f: white solid, melting point: 53 °C.

^1H NMR (400 MHz, CHLOROFORM-D) δ 7.34 - 7.29 (m, 4H), 7.27 - 7.22 (m, 4H), 2.57 (t, J = 7.0 Hz, 4H), 1.94 - 1.84 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 133.8($2\times\text{C}$), 132.9($4\times\text{CH}$), 128.7($4\times\text{CH}$), 122.4($2\times\text{C}$), 90.3($2\times\text{C}\equiv\text{C}$), 80.4($2\times\text{C}\equiv\text{C}$), 27.9, 18.8($2\times\text{CH}_2$).

ESI-HRMS: m/z calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_2$ $[\text{M}+\text{H}]^+$: 313.0545; found: 313.0543.

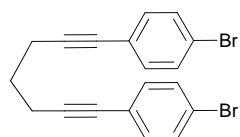


1,8-bis(4-bromophenyl)octa-1,7-diyne 1g: white solid, melting point: 95 °C.

^1H NMR (301 MHz, CHLOROFORM-D) δ 7.46 - 7.36 (m, 4H), 7.28 - 7.23 (m, 4H), 2.45 (t, J = 6.0 Hz, 4H), 1.82 - 1.73 (m, 4H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 133.2($4\times\text{CH}$), 131.6($4\times\text{CH}$), 123.0($2\times\text{C}$), 121.8($2\times\text{C}$), 91.2($2\times\text{C}\equiv\text{C}$), 80.1($2\times\text{C}\equiv\text{C}$), 27.9($2\times\text{CH}_2$), 19.2($2\times\text{CH}_2$).

ESI-HRMS: m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Br}_2$ $[\text{M}+\text{H}]^+$: 416.9672; found: 416.9673.

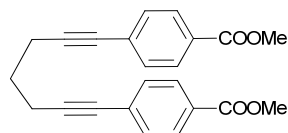


1,7-bis(4-bromophenyl)hepta-1,6-diyne 1h: white solid, melting point: 63 °C.

¹H NMR (301 MHz, CHLOROFORM-D) δ 7.41 (d, *J* = 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 4H), 2.57 (t, *J* = 7.0 Hz, 4H), 1.97 - 1.83 (m, 2H).

¹³C NMR (76 MHz, CHLOROFORM-D) δ 133.2(4×CH), 131.6(4×CH), 122.9(2×C), 121.9(2×C), 90.5(2×C≡C), 80.5(2×C≡C), 27.8, 18.8(2×CH₂).

ESI-HRMS: *m/z* calcd for C₁₉H₁₄Br₂ [M+H]⁺: 402.9515; found: 402.9516.

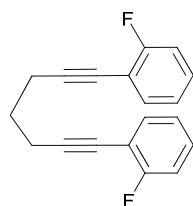


dimethyl 4,4'-(hepta-1,6-diyne-1,7-diyl)dibenzoate 1i: white solid, melting point: 105 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.96 (d, *J* = 8.5 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 4H), 3.91 (s, 6H), 2.63 (t, *J* = 7.0 Hz, 4H), 1.98 - 1.89 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 166.8(2×C=O), 131.7(4×CH), 129.6(4×CH), 129.2(2×C), 128.7(2×C), 92.6(2×C≡C), 81.0(2×C≡C), 52.3(2×OCH₃), 27.7, 18.9(2×CH₂).

ESI-HRMS: *m/z* calcd for C₂₃H₂₀O₄ [M+H]⁺: 361.1434; found: 361.1436.

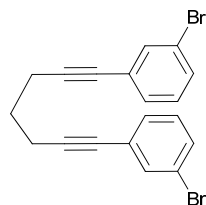


1,7-bis(2-fluorophenyl)hepta-1,6-diyne 1j: oil.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.44 - 7.35 (m, 2H), 7.28 - 7.19 (m, 2H), 7.10 - 7.00 (m, 4H), 2.65 (t, *J* = 7.0 Hz, 4H), 1.99 - 1.91 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 163.0 (d, *J* = 250.3 Hz, 2×C), 133.7(2×CH), 129.4 (d, *J* = 7.8 Hz, 2×CH), 123.9 (d, *J* = 3.6 Hz, 2×CH), 115.5 (d, *J* = 21.1 Hz, 2×CH), 112.4 (d, *J* = 16.0 Hz, 2×C), 94.7 (d, *J* = 3.0 Hz, 2×C≡C), 74.8(2×C≡C), 27.8, 19.0(2×CH₂).

ESI-HRMS: *m/z* calcd for C₁₉H₁₄F₂ [M+H]⁺: 281.1136; found: 281.1134.

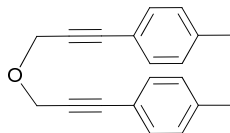


1,7-bis(3-bromophenyl)hepta-1,6-diyne 1k: oil.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.55 (t, *J* = 1.7 Hz, 2H), 7.43 - 7.37 (m, 2H), 7.34 - 7.29 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.0 Hz, 4H), 1.93 - 1.84 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 134.5(2 \times CH), 131.0(2 \times CH), 130.3(2 \times CH), 129.8(2 \times CH), 125.9(2 \times C), 122.2(2 \times C), 90.7(2 \times C \equiv C), 80.1(2 \times C \equiv C), 27.8, 18.8(2 \times CH₂).

ESI-HRMS: m/z calcd for C₁₉H₁₄Br₂ [M+H]⁺: 402.9515; found: 402.9515.



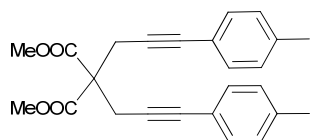
4,4'-(oxybis(prop-1-yn-3,1-diyl))bis(methylbenzene) 1l: oil.

^1H NMR (301 MHz, CHLOROFORM-D) δ 7.34 (d, J = 8.0 Hz, 4H), 7.10 (d, J = 8.0 Hz, 4H), 4.52 (s, 4H), 2.32 (s, 6H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 138.7(2 \times C), 131.8(4 \times CH), 129.1(4 \times CH), 119.5(2 \times C), 87.0(2 \times C \equiv C), 83.8(2 \times C \equiv C), 57.5(2 \times CH₂), 21.5(2 \times CH₃).

ESI-HRMS: m/z calcd for C₂₀H₁₈O [M+H]⁺: 275.1430; found: 275.1431.

GC-MS m/z : 274

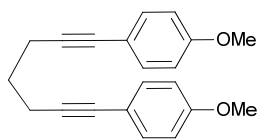


dimethyl 2,2-bis(3-(p-tolyl)prop-2-yn-1-yl)malonate 1m: ^{1b}

^1H NMR (400 MHz, CHLOROFORM-D) δ 7.26 (d, J = 8.0 Hz, 4H), 7.08 (d, J = 8.0 Hz, 4H), 3.79 (s, 6H), 3.25 (s, 4H), 2.32 (s, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 169.6(2 \times C=O), 138.2(2 \times C), 131.7(4 \times CH), 129.1(4 \times CH), 120.1(2 \times C), 84.0(2 \times C \equiv C), 83.3(2 \times C \equiv C), 57.5, 53.2(2 \times CH₃), 24.0(2 \times CH₂), 21.6(2 \times CH₃).

ESI-HRMS: m/z calcd for C₂₅H₂₄O₄ [M+H]⁺: 389.1747; found: 389.1746.

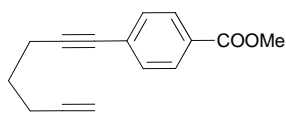


1,7-bis(4-methoxyphenyl)hepta-1,6-diyne 1i: white solid, melting point: 49 °C.

^1H NMR (400 MHz, CHLOROFORM-D) δ 7.36 - 7.30 (m, 4H), 6.87 - 6.76 (m, 4H), 3.79 (s, 6H), 2.56 (t, J = 7.0 Hz, 4H), 1.94 - 1.83 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 159.2(2 \times C), 133.0(4 \times CH), 116.1(2 \times C), 114.0(4 \times CH), 87.8(2 \times C \equiv C), 81.0(2 \times C \equiv C), 55.4(2 \times OCH₃), 28.3, 18.8(2 \times CH₂).

ESI-HRMS: m/z calcd for C₂₁H₂₀O₂ [M+H]⁺: 305.1536; found: 305.1539.

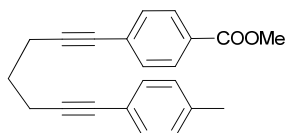


methyl 4-(hepta-1,6-diyne-1-yl)benzoate 1p: oil.

^1H NMR (400 MHz, CHLOROFORM-D) δ 7.95 (d, $J = 8.3$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 3.90 (s, 3H), 2.57 (t, $J = 7.0$ Hz, 2H), 2.38 (td, $J = 7.0, 2.6$ Hz, 2H), 2.00 (t, $J = 2.6$ Hz, 1H), 1.88 - 1.80(m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 166.7, 131.6(2 \times CH), 129.5(2 \times CH), 129.1, 128.7, 92.5, 83.5, 80.9, 69.2, 52.3, 27.6, 18.7, 17.8.

ESI-HRMS: m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2$ $[\text{M}+\text{H}]^+$: 227.1067; found: 227.1067.



methyl 4-(7-(p-tolyl)hepta-1,6-diyn-1-yl)benzoate 1o: white solid, melting point: 119 °C.

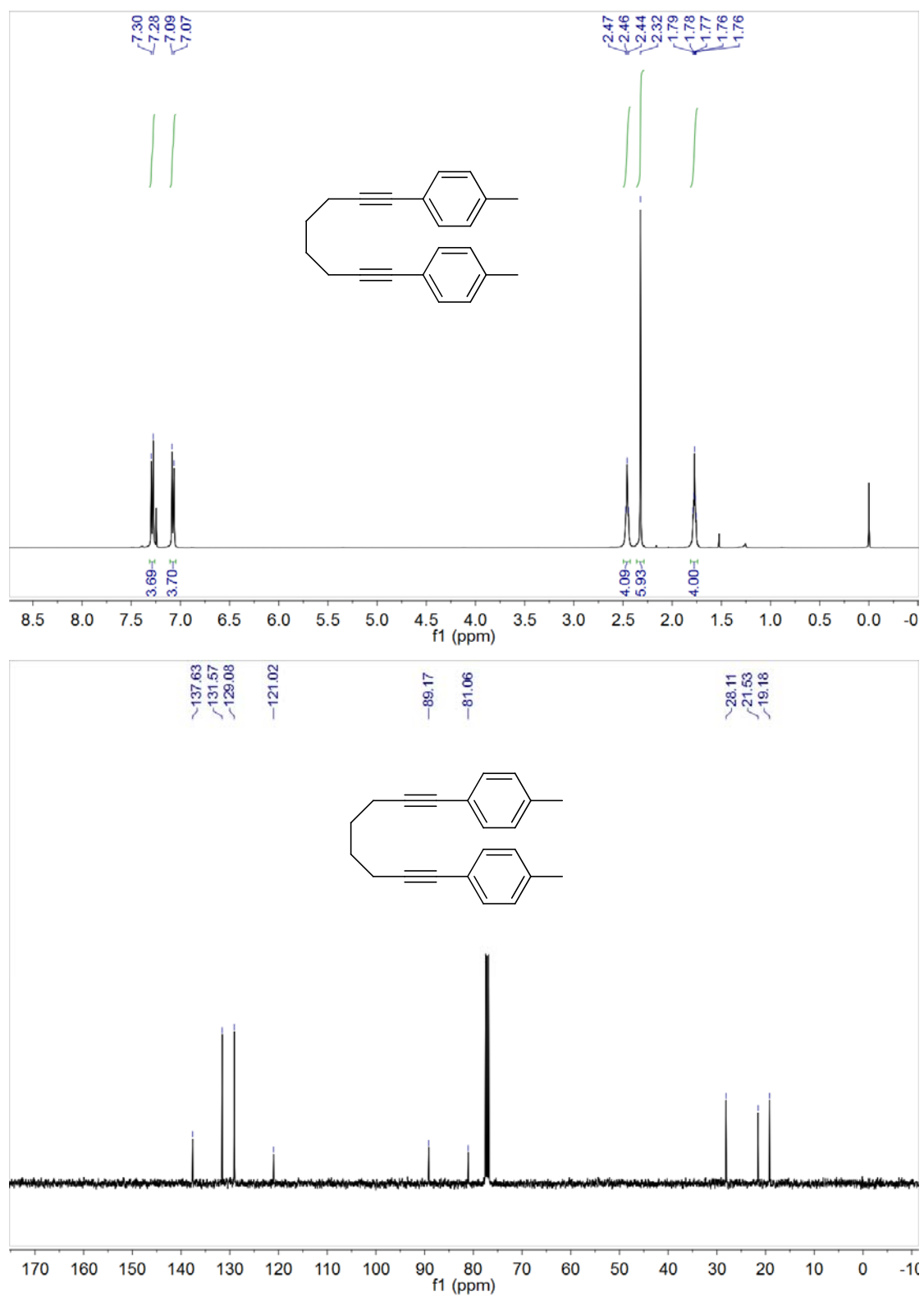
^1H NMR (301 MHz, CHLOROFORM-D) δ 7.95 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 3.91 (s, 3H), 2.66 - 2.55 (m, 4H), 2.33 (s, 3H), 1.98 - 1.85 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 166.8, 137.8, 131.7(2 \times CH), 131.6(2 \times CH), 129.6(2 \times CH), 129.1(2 \times CH, C), 128.8, 120.8, 92.9, 88.3, 81.5, 80.8, 52.3, 28.0, 21.6, 18.9.

ESI-HRMS: m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$: 317.1536; found: 317.1534.

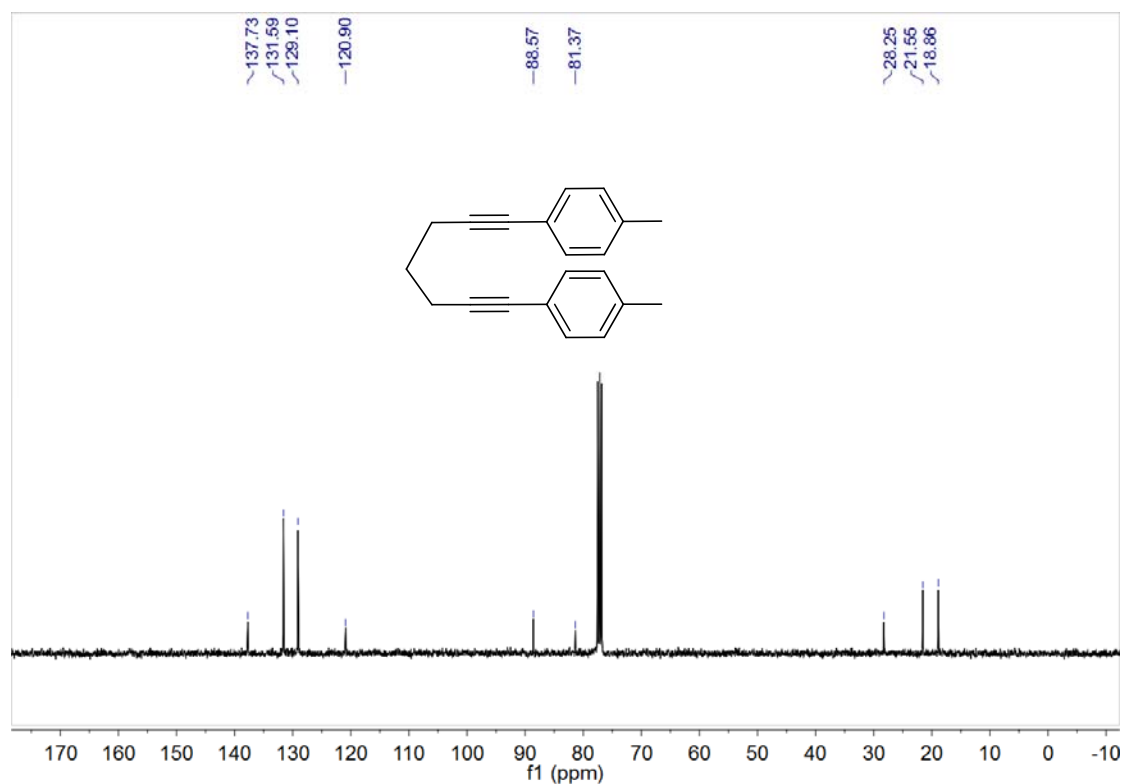
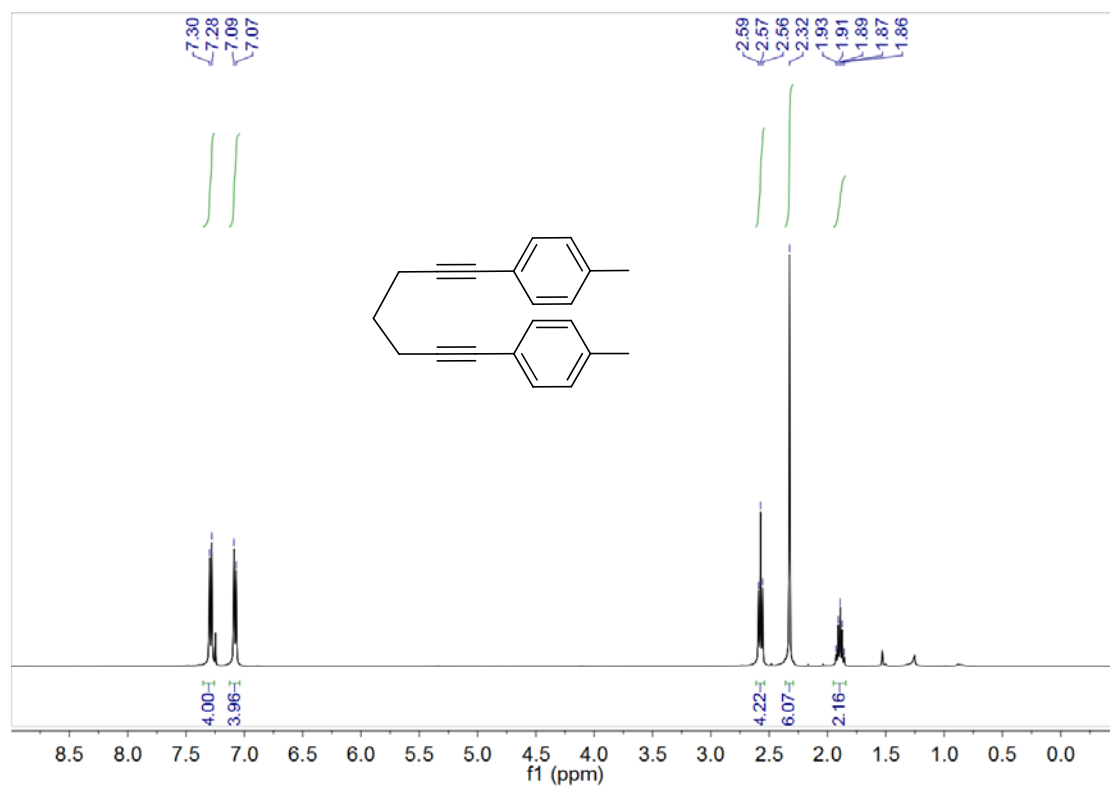
4. NMR spectra of starting materials **1**

1a



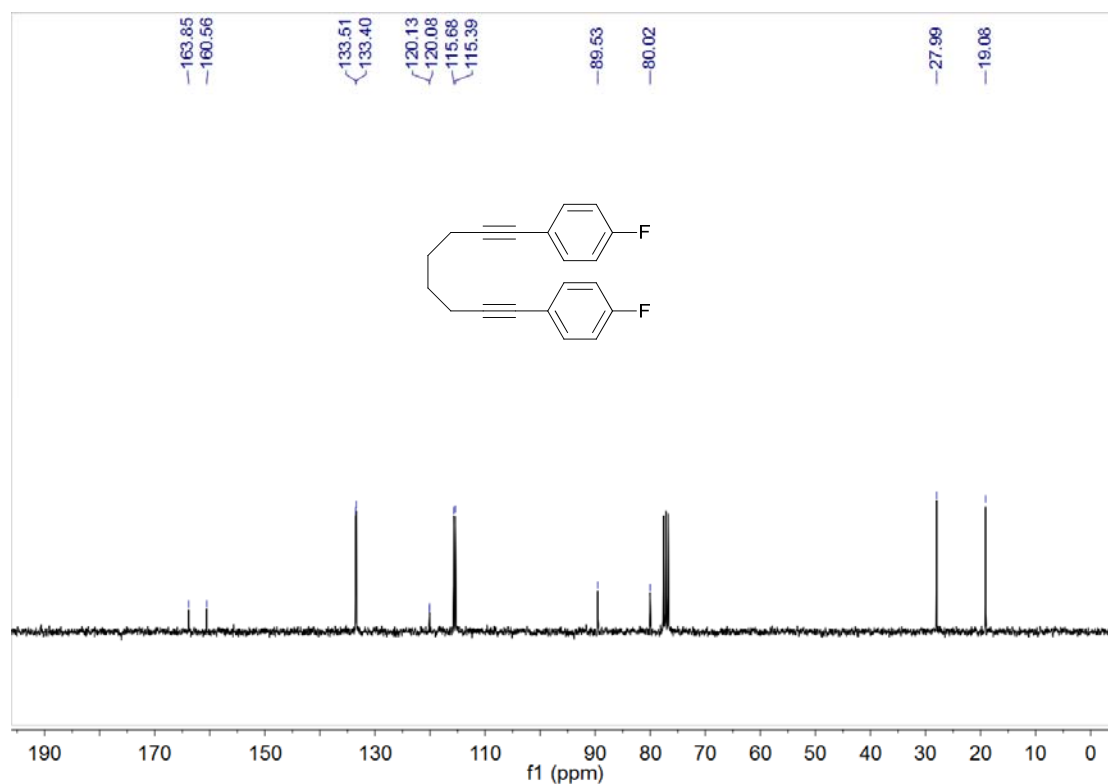
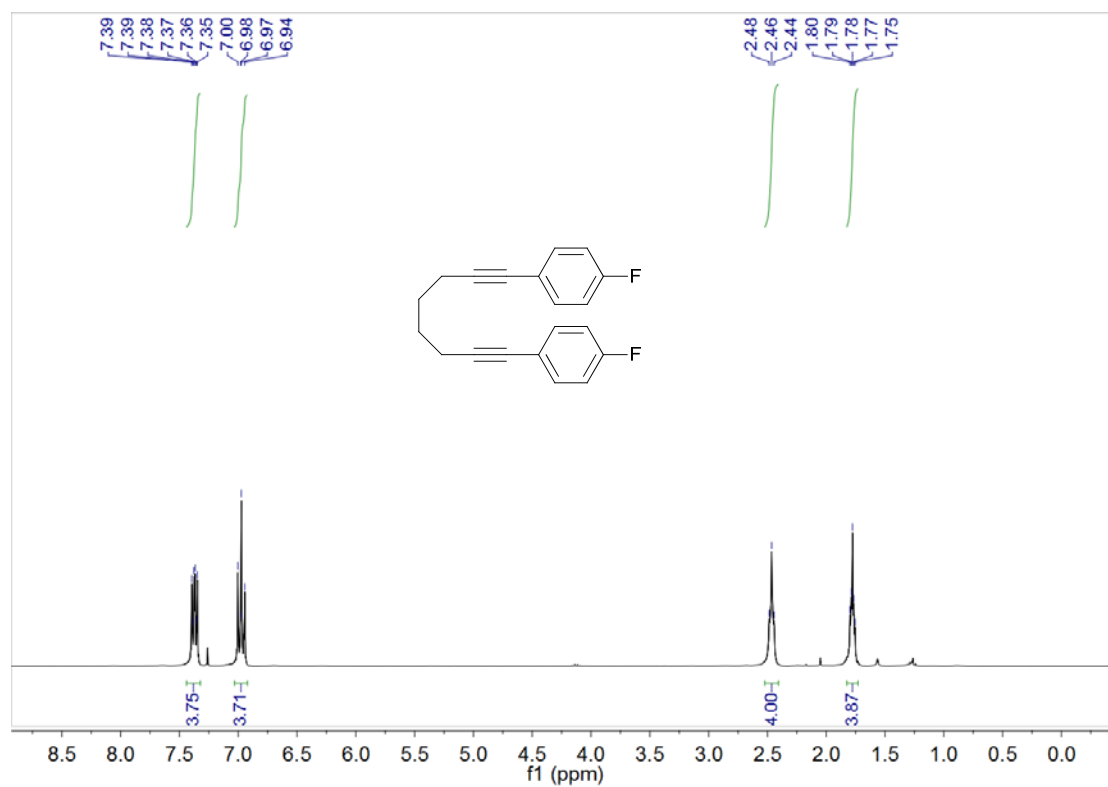
^1H NMR (400 MHz, CDCl_3) (up) and ^{13}C NMR (101 MHz, CDCl_3) (down)

1b



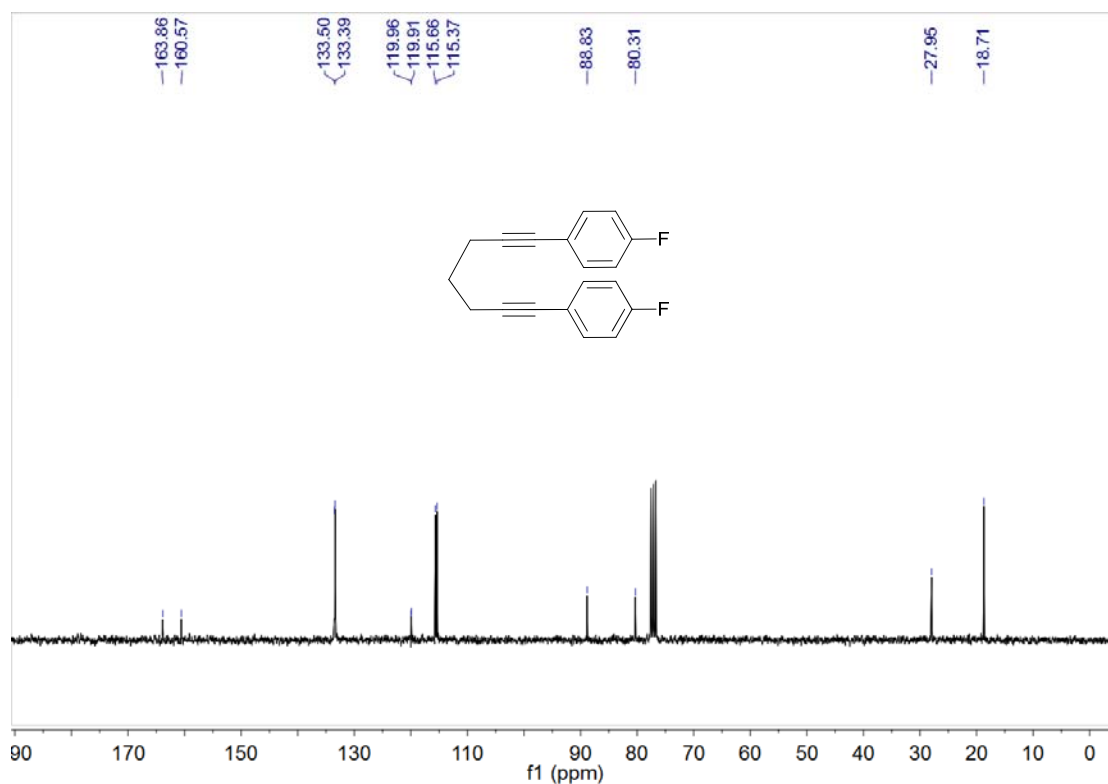
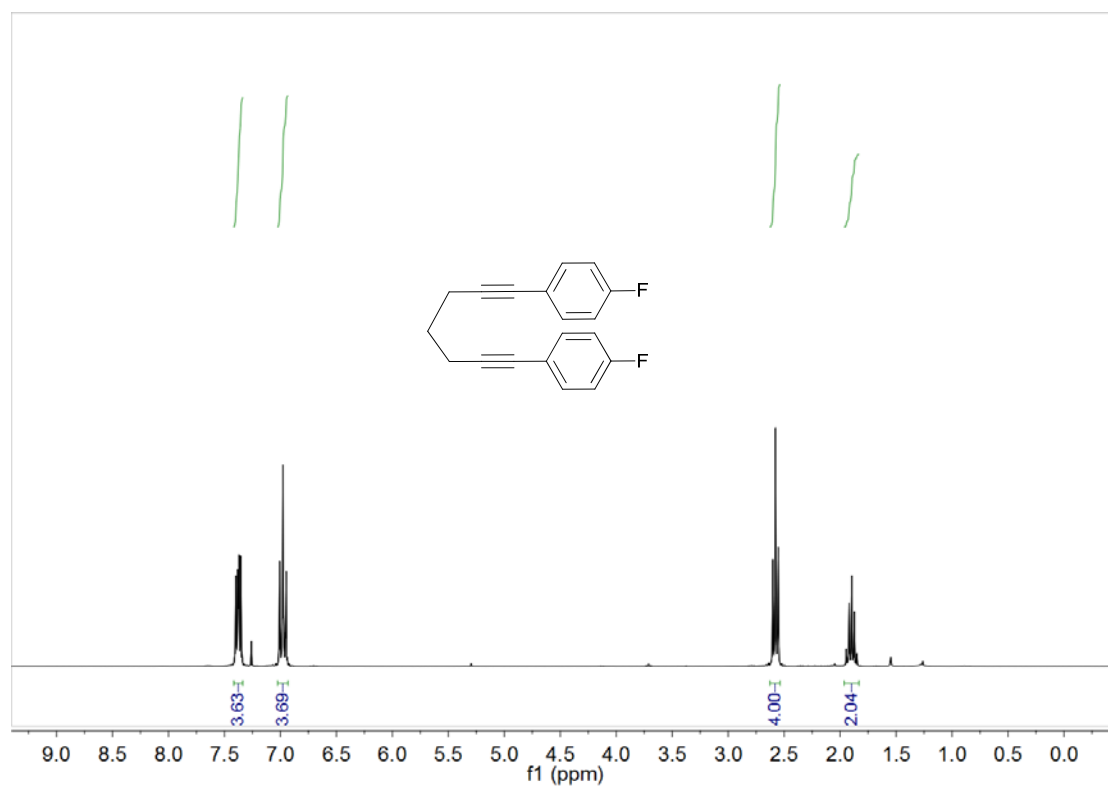
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

1c



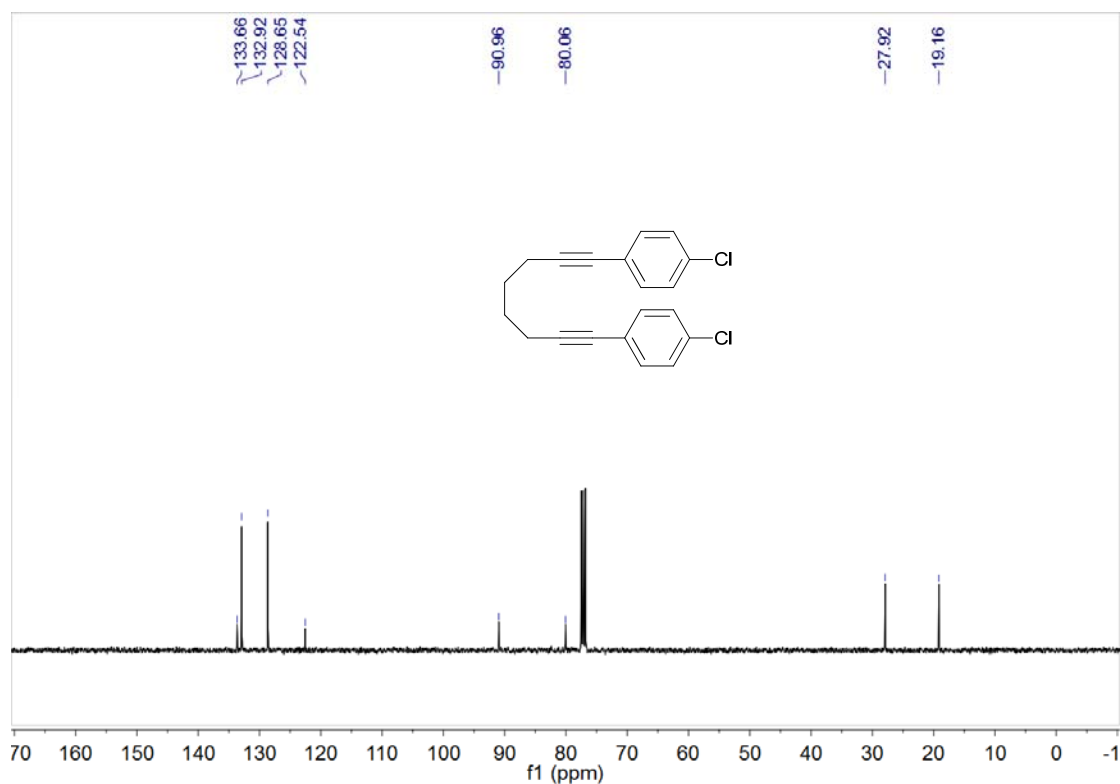
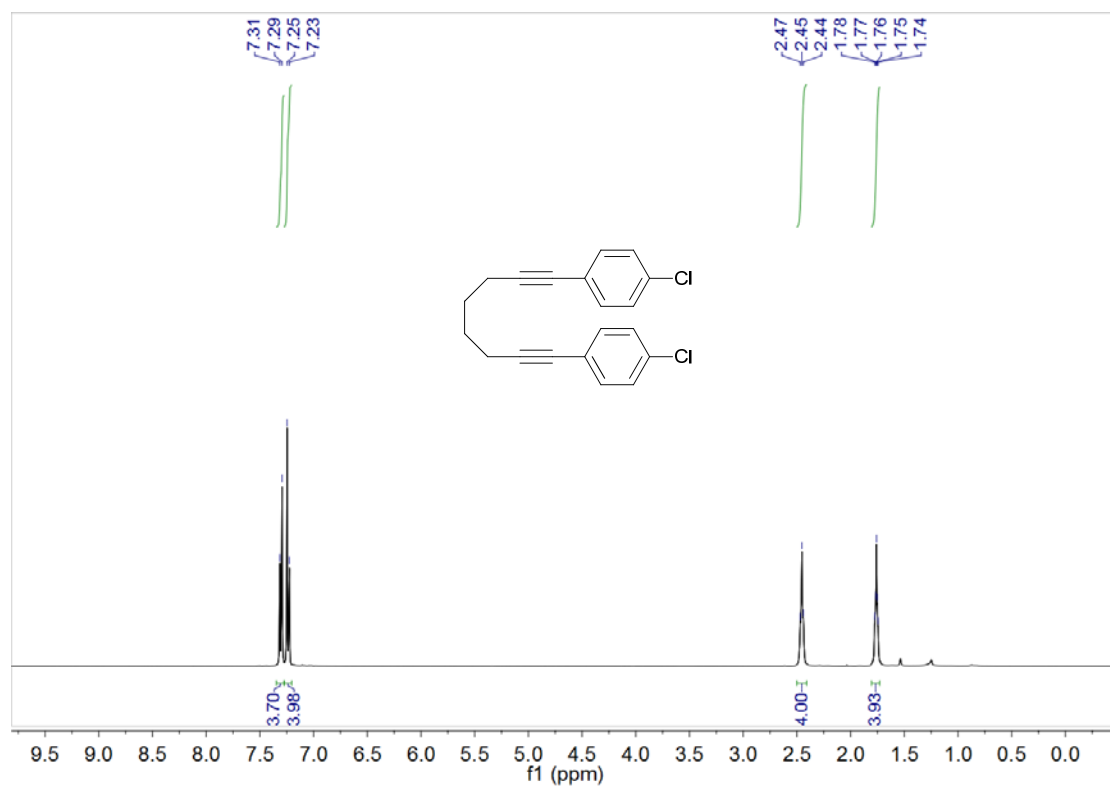
¹H NMR (300 MHz, CDCl₃) (up) and ¹³C NMR (76 MHz, CDCl₃) (down)

1d



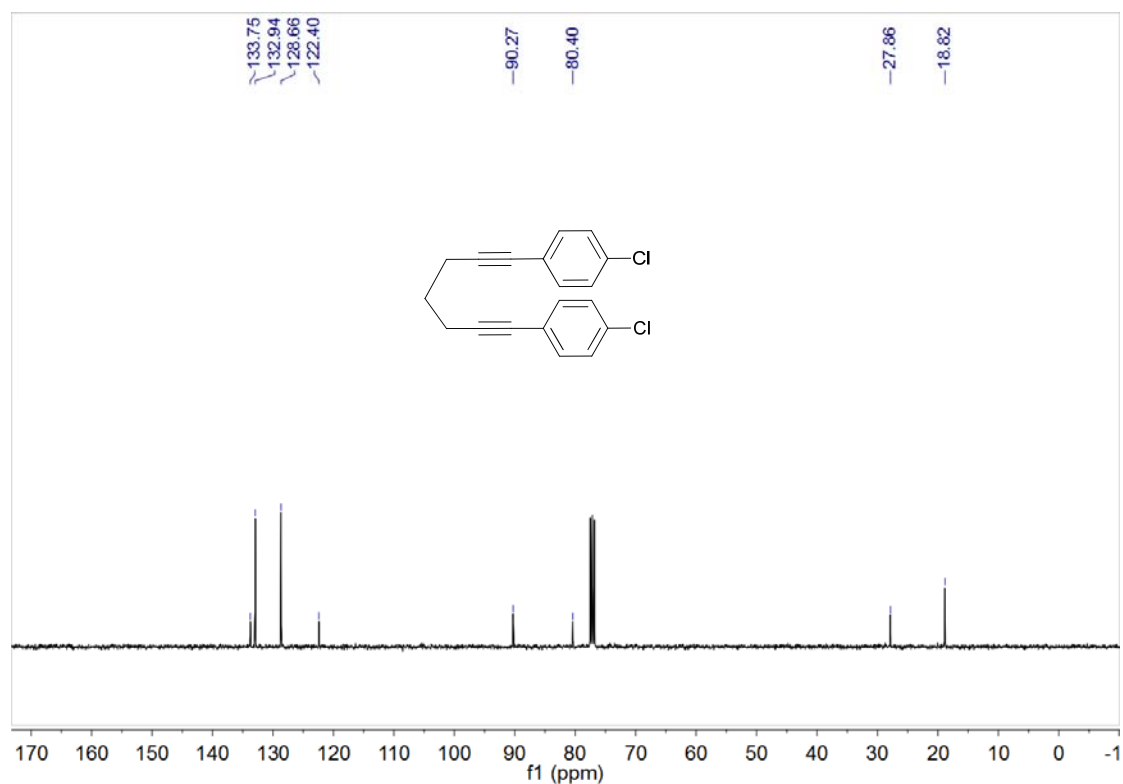
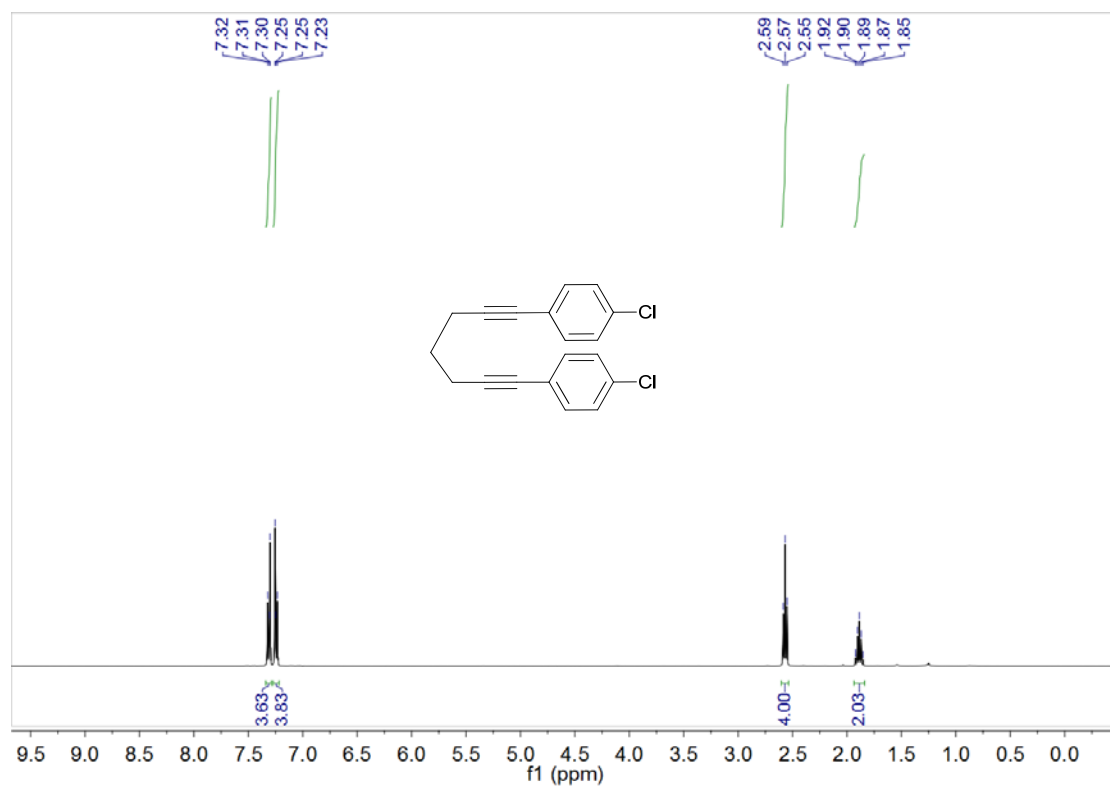
¹H NMR (300 MHz, CDCl₃) (up) and ¹³C NMR (76 MHz, CDCl₃) (down)

1e



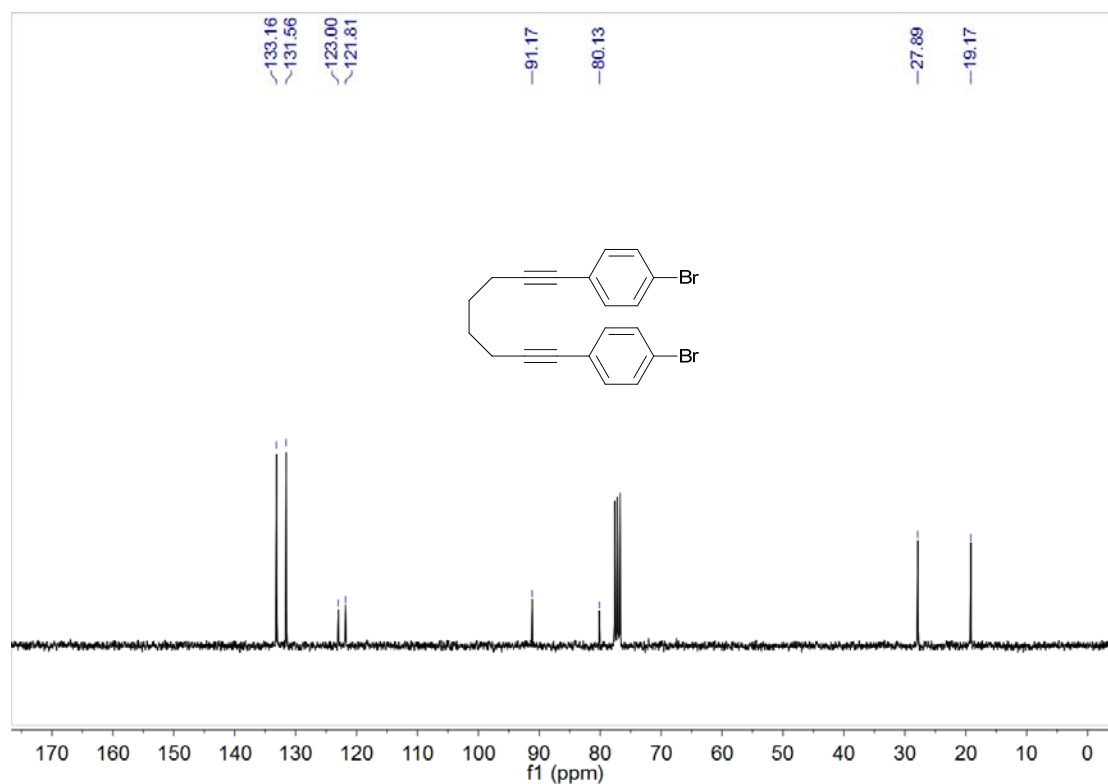
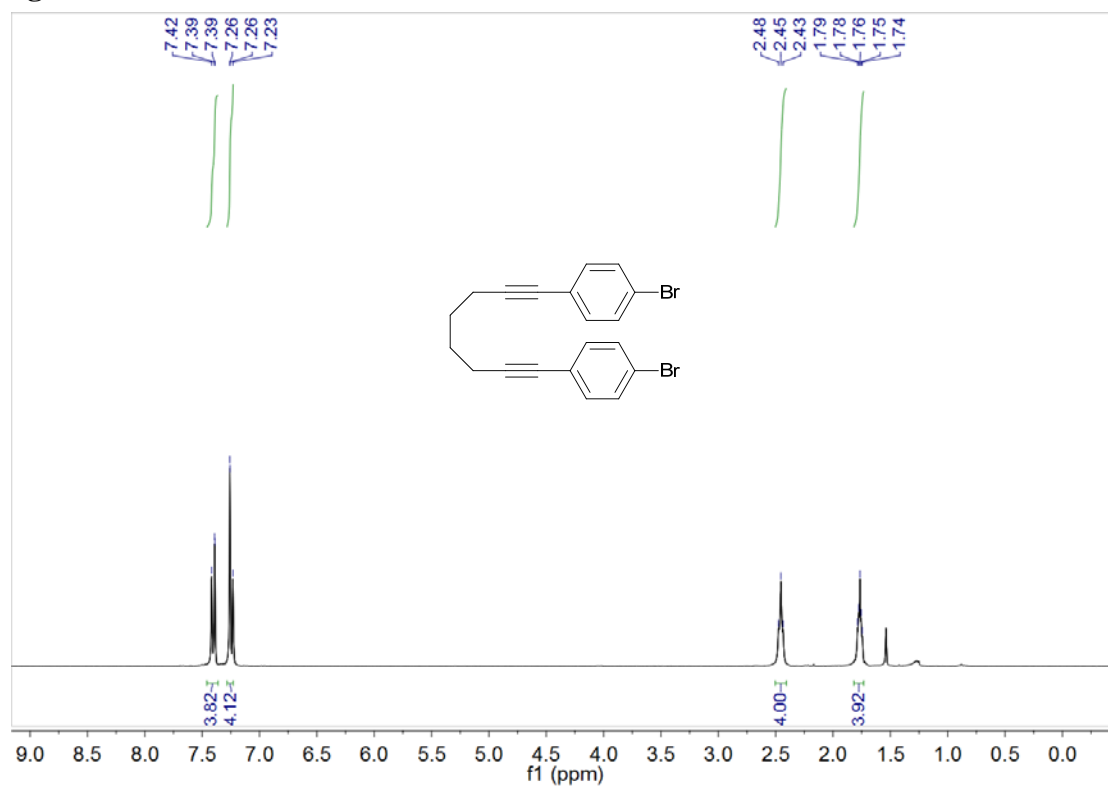
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

1f



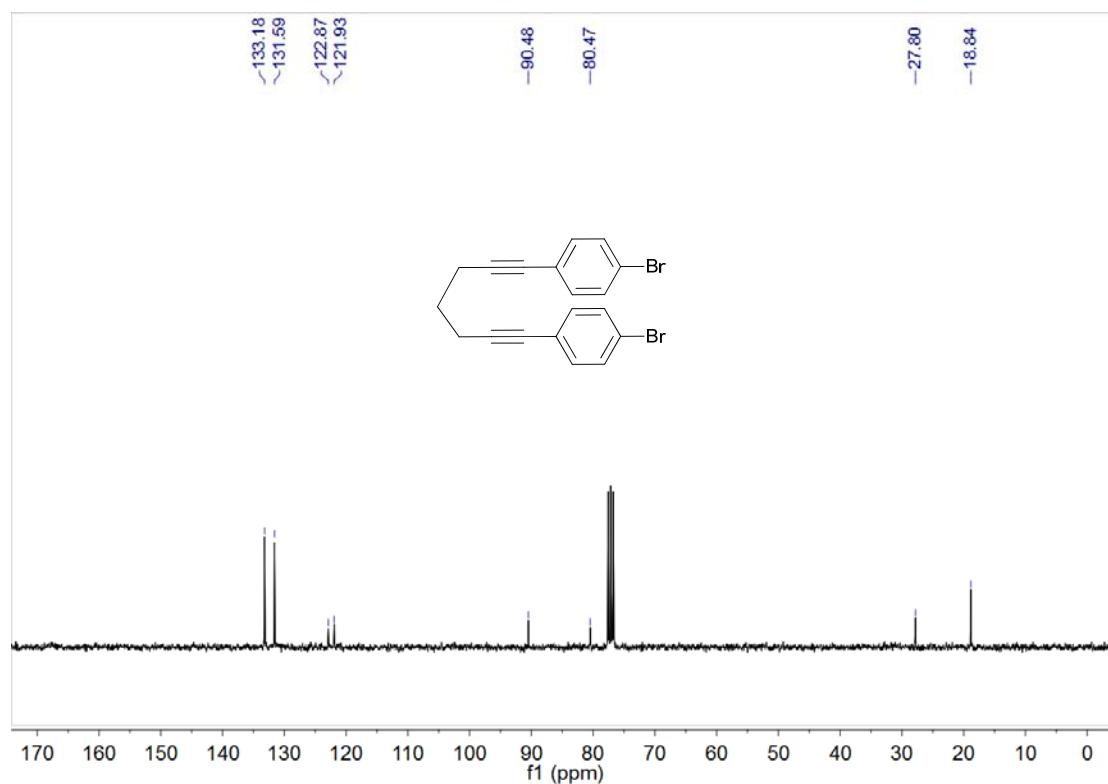
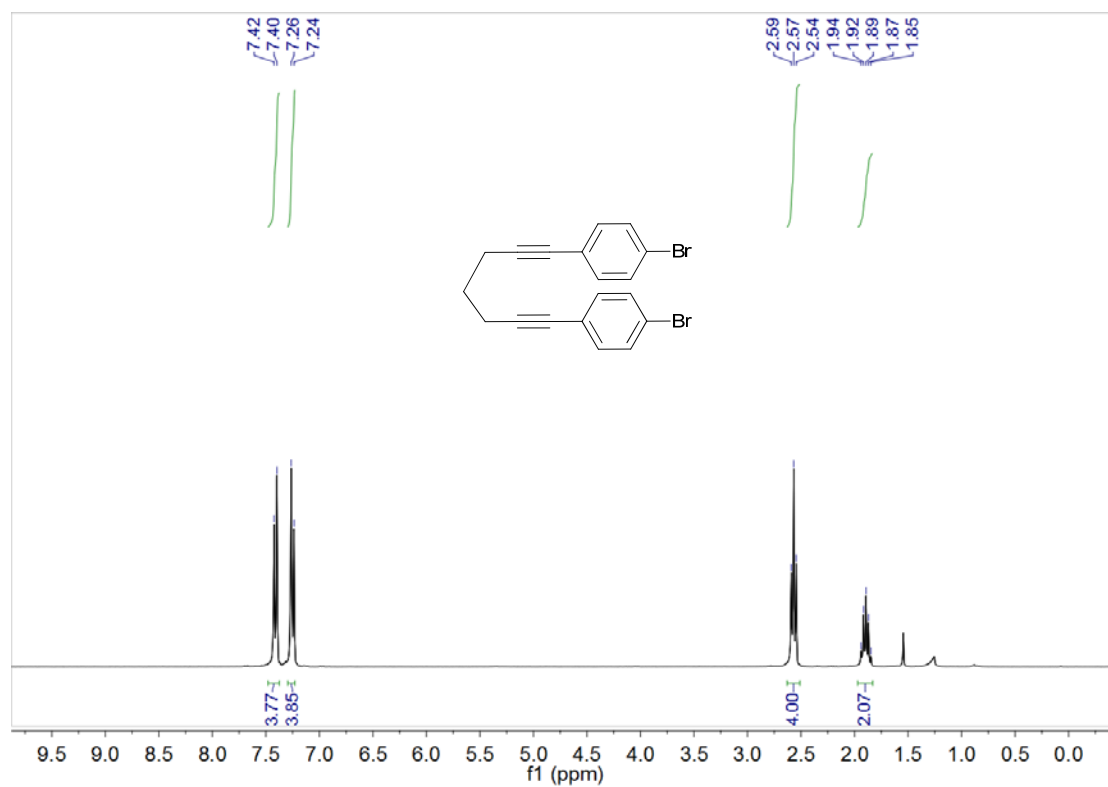
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

1g



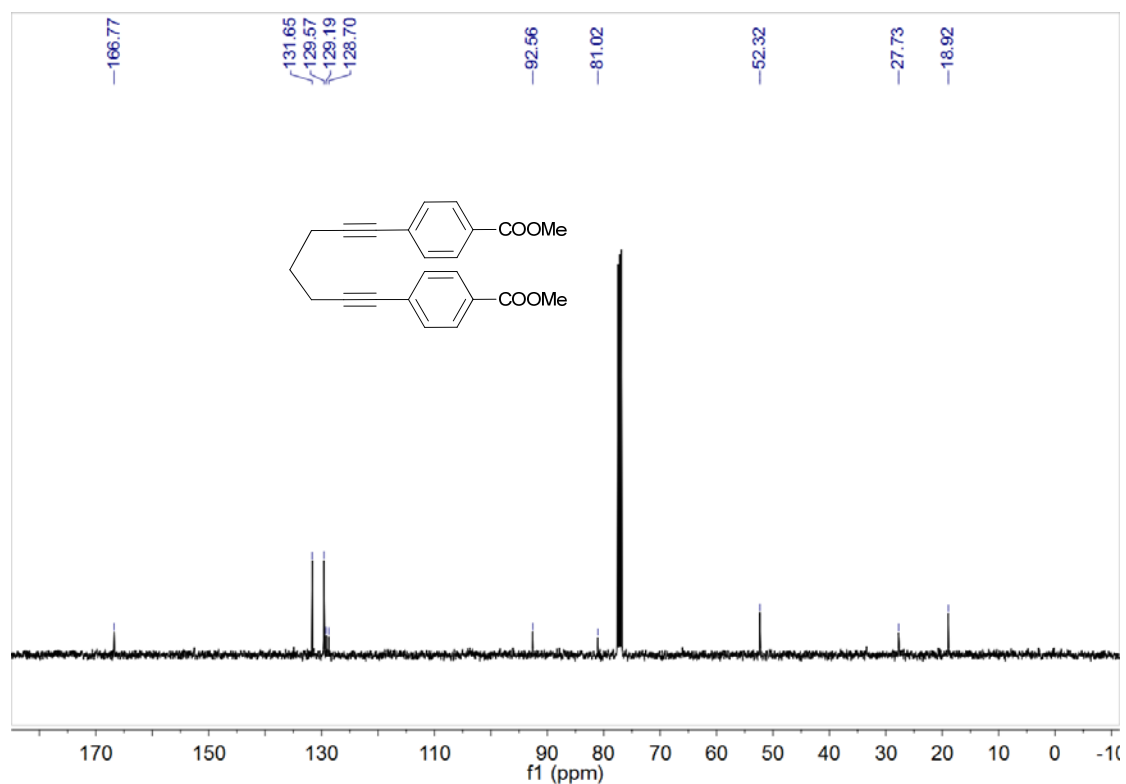
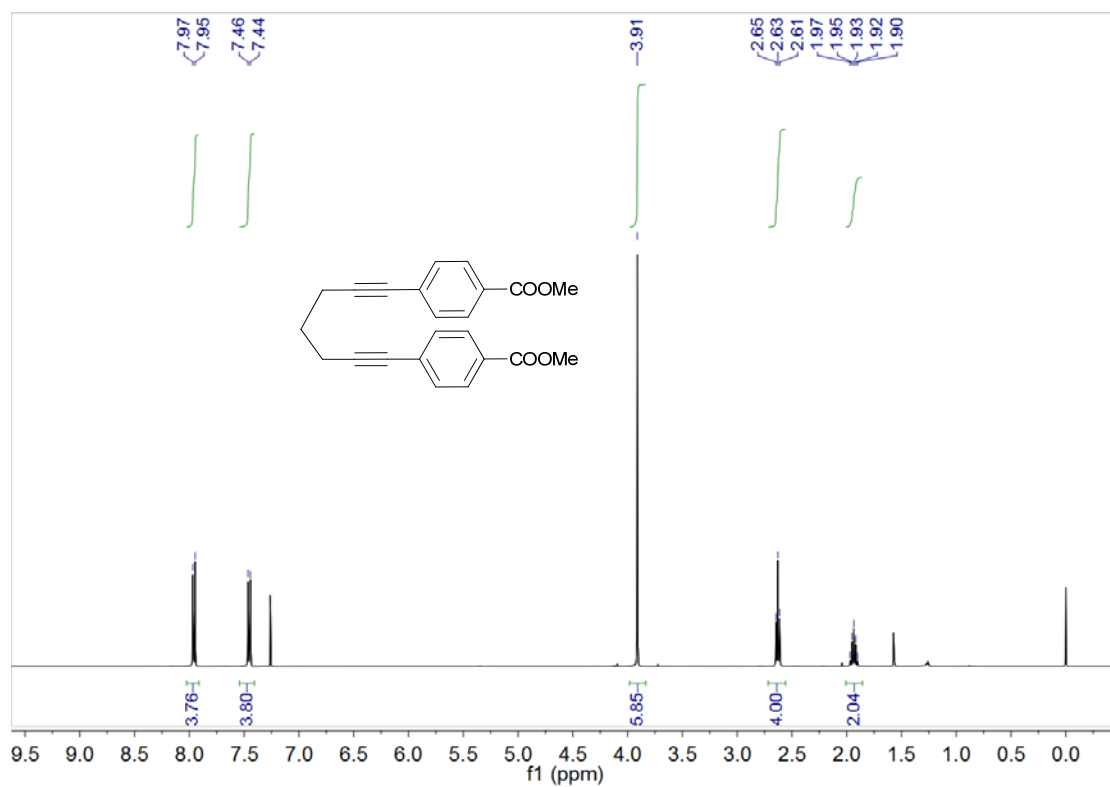
¹H NMR (300 MHz, CDCl₃) (up) and ¹³C NMR (76 MHz, CDCl₃) (down)

1h



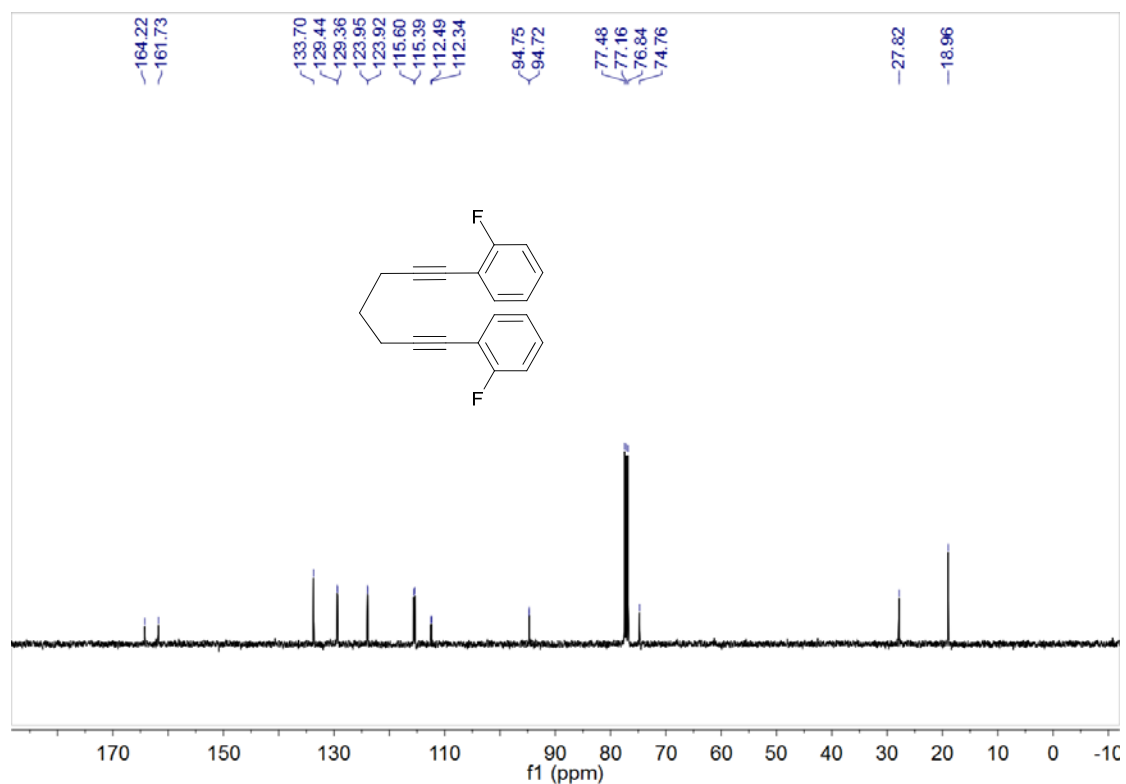
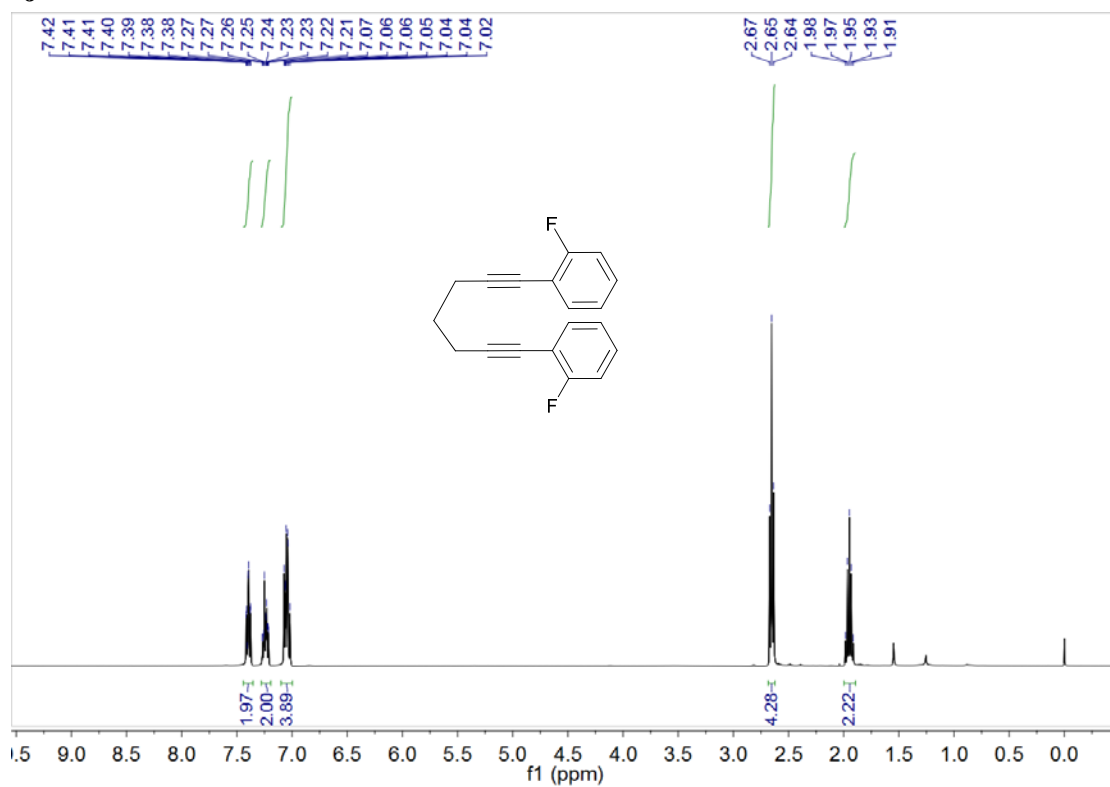
¹H NMR (300 MHz, CDCl₃) (up) and ¹³C NMR (76 MHz, CDCl₃) (down)

1i



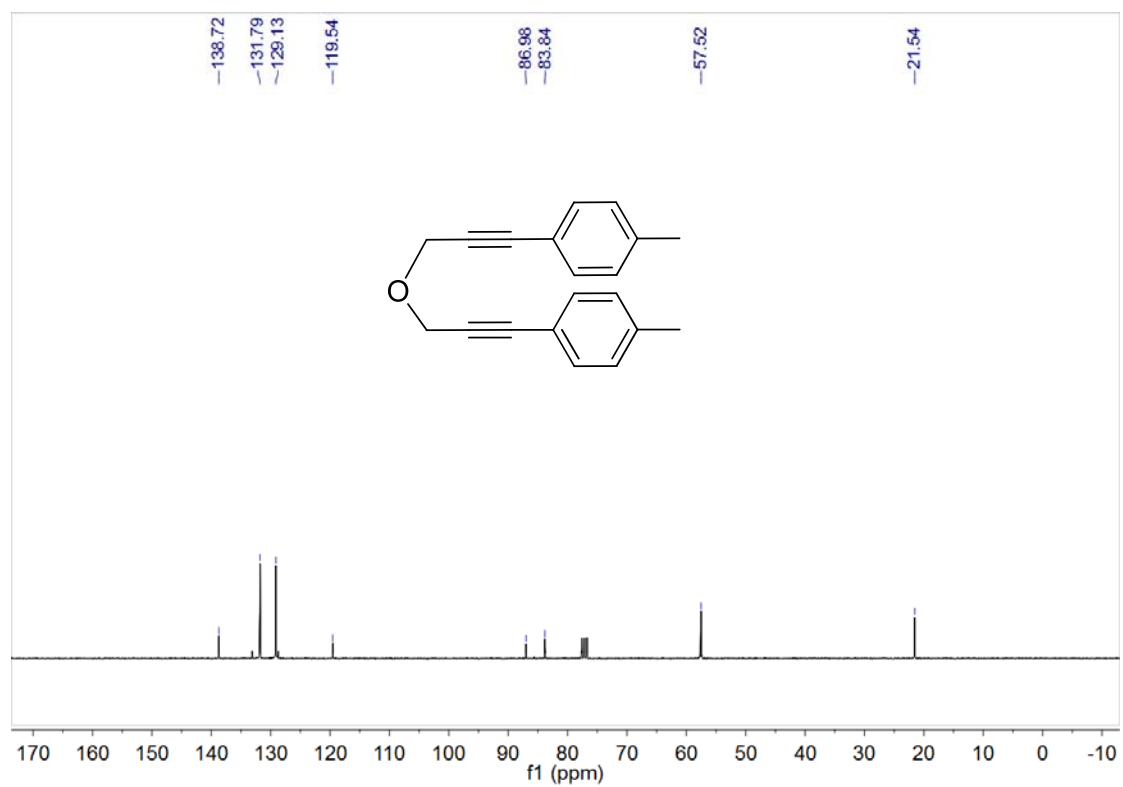
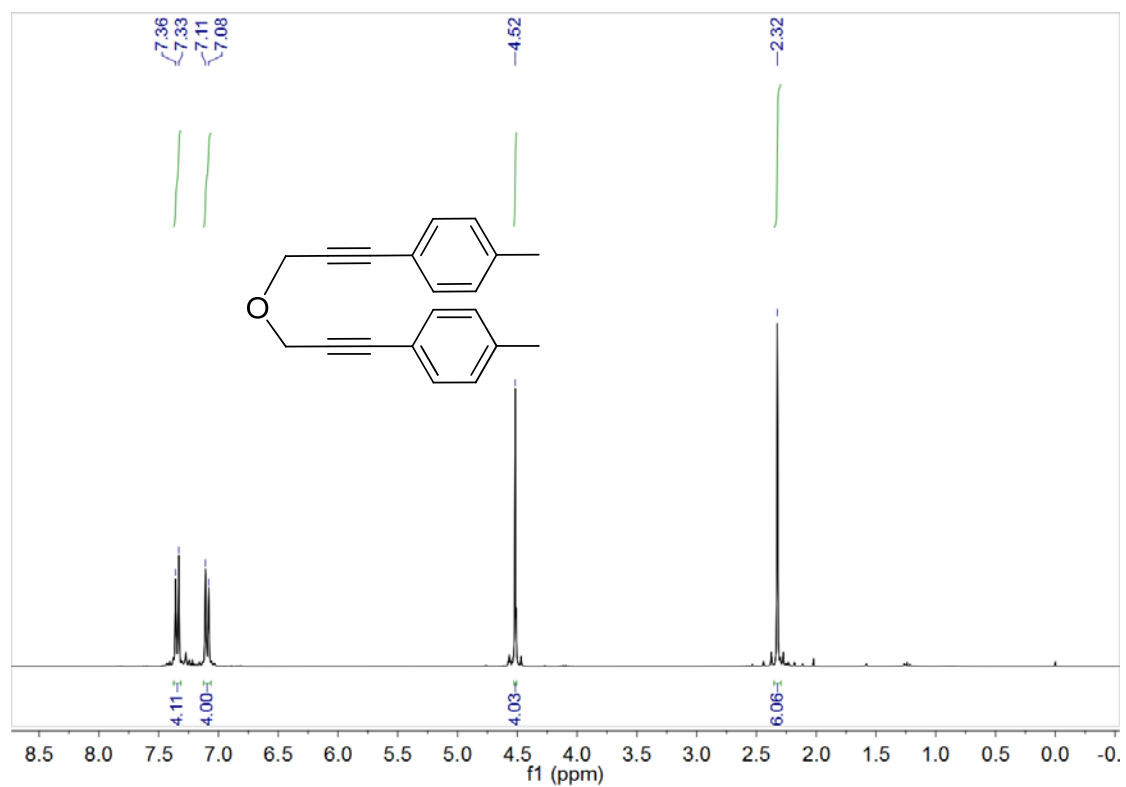
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

1j



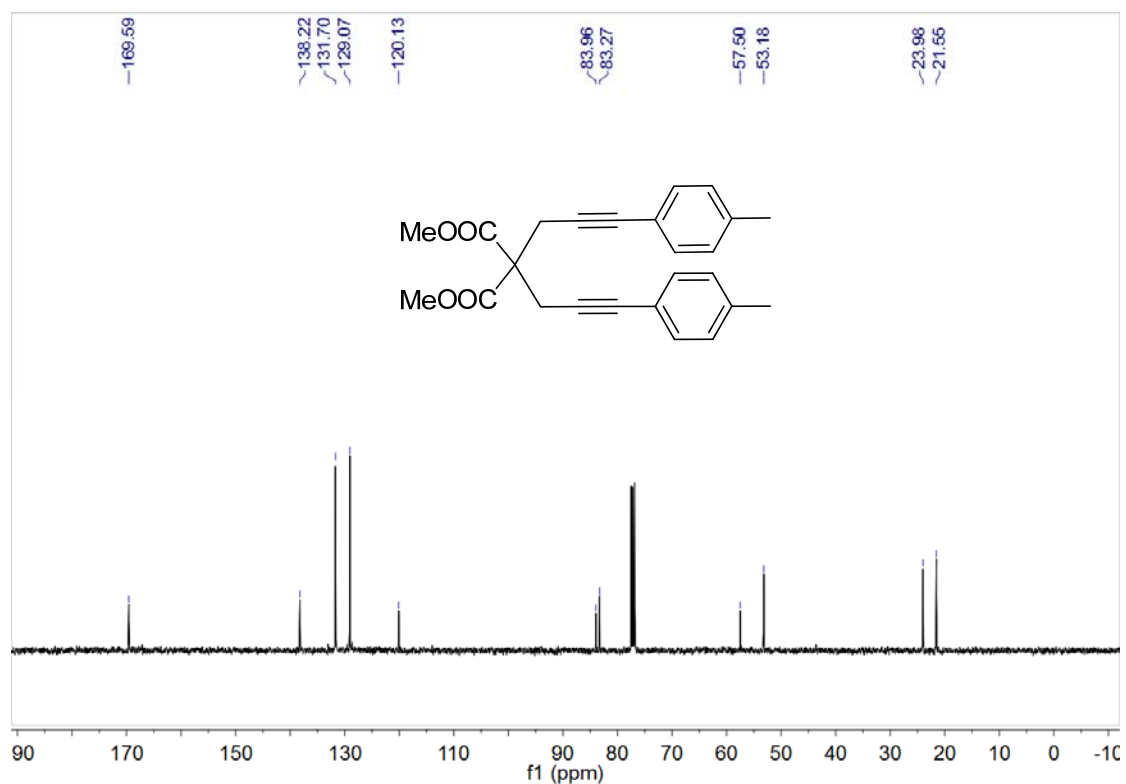
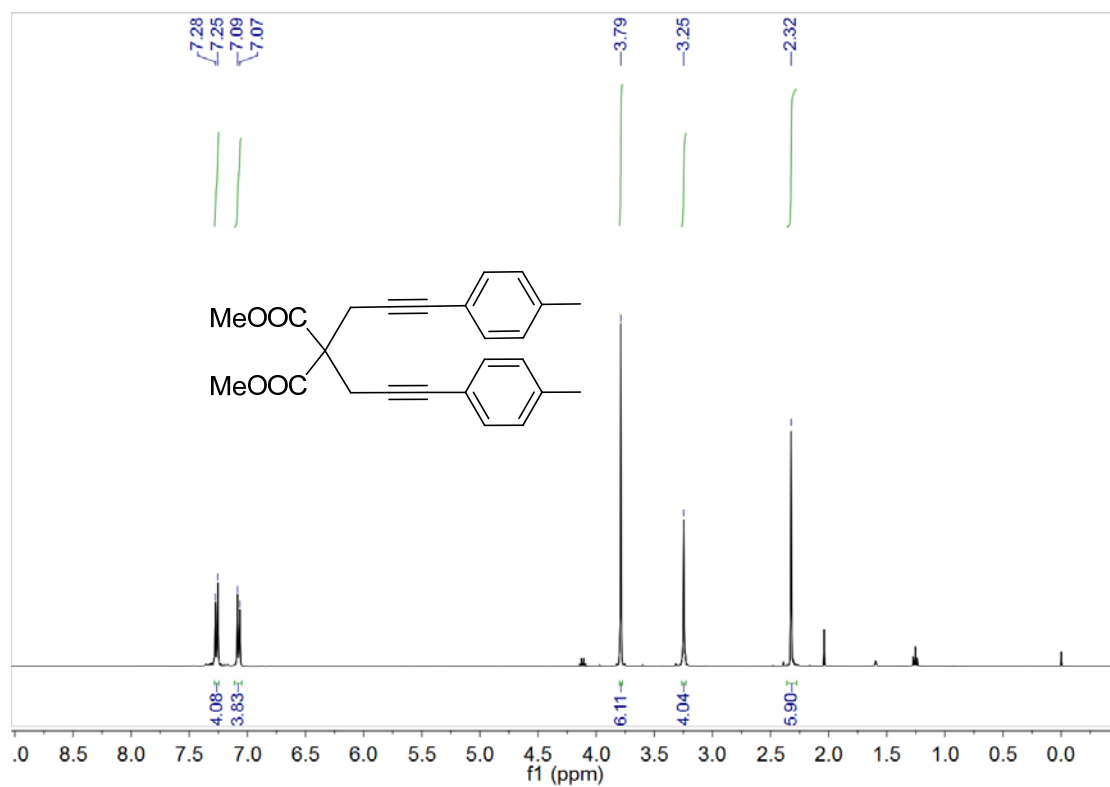
^1H NMR (400 MHz, CDCl_3) (up) and ^{13}C NMR (101 MHz, CDCl_3) (down)

11



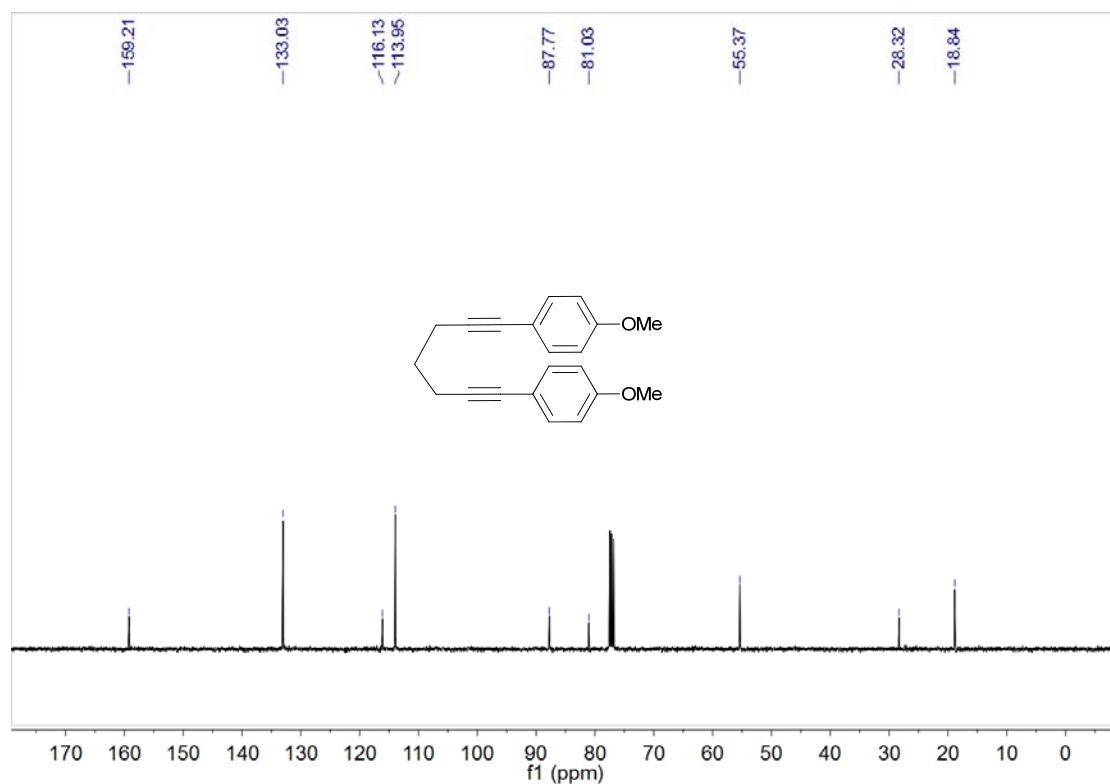
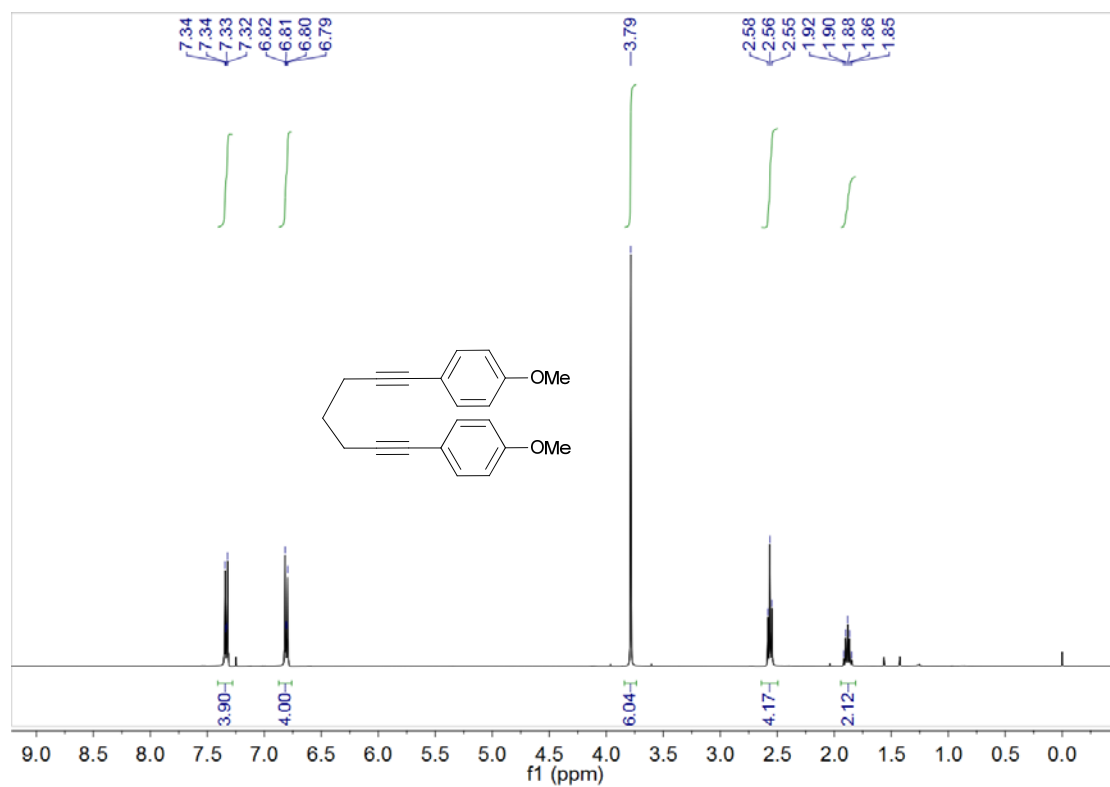
¹H NMR (300 MHz, CDCl₃) (up) and ¹³C NMR (76 MHz, CDCl₃) (down)

1m



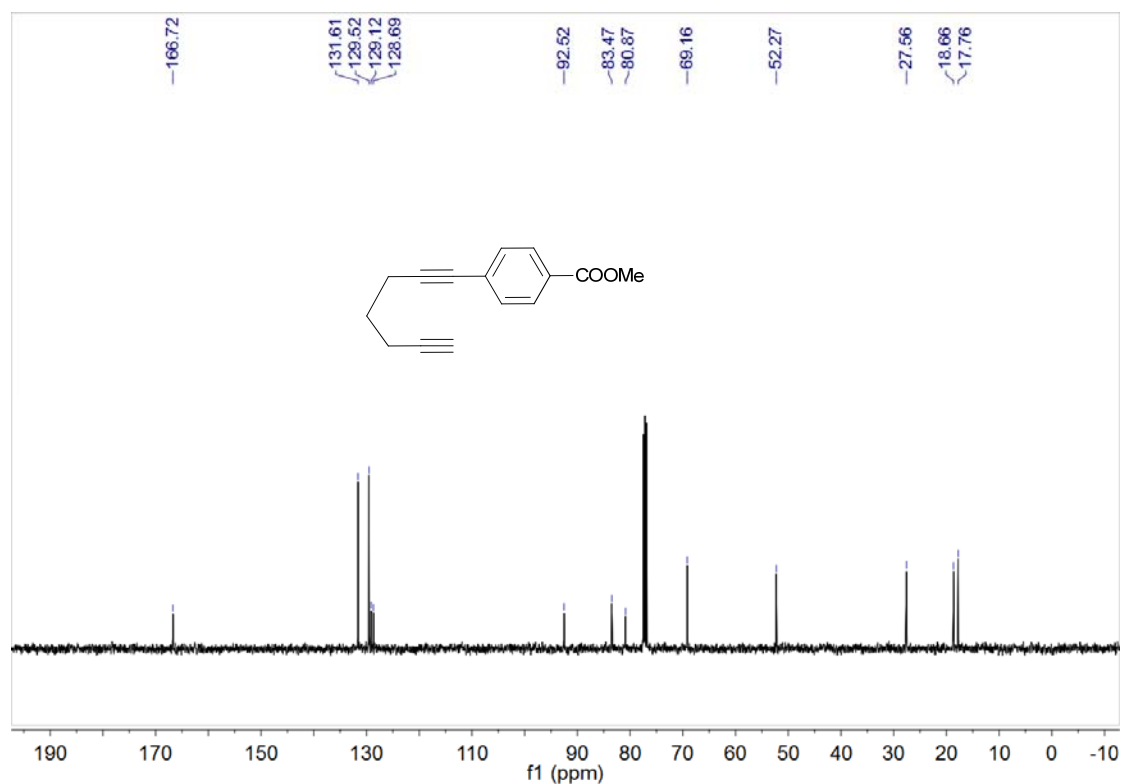
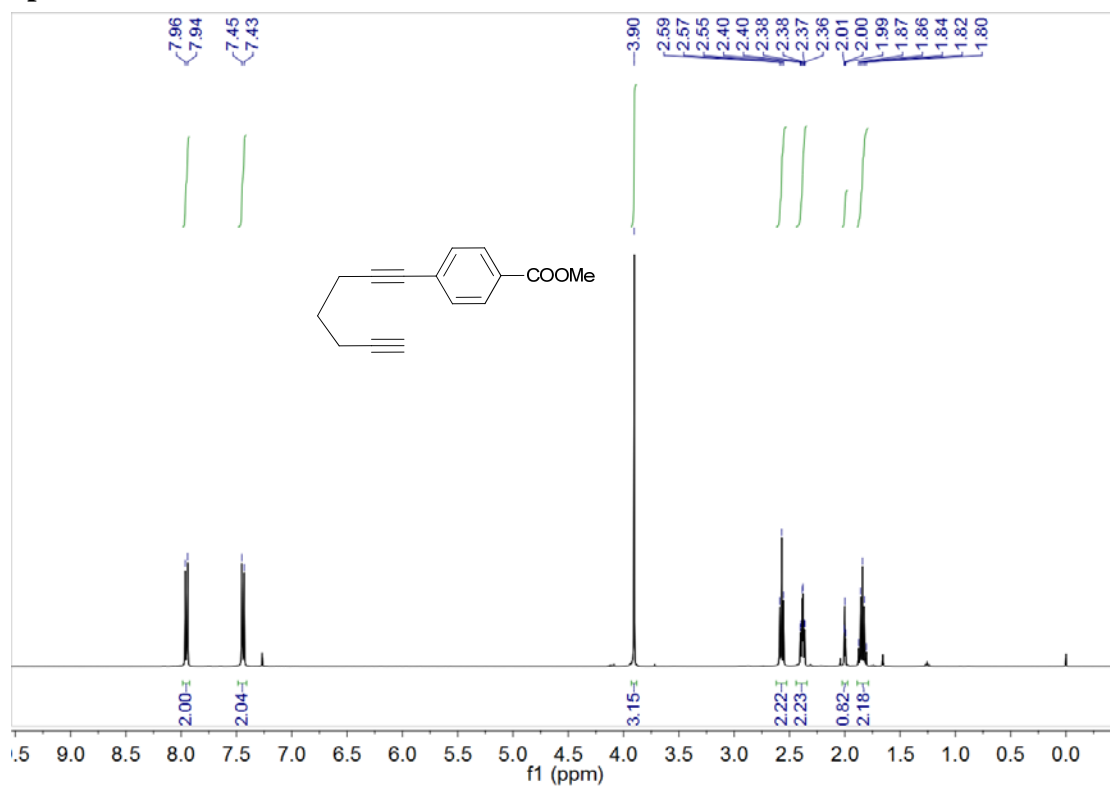
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

1n



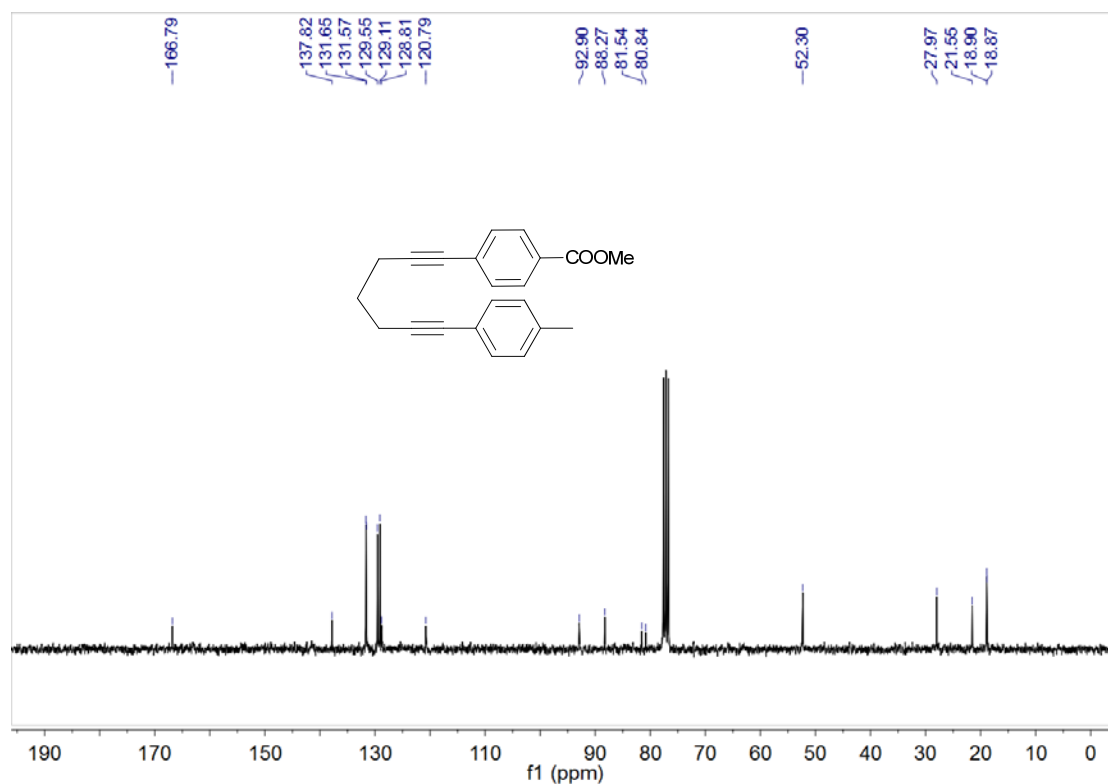
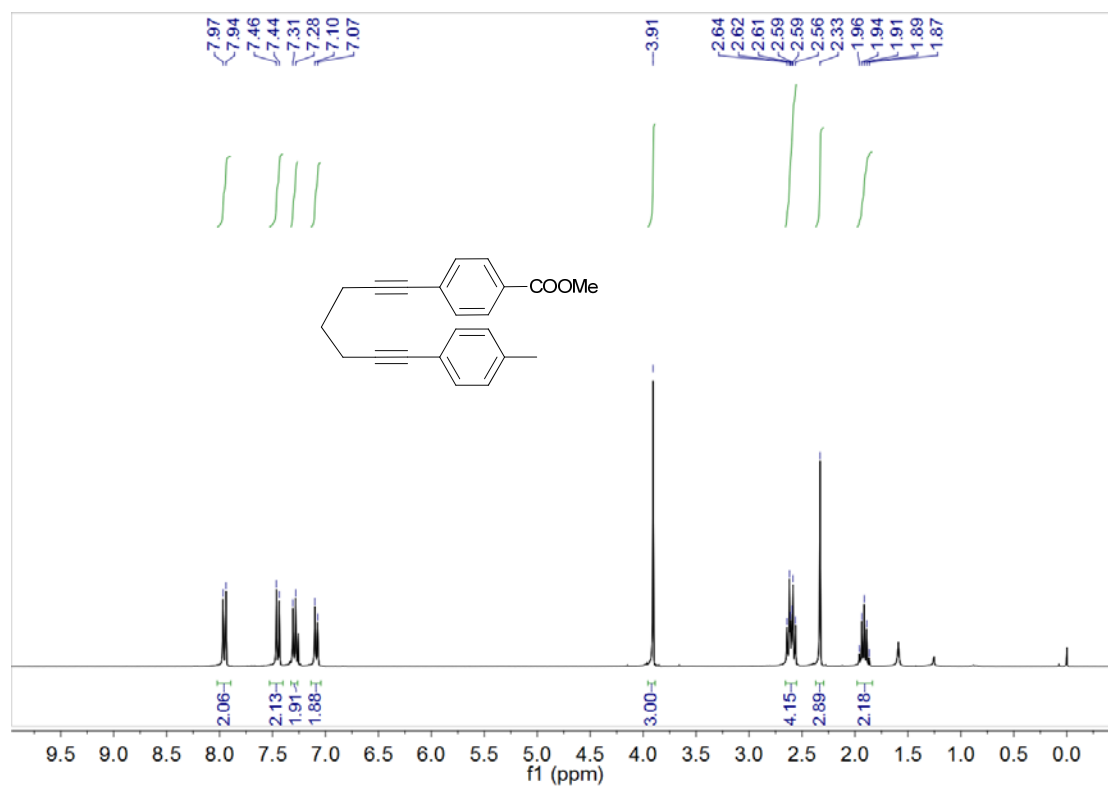
^1H NMR (400 MHz, CDCl_3) (up) and ^{13}C NMR (101 MHz, CDCl_3) (down)

1p



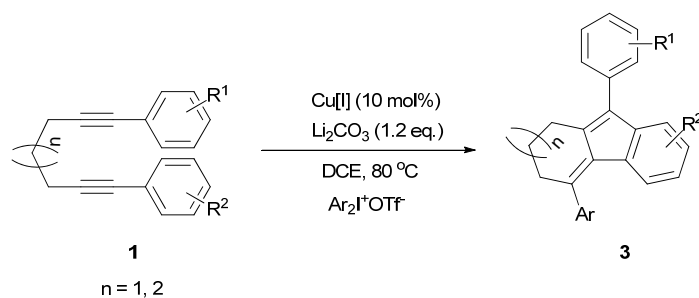
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

1o



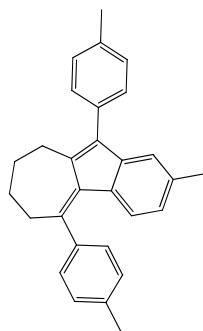
¹H NMR (300 MHz, CDCl₃) (up) and ¹³C NMR (76 MHz, CDCl₃) (down)

5. General procedure for the synthesis of products



A sealed tube was charged with the mixture of prepared diyne **1** (0.2 mmol), diaryliodonium salt **2** (0.24 mmol), Li_2CO_3 (0.24 mmol, 18 mg), CuBr ($n=2$, 0.02 mmol, 3 mg) or CuCl ($n=1$, 0.02 mmol, 2 mg). The tube was evacuated and recharged with N_2 for 4 times. Then dichloroethane (2.0 mL) were added, the tube was sealed and the mixture was allowed to stir at $80\text{ }^\circ\text{C}$ for 12 h. After completion, the mixture was cooled to room temperature, then water (4 mL) was added and the mixture was extracted with EA ($4\text{ mL} \times 3$), dried by anhydrous Na_2SO_4 . Evaporation of the solvent followed by purification on silica gel (PE or PE/EA) provided the corresponding product as a yellow solid. Or evaporation of the solvent and the yellow products were recrystallized from the dichloromethane or diethyl ether.

6. Characterization data of polycyclic products



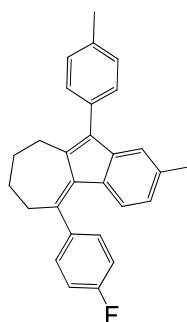
2-methyl-5,10-di-*p*-tolyl-6,7,8,9-tetrahydrobenzo[*a*]azulene (3aa): yellow solid, 50 mg, yield: 66%, melting point: 177 °C.

¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.23 - 7.37 (m, 8H), 6.96 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.25 (d, *J* = 7.9 Hz, 1H), 2.91 - 2.84 (m, 2H), 2.81 - 2.75 (m, 2H), 2.44 (s, 3H), 2.43 (s, 3H), 2.23 (s, 3H), 2.06 - 1.92 (m, 2H), 1.91 - 1.71 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 150.3, 143.8, 141.8, 139.9, 139.3, 139.1, 137.6, 136.9, 136.2, 133.4, 132.7, 129.5(2×CH), 129.5(2×CH), 129.2(2×CH), 128.3(2×CH), 124.8, 122.7, 119.9, 36.2, 26.9, 25.7, 25.5, 21.6, 21.5(2×CH₃).

ESI-HRMS: *m/z* calcd for C₂₉H₂₈ [M+H]⁺: 377.2264; found: 377.2266.

GC-MS *m/z*: 376



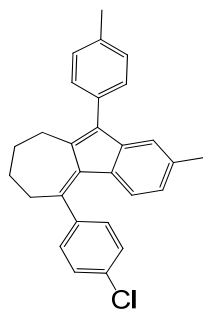
5-(4-fluorophenyl)-2-methyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3ab): yellow solid, 44 mg, yield: 58%, melting point: 202 °C.

¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.40 - 7.26 (m, 6H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.97 (s, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 7.8 Hz, 1H), 2.88 - 2.81 (m, 2H), 2.81 - 2.73 (m, 2H), 2.43 (s, 3H), 2.24 (s, 3H), 2.05 - 1.95 (m, 2H), 1.87 - 1.77 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 162.6 (d, *J* = 246.8 Hz), 148.6, 143.9, 140.7 (d, *J* = 3.4 Hz), 139.8, 139.7, 139.6, 137.1, 136.6, 133.2, 132.5, 130.1 (d, *J* = 7.8 Hz, 2×CH), 129.5(2×CH), 129.3(2×CH), 124.9, 122.6, 120.1, 115.8 (d, *J* = 21.2 Hz, 2×CH), 36.2, 26.9, 25.6, 25.4, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₂₈H₂₅F [M+H]⁺: 381.2013; found: 381.2015.

GC-MS *m/z*: 380



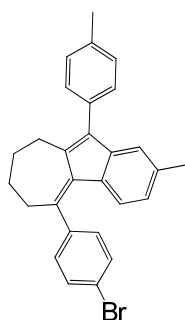
5-(4-chlorophenyl)-2-methyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3ac):

yellow solid, 45 mg, yield: 57%, melting point: 180 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 - 7.28 (m, 8H), 6.96 (s, 1H), 6.62 (d, J = 7.9 Hz, 1H), 6.23 (d, J = 7.9 Hz, 1H), 2.86 - 2.80 (m, 2H), 2.74 - 2.80 (m, 2H), 2.43 (s, 3H), 2.24 (s, 3H), 2.05 - 1.96 (m, 2H), 1.87 - 1.77 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 148.2, 143.9, 143.2, 139.9, 139.7, 139.7, 137.1, 136.7, 133.7, 133.0, 132.5, 129.8(2×CH), 129.5(2×CH), 129.3(2×CH), 129.1(2×CH), 125.0, 122.6, 120.1, 36.0, 26.9, 25.6, 25.4, 21.6, 21.5.

ESI-HRMS: m/z calcd for C₂₈H₂₅Cl [M+H]⁺: 397.1718; found: 397.1717.



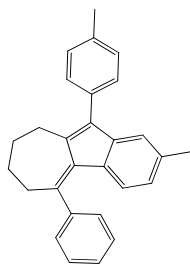
5-(4-bromophenyl)-2-methyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3ad):

yellow solid, 52 mg, yield: 59%, melting point: 172 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.60 - 7.53 (m, 2H), 7.31 (dd, J = 15.4, 7.3 Hz, 4H), 7.26 - 7.23 (m, 2H), 6.96 (s, 1H), 6.63 (d, J = 7.8 Hz, 1H), 6.23 (d, J = 7.8 Hz, 1H), 2.87 - 2.80 (m, 2H), 2.80 - 2.73 (m, 2H), 2.43 (s, 3H), 2.24 (s, 3H), 2.05 - 1.96 (m, 2H), 1.86 - 1.77 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 148.1, 144.0, 143.7, 139.8, 139.8, 139.7, 137.1, 136.7, 133.0, 132.5, 132.0(2×CH), 130.1(2×CH), 129.5(2×CH), 129.3(2×CH), 125.0, 122.6, 121.9, 120.1, 36.0, 26.9, 25.6, 25.4, 21.6, 21.5.

ESI-HRMS: m/z calcd for C₂₈H₂₅Br [M+H]⁺: 443.1196; found: 443.1197.



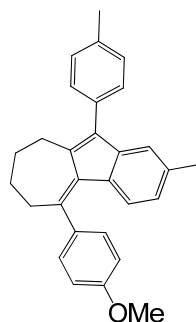
2-methyl-5-phenyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3ae): yellow solid, 45 mg, yield: 62% , melting point: 192°C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.45 - 7.26 (m, 9H), 6.96 (s, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 7.8 Hz, 1H), 2.91 - 2.84 (m, 2H), 2.82 - 2.75 (m, 2H), 2.42 (s, 3H), 2.22 (s, 3H), 2.06 - 1.97 (m, 2H), 1.88 - 1.78 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 150.0, 144.9, 143.9, 139.9, 139.4, 139.4, 137.0, 136.4, 133.3, 132.7, 129.5(2×CH), 129.3(2×CH), 128.8(2×CH), 128.2(2×CH), 127.8, 124.8, 122.7, 119.9, 36.2, 26.9, 25.7, 25.5, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₂₈H₂₆ [M+H]⁺: 363.2107; found: 363.2108.

GC-MS *m/z*: 362

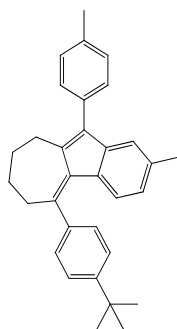


5-(4-methoxyphenyl)-2-methyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3af): yellow solid, 34.5 mg, yield: 44%, melting point: 108°C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.28 - 7.39 (m, 6H), 7.02 - 6.95 (m, 3H), 6.63 (dd, *J* = 7.8, 0.7 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 2.92 - 2.85 (m, 2H), 2.83 - 2.76 (m, 2H), 2.45 (s, 3H), 2.26 (s, 3H), 2.07 - 1.97 (m, 2H), 1.89 - 1.80 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 159.5, 150.0, 143.8, 139.8, 139.3, 139.1, 137.0, 136.9, 136.2, 133.4, 132.8, 129.9(2×CH), 129.5(2×CH), 129.2(2×CH), 124.8, 122.6, 119.9, 114.2(2×CH), 55.5, 36.2, 26.8, 25.6(2×CH₂), 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₂₉H₂₈O [M+H]⁺: 393.2213; found: 393.2211.



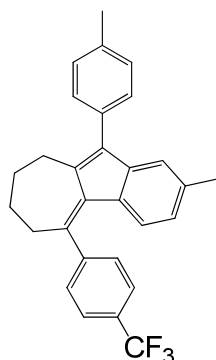
5-(4-(tert-butyl)phenyl)-2-methyl-10-(p-tolyl)-6,7,8,9-tetrahydrobenzo[a]azulene

(3ag): yellow solid, 33.5 mg, yield: 40%, melting point: 139°C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 (d, 2H), 7.34 (d, 2H), 7.31 - 7.26 (m, 4H), 6.96 (s, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 2.90 - 2.85 (m, 2H), 2.81 - 2.75 (m, 2H), 2.42 (s, 3H), 2.22 (s, 3H), 2.05 - 1.96 (m, 2H), 1.86 - 1.78 (m, 2H), 1.39 (s, 9H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 151.0, 150.4, 143.8, 141.8, 139.9, 139.3, 139.1, 136.9, 136.2, 133.4, 132.8, 129.5(2×CH), 129.2(2×CH), 128.0(2×CH), 125.6(2×CH), 124.8, 122.7, 119.8, 36.2, 34.8, 31.6(3×CH₃), 26.9, 25.7, 25.5, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₃₂H₃₄ [M+H]⁺: 419.2733; found: 419.2734.



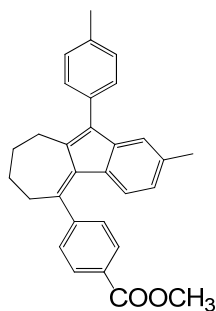
2-methyl-10-(p-tolyl)-5-(4-(trifluoromethyl)phenyl)-6,7,8,9-tetrahydrobenzo[a]azulene

(3ah): yellow solid, 48 mg, yield: 56%, melting point: 141 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (q, *J* = 8.0 Hz, 4H), 6.96 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.09 (d, *J* = 7.8 Hz, 1H), 2.87 - 2.81 (m, 2H), 2.81 - 2.75 (m, 2H), 2.43 (s, 3H), 2.23 (s, 3H), 2.07 - 1.97 (m, 2H), 1.87 - 1.79 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 148.6, 147.5, 144.1, 140.1, 140.1, 139.6, 137.2, 136.9, 132.9, 132.4, 129.9 (q, *J* = 32.6 Hz), 129.5(2×CH), 129.3(2×CH), 128.7(2×CH), 125.9 (q, *J* = 3.5 Hz, 2×CH), 125.0, 124.4 (q, *J* = 272.2 Hz), 122.6, 120.2, 35.9, 27.0, 25.7, 25.3, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₂₉H₂₅F₃ [M+H]⁺: 431.1981; found: 431.1980.

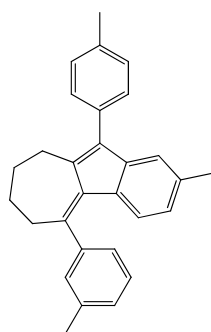


methyl 4-(2-methyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulen-5-yl)benzoate (3ai): yellow solid, 54 mg, yield: 64%, melting point: 136°C.

^1H NMR (400 MHz, CHLOROFORM- D) δ 8.11 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.36 - 7.27 (m, 4H), 6.95 (s, 1H), 6.57 (d, $J = 7.8$ Hz, 1H), 6.12 (d, $J = 7.8$ Hz, 1H), 3.97 (s, 3H), 2.91 - 2.82 (m, 2H), 2.82 - 2.74 (m, 2H), 2.44 (s, 3H), 2.23 (s, 3H), 2.08 - 1.96 (m, 2H), 1.88 - 1.79 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM- D) δ 167.1, 149.8, 148.2, 144.0, 140.0, 139.9, 139.7, 137.2, 136.8, 132.9, 132.4, 130.2(2 \times CH), 129.5(2 \times CH), 129.4, 129.3(2 \times CH), 128.4(2 \times CH), 125.0, 122.7, 120.1, 52.4, 35.8, 27.0, 25.7, 25.3, 21.6, 21.5.

ESI-HRMS: m/z calcd for $\text{C}_{30}\text{H}_{28}\text{O}_2$ $[\text{M}+\text{H}]^+$: 421.2162; found: 421.2160.



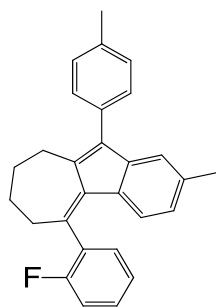
2-methyl-5-(*m*-tolyl)-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3aj): yellow solid, 37.5 mg, yield: 50%, melting point: 161°C.

^1H NMR (400 MHz, CHLOROFORM- D) δ 7.37 - 7.27 (m, 5H), 7.23 - 7.13 (m, 3H), 6.96 (s, 1H), 6.59 (d, $J = 7.9$ Hz, 1H), 6.19 (d, $J = 7.9$ Hz, 1H), 2.91 - 2.84 (m, 2H), 2.81 - 2.75 (m, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 2.23 (s, 3H), 2.06 - 1.97 (m, 2H), 1.87 - 1.78 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM- D) δ 150.3, 144.9, 143.8, 139.9, 139.2, 138.4, 137.0, 136.3, 133.3, 132.7, 129.5(2 \times CH), 129.2(2 \times CH), 128.8, 128.7, 128.5, 125.2, 124.8, 122.7, 119.9, 36.2, 26.9, 25.7, 25.5, 21.6(2 \times CH $_3$), 21.5.

ESI-HRMS: m/z calcd for $\text{C}_{29}\text{H}_{28}$ $[\text{M}+\text{H}]^+$: 377.2264; found: 377.2266.

GC-MS m/z : 376



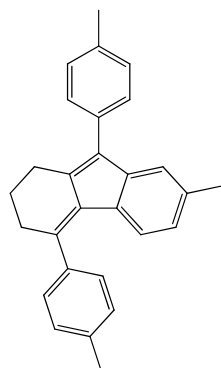
5-(2-fluorophenyl)-2-methyl-10-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene (3ak): yellow solid, 22 mg, yield: 29%, melting point: 187°C.

¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.43 - 7.28 (m, 6H), 7.22 - 7.16 (m, 2H), 6.95 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.15 (d, *J* = 7.9 Hz, 1H), 2.87 - 2.72 (m, 4H), 2.43 (s, 3H), 2.23 (s, 3H), 2.09 - 1.99 (m, 2H), 1.89 - 1.78 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 159.2 (d, *J* = 246.2 Hz), 144.1, 143.2, 140.8, 139.8, 137.1, 136.7, 133.0, 132.4 (d, *J* = 21.6 Hz), 130.7, 130.6, 129.6 (d, *J* = 7.6 Hz), 129.5(2×CH), 129.3(2×CH), 125.0, 124.5, 124.5, 122.2, 120.1, 116.3 (d, *J* = 21.8 Hz), 35.0, 26.7, 25.6, 25.2, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₂₈H₂₅F [M+H]⁺: 381.2013; found: 381.2015.

GC-MS *m/z*: 380



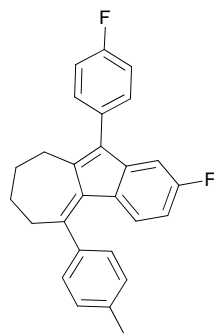
7-methyl-4,9-di-*p*-tolyl-2,3-dihydro-1H-fluorene (3ba): yellow solid, 58 mg, yield: 80%, melting point: 125°C.

¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.34 - 7.21 (m, 6H), 7.09 (s, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 2.79 - 2.73 (m, 2H), 2.69 (t, *J* = 5.9 Hz, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 2.27 (s, 3H), 2.00 - 1.91 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-*D*) δ 145.2, 144.1, 139.2, 137.8, 136.7, 136.7, 135.6, 135.3, 134.8, 132.6, 131.8, 129.4(2×CH), 129.2 (2×CH), 129.0(2×CH), 128.2(2×CH), 124.6, 122.4, 119.8, 34.8, 24.8, 24.1, 21.8, 21.5, 21.4.

ESI-HRMS: *m/z* calcd for C₂₈H₂₆ [M+H]⁺: 363.2107; found: 363.2107.

GC-MS *m/z*: 362



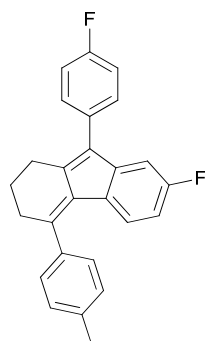
2-fluoro-10-(4-fluorophenyl)-5-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene 3ca:

yellow solid, 32 mg, yield: 42%, melting point: 187 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.45 - 7.37 (m, 2H), 7.28 (s, 4H), 7.23 - 7.15 (m, 2H), 6.85 - 6.78 (m, 1H), 6.54 - 6.46 (m, 1H), 6.39 - 6.36 (m, 1H), 2.94 - 2.88 (m, 2H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.48 (s, 3H), 2.09 - 2.00 (m, 2H), 1.91 - 1.82 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 162.3 (d, *J* = 246.6 Hz, 2×C), 152.0, 145.2 (d, *J* = 8.2 Hz), 141.8, 141.3, 138.2, 138.1, 137.5, 131.6, 131.1 (d, *J* = 7.9 Hz, 2×CH, C), 129.6 (2×CH), 128.1 (2×CH), 123.9 (d, *J* = 8.6 Hz), 115.7 (d, *J* = 21.3 Hz, 2×CH), 110.5 (d, *J* = 22.5 Hz), 106.0 (d, *J* = 23.6 Hz), 36.3, 26.7, 25.7, 25.3, 21.5.

ESI-HRMS: *m/z* calcd for C₂₇H₂₂F₂ [M+H]⁺: 385.1762; found: 385.1764.

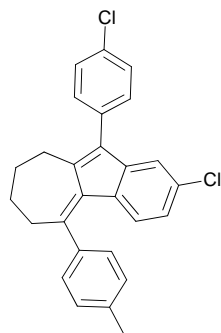


7-fluoro-9-(4-fluorophenyl)-4-(*p*-tolyl)-2,3-dihydro-1H-fluorene 3da: yellow solid, 63 mg, yield: 85%, melting point: 202 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.45 - 7.38 (m, 2H), 7.32 - 7.24 (m, 4H), 7.19 - 7.11 (m, 2H), 6.91 (d, *J* = 9.3 Hz, 1H), 6.80 - 6.72 (m, 1H), 6.57 - 6.49 (m, 1H), 2.78 - 2.68 (m, 4H), 2.44 (s, 3H), 2.03 - 1.93 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 162.7 (d, *J* = 243.8 Hz), 162.1 (d, *J* = 246.5 Hz), 147.0, 145.7 (d, *J* = 8.5 Hz), 138.6, 138.2, 137.6, 134.3, 133.3 (d, *J* = 1.7 Hz), 130.9 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 7.9 Hz, 2×CH), 130.1, 129.5 (2×CH), 128.0 (2×CH), 123.6 (d, *J* = 8.9 Hz), 115.6 (d, *J* = 21.3 Hz, 2×CH), 110.3 (d, *J* = 22.8 Hz), 106.1 (d, *J* = 23.9 Hz), 34.8, 24.6, 24.1, 21.5.

ESI-HRMS: *m/z* calcd for C₂₆H₂₀F₂ [M+H]⁺: 371.1606; found: 371.1607.

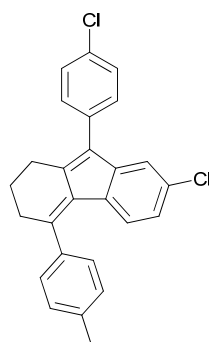


2-chloro-10-(4-chlorophenyl)-5-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene 3ea: yellow solid, 32 mg, yield: 38%, melting point: 165 °C.

^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.45 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.25 (s, 4H), 7.06 (d, J = 2.0 Hz, 1H), 6.77 - 6.73 (m, 1H), 6.26 (d, J = 8.3 Hz, 1H), 2.92 - 2.86 (m, 2H), 2.79 - 2.73 (m, 2H), 2.45 (s, 3H), 2.04 - 1.97 (m, 2H), 1.88 - 1.79 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 153.5, 144.6, 141.8, 141.1, 138.3 (2 \times C), 137.2, 134.1, 133.4, 133.4, 132.3, 130.8 (2 \times CH), 129.7(2 \times CH), 129.0(2 \times CH), 128.1(2 \times CH), 124.0, 123.8, 118.9, 36.5, 26.7, 25.7, 25.3, 21.5.

ESI-HRMS: m/z calcd for $\text{C}_{27}\text{H}_{22}\text{Cl}_2$ $[\text{M}+\text{H}]^+$: 417.1171; found: 417.1170.

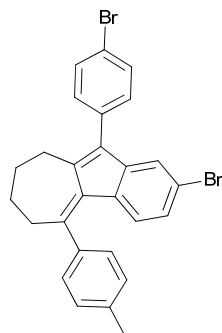


7-chloro-9-(4-chlorophenyl)-4-(*p*-tolyl)-2,3-dihydro-1H-fluorene 3fa: yellow solid, yield: 66% or 85% when use 2.4 eq. iodonium salt, melting point: 204 °C.

^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.46 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.33 - 7.26 (m, 4H), 7.20 (s, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 2.79 - 2.71 (m, 4H), 2.46 (s, 3H), 2.04 - 1.96 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 148.3, 145.0, 138.5, 138.4, 137.6, 134.4, 133.3, 133.1, 133.0, 132.8, 132.5, 130.3 (2 \times CH), 129.5 (2 \times CH), 128.9 (2 \times CH), 128.0 (2 \times CH), 123.8, 123.5, 118.9, 34.9, 24.5, 24.0, 21.5.

ESI-HRMS: m/z calcd for $\text{C}_{26}\text{H}_{20}\text{Cl}_2$ $[\text{M}+\text{H}]^+$: 403.1015; found: 403.1017.



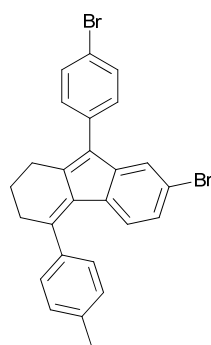
2-bromo-10-(4-bromophenyl)-5-(*p*-tolyl)-6,7,8,9-tetrahydrobenzo[*a*]azulene 3ga:

yellow solid, 36 mg, yield: 36%, melting point: 198 °C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.30 - 7.19 (m, 7H), 6.90 (dd, *J* = 8.2, 4.1 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 2.91 - 2.85 (m, 2H), 2.79 - 2.73 (m, 2H), 2.44 (s, 3H), 2.05 - 1.96 (m, 2H), 1.87 - 1.78 (m, 2H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 153.8, 144.8, 141.6, 141.1, 138.4, 138.3, 137.2, 134.5, 133.9, 131.9 (2×CH), 131.2 (2×CH), 129.7 (2×CH), 128.1 (2×CH), 126.9, 124.2, 121.8, 121.6, 120.5, 36.5, 26.6, 25.7, 25.3, 21.5.

ESI-HRMS: *m/z* calcd for C₂₇H₂₂Br₂ [M+H]⁺: 507.0142; found: 507.0141.

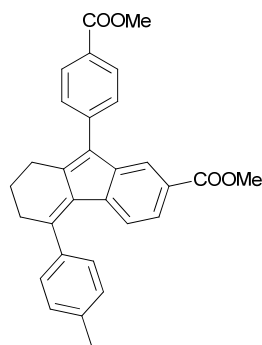


7-bromo-9-(4-bromophenyl)-4-(*p*-tolyl)-2,3-dihydro-1H-fluorene 3ha: yellow solid, 63 mg, yield: 64%, melting point: 197 °C.

¹H NMR (301 MHz, CHLOROFORM-D) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.36 - 7.24 (m, 7H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 2.79 - 2.66 (m, 4H), 2.44 (s, 3H), 2.03 - 1.87 (m, 2H).

¹³C NMR (76 MHz, CHLOROFORM-D) δ 148.6, 145.2, 138.5, 138.4, 137.5, 134.5, 133.7, 133.0 (2×C), 131.9 (2×CH), 130.6 (2×CH), 129.5 (2×CH), 128.0 (2×CH), 126.7, 123.9, 121.8, 121.3, 121.0, 34.9, 24.5, 24.0, 21.5.

ESI-HRMS: *m/z* calcd for C₂₆H₂₀Br₂ [M+H]⁺: 492.9986; found: 492.9988.

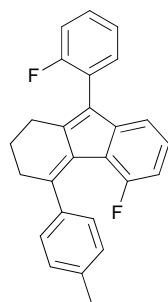


methyl 9-(4-(methoxycarbonyl)phenyl)-4-(p-tolyl)-2,3-dihydro-1H-fluorene-7-carboxylate 3ia: yellow solid, 17 mg, yield: 19%, melting point: 173 °C.

^1H NMR (400 MHz, CHLOROFORM- D) δ 8.17 (d, J = 8.1 Hz, 2H), 7.91 (s, 1H), 7.62 - 7.55 (m, 3H), 7.31 (q, J = 8.1 Hz, 4H), 6.91 (d, J = 8.1 Hz, 1H), 3.96 (s, 3H), 3.85 (s, 3H), 2.85 - 2.75 (m, 4H), 2.46 (s, 3H), 2.06 - 1.97 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM- D) δ 167.6, 167.2, 150.7, 143.1, 139.9, 138.7, 138.6, 138.3, 137.9, 134.9, 133.7, 130.0(2 \times CH), 129.6(2 \times CH), 129.0(2 \times CH), 128.9, 128.4, 128.0(2 \times CH), 126.0, 122.4, 119.7, 52.3, 52.1, 35.2, 24.4, 24.1, 21.6.

ESI-HRMS: m/z calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4$ $[\text{M}+\text{H}]^+$: 451.1904; found: 451.1905.

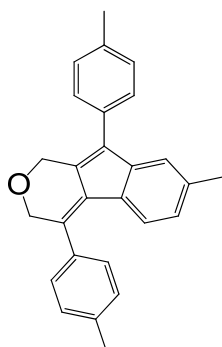


5-fluoro-9-(2-fluorophenyl)-4-(p-tolyl)-2,3-dihydro-1H-fluorene 3ja: yellow solid, 27 mg, yield: 36%, melting point: 192 °C.

^1H NMR (400 MHz, CHLOROFORM- D) δ 7.47 - 7.34 (m, 2H), 7.32 - 7.19 (m, 6H), 7.15 - 7.08 (m, 1H), 6.93 (d, J = 7.4 Hz, 1H), 6.68 - 6.61 (m, 1H), 2.82 (t, J = 5.9 Hz, 2H), 2.66 (s, 2H), 2.44 (s, 3H), 2.06 - 1.95 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM- D) δ 160.3 (d, J = 247.3 Hz), 157.2 (d, J = 254.0 Hz), 149.5, 146.8 (d, J = 6.2 Hz), 140.6 (d, J = 4.5 Hz), 139.5, 137.8, 133.4 (d, J = 4.6 Hz), 131.5 (d, J = 3.8 Hz), 129.3 (d, J = 8.0 Hz), 128.9 (d, J = 1.9 Hz), 128.6 - 128.3 (multi-peaks), 124.1 (d, J = 3.4 Hz), 122.8 (d, J = 16.4 Hz), 119.4 (d, J = 14.9 Hz), 116.2 (d, J = 22.3 Hz), 115.1, 112.3 (d, J = 23.8 Hz), 35.6, 24.2 (d, J = 2.3 Hz), 23.8, 21.5.

ESI-HRMS: m/z calcd for $\text{C}_{26}\text{H}_{20}\text{F}_2$ $[\text{M}+\text{H}]^+$: 371.1606; found: 371.1607.



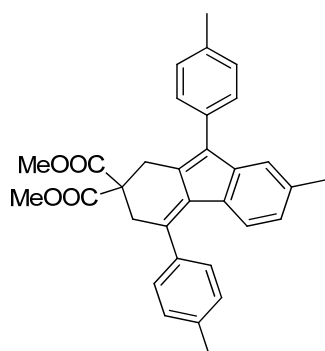
7-methyl-4,9-di-p-tolyl-1,3-dihydroindeno[2,1-c]pyran (3la): orange solid, 47.5 mg, yield: 65%, melting point: 105°C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.31 - 7.25 (m, 4H), 7.18 (s, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.85 (s, 2H), 4.57 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 143.8, 141.1, 139.0, 137.5, 137.4, 134.2, 134.0, 132.7, 131.6, 131.1, 130.8, 129.6(2×CH), 129.5(2×CH), 128.8(2×CH), 128.6(2×CH), 125.3, 122.5, 120.6, 69.8, 64.6, 21.9, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₂₇H₂₄O [M+H]⁺: 365.1900; found: 365.1901.

GC-MS *m/z*: 364

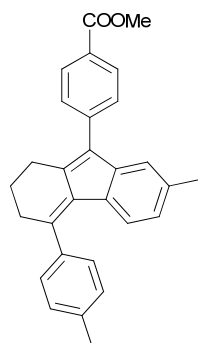


dimethyl 7-methyl-4,9-di-p-tolyl-1H-fluorene-2,2(3H)-dicarboxylate (3ma): yellow solid, 18 mg, yield: 19%, melting point: 70°C.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 - 7.36 (m, 4H), 7.33 - 7.25 (m, 4H), 7.04 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 6H), 3.35 (s, 2H), 3.27 (s, 2H), 2.44 (s, 3H), 2.43 (s, 3H), 2.26 (s, 3H).

¹³C NMR (101 MHz, CHLOROFORM-D) δ 171.2(2×C), 144.5, 140.5, 138.2, 137.8, 137.3, 137.2, 137.1, 134.7, 131.9, 131.5, 131.1, 129.4(4×CH), 128.9(2×CH), 128.3(2×CH), 125.1, 122.5, 120.2, 56.9, 53.0(2×CH₃), 40.1, 29.9, 21.7, 21.6, 21.5.

ESI-HRMS: *m/z* calcd for C₃₂H₃₀O₄ [M+H]⁺: 479.2217; found: 479.2217.

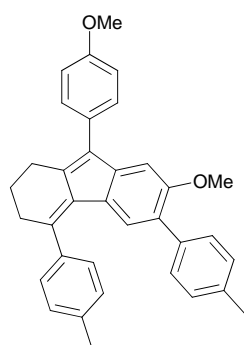


methyl 4,9-di-p-tolyl-2,3-dihydro-1H-fluorene-7-carboxylate 30a: yellow solid, melting point: 147 °C.

^1H NMR (400 MHz, CHLOROFORM-D) δ 8.14 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.07 (s, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 1H), 3.95 (s, 3H), 2.81 - 2.75 (m, 2H), 2.74 - 2.69 m, 2H), 2.44 (s, 3H), 2.28 (s, 3H), 2.03 - 1.94 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.2, 146.7, 143.4, 140.6, 138.9, 138.1, 137.2, 136.9, 135.2, 134.0, 131.7, 129.8(2 \times CH), 129.4(2 \times CH), 129.1(2 \times CH), 128.6, 128.1(2 \times CH), 124.9, 122.6, 119.6, 52.3, 34.8, 24.7, 24.2, 21.8, 21.5.

ESI-HRMS: m/z calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{H}]^+$: 407.2006; found: 407.2008.



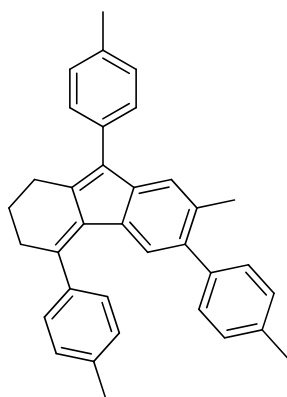
7-methoxy-9-(4-methoxyphenyl)-4,6-di-p-tolyl-2,3-dihydro-1H-fluorene 4na:

yellow solid, yield: 22% or 48% when 2.0 eq. iodonium salt was used, melting point: 186 °C.

^1H NMR (600 MHz, CHLOROFORM-D) δ 7.46 (d, $J = 8.6$ Hz, 2H), 7.35 (d, $J = 7.9$ Hz, 2H), 7.26 - 7.22 (m, 4H), 7.10 (d, $J = 7.9$ Hz, 2H), 7.04 (d, $J = 8.6$ Hz, 2H), 6.91 (s, 1H), 6.86 (s, 1H), 3.88 (s, 3H), 3.73 (s, 3H), 2.77 (t, $J = 6.3$ Hz, 2H), 2.72 (t, $J = 5.9$ Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H), 2.01 - 1.95 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.8, 156.3, 144.7, 144.6, 139.0, 138.0, 136.4(2 \times C), 135.9, 135.2, 134.3, 130.2(2 \times CH), 129.4(2 \times CH), 129.3(2 \times CH), 128.6(2 \times CH), 128.3(2 \times CH), 127.9, 127.3, 125.7, 125.1, 114.1(2 \times CH), 102.8, 56.0, 55.5, 34.5, 24.8, 24.3, 21.4, 21.3.

ESI-HRMS: m/z calcd for $\text{C}_{35}\text{H}_{32}\text{O}_2$ $[\text{M}+\text{H}]^+$: 485.2475; found: 485.2478.

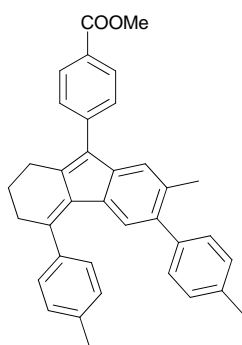


7-methyl-4,6,9-tri-p-tolyl-2,3-dihydro-1H-fluorene (4ba): yellow solid, 9 mg, yield: 10 % or 54% when 2.4 eq. iodonium salts were used

^1H NMR (600 MHz, CHLOROFORM-D) δ 7.42 (d, $J = 7.6$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.30 (d, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 7.6$ Hz, 2H), 7.18 (s, 1H), 7.12 - 7.04 (m, 4H), 6.83 (s, 1H), 2.78 (t, $J = 6.1$ Hz, 2H), 2.71 (t, $J = 5.7$ Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H), 2.23 (s, 3H), 1.97 (dt, $J = 13.2, 6.5$ Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 145.5, 142.9, 139.8, 138.9, 138.0, 137.3, 136.8, 136.0, 135.8, 135.5, 134.6, 134.0, 132.7, 132.4, 129.4(2 \times CH), 129.3(4 \times CH), 129.0(2 \times CH), 128.7(2 \times CH), 128.3(2 \times CH), 124.4, 121.0, 34.7, 24.7, 24.2, 21.5, 21.4, 21.3, 21.2.

ESI-HRMS: m/z calcd for $\text{C}_{35}\text{H}_{32}$ $[\text{M}+\text{H}]^+$: 453.2577; found: 453.2576.



methyl 4-(7-methyl-4,6-di-p-tolyl-2,3-dihydro-1H-fluoren-9-yl)benzoate 40a: yellow solid, melting point: 213 $^{\circ}\text{C}$.

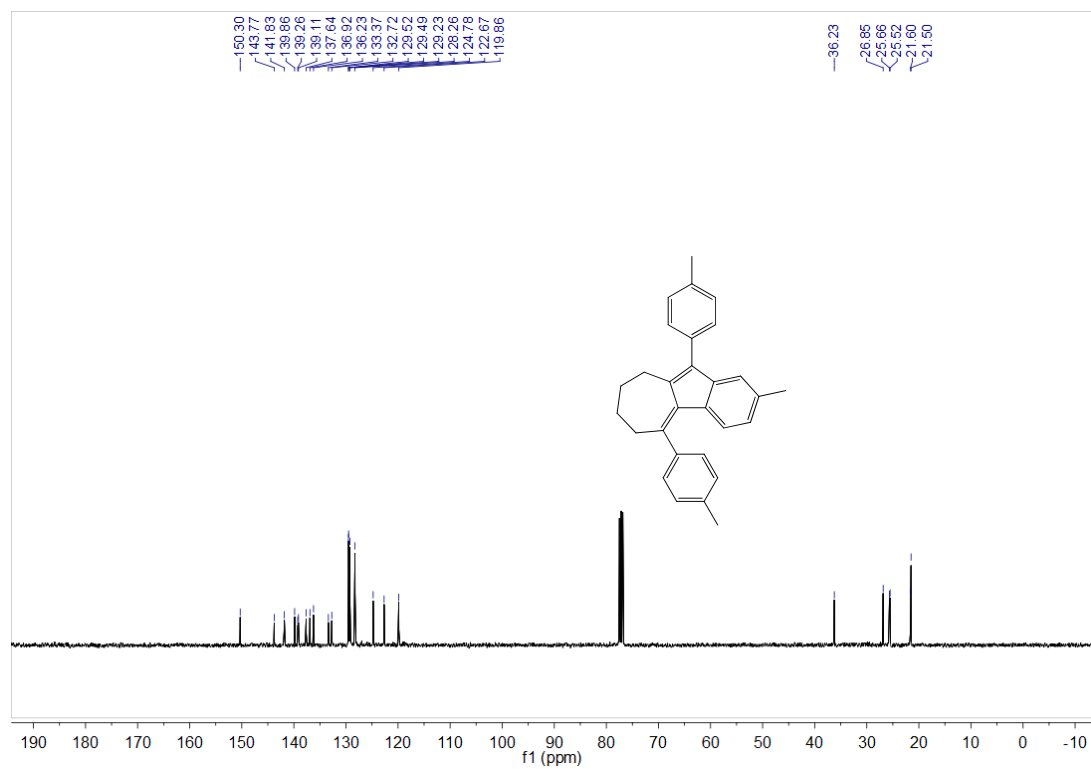
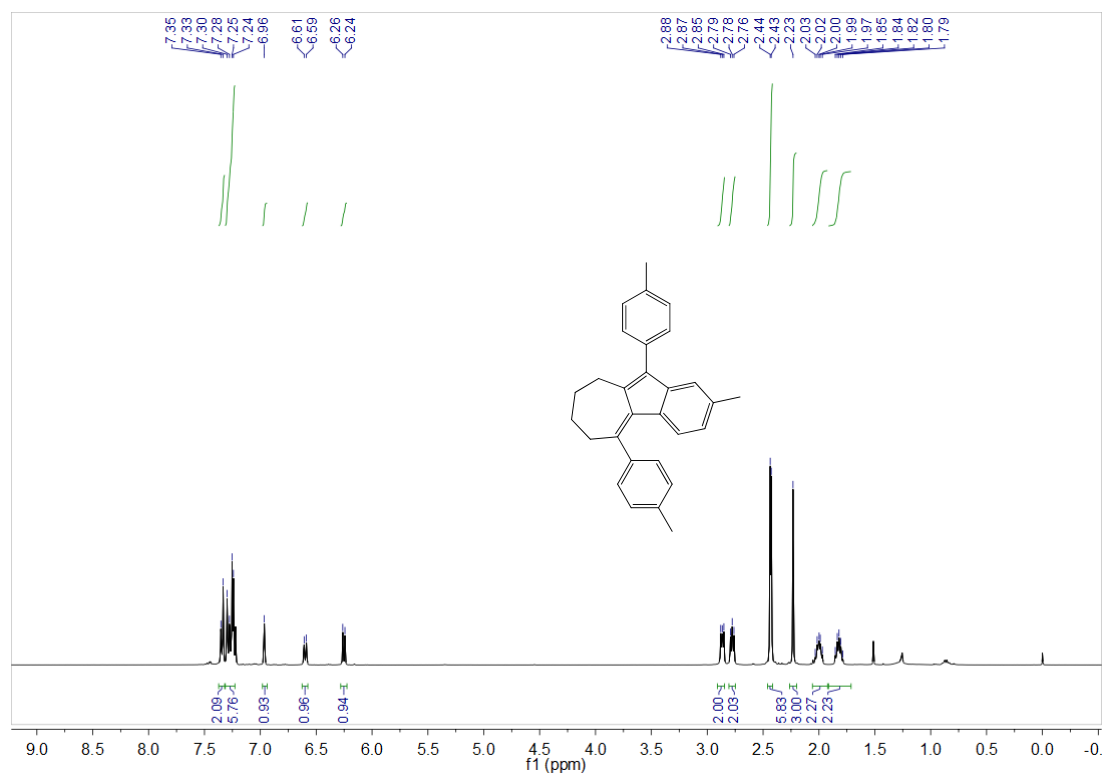
^1H NMR (400 MHz, CHLOROFORM-D) δ 8.16 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 7.15 (s, 1H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 7.9$ Hz, 2H), 6.84 (s, 1H), 3.96 (s, 3H), 2.82 - 2.70 (m, 4H), 2.37 (s, 3H), 2.36 (s, 3H), 2.24 (s, 3H), 2.03 - 1.95 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.2, 146.9, 142.2, 140.7, 139.6, 138.7, 138.2, 137.6, 137.5, 135.9, 135.4, 134.2, 133.8, 132.3, 129.9(2 \times CH), 129.3(4 \times CH), 129.1(2 \times CH), 128.7(2 \times CH), 128.6(2 \times CH), 128.2, 124.5, 120.8, 52.2, 34.7, 24.7, 24.3, 21.5, 21.3, 21.2.

ESI-HRMS: m/z calcd for $\text{C}_{36}\text{H}_{32}\text{O}_2$ $[\text{M}+\text{H}]^+$: 497.2475; found: 497.2473.

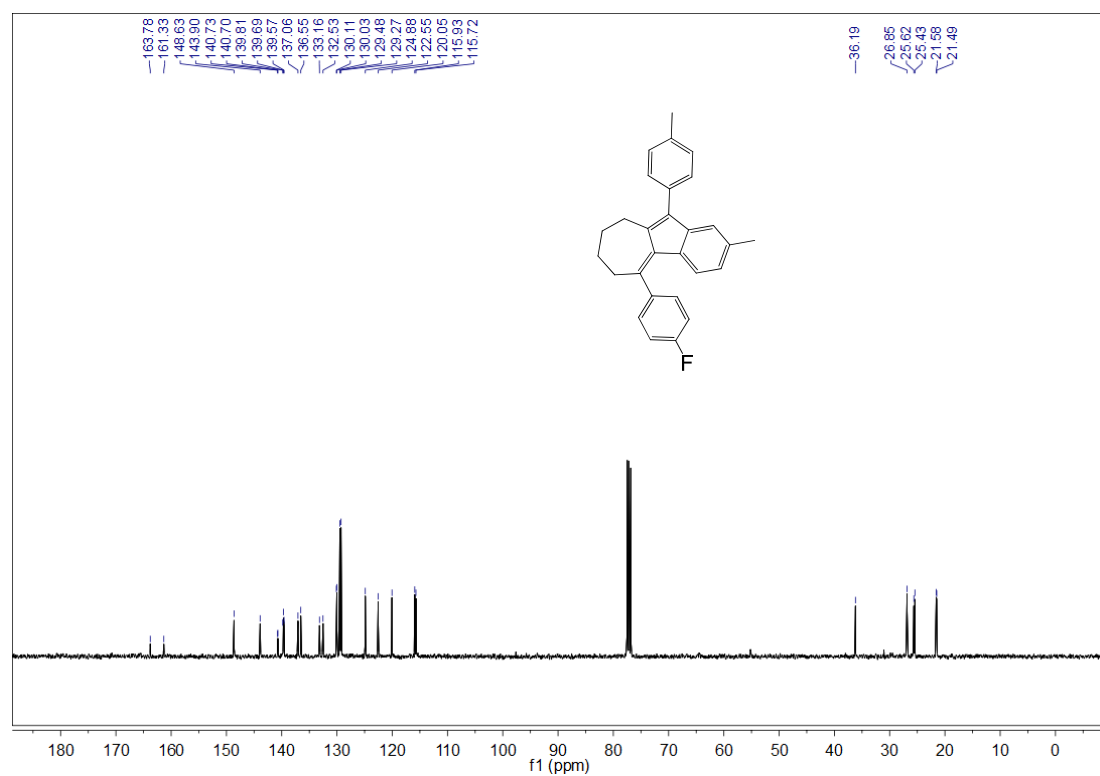
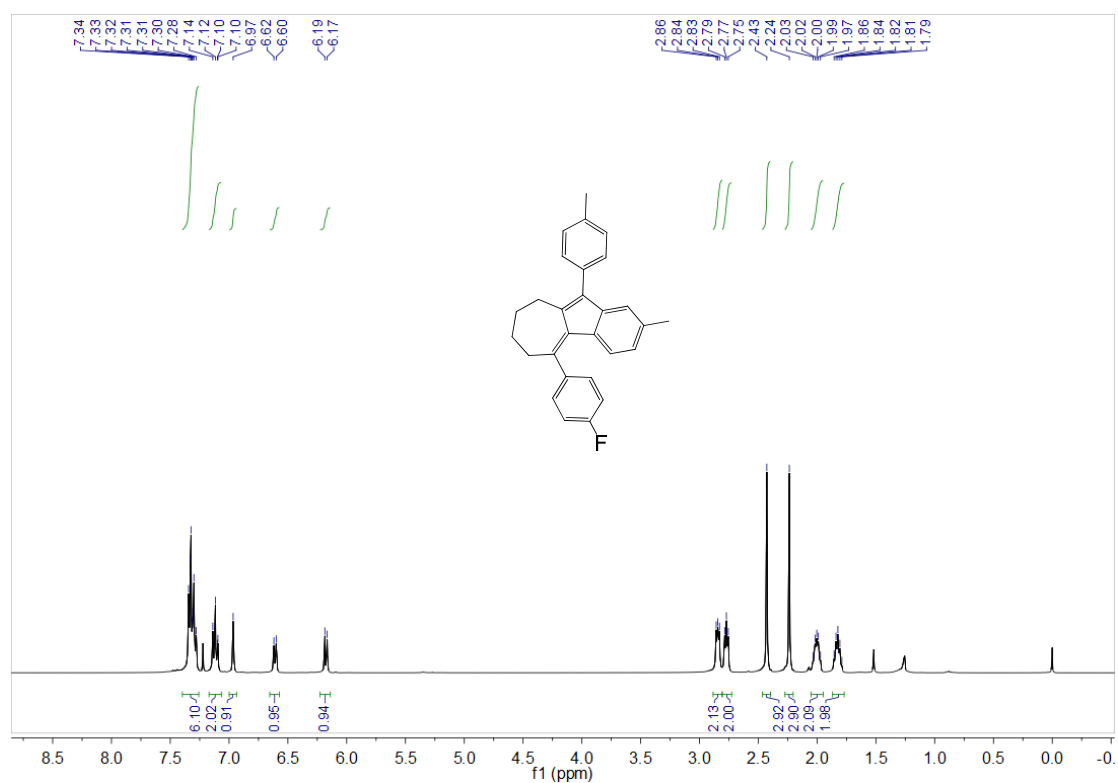
7. NMR spectra of polycyclic products

3aa



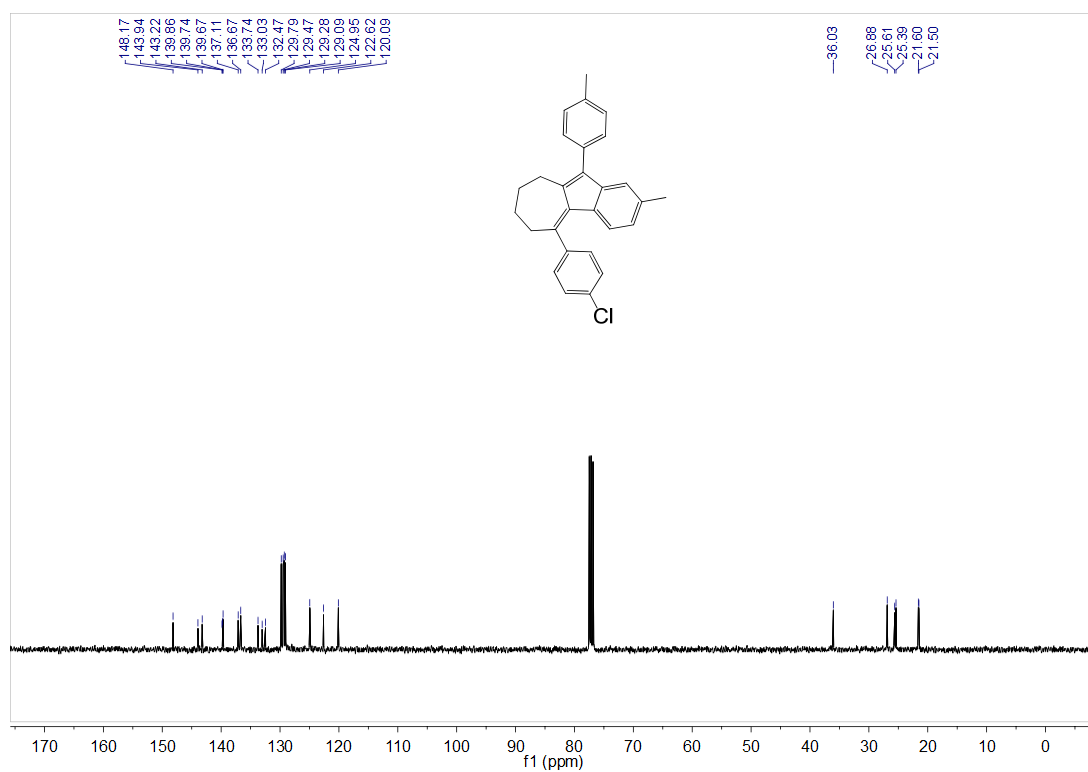
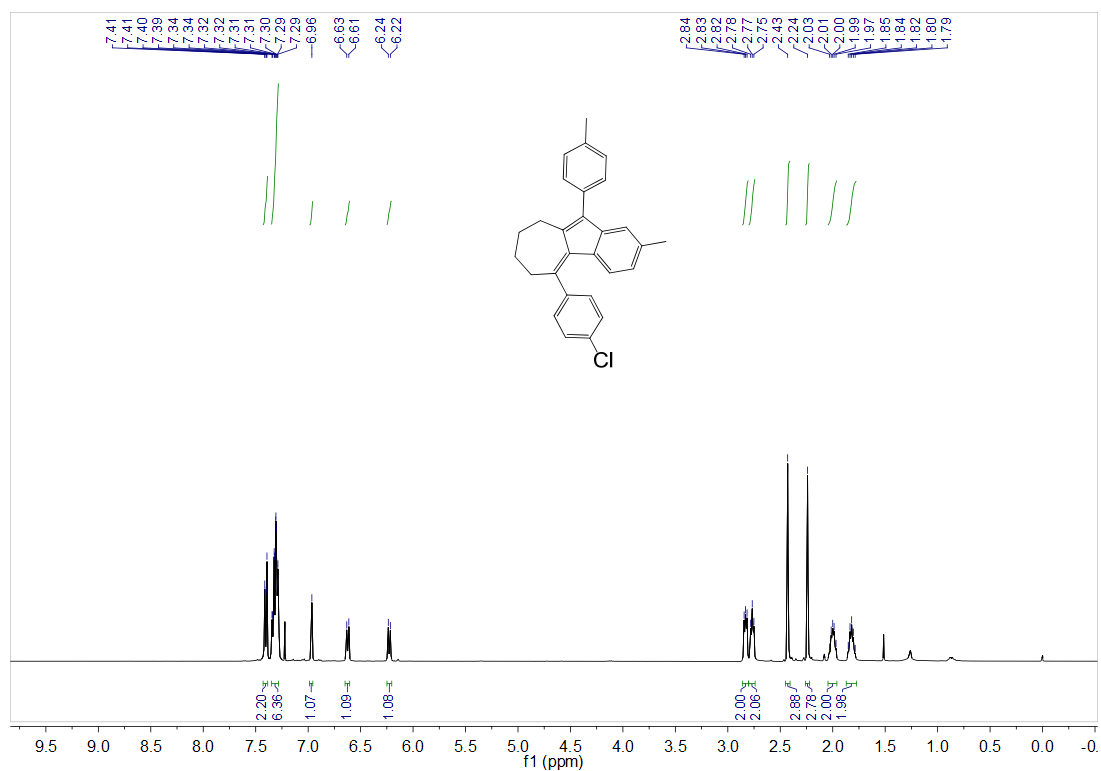
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ab



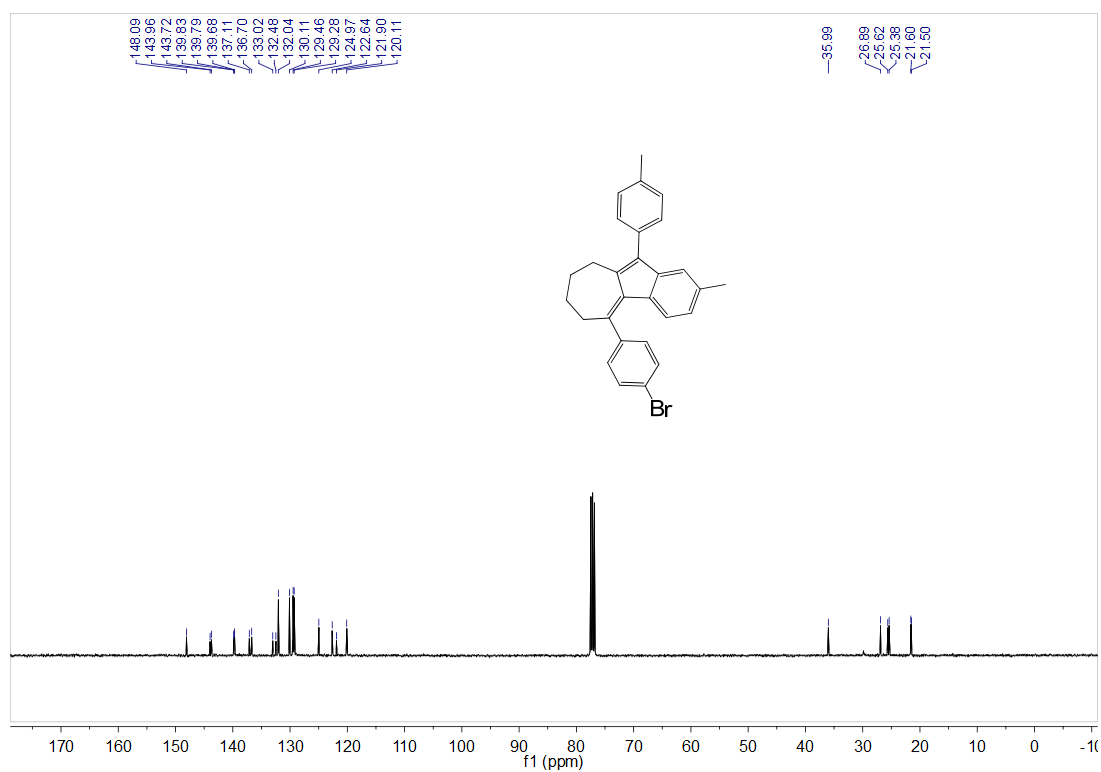
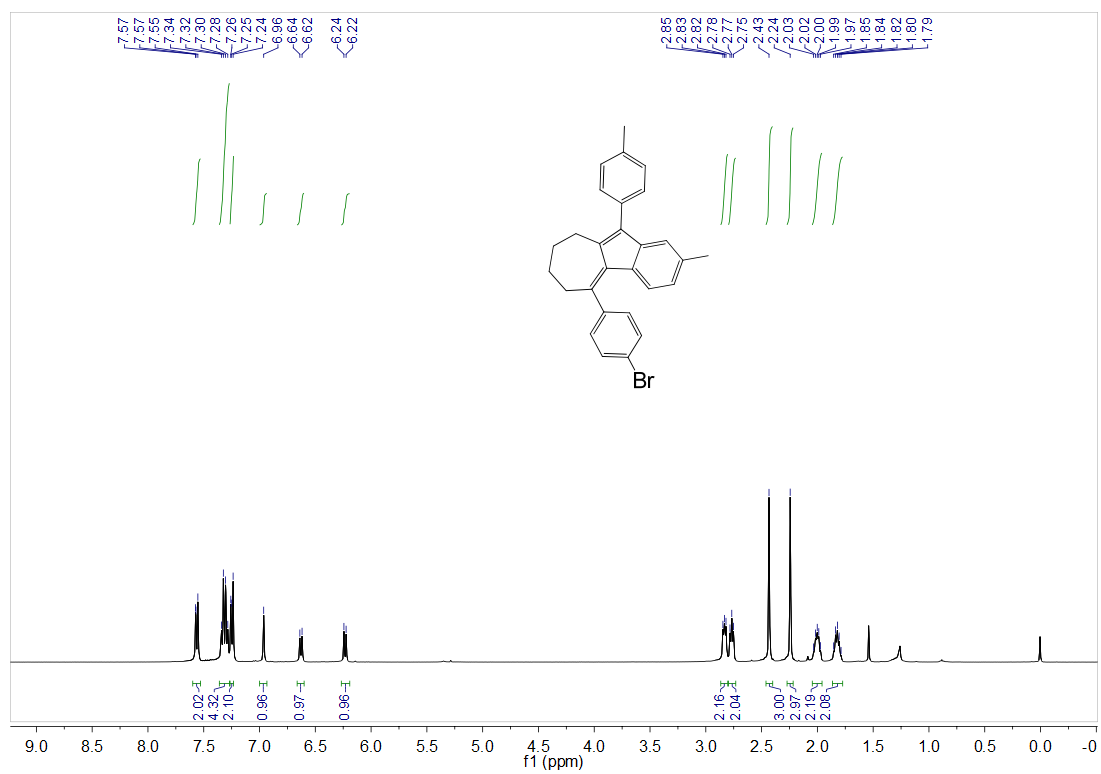
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ac



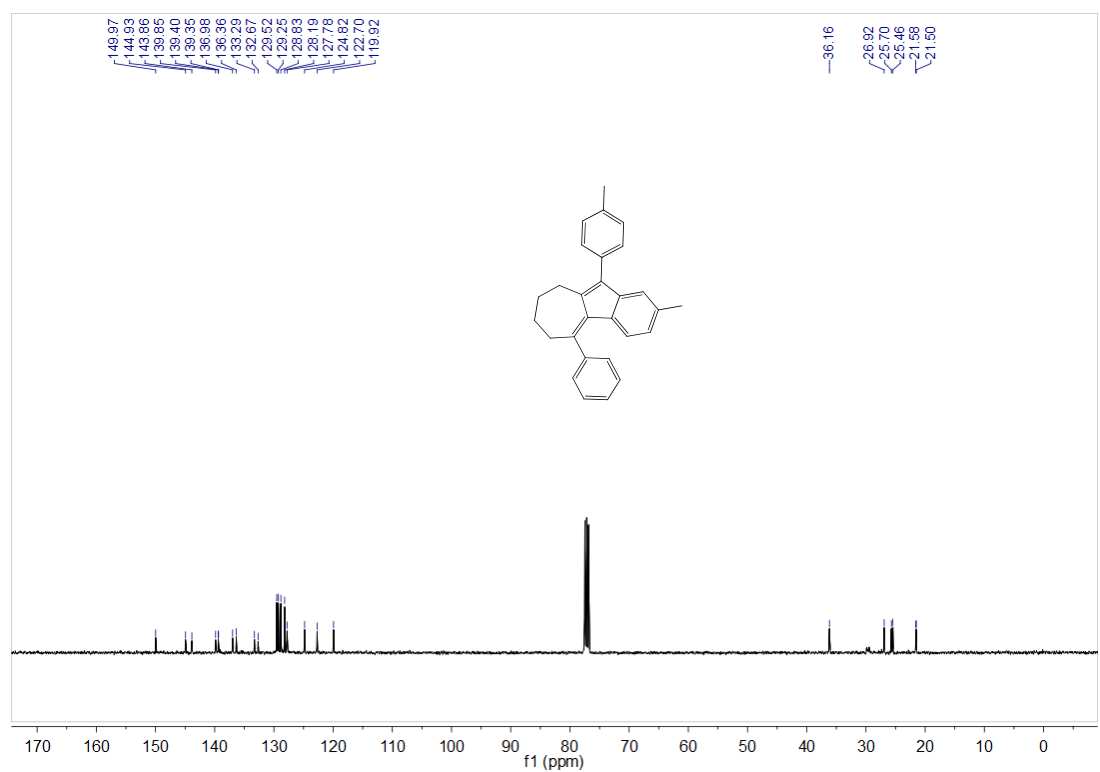
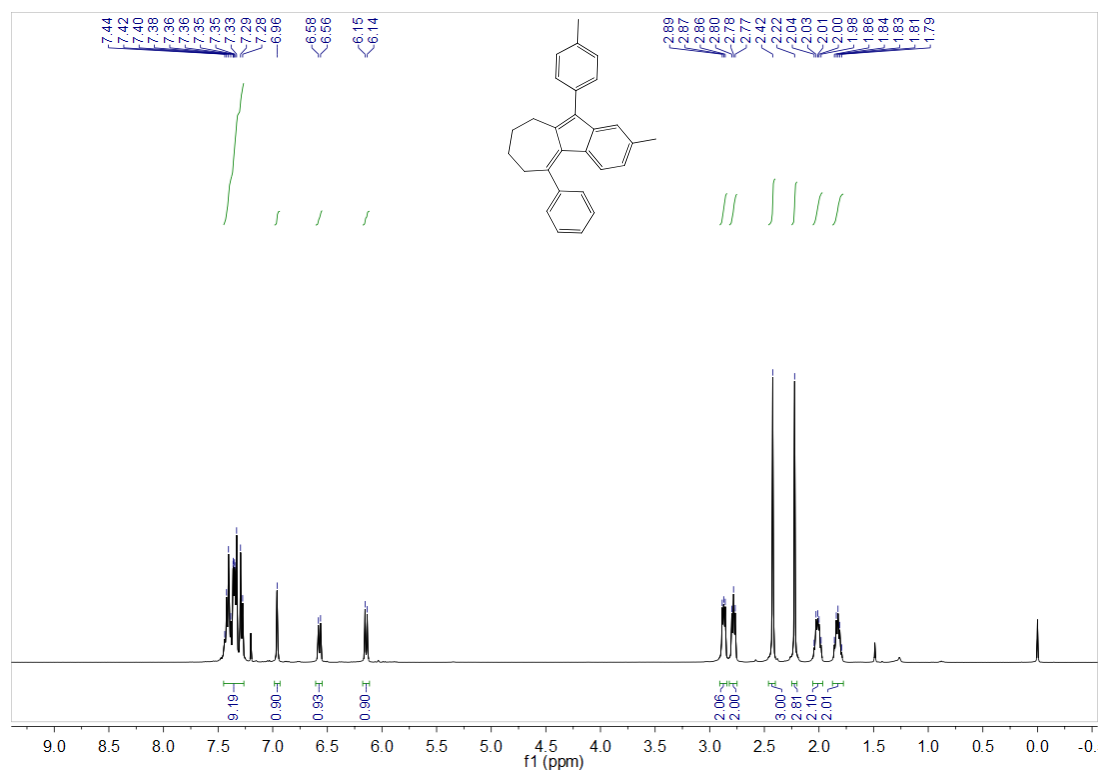
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ad



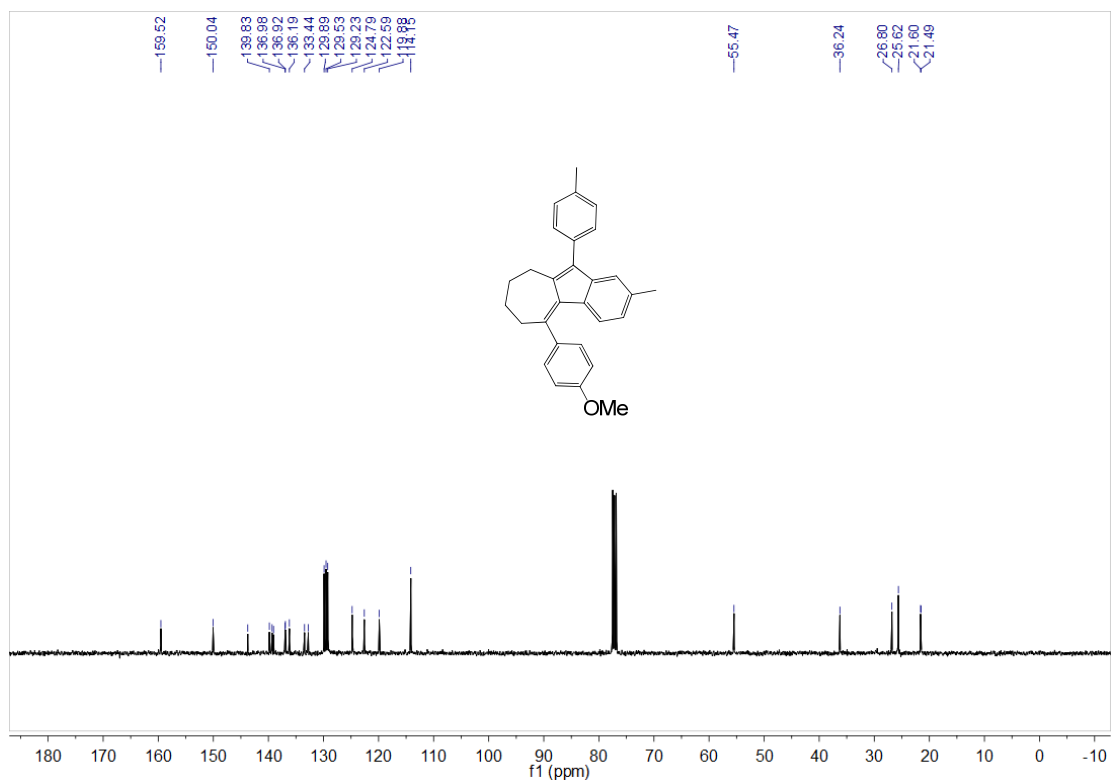
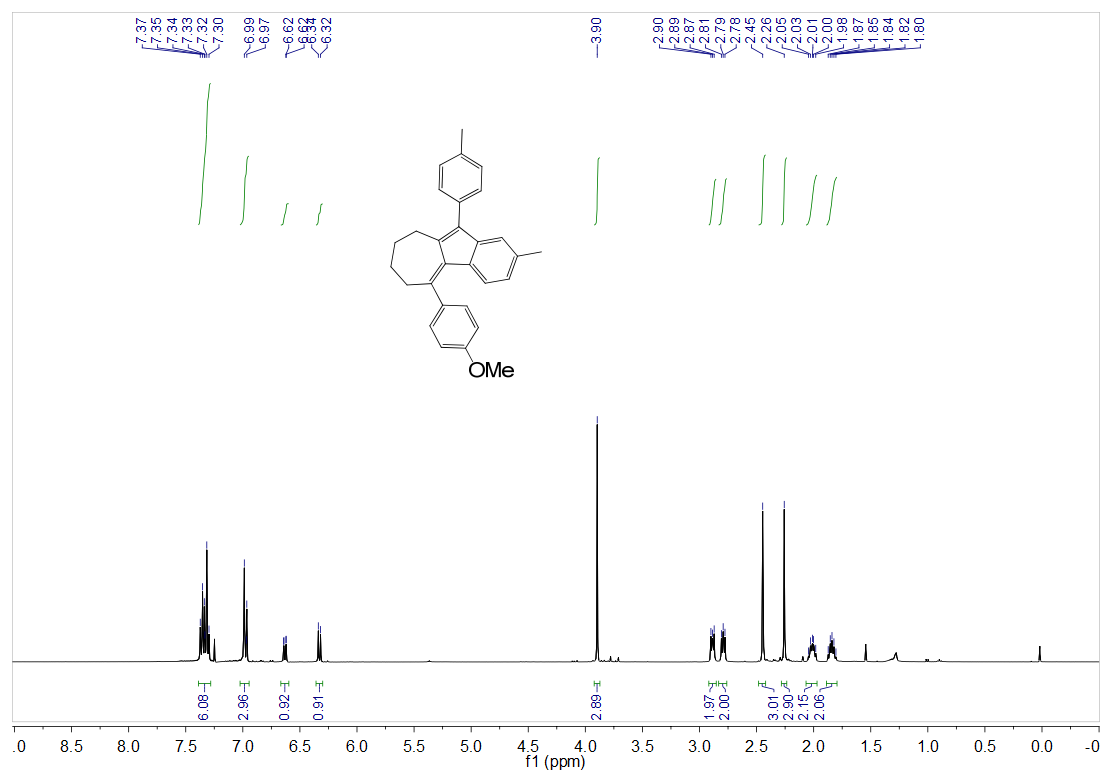
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ae



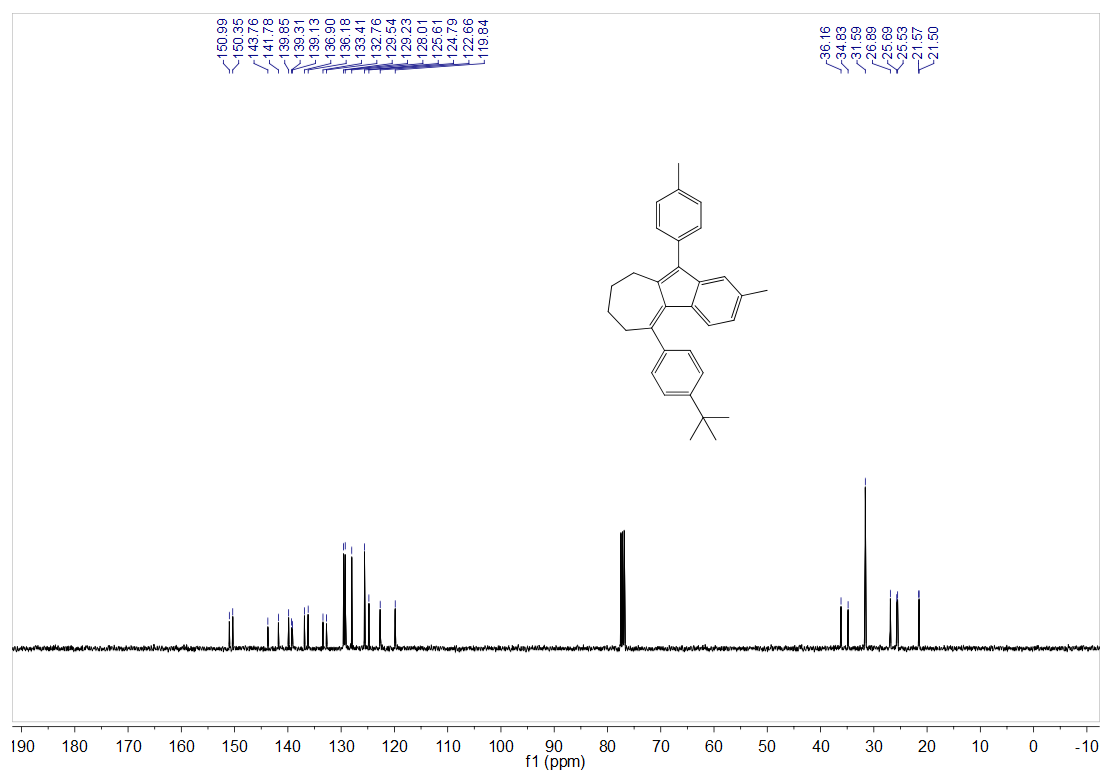
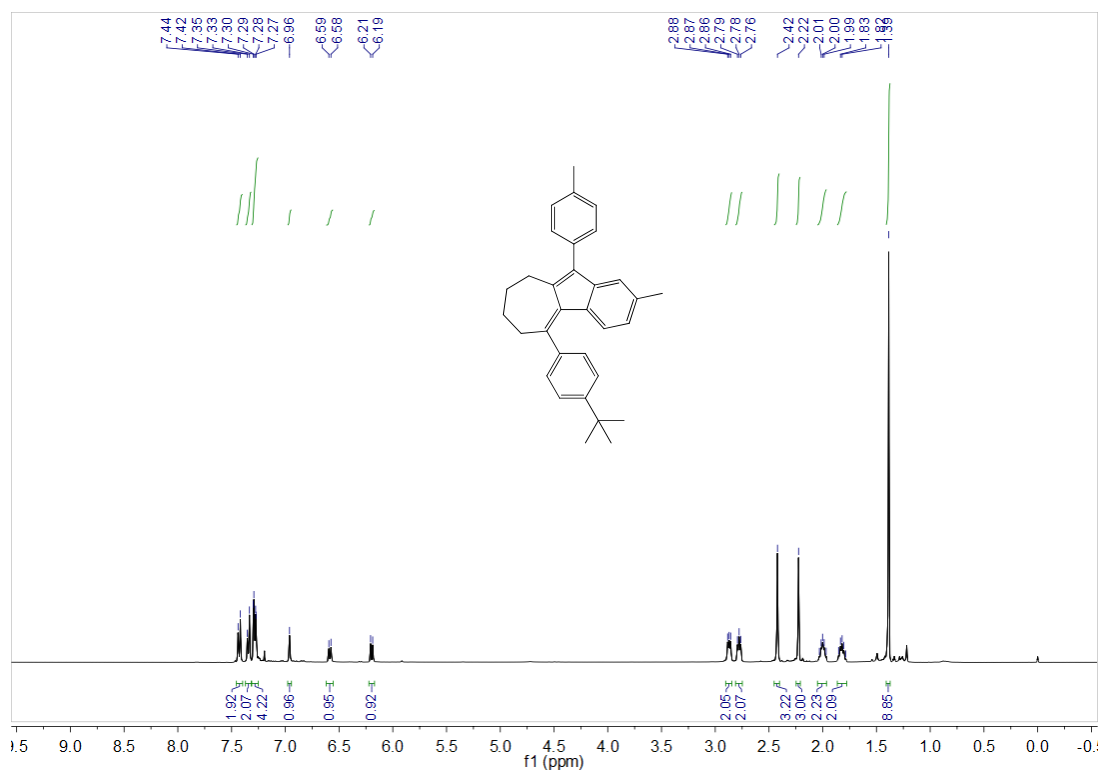
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3af



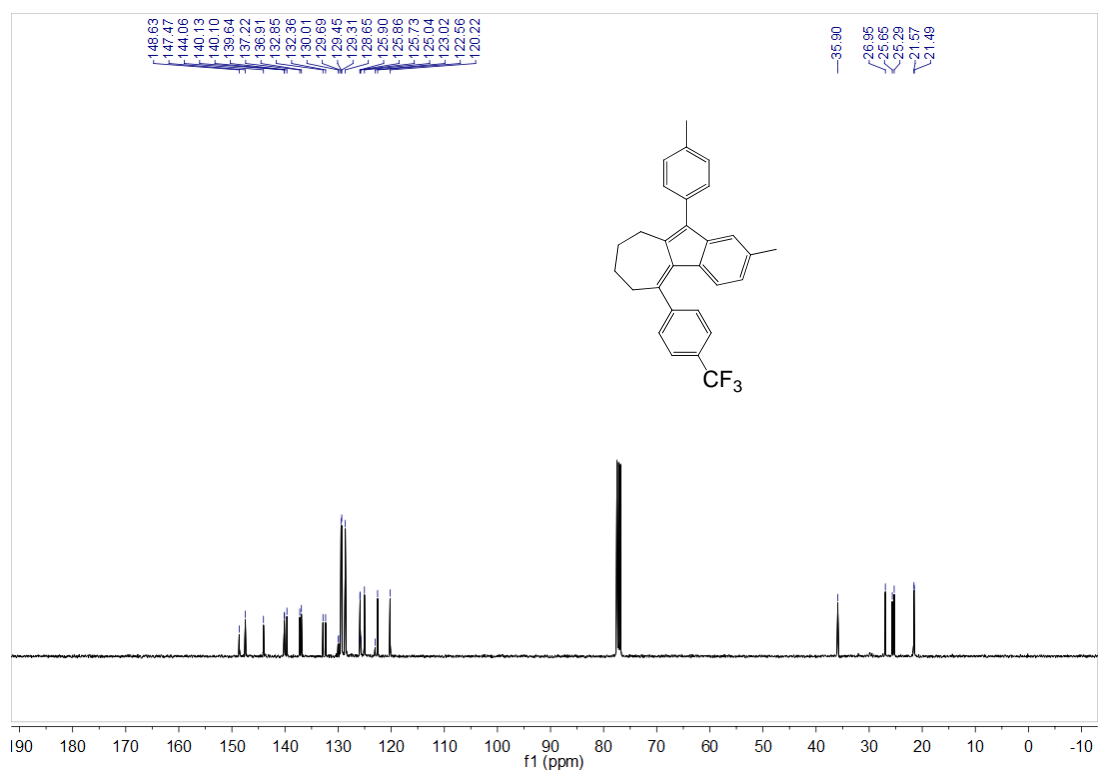
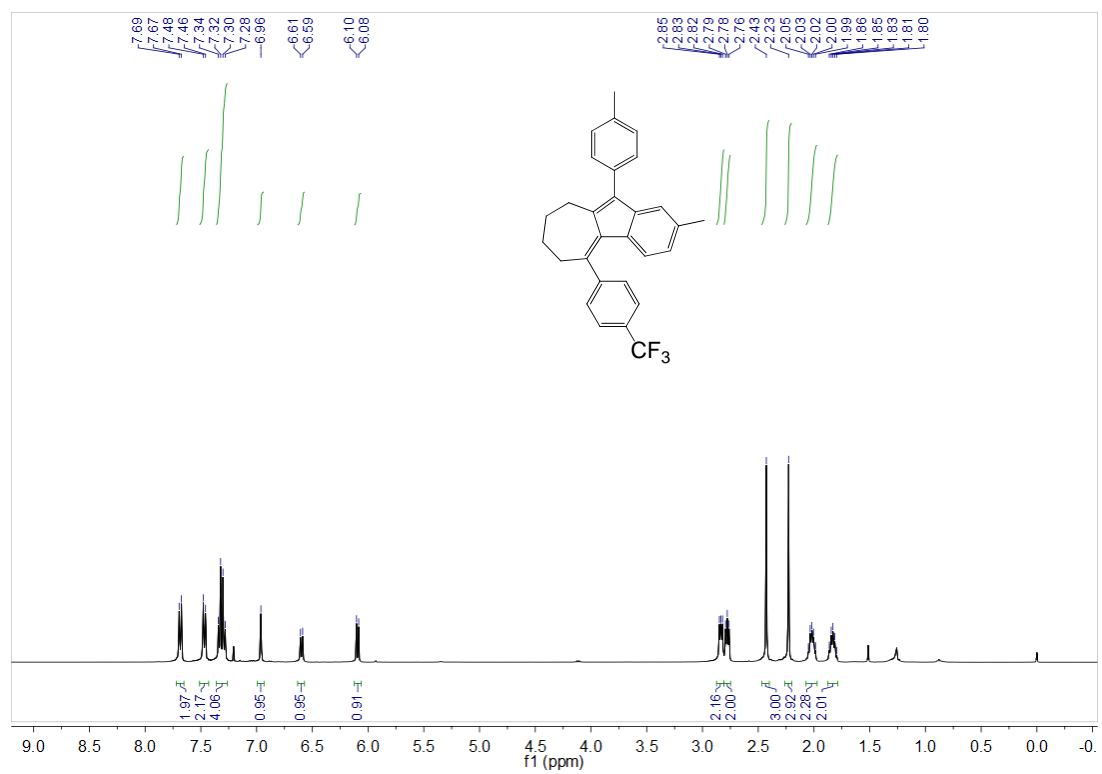
^1H NMR (400 MHz, CDCl_3) (up) and ^{13}C NMR (101 MHz, CDCl_3) (down)

3ag



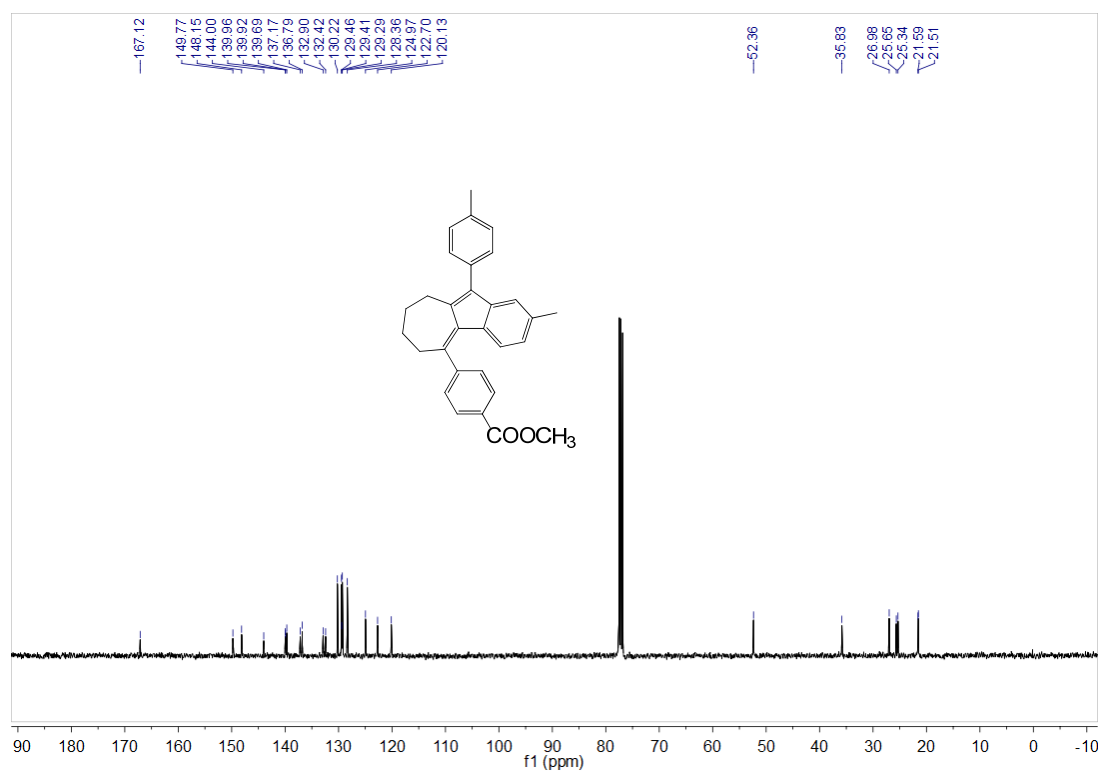
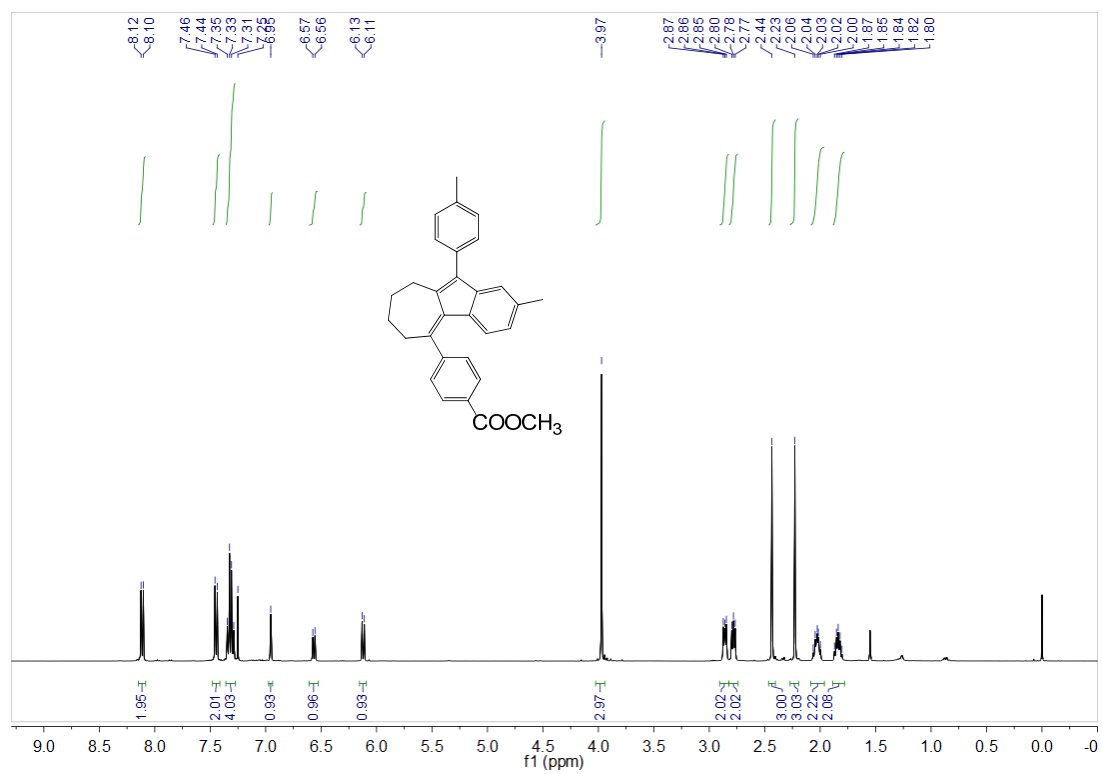
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ah



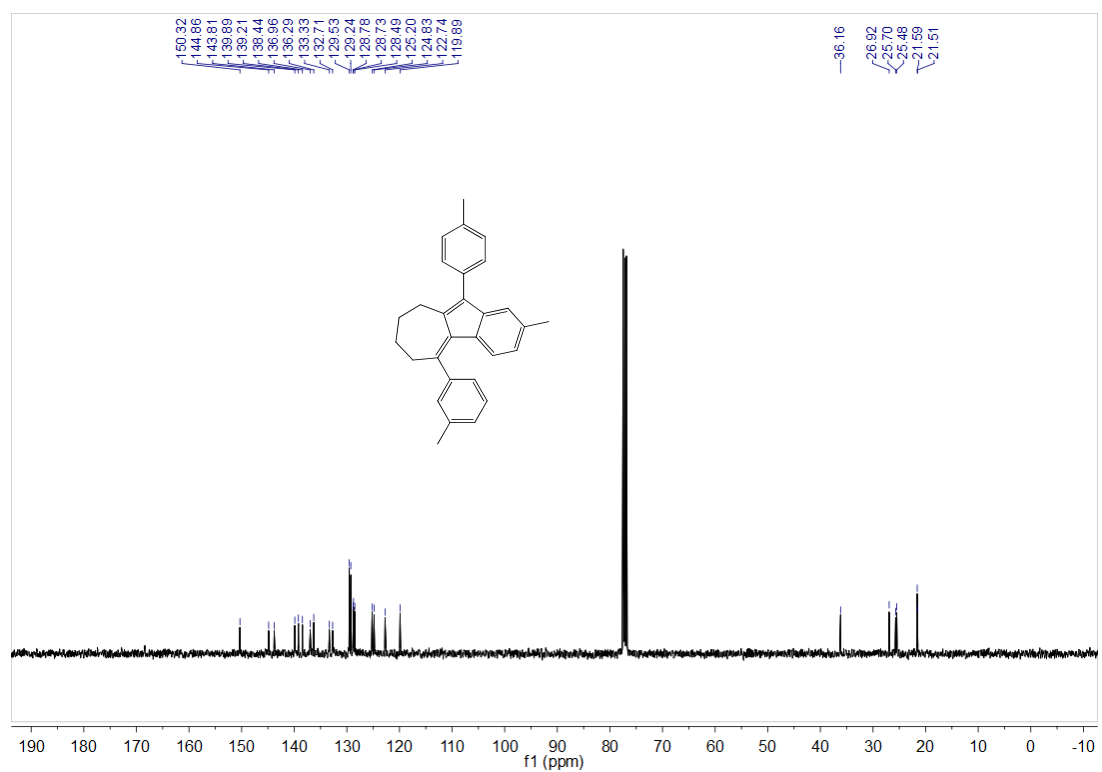
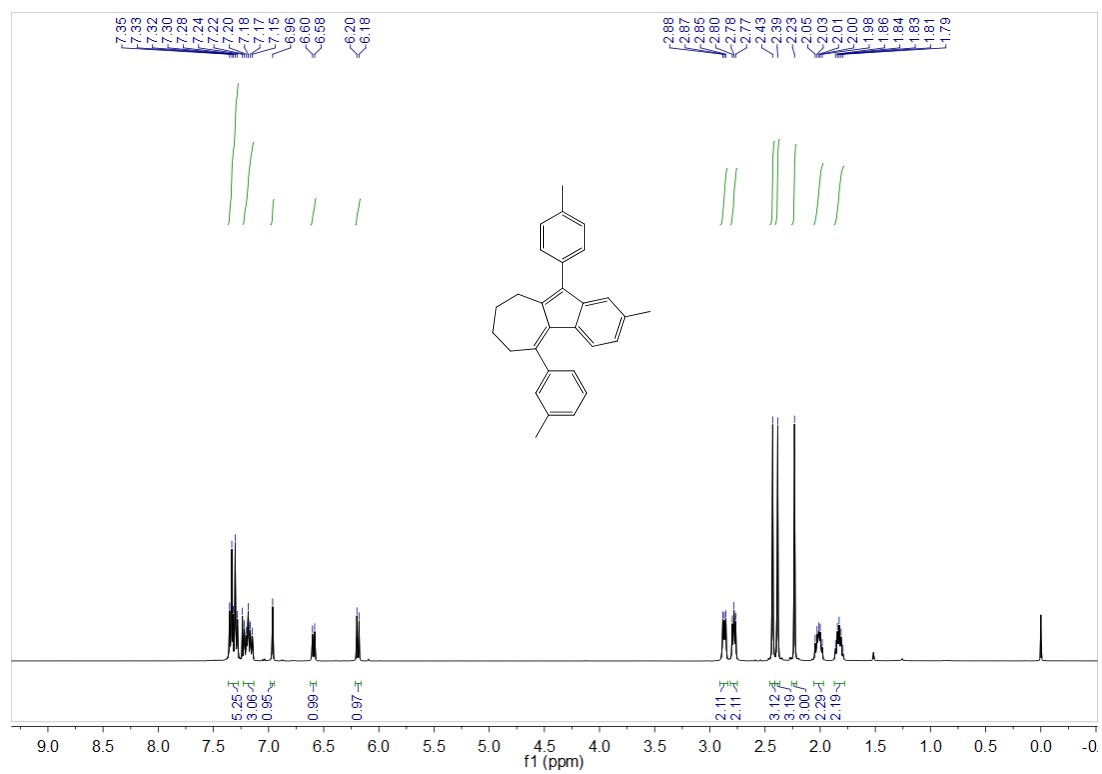
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ai



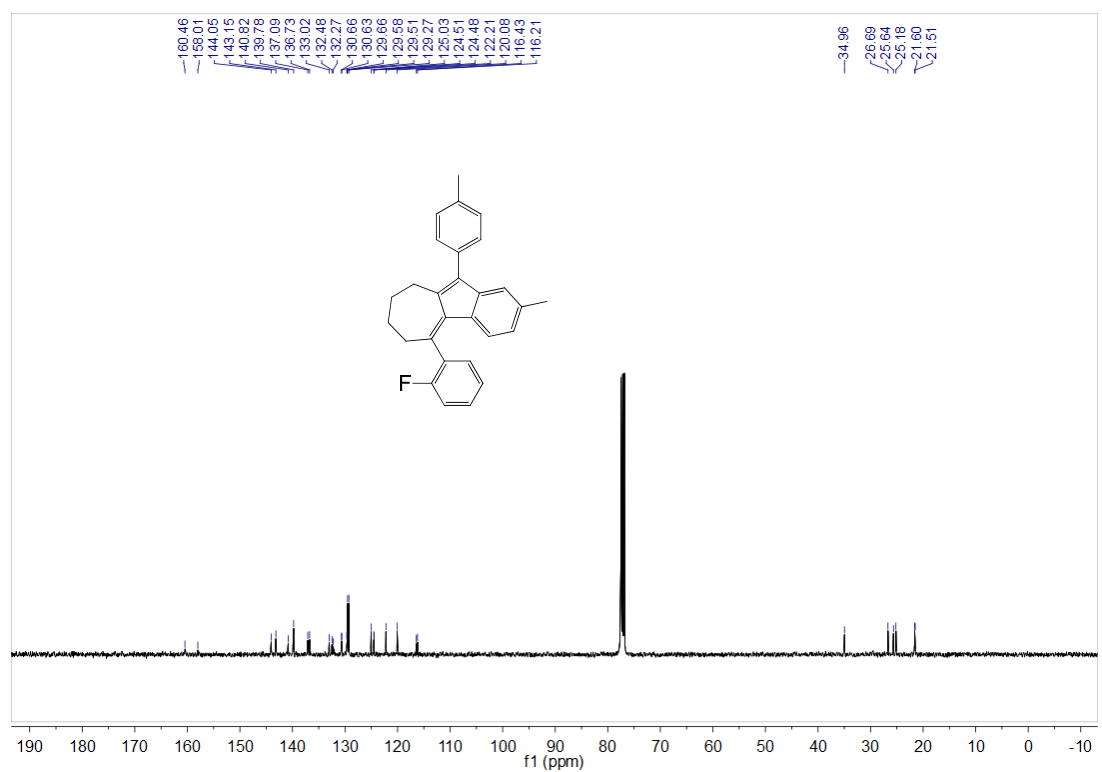
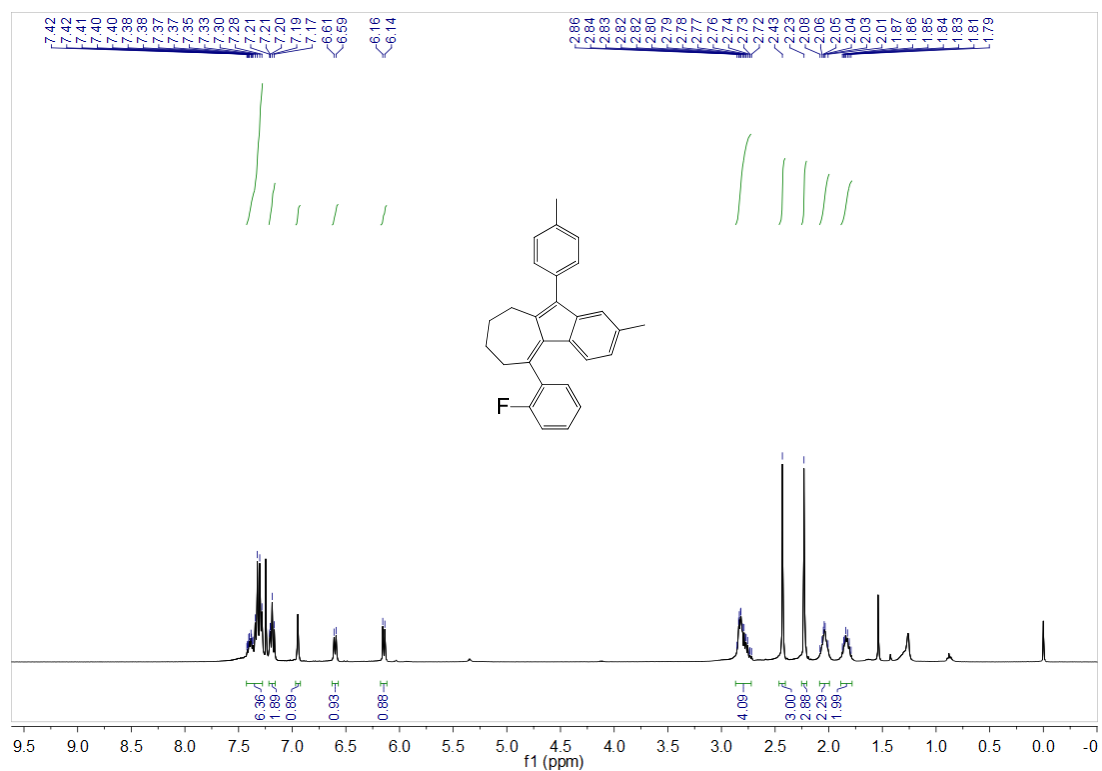
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3aj



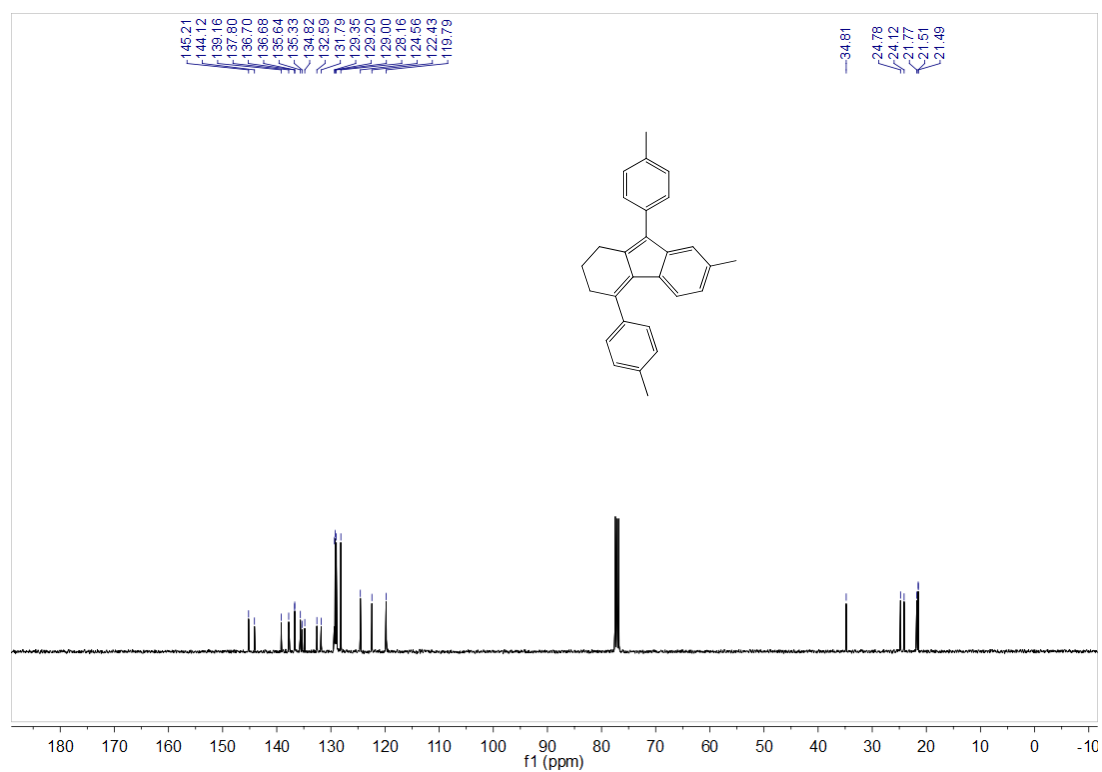
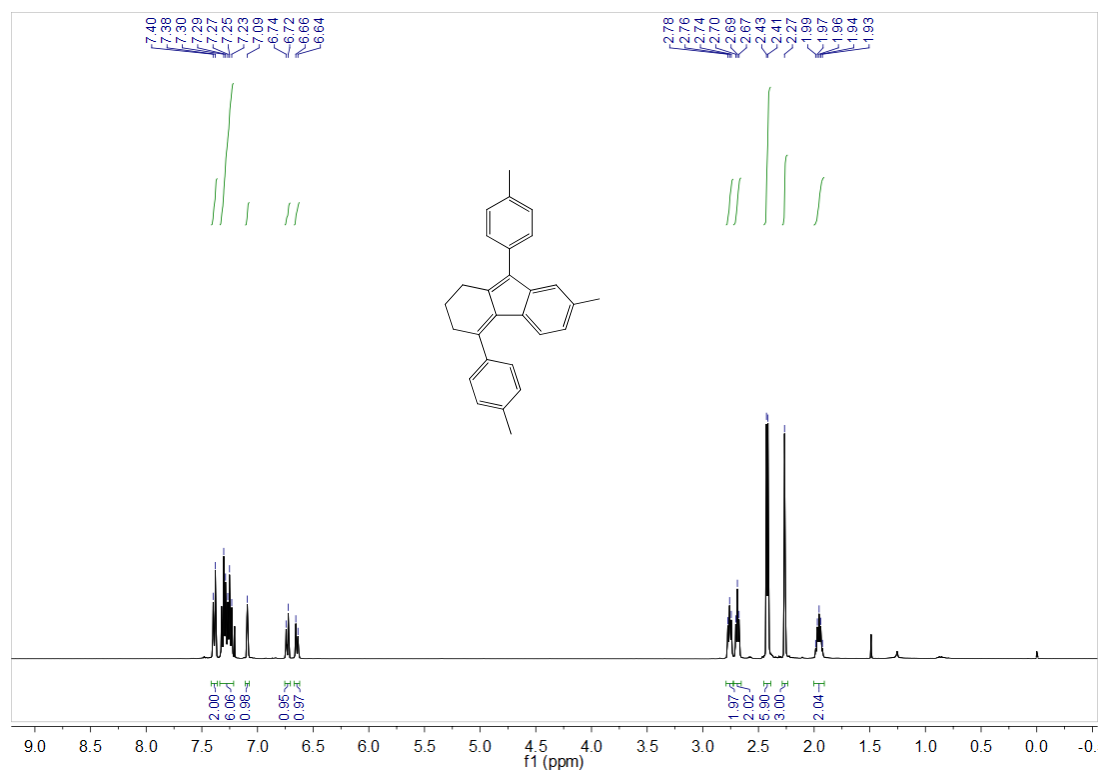
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ak

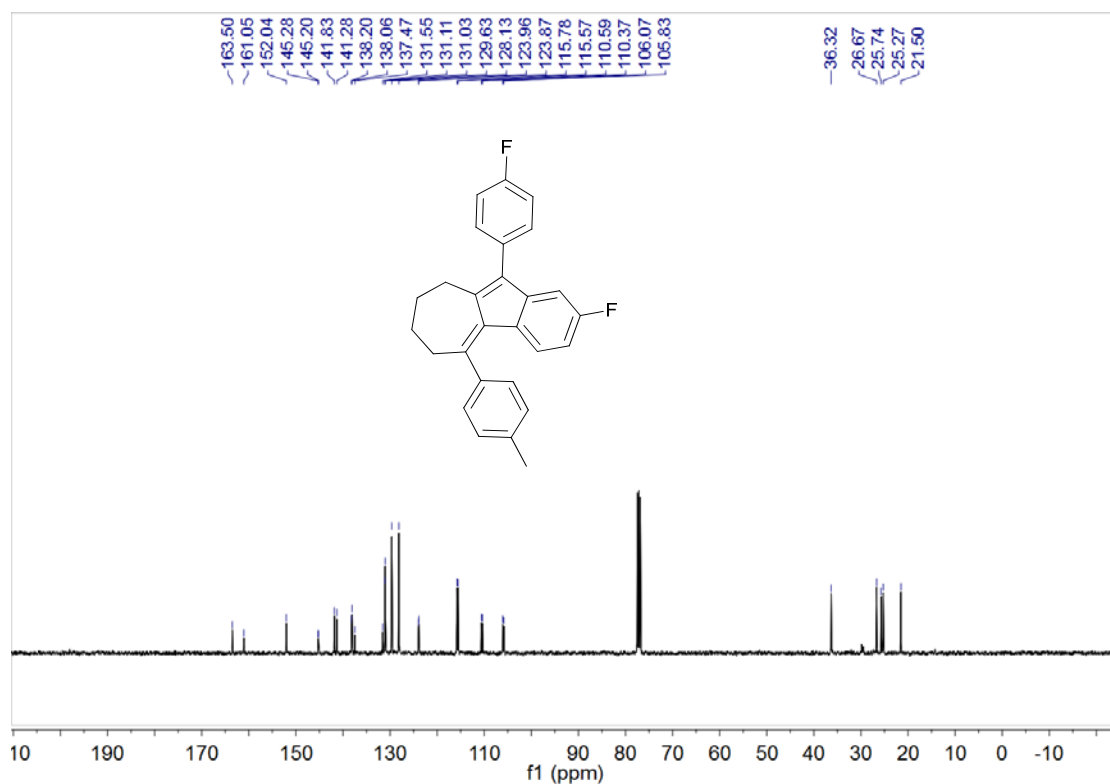
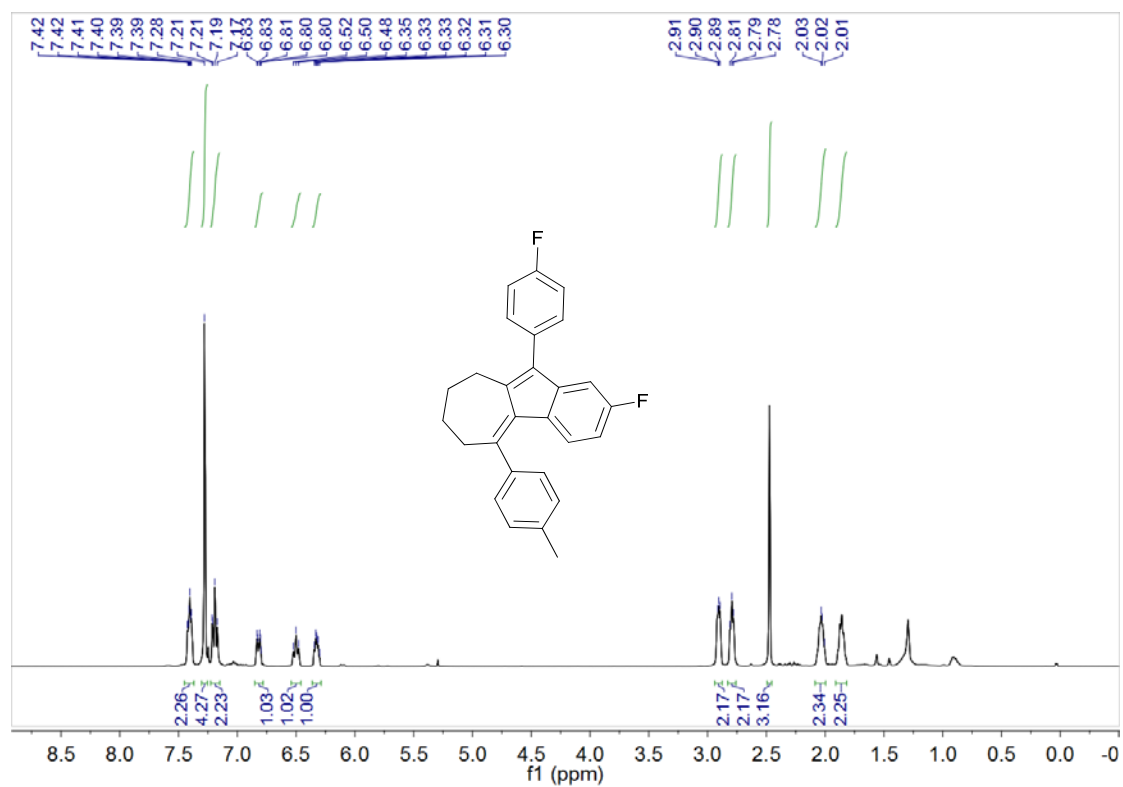


¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ba

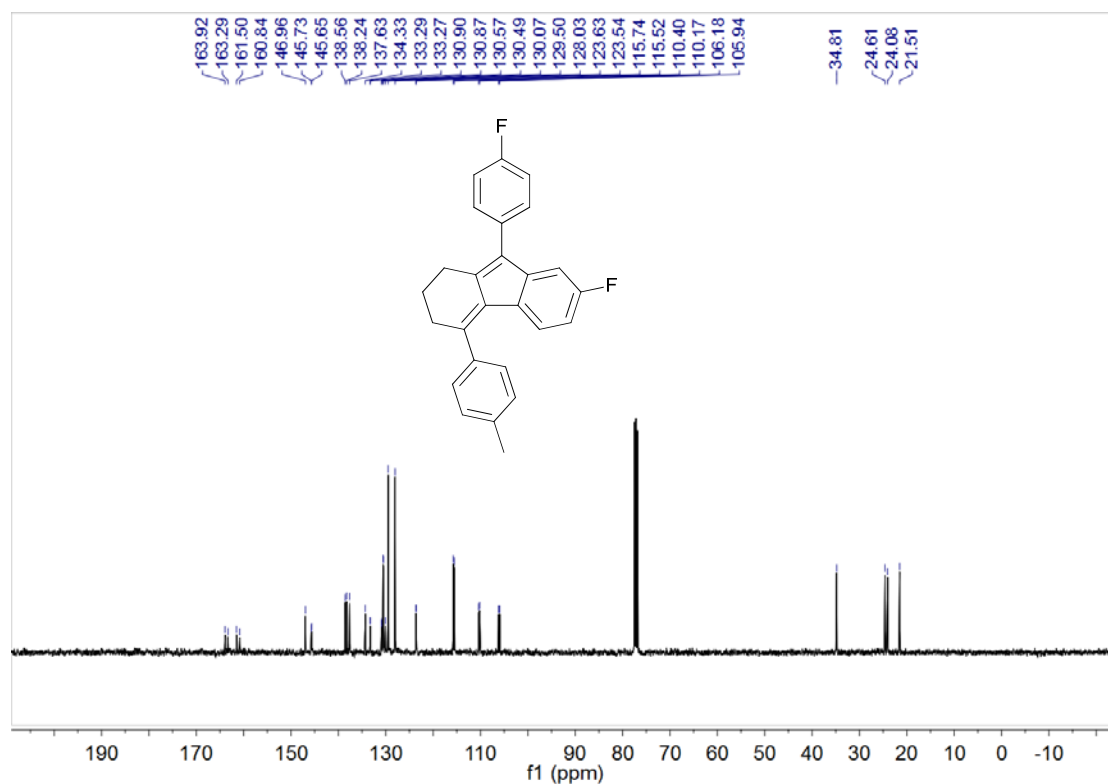
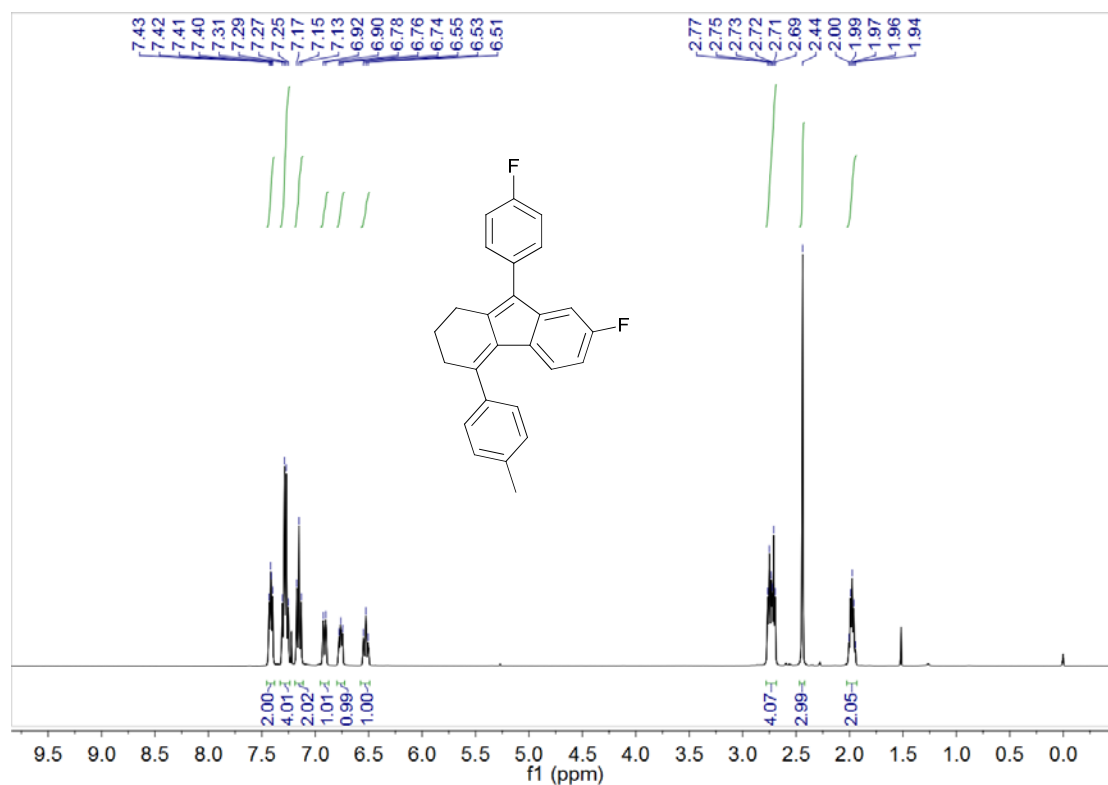


¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ca

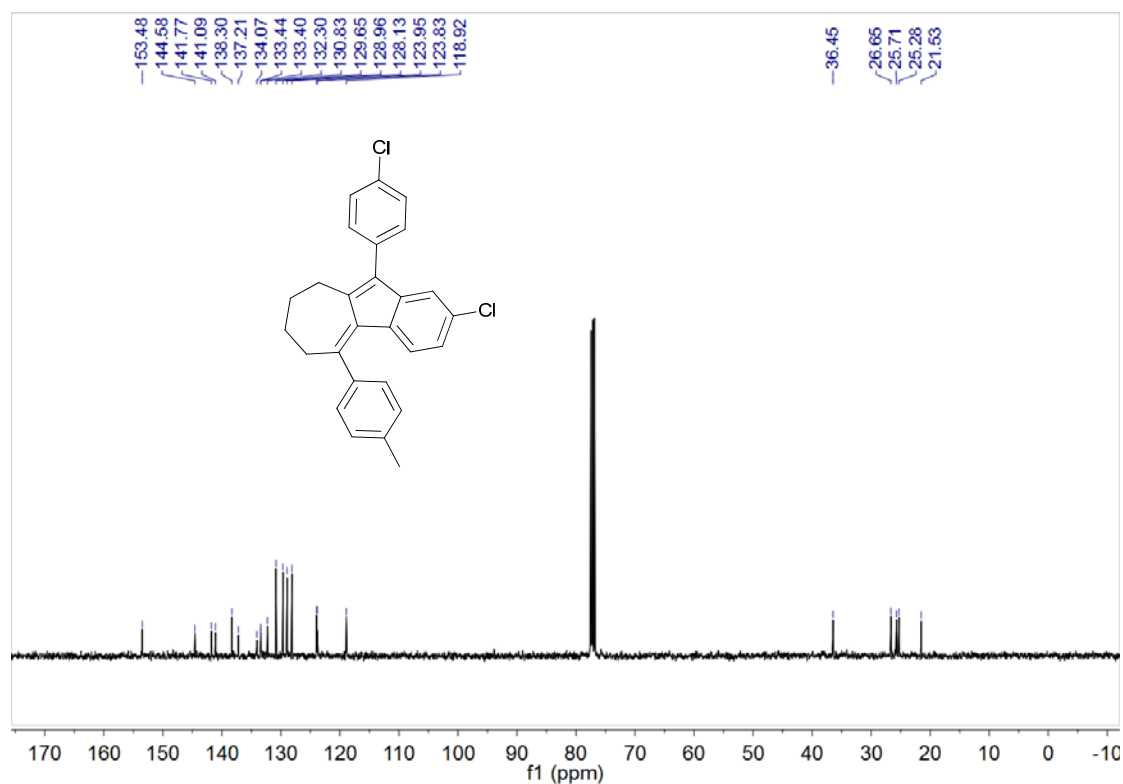
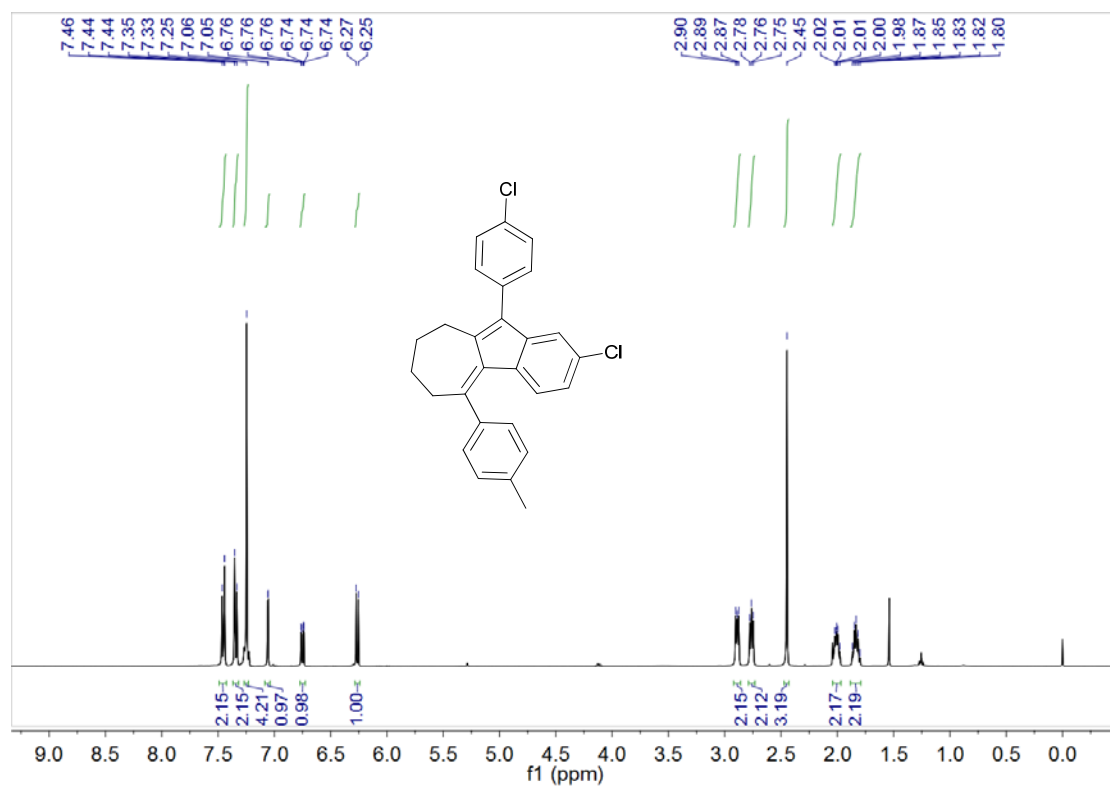
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3da



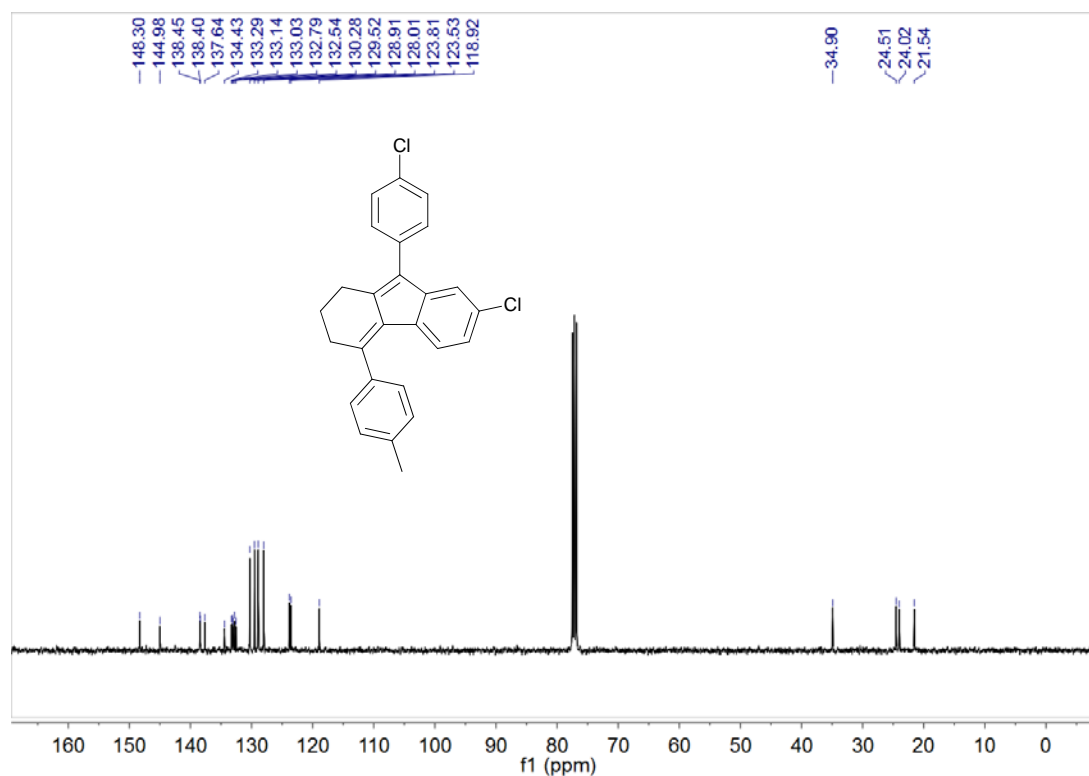
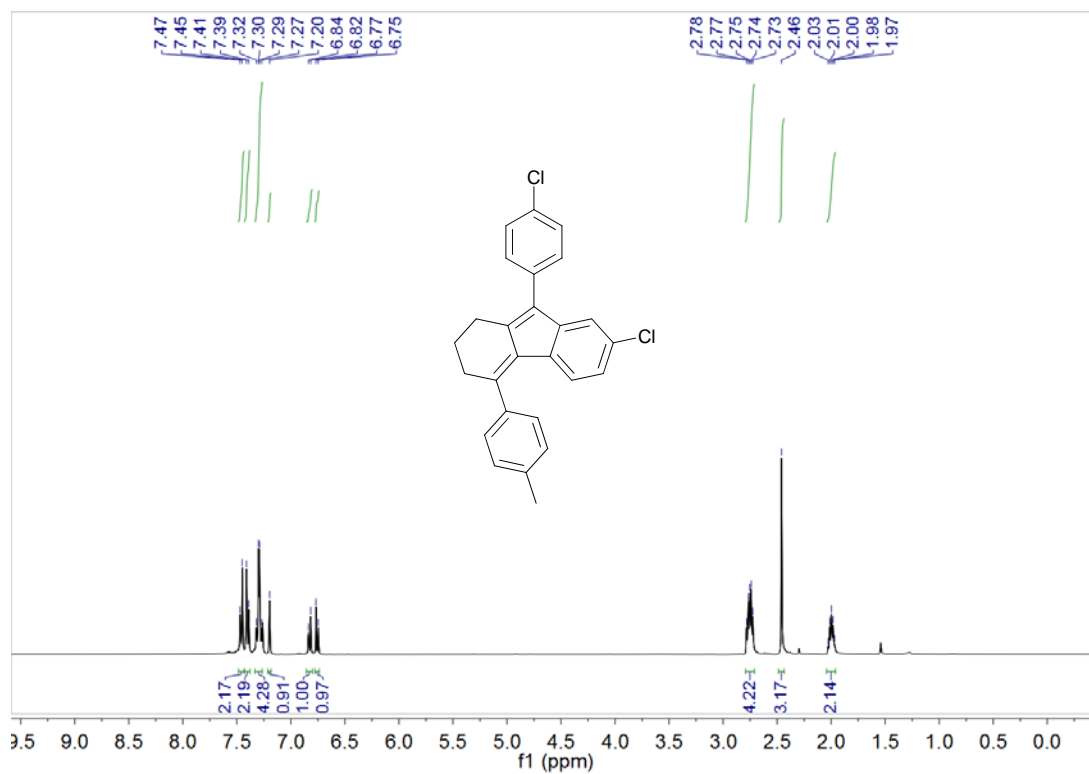
^1H NMR (400 MHz, CDCl_3) (up) and ^{13}C NMR (101 MHz, CDCl_3) (down)

3ea



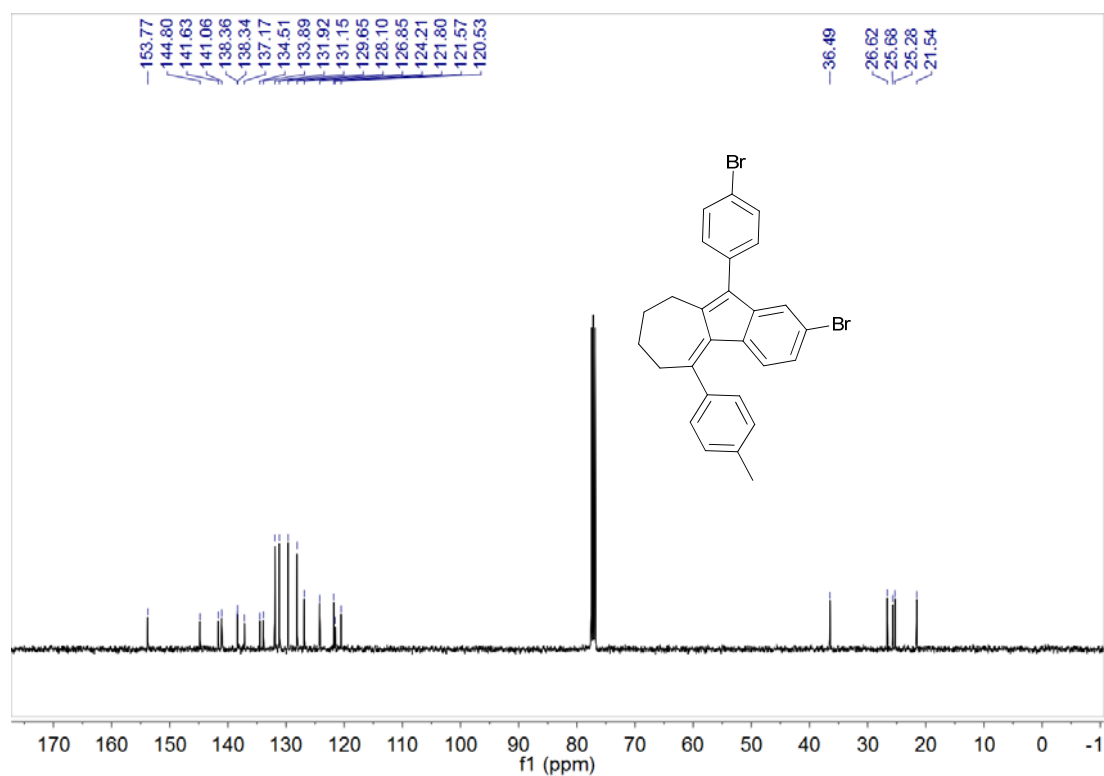
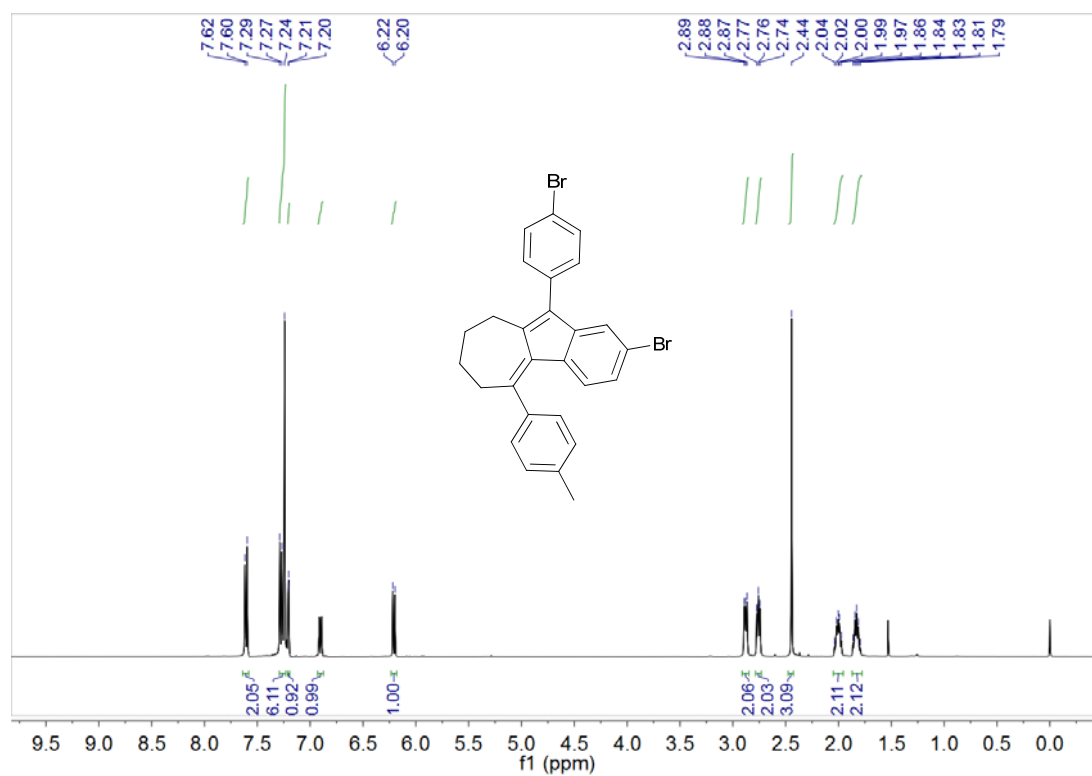
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3fa



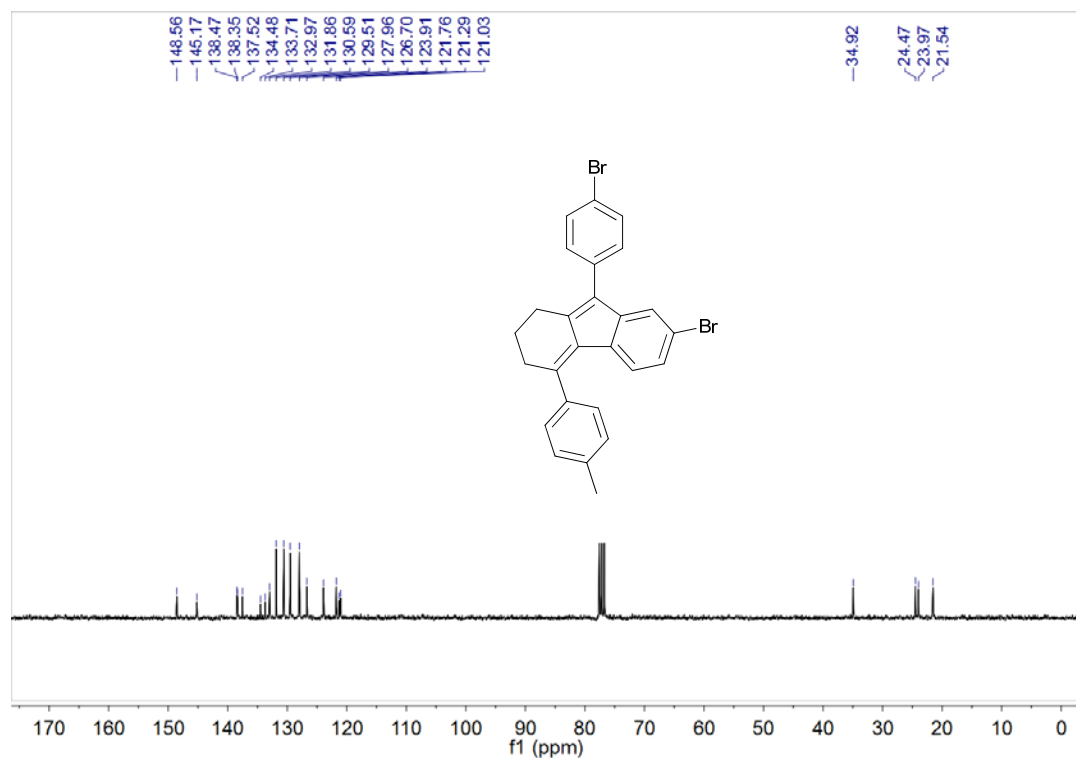
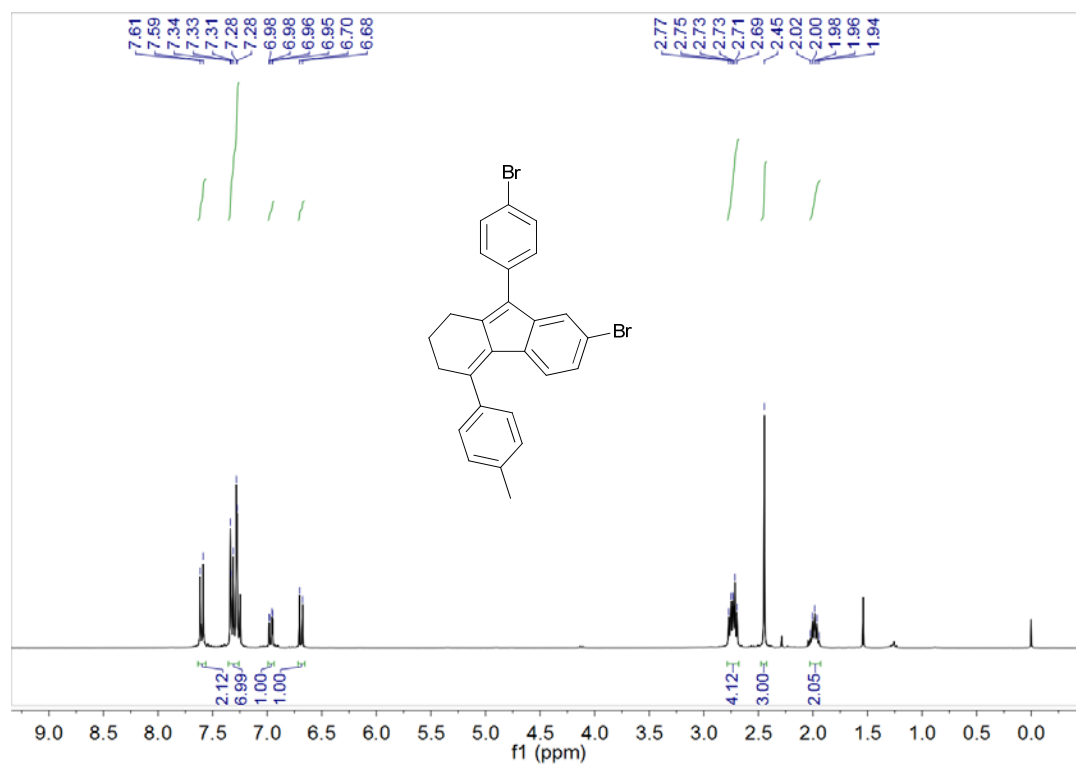
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ga



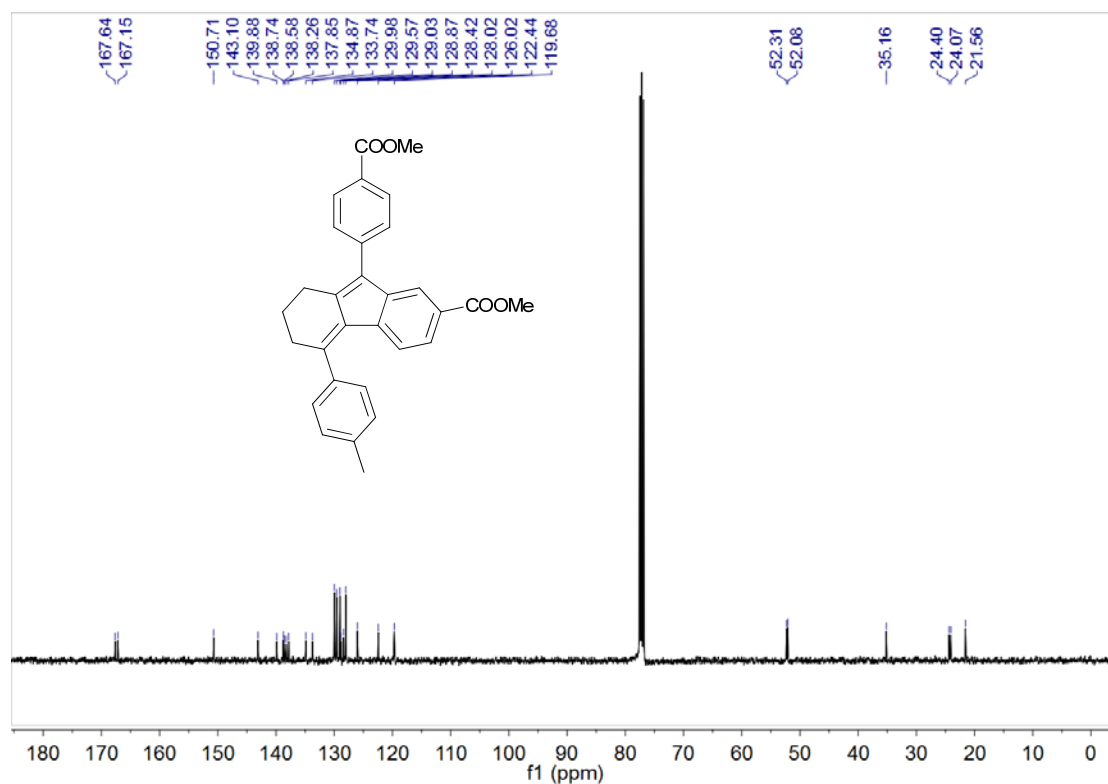
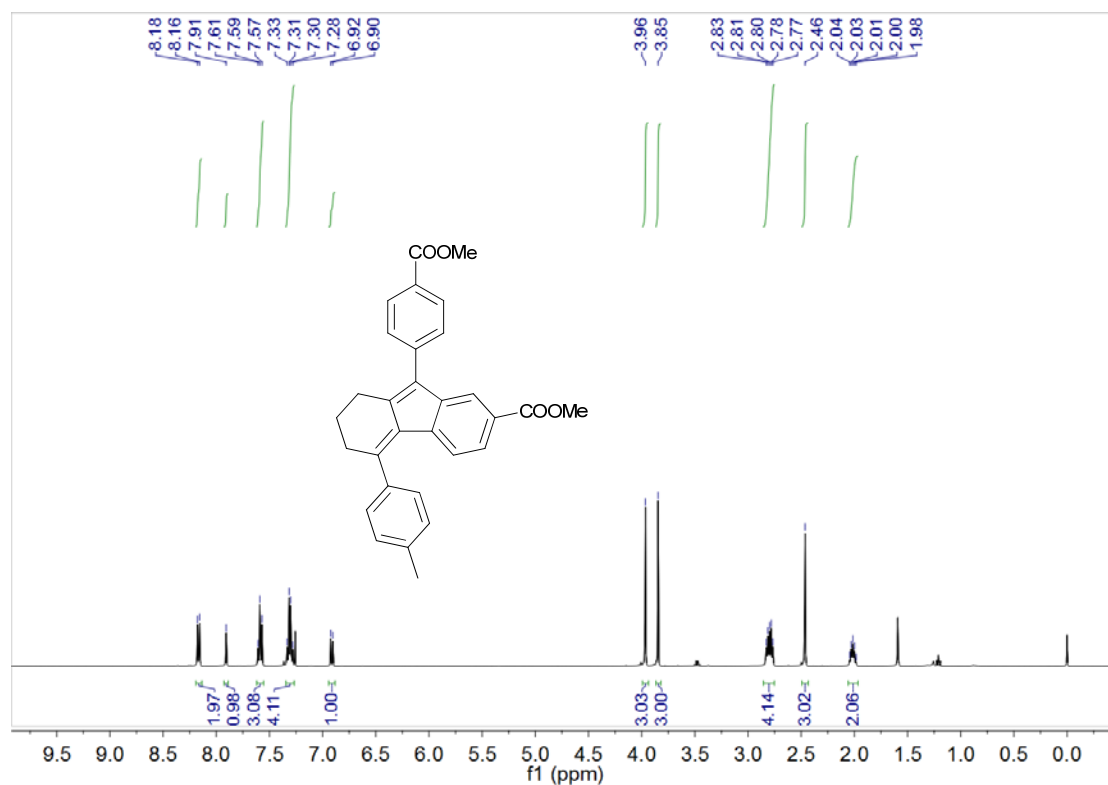
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ha



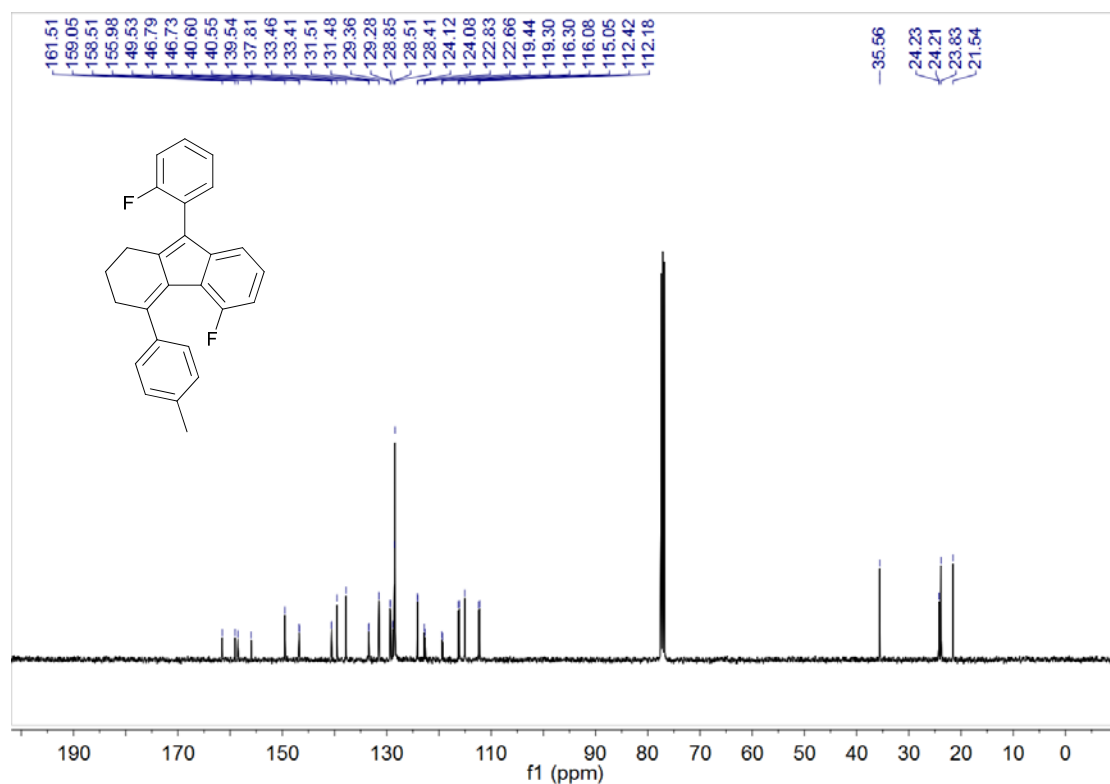
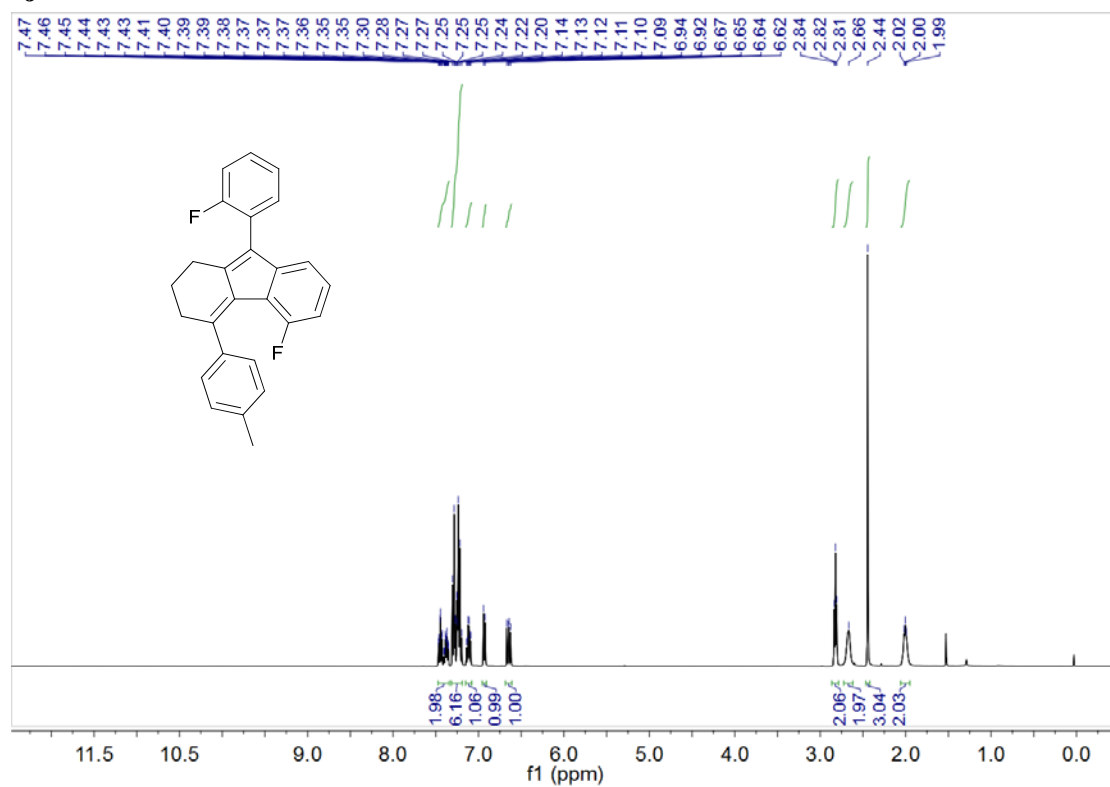
^1H NMR (300 MHz, CDCl_3) (up) and ^{13}C NMR (76 MHz, CDCl_3) (down)

3ia



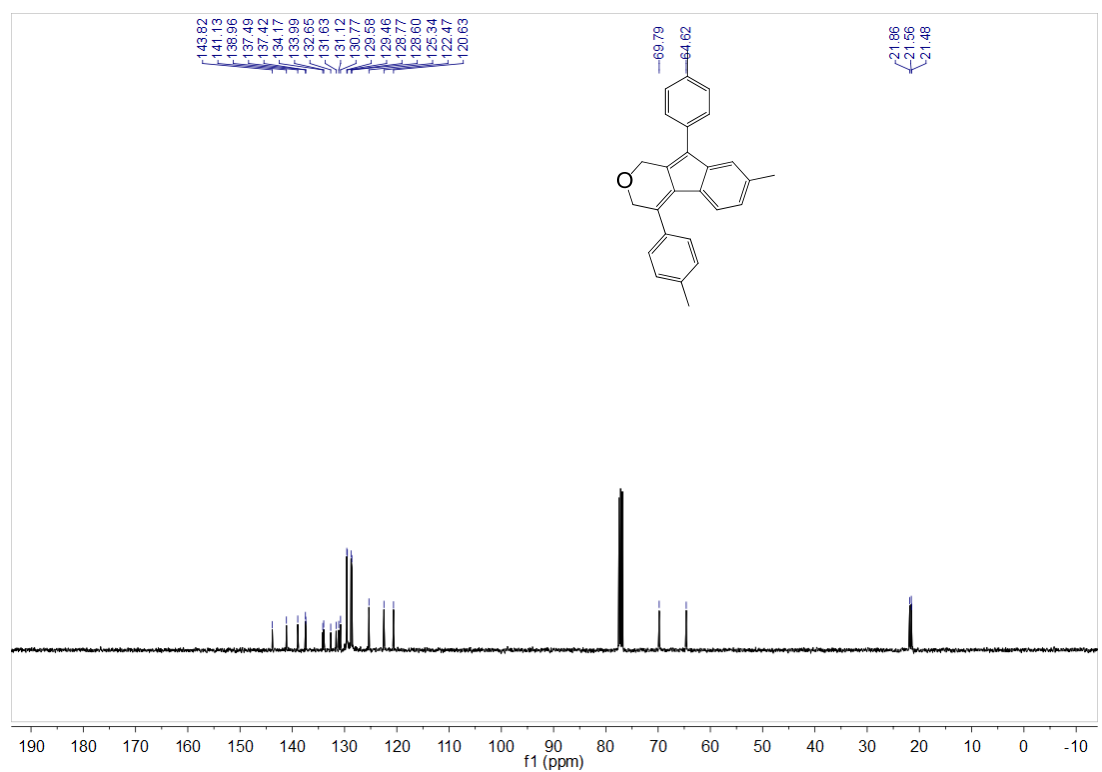
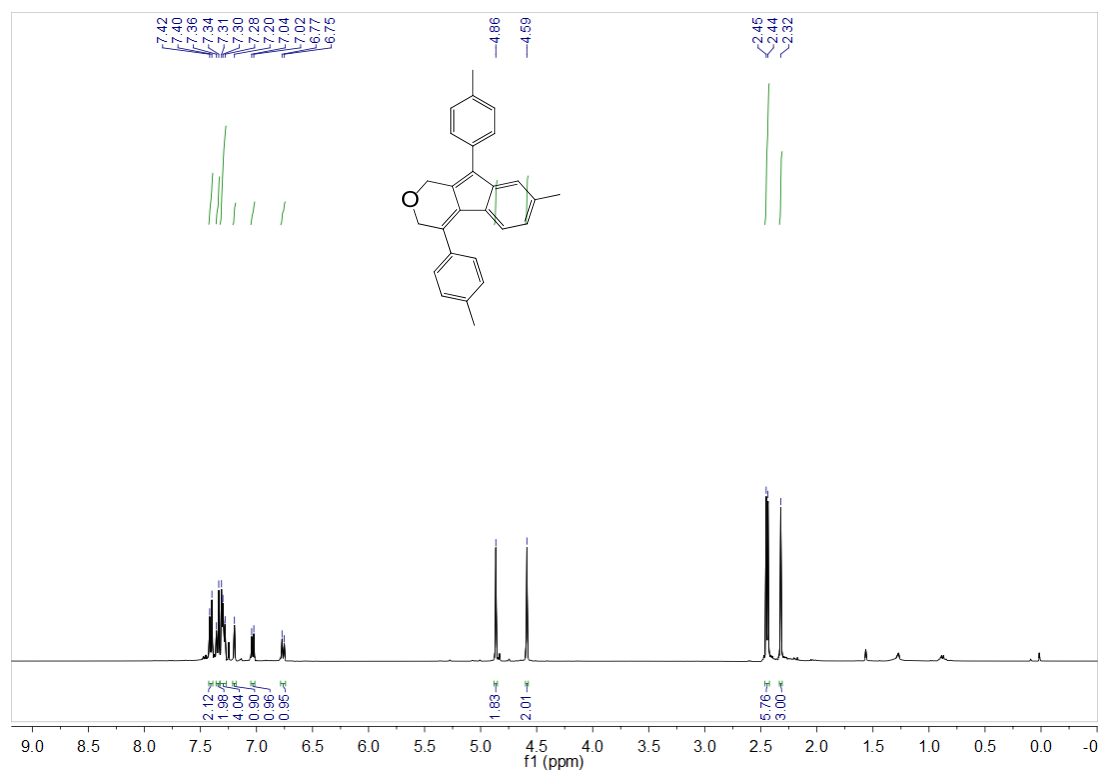
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ja



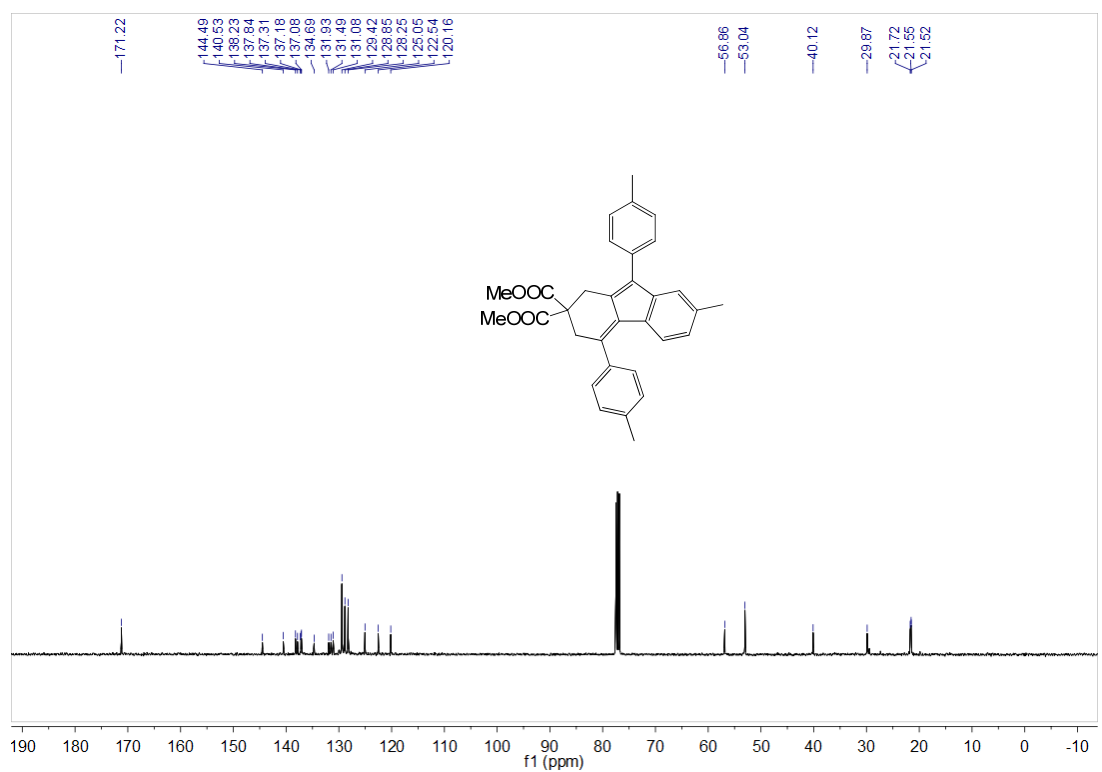
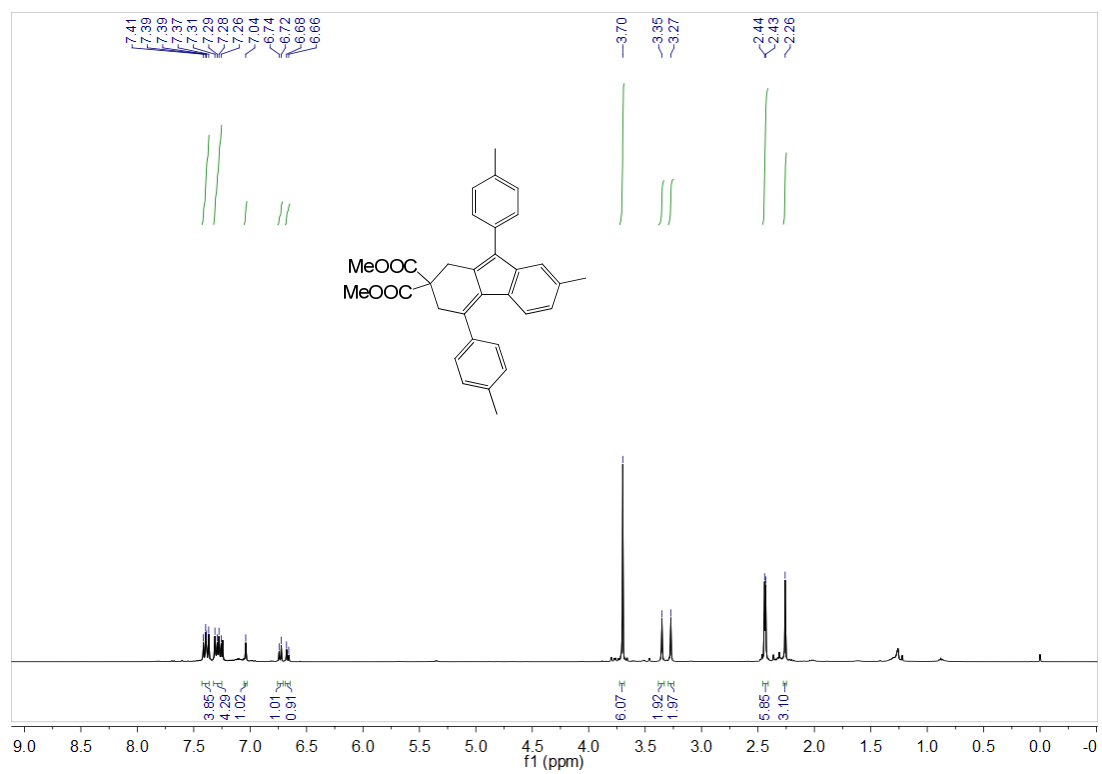
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3la



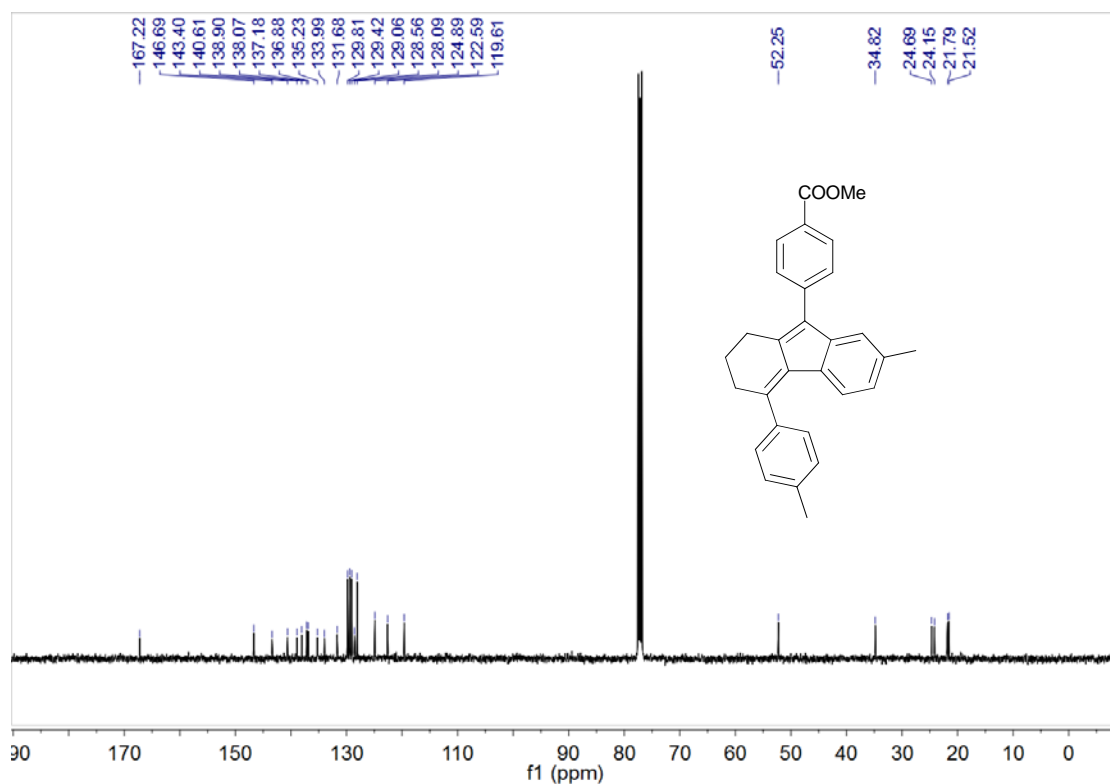
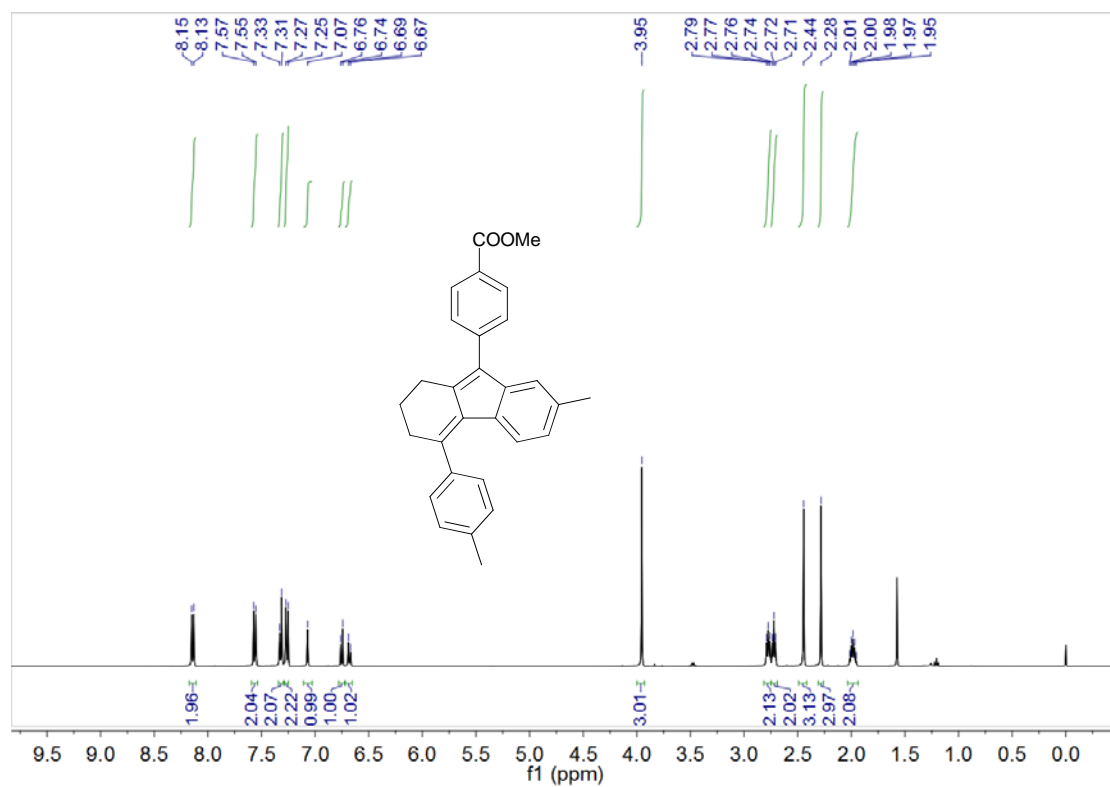
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

3ma



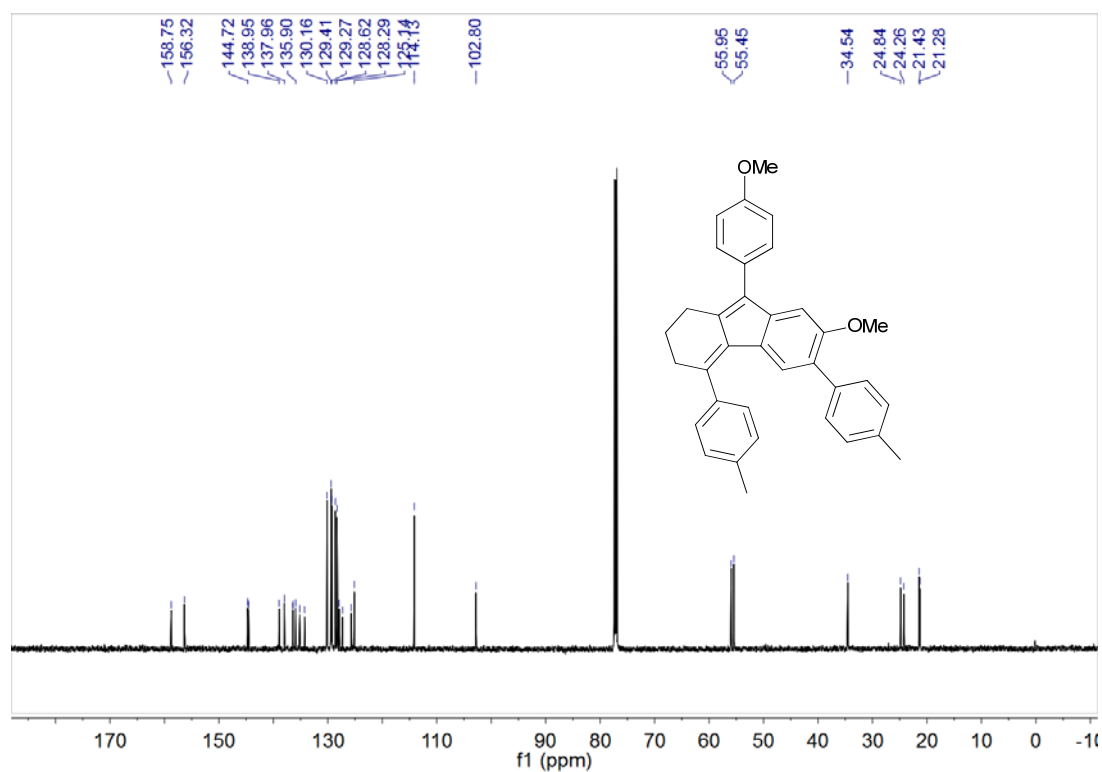
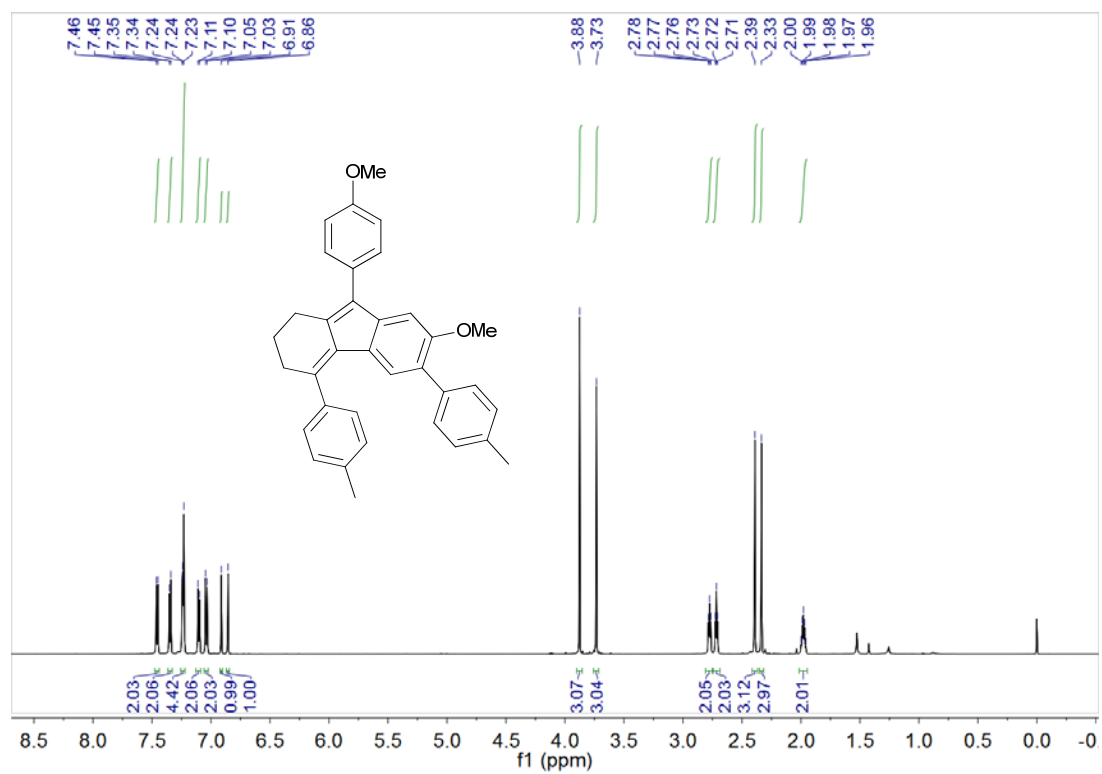
¹H NMR (400 MHz, CDCl₃) (up) and ¹³C NMR (101 MHz, CDCl₃) (down)

30a



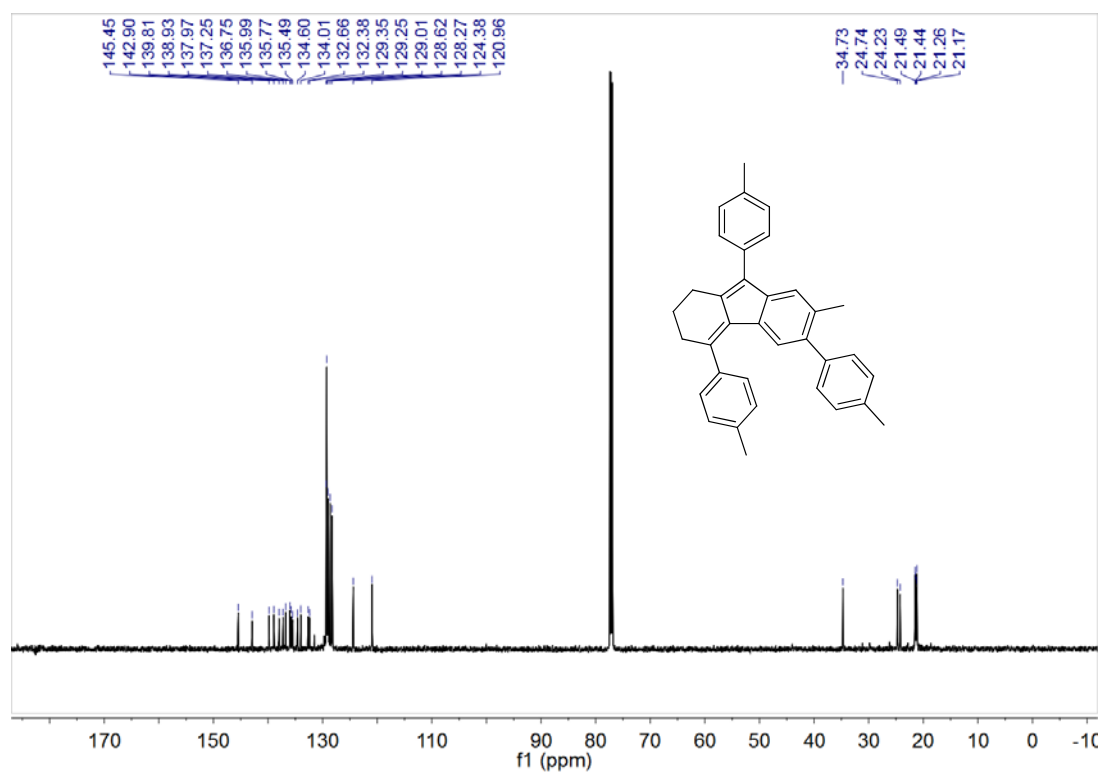
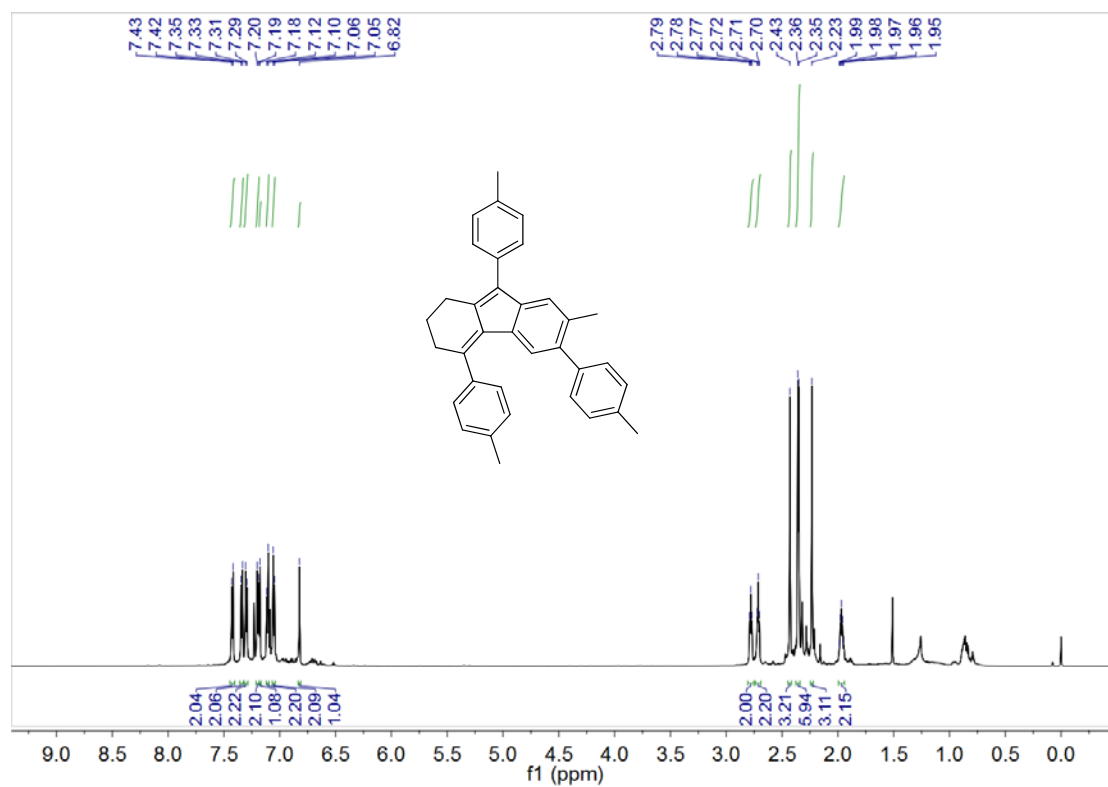
^1H NMR (400 MHz, CDCl_3) (up) and ^{13}C NMR (101 MHz, CDCl_3) (down)

4na



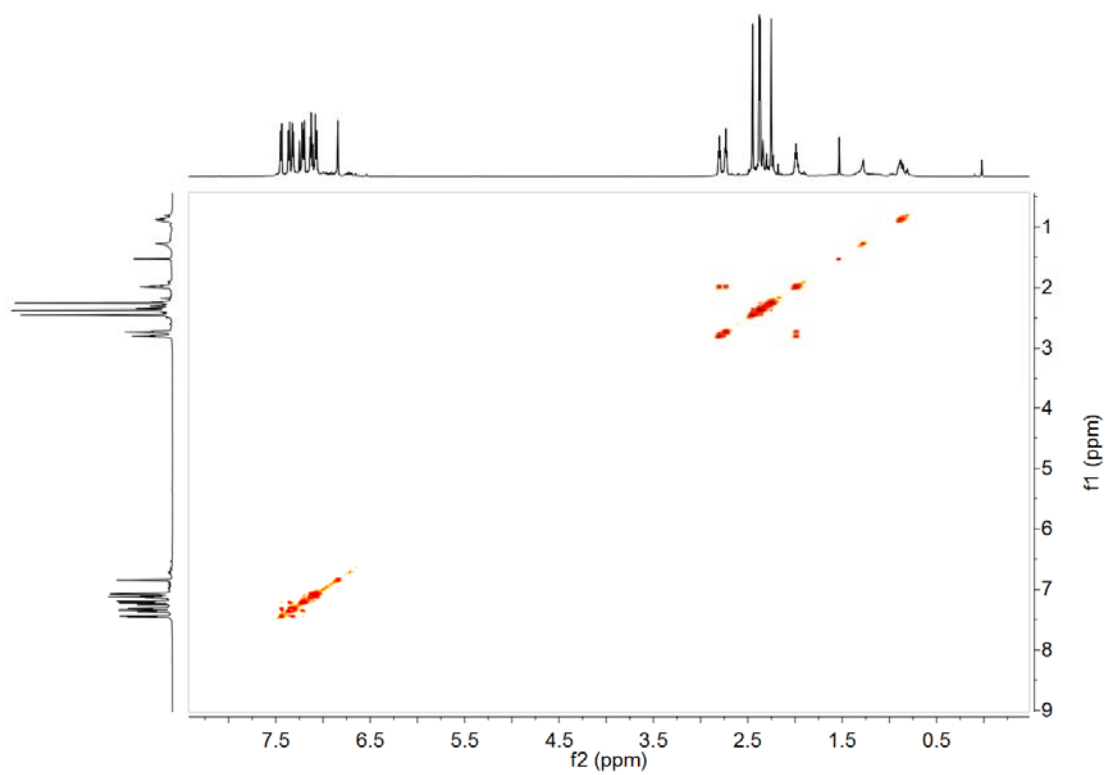
¹H NMR (600 MHz, CDCl₃) (up) and ¹³C NMR (151 MHz, CDCl₃) (down)

4ba

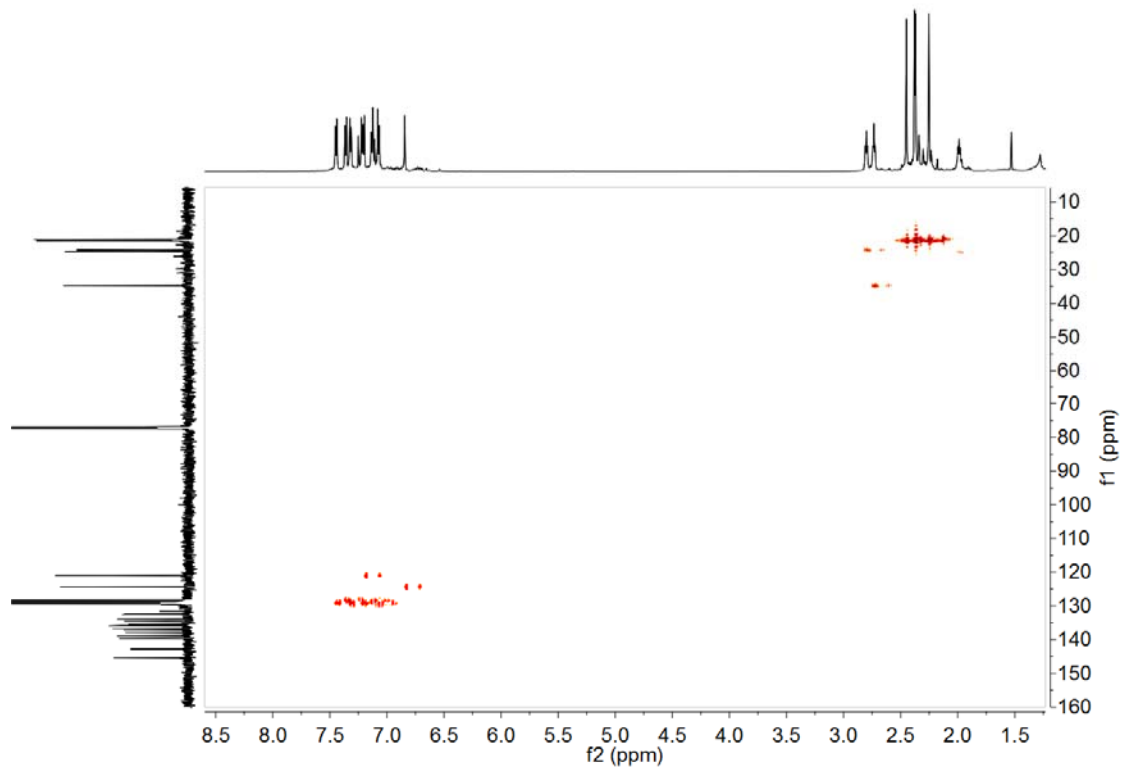


¹H NMR (600 MHz, CDCl₃) (up) and ¹³C NMR (151 MHz, CDCl₃) (down)

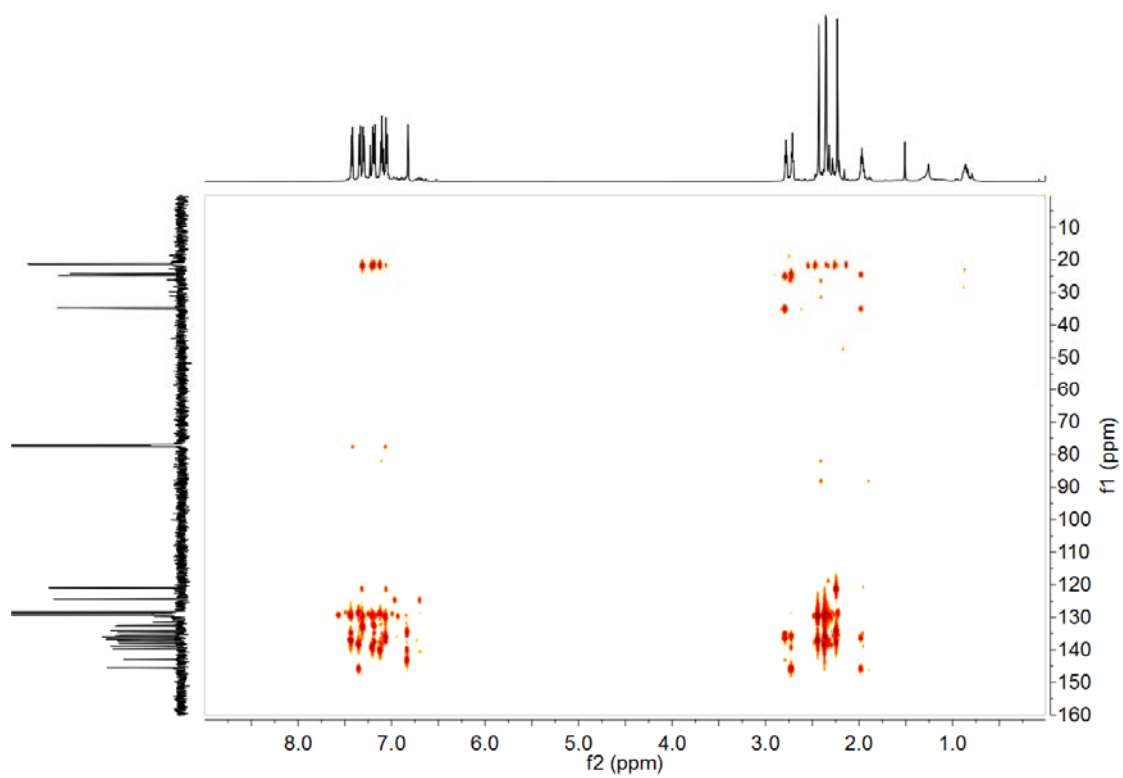
4ba-600M-H-H-COSY



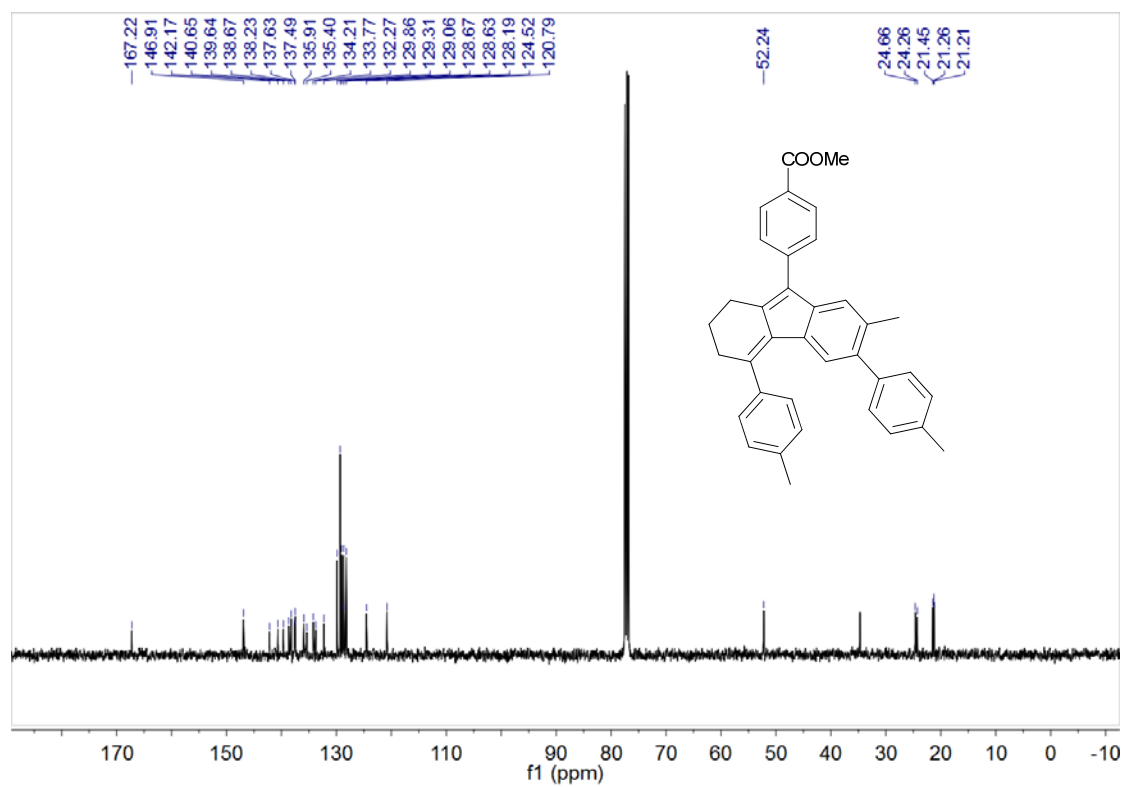
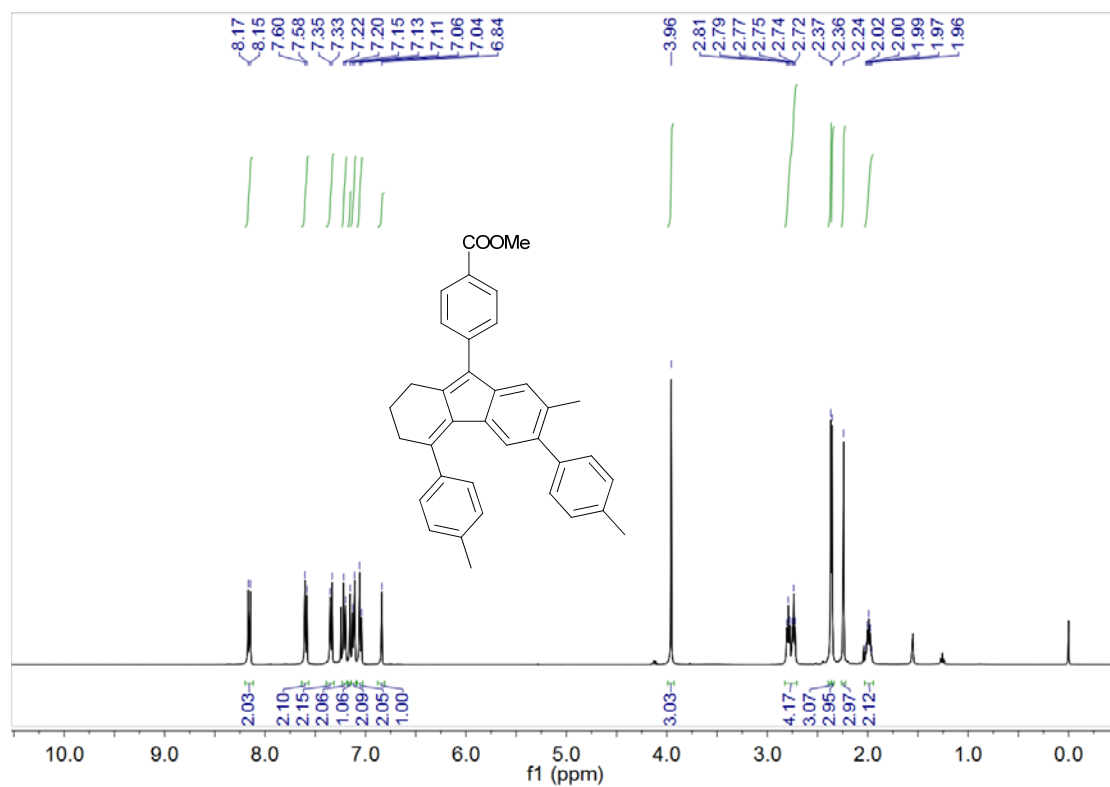
4ba-600M-C-H-HMQC



4ba-600M-C-H-HMBC

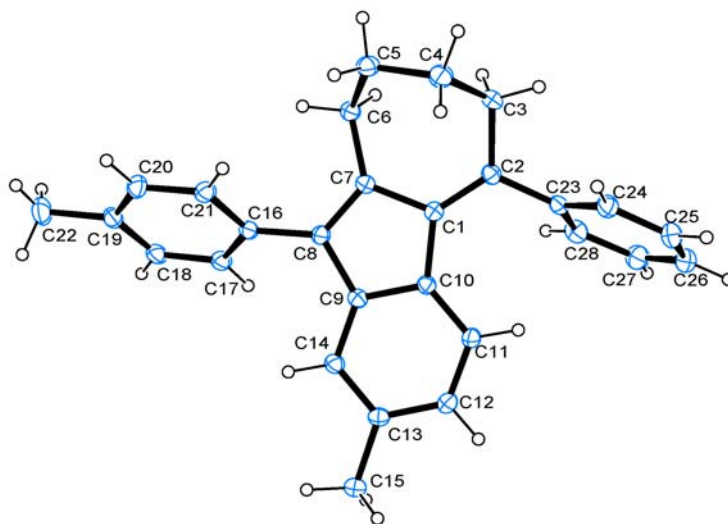


40a



8. X-ray single crystallographic data of compound **3ae**

Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in EA/ n-hexane. Formula: $C_{28}H_{26}$, $M = 362.20$, yellow crystal, $a = 20.325(14)$, $b = 11.622(2)$, $c = 8.5200(17)$ Å, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 2012.6(7)$ Å³, $\rho(\text{calcd}) = 1.196$ g/cm³, $\mu = 0.067$ mm⁻¹, $Z = 4$, Orthorhombic, space group $Pc a 2_1$, $\lambda = 0.71073$ Å, $T = 173 \pm 2$ K. Theta (max) = 27.4606° , $R(\text{reflections}) = 0.0547(3962)$, $wR2(\text{reflections}) = 0.1625(4122)$. CCDC number: 1471734



9. References

- 1 (a) C. Cheng, C. Chang, Y. Hsu, T. Lee, L. Chang, S. Liu and Y. Wu, *Eur. J. Org. Chem.*, 2010, 672. (b) M. K. Thorson, K. L. Klinkel, J. Wang and T. J. Williams, *Eur. J. Inorg. Chem.*, 2009, **2009**, 295.
- 2 B. M. Zhu and B. Olofsson, *Adv. Synth. Catal.*, 2007, **349**, 2610; M. Bielawski, D. Aili and B. Olofsson, *J. Org. Chem.*, 2008, **73**, 4602.