A simply and efficient synthesis of 9-arylfluorenes via metal-free reductive coupling of arylboronic acids and *N*-tosylhydrazones *in situ*

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Supporting Information

1. Materials and instruments

Chemicals were obtained commercially and used as received. NMR spectra were recorded on a Bruker DPX–400 spectrometer using TMS as the internal standard. EI–Mass spectrum was measured on a LC/Q–TOF MS (Micromass, England) or GC-MS (Agilent 7890A/5975C) instrument. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Arylboronic acids and aryl bromides were of analytical grade quality, purchased from Adamas-beta Pharmaceuticals, Inc. Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

2. General procedure for the one-pot two-steps reductive coupling of *N*-tosylhydrazones and arylboronic acids

A solution of the 9-fluorenone derivatives 1 (0.5 mmol) and tosylhydrazide (0.75 mmol) in 5 mL of toluene was stirred at 80 ºC for 2 h in a reaction tube. Potassium carbonate (1.0 mmol) and the appropriate boronic acid 2 (0.75 mmol) were added to the reaction mixture. The system was refluxed at 110 ºC for 5 h with stirring. When the reaction was complete, the crude mixture was allowed to reach room temperature. Dichloromethane and a saturated solution of $NaHCO_3$ were added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with a saturated solution of $NaHCO_3$, one portion of brine and then dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The products were purified by chromatography on silica gel.

3. The NMR Spectra Data

9-phenyl-9H-fluorene[3a][1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.26 (d, *J* = 4.9 Hz, 6H), 7.09 (d, *J* = 6.4 Hz, 2H), 5.05 (s, 1H).

9-(p-tolyl)-9H-fluorene[3b][2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 5.01 (s, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.09, 140.97, 138.52, 136.39, 129.40, 128.20, 127.29, 127.23, 125.29, 119.83, 77.35, 77.03, 76.71, 54.09, 21.10.

9-(4-methoxyphenyl)-9H-fluorene[3c][2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 7.6, 0.6 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.25 (dd, *J* = 7.2, 1.1 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.99 (s, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.53 (s), 148.22 (s), 140.92 (s), 133.55 (s), 129.31 (s), 127.28 (d, *J* = 5.2 Hz), 125.29 (s), 119.86 (s), 114.12 (s), 77.37 (s), 77.06 (s), 76.74 (s), 55.25 (s), 53.70 (s).

9-(4-propylphenyl)-9H-fluorene[3d]

Mp. 88-89 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.29 – 7.22 (m, 2H), 7.03 (ddd, *J* = 9.8, 7.2, 1.9 Hz, 4H), 5.02 (s, 1H), 2.57 – 2.51 (m, 2H), 1.61 (ddd, *J* = 9.1, 7.5, 4.1 Hz, 2H), 0.96 – 0.90 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09 (s), 141.20 (s), 140.98 (s), 138.68 (s), 128.76 (s), 128.13 (s), 127.25 (dd, *J* = 3.0, 2.1 Hz), 125.35 (s), 119.83 (s), 77.36 (s), 77.04 (s), 76.72 (s), 54.13 (s), 37.74 (s), 24.52 (s), 13.94 (s).

HRMS(EI):m/z calcd for $C_{22}H_{24}$ $[M]^+$ 284.1565,found 284.1563.

IR (KBr, cm^{-1}): 2953, 2928, 2826, 1510, 1448, 738.

9-(4-pentylphenyl)-9H-fluorene[3e]

Mp.74-75 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.25 (td, *J* = 7.2, 1.1 Hz, 3H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.97 (m, 2H), 5.02 (s, 1H), 2.58 – 2.52 (m, 2H), 1.63 – 1.53 (m, 3H), 1.34 – 1.24 (m, 5H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.07 (s), 141.45 (s), 140.97 (s), 138.61 (s), 128.68 (s), 128.13 (s), 127.23 (d, *J* = 4.2 Hz), 125.34 (s), 119.82 (s), 77.34 (s), 77.02 (s), 76.71 (s), 54.11 (s), 35.61 (s), 31.61 (s), 31.14 (s), 22.56 (s), 14.05 (s).

HRMS(EI):m/z calcd for $C_{24}H_{24}$ $[M]^+$ 312.1878, found 312.1873.

IR (KBr, cm^{-1}): 3048, 2951, 2876, 1510, 1449, 739.

9-(4-fluorophenyl)-9H-fluorene[3f][1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.35 – 7.27 (m, 4H), 7.12 – 7.06 (m, 2H), 6.99 (ddd, *J* = 8.8, 5.8, 2.5 Hz, 2H), 5.06 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.05 (s), 141.07 (s), 128.77 – 128.55 (m), 127.60 (d, *J* = 19.1 Hz), 125.67 (d, *J* = 3.8 Hz), 125.25 (s), 120.08 (s), 77.35 (s), 77.03 (s), 76.71 (s), 54.07 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.17 (d, *J* = 1.8 Hz).

9-(4-(trifluoromethyl)phenyl)-9H-fluorene[3g][3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.29 – 7.24 (m, 4H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.09 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.05 (s), 145.94 (s), 141.07 (s), 129.33 (s), 129.01 (s), 128.78 – 128.55 (m), 127.60 (d, *J* = 19.1 Hz), 125.83 – 125.46 (m), 125.26 (d, *J* = 1.0 Hz), 122.86 (s), 120.08 (d, *J* = 1.0 Hz), 77.35 (s), 77.03 (s), 76.71 (s), 54.07 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44 (s).

9-(3,4,5-trifluorophenyl)-9H-fluorene[3h]

Mp.115.7-116.8 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.9, 0.7 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.30 – 7.27 (m, 4H), 6.70 (dd, *J* = 8.5, 6.5 Hz, 2H), 4.95 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.28 (s), 140.94 (s), 127.96 (s), 127.62 (s), 125.14 (s), 120.18 (s), 112.20 (dd, *J* = 15.6, 5.8 Hz), 86.82 (s), 77.35 (s), 77.03 (s), 76.71 (s), 53.39 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.06 (d, *J* = 20.7 Hz), -162.77 (t, *J* = 20.6 Hz).

HRMS(EI):m/z calcd for $C_{19}H_{11}F_3$ $[M]^+$ 296.0813, found 296.0810.

IR (KBr, cm^{-1}): 3048, 2951, 2876, 1510, 1449, 739.

9-(m-tolyl)-9H-fluorene[3i][4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.37 (ddd, *J* = 7.6, 1.2, 0.6 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 0.5 Hz, 1H), 6.93 – 6.86 (m, 2H), 5.00 (s, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.00 (s), 141.48 (s), 141.02 (s), 138.31 (s), 128.92 (s), 128.55 (s), 127.67 (s), 127.29 (d, *J* = 3.6 Hz), 125.45 (d, *J* = 16.9 Hz), 119.86 (s), 77.38 (s), 77.06 (s), 76.74 (s), 54.45 (s), 21.45 (s).

9-(naphthalen-2-yl)-9H-fluorene[3j][5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 5H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.34 – 7.23 (m, 4H), 6.90 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.21 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.92 (d, *J* = 0.9 Hz), 141.13 (s), 139.11 (s), 133.63 (s), 132.61 (s), 128.52 (s), 127.89 – 127.14 (m), 126.17 (d, *J* = 11.7 Hz), 125.55 (d, *J* = 12.8 Hz), 119.96 (d, *J* = 0.9 Hz), 77.37 (s), 77.05 (s), 76.73 (s), 54.63 (s).

9-(o-tolyl)-9H-fluorene[3k][3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 3H), 7.42 (s, 3H), 7.33 – 7.28 (m, 7H), 5.46 (s, 1H), 2.82 (s, 3H).

9-(2,3-difluorophenyl)-9H-fluorene[3l]

Mp. 100-101 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.28 (td, *J* = 7.4, 1.1 Hz, 2H), 7.07 – 6.98 (m, 1H), 6.84 (tdd, *J* = 8.1, 5.0, 1.7 Hz, 1H), 6.42 (dd, *J* = 7.7, 6.3 Hz, 1H), 5.49 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.20 (d, *J* = 1.1 Hz), 141.16 (s), 131.22 (d, *J* = 11.9 Hz), 127.57 (d, *J* = 17.4 Hz), 125.19 (d, *J* = 1.2 Hz), 124.15 (dd, *J* = 7.0, 4.7 Hz), 123.80 (s), 120.07 (s), 115.58 (d, *J* = 17.0 Hz), 77.34 (s), 77.02 (s), 76.71 (s), 29.72 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.94 – -138.01 (m), -143.90 (d, *J* = 19.9 Hz).

HRMS(EI):m/z calcd for $C_{19}H_{12}F_2$ $[M]^+$ 278.0907, found 278.0909.

IR (KBr, cm^{-1}): 1485, 1446, 1280, 945, 800, 779, 742.

9-(2,4-difluorophenyl)-9H-fluorene[3m]

Mp. 94.6-95.3 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.28 (dd, *J* = 7.4, 1.0 Hz, 2H), 6.94 – 6.87 (m, 1H), 6.70 – 6.59 (m, 2H), 5.42 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.55 (s), 141.11 (s), 127.51 (d, *J* = 12.4 Hz), 125.13 (d, *J* = 1.2 Hz), 120.05 (s), 111.74 – 111.25 (m), 104.12 (s), 103.87 (s), 77.34 (s), 77.02 (s), 76.70 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.22 (dd, *J* = 6.8, 1.1 Hz), -114.77 (s).

HRMS(EI):m/z calcd for $C_{19}H_{12}F_2$ $[M]^+$ 278.0907, found 278.0909.

IR (KBr, cm^{-1}): 1620, 1604, 1500, 1447, 1267, 964, 852, 739.

3-(9H-fluoren-9-yl)thiophene[3n][6]

^{1}H NMR (400 MHz, DMSO) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.38 (ddd, *J* = 11.4, 6.2, 3.4 Hz, 5H), 7.44 – 7.23 (m, 8H), 7.32 – 7.24 (m, 3H), 6.64 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.64 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.30 (s, 1H), 5.30 (s, 1H).

^{13}C NMR (101 MHz, DMSO) δ 147.14 (s), 141.48 (s), 140.62 (s), 127.83 (d, *J* = 6.4 Hz), 127.46 (s), 127.11 (s), 125.59 (s), 122.32 (s), 120.63 (s), 49.12 (s), 40.80 (s), 40.74 (s), 40.53 (d, *J* = 21.4 Hz), 40.10 (d, *J* = 21.1 Hz), 39.68 (d, *J* = 21.3 Hz), 39.36 (s), 39.04 – 33.96 (m).

2-(9H-fluoren-9-yl)furan[3o][7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 3H), 6.29 (s, 1H), 6.03 (s, 1H), 5.21 (s, 1H).

9-butyl-9H-fluorene[3p][8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.5, 0.7 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.37 – 7.27 (m, 4H), 3.96 (t, *J* = 5.9 Hz, 1H), 2.03 – 1.96 (m, 2H), 1.31 – 1.11 (m, 5H), 0.82 (td, *J* = 7.2, 1.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.65 (s), 141.15 (s), 126.82 (d, *J* = 4.9 Hz), 124.37 (s), 119.79 (s), 77.39 (s), 77.22 (d, *J* = 32.0 Hz), 76.74 (s), 47.50 (s), 32.84 (s), 27.84 (s), 23.06 (s), 13.96 (s).

2-bromo-9-(4-methoxyphenyl)-9H-fluorene[3q]

Mp. 107-108 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.49 (ddd, *J* = 8.1, 1.8, 0.7 Hz, 1H), 7.44 – 7.32 (m, 2H), 7.32 – 7.23 (m, 2H), 7.02 – 6.94 (m, 2H), 6.86 – 6.79 (m, 2H), 4.97 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.74 (s), 150.23 (s), 147.90 (s), 139.88 (d, *J* = 2.1 Hz), 132.57 (s), 130.43 (s), 129.29 (s), 128.54 (s), 127.73 (s), 127.47 (s), 125.35 (s), 121.11 (d, *J* = 14.6 Hz), 119.92 (s), 114.26 (s), 55.27 (s), 53.61 (s).

HRMS(EI): m/z calcd for $C_{20}H_{15}BrO$, $[M]^+$ 350.0306, found 350.0305.

IR (KBr, cm^{-1}): 1508, 1460, 1258, 1176, 742.

2,7-dibromo-9-(4-methoxyphenyl)-9H-fluorene[3r]

Mp. 153.5-155.5 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 (ddd, *J* = 8.1, 1.8, 0.7 Hz, 2H), 7.40 – 7.36 (m, 2H), 6.92 (s, 2H), 6.81 (s, 2H), 4.92 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95 (s), 149.88 (s), 138.85 (s), 131.60 (s), 130.69 (s), 129.29 (d, *J* = 1.0 Hz), 128.61 (s), 121.52 (s), 121.25 (s), 114.42 (s), 77.36 (s), 77.04 (s), 76.73 (s), 55.30 (s), 53.50 (s).

HRMS(EI):m/z calcd for $C_{20}H_{14}Br_2O$ $[M]^+$ 429.9391, found 429.9387.

IR (KBr, cm^{-1}): 1510, 1456, 1258, 964, 806.

9-(4-methoxyphenyl)-2-nitro-9H-fluorene[3s]

Mp. 149.8-151.1 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 15.8 Hz, 1H), 8.15 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 5.8, 1.0 Hz, 3H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.09 (s, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98 (s), 149.76 (s), 149.22 (s), 147.22 (s), 138.63 (s), 131.39 (s), 129.33 (d, *J* = 19.9 Hz), 127.90 (s), 125.70 (s), 123.57 (s), 121.26 (s), 120.77 (s), 119.97 (s), 114.46 (s), 77.33 (s), 77.01 (s), 76.69 (s), 55.29 (s), 53.72 (s).

HRMS(EI):m/z calcd for $C_{20}H_{15}NO_3$ $[M-H]^+$ 316.0968, found 316.0973.

IR (KBr, cm^{-1}): 1510, 1333, 1258, 1030, 752.

2-bromo-9-(4-methoxyphenyl)-7-nitro-9H-fluorene[3t]

Mp. 191.5-192.8 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.16 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.03 – 6.98 (m, 2H), 6.90 – 6.85 (m, 2H), 5.10 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.20 (s), 151.59 (s), 148.94 (s), 147.48 (s), 146.10 (s), 137.55 (s), 131.23 (s), 130.45 (s), 129.24 (s), 129.02 (s), 123.70 (d, *J* = 8.0 Hz), 122.50 (s), 120.85 (s), 120.12 (s), 114.63 (s), 77.33 (s), 77.01 (s), 76.69 (s), 55.32 (s), 53.64 (s).

HRMS(EI):m/z calcd for $C_{20}H_{14}BrNO_3$ $[M-H]^+$ 394.0073, found 394.0080.

IR (KBr, cm^{-1}): 1600, 1510, 1337, 1250, 1028, 818, 737.

9-(4-methoxyphenyl)-9H-fluoren-2-amine[3u]

Mp. 161.4-162 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.14 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.83 – 6.78 (m, 2H), 6.70 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.63 (s, 1H), 4.89 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.45 (s), 150.13 (s), 147.34 (s), 141.36 (s), 133.98 (s), 129.35 (s), 127.13 (s), 125.63 (s), 125.00 (s), 120.68 (s), 118.54 (s), 114.42 (s), 114.05 (s), 112.01 (s), 77.34 (s), 77.02 (s), 76.71 (s), 55.24 (s), 53.54 (s).

HRMS(EI):m/z calcd for $C_{20}H_{17}NO$ $[M]^+$ 287.1305, found 287.1311.

IR (KBr, cm^{-1}): 3564, 3412, 1609, 1510, 1456, 1252, 1179, 1034, 825, 741.

9-(3-(9H-fluoren-9-yl)phenyl)-9H-carbazole[3v]

Mp. 200.3-201.1 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.00 (m, 2H), 7.79 (dd, *J* = 7.5, 0.8 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.23 (m, 14H), 7.19 (s, 1H), 5.15 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.39 (s), 143.82 (s), 141.08 (s), 140.69 (s), 137.96 (s), 130.13 (s), 127.53 (d, *J* = 15.0 Hz), 127.24 (s), 126.88 (s), 125.89 (s), 125.29 (d, *J* = 2.2 Hz), 123.35 (s), 120.38 – 119.80 (m), 109.76 (s), 77.36 (s), 77.04 (s), 76.72 (s), 54.17 (s).

HRMS(EI):m/z calcd for $C_{31}H_{21}N$ $[M]^+$ 407.1674, found 407.1672.

IR (KBr, cm^{-1}): 3045, 1599, 1449, 1334, 1226, 1179, 1034, 825, 741.

3-(9H-fluoren-9-yl)-9-phenyl-9H-carbazole[3w]

Mp. 101.1-101.9 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.51 (m, 4H), 7.39 (ddd, *J* = 11.5, 9.8, 7.3 Hz, 7H), 7.29 – 7.25 (m, 3H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 1H), 5.24 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72 (s), 141.04 (d, *J* = 19.5 Hz), 137.73 (s), 133.02 (s), 129.83 (s), 127.25 (dd, *J* = 22.9, 11.6 Hz), 126.33 (s), 125.92 (s), 125.47 (s), 123.61 (s), 123.14 (s), 120.37 (s), 120.07 (s), 119.86 (d, *J* = 2.3 Hz), 110.08 (s), 109.77 (s), 77.35 (s), 77.03 (s), 76.71 (s), 54.64 (s).

HRMS(EI):m/z calcd for $C_{31}H_{21}N$ $[M]^+$ 407.1674, found 407.1672.

IR (KBr, cm^{-1}): 3267, 1595, 1501, 1448, 1323, 1234, 806, 735.

9-(4-(9H-fluoren-9-yl)phenyl)-9H-carbazole[3x]

Mp. 243.5-244.7 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 0.8 Hz, 2H), 7.84 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.48 – 7.38 (m, 10H), 7.37 – 7.25 (m, 6H), 5.18 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.53 (s), 141.19 – 140.76 (m), 136.35 (s), 129.70 (s), 127.82 – 127.10 (m), 125.87 (s), 125.43 (s), 123.32 (s), 120.28 (s), 119.96 (d, *J* = 20.0 Hz), 109.85 (s), 77.35 (s), 77.04 (s), 76.72 (s), 54.07 (s).

HRMS(EI):m/z calcd for $C_{31}H_{21}N$ $[M]^+$ 407.1674, found 407.1672.

IR (KBr, cm^{-1}): 3059, 1599, 1510, 1450, 1223, 745.

4-(9H-fluoren-9-yl)-N,N-diphenylaniline[3y]

Mp. 174.2-175.1 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.38 (d, *J* = 8.3 Hz, 4H), 7.29 (s, 2H), 7.19 (s, 4H), 7.05 (ddd, *J* = 4.4, 3.4, 1.8 Hz, 4H), 6.95 (s, 6H), 5.00 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.85 (d, *J* = 10.8 Hz), 140.96 (s), 129.09 (d, *J* = 15.2 Hz), 127.26 (d, *J* = 2.8 Hz), 125.36 (s), 124.16 (d, *J* = 7.2 Hz), 122.61 (s), 119.87 (s), 77.34 (s), 77.02 (s), 76.70 (s), 53.84 (s).

HRMS(EI):m/z calcd for $C_{31}H_{23}N$ $[M]^+$ 409.1830, found 409.1823.

IR (KBr, cm^{-1}): 3036, 1585, 1495, 1448, 1328, 1273, 738, 649.

4. References

[1] S. Sarkar, S. Maiti, K. Bera, S. Jalal and U. Jana. *Tetrahedron Lett.*, 2012, 53, 5544.

[2] G. J. Li, E. J. Wang, H. Y. Chen, H. F. Li, Y. H. Liu and P. G. Wang. *Tetrahedron.*, 2008, 64, 9033.

[3] J. J. Chen, O. Satoru, Y. C. Hsieh, C. C. Hsiao, H. Shuhei, H. Sakurai and Y. T. Wu. Adv. Synth. Catal., 2012, 354, 1551.

[4] K. Fuchibe, T. Akiyama. *J. Am. Chem. Soc*., 2006 , 128, 1434.

[5] V. Carlos, H. Valentin, G. Massimo, F. M. Martin and F. L. Ben. Chem - Eur. J., 2014 , 20, 13078.

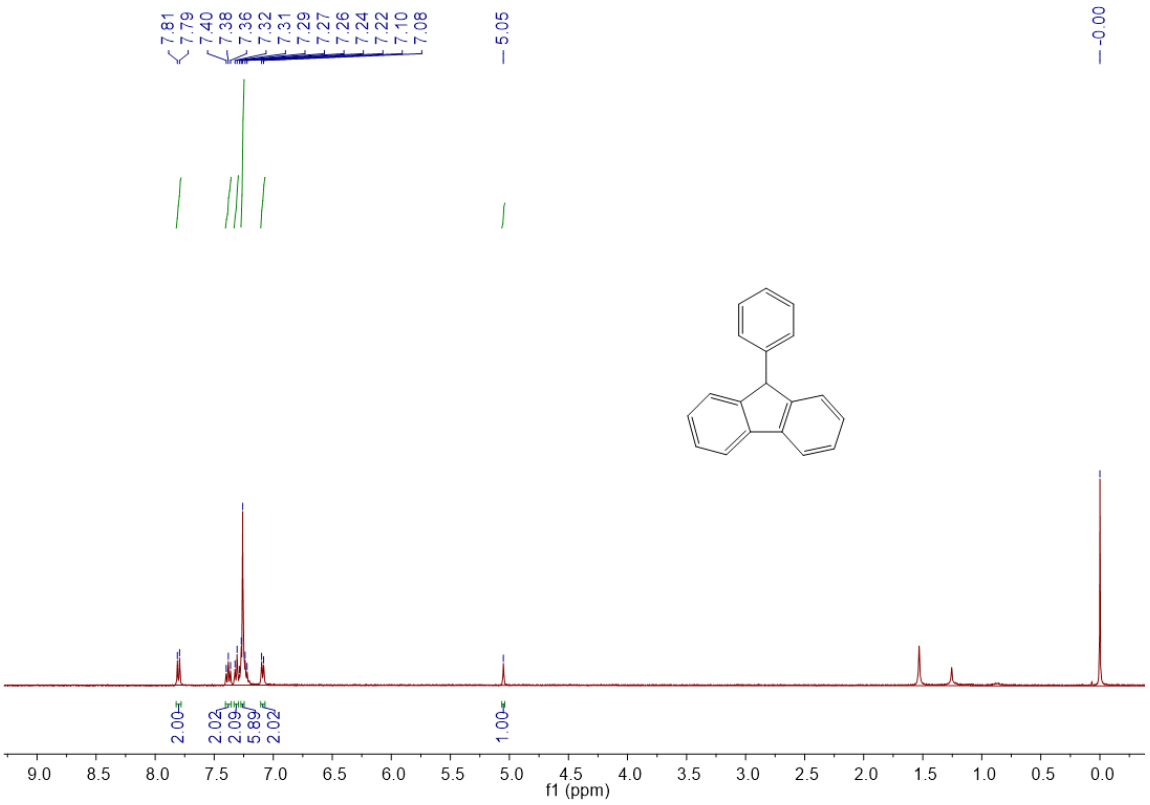
[6] T. Das, A. Chakraborty, A. Sarkar. Tetrahedron Lett., 2014, 55, 5174.

[7] N. Kanbe, J. Terao, K. Adachi and T. Nagai. Jpn. Kokai. Tokkyo. Koho., 2010, JP 2010138088.

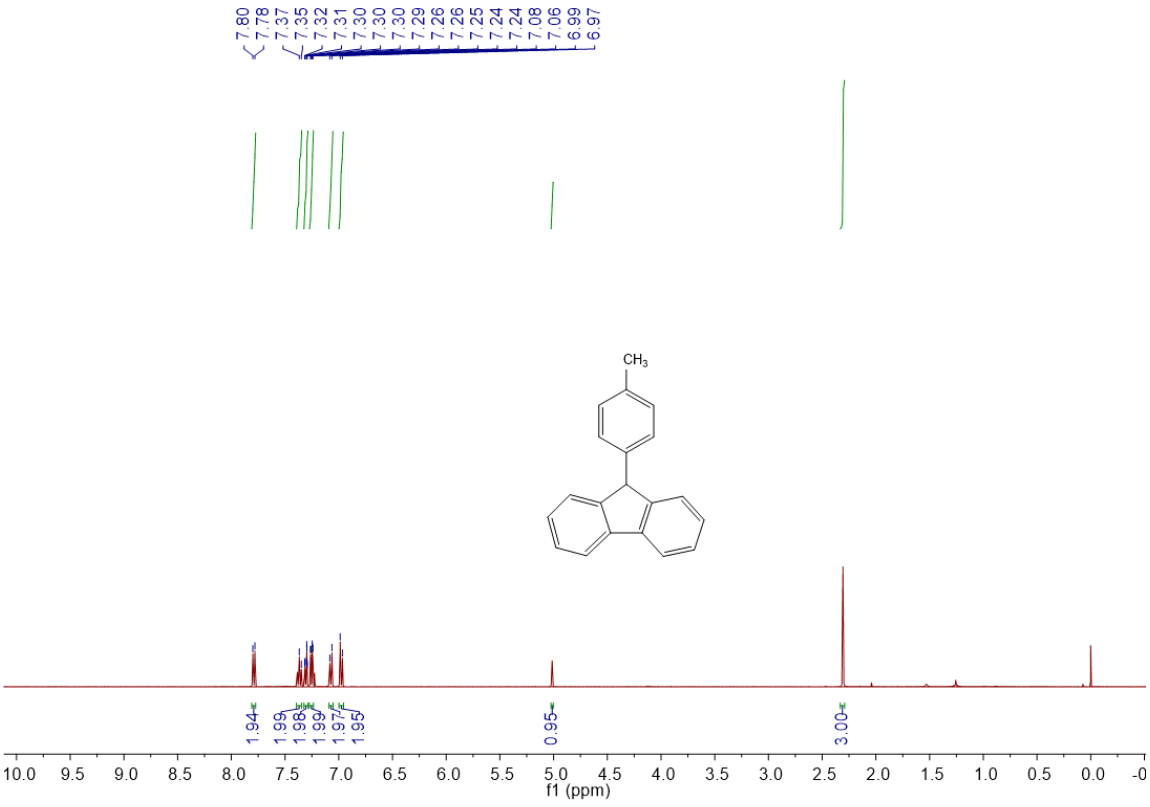
[8] H. Li, A. J. A. Aquino, D. B. Cordes, L. F. Hung, W. L. Hase and K. Clemens. J. Am. Chem. Soc., 2013, 135, 16066.

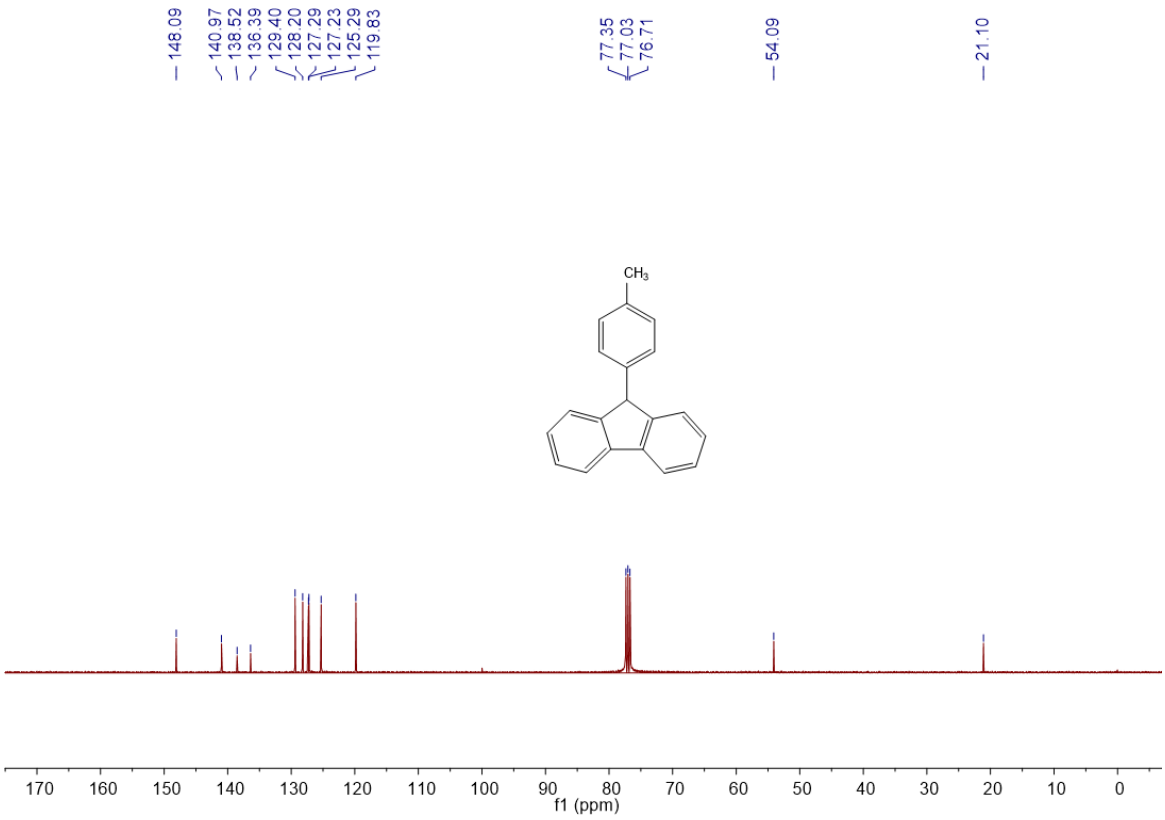
5. Copies of Spectra

9-phenyl-9H-fluorene[3a]

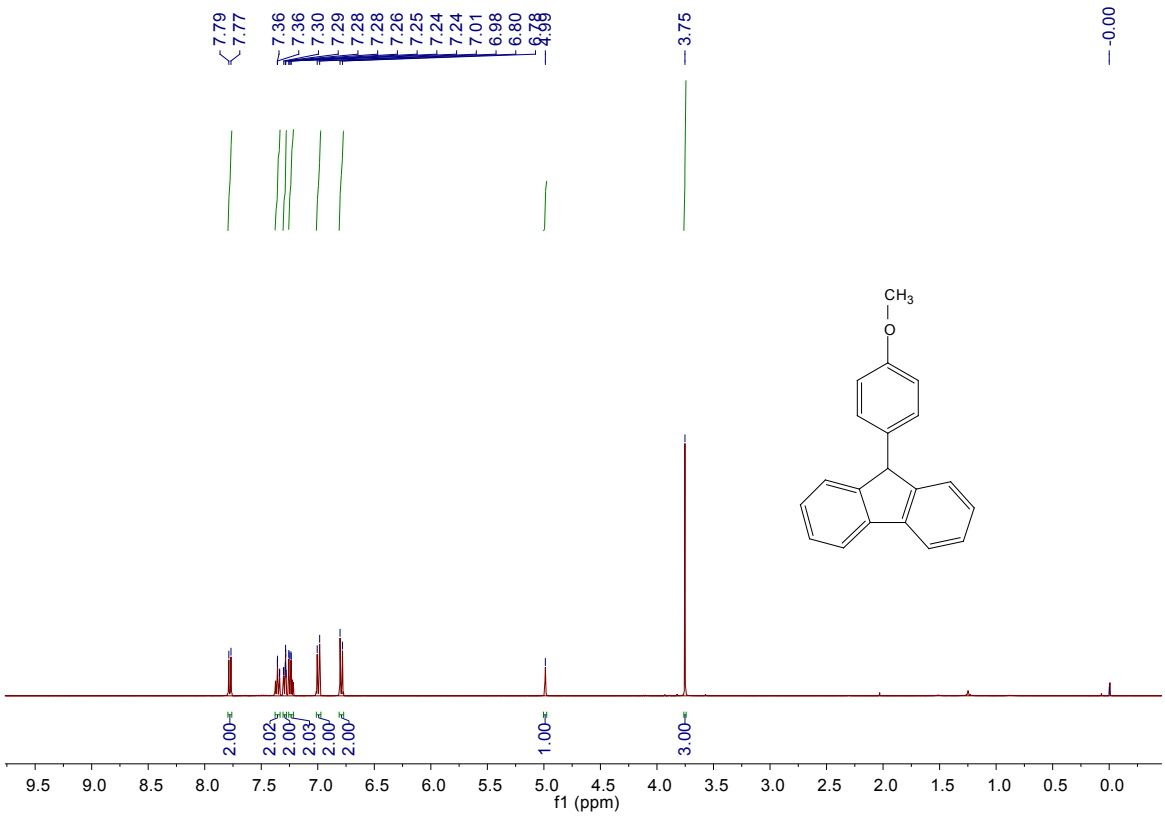


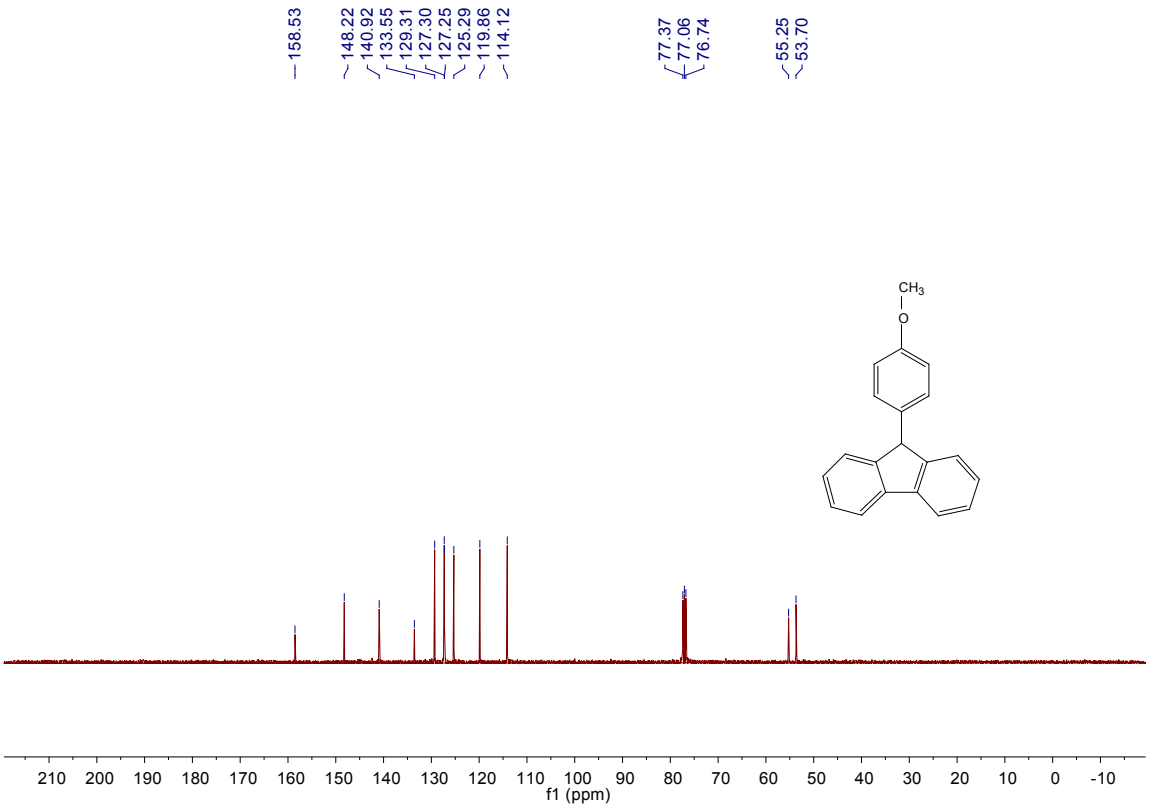
9-(p-tolyl)-9H-fluorene[3b]



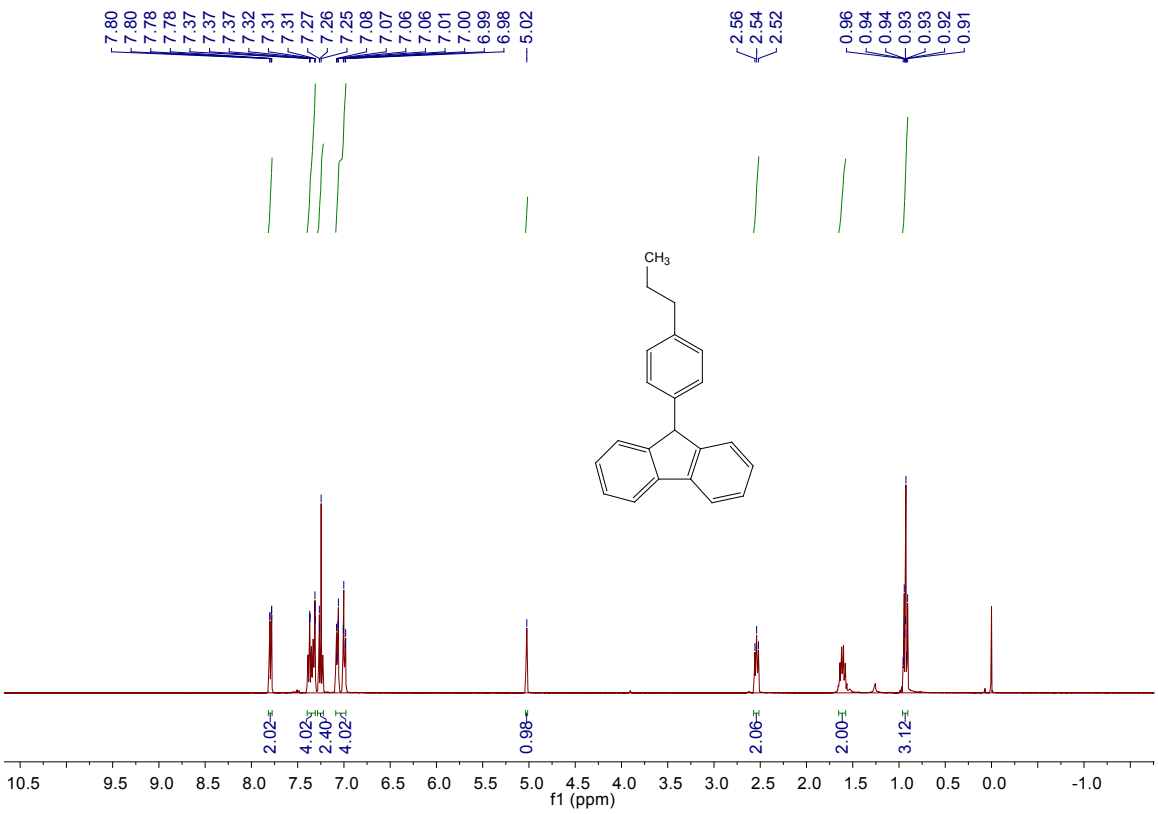


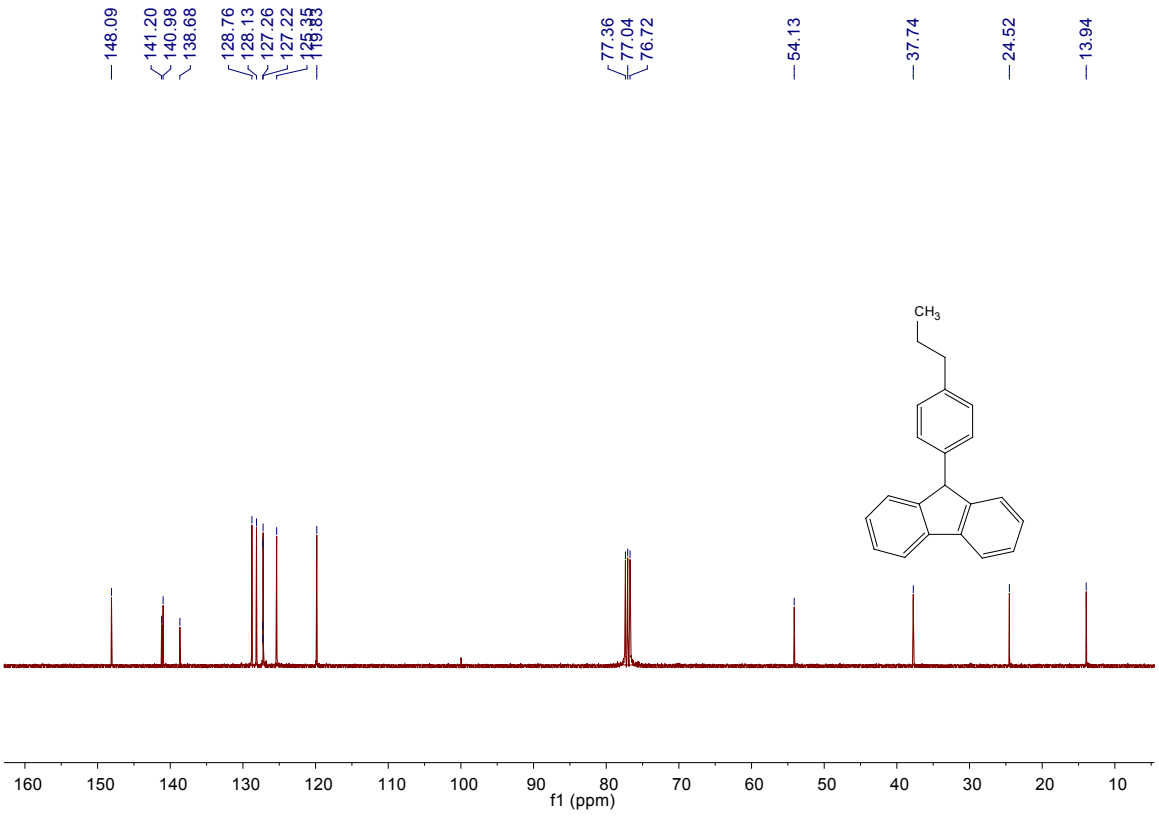
9-(4-methoxyphenyl)-9H-fluorene[3c]





9-(4-propylphenyl)-9H-fluorene[3d]

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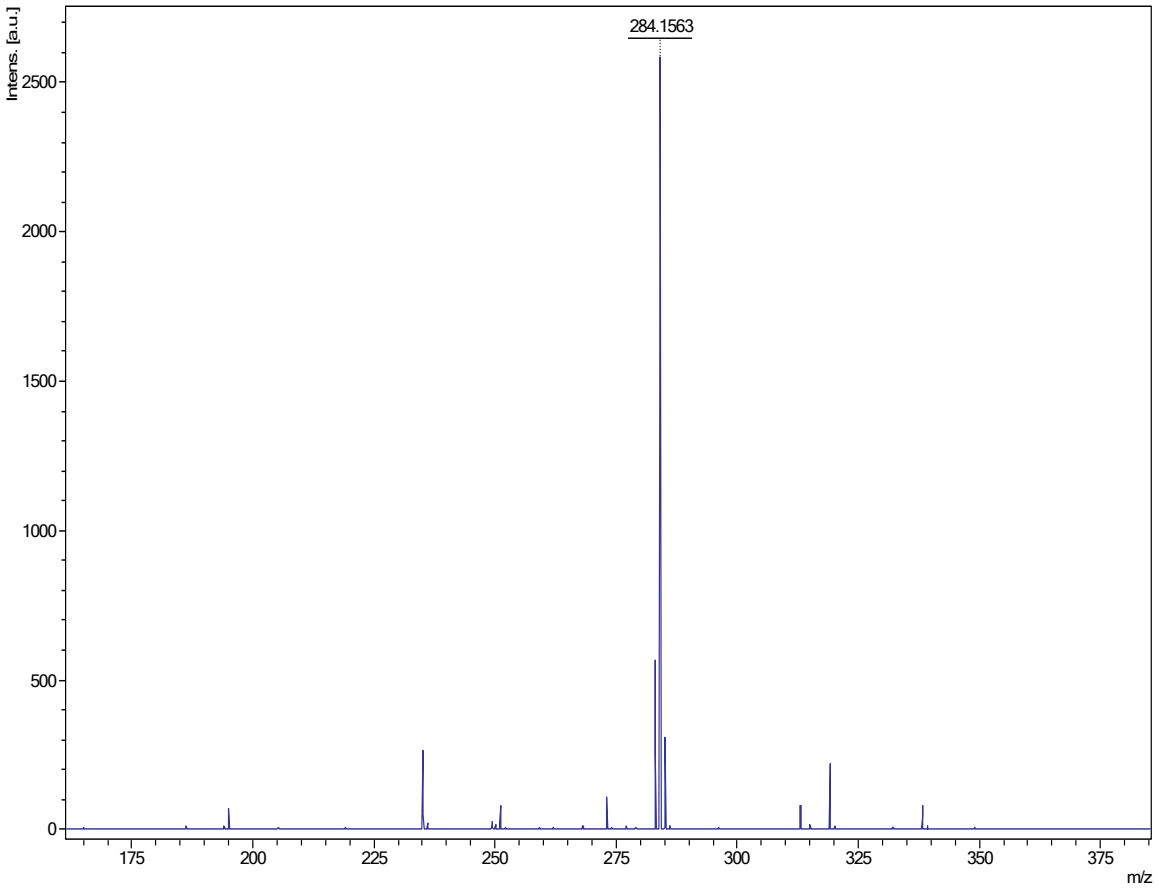
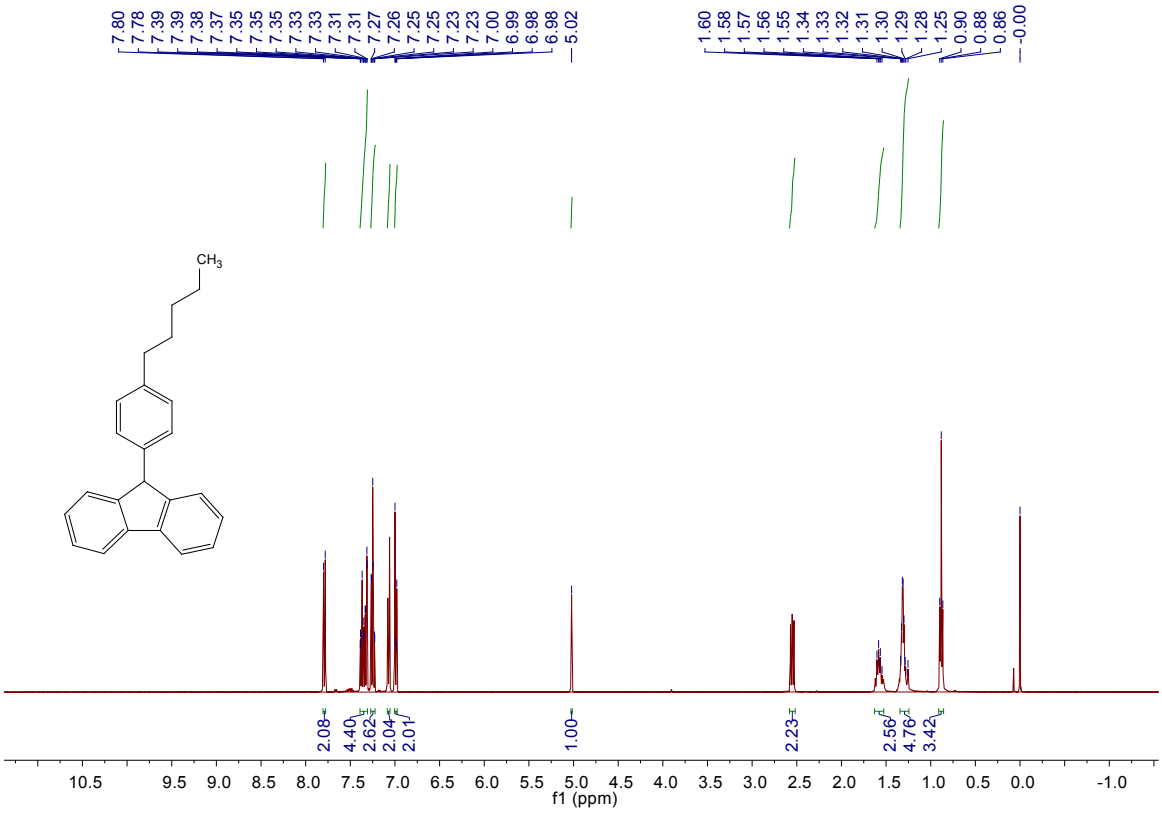
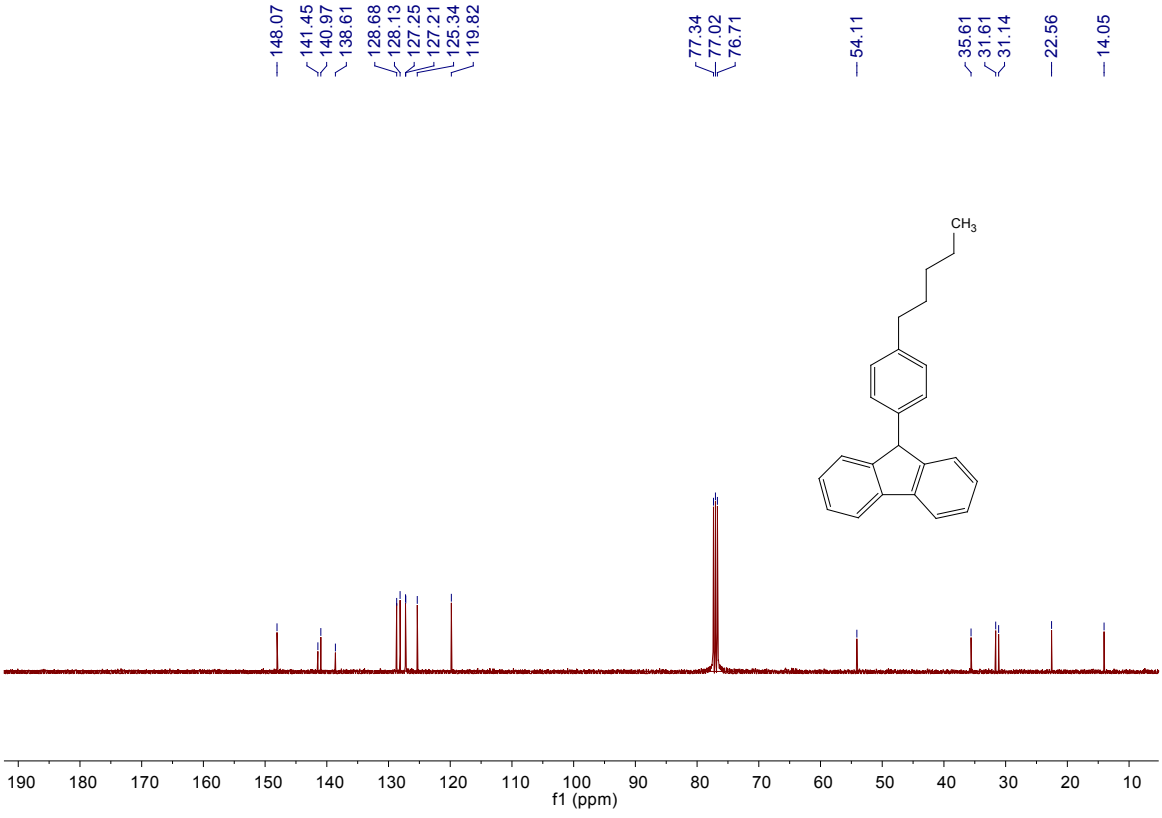
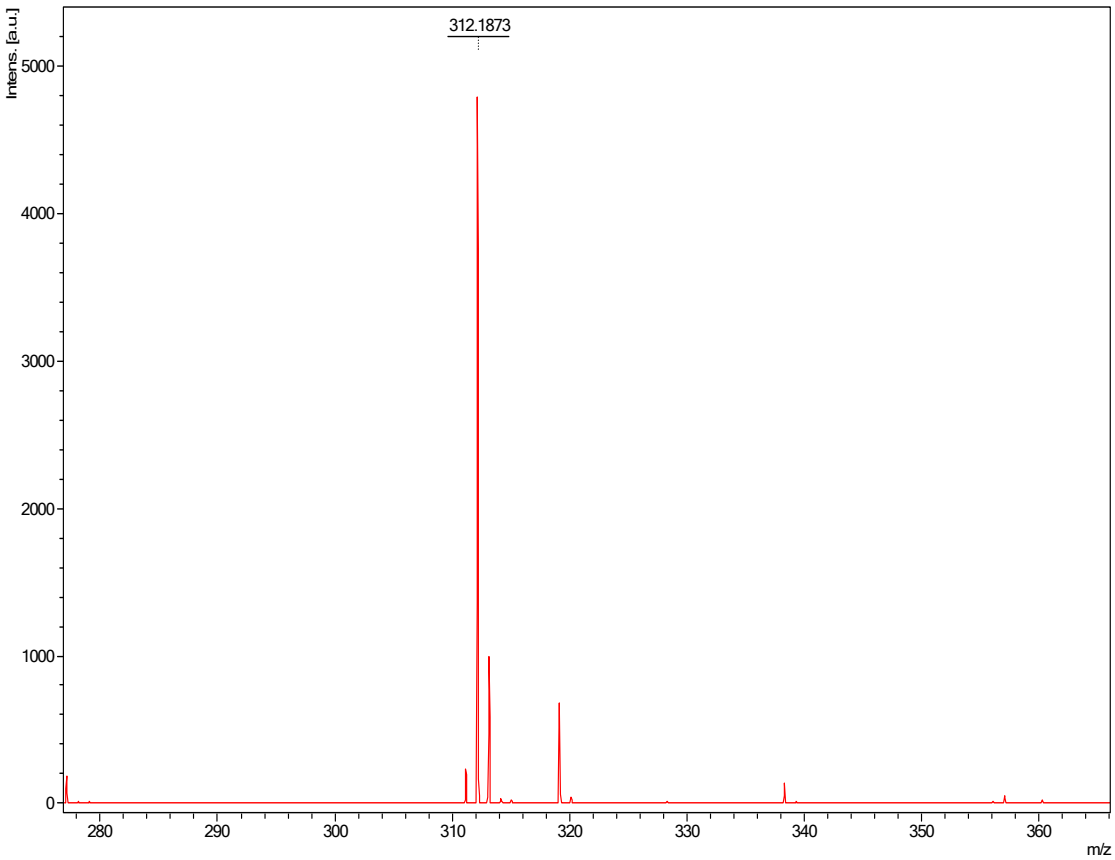
141.20
140.98
138.68
128.76
128.13
127.26
127.22
125.35
119.83
77.36
77.04
76.72
54.13
37.74
24.52
13.94
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


284.1563
Intens. [a.u.]
2500
2000
1500
1000
500
0
175
200
225
250
275
300
325
350
375
m/z

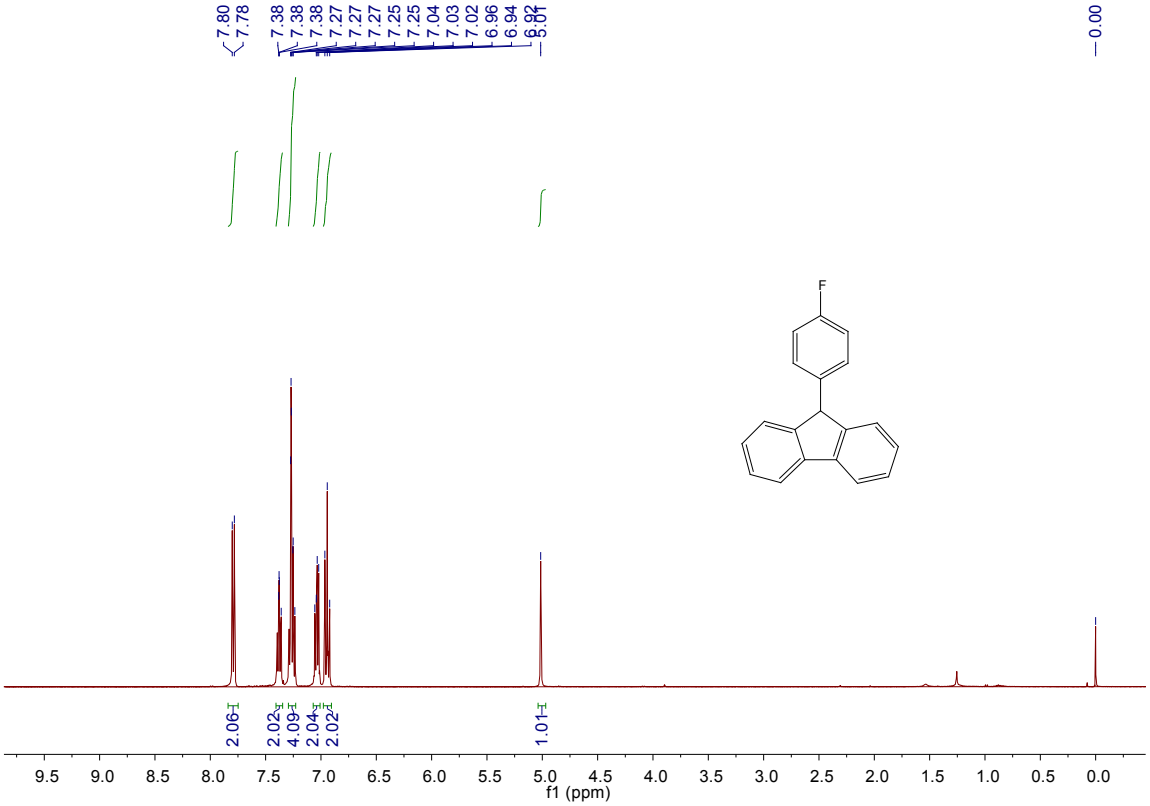
9-(4-pentylphenyl)-9H-fluorene[3e]

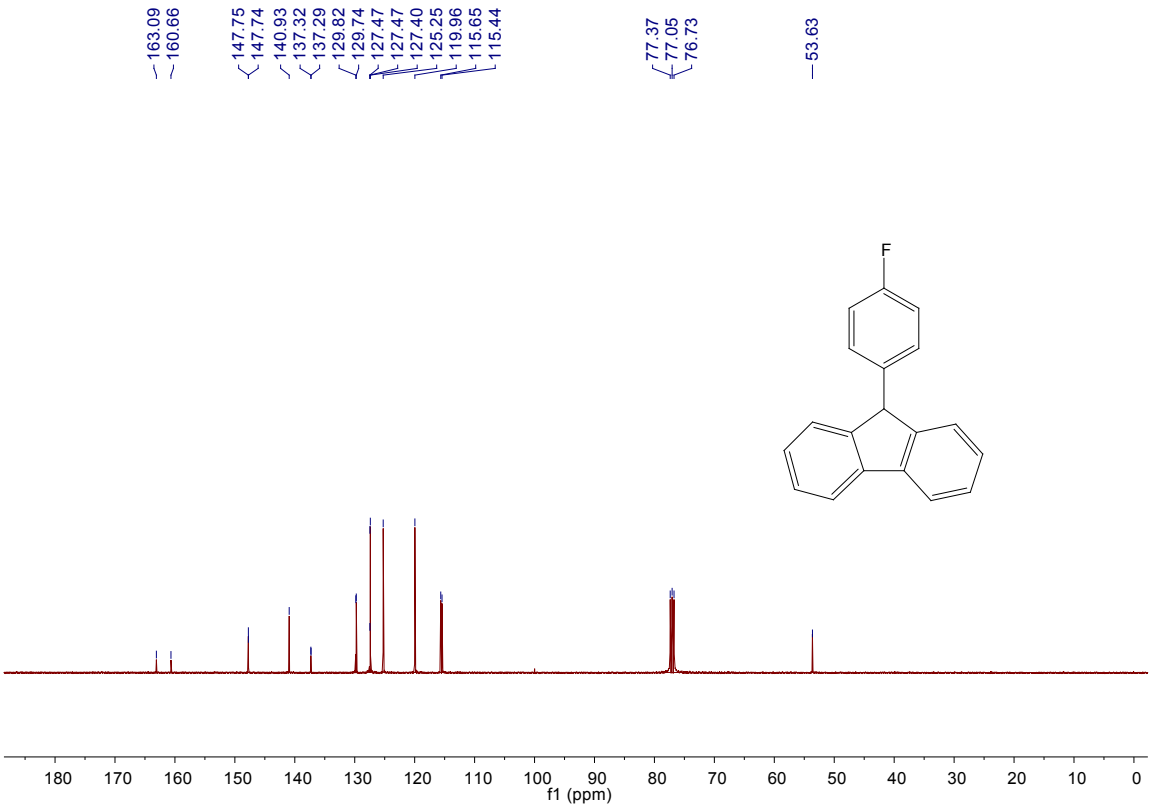


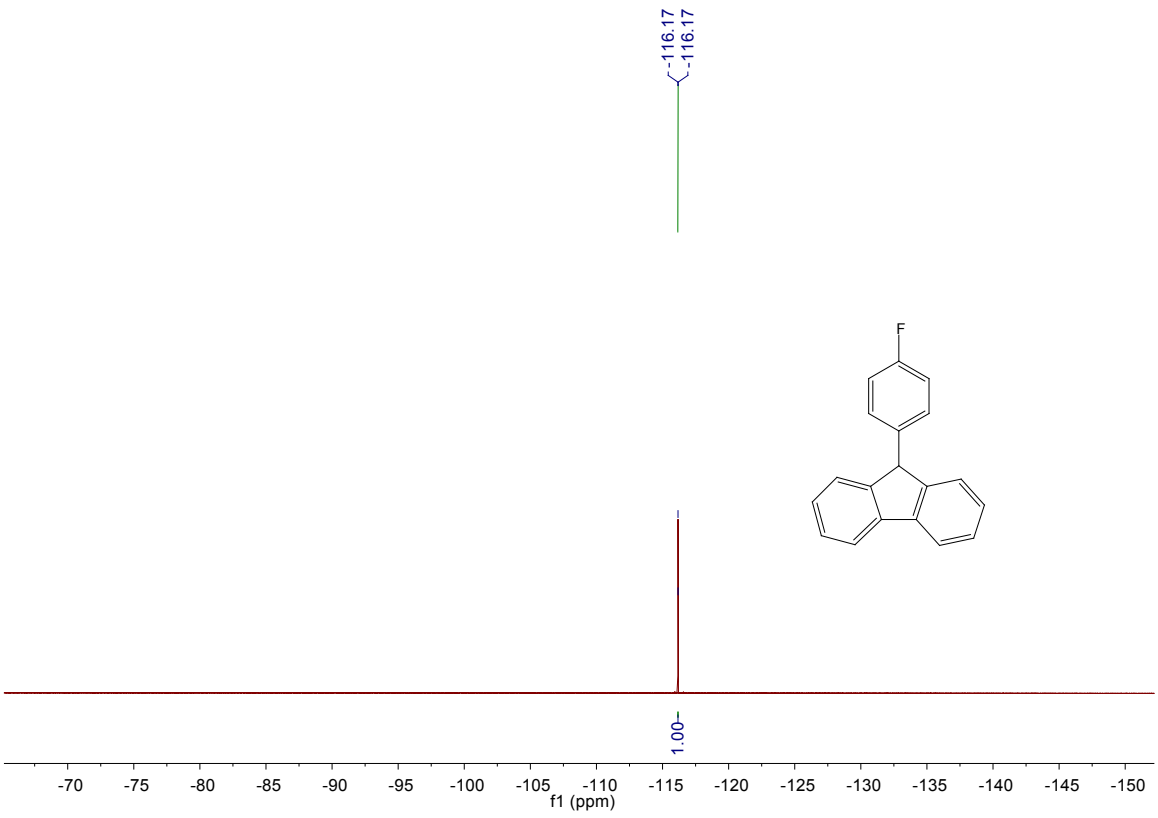




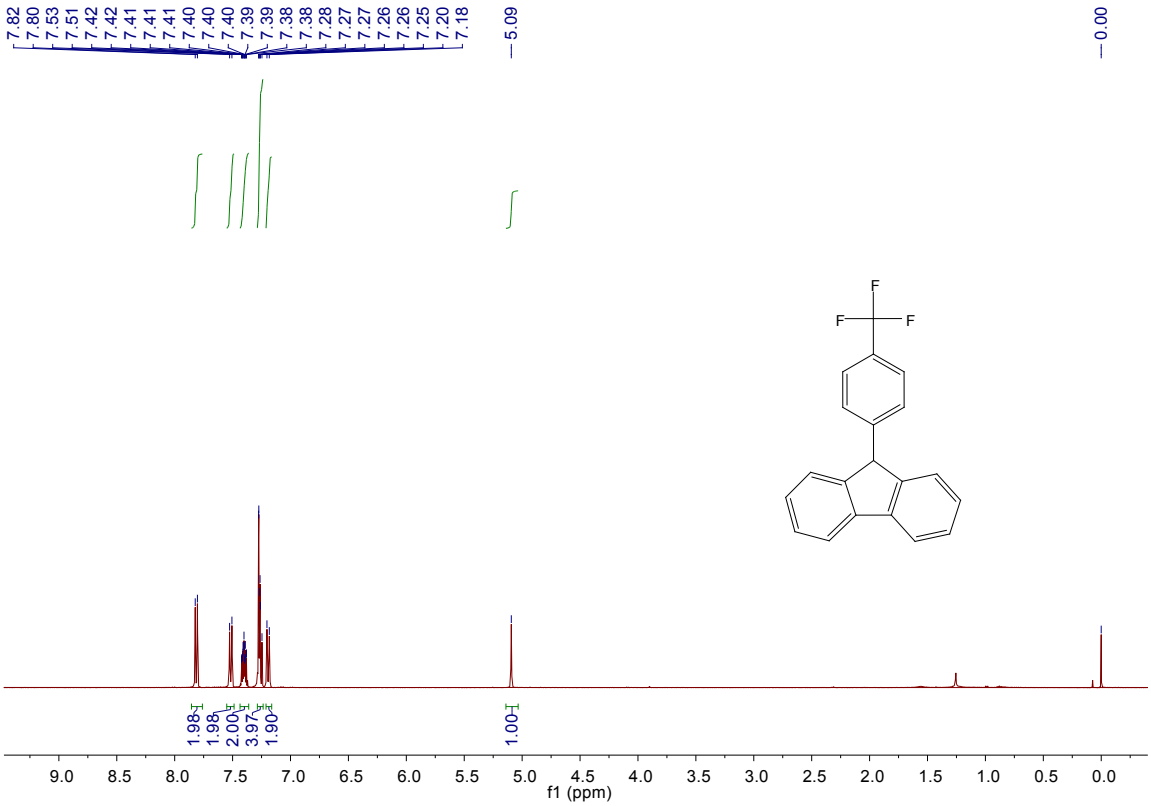
9-(4-fluorophenyl)-9H-fluorene[3f]

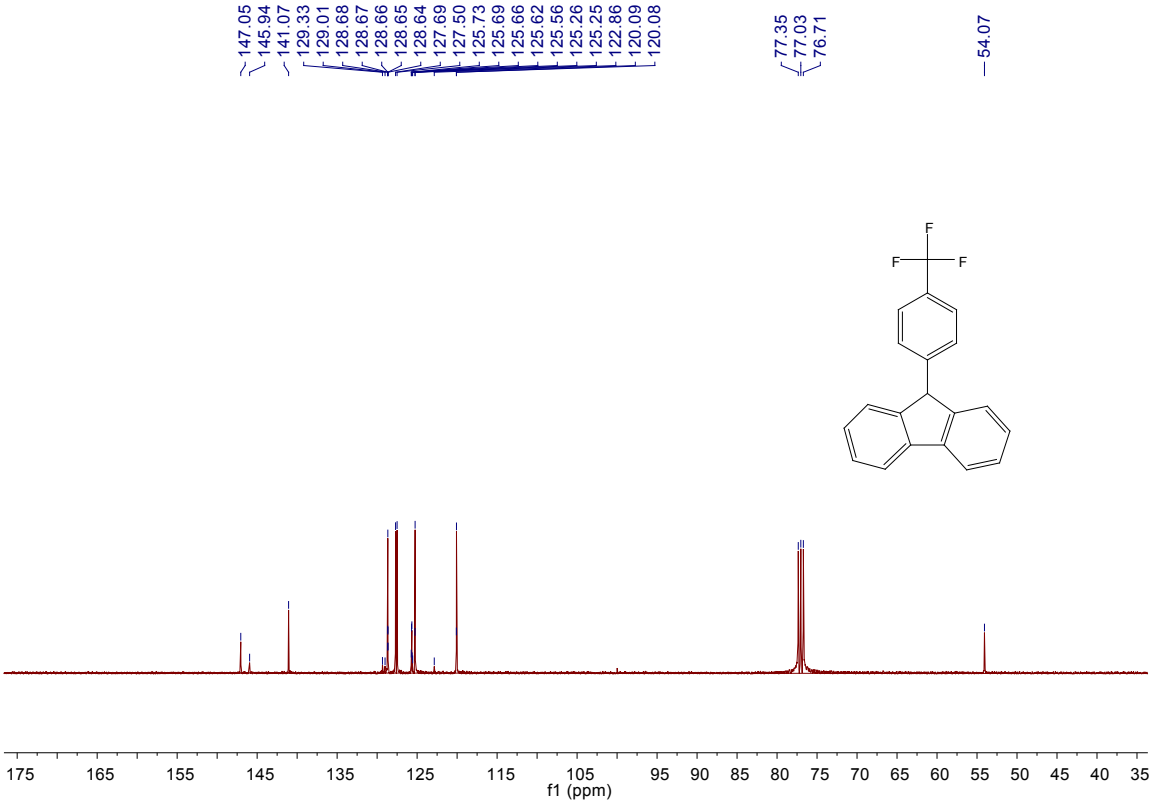


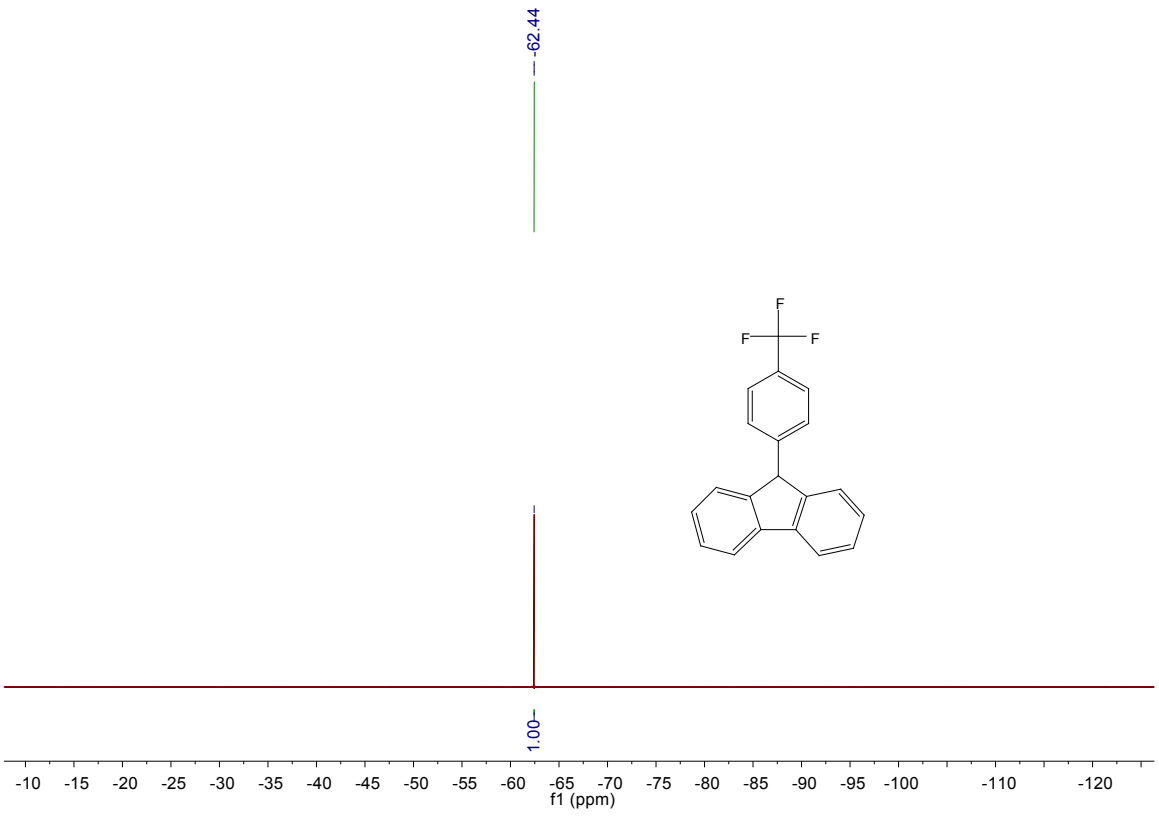

163.09
160.66
147.75
147.74
140.93
137.32
137.29
129.82
129.74
127.47
127.47
127.40
125.25
119.96
115.65
115.44
77.37
77.05
76.73
53.63
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-116.17
-116.17
F
1.00
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

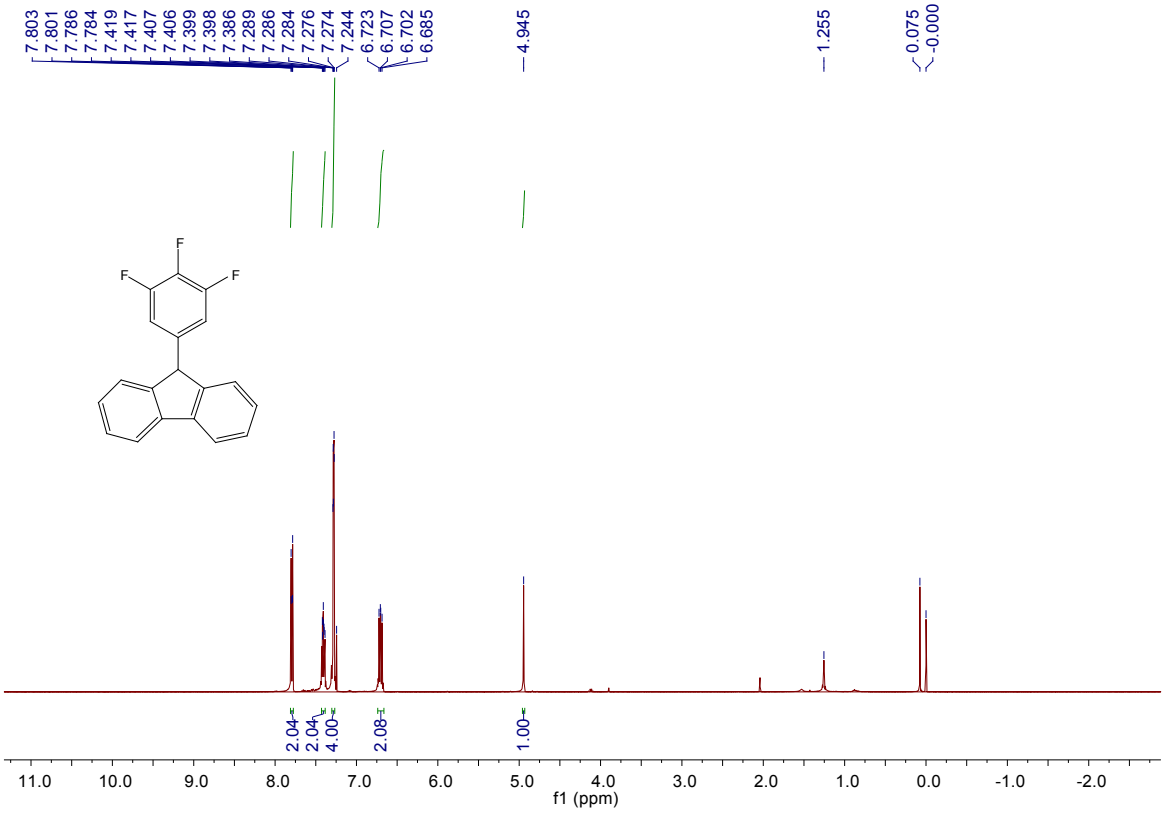
9-(4-(trifluoromethyl)phenyl)-9H-fluorene[3g]

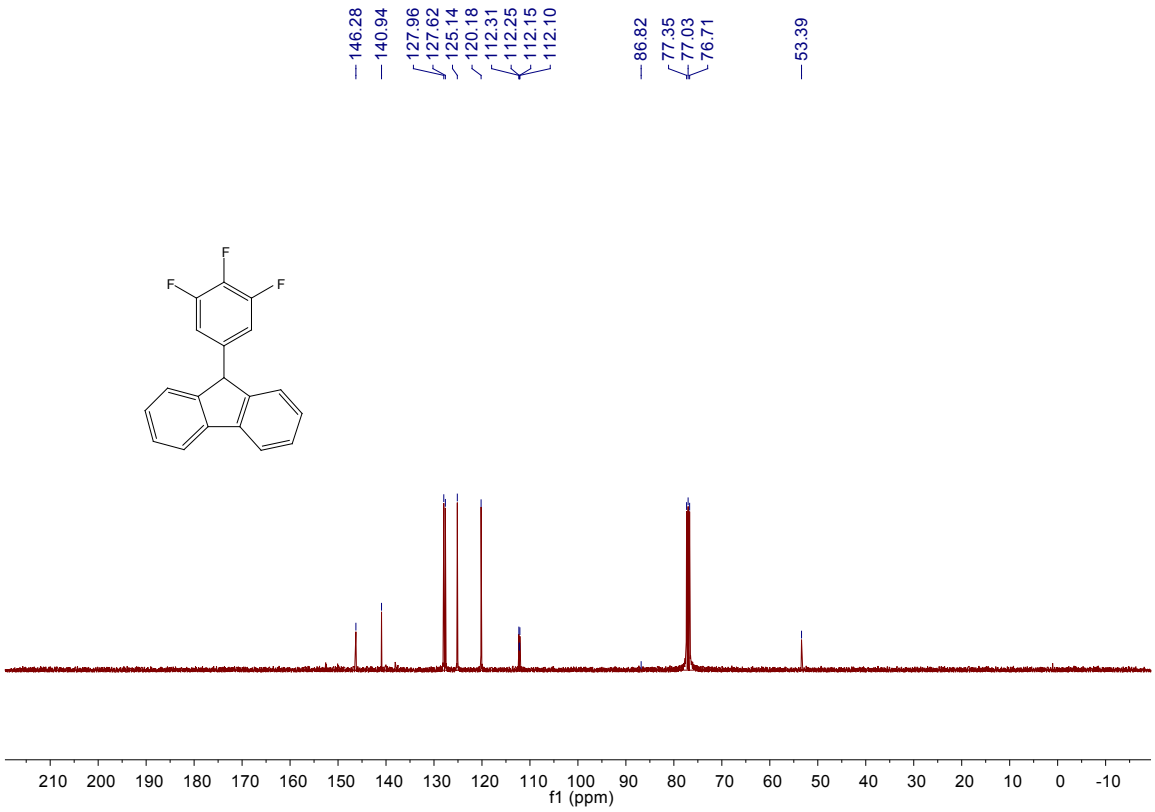


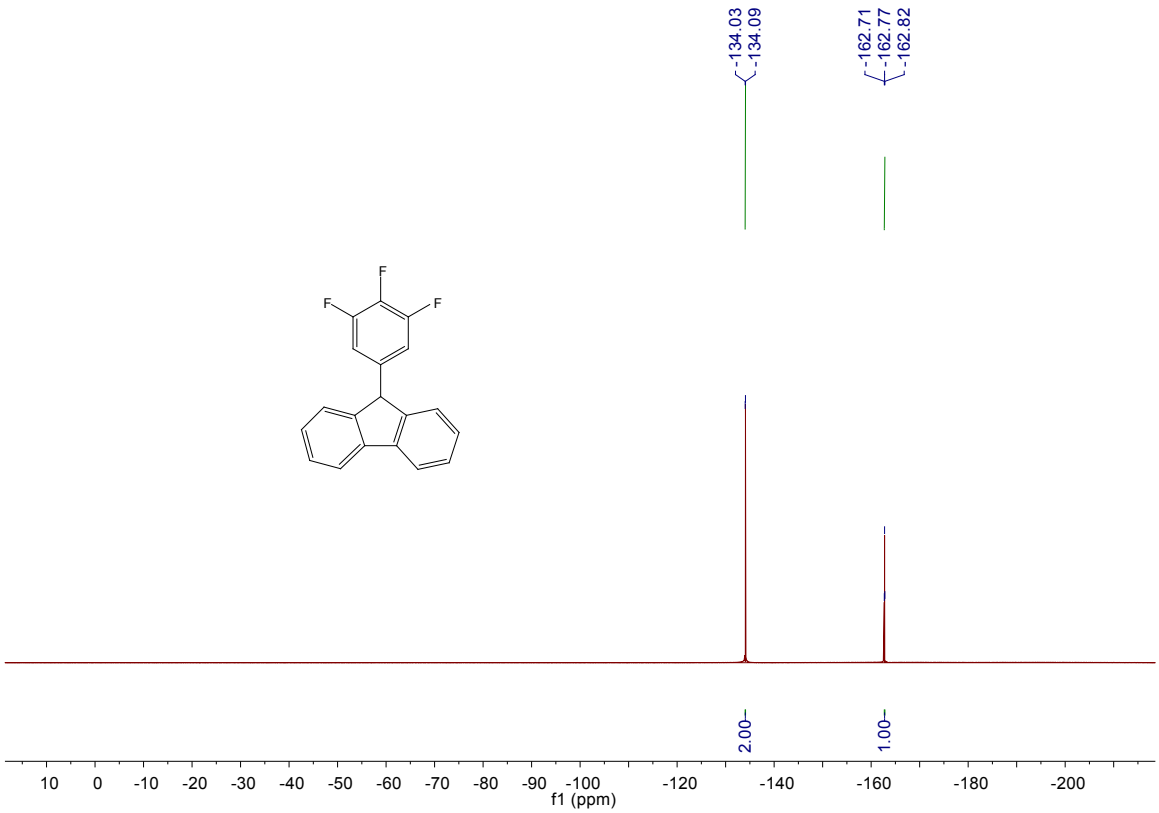




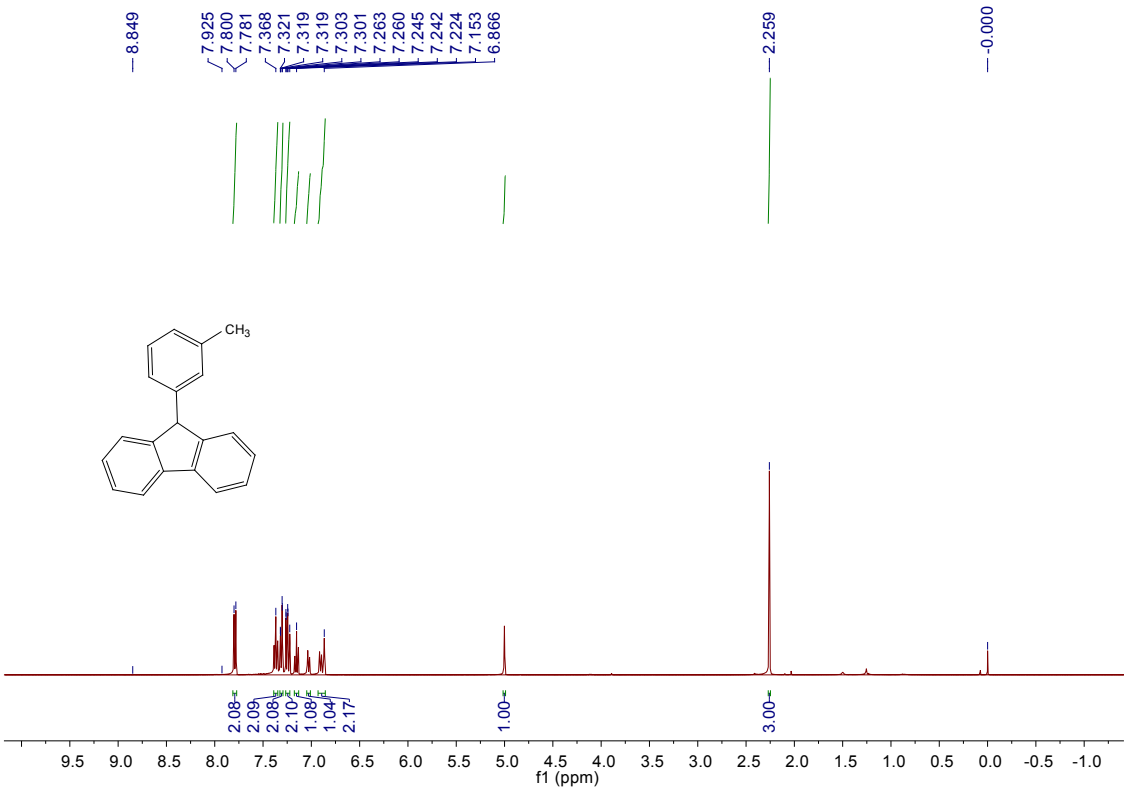
9-(3,4,5-trifluorophenyl)-9H-fluorene[3h]

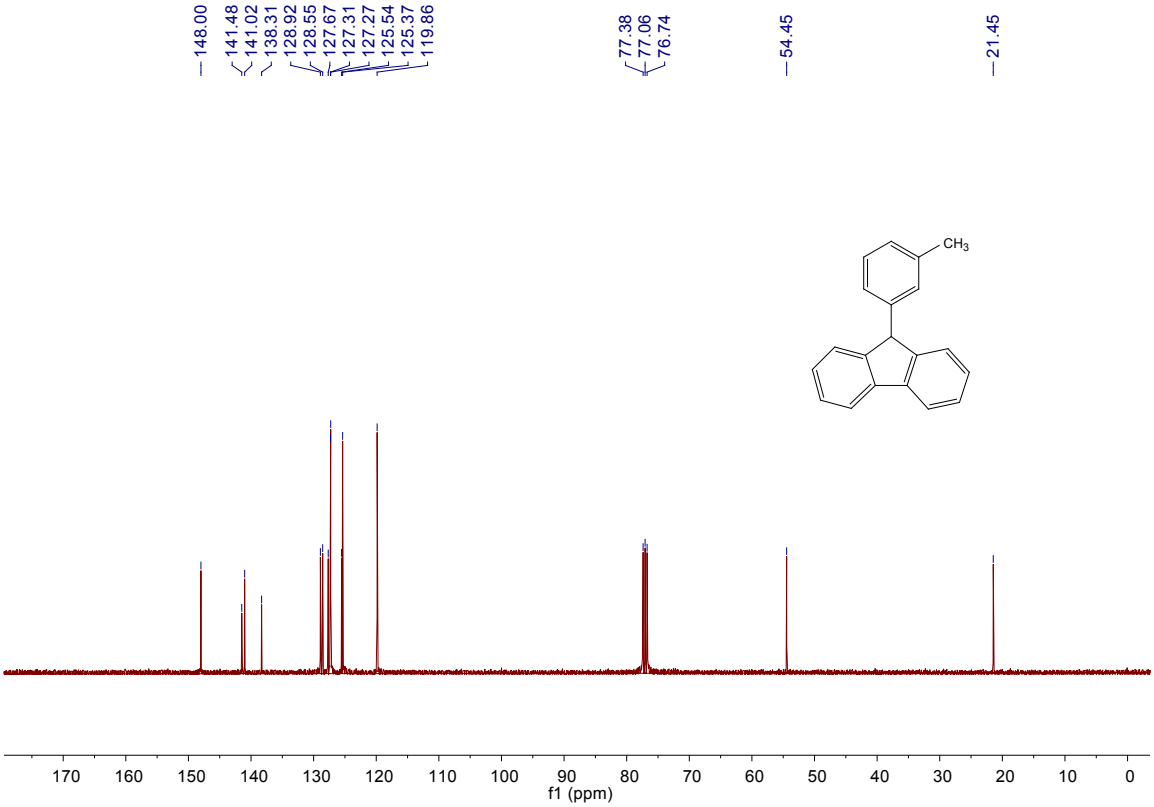



146.28
140.94
127.96
127.62
125.14
120.18
112.31
112.25
112.15
112.10
86.82
77.35
77.03
76.71
53.39
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

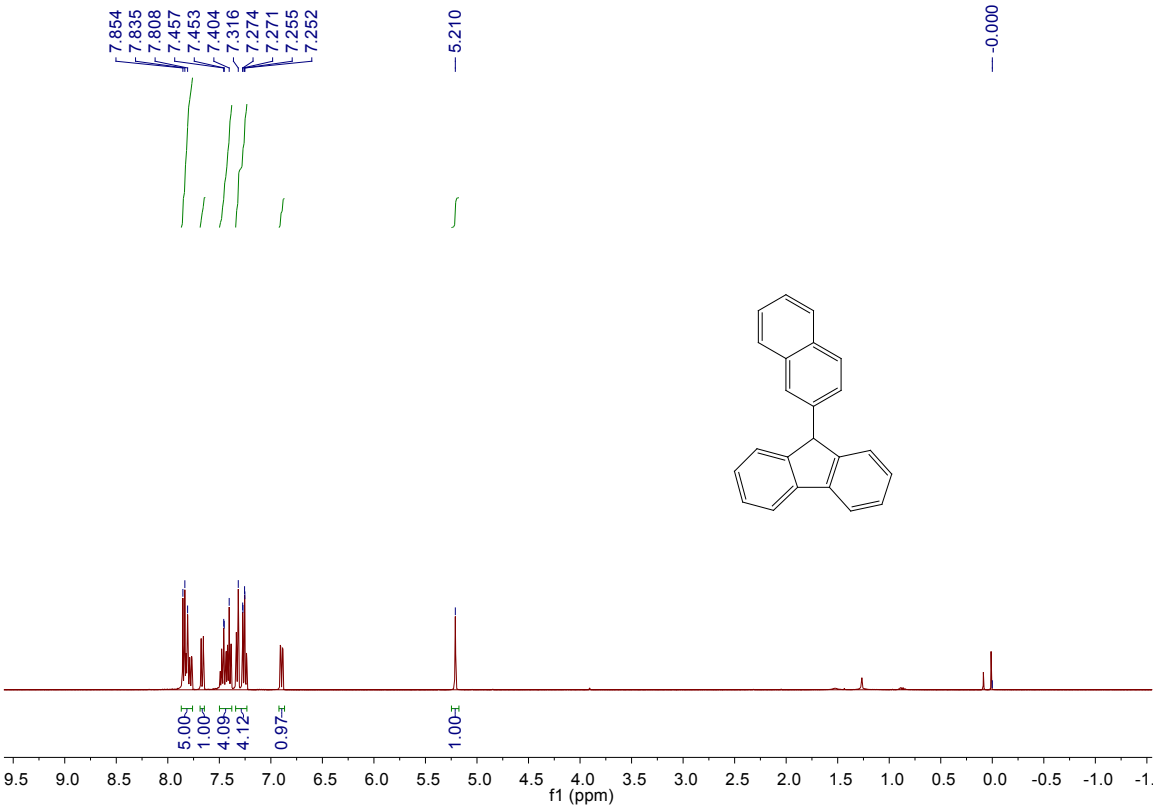

-134.03
-134.09
-162.71
-162.77
-162.82
F
F
F
2.00
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

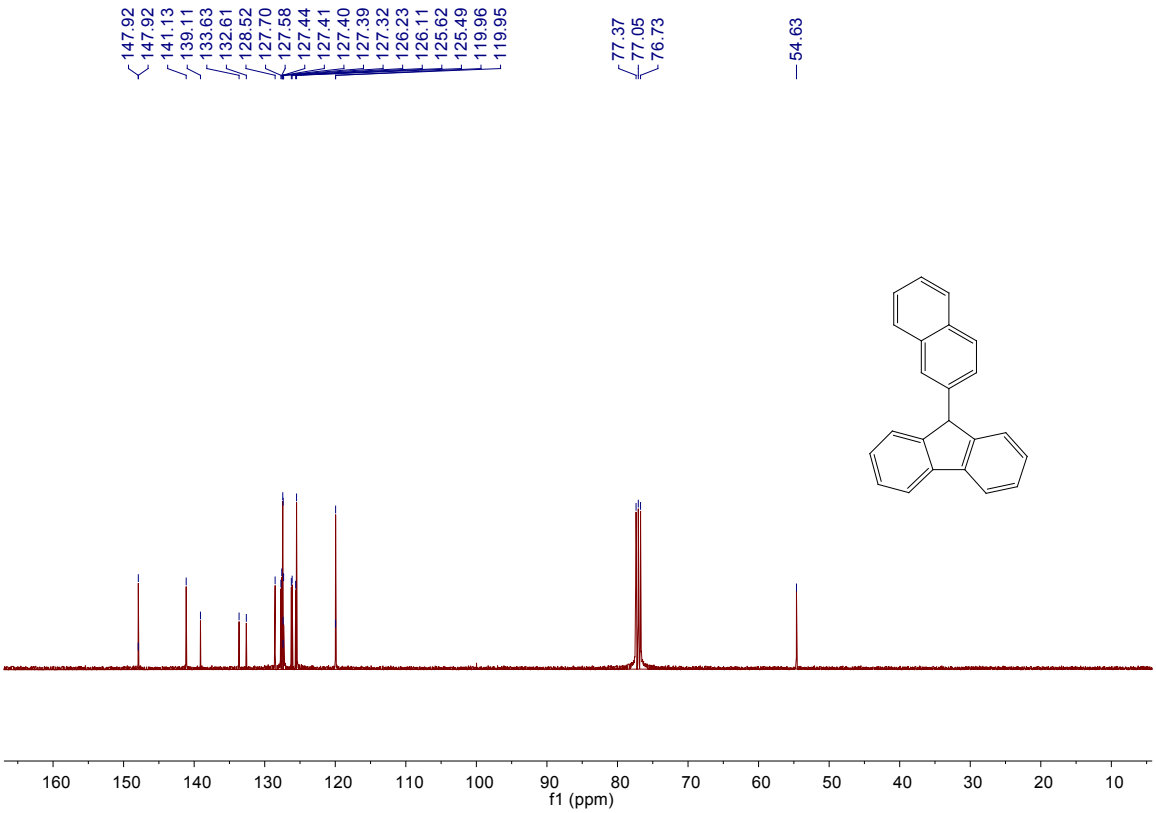
9-(m-tolyl)-9H-fluorene[3i]



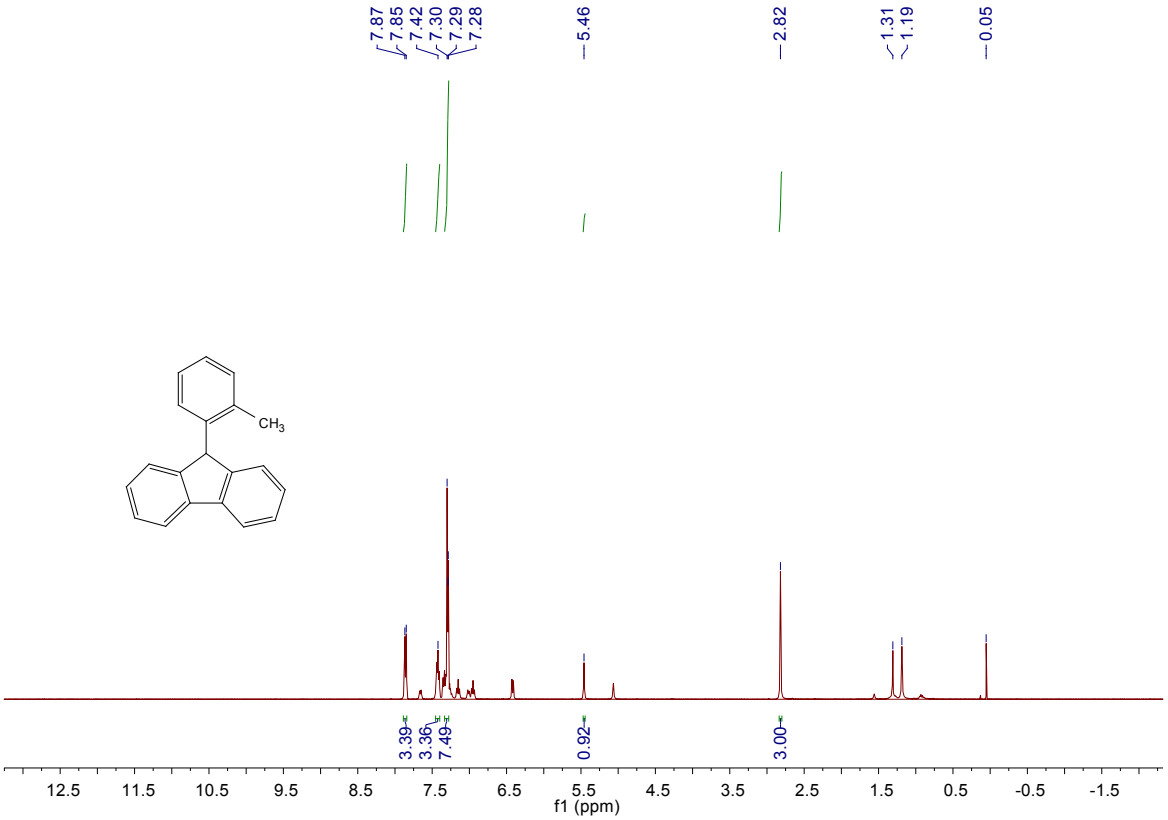


9-(naphthalen-2-yl)-9H-fluorene[3j]

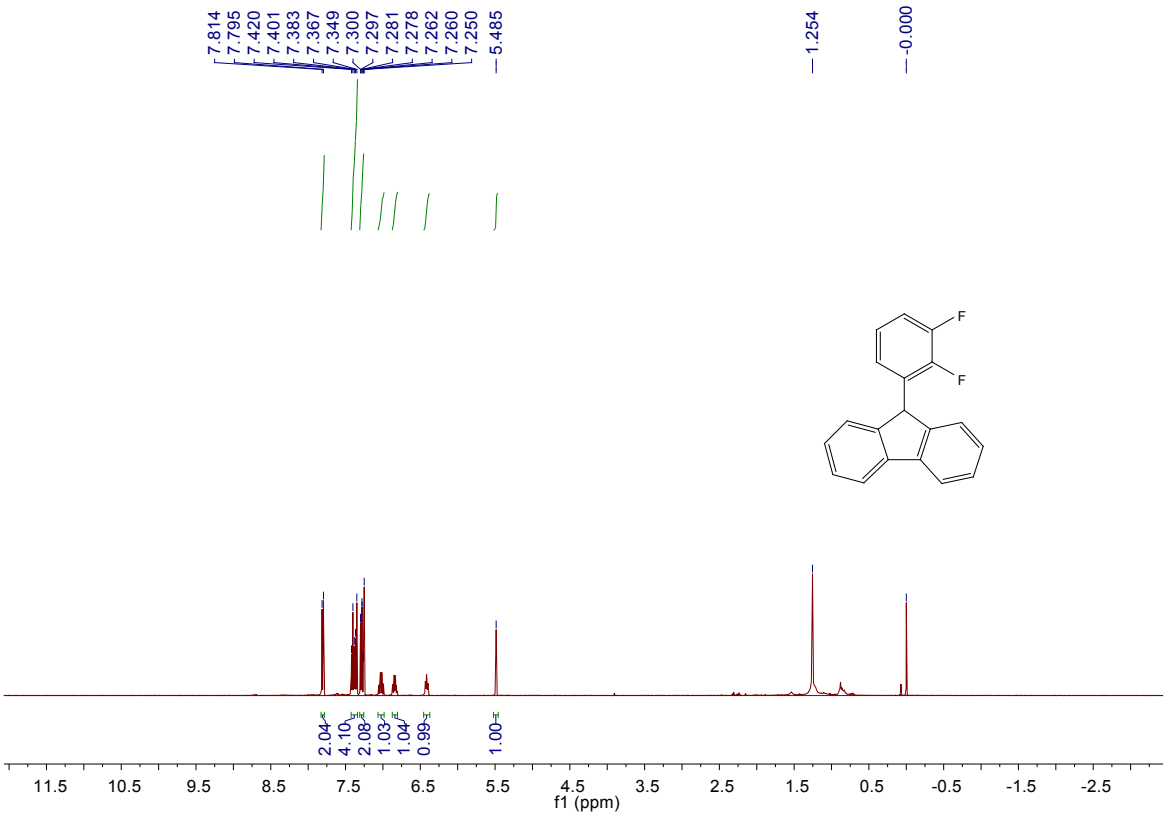


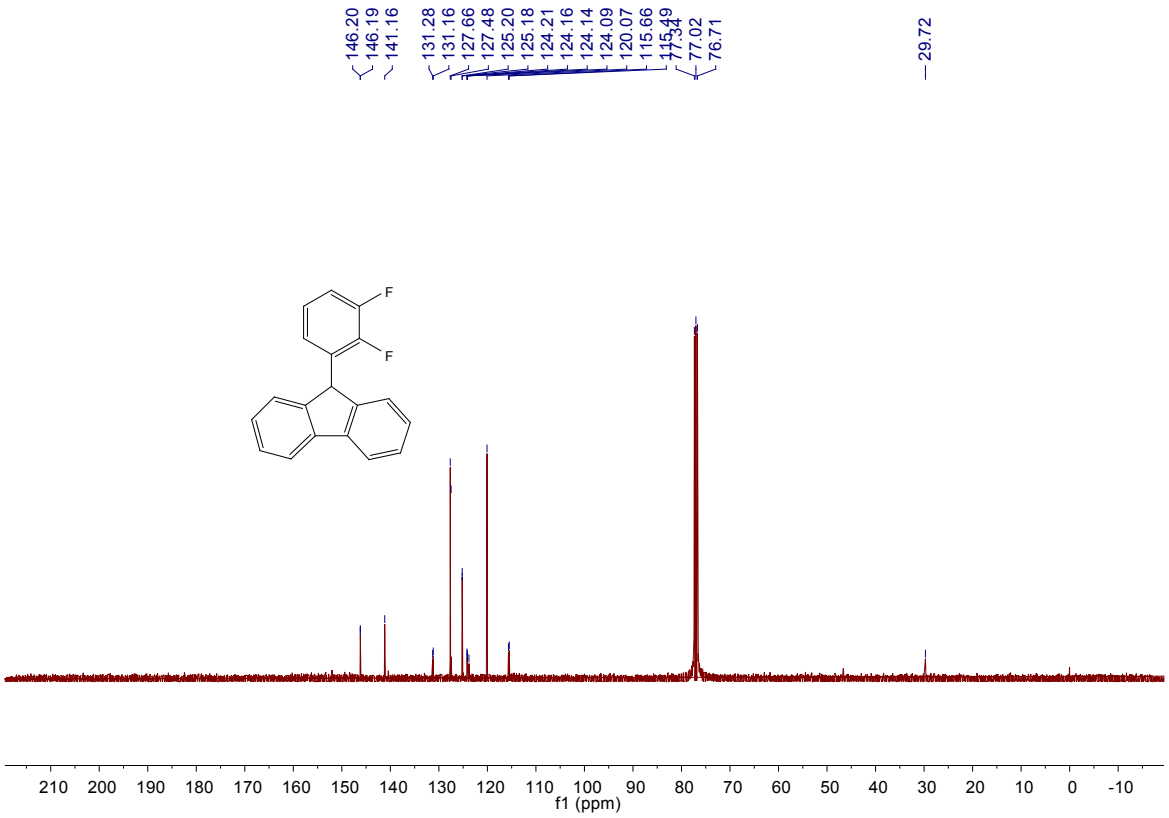


9-(o-tolyl)-9H-fluorene[3k]



9-(2,3-difluorophenyl)-9H-fluorene[3l]

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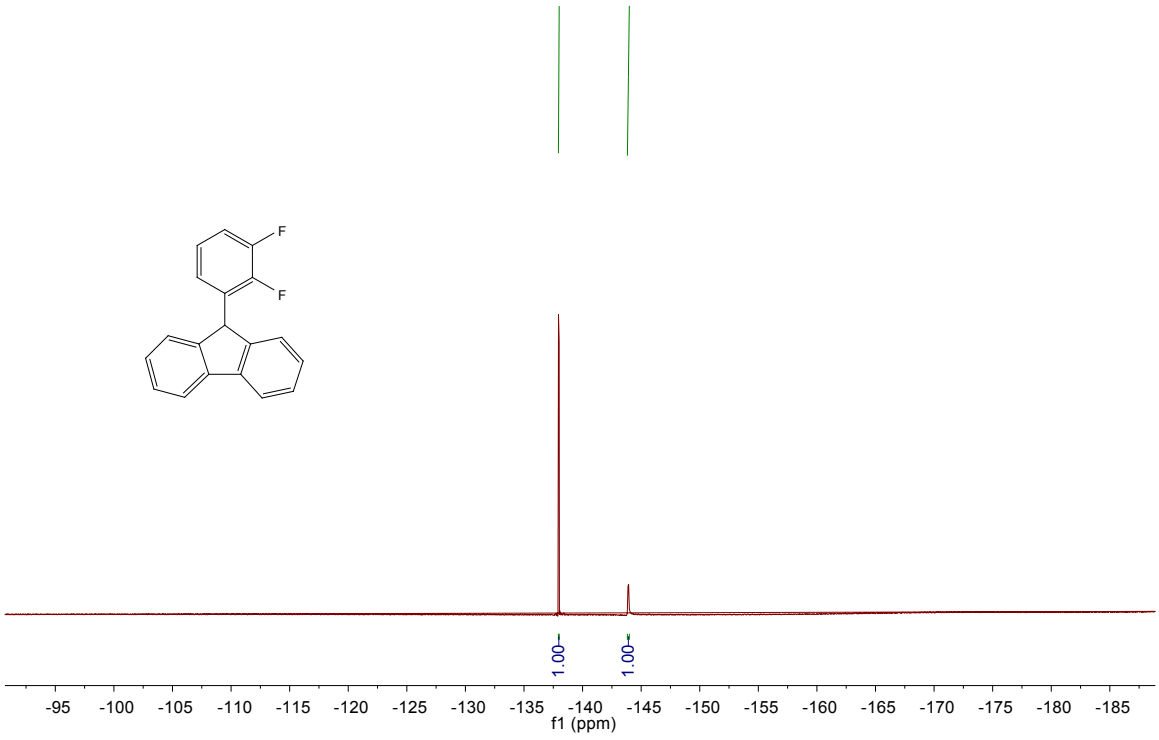
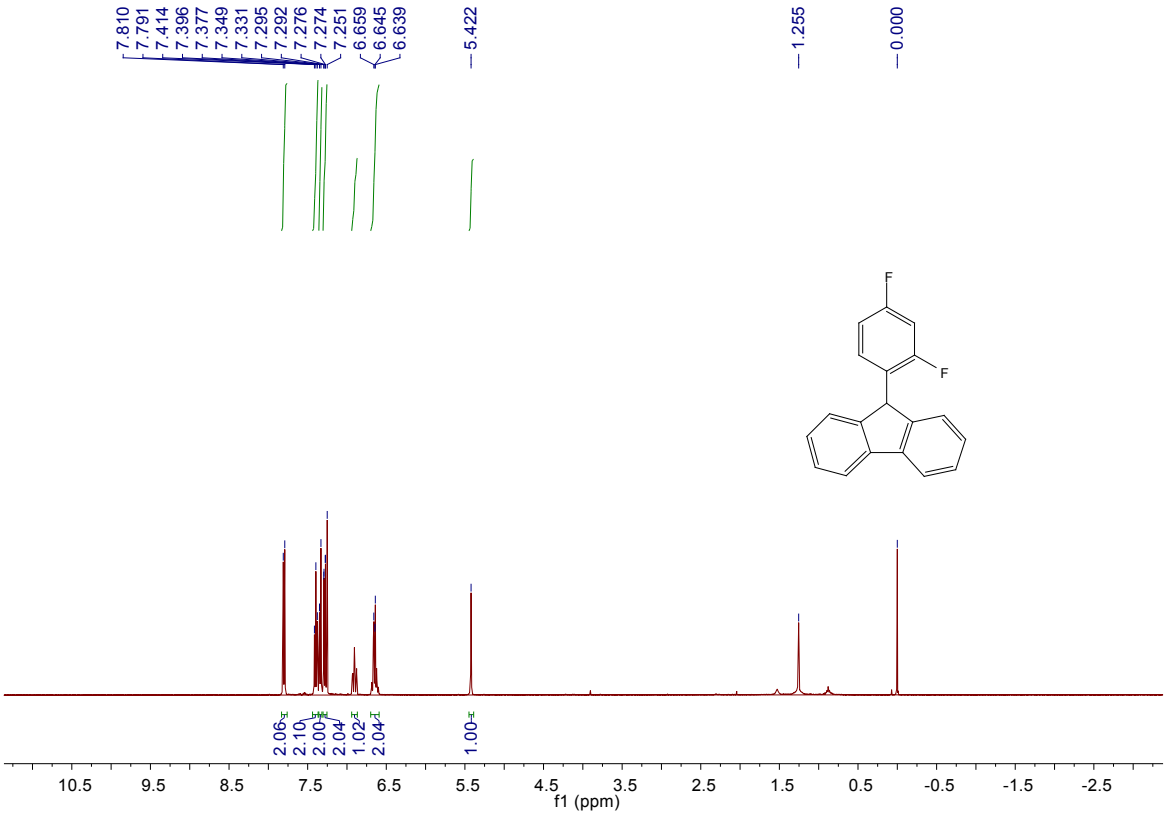
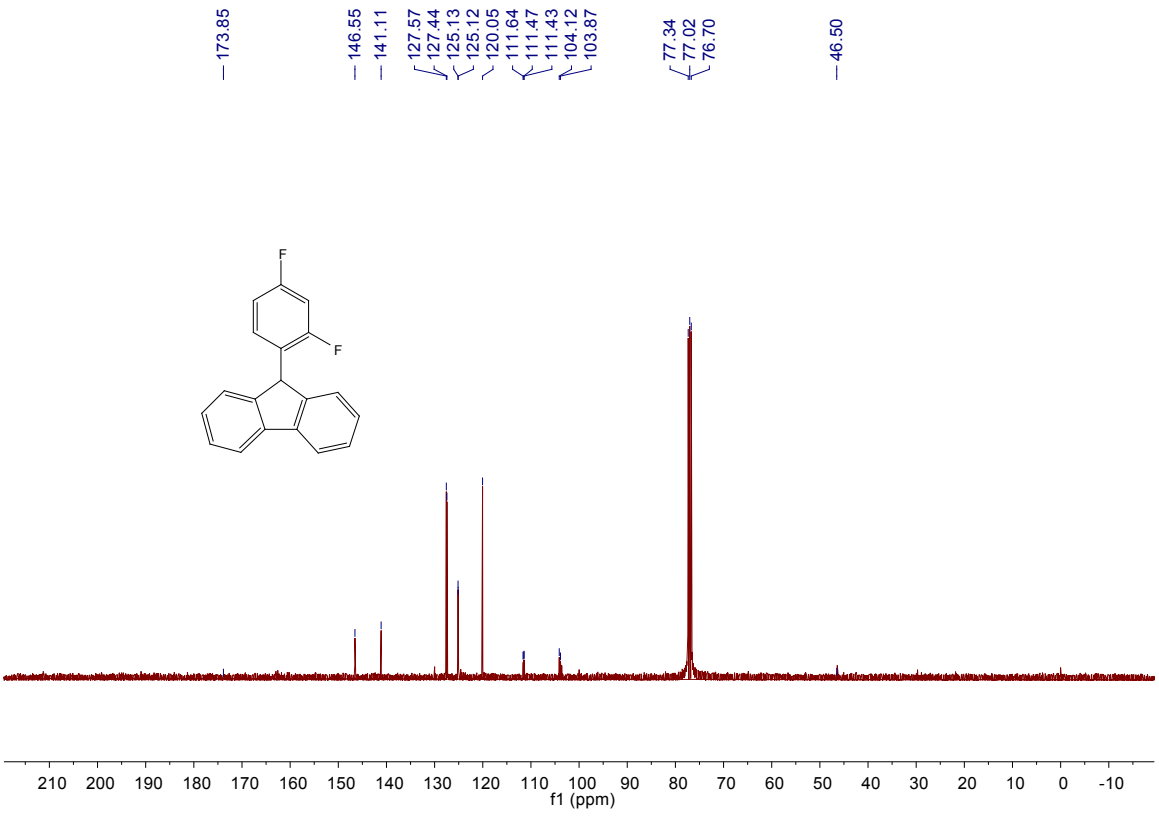
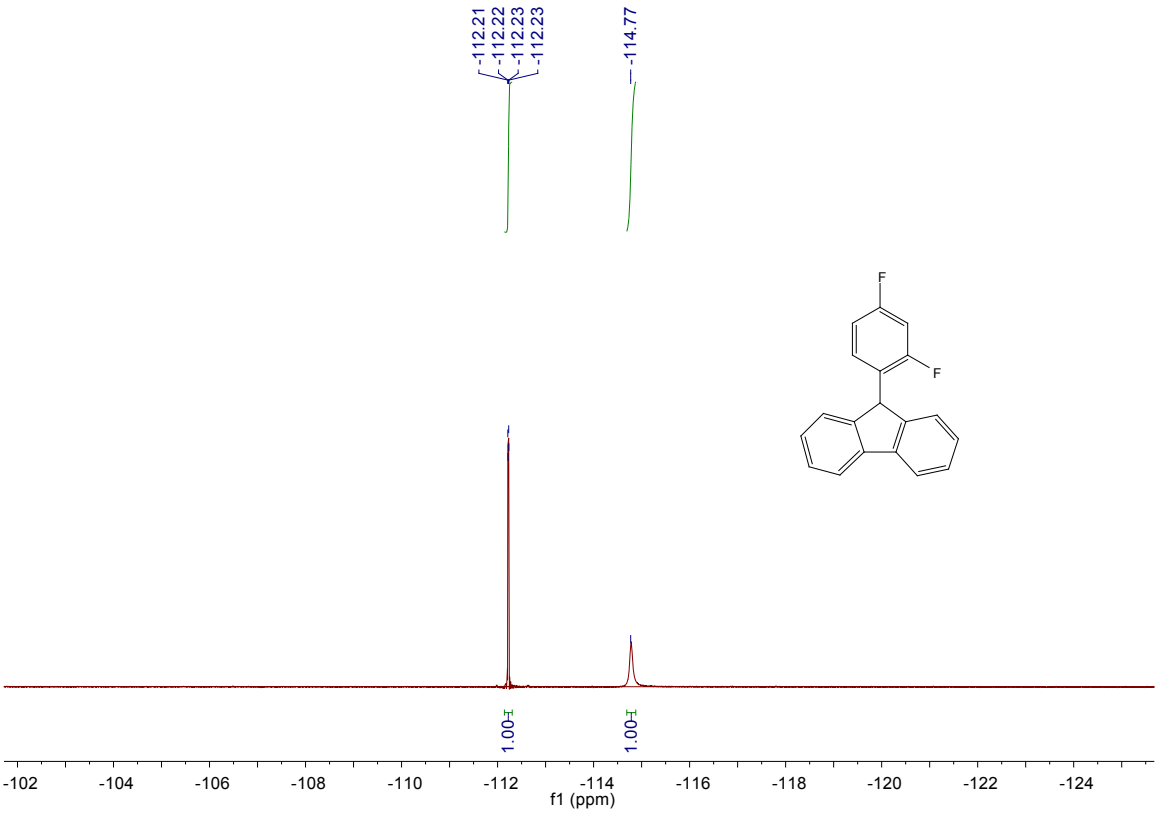
146.19
141.16
131.28
131.16
127.66
127.48
125.20
125.18
124.21
124.16
124.14
124.09
120.07
115.66
115.49
77.34
77.02
76.71
29.72
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
1.00
1.00
-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)

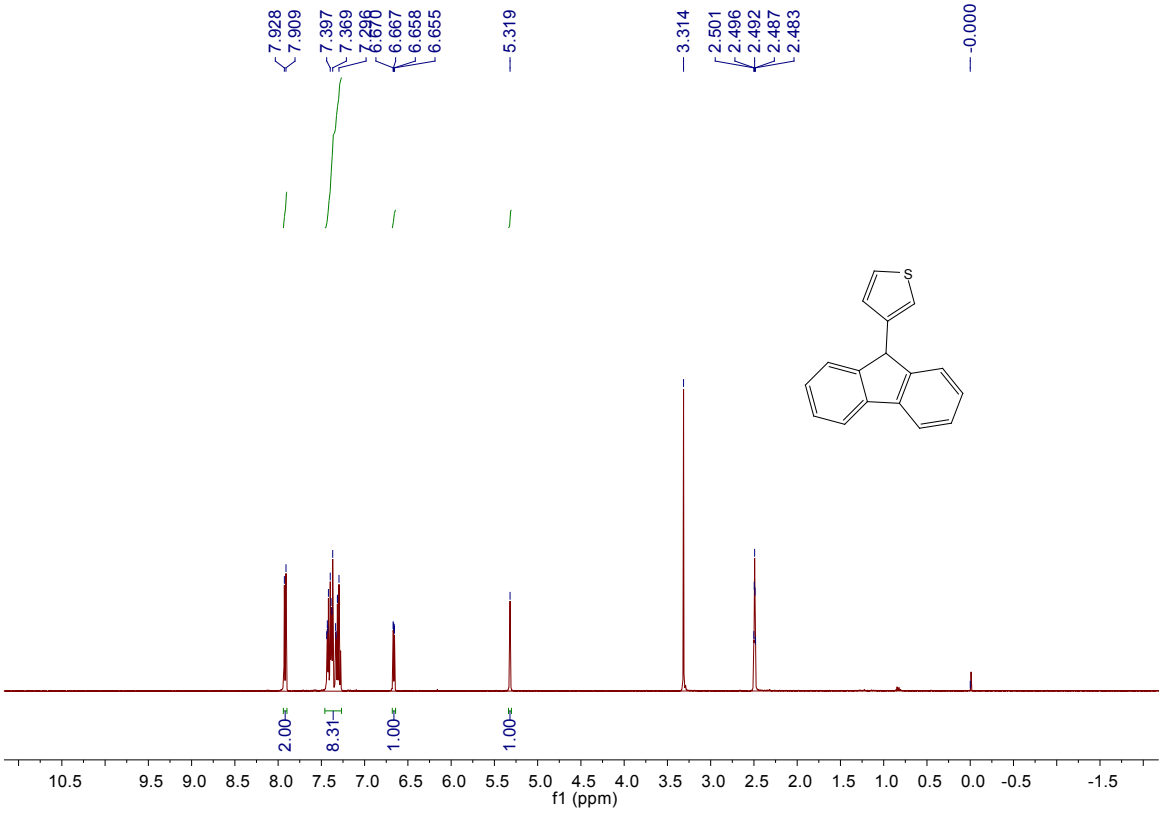
9-(2,4-difluorophenyl)-9H-fluorene[3m]

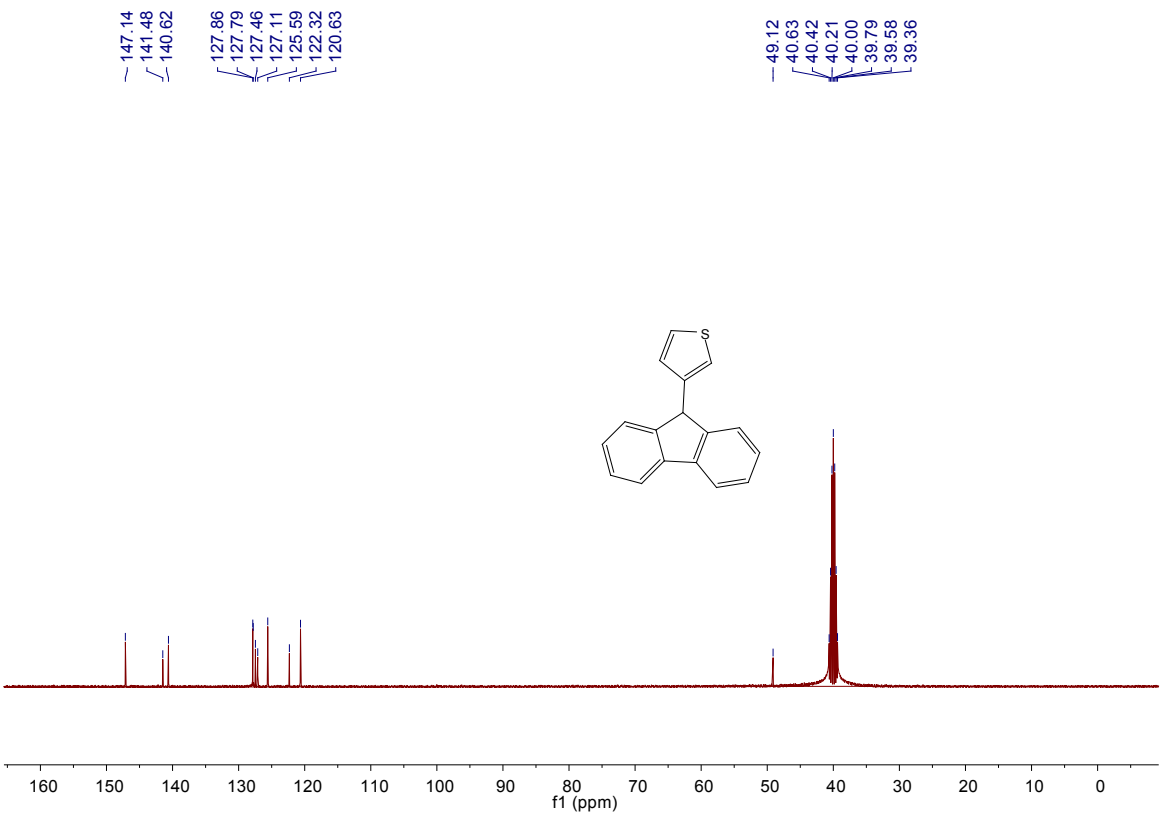




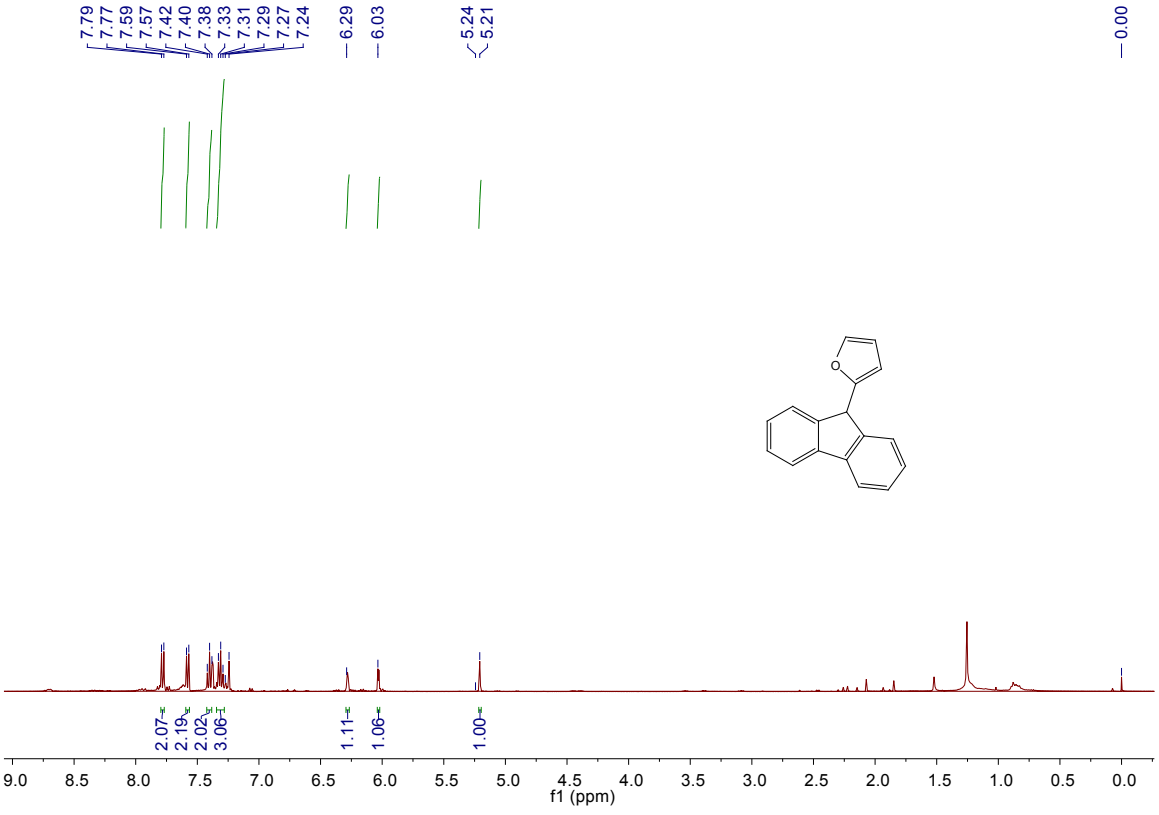


3-(9H-fluoren-9-yl)thiophene[3n]

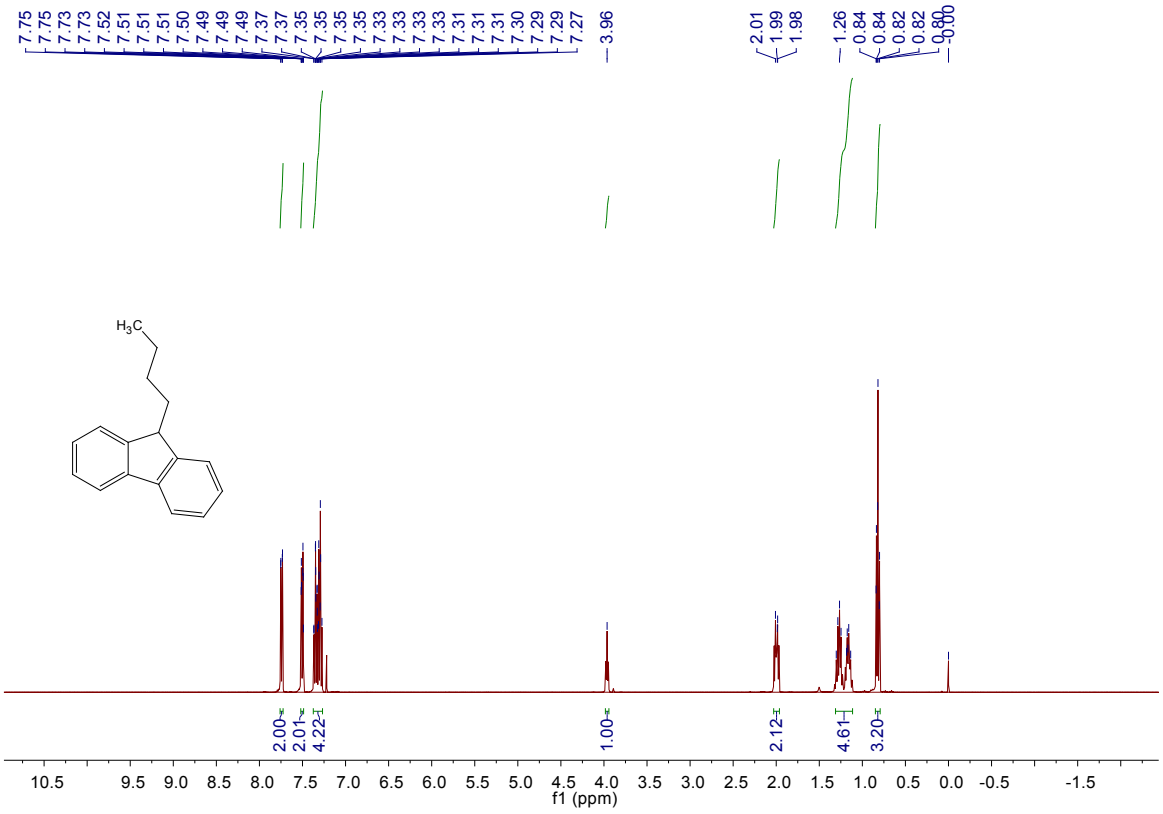


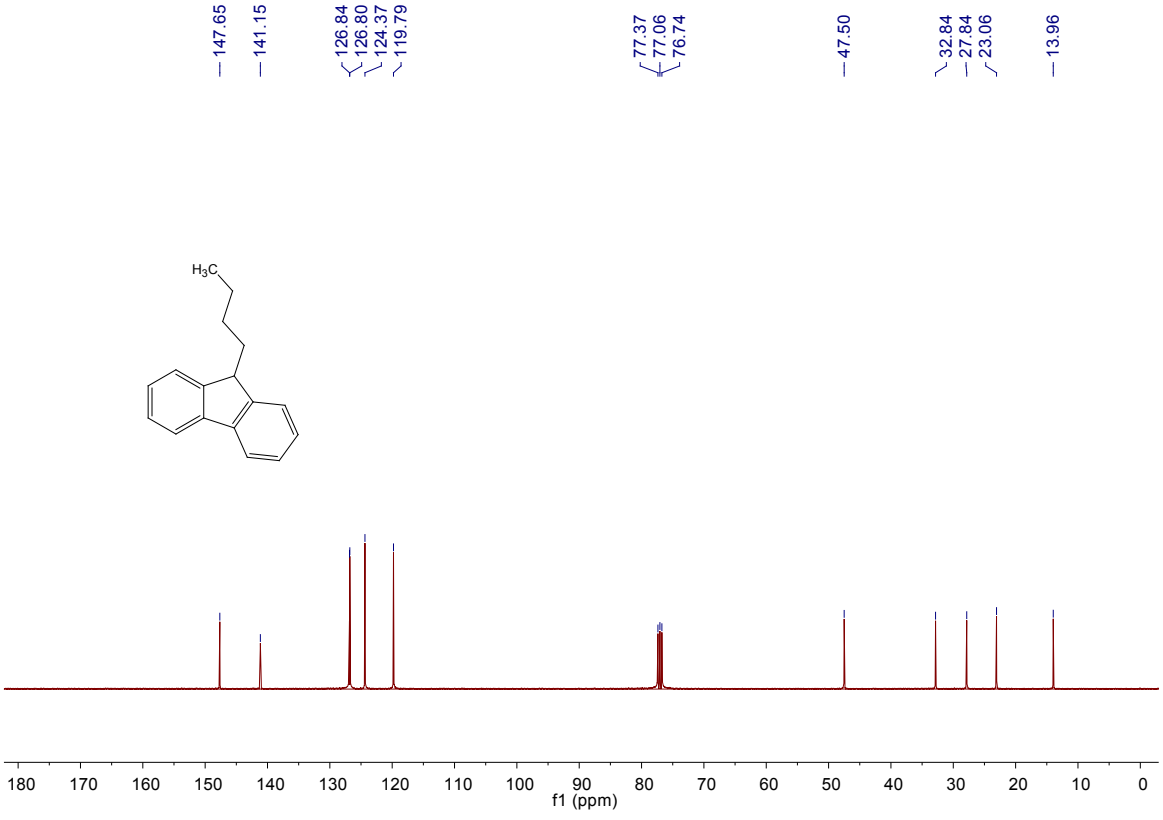


2-(9H-fluoren-9-yl)furan[3o]

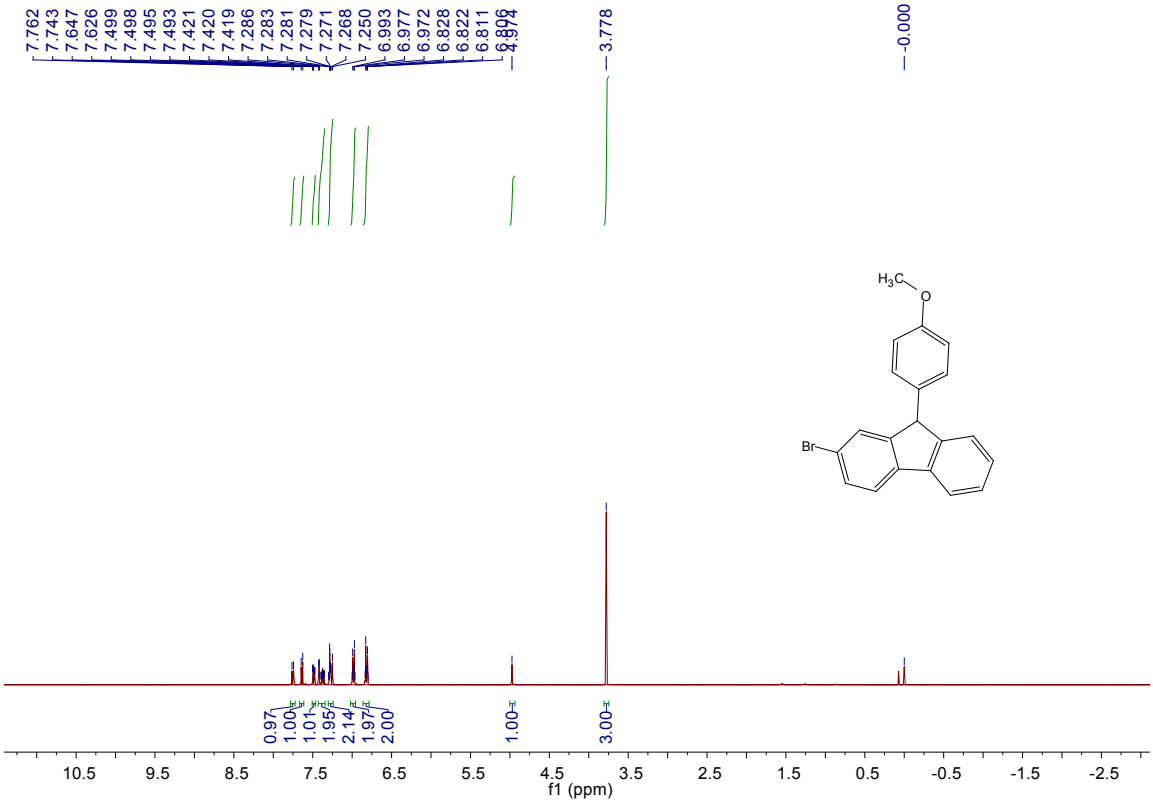


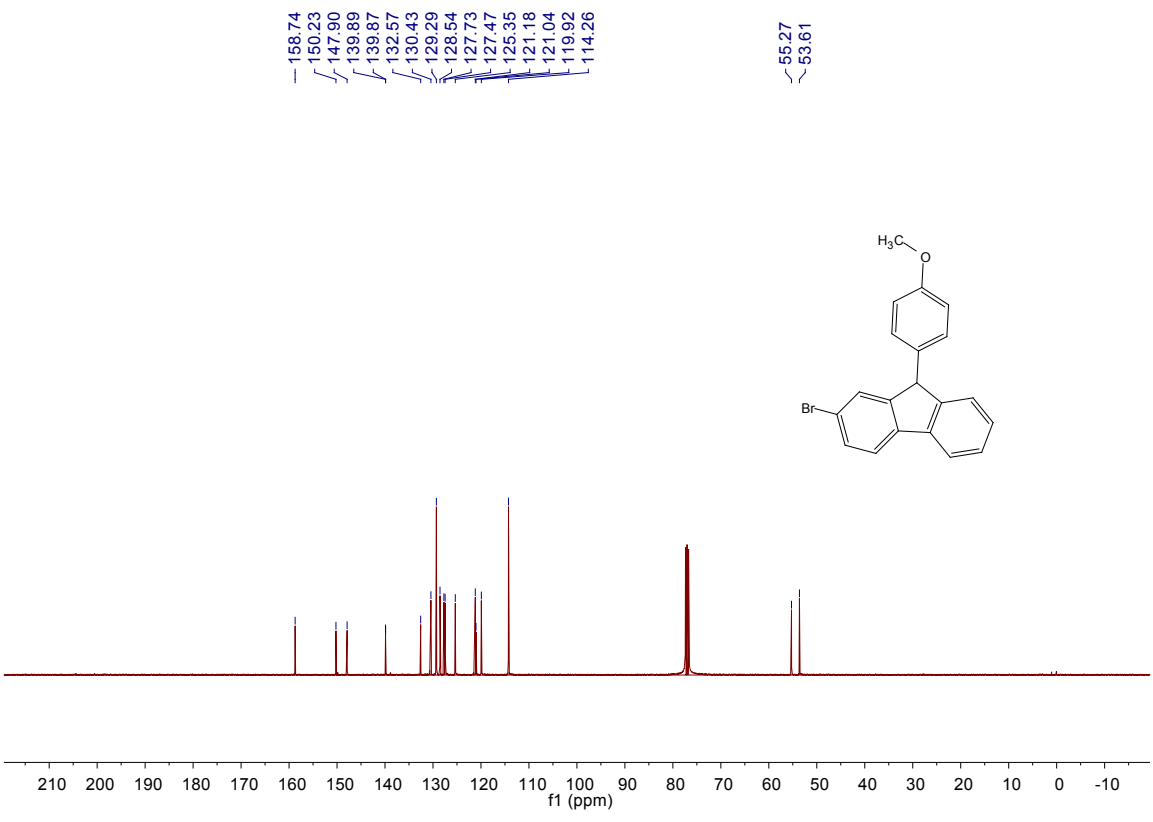
9-butyl-9H-fluorene[3p]

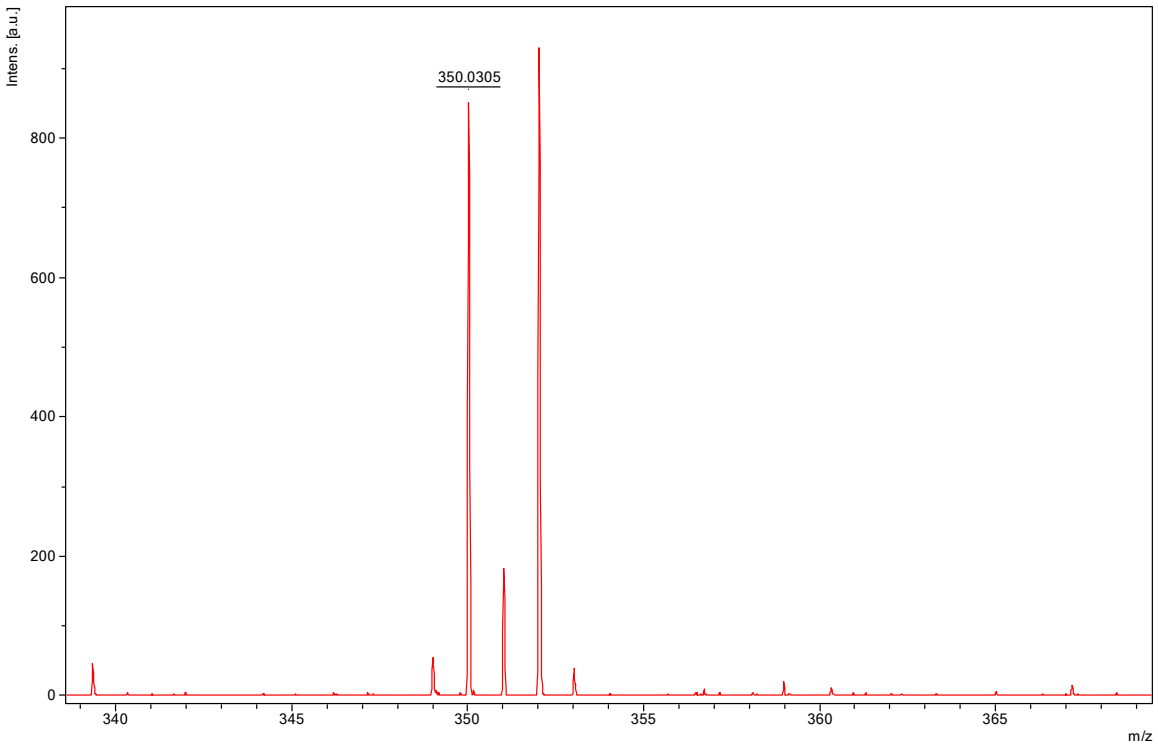




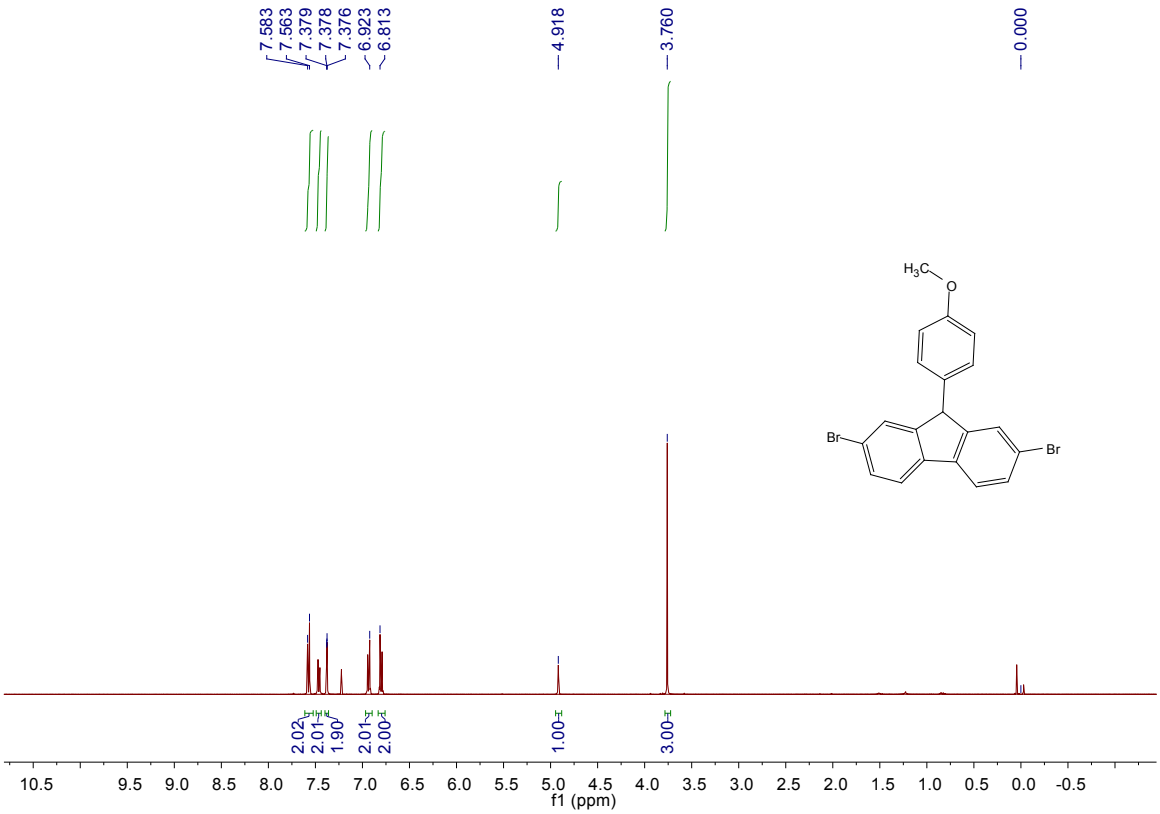
2-bromo-9-(4-methoxyphenyl)-9H-fluorene[3q]

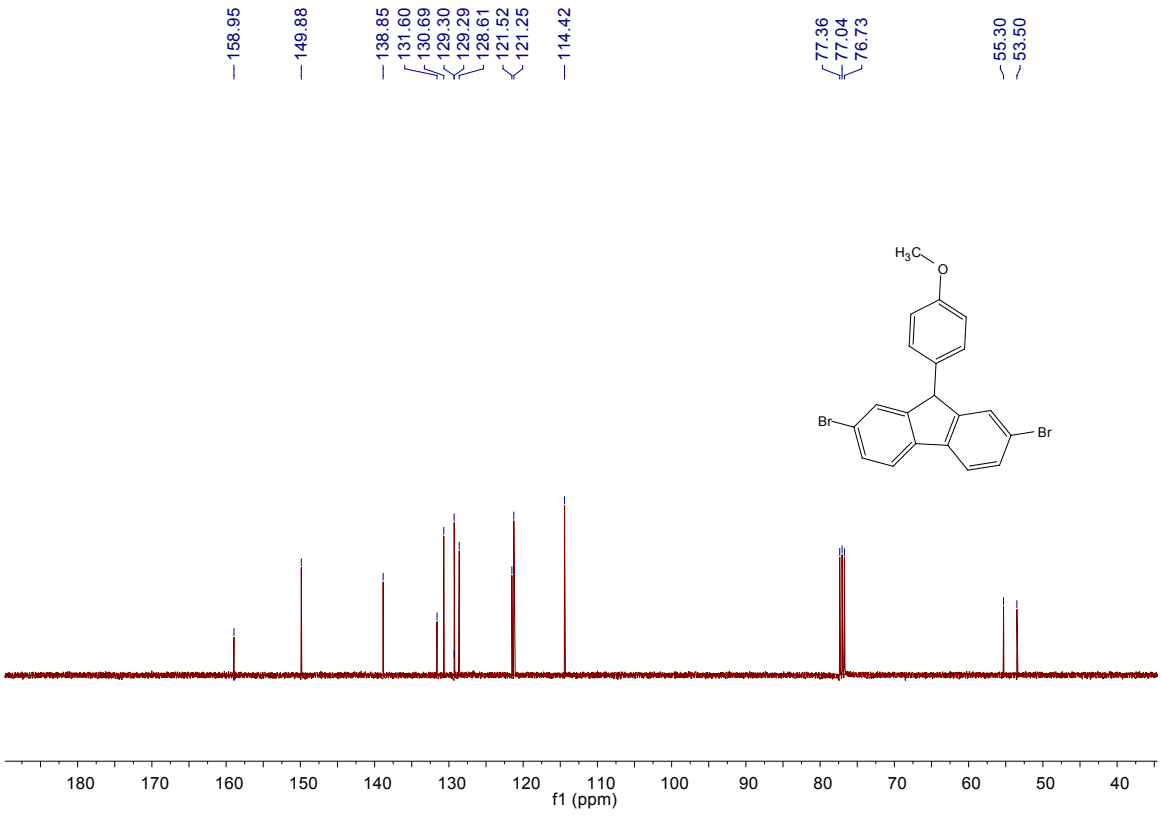


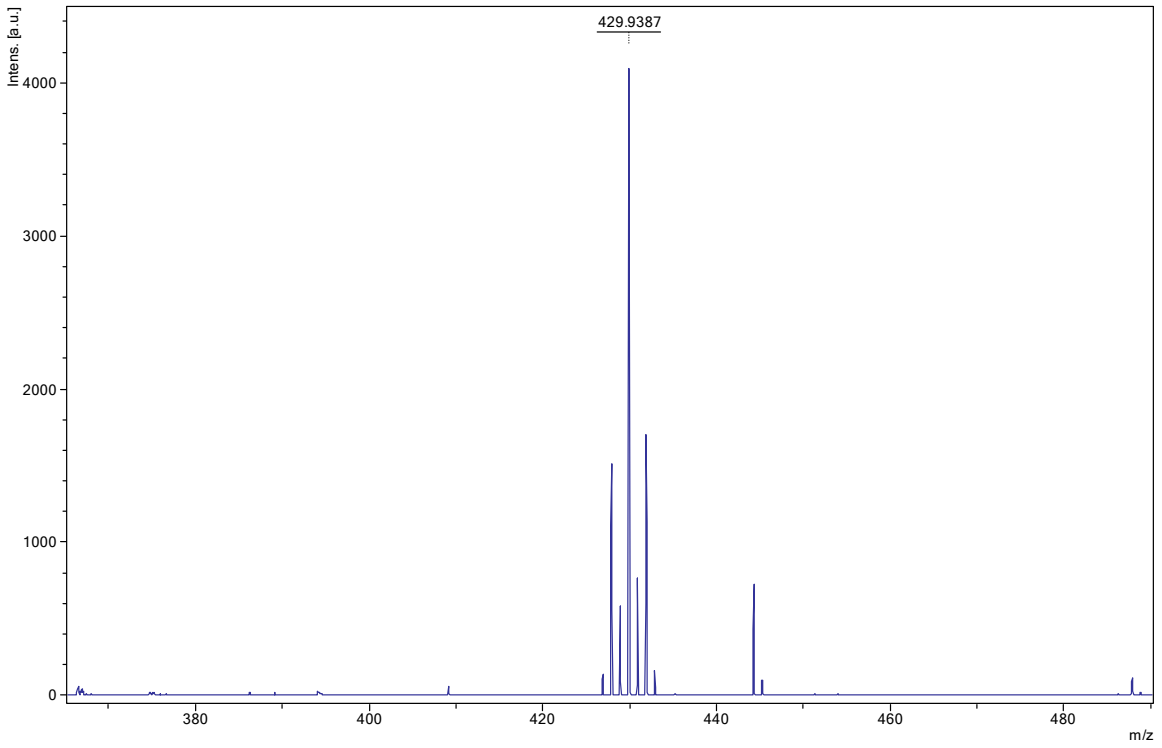




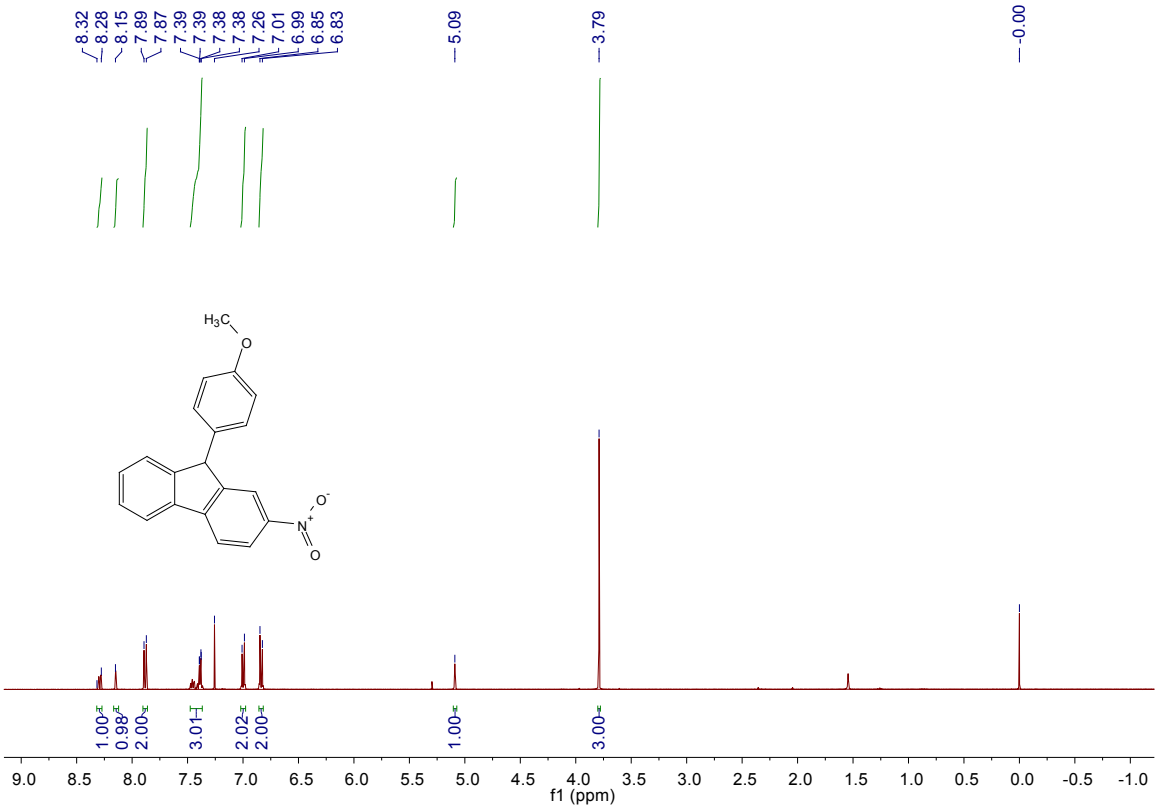
2,7-dibromo-9-(4-methoxyphenyl)-9H-fluorene[3r]

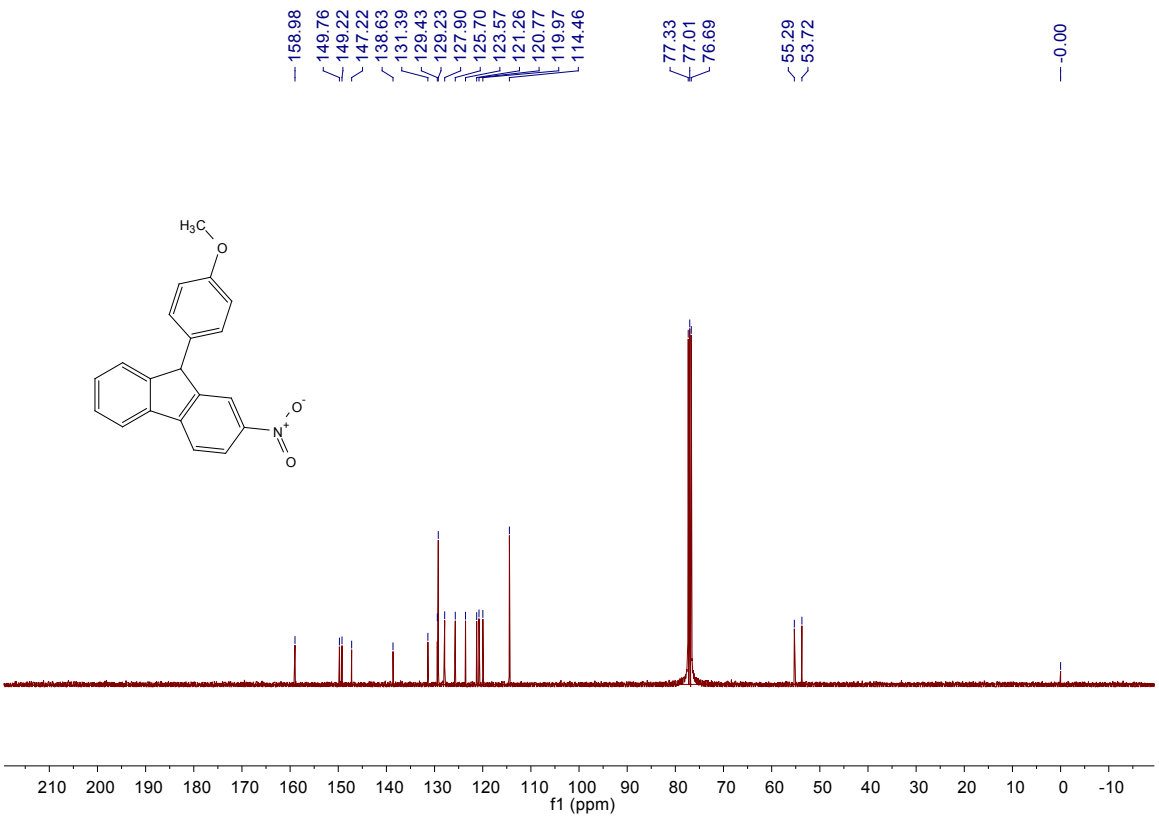


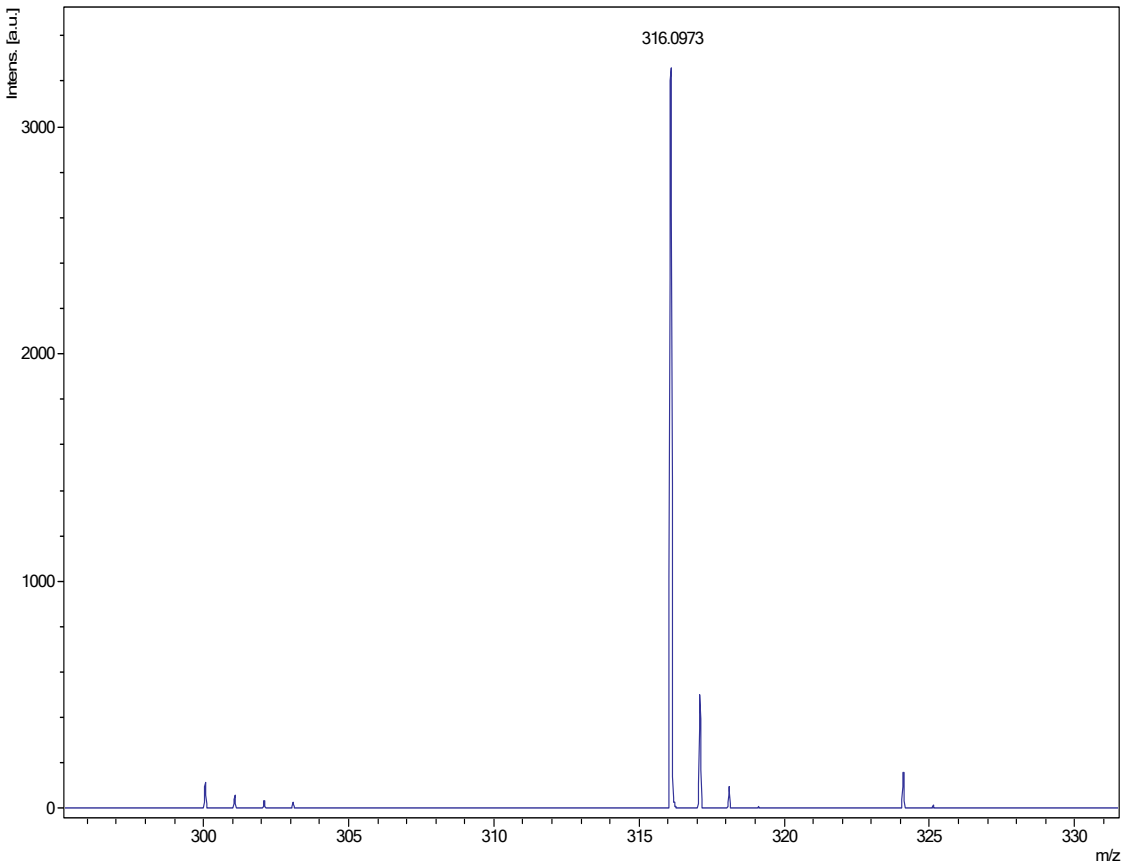

158.95
149.88
138.85
131.60
130.69
129.30
129.29
128.61
121.52
121.25
114.42
77.36
77.04
76.73
55.30
53.50
H3C
O
Br
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)


429.9387
Intens. [a.u.]
4000
3000
2000
1000
0
380
400
420
440
460
480
m/z

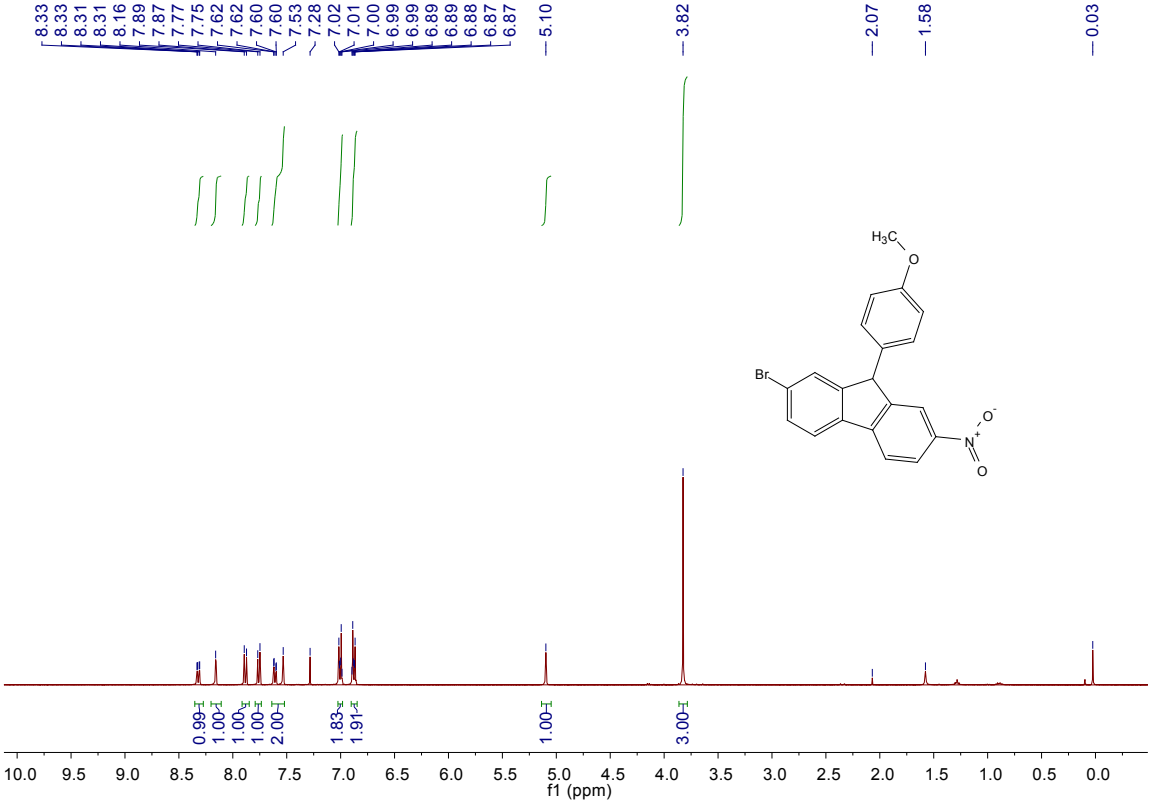
9-(4-methoxyphenyl)-2-nitro-9H-fluorene[3s]

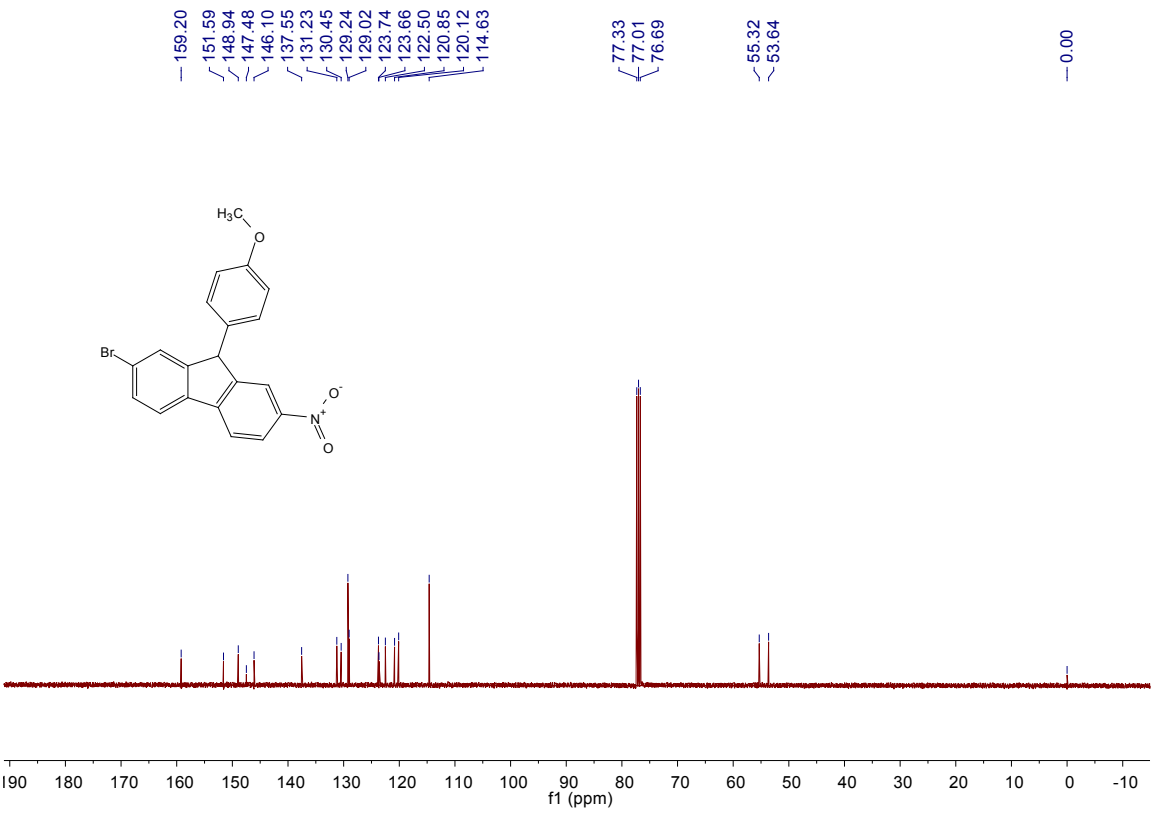


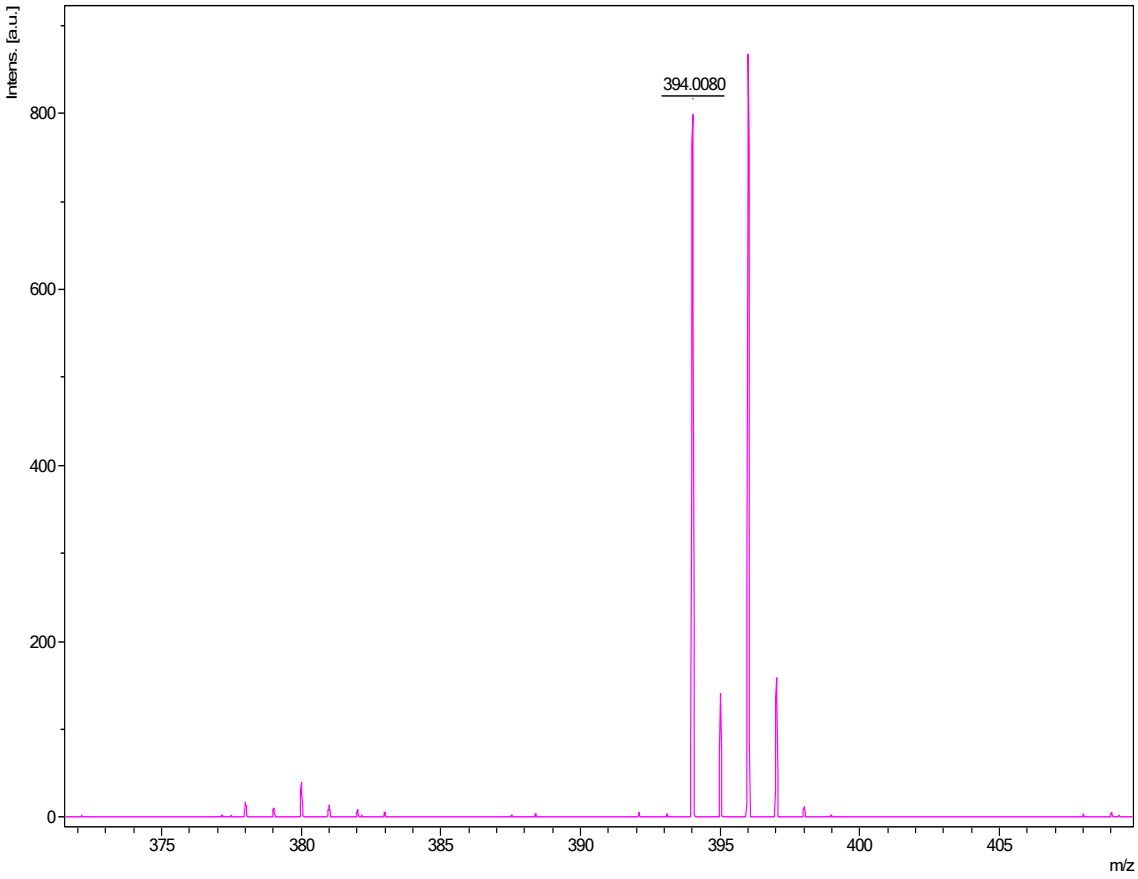




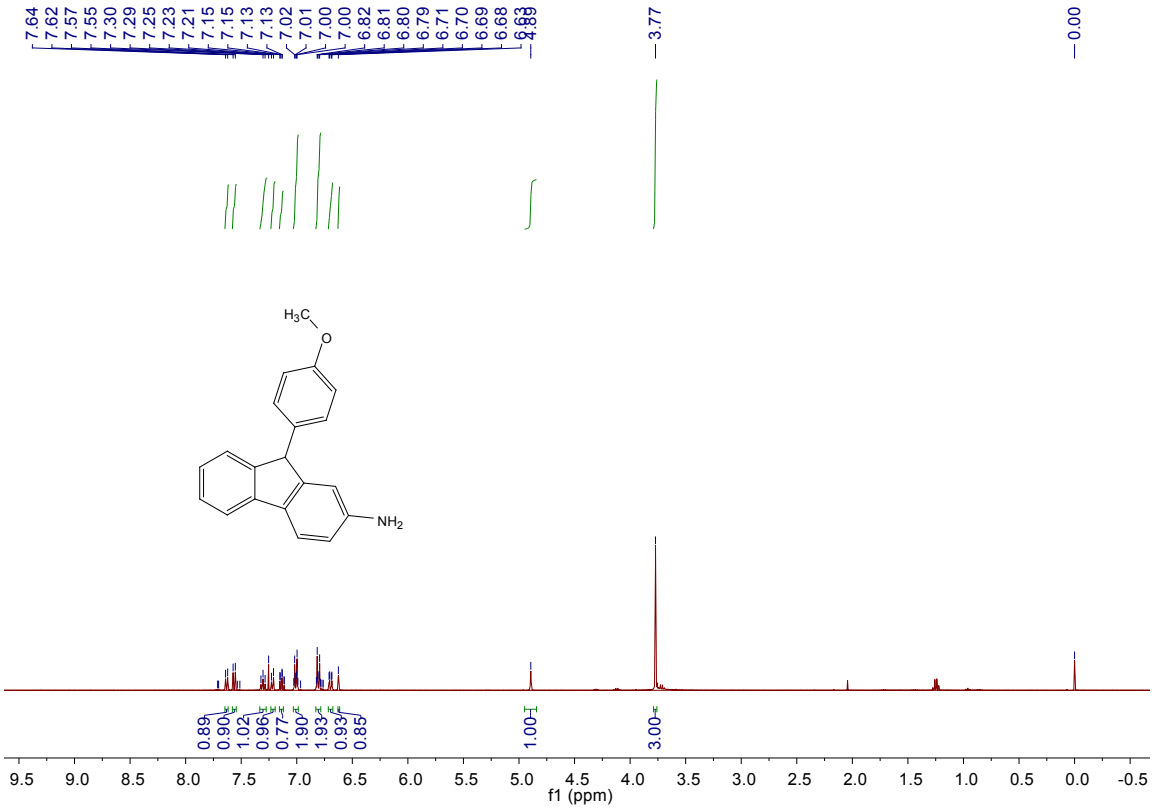
2-bromo-9-(4-methoxyphenyl)-7-nitro-9H-fluorene[3t]

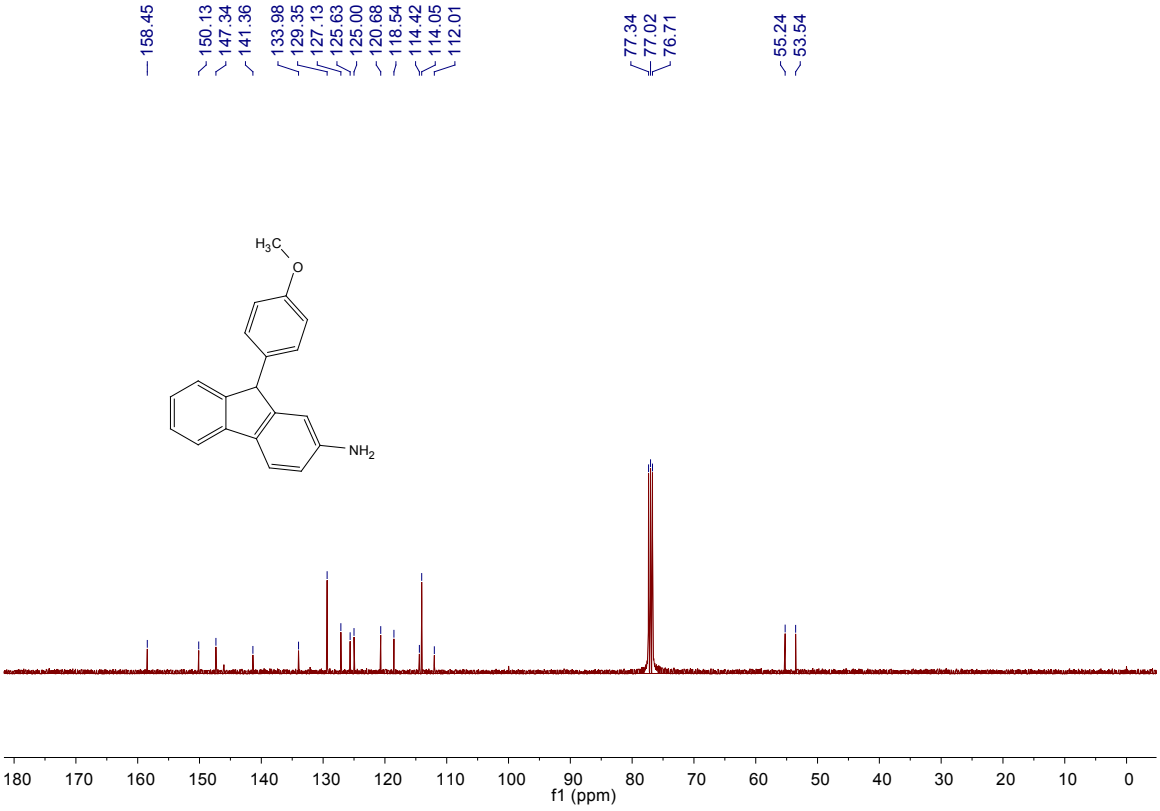


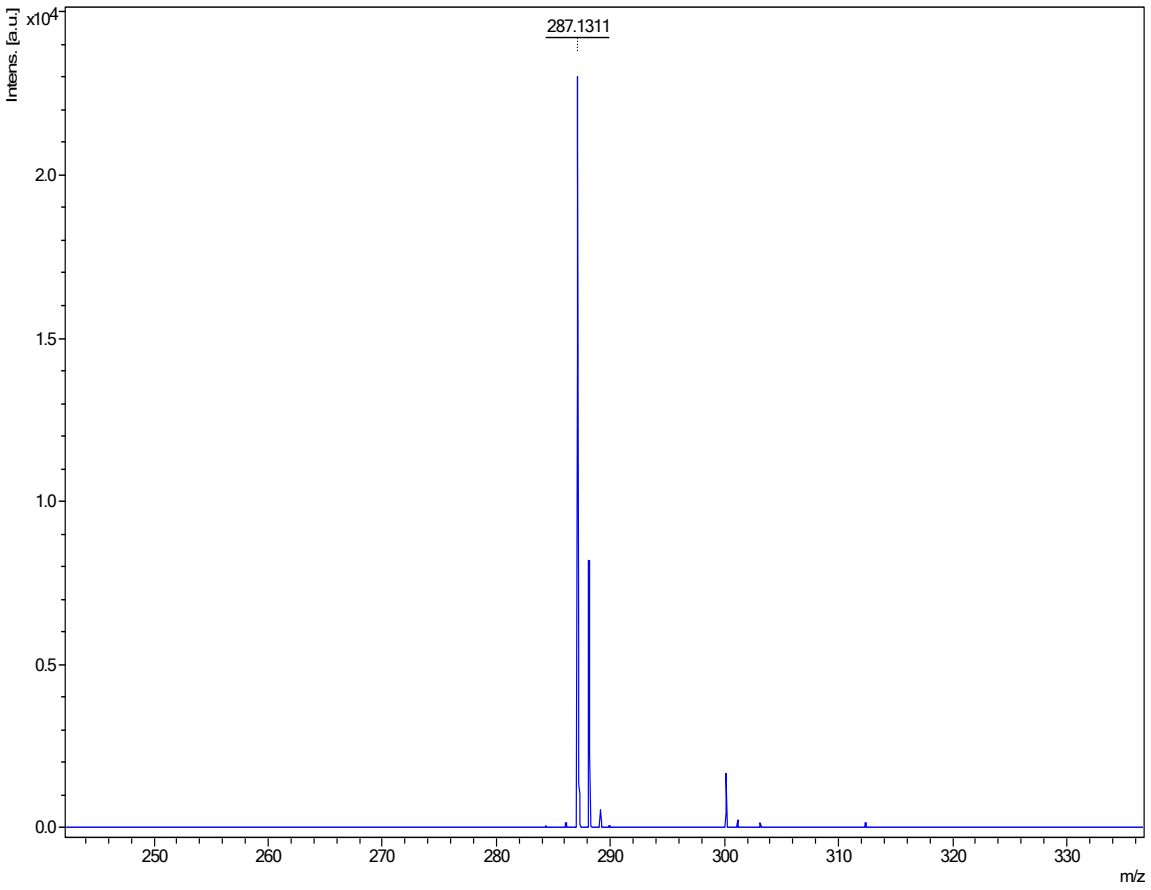

159.20
151.59
148.94
147.48
146.10
137.55
131.23
130.45
129.24
129.02
123.74
123.66
122.50
120.85
120.12
114.63
77.33
77.01
76.69
55.32
53.64
0.00
H3C
O
Br
O-
N+
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens. [a.u.]
394.0080
800
600
400
200
0
375 380 385 390 395 400 405
m/z

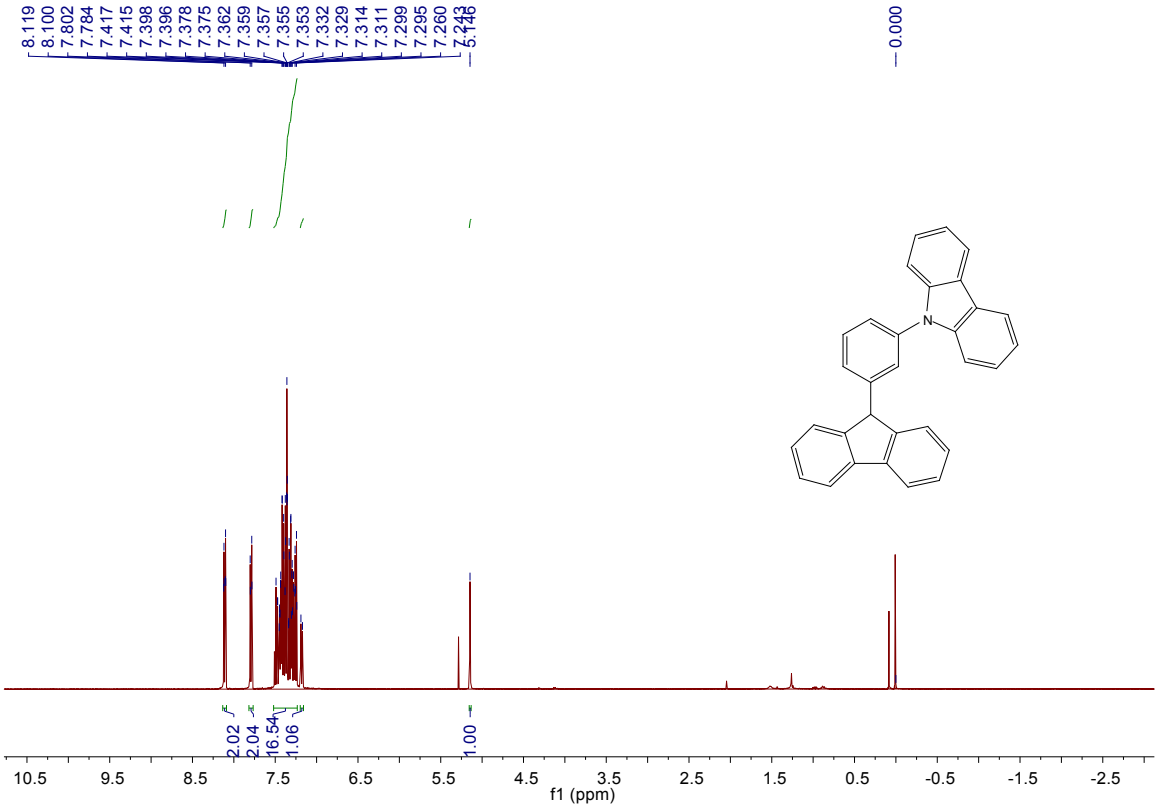
9-(4-methoxyphenyl)-9H-fluoren-2-amine[3u]

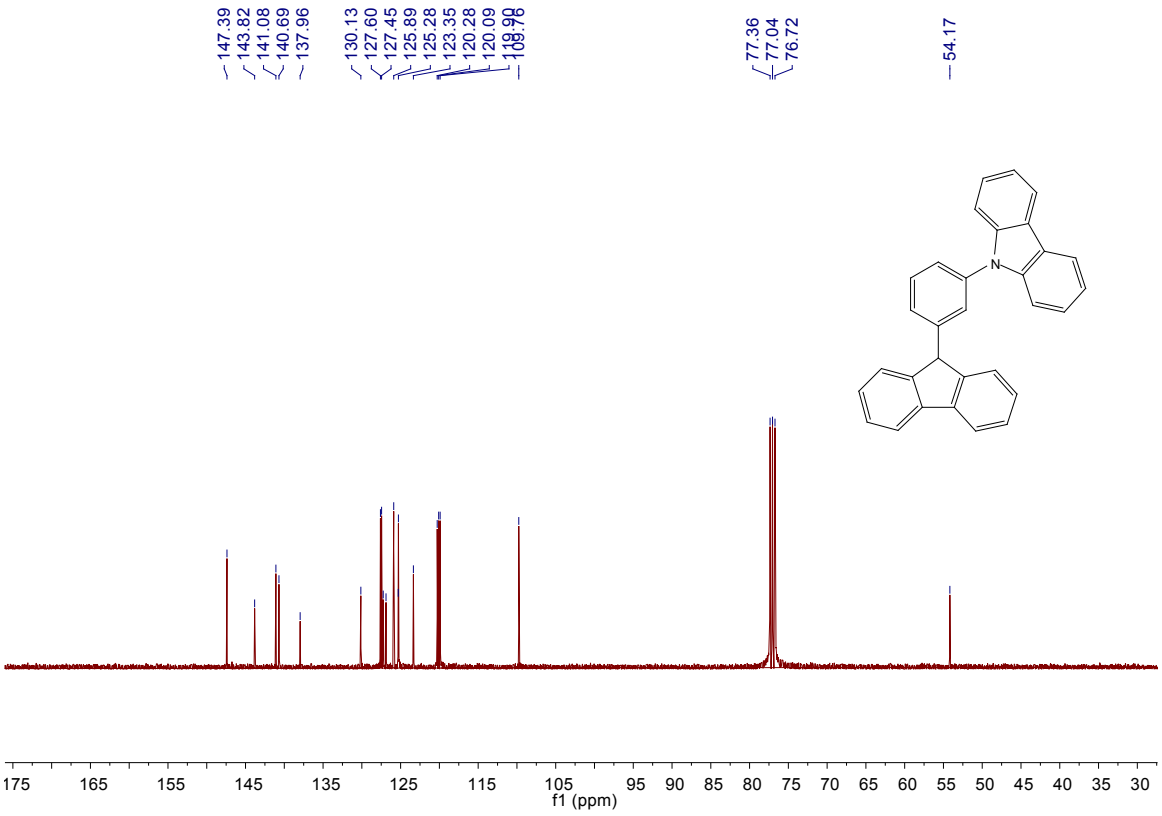


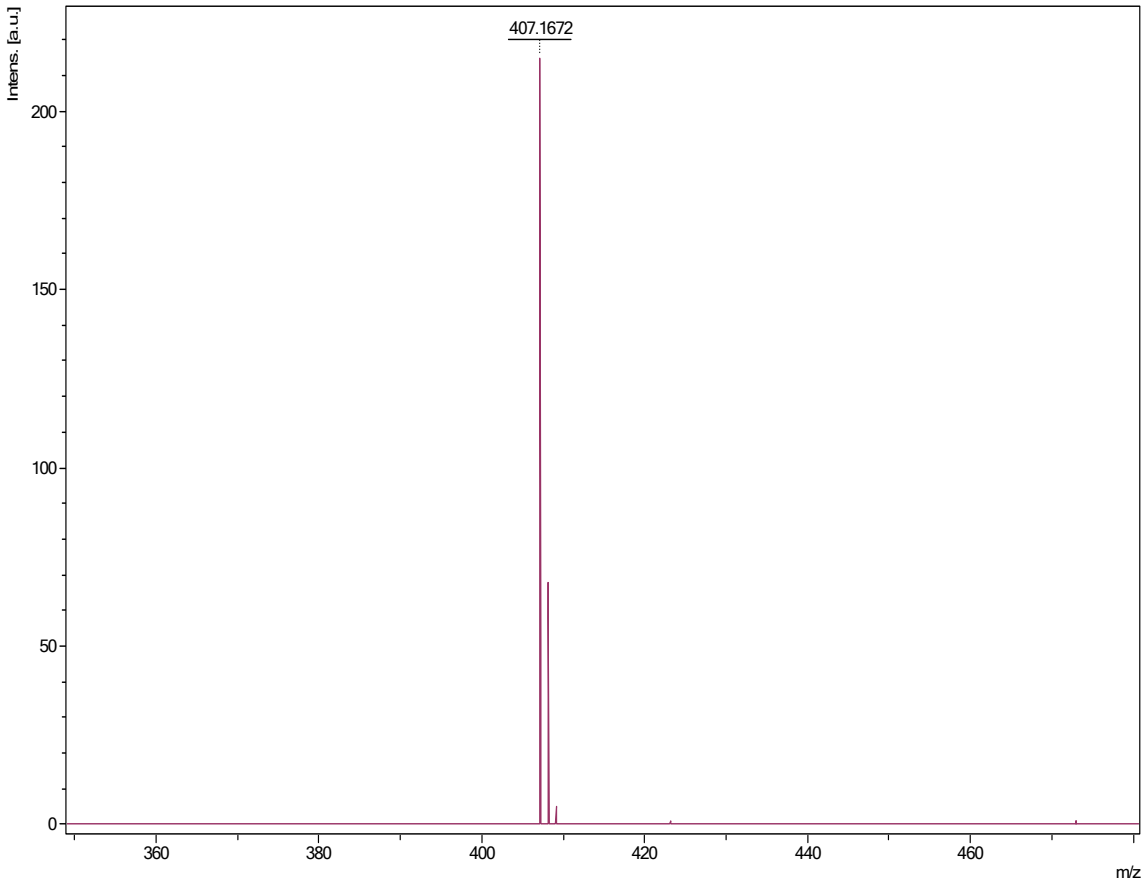




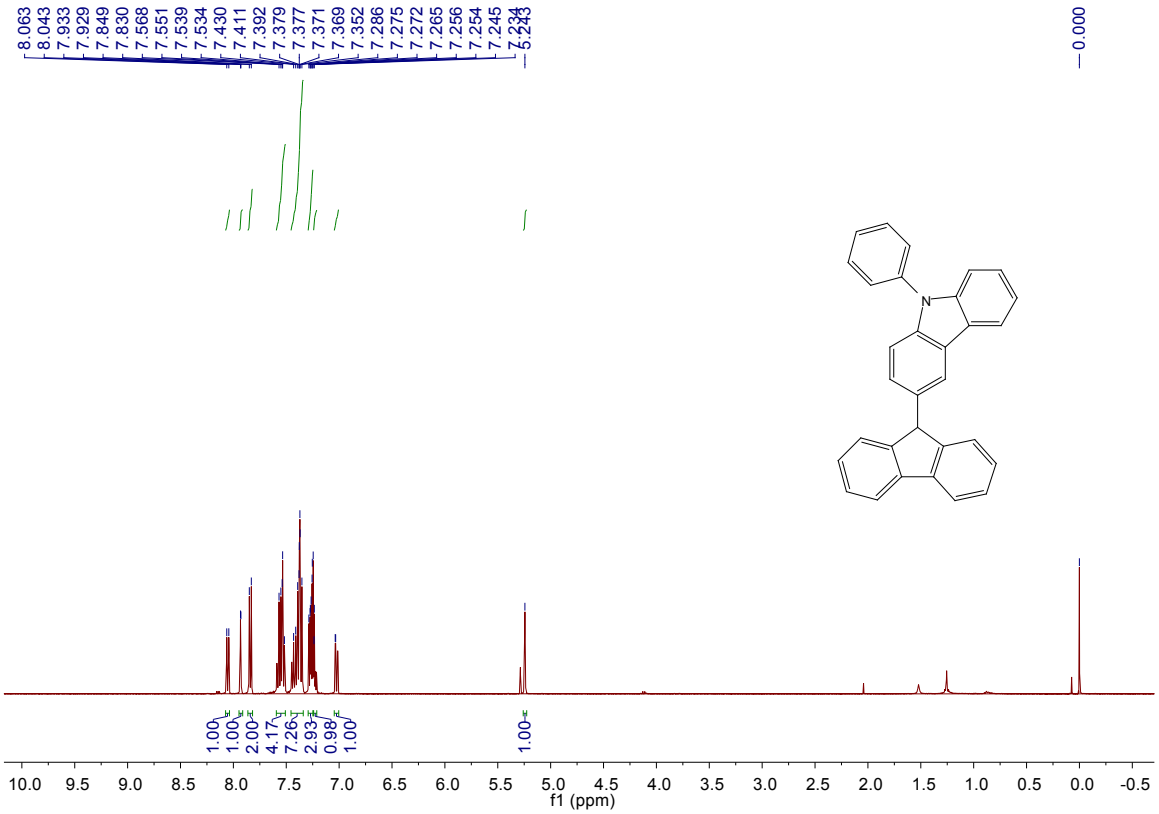
9-(3-(9H-fluoren-9-yl)phenyl)-9H-carbazole[3v]

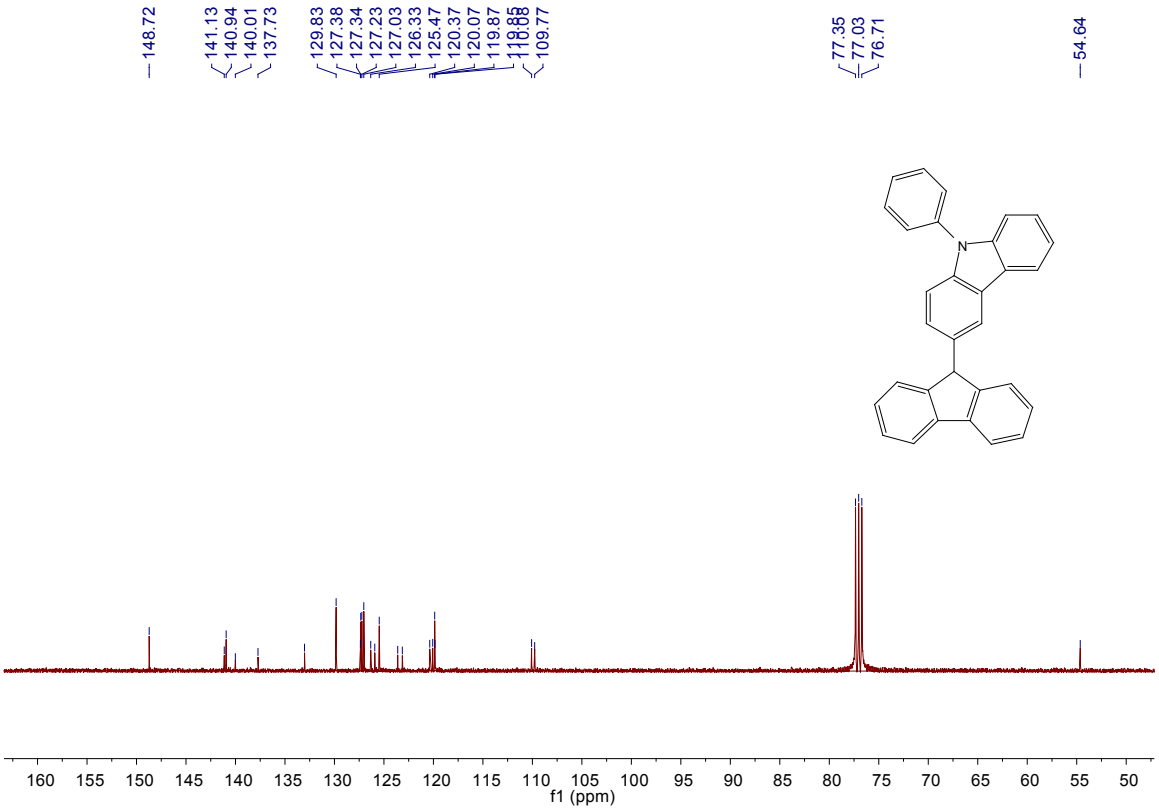


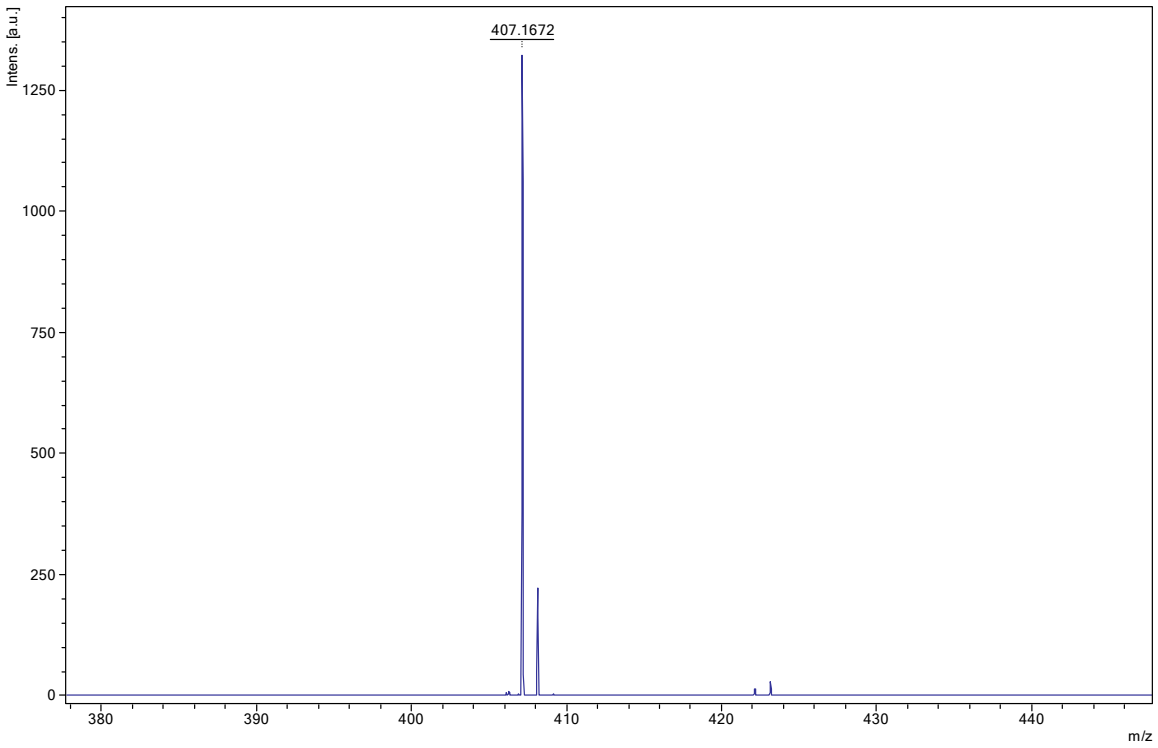

147.39
143.82
141.08
140.69
137.96
130.13
127.60
127.45
125.89
125.28
123.35
120.28
120.09
119.90
108.76
77.36
77.04
76.72
54.17
N
175 165 155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)


Intens. [a.u.]
407.1672
200
150
100
50
0
360 380 400 420 440 460
m/z

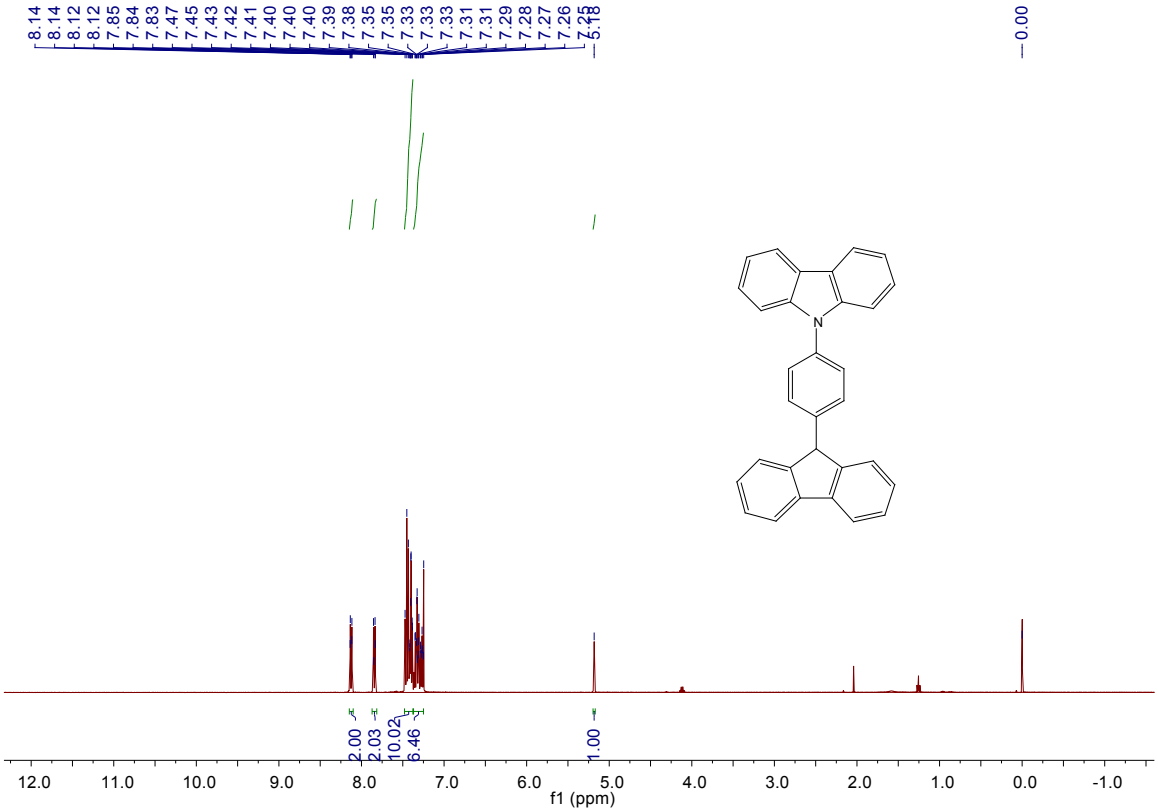
3-(9H-fluoren-9-yl)-9-phenyl-9H-carbazole[3w]

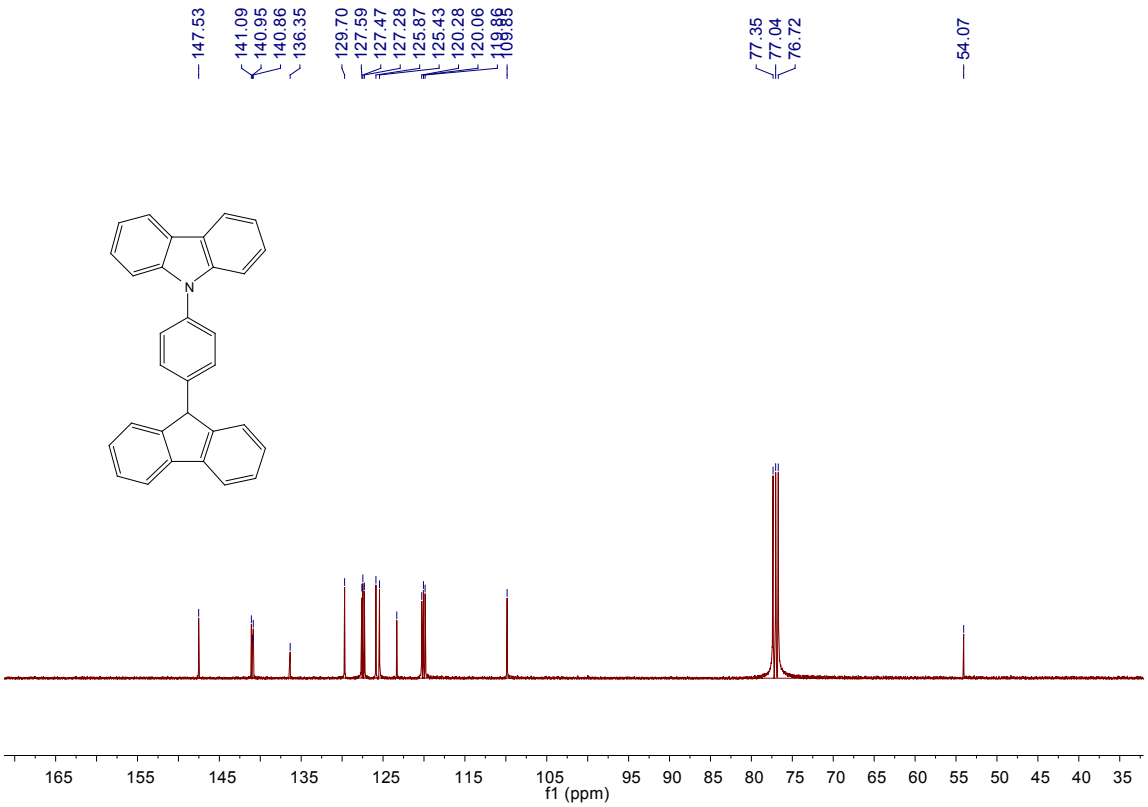


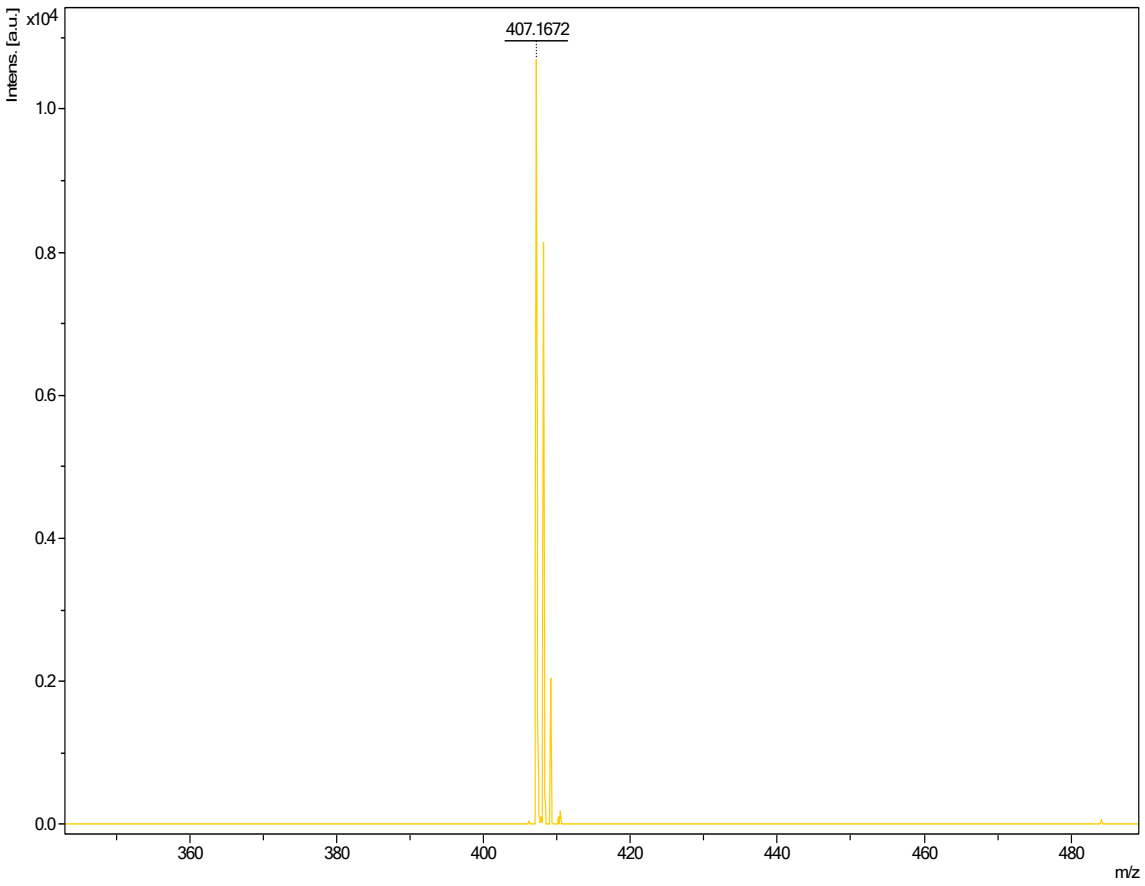




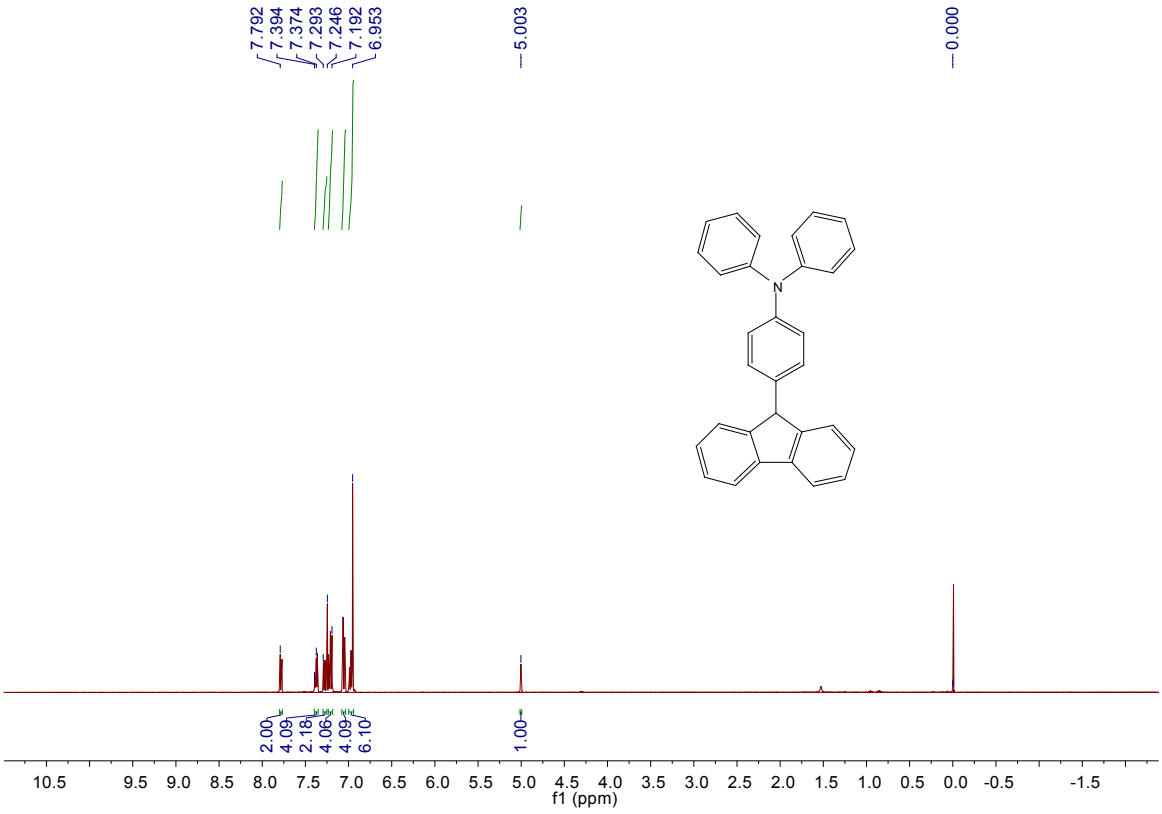
9-(4-(9H-fluoren-9-yl)phenyl)-9H-carbazole[3x]

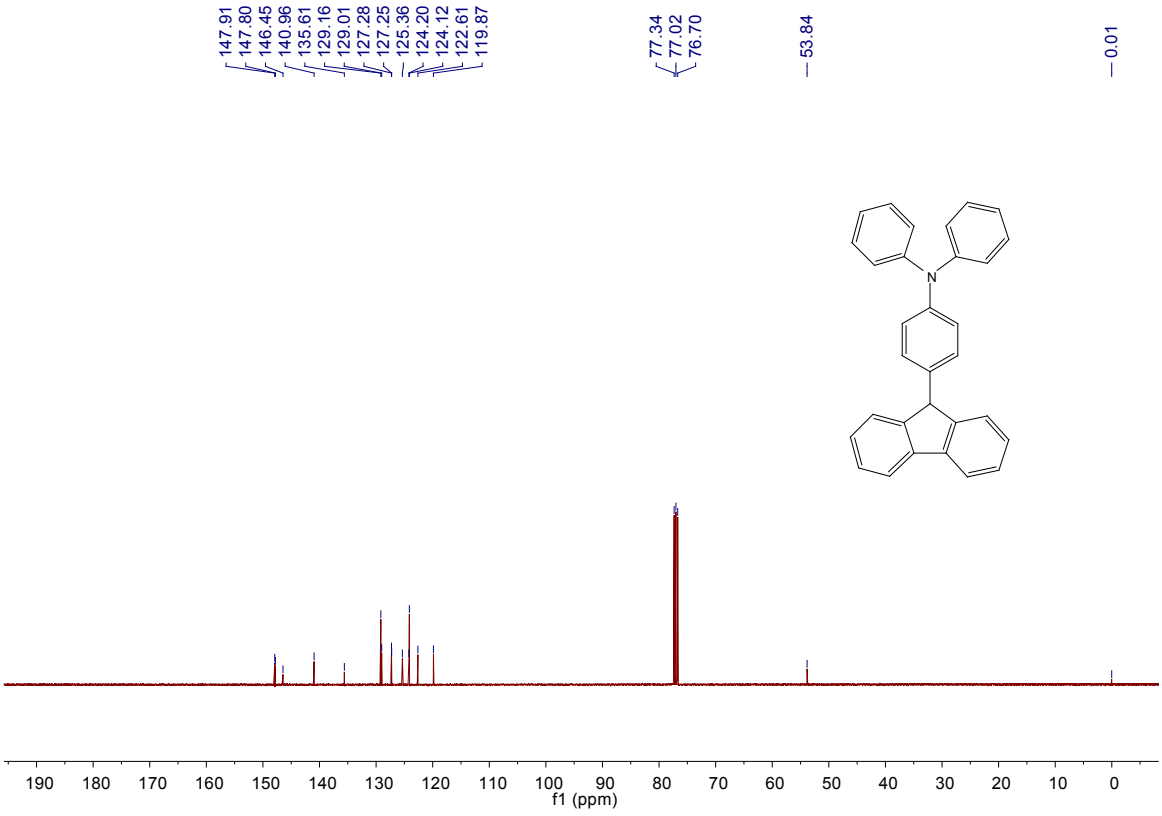


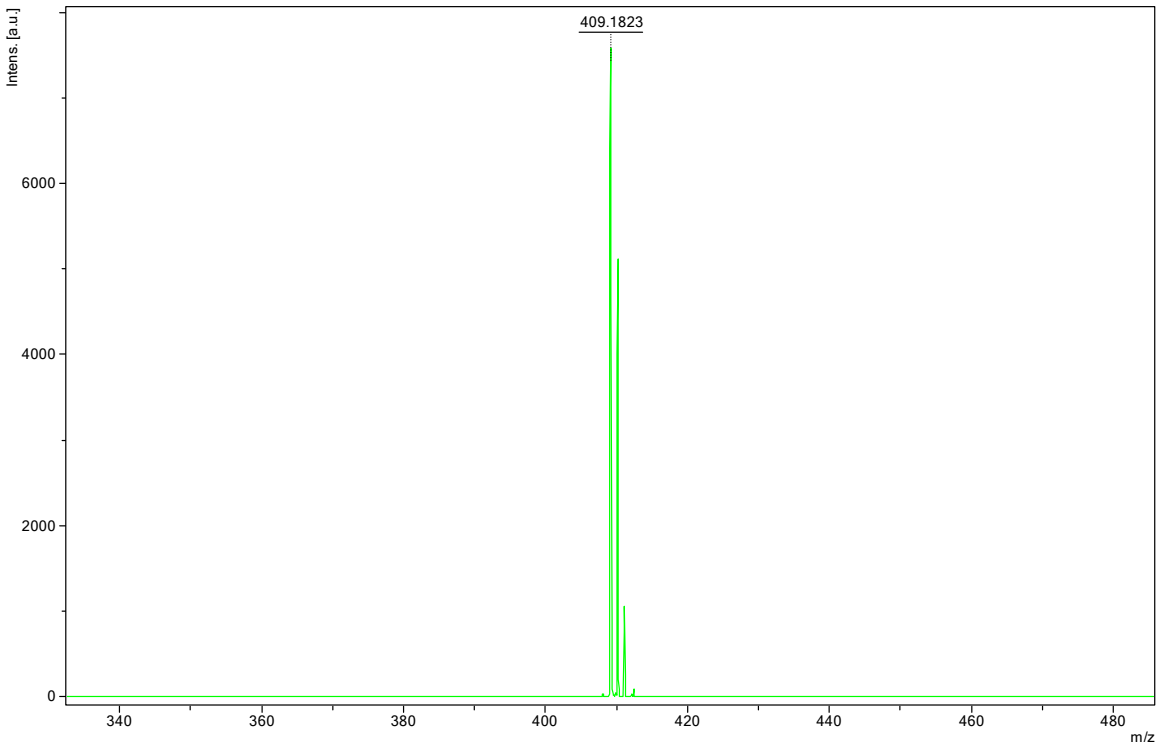

147.53
141.09
140.95
140.86
136.35
129.70
127.59
127.47
127.28
125.87
125.43
120.28
120.06
77.35
77.04
76.72
54.07
N
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)


Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
407.1672
360
380
400
420
440
460
480
m/z

4-(9H-fluoren-9-yl)-N,N-diphenylaniline[3y]






409.1823
Intens. [a.u.]
6000
4000
2000
0
340
360
380
400
420
440
460
480
m/z