Supporting Information

Radical-Radical Cross Coupling Reactions of Photo-excited Fluorenones

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General information

Reagents and solvents used were generally AR grade. Thin layer chromatography was performed on silica gel coated plates. ^{1}H spectra were recorded on FT-NMR 500 and 400 MHz instruments. Chemical data for ^{1}H NMR are reported in parts per million (ppm) downfield from tetramethylsilane and are internally referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz or 125 MHz. Chemical data for ^{13}C NMR are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent.

General experimental procedure for decarboxylative radical addition to 9-fluorenone. 9-fluorenone (1 mmol) was taken in an oven-dried round bottom flask and dissolved in 1 ml of DMF followed by the addition of carboxylic acid (2.0 mmol, 2 equiv.) and CsF (3.0 mmol, 3 equiv.). The stirred reaction mixture was irradiated under 27W CFL for 48 h at room temperature. The reaction was monitored by TLC. After completion, the reaction mixture was diluted with cold water and extracted with ethyl acetate (3 x 20 ml). The combined organic layers were concentrated under vacuum and dried with $NaSO_4$. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane to give pure product.

9-benzyl-9H-fluoren-9-ol (2a).[i] The title compound was prepared according to general procedure described above using phenyl acetic acid (272.2 mg, 2.0 mmol) and 9-fluorenone (180.0 mg, 1.0 mmol) in DMF, and purified by column chromatography (5% EtOAc /hexane) yields pure compound **2a** (163 mg, 60%). White solid; m. p. 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.21 (m, 6H), 7.16 –7.09 (m, 3H), 6.98 – 6.94 (m, 2H), 3.28 (s, 2H), 2.20 (s, 1H); ^{13}C NMR (125 MHz, ($CDCl_3$) δ 148.2 (2C), 139.3(2C), 136.3, 130.8

(2C), 128.9 (2C), 127.6 (2C), 127.5 (2C), 126.5, 124.3 (2C), 119.9 (2C), 82.3, 45.8. HRMS (m/z)$[M+H-H_2O]^+$ calculated for $[C_{20}H_{15}]^+$ 255.1168; found 255.1170. Solid, M.P.

9-(4-bromobenzyl)-9H-fluoren-9-ol (2b). The title compound was prepared according to general procedure described above using *p*-bromophenylacetic acid (430.2mg, 2.0mmol) and 9-fluorenone (180.0mg, 1.0mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2b** (193 mg, 55%). White solid; m. p. 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.27 (d, *J* = 6.4 Hz, 2H), 7.23(d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 3.26 (s, 2H), 2.14 (s, 1H), 1.57 (s, 1H); ^{13}C NMR (125 MHz, ($CDCl_3$) δ 146.8 (2C), 138.2 (2C), 134.2, 131.3 (2C), 129.5 (2C), 128.1 (2C), 126.6 (2C), 123.1 (2C), 119.5, 118.9 (2C), 81.2, 44.1. HRMS (m/z) $[M + H\text{-}H_2O]^+$ calculated for $[C_{20}H_{14}Br]^+$ 333.0273; found 333.0276.

9-(4-(trifluoromethyl)benzyl)-9H-fluoren-9-ol (2c). The title compound was prepared according to general procedure described above using *p*-trifluoreomethylphenylacetic acid (204.1 mg, 1.0 mmol) and 9-fluorenone (90.0mg, 0.5mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2c** (88 mg, 52%). White solid; m. p. 135-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 11.5 Hz, 2H), 7.35-7.19 (m, 8H), 7.02 (t, *J* = 7.5 Hz, 2H), 3.30 (s, 2H), 2.10 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8(2C), 140.4, 139.2 (2C), 131.0 (2C), 129.2 (2C), 128.7, 128.5, 127.7 (2C), 124.3 (2C), 124.1 (2C), 120.1 (2C), 82.2, 45.5. HRMS (m/z) $[M + H\text{-}H_2O]^+$ calculated for $[C_{21}H_{14}F_3]^+$ 323.1042; found 323.1042.

9-(4-methoxybenzyl)-9H-fluoren-9-ol (2d).[ii] The title compound was prepared according to general procedure described above using *p*-methoxyphenylacetic acid (166.1 mg, 1.0 mmol) and 9-fluorenone (90.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2d** (74 mg, 49 %). White solid; m. p. 135-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 11.3 Hz, 2H), 7.31 – 7.14 (m, 6H), 6.83 (t, *J* = 11.4 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 3.68 (d, *J* = 22.0 Hz, 3H), 3.16 (s, 2H), 2.30 (d, *J* = 38.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 148.4 (2C), 139.4 (2C), 131.7 (2C), 128.8 (2C), 128.5, 127.5 (2C), 124.4 (2C), 119.9 (2C), 112.9 (2C), 82.4, 55.1, 44.9.HRMS (m/z) $[M+H\text{-}H_2O]^+$ calculated for $[C_{21}H_{17}O]^+$ 285.1274; found 285.1269.

9-(4-chlorobenzyl)-9H-fluoren-9-ol (2e).[iii] The title compound was prepared according to general procedure described above using *p*-chlorophenylacetic acid (170.6 mg, 1.0 mmol) and 9-

fluorenone (90.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2e** (81 mg, 53%). White solid; m. p. 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 3.28 (s, 2H), 2.14 (s, 1H); ^{13}C NMR (125 MHz, ($CDCl_3$) δ 146.9 (2C), 138.3 (2C), 133.7, 131.3, 130.9 (2C), 128.0 (2C), 126.6 (2C), 126.5 (2C), 123.1 (2C), 118.9 (2C), 81.2 and 44.0. HRMS (m/z) $[M+H-H_2O]^+$ calculated for $[C_{20}H_{14}Cl]^+$ 289.0779; found 289.0767.

9-(2-methoxybenzyl)-9H-fluoren-9-ol (2f). The title compound was prepared according to general procedure described above using 2-methoxyphenylacetic acid (166.1 mg, 1.0 mmol) and 9-fluorenone (90.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2f** (64 mg, 42%). White solid; m. p. 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 –7.48 (m, 2H), 7.31 – 7.13 (m, 7H), 6.87 – 6.74 (m, 3H), 3.80 – 3.72 (m, 1H), 3.69 (s, 3H), 3.28 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 149.0 (2C), 139.2 (2C), 133.0, 128.6 (2C), 128.3, 127.3 (2C), 125.3, 124.3 (2C), 120.5, 119.8 (2C), 110.5, 82.9, 55.4, 40.7. HRMS (m/z) $[M + H-H_2O]^+$ calculated for $[C_{21}H_{17}O]^+$ 285.1274; found 285.1277.

9-(2-chlorobenzyl)-9H-fluoren-9-ol (2g). The title compound was prepared according to general procedure described above using 2-chlorophenylacetic acid (171 mg, 1.0 mmol) and 9-fluorenone (90.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2g** (66 mg, 43%). White solid; m. p. 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.37 – 7.30 (m, 3H), 7.27 –7.25 (m, 1H), 7.24 – 7.21 (m, 4H), 7.17 – 7.13(m, 2H), 3.47 (s, 2H), 2.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2 (2C), 138.0 (2C), 134.4, 133.6, 131.6, 128.2, 128.0 (2C), 127.0, 126.6 (2C), 125.0, 123.1 (2C), 118.9 (2C), 81.17, 40.78. HRMS (m/z) $[M+H-H_2O]^+$ calculated for $[C_{20}H_{14}Cl]^+$ 289.0779; found 289.0810.

9-benzhydryl-9H-fluoren-9-ol (2h).[iv] The title compound was prepared according to general procedure described above using diphenyl acetic acid (212.2 mg, 1.0mmol) and 9-fluorenone (90.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2h** (101 mg, 58%). White solid; m. p. 183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.25 (dd, *J* = 13.8, 6.3 Hz, 2H), 7.22 – 7.14 (m, 6H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 7.5 Hz, 2H), 4.37 (s, 1H), 2.33 (s, 1H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 148.0 (2C), 140.7 (2C), 139.8 (2C), 130.2 (4C), 128.9 (2C), 127.9 (4C), 127.3 (2C), 126.7 (2C), 125.4 (2C), 119.8 (2C), 84.4, 60.3. HRMS (m/z) $[M+H-H_2O]^+$ calculated for $[C_{26}H_{19}]^+$ 331.1481; found 331.1474.

9-(1-phenylpropyl)-9H-fluoren-9-ol (2i). The title compound was prepared according to general procedure described above using 2-phenylbutyric acid (164.2 mg, 1.0 mmol) and 9-fluorenone (90.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2i** (67 mg, 45%). White solid; m. p. 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 1H), 7.51 – 7.47 (m, 1H), 7.41 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.24 – 7.13 (m, 3H), 7.10 – 7.04 (m, 3H), 6.87 (dt, *J* = 4.1, 3.2 Hz, 2H), 3.25 (dd, *J* = 12.1, 2.9 Hz, 1H), 2.22 (s, 1H), 1.93 – 1.54 (m, 2H), 0.65 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 149.5, 141.8, 141.2, 140.1, 131.4(2C), 130.4, 130.0, 129.0, 128.8(2C), 128.6, 128.0, 126.0, 125.7, 121.2, 121.1, 85.9, 58.2, 23.2, 13.9. HRMS (m/z) $[M+H-H_2O]^+$ calculated for $[C_{22}H_{19}]^+$ 283.1481; found 283.1464.

9-benzyl-2-fluoro-9H-fluoren-9-ol (2j). The title compound was prepared according to general procedure described above using phenyl acetic acid (136.1 mg, 1.0 mmol) and 2-fluoro-9-fluorenone (99.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (5% EtOAc/hexane) yields pure compound **2j** (69 mg, 48%). White solid; m. p. 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.35-7.29 (m, 2H), 7.27-7.24 (m, 1H), 7.19 – 7.11 (m, 3H), 7.03 – 6.93 (m, 4H), 3.27 (d, *J* = 13.9 Hz, 2H), 2.19 (d, *J* = 14.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6 (d, *J* = 245 Hz), 148.3 (d, *J* = 312 Hz), 137.5, 134.7, 134.1, 129.7 (2C), 128.1, 126.6 (2C), 126.2, 125.6, 123.2, 120.0, 119.9 (d, *J* = 8.7 Hz), 118.6, 114.7 (d, *J* = 22.5 Hz), 110.9 (d, *J* = 23.7 Hz), 81.1, 44.8. HRMS (m/z) $[M+H-H_2O]^+$ calculated for $[C_{20}H_{14}F]^+$ 273.1074; found 273.1084.

Methyl 9-benzyl-9-hydroxy-9H-fluorene-2-carboxylate (2k). The title compound was prepared according to general procedure described above using phenylacetic acid (136.1 mg, 1.0 mmol) and methyl 9-oxo-9-fluorene-2-carboxylate (119.0 mg, 0.5 mmol) in DMF, and purified by column chromatography (10% EtOAc/hexane) yields pure compound **2k** (61 mg, 37%). White solid; m. p. 147-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01– 7.94 (m, 1H), 7.48– 7.52 (m, 1H), 7.31–7.26 (m, 5H), 7.12–7.02 (m, 3H), 6.85 (dd, *J* = 7.9 Hz, 1.3 Hz, 5H), 3.88 – 3.83 (m, 3H), 3.62 (s, 1H), 3.38 – 3.23 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 149.1, 148.5, 143.9, 138.2, 135.8, 130.9, 130.6 (2C), 129.1, 128.7, 128.3, 127.6 (2C), 126.5, 125.4, 124.6, 120.8, 119.6, 82.2, 52.1, 45.8. HRMS (m/z) $[M+H-H_2O]^+$ calculated for $[C_{22}H_{17}O_2]^+$ 313.1223; found 313.1212.

***tert*-Butyl 2-(9-hydroxy-9H-fluoren-9-yl)pyrrolidine-1-carboxylate (2l).** The title compound was prepared according to general procedure described above using boc-l-proline (215.1mg, 1.0mmol) and 9-fluorenone (90.0mg, 0.5mmol) in MeCN, and purified by column chromatography (5% EtOAc /hexane) yields pure compound **2l** (84 mg, 48%). White solid, m. p. 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 –7.50 (m, 3H), 7.48-7.44 (m, 1H), 7.36 – 7.23 (m, 4H), 4.68 (dd, *J* = 8.1, 5.6 Hz, 1H), 3.26 (dtd, *J* = 13.3, 10.9, 6.9 Hz, 2H), 1.59 (s, 9H), 1.52 – 1.31 (m, 2H), 0.98 – 0.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 148.5, 146.9, 140.8, 139.9, 128.7 (2C), 128.1 (2C), 127.7 (2C), 125.0 (2C), 123.6, 119.7 (2C), 85.4, 81.3, 65.93, 48.7, 28.6 (2C), 23.8. HRMS (m/z) $[M+H]^+$ calculated for $[C_{22}H_{26}NO_3]^+$ 352.1907; found 352.1911.

1-(2-(9-hydroxy-9H-fluoren-9-yl) pyrrolidin-1-yl) ethan-1-one (2m). The title compound was prepared according to general procedure described above using N-acetyl-l-proline (157.0mg,1.0mmol) and 9-fluorenone (90.0mg, 0.5mmol) in MeCN, and purified by column chromatography (5% EtOAc /hexane) yields pure compound **2m** (73 mg, 50%). White solid; m. p. 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 31.5, 11.2 Hz, 3H), 7.37 – 7.18 (m, 5H), 4.95 – 4.80 (m, 1H), 3.50 – 3.06 (m, 2H), 2.26 (d, *J* = 18.3 Hz, 3H), 1.53 – 1.35 (m, 2H), 1.05 – 0.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 148.4, 146.8, 140.7, 139.8, 128.9, 128.8, 128.2, 127.8, 124.6, 123.5, 119.9, 119.8, 85.2, 66.5, 50.2, 28.3, 24.0, 23.1. HRMS (m/z) $[M+H]^+$ calculated for $[C_{19}H_{20}NO_2]^+$ 294.1489; found 294.1484.

***tert*-butyl (1-(9-hydroxy-9H-fluoren-9-yl) ethyl)carbamate (2n).** The title compound was prepared according to general procedure described above using boc-l-alanine (189.0 mg, 1.0 mmol) and 9-fluorenone (90.0 mg, 0.5 mmol) in MeCN, and purified by column chromatography (5% EtOAc /hexane) yields pure compound **2n** (54 mg, 33%). Semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 4H), 7.39 – 7.23 (m, 4H), 4.69 (s, 1H), 4.37 (s, 1H), 1.45 (s, 9H), 0.71 (s, 3H); ^{13}C NMR (125 MHz, ($CDCl_3$) δ 156.9, 147.1, 145.4, 140.0, 139.5, 134.1, 128.6, 128.6, 127.5, 127.1, 124.0, 123.8, 123.1, 119.8, 119.4, 84.7, 79.7, 53.4, 27.9 and 15.8. HRMS (m/z) $[M+H]^+$ calculated for $[C_{20}H_{24}NO_3]^+$ 326.1751; found 326.1759.

***tert*-Butyl 2-(2-fluoro-9-hydroxy-9H-fluoren-9-yl)pyrrolidine-1-carboxylate (2o).** The title compound was prepared according to general procedure described above using L-boc-proline (215.1 mg, 1.0 mmol) and 2-fluoro-9-fluorenone (99.0 mg, 0.5 mmol) in MeCN, and purified by column chromatography (5% EtOAc /hexane) yields pure compound **2o** (74 mg, 40%). Yellowish white solid; m. p. 153-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.35 – 7.21 (m, 2H), 7.16 – 6.96 (m, 2H), 4.72 – 4.56 (m, 1H), 3.60 – 3.41 (m, 1H), 3.10-2.98 (m, 1H), 1.64 – 1.37 (m, 11H), 1.07 – 0.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 160.2 (d, *J* = 277 Hz), 149.04, 148.4, 139.1, 136.8, 128.8, 127.7, 127.4 (d, *J* = 27 Hz), 125.0, 123.6, 120.6 (d, *J* = 8 Hz), 119.4, 115.6 (d, *J* = 20 Hz), 112.7 (d, *J* = 20 Hz), 85.0, 81.6, 65.8, 48.7, 28.5(2C), 23.8. HRMS (m/z) $[M+H]^+$ calculated for $[C_{22}H_{25}FNO_3]^+$ 370.1813; found 370.1816.

***tert*-Butyl2-(9-hydroxy-2-(methoxycarbonyl)-9H-fluoren-9-yl)pyrrolidine-1-carboxylate (2p).** The title compound was prepared according to general procedure described above using l-boc-proline (215.1 mg, 1.0 mmol) and methyl 9-oxo-9-fluorene-2-carboxylate (120 mg, 0.5 mmol) in MeCN, and purified by column chromatography (10% EtOAc /hexane) yields mixture of distereomers **2p** (66 mg, 32%) in ratio (1:1) confirmed from ^{13}C spectra. Yellow solid; m.p. 148-149°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 1H), 7.65 – 7.36 (m, 4H), 7.33 – 7.22 (m, 2H), 4.72 – 4.55 (m, 1H), 3.87 (d, *J* = 11.0 Hz, 3H), 3.44 (d, *J* = 6.2 Hz, 1H), 3.03 – 2.89 (m, 1H), 1.95 – 1.71 (m, 2H), 1.63 – 1.48 (m, 9H), 0.92 – 0.81 (m, 1H), 0.73 – 0.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 158.8, 149.0, 147.5, 145.0, 139.2, 130.7, 129.6, 129.3, 128.9, 126.3, 125.3, 124.8, 123.8, 120.6, 119.5, 85.1, 81.6, 65.8, 52.1, 48.6, 28.8, 28.6, 23.8. HRMS (m/z) $[M+H]^+$ calculated. For $[C_{24}H_{28}NO_5]^+$ 410.1962; found 410.1951.

General procedure for reaction with cyclopropyl amine. To a solution of 9-fluorenone (1.0 mmol) in 2 ml MeCN was added cyclic amine (2.0 mmol). The stirred reaction mixture was irradiated under 27W CFL for 10- 48 h at room temperature. The reaction was monitored by TLC. After completion, the solvent was evaporated and the crude reaction mixture was subjected to silica gel column chromatography using hexane/ethyl acetate to give pure product.

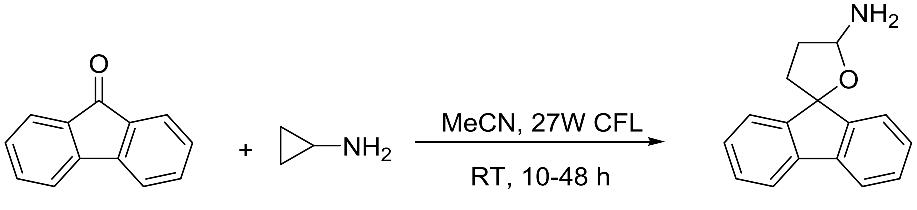
4',5'-Dihydro-3'H-spiro[fluorene-9,2'-furan]-5'-amine (3a). The title compound was prepared according to the general procedure described above using 9-fluorenone (180 mg, 1.0 mmol) and cyclopropyl amine (142.75 µl, 2.0 mmol) and purified by column chromatography as whitish yellow solid (114 mg, 48%). Yellow solid; m. p. 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 6.6, 1.3 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.41 – 7.26 (m, 4H), 5.92 (d, *J* = 4.6 Hz, 1H), 2.76 – 2.65 (m, 1H), 2.49 (tdd, *J* = 13.0, 8.6, 4.7 Hz, 1H), 2.39 – 2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 148.7, 139.7, 139.1, 128.9, 128.8, 128.2, 128.0, 124.7, 123.1, 119.9, 119.7, 99.7, 91.3, 35.4, 35.0; GC-MS (EI) m/z (%) 238 (17), 220 (33.7), 189 (41), 181 (100), 165 (46.5). HRMS (m/z) $[M+H]^+$ calculated. For $[C_{16}H_{16}NO]^+$ 238.1226; found 238.1223.

2-fluoro-4', 5'-dihydro-3'H-spiro[fluorene-9,2'-furan]-5'-amine (3b). The title compound was prepared according to the general procedure described above using 2-fluoro-9-fluorenone (198 mg, 1.0 mmol) andcyclopropyl amine (142.75 µl, 2.0 mmol) and purified by column chromatography (133 mg, 52%). White solid; m. p. 126-127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.40 (m, 3H), 7.39 – 7.22 (m, 3H), 7.05 (ddt, *J* = 7.0, 6.3, 3.5 Hz, 1H), 5.89 (s, 1H), 2.73 – 2.61 (m, 1H), 2.51 – 2.38 (m, 1H), 2.36 – 2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, *J*=246.3), 151.3, 148.7 (d, *J* = 12.6 Hz), 136.9 (d, *J* = 381.8 Hz), 128.4 (d, *J*= 156.8 Hz), 124.7, 123.1, 120.8 (d, *J* = 23.9 Hz), 119.5 (d, *J* = 21.4 Hz), 115.7(d, *J* = 23.3 Hz), 112.4 (d, *J* = 23.9 Hz), 110.8 (d, *J* = 23.9 Hz), 99.8, 90.9, 35.5(d, *J* = 7.6 Hz), 34.8; HRMS (m/z) $[M+H]^+$ calculated for $C_{16}H_{15}FNO$: 256.1132, found 256.1123.

Methyl 5'-amino-4', 5'-dihydro-3'H-spiro[fluorene-9,2'-furan]-2-carboxylate (3c). The title compound was prepared according to the general procedure described above using methyl 9-oxo-9-fluorene-2-carboxylate (295 mg, 1.0 mmol) and cyclopropyl amine (142.75 µl, 2.0 mmol) and purified by column chromatography (89 mg, 30%).Yellowish white solid; m. p. 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.01 (m, 2H), 7.77 – 7.29 (m, 5H), 6.02 – 5.89 (m, 1H), 4.00 – 3.86 (m, 3H), 2.80 – 2.65 (m, 1H), 2.62 – 2.46 (m, 1H), 2.43 – 2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 149.4, 143.9, 138.5, 130.9, 129.3, 129.1, 125.9, 124.7, 123.3, 120.6, 119.5, 99.9, 90.9, 52.1, 35.2, 34.9. HRMS (m/z) $[M+H]^+$ calculated. For $[C_{18}H_{18}NO_3]^+$ 296.1281; found 296.1282.

Optimization studies

Table S1: Optimization of reaction conditions for ring expansion reactions.



S.No	Light source	Solvent	Yield (%)
1	27W CFL	MeCN	48
2	27W CFL	DMF	44
3	27W CFL	DMSO	37
4	Blue LED	MeCN	46
5	-	MeCN	Traces

NMR Spectra's

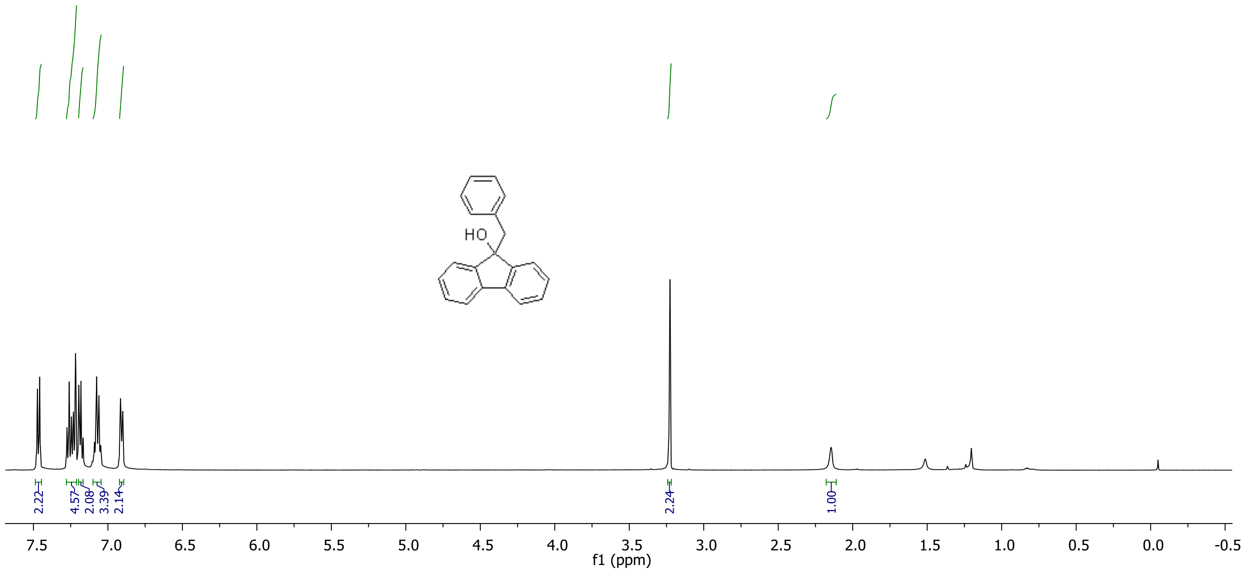


Figure S1. ^{1}H NMR spectrum of **2a**

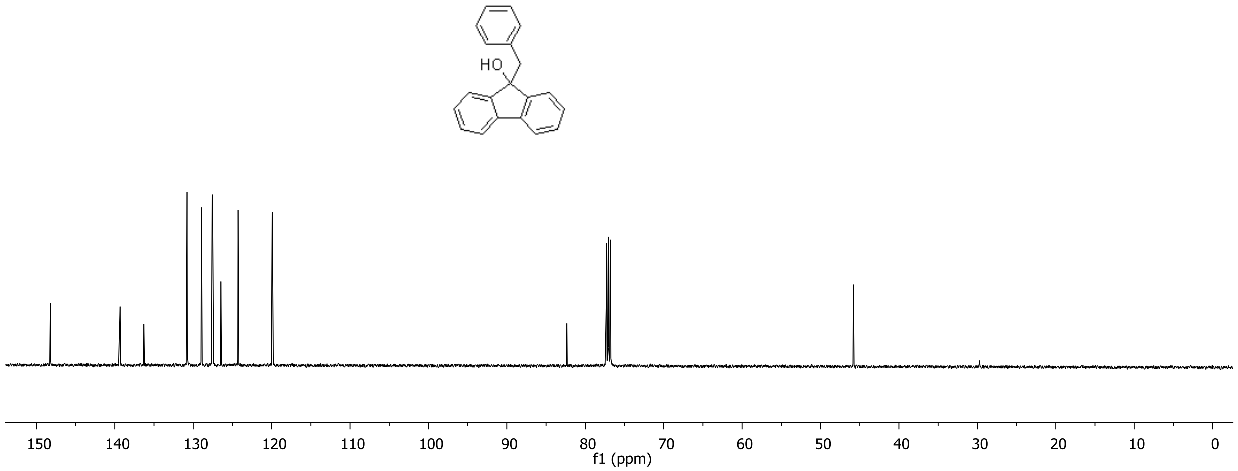


Figure S2. ^{13}C NMR spectrum of **2a**

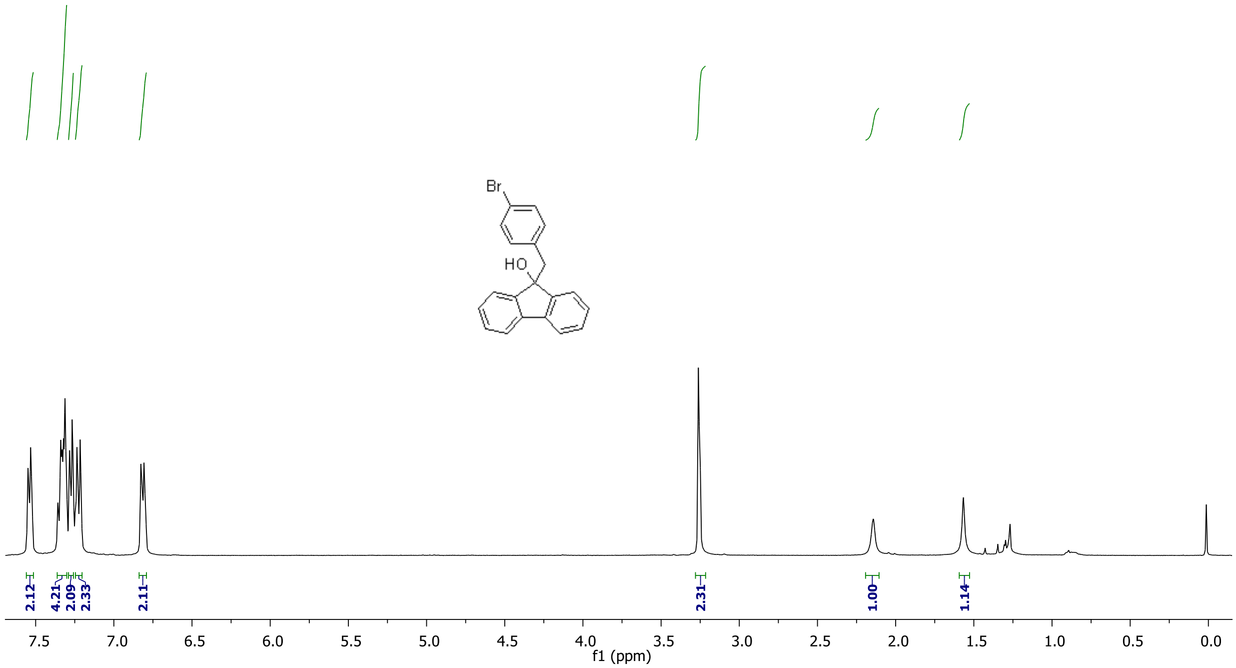


Figure S3. ^{1}H NMR spectrum of **2b**

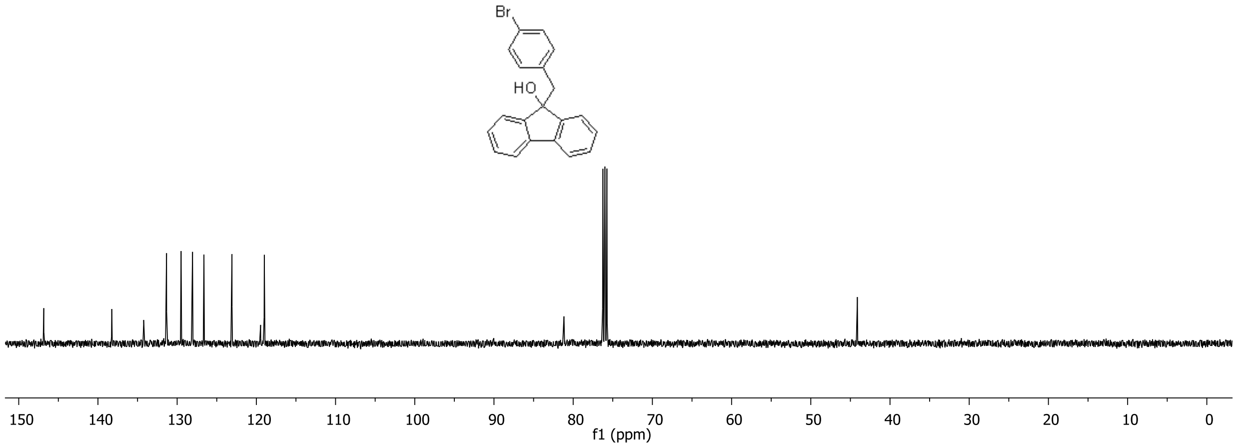


Figure S4. ^{13}C NMR spectrum of **2b**

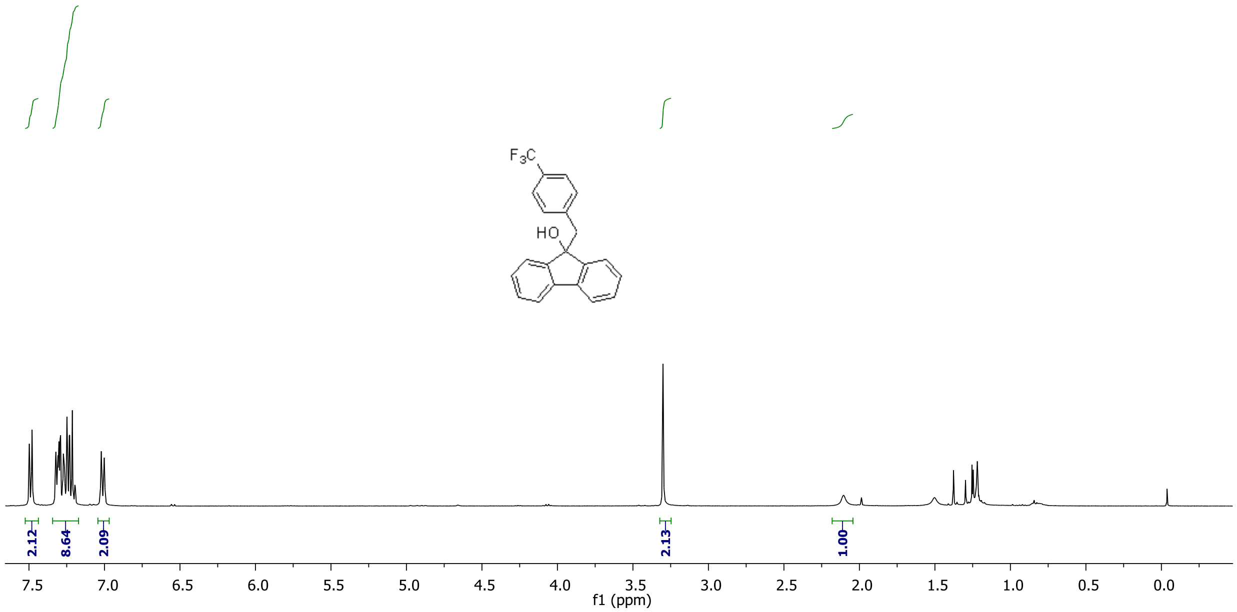


Figure S5. ^{1}H NMR spectrum of **2c**

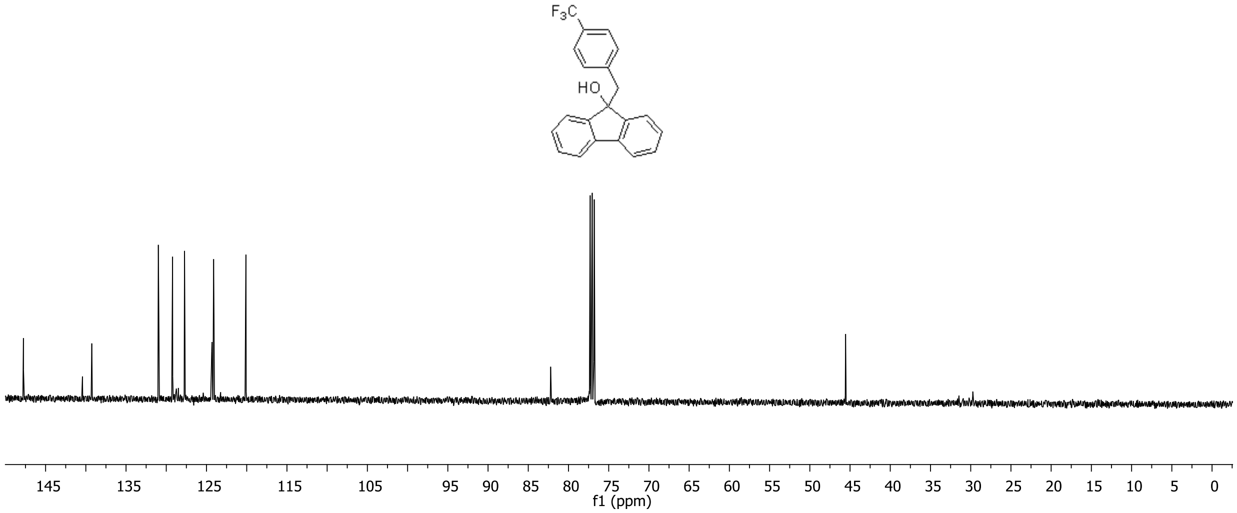


Figure S6. ^{13}C NMR spectrum of **2c**

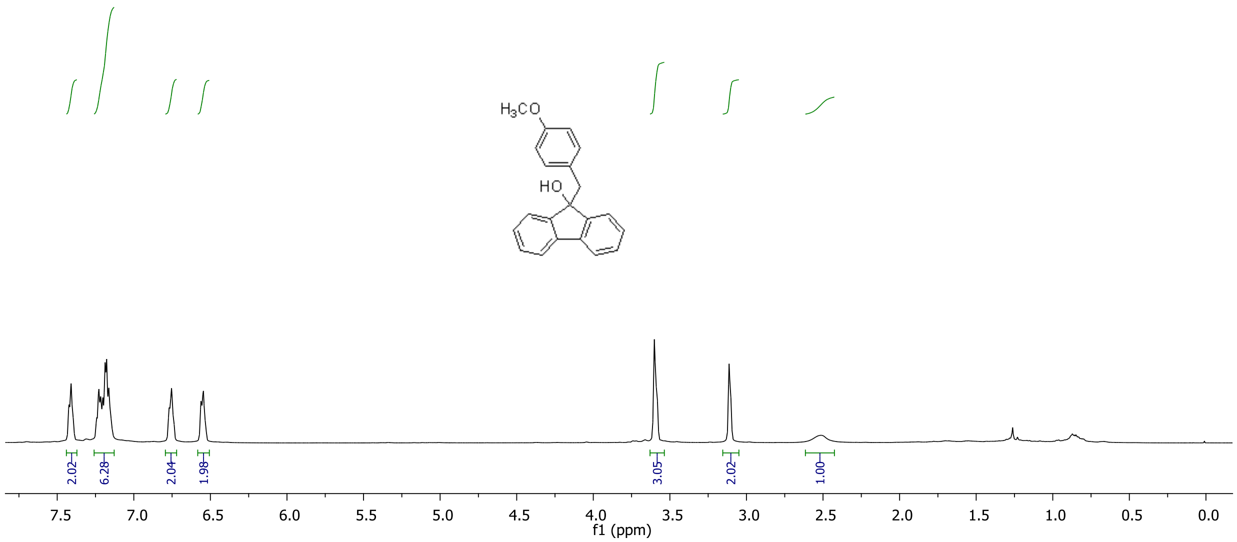


Figure S7. ^{1}H NMR spectrum of **2d**

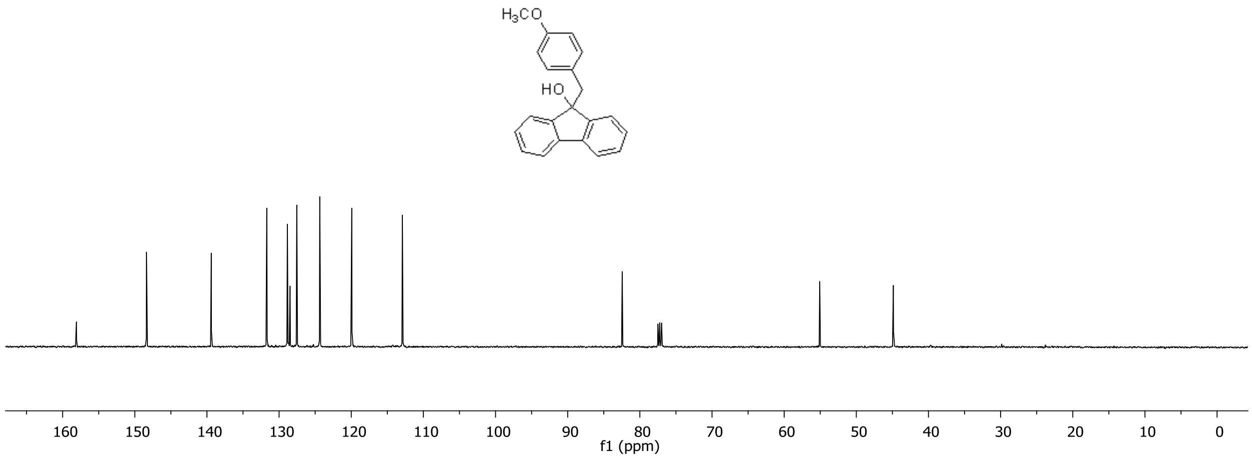


Figure S8. ^{13}C NMR spectrum of **2d**

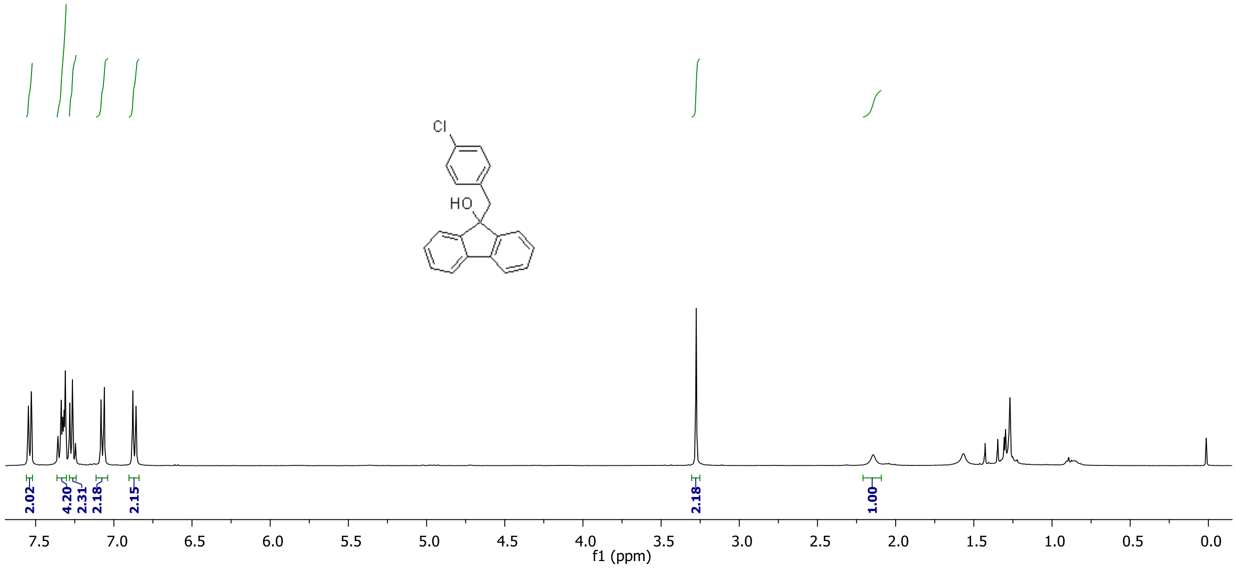


Figure S9. ^{1}H NMR spectrum of **2e**

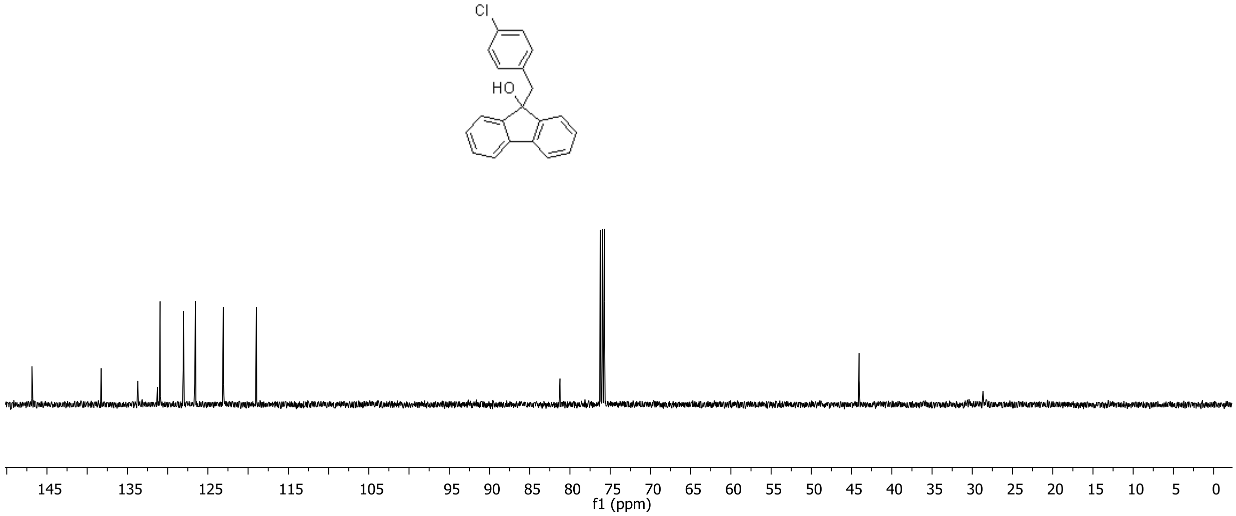


Figure S10. ^{13}C NMR spectrum of **2e**

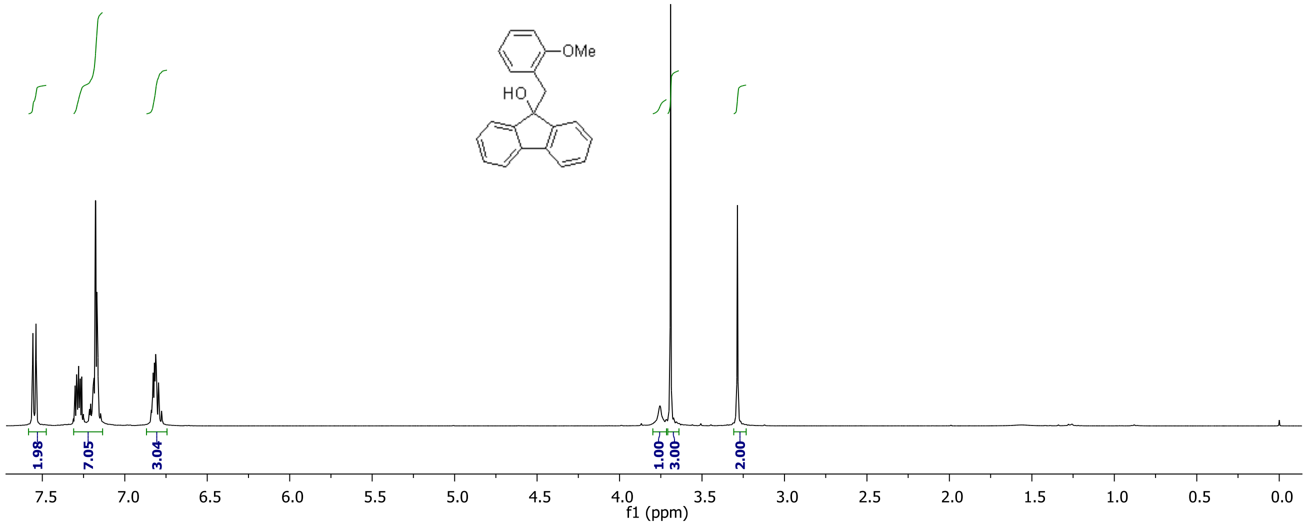


Figure S11. ^{1}H NMR spectrum of **2f**

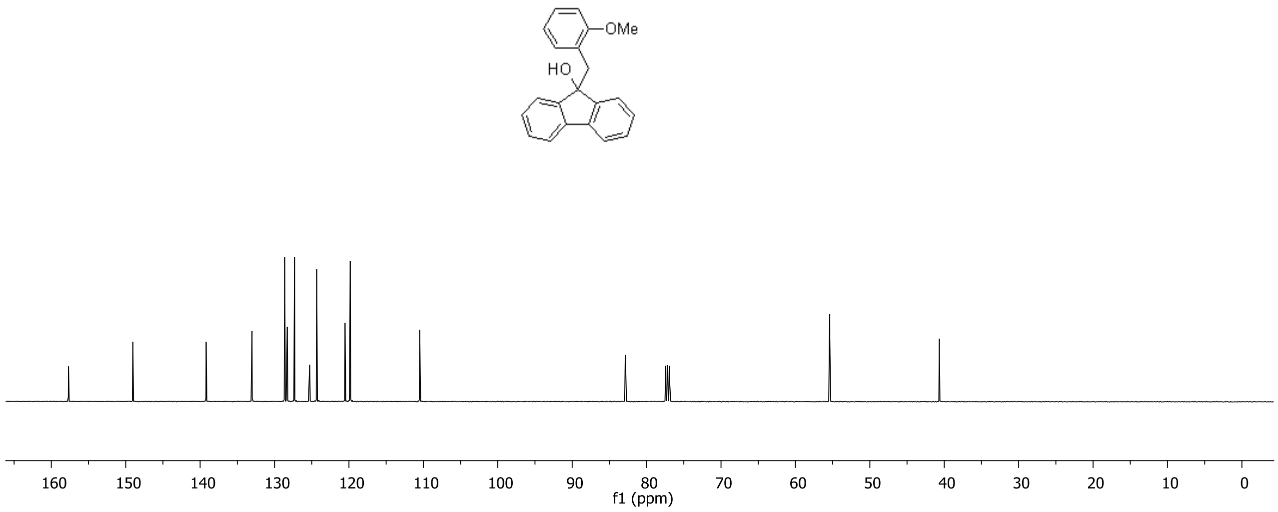


Figure S12. ^{13}C NMR spectrum of **2f**

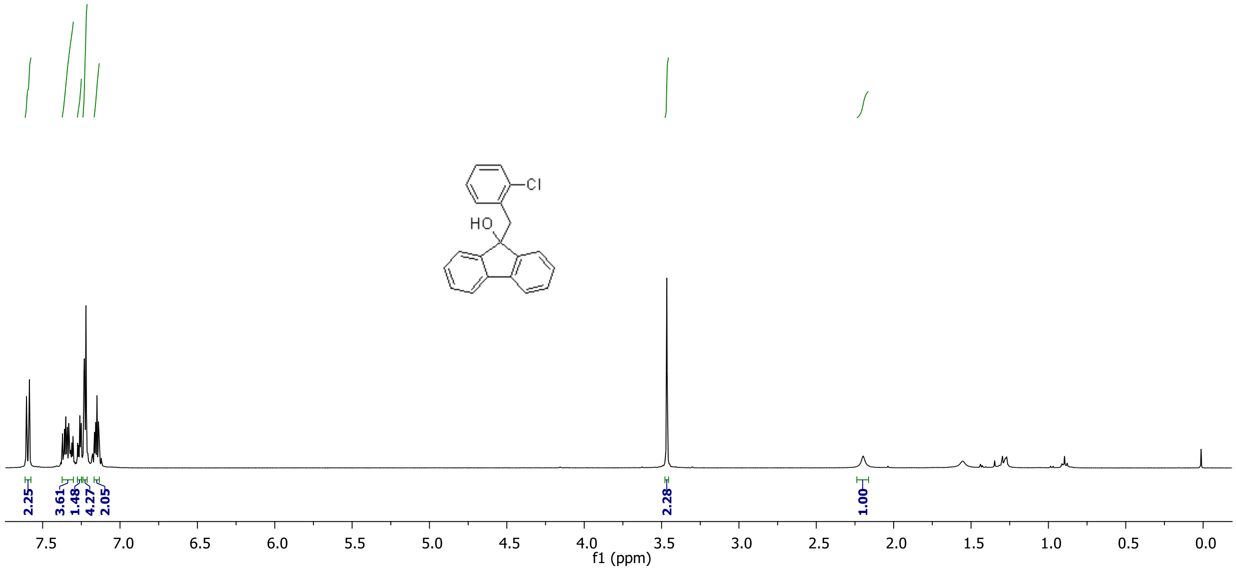


Figure S13. ^{1}H NMR spectrum of **2g**

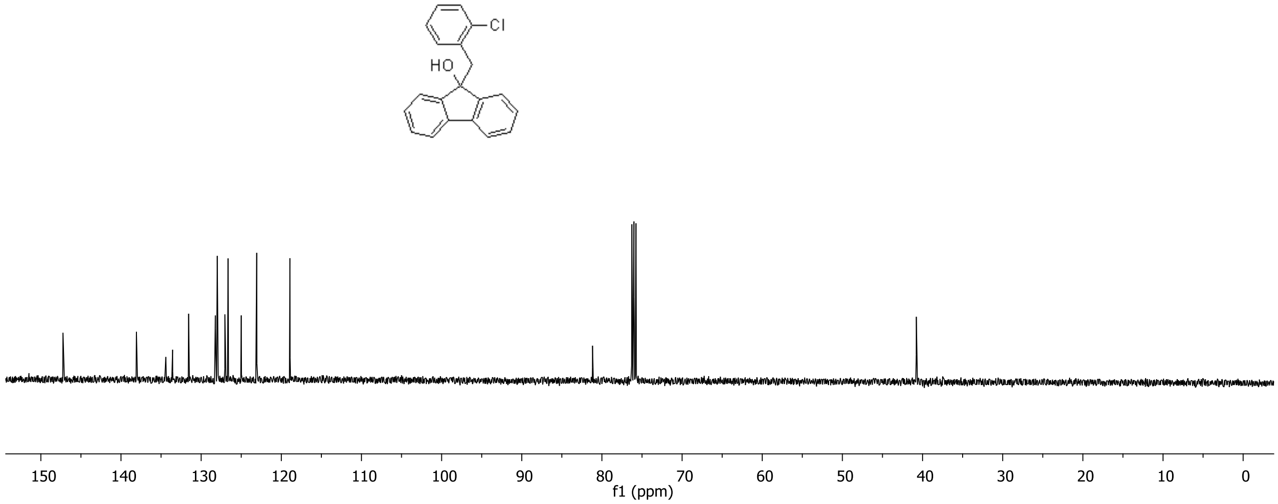


Figure S14. ^{13}C NMR spectrum of **2g**

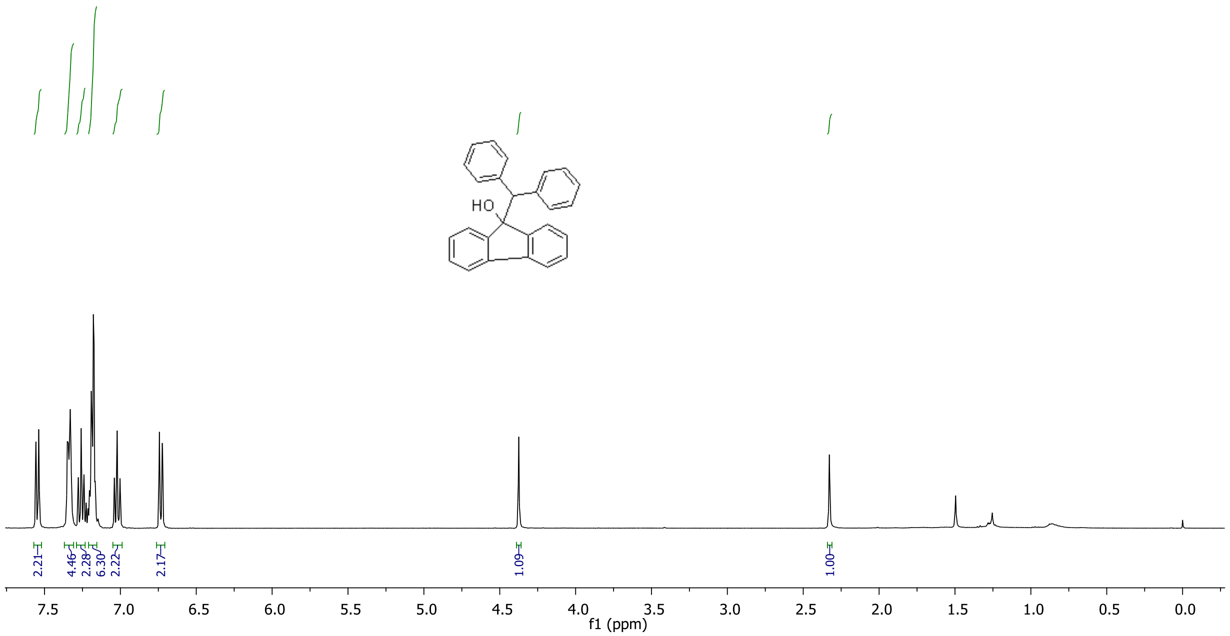


Figure S15. ^{1}H NMR spectrum of **2h**

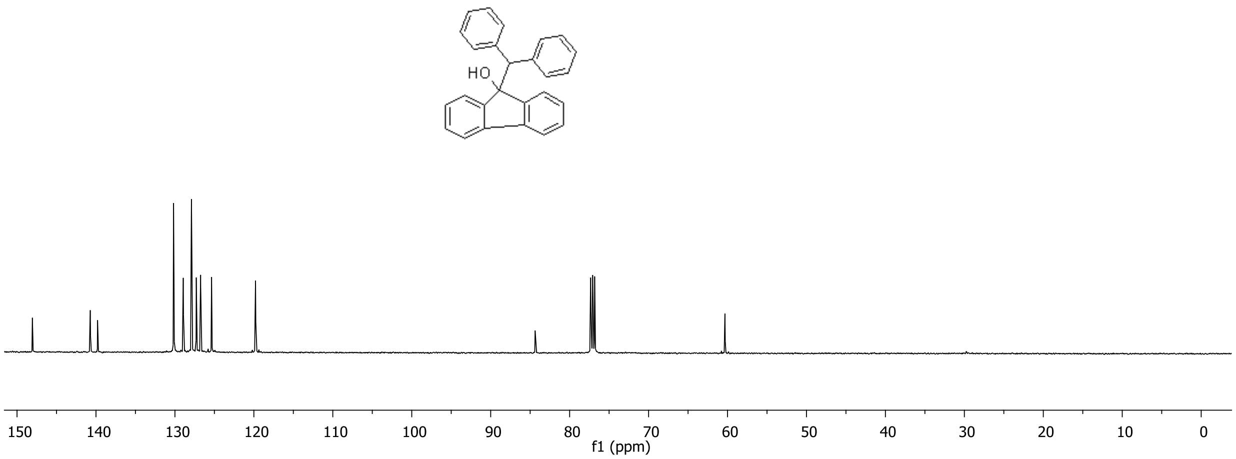


Figure S16. ^{13}C NMR spectrum of **2h**

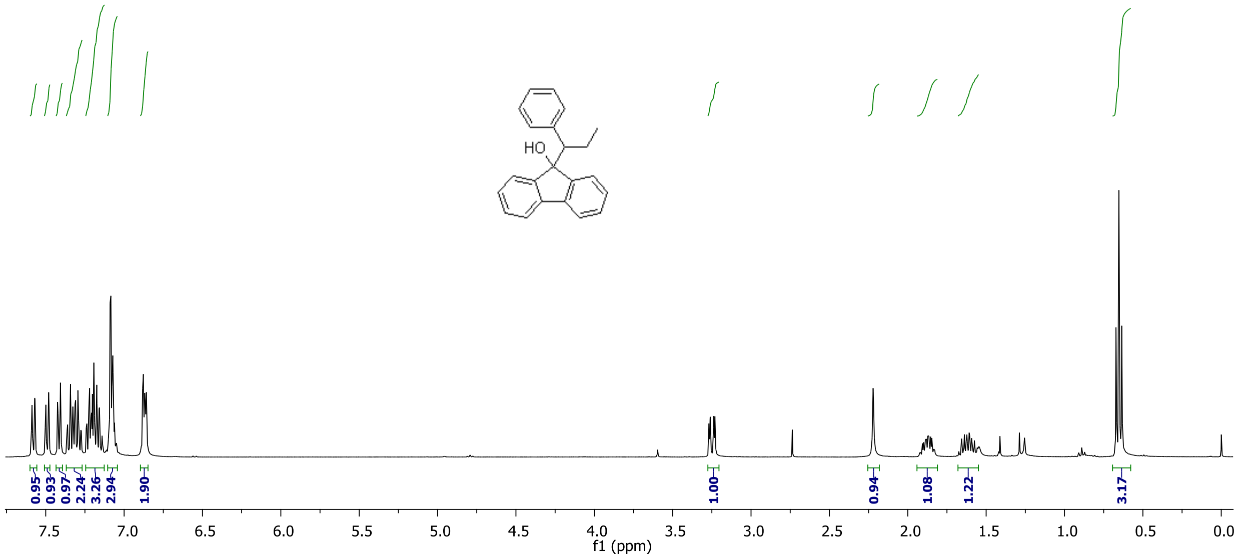


Figure S17. ^{1}H NMR spectrum of **2i**

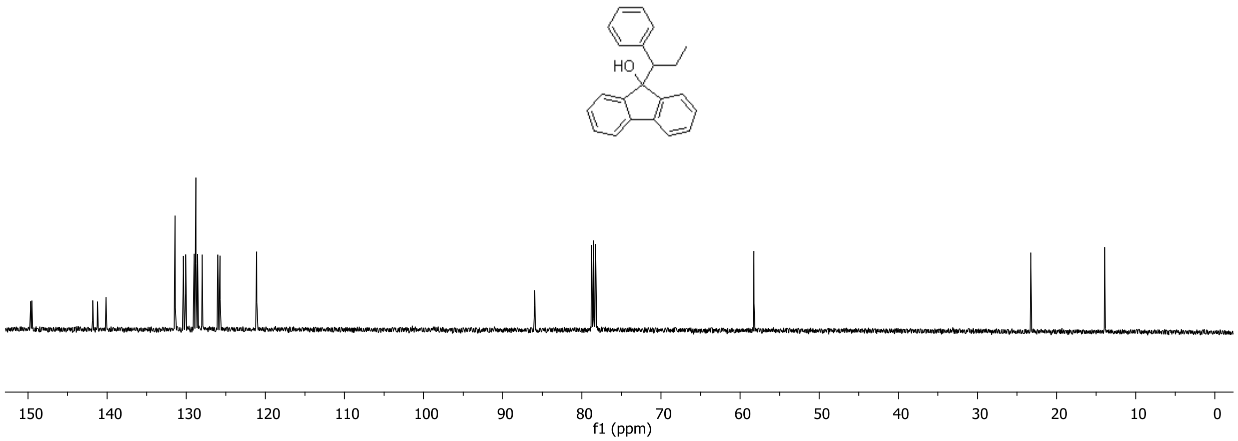


Figure S18. ^{13}C NMR spectrum of **2i**

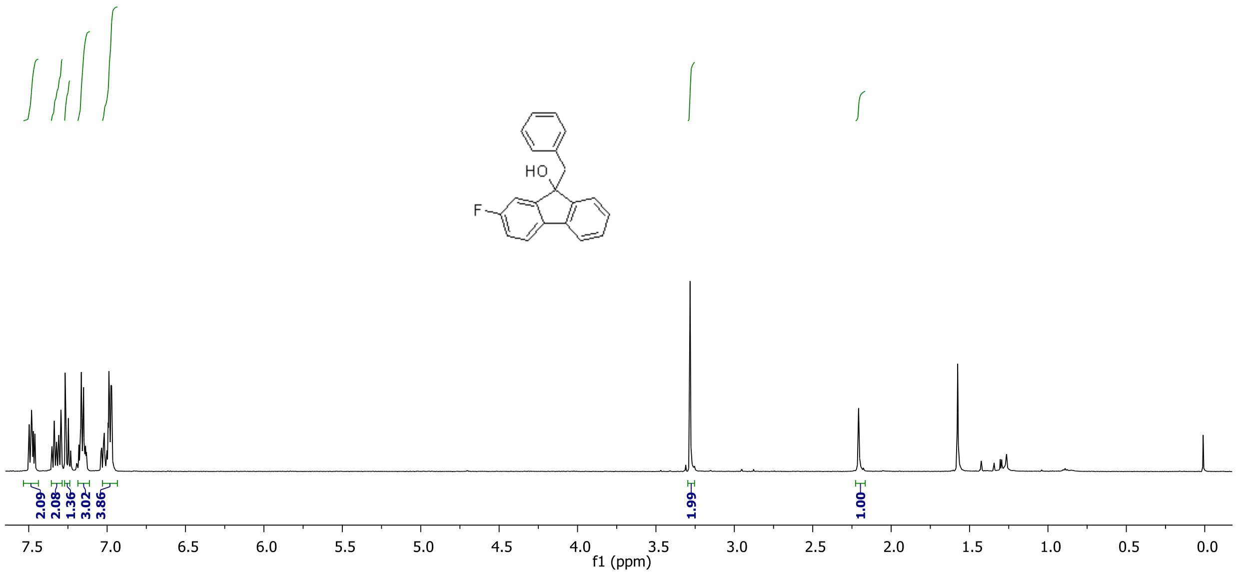


Figure S19. ^{1}H NMR spectrum of **2j**

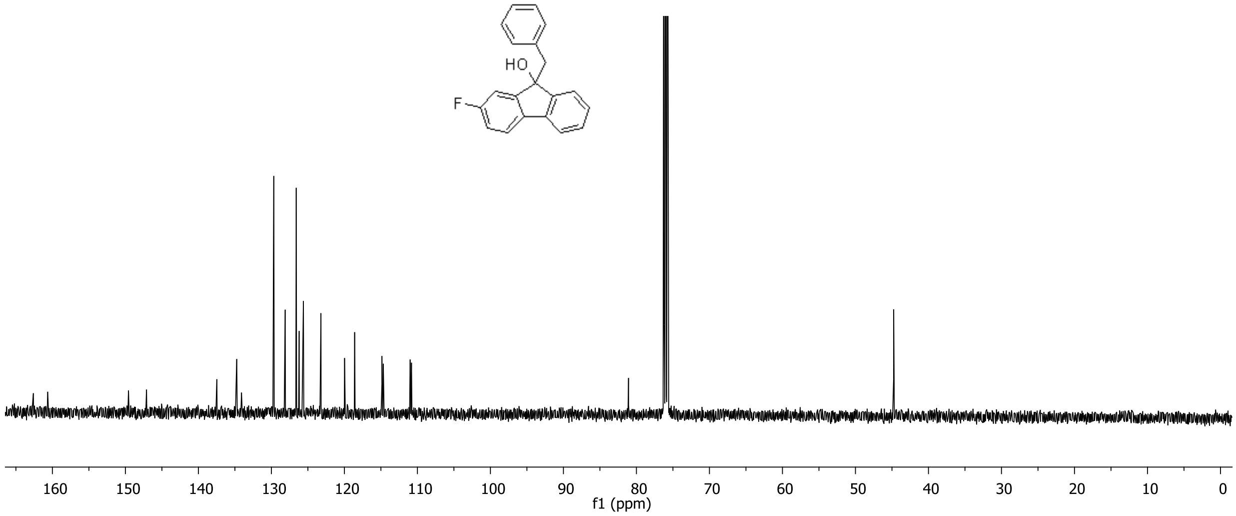


Figure S20. ^{13}C NMR spectrum of **2j**

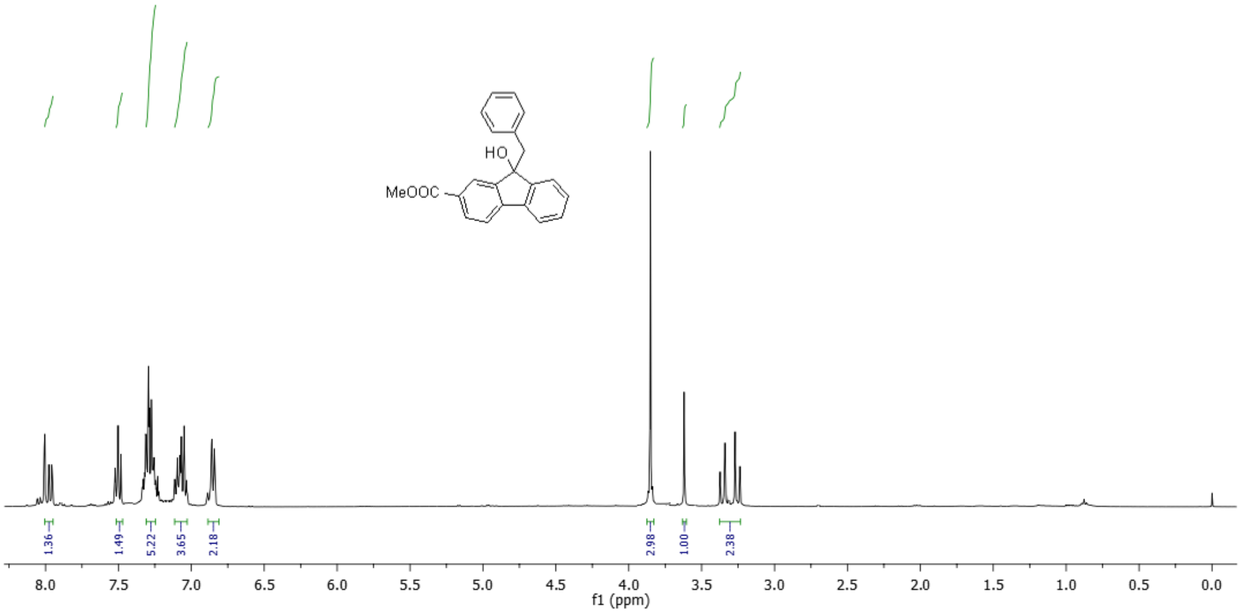


Figure S21. ^{1}H NMR spectrum of **2k**

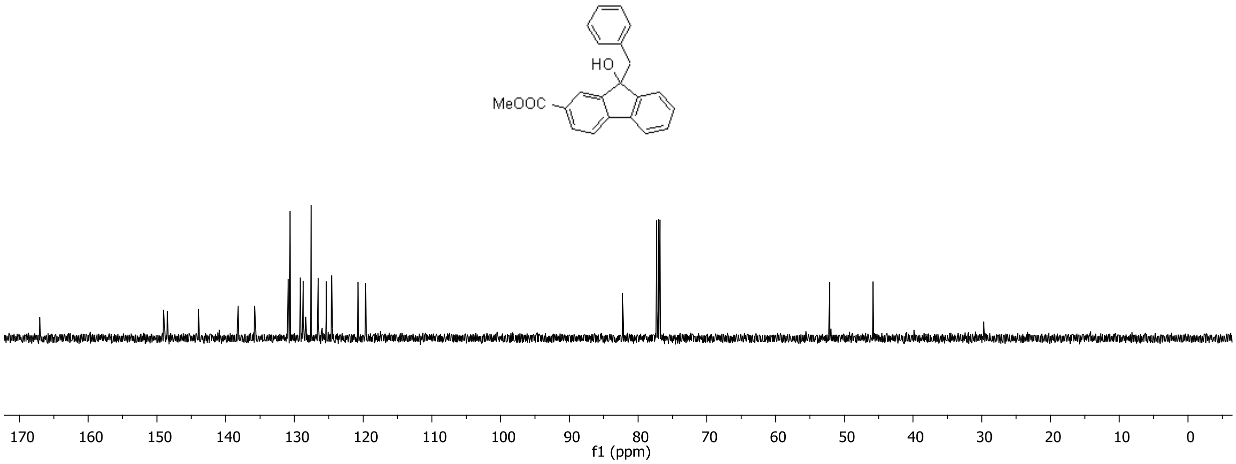


Figure S22. ^{13}C NMR spectrum of **2k**

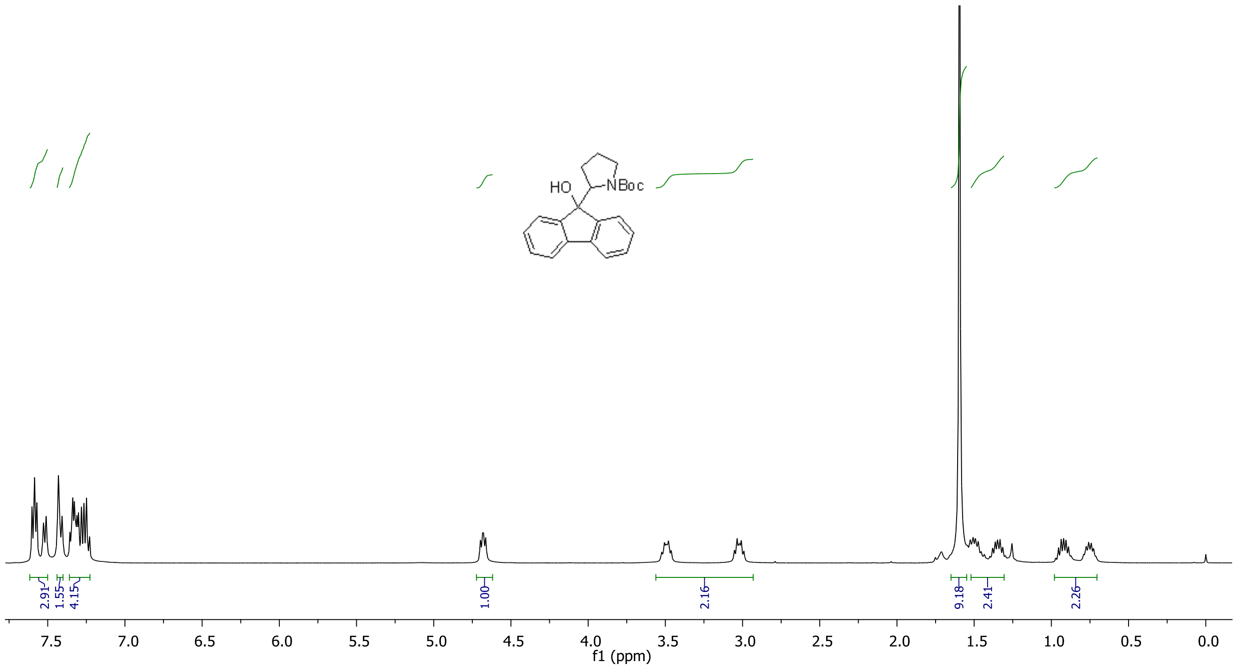


Figure S23. ^{1}H NMR spectrum of **2l**

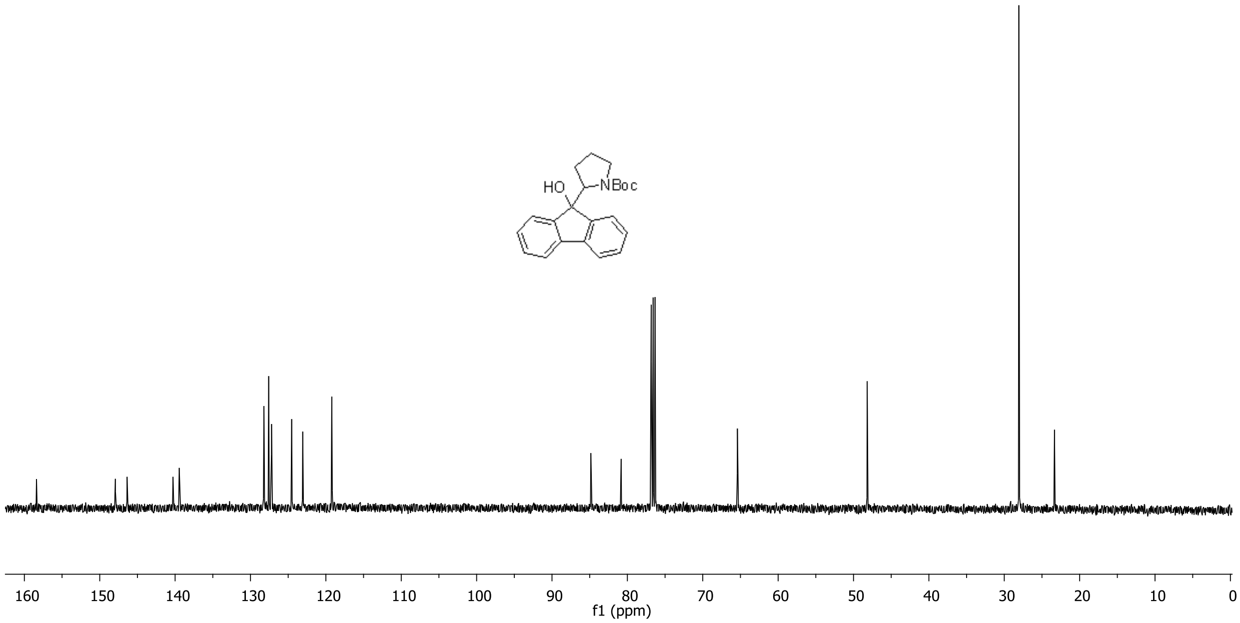


Figure S24. ^{13}C NMR spectrum of **2l**

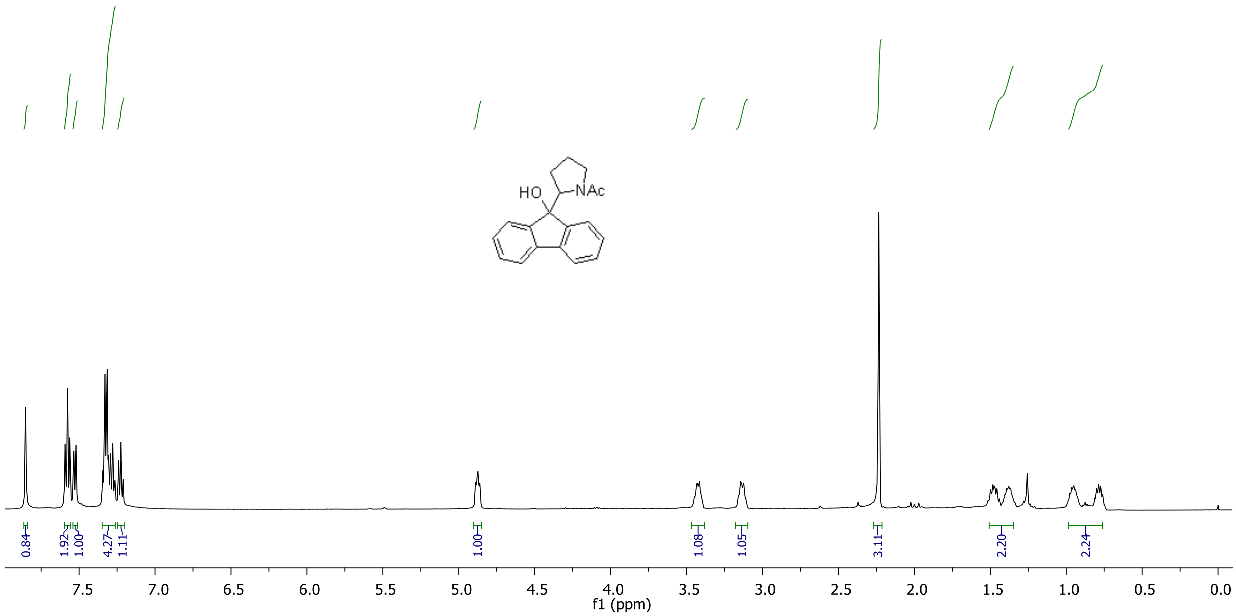


Figure S25. ^{1}H NMR spectrum of **2m**

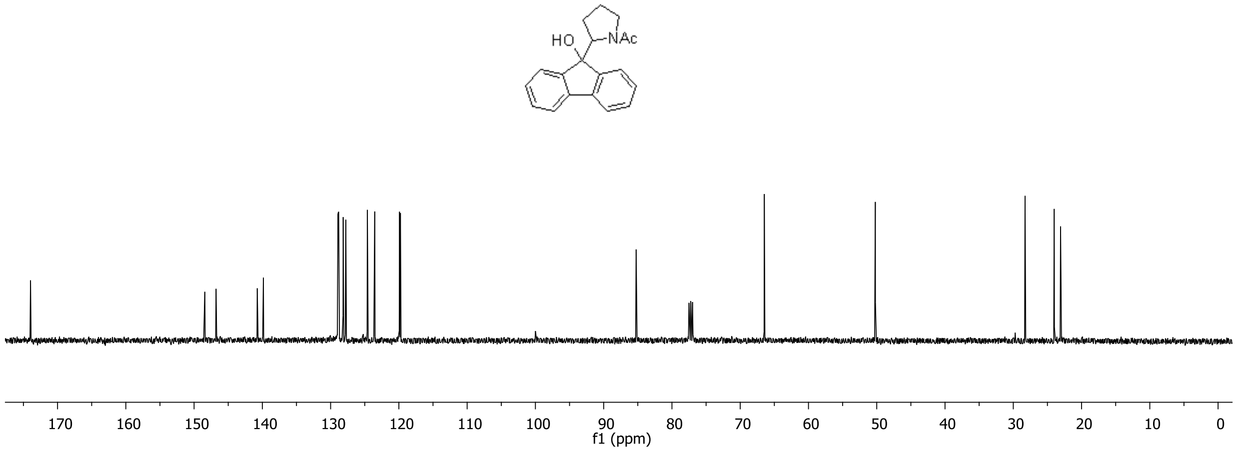


Figure S26. ^{13}C NMR spectrum of **2m**

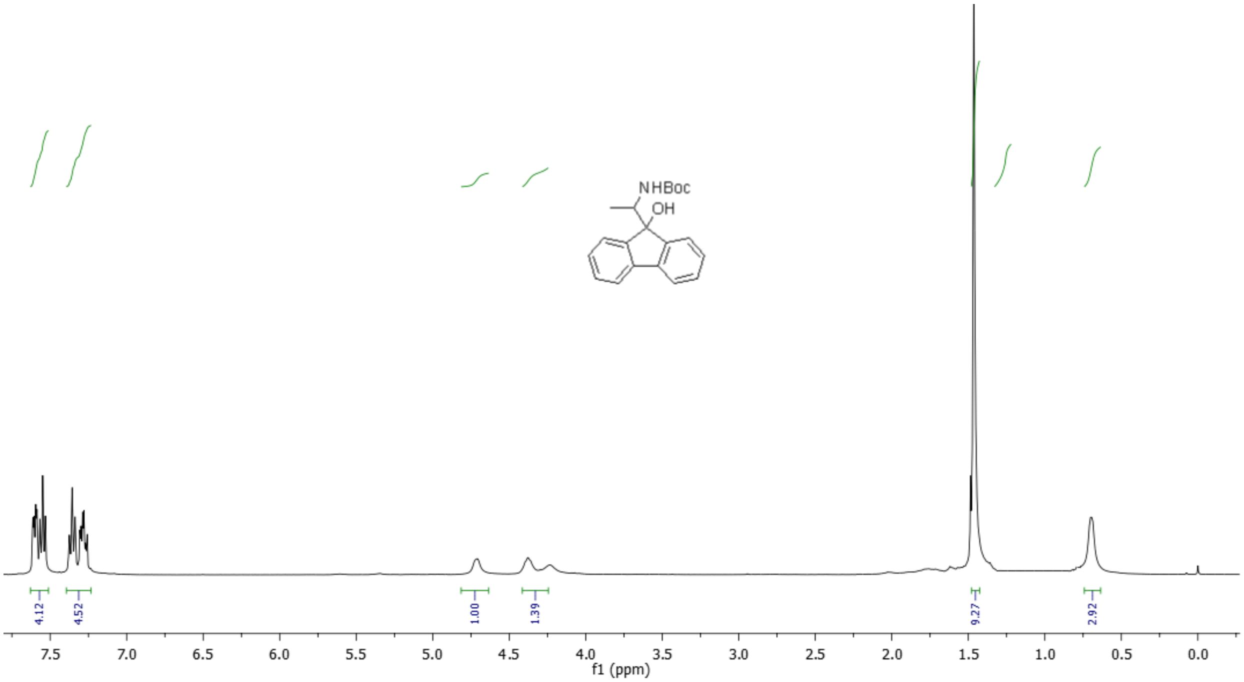


Figure S27. ^{1}H NMR spectrum of **2n**

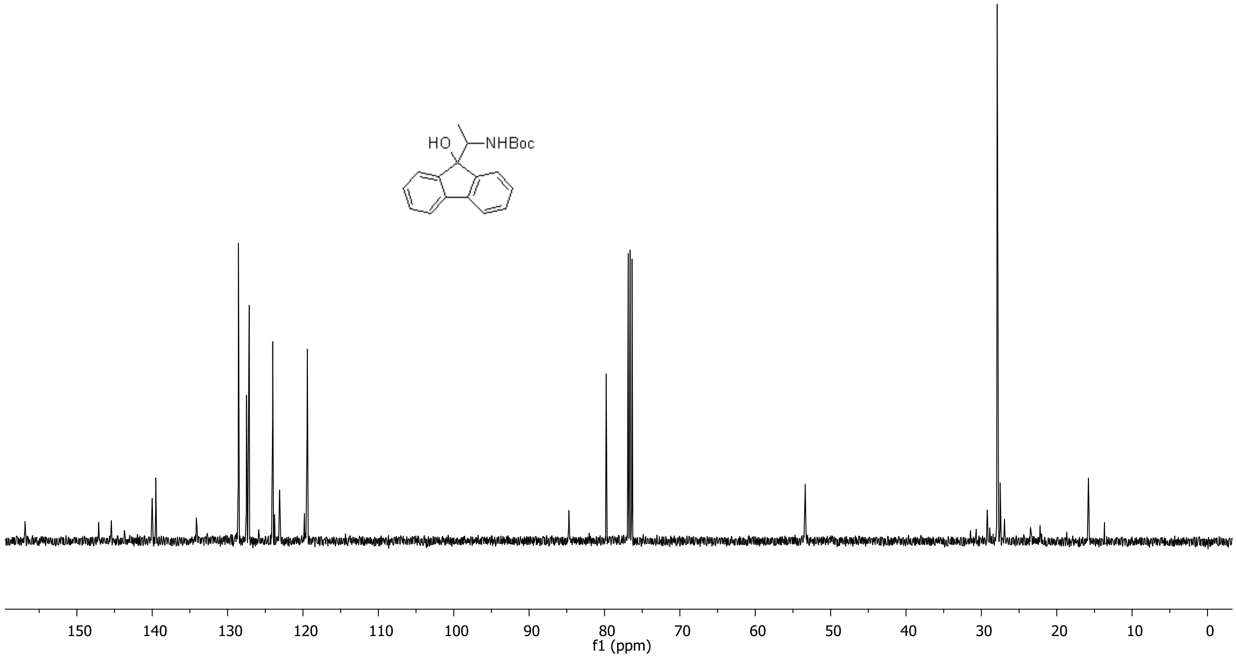


Figure S28. ^{13}C NMR spectrum of **2n**

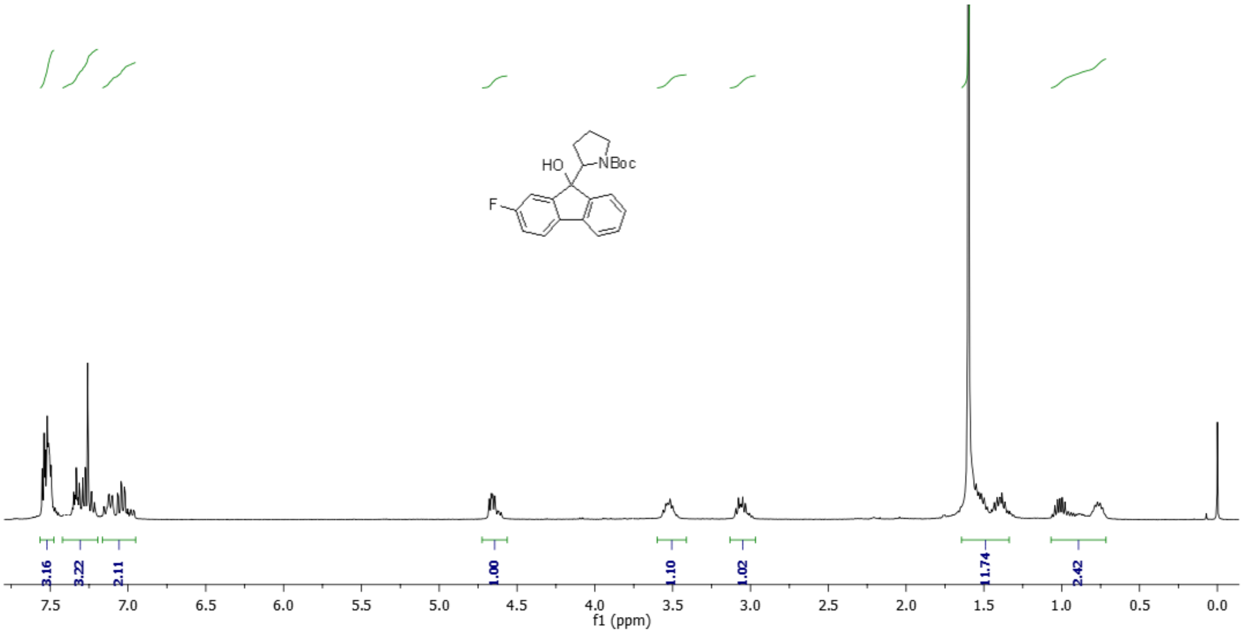


Figure S29. ^{1}H NMR spectrum of **2o**

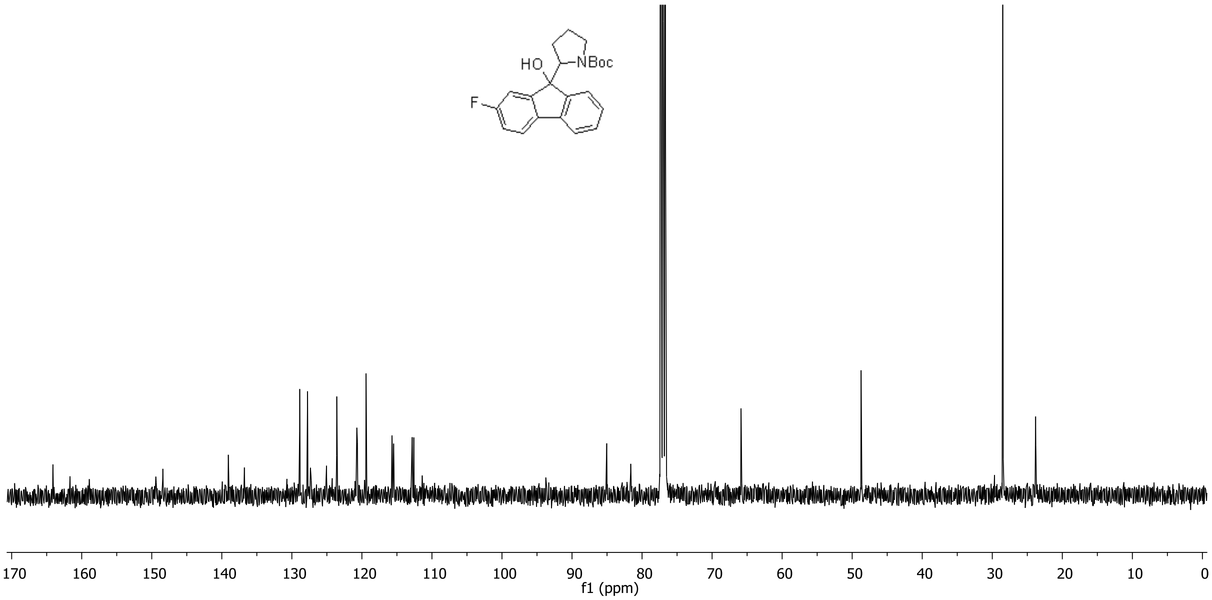


Figure S30. ^{13}C NMR spectrum of **2o**

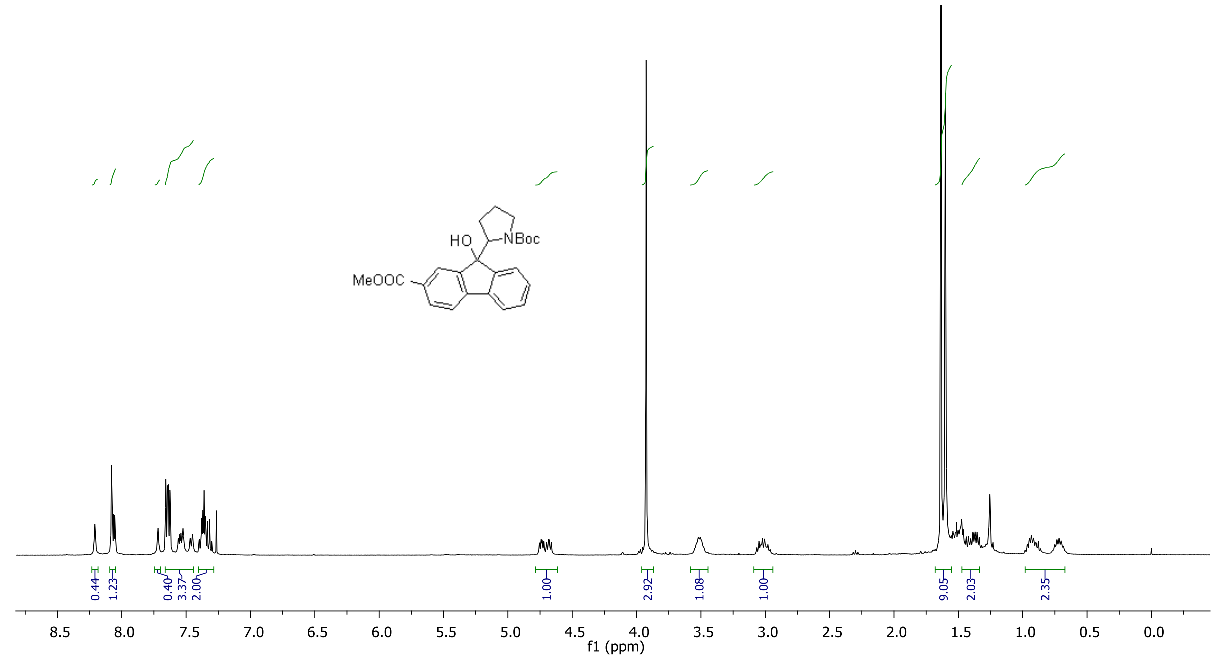


Figure S31. ^{1}H NMR spectrum of **2p**

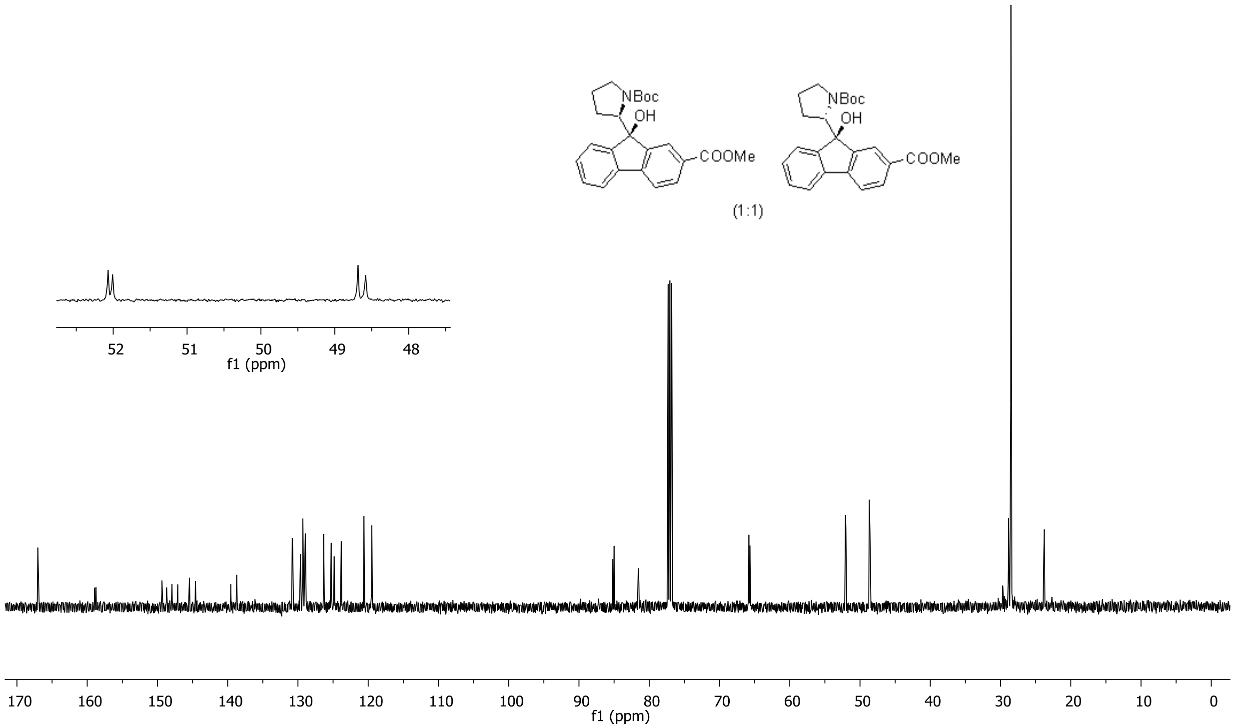


Figure S32. ^{13}C NMR spectrum of **2p**

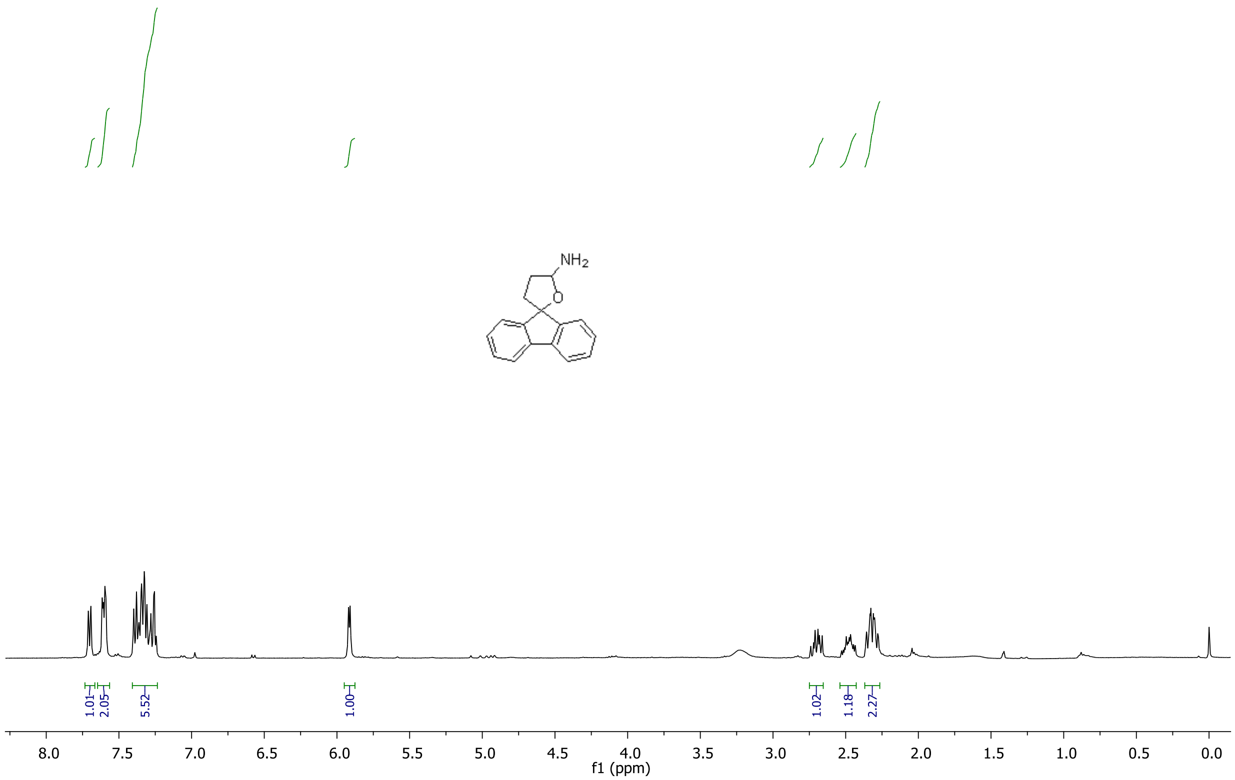


Fig. S33. ^{1}H NMR spectrum of **3a**

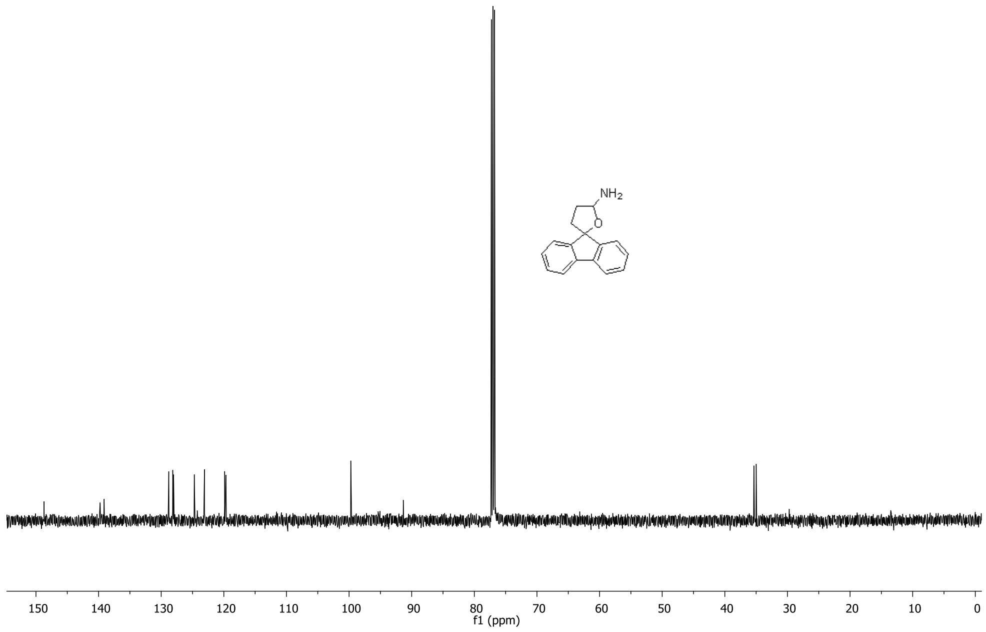


Fig. S34. ^{13}C NMR spectrum of **3a**

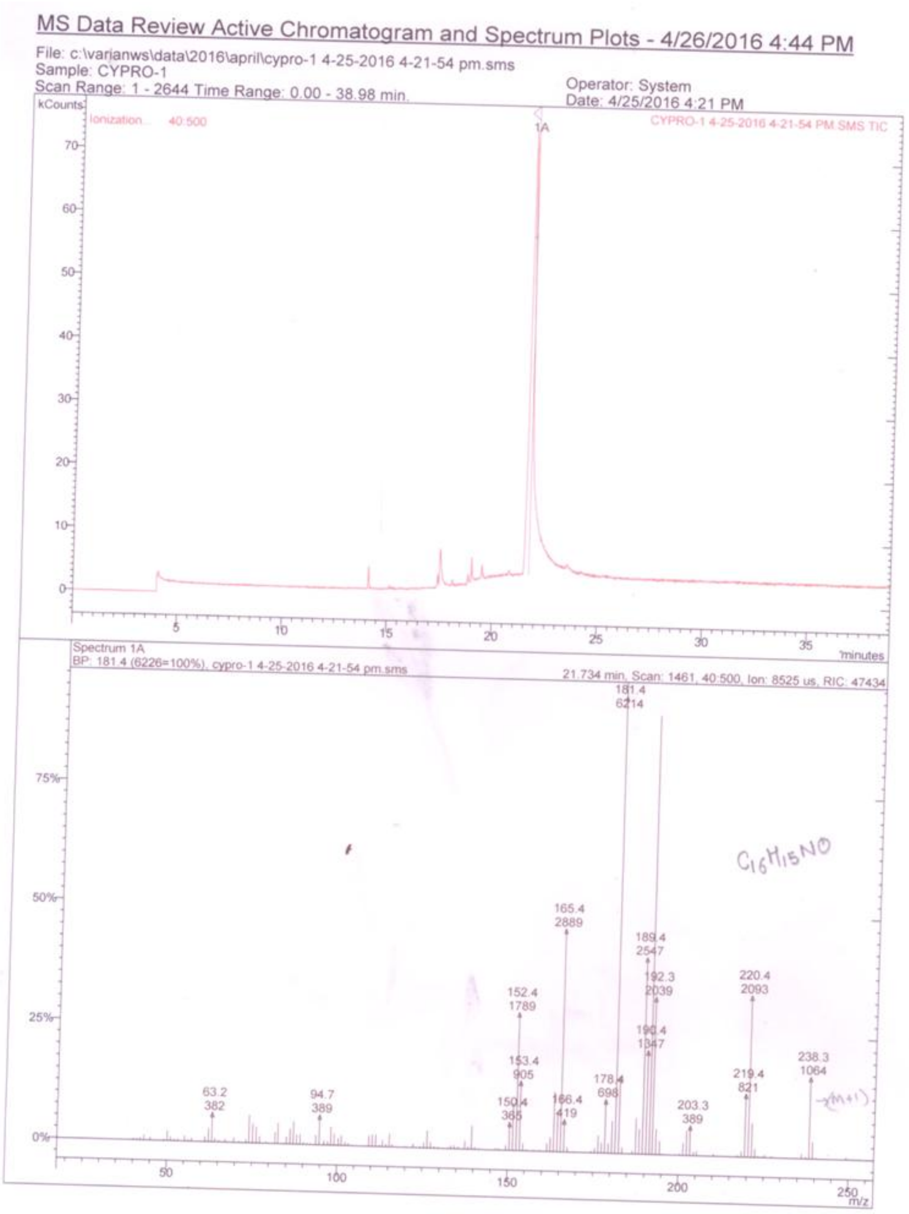


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Fig S35 GC-MS spectra of **3a**

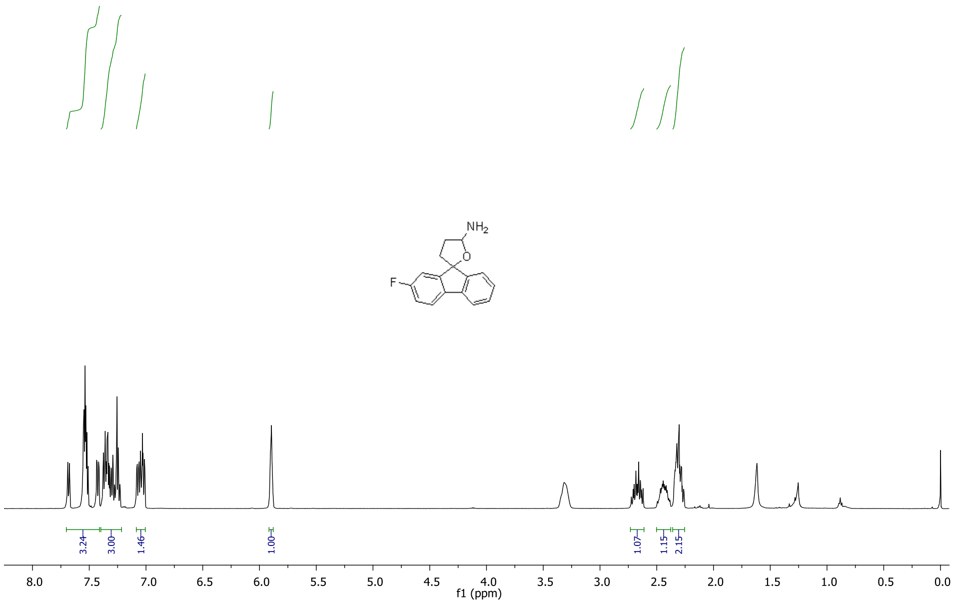

Fig. S36. ^{1}H NMR spectrum of **3b**

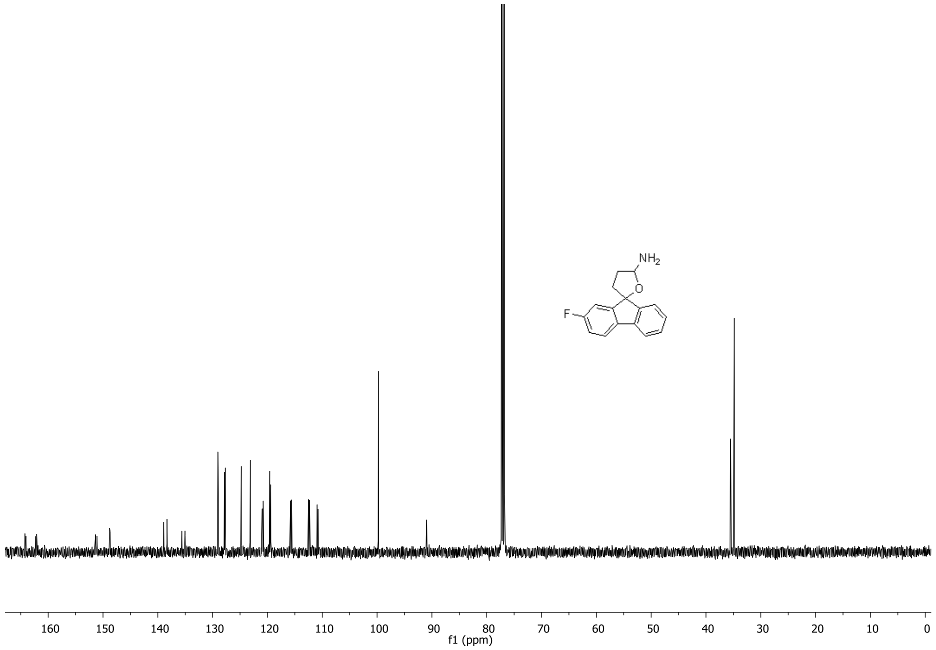

Fig. S37. ^{13}C NMR spectrum of **3b**

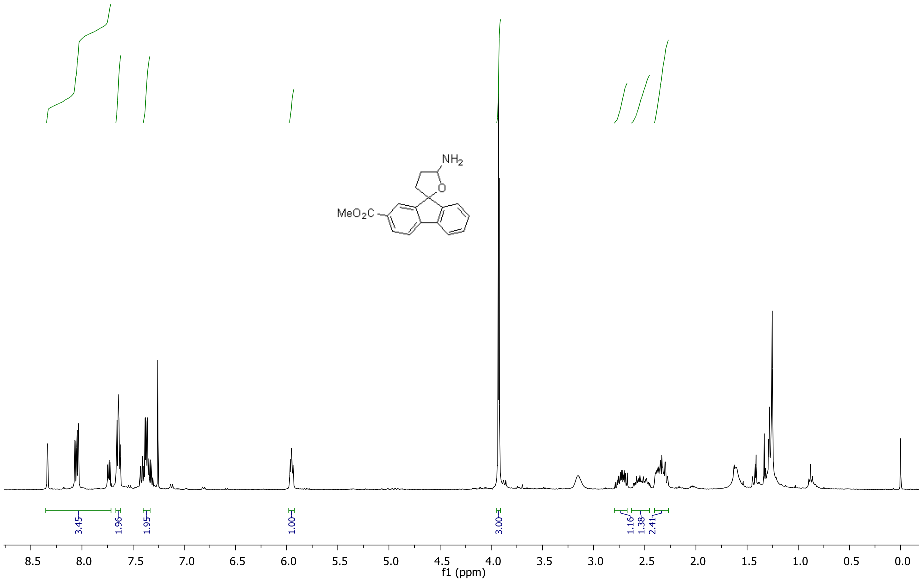

Fig. S38. ^{1}H NMR spectrum of **3c**

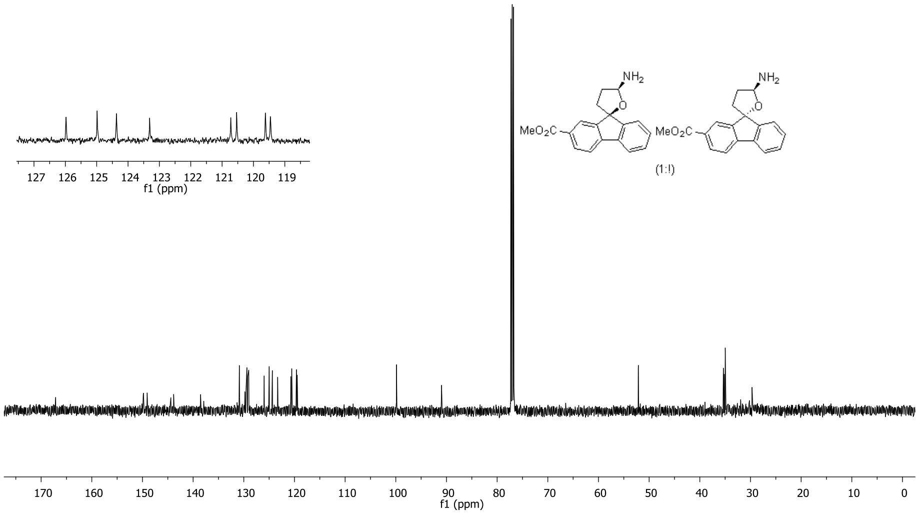

Fig. S39. ^{13}C NMR spectrum of **3c**

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[i] Wei, B.; Li, H.; Zhang, W.-X.; Xi, Z. *Organometallics* **2015**, *34*, 1339-1344.

[ii] Sprinzak, Y. r. *J. Am. Chem. Soc.* **1958**, *80*, 5449-5455.

[iii] Fox, H. H.; Gibas, J. T.; Lee, H. L.; Boris, A. *J. Med. Chem.* **1964**, *7*, 790-792.

[iv] Mladenova, G.; Chen, L.; Rodriquez, C. F.; Siu, K. W. M.; Johnston, L. J.; Hopkinson, A. C.; Lee-Ruff, E. *J. Org. Chem.* **2001**, *66*, 1109-1114.