

Supplementary Information

One-Step Synthesis of Diazaspiro[4.5]decane Scaffolds with Exocyclic Double Bonds

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1. General Experimental Procedures

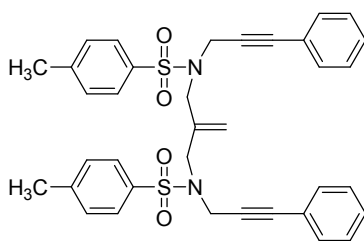
All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance 300 spectrometer with CDCl_3 as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^1H NMR spectra as 0.00 ppm and CDCl_3 resonance in the ^{13}C spectra as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from CHCl_3 on the NaCl window in the 4000–400 cm^{-1} ranges on a Nicolet 5DX spectrometer. All HRMS spectra were recorded using EI or APCI at 70 eV. X-ray Crystallography diffraction data of **fa**, **ga**, and **gb** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator using the ω -scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

General procedures:

Substrate yne-en-yne^[1] **a-g** (1.0 mmol), aryl halide (1.1 mmol), $\text{Pd}(\text{OAc})_2$ (2 mol%), and PPh_3 (4 mol%) were added to the degassed solution of $(n\text{-Bu})_3\text{N}$ (2 mmol) in DMF (10 mL). and the mixture was stirred at room temperature for half an hour, and then heated at 130°C for 20 h, The reaction mixture was cooled, and then quenched with water and extracted with EtOAc ($3 \times 5 \text{ mL}$). The combined organic layers were washed with hydrochloric acid (5%), sodium carbonate (5%), and saturated sodium chloride solution. After separation, the organic layer was dried over MgSO_4 and then concentrated. The residue was loaded onto a silica gel column and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate) to give the corresponding product **aa-gd**.

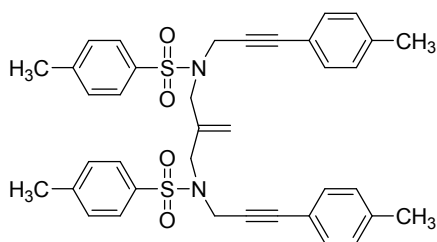
[1] T. J. Meng, Y. M. Hu, Q. S. Zhao, T. Yu, S. Wang, *Tetrahedron*, **2011**, 67, 8710-8716.

2. Characterization Data for the New Compounds



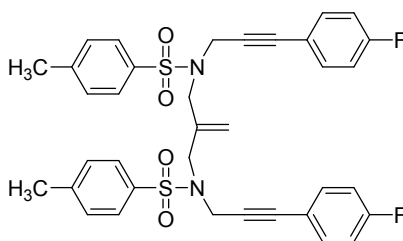
***N, N'*-2-methylenepropane-1,3-diylbis(4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (a)**

White solid; 82 % yield; m.p. 116-117 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.45; ^1H NMR (300 MHz, CDCl_3): δ 7.76 - 7.78 (d, 4H, J = 7.8 Hz; Ar-H), 7.23 (s, 10H, Ar-H), 7.05 - 7.07 (d, 4H, J = 6.3 Hz; Ar-H), 5.41 (s, 2H; $\text{C}=\text{CH}_2$), 4.33 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.92 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$), 2.31 (s, 6H; Ar- CH_3); ^{13}C NMR (75.5 MHz, CDCl_3): δ 143.7, 137.3, 135.5, 131.6, 129.6, 128.5, 128.1, 127.9, 122.1, 117.6, 86.1, 81.4, 49.3, 37.4, 21.4 ppm; FT-IR (neat): ν 3053.3, 2993.5, 2908.7, 2862.4, 2337.4, 2198.9, 1595.1, 1442.8, 1350.2, 1329.0, 1163.1, 1089.8, 981.8, 904.6, 850.6, 758.0, 692.4, 659.7 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 623.2033; found: 623.2028.



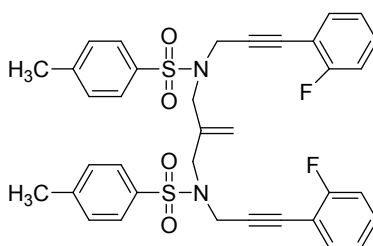
***N, N'*-2-methylenepropane-1,3-diylbis(4-methyl-*N*-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (b)**

White solid; 78 % yield; m.p. 127 - 128 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.50; ^1H NMR (300 MHz, CDCl_3): δ 7.75 - 7.78 (d, 4H, J = 7.8 Hz; Ar-H), 7.23 - 7.25 (d, 4H, J = 5.7 Hz; Ar-H), 7.02 - 7.05 (d, 4H, J = 7.8 Hz; Ar-H), 6.94 - 6.97 (d, 4H, J = 8.1 Hz; Ar-H), 5.39 (s, 2H; $\text{C}=\text{CH}_2$), 4.32 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.91 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$), 2.33 (s, 6H; Ar- CH_3), 2.32 (s, 6H; Ar- CH_3); ^{13}C NMR (75.5 MHz, CDCl_3): δ 143.6, 138.6, 137.4, 135.6, 131.5, 129.6, 128.9, 127.9, 119.0, 117.5, 86.2, 80.7, 49.3, 37.5, 21.5 ppm; FT-IR (neat): ν 3028.2, 2972.3, 2918.3, 2862.4, 2243.2, 1597.1, 1508.3, 1438.8, 1344.4, 1089.8, 902.7, 815.9, 744.5, 677.0, 657.7 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{38}\text{H}_{38}\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 651.2346; found: 651.2336.



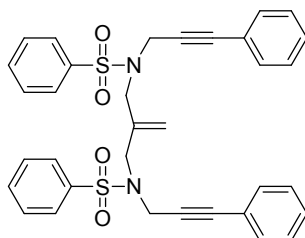
***N, N'*-2-methylenepropane-1,3-diylbis(*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (c)**

White solid; 83 % yield; m.p. 139 -140 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.48; ^1H NMR (300 MHz, CDCl_3): δ 7.74 - 7.77 (d, 4H, J = 8.7 Hz; Ar-H), 7.23 (s, 4H; Ar-H), 7.02 - 7.05 (m, 4H; Ar-H), 6.89 - 6.95 (t, 4H; Ar-H), 5.40 (s, 2H; $\text{C}=\text{CH}_2$), 4.30 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.92 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$), 2.32 (s, 6H; Ar- CH_3); ^{13}C NMR (75.5 MHz, CDCl_3): δ 164.2, 143.7, 137.4, 135.6, 133.4, 129.6, 127.9, 118.0, 115.6, 115.3, 85.0, 81.1, 49.4, 37.4, 21.4 ppm; FT-IR (neat): ν 3049.5, 2980.0, 2908.7, 2858.5, 2250.9, 1599.0, 1442.8, 1354.0, 1305.8, 1213.2, 1091.7, 983.7, 910.4, 837.1, 814.0, 773.5, 655.8 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{36}\text{H}_{32}\text{F}_2\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 659.1844; found: 659.1837.



***N, N'*-2-methylenepropane-1,3-diylbis(*N*-(3-(2-fluorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (d)**

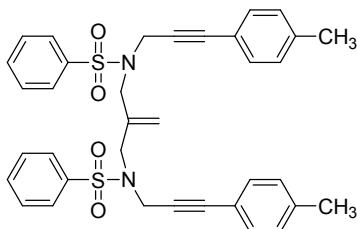
White solid; 71 % yield; m.p. 141 - 142 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.40; ^1H NMR (300 MHz, CDCl_3): δ 7.75 - 7.77 (d, 4H, J = 8.4 Hz; Ar-H), 7.21 - 7.27 (m, 7H; Ar-H), 7.00 - 7.06 (m, 5H; Ar-H), 5.43 (s, 2H; $\text{C}=\text{CH}_2$), 4.36 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.92 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$), 2.26 (s, 6H; Ar- CH_3); ^{13}C NMR (75.5 MHz, CDCl_3): δ 164.3, 143.7, 137.1, 135.4, 133.5, 130.2, 129.6, 127.8, 123.8, 117.9, 115.5, 115.2, 86.7, 79.6, 49.3, 37.5, 21.4 ppm; FT-IR (neat): ν 3043.7, 2980.0, 2914.4, 2854.7, 1595.1, 1435.0, 1346.3, 1259.5, 1215.2, 1093.6, 941.3, 908.5, 817.8, 761.9, 734.9, 696.3, 661.6 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{36}\text{H}_{32}\text{F}_2\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 659.1844; found: 659.1839.



***N, N'*-2-methylenepropane-1,3-diylbis(*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (e)**

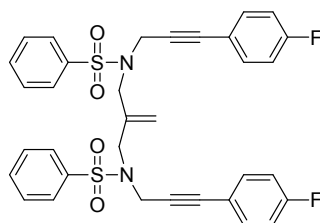
White solid; 75 % yield; m.p. 104 - 105 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.45; ^1H NMR (300 MHz, CDCl_3): δ 7.89 - 7.92 (d, 4H, J = 8.1 Hz; Ar-H), 7.45 - 7.53 (m, 6H; Ar-H), 7.10 - 7.28 (m, 6H; Ar-H), 7.07 - 7.08 (d, 4H, J = 1.8 Hz; Ar-H), 5.42 (s, 2H; $\text{C}=\text{CH}_2$), 4.37 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.94 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$); ^{13}C NMR (75.5 MHz, CDCl_3): δ 138.7, 137.2, 132.9, 131.6, 129.0, 128.6, 128.2, 127.8,

121.9, 117.8, 86.2, 81.3, 55.3, 49.3, 37.5 ppm; FT-IR (neat): ν 3055.2, 2968.5, 2908.7, 2858.5, 2239.4, 1597.1, 1491.0, 1446.6, 1330.9, 1093.6, 979.8, 898.8, 788.9, 814.0, 758.0, 721.4, 690.5 cm^{-1} ; cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 595.1720; found: 595.1713.



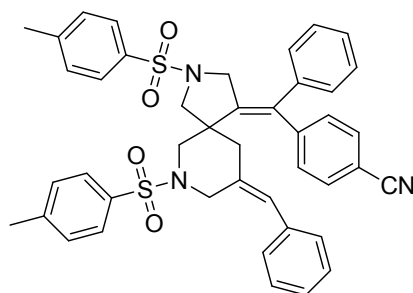
***N, N'*-2-methylenepropane-1,3-diylbis(*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide (f)**

White solid; 82 % yield; m.p. 109 - 110 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.45; ^1H NMR (300 MHz, CDCl_3): δ 7.88 - 7.90 (d, 4H, J = 5.4 Hz; Ar-H), 7.45 - 7.57 (m, 6H; Ar-H), 7.02 - 7.05 (d, 4H, J = 7.5 Hz; Ar-H), 6.96 - 6.99 (d, 4H, J = 8.4 Hz; Ar-H), 5.41 (s, 2H; $\text{C}=\text{CH}_2$), 4.35 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.93 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$), 2.31 (s, 6H; Ar- CH_3); ^{13}C NMR (75.5 MHz, CDCl_3): δ 138.7, 138.6, 137.2, 132.8, 131.5, 129.0, 128.9, 127.8, 118.9, 117.7, 86.3, 80.5, 49.3, 37.5, 21.5 ppm; FT-IR (neat): ν 3072.6, 2974.2, 2912.5, 2862.4, 2241.3, 2206.6, 1604.8, 1508.3, 1446.6, 1334.7, 1091.7, 1062.8, 974.5, 896.9, 821.7, 814.0, 744.5, 686.7 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 623.2033; found: 623.2023.



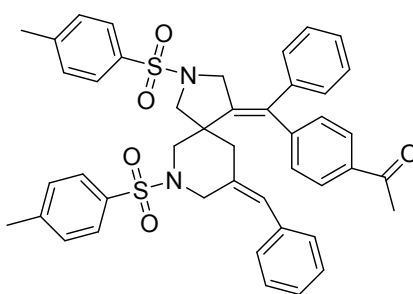
***N, N'*-2-methylenepropane-1,3-diylbis(*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)benzenesulfonamide (g)**

White solid; 87 % yield; m.p. 83 - 84 °C; TLC (petroleum ether/EtOAc = 5:1): R_f = 0.48; ^1H NMR (300 MHz, CDCl_3): δ 7.88 - 7.90 (d, 4H, J = 6.6 Hz; Ar-H), 7.45 - 7.87 (m, 6H; Ar-H), 7.04 - 7.08 (m, 4H; Ar-H), 6.89 - 6.95 (m, 4H; Ar-H), 5.41 (s, 2H; $\text{C}=\text{CH}_2$), 4.34 (s, 4H; $\text{C}\equiv\text{C}-\text{CH}_2$), 3.93 (s, 4H; $\text{C}=\text{C}-\text{CH}_2$); ^{13}C NMR (75.5 MHz, CDCl_3): δ 164.3, 138.6, 137.2, 133.6, 132.9, 129.0, 127.8, 117.8, 115.6, 115.3, 85.1, 81.0, 49.3, 37.4 ppm; FT-IR (neat): ν 3064.9, 2982.0, 2914.4, 2866.2, 2250.9, 2212.4, 1599.0, 1429.3, 1334.7, 1097.5, 981.8, 896.9, 842.9, 690.5, 661.6 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{34}\text{H}_{28}\text{F}_2\text{N}_2\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 631.1531; found: 631.1524.



4-((E)-((Z)-9-benzylidene-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(phenyl)methyl)benzonitrile(aa)

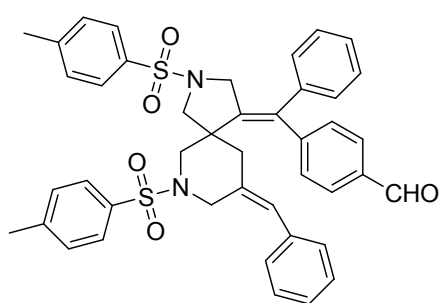
White solid; 623 mg (86 % yield); m.p. 252 - 253 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ^1H NMR (300 MHz, CDCl_3): δ 7.64 - 7.67 (d, J = 7.8 Hz, 2H; Ar-H), 7.45 - 7.47 (d, J = 7.8 Hz, 2H; Ar-H), 7.25 - 7.35 (m, 8H; Ar-H), 7.24 - 7.25 (m, 6H; Ar-H), 7.04 - 7.11 (m, 4H; Ar-H), 6.34 (s, 1H; C=CH), 4.55 - 4.59 (d, J = 12.3 Hz, 1H; N-CH₂-C=C), 4.02 - 4.07 (d, J = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.66 - 3.71 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.57 - 3.61 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 3.38 - 3.42 (d, J = 11.7 Hz, 1H; N-CH₂-C=CH), 2.91 - 2.94 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 2.53 - 2.57 (d, J = 13.8 Hz, 1H; C-CH₂-C=CH), 2.50 (s, 3H; Ar-CH₃), 2.43 (s, 3H; Ar-CH₃), 2.14 - 2.18 (d, J = 13.2 Hz, 1H; N-CH₂-C=C), 2.04 - 2.09 (d, J = 16.2 Hz, 1H; C-CH₂-C=CH), 1.72 - 1.76 (d, J = 11.1 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 145.4, 144.4, 144.1, 140.8, 139.1, 137.1, 135.6, 132.2, 132.1, 131.6, 130.3, 129.9, 129.7, 129.6, 129.4, 129.2, 128.7, 128.5, 128.2, 128.2, 128.0, 127.5, 127.4, 127.1, 118.2, 111.3, 56.4, 53.0, 52.7, 48.0, 47.3, 43.5, 21.7, 21.6 ppm; FT-IR (neat): ν 3055.2, 3028.2, 2926.0, 2873.9, 2837.3, 2227.8, 1597.1, 1564.3, 1491.0, 1442.8, 1334.7, 1091.7, 1010.7, 842.9, 815.9, 758.0, 702.1, 667.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{39}\text{N}_3\text{O}_4\text{S}_2$ [$\text{M} + \text{H}$]⁺, 726.2455; found: 726.2443.



1-(4-((E)-((Z)-9-benzylidene-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(phenyl)methyl)phenyl)ethanone(ab)

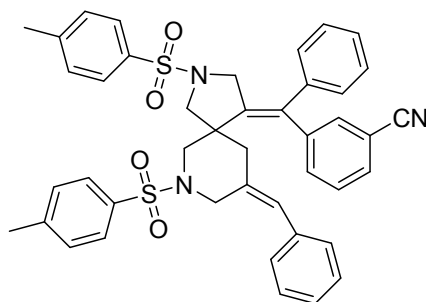
White solid; 564 mg (76 % yield); m.p. 254 - 255 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.40; ^1H NMR (300 MHz, CDCl_3): δ 7.76 - 7.78 (d, J = 9.9 Hz, 2H; Ar-H), 7.64 - 7.67 (d, J = 7.2 Hz, 2H; Ar-H), 7.31 - 7.33 (d, J = 5.1 Hz, 8H; Ar-H), 7.20 - 7.22 (d, J = 9.3 Hz, 6H; Ar-H), 7.09 - 7.11 (d, J = 7.5 Hz, 4H; Ar-H), 6.34 (s, 1H; C=CH), 4.49 - 4.53 (d, J = 12.0 Hz, 1H; N-CH₂-C=C), 4.01 - 4.06 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.65 - 3.70 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.53 -

3.56 (d, $J = 9.6$ Hz, 1H; N-CH₂-C-C=C), 3.44 - 3.48 (d, $J = 10.5$ Hz, 1H; N-CH₂-C=CH), 2.92 - 2.95 (d, $J = 9.3$ Hz, 1H; N-CH₂-C-C=C), 2.50 - 2.54 (d, $J = 13.5$ Hz, 1H; C-CH₂-C=CH), 2.50 (s, 3H; O=C-CH₃), 2.43 (s, 3H; Ar-CH₃), 2.39 (s, 3H; Ar-CH₃), 2.12 - 2.15 (t, 2H; N-CH₂-C=C, C-CH₂-C=CH), 1.92 - 1.95 (d, $J = 10.8$ Hz, 1H; N-CH₂-C=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ 197.0, 145.5, 144.0, 143.9, 141.4, 138.2, 138.1, 135.8, 132.2, 131.9, 130.0, 129.9, 129.7, 129.1, 128.9, 128.8, 128.5, 128.4, 128.1, 127.8, 127.6, 127.3, 127.2, 56.6, 53.1, 52.8, 48.0, 47.2, 43.5, 26.6, 21.7, 21.5 ppm; FT-IR (neat): ν 3053.3, 3028.2, 2941.4, 2877.8, 2837.3, 1685.8 (C=O), 1599.0, 1492.9, 1460.1, 1400.3, 1350.2, 1265.3, 1091.7, 1012.6, 964.4, 815.9, 756.1, 704.0, 667.4 cm⁻¹; HRMS (APCI): m/z calcd for C₄₄H₄₂N₂O₅S₂ [M + H]⁺, 743.2608; found: 743.2597.



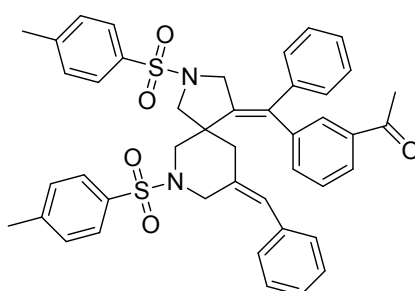
4-((E)-(Z)-9-benzylidene-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(phenyl)methylbenzaldehyde(ac)

White solid; 568 mg (78 % yield); m.p. 249 - 250 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.42; ¹H NMR (300 MHz, CDCl₃): δ 9.88 (s, 1H; CHO), 7.65 - 7.70 (t, 4H; Ar-H), 7.30 - 7.36 (t, 9H; Ar-H), 7.23 - 7.27 (t, 2H; Ar-H), 7.17 - 7.20 (d, $J = 8.4$ Hz, 3H; Ar-H), 7.07 - 7.12 (t, 4H; Ar-H), 6.36 (s, 1H; C=CH), 4.51 - 4.55 (d, $J = 11.7$ Hz, 1H; N-CH₂-C=C), 4.03 - 4.08 (d, $J = 15.0$ Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.65 - 3.69 (d, $J = 14.4$ Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.56 - 3.60 (d, $J = 9.9$ Hz, 1H; N-CH₂-C-C=C), 3.41 - 3.45 (d, $J = 11.1$ Hz, 1H; N-CH₂-C=CH), 2.89 - 2.93 (d, $J = 10.2$ Hz, 1H; N-CH₂-C-C=C), 2.53 - 2.58 (d, $J = 13.2$ Hz, 1H; C-CH₂-C=CH), 2.44 (s, 3H; Ar-CH₃), 2.40 (s, 3H; Ar-CH₃), 2.09 - 2.19 (t, 2H; N-CH₂-C=C, C-CH₂-C=CH), 1.82 - 1.85 (d, $J = 11.1$ Hz, 1H; N-CH₂-C=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ 191.1, 146.9, 143.9, 141.1, 138.6, 137.8, 135.7, 135.1, 132.4, 132.3, 131.8, 130.1, 129.8, 129.7, 129.5, 129.3, 129.2, 128.7, 128.5, 128.0, 127.9, 127.5, 127.3, 127.2, 56.5, 53.0, 52.7, 48.0, 47.2, 43.5, 21.6, 21.5 ppm; FT-IR (neat): ν 3053.3, 3026.3, 2962.7, 2931.8, 2873.9, 1699.3 (CHO), 1599.0, 1492.9, 1456.3, 1350.2, 1091.7, 1045.4, 815.9, 758.0, 702.1, 667.4 cm⁻¹; HRMS (APCI): m/z calcd for C₄₃H₄₀N₂O₅S₂ [M + H]⁺, 729.2451; found: 729.2449.



3-((E)-((Z)-9-benzylidene-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(phenyl)methyl)benzonitrile(ad)

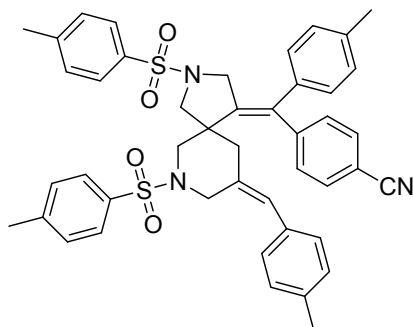
White solid; 558 mg (77 % yield); m.p. 133 - 134 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.48; ^1H NMR (300 MHz, CDCl_3): δ 7.65 - 7.67 (d, J = 7.8 Hz, 2H; Ar-H), 7.36 - 7.41 (m, 7H; Ar-H), 7.25 - 7.34 (m, 9H; Ar-H), 7.11 - 7.13 (d, J = 7.2 Hz, 2H; Ar-H), 7.03 - 7.06 (d, J = 6.9 Hz, 2H; Ar-H), 6.36 (s, 1H; C=CH), 4.55 - 4.59 (d, J = 12.0 Hz, 1H; N-CH₂-C=C), 4.00 - 4.05 (d, J = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.66 - 3.71 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.52 - 3.55 (d, J = 9.9 Hz, 1H; N-CH₂-C=C), 3.45 - 3.48 (d, J = 11.1 Hz, 1H; N-CH₂-C=CH), 2.96 - 2.99 (d, J = 10.2 Hz, 1H; N-CH₂-C=C), 2.50 - 2.55 (d, J = 13.8 Hz, 1H; C-CH₂-C=CH), 2.45 (s, 3H; Ar-CH₃), 2.45 (s, 3H; Ar-CH₃), 2.19 - 2.23 (d, J = 12.6 Hz, 1H; N-CH₂-C=C), 2.06 - 2.11 (d, J = 12.9 Hz, 1H; C-CH₂-C=CH), 1.82 - 1.86 (d, J = 11.4 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 144.1, 143.9, 141.8, 141.0, 139.5, 136.7, 135.6, 133.0, 132.2, 131.9, 130.9, 130.2, 129.9, 129.8, 129.3, 129.3, 128.7, 128.5, 128.0, 127.4, 127.4, 127.1, 118.1, 112.7, 56.5, 52.9, 52.8, 48.1, 47.2, 43.6, 21.6 ppm; FT-IR (neat): ν 3055.2, 3026.3, 2955.0, 2924.1, 2870.1, 1597.1, 1492.9, 1462.0, 1442.8, 1348.2, 1091.7, 1043.5, 962.5, 814.0, 748.4, 706.0, 665.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{39}\text{N}_3\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 726.2455; found: 726.2462.



1-(3-((E)-((Z)-9-benzylidene-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(phenyl)methyl)phenyl)ethanone(ae)

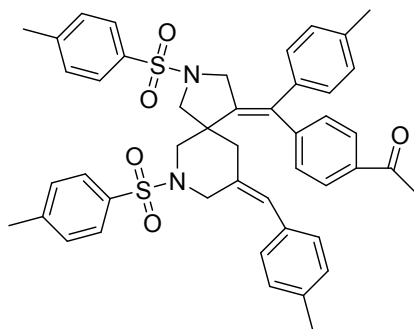
White solid; 527 mg (71 % yield); m.p. 239 - 240 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.48; ^1H NMR (300 MHz, CDCl_3): δ 7.65 - 7.74 (m, 4H; Ar-H), 7.32-7.42 (m, 8H; Ar-H), 7.14 - 7.20 (m, 6H; Ar-H), 7.05 - 7.10 (t, 4H; Ar-H), 6.32 (s, 1H; C=CH), 4.50 - 4.54 (d, J = 12.0 Hz, 1H; N-CH₂-C=C), 4.00 - 4.05 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.68 - 3.73 (d, J = 13.5 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.45 - 3.55 (t, 2H; N-CH₂-C=C, N-CH₂-C=CH), 2.96 - 2.99 (d, J = 9.0 Hz, 1H; N-CH₂-C=C), 2.51 (s, 4H; C-CH₂-C=CH, O=C-CH₃), 2.44 (s, 3H; Ar-CH₃), 2.43 (s, 3H; Ar-CH₃), 2.15 (s, 2H;

N-CH₂-C=C, C-CH₂-C=CH), 1.92 - 1.96 (d, *J* = 11.1 Hz, 1H; N-CH₂-C=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ 197.1, 144.0, 143.6, 141.7, 141.0, 138.3, 138.1, 136.8, 135.7, 133.2, 132.4, 132.3, 129.9, 129.6, 129.1, 128.7, 128.6, 128.5, 128.1, 128.0, 127.7, 127.5, 127.4, 127.3, 127.2, 56.5, 52.9, 52.8, 48.0, 47.1, 43.5, 26.7, 21.6, 21.6 ppm; FT-IR (neat): ν 3059.1, 3024.4, 2955.0, 2924.1, 2872.0, 2837.3, 1685.8 (C=O), 1597.1, 1491.0, 1423.5, 1352.1, 1249.9, 1091.7, 1043.5, 966.3, 815.9, 667.4 cm⁻¹; HRMS (APCI): *m/z* calcd for C₄₄H₄₂N₂O₅S₂ [M + H]⁺, 743.2608; found: 743.2619.



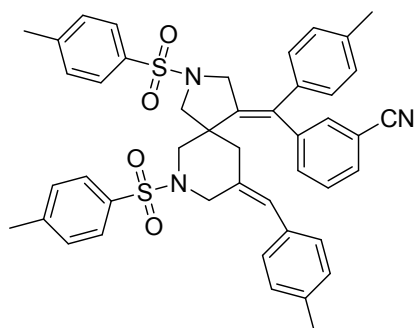
4-((E)-((Z)-9-(4-methylbenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(p-tolyl)methyl)benzonitrile(ba)

White solid; 572 mg (76 % yield); m.p. 267 - 268 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ¹H NMR (300 MHz, CDCl₃): δ 7.65 - 7.67 (d, *J* = 8.1 Hz, 2H; Ar-H), 7.44 - 7.46 (d, *J* = 7.8 Hz, 2H; Ar-H), 7.27 - 7.35 (m, 6H; Ar-H), 7.11 - 7.22 (m, 6H; Ar-H), 7.00 - 7.02 (d, *J* = 7.2 Hz, 2H; Ar-H), 6.91 - 6.93 (d, *J* = 7.8 Hz, 2H; Ar-H), 6.31 (s, 1H; C=CH), 4.55 - 4.59 (d, *J* = 12.0 Hz, 1H; N-CH₂-C=C), 4.03 - 4.08 (d, *J* = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.66 - 3.71 (d, *J* = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.56 - 3.59 (d, *J* = 9.9 Hz, 1H; N-CH₂-C=C), 3.35 - 3.39 (d, *J* = 11.1 Hz, 1H; N-CH₂-C=CH), 2.88 - 2.91 (d, *J* = 9.9 Hz, 1H; N-CH₂-C=C), 2.50 - 2.55 (d, *J* = 14.4 Hz, 4H; C-CH₂-C=CH, Ar-CH₃), 2.44 (s, 3H; Ar-CH₃), 2.35 (s, 3H; Ar-CH₃), 2.32 (s, 3H; Ar-CH₃), 2.06 - 2.16 (t, 2H; N-CH₂-C=C, C-CH₂-C=CH), 1.70 - 1.74 (d, *J* = 14.7 Hz, 1H; N-CH₂-C=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ 145.7, 144.4, 144.0, 138.9, 137.9, 137.1, 137.0, 132.7, 132.3, 132.0, 131.7, 130.3, 129.9, 129.7, 129.4, 129.2, 128.6, 128.6, 128.0, 127.5, 127.0, 118.2, 111.2, 56.5, 53.1, 52.7, 47.9, 47.3, 43.6, 21.7, 21.6, 21.2, 21.2 ppm; FT-IR (neat): ν 3066.5, 3026.2, 2968.7, 2910.3, 2867.2, 2308.8, 1599.1, 1514.2, 1456.6, 1438.7, 1348.7, 1091.7, 1008.9, 850.1, 813.7, 753.7, 710.2, 665.6 cm⁻¹; HRMS (APCI): *m/z* calcd for C₄₅H₄₃N₃O₄S₂ [M + H]⁺, 754.2768; found: 754.2756.



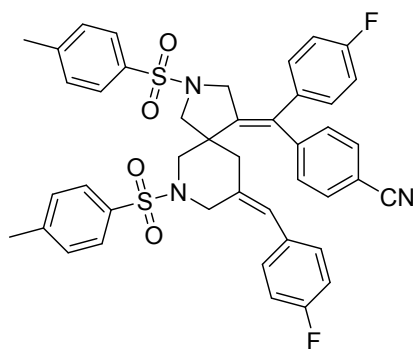
1-(4-((E)-((Z)-9-(4-methylbenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(p-tolyl)methyl)phenyl)ethanone(bb)

White solid; 570 mg (74 % yield); m.p. 142 - 143 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.41; ^1H NMR (300 MHz, CDCl_3): δ 7.74 - 7.77 (d, J = 8.7 Hz, 2H; Ar-H), 7.65 - 7.68 (d, J = 8.1 Hz, 2H; Ar-H), 7.31 - 7.36 (m, 4H; Ar-H), 7.10 - 7.20 (m, 8H; Ar-H), 6.93 - 7.10 (m, 4H; Ar-H), 6.30 (s, 1H; C=CH), 4.50 - 4.54 (d, J = 9.3 Hz, 1H; N-CH₂-C=C), 4.02 - 4.07 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.67 - 3.71 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.52 - 3.55 (d, J = 10.2 Hz, 1H; N-CH₂-C-C=C), 3.42 - 3.45 (d, J = 10.5 Hz, 1H; N-CH₂-C=CH), 2.91 - 2.95 (d, J = 11.1 Hz, 1H; N-CH₂-C-C=C), 2.47 - 2.50 (t, 4H; C-CH₂-C=CH, O=C-CH₃), 2.44 (s, 3H; Ar-CH₃), 2.39 (s, 3H; Ar-CH₃), 2.34 (s, 3H; Ar-CH₃), 2.31 (s, 3H; Ar-CH₃), 2.10 - 2.17 (t, 2H; N-CH₂-C=C, C-CH₂-C=CH), 1.90 - 1.93 (d, J = 9.0 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 196.9, 145.8, 143.9, 143.8, 138.5, 138.0, 137.9, 137.6, 137.0, 135.7, 132.8, 132.3, 131.9, 129.9, 129.8, 129.7, 129.6, 129.2, 129.0, 128.9, 128.6, 128.3, 128.0, 127.6, 127.0, 56.6, 53.0, 52.8, 47.9, 47.2, 43.4, 26.5, 21.6, 21.4, 21.2, 21.1 ppm; FT-IR (neat): ν 3066.7, 3023.6, 2957.8, 2906.2, 2865.3, 1683.9 (C=O), 1599.7, 1508.2, 1446.7, 1415.6, 1352.6, 1265.5, 1091.7, 1010.8, 959.4, 817.8, 756.5, 708.2, 669.7 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{46}\text{H}_{46}\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 771.2921; found: 771.2911.



3-((E)-((Z)-9-(4-methylbenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(p-tolyl)methyl)benzonitrile(bc)

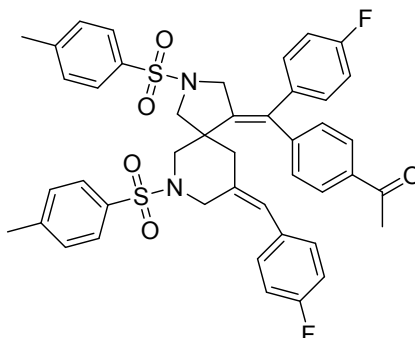
White solid; 587 mg (78 % yield); m.p. 138 - 140 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.48; ^1H NMR (300 MHz, CDCl_3): δ 7.65 - 7.68 (d, J = 8.1 Hz, 2H; Ar-H), 7.37 - 7.38 (t, 4H; Ar-H), 7.28 - 7.35 (m, 6H; Ar-H), 7.12 - 7.16 (m, 4H; Ar-H), 7.00 - 7.03 (d, J = 8.1 Hz, 2H; Ar-H), 6.91 - 6.93 (d, J = 8.1 Hz, 2H; Ar-H), 6.31 (s, 1H; C=CH), 4.55 - 4.59 (d, J = 12.9 Hz, 1H; N-CH₂-C=C), 4.00 - 4.05 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.67 - 3.72 (d, J = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.49 - 3.54 (d, J = 12.9 Hz, 1H; N-CH₂-C-C=C), 3.42 - 3.45 (d, J = 9.6 Hz, 1H; N-CH₂-C=CH), 2.94 - 2.98 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 2.45 - 2.50 (d, 7H; C-CH₂-C=CH, Ar-CH₃), 2.35 (s, 3H; Ar-CH₃), 2.33 (s, 3H; Ar-CH₃), 2.16 - 2.20 (d, J = 12.0 Hz, 1H; N-CH₂-C-C=C), 2.03 - 2.08 (d, J = 12.9 Hz, 1H; C-CH₂-C=CH), 1.79 - 1.83 (d, J = 11.1 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 144.0, 143.9, 142.1, 139.2, 138.2, 137.9, 137.1, 136.6, 133.0, 132.7, 132.2, 131.9, 130.8, 130.1, 129.9, 129.8, 129.2, 128.7, 128.7, 128.1, 127.4, 127.0, 118.1, 112.6, 56.5, 53.0, 52.9, 47.9, 47.2, 43.6, 21.6, 21.6, 21.2, 21.2 ppm; FT-IR (neat): ν 3055.2, 3020.5, 2953.0, 2881.7, 2310.7, 1595.1, 1535.3, 1489.1, 1456.3, 1338.6, 1159.2, 1085.9, 1014.6, 839.0, 808.2, 754.2, 688.6 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{45}\text{H}_{43}\text{N}_3\text{O}_4\text{S}_2$ [$\text{M} + \text{H}$]⁺, 754.2768; found: 754.2780.



4-((Z)-((Z)-9-(4-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(4-fluorophenyl)methyl)benzonitrile(ca)

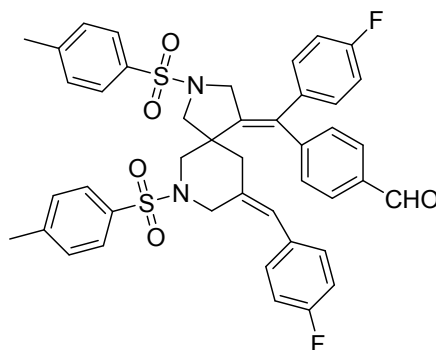
White solid; 646 mg (85 % yield); m.p. 257 - 258 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.52; ^1H NMR (300 MHz, CDCl_3): δ 7.66 - 7.68 (d, J = 8.0 Hz, 2H; Ar-H), 7.47 - 7.49 (d, J = 8.4 Hz, 2H; Ar-H), 7.26 - 7.36 (m, 6H; Ar-H), 7.20 - 7.22 (d, J = 8.4 Hz, 2H; Ar-H), 7.06 - 7.12 (m, 4H; Ar-H), 7.02 - 7.04 (d, J = 6.8 Hz, 2H; Ar-H), 6.33 (s, 1H; C=CH), 4.48 - 4.51 (d, J = 12.4 Hz, 1H; N-CH₂-C=C), 4.03 - 4.06 (d, J = 14.8 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.59 - 3.66 (t, 2H; C-CH₂-N-CH₂-C=CH, N-CH₂-C-C=C), 3.38 - 3.41 (d, J = 11.2 Hz, 1H; N-CH₂-C=CH), 2.89 - 2.91 (d, J = 10.0 Hz, 1H; N-CH₂-C-C=C), 2.51 - 2.55 (d, J = 11.6 Hz, 1H; C-CH₂-C=CH), 2.51 (s, 3H; Ar-CH₃), 2.45 (s, 3H; Ar-CH₃), 2.12 - 2.17 (t, 2H; N-CH₂-C-C=C, C-CH₂-C=CH), 1.73 - 1.76 (d, J = 11.2 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 163.8 (d, $J_{\text{C-F}}$ = 249.2 Hz), 163.6 (d, $J_{\text{C-F}}$ = 247.4 Hz), 145.2, 144.5, 144.2, 139.7, 136.7, 136.7, 136.2, 132.1, 131.7, 130.5, 130.4, 129.9, 129.8, 129.4, 129.3, 129.1, 129.0, 128.0, 127.5, 118.1, 116.4, 116.2, 115.6, 115.4, 111.6, 56.4, 52.9, 52.6, 48.1, 47.2, 43.4, 21.6,

21.6 ppm; FT-IR (neat): ν 3074.5, 3045.6, 2974.2, 2937.6, 2881.7, 2308.8, 2227.8, 1600.9, 1508.3, 1338.6, 1222.9, 1161.2, 1091.7, 815.9, 667.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{37}\text{F}_2\text{N}_3\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 762.2266; found: 762.2252.



1-(4-((Z)-((Z)-9-(4-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(4-fluorophenyl)methyl)phenyl)ethanone(cb)

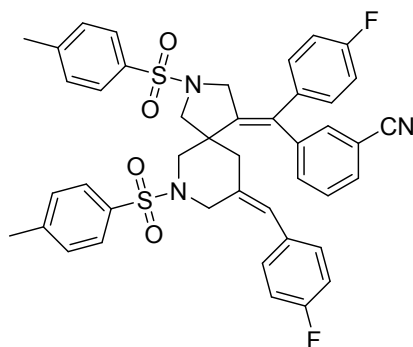
White solid; 646 mg (83 % yield); m.p. 137 - 138 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.42; ^1H NMR (300 MHz, CDCl_3): δ 7.77 - 7.79 (d, J = 7.8 Hz, 2H; Ar-H), 7.65 - 7.67 (d, J = 8.1 Hz, 2H; Ar-H), 7.30 - 7.36 (t, 5H; Ar-H), 7.17 - 7.21 (m, 5H; Ar-H), 6.98 - 7.07 (m, 6H; Ar-H), 6.32 (s, 1H; C=CH), 4.41 - 4.45 (d, J = 12.6 Hz, 1H; N- CH_2 -C=C), 4.00 - 4.05 (d, J = 14.4 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.59 - 3.64 (d, J = 14.4 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.54 - 3.57 (d, J = 10.2 Hz, 1H; N- CH_2 -C-C=C), 3.42 - 3.46 (d, J = 10.2 Hz, 1H; N- CH_2 -C=CH), 2.89 - 2.92 (d, J = 9.6 Hz, 1H; N- CH_2 -C-C=C), 2.56 - 2.61 (d, J = 16.2 Hz, 1H; C- CH_2 -C=CH), 2.51 (s, 3H; O=C- CH_3), 2.44 (s, 3H; Ar- CH_3), 2.39 (s, 3H; Ar- CH_3), 2.07 - 2.17 (t, 2H; N- CH_2 -C-C=C, C- CH_2 -C=CH), 1.89 - 1.93 (d, J = 11.4 Hz, 1H; N- CH_2 -C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 196.8, 163.7 (d, $J_{\text{C-F}}$ = 248.3 Hz), 163.5 (d, $J_{\text{C-F}}$ = 247.0 Hz), 145.2, 144.1, 144.0, 138.7, 137.1, 135.9, 132.1, 131.8, 130.5, 130.4, 129.9, 129.7, 129.7, 129.1, 128.9, 128.8, 128.4, 128.0, 127.5, 116.3, 116.0, 115.6, 115.3, 56.5, 52.9, 52.7, 48.0, 47.0, 43.3, 26.5, 21.6, 21.4 ppm; FT-IR (neat): ν 3063.0, 3043.7, 2956.9, 2926.0, 2870.1, 2351.2, 2308.8, 1683.9 (C=O), 1600.9, 1508.3, 1350.2, 1265.3, 1226.7, 1091.7, 1041.6, 958.6, 815.9, 663.5 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{44}\text{H}_{40}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 779.2420; found: 779.2404.



4-((Z)-((Z)-9-(4-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(4-

fluorophenyl)methyl)benzaldehyde(cc)

White solid; 581 mg (76 % yield); m.p. 146 - 147 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.48; ^1H NMR (300 MHz, CDCl_3): δ 9.88 (s, 1H; CHO), 7.68 - 7.71 (d, J = 8.7 Hz, 2H; Ar-H), 7.65 - 7.67 (d, J = 8.4 Hz, 2H; Ar-H), 7.29 - 7.36 (m, 6H; Ar-H), 7.17 - 7.26 (m, 2H; Ar-H), 7.01 - 7.11 (m, 8H; Ar-H), 6.33 (s, 1H; C=CH), 4.43 - 4.47 (d, J = 13.2 Hz, 1H; N-CH₂-C=C), 4.02 - 4.06 (d, J = 14.4 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.56 - 3.64 (t, 2H; C-CH₂-N-CH₂-C=CH, N-CH₂-C-C=C), 3.39 - 3.42 (d, J = 10.2 Hz, 1H; N-CH₂-C=CH), 2.87 - 2.90 (d, J = 9.0 Hz, 1H; N-CH₂-C-C=C), 2.53 - 2.57 (d, J = 11.1 Hz, 1H; C-CH₂-C=CH), 2.44 (s, 3H; Ar-CH₃), 2.39 (s, 3H; Ar-CH₃), 2.07 - 2.16 (t, 2H; N-CH₂-C=C, C-CH₂-C=CH), 1.79 - 1.83 (d, J = 13.2 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 190.9, 163.7 (d, $J_{\text{C-F}}$ = 248.1 Hz), 163.6 (d, $J_{\text{C-F}}$ = 247.0 Hz), 146.6, 144.0, 139.2, 136.9, 135.3, 132.3, 131.9, 131.6, 130.5, 130.3, 129.9, 129.7, 129.3, 129.1, 129.0, 128.0, 127.5, 116.4, 116.1, 115.6, 115.3, 56.5, 52.9, 52.7, 48.1, 47.1, 43.3, 21.6, 21.5 ppm; FT-IR (neat): ν 3066.8, 3047.5, 2956.9, 2926.0, 2870.1, 2374.4, 1701.2(CHO), 1600.9, 1506.4, 1348.2, 1226.7, 1091.7, 815.9, 663.5 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{38}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 765.2263; found: 765.2256.

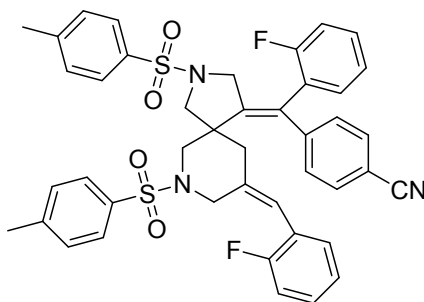


3-((E)-((Z)-9-(4-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(4-

fluorophenyl)methyl)benzonitrile(cd)

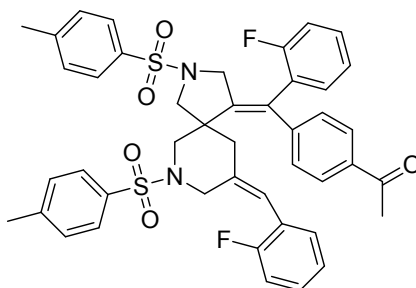
White solid; 594 mg (78 % yield); m.p. 149 - 150 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ^1H NMR (300 MHz, CDCl_3): δ 7.65 - 7.68 (d, J = 8.1 Hz, 2H; Ar-H), 7.36 - 7.37 (d, J = 4.5 Hz, 4H; Ar-H), 7.29 - 7.34 (m, 6H; Ar-H), 7.06 - 7.09 (t, 3H; Ar-H), 7.01 - 7.04 (t, 5H; Ar-H), 6.33 (s, 1H; C=CH), 4.67 - 4.51 (d, J = 12.0 Hz, 1H; N-CH₂-C=C), 3.99 - 4.04 (d, J = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.61 - 3.66 (d, J = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.52 - 3.55 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 3.43 - 3.46 (d, J = 7.8 Hz, 1H; N-CH₂-C=CH), 2.94 - 2.97 (d, J = 9.3 Hz, 1H; N-CH₂-C-C=C), 2.48 - 2.54 (d, J = 18.6 Hz, 4H; C-CH₂-C=CH, Ar-CH₃), 2.45 (s, 3H; Ar-CH₃), 2.16 - 2.20 (d, J = 12.0 Hz, 1H; N-CH₂-C-C=C), 2.04 - 2.08 (d, J = 14.1 Hz, 1H; C-CH₂-C=CH), 1.78 - 1.84 (d, J = 17.8 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 163.8 (d, $J_{\text{C-F}}$ = 258.8 Hz), 163.6 (d, $J_{\text{C-F}}$ = 271.0

Hz), 144.2, 144.1, 141.6, 140.0, 136.9, 135.8, 132.9, 131.9, 131.0, 130.5, 130.4, 129.9, 129.8, 129.5, 129.4, 129.1, 129.0, 128.0, 127.4, 118.0, 116.5, 116.2, 115.7, 115.4, 112.8, 56.5, 52.8, 48.1, 47.1, 43.4, 21.6, 21.6 ppm; FT-IR (neat): ν 3064.9, 3043.7, 2956.9, 2926.0, 2872.0, 2378.2, 2308.8, 1599.0, 1508.3, 1458.2, 1350.2, 1220.9, 1153.4, 1091.7, 1043.5, 1010.7, 964.4, 815.9, 771.5, 667.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{37}\text{F}_2\text{N}_3\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 762.2266; found: 762.2274.



4-((Z)-((Z)-9-(2-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(2-fluorophenyl)methyl)benzonitrile(da)

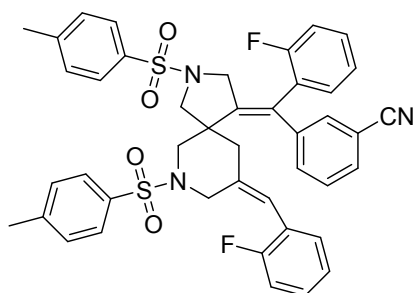
White solid; 632 mg (83 % yield); m.p. 265 - 266 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.42; ^1H NMR (300 MHz, CDCl_3): δ 7.64 - 7.67 (d, J = 8.1 Hz, 2H; Ar-H), 7.45 - 7.48 (d, J = 8.1 Hz, 2H; Ar-H), 7.29-7.35 (t, 6H; Ar-H), 7.27 (s, 4H; Ar-H), 7.03 - 7.15 (m, 6H; Ar-H), 6.26 (s, 1H; C=CH), 4.31 - 4.35 (d, J = 12.6 Hz, 1H; N- CH_2 -C=C), 3.96 - 4.00 (d, J = 14.7 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.58 - 3.63 (t, 2H; C- CH_2 -N- CH_2 -C=CH, N- CH_2 -C-C=C), 3.39 - 3.42 (d, J = 11.1 Hz, 1H; N- CH_2 -C=CH), 2.92 - 2.95 (d, J = 9.9 Hz, 1H; N- CH_2 -C-C=C), 2.58 - 2.63 (d, J = 13.5 Hz, 1H; C- CH_2 -C=CH), 2.50 (s, 3H; Ar- CH_3), 2.43 (s, 3H; Ar- CH_3), 2.11 - 2.25 (t, 2H; N- CH_2 -C-C=C, C- CH_2 -C=CH), 1.69 - 1.73 (d, J = 11.4 Hz, 1H; N- CH_2 -C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 161.5 (d, $J_{\text{C-F}}$ = 247.6 Hz), 159.7 (d, $J_{\text{C-F}}$ = 246.6 Hz), 144.5, 144.3, 144.1, 141.7, 132.1, 131.4, 130.8, 130.6, 130.4, 130.3, 129.9, 129.8, 129.6, 129.4, 129.1, 127.9, 127.5, 125.1, 124.3, 124.2, 123.3, 118.2, 116.7, 116.5, 115.8, 115.5, 111.6, 56.4, 52.8, 52.6, 48.0, 47.6, 43.3, 21.7, 21.6 ppm; FT-IR (neat): ν 3061.0, 3030.2, 2926.0, 2877.8, 2833.4, 2349.3, 2306.9, 1595.1, 1487.1, 1452.4, 1340.5, 1093.6, 1012.6, 916.2, 815.9, 765.7, 707.9, 665.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{37}\text{F}_2\text{N}_3\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 762.2266; found: 762.2257.



1-(4-((Z)-((Z)-9-(2-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(2-

fluorophenyl)methyl)phenyl)ethanone(db)

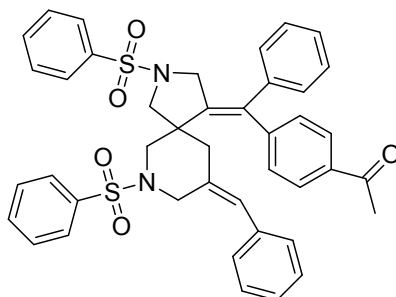
White solid; 654 mg (84 % yield); m.p. 235 - 236 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.36; ^1H NMR (300 MHz, CDCl_3): δ 7.76 - 7.79 (d, J = 8.1 Hz, 2H; Ar-H), 7.65 - 7.67 (d, J = 8.1 Hz, 2H; Ar-H), 7.32 - 7.35 (d, J = 8.7 Hz, 4H; Ar-H), 7.25 - 7.29 (t, 4H; Ar-H), 7.17 - 7.19 (d, J = 7.8 Hz, 2H; Ar-H), 7.00 - 7.14 (m, 6H; Ar-H), 6.25 (s, 1H; C=CH), 4.27 - 4.31 (d, J = 12.3 Hz, 1H; N-CH₂-C=C), 3.95 - 4.00 (d, J = 14.4 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.59 - 3.64 (d, J = 14.4 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.53 - 3.56 (d, J = 9.6 Hz, 1H; N-CH₂-C-C=C), 3.45 - 3.49 (d, J = 11.4 Hz, 1H; N-CH₂-C=CH), 2.96 - 2.99 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 2.55 - 2.59 (d, J = 13.5 Hz, 1H; C-CH₂-C=CH), 2.50 (s, 3H; O=C-CH₃), 2.43 (s, 3H; Ar-CH₃), 2.38 (s, 3H; Ar-CH₃), 2.12 - 2.21 (t, 2H; N-CH₂-C-C=C, C-CH₂-C=CH), 1.89 - 1.92 (d, J = 11.1 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 196.8, 161.5 (d, $J_{\text{C-F}}$ = 246.8 Hz), 159.7 (d, $J_{\text{C-F}}$ = 245.8 Hz), 144.4, 144.1, 143.9, 140.8, 135.9, 132.2, 131.8, 131.7, 131.4, 130.9, 130.8, 129.9, 129.7, 129.5, 129.1, 128.9, 128.4, 128.0, 127.5, 125.0, 124.2, 122.9, 116.6, 116.4, 115.7, 115.4, 56.5, 52.8, 52.7, 48.0, 47.4, 43.2, 26.5, 21.6, 21.4 ppm; FT-IR (neat): ν 3078.4, 3032.1, 2941.4, 2877.8, 2833.4, 2349.3, 2308.8, 1685.8 (C=O), 1600.9, 1487.1, 1450.5, 1400.3, 1352.1, 1265.3, 1091.7, 1010.7, 964.4, 814.0, 754.2, 667.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{44}\text{H}_{40}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 779.2420; found: 779.2410.

**3-((Z)-((Z)-9-(2-fluorobenzylidene)-2,7-ditosyl-2,7-diazaspiro[4.5]decan-4-ylidene)(2-****fluorophenyl)methyl)benzonitrile(dc)**

White solid; 517 mg (68 % yield); m.p. 149 - 150 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.38; ^1H NMR (300 MHz, CDCl_3): δ 7.65 - 7.68 (d, J = 8.1 Hz, 2H; Ar-H), 7.40 - 7.44 (t, 3H; Ar-H), 7.36 - 7.41 (t, 3H; Ar-H), 7.28 - 7.33 (m, 6H; Ar-H), 7.11 - 7.17 (m, 3H; Ar-H), 7.02 - 7.08 (m, 3H; Ar-H), 6.27 (s, 1H; C=CH), 4.33 - 4.38 (d, J = 12.6 Hz, 1H; N-CH₂-C=C), 3.94 - 3.98 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.59 - 3.64 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.50 - 3.55 (d, J = 15.0 Hz, 1H; N-CH₂-C-C=C), 3.46 - 3.48 (d, J = 7.2 Hz, 1H; N-CH₂-C=CH), 3.00 - 3.03 (d, J = 9.6 Hz, 1H; N-CH₂-C-C=C), 2.54 - 2.59 (d, J = 13.5 Hz, 1H; C-CH₂-C=CH), 2.45 (s, 3H; Ar-CH₃), 2.44 (s, 3H; Ar-CH₃), 2.20 - 2.24 (d, J = 13.5 Hz, 1H; N-CH₂-C-C=C), 2.08 - 2.12 (d, J = 13.2 Hz, 1H; C-CH₂-C=CH), 1.77 - 1.83 (d, J = 18.0 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 161.5 (d, $J_{\text{C-F}}$ = 241.3

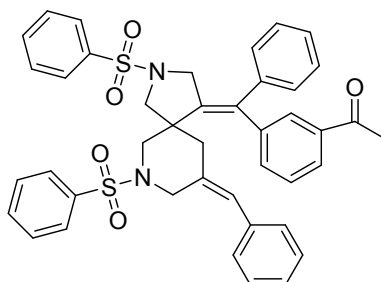
ylidene)(phenyl)methyl)benzonitrile(ea)

White solid; 425 mg (57 % yield); m.p. 240 - 241 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.45; ^1H NMR (300 MHz, CDCl_3): δ 7.77 - 7.79 (d, J = 6.6 Hz, 2H; Ar-H), 7.56 - 7.68 (m, 4H; Ar-H), 7.43 - 7.53 (m, 6H; Ar-H), 7.25 - 7.35 (m, 6H; Ar-H), 7.20 - 7.22 (d, J = 7.5 Hz, 2H; Ar-H), 7.12 - 7.14 (d, J = 6.9 Hz, 2H; Ar-H), 7.03 - 7.05 (d, J = 6.0 Hz, 2H; Ar-H), 6.37 (s, 1H; C=CH), 4.59 - 4.63 (d, J = 12.0 Hz, 1H; N- CH_2 -C=C), 4.04 - 4.09 (d, J = 15.0 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.68 - 3.73 (d, J = 15.0 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.59 - 3.62 (d, J = 9.6 Hz, 1H; N- CH_2 -C-C=C), 3.39 - 3.42 (d, J = 11.1 Hz, 1H; N- CH_2 -C=CH), 2.97 - 3.00 (d, J = 9.6 Hz, 1H; N- CH_2 -C-C=C), 2.51 - 2.56 (d, J = 12.9 Hz, 1H; C- CH_2 -C=CH), 2.19 - 2.23 (d, J = 12.0 Hz, 1H; N- CH_2 -C=C), 2.09 - 2.13 (d, J = 13.5 Hz, 1H; C- CH_2 -C=CH), 1.73 - 1.77 (d, J = 11.7 Hz, 1H; N- CH_2 -C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 145.3, 140.7, 138.9, 137.3, 135.5, 134.8, 133.3, 133.1, 132.1, 130.4, 129.3, 129.3, 129.1, 129.1, 128.8, 128.6, 128.1, 127.9, 127.4, 127.1, 118.1, 111.5, 56.4, 52.9, 52.6, 48.0, 47.3, 43.5 ppm; FT-IR (neat): ν 3053.3, 3026.3, 2873.9, 2225.9, 1597.1, 1491.0, 1462.0, 1440.8, 1352.1, 1334.7, 1163.1, 1091.7, 815.9, 758.0, 702.1, 667.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{41}\text{H}_{35}\text{N}_3\text{O}_4\text{S}_2$ [$\text{M} + \text{H}$] $^+$, 698.2142; found: 698.2137.

**1-(4-((E)-((Z)-9-benzylidene-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-****ylidene)(phenyl)methyl)phenyl)ethanone(eb)**

White solid; 443 mg (62 % yield); m.p. 136 - 137 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.43; ^1H NMR (300 MHz, CDCl_3): δ 7.74 - 7.80 (t, 4H; Ar-H), 7.49 - 7.67 (m, 4H; Ar-H), 7.40 - 7.47 (m, 4H; Ar-H), 7.23 - 7.37 (m, 4H; Ar-H), 7.18 - 7.21 (d, J = 8.4 Hz, 2H; Ar-H), 7.05 - 7.13 (m, 6H; Ar-H), 6.36 (s, 1H; C=CH), 4.54 - 4.58 (d, J = 12.6 Hz, 1H; N- CH_2 -C=C), 4.03 - 4.08 (d, J = 14.4 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.68 - 3.73 (d, J = 15.0 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.56 - 3.59 (d, J = 9.9 Hz, 1H; N- CH_2 -C-C=C), 3.44 - 3.47 (d, J = 11.1 Hz, 1H; N- CH_2 -C=CH), 2.97 - 3.01 (d, J = 9.6 Hz, 1H; N- CH_2 -C-C=C), 2.54 - 2.56 (d, J = 7.5 Hz, 1H; C- CH_2 -C=CH), 2.49 (s, 3H; O=C- CH_3), 2.16 - 2.20 (d, J = 12.3 Hz, 2H; N- CH_2 -C=C, C- CH_2 -C=CH), 1.90 - 1.94 (d, J = 11.7 Hz, 1H; N- CH_2 -C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 197.0, 145.4, 141.3, 138.1, 135.6, 135.2, 133.1, 132.8, 130.1, 129.5, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.1, 127.9, 127.8, 127.5, 127.5, 127.3, 127.1, 56.5, 52.9, 52.7, 48.0, 47.2, 43.4, 26.5 ppm; FT-IR (neat): ν 3057.2, 3024.4, 2956.9, 2829.9, 2850.8, 2347.4,

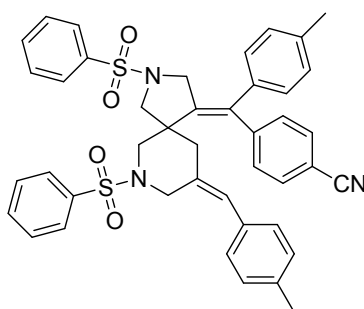
2308.8, 1681.9 (C=O), 1600.9, 1462.0, 1444.7, 1350.2, 1265.3, 1166.9, 1091.7, 1014.6, 960.6, 925.8, 823.6, 752.2, 690.5 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{42}\text{H}_{38}\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 715.2295; found: 715.2296.



1-(3-((E)-((Z)-9-benzylidene-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-

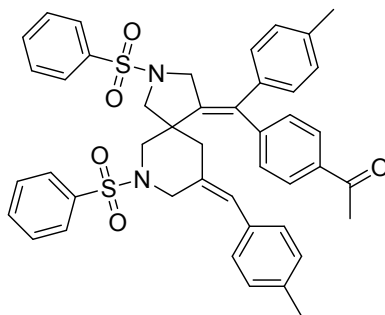
ylidene)(phenyl)methyl)phenyl)ethanone(ec)

White solid; 364 mg (51 % yield); m.p. 204 - 205 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.45; ^1H NMR (300 MHz, CDCl_3): δ 7.77 - 7.80 (d, J = 7.2 Hz, 2H; Ar-H), 7.65 - 7.68 (t, 3H; Ar-H), 7.54 - 7.59 (m, 3H; Ar-H), 7.41 - 7.47 (m, 4H; Ar-H), 7.24 - 7.36 (m, 8H; Ar-H), 7.08 - 7.13 (t, 4H; Ar-H), 6.34 (s, 1H; C=CH), 4.54 - 4.58 (d, J = 12.3 Hz, 1H; N- CH_2 -C=C), 4.03 - 4.08 (d, J = 14.4 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.71 - 3.76 (d, J = 14.4 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.48 - 3.55 (t, 2H; N- CH_2 -C-C=C, N- CH_2 -C=CH), 3.02 - 3.06 (d, J = 10.2 Hz, 1H; N- CH_2 -C-C=C), 2.46 - 2.50 (d, J = 12.9 Hz, 1H; C- CH_2 -C=CH), 2.46 (s, 3H; O=C- CH_3), 2.11 - 2.21 (t, 2H; N- CH_2 -C=C, C- CH_2 -C=CH), 1.93 - 1.97 (d, J = 11.4 Hz, 1H; N- CH_2 -C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 197.1, 141.6, 140.9, 138.2, 136.9, 135.7, 135.6, 135.5, 133.1, 132.7, 129.9, 129.5, 129.2, 129.1, 129.0, 128.7, 128.5, 128.1, 127.9, 127.7, 127.5, 127.4, 127.3, 127.2, 56.5, 52.9, 52.7, 48.1, 47.1, 43.5, 26.7 ppm; FT-IR (neat): ν 3057.2, 3026.3, 2958.8, 2933.7, 2877.8, 2345.4, 1685.8 (C=O), 1597.1, 1491.0, 1444.7, 1346.3, 1249.9, 1168.9, 1091.7, 1014.6, 964.4, 927.8, 819.8, 754.2, 692.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{42}\text{H}_{38}\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 715.2295; found: 715.2304.



4-((E)-((Z)-9-(4-methylbenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(p-tolyl)methyl)benzonitrile(fa)

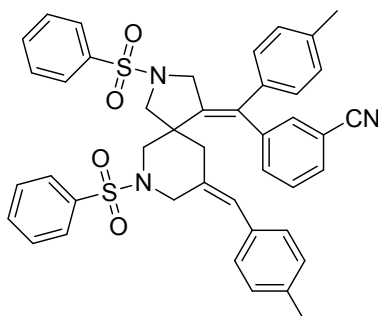
White solid; 537 mg (74 % yield); m.p. 154 - 155 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ^1H NMR (300 MHz, CDCl_3): δ 7.77 - 7.79 (d, J = 7.2 Hz, 2H; Ar-H), 7.53 - 7.68 (m, 4H; Ar-H), 7.42 - 7.50 (m, 6H; Ar-H), 7.11 - 7.19 (m, 6H; Ar-H), 7.01 - 7.04 (d, J = 7.8 Hz, 2H; Ar-H), 6.90 - 6.92 (d, J = 8.1 Hz, 2H; Ar-H), 6.32 (s, 1H; C=CH), 4.59 - 4.63 (d, J = 11.4 Hz, 1H; N-CH₂-C=C), 4.04 - 4.08 (d, J = 14.1 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.69 - 3.74 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.57 - 3.60 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 3.35 - 3.39 (d, J = 11.7 Hz, 1H; N-CH₂-C=CH), 2.95 - 2.98 (d, J = 10.2 Hz, 1H; N-CH₂-C-C=C), 2.48 - 2.52 (d, J = 14.4 Hz, 1H; C-CH₂-C=CH), 2.35 (s, 3H; Ar-CH₃), 2.32 (s, 3H; Ar-CH₃), 2.16 - 2.20 (d, J = 14.4 Hz, 1H; N-CH₂-C=C), 2.04 - 2.10 (d, J = 18.9 Hz, 1H; C-CH₂-C=CH), 1.70 - 1.73 (d, J = 11.1 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 145.5, 138.6, 137.9, 137.9, 137.2, 137.2, 135.5, 134.8, 133.3, 132.7, 132.1, 130.3, 129.9, 129.3, 129.3, 129.1, 128.7, 128.5, 127.9, 127.5, 127.0, 118.2, 111.3, 56.4, 53.0, 52.7, 48.0, 47.4, 43.6, 21.3, 21.2 ppm; FT-IR (neat): ν 3057.2, 3022.5, 2953.0, 2922.2, 2868.2, 2380.2, 2308.8, 1602.9, 1446.6, 1350.2, 1165.0, 1091.7, 1041.6, 1012.6, 823.6, 719.5, 690.5 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{39}\text{N}_3\text{O}_4\text{S}_2$ [$\text{M} + \text{H}$]⁺, 726.2455; found: 726.2456.



1-(4-((E)-((Z)-9-(4-methylbenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(p-tolyl)methyl)phenyl)ethanone(fb)

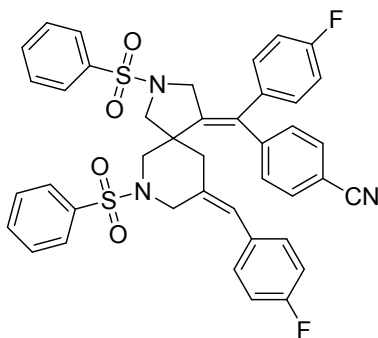
White solid; 497 mg (67 % yield); m.p. 161 - 162 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.42; ^1H NMR (300 MHz, CDCl_3): δ 7.76 - 7.80 (d, J = 7.2 Hz, 2H; Ar-H), 7.72-7.75 (d, J = 7.8 Hz, 2H; Ar-H), 7.51-7.65 (m, 5H; Ar-H), 7.40-7.46 (m, 3H; Ar-H), 7.10 - 7.18 (m, 5H; Ar-H), 7.00 - 7.02 (d, J = 7.5 Hz, 2H; Ar-H), 6.93 - 6.95 (d, J = 7.2 Hz, 2H; Ar-H), 6.31 (s, 1H; C=CH), 4.53 - 4.59 (d, J = 19.2 Hz, 1H; N-CH₂-C=C), 4.04 - 4.09 (d, J = 14.4 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.70 - 3.75 (d, J = 15.0 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.54 - 3.57 (d, J = 9.9 Hz, 1H; N-CH₂-C-C=C), 3.41 - 3.45 (d, J = 7.8 Hz, 1H; N-CH₂-C=CH), 2.96 - 3.00 (d, J = 10.2 Hz, 1H; N-CH₂-C-C=C), 2.46 - 2.49 (d, J = 9.9 Hz, 4H; C-CH₂-C=CH, O=C-CH₃), 2.34 (s, 3H; Ar-CH₃), 2.31 (s, 3H; Ar-CH₃), 2.14 - 2.17 (d, J = 10.5 Hz, 2H; N-CH₂-C=C, C-CH₂-C=CH), 1.87 - 1.91 (d, J = 9.6 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 197.0, 145.6, 138.4, 138.0, 137.8, 137.6, 137.1, 135.7, 135.5, 135.0, 133.1, 132.8, 130.0,

129.7, 129.2, 129.0, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.7, 127.5, 127.0, 56.5, 53.0, 52.8, 47.9, 47.2, 43.4, 26.5, 21.2, 21.1 ppm; FT-IR (neat): ν 3061.0, 3024.4, 2953.0, 2920.2, 2868.2, 2349.3, 2306.9, 1683.9 (C=O), 1602.9, 1510.3, 1446.6, 1348.2, 1265.3, 1166.9, 1091.7, 1008.8, 964.4, 821.7, 754.2, 692.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{44}\text{H}_{42}\text{N}_2\text{O}_5\text{S}_2$ $[\text{M} + \text{H}]^+$, 743.2608; found: 743.2604.



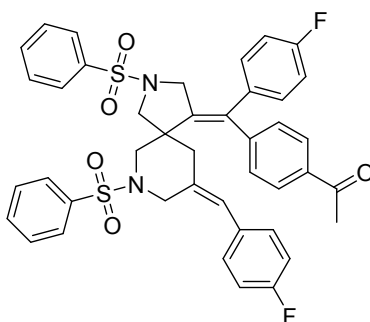
3-((E)-((Z)-9-(4-methylbenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(p-tolyl)methyl)benzonitrile(fc)

White solid; 500 mg (69 % yield); m.p. 141 - 142 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ^1H NMR (300 MHz, CDCl_3): δ 7.78 - 7.80 (d, J = 6.9 Hz, 2H; Ar-H), 7.51 - 7.65 (m, 8H; Ar-H), 7.27 - 7.38 (m, 4H; Ar-H), 7.12 - 7.17 (t, 4H; Ar-H), 7.01 - 7.04 (d, J = 7.8 Hz, 2H; Ar-H), 6.91 - 6.93 (d, J = 8.1 Hz, 2H; Ar-H), 6.33 (s, 1H; C=CH), 4.59 - 4.63 (d, J = 12.3 Hz, 1H; N- CH_2 -C=C), 4.03 - 4.08 (d, J = 15.0 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.70 - 3.75 (d, J = 14.4 Hz, 1H; C- CH_2 -N- CH_2 -C=CH), 3.53 - 3.56 (d, J = 9.6 Hz, 1H; N- CH_2 -C-C=C), 3.44 - 3.48 (d, J = 11.1 Hz, 1H; N- CH_2 -C=CH), 3.01 - 3.04 (d, J = 9.9 Hz, 1H; N- CH_2 -C-C=C), 2.45 - 2.50 (d, J = 13.2 Hz, 1H; C- CH_2 -C=CH), 2.35 (s, 3H; Ar- CH_3), 2.31 (s, 3H; Ar- CH_3), 2.19 - 2.23 (d, J = 12.6 Hz, 1H; N- CH_2 -C=C), 2.03 - 2.08 (d, J = 12.9 Hz, 1H; C- CH_2 -C=CH), 1.80 - 1.83 (d, J = 10.8 Hz, 1H; N- CH_2 -C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 142.0, 139.0, 138.1, 137.9, 137.2, 136.8, 135.2, 134.8, 133.1, 133.1, 132.9, 132.7, 131.9, 131.0, 129.9, 129.3, 129.2, 128.6, 128.5, 127.9, 127.4, 127.0, 118.1, 112.6, 56.5, 53.0, 52.8, 48.1, 47.3, 43.6, 21.2, 21.2 ppm; FT-IR (neat): ν 3063.0, 3024.4, 2955.0, 2922.2, 2866.2, 2378.2, 2229.7, 1610.6, 1510.3, 1446.6, 1350.2, 1091.7, 1043.5, 1012.6, 962.5, 825.5, 804.3, 756.1, 719.5, 690.5 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{43}\text{H}_{39}\text{N}_3\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 726.2455; found: 726.2463.



4-((Z)-((Z)-9-(4-fluorobenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(4-fluorophenyl)methyl)benzonitrile(ga)

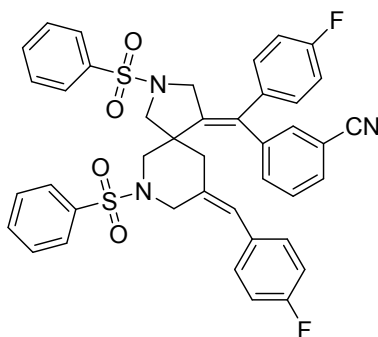
White solid; 564 mg (77 % yield); m.p. 168 - 169 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ^1H NMR (300 MHz, CDCl_3): δ 7.78 (s, 2H; Ar-H), 7.63 - 7.67 (t, 5H; Ar-H), 7.48 - 7.57 (m, 6H; Ar-H), 7.18 - 7.20 (d, J = 6.3 Hz, 2H; Ar-H), 7.02 - 7.20 (m, 7H; Ar-H), 6.34 (s, 1H; C=CH), 4.52 - 4.55 (d, J = 14.7 Hz, 1H; N-CH₂-C=CH), 4.03 - 4.08 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.60 - 3.69 (t, 2H; C-CH₂-N-CH₂-C=CH, N-CH₂-C-C=CH), 3.37 - 3.41 (d, J = 10.8 Hz, 1H; N-CH₂-C=CH), 2.94 - 2.97 (d, J = 9.0 Hz, 1H; N-CH₂-C-C=CH), 2.52 - 2.56 (d, J = 12.6 Hz, 1H; C-CH₂-C=CH), 2.17 - 2.21 (d, J = 12.0 Hz, 1H; N-CH₂-C-C=CH), 2.06 - 2.11 (d, J = 13.8 Hz, 1H; C-CH₂-C=CH), 1.71 - 1.75 (d, J = 10.5 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 163.8 (d, $J_{\text{C-F}}$ = 249.0 Hz), 163.6 (d, $J_{\text{C-F}}$ = 247.4 Hz), 145.0, 139.4, 136.3, 135.4, 134.7, 133.4, 133.2, 131.5, 130.5, 130.4, 129.3, 129.2, 129.1, 129.0, 128.0, 127.9, 127.4, 118.0, 116.5, 116.2, 115.7, 115.4, 111.7, 56.4, 52.8, 52.6, 48.1, 47.2, 43.4 ppm; FT-IR (neat): ν 3056.6, 2957.3, 2871.5, 2347.9, 2308.8, 1600.7, 1504.4, 1438.2, 1346.3, 1223.7, 1163.8, 1091.7, 1008.4, 962.6, 815.9, 742.7, 714.6, 692.5 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{41}\text{H}_{33}\text{F}_2\text{N}_3\text{O}_4\text{S}_2$ $[\text{M} + \text{H}]^+$, 734.1953; found: 734.1943.



1-(4-((Z)-((Z)-9-(4-fluorobenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(4-fluorophenyl)methyl)phenyl)ethanone(gb)

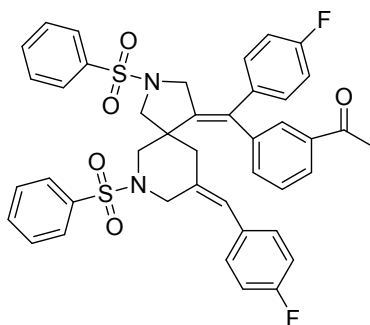
White solid; 540 mg (72 % yield); m.p. 150 - 151 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.44; ^1H NMR (300 MHz, CDCl_3): δ 7.74 - 7.80 (t, 4H; Ar-H), 7.50 - 7.65 (m, 4H; Ar-H), 7.41 - 7.47 (m, 4H; Ar-H), 7.15 - 7.18 (d, J = 8.1 Hz, 2H; Ar-H), 7.00 - 7.08 (m, 8H; Ar-H), 6.32 (s, 1H; C=CH), 4.46 -

4.50 (d, $J = 12.3$ Hz, 1H; N-CH₂-C=C), 4.02 - 4.07 (d, $J = 14.7$ Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.65 - 3.70 (d, $J = 14.7$ Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.56 - 3.59 (d, $J = 9.9$ Hz, 1H; N-CH₂-C-C=C), 3.42 - 3.46 (d, $J = 11.7$ Hz, 1H; N-CH₂-C=CH), 2.97 - 3.00 (d, $J = 9.9$ Hz, 1H; N-CH₂-C-C=C), 2.49 - 2.53 (d, $J = 9.6$ Hz, 4H; C-CH₂-C=CH, O=C-CH₃), 2.14 - 2.18 (d, $J = 12.6$ Hz, 2H; N-CH₂-C-C=C, C-CH₂-C=CH), 1.88 - 1.92 (d, $J = 14.4$ Hz, 1H; N-CH₂-C=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ 196.9, 163.7 (d, $J_{C-F} = 248.3$ Hz), 163.6 (d, $J_{C-F} = 246.7$ Hz), 145.1, 138.5, 137.2, 135.9, 134.9, 133.2, 132.9, 130.5, 130.4, 129.6, 129.3, 129.1, 129.0, 128.9, 128.8, 128.4, 127.9, 127.4, 116.3, 116.0, 115.7, 115.4, 56.5, 52.9, 52.6, 48.1, 47.1, 43.3, 26.5 ppm; FT-IR (neat): ν 3064.9, 2955.0, 2872.0, 2310.7, 1687.7 (C=O), 1602.9, 1506.4, 1446.6, 1348.2, 1265.3, 1226.7, 1165.0, 1091.7, 1012.6, 960.6, 817.8, 748.4, 719.5, 690.5 cm⁻¹; HRMS (APCI): m/z calcd for C₄₂H₃₆F₂N₂O₅S₂ [M + H]⁺, 751.2107; found: 751.2105.



3-((E)-((Z)-9-(4-fluorobenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(4-fluorophenyl)methyl)benzonitrile(gc)

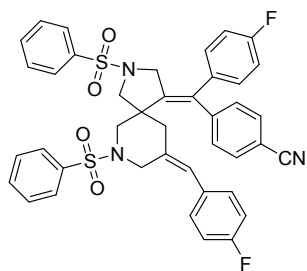
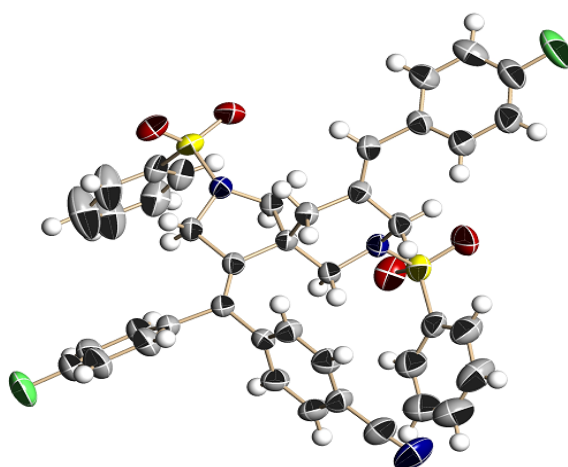
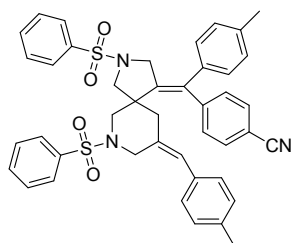
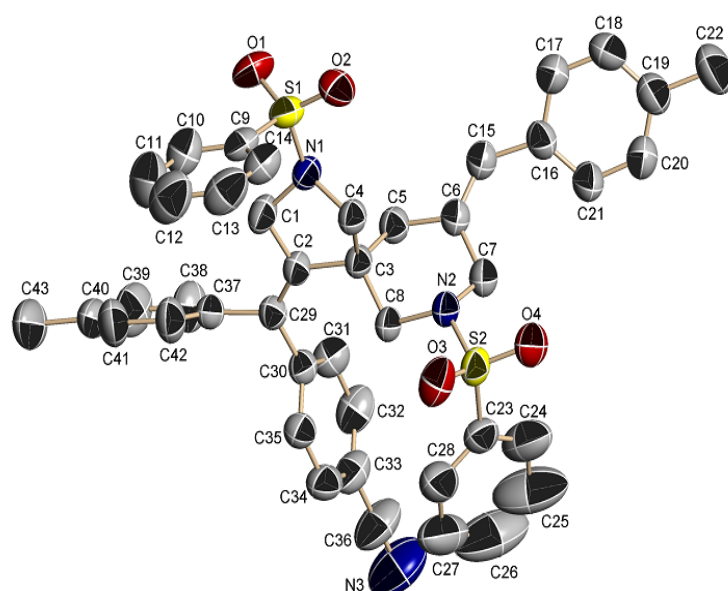
White solid; 550 mg (75 % yield); m.p. 153 - 154 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.50; ¹H NMR (300 MHz, CDCl₃): δ 7.78 - 7.80 (d, $J = 6.9$ Hz, 2H; Ar-H), 7.58 - 7.66 (m, 5H; Ar-H), 7.51 - 7.55 (m, 4H; Ar-H), 7.30 - 7.38 (m, 4H; Ar-H), 7.07 - 7.11 (m, 3H; Ar-H), 7.02 - 7.04 (d, $J = 6.9$ Hz, 4H; Ar-H), 6.34 (s, 1H; C=CH), 4.51 - 4.55 (d, $J = 12.0$ Hz, 1H; N-CH₂-C=C), 4.01 - 4.07 (d, $J = 15.0$ Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.64 - 3.69 (d, $J = 15.0$ Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.55 - 3.59 (d, $J = 10.2$ Hz, 1H; N-CH₂-C-C=C), 3.45 - 3.49 (d, $J = 11.4$ Hz, 1H; N-CH₂-C=CH), 2.99 - 3.03 (d, $J = 9.9$ Hz, 1H; N-CH₂-C-C=C), 2.50 - 2.54 (d, $J = 13.5$ Hz, 1H; C-CH₂-C=CH), 2.18 - 2.22 (d, $J = 12.6$ Hz, 1H; N-CH₂-C-C=C), 2.04 - 2.08 (d, $J = 13.5$ Hz, 1H; C-CH₂-C=CH), 1.80 - 1.83 (d, $J = 11.1$ Hz, 1H; N-CH₂-C=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ 164.1 (d, $J_{C-F} = 273.4$ Hz), 163.7 (d, $J_{C-F} = 269.9$ Hz), 141.5, 139.8, 135.9, 135.3, 135.1, 133.3, 133.2, 132.9, 131.8, 131.2, 130.5, 130.4, 129.3, 129.3, 129.0, 128.9, 127.9, 127.4, 118.0, 116.5, 116.2, 115.7, 115.4, 112.8, 56.4, 52.8, 52.7, 48.2, 47.1, 43.4 ppm; FT-IR (neat): ν 3066.8, 2955.0, 2935.7, 2875.9, 2380.2, 2208.8, 1600.9, 1506.4, 1446.6, 1348.2, 1222.9, 1166.9, 1091.7, 1010.7, 964.4, 927.8, 875.7, 817.8, 756.1, 717.5, 692.4 cm⁻¹; HRMS (APCI): m/z calcd for C₄₁H₃₃F₂N₃O₄S₂ [M + H]⁺, 734.1953; found: 734.1965.

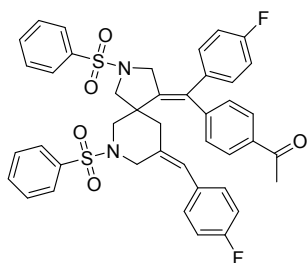
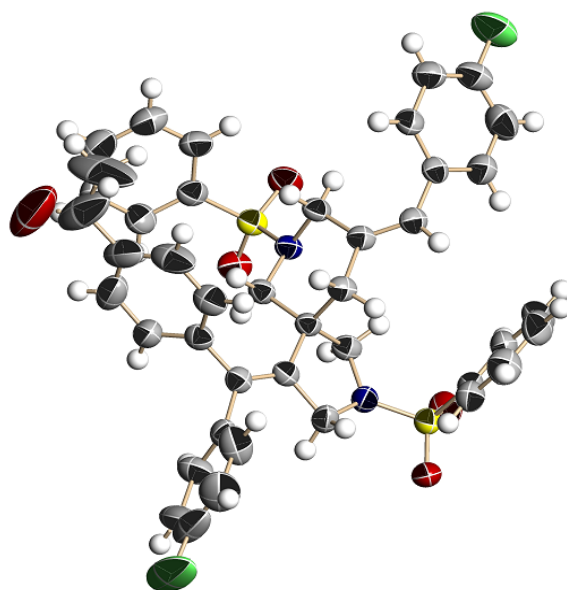


1-(3-((E)-((Z)-9-(4-fluorobenzylidene)-2,7-bis(phenylsulfonyl)-2,7-diazaspiro[4.5]decan-4-ylidene)(4-fluorophenyl)methyl)phenyl)ethanone(gd)

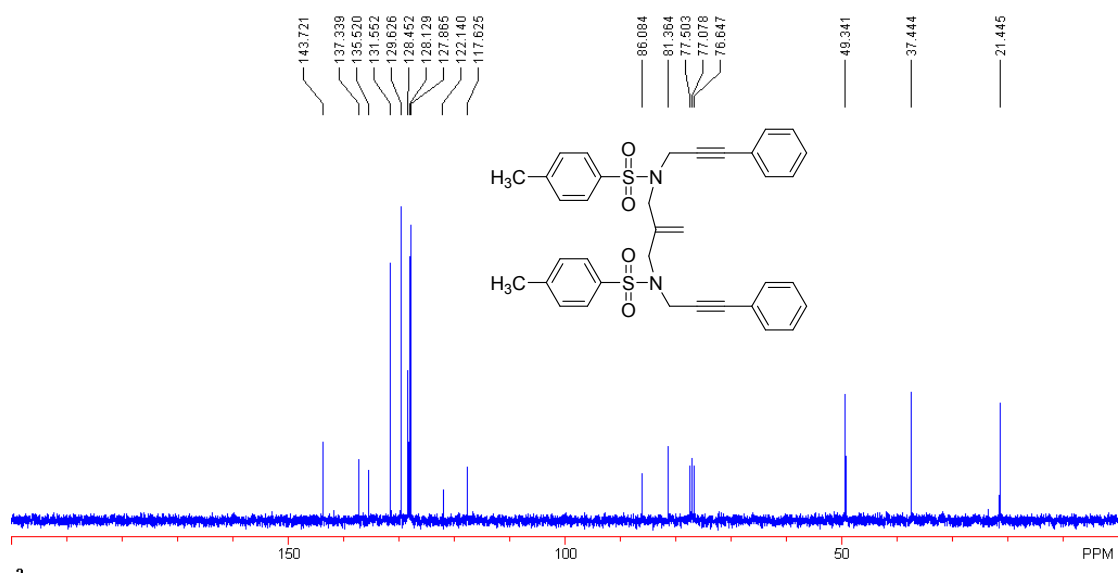
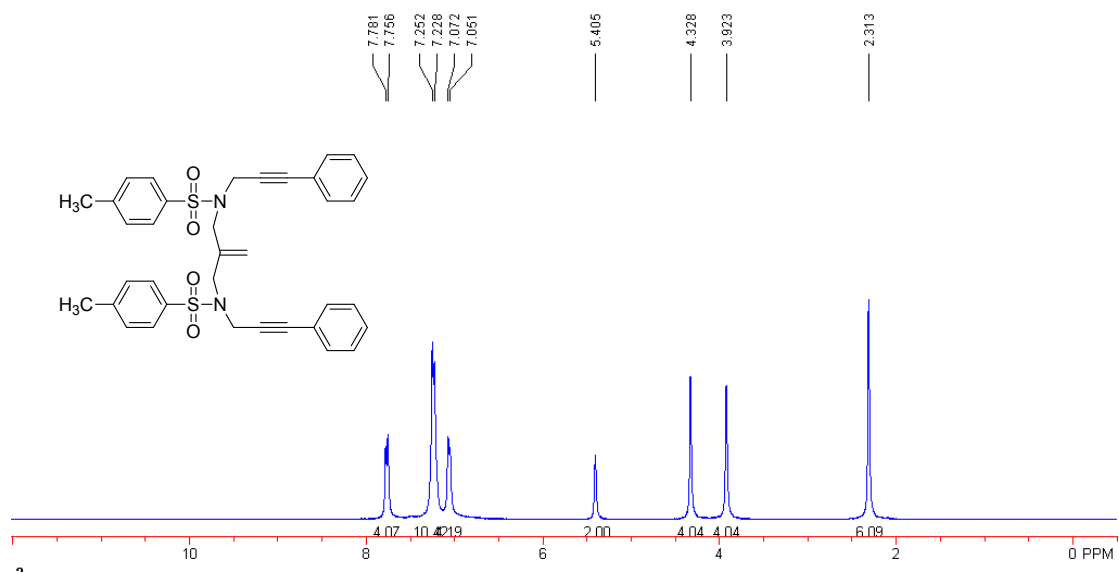
White solid; 503 mg (67 % yield); m.p. 159 - 160 °C; TLC (petroleum ether/EtOAc = 3:1): R_f = 0.44; ^1H NMR (300 MHz, CDCl_3): δ 7.78 - 7.81 (d, J = 7.5 Hz, 2H; Ar-H), 7.55 - 7.68 (m, 6H; Ar-H), 7.42 - 7.47 (m, 4H; Ar-H), 7.28 - 7.30 (d, J = 6.0 Hz, 2H; Ar-H), 6.98 - 7.08 (m, 8H; Ar-H), 6.31 (s, 1H; C=CH), 4.46 - 4.50 (d, J = 12.6 Hz, 1H; N-CH₂-C=C), 4.02 - 4.07 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.67 - 3.72 (d, J = 14.7 Hz, 1H; C-CH₂-N-CH₂-C=CH), 3.53 - 3.57 (d, J = 9.6 Hz, 1H; N-CH₂-C-C=C), 3.46 - 3.50 (d, J = 12.9 Hz, 1H; N-CH₂-C=CH), 3.00 - 3.03 (d, J = 9.6 Hz, 1H; N-CH₂-C-C=C), 2.49 - 2.53 (d, J = 12.0 Hz, 4H; C-CH₂-C=CH, O=C-CH₃), 2.10 - 2.18 (t, 2H; N-CH₂-C-C=C, C-CH₂-C=CH), 1.91 - 1.95 (d, J = 11.4 Hz, 1H; N-CH₂-C=CH); ^{13}C NMR (75.5 MHz, CDCl_3): δ 197.1, 163.6 (d, $J_{\text{C-F}}$ = 255.0 Hz), 163.4 (d, $J_{\text{C-F}}$ = 247.1 Hz), 140.7, 138.6, 137.3, 136.9, 135.4, 133.2, 133.0, 132.8, 131.6, 130.5, 130.4, 129.7, 129.3, 129.1, 128.9, 128.9, 128.7, 127.9, 127.7, 127.4, 116.3, 116.0, 115.7, 115.4, 56.5, 52.8, 52.7, 48.1, 47.0, 43.3, 26.7 ppm; FT-IR (neat): 3070.7, 2935.7, 2885.5, 2812.2, 2351.2, 2306.9, 1681.9 (C=O), 1600.9, 1446.6, 1348.2, 1226.7, 1170.8, 1091.7, 1012.6, 966.3, 817.8, 760.0, 719.5, 694.4 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{42}\text{H}_{36}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$ [$\text{M} + \text{H}$]⁺, 751.2107; found: 751.2101.

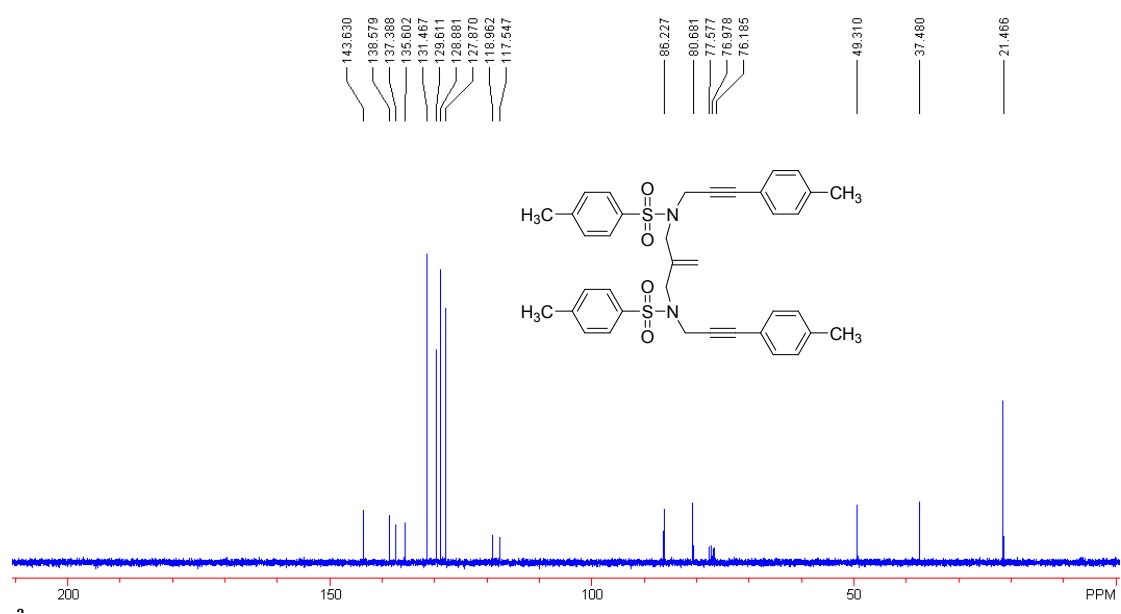
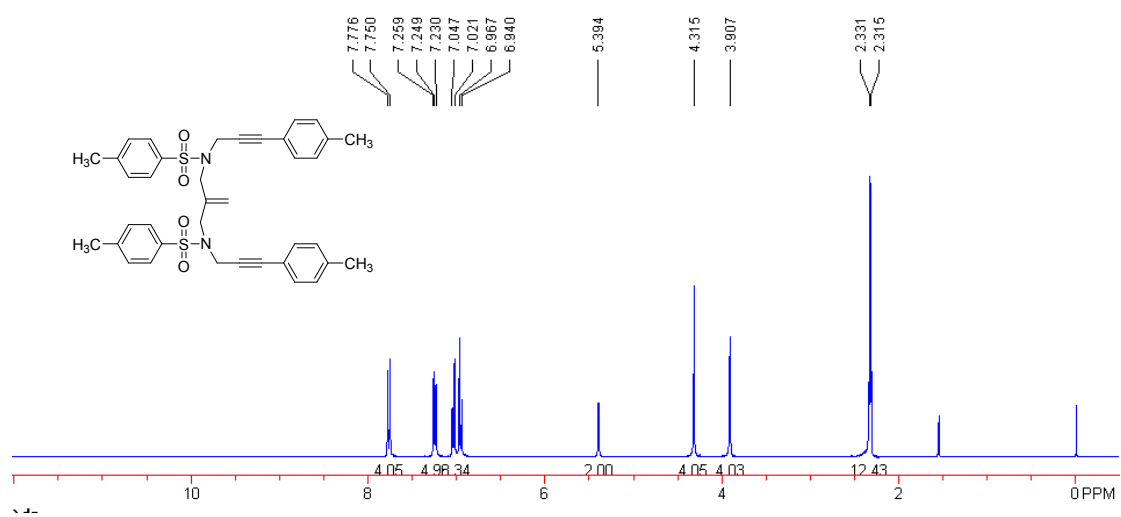
3. X-Ray Structure for fa, ga, and gb

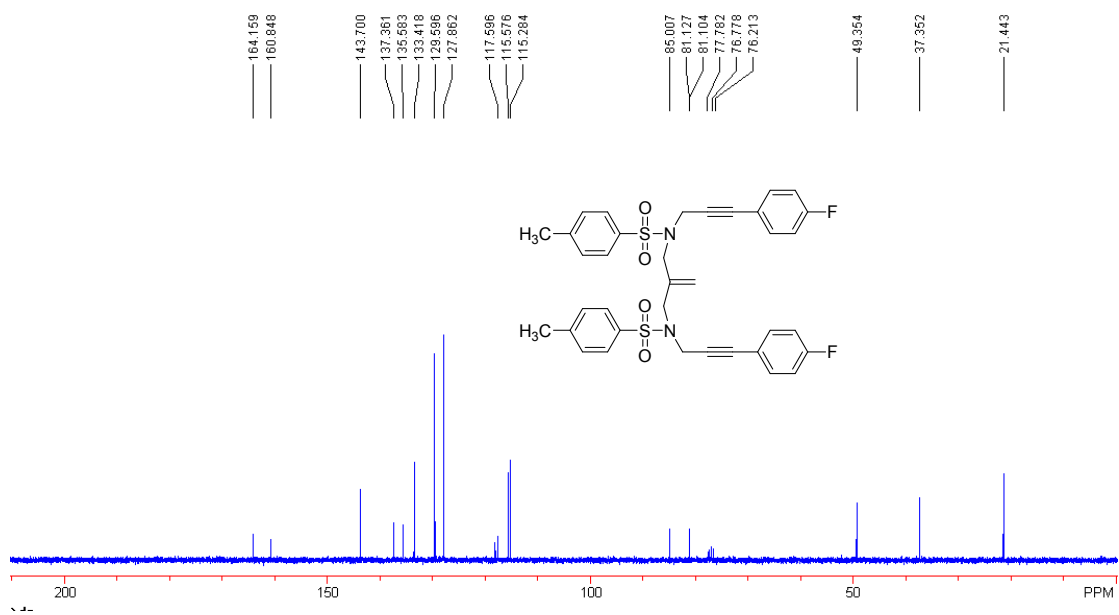
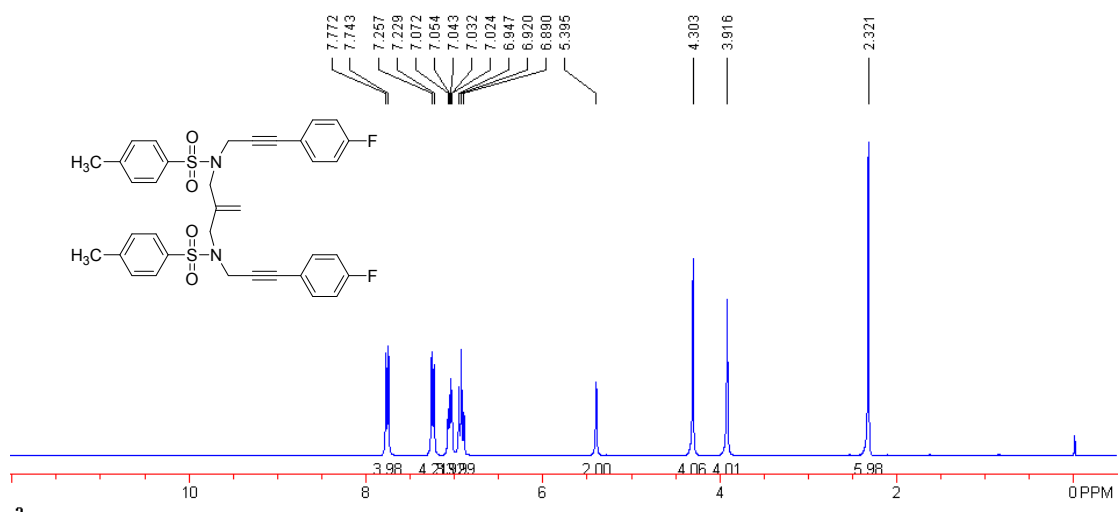


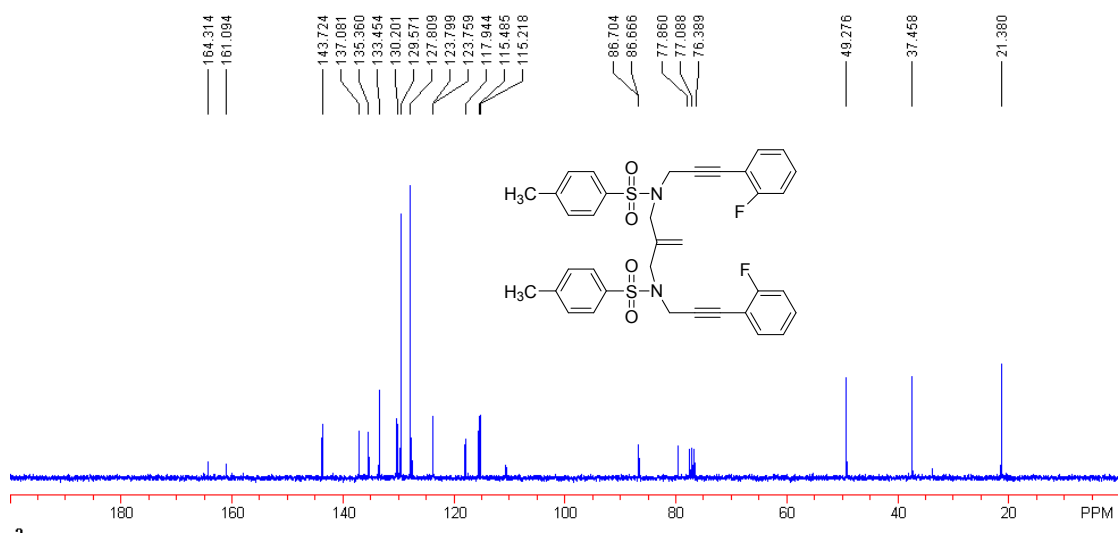
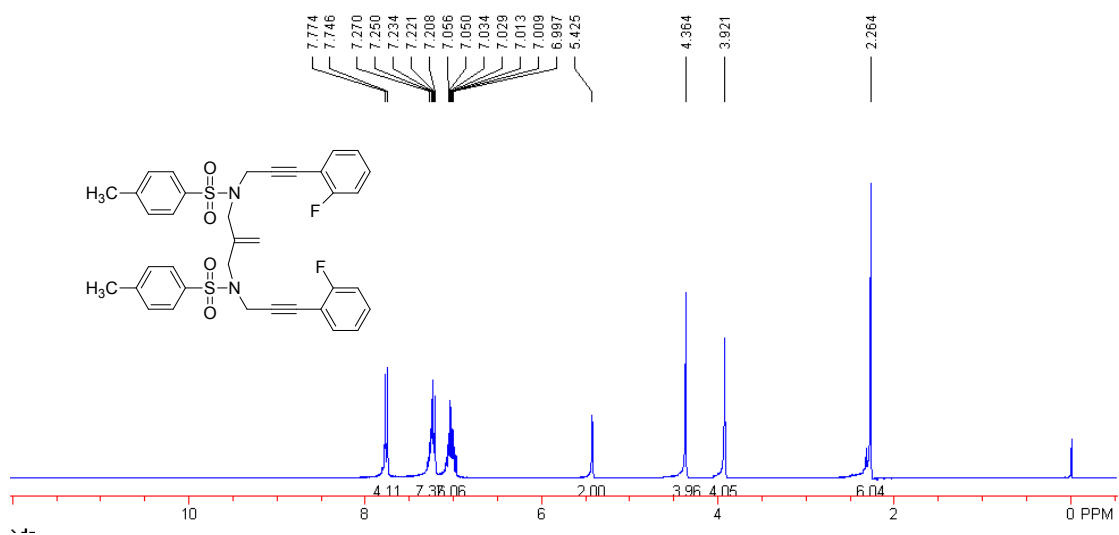


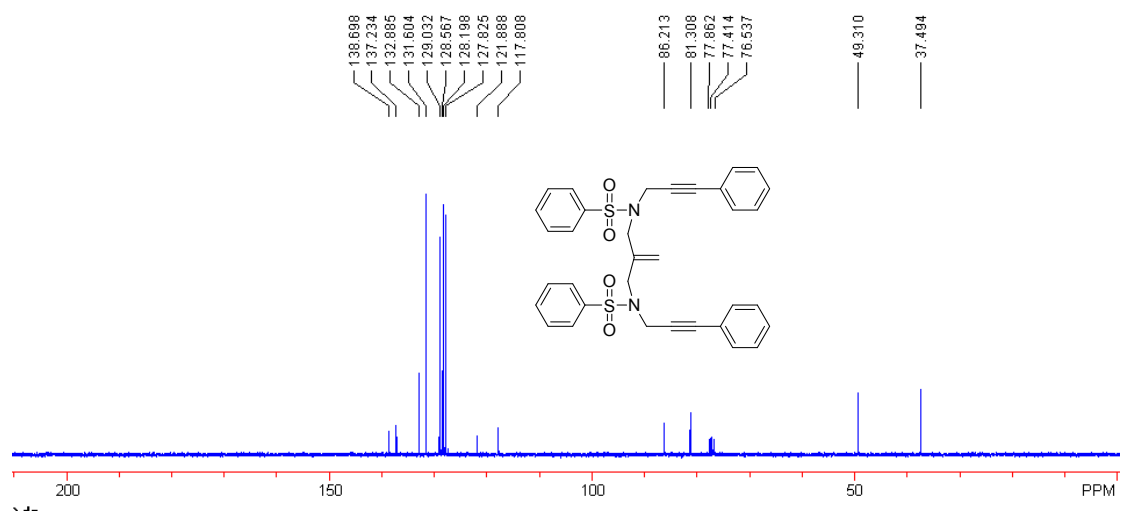
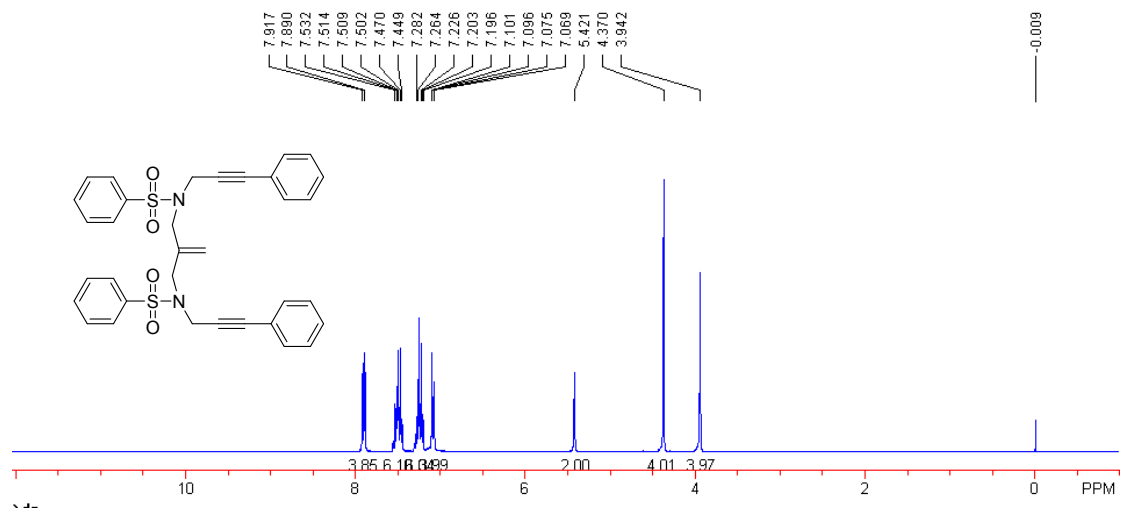
4. ^1H NMR & ^{13}C NMR Spectra for New Compounds

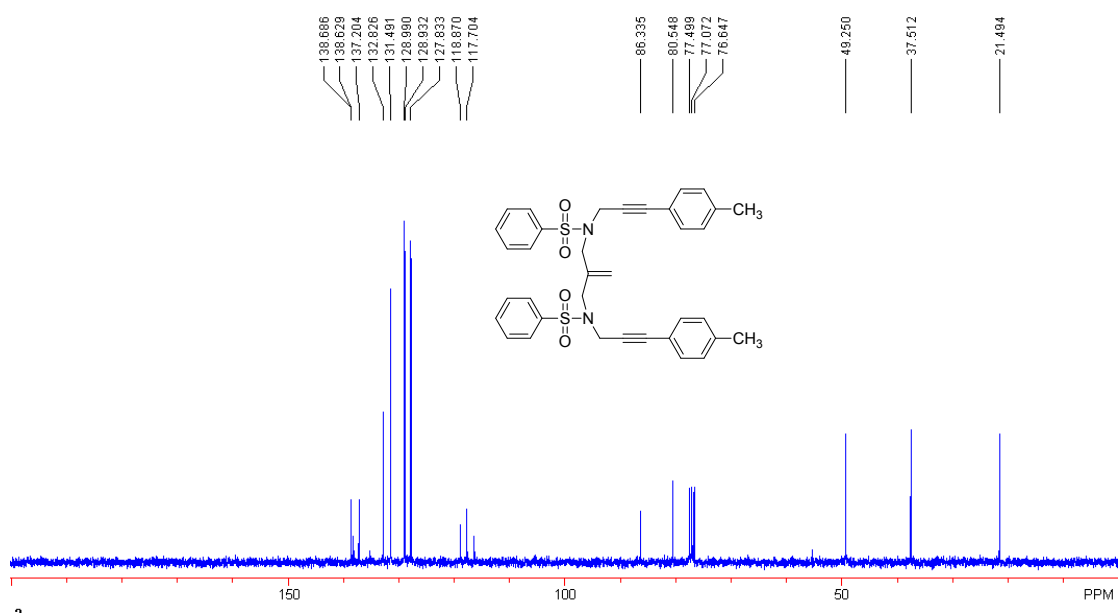
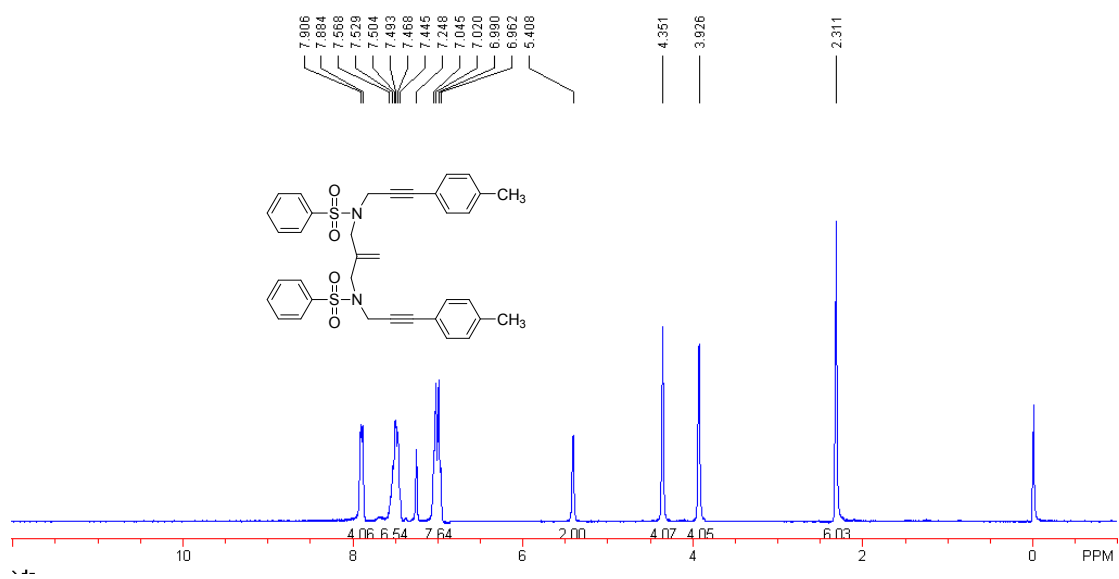


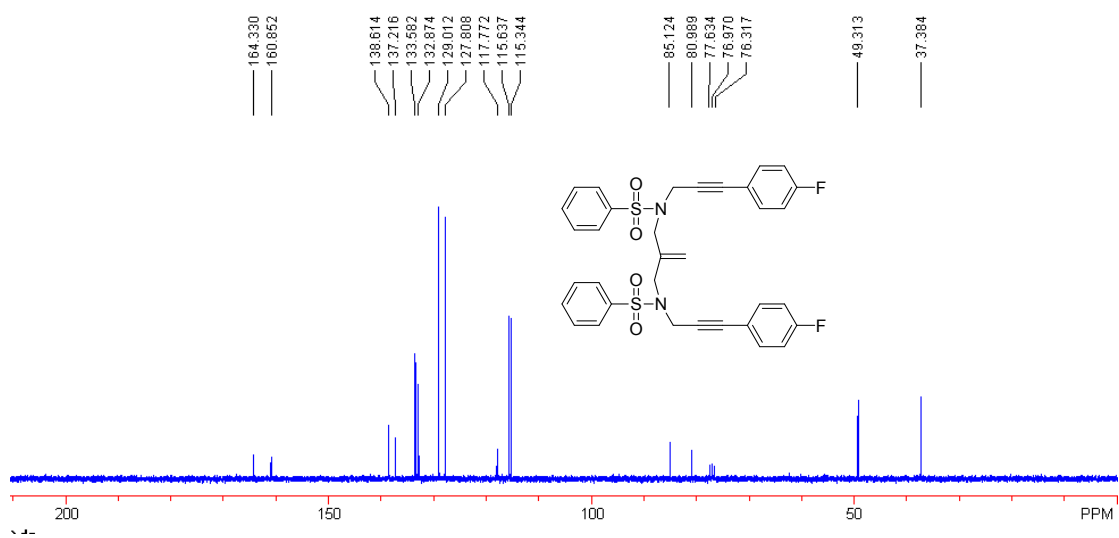
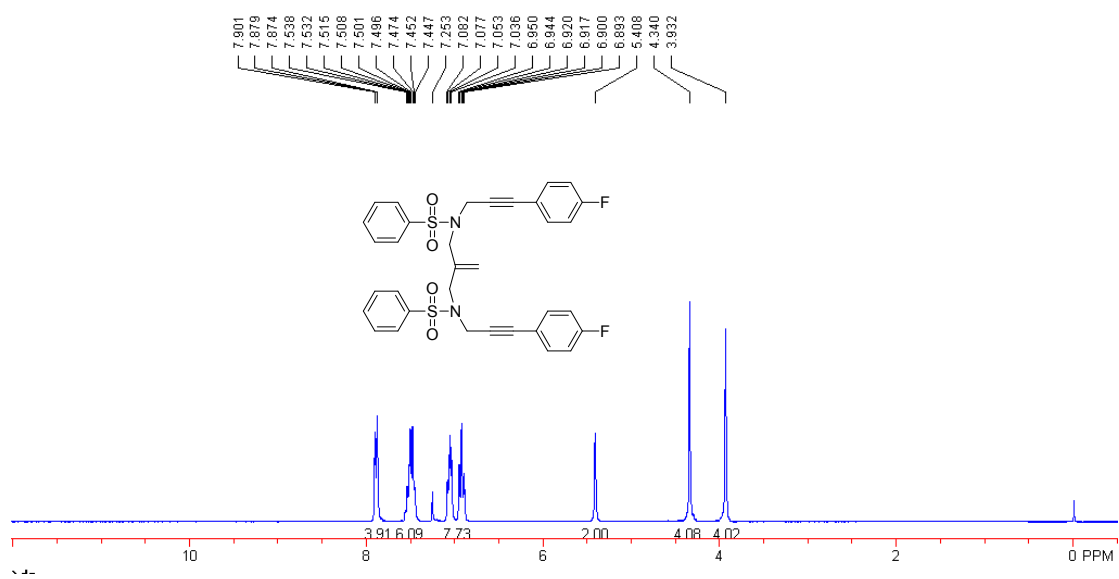


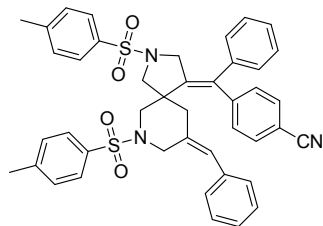
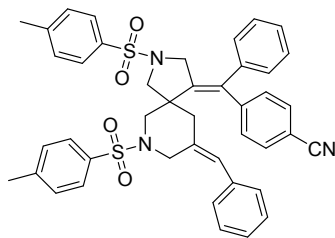


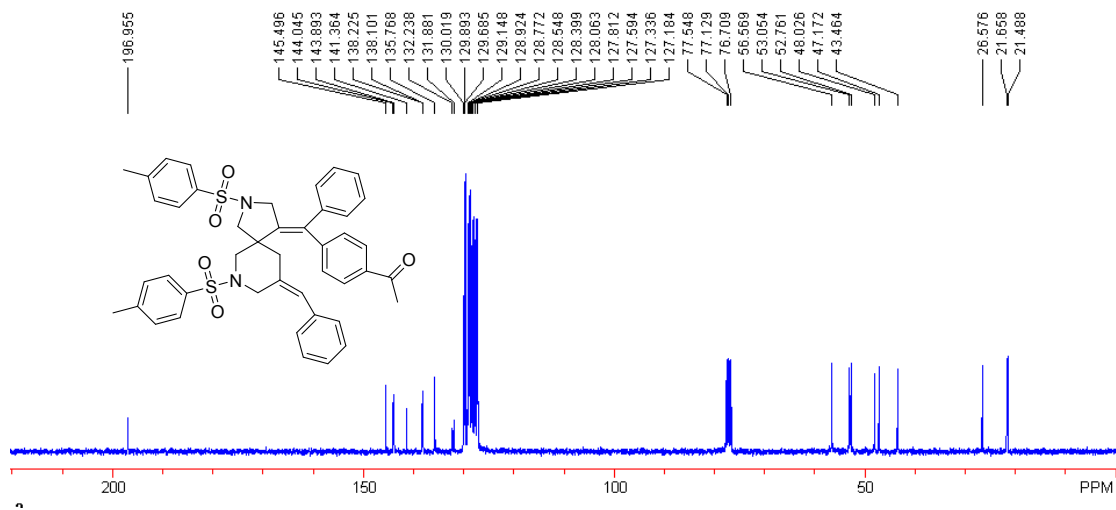
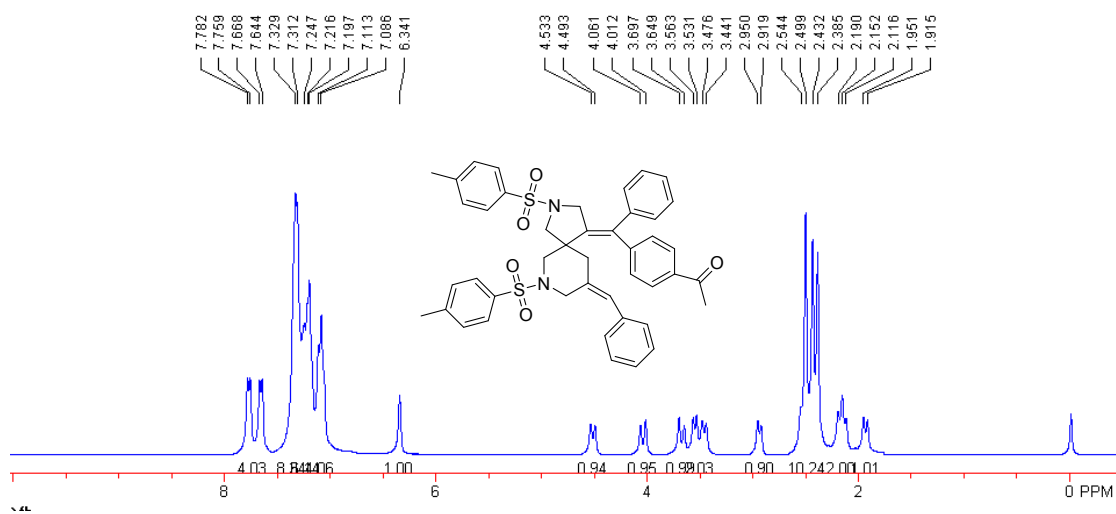


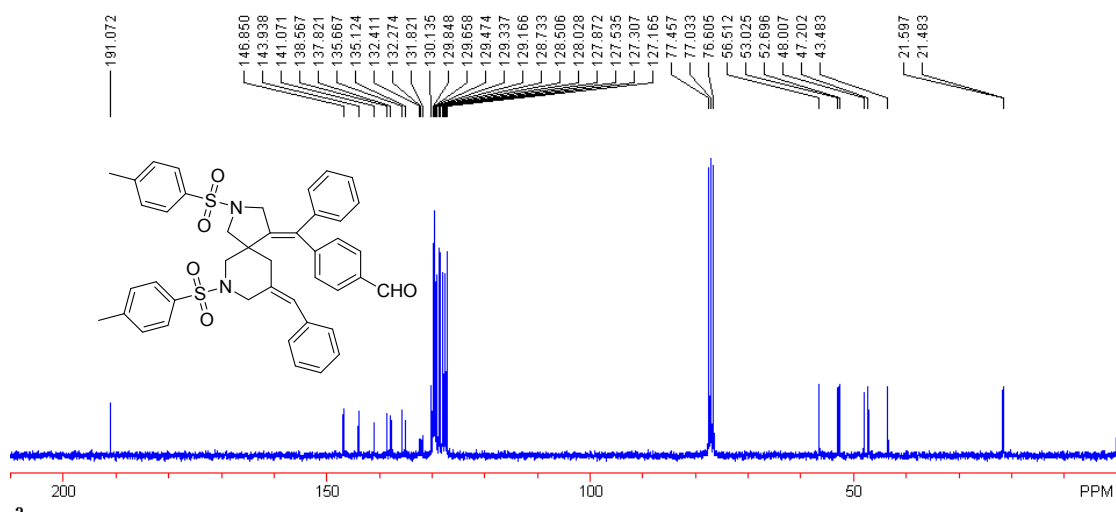
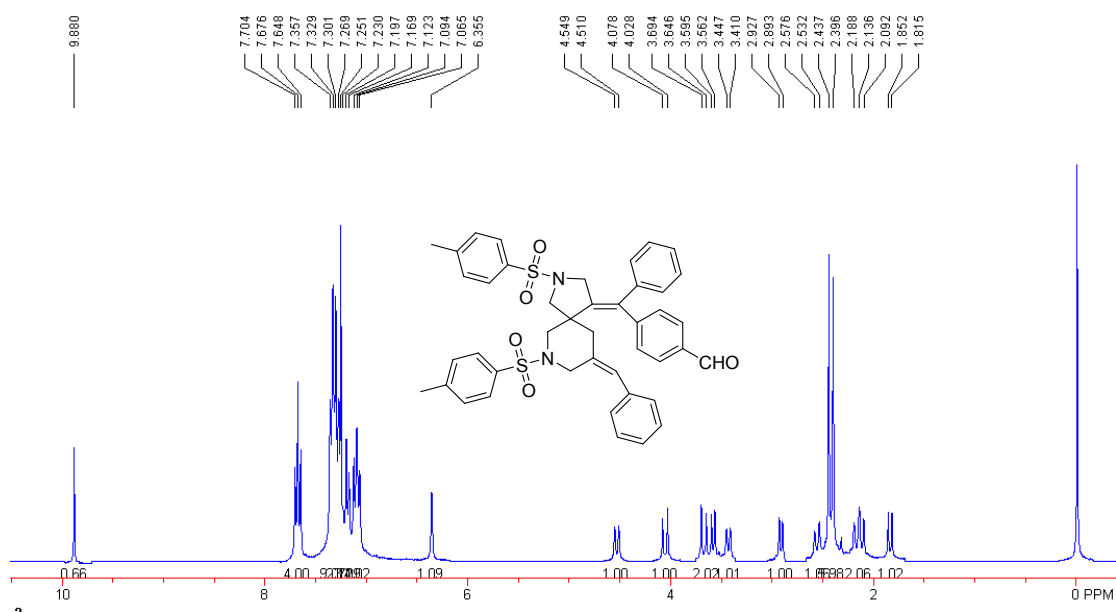


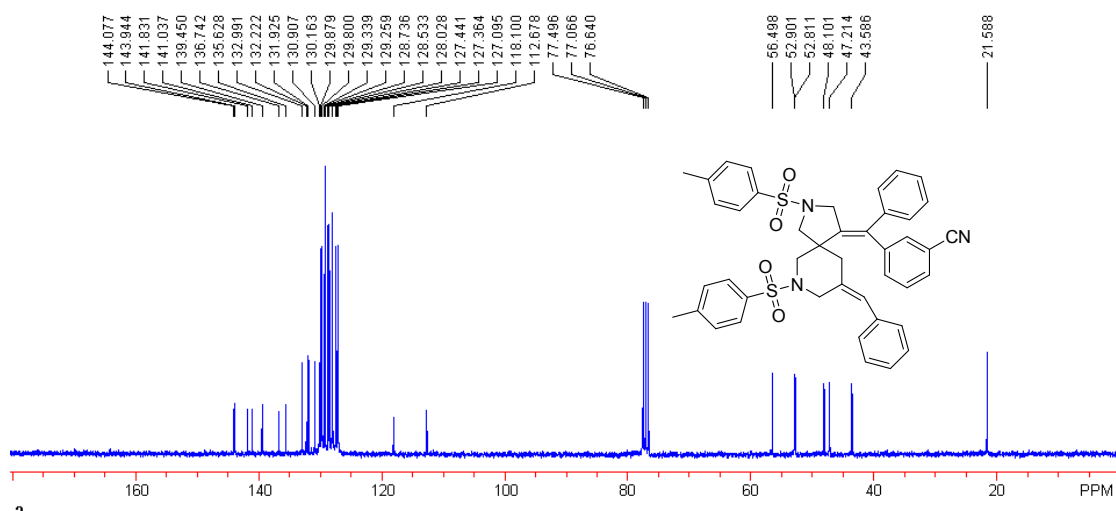
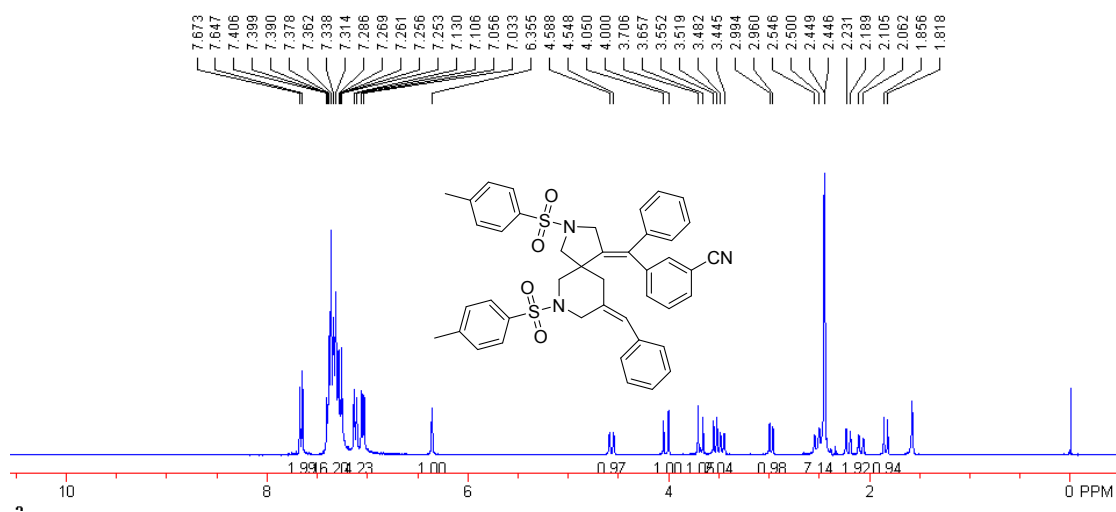


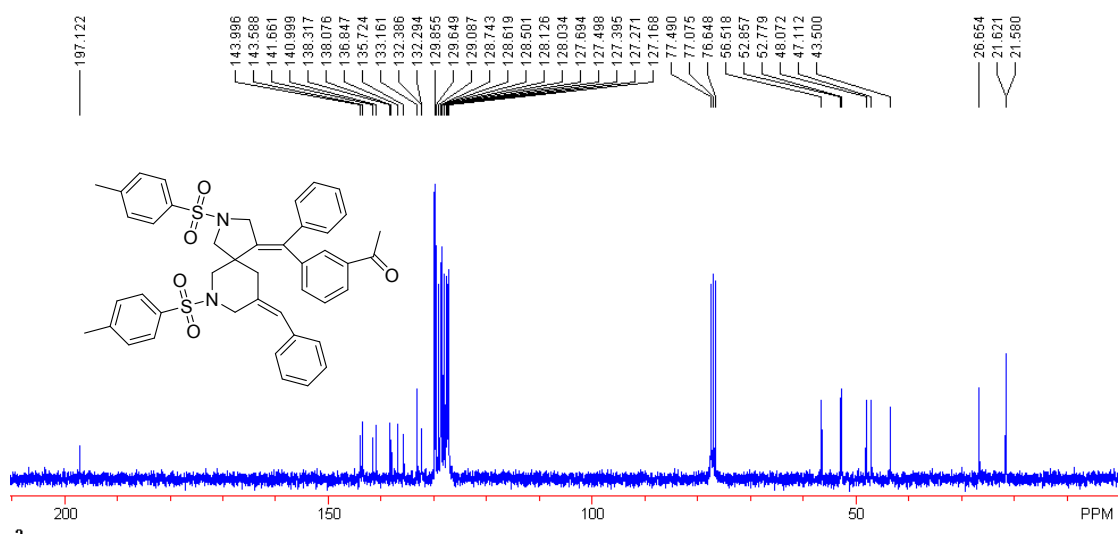
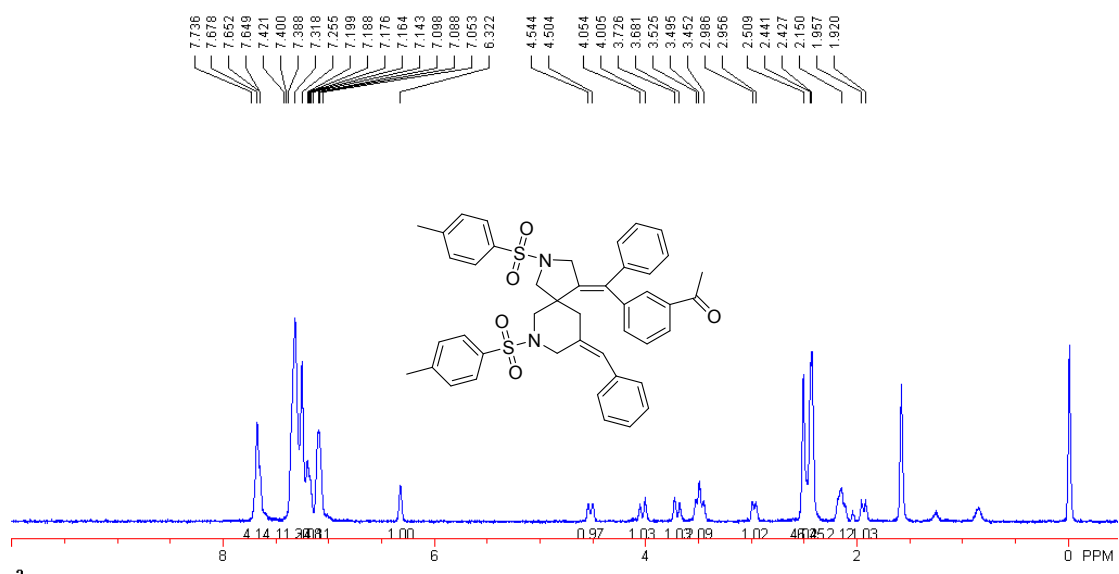


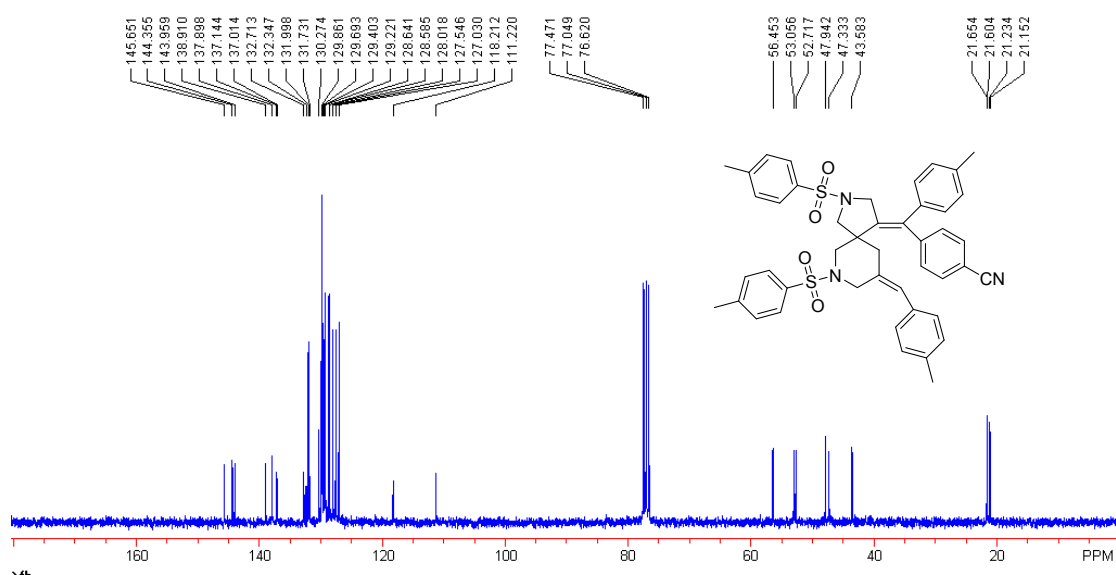
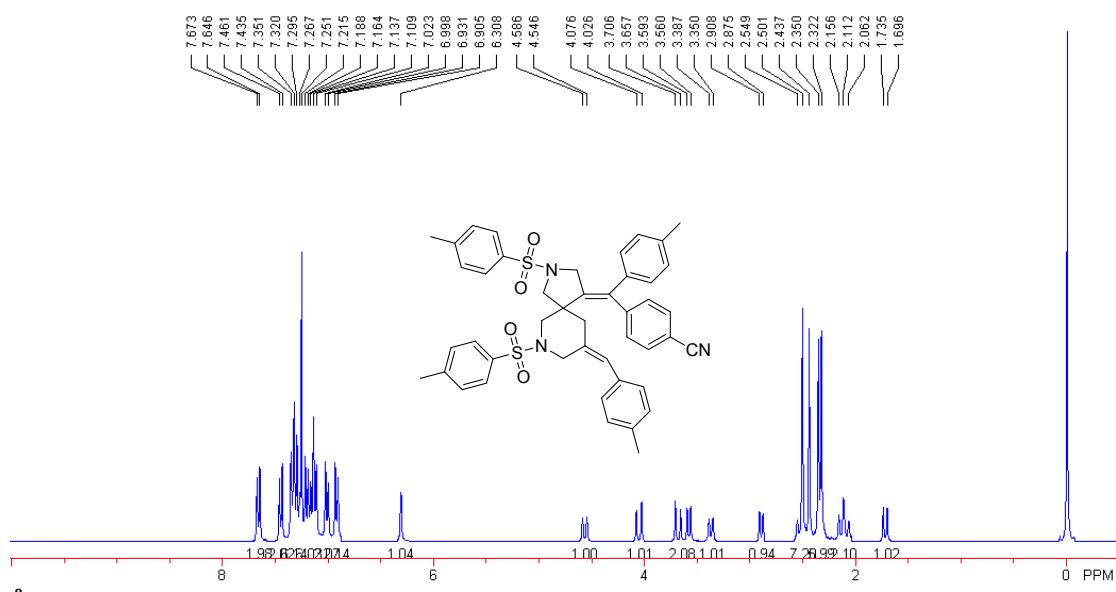


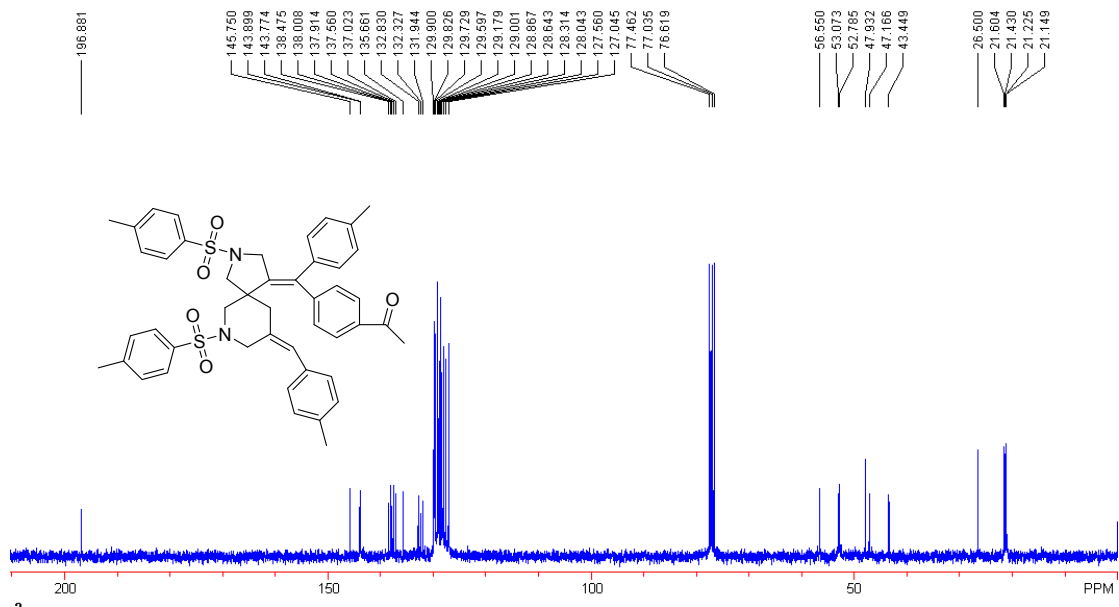
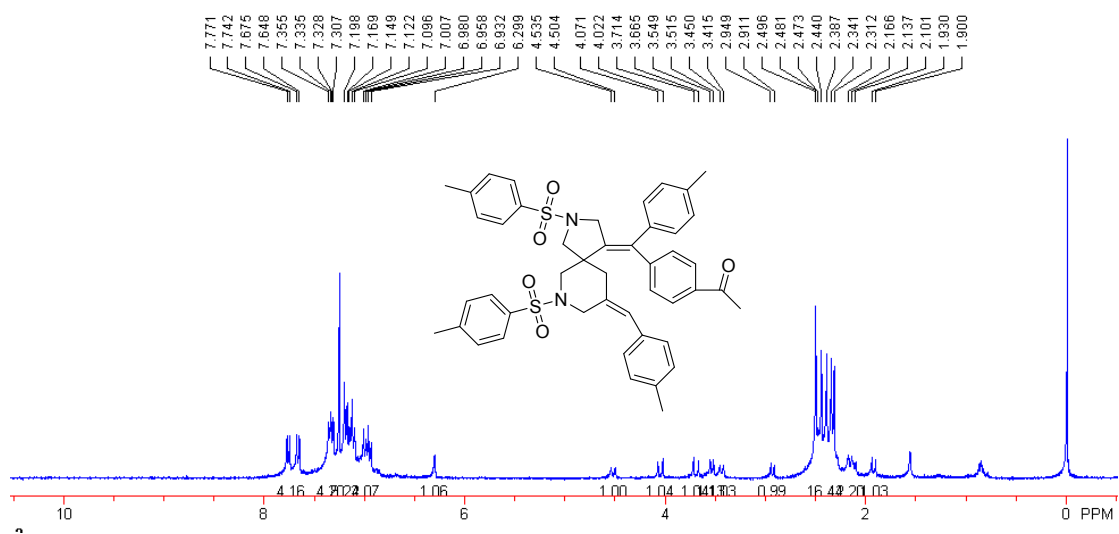


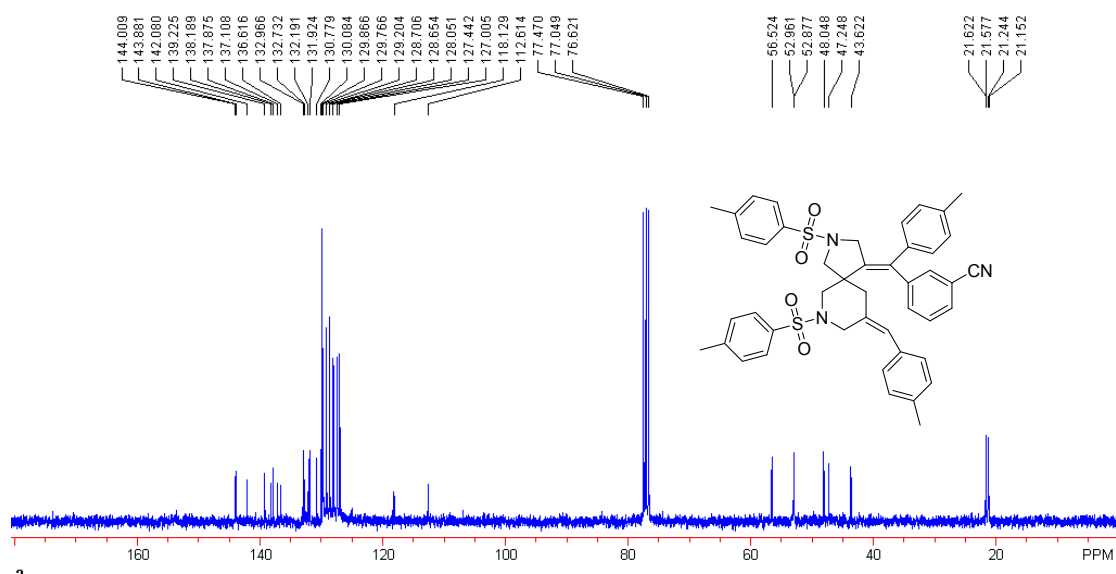
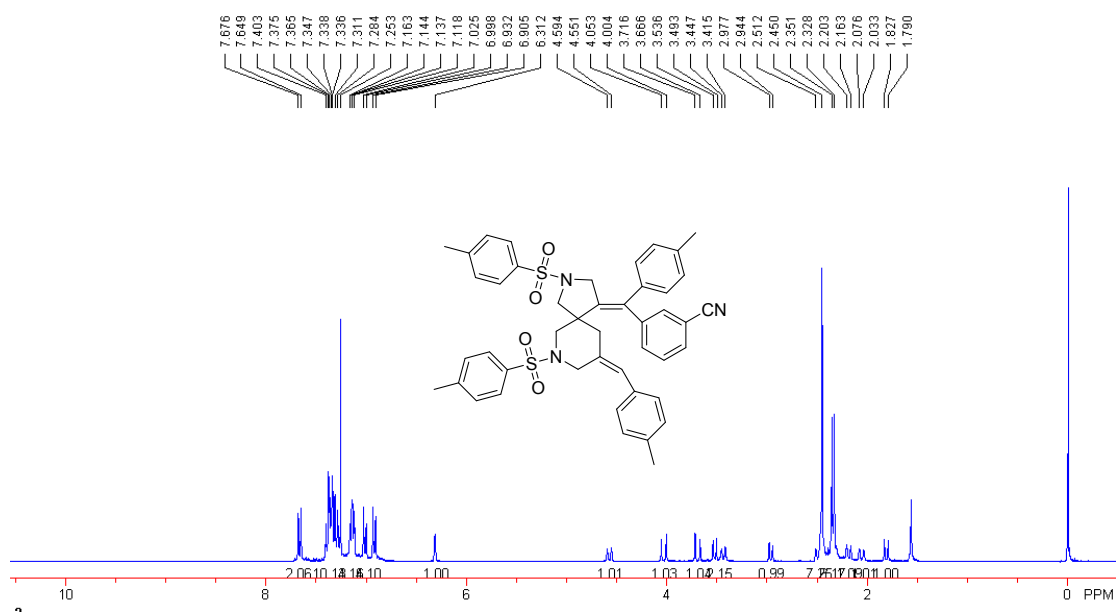


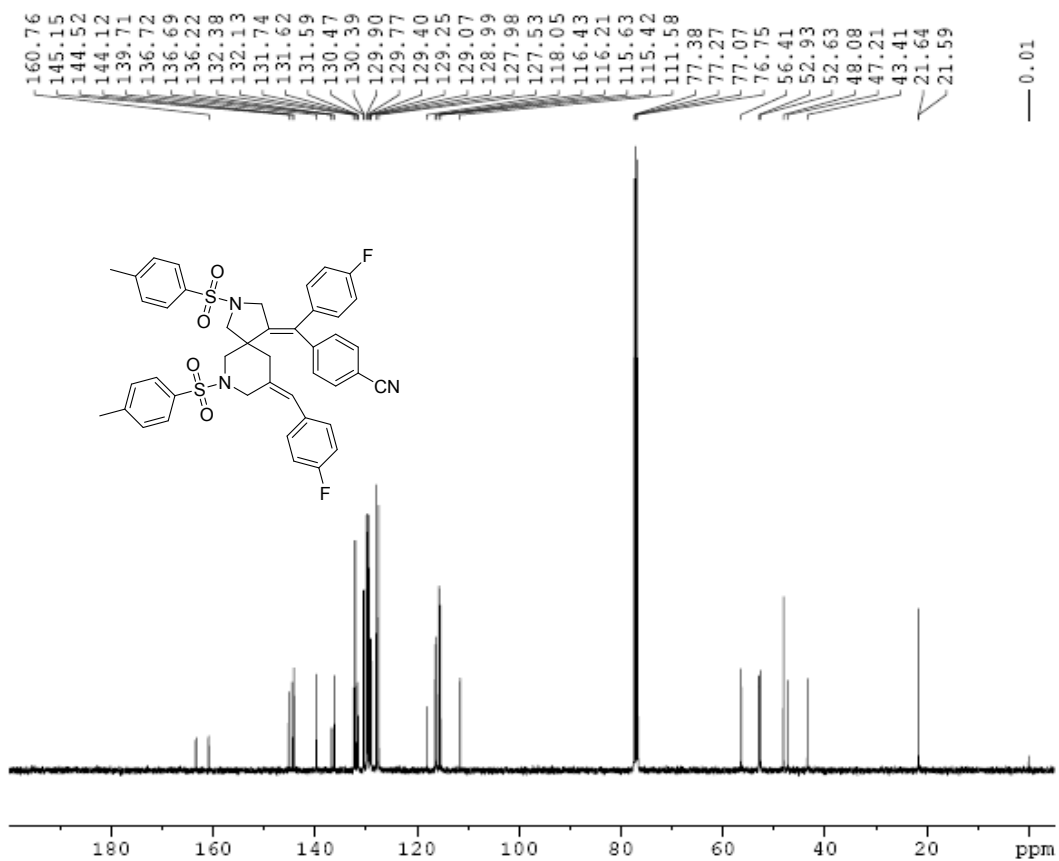
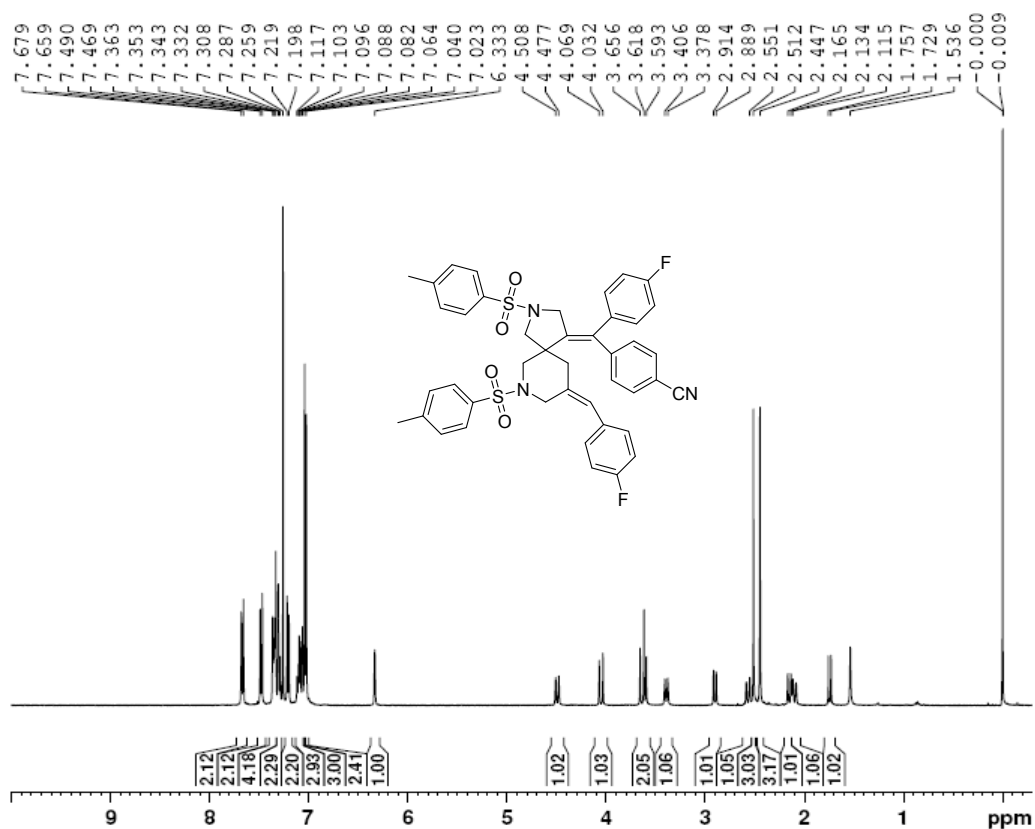


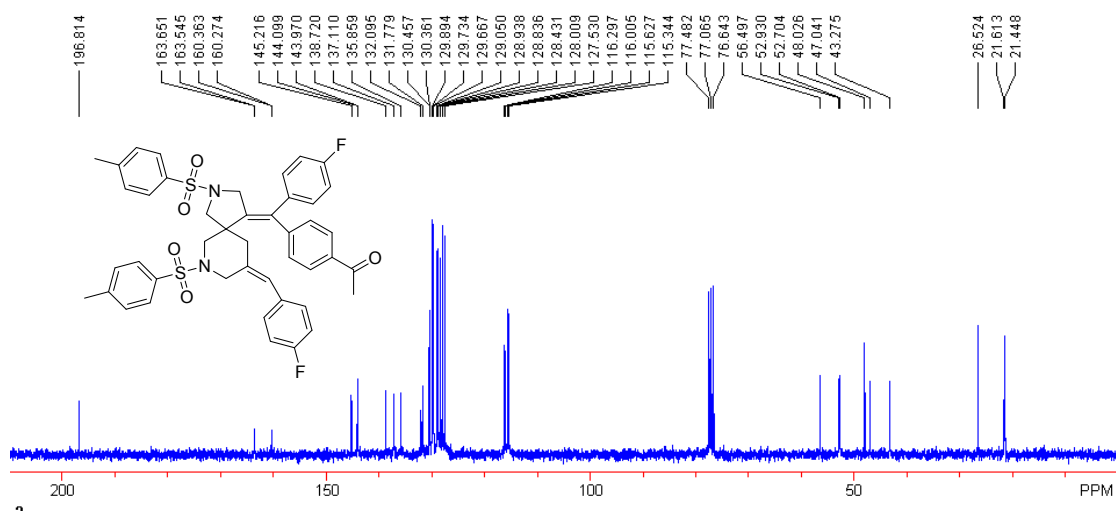
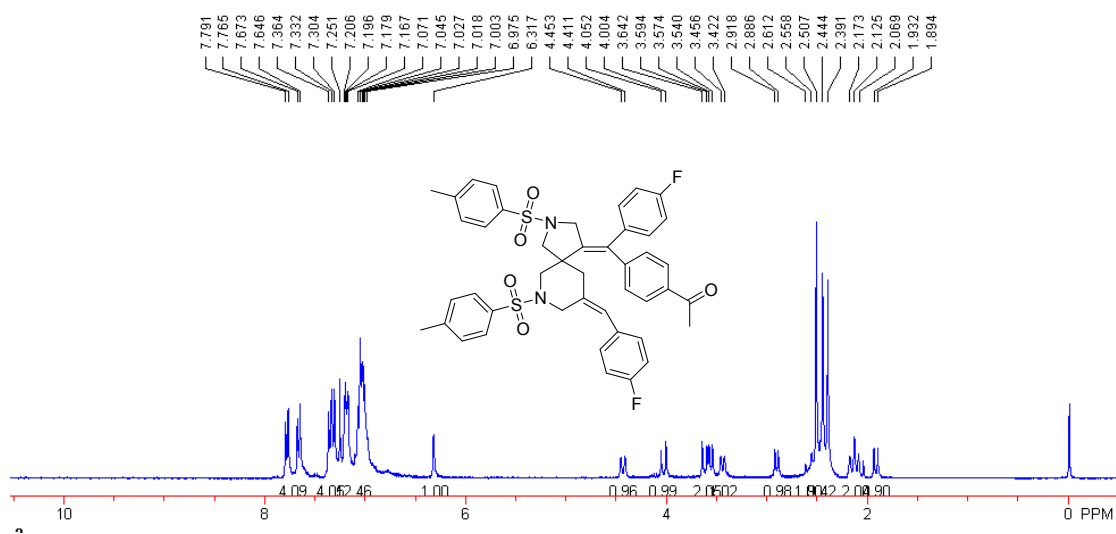


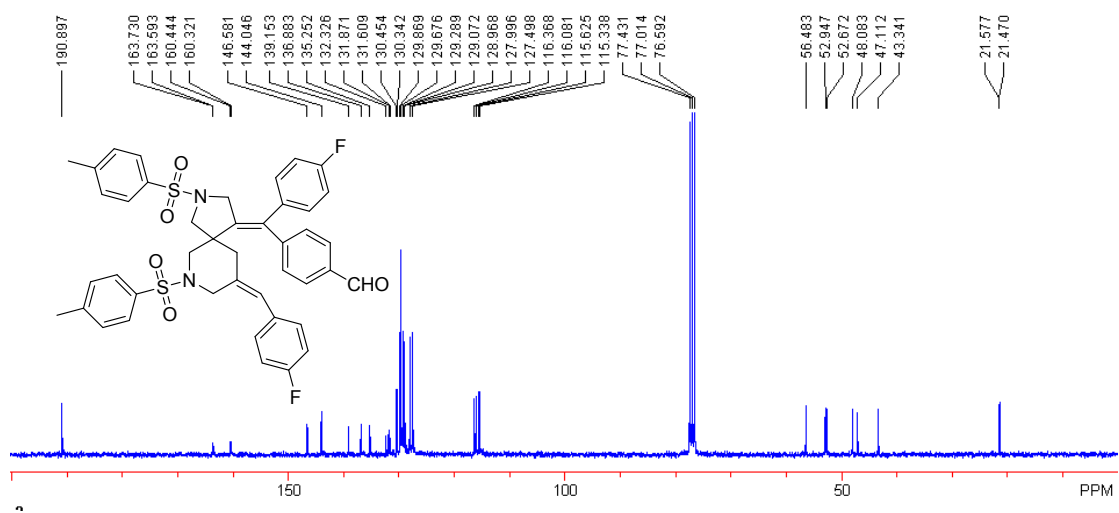
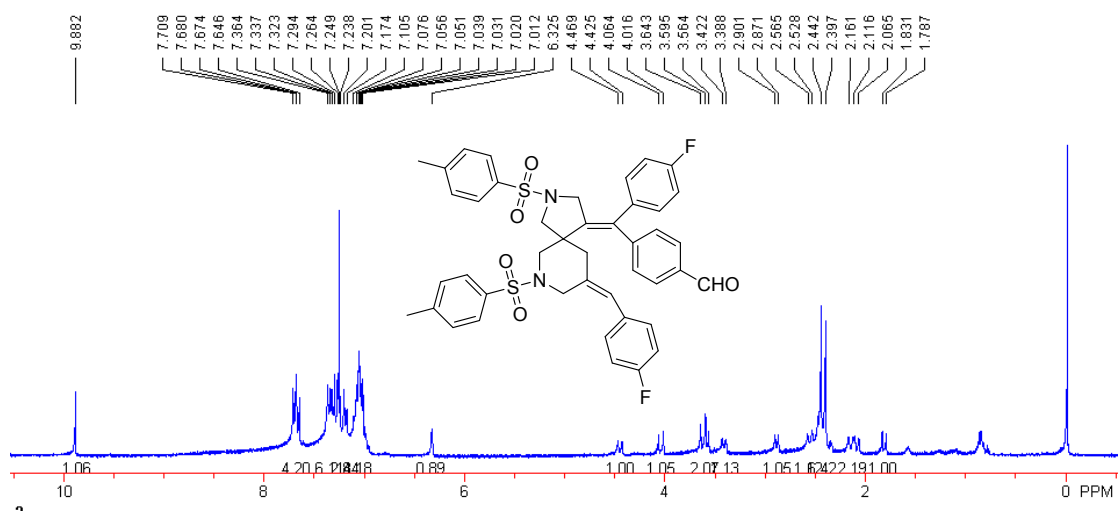


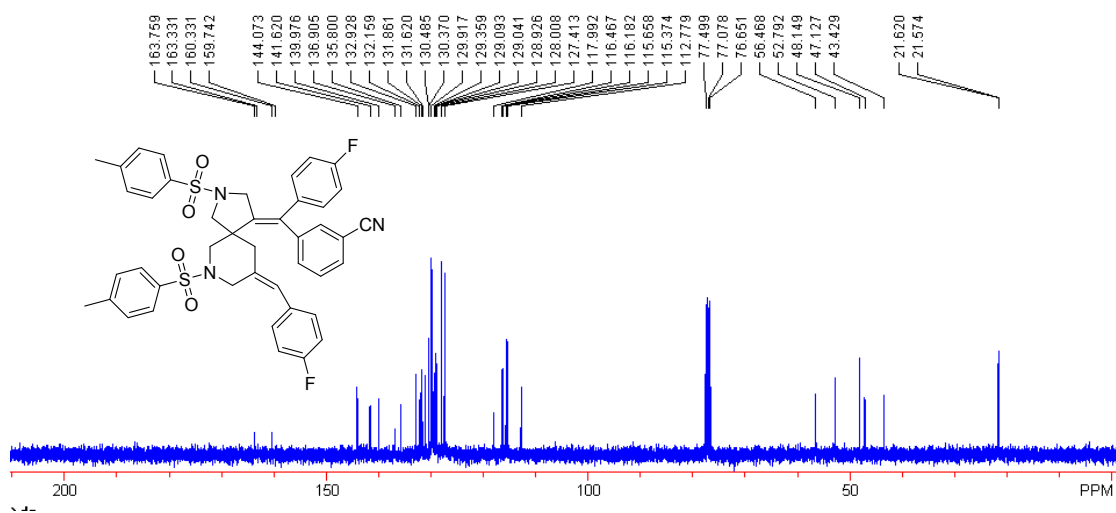
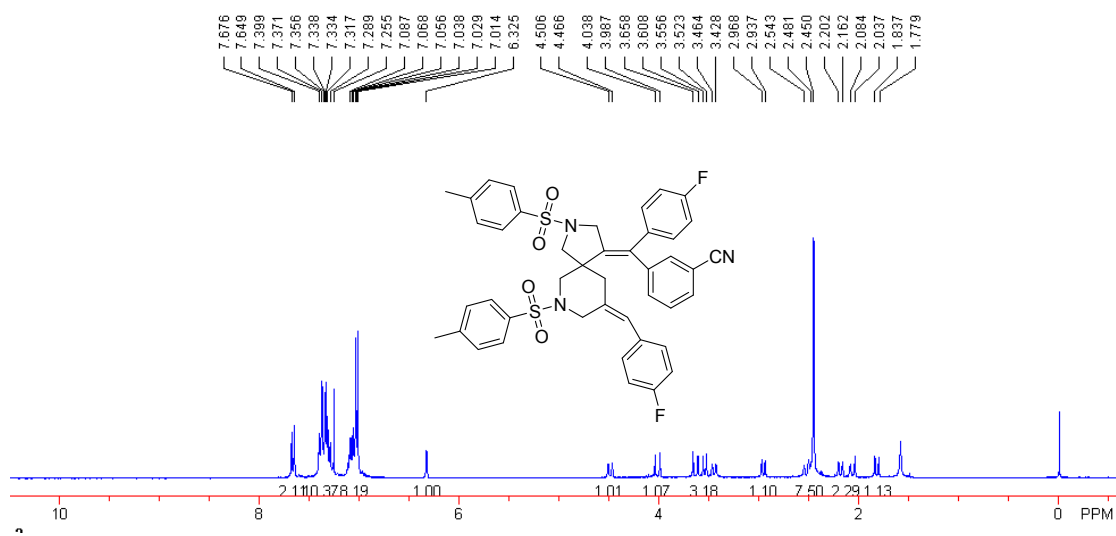


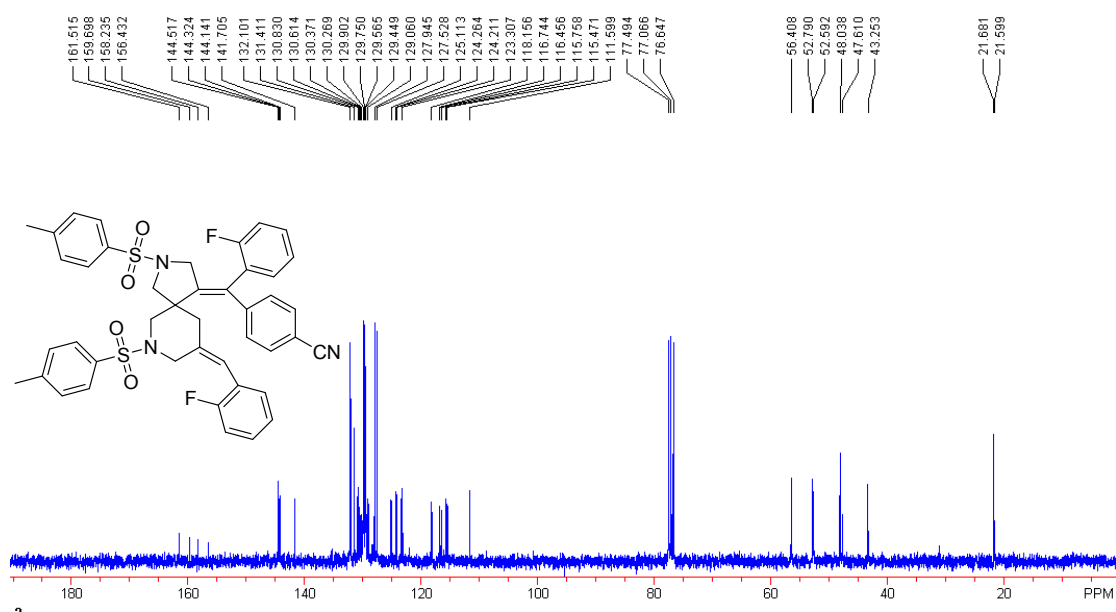
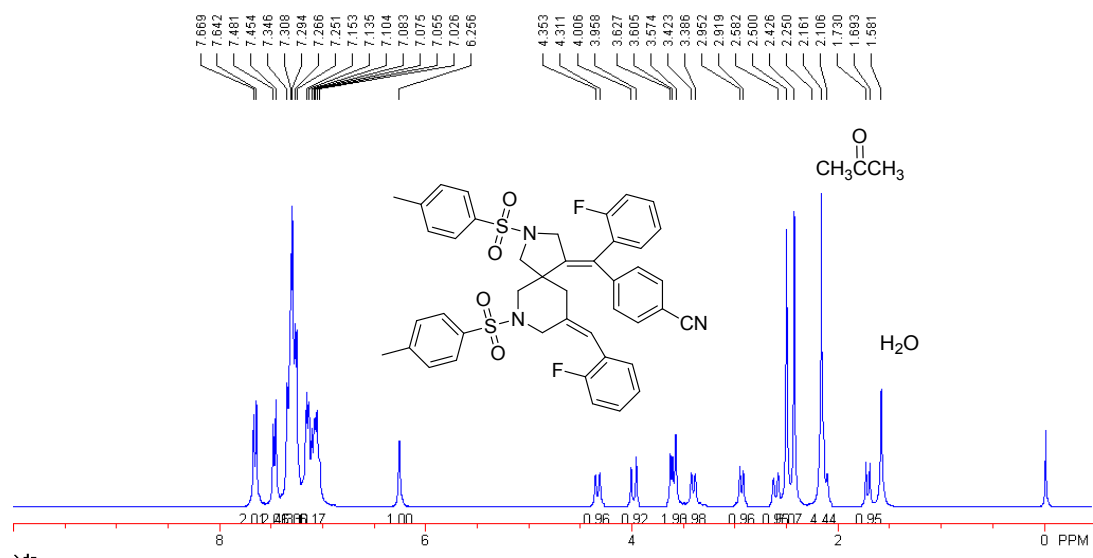


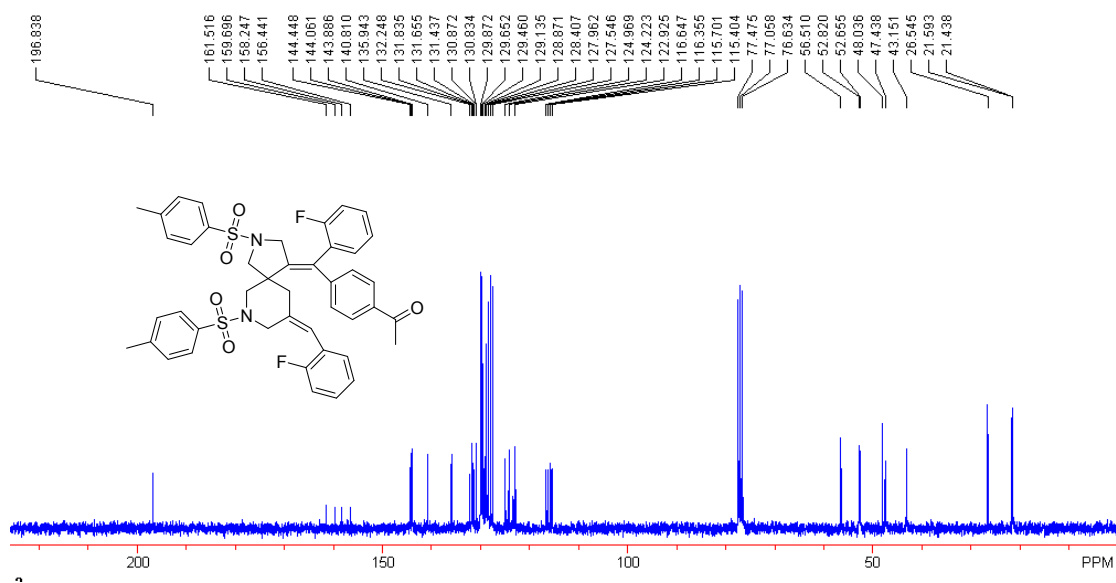
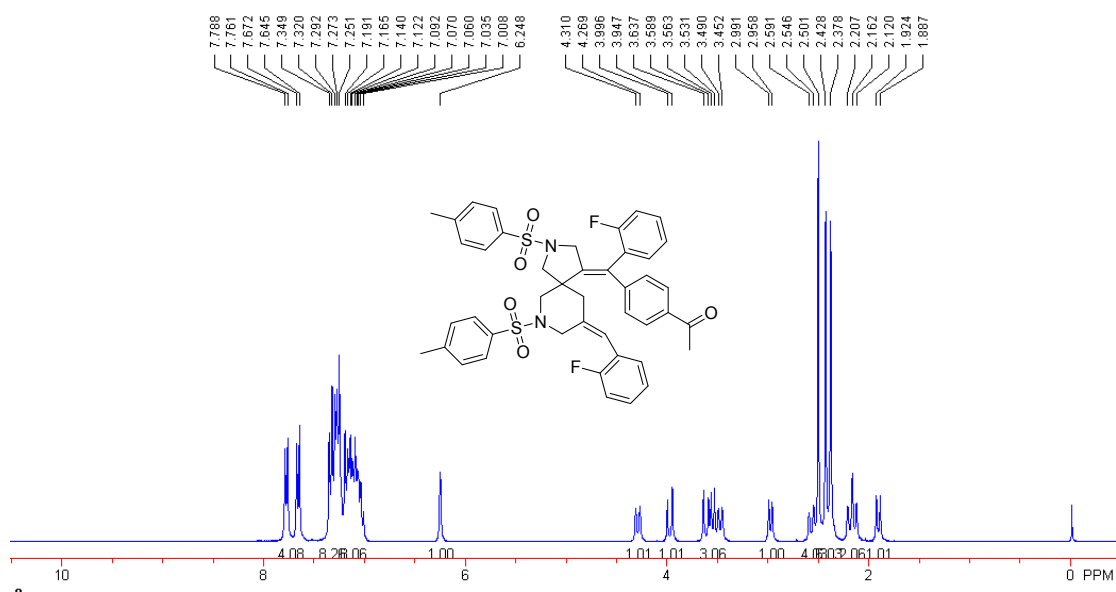


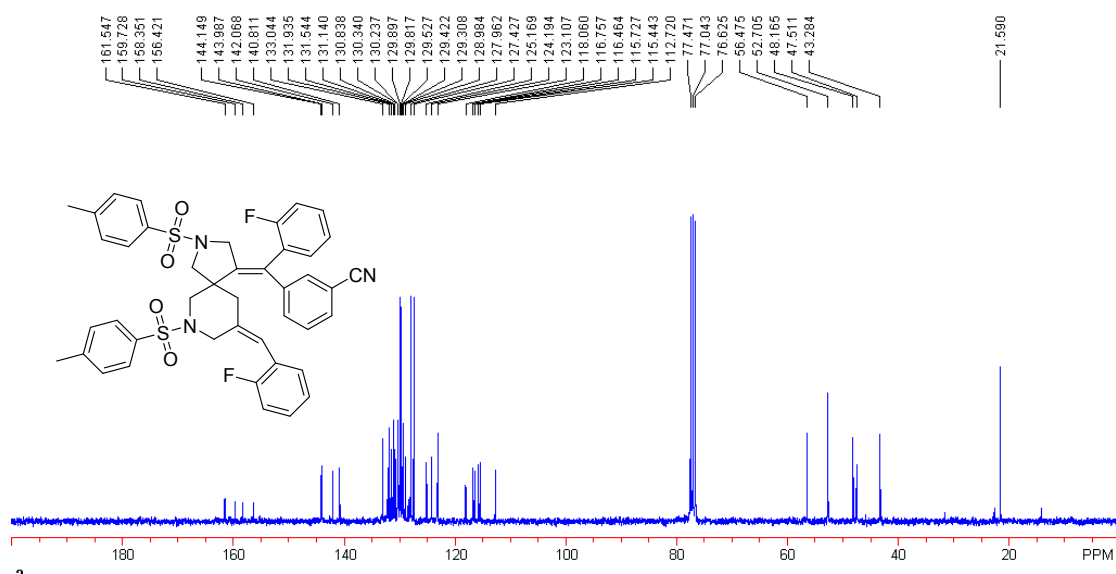
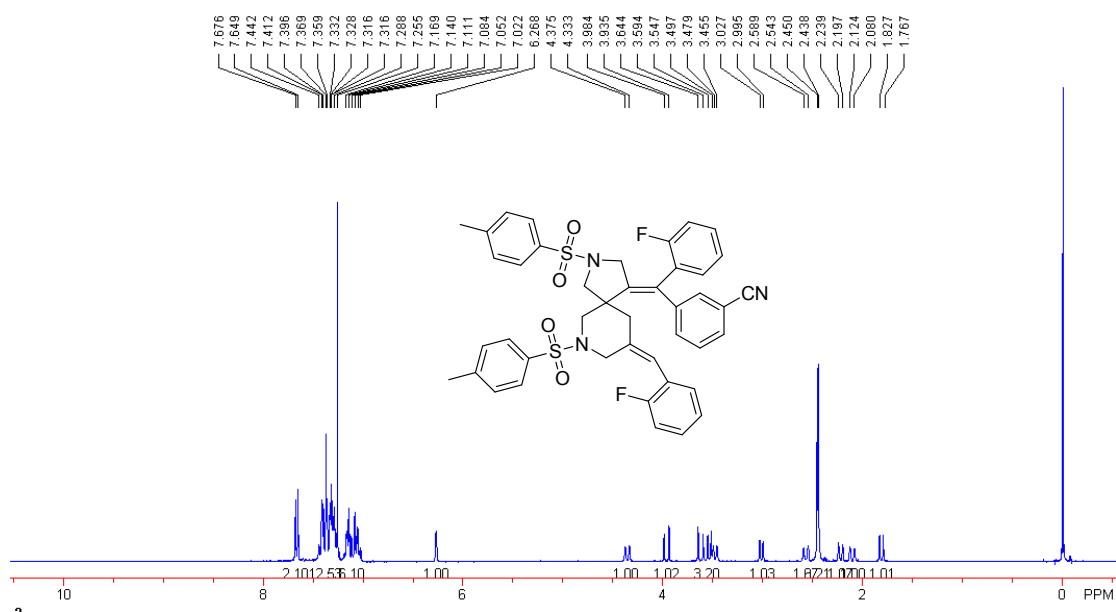


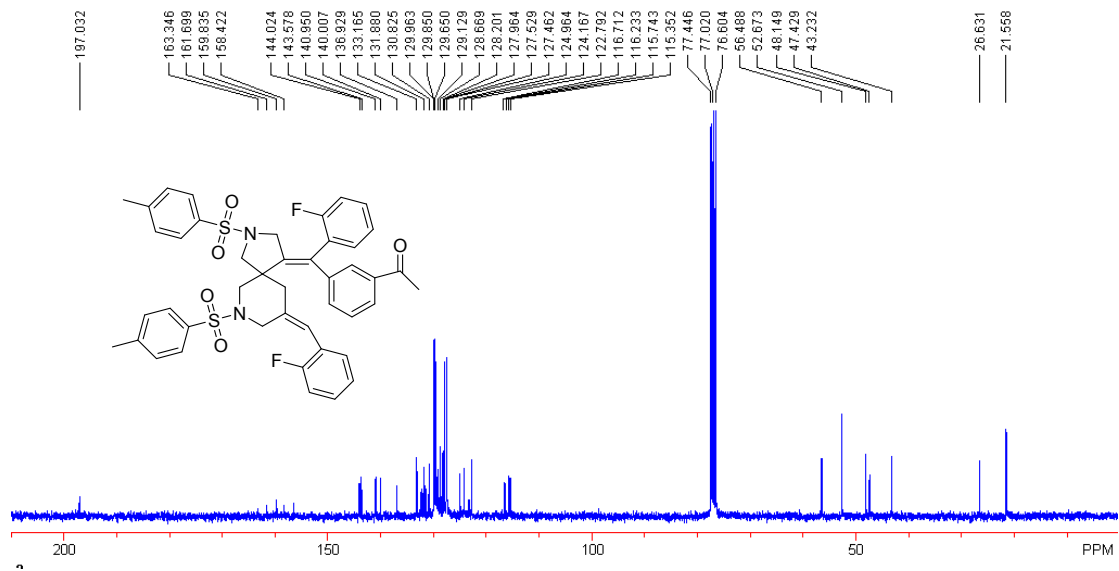
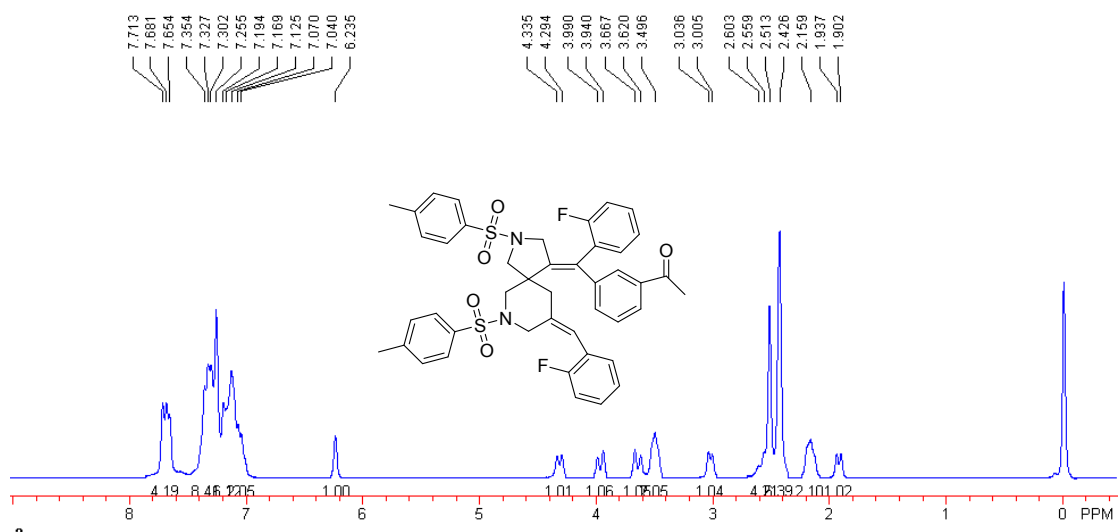


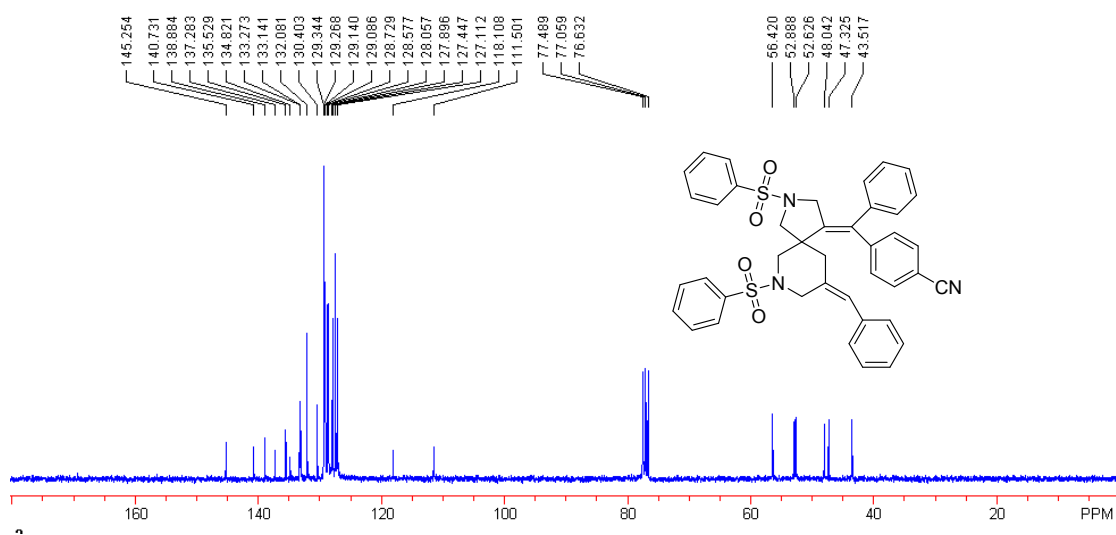
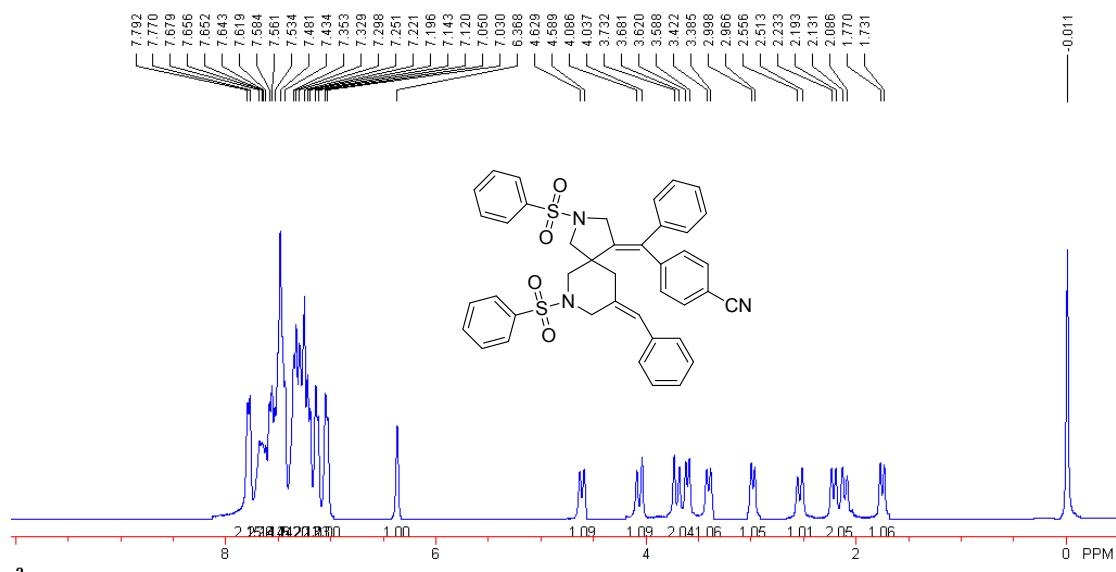


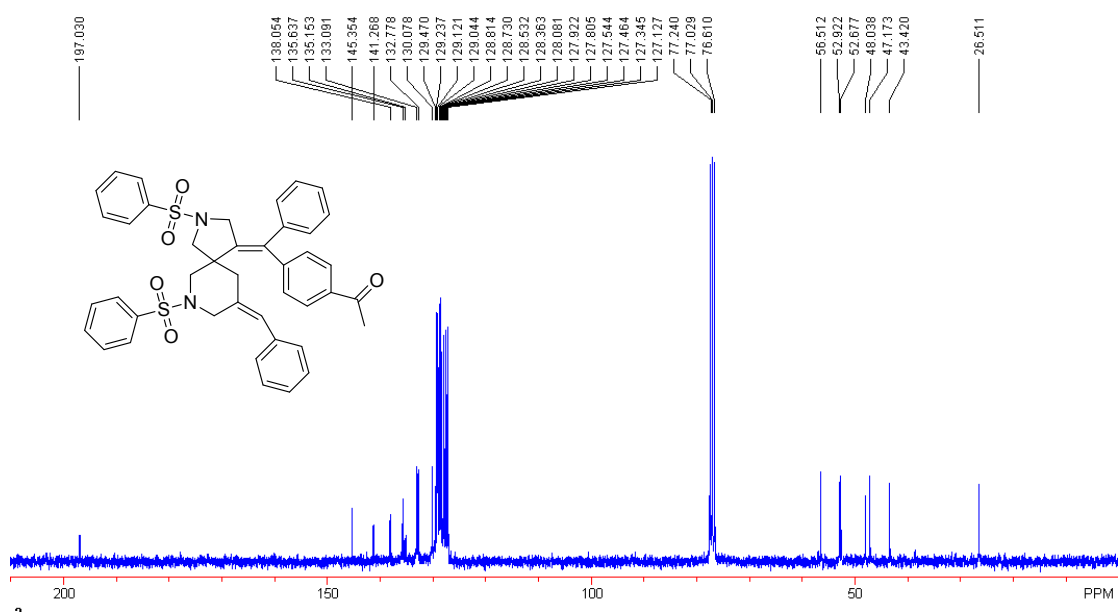
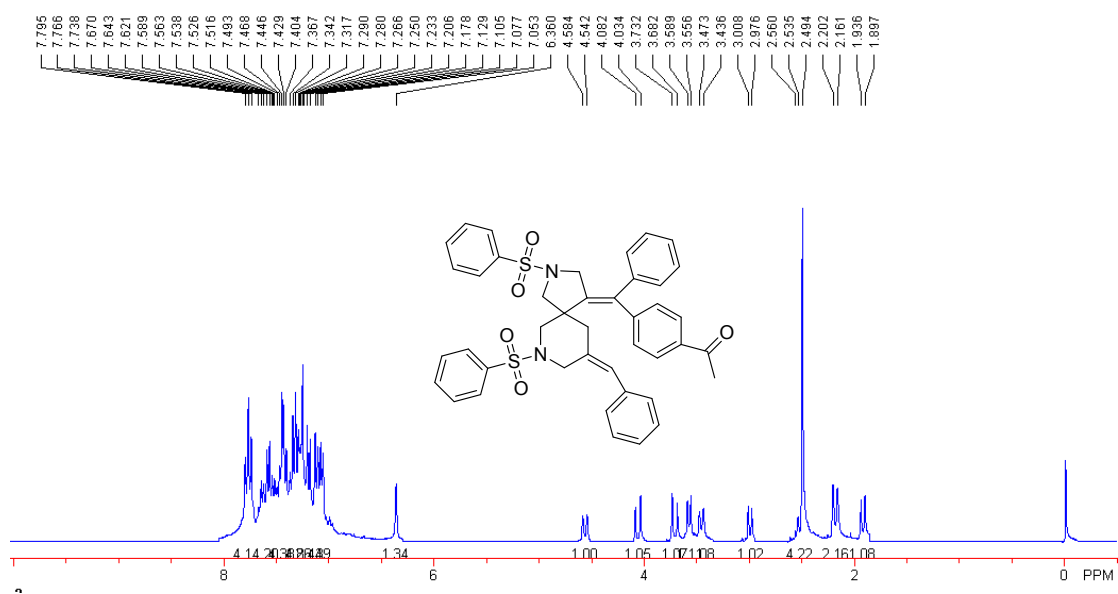


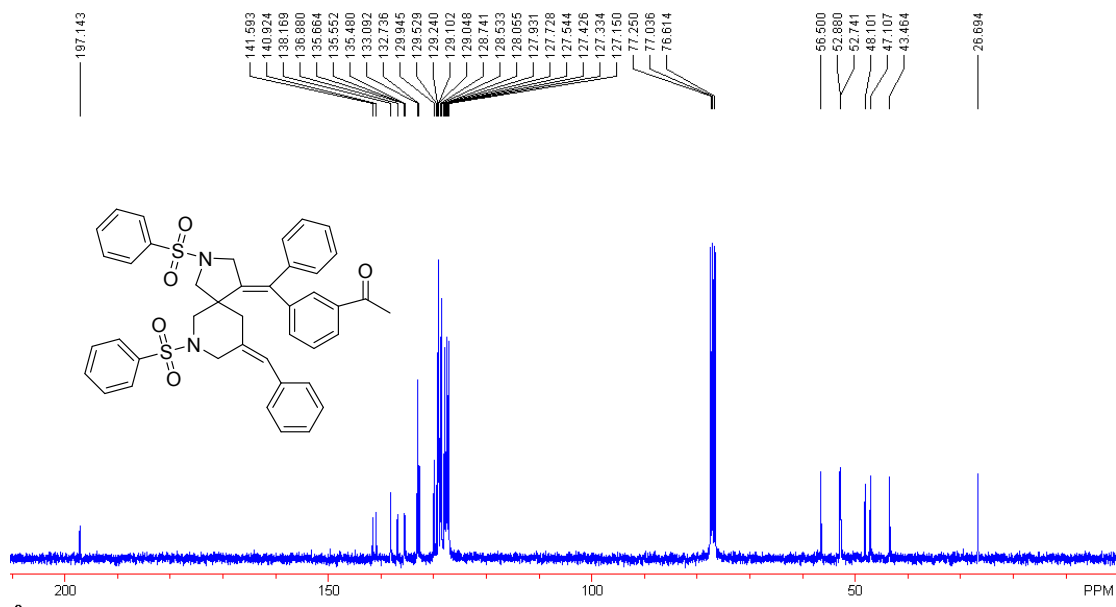
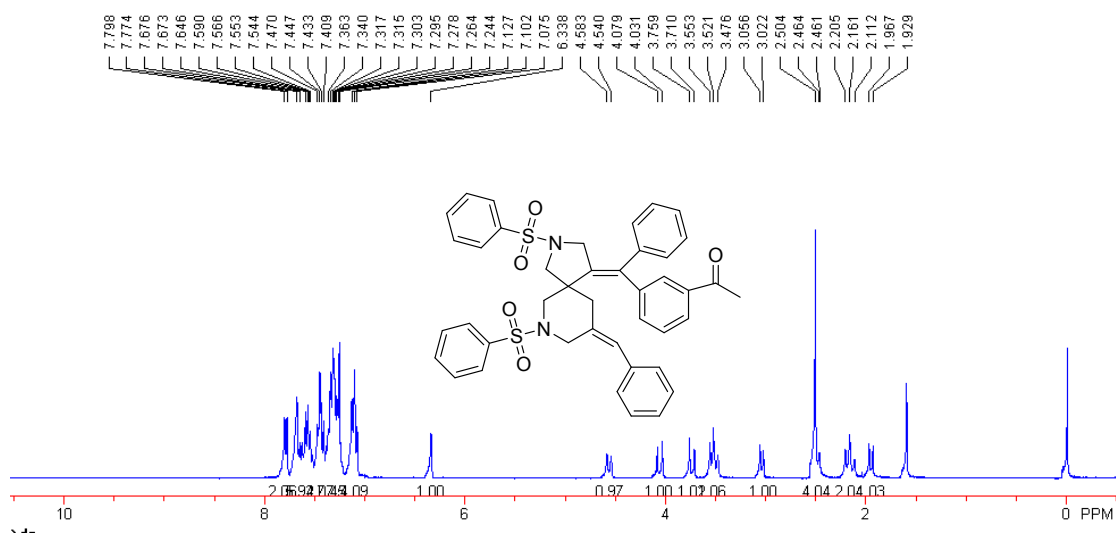


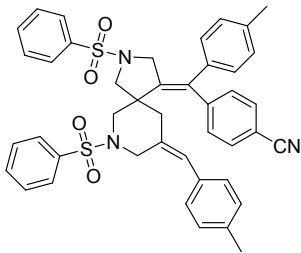
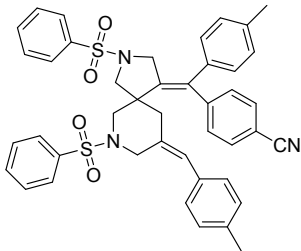


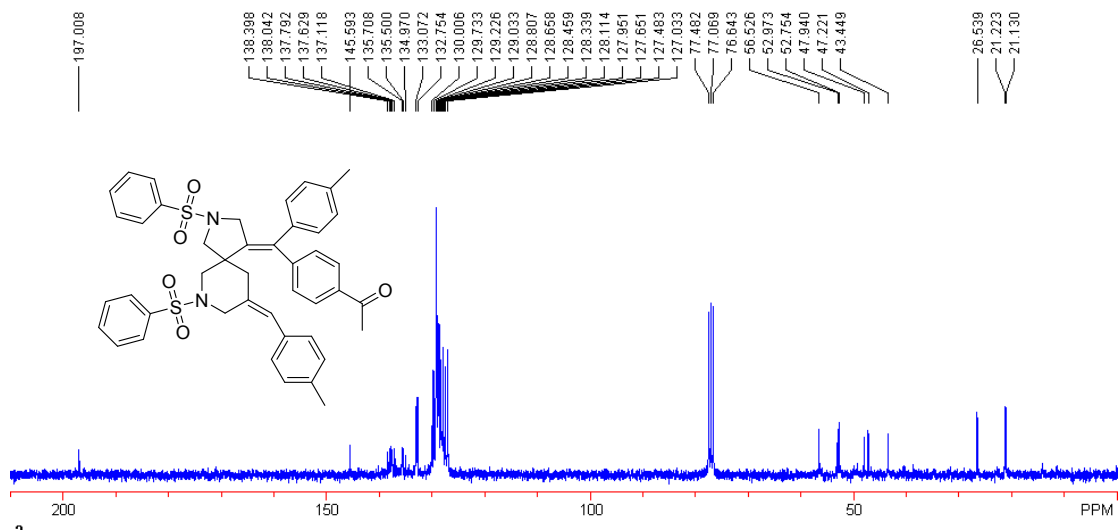
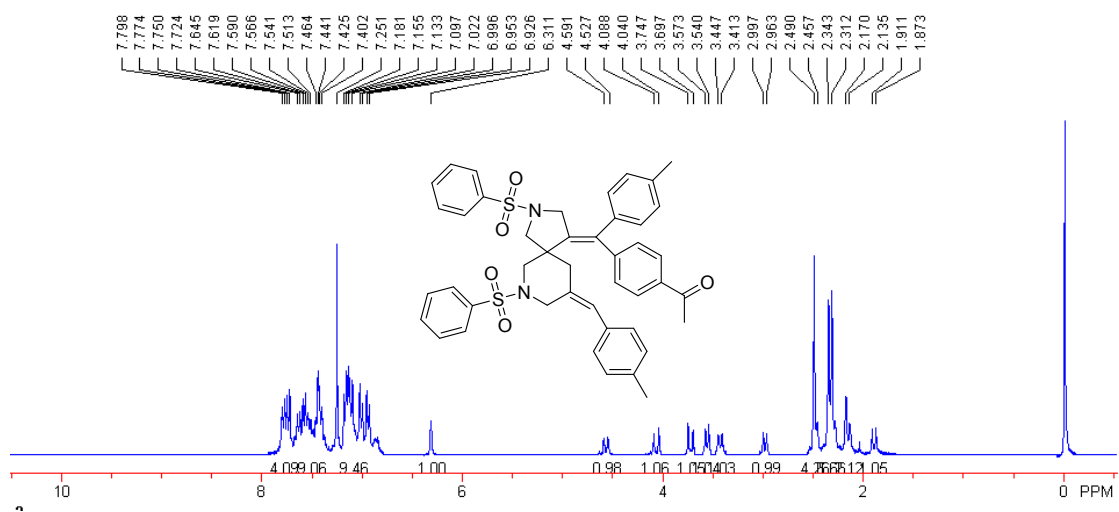


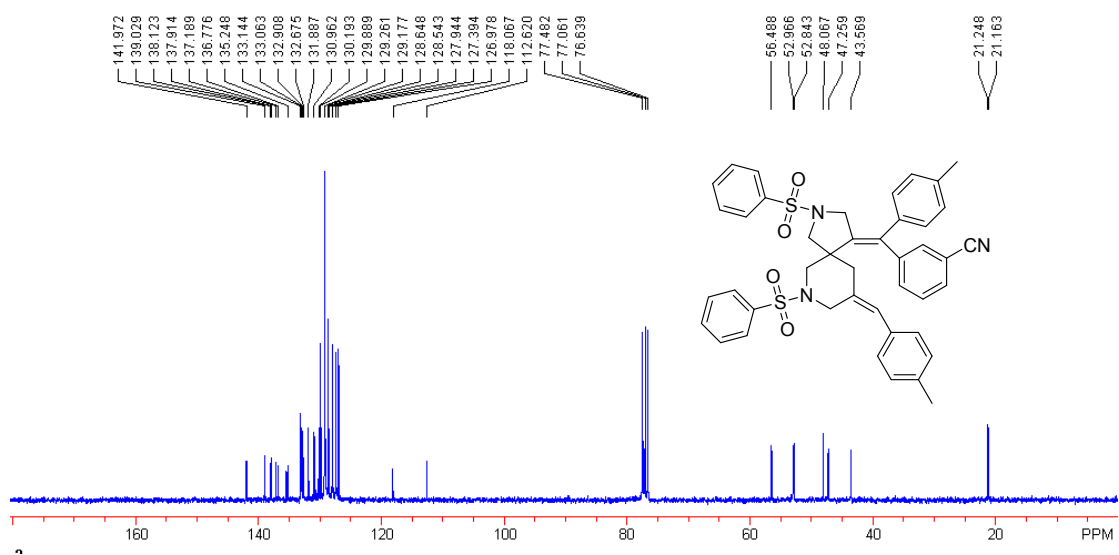
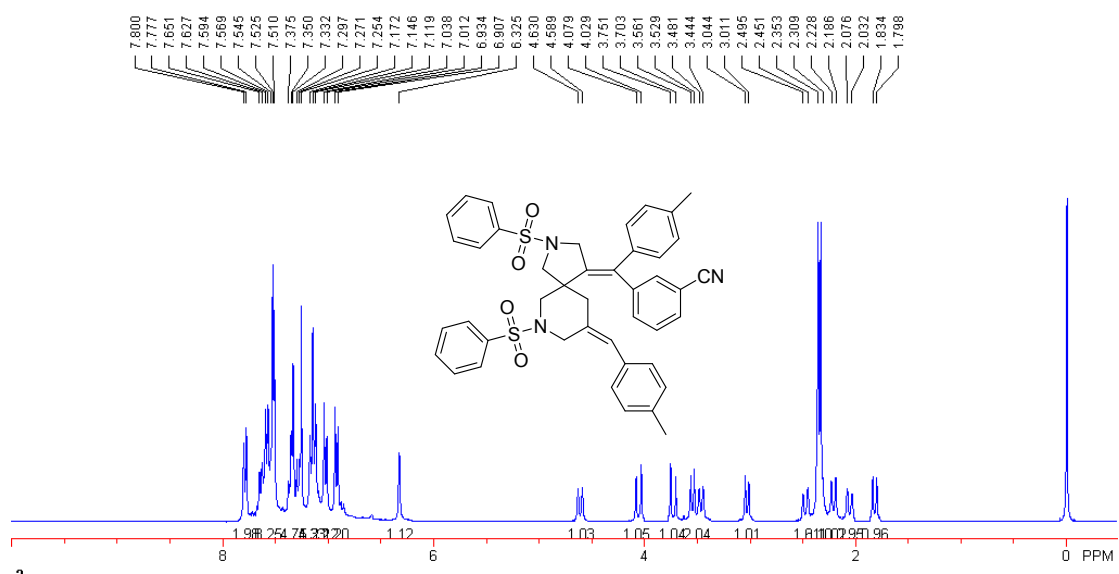


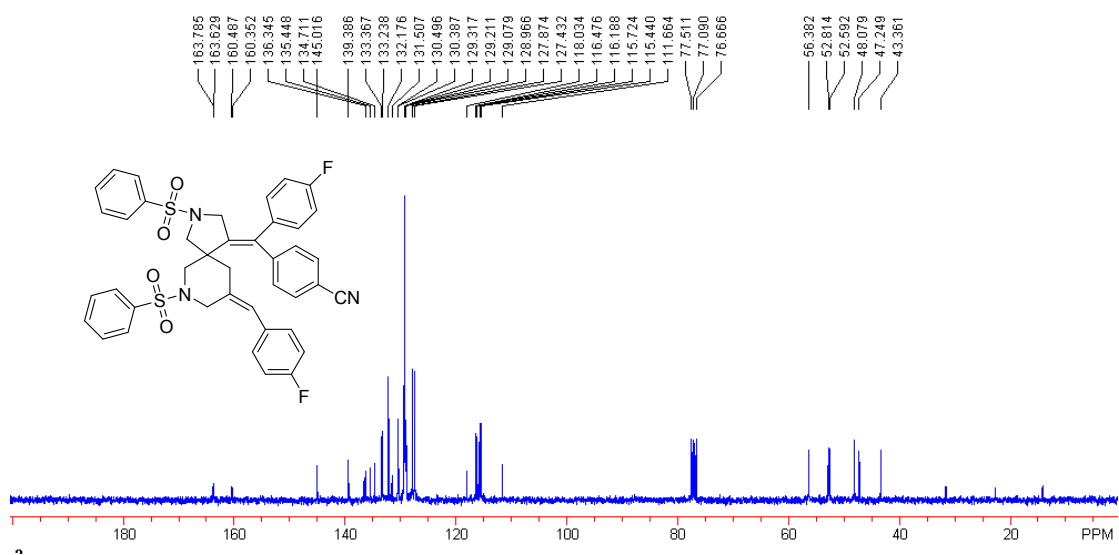
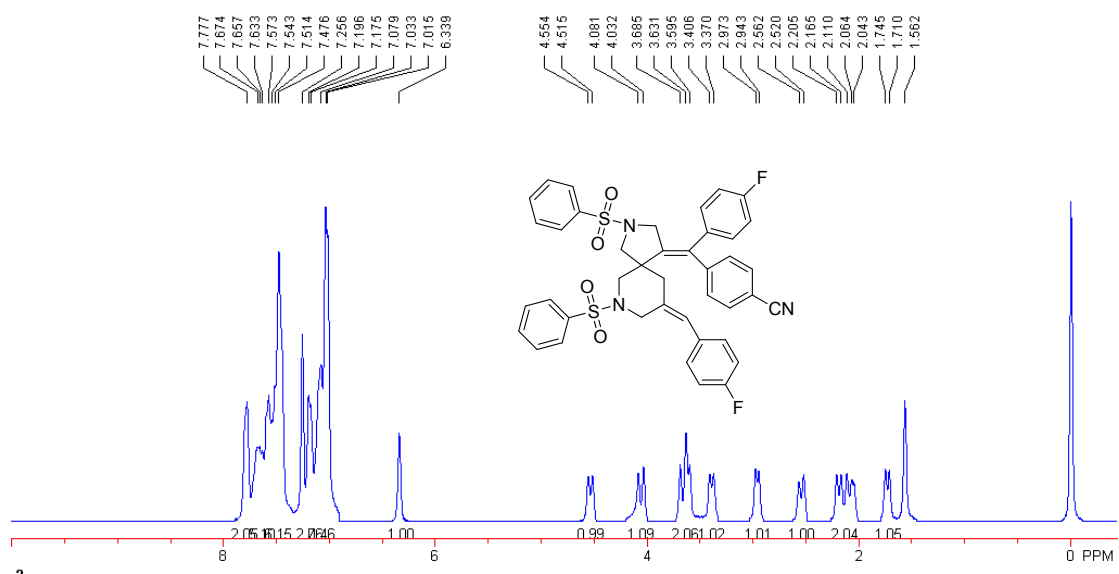


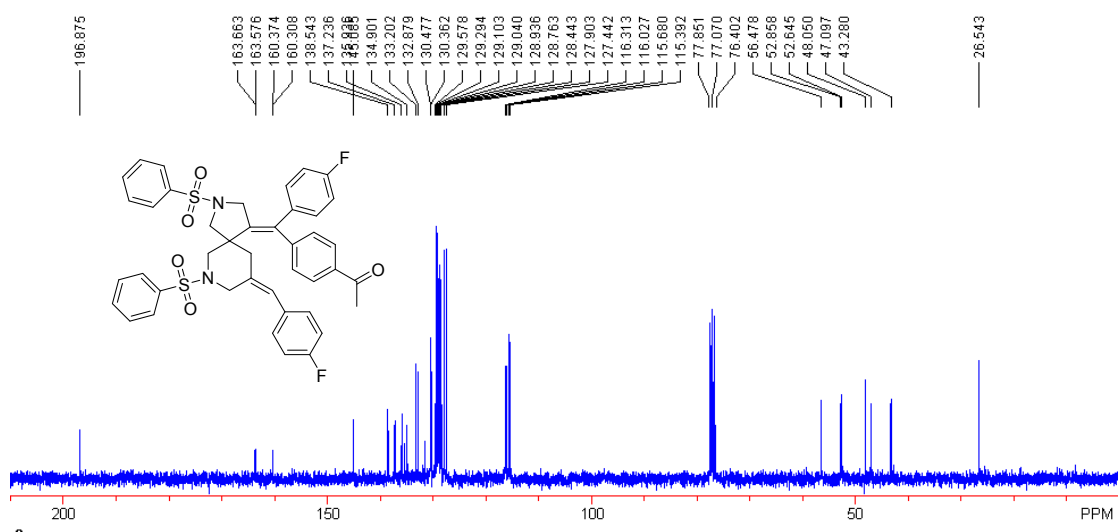
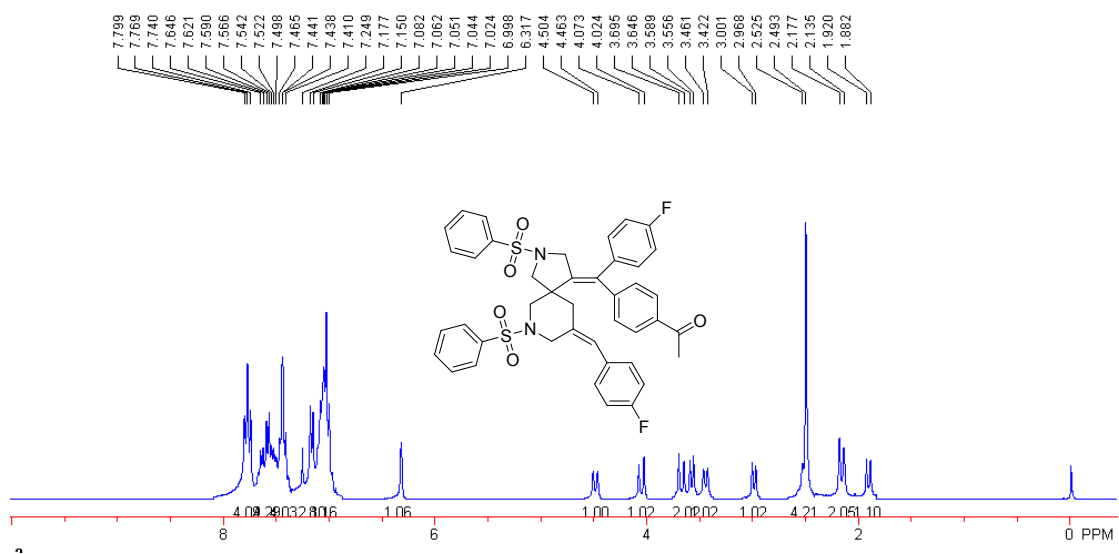


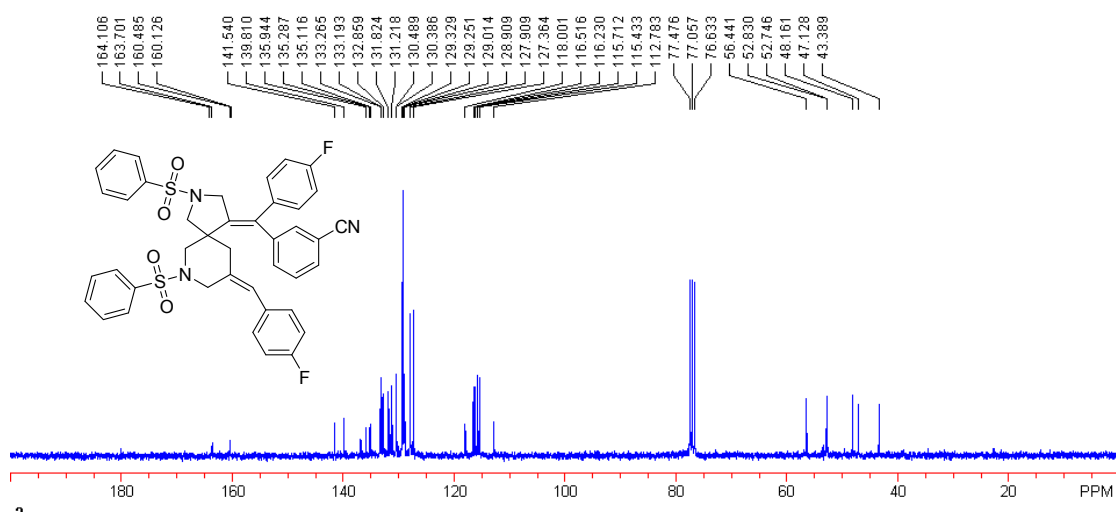
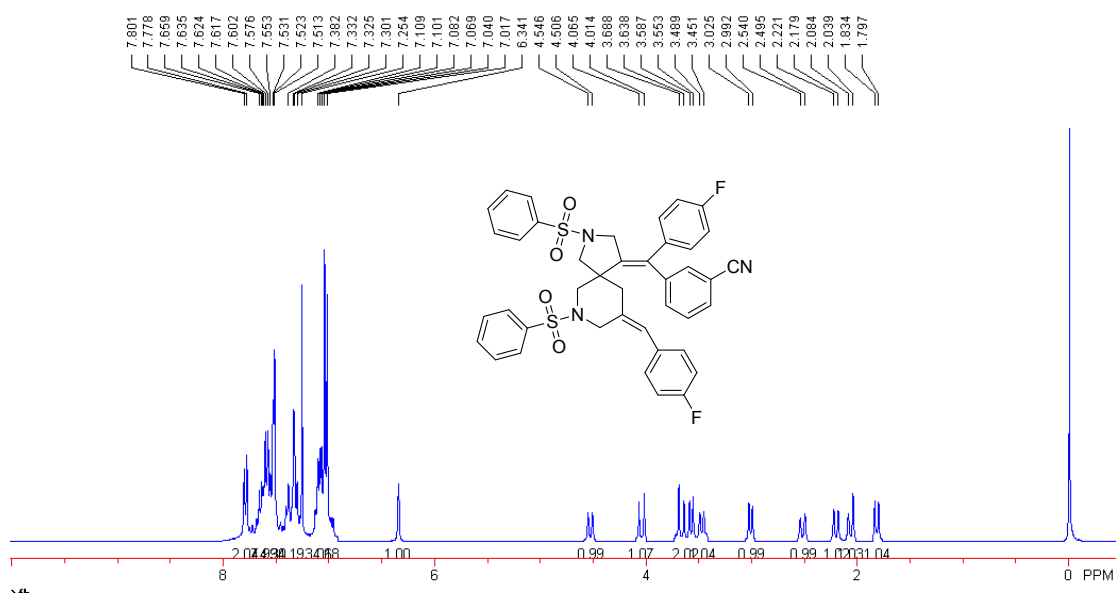


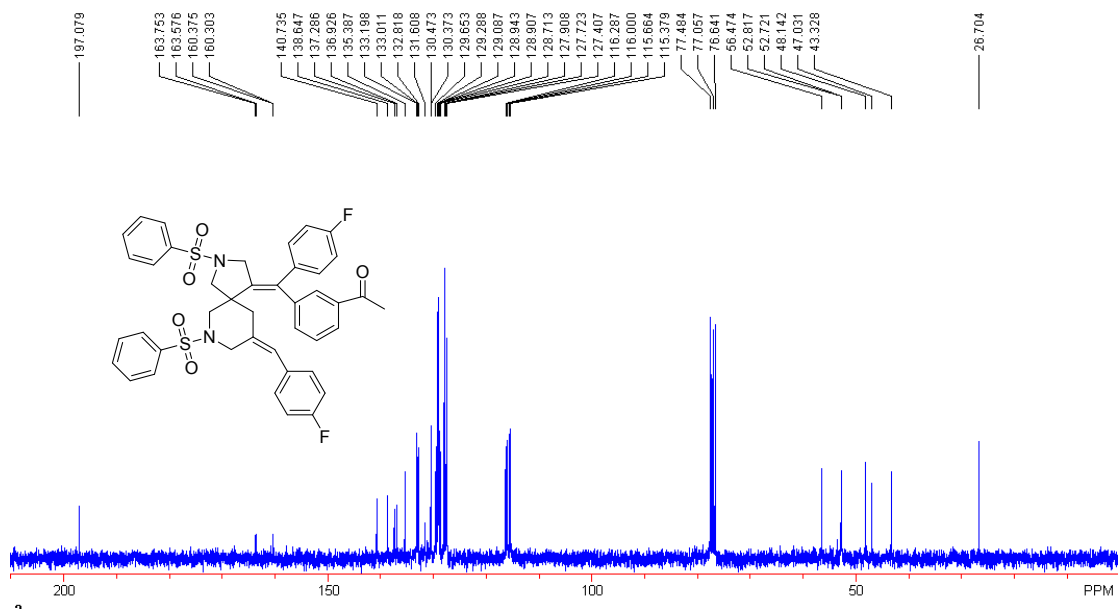
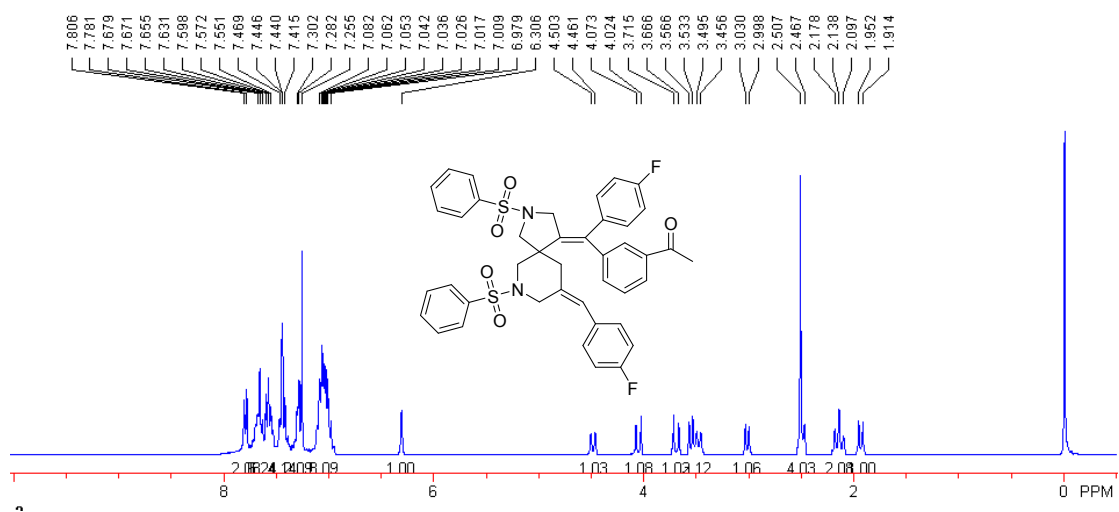




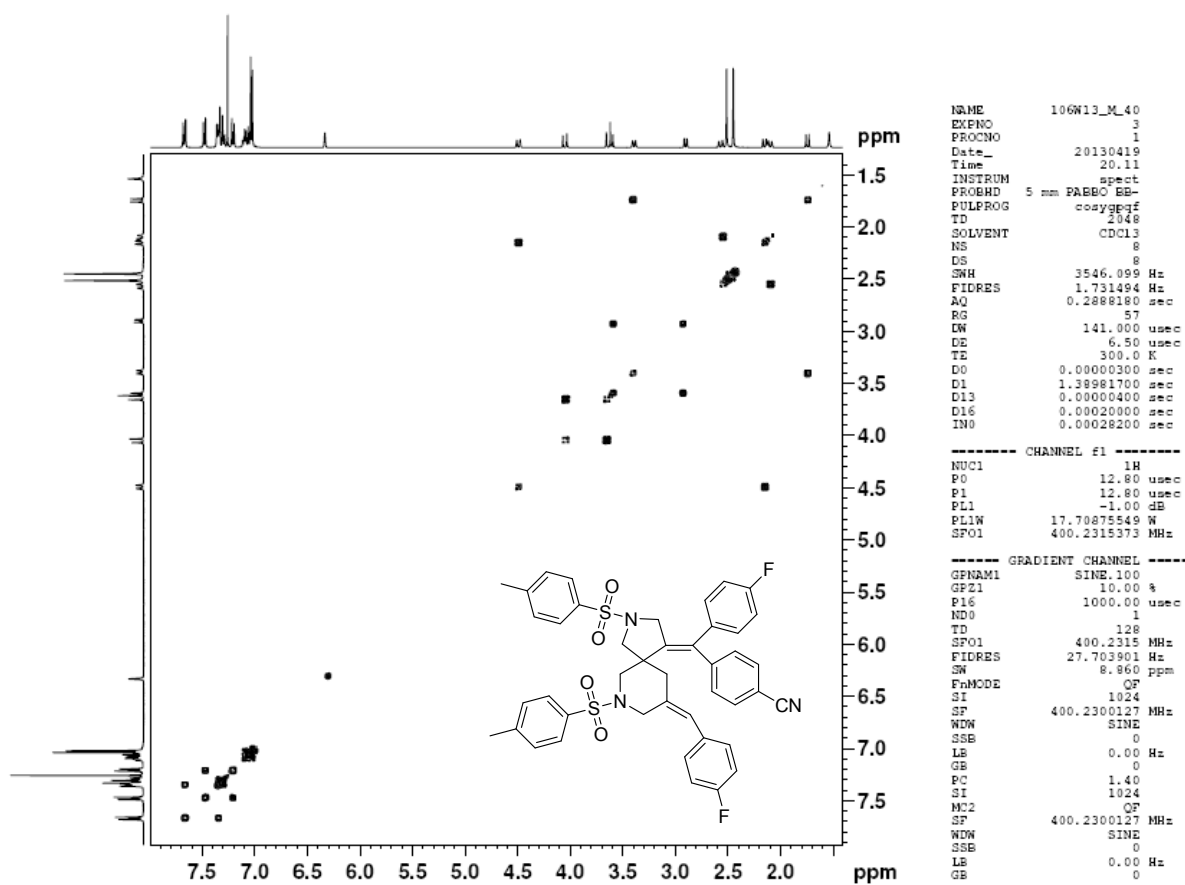


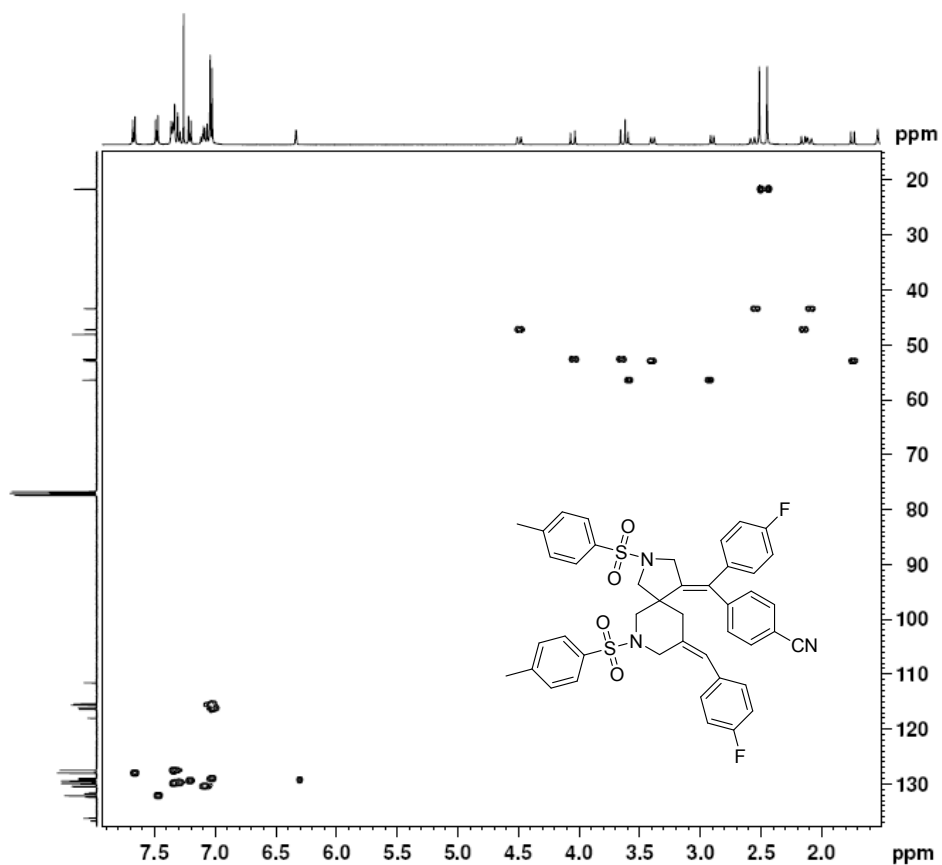






5. 2D COSY Spectra for ca and db

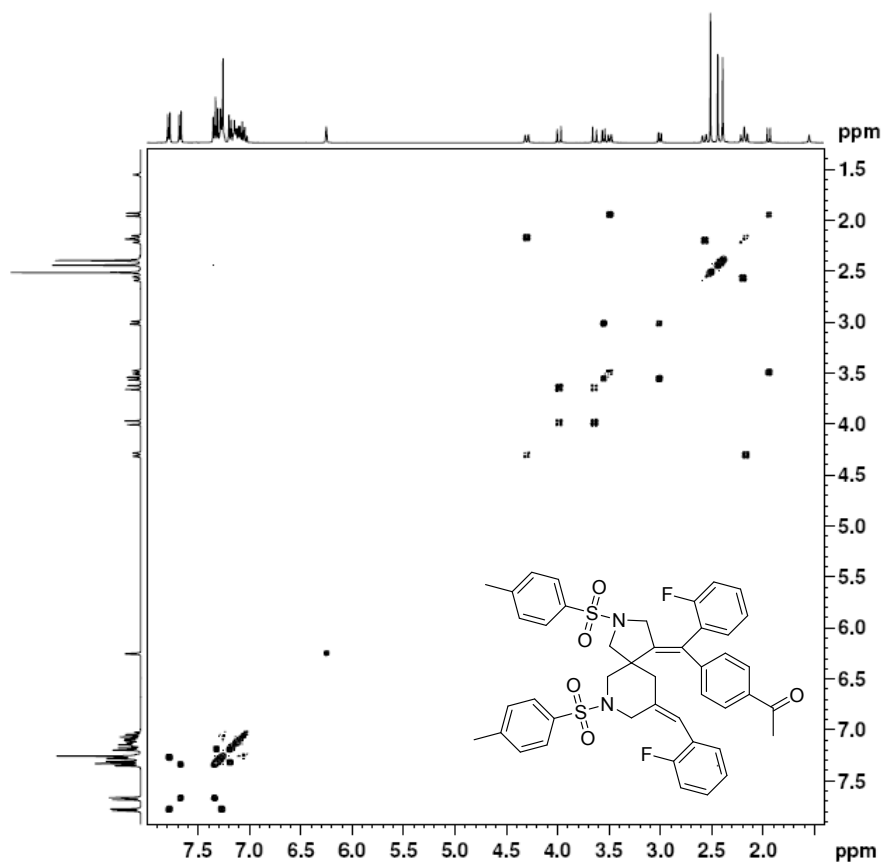




```

NAME      106M13_M_40
EXPNO     4
PROCNO    20130419
Time      20.42
INSTRUM    spect
PROBHD     5 mm DABBO BB-
PULPROG    zgpg30
TD         1024
SOLVENT    CDCl3
NS         16
DS         16
SWH         3546.099 Hz
FIDRES     0.462098 Hz
AQ         0.1444340 sec
RG         203
DM         141.000 usec
DE         6.50 usec
TE         300.1 K
CNS12      145.0000000
D0         0.0000000 sec
D1         1.45146203 sec
D4         0.00172414 sec
D11        0.03000000 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00030000 sec
ZGPG30     CHANNEL f1
=====
NUC1       1H
P1         12.80 usec
P2         25.60 usec
P28        1.00 usec
PL1        -1.00 dB
PL1W       17.78875549 W
SF01       400.2315373 MHz
=====
CHANNEL f2
=====
CPDPRG2    gpg3
NUC2       13C
P3         11.70 usec
P4         23.40 usec
PCPD2      80.00 usec
PL2        3.00 dB
PL12       19.70 dB
PL1W       41.9221451 W
PL12W      0.89628094 W
SF02       100.6454196 MHz
=====
GRADIENT CHANNEL
=====
GNAME1     SINE.100
GNAME2     SINE.100
GP11       80.00 %
GP12       20.10 %
P16        1000.00 usec
ND0        2
TD         256
SF01       100.6454 MHz
FIDRES     65.120439 Hz
SM         165.639 ppm
PRMODE     Echo-AntiEcho
SI         1024
SF         400.2300127 MHz
MCM        QSIGN
SSB         2
LB         0.00 Hz
GB         0
PC         1.40
SI         1024
MT2        echo-antiEcho
SF         100.6379140 MHz
MCM        QSIGN
SSB         2
LB         0.00 Hz
GB         0

```



```

NAME      106W13_M_26
EXPNO     3
PROCNO    1
Date_     20130419
Time      13.47
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         2048
SOLVENT   CDCl3
NS         8
DS         8
SWH        2958.580 Hz
FIDRES     1.444619 Hz
AQ         0.3461620 sec
RG         64
DM         169.000 usec
DE         6.50 usec
TE         300.0 K
D0         0.00000300 sec
D1         1.33247304 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00033800 sec

```

```

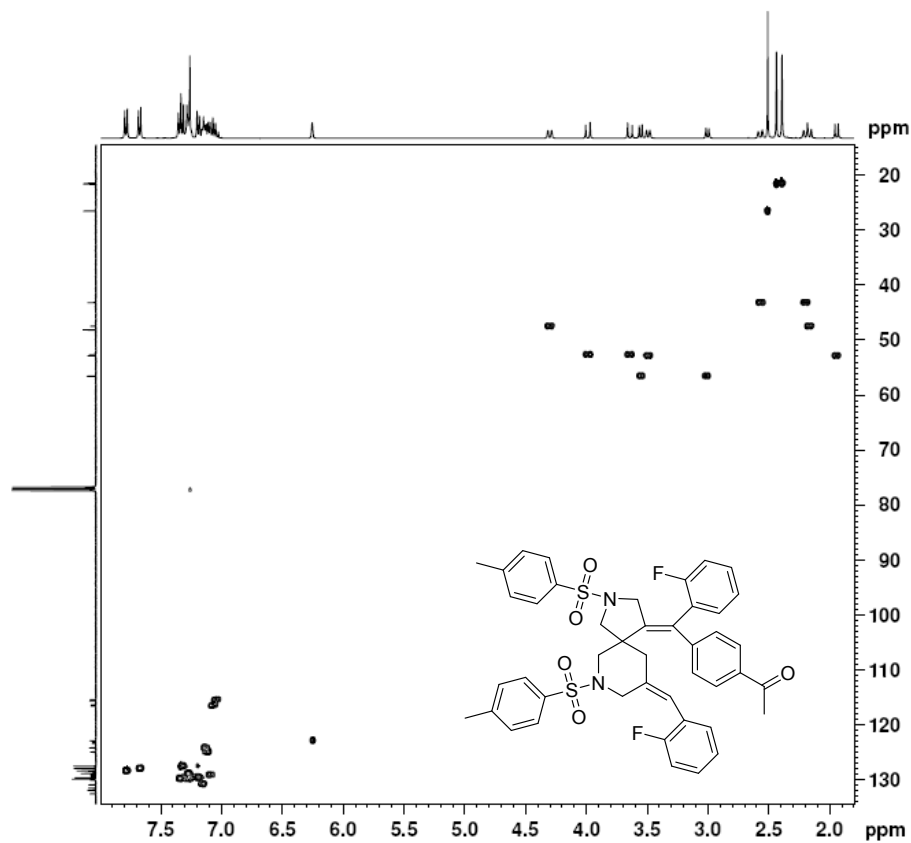
----- CHANNEL f1 -----
NUC1       1H
P0         12.80 usec
P1         12.80 usec
PL1        -1.00 dB
PL1W       17.70875549 W
SFO1       400.2318912 MHz

```

```

----- GRADIENT CHANNEL -----
GPNAM1     SINE.100
GP21       10.00 %
P16        1000.00 usec
ND0         1
TD          128
SFO1       400.2319 MHz
FIDRES     23.113905 Hz
SW          7.392 ppm
FnMODE     QF
SI          1024
SF         400.2300127 MHz
WDW         SINE
SSB         0
LB          0.00 Hz
GB          0
PC          1.40
SI          1024
MC2         QF
SF         400.2300127 MHz
WDW         SINE
SSB         0
LB          0.00 Hz
GB          0

```



```

NAME      106W13_M_26
EXPNO     4
PROCNO    1
Date_     20130419
Time      14.17
INSTRUM    spect
PROBHD     5 mm DABBO BB-
PULPROG    zgpg30
TD         1024
SOLVENT    CDCl3
NS         16
DS         16
SMB        2958.580 Hz
FIDRES     2.869238 Hz
AQ         0.1731060 sec
RG         203
DM         169.000 usec
DE         6.50 usec
TE         300.0 K
CNS2       145.000000
D0         0.0000300 sec
D1         1.4279005 sec
D4         0.00172414 sec
D11        0.0000000 sec
D13        0.0000000 sec
D16        0.0002000 sec
CNS        0.0000300 sec
ZGPGTMS

===== CHANNEL f1 =====
NUC1       1H
P1         12.80 usec
P2         25.60 usec
P2a        1.00 usec
PL1        -1.00 dB
PL1a       17.70875549 W
SFO1       400.2319812 MHz

===== CHANNEL f2 =====
CPDPRG2    gpgp
NUC2       13C
P3         11.70 usec
P4         23.40 usec
PCPD2      90.00 usec
PL2        3.00 dB
PL12       19.70 dB
PL1a       41.02221451 W
PL12a      0.89628094 W
SFO2       100.6454196 MHz

===== GRADIENT CHANNEL =====
GRNAM1     SINE.100
GRNAM2     SINE.100
GD1        80.00 %
GD2        20.10 %
P16        1000.00 usec
MD0        2
TD          256
SFO1       100.6454 MHz
FIDRES     65.120439 Hz
SM         165.639 ppm
FNUC2      Echo-AntiEcho
SI         1024
SF         400.2300127 MHz
MEM        2
SSB        0
LB          0.00 Hz
GB          0
PC          1.40
SI         1024
WC2        Echo-AntiEcho
SF         100.6379140 MHz
MEM        2
SSB        0
LB          0.00 Hz
GB          0

```