

**Copper-catalyzed intermolecular and regioselective
aminofluorination of Styrenes: Facile access to β -fluoro-
N-protected phenethylamines**

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Supporting Information

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1. Experimental Section

1.1. General

All solvents and all deuterated solvents were purchased from Merck, reagents from Aldrich, Merck and AK Scientific. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2 mm). NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. All chemical shifts in NMR experiments were reported as ppm downfield from TMS. The following calibrations were used: CDCl_3 δ = 7.26 and 77.0 ppm. Infrared spectra were recorded on a JASCO FT/IR-400 spectrophotometer. HPLC-HR-MS experiments were performed on an Exactive Plus Orbitrap MS (Thermo Scientific). The accurate mass measurements were performed at a resolution of 140,000. Melting points were determined on a Reichert Galen III hot plate microscope apparatus and are uncorrected.

1.2. General procedure for the Aminofluorination of Styrenes

In a 10 mL vial, $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (32 mg, 0.1 mmol), neocuproin (21 mg 0.1 mmol), 1,2-dichloroethane (3.0 mL) were stirred for 3 min and Ph-I=N-Ts (560 mg, 1.5 mmol) was added to the red solution. The suspension was stirred for 3 min and $\text{Et}_3\text{N}\cdot 3\text{HF}$ (0.97 mL, 6 mmol) was added. A clear green solution is obtained. Styrene (**1a**, 104 mg, 1 mmol) and $\text{Mo}(\text{CO})_6$ (65 mg, 0.25 mmol) were then added. The mixture was heated to 70 °C (oil bath) for 15 min. Gas was evolved during the reaction and a red solution was obtained. The mixture was added to silica gel (5 g), the solvent was removed under reduced pressure, and the powder was placed on the top of a chromatographic column. The column was eluted with a gradient of petroleum ether/ethyl acetate (4:1) affording the product **2a** (209 mg, 71%).

1.3. Protocols for *N*-alkylation of fluorosulfonamides **2a**, **2c**, **3a**, **3d**, **3e** and **3g**.

Conditions A, basic alkylation.

A flame-dried, 25-mL, round-bottomed flask fitted with a magnetic stirbar is charged with **2a** (147 mg, 0.5 mmol) and anhydrous DMF (10 mL). The solution is stirred at 0 °C and NaH (13 mg, 0.55 mmol) was added in one portion. The suspension was stirred at 0 °C for 0.5 h and then at room temperature for 0.5 h. The suspension was cooled at 0 °C and benzyl chloride (70 mg, 0.55 mmol) in anhydrous DMF (5 mL) was added dropwise over 5 min. The mixture was warmed to room temperature and stirred for 2 h. After that, ice (10 g) was added and the mixture was extracted with $(\text{Et})_2\text{O}$ (3 x 15 mL). The combined organic phase was washed with H_2O (2 x 10 mL), dried over anhydrous Na_2SO_4 , filtered, and evaporated to give the crude product. The residue was directly loaded on silica gel and purified (hexane/EtOAc = 15/1) to give **4a** (155 mg, 81 %) as a pale yellow solid.

Conditions B, Mitsunobu alkylation.

A flame-dried, 25-mL, round-bottomed flask fitted with a magnetic stirbar is charged with **2a** (147 mg, 0.5 mmol), anhydrous THF (10 mL), triphenylphosphine (184 mg, 0.7 mmol) and benzyl alcohol (76 mg, 0.7 mmol). The solution is cooled at 0 °C and DEAD (174 mg, 1 mmol) in anhydrous THF (5 mL) was added dropwise over 10 min. The mixture was stirred at 0 °C for 2 h. The mixture was concentrated to dryness and The residue was directly loaded on silica gel and purified (hexane/EtOAc = 15/1) to give **4a** (105 mg, 55 %) as a pale yellow solid.

1.4. Protocols for Deprotection of tosyl and Nosyl groups

Conditions A.^[1]

To a suspension of Mg (40 mg, 1.6 mmol) in anhydrous MeOH (5 mL) was added *N*-benzyl-*N*-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (**4a**, 115 mg, 0.3 mmol). The resulting suspension was sonicated for 1 h until consumption of the starting material (reaction monitored by TLC) was complete. The reaction was then diluted with brine (5 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated. The resulting residue was purified by flash chromatography (silica gel, DCM/MeOH, 99/1) afforded the pure product **5a** as a colorless liquid, 55 mg (80% yield).

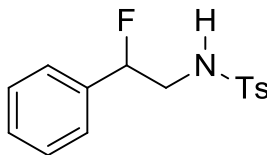
Conditions B.^[2]

A solution of *N*-benzyl-*N*-(2-(4-chlorophenyl)-2-fluoroethyl)-2-nitrobenzenesulfonamide (**4i**, 135 mg, 0.3 mmol) in dry DMF (1 mL) was added to a solution of DBU (274 mg, 1.8 mmol) and 2-mercaptoethanol (140 mg, 1.8 mmol) in DMF (2 mL). The reaction mixture was stirred for 12 h, diluted with water (10 mL) and extracted with ether (3 × 5 mL). The organic phase was washed with water (3 × 10 mL), dried (anhydrous MgSO₄), and evaporated to afford the crude product. Purification by flash chromatography (silica gel, DCM/MeOH, 99/1) afforded the pure product **5b** as a colorless liquid, 51 mg (65% yield).

References.

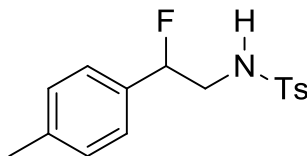
- [1] a) B. Nyasse, L. Grehn, U. Ragnarsson, *Chem. Commun.* **1997**, 1017; b) D. A. Alonso, P. G. Andersson, *J. Org. Chem.* **1998**, 63, 9455.
- [2] a) T. Kan, T. Fukuyama, *Chem. Commun.* **2004**, 353; b) R. De Marco, M. L. Di Gioia, A. Leggio, A. Liguori, M. C. Viscomi, *Eur. J. Org. Chem.* **2009**, 3795.

2. Analytical data of New Compounds.



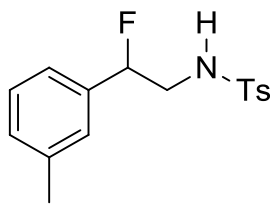
***N*-(2-Fluoro-2-phenylethyl)-*N*-tolylsulfonamide (2a)**

Pale yellow solid; mp: 83-85 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, J = 8.0 Hz, 2H), 7.29 – 7.14 (m, 7H), 5.38 (ddd, J = 48.1, 8.3, 3.4 Hz, 1H), 5.16 (dd, J = 7.8, 4.8 Hz, 1H), 3.32 – 3.17 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.69, 136.90, 136.51 (d, J = 19.5 Hz), 129.85, 129.04 (d, J = 1.6 Hz), 128.70, 127.07, 125.60, 125.54, 92.76 (d, J = 174.1 Hz), 48.62 (d, J = 25.2 Hz), 21.52. ^{19}F NMR (376 MHz, CDCl_3) δ -182.75 (ddd J = 46.9, 30.2, 16.8 Hz). IR (film) ν (cm^{-1}) 3301, 3089, 2938, 2360, 1927, 1598, 1455, 1305, 1288, 1092, 916, 698. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{15}\text{H}_{17}\text{FNO}_2\text{S}$: 294.0959, Found: 294.0927.



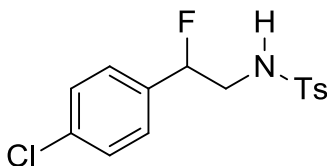
***N*-(2-fluoro-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (2b).**

Colorless solid; mp: 115-118 °C ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.59 (ddd, J = 47.7, 7.8, 3.4 Hz, 1H), 5.16 (dd, J = 7.4, 4.7 Hz, 1H), 3.75 – 3.40 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.10, 145.87, 139.37, 132.86 (d, J = 19.8 Hz), 129.48, 128.23, 125.46, 125.39, 124.42, 92.47 (d, J = 174.3 Hz), 48.57 (d, J = 25.2 Hz), 21.18. ^{19}F NMR (376 MHz, CDCl_3) δ -181.54 (ddd, J = 46.4, 30.0, 16.5 Hz). IR (film) ν (cm^{-1}) 3267, 3037, 2921, 2854, 2360, 1916, 1597, 1434, 1254, 1092, 809, 775. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{FNO}_2\text{S}$: 308.1115. Found: 308.1079.



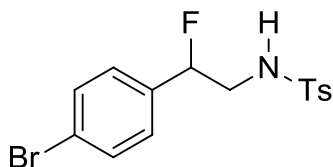
***N*-(2-fluoro-2-(*m*-tolyl)ethyl)-4-methylbenzenesulfonamide (2c).**

Colorless solid; mp: 93-97 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.45 – 7.37 (m, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 7.8 Hz, 2H), 5.63 (ddd, J = 48.2, 8.4, 3.4 Hz, 1H), 5.27 (dd, J = 8.1, 4.4 Hz, 1H), 3.71 – 3.31 (m, 2H), 2.60 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.69, 138.51, 136.93, 136.39 (d, J = 19.2 Hz), 129.84, 128.63, 127.08, 126.19 (d, J = 6.8 Hz), 122.61 (d, J = 6.9 Hz), 92.81 (d, J = 173.8 Hz), 48.64 (d, J = 25.2 Hz), 21.54, 21.37. ^{19}F NMR (376 MHz, CDCl_3) δ -182.65 (dd, J = 47.0, 30.3, 16.7 Hz). IR (film) ν (cm^{-1}) 3265, 3030, 2911, 2859, 2370, 1914, 1597, 1433, 1251, 1092, 799. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{FNO}_2\text{S}$: 308.1115 Found: 308.1089.



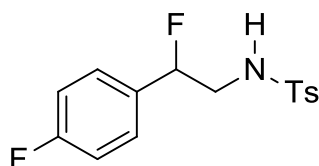
***N*-(2-(4-chlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (2d).**

Yellow solid; mp: 139-141 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.3 Hz, 4H), 7.10 (d, J = 8.3 Hz, 2H), 5.40 (ddd, J = 47.6, 8.0, 3.5 Hz, 1H), 4.89 (dd, J = 7.9, 4.8 Hz, 1H), 3.43 – 3.09 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.83, 136.79, 135.00, 134.80, 129.86, 128.92, 127.01, 126.92 (d, J = 7.0 Hz), 92.09 (d, J = 174.7 Hz), 48.43 (d, J = 25.1 Hz), 21.55. ^{19}F NMR (376 MHz, CDCl_3) δ -183.19 (ddd, J = 46.4, 28.8, 17.7 Hz). IR (film) ν (cm^{-1}) 3269, 3070, 2923, 2853, 2360, 1599, 1433, 1326, 1251, 1090, 820, 713. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{ClFNO}_2\text{S}$: 328.0569. Found: 328.0534.



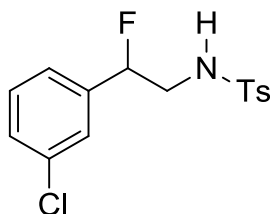
***N*-(2-(4-bromophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (2e).**

Colorless crystals; mp: 149-153 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 5.56 (ddd, J = 47.6, 8.0, 3.5 Hz, 1H), 5.17 (m, 1H), 3.67 – 3.19 (m, 2H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.83, 136.77, 135.45 (d, J = 20.0 Hz), 131.86, 129.87, 127.20 (d, J = 7.0 Hz), 127.01, 123.12, 92.11 (d, J = 174.8 Hz), 48.35 (d, J = 25.1 Hz), 21.56. ^{19}F NMR (376 MHz, CDCl_3) δ -183.82 (ddd, J = 46.6, 28.9, 17.8 Hz). IR (film) ν (cm^{-1}) 3274, 2916, 2360, 1653, 1373, 1274, 1163, 1092, 1055, 915, 813. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{BrFNO}_2\text{S}$: 372.0064. Found: 372.0042.



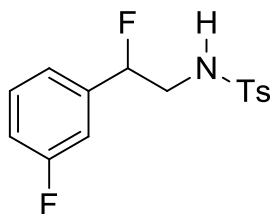
***N*-(2-fluoro-2-(4-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (2f).**

Pale yellow solid; mp: 116-119 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.15 (dd, J = 8.2, 5.4 Hz, 2H), 6.95 (t, J = 8.6 Hz, 2H), 5.39 (ddd, J = 47.6, 8.1, 3.6 Hz, 1H), 5.05 (dd, J = 7.8, 4.9 Hz, 1H), 3.46 – 3.07 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.26, 161.79, 143.80, 136.82, 132.31 (dd, J = 20.1, 3.3 Hz), 129.86, 127.57 (dd, J = 8.3, 6.8 Hz), 127.03, 115.71 (d, J = 21.8 Hz), 92.18 (d, J = 174.1 Hz), 48.49 (d, J = 25.7 Hz), 21.52. ^{19}F NMR (376 MHz, CDCl_3) δ -112.25 (ddd, J = 8.5, 5.9, 3.0 Hz), -181.13 (ddd, J = 46.1, 29.2, 17.0 Hz). IR (film) ν (cm^{-1}) 3275, 3072, 2925, 2360, 1601, 1514, 1327, 1227, 1159, 902, 883, 778. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_2\text{NO}_2\text{S}$: 312.0865. Found: 312.0836.



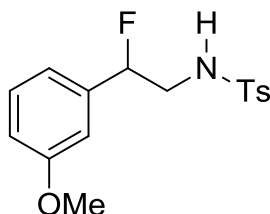
***N*-(2-(3-chlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (2g).**

White solid; mp: 83-86 °C ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 6.8 Hz, 4H), 7.16 (s, 1H), 7.06 (d, J = 6.8 Hz, 1H), 5.40 (ddd, J = 47.7, 8.1, 3.4 Hz, 1H), 5.01 (dd, J = 8.1, 4.7 Hz, 1H), 3.47 – 3.15 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.84, 138.45 (d, J = 19.9 Hz), 136.77, 134.73, 130.05, 129.89, 129.15 (d, J = 1.3 Hz), 127.02, 125.66 (d, J = 7.8 Hz), 123.65 (d, J = 7.0 Hz), 91.96 (d, J = 175.7 Hz), 48.44 (d, J = 24.8 Hz), 21.55. ^{19}F NMR (376 MHz, CDCl_3) δ -184.44 (ddd, J = 46.9, 29.5, 17.4 Hz). IR (film) ν (cm^{-1}) 3300, 3033, 2934, 2360, 1597, 1480, 1288, 1184, 1093, 934, 889, 781. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{ClFNO}_2\text{S}$: 328.0569 Found: 328.0537.



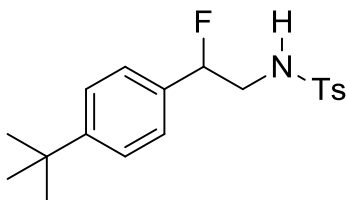
***N*-(2-fluoro-2-(3-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (2h).**

Colorless solid; mp: 86-89 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 3H), 6.95 (dd, J = 10.9, 5.1 Hz, 2H), 6.86 (d, J = 9.3 Hz, 1H), 5.40 (ddd, J = 47.8, 8.2, 3.3 Hz, 1H), 4.82 (dd, J = 8.1, 4.4 Hz, 1H), 3.45 – 3.11 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.85 (d, J = 247.3 Hz), 143.86, 139.46 – 138.28 (m), 136.80, 130.44 (d, J = 8.1 Hz), 129.88, 127.03, 121.06 (dd, J = 7.2, 3.1 Hz), 115.97 (d, J = 22.3 Hz), 112.58 (dd, J = 22.8, 7.9 Hz), 91.98 (d, J = 175.6 Hz), 48.47 (d, J = 24.7 Hz), 21.53. ^{19}F NMR (376 MHz, CDCl_3) δ -111.69 (td, J = 9.0, 5.8 Hz), -184.42 (ddd, J = 46.9, 29.7, 17.3 Hz). IR (film) ν (cm^{-1}) 3300, 2925, 2855, 2360, 1657, 1596, 1492, 1327, 1287, 1230, 1109, 835. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_2\text{NO}_2\text{S}$: 312.0865 Found: 312.0852.



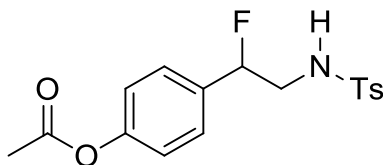
***N*-(2-fluoro-2-(3-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (2i).**

waxy solid. ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.18 (t, J = 3.9 Hz, 1H), 6.79 (dd, J = 8.3, 2.5 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.70 (d, J = 1.6 Hz, 1H), 5.37 (ddd, J = 48.1, 8.3, 3.4 Hz, 1H), 4.85 (dd, J = 8.2, 4.2 Hz, 1H), 3.70 (s, 3H), 3.46 – 3.11 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.84, 143.74, 137.94 (d, J = 19.5 Hz), 136.87, 129.87, 129.85, 127.05, 117.64 (d, J = 7.0 Hz), 114.53, 111.05 (d, J = 7.7 Hz), 92.56 (d, J = 174.6 Hz), 55.30, 48.59 (d, J = 25.1 Hz), 21.53. ^{19}F NMR (376 MHz, CDCl_3) δ -183.44 (ddd, J = 47.3, 30.3, 17.1 Hz). IR (film) ν (cm^{-1}) 3432, 2923, 2360, 2341, 1598, 1492, 1327, 1160, 1043, 814, 698. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{FNO}_3\text{S}$: 324.1064 Found: 324.1033.



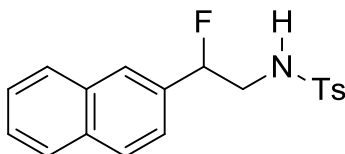
***N*-(2-(4-(*tert*-butyl)phenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (2j).**

Yellow solid; mp: 129-132 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 5.32 (ddd, J = 48.2, 8.4, 3.5 Hz, 1H), 4.87 (dd, J = 8.3, 4.4 Hz, 1H), 3.39 – 3.07 (m, 2H), 2.29 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.29 (d, J = 1.8 Hz), 152.28, 143.70, 133.37 (d, J = 19.6 Hz), 133.28, 129.84, 127.10, 125.65, 125.43 (d, J = 6.5 Hz), 92.67 (d, J = 173.1 Hz), 48.52 (d, J = 25.5 Hz), 34.67, 31.25, 21.54. ^{19}F NMR (376 MHz, CDCl_3) δ -181.43 (ddd, J = 46.8, 30.4, 16.5 Hz). IR (film) ν (cm^{-1}) 3267, 2961, 2866, 2360, 1598, 1424, 1322, 1286, 1160, 1019, 863, 708. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{19}\text{H}_{25}\text{FNO}_2\text{S}$: 350.1585. Found: 350.1546.



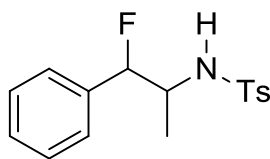
4-(1-fluoro-2-(4-methylphenylsulfonamido)ethyl)phenyl acetate (2k).

Pale yellow solid, 116-118 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 5.46 (ddd, J = 47.9, 8.3, 3.2 Hz, 1H), 5.02 (dd, J = 7.9, 4.5 Hz, 1H), 3.50 – 3.13 (m, 2H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.35, 151.08, 143.77, 136.79, 134.03 (d, J = 20.0 Hz), 129.87, 127.06, 126.79 (d, J = 6.9 Hz), 121.96, 92.29 (d, J = 174.4 Hz), 48.58 (d, J = 25.3 Hz), 21.53, 21.10. ^{19}F NMR (376 MHz, CDCl_3) δ -182.43 (ddd, J = 45.2, 29.0, 16.2 Hz). IR (film) ν (cm^{-1}) 3310, 2938, 2360, 1762, 1597, 1327, 1288, 1158, 1073, 948, 849, 778. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{18}\text{H}_{19}\text{FNO}_4\text{S}$: 352.1014 Found: 352.0984.



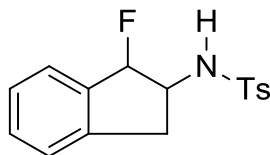
N-(2-fluoro-2-(naphthalen-2-yl)ethyl)-4-methylbenzenesulfonamide (2l).

White solid; mp: 113-116 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.76 (m, 3H), 7.71 (d, J = 8.1 Hz, 2H), 7.49 (dd, J = 6.3, 3.2 Hz, 2H), 7.31 (dd, J = 8.5, 1.2 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 5.64 (ddd, J = 47.8, 8.0, 3.6 Hz, 1H), 5.14 (dd, J = 7.9, 4.8 Hz, 1H), 3.60 – 3.22 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.68, 136.87, 133.79 (d, J = 19.4 Hz), 133.47 (d, J = 1.0 Hz), 132.93, 129.80, 128.68, 128.14, 127.78, 127.04, 126.70, 126.64, 122.72 (d, J = 6.1 Hz), 92.89 (d, J = 174.4 Hz), 48.56 (d, J = 25.4 Hz), 21.53. ^{19}F NMR (376 MHz, CDCl_3) δ -182.67 (ddd, J = 46.5, 29.1, 17.4 Hz). IR (film) ν (cm^{-1}) 3262, 2947, 2360, 1597, 1492, 1448, 1331, 1264, 1331, 1264, 953, 864. HRMS: m/z $[[\text{M}-\text{H}]^+]$ Calcd. for $\text{C}_{19}\text{H}_{19}\text{FNO}_2\text{S}$: 344.1115 Found: 344.1096.



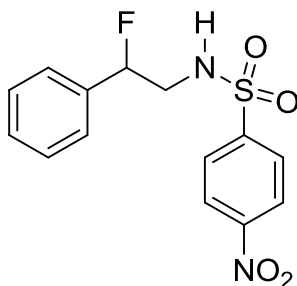
N-(1-fluoro-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (2m).

Waxy solid. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 8.3 Hz, 2H), 7.32 – 7.18 (m, 5H), 7.18 – 7.10 (m, 2H), 5.43 (dd, J = 47.1, 3.0 Hz, 1H), 5.32 (d, J = 9.0 Hz, 1H), 3.82 – 3.53 (m, 2H), 2.33 (s, 3H), 0.91 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.50, 138.04, 136.70 (d, J = 20.3 Hz), 129.81, 129.63, 128.47, 128.46, 128.33, 127.00, 125.16 (d, J = 8.5 Hz), 95.48 (d, J = 179.1 Hz), 54.13 (d, J = 23.5 Hz), 21.52, 14.28 (d, J = 6.1 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -186.50 (ddd, J = 45.8, 15.6 Hz), -198.76 (dd, J = 47.1, 24.6 Hz). IR (film) ν (cm^{-1}) 3258, 2980, 2877, 2360, 1655, 1496, 1380, 1331, 1289, 1122, 957, 852. HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{FNO}_2\text{S}$: 308.1115 Found: 308.1093.



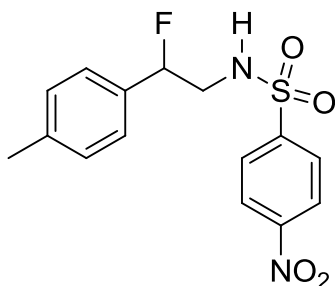
N-(1-fluoro-2,3-dihydro-1H-inden-2-yl)-4-methylbenzenesulfonamide (2n).

Waxy solid. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 8.2 Hz, 2H), 7.31 – 7.18 (m, 4H), 7.11 (dd, J = 15.7, 7.8 Hz, 2H), 5.34 (d, J = 9.9 Hz, 1H), 5.20 (dd, J = 57.8, 4.6 Hz, 1H), 4.08 – 3.88 (m, 1H), 2.98 (dd, J = 15.8, 7.7 Hz, 1H), 2.86 – 2.72 (m, 1H), 2.33 (3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.76, 142.29 (d, J = 5.3 Hz), 136.78 (d, J = 15.4 Hz), 131.05 (d, J = 4.5 Hz), 129.89, 127.51 (d, J = 3.7 Hz), 127.16, 126.43 (d, J = 2.6 Hz), 125.10 (d, J = 3.0 Hz), 93.61 (d, J = 178.4 Hz), 55.82 (d, J = 20.4 Hz), 36.84, 21.61. ^{19}F NMR (376 MHz, CDCl_3) δ -177.89 (ddd, J = 58.0, 24.5 Hz). HRMS: m/z $[[\text{M}+\text{H}]^+]$ Calcd. for $\text{C}_{16}\text{H}_{17}\text{FNO}_2\text{S}$: 306.0959 Found: 306.0922.



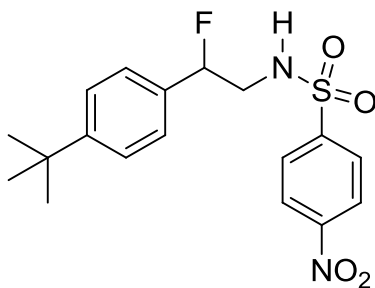
***N*-(2-fluoro-2-phenylethyl)-4-nitrobenzenesulfonamide (3a).**

Pale yellow solid; mp: 126-130 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.7 Hz, 2H), 7.40 – 7.19 (m, 3H), 7.13 (dd, J = 8.1, 4.7 Hz, 2H), 5.42 (ddd, J = 47.8, 7.9, 3.1 Hz, 1H), 5.18 (dd, J = 7.5, 4.5 Hz, 1H), 3.55 – 3.12 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.12, 145.81, 135.92 (d, J = 19.6 Hz), 129.28, 128.83, 128.24, 125.42 (d, J = 7.0 Hz), 124.46, 92.56 (d, J = 174.9 Hz), 48.61 (d, J = 24.7 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -183.39 (ddd, J = 46.8, 28.6, 18.3 Hz). IR (film) ν (cm^{-1}) 3280, 3104, 3039, 2924, 2360, 1944, 1697, 1478, 1373, 1241, 1089, 889. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{FN}_2\text{O}_4\text{S}$, 323.0507 Found: 323.0474.



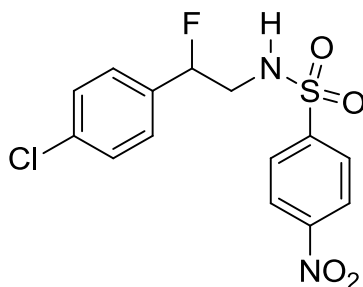
***N*-(2-fluoro-2-(*p*-tolyl)ethyl)-4-nitrobenzenesulfonamide (3b).**

Pale yellow solid; mp: 151-154. ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.59 (ddd, J = 47.7, 7.8, 3.4 Hz, 1H), 5.16 (dd, J = 7.4, 4.7 Hz, 1H), 3.75 – 3.32 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.10, 145.87, 139.37, 132.86 (d, J = 19.8 Hz), 129.48, 128.23, 125.43 (d, J = 6.8 Hz), 124.42, 92.47 (d, J = 174.3 Hz), 48.57 (d, J = 25.2 Hz), 21.18. ^{19}F NMR (376 MHz, CDCl_3) δ -182.09 (ddd, J = 46.4, 28.0, 18.4 Hz). IR (film) ν (cm^{-1}) 3272, 3113, 2948, 2360, 1615, 1533, 1402, 1252, 1165, 1091, 907, 826. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{14}\text{FN}_2\text{O}_4\text{S}$: 337.0664 Found: 337.0656.



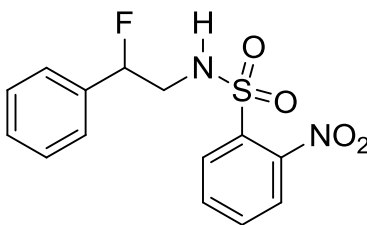
***N*-(2-(4-(*tert*-butyl)phenyl)-2-fluoroethyl)-4-nitrobenzenesulfonamide (3c).**

Pale yellow solid; mp: 158-160 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 5.35 (ddd, J = 47.9, 8.1, 3.3 Hz, 1H), 5.01 (dd, J = 8.0, 4.4 Hz, 1H), 3.48 – 3.08 (m, 1H), 1.15 (s, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.62 (d, J = 1.8 Hz), 150.15, 145.85, 132.81 (d, J = 19.7 Hz), 128.29, 125.80, 125.32 (d, J = 6.6 Hz), 124.46, 92.52 (d, J = 174.1 Hz), 48.53 (d, J = 25.1 Hz), 34.70, 31.23. ^{19}F NMR (376 MHz, CDCl_3) δ -181.67 (ddd, J = 46.7, 29.1, 17.6 Hz). IR (film) ν (cm^{-1}) 3279, 3107, 2959, 2868, 2360, 1607, 1530, 1465, 1310, 1165, 1010, 882. HRMS: m/z $[\text{M-H}]^-$ Calcd. for $\text{C}_{18}\text{H}_{20}\text{FN}_2\text{O}_4\text{S}$: 379.1133 Found: 379.1122.



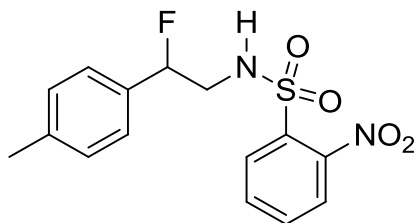
***N*-(2-(4-chlorophenyl)-2-fluoroethyl)-4-nitrobenzenesulfonamide (3d).**

White solid; mp: 138-141 °C. ^1H NMR (200 MHz, CDCl_3) δ 8.36 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 8.9 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 5.55 (ddd, J = 47.6, 7.7, 3.4 Hz, 1H), 5.27 – 4.94 (m, 1H), 3.77 – 2.91 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.12, 145.84, 135.23, 134.44 (d, J = 20.1 Hz), 129.03, 128.17, 126.82 (d, J = 7.1 Hz), 124.46, 92.00 (d, J = 175.6 Hz), 48.48 (d, J = 24.8 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -183.81 (ddd, J = 46.6, 27.8, 18.9 Hz). IR (film) ν (cm^{-1}) 3271, 3099, 2915, 2360, 1607, 1542, 1330, 1254, 1165, 964, 911, 714. HRMS: m/z $[\text{M-H}]^-$ Calcd. for $\text{C}_{14}\text{H}_{11}\text{ClFN}_2\text{O}_4\text{S}$: 357.0117 Found: 357.0088.



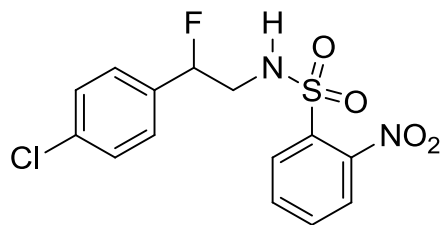
***N*-(2-fluoro-2-phenylethyl)-2-nitrobenzenesulfonamide (3e).**

Pale yellow solid; mp: 105-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.06 – 7.94 (m, 1H), 7.83 – 7.72 (m, 1H), 7.69 – 7.56 (m, 2H), 7.24 (dd, J = 5.3, 1.3 Hz, 3H), 7.20 – 7.09 (m, 2H), 5.82 – 5.62 (m, 1H), 5.45 (ddd, J = 47.8, 7.9, 3.3 Hz, 1H), 3.69 – 3.27 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.89 (s), 136.12 (d, J = 19.6 Hz), 133.91 (s), 133.73 (s), 133.00 (s), 130.77 (s), 129.18 (s), 128.76 (s), 125.49 (d, J = 7.6 Hz), 125.38 (s), 92.55 (d, J = 175.3 Hz), 49.18 (d, J = 24.8 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -183.22 (ddd, J = 46.6, 28.7, 18.1 Hz). IR (film) ν (cm^{-1}) 3353, 2953, 2359, 1535, 1445, 1350, 1201, 1127, 927, 879, 770. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{14}\text{H}_{12}\text{FN}_2\text{O}_4\text{S}$: 323.0507 Found: 323.0497.



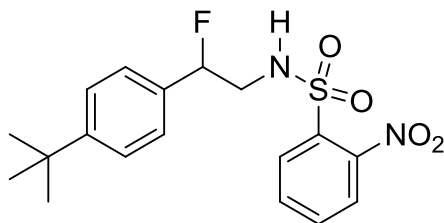
***N*-(2-fluoro-2-(p-tolyl)ethyl)-2-nitrobenzenesulfonamide (3f).**

Pale yellow solid; mp: 105-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.88 – 7.75 (m, 2H), 7.23 (s, 4H), 5.91 (dd, J = 7.1, 5.1 Hz, 1H), 5.61 (ddd, J = 47.8, 7.8, 3.4 Hz, 1H), 3.91 – 3.42 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.83, 139.11 (d, J = 1.8 Hz), 133.81, 133.75, 133.25, 133.05, 130.76, 129.41, 125.56, 125.49 (d, J = 1.3 Hz), 92.56 (d, J = 174.4 Hz), 49.12 (d, J = 25.3 Hz), 21.20. ^{19}F NMR (376 MHz, CDCl_3) δ -181.30 (ddd, J = 47.8, 28.4, 18.4 Hz). IR (film) ν (cm^{-1}) 3355, 2952, 2360, 1616, 1441, 1347, 1242, 1125, 1056, 905, 816. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{14}\text{FN}_2\text{O}_4\text{S}$: 337.0664 Found: 337.0647.



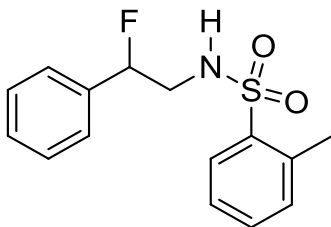
***N*-(2-(4-chlorophenyl)-2-fluoroethyl)-2-nitrobenzenesulfonamide (3g).**

Pale yellow solid; mp: 111-114 °C ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.77 – 7.62 (m, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 5.87 (dd, J = 7.1, 5.1 Hz, 1H), 5.54 (ddd, J = 47.3, 7.3, 3.3 Hz, 1H), 3.57 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.69, 134.88, 134.67, 133.83, 133.71, 133.15, 130.62, 128.87, 126.97 (d, J = 7.2 Hz), 125.45, 91.94 (d, J = 175.7 Hz), 48.92 (d, J = 24.8 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -183.43 (ddd, J = 46.5, 27.0, 19.6 Hz). IR (film) ν (cm^{-1}) 3344, 3097, 2930, 2360, 1567, 1422, 1202, 1160, 1055, 912, 827, 787. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{14}\text{H}_{11}\text{ClFN}_2\text{O}_4\text{S}$: 357.0111 Found: 357.0111.



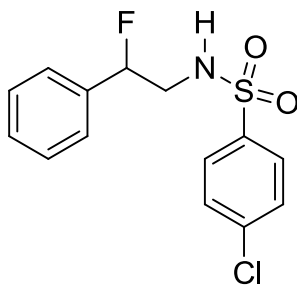
***N*-(2-(4-(tert-butyl)phenyl)-2-fluoroethyl)-2-nitrobenzenesulfonamide (3h).**

Pale yellow waxy solid. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, J = 5.8, 3.4 Hz, 1H), 7.71 (dd, J = 5.7, 3.6 Hz, 1H), 7.58 (dd, J = 5.9, 3.4 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 5.72 (dd, J = 7.1, 5.1 Hz, 1H), 5.40 (ddd, J = 48.0, 8.1, 3.3 Hz, 1H), 3.60 – 3.22 (m, 2H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.35 (d, J = 1.7 Hz), 147.89, 133.92, 133.70, 133.28, 133.08, 130.84, 125.72, 125.57 – 125.18 (m), 92.60 (d, J = 174.3 Hz), 49.08 (d, J = 25.1 Hz), 34.68, 31.27. ^{19}F NMR (376 MHz, CDCl_3) δ -181.02 (ddd, J = 47.1, 29.5, 17.6 Hz). IR (film) ν (cm^{-1}) 3373, 2962, 2361, 1594, 1541, 1442, 1362, 1243, 1168, 1057, 836, 783. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{18}\text{H}_{20}\text{FN}_2\text{O}_4\text{S}$: 379.1133 Found: 379.1120.



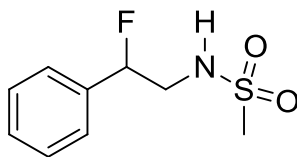
***N*-(2-fluoro-2-phenylethyl)-2-methylbenzenesulfonamide (3i).**

Waxy solid. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.30 – 7.17 (m, 5H), 7.15 – 7.05 (m, 2H), 5.35 (ddd, J = 48.1, 8.1, 3.6 Hz, 1H), 5.16 (dd, J = 7.5, 4.9 Hz, 1H), 3.51 – 3.11 (m, 2H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.81, 137.21, 136.41 (d, J = 19.5 Hz), 133.01, 132.74, 129.34, 129.08, 129.06, 128.72, 126.25, 125.50 (d, J = 7.0 Hz), 92.71 (d, J = 174.0 Hz), 48.41 (d, J = 25.2 Hz), 20.22. ^{19}F NMR (376 MHz, CDCl_3) δ -183.98 (ddd, J = 47.0, 29.5, 17.5 Hz). IR (film) ν (cm^{-1}) 3388, 2917, 2360, 1639, 1423, 1255, 1054, 918, 874, 771, 698. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{15}\text{H}_{17}\text{FNO}_2\text{S}$: 294.0959 Found: 294.0932.



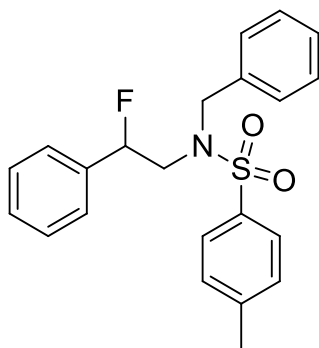
4-chloro-*N*-(2-fluoro-2-phenylethyl)benzenesulfonamide (3j).

White solid; mp: 126-129 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.24 (dd, J = 4.9, 1.6 Hz, 3H), 7.17 – 7.09 (m, 2H), 5.39 (ddd, J = 48.0, 8.2, 3.4 Hz, 1H), 5.10 (dd, J = 7.9, 4.7 Hz, 1H), 3.51 – 2.98 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.37, 138.42, 136.22 (d, J = 19.5 Hz), 129.52, 129.17, 129.15, 128.77, 128.49, 125.51 (d, J = 7.0 Hz), 92.66 (d, J = 174.4 Hz), 48.57 (d, J = 25.0 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -183.02 (ddd, J = 46.8, 29.5, 17.4 Hz). IR (film) ν (cm^{-1}) 3277, 3092, 2926, 2852, 2360, 1587, 1496, 1453, 1398, 1279, 1160, 904. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{14}\text{H}_{12}\text{ClFNO}_2\text{S}$: 314.0413 Found: 314.0398.



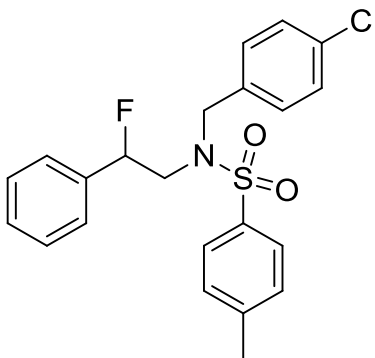
***N*-(2-fluoro-2-phenylethyl)methanesulfonamide (3k).**

Brown liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (dt, J = 12.9, 5.7 Hz, 5H), 5.33 (ddd, J = 48.0, 6.8, 4.4 Hz, 1H), 5.14 (t, J = 6.2 Hz, 1H), 3.61 – 3.27 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.56 (d, J = 19.6 Hz), 129.10 (d, J = 1.5 Hz), 128.78, 125.63 (d, J = 7.0 Hz), 93.18 (d, J = 174.4 Hz), 48.60 (d, J = 24.7 Hz), 40.83 (d, J = 1.4 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -182.63 – -183.05 (m). IR (film) ν (cm^{-1}) 2981, 3072, 2925, 2362, 1912, 1611, 1450, 1300, 1299, 1092, 910, 690. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_9\text{H}_{13}\text{FNO}_2\text{S}$: 218.0646 Found: 218.0617.



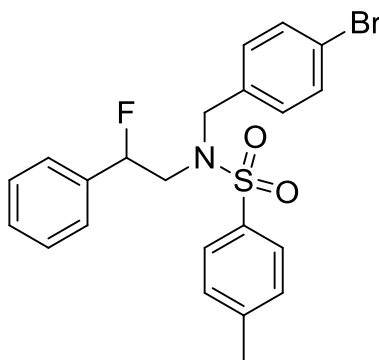
***N*-benzyl-*N*-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (4a).**

Pale yellow solid; mp: 96-99 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.1 Hz, 2H), 7.23 (m, 8H), 7.15 – 7.03 (m, 4H), 5.46 (ddd, J = 48.7, 7.2, 4.6 Hz, 1H), 4.41 (q, J = 15.0 Hz, 2H), 3.54 – 3.26 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.55, 137.41, 137.33, 135.67, 129.81, 128.79 (d, J = 1.4 Hz), 128.65, 128.60, 127.91, 127.29, 125.43 (d, J = 7.0 Hz), 93.33 (d, J = 176.1 Hz), 52.39 (d, J = 2.1 Hz), 52.31 (d, J = 25.7 Hz), 21.56. ^{19}F NMR (376 MHz, CDCl_3) δ -180.28 – -180.77 (m). IR (film) ν (cm^{-1}) 3447, 3089, 2360, 1598, 1495, 1454, 1370, 1253, 1189, 881, 774. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{22}\text{H}_{23}\text{FNO}_2\text{S}$: 384.1428 Found: 384.1395.



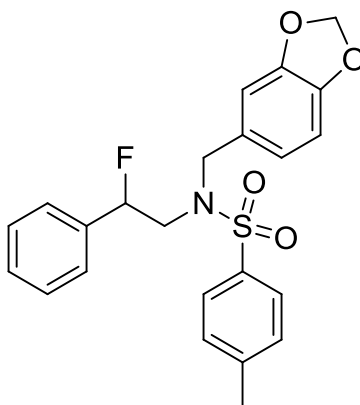
***N*-(4-chlorobenzyl)-*N*-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (4b).**

White solid; mp: 130-133 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 7.1 Hz, 5H), 7.17 (d, J = 8.3 Hz, 2H), 7.08 (t, J = 8.0 Hz, 4H), 5.47 (ddd, J = 48.7, 8.3, 3.0 Hz, 1H), 4.36 (q, J = 15.2 Hz, 2H), 3.58 – 3.20 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.80, 137.13 (d, J = 7.4 Hz), 136.98, 134.41, 133.74, 129.92, 128.91 (d, J = 1.3 Hz), 128.79, 128.67, 127.26, 125.44 (d, J = 6.9 Hz), 93.42 (d, J = 175.8 Hz), 52.65 (d, J = 25.8 Hz), 51.94 (d, J = 2.1 Hz), 21.57. ^{19}F NMR (376 MHz, CDCl_3) δ -179.89 (ddd, J = 47.5, 32.1, 15.5 Hz). IR (film) ν (cm^{-1}) 3064, 2929, 2360, 1800, 1648, 1597, 1490, 1362, 1202, 1155, 914, 815. HRMS: m/z $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{22}\text{H}_{22}\text{ClFNO}_2\text{S}$: 418.1039 Found: 418.1010.



***N*-(4-bromobenzyl)-*N*-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (4c).**

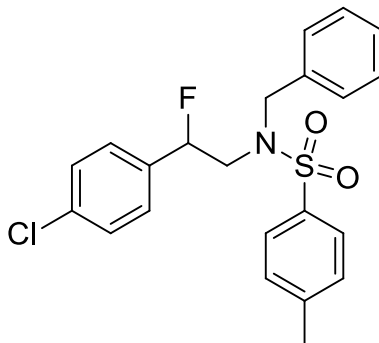
White solid; mp: 98-101 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 7.0 Hz, 5H), 7.13 – 7.06 (m, 2H), 7.00 (d, J = 8.1 Hz, 2H), 5.47 (ddd, J = 48.6, 8.4, 2.9 Hz, 1H), 4.34 (q, J = 15.3 Hz, 2H), 3.56 – 3.22 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.78, 137.14, 137.03 (d, J = 15.6 Hz), 134.90, 131.74, 130.23, 129.91, 128.89, 128.64 (d, J = 5.7 Hz), 127.25, 125.42 (d, J = 7.0 Hz), 121.90, 93.45 (d, J = 175.8 Hz), 52.62 (d, J = 25.8 Hz), 51.98 (d, J = 2.3 Hz), 21.58. ^{19}F NMR (376 MHz, CDCl_3) δ -179.93 (ddd, J = 47.5, 32.3, 15.2 Hz). IR (film) ν (cm^{-1}) 3442, 3066, 2360, 1596, 1488, 1375, 1292, 967, 857, 774. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{22}\text{H}_{20}\text{BrFNO}_2\text{S}$: 460.0387 Found: 460.0363.



***N*-(benzo[d][1,3]dioxol-5-ylmethyl)-*N*-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (4d).**

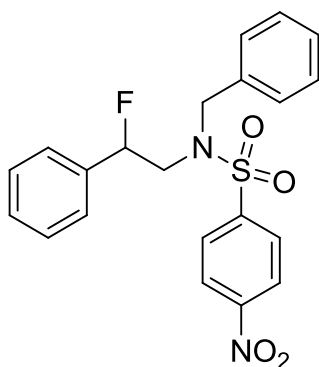
White solid; mp: 98-101 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 7.2 Hz, 5H), 7.14 – 7.05 (m, 2H), 6.63 (d, J = 7.7 Hz, 1H), 6.57 (d, J = 9.6 Hz, 2H), 5.84 (s, 2H), 5.61 – 5.30 (m, 1H), 4.28 (dd, J = 38.6, 14.8 Hz, 2H), 3.52 – 3.28 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.03, 147.40, 143.59, 137.35, 137.14, 129.82, 129.35, 128.81, 128.58, 127.25, 125.46 (d, J = 7.0

Hz), 122.21, 101.13, 93.34 (d, $J = 175.8$ Hz), 52.23 (d, $J = 2.1$ Hz), 52.04 (d, $J = 26.0$ Hz), 21.55. ^{19}F NMR (376 MHz, CDCl_3) δ -180.14 – -180.48 (m). IR (film) ν (cm^{-1}) 2954, 2360, 2341, 1734, 1598, 1505, 1498, 1447, 1330, 1256, 1101, 987. HRMS: m/z $[\text{M-H}]^-$ Calcd. for $\text{C}_{23}\text{H}_{21}\text{FNO}_4\text{S}$: 426.1181 Found: 426.1170.



***N*-benzyl-*N*-(2-(4-chlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (4e).**

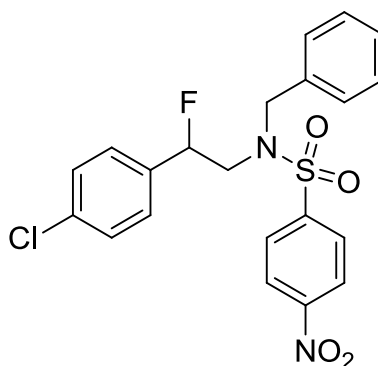
White solid; mp: 105-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.25 – 7.19 (m, 5H), 7.18 – 7.09 (m, 2H), 7.04 (d, $J = 8.2$ Hz, 2H), 5.67 – 5.35 (m, 1H), 4.40 (dd, $J = 45.7, 14.9$ Hz, 2H), 3.54 – 3.29 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.71, 136.98, 135.69 (d, $J = 19.9$ Hz), 135.47, 134.66 (d, $J = 1.9$ Hz), 129.86, 128.78, 128.68, 128.62, 127.98, 127.30, 126.92 (d, $J = 7.0$ Hz), 92.70 (d, $J = 176.3$ Hz), 52.69 (d, $J = 1.7$ Hz), 52.31 (d, $J = 26.7$ Hz), 21.57. ^{19}F NMR (376 MHz, CDCl_3) δ -180.22 – -180.64 (m). IR (film) ν (cm^{-1}) 3065, 2954, 2922, 2361, 1663, 1599, 1492, 1339, 1273, 1248, 1123, 929. HRMS: m/z $[\text{M+H}]^+$ Calcd. for $\text{C}_{22}\text{H}_{22}\text{ClFNO}_2\text{S}$: 418.1039 Found: 418.1007.



***N*-benzyl-*N*-(2-fluoro-2-phenylethyl)-4-nitrobenzenesulfonamide (4f).**

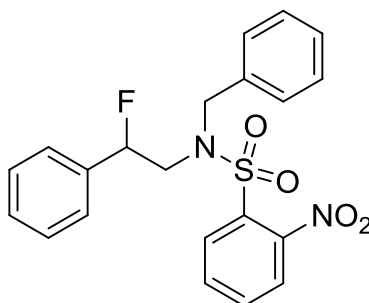
White solid; mp: 102-104 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.8$ Hz, 2H), 7.89 (d, $J = 8.8$ Hz, 2H), 7.31 – 7.18 (m, 6H), 7.17 – 7.10 (m, 2H), 7.11 – 7.04 (m,

2H), 5.44 (ddd, $J = 48.8, 9.0, 2.6$ Hz, 1H), 4.48 (q, $J = 15.1$ Hz, 2H), 3.58 (td, $J = 15.2, 9.0$ Hz, 1H), 3.41 (ddd, $J = 32.6, 15.8, 2.7$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.92, 146.33, 136.55 (d, $J = 19.5$ Hz), 134.70, 129.10 (d, $J = 1.5$ Hz), 128.90, 128.76, 128.56, 128.39, 125.36 (d, $J = 6.9$ Hz), 124.29, 92.73 (d, $J = 176.8$ Hz), 52.35 (d, $J = 16.8$ Hz), 52.21 (d, $J = 6.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -180.48 (ddd, $J = 48.0, 33.0, 15.0$ Hz). IR (film) ν (cm^{-1}) 3066, 2922, 2854, 2361, 1808, 1690, 1543, 1476, 1349, 1312, 1208, 989. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{21}\text{H}_{18}\text{FN}_2\text{O}_4\text{S}$: 413.0977 Found: 413.0971.



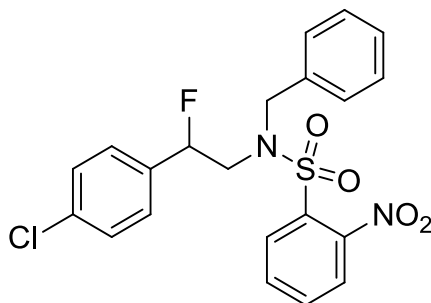
***N*-benzyl-*N*-(2-(4-chlorophenyl)-2-fluoroethyl)-4-nitrobenzenesulfonamide (4g).**

White solid; mp: 153-155 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.8$ Hz, 2H), 7.90 (d, $J = 8.8$ Hz, 2H), 7.22 (m, 5H), 7.12 (m, 2H), 7.03 (d, $J = 8.2$ Hz, 2H), 5.45 (ddd, $J = 48.4, 8.7, 2.7$ Hz, 1H), 4.47 (s, 2H), 3.55 (td, $J = 15.1, 8.8$ Hz, 1H), 3.38 (ddd, $J = 31.6, 15.7, 2.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.98, 146.06, 135.07 (d, $J = 5.1$ Hz), 134.90, 134.51, 128.95 (d, $J = 4.4$ Hz), 128.54, 128.44, 128.39, 126.77 (d, $J = 7.0$ Hz), 124.33, 92.24 (d, $J = 177.3$ Hz), 52.49 (d, $J = 1.8$ Hz), 52.31 (d, $J = 25.6$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -180.64 (ddd, $J = 47.4, 32.3, 15.2$ Hz). IR (film) ν (cm^{-1}) 3092, 2922, 2854, 2361, 1604, 1587, 1527, 1349, 1270, 1161, 1109, 855. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{21}\text{H}_{17}\text{ClFN}_2\text{O}_4\text{S}$: 447.1355 Found: 447.1337.



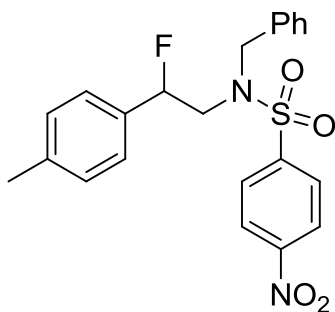
***N*-benzyl-*N*-(2-fluoro-2-phenylethyl)-2-nitrobenzenesulfonamide (4h).**

White solid; mp: 99-102 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 7.5 Hz, 1H), 7.71 – 7.52 (m, 3H), 7.23 (qdd, J = 14.1, 11.8, 6.6 Hz, 1H), 5.56 (ddd, J = 48.9, 7.5, 4.2 Hz, 1H), 4.67 (s, 2H), 3.65 – 3.60 (m, 1H), 3.56 (dd, J = 5.8, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.60, 147.89, 136.76 (d, J = 19.5 Hz), 135.04, 133.90, 133.71, 131.87, 131.00, 128.99 (d, J = 1.4 Hz), 128.82, 128.68, 128.49, 128.14, 125.43 (d, J = 7.0 Hz), 124.35, 93.34 (d, J = 176.4 Hz), 52.33 (d, J = 2.6 Hz), 52.08 (d, J = 24.4 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -180.43 – -180.99 (m). IR (film) ν (cm^{-1}) 3338, 3075, 3035, 2921, 2360, 1855, 1588, 1454, 1379, 1258, 1136, 126. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{21}\text{H}_{18}\text{FN}_2\text{O}_4\text{S}$: 413.0977 Found: 413.0963.



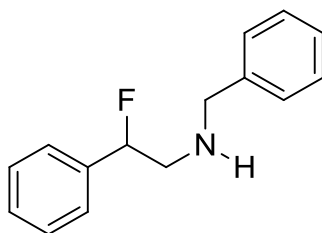
***N*-benzyl-*N*-(2-(4-chlorophenyl)-2-fluoroethyl)-2-nitrobenzenesulfonamide (4i).**

Pale yellow solid m.p. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 7.9 Hz, 1H), 7.73 – 7.50 (m, 3H), 7.20 (dt, J = 7.5, 5.5 Hz, 7H), 7.09 (d, J = 8.2 Hz, 2H), 5.68 – 5.38 (m, 1H), 4.66 (s, 2H), 3.67 – 3.51 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.83, 135.26 (d, J = 20.0 Hz), 134.86, 134.80 (d, J = 1.9 Hz), 133.75, 133.70, 131.90, 130.99, 128.85, 128.20, 126.88 (d, J = 7.1 Hz), 124.35, 92.82 (d, J = 177.0 Hz), 52.47 (d, J = 2.7 Hz), 51.98 (d, J = 24.7 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -181.01 (ddd, J = 47.8, 30.1, 17.8 Hz). IR ν (cm^{-1}) 3423, 2924, 2360, 2341, 1543, 1495, 1439, 1206, 1091, 937, 851, 777. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{21}\text{H}_{17}\text{ClFN}_2\text{O}_4\text{S}$: 447.1355 Found: 447.1332.



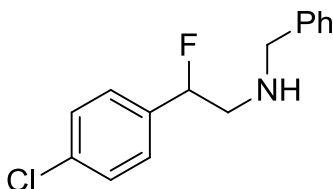
***N*-benzyl-*N*-(2-fluoro-2-(*p*-tolyl)ethyl)-4-nitrobenzenesulfonamide (4j).**

Pale yellow solid m.p. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.5$ Hz, 2H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 4.9$ Hz, 3H), 7.20 – 7.13 (m, 2H), 7.06 (d, $J = 7.8$ Hz, 2H), 6.98 (d, $J = 7.8$ Hz, 2H), 5.42 (dd, $J = 48.7, 7.5$ Hz, 1H), 4.50 (q, $J = 15.1$ Hz, 2H), 3.61 (td, $J = 15.0, 9.0$ Hz, 1H), 3.40 (dd, $J = 30.7, 15.5$ Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.88, 146.36, 139.11 (d, $J = 1.7$ Hz), 134.77, 133.55 (d, $J = 19.6$ Hz), 129.40, 128.88, 128.56, 128.39, 128.34, 125.44 (d, $J = 6.6$ Hz), 124.27, 92.64 (d, $J = 176.0$ Hz), 21.20. ^{19}F NMR (376 MHz, CDCl_3) δ -178.60 (ddd, $J = 47.5, 32.7, 14.9$ Hz). IR ν (cm^{-1}) 3093, 2921, 2360, 1805, 1588, 1530, 1477, 1349, 1256, 1085, 881, 766. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{22}\text{H}_{20}\text{FN}_2\text{O}_4\text{S}$: 429.1279 Found: 429.1266.



N-benzyl-2-fluoro-2-phenylethanamine (5a).

Brown liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.07 (m, 10H), 5.53 (ddd, J = 48.7, 8.6, 3.2 Hz, 1H), 3.78 (s, 2H), 3.04 (ddd, J = 16.5, 13.3, 8.6 Hz, 1H), 2.83 (ddd, J = 31.8, 13.3, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.92, 138.42 (d, J = 19.5 Hz), 128.52, 128.50, 128.13, 127.11, 125.61 (d, J = 7.0 Hz), 93.98 (d, J = 171.1 Hz), 54.96 (d, J = 24.0 Hz), 53.68. ^{19}F NMR (376 MHz, CDCl_3) δ -182.02 (dd, J = 48.4, 31.9, 16.6 Hz). IR ν (cm^{-1}) 3447, 3089, 2360, 1598, 1495, 1454, 1370, 1253, 1189, 881, 774. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{17}\text{FN}$: 230.1340 Found: 230.1321.



N-benzyl-2-(4-chlorophenyl)-2-fluoroethanamine (5b).

^1H NMR (400 MHz, CDCl_3) δ 7.24 (dt, J = 12.7, 4.9 Hz, 6H), 7.17 (d, J = 8.7 Hz, 3H), 5.49 (ddd, J = 48.4, 8.4, 3.3 Hz, 1H), 3.77 (s, 2H), 3.00 (ddd, J = 16.9, 13.3, 8.4 Hz, 1H), 2.89 – 2.71 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.77, 136.93 (d, J = 20.0 Hz), 134.35 (d, J = 2.1 Hz), 128.72, 128.54, 128.13, 127.19, 127.04 (d, J = 7.0 Hz), 93.29 (d, J = 172.0 Hz), 54.74 (d, J = 23.9 Hz), 53.66. ^{19}F NMR (376 MHz, CDCl_3) δ -182.17 (ddd, J = 48.1, 31.2, 17.0 Hz). IR ν (cm^{-1}) 3331, 2917, 2848, 1738, 1600, 1494, 1453, 1092, 1015, 908, 828, 734. HRMS: m/z $[\text{M}-\text{H}]^-$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{ClFN}$: 264.0950 Found: 264.0933.

3. X-Ray Analytical Data for Compound 2e

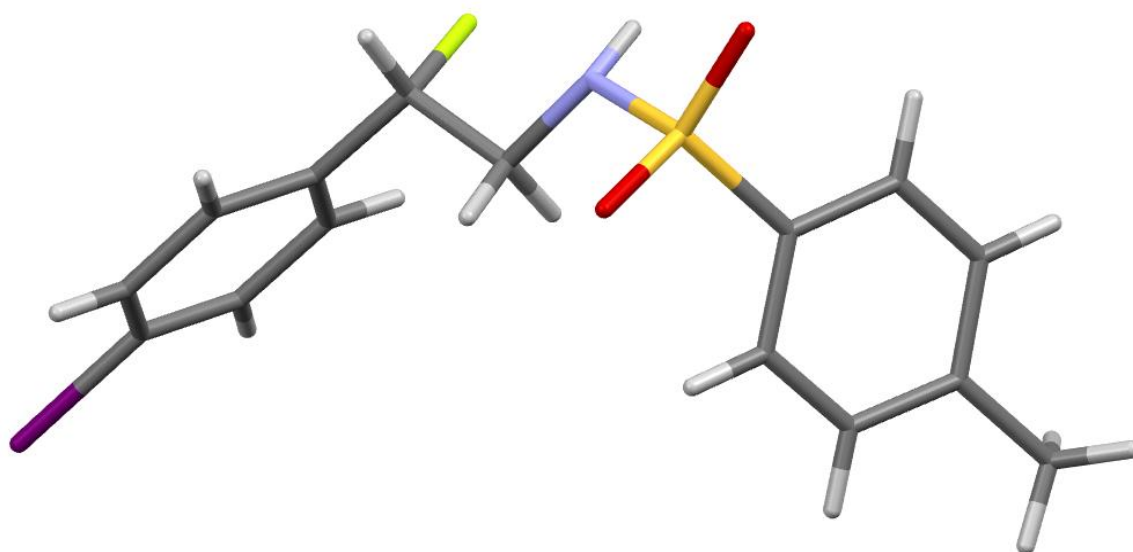
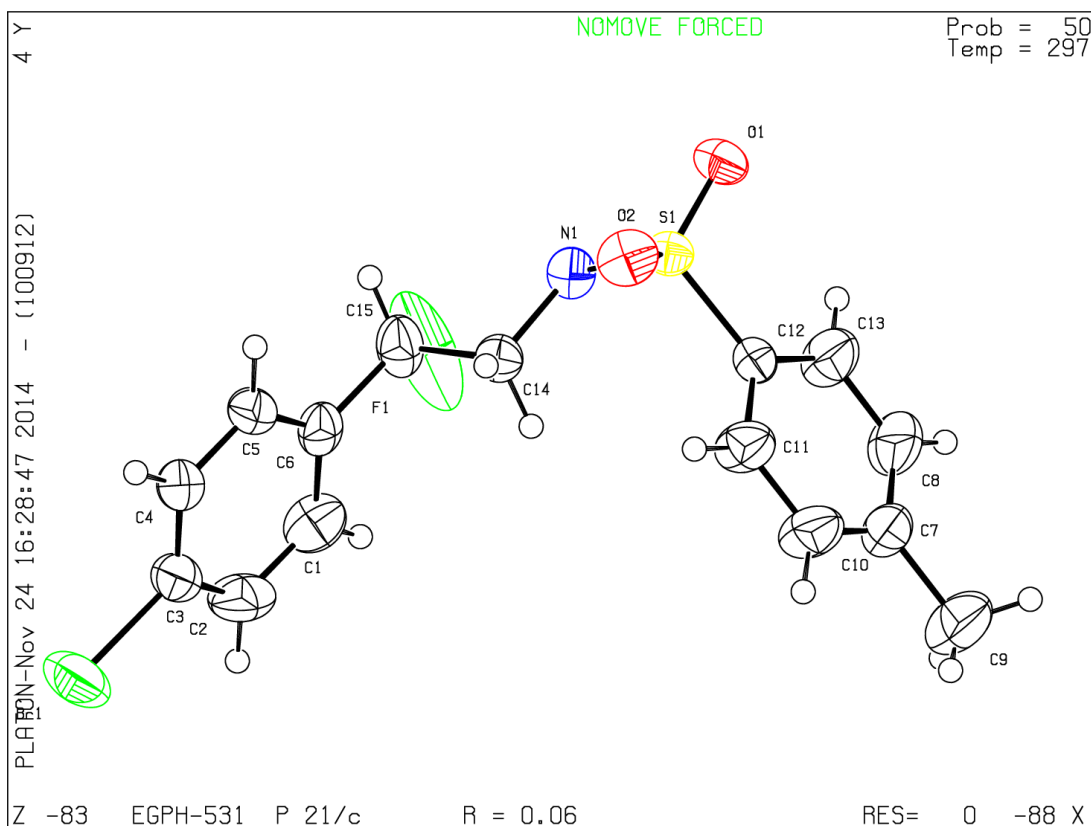


Figure 1. X-ray structure of **2e**. C gray, H white, N blue, O red, S yellow, Br purple, F green.



Bond precision: C-C = 0.0064 Å Wavelength=0.71073

Cell: a=11.571(2) b=5.2088(10) c=26.139(5)

$\alpha=90$ $\beta=93.278(2)$ $\gamma=90$

Temperature: 297 K

	Calculated	Reported
Volume	1572.9(5)	1572.9(5)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₁₅ H ₁₅ Br F N O ₂ S	C ₁₅ H ₁₅ Br F N O ₂ S
Sum formula	C ₁₅ H ₁₅ Br F N O ₂ S	C ₁₅ H ₁₅ Br F N O ₂ S
Mr	372.24	372.24
Dx, g cm ⁻³	1.572	1.572
Z	4	4
Mu (mm ⁻¹)	2.759	2.759
F ₀₀₀	752.0	752.0
F ₀₀₀ '	751.68	

h,k,lmax	15,6,35	15,6,35
Nref	3927	3927
Tmin,Tmax	0.337,0.516	0.337,0.516
Tmin'	0.049	

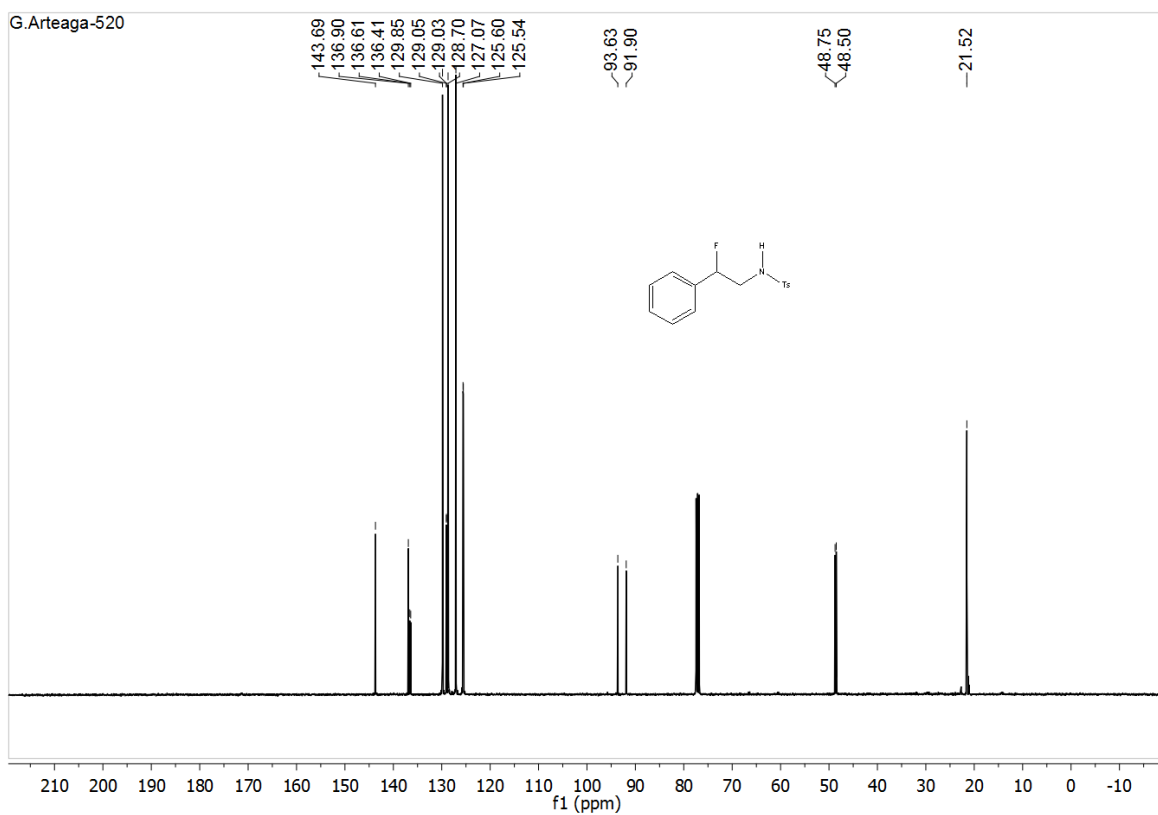
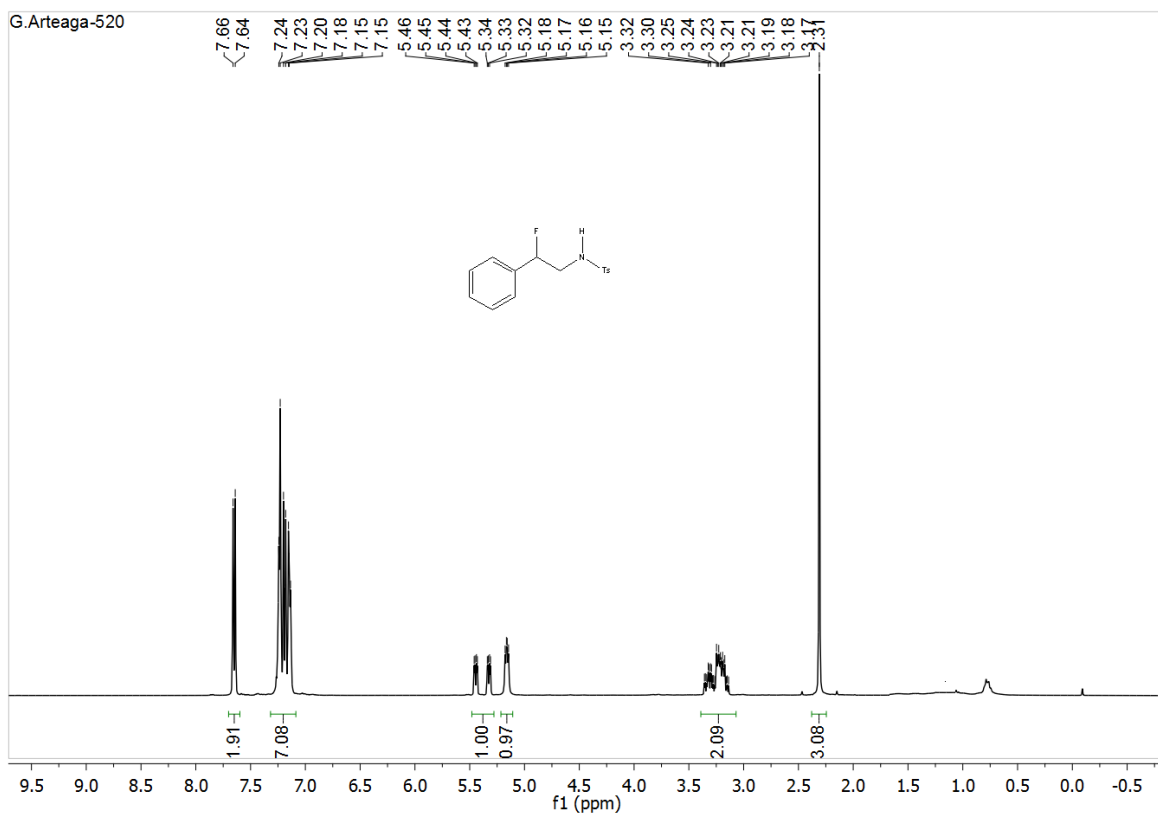
Correction method= MULTI-SCAN

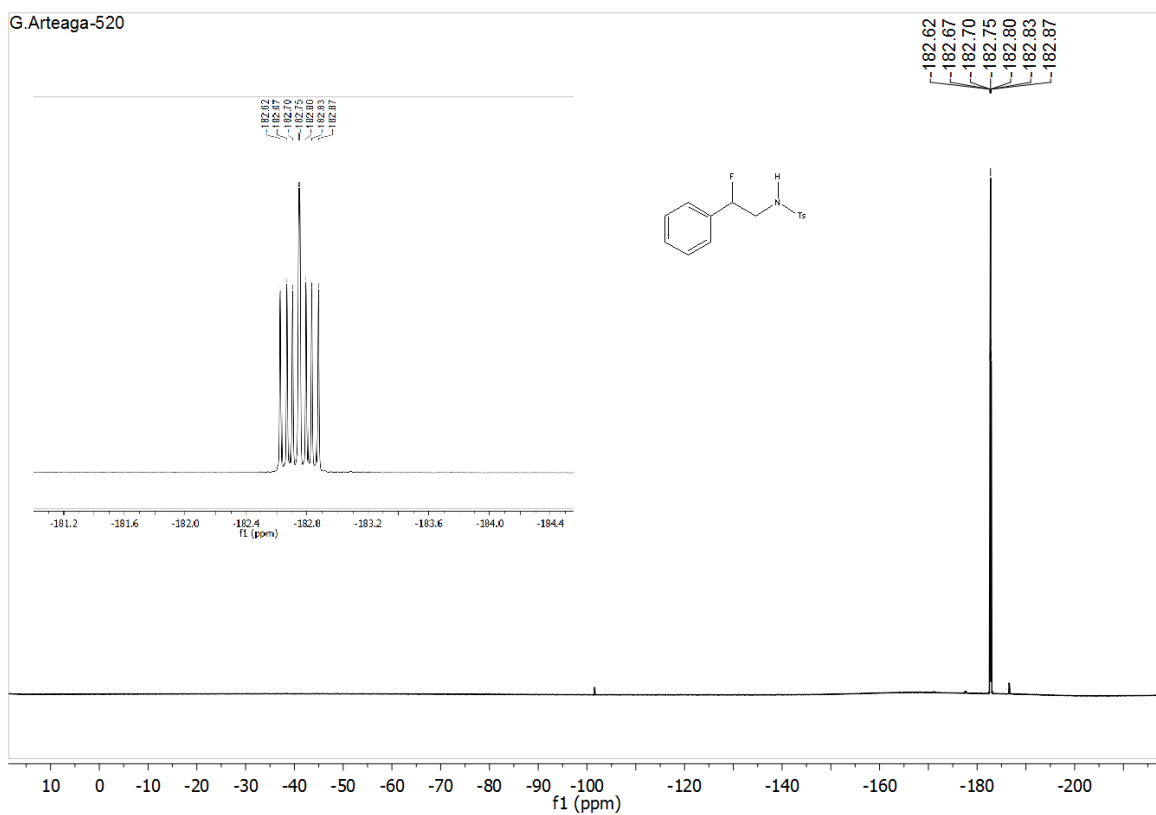
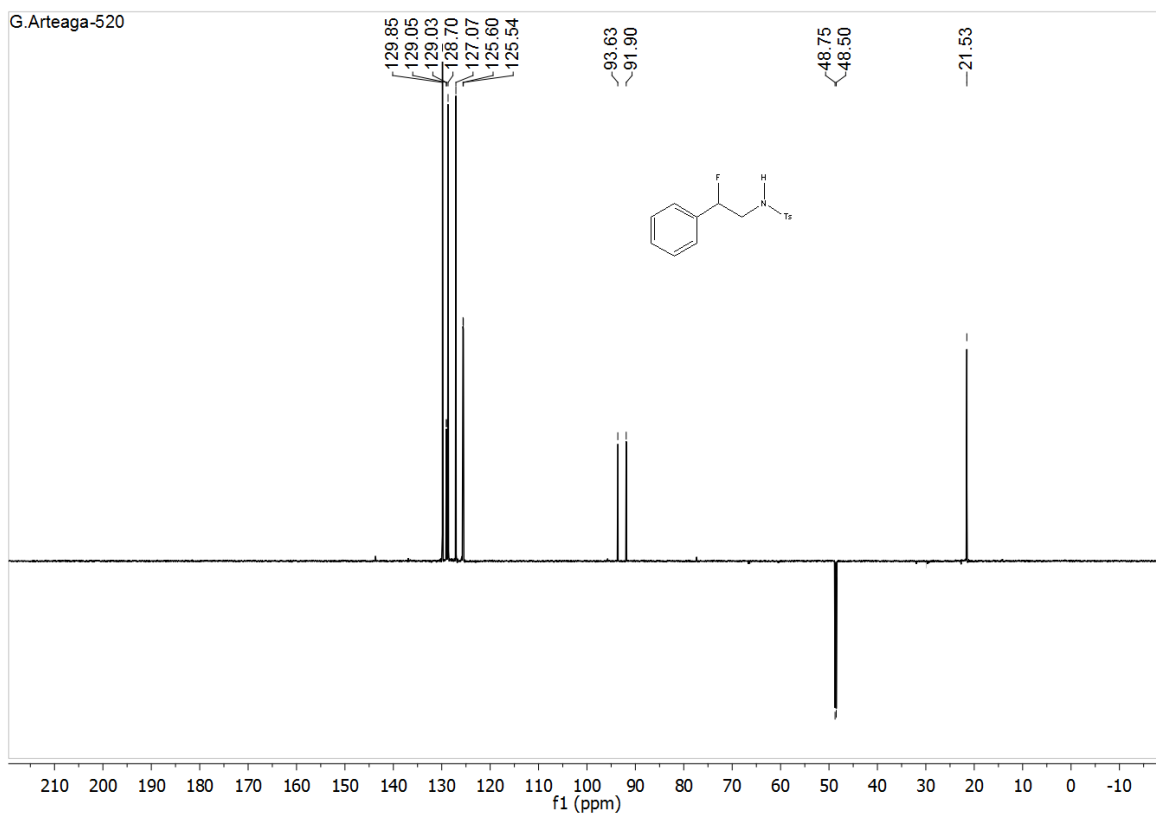
Data completeness= 1.000 Theta(max)= 28.420

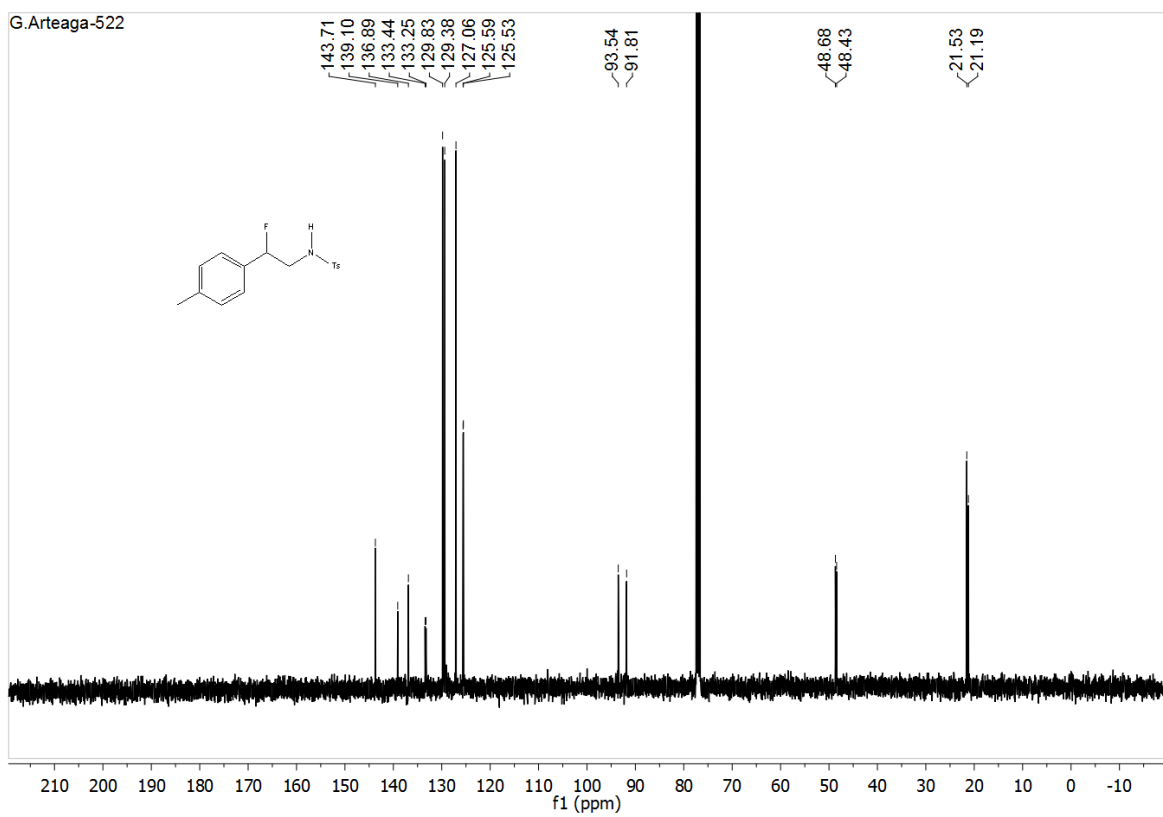
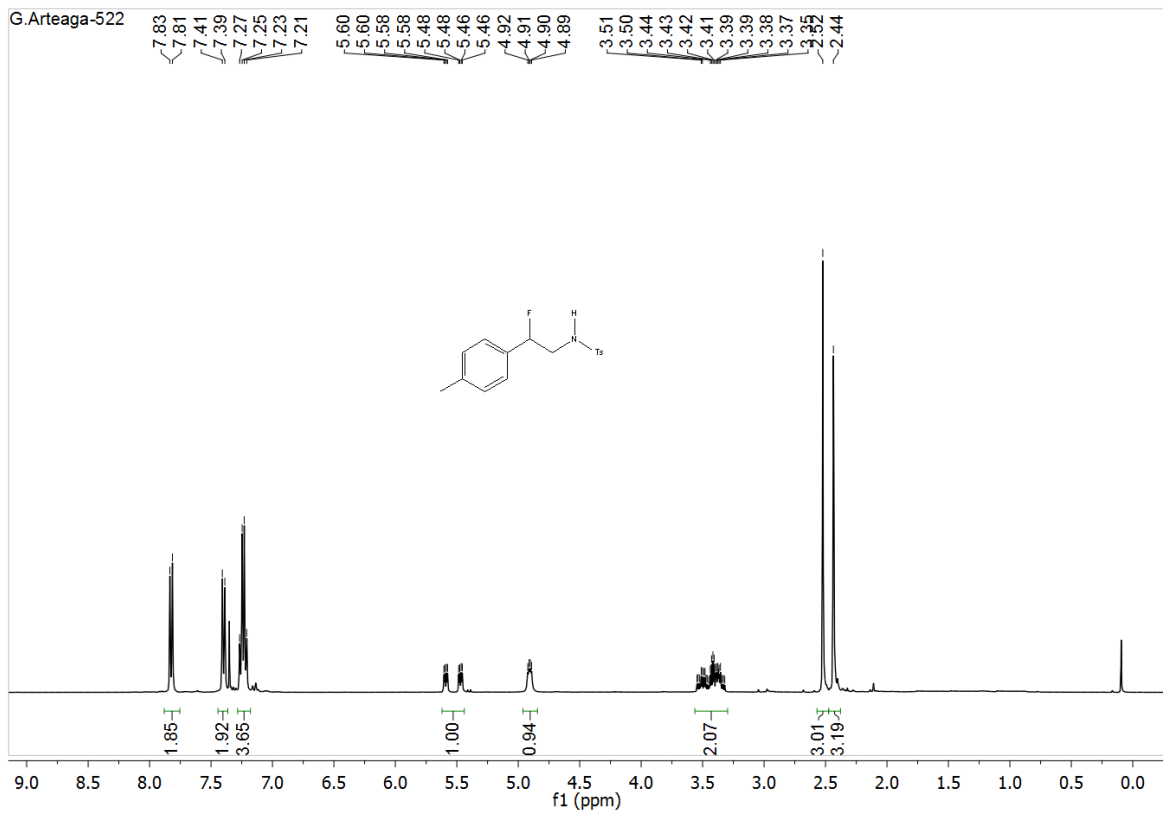
R(reflections)= 0.0581(2329) wR2(reflections)= 0.1757(3098)

S = 1.230 Npar= 195

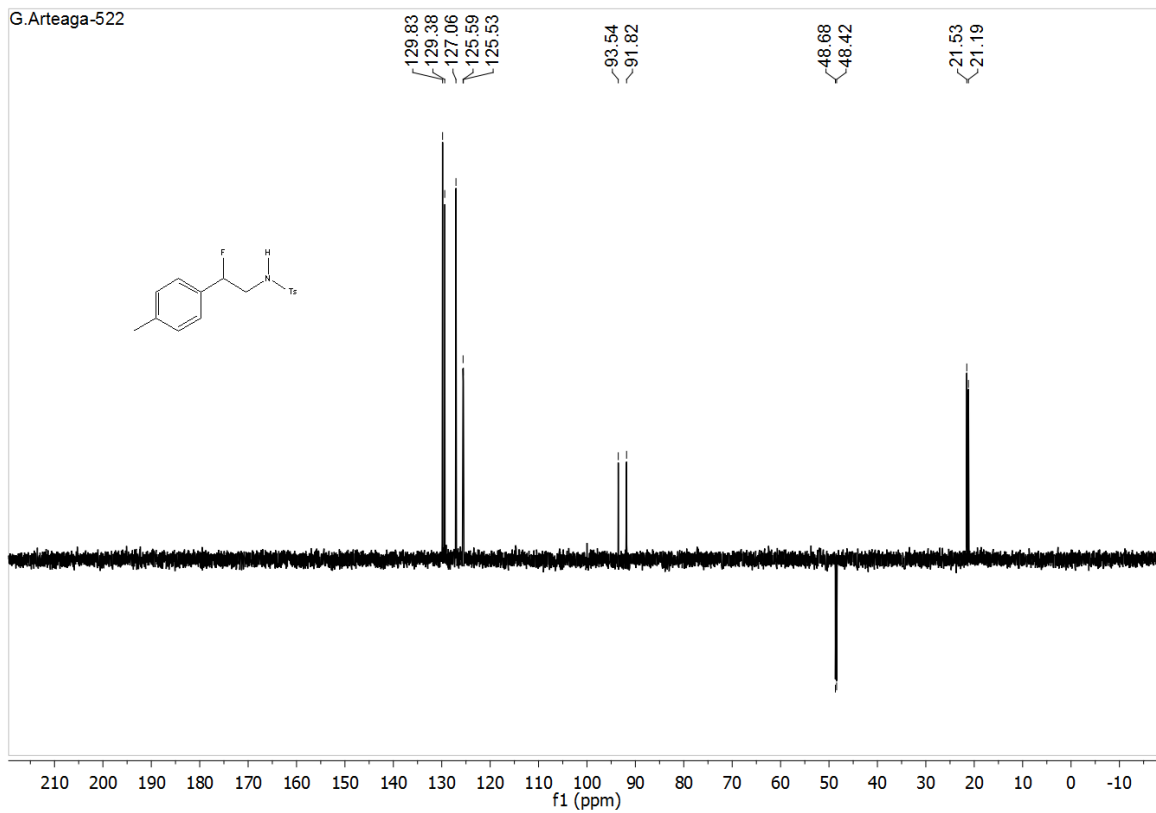
4. Spectral Characterization of Products



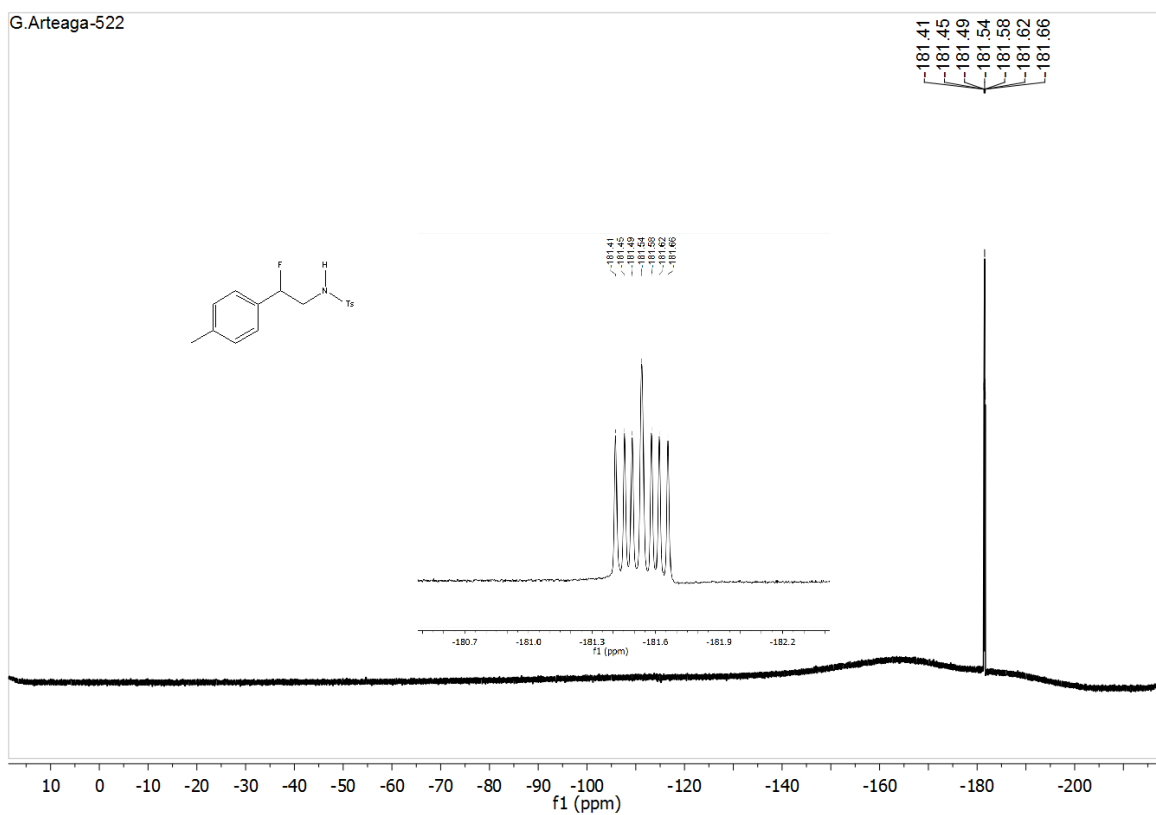


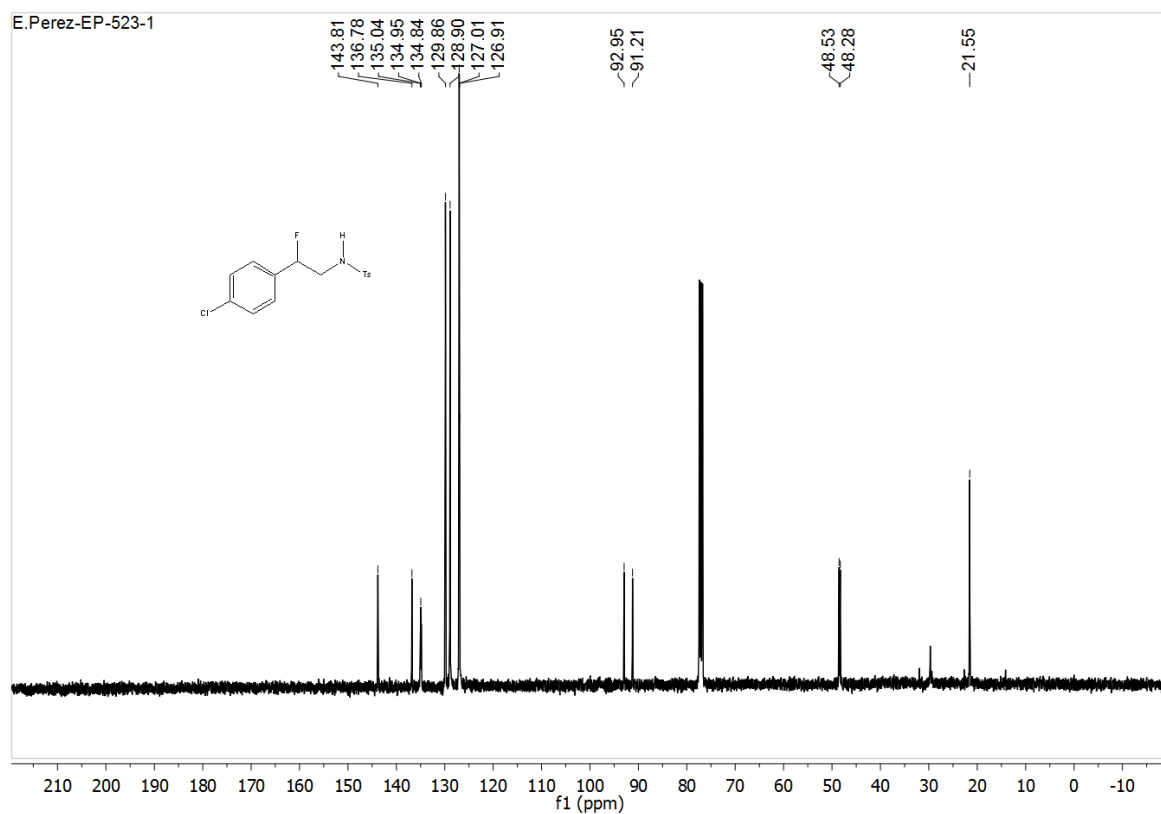
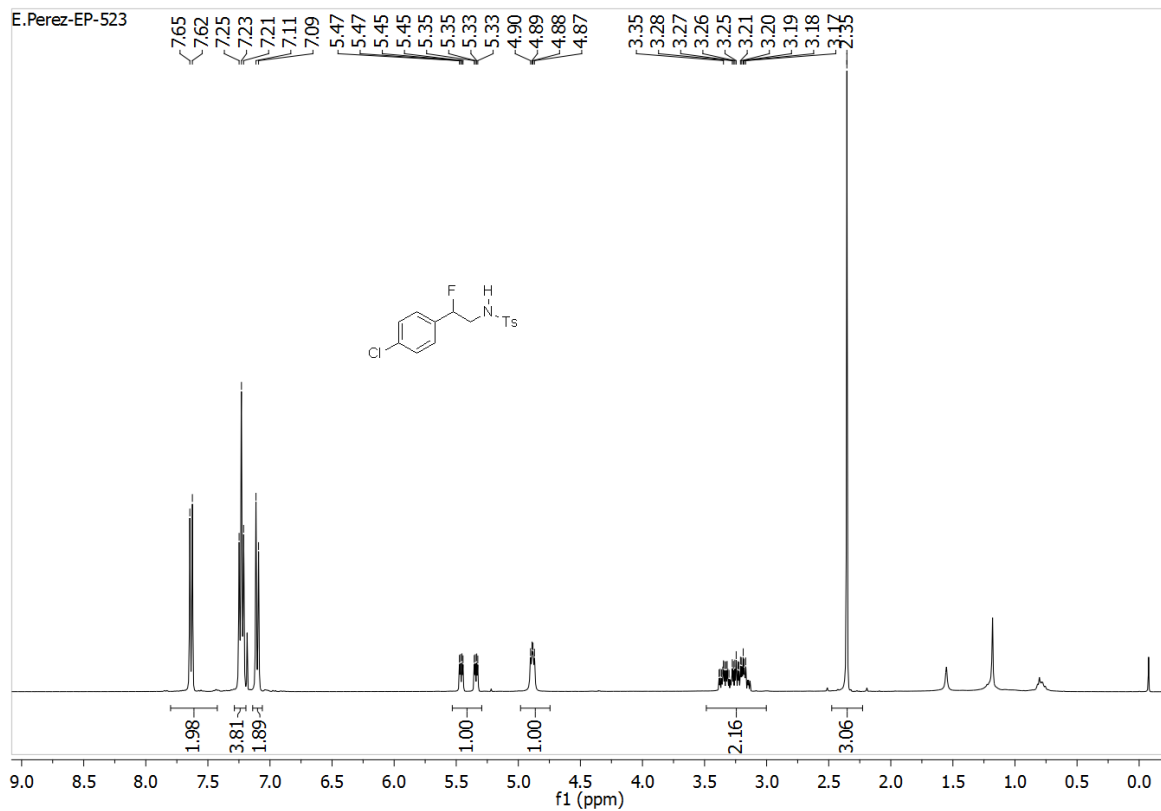


G.Arteaga-522

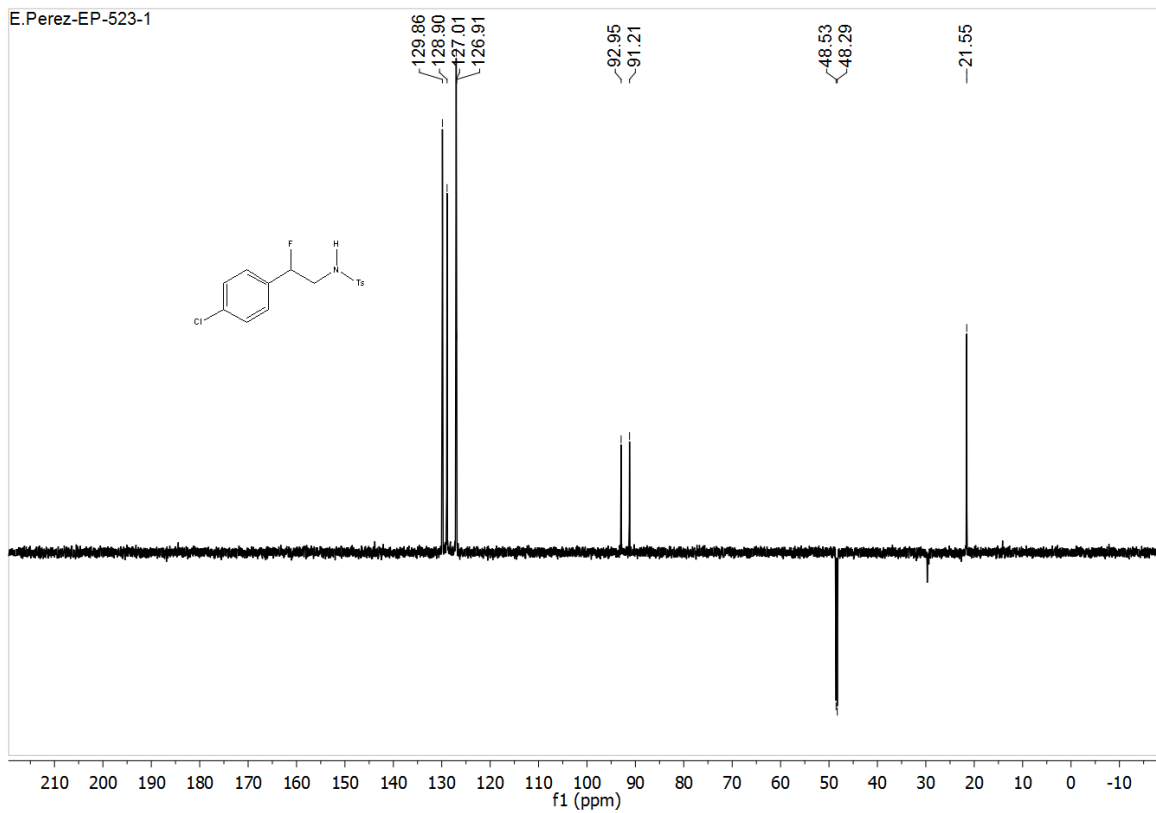


G.Arteaga-522

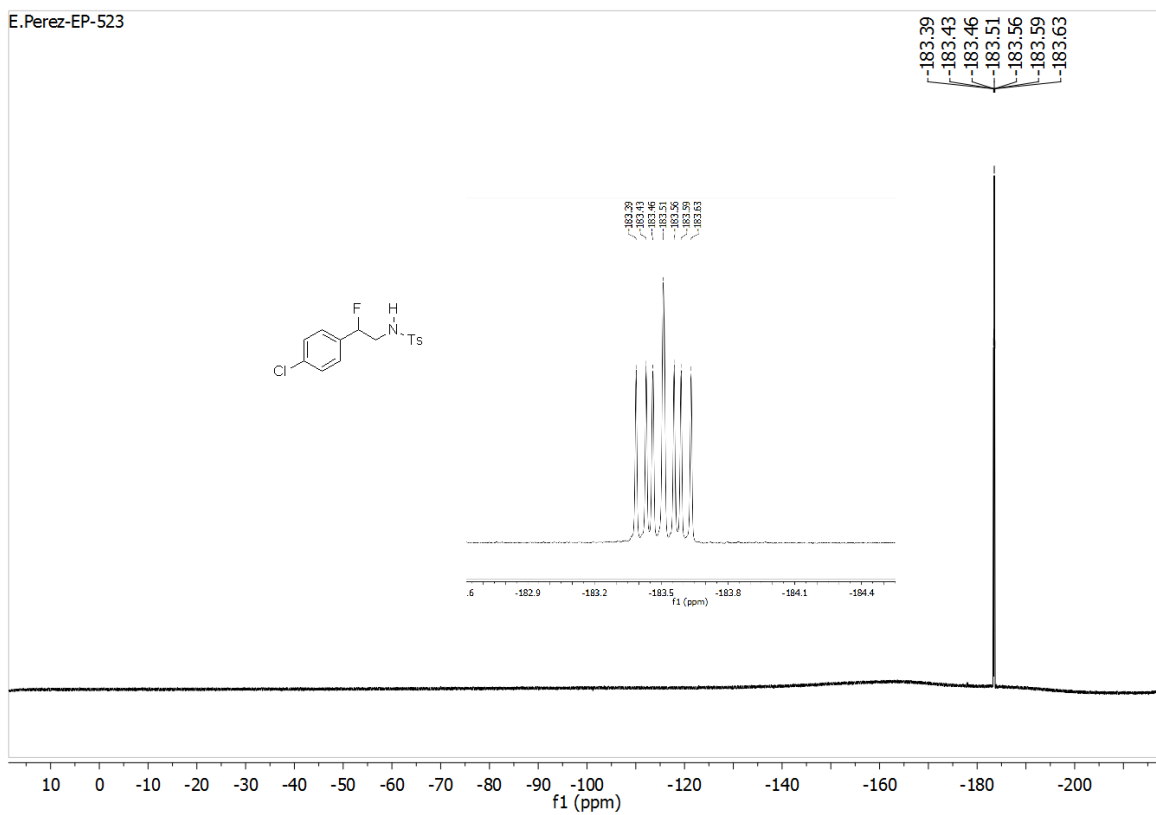


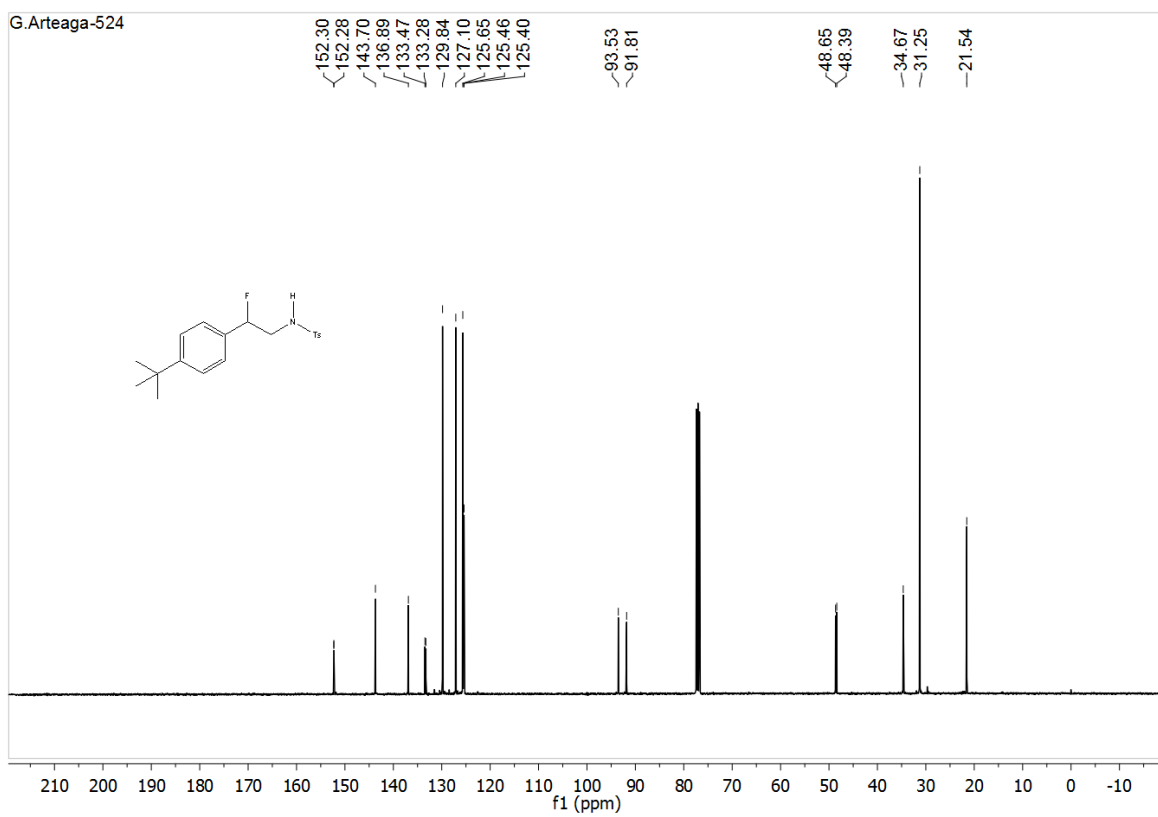
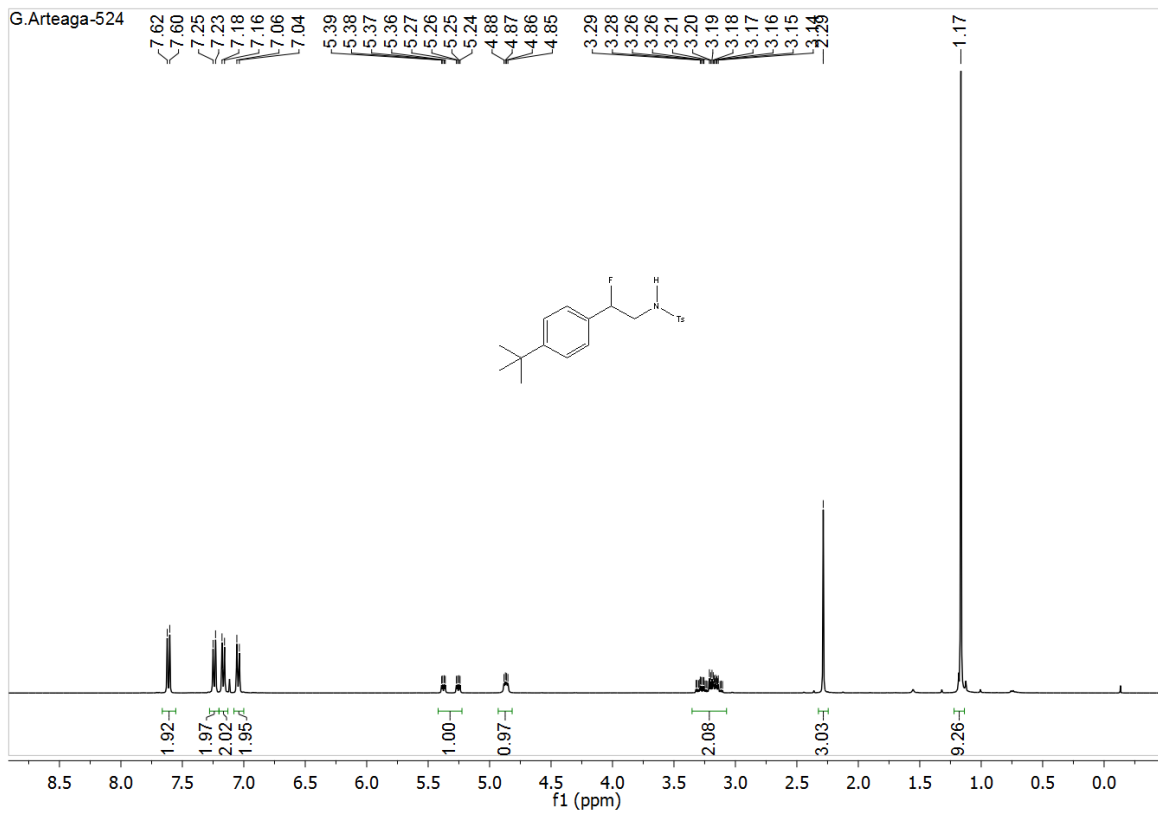


E.Perez-EP-523-1

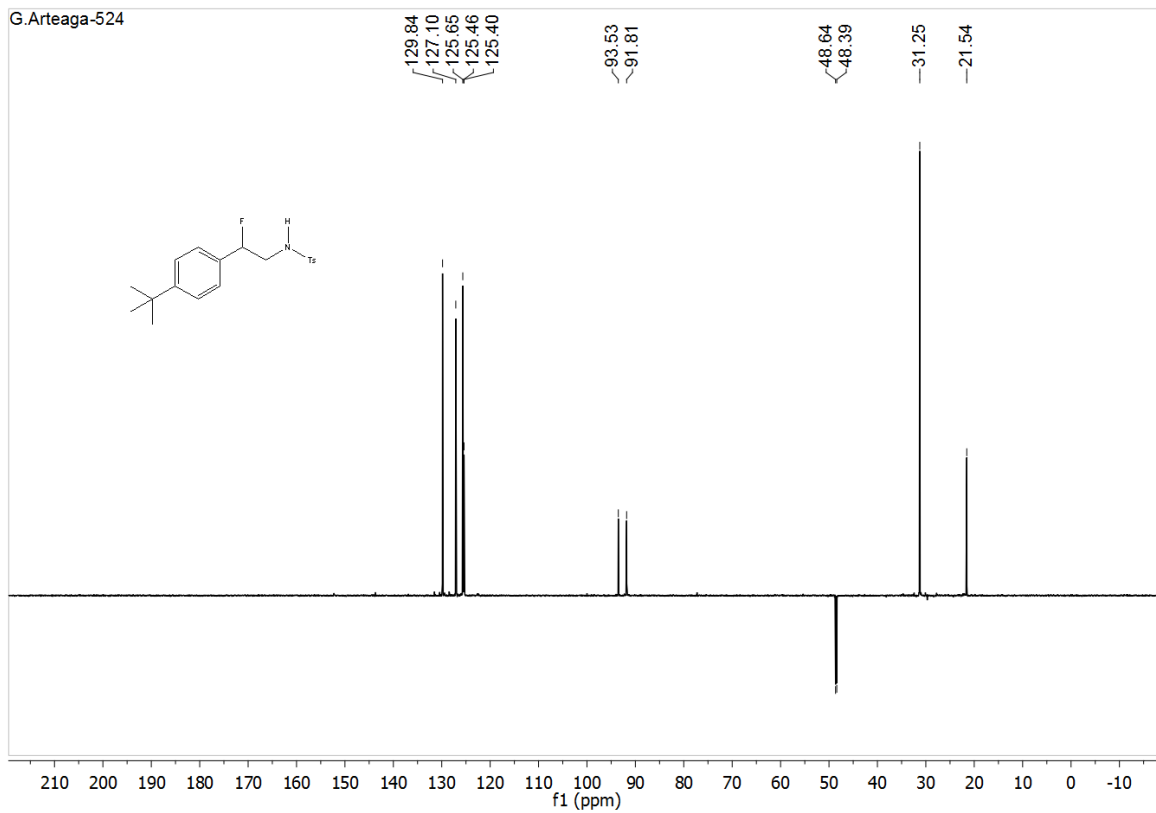


E.Perez-EP-523

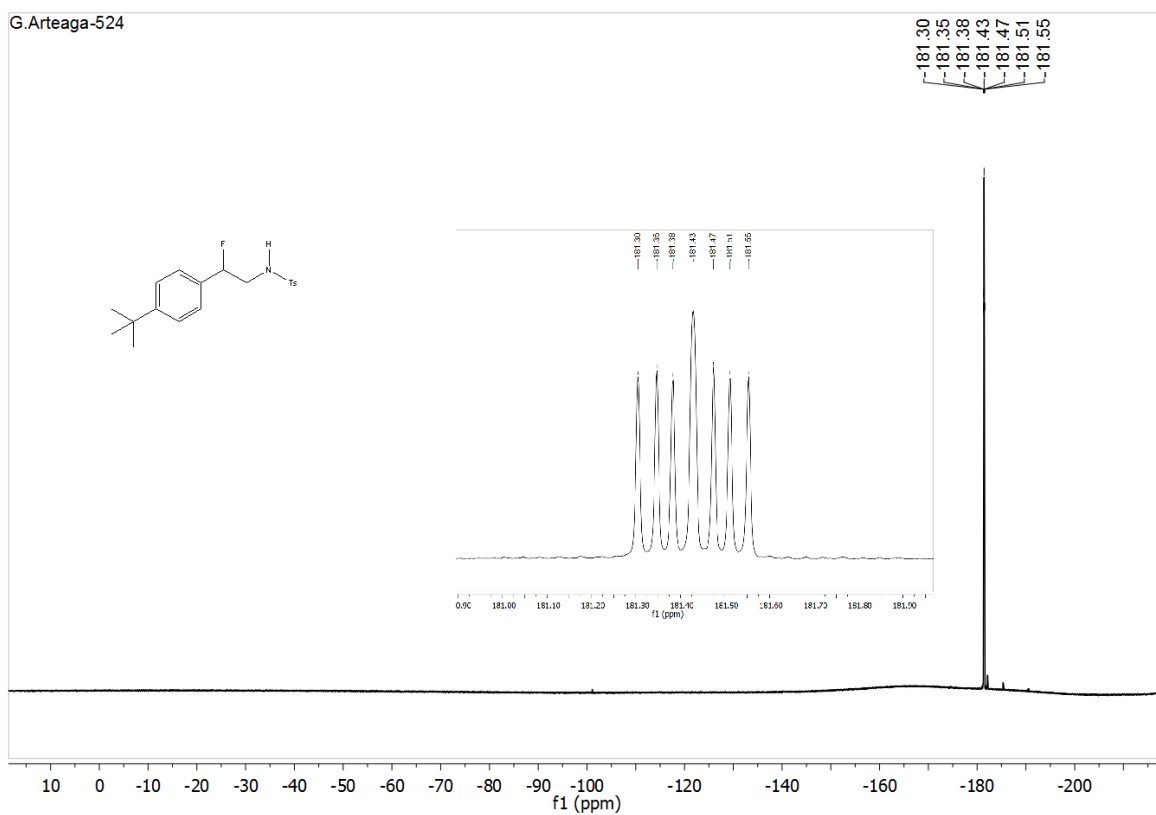


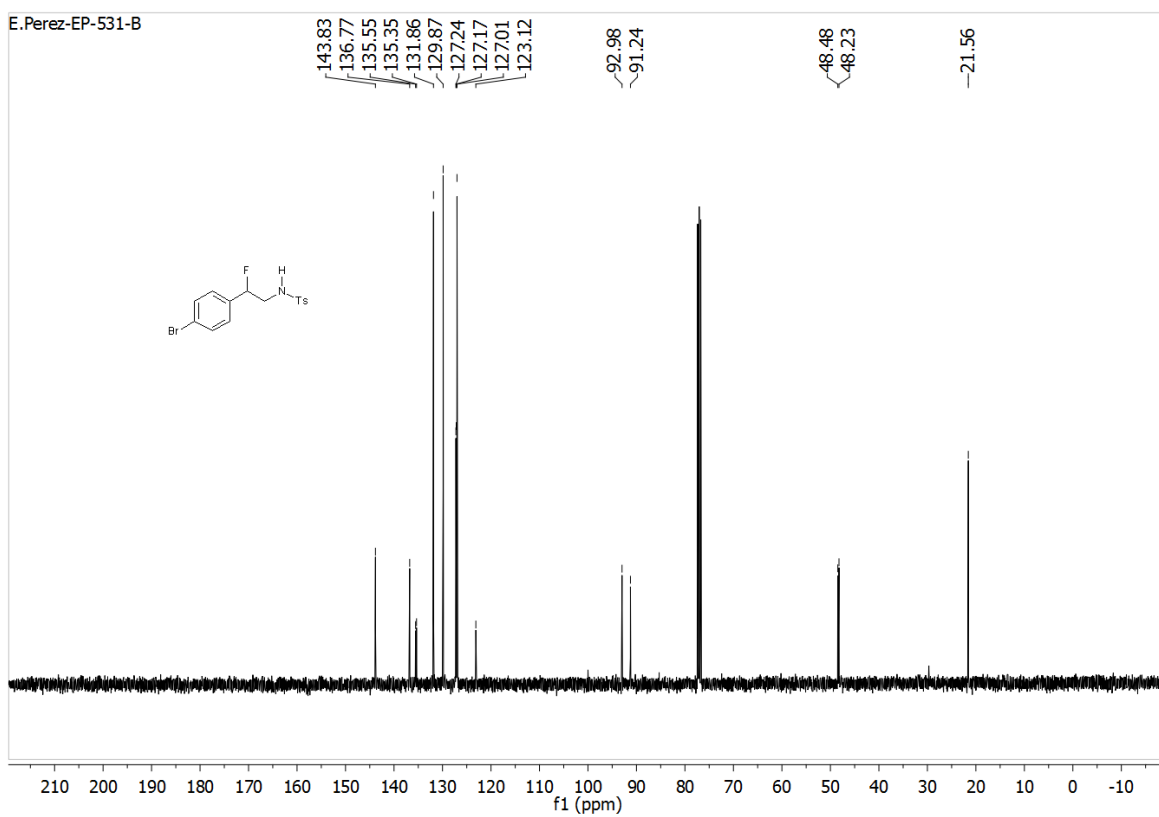
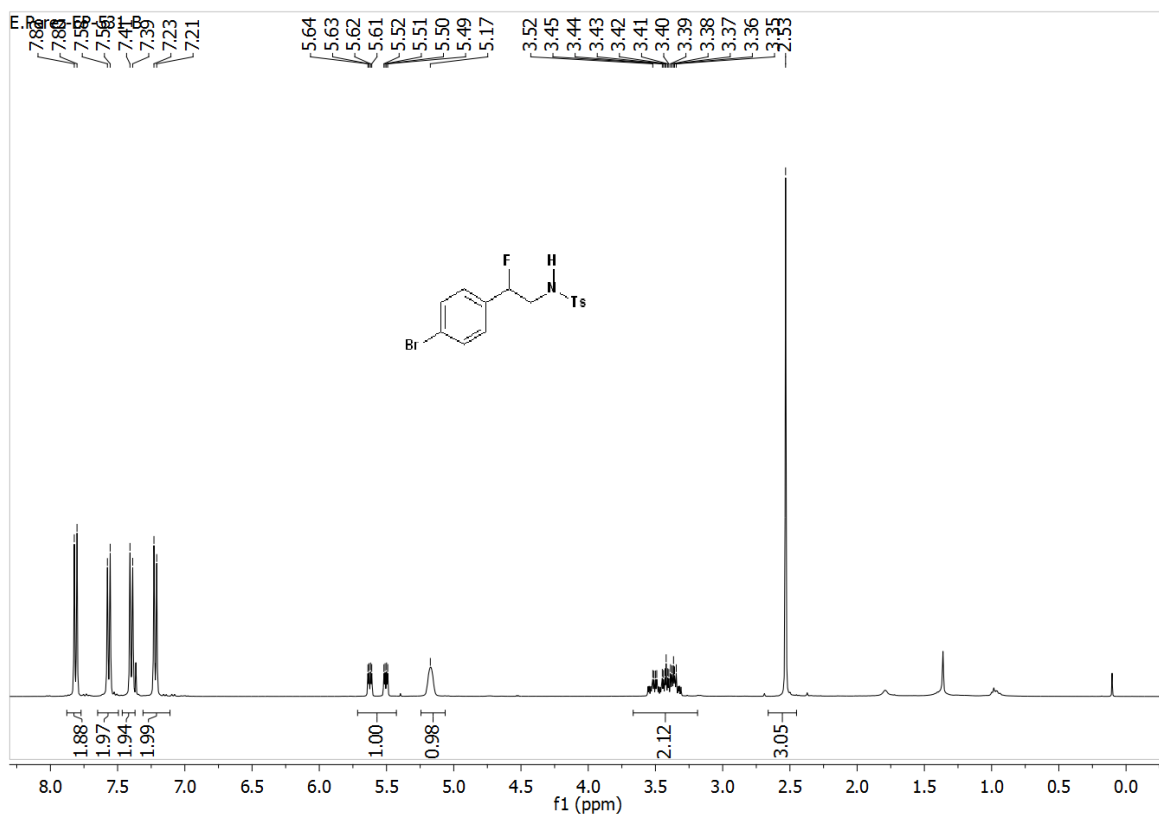


G.Arteaga-524

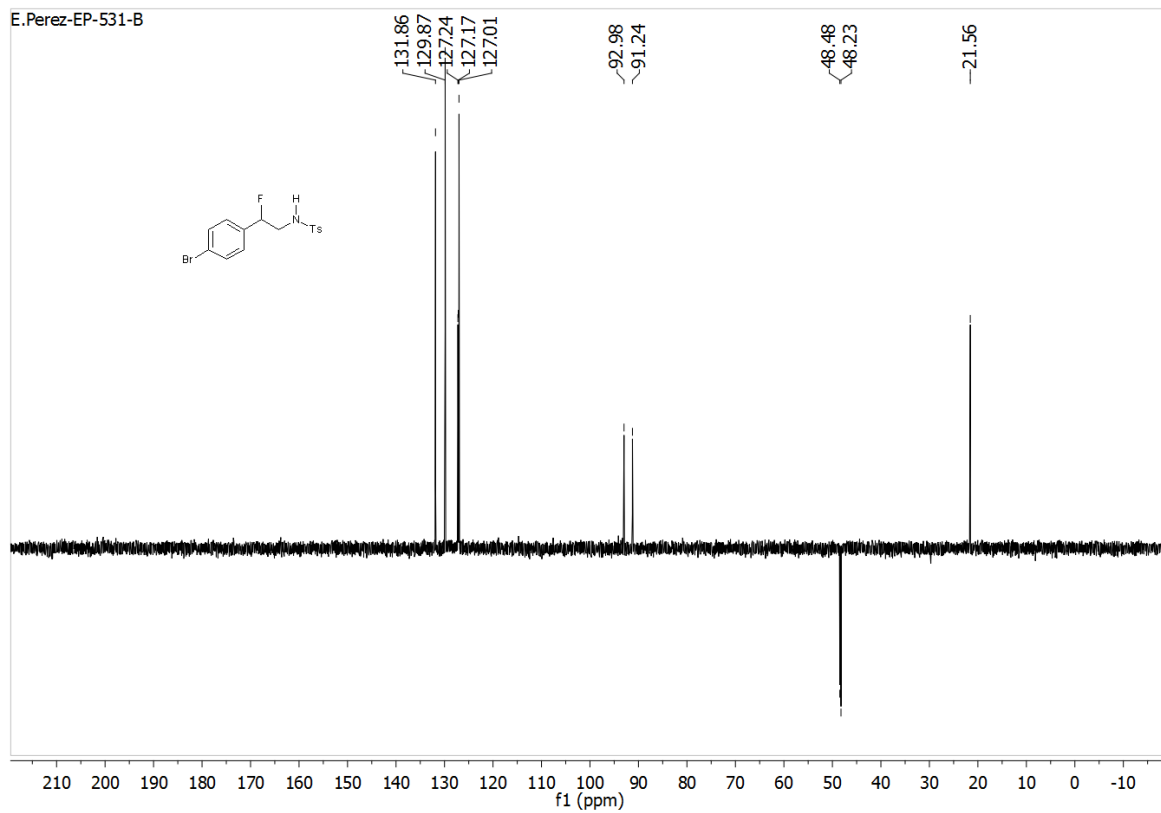


G.Arteaga-524

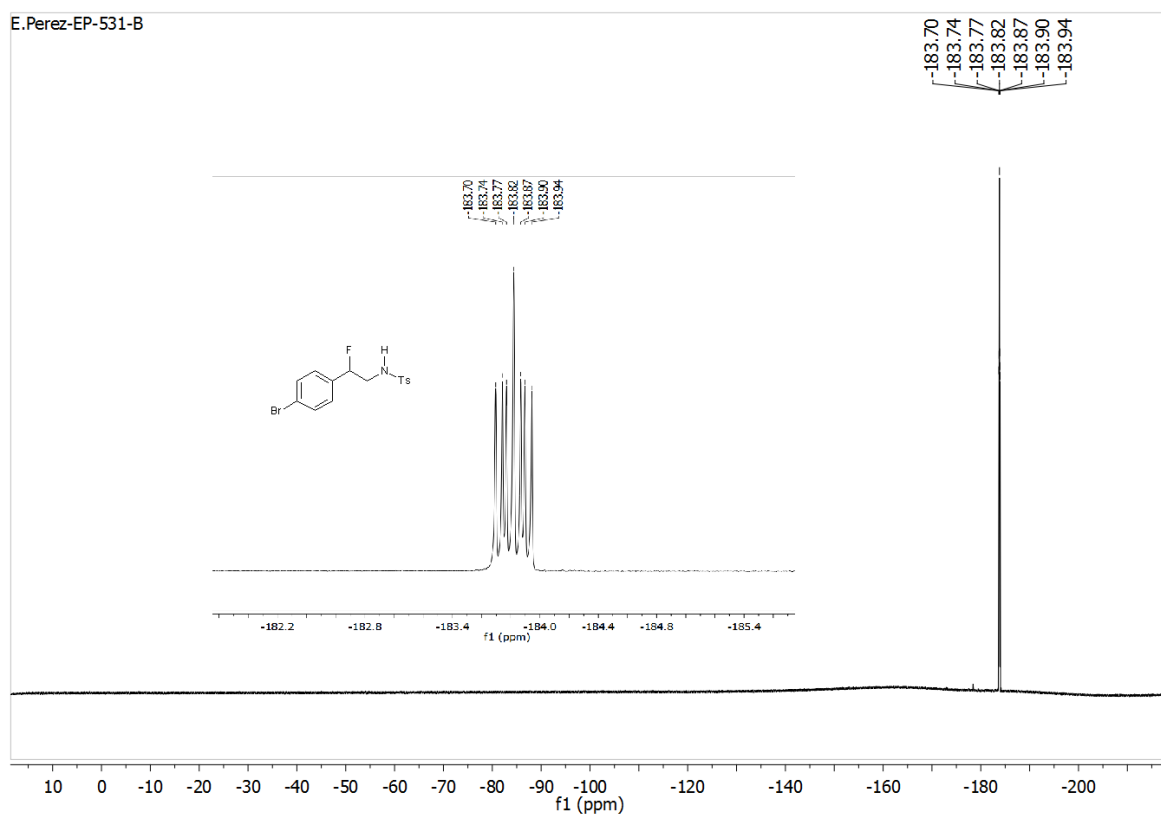


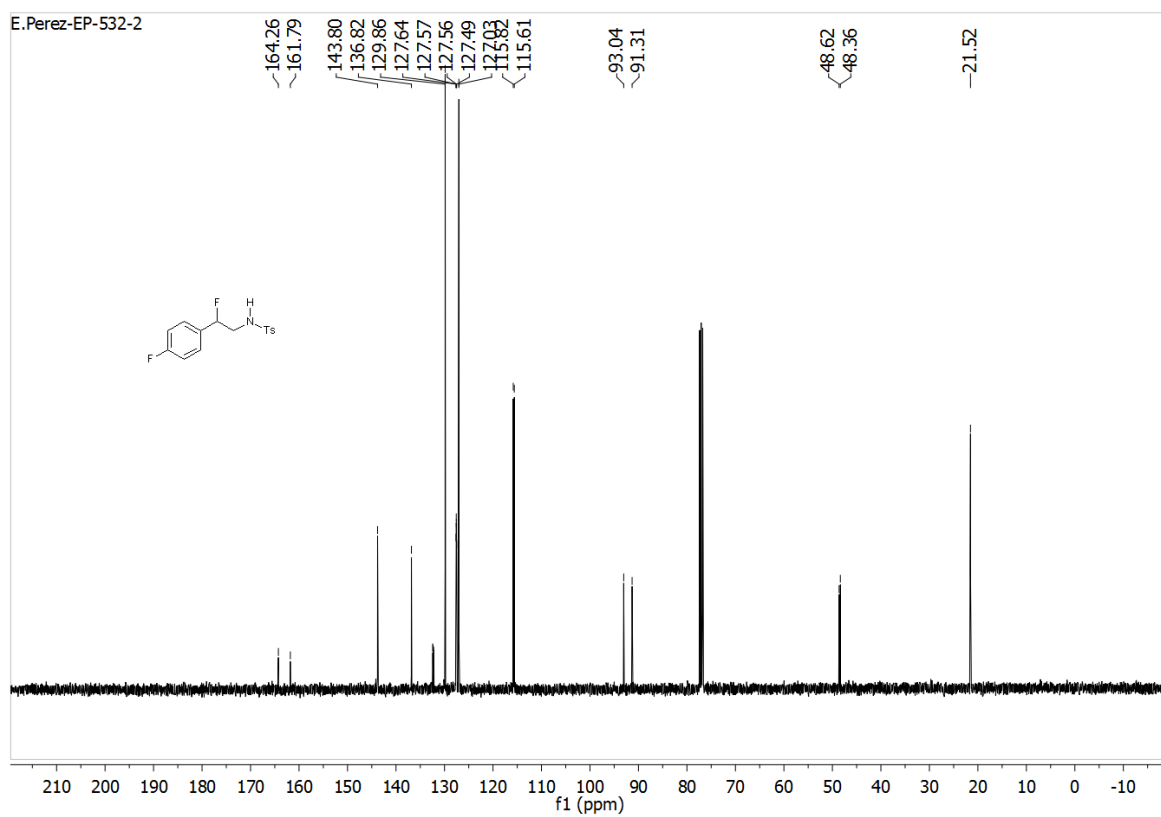
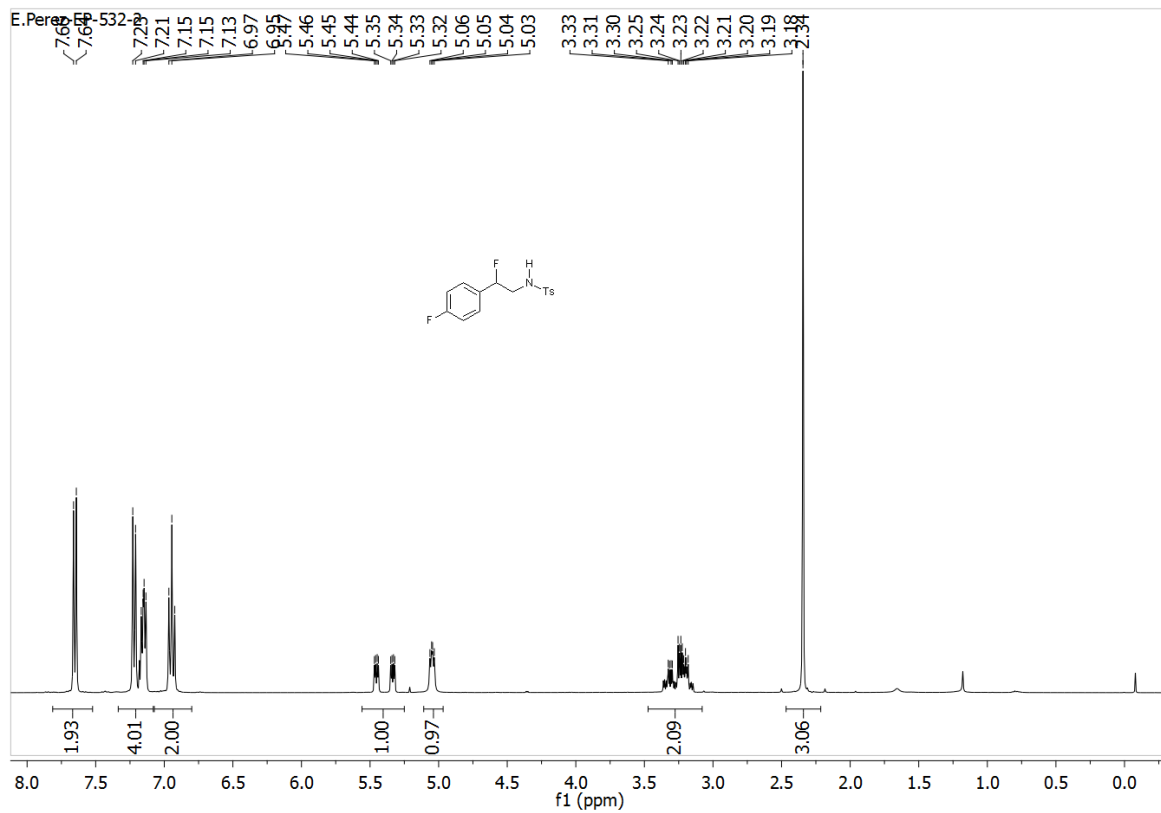


E.Perez-EP-531-B

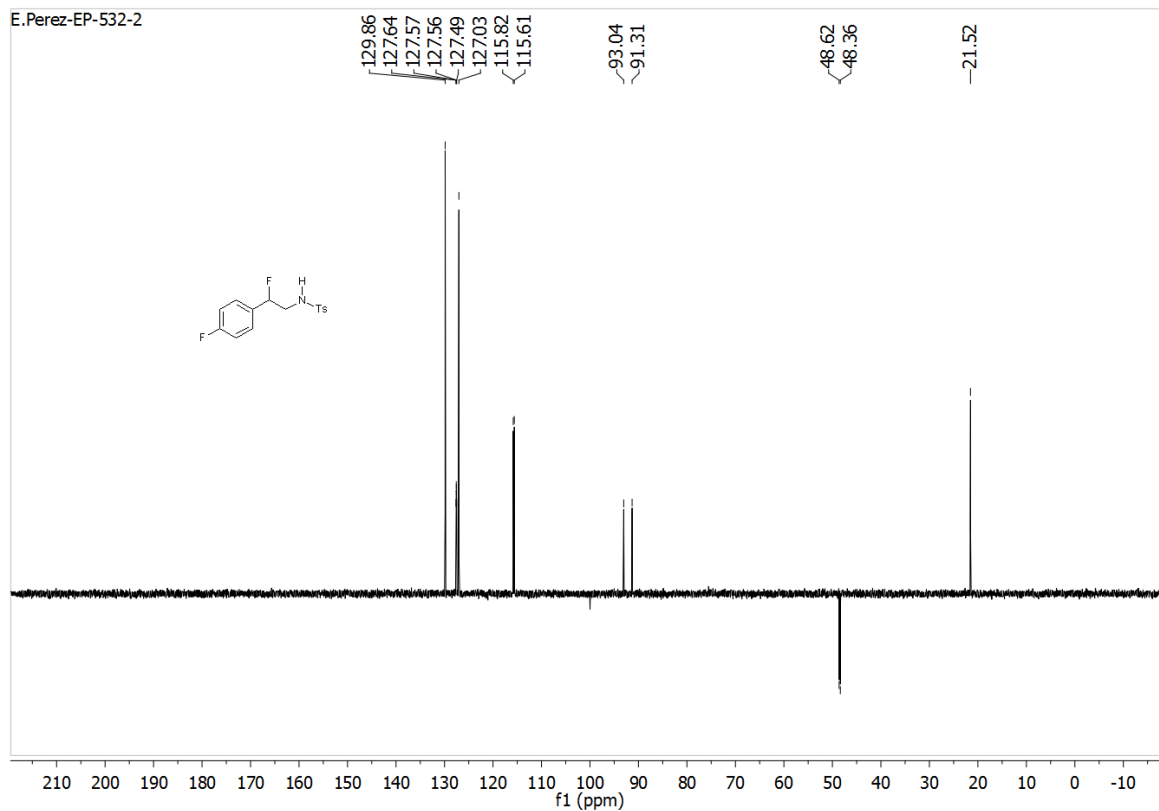


E.Perez-EP-531-B

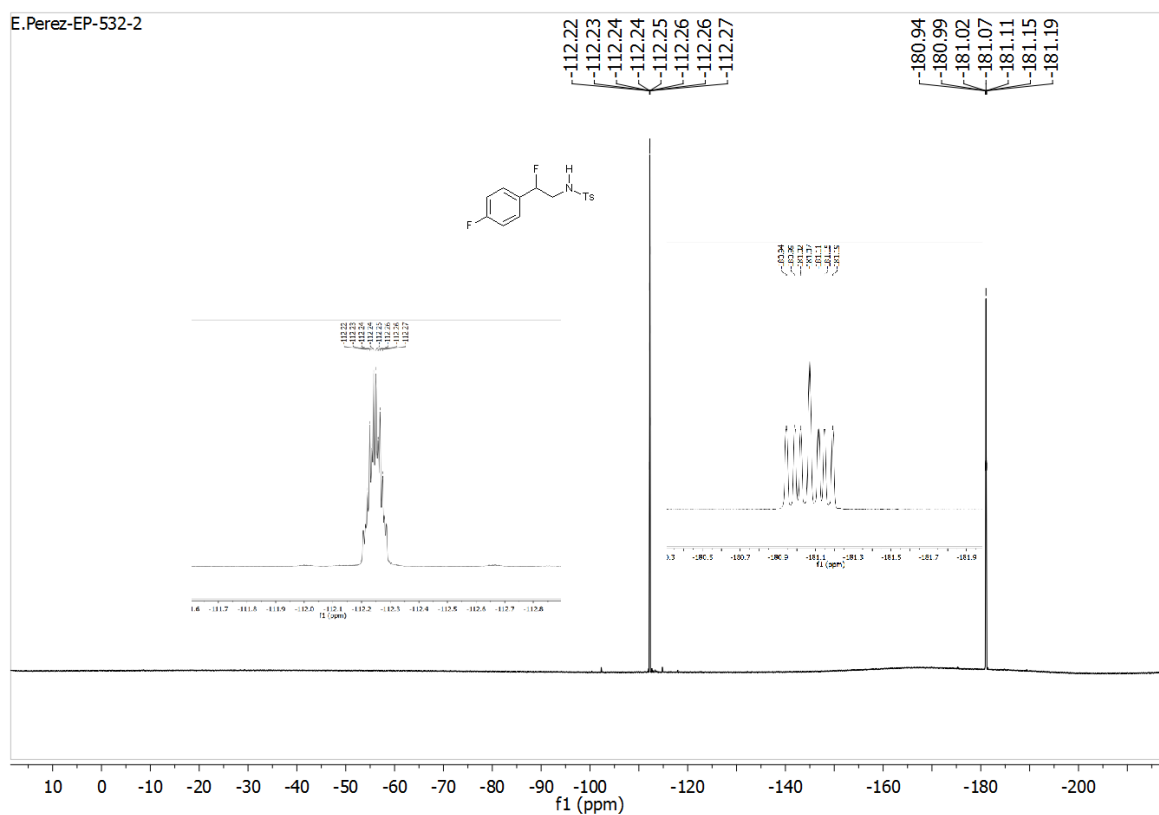


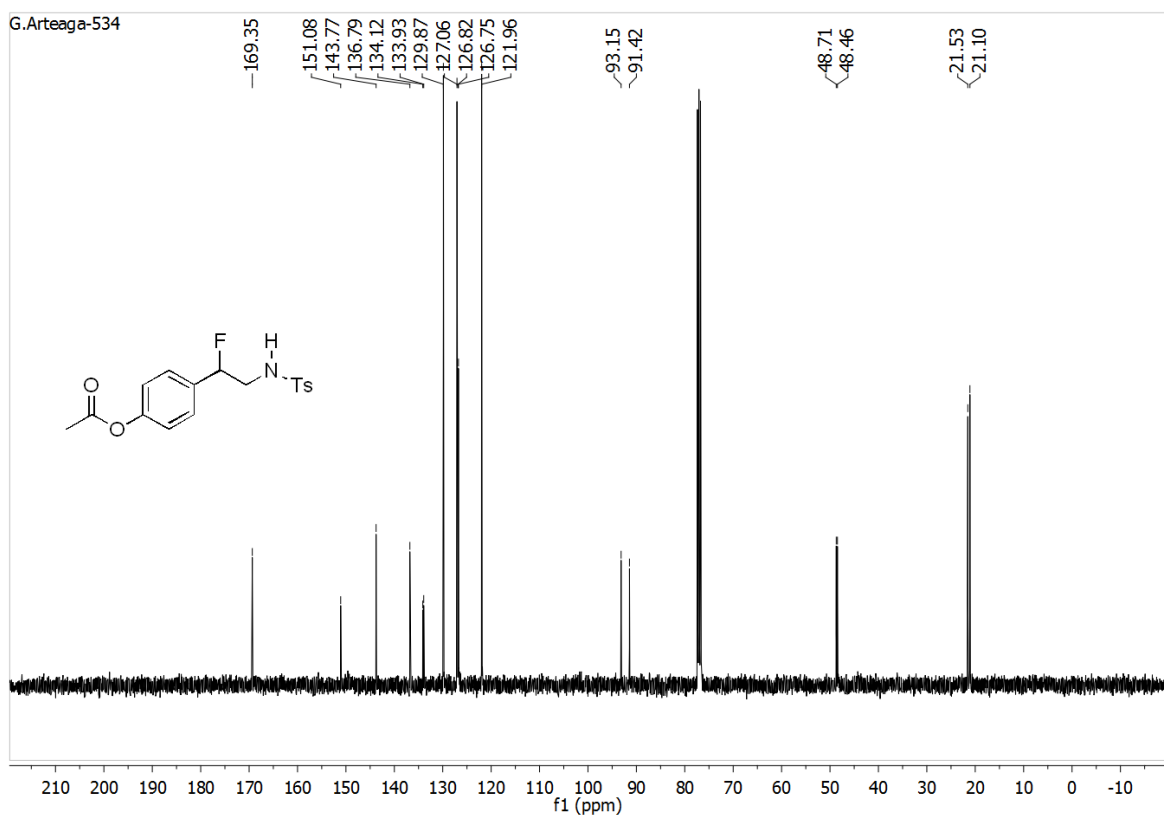
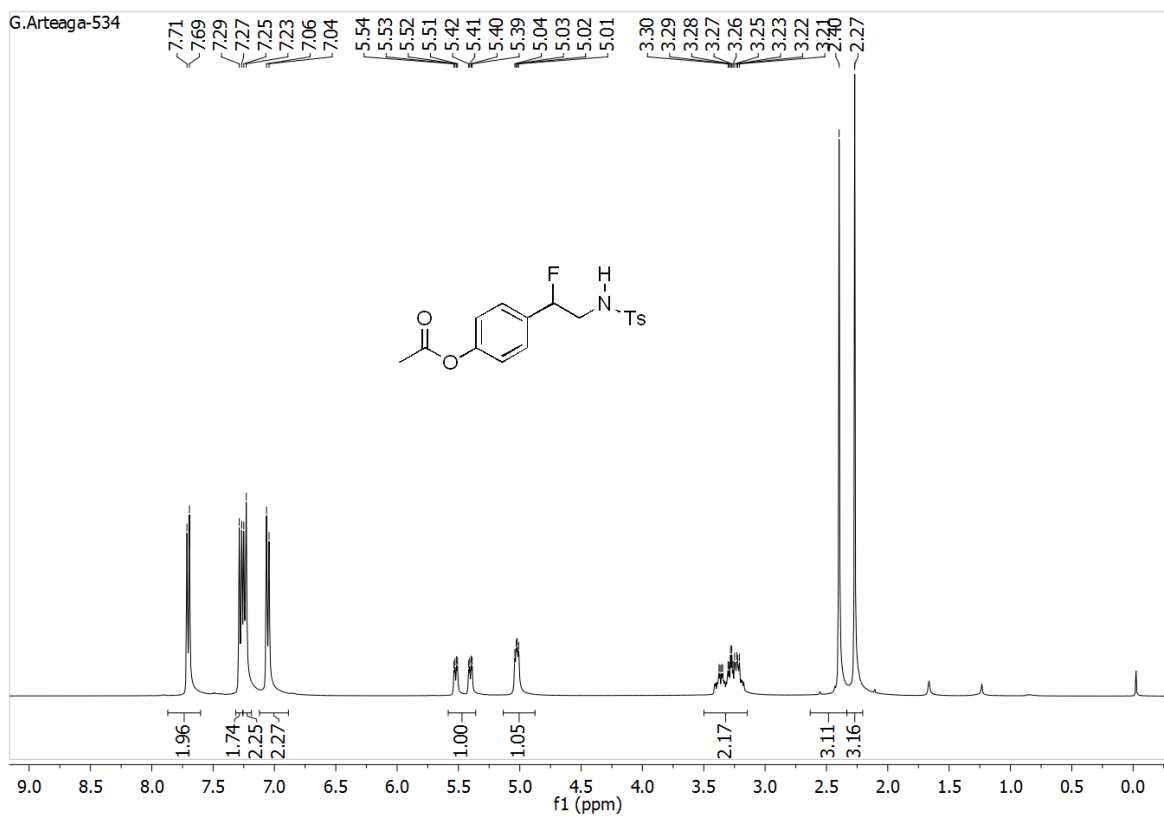


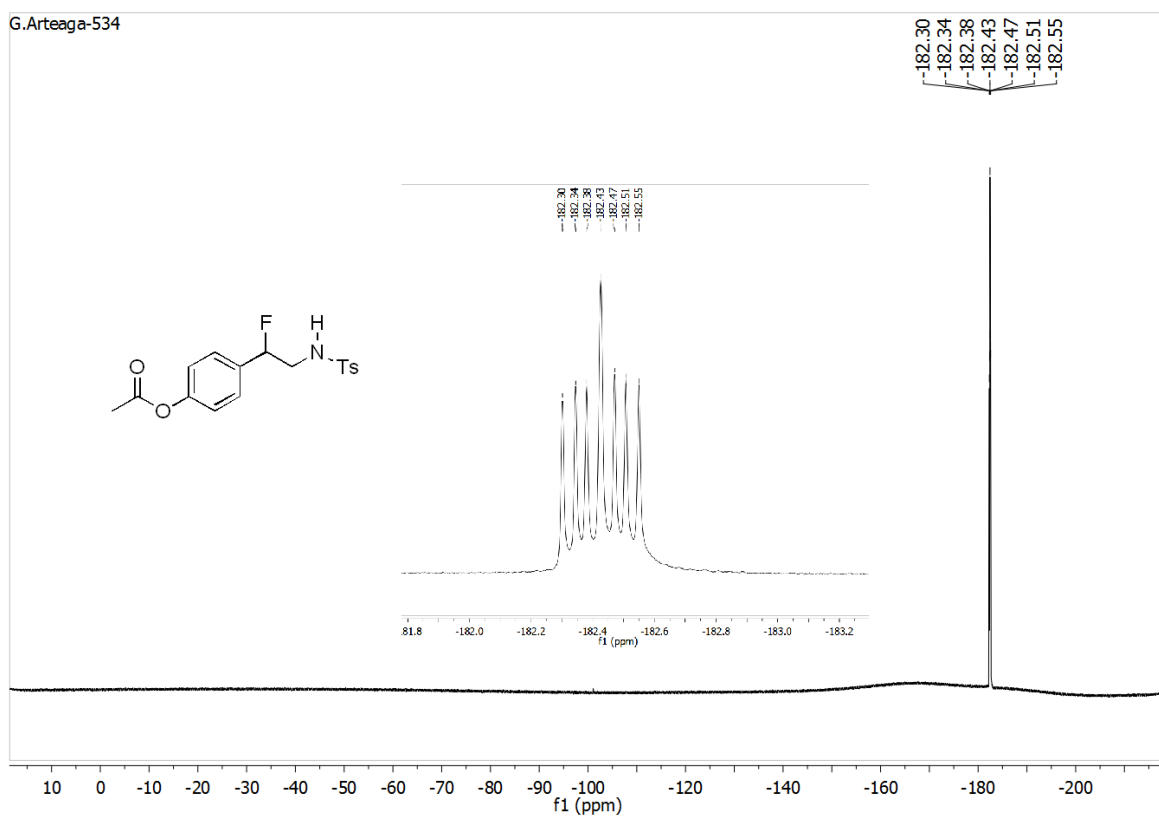
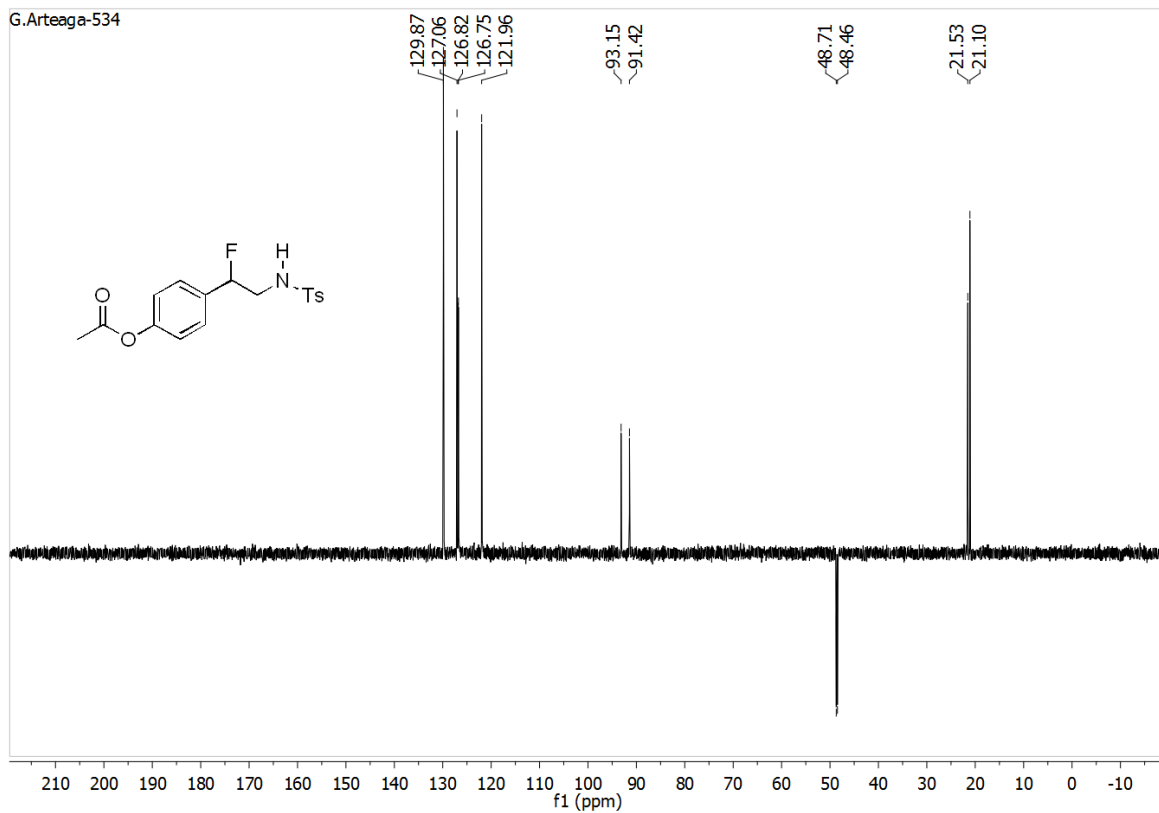
E.Perez-EP-532-2

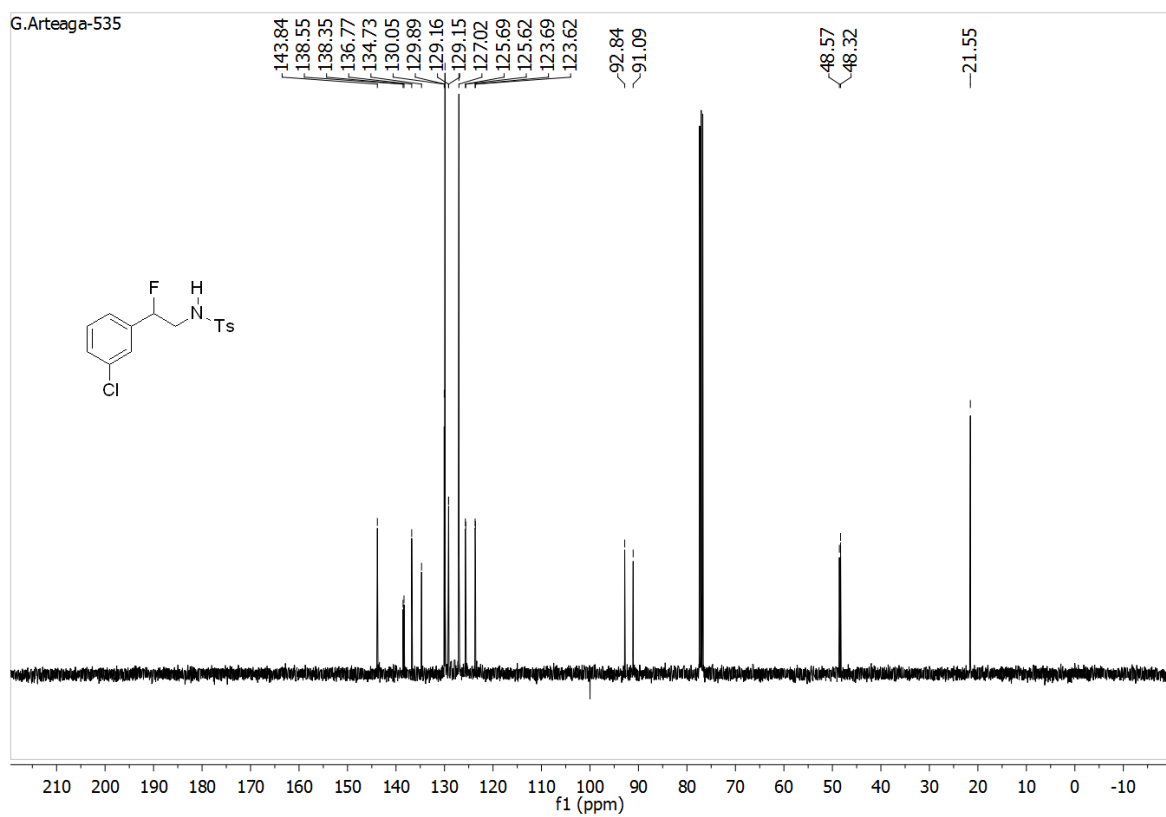
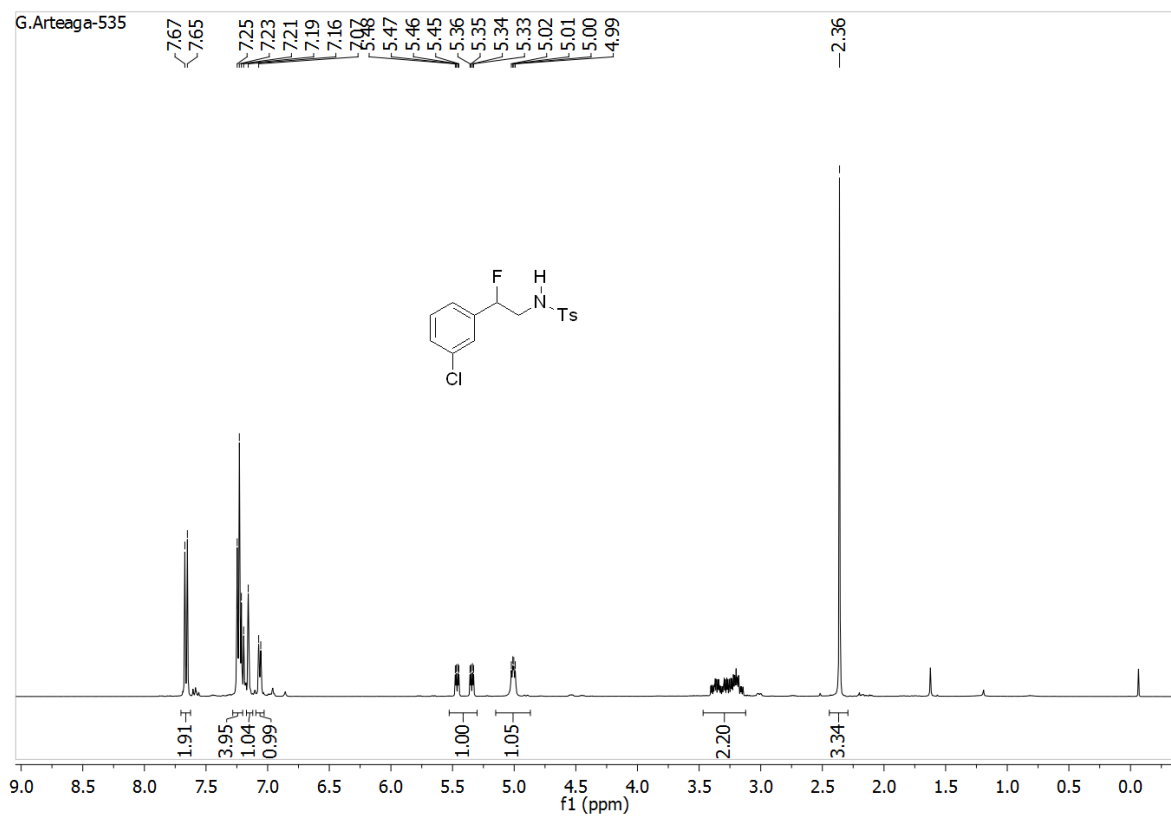


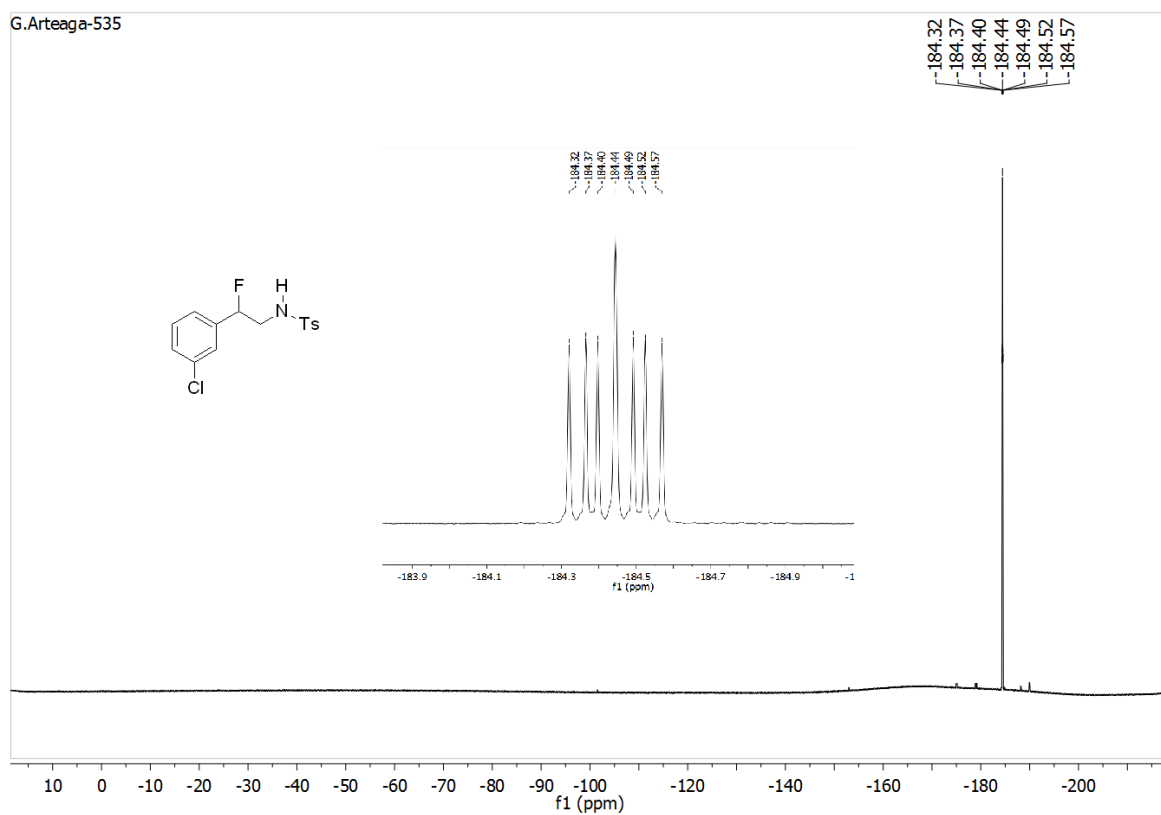
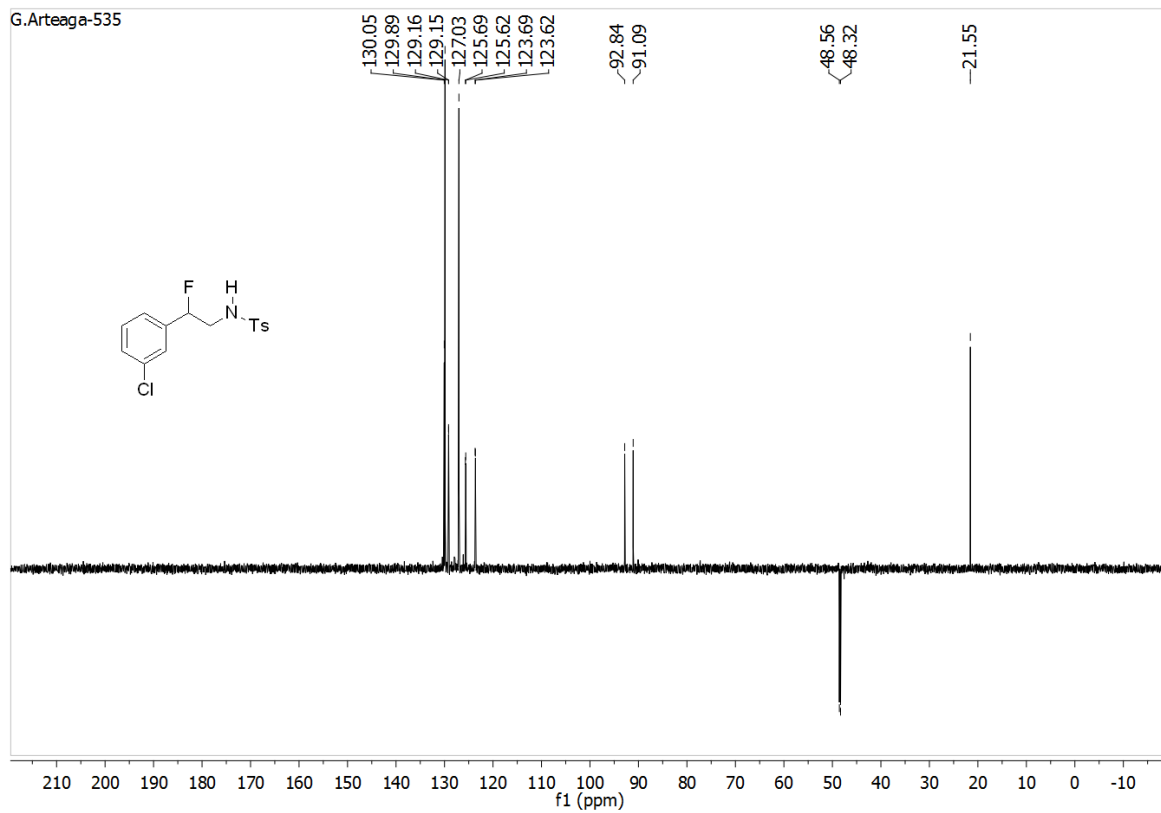
E.Perez-EP-532-2

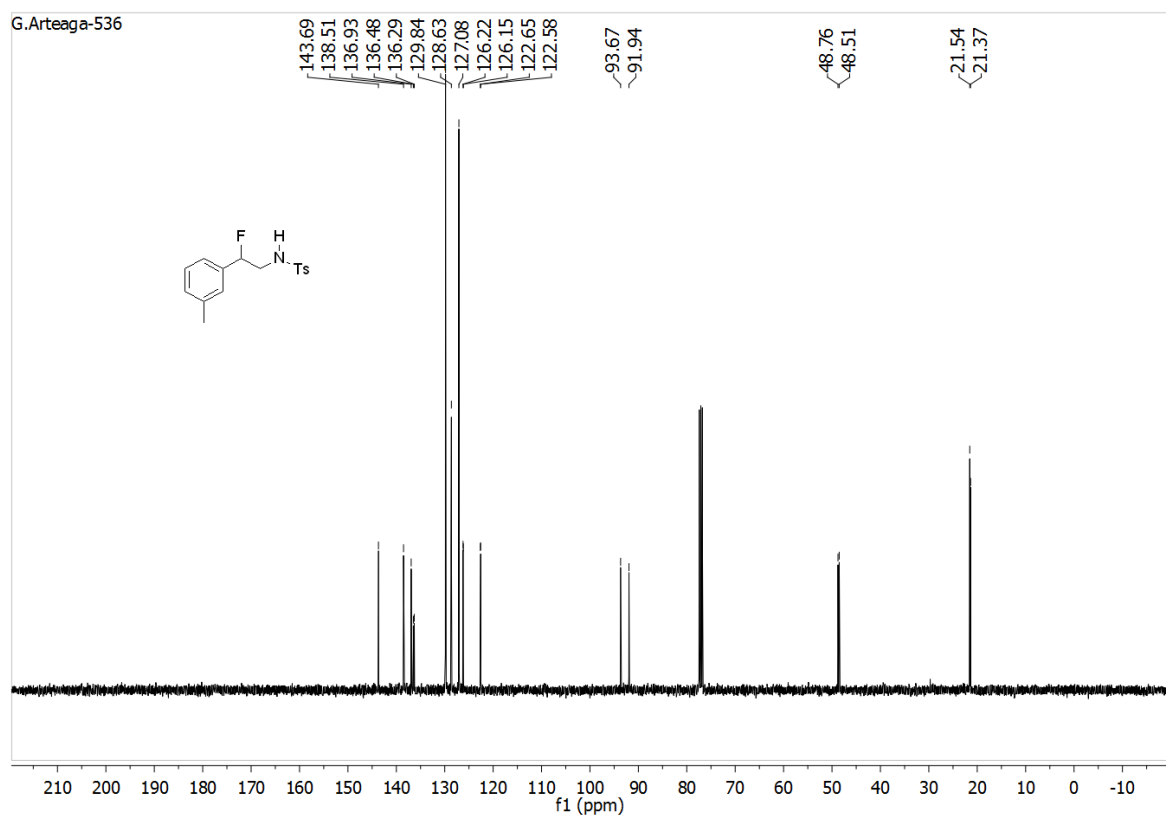
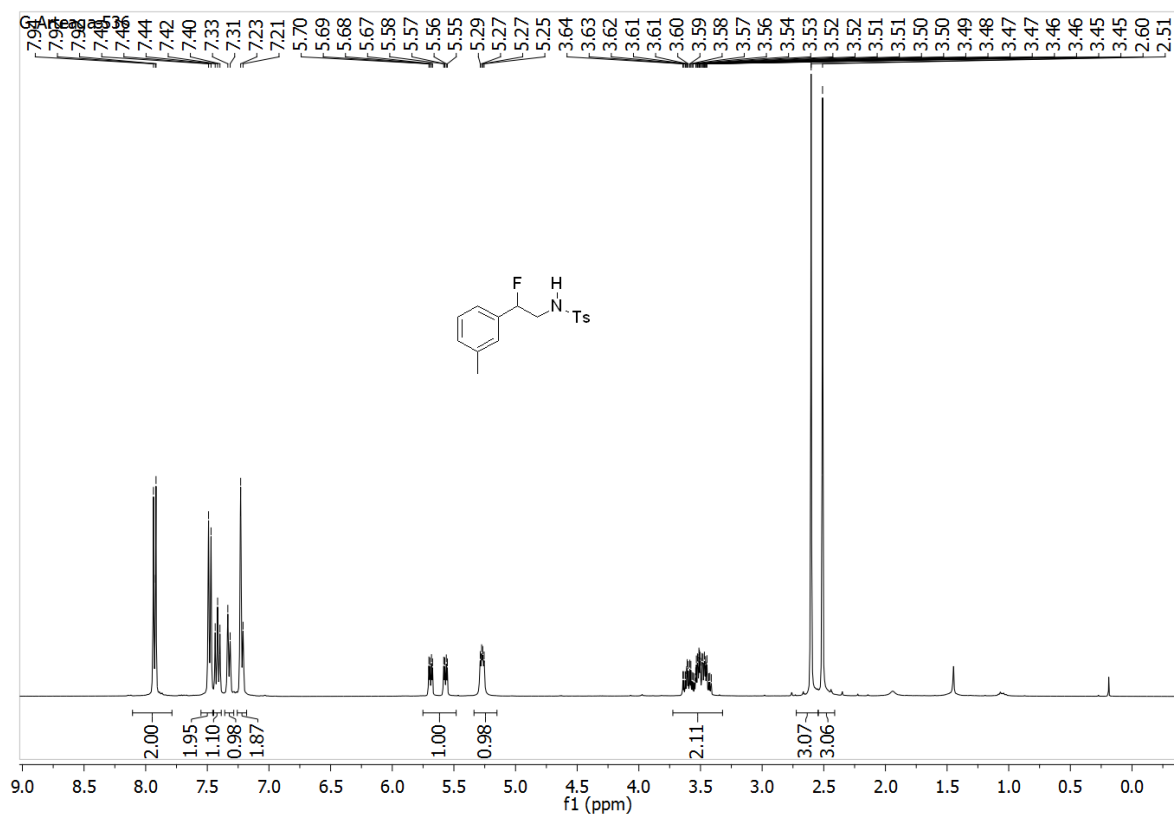


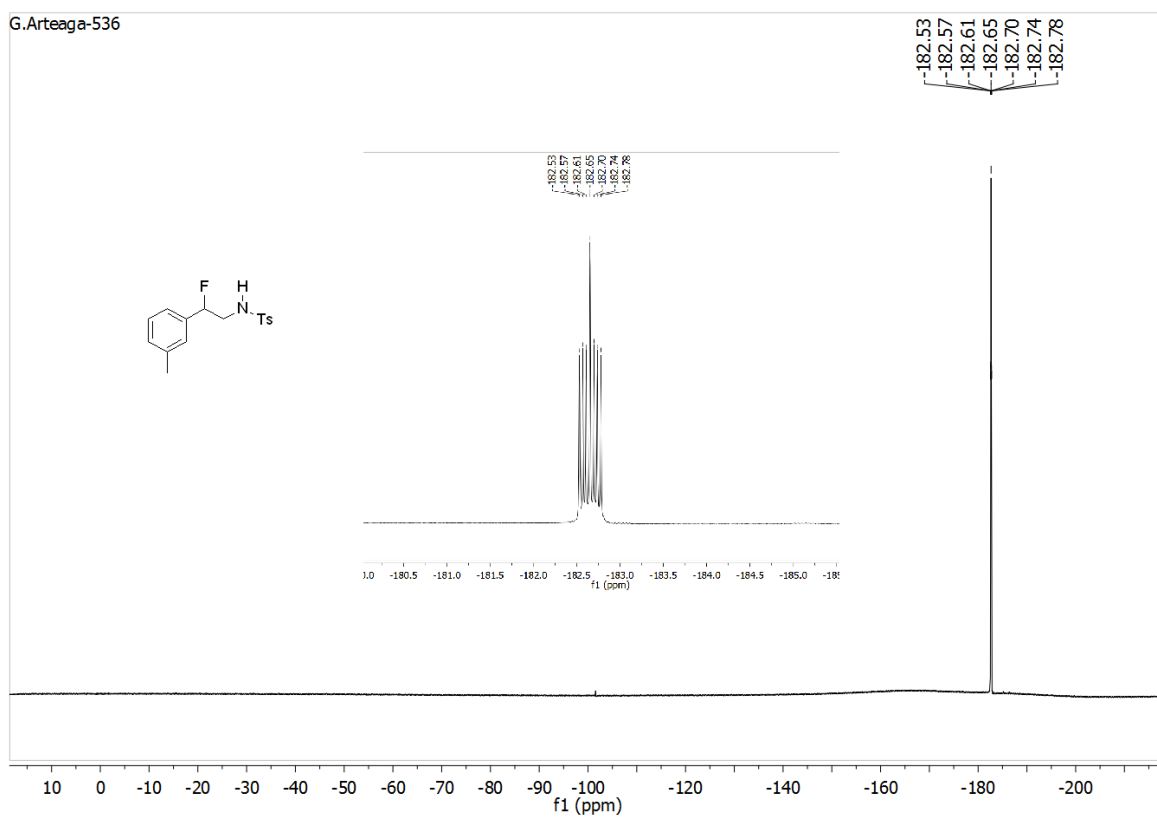
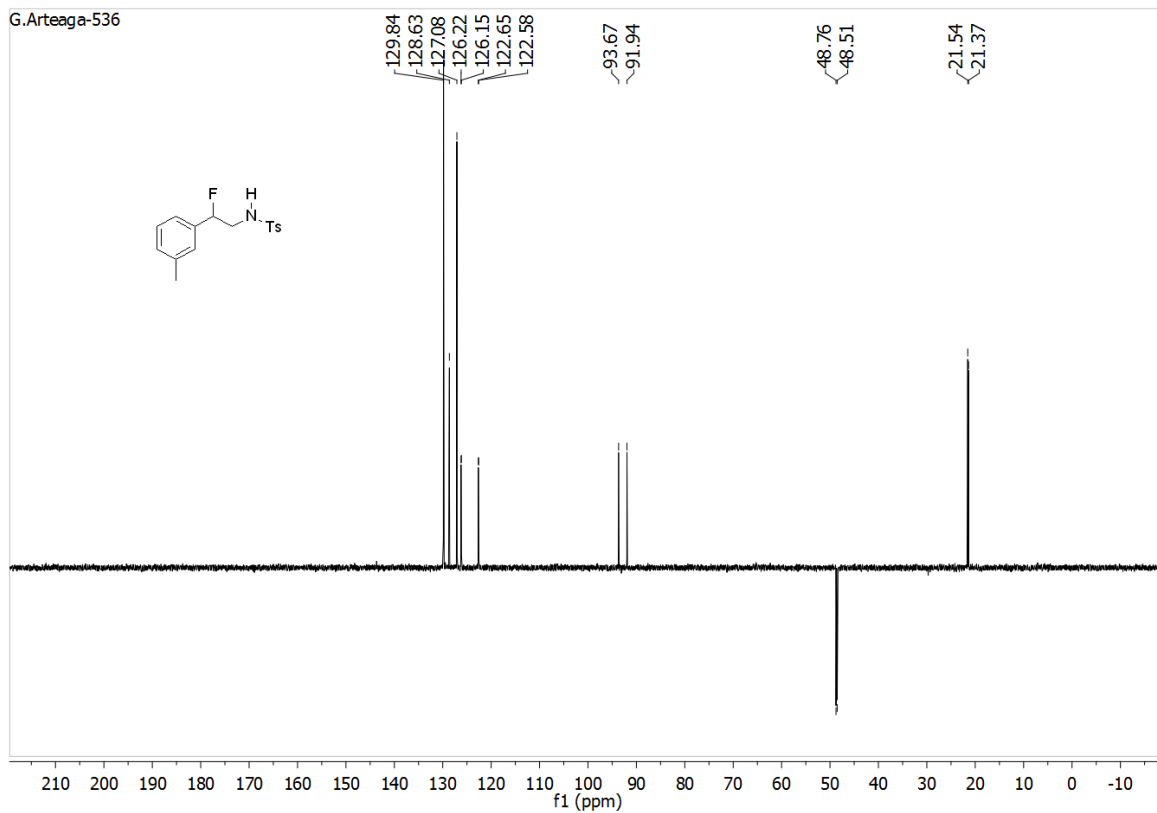


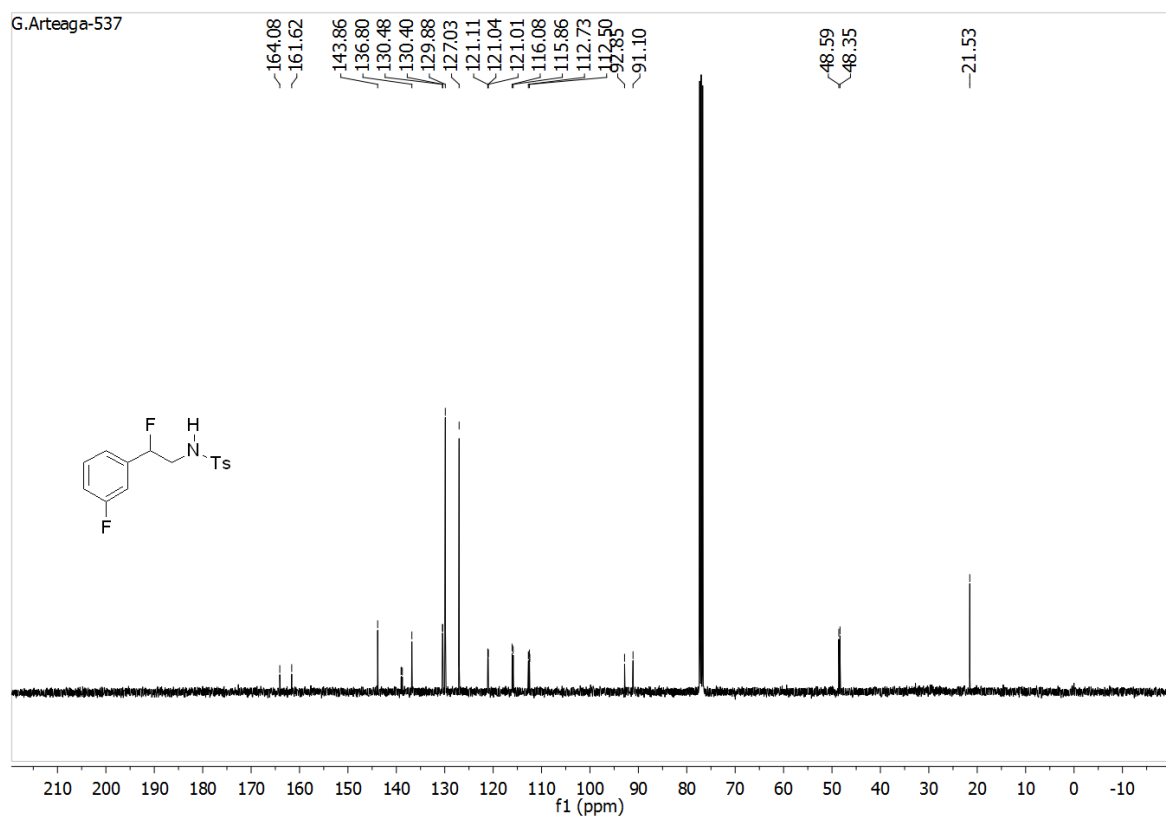
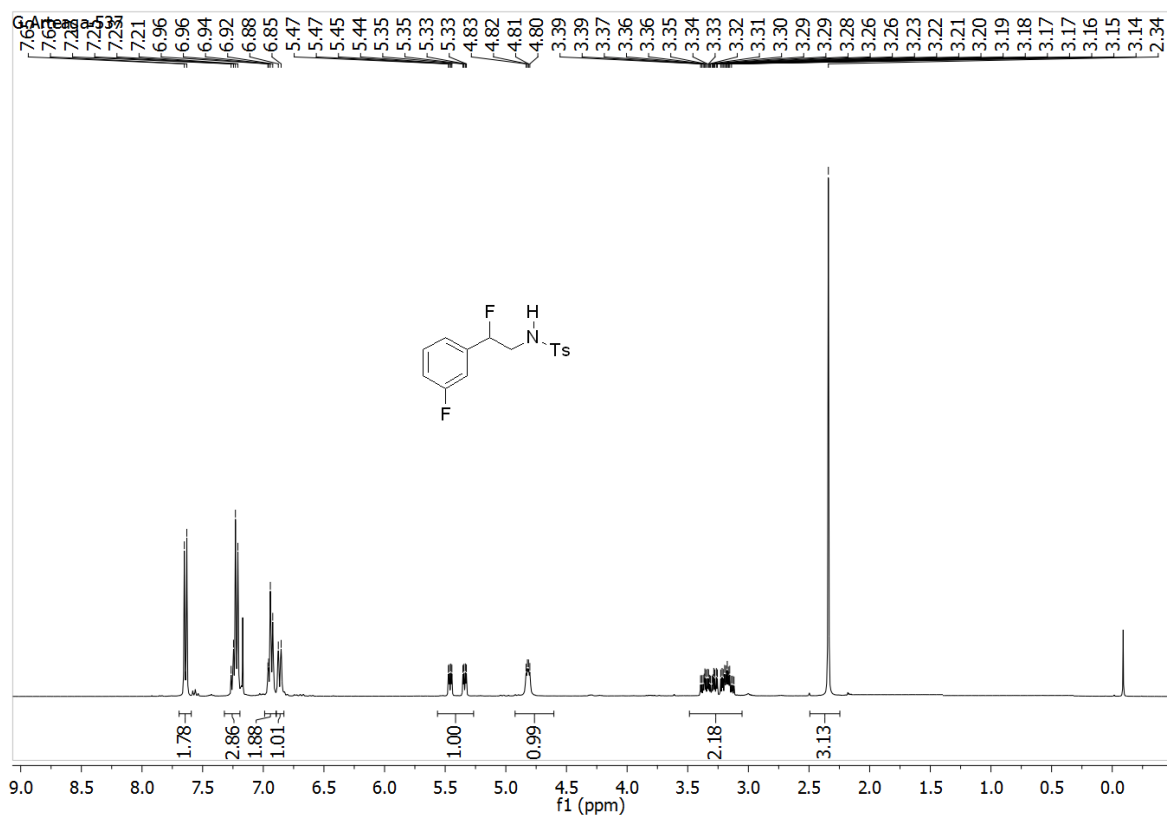


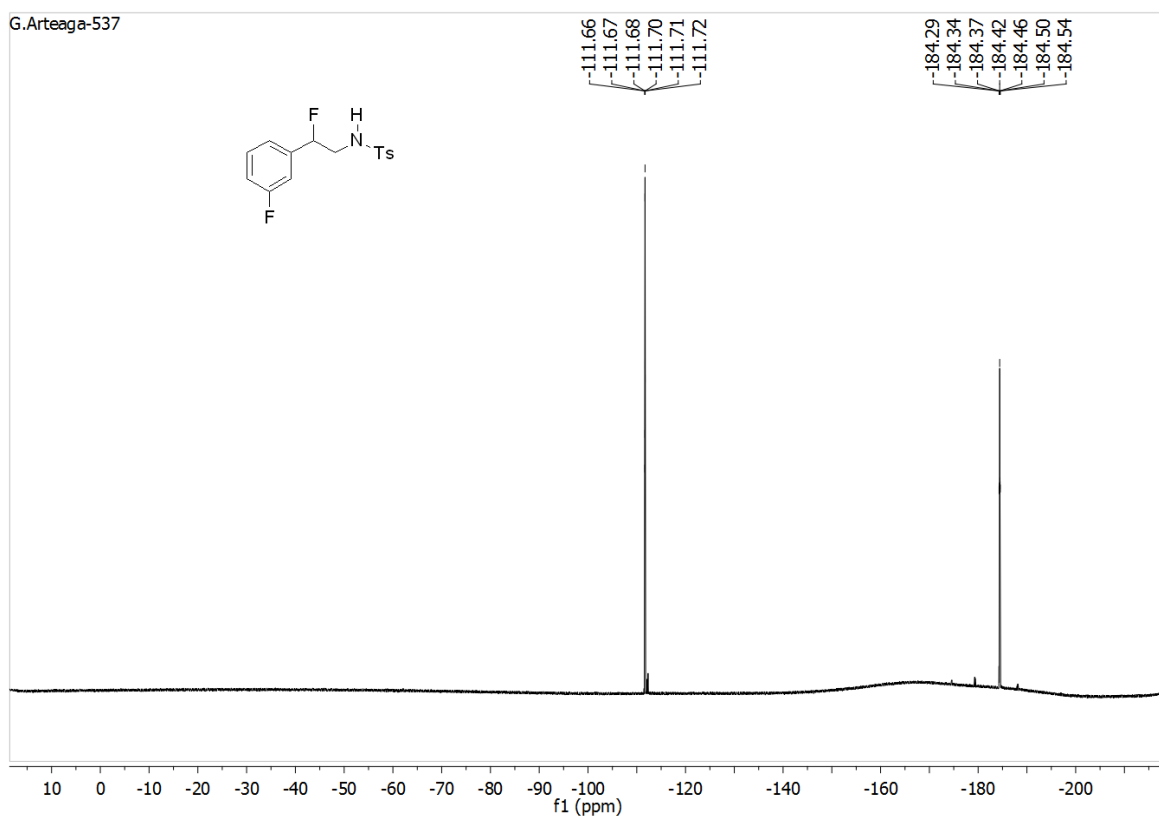
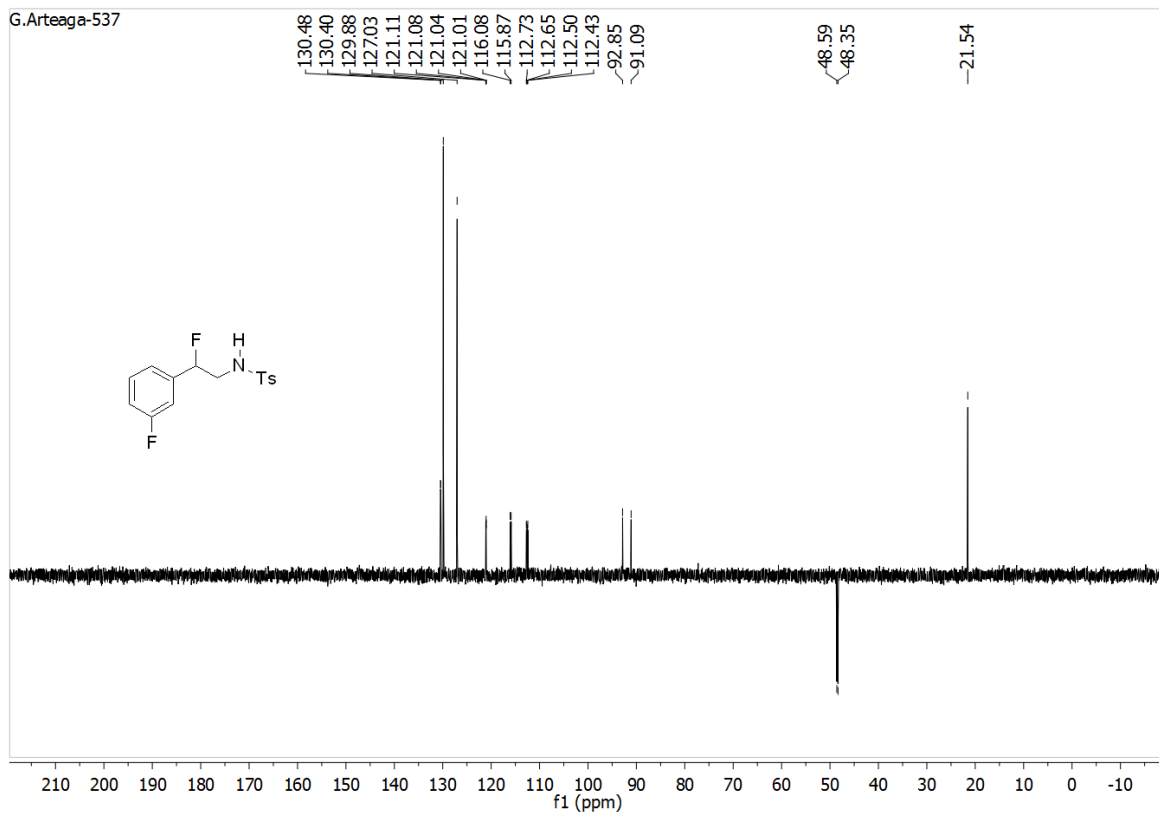


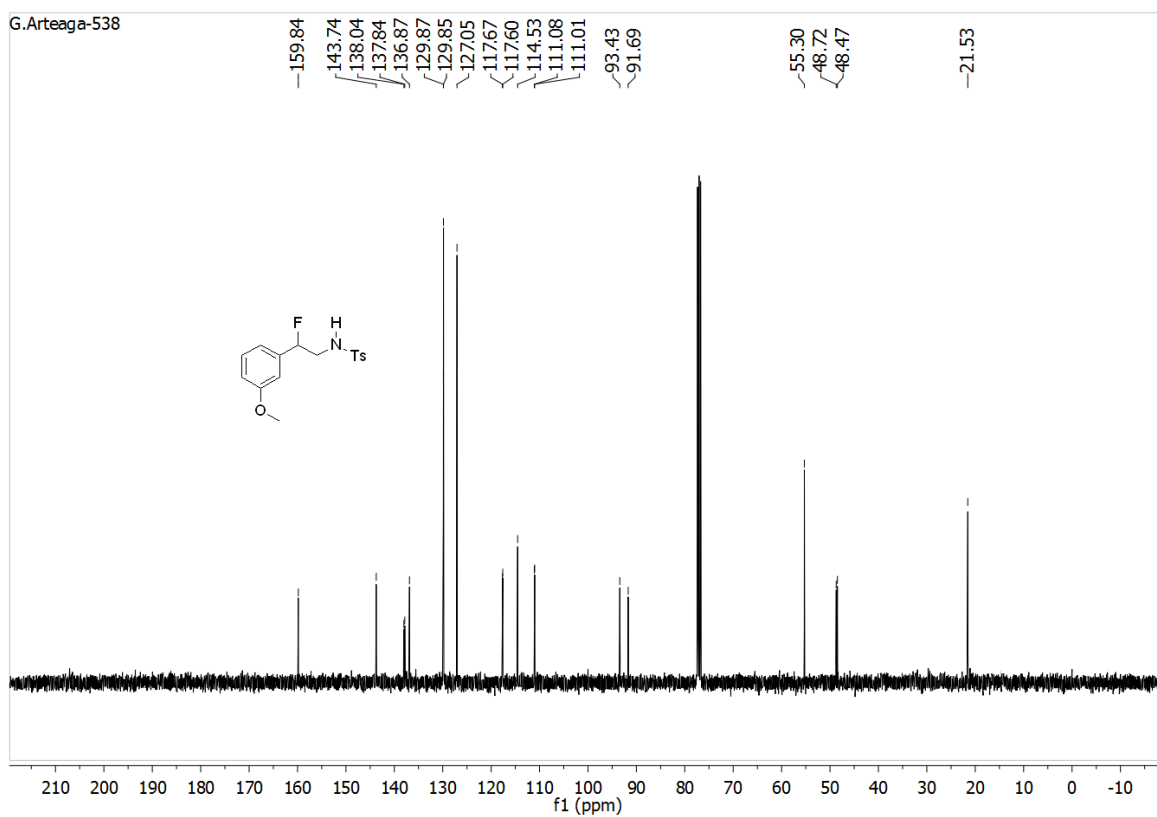
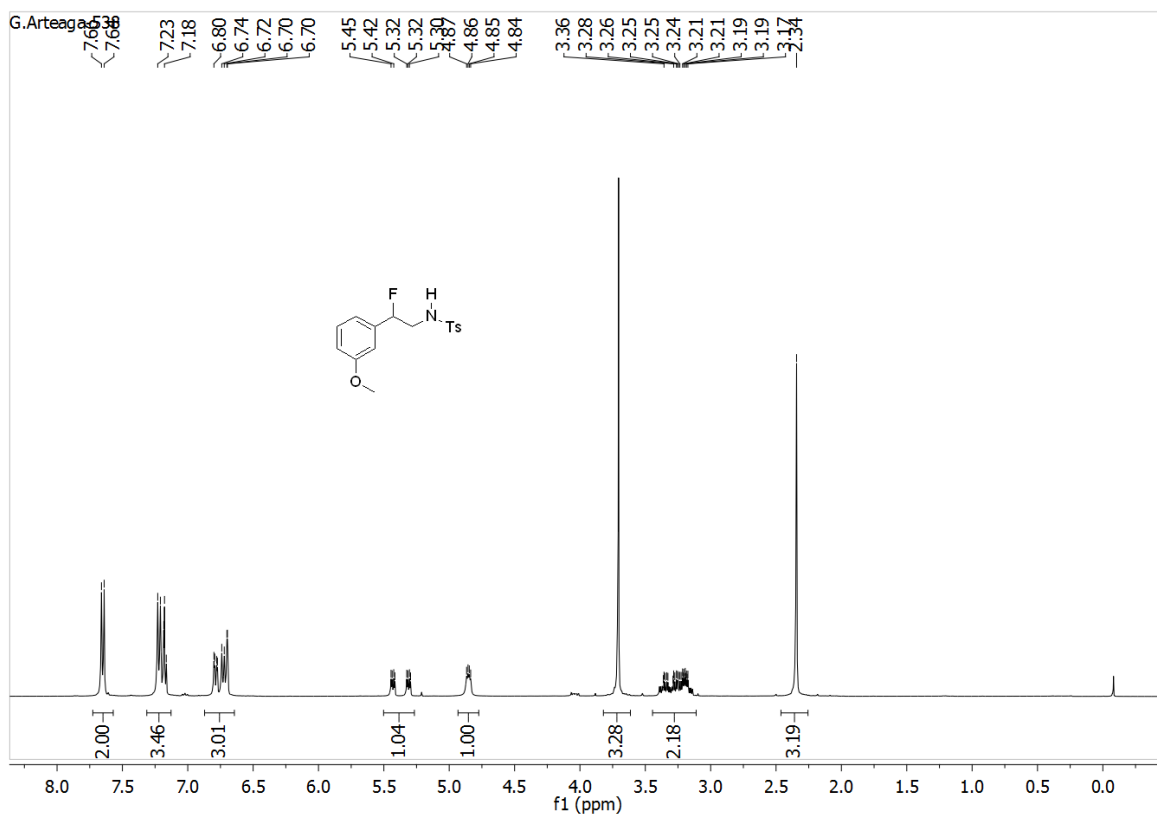


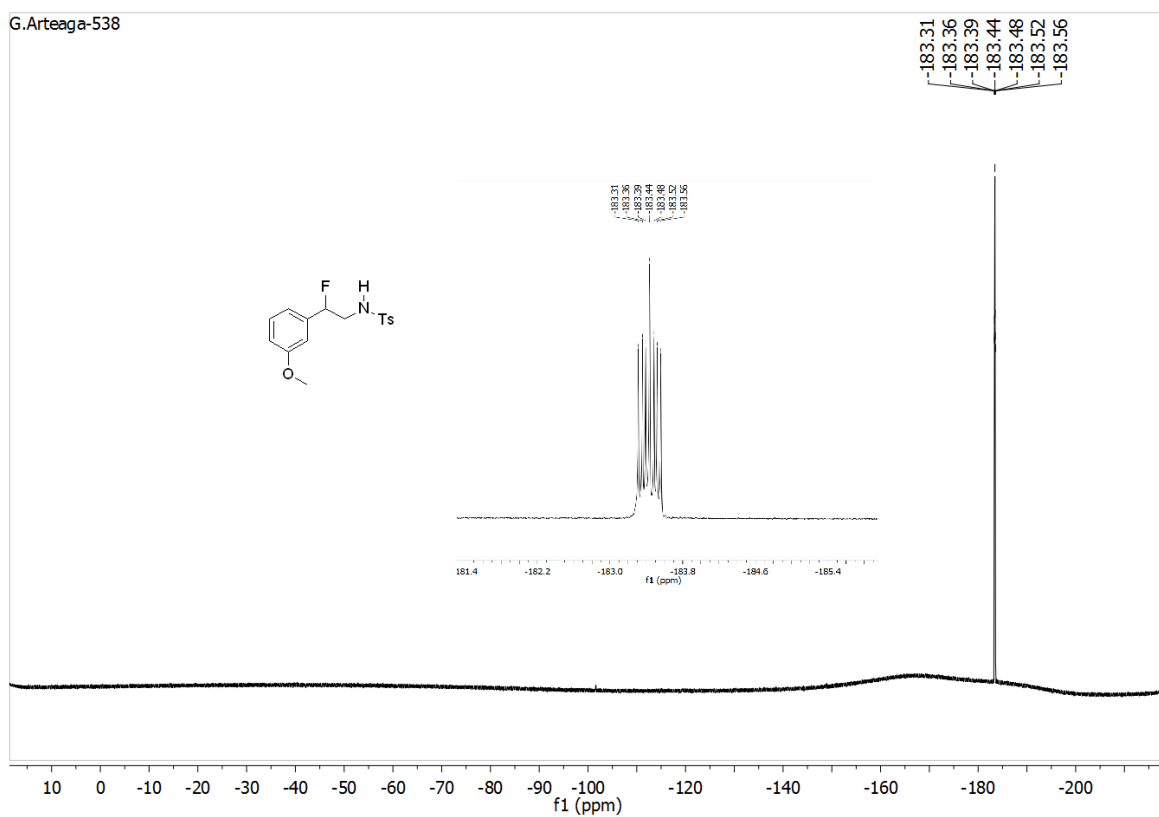
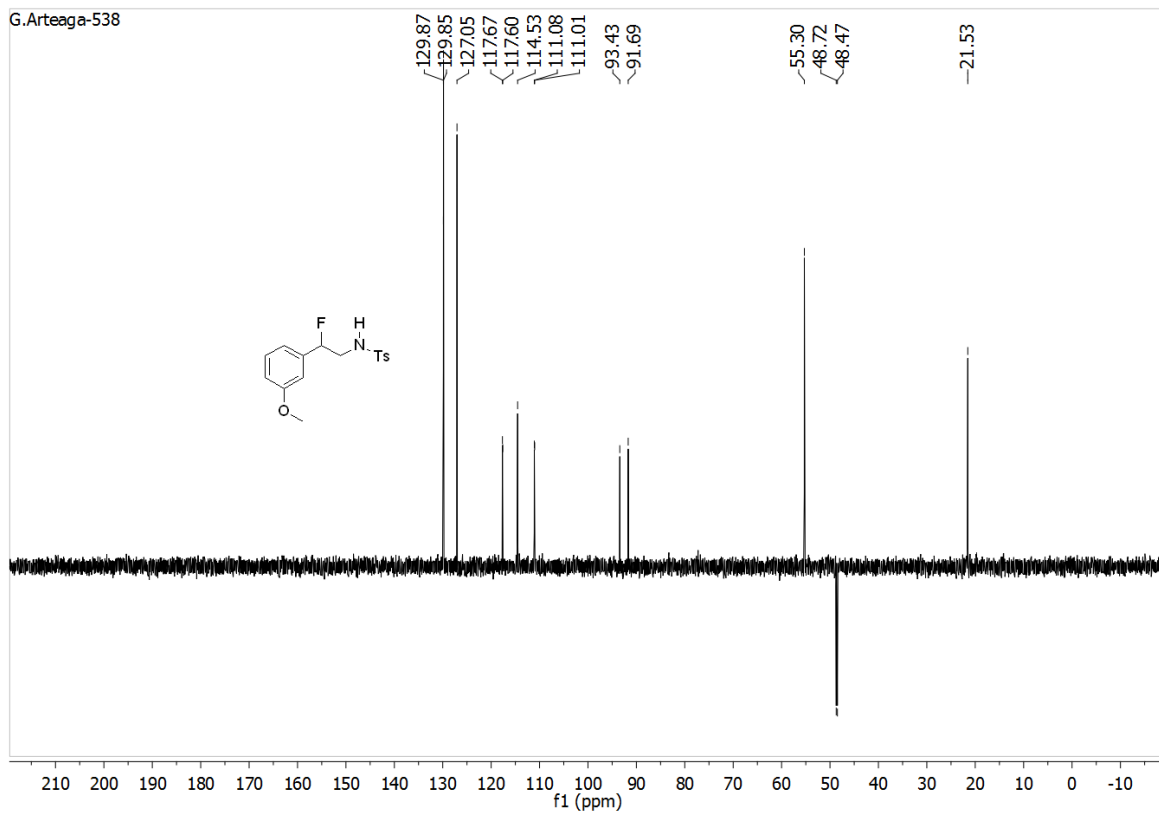


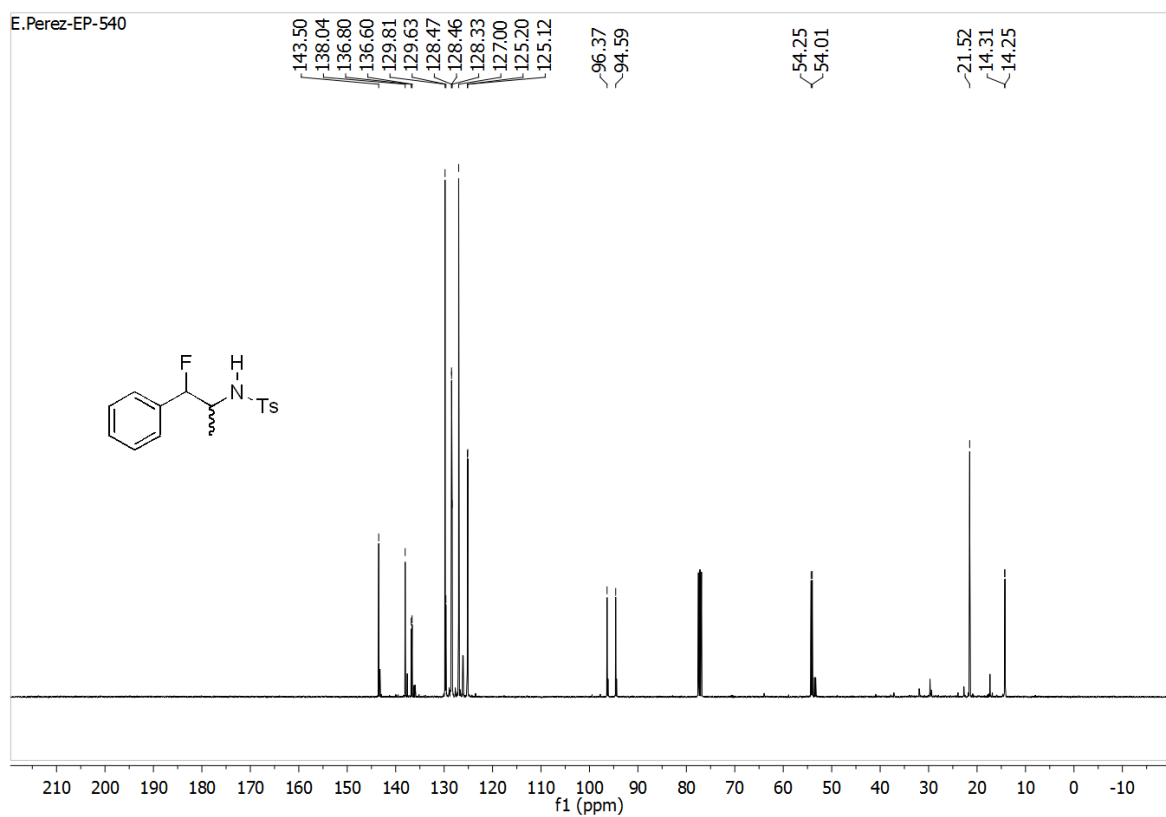
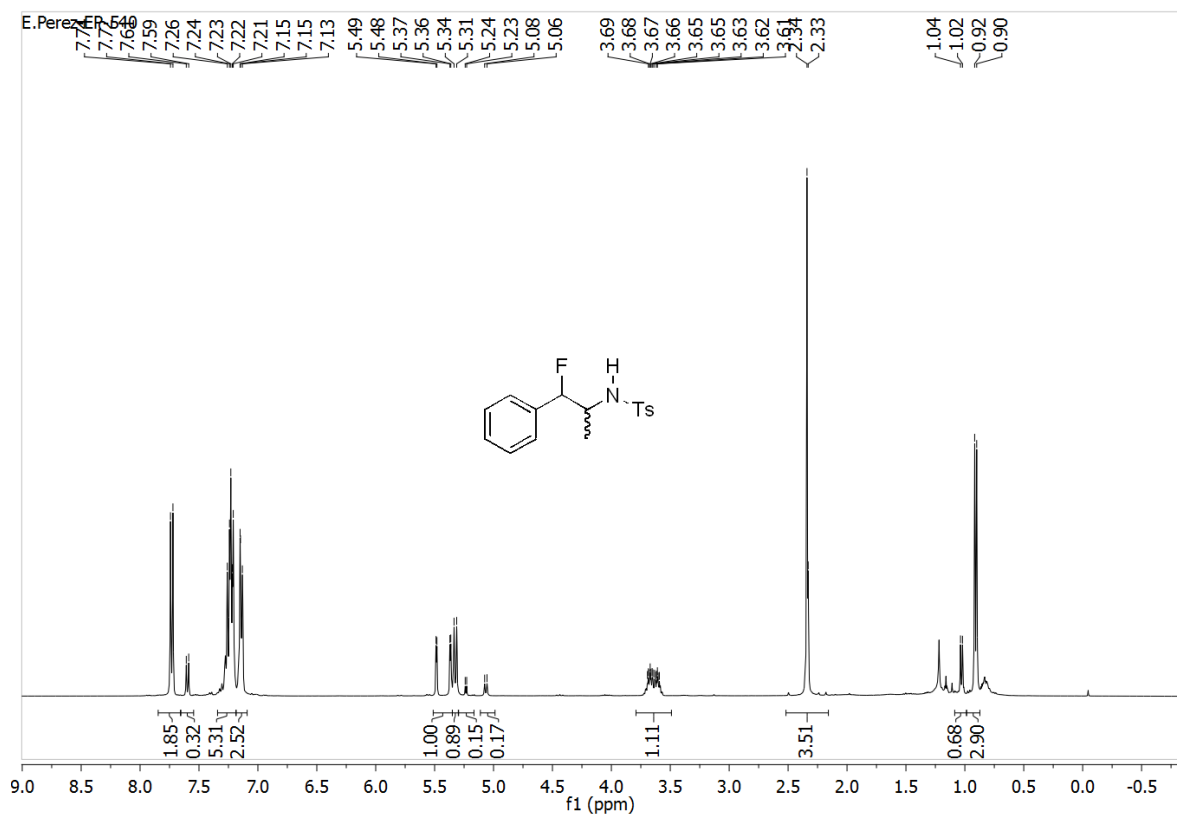


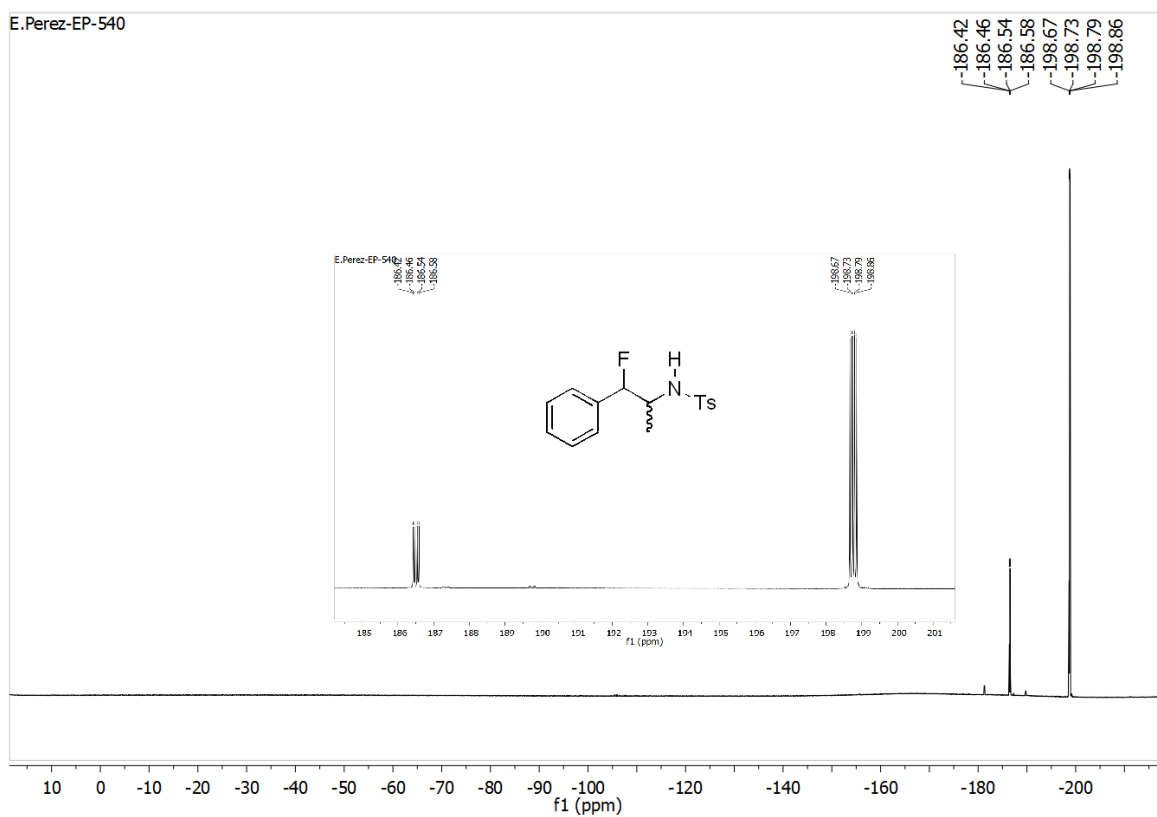
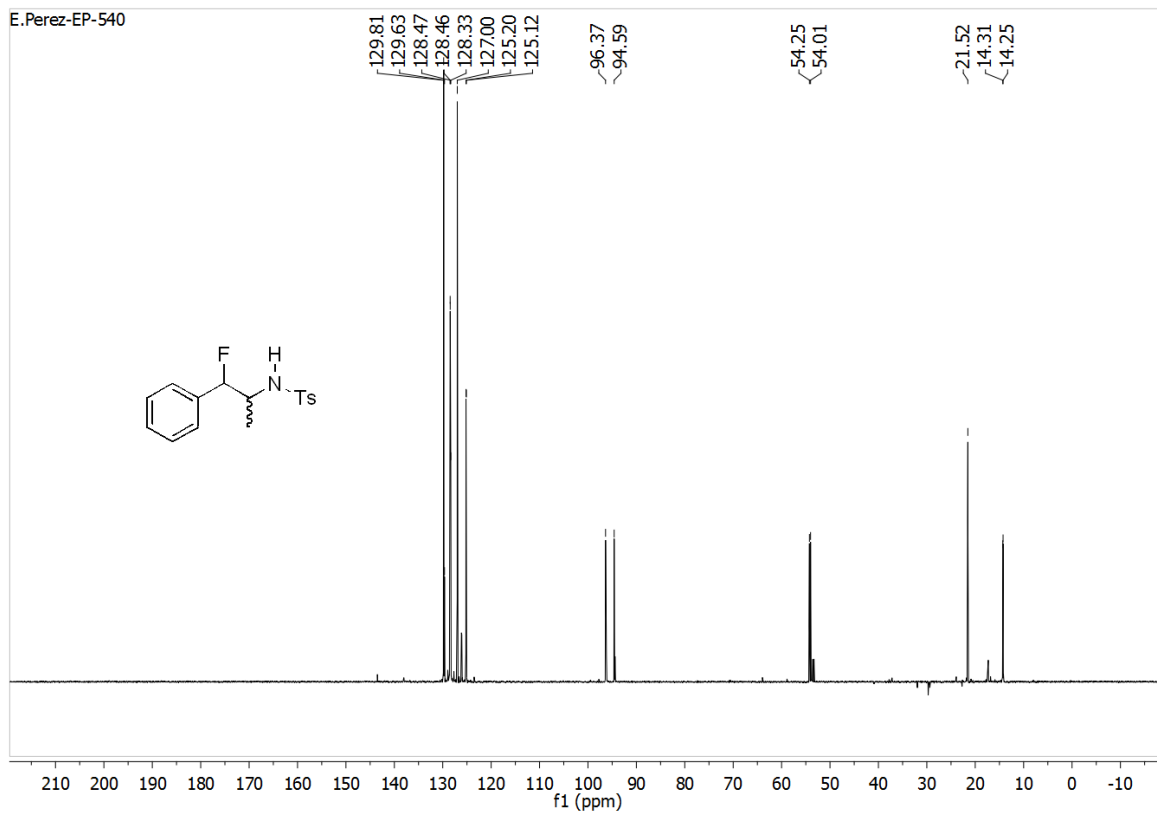


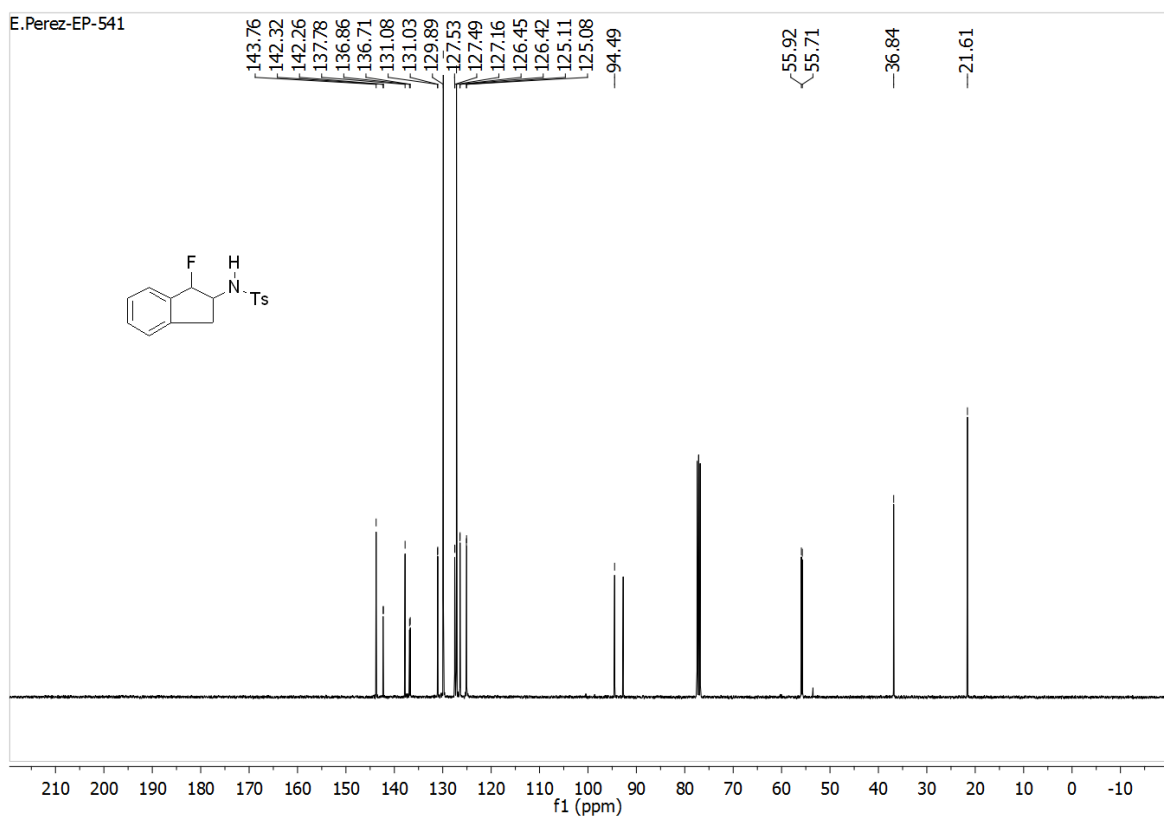
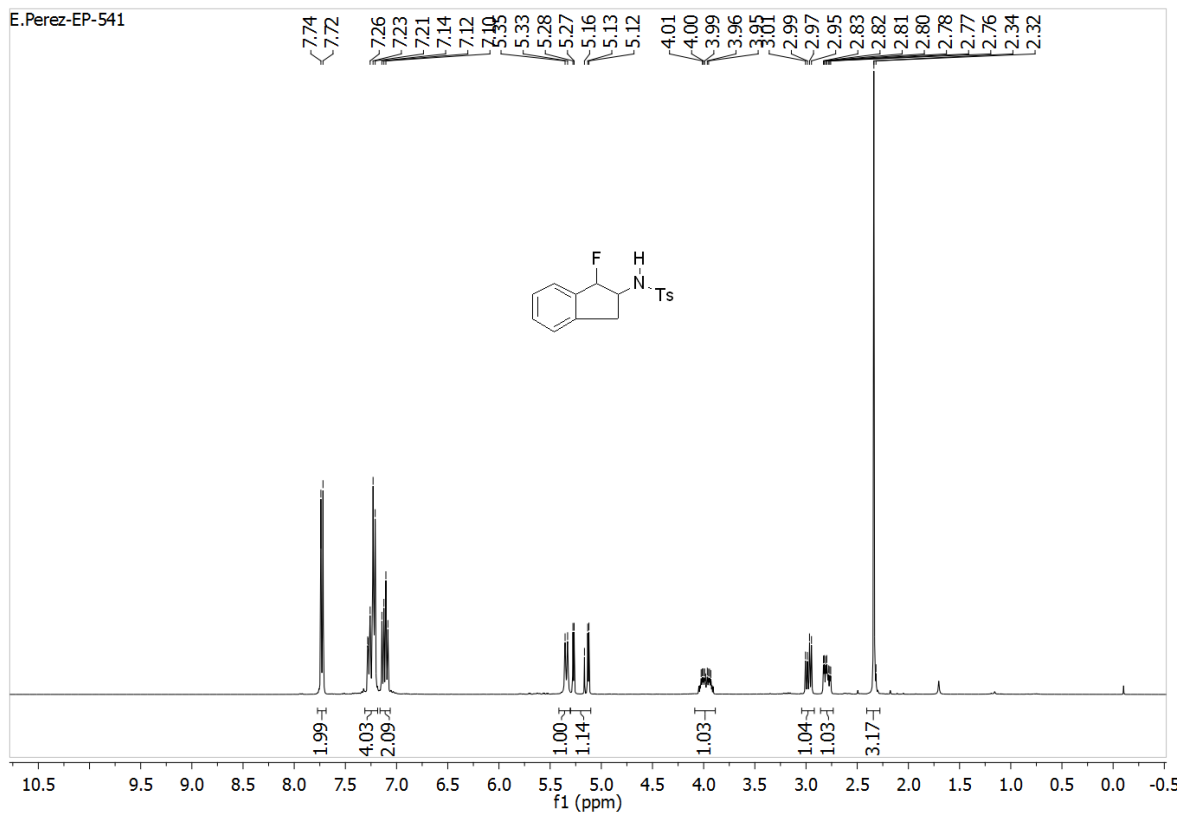


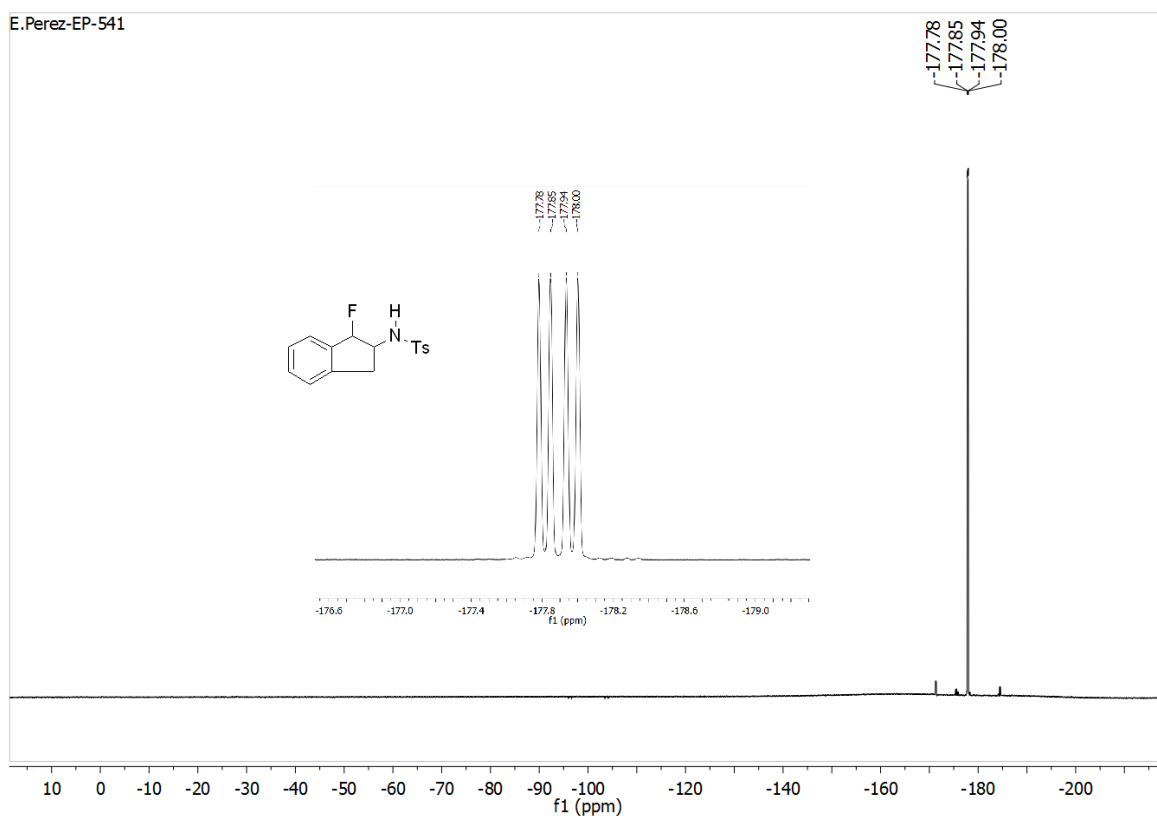
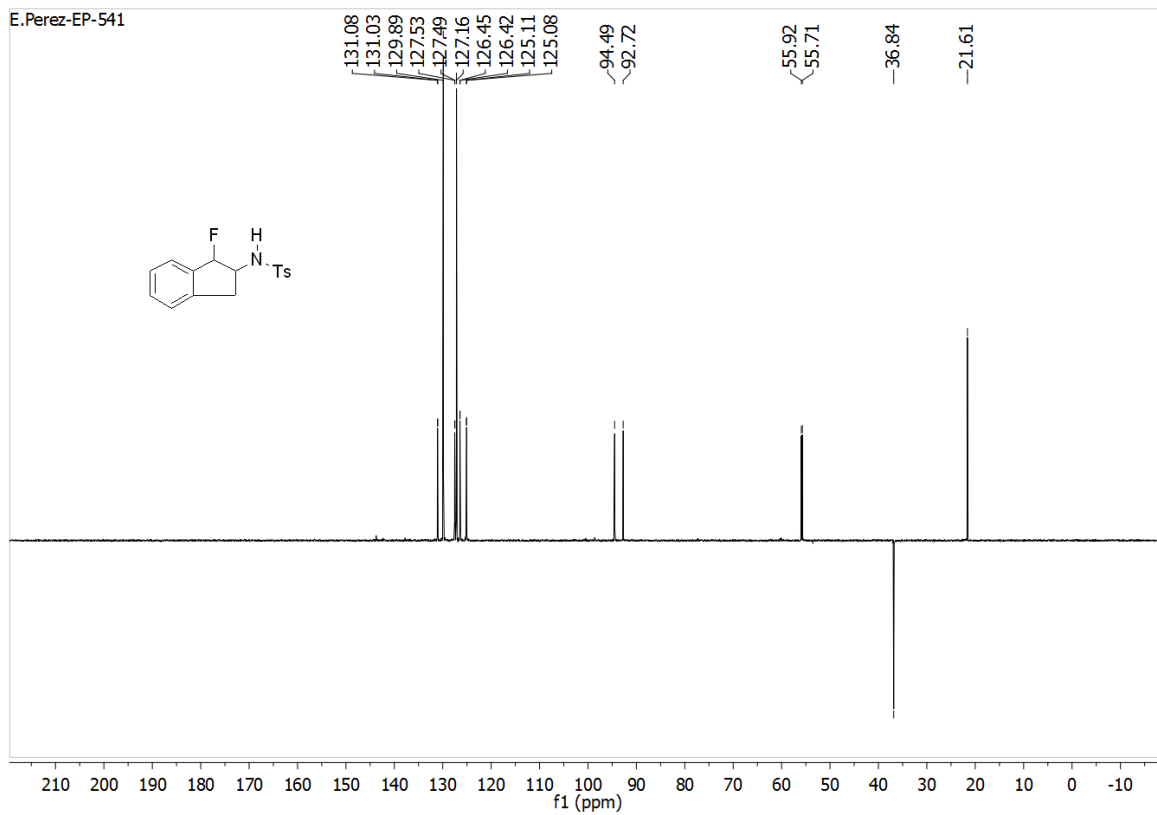


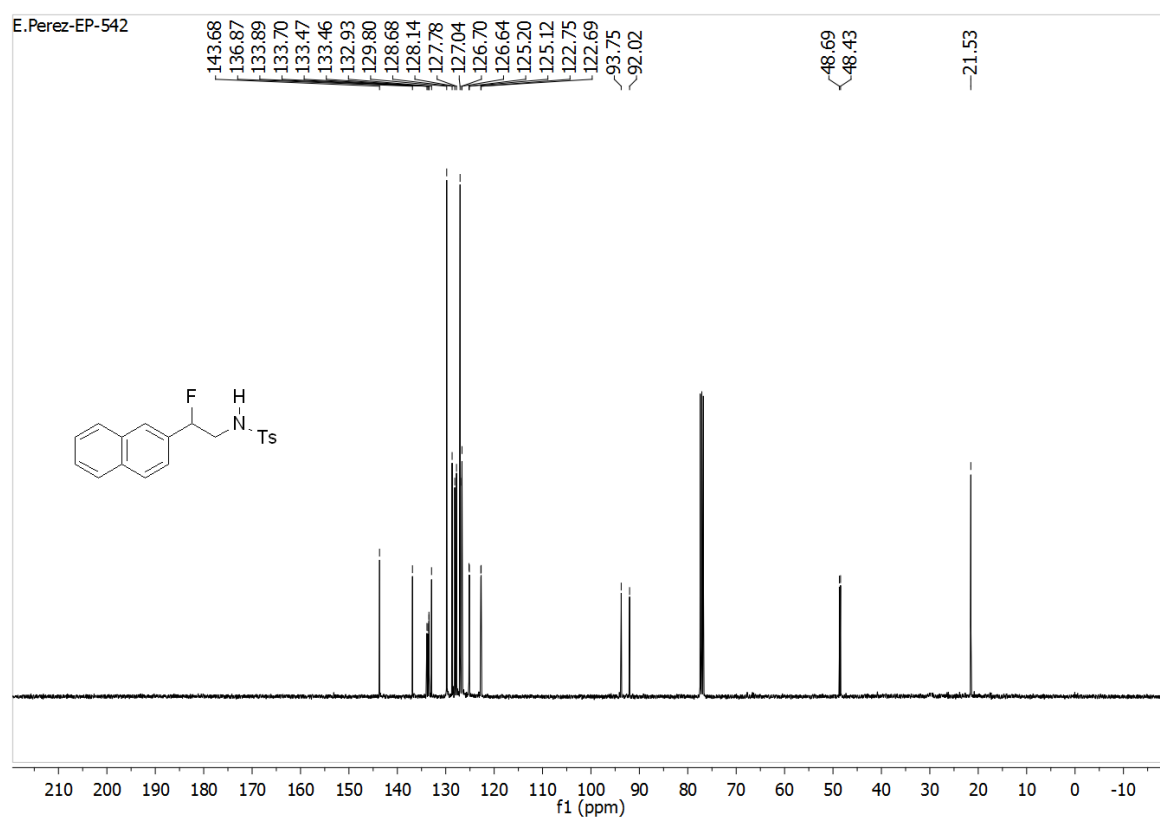
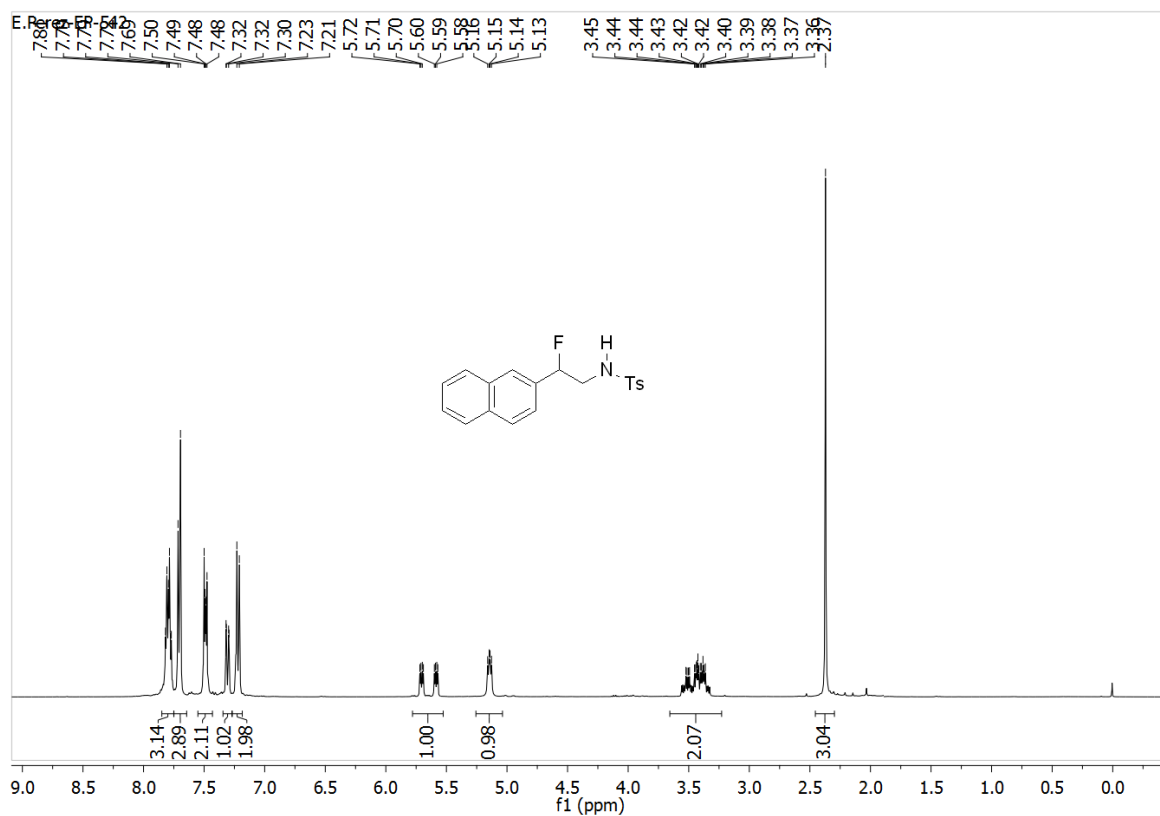




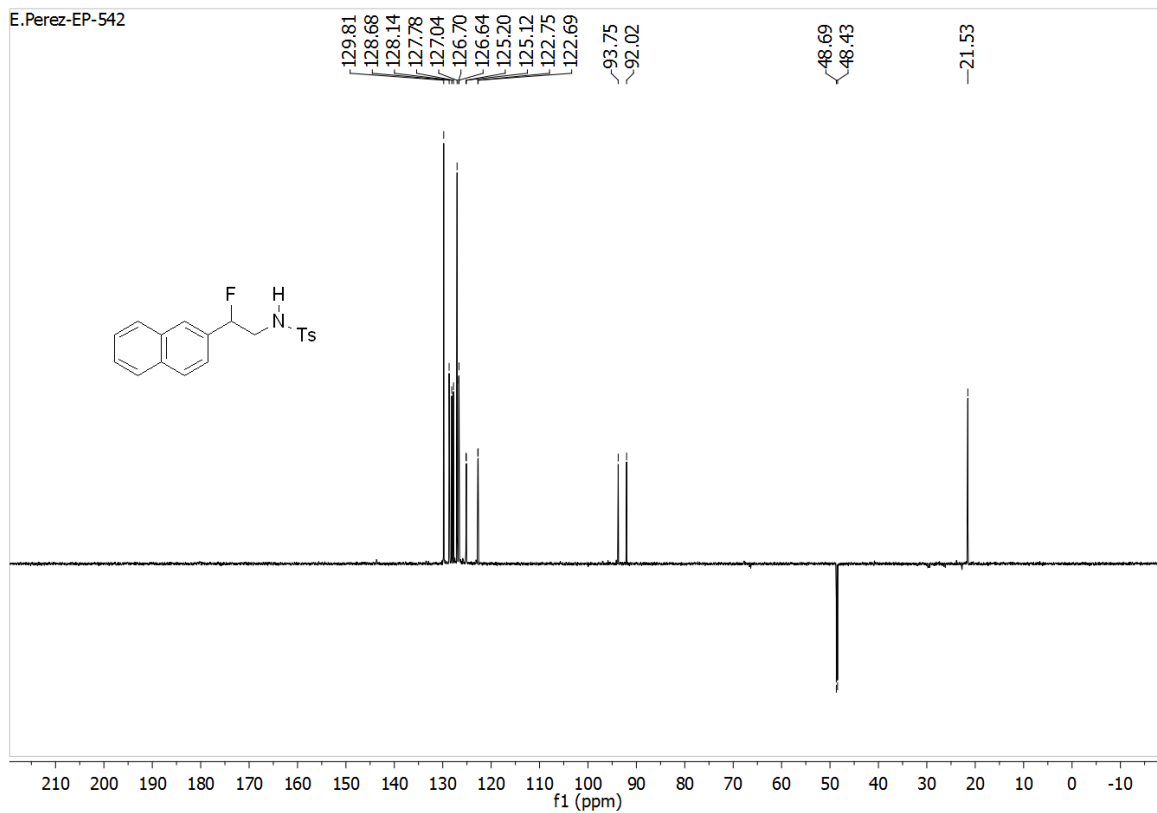




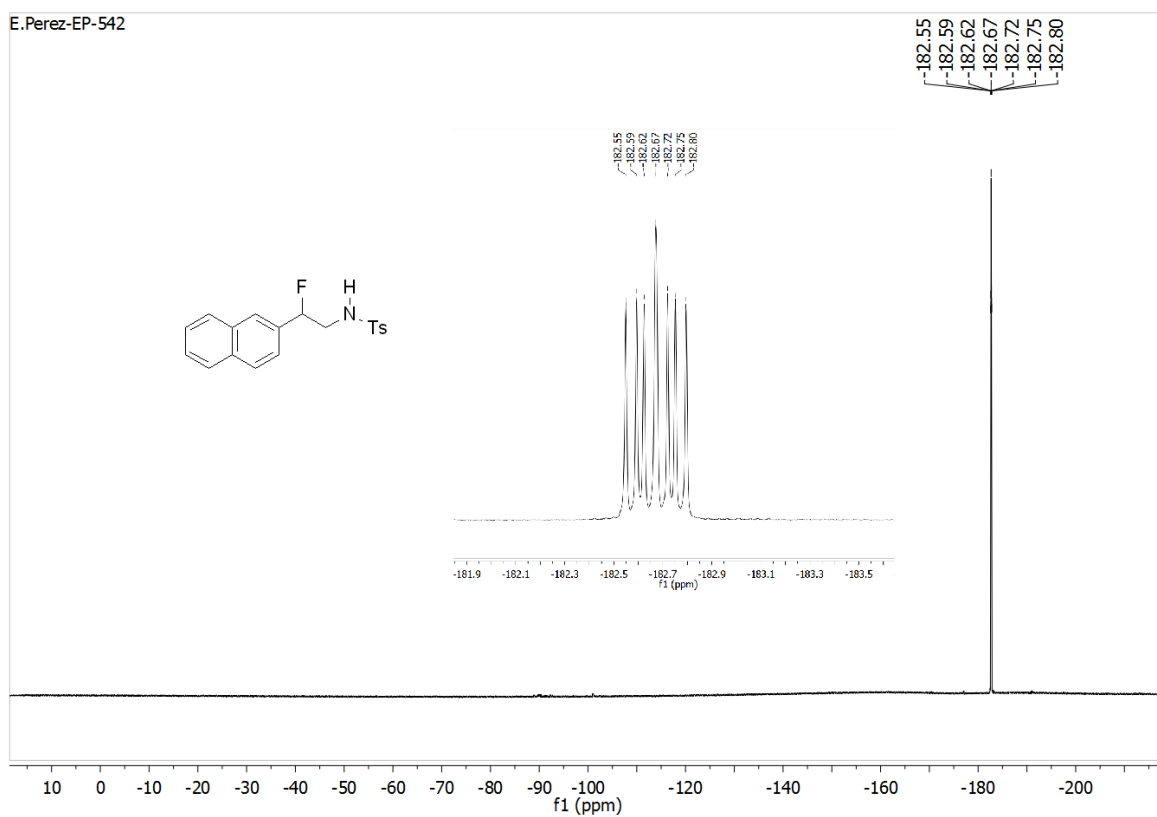


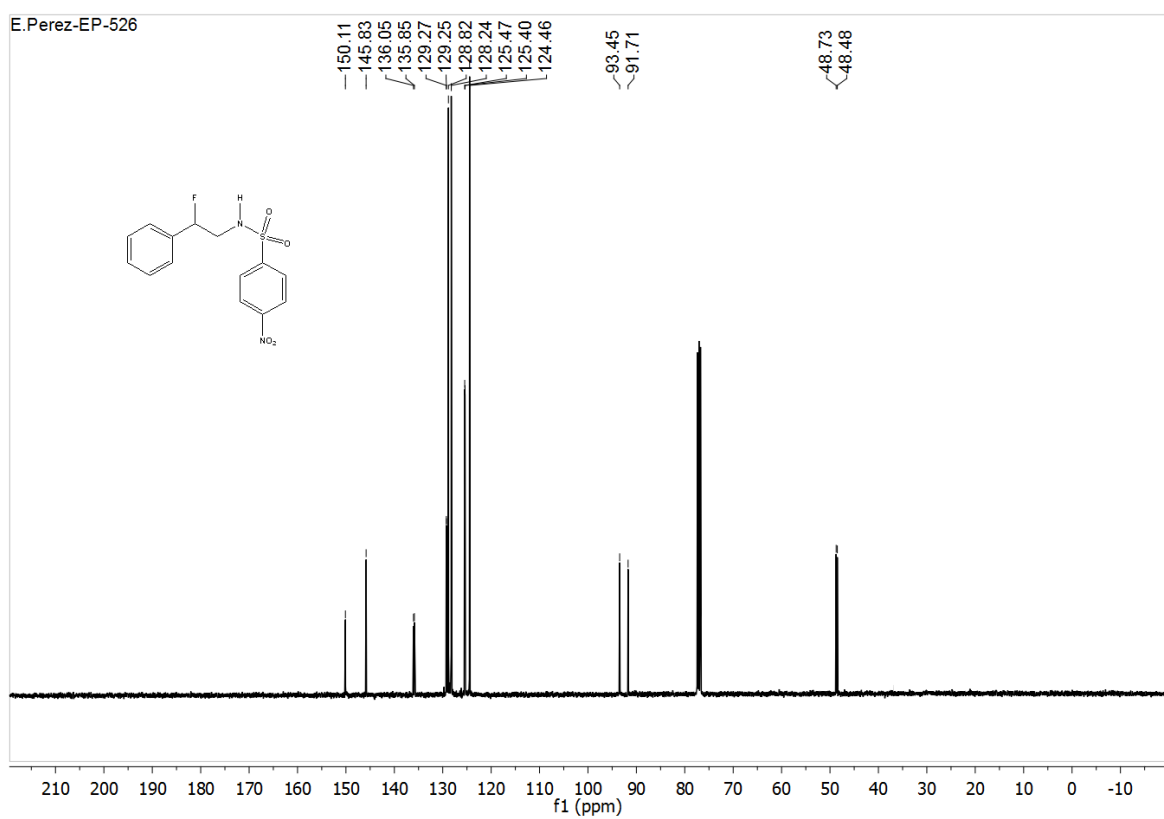
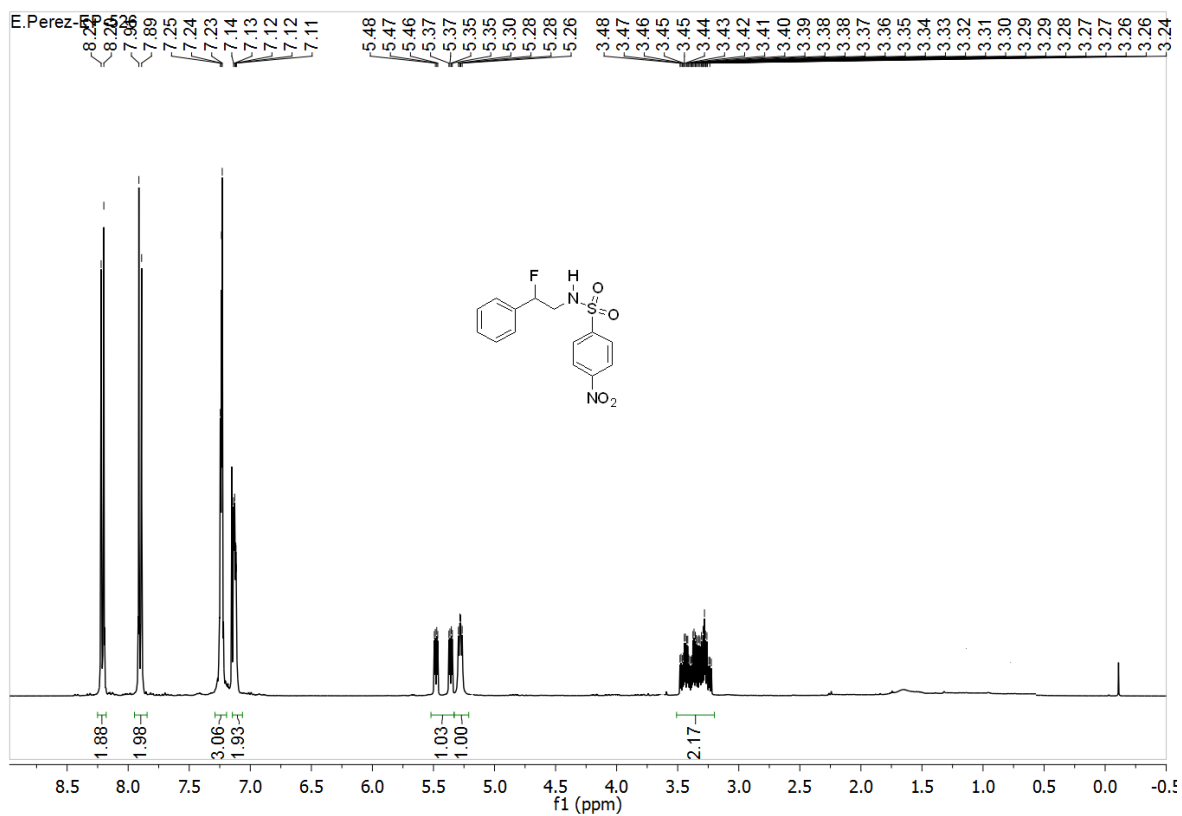


E.Perez-EP-542

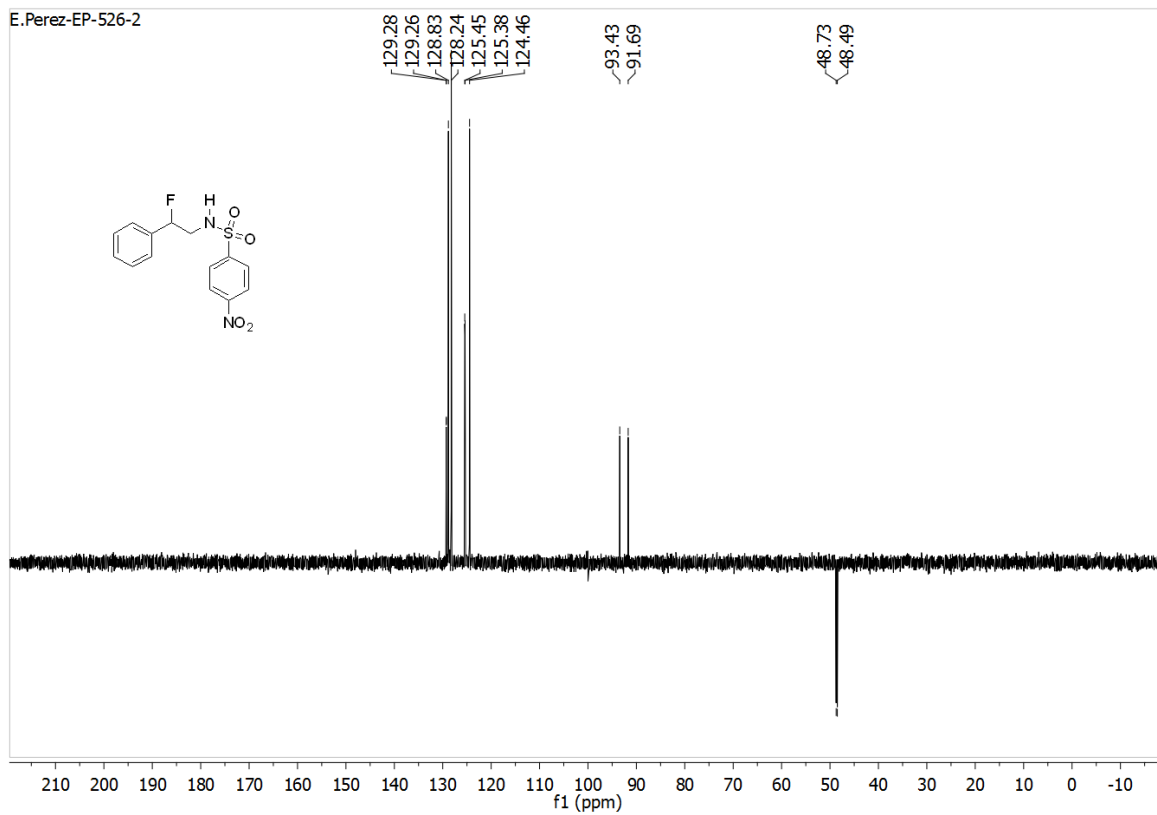


E.Perez-EP-542

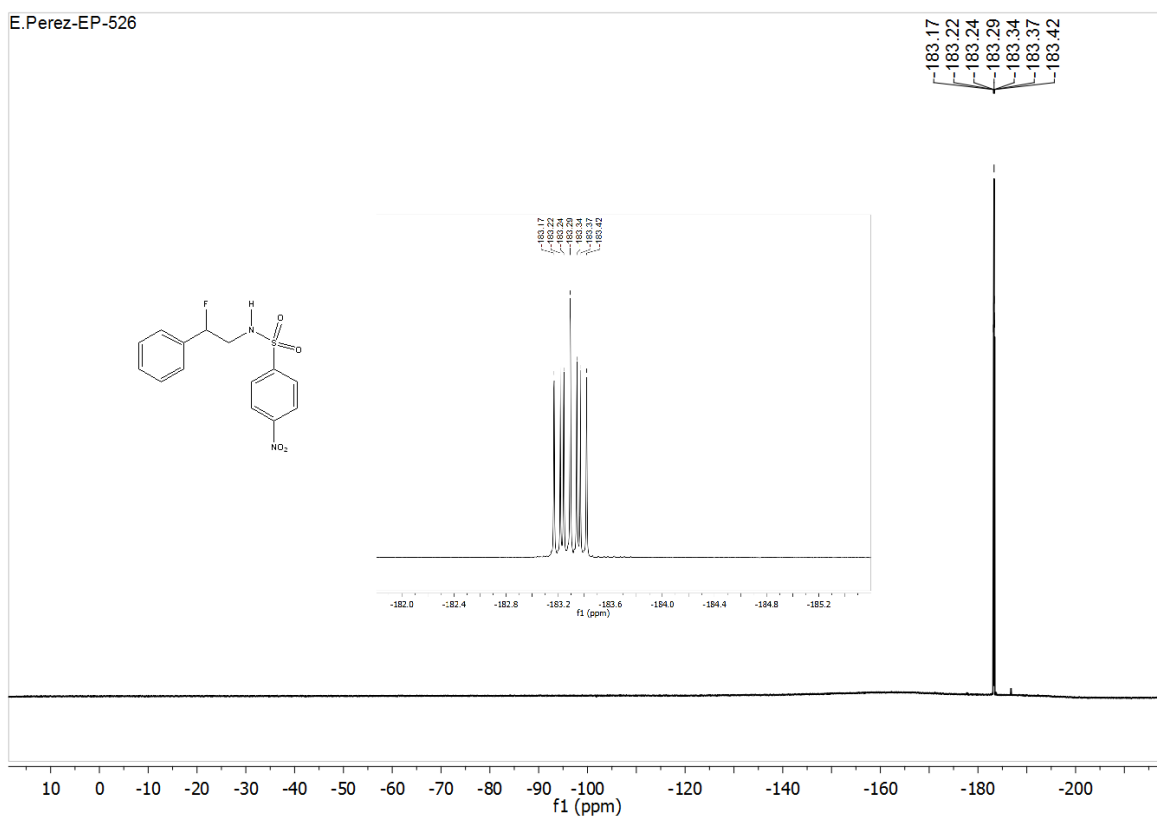


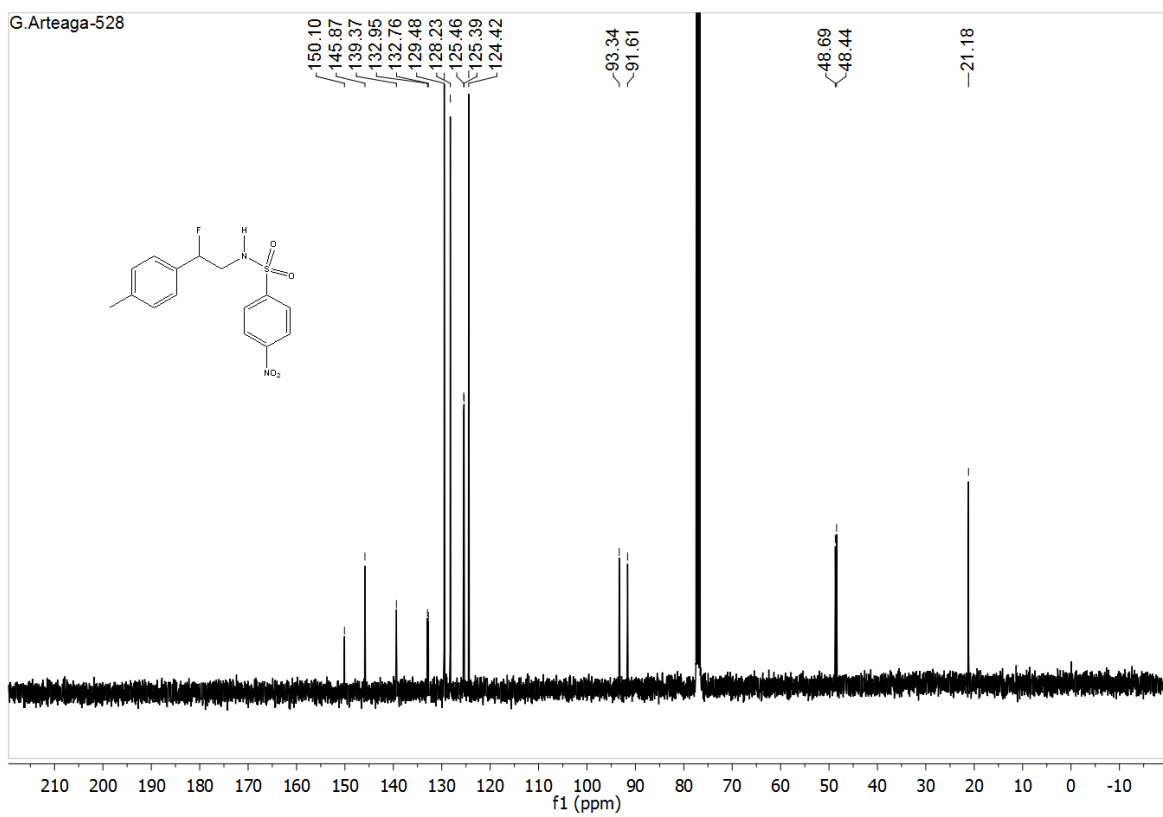
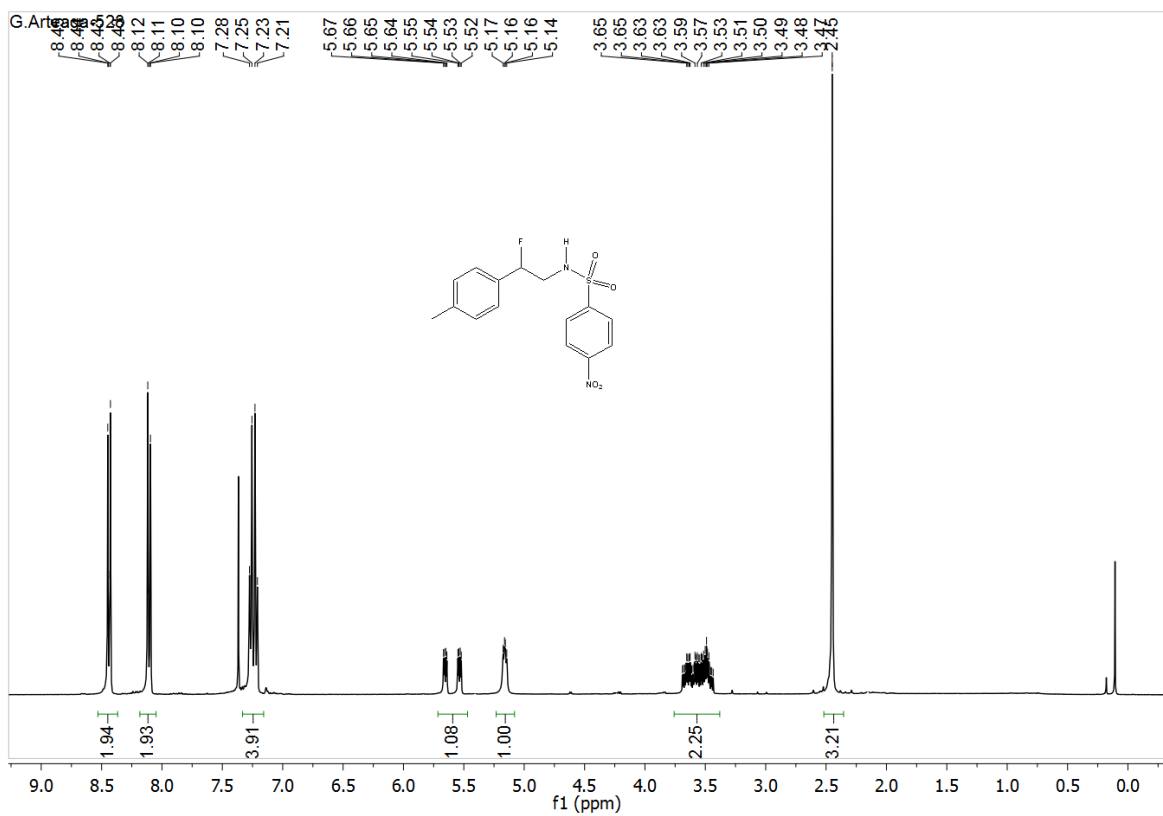


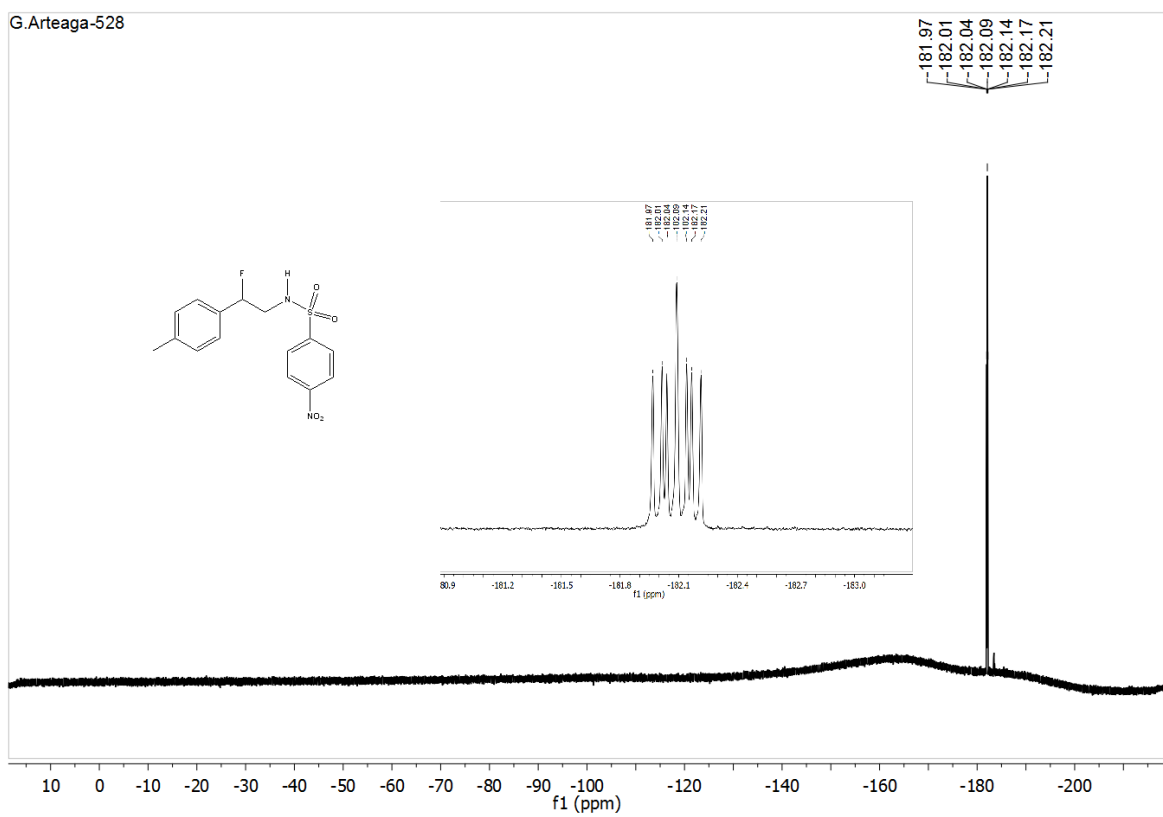
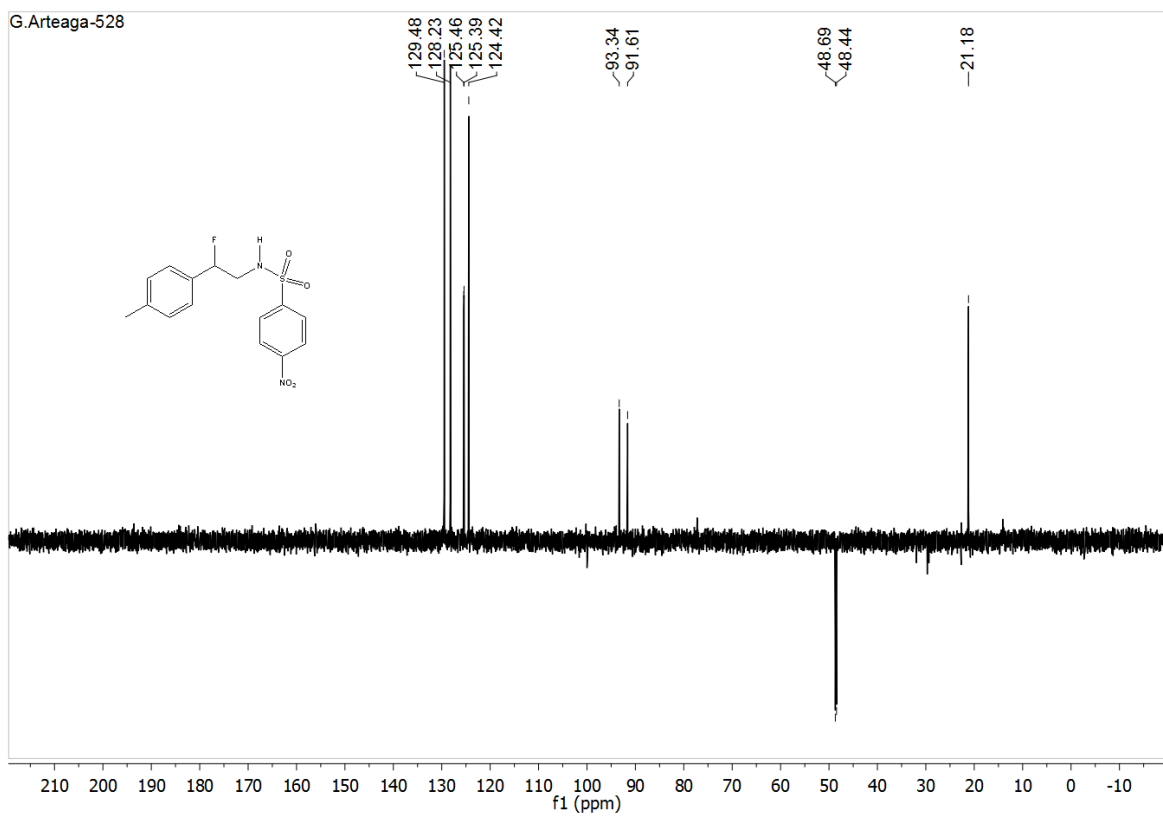
E.Perez-EP-526-2

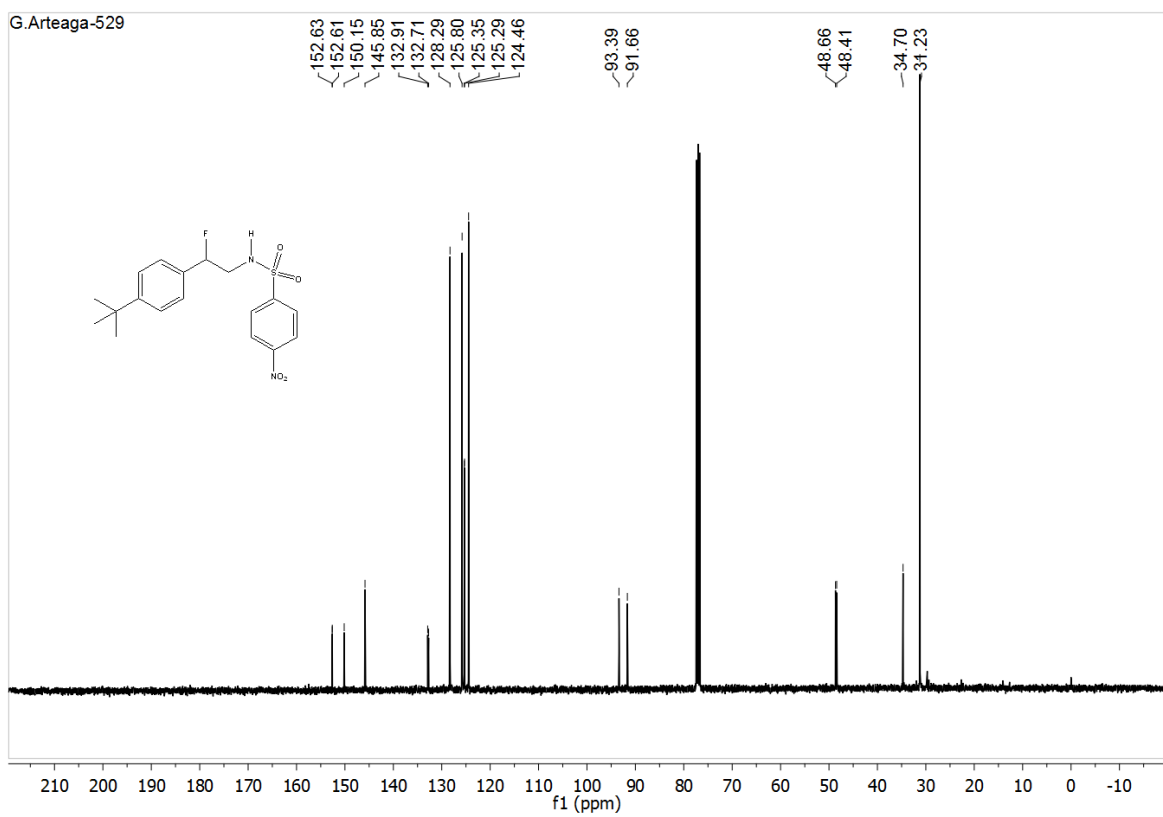
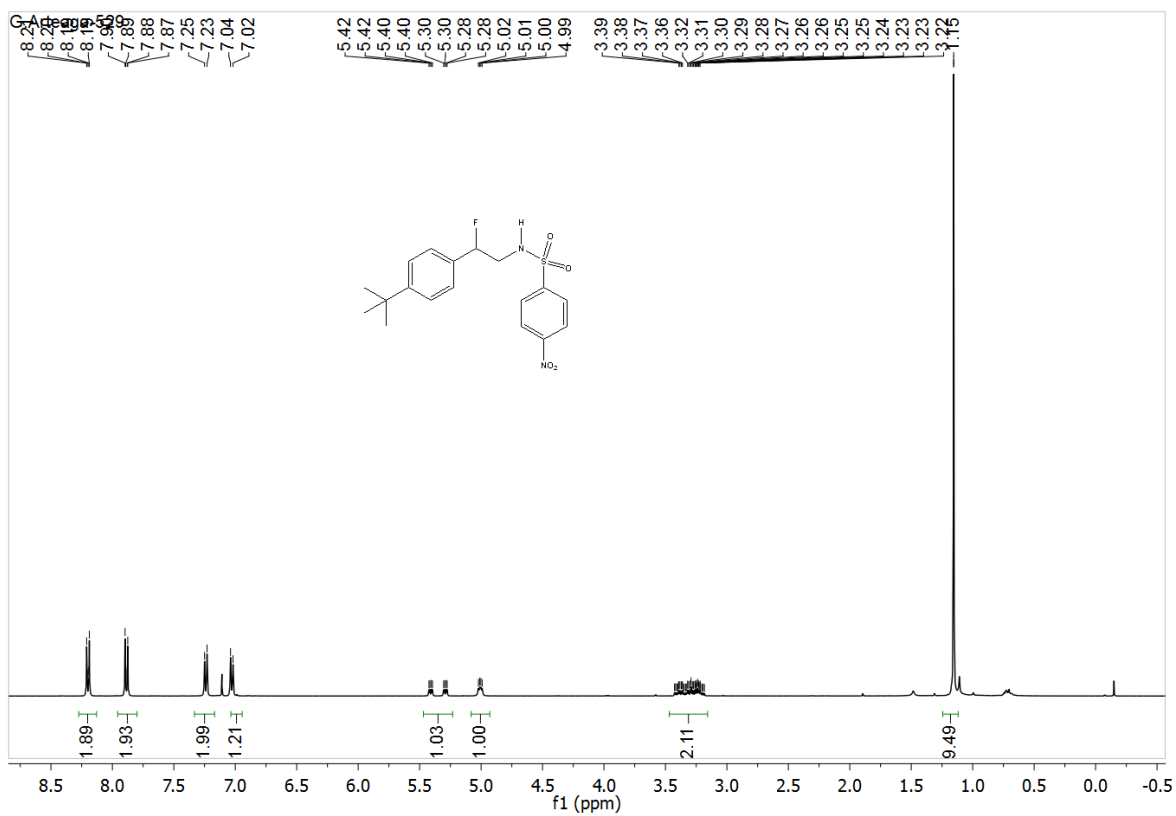


E.Perez-EP-526

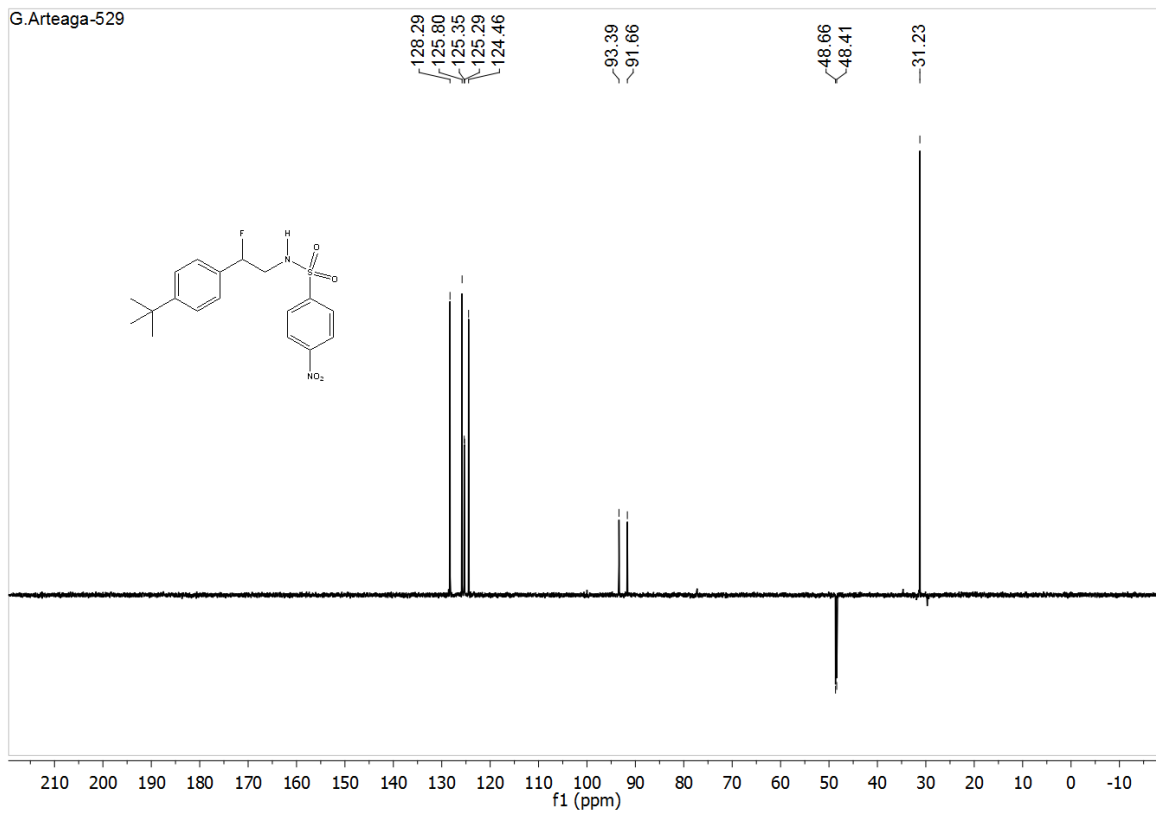




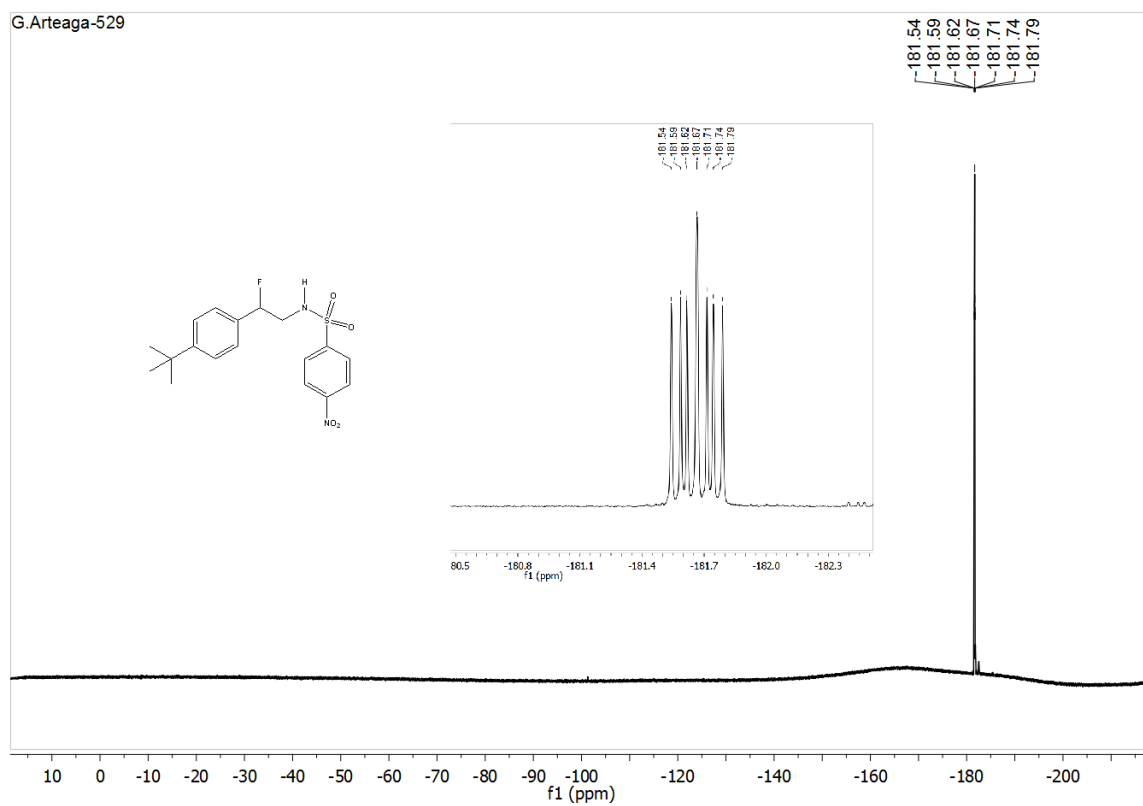


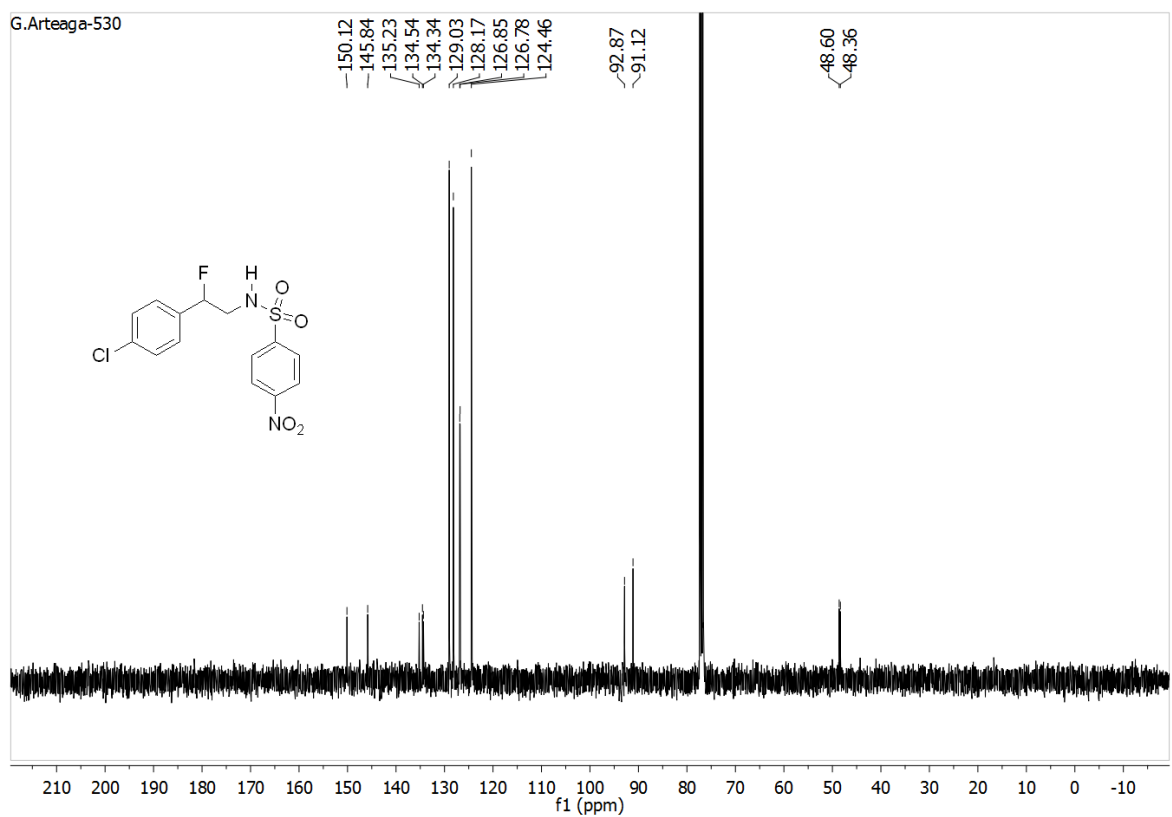
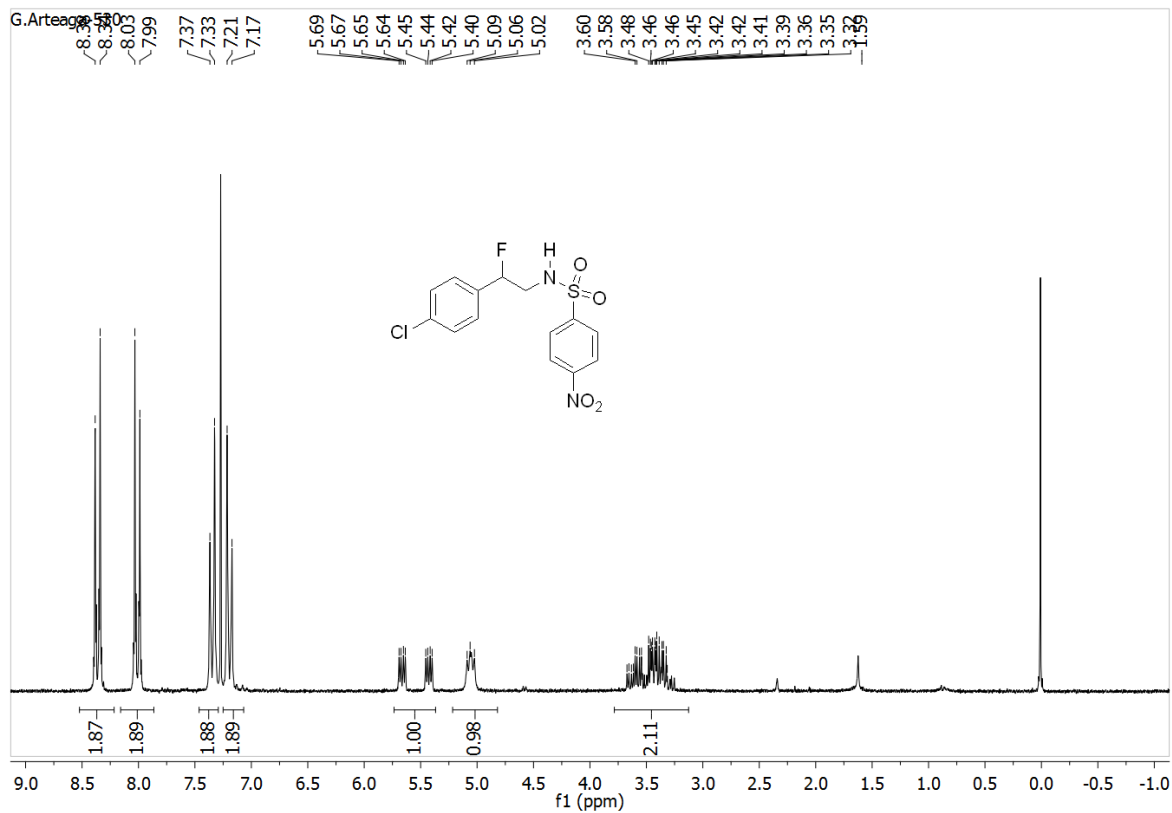


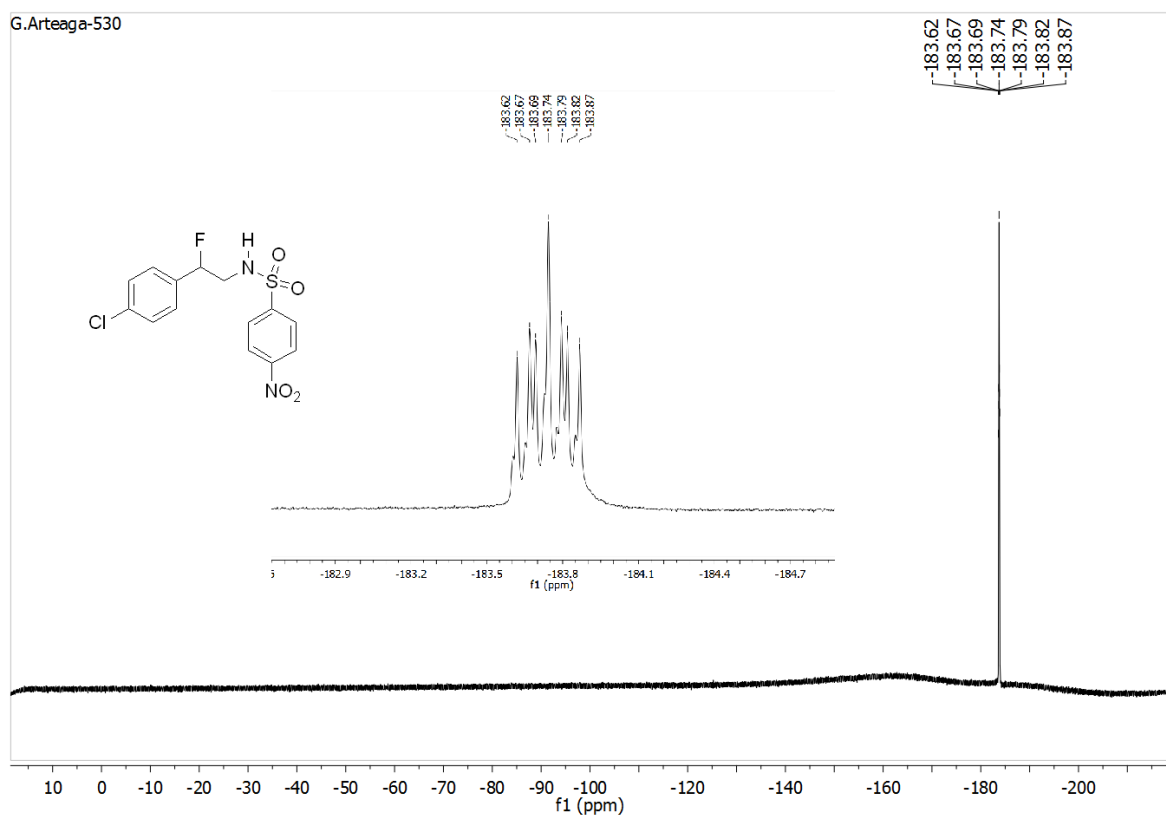
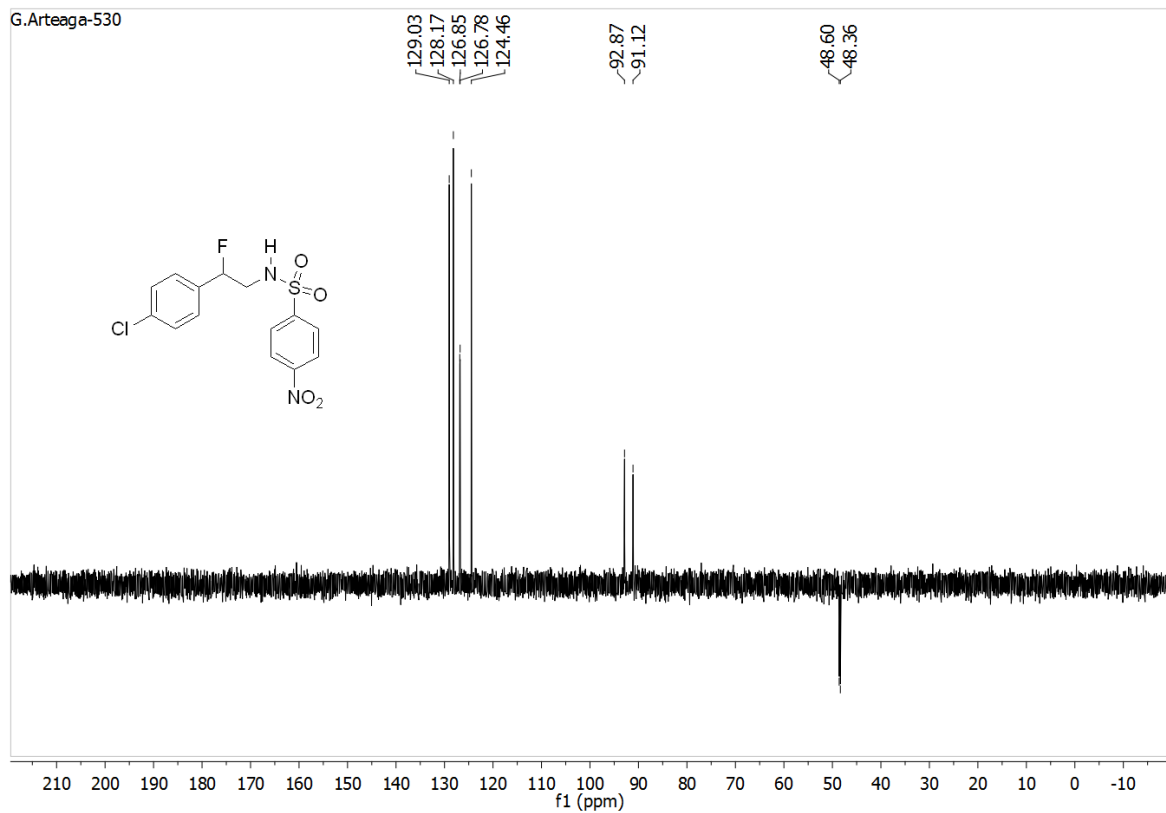
G.Arteaga-529

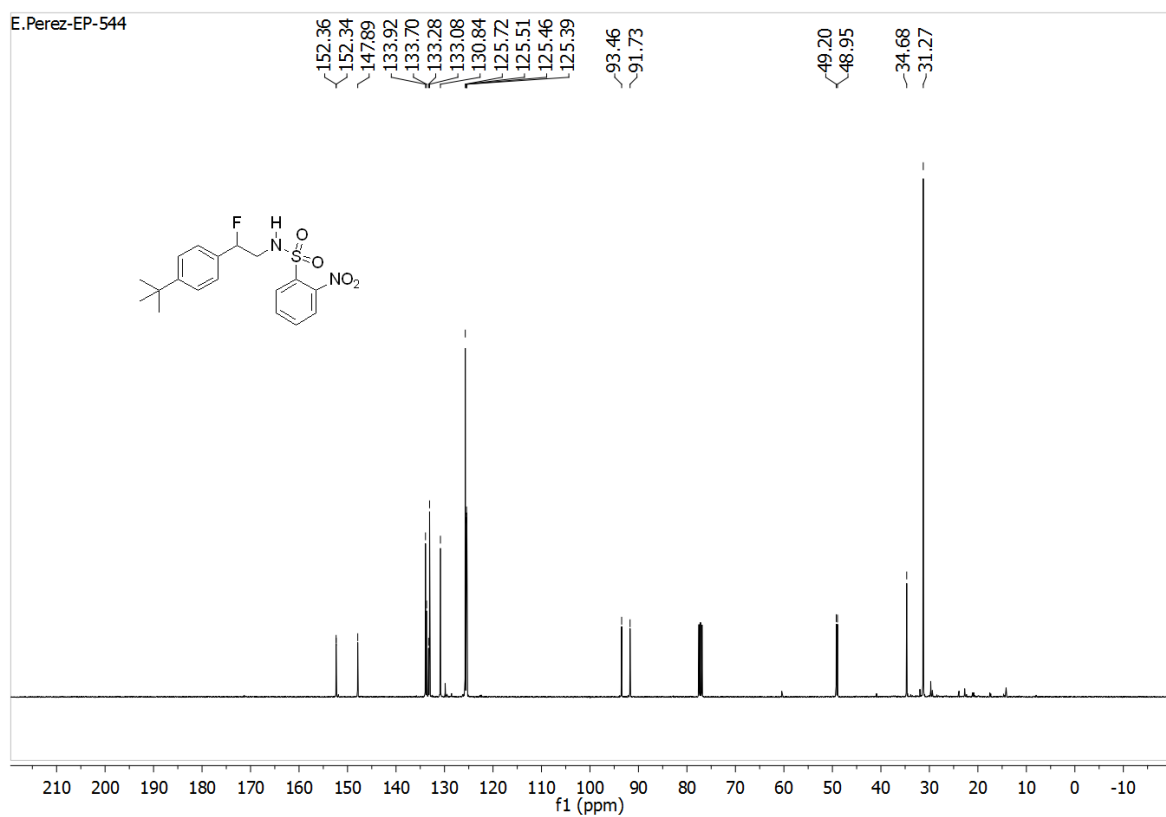
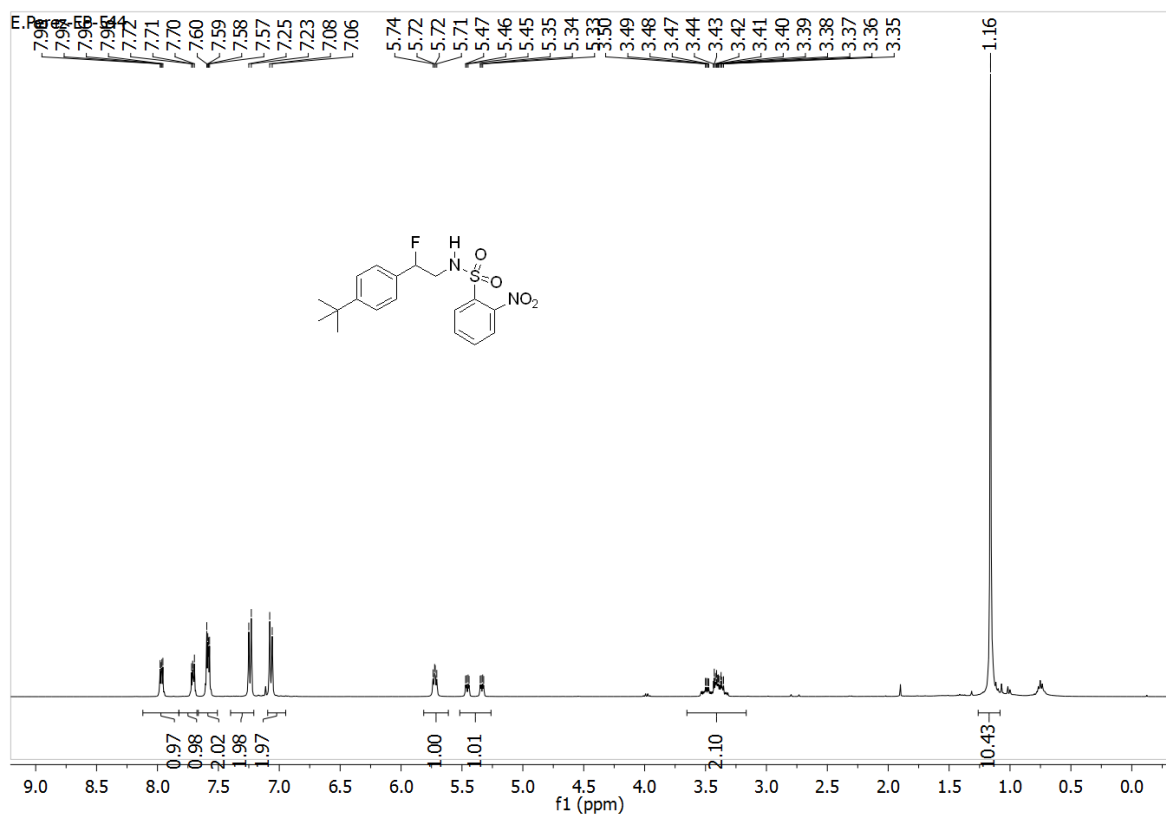


G.Arteaga-529

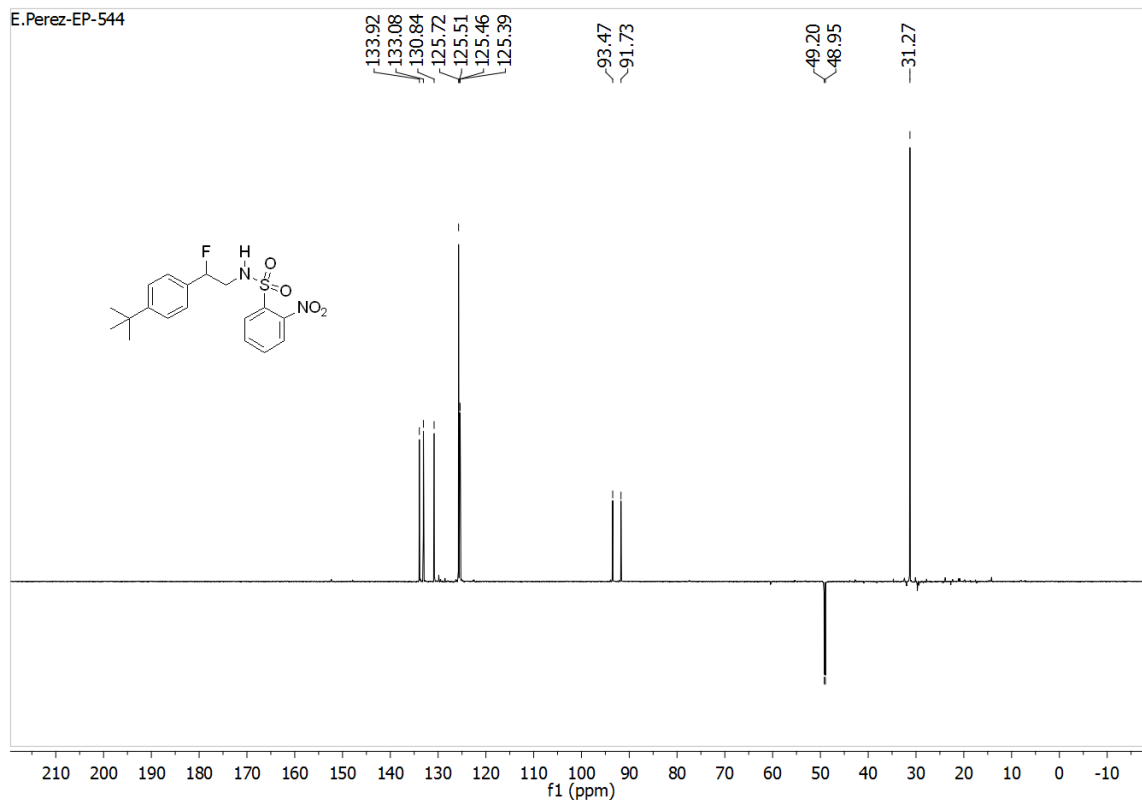




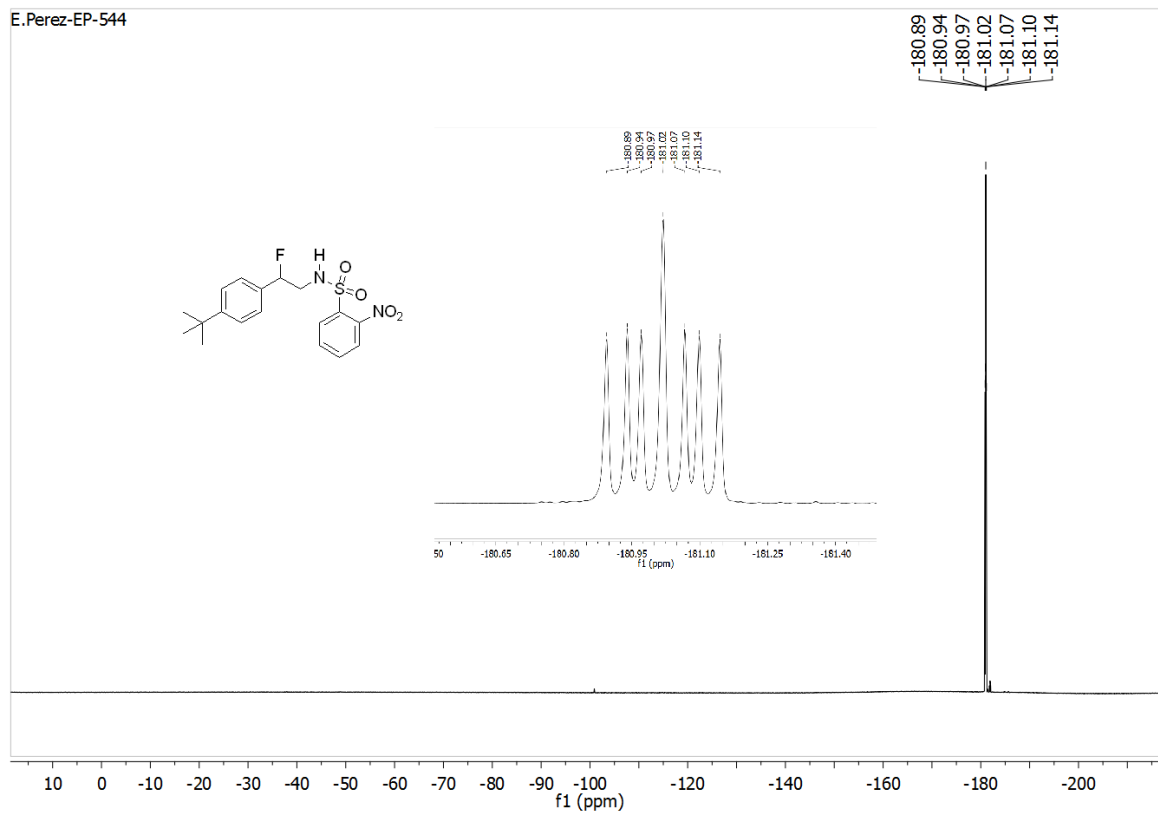


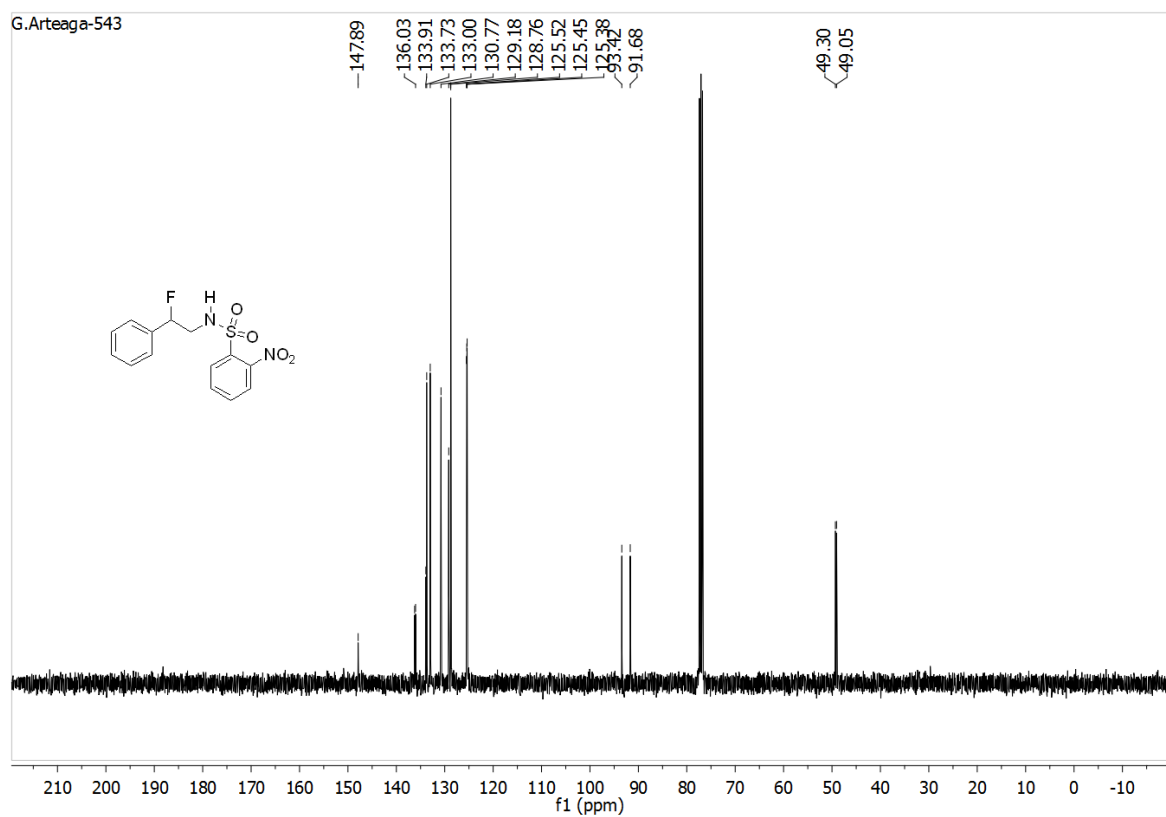
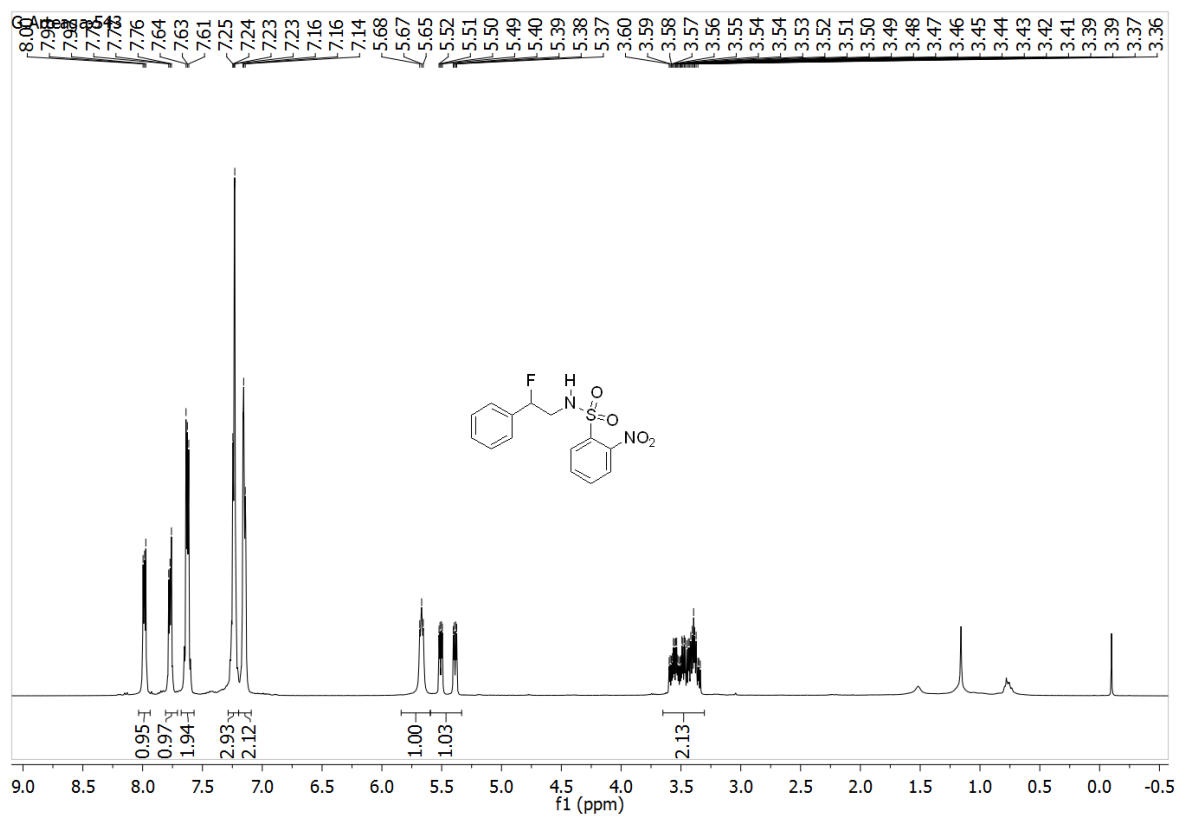


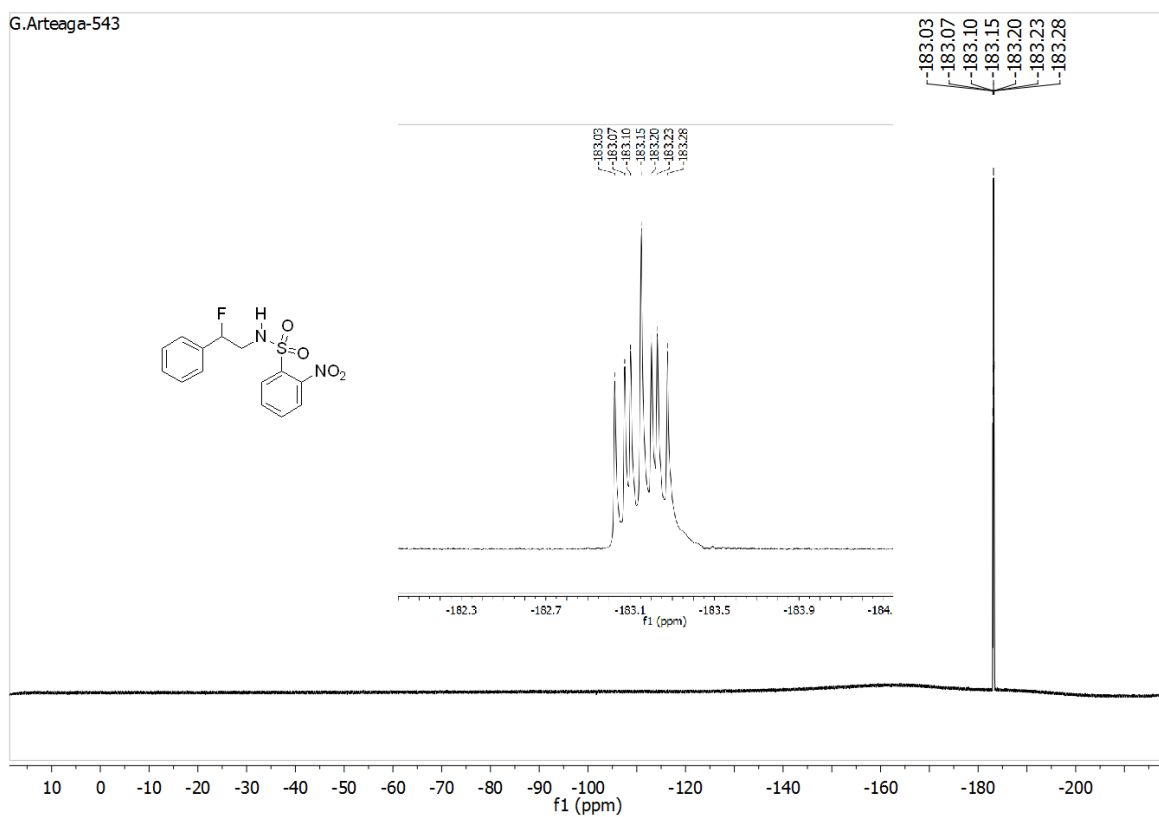
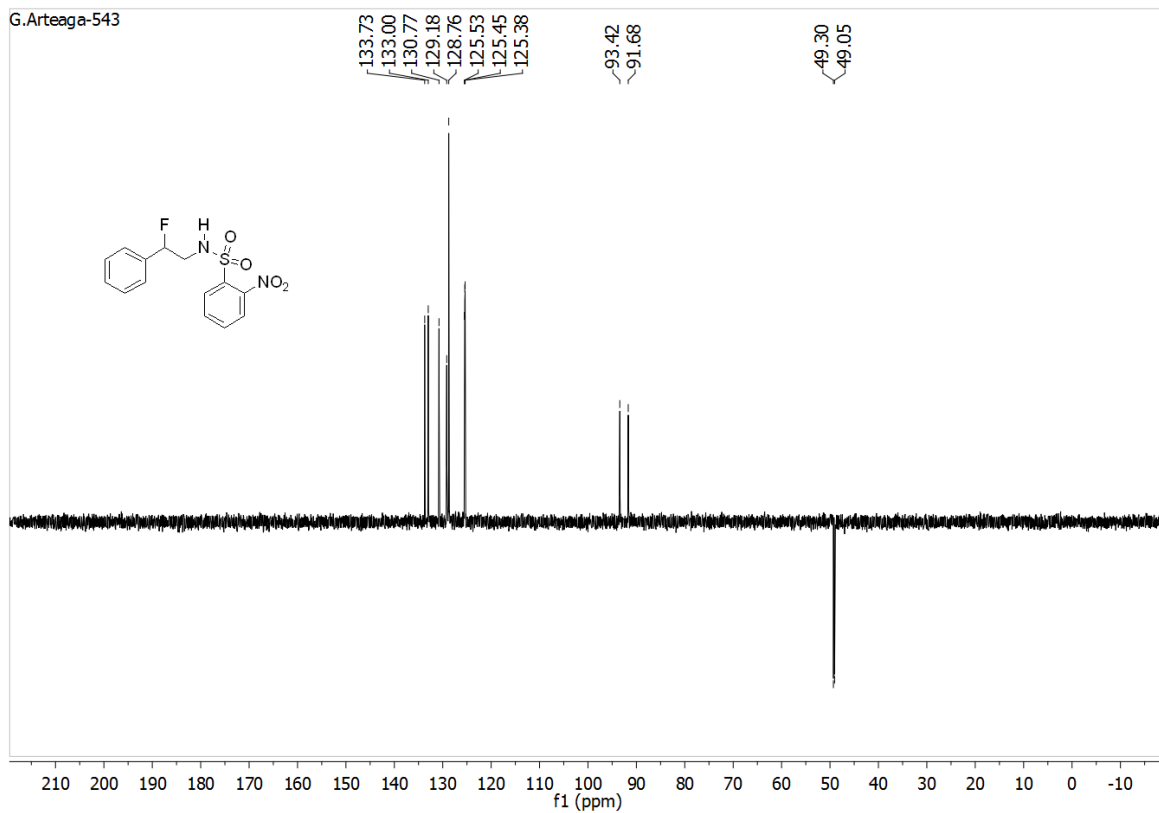
E.Perez-EP-544

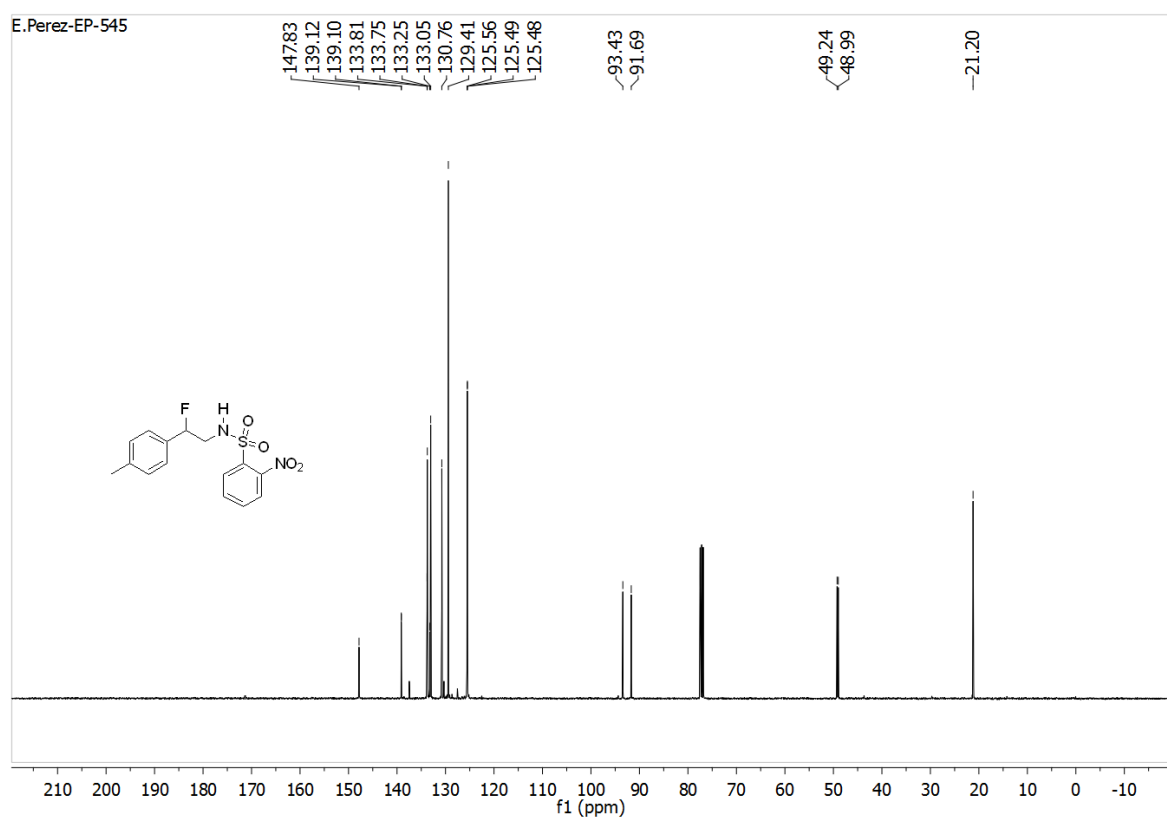
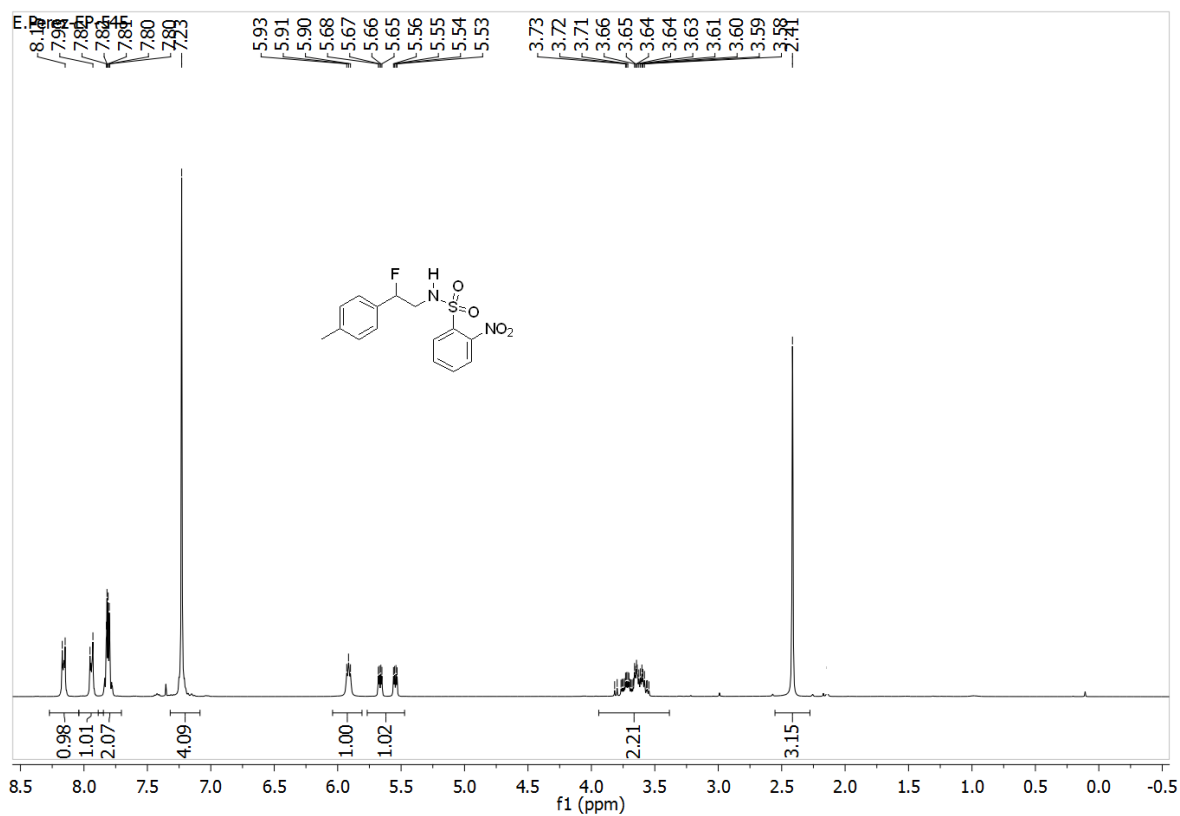


E.Perez-EP-544

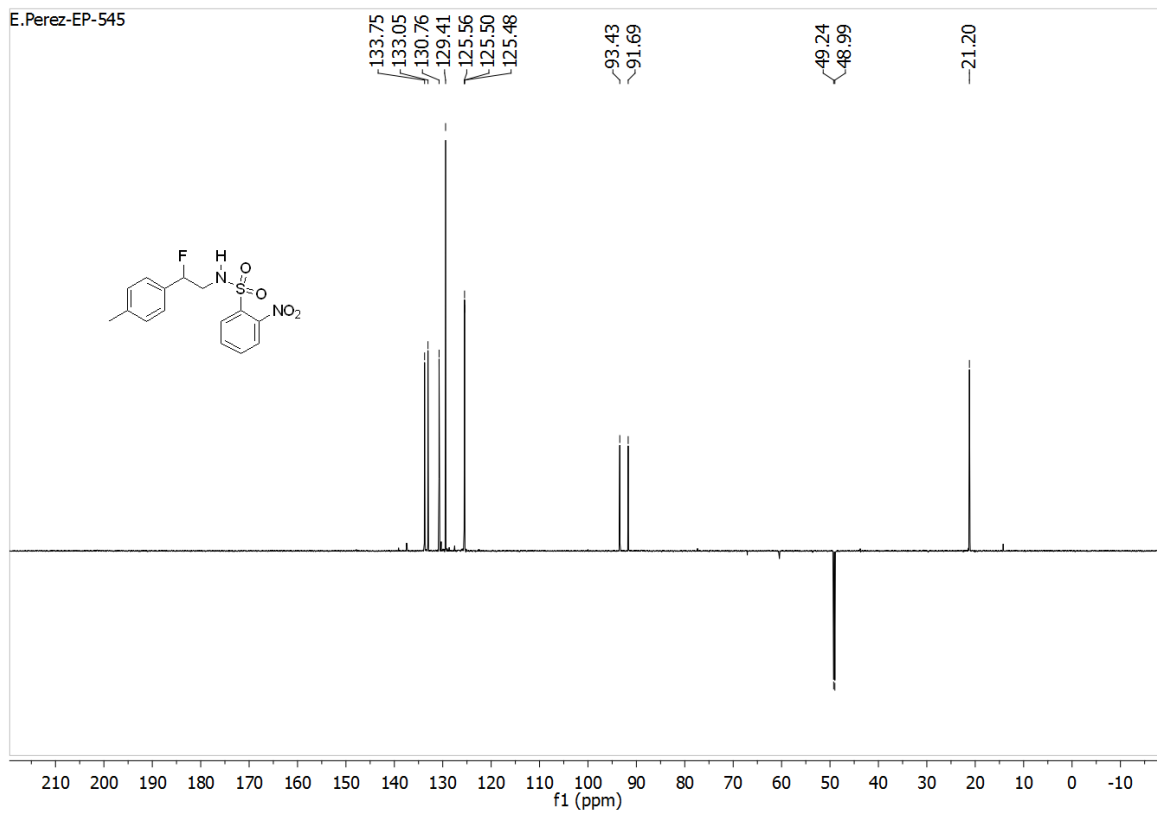




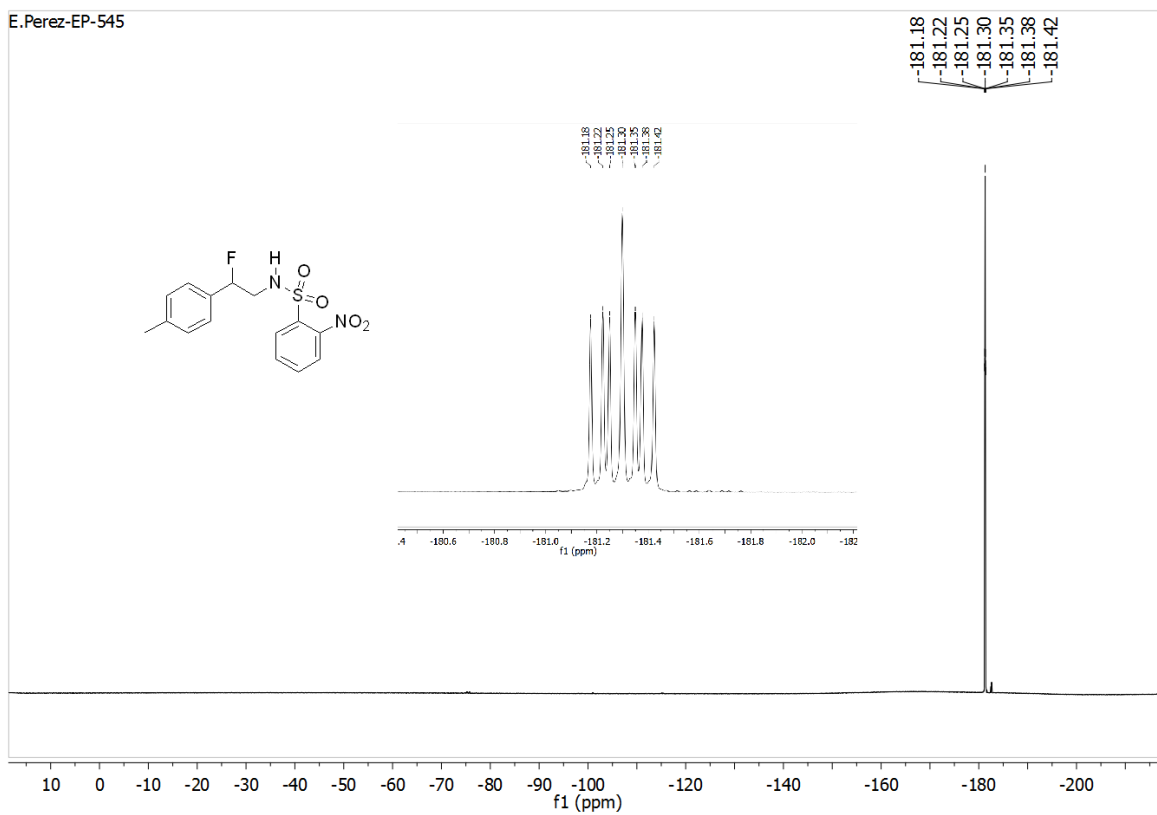


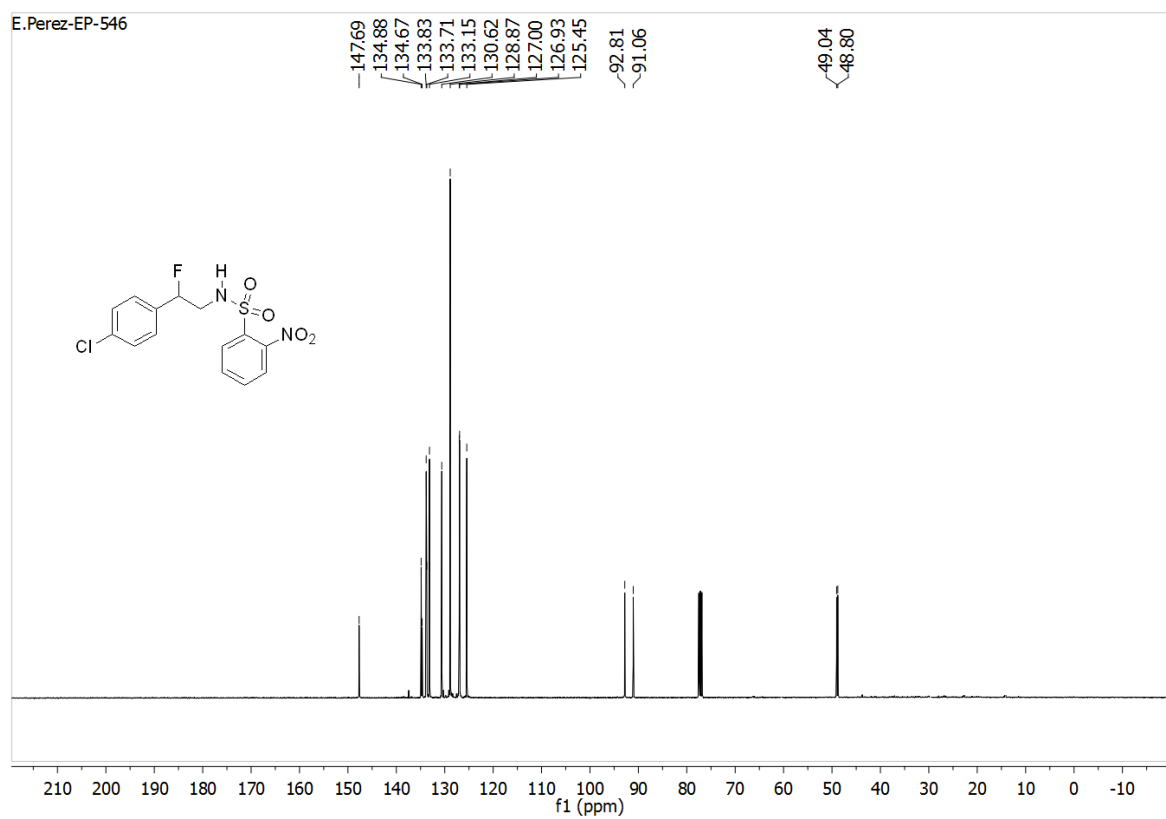
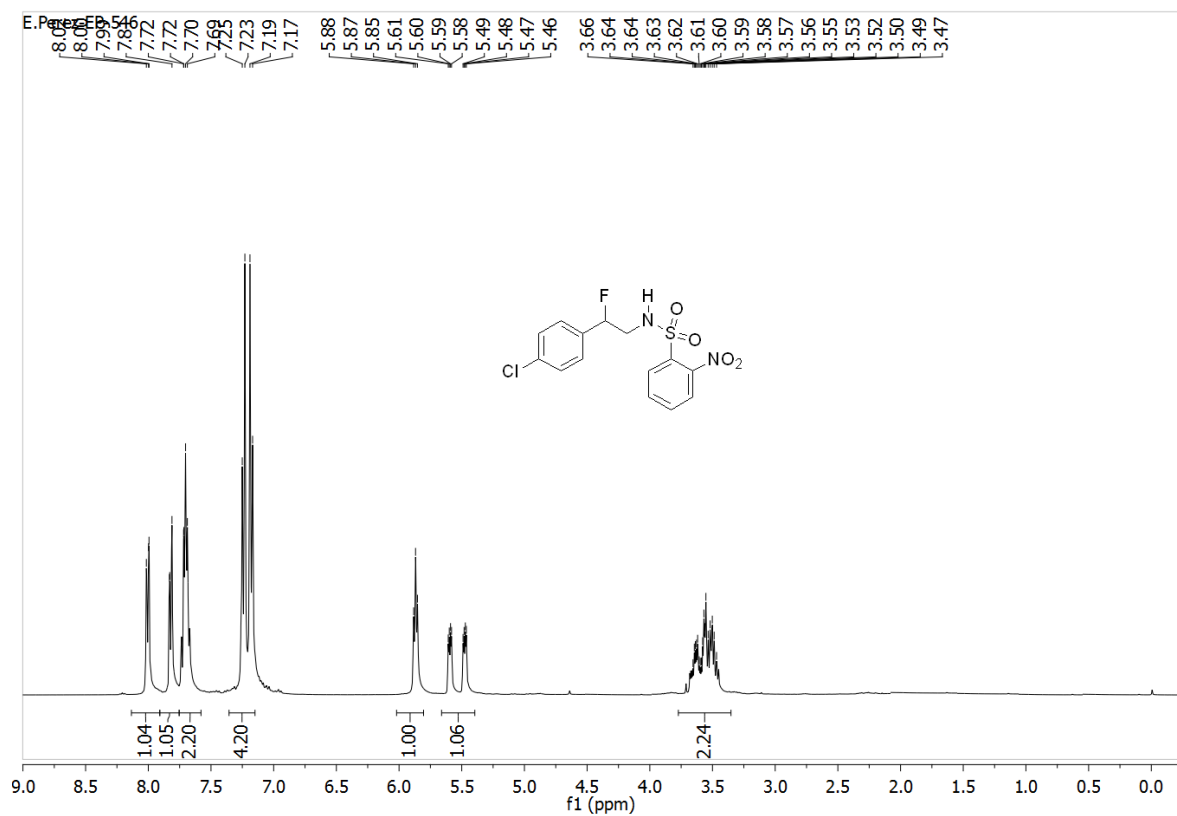


E.Perez-EP-545

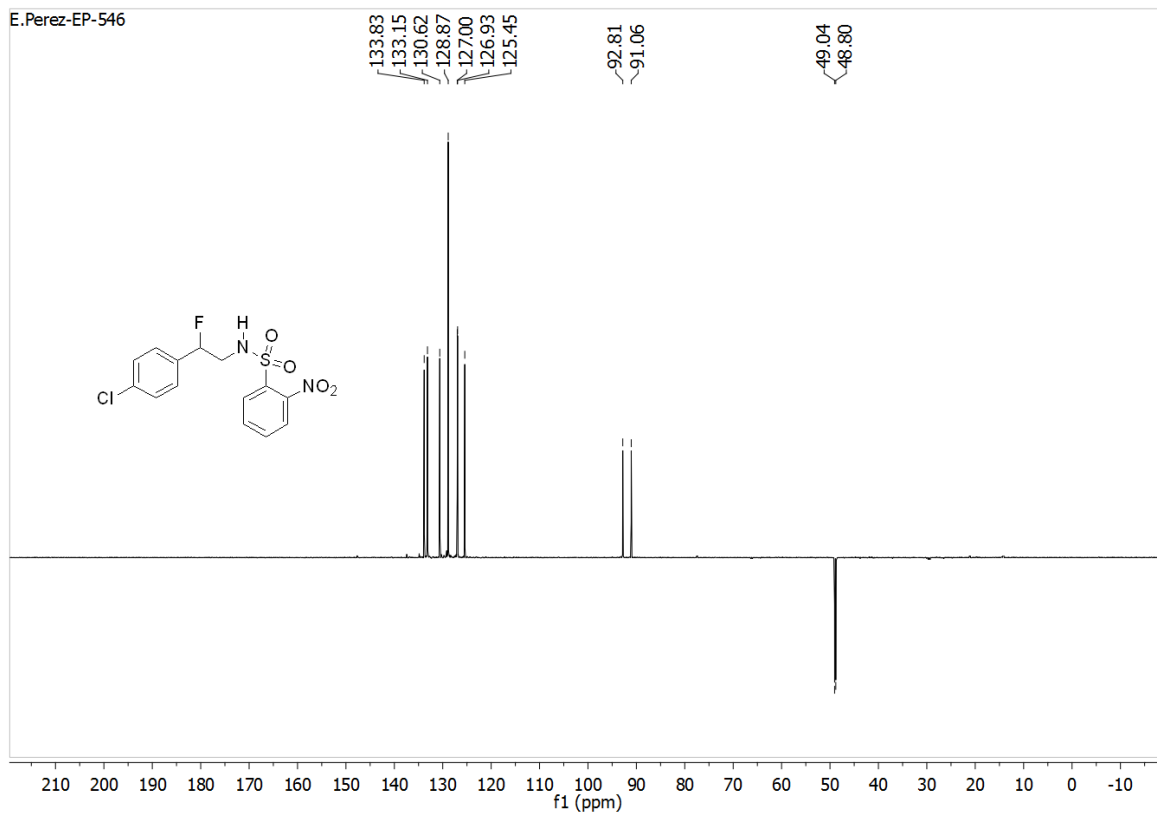


E.Perez-EP-545

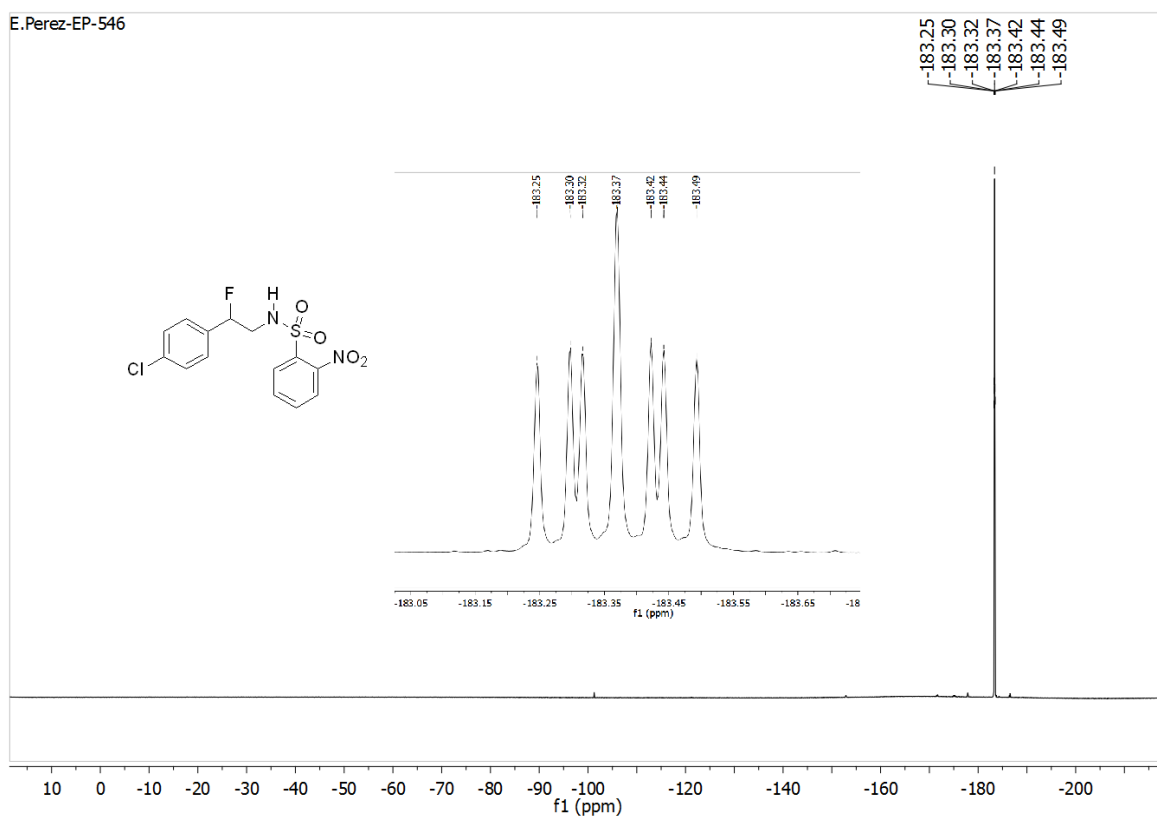


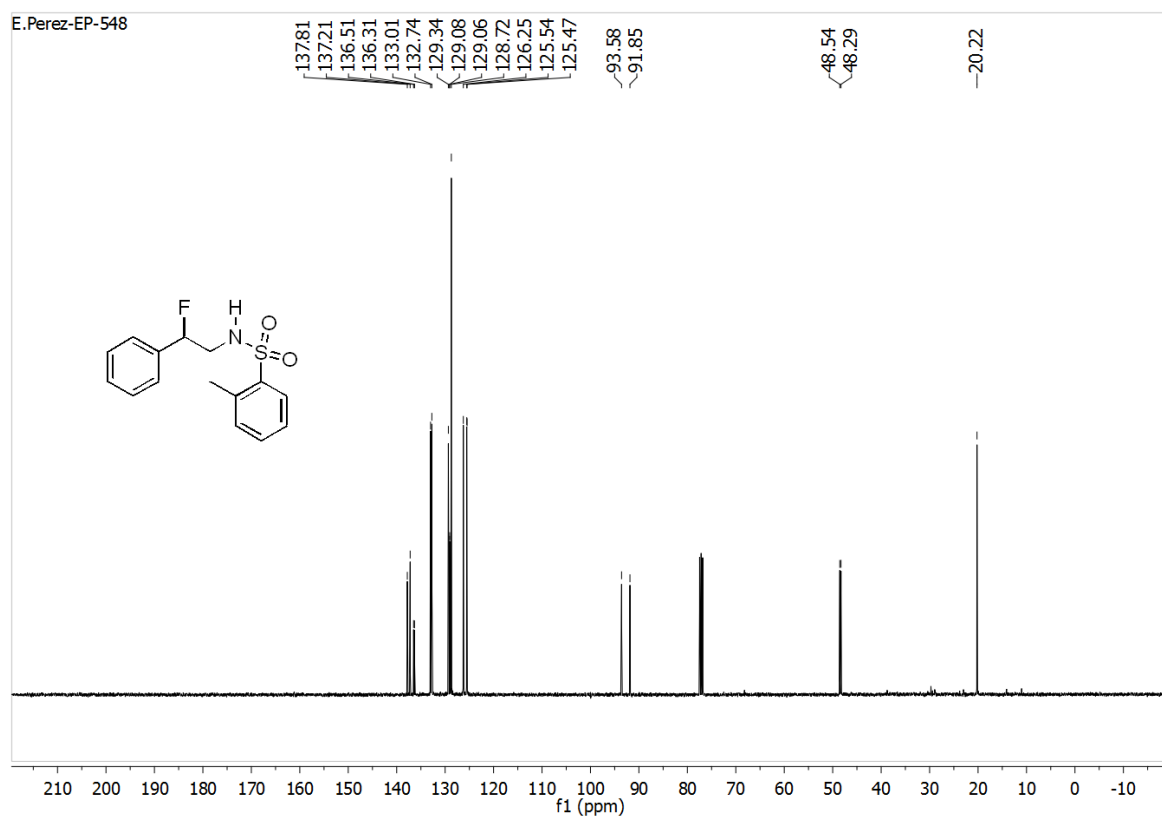
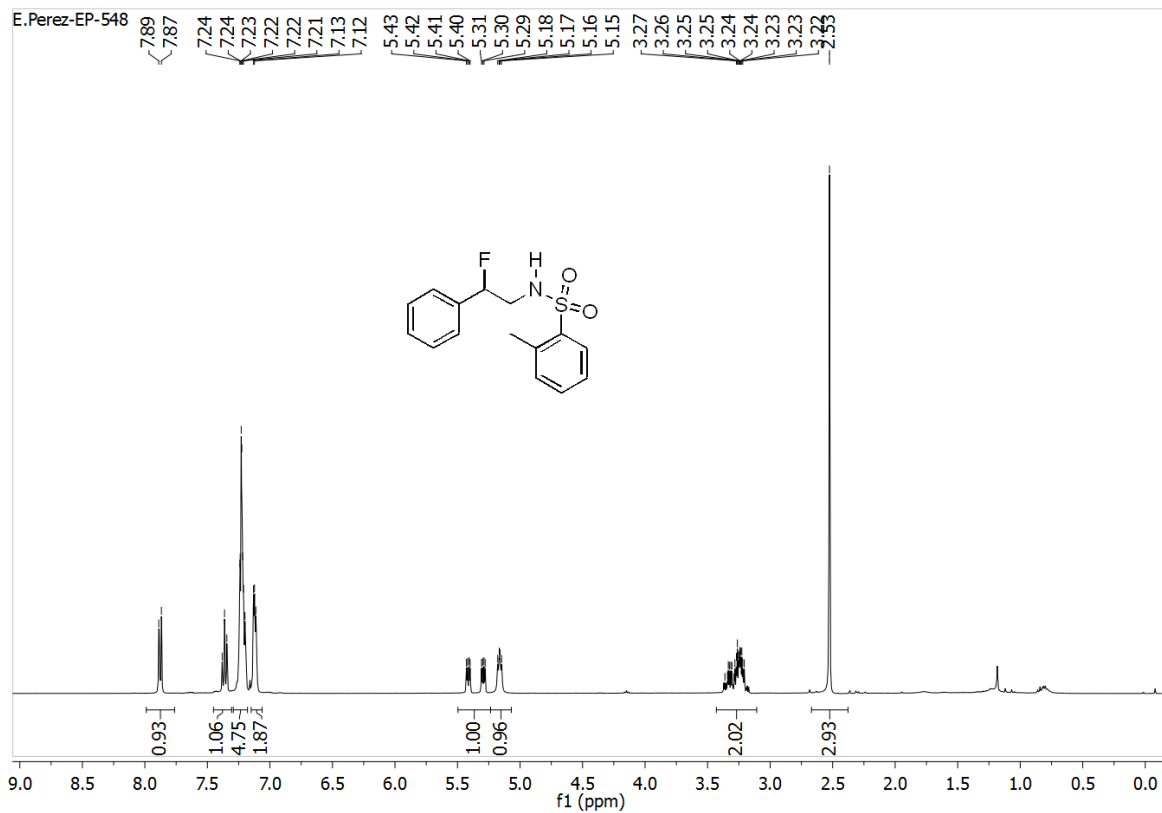


E.Perez-EP-546

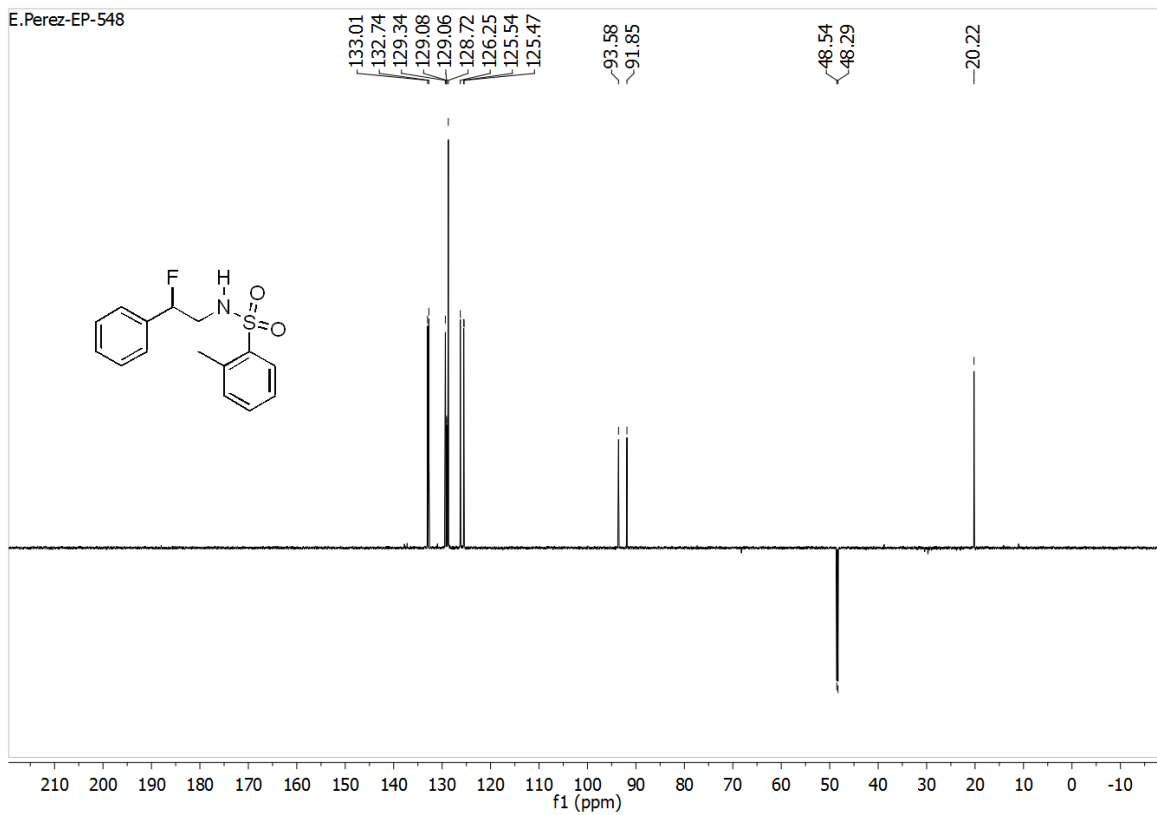


E.Perez-EP-546

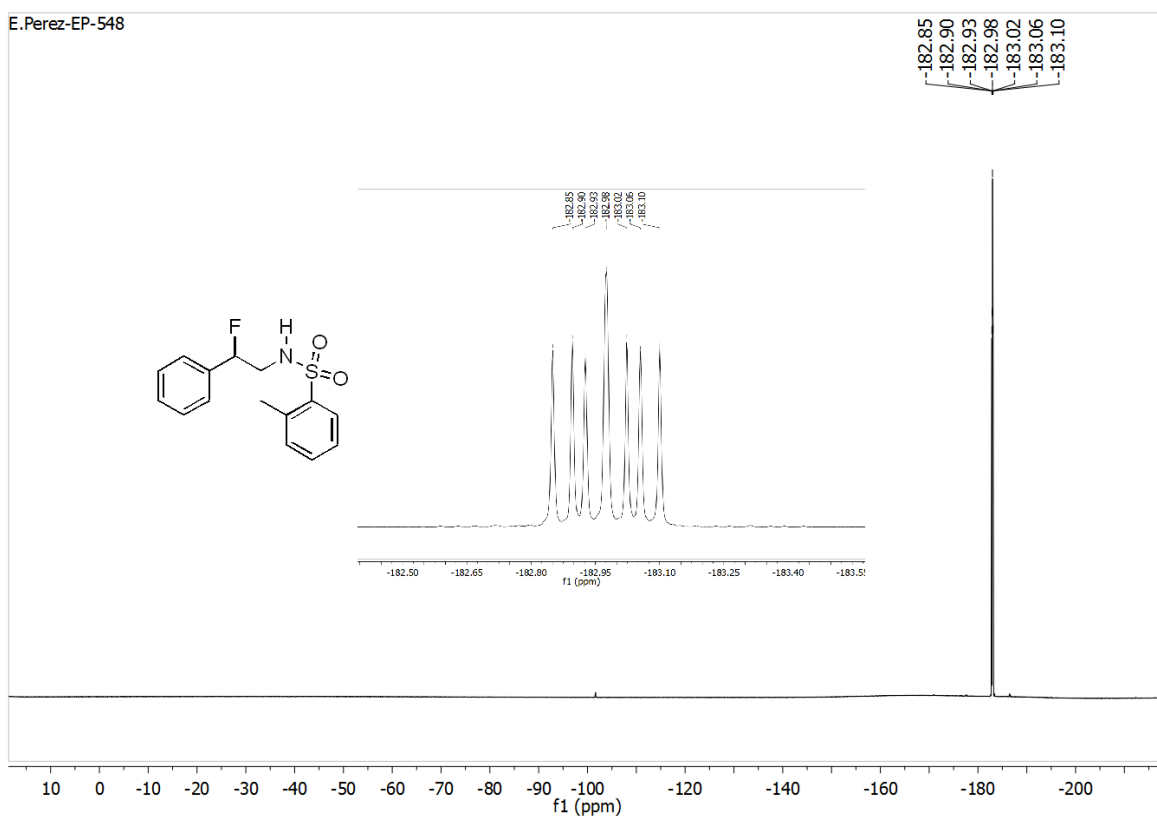


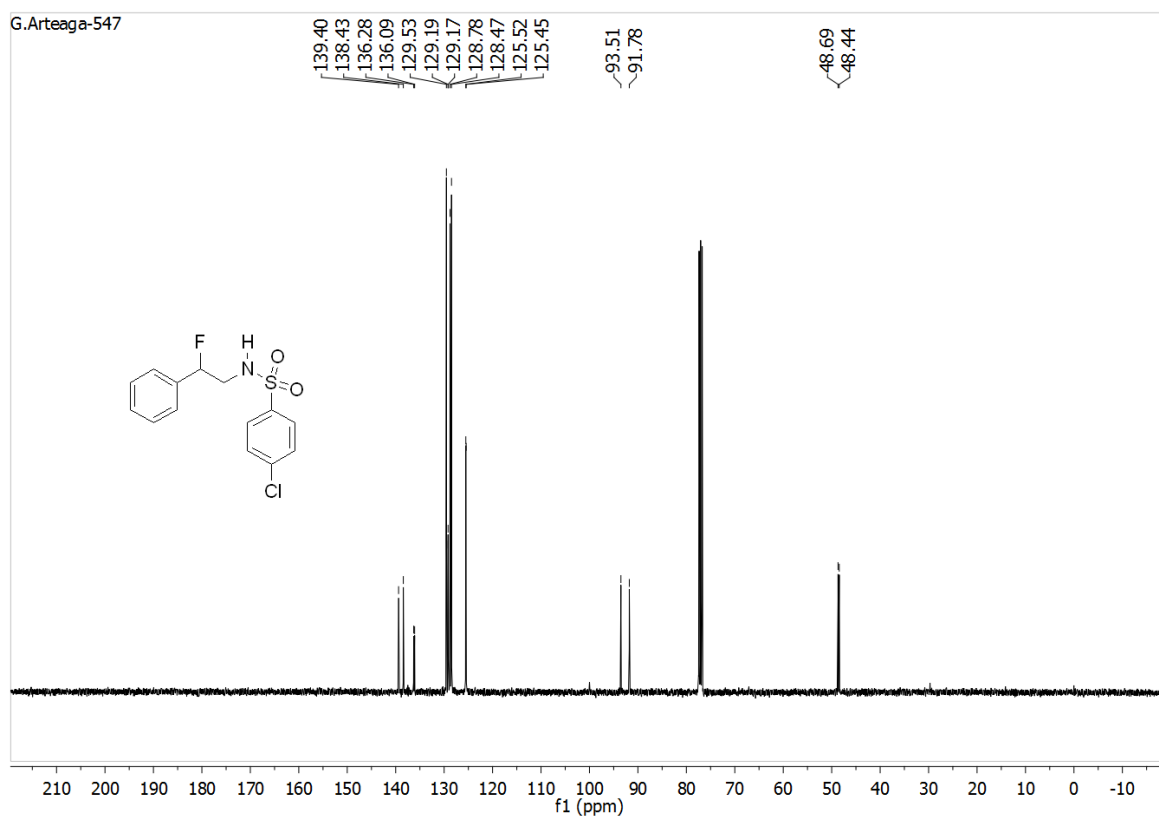
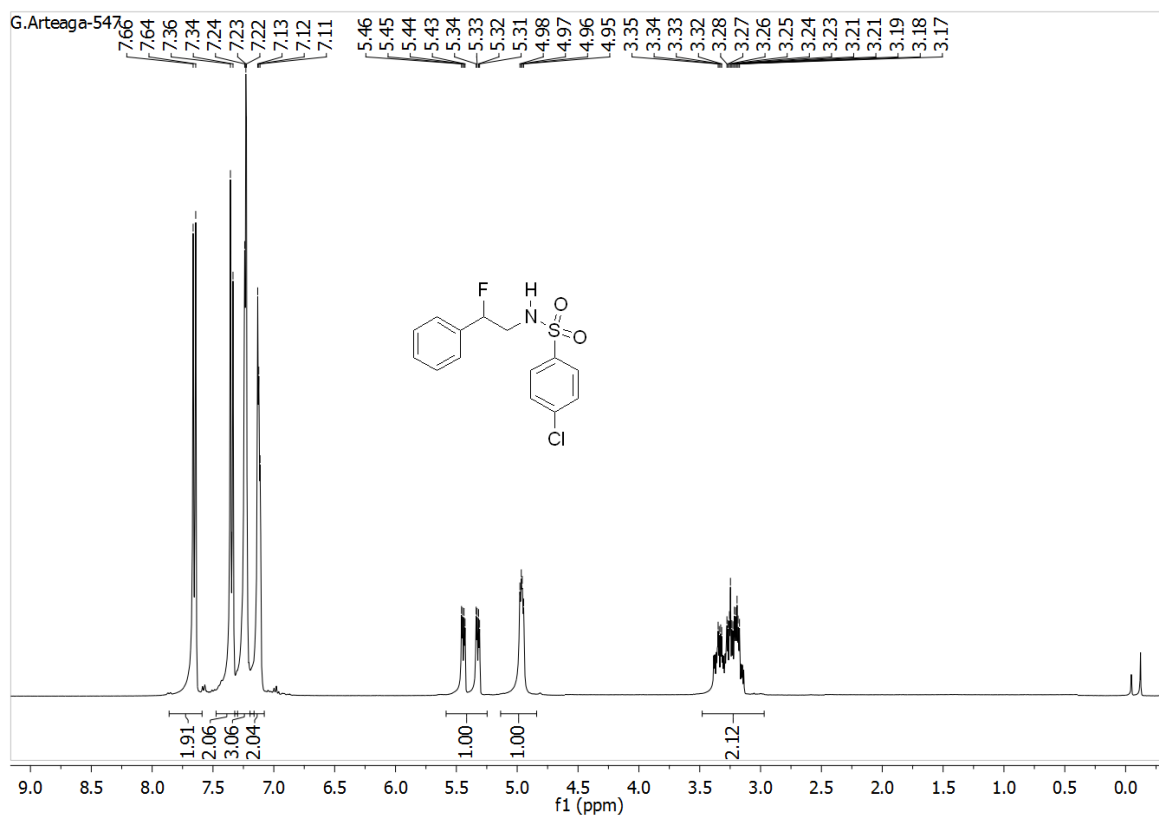


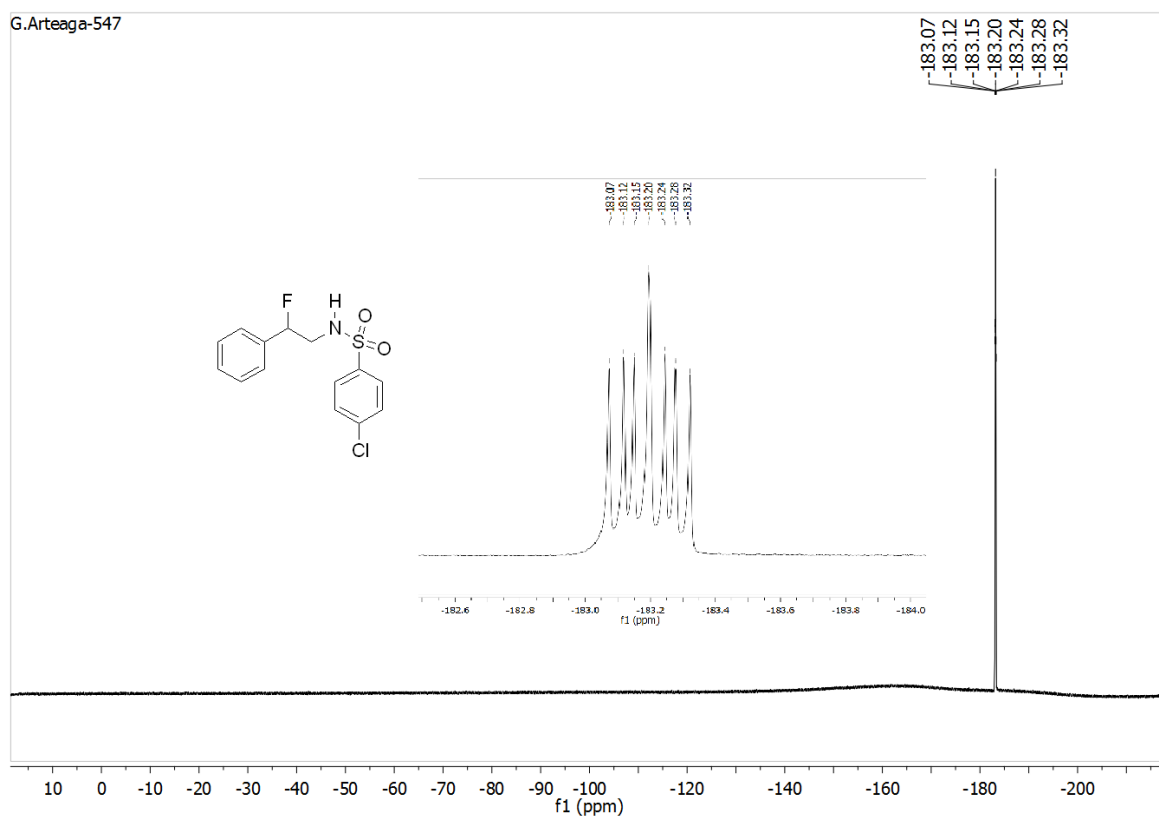
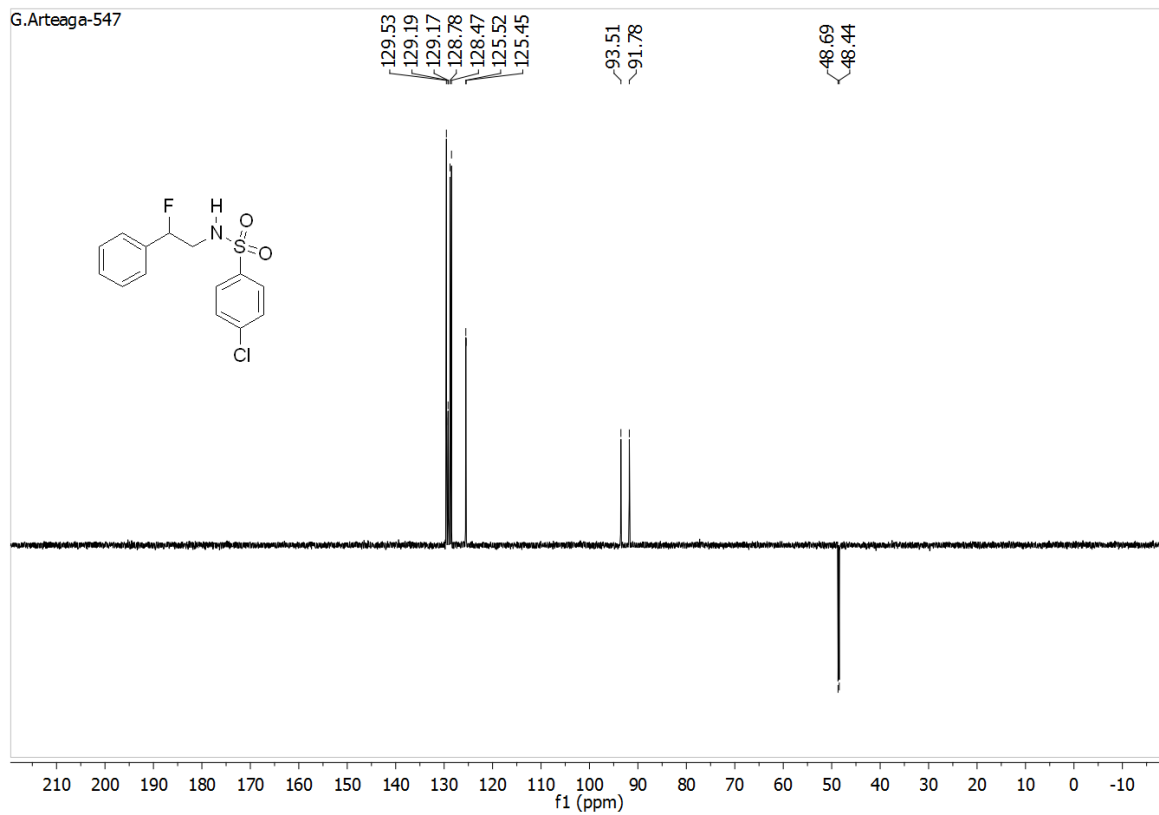
E.Perez-EP-548

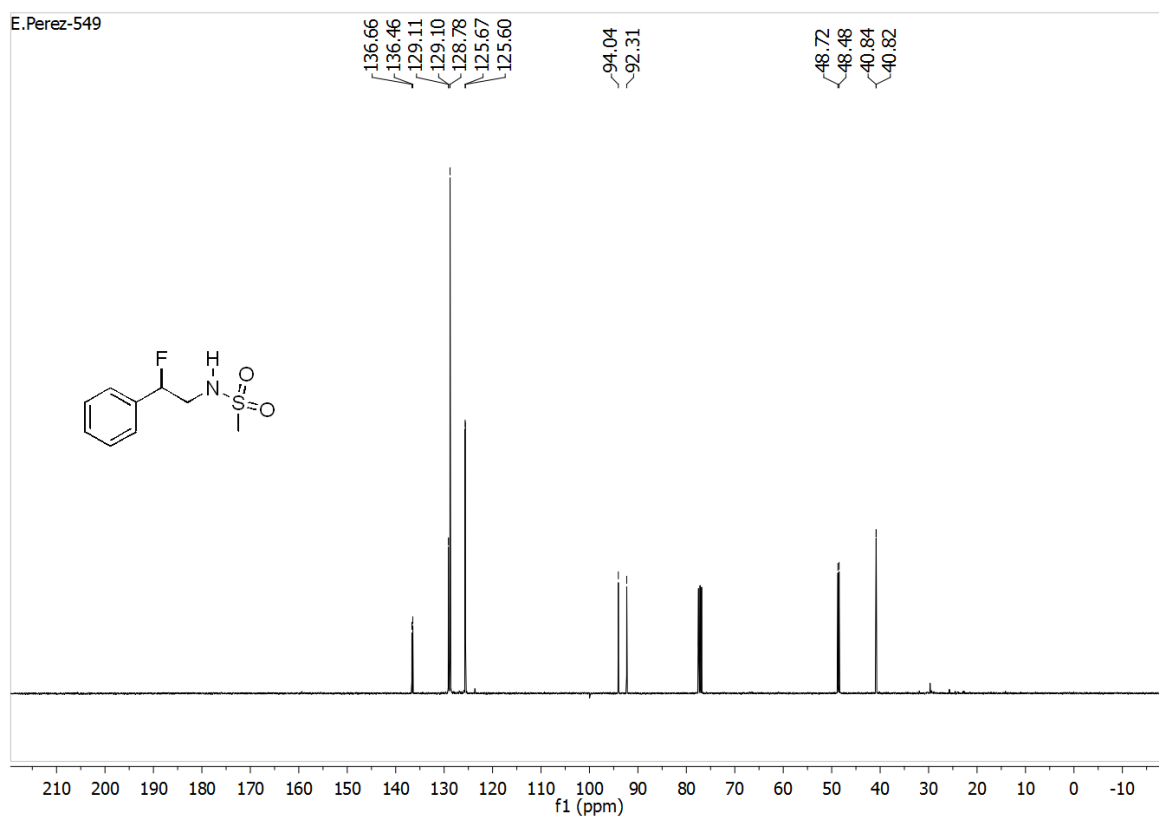
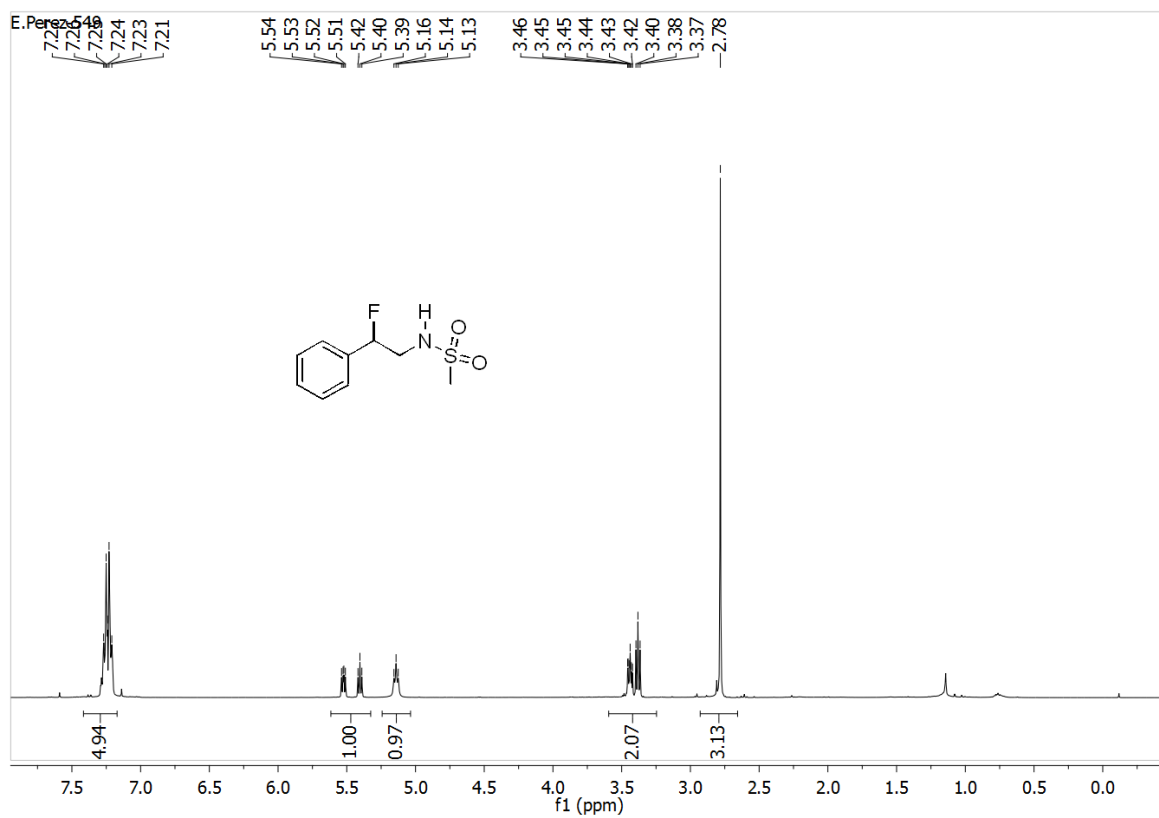


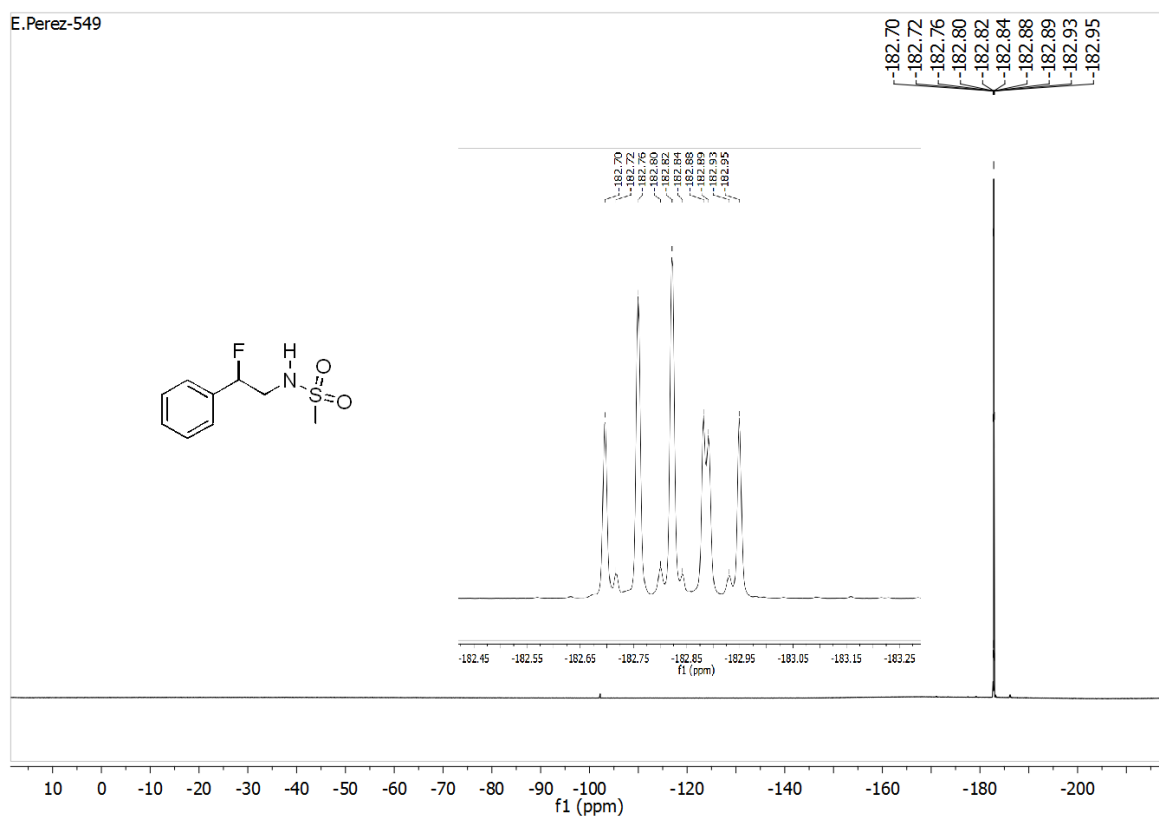
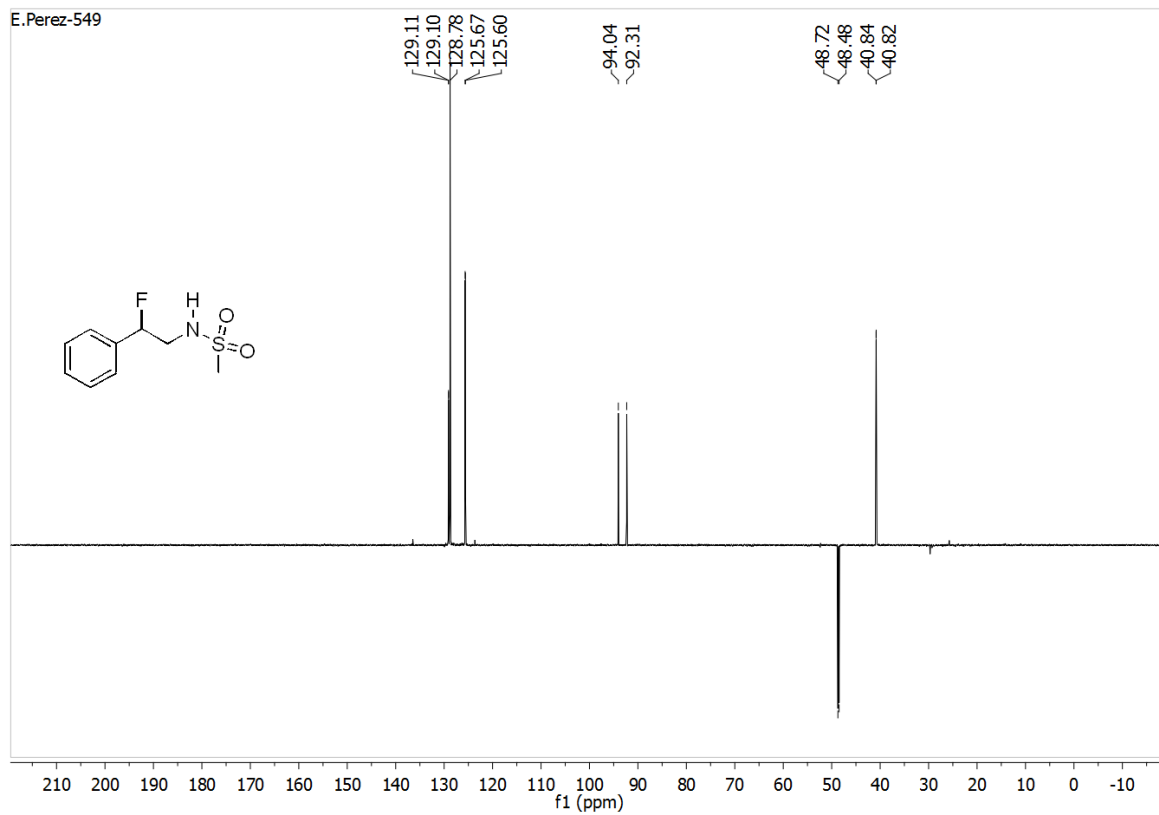
E.Perez-EP-548

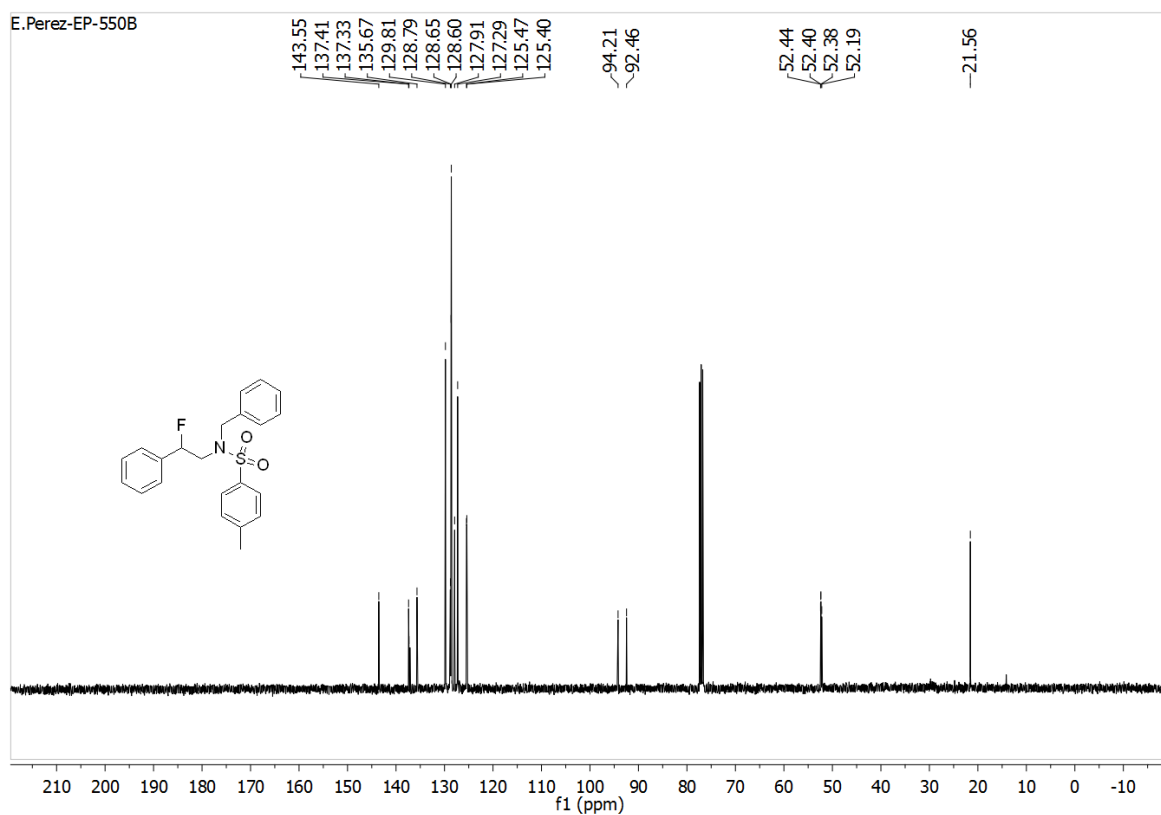
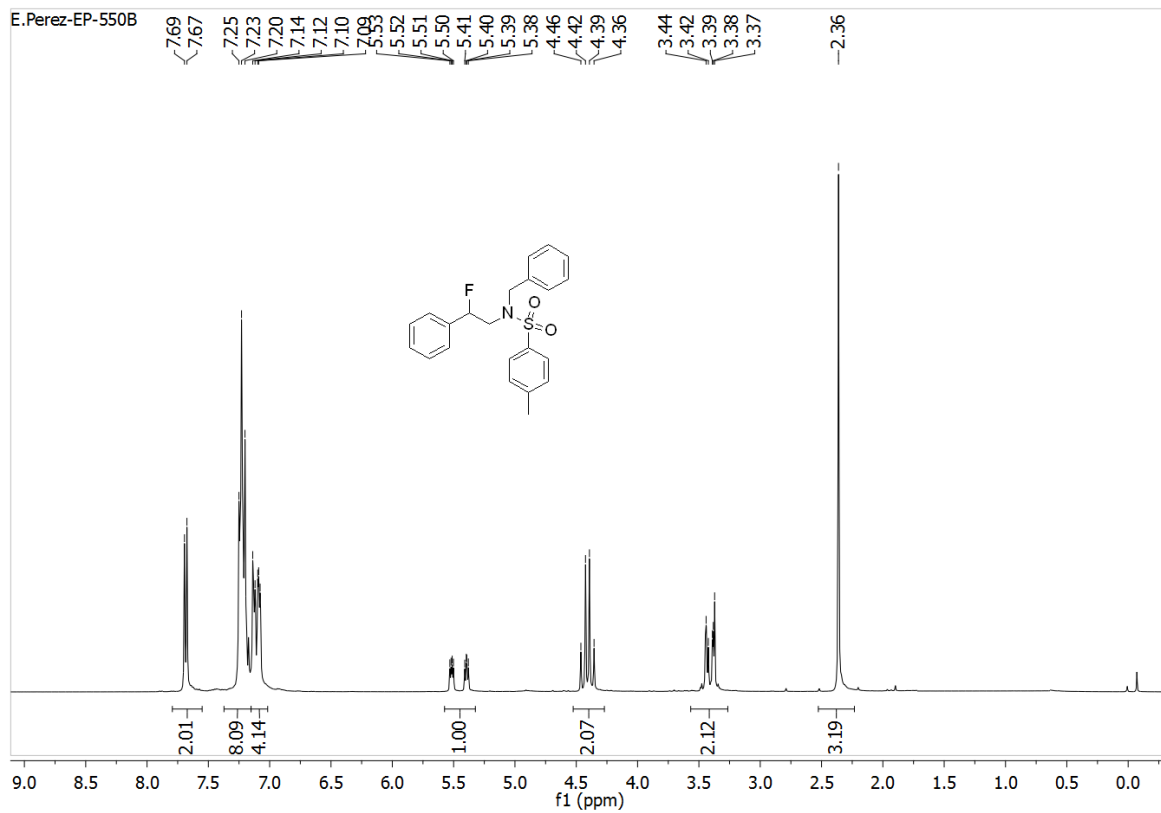




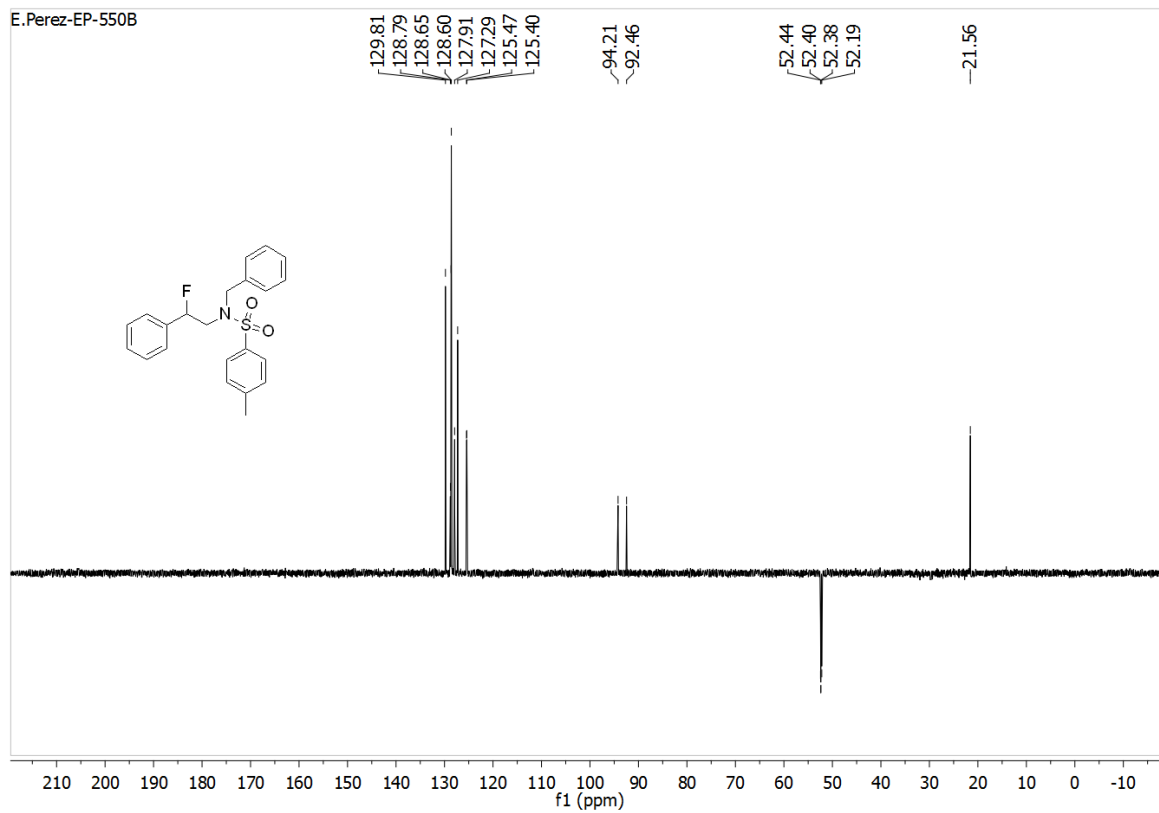




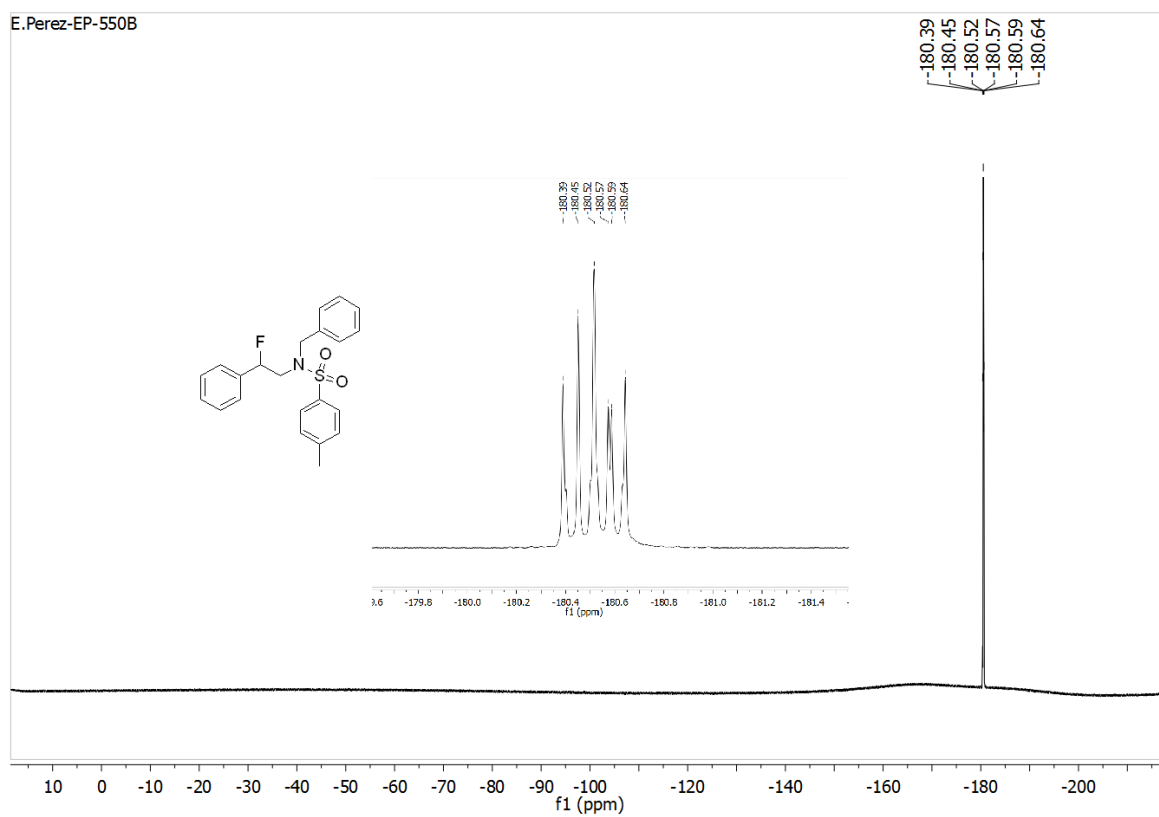


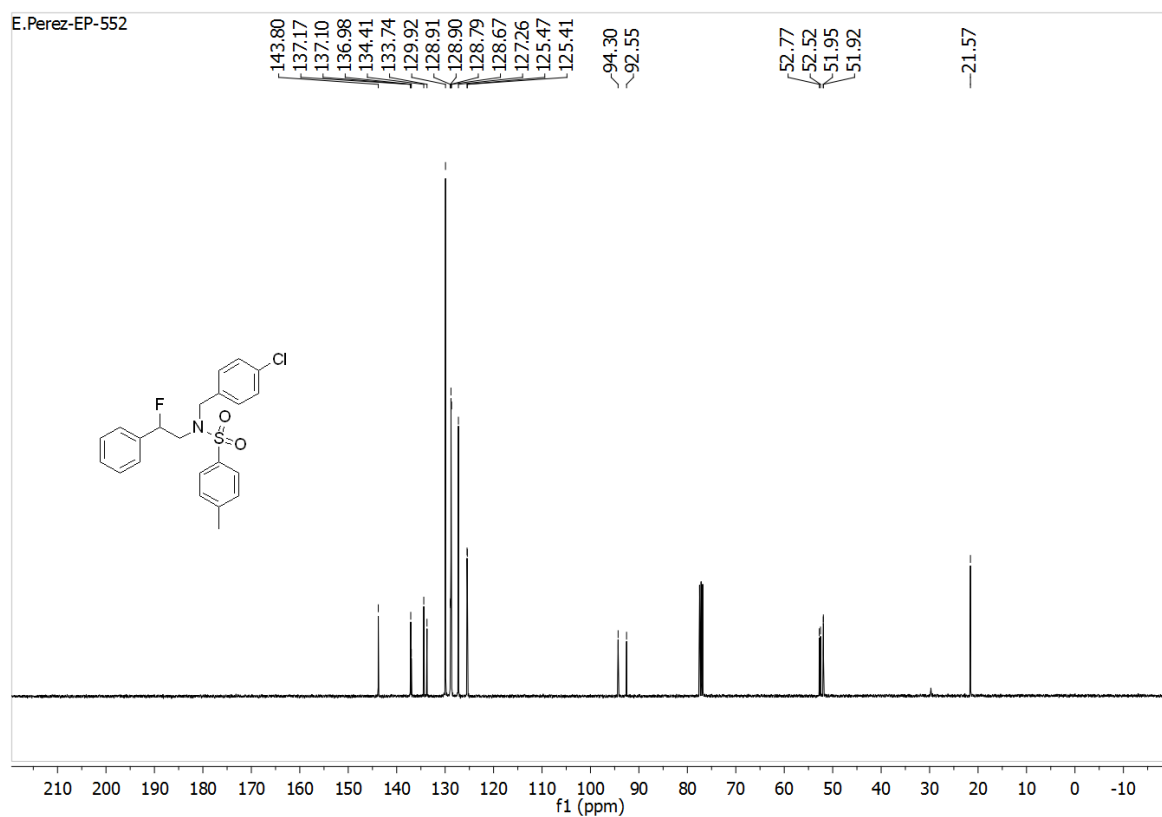
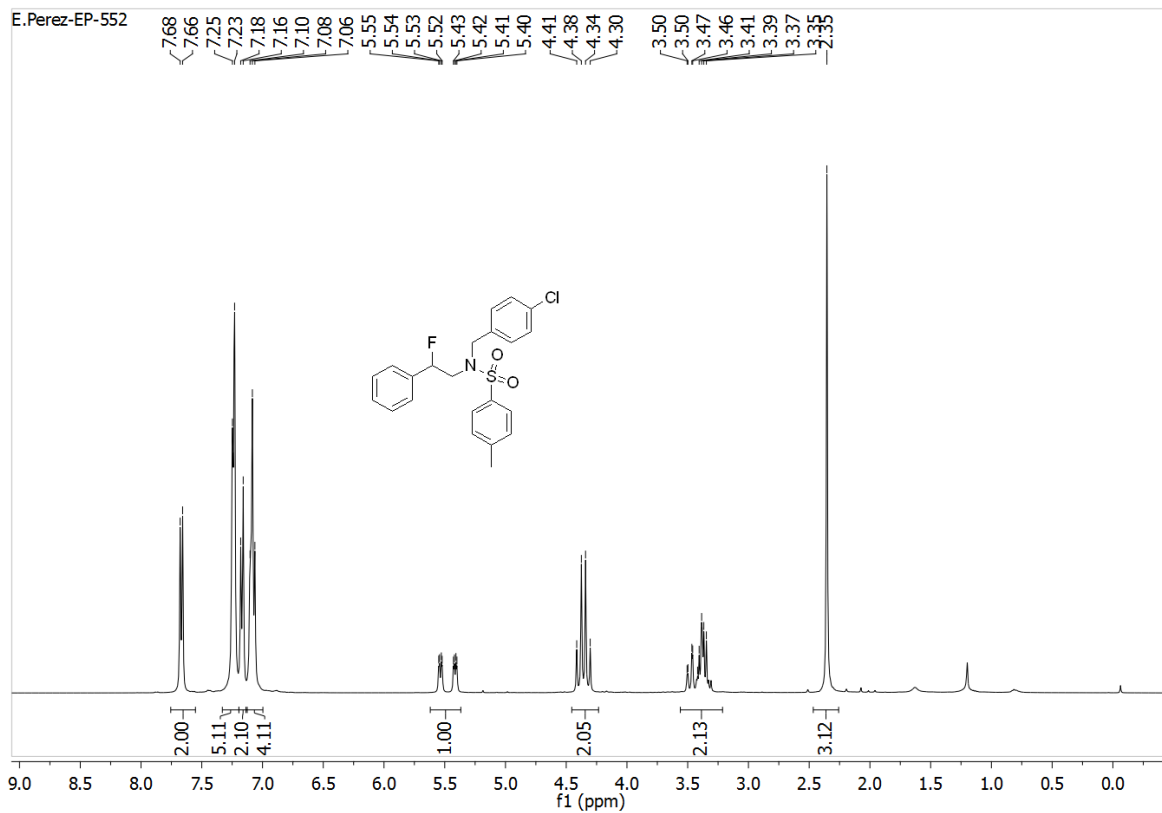


E.Perez-EP-550B

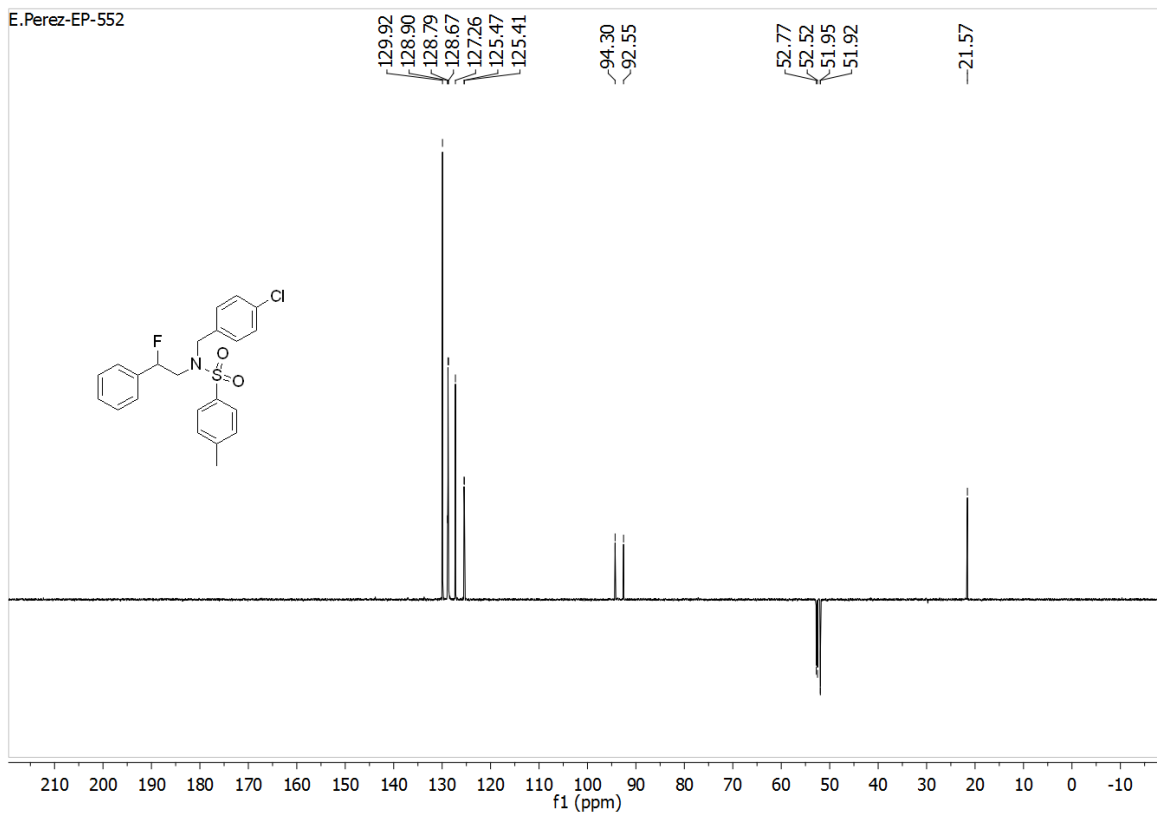


E.Perez-EP-550B

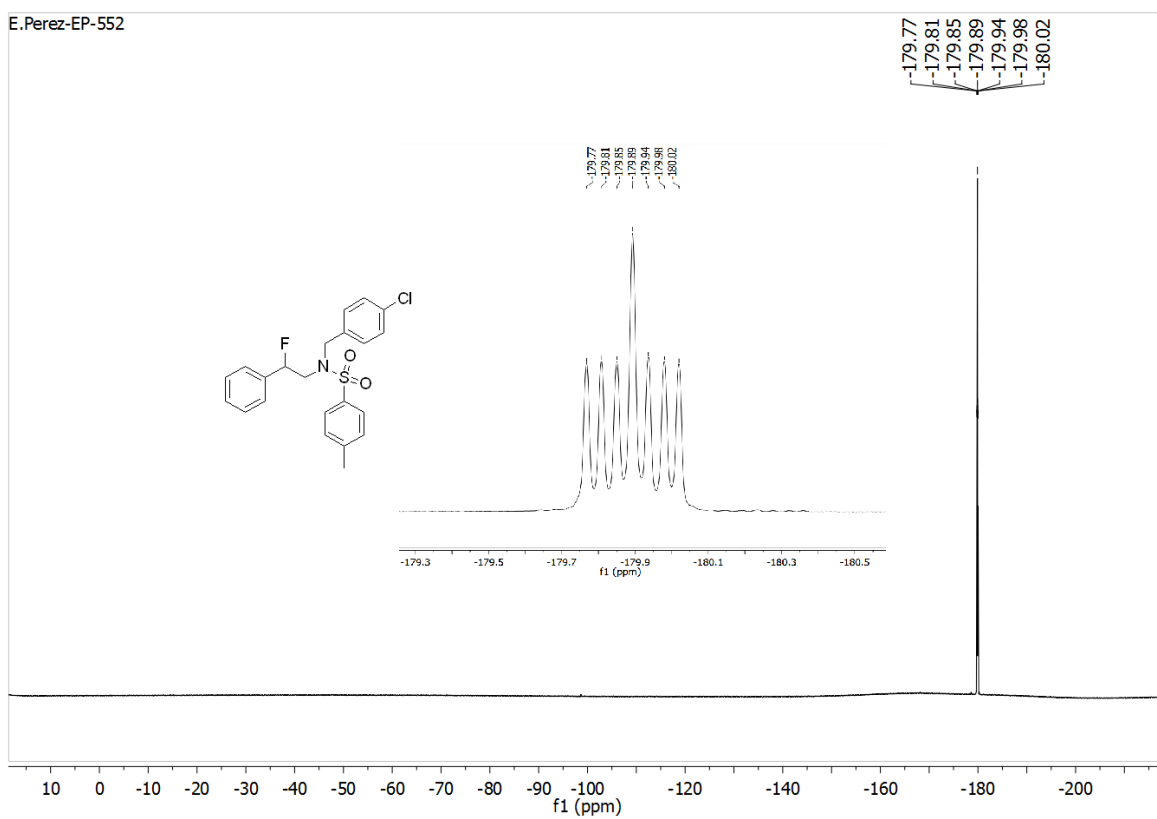


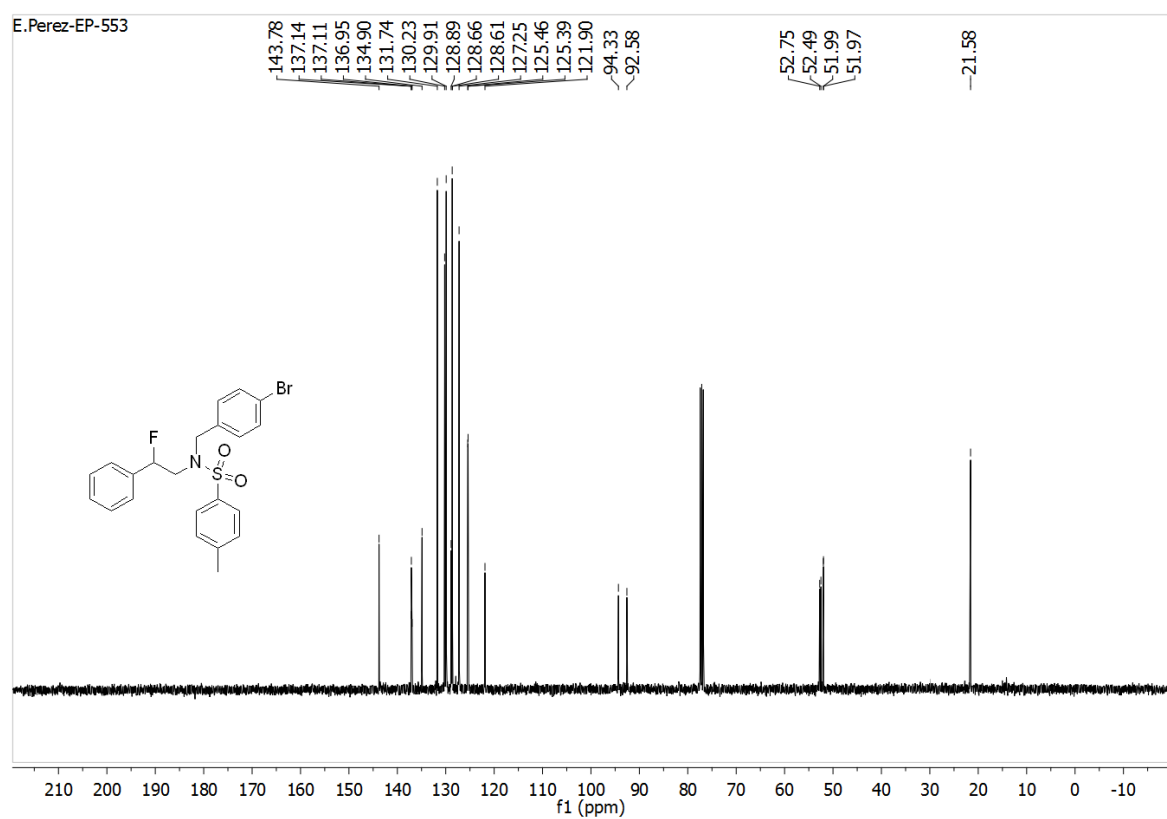
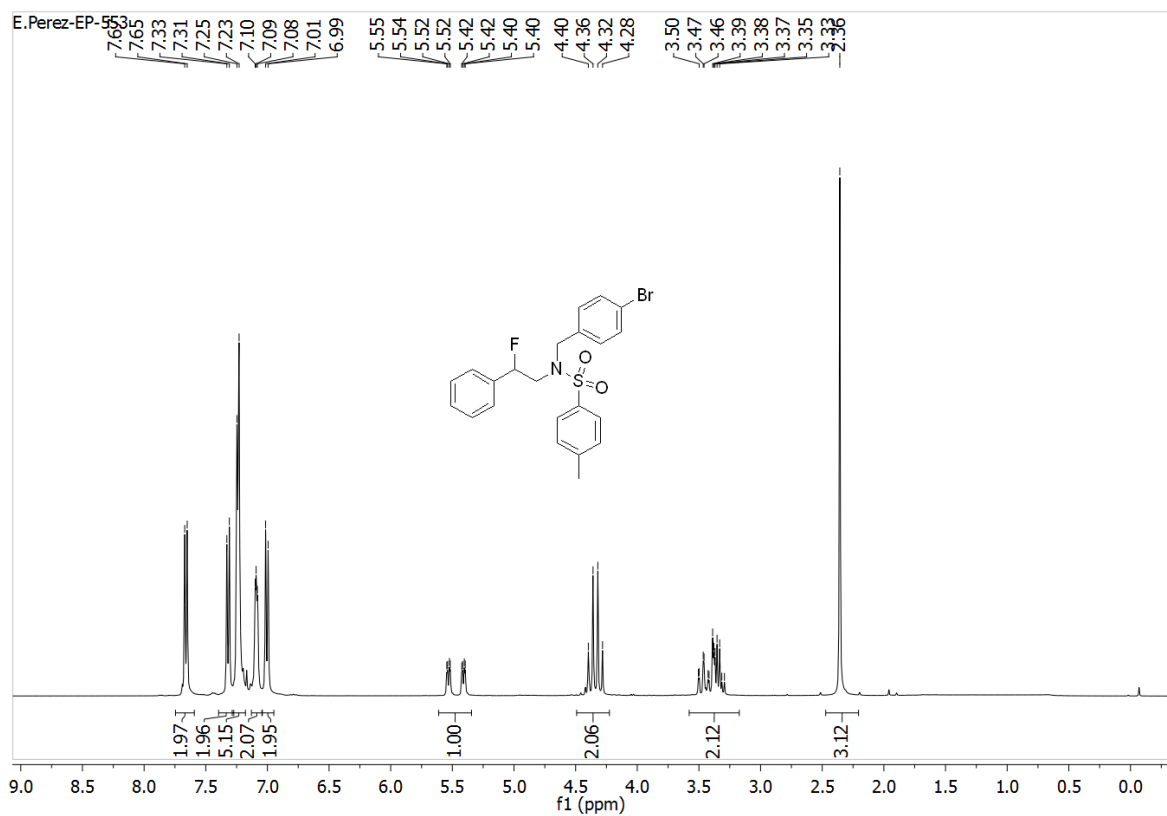


E.Perez-EP-552

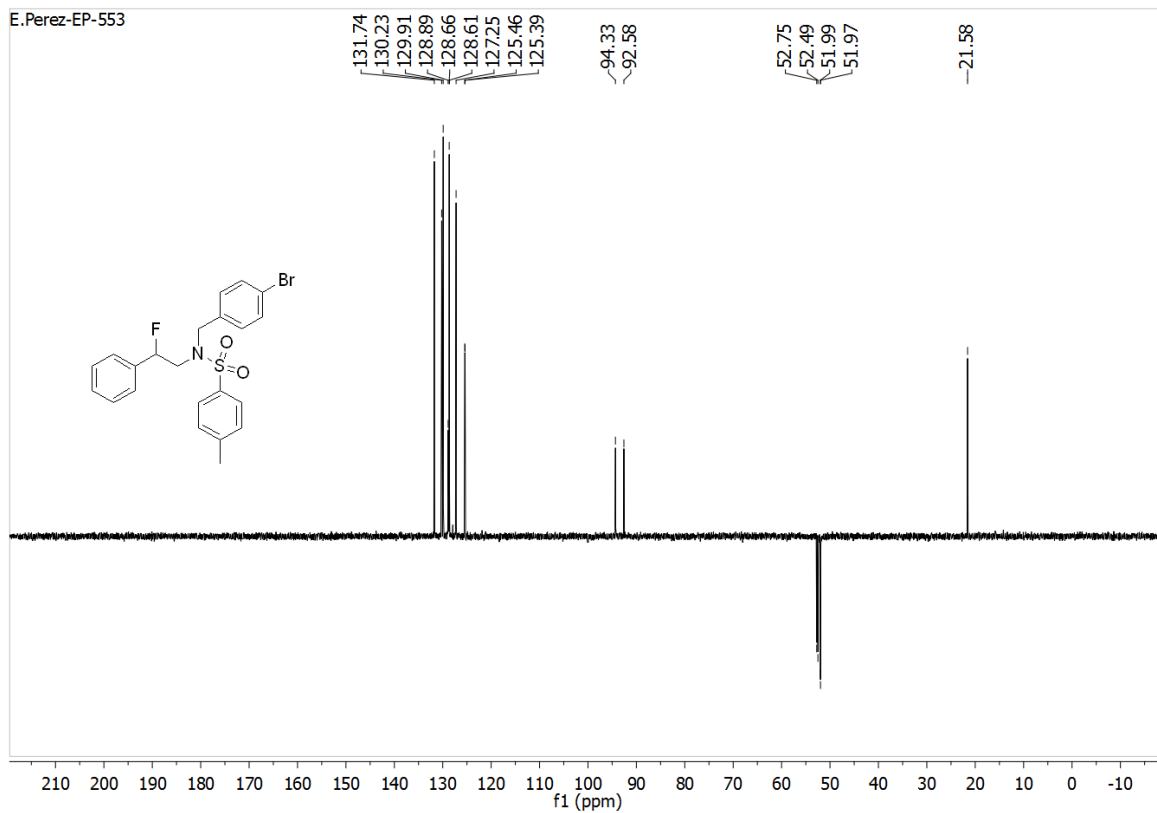


E.Perez-EP-552

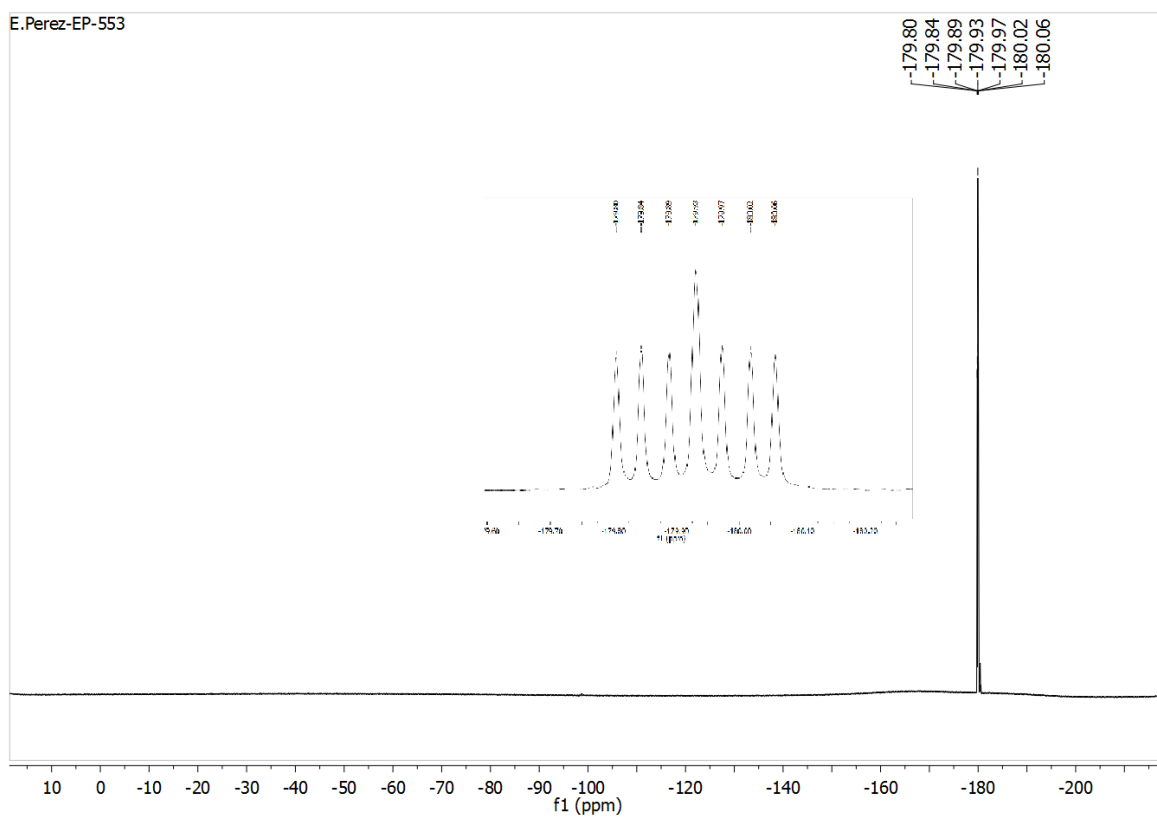


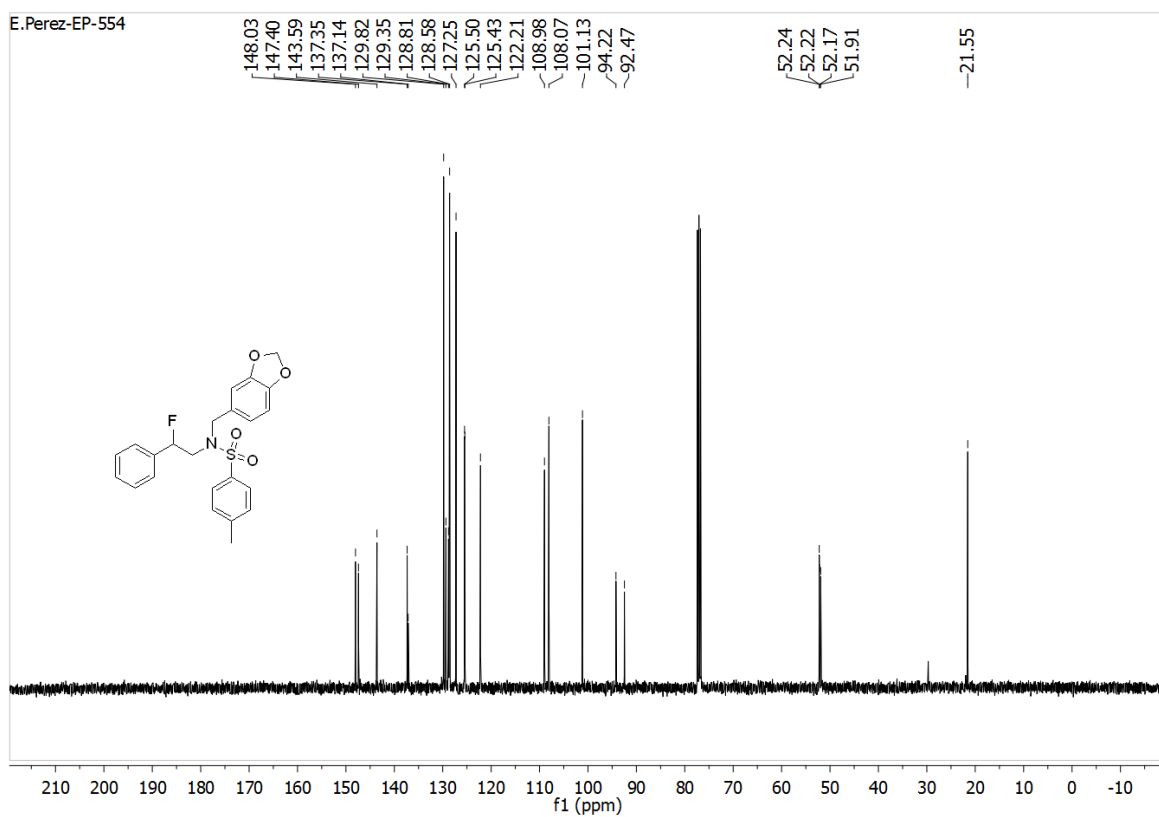
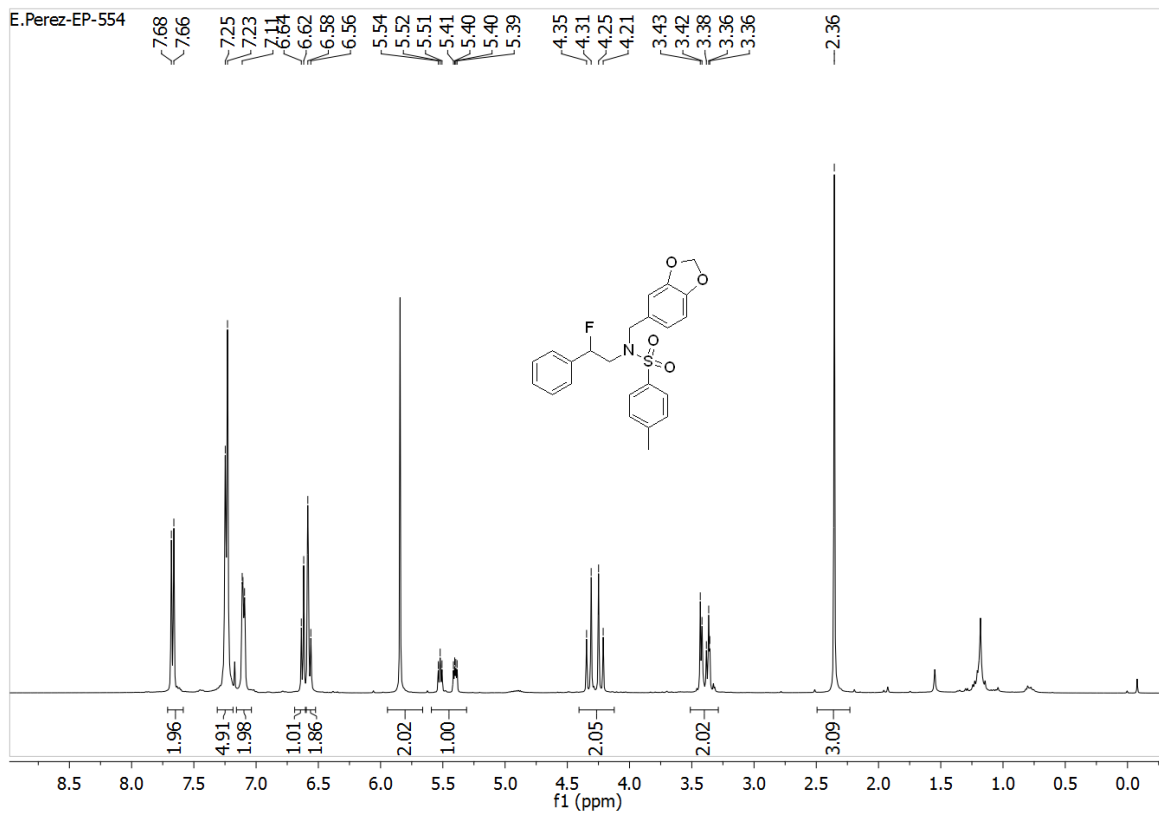


E.Perez-EP-553

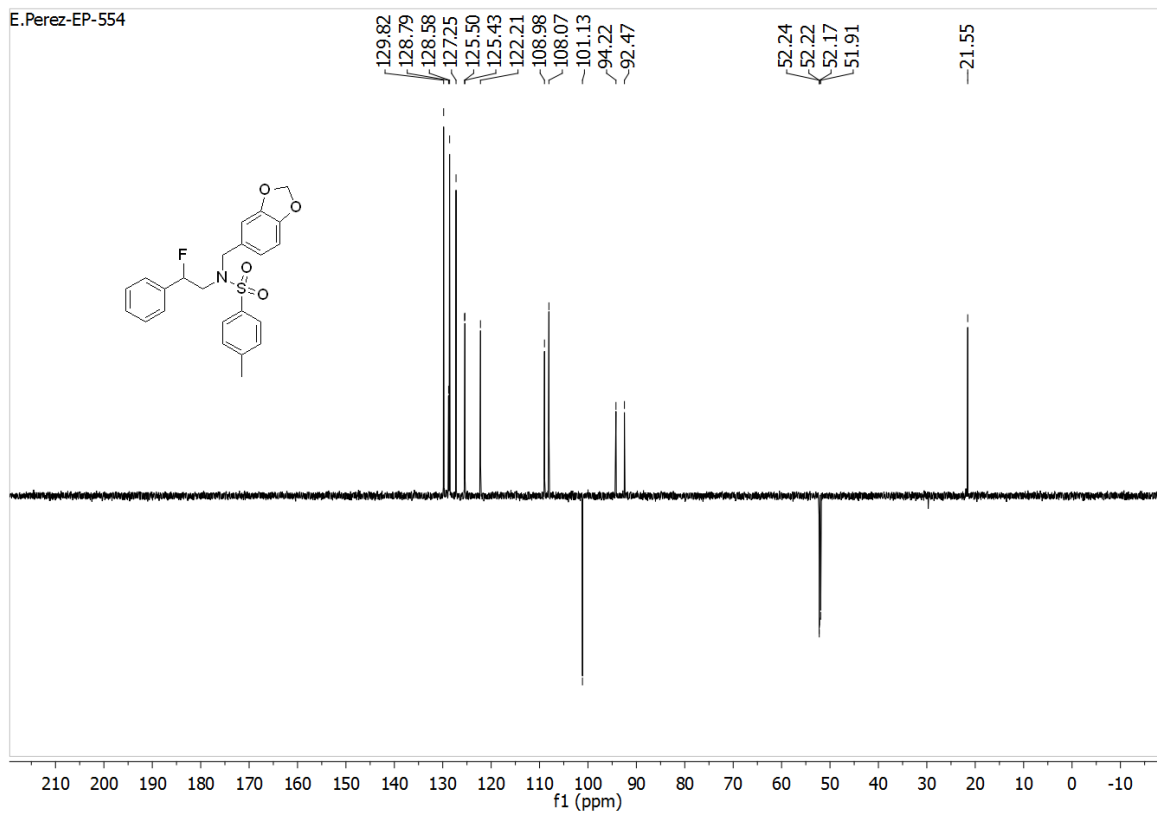


E.Perez-EP-553

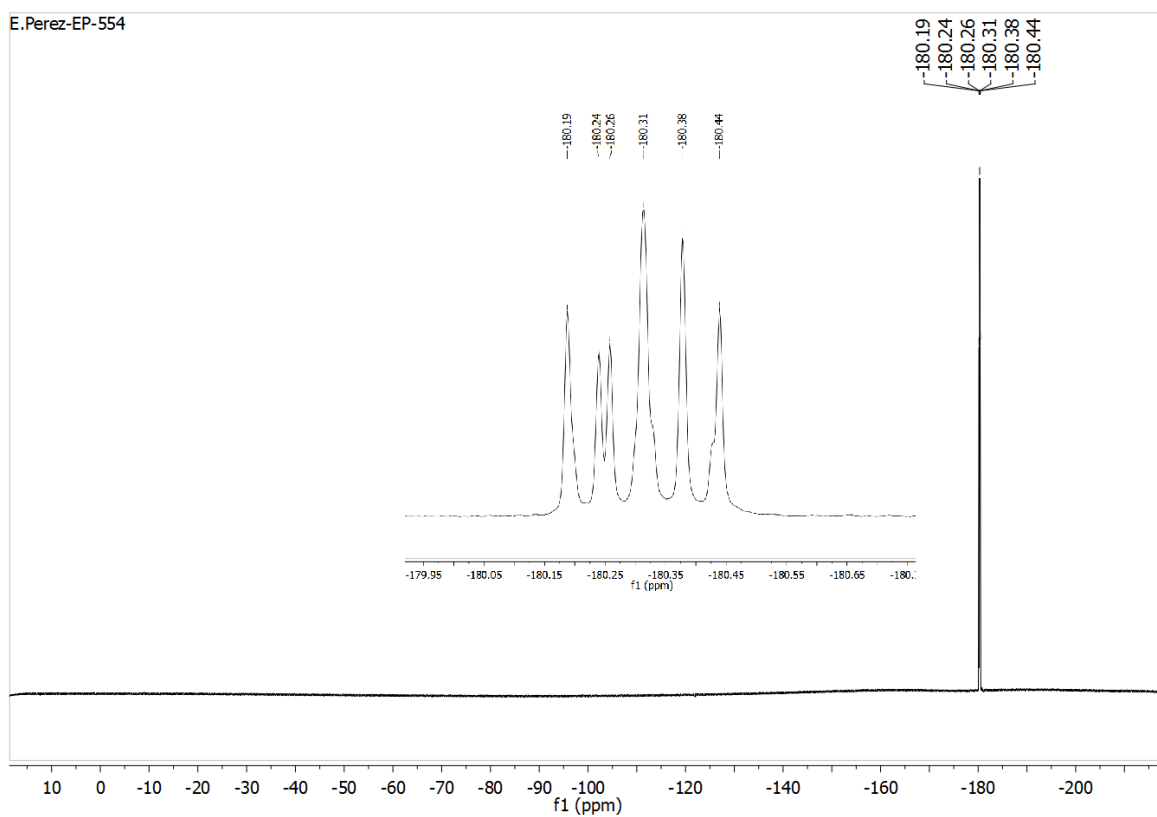


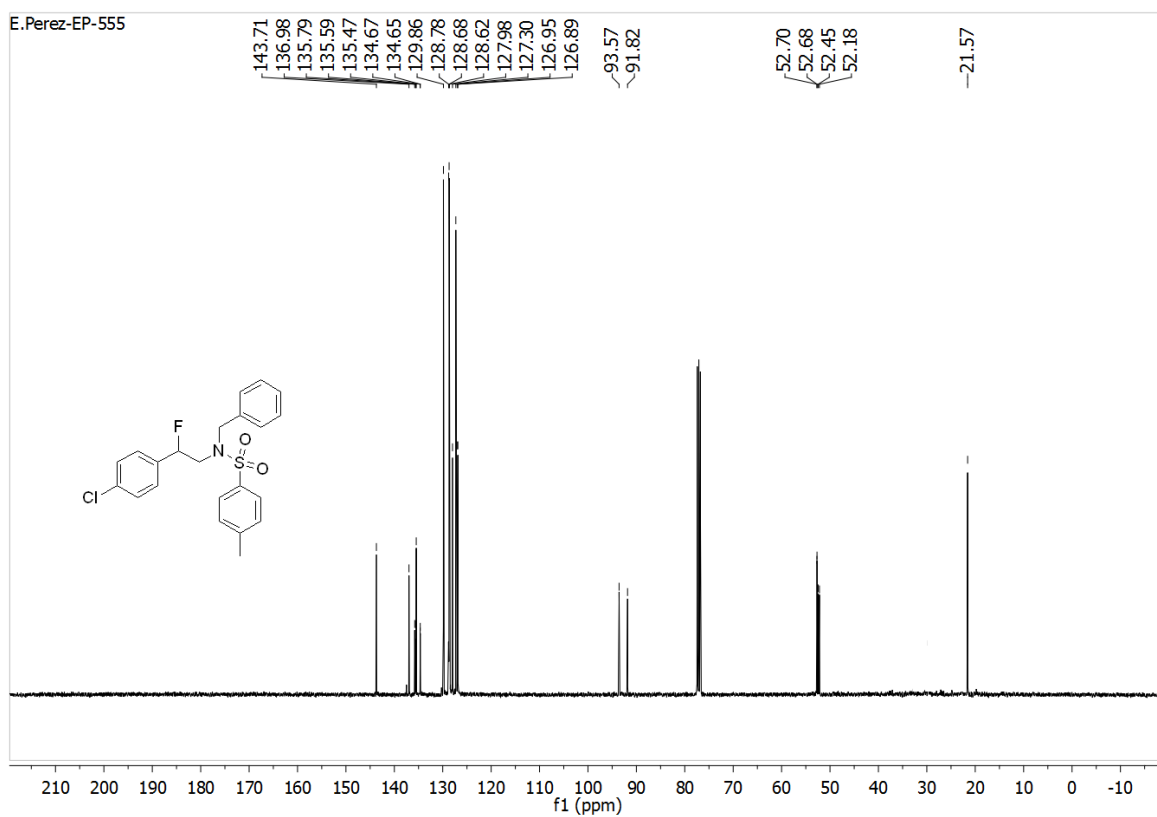
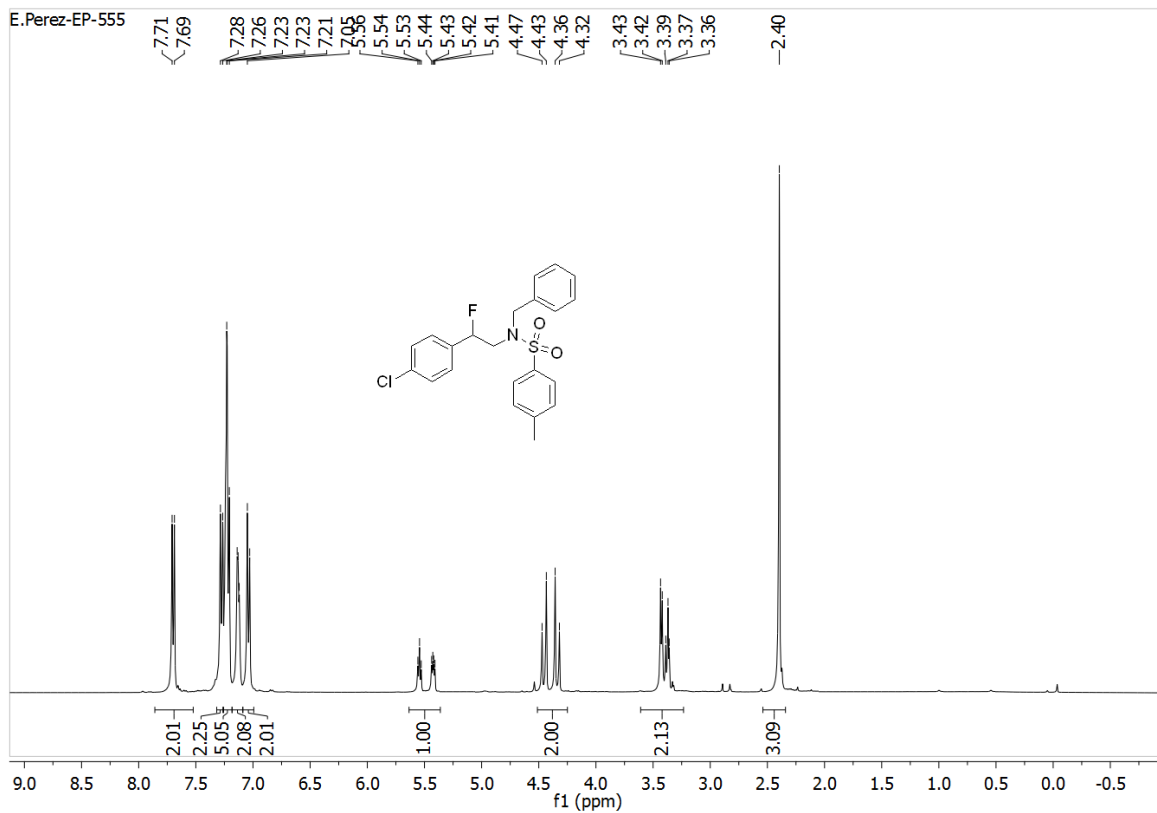


E.Perez-EP-554

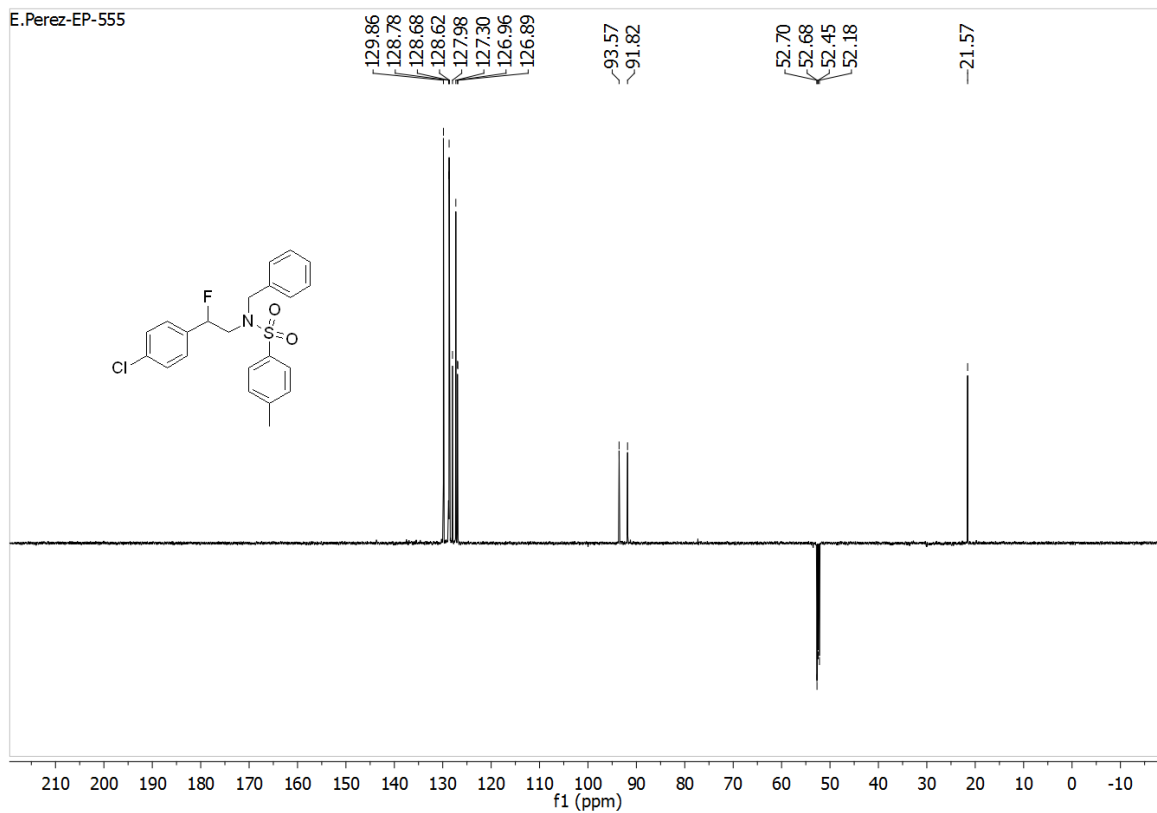


E.Perez-EP-554

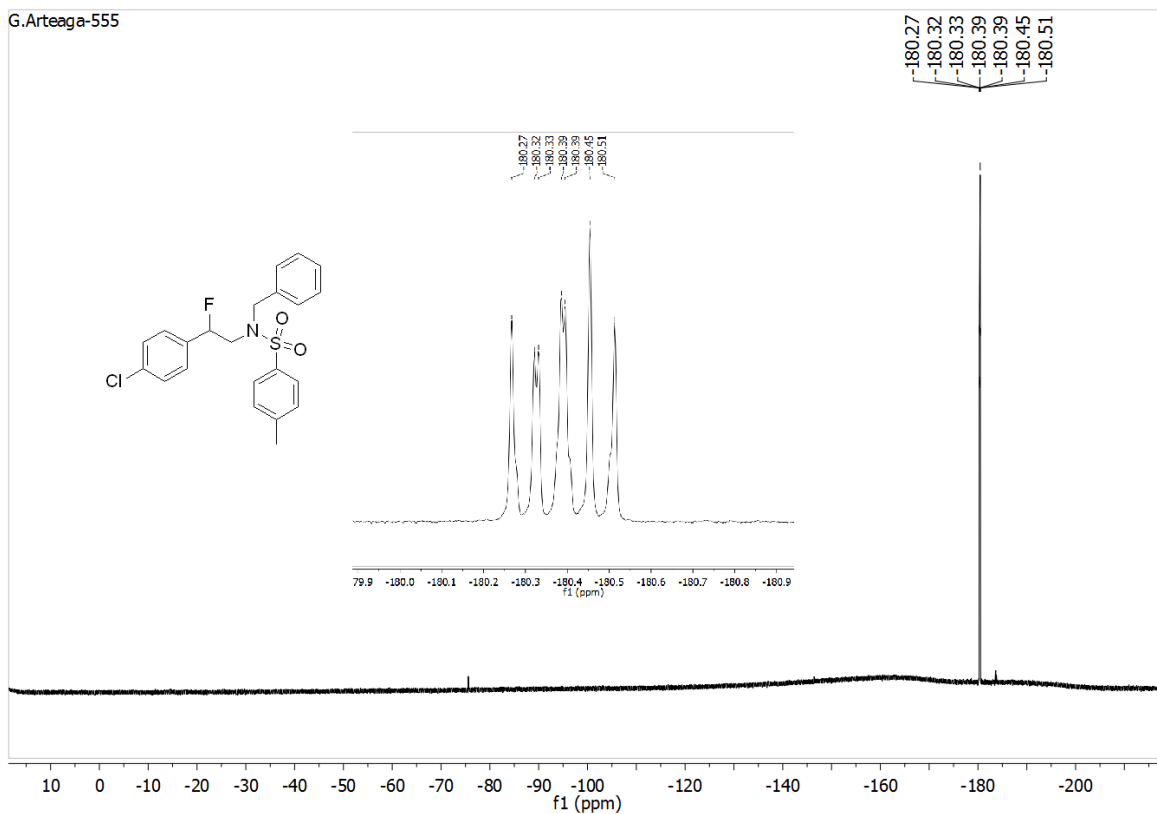


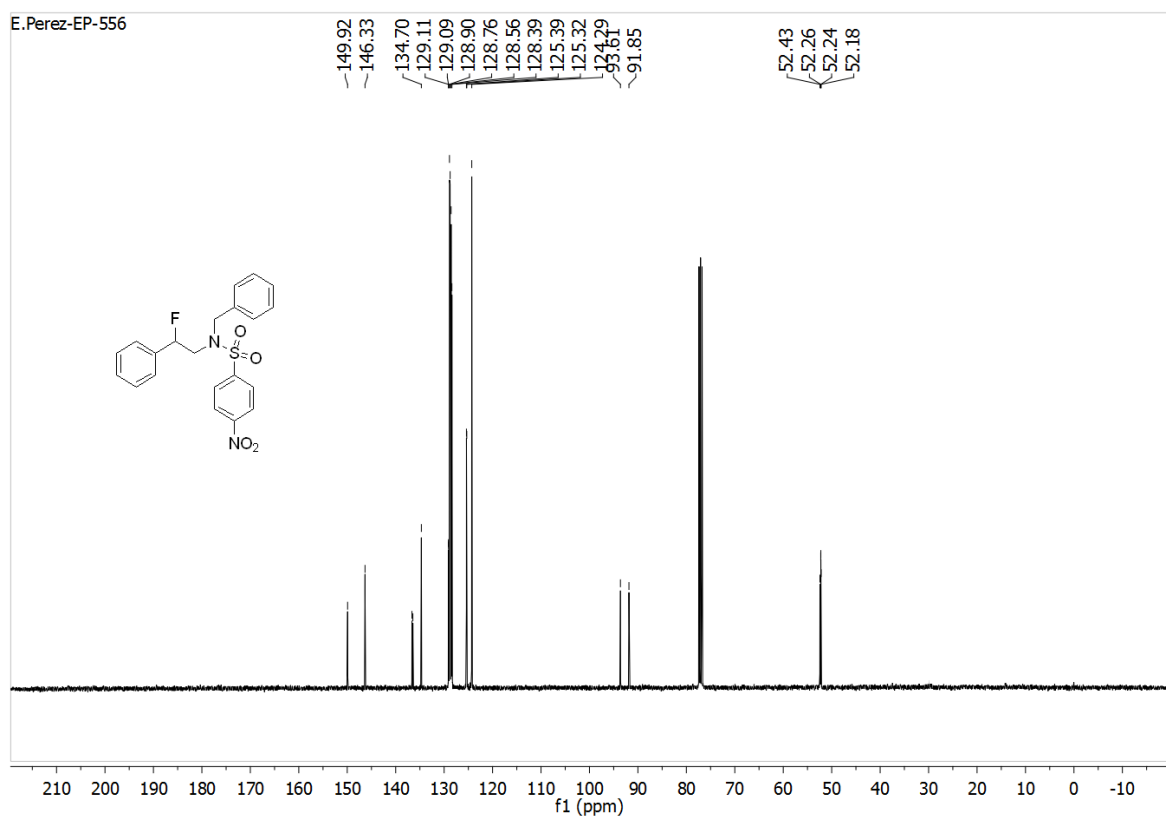
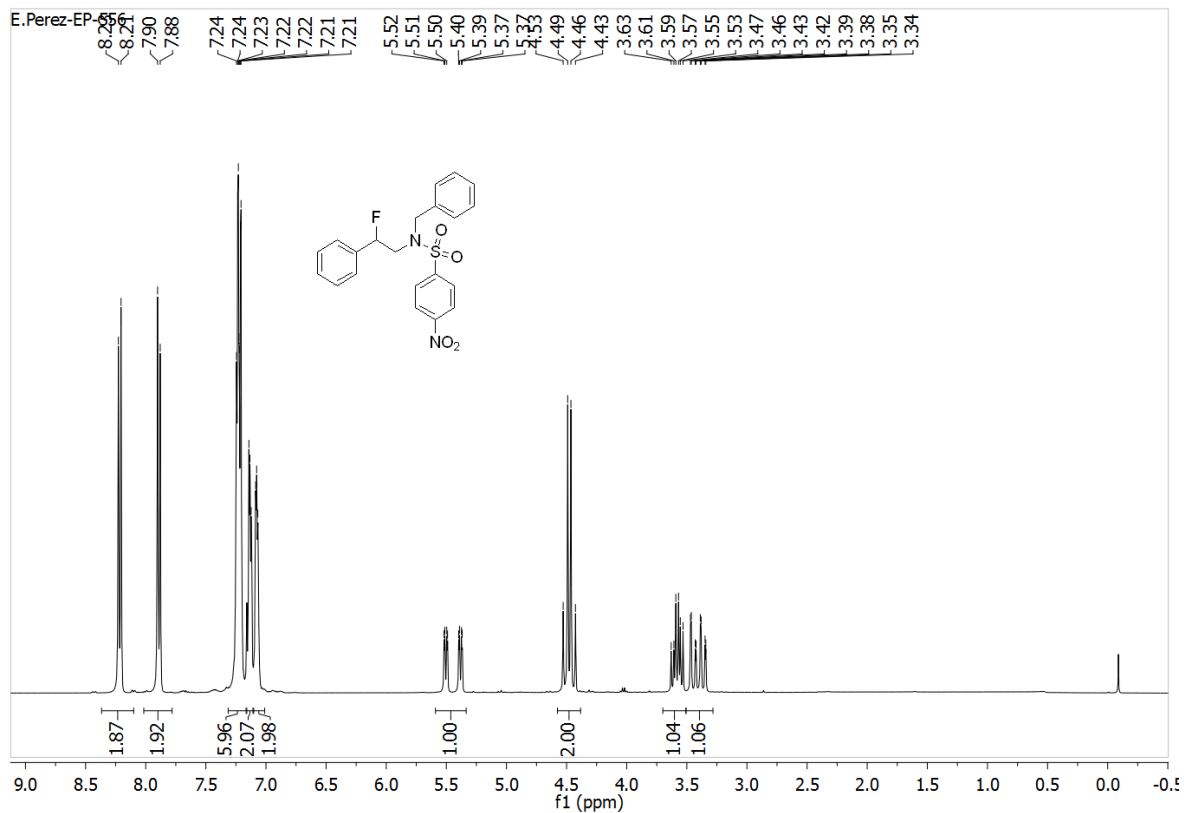


E.Perez-EP-555

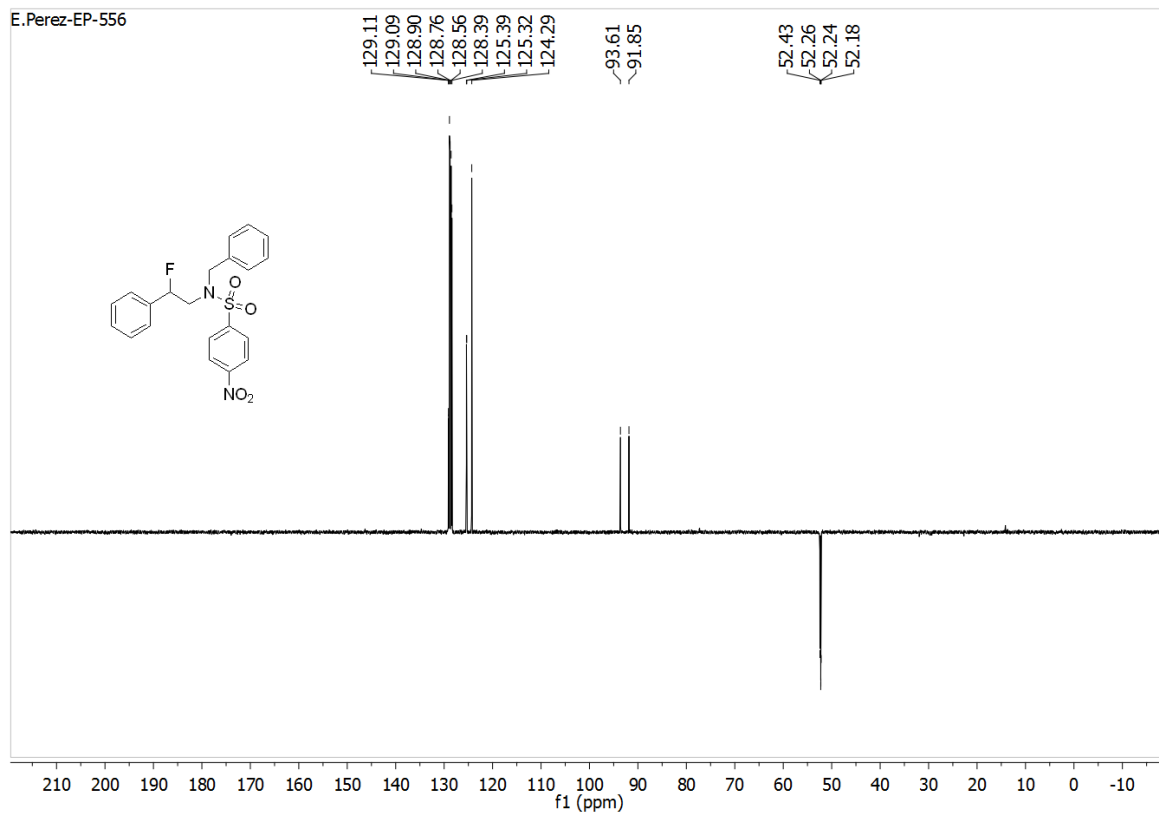


G.Arteaga-555

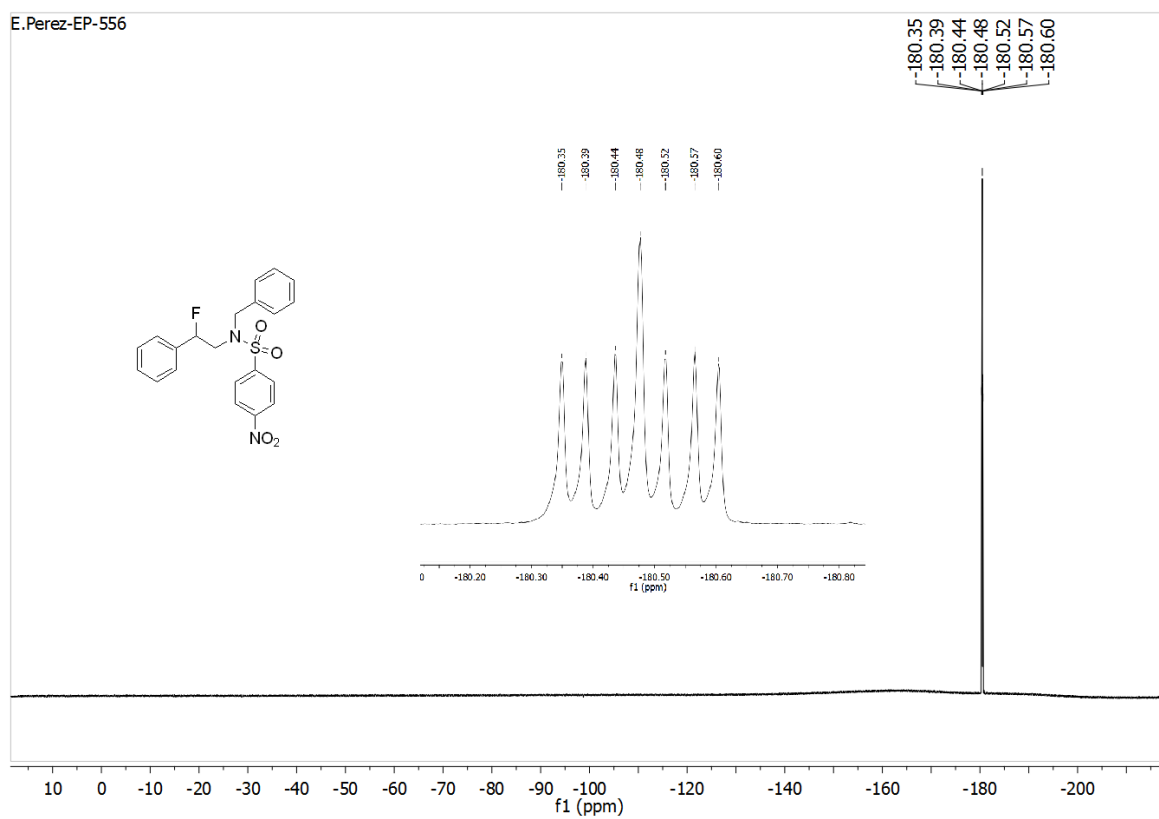


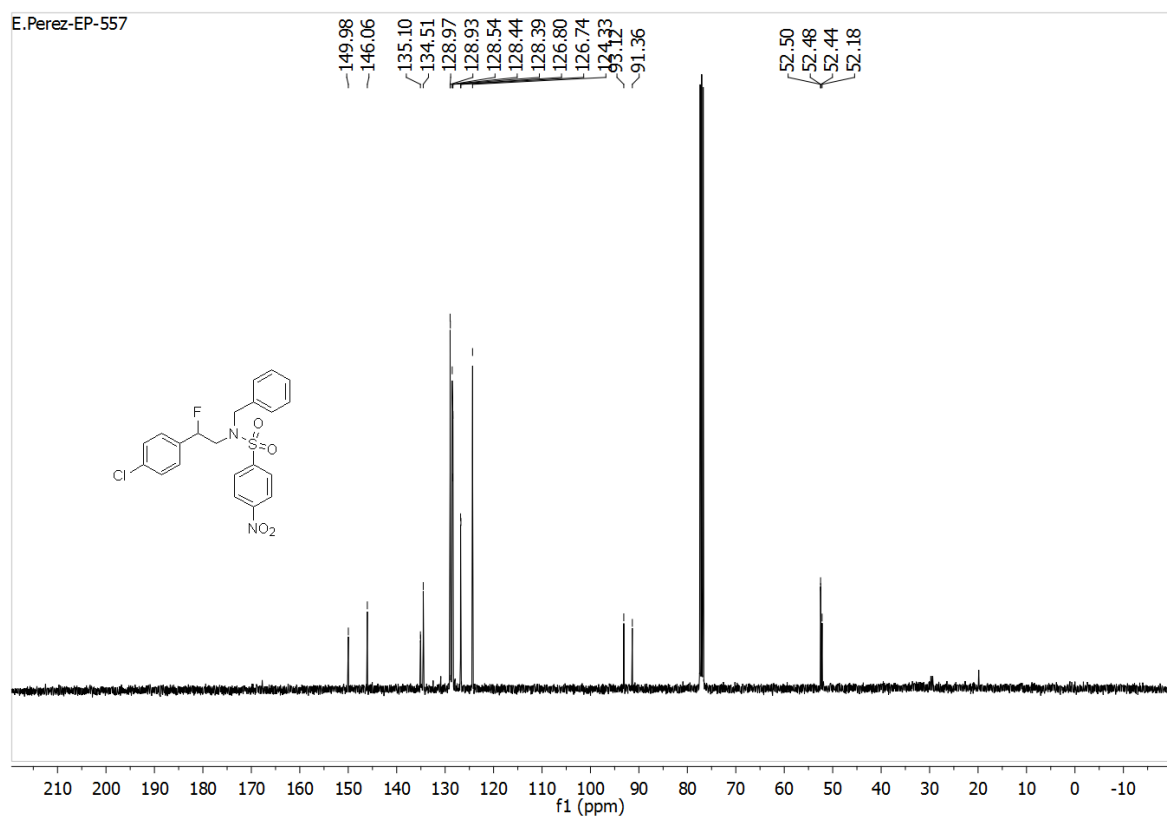
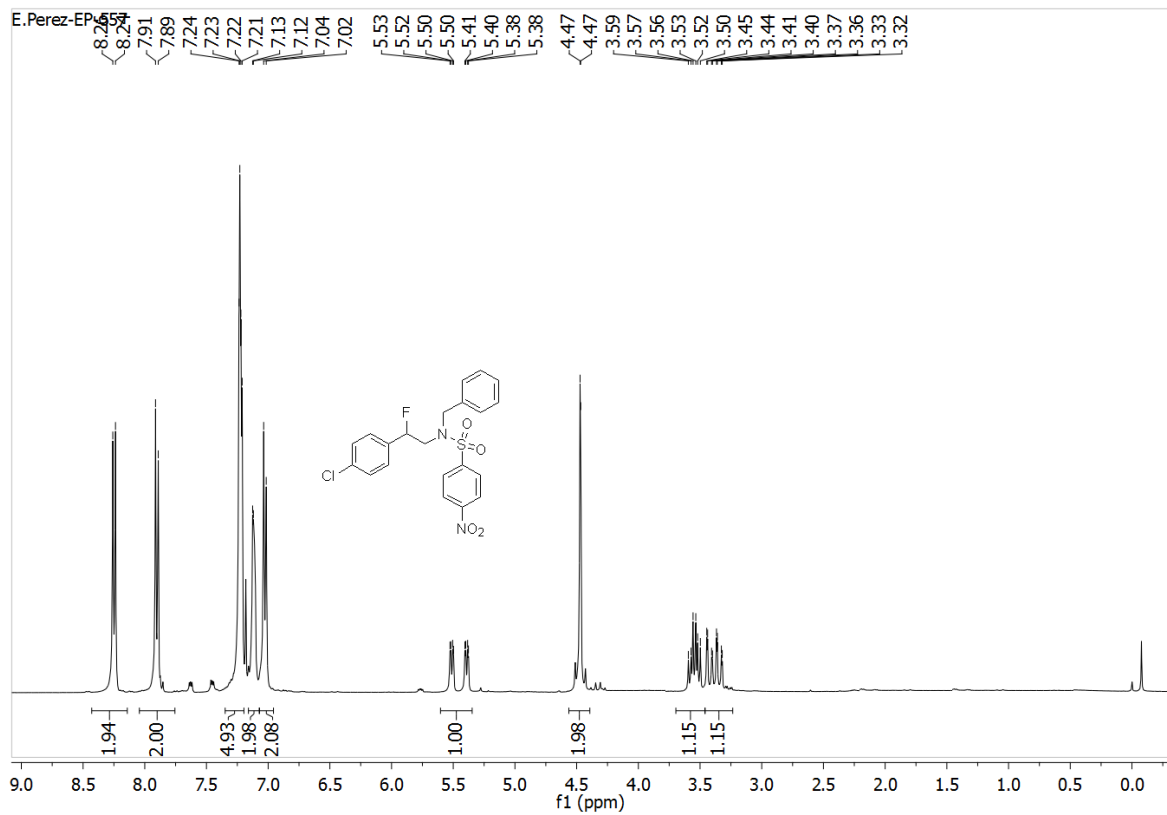


E.Perez-EP-556

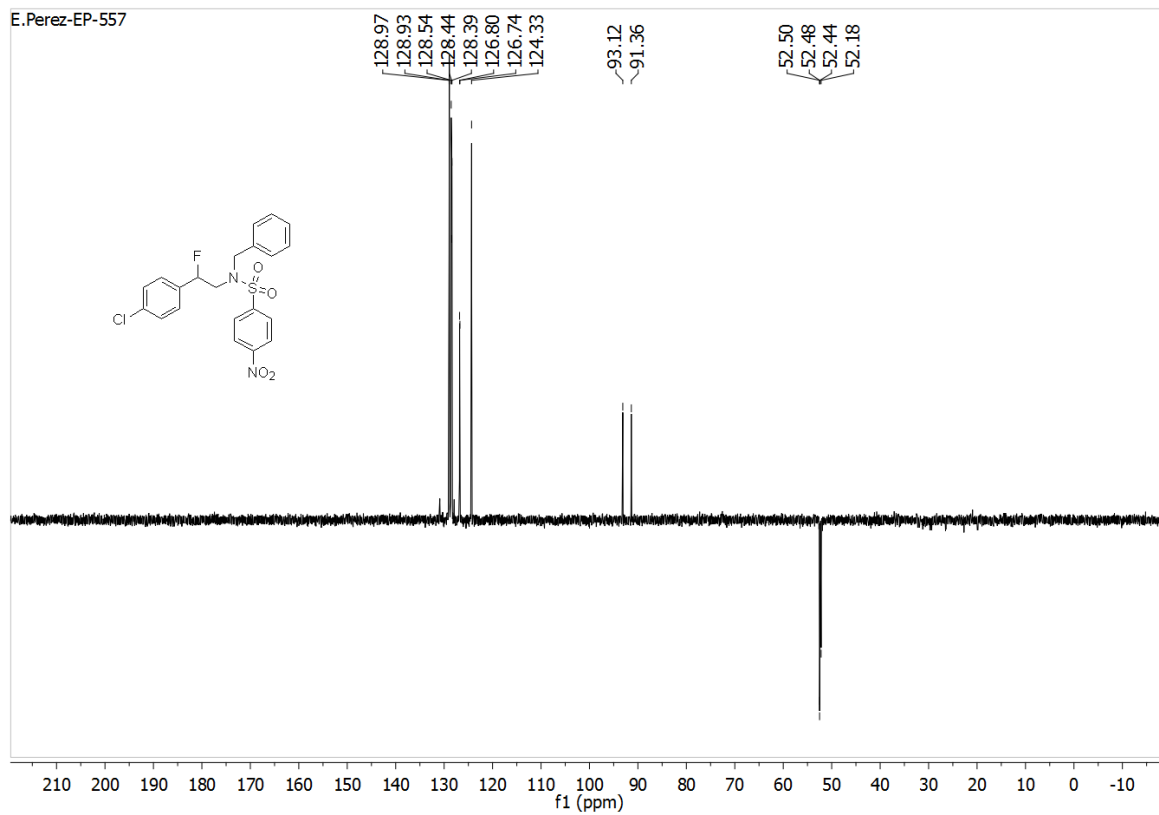


E.Perez-EP-556

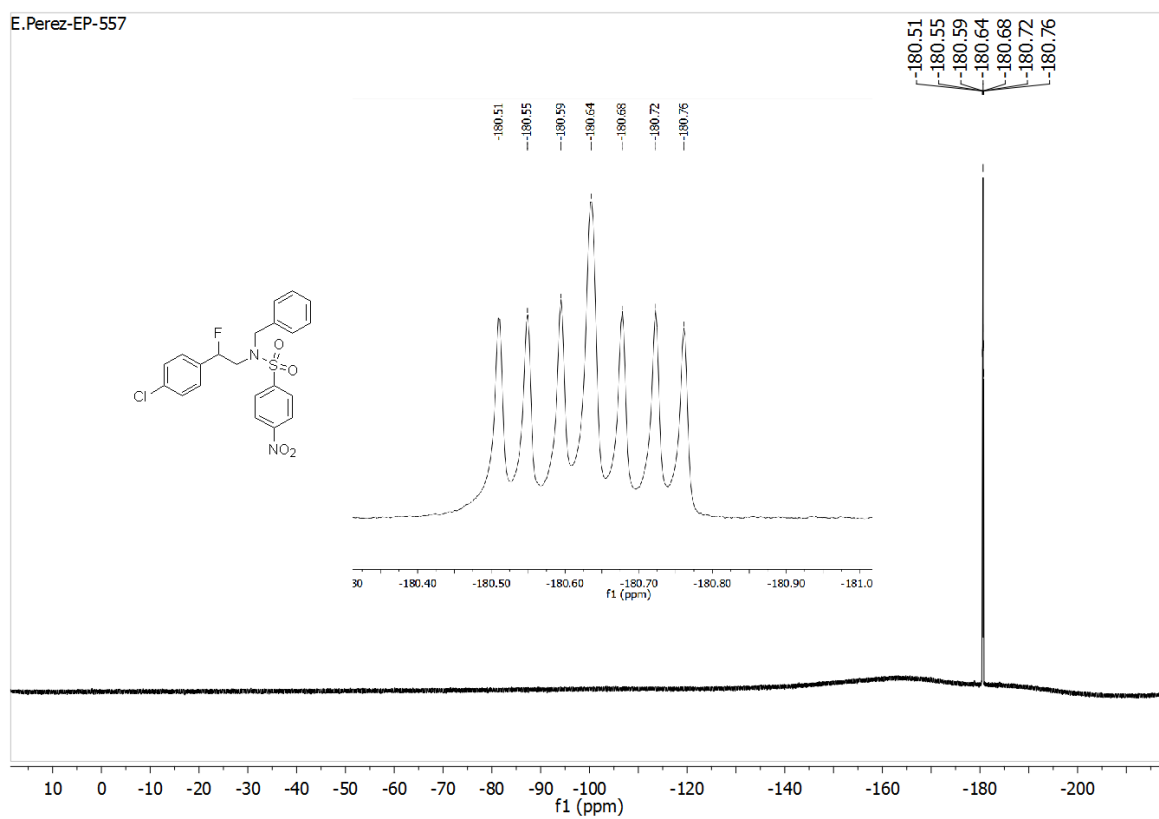


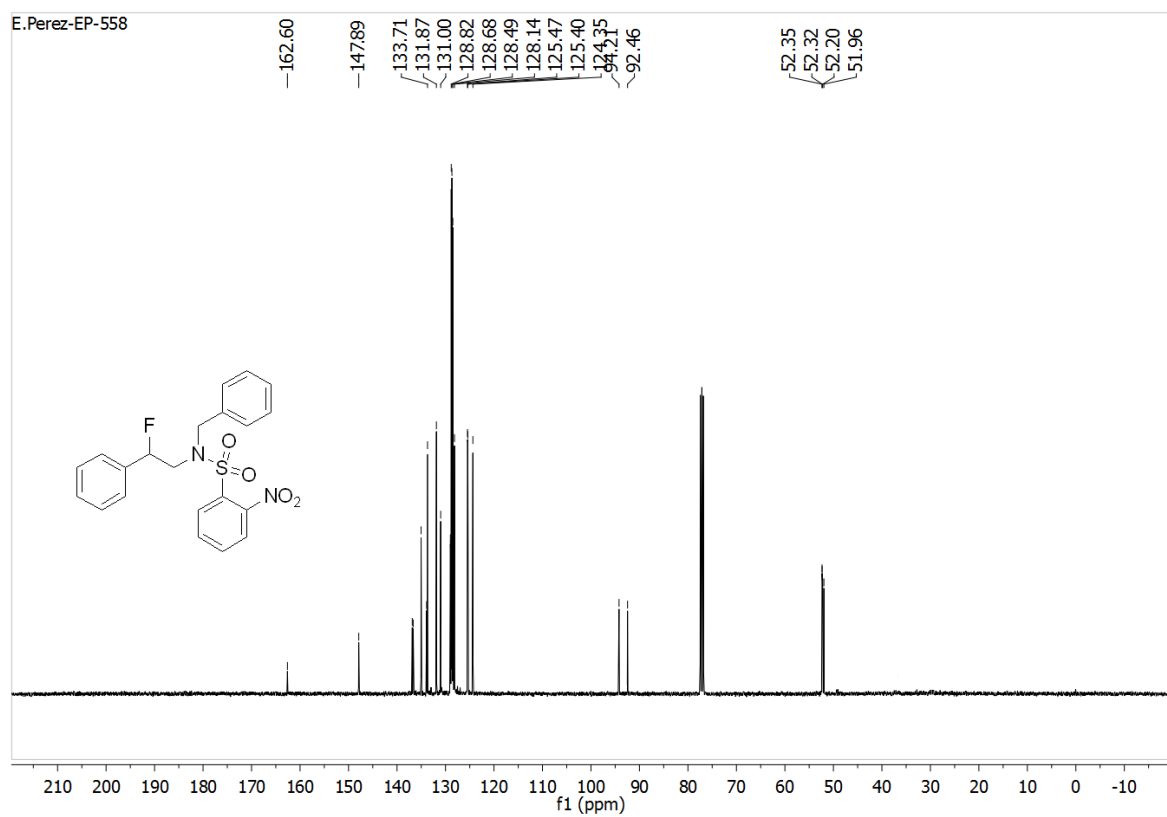
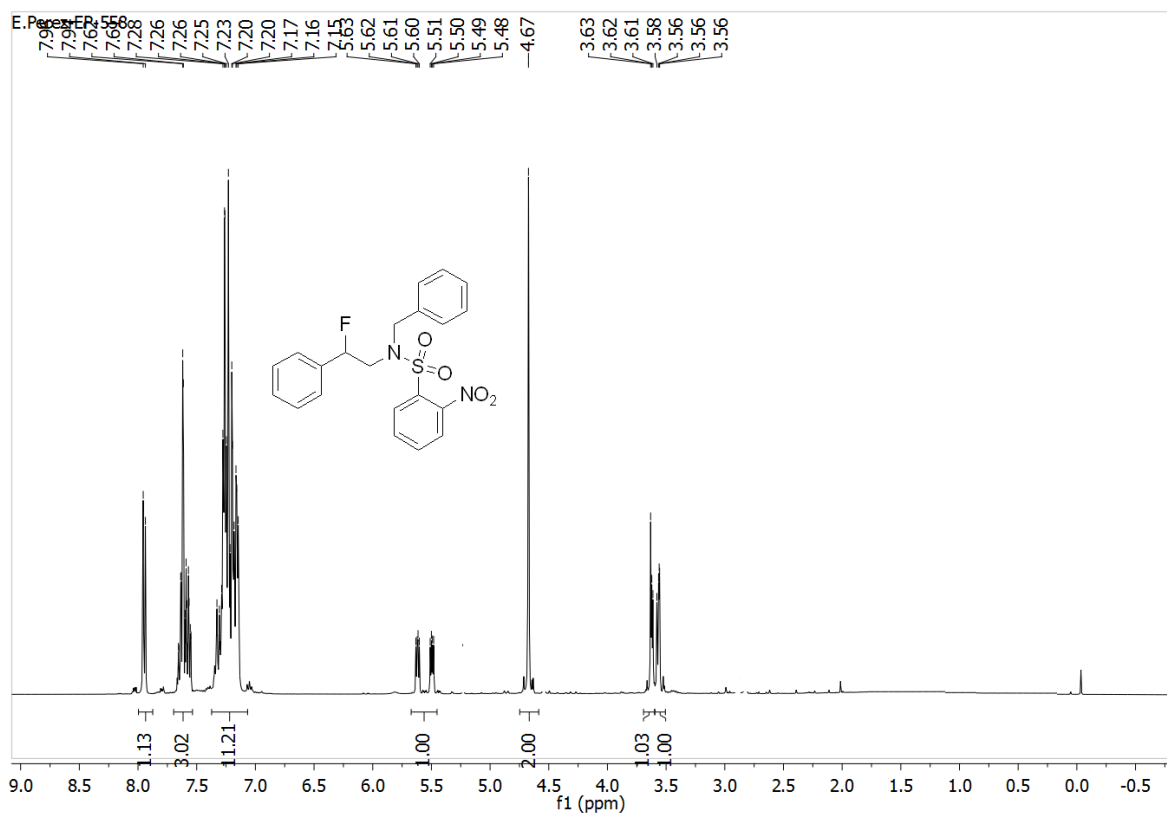


E.Perez-EP-557

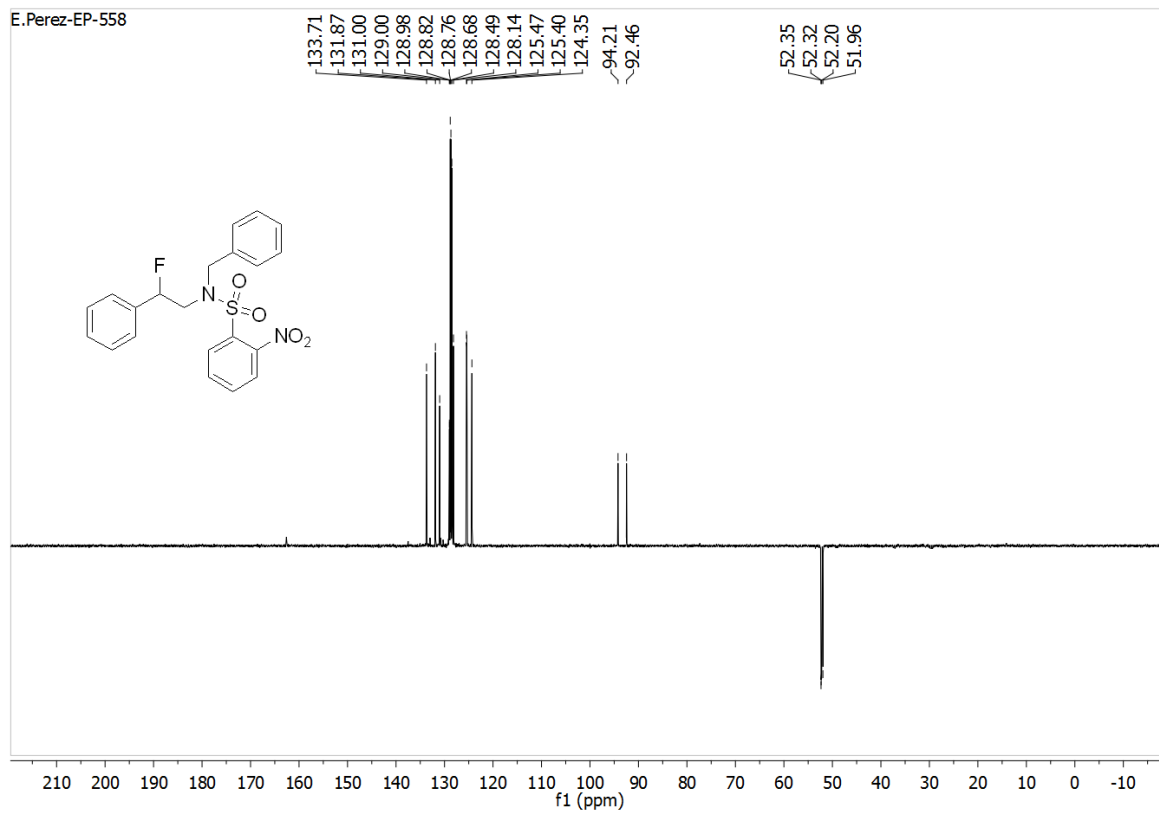


E.Perez-EP-557

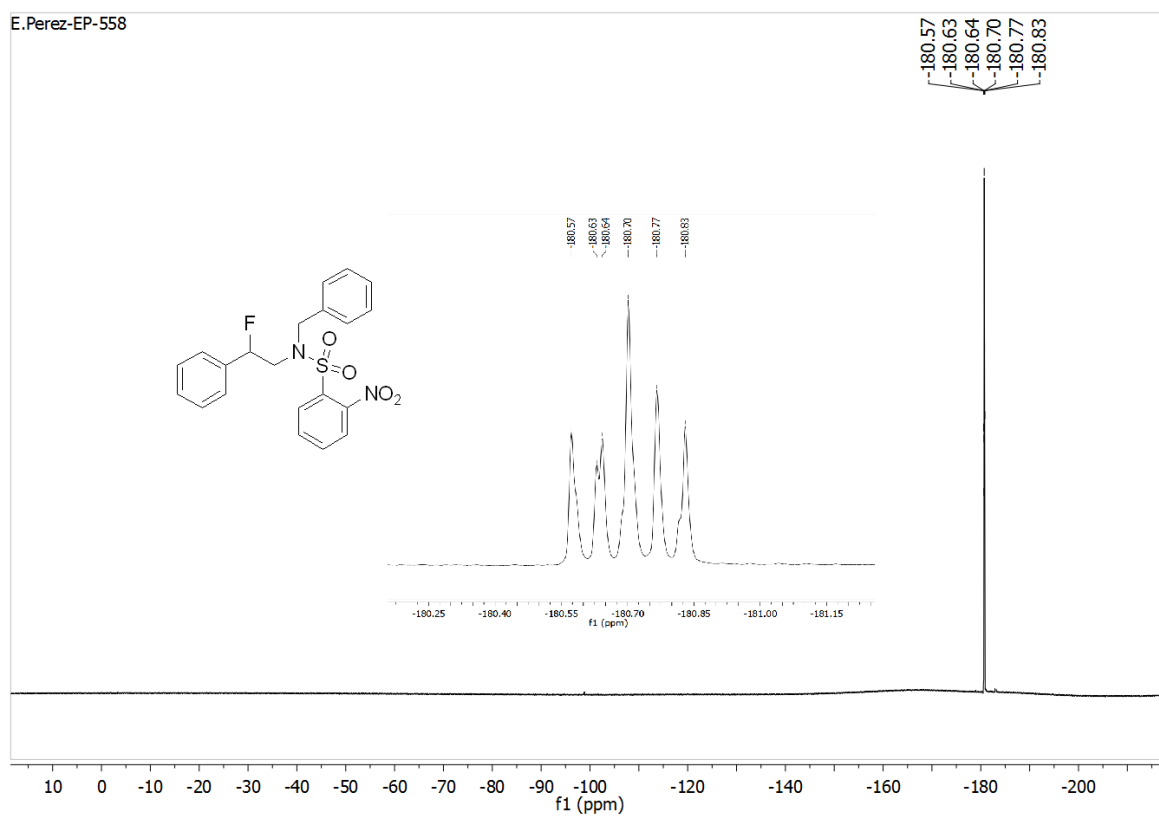


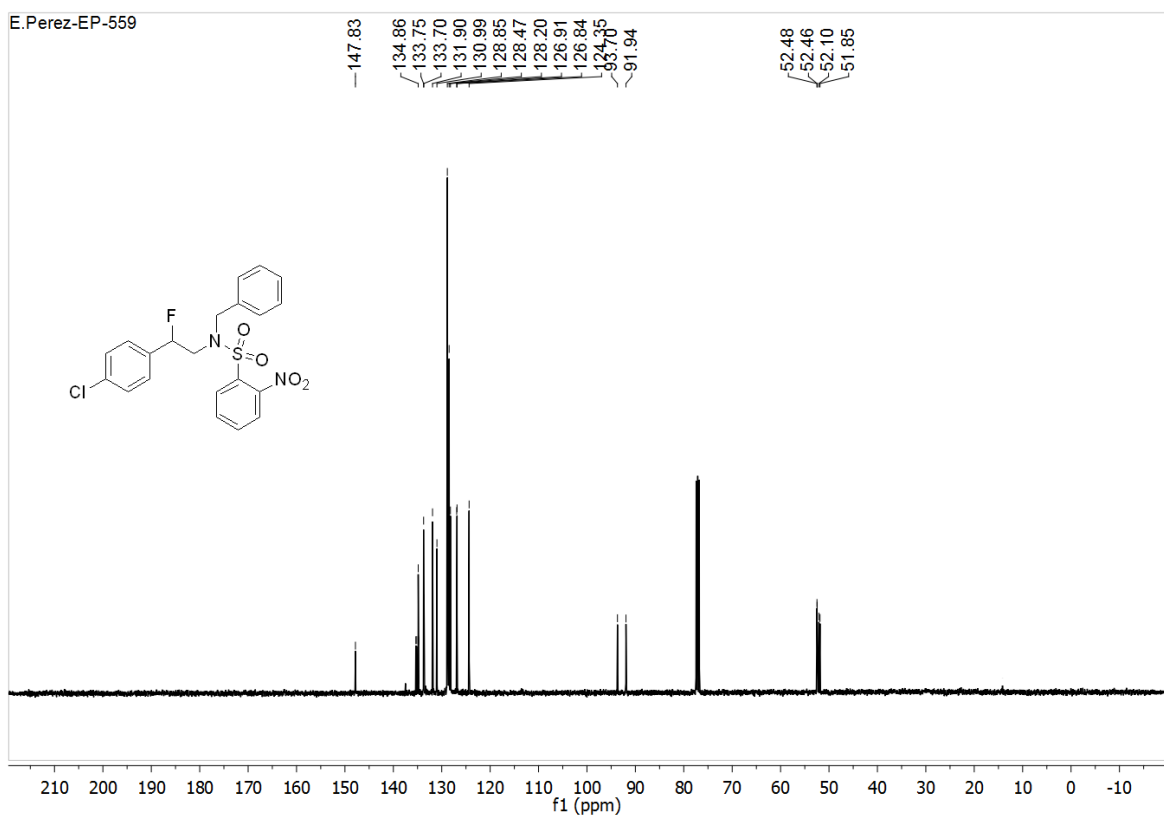
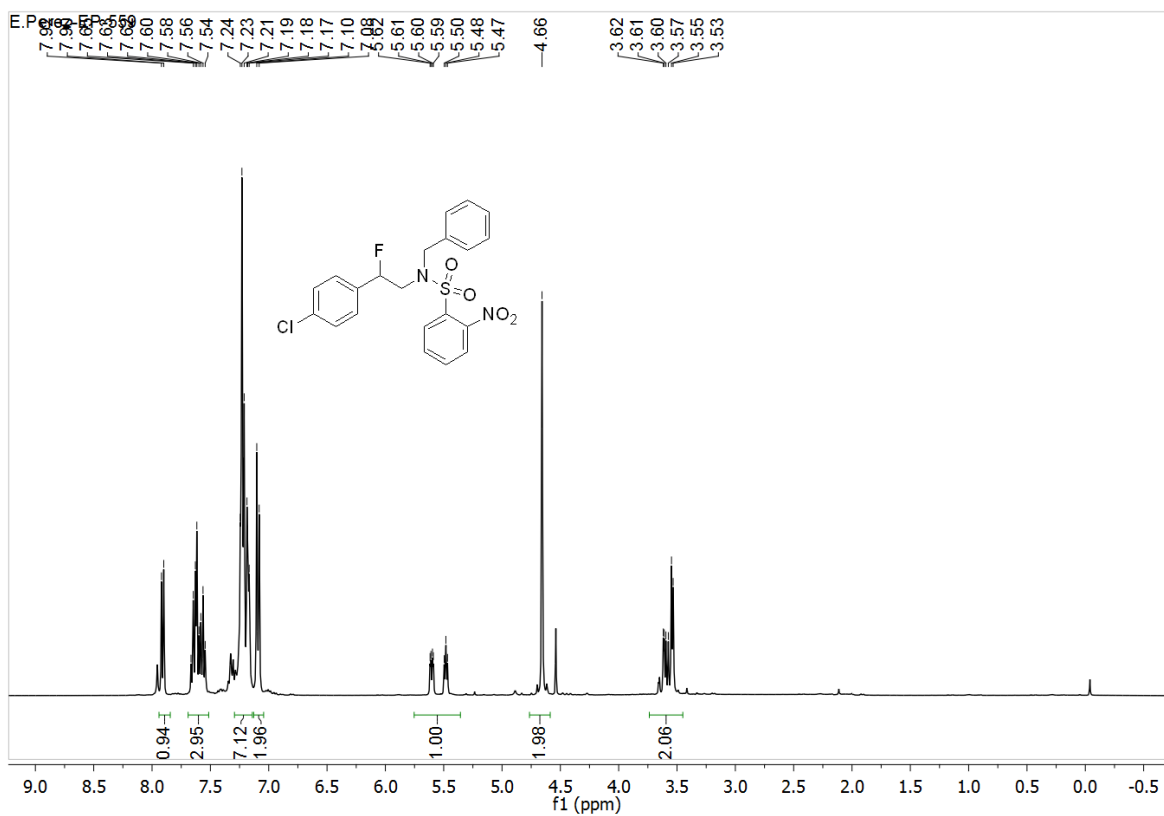


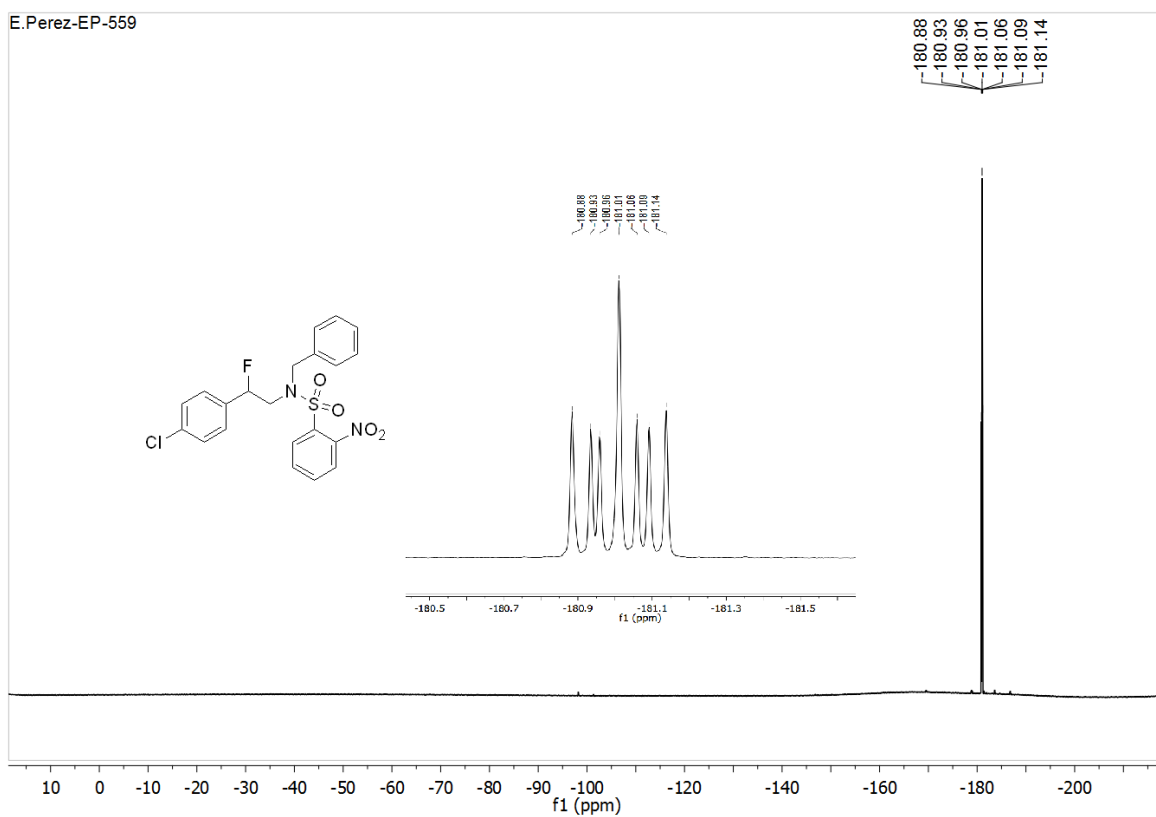
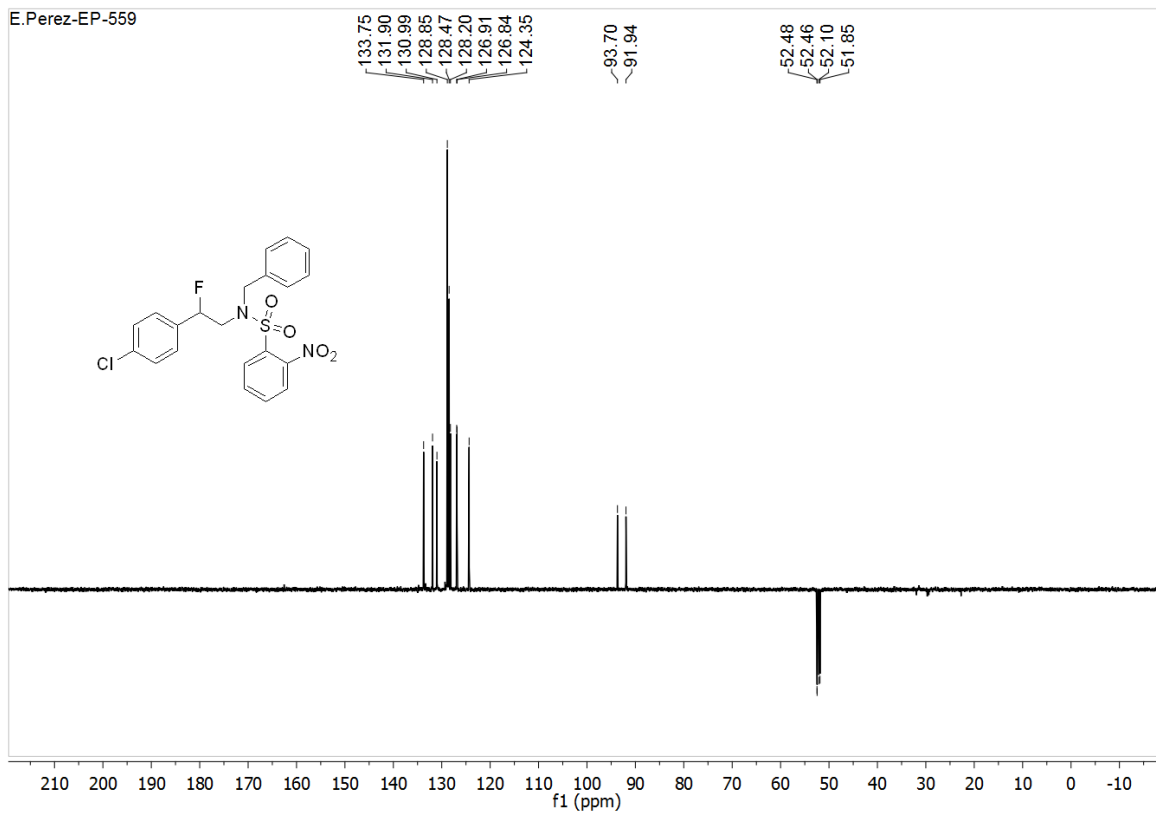
E.Perez-EP-558

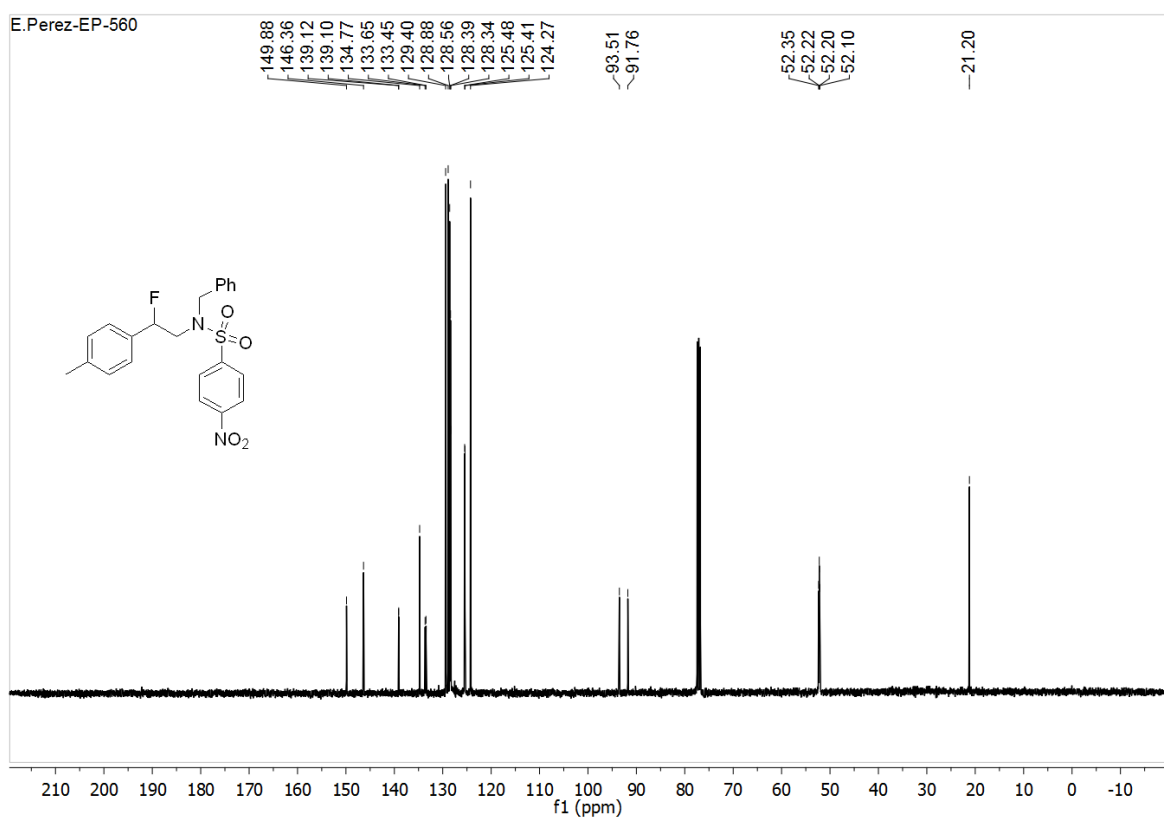
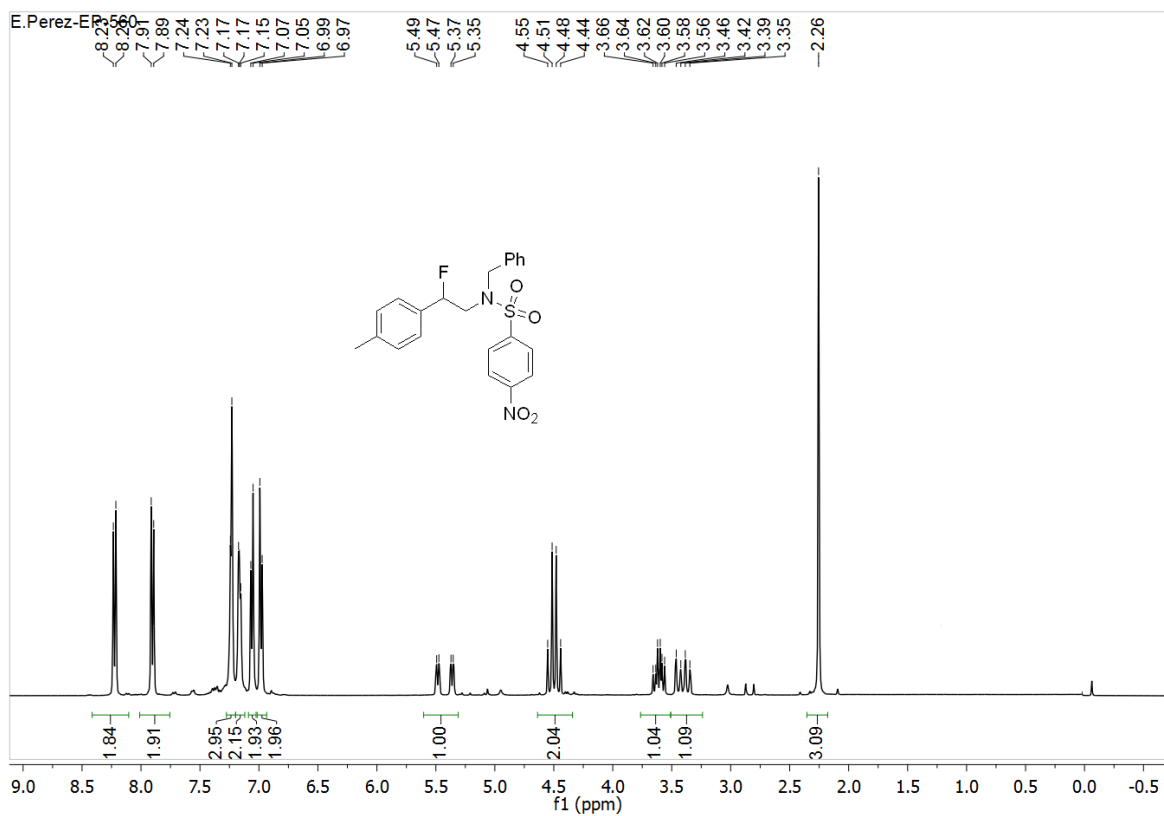


E.Perez-EP-558

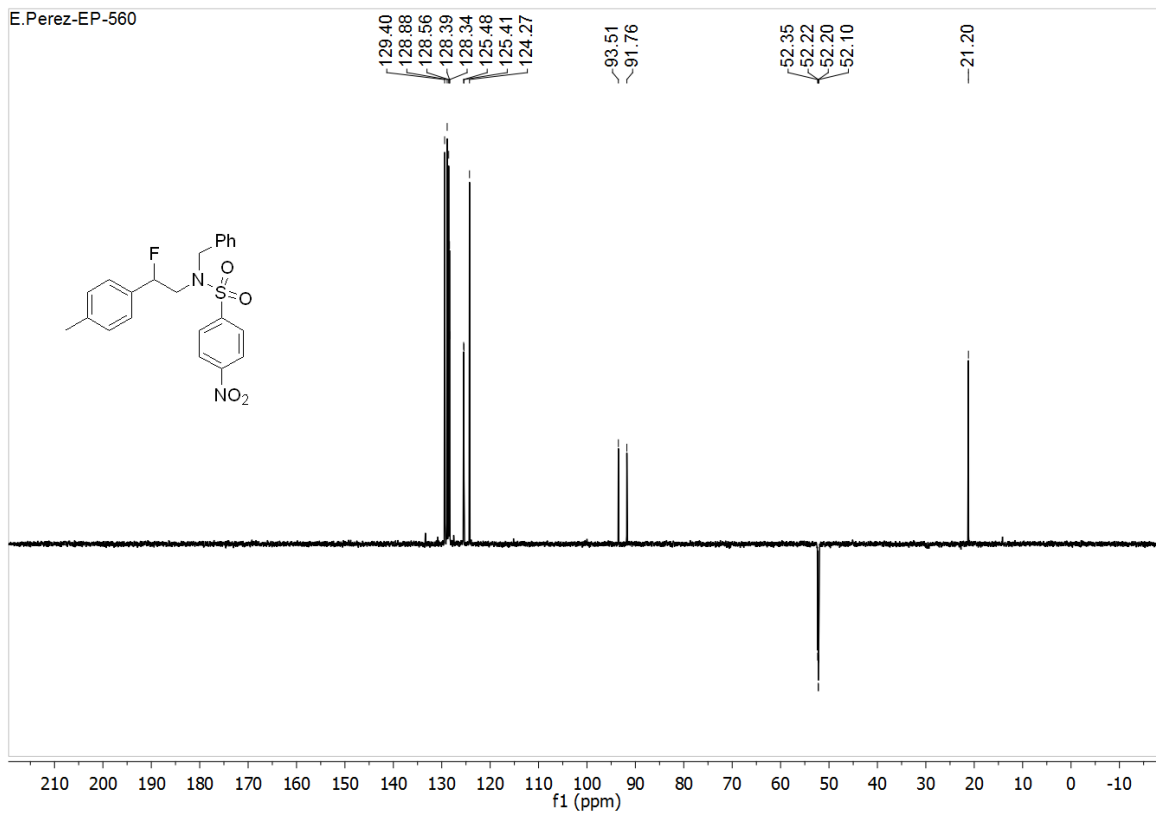








E.Perez-EP-560



E.Perez-EP-560

