Supporting Information for

Transition-Metal-Free, Room-Temperature Radical Azidofluorination of Unactivated Alkenes in Aqueous Solution

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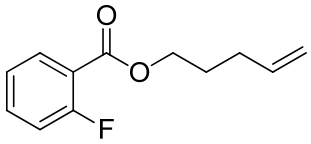
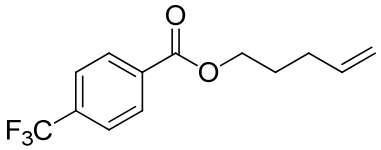
1. Synthesis and Characterizations of New Substrates.

n-Butylbenzene (**A-2**), 4-bromostyrene (**A-28**) and dimethyl *cis*-norbornene-*endo*-2,3-dicarboxylate (**A-29**) were commercially available and used directly without further purification. The rest of substrate alkenes were prepared according to the conventional methods.

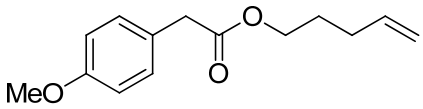
Characterizations of new substrate alkenes:



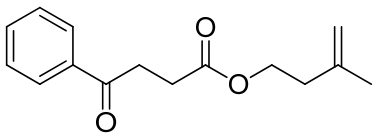
Pent-4-en-1-yl 2-fluorobenzoate (A-4). 2-Fluorobenzoic acid (1.90 g, 10 mmol) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC, 2.50 g, 13 mmol) and DMAP (122 mg, 1.0 mmol) in CH_2Cl_2 (25 mL) at 0 ^oC. Pent-4-en-1-ol (1.03 g, 12 mmol) was then added. The resulting mixture was allowed to warm up to room temperature and stirred for another 12 h. The solution was diluted with Et_2O (150 mL) and washed with 1N HCl solution. The aqueous layer was then extracted twice with Et_2O (100 mL). The combined organic layer was dried over anhydrous $Na_2S_2O_4$. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:5, v:v) as the eluent to give pure **A-4** as a colorless oil. Yield: 1.98 g (95%). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91-7.95 (m, 1H), 7.50-7.52 (m, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.11-7.16 (m, 1H), 5.80-6.00 (m, 1H), 5.00-5.10 (m, 2H), 4.35 (t, J = 6.4 Hz, 2H), 2.20-2.26 (m, 2H), 1.83-1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5 (d, J = 3.8 Hz), 161.9 (d, J = 258.9 Hz), 137.4, 134.3 (d, J = 8.3 Hz), 132.0, 123.9 (d, J = 3.8 Hz), 118.9 (d, J = 9.9 Hz), 116.9 (d, J = 22.0 Hz), 115.4, 64.6, 30.0, 27.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.9 (m, 1F); IR (neat): ν (cm^{-1}) 3079, 2957, 1731, 1614, 1489, 1457, 1298, 1251, 1128, 1085, 915, 757. EIMS: *m/z* (rel intensity) 208 (M^+, 1), 141 (6), 124 (9), 123 (100), 95 (23), 75 (10), 69 (4), 68 (38), 67 (17); HRMS calcd for $C_9H_8O_2F$ ($M-C_3H_5$): 167.0508, found 167.0507.



Pent-4-en-1-yl 4-(trifluoromethyl)benzoate (A-5). This compound was prepared in 95% yield from the condensation of 4-(trifluoromethyl)benzoic acid and pent-4-en-1-ol according to the procedure outlined in the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 5.80-5.90 (m, 1H), 5.00-5.10 (m, *2*H), 4.38 (t, *J* = 6.4 Hz, 2H), 2.20-2.26 (m, 2H), 1.86-1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 137.2, 134.3 (q, *J* = 32.6 Hz), 133.6, 129.9, 125.3 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 271.0 Hz), 115.4, 64.9, 30.1, 27.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.1 (m, 3F); IR (neat): ν (cm^{-1}) 3081, 2958, 1725, 1642, 1515, 1412, 1327, 1276, 1170, 1067, 1018, 916, 863, 776; EIMS: *m/z* (rel intensity) 239 (M-F, 7), 191 (2), 173 (100), 145 (53), 125 (5), 95 (6), 68 (54), 67 (30); HRMS calcd for $C_{13}H_{13}O_2F_2$ (M-F): 239.0884, found 239.0887.

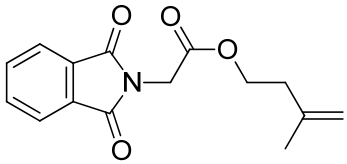


Pent-4-en-1-yl 2-(4-methoxyphenyl)acetate (A-6). This compound was prepared in 96% yield from the condensation of 4-methoxybenzoic acid and pent-4-en-1-ol according to the procedure outlined in the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.72-5.82 (m, 1H), 4.96-5.02 (m, 2H), 4.09 (t, *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 3.55 (s, 2H), 2.05-2.10 (m, 2H), 1.68-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 158.7, 137.4, 130.2, 126.2, 115.3, 113.9, 64.2, 55.2, 40.5, 30.0, 27.7; IR (neat): ν (cm^{-1}) 2956, 1736, 1612, 1513, 1248, 1153, 1035, 997, 916, 820; EIMS: *m/z* (rel intensity) 234 (M^+, 56), 166 (84), 148 (34), 121 (100), 106 (6), 91 (16), 78 (30); HRMS calcd for $C_{14}H_{18}O_3$ (M): 234.1256, found 234.1261.



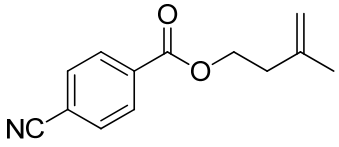
3-Methylbut-3-en-1-yl 4-oxo-4-phenylbutanoate (A-11). This compound was prepared from 4-oxo-4-phenylbutanoic acid and 3-methylbut-3-en-1-ol in 97% yield according to the

procedure outlined for the synthesis of **A-4**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.79 (s, 1H), 4.73 (s, 1H), 4.22 (t, *J* = 7.2 Hz, 2H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 172.8, 141.6, 136.5, 133.2, 128.6, 128.0, 112.2, 62.8, 36.6, 33.4, 28.2, 22.4; IR (neat): ν (cm^{-1}) 3075, 2968, 1733, 1581, 1597, 1323, 1217, 1166, 893, 749, 691. ESI-MS: (*m/z*) 247 (M^{+}+H), 269 (M^{+}+Na); HRMS calcd for $C_{15}H_{18}NaO_3$ (M+Na): 269.1148, found 269.1150.

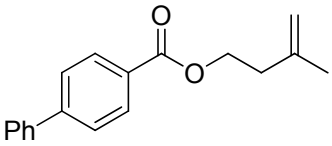


3-Methylbut-3-en-1-yl 2-(1,3-dioxoisoindolin-2-yl)acetate (A-12). In a three-necked round-bottom flask were palced glycine (2.25 g, 20 mmol), phthalic anhydride (4.44 g, 30 mmol), triethylamine (3.04 g, 30 mmol) and toluene (60 mL). The flask was equipped with a stirring bar, a Dean-Stark trap and a refluc condenser. The mixture was heated to reflux and stirred for 10 h with azeotropic removal of water. After the completion of reaction the solvent was removed in a rotary evaporator. The resulting white solid was taken up in water (250 mL) and the mixture was acidified with conc. HCl (6.0 mL). The product was collected by filtration, washed with water (2 × 30 mL) and dried to give 6.09 g (98% yield) of phthalimidoacetic acid as a white power.

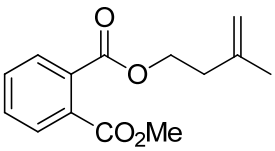
Compound **A-12** was then prepared from phthalimidoacetic acid and 3-methylbut-3-en-1-ol in 98% yield according to the procedure outlined for the synthesis of **A-4**. White solid, 56-58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.90 (m, 2H), 7.74-7.76 (m, 2H), 4.76 (s, 1H), 4.69 (s, 1H), 4.44 (s, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 167.2, 141.0, 134.2, 132.0, 123.6, 112.6, 63.9, 38.9, 36.5, 22.3; IR (KBr): ν (cm^{-1}) 3077, 2969, 1778, 1751, 1724, 1418, 1194, 1114, 956, 735, 714. Anal. calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13; Found: C, 65.64; H, 5.48; N, 5.15.



3-Methylbut-3-en-1-yl 4-cyanobenzoate (A-13). This compound was prepared from 4-cyanobenzoic acid and 3-methylbut-3-en-1-ol in 97% yield according to the procedure outlined for the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 4.86 (s, 1H), 4.81 (s, 1H), 4.48 (t, *J* = 6.8 Hz, 2H), 2.50 (t, *J* = 6.4 Hz, 2H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 141.3, 134.1, 132.1, 130.0, 117.9, 116.3, 112.6, 63.8, 36.6, 22.4; IR (neat): ν (cm^{-1}) 3075, 2970, 2232, 1725, 1651, 1406, 1377, 1275, 1108, 1020, 862, 767, 692. EIMS: *m/z* (rel intensity) 148 (4), 130 (100), 102 (70), 75 (14), 68 (94), 51 (8), 39 (9); HRMS calcd for C_8H_6NO (M-C_5H_7): 148.0399, found 148.0400.

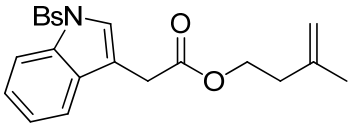


3-Methylbut-3-en-1-yl [1,1'-biphenyl]-4-carboxylate (A-14). This compound was prepared from 4-phenylbenzoic acid and 3-methylbut-3-en-1-ol in 95% yield according to the procedure outlined for the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.61-7.67 (m, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 4.86 (s, 1H), 4.83 (s, 1H), 4.46 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 6.8 Hz, 2H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 145.6, 141.7, 130.0, 128.9, 128.1, 127.3, 127.0, 112.4, 63.2, 36.8, 22.5; IR (neat): ν (cm^{-1}) 2960, 1720, 1609, 1277, 1113, 1008, 893, 748, 698. EIMS: *m/z* (rel intensity) 266 (M^+, 10), 198 (100), 181 (100), 152 (100), 127 (12), 76 (12), 68 (10); HRMS calcd for $C_{18}H_{18}O_2$ (M): 266.1307, found 266.1308.



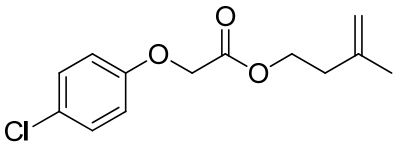
Methyl (3-methylbut-3-en-1-yl) phthalate (A-15). This compound was prepared from 2-methoxycarbonylbenzoic acid and 3-methylbut-3-en-1-ol in 97% yield according to the procedure outlined for the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.73 (m, 2H), 7.52-7.54 (m, 2H), 4.84 (s, 1H), 4.79 (s, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 2.46 (t, *J* = 6.8 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 167.5,

141.4, 132.1, 131.02, 131.00, 128.9, 128.8, 112.4, 63.8, 52.6, 36.5, 22.5; IR (neat): ν (cm^{-1}) 2953, 1736, 1728, 1434, 1291, 1125, 1072, 744. EIMS: *m/z* (rel intensity) 248 (M^+, 2), 216 (4), 181 (54), 163 (100), 149 (68), 133 (16), 104 (18), 92 (20), 77 (36), 68 (83); HRMS calcd for $C_{14}H_{16}O_4$ (M): 248.1049, found 248.1047.

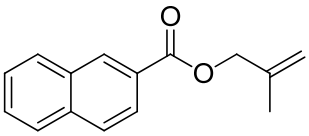


3-Methylbut-3-en-1-yl 2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)acetate (A-16). 3-Methylbut-3-en-1-yl 2-(1*H*-indol-3-yl)acetate was first prepared in 95% yield from the condensation of 2-(1*H*-indol-3-yl)acetic acid and 3-methylbut-3-en-1-ol according to the procedure outlined in the synthesis of **A-4**.

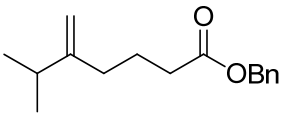
To a suspended solution of NaH (480 mg, 60% dispersion in mineral oil, 12 mmol) in THF (20 mL) at 0 °C was added dropwise 3-methylbut-3-en-1-yl 2-(1*H*-indol-3-yl)acetate (1.94 g, 8 mmol) in THF (5 mL). The reaction mixture was then stirred for 30 min at room temperature. The mixture was cooled down to 0 °C. Benzenesulfonyl chloride (1.22 mL, 9.6 mmol) was added and the resulting mixture was stirred for 12 h at rt. CH_2Cl_2 (20 mL) was added and the organic phase was washed with saturated Na_2CO_3 solution (3×15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel with hexane/ethyl acetate (6:1, v:v) as the eluent to afford **A-16** (2.77 g, 75% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.41-7.57 (m, 5H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 6.4 Hz, 1H), 4.73 (s, 1H), 4.64 (s, 1H), 4.22 (t, *J* = 6.8 Hz, 2H), 3.68 (s, 2H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 141.3, 138.2, 135.0, 133.8, 130.5, 129.2, 126.8, 124.9, 124.6, 123.3, 119.6, 115.3, 113.6, 112.4, 63.2, 36.6, 31.0, 22.3; IR (neat): ν (cm^{-1}) 2968, 1737, 1448, 1373, 1175, 1121, 981, 746; ESI-MS: (*m/z*) 406 (M^++Na); HRMS calcd for $C_{21}H_{21}NNaO_4S$ (M+Na): 406.1083, found 406.1073.



3-Methylbut-3-en-1-yl 2-(4-chlorophenoxy)acetate (A-18). This compound was prepared from 2-(4-chlorophenoxy)acetic acid and 3-methylbut-3-en-1-ol in 95% yield according to the procedure outlined for the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.81 (s, 1H), 4.72 (s, 1H), 4.59 (s, 2H), 4.33 (t, *J* = 6.8 Hz, 2H), 2.37 (t, *J* = 6.8 Hz, 2H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 156.4, 141.1, 129.4, 126.7, 116.0, 112.6, 65.5, 63.4, 36.6, 22.3; IR (neat): ν (cm^{-1}) 2969, 1760, 1738, 1595, 1492, 1294, 1192, 1080, 895, 825, 642. EIMS: *m/z* (rel intensity) 254 (M^+, 46), 186 (100), 141 (58), 128 (22), 111 (44), 99 (7), 75 (18), 68 (24); HRMS calcd for $C_{13}H_{15}O_3Cl$ (M): 254.0710, found 254.0708.



2-methylallyl 2-naphthoate (A-19). This compound was prepared from 2-naphthoic acid and 2-methylprop-2-en-1-ol in 95% yield according to the procedure outlined for the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.52-7.61 (m, 2H), 5.13 (s, 1H), 5.02 (s, 1H), 4.82 (s, 2H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 140.1, 135.6, 132.5, 131.1, 129.4, 128.25, 128.17, 127.8, 127.4, 126.6, 125.2, 113.0, 68.2, 19.6; IR (neat): ν (cm^{-1}) 3060, 2974, 1721, 1631, 1467, 1280, 1225, 1195, 1097, 778, 762, 474; EIMS: *m/z* (rel intensity) 226 (M^+, 56), 181 (17), 172 (14), 155 (100), 127 (100), 101 (12), 77 (14); HRMS calcd for $C_{15}H_{14}O_2$ (M): 226.0994, found 226.0992.

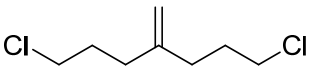


Benzyl 6-methyl-5-methyleneheptanoate (A-21). To the solution of glutaric anhydride (5 g, 43.9 mmol) in THF (20 mL) at 0 °C was added isopropylmagnesium bromide (2.0 M in THF, 43.9 mmol, 21.9 mL) dropwise. The mixture was refluxed for 10 h and then cooled down to

room temperature. The reaction was then quenched with saturated NH_4Cl solution (10 mL). The resulting mixture was partitioned between CH_2Cl_2 (50 mL) and 1 M HCl (50 mL). The organic layer was then separated, dried over anhydrous Na_2SO_4, and concentrated to give a yellow oil, which was purified by column chromatography on silica gel with hexane/ethyl acetate (4:1, v:v) as the eluent to afford 6-methyl-5-oxoheptanoic acid (56% yield) as a colorless oil.

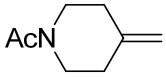
6-Methyl-5-methyleneheptanoic acid was then prepared in 77% yield as a colorless liquid via Wittig reaction of 6-methyl-5-oxoheptanoic acid and methyltriphenylphosphonium bromide following the procedure outlined in the synthesis of **A-23**.

Compound **A-22** was then prepared in 95% yield from the condensation of 6-methyl-5-methyleneheptanoic acid with benzyl alcohol according to the procedure outlined in the synthesis of **A-4**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.39 (m, 5H), 5.12 (s, 2H), 4.77 (s, 1H), 4.68 (s, 1H), 2.37 (t, J = 7.6 Hz, 2H), 2.17-2.25 (m, 1H), 2.06 (t, J = 7.6 Hz, 2H), 1.76-1.84 (m, 2H), 1.01 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 136.1, 128.5, 128.17, 128.16, 107.0, 66.1, 33.9, 33.6, 33.5, 23.3, 21.8; IR (neat): ν (cm^{-1}) 2962, 1736, 1698, 1685, 1559, 1541, 1458, 1158, 892, 750, 697; ESI-MS: (*m/z*) 269 (M^++Na); HRMS calcd for $C_{16}H_{22}O_2Na$ (M+Na): 269.1512, found 269.1509.



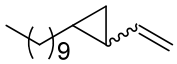
1,7-Dichloro-4-methyleneheptane (A-23). To a stirred solution of methyltriphenylphosphonium bromide (10.7 g, 30 mmol) in anhydrous THF (40 mL) was added *n*-butyllithium (12 mL, 30 mmol, 2.5 M in hexane) dropwise at 0 °C under nitrogen atmosphere. After addition, the solution was then warmed to room temperature and stirred for 30 min. 1,7-Dichloroheptan-4-one (1.83 g, 10.0 mmol) in anhydrous THF (10 mL) was then added dropwise. The solution was stirred at room temperature for 24 h. The resulting mixture was then diluted with CH_2Cl_2 (40 mL) and H_2O (20 mL). The two layers were separated and the aqueous phase was extracted by CH_2Cl_2 (15 mL × 3). The combined organic phase was then dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Purification by column chromatography on silica gel with hexane as the eluent afforded **A-23** (1.44 g, 80% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.82 (s, 2H), 3.55 (t, J =

6.8 Hz, 4H), 2.17 (t, J = 7.2 Hz, 4H), 1.88-1.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 110.8, 44.5, 32.9, 30.5; IR (neat): ν (cm^{-1}) 3078, 2957, 1646, 1443, 1308, 897, 777, 724, 654. EIMS: *m/z* (rel intensity) 180 (M^+, 6), 131 (5), 118 (71), 95 (12), 79 (18), 67 (37), 56 (100); HRMS calcd for $C_8H_{14}Cl_2$ (M): 180.0473, found 180.0469.



1-(4-Methylenepiperidin-1-yl)ethanone (A-24). To piperidin-4-one hydrochloride (2.73 g, 20 mmol) in CH_2Cl_2 (30 mL) was added dry triethylamine (8.3 mL, 60 mmol) at 0 °C. The mixture was stirred at room temperature for 15 min. Acetyl chloride (1.95 g, 25 mmol) was then added dropwise. The mixture was then stirred at room temperature for 3 h. The resulting mixture was partitioned between CH_2Cl_2 (30 mL) and saturated Na_2CO_3 (20 mL) solution. The aqueous phase was extracted with CH_2Cl_2 (30 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (1:1, v:v) as the eluent to afford pure 1-acetylpiperidin-4-one (2.68 g, 95%) as a colorless oil.

Compound **A-24** was then prepared in 75% yield from 1-acetylpiperidin-4-one and methyltriphenylphosphonium bromide via Wittig reaction following the procedure outlined in the synthesis of **A-23**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.77 (s, 2H), 3.58 (t, J = 5.6 Hz, 2H), 3.43 (t, J = 5.6 Hz, 2H), 2.17-2.24 (m, 4H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 144.4, 109.7, 47.8, 43.0, 34.9, 34.1, 21.4; IR (neat): ν (cm^{-1}) 3074, 2943, 1645, 1429, 1266, 1237, 989, 893, 660, 585. ESI-MS: (*m/z*) 140 (M^++H); HRMS calcd for $C_8H_{13}NONa$ (M+Na): 162.0889, found 162.0887.



1-Decyl-2-vinylcyclopropane (A-33). $Cu(OTf)_2$ (540 mg, 1.5 mmol, 5 mol%) and dodec-1-ene (20 mL, 90 mmol) were placed into a flame-dried flask, dissolved in anhydrous CH_2Cl_2 (100 mL) under N_2 atmosphere. Then ethyl diazoacetate (3.43 g, 30 mmol) dissolved in anhydrous CH_2Cl_2 (50 mL) was added slowly via a syringe pump within 5 h. After completion, the reaction mixture was stirred for additional 18 h. The solvent was removed and the reaction mixture was partitioned between CH_2Cl_2 (50 mL) and saturated NaCl (20 mL)

solution. The aqueous phase was extracted with CH_2Cl_2 (50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (50:1, v:v) as the eluent to afford pure ethyl 2-decylcyclopropanecarboxylate (*trans*/*cis* = 1:1, 5.33 g, 70%) as colorless oil.

To a solution of ethyl 2-decylcyclopropanecarboxylate (5.08 g, 20 mmol) in CH_2Cl_2 (50 mL) at -78° C was added a 1.5 M solution of DIBAL-H (13.5 mL, 20 mmol) in toluene. The mixture was stirred at -78° C until TLC indicated the completion of the reaction. A saturated solution of sodium tartrate was added and the reaction mixture was stirred overnight. The resulting mixture was extracted three times with dichloromethane (100 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered and evaporated. The 2-decylcyclopropanecarbaldehyde was obtained as colorless oil (4.07g, 97% yield) and was used for the next transformation without further purification.

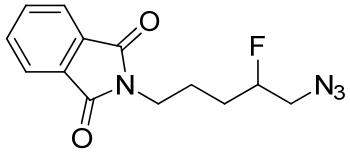
Finally, compound **A-33** was prepared from 2-decylcyclopropanecarbaldehyde and methyltriphenylphosphonium bromide via Wittig reaction according to the procedure outlined in the synthesis of **A-23** in 90% yield as the mixture of two stereoisomers in about 1:1 ratio. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34-5.62 (m, 1H), 4.79-5.12 (m, 2H), 0.19-1.56 (m, 25H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3/138.6, 113.6/110.8, 33.8/31.9, 29.7, 29.65, 29.63, 29.5, 29.4, 29.3, 29.1, 22.7/22.5, 21.1/19.8, 18.8, 14.1/13.9, 12.7; IR (neat): ν (cm^{-1}) 3067, 2924, 2854, 1635, 1466, 1027, 985, 892; EIMS: *m/z* (rel intensity) 208 (M^+, 6), 180 (10), 166 (3), 123 (13), 109 (27), 96 (56), 81 (80), 67 (86), 54 (100), 41 (62); HRMS calcd for $C_{15}H_{28}$ (M): 208.2191, found 208.2190.

2. Typical Procedure for the Azidofluorination.

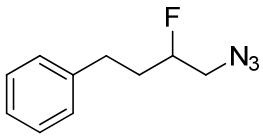
Typical Procedure for the Azidofluorination of Unactivated Alkenes. 2-(Pent-4-en-1-yl)-isoindoline-1,3-dione (**A-1**, 64.5 mg, 0.3 mmol), Selectfluor (212 mg, 0.6 mmol) were placed in a Schlenk-tube under nitrogen atmosphere, CF_3CO_2H (69 uL, 0.9 mmol), $TMSN_3$ (78 uL, 0.6 mmol), CH_3CN (1 mL) and water (2 mL) was then added successively at rt. The reaction mixture was then stirred at rt for 18 h. The resulting mixture was extracted with

dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (7:1, v:v) as the eluent to give the pure product 2-(5-azido-4-fluoropentyl)isoindoline-1,3-dione (**1**) as a yellow oil. Yield: 68 mg (83%).

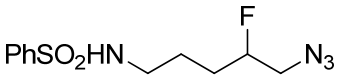
3. Characterizations of Products.



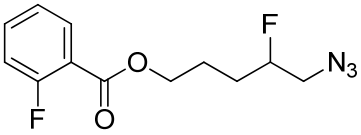
2-(5-Azido-4-fluoropentyl)isoindoline-1,3-dione (1). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.86 (m, 2H), 7.71-7.75 (m, 2H), 4.61-4.77 (m, 1H), 3.71-3.76 (m, 2H), 3.32-3.42 (m, 2H), 1.61-1.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 134.0, 132.0, 123.3, 92.0 (d, J = 173.1 Hz), 54.2 (d, J = 22.1 Hz), 37.3, 29.5 (d, J = 20.5 Hz), 24.1 (d, J = 4.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -185.7 (m, 1F); IR (neat): ν (cm^{-1}) 2929, 2103, 1773, 1712, 1467, 1438, 1398, 1050, 720; ESI-MS: (*m/z*) 299 (M^++Na); HRMS calcd for $C_{13}H_{13}FN_4NaO_2$ (M+Na): 299.0915, found 299.0919.



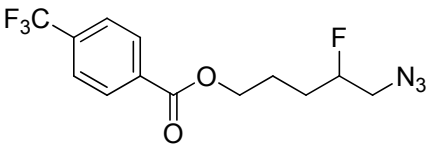
(4-Azido-3-fluorobutyl)benzene (2). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.2 Hz, 2H), 7.18-7.24 (m, 3H), 4.54-4.70 (m, 1H), 3.30-3.45 (m, 2H), 2.79-2.87 (m, 1H), 2.67-2.75 (m, 1H), 2.02-2.12 (m, 1H), 1.79-1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 128.6, 128.4, 126.3, 91.7 (d, J = 172.3 Hz), 54.3 (d, J = 22.0 Hz), 33.9 (d, J = 20.5 Hz), 30.9 (d, J = 4.6 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -186.0 (m, 1F); IR (neat): ν (cm^{-1}) 3028, 2930, 2103, 1497, 1455, 1281, 749, 700; EIMS: *m/z* (rel intensity) 164 (22), 144 (8), 135 (8), 118 (95), 104 (13), 91 (100), 77 (9), 65 (20); HRMS calcd for $C_{10}H_{11}NF$ (M-N_2H): 164.0876, found 164.0874.



***N*-(5-Azido-4-fluoropentyl)benzenesulfonamide (3).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.51-7.62 (m, 3H), 4.89 (br s, 1H), 4.52-4.65 (m, 1H), 3.26-3.41 (m, 2H), 2.98-3.03 (m, 2H), 1.57-1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 132.8, 129.2, 127.0, 92.1 (d, *J* = 173.1 Hz), 54.1 (d, *J* = 21.2 Hz), 42.6, 29.0 (d, *J* = 20.5 Hz), 25.1 (d, *J* = 3.8 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -185.3 (m, 1F); IR (neat): ν (cm^{-1}); IR (neat): ν (cm^{-1}) 3288, 2933, 2102, 1447, 1326, 1157, 1093, 755, 720; ESI-MS: (*m/z*) 309 (M^++Na); HRMS calcd for $C_{11}H_{15}FN_4NaO_2S$ (M+Na): 309.0792, found 309.0789.

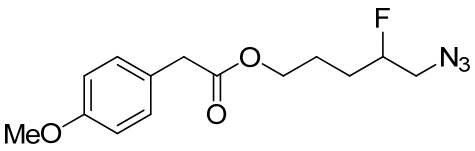


5-Azido-4-fluoropentyl 2-fluorobenzoate (4). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.95 (m, 1H), 7.50-7.55 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.11-7.16 (m, 1H), 4.64-4.80 (m, 1H), 4.34-4.44 (m, 2H), 3.36-3.46 (m, 2H), 1.71-2.01 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4 (d, *J* = 3.8 Hz), 161.9 (d, *J* = 258.1 Hz), 134.5 (d, *J* = 9.1 Hz), 132.1, 124.0 (d, *J* = 4.6 Hz), 118.6 (d, *J* = 9.9 Hz), 117.0 (d, *J* = 22.8 Hz), 92.2 (d, *J* = 173.1 Hz), 64.5, 54.2 (d, *J* = 22.0 Hz), 28.9 (d, *J* = 20.5 Hz), 24.2 (d, *J* = 4.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -109.3 (m, 1F), -185.4 (m, 1F); IR (neat): ν (cm^{-1}) 2961, 2103, 1728, 1613, 1489, 1457, 1299, 1130, 1084, 757; ESI-MS: (*m/z*) 292 (M^++Na); HRMS calcd for $C_{12}H_{13}F_2N_3NaO$ (M+Na): 292.0868, found 292.0861.

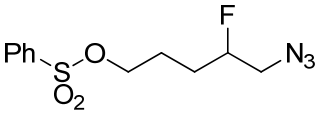


5-Azido-4-fluoropentyl 4-(trifluoromethyl)benzoate (5). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 4.64-4.79 (m, 1H), 4.36-4.46 (m, 2H), 3.38-3.48 (m, 2H), 1.69-2.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 134.6 (q, *J* = 32.4 Hz), 133.4, 130.0, 125.5 (q, *J* = 4.0 Hz), 123.6 (q, *J* = 270.9 Hz), 92.1 (d, *J* = 173.0 Hz), 64.8, 54.2 (d, *J* = 22.1 Hz), 29.0 (d, *J* = 21.3 Hz), 24.3 (d, *J* = 3.9 Hz); ^{19}F NMR (282

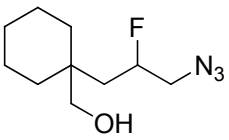
MHz , $CDCl_3$): δ -63.4 (s, 3F), -185.7 (m, 1F); IR (KBr): ν (cm^{-1}) 2928, 2105, 1725, 1327, 1277, 1130, 863, 776; EIMS: *m/z* (rel intensity) 300 (5), 190 (18), 173 (100), 145 (53), 95 (5), 88 (7), 73 (7), 55 (7); HRMS calcd for $C_{13}H_{13}F_3N_3O_2$ (M-F): 300.0960, found 300.0956.



5-Azido-4-fluoropentyl 2-(4-methoxyphenyl)acetate (6). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.51-4.67 (m, 1H), 4.07-4.17 (m, 2H), 3.79 (s, 3H), 3.55 (s, 2H), 3.27-3.37 (m, 2H), 1.49-1.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 158.7, 130.2, 126.0, 114.0, 92.1 (d, *J* = 173.1 Hz), 63.9, 55.2, 54.2 (d, *J* = 22.0 Hz), 40.5, 28.7 (d, *J* = 20.5 Hz), 24.1 (d, *J* = 4.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -185.8 (m, 1F); IR (neat): ν (cm^{-1}) 2958, 2103, 1732, 1613, 1514, 1464, 1248, 1157, 1033, 821; ESI-MS: (*m/z*) 318 (M^++Na); HRMS calcd for $C_{14}H_{18}FN_3NaO_3$ (M+Na): 318.1224, found 318.1226.

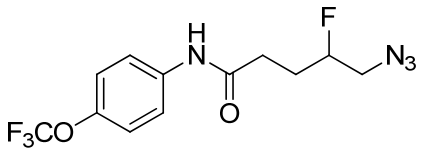


5-Azido-4-fluoropentyl benzenesulfonate (7). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 4.51-4.66 (m, 1H), 4.05-4.16 (m, 2H), 3.30-3.39 (m, 2H), 1.61-1.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.9, 129.3, 127.8, 91.8 (d, *J* = 173.1 Hz), 69.8, 54.1 (d, *J* = 21.3 Hz), 28.2 (d, *J* = 21.2 Hz), 24.5 (d, *J* = 3.8 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -186.1 (m, 1F); IR (neat): ν (cm^{-1}) 3068, 2929, 2104, 1448, 1360, 1290, 1187, 1097, 965, 755, 689, 589; ESI-MS: (*m/z*) 310 (M^++Na); HRMS calcd for $C_{11}H_{14}FN_3NaO_3S$ (M+Na): 310.0632, found 310.0623.

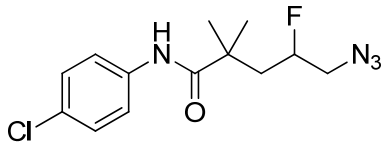


(1-(3-Azido-2-fluoropropyl)cyclohexyl)methanol (8). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.81-4.99 (m, 1H), 3.27-3.56 (m, 4H), 1.78-1.90 (m, 1H), 1.39-1.61 (m, 11H); ^{13}C

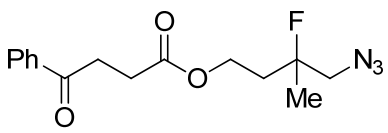
NMR (100 MHz, $CDCl_3$): δ 90.6 (d, *J* = 169.3 Hz), 68.3, 55.4 (d, *J* = 22.8 Hz), 36.8, 33.4 (d, *J* = 1.5 Hz), 32.4, 26.2, 21.3 (d, *J* = 5.3 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -180.0 (m, 1F); IR (neat): ν (cm^{-1}) 3422, 2930, 2857, 2104, 1454, 1290, 1043, 929, 862; ESI-MS: (*m/z*) 238 (M^++Na); HRMS calcd for $C_{10}H_{18}FN_3NaO$ (M+Na): 238.1326, found 238.1318.



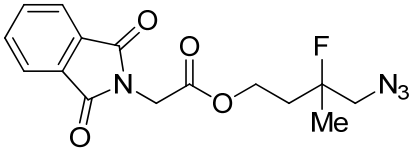
5-Azido-4-fluoro-*N*-(4-(trifluoromethoxy)phenyl)pentanamide (9). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.26 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.67-4.83 (m, 1H), 3.41-3.48 (m, 2H), 2.51-2.62 (m, 2H), 2.03-2.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 145.4, 136.2, 121.7, 121.1, 120.4 (q, *J* = 255.8 Hz), 91.8 (d, *J* = 173.1 Hz), 54.2 (d, *J* = 21.2 Hz), 32.2 (d, *J* = 3.8 Hz), 27.6 (d, *J* = 20.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -58.1 (s, 3F), -187.4 (m, 1F); IR (neat): ν (cm^{-1}) 3311, 2932, 2104, 1668, 1609, 1511, 1411, 1221, 1069, 847; ESI-MS: (*m/z*) 321 (M^++H), 343 (M^++Na); HRMS calcd for $C_{12}H_{12}F_4N_4NaO_2$ (M+Na): 343.0789, found 343.0794.



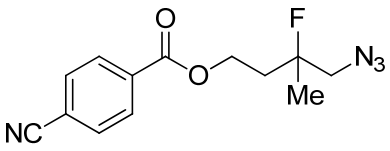
5-Azido-*N*-(4-chlorophenyl)-4-fluoro-2,2-dimethylpentanamide (10). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.41 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.73-4.88 (m, 1H), 3.34-3.43 (m, 2H), 1.91-2.01 (m, 2H), 1.41 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 136.1, 129.6, 129.0, 121.6, 91.0 (d, *J* = 172.3 Hz), 54.9 (d, *J* = 22.0 Hz), 42.5 (d, *J* = 19.0 Hz), 42.0, 26.8, 25.4 (d, *J* = 2.3 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -183.6 (m, 1F); IR (KBr): ν (cm^{-1}) 3339, 2970, 2105, 1662, 1593, 1521, 1493, 1397, 1090, 828; EIMS: *m/z* (rel intensity) 298 (M, 40), 278 (32), 250 (18), 197 (84), 138 (35), 127 (100), 96 (91), 81 (88), 41 (36); HRMS calcd for $C_{13}H_{16}N_4OFCl$ (M): 298.0997, found 298.0998.



4-Azido-3-fluoro-3-methylbutyl 4-oxo-4-phenylbutanoate (11). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.37 (dd, *J* = 19.2, 3.8 Hz, 2H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.76 (d, *J* = 6.8 Hz, 1H), 1.97-2.15 (m, 2H) , 1.43 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 172.7, 136.4, 133.3, 128.6, 128.0, 95.5 (d, *J* = 172.8 Hz), 59.8 (d, *J* = 6.6 Hz), 58.1 (d, *J* = 23.7 Hz), 35.9 (d, *J* = 22.8 Hz), 33.3, 28.2, 22.5 (d, *J* = 23.7 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -149.7 (m, 1F); IR (neat): ν (cm^{-1}) 2925, 2104, 1732, 1682, 1597, 1449, 1359, 1075, 987, 749, 691; ESI-MS: (*m/z*) 330 (M^++Na); HRMS calcd for $C_{15}H_{18}FN_3NaO_3$ (M+Na): 330.1224, found 330.1237.

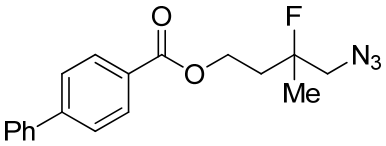


4-Azido-3-fluoro-3-methylbutyl 2-(1,3-dioxoisoindolin-2-yl)acetate (12). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.91 (m, 2H), 7.75-7.77 (m, 2H), 4.45 (s, 2H), 4.33 (t, *J* = 6.8 Hz, 2H), 3.33 (d, *J* = 18.8 Hz, 2H), 1.95-2.18 (m, 2H), 1.40 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 167.1, 134.3, 131.9, 123.6, 95.2 (d, *J* = 173.1 Hz), 61.0 (d, *J* = 6.8 Hz), 58.0 (d, *J* = 25.1 Hz), 38.9, 35.7 (d, *J* = 22.0 Hz), 22.4 (d, *J* = 23.6 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -150.4 (m, 1F); IR (neat): ν (cm^{-1}) 3482, 2985, 2107, 1778, 1724, 1469, 1418, 1312, 1193, 1115, 956, 735; ESI-MS: (*m/z*) 357 (M^++Na); HRMS calcd for $C_{15}H_{15}FN_4NaO_4$ (M+Na): 357.0970, found 357.0957.

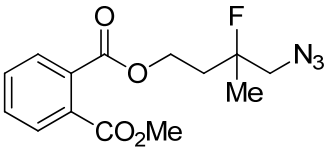


4-Azido-3-fluoro-3-methylbutyl 4-cyanobenzoate (13). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 4.53 (t, *J* = 6.8 Hz, 2H), 3.34-3.47 (m, 2H), 2.08-2.33 (m, 2H), 1.48 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 133.7, 132.3, 130.0, 117.9, 116.6, 95.3 (d, *J* = 173.1 Hz), 60.9 (d, *J* = 6.8 Hz), 58.1 (d, *J* = 25.0 Hz), 35.7 (d, *J* = 22.8 Hz), 22.6 (d, *J* = 23.6 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -150.4 (m, 1F); IR (neat): ν (cm^{-1}) 2985, 2231, 2105, 1725, 1459, 1277, 1108, 862,

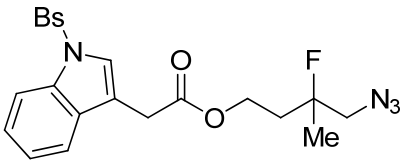
767; ESI-MS: (*m/z*) 299 (M^++Na); HRMS calcd for $C_{13}H_{13}FN_4O_2Na$ (M+Na): 299.0915, found 299.0911.



4-Azido-3-fluoro-3-methylbutyl [1,1'-biphenyl]-4-carboxylate (14). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 4.50 (t, *J* = 6.4 Hz, 2H), 3.35-3.47 (m, 2H), 2.10-2.31 (m, 2H), 1.49 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 145.8, 140.0, 130.1, 128.9, 128.7, 128.2, 127.3, 127.1, 95.5 (d, *J* = 172.3 Hz), 60.1 (d, *J* = 6.8 Hz), 58.2 (d, *J* = 24.3 Hz), 36.0 (d, *J* = 22.7 Hz), 22.6 (d, *J* = 23.6 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -150.1 (m, 1F); IR (neat): ν (cm^{-1}) 3058, 3032, 2983, 2104, 1713, 1609, 1386, 1276, 1113, 1077, 859, 749, 699; ESI-MS: (*m/z*) 350 (M^++Na); HRMS calcd for $C_{18}H_{18}FN_3NaO_2$ (M+Na): 350.1275, found 350.1281.

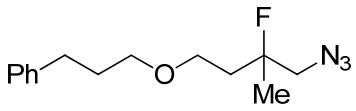


4-Azido-3-fluoro-3-methylbutyl methyl phthalate (15). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.76 (m, 1H), 7.67-7.71 (m, 1H), 7.53-7.57 (m, 2H), 4.48 (t, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 3.31-3.44 (m, 2H), 2.05-2.25 (m, 2H), 1.45 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 167.5, 132.1, 131.5, 131.3, 131.1, 129.0, 128.6, 95.4 (d, *J* = 173.1 Hz), 60.8 (d, *J* = 6.8 Hz), 58.1 (d, *J* = 24.2 Hz), 52.6, 35.8 (d, *J* = 22.0 Hz), 22.4 (d, *J* = 23.6 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -150.4 (m, 1F); IR (neat): ν (cm^{-1}) 2954, 2104, 1728, 1595, 1434, 1277, 1126, 1076, 959, 746; ESI-MS: (*m/z*) 332 (M^++Na); HRMS calcd for $C_{14}H_{16}FN_3NaO_4$ (M+Na): 331.1017, found 331.1017.

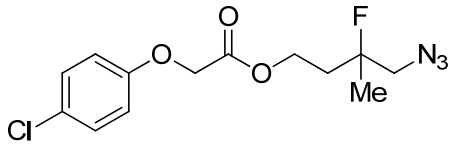


4-Azido-3-fluoro-3-methylbutyl 2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)acetate (16). Yellow

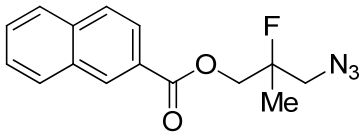
oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.42-7.57 (m, 5H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24-7.28 (m, 1H), 4.25 (t, *J* = 6.4 Hz, 2H), 3.70 (s, 3H), 3.21 (d, *J* = 18.8 Hz, 2H), 1.89-2.08 (m, 2H), 1.28 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 138.2, 135.0, 133.8, 130.3, 129.3, 126.8, 125.0, 124.6, 123.4, 119.5, 115.0, 113.7, 95.3 (d, *J* = 173.1 Hz), 60.2 (d, *J* = 6.9 Hz), 58.0 (d, *J* = 24.3 Hz), 35.7 (d, *J* = 22.8 Hz), 31.0, 22.3 (d, *J* = 23.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -150.1 (m, 1F); IR (neat): ν (cm^{-1}) 3065, 2982, 2104, 1732, 1447, 1372, 1277, 1174, 979, 748; ESI-MS: (*m/z*) 467 (M^++Na); HRMS calcd for $C_{21}H_{21}FN_4NaO_4S$ (M+Na): 467.1160, found 467.1154.



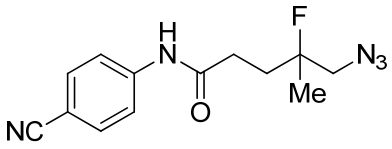
(3-(4-Azido-3-fluoro-3-methylbutoxy)propyl)benzene (17). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.30 (m, 5H), 3.30-3.57 (m, 6H), 2.68 (d, *J* = 7.2 Hz, 2H), 1.95-2.03 (m, 2H), 1.85-1.92 (m, 2H), 1.42 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 128.4, 128.3, 125.8, 96.2 (d, *J* = 170.8 Hz), 70.2, 65.8 (d, *J* = 7.6 Hz), 58.3 (d, *J* = 23.5 Hz), 37.2 (d, *J* = 22.1 Hz), 32.4, 31.2, 22.6 (d, *J* = 24.3 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -148.1 (m, 1F); IR (neat): ν (cm^{-1}) 2938, 2104, 1497, 1454, 1382, 1294, 1113, 747, 700; ESI-MS: (*m/z*) 288 (M^++Na); HRMS calcd for $C_{14}H_{20}FN_3NaO$ (M+Na): 288.1483, found 288.1479.



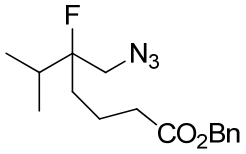
4-Azido-3-fluoro-3-methylbutyl 2-(4-chlorophenoxy)acetate (18). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 9.2 Hz, 2H), 6.83 (d, *J* = 9.2 Hz, 2H), 4.61 (s, 2H), 4.35-4.39 (m, 2H), 3.33 (d, *J* = 18.8 Hz, 2H), 1.95-2.18 (m, 2H), 1.40 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 156.3, 129.5, 126.8, 115.9, 95.3 (d, *J* = 173.1 Hz), 65.5, 60.5 (d, *J* = 6.8 Hz), 58.0 (d, *J* = 24.3 Hz), 35.7 (d, *J* = 22.8 Hz), 22.5 (d, *J* = 23.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -150.5 (m, 1F); IR (neat): ν (cm^{-1}) 2983, 2105, 1762, 1595, 1492, 1294, 1194, 1081, 826, 642; ESI-MS: (*m/z*) 338 (M^++Na); HRMS calcd for $C_{13}H_{15}ClFN_3NaO_3$ (M+Na): 338.0678, found 338.0670.



3-Azido-2-fluoro-2-methylpropyl 2-naphthoate (19). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.06 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.88-7.91 (m, 2H), 7.55-7.63 (m, 2H), 4.45-4.57 (m, 2H), 3.51-3.64 (m, 2H), 1.55 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 135.7, 132.4, 131.4, 129.4, 128.5, 128.4, 127.8, 126.8, 126.6, 125.1, 94.6 (d, *J* = 175.3 Hz), 66.4 (d, *J* = 26.6 Hz), 55.6 (d, *J* = 25.8 Hz), 20.2 (d, *J* = 23.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -158.4 (m, 1F); IR (neat): ν (cm^{-1}) 2927, 2106, 1722, 1630, 1465, 1390, 1281, 1195, 1096, 778; ESI-MS: (*m/z*) 310 (M^++Na); HRMS calcd for $C_{15}H_{14}FN_3NaO_2$ (M+Na): 310.0962, found 310.0967.

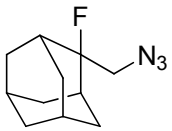


5-Azido-*N*-(4-cyanophenyl)-4-fluoro-4-methylpentanamide (20). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (br s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 3.37 (d, *J* = 18.8 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.16-2.27 (m, 1H), 1.98-2.11 (m, 1H), 1.41 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 142.0, 133.3, 119.5, 118.8, 107.0, 96.0 (d, *J* = 173.1 Hz), 58.1 (d, *J* = 24.3 Hz), 32.2 (d, *J* = 21.8 Hz), 31.3 (d, *J* = 4.5 Hz), 22.1 (d, *J* = 23.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -152.7 (m, 1F); IR (neat): ν (cm^{-1}) 3327, 2986, 2226, 2105, 1681, 1594, 1525, 1312, 1176, 840, 549; ESI-MS: (*m/z*) 274 (M^+-H); HRMS calcd for $C_{13}H_{13}FN_5O$ (M-H): 274.1110, found 274.1112.

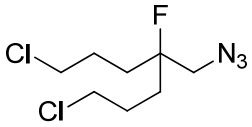


Benzyl 5-(azidomethyl)-5-fluoro-6-methylheptanoate (21). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.38 (m, 5H), 5.12 (s, 2H), 3.29-3.46 (m, 2H), 2.40 (t, *J* = 6.4 Hz, 2H), 2.07-2.16 (m, 1H), 1.61-1.75 (m, 4H), 0.92-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 135.9, 128.6, 128.3, 99.8 (d, *J* = 176.2 Hz), 66.3, 54.1 (d, *J* = 25.1 Hz), 34.2, 32.3 (d, *J* = 21.2 Hz), 31.6 (d, *J* = 22.8 Hz), 18.4 (d, *J* = 6.1 Hz), 16.8 (d, *J* = 6.1 Hz), 16.5 (d, *J* = 5.3

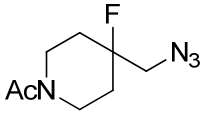
Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -163.1 (m, 1F); IR (neat): ν (cm^{-1}) 3034, 2968, 2103, 1738, 1456, 1294, 1260, 1161, 750, 698; ESI-MS: (*m/z*) 330 (M^++Na); HRMS calcd for $C_{16}H_{22}FN_3NaO_2$ (M+Na): 330.1588, found 330.1586.



2-(Azidomethyl)-2-fluoroadamantane (22). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (d, *J* = 25.2 Hz, 2H), 2.13-2.19 (m, 4H), 1.82-1.86 (m, 4H), 1.72 (s, 2H), 1.64 (t, *J* = 13.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 99.8 (d, *J* = 179.2 Hz), 55.0 (d, *J* = 23.6 Hz), 37.5, 34.9 (d, *J* = 8.4 Hz), 33.8 (d, *J* = 19.0 Hz), 32.6 (d, *J* = 3.1 Hz), 26.9 (d, *J* = 2.3 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -151.2 (m, 1F); IR (neat): ν (cm^{-1}) 2920, 2100, 1458, 1291, 1253, 1102, 923, 893, 859, 511; EIMS: *m/z* (rel intensity) 181 (6), 166 (6), 153 (100), 138 (13), 133 (34), 91 (44), 79 (22), 67 (14); HRMS calcd for $C_{11}H_{16}FN$ (M-N_2): 181.1267, found 181.1269.

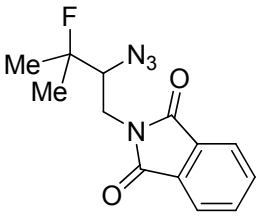


4-(Azidomethyl)-1,7-dichloro-4-fluoroheptane (23). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (t, *J* = 5.6 Hz, 4H), 3.37 (d, *J* = 18.0 Hz, 2H), 1.81-1.89 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 97.4 (d, *J* = 174.6 Hz), 55.9 (d, *J* = 25.8 Hz), 44.7, 32.5 (d, *J* = 22.0 Hz), 26.3 (d, *J* = 6.0 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -157.4 (m, 1F); IR (neat): ν (cm^{-1}) 2963, 2106, 1446, 1280, 922, 765, 653; EIMS: *m/z* (rel intensity) 185 (48), 164 (52), 149 (48), 129 (26), 113 (42), 93 (97), 73 (100), 59 (50); HRMS calcd for $C_7H_{12}Cl_2F$ (M-CH_2N_3): 185.0300, found 185.0299.

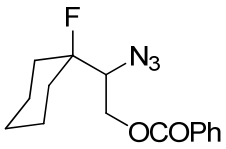


1-(4-(Azidomethyl)-4-fluoropiperidin-1-yl)ethanone (24). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49-4.54 (m, 1H), 3.69-3.74 (m, 1H), 3.26-3.49 (m, 3H), 2.90-2.97 (m, 1H), 2.11 (s, 3H), 1.91-2.05 (m, 2H), 1.48-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 93.6 (d, *J* = 175.3 Hz), 58.1 (d, *J* = 23.6 Hz), 41.9 (d, *J* = 2.3 Hz), 36.9 (d, *J* = 2.3 Hz), 32.8 (d, *J* =

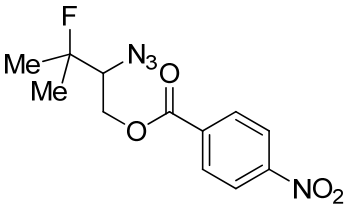
21.2 Hz), 32.1 (d, *J* = 21.3 Hz), 21.3; ^{19}F NMR (282 MHz , $CDCl_3$): δ -166.2 (m, 1F); IR (neat): ν (cm^{-1}) 2926, 2103, 1643, 1442, 1276, 971, 869, 738; ESI-MS: (*m/z*) 201 (M^++H), 223 (M^++Na); HRMS calcd for $C_8H_{13}FN_4NaO$ (M+Na): 223.0966, found 223.0962.



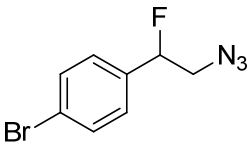
2-(2-Azido-3-fluoro-3-methylbutyl)isoindoline-1,3-dione (25). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.90 (m, 2H), 7.74-7.78 (m, 2H), 3.76-3.91 (m, 3H), 1.52 (d, *J* = 21.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 134.2, 131.8, 123.5, 96.4 (d, *J* = 171.6 Hz), 66.3 (d, *J* = 23.5 Hz), 37.5 (d, *J* = 6.9 Hz), 23.8 (d, *J* = 11.4 Hz), 23.6 (d, *J* = 11.4 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -142.7 (m, 1F); IR (neat): ν (cm^{-1}) 2988, 2114, 1775, 1713, 1468, 1399, 1254, 1010, 720; ESI-MS: (*m/z*) 299 (M^++Na); HRMS calcd for $C_{13}H_{13}FN_4NaO_2$ (M+Na): 299.0915, found 299.0911.



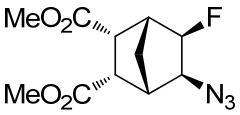
2-Azido-2-(1-fluorocyclohexyl)ethyl benzoate (26). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.74 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.36 (dd, *J* = 11.2, 9.2 Hz, 1H), 3.74-3.80 (m, 1H), 1.91-1.98 (m, 2H), 1.48-1.72 (m, 7H), 1.22-1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 133.3, 129.8, 129.4, 128.5, 95.9 (d, *J* = 175.4 Hz), 67.1 (d, *J* = 24.3 Hz), 63.8 (d, *J* = 5.3 Hz), 32.4 (d, *J* = 22.0 Hz), 31.5 (d, *J* = 22.0 Hz), 24.9, 21.3 (d, *J* = 2.3 Hz), 21.2 (d, *J* = 2.3 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -165.3 (m, 1F); IR (neat): ν (cm^{-1}) 2939, 2105, 1726, 1450, 1271, 1114, 711; ESI-MS: (*m/z*) 314 (M^++Na); HRMS calcd for $C_{15}H_{18}FN_3NaO_2$ (M+Na): 314.1275, found 314.1275.



2-Azido-3-fluoro-3-methylbutyl 4-nitrobenzoate (27). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H), 4.73 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.39 (dd, *J* = 11.6, 9.2 Hz, 1H), 3.84-3.90 (m, 1H), 1.51 (d, *J* = 20.4 Hz, 3H), 1.46 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 150.8, 134.7, 130.9, 123.7, 95.2 (d, *J* = 170.8 Hz), 67.1 (d, *J* = 25.0 Hz), 64.8 (d, *J* = 5.3 Hz), 24.6 (d, *J* = 23.5 Hz), 23.4 (d, *J* = 23.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -143.8 (m, 1F); IR (neat): ν (cm^{-1}) 2925, 2105, 1731, 1608, 1530, 1350, 1269, 1103, 719; EIMS: *m/z* (rel intensity) 230 (2), 207 (70), 177 (9), 164 (11), 150 (100), 134 (14), 104 (21), 76 (15); HRMS calcd for $C_9H_7N_4O_4$ (M-C_3H_6F): 235.0467, found 235.0468.

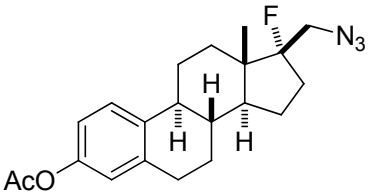


1-(2-Azido-1-fluoroethyl)-4-bromobenzene (28). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.50-5.65 (m, 1H), 3.60-3.70 (m, 1H), 3.40-3.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6 (d, *J* = 20.5 Hz), 132.0, 127.2 (d, *J* = 7.1 Hz), 123.2 (d, *J* = 1.6 Hz), 92.4 (d, *J* = 177.0 Hz), 55.7 (d, *J* = 24.5 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -182.8 (m, 1F); IR (neat): ν (cm^{-1}) 2926, 2107, 1596, 1490, 1405, 1261, 1011, 873, 821; EIMS: *m/z* (rel intensity) 243 (M^+, 11), 187 (100), 136 (12), 116 (4), 108 (38), 89 (9), 63 (6), 50 (5); HRMS calcd for $C_8H_7BrFN_3$ (M): 242.9807, found 242.9809.

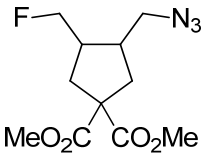


(1*R,2*S**,3*S**,4*S**,5*S**,6*R**)-Dimethyl 5-azido-6-fluorobicyclo[2.2.1]heptane-2,3-dicarboxylate (29).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (dd, *J* = 53.2, 5.6 Hz, 1H), 4.31 (t, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.12-3.17 (m, 1H), 3.00 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.78-2.81 (m, 1H), 2.55 (s, 1), 2.13 (d, *J* = 11.2 Hz, 1H), 1.39 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 171.4, 91.8 (d, *J* = 191.3 Hz), 61.2 (d, *J* = 13.7

Hz), 52.0, 51.9, 45.3 (d, J = 22.8 Hz), 44.9, 44.7, 43.5 (d, J = 9.1 Hz), 34.4; ^{19}F NMR (282 MHz , $CDCl_3$): δ -182.8 (m, 1F); IR (neat): ν (cm^{-1}) 2955, 2112, 1740, 1353, 1220, 1174; EIMS: *m/z* (rel intensity) 240 (15), 191 (11), 163 (19), 145 (48), 113 (100), 97 (36), 77 (15), 59 (42); HRMS calcd for $C_{10}H_{11}FN_3O_3$ (M-CH_3O): 240.0784, found 240.0788. The configuration was confirmed by the 2D NOESY experiments.

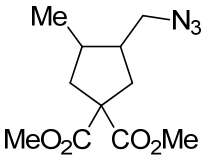


(8*R*,9*S*,13*S*,14*S*,17*R*)-17-(Azidomethyl)-17-fluoro-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl acetate (30). White solid, Mp 60-62 °C; $[\alpha]_D^{28}$ = -12.3 (c 1.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.79 (s, 1H), 3.37-3.54 (m, 2H), 2.87 (br s, 2H), 2.28-2.39 (m, 5H), 1.82-2.08 (m, 7H), 1.42-1.56 (m, 3H), 1.29-1.35 (m, 1H), 0.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 148.4, 138.1, 137.7, 126.4, 121.5, 118.6, 107.7 (d, J = 181.5 Hz), 54.1 (d, J = 23.5 Hz), 49.5, 47.0 (d, J = 19.0 Hz), 43.7, 38.2, 33.3 (d, J = 22.8 Hz), 30.7 (d, J = 5.3 Hz), 29.5, 27.5, 25.8, 23.4, 21.1, 14.7 (d, J = 5.3 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -155.4 (m, 1F); IR (KBr): ν (cm^{-1}) 2931, 2097, 1763, 1369, 1261, 1203, 1153, 1016, 894. ESI-MS: (*m/z*) 394 (M^++Na); HRMS calcd for $C_{21}H_{26}FN_3NaO_2$ (M+Na): 394.1901, found 394.1908. The configuration was confirmed by the 2D NOESY experiments.

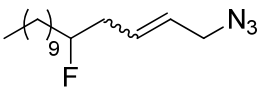


Dimethyl 3-(azidomethyl)-4-(fluoromethyl)cyclopentane-1,1-dicarboxylate (31). This compound was isolated as the mixture of two stereoisomers (*cis*/*trans* = 5:1 determined by ^{1}H NMR). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.35-4.52 (m, 2H), 3.72-3.76 (m, 6H), 3.34-3.49 (m, 2H), 2.39-2.53 (m, 4H), 2.04-2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 172.18/172.15, 84.8 (d, J = 168.5 Hz)/83.3 (d, J = 167.8 Hz), 58.7/54.3, 53.0/52.9, 51.82/51.80, 46.0/45.8, 42.7 (d, J = 18.9 Hz)/40.6 (d, J = 19.0 Hz), 41.1 (d, J = 3.8 Hz)/40.4 (d, J = 1.5 Hz), 38.1/37.7, 36.0 (d, J = 6.1 Hz)/35.4 (d, J = 7.6 Hz); ^{19}F NMR (282 MHz ,

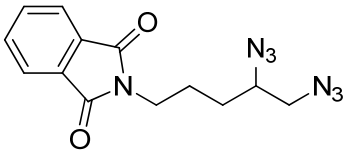
$CDCl_3$): δ -220.5/-222.0 (2m, 1F); IR (neat): ν (cm^{-1}) 2956, 2101, 1732, 1435, 1260, 1201, 996; ESI-MS: (*m/z*) 296 (M^++Na); HRMS calcd for $C_{11}H_{16}FN_3NaO_4$ (M+Na): 296.1017, found 296.1018. The relative configurations were confirmed by the 2D NOESY experiments.



Dimethyl 3-(azidomethyl)-4-methylcyclopentane-1,1-dicarboxylate (32). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 6H), 3.21-3.31 (m, 2H), 2.40-2.49 (m, 2H), 2.25-2.29 (m, 2H), 2.07-2.12 (m, 1H), 1.95-2.00 (m, 1H), 1.03 (d, *J* = 5.6 Hz, 0.5H)/0.91 (d, *J* = 6.8 Hz, 2.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.93, 172.87, 58.8/54.0, 52.8/52.7, 51.9, 46.3/45.7, 42.5/41.9, 41.2, 38.4/36.9, 37.4/35.0, 17.9/14.7; IR (neat): ν (cm^{-1}) 2956, 2102, 1740, 1435, 1270, 1201, 1173, 1149; ESI-MS: (*m/z*) 278 (M^++Na); HRMS calcd for $C_{11}H_{17}N_3NaO_4$ (M+Na): 278.1111, found 278.1111.

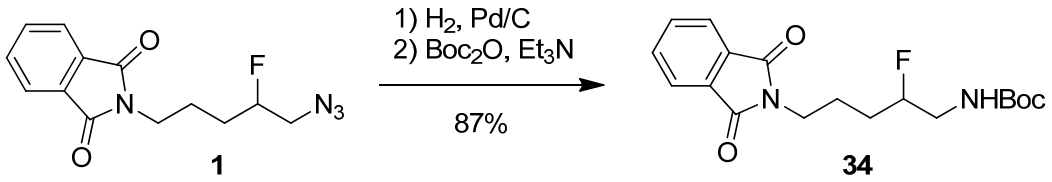


1-Azido-5-fluoropentadec-2-ene (33). This compound was isolated as the mixture of two stereoisomers (*E*/*Z* = 8:1 determined by ^{1}H NMR). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (major isomer) 5.75-5.83 (m, 1H), 5.59-5.66 (m, 1H), 4.42-4.61 (m, 1H), 3.74 (d, *J* = 6.4 Hz, 2H), 2.31-2.44 (m, 2H), 1.26-1.72 (m, 18H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (major isomer) 131.1 (d, *J* = 5.3 Hz), 126.1, 93.2 (d, *J* = 169.3 Hz), 52.6, 37.9 (d, *J* = 21.2 Hz), 34.6 (d, *J* = 20.5 Hz), 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 25.0 (d, *J* = 3.8 Hz), 22.6 (d, *J* = 1.6 Hz), 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ -185.4/188.7 (2m, 1F); IR (neat): ν (cm^{-1}) 2926, 2099, 1466, 1432, 1379, 1236, 972; EIMS: *m/z* (rel intensity) 240 (4), 221 (15), 180 (20), 128 (25), 108 (52), 94 (71), 80 (100), 68 (85); HRMS calcd for $C_{15}H_{27}NF$ (M-N_2H): 240.2128, found 240.2127.

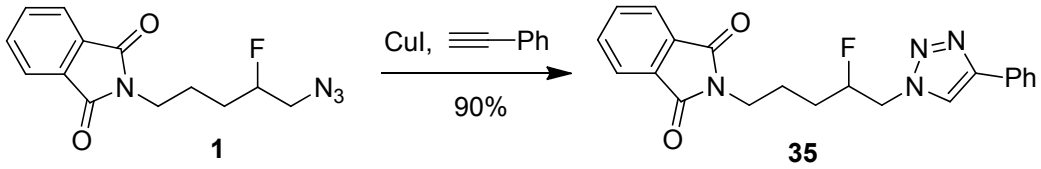


2-(3,4-Diazidopentyl)isoindoline-1,3-dione (1D). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.87 (m, 2H), 7.71-7.75 (m, 2H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.52-3.58 (m, 1H), 3.03-3.43 (m, 2H), 1.74-1.92 (m, 2H), 1.54-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 134.0, 132.0, 123.3, 61.5, 54.8, 37.2, 29.0, 25.1; IR (neat): ν (cm^{-1}) 2936, 2101, 1772, 1712, 1467, 1438, 1397, 1363, 1276, 1046, 720; ESI-MS: (*m/z*) 322 (M^++Na); HRMS calcd for $C_{13}H_{13}N_7NaO_2$ (M+Na): 322.1023, found 322.1017.

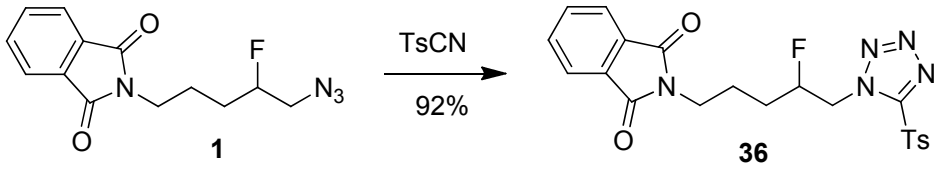
4. Procedures for Further Transformations of Azidofluorination Products.



***tert*-Butyl (5-(1,3-dioxoisoindolin-2-yl)-2-fluoropentyl)carbamate (34).** A solution of 2-(5-azido-4-fluoropentyl)isoindoline-1,3-dione (**1**, 82.9 mg, 0.3 mmol) in methanol (3 mL) was hydrogenated over 10% Pd/C for 6 h. The catalyst was removed by filtration and the solvent was evaporated to give a yellow residue. The residue was then treated with Boc_2O (131 mg, 0.6 mmol), Et_3N (83 uL, 0.6 mmol) and CH_2Cl_2 (3 mL). The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, v:v) as the eluent to afford pure product **34** (91.4 mg, 87% yield from two steps) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.84 (m, 4H), 4.85 (br, 1H), 4.51-4.64 (m, 1H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.39-3.46 (m, 1H), 3.13-3.23 (m, 1H), 1.51-1.89 (m, 4H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 155.9, 134.0, 132.0, 123.2, 92.8 (d, *J* = 169.3 Hz), 79.6, 44.4 (d, *J* = 20.5 Hz), 37.5, 29.6 (d, *J* = 3.8 Hz), 28.3, 24.2 (d, *J* = 3.8 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -187.7 (m, 1F); IR (neat): ν (cm^{-1}) 2929, 1773, 1713, 1515, 1397, 1366, 1172, 1052, 721; ESI-MS: (*m/z*) 373 (M^++Na); HRMS calcd for $C_{18}H_{23}FN_2O_4$ (M+Na): 373.1534, found 373.1522.



(2-(4-Fluoro-5-(4-phenyl-1H-1,2,3-triazol-1-yl)pentyl)isoindoline-1,3-dione (35). In a round bottom flask were added 2-(5-azido-4-fluoropentyl)isoindoline-1,3-dione (**1**, 82.9 mg, 0.3 mmol), phenylacetylene (49 uL, 0.45 mmol), CuI (11.4 mg, 0.06 mmol) and dimethylsulfoxide (1 mL) . The mixture was stirred at room temperature for 4 h. Water (10 mL) was added and the mixture was acidified with 1 N HCl and extracted with ethyl acetate (15 × 3 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:2, v:v) as the eluent to afford pure product **35** (102 mg, 90% yield) as white solid. Mp: 134-136 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82-7.87 (m, 5H), 7.70-7.72 (m, 2H), 7.42 (t, *J* = 6.8 Hz, 2H), 7.32-7.35 (m, 1H), 4.89-5.02 (m, 1H), 4.50-4.73 (m, 2H), 3.75 (t, *J* = 6.8 Hz, 2H), 1.85-1.97 (m, 2H), 1.69-1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 148.0, 134.0, 131.9, 130.4, 128.8, 128.2, 125.7, 123.2, 120.8, 91.3 (d, *J* = 173.9 Hz), 53.6 (d, *J* = 21.3 Hz), 37.1, 29.2 (d, *J* = 20.5 Hz), 23.9 (d, *J* = 3.8 Hz); ^{19}F NMR (282 MHz , $CDCl_3$): δ -184.8 (m, 1F); IR (KBr): ν (cm^{-1}) 3086, 2943, 1772, 1705, 1465, 1398, 1224, 1042, 770, 720; ESI-MS: (*m/z*) 379 (M^++H), 401 (M^++Na); HRMS calcd for $C_{21}H_{20}FN_4O_2$ (M+H): 379.1565, found 379.1554.



2-(4-Fluoro-5-(5-tosyl-1*H*-tetrazol-1-yl)pentyl)isoindoline-1,3-dione (36). 2-(5-Azido-4-fluoropentyl)isoindoline-1,3-dione (**1**, 82.9 mg, 0.3 mmol) and *p*-toluenesulfonyl cyanide (81.5 mg, 0.45 mmol) were placed in a vial and stirred neat for 5 h in an oil bath set to 100 ^oC. After completion of reaction, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, v:v) as the eluent afforded pure product **36** (126 mg, 92% yield) as white solid. Mp: 116-118 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.85-7.86 (m, 2H), 7.74-7.75 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 4.98-5.12 (m, 2H),

4.78-4.88 (m, 1H), 3.79 (t, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 1.79-2.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 155.3, 147.5, 134.2, 134.1, 132.0, 130.4, 129.3, 123.3, 90.5 (d, *J* = 177.7 Hz), 52.7 (d, *J* = 22.0 Hz), 37.1, 29.7 (d, *J* = 20.5 Hz), 23.9 (d, *J* = 3.0 Hz), 21.9; ^{19}F NMR (282 MHz , $CDCl_3$): δ -185.2 (m, 1F); IR (KBr): ν (cm^{-1}) 2931, 1774, 1711, 1594, 1399, 1352, 1160, 750, 664, 598, 533; ESI-MS: (*m/z*) 458 (M^++H), 480 (M^++Na); HRMS calcd for $C_{21}H_{20}FN_5NaO_4S$ (M+Na): 480.1112, found 480.1108.

5. References for Known Compounds.

entry	reference	compound
1	Whittaker, A. M; Lalic, G. *Org. Lett.* **2013**, *9*, 1112.	**A-1**
2	Zeng , W.; Chemler, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 12948.	**A-3**
3	Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 16410.	**A-7**
4	Zheng, T.; Narayan, R. S.; Schomaker, J. M.; Borhan, B. *J. Am. Chem. Soc*. **2005**, *127*, 6946.	**A-8**
5	Li, Z.; Song, L.; Li, C. *J. Am. Chem. Soc*. **2013**, *135*, 4640.	**A-9, A-10, A-20**
6	Murphy, J. A.; Schoenebeck, F.; Findlay, N. J.; Thomson, D. W.; Zhou, S.; Garnier, J. *J. Am. Chem. Soc*. **2009**, *131*, 6475.	**A-17**
7	Hughes, L.; Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc*. **1988**, *110*, 7494.	**A-22**
8	Takahashi, M.; McLaughlin, M.; Micalizio, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 3648.	**A-25**
9	Toshihiro, T.; Tohru, Y.; Teruaki, M. *Chem. Lett*. **1991**, 1499.	**A-26**
10	Traber, B.; Pfander, H. *Helv. Chim. Acta*, **1996,** *79*, 499.	**A-27**
11	Forcellese, M. L.; Camerini, E.; Ruffini, B.; Mincione, E. *J. Org. Chem*. **1981**, *46*, 3326.	**A-30**
12	Oliveira, C. C.; Dos Santos, E. A. F.; Bormio Nunes, J. H.;	**A-33**

	Correia, C. R. D. *J. Org. Chem.* **2012**, *77*, 8182.	

6. Complete References 4a, 11b and 23f.

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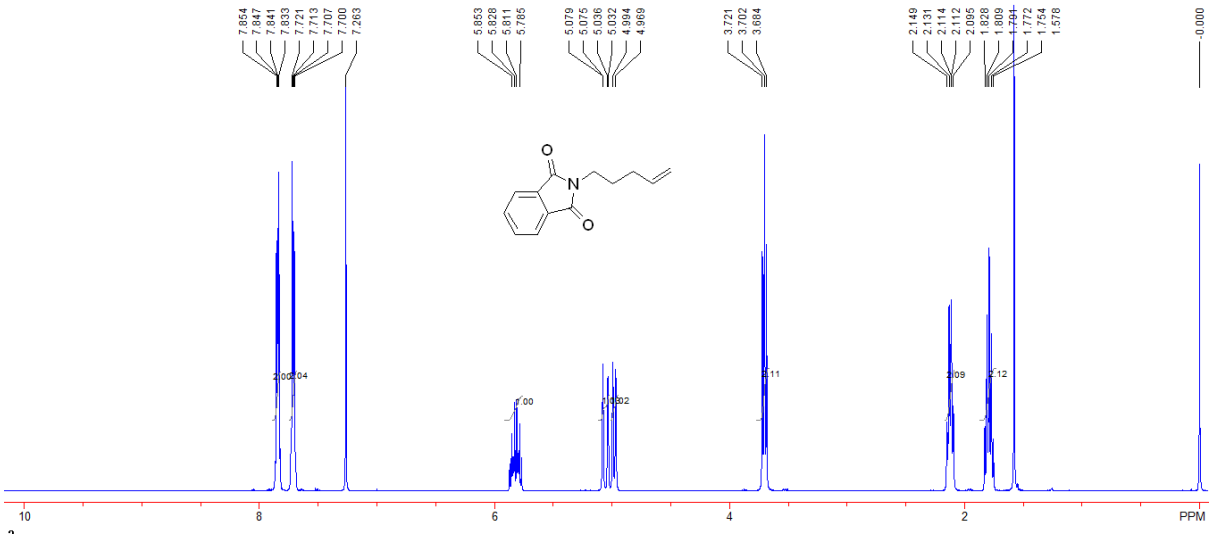
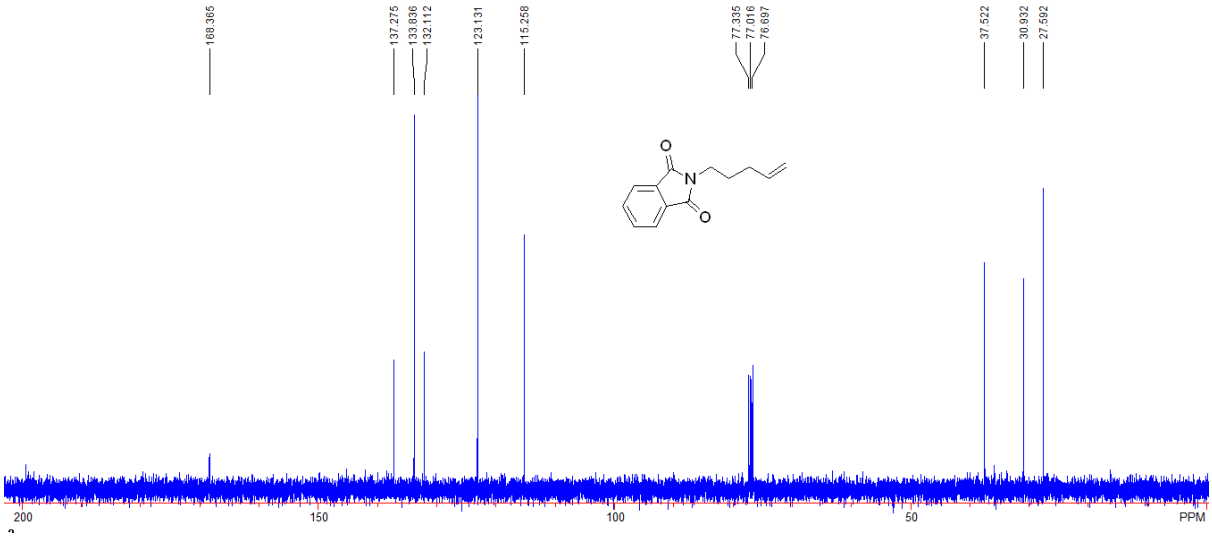
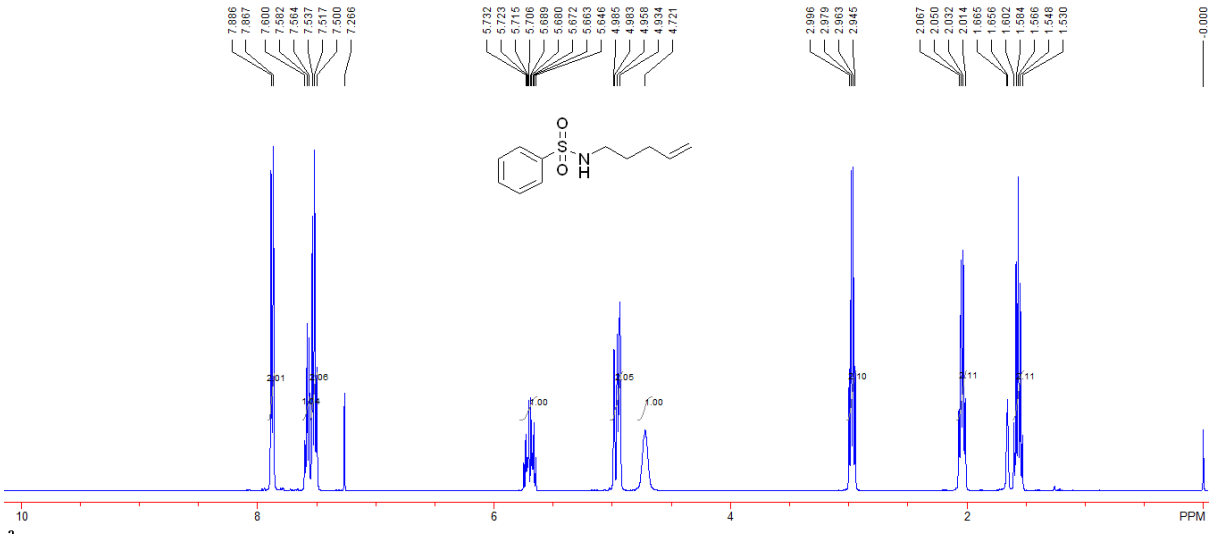
7. ^{1}H and ^{13}C NMR Spectra of Substrates.

Compound **A-1**





Compound **A-3**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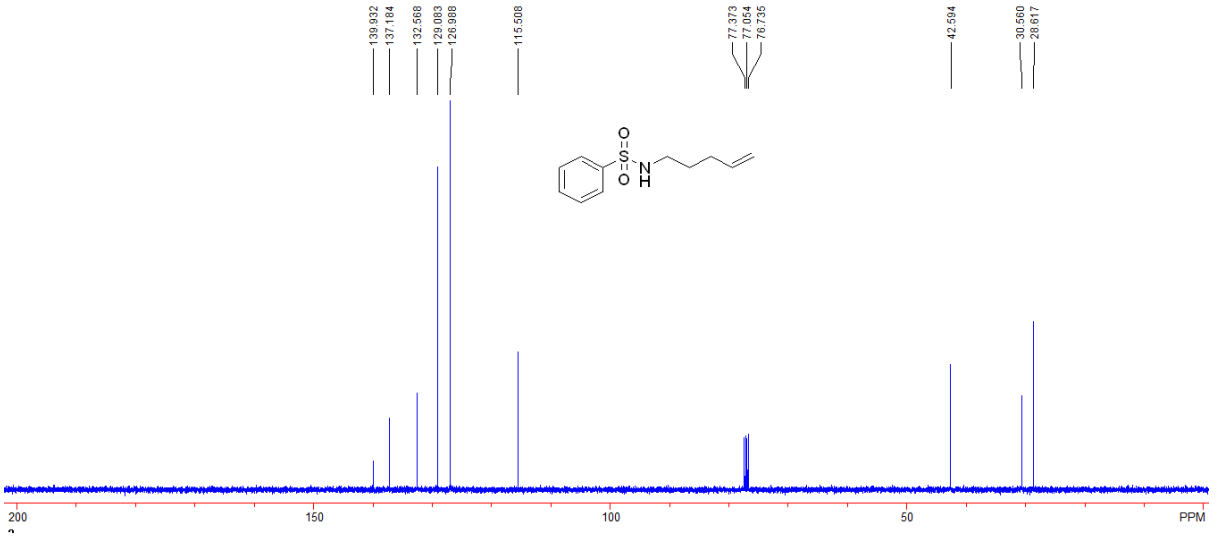
5.715
5.706
5.689
5.680
5.672
5.663
5.646
4.985
4.983
4.958
4.934
4.721
2.996
2.979
2.963
2.945
2.067
2.050
2.032
2.014
1.665
1.656
1.602
1.584
1.566
1.548
1.530
0.000
2.01
2.06
1.00
1.05
1.00
2.10
2.11
2.11
10
8
6
4
2
PPM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132.568
129.083
126.988
115.508
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77.054
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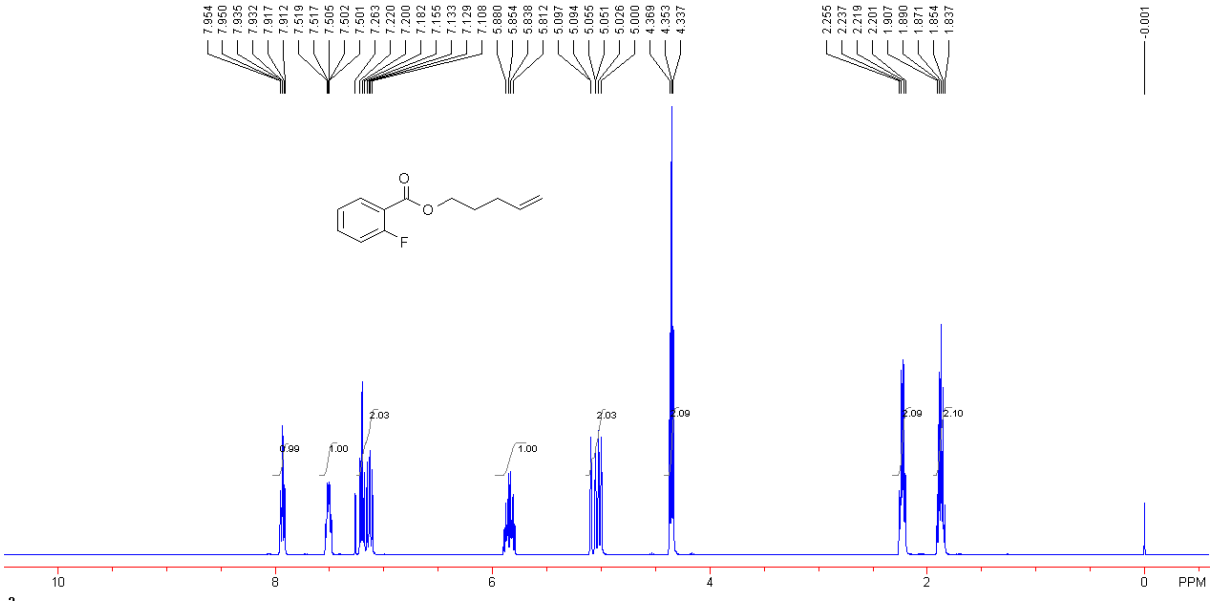
30.560
28.617
200
150
100
50
PPM

Compound **A-4**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7.935
7.932
7.917
7.912
7.519
7.517
7.505
7.502
7.501
7.263
7.220
7.200
7.182
7.155
7.133
7.129
7.108
5.880
5.854
5.838
5.812
5.097
5.094
5.055
5.051
5.026
5.000
4.369
4.353
4.337
2.255
2.237
2.219
2.201
1.907
1.890
1.871
1.854
1.837
0.001
O
O
F
0.99
1.00
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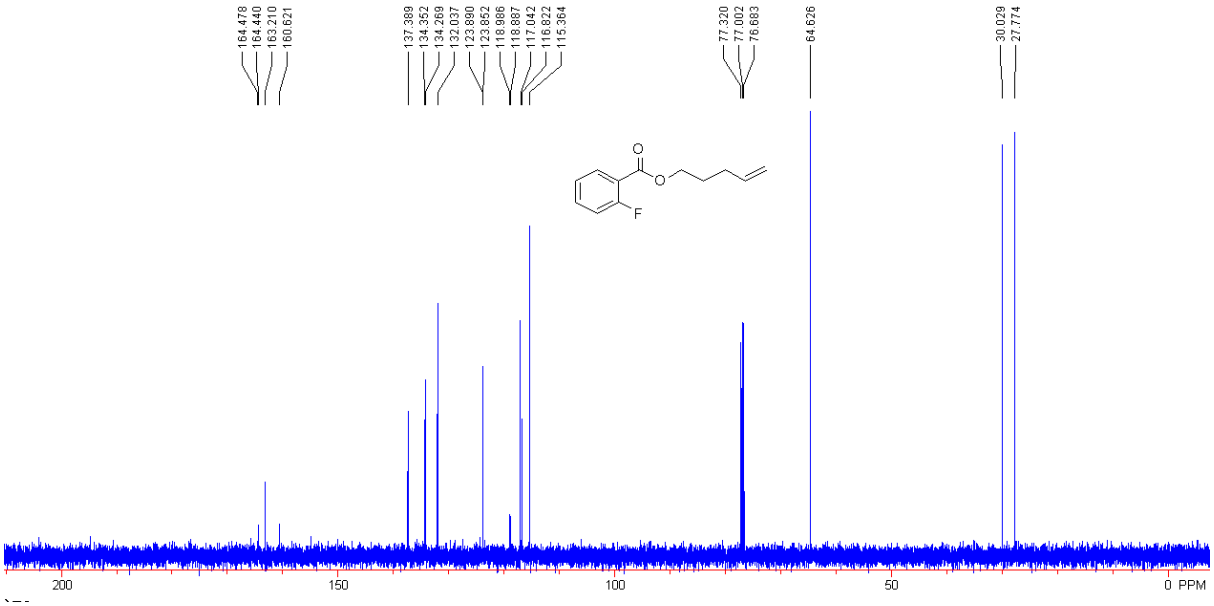
1.00
2.03
2.09
2.09
2.10
10
8
6
4
2
0
PPM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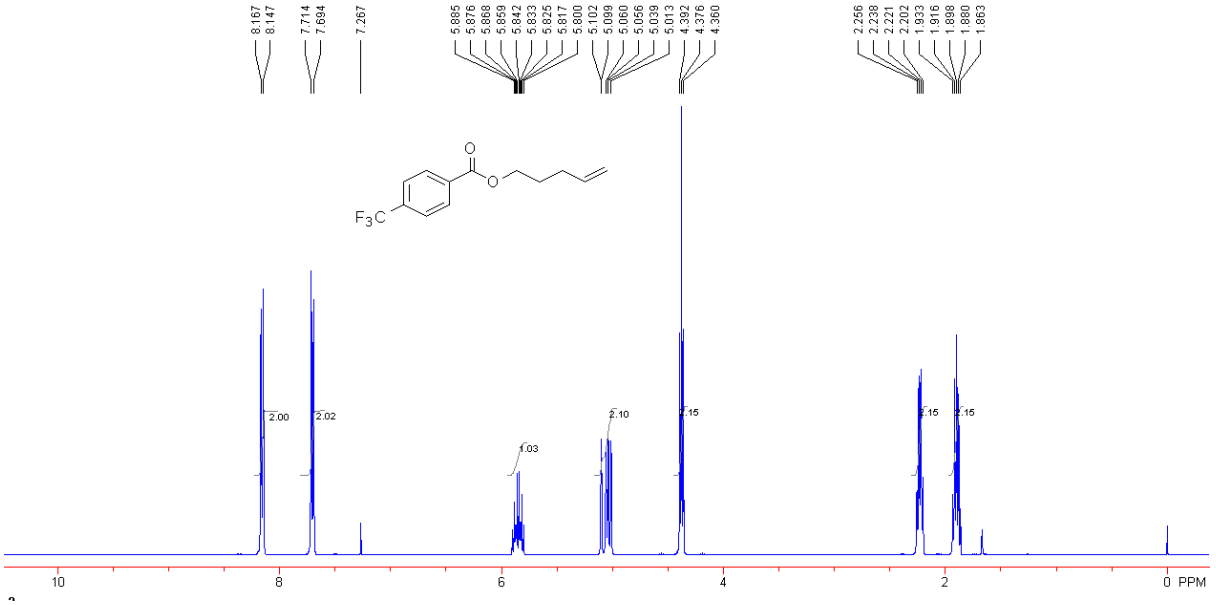
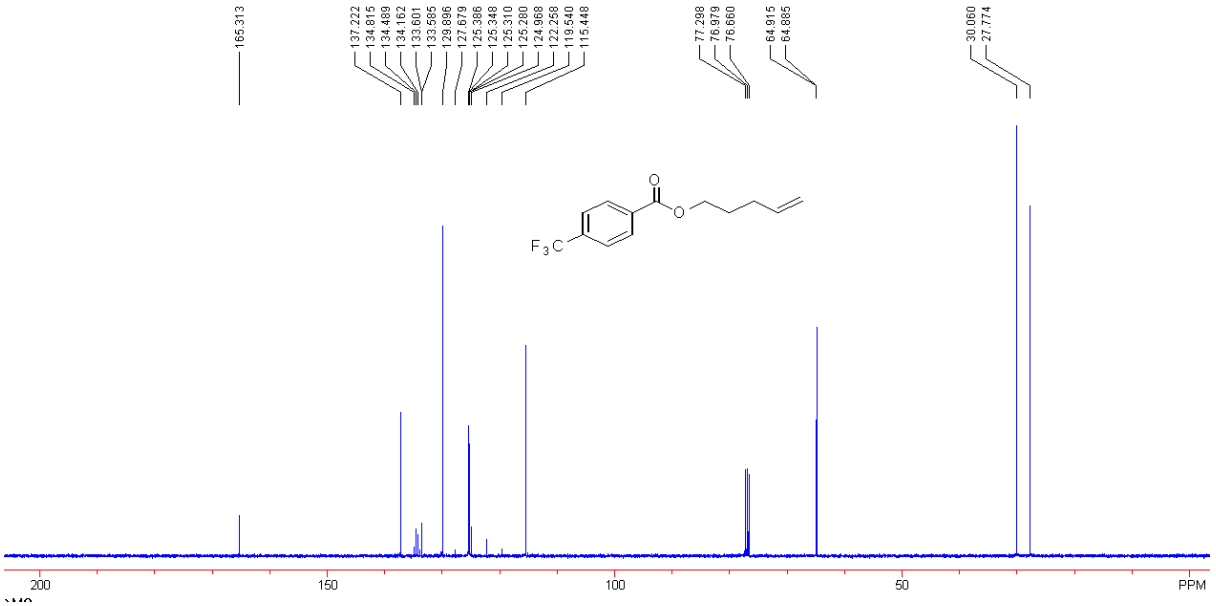
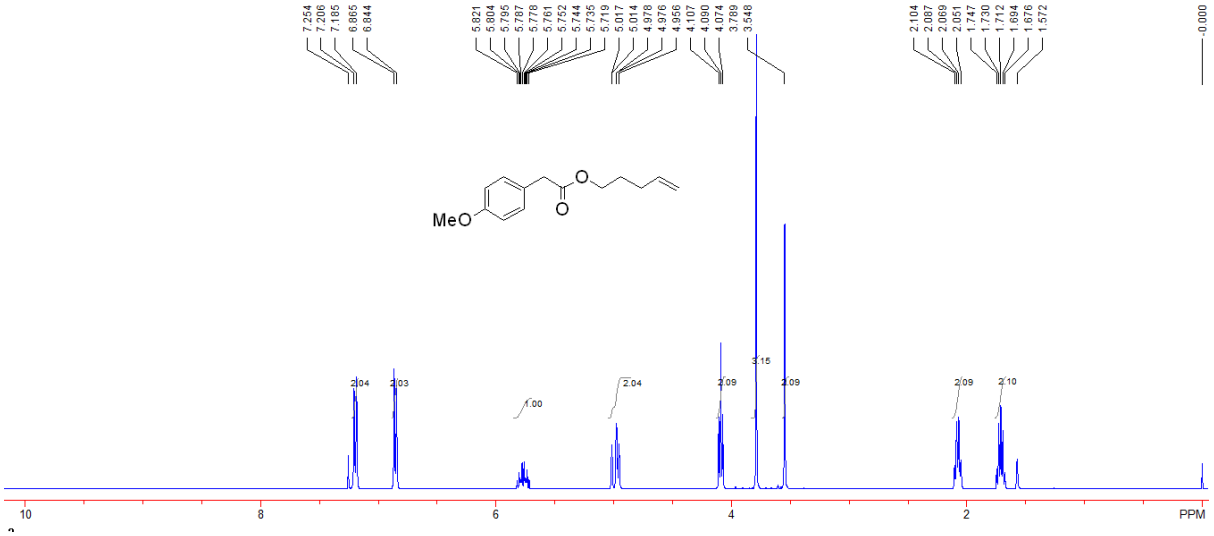
163.210
160.621
137.389
134.352
134.269
132.037
123.890
123.852
118.986
118.887
117.042
116.822
115.364
77.320
77.002
76.683
64.626
30.029
27.774
O
O
F
200
150
100
50
0 PPM

Compound **A-5**





Compound **A-6**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5.787
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5.761
5.752
5.744
5.735
5.719
5.017
5.014
4.978
4.976
4.956
4.107
4.090
4.074
3.789
3.548
2.104
2.087
2.069
2.051
1.747
1.730
1.712
1.694
1.676
1.572
0.000
MeO
O
O
2.04
2.03
1.00
2.04
2.09
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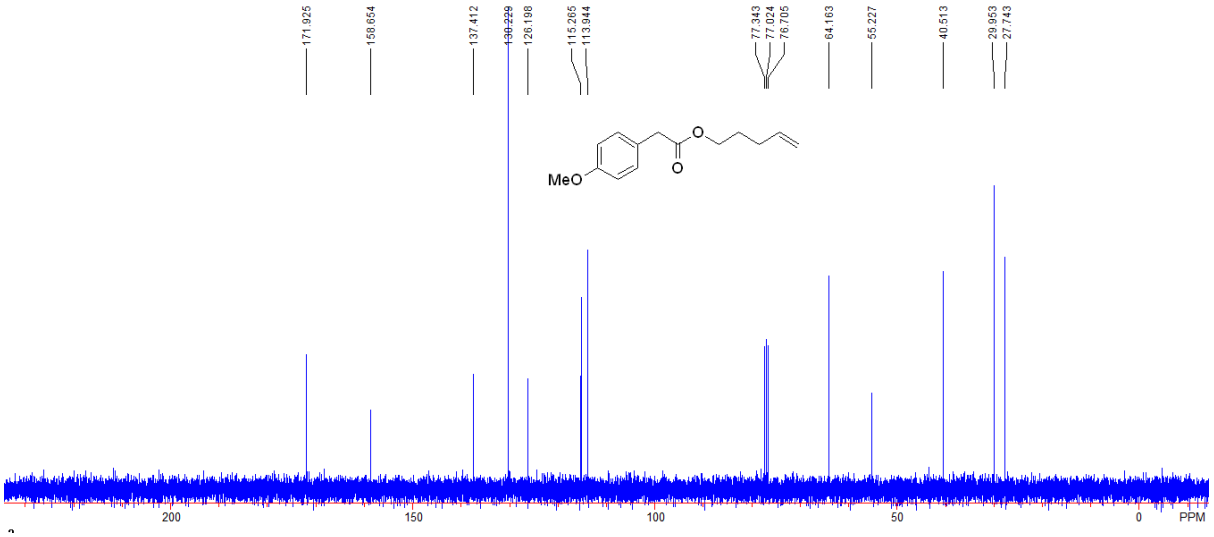
2.09
2.09
2.10
10
8
6
4
2
PPM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130.229
126.198
115.265
113.944
77.343
77.024
76.705
64.163
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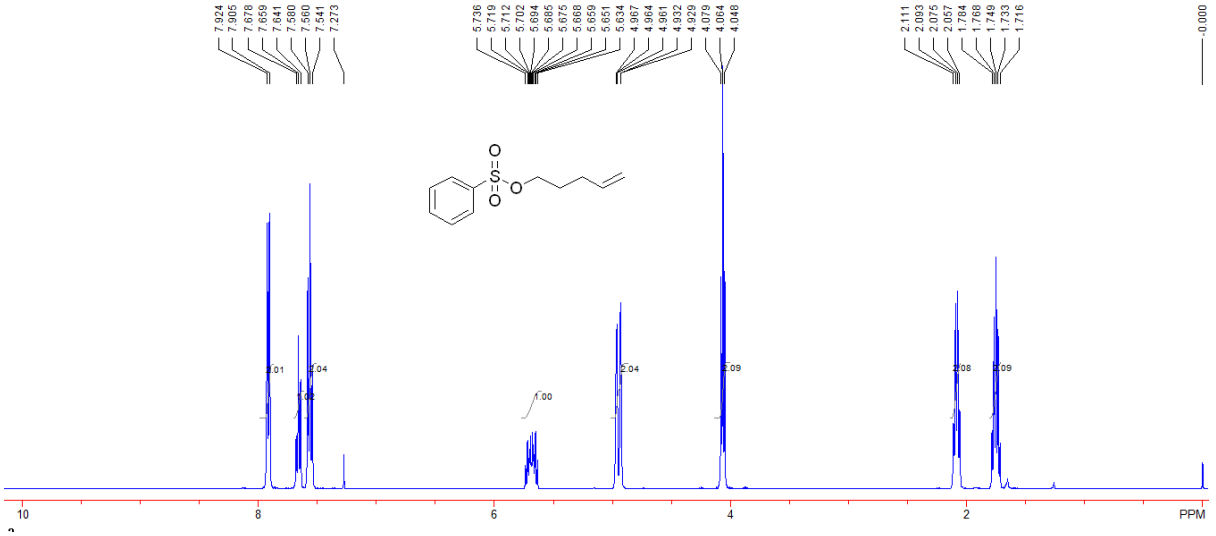
29.953
27.743
MeO
O
O
200
150
100
50
0
PPM

Compound **A-7**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7.641
7.560
7.560
7.541
7.273
5.736
5.719
5.712
5.702
5.694
5.685
5.675
5.668
5.659
5.651
5.634
4.967
4.964
4.961
4.932
4.929
4.079
4.064
4.048
2.111
2.093
2.075
2.057
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1.749
1.733
1.716
0.000
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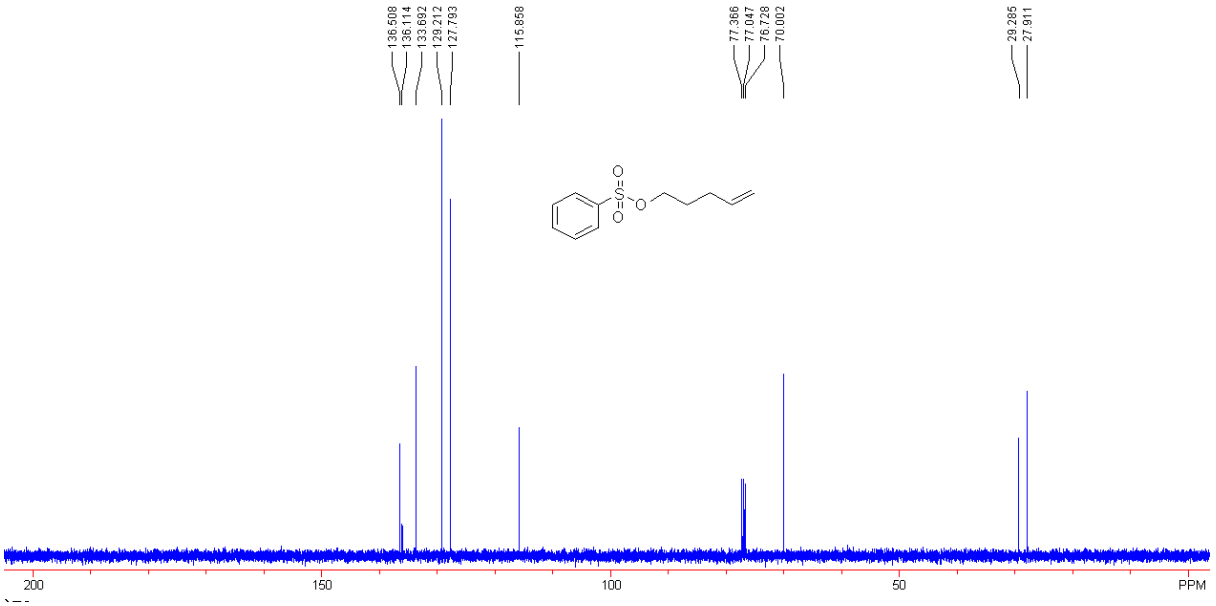
1.00
2.04
3.09
2.08
3.09
10
8
6
4
2
PPM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133.692
129.212
127.793
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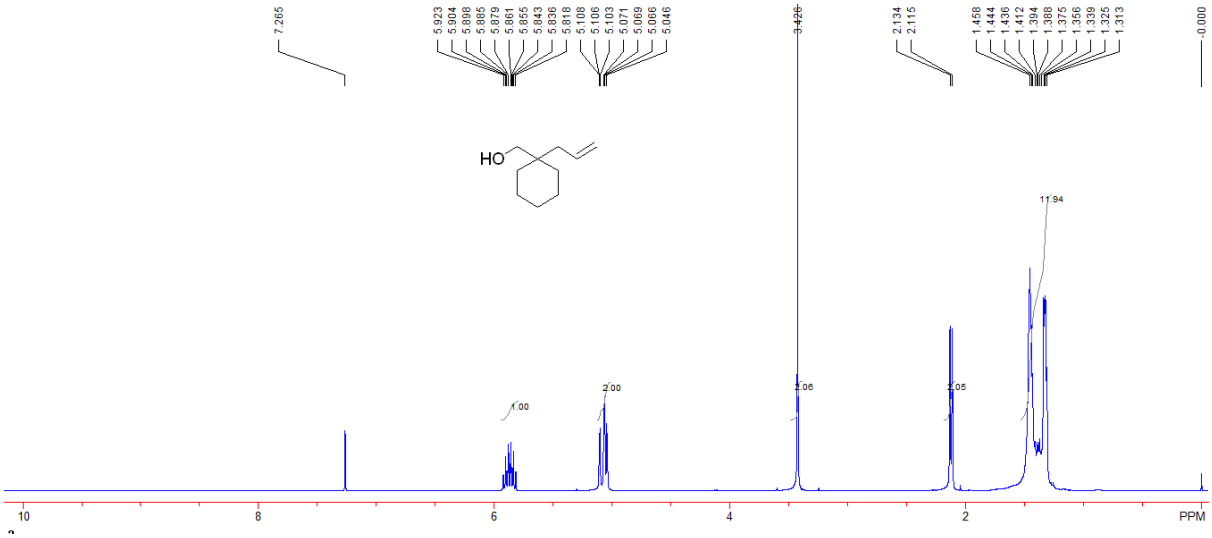
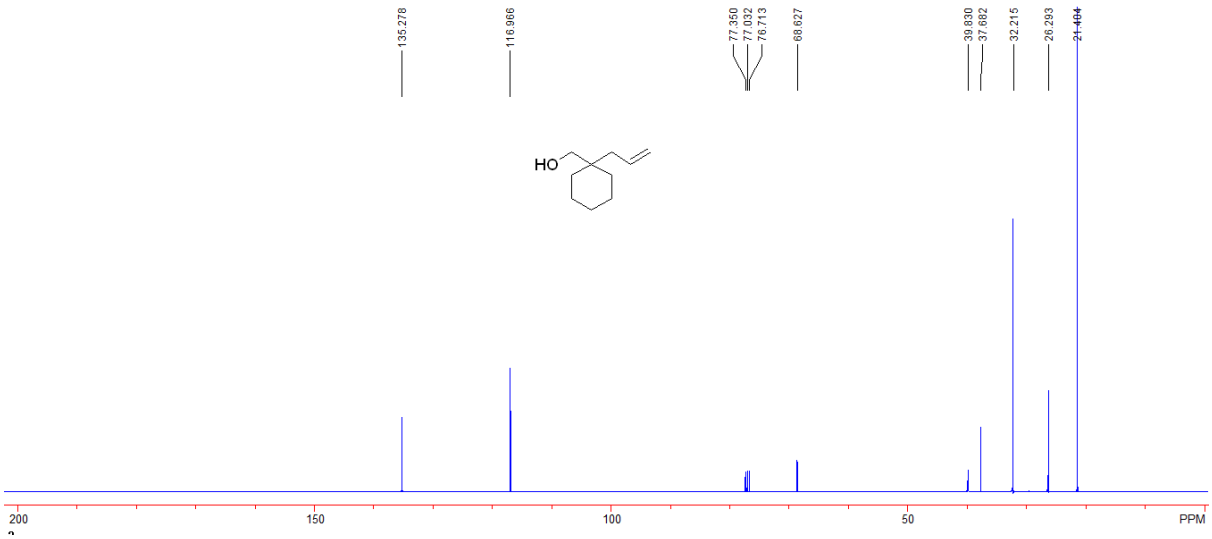
77.047
76.728
70.002
29.285
27.911
200
150
100
50
PPM

Compound **A-8**





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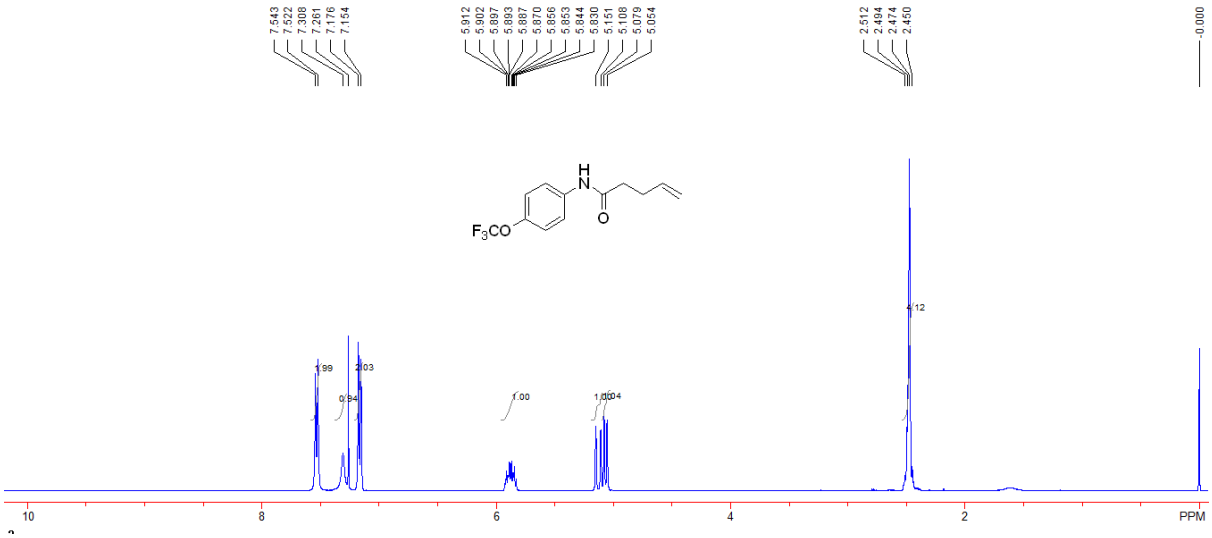
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7.154
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5.902
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5.893
5.887
5.870
5.856
5.853
5.844
5.830
5.151
5.108
5.079
5.054
2.512
2.494
2.474
2.450
0.000
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2.03
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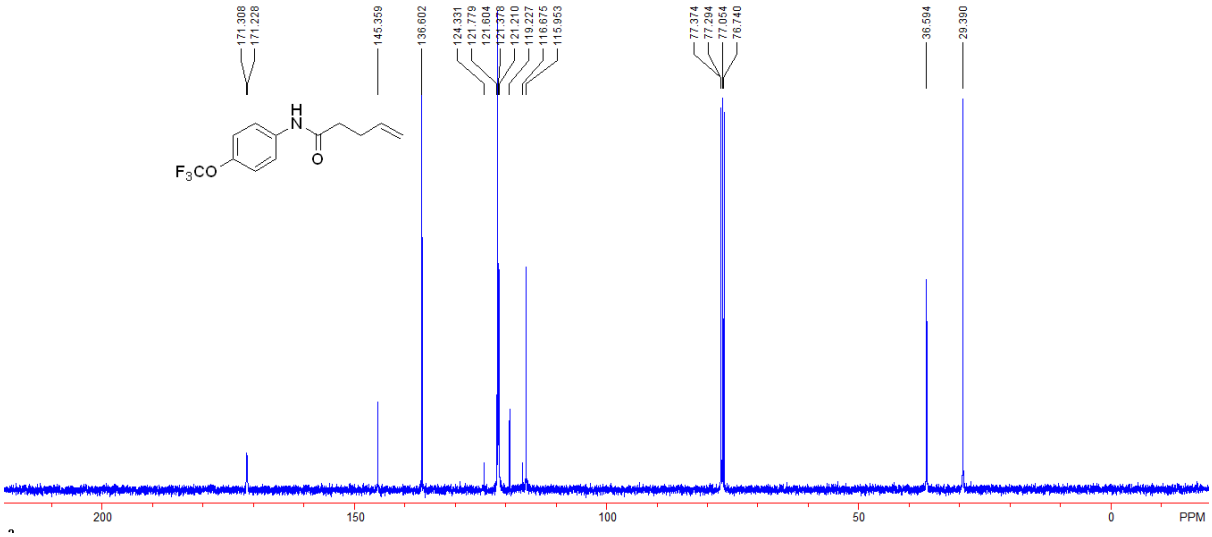
1.004
10
8
6
4
2
PPM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121.604
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119.227
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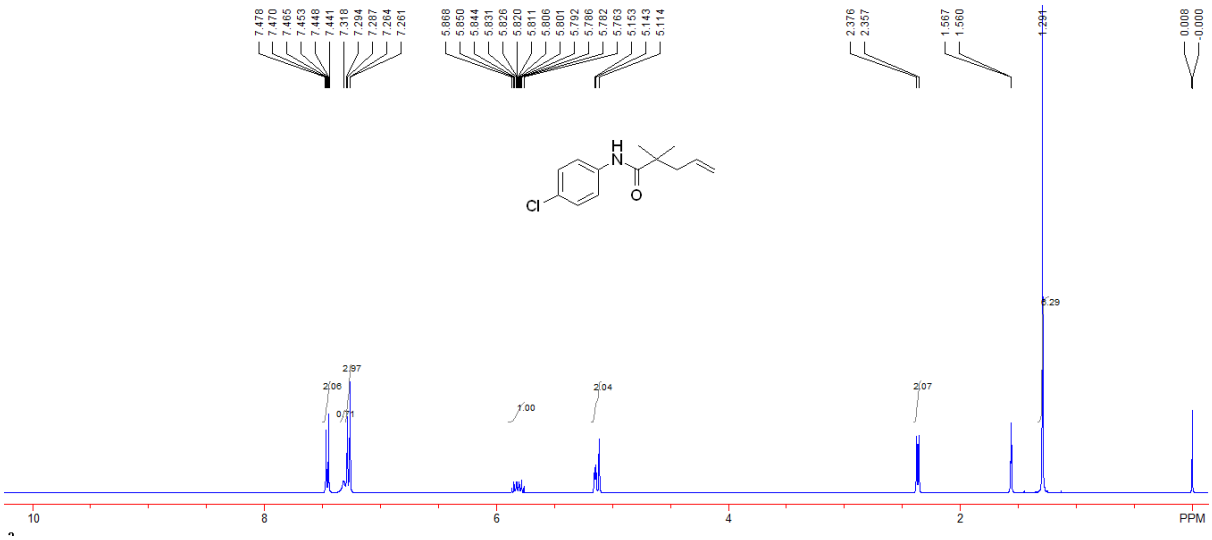
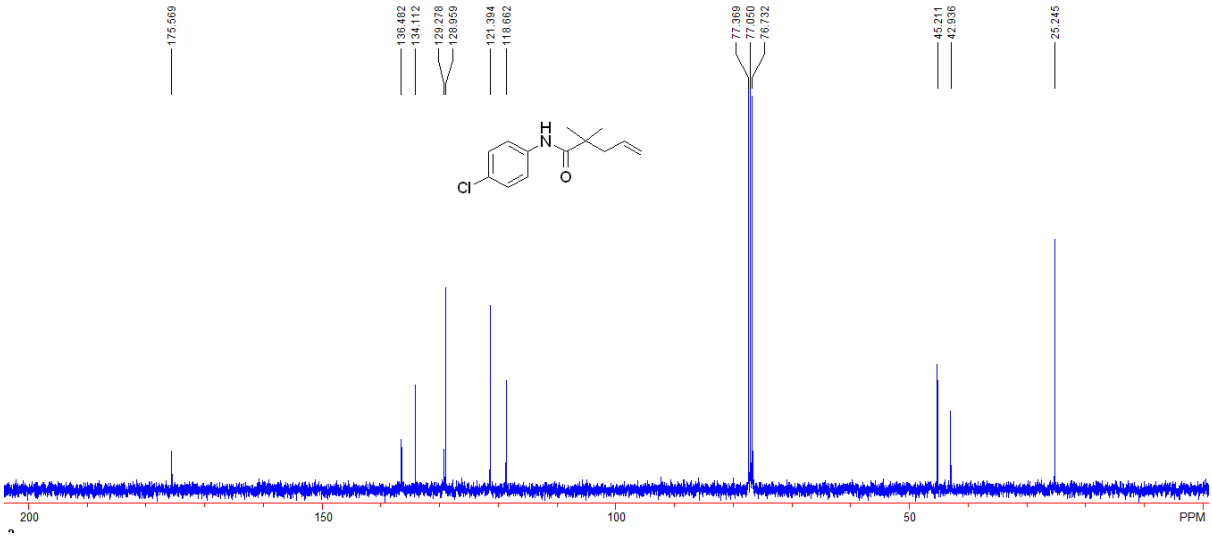
115.953
77.374
77.294
77.054
76.740
36.594
29.390
H
N
O
F3CO
200
150
100
50
0
PPM

Compound **A-10**





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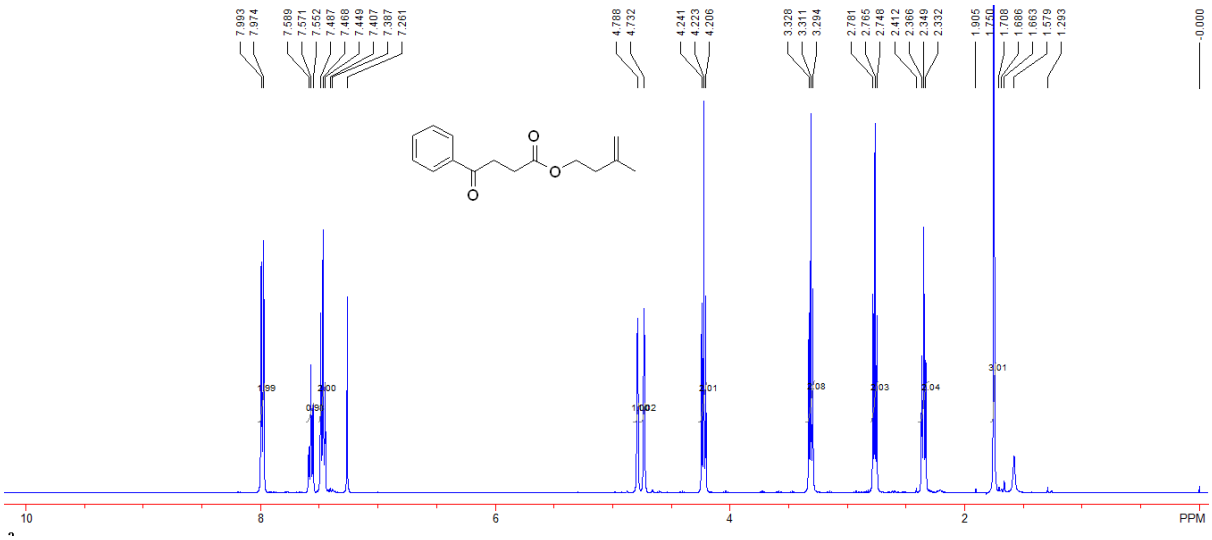

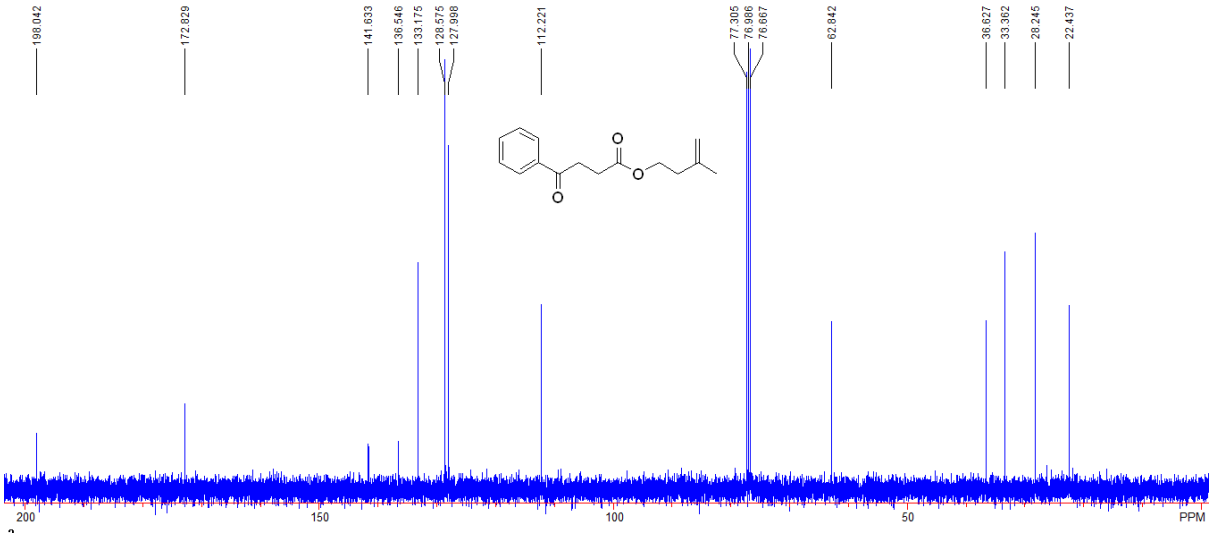

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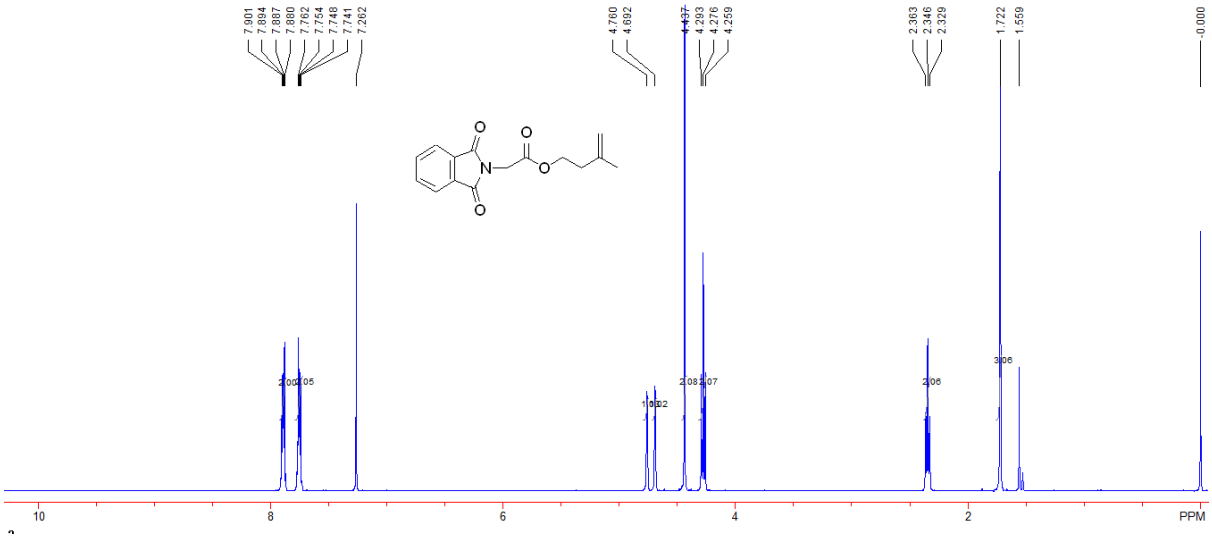

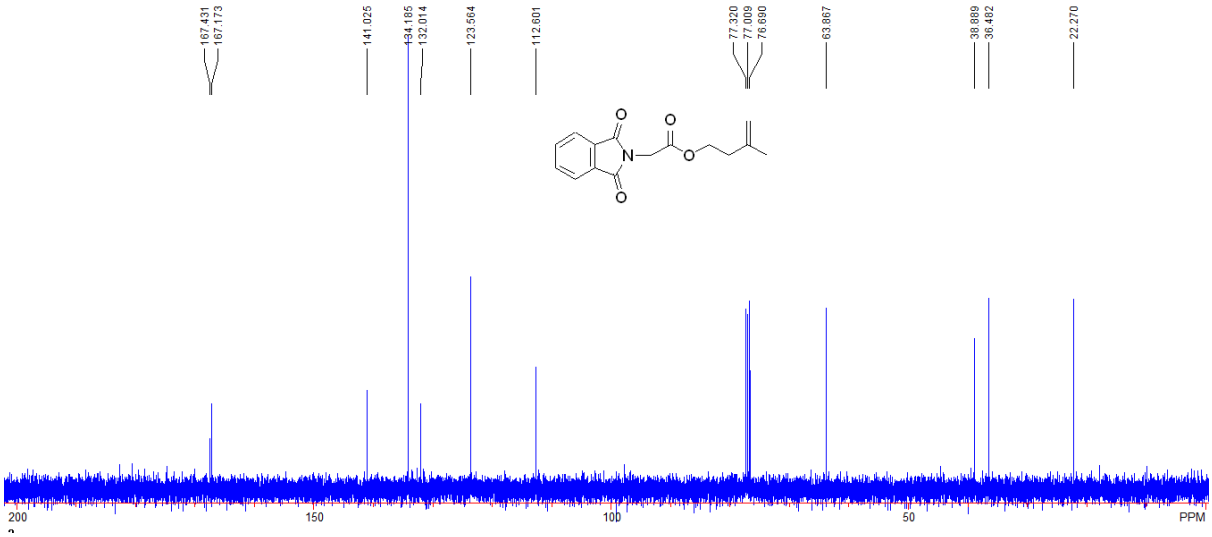

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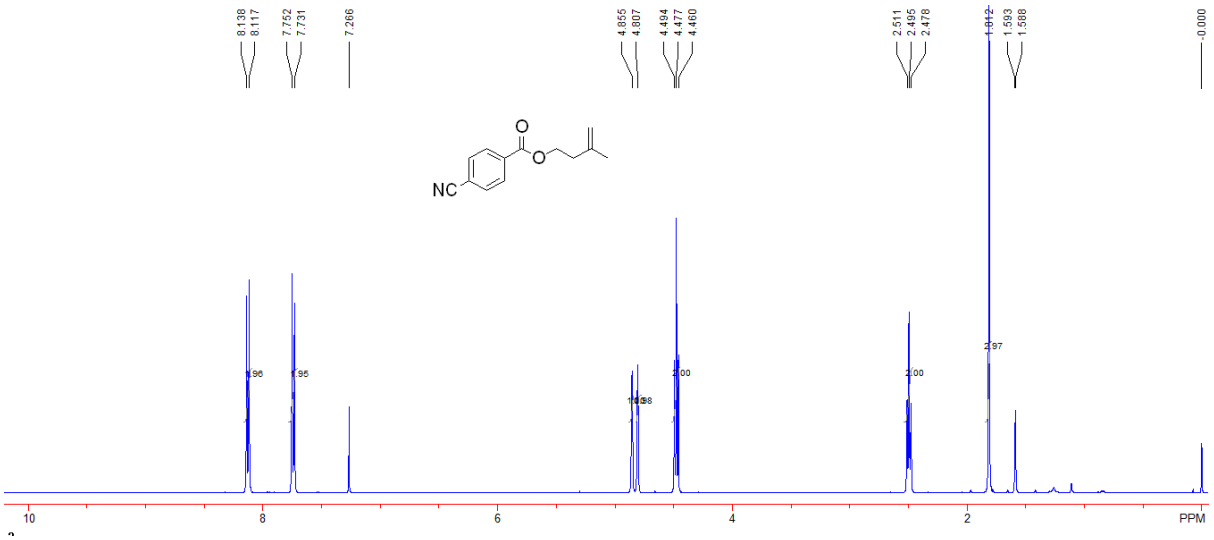

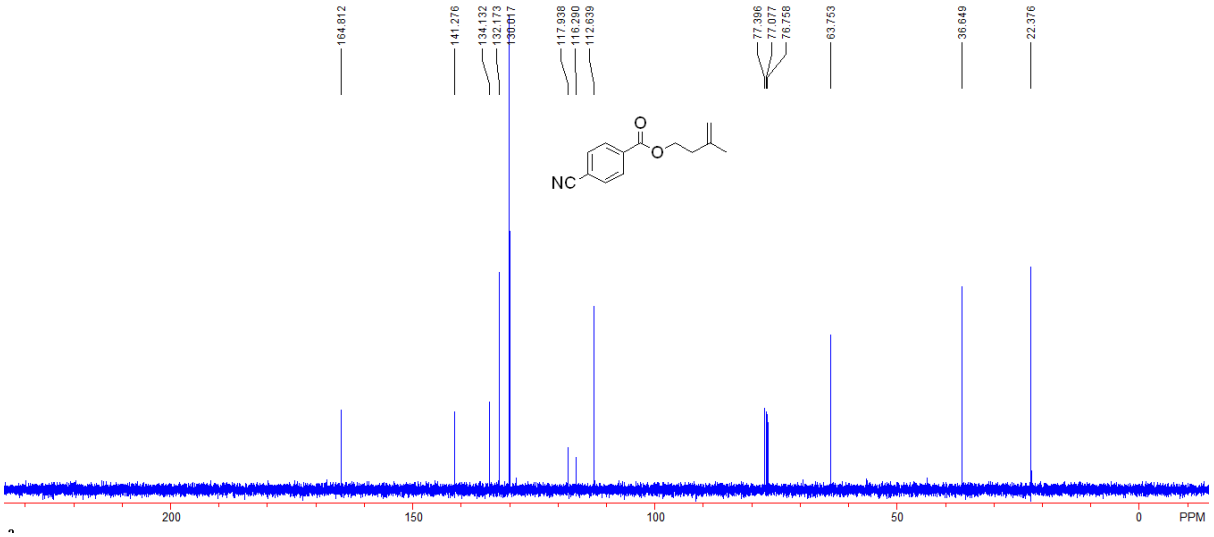

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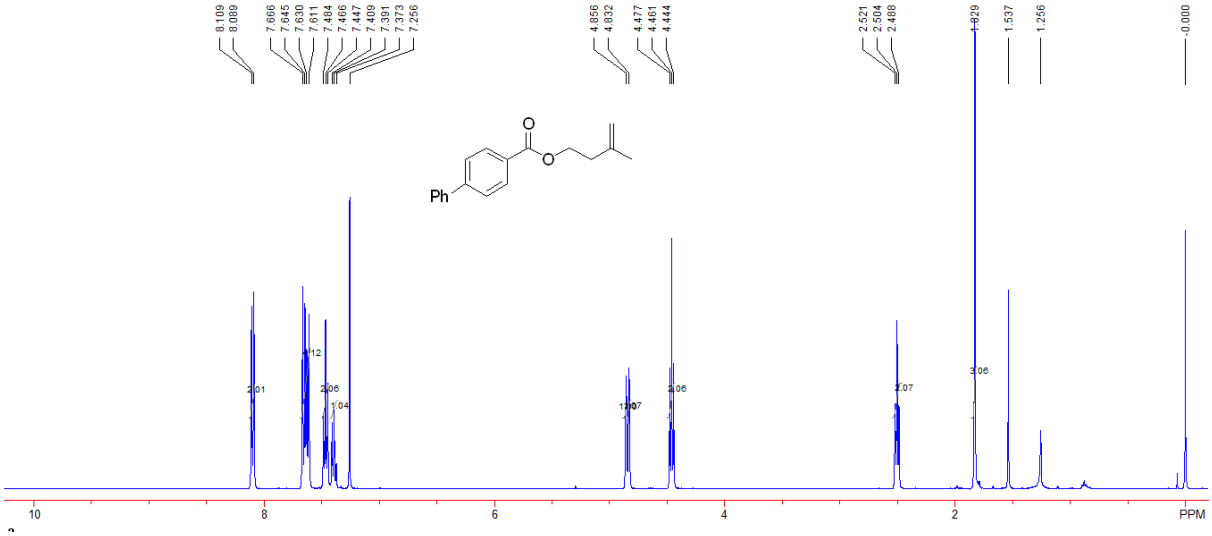

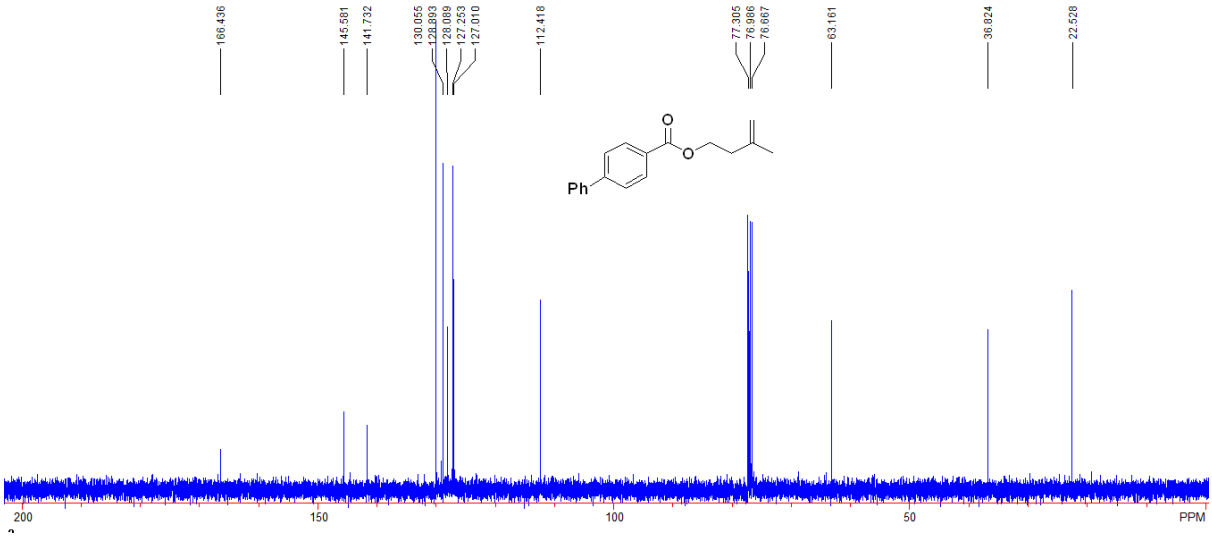

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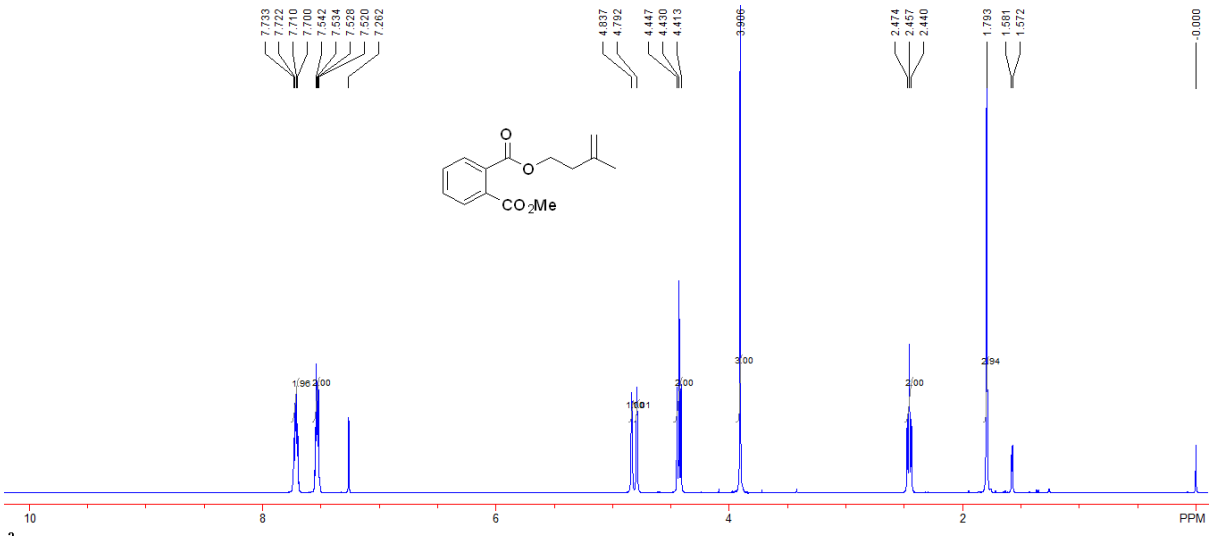

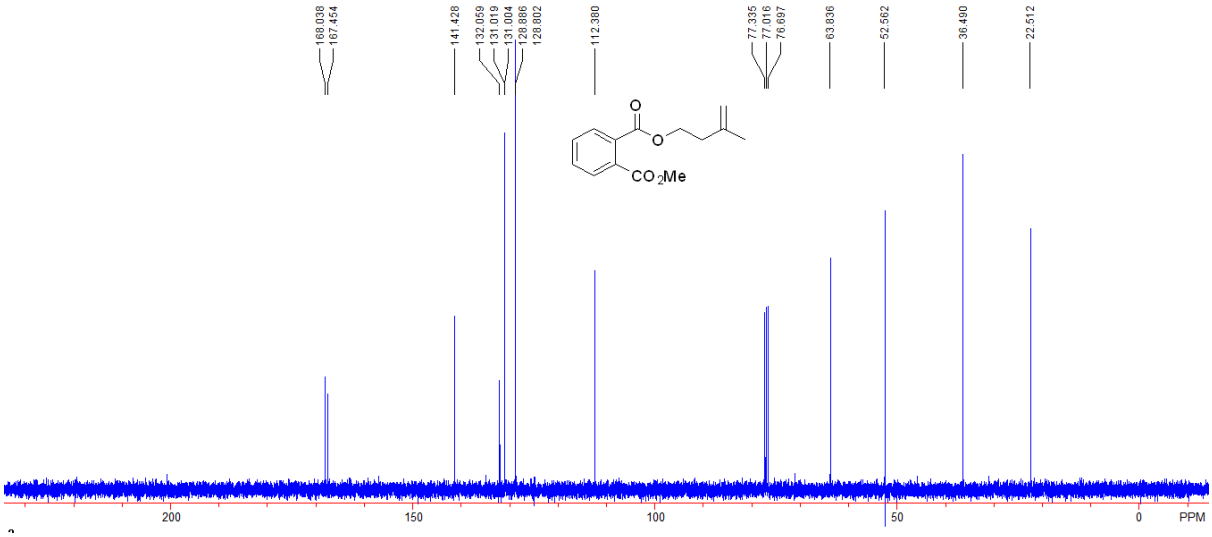

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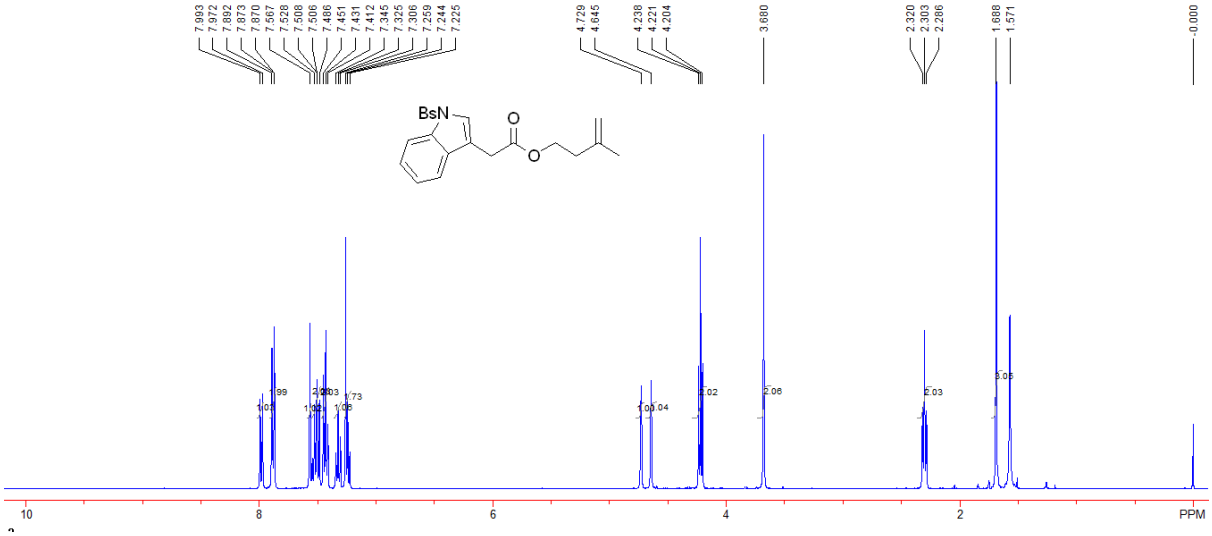

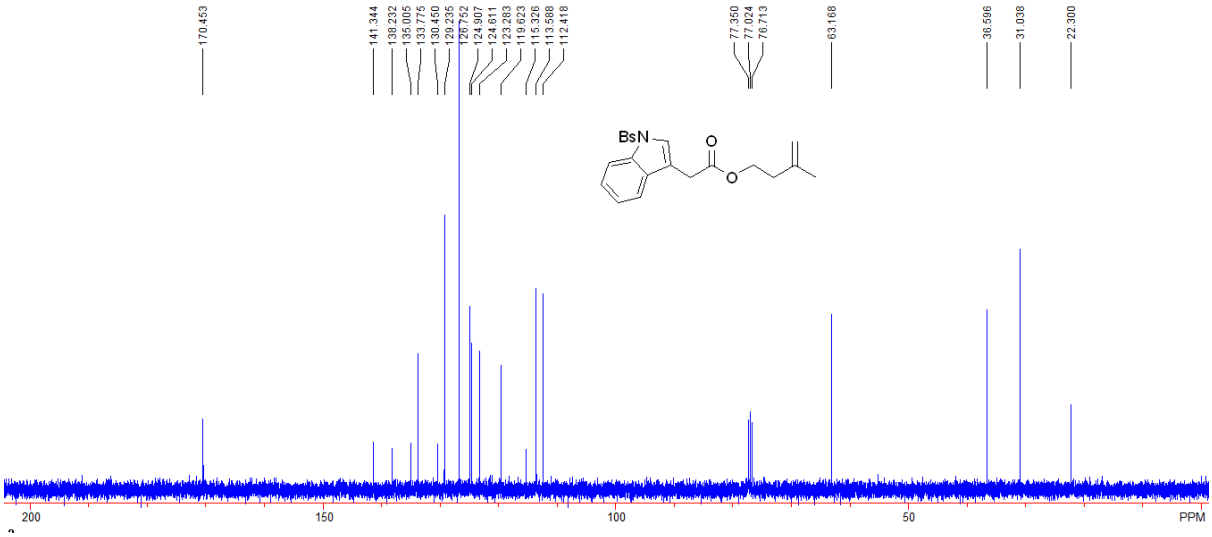

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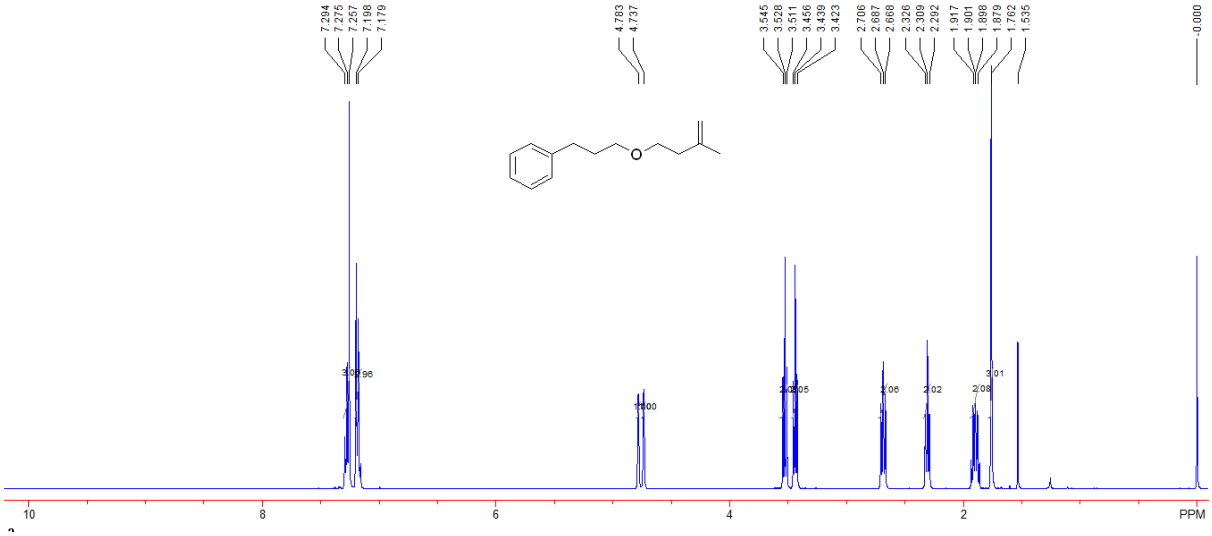

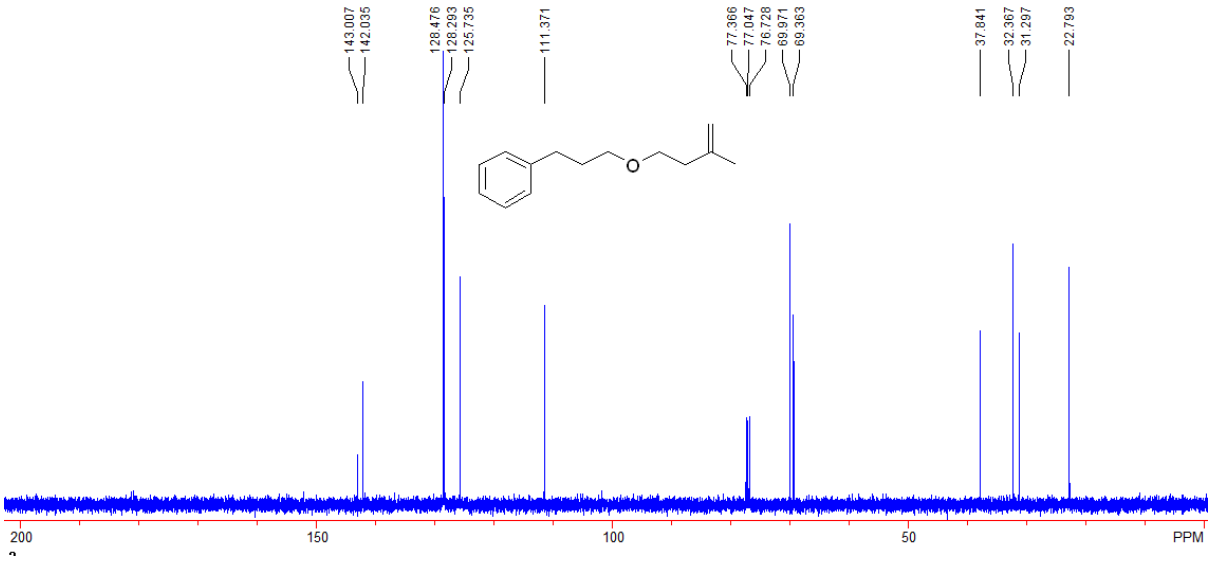

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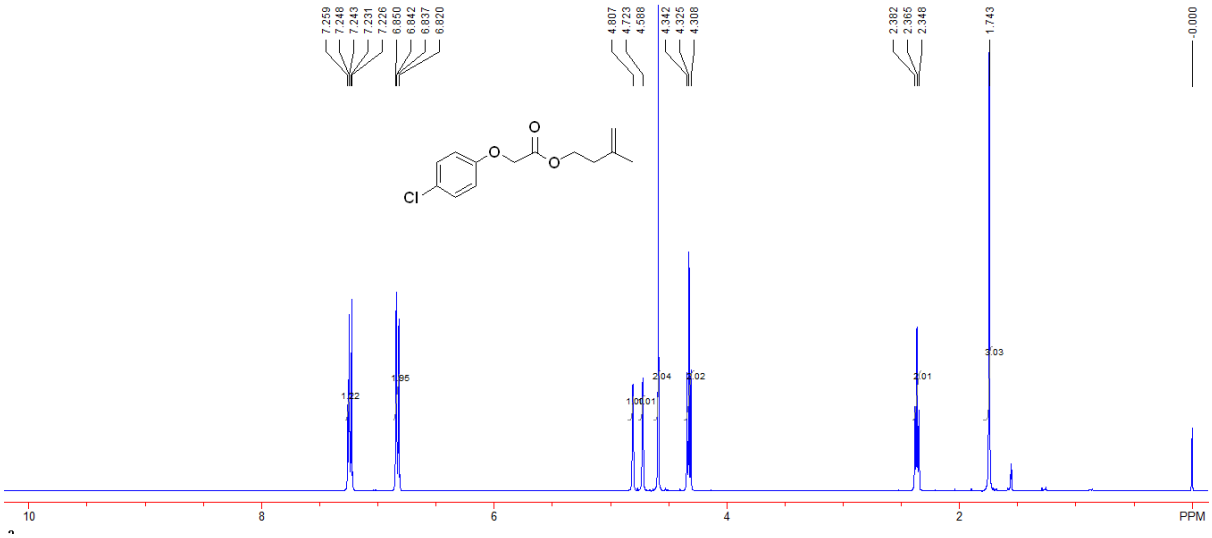

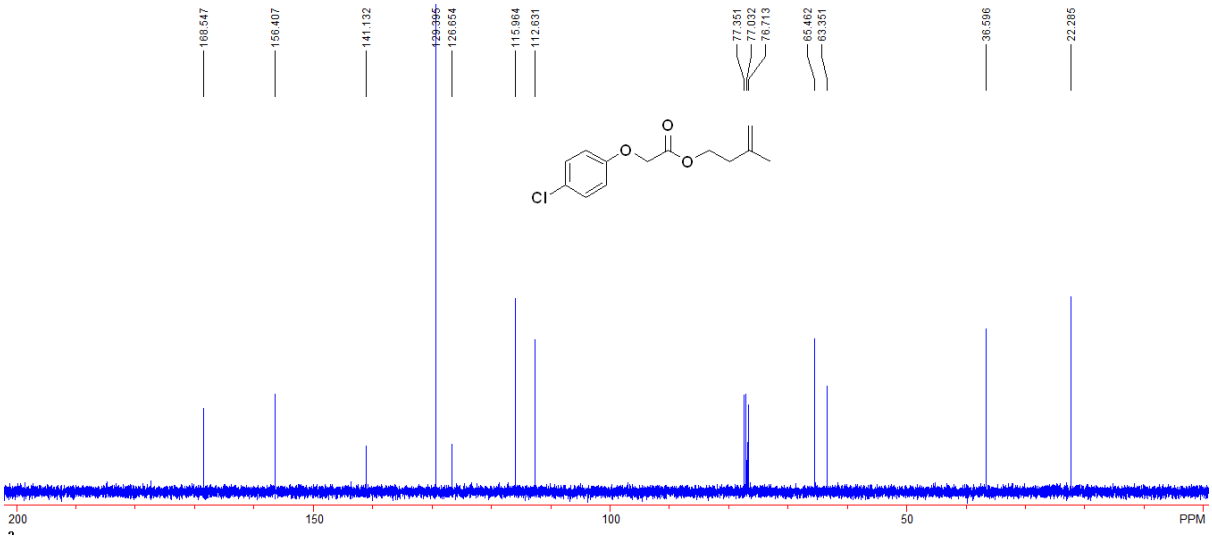

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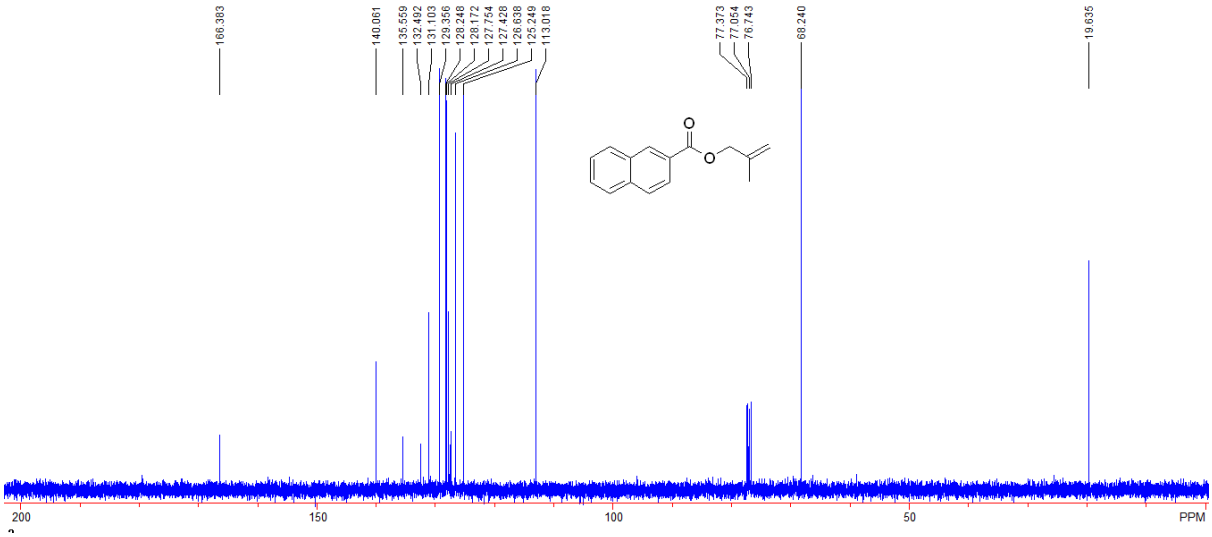

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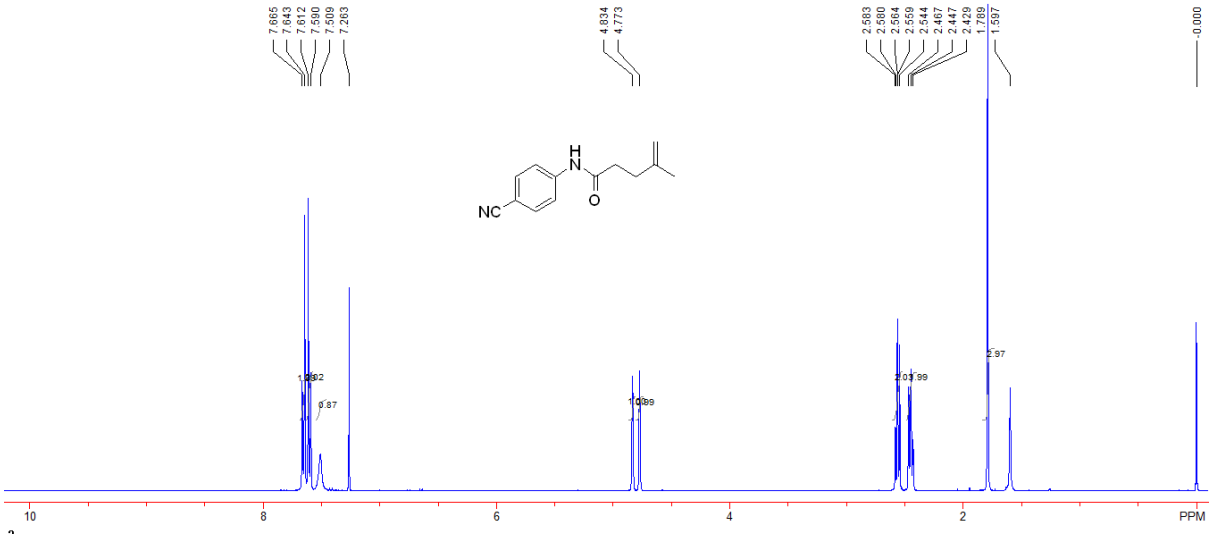

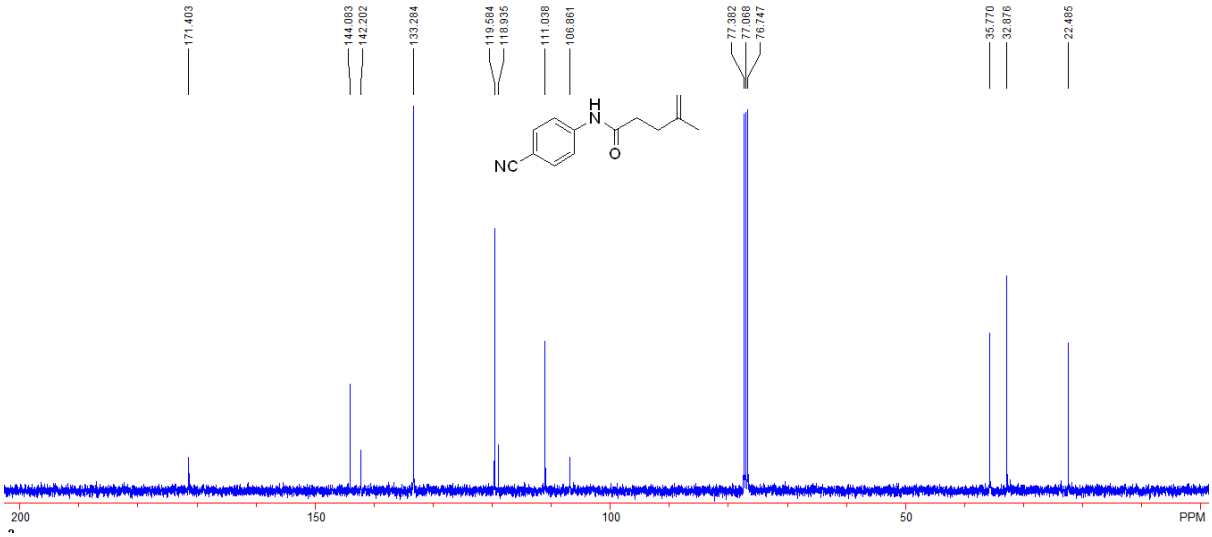

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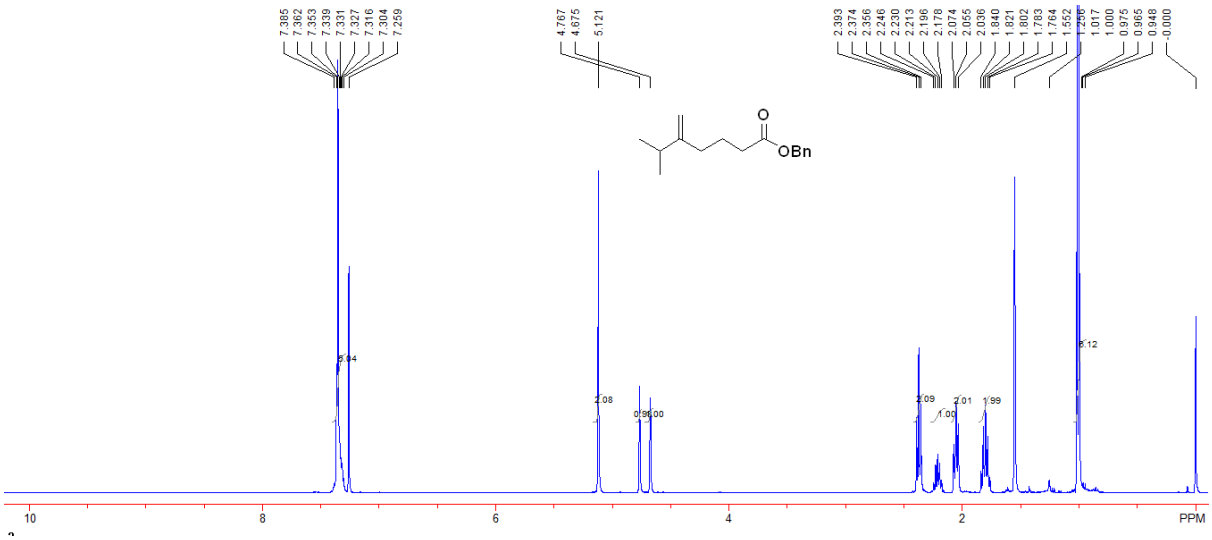

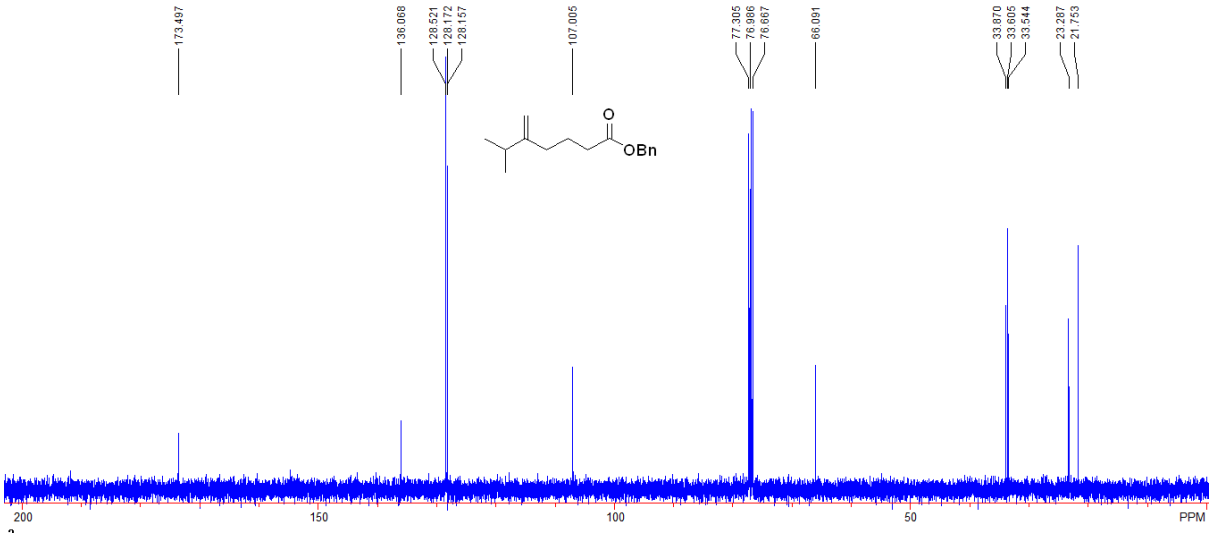

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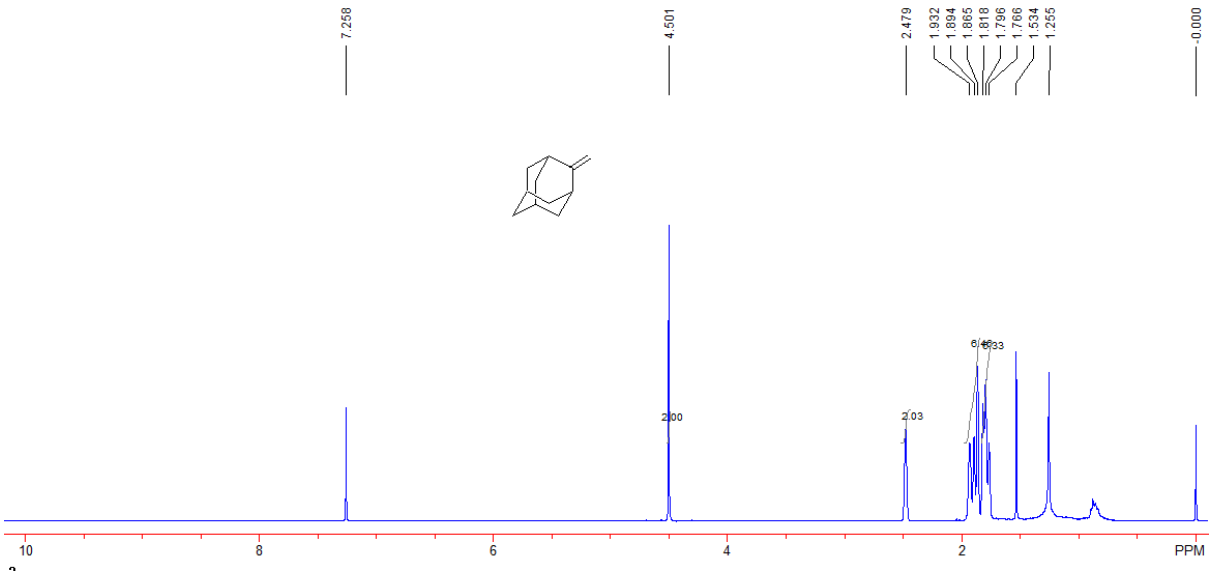
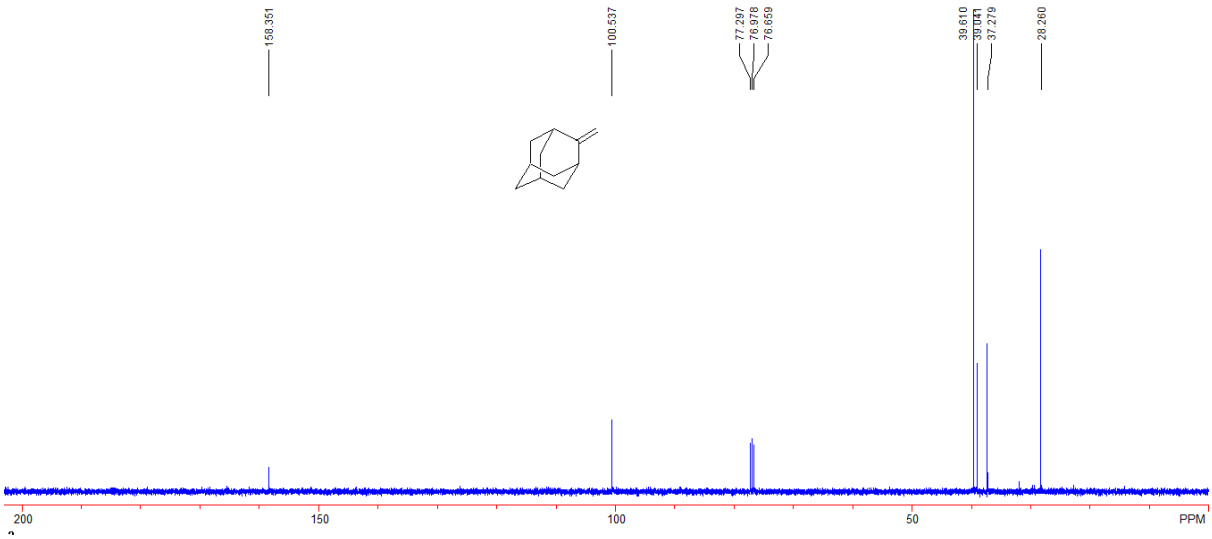
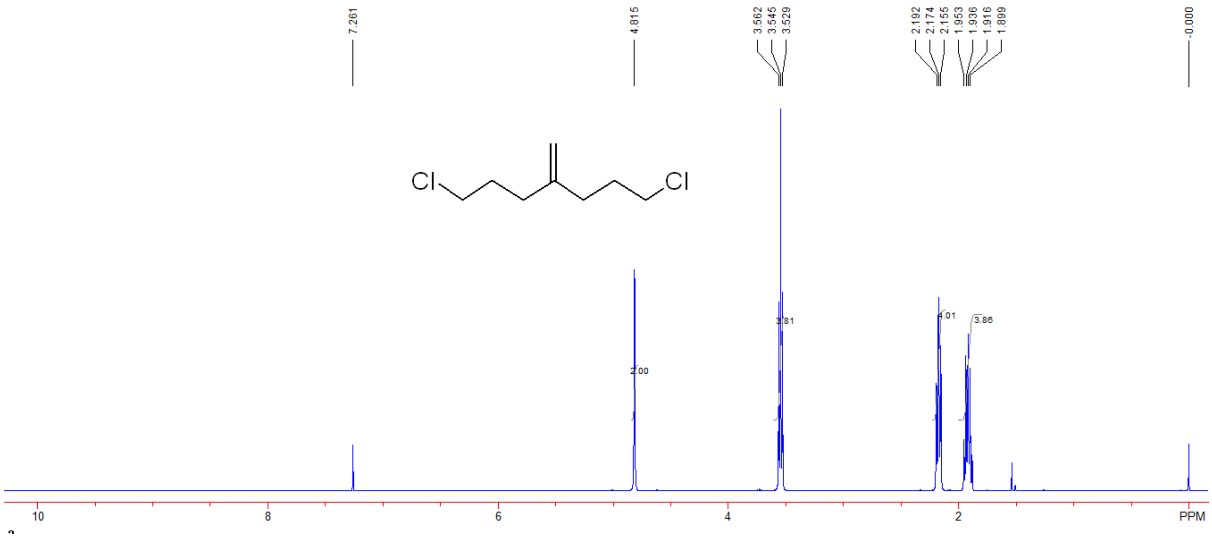
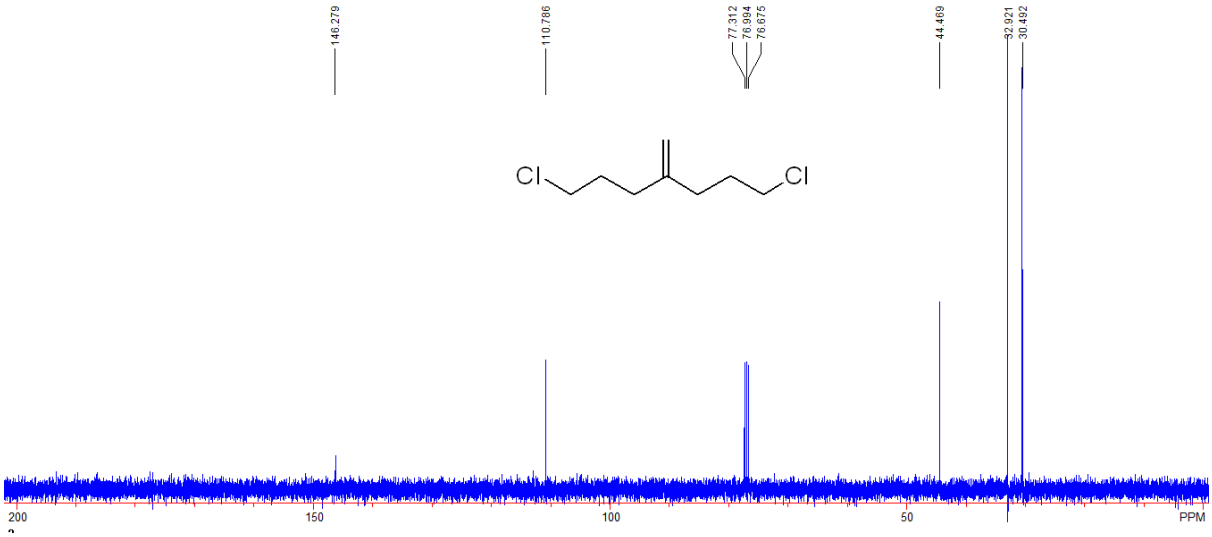


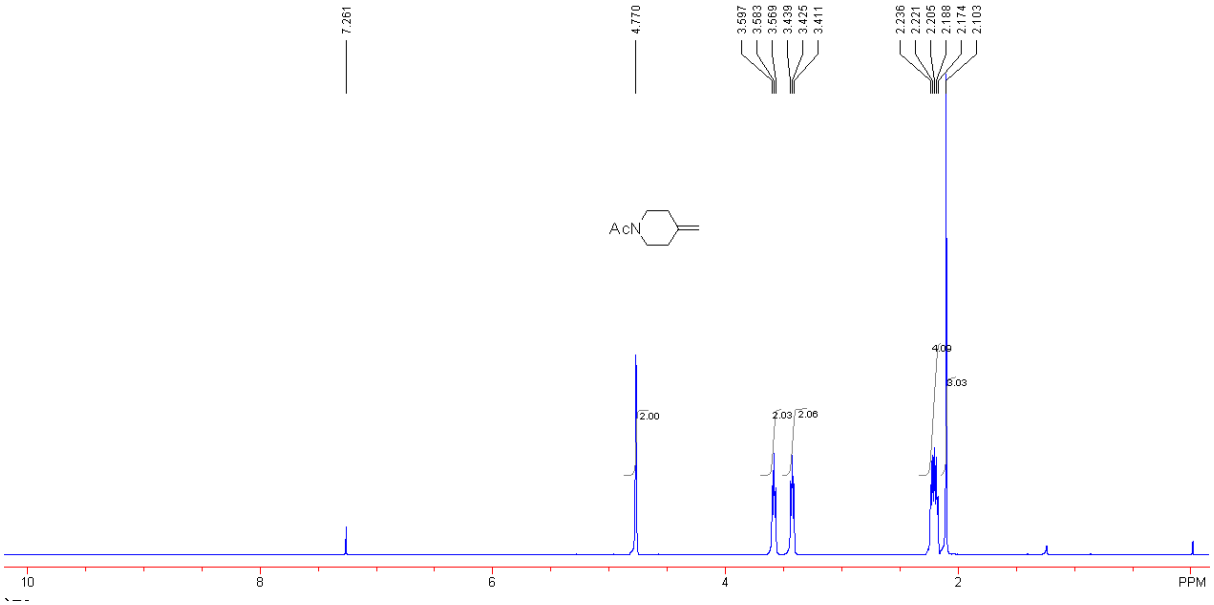


Compound **A-23**





Compond **A-24**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3.411
2.236
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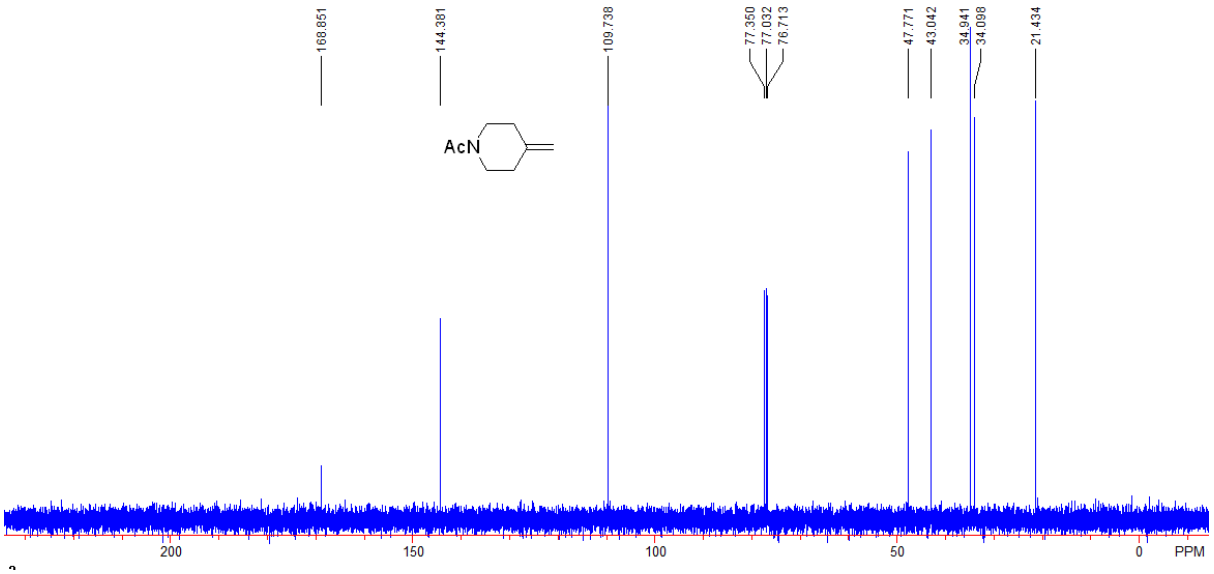
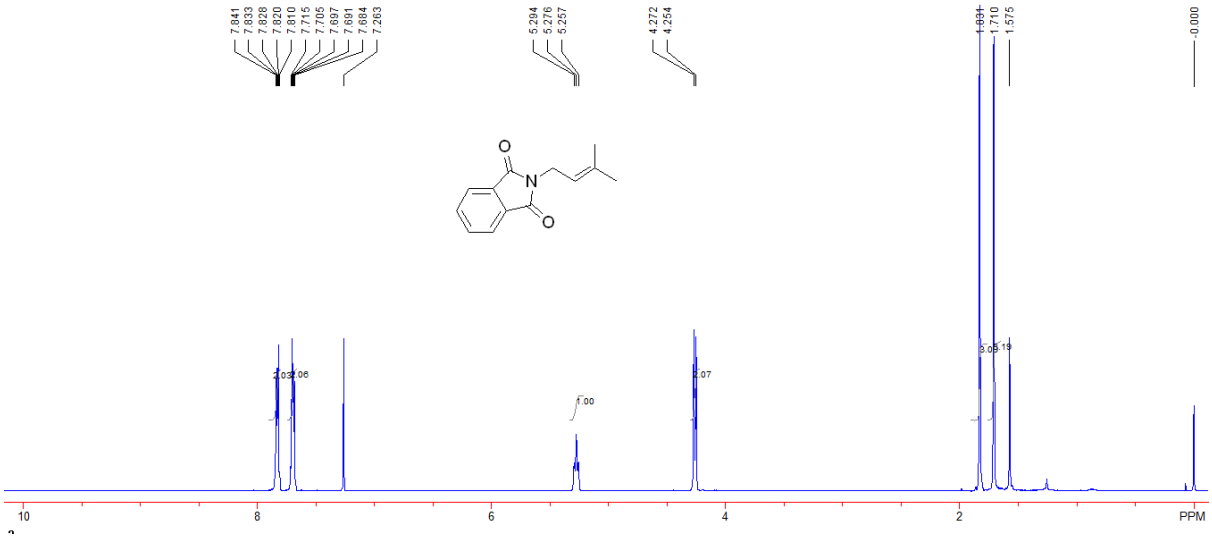
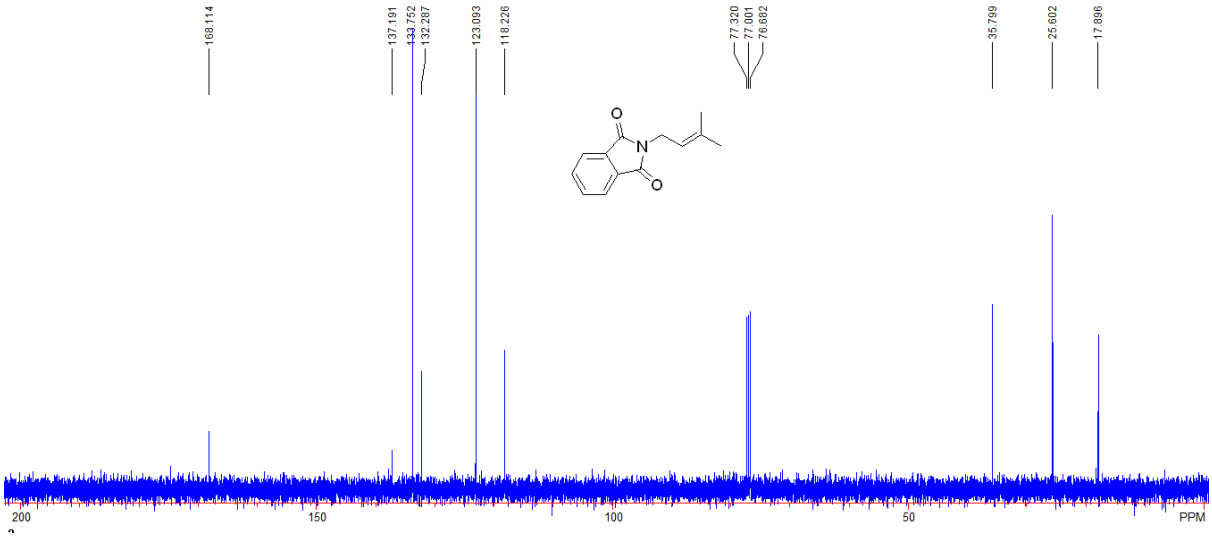
2.103
AcN
2.00
2.03
2.06
4.09
3.03
10
8
6
4
2
PPM

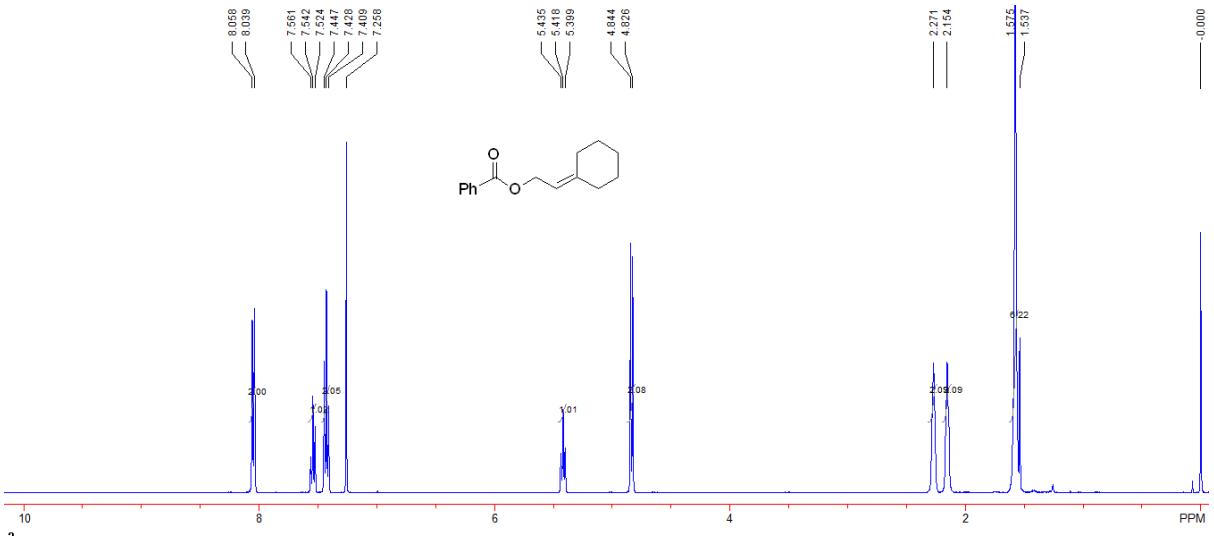

168.851
144.381
109.738
77.350
77.032
76.713
47.771
43.042
34.941
34.098
21.434
AcN
200
150
100
50
0
PPM

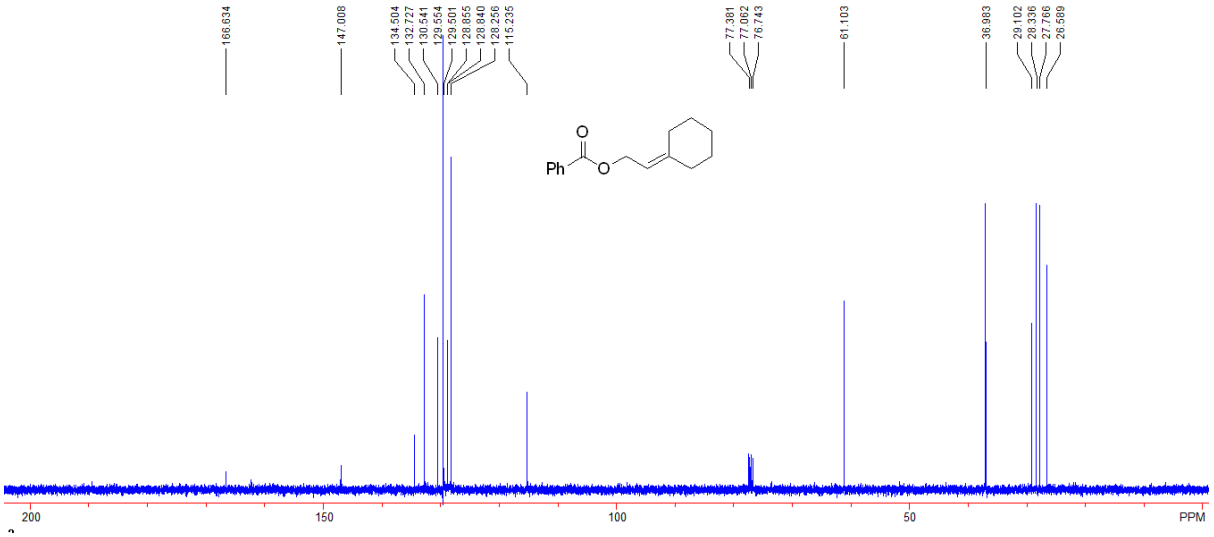
Compound **A-25**



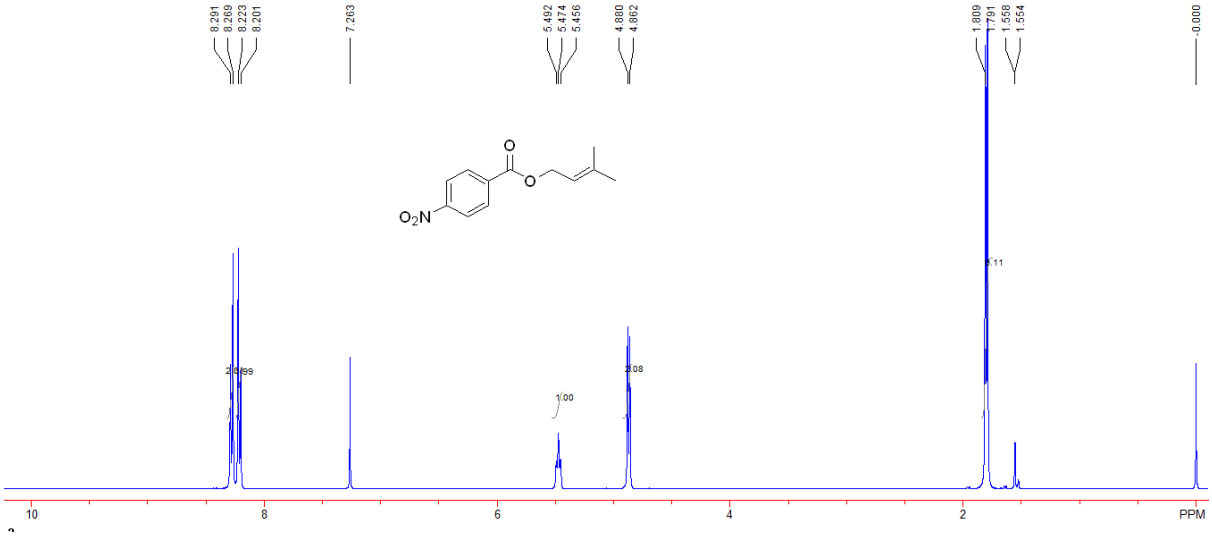


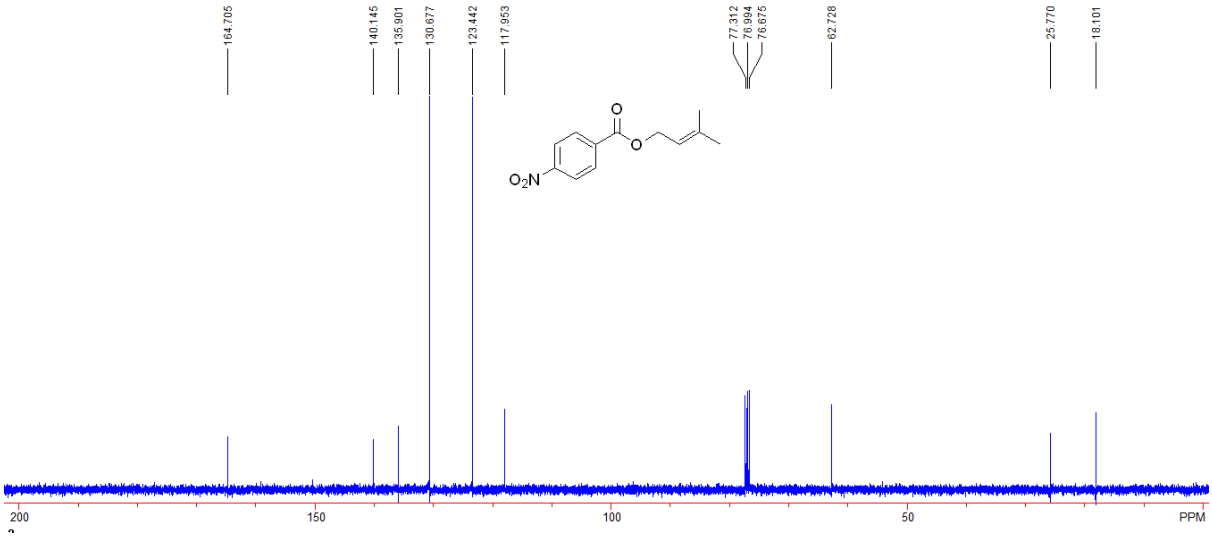
Compound **A-26**



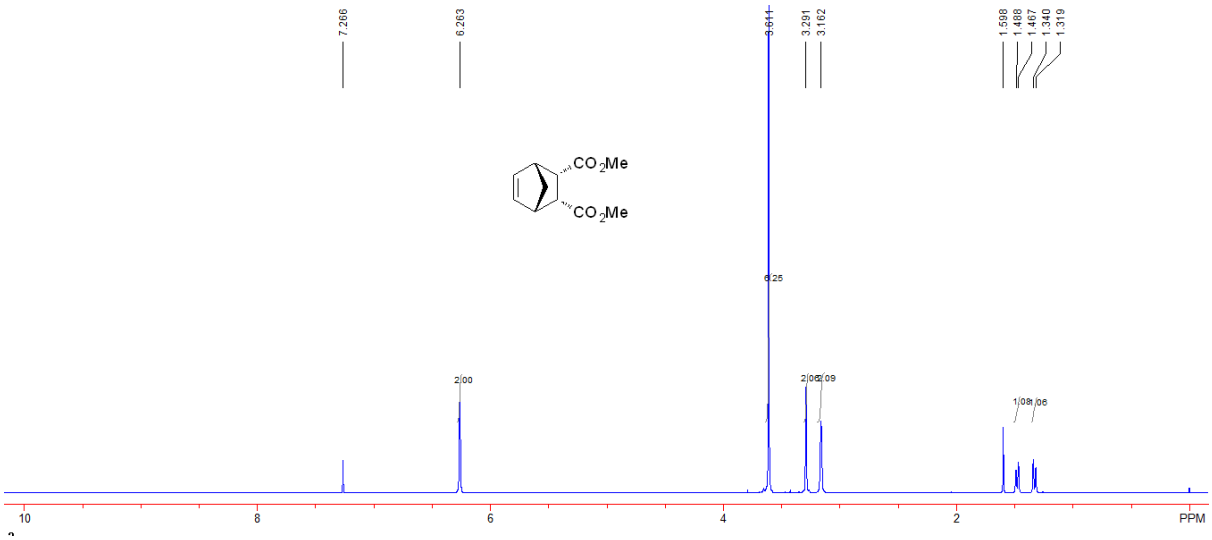


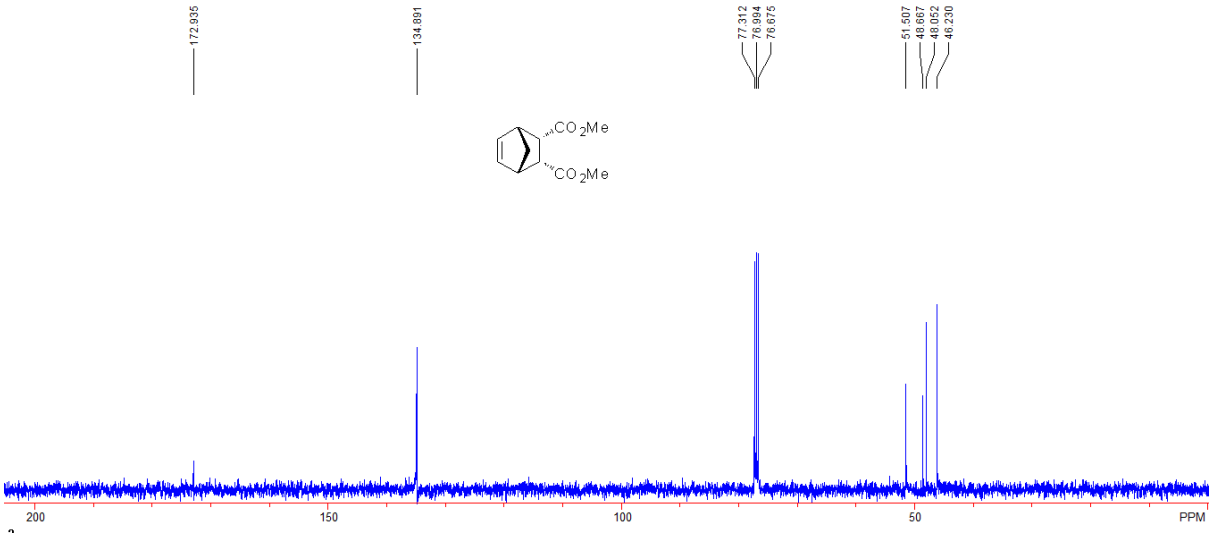
Compound **A-27**



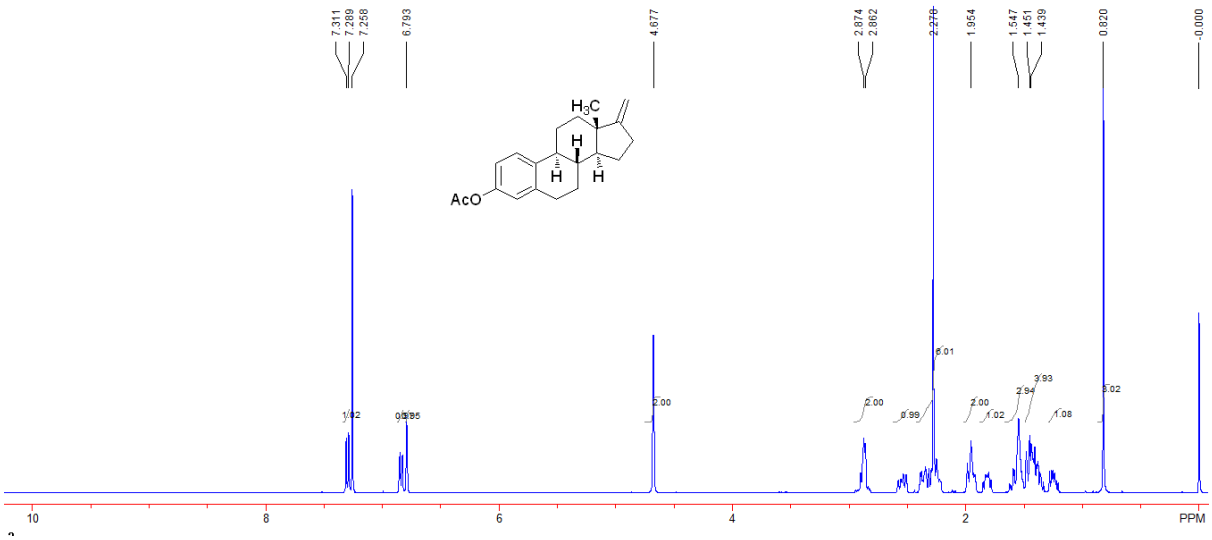


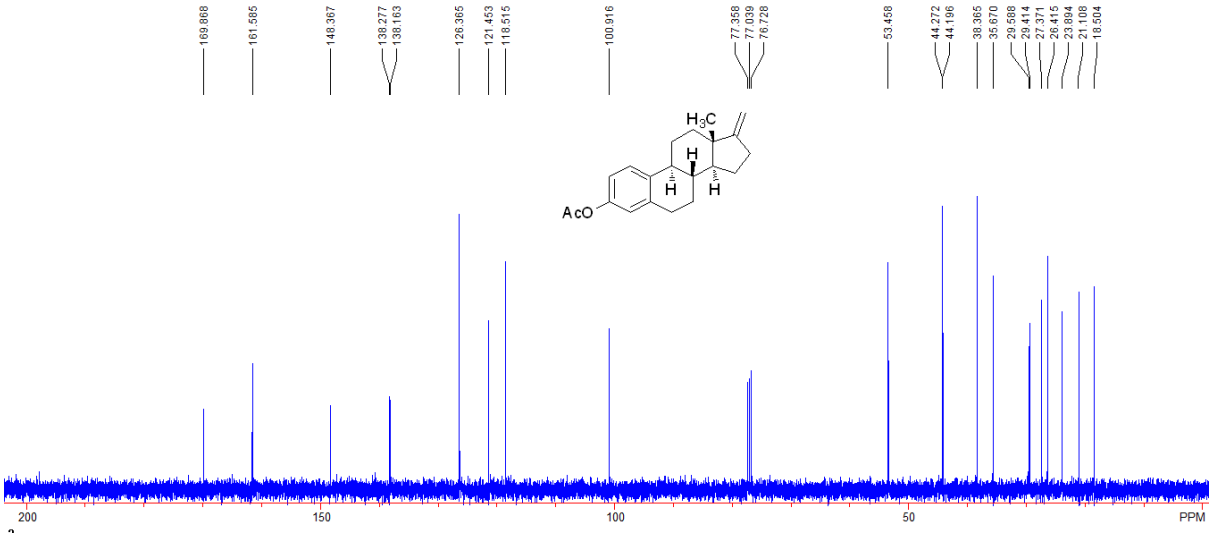
Compound **A-29**



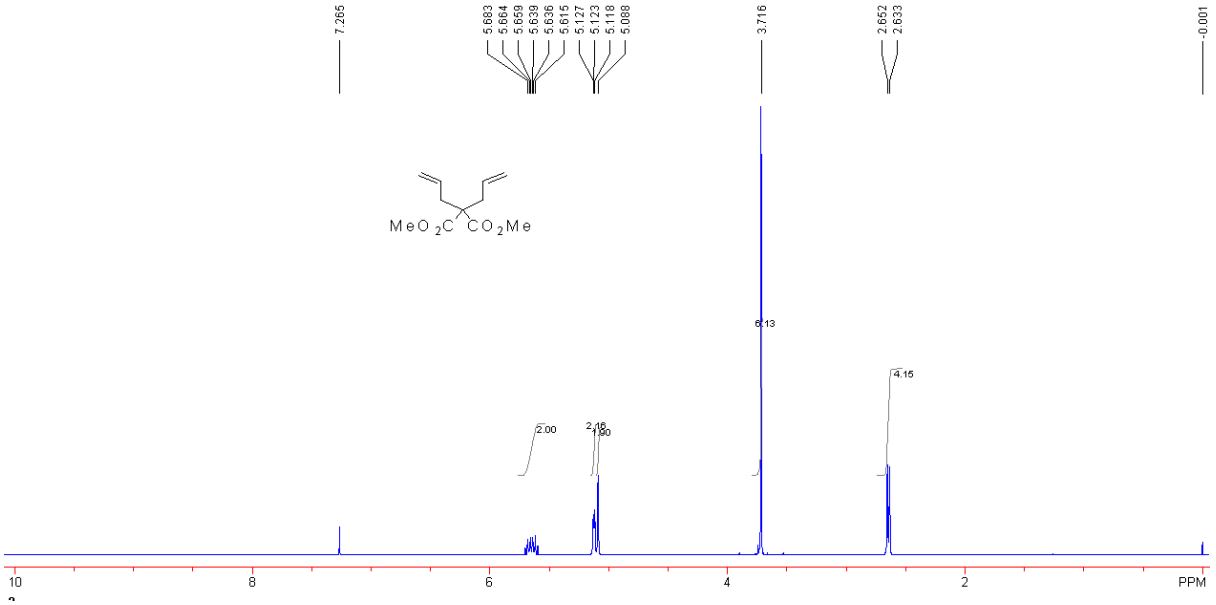


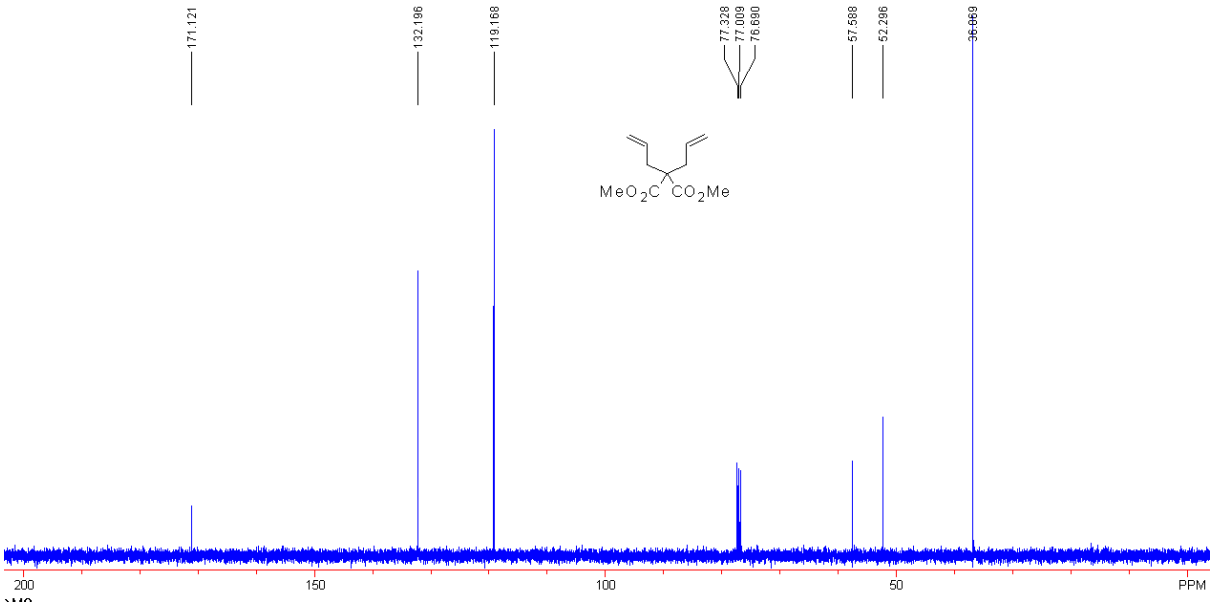
Compound **A-30**



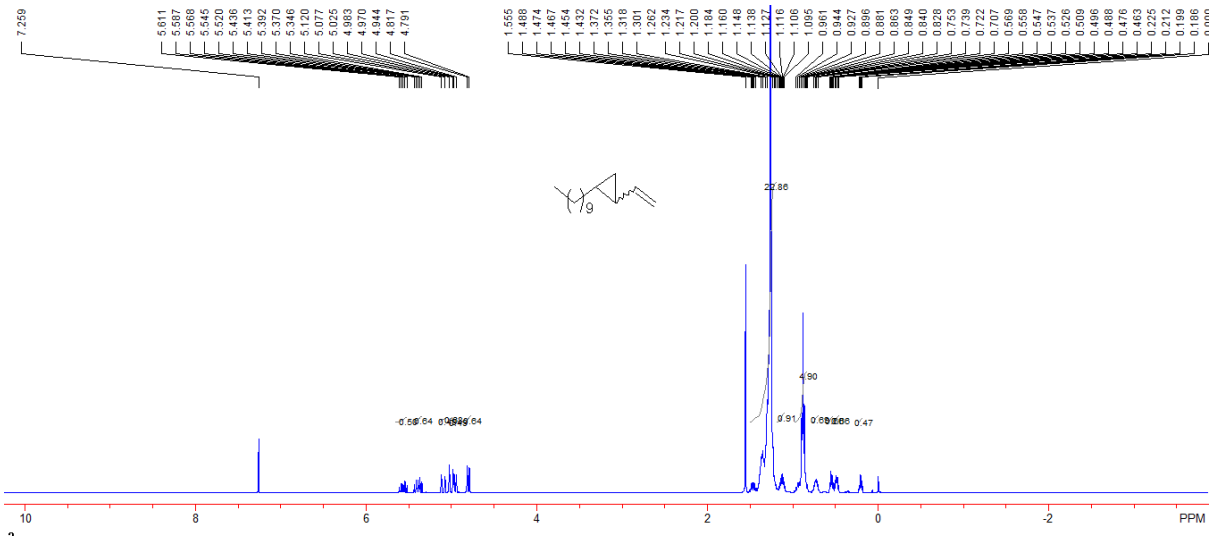


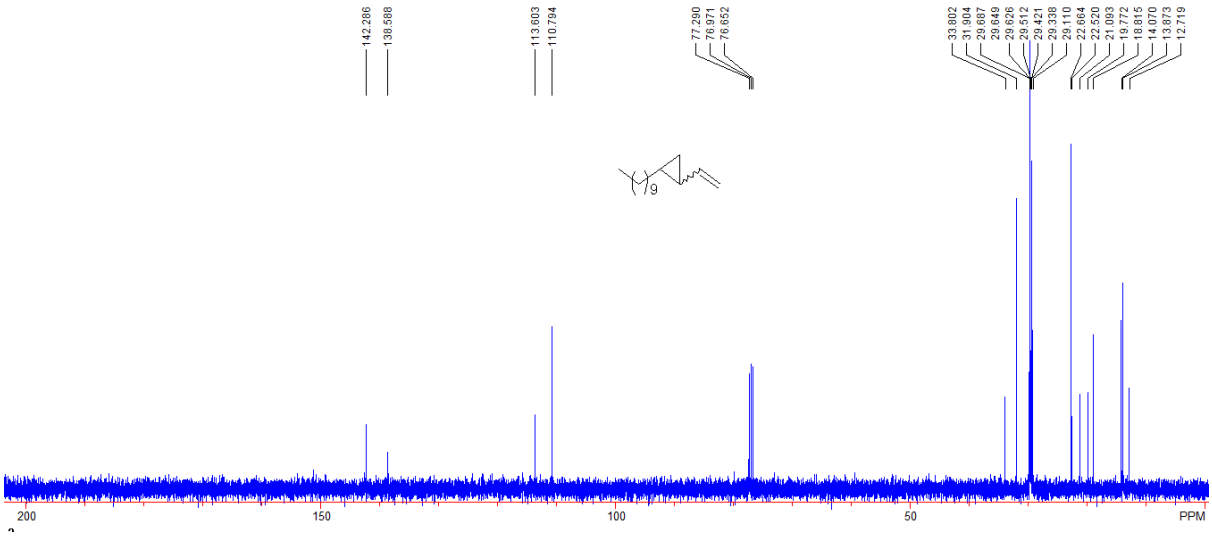
Compound **A-31**





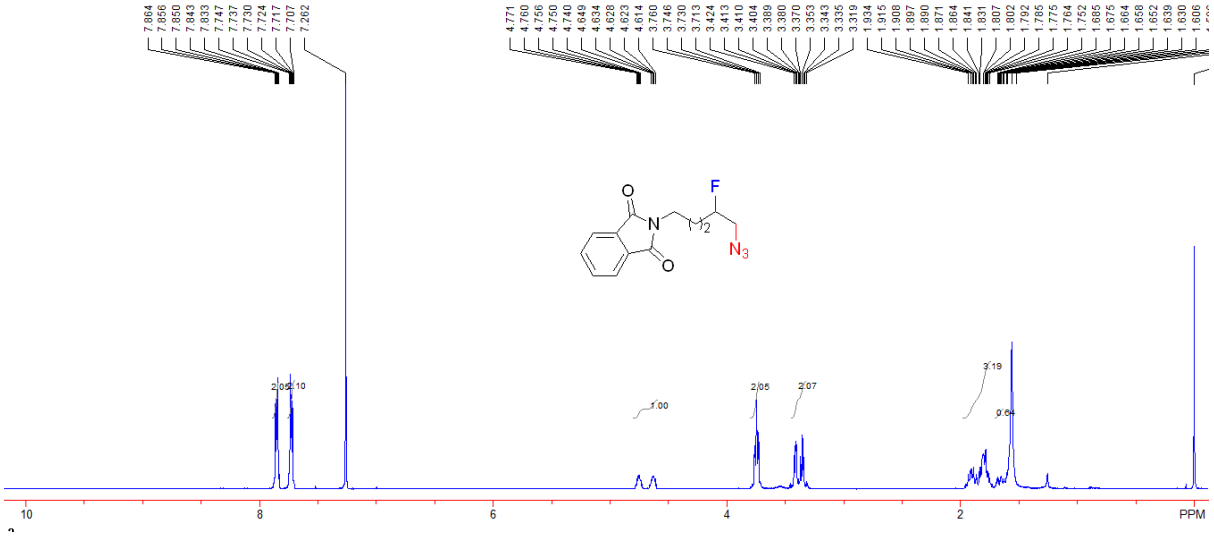
Compound **A-33**

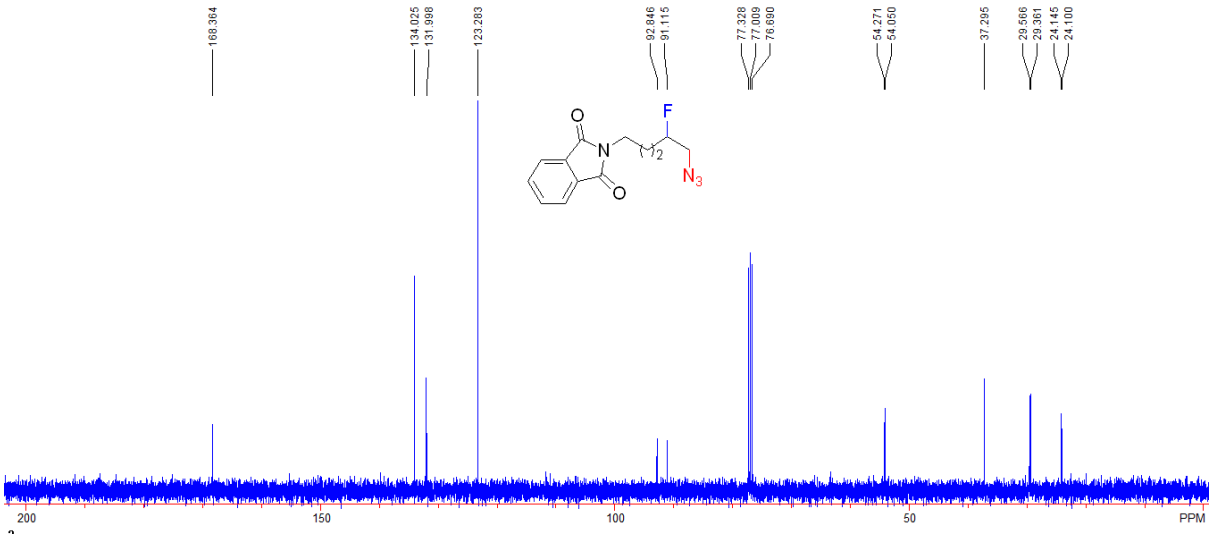


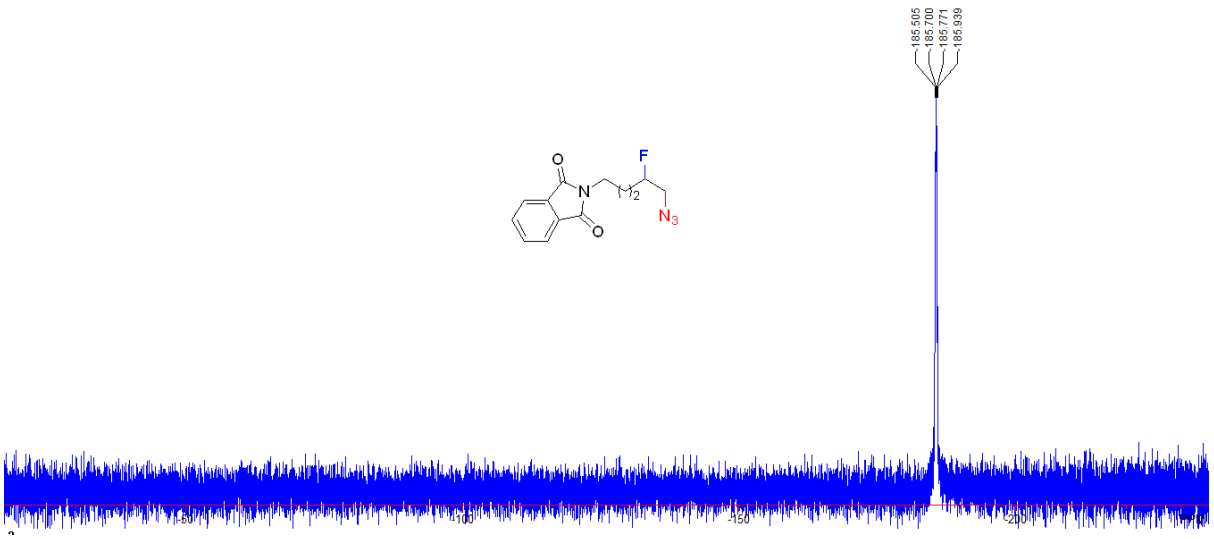


8. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products.

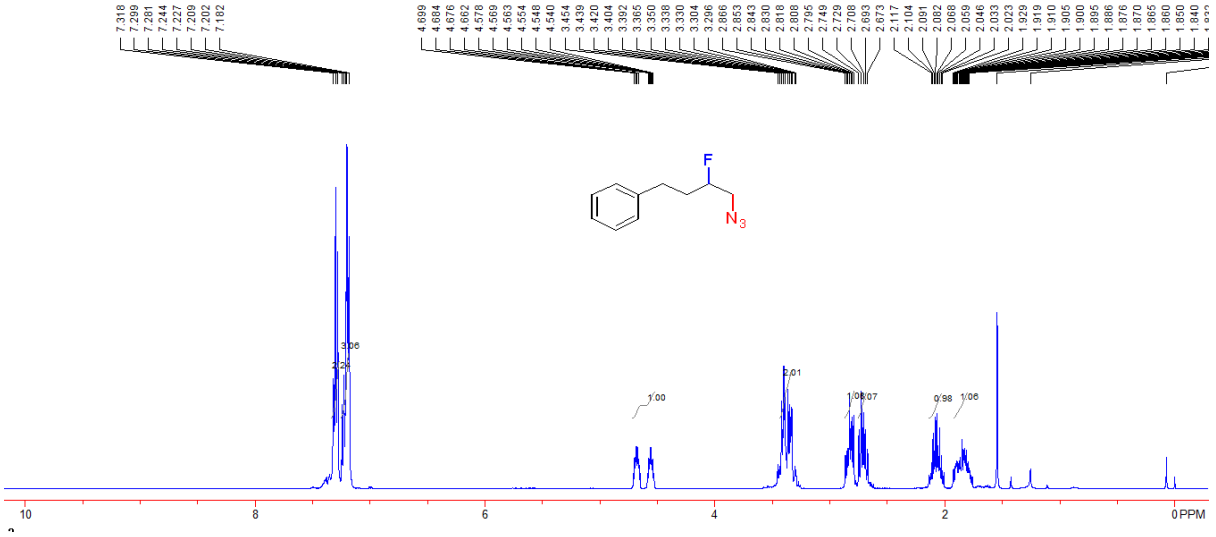
Compound **1**

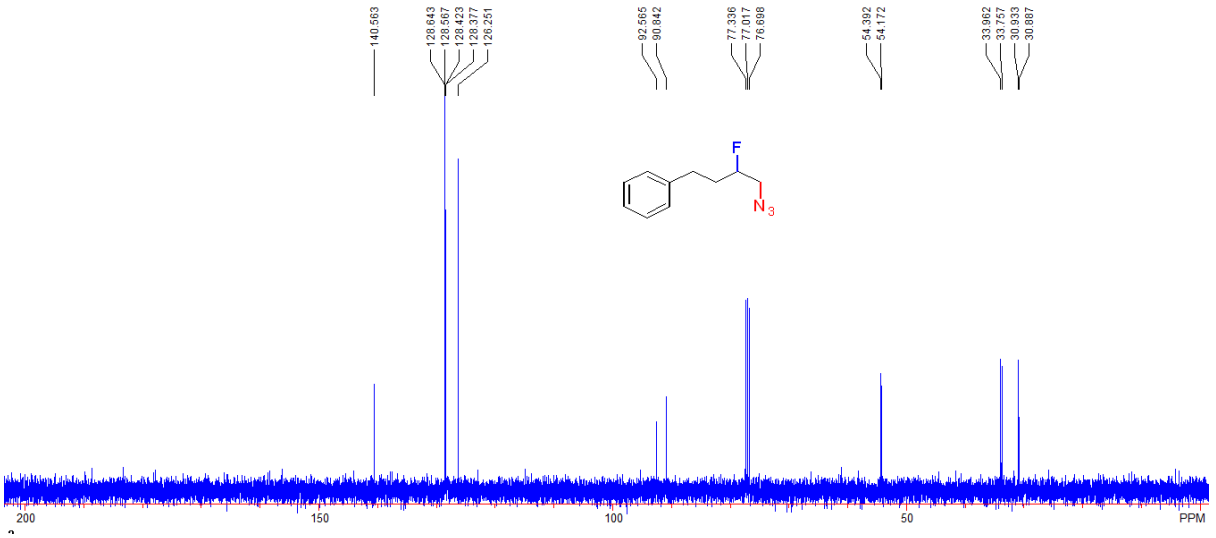

7.864
7.856
7.850
7.843
7.833
7.747
7.737
7.730
7.724
7.717
7.707
7.262
4.771
4.760
4.756
4.750
4.740
4.649
4.634
4.628
4.623
4.614
3.760
3.746
3.730
3.713
3.424
3.413
3.410
3.404
3.389
3.380
3.370
3.353
3.343
3.335
3.319
1.934
1.915
1.908
1.897
1.890
1.871
1.864
1.841
1.831
1.807
1.802
1.792
1.785
1.775
1.764
1.752
1.685
1.675
1.664
1.658
1.652
1.639
1.630
1.806
O
N
F
N3
2.05
2.10
1.00
2.05
2.07
3.19
9.64
10
8
6
4
2
PPM

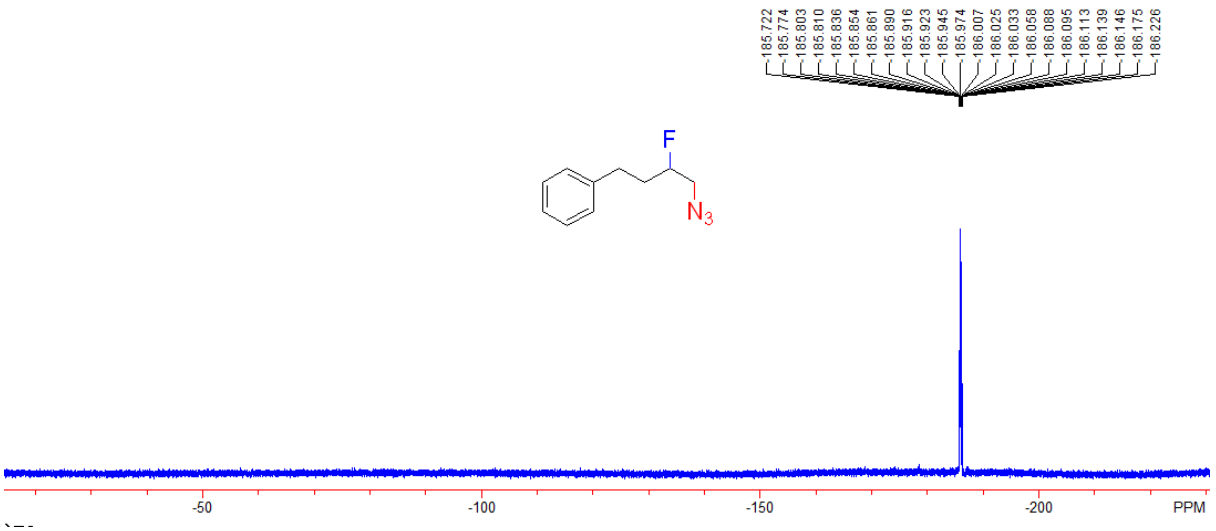

168.364
134.025
131.998
123.283
92.846
91.115
77.328
77.009
76.690
54.271
54.050
37.295
29.566
29.361
24.145
24.100
O
N
F
N3
200
150
100
50
PPM


185.505
185.700
185.771
185.939
O
N
F
N3
-50
-100
-150
-200
PPM

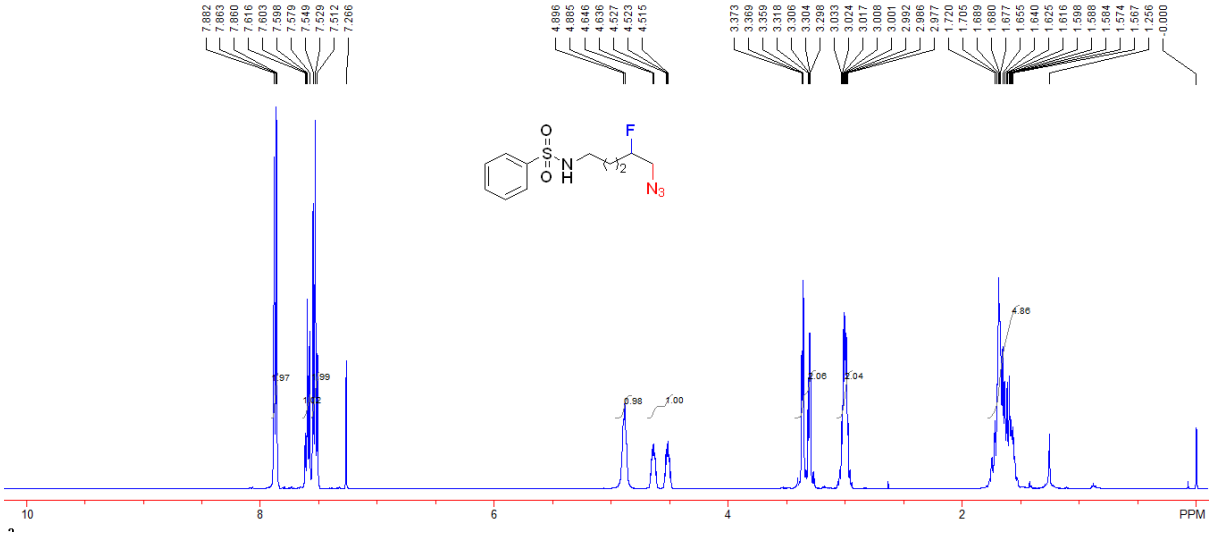
Compound **2**

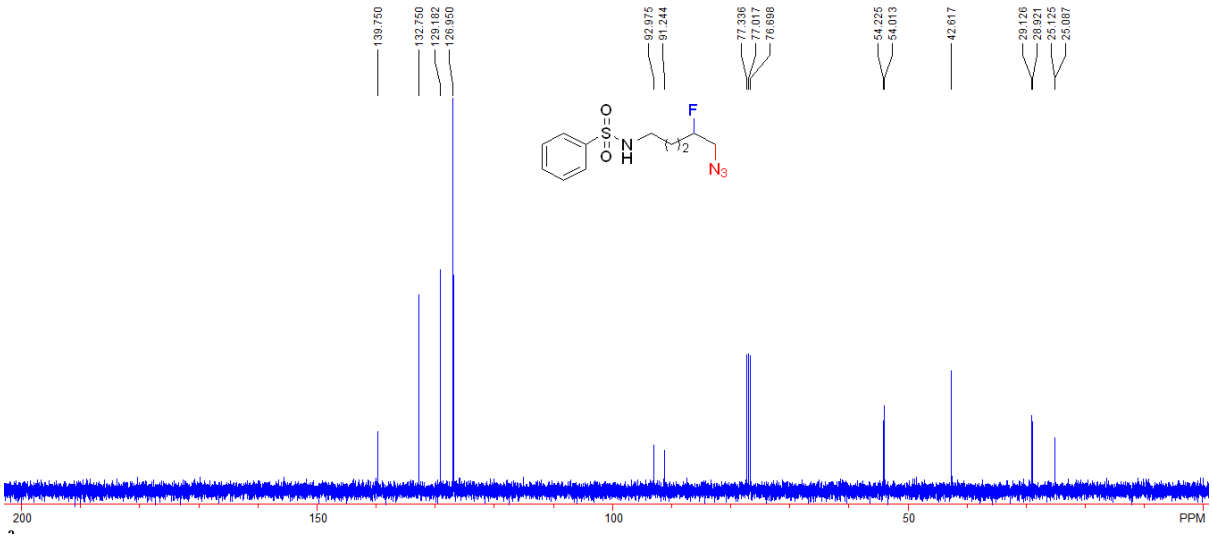


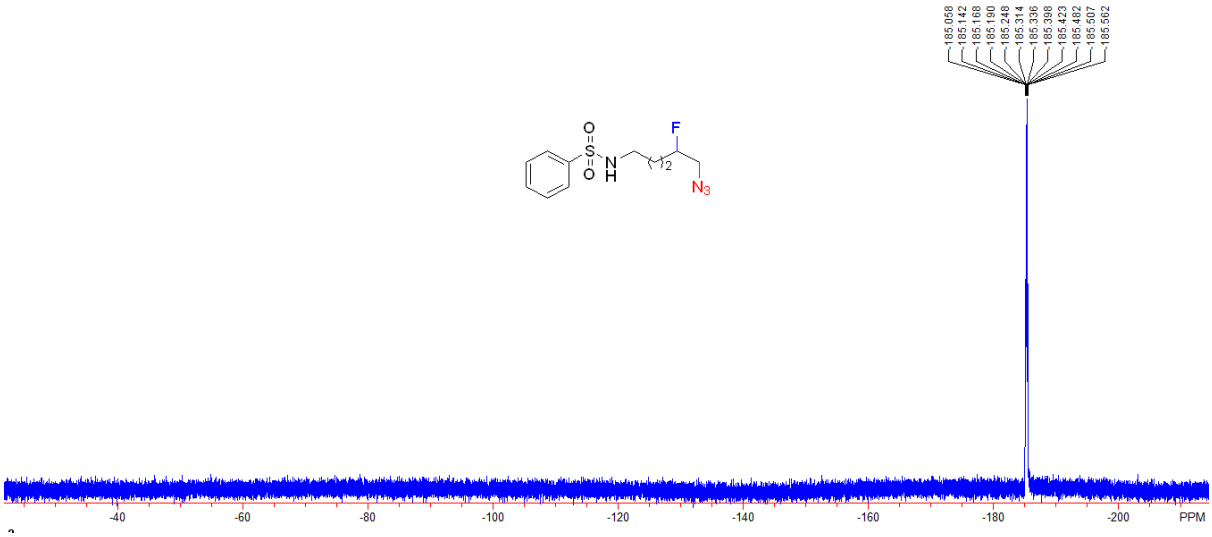




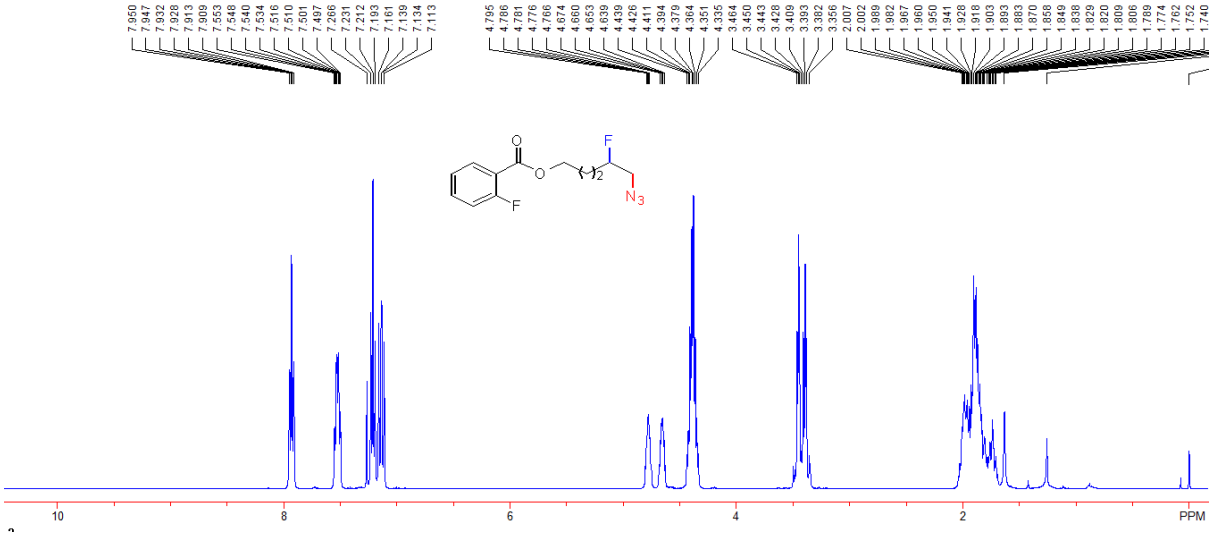
Compound **3**

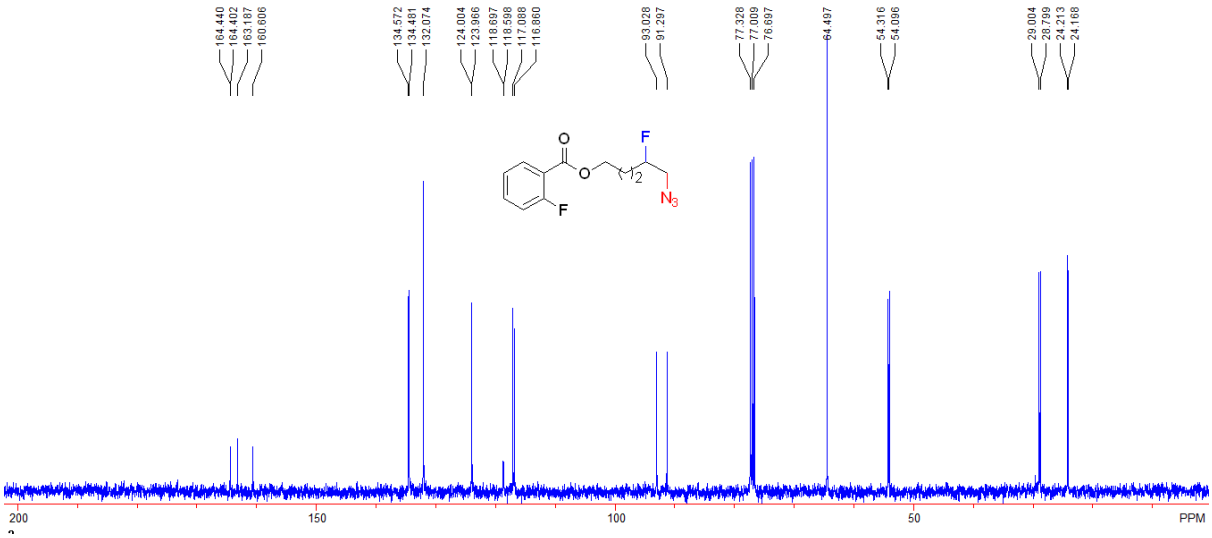

7.882
7.863
7.860
7.616
7.603
7.598
7.579
7.549
7.529
7.512
7.266
4.896
4.885
4.646
4.636
4.527
4.523
4.515
3.373
3.369
3.359
3.318
3.306
3.304
3.298
3.033
3.024
3.017
3.008
3.001
2.992
2.986
2.977
2.720
1.705
1.689
1.680
1.677
1.655
1.640
1.625
1.616
1.598
1.588
1.584
1.574
1.567
1.256
0.000
O
O=S=O
N
H
2
F
N3
4.86
1.97
1.99
0.98
1.00
1.06
2.04
10
8
6
4
2
PPM

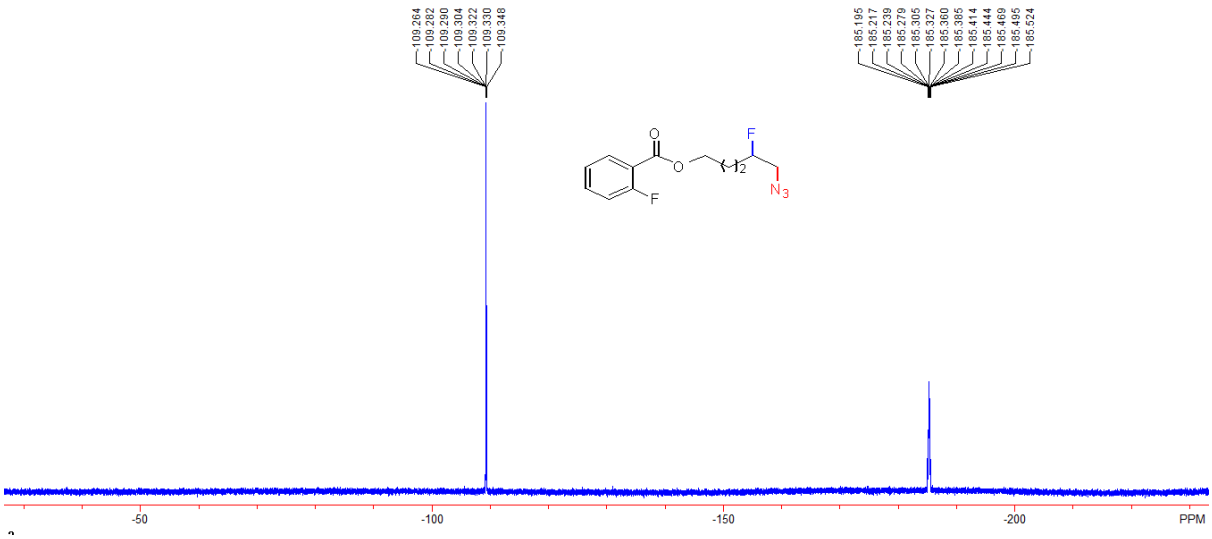

139.750
132.750
129.182
126.950
92.975
91.244
77.336
77.017
76.698
54.225
54.013
42.617
29.126
28.921
25.125
25.087
O
O=S=O
N
H
2
F
N3
200
150
100
50
PPM


185.058
185.142
185.168
185.190
185.248
185.314
185.336
185.398
185.423
185.482
185.507
185.562
O
O=S=O
N
H
2
F
N3
-40
-60
-80
-100
-120
-140
-160
-180
-200
PPM

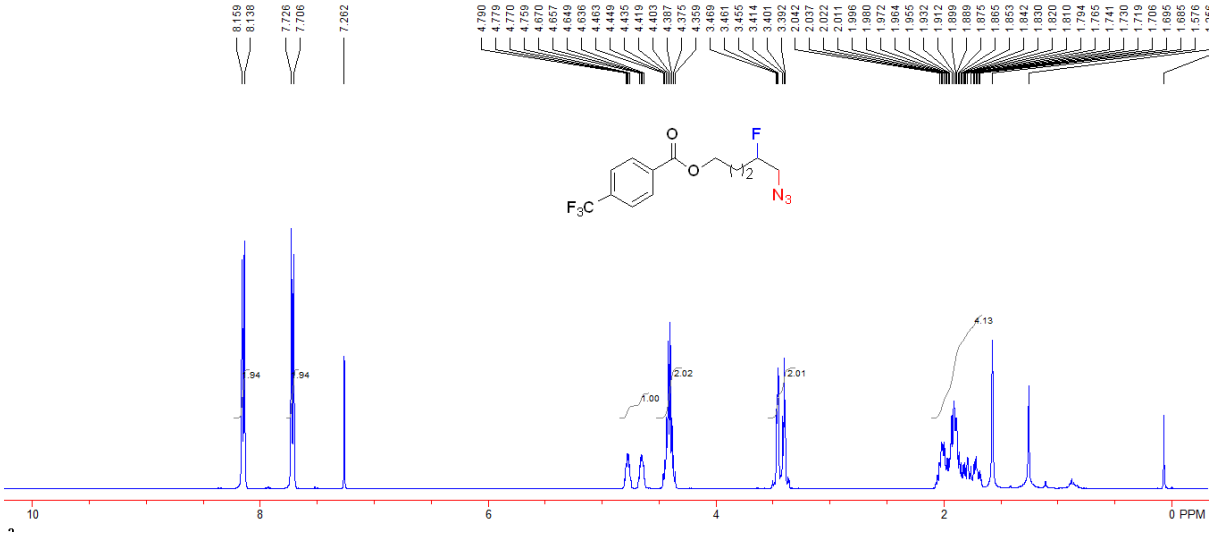
Compound **4**

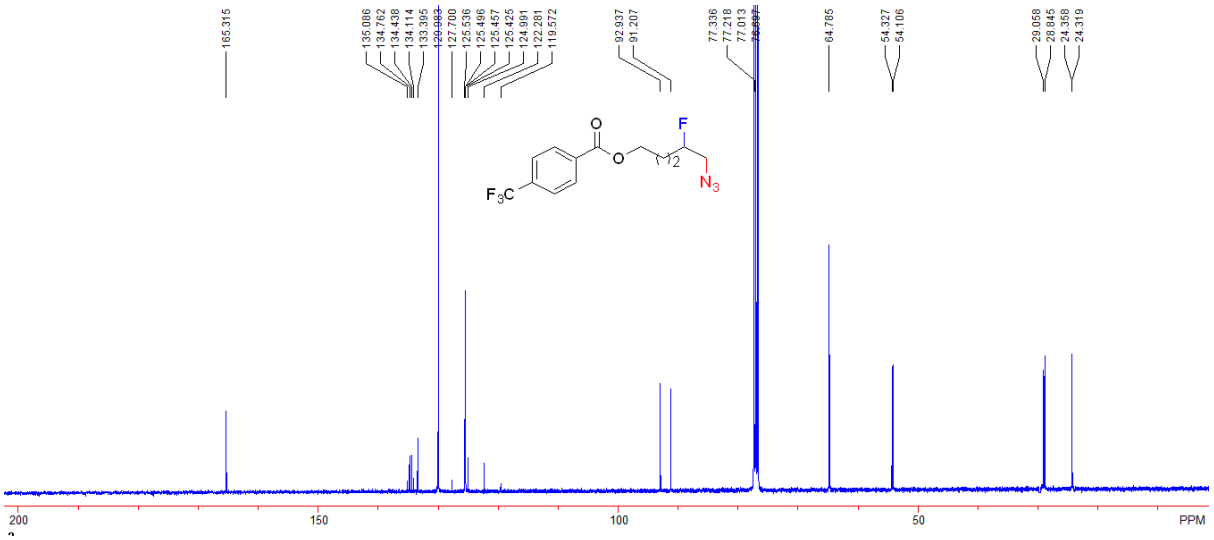

7.950
7.947
7.932
7.928
7.913
7.909
7.553
7.548
7.540
7.534
7.516
7.510
7.501
7.497
7.266
7.231
7.212
7.193
7.181
7.139
7.134
7.113
4.795
4.786
4.781
4.776
4.766
4.674
4.660
4.653
4.639
4.439
4.426
4.411
4.394
4.379
4.364
4.351
4.335
3.464
3.450
3.443
3.428
3.409
3.393
3.382
3.356
2.007
2.002
1.989
1.982
1.967
1.960
1.950
1.941
1.928
1.918
1.903
1.893
1.883
1.870
1.858
1.849
1.838
1.829
1.820
1.809
1.806
1.789
1.774
1.762
1.752
1.740
O
O
F
F
N3
2
10
8
6
4
2
PPM

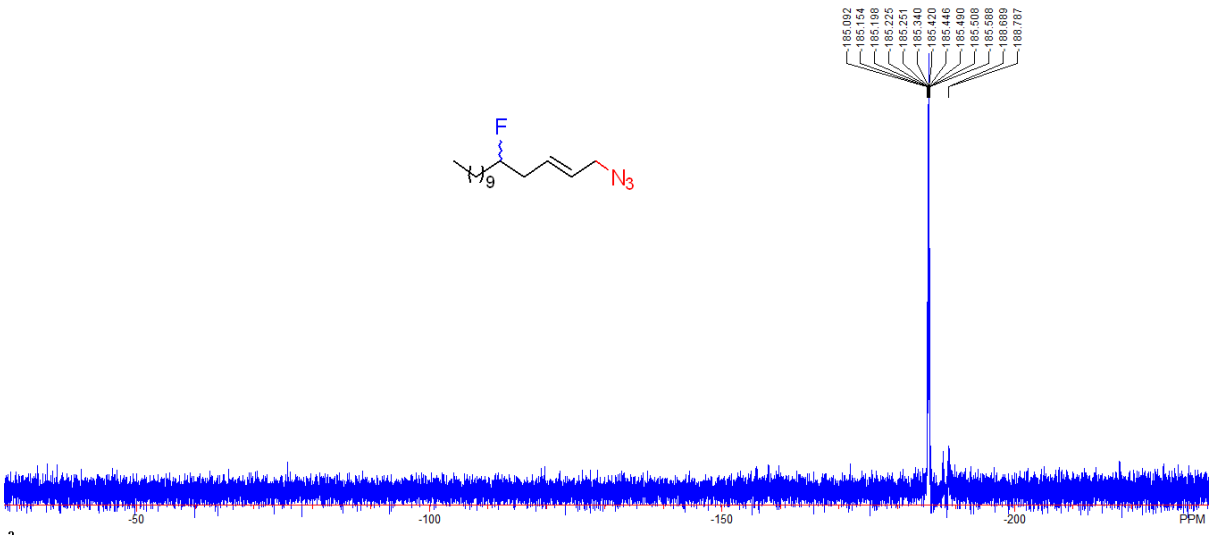

164.440
164.402
163.187
160.606
134.572
134.481
132.074
124.004
123.966
118.697
118.598
117.088
116.860
93.028
91.297
77.328
77.009
76.697
64.497
54.316
54.096
29.004
28.799
24.213
24.168
O
O
F
F
N3
2
200
150
100
50
PPM


109.264
109.282
109.290
109.304
109.322
109.330
109.348
185.195
185.217
185.239
185.279
185.305
185.327
185.360
185.385
185.414
185.444
185.469
185.495
185.524
O
O
F
F
N3
2
-50
-100
-150
-200
PPM

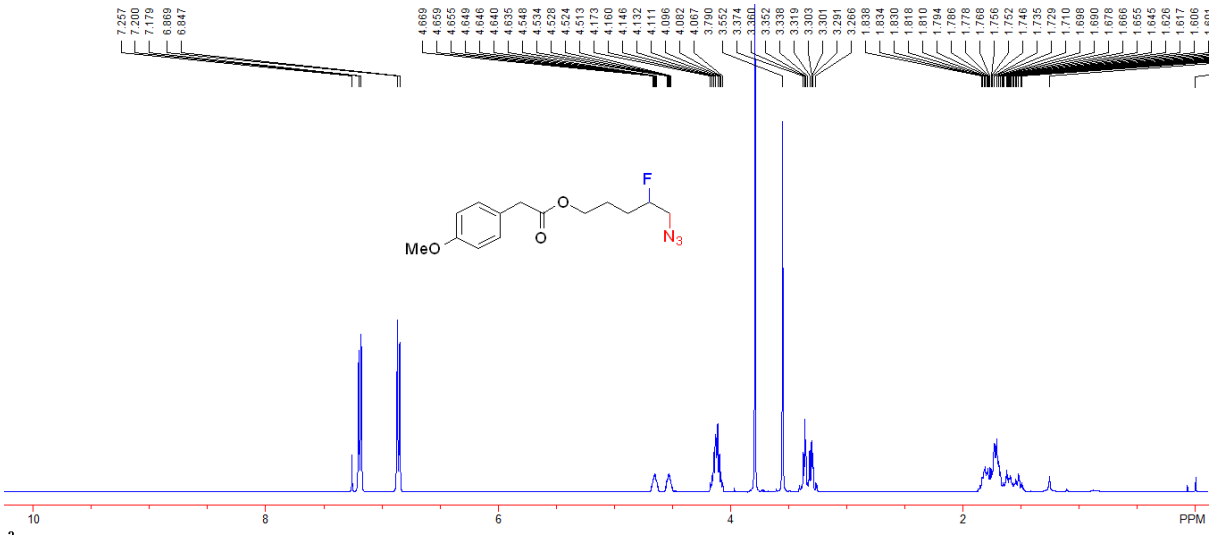
Compound **5**

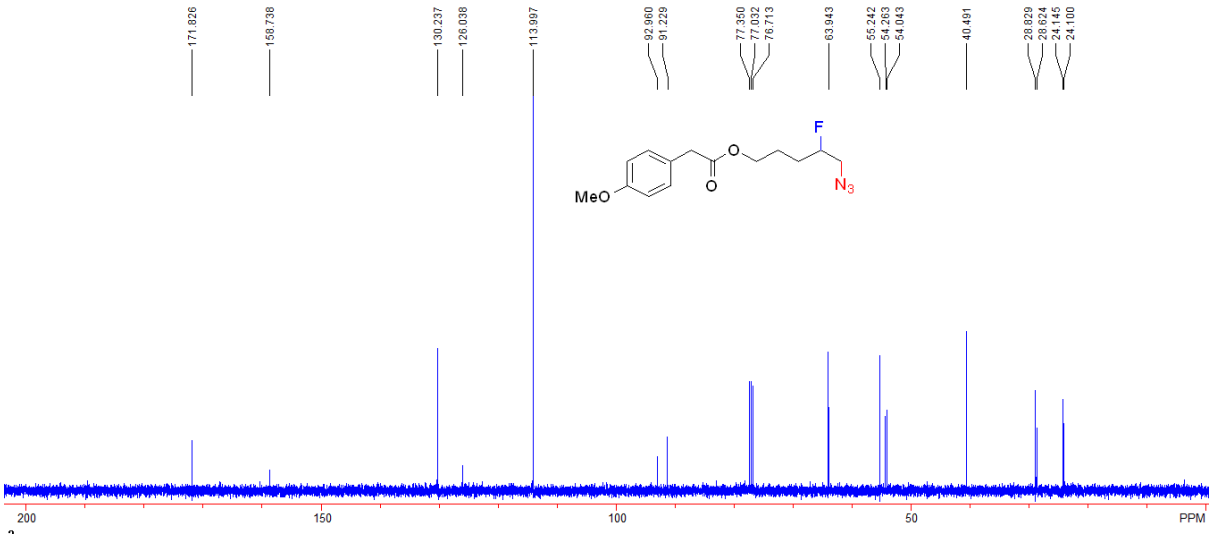


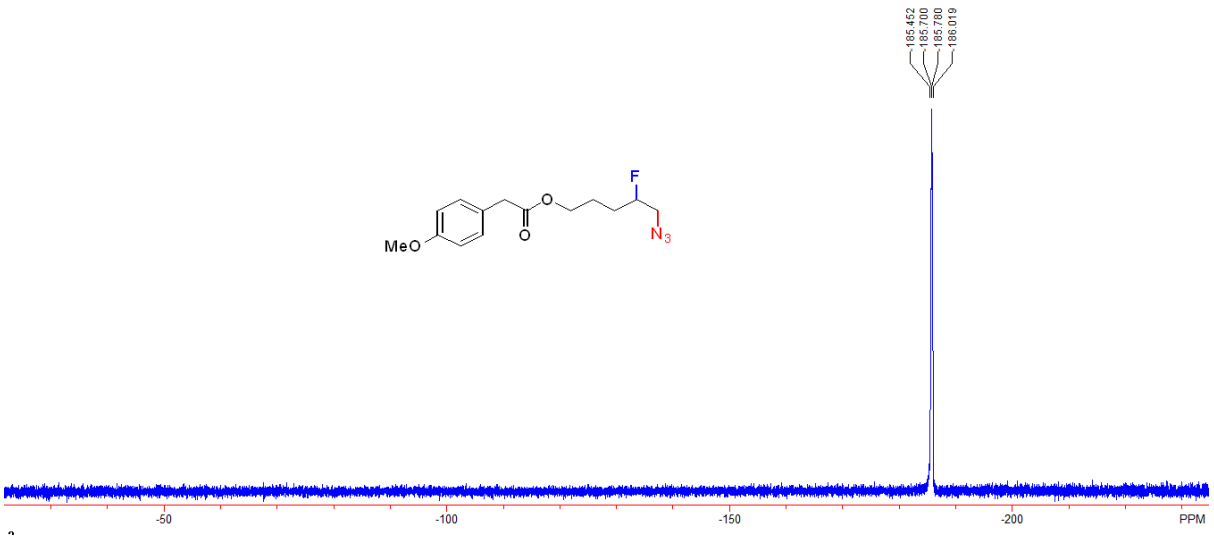




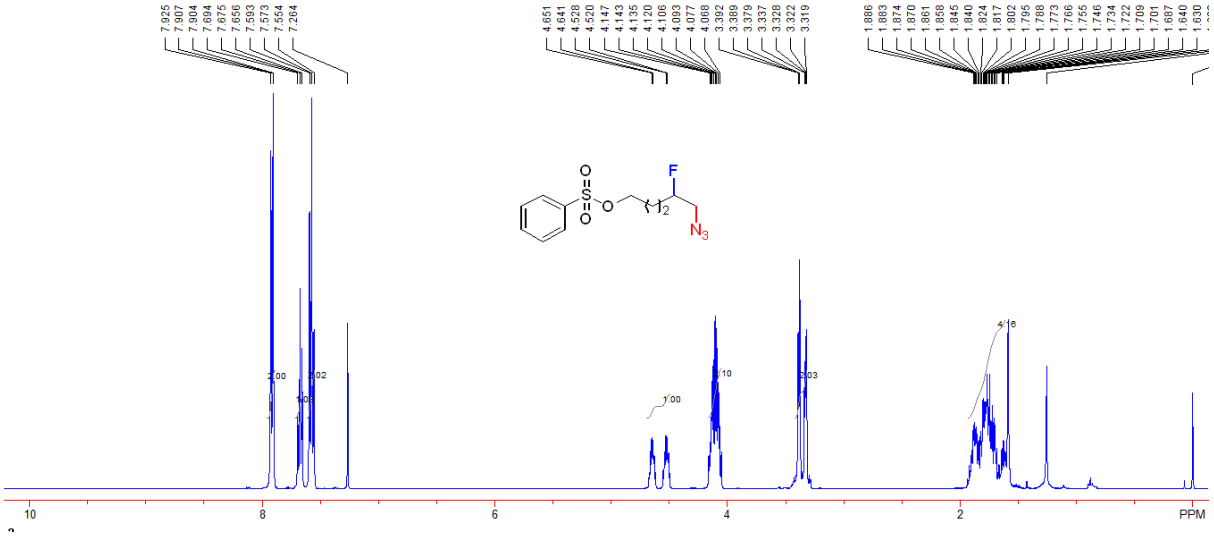
Compound **6**

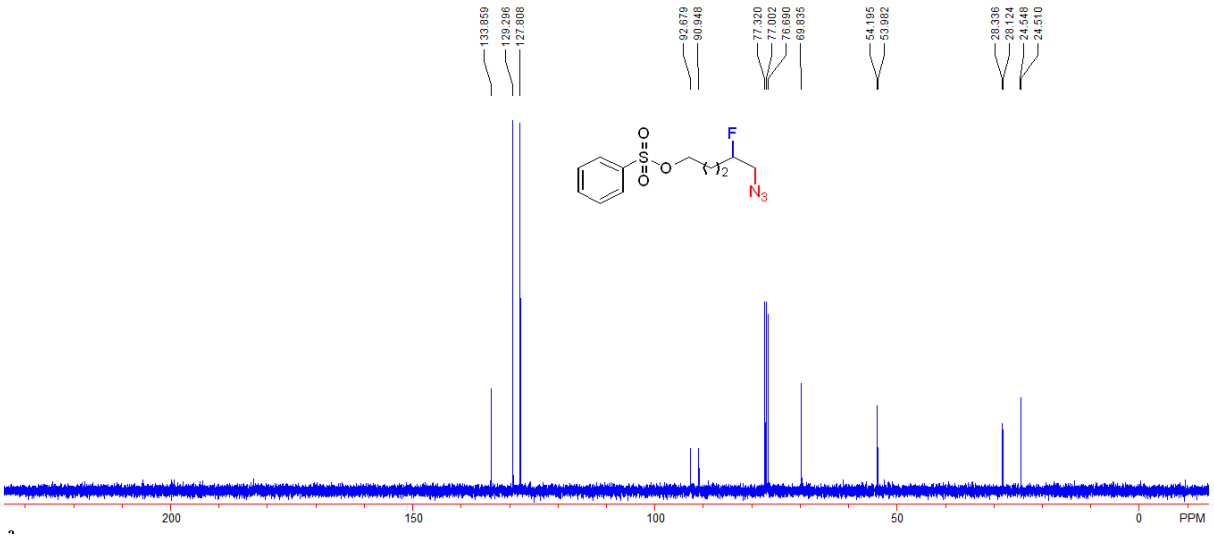

7.257
7.200
7.179
6.869
6.847
4.669
4.659
4.655
4.649
4.646
4.640
4.635
4.548
4.534
4.528
4.524
4.513
4.173
4.160
4.146
4.132
4.111
4.096
4.082
4.067
3.790
3.552
3.374
3.360
3.352
3.338
3.319
3.303
3.301
3.291
3.266
1.838
1.834
1.830
1.818
1.810
1.794
1.786
1.778
1.768
1.756
1.752
1.746
1.735
1.729
1.710
1.698
1.690
1.678
1.666
1.655
1.645
1.626
1.617
1.606
F
O
O
N3
MeO
10
8
6
4
2
PPM

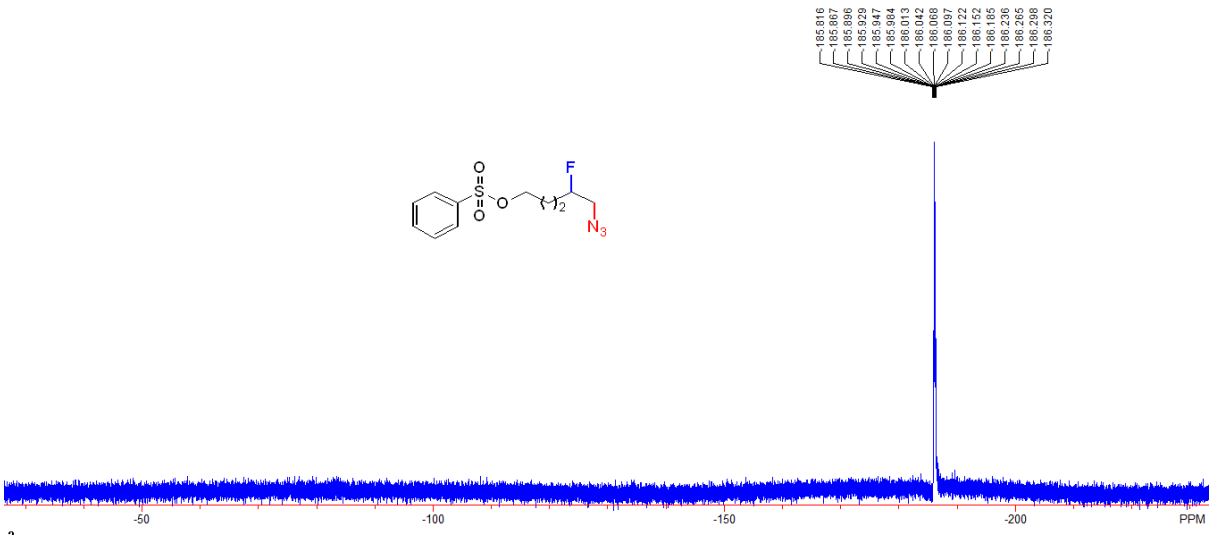

171.826
158.738
130.237
126.038
113.997
92.960
91.229
77.350
77.032
76.713
63.943
55.242
54.263
54.043
40.491
28.829
28.624
24.145
24.100
F
O
O
N3
MeO
200
150
100
50
PPM


185.452
185.700
185.780
186.019
F
O
O
N3
MeO
-50
-100
-150
-200
PPM

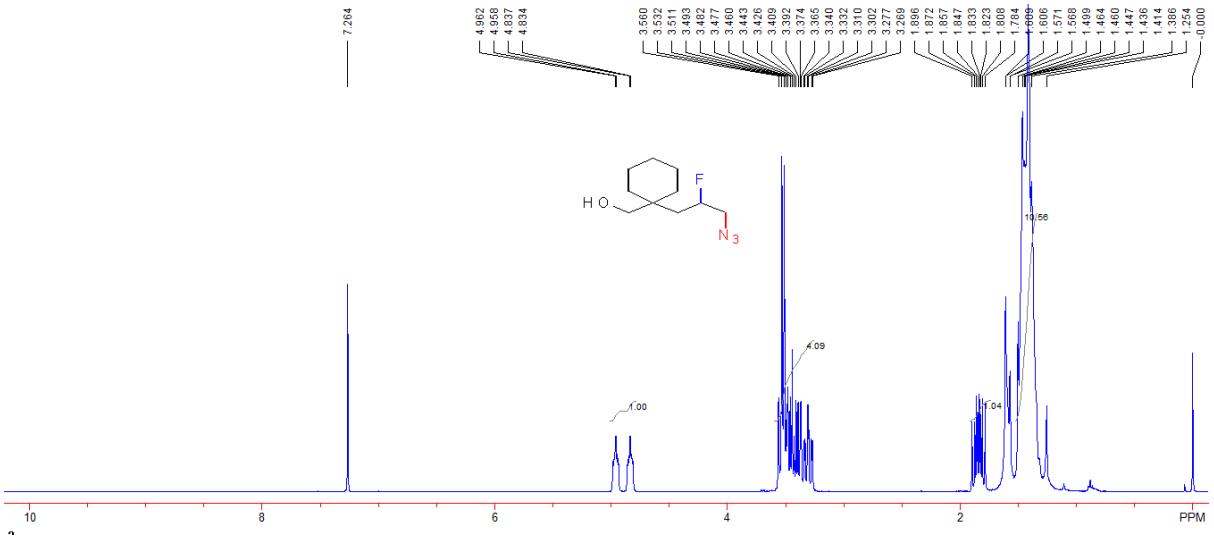
Compound **7**

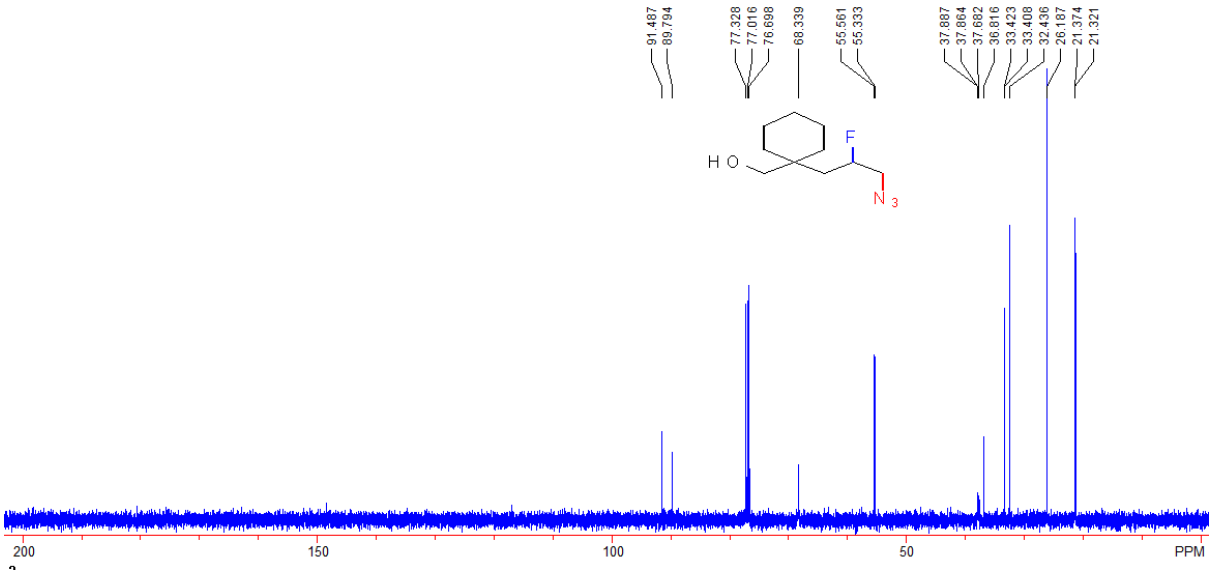


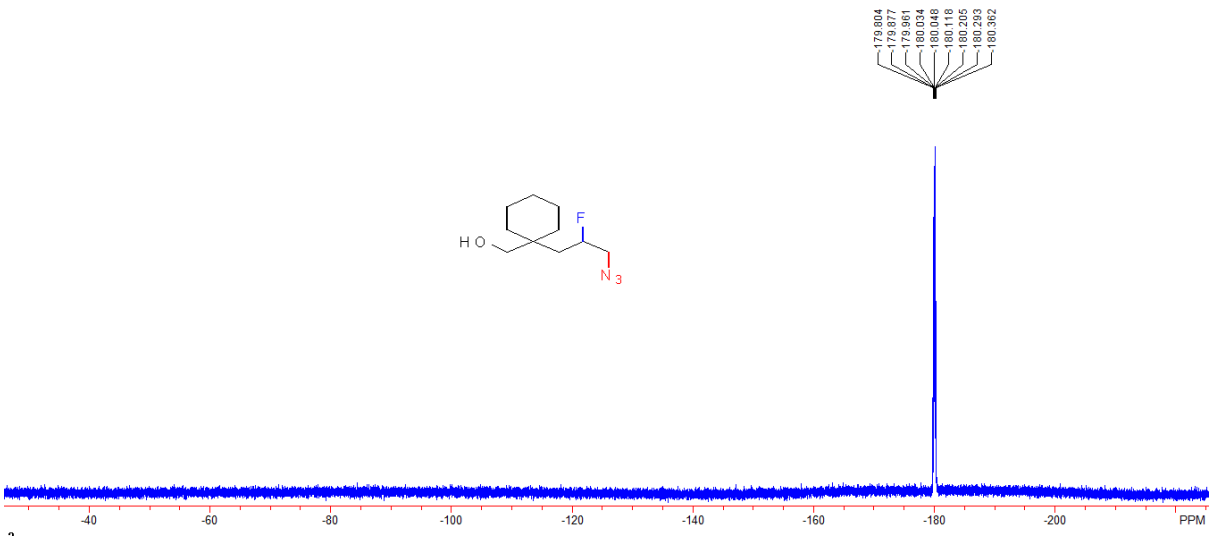




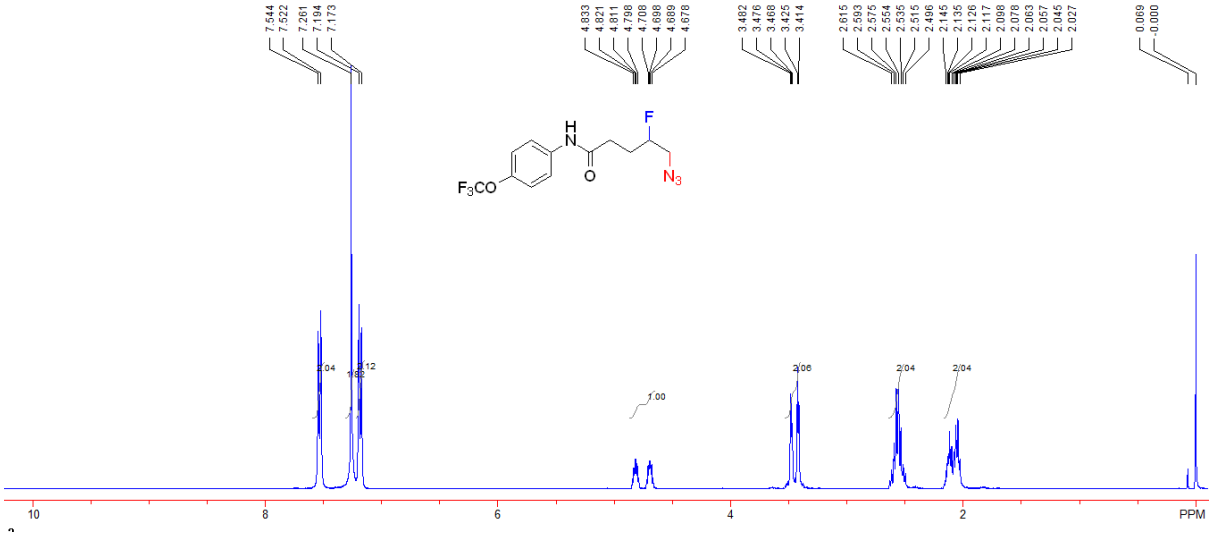
Compound **8**


7.264
4.962
4.958
4.837
4.834
3.560
3.532
3.511
3.493
3.482
3.477
3.460
3.443
3.426
3.409
3.392
3.374
3.365
3.340
3.332
3.310
3.302
3.277
3.269
1.896
1.872
1.857
1.847
1.833
1.823
1.808
1.784
1.606
1.571
1.568
1.499
1.464
1.460
1.447
1.436
1.414
1.386
1.254
0.000
HO
F
N3
1.00
4.09
10.56
1.04
10
8
6
4
2
PPM


91.487
89.794
77.328
77.016
76.698
68.339
55.561
55.333
37.887
37.864
37.682
36.816
33.423
33.408
32.436
26.187
21.374
21.321
HO
F
N3
200
150
100
50
PPM


179.804
179.877
179.961
180.034
180.048
180.118
180.205
180.293
180.362
HO
F
N3
-40
-60
-80
-100
-120
-140
-160
-180
-200
PPM

Compound **9**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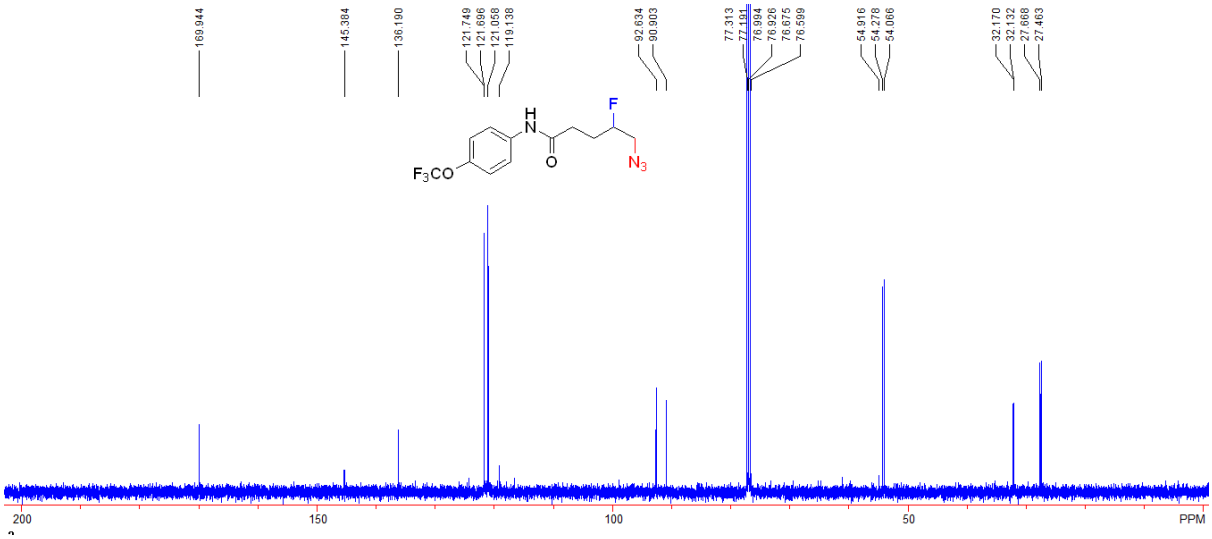
7.261
7.194
7.173
4.833
4.821
4.811
4.798
4.708
4.698
4.689
4.678
3.482
3.476
3.468
3.425
3.414
2.615
2.593
2.575
2.554
2.535
2.515
2.496
2.145
2.135
2.126
2.117
2.098
2.078
2.063
2.057
2.045
2.027
0.089
0.000
2.04
2.12
1.00
2.06
2.04
2.04
F
H
N
O
F3CO
N3
10
8
6
4
2
PPM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136.190
121.749
121.696
121.058
119.138
92.634
90.903
77.313
77.191
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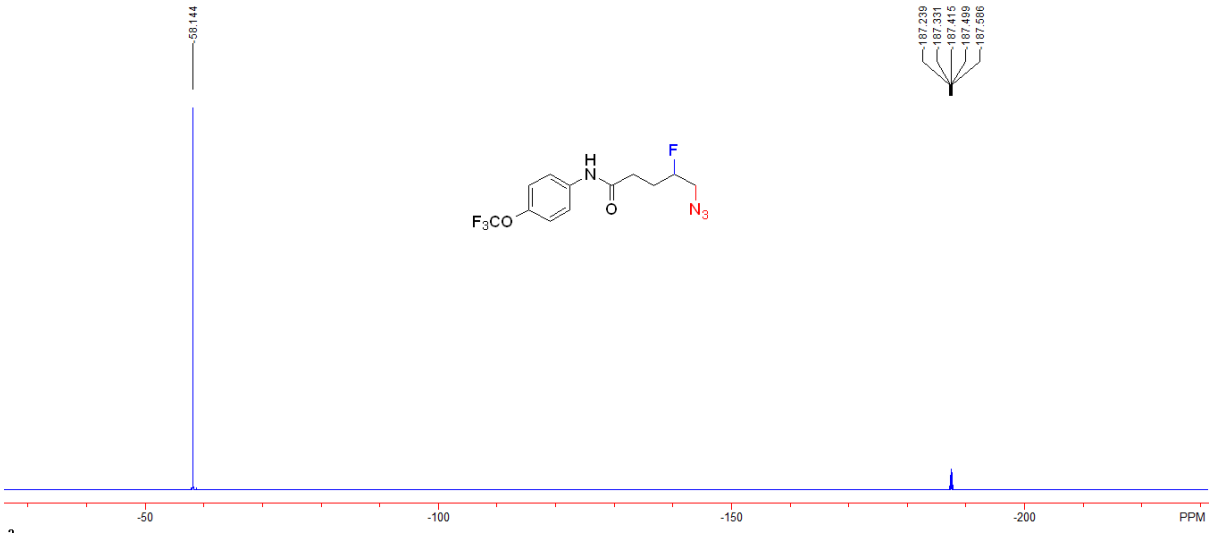
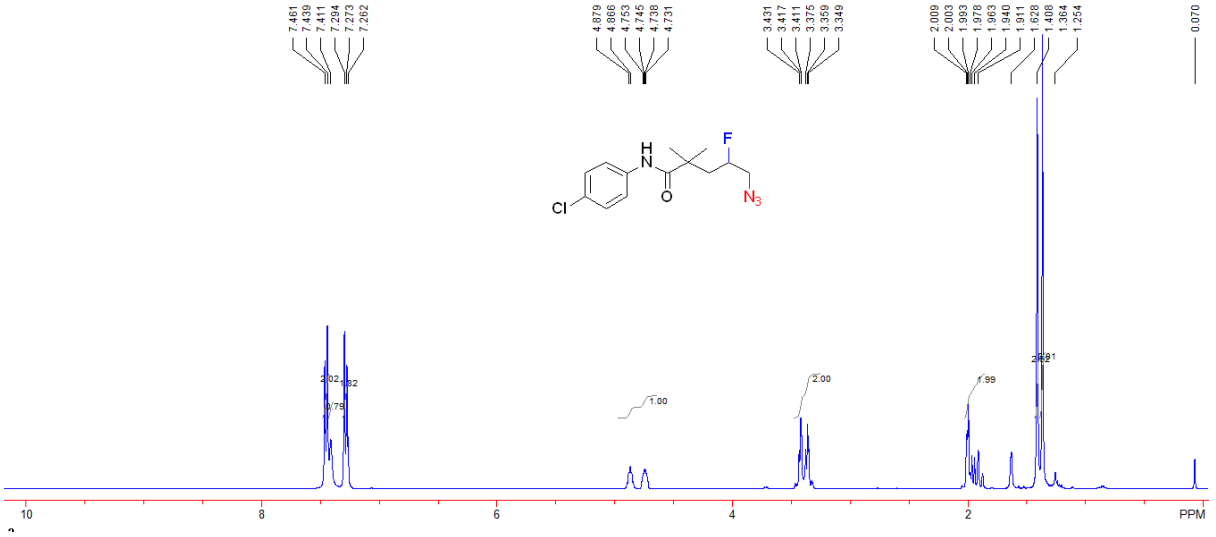
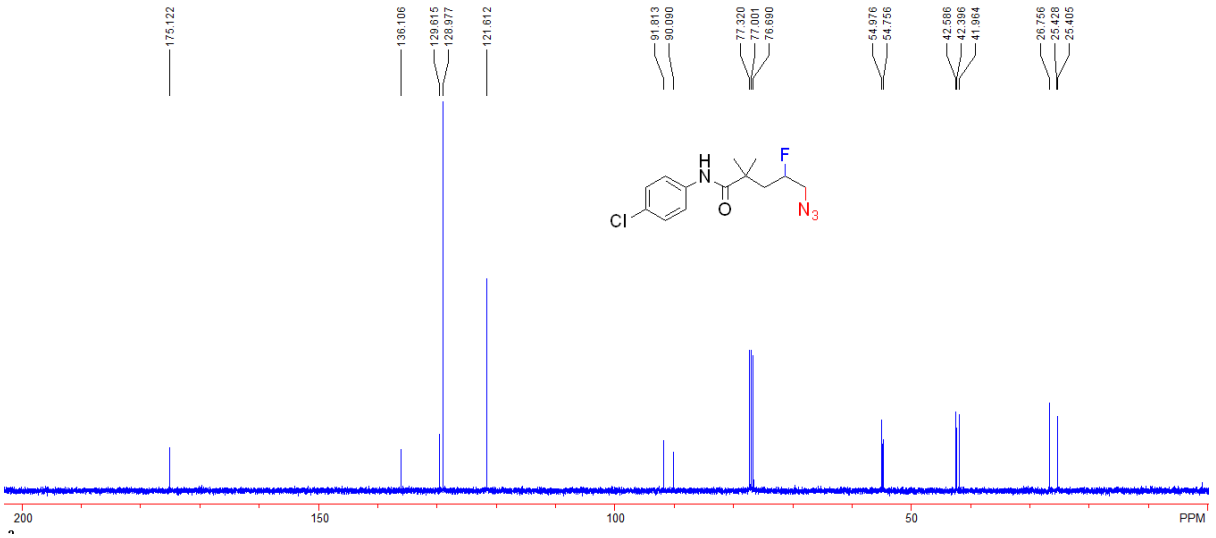
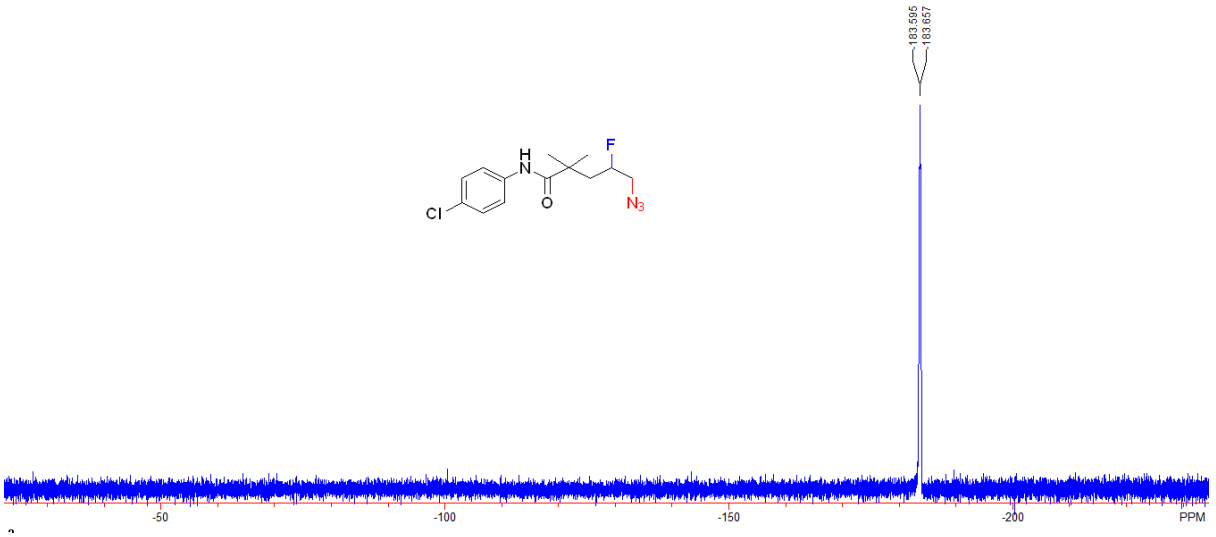
76.926
76.675
76.599
54.916
54.278
54.066
32.170
32.132
27.668
27.463
F
H
N
O
F3CO
N3
200
150
100
50
PPM


58.144
187.239
187.331
187.415
187.499
187.586
F
H
N
O
F3CO
N3
-50
-100
-150
-200
PPM

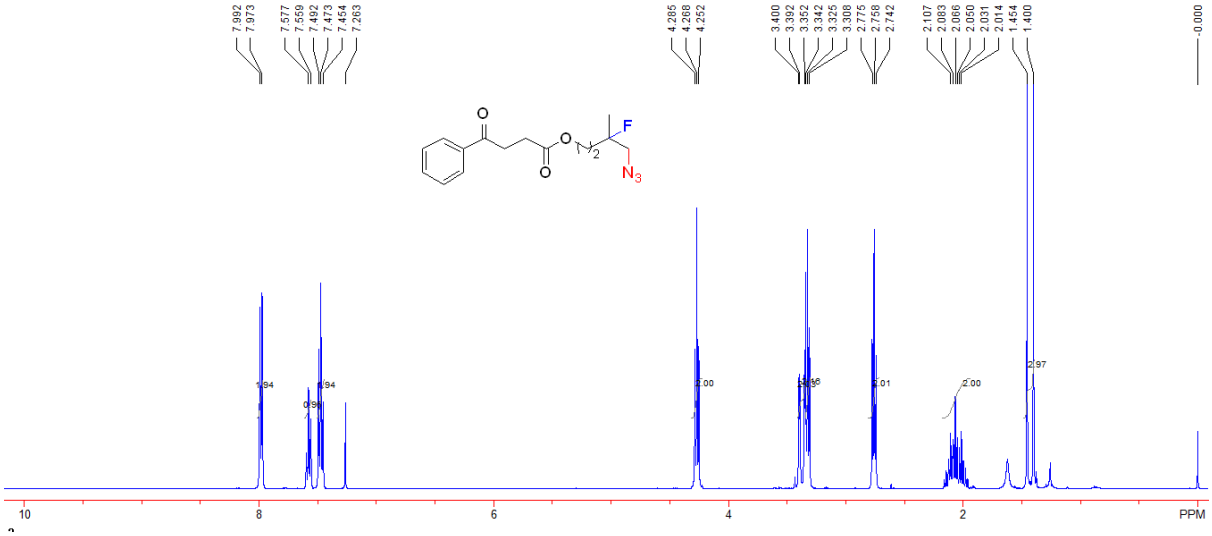
Compound **10**

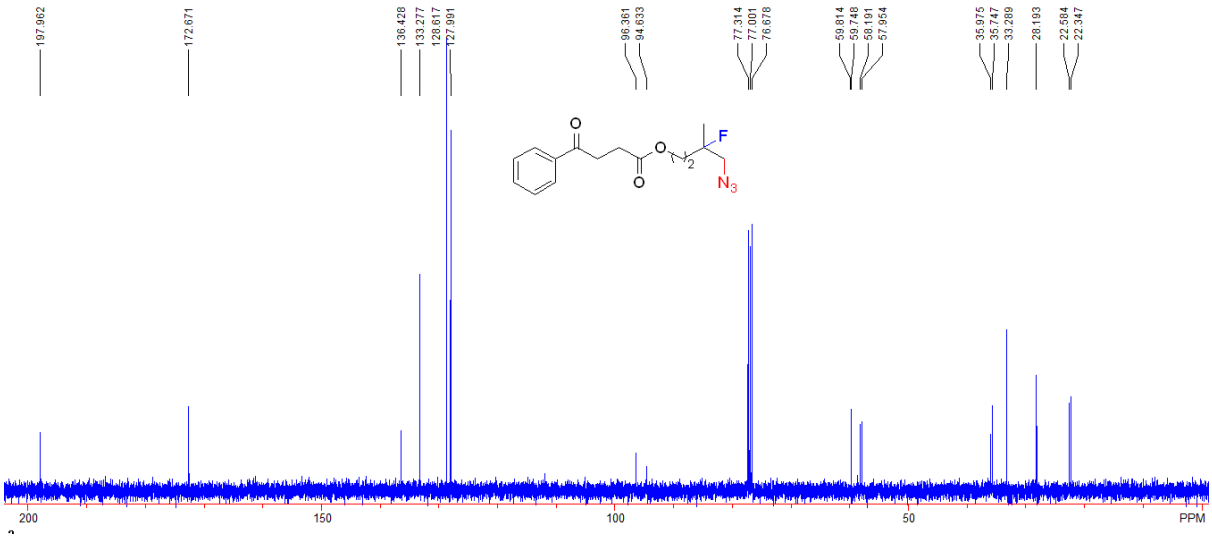


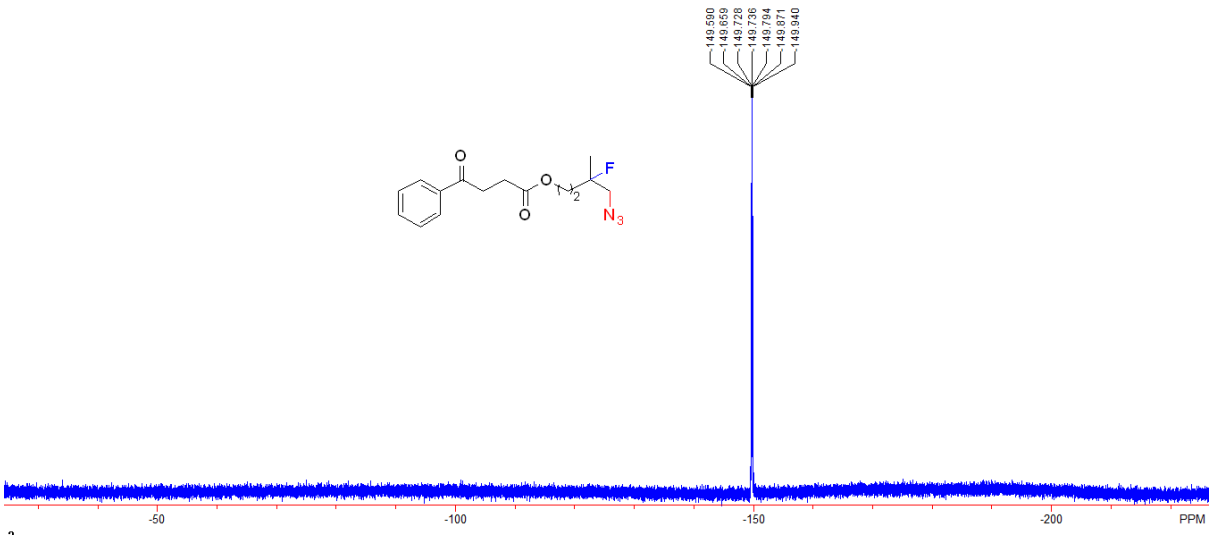




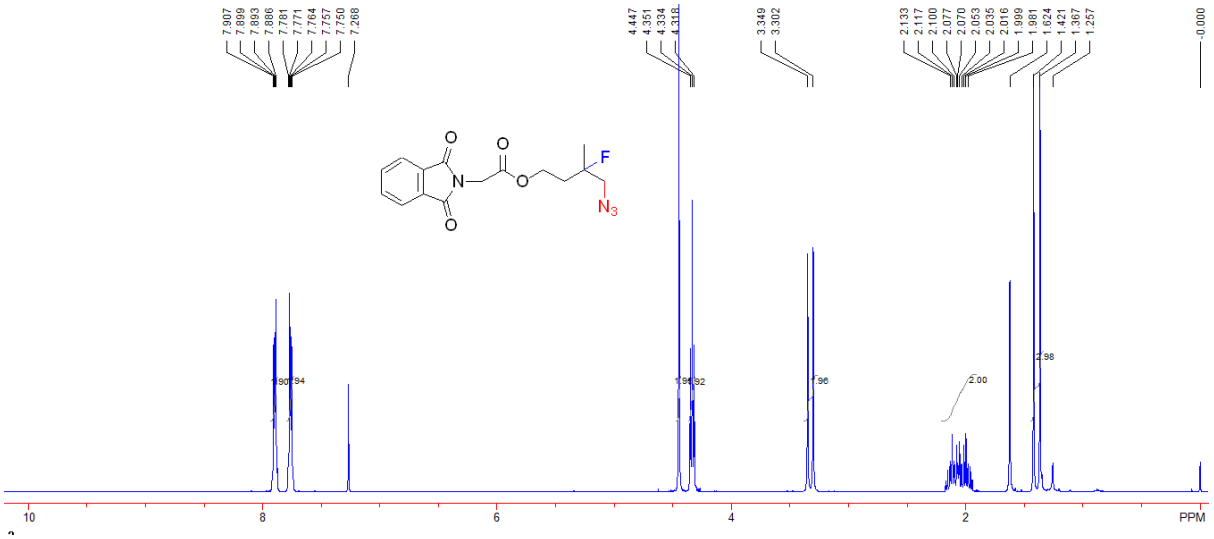
Compound **11**

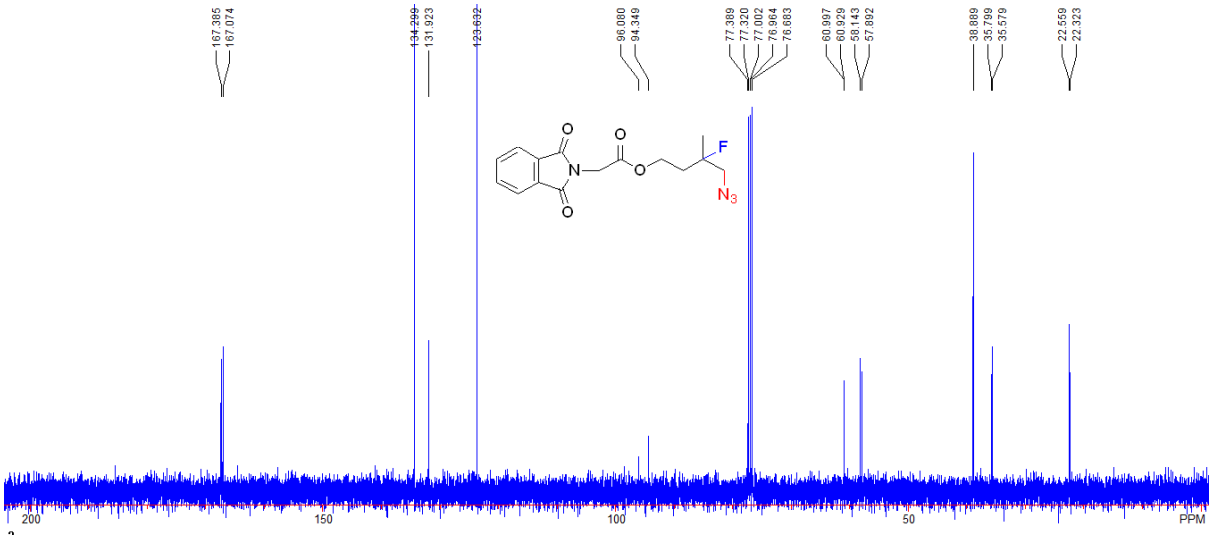


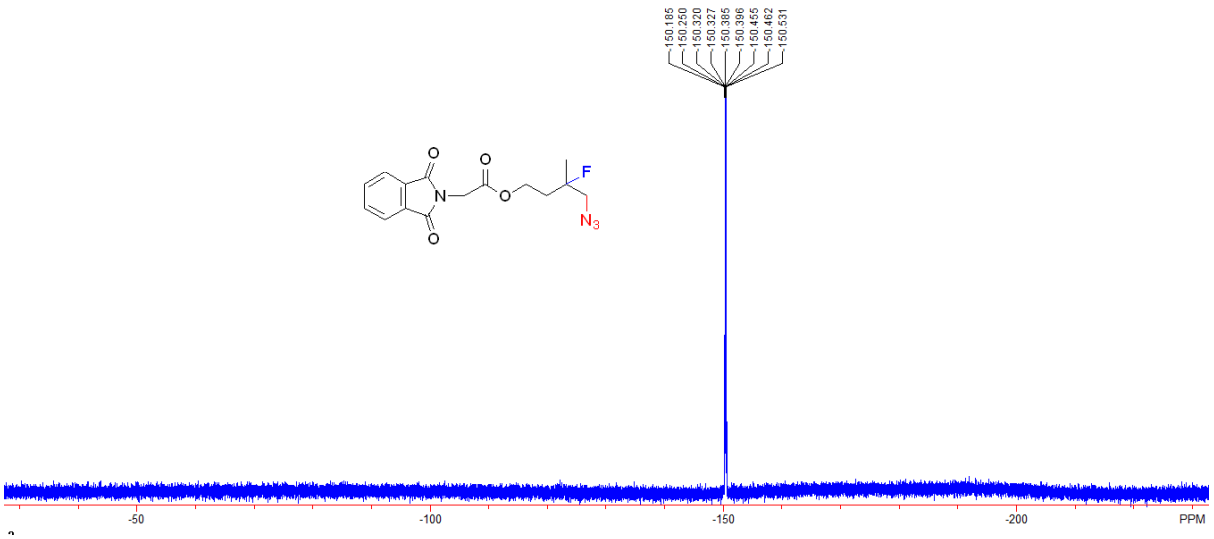




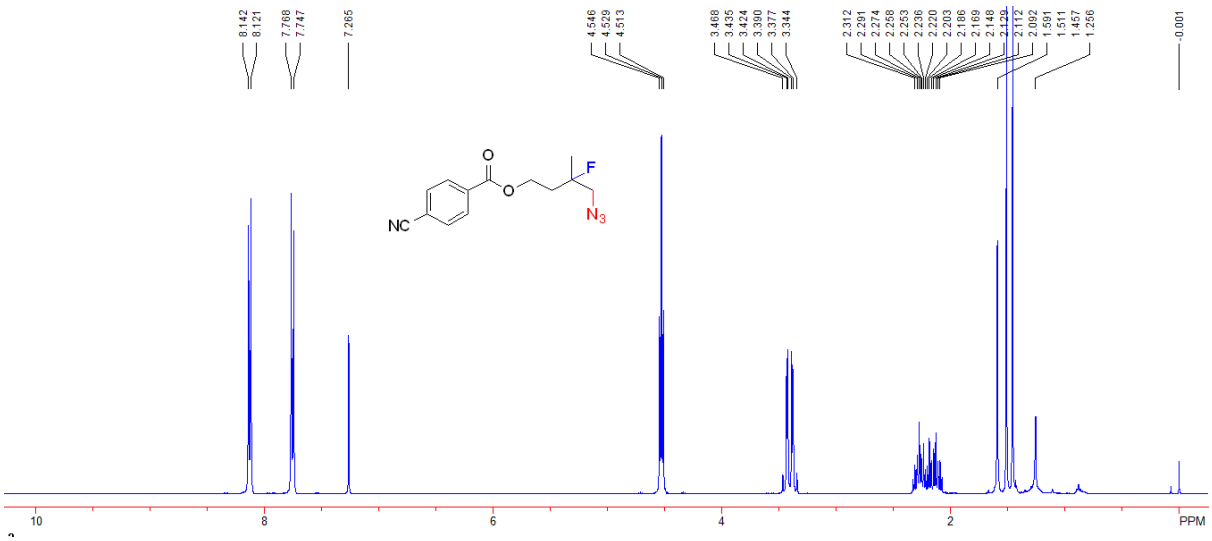
Compound **12**







Compound **13**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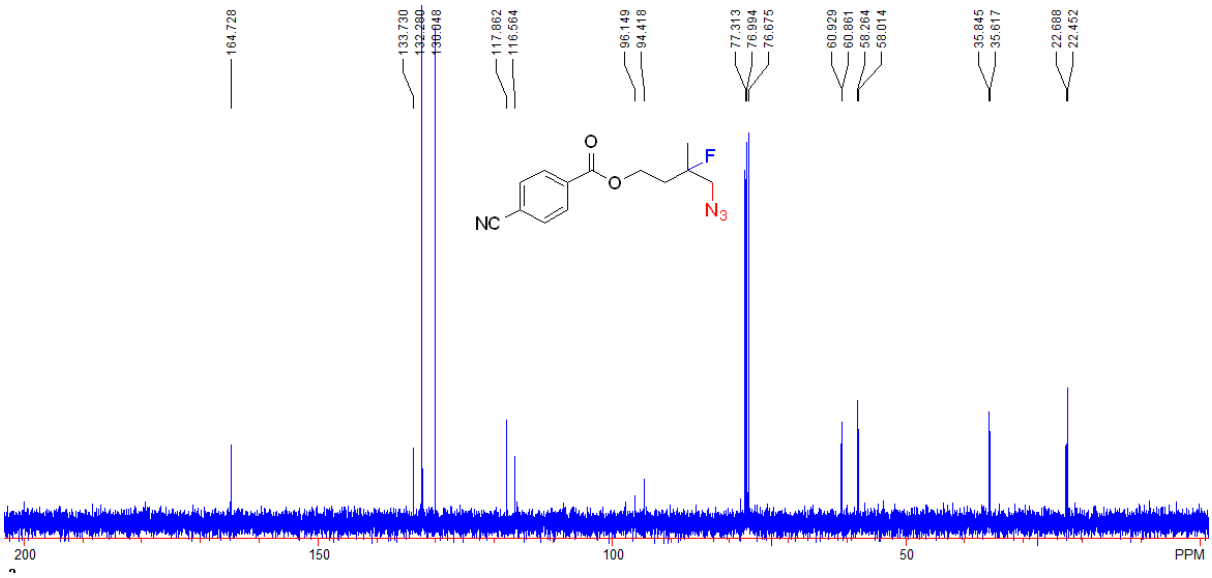
7.747
7.265
4.546
4.529
4.513
3.468
3.435
3.424
3.390
3.377
3.344
2.312
2.291
2.274
2.258
2.253
2.236
2.220
2.203
2.186
2.169
2.148
2.129
2.112
2.092
1.591
1.511
1.457
1.256
0.001
O
O
F
NC
N3
10
8
6
4
2
PPM


164.728
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130.048
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116.564
96.149
94.418
77.313
76.994
76.675
60.929
60.861
58.264
58.014
35.845
35.617
22.688
22.452
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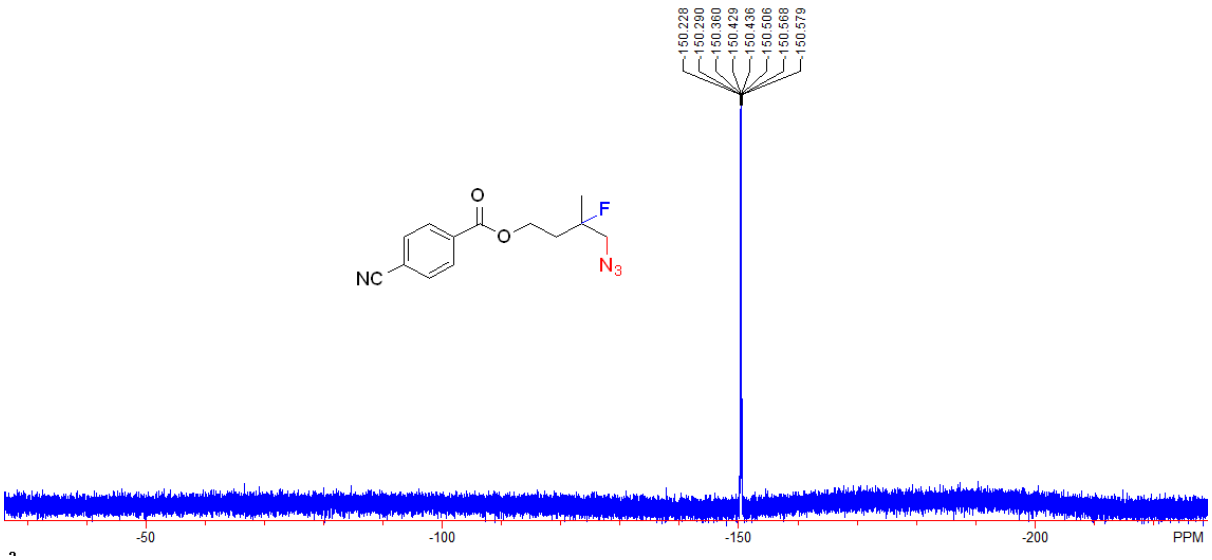
O
F
NC
N3
200
150
100
50
PPM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150.360
150.429
150.436
150.506
150.568
150.579
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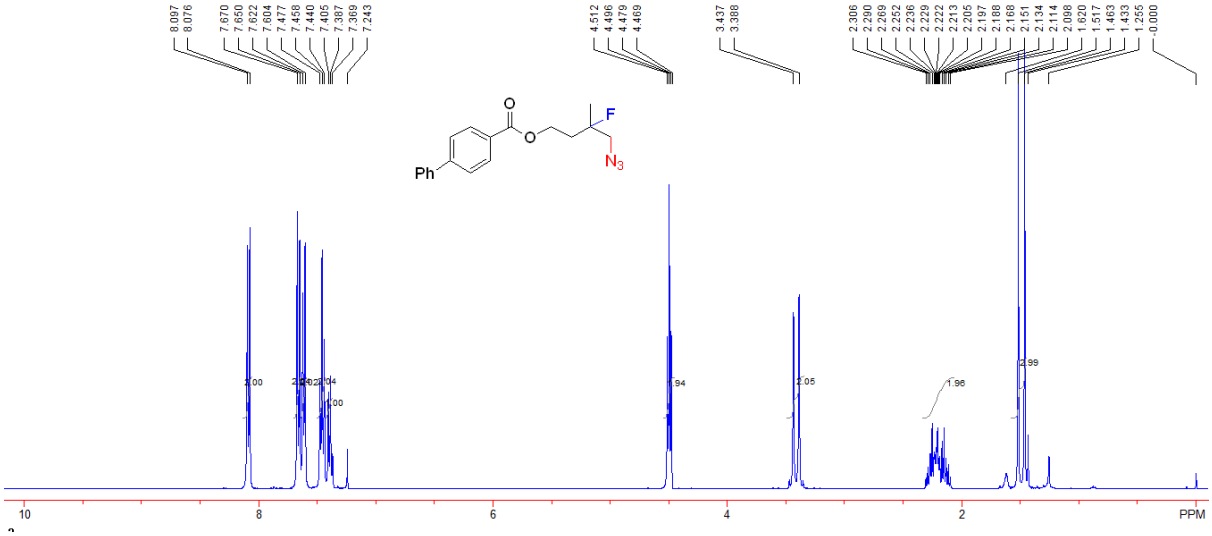
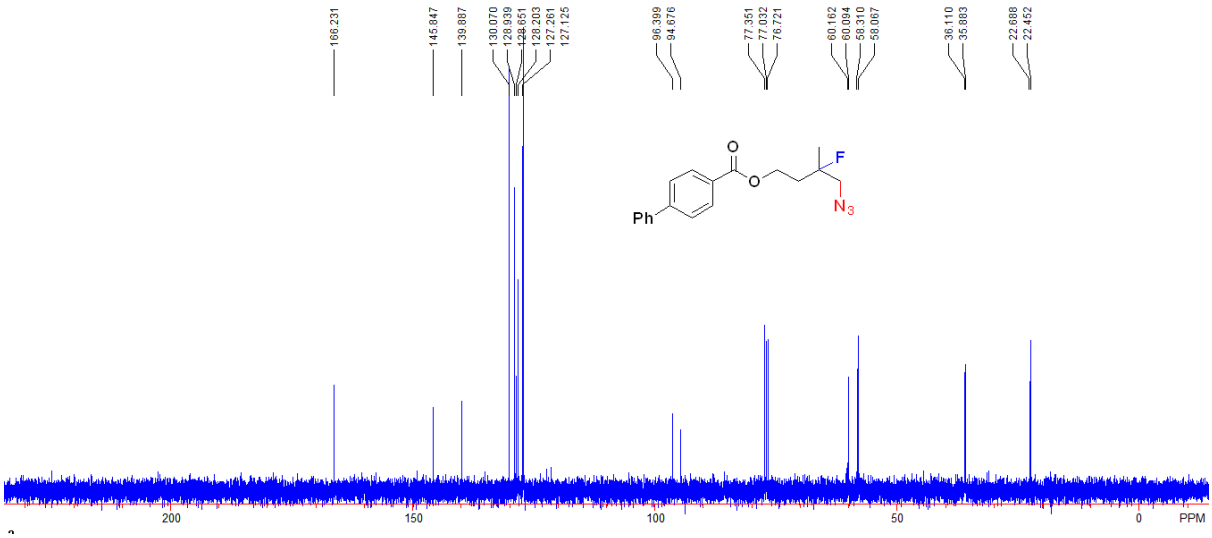
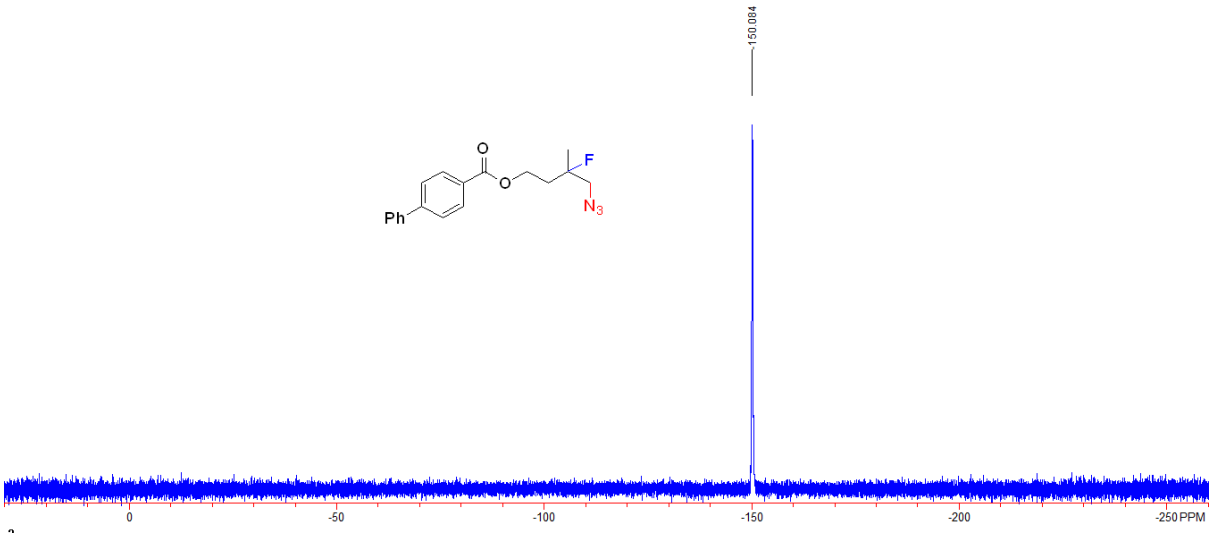
O
F
NC
N3
-50
-100
-150
-200
PPM

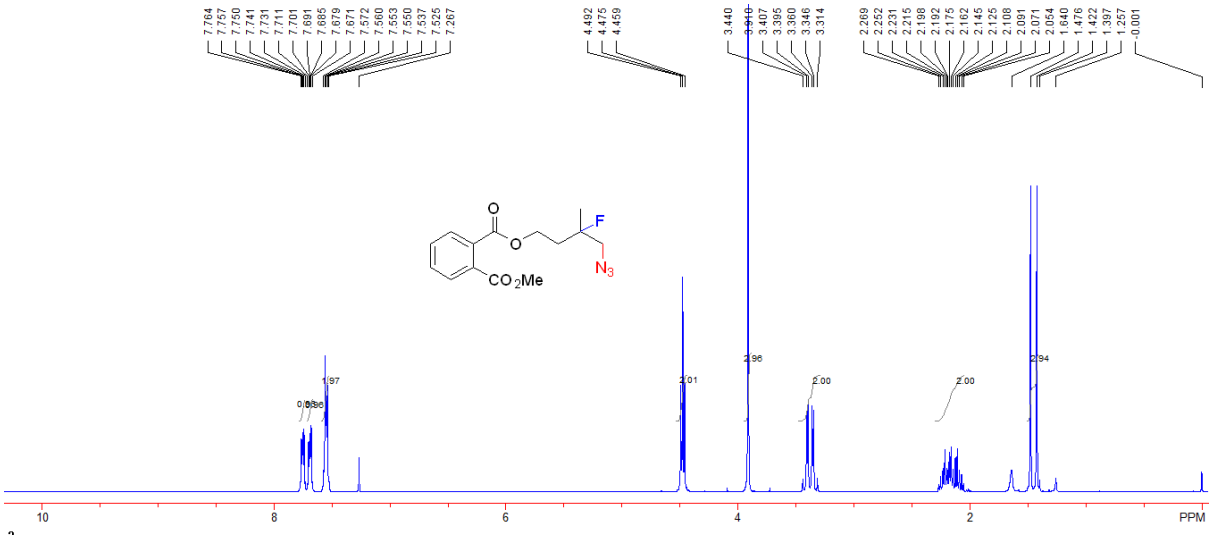
Compound **14**

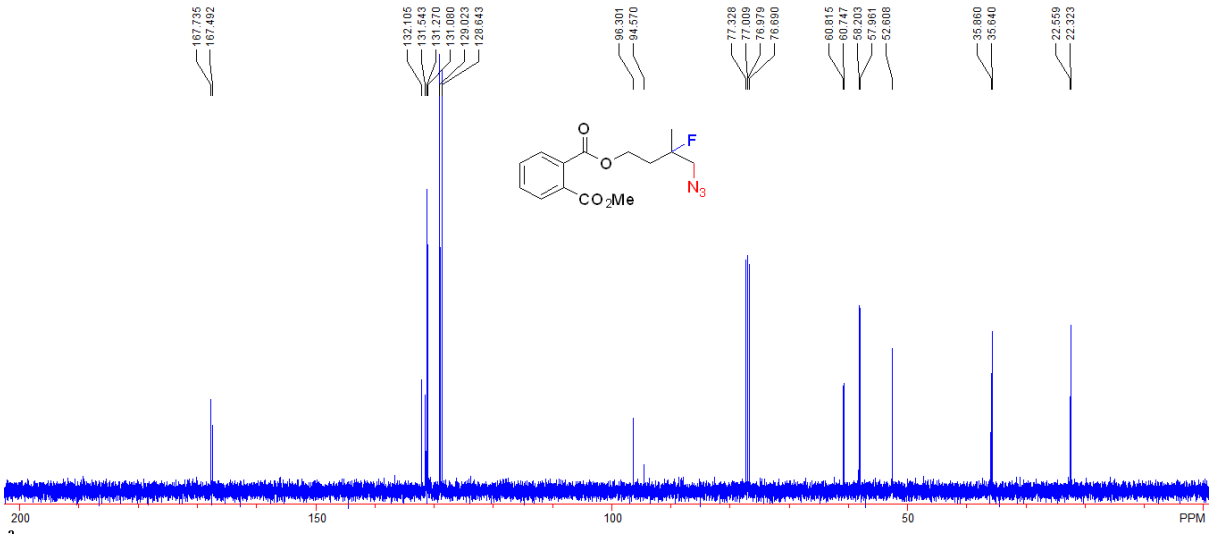


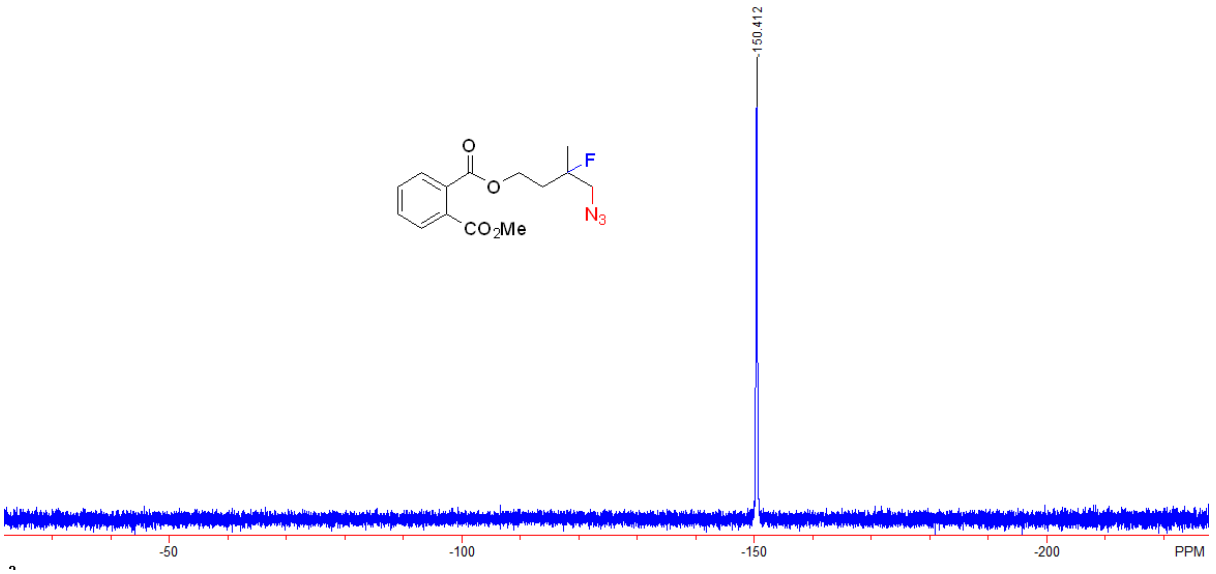




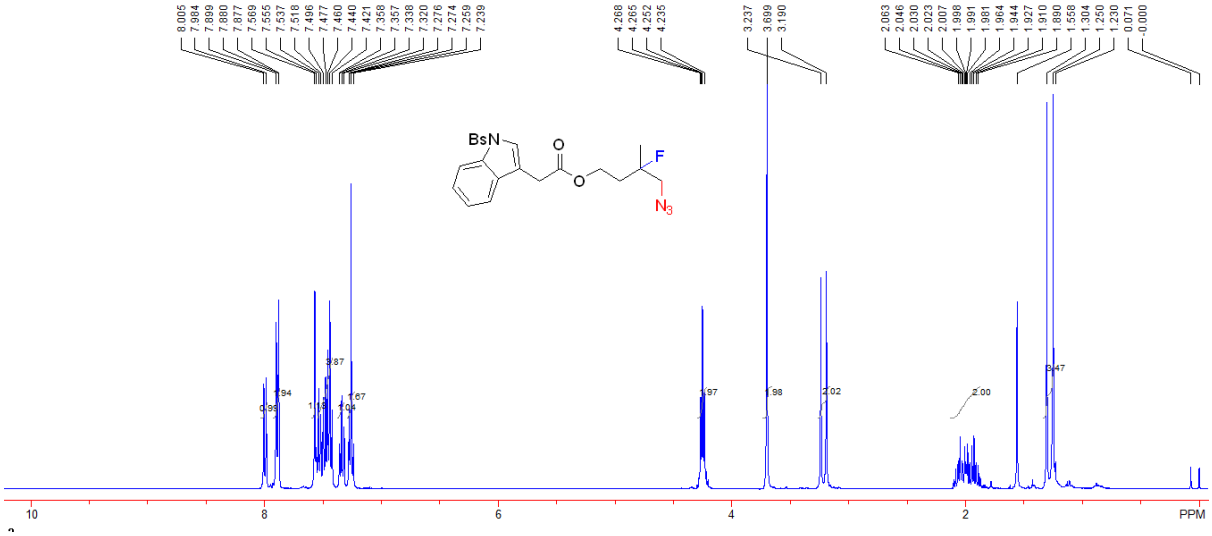
Compound **15**







Compound **16**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7.537
7.518
7.496
7.477
7.460
7.440
7.421
7.358
7.357
7.338
7.320
7.276
7.274
7.259
7.239
4.268
4.265
4.252
4.235
3.237
3.699
3.190
2.063
2.046
2.030
2.023
2.007
1.998
1.991
1.981
1.964
1.944
1.927
1.910
1.890
1.558
1.304
1.250
1.230
0.071
0.000
BsN
O
O
F
N3
0.99
1.94
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1.04
1.97
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2.02
2.00
3.47
10
8
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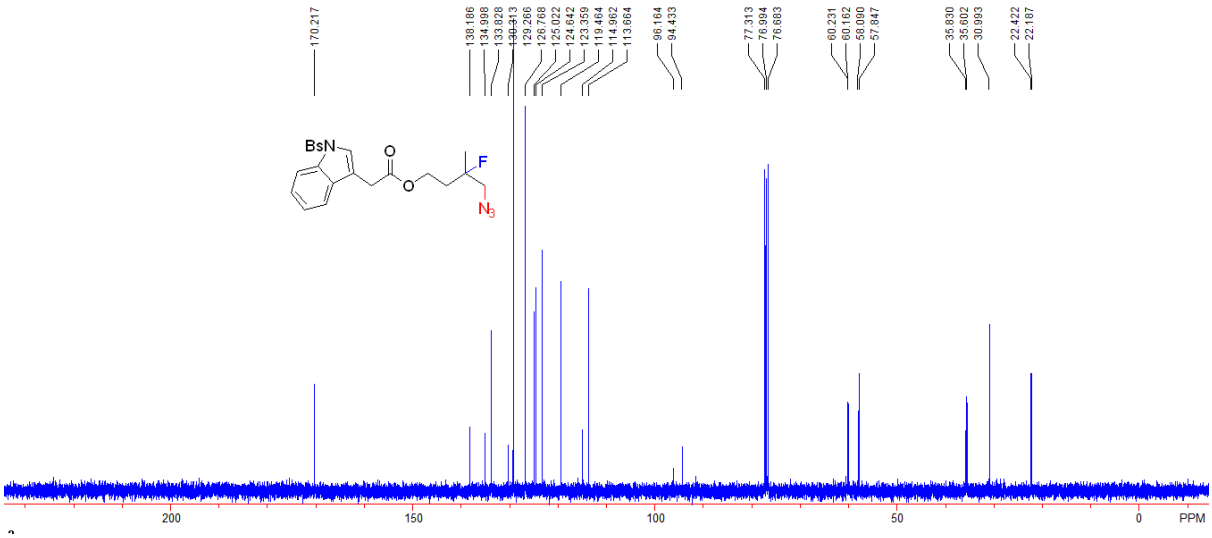
4
2
PPM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129.266
126.768
125.022
124.642
123.359
119.464
114.962
113.664
96.164
94.433
77.313
76.994
76.683
60.231
60.162
58.090
57.847
35.830
35.602
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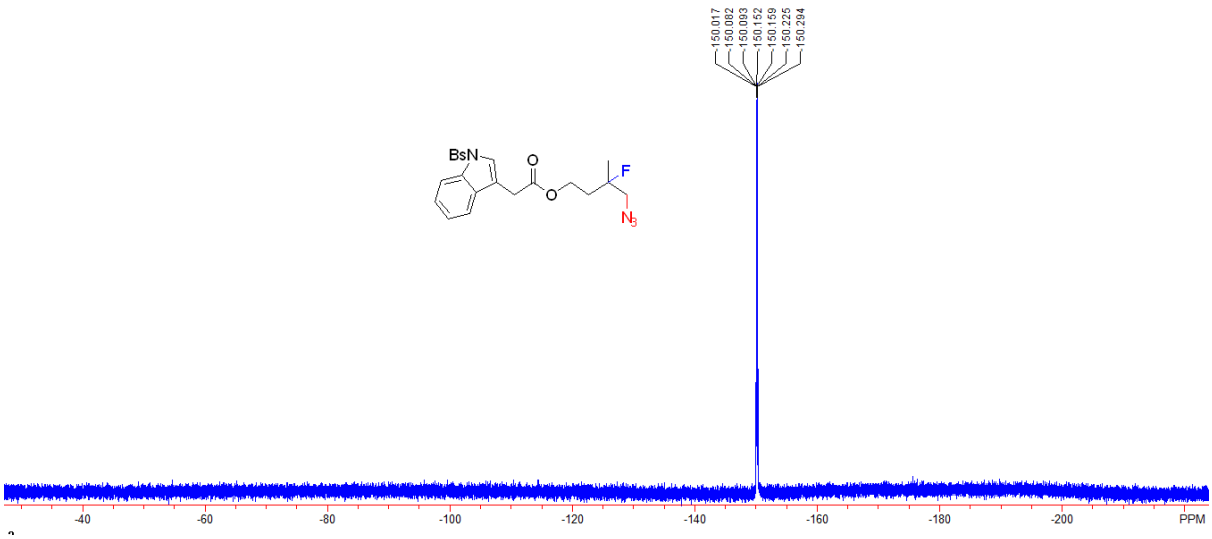
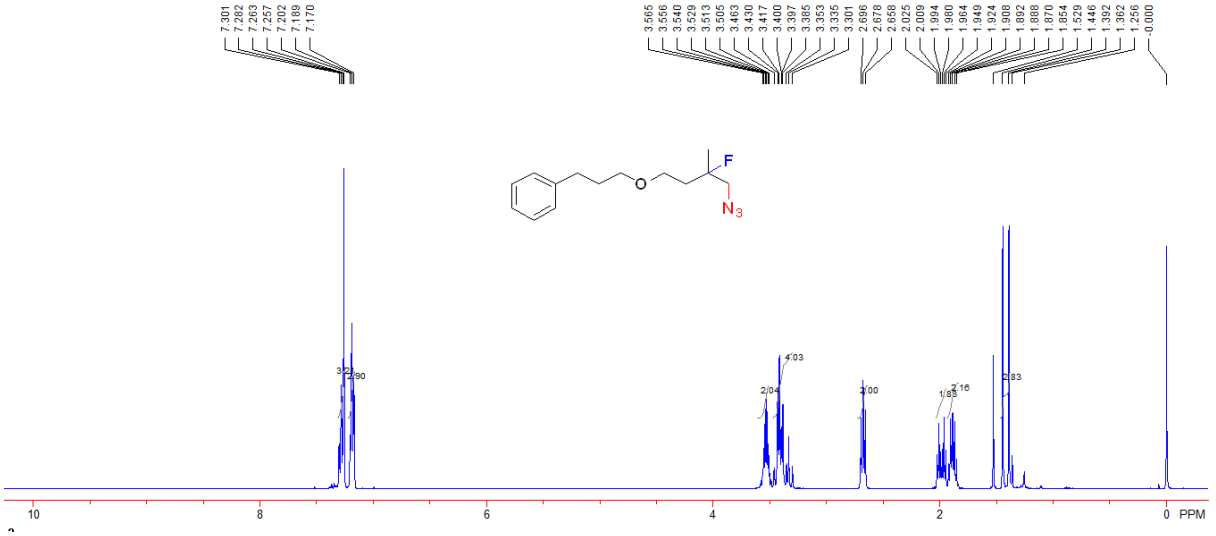
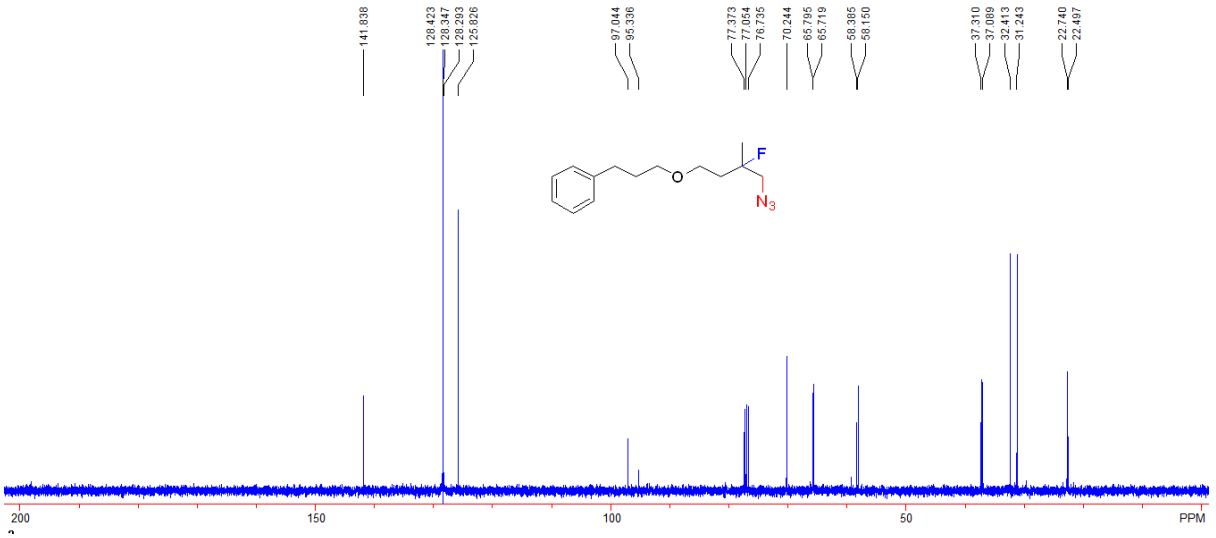
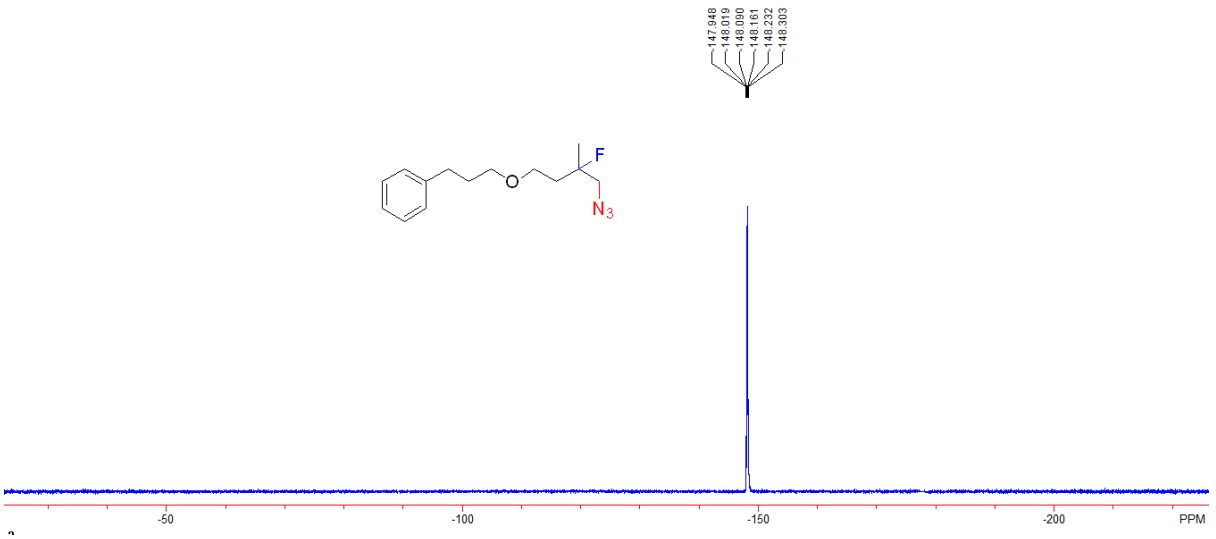
22.422
22.187
BsN
O
O
F
N3
200
150
100
50
0
PPM


150.017
150.082
150.093
150.152
150.159
150.225
150.294
BsN
O
O
F
N3
-40
-60
-80
-100
-120
-140
-160
-180
-200
PPM

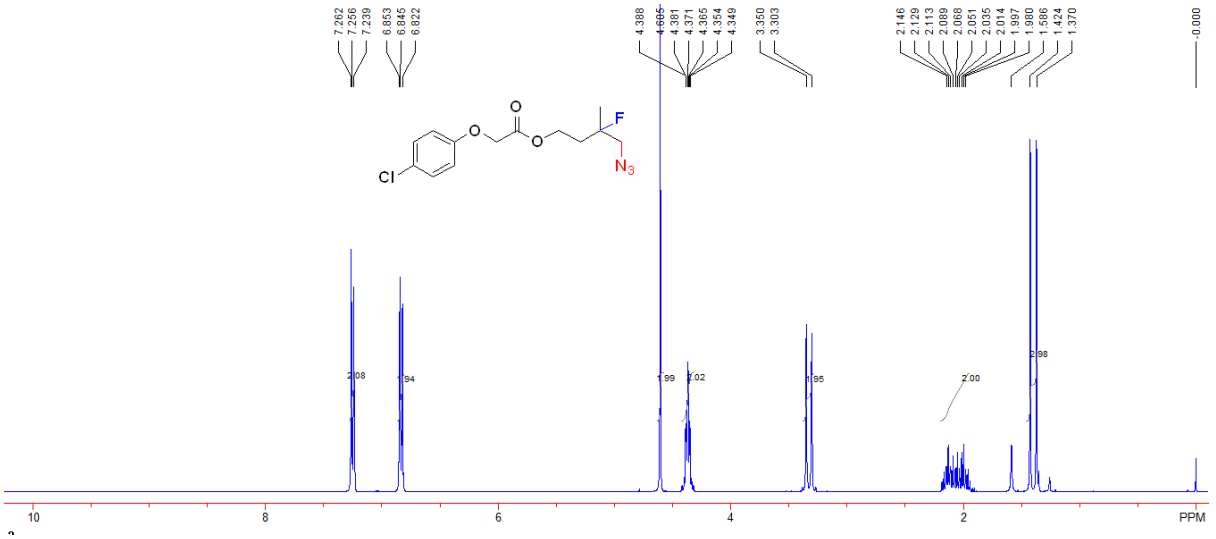
Compound **17**

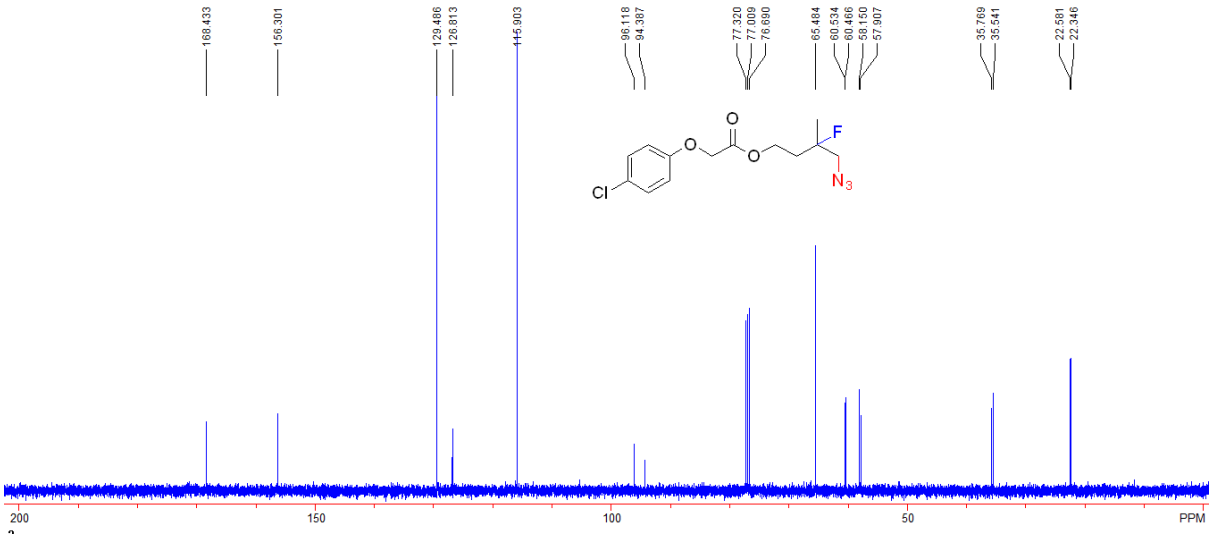


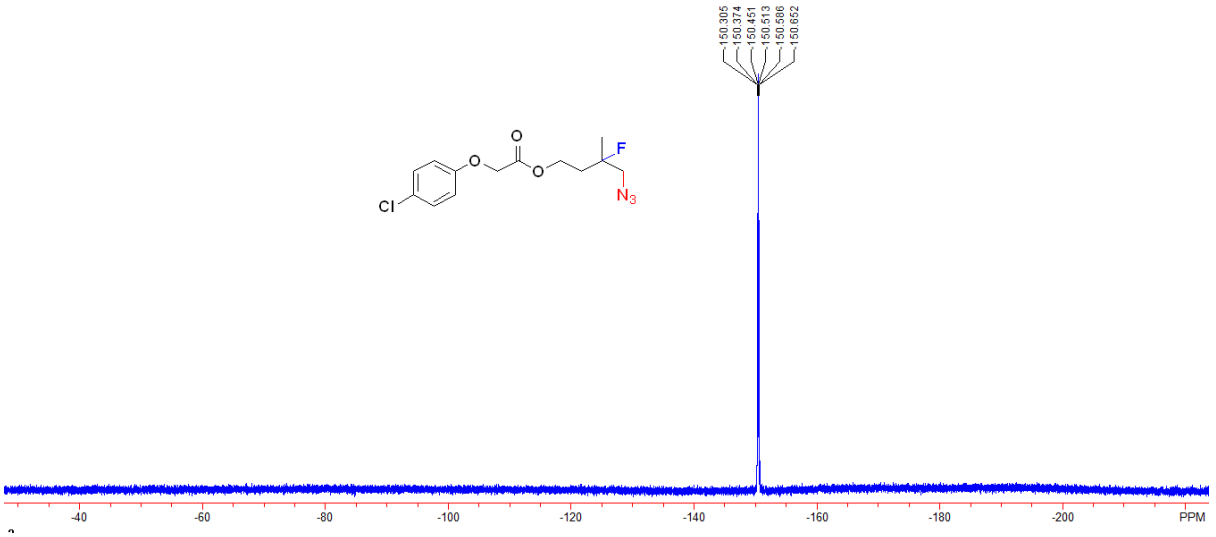




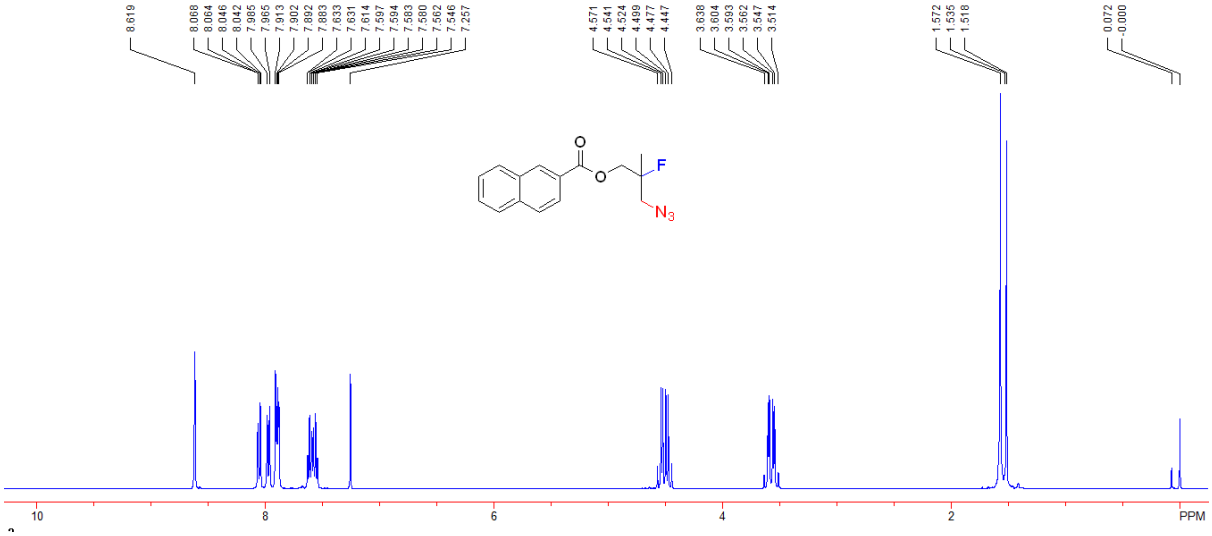
Compound **18**

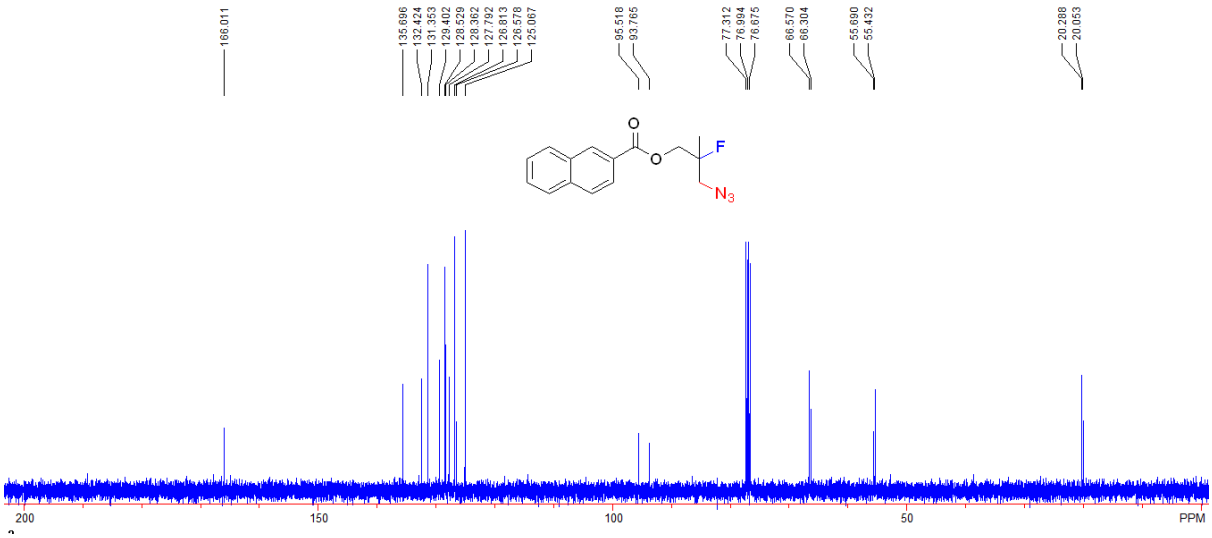


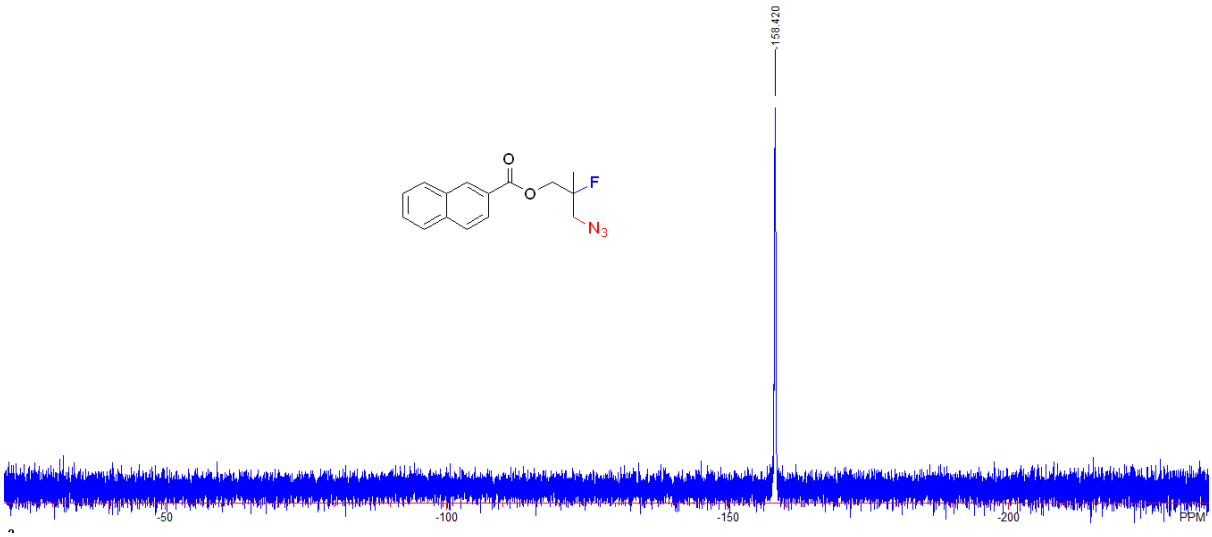




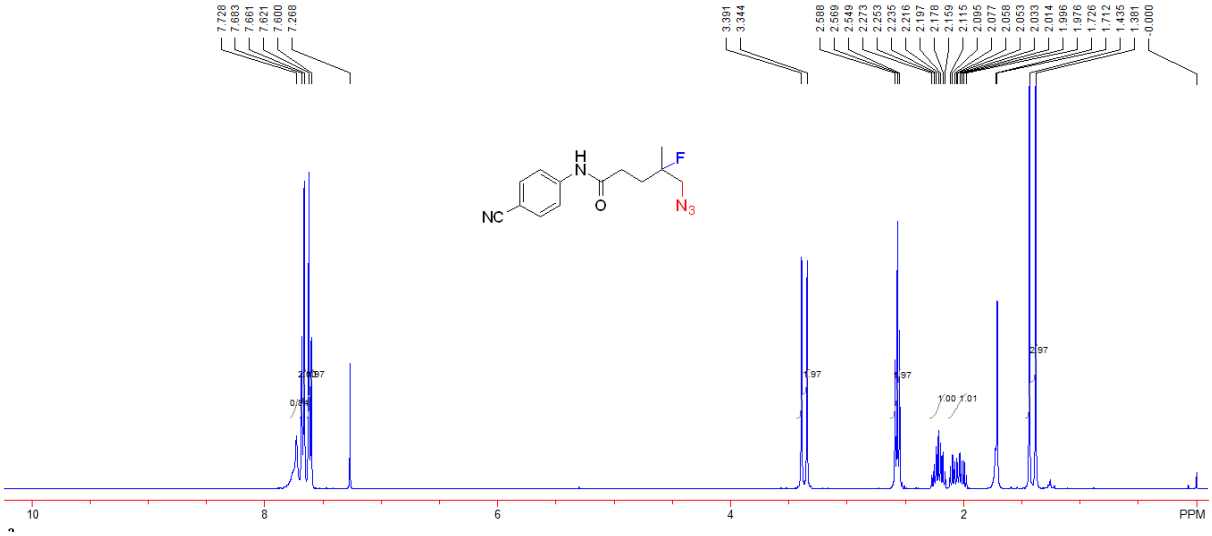
Compound **19**

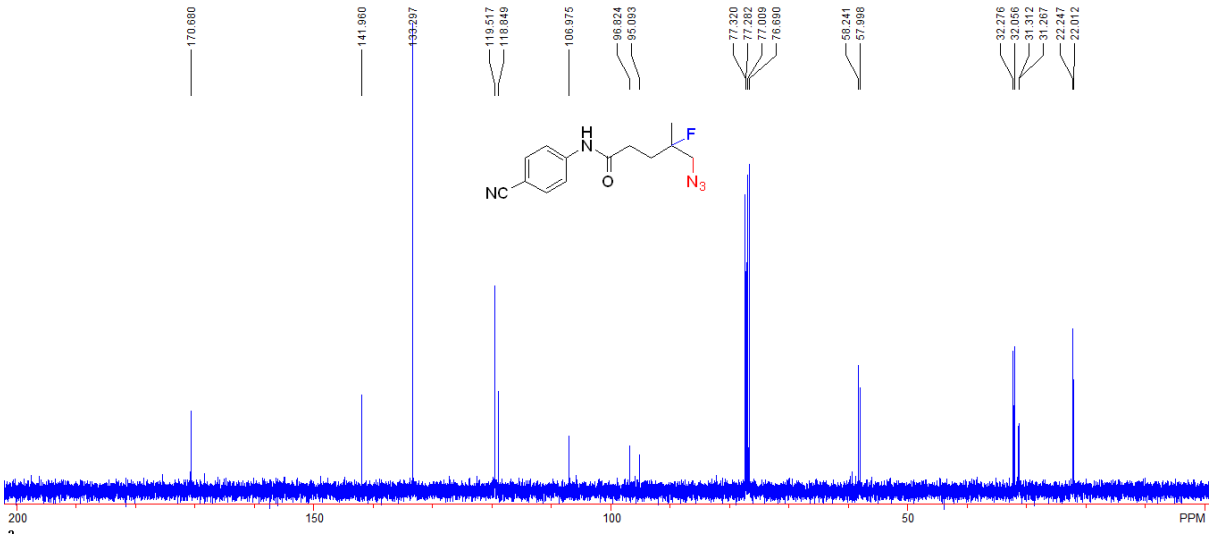


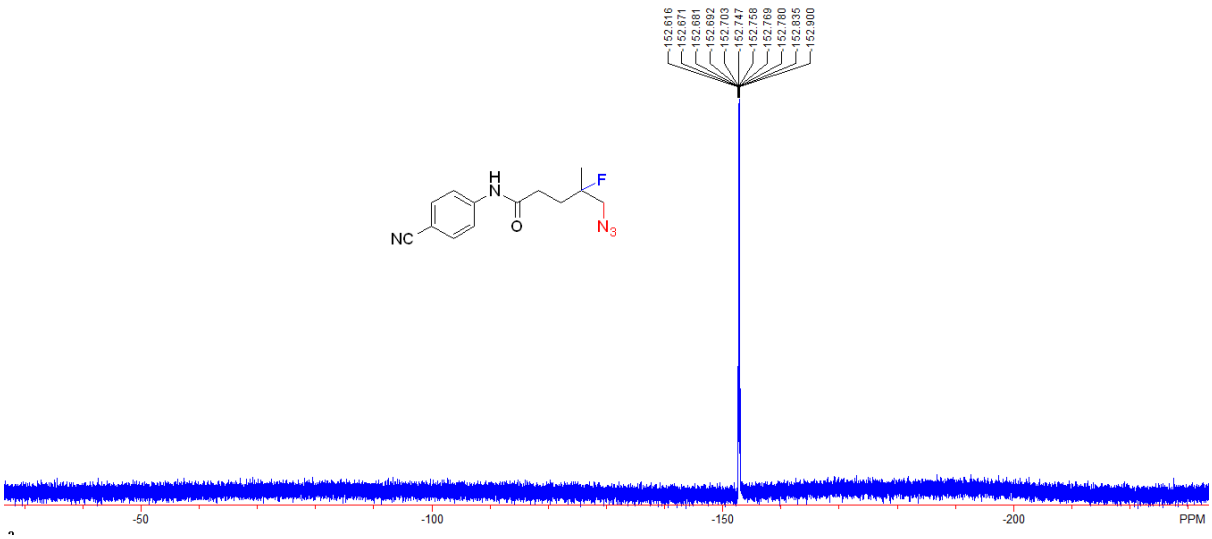




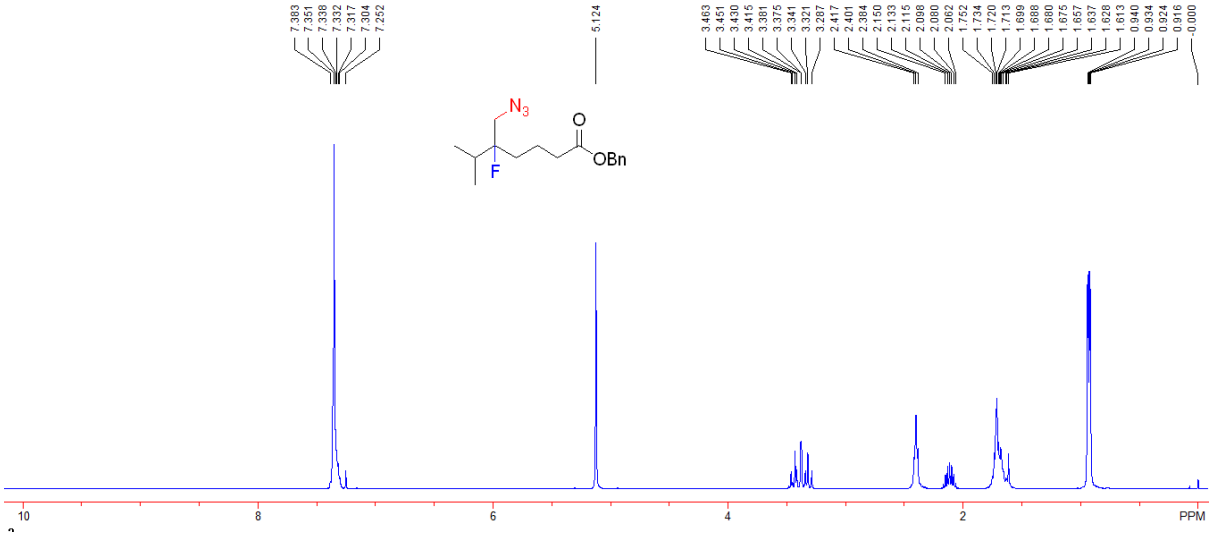
Compound **20**

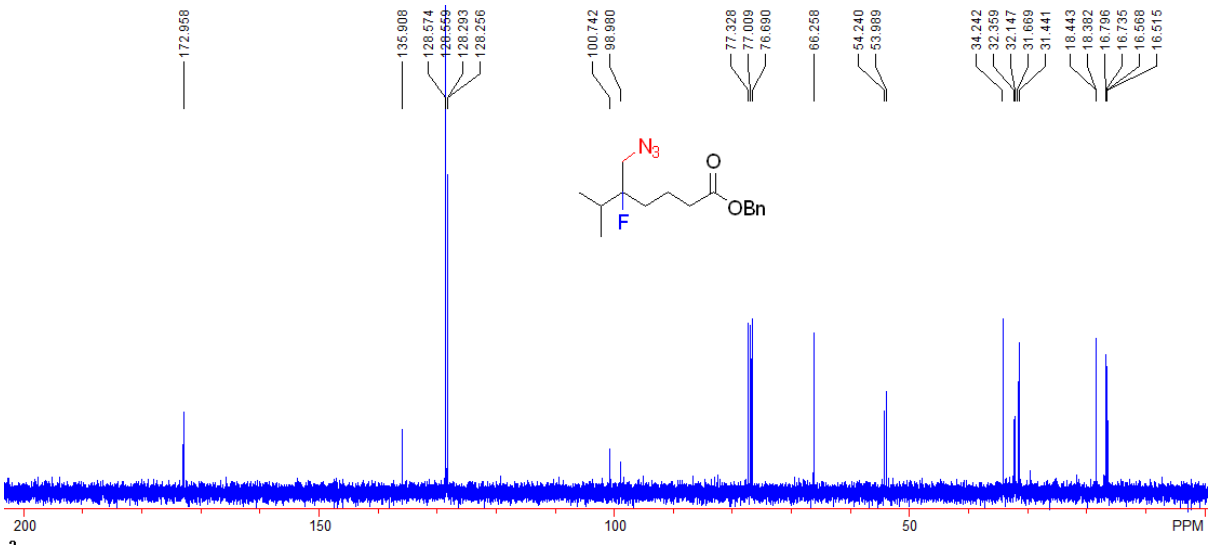


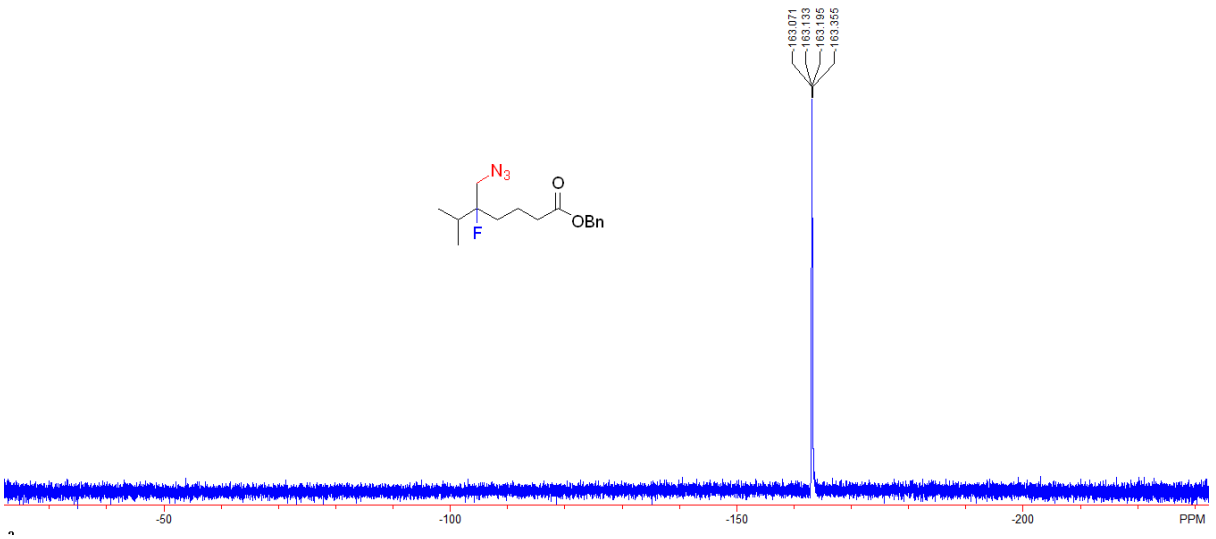




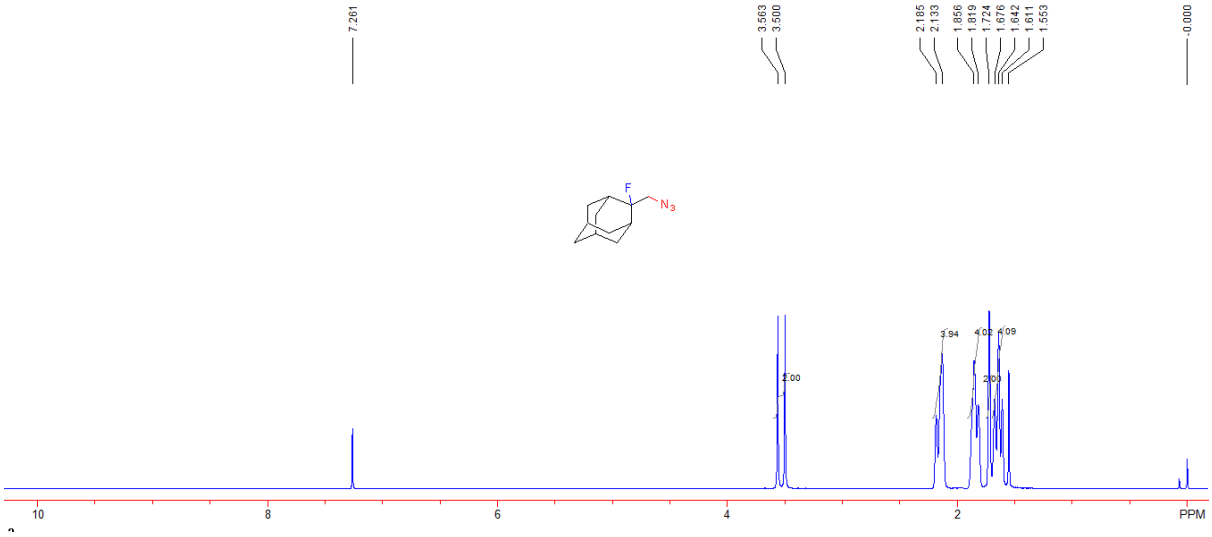
Compound **21**

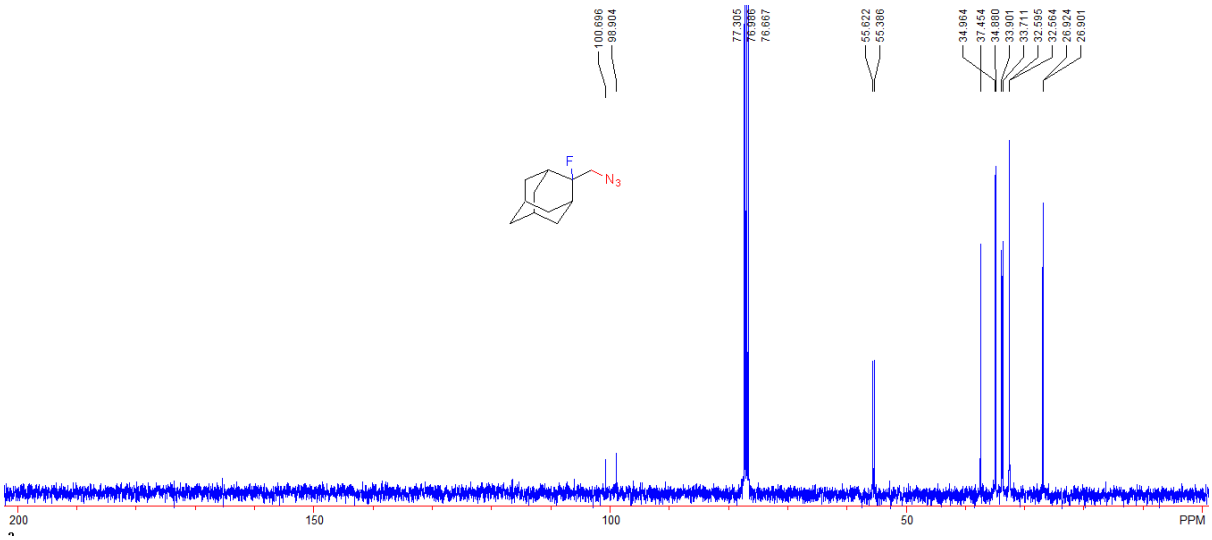


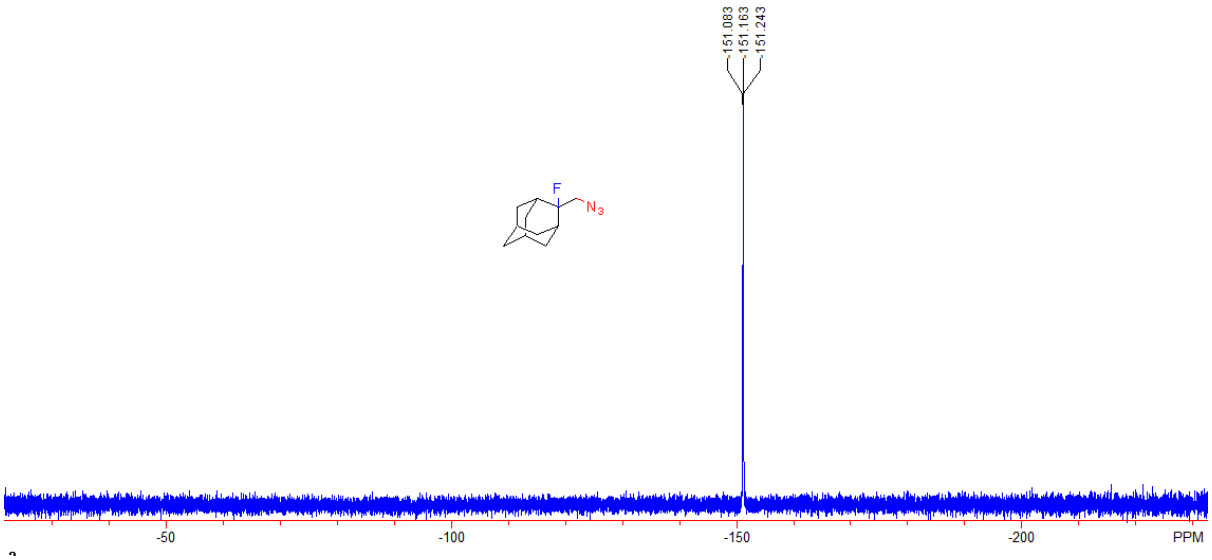




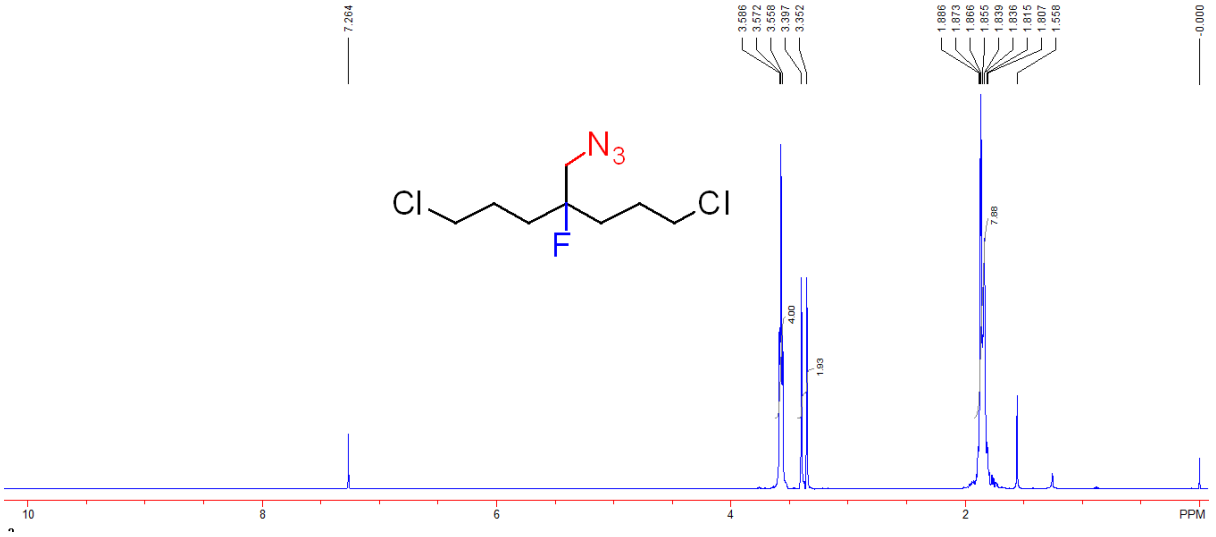
Compound **22**

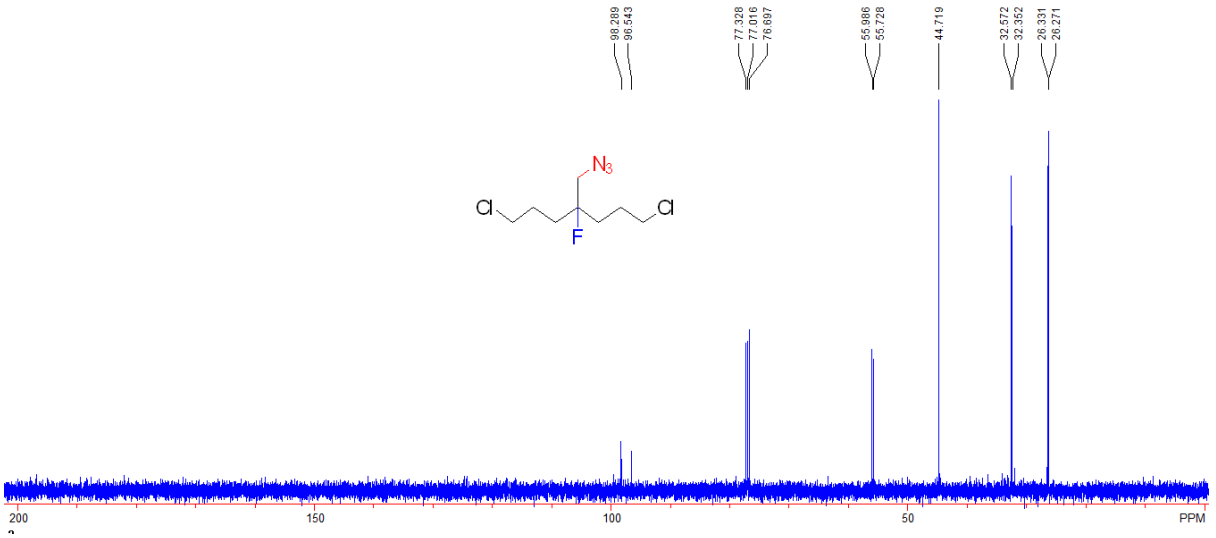


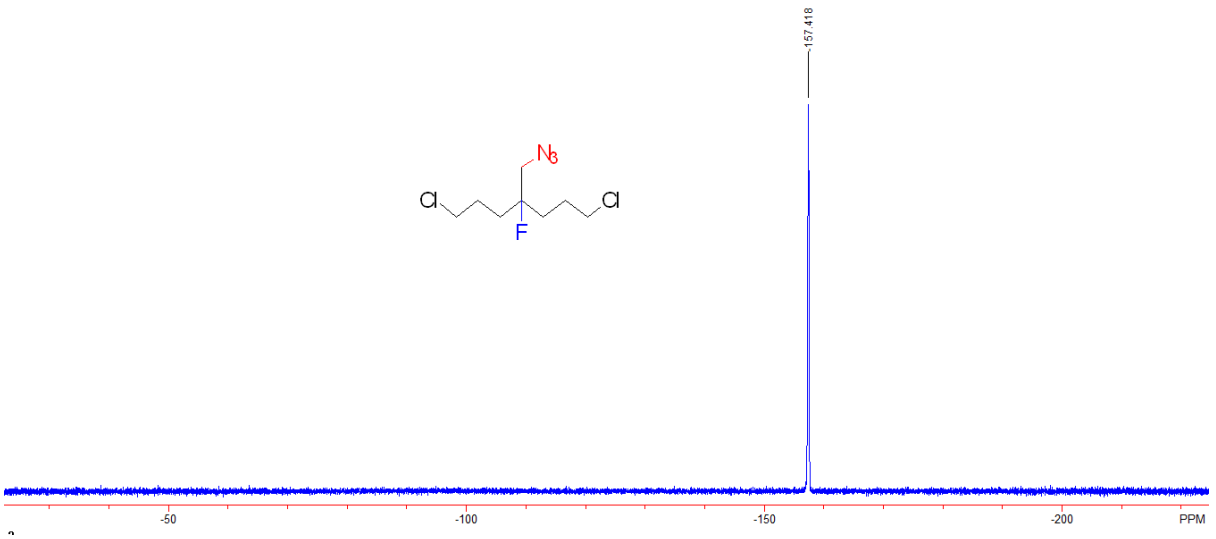




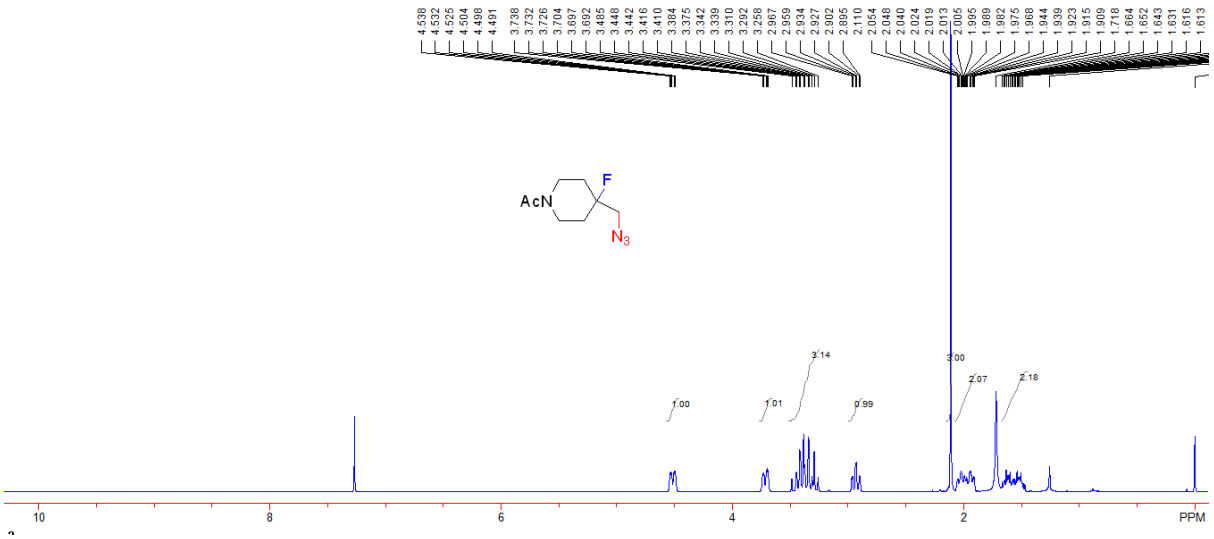
Compound **23**

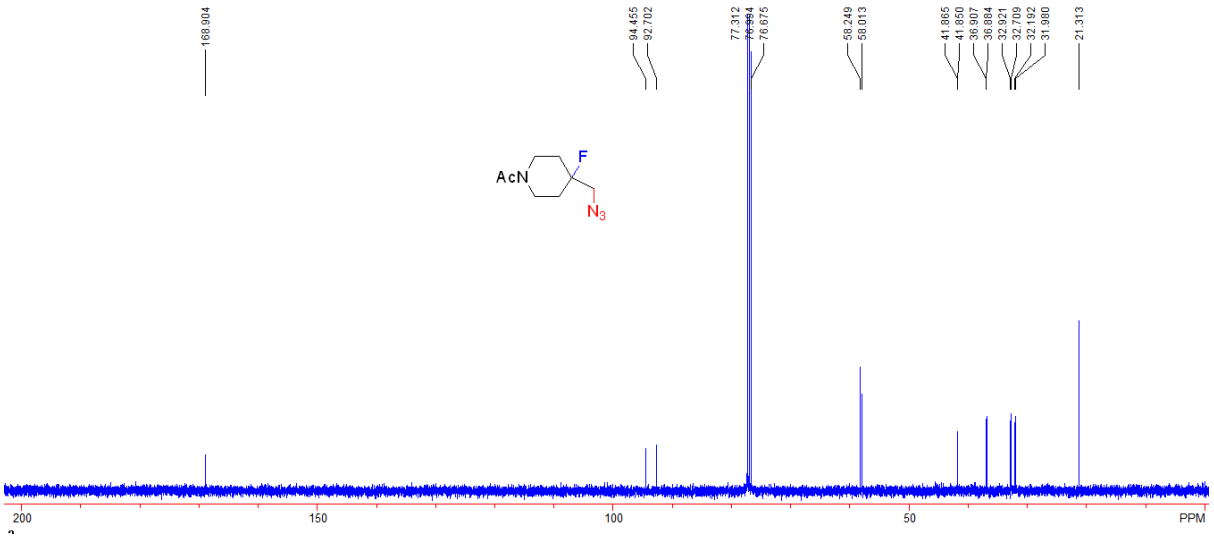


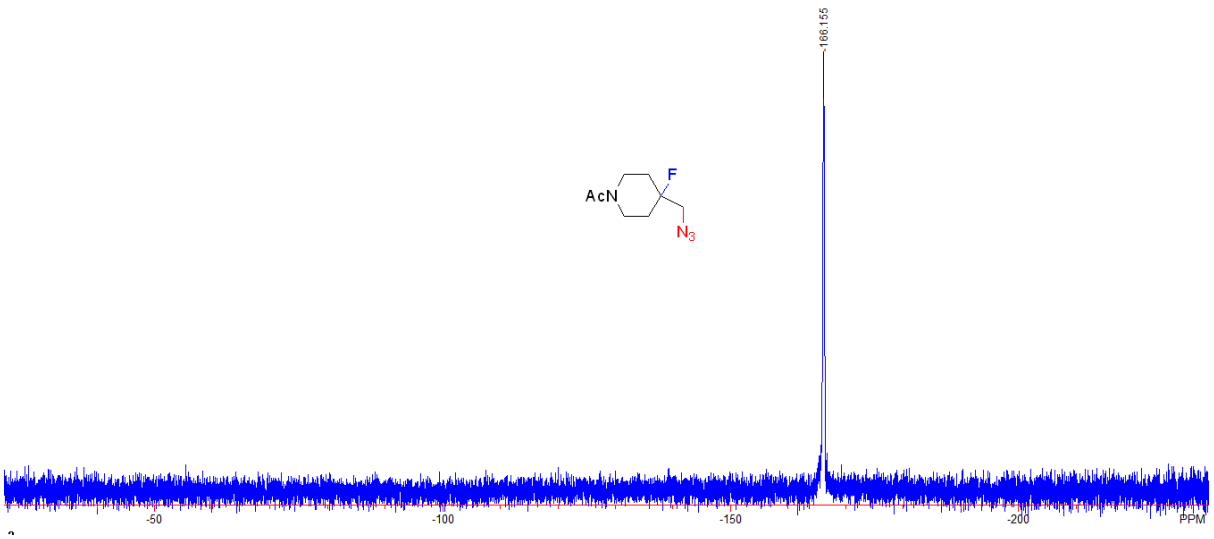




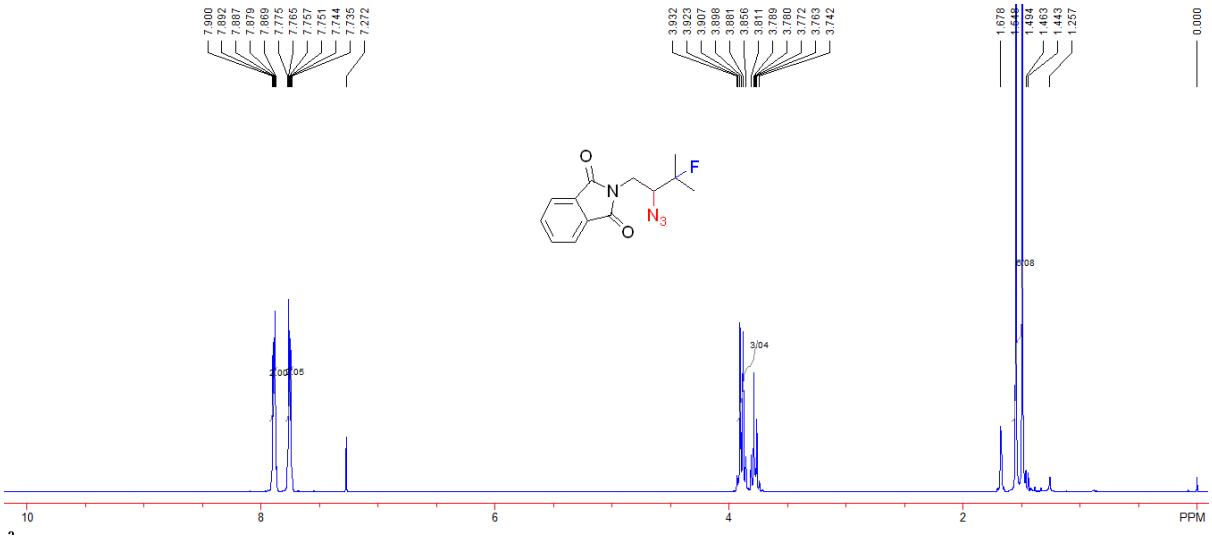
Compound **24**

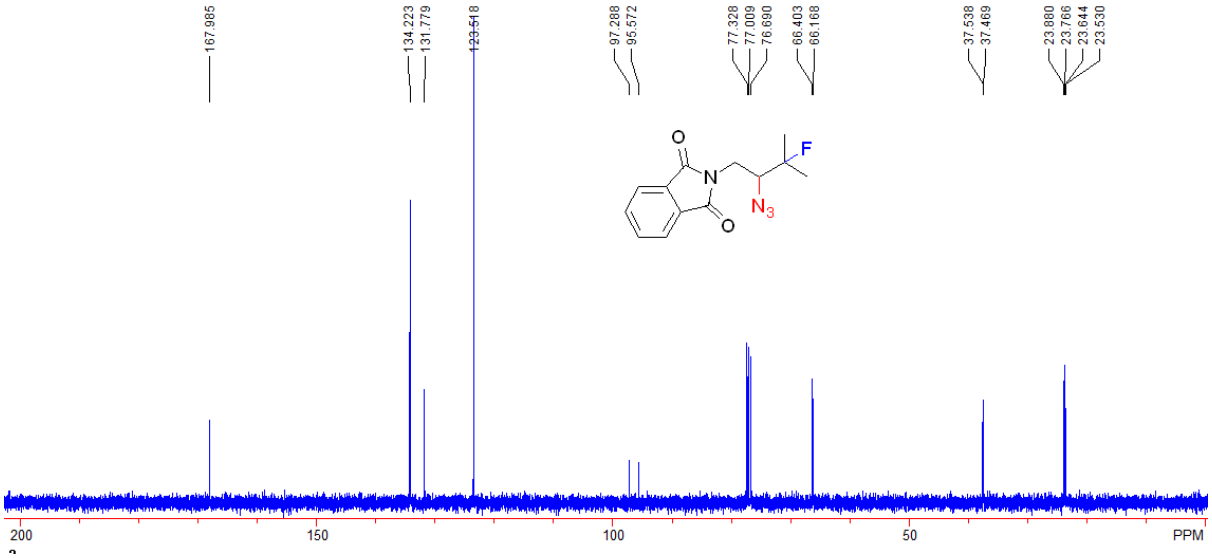


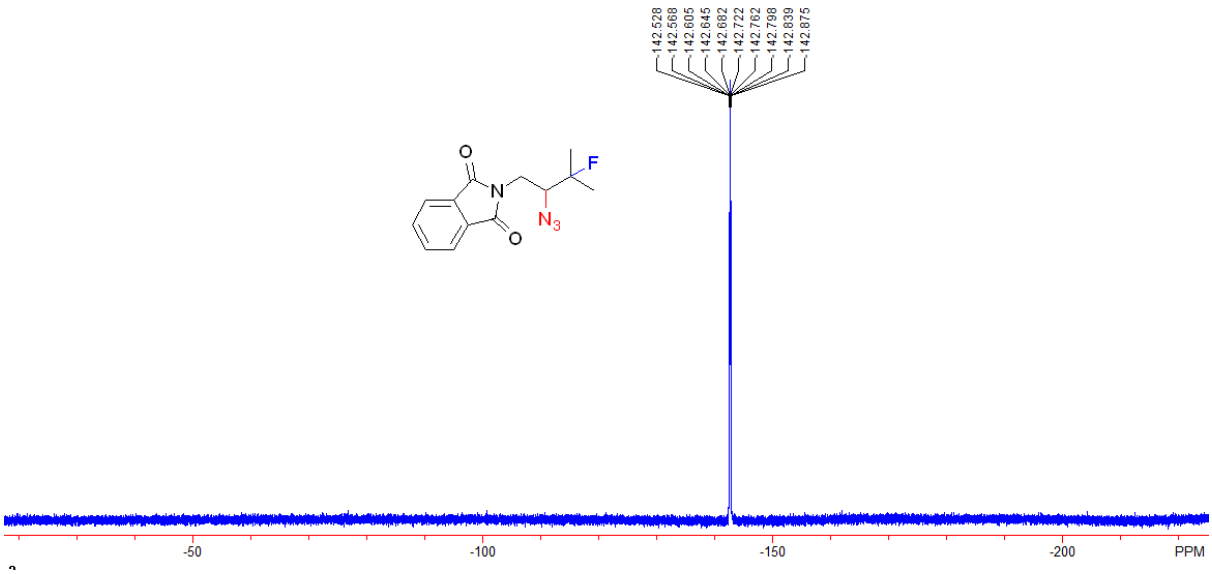




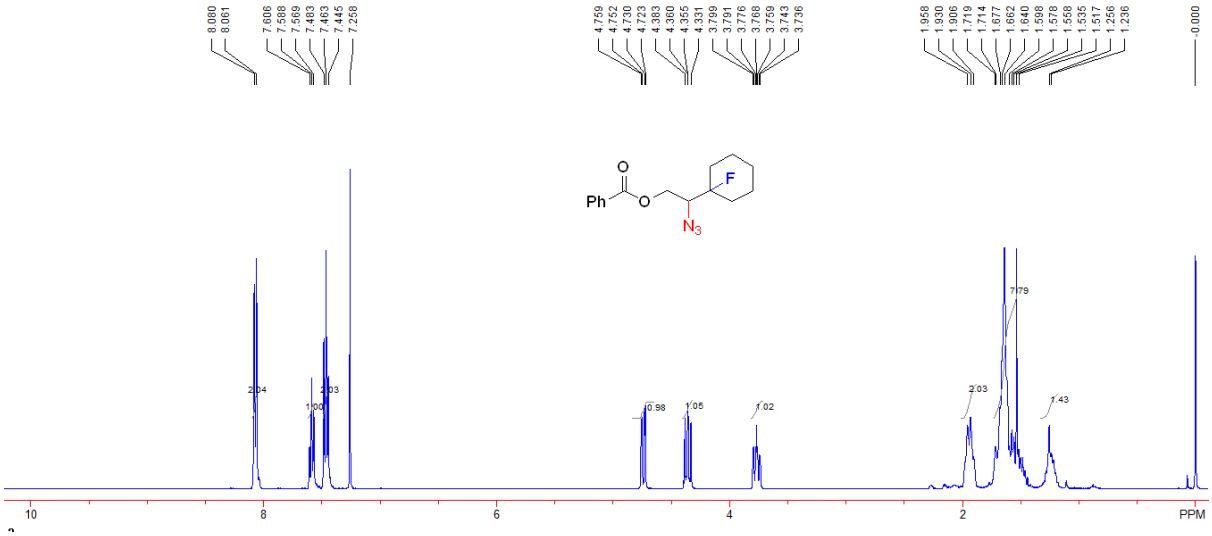
Compound **25**

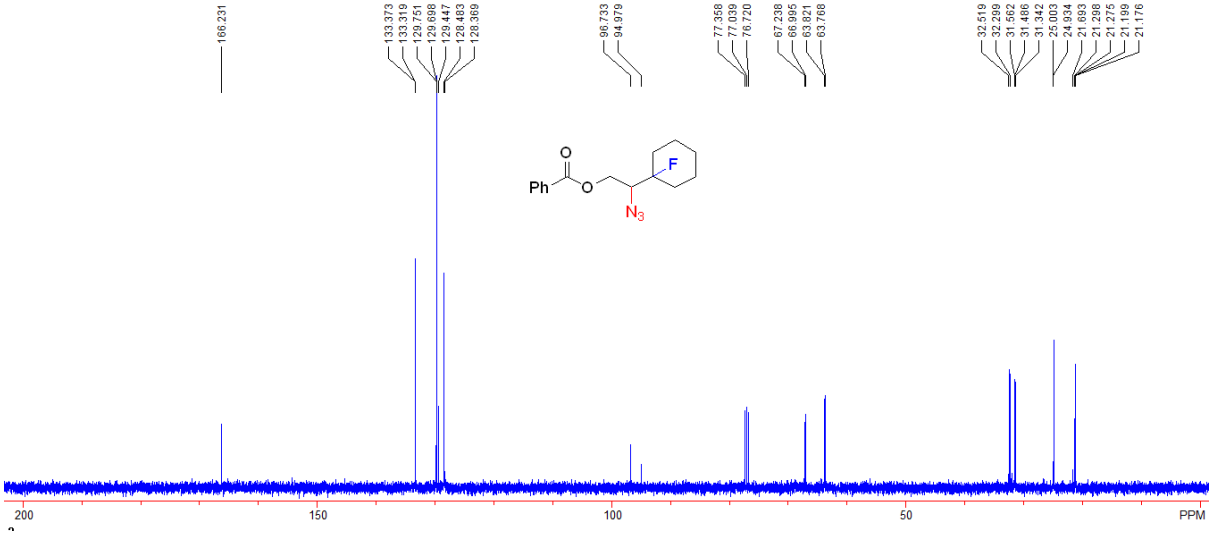


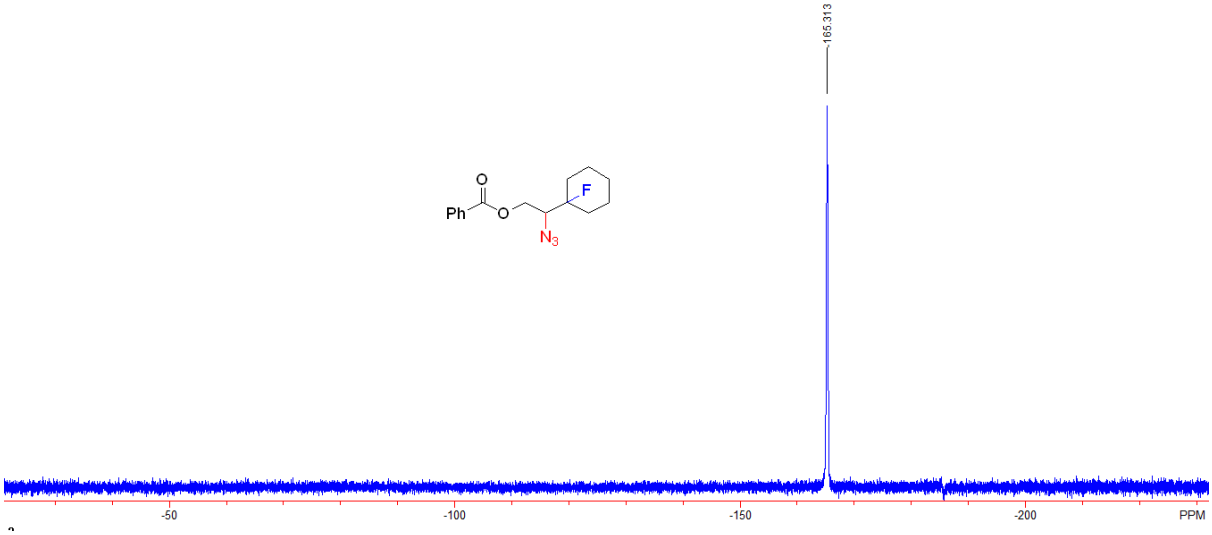




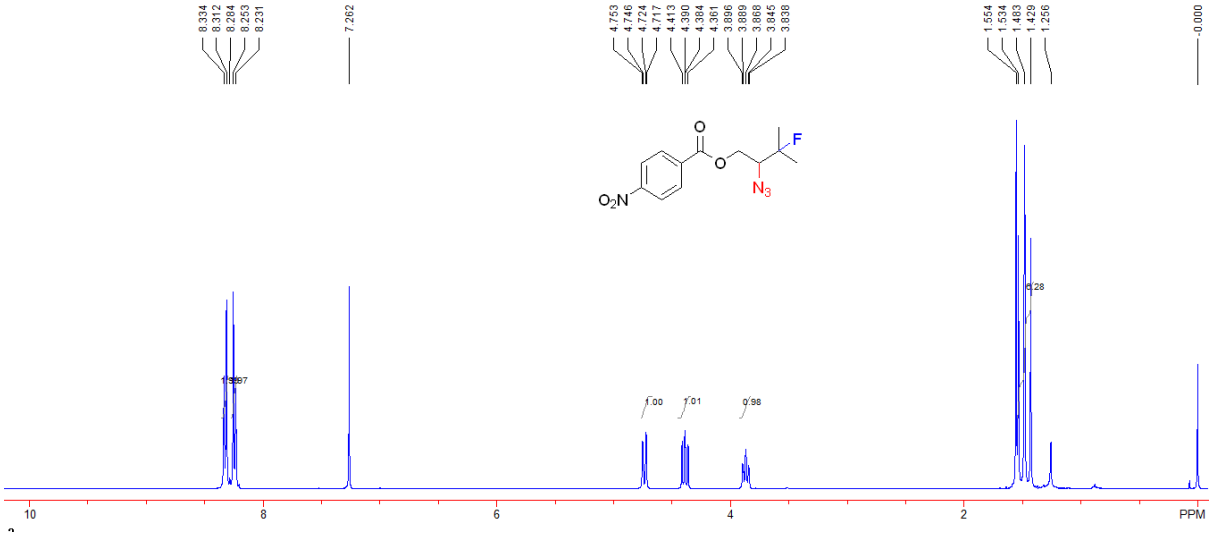
Compound **26**







Compound **27**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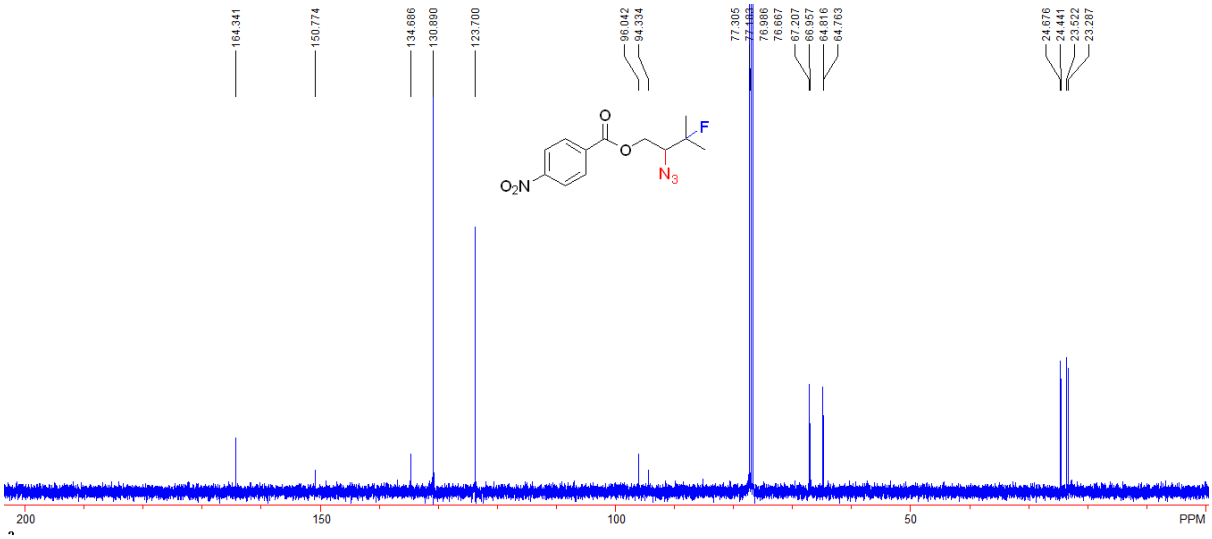
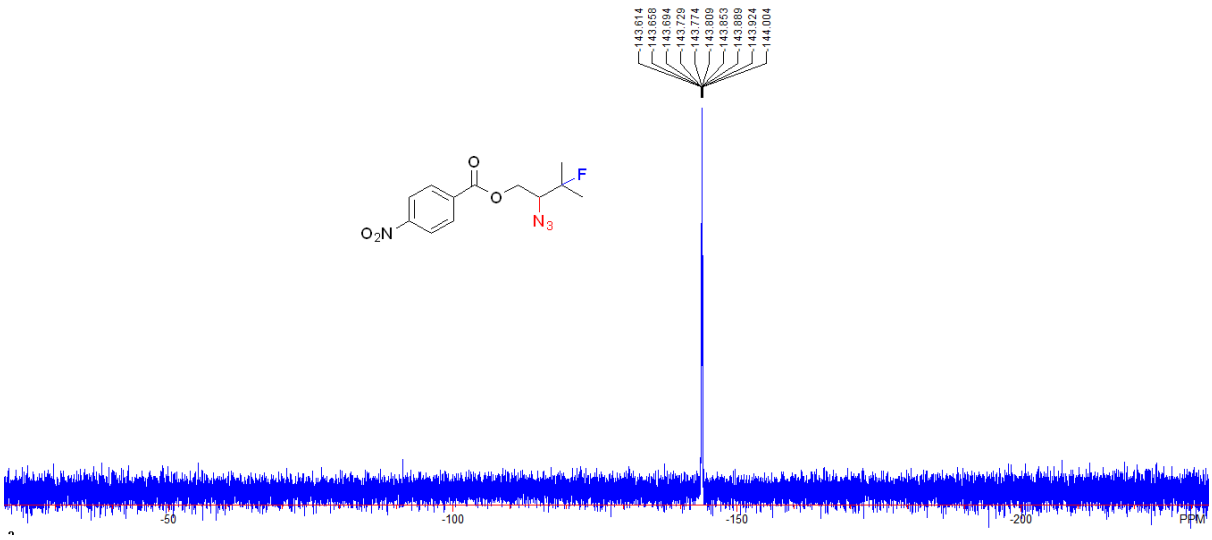
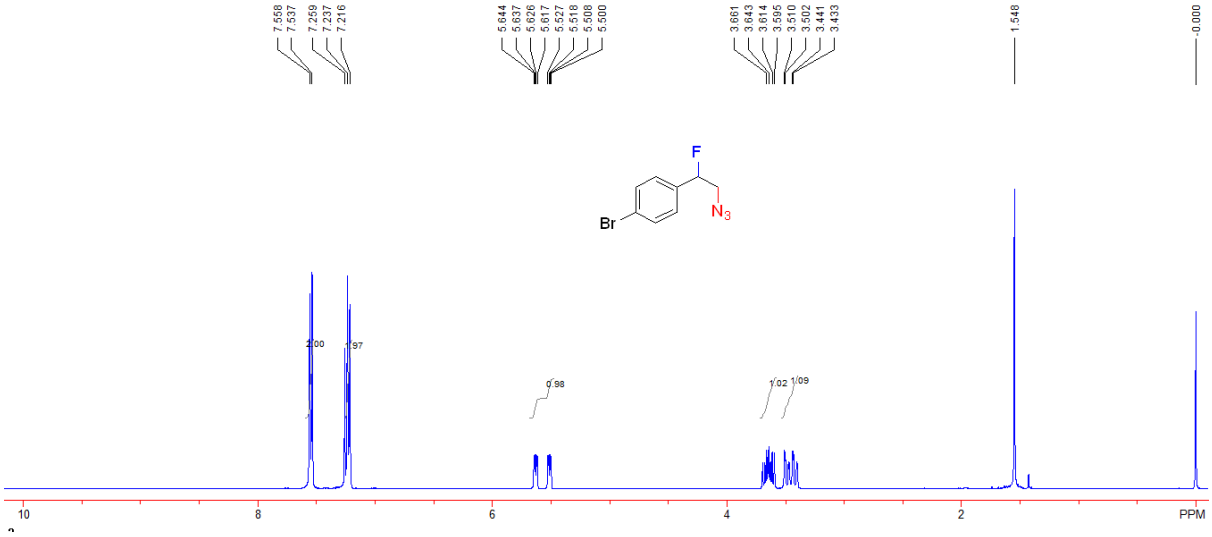
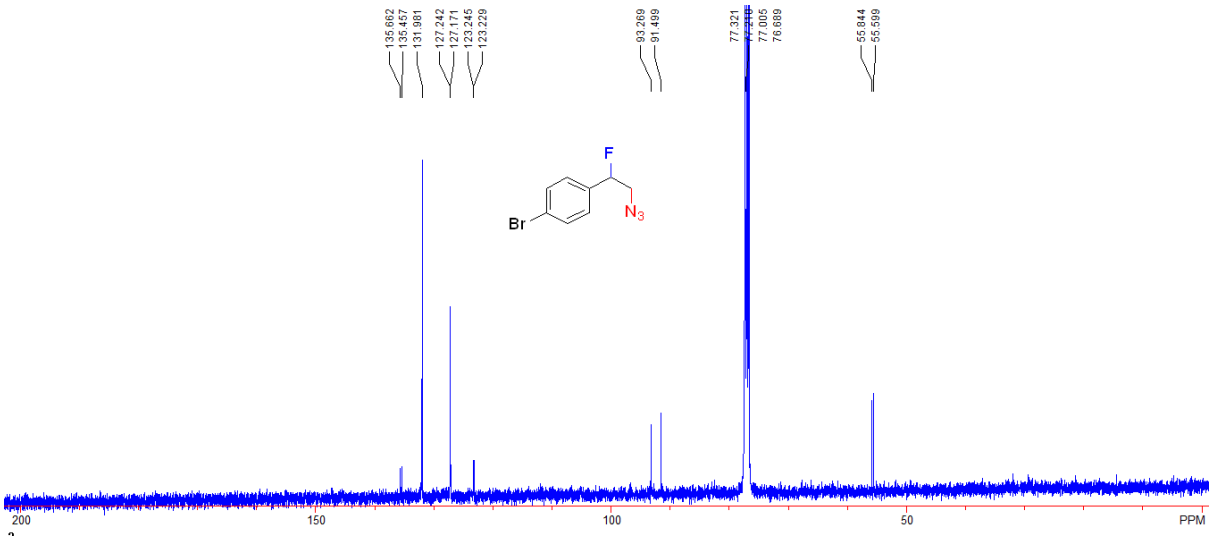
8.312
8.284
8.253
8.231
7.262
4.753
4.746
4.724
4.717
4.413
4.390
4.384
4.361
3.886
3.869
3.868
3.845
3.838
1.554
1.534
1.483
1.429
1.256
0.000
6.28
1.00
1.01
0.98
O2N
F
N3
10
8
6
4
2
PPM

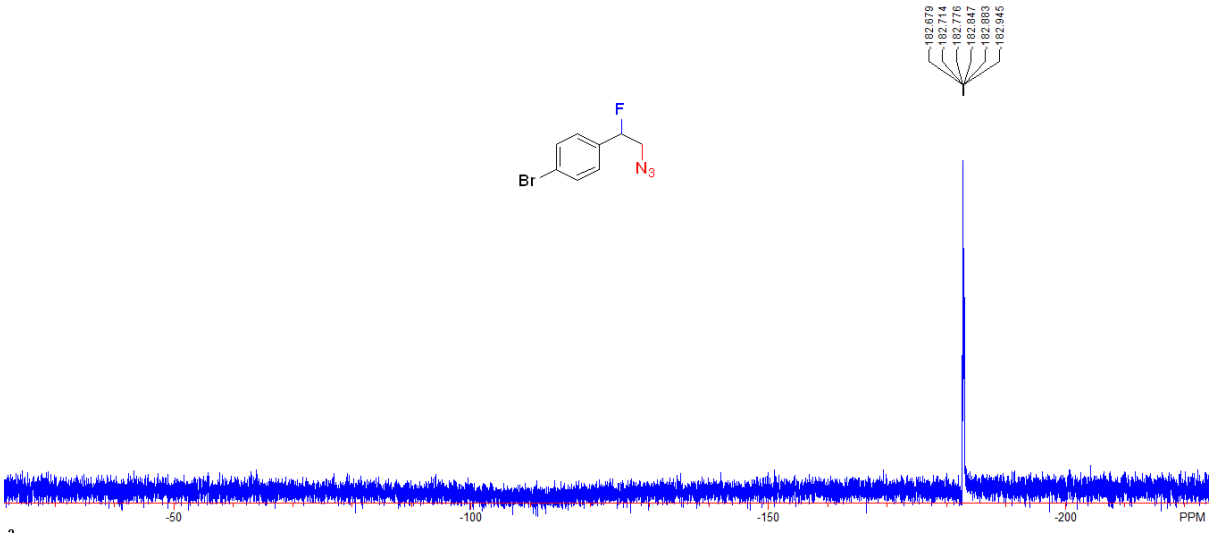

164.341
150.774
134.686
130.890
123.700
96.042
94.334
77.305
76.986
76.667
67.207
66.957
64.816
64.763
24.676
24.441
23.522
23.287
O2N
F
N3
200
150
100
50
PPM


143.614
143.658
143.694
143.729
143.774
143.809
143.853
143.889
143.924
144.004
O2N
F
N3
-50
-100
-150
-200
PPM

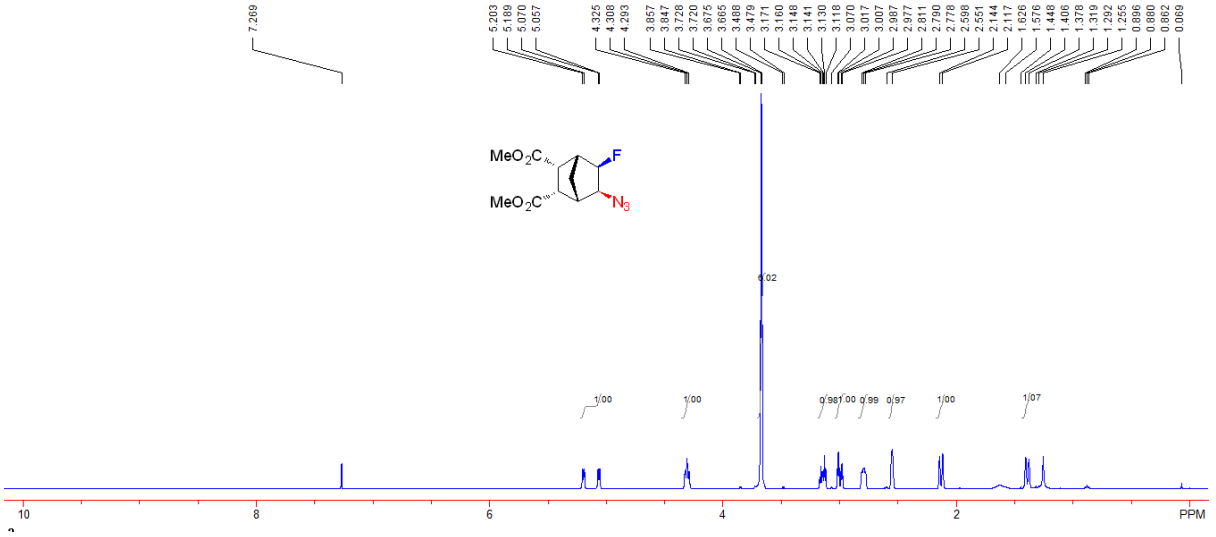
Compound **28**

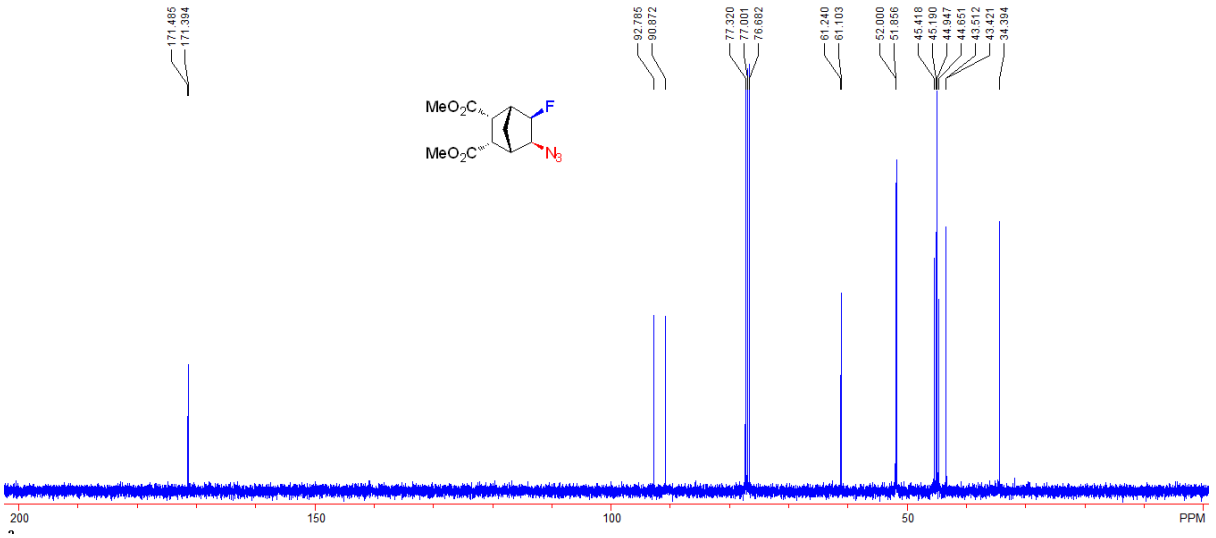


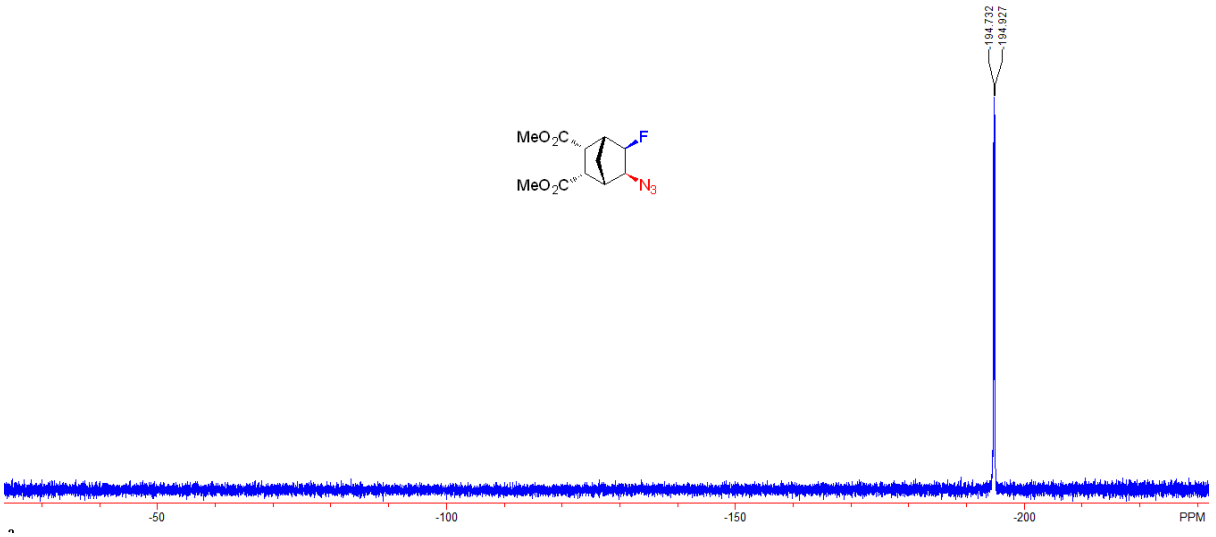




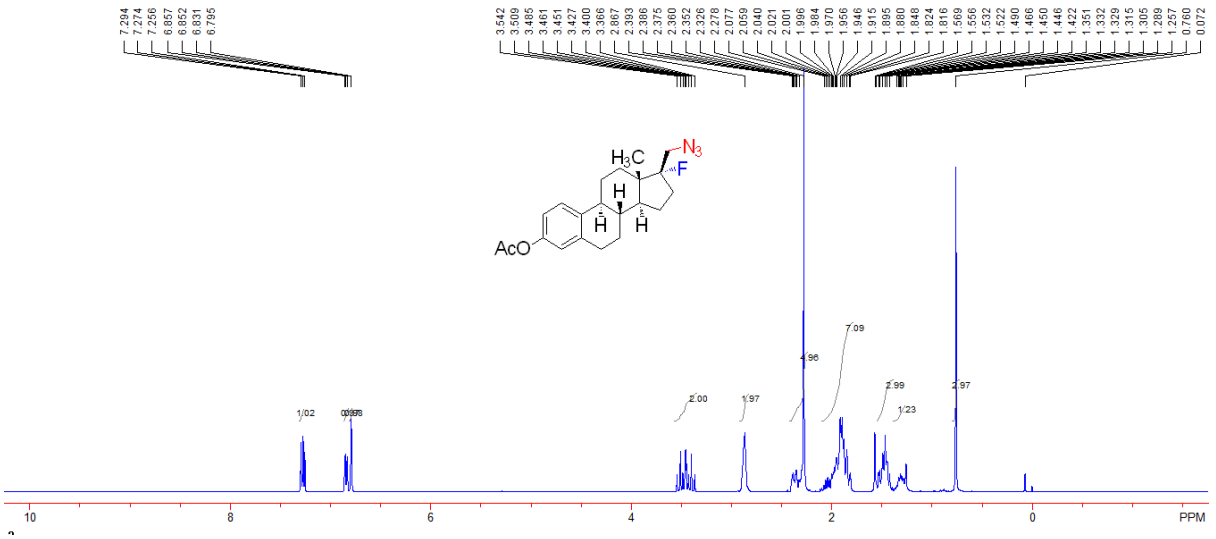
Compound **29**

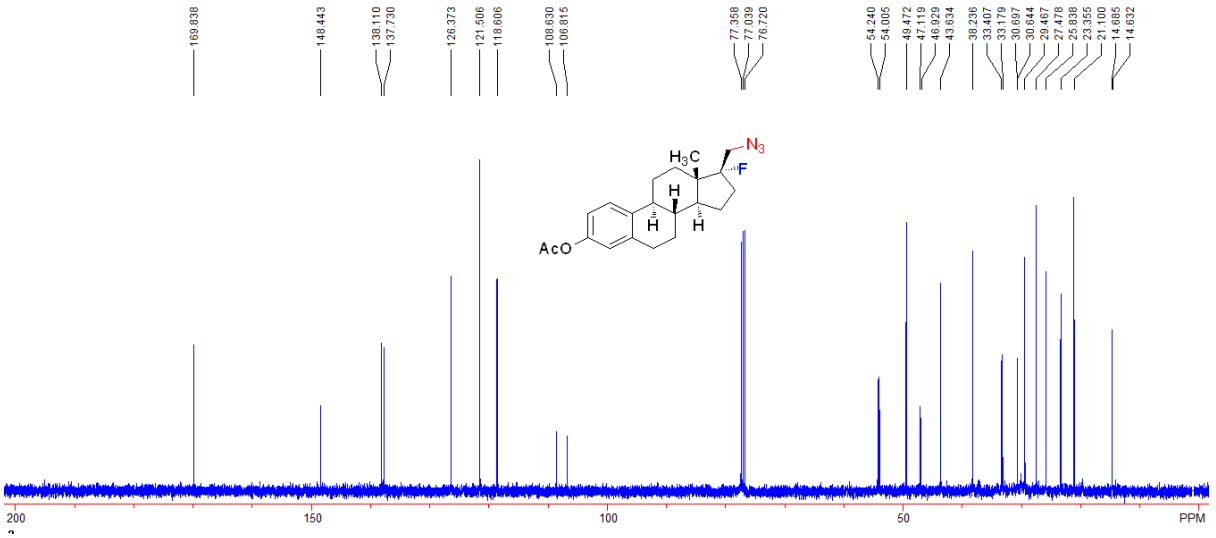


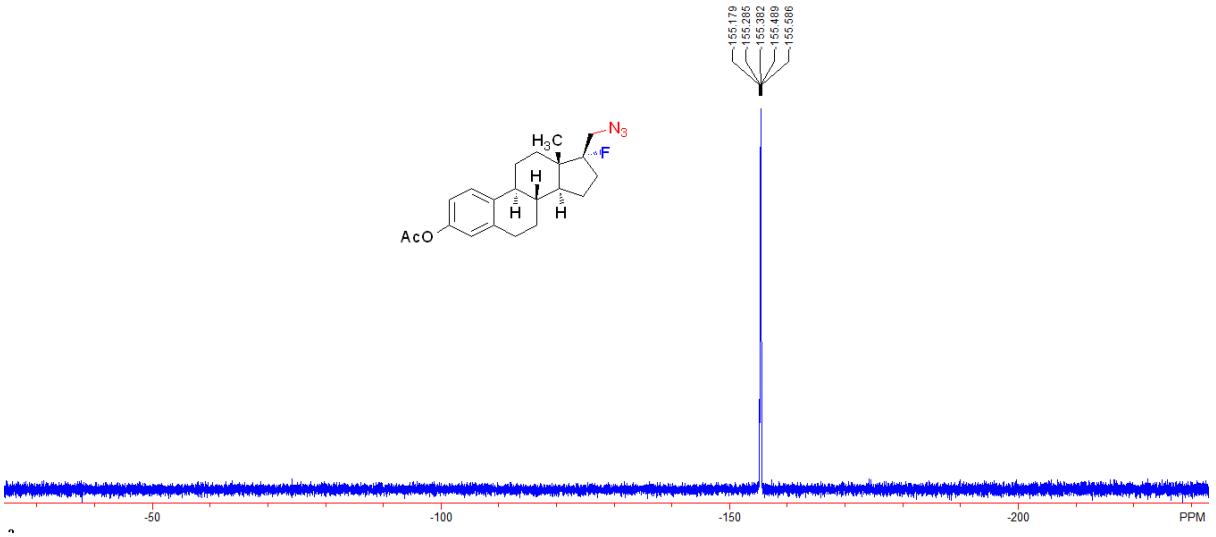




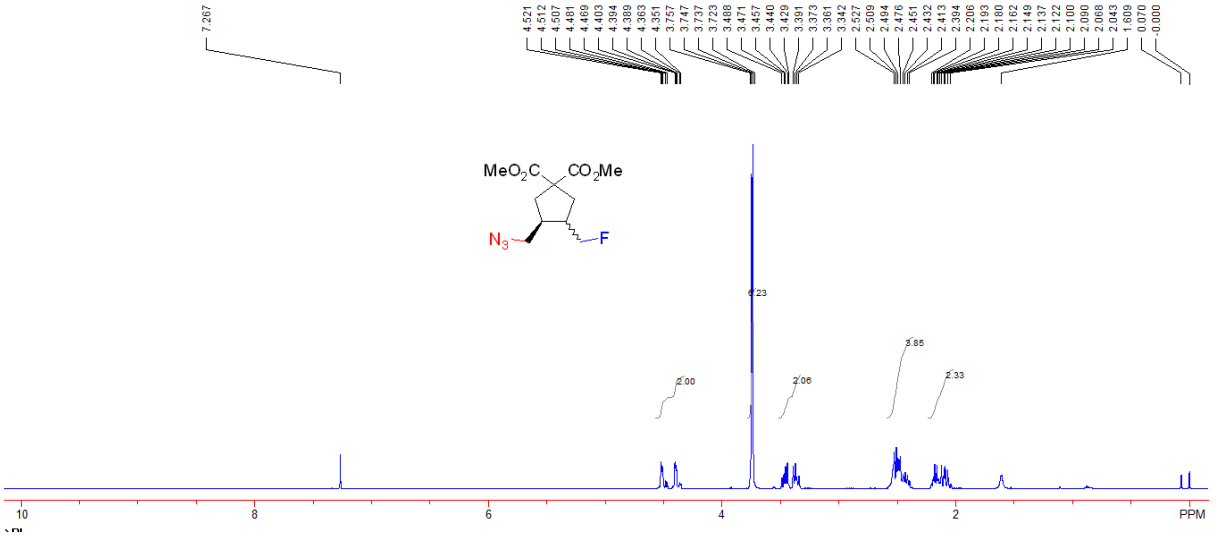
Compound **30**

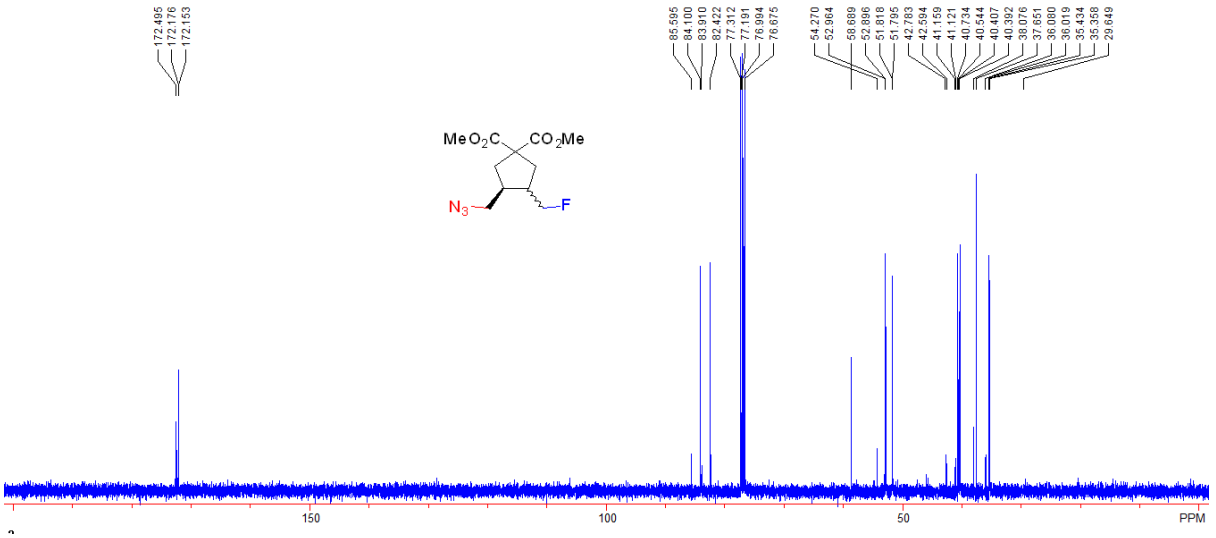


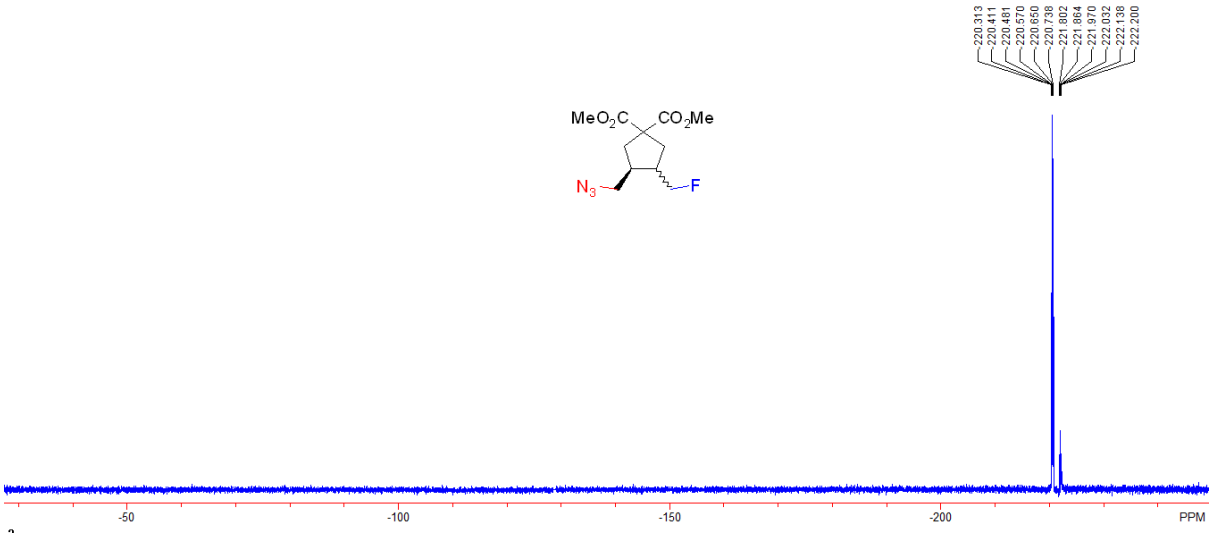




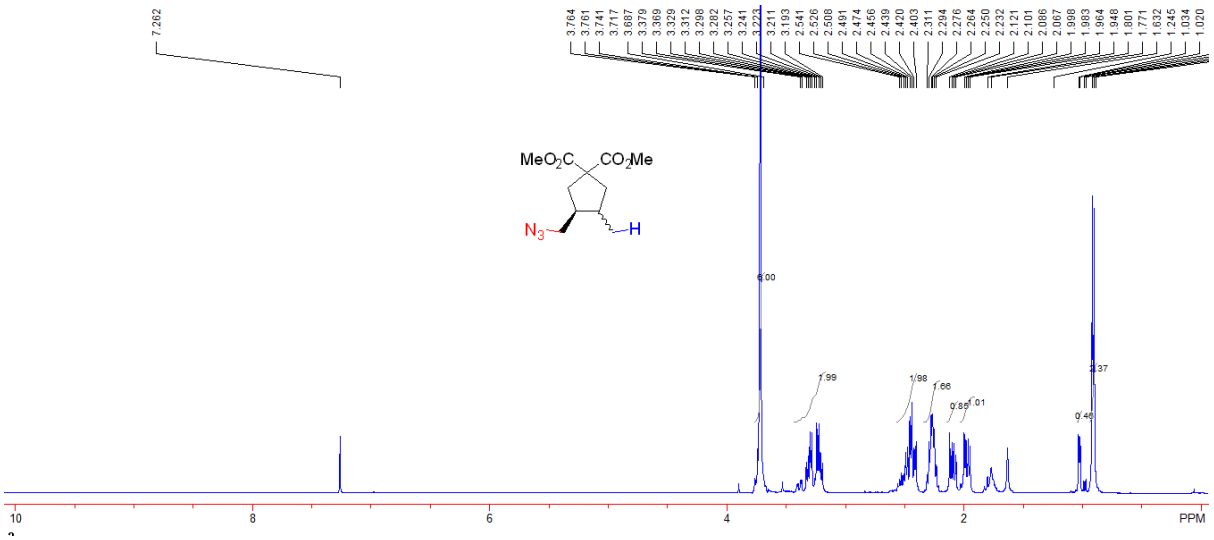
Compound **31**

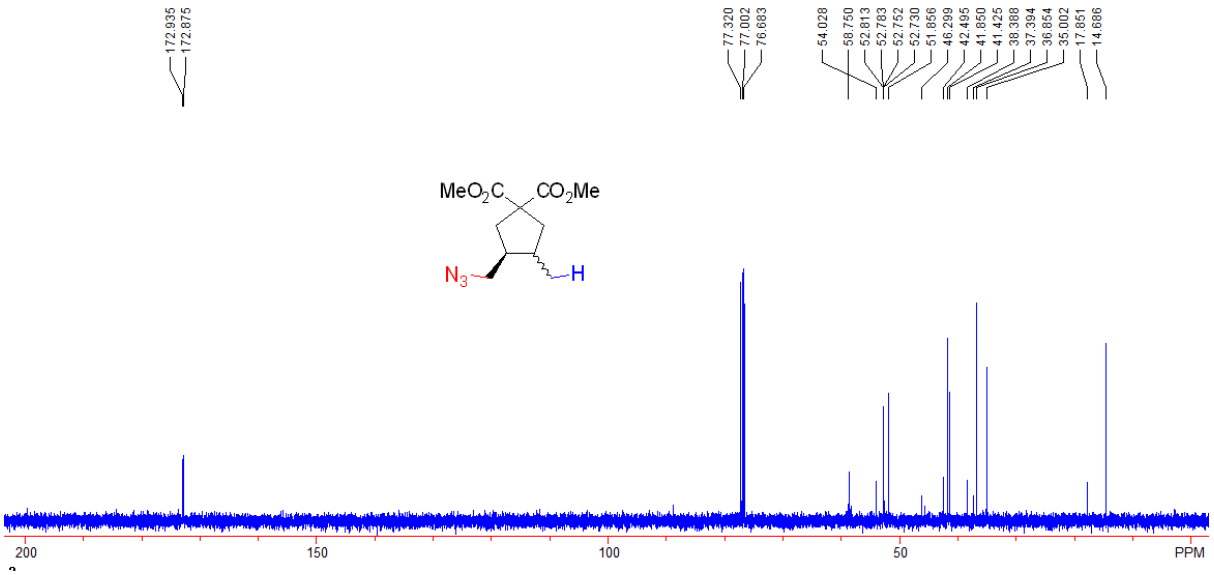




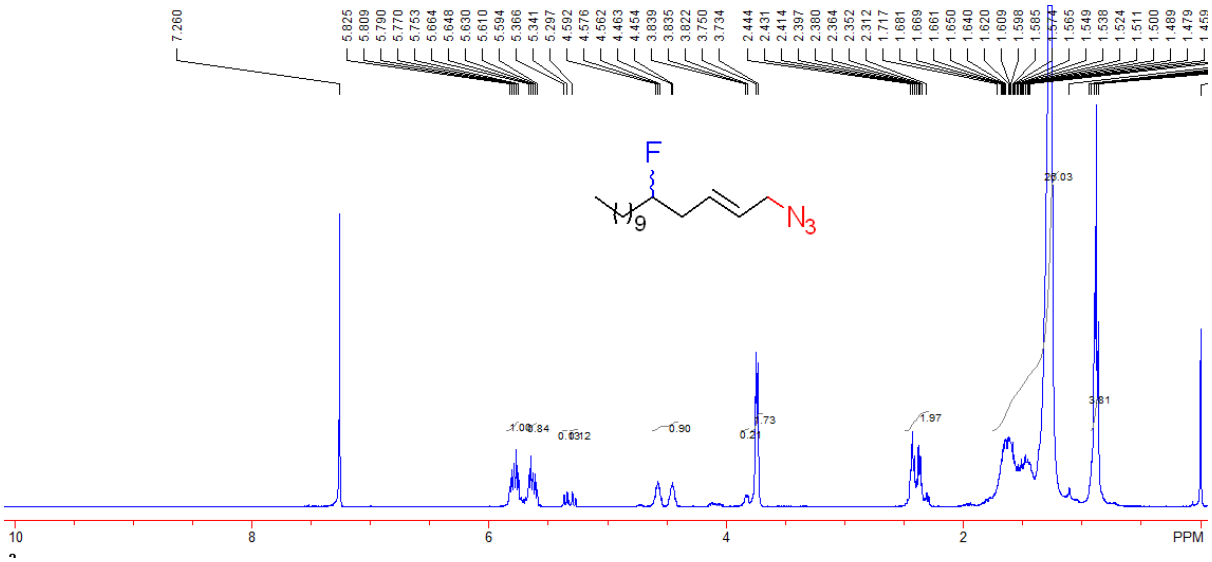


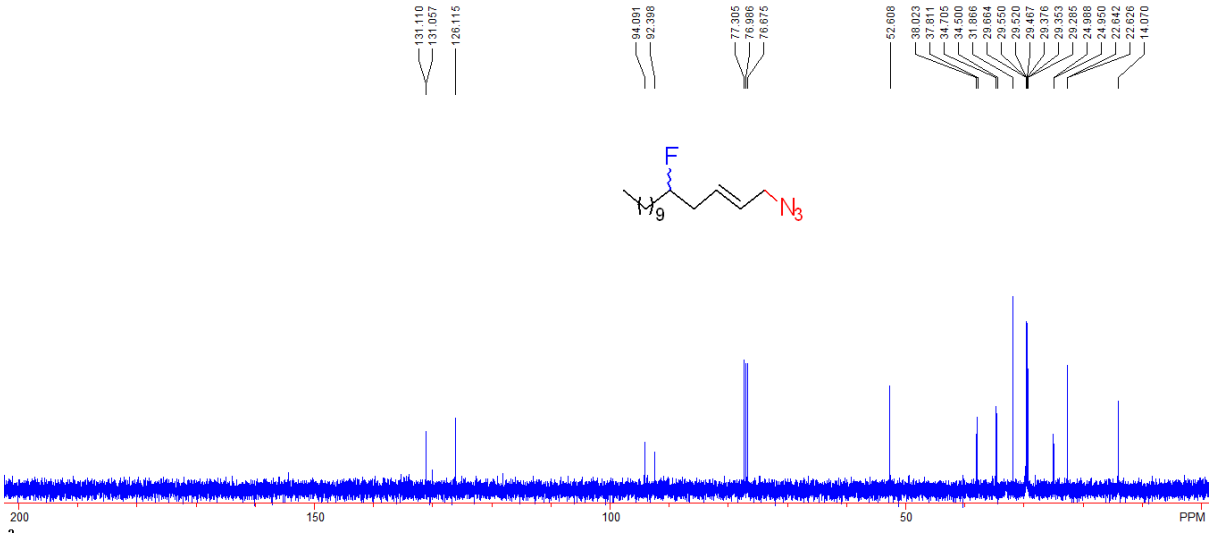
Compound **32**

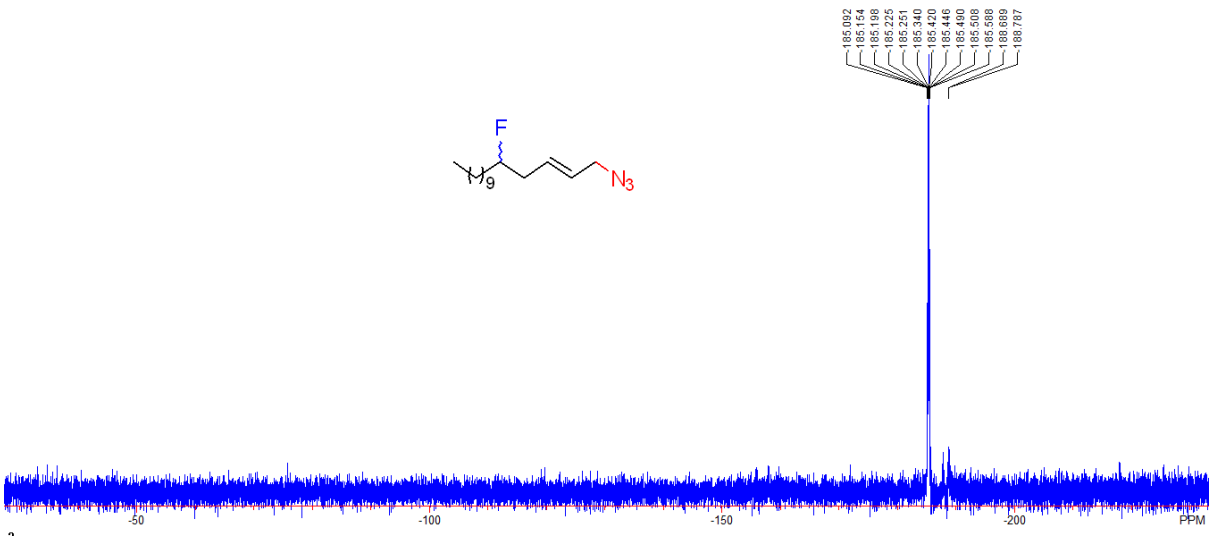

7.262
3.764
3.761
3.741
3.717
3.687
3.379
3.369
3.329
3.312
3.298
3.282
3.257
3.241
3.223
3.211
3.193
2.541
2.526
2.508
2.491
2.474
2.456
2.439
2.420
2.403
2.311
2.294
2.276
2.264
2.250
2.232
2.121
2.101
2.086
2.067
1.998
1.983
1.964
1.948
1.801
1.771
1.632
1.245
1.034
1.020
MeO2C
CO2Me
N3
H
6.00
1.99
1.98
1.66
0.85
1.01
2.37
0.46
10
8
6
4
2
PPM


172.935
172.875
77.320
77.002
76.683
54.028
53.750
52.813
52.783
52.752
52.730
51.856
46.299
42.495
41.850
41.425
38.388
37.394
36.854
35.002
17.851
14.686
MeO2C
CO2Me
N3
H
200
150
100
50
PPM

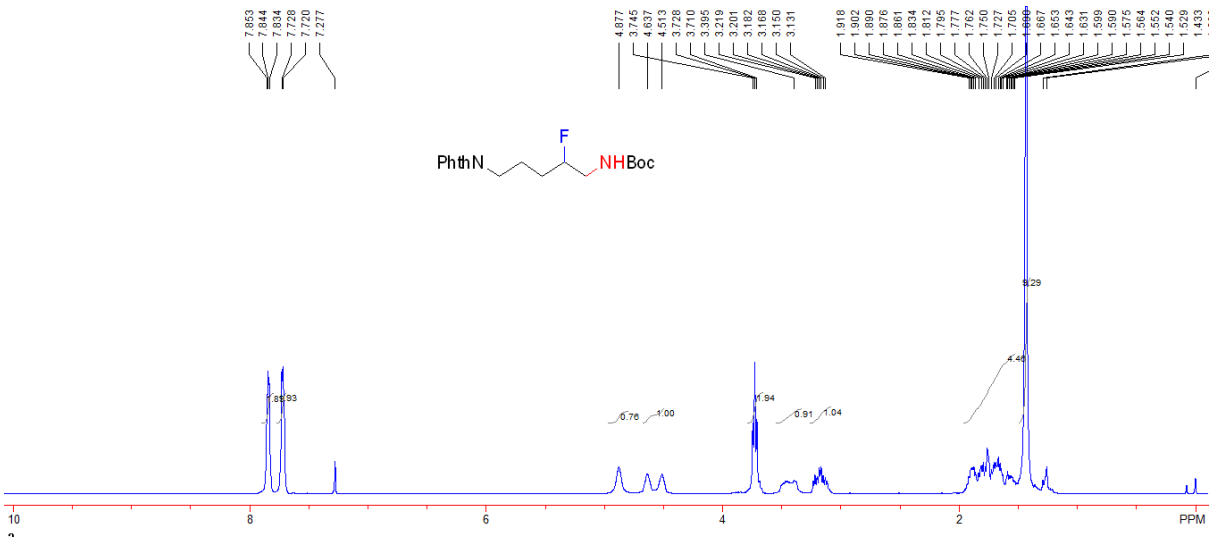
Compound **33**

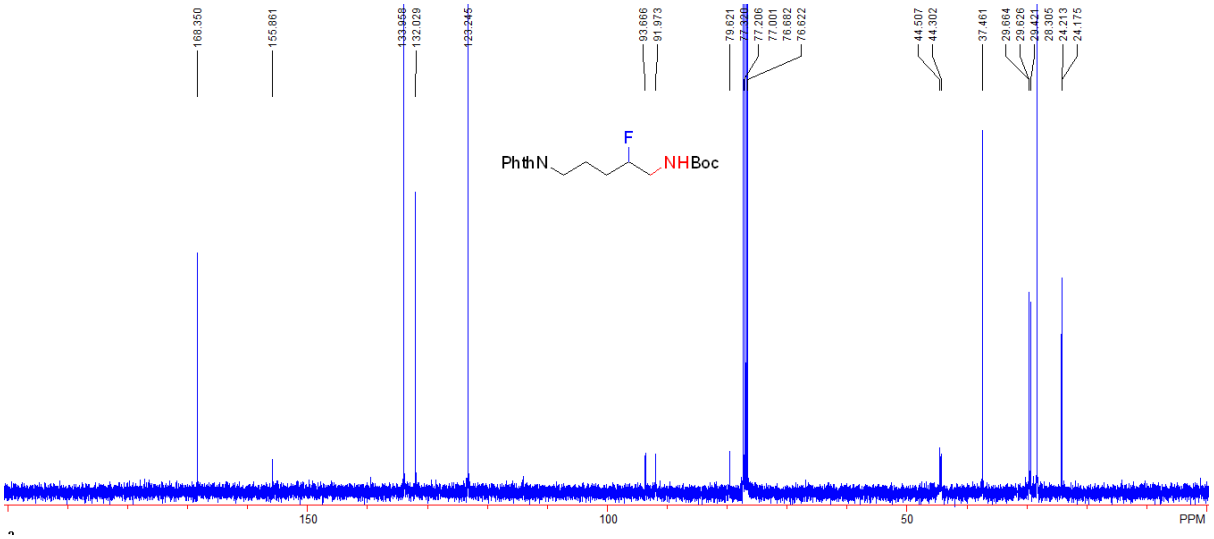


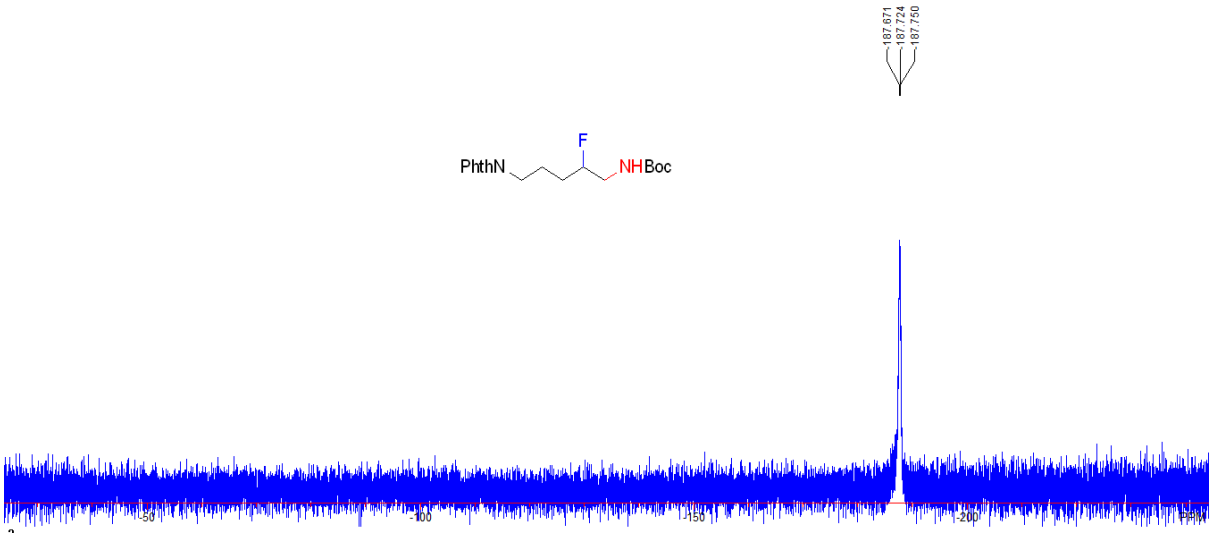




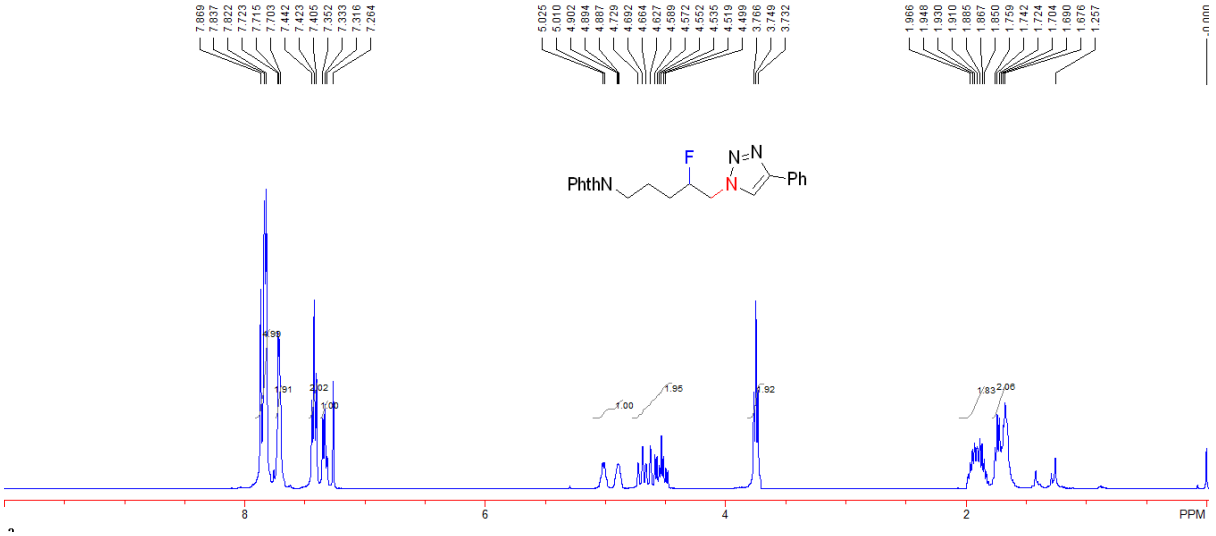
Compound **34**







Compound **35**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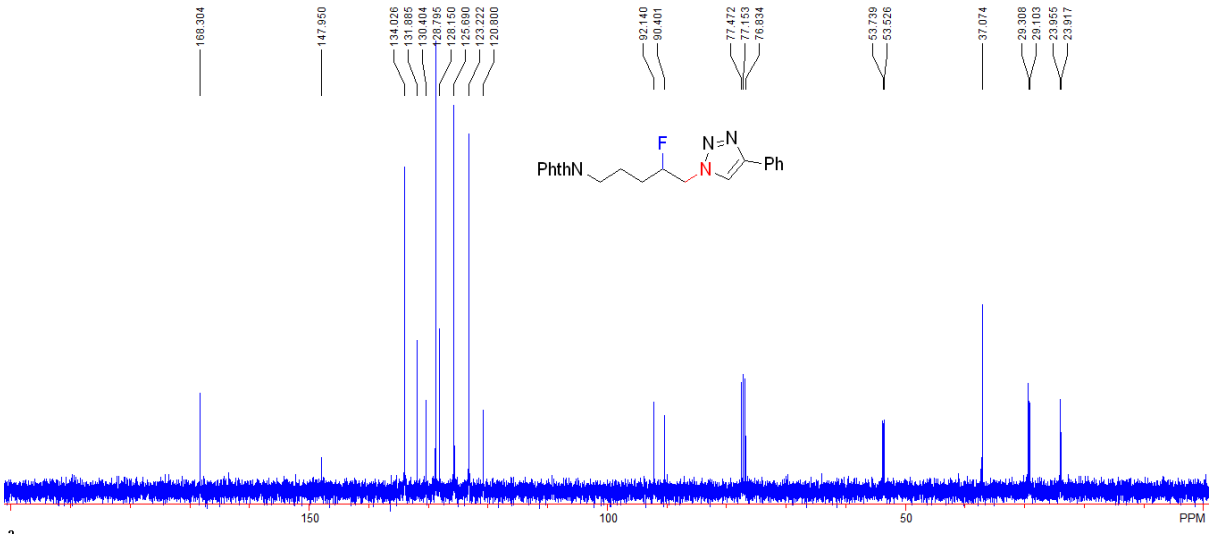
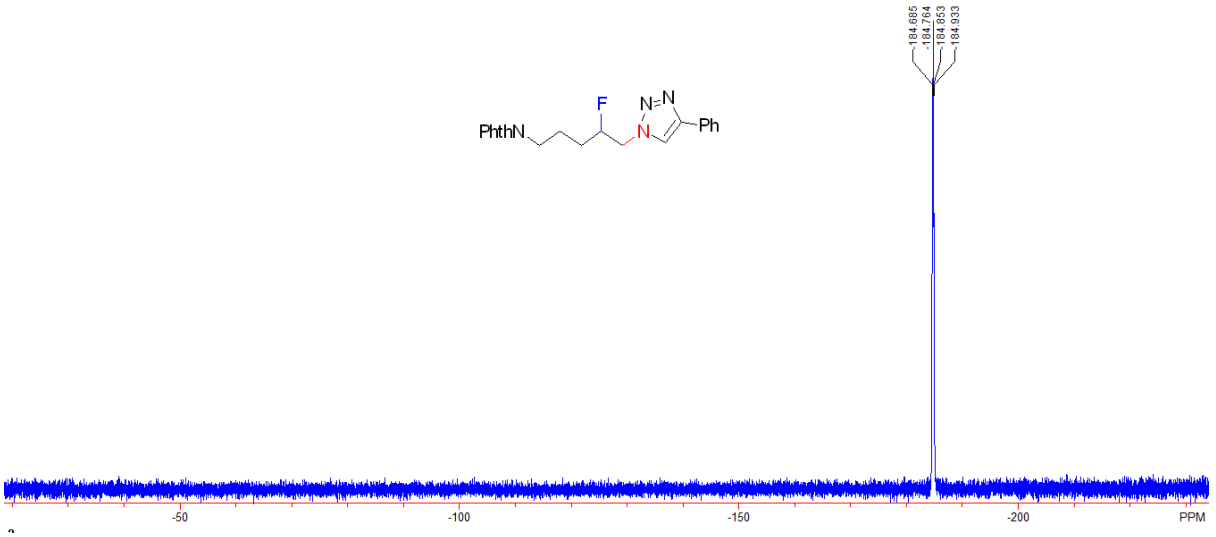
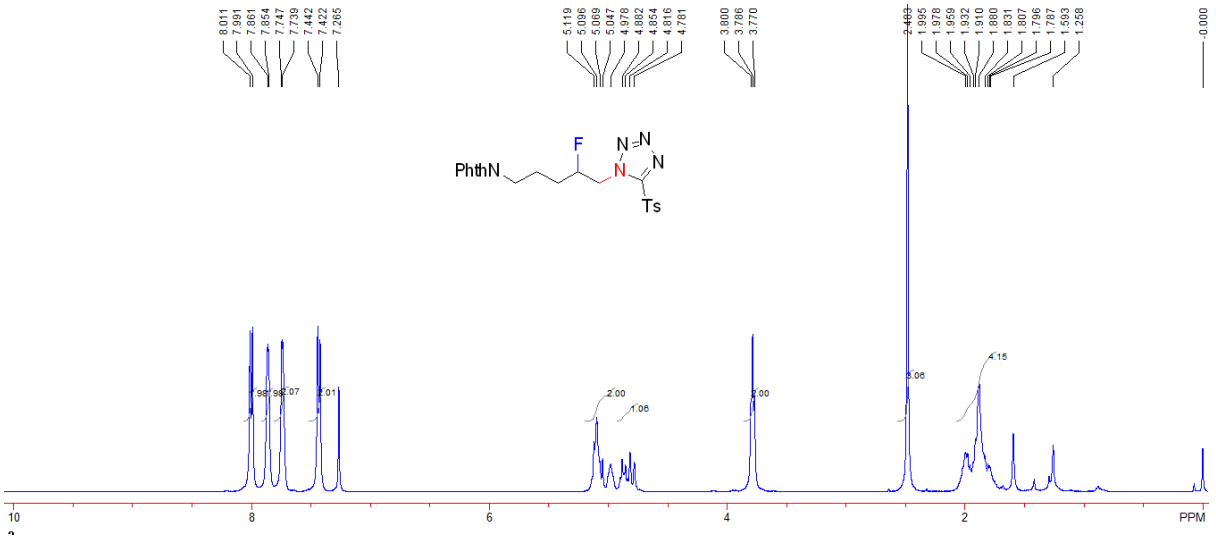
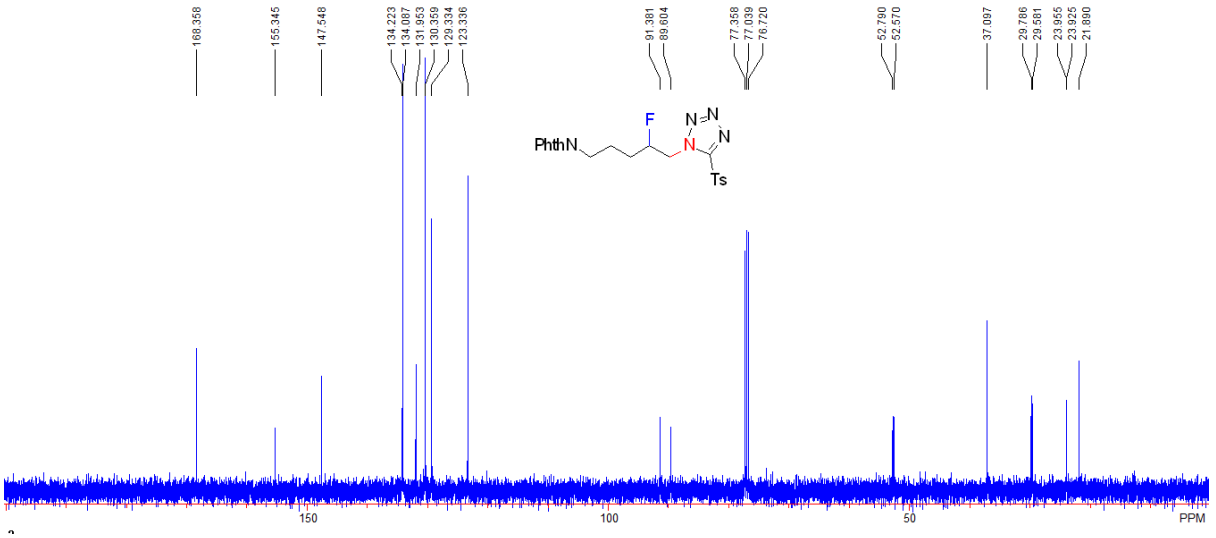
7.822
7.723
7.715
7.703
7.442
7.423
7.405
7.352
7.333
7.316
7.264
5.025
5.010
4.902
4.884
4.687
4.729
4.692
4.664
4.627
4.589
4.572
4.552
4.535
4.519
4.499
3.766
3.749
3.732
1.966
1.948
1.930
1.910
1.885
1.867
1.850
1.759
1.742
1.724
1.704
1.680
1.676
1.257
F
N=N
PhthN
N
Ph
4.98
1.91
2.02
1.00
1.00
1.95
1.92
1.83
2.06
8
6
4
2
PPM

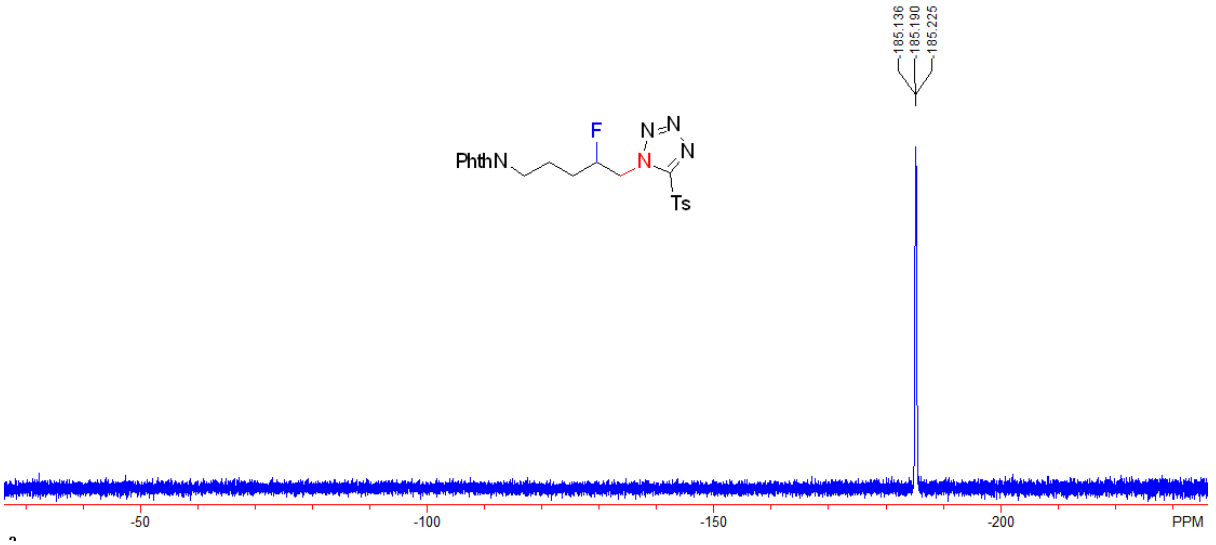

168.304
147.950
134.026
131.885
130.404
128.795
128.150
125.690
123.222
120.800
92.140
90.401
77.472
77.153
76.834
53.739
53.526
37.074
29.308
29.103
23.955
23.917
F
N=N
PhthN
N
Ph
150
100
50
PPM


184.685
184.764
184.853
184.933
F
N=N
PhthN
N
Ph
-50
-100
-150
-200
PPM

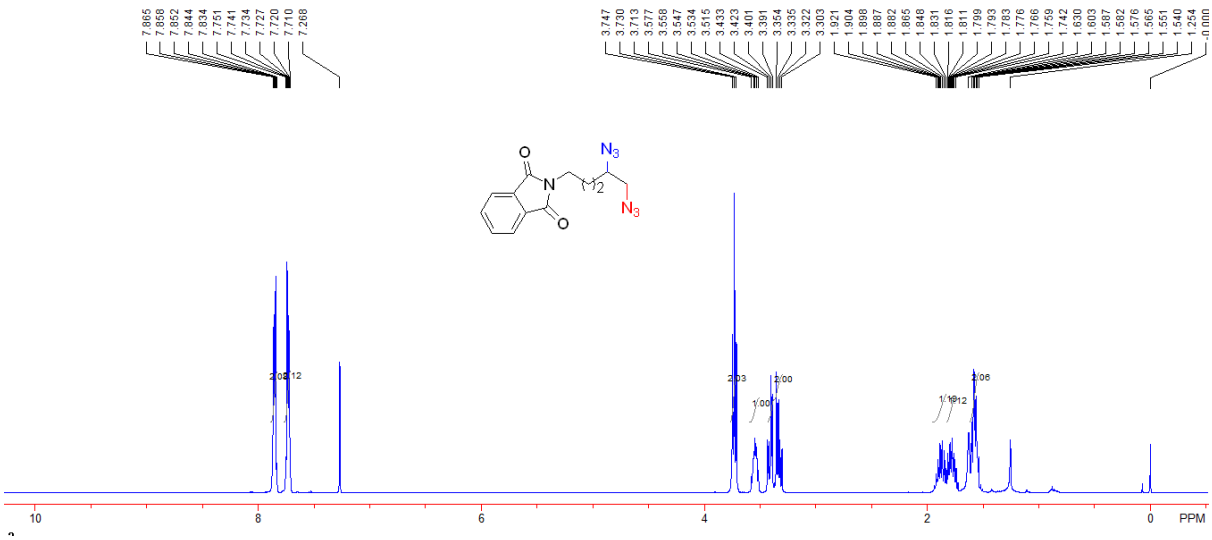
Compound **36**







Compound **1D**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7.858
7.852
7.844
7.834
7.751
7.741
7.734
7.727
7.720
7.710
7.268
3.747
3.730
3.713
3.577
3.558
3.547
3.534
3.515
3.433
3.423
3.401
3.391
3.354
3.335
3.322
3.303
1.921
1.904
1.898
1.887
1.882
1.865
1.848
1.831
1.816
1.811
1.799
1.793
1.783
1.776
1.766
1.759
1.742
1.630
1.603
1.587
1.582
1.576
1.565
1.551
1.540
1.254
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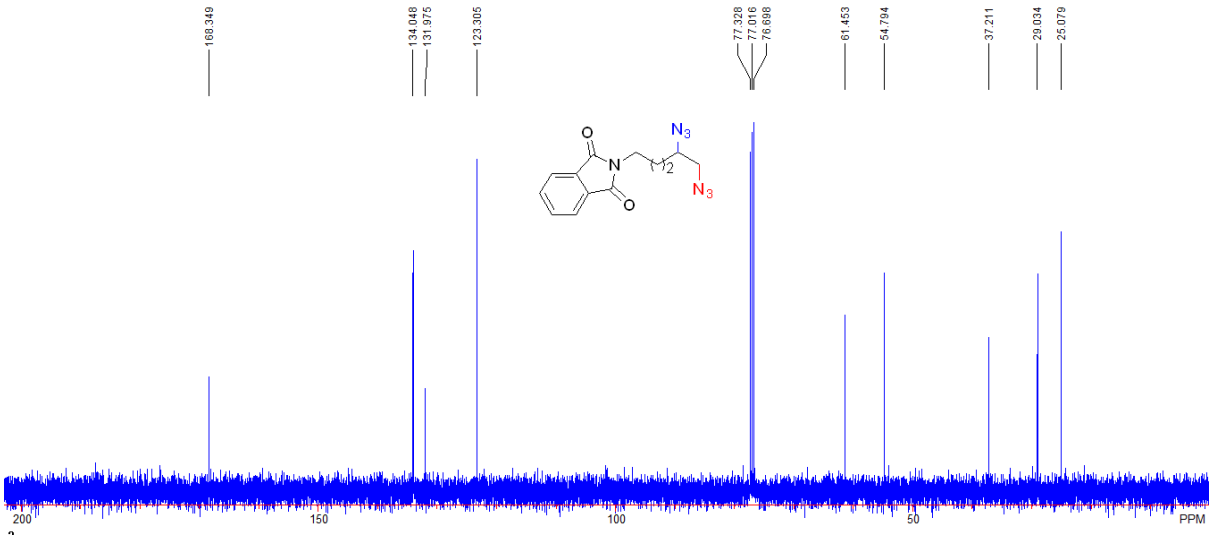
N3
2.00
2.12
2.03
2.00
1.00
1.00
1.12
2.06
10
8
6
4
2
0
PPM


168.349
134.048
131.975
123.305
77.328
77.016
76.698
61.453
54.794
37.211
29.034
25.079
N3
N3
200
150
100
50
PPM