Supplementary Material

Dehydrogenative C(sp3)–H Bond Functionalization of Tetrahydroisoquinolines Mediated by Organic Oxidants under Mild Conditions

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General Remarks:

All reactions were monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plates (0.25 mm thickness). Preparative thin layer chromatography was performed using Merck 60 F254 silica gel purchased from Merck KGA. Column chromatography was carried out on silica gel (12-26, ICN Biomedicals) using petrol ether/ethyl acetate as eluents. 1H-NMR and 13C-NMR spectra were measured on a on a Bruker Ultrashield Advance III spectrometer (^{1}H at 500.26 MHz, ^{13}C at 125.79 MHz) using $CDCl_3$ as solvent with $CHCl_3$ as internal standard. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in Hertz (Hz).The proton spectra are reported as follows δ/ppm (multiplicity, number of protons, coupling constant J/Hz). Two dimensional spectra (COSY, HSQC, HMBC) were used where appropriate to aid the assignments in ^{1}H and ^{13}C spectra. High-resolution mass spectral analyses (HRMS) were carried out using Bruker ESI-TOF MS. IR spectra were measured on a PerkineElmer FT-IR 1725X spectrophotometer using ATR technique. The peak intensities are defined as very strong (vs), strong (s), middle (m) or weak (w).

General procedure I for DDQ oxidation/Mannich reaction of *N*-Aryl substituted THIQs

To a stirred solution of tetrahydroisoquinoline (0.25 mmol, 1 equiv.) in acetonitrile (2ml) was added DDQ (0.263 mmol, 1.05 equiv.) and solution was allowed to stirr at room temperature next 30 min. Subsequently L-Proline (0.075 mmol, 0.3 equiv.), acetone (0.185 ml, 10 equiv.) and TFA (0.15 mmol) were added and solution stirred until TLC showed full conversion. Upon completion of reaction, excess of solvent was evaporated under reduced pressure on the vacuum evaporator. Residue was redisolved in CH_2Cl_2 and solids were removed by filtration through cellite, solvent evaporated and remaining organic material was purified using SiO_2 column chromatography with Petrol ether/Ethyl acetate as an eluents.

General procedure II for DDQ oxidation/Mannich reaction of *N*-unsubstituted THIQs

2-Iodoxybenzoic acid (IBX) (70 mg, 0.25 mmol) was dissolved in DMSO (0.5 mL) with vigorous stirring for approximately 20 min at ambient temperature. This IBX solution was then added to a solution of amine (0.25 mmol) in DMSO (0.5 mL) and allowed to stir at room temperature for 10-20 min. The mixture was quenched by addition of saturated aqueos $Na_2S_2O_3$ (1 mL) and then basified with saturated aqueos $NaHCO_3$ (1 mL). Following extraction with EtOAc (5 mL) the organic phase was washed with water (3 x10 mL) and brine (1 x10 mL) and then dried over MgSO4 and concentrated under reduced pressure in vacuum evaporator to yield the corresponding imine wich was used in the next step without purification.

To the solution of crude imine in the 2 ml of ketone was added L-Proline (0.075 mmol, 0.3 equiv.), and TFA (0.15 mmol) and solution stirred until TLC showed full conversion. Upon completion of reaction, reaction was quenched with $NaHCO_3$ and water phase was extracted with CH_2Cl_2 (3 x15 ml), organic phase was washed once more with $NaHCO_3$ and then dried over MgSO4 and concentrated under reduced pressure in vacuum evaporator. Remaining organic material was purified using SiO_2 column chromatography with Petrol ether/Ethyl acetate as an eluents.

General procedure III for DDQ oxidation/Strecker reaction of *N*-Aryl substituted THIQs

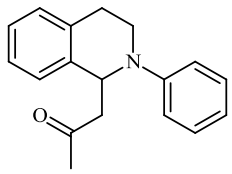
To a stirred solution of tetrahydroisoquinoline (0.25 mmol, 1 equiv.) in acetonitrile (2ml) was added DDQ (0.263 mmol, 1.05 equiv.) and solution was allowed to stirr at room temperature for 30 min. Subsequently TMSCN (0.3 mmol, 1.2 equiv.) was added and solution stirred until

TLC showed full conversion. Upon completion of reaction, excess of solvent and TMSCN was evaporated under reduced pressure on the vacuum evaporator. Residue was redisolved in CH_2Cl_2 and solids were removed by filtration through cellite, solvent was evaporated and remaining organic material was purified using SiO_2 column chromatography with Petrol ether/Ethyl acetate as an eluents.

General procedure IV for Ru catalyzed photoredox oxidation/Mannich reaction of *N*-Aryl substituted pyrrolidines

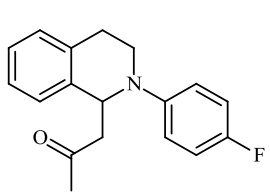
To a stirred solution of N-aryl-substituted pyrrolidine (0.3 mmol, 1 equiv.) in acetonitrile (2ml) was added $Ru(bpy)_3Cl_2*6H_2O$ (0.003 mmol, 1 mol %), L-Proline (0.09 mmol, 0.3 equiv.), and acetone (10 equiv.). Solution was irradiated with 14W CFL lamp. After first 24h additional 1 mol% of $Ru(bpy)_3Cl_2*6H_2O$ catalyst was added. Solution was stirred for the next 24-96h. After this time excess of solvent was evaporated under reduced pressure on the vacuum evaporator. Remaining organic material was purified using SiO_2 column chromatography with Petrol ether/Ethyl acetate as an eluents.

1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (1a)



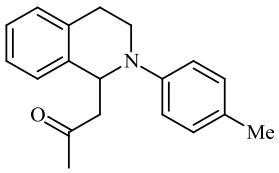
General procedure I was followed with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.3 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (52 mg, 78 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.24 (t, 2H, ArH, *J* = 7.8 Hz), 7.12-7.15 (m, 4H, ArH), 6.93 (d, 2H, ArH, *J* = 8.5 Hz), 6.77 (t, 1H, *J* = 7.0 Hz), 5.39 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.64 (dt, 1H, *J* = 5.5 Hz, 13.0 Hz), 3.52 (ddd, 1H, *J* = 4.4 Hz, 8.9 Hz, 12.5 Hz), 3.02-3.07 (m, 2H), 2.81 (dd, 2H, *J* = 7.2, 16.2 Hz), 2.06 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.2, 148.8, 138.3, 134.4, 129.3, 128.6, 126.83, 126.78, 126.3, 118.2, 114.8, 54.8, 50.2, 42.0, 31.1, 27.2. **IR** (ATR): ν = 3060 (m), 3025 (m), 2913 (m), 2836 (m), 1711 (vs), 1599 (vs), 1501 (vs), 1393 (s), 1355 (s), 1275 (m), 1230 (m) 1159 (m), 1033 (m), 928 (w), 755 (s), 695 (m) cm^{-1}; **MS** (ESI) *m*/*z* 266 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S1]

1-(2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (2a)



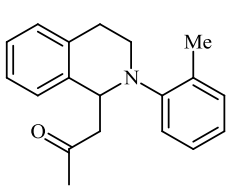
General procedure I was followed with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (69.3 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (52 mg, 73 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.13-7.20 (m, 4H, ArH), 6.89-6.97 (m, 4H, ArH), 5.31 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.59 (dt, 1H, *J* = 4.9, 12.5 Hz), 3.48-3.53 (m, 1H), 3.00-3.06 (m, 2H), 2.76-2.83 (m, 2H), 2.09 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.1, 156.4 (d, *J* = 237.6 Hz), 145.7, 138.0, 134.1, 128.8, 126.74, 126.72, 126.3, 117.1 (d, *J* = 7.6 Hz), 115.6 (d, *J* = 22.1 Hz), 55.5, 50.0, 42.6, 30.9, 26.7; **IR** (ATR): ν = 3055 (m), 2915 (m), 2836 (m), 1711 (s), 1510 (vs), 1357 (m), 1231 (s), 1161 (m), 1033 (w), 926 (w), 815 (m), 754 (m) cm^{-1}; **MS** (ESI) *m*/*z* 284 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S1]

1-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3a)



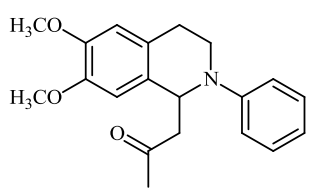
General procedure I was followed with 2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (55.8 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (49 mg, 71 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.15-7.19 (m, 3H, ArH), 7.12-7.14 (m, 1H, ArH), 7.06 (d, 2H, ArH, *J* = 8.5 Hz), 6.87 (d, 2H, ArH, *J* = 8.5 Hz), 5.35 (t, 1H, C(1)H, *J* = 6.5 Hz), 3.64 (dt, 1H, *J* = 5.0 Hz, 12.5 Hz), 3.01-3.08 (m, 2H), 2.76-2.83 (m, 2H), 2.26 (s, 3H, Ar$C\underline{H}_3$), 2.08 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.3, 146.9, 138.3, 134.4, 129.8, 128.8, 127.9, 126.8, 126.7, 126.2, 115.6, 55.1, 50.1, 42.2, 31.0, 27.0, 20.3; **MS** (ESI) *m*/*z* 280 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S1]

1-(2-(*o*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (4a)



General procedure I was followed with 2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline (55.8 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 24 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (36 mg, 52 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.13-7.23 (m, 5H, ArH), 7.04 (t, 1H, ArH, *J* = 7.5 Hz), 6.98 (t, 1H, ArH, *J* = 7.2 Hz), 6.84 (d, 1H, ArH, *J* = 8.0 Hz), 4.97 (dd, 1H, C(1)H, *J* = 5.0 Hz, 8.0 Hz), 3.44-3.50 (m, 1H), 3.19 (dd, 1H, *J* = 3.2 Hz, 13.2 Hz), 3.02 (dd, 1H, *J* = 8.5 Hz, 15.5 Hz), 2.84 (ddd, 1H, *J* = 5.5 Hz, 11.0 Hz, 16.5 Hz), 2.74 (dd, 1H, *J* = 5.0, 15.5 Hz), 2.64 (brd, 1H, *J* = 16.5 Hz), 2.30 (s, 3H, CH_3), 2.03 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.0, 149.7, 138.5, 135.0, 133.5, 131.1, 129.2, 126.5, 126.4, 126.3, 126.2, 123.6, 122.3, 57.1, 50.6, 43.7, 30.0, 26.1, 17.9; **IR** (ATR): ν = 3061 (m), 3019 (m), 2923 (s), 2830 (m), 1711 (vs), 1598 (m), 1492 (vs), 1455 (m), 1356 (s), 1279 (m), 1214 (m), 1035 (w), 926 (w), 762 (s), 731 (m) cm^{-1}; **MS** (ESI) *m*/*z* 280 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S1]

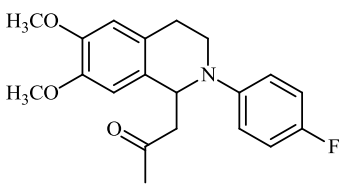
1-(6,7-Dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (5a)



General procedure I was followed with 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (67.3 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (58 mg, 71 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.24 (t, 2H, ArH, *J* = 8.0 Hz), 6.93 (d, 2H, ArH, *J* = 8.0 Hz), 6.78 (t, 1H, ArH, *J* = 7.2 Hz), 6.69 (s, 1H, C(5)H or C(8)H), 6.61 (s, 1H, C(5)H or C(8)H), 5.30 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.84 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.66 (dt, 1H, *J* = 5.0 Hz, 13.0 Hz), 3.49 (ddd, 1H, *J* = 4.5 Hz, 9.7 Hz, 12.8 Hz), 3.04 (dd, 1H, *J* = 5.5 Hz, 16.5 Hz), 2.97 (ddd, 1H, *J* = 5.8 Hz, 9.8 Hz, 15.8 Hz), 2.82 (dd, 1H, *J* = 6.8 Hz, 12.2 Hz), 2.70 (dt, 1H, *J* = 4.2 Hz, 16.0 Hz), 2.08 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.6, 148.9, 147.7, 147.3, 130.1, 129.2, 126.2, 118.4, 115.1, 111.3, 109.7, 55.9, 55.8, 54.5, 50.1, 41.9, 31.1, 26.5; **IR** (ATR): ν = 2998 (m), 2935

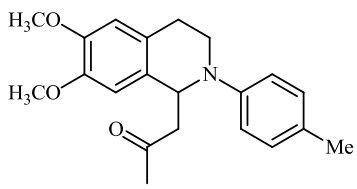
(m), 2835 (m), 2253 (w), 1710 (s), 1599 (s), 1510 (vs), 1464 (m), 1388 (m), 1356 (m), 1248 (s), 1115 (m), 1034 (m), 929 (w), 862 (w), 803 (w), 754 (m), 696 (m) cm^{-1}; **MS** (ESI) *m*/*z* 326 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S1]

1-(2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6a)



General procedure I was followed with 2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (71.8 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 µL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (56 mg, 65 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.86-6.94 (m, 4H, ArH), 6.66 (s, 1H, C(5)H or C(8)H), 6.59 (s, 1H, C(5)H or C(8)H), 5.18 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.838 (s, 3H, OCH_3), 3.831 (s, 3H, OCH_3), 3.58 (ddd, 1H, *J* = 3.8 Hz, 5.2 Hz, 12.8 Hz), 3.46 (ddd, 1H, *J* = 4.2 Hz, 10.5 Hz, 16.0 Hz), 3.01 (dd, 1H, *J* = 6.2 Hz, 16.2 Hz), 2.92 (ddd, 1H, *J* = 5.8 Hz, 10.2 Hz, 16.0 Hz), 2.78 (dd, 1H, *J* = 6.5 Hz, 16.0 Hz), 2.64 (dt, 1H, *J* = 7.2 Hz, 16.0 Hz), 2.09 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.5, 156.6 (d, *J* = 238.0 Hz), 147.8, 147.5, 145.9, 129.8, 126.0, 117.5 (d, *J* = 7.4 Hz), 115.6 (d, *J* = 22.4 Hz), 111.4, 109.6, 55.9, 55.8, 55.3, 50.0, 42.6, 31.0, 26.0; **IR** (ATR): ν = 2999 (w), 2937 (m), 2836 (m), 2253 (w), 1711 (s), 1610 (m), 1511 (vs), 1465 (m), 1357 (m), 1246 (s), 1116 (m), 1036 (w), 930 (w), 811 (m), 732 (w) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{20}H_{22}FNO_3Na$ $(M+Na^+)$ 366.1476, found 366.1469;

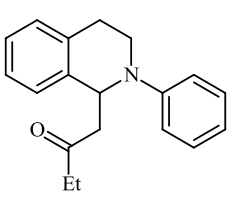
1-(6,7-Dimethoxy-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (7a)



General procedure I was followed with 6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (70.8 mg, 0.25 mmol), acetone (145.2 mg, 0.185 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 µL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (59 mg, 70 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.05 (d, 2H, ArH, *J* = 8.0 Hz), 6.86 (d, 2H, ArH, *J* = 8.0 Hz), 6.68 (s, 1H, C(5)H or C(8)H), 6.59 (s,

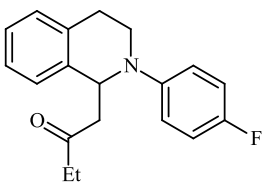
1H, C(5)H or C(8)H), 5.24 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.842 (s, 3H, OCH_3), 3.838 (s, 3H, OCH_3), 3.64 (ddd, 1H, *J* = 4.0 Hz, 5.0 Hz, 12.9 Hz), 3.46 (ddd, 1H, *J* = 4.1 Hz, 10.1 Hz, 13.1 Hz), 3.02 (dd, 1H, *J* = 6.0 Hz, 16.0 Hz), 2.95 (ddd, 1H, *J* = 5.8 Hz, 10.2 Hz, 16.0 Hz), 2.79 (dd, 1H, *J* = 7.0 Hz, 16.0 Hz), 2.66 (brdt, 1H, *J* = 3.5 Hz, 16.0 Hz), 2.25 (s, 3H, $ArC\underline{H}_3$), 2.08 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.7, 147.7, 147.3, 147.0, 130.1, 129.8, 128.1, 126.2, 116.0, 111.4, 109.7, 55.9, 55.8, 54.9, 49.9, 42.1, 31.0, 26.3, 20.3; **IR** (ATR): ν = 2999 (m), 2915 (m), 2834 (m), 2252 (w), 1710 (s), 1613 (m), 1515 (vs), 1463 (m), 1387 (m), 1355 (m) 1248 (s), 1116 (m), 1037 (m), 929 (w), 861 (w), 806 (m), 733 (m) cm^{-1}; **MS** (ESI) *m*/*z* 340 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S2]

1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (1b)



General procedure I was followed with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.3 mg, 0.25 mmol), ethyl methyl ketone (180.3 mg, 0.224 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (43 mg, 62 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.26 (t, 2H, ArH, *J* = 8.0 Hz), 7.13-7.18 (m, 4H, ArH), 6.95 (d, 2H, ArH, *J* = 8.5 Hz), 6.78 (t, 1H, ArH, *J* = 7.2 Hz), 5.43 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.65 (dt, 1H, *J* = 5.2 Hz, 12.5 Hz), 3.54 (ddd, 1H, *J* = 4.5 Hz, 8.6 Hz, 12.9 Hz), 3.02-3.10 (m, 2H), 2.77-2.87 (m, 2H), 2.36 (dq, 1H, *J* = 7.3, 17.9 Hz), 2.26 (dq, 1H, *J* = 7.3, 17.9 Hz), 0.99 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 209.9, 148.8, 138.3, 134.4, 129.3, 128.6, 126.8, 126.7, 126.2, 118.1, 114.6, 55.1, 48.9, 41.9, 37.2, 27.2, 7.5; **IR** (ATR): ν = 3060 (m), 3026 (m), 2975 (m), 2936 (m), 2837 (m), 1710 (vs), 1598 (vs), 1501 (vs), 1393 (s), 1350 (m), 1272 (m), 1228 (m), 1112 (m), 1038 (w), 944 (w), 752 (s), 695 (m) cm^{-1}; **MS** (ESI) *m*/*z* 280 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S1]

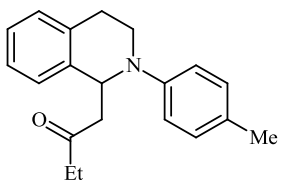
1-(2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (2b)



General procedure I was followed with 2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (71.8 mg, 0.25 mmol), ethyl methyl ketone (180.3 mg, 0.224 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075

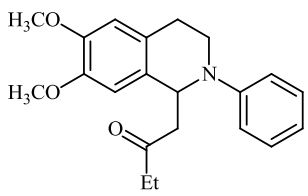
mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (40 mg, 54%) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.12-7.18 (m, 4H, ArH), 6.88-6.96 (m, 4H, ArH), 5.32 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.58 (dt, 1H, *J* = 5.0 Hz, 13.0 Hz), 3.48-3.53 (m, 1H), 2.99-3.07 (m, 2H), 2.74-2.81 (m, 2H), 2.36 (dq, 1H, *J* = 7.2, 17.7 Hz), 2.28 (dq, 1H, *J* = 7.2, 17.7 Hz), 0.99 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 209.8, 156.4 (d, *J* = 237.8 Hz), 145.7, 138.1, 134.2, 128.8, 126.8, 126.2, 116.9 (d, *J* = 7.2 Hz), 115.6 (d, *J* = 22.0 Hz), 55.8, 48.8, 42.5, 37.2, 26.8, 7.5; **IR** (ATR): ν = 3054 (w), 2975 (m), 2936 (m), 2837 (w), 1710 (s), 1510 (vs), 1456 (m), 1394 (m), 1354 (m), 1232 (s), 1112 (m), 945 (w), 814 (m), 760 (m) cm^{-1}; **MS** (ESI) *m*/*z* 298 $[M+H]^+$. Spectroscopic data are in agreement with the published data. [S3]

1-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (3b)



General procedure I was followed with 2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (55.8 mg, 0.25 mmol), ethyl methyl ketone (180.3 mg, 0.224 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (40 mg, 55%) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.12-7.15 (m, 4H, ArH), 7.05 (d, 2H, ArH, *J* = 8.2 Hz), 6.86 (d, 2H, ArH, *J* = 8.2 Hz), 5.36 (t, 1H, C(1)H, *J* = 6.5 Hz), 3.62 (dt, 1H, *J* = 5.1 Hz, 12.5 Hz), 3.47-3.52 (m, 1H), 2.99-3.08 (m, 2H), 2.73-2.81 (m, 2H), 2.27-2.37 (m, 2H), 2.24 (s, 3H, CH_3), 0.99 (t, 3H, CH_3, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 210.0, 146.9, 138.4, 134.4, 129.8, 128.7, 126.8, 126.7, 126.1, 118.3, 115.5, 55.4, 48.8, 42.0, 37.1, 27.0, 20.3, 7.5; **IR** (ATR): ν = 3025 (m), 2973 (m), 2914 (m), 1710 (vs), 1616 (s), 1517 (vs), 1455 (m), 1392 (m), 1275 (m), 1269 (m), 1205 (m), 1111 (m), 1042 (w), 944 (m), 807 (m), 759 (m) cm^{-1}; **MS** (ESI) *m*/*z* 294 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S3]

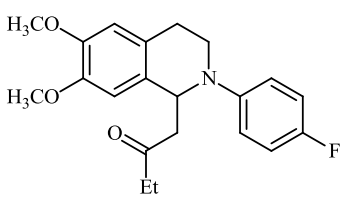
1-(6,7-Dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (5b)



General procedure I was followed with 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (67.3 mg, 0.25 mmol), ethyl methyl ketone (180.3 mg, 0.224 ml, 2.5 mmol), DDQ (56.7 mg, 0.25

mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (52 mg, 61 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.24 (t, 2H, ArH, *J* = 8.2 Hz), 6.95 (d, 2H, ArH, *J* = 8.5 Hz), 6.78 (t, 1H, ArH, *J* = 7.0 Hz), 6.66 (s, 1H, C(5)H or C(8)H), 6.61 (s, 1H, C(5)H or C(8)H), 5.32 (t, 1H, C(1)H, *J* = 6.5 Hz), 3.85 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.66 (dt, 1H, *J* = 5.0 Hz, 13.0 Hz), 3.50 (ddd, 1H, *J* = 4.2 Hz, 9.2 Hz, 12.5 Hz), 3.02 (dd, 1H, *J* = 5.2 Hz, 15.8 Hz), 2.96-3.02 (m, 1H), 2.78 (dd, 1H, *J* = 7.0 Hz, 16.0 Hz), 2.72 (dt, 1H, *J* = 4.4 Hz, 16.0 Hz), 2.37 (dq, 1H, *J* = 7.4 Hz, 17.8 Hz), 2.28 (dq, 1H, *J* = 7.2 Hz, 17.8 Hz), 0.99 (t, 3H, $COCH_2C\underline{H}_3$, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 210.3, 148.9, 147.7, 147.3, 130.2, 129.3, 126.2, 118.2, 114.9, 111.3, 109.7, 55.9, 55.8, 54.9, 48.8, 41.8, 37.4, 26.6, 7.5; **IR** (ATR): ν = 2936 (s), 2835 (m), 1709 (s), 1599 (s), 1511 (vs), 1463 (m), 1388 (m), 1354 (m), 1253 (s), 1115 (m), 1031 (m), 864 (w), 753 (m), 696 (m) cm^{-1}; **MS** (ESI) *m*/*z* 340 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S4]

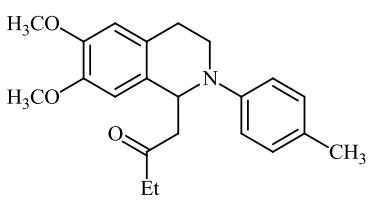
1-(2-(4-Fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (6b)



General procedure I was followed with 2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (71.8 mg, 0.25 mmol), ethyl methyl ketone (180.3 mg, 0.224 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (49 mg, 55 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.87-6.94 (m, 4H, ArH), 6.62 (s, 1H, C(5)H or C(8)H), 6.59 (s, 1H, C(5)H or C(8)H), 5.20 (t, 1H, C(1)H, *J* = 6.5 Hz), 3.84 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.57 (ddd, 1H, *J* = 3.9 Hz, 5.4 Hz, 12.9 Hz), 3.43-3.49 (m, 1H), 2.99 (dd, 1H, *J* = 6.5 Hz, 16.0 Hz), 2.88-2.98 (m, 1H), 2.74 (dd, 1H, *J* = 6.5 Hz, 15.5 Hz), 2.66 (dt, 1H, *J* = 3.8 Hz, 16.0 Hz), 2.26-2.40 (m, 2H, $COC\underline{H}_2CH_3$), 0.99 (t, 3H, $COCH_2C\underline{H}_3$, J = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 210.2, 156.5 (d, *J* = 238.1 Hz), 147.8, 147.4, 145.8, 129.9, 126.0, 117.25 (d, *J* = 7.4 Hz), 115.6 (d, *J* = 22.0 Hz), 111.4, 109.5, 55.9, 55.8, 55.6, 48.7, 42.4, 37.3, 26.2, 7.5; **IR** (ATR): ν = 2936 (m), 2835 (m), 2254 (w), 1709 (s), 1610 (m), 1511 (vs), 1463 (m), 1355 (m), 1230 (s),

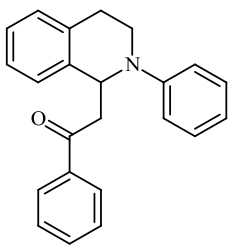
1115 (m), 1028 (w), 945 (w), 813 (m), 733 (w) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{21}H_{24}FNO_3Na$ ($M+Na^+$) 380.1632, found 380.1620;

1-(6,7-Dimethoxy-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (7b)



General procedure I was followed with 6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (70.8 mg, 0.25 mmol), ethyl methyl ketone (180.3 mg, 0.224 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 µL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (51 mg, 58 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.05 (d, 2H, ArH, *J* = 8.2 Hz), 6.86 (d, 2H, ArH, *J* = 8.2 Hz), 6.65 (s, 1H, C(5)H or C(8)H), 6.29 (s, 1H, C(5)H or C(8)H), 5.26 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.84 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.63 (dt, 1H, *J* = 4.8 Hz, 12.0 Hz), 3.46 (ddd, 1H, *J* = 4.2 Hz, 10.2 Hz, 12.5 Hz), 2.94-3.01 (m, 2H), 2.75 (dd, 1H, *J* = 7.0 Hz, 15.5 Hz), 2.67 (brdt, 1H, *J* = 3.5 Hz, 16.0 Hz), 2.36 (dq, 1H, *J* = 7.3 Hz, 17.9 Hz), 2.28 (dq, partially hidden by $COCH_2C\underline{H}_3$ signal, 1H, *J* = 7.3 Hz, 17.9 Hz), 0.98 (t, 3H, $COCH_2C\underline{H}_3$, *J* = 7.5 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 210.4, 147.7, 147.3, 147.0, 130.2, 129.8, 127.9, 126.2, 115.8, 111.3, 109.6, 55.9, 55.8, 55.3, 48.6, 41.9, 37.3, 26.5, 20.3, 7.5; **IR** (ATR): ν = 2935 (s), 2834 (m), 1709 (s), 1613 (m), 1516 (vs), 1462 (m), 1387 (m), 1355 (m), 1252 (s), 1114 (m), 1030 (w), 947 (w), 814 (m), 732 (w) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{22}H_{27}NO_3Na$ ($M+Na^+$) 376.1883, found 376.1880;

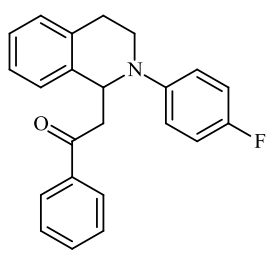
1-Phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (1c)



General procedure I was followed with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.3 mg, 0.25 mmol), acetophenone (300.4 mg, 0.292 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 µL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. over night. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (49 mg, 60 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.87 (d, 2H, ArH, *J* = 7.5 Hz), 7.54 (t, 1H, ArH, *J* = 7.2 Hz), 7.42 (t, 2H, ArH, *J* = 7.8 Hz), 7.11-7.27 (m, 7H, ArH), 6.99 (d, 1H, ArH, *J* = 8.0 Hz), 6.77 (t, 1H, ArH, *J* = 7.2 Hz), 5.69 (dd, 1H, C(1)H, *J* =

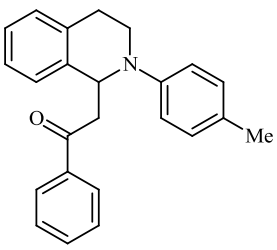
5.5 Hz, 7.0 Hz), 3.63-3.71 (m, 2H) 3.60 (dd, 1H, *J* = 4.8 Hz, 16.8 Hz), 3.42 (dd, 1H, *J* = 7.2, 16.8 Hz), 3.10-3.16 (m, 1H), 2.95 (dt, 1H, *J* = 5.0 Hz, 16.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 198.6, 148.7, 138.5, 137.2, 134.5, 133.1, 129.3, 128.5, 128.1, 127.1, 126.8, 126.2, 117.9, 114.3, 55.0, 45.3, 42.1, 27.5; **IR** (ATR): ν = 3060 (m), 3028 (m), 2906 (m), 2838 (m), 1680 (vs), 1598 (vs), 1501 (vs), 1449 (m), 1393 (m), 1349 (m), 1282 (s), 1206 (m), 1032 (m), 751 (s), 693 (m) cm^{-1}; **MS** (ESI) *m*/*z* 328 $[M+H]^+$. Spectroscopic data are in agreement with the published data. [S5]

2-(2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (2c)



General procedure I was followed with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (69.3 mg, 0.25 mmol), acetophenone (300.4 mg, 0.292 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t over night. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (62 mg, 61 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.85 (d, 2H, ArH, *J* = 7.5 Hz), 7.53 (t, 1H, ArH, *J* = 7.5 Hz), 7.41 (t, 2H, ArH, *J* = 7.8 Hz), 7.21 (d, 1H, ArH, *J* = 7.5 Hz), 7.12-7.17 (m, 3H, ArH), 6.92 (d, 4H, ArH, *J* = 6.5 Hz), 5.57 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.56-3.61 (m, 3H), 3.34 (dd, 1H, *J* = 6.5 Hz, 16.5 Hz), 3.06-3.12 (m, 1H), 2.87 (dt, 1H, *J* = 4.1 Hz, 16.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 198.6, 156.3 (d, *J* = 237.0 Hz), 145.6, 138.3, 137.2, 134.2, 133.1, 128.7, 128.5, 128.1, 127.0, 126.8, 126.3, 116.6 (d, *J* = 7.2 Hz), 115.6 (d, *J* = 22.1 Hz), 55.8, 45.1, 42.6, 27.1; **IR** (ATR): ν = 3059 (w), 2906 (w), 2836 (w), 1681 (s), 1512 (vs), 1450 (m), 1280 (m), 1232 (m), 818 (m), 756 (m), 693 (w) cm^{-1}; **MS** (ESI) *m*/*z* 346 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S5]

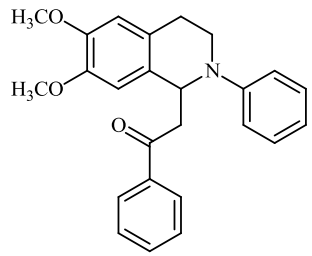
1-Phenyl-2-(2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3c)



General procedure I was followed with 2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (55.8 mg, 0.25 mmol), acetophenone (300.4 mg, 0.292 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. over night. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the

title compound (49 mg, 57 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.84 (d, 2H, ArH, *J* = 7.0 Hz), 7.52 (t, 1H, ArH, *J* = 7.5 Hz), 7.40 (t, 2H, ArH, *J* = 7.8 Hz), 7.21 (d, 1H, ArH, *J* = 7.5 Hz), 7.09-7.15 (m, 3H, ArH), 7.04 (d, 2H, ArH, *J* = 8.5 Hz), 6.89 (d, 2H, ArH, *J* = 8.5 Hz), 5.61 (t, 1H, C(1)H, *J* = 6.0 Hz), 3.54-3.67 (m, 3H), 3.36 (dd, 1H, *J* = 7.2 Hz, 16.2 Hz), 3.10 (ddd, 1H, *J* = 6.2 Hz, 9.2 Hz, 15.8 Hz), 2.88 (dt, 1H, *J* = 4.5 Hz, 16.0 Hz), 2.23 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 198.7, 146.8, 138.6, 137.3, 134.4, 133.0, 129.8, 128.6, 128.5, 128.1, 127.6, 127.1, 126.7, 126.1, 115.2, 55.4, 45.1, 42.2, 27.4, 20.3; **IR** (ATR): ν = 3060 (m), 3027 (m), 2917 (m), 2858 (m), 1680 (vs), 1615 (m), 1517 (vs), 1459 (m), 1393 (m), 1278 (m), 1205 (m), 1020 (w), 937 (w), 804 (m), 754 (m), 692 (m) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{24}H_{23}NONa$ ($M+Na^+$) 364.1672, found 364.1665;

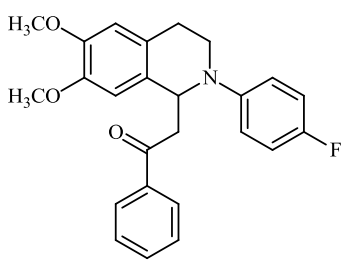
2-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (5c)



General procedure I was followed with 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (67.3 mg, 0.25 mmol), acetophenone (300.4 mg, 0.292 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. over night. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (58 mg, 60 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.85 (d, 2H, ArH, *J* = 7.5 Hz), 7.52 (t, 1H, ArH, *J* = 7.5 Hz), 7.41 (t, 2H, ArH, *J* = 7.8 Hz), 7.24 (t, 2H, ArH, *J* = 7.5 Hz), 6.98 (d, 2H, ArH, *J* = 8.5 Hz), 6.76 (t, 1H, ArH, *J* = 7.2 Hz), 6.70 (s, 1H, C(5)H or C(8)H), 6.63 (s, 1H, C(5)H or C(8)H), 5.36 (dd, 1H, C(1)H, *J* = 5.0 Hz, 7.0 Hz), 3.84 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.68 (dt, 1H, *J* = 5.2 Hz, 12.5 Hz), 3.32-3.61 (m, 2H), 3.39 (dd, 1H, *J* = 7.5 Hz, 16.0 Hz), 3.03 (ddd, 1H, *J* = 5.8 Hz, 8.4 Hz, 15.6 Hz), 2.81 (dt, 1H, *J* = 4.4 Hz, 16.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 199.1, 148.9, 147.8, 147.3, 137.3, 133.1, 130.4, 129.3, 128.5, 128.1, 126.3, 118.1, 114.7, 111.3, 110.1, 55.9 (2C overlapped), 55.0, 45.1, 42.0, 27.0; **IR** (ATR): ν = 3059 (m), 2999 (m), 2934 (m), 2835 (m), 1679 (s), 1599 (s), 1510 (vs), 1464 (m), 1389 (m), 1354 (m) 1251 (s), 1116 (m), 1031 (m), 912 (w), 865 (w), 759 (m), 694 (m) cm^{-1}; **MS** (ESI) *m/z* 388 $[M+H]^+$. Spectroscopic data are in agreement with the published d

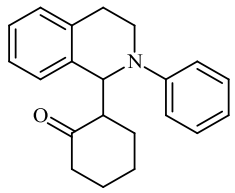
ata.[S6]

2-(2-(4-Fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (6c)



General procedure I was followed with 2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (71.8 mg, 0.25 mmol), acetophenone (300.4 mg, 0.292 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 6 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (72 mg, 71 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.85 (d, 2H, ArH, *J* = 7.5 Hz), 7.53 (d, 1H, ArH, *J* = 7.5 Hz), 7.41 (t, 2H, ArH, *J* = 7.5 Hz), 6.92 (d, 4H, ArH, *J* = 6.5 Hz), 6.67 (s, 1H, C(5)H or C(8)H), 6.62 (s, 1H, C(5)H or C(8)H), 5.44 (t, 1H, C(1)H, *J* = 6.0 Hz), 3.84 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.52-3.63 (m, 3H), 3.33 (dd, 1H, *J* = 6.8 Hz, 16.2 Hz), 3.00 (ddd, 1H, *J* = 6.1 Hz, 9.6 Hz, 15.9 Hz), 2.74 (brd, 1H, *J* = 16.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 199.0, 156.4 (d, *J* = 237.5 Hz), 147.8, 147.4, 145.8, 137.3, 133.2, 130.1, 128.6, 128.1, 126.1, 117.1 (d, *J* = 7.3 Hz), 115.6 (d, *J* = 22.1 Hz), 111.4, 109.9, 55.9 (3C overlapped), 44.9, 42.6.3, 26.6; **IR** (ATR): ν = 3060 (w), 2935 (m), 2837 (m), 2253 (w), 1680 (s), 1511 (vs), 1465 (m), 1355 (m), 1248 (s), 1116 (m), 1023 (w), 913 (w), 821 (w), 733 (w), 694 (w) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{25}H_{24}FNO_3Na$ ($M+Na^+$) 428.1632, found 428.1625;

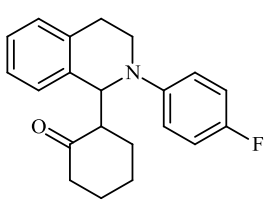
2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone (1d)



General procedure I was followed with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.3 mg, 0.25 mmol), cyclohexanone (245.4 mg, 0.259 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 12 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (37 mg, 48 %) as colorless oil.Major isomer is marked with *. **^{1}H NMR** ($CDCl_3$, 500 MHz, 1: 1.37 diastereomeric mixture): δ 5.68 (d, 1H, C(1)H, *J* = 8.5 Hz), 5.63* (d, 1H, C(1)H, *J* = 5.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz, 1: 1.37 diastereomeric mixture): δ 211.87*, 211.80, 149.3*, 149.2, 140.3*, 135.9, 135.0, 134.5*, 129.3, 129.2*, 128.6, 127.9, 127.8*, 127.2*, 126.6*, 126.3*, 125.7, 118.1, 116.3*, 114.8, 112.3*, 59.3*, 56.4, 54.9, 54.0*, 43.5*, 43.1*, 42.6, 41.3,

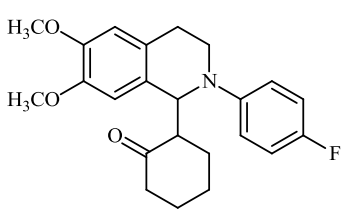
32.7*, 30.1, 28.6*, 27.7*, 27.3, 27.2, 25.6*, 23.8. **MS** (ESI) *m*/*z* 306 $[M+H]^+$. Spectroscopic data are in agreement with the published data. [S7]

2-(2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone (2d)



General procedure I was followed with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (69.3 mg, 0.25 mmol), cyclohexanone (245.4 mg, 0.259 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 12 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (46 mg, 57 %) as colorless oil. Major isomer is marked with *. **^{1}H NMR** ($CDCl_3$, 500 MHz, 1: 1.34 diastereomeric mixture): δ 5.52 (d, 1H, C(1)H, *J* = 8.5 Hz), 5.44* (d, 1H, C(1)H, *J* = 5.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz, 1: 1.37 diastereomeric mixture): δ 211.89, 211.70*, 156.3* (d, *J* = 237.9 Hz), 155.1 (d, *J* = 235.4 Hz), 146.0*, 139.9, 135.7*, 134.8*, 134.3, 128.7*, 127.9, 127.8*, 127.1, 126.6*, 126.2, 125.7*, 117.1* (d, *J* = 7.4 Hz), 115.5* (d, *J* = 22.0 Hz), 115.4 (d, *J* = 21.9 Hz), 113.6 (d, *J* = 7.2 Hz), 59.2, 56.3*, 55.6*, 54.5, 43.9, 43.3*, 43.0, 41.2*, 32.6, 30.3*, 28.6, 27.3*, 27.2, 26.6*, 25.5, 23.6*; **MS** (ESI) *m*/*z* 324 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S7]

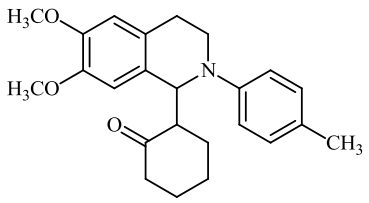
2-(2-(4-Fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone (6d)



General procedure I was followed with 2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (71.8 mg, 0.25 mmol), cyclohexanone (245.4 mg, 0.259 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 12 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (53 mg, 55 %) as colorless oil. Major isomer is marked with *.**^{1}H NMR** ($CDCl_3$, 500 MHz, 1: 1.29 diastereomeric mixture): δ 5.40* (d, 1H, C(1)H, *J* = 4.5 Hz), 5.35 (d, 1H, C(1)H, *J* = 8.5 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz, 1: 1.29 diastereomeric mixture): δ 212.52, 212.12*, 156.6* (d, *J* = 237.8 Hz), 155.4 (d, *J* = 235.7 Hz), 147.7*, 147.5, 147.08, 147.04*, 146.2, 146.0*, 132.0, 127.5*, 127.0*, 126.1, 117.1* (d, *J* = 7.4 Hz), 115.6* (d, *J* = 21.9 Hz), 115.4 (d, *J* = 21.7 Hz), 114.4 (d, *J* = 7.2 Hz),

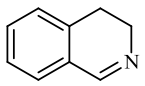
111.2*, 111.1, 110.84*, 110.77; **HRMS**: m/z (ESI/TOF) calc for $C_{23}H_{26}FNO_3Na$ ($M+Na^+$) 406.1789, found 406.1778;

2-(6,7-Dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone (7d)



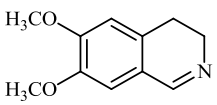
General procedure I was followed with 6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (70.8 mg, 0.25 mmol), cyclohexanone (245.4 mg, 0.259 ml, 2.5 mmol), DDQ (56.7 mg, 0.25 mmol), TFA (5.7 μL, 0.075 mmol) and L-proline (8.6 mg, 0.075 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 12 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (42 mg, 44 %) as colorless oil. Signals that can be certainly assigned to major isomer are marked with *, and signals that can be certainly assigned to minor isomer are marked with +. **^{1}H NMR** ($CDCl_3$, 500 MHz, 1: 1.29 diastereomeric mixture): δ 5.47* (d, 1H, C(1)H, *J* = 3.5 Hz), 5.42 (d, 1H, C(1)H, *J* = 8.5 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz, 1: 1.29 diastereomeric mixture): δ 212.62, 211.27, 147.6$^+$, 147.4*, 147.2$^+$, 147.0*, 132.3, 129.8, 129.7, 127.9, 127.6, 127.2, 126.3, 125.9, 115.6, 113.2, 111.2*, 111.1$^+$, 110.93*, 110.88$^+$, 59.4, 56.5, 56.0*, 55.93$^+$, 55.85$^+$, 55.76*, 54.8, 54.0, 43.29, 43.23, 43.16, 41.5, 32.8, 30.2, 28.9, 27.3, 26.9, 26.5, 25.7$^+$, 24.0*, 20.27*, 20.15$^+$; **HRMS**: m/z (ESI/TOF) calc for $C_{24}H_{29}NO_3Na$ ($M+Na^+$) 402.2040, found 402.2029;

3,4-Dihydroisoquinoline (9a)



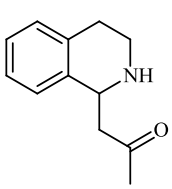
General procedure II was followed with 1,2,3,4-tetrahydroisoquinoline (266.4 mg, 2.0 mmol), IBX (560.0 mg, 2.0 mmol), in DMSO (2 + 2 mL) to yield the title compound (188 mg, 72 %) as brownish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.31 (s, 1H, C(1)H), 7.33 (t, 1H, ArH, *J* = 7.2 Hz), 7.23-7.28 (m, 2H, ArH), 7.13 (d, 1H, ArH, *J* = 7.5 Hz), 3.73-3.76 (m, 2H, C(2)H_2), 2.72 (t, 2H, C(4)H_2, *J* = 7.5 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 160.3, 136.2, 131.0, 128.4, 127.3, 127.1, 127.0, 47.3, 24.9. **IR** (ATR): ν = 3396 (m), 3021 (m), 2942 (s), 2896 (m), 2847 (m), 1627 (vs), 1576 (m), 1452 (m), 1210 (m), 1005 (m), 880 (m), 755 (vs), 694 (m), 592 (m) cm^{-1}; **MS** (ESI) *m/z* 132 $[M+H]^+$. Spectroscopic data are in agreement with the published data. [S8]

6,7-Dimethoxy-3,4-dihydroisoquinoline (9b)



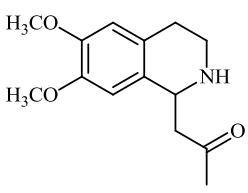
General procedure II was followed with 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (386.5 mg, 2.0 mmol), IBX (560.0 mg, 2.0 mmol), in DMSO (2 + 2 mL) to yield the title compound (281 mg, 73 %) as brownish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.18 (s, 1H, C(1)H), 6.76 (s, 1H, C(5)H or C(8)H), 6.63 (s, 1H, C(5)H or C(8)H), 3.86 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.68 (td, 2H, C(3)H_2, *J* = 2.0 Hz, 8.5 Hz), 2.63 (t, 2H, C(4)H_2, *J* = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 129.3, 150.9, 147.5, 129.5, 121.2, 110.08, 110.07, 55.8, 55.7, 47.0, 24.4; **IR** (ATR): ν = 3376 (m), 2939 (m), 2836 (m), 1574 (m), 1515 (s), 1462 (m), 1280 (s), 1120 (vs), 1015 (m), 858 (m), 731 (m) cm^{-1}; **MS** (ESI) *m*/*z* 192 $[M+H]^+$.Spectroscopic data are in agreement with the published data. [S9]

1-(1,2,3,4-Tetrahydroisoquinolin-1-yl)propan-2-one (10)



General procedure II was followed with 3,4-dihydroisoquinoline (33.3 mg, 0.25 mmol), L-proline (8.6 mg, 0.075 mmol), trifluoroacetic acid (8.6 mg, 5.6 μL, 0,075 mmol), and acetone (2 mL). The reaction was conducted overnight at room temperature. After reaction work-up the crude product was purified by column chromatography on silica gel (petrolether/ethylacetate/Et_3N = 60/40/1) to give the title compound (23.3 mg, 49 %) as slightly yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.12-7.14 (m, 2H, ArH), 7.08-7.10 (m, 1H, ArH), 7.04-7.05 (m, 1H, ArH), 4.49 (dd, 1H, C(1)H, *J* = 2.5, 9.0 Hz), 3.16 (dt, 1H, *J* = 5.5, 12.0 Hz), 2.83-3.02 (m, 4H), 2.73 (dt, 1H, *J* = 4.8, 16.5 Hz), 2.40 (brs, 1H, NH), 2.20 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 208.3, 137.8, 135.5, 129.4, 126.1, 125.8, 125.5, 51.8, 50.5, 41.0, 30.6, 29.8; **IR** (ATR): ν = 3334 (m), 3062 (m), 3020 (m), 2920 (s), 2833 (m), 1711 (vs), 1493 (m), 1454 (m), 1360 (m), 1163 (m), 1125 (w), 756 (m) cm^{-1}; **MS** (ESI) *m*/*z* 190 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S10]

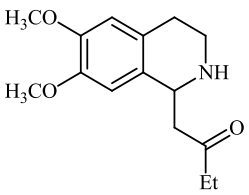
1-(6,7-Dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (11a)



General procedure II was followed with 6,7-dimethoxy-3,4-dihydroisoquinoline (47.8 mg, 0.25 mmol), L-proline (8.6 mg, 0.075 mmol), trifluoroacetic acid (8.6 mg, 5.6 μL, 0,075 mmol), and acetone (2 mL). The reaction was conducted overnight at room temperature. After reaction work-up the crude product was purified by column chromatography on silica

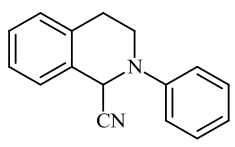
gel (petrolether/ethylacetate/Et_3N = 50/50/1) to give the title compound (25.7 mg, 41 %) as slightly yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.57 (s, 1H, C(5)H or C(8)H), 6.52 (s, 1H, C(5)H or C(8)H), 4.43 (t, 1H, C(1)H, *J* = 6.2 Hz), 3.84 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.13 (dt, 1H, *J* = 5.5, 12.0 Hz), 2.98 (ddd, 1H, *J* = 4.8 Hz, 7.5 Hz, 12.2 Hz), 2.89 (brd, 2H, *J* = 6.0 Hz), 2.64 (dt, 1H, *J* = 5.2 Hz, 16.5 Hz), 2.21 (s, 3H, $COCH_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 208.4, 147.5, 147.3, 129.6, 127.6, 111.9, 108.8, 56.0, 55.8, 51.5, 50.6, 40.9, 30.8, 29.3; **IR** (ATR): ν = 3335 (m), 2936 (s), 2835 (m), 1709 (s), 1608 (m), 1516 (vs), 1463 (m), 1358 (m), 1260 (s), 1224 (s), 1117 (s), 1036 (m), 855 (w) 781 (w), 734 (w) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{14}H_{19}NO_3Na$ ($M+Na^+$) 272.1257, found 272.1252;

1-(6,7-Dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (11b)



General procedure II was followed with 6,7-dimethoxy-3,4-dihydroisoquinoline (47.8 mg, 0.25 mmol), L-proline (8.6 mg, 0.075 mmol), trifluoroacetic acid (8.6 mg, 5.6 μL, 0,075 mmol), and acetone (2 mL). The reaction was conducted overnight at room temperature. After reaction work-up the crude product was purified by column chromatography on silica gel (petrolether/ethylacetate/Et_3N = 50/50/1) to give the title compound (24.8 mg, 38 %) as slightly yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.57 (s, 1H, C(5)H or C(8)H), 6.52 (s, 1H, C(5)H or C(8)H), 4.44 (dd, 1H, C(1)H, *J* = 5.0, 7.5 Hz), 3.84 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.54 (dt, 1H, *J* = 2.8, 6.8 Hz) 3.13 (dt, 1H, *J* = 5.9, 12.5 Hz), 2.98 (ddd, 1H, *J* = 4.8 Hz, 7.5 Hz, 12.2 Hz), 2.93 (brt, 1H, *J* = 6.8 Hz), 2.87 (brd, 2H, *J* = 5.0 Hz), 2.76 (dt, 1H, *J* = 6.2 Hz, 16.0 Hz), 2.64 (dt, 1H, *J* = 5.5 Hz, 16.0 Hz), 2.42-2.55 (m, 2H, $COC\underline{H}_2CH_3$) 1.08 (t, 3H, $COCH_2C\underline{H}_3$, *J* = 7.5 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 211.0, 147.5, 147.3, 129.8, 127.6, 111.9, 108.8, 56.0, 55.8, 51.6, 49.3, 40.8, 36.9, 29.3, 7.6. **IR** (ATR): ν = 3343 (m), 2937 (s), 2835 (m), 1708 (s), 1662 (s), 1607 (s), 1516 (vs), 1461 (s), 1272 (m), 1224 (s), 1119 (s), 1023 (w), 858 (w) 802 (w), 732 (w) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{15}H_{21}NO_3Na$ ($M+Na^+$) 286.1414, found 286.1406;

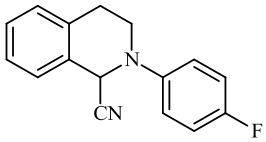
2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (12a)



General procedure III was followed with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.3 mg, 0.25 mmol), trimethylsilyl cyanide (29.8 mg, 0.038 ml, 0.3 mmol), and DDQ (56.7 mg, 0.25 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 72 h. The mixture was purified by

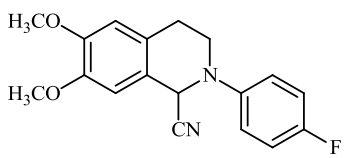
column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (44 mg, 75 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.36 (t, 2H, ArH, *J* = 8.0 Hz), 7.22-7.32 (m, 4H, ArH), 7.08 (d, 2H, ArH, *J* = 8.0 Hz), 7.02 (t, 1H, ArH, *J* = 7.2 Hz), 5.51 (s, 1H, C(1)H), 3.76 (dddd, 1H, *J* = 1.0 Hz, 3.0 Hz, 6.0 Hz, 12.5 Hz), 3.47 (ddd, 1H, *J* = 3.9 Hz, 10.9 Hz, 12.1 Hz), 3.14 (ddd, 1H, *J* = 5.9 Hz, 10.6 Hz, 16.4 Hz), 2.95 (dt, 1H, *J* = 3.4 Hz, 16.5 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 148.3, 134.5, 129.5 (2C overlapped), 129.3, 128.7, 127.0, 126.8, 121.8, 117.7, 117.5, 53.1, 44.1, 28.4; **IR** (ATR): ν = 3063 (m), 3030 (m), 2927 (m), 2833 (m), 1934 (w), 1598 (vs), 1500 (vs), 1456 (m), 1378 (s), 1204 (s), 1146 (m), 1029 (m), 940 (m), 909 (s), 737 (vs), 694 (m) cm^{-1}; **MS** (ESI) *m*/*z* 235 $[M+H]^+$. Spectroscopic data are in agreement with the published data. [S11]

2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (12b)



General procedure III was followed with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (69.3 mg, 0.25 mmol), trimethylsilyl cyanide (29.8 mg, 0.038 ml, 0.3 mmol), and DDQ (56.7 mg, 0.25 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 72 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (37 mg, 58 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.21-7.31 (m, 4H, ArH), 7.02-7.08 (m, 4H, ArH), 5.38 (s, 1H, C(1)H), 3.61 (dddd, 1H, *J* = 1.0 Hz, 2.2 Hz, 6.2 Hz, 12.3 Hz), 3.44 (dt, 1H, *J* = 4.0 Hz, 11.8 Hz), 3.14 (ddd, 1H, *J* = 6.0 Hz, 10.8 Hz, 16.5 Hz), 2.93 (dt, 1H, *J* = 3.0 Hz, 16.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 158.6 (d, *J* = 242.2 Hz), 145.1, 134.2, 129.42, 129.36, 128.8, 127.0, 126.8, 120.4 (d, *J* = 7.9 Hz), 117.4, 116.2 (d, *J* = 22.4 Hz), 54.7, 44.7, 28.5; **IR** (ATR): ν = 3067 (m), 2929 (m), 2835 (m), 1725 (w), 1510 (vs), 1459 (m), 1380 (m), 1234 (s), 1163 (m), 942 (m), 825 (m), 758 (m) cm^{-1}; **MS** (ESI) *m*/*z* 253 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S12]

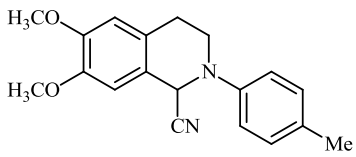
2-(4-Fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (12c)



General procedure III was followed with 2-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (71.8 mg, 0.25 mmol), trimethylsilyl cyanide (29.8 mg, 0.038 ml, 0.3 mmol), and DDQ (56.7 mg, 0.25 mmol), in acetonitrile (2 mL). The reaction was conducted at r.t. for 72 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (52 mg, 67 %) as yellowish oil. **^{1}H**

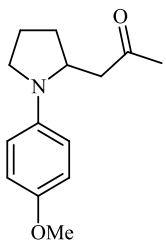
NMR ($CDCl_3$, 500 MHz): δ 7.05-7.06 (m, 4H, ArH), 6.72 (s, 1H, C(5)H or C(8)H), 6.68 (s, 1H, C(5)H or C(8)H), 5.33 (s, 1H, C(1)H), 3.882 (s, 3H, OCH_3), 3.876 (s, 3H, OCH_3), 3.61 (brdd, 1H, *J* = 5.5 Hz, 12.5 Hz), 3.41 (dt, 1H, *J* = 4.0 Hz, 11.8 Hz), 3.08 (ddd, 1H, *J* = 5.8 Hz, 10.8 Hz, 16.2 Hz), 2.83 (dt, 1H, *J* = 2.5 Hz, 15.0 Hz); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 158.6 (d, *J* = 242.2 Hz), 149.4, 148.1, 145.1 (d, *J* = 2.1 Hz), 126.5, 120.9, 120.5 (d, *J* = 8.1 Hz), 117.6, 116.1 (d, *J* = 22.4 Hz), 111.5, 109.3, 56.0, 55.9, 54.5, 44.8, 28.1. **IR** (ATR): ν = 3004 (w), 2936 (m), 2836 (m), 2254 (w), 1612 (m), 1515 (vs), 1464 (m), 1379 (m), 1244 (s), 1120 (m), 1029 (m), 824 (m), 734 (m) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{18}H_{17}FN_2O_2Na$ ($M+Na^+$) 335.1166, found 335.1158;

6,7-Dimethoxy-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (12d)



General procedure III was followed with 6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (70.8 mg, 0.25 mmol), trimethylsilyl cyanide (29.8 mg, 0.038 ml, 0.3 mmol), and DDQ (56.7 mg, 0.25 mmol), in acetonitrile (2 mL). The reaction was conducted at r.t. for 72 h. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (48 mg, 62 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.16 (d, 2H, ArH, *J* = 8.5 Hz), 6.99 (d, 2H, ArH, *J* = 8.5 Hz), 6.73 (s, 1H, C(5)H or C(8)H), 6.67 (s, 1H, C(5)H or C(8)H), 5.38 (s, 1H, C(1)H), 3.88 (s, 6H, $2OCH_3$), 3.69 (brdd, 1H, *J* = 5.5 Hz, 12.5 Hz), 3.40 (td, 1H, *J* = 3.8 Hz, 10.9 Hz), 3.07 (ddd, 1H, *J* = 5.8 Hz, 11.0 Hz, 16.2 Hz), 2.82 (brdt, 1H, *J* = 2.2 Hz, 15.5 Hz), 2.31 (s, 3H, $ArC\underline{H}_3$); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 149.3, 148.0, 146.3, 131.8, 130.0, 126.8, 121.2, 118.4, 117.8, 111.5, 109.3, 56.0, 55.9, 53.9, 44.4, 28.1, 20.5; **IR** (ATR): ν = 3004 (w), 2934 (m), 2835 (m), 2254 (w), 1614 (m), 1518 (vs), 1464 (m), 1380 (m), 1247 (s), 1120 (m), 1029 (m), 860 (w), 734 (m) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{19}H_{20}N_2O_2Na$ ($M+Na^+$) 331.1417, found 331.1410;

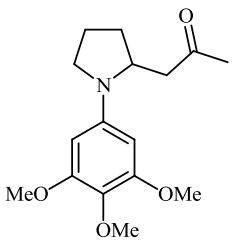
1-(1-(4-Methoxyphenyl)pyrrolidin-2-yl)propan-2-one (13a)



General procedure IV was followed with 1-(4-methoxyphenyl)pyrrolidine (53.2 mg, 0.30 mmol), acetone (174.2 mg, 0.222 ml, 3.0 mmol), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (4.5 mg, 0.006 mmol), and L-proline (10.4 mg, 0.09 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 days. The mixture was purified by column

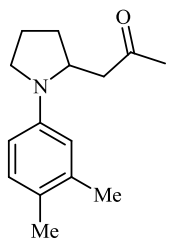
chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (20 mg, 34 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.85 (d, 2H, ArH, *J* = 9.0 Hz), 6.52 (d, 2H, ArH, *J* = 9.0 Hz), 4.13-4.16 (m, 1H), 3.75 (s, 3H, OCH_3), 3.36-3.40 (m, 1H), 3.13 (dd, 1H, *J* = 8.0 Hz, 16.5 Hz), 2.85 (dd, 1H, *J* = 2.0 Hz, 17.0 Hz), 2.43 (dd, 1H, *J* = 10.0 Hz, 16.5 Hz), 2.16 (s, 3H, $COCH_3$), 2.08-2.14 (m, 1H), 1.96-2.02 (m, 2H), 1.72-1.74 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 208.3, 151.0, 141.4, 115.1, 112.8, 55.9, 54.5, 48.5, 46.7, 31.4, 30.9, 23.2; **IR** (ATR): ν = 2957 (m), 2905 (m), 2832 (m), 1710 (s), 1515 (vs), 1364 (m), 1242 (s), 1181 (m), 1152 (m), 1042 (m), 816 (m) cm^{-1}; **MS** (ESI) *m/z* 234 $[M+H]^+$. Spectroscopic data are in agreement with the published data. [S13]

1-(1-(3,4,5-Trimethoxyphenyl)pyrrolidin-2-yl)propan-2-one (13b)



General procedure IV was followed with 1-(3,4,5-trimethoxyphenyl)pyrrolidine (71.2 mg, 0.30 mmol), acetone (174.2 mg, 0.222 ml, 3.0 mmol), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (4.5 mg, 0.006 mmol), and L-proline (10.4 mg, 0.09 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 days. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 3/1) to give the title compound (13 mg, 18 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 5.78 (s, 2H, ArH), 4.21 (brdd, 1H, *J* = 7.5 Hz, 9.0 Hz), 3.84 (s, 6H, $2OCH_3$), 3.77 (s, 3H, OCH_3), 3.38-3.41 (m, 1H), 3.19 (dd, 1H, *J* = 8.5 Hz, 16.5 Hz), 2.86 (dd, 1H, *J* = 2.2 Hz, 16.8 Hz), 2.47 (dd, 1H, *J* = 9.5 Hz, 17.0 Hz), 2.18 (s, 3H, $COCH_3$), 2.08-2.14 (m, 1H), 2.00-2.04 (m, 2H), 1.73-1.76 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 208.4, 154.3, 143.7, 129.5, 89.9, 61.4, 56.3, 54.6, 48.4, 42.2, 32.0, 31.3, 23.5; **IR** (ATR): ν = 2956 (m), 2827 (w), 1708 (s), 1611 (s), 1512 (vs), 1456 (s), 1362 (m), 1252 (vs), 1126 (vs), 1011 (m), 924 (w), 792 (m) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{16}H_{23}NO_4Na$ $(M+Na^+)$ 316.1519, found 316.1500;

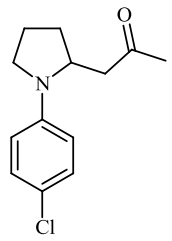
1-(1-(3,4-Dimethylphenyl)pyrrolidin-2-yl)propan-2-one (13c)



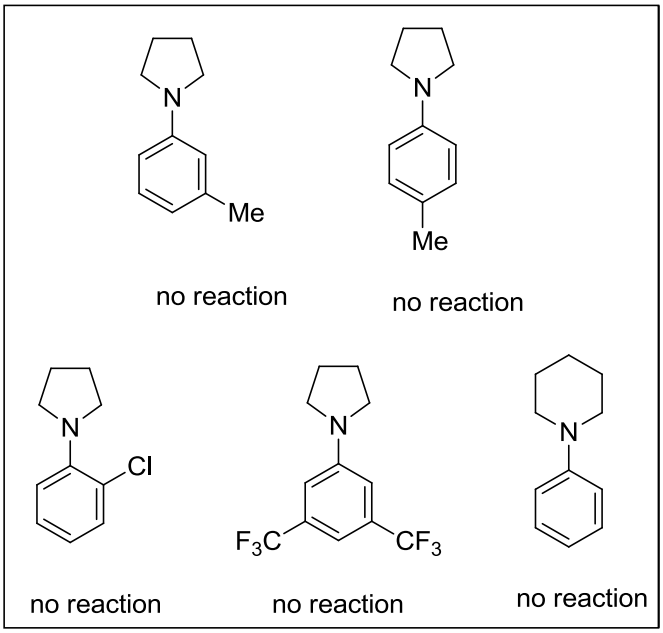
General procedure IV was followed with 1-(3,4-dimethylphenyl)pyrrolidine (52.6 mg, 0.30 mmol), acetone (174.2 mg, 0.222 ml, 3.0 mmol), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (4.5 mg, 0.006 mmol), and L-proline (10.4 mg, 0.09 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 days. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (21

mg, 36 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.00 (d, 1H, HC(5)Ar, *J* = 8.5 Hz), 6.41 (s, 1H, HC(2)Ar), 6.35 (dd, 1H, HC(6)Ar, *J* = 2.2 Hz, 8.2 Hz), 4.19-4.22 (m, 1H), 3.39-3.42 (m, 1H), 3.16 (dd, 1H, *J* = 8.2 Hz, 16.8 Hz), 2.90 (dd, 1H, *J* = 2.2 Hz, 16.8 Hz), 2.44 (dd, 1H, *J* = 10.0 Hz, 17.0 Hz), 2.25 (s, 3H, CH_3), 2.19 (s, 6H, $2CH_3$), 2.09-2.13 (m, 1H), 1.98-2.03 (m, 2H), 1.74-1.77 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 208.4, 144.9, 137.3, 130.4, 123.8, 113.5, 109.4, 54.0, 48.0, 46.6, 31.3, 30.9, 23.1, 20.3, 18.5; **IR** (ATR): ν = 2962 (m), 2919 (m), 1707 (s), 1613 (s), 1508 (vs), 1453 (m) 1357 (vs), 1288 (m), 1148 (s), 1014 (m), 836 (m), 797 (s), 704 (m) cm^{-1}; **HRMS**: m/z (ESI/TOF) calc for $C_{15}H_{21}NONa$ ($M+Na^+$) 254.1515, found 254.1507;

1-(1-(4-Chlorophenyl)pyrrolidin-2-yl)propan-2-one (13d)



General procedure IV was followed with 1-(4-chlorophenyl)pyrrolidine (54.5 mg, 0.30 mmol), acetone (174.2 mg, 0.222 ml, 3.0 mmol), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (4.5 mg, 0.006 mmol), and L-proline (10.4 mg, 0.09 mmol) in acetonitrile (2 mL). The reaction was conducted at r.t. for 4 days. The mixture was purified by column chromatography on silica gel (petrolether/ethylacetate = 7/1) to give the title compound (8 mg, 13 %) as yellowish oil. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.15 (d, 2H, *m*-ArH, *J* = 8.5 Hz), 6.45 (brd, 2H, *o*-ArH, *J* = 7.5 Hz), 4.18 (t, 1H, *J* = 8.8 Hz), 3.14 (dd, 1H, *J* = 8.5 Hz, 16.5 Hz), 2.82 (d, 1H, *J* = 17.0 Hz), 2.44 (dd, 1H, *J* = 10.2 Hz, 15.5 Hz), 2.17 (s, 3H, CH_3), 2.08-2.14 (m, 1H), 1.97-2.04 (m, 2H), 1.74-1.77 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ 207.9, 145.0, 129.1, 120.6, 112.9, 54.1, 48.0, 46.2, 31.4, 30.9, 23.1; **IR** (ATR): ν = 2968 (m), 1711 (s), 1599 (s), 1501 (vs), 1367 (s), 1153 (m), 1097 (m), 976 (w), 811 (m), 707 (w) cm^{-1}; **MS** (ESI) *m*/*z* 238 $[M+H]^+$. Spectroscopic data are in agreement with the published data.[S13]



Scheme S1. Substrates that did not react under photoredox reaction conditions of C-H oxidation/Mannich reaction.

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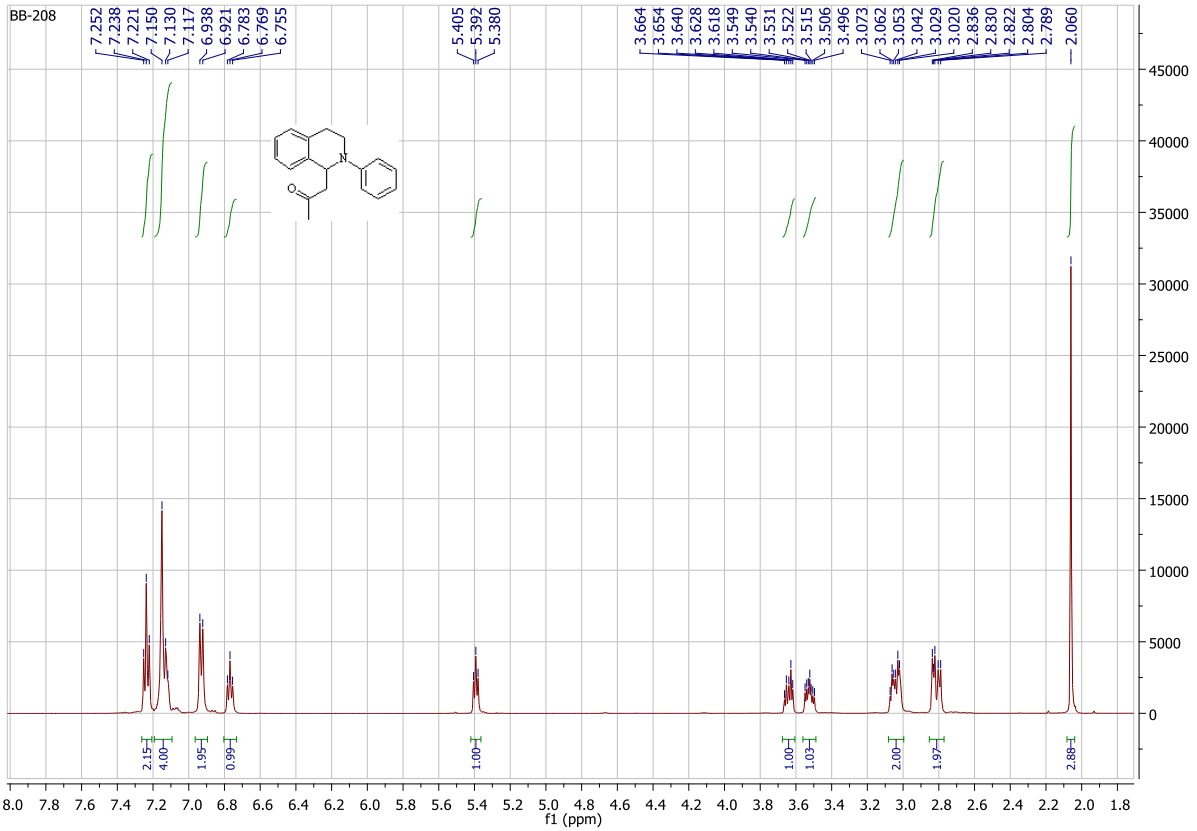
1a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5.405
5.392
5.380
3.664
3.654
3.640
3.628
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3.549
3.540
3.531
3.522
3.515
3.506
3.496
3.073
3.062
3.053
3.042
3.029
3.020
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2.830
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2.804
2.789
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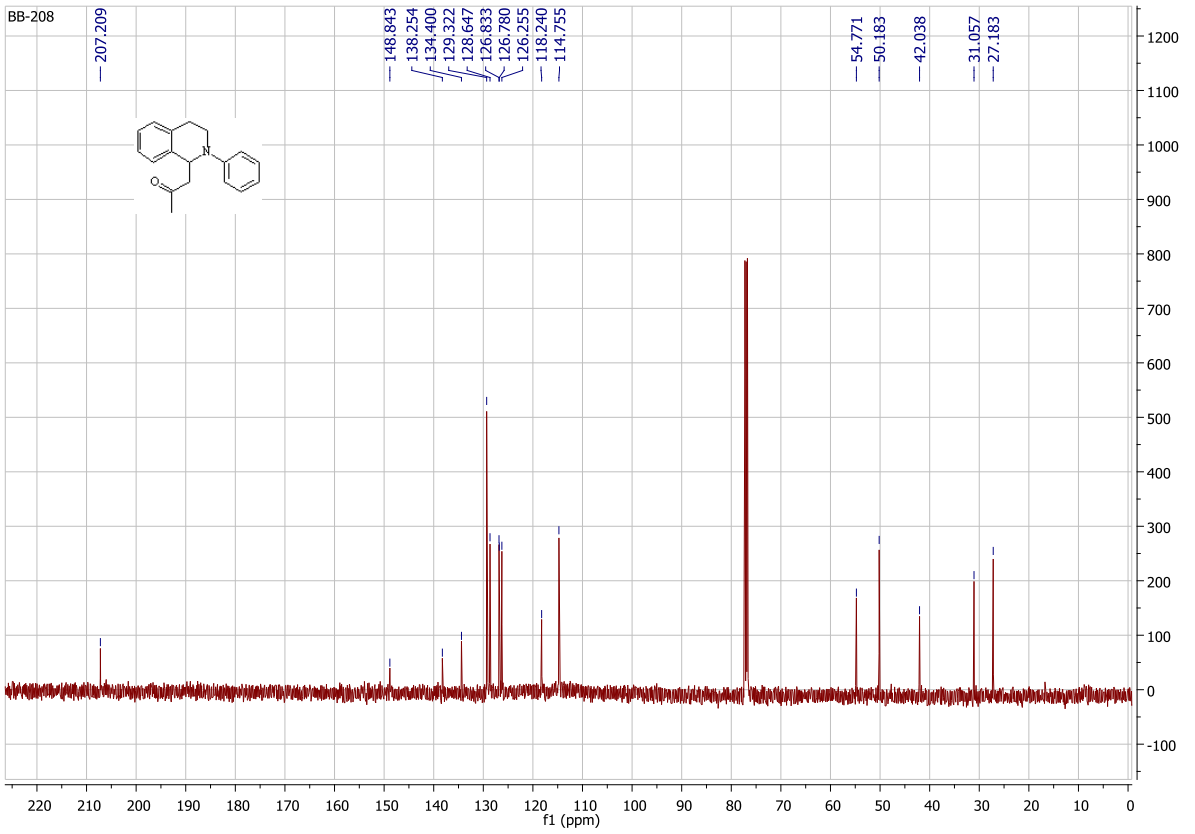
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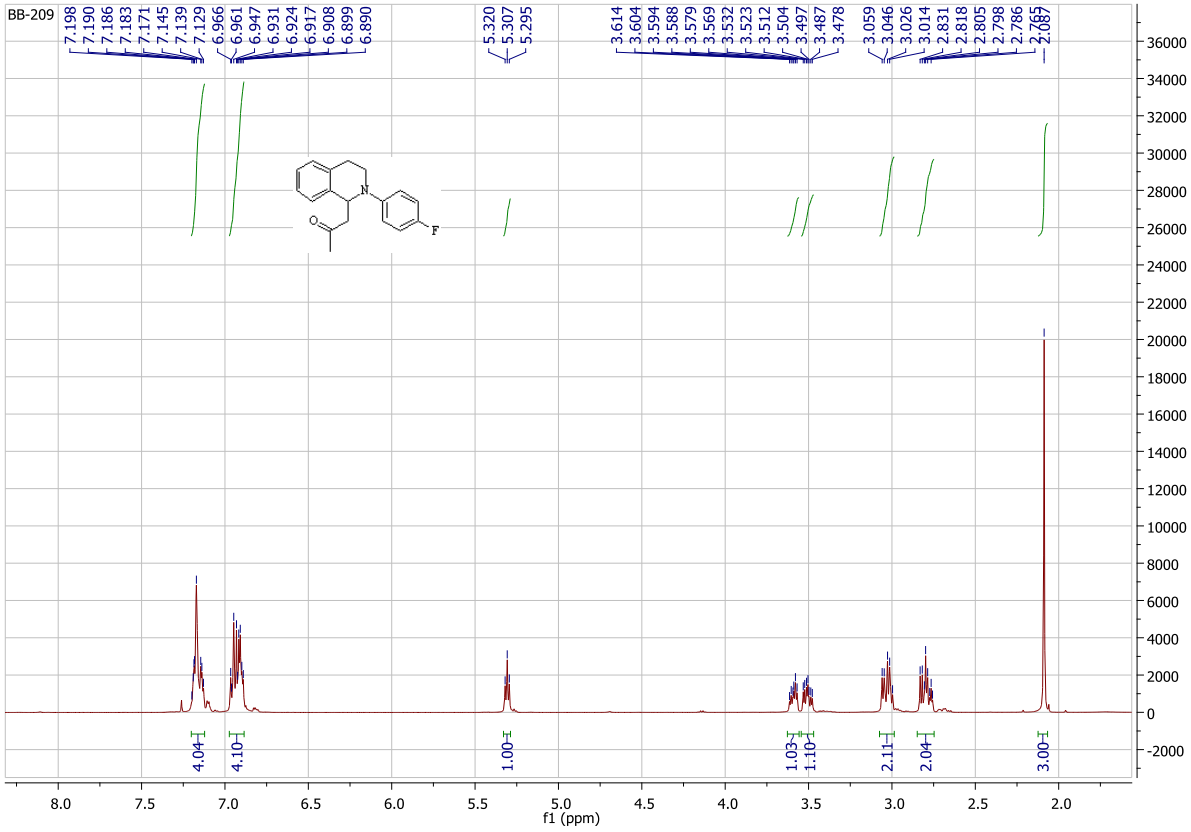
f1 (ppm)

2a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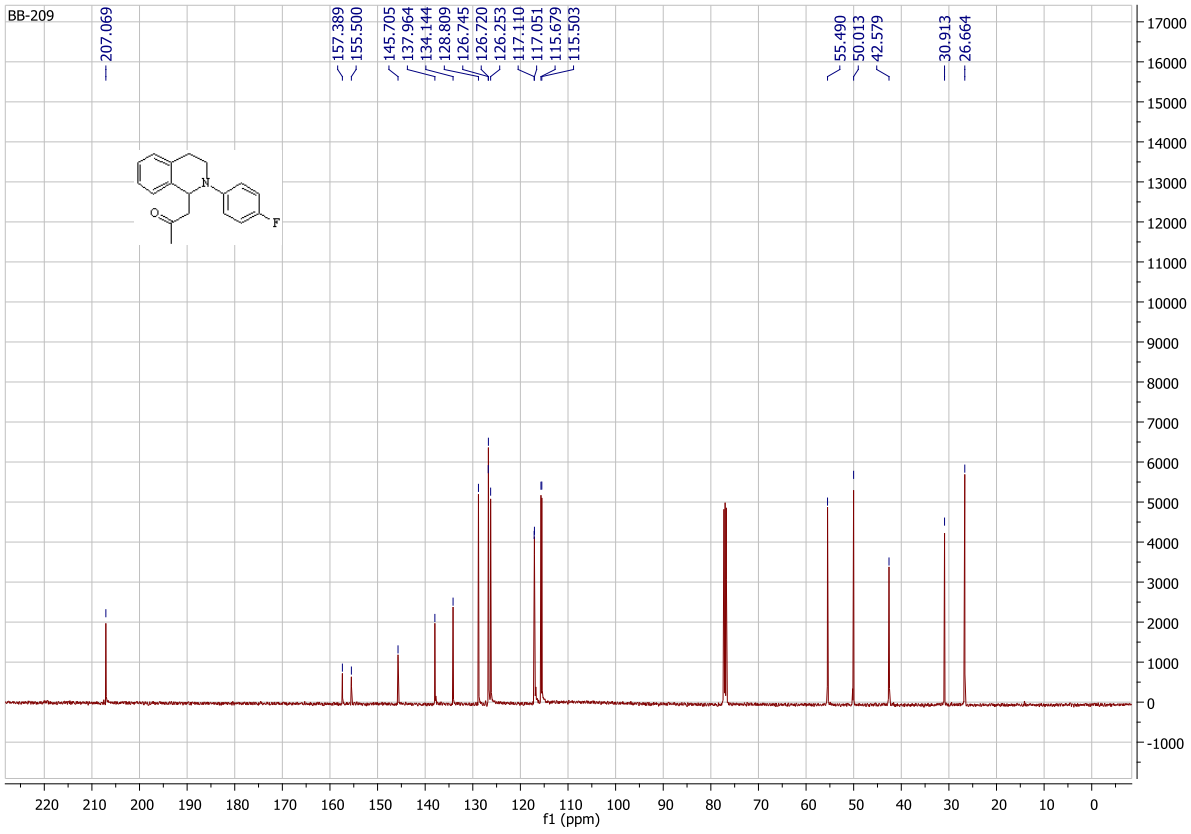
3.00
f1 (ppm)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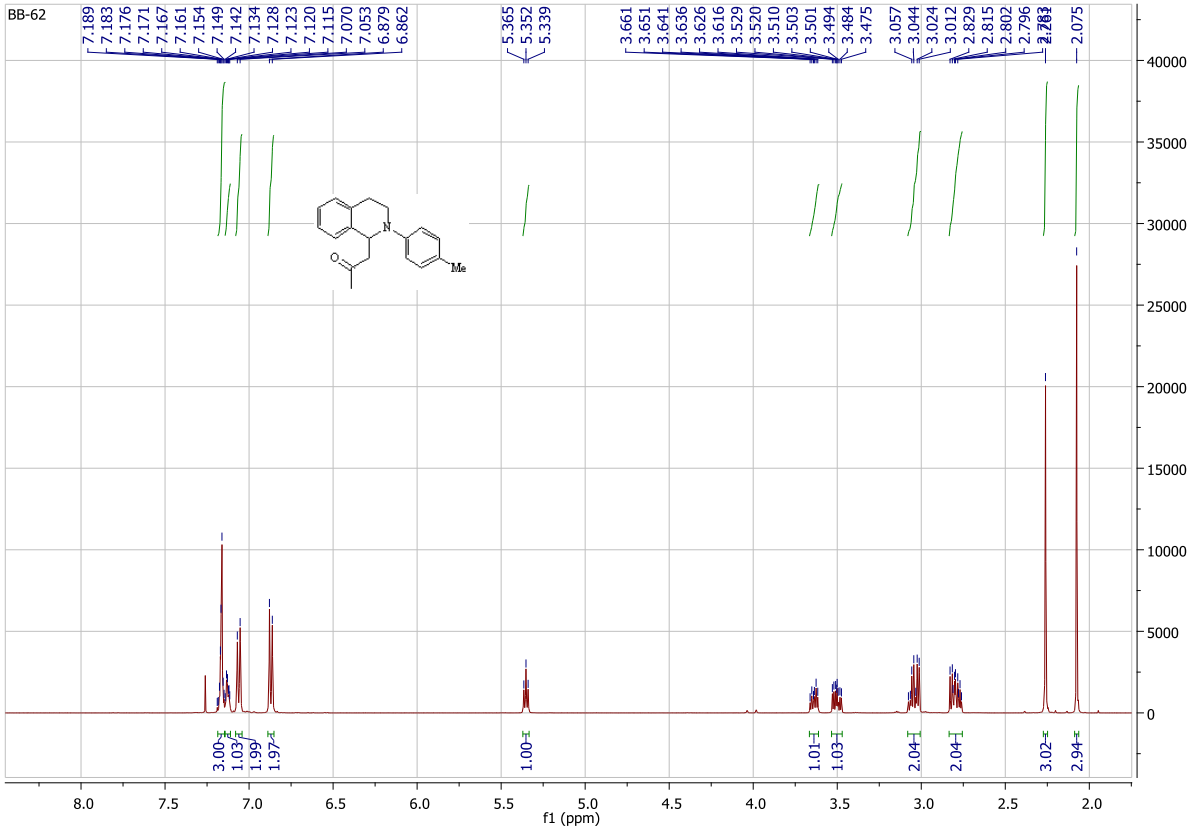
f1 (ppm)

3a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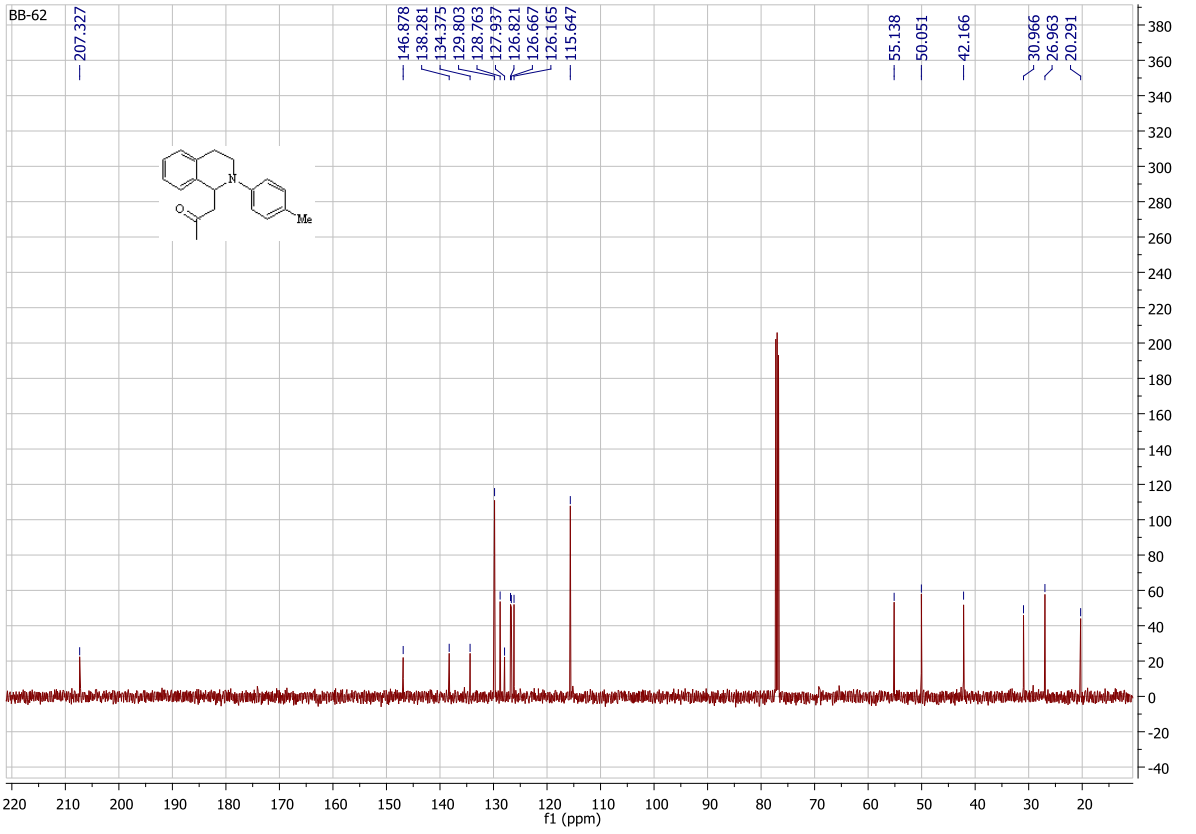
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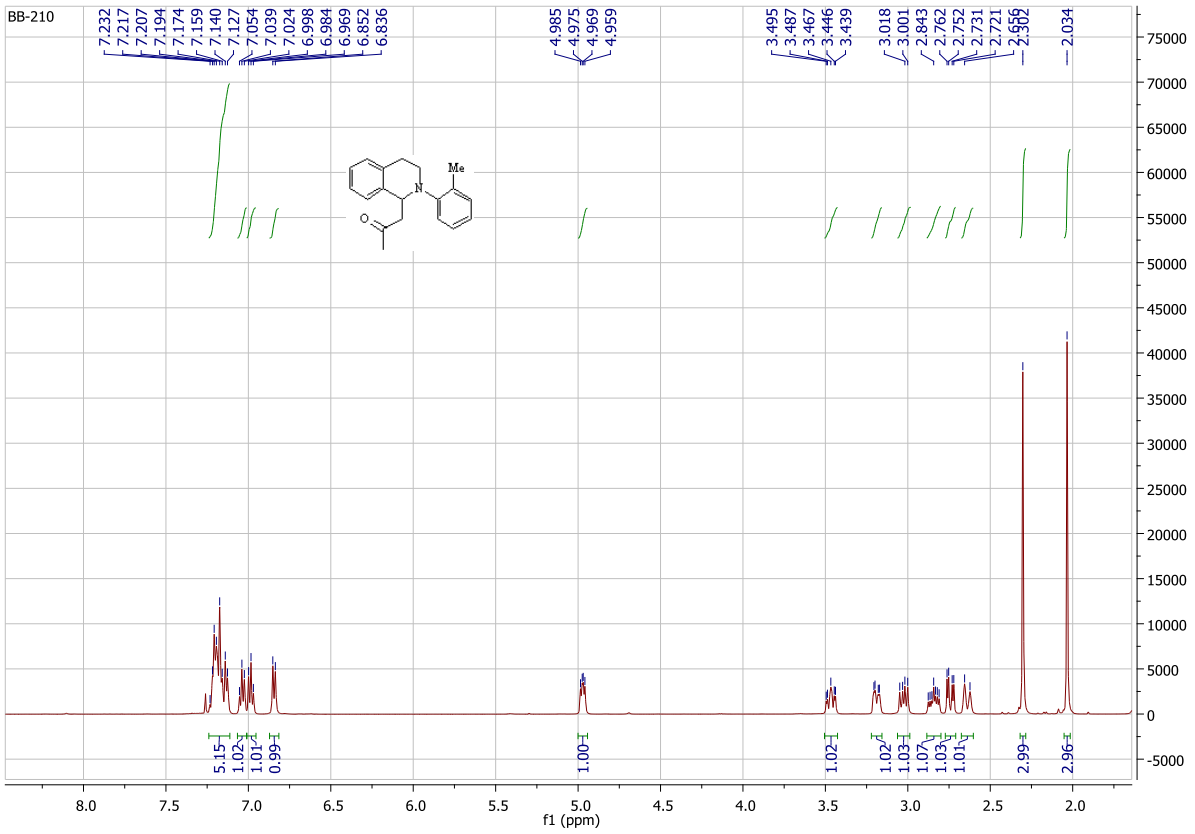
Me
f1 (ppm)

4a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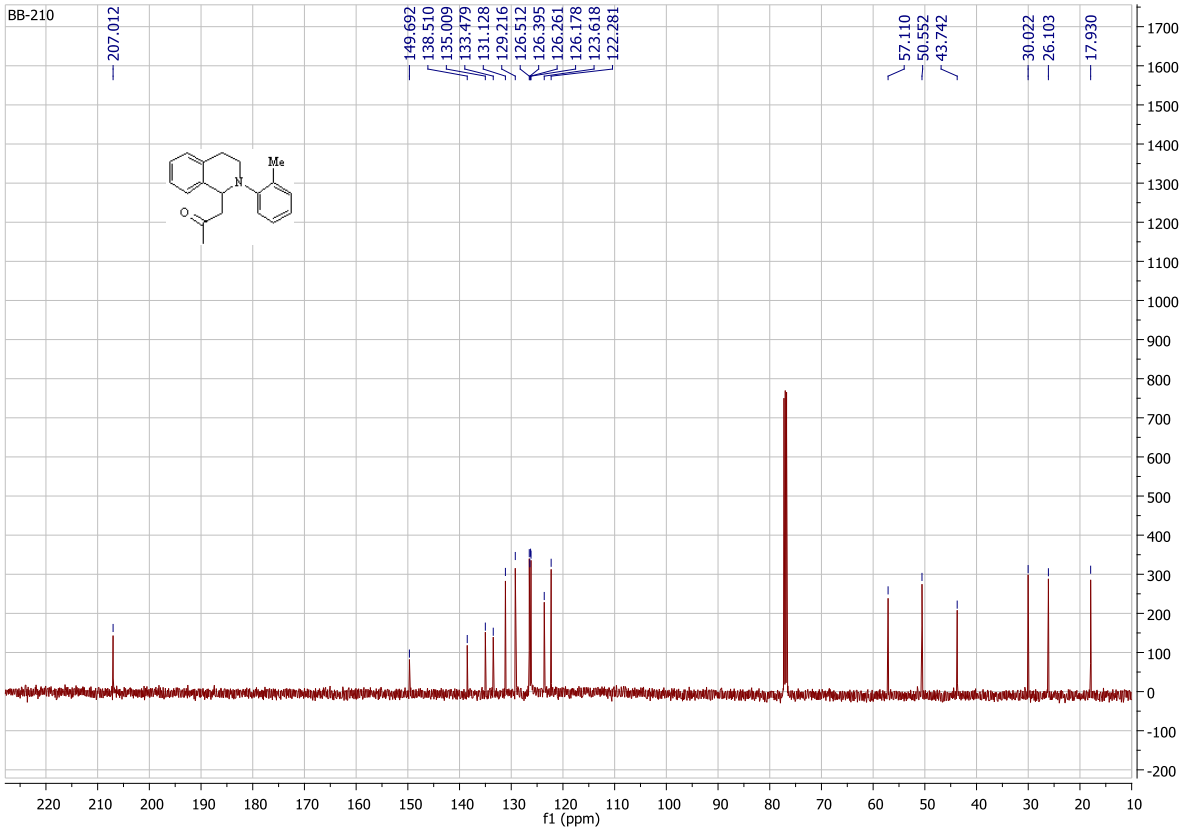
6.984
6.969
6.852
6.836
4.985
4.975
4.969
4.959
3.495
3.487
3.467
3.446
3.439
3.018
3.001
2.843
2.762
2.752
2.731
2.721
2.656
2.502
2.034
Me
N
O
5.15
1.02
1.01
0.99
1.00
1.02
1.02
1.03
1.07
1.03
1.01
2.99
2.96
f1 (ppm)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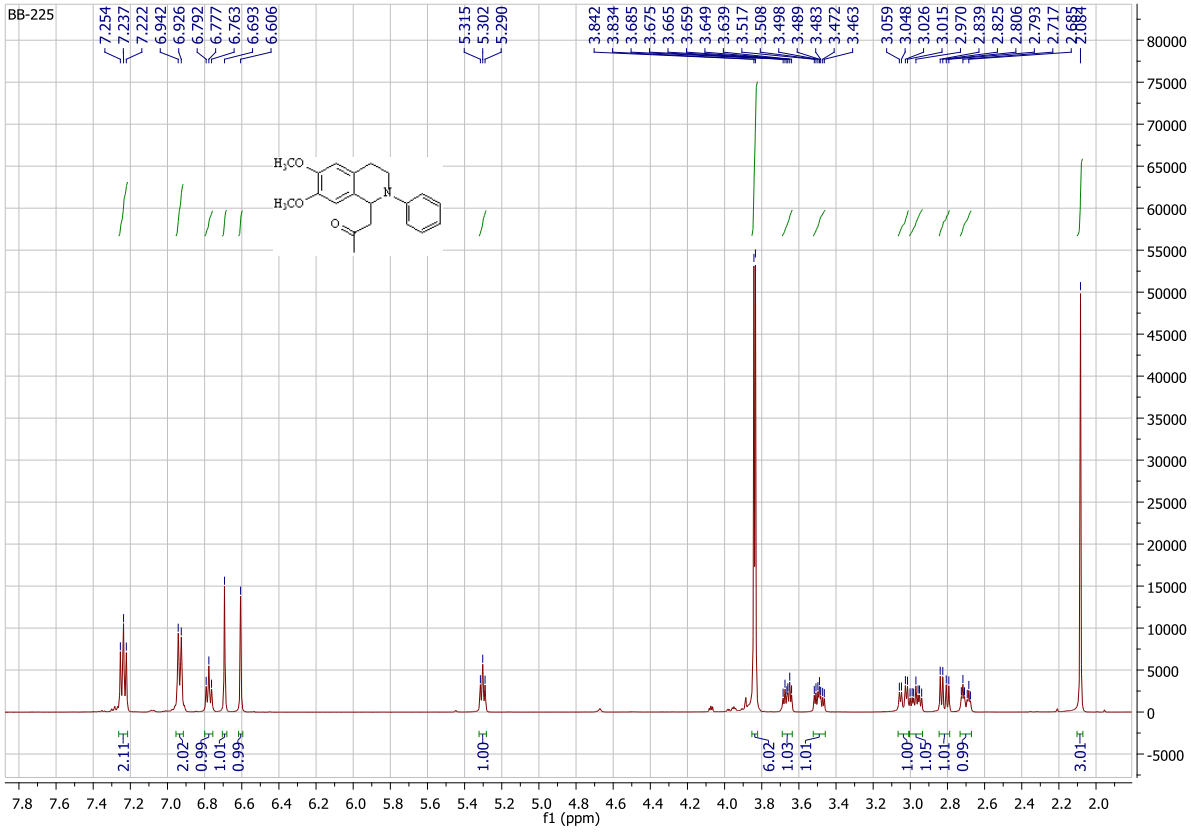
149.692
138.510
135.009
133.479
131.128
129.216
126.512
126.395
126.261
126.178
123.618
122.281
57.110
50.552
43.742
30.022
26.103
17.930
Me
N
O
f1 (ppm)

5a


BB-225
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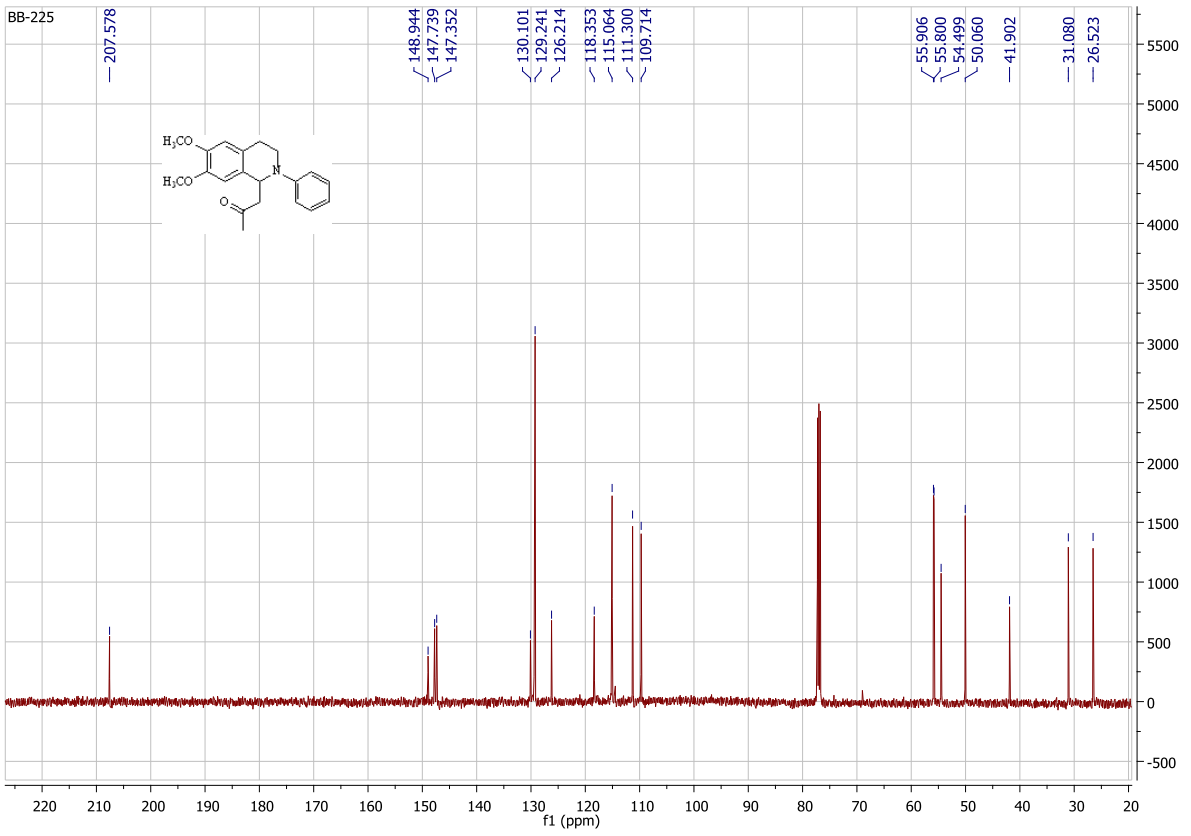
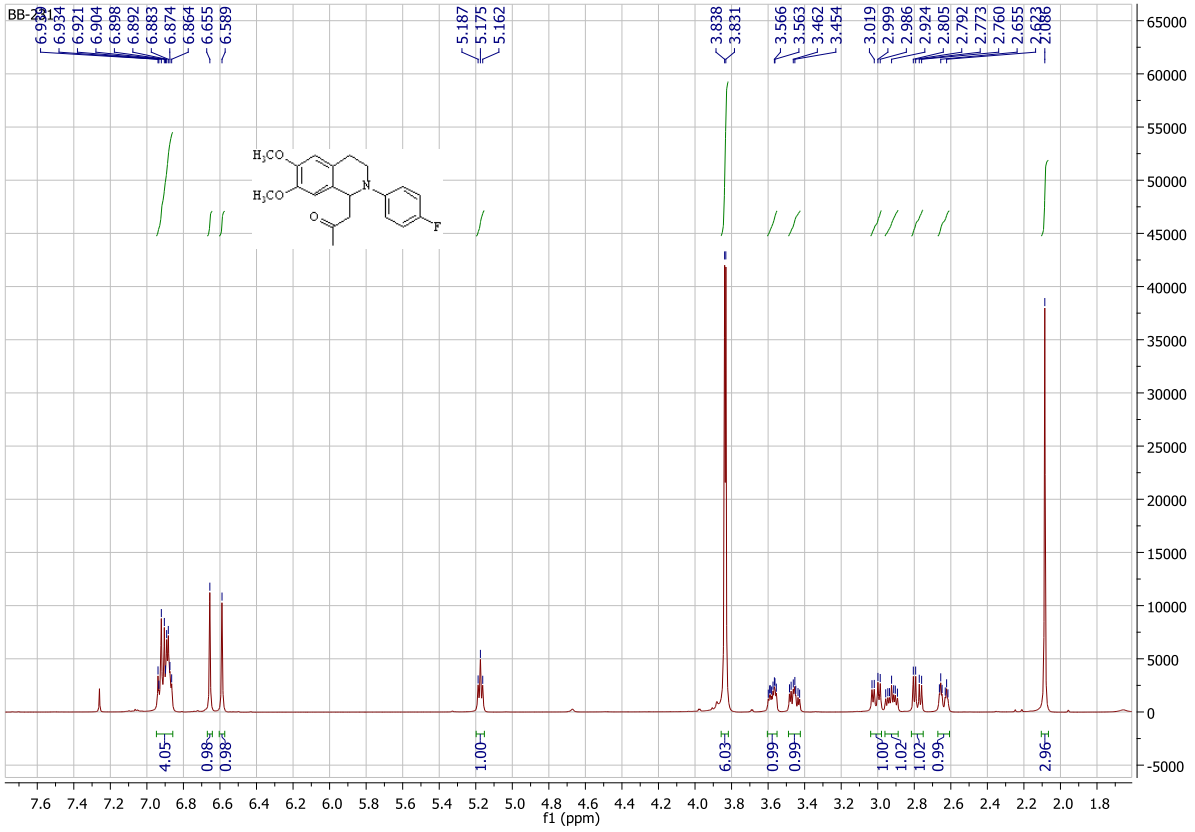
7.237
7.222
6.942
6.926
6.792
6.777
6.763
6.693
6.606
5.315
5.302
5.290
3.842
3.834
3.685
3.675
3.665
3.659
3.649
3.639
3.517
3.508
3.498
3.489
3.483
3.472
3.463
3.059
3.048
3.026
3.015
2.970
2.839
2.825
2.806
2.793
2.717
2.685
2.084
2.11
2.02
0.99
1.01
0.99
1.00
6.02
1.03
1.01
1.00
1.05
1.01
0.99
3.01
f1 (ppm)


BB-225
207.578
148.944
147.739
147.352
130.101
129.241
126.214
118.353
115.064
111.300
109.714
55.906
55.800
54.499
50.060
41.902
31.080
26.523
f1 (ppm)

6a


BB-231
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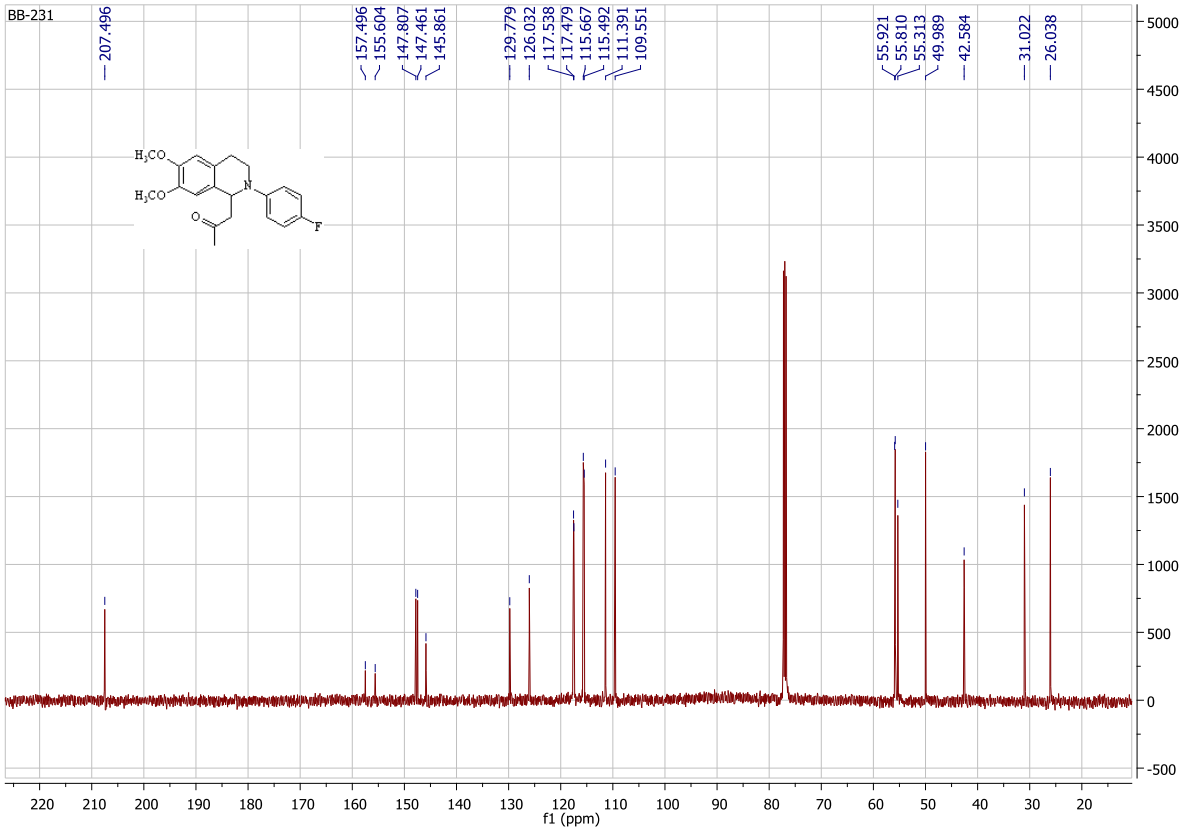
6.934
6.921
6.904
6.898
6.892
6.883
6.874
6.864
6.655
6.589
5.187
5.175
5.162
3.838
3.831
3.566
3.563
3.462
3.454
3.019
2.999
2.986
2.924
2.805
2.792
2.773
2.760
2.655
2.623
2.086
4.05
0.98
0.98
1.00
6.03
0.99
0.99
1.00
1.02
1.02
0.99
2.96
f1 (ppm)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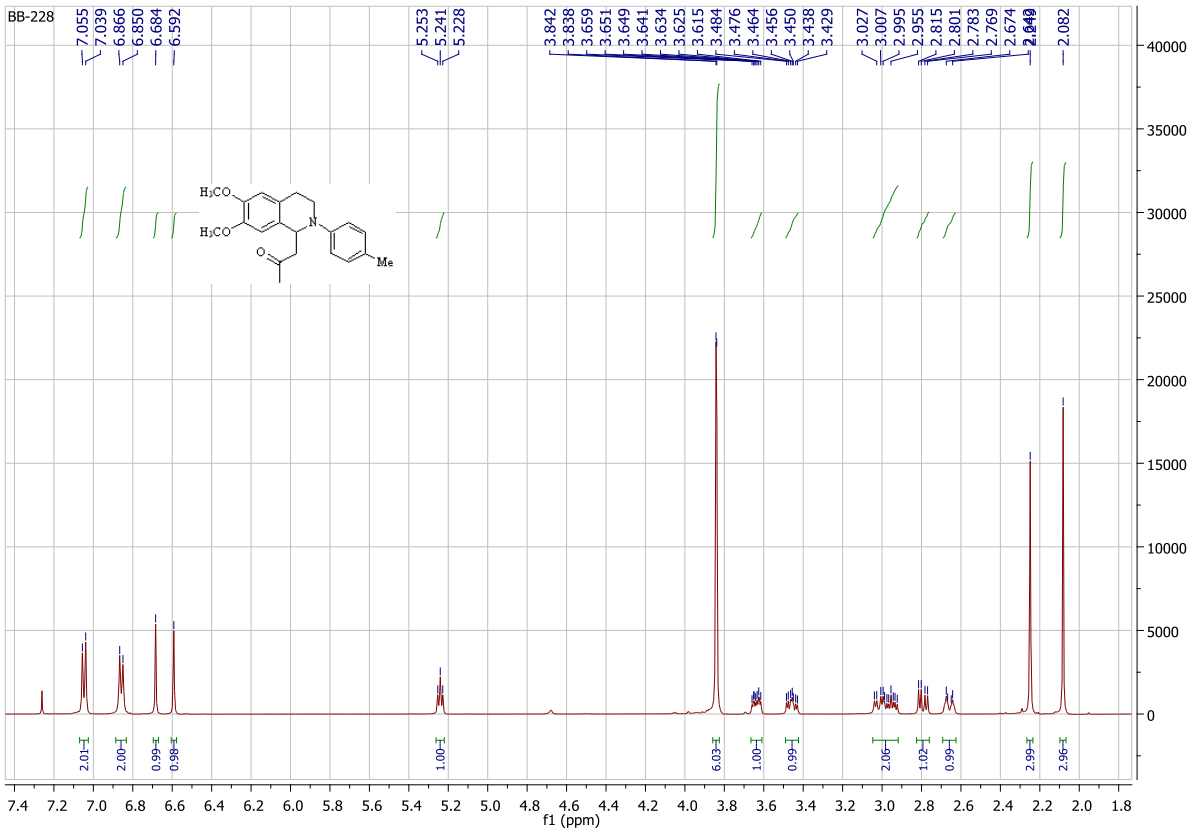
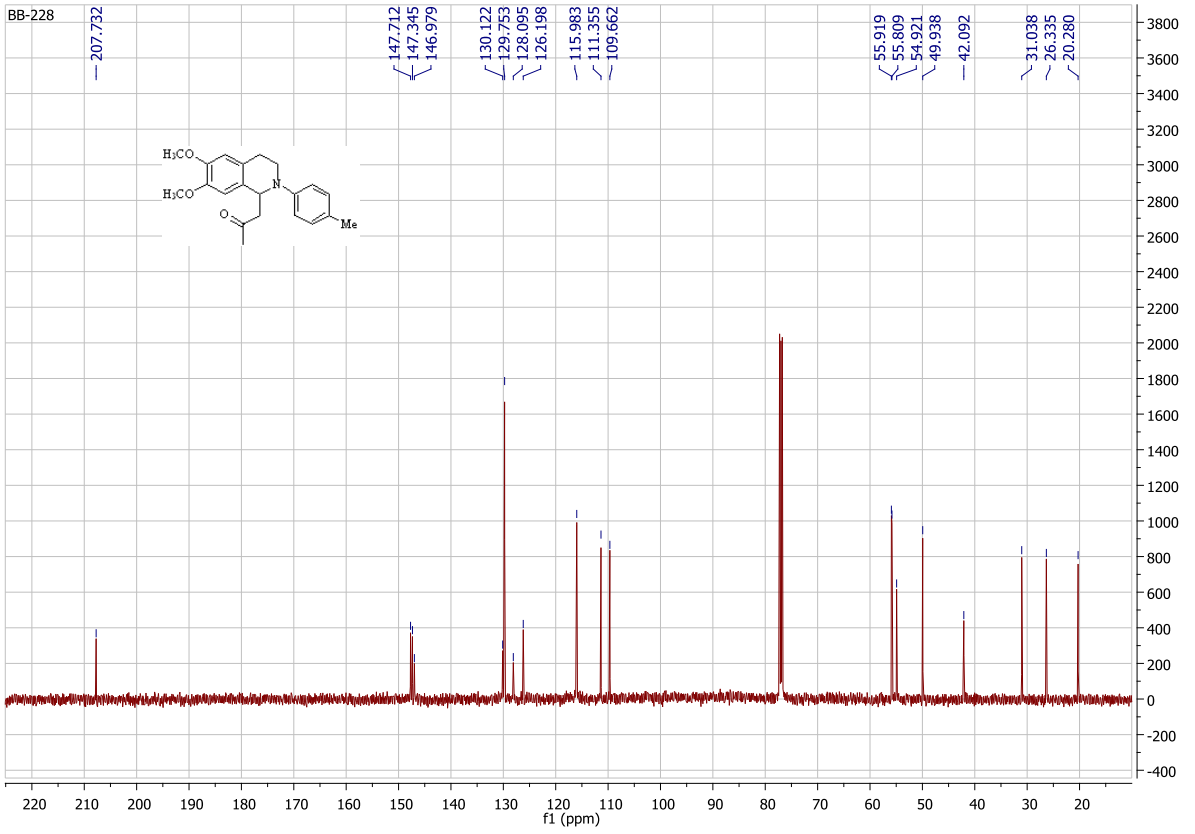
157.496
155.604
147.807
147.461
145.861
129.779
126.032
117.538
117.479
115.667
115.492
111.391
109.551
55.921
55.810
55.313
49.989
42.584
31.022
26.038
f1 (ppm)

7a


BB-228
7.055
7.039
6.866
6.850
6.684
6.592
5.253
5.241
5.228
3.842
3.838
3.659
3.651
3.649
3.641
3.634
3.625
3.615
3.484
3.476
3.464
3.456
3.450
3.438
3.429
3.027
3.007
2.995
2.955
2.815
2.801
2.783
2.769
2.674
2.649
2.082
H3CO
H3CO
N
O
Me
2.01
2.00
0.99
0.98
1.00
6.03
1.00
0.99
2.06
1.02
0.99
2.99
2.96
f1 (ppm)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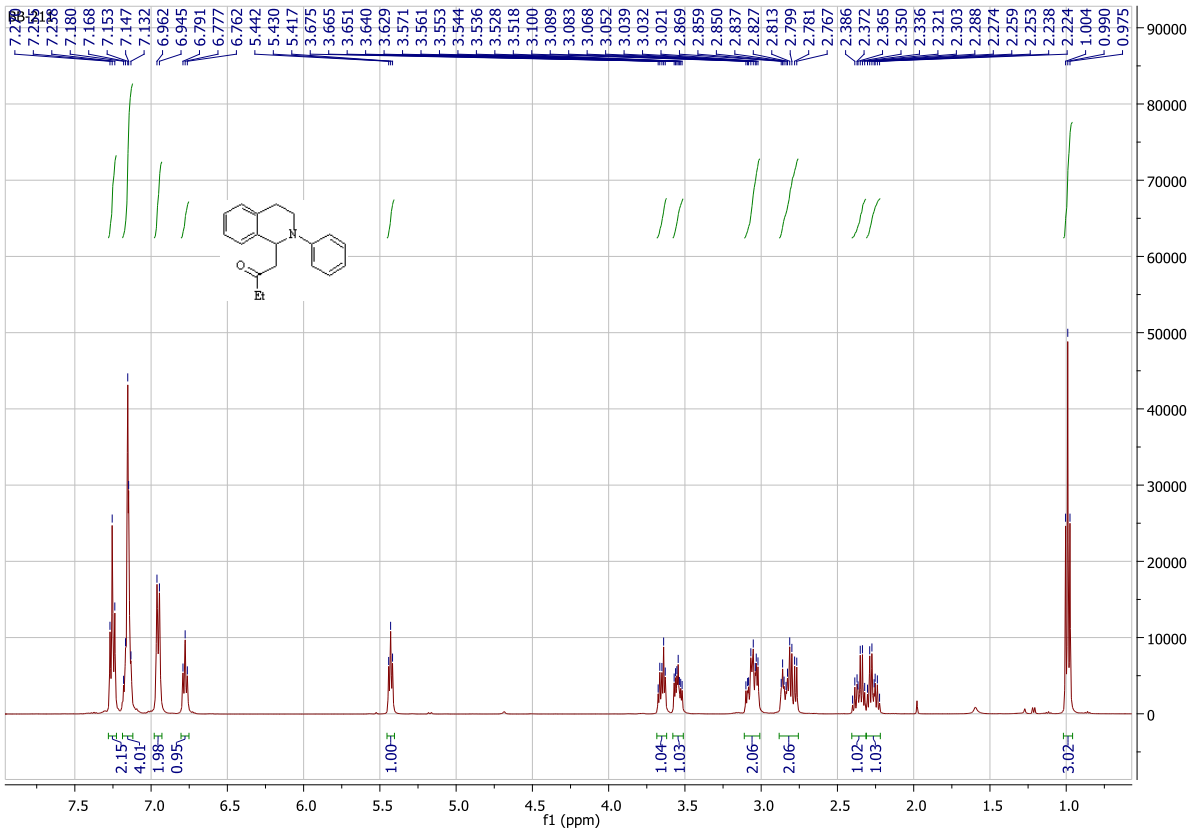
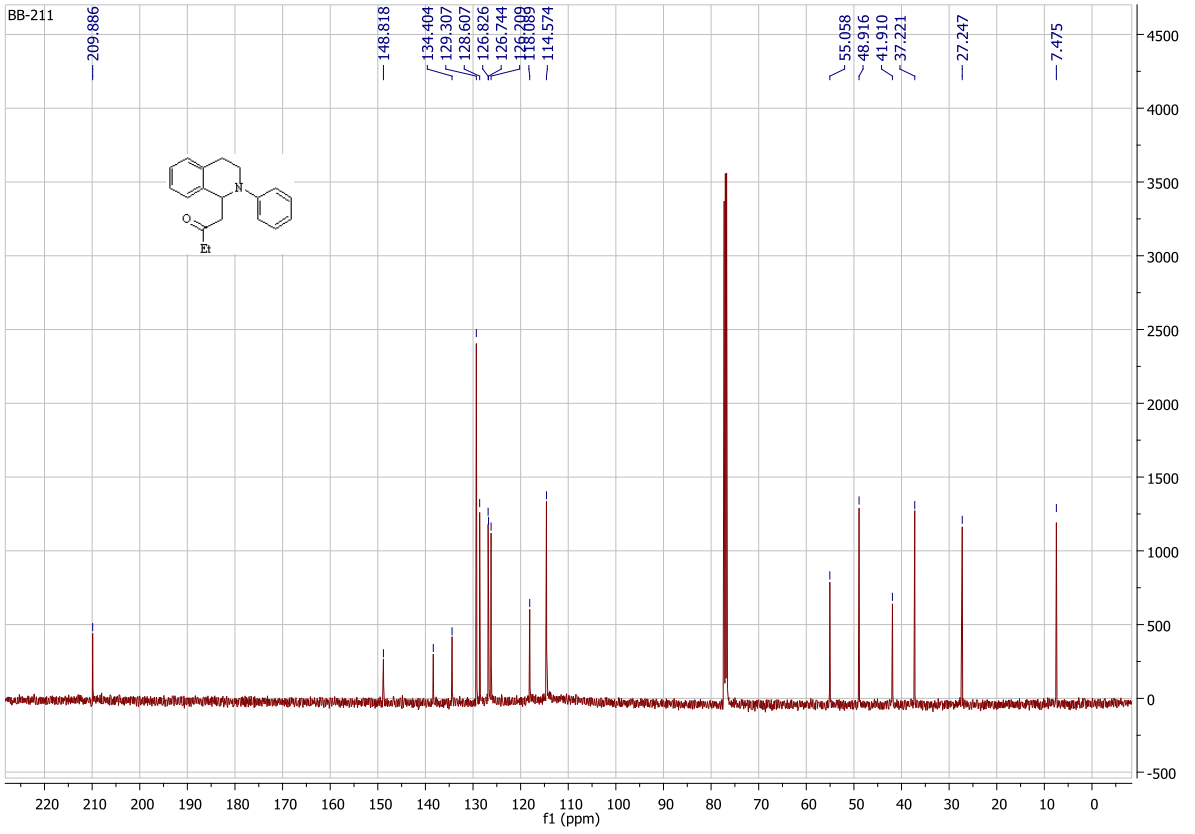
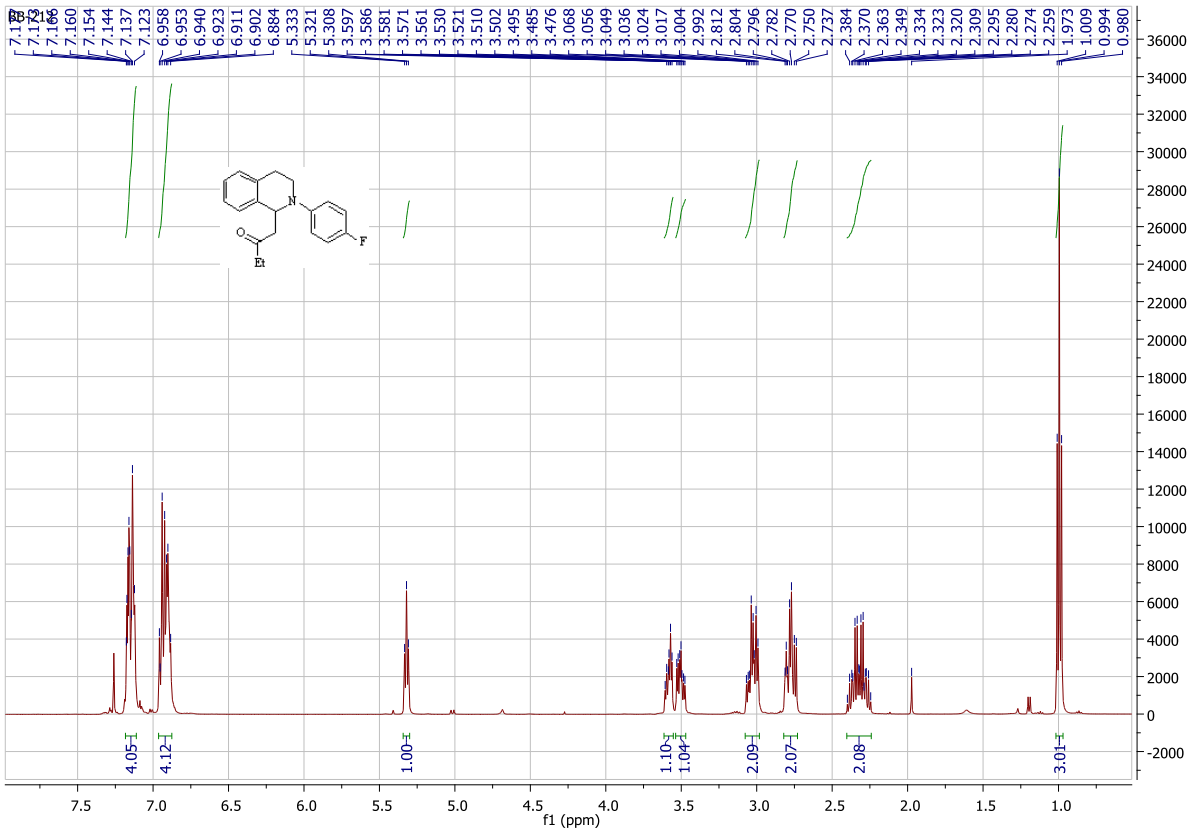
147.345
146.979
130.122
129.753
128.095
126.198
115.983
111.355
109.662
55.919
55.809
54.921
49.938
42.092
31.038
26.335
20.280
H3CO
H3CO
N
O
Me
f1 (ppm)

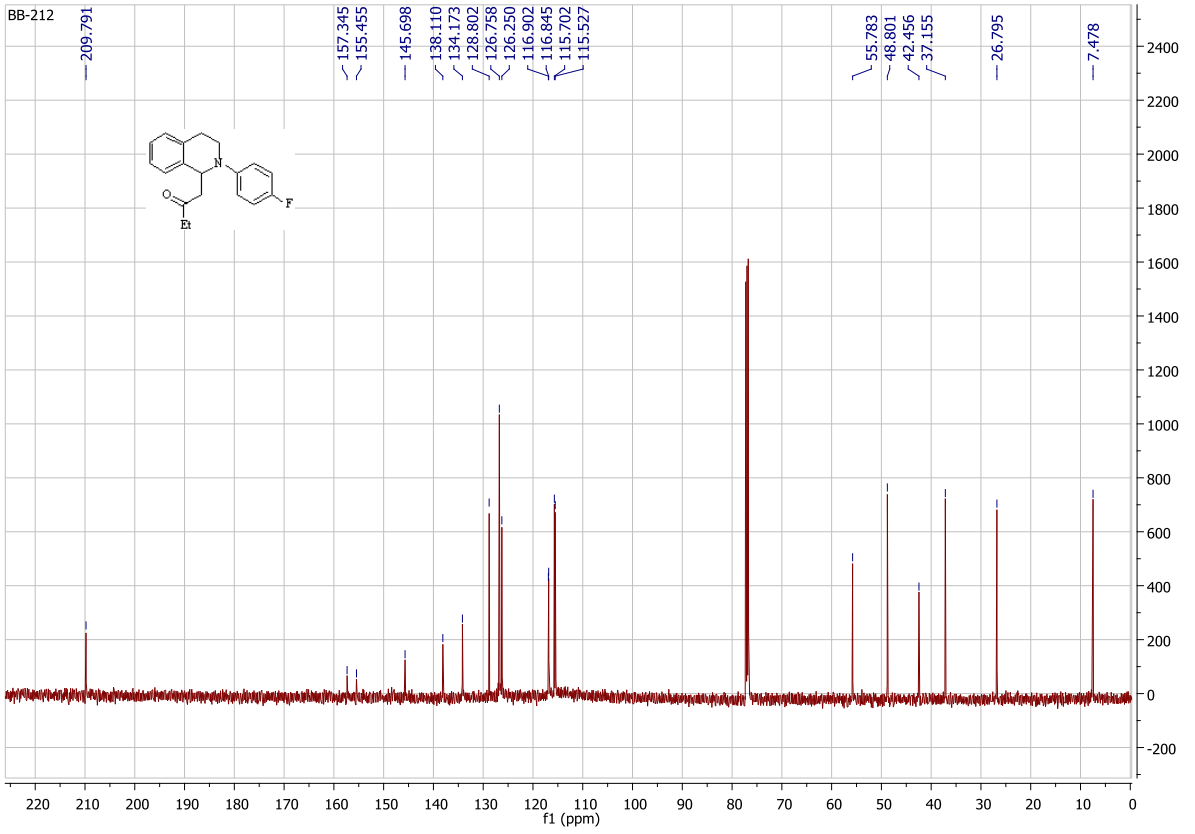
1b


7.260
7.252
7.238
7.180
7.168
7.153
7.147
7.132
6.962
6.945
6.791
6.777
6.762
5.442
5.430
5.417
3.675
3.665
3.651
3.640
3.629
3.571
3.561
3.553
3.544
3.536
3.528
3.518
3.100
3.089
3.083
3.068
3.052
3.039
3.032
3.021
2.869
2.859
2.850
2.837
2.827
2.813
2.799
2.781
2.767
2.386
2.372
2.365
2.350
2.336
2.321
2.303
2.288
2.274
2.259
2.253
2.238
2.224
1.004
0.990
0.975
2.15
4.01
1.98
0.95
1.00
1.04
1.03
2.06
2.06
1.02
1.03
3.02
f1 (ppm)

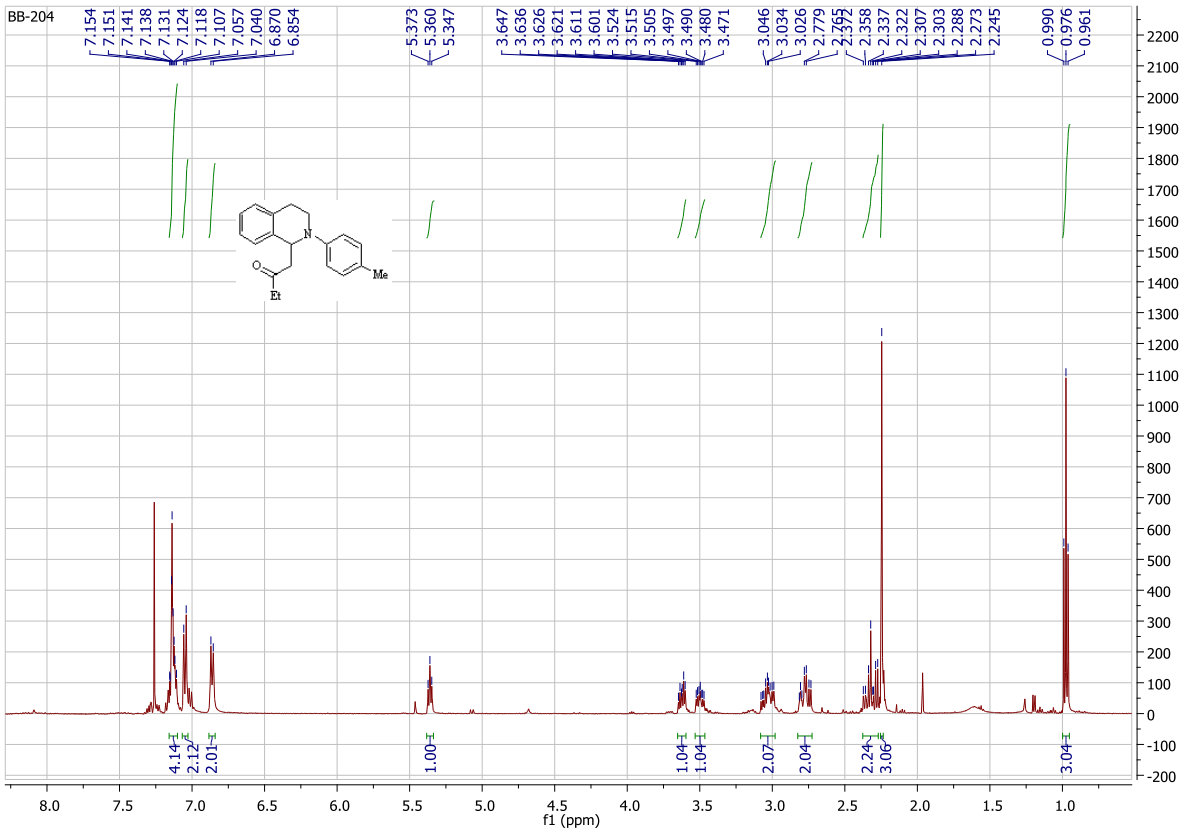

BB-211
209.886
148.818
134.404
129.307
128.607
126.826
126.744
126.209
118.089
114.574
55.058
48.916
41.910
37.221
27.247
7.475
f1 (ppm)

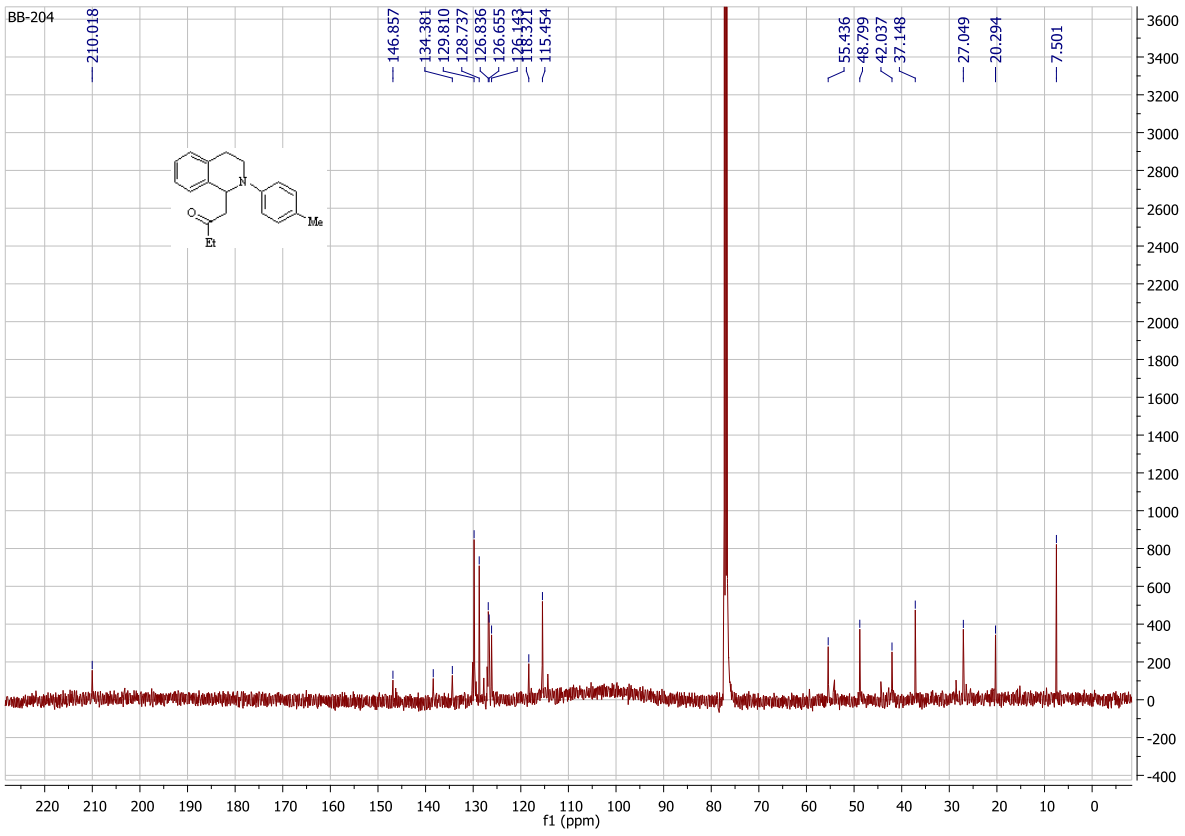
2b


BB-212
7.123
6.958
6.953
6.940
6.923
6.911
6.902
6.884
5.333
5.321
5.308
3.597
3.586
3.581
3.571
3.561
3.530
3.521
3.510
3.502
3.495
3.485
3.476
3.068
3.056
3.049
3.036
3.024
3.017
3.004
2.992
2.812
2.804
2.796
2.782
2.770
2.750
2.737
2.384
2.370
2.363
2.349
2.334
2.323
2.320
2.309
2.295
2.280
2.274
2.259
1.973
1.009
0.994
0.980
4.05
4.12
1.00
1.10
1.04
2.09
2.07
2.08
3.01
f1 (ppm)

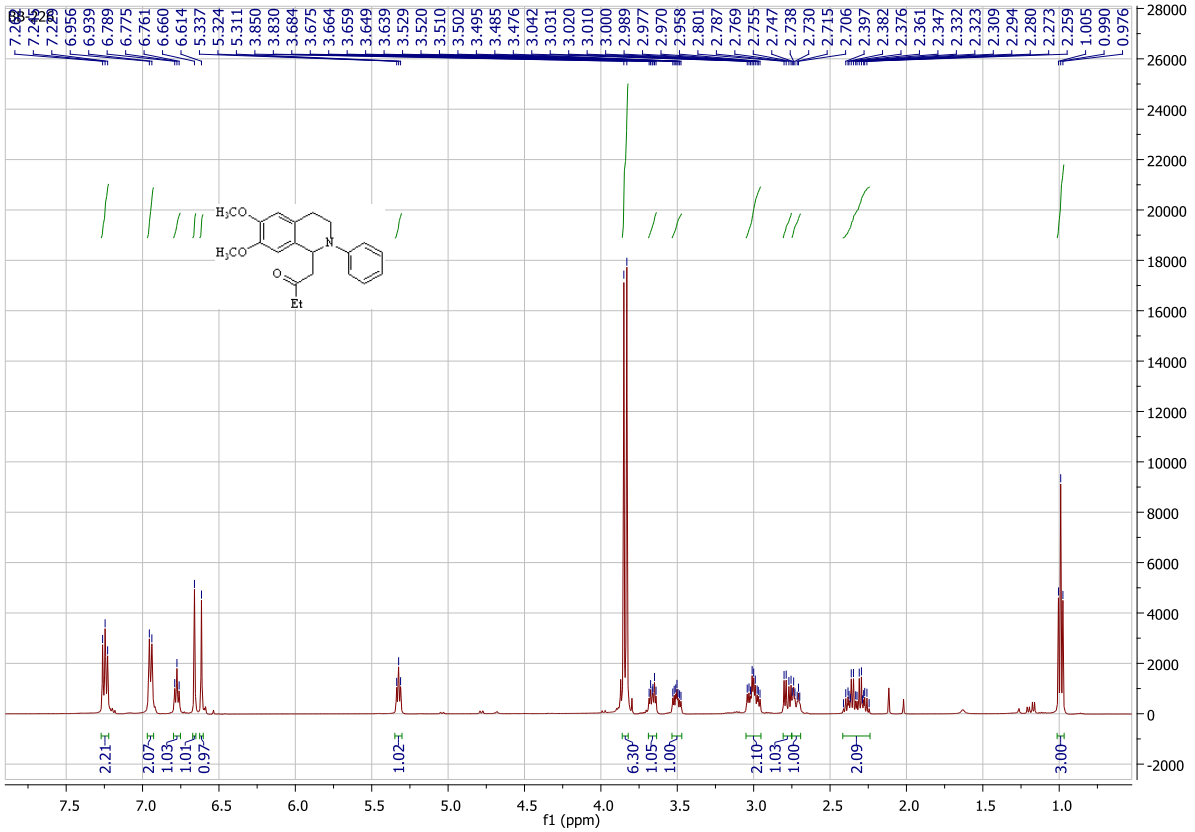

BB-212
209.791
157.345
155.455
145.698
138.110
134.173
128.802
126.758
126.250
116.902
116.845
115.702
115.527
55.783
48.801
42.456
37.155
26.795
7.478
f1 (ppm)

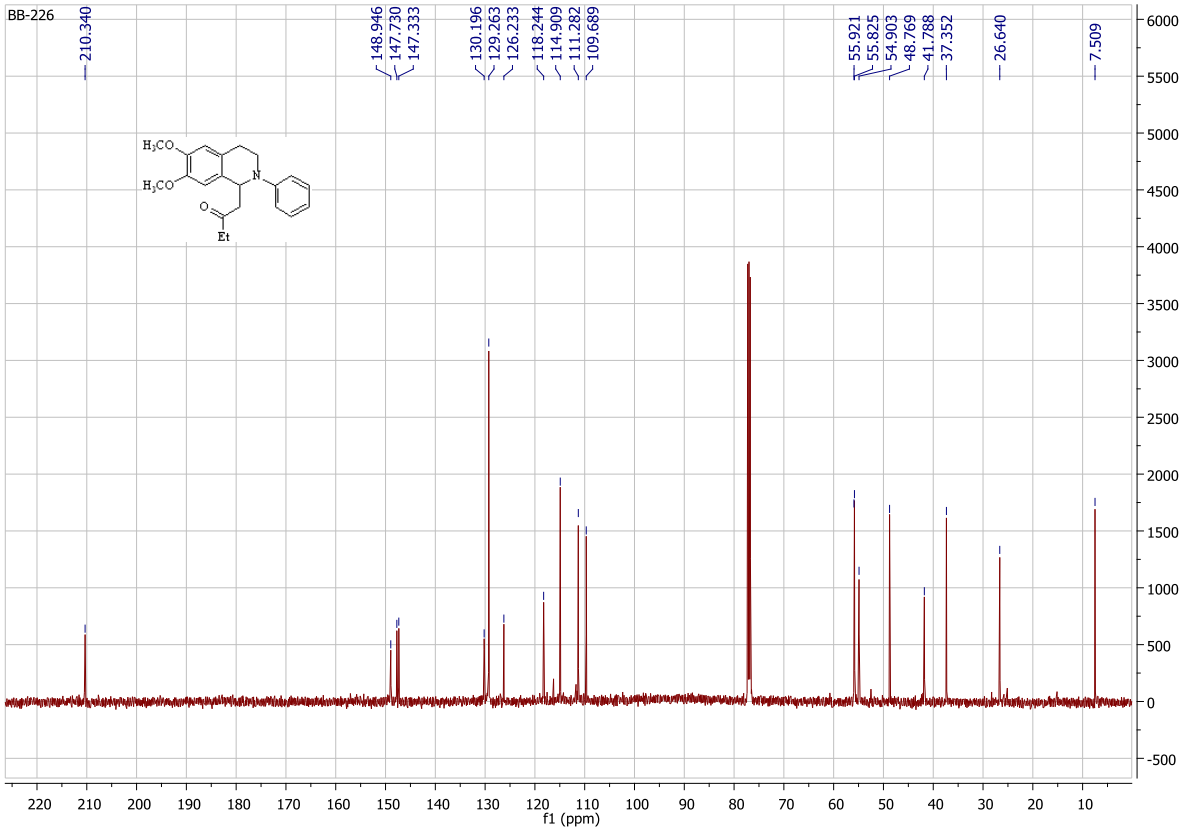
3b


BB-204
7.154
7.151
7.141
7.138
7.131
7.124
7.118
7.107
7.057
7.040
6.870
6.854
5.373
5.360
5.347
3.647
3.636
3.626
3.621
3.611
3.601
3.524
3.515
3.505
3.497
3.490
3.480
3.471
3.046
3.034
3.026
2.779
2.765
2.372
2.358
2.337
2.322
2.307
2.303
2.288
2.273
2.245
0.990
0.976
0.961
4.14
2.12
2.01
1.00
1.04
1.04
2.07
2.04
2.24
3.06
3.04
f1 (ppm)


BB-204
210.018
146.857
134.381
129.810
128.737
126.836
126.655
126.143
118.321
115.454
55.436
48.799
42.037
37.148
27.049
20.294
7.501
f1 (ppm)

5b


7.266
7.422
7.229
6.956
6.939
6.789
6.775
6.761
6.660
6.614
5.337
5.324
5.311
3.850
3.830
3.684
3.675
3.664
3.659
3.649
3.639
3.529
3.520
3.510
3.502
3.495
3.485
3.476
3.042
3.031
3.020
3.010
3.000
2.989
2.977
2.970
2.958
2.801
2.787
2.769
2.755
2.747
2.738
2.730
2.715
2.706
2.397
2.382
2.376
2.361
2.347
2.332
2.323
2.309
2.294
2.280
2.273
2.259
1.005
0.990
0.976
H3CO
H3CO
N
O
Et
2.21
2.07
1.03
1.01
0.97
1.02
6.30
1.05
1.00
2.10
1.03
1.00
2.09
3.00
f1 (ppm)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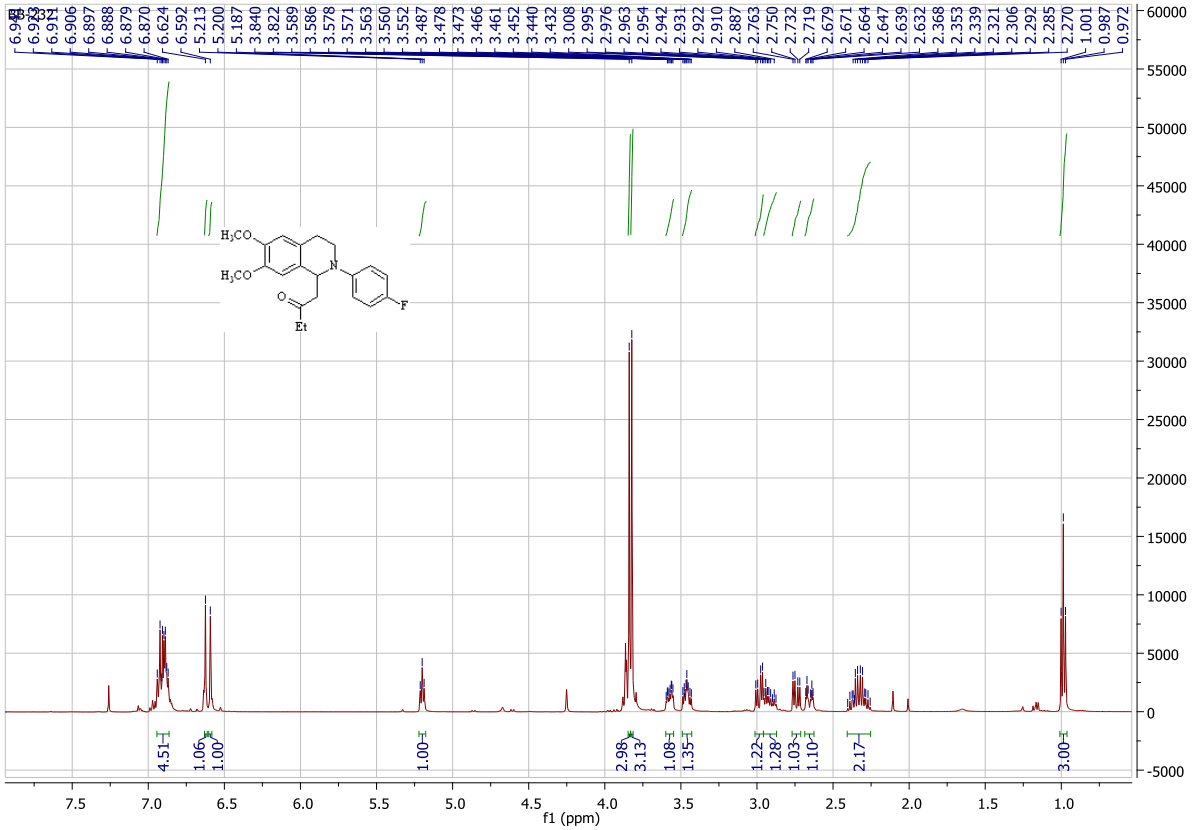
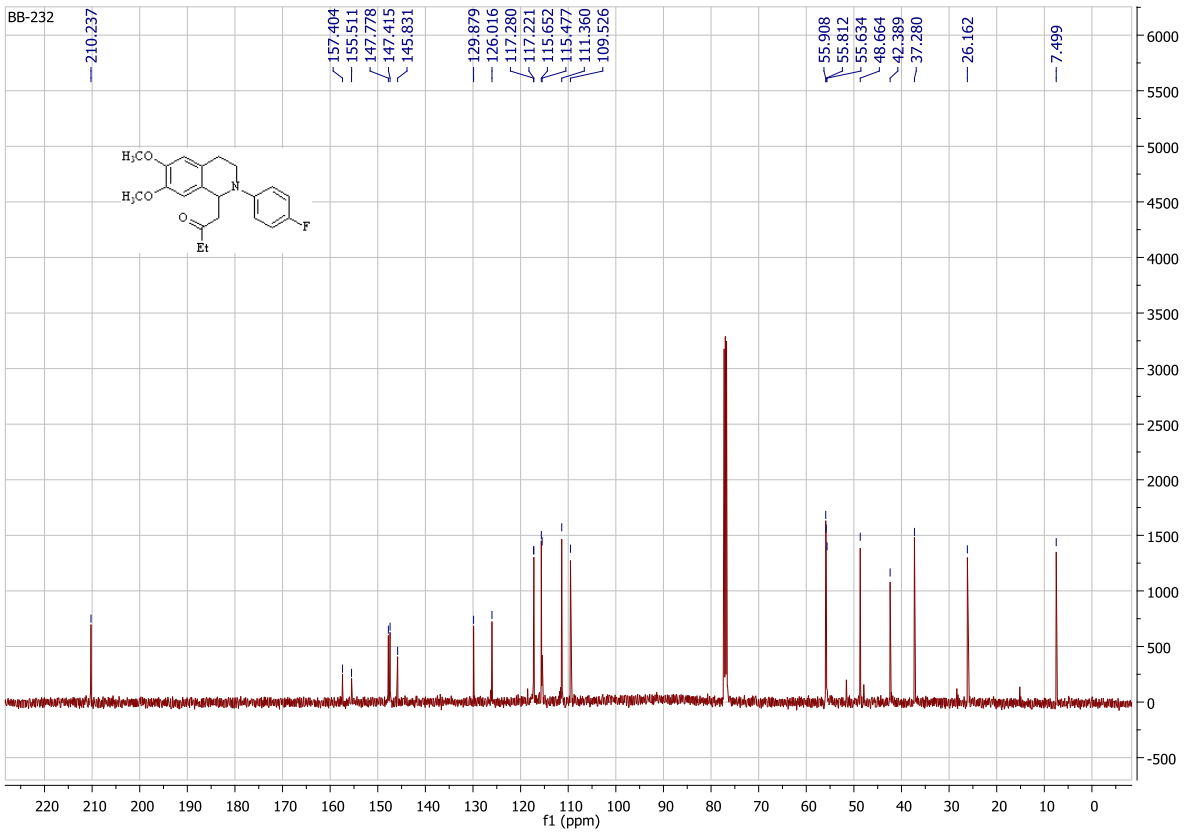
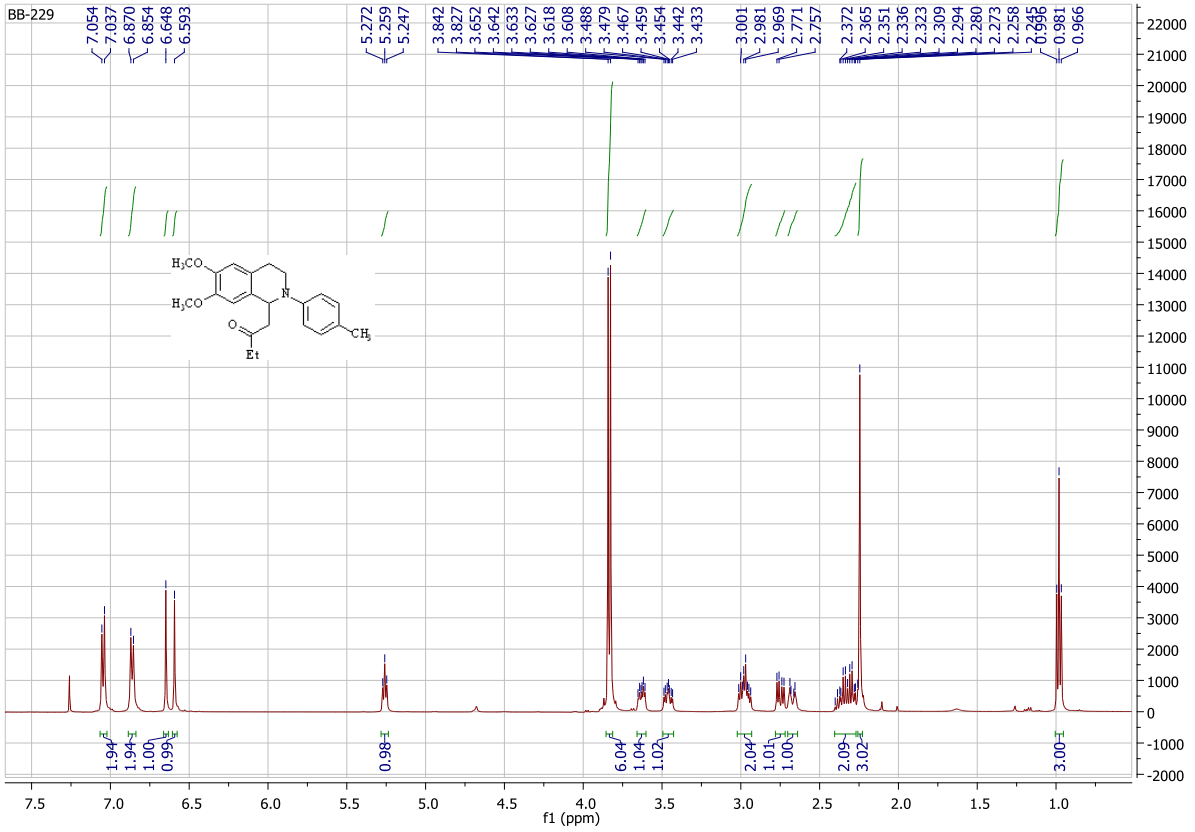
148.946
147.730
147.333
130.196
129.263
126.233
118.244
114.909
111.282
109.689
55.921
55.825
54.903
48.769
41.788
37.352
26.640
7.509
H3CO
H3CO
N
O
Et
f1 (ppm)

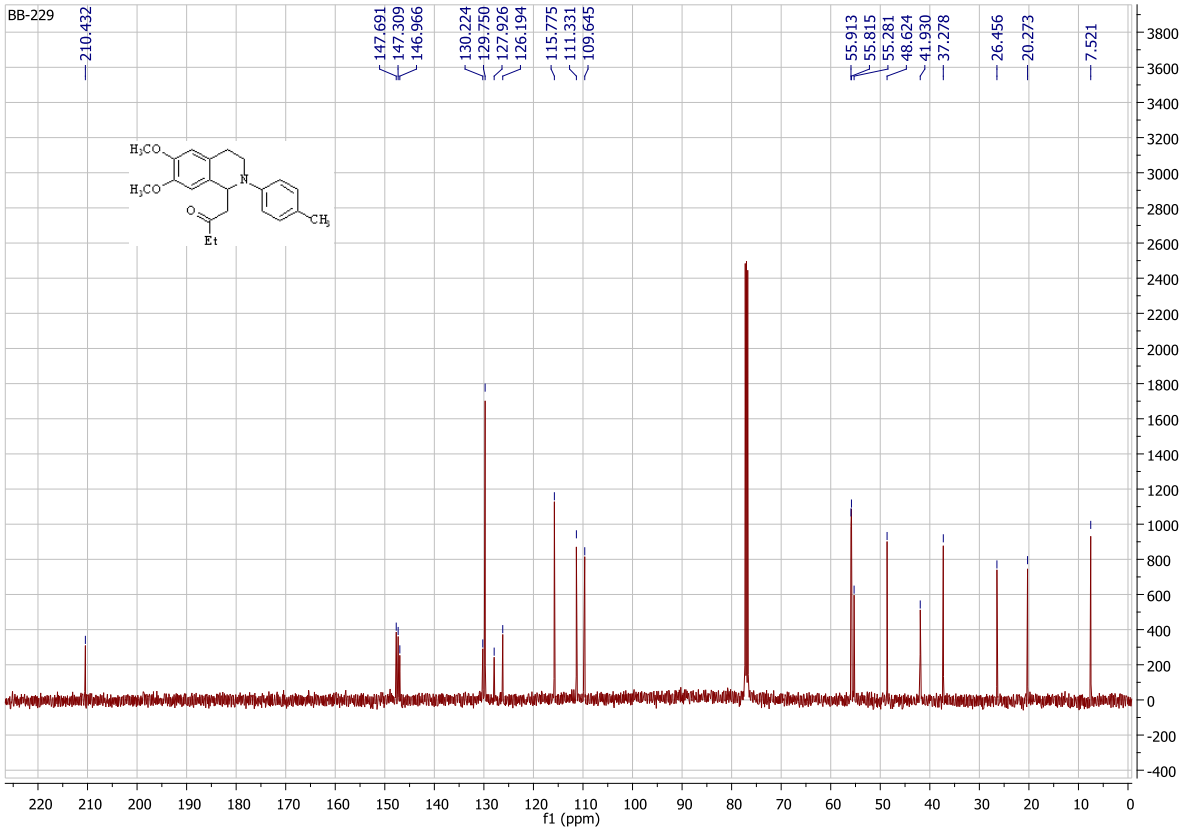
6b


BB-232
6.946
6.923
6.915
6.906
6.897
6.888
6.879
6.870
6.624
6.592
5.213
5.200
5.187
3.840
3.822
3.589
3.586
3.578
3.571
3.563
3.560
3.552
3.487
3.478
3.473
3.466
3.461
3.452
3.440
3.432
3.008
2.995
2.976
2.963
2.954
2.942
2.931
2.922
2.910
2.887
2.763
2.750
2.732
2.719
2.679
2.671
2.664
2.647
2.639
2.632
2.368
2.353
2.339
2.321
2.306
2.292
2.285
2.270
1.001
0.987
0.972
4.51
1.06
1.00
1.00
2.98
3.13
1.08
1.35
1.22
1.28
1.03
1.10
2.17
3.00
f1 (ppm)


BB-232
210.237
157.404
155.511
147.778
147.415
145.831
129.879
126.016
117.280
117.221
115.652
115.477
111.360
109.526
55.908
55.812
55.634
48.664
42.389
37.280
26.162
7.499
f1 (ppm)

7b


BB-229
7.054
7.037
6.870
6.854
6.648
6.593
5.272
5.259
5.247
3.842
3.827
3.652
3.642
3.633
3.627
3.618
3.608
3.488
3.479
3.467
3.459
3.454
3.442
3.433
3.001
2.981
2.969
2.771
2.757
2.372
2.365
2.351
2.336
2.323
2.309
2.294
2.280
2.273
2.258
2.245
0.996
0.981
0.966
1.94
1.94
1.00
0.99
0.98
6.04
1.04
1.02
2.04
1.01
1.00
2.09
3.02
3.00
f1 (ppm)


BB-229
210.432
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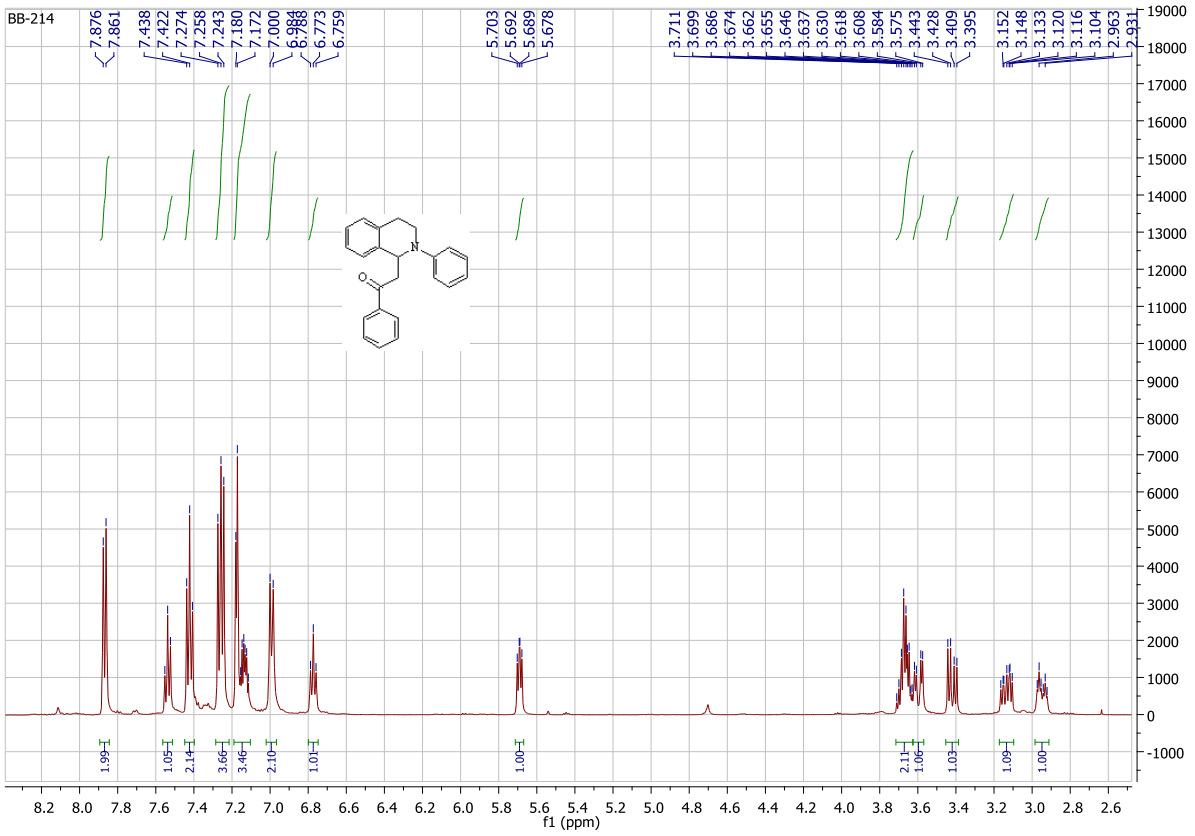
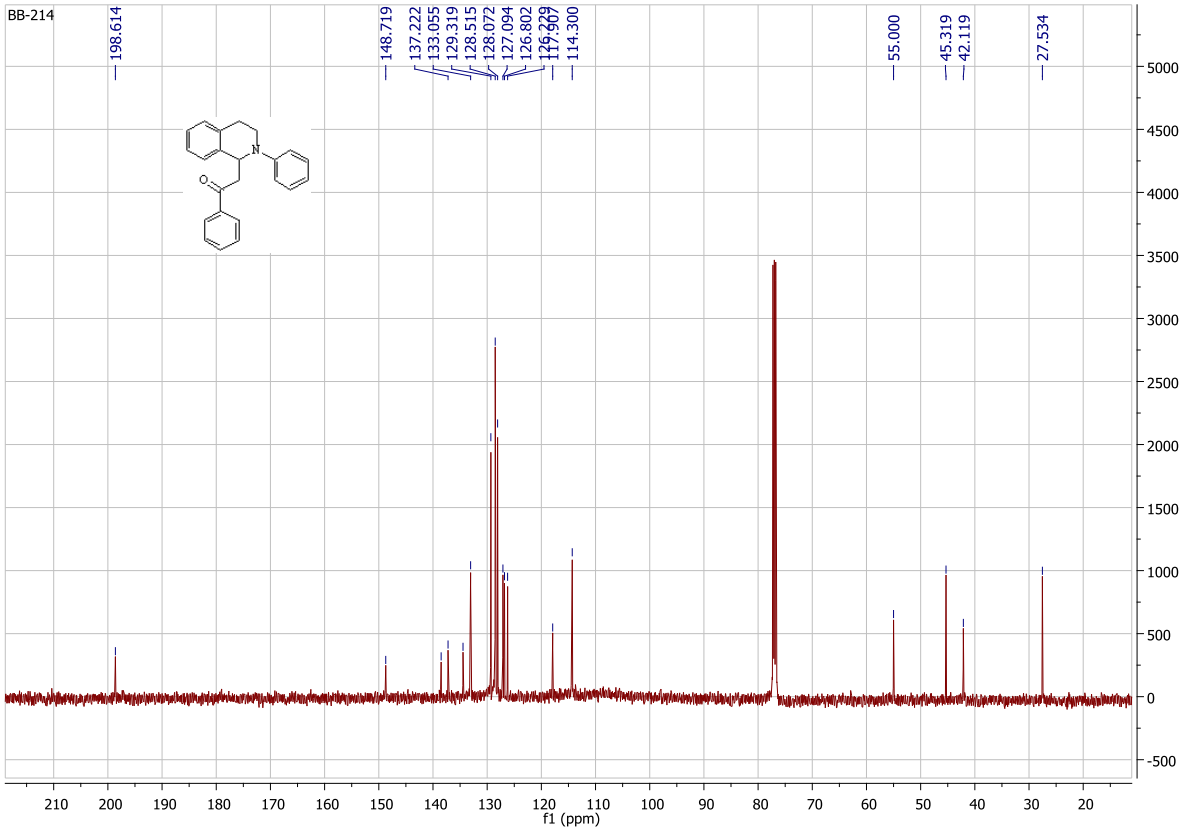
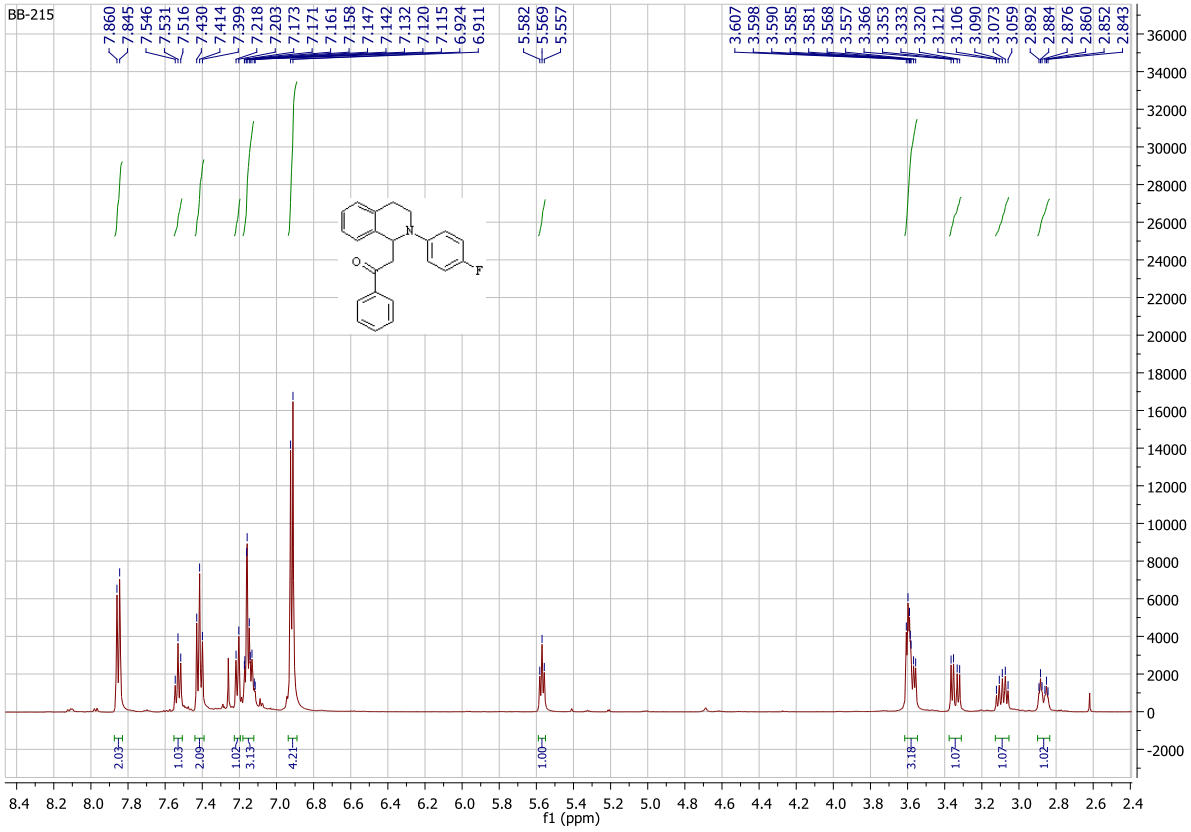
147.309
146.966
130.224
129.750
127.926
126.194
115.775
111.331
109.645
55.913
55.815
55.281
48.624
41.930
37.278
26.456
20.273
7.521
f1 (ppm)

1c


BB-214
7.876
7.861
7.438
7.422
7.274
7.258
7.243
7.180
7.172
7.000
6.984
6.788
6.773
6.759
5.703
5.692
5.689
5.678
3.711
3.699
3.686
3.674
3.662
3.655
3.646
3.637
3.630
3.618
3.608
3.584
3.575
3.443
3.428
3.409
3.395
3.152
3.148
3.133
3.120
3.116
3.104
2.963
2.931
1.99
1.05
2.14
3.66
3.46
2.10
1.01
1.00
2.11
1.06
1.03
1.09
1.00
f1 (ppm)


BB-214
198.614
148.719
137.222
133.055
129.319
128.515
128.072
127.094
126.802
126.229
117.907
114.300
55.000
45.319
42.119
27.534
f1 (ppm)

2c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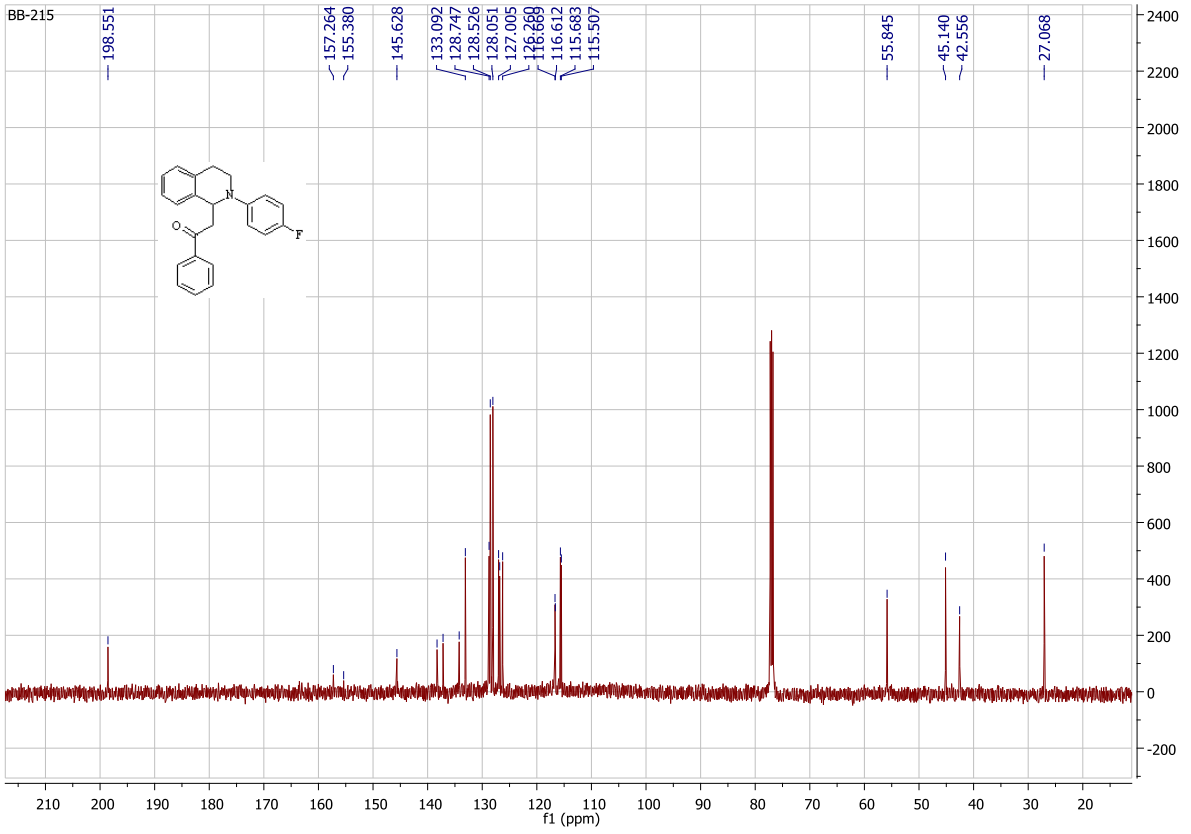
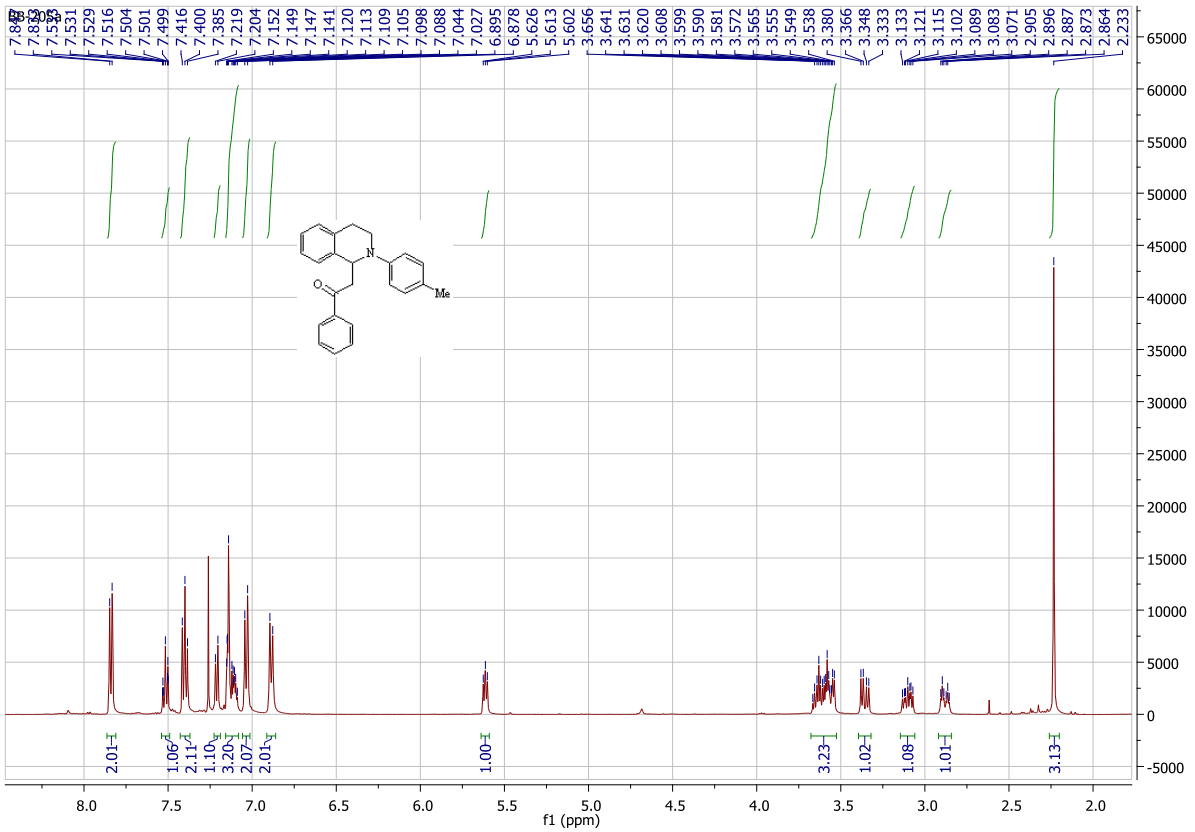
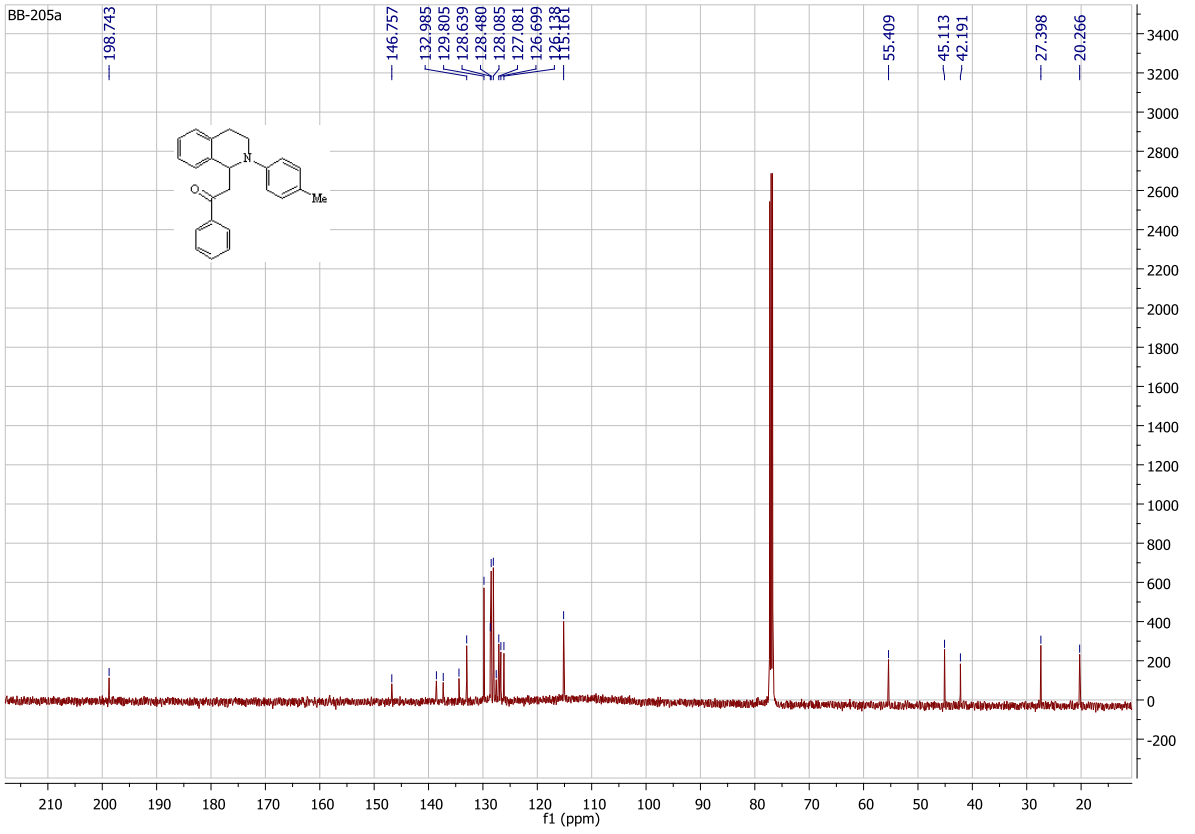
7.546
7.531
7.516
7.430
7.414
7.399
7.218
7.203
7.173
7.171
7.161
7.158
7.147
7.142
7.132
7.120
7.115
6.924
6.911
5.582
5.569
5.557
3.607
3.598
3.590
3.585
3.581
3.568
3.557
3.366
3.353
3.333
3.320
3.121
3.106
3.090
3.073
3.059
2.892
2.884
2.876
2.860
2.852
2.843
2.03
1.03
2.09
1.02
3.13
4.21
1.00
3.18
1.07
1.07
1.02
f1 (ppm)

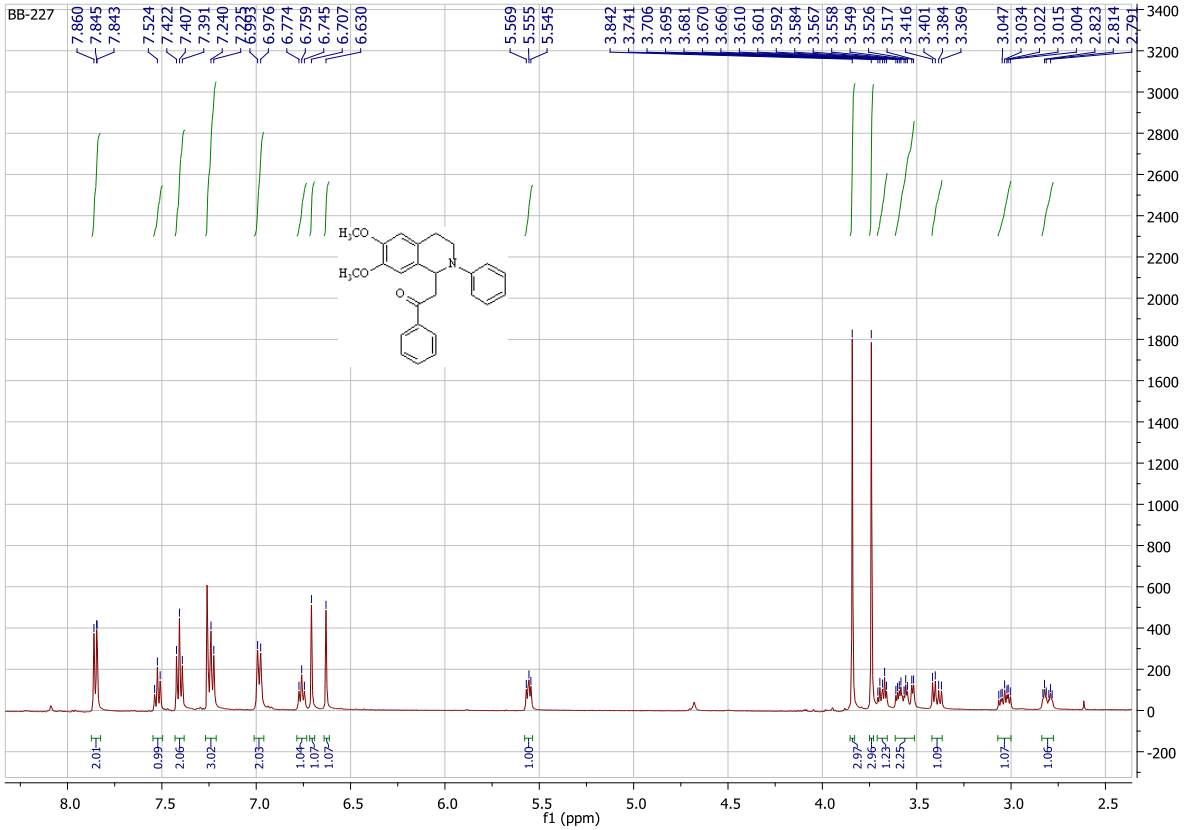

BB-215
198.551
157.264
155.380
145.628
133.092
128.747
128.526
128.051
127.005
126.260
116.669
116.612
115.683
115.507
55.845
45.140
42.556
27.068
f1 (ppm)

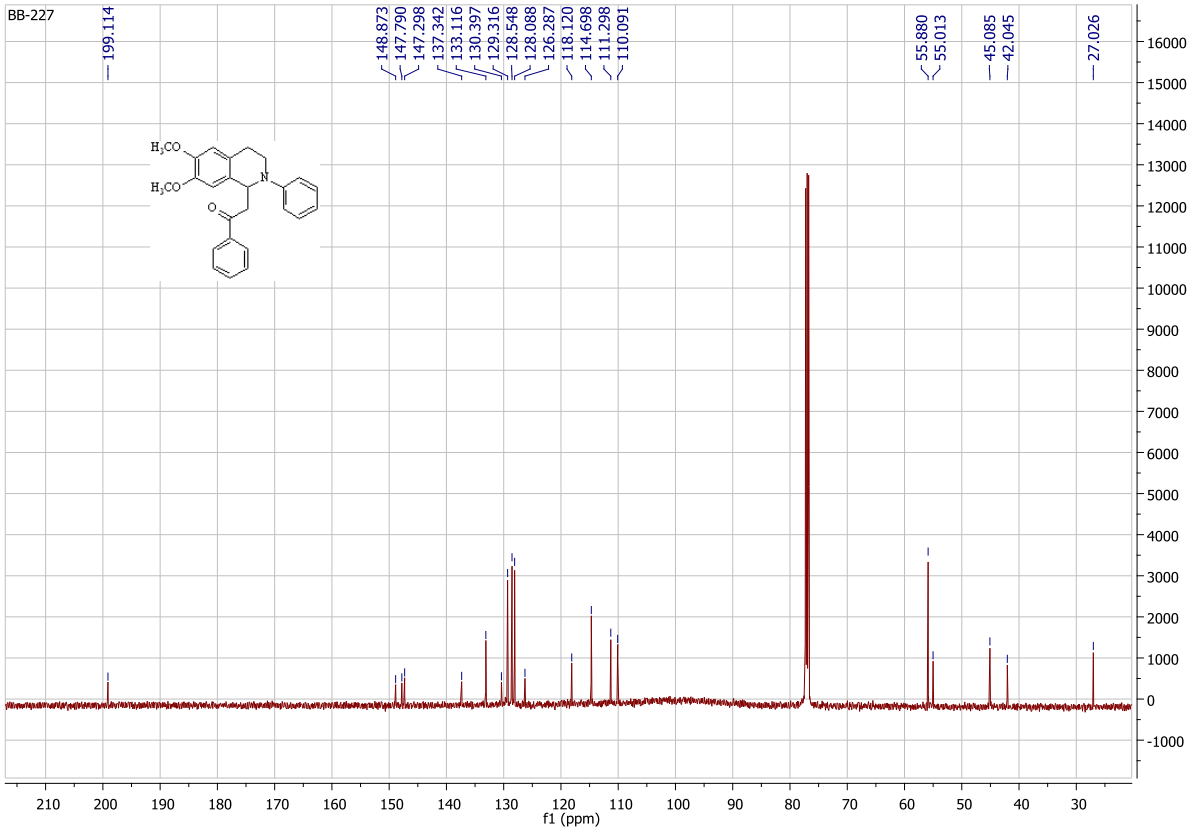
3c


BB-205
7.846
7.833
7.553
7.531
7.529
7.516
7.504
7.501
7.499
7.416
7.400
7.385
7.219
7.204
7.152
7.149
7.147
7.141
7.120
7.113
7.109
7.105
7.098
7.088
7.044
7.027
6.895
6.878
6.626
5.613
5.602
3.656
3.641
3.631
3.620
3.608
3.599
3.590
3.581
3.572
3.565
3.555
3.549
3.538
3.380
3.366
3.348
3.333
3.133
3.121
3.115
3.102
3.089
3.083
3.071
2.905
2.896
2.887
2.873
2.864
2.233
Me
2.01
1.06
2.11
1.10
3.20
2.07
2.01
1.00
3.23
1.02
1.08
1.01
3.13
f1 (ppm)

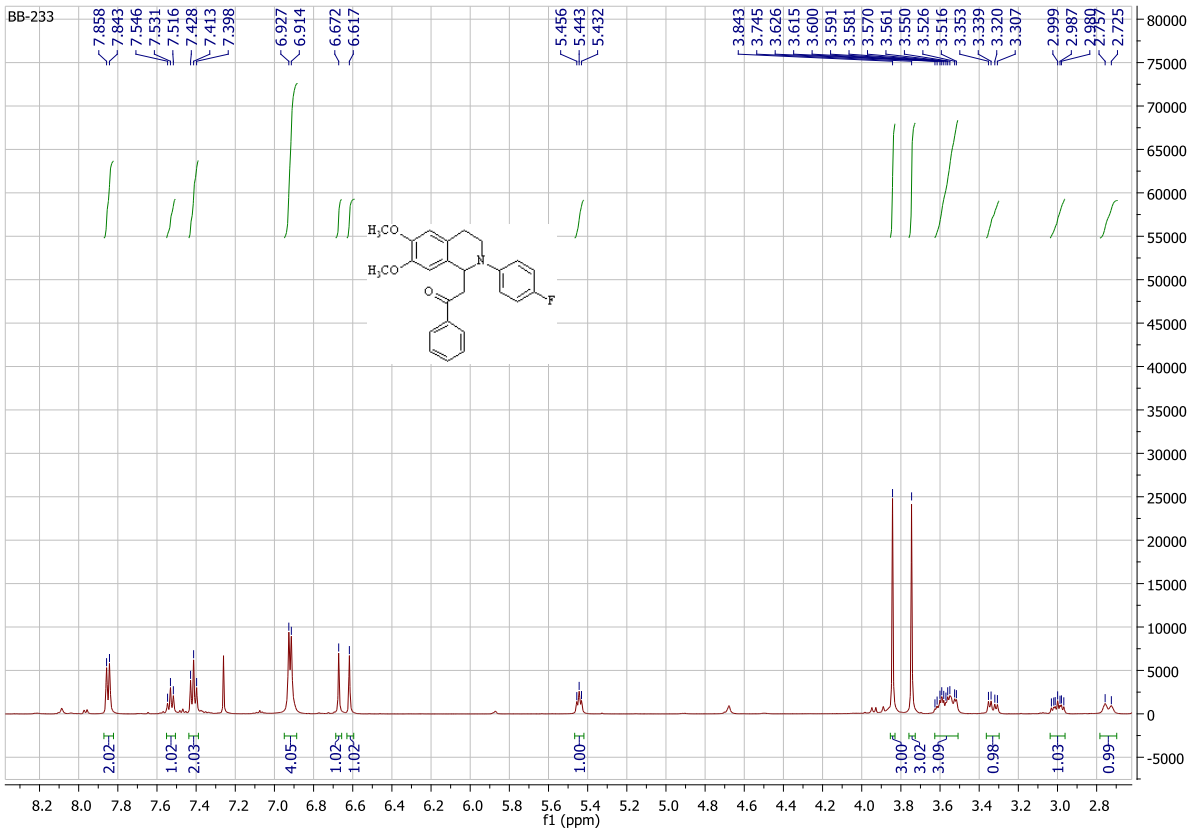

BB-205a
198.743
146.757
132.985
129.805
128.639
128.480
128.085
127.081
126.699
126.138
115.161
55.409
45.113
42.191
27.398
20.266
Me
f1 (ppm)

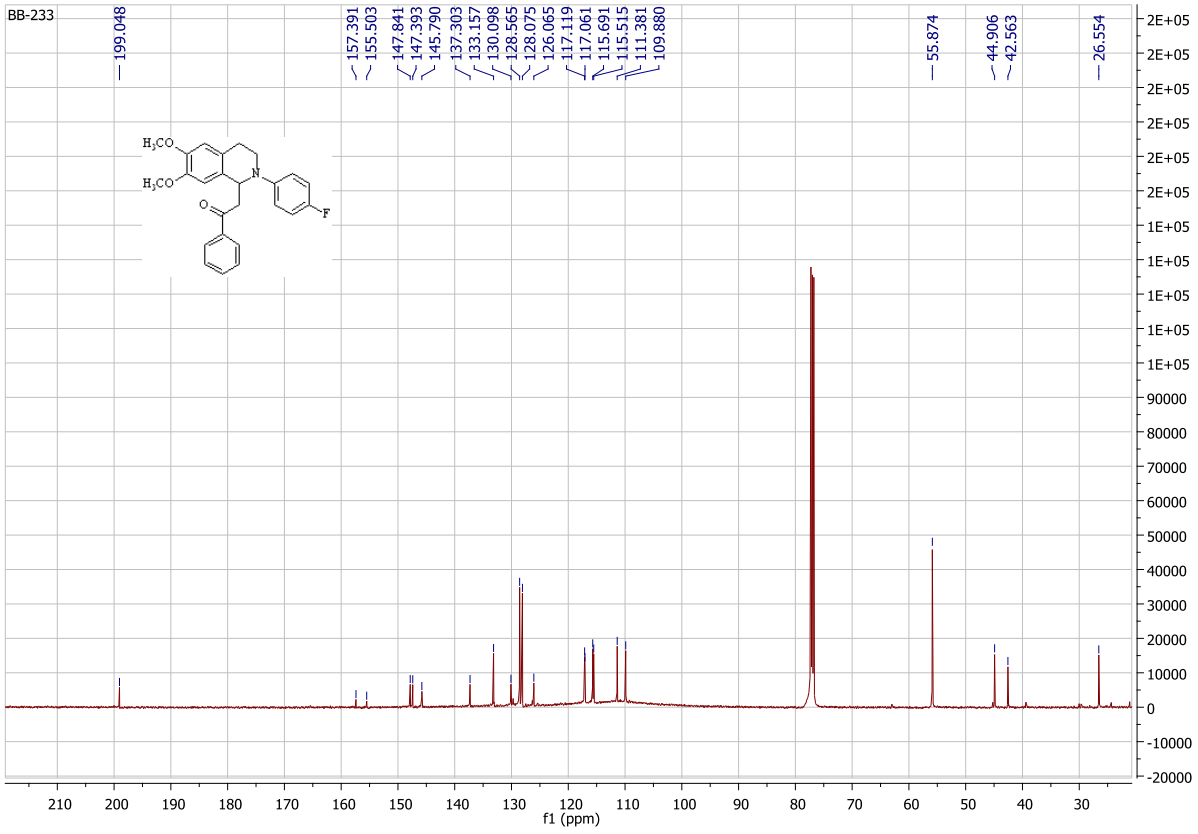
5c


BB-227
7.860
7.845
7.843
7.524
7.422
7.407
7.391
7.240
6.976
6.774
6.759
6.745
6.707
6.630
5.569
5.555
5.545
3.842
3.741
3.706
3.695
3.681
3.670
3.660
3.610
3.601
3.592
3.584
3.567
3.558
3.549
3.526
3.517
3.416
3.401
3.384
3.369
3.047
3.034
3.022
3.015
3.004
2.823
2.814
2.791
f1 (ppm)

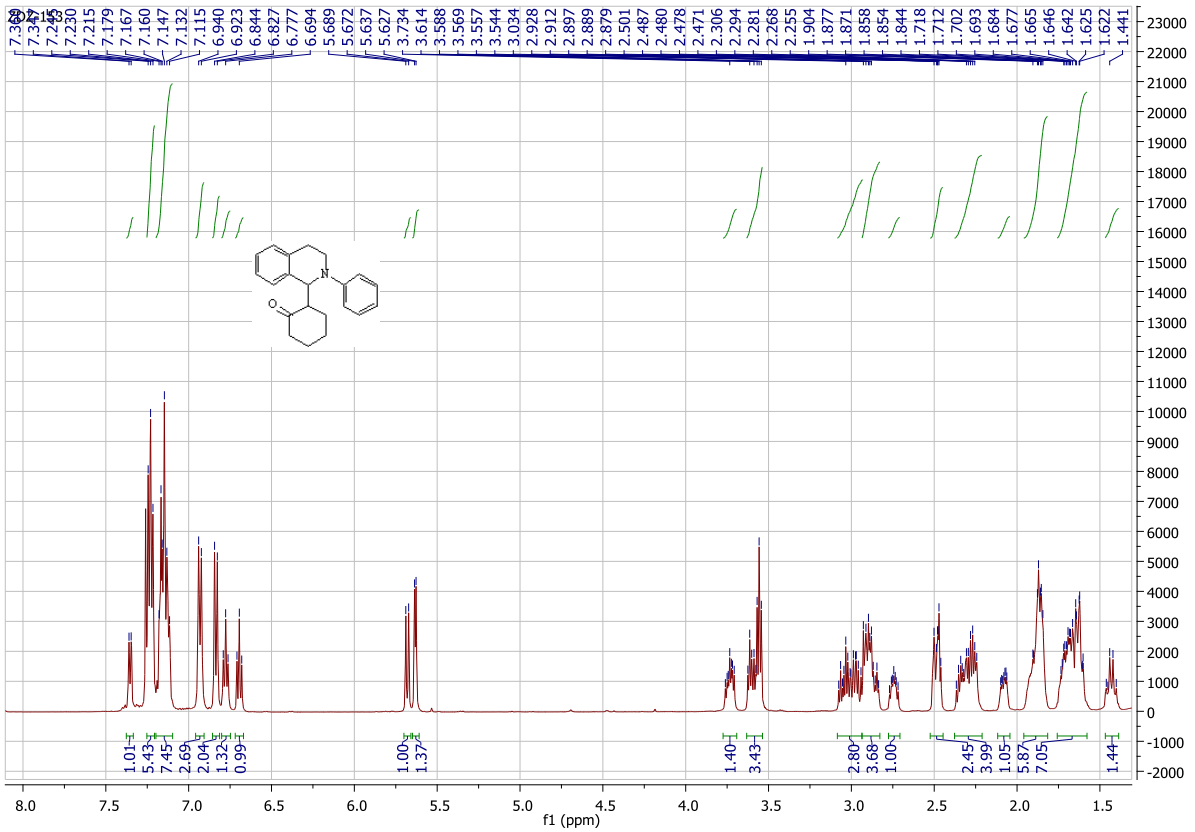

BB-227
199.114
148.873
147.790
147.298
137.342
133.116
130.397
129.316
128.548
128.088
126.287
118.120
114.698
111.298
110.091
55.880
55.013
45.085
42.045
27.026
f1 (ppm)

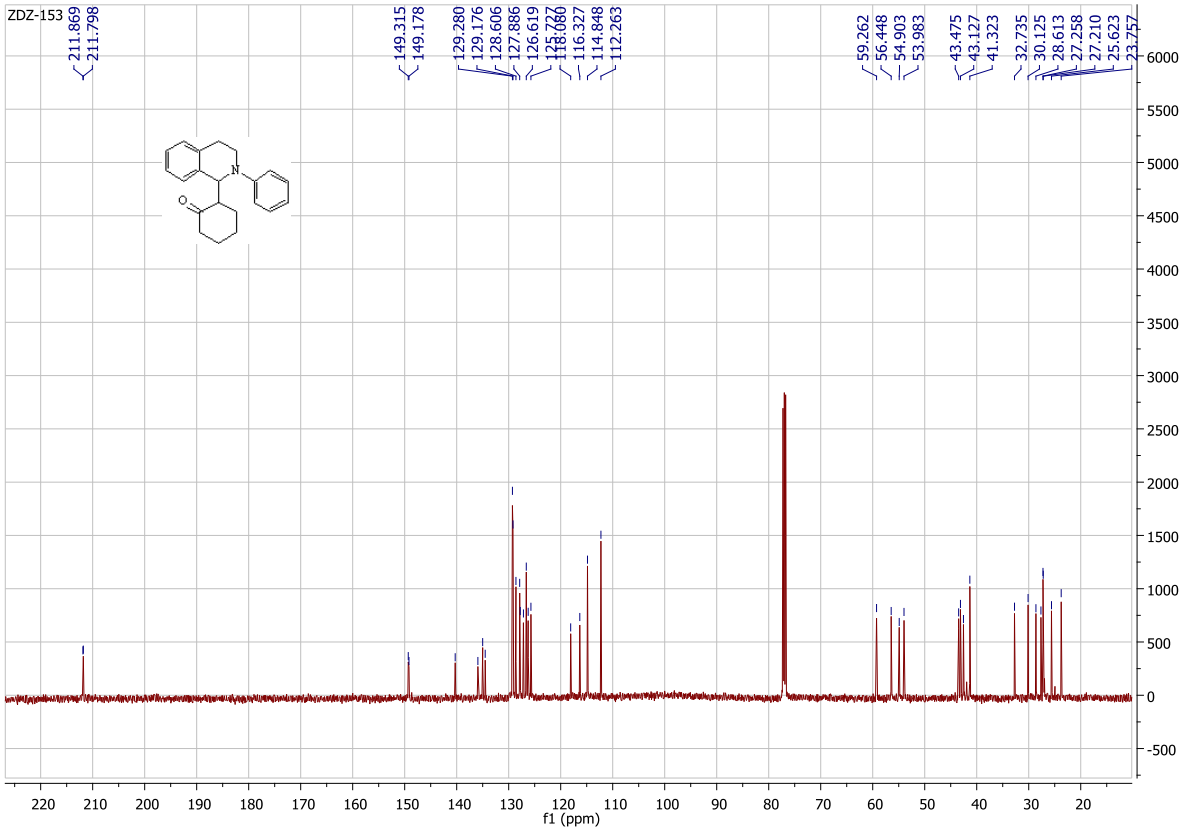
6c


BB-233
7.858
7.843
7.546
7.531
7.516
7.428
7.413
7.398
6.927
6.914
6.672
6.617
5.456
5.443
5.432
3.843
3.745
3.626
3.615
3.600
3.591
3.581
3.570
3.561
3.550
3.526
3.516
3.353
3.339
3.320
3.307
2.999
2.987
2.980
2.757
2.725
2.02
1.02
2.03
4.05
1.02
1.02
1.00
3.00
3.02
3.09
0.98
1.03
0.99
f1 (ppm)

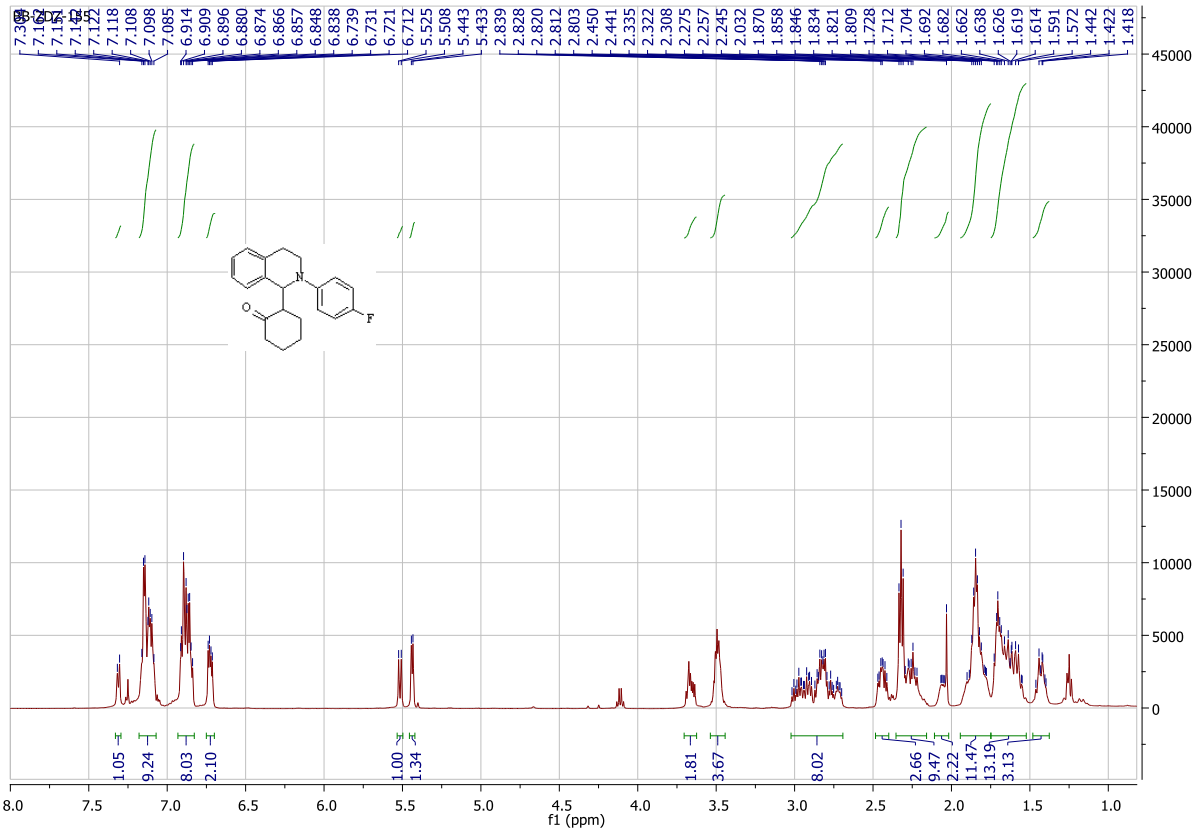

BB-233
199.048
157.391
155.503
147.841
147.393
145.790
137.303
133.157
130.098
128.565
128.075
126.065
117.119
117.061
115.691
115.515
111.381
109.880
55.874
44.906
42.563
26.554
f1 (ppm)

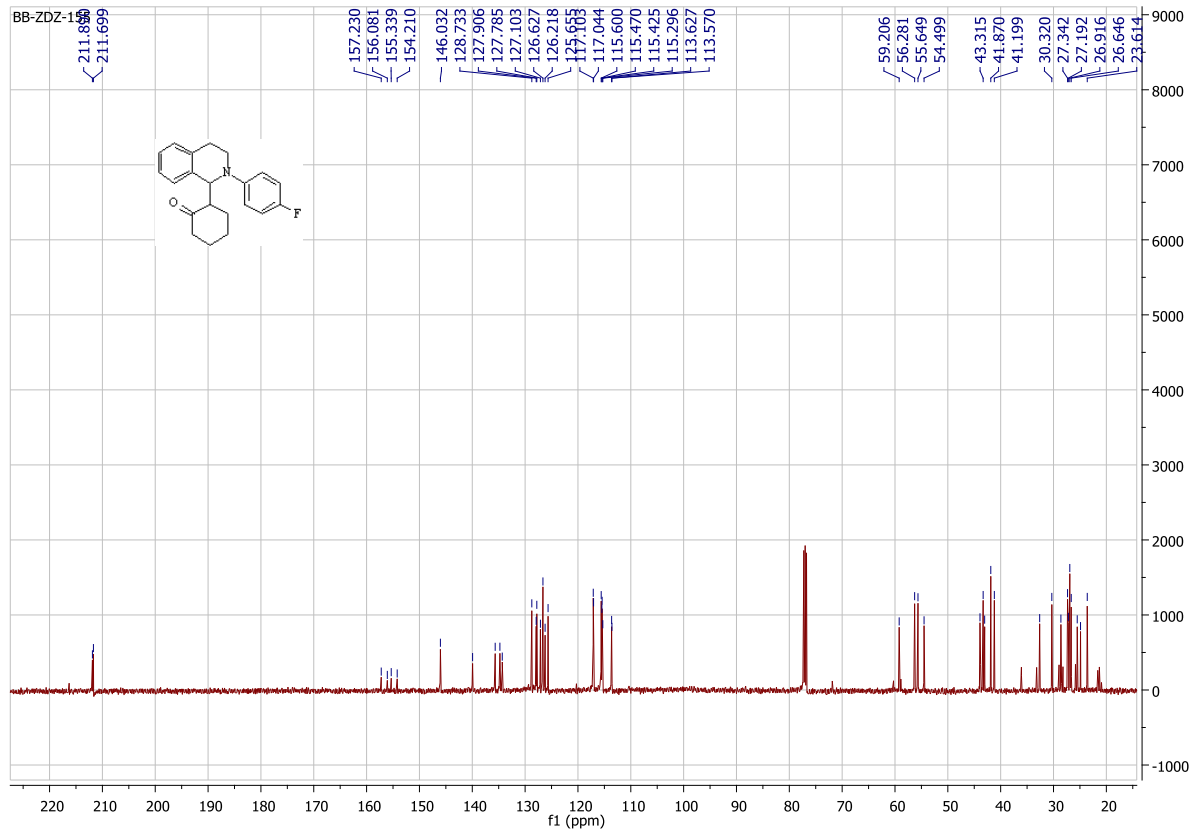
1d



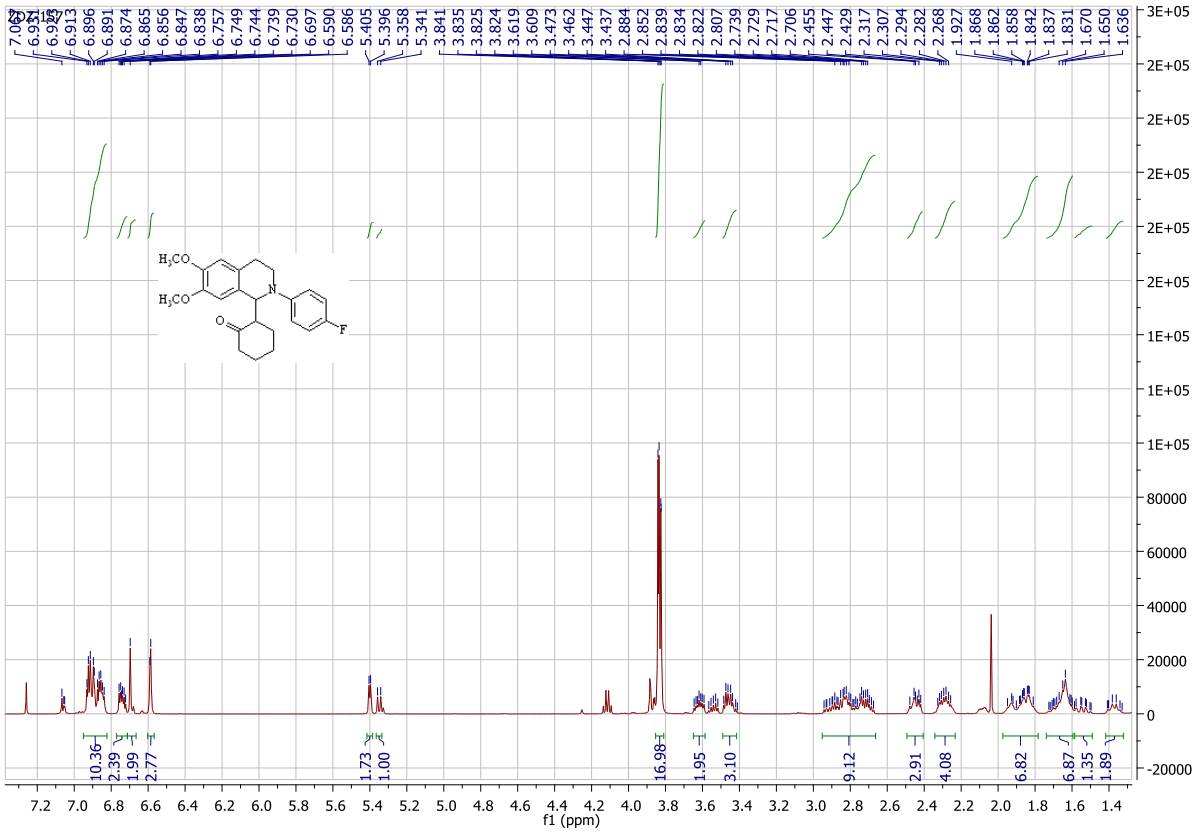


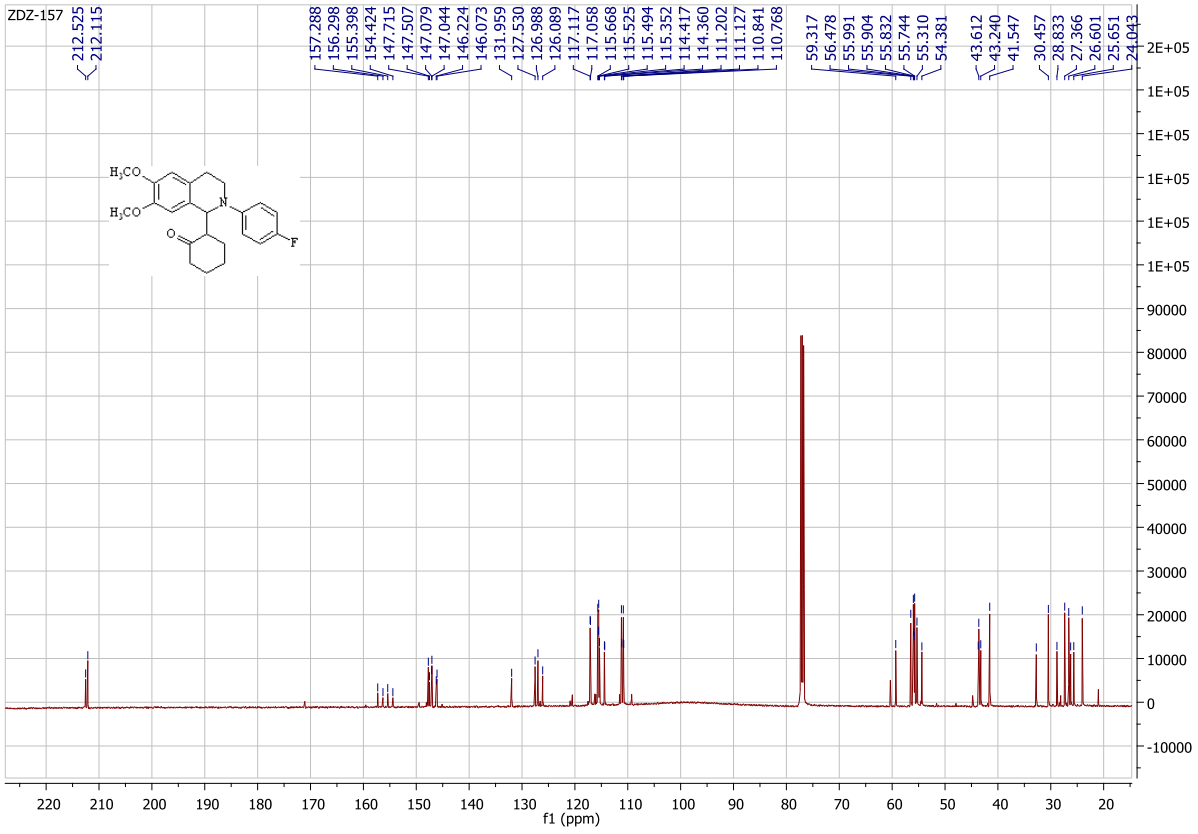
2d


7.306
7.163
7.153
7.144
7.122
7.118
7.108
7.098
7.085
6.914
6.909
6.896
6.880
6.874
6.866
6.857
6.848
6.838
6.739
6.731
6.721
6.712
5.525
5.508
5.443
5.433
2.839
2.828
2.820
2.812
2.803
2.450
2.441
2.335
2.322
2.308
2.275
2.257
2.245
2.032
1.870
1.858
1.846
1.834
1.821
1.809
1.728
1.712
1.704
1.692
1.682
1.662
1.638
1.626
1.619
1.614
1.591
1.572
1.442
1.422
1.418
1.05
9.24
8.03
2.10
1.00
1.34
1.81
3.67
8.02
2.66
9.47
2.22
11.47
13.19
3.13
f1 (ppm)

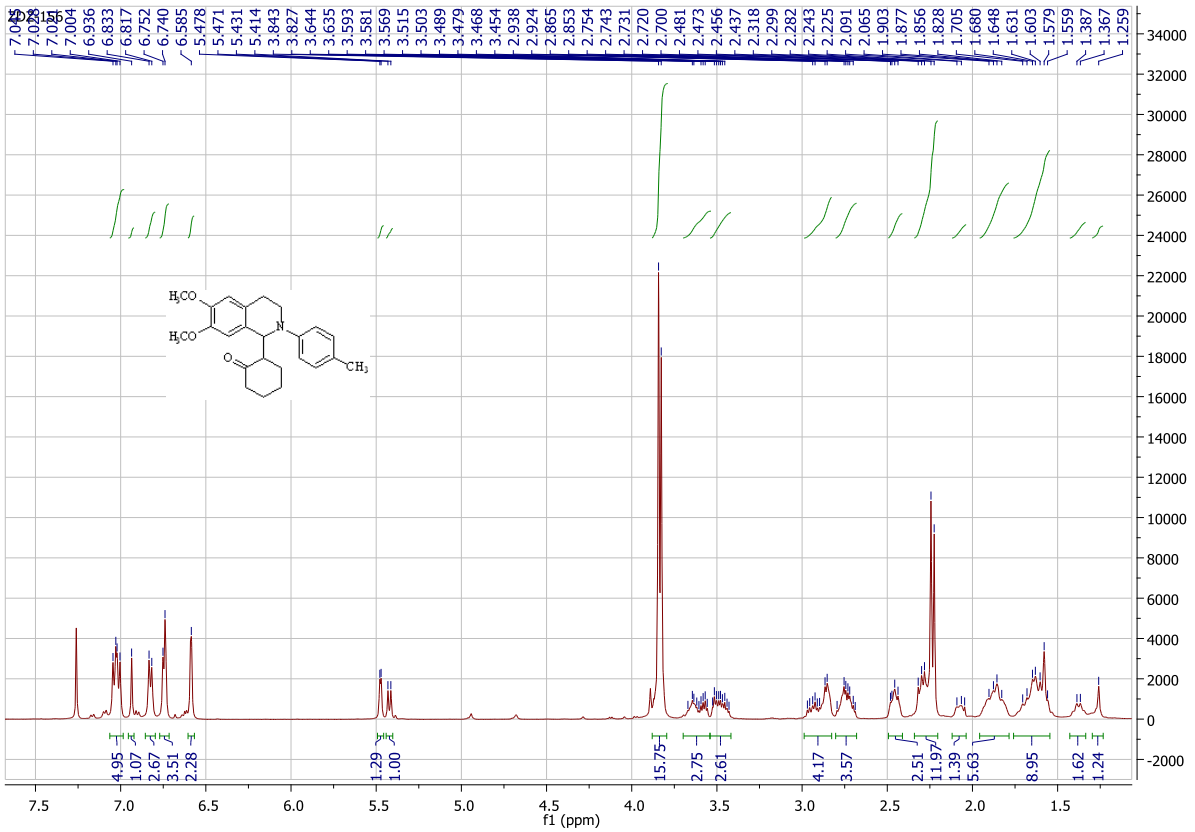

BB-ZDZ-158
211.856
211.699
157.230
156.081
155.339
154.210
146.032
128.733
127.906
127.785
127.103
126.627
126.218
125.655
117.103
117.044
115.600
115.470
115.425
115.296
113.627
113.570
59.206
56.281
55.649
54.499
43.315
41.870
41.199
30.320
27.342
27.192
26.916
26.646
23.614
f1 (ppm)

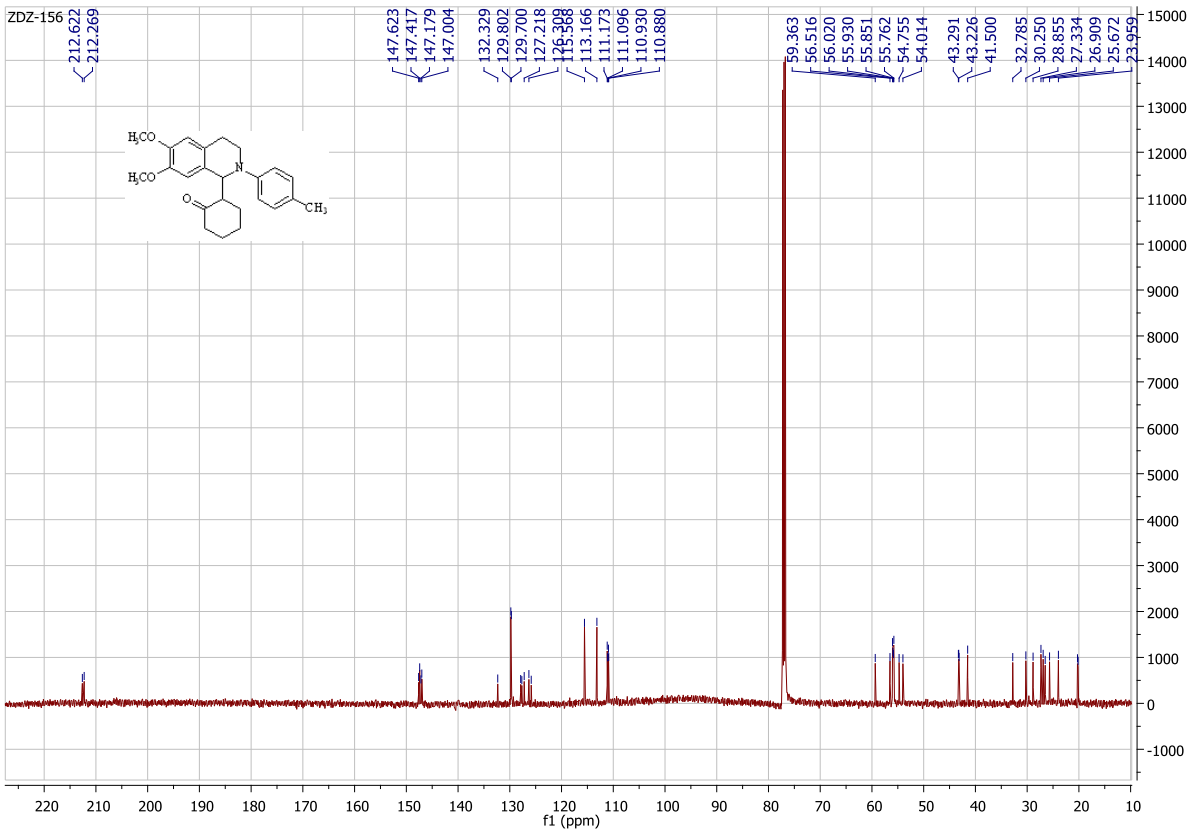
5c


ZDZ-157
7.062
6.931
6.925
6.913
6.896
6.891
6.874
6.865
6.856
6.847
6.838
6.757
6.749
6.744
6.739
6.730
6.697
6.590
6.586
5.405
5.396
5.358
5.341
3.841
3.835
3.825
3.824
3.619
3.609
3.473
3.462
3.447
3.437
2.884
2.852
2.839
2.834
2.822
2.807
2.739
2.729
2.717
2.706
2.455
2.447
2.429
2.317
2.307
2.294
2.282
2.268
1.927
1.868
1.862
1.858
1.842
1.837
1.831
1.670
1.650
1.636
10.36
2.39
1.99
2.77
1.73
1.00
16.98
1.95
3.10
9.12
2.91
4.08
6.82
6.87
1.35
1.89
f1 (ppm)

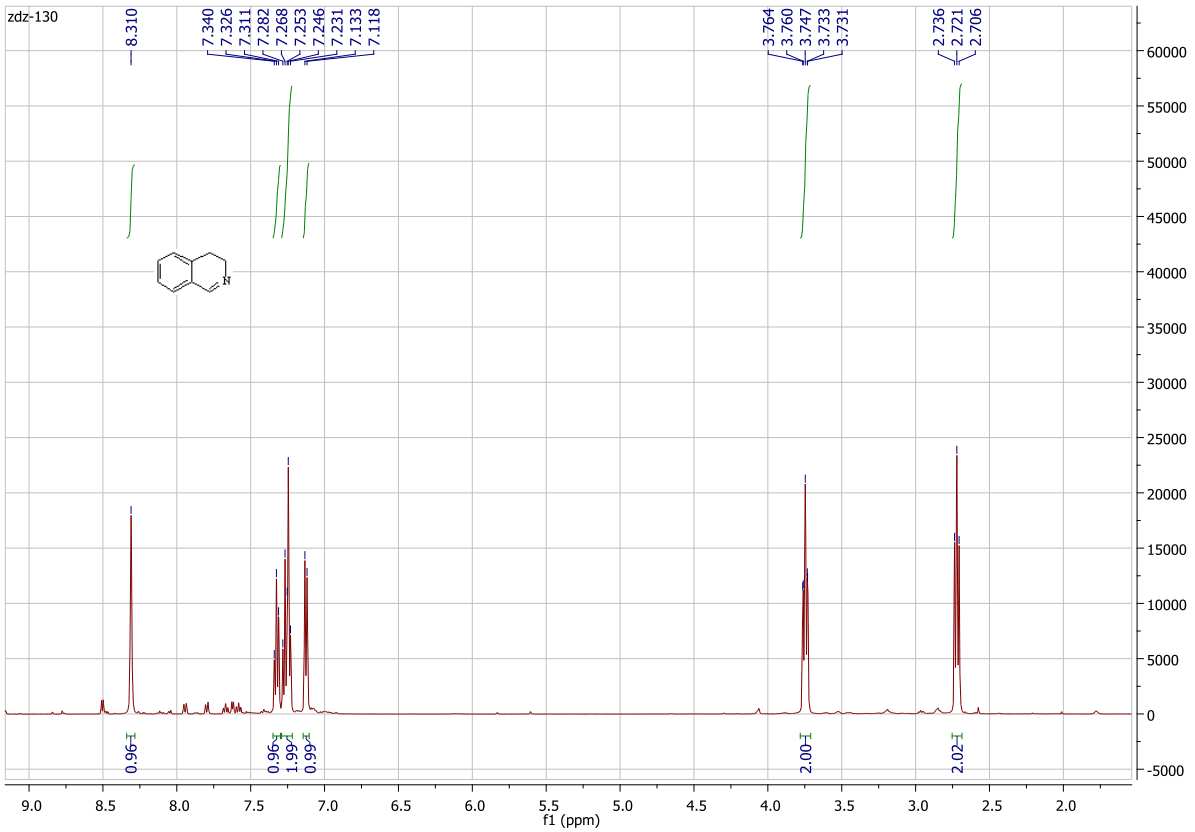

ZDZ-157
212.525
212.115
157.288
156.298
155.398
154.424
147.715
147.507
147.079
147.044
146.224
146.073
131.959
127.530
126.988
126.089
117.117
117.058
115.668
115.525
115.494
115.352
114.417
114.360
111.202
111.127
110.841
110.768
59.317
56.478
55.991
55.904
55.832
55.744
55.310
54.381
43.612
43.240
41.547
30.457
28.833
27.366
26.601
25.651
24.043
f1 (ppm)

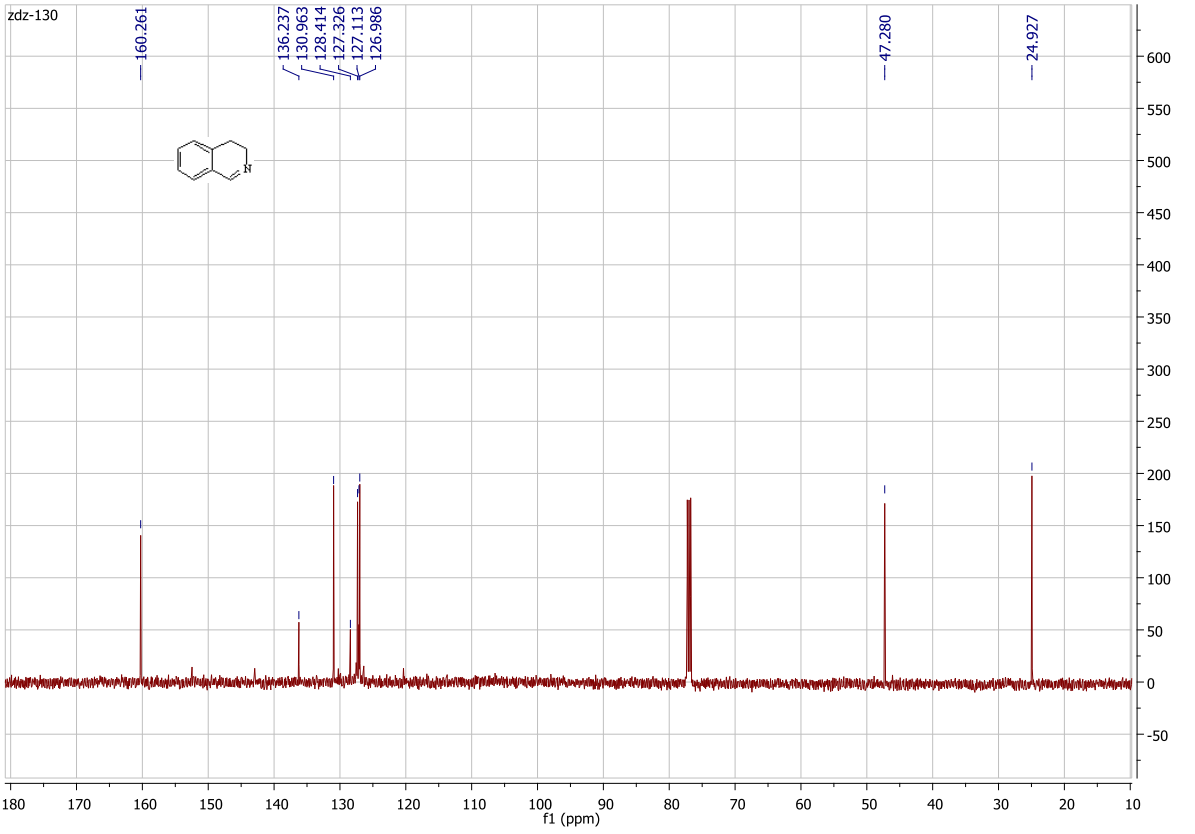
6c


ZDZ-156
7.042
7.028
7.015
7.007
7.004
6.936
6.833
6.817
6.752
6.740
6.585
5.478
5.471
5.431
5.414
3.843
3.827
3.644
3.635
3.593
3.581
3.569
3.515
3.503
3.489
3.479
3.468
3.454
2.938
2.924
2.865
2.853
2.754
2.743
2.731
2.720
2.700
2.481
2.473
2.456
2.437
2.318
2.299
2.282
2.243
2.225
2.091
2.065
1.903
1.877
1.856
1.828
1.705
1.680
1.648
1.631
1.603
1.579
1.559
1.387
1.367
1.259
4.95
1.07
2.67
3.51
2.28
1.29
1.00
15.75
2.75
2.61
4.17
3.57
2.51
11.97
1.39
5.63
8.95
1.62
1.24
f1 (ppm)

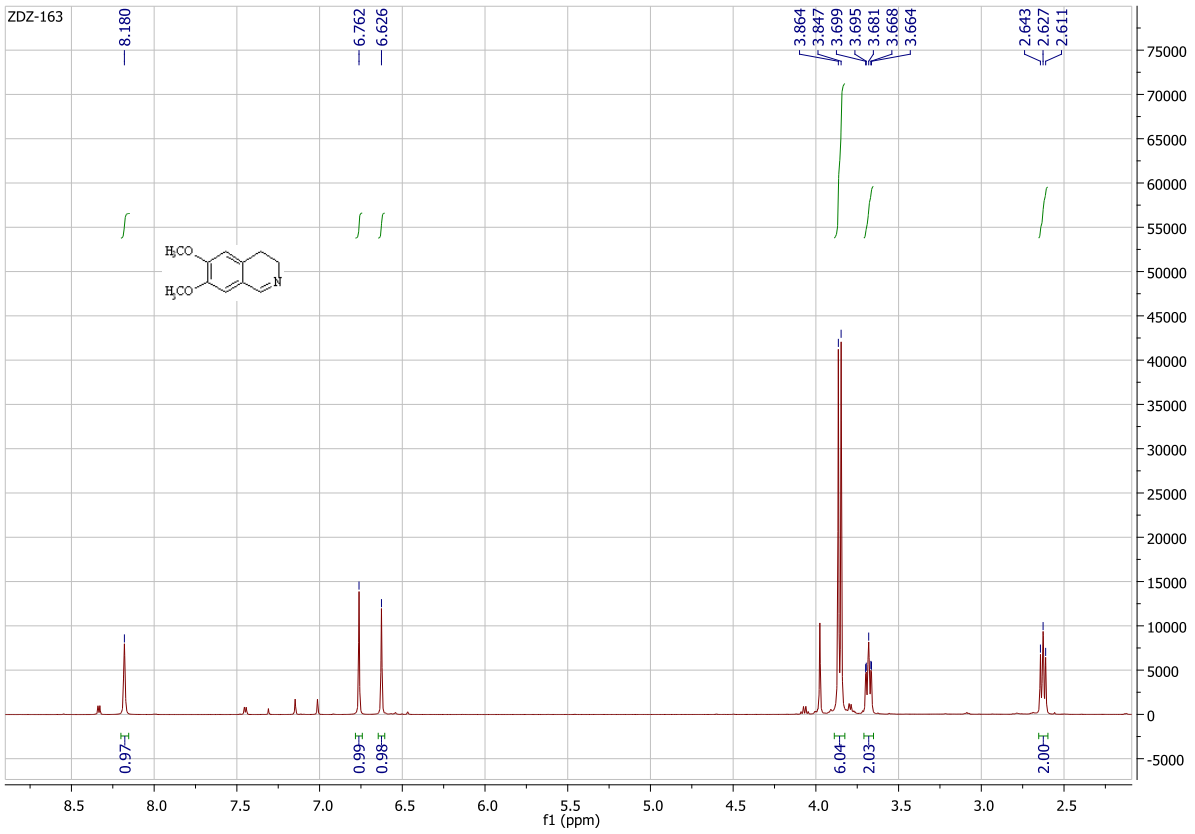

ZDZ-156
212.622
212.269
147.623
147.417
147.179
147.004
132.329
129.802
129.700
127.218
126.309
115.588
113.166
111.173
111.096
110.930
110.880
59.363
56.516
56.020
55.930
55.851
55.762
54.755
54.014
43.291
43.226
41.500
32.785
30.250
28.855
27.334
26.909
25.672
23.959
f1 (ppm)

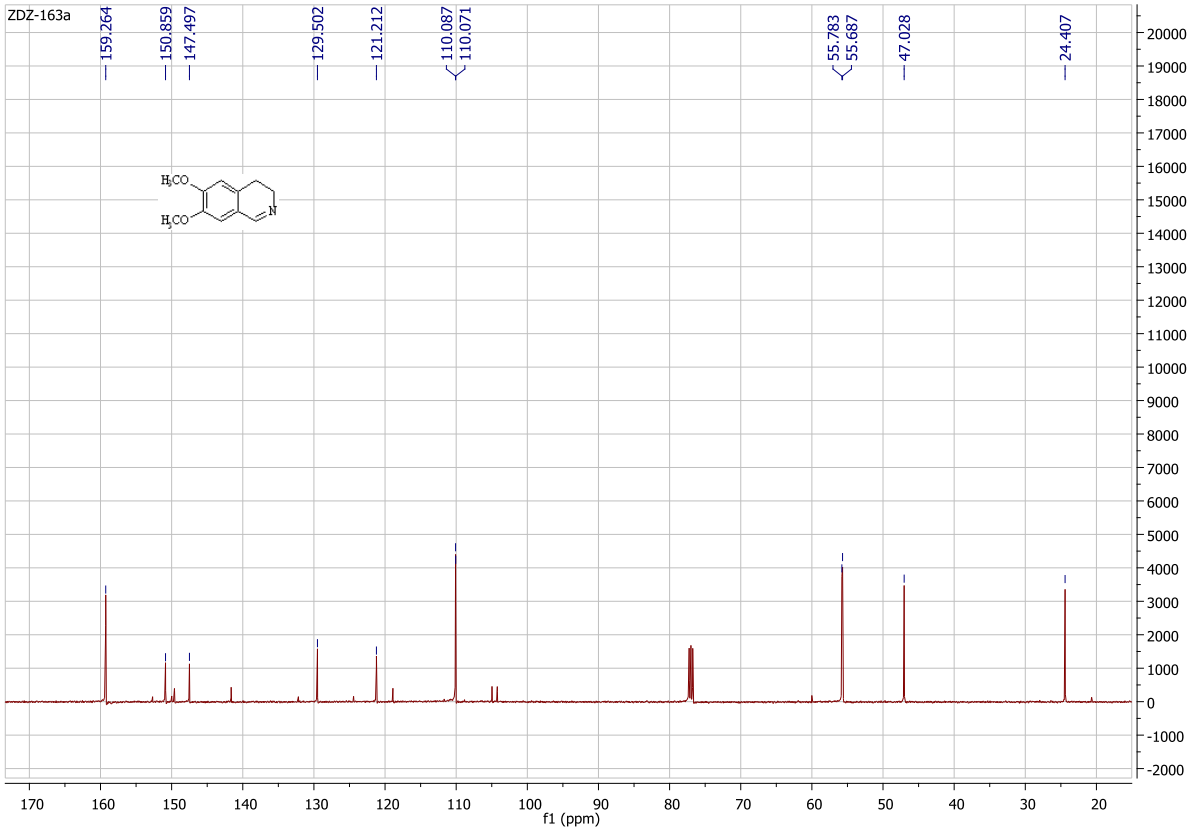
9a


zdz-130
8.310
7.340
7.326
7.311
7.282
7.268
7.253
7.246
7.231
7.133
7.118
3.764
3.760
3.747
3.733
3.731
2.736
2.721
2.706
0.96
0.96
1.99
0.99
2.00
2.02
f1 (ppm)

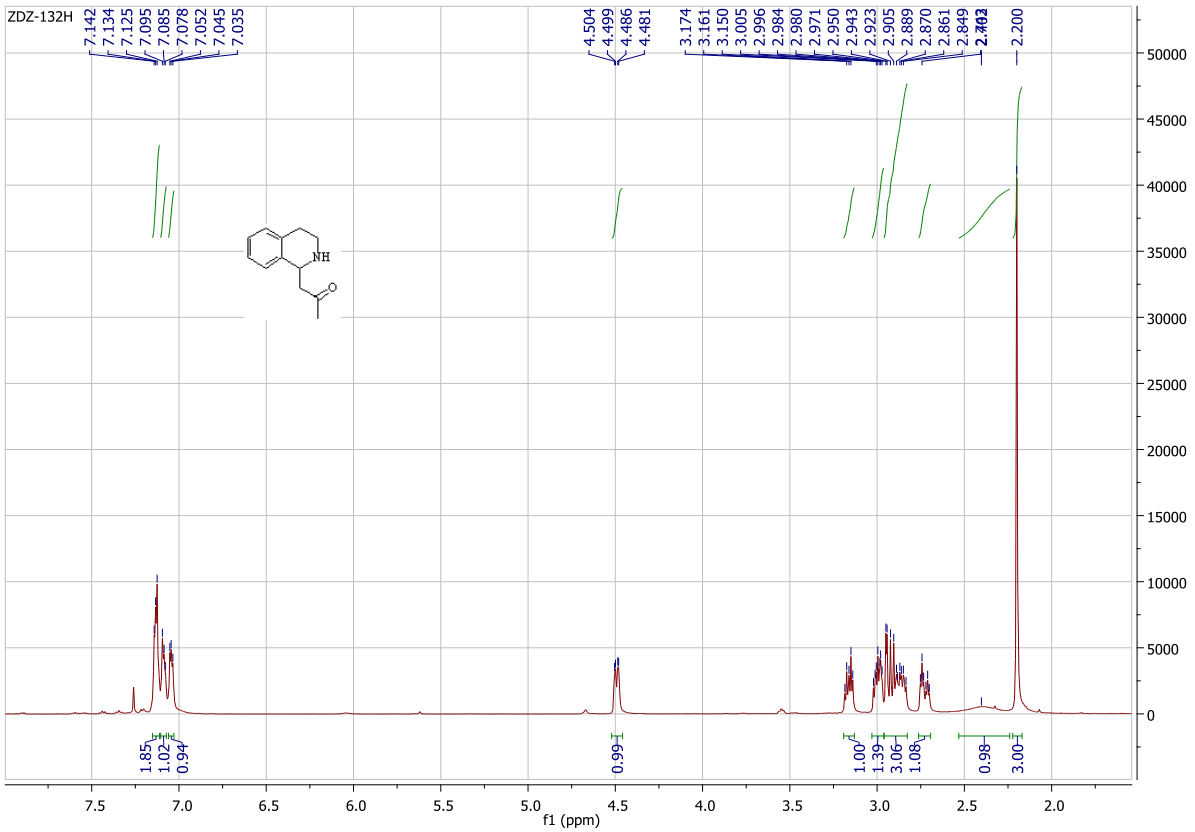

zdz-130
160.261
136.237
130.963
128.414
127.326
127.113
126.986
47.280
24.927
f1 (ppm)

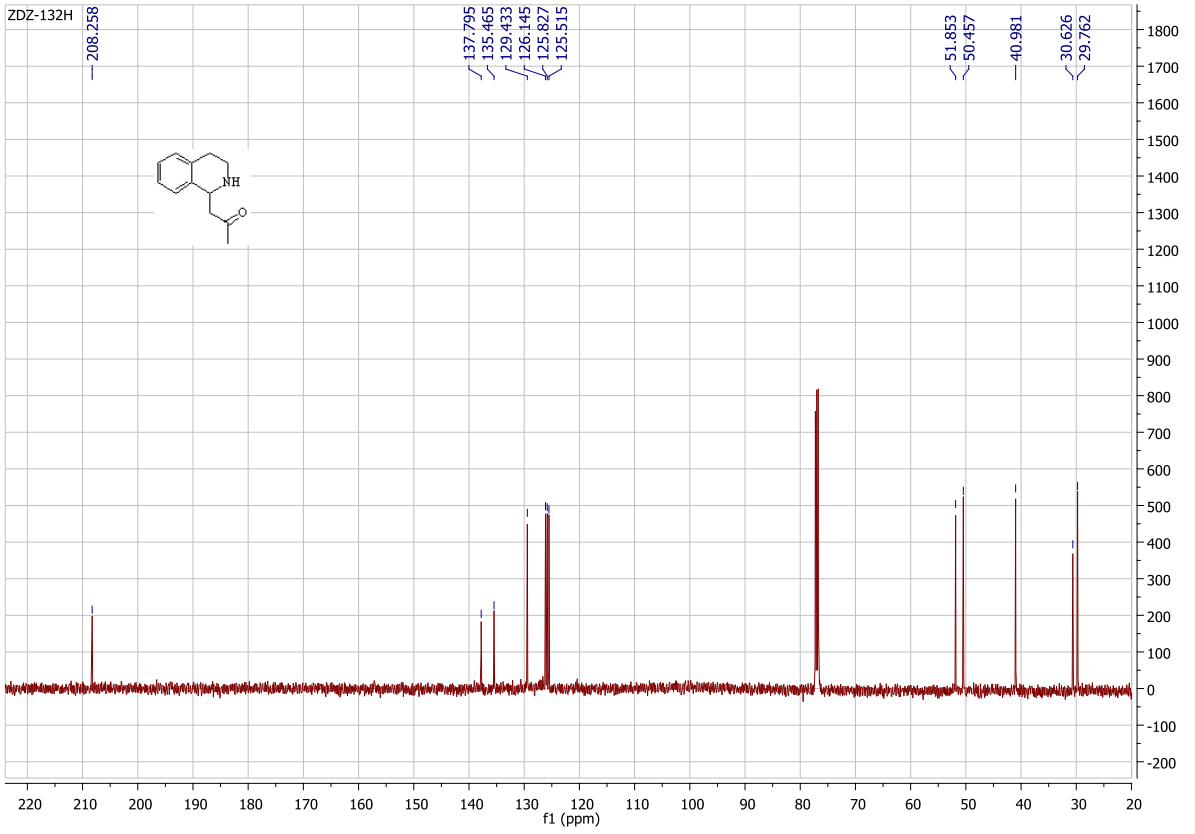
9b


ZDZ-163
8.180
6.762
6.626
3.864
3.847
3.699
3.695
3.681
3.668
3.664
2.643
2.627
2.611
0.97
0.99
0.98
6.04
2.03
2.00
f1 (ppm)

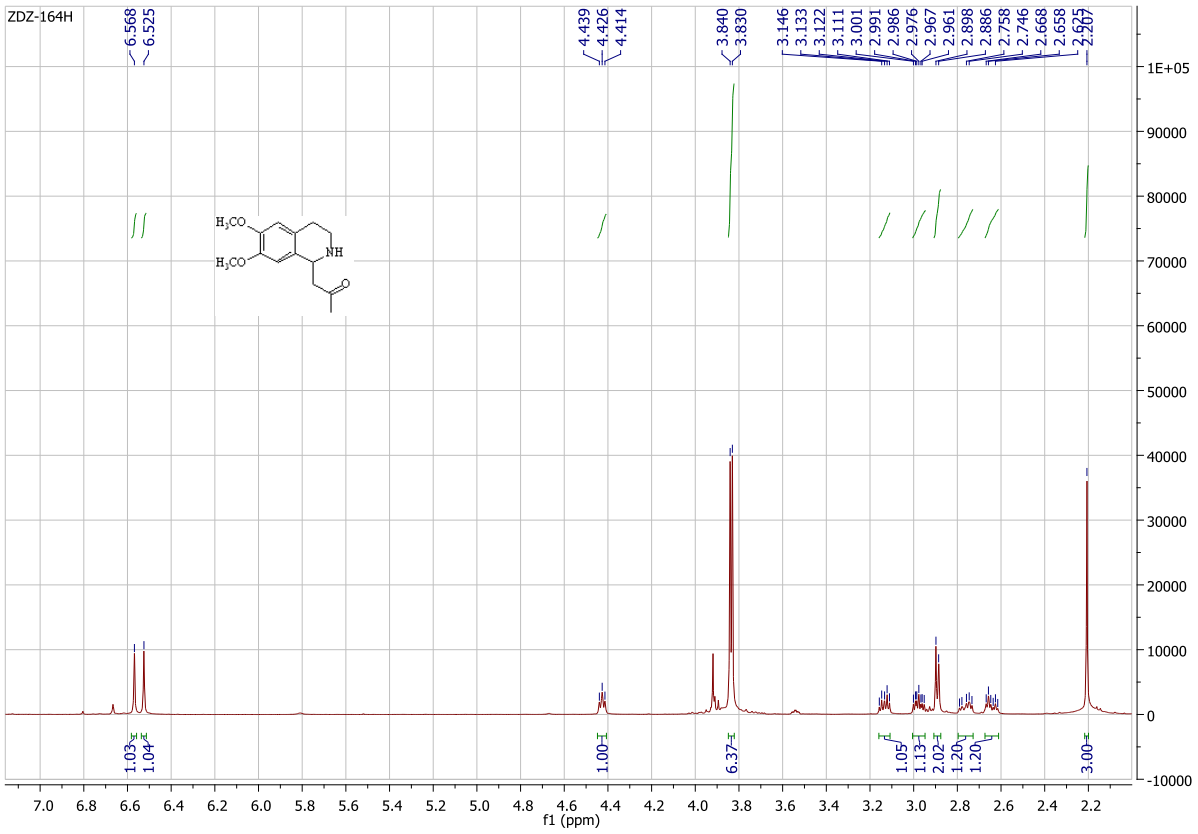

ZDZ-163a
159.264
150.859
147.497
129.502
121.212
110.087
110.071
55.783
55.687
47.028
24.407
f1 (ppm)

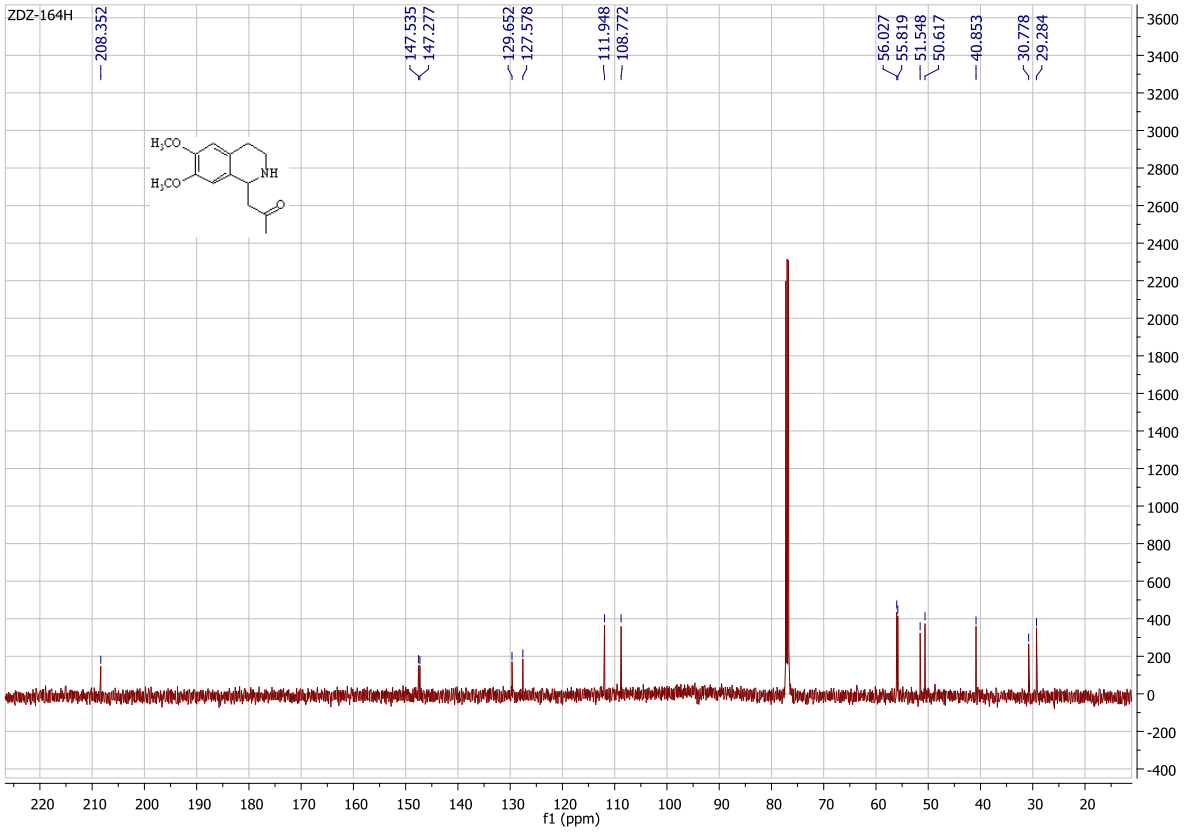
10


ZDZ-132H
7.142
7.134
7.125
7.095
7.085
7.078
7.052
7.045
7.035
4.504
4.499
4.486
4.481
3.174
3.161
3.150
3.005
2.996
2.984
2.980
2.971
2.950
2.943
2.923
2.905
2.889
2.870
2.861
2.849
2.200
NH
O
1.85
1.02
0.94
0.99
1.00
1.39
3.06
1.08
0.98
3.00
f1 (ppm)

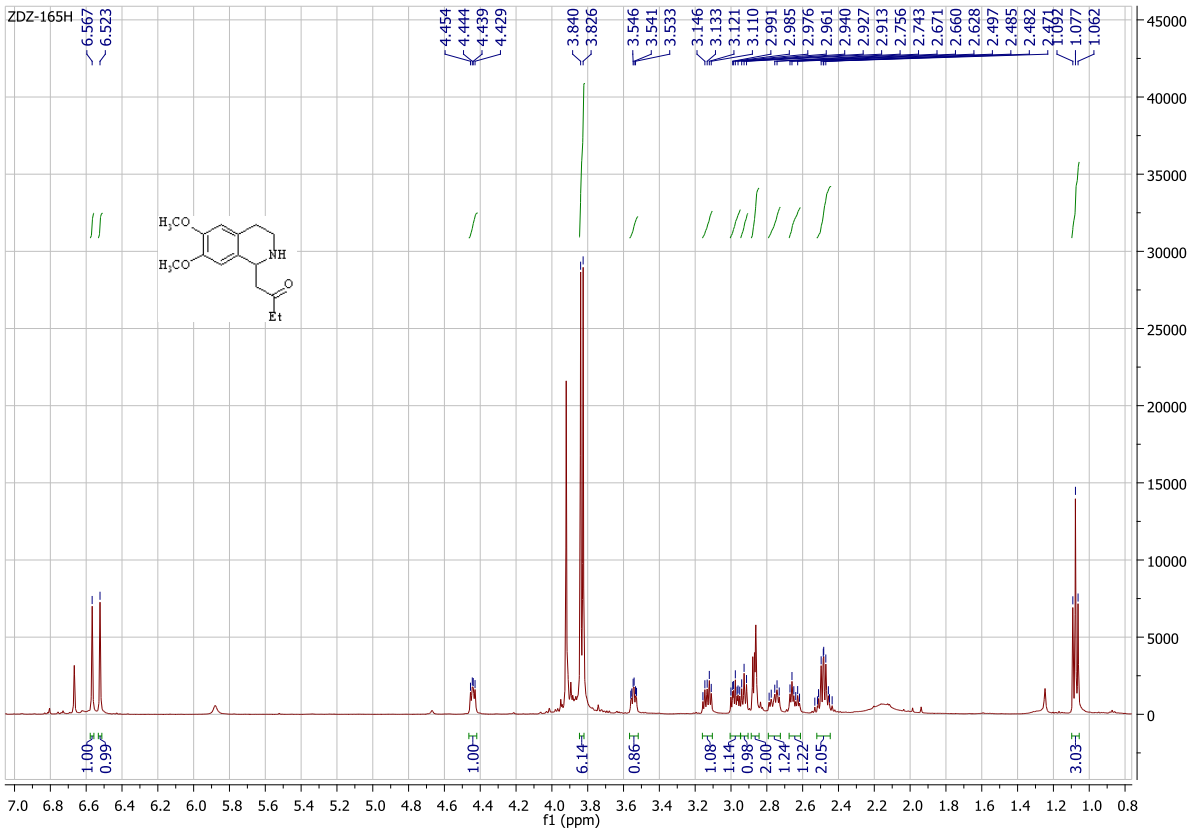

ZDZ-132H
208.258
137.795
135.465
129.433
126.145
125.827
125.515
51.853
50.457
40.981
30.626
29.762
NH
O
f1 (ppm)

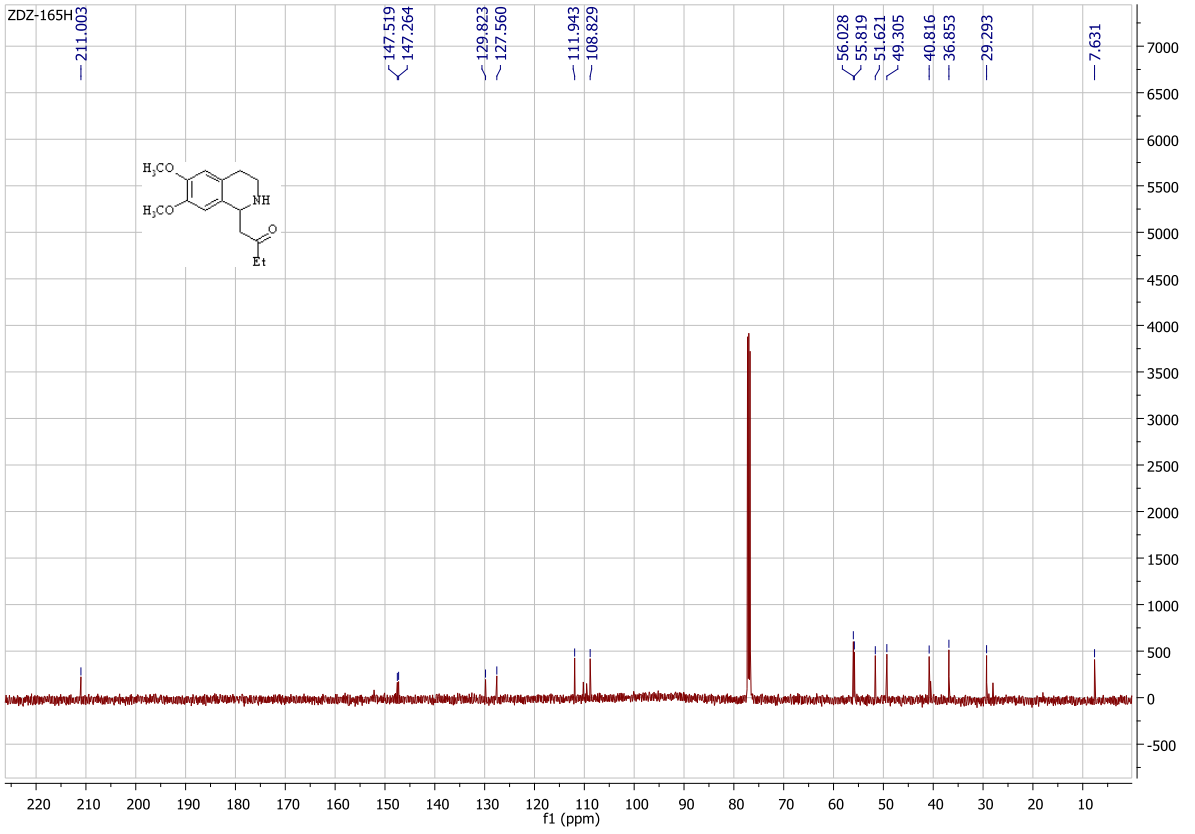
11a


ZDZ-164H
6.568
6.525
4.439
4.426
4.414
3.840
3.830
3.146
3.133
3.122
3.111
3.001
2.991
2.986
2.976
2.967
2.961
2.898
2.886
2.758
2.746
2.668
2.658
2.625
2.267
1.03
1.04
1.00
6.37
1.05
1.13
2.02
1.20
1.20
3.00
f1 (ppm)

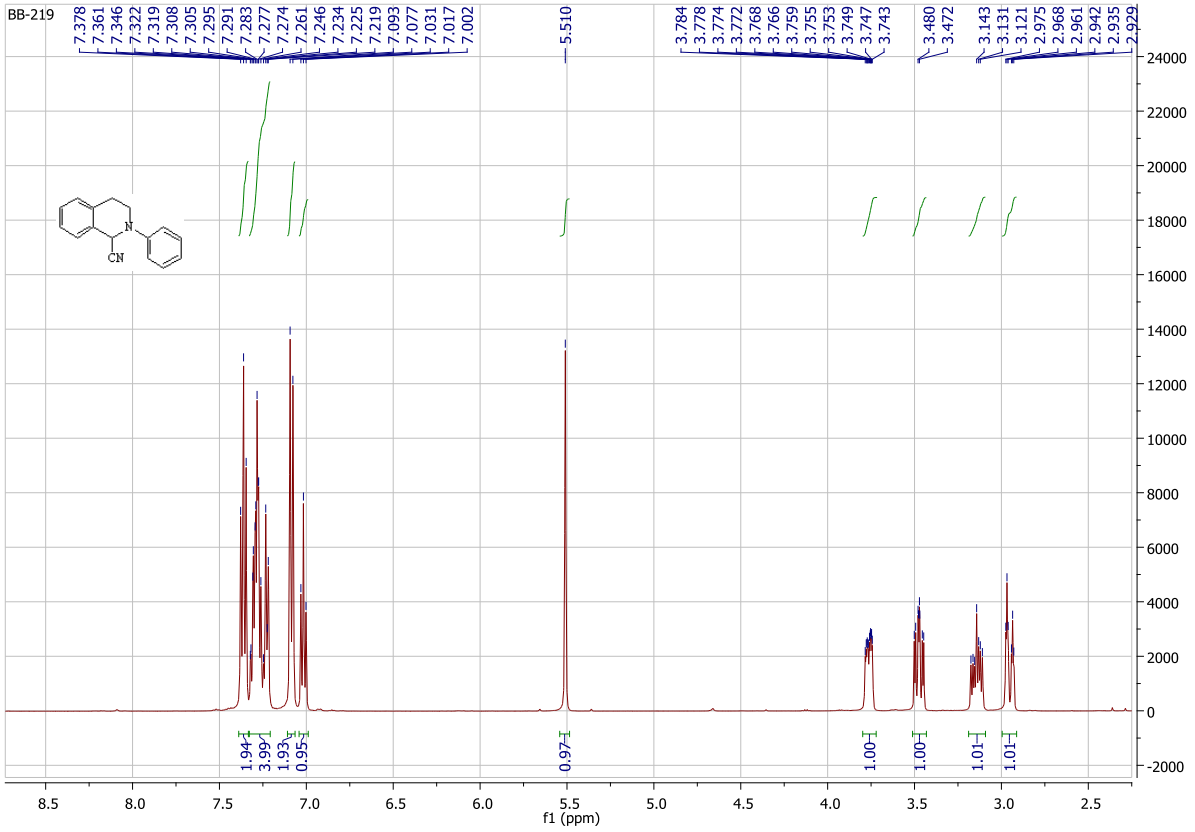

ZDZ-164H
208.352
147.535
147.277
129.652
127.578
111.948
108.772
56.027
55.819
51.548
50.617
40.853
30.778
29.284
f1 (ppm)

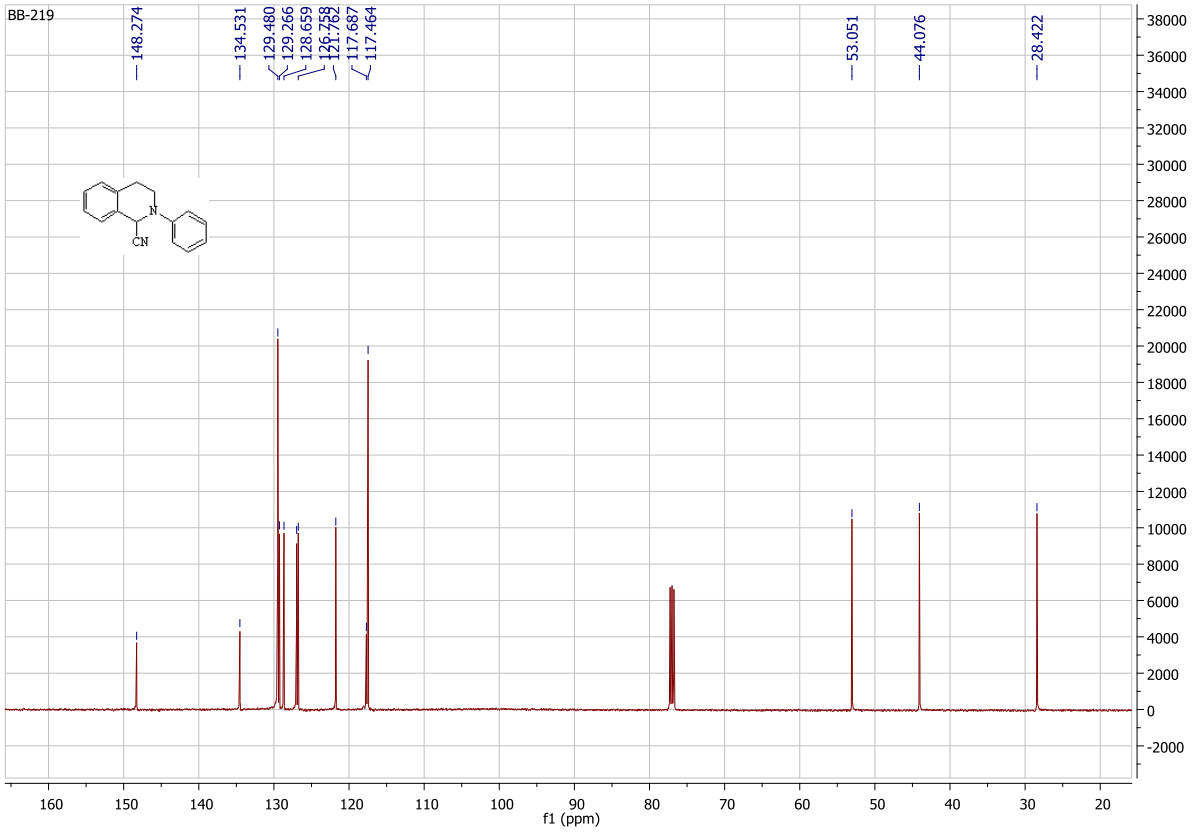
11b


ZDZ-165H
6.567
6.523
4.454
4.444
4.439
4.429
3.840
3.826
3.546
3.541
3.533
3.146
3.133
3.121
3.110
2.991
2.985
2.976
2.961
2.940
2.927
2.913
2.756
2.743
2.671
2.660
2.628
2.497
2.485
2.482
2.471
1.092
1.077
1.062
1.00
0.99
1.00
6.14
0.86
1.08
1.14
0.98
2.00
1.24
1.22
2.05
3.03
f1 (ppm)

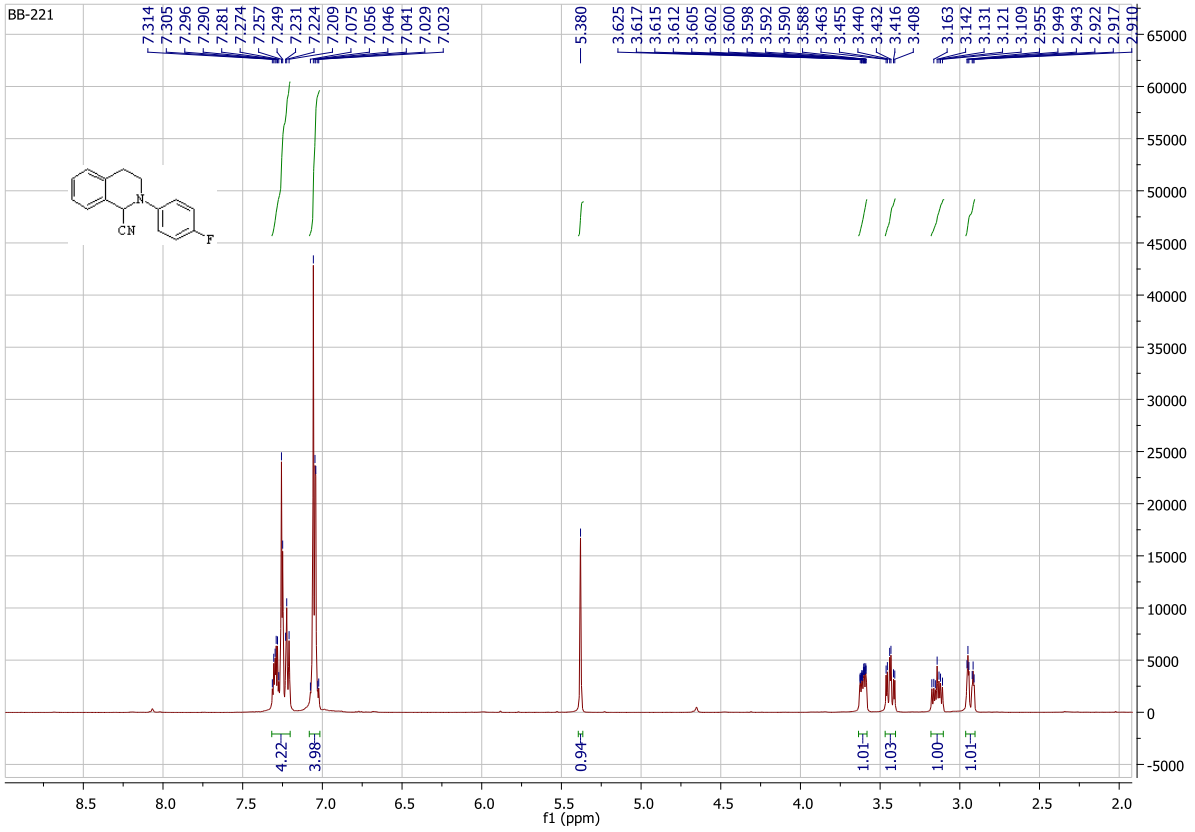

ZDZ-165H
211.003
147.519
147.264
129.823
127.560
111.943
108.829
56.028
55.819
51.621
49.305
40.816
36.853
29.293
7.631
f1 (ppm)

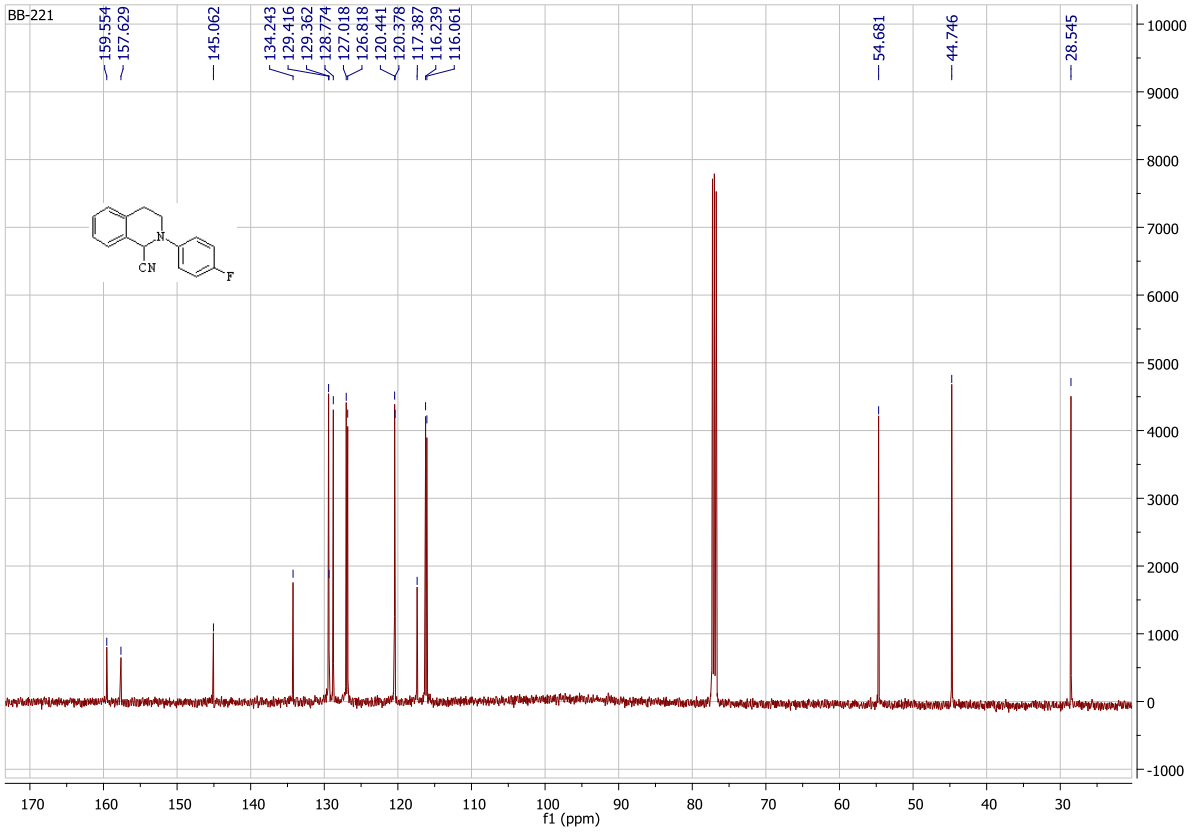
12a


BB-219
7.378
7.361
7.346
7.322
7.319
7.308
7.305
7.295
7.291
7.283
7.277
7.274
7.261
7.246
7.234
7.225
7.219
7.093
7.077
7.031
7.017
7.002
5.510
3.784
3.778
3.774
3.772
3.768
3.766
3.759
3.755
3.753
3.749
3.747
3.743
3.480
3.472
3.143
3.131
3.121
2.975
2.968
2.961
2.942
2.935
2.929
CN
1.94
3.99
1.93
0.95
0.97
1.00
1.00
1.01
1.01
f1 (ppm)

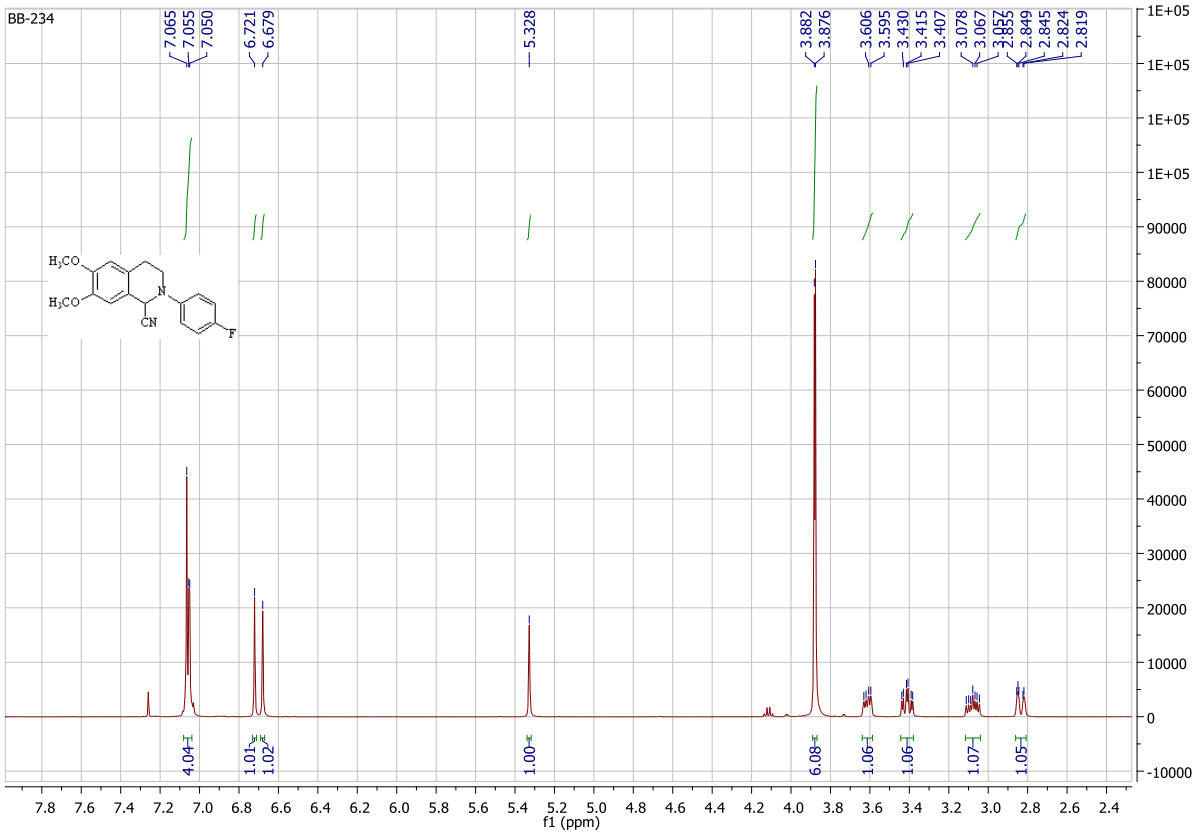

BB-219
148.274
134.531
129.480
129.266
128.659
126.758
126.762
117.687
117.464
53.051
44.076
28.422
CN
f1 (ppm)

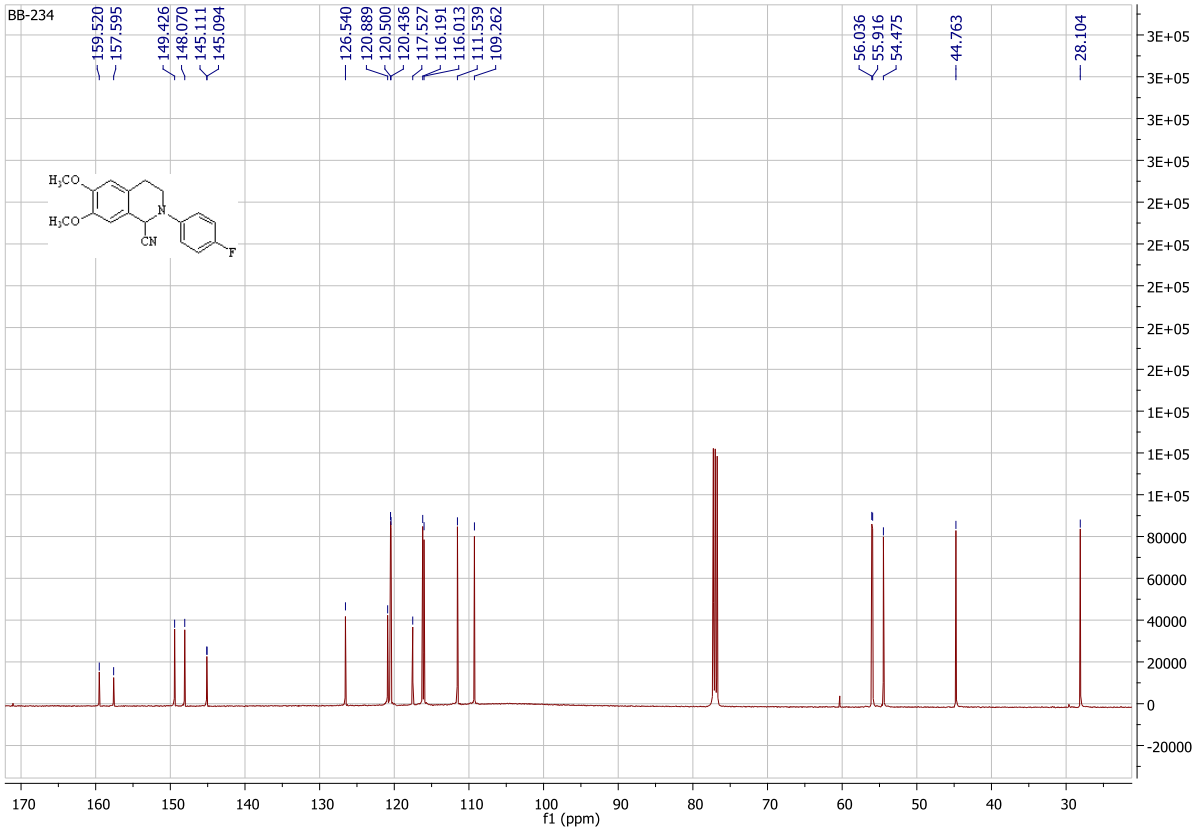
12b


BB-221
7.314
7.305
7.296
7.290
7.281
7.274
7.257
7.249
7.231
7.224
7.209
7.075
7.056
7.046
7.041
7.029
7.023
5.380
3.625
3.617
3.615
3.612
3.605
3.602
3.600
3.598
3.592
3.590
3.588
3.463
3.455
3.440
3.432
3.416
3.408
3.163
3.142
3.131
3.121
3.109
2.955
2.949
2.943
2.922
2.917
2.910
CN
F
4.22
3.98
0.94
1.01
1.03
1.00
1.01
f1 (ppm)

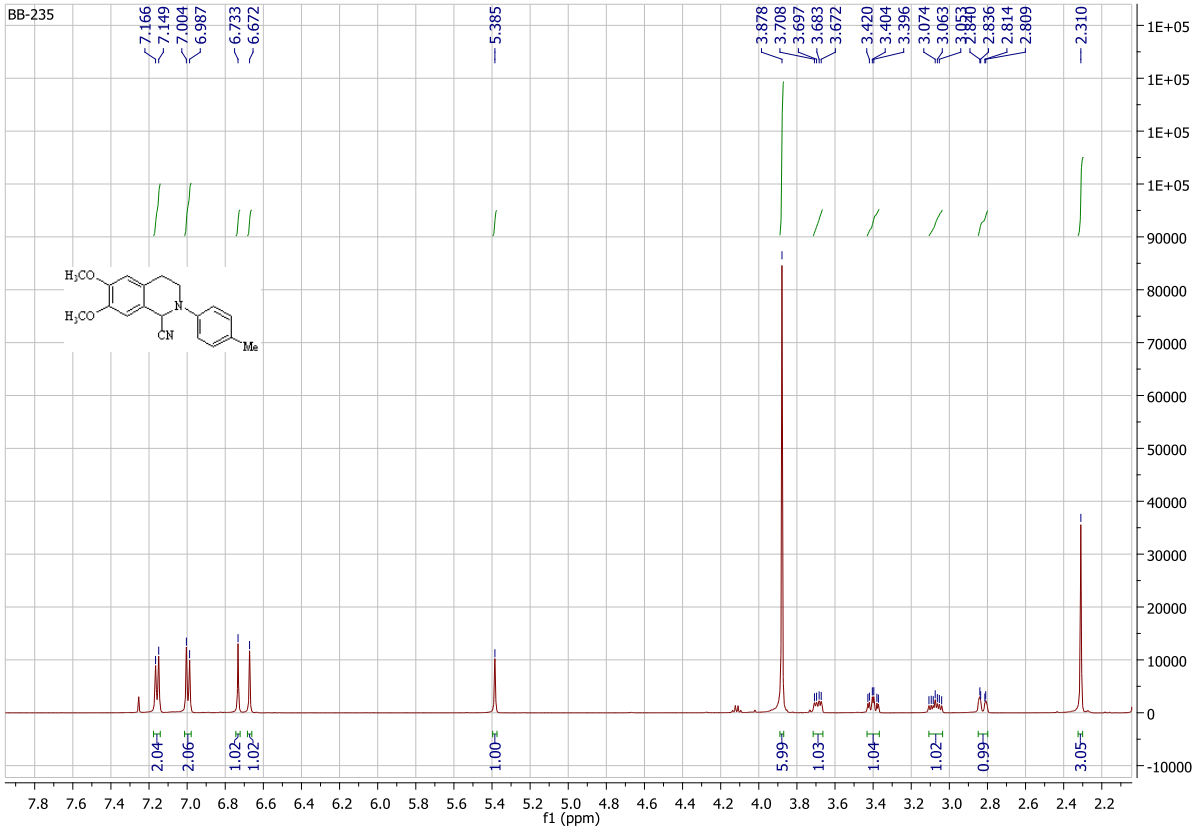

BB-221
159.554
157.629
145.062
134.243
129.416
129.362
128.774
127.018
126.818
120.441
120.378
117.387
116.239
116.061
54.681
44.746
28.545
CN
F
f1 (ppm)

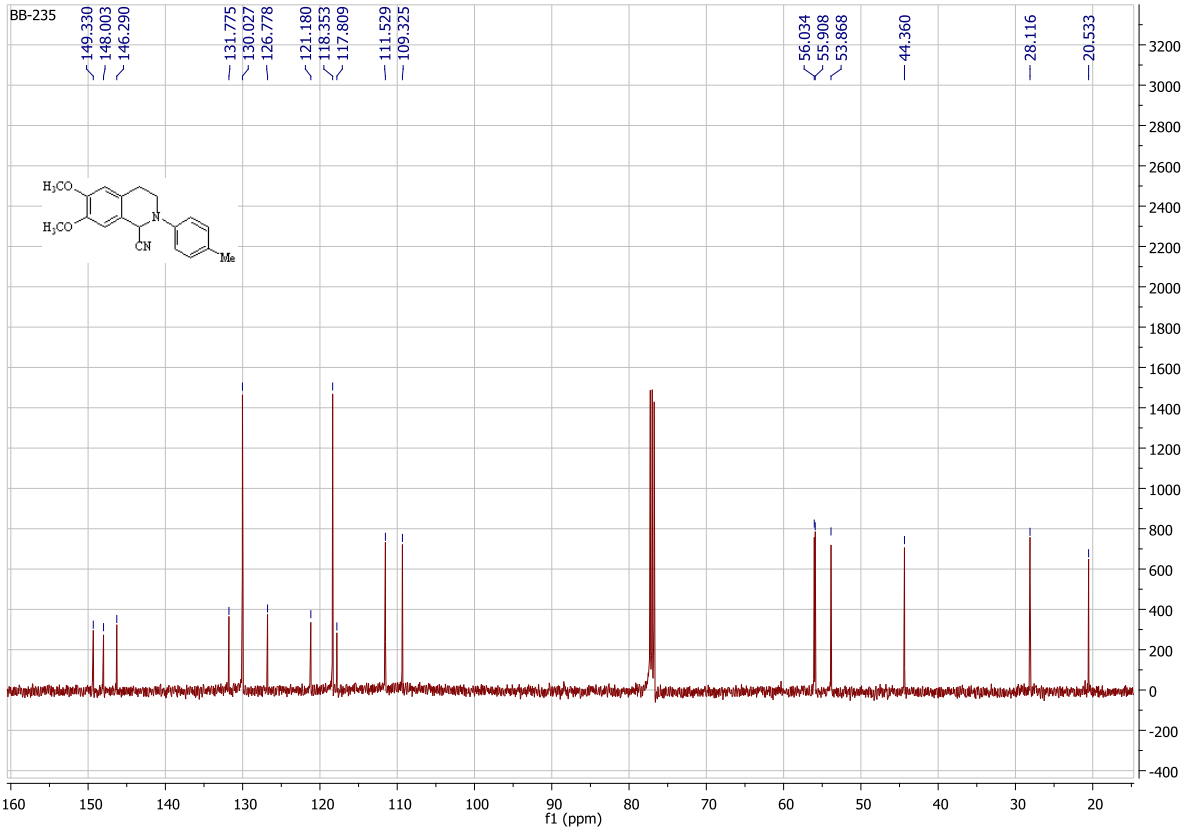
12c


BB-234
7.065
7.055
7.050
6.721
6.679
5.328
3.882
3.876
3.606
3.595
3.430
3.415
3.407
3.078
3.067
2.855
2.849
2.845
2.824
2.819
4.04
1.01
1.02
1.00
6.08
1.06
1.06
1.07
1.05
f1 (ppm)

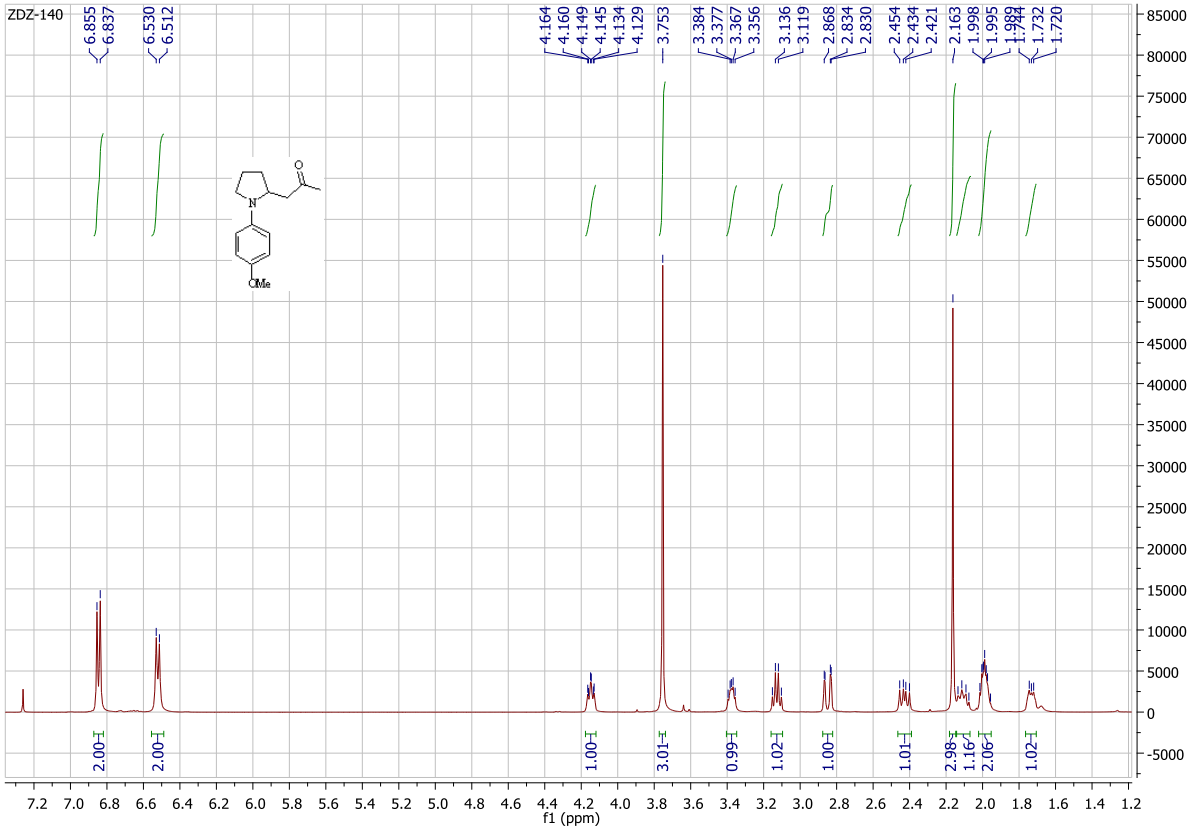

BB-234
159.520
157.595
149.426
148.070
145.111
145.094
126.540
120.889
120.500
120.436
117.527
116.191
116.013
111.539
109.262
56.036
55.916
54.475
44.763
28.104
f1 (ppm)

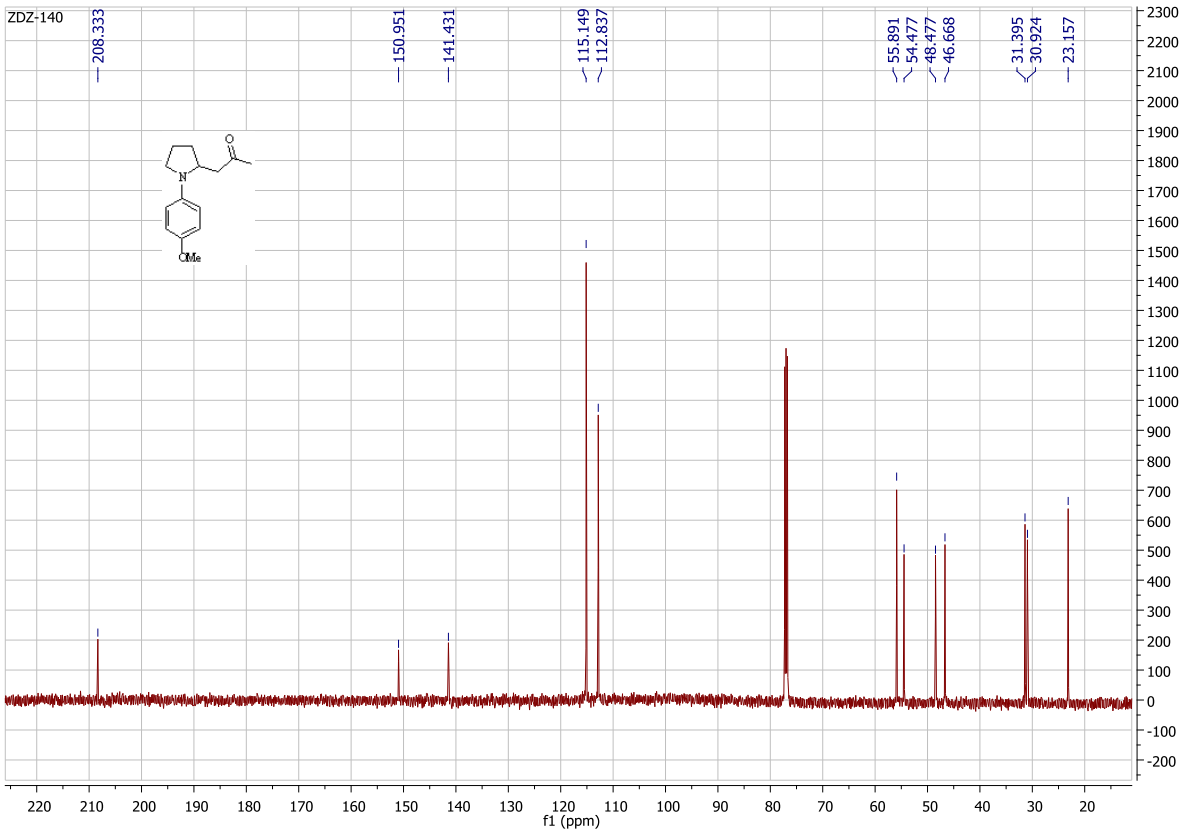
12d


BB-235
7.166
7.149
7.004
6.987
6.733
6.672
5.385
3.878
3.708
3.697
3.683
3.672
3.420
3.404
3.396
3.074
3.063
2.840
2.836
2.814
2.809
2.310
2.04
2.06
1.02
1.02
1.00
5.99
1.03
1.04
1.02
0.99
3.05
f1 (ppm)

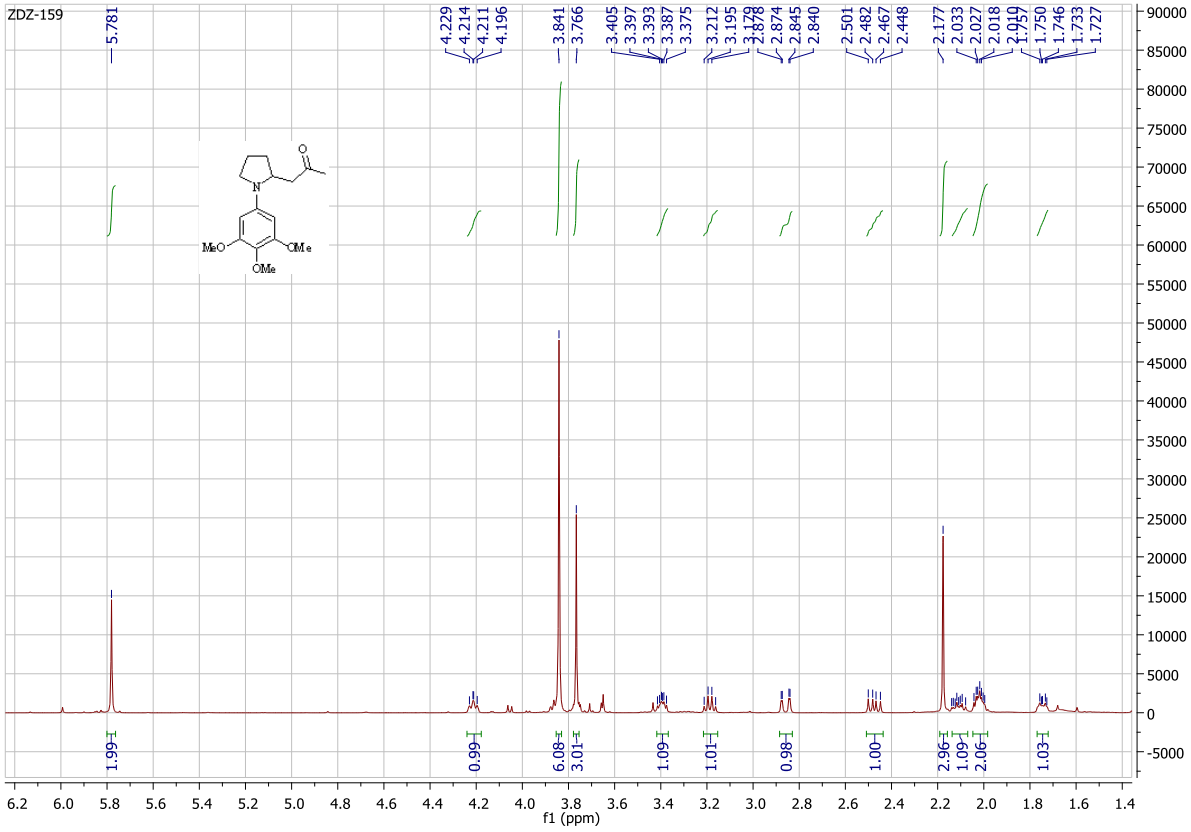

BB-235
149.330
148.003
146.290
131.775
130.027
126.778
121.180
118.353
117.809
111.529
109.325
56.034
55.908
53.868
44.360
28.116
20.533
f1 (ppm)

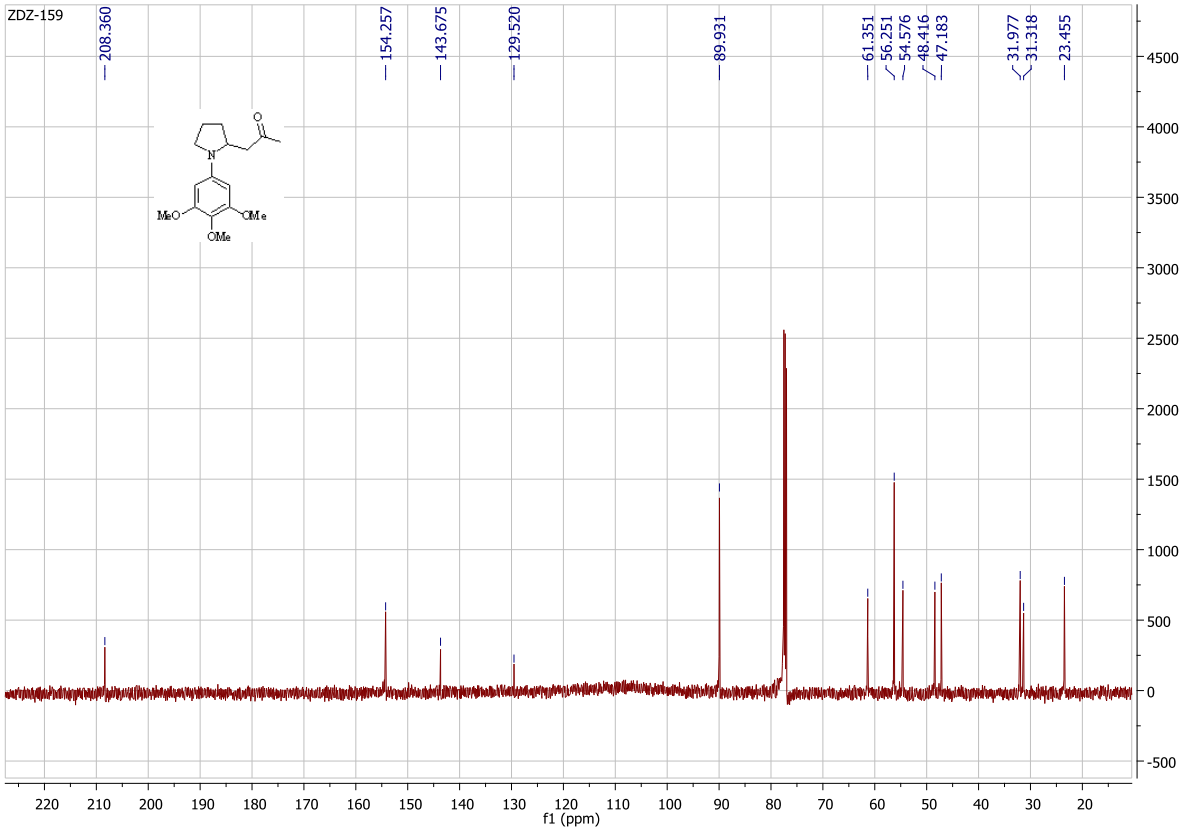
13a


ZDZ-140
6.855
6.837
6.530
6.512
4.164
4.160
4.149
4.145
4.134
4.129
3.753
3.384
3.377
3.367
3.356
3.136
3.119
2.868
2.834
2.830
2.454
2.434
2.421
2.163
1.998
1.995
1.989
1.732
1.720
OMe
2.00
2.00
1.00
3.01
0.99
1.02
1.00
1.01
2.98
1.16
2.06
1.02
f1 (ppm)

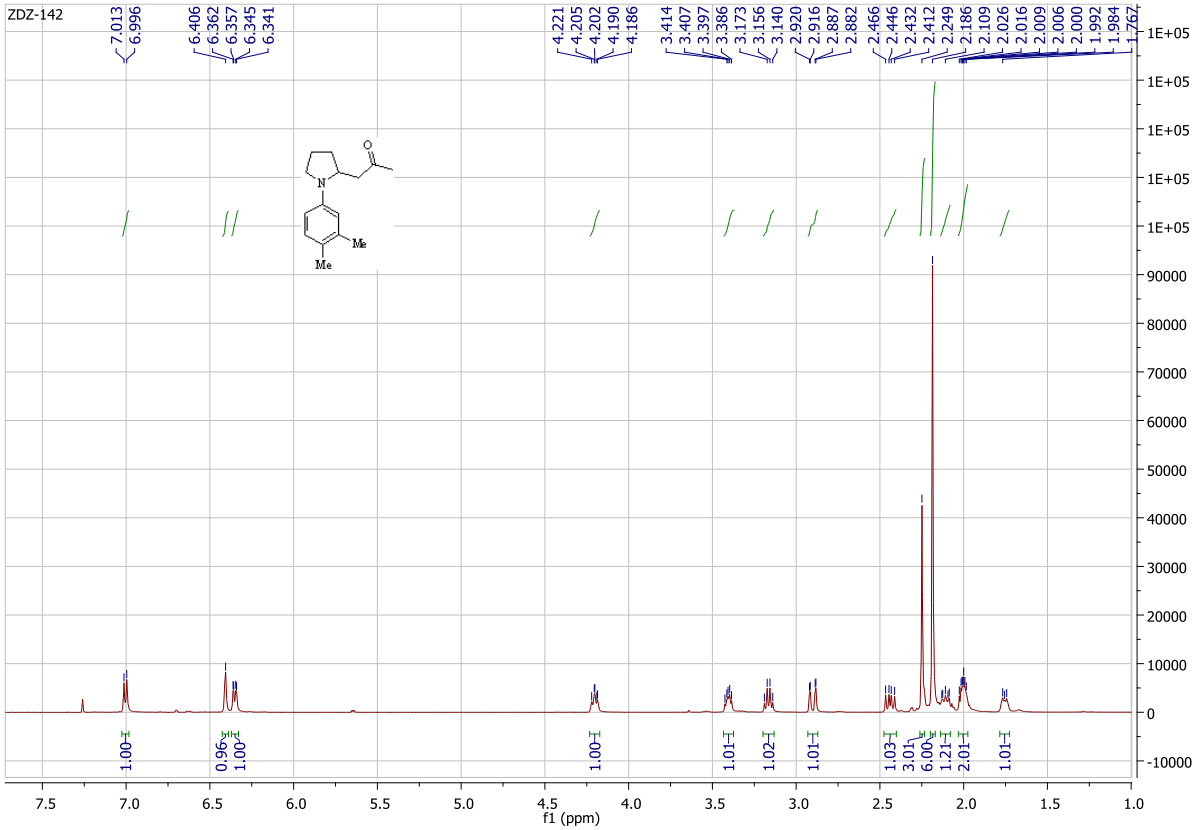

ZDZ-140
208.333
150.951
141.431
115.149
112.837
55.891
54.477
48.477
46.668
31.395
30.924
23.157
OMe
f1 (ppm)

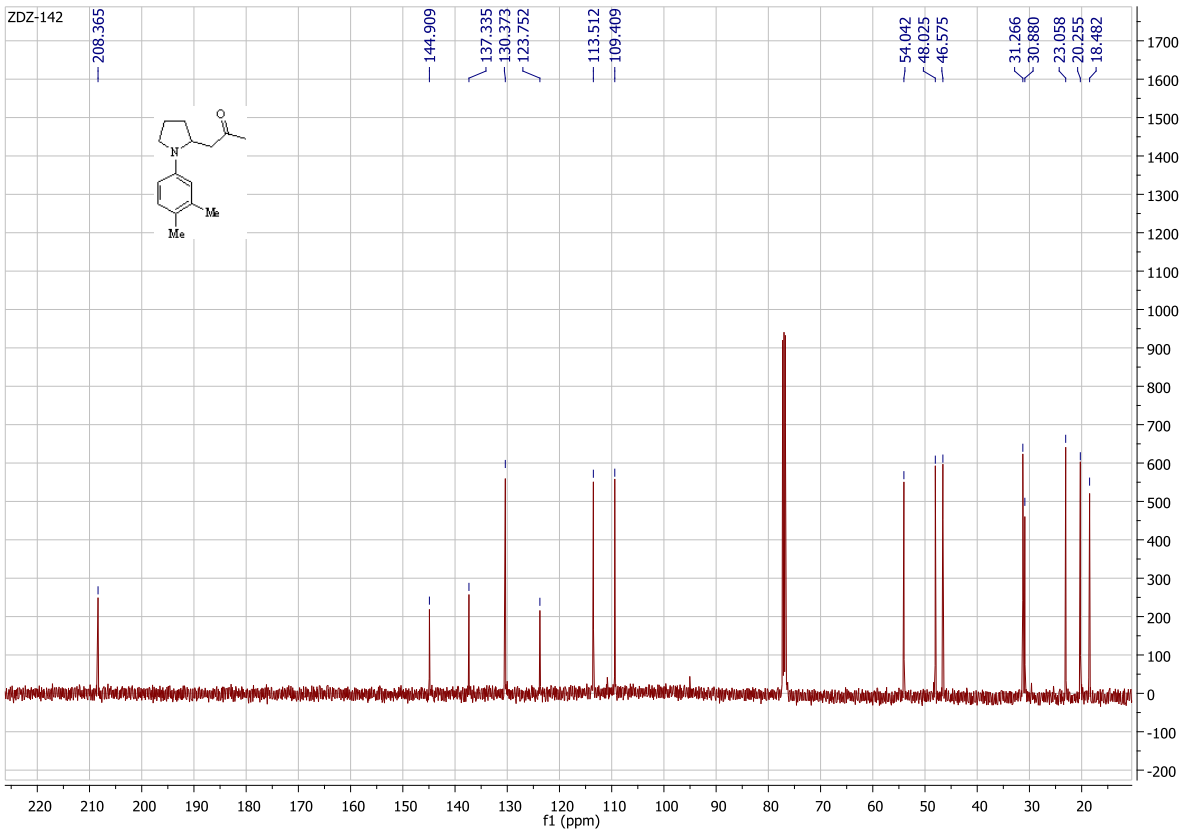
13b


ZDZ-159
5.781
4.229
4.214
4.211
4.196
3.841
3.766
3.405
3.397
3.393
3.387
3.375
3.212
3.195
3.179
2.878
2.874
2.845
2.840
2.501
2.482
2.467
2.448
2.177
2.033
2.027
2.018
2.010
1.757
1.750
1.746
1.733
1.727
MeO
OMe
OMe
1.99
0.99
6.08
3.01
1.09
1.01
0.98
1.00
2.96
1.09
2.06
1.03
f1 (ppm)

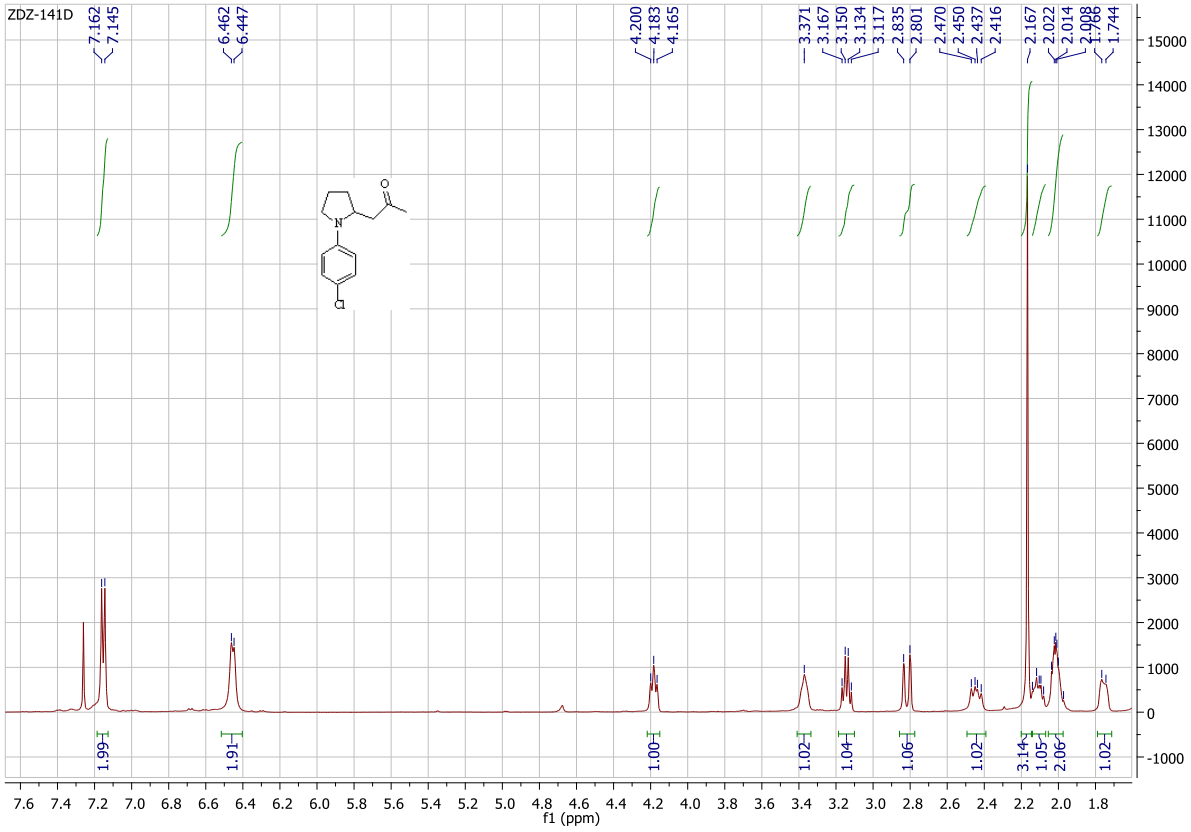

ZDZ-159
208.360
154.257
143.675
129.520
89.931
61.351
56.251
54.576
48.416
47.183
31.977
31.318
23.455
MeO
OMe
OMe
f1 (ppm)

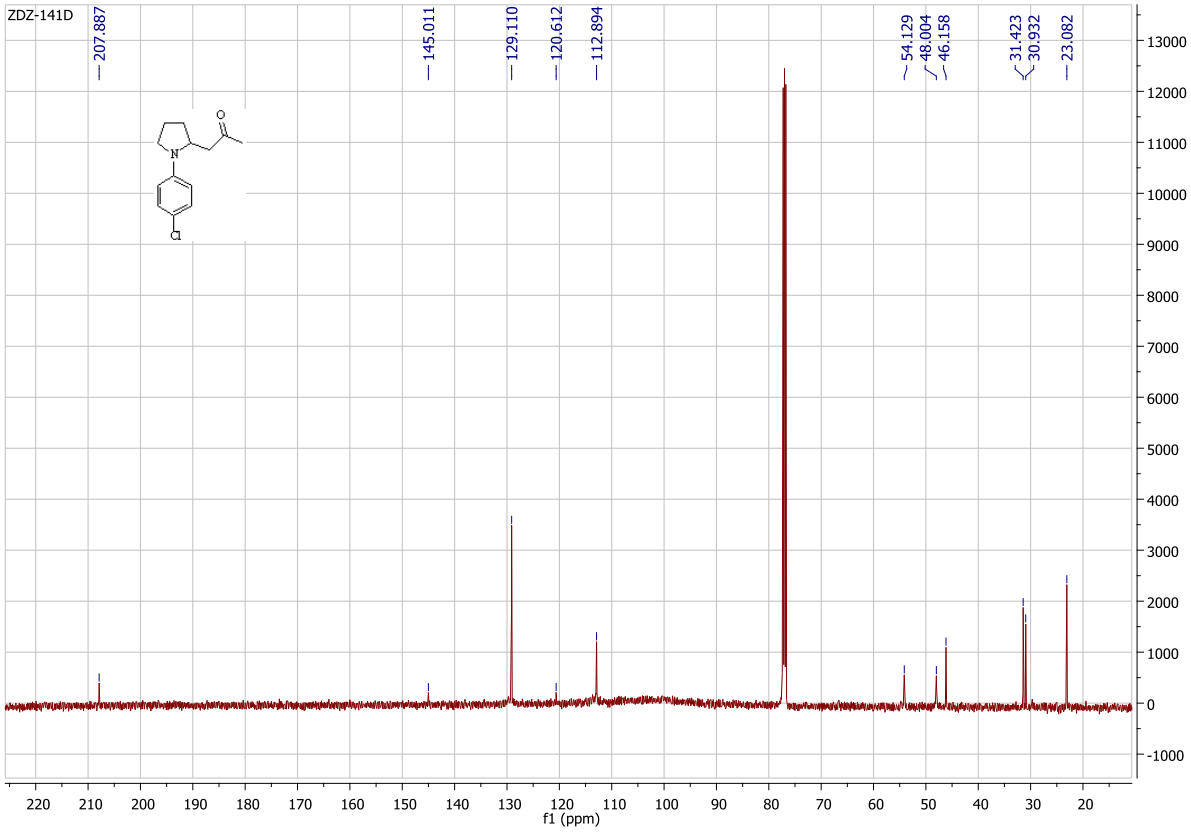
13c


ZDZ-142
7.013
6.996
6.406
6.362
6.357
6.345
6.341
4.221
4.205
4.202
4.190
4.186
3.414
3.407
3.397
3.386
3.173
3.156
3.140
2.920
2.916
2.887
2.882
2.466
2.446
2.432
2.412
2.249
2.186
2.109
2.026
2.016
2.009
2.006
2.000
1.992
1.984
1.767
Me
Me
1.00
0.96
1.00
1.00
1.01
1.02
1.01
1.03
3.01
6.00
1.21
2.01
1.01
f1 (ppm)


ZDZ-142
208.365
144.909
137.335
130.373
123.752
113.512
109.409
54.042
48.025
46.575
31.266
30.880
23.058
20.255
18.482
Me
Me
f1 (ppm)

13d


ZDZ-141D
7.162
7.145
6.462
6.447
4.200
4.183
4.165
3.371
3.167
3.150
3.134
3.117
2.835
2.801
2.470
2.450
2.437
2.416
2.167
2.022
2.014
2.008
1.766
1.744
1.99
1.91
1.00
1.02
1.04
1.06
1.02
3.14
1.05
2.06
1.02
f1 (ppm)


ZDZ-141D
207.887
145.011
129.110
120.612
112.894
54.129
48.004
46.158
31.423
30.932
23.082
f1 (ppm)