Asymmetric Synthesis of Bicyclic Amidines via Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Carbodiimides.

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Supporting Information

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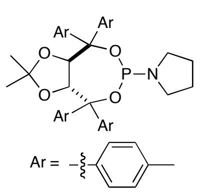
General Methods. All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Triethylamine (peptide synthesis grade) was purchased from Fisher Scientific and used without further purification. Column chromatography was performed on Silicycle Inc. silica gel 60 (230-400 mesh). Thin layer chromatography was performed on Silicycle Inc. 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light (254 nm) and/or potassium permanganate.

Alkynes **1a – 1d, 1f, 1h – 1l, 1p,** and **1q** were purchased from Aldrich Chemicals Co. and used without further purification. Alkynes **1e** and **1g** are known compounds and can be synthesized from the corresponding aryl bromide or iodide via a typical Sonogashira procedure described previously.[1] Alkyne **1m** was prepared by a typical methylation using (trimethylsilyl)diazomethane solution (2.0 M in Et_2O) of the corresponding carboxylic acid, which was purchased from Aldrich Chemicals Co. Alkyne **1n** and **1o** were prepared by typical TBS-protection of the corresponding alcohols, which were purchased from Aldrich Chemicals Co. $[Rh(C_2H_4)_2Cl]_2$ and **L1** were purchased from Strem Chemical, Inc. and used without further purification. Synthesis of **L2** was described previously while **L3** – **L5** can be synthesized by the procedure described within. All racemate products are obtained via the same cycloaddition using the *rac*-**L3** as the ligand. Carbodiimides **2a** – **2f**, **5**, and **8** can be synthesized by the procedures described within.

General procedure for synthesis of ligands:

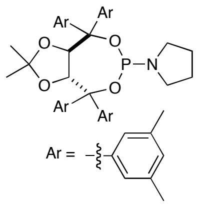
To a flame-dried round bottom flask charged with a magnetic stir bar was added 4 Å molecular sieves, the diol (2.11 mmol) and 9 ml of THF. To the reaction mixture was added Et_3N (3.40 eq, 7.17 mmol) and phosphorus trichloride (1.2 eq, 2.53 mmol) dropwise at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 40 minutes. A solution of amine (10 eq, 21.10 mmol) in 11 ml of THF was added slowly at 0 °C. The reaction was allowed to stir overnight at ambient temperature before it was diluted with diethyl ether and filtered. The filtrate was concentrated in vacuo and the resulting crude material was purified by flash column chromatography (4:96 EtOAc:Hexane) to afford the desired phosphoramidite as a white solid.



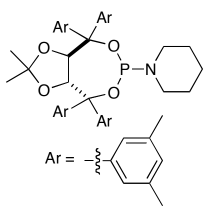
1-[4,4,8,8-Tetrakis-(4-methyl-phenyl)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl]-pyrrolidine (L3). Flash Chromatography (96:4 Hexanes:EtOAc) yielded a white solid (45%). R_f = 0.50 (90:10 Hexanes:EtOAc); $[\alpha]_D^{20}$ = -109.4 (c=1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (2H, d, *J* = 8.1 Hz), 7.46 (2H, d, *J* = 8.3 Hz), 7.34 (2H, d, *J* = 8.1 Hz), 7.29 (2H, d, *J* = 8.1 Hz), 7.11-7.01 (6H, m) 7.04 (2H, d, 8.1 Hz), 5.15 (1H, dd, *J* = 8.5, 3.4 Hz), 4.76 (1H, d, *J* = 8.5 Hz), 3.41-3.37 (2H, m), 3.25-3.21 (2H, m), 2.31 (3H, s), 2.31 (3H, s), 2.30 (3H, s), 2.28 (3H, s) 1.83-1.78 (4H, m), 1.31 (3H, s), 0.29 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 144.2,

[1] Yu, R. T.; Rovis, T. *J. Am. Chem. Soc.* **2006,** *128,* 12370.

139.6, 139.5, 137.0, 136.8, 136.6, 129.1, 129.0, 128.8, 128.5, 128.4, 128.0, 127.2, 127.2, 126.3, 111.6, 83.1, 82.8, 82.6, 81.6, 81.1, 45.2, 45.0, 27.8, 26.2, 26.2, 25.6, 21.3, 21.3, 21.2; ^{31}P NMR (75 MHz, $CDCl_3$) δ 138.74; IR (Thin Film). 2924, 2862, 1507, 1452, 1377, 1247, 1161, 1044, 907 cm^{-1}.

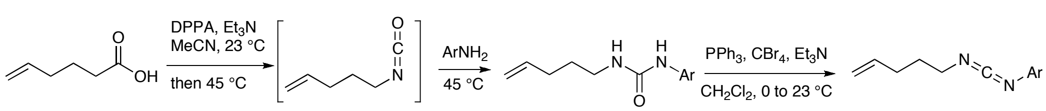


1-[4,4,8,8-Tetrakis-(3,5-dimethyl-phenyl)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl]-pyrrolidine (L4). Flash Chromatography (96:4 Hexanes:EtOAc) yielded a white solid (50%). R_f = 0.50 (90:10 Hexanes:EtOAc); $[\alpha]_D^{20}$ = -108.0 (c=1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, s), 7.16 (2H, s), 7.04 (2H, s), 7.02 (2H, s), 6.84 (3H, s), 6.80 (1H, s), 5.08 (1H, dd, *J* = 8.5, 2.5 Hz), 4.74 (1H, d, *J* = 8.0 Hz), 3.47-3.35 (2H, m), 3.35-3.15 (2H, m), 2.27 (6H, s), 2.25 (12H, s), 2.24 (6H, s), 1.86-1.72 (4H, m), 1.32 (3H, s), 0.25 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.9, 142.2, 142.1, 137.3, 136.9, 136.7, 136.3, 129.2, 128.9, 128.7, 127.9, 127.0, 126.8, 125.3, 125.2, 111.7, 83.1 (d, *J* = 4.5 Hz), 82.9, 82.7, 81.8, 81.1 (d, *J* = 5.5 Hz), 45.1 (d, *J* = 19.0 Hz), 27.9, 26.3, 26.2, 25.7, 21.9, 21.8; ^{31}P NMR (75 MHz, $CDCl_3$) δ 138.40; IR (Thin Film). 2917, 2866, 1601, 1456, 1379, 1214, 1159, 1042, 854 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 678.3707, found 678.3702.

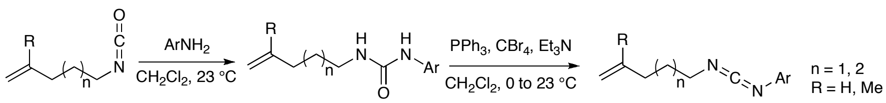


(*R*,*R*)-1-[4,4,8,8-Tetrakis-(3,5-dimethyl-phenyl)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl]-piperidine (L5) Flash Chromatography (96:4 Hexanes:EtOAc) yielded a white solid (52%); R_f = 0.50 (90:10 Hexanes:EtOAc); $[\alpha]_D^{20}$ = -108.0 (c=1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (2H, s), 7.20 (2H, s), 7.04 (4H, s), 6.84 (3H, s), 6.79 (1H, s), 5.02 (1H, dd, *J* = 8.5, 3.0 Hz), 4.67 (1H, d, *J* = 8.5 Hz), 3.34-3.27 (2H, m), 3.20-3.08 (2H, m), 2.26 (6H, s), 2.26 (6H, s), 2.25 (6H, s), 2.24 (6H, s), 1.65-1.50 (6H, m), 1.37 (3H, s), 0.25 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.0, 142.1, 137.3, 136.9, 136.7, 136.4, 129.2, 128.9, 128.8, 128.7, 127.1, 126.8, 125.3, 111.5, 83.3, 82.9, 82.7, 81.4, 81.3, 81.2, 77.4, 45.3, 45.1, 27.9, 27.2, 27.2, 25.7, 25.5, 21.9, 21.8, 21.7; ^{31}P NMR (75 MHz, $CDCl_3$) δ 138.76; IR (Thin Film) 2931, 2851, 1600, 1448, 1370, 1215, 1159, 1040, 940 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 692.3863, found 692.3843.

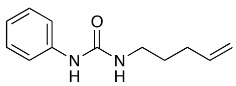
General procedure for synthesis of carbodiimides:



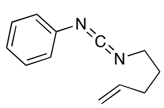
Procedure A: To a solution of 5-hexenoic acid (5.26 mmol) in 6 ml of MeCN (ca. 1 M) was added 0.77 ml of Et_3N (1.06 eq, 5.57 mmol) slowly, followed by 1.2 ml of diphenyl phosphoryl azide (1.06 eq, 5.57 mmol) dropwise at ambient temperature. The reaction mixture was stirred at ambient temperature for 30 minutes before heated to 45 °C in an oil bath. The reaction mixture was stirred at 45 °C for additional two hours to ensure complete conversion to the isocyanate. The amine (1.2 eq, 6.31 mmol) was added, and the resulting reaction mixture was stirred at 45 °C for 12 hours fitted with a reflux condenser. The reaction was diluted with Et_2O (40 ml), washed with 1M HCl (2x20 ml) and brine (20 ml). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The urea was then purified by silica gel flash chromatography (70:30 Hexane:EtOAc). To a solution of the urea (1.76 mmol) in 14 ml of CH_2Cl_2 was added triphenyl phosphine (2.0 eq, 3.53 mmol), 1.0 ml of Et_3N (4.0 eq, 7.05 mmol), followed by a solution of CBr_4 (2.0 eq, 3.53 mmol) in 5 ml of CH_2Cl_2 slowly at 0 °C. The reaction mixture was stirred at ambient temperature for 12 hours and then concentrated *in vacuo*. The target carbodiimide was purified by silica gel flash chromatography (96:4 Hexane:EtOAc). Note: Two consecutive purifications of flash chromatography are recommended, as the purity of carbodiimides is vital to the success of cycloaddition.



Procedure B: To a solution of isocyanate[2] (2.70 mmol) in 12 ml of CH_2Cl_2 was added the amine (1.05 eq, 2.83 mmol). The reaction mixture was stirred at ambient temperature for 12 hours and then concentrated *in vacuo*. The crude material was dissolved in Et_2O followed by addition of Hexane. The urea was then precipitated and filtered as a white solid. To a solution of the urea (1.76 mmol) in 14 ml of CH_2Cl_2 was added triphenyl phosphine (2.0 eq, 3.53 mmol), 1.0 ml of Et_3N (4.0 eq, 7.05 mmol), followed by a solution of CBr_4 (2.0 eq, 3.53 mmol) in 5 ml of CH_2Cl_2 slowly at 0 °C. The reaction mixture was stirred at ambient temperature for 12 hours and then concentrated *in vacuo*. The target carbodiimide was purified by silica gel flash chromatography (96:4 Hexane:EtOAc). Note: Two consecutive purifications of flash chromatography are recommended, as the purity of carbodiimides is vital to the success of cycloaddition.

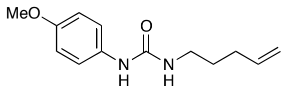


1-(pent-4-enyl)-3-phenylurea. Procedure B yielded a white solid (81%); R_f = 0.56 (1:1 Hex/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (br s, 1H), 7.26 – 7.22 (m, 4H), 7.01 (m, 1H), 5.73 (ddt, 1H, *J* = 6.6, 10.2, 16.6 Hz), 5.58 (m, 1H), 4.99 – 4.92 (m, 2H), 3.18 (dt, 2H, *J* = 6.4, 6.4 Hz), 2.03 (dt, 2H, *J* = 7.2, 7.2 Hz), 1.54 (tt, 2H, *J* = 7.2, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 139.1, 138.0, 129.3, 123.5, 120.8, 115.3, 39.9, 31.2, 29.5; IR (Thin Film) 3338, 2925, 1647, 1596, 1558, 1500, 1443, 1310, 1240 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 205.13353, found 205.13350.

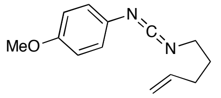


***N*-((pent-4-enylimino)methylene)aniline (2a).** Procedure B yielded an clear oil (66%); R_f = 0.63 (95:5 Hex/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, 2H, *J* = 7.5 Hz), 7.13 – 7.09 (m, 3H), 5.80 (ddt, 1H, *J* = 6.8, 10.2, 17.0 Hz), 5.07 (dm, 1H, *J* = 17.1 Hz), 5.02 (dm, 1H, *J* = 10.0 Hz), 3.44 (t, 2H, *J* = 6.8 Hz), 2.20 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.78 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 137.4, 136.3, 129.6, 124.8, 123.7, 115.9, 46.3, 31.0, 30.6; IR (Thin Film) 2931, 2135, 1595, 1502, 1344, 1153 cm^{-1}.

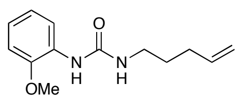
[2] (a) Yu, R. T.; Rovis, T. *J. Am. Chem. Soc.* **2006,** *128,* 2782. (b) Lee, E. E.; Rovis, T. *Org. Lett. In press*.



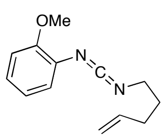
1-(4-methoxyphenyl)-3-(pent-4-enyl)urea. Procedure A yielded a white solid (52%); R_f = 0.33 (1:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, 2H, *J* = 7.7 Hz), 6.92 (m, 1H), 6.79 (d, 2H, *J* = 7.8 Hz), 5.73 (m, 1H), 5.16 (m, 1H), 4.97 – 4.89 (m, 2H), 3.74 (s, 3H), 3.16 (m, 2H), 2.01 (dt, 2H, *J* = 6.2, 6.2 Hz), 1.52 (tt, 2H, *J* = 6.6, 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 156.8, 138.1, 131.4, 124.5, 115.2, 114.6, 55.7, 40.0, 31.3, 29.5; IR (Thin Film) 3313, 2938, 1634, 1570, 1513, 1297, 1246, 1176, 1030 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 235.14410, found 235.14350.



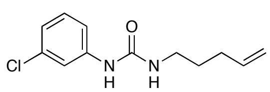
4-methoxy-*N*-((pent-4-enylimino)methylene)aniline (2b). Procedure A yielded an clear oil (46%); R_f = 0.26 (95:5 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, 2H, *J* = 8.7 Hz), 6.82 (d, 2H, *J* = 8.7 Hz), 5.80 (ddt, 1H, *J* = 6.6, 10.0, 16.8 Hz), 5.05 (dm, 1H, *J* = 17.3 Hz), 5.01 (dm, 1H, *J* = 10.0 Hz), 3.78 (s, 3H), 3.40 (t, 2H, *J* = 6.8 Hz), 2.19 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.76 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 137.5, 137.3, 133.2, 124.5, 115.8, 114.8, 55.7, 46.4, 31.0, 30.6; IR (Thin Film) 2936, 2129, 1582, 1507, 1289, 1240, 1170, 1033 cm^{-1}.



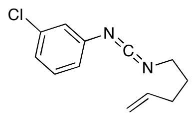
1-(2-methoxyphenyl)-3-(pent-4-enyl)urea. Procedure A yielded a white solid (59%); R_f = 0.53 (1:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, 1H, *J* = 1.9, 7.7 Hz), 7.03 (s, 1H), 6.98 – 6.90 (m, 2H), 6.84 (dd, 2H, *J* = 1.7, 7.7 Hz), 5.78 (ddt, 1H, *J* = 6.6, 10.2, 17.1 Hz), 5.21 (m, 1H), 5.01 (dm, 1H, *J* = 17.0 Hz), 4.96 (dm, 1H, *J* = 10.2 Hz), 3.81 (s, 3H), 3.26 (dt, 2H, *J* = 6.7, 6.7 Hz), 2.09 (dt, 2H, *J* = 7.2, 7.2 Hz), 1.62 (tt, 2H, *J* = 7.2, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.5, 138.1, 128.9, 122.7, 121.4, 119.9, 115.3, 110.4, 55.8, 40.0, 31.3, 29.5; IR (Thin Film) 3326, 2933, 1640, 1602, 1564, 1462, 1284, 1252, 1170, 1025 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 235.14410, found 235.14318.



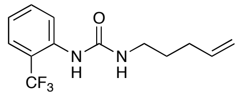
2-methoxy-*N*-((pent-4-enylimino)methylene)aniline (2c). Procedure A yielded an clear oil (72%); R_f = 0.29 (95:5 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (ddd, 1H, *J* = 1.5, 7.7, 7.7 Hz), 7.02 (dd, 1H, *J* = 1.6, 8.1 Hz), 6.89 – 6.85 (m, 2H), 5.81 (ddt, 1H, *J* = 6.6, 10.0, 16.8 Hz), 5.07 (dm, 1H, *J* = 17.0 Hz), 5.00 (dm, 1H, *J* = 10.2 Hz), 3.89 (s, 3H), 3.41 (t, 2H, *J* = 6.8 Hz), 2.20 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.77 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 137.7, 137.1, 129.1, 125.5, 124.8, 121.2, 115.6, 111.3, 56.1, 46.4, 31.1, 30.4; IR (Thin Film) 2936, 2135, 1589, 1502, 1464, 1344, 1245, 1109, 1027 cm^{-1}.



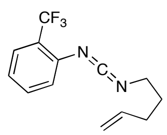
1-(3-chlorophenyl)-3-(pent-4-enyl)urea. Procedure A yielded a yellow oil (51%); R_f = 0.63 (1:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.33 (s, 1H), 7.13 – 7.11 (m, 2H), 6.96 (m, 1H), 5.77 (m, 1H), 5.73 (ddt, 1H, *J* = 6.6, 10.0, 16.8 Hz), 5.00 – 4.85 (m, 2H), 3.18 (dt, 2H, *J* = 6.8, 6.8 Hz), 2.03 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.53 (tt, 2H, *J* = 7.2, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 140.4, 137.8, 134.8, 130.2, 123.1, 120.1, 118.0, 115.4, 39.9, 31.2, 29.3; IR (Thin Film) 3326, 2931, 1653, 1595, 1558, 1475, 1271, 1233, 1093, 1074 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 239.09456, found 239.09391.



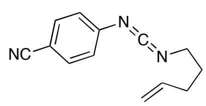
3-chloro-*N*-((pent-4-enylimino)methylene)aniline (2d). Procedure A yielded an clear oil (55%); R_f = 0.57 (10:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 1H), 7.08 – 7.06 (m, 2H), 6.96 (dm, 1H, *J* = 8.1 Hz), 5.80 (ddt, 1H, *J* = 6.8, 10.2, 17.1 Hz), 5.09 – 5.01 (m, 2H), 3.46 (t, 2H, *J* = 6.8 Hz), 2.20 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.78 (tt, 2H, *J* = 6.8, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.2, 134.9, 134.8, 130.4, 124.9, 123.9, 121.9, 116.0, 46.2, 31.0, 30.5; IR (Thin Film) 2936, 2140, 1589, 1485, 1344, 1164, 1109 cm^{-1}.



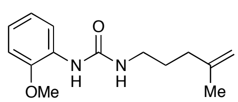
1-(pent-4-enyl)-3-(2-(trifluoromethyl)phenyl)urea. Procedure A yielded a white solid (70%); R_f = 0.47 (7:3 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 1H, *J* = 7.9 Hz), 7.56 (d, 1H, *J* = 7.7 Hz), 7.47 (dd 1H, *J* = 7.7, 7.7 Hz), 7.20 – 7.16 (m, 2H), 6.85 (m, 1H), 5.75 (ddt, 1H, *J* = 6.6, 10.2, 16.8 Hz), 5.01 – 4.92 (m, 2H), 3.17 (dt, 2H, *J* = 6.8, 6.8 Hz), 2.04 (dt, 2H, *J* = 6.8, 6.8 Hz), 1.56 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 137.9, 136.5, 133.0, 129.6, 126.3, 125.5, 124.0, 120.4, 115.4, 40.2, 31.2, 29.1; IR (Thin Film) 3326, 2938, 1650, 1564, 1456, 1322, 1284, 1175, 1119, 1030 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 273.12092, found 273.12023.



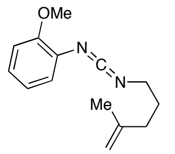
***N*-((pent-4-enylimino)methylene)-2-(trifluoromethyl)aniline (2e).** Procedure A yielded an clear oil (60%); R_f = 0.52 (95:5 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 1H, *J* = 7.9 Hz), 7.46 (dd, 1H, *J* = 7.9, 7.9 Hz), 7.25 (d, 1H, *J* = 7.7 Hz), 7.15 (dd, 1H, *J* = 7.7, 7.7 Hz), 5.79 (ddt, 1H, *J* = 6.8, 10.2, 17.0 Hz), 5.05 (dm, 1H, *J* = 17.3 Hz), 5.01 (dm, 1H, *J* = 10.8 Hz), 3.47 (t, 2H, *J* = 6.8 Hz), 2.19 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.78 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.3, 132.8, 132.6, 127.0, 126.9, 125.5, 124.1, 122.4, 116.0, 46.0, 30.9, 30.4; IR (Thin Film) 2942, 2151, 1581, 1507, 1462, 1315, 1130, 1056 cm^{-1}.



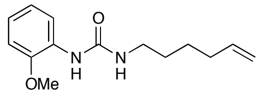
4-((pent-4-enylimino)methyleneamino)benzonitrile (2f). After a quick flash chromatography, the crude urea was converted to the target carbodiimide according to Procedure A as an clear oil (25% overall); R_f = 0.18 (95:5 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, *J* = 8.3 Hz), 7.12 (d, 2H, *J* = 8.3 Hz), 5.79 (ddt, 1H, *J* = 6.6, 10.2, 17.1 Hz), 5.08 – 5.01 (m, 2H), 3.50 (t, 2H, *J* = 6.8 Hz), 2.19 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.79 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 137.0, 133.6, 132.5, 124.3, 119.1, 116.2, 107.7, 46.0, 30.9, 30.4; IR (Thin Film) 2936, 2230, 2150, 1594, 1507, 1340, 1155 cm^{-1}.



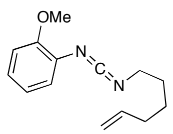
1-(2-methoxyphenyl)-3-(4-methylpent-4-enyl)urea. Procedure B yielded a white solid (67%); R_f = 0.54 (1:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 1H, *J* = 7.7 Hz), 6.98 – 6.90 (m, 3H), 6.84 (d, 2H, *J* = 7.9 Hz), 5.15 (m, 1H), 4.70 (s, 1H), 4.67 (s, 1H), 3.82 (s, 3H), 3.25 (dt, 2H, *J* = 6.7, 6.7 Hz), 2.05 (t, 2H, *J* = 7.6 Hz), 1.70 (s, 3H), 1.67 (tt, 2H, *J* = 7.3, 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 148.5, 145.3, 128.8, 122.7, 121.4, 120.0, 110.5, 110.4, 55.8, 40.3, 35.2, 28.2, 22.6; IR (Thin Film) 3326, 2938, 1640, 1602, 1558, 1462, 1431, 1246, 1106, 1025 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 249.15975, found 249.15873.



2-methoxy-*N*-((4-methylpent-4-enylimino)methylene)aniline (5). Procedure B yielded an clear oil (68%); R_f = 0.34 (95:5 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (ddd, 1H, *J* = 1.5, 7.7, 7.7 Hz), 7.02 (dd, 1H, *J* = 1.5, 8.3 Hz), 6.88 – 6.85 (m, 2H), 4.75 (s, 1H), 4.71 (s, 1H), 3.89 (s, 3H), 3.40 (t, 2H, *J* = 6.8 Hz), 2.15 (t, 2H, *J* = 7.5 Hz), 1.82 (tt, 2H, *J* = 7.0, 7.0 Hz), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 144.9, 137.1, 129.2, 125.5, 124.8, 121.2, 111.3, 110.8, 56.0, 46.6, 35.1, 29.2, 22.6; IR (Thin Film) 2940, 2131, 1588, 1501, 1465, 1347, 1245, 1107, 1020 cm^{-1}.



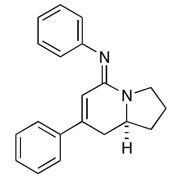
1-(hex-5-enyl)-3-(2-methoxyphenyl)urea. Procedure B yielded a white solid (80%); R_f = 0.53 (1:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, 1H, *J* = 1.9, 7.7 Hz), 7.00 (s, 1H), 6.99 – 6.90 (m, 2H), 6.84 (dd, 2H, *J* = 1.7, 7.7 Hz), 5.77 (ddt, 1H, *J* = 6.8, 10.2, 17.1 Hz), 5.13 (m, 1H), 4.99 (dm, 1H, *J* = 17.1 Hz), 4.94 (dm, 1H, *J* = 10.2 Hz), 3.81 (s, 3H), 3.25 (dt, 2H, *J* = 6.7, 6.7 Hz), 2.05 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.58 – 1.48 (m, 2H), 1.46 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 148.4, 138.7, 128.9, 122.6, 121.4, 119.8, 114.9, 110.3, 55.8, 40.4, 33.6, 29.8, 26.3; IR (Thin Film) 3319, 2931, 1640, 1602, 1551, 1456, 1240, 1214, 1170, 1030 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 249.15975, found 249.15959.



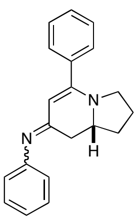
***N*-((hex-5-enylimino)methylene)-2-methoxyaniline (8).** Procedure B yielded an clear oil (70%); R_f = 0.32 (95:5 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.02 (d, 1H, *J* = 8.1 Hz), 6.89 – 6.85 (m, 2H), 5.80 (ddt, 1H, *J* = 6.8, 10.2, 17.1 Hz), 5.01 (dm, 1H, *J* = 17.1 Hz), 4.96 (dm, 1H, *J* = 10.2 Hz), 3.88 (s, 3H), 3.40 (t, 2H, *J* = 6.8 Hz), 2.10 (dt, 2H, *J* = 6.9, 6.9 Hz), 1.74 – 1.66 (m, 2H), 1.58 – 1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 138.6, 137.1, 129.2, 125.5, 124.8, 121.2, 115.0, 111.3, 56.1, 47.0, 33.5, 30.8, 26.3; IR (Thin Film) 2936, 2132, 1594, 1501, 1464, 1342, 1242, 1107, 1025 cm^{-1}.

General procedure for the Rh-catalyzed [2+2+2] cycloaddition of alkenyl carbodiimides and terminal alkynes:

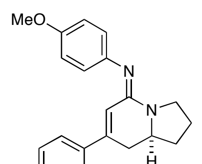
A flame-dried round bottom flask was charged with $[Rh(C_2H_4)_2Cl]_2$ (1.8 mg, 0.0048 mmol) and the phosphoramidite ligand **L4** (6.5 mg, 0.0097 mmol), and was fitted with a flame-dried reflux condenser in an inert atmosphere (N_2) glove box. Upon removal from the glove box, 1.0 ml toluene was added via syringe and the resulting yellow solution was stirred at ambient temperature under argon flow for 15 minutes. To this solution was added a solution of alkyne **1** (0.322 mmol) and carbodiimide **2**, **5,** or **8** (0.161 mmol) in 1 ml of toluene via syringe or cannula. After an additional 1 ml of toluene to wash down the remaining residue, the resulting solution was heated to 110 °C in an oil bath, and maintained at reflux for *ca.* 3 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography (gradient elution typically 50:50 Hex:EtOAC, then 100% EtOAc, followed by 60:40:4 Hex:EtOAc:Et_3N). Evaporation of solvent afforded the analytically pure product **3**, **6**, or **9**. The minor products **4**, **7**, **10** were much more polar (basic), requiring 96:4 EtOAc:Et_3N for isolation. The minor products were typically a 2:1 or 3:1 mixture of imine isomers, and often contaminated with other by-products. For characterization purpose, products that can be isolated relatively clean such as **4aa, 4ab, 4ac, 7a, 4ke,** and **4kc**, analytical data are provided. Others are not provided due to the impurities.



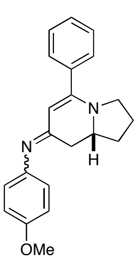
(*S*,*E*)-*N*-(7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3aa). General procedure with alkyne **1a** and carbodiimide **2a** yielded 32.5 mg of the cycloadduct (70%); R_f = 0.46 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 430.8 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 8.34 minutes, Minor: 7.22 minutes, 254 nm detection light, *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 7H), 6.99 (t, 1H, *J* = 7.5 Hz), 6.88 (d, 2H, *J* = 7.5 Hz), 6.42 (d, 1H, *J* = 2.6 Hz), 3.78 (m, 1H), 3.70 (m, 1H), 3.64 (m, 1H), 2.92 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.59 (ddd, 1H, *J* = 2.8, 13.2, 16.0 Hz), 2.29 (ddd, 1H, *J* = 5.5, 5.5, 11.3 Hz), 2.14 (m, 1H), 1.94 (m, 1H), 1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.7, 145.4, 139.2, 129.0, 128.8, 126.0, 123.4, 122.0, 114.6, 56.4, 45.6, 33.8, 33.7, 23.3; IR (Thin Film) 2959, 1629, 1573, 1454, 1350, 1328 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 289.16992, found 289.16896.



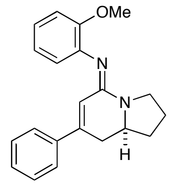
(*R*)-*N*-(5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1*H*)-ylidene)aniline (4aa). General procedure with alkyne **1a** and carbodiimide **2a** yielded 8.5 mg of the cycloadduct (18%) as a 3:1 mixture of the imine isomers; R_f = 0.28 (96:4 EtOAc/Et_3N); *ee* not determined; See spectra for its ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$); IR (Thin Film) 2967, 1600, 1575, 1489, 1452, 1235, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 289.16992, found 289.1702.



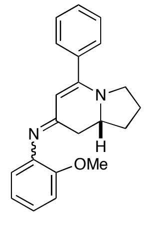
(*S*,*E*)-4-methoxy-*N*-(7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3ab). General procedure with alkyne **1a** and carbodiimide **2b** yielded 36.0 mg of the cycloadduct (70%); R_f = 0.43 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 329.0 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH with 0.1% diethyl amine, 1.0 ml/min, Major: 9.05 minutes, Minor: 8.06 minutes, 254 nm detection light, *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 6.83 – 6.78 (m, 4H), 6.42 (d, 1H, *J* = 2.1 Hz), 3.79 (s, 3H), 3.75 (m, 1H), 3.68 (m, 1H), 3.60 (m, 1H), 2.90 (dd, 1H, *J* = 4.1, 16.2 Hz), 2.56 (m, 1H), 2.27 (ddd, 1H, *J* = 5.7, 5.7, 11.5 Hz), 2.13 (m, 1H), 1.92 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 152.5, 145.1, 144.0, 139.3, 128.9, 128.8, 125.9, 124.1, 114.6, 114.1, 56.4, 55.6, 45.5, 33.8, 33.6, 23.2; IR (Thin Film) 2954, 1627, 1571, 1496, 1446, 1322, 1235 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 319.18048, found 319.17926.



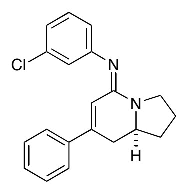
(*R*)-4-methoxy-*N*-(5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1*H*)-ylidene)aniline (4ab). General procedure with alkyne **1a** and carbodiimide **2b** yielded 9.2 mg of the cycloadduct (18%) as a 3:1 mixture of the imine isomers; R_f = 0.17 (96:4 EtOAc/Et_3N); *ee* not determined; See spectra for its ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$); IR (Thin Film) 2961, 1600, 1581, 1544, 1489, 1452, 1235, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 319.18048, found 319.1812.



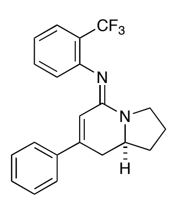
(*S*,*E*)-2-methoxy-*N*-(7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3ac). General procedure with alkyne **1a** and carbodiimide **2c** yielded 35.0 mg of the cycloadduct (68%); R_f = 0.49 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 330.1 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 12.35 minutes, Minor: 8.67 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 6.96 (m, 1H), 6.88 – 6.83 (m, 2H), 6.77 (d, 1H, *J* = 7.5 Hz), 6.34 (m, 1H), 3.83 (m, 1H), 3.81 (s, 3H), 3.75 – 3.63 (m, 2H), 2.89 (dd, 1H, *J* = 4.0, 16.2 Hz), 2.57 (ddd, 1H, *J* = 2.3, 12.2, 15.8 Hz), 2.27 (ddd, 1H, *J* = 6.0, 6.0, 11.5 Hz), 2.12 (m, 1H), 1.92 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 146.1, 139.0, 134.3, 129.7, 129.2, 128.9, 126.0, 123.5, 121.9, 121.7, 114.3, 56.4, 45.5, 33.8, 33.7, 23.2; IR (Thin Film) 2946, 1635, 1579, 1491, 1441, 1328, 1240 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 319.18048, found 319.17991.



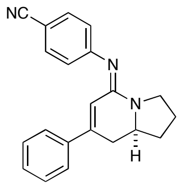
(*R*)-2-methoxy-*N*-(5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1*H*)-ylidene)aniline (4ac). General procedure with alkyne **1a** and carbodiimide **2c** yielded 7.2 mg of the cycloadduct (14%) as a 3:1 mixture of the imine isomers; R_f = 0.15 (96:4 EtOAc/Et_3N); *ee* not determined; See spectra for its ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$); IR (Thin Film) 2955, 1600, 1575, 1551, 1489, 1452, 1235, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 319.18048, found 319.1801.



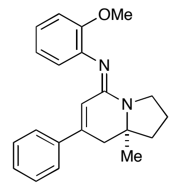
(*S*,*E*)-3-chloro-*N*-(7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3ad). General procedure with alkyne **1a** and carbodiimide **2d** yielded 34.9 mg of the cycloadduct (67%); R_f = 0.60 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 391.8 (c = 1, $CHCl_3$); HPLC analysis – Chiracel AD-H column 99:1 hexane:iPrOH, 1.0 ml/min, Major: 8.90 minutes, Minor: 8.21 minutes, 254 nm detection light, *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 5H), 7.15 (dd, 1H, *J* = 7.9, 8.1 Hz), 6.94 (d, 1H, *J* = 8.1 Hz), 6.93 (s, 1H), 6.74 (d, 1H, *J* = 7.9 Hz), 6.36 (d, 1H, *J* = 2.3 Hz), 3.76 – 3.67 (m, 2H), 3.57 (m, 1H), 2.92 (dd, 1H, *J* = 4.1, 16.2 Hz), 2.57 (ddd, 1H, *J* = 2.6, 13.6, 16.0 Hz), 2.28 (m, 1H), 2.13 (m, 1H), 1.93 (m, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 146.1, 139.0, 134.3, 129.7, 129.2, 128.9, 126.0, 123.5, 121.9, 121.7, 114.3, 56.4, 45.5, 33.8, 33.7, 23.3; IR (Thin Film) 2959, 1623, 1573, 1447, 1353, 1328, 1278 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 323.13095, found 323.12911.



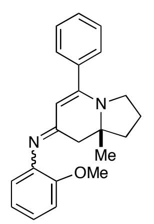
(*S*,*E*)-*N*-(7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-(trifluoromethyl)aniline (3ae). General procedure with alkyne **1a** and carbodiimide **2e** yielded 47.0 mg of the cycloadduct (82%); R_f = 0.56 (EtOAc); $[\alpha]_D^{20}$ = – 212.7 (c = 1, $CHCl_3$); HPLC analysis – Chiracel AD-H column 99:1 hexane:iPrOH, 1.0 ml/min, Major: 5.24 minutes, Minor: 5.54 minutes, 210 nm detection light, *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 1H, *J* = 7.7 Hz), 7.38 – 7.32 (m, 6H), 7.01 (dd, 1H, *J* = 7.5, 7.7 Hz), 6.81 (d, 1H, *J* = 7.9 Hz), 6.16 (d, 1H, *J* = 2.6 Hz), 3.76 – 3.68 (m, 2H), 3.62 (m, 1H), 2.90 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.58 (m, 1H), 2.29 (m, 1H), 2.13 (m, 1H), 1.94 (m, 1H), 1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 150.2, 146.1, 139.1, 132.1, 129.0, 128.8, 126.5, 126.4, 126.1, 126.0, 124.7, 123.4, 123.1, 121.3, 114.7, 56.4, 45.3, 33.9, 33.7, 23.2; IR (Thin Film) 2963, 1633, 1578, 1559, 1443, 1248, 1126 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 357.15730, found 357.15647.



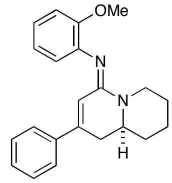
(*S*,*E*)-4-(7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylideneamino)benzonitrile (3af). General procedure with alkyne **1a** and carbodiimide **2f** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 28.0 mg of the cycloadduct (55%); R_f = 0.12 (EtOAc); $[\alpha]_D^{20}$ = – 413.2 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 11.26 minutes, Minor: 12.37 minutes, 210 nm detection light, *ee* = 92%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2H, *J* = 8.3 Hz), 7.38 – 7.34 (m, 5H), 6.88 (d, 2H, *J* = 8.3 Hz), 6.29 (d, 1H, *J* = 2.6 Hz), 3.78 – 3.70 (m, 2H), 3.56 (m, 1H), 2.95 (dd, 1H, *J* = 4.3, 16.4 Hz), 2.60 (ddd, 1H, *J* = 2.8, 13.4, 16.2 Hz), 2.32 (ddd, 1H, *J* = 6.0, 6.0, 11.9 Hz), 2.15 (m, 1H), 1.93 (m, 1H), 1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 152.0, 146.8, 138.7, 133.1, 129.4, 129.0, 125.9, 124.0, 120.4, 114.1, 104.2, 56.3, 45.6, 33.7, 23.2; IR (Thin Film) 2963, 2218, 1626, 1553, 1456, 1322, 1273, 1163 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 314.16468, found 314.16517.



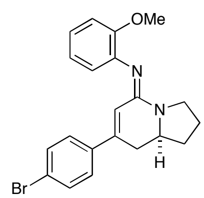
(*S*,*E*)-2-methoxy-*N*-(8a-methyl-7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (6a). General procedure with alkyne **1a** and carbodiimide **5** yielded 34.3 mg of the cycloadduct (64%); R_f = 0.44 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 249.8 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 6.74 minutes, Minor: 8.76 minutes, 210 nm detection light, *ee* = 99%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 6.95 (m, 1H), 6.87 – 6.83 (m, 2H), 6.77 (d, 1H, *J* = 7.7 Hz), 6.30 (m, 1H), 3.79 (s, 3H), 3.79 – 3.65 (m, 2H), 2.83 (d, 1H, *J* = 16.2 Hz), 2.77 (dd, 1H, *J* = 2.1, 16.2 Hz), 2.11 – 2.04 (m, 3H), 1.93 (m, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.8, 143.3, 140.4, 139.9, 128.7, 126.0, 124.6, 122.6, 120.8, 114.7, 111.5, 60.2, 55.9, 45.1, 40.9, 40.8, 23.1, 21.7; IR (Thin Film) 2963, 1626, 1578, 1486, 1431, 1236, 1169 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 333.19614, found 333.19614.



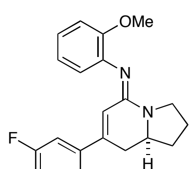
(*R*)-2-methoxy-*N*-(8a-methyl-5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1*H*)-ylidene)aniline (7a). General procedure with alkyne **1a** and carbodiimide **5** yielded 10.8 mg of the cycloadduct (20%) as a 2:1 mixture of the imine isomers; R_f = 0.36 (96:4 EtOAc/Et_3N); *ee* not determined; See spectra for its ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$); IR (Thin Film) 2967, 1600, 1575, 1551, 1489, 1452, 1241, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 333. 19614, found 333.1963.



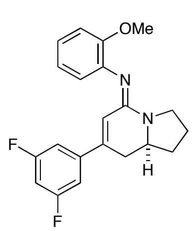
(*S*,*E*)-2-methoxy-*N*-(2-phenyl-1*H*-quinolizin-4(6*H*,7*H*,8*H*,9*H*,9a*H*)-ylidene)aniline (9a). General procedure with alkyne **1a** and carbodiimide **8** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 23.0 mg of the cycloadduct (43%); R_f = 0.55 (65:35:4 Hex/EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 240.1 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 20.39 minutes, Minor: 11.03 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 5H), 6.97 (m, 1H), 6.89 – 6.86 (m, 2H), 6.74 (d, 1H, *J* = 6.6 Hz), 6.26 (d, 1H, *J* = 1.7 Hz), 4.62 (dm, 1H, *J* = 12.8 Hz), 3.79 (s, 3H), 3.37 (m, 1H), 2.78 (dd, 1H, *J* = 4.9, 17.1 Hz), 2.71 (dd, 1H, *J* = 3.2, 13.2 Hz), 2.61 (ddd, 1H, *J* = 1.7, 10.4, 16.8 Hz), 1.87 – 1.80 (m, 3H), 1.72 – 1.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 151.7, 143.4, 140.4, 139.1, 128.9, 128.7, 125.8, 123.6, 122.8, 121.0, 113.7, 111.6, 56.0, 55.1, 45.3, 34.6, 33.6, 24.8, 24.1; IR (Thin Film) 2930, 1637, 1581, 1489, 1440, 1328, 1260 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 333.19614, found 333.19535.



(*S*,*E*)-*N*-(7-(4-bromophenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3bc). General procedure with alkyne **1b** and carbodiimide **2c** yielded 47.7 mg of the cycloadduct (75%); R_f = 0.45 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 345.1 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 12.44 minutes, Minor: 9.03 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 2H, *J* = 8.3 Hz), 7.20 (d, 2H, *J* = 8.3 Hz), 6.98 (m, 1H), 6.88 – 6.83 (m, 2H), 6.77 (d, 1H, *J* = 7.2 Hz), 6.32 (m, 1H), 3.86 (m, 1H), 3.80 (s, 3H), 3.75 – 3.63 (m, 2H), 2.83 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.55 (ddd, 1H, *J* = 2.3, 13.2, 15.8 Hz), 2.27 (ddd, 1H, *J* = 6.0, 6.0, 11.5 Hz), 2.24 (m, 1H), 1.92 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 143.7, 138.1, 131.9, 127.5, 124.5, 123.0, 120.8, 115.5, 111.3, 56.4, 55.9, 45.7, 33.6, 23.2; IR (Thin Film) 2938, 1620, 1578, 1431, 1320, 1230, 1108 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 397.09100, found 397.08916. X-ray data is attached at the end of this manuscript.

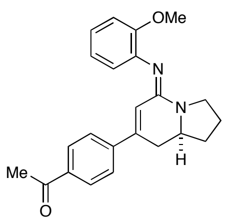


(*S*,*E*)-*N*-(7-(3-fluorophenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3cc). General procedure with alkyne **1c** and carbodiimide **2c** yielded 41.9 mg of the cycloadduct (77%); R_f = 0.48 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 359.1 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 11.83 minutes, Minor: 8.45 minutes, 210 nm detection light, *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 1H), 7.12 (d, 1H, *J* = 7.9 Hz), 7.04 -- 6.95 (m, 3H), 6.88 – 6.83 (m, 2H), 6.74 (dd, 1H, *J* = 1.7, 7.7 Hz), 6.34 (d, 1H, *J* = 2.4 Hz), 3.82 (m, 1H), 3.81 (s, 3H), 3.73 – 3.61 (m, 2H), 2.83 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.55 (ddd, 1H, *J* = 2.6, 13.0, 15.8 Hz), 2.27 (ddd, 1H, *J* = 5.8, 5.8, 11.3 Hz), 2.12 (m, 1H), 1.92 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.8, 152.2, 152.1, 143.3, 141.8, 141.7, 139.9, 130.3, 130.2, 124.3, 122.8, 121.6, 120.8, 116.2, 115.7, 115.5, 113.0, 112.8, 111.3, 56.3, 55.9, 45.5, 33.8, 33.6, 23.2; IR (Thin Film) 2953, 1636, 1579, 1485, 1435, 1328, 1247, 1109 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 337.17106, found 337.17014.

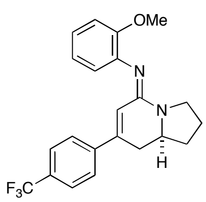


(*S*,*E*)-*N*-(7-(3,5-difluorophenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3dc). General procedure with alkyne **1d** and carbodiimide **2c** yielded 37.7 mg of the cycloadduct (66%); R_f = 0.43 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 341.4 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 11.40 minutes, Minor: 8.20 minutes, 210 nm detection light, *ee* =

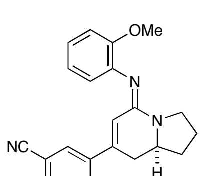
99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (m, 1H), 6.89 – 6.86 (m, 4H), 6.75 – 6.71 (m, 2H), 6.33 (d, 1H, *J* = 2.6 Hz), 3.81 (m, 1H), 3.81 (s, 3H), 3.73 – 3.60 (m, 2H), 2.78 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.54 (ddd, 1H, *J* = 2.6, 13.0, 16.0 Hz), 2.27 (ddd, 1H, *J* = 6.2, 6.2, 12.1 Hz), 2.13 (m, 1H), 1.92 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 152.2, 151.7, 142.2, 139.7, 124.2, 123.0, 120.8, 117.0, 111.4, 109.0, 108.8, 104.2, 103.9, 103.7, 56.2, 55.9, 45.6, 33.7, 33.6, 23.2; IR (Thin Film) 2938, 1626, 1596, 1443, 1322, 1242, 1120 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 355.16164, found 355.16026.



(*S*,*E*)-1-(4-(5-(2-methoxyphenylimino)-1,2,3,5,8,8a-hexahydroindolizin-7-yl)phenyl)ethanone (3ec). General procedure with alkyne **1e** and carbodiimide **2c** yielded 45.2 mg of the cycloadduct (78%); R_f = 0.37 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 352.8 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 25.11 minutes, Minor: 17.29 minutes, 210 nm detection light, *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 2H, *J* = 7.0 Hz), 7.42 (d, 2H, *J* = 7.0 Hz), 6.97 (m, 1H), 6.88 – 6.82 (m, 2H), 6.74 (d, 1H, *J* = 7.5 Hz), 6.42 (m, 1H), 3.82 (m, 1H), 3.81 (s, 3H), 3.75 – 3.66 (m, 2H), 2.88 (dd, 1H, *J* = 4.1, 16.0 Hz), 2.59 (m, 1H), 2.57 (s, 3H), 2.28 (ddd, 1H, *J* = 6.6, 6.6, 11.9 Hz), 2.13 (m, 1H), 1.92 (m, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 152.2, 152.0, 143.9, 143.3, 139.8, 136.9, 128.8, 126.1, 124.3, 122.9, 120.8, 117.1, 111.3, 56.3, 55.9, 45.6, 33.7, 26.9, 23.2; IR (Thin Film) 2954, 1683, 1627, 1577, 1434, 1353, 1271, 1235, 1116 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 361.19105, found 361.19049.

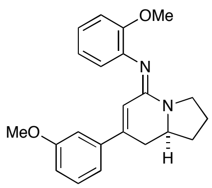


(*S*,*E*)-2-methoxy-*N*-(7-(4-(trifluoromethyl)phenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3fc). General procedure with alkyne **1f** and carbodiimide **2c** yielded 42.5 mg of the cycloadduct (68%); R_f = 0.44 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 303.4 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 9.49 minutes, Minor: 7.13 minutes, 210 nm detection light, *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, *J* = 8.3 Hz), 7.43 (d, 2H, *J* = 8.1 Hz), 6.98 (m, 1H), 6.88 – 6.83 (m, 2H), 6.76 (d, 1H, *J* = 6.8 Hz), 6.38 (d, 1H, *J* = 2.3 Hz), 3.83 (m, 1H), 3.80 (s, 3H), 3.78 – 3.63 (m, 2H), 2.86 (dd, 1H, *J* = 4.3, 16.0 Hz), 2.60 (ddd, 1H, *J* = 2.4, 13.2, 15.8 Hz), 2.28 (ddd, 1H, *J* = 5.8, 5.8, 11.3 Hz), 2.14 (m, 1H), 1.93 (m, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 152.0, 143.3, 142.9, 131.1, 130.5 126.2, 125.7, 125.7, 124.4, 123.1, 120.8, 117.0, 111.4, 56.3, 55.9, 45.7, 33.7, 33.6, 23.2; IR (Thin Film) 2948, 1625, 1581, 1439, 1328, 1235, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 387.16787, found 387.16857.

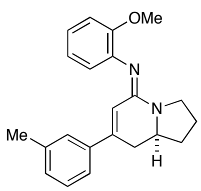


(*S*,*E*)-3-(5-(2-methoxyphenylimino)-1,2,3,5,8,8a-hexahydroindolizin-7-yl)benzonitrile (3gc). General procedure with alkyne **1g** and carbodiimide **2c** yielded 34.3 mg of the cycloadduct (62%); R_f = 0.49 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 280.9 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 21.14 minutes, Minor: 15.22 minutes, 210 nm detection light, *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.57 – 7.54 (m, 2H), 7.42 (dd, 1H, *J* = 7.9, 7.9 Hz), 6.98 (m, 1H), 6.89 – 6.84 (m, 2H), 6.73 (dd, 1H, *J* = 7.5 Hz), 6.35 (d, 1H, *J* = 2.3

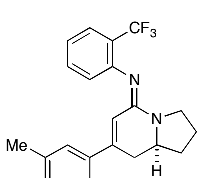
Hz), 3.82 (m, 1H), 3.81 (s, 3H), 3.76 – 3.61 (m, 2H), 2.82 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.59 (ddd, 1H, *J* = 2.6, 13.2, 15.8 Hz), 2.28 (m, 1H), 2.12 (m, 1H), 1.93 (m, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 151.7, 142.2, 140.8, 139.7, 132.0, 130.2, 129.7, 129.5, 124.2, 123.0, 120.9, 118.7, 117.1, 113.1, 111.4, 56.2, 55.9, 45.6, 33.7, 33.6, 23.2; IR (Thin Film) 2953, 2225, 1629, 1573, 1485, 1435, 1328, 1234, 1115 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 344.17573, found 344.17469.



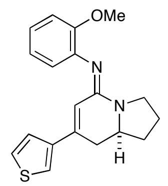
(*S*,*E*)-2-methoxy-*N*-(7-(3-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3hc). General procedure with alkyne **1h** and carbodiimide **2c** yielded 38.8 mg of the cycloadduct (69%); R_f = 0.40 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 280.9 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 15.51 minutes, Minor: 11.07 minutes, 210 nm detection light, *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, 1H, *J* = 7.9, 7.9 Hz), 6.98 – 6.93 (m, 2H), 6.87 – 6.84 (m, 2H), 6.83 (s, 1H), 6.77 (dd, 1H, *J* = 7.5 Hz), 6.33 (m, 1H), 3.82 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.76 – 3.63 (m, 2H), 2.86 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.56 (ddd, 1H, *J* = 2.1, 13.0, 15.6 Hz), 2.26 (ddd, 1H, *J* = 6.0, 6.0, 11.7 Hz), 2.12 (m, 1H), 1.92 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 152.5, 152.4, 144.7, 140.9, 129.8, 124.5, 122.9, 120.8, 118.5, 115.5, 113.8, 112.0, 111.3, 56.4, 55.9, 55.5, 45.7, 33.9, 33.6, 23.2; IR (Thin Film) 2947, 1633, 1583, 1490, 1440, 1328, 1253, 1116 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 349.19105, found 349.19044.



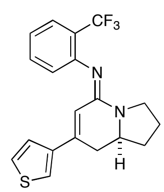
(*S*,*E*)-2-methoxy-*N*-(7-*m*-tolyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3ic). General procedure with alkyne **1i** and carbodiimide **2c** yielded 32.8 mg of the cycloadduct (61%); R_f = 0.47 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 349.2 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 11.50 minutes, Minor: 8.21 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 – 7.16 (m, 3H), 7.11 (d, 1H, *J* = 7.3 Hz), 6.97 (m, 1H), 6.88 – 6.83 (m, 2H), 6.78 (d, 1H, *J* = 7.5 Hz), 6.32 (d, 1H, *J* = 2.1 Hz), 3.84 (m, 1H), 3.82 (s, 3H), 3.74 – 3.63 (m, 2H), 2.88 (dd, 1H, *J* = 4.3, 16.2 Hz), 2.57 (ddd, 1H, *J* = 2.6, 13.2, 16.0 Hz), 2.32 (s, 3H), 2.26 (ddd, 1H, *J* = 5.8, 5.8, 11.7 Hz), 2.12 (m, 1H), 1.92 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 152.4, 145.0, 139.4, 138.4, 129.6, 128.7, 126.7, 124.5, 123.1, 122.8, 120.8, 115.1, 111.2, 56.4, 55.9, 45.7, 33.9, 33.7, 23.2, 21.7; IR (Thin Film) 2942, 1631, 1569, 1489, 1439, 1322, 1235, 1114 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 333.19614, found 333.19545.



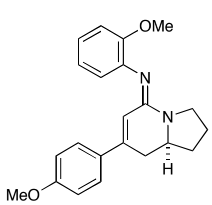
(*S*,*E*)-*N*-(7-*m*-tolyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-(trifluoromethyl)aniline (3ie). General procedure with alkyne **1i** and carbodiimide **2e** yielded 44.0 mg of the cycloadduct (74%); R_f = 0.51 (EtOAc); $[\alpha]_D^{20}$ = – 230.2 (c = 1, $CHCl_3$); HPLC analysis – Chiracel AD-H column 99:1 hexane:iPrOH, 1.0 ml/min, Major: 4.81 minutes, Minor: 5.41 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J* = 7.5 Hz), 7.33 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.18 (dd, 1H, *J* = 7.0, 7.0 Hz), 7.14 – 7.08 (m, 3H), 6.98 (dd, 1H, *J* = 7.5, 7.5 Hz), 6.79 (d, 1H, *J* = 7.5 Hz), 6.11 (m, 1H), 3.74 – 3.65 (m, 2H), 3.58 (m, 1H), 2.86 (dm, 1H, *J* = 6.4 Hz), 2.55 (m, 1H), 2.30 (s, 3H), 2.25 (m, 1H), 2.10 (m, 1H), 1.91 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 146.3, 139.2, 138.4, 132.1, 129.8, 128.7, 126.6, 126.5, 126.4, 124.7, 123.1, 121.2, 114.5, 56.4, 45.3, 34.1, 33.7, 23.2, 21.6; IR (Thin Film) 2961, 1631, 1594, 1563, 1439, 1310, 1124 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 371.17296, found 371.1734.



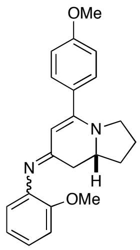
(*S*,*E*)-2-methoxy-*N*-(7-(thiophen-3-yl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3jc). General procedure with alkyne **1j** and carbodiimide **2c** yielded 30.6 mg of the cycloadduct (58%); R_f = 0.46 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 311.5 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 16.30 minutes, Minor: 10.22 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.10 (d, 1H, *J* = 4.9 Hz), 6.98 (m, 1H), 6.88 – 6.86 (m, 2H), 6.78 (d, 1H, *J* = 7.5 Hz), 6.32 (m, 1H), 3.82 (m, 1H), 3.80 (s, 3H), 3.72 – 3.64 (m, 2H), 2.89 (dd, 1H, *J* = 4.0, 16.2 Hz), 2.50 (ddd, 1H, *J* = 1.7, 10.2, 15.3 Hz), 2.27 (ddd, 1H, *J* = 5.8, 5.8, 11.3 Hz), 2.10 (m, 1H), 1.91 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.4, 141.0, 139.3, 126.6, 125.4, 124.9, 122.8, 120.8, 113.8, 111.3, 56.2, 55.9, 45.7, 33.6, 23.2; IR (Thin Film) 2948, 1625, 1575, 1495, 1439, 1328, 1235, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 325.13691, found 325.13691.



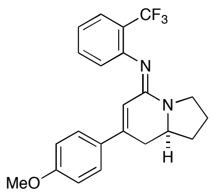
(*S*,*E*)-*N*-(7-(thiophen-3-yl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-(trifluoromethyl)aniline (3je). General procedure with alkyne **1j** and carbodiimide **2e** yielded 46.1 mg of the cycloadduct (79%); R_f = 0.46 (EtOAc); $[\alpha]_D^{20}$ = – 265.9 (c = 1, $CHCl_3$); HPLC analysis – Chiracel AD-H column 99:1 hexane(with 0.01% diethyl amine):iPrOH, 1.0 ml/min, Major: 6.31 minutes, Minor: 6.66 minutes, 254 nm detection light, *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J* = 6.8 Hz), 7.34 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.25 – 7.23 (m, 2H), 7.04 (m, 1H), 6.99 (dd, 1H, *J* = 7.5, 7.5 Hz), 6.78 (d, 1H, *J* = 7.5 Hz), 6.11 (m, 1H), 3.74 – 3.64 (m, 2H), 3.57 (m, 1H), 2.88 (dm, 1H, *J* = 16.2 Hz), 2.49 (m, 1H), 2.26 (m, 1H), 2.08 (m, 1H), 1.91 (m, 1H), 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 140.8, 132.1, 126.7, 126.4, 125.3, 124.7, 123.1, 121.3, 113.1, 56.2, 45.4, 33.8, 33.7, 23.1; IR (Thin Film) 2967, 1631, 1587, 1563, 1439, 1315, 1247, 1123, 1031 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 363.11373, found 363.11471.



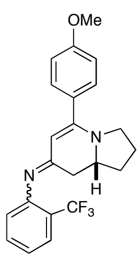
(*S*,*E*)-2-methoxy-*N*-(7-(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3kc). General procedure with alkyne **1k** and carbodiimide **2c** yielded 11.2 mg of the cycloadduct (20%); R_f = 0.43 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 165.2 (c = 0.73, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 18.71 minutes, Minor: 12.56 minutes, 210 nm detection light, *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, 2H, *J* = 8.8 Hz), 6.98 (m, 1H), 6.88 – 6.78 (m, 5H), 6.27 (m, 1H), 3.85 (m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.75 – 3.66 (m, 2H), 2.89 (dd, 1H, *J* = 4.0, 16.0 Hz), 2.52 (ddd, 1H, *J* = 2.4, 11.6, 16.0 Hz), 2.27 (ddd, 1H, *J* = 6.0, 6.0, 11.2 Hz), 2.12 (m, 1H), 1.92 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 160.3, 152.9, 152.5, 140.1, 131.4, 127.3, 124.7, 122.9, 120.8, 114.1, 113.3, 111.3, 56.5, 55.9, 55.5, 45.8, 33.6, 23.2; IR (Thin Film) 2954, 1627, 1577, 1515, 1440, 1241, 1179, 1116 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 349.19105, found 349.18953.



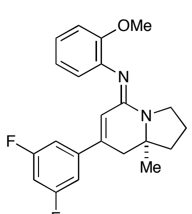
(*R*)-2-methoxy-*N*-(5-(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-ylidene)aniline (4kc). General procedure with alkyne **1k** and carbodiimide **2c** yielded 29.3 mg of the cycloadduct (52%) as a 2:1 mixture of the imine isomers; R_f = 0.17 (96:4 EtOAc/Et_3N); *ee* not determined; See spectra for its ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$); IR (Thin Film) 2954, 1602, 1577, 1509, 1453, 1247, 1172, 1116 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 349.19105, found 349.18960.



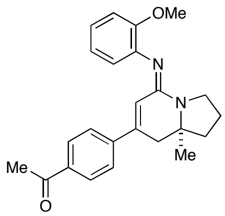
(*S*,*E*)-*N*-(7-(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-(trifluoromethyl)aniline (3ke). General procedure with alkyne **1k** and carbodiimide **2e** yielded 23.0 mg of the cycloadduct (37%); R_f = 0.79 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 236.7 (c = 1.0, $CHCl_3$); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 4.98 minutes, Minor: 5.45 minutes, 210 nm detection light, *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J* = 7.9 Hz), 7.34 (dd, 1H, *J* = 7.7, 7.7 Hz), 7.32 – 7.23 (m, 2H), 6.98 (dd, 1H, *J* = 7.6, 7.6 Hz), 6.84 – 6.78 (m, 3H), 6.60 (m, 1H), 3.77 (s, 3H), 3.75 – 3.63 (m, 2H), 3.58 (m, 1H), 2.87 (dd, 1H, *J* = 4.0, 16.2 Hz), 2.41 (m, 1H), 2.25 (m, 1H), 2.09 (m, 1H), 1.91 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 151.6, 145.5, 132.1, 131.3, 127.3, 126.4, 124.8, 121.2, 114.1, 112.9, 56.4, 55.6, 45.3, 33.8, 33.7, 23.2; IR (Thin Film) 2945, 1631, 1557, 1510, 1439, 1247, 1179, 1124 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 387.16787, found 387.16883.



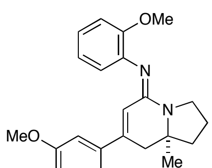
(*R*)-*N*-(5-(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-ylidene)-2-(trifluoromethyl)aniline (4ke). General procedure with alkyne **1k** and carbodiimide **2e** yielded 22.3 mg of the cycloadduct (36%) as a 3:1 mixture of the imine isomers; R_f = 0.56 (96:4 EtOAc/Et_3N); *ee* not determined; See spectra for its ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$); IR (Thin Film) 2961, 1600, 1563, 1513, 1443, 1247, 1172, 1117 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 387.16787, found 387.16797.



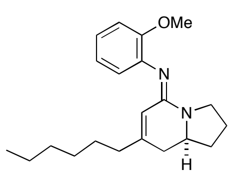
(*S*,*E*)-*N*-(7-(3,5-difluorophenyl)-8a-methyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (6d). General procedure with alkyne **1d** and carbodiimide **5** yielded 47.0 mg of the cycloadduct (79%); R_f = 0.53 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 253.6 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 6.41 minutes, Minor: 7.96 minutes, 210 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (m, 1H), 6.88 – 6.83 (m, 4H), 6.75 – 6.70 (m, 2H), 6.29 (m, 1H), 3.78 (s, 3H), 3.78 – 3.64 (m, 2H), 2.76 – 2.68 (m, 2H), 2.11 – 2.06 (m, 3H), 1.93 (m, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 162.1, 152.1, 151.0, 124.4, 122.9, 120.9, 116.3, 111.6, 109.0, 108.8, 104.2, 103.9, 103.7, 60.1, 55.9, 45.1, 40.8, 40.6, 23.2, 21.7; IR (Thin Film) 2969, 1626, 1585, 1571, 1431, 1242, 1174, 1120 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 369.17729, found 369.17689.



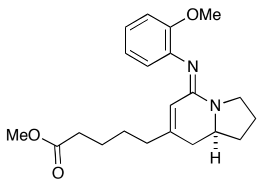
(*S*,*E*)-1-(4-(5-(2-methoxyphenylimino)-8a-methyl-1,2,3,5,8,8a-hexahydroindolizin-7-yl)phenyl)ethanone (6e). General procedure with alkyne **1e** and carbodiimide **5** yielded 45.0 mg of the cycloadduct (74%); R_f = 0.43 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 245.8 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 13.21 minutes, Minor: 16.64 minutes, 210 nm detection light, *ee* = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J* = 8.5 Hz), 7.42 (d, 2H, *J* = 8.1 Hz), 6.96 (m, 1H), 6.88 – 6.84 (m, 2H), 6.76 (d, 1H, *J* = 7.5 Hz), 6.38 (m, 1H), 3.79 (s, 3H), 3.79 – 3.65 (m, 2H), 2.83 – 2.78 (m, 2H), 2.58 (s, 3H), 2.14 – 2.06 (m, 3H), 1.93 (m, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 152.2, 151.3, 144.4, 142.1, 140.2, 136.9, 128.8, 126.1, 124.5, 122.8, 120.9, 116.5, 111.5, 60.1, 55.9, 45.1, 40.9, 40.6, 26.9, 23.2, 21.7; IR (Thin Film) 2967, 1680, 1625, 1569, 1427, 1266, 1111 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 375.20670, found 375.20550.



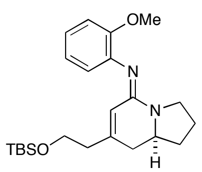
(*S*,*E*)-2-methoxy-*N*-(7-(3-methoxyphenyl)-8a-methyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (6h). General procedure with alkyne **1h** and carbodiimide **5** yielded 38.7 mg of the cycloadduct (66%); R_f = 0.49 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 244.0 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 7.95 minutes, Minor: 10.68 minutes, 210 nm detection light, *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, 1H, *J* = 8.0, 8.0 Hz), 6.96 – 6.92 (m, 2H), 6.86 – 6.82 (m, 4H), 6.77 (d, 1H, *J* = 7.7 Hz), 6.29 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.78 – 3.63 (m, 2H), 2.81 – 2.73 (m, 2H), 2.11 – 2.06 (m, 3H), 1.92 (m, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 159.8, 152.3, 151.7, 143.2, 141.4, 129.8, 124.6, 122.6, 120.8, 118.5, 115.0, 113.7, 112.1, 111.4, 60.2, 55.9, 55.5, 45.1, 40.9, 23.1, 21.7; IR (Thin Film) 2957, 1626, 1577, 1492, 1430 1242, 1162, 1108 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H$^+$) 363.20670, found 363.20638.



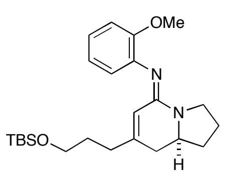
(*S*,*E*)-*N*-(7-hexyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3lc). General procedure with alkyne **1l** and carbodiimide **2c** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 38.8 mg of the cycloadduct (74%); R_f = 0.41 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 211.9 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 8.59 minutes, Minor: 7.05 minutes, 230 nm detection light, *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (m, 1H), 6.85 – 6.82 (m, 2H), 6.74 (d, 1H, *J* = 7.0 Hz), 5.72 (m, 1H), 3.79 (s, 3H), 3.77 (m, 1H), 3.62 – 3.51 (m, 2H), 2.29 (dd, 1H, *J* = 4.5, 16.2 Hz), 2.18 – 2.14 (m, 2H), 2.10 – 2.05 (m, 3H), 1.85 (m, 1H), 1.61 (m, 1H), 1.37 – 1.21 (m, 8H), 0.86 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.4, 149.3, 124.5, 122.5, 120.6, 114.5, 111.2, 56.5, 55.8, 45.5, 37.2, 34.7, 33.6, 31.8, 29.0, 27.2, 23.2, 22.8, 14.3; IR (Thin Film) 2928, 1651, 1583, 1490, 1440, 1322, 1247, 1116 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 327.24309, found 327.24281.



(*S*,*E*)-methyl 5-(5-(2-methoxyphenylimino)-1,2,3,5,8,8a-hexahydroindolizin-7-yl)pentanoate (3mc). General procedure with alkyne **1m** and carbodiimide **2c** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 39.0 mg of the cycloadduct (68%); R_f = 0.42 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 212.4 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 19.00 minutes, Minor: 13.29 minutes, 230 nm detection light, *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (m, 1H), 6.85 – 6.81 (m, 2H), 6.70 (d, 1H, *J* = 7.7 Hz), 5.73 (m, 1H), 3.78 (s, 3H), 3.73 (m, 1H), 3.64 (s, 3H), 3.61 – 3.51 (m, 2H), 2.30 – 2.25 (m, 3H), 2.19 – 2.14 (m, 2H), 2.10 – 2.03 (m, 3H), 1.84 (m, 1H), 1.64 – 1.54 (m, 3H), 1.44 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 152.6, 152.3, 148.1, 140.3, 124.4, 122.4, 120.6, 115.0, 111.2, 56.4, 55.8, 51.7, 45.4, 36.8, 34.6, 33.9, 33.6, 26.7, 24.5, 23.2; IR (Thin Film) 2942, 1736, 1649, 1575, 1489, 1439, 1328, 1235, 1173 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 357.21726, found 357.21669.

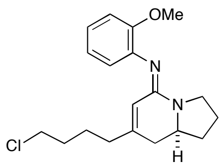


(*S*,*E*)-*N*-(7-(2-(*tert*-butyldimethylsilyloxy)ethyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3nc). General procedure with alkyne **1n** and carbodiimide **2c** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 49.3 mg of the cycloadduct (76%); R_f = 0.48 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 169.9 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 8.24 minutes, Minor: 5.98 minutes, 230 nm detection light, *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (m, 1H), 6.84 – 6.81 (m, 2H), 6.70 (d, 1H, *J* = 7.7 Hz), 5.78 (d, 1H, *J* = 1.7 Hz), 3.79 (s, 3H), 3.73 (m, 1H), 3.65 (m, 2H), 3.62 – 3.52 (m, 2H), 2.38 (dd, 1H, *J* = 4.3, 16.4 Hz), 2.28 (t, 2H, *J* = 6.4 Hz), 2.21 – 2.13 (m, 2H), 2.04 (m, 1H), 1.85 (m, 1H), 1.60 (m, 1H), 0.85 (s, 9H), 0.003 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 152.4, 146.4, 140.3, 124.4, 122.4, 120.7, 116.0, 111.2, 61.8, 56.3, 55.8, 45.4, 40.4, 35.3, 33.6, 26.1, 23.1, 18.4, -5.22; IR (Thin Film) 2947, 1652, 1577, 1490, 1465, 1434, 1328, 1253, 1097 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 401.26188, found 401.26217.

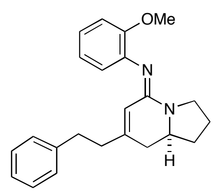


***(S,E)-N-*(7-(3-(tert-butyldimethylsilyloxy)propyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3oc).** General procedure with alkyne **1o** and carbodiimide **2c** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 48.5 mg of the cycloadduct (73%); R_f = 0.49 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 181.1 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 7.21 minutes, Minor: 5.69 minutes, 230 nm detection light, *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (m, 1H), 6.85 – 6.81 (m, 2H), 6.71 (d, 1H, *J* = 7.6 Hz), 5.75 (m, 1H), 3.79 (s, 3H), 3.73 (m, 1H), 3.62 – 3.51 (m, 4H), 2.30 (dd, 1H, *J* = 4.4, 16.4 Hz), 2.20 – 2.10 (m, 5H), 2.05 (m, 1H), 1.85 (m, 1H), 1.66 – 1.56 (m, 3H), 0.86 (s, 9H), 0.006 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 152.4, 148.6, 140.4, 124.4, 122.4, 120.7, 114.6, 111.2, 62.6, 56.4, 55.8, 45.4, 34.9, 33.6, 30.5, 26.1, 23.2, 18.5, -5.13; IR

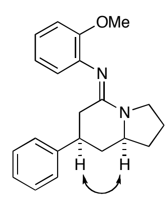
(Thin Film) 2940, 1654, 1579, 1441, 1322, 1252, 1102 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 415.27753, found 415.27832.



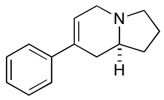
(*S*,*E*)-*N*-(7-(4-chlorobutyl)-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)-2-methoxyaniline (3pc). General procedure with alkyne **1p** and carbodiimide **2c** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 32.1 mg of the cycloadduct (60%); R_f = 0.46 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 179.6 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 13.88 minutes, Minor: 11.04 minutes, 230 nm detection light, *ee* = 88%; ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (m, 1H), 6.86 – 6.83 (m, 2H), 6.73 (d, 1H, *J* = 7.5 Hz), 5.74 (m, 1H), 3.79 (s, 3H), 3.76 (m, 1H), 3.62 – 3.53 (m, 2H), 3.49 (t, 2H, *J* = 6.4 Hz), 2.30 (dd, 1H, *J* = 4.5, 16.4 Hz), 2.20 – 2.05 (m, 5H), 1.86 (m, 1H), 1.74 – 1.52 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.4, 140.0, 124.4, 122.6, 120.7, 115.1, 111.2, 56.4, 55.8, 45.5, 44.8, 36.3, 34.6, 33.6, 32.0, 24.4, 23.2; IR (Thin Film) 2942, 1649, 1581, 1489, 1439, 1328, 1241, 1173, 1118 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 333.17281, found 333.17217.



(*S*,*E*)-2-methoxy-*N*-(7-phenethyl-2,3,8,8a-tetrahydroindolizin-5(1*H*)-ylidene)aniline (3qc). General procedure with alkyne **1q** and carbodiimide **2c** in the presence of 5 mol% $[Rh(C_2H_4)_2Cl]_2$ and 10 mol% **L4** yielded 39.3 mg of the cycloadduct (70%); R_f = 0.47 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 219.8 (c = 1, $CHCl_3$); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 17.02 minutes, Minor: 12.63 minutes, 230 nm detection light, *ee* = 92%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.18 (m, 1H), 7.10 (d, 2H, *J* = 7.9 Hz), 6.93 (m, 1H), 6.84 – 6.78 (m, 2H), 6.58 (d, 1H, *J* = 7.7 Hz), 5.75 (m, 1H), 3.78 (s, 3H), 3.74 (m, 1H), 3.61 – 3.52 (m, 2H), 2.72 – 2.61 (m, 2H), 2.42 – 2.38 (m, 2H), 2.31 (dd, 1H, *J* = 4.5, 16.4 Hz), 2.22 – 2.14 (m, 2H), 2.04 (m, 1H), 1.85 (m, 1H), 1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.4, 147.7, 141.2, 140.2, 128.6, 128.5, 126.3, 124.4, 122.4, 120.6, 115.2, 111.2, 56.3, 55.8, 45.4, 39.0, 35.0, 33.8, 33.6, 23.2; IR (Thin Film) 2930, 1649, 1581, 1489, 1439, 1328, 1247, 1118 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 342.21179, found 342.21059.



(*E*)-2-methoxy-*N*-((7*R*,8a*S*)-7-phenylhexahydroindolizin-5(1*H*)-ylidene)aniline (11). A mixture of **3ac** (29.1 mg, 0.0914 mmol) and 34 mg of 10% Pd/C in 3 ml of MeOH was stirred at ambient temperature under hydrogen atmosphere (1 atm) for 3 hours. The reaction mixture was filtered through celite and concentrated *in vacuo*. Upon purification by column chromatography 27.0 mg (92%) of the desired product was isolated; R_f = 0.44 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = – 155.0 (c = 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.19 – 7.12 (m, 3H), 6.87 (ddd, 1H, *J* = 1.7, 7.7, 7.7 Hz), 6.82 – 6.74 (m, 3H), 3.79 (s, 3H), 3.74 – 3.66 (m, 2H), 3.54 (dddd, 1H, *J* = 4.1, 4.1, 10.9, 10.9 Hz), 2.94 (dddd, 1H, *J* = 3.3, 5.3, 12.2, 17.7 Hz), 2.55 (dd, 1H, *J* = 5.3, 16.8 Hz), 2.27 – 2.20 (m, 2H), 2.12 (m, 1H), 2.05 (m, 1H), 1.87 (m, 1H), 1.66 – 1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 151.6, 145.0, 140.5, 128.8, 126.9, 126.8, 124.1, 122.4, 121.1, 111.5, 59.3, 55.8, 46.4, 39.9, 36.8, 34.3, 33.7, 22.8; IR (Thin Film) 2932, 1602, 1584, 1462, 1443, 1320, 1242, 1110 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 321.19614, found 321.19721.



(*S*)-7-phenyl-1,2,3,5,8,8a-hexahydroindolizine (12). To a solution of **3ac** (33.0 mg, 0.104 mmol) in 2 ml of anhydrous THF was added 0.5 ml of 1M DIBAL solution (in hexane) at 0 °C. The reaction mixture was stirred at ambient temperature until the disappearance of starting material. The reaction was quenched with H_2O and then 2N NaOH, and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Upon purification by column chromatography 15.0 mg (72%) of the desired product was isolated; R_f = 0.36 (96:4 EtOAc/Et_3N); $[\alpha]_D^{20}$ = + 85.3 (c = 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, 2H, *J* = 7.6 Hz), 7.32 (t, 2H, *J* = 7.6 Hz), 7.23 (t, 1H, *J* = 7.2 Hz), 6.08 (m, 1H), 3.69 (dm, 1H, *J* = 16.4 Hz), 3.25 (ddd, 1H, *J* = 2.0, 8.8, 8.8 Hz), 2.93 (dm, 1H, *J* = 16.4 Hz), 2.67 (ddd, 1H, *J* = 2.8, 2.8, 16.0 Hz), 2.40 (m, 1H), 2.30 (m, 1H), 2.20 (q, 1H, 8.9 Hz), 2.07 (m, 1H), 1.92 (m, 1H), 1.80 (m, 1H), 1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 135.9, 128.5, 127.1, 125.4, 122.6, 60.4, 54.5, 53.1, 35.0, 31.1, 21.7; IR (Thin Film) 2960, 2910, 2779, 1496, 1446, 1384, 1328, 1147 cm^{-1}; HRMS (ESI) *m/e* calcd ($M+H^+$) 200.14337, found 200.14313.

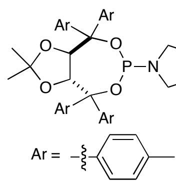
^1H NMR and ^{13}C NMR spectra of new compounds are attached:

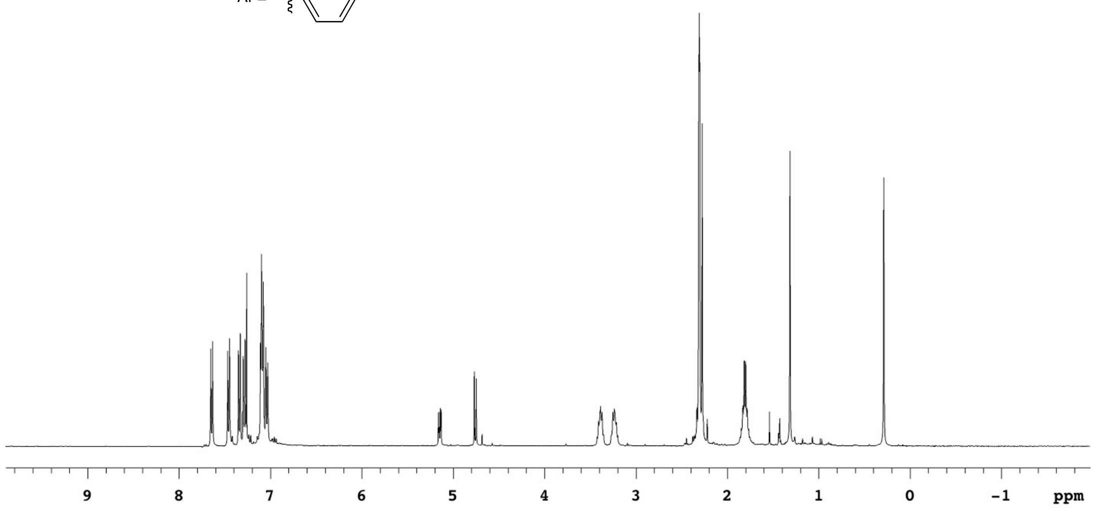
X-ray data of **3bc** is attached following the spectra

L3

STANDARD 1H OBSERVE

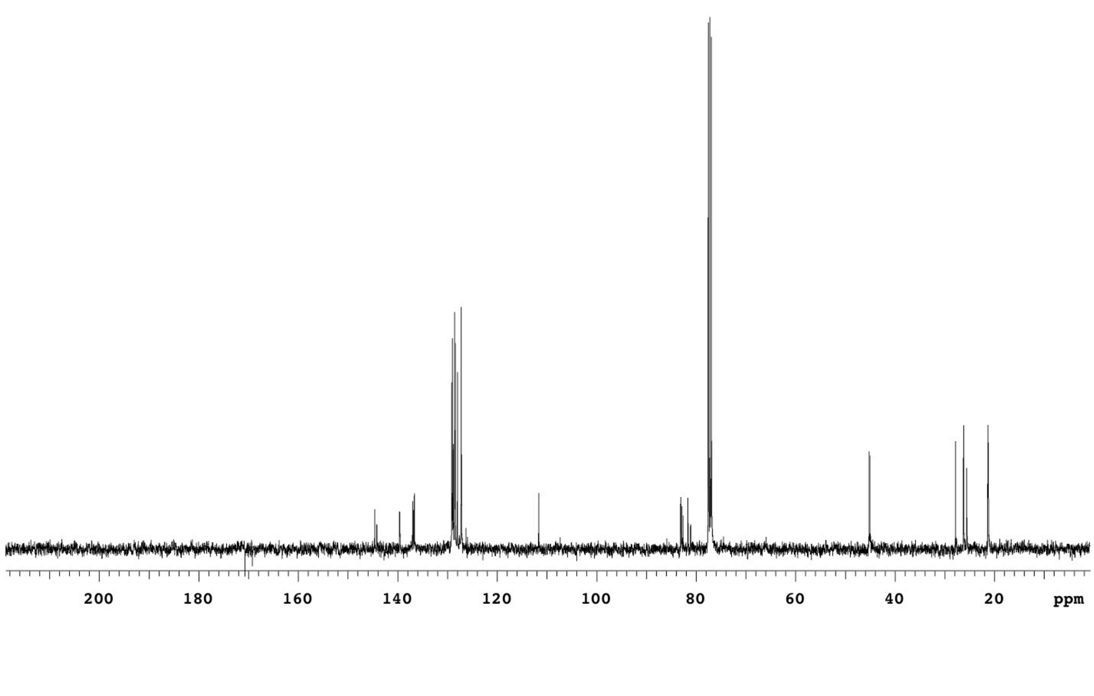
yu3-55
yu3-55



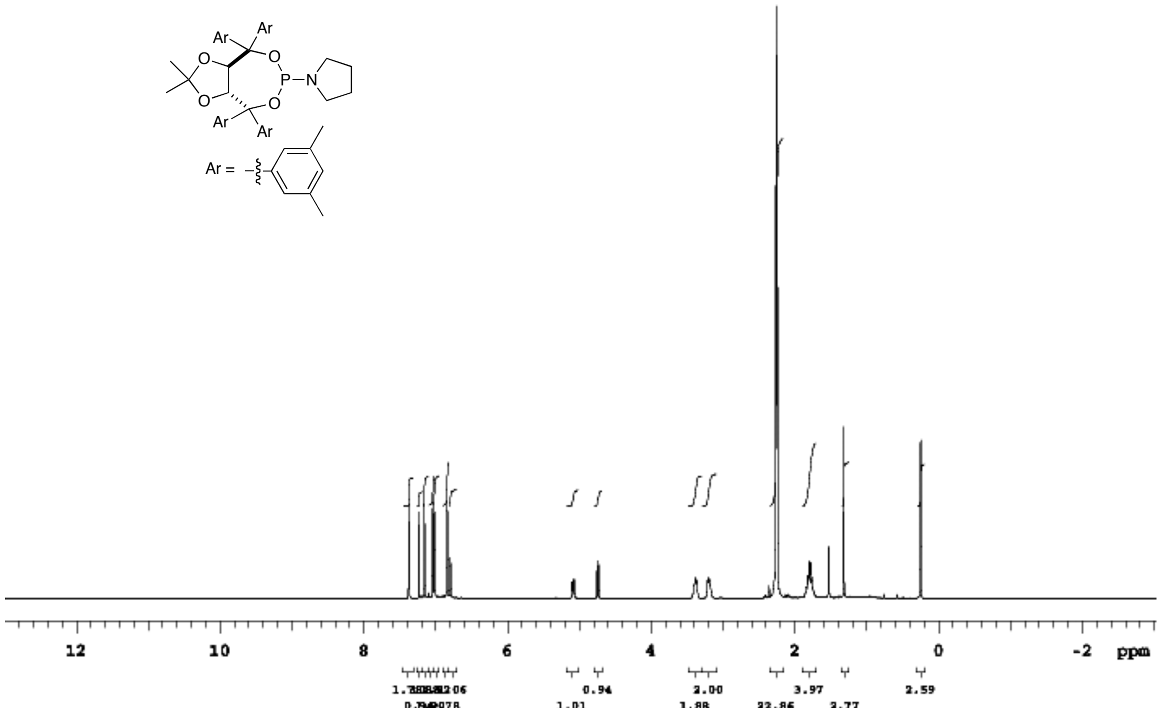


13C OBSERVE

yu3-55
yu3-55



L4



Ar
Ar
O
O
P
N
O
O
Ar
Ar
Ar =
12
10
8
6
4
2
0
-2
ppm
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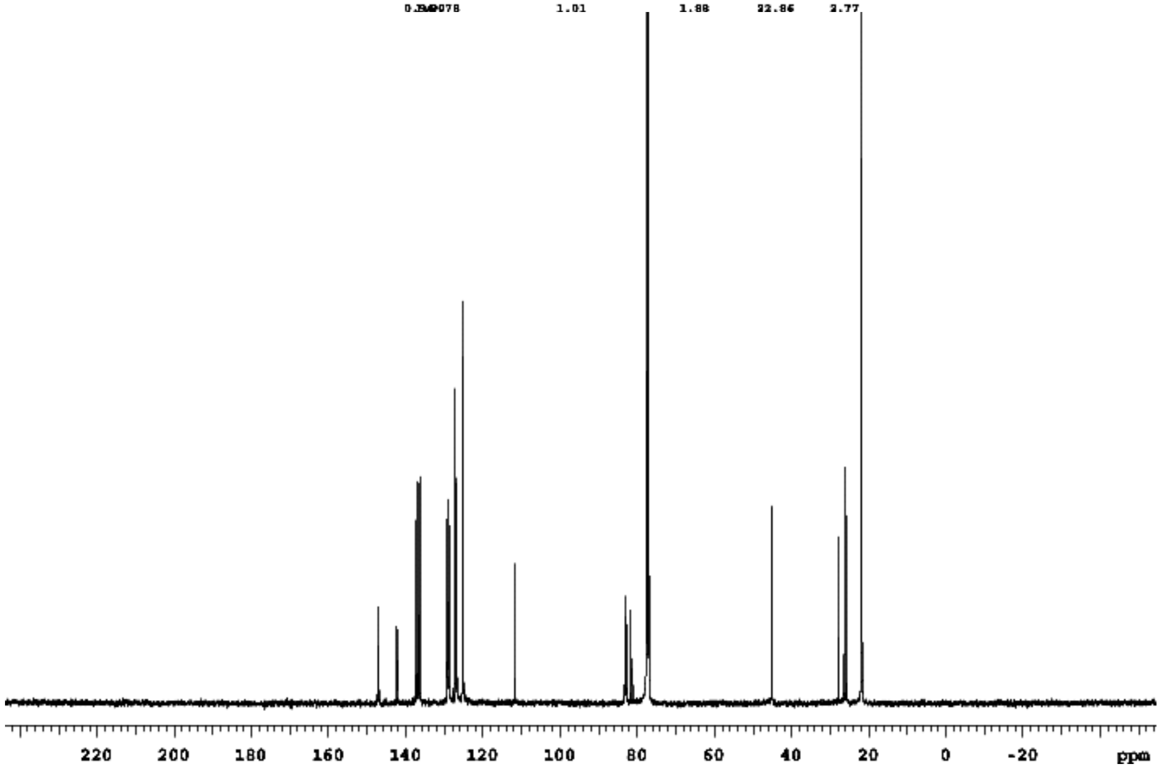
2.00
3.97
2.59
1.01
1.88
22.86
2.77



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40
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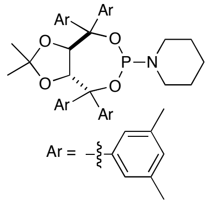
-20
ppm

L5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P
N
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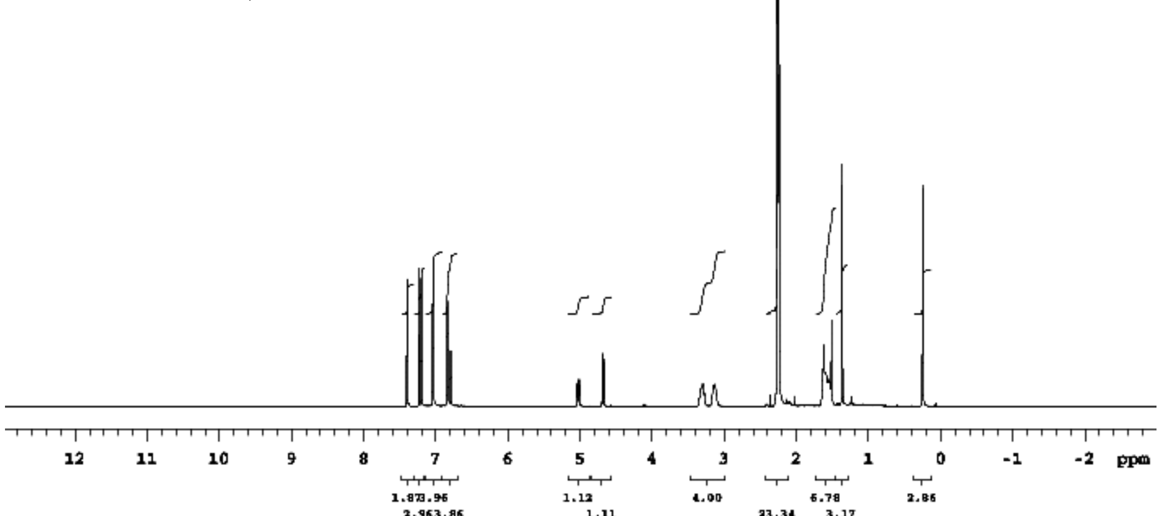
Ar
Ar
Ar =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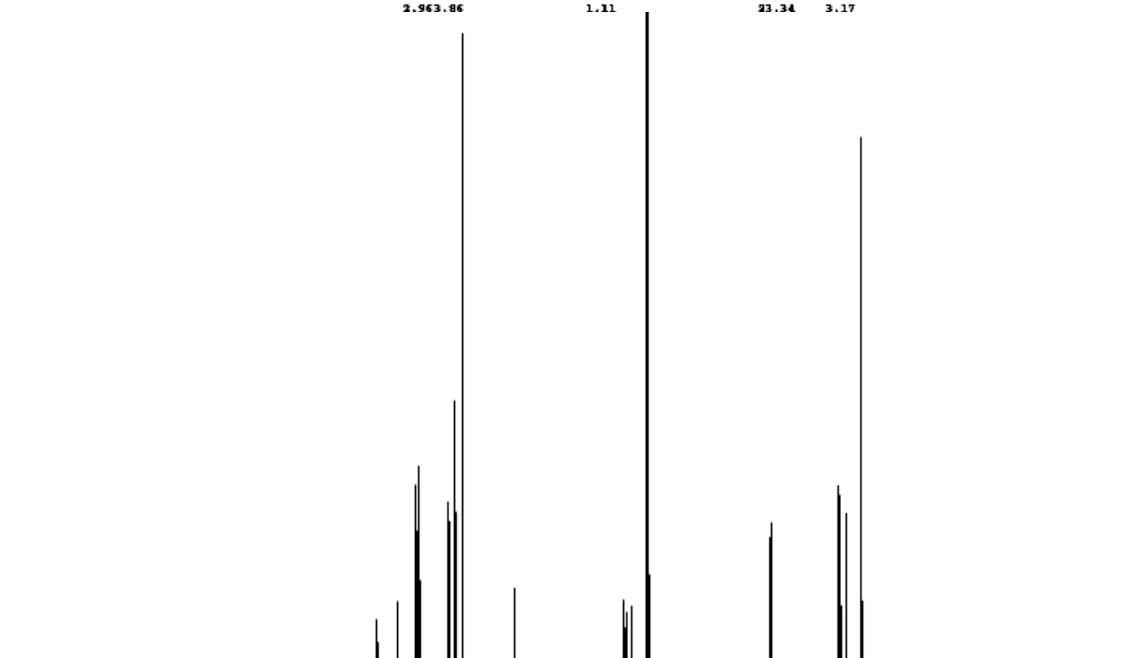
2.96 3.86
1.12
1.11
4.00
23.34
6.78
3.17
2.86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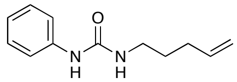
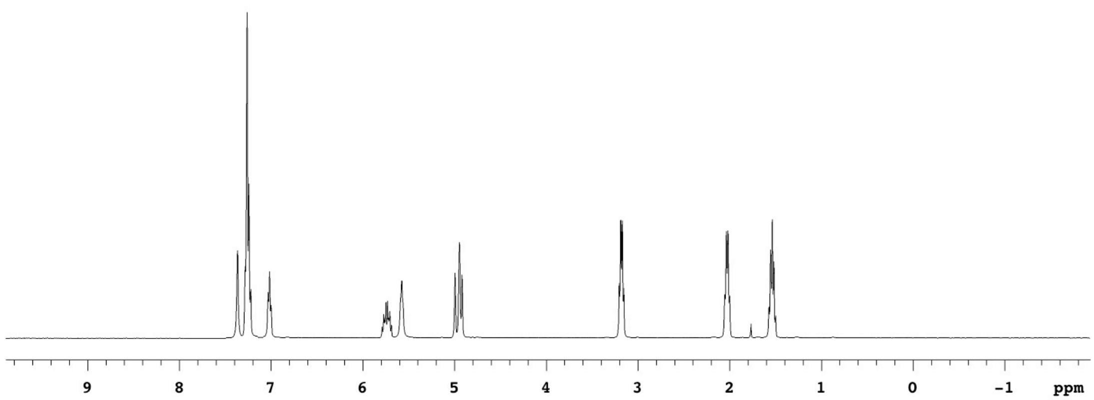
STANDARD 1H OBSERVE

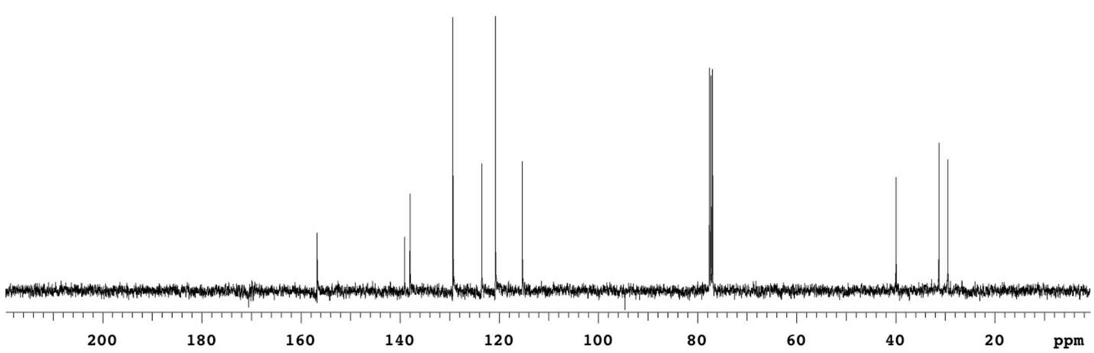
yu3-58





13C OBSERVE

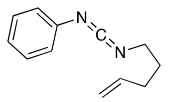
yu3-58

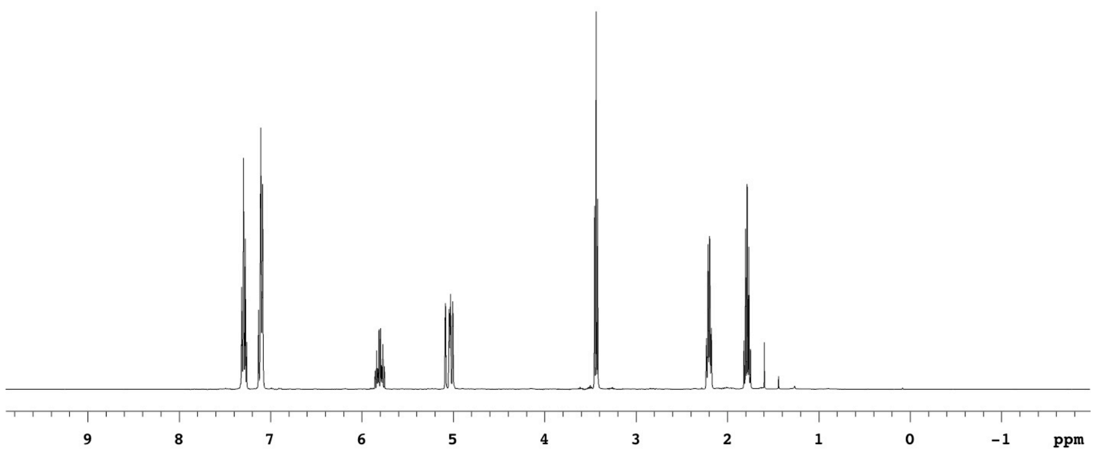


2a

STANDARD 1H OBSERVE

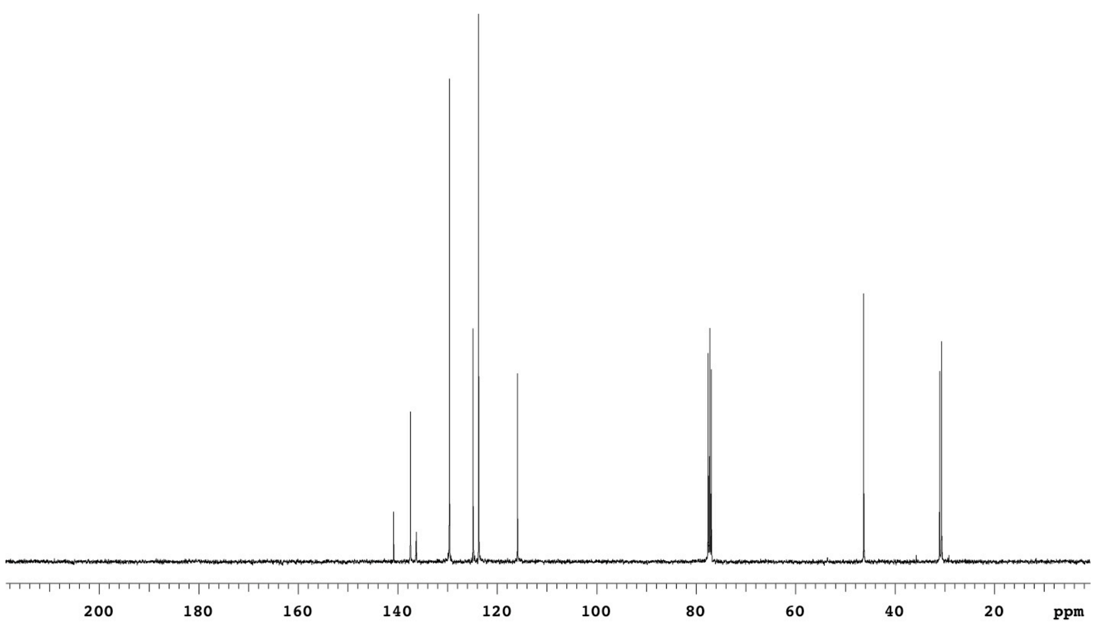
yu3-60





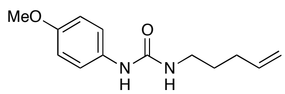
13C OBSERVE

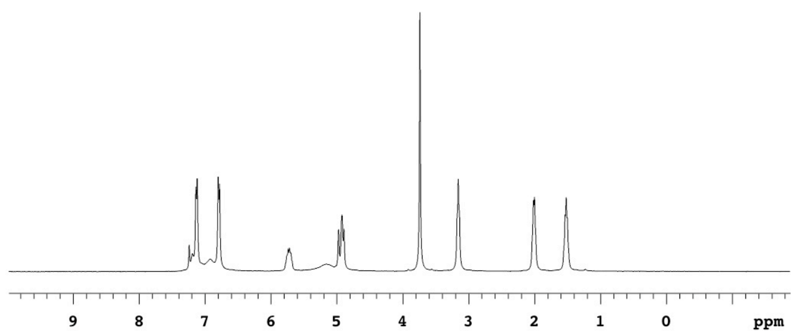
yu3-60
yu3-60



STANDARD 1H OBSERVE

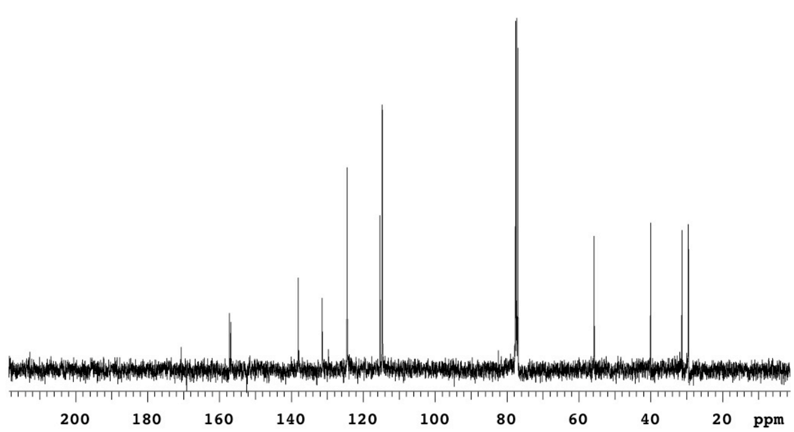
yu3-26



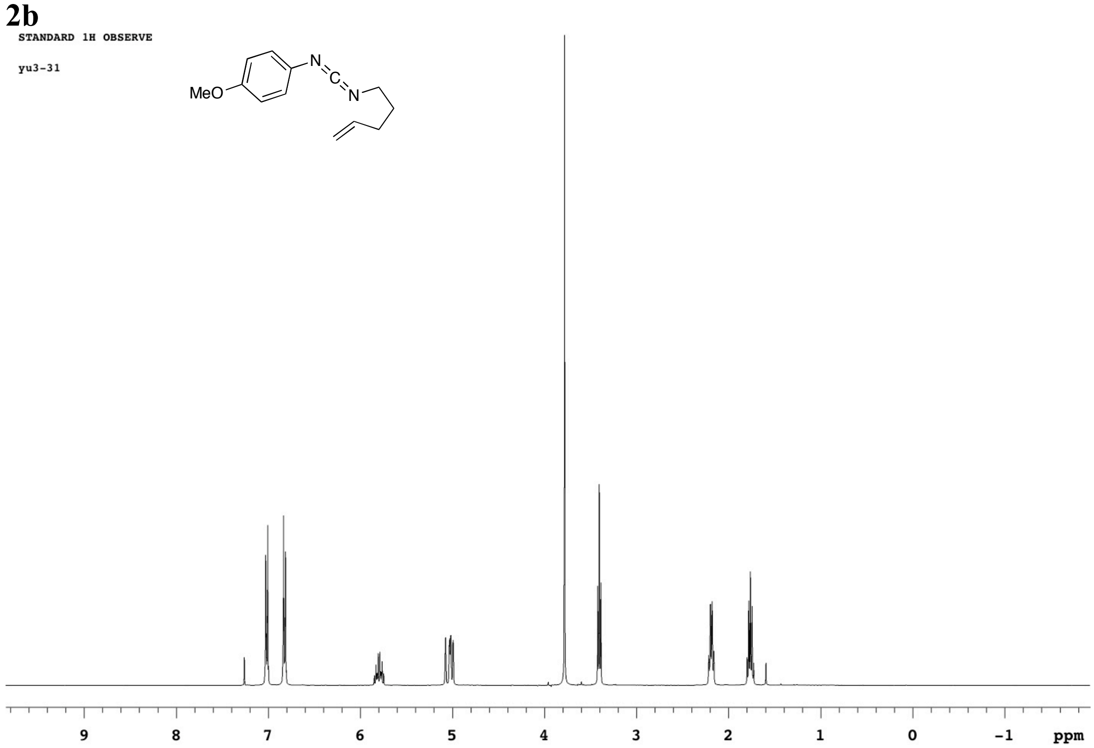


13C OBSERVE

yu3-26



2b


STANDARD 1H OBSERVE
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7
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4
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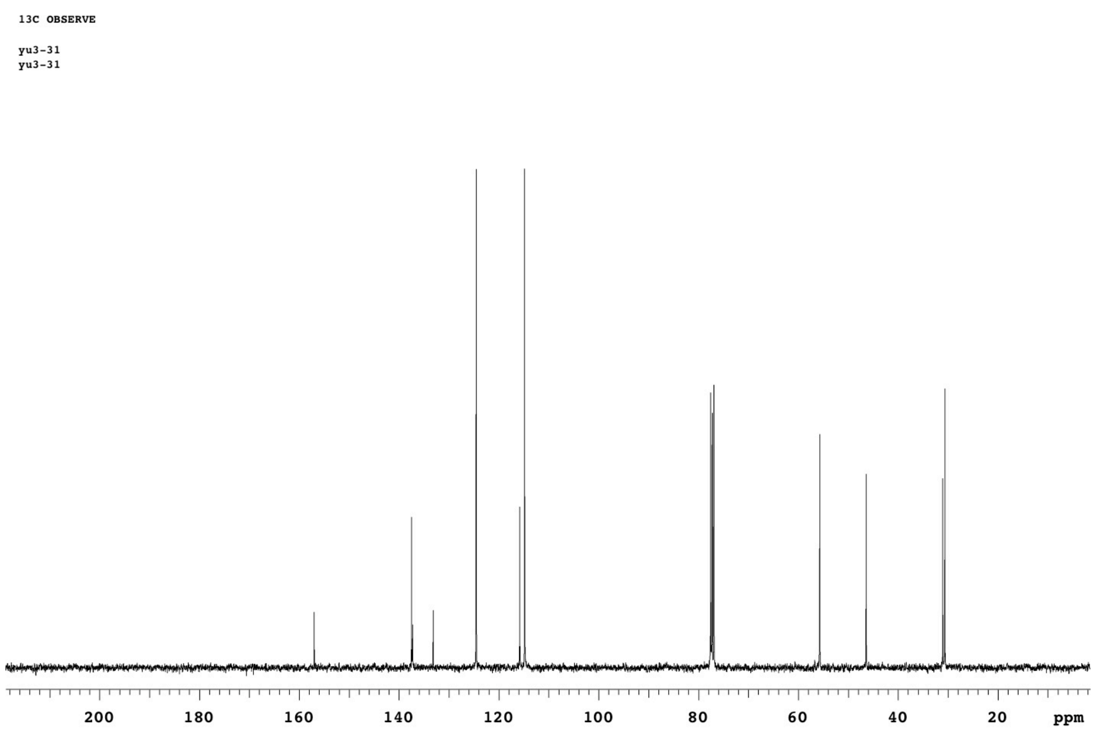
-1
ppm


13C OBSERVE
yu3-31
yu3-31
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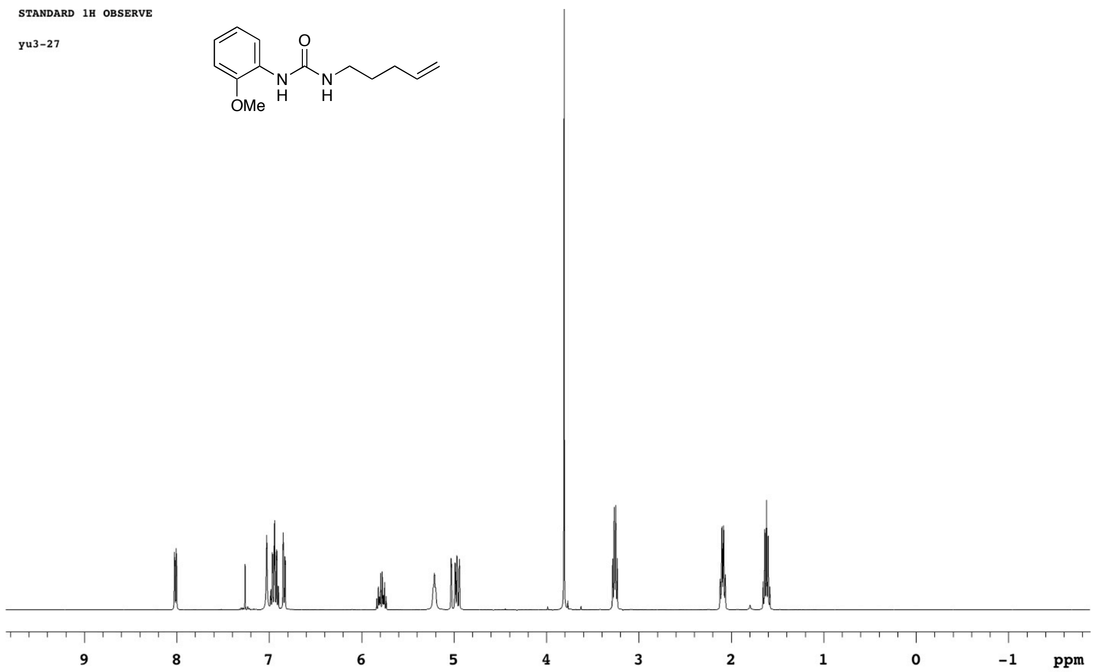
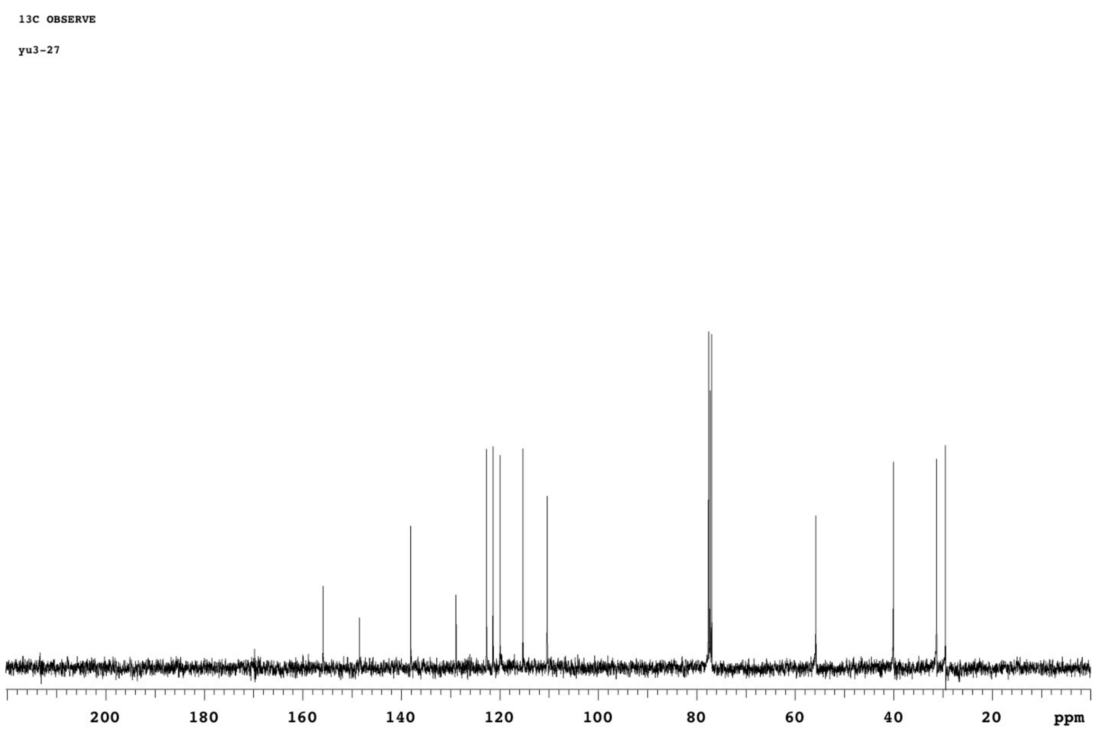
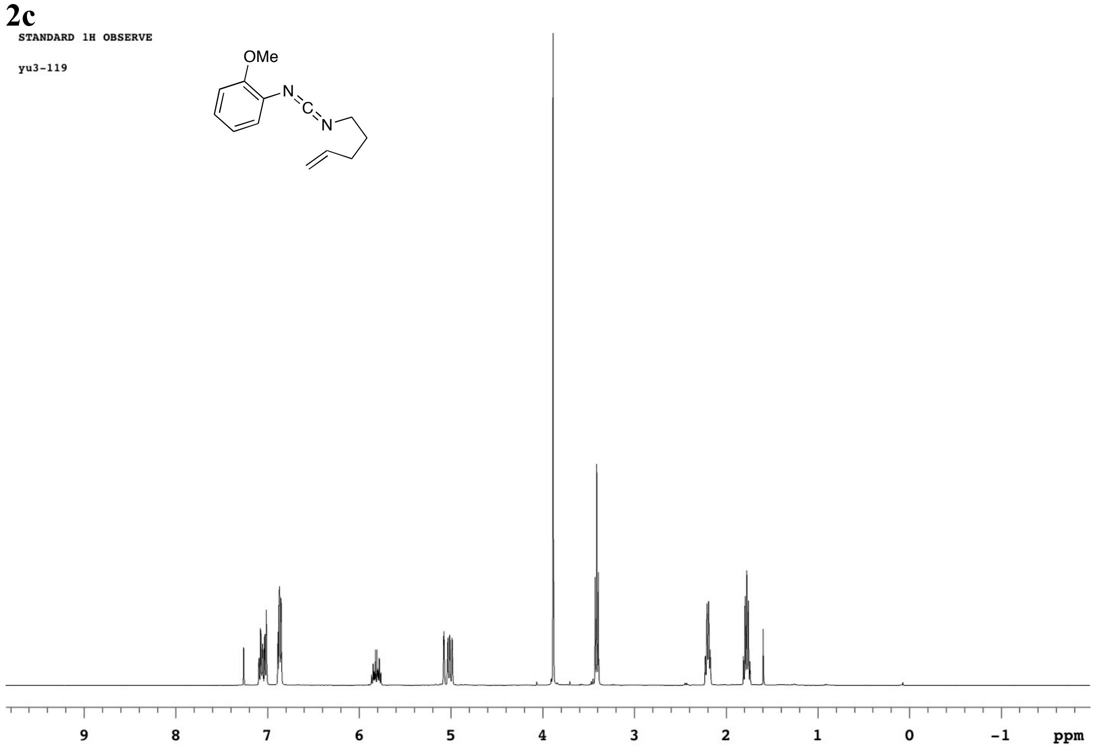
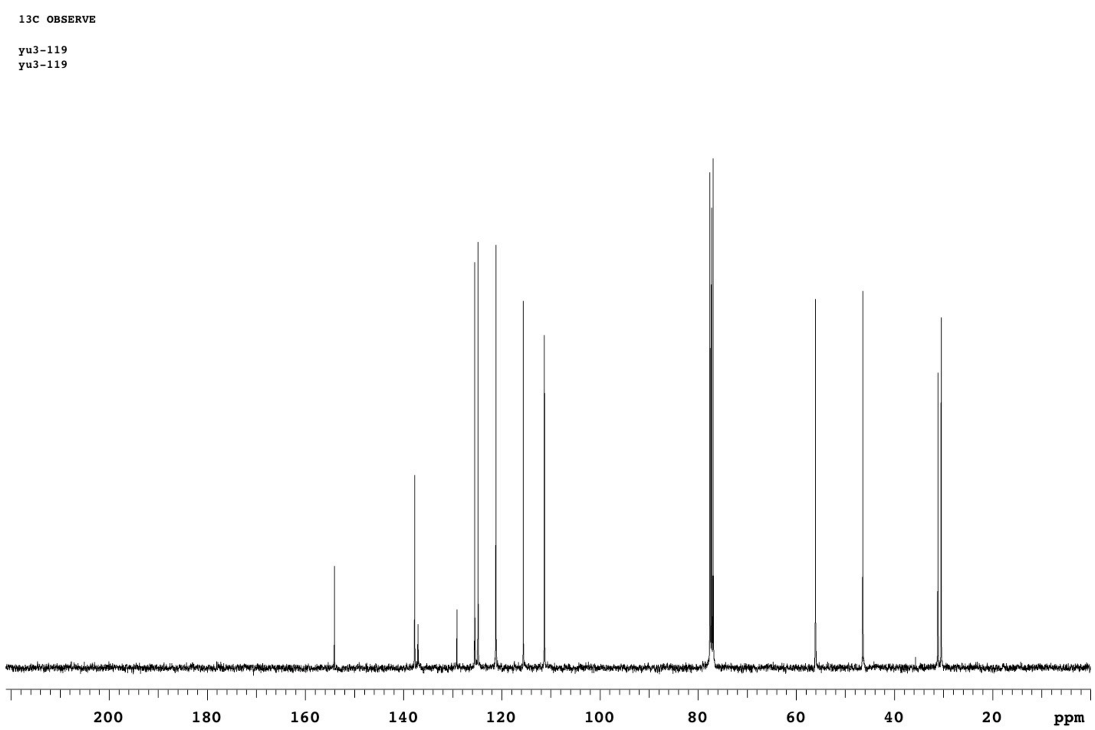
180
160
140
120
100
80
60
40
20
ppm


STANDARD 1H OBSERVE
yu3-27
O
N
H
N
H
OMe
9 8 7 6 5 4 3 2 1 0 -1 ppm


13C OBSERVE
yu3-27
200 180 160 140 120 100 80 60 40 20 ppm

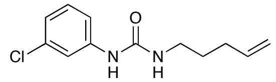
2c

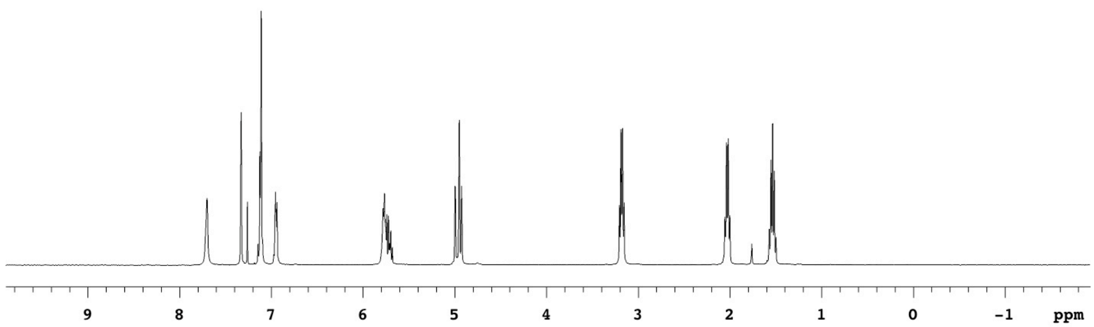

STANDARD 1H OBSERVE
yu3-119
OMe
N
C
N
9 8 7 6 5 4 3 2 1 0 -1 ppm


13C OBSERVE
yu3-119
yu3-119
200 180 160 140 120 100 80 60 40 20 ppm

STANDARD 1H OBSERVE

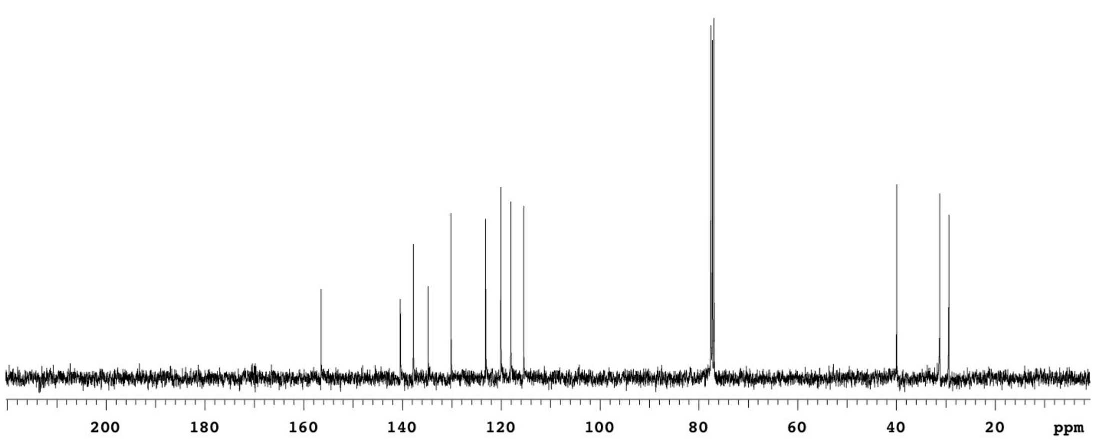
yu3-59
yu3-59





13C OBSERVE

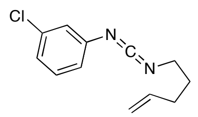
yu3-59
yu3-59

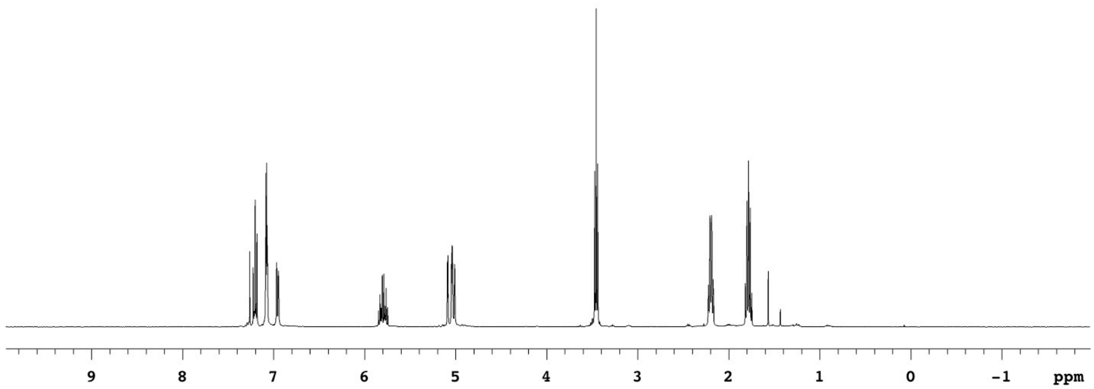


2d

STANDARD 1H OBSERVE

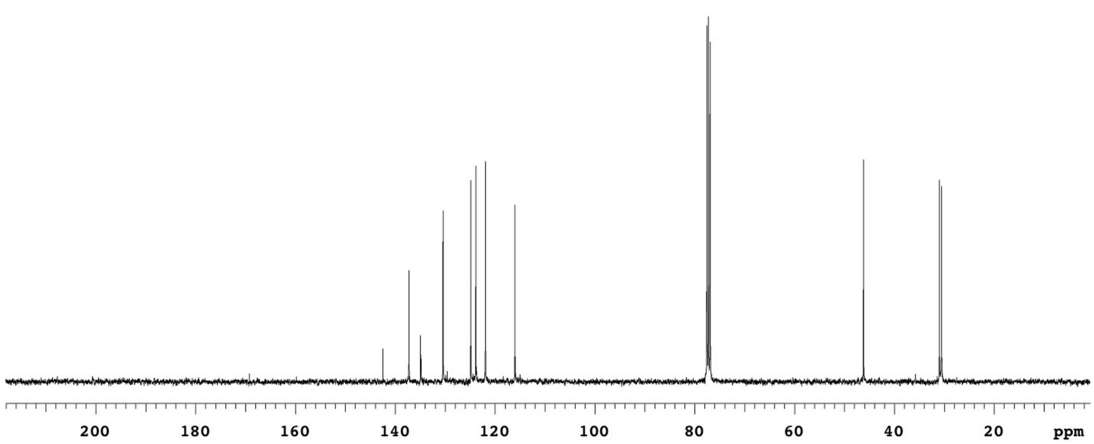
yu3-111
yu3-111





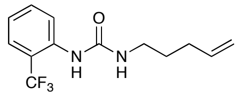
13C OBSERVE

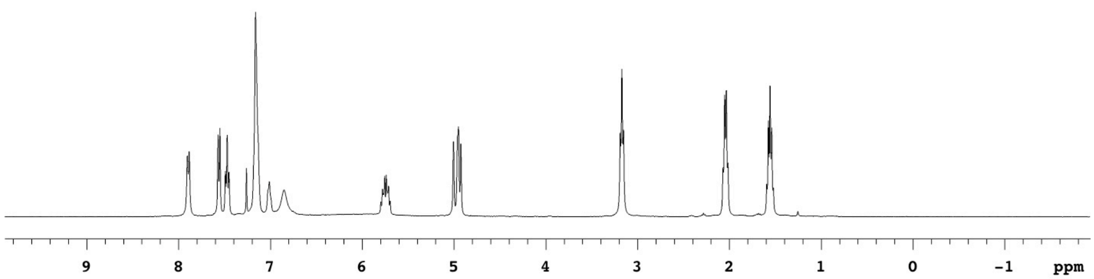
yu3-111
yu3-111



STANDARD 1H OBSERVE

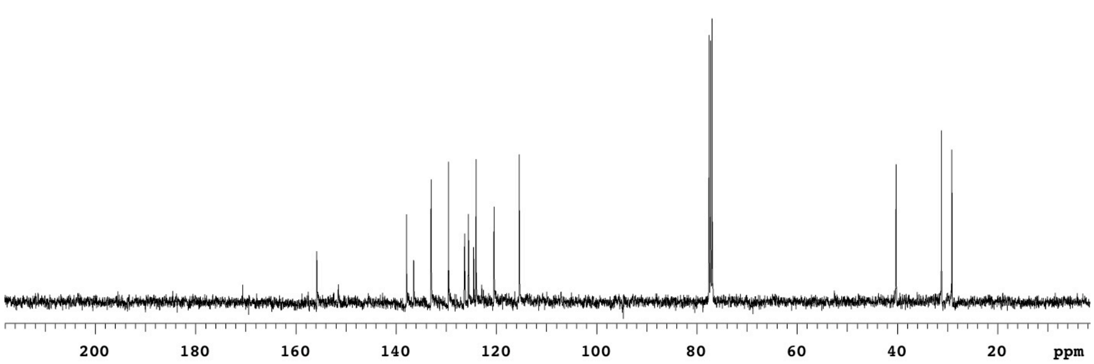
yu3-78





13C OBSERVE

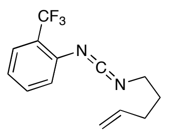
yu3-78

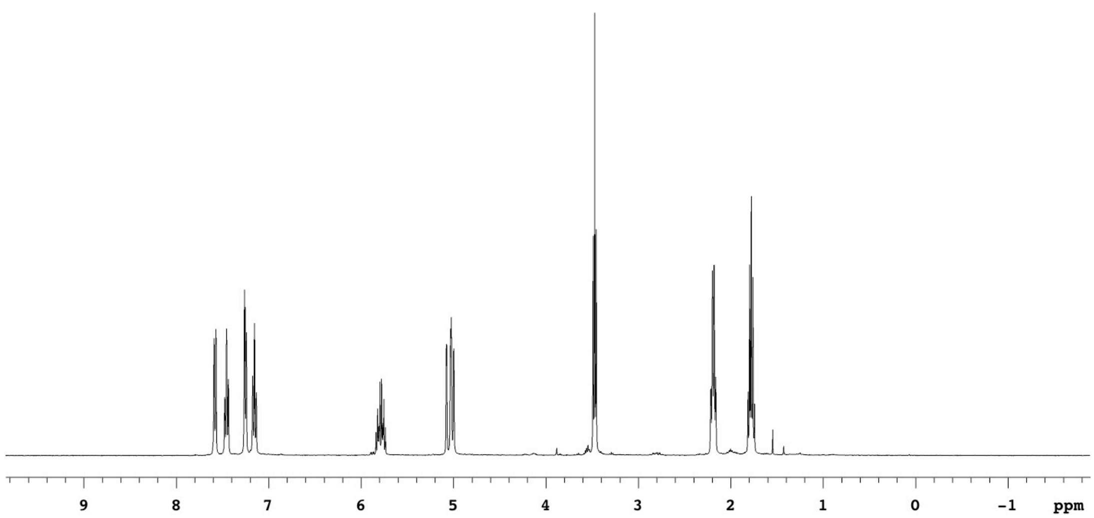


2e

STANDARD 1H OBSERVE

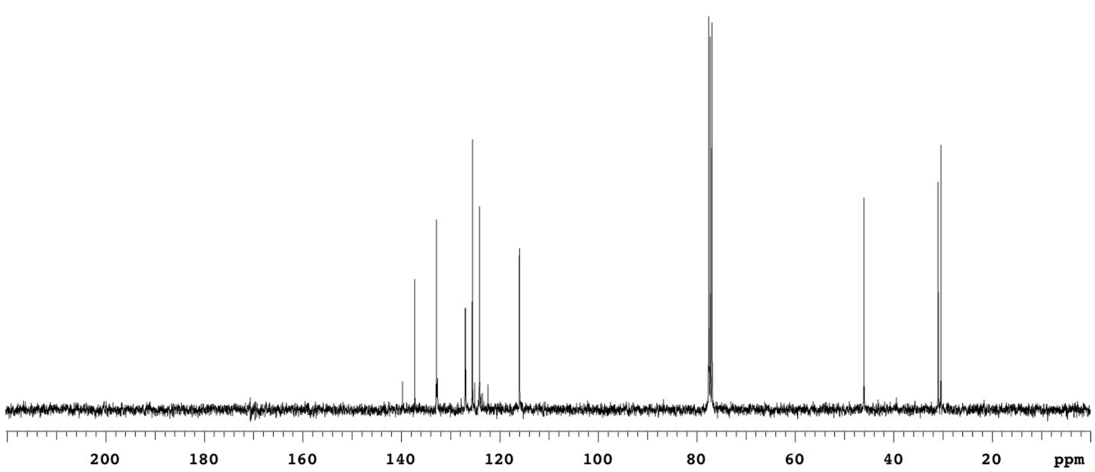
yu3-175
yu3-175





13C OBSERVE

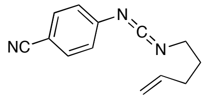
yu3-175

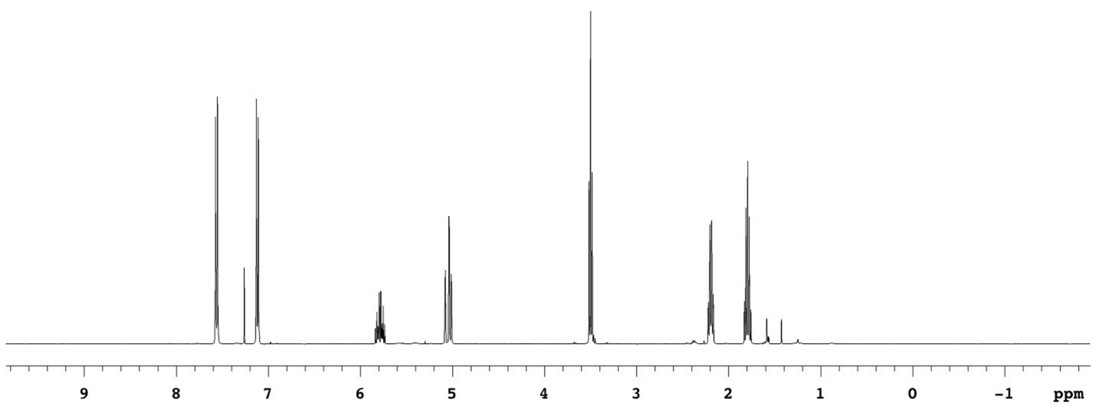


2f

STANDARD 1H OBSERVE

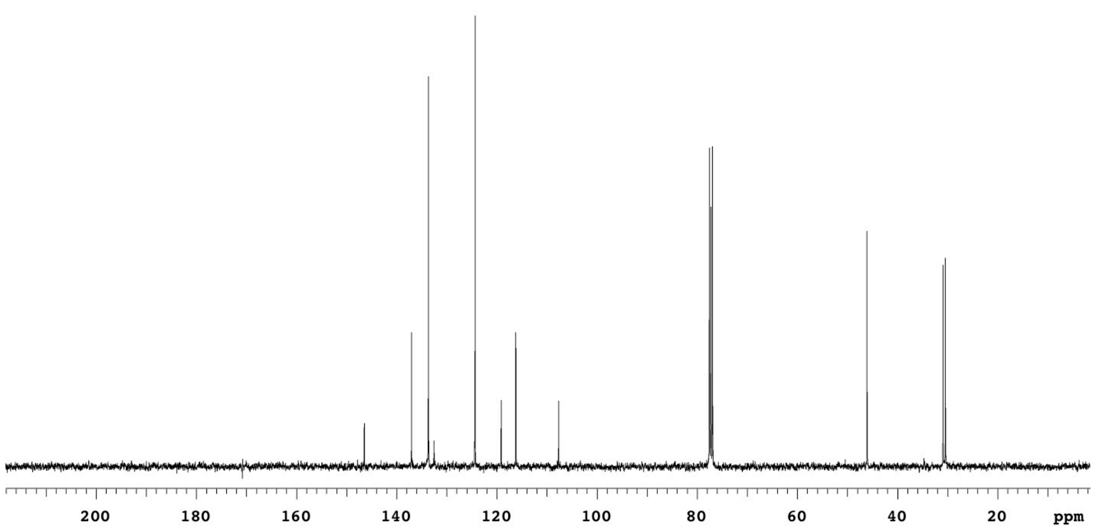
yu3-197
yu3-197

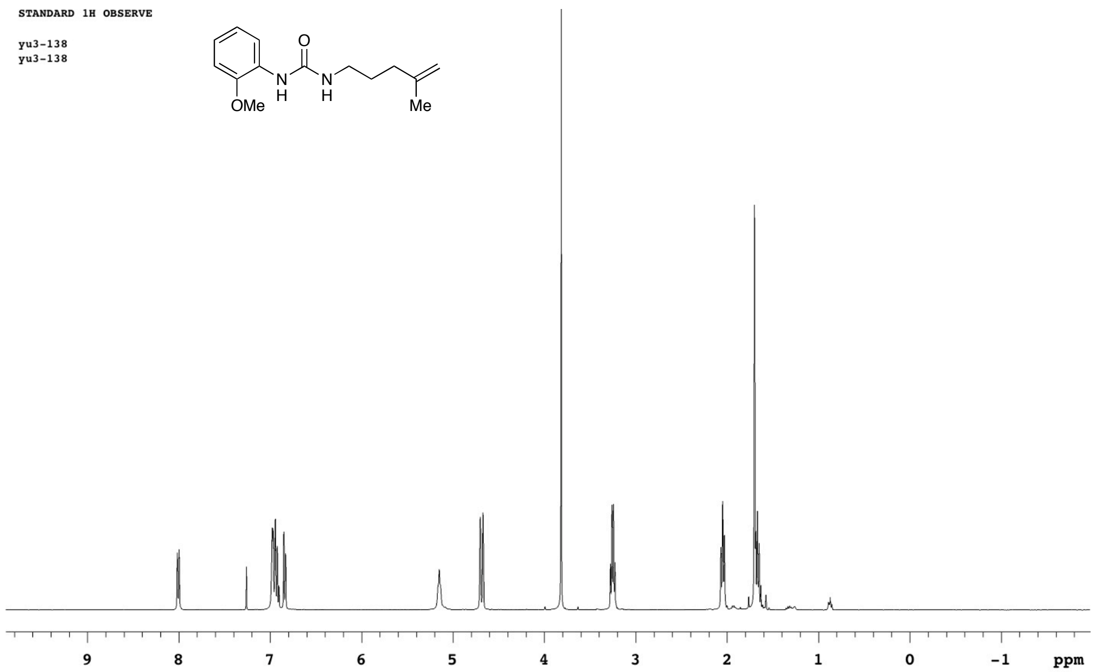


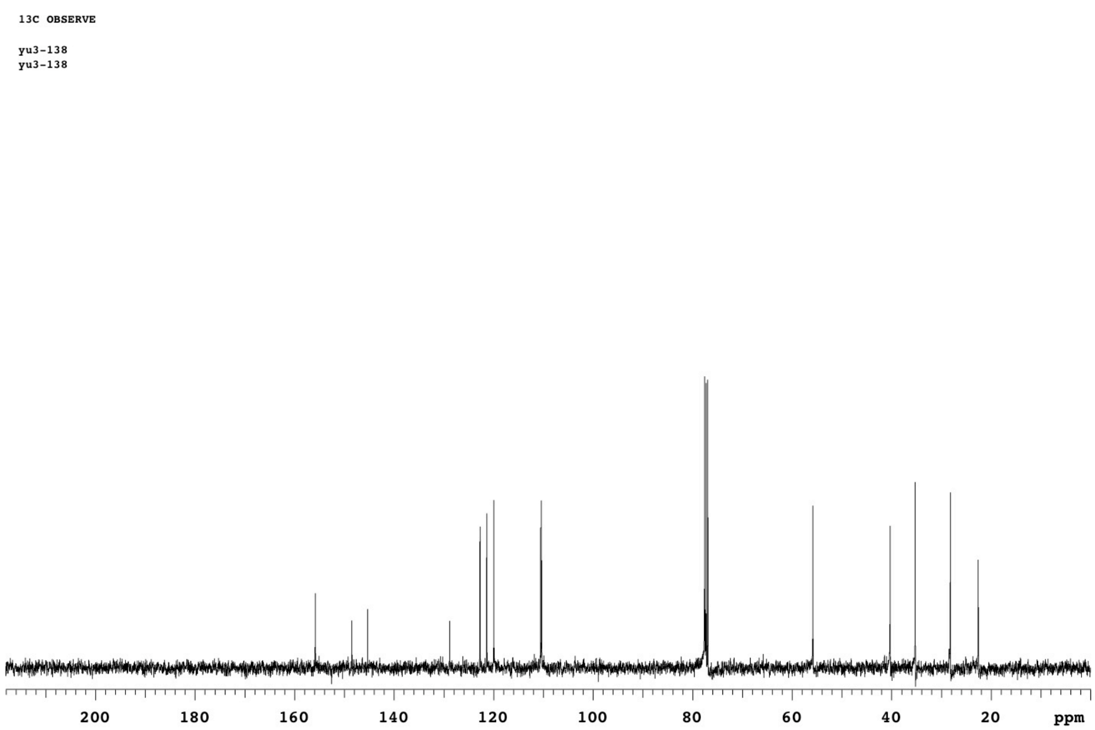


13C OBSERVE

yu3-197
yu3-197



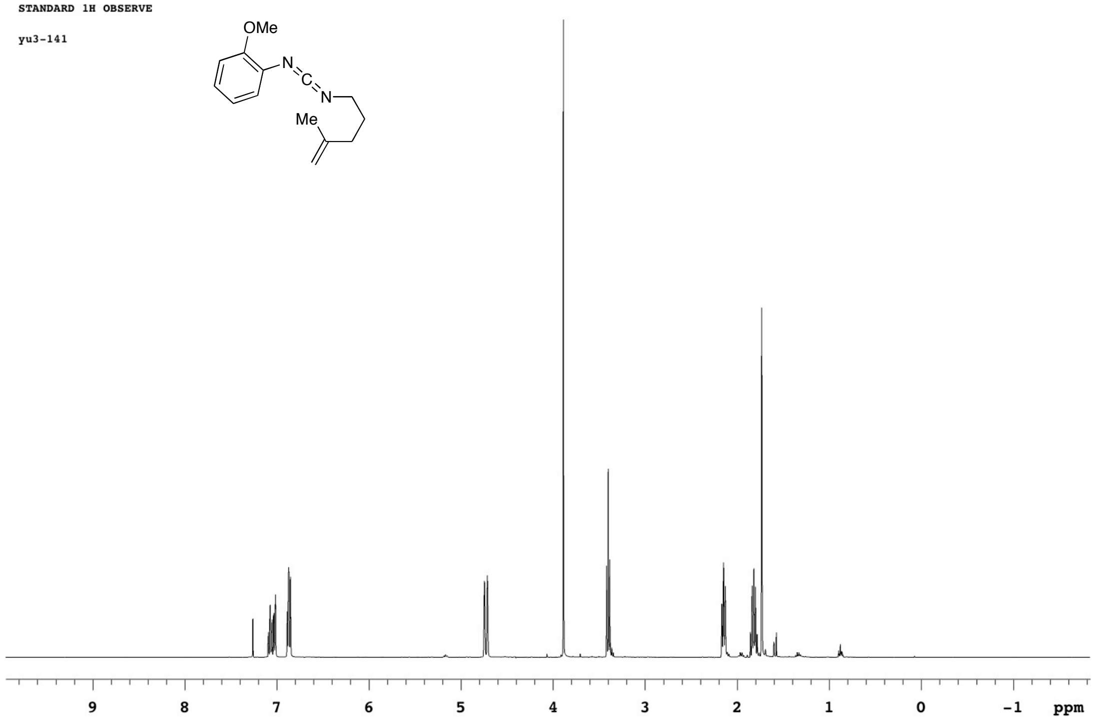

STANDARD 1H OBSERVE
yu3-138
yu3-138
O
N
H
N
H
OMe
Me
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-138
yu3-138
200
180
160
140
120
100
80
60
40
20
ppm

5

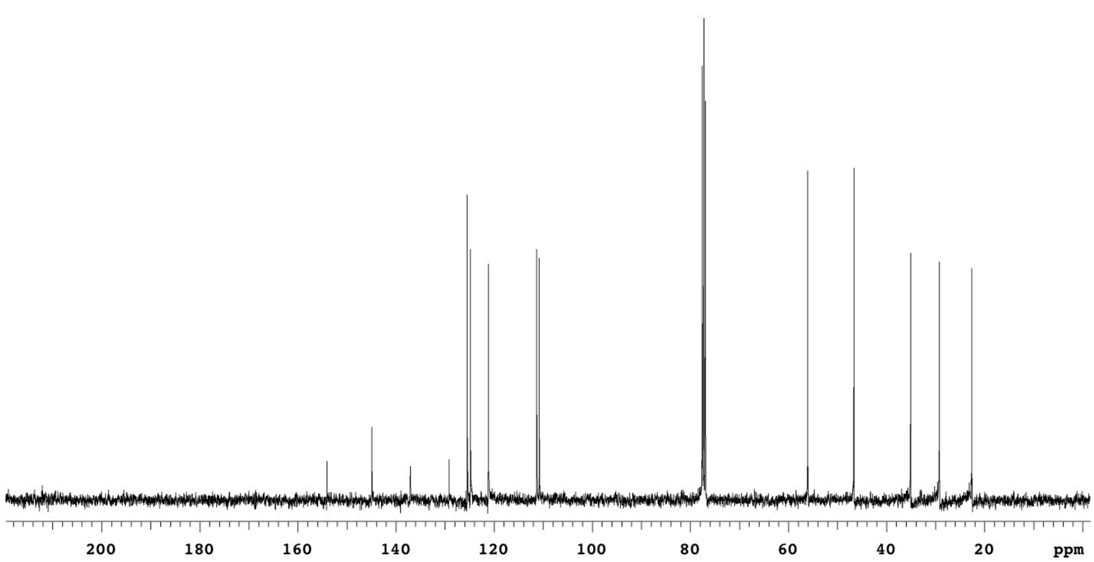
STANDARD 1H OBSERVE

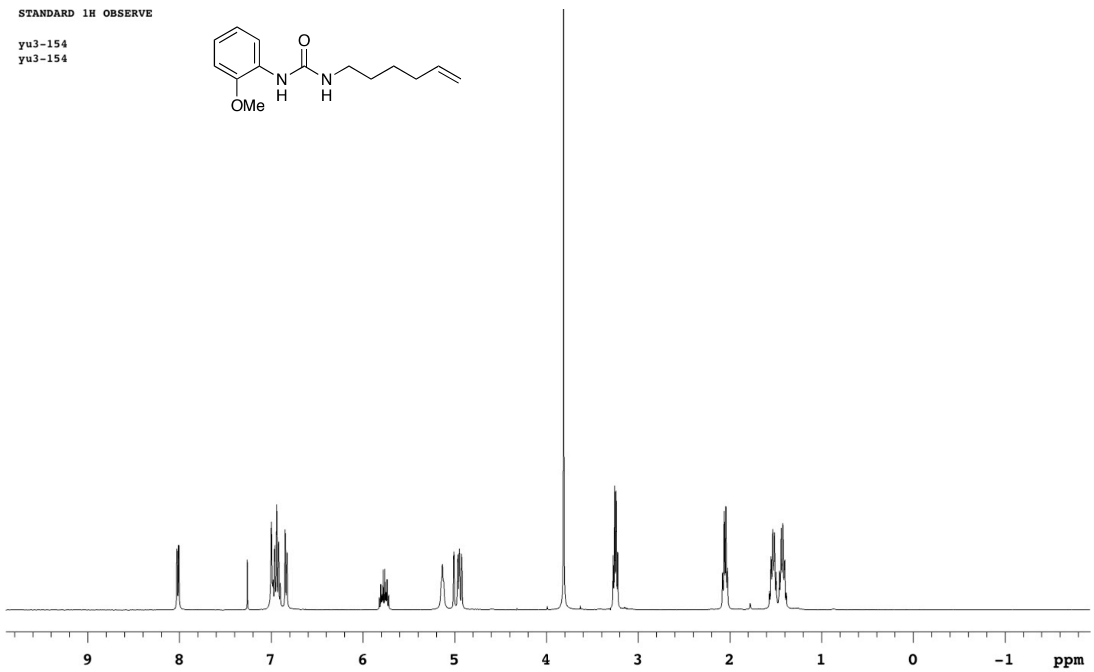
yu3-141

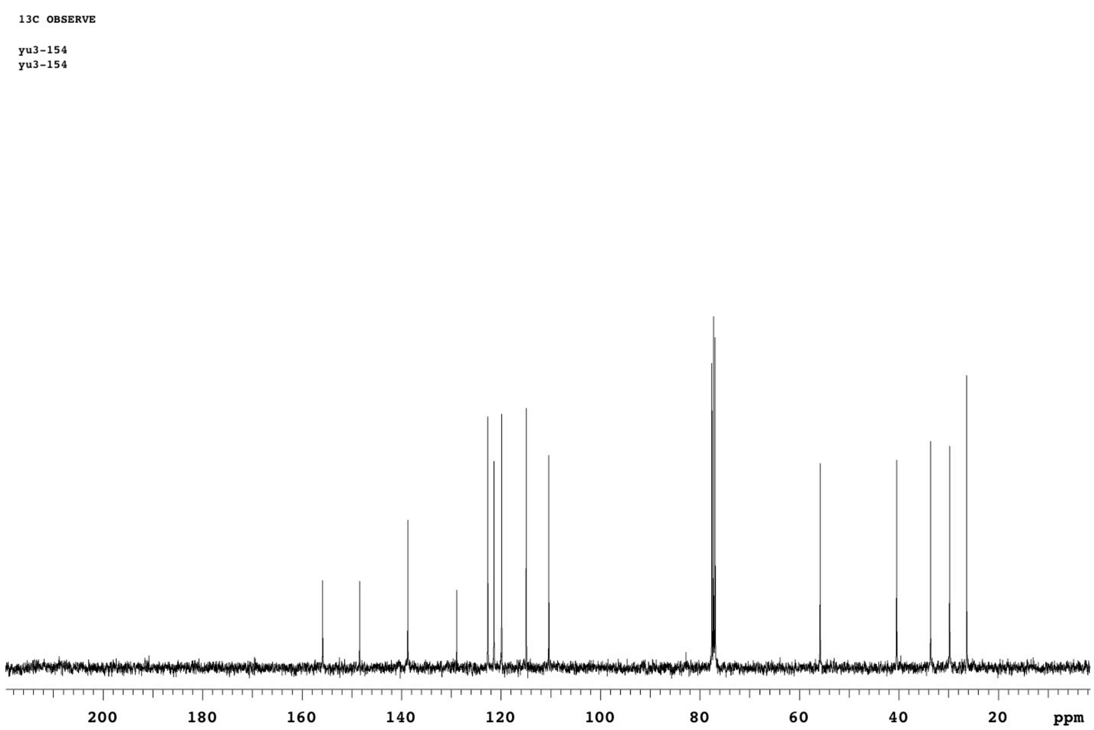


13C OBSERVE

yu3-141
yu3-141



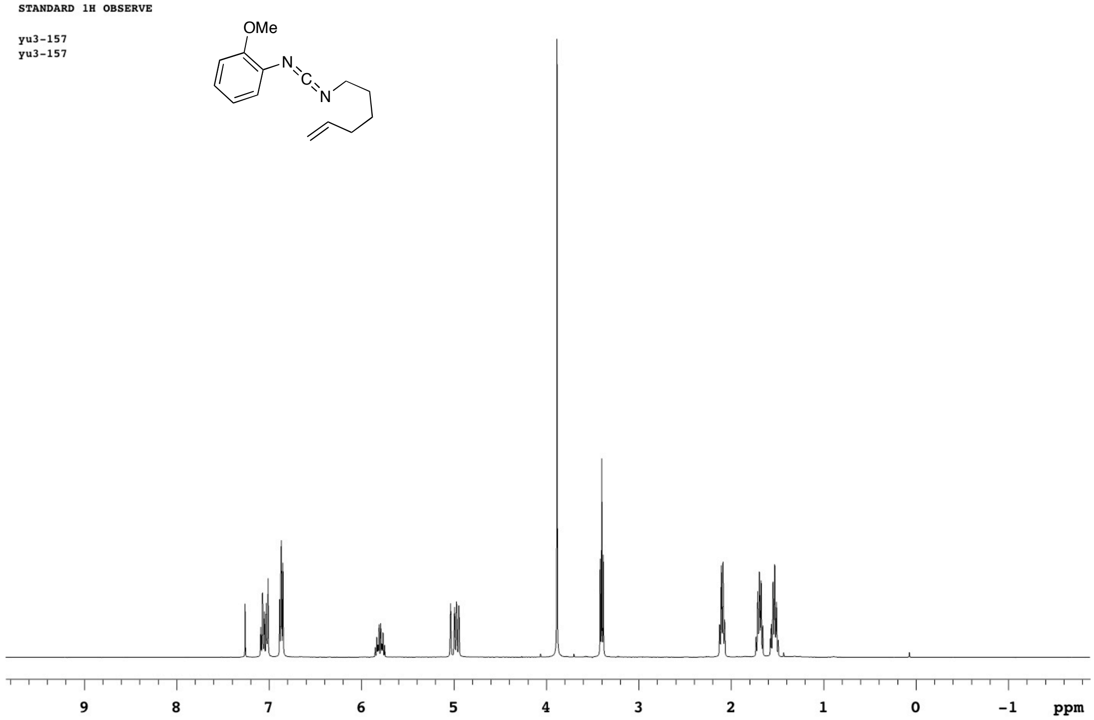

STANDARD 1H OBSERVE
yu3-154
yu3-154
O
N
H
N
H
OMe
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-154
yu3-154
200
180
160
140
120
100
80
60
40
20
ppm

8

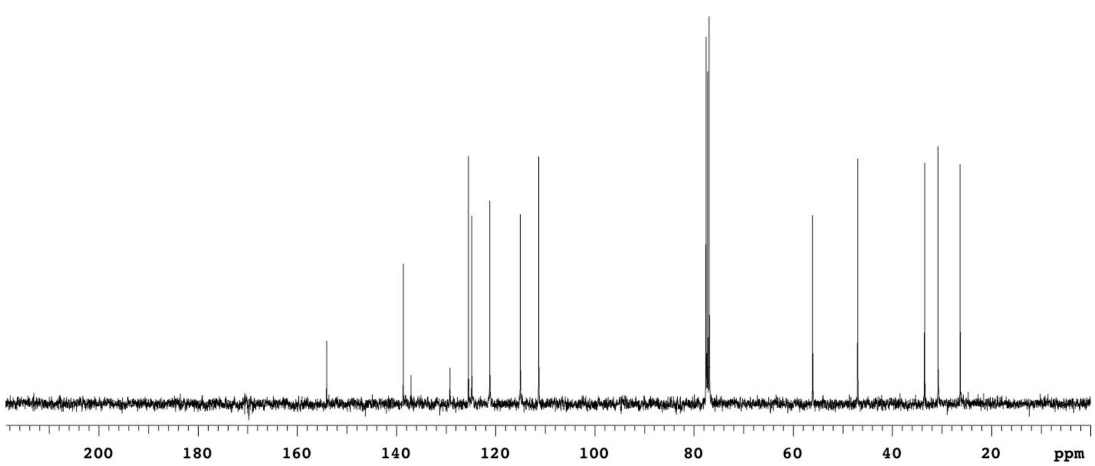
STANDARD 1H OBSERVE

yu3-157
yu3-157



13C OBSERVE

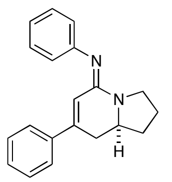
yu3-157
yu3-157

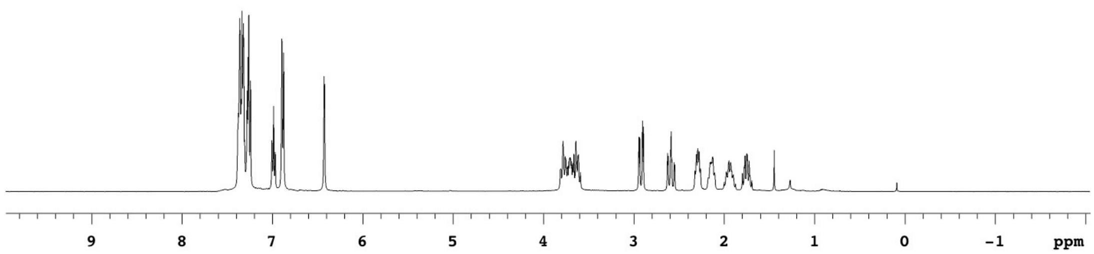


3aa

STANDARD 1H OBSERVE

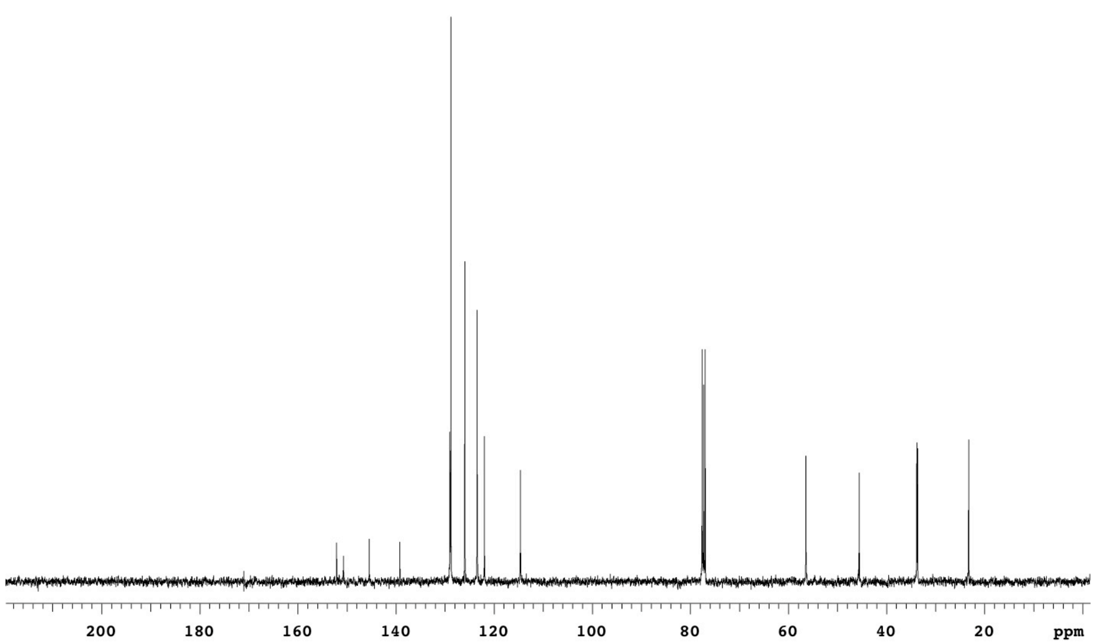
yu3-62-1





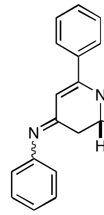
13C OBSERVE

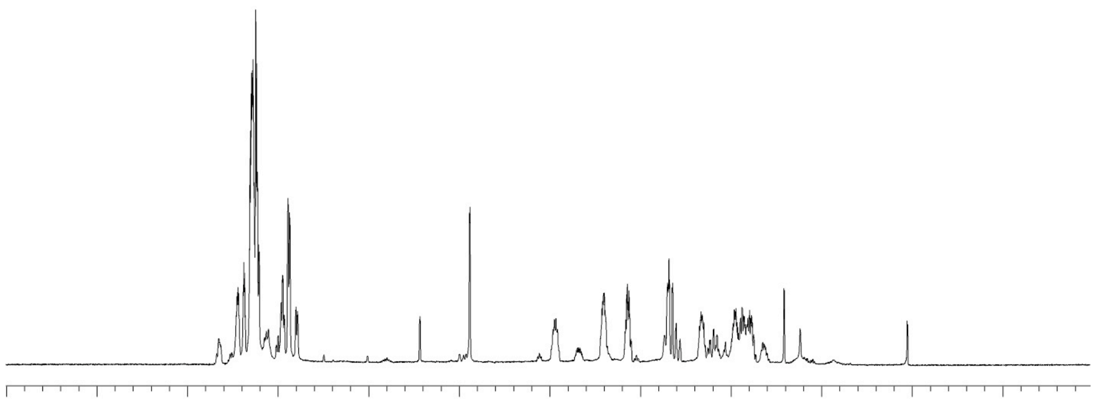
yu3-62-1



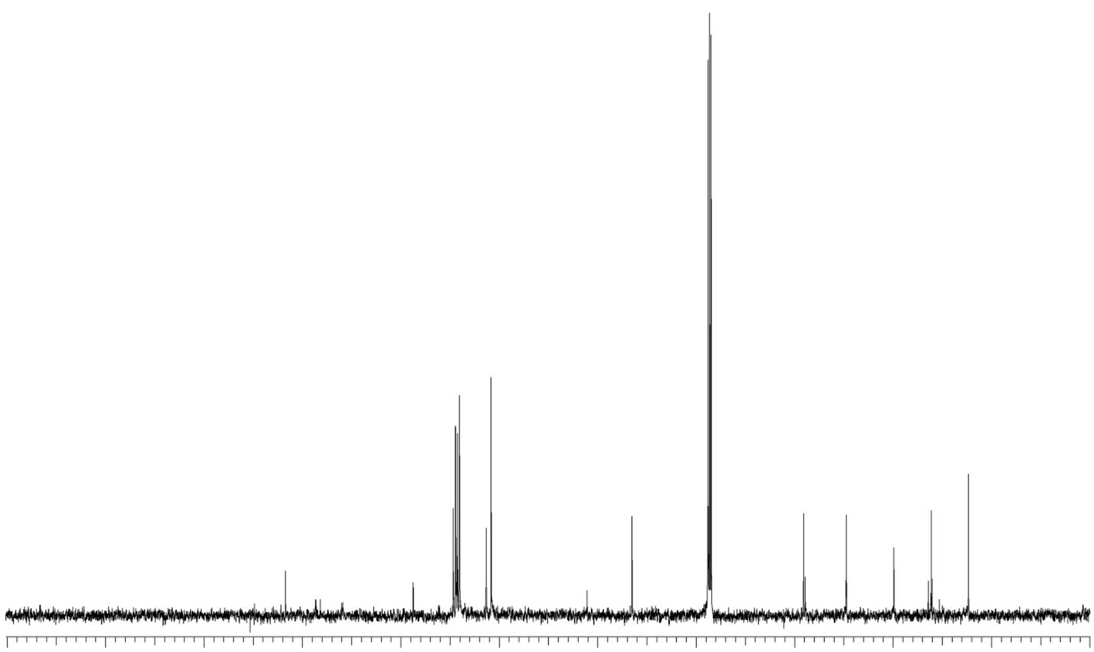
4aa

STANDARD 1H OBSERVE

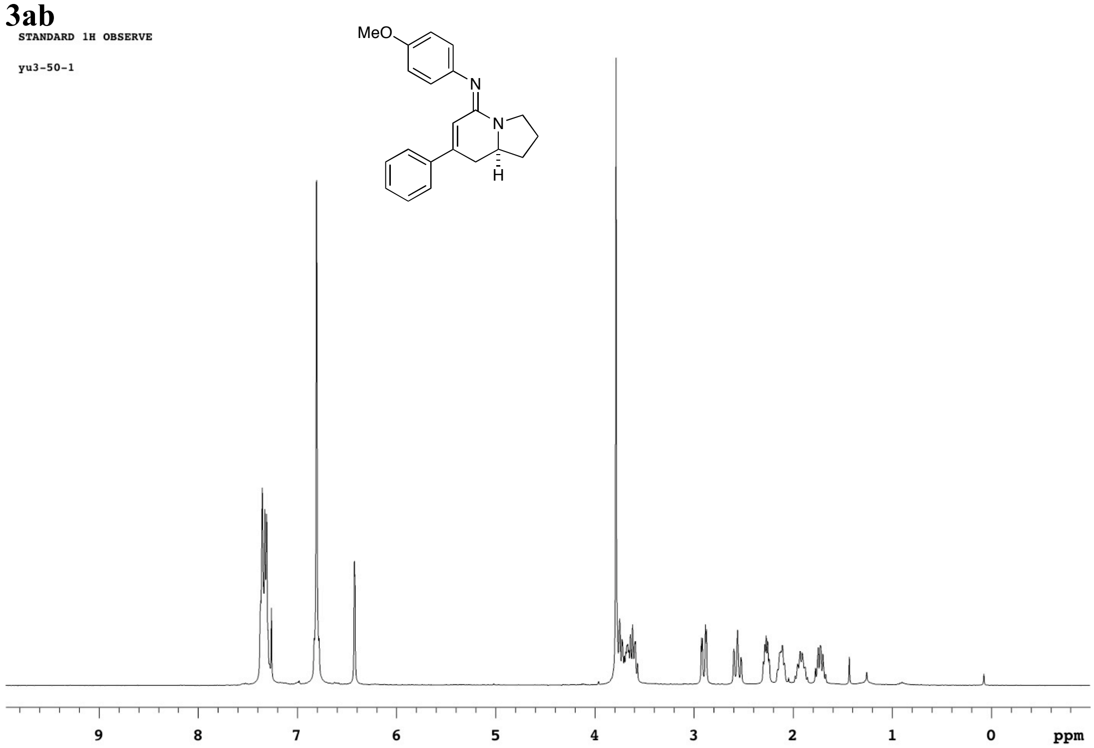


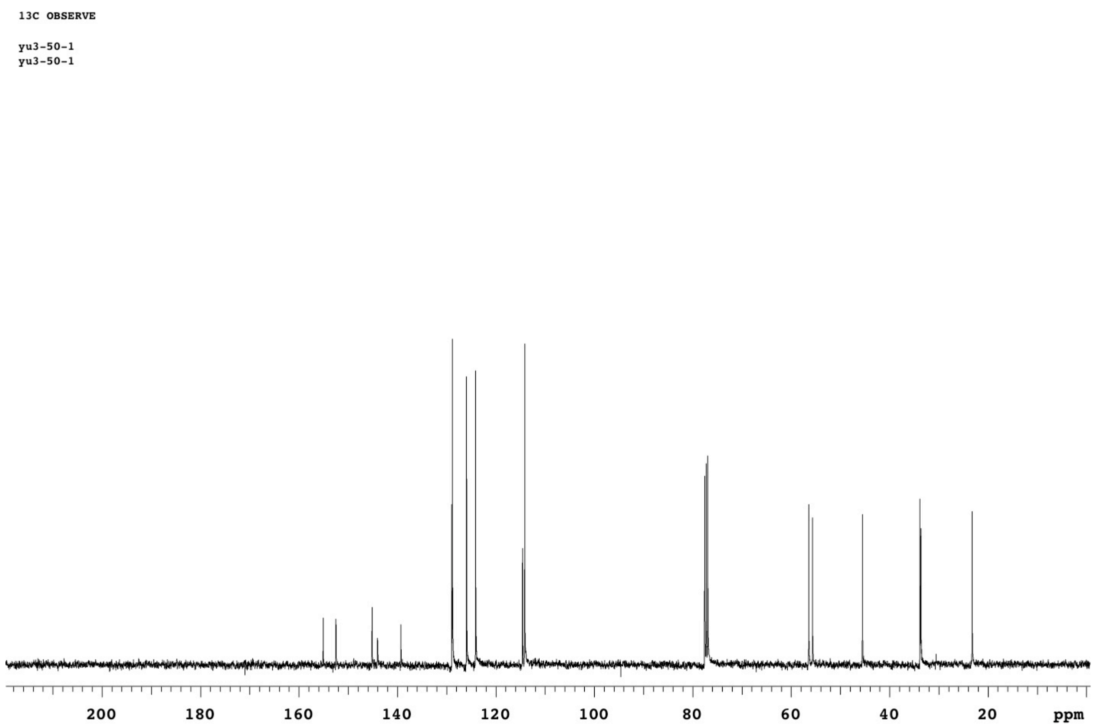


13C OBSERVE



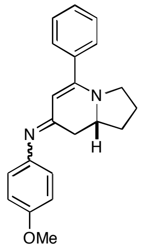
3ab

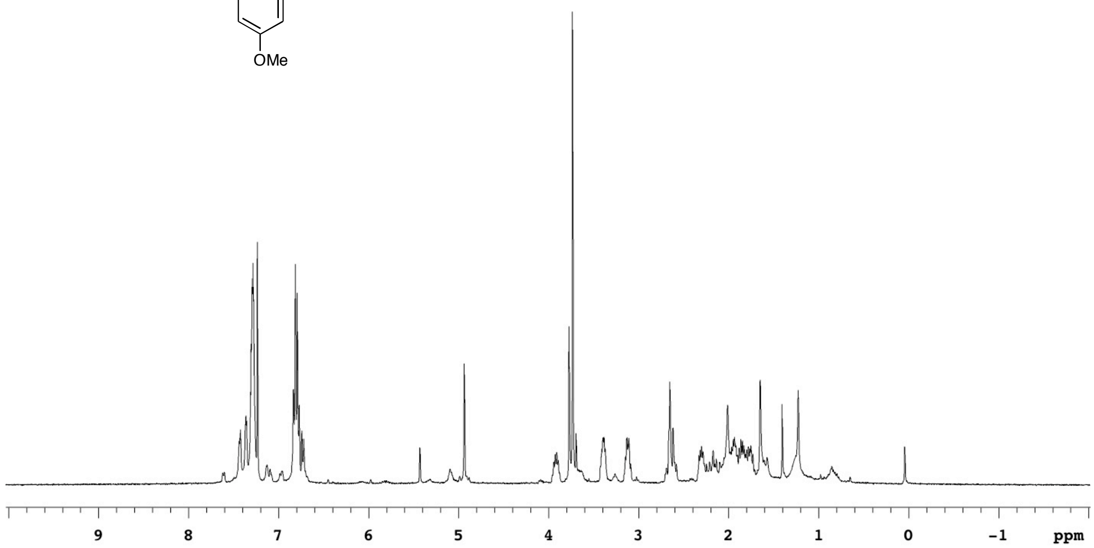

STANDARD 1H OBSERVE
yu3-50-1
MeO
N
N
H
9
8
7
6
5
4
3
2
1
0
ppm


13C OBSERVE
yu3-50-1
yu3-50-1
200
180
160
140
120
100
80
60
40
20
ppm

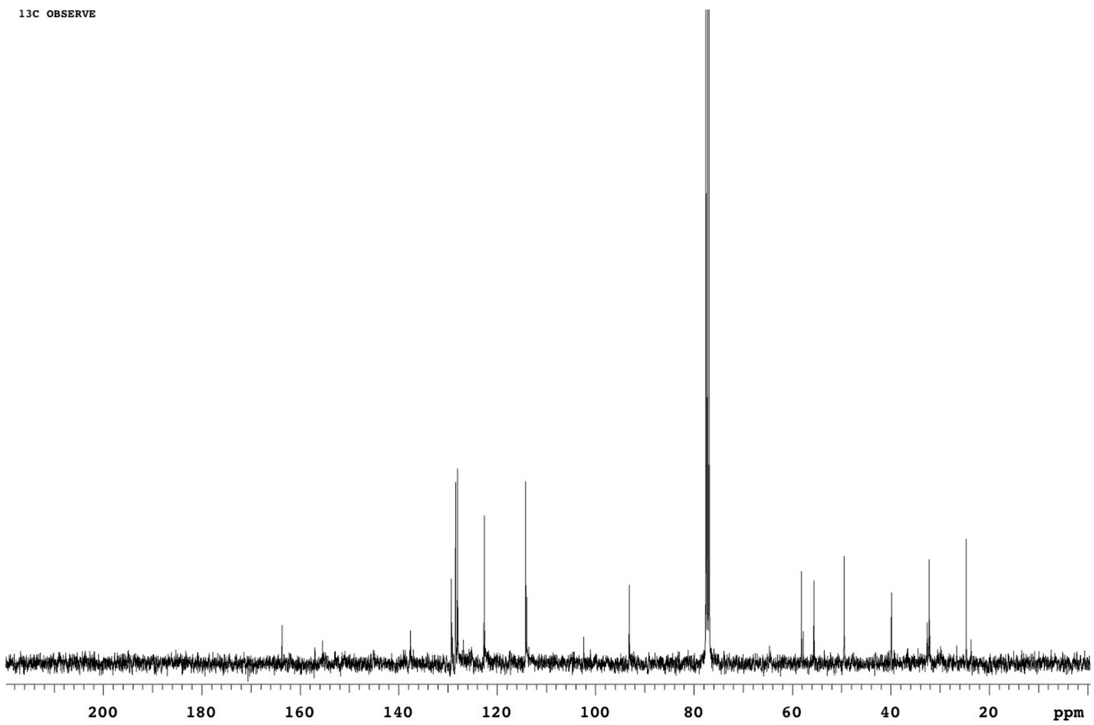
4ab

STANDARD 1H OBSERVE





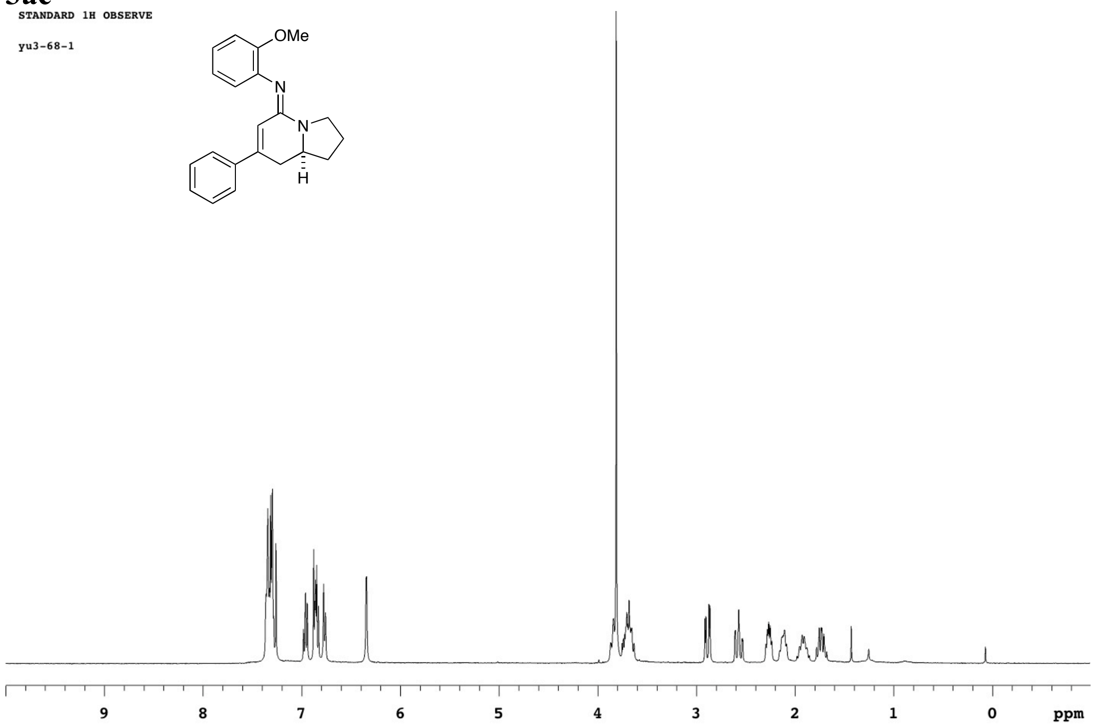
13C OBSERVE



3ac

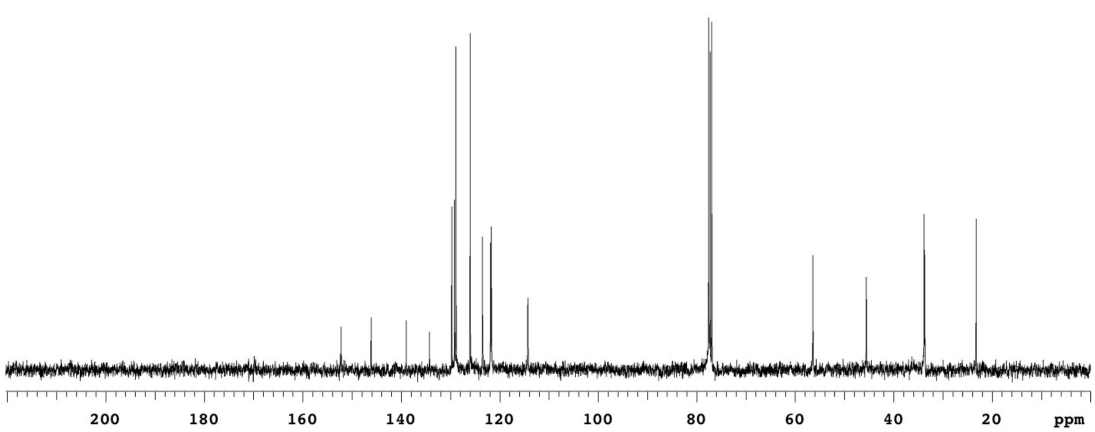
STANDARD 1H OBSERVE

yu3-68-1



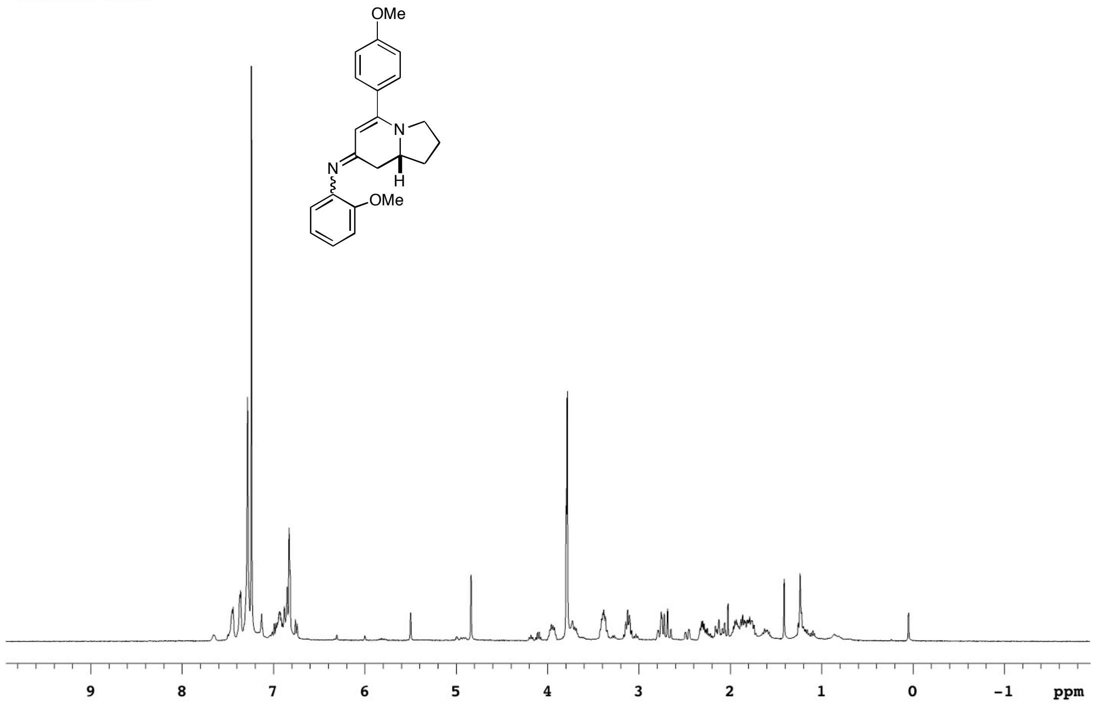
13C OBSERVE

yu3-68-1

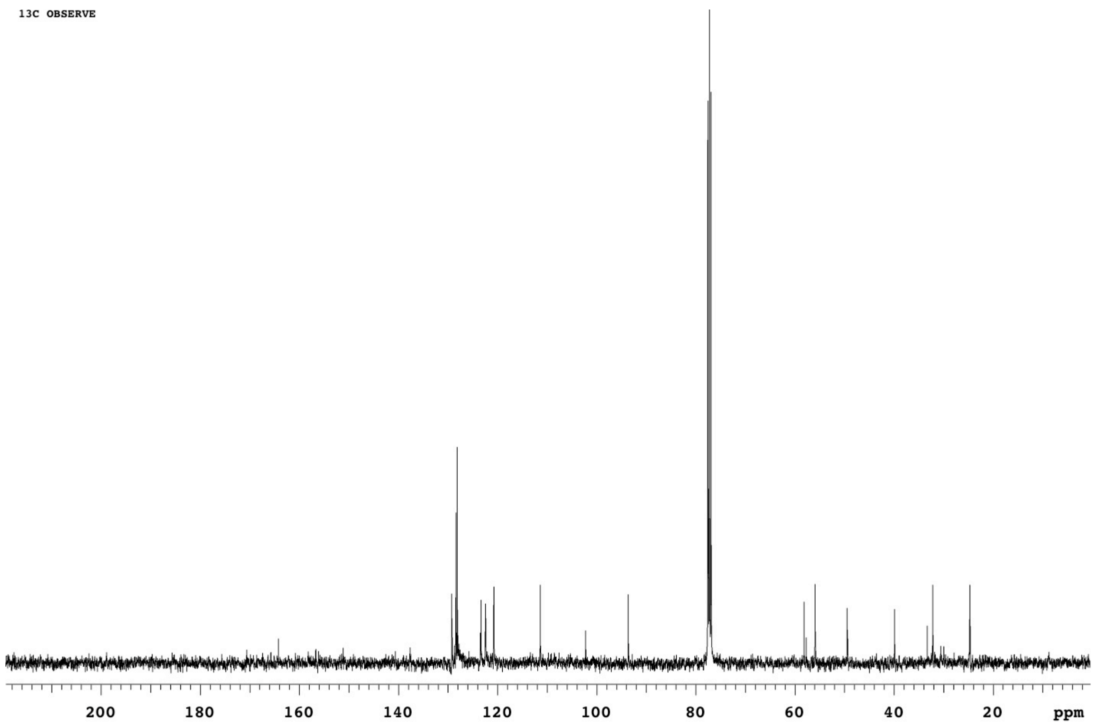


4ac

STANDARD 1H OBSERVE



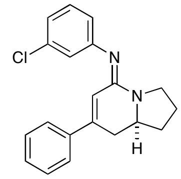
13C OBSERVE

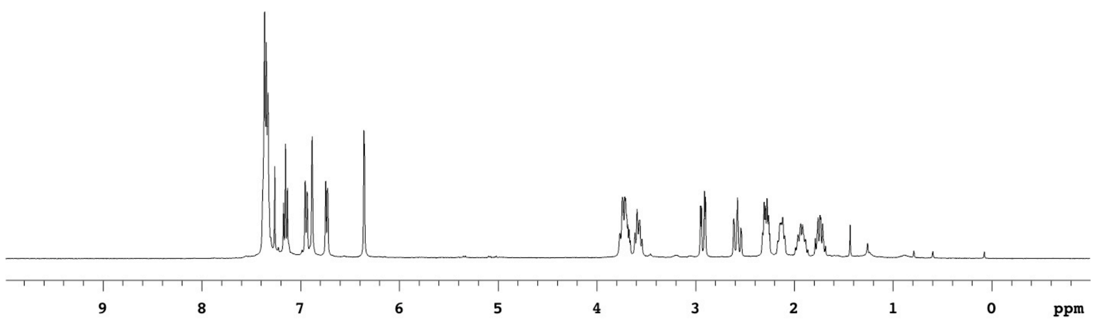


3ad

STANDARD 1H OBSERVE

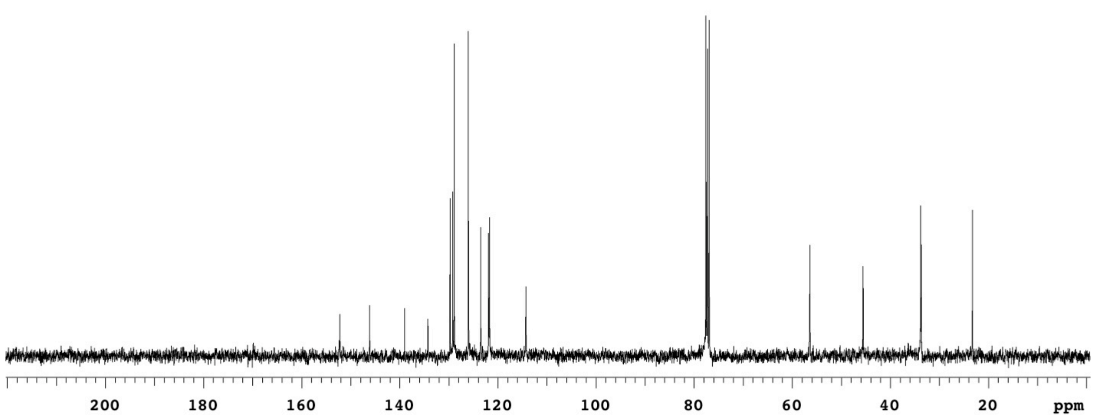
yu3-63-1





13C OBSERVE

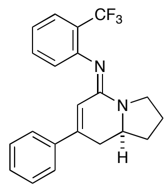
yu3-63-1

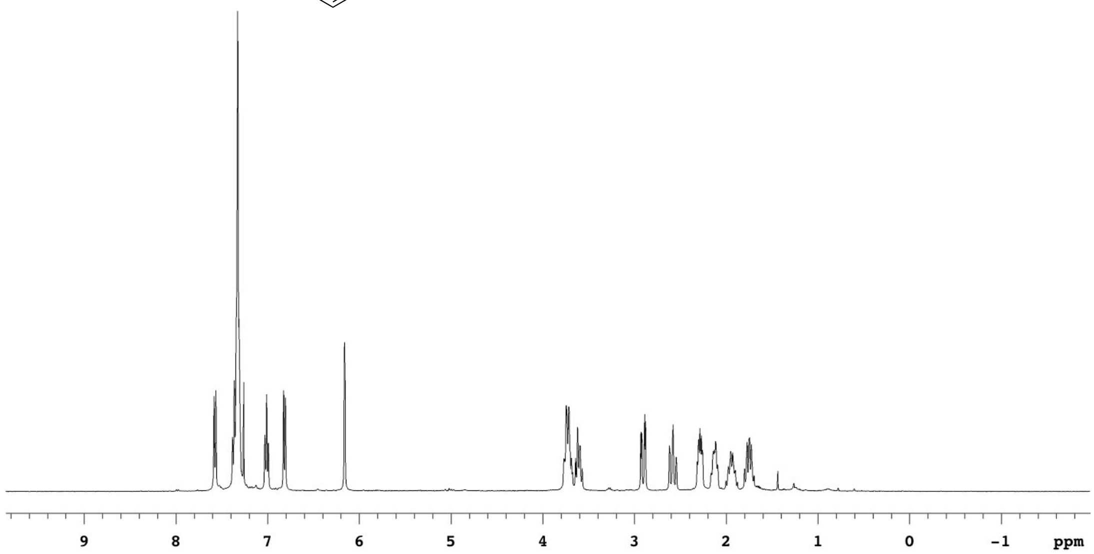


3ae

STANDARD 1H OBSERVE

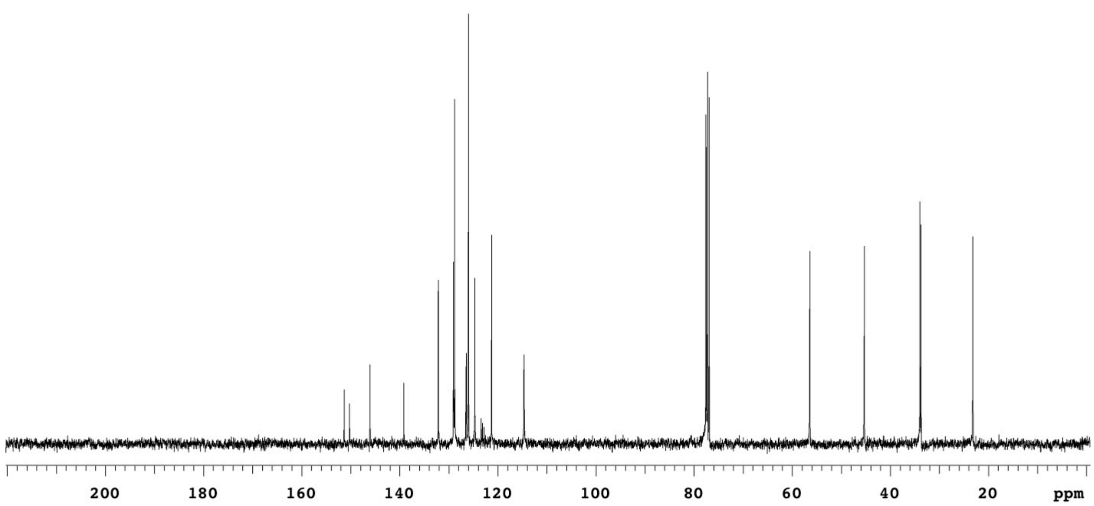
yu3-113-1





13C OBSERVE

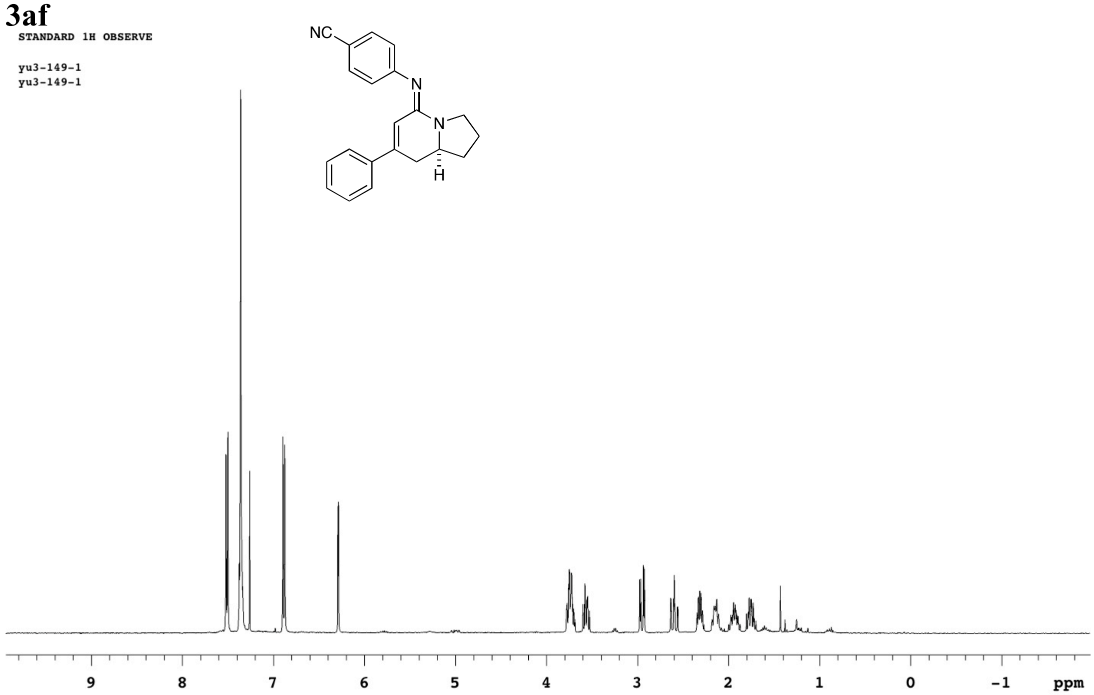
yu3-113
yu3-113-1



3af

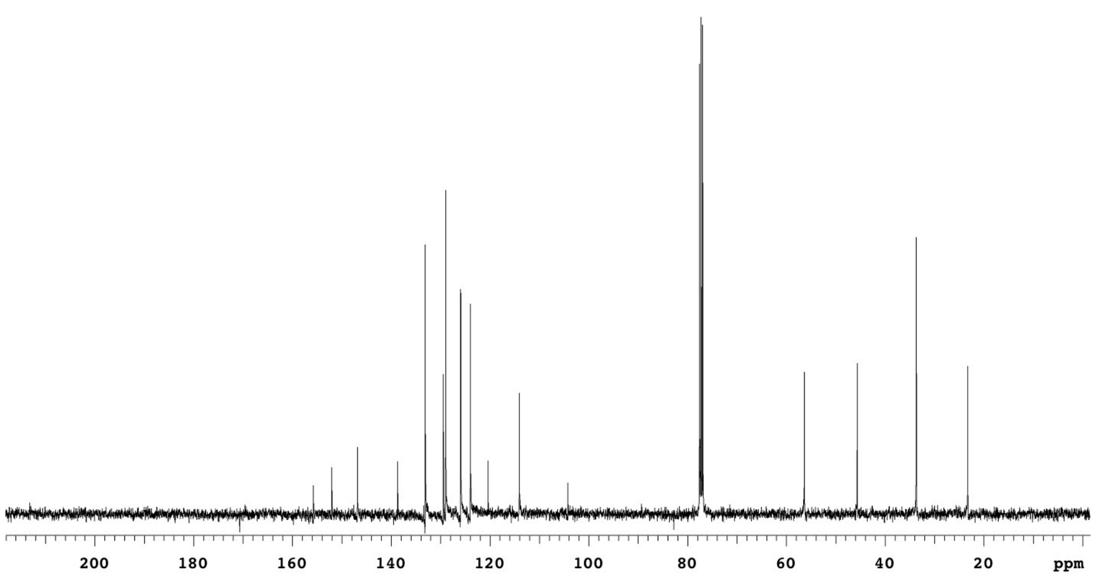
STANDARD 1H OBSERVE

yu3-149-1
yu3-149-1

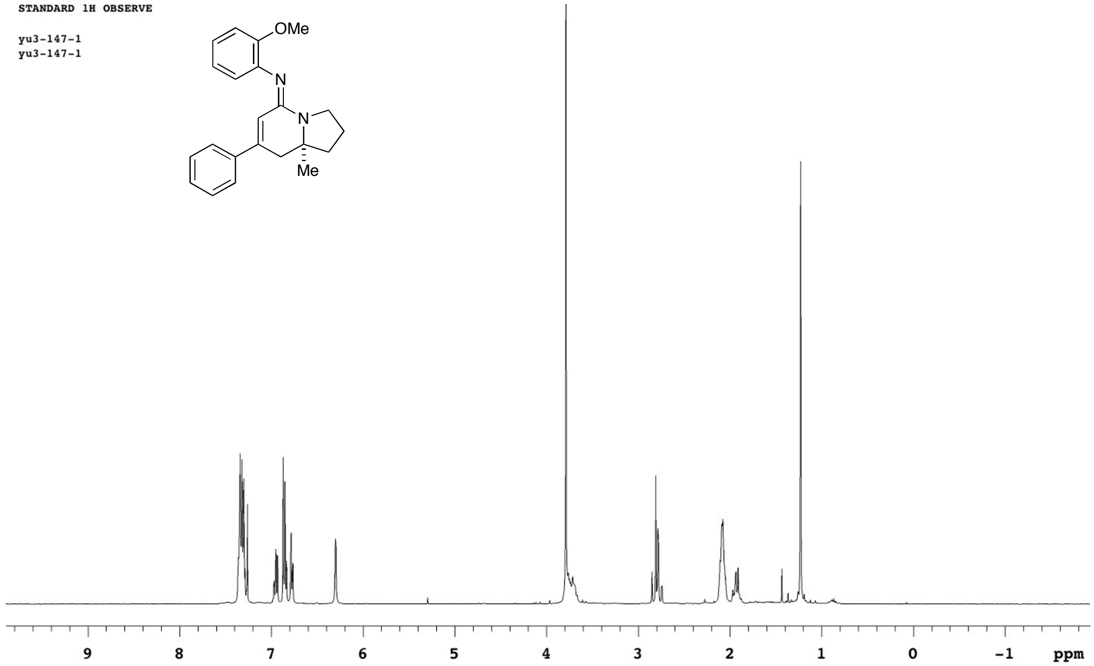


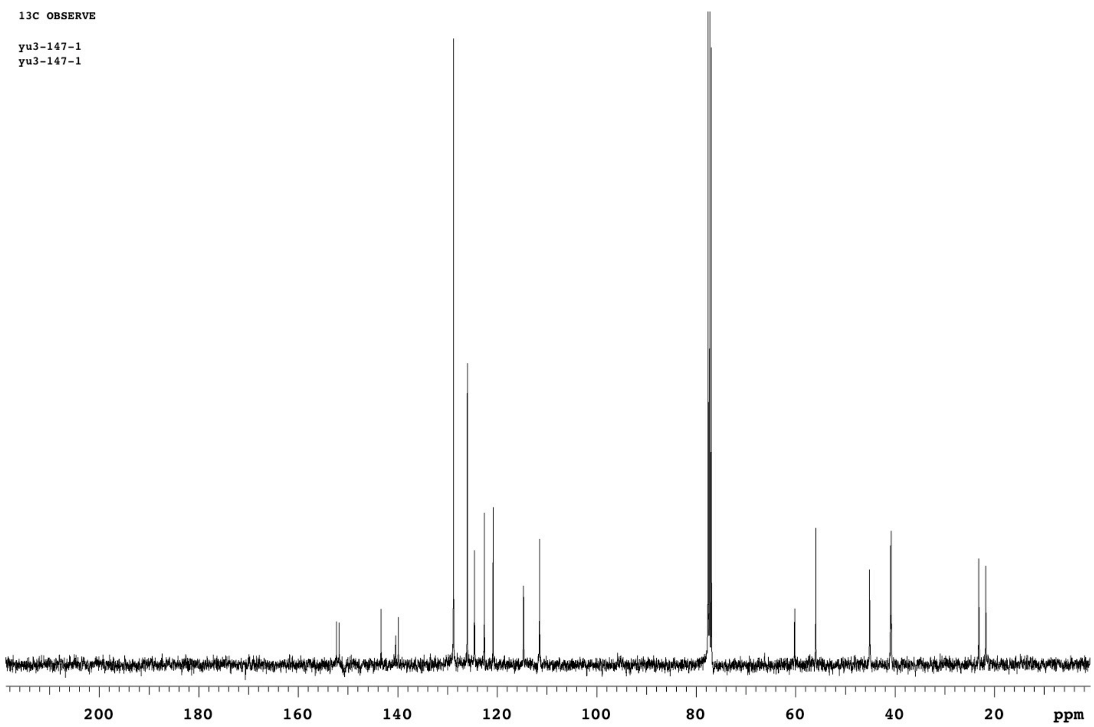
13C OBSERVE

yu3-149-1
yu3-149-1



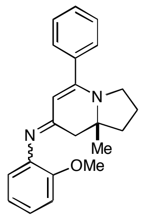
6a

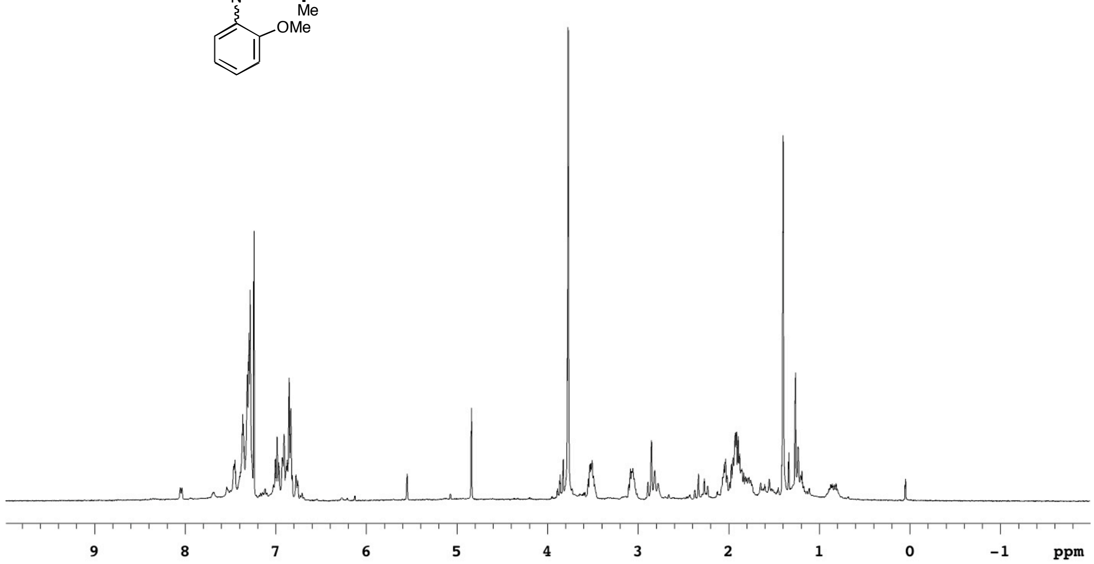

STANDARD 1H OBSERVE
yu3-147-1
yu3-147-1
OMe
N
N
Me
9 8 7 6 5 4 3 2 1 0 -1 ppm


13C OBSERVE
yu3-147-1
yu3-147-1
200 180 160 140 120 100 80 60 40 20 ppm

7a

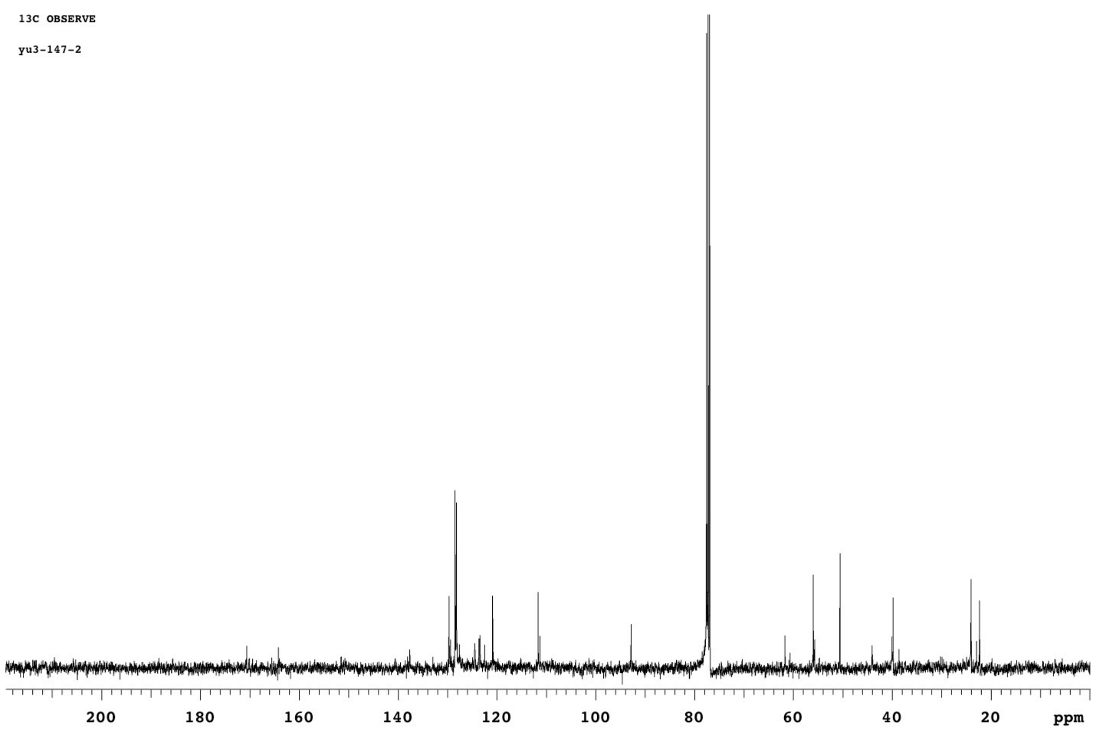
STANDARD 1H OBSERVE



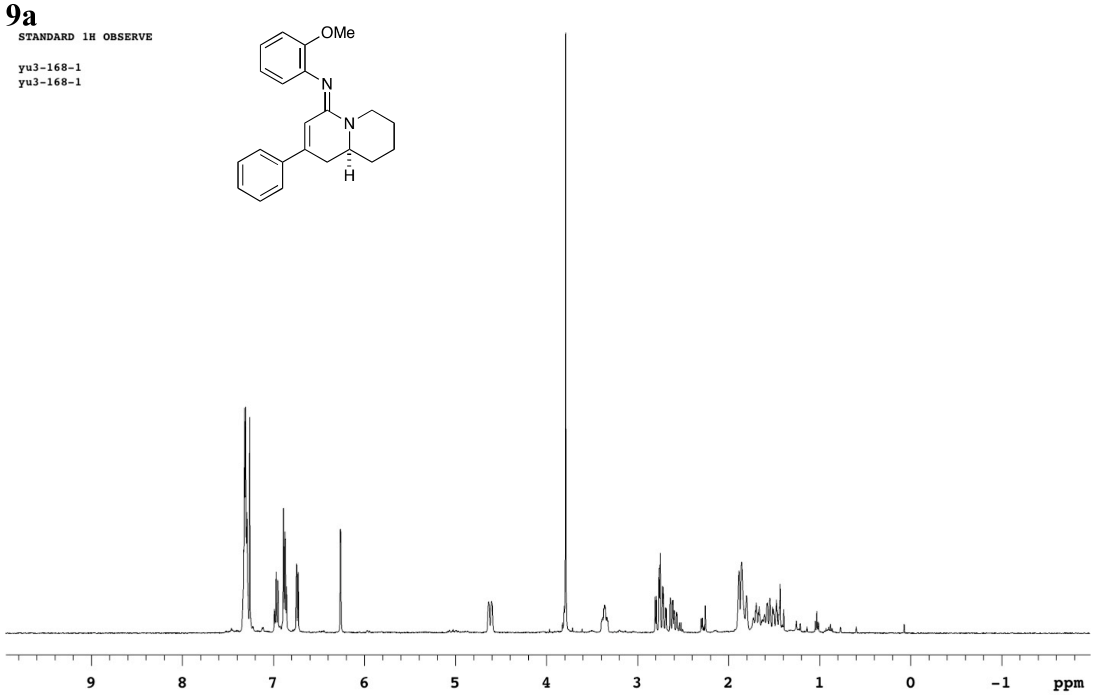


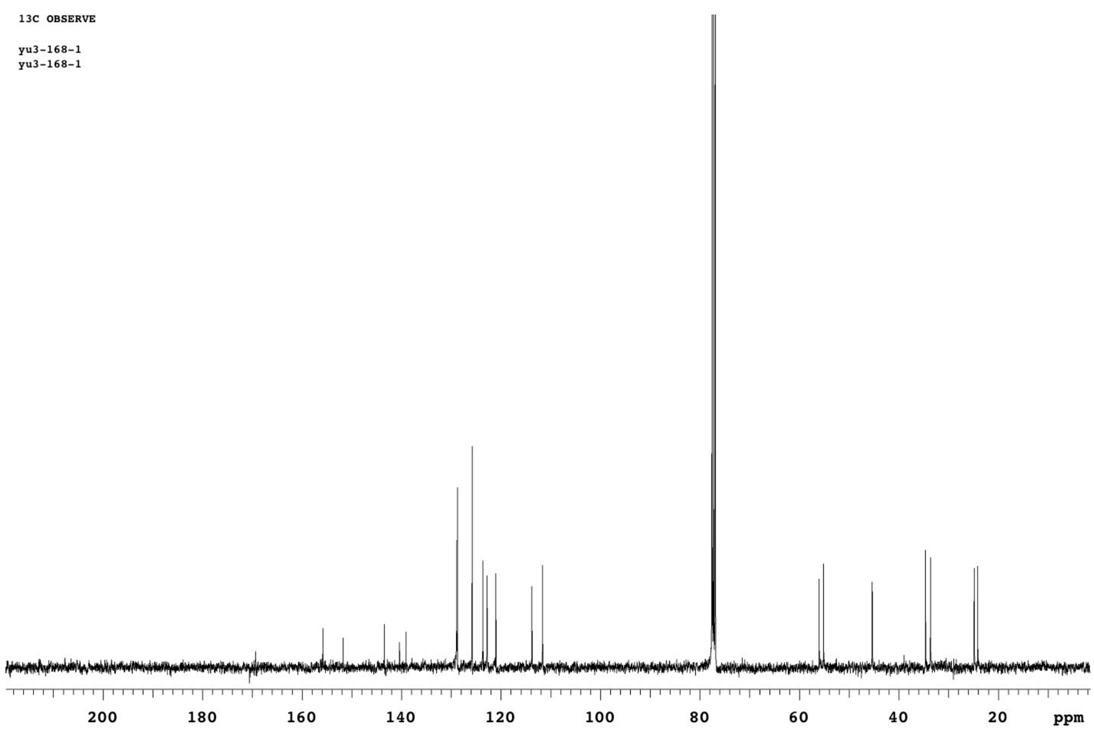
13C OBSERVE

yu3-147-2



9a

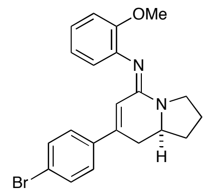

STANDARD 1H OBSERVE
yu3-168-1
yu3-168-1
OMe
N
N
H
9 8 7 6 5 4 3 2 1 0 -1 ppm

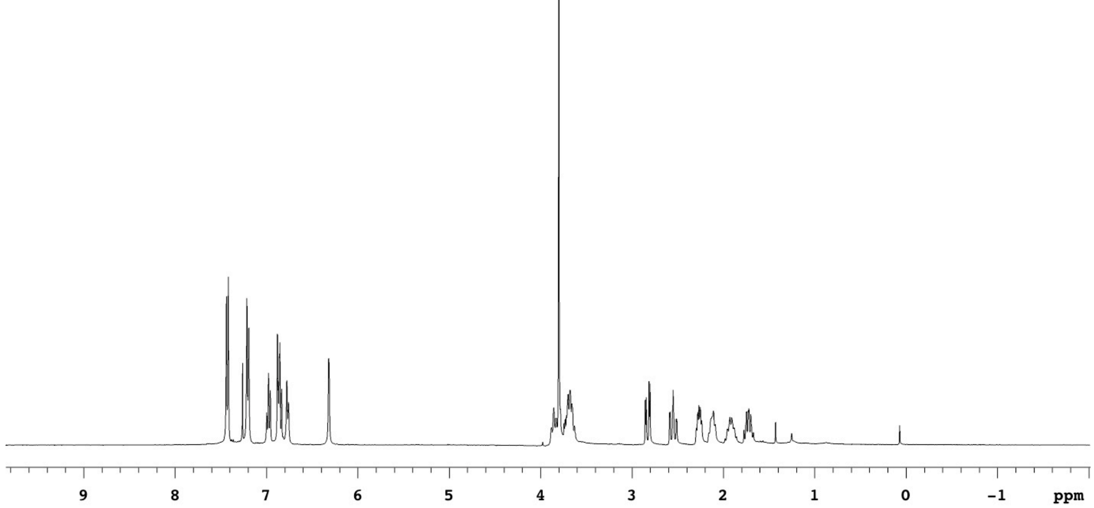

13C OBSERVE
yu3-168-1
yu3-168-1
200 180 160 140 120 100 80 60 40 20 ppm

3bc

STANDARD 1H OBSERVE

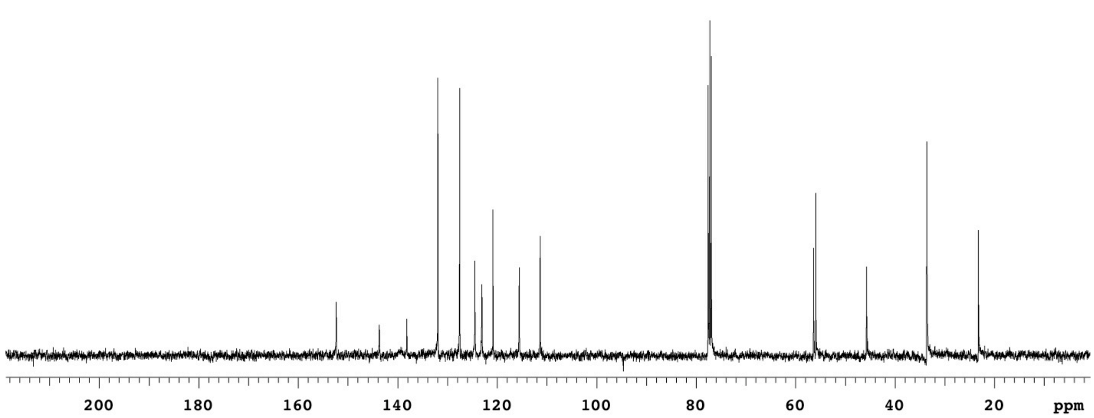
yu3-73





13C OBSERVE

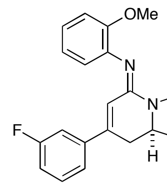
yu3-73

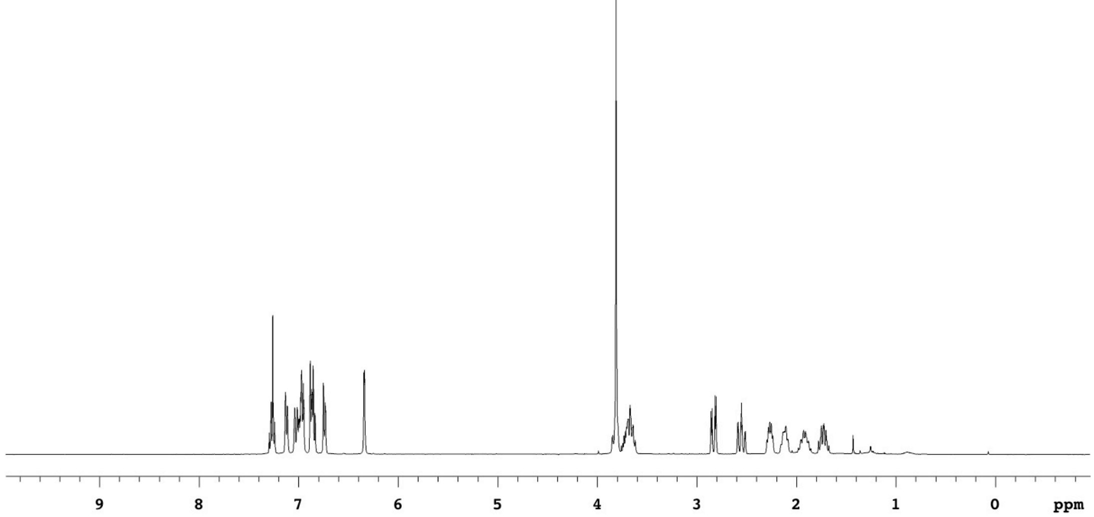


3cc

STANDARD 1H OBSERVE

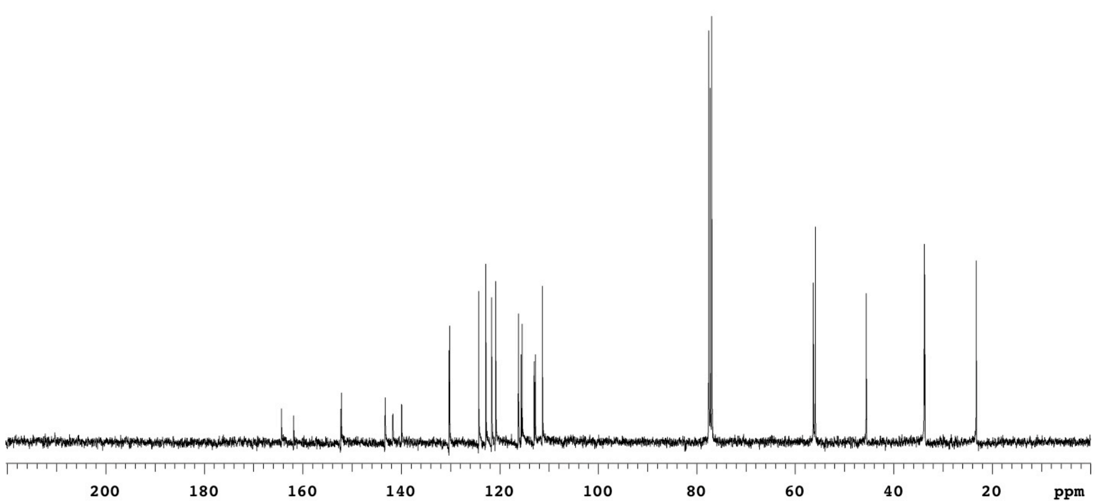
yu3-117-1



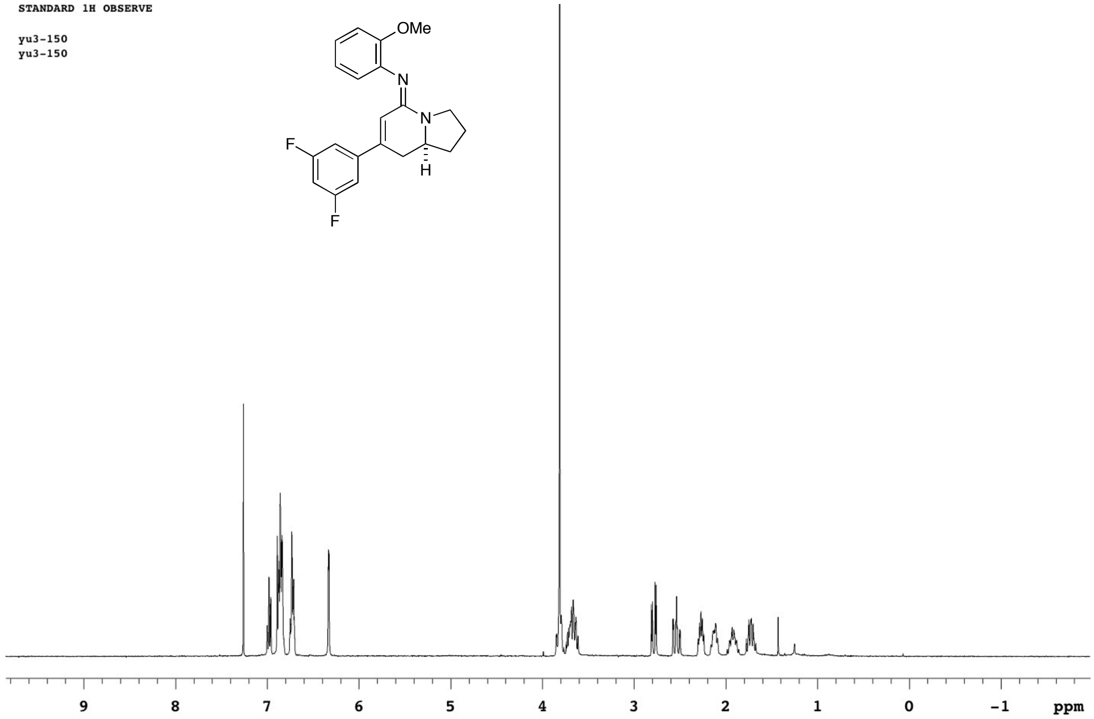


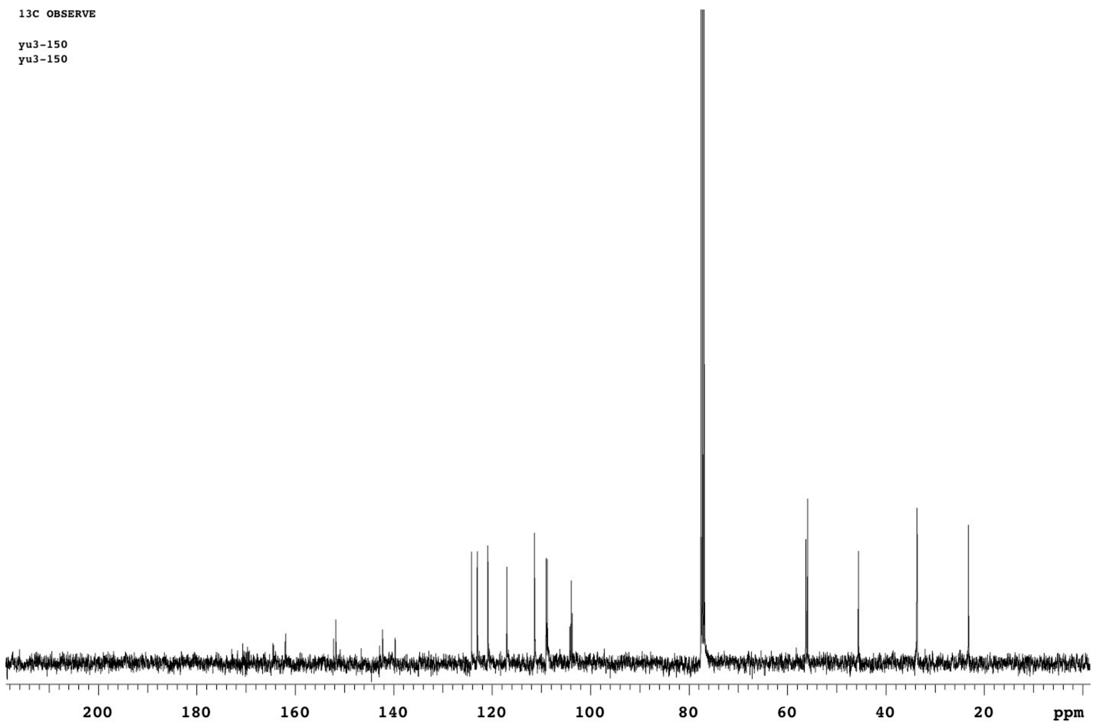
13C OBSERVE

yu3-117-1
yu3-117

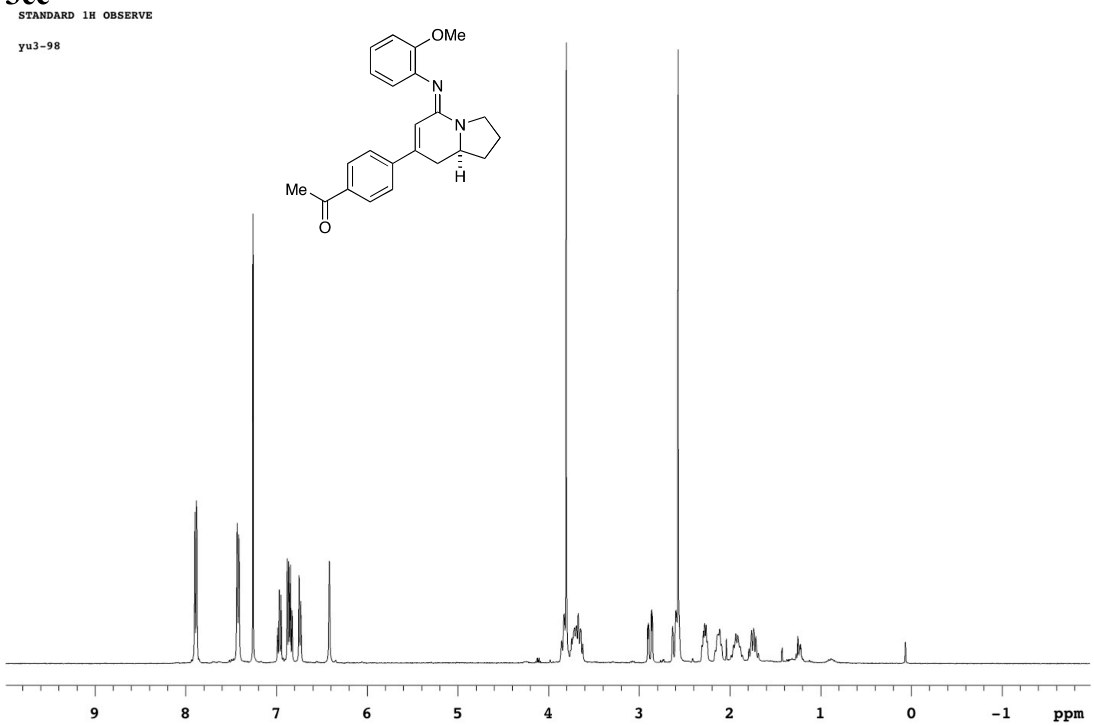


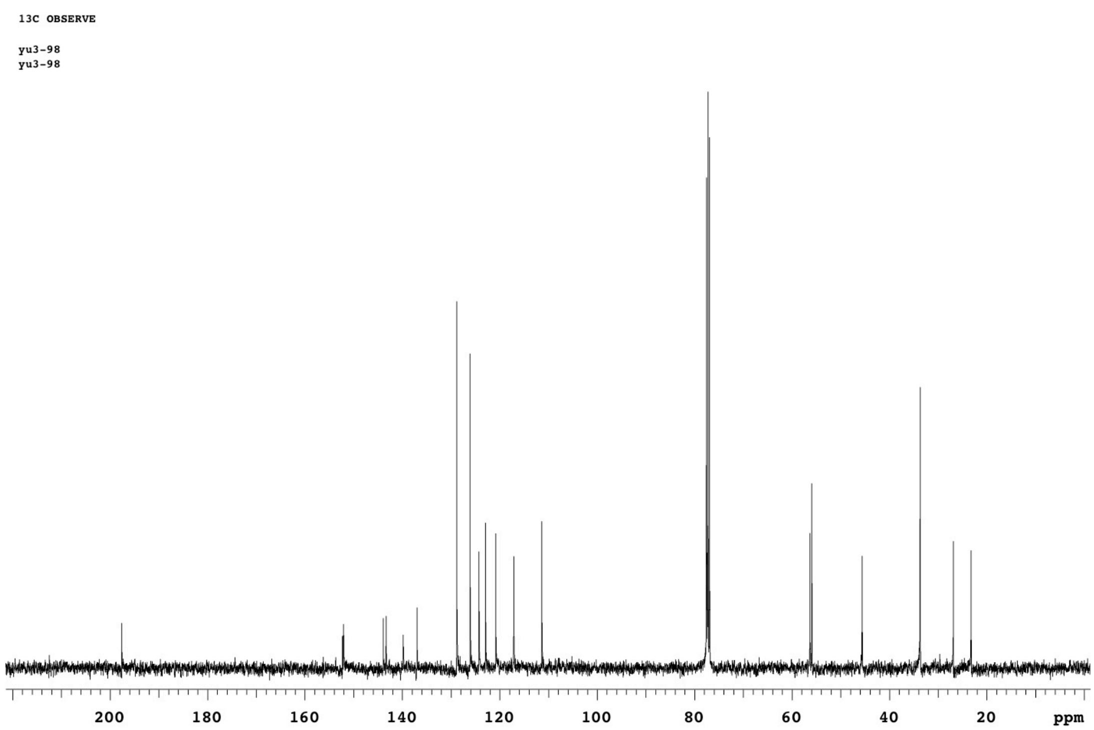
3dc


STANDARD 1H OBSERVE
yu3-150
yu3-150
OMe
N
N
F
F
H
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-150
yu3-150
200
180
160
140
120
100
80
60
40
20
ppm

3ec

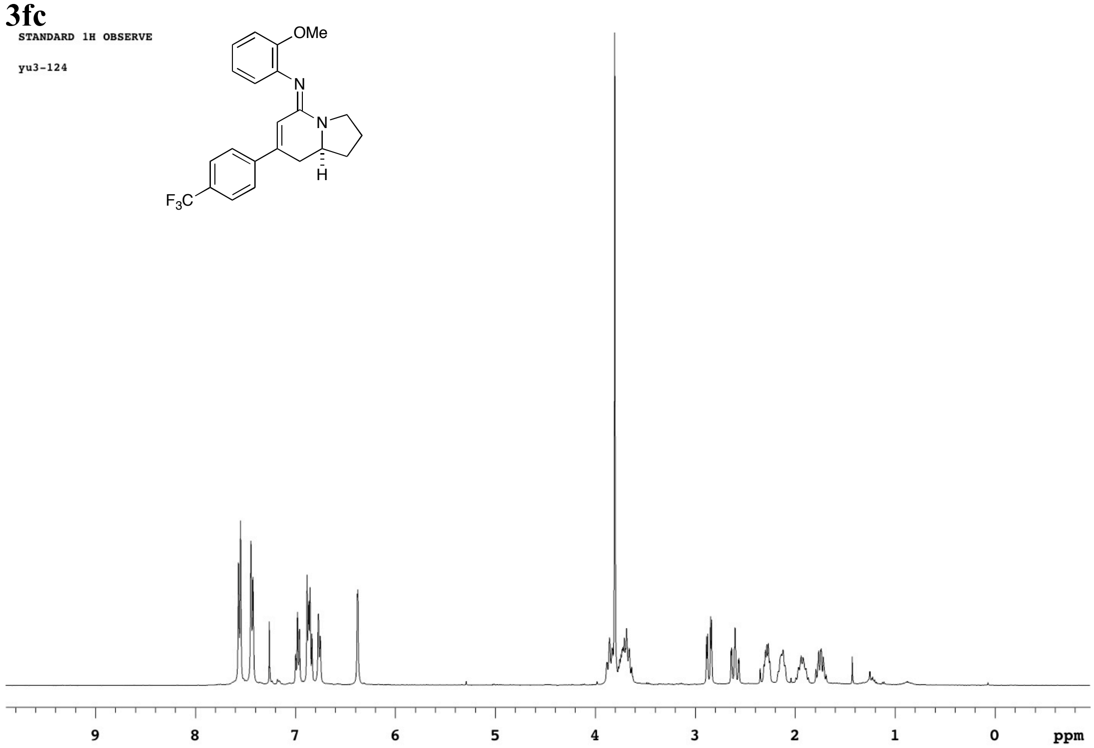

STANDARD 1H OBSERVE
yu3-98
OMe
N
N
H
Me
O
9 8 7 6 5 4 3 2 1 0 -1 ppm


13C OBSERVE
yu3-98
yu3-98
200 180 160 140 120 100 80 60 40 20 ppm

3fc

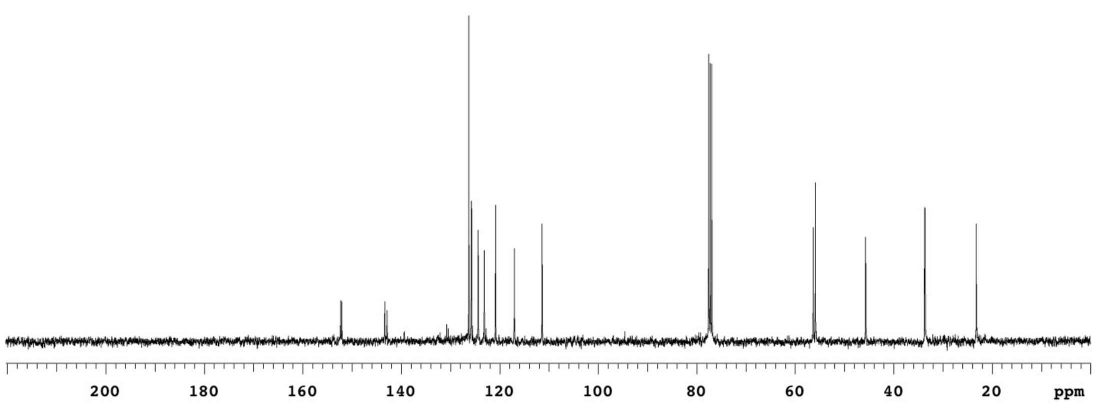
STANDARD 1H OBSERVE

yu3-124

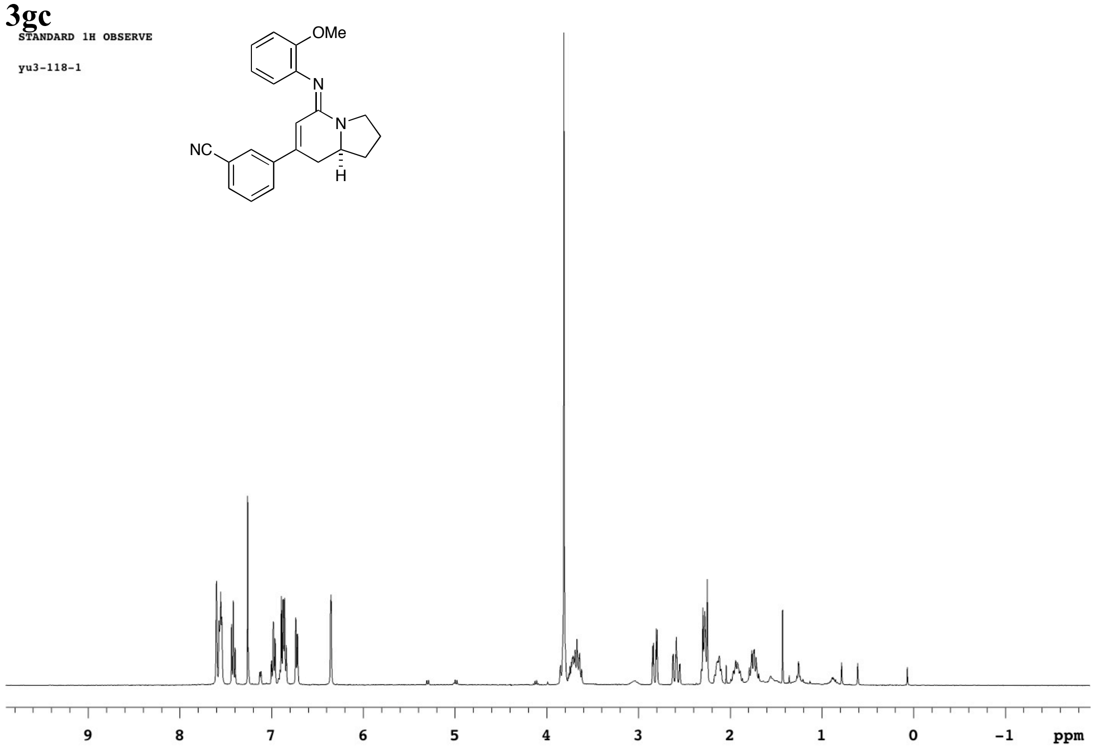


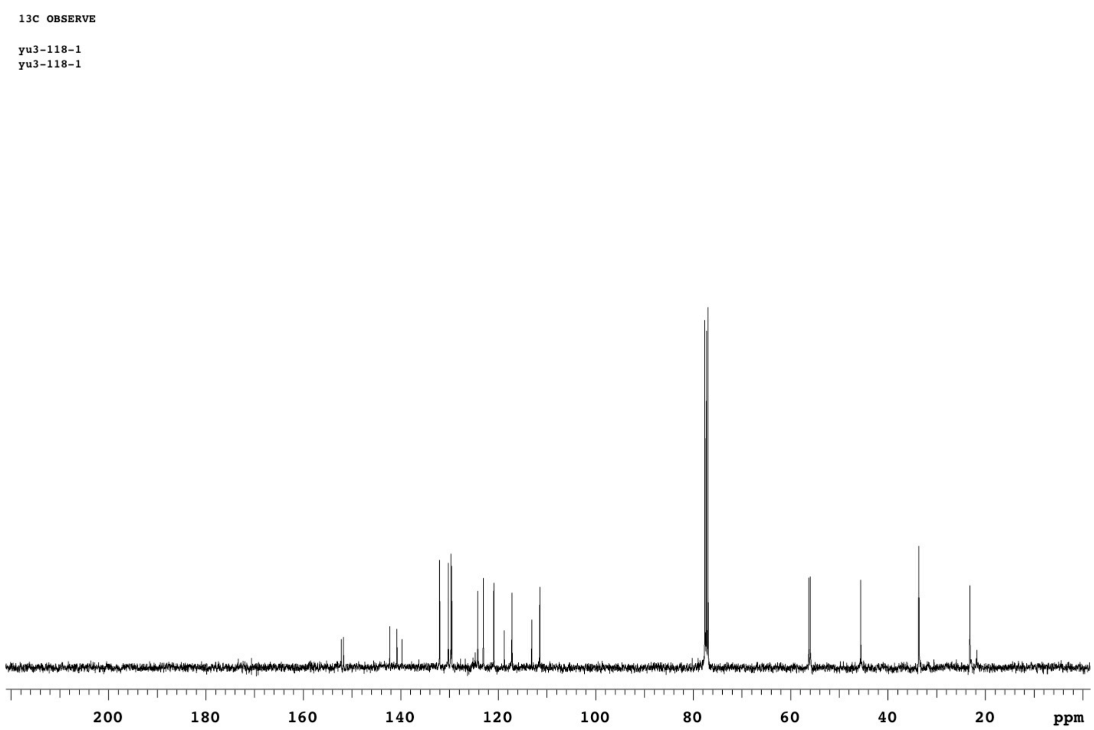
13C OBSERVE

yu3-124
yu3-124

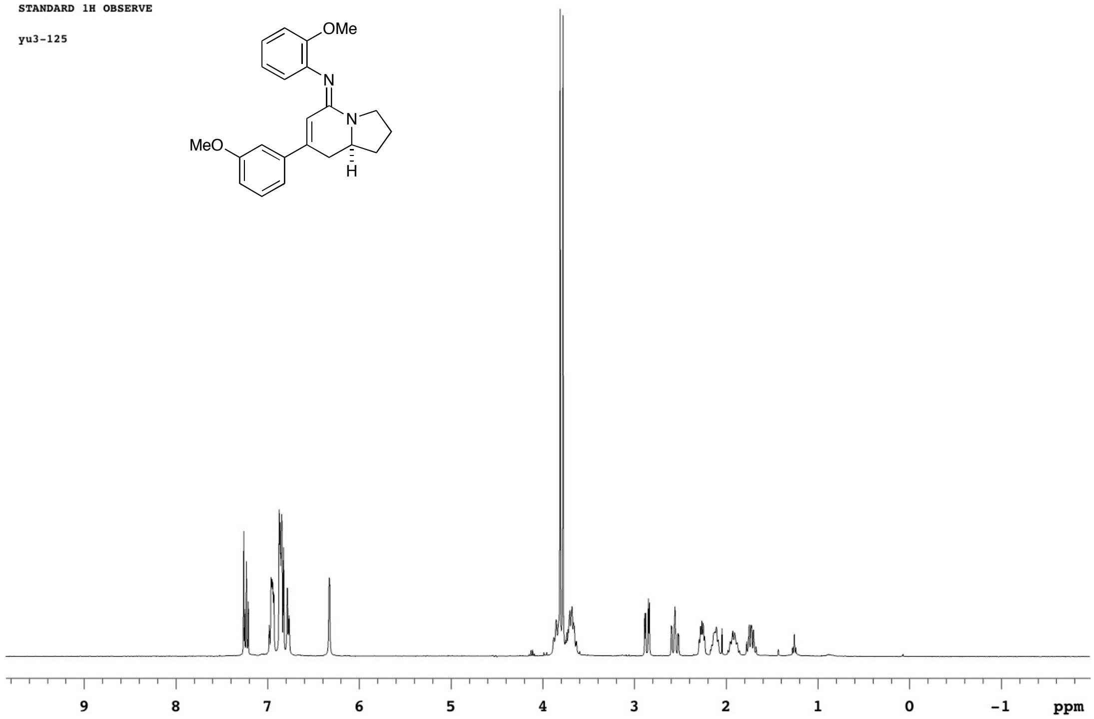


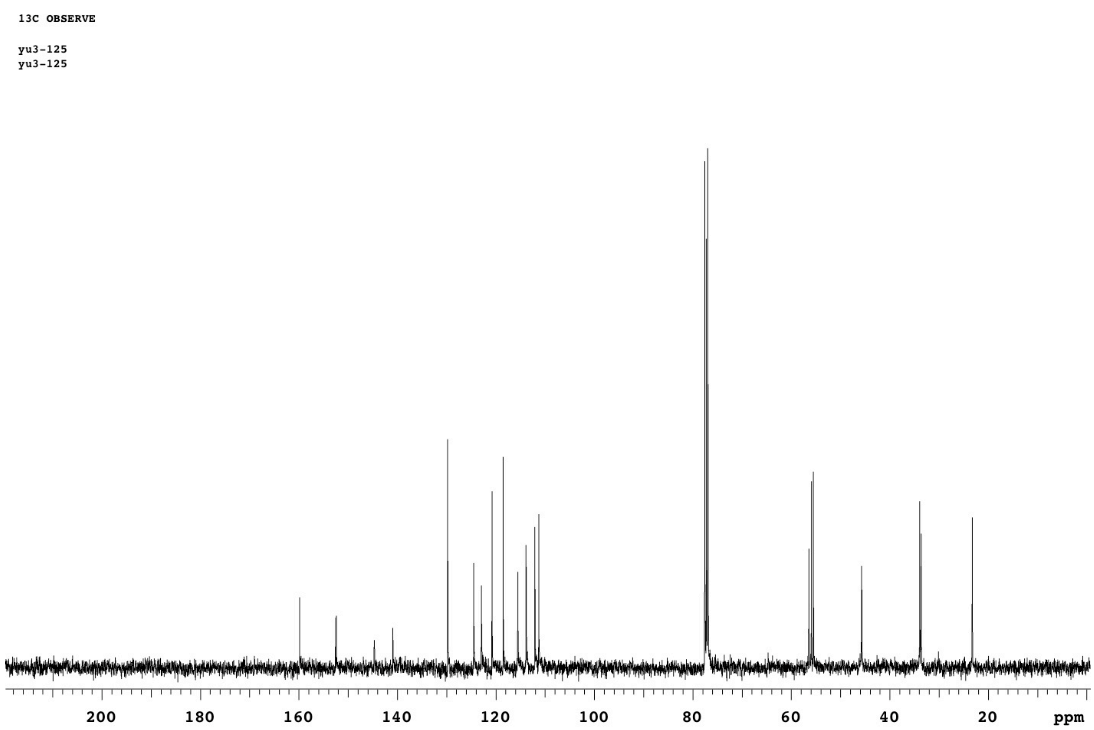
3gc


STANDARD 1H OBSERVE
yu3-118-1
OMe
N
N
NC
H
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-118-1
yu3-118-1
200
180
160
140
120
100
80
60
40
20
ppm

3hc

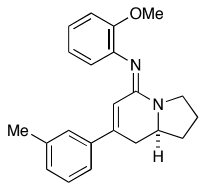

STANDARD 1H OBSERVE
yu3-125
OMe
N
N
MeO
H
9
8
7
6
5
4
3
2
1
0
-1
ppm

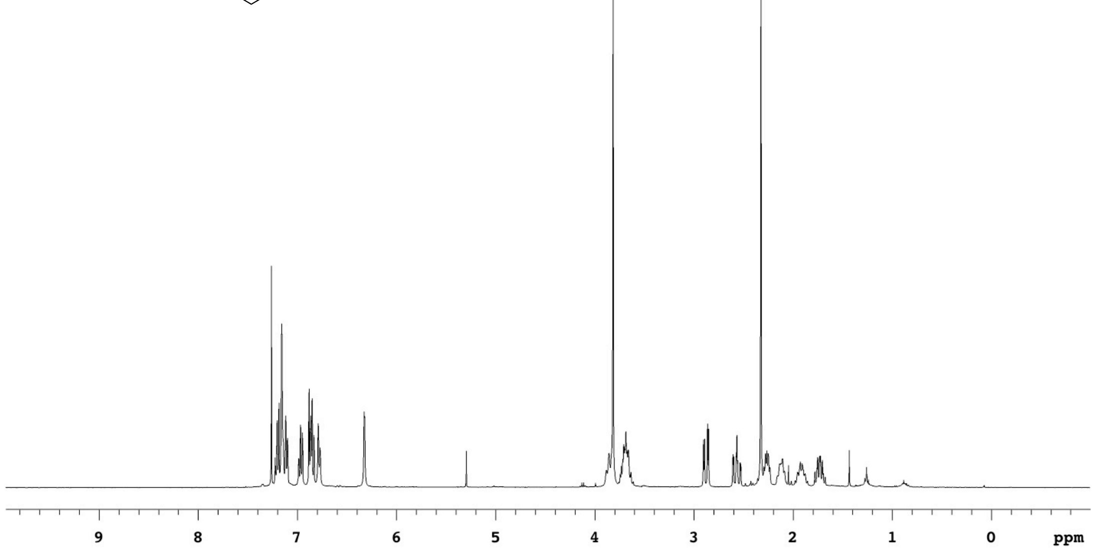

13C OBSERVE
yu3-125
yu3-125
200
180
160
140
120
100
80
60
40
20
ppm

3ic

STANDARD 1H OBSERVE

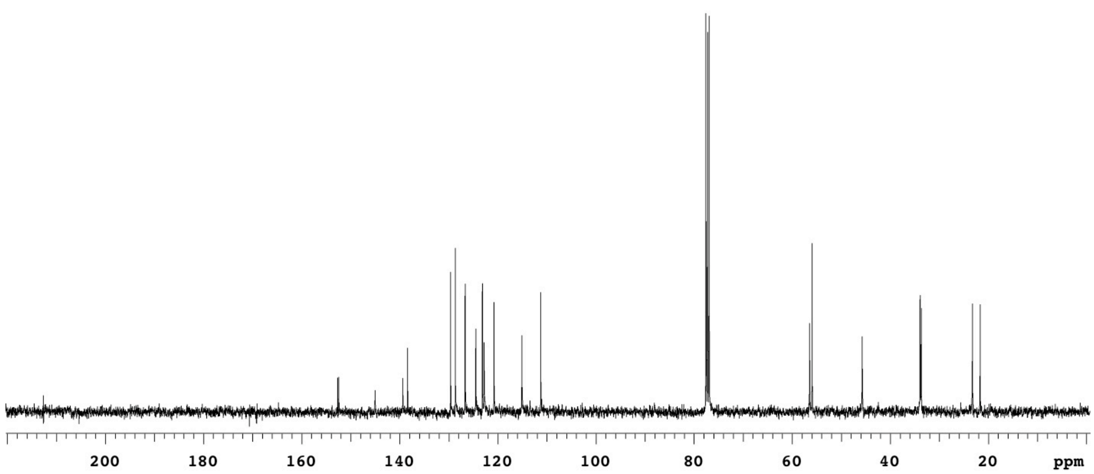
yu3-123-1



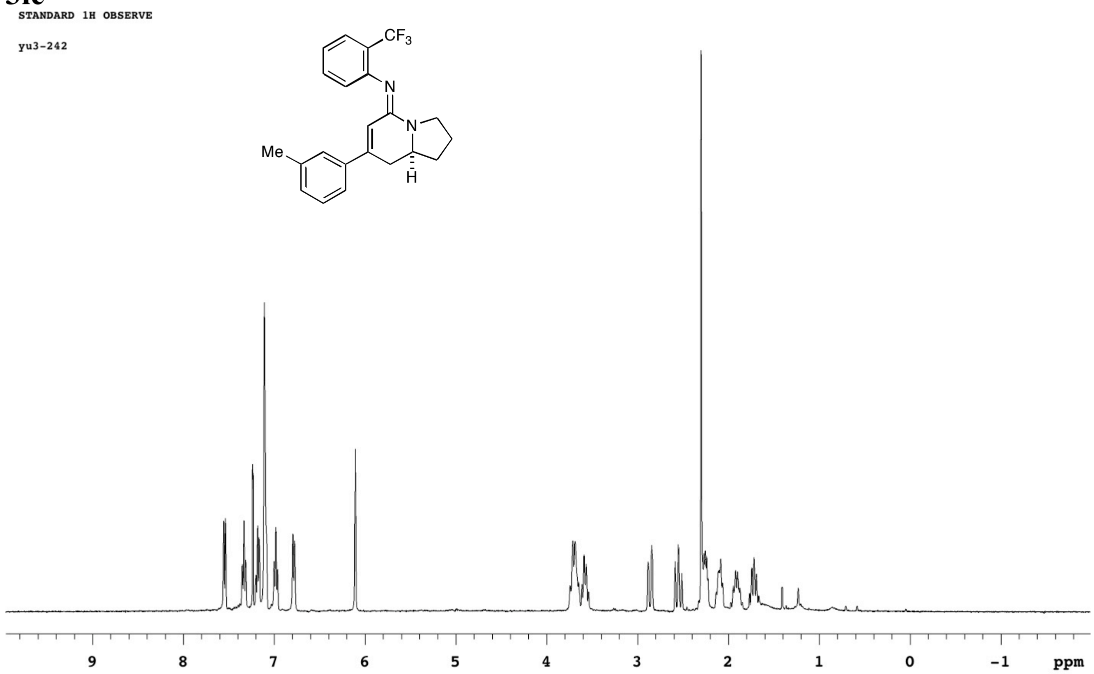


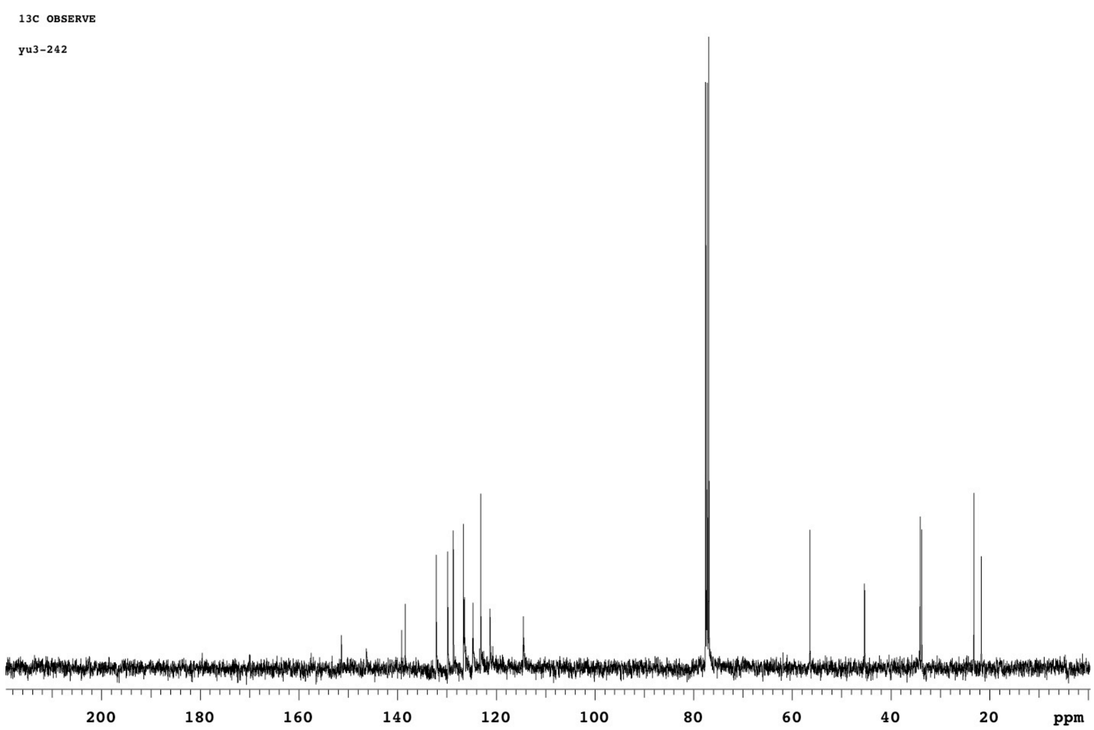
13C OBSERVE

yu3-123-1
yu3-123-1

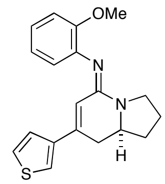


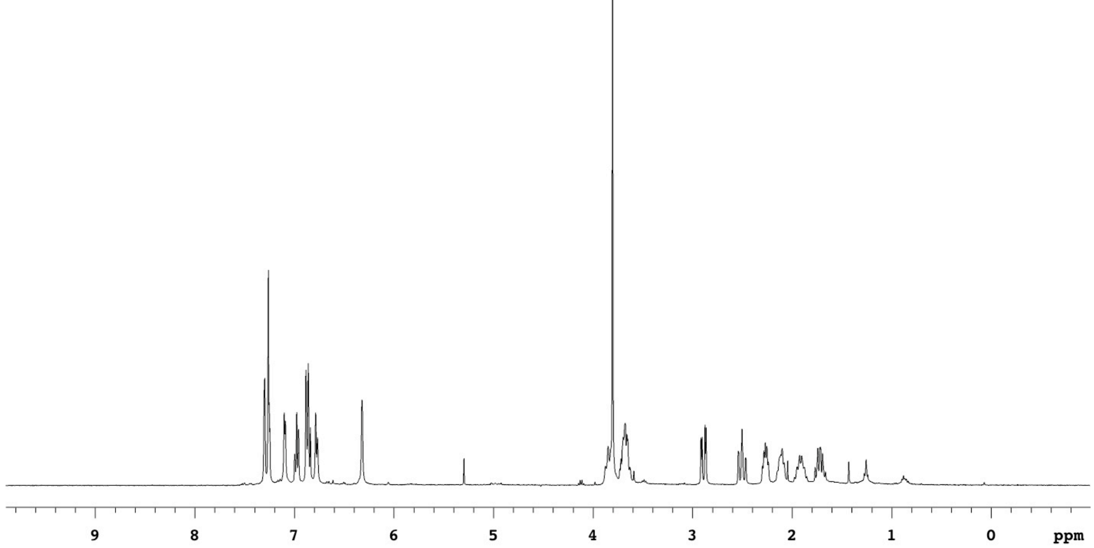
3ie

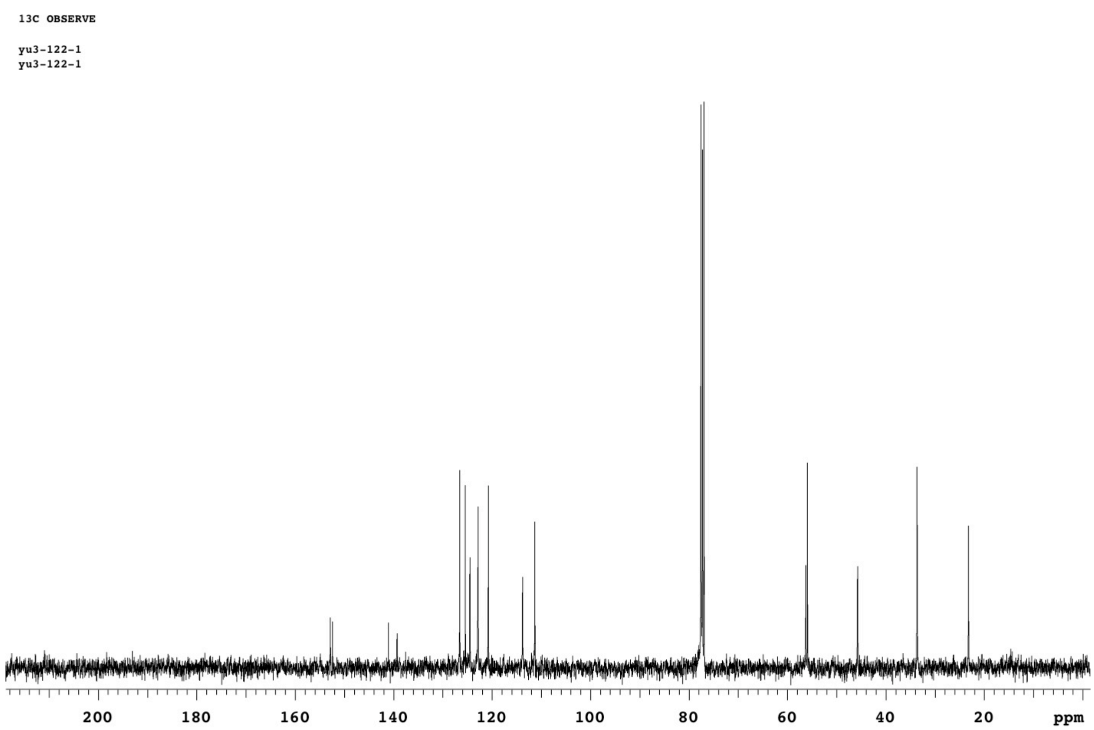

STANDARD 1H OBSERVE
yu3-242
CF3
N
N
Me
H
9 8 7 6 5 4 3 2 1 0 -1 ppm


13C OBSERVE
yu3-242
200 180 160 140 120 100 80 60 40 20 ppm

3jc



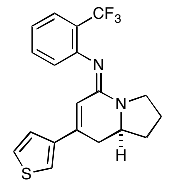

STANDARD 1H OBSERVE
yu3-122-1
9
8
7
6
5
4
3
2
1
0
ppm

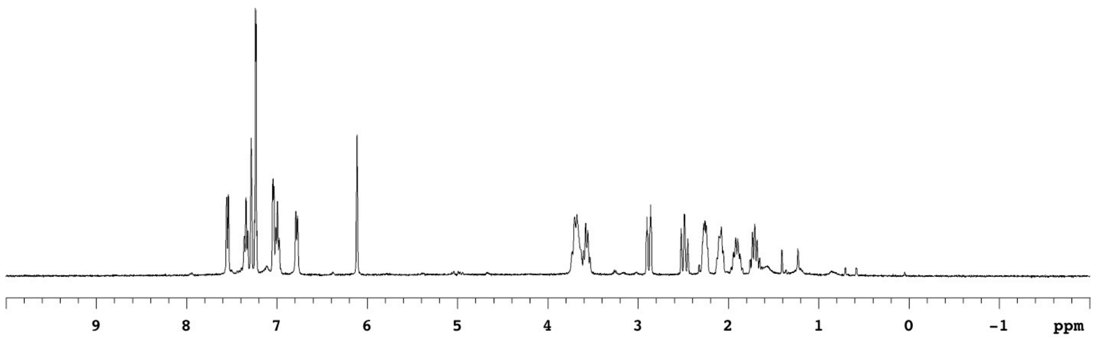

13C OBSERVE
yu3-122-1
yu3-122-1
200
180
160
140
120
100
80
60
40
20
ppm

3je

STANDARD 1H OBSERVE

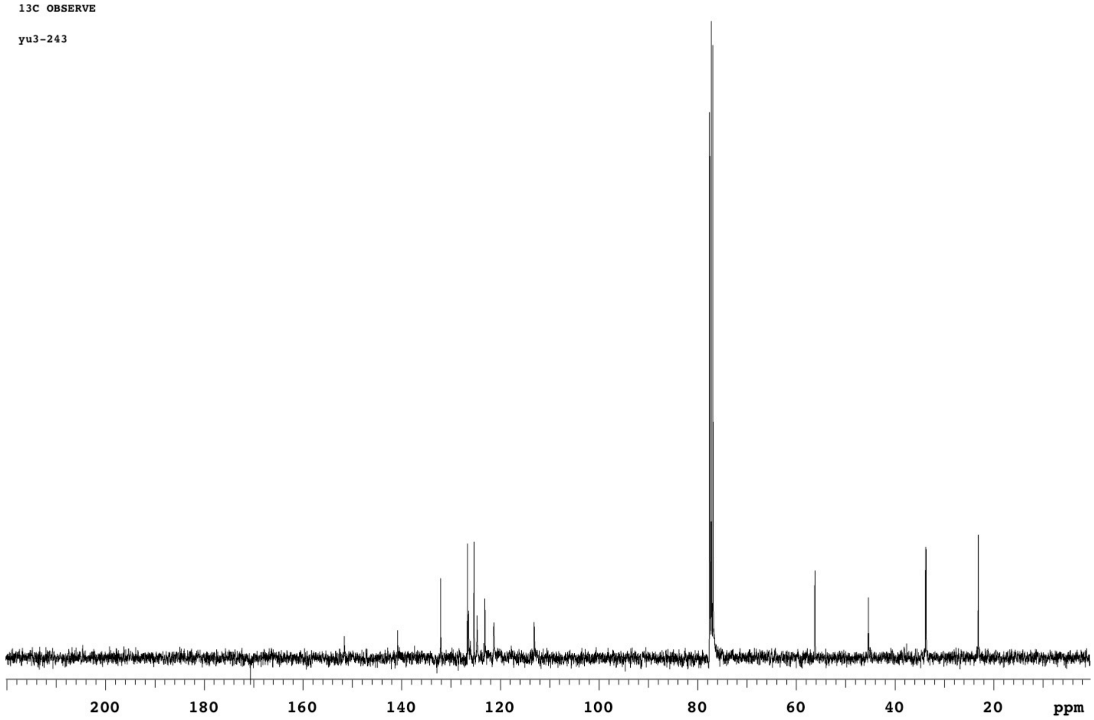
yu3-243





13C OBSERVE

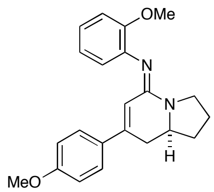
yu3-243

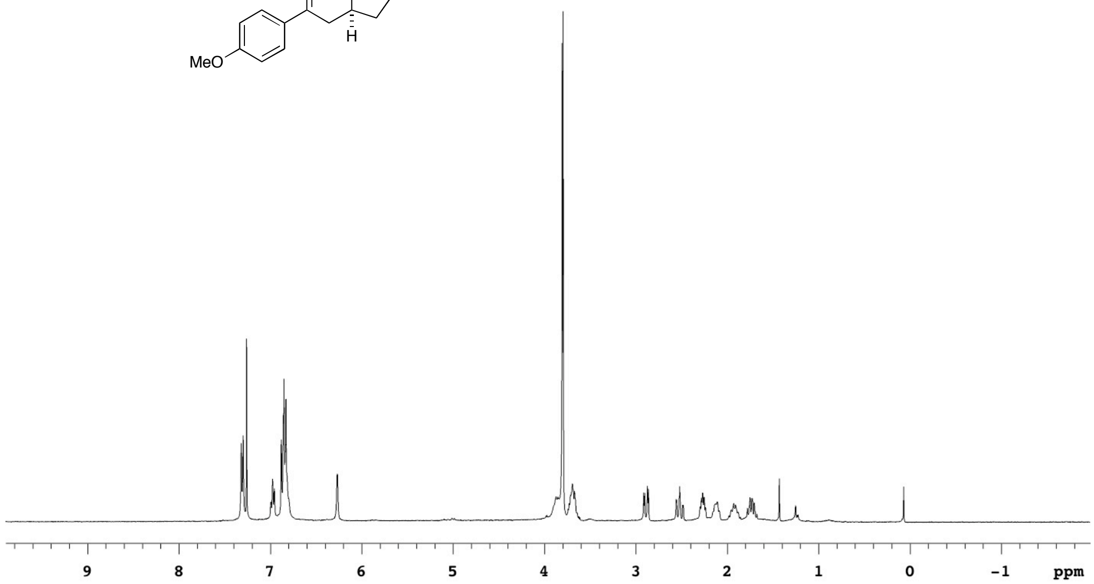


3kc

STANDARD 1H OBSERVE

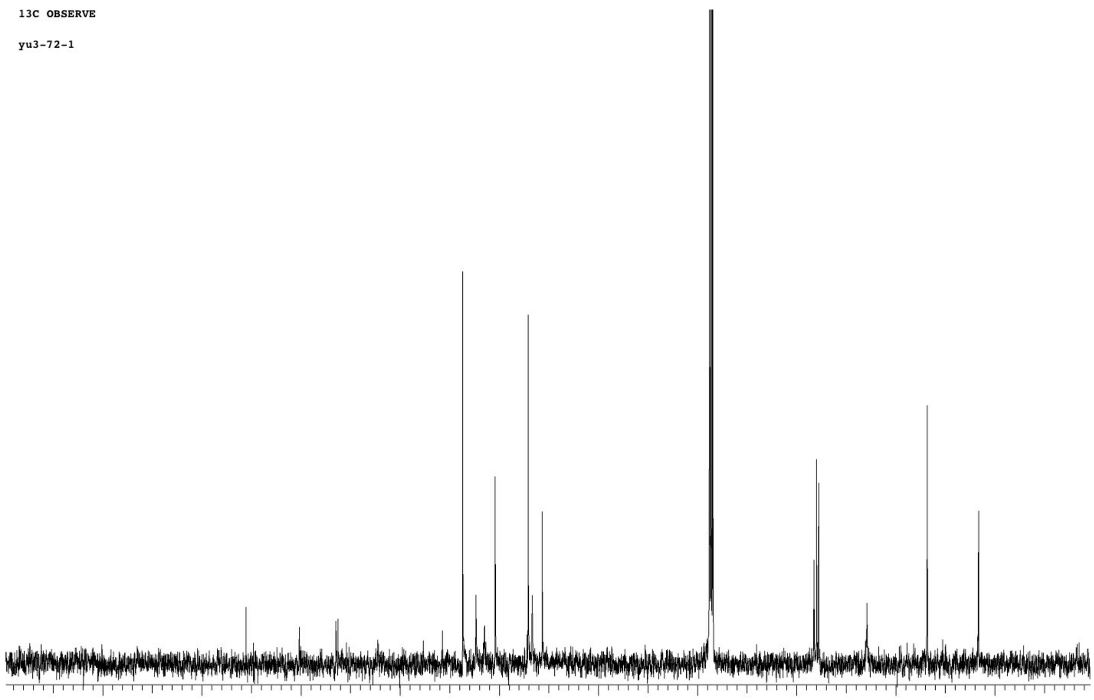
yu3-72-1



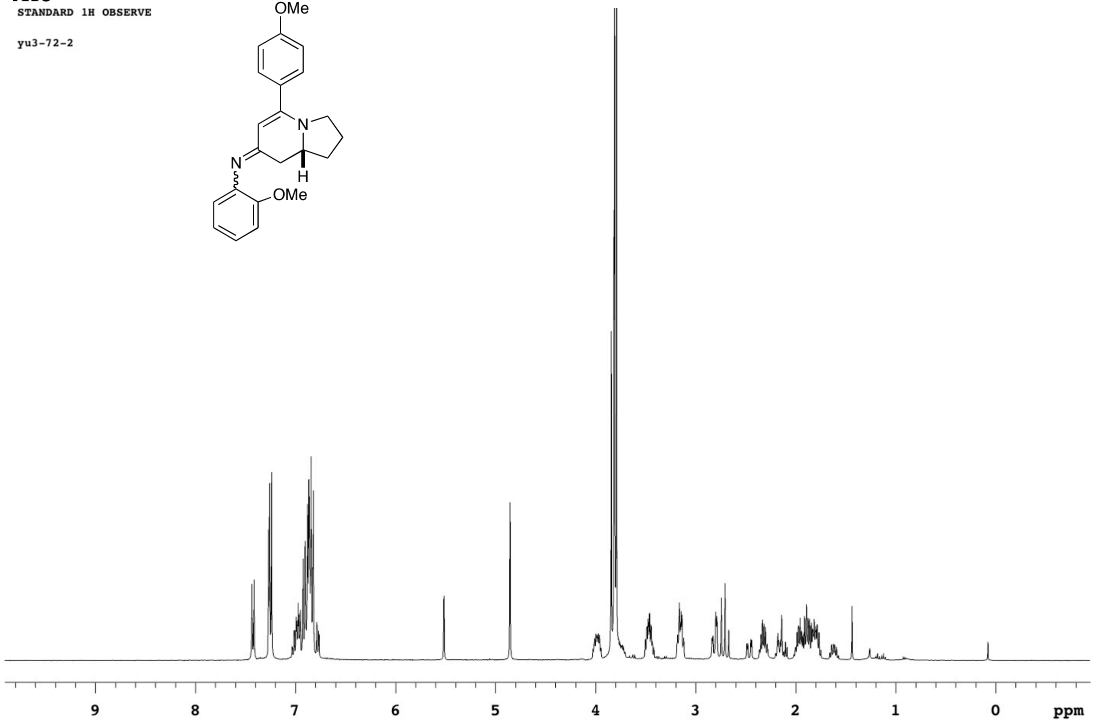


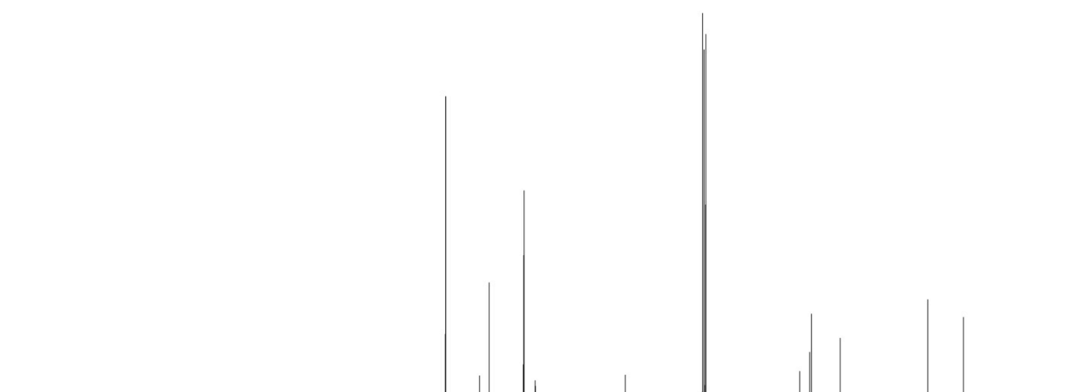
13C OBSERVE

yu3-72-1



4kc

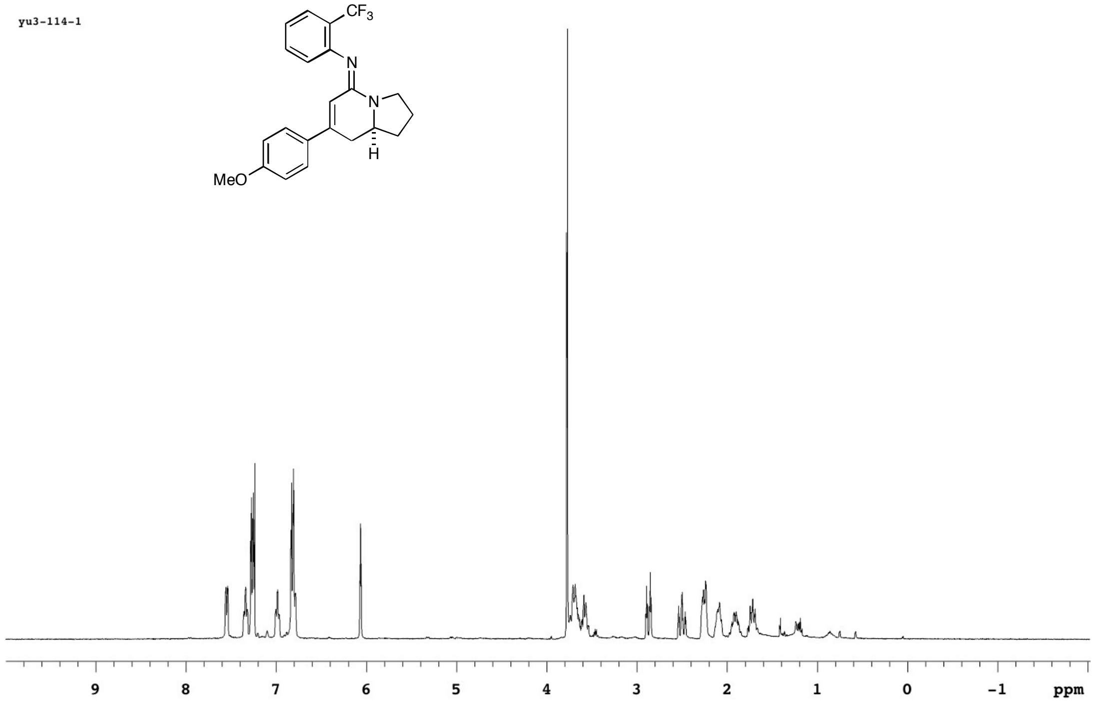

STANDARD 1H OBSERVE
yu3-72-2
OMe
N
N
H
OMe
9
8
7
6
5
4
3
2
1
0
ppm


13C OBSERVE
yu3-72-2
200
180
160
140
120
100
80
60
40
20
ppm

3ke

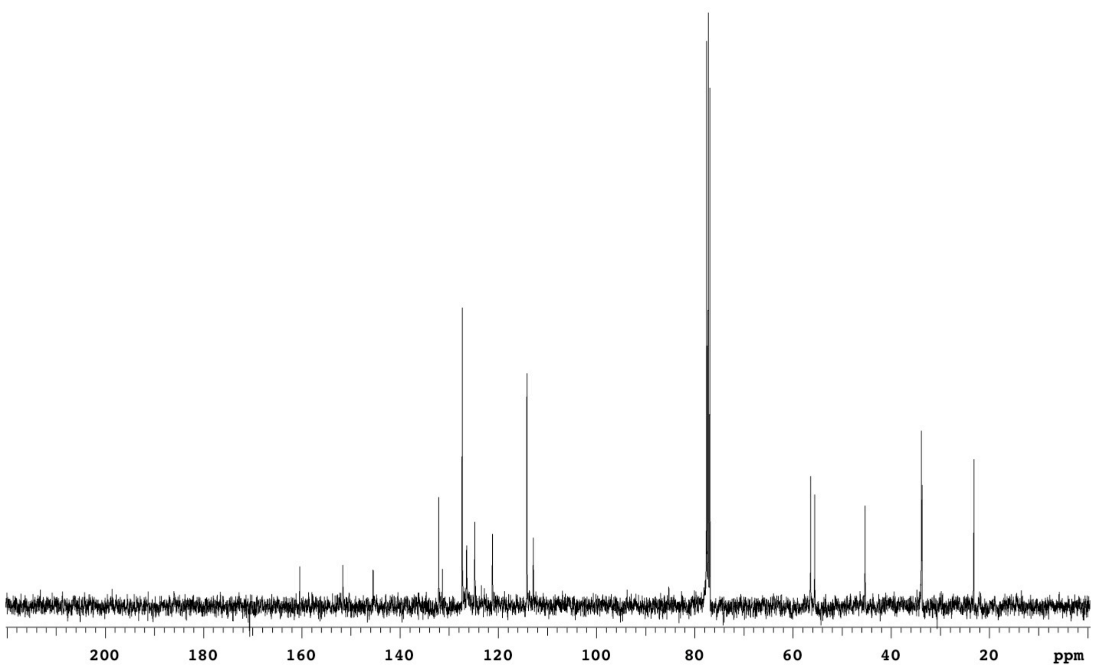
STANDARD 1H OBSERVE

yu3-114-1



13C OBSERVE

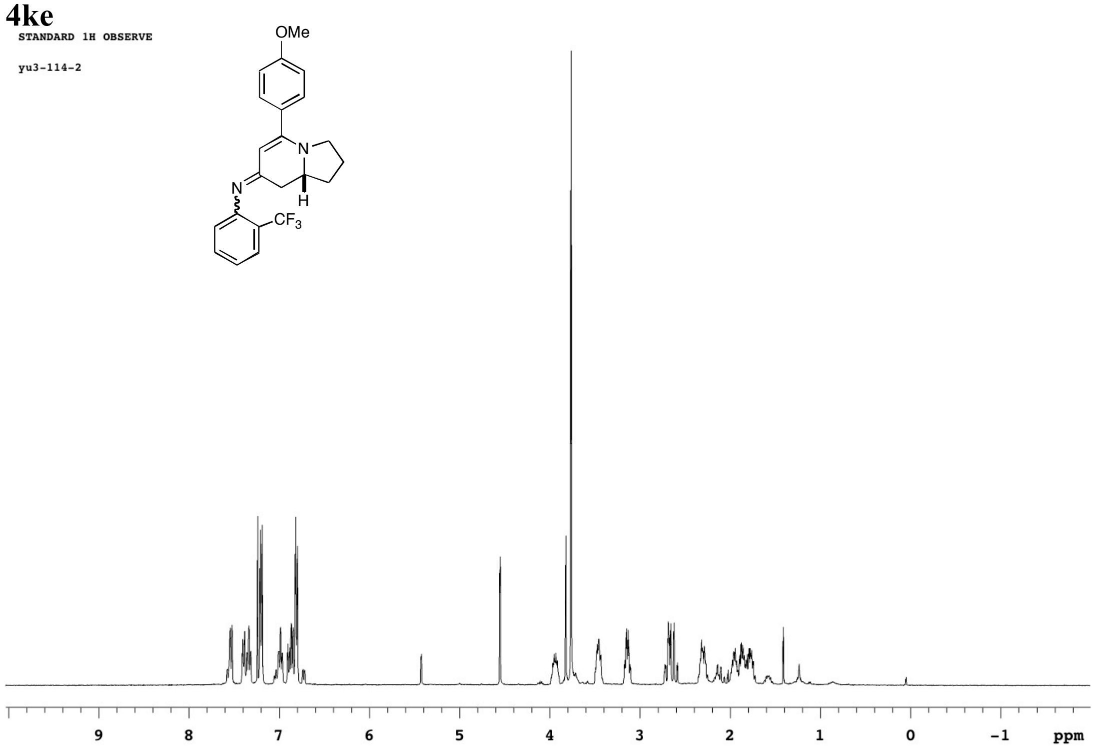
yu3-114-1



4ke

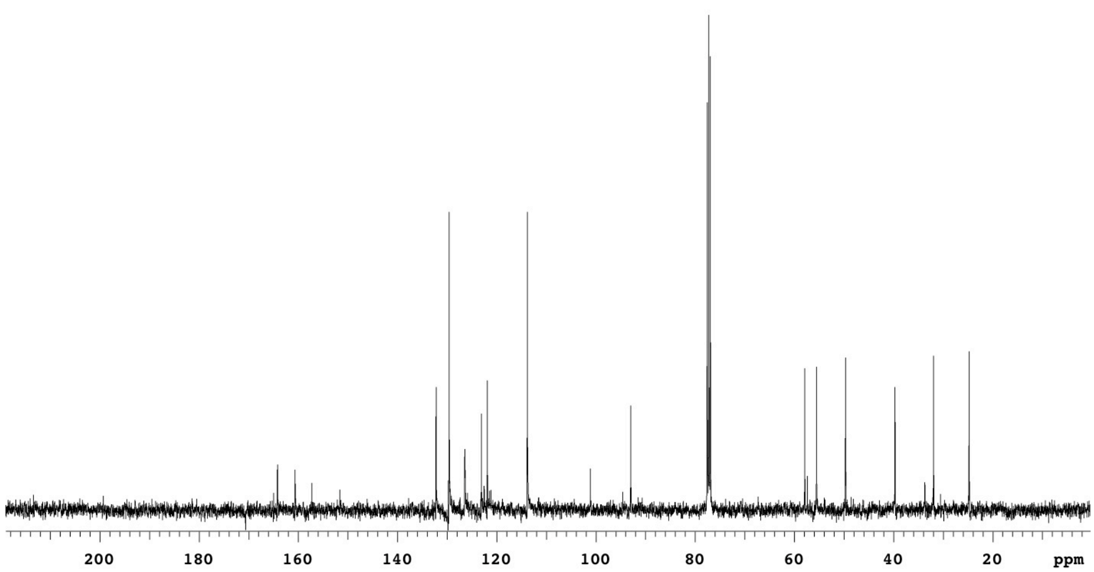
STANDARD 1H OBSERVE

yu3-114-2

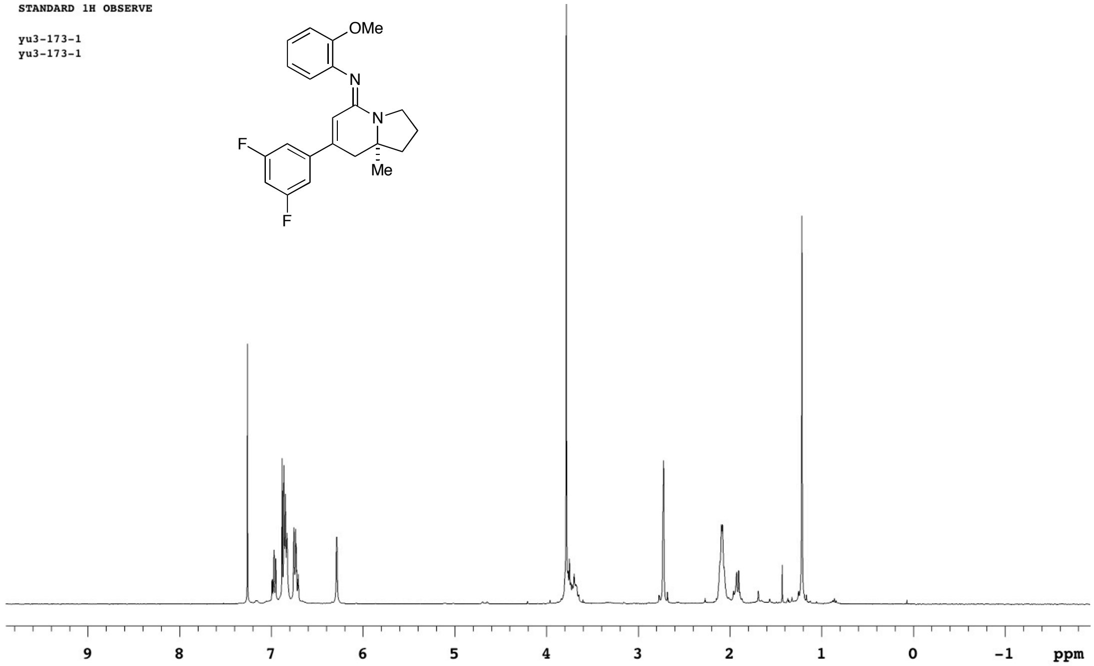


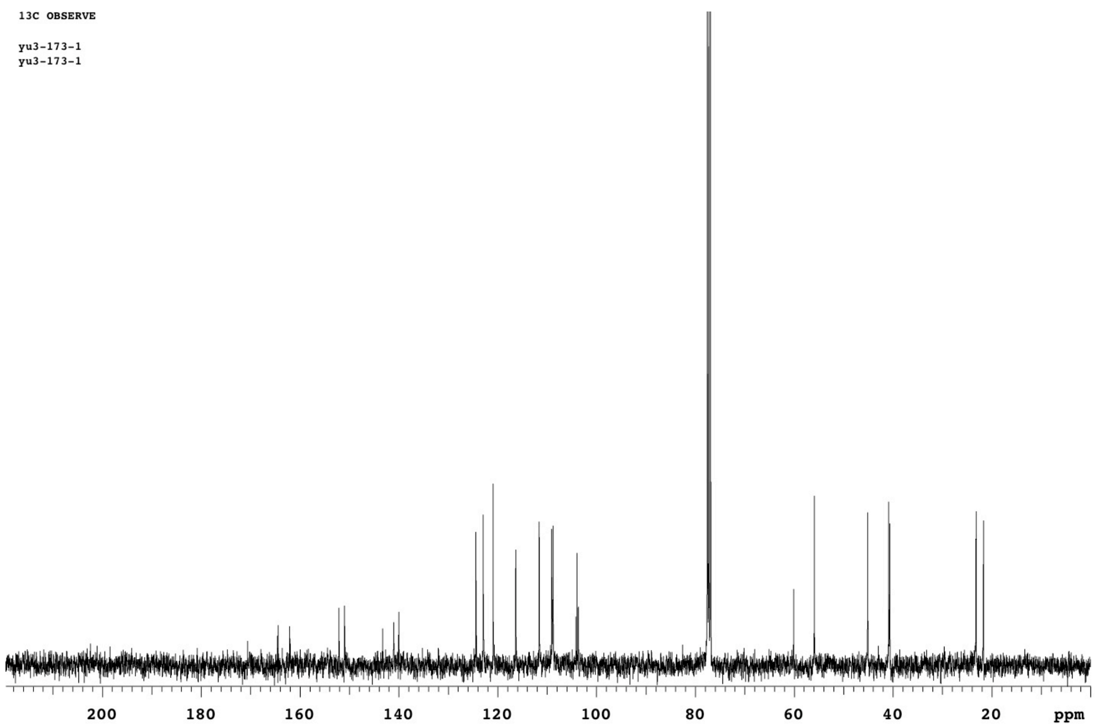
13C OBSERVE

yu3-114-2



6d

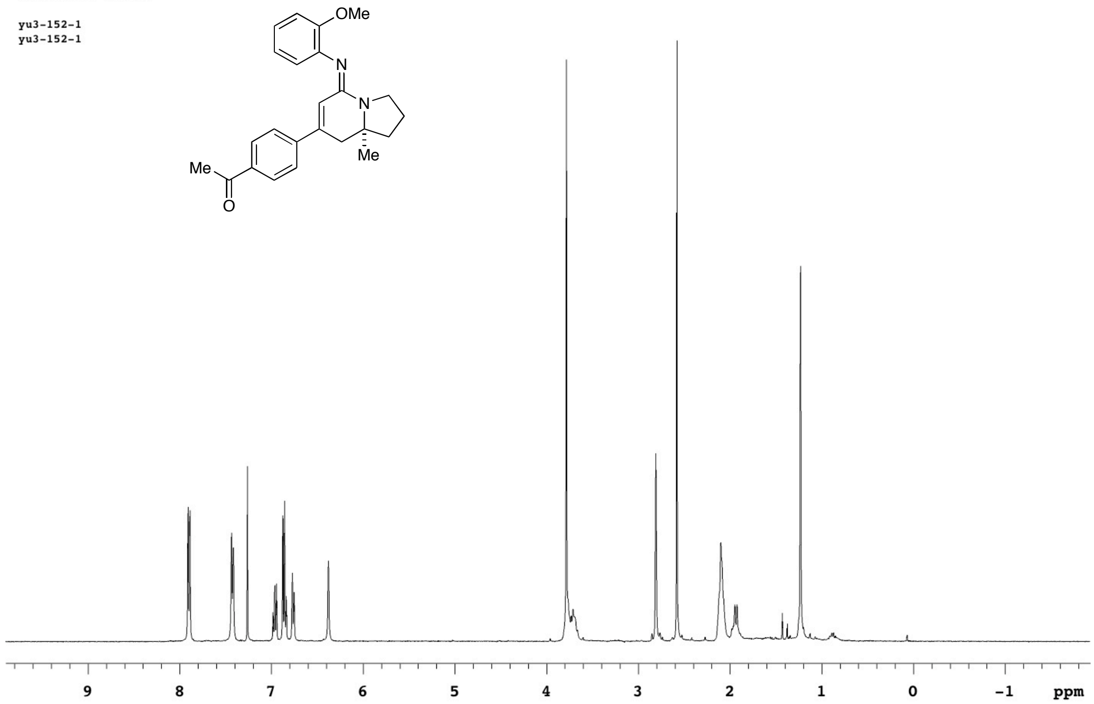

STANDARD 1H OBSERVE
yu3-173-1
yu3-173-1
OMe
N
N
F
F
Me
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-173-1
yu3-173-1
200
180
160
140
120
100
80
60
40
20
ppm

6e

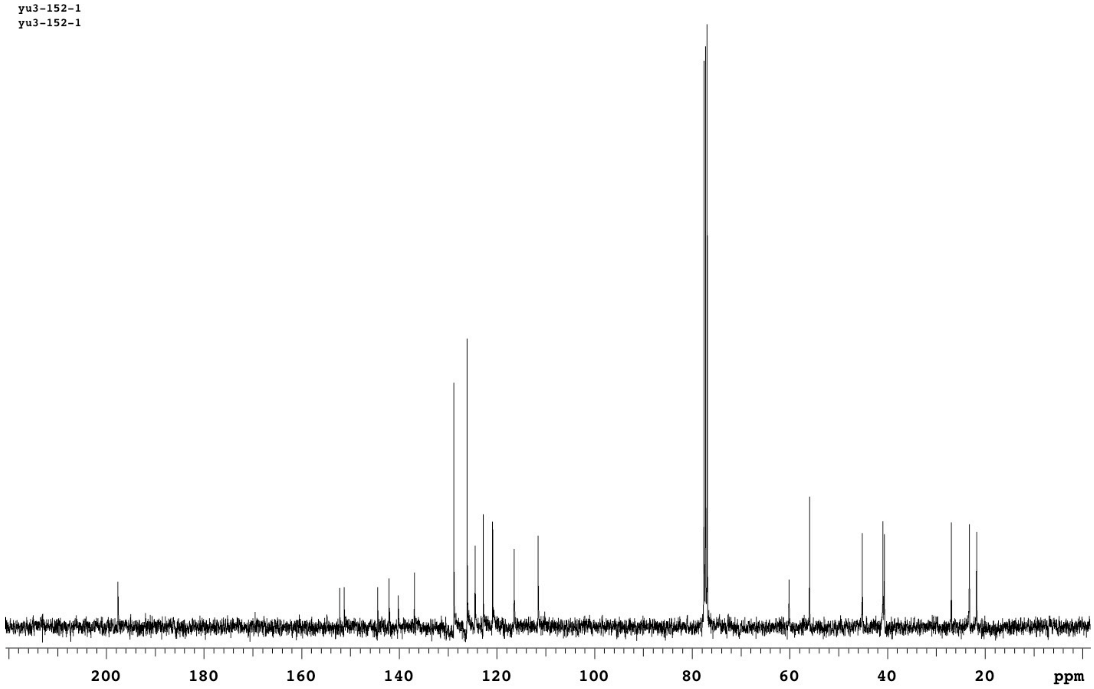
STANDARD 1H OBSERVE

yu3-152-1
yu3-152-1

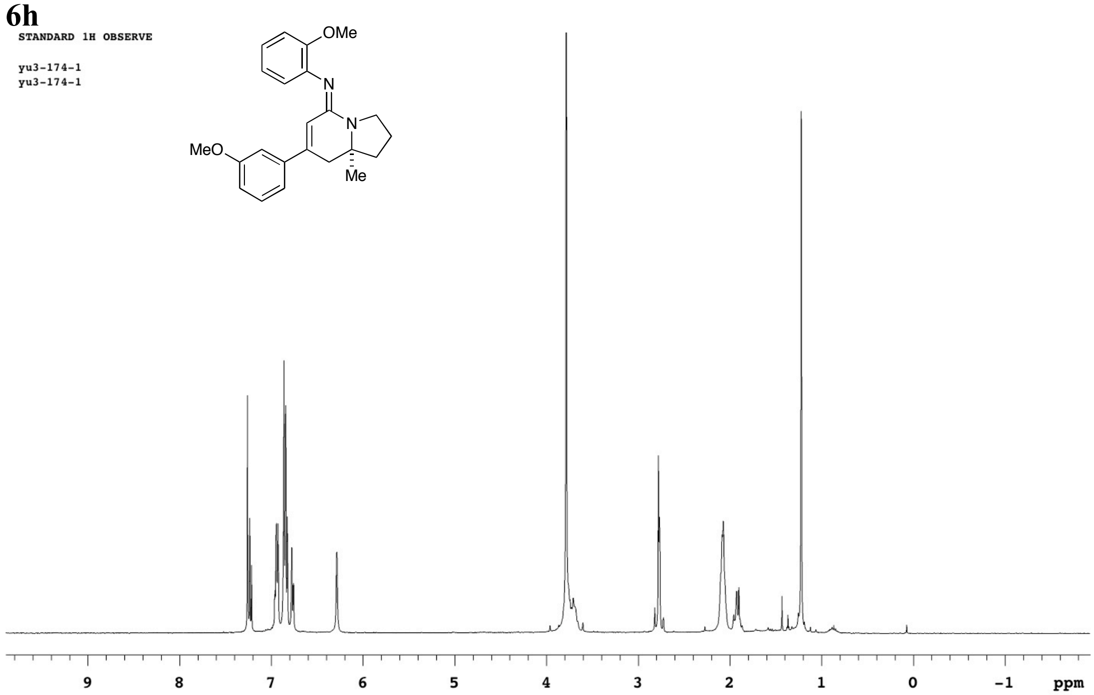


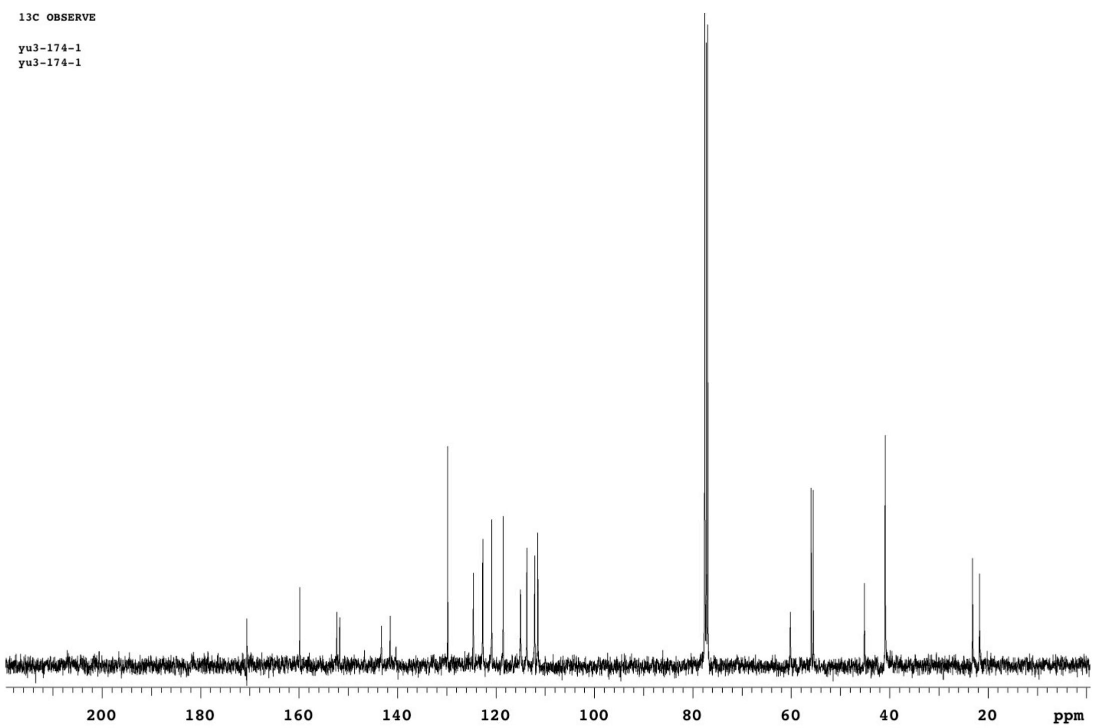
13C OBSERVE

yu3-152-1
yu3-152-1

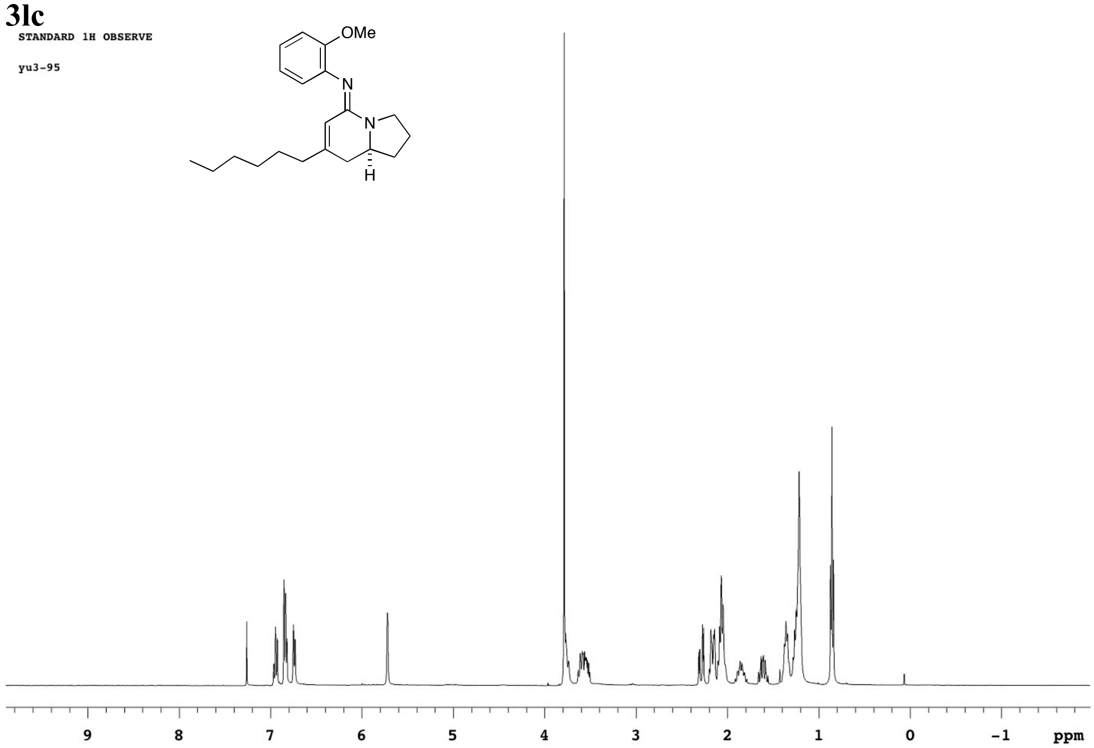


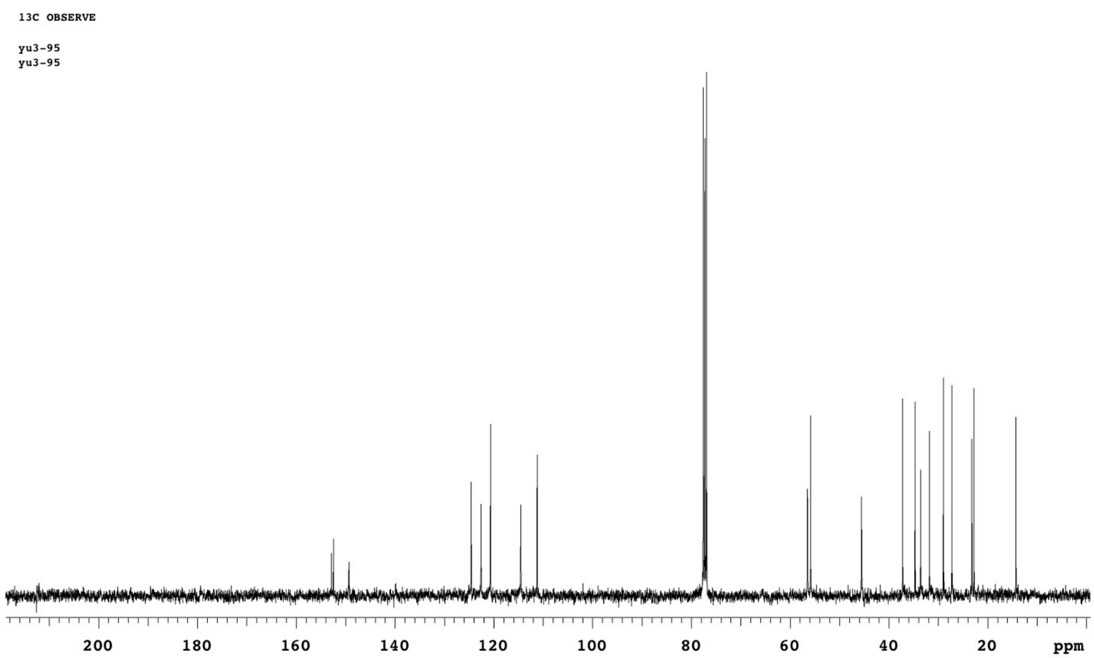
6h


STANDARD 1H OBSERVE
yu3-174-1
yu3-174-1
OMe
N
N
MeO
Me
9
8
7
6
5
4
3
2
1
0
-1
ppm

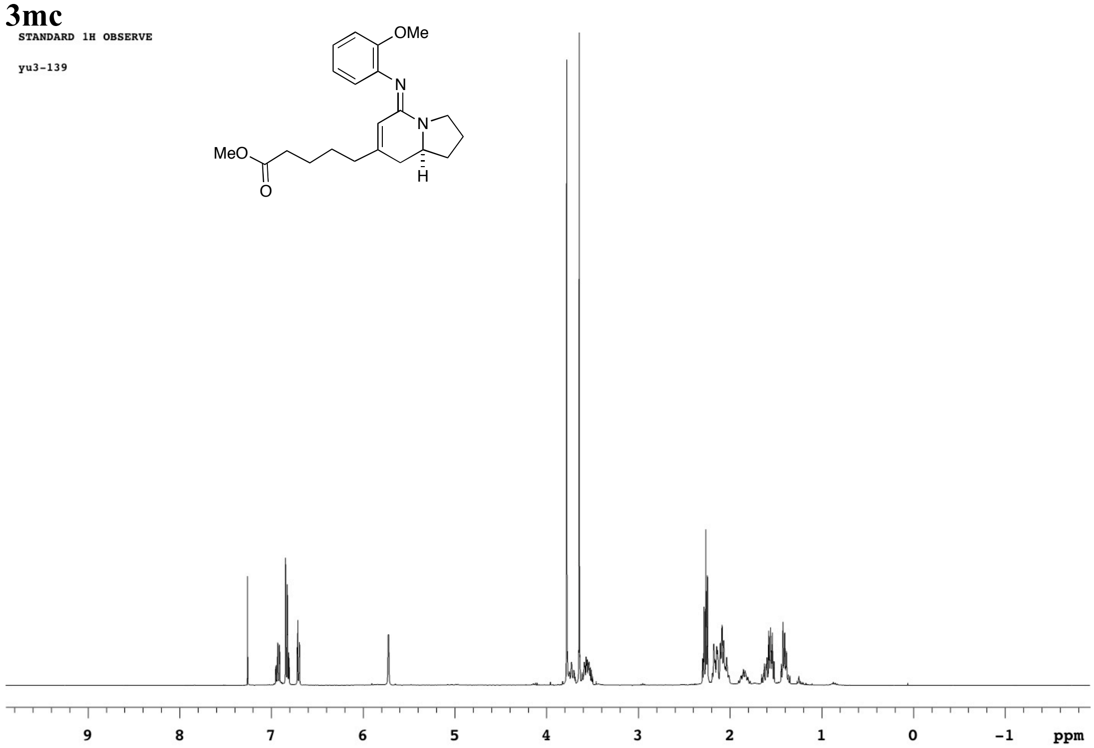

13C OBSERVE
yu3-174-1
yu3-174-1
200
180
160
140
120
100
80
60
40
20
ppm

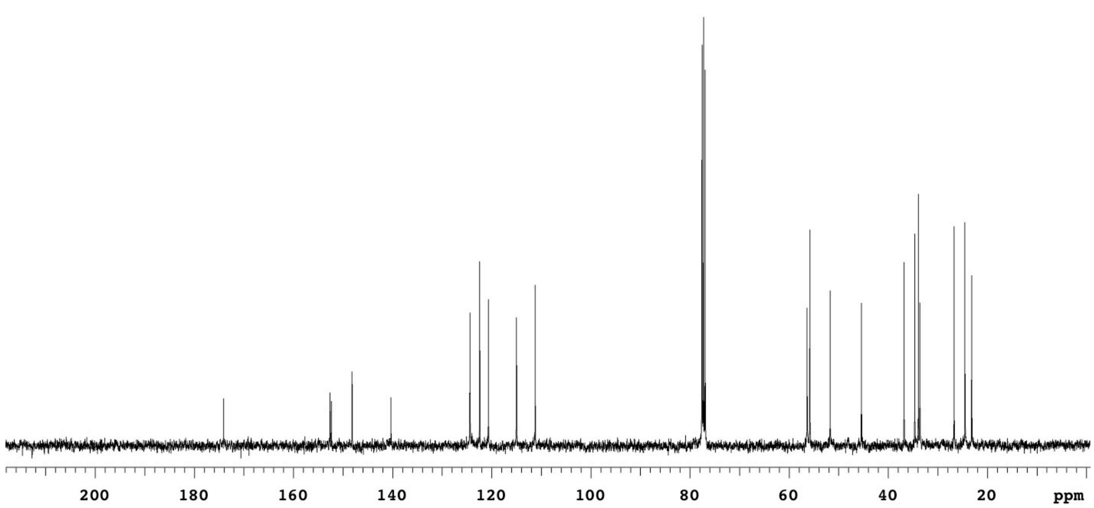
3lc


STANDARD 1H OBSERVE
yu3-95
OMe
N
N
H
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-95
yu3-95
200
180
160
140
120
100
80
60
40
20
ppm

3mc

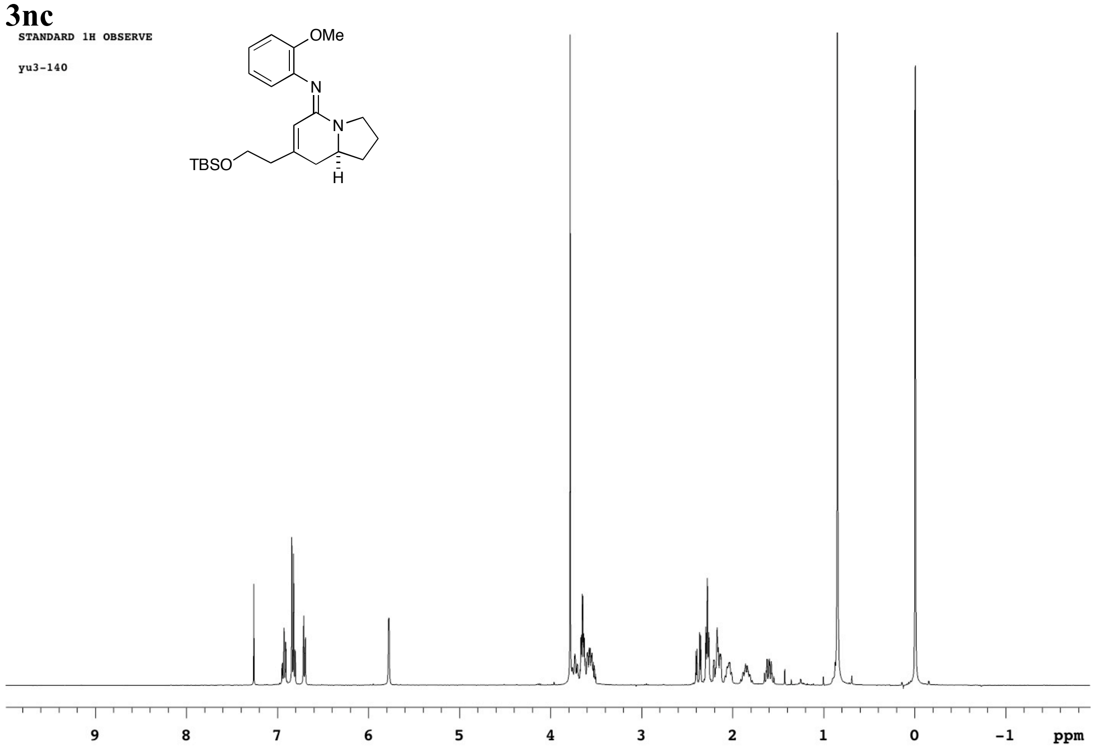

STANDARD 1H OBSERVE
yu3-139
OMe
N
N
MeO
O
H
9
8
7
6
5
4
3
2
1
0
-1
ppm


13C OBSERVE
yu3-139
yu3-139
200
180
160
140
120
100
80
60
40
20
ppm

3nc

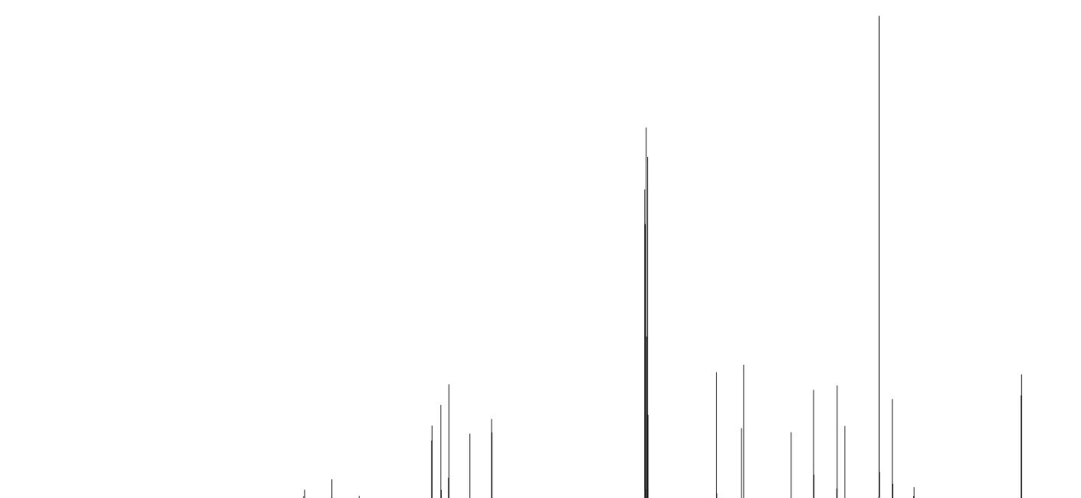
STANDARD 1H OBSERVE

yu3-140

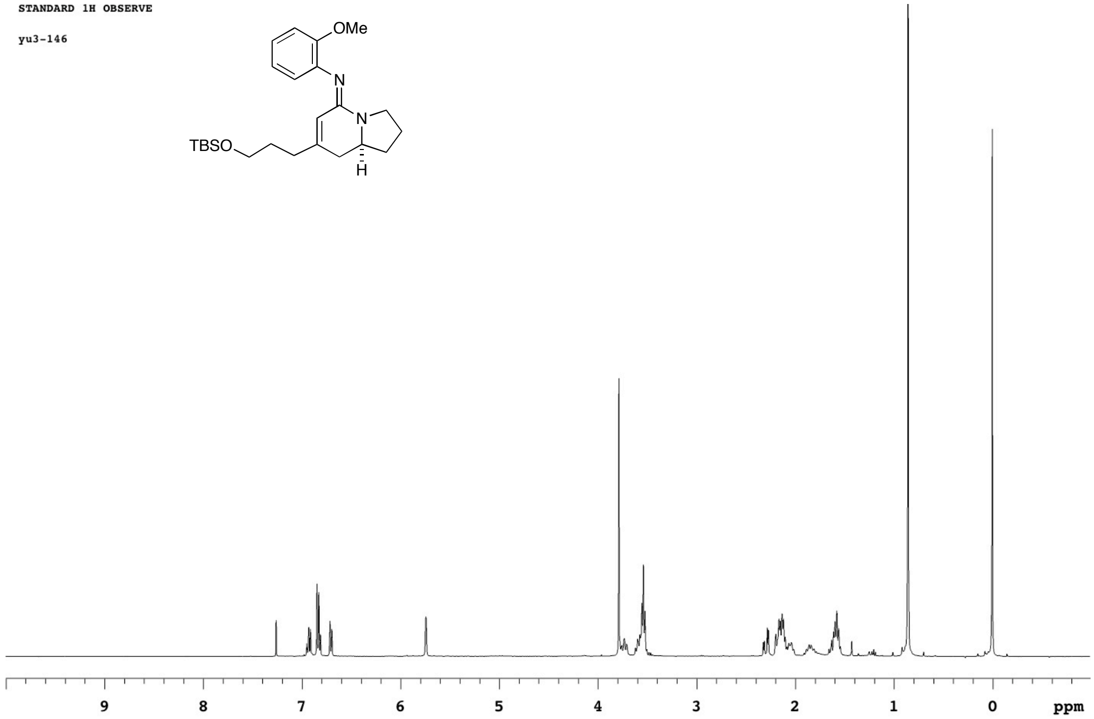


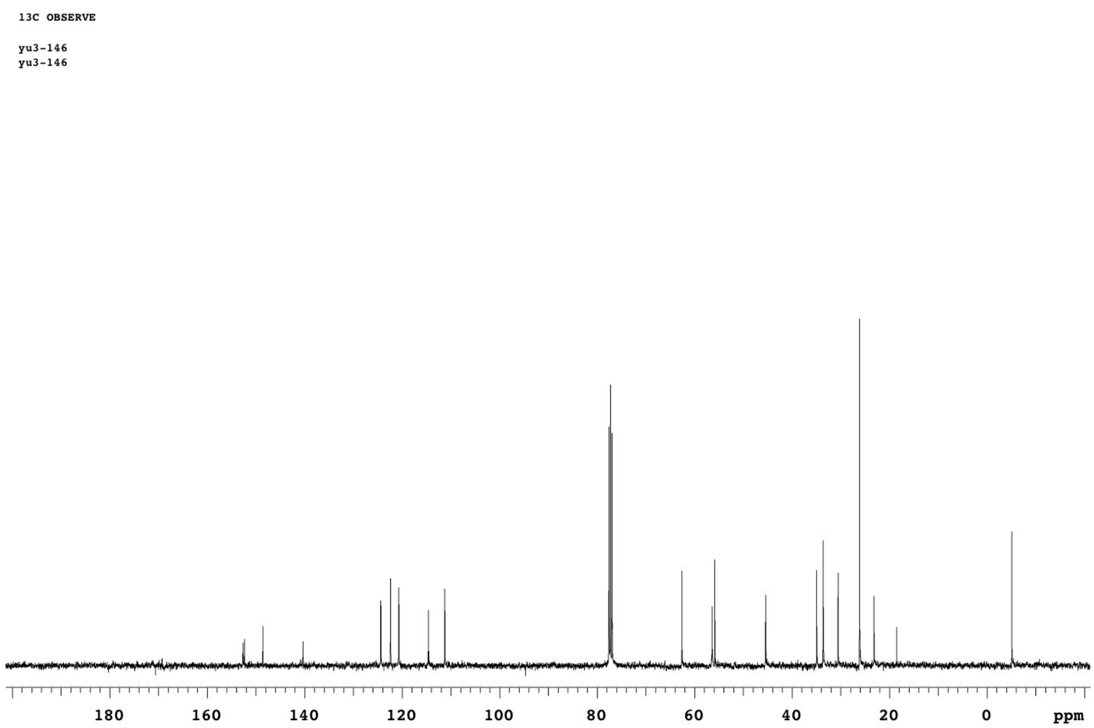
13C OBSERVE

yu3-140
yu3-140



3oc

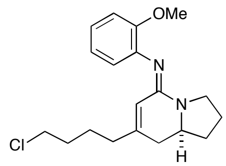

STANDARD 1H OBSERVE
yu3-146
OMe
N
N
TBSO
H
9
8
7
6
5
4
3
2
1
0
ppm

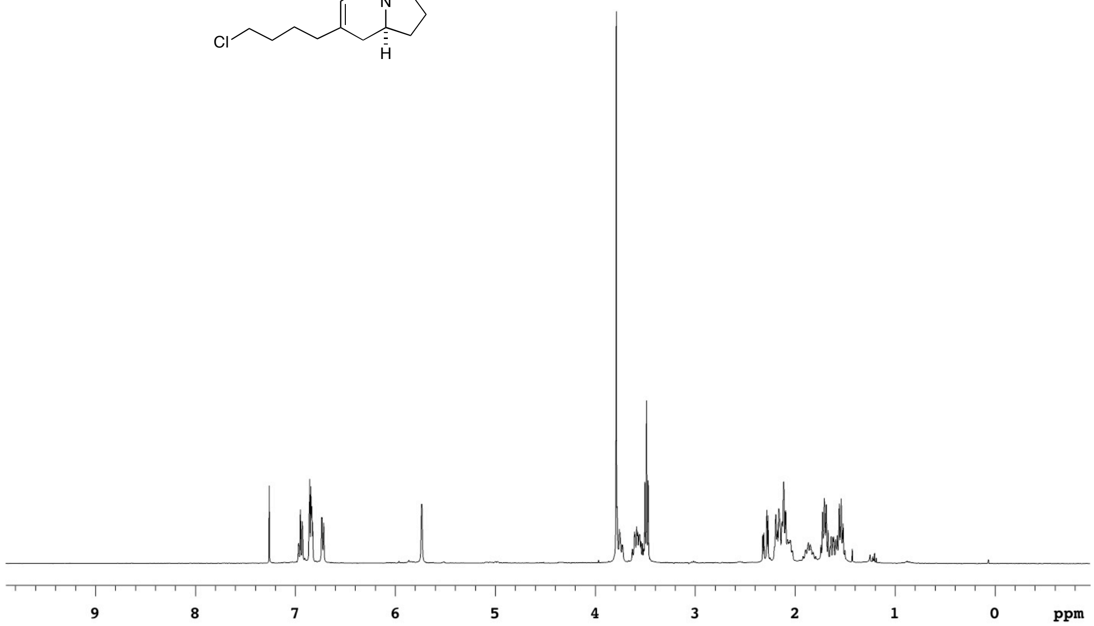

13C OBSERVE
yu3-146
yu3-146
180
160
140
120
100
80
60
40
20
0
ppm

3pc

STANDARD 1H OBSERVE

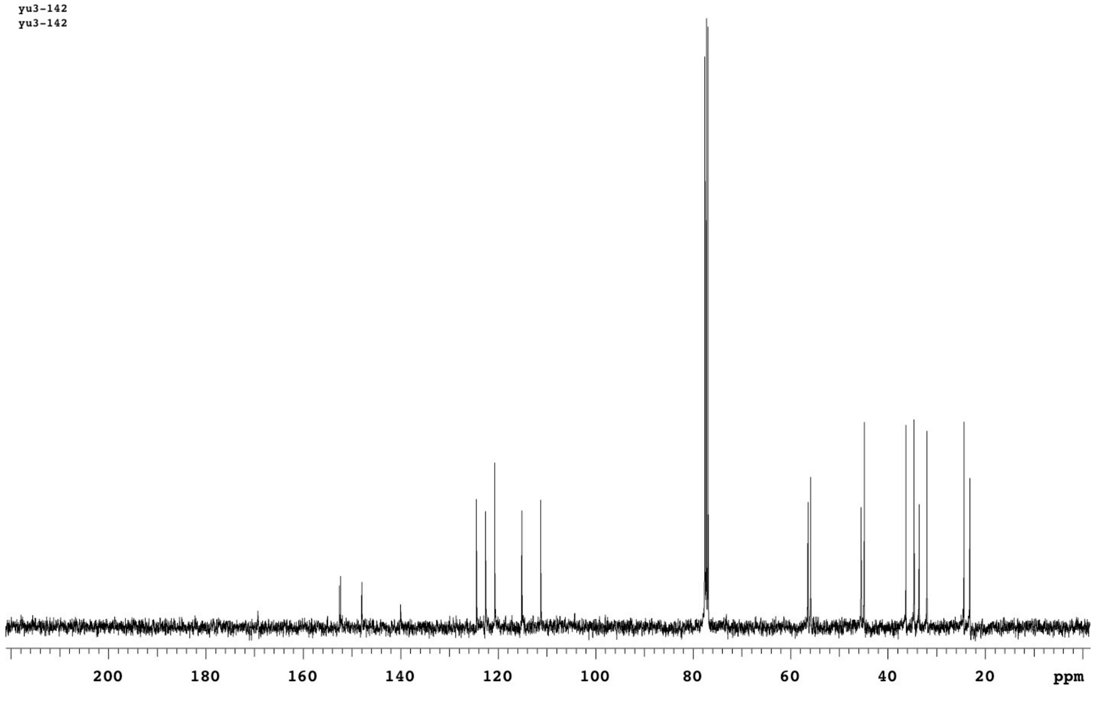
yu3-142





13C OBSERVE

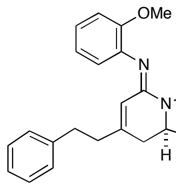
yu3-142
yu3-142

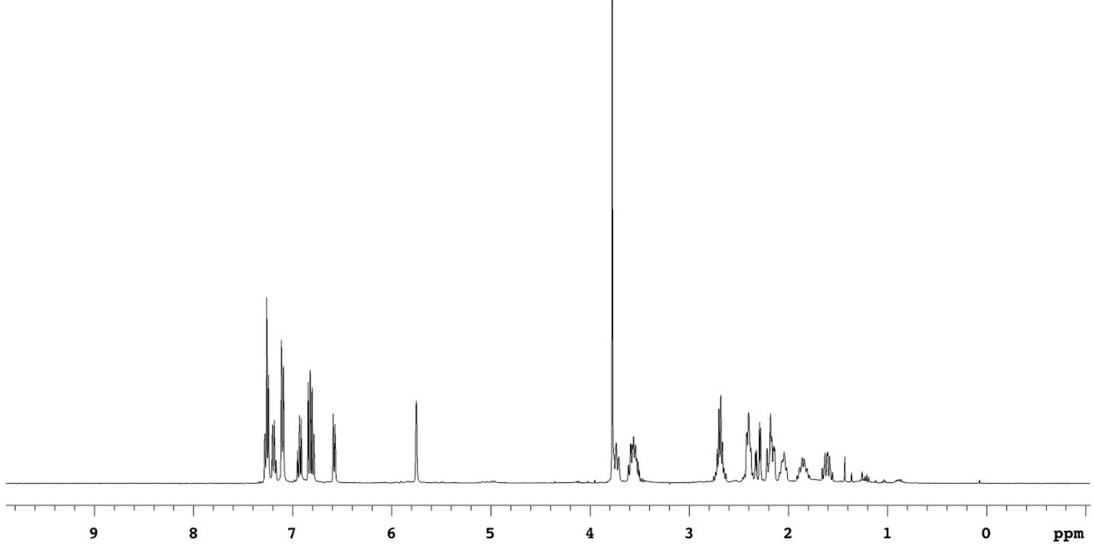


3qc

STANDARD 1H OBSERVE

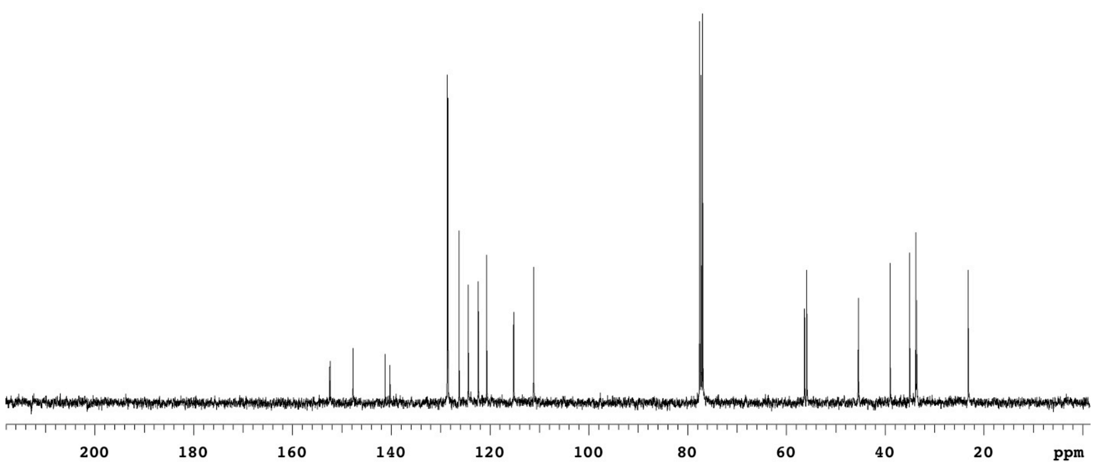
yu3-145



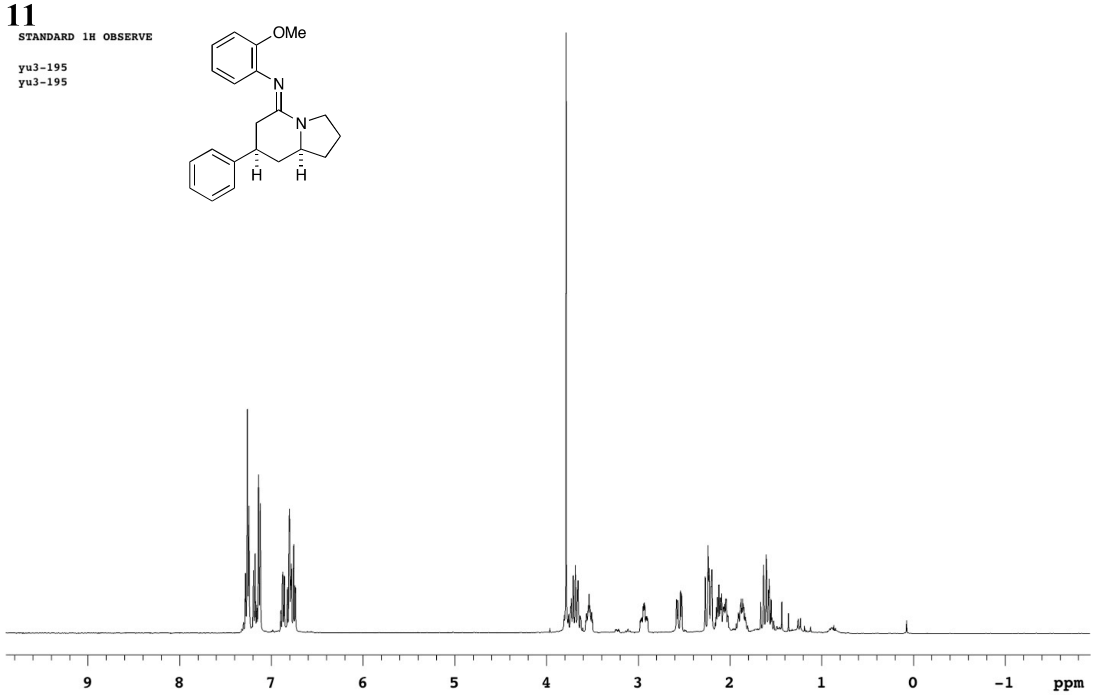


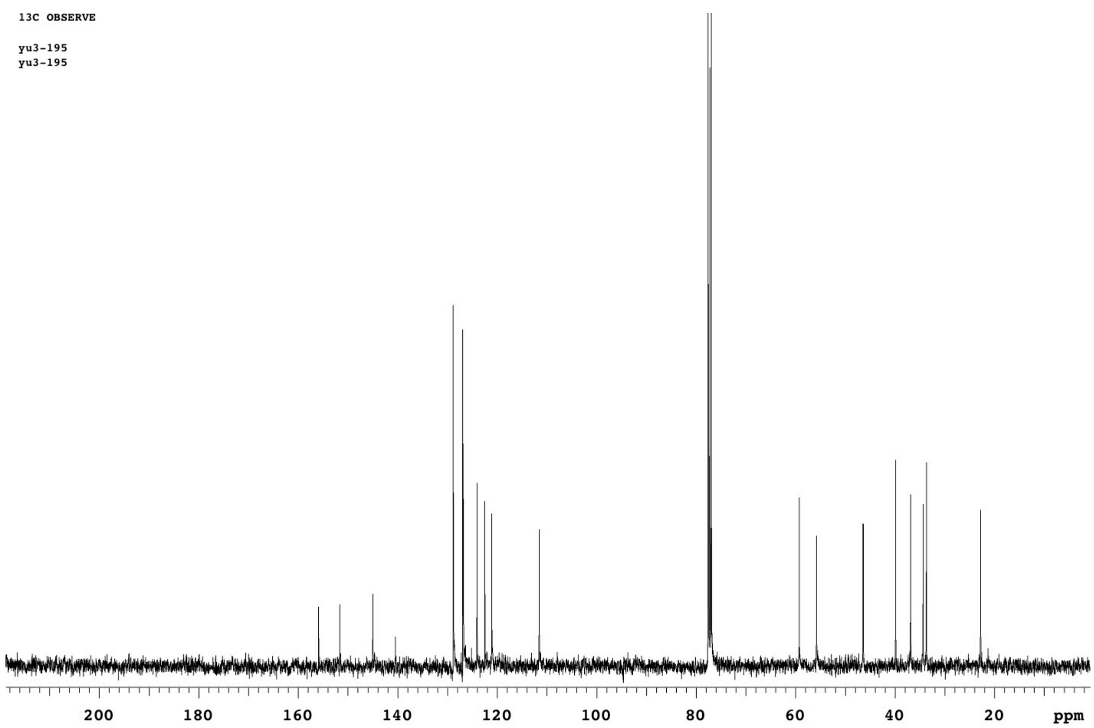
13C OBSERVE

yu3-145
yu3-145

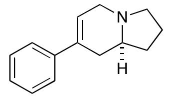


11


STANDARD 1H OBSERVE
yu3-195
yu3-195
OMe
N
N
H
H
9
8
7
6
5
4
3
2
1
0
-1
ppm

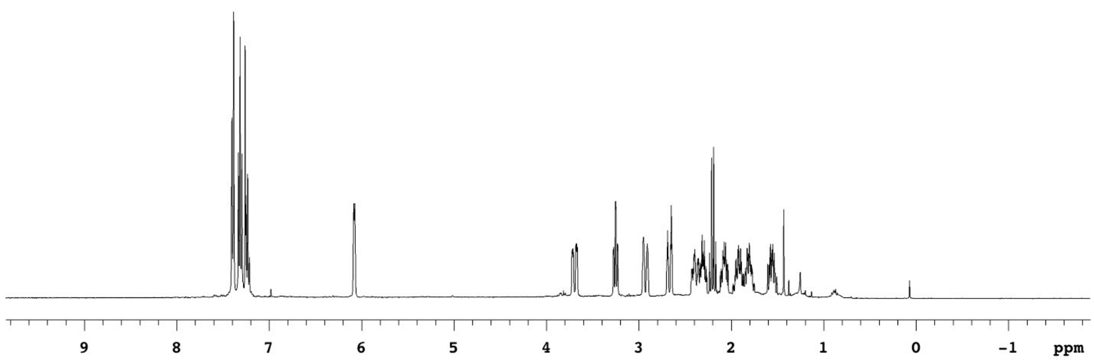

13C OBSERVE
yu3-195
yu3-195
200
180
160
140
120
100
80
60
40
20
ppm

12



STANDARD 1H OBSERVE

yu3-183
yu3-183



13C OBSERVE

yu3-183
yu3-183

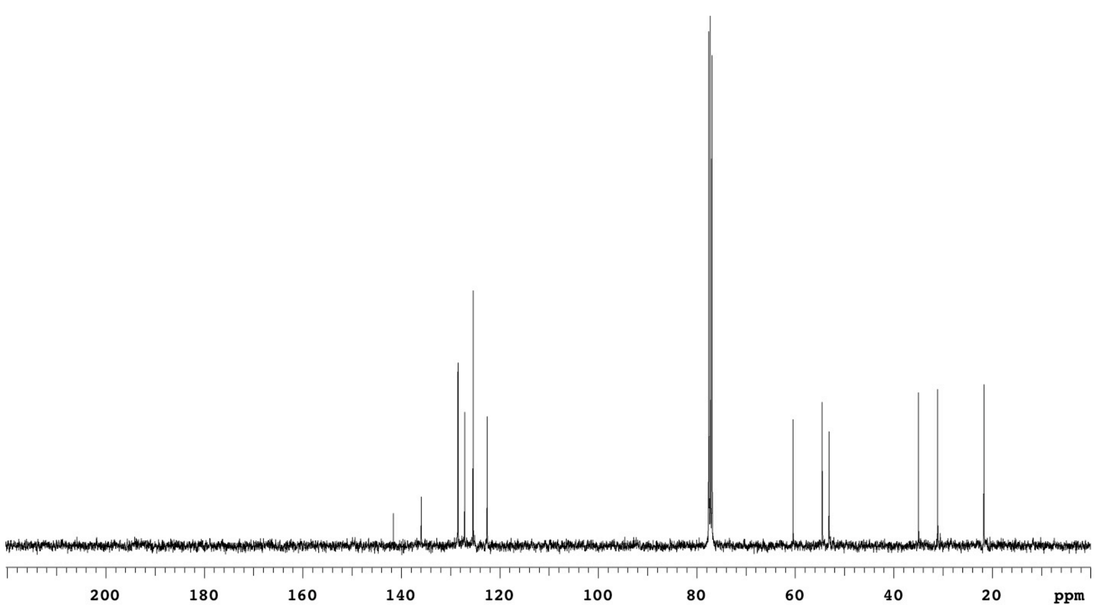


Table 7. Crystal data and structure refinement for rovis29_0m (**3bc**).

Identification code	rovis29_0m	
Empirical formula	C21 H21 Br N2 O	
Formula weight	397.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.4508(13) Å	α= 90°.
	b = 14.332(3) Å	β= 90°.
	c = 38.051(8) Å	γ = 90°.
Volume	3518.0(13) Å^3	
Z	8	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	2.348 mm^{-1}	
F(000)	1632	
Crystal size	0.27 x 0.26 x 0.04 mm^3	
Theta range for data collection	3.50 to 30.03°.	
Index ranges	-3<=h<=9, -20<=k<=19, -47<=l<=53	
Reflections collected	22084	
Independent reflections	10257 [R(int) = 0.1359]	
Completeness to theta = 30.03°	99.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9161 and 0.5729	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10257 / 0 / 452	
Goodness-of-fit on F^2	0.923	
Final R indices [I>2sigma(I)]	R1 = 0.0705, wR2 = 0.1039	
R indices (all data)	R1 = NaN, wR2 = 0.1405	
Absolute structure parameter	-0.016(19)	
Largest diff. peak and hole	0.580 and -0.573 e.Å^{-3}	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for rovis29_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	6942(1)	1906(1)	9840(1)	34(1)
N(1)	-4066(10)	-430(4)	8700(2)	22(2)
N(2)	-4005(10)	789(5)	8314(2)	21(2)
O(1)	-264(8)	525(4)	7987(1)	21(1)
C(1)	-3191(12)	376(5)	8581(2)	16(2)
C(2)	-1368(12)	688(5)	8784(2)	17(2)
C(3)	-476(13)	201(6)	9034(2)	21(2)
C(4)	-1302(12)	-773(5)	9122(2)	29(2)
C(5)	-3555(13)	-848(5)	9045(2)	27(2)
C(6)	-4437(14)	-1821(6)	9009(2)	45(2)
C(7)	-6198(14)	-1747(6)	8747(2)	45(3)
C(8)	-5943(13)	-846(5)	8548(2)	21(2)
C(9)	1370(13)	559(5)	9229(2)	19(2)
C(10)	2785(13)	1157(5)	9058(2)	22(2)
C(11)	4423(12)	1554(6)	9238(2)	22(2)
C(12)	4651(12)	1359(6)	9590(2)	25(2)
C(13)	3366(12)	748(6)	9764(2)	25(2)
C(14)	1711(13)	372(6)	9583(2)	25(2)
C(15)	-2933(12)	1559(5)	8165(2)	19(2)
C(16)	-3856(13)	2434(6)	8161(2)	23(2)
C(17)	-2835(12)	3187(6)	7993(2)	24(2)
C(18)	-1019(13)	3045(6)	7815(2)	25(2)
C(19)	-70(12)	2168(5)	7810(2)	19(2)
C(20)	-1002(12)	1434(5)	7986(2)	18(2)
C(21)	1536(13)	343(6)	7776(2)	24(2)
Br(1A)	8267(1)	6859(1)	9885(1)	33(1)
N(1A)	19162(9)	4583(5)	8687(2)	17(2)
N(2A)	18968(10)	5791(5)	8303(2)	19(2)
O(1A)	15297(8)	5531(4)	7948(1)	21(1)
C(1A)	18143(12)	5312(5)	8553(2)	18(2)
C(2A)	16175(11)	5592(5)	8735(2)	18(2)

C(3A)	15619(12)	5207(5)	9047(2)	15(2)
C(4A)	16957(11)	4457(5)	9207(2)	23(2)
C(5A)	18192(13)	3926(5)	8935(2)	23(2)
C(6A)	20053(11)	3372(5)	9062(2)	20(2)
C(7A)	21352(13)	3295(6)	8733(2)	26(2)
C(8A)	21086(12)	4224(5)	8543(2)	20(2)
C(9A)	13775(13)	5564(5)	9240(2)	19(2)
C(10A)	12229(12)	6090(5)	9080(2)	18(2)
C(11A)	10607(12)	6470(5)	9267(2)	22(2)
C(12A)	10464(13)	6315(6)	9628(2)	24(2)
C(13A)	11941(12)	5774(6)	9797(2)	28(2)
C(14A)	13570(13)	5395(5)	9601(2)	23(2)
C(15A)	17886(12)	6553(5)	8145(2)	17(2)
C(16A)	18764(13)	7448(6)	8154(2)	21(2)
C(17A)	17804(13)	8187(7)	7987(2)	29(2)
C(18A)	15990(13)	8051(7)	7797(2)	25(2)
C(19A)	15122(12)	7167(6)	7781(2)	21(2)
C(20A)	16082(13)	6406(5)	7954(2)	19(2)
C(21A)	13456(12)	5348(6)	7748(2)	28(2)

Table 9. Bond lengths [Å] and angles [°] for rovis29_0m.

Br(1)-C(12)	1.924(9)
N(1)-C(1)	1.365(9)
N(1)-C(8)	1.468(10)
N(1)-C(5)	1.478(9)
N(2)-C(1)	1.288(9)
N(2)-C(15)	1.421(9)
O(1)-C(20)	1.387(9)
O(1)-C(21)	1.435(9)
C(1)-C(2)	1.476(10)
C(2)-C(3)	1.312(10)
C(3)-C(9)	1.494(12)
C(3)-C(4)	1.531(11)
C(4)-C(5)	1.486(11)
C(5)-C(6)	1.512(11)
C(6)-C(7)	1.516(11)
C(7)-C(8)	1.505(11)
C(9)-C(14)	1.390(10)
C(9)-C(10)	1.411(11)
C(10)-C(11)	1.380(11)
C(11)-C(12)	1.378(10)
C(12)-C(13)	1.376(11)
C(13)-C(14)	1.381(11)
C(15)-C(16)	1.388(10)
C(15)-C(20)	1.431(11)
C(16)-C(17)	1.418(10)
C(17)-C(18)	1.367(11)
C(18)-C(19)	1.399(11)
C(19)-C(20)	1.385(10)
Br(1A)-C(12A)	1.891(8)
N(1A)-C(1A)	1.335(9)
N(1A)-C(8A)	1.451(9)
N(1A)-C(5A)	1.472(9)
N(2A)-C(1A)	1.289(9)
N(2A)-C(15A)	1.430(9)

O(1A)-C(20A)	1.353(9)
O(1A)-C(21A)	1.435(9)
C(1A)-C(2A)	1.500(10)
C(2A)-C(3A)	1.360(10)
C(3A)-C(9A)	1.488(11)
C(3A)-C(4A)	1.507(10)
C(4A)-C(5A)	1.513(10)
C(5A)-C(6A)	1.518(10)
C(6A)-C(7A)	1.510(10)
C(7A)-C(8A)	1.526(10)
C(9A)-C(10A)	1.391(10)
C(9A)-C(14A)	1.403(10)
C(10A)-C(11A)	1.377(10)
C(11A)-C(12A)	1.394(11)
C(12A)-C(13A)	1.387(11)
C(13A)-C(14A)	1.398(11)
C(15A)-C(20A)	1.388(11)
C(15A)-C(16A)	1.402(10)
C(16A)-C(17A)	1.381(11)
C(17A)-C(18A)	1.389(11)
C(18A)-C(19A)	1.387(11)
C(19A)-C(20A)	1.415(10)

C(1)-N(1)-C(8)	123.6(7)
C(1)-N(1)-C(5)	123.1(6)
C(8)-N(1)-C(5)	111.7(6)
C(1)-N(2)-C(15)	118.2(7)
C(20)-O(1)-C(21)	116.6(6)
N(2)-C(1)-N(1)	118.9(7)
N(2)-C(1)-C(2)	126.8(7)
N(1)-C(1)-C(2)	114.3(7)
C(3)-C(2)-C(1)	124.6(8)
C(2)-C(3)-C(9)	121.8(8)
C(2)-C(3)-C(4)	119.3(8)
C(9)-C(3)-C(4)	118.8(7)
C(5)-C(4)-C(3)	111.3(6)

N(1)-C(5)-C(4)	111.3(6)
N(1)-C(5)-C(6)	102.1(6)
C(4)-C(5)-C(6)	116.9(7)
C(5)-C(6)-C(7)	106.1(7)
C(8)-C(7)-C(6)	108.0(7)
N(1)-C(8)-C(7)	103.9(7)
C(14)-C(9)-C(10)	117.4(8)
C(14)-C(9)-C(3)	122.8(8)
C(10)-C(9)-C(3)	119.8(7)
C(11)-C(10)-C(9)	121.3(7)
C(12)-C(11)-C(10)	118.6(8)
C(13)-C(12)-C(11)	122.2(8)
C(13)-C(12)-Br(1)	119.1(6)
C(11)-C(12)-Br(1)	118.7(7)
C(12)-C(13)-C(14)	118.3(7)
C(13)-C(14)-C(9)	122.1(8)
C(16)-C(15)-N(2)	119.8(7)
C(16)-C(15)-C(20)	118.8(7)
N(2)-C(15)-C(20)	121.1(7)
C(15)-C(16)-C(17)	119.5(8)
C(18)-C(17)-C(16)	120.6(8)
C(17)-C(18)-C(19)	121.1(8)
C(20)-C(19)-C(18)	119.0(7)
C(19)-C(20)-O(1)	124.4(7)
C(19)-C(20)-C(15)	120.9(7)
O(1)-C(20)-C(15)	114.6(7)
C(1A)-N(1A)-C(8A)	123.6(6)
C(1A)-N(1A)-C(5A)	122.4(6)
C(8A)-N(1A)-C(5A)	112.3(6)
C(1A)-N(2A)-C(15A)	121.2(7)
C(20A)-O(1A)-C(21A)	119.1(6)
N(2A)-C(1A)-N(1A)	119.7(7)
N(2A)-C(1A)-C(2A)	123.1(7)
N(1A)-C(1A)-C(2A)	116.8(7)
C(3A)-C(2A)-C(1A)	121.2(7)
C(2A)-C(3A)-C(9A)	120.2(7)

C(2A)-C(3A)-C(4A)	119.4(7)
C(9A)-C(3A)-C(4A)	120.3(7)
C(3A)-C(4A)-C(5A)	112.6(6)
N(1A)-C(5A)-C(4A)	110.0(6)
N(1A)-C(5A)-C(6A)	101.7(6)
C(4A)-C(5A)-C(6A)	117.4(6)
C(7A)-C(6A)-C(5A)	102.3(6)
C(6A)-C(7A)-C(8A)	105.5(6)
N(1A)-C(8A)-C(7A)	103.0(6)
C(10A)-C(9A)-C(14A)	117.1(8)
C(10A)-C(9A)-C(3A)	123.0(7)
C(14A)-C(9A)-C(3A)	119.9(8)
C(11A)-C(10A)-C(9A)	122.2(7)
C(10A)-C(11A)-C(12A)	119.8(8)
C(13A)-C(12A)-C(11A)	120.1(8)
C(13A)-C(12A)-Br(1A)	120.3(6)
C(11A)-C(12A)-Br(1A)	119.6(7)
C(12A)-C(13A)-C(14A)	119.0(8)
C(13A)-C(14A)-C(9A)	121.8(8)
C(20A)-C(15A)-C(16A)	119.4(7)
C(20A)-C(15A)-N(2A)	120.9(7)
C(16A)-C(15A)-N(2A)	119.4(7)
C(17A)-C(16A)-C(15A)	120.5(8)
C(16A)-C(17A)-C(18A)	120.7(9)
C(19A)-C(18A)-C(17A)	119.3(9)
C(18A)-C(19A)-C(20A)	120.5(8)
O(1A)-C(20A)-C(15A)	117.6(7)
O(1A)-C(20A)-C(19A)	122.9(7)
C(15A)-C(20A)-C(19A)	119.5(7)

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters ($Å^2$x 10^3)for rovis29_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

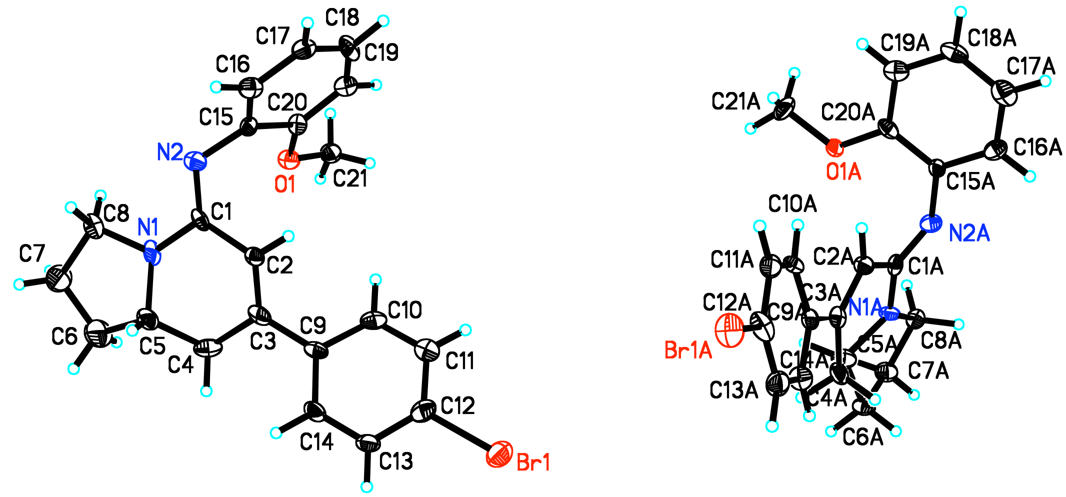
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	31(1)	42(1)	31(1)	-2(1)	-6(1)	-3(1)
N(1)	20(3)	6(4)	38(4)	0(3)	2(3)	-6(3)
N(2)	21(4)	20(4)	20(4)	3(3)	3(3)	5(3)
O(1)	20(3)	23(3)	18(3)	1(2)	3(2)	4(3)
C(1)	19(4)	7(4)	23(4)	1(3)	11(4)	0(3)
C(2)	16(4)	19(4)	16(4)	2(3)	6(3)	2(3)
C(3)	24(4)	26(5)	14(4)	4(4)	13(4)	4(4)
C(4)	33(5)	26(4)	26(4)	6(4)	-4(4)	8(4)
C(5)	33(5)	23(4)	24(4)	6(3)	-2(4)	-12(4)
C(6)	56(6)	30(5)	48(5)	6(5)	-12(5)	-19(5)
C(7)	39(5)	26(5)	69(6)	20(5)	-15(5)	-9(5)
C(8)	22(4)	13(4)	29(5)	-2(4)	10(4)	3(4)
C(9)	25(4)	19(5)	14(4)	3(3)	4(4)	6(4)
C(10)	29(4)	14(4)	24(4)	4(3)	-6(4)	11(4)
C(11)	22(4)	20(5)	24(4)	-2(3)	7(4)	11(4)
C(12)	20(4)	29(5)	28(5)	1(4)	-3(4)	11(4)
C(13)	21(4)	36(5)	16(4)	11(4)	2(4)	3(4)
C(14)	20(4)	35(5)	21(4)	9(4)	7(4)	0(4)
C(15)	18(4)	23(5)	15(4)	1(3)	-5(4)	-7(4)
C(16)	28(5)	19(5)	21(4)	-1(4)	-5(4)	0(4)
C(17)	30(4)	14(4)	29(4)	1(4)	-12(4)	-1(5)
C(18)	36(5)	14(5)	26(4)	-2(4)	1(4)	-13(4)
C(19)	23(4)	20(5)	15(4)	-5(3)	2(3)	5(4)
C(20)	16(4)	16(4)	21(4)	-2(3)	1(3)	2(3)
C(21)	20(4)	23(5)	29(4)	6(4)	-1(4)	3(4)
Br(1A)	26(1)	35(1)	38(1)	-6(1)	10(1)	3(1)
N(1A)	16(3)	25(4)	12(3)	8(3)	2(3)	3(3)
N(2A)	17(4)	19(4)	21(4)	2(3)	-2(3)	6(3)
O(1A)	17(3)	16(3)	29(3)	8(2)	-5(2)	-2(2)
C(1A)	16(4)	21(4)	16(4)	-7(3)	1(4)	-5(3)
C(2A)	14(4)	20(4)	19(4)	3(3)	1(3)	2(3)

C(3A)	17(4)	7(4)	22(4)	-6(3)	1(3)	-2(3)
C(4A)	24(4)	14(4)	29(4)	6(3)	1(4)	-4(3)
C(5A)	30(4)	19(4)	21(4)	2(3)	1(4)	8(4)
C(6A)	20(4)	20(4)	21(4)	4(3)	0(3)	8(3)
C(7A)	27(4)	22(5)	30(4)	6(4)	-5(4)	4(4)
C(8A)	19(4)	15(4)	25(4)	-1(4)	-3(3)	5(3)
C(9A)	24(4)	13(4)	19(4)	-1(3)	-3(4)	-6(4)
C(10A)	23(4)	14(4)	18(4)	6(3)	0(3)	0(3)
C(11A)	19(4)	16(4)	31(5)	1(4)	-3(4)	1(3)
C(12A)	29(4)	13(4)	30(5)	-6(4)	13(4)	1(4)
C(13A)	27(4)	35(5)	21(4)	-3(4)	0(4)	-8(4)
C(14A)	22(4)	24(5)	22(4)	-2(4)	5(4)	1(4)
C(15A)	20(4)	15(5)	15(4)	0(3)	-1(3)	-5(3)
C(16A)	21(4)	26(5)	16(4)	-5(4)	0(4)	5(4)
C(17A)	37(5)	31(5)	18(4)	-3(4)	11(4)	-3(5)
C(18A)	34(5)	24(5)	18(4)	6(4)	9(3)	7(5)
C(19A)	22(4)	27(5)	15(4)	-1(4)	9(3)	7(4)
C(20A)	27(4)	10(4)	20(4)	1(3)	4(3)	1(3)
C(21A)	15(4)	35(5)	33(5)	0(4)	-11(4)	0(4)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for rovis29_0m.

	x	y	z	U(eq)
H(2B)	-800	1282	8730	21
H(4A)	-539	-1244	8982	34
H(4B)	-1059	-906	9374	34
H(5A)	-4342	-509	9232	32
H(6A)	-4955	-2048	9238	54
H(6B)	-3363	-2258	8923	54
H(7A)	-6159	-2282	8582	53
H(7B)	-7547	-1754	8871	53
H(8A)	-5763	-963	8293	26
H(8B)	-7158	-434	8583	26
H(10A)	2607	1290	8816	27
H(11A)	5374	1953	9120	26
H(13A)	3610	588	10003	29
H(14A)	775	-27	9703	30
H(16A)	-5162	2528	8271	27
H(17A)	-3418	3795	8003	29
H(18A)	-391	3551	7694	30
H(19A)	1195	2076	7686	23
H(21A)	1917	-317	7797	36
H(21B)	2689	732	7857	36
H(21C)	1232	489	7530	36
H(2AB)	15302	6047	8629	21
H(4AA)	16065	4014	9337	27
H(4AB)	17924	4745	9377	27
H(5AA)	17241	3502	8802	28
H(6AA)	20804	3709	9250	24
H(6AB)	19635	2750	9149	24
H(7AA)	20863	2773	8584	31
H(7AB)	22826	3188	8793	31
H(8AA)	22257	4650	8593	24

H(8AB)	20977	4132	8285	24
H(10B)	12293	6191	8833	22
H(11B)	9591	6837	9151	26
H(13B)	11847	5663	10043	34
H(14B)	14564	5012	9716	27
H(16B)	20030	7547	8276	25
H(17B)	18389	8793	8002	35
H(18B)	15351	8559	7678	30
H(19B)	13872	7071	7654	25
H(21D)	13094	4686	7768	42
H(21E)	13703	5505	7501	42
H(21F)	12314	5729	7839	42


C17
C18
C19
C16
C15
C20
N2
O1
C21
C8
N1
C1
C7
C2
C10
C9
C6
C5
C3
C11
C4
C12
C14
C13
Br1
C19A
C18A
C17A
C21A
C20A
C16A
O1A
C15A
C10A
N2A
C11A
C2A
C1A
C12A
C3A
C9A
N1A
Br1A
C5A
C8A
C14A
C7A
C13A
C4A
C6A