ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

A convenient synthesis of quinoline fused triazolo-azepine/oxepine derivatives through Pd-catalyzed C-H functionalisation of triazoles

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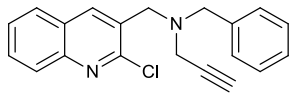
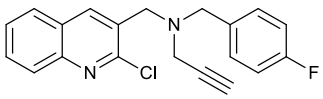
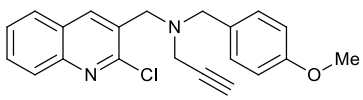
General Experimental

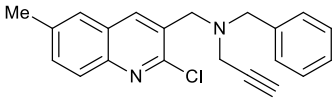
All reagents were purchased from Sigma-Aldrich, Alfa Aesar, SDFine, Spectrochem or AVRA and used without further purification unless otherwise stated. Silicon oil baths on stirrer hotplates were employed with temperature control *via* thermometer. Reaction progress was monitored by Thin Layer Chromatography (TLC) using TLC Silica gel 60 F254. Flash column chromatography was performed using silica gel (60-120 or 100-200 mesh) as a stationary phase. Melting points were measured in open capillaries using melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR's were recorded using Bruker AVIII 300 MHz, 400 MHz and 500 MHz spectrometers at 300 K. Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) are quoted in Hz to one decimal place. For spectra recorded in chloroform-*d* ($CDCl_3$) the 7.26 ppm resonance of residual $CHCl_3$ for proton spectra and 77.16 ppm resonance of $CDCl_3$ for carbon spectra were used as internal references. Spectral data for ^{1}H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for ^{13}C NMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in ^{1}H NMR: s (singlet), d (doublet), t (triplet), q (quartert), dd (doublet of doublets), td (triplet of doublets), quin (quintuplet), bs (broad singlet), m (multiplet). All NMR spectra are processed using MestReNova version 6.0.2 (*v*). ESI mass spectra were recorded on Micro mass Quattro LC using ESI^{+} software with capillary voltage 3.98 kV and an ESI mode positive ion trap detector.High resolution mass spectra (HRMS) were recorded using ESI-TOF techniques and was obtained using a lock-mass to adjust the calibrated mass scale. 005233.

General procedure for the preparation of *N*-aralkyl-N-((2-chloroquinolin-3-yl)methyl) prop-2-yn-1-amines (2a-e): To a solution of the compound N-aralkyl-1-(2-chloroquinolin-3-yl)methanamine (**1,** 1. 25 mmol) in DMF (10 ml) was added potassium carbonate (241 mg, 1.75 mmol) and stirred at room temperature for about 30 min. Then propargyl bromide (80% solution in toluene, 147 mg1.25 mmol)/ (188mg 1.62mmol,) was added to the reaction mixture and continued stirring at room temperature for about 15 h. After the completion of reaction (monitored by TLC), the reaction mixture poured into cold water. The solid seperated was filetered, washed with water and dried. The products obtained were pure enough and hence directly taken for further reaction without purification.

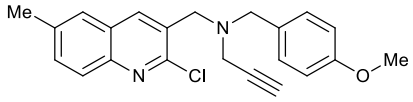
N-Benzyl-1-(2-chloroquinolin-3-yl)methanamine (2a): Colourless solid, yield:316 mg, 90%;  m.p. 49-51°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.02 (s, 1H), 7.84 (s, 1H), 7.71 (s, 1H), 7.56 (s, 1H), 7.49 – 7.15 (m, 5H), 3.97 (s, 2H), 3.82 (s, 2H), 3.34 (s, 2H), 2.35 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.5, 147.0, 138.4, 138.3, 130.6, 130.3, 129.1(2C), 128.6(2C), 128.4, 127.6(2C), 127.4, 127.2, 78.3, , 74.0, 57.9, 54.8, 41.4.

1-(2-Chloroquinolin-3-yl)-N-(4-fluorobenzyl) methanamine (2b): Pale yellow solid, yield:  345 mg, 92% ; m.p. 47-49°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.02 (d, *J*= 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.4 Hz,1H), 7.42 – 7.34 (m, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 3.95 (s, 2H), 3.78 (s, 2H), 3.31 (d, *J* = 1.6 Hz, 2H), 2.35 (s, 1H); ^{13}C NMR (101 MHz,$CDCl_3$) : δ 162.3 (d, *J* = 245.3 Hz), 151.5, 147.1, 138.5, 134.0 (d, *J* = 3.1 Hz, 2C), 130.7 (*J* = 8.0 Hz) , 130.4, 130.3, 128.4, 127.5, 127.4, 127.2, 115.4 (d, *J* = 21.3 Hz, 2C).78.1, 74.2, 57.1, 54.8, 41.1.

N-((2-Chloroquinolin-3-yl)methyl)-N-(4-methoxybenzyl)prop-2-yn-1-amine (2c):  Colourless solid, yield: 389 mg, 89% ; m.p. 52-54°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.86 (d*J* = 8.4 Hz, 2H), 3.94 (s, 2H), 3.79 (s, 3H), 3.76 (s, 2H), 3.32 (d, *J* = 1.7 Hz, 2H), 2.34 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 151.5, 147.0, 138.4, 130.7, 130.3(2C), 130.3, 130.2, 128.4, 127.5, 127.4, 127.1, 113.9 (2C), 78.4, 74.0, 57.3, 55.4, 54.6, 41.2.

N-Benzyl-N-((2-chloro-6-methylquinolin-3-yl)methyl)prop-2-yn-1-amine (2d): Light brown  solid, yield: 375 mg, 90% ; m.p. 46-48°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.60 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 3.95 (s, 2H), 3.82 (s, 2H), 3.33 (d, *J* = 1.8 Hz, 2H), 2.53 (s, 3H), 2.34 (s, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 145.6, 138.4, 137.9, 137.2, 132.5, 130.5, 129.2 (2C), 128.5 (2C), 128.0, 127.5, 127.5, 126.5, 78.4, 74.0, 57.8, 54.8, 41.3, 21.7.

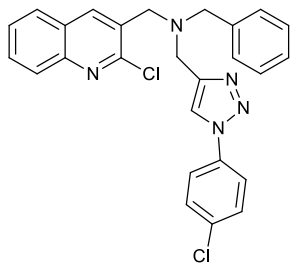
N-((2-Chloro-6-methylquinolin-3-yl)methyl)-N-(4-methoxybenzyl)prop-2-yn-1-amine (2e):



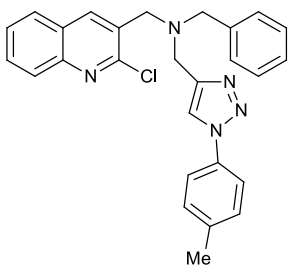
Light brown solid, yield: 409 mg, 90% ; m.p. 43-45^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.19 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.59 (s, 1H), 7.53 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 2H), 3.79 (s, 3H), 3.75 (s, 2H), 3.31 (d, *J* = 2.3 Hz, 2H), 2.53 (s, 3H), 2.33 (t, *J* = 2.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 150.6, 145.6, 137.9, 137.1, 132.5, 130.5, 130.4, 130.4(2C), 128.0, 127.5, 126.4, 113.9 (2C), 78.4, 73.9, 57.2, 55.4, 54.6, 41.2, 21.7.

General procedure for the preparation of N-aralkyl-1-(2-chloroquinolin-3-yl)-N-((1-aryl-1H-1,2,3-triazol-4-yl)methyl)methanamines(4a-m): *N*-aralkyl-*N*-((2-chloroquinolin-3-yl)-methyl)prop-2-yn-1-amine (2, 0.5 mmol) was dissolved in DMF (5 mL) and then aryl azide (0.75 mmol) was added. To this solution, $CuSO_4.5H_2O$ (2.5 mg, 0.01 mmol) and then sodium ascorbate (20.0 mg, 0.1 mmol in 1 mL water) were added. The resulting mixture was stirred at room temperature for 6 hours. After the completion of thereaction (monitored by TLC), the reaction mixture was poured into cold water. Solid obtained was filtered, washed with hexane dried and directly used for the next step as it is sufficiently pure.

N-Benzyl-1-(1-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl)-N-((2-chloroquinolin-3yl)methyl) methanamine (4a): Light brown solid, yield: 206 mg,87% ; m.p. 85-87 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.43 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H),7.69 (t, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.8Hz, 2H), 7.55(t, *J* = 7.2 Hz, 1H), 7.49-7.44 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 2.1 Hz, 1H), 3.96(s, 2H), 3.94 (s, 2H), 3.82 (s, 2H);^{13}C NMR (101 MHz,$CDCl_3$): δ 151.1, 146.9, 145.7, 138.6, 138.5, 135.6, 134.5, 130.9,130.2 (2C), 130.0, 128.9 (2C), 128.6 (2C), 128.2 127.6, 127.5, 127.4, 127.2, 121.7 (2C), 120.8, 58.6, 55.2, 48.2.

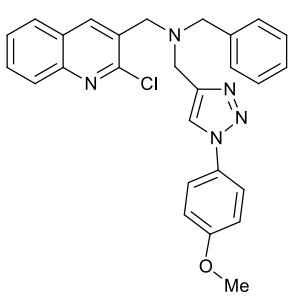


N-Benzyl-1-(2-chloroquinolin-3-yl)-N-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl) methanamine (4b): Colorless solid, yield: 192 mg, 85% ; m.p. 69-71^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 3H), 7.45

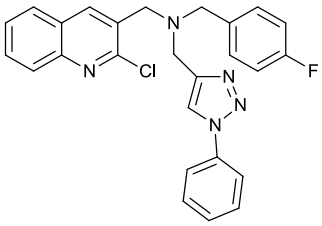


(d, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 16.2, 8.0 Hz, 4H), 7.26 (d, *J* = 4.0 Hz, 1H), 3.96 (s, 2H), 3.94 (s, 2H), 3.82 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.2, 146.9, 145.2, 138.9, 138.7, 138.6, 134.9, 131.1, 130.3(2C), 130.2, 128.9 (2C), 128.6 (2C), 128.3, 127.7, 127.5, 127.4, 127.1, 120.9, 120.5 (2C), 58.5, 55.0, 48.1, 21.2.

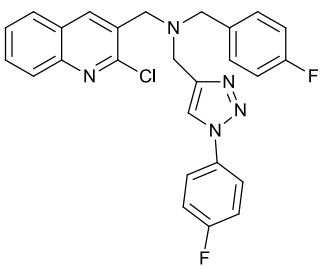
N-Benzyl-1-(2-chloroquinolin-3-yl)-N-((1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl) methyl) methanamine (4c): Light orange solid, yield: 196 mg, 84% ; m.p. 81-83ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ8.45 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.67 (dd, *J* = 11.8, 4.6 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.99 (d, *J* = 8.9 Hz, 2H) 3.95 (s, 2H), 3.92 (s, 2H), 3.85 (s, 3H), 3.81 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 151.2, 146.8, 145.1, 138.7, 138.6, 131.0, 130.6, 130.1, 128.9(2C), 128.5(2C), 128.2, 127.6, 127.4, 127.4, 127.1, 122.2(2C), 121.1, 114.8(2C) 58.5, 55.7, 55.0, 48.1



1-(2-Chloroquinolin-3-yl)-N-(4-fluorobenzyl)-N-((1-phenyl-1H-1,2,3-triazol-4-yl) methyl) methanamine (4d): Light brown solid, yield: 187 mg, 82% ; m.p. 64-66ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.82 (s, 1H), 7.73 – 7.63 (m, 3H), 7.59 – 7.48 (m, 3H), 7.48 – 7.37 (m, 3H), 7.02 (t, *J* = 8.7 Hz, 2H), 3.95 (s, 2H), 3.92 (s, 2H), 3.79 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2 (d, *J* =245.4 Hz), 151.1, 147.0, 145.1, 138.7, 137.1, 134.3, 130.8, 130.5 (d, *J* = 7.9 Hz, 2C), 130.3, 129.9(2C), 128.9, 128.3, 127.6, 127.4, 127.2, 120.9, 120.6 (2C), 115.4 (d, *J* = 21.3 Hz, 2C), 57.7, 55.1, 47.9.

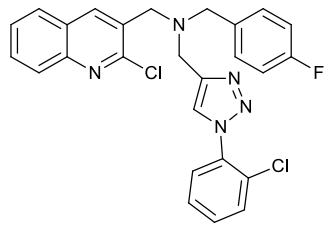


1-(2-Chloroquinolin-3-yl)-N-(4-fluorobenzyl)-N-((1-(4-fluorophenyl)-1H-1,2,3-triazol-4-yl)methyl)methanamine (4e): Light brown solid, yield: 201 mg, 85% ; m.p. 67-69ºC; ^{1}H NMR (400 MHz$CDCl_3$): δ 8.40 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.75 (s, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 9.1, 4.6 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.41(dd, *J* = 8.6, 5.5 Hz, 2H), 7.24–7.16 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 3.94 (s, 2H), 3.91(s, 2H), 3.79 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) : δ 162.5 (d,



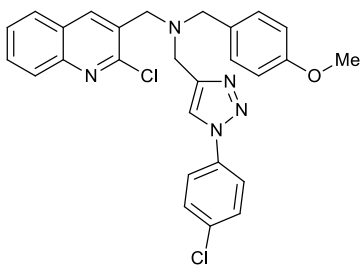
J = 249.3 Hz), 162.2 (d, *J* = 245.3 Hz), 151.1,146.9, 145.3, 138.7, 134.3 (d, *J* = 3.0 Hz), 133.4 (d, *J* = 3.1 Hz),130.8, 130.5 (d, *J* = 7.9 Hz, 2C), 130.3, 128.3, 127.6, 127.4, 127.2, 122.6 (d, *J* = 8.6 Hz, 2C), 121.1, 116.8 (d, *J* = 23.2 Hz, 2C), 116.8 (d, *J* = 23.2 Hz, 2C), 57.8, 55.1, 48.0.

1-(1-(2-Chlorophenyl)-1H-1,2,3-triazol-4-yl)-N-((2-chloroquinolin-3-yl)methyl)-N-(4-fluoro benzyl) methanamine (4f): Light brown solid, yield: 196 mg, 80% ; m.p. 64-66°C; ^{1}H NMR^{1}H



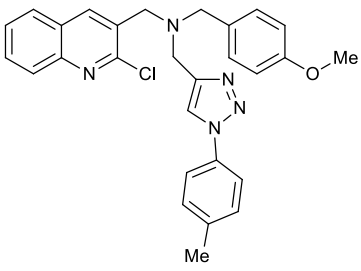
NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.71 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.59-7.54 (m, 3H), 7.48 – 7.39 (m, 4H), 7.01 (t, *J* = 8.7 Hz, 2H), 3.97 (s, 2H), 3.94 (s, 2H), 3.79 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2 (d, *J* = 244.8 Hz), , 151.2, 147.0, 144.2, 138.7, 135.0, 134.4, 130.9(2C) , 130.5 (d, *J* = 7.7 Hz, 2C), 130.3, 128.7, 128.3, 128.1, 127.9, 127.6, 127.4, 127.2, 125.0, 120.2,115.4 (d, *J* = 21.3 Hz, 2C), 57.6, 55.1, 47.9.

1- (1-(4-Chlorophenyl)-1H-1,2,3-triazol-4-yl)-N-((2-chloroquinolin-3-yl)methyl)-N-(4-methoxybenzyl)methanamine (4g) : Light yellowsolid, yield: 216 mg, 86% ; m.p. 68-70°C;



^{1}H NMR(400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.98 (d, *J* = 8.5 Hz,1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 (s, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 2H), 7.55 (t, *J* = 8.1 Hz, 1H), 7.48 (d, *J*= 9.0 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 2H), 3.92 (s, 2H), 3.78 (s, 3H), 3.76(s, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 146.3, 146.1, 145.9, 138.2, 136.6, 134.8, 132.3, 131.7, 130.2, 130.1(2C), 129.9, 129.0, 128.7(2C), 128.1(2C), 127.5, 127.2, 127.0, 113.9(2C), 58.5, 56.6, 55.4, 54.0.

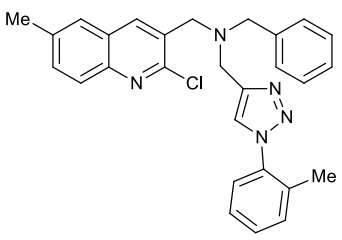
1-(2-Chloroquinolin-3-yl)-N-(4-methoxybenzyl)-N-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl) methanamine (4h): Light brownsolid, yield: 207 mg, 86% ; m.p. 59-61°C;^{1}H



NMR(400 MHz, $CDCl_3$):δ 8.44 (s, 1H), 8.00 (d, *J* = 8.5 Hz,1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.79 (s, 1H), 7.70 (t, *J* = 7.7 Hz, 1H)7.56 (t, *J* = 8.1 Hz, 3H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.33–7.28 (m,2H), 6.87 (d, *J*= 8.7 Hz, 2H), 3.95 (s, 2H), 3.93 (s, 2H), 3.79 (s,3H), 3.77 (s, 2H), 2.43 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0,

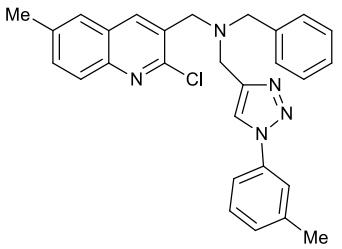
146.4, 146.3, 145.8, 138.8, 137.1, 136.5, 132.2, 131.6, 130.3, 130.2(2C), 129.6, 129.2, 129.1 (2C), 127.3, 127.1, 126.9, 126.5 (2C), 113.8 (2C), 58.5, 56.5, 55.4, 53.9, 21.4

N-Benzyl-1-(2-chloro-6-methylquinolin-3-yl)-N-((1-(o-tolyl)-1H-1,2,3-triazol-4-yl) methyl)methanamine(4i): Pale yellowsolid, yield: 194 mg, 83% ; m.p. 65-67^{o}C;^{1}H NMR(400



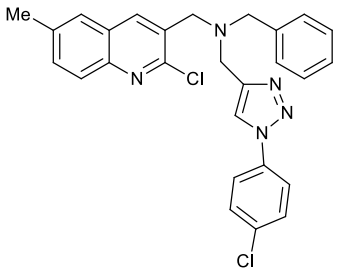
MHzCDCl$_3$): δ 8.37 (s, 1H), 7.88 (s & d, *J* = 8.6 Hz, 1H), 7.61 (d,*J*=3.6 Hz, 2H), 7.52 (d, *J*=10.3 Hz, 1H), 7.45 (d,*J* =7.2 Hz, 2H), 7.40 (d, *J* =7.6 Hz,1H), 7.37–7.30 (m, 4H), 7.25(d, *J*=4.9 Hz, 2H),3.95 (s, 4H), 3.83 (s, 2H), 2.52 (s, 3H), 2.16 (s, 3H); ^{13}C NMR(101 MHz, CDCl$_3$): δ 150.2, 145.5, 144.5, 138.8, 138.0, 137.1, 136.6, 133.8, 132.4, 131.5, 130.9, 129.9, 128.9(2C), 128.6 (2C), 127.2, 127.5, 127.4, 126.9, 126.5, 126.1, 124.3, 58.6, 55.2, 48.2, 21.8, 17.9.

N-Benzyl-1-(2-chloro-6-methylquinolin-3-yl)-N-((1-(m-tolyl)-1H-1,2,3-triazol-4-yl) methyl) methanamine (4j): Light brown solid, yield: 196 mg, 84%; m.p. 69-71^{o}C;^{1}H NMR (400



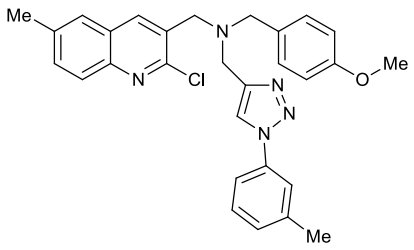
MHzCDCl$_3$): δ 8.35 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.80 (s, 1H), 7.62 (s, 1H), 7.52-7.50 (m, 2H), 7.45(d, *J* = 7.2 Hz, 3H), 7.39(d, *J* = 7.6 Hz, 1H), 7.34-7.32 (m, 2H), 7.29 – 7.18 (m, 2H),3.93 (2s, 4H), 3.82 (s, 2H), 2.52 (s, 3H), 2.44 (s, 3H); ^{13}C NMR(101 MHz, CDCl$_3$): δ 150.3, 145.5, 145.3, 140.1, 138.7, 138.0, 137.1, 137.1, 132.4, 130.9, 129.6, 129.5, 128.9(2C), 128.6 (2C), 127.9, 127.5, 127.4, 126.5, 121.3, 120.9, 117.7, 58.5, 55.1, 48.2, 21.7, 21.5.

N-Benzyl-1-(2-chloro-6-methylquinolin-3-yl)-N-((1-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl) methyl)methanamine (4k) : Light yellow solid, yield: 207 mg, 85% ; m.p. 93-

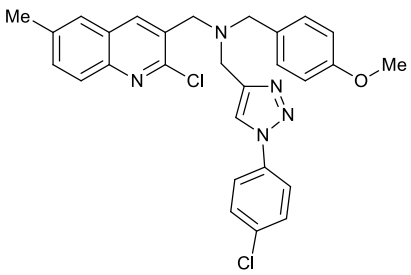


95^{e}C;^{1}H NMR (400 MHz, CDCl$_3$): δ 8.33 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.78 (s, 1H), 7.65 – 7.59 (m, 3H), 7.54 – 7.42 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 1H), 3.93 (s, s, 4H), 3.82 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 150.2, 145.8, 145.5, 138.6, 138.0, 137.2, 135.6, 134.5, 132.5, 130.8, 130.0(2C), 128.9(2C), 128.6(2C), 127.9, 127.5, 127.4, 126.5, 121.7 (2C), 120.8, 58.6, 55.2, 48.2, 21.7

1-(2-Chloro-6-methylquinolin-3-yl)-N-(4-methoxybenzyl)-N-((1-(m-tolyl)-1H-1,2,3-triazol-4-yl)methyl)methanamine (4l): Light brown solid, yield: 196 mg, 84% ; m.p. 85-87^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.79 (s, 1H), 7.61 (s, 1H), 7.55–7.47 (m, 2H), 7.45(d, *J* = 8.6 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.23 (d, *J* = 7.5 Hz,1H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 4H), 3.78 (s,3H), 3.75 (s, 2H), 2.52 (s, 3H), 2.44 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 150.2, 145.3, 140.0, 138.7, 138.0, 137.1, 132.4, 130.9, 130.1, 129.5(2C), 128.9(2C), 128.5(2C), 127.9, 127.5, 127.4, 126.5, 120.9, 117.7(2C), 58.5, 55.3, 55.1, 48.2, 21.7, 21.5.



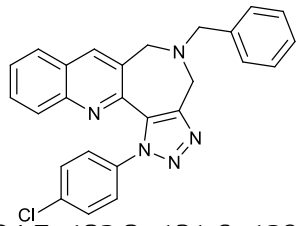
1-(2-Chloro-6-methylquinolin-3-yl)-N-((1-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl)methyl)-N-(4-Methoxybenzyl)methanamine(4m) : Light brown solid, yield: 258 mg, 84% ; m.p. 96-98^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.76 (s, 1H), 7.65–7.58 (m, 3H), 7.49-7.46(m, 3H), 7.35 (d, *J* =8.7 Hz, 2H), 6.87 (d,*J* = 8.7 Hz, 2H), 3.93(s,2H), 3.91 (s, 2H), 3.78 (s, 3H), 3.75 (s, 2H), 2.52 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 150.2, 145.9, 145.4,138.0, 137.1, 135.6, 134.5, 132.4, 130.9, 130.5, 130.1 (2C), 130.0 (2C), 127.9, 127.5, 126.5, 121.7 (2C), 120.7, 113.9 (2C), 58.0, 55.4, 55.1, 48.1, 21.7



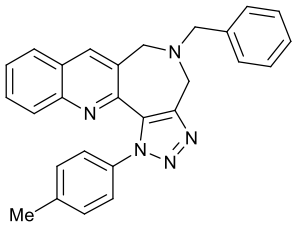
General procedure for the preparation of 5-arylalkyl-1-aryl-1,4,5,6-tetrahydro[1,2,3] triazolo [4',5':5,6] azepino[*4,3-b*]quinolines (6a-m).

To the solution N-aralkyl-1-(2-chloroquinolin-3-yl)-N-((1-aryl-1H-1,2,3-triazol-4-yl)methyl)-methanamines (**4a**, 0.25 mmol) in DMF (3mL) was added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 10 mol%), triphenylphosphine (13.0 mg, 0.05 mmol, 20 mol%), and then cesium carbonate (162.0 mg, 0.5 mmol) were added. The reaction mixture was heated with stirring at 130 ^{o}C for 25h. After completion of the reaction monitored by TLC, the reaction mixture was cooled and extracted with EtOAc (2 x20 mL).The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluted with 10% hexane/EtOAc) to afford the title compounds.

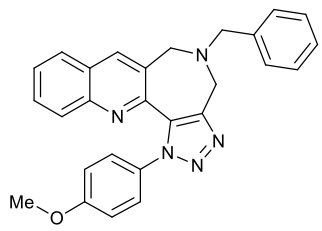
5-Benzyl-1-(4-chlorophenyl)-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*]quinoline (6a): Light brownsolid, yield: 94 mg, 86% ; m.p. 118-120ºC;^{1}H NMR (400MHz, $CDCl_3$): δ 7.70 –7.62 (m, 2H), 7.60 (dd, *J* = 8.2, 7.0 Hz,1H), 7.51-7.46 (m, 3H), 7.44 – 7.37 (m, 3H),7.30 -7.26 (m, 3H), 7.24-7.22 (m, 2H).4.53(s, 2H), 4.12 (s,2H), 3.77(s, 2H);^{13}C NMR (101 MHz, $CDCl_3$): δ 146.2, 146.0, 145.9, 138.1, 138.1, 136.6, 134.7, 132.3, 131.6, 129.9, 129.0, 128.9 (2C), 128.7 (2C), 128.5 (2C), 128.1 (2C), 127.5(2C), 127.2, 127.0, 59.1, 56.7, 54.1; HRMS (ESI) calculated for $C_{26}H_{20}ClN_5[M+H]^+$*m/z* 438.1485; found 438.1485.



5-Benzyl-1-(p-tolyl)-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*]quinoline(6b): Light orange solid, yield: 86 mg, 83% ; m.p. 110-112ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.67 (m, 2H), 7.59–7.52 (m,1H), 7.51-7.48 (m, 1H), 7.45–7.31 (m,3H), 7.33 – 7.17 (m, 7H), 4.52 (s, 2H), 4.11 (s, 2H), 3.78 (s, 2H), 2.50 (s, 3H); (101 MHz, $CDCl_3$): δ 146.4, 146.3, 145.8, 138.8, 138.3, 137.1, 136.5, 132.2, 131.6, 129.6, 129.2, 129.1(2C), 129.0(2C), 128.5 (2C), 127.5, 127.3, 127.1, 127.0, 126.5 (2C), 59.2, 56.7, 54.0, 21.5; HRMS (ESI) calculated for $C_{27}H_{23}N_5[M+H]^+$*m/z* 418.2032; found 418.2021.



5-Benzyl-1-(4-methoxyphenyl)-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*]quinoline (6c): Light brownsolid, yield: 92 mg, 85% ; m.p. 121-123ºC; ^{1}H NMR (400 MHz,$CDCl_3$):δ 7.69 – 7.64 (m, 1H), 7.64 (s, 1H), 7.60 – 7.53 (m, 1H), 7.51 – 7.44 (m, 1H), 7.44 – 7.37 (m, 3H), δ 7.31 – 7.26 (m, 3H), 7.24-7.22 (m, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 4.52 (s, 2H), 4.10 (s, 2H), 3.91 (s, 3H), 3.77 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 146.4, 146.3, 145.8,138.3, 136.5, 132.6, 132.3, 131.6, 129.7, 129.3, 129.0(2C), 128.5(2C), 128.0(2C), 127.5, 127.3, 127.1, 127.0, 113.7 (2C), 59.2, 56.7, 55.8, 54.1; HRMS (ESI) calculated for $C_{27}H_{23}N_5O[M+H]^+$*m/z* 434.1981; found 434.1981.



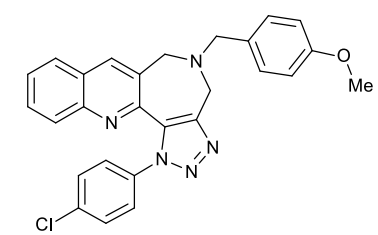
5-(4-Fluorobenzyl)-1-phenyl-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*]quinoline (6d): Light orange solid, yield: 84 mg, 80% ; m.p. 117-118^{e}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.63 (s, 1H), 7.55 – 7.43(m, 7H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.19 (dd,*J* = 8.7, 5.5 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 4.52 (s, 2H), 4.11 (s, 2H), 3.72 (s, 2H); ^{13}CNMR (101 MHz, $CDCl_3$): δ 162.2 (d, *J* = 245.3 Hz), 146.31, 146.1, 145.7, 139.6, 136.5, 134.0(d, *J* = 3.1Hz,) , 132.3, 131.4, 130.4 (d, *J* = 7.9 Hz, 2C) 129.7, 129.1, 128.9, 128.6 (2C), 127.4, 127.1, 126.9, 126.8 (2C), 115.3 (d, *J* = 21.3 Hz, 2C)., 58.2, 56.6, 54.0; HRMS (ESI) calculated for $C_{26}H_{20}FN_5[M+H]^+$ *m/z* 422.1781; found 422.1781.

5-(4-Fluorobenzyl)-1-(4-fluorophenyl)-1,4,5,6-tetrahydro[1,2,3]triazolo[4',5':5,6]azepino [*4,3-b*]quinoline (6e): Light brown solid, yield: 99 mg, 90%; m.p. 145-147^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.63 (s, 1H), 7.61 – 7.53 (m, 1H), 7.52-7.47 (m, 1H), 7.47-7.43 (m, 2H), 7.38 (d, *J* =8.4 Hz, 1H), 7.22 – 7.16 (m 4H), 6.98 (t, *J* = 8.7 Hz, 2H), 4.52 (s, 2H), 4.10 (s, 2H), 3.73 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8 (d, *J* = 248.5 Hz), 162.3 (d, *J* = 245.4 Hz) 146.3, 146.0, 145.8, 136.5, 135.7 (d, *J* = 3.3 Hz), 133.9 (d, *J* = 3.1 Hz), 131.5, 130.4 (d, *J* = 8.0 Hz, 2C), 129.9, 129.1, 128.7 (d, *J* = 8.8 Hz, 2C), 127.6, 127.1, 126.9, 115.5 (d, *J* = 23.1 Hz, 2C), 115.3 (d, *J* = 21.3 Hz, 2C), 77.2, 58.2, 56.7, 54.1; HRMS (ESI) calculated for $C_{26}H_{19}F_2N_5[M+H]^+$ *m/z* 422.1687; found 440.1687.

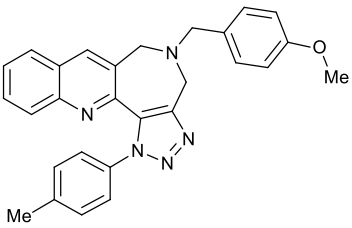
1-(2-Chlorophenyl)-5-(4-fluorobenzyl)-1,4,5,6-tetrahydro[1,2,3]triazolo[4',5':5,6]azepino [*4,3-b*] quinoline (6f): Light brown solid, yield: 89 mg, 78% ; m.p. 117-119^{e}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.55 – 7.48 (m, 4H), 7.45 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.21-7.18 (m, 3H), 7.03 – 6.93 (m, 2H), 4.56 (s, 2H), 4.14 (s, 2H), 3.75 (s, 2H);^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2(d, *J* = 245.3 Hz), 146.28, 145.82, 145.21, 138.16, 136.34, 133.94 (d, *J* = 3.1Hz),

133.3, 132.0, 131.0, 130.5, 130.4(2C), 129.6, 129.6, 129.1, 129.1, 127.4 (d, *J* = 4.8 Hz, 2C), 127.1, 126.9, 115.3 (d, *J* = 21.3 Hz, 2C) 8.84, 57.0, 54.2; HRMS (ESI) calculated for $C_{26}H_{19}ClFN_5[M+H]^+$ *m/z* 456.1391; found 456.1391.

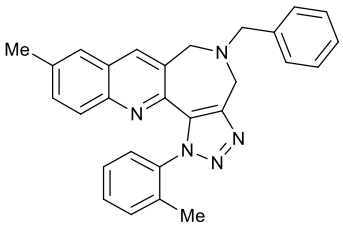
1-(4-Chlorophenyl)-5(4methoxybenzyl)1,4,5,6-tetrahydro[1,2,3]triazolo[4',5':5,6]azepino [*4,3-b*]quinoline (6g): Brown solid, yield: 99 mg, 85% ; m.p. 116-118ºC; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.67 (d & s, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.50-7.45 (m, 3H), 7.44–7.34 (m, 3H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.50 (s, 2H), 4.10 (s, 2H), 3.81 (s, 3H), 3.70 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) : δ 159.0, 151.2, 146.9, 145.9, 138.6, 135.62, 134.6, 131.1, 130.5, 130.2, 130.2(2C) , 130.0(2C) , 128.3, 127.6, 127.5, 127.2, 121.8(2C) , 120.8, 114.0(2C) , 58.1, 55.4, 55.1, 48.1; HRMS (ESI) calculated for $C_{27}H_{22}ClN_5O[M+H]^+$ *m/z* 468.1591; found 468.1591.



5-(4-Methoxybenzyl)-1-(p-tolyl)-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*] quinoline (6h): Light brown solid, yield: 94 mg, 84% ; m.p. 118-120ºC;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d & s, 2H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.46 (t, *J* =7.5 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.28 (d, *J* = 8.1 Hz,2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.50 (s, 2H), 4.09 (s, 2H), 3.81 (s, 3H), 3.70 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz,$CDCl_3$): δ 159.0, 151.2, 146.9, 145.3, 138.9, 138.6, 134.9, 131.1, 130.6, 130.3(2C), 130.1(2C), 128.2, 127.6, 127.5, 127.1, 120.9, 120.6(2C), 114.0 (2C), 77.2, 57.8, 55.3, 54.9, 48.0, 21.2; HRMS (ESI) calculated for $C_{28}H_{25}N_5O[M+H]^+$ *m/z* 448.2137; found 448.2139.

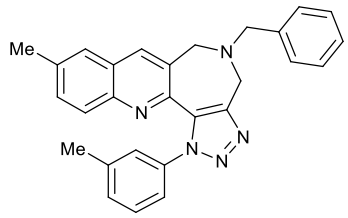


5-Benzyl-9-methyl-1-(o-tolyl)-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*]quinoline (6i): Pale yellowsolid, yield: 88 mg, 82% ; m.p. 101-103ºC;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.33 – 7.27 (m, 5H), 7.25-7.23 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 4.56 (s, 2H), 4.09 (s, 2H), 3.80 (s, 2H), 2.46 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 145.1, 145.1, 139.5, 138.3, 137.4, 135.9, 135.5, 133.0, 131.8, 131.3, 130.2, 129.3,

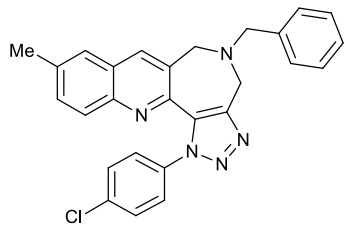


129.0, 128.9(2C), 128.5(2C), 127.5, 127.4, 126.9, 126.2, 125.8, 59.1, 57.0, 54.5, 21.8, 17.8); HRMS (ESI) calculated for $C_{28}H_{25}N_5[M+H]^+$ *m/z* 432.2188; found 432.2188.

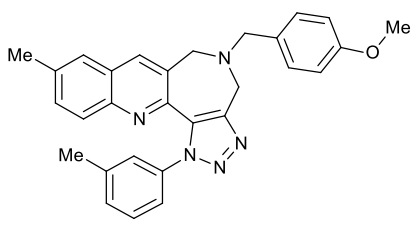
5-Benzyl-9-methyl-1-(m-tolyl)-1,4,5,6-tetrahydro-[1,2,3]triazolo[4',5':5,6]azepino[*4,3-b*] quinoline (6j): Light brown solid, yield: 88 mg, 82% ; m.p. 89-91^oC;^1H NMR (400 MHz, $CDCl_3$) : δ 7.59 (s, 1H), 7.43 (s, 1H), 7.38-7.36 (m, 3H), 7.34 – 7.26 (m, 7H), 7.20 (s, 1H), 4.51 (s, 2H), 4.11 (s, 2H), 3.77 (s, 2H), 2.49 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.6, 145.3, 145.0, 139.4, 138.6, 138.3, 137.4, 135.9, 132.3, 132.0, 131.5, 129.5, 129.0(2C), 128.8, 128.5 (2C), 128.2, 127.5, 127.2, 127.0, 126.0, 123.8, 59.0, 56.7, 53.9, 21.89, 21.4;HRMS (ESI) calculated for $C_{28}H_{25}N_5[M+H]^+$ *m/z* 432.2188; found 432.2188.



5-Benzyl-1-(4-chlorophenyl)-9-methyl-1,4,5,6-tetrahydro[1,2,3]triazolo[4',5':5,6]azepino [*4,3-b*]quinoline (6k): Light brown solid, yield: 99 mg, 88% ; m.p. 123-125^oC;^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.48 – 7.44 (m, 2H), 7.44 – 7.39 (m, 4H), 7.31 – 7.26 (m, 4H), 7.22 (dd, *J* = 7.3, 2.0 Hz, 2H), 4.51 (s, 2H), 4.09 (s, 2H), 3.76 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.8, 145.0, 144.9, 138.2, 138.2, 137.7, 136.0,134.7, 132.4, 132.2, 131.5, 129.0(2C), 128.7, 128.7(2C), 128.5(2C), 128.1 (2C), 127.5, 127.1, 126.0, 59.1, 56.7, 54.0, 21.8;HRMS (ESI) calculated for $C_{27}H_{22}ClN_5[M+H]^+$ *m/z* 452.1642; found 452.1642.

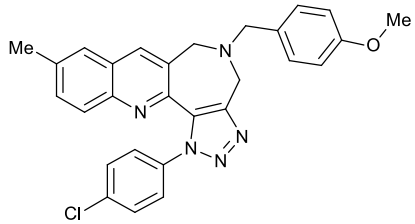


5-(4-Methoxybenzyl)-9methyl-1(m-tolyl)1,4,5,6-tetrahydro[1,2,3]triazolo[4',5':5,6]azepino [*4,3-b*]quinoline (6l): Light brown solid, yield: 93 mg, 81%; m.p. 107-109^oC;^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.43 (s, 1H), 7.38- 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.23-7.16 (m, 2H), 7.13 (d, *J*= 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.50 (s, 2H), 4.08 (s, 2H), 3.81 (s, 3H), 3.69 (s, 2H), 2.49 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) : δ 159.0, 145.6, 145.3, 144.9, 139.4, 138.6, 137.4, 135.9, 132.3, 132.0, 131.5, 130.3, 130.2(2C), 129.5, 128.8, 128.2, 127.2, 127.0,



126.0, 123.8, 113.8 (2C), 58.3, 56.5, 55.4, 53.8, 21.8, 21.4;HRMS (ESI) calculated for $C_{29}H_{27}N_5O[M+H]^+$ *m/z* 462.2294; found 462.2292.

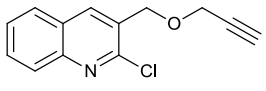
1-(4-Chlorophenyl)5-(4methoxybenzyl)-9-methyl-1,4,5,6-tetrahydro[1,2,3]triazolo[4',5':5,6] azepino[*4,3-b*]quinoline (6m): Brown solid, yield: 98 mg, 82% ; m.p. 118-120°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.48 – 7.38 (m, 6H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.49 (s, 2H), 4.08 (s, 2H), 3.81 (s, 3H), 3.69 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 145.7, 145.0, 144.9, 138.1, 137.7, 136.1, 134.7, 132.5, 132.2, 131.5, 130.2(2C), 130.1, 128.7, 128.7(2C), 128.1 (2C), 127.1, 126.0, 113.9(2C), 58.4, 56.5, 55.4, 53.7, 21.8; HRMS (ESI) calculated for $C_{28}H_{24}ClN_5O[M+]^+$ *m/z* 481.1669; found 481.1650.



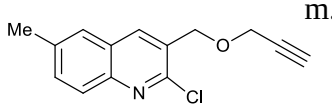
General procedure for the preparation of 2-chloro-3-((prop-2-yn-1-yloxy)methyl)quinolines (3a-d).

To a solution of the compound (2-chloroquinolin-3-yl)methanol (1.5 mmol) in DMF (10 ml) was cooled in ice and then added sodium hydride (90.0 mg, 2.25 mmol) followed by propargyl bromide 223.0 mg, 1.5 mmol). To the resulting reaction mixture TEBA (68.0 mg, 20 mol%) was added and stirred at room temperature for about 6 h. After the completion of reaction (monitored by TLC), the reaction mixture poured into cold water. The solid seperated was filetered, washed with water and dried. The products obtained were pure enough and hence directly taken for further reaction without purification.

2-Chloro-3-((prop-2-yn-1-yloxy)methyl)quinoline (3a): Colourlesssolid, yield: 320 mg, 90% ; m.p.118-20°C; ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.27 (d, *J* = 0.6 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.83 (dd, *J* =8.2, 1.0 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.56 (ddd,*J* = 8.1, 7.0, 1.1 Hz, 1H), 4.82 (d, *J* = 1.1 Hz, 2H), 4.38 (d, *J* = 2.4 Hz, 2H), 2.54 (t, *J* = 2.4 Hz, 1H);^{13}C NMR (126 MHz, $CDCl_3$): δ 149.2, 147.1, 136.9, 130.4, 129.8, 128.4, 127.7, 127.3, 127.3, 76.9, 75.5, 68.3, 58.5.

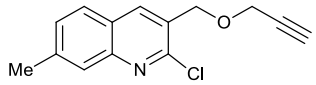


2-Chloro-3-((prop-2-yn-1-yloxy)methyl)quinoline(3b): Colourless solid, yield: 330 mg, 90%; m.p. 41-43°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.57 (s, 1H), 7.53 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.79 (d, *J* =



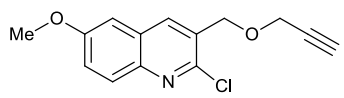
1.0 Hz, 2H), 4.36(d, *J* = 2.4 Hz, 2H), 2.53(t,*J*2.4 Hz, 1H), 2.51 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 145.7, 137.3, 136.3, 132.7, 129.6, 128.0, 127.4, 126.4, 79.2, 75. 4, 68.4, 58.4, 21.7.

2-Chloro-7-methyl-3-((prop-2-yn-1-yloxy)methyl)quinoline (3c): Light brown solid, yield:



334 mg, 91% ; m.p. 52-54ºC; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.20 (d, *J* = 0.6 Hz, 1H), 7.77(d, *J*= 0.7 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.38 (dd, *J* = 8.3, 1.5 Hz,1H), 4.79 (d, *J* = 0.9 Hz, 2H),4.36 (d, *J* = 2.4 Hz, 2H), 2.54 (s, 2H), 2.53 (t, *J* = 2.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 147.4, 141.0, 136.7, 129.5, 128.7, 127.4, 127.3, 125.4, 79.2, 75.4, 68.4, 58.4, 22.0.

2-Chloro-6-methoxy-3-((prop-2-yn-1-yloxy)methyl)quinoline (3d): Light yellow solid , yield:



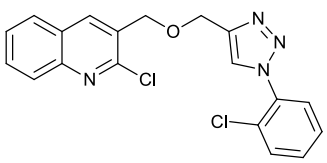
334 mg, 89% ; m.p.64-66ºC; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.17 (s, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.09 (s, 1H), 4.80 (s, 2H), 4.37 (s, 2H), 3.92 (s, 3H), 2.53 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4, 146.6, 143.1, 135.7, 129.9, 129.8, 128.5, 123.0, 105.3, 79.2, 75.4, 68.3, 58.5, 55.7.

General procedure for the preparation of 2-chloro-3-(((1-aryl/arylalkyl-1H-1,2,3-triazol-4-yl) methoxy)methyl)quinolines (5a-h)

2-chloro-3-((prop-2-yn-1-yloxy)methyl)quinolines (**3**, 0.5 mmol) was dissolved in DMF (5mL) and then aryl azide(0.75 mmol) was added. To this solution, $CuSO_4.5H_2O$ (2.5 mg, 0.01 mmol) and then sodium ascorbate (20.0 mg, 0.1 mmol in 1 mL water) were added. The resulting mixture was stirred at room temperature for 6 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was poured into cold water. Solid obtained was filtered, washed with hexane dried and directly used for the next step as it is sufficiently pure.

2-Chloro-3-(((1-(2-chlorophenyl)-1H-1,2,3-triazol-4-yl)methoxy)methyl)quinoline(5a):

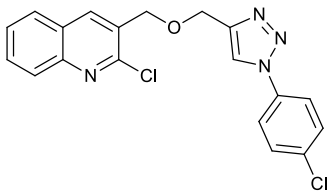
Pale yellow solid, yield: 155 mg, 81% ; m.p. 82-84ºC;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32



(s,1H), 8.08 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.75 –7.68 (m, 1H), 7.65 –7.60 (m, 1H), 7.60 –7.52 (m, 2H), 7.48 –7.43 (m, 2H),4.97 (s, 2H),4.87 (s, 2H);^{13}C NMR (101 MHz,

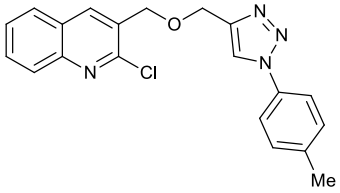
$CDCl_3$): δ 149.4, 147.2, 144.5, 137.2, 135.0, 131.0, 131.0, 130.4, 130.0, 128.7, 128.4, 128.1, 127.9, 127.8, 127.4, 127.3, 125.0, 69.2, 64.5.

2-Chloro-3-(((1-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl)methoxy)methyl)quinoline(5b):



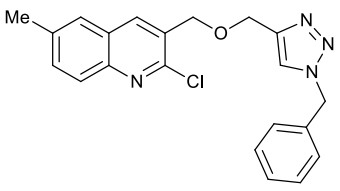
Light brown solid, yield: 163 mg, 85% ; m.p. 87-89°C;^{1}H NMR(500 MHz, $CDCl_3$) :δ8.30(s, 1H), 8.04 (s, 1H),8.01(d,*J*=8.5Hz,1H), 7.84 (d, *J* = 8.0 Hz, 1H),7.72-7.69 (m , 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.51(d, *J* = 8.8 Hz, 2H), 4.94 (s, 2H), 4.87(s, 2H);^{13}CNMR(126 MHz, $CDCl_3$) : δ149.4,147.2, 145.8, 137.1, 135.6, 134.9, 130.5, 130.1(2C), 129.8, 128.4, 127.7, 127.2 (2C), 121.9(2C), 121.0, 69.3, 64.5.

2-Chloro-3-(((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methoxy)methyl)quinoline (5c):



Light yellow solid, yield: 160 mg, 88% ; m.p. 84-86°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s1H), 8.01 (s and d, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.31 (d, *J* = 7.2Hz, 2H), 4.93 (s, 2H), 4.86 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 147.1, 139.2, 137.1, 134.8, 130.4(3C), 130.0, 128.4, 127.7, 127.4(2C), 127.3, 121.2, 120.7 (2C), 69.1, 64.6, 21.2.

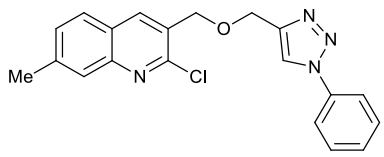
3-(((1-Benzyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-2-chloro-6-methylquinoline (5d) :



Colourlesssolid, yield: 143 mg, 76% ; m.p. 81-83°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s,1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.59 – 7.47 (m, 3H), 7.40 – 7.32 (m, 3H), 7.32 – 7.26 (m, 2H), 5.54 (s, 2H), 4.81 (s, 2H), 4.76 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.5, 145.7, 137.3, 136.6, 134.6, 132.6 (2C), 129.8, 129.3 (2C), 129.0, 128.3 (2C), 128.0, 127.4, 126.6 (2C),69.1, 64.6, 54.4, 21.7.

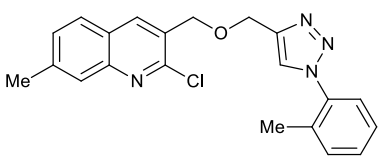
2-Chloro-7-methyl-3-(((1-phenyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)quinoline (5e):

Colourlesssolid, yield: 149 mg, 82% ; m.p. 67-69°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.07 (s, 1H), 7.77-7.74 (m, 4H), 7.59–7.36 (m, 4H), 4.94 (s, 2H), 4.85 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz,



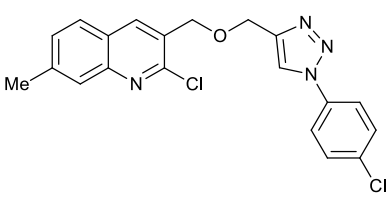
$CDCl_3$): δ 148.4, 146.5, 140.0, 136.0, 136.2, 129.0 (3C), 128.6, 128.0 , 127.9, 126.5 , 126.4, 124.4, 120.2, 119.8 (2C),68.3, 63.5, 21.1.

2-Chloro-7-methyl-3-(((1-(o-tolyl)-1H-1,2,3-triazol-4-yl)methoxy)methyl)quinoline (5f):



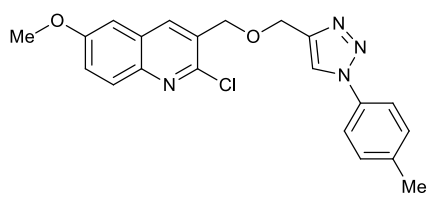
Light brownsolid, yield: 151 mg, 80% ; m.p. 82-84°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s,1H), 7.82 (s, 1H), 7.73 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.41 –7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 4.92 (s, 2H), 4.81 (s, 2H), 2.51 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$):δ 149.3, 147.3, 144.5, 140.9, 137.0, 136.4, 133.7, 131.5, 130.0, 129.4, 128.8, 127.3, 127.2, 126.9, 126.0 125.3, 124.4, 69.2, 64.4, 21.9, 17.9.

2-Chloro-3-(((1-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl)methoxy)methyl)-7-methylquinoline



(5g): Colorless solid, yield: 169 mg, 85% ; m.p. 93-95°C;^{1}H NMR (400 MHz, $CDCl_3$):δ 8.21 (s, 1H), 8.03 (s, 1H), 7.77 (s, 1H), 7.73 – 7.63 (m, 3H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 4.91 (s, 2H), 4.82 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$):δ 149.5, 147.5, 145.9, 141.1, 137.1, 135.6, 134.9, 130.1(2C), 129.6, 128.8, 127.5, 127.3, 125.4, 121.9 (2C), 121.0, 69.4, 64.5, 22.1.

2-Chloro-6-methoxy-3-(((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methoxy)methyl)quinoline(5h):



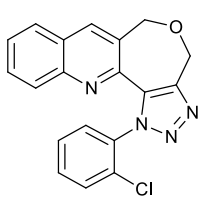
Light brown solid, yield: 157 mg, 80% ; m.p. 98-100°C;^{1}H NMR (400 MHz, $CDCl_3$):δ 8.21 (s, 1H), 8.03 (s, 1H), 7.90 (s, 1H), 7.60 (s, 2H), 7.44 –7.21 (m, 3H), 7.09 (s, 1H), 4.92 (s, 2H), 4.84 (s, 2H), 3.91 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4, 146.7, 143.1, 139.2, 136.0 (2C), 134.9, 130.5, 130.1(2C),129.8, 128.5, 123.1, 121.2, 120.7(2C), 105.3, 69.2, 64.5, 55.8, 21.3.

General procedure for the preparation of 1-aryl/aralkyl-4,6-dihydro-*1H*-[1,2,3] triazolo [4',5':5,6]oxepino[*4,3-b*]quinolines (7a-h).

To the solution of 2-chloro-3-(((1-aryl/aralkyl-1H-1,2,3-triazol-4-yl) methoxy)methyl)quinolines (**5a**, 0.3 mmol) in DMF (3mL) was added $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol%), triphenylphosphine (15.6 mg, 0.06 mmol, 20 mol%), and then cesium carbonate (194 mg, 0.6 mmol) were added. The reaction mixture was heated with stirring at 130 °C for 25h. After completion of the

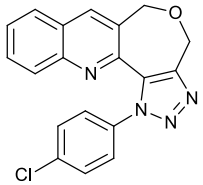
reaction monitored by TLC , the reaction mixture was cooled and extracted with EtOAc (2 x20 mL).The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluted with 10% hexane/EtOAc) to afford the title compounds.

1-(2-Chlorophenyl)-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*]quinoline(7a):



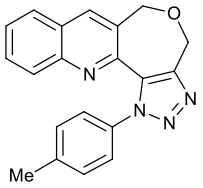
Light brown solid, yield: 78 mg, 75% ; m.p. 113-115^oC;^1H NMR (400 MHz, $CDCl_3$):δ 7.96 (s, 1H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.43 (m, 5H), 7.24 (d, *J* = 8.3 Hz, 1H), 5.41 (s, 2H), 4.94 (d, *J* = 10.5 Hz, 2H);^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 146.1, 145.5, 137.6, 135.2, 133.1, 132.2, 131.3, 130.6, 130.0, 129.7, 129.3, 129.3, 127.6, 127.4, 127.4, 126.7, 72.2, 69.34; HRMS (ESI) calculated for $C_{19}H_{13}ClN_4O[M+Na]^+$*m/z* 371.0676; found 371.0761.

1-(4-Chlorophenyl)-4,6-dihydro-1H-[1,2,3]triazolo[4',5':5,6]oxepino[4,3-b]quinoline (7b):



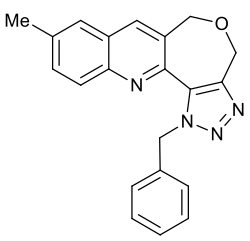
Colourlesssolid, yield: 86 mg, 83%; m.p. 138-140^oC;^1H NMR (400 MHz, $CDCl_3$):δ 7.99 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.51–7.44 (m, 3H), 7.42 (d, *J* = 8.7 Hz, 2H), 5.38 (s, 2H), 4.93 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 146.6, 145.4, 137.7, 135.6, 135.1, 132.0, 131.7, 130.3, 129.2, 128.7(2C), 128.3 (2C), 127.8, 127.5, 126.8, 71.8, 69.2; HRMS (ESI) calculated for $C_{19}H_{13}ClN_4O[M+Na]^+$*m/z* 371.0676; found 371.0712.

1-(p-Tolyl)-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*]quinoline(7c): Light



brown solid, yield: 78 mg, 80% ; m.p. 123-125^oC;^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.38 (s, 2H), 4.91 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 146.4, 145.8, 139.1, 136.6, 135.4, 131.9, 131.7, 130.1, 129.3, 129.1(2C), 127.6, 127.4, 127.2, 126.7 (2C), 71.7, 69.2, 21.5;HRMS (ESI) calculated for $C_{20}H_{16}N_4O[M+H]^+$*m/z* 329.1402; found 329.1407.

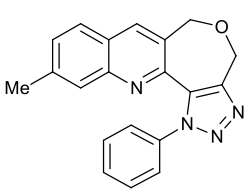
1-Benzyl-9-methyl-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*]quinoline (7d):



Colourlesssolid, yield: 82 mg, 80% ; m.p. 133-135^oC;^1H NMR (400 MHz, $CDCl_3$):δ 7.98 (d, *J*= 8.6 Hz, 1H), 7.84 (s, 1H), 7.58 (dd, *J* = 8.6,

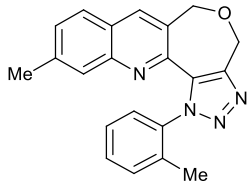
1.8 Hz, 1H), 7.54 (s, 1H)7.33 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.15 (m, 3H), 6.47 (s, 2H), 5.30 (s, 2H), 4.77 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 145.6, 145.5, 137.8, 136.8, 135.0, 132.7, 131.7, 130.6, 128.7, 128.6 (2C), 127.9 (2C), 127.8, 126.8, 126.5, 71.9, 69.4, 54.4, 21.8; HRMS (ESI) calculated for $C_{21}H_{18}N_4O[M+H]^+$ *m/z* 343.1559; found 343.1554.

10-Methyl-1-phenyl-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*]quinoline (7e):



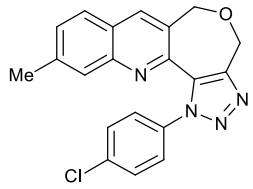
Colourless solid, yield: 78 mg, 80% ; m.p. 152-154^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.55-7.45 (m, 5H), 7.33 (d, *J* = 9.7 Hz, 1H),7.13 (s, 1H), 5.38 (s, 2H), 4.90 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.0, 146.4, 145.6, 140.5, 139.2, 135.2, 132.1, 130.9, 130.0, 129.1, 128.6 (2C), 128.2, 127.1, 126.9 (2C), 124.8, 71.8, 69.1, 21.9;HRMS (ESI) calculated for $C_{20}H_{16}N_4O[M+H]^+$ *m/z* 329.1402; found 329.1428.

10-Methyl-1-(o-tolyl)-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*]quinoline (7f):



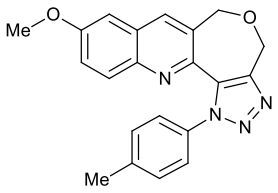
Light brownsolid, yield: 82 mg, 80%; m.p. 108-109^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s,1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 7.6Hz, 1H), 7.33 – 7.27 (m, 3H), 7.02 (s, 1H), 5.40 (s, 2H), 4.91 (s, 2H), 2.44 (s, 3H), 2.02 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ 147.2, 146.1, 145.5, 140.4, 138.9, 136.2, 134.9, 132.7, 130.6, 130.3, 129.9, 129.6, 128.3, 127.4, 127.00, 126.3, 124.6, 72.2, 69.4, 22.0, 17.9.

1-(4-Chlorophenyl)-10-methyl-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*] quinoline (7g): Light yellow solid, yield: 92 mg, 85% ; m.p. 161-163^{o}C;^{1}H NMR (400 MHz,



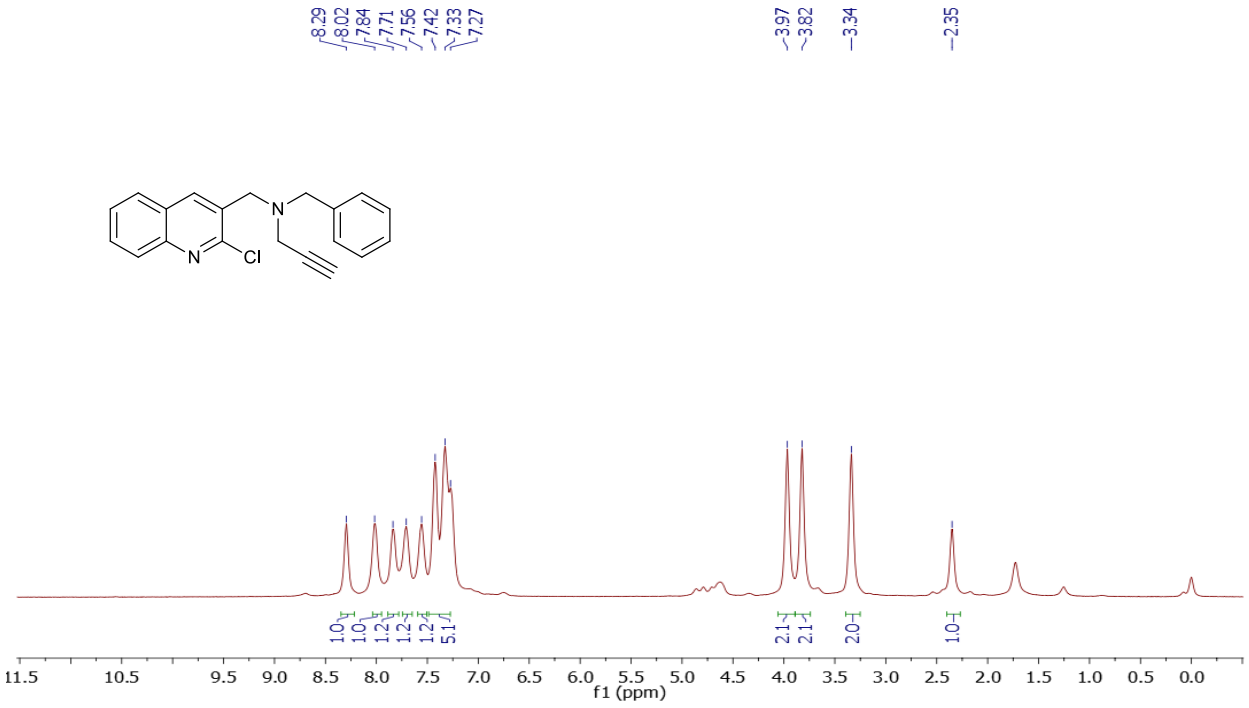
$CDCl_3$): δ 7.94 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J*=8.8 Hz, 2H), 7.36 (d, *J* =9.7 Hz, 1H), 7.21 (s, 1H), 5.37 (s, 2H), 4.90 (s, 2H), 2.49 (s, 3H); ^{3}C NMR (101 MHz, $CDCl_3$):δ 147.0, 146.5,145.4, 140.8, 137.7, 135.3, 135.0, 132.1, 130.8, 130.2, 128.8(2C), 128.2 (2C), 128.1, 127.1, 124.8, 71.7, 69.1, 22.0; HRMS (ESI) calculated for $C_{20}H_{15}ClN_4O[M+H]^+$ *m/z* 363.1013; found 363.1012.

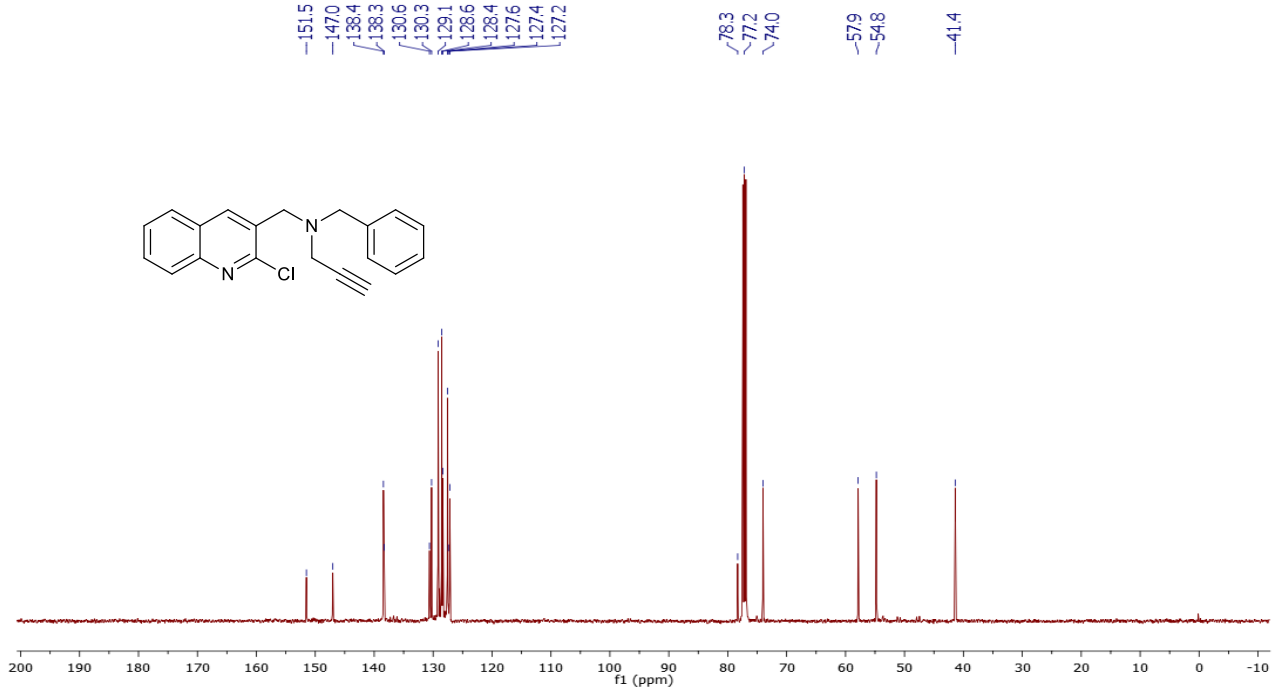
9-Methoxy-1-(p-tolyl)-4,6-dihydro-*1H*-[1,2,3]triazolo[4',5':5,6]oxepino[*4,3-b*]quinoline(7h): Light brown solid, yield: 88 mg, 82% ; m.p. 180-182^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ7.86 (s,

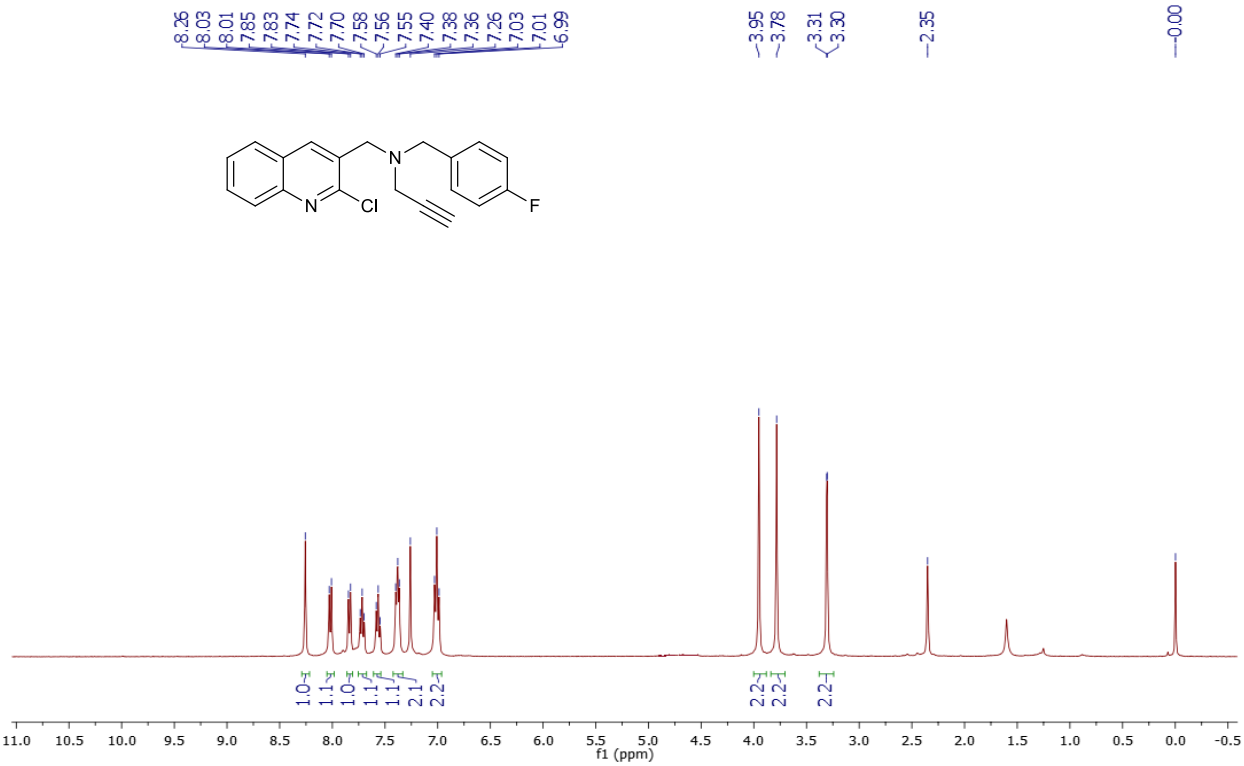


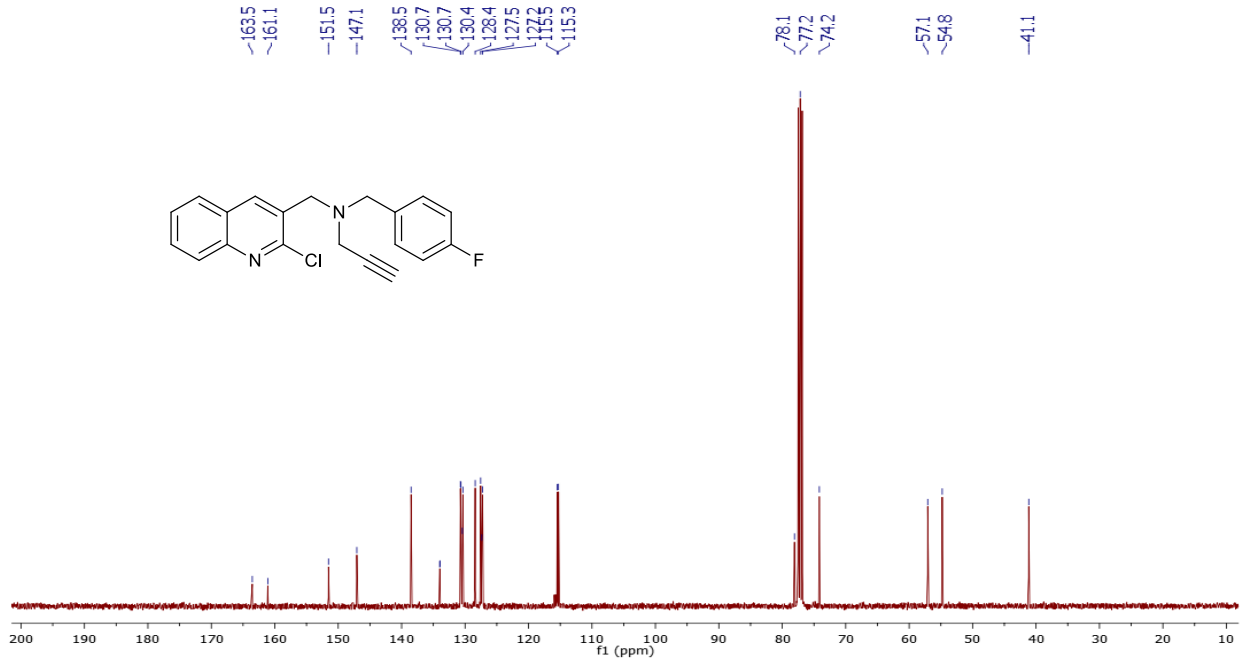
1H), 7.39-7.31 (m, 5H), 7.23 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 5.37 (s, 2H), 4.89 (s, 2H), 3.91 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 145.9, 143.4, 143.0, 139.1, 136.7, 134.2(2C), 132.1, 130.9, 129.1 (2C), 128.0, 126.8 (2C), 123.0, 105.0, 71.9, 69.2, 55.8, 21.5; HRMS (ESI) calculated for $C_{21}H_{18}ClN_4O[M+H]^+$*m/z* 359.1508.; found 359.1521.

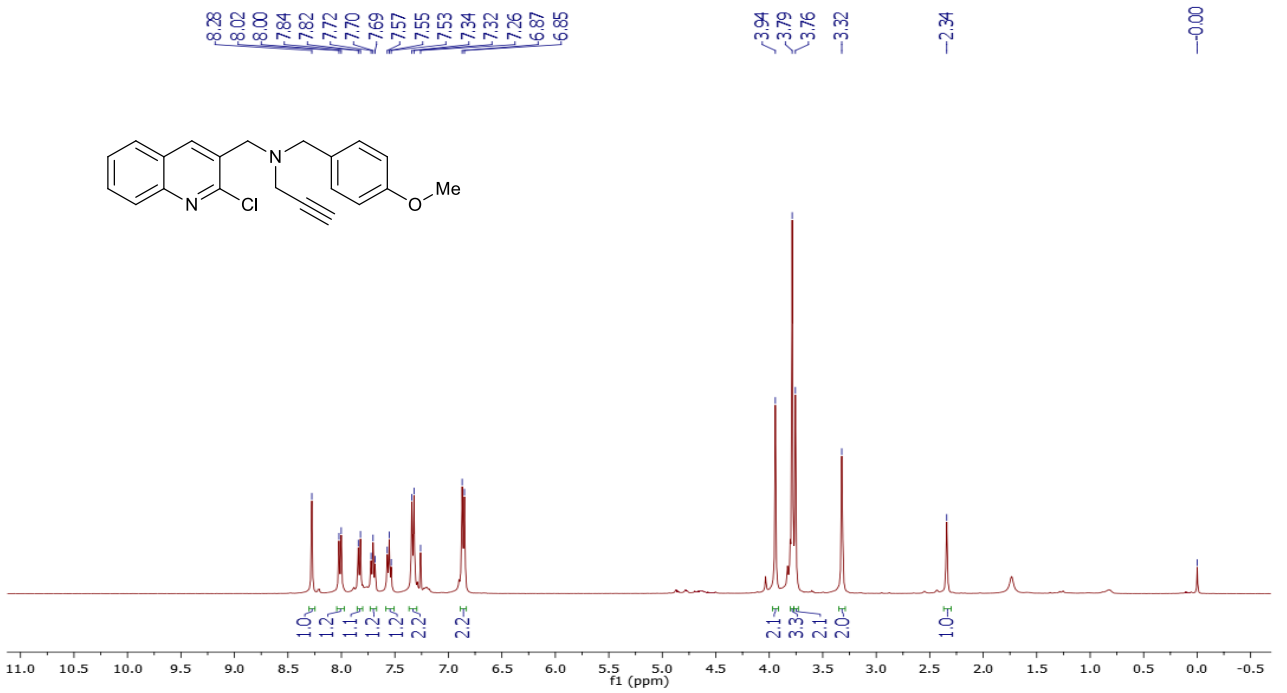
^{1}H-NMR and ^{13}C-NMR spectra of the compounds (2a-e)






8.26
8.03
8.01
7.85
7.83
7.74
7.72
7.70
7.58
7.56
7.55
7.40
7.38
7.36
7.26
7.03
7.01
6.99
3.95
3.78
3.31
3.30
2.35
0.00
N
Cl
N
F
1.0
1.1
1.0
1.1
1.1
2.1
2.2
2.2
2.2
2.2
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.5
161.1
151.5
147.1
138.5
130.7
130.7
130.4
128.4
127.5
127.2
115.5
115.3
78.1
77.2
74.2
57.1
54.8
41.1
N
Cl
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.00
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7.72
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7.69
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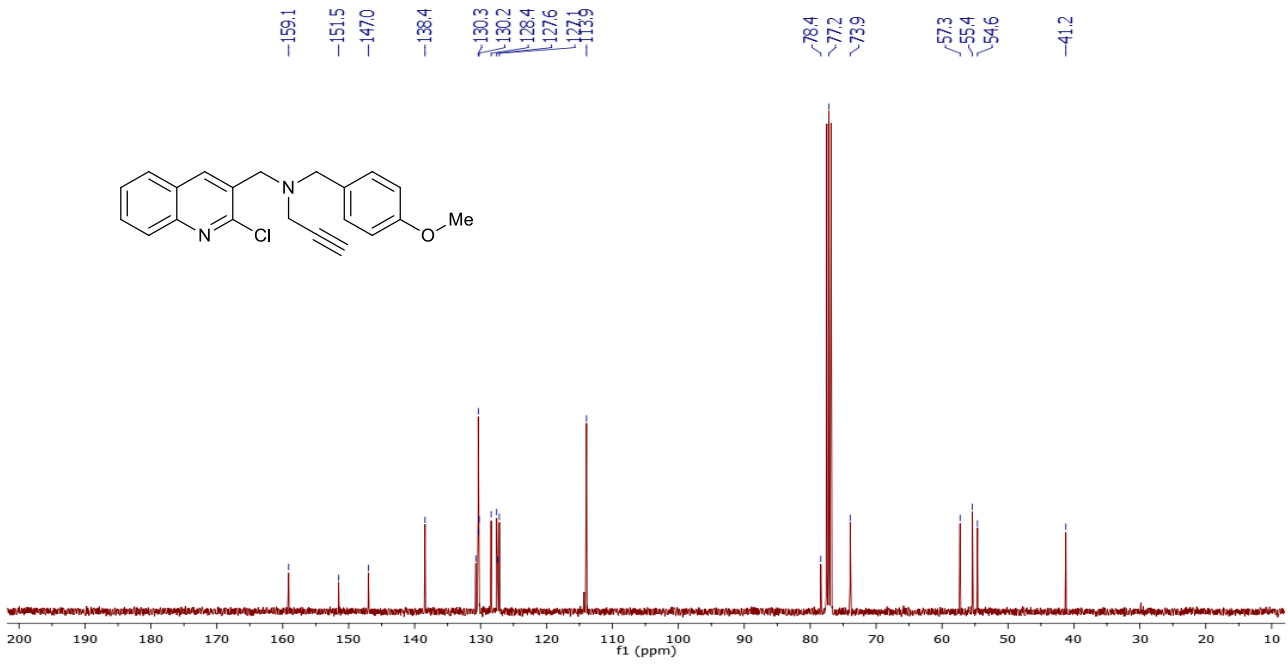
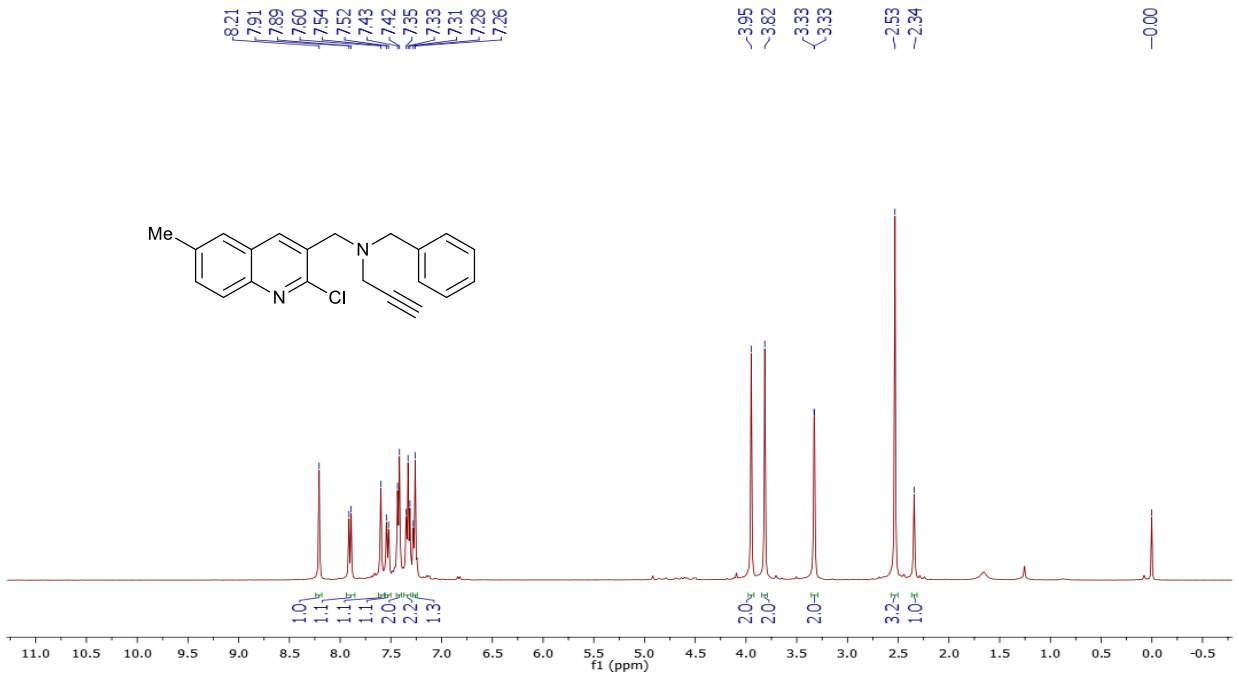
7.55
7.53
7.34
7.32
7.26
6.87
6.85
3.94
3.79
3.76
3.32
2.34
0.00
N
Cl
N
O
Me
1.0
1.2
1.1
1.2
1.2
2.2
2.2
2.1
3.3
2.1
2.0
1.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.1
151.5
147.0
138.4
130.3
130.2
128.4
127.6
127.1
113.9
78.4
77.2
73.9
57.3
55.4
54.6
41.2
N
Cl
N
O
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.21
7.91
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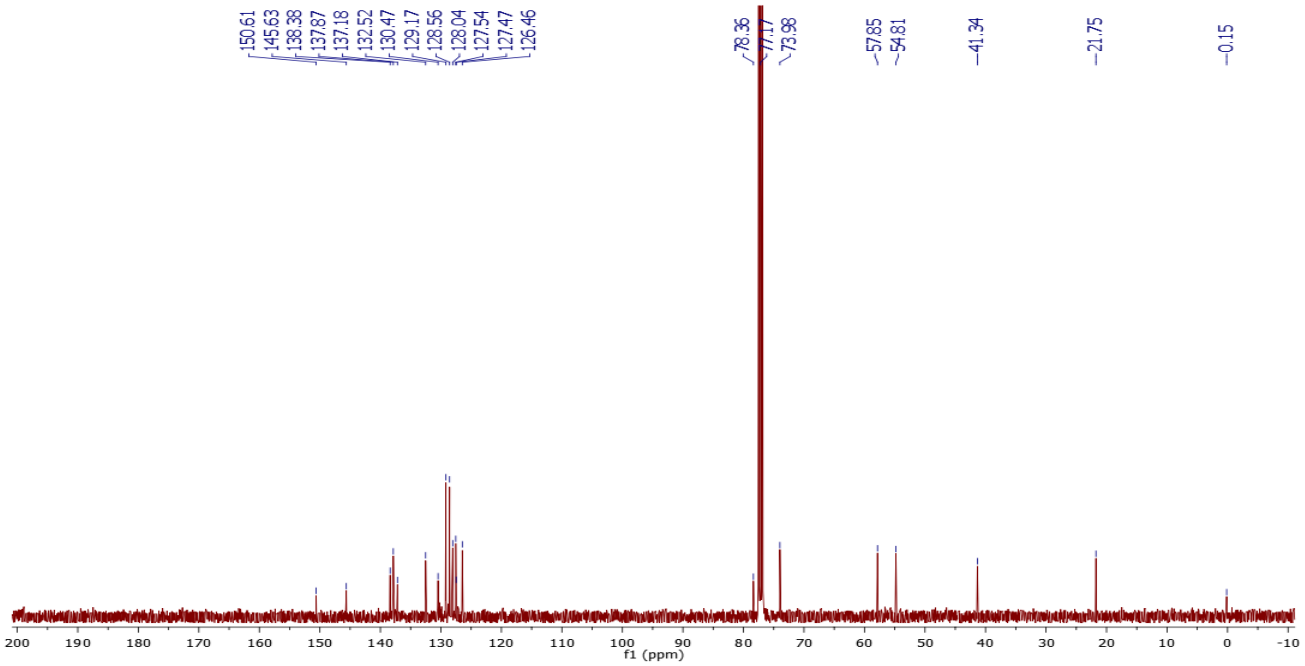
7.60
7.54
7.52
7.43
7.42
7.35
7.33
7.31
7.28
7.26
3.95
3.82
3.33
3.33
2.53
2.34
0.00
Me
N
N
Cl
1.0
1.1
1.1
1.1
2.0
2.2
1.3
2.0
2.0
2.0
3.2
1.0
f1 (ppm)


150.61
145.63
138.38
137.87
137.18
132.52
130.47
129.17
128.56
128.04
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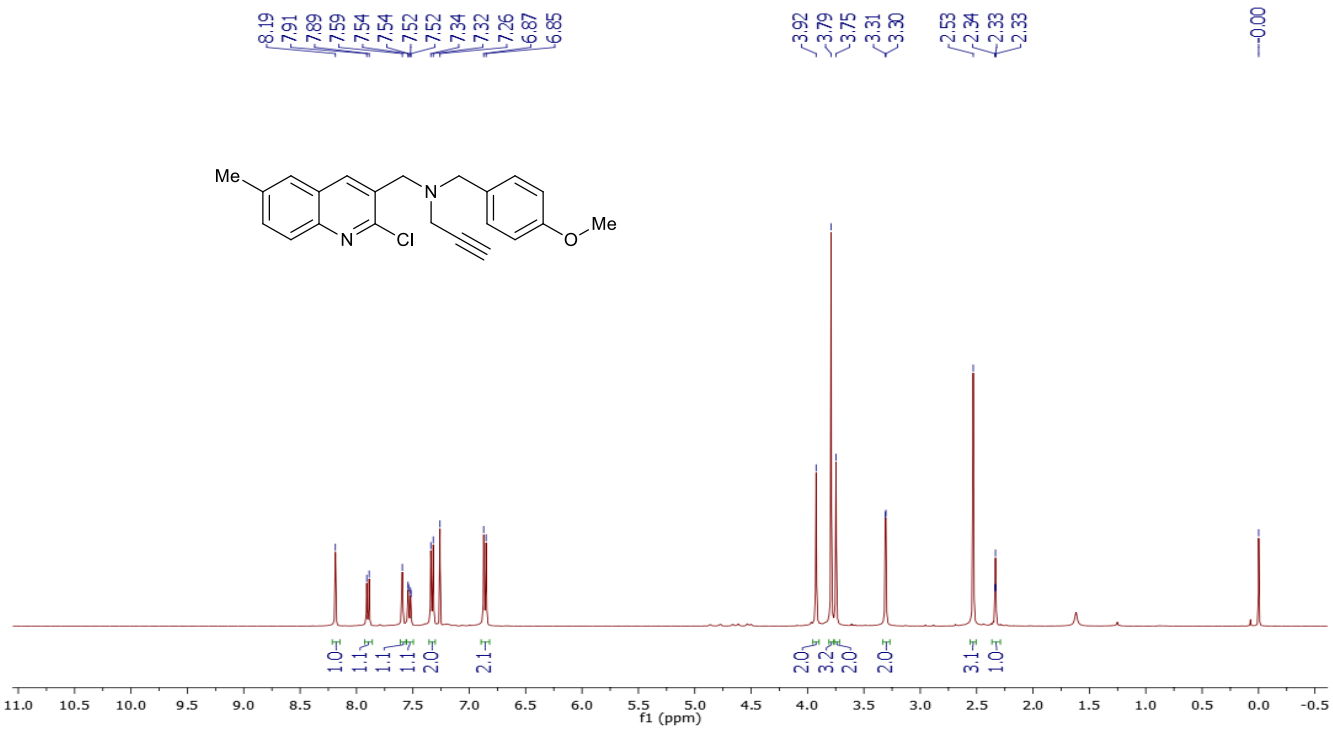
77.17
73.98
57.85
54.81
41.34
21.75
0.15
f1 (ppm)


8.19
7.91
7.89
7.59
7.54
7.54
7.52
7.52
7.34
7.32
7.26
6.87
6.85
3.92
3.79
3.75
3.31
3.30
2.53
2.34
2.33
2.33
0.00
Me
N
Cl
O
Me
1.0
1.1
1.1
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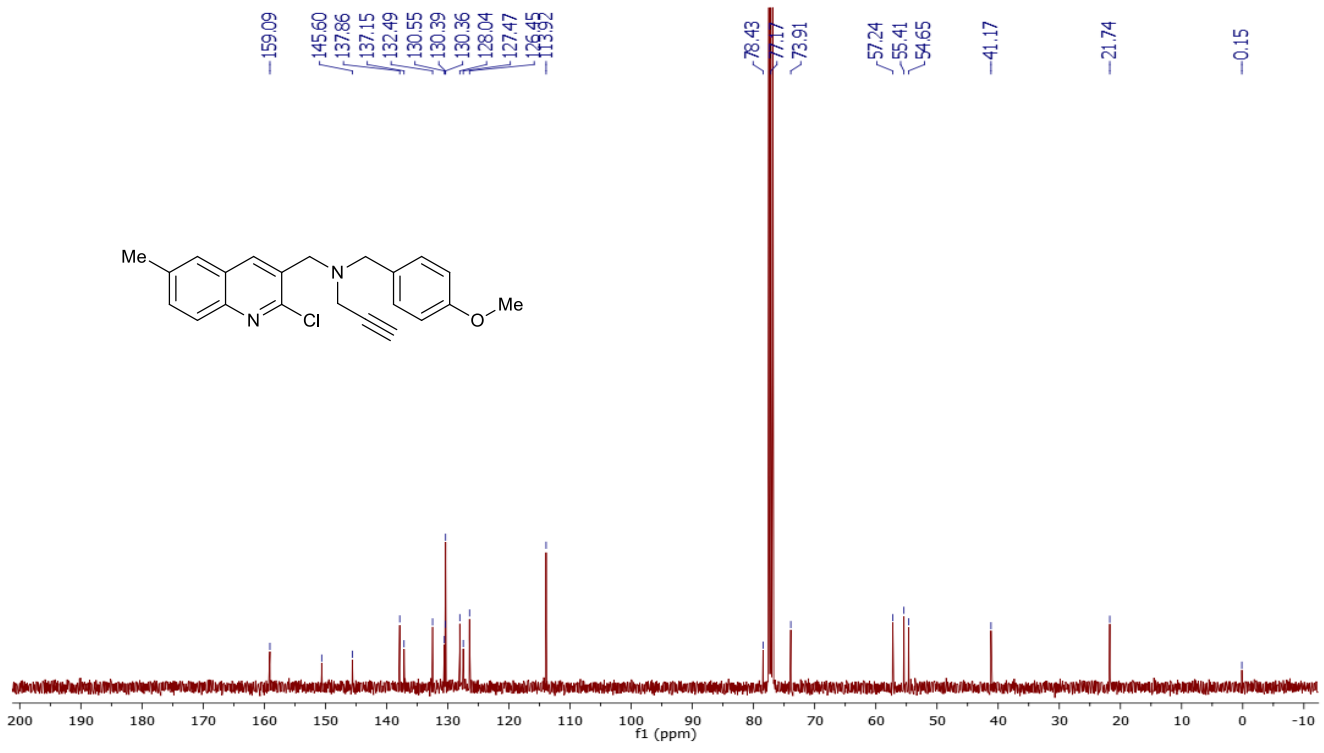
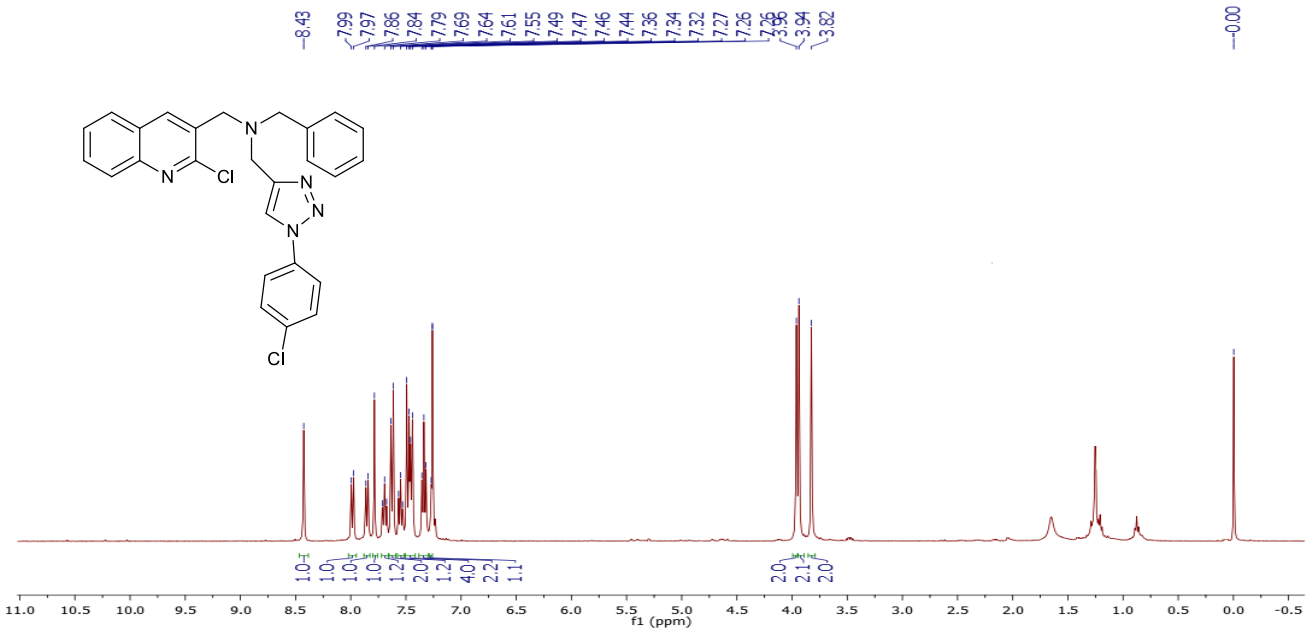
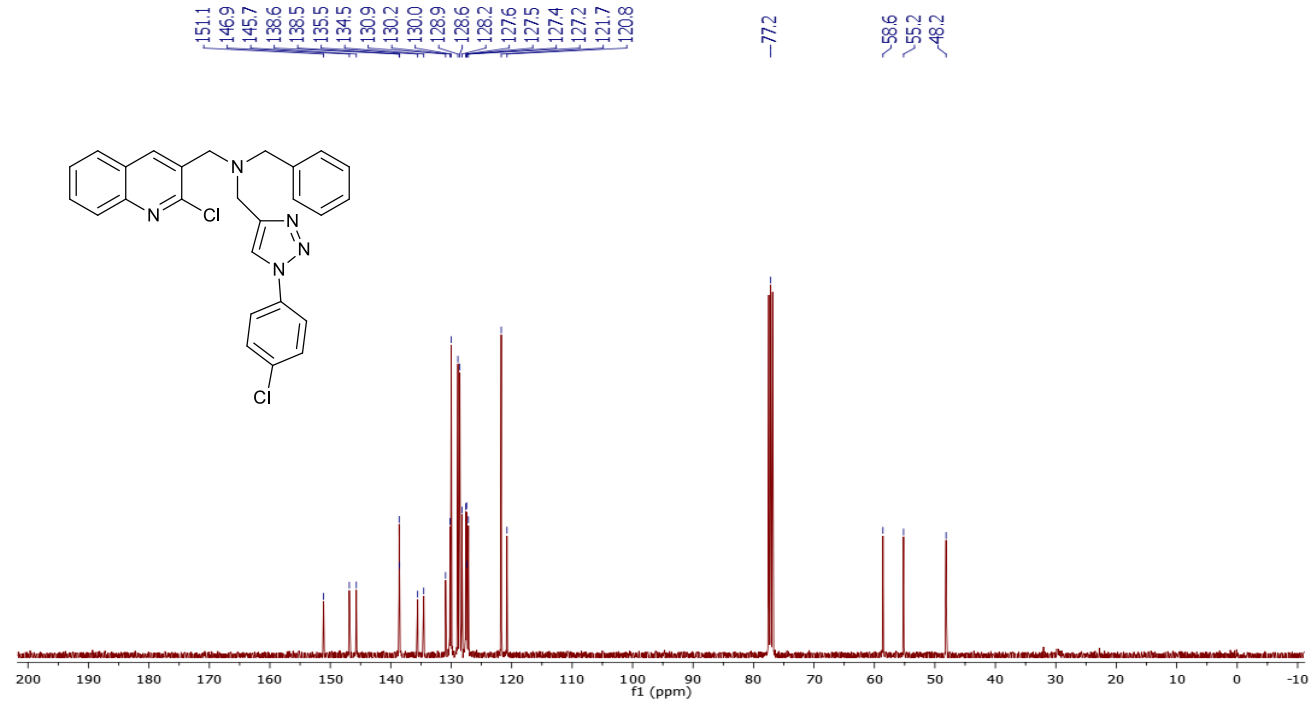
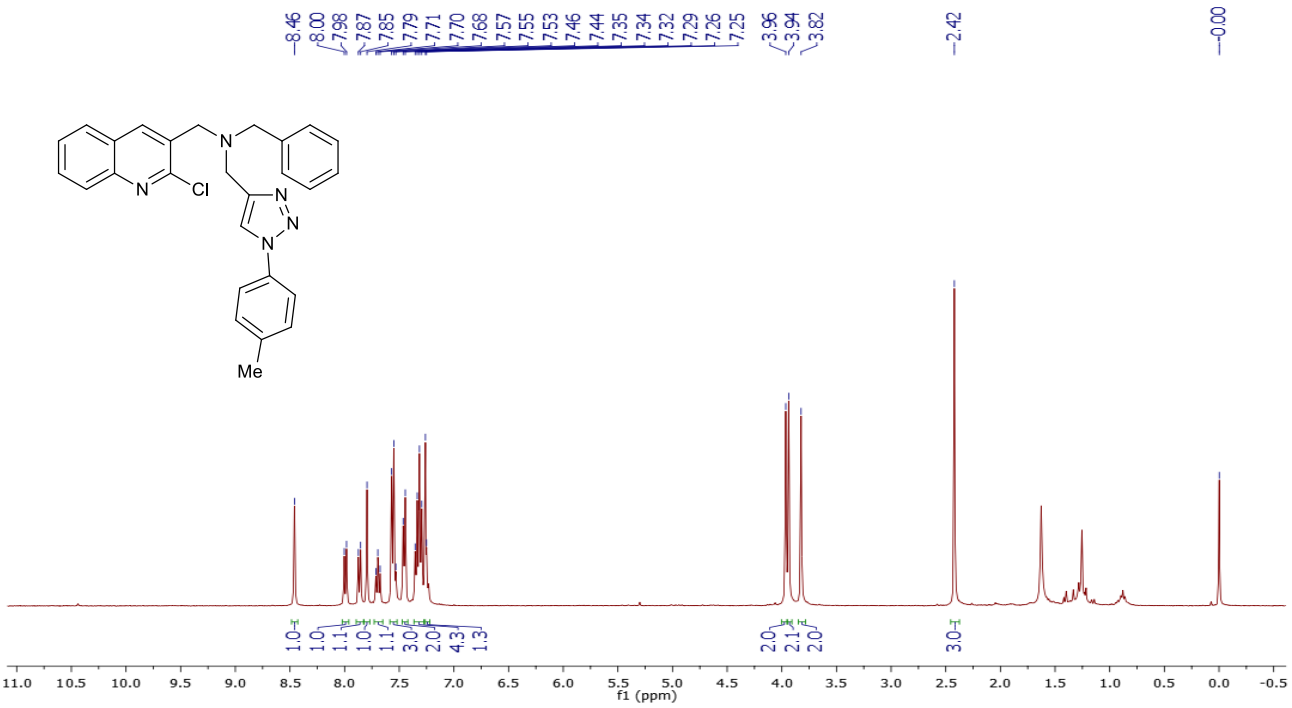
2.0
2.1
2.0
3.2
2.0
2.0
3.1
1.0
f1 (ppm)


159.09
145.60
137.86
137.15
132.49
130.55
130.39
130.36
128.04
127.47
126.45
113.92
78.43
77.17
73.91
57.24
55.41
54.65
41.17
21.74
0.15
Me
N
Cl
O
Me
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of the compounds (4a-m)






8.46
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7.68
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7.55
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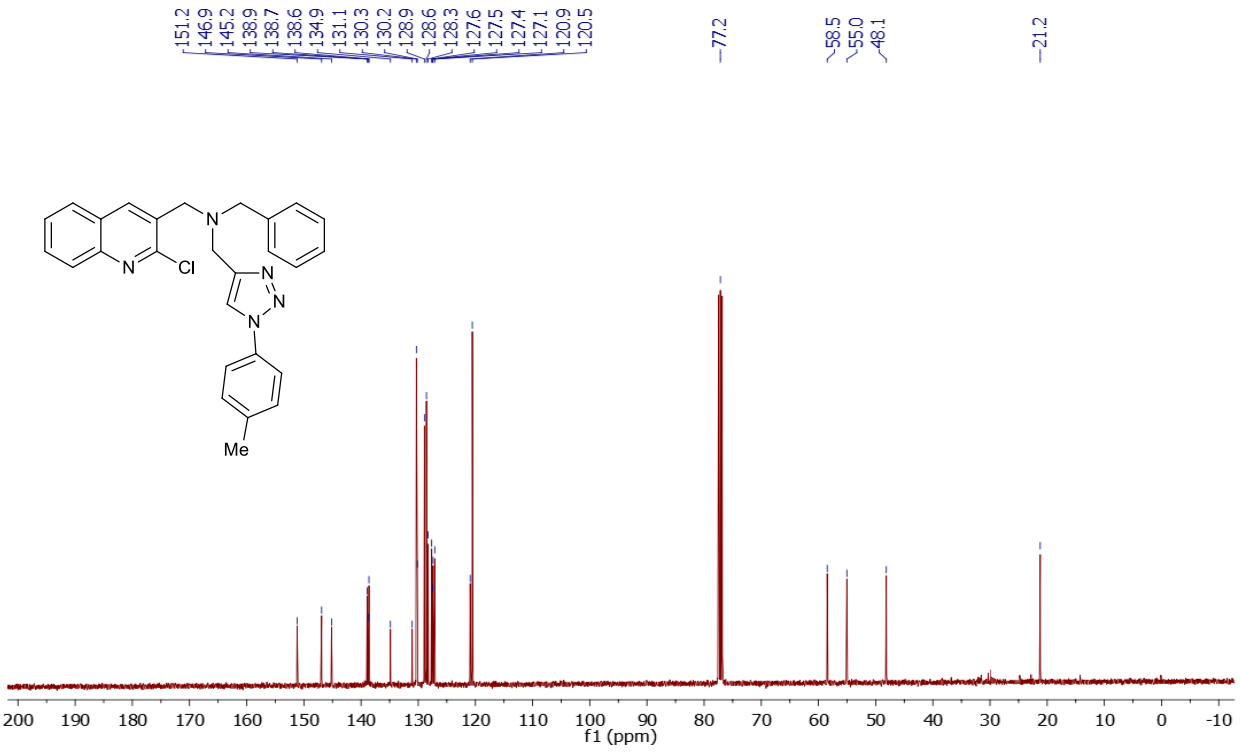
7.44
7.35
7.34
7.32
7.29
7.26
7.25
3.96
3.94
3.82
2.42
0.00
N
Cl
N
N
N
Me
1.0
1.0
1.1
1.0
1.1
3.0
2.0
4.3
1.3
2.0
2.1
2.0
3.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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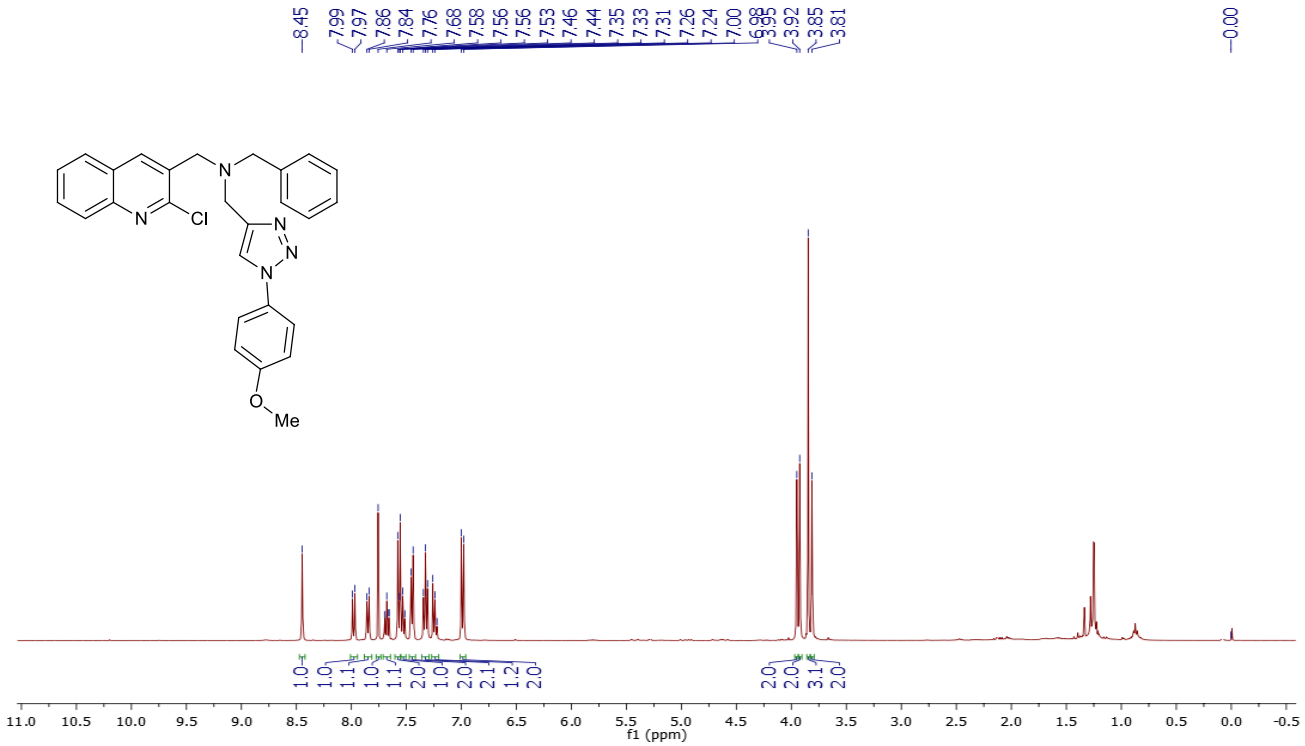
146.9
145.2
138.9
138.7
138.6
134.9
131.1
130.3
130.2
128.9
128.6
128.3
127.6
127.5
127.4
127.1
120.9
120.5
77.2
58.5
55.0
48.1
21.2
N
Cl
N
N
N
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.45
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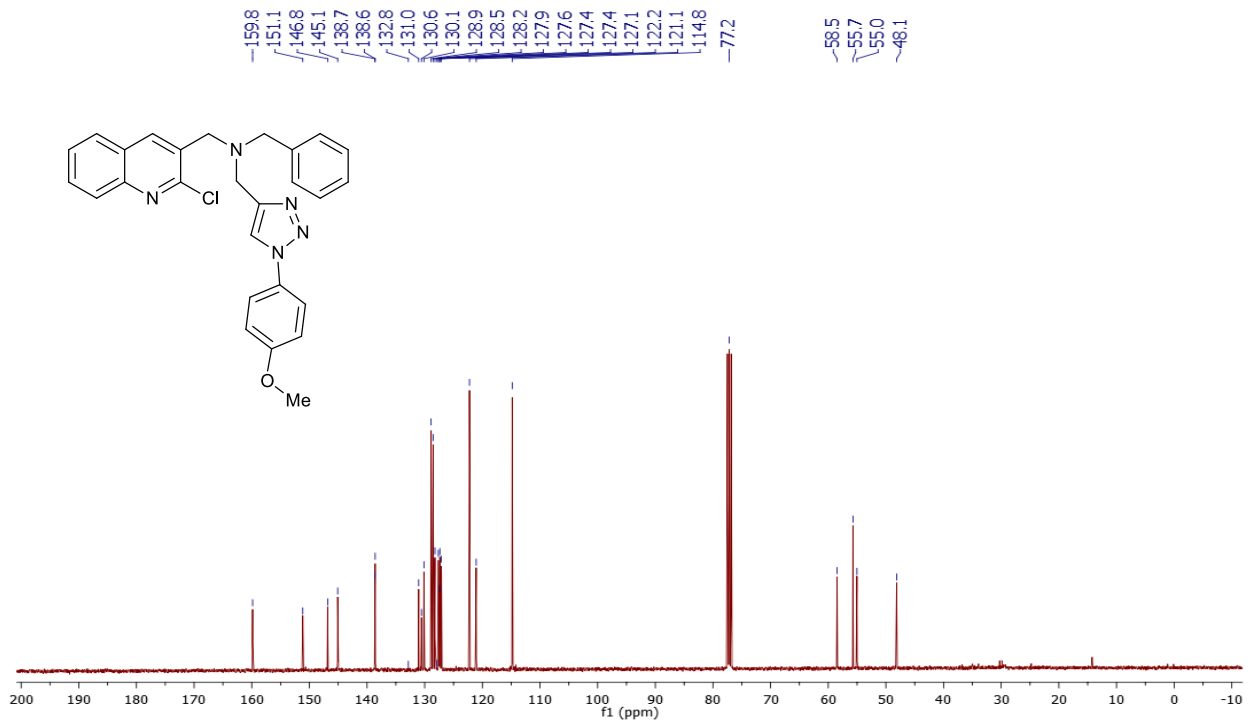
7.68
7.58
7.56
7.56
7.53
7.46
7.44
7.35
7.33
7.31
7.26
7.24
7.00
6.98
6.95
3.92
3.85
3.81
0.00
Cl
N
N
N
N
O
Me
1.0
1.0
1.1
1.0
1.1
2.0
1.0
2.0
2.1
1.2
2.0
2.0
2.0
3.1
2.0
f1 (ppm)


159.8
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146.8
145.1
138.7
138.6
132.8
131.0
130.6
130.1
128.9
128.5
128.2
127.9
127.6
127.4
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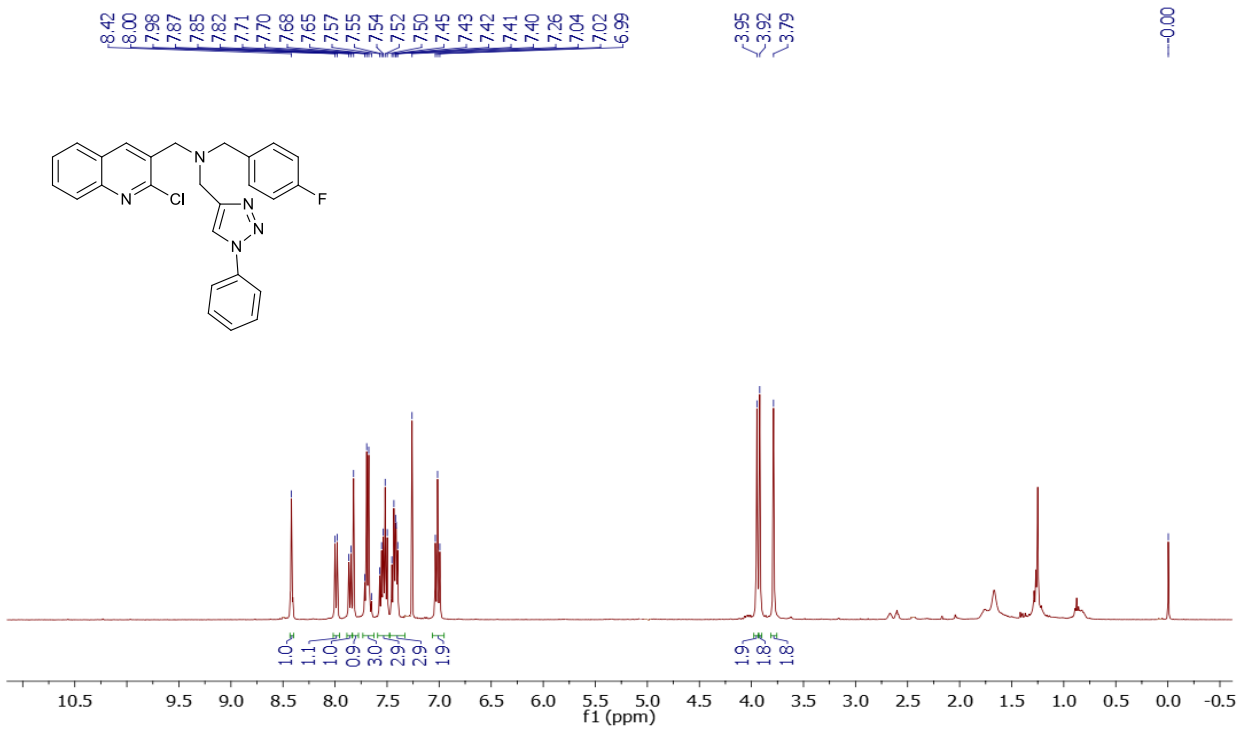
N
O
Me
f1 (ppm)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7.40
7.26
7.04
7.02
6.99
3.95
3.92
3.79
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1.0
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1.9
1.9
1.8
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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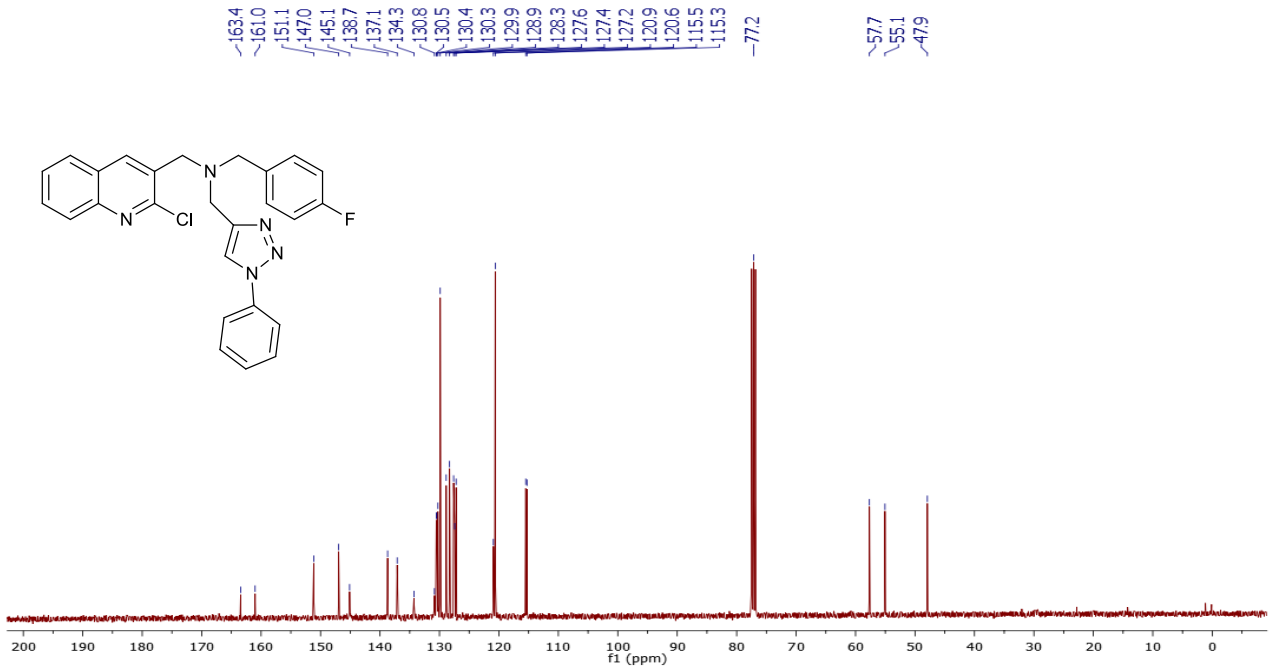
f1 (ppm)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128.9
128.3
127.6
127.4
127.2
120.9
120.6
115.5
115.3
77.2
57.7
55.1
47.9
Cl
F
200
190
180
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110
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90
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50
40
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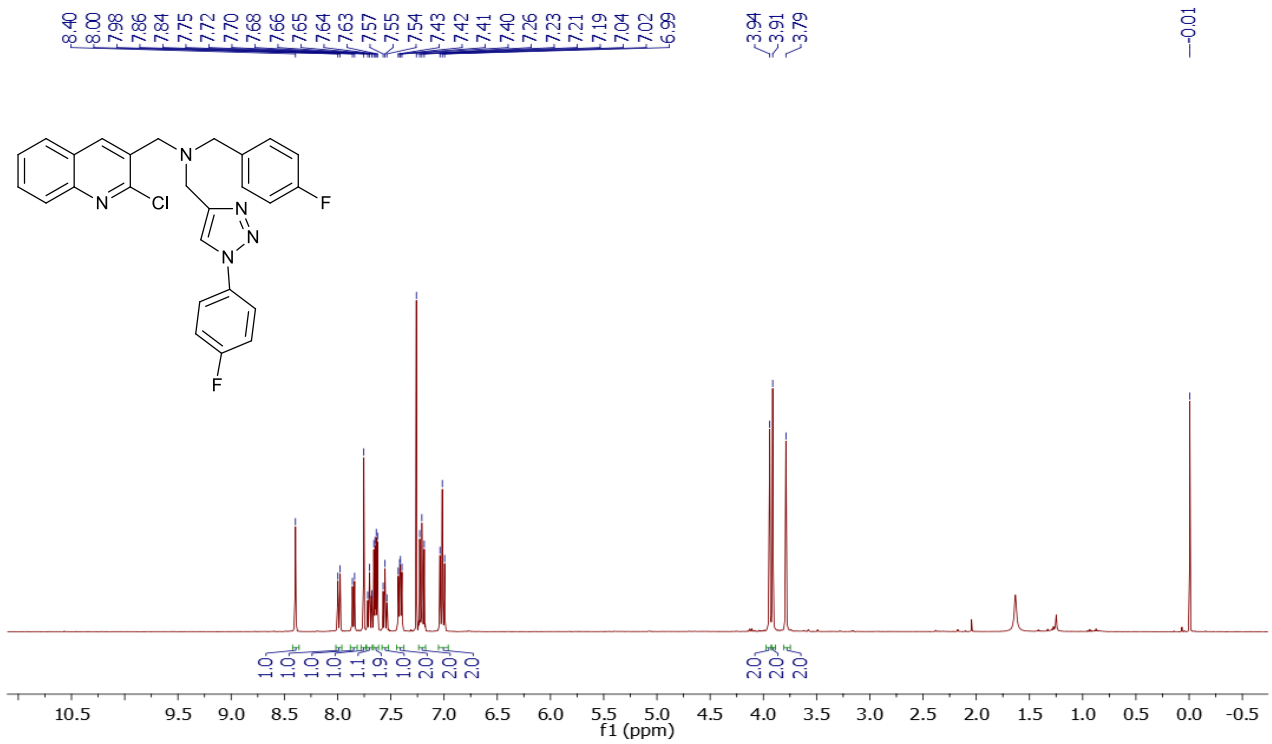
f1 (ppm)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7.55
7.54
7.43
7.42
7.41
7.40
7.26
7.23
7.21
7.19
7.04
7.02
6.99
3.94
3.91
3.79
0.01
Cl
F
F
1.0
1.0
1.0
1.0
1.1
1.9
1.0
2.0
2.0
2.0
2.0
2.0
2.0
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7.0
6.5
6.0
5.5
5.0
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2.0
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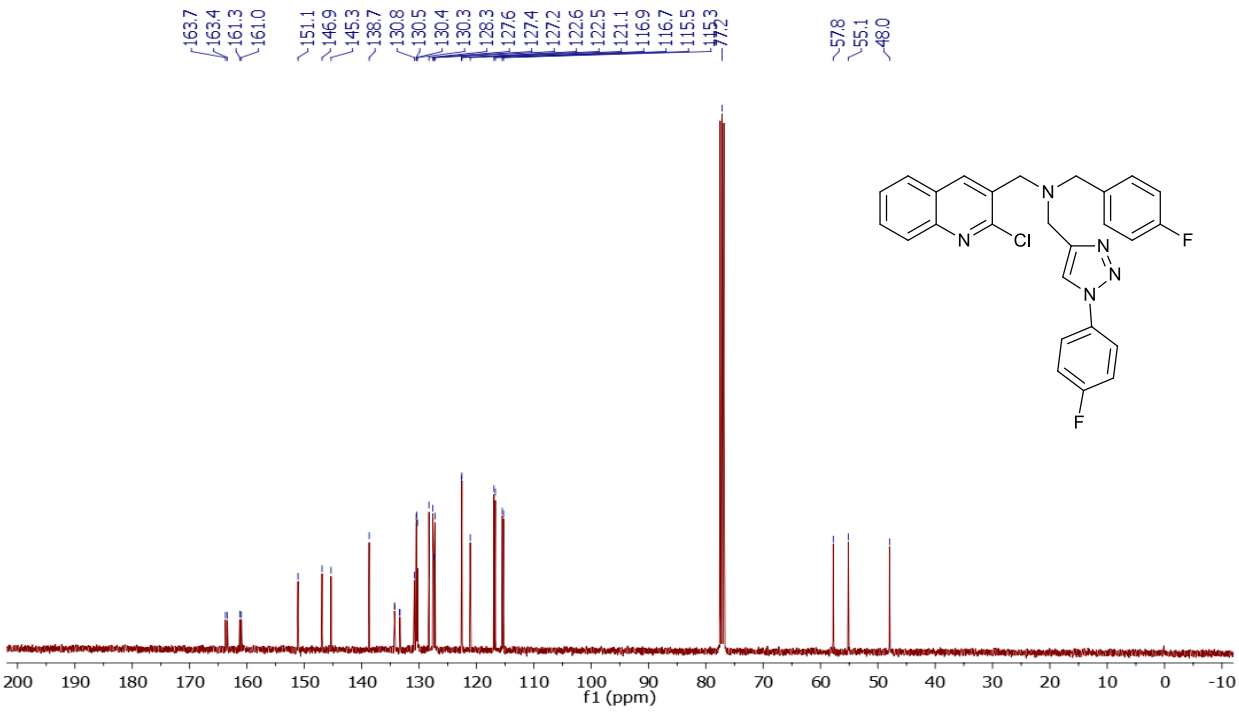
-0.5
f1 (ppm)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127.4
127.2
122.6
122.5
121.1
116.9
116.7
115.5
115.3
77.2
57.8
55.1
48.0
Cl
F
F
200
190
180
170
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100
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80
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40
30
20
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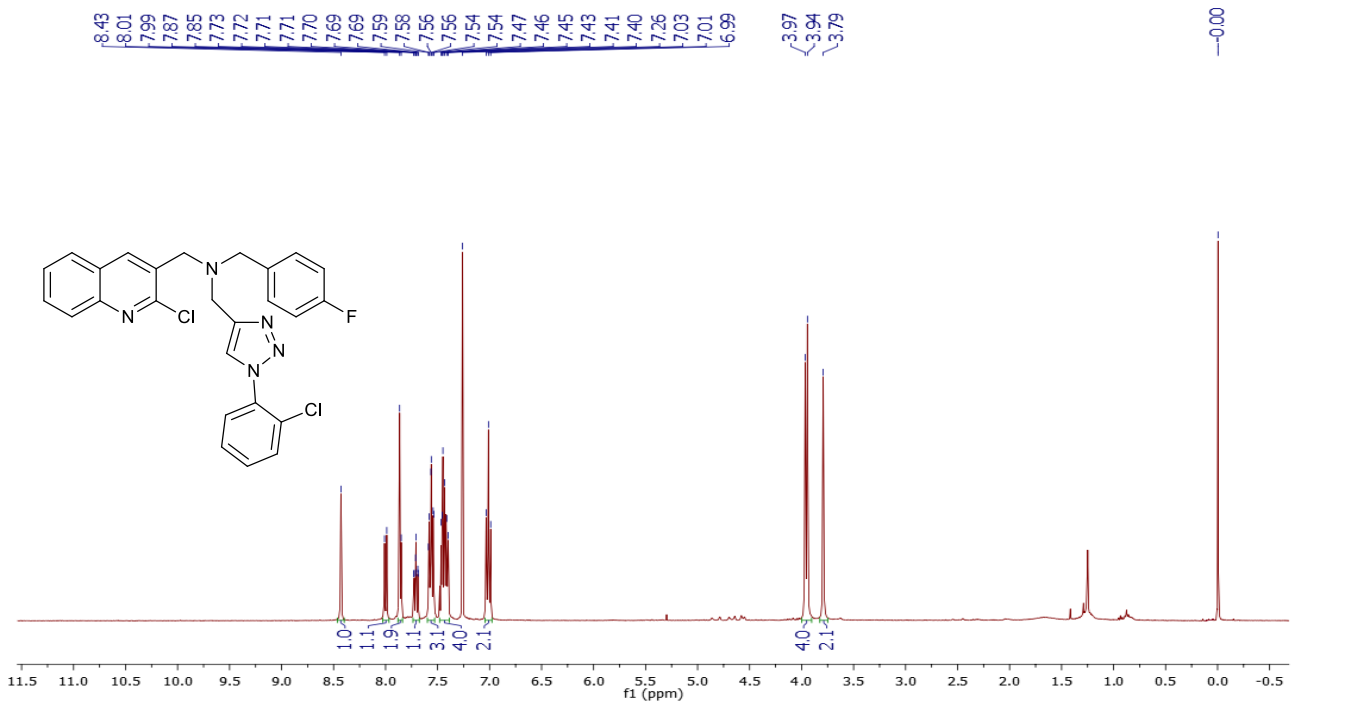
-10
f1 (ppm)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7.58
7.56
7.56
7.54
7.54
7.47
7.46
7.45
7.43
7.41
7.40
7.26
7.03
7.01
6.99
3.97
3.94
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1.1
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1.1
3.1
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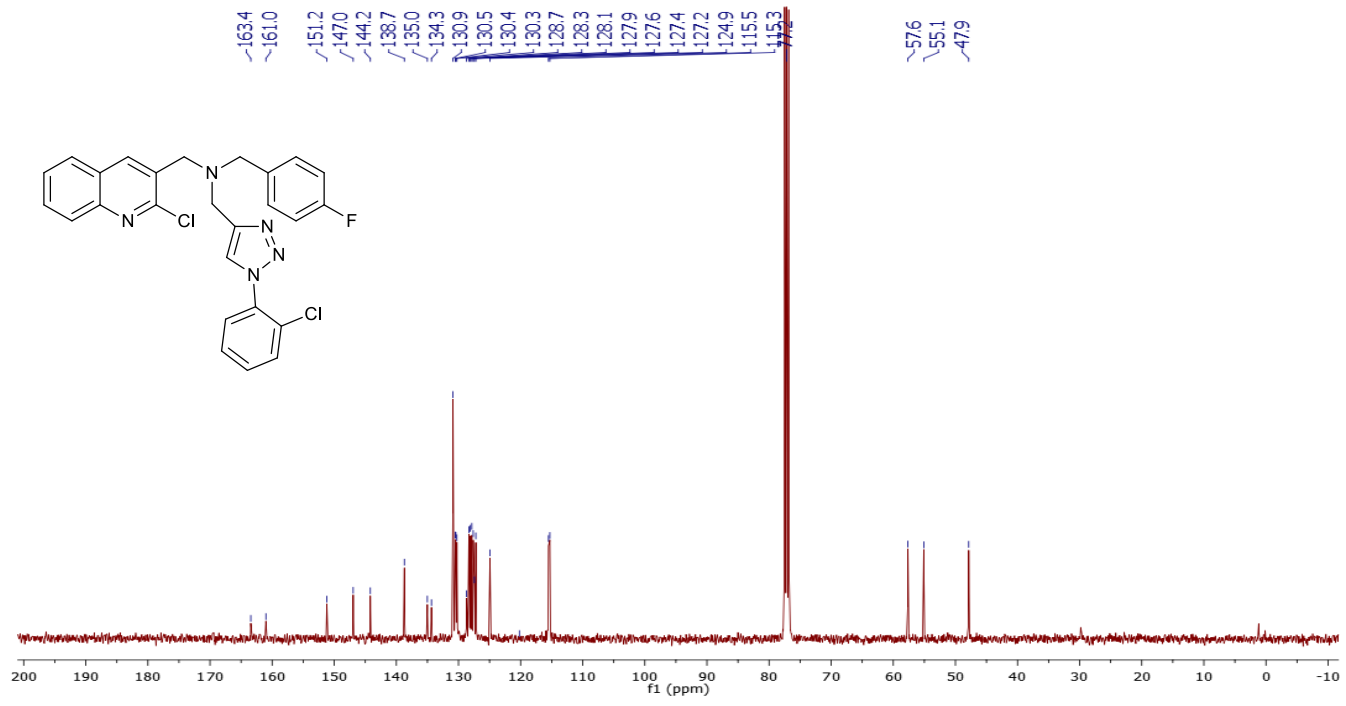
2.1
4.0
2.1
f1 (ppm)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127.2
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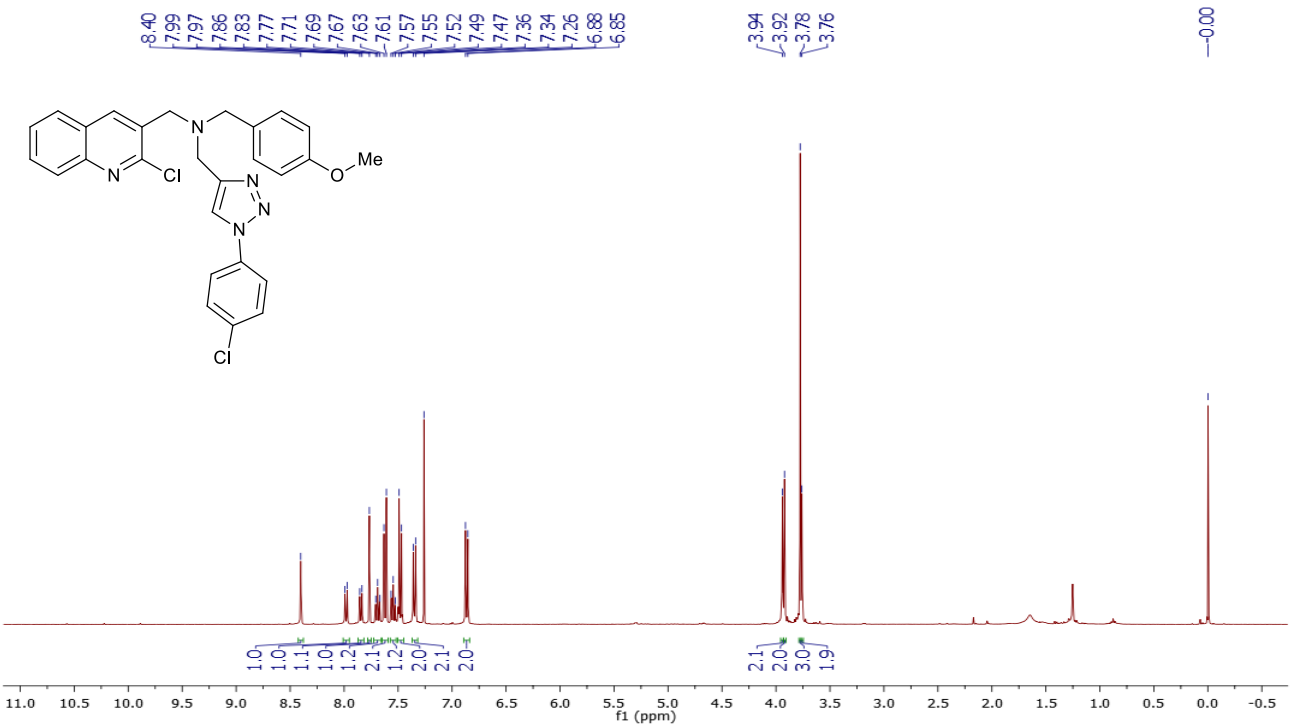
115.5
57.6
55.1
47.9
f1 (ppm)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7.55
7.52
7.49
7.47
7.36
7.34
7.26
6.88
6.85
3.94
3.92
3.78
3.76
0.00
Cl
N
N
N
O
Me
Cl
1.0
1.0
1.1
1.0
1.2
2.1
1.2
2.0
2.1
2.0
2.1
2.0
3.0
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6.5
6.0
5.5
5.0
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2.0
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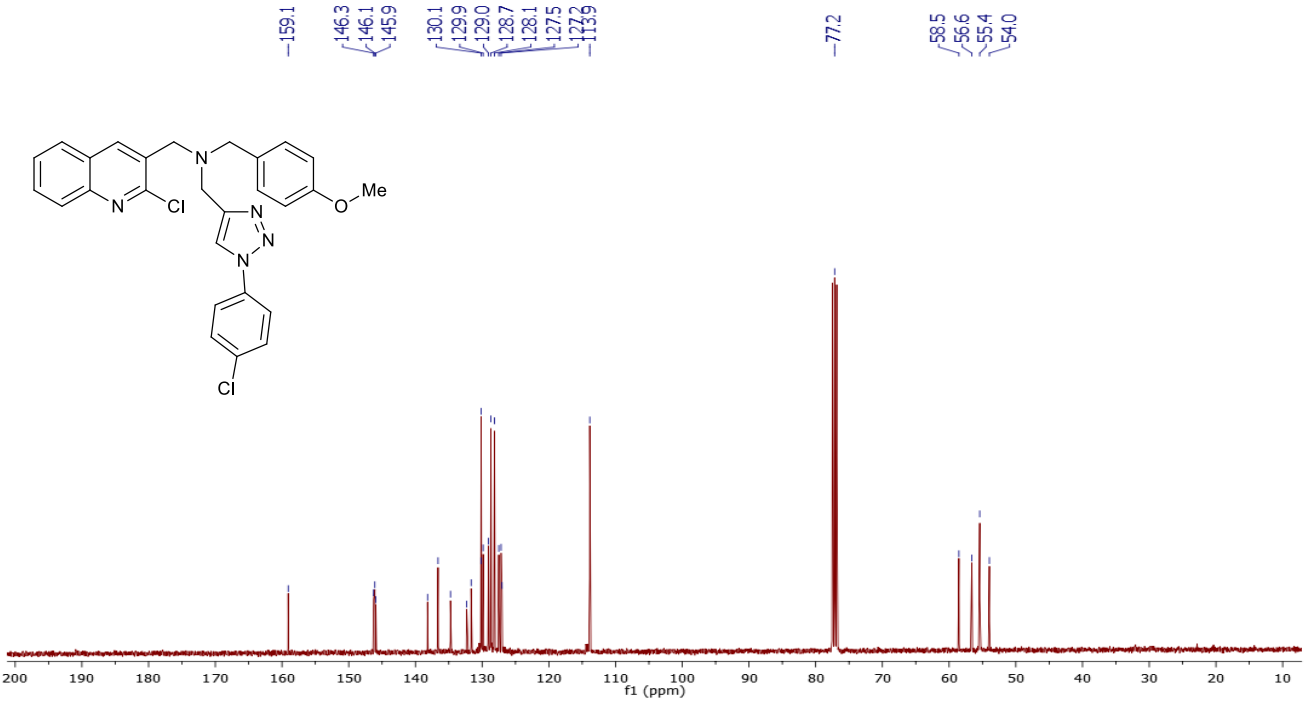
-0.5
f1 (ppm)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146.3
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129.9
129.0
128.7
128.1
127.5
127.2
113.9
77.2
58.5
56.6
55.4
54.0
Cl
N
N
N
O
Me
Cl
200
190
180
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160
150
140
130
120
110
100
90
80
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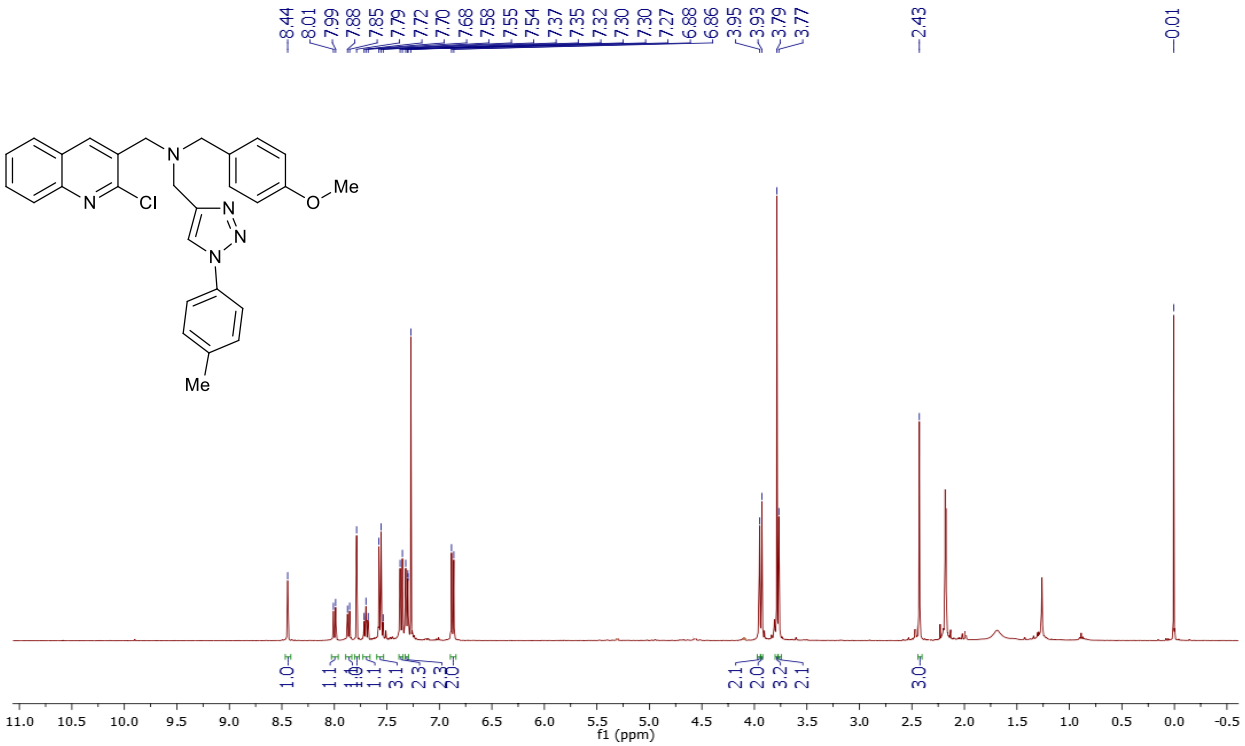
60
50
40
30
20
10
f1 (ppm)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7.37
7.35
7.32
7.30
7.30
7.27
6.88
6.86
3.95
3.93
3.79
3.77
2.43
0.01
Cl
N
O
Me
Me
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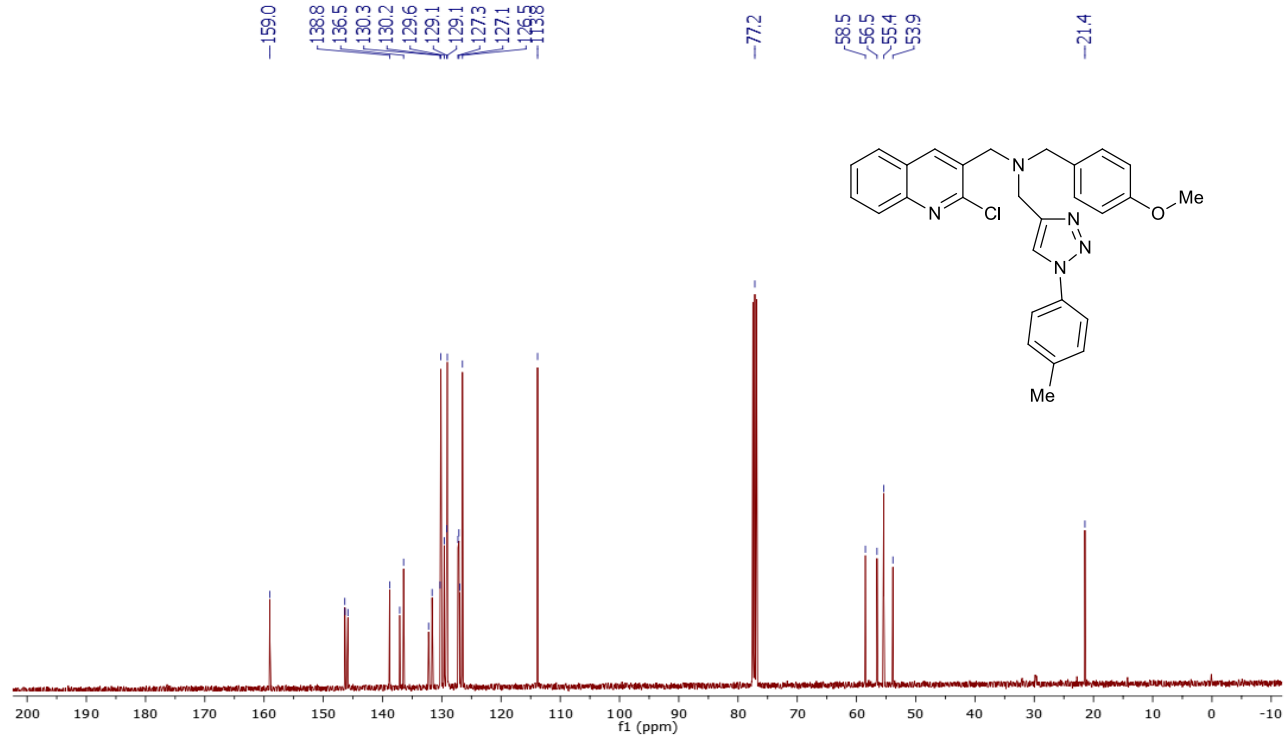
3.1
2.3
2.0
2.1
2.0
3.2
2.1
3.0
f1 (ppm)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136.5
130.3
130.2
129.6
129.1
129.1
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127.1
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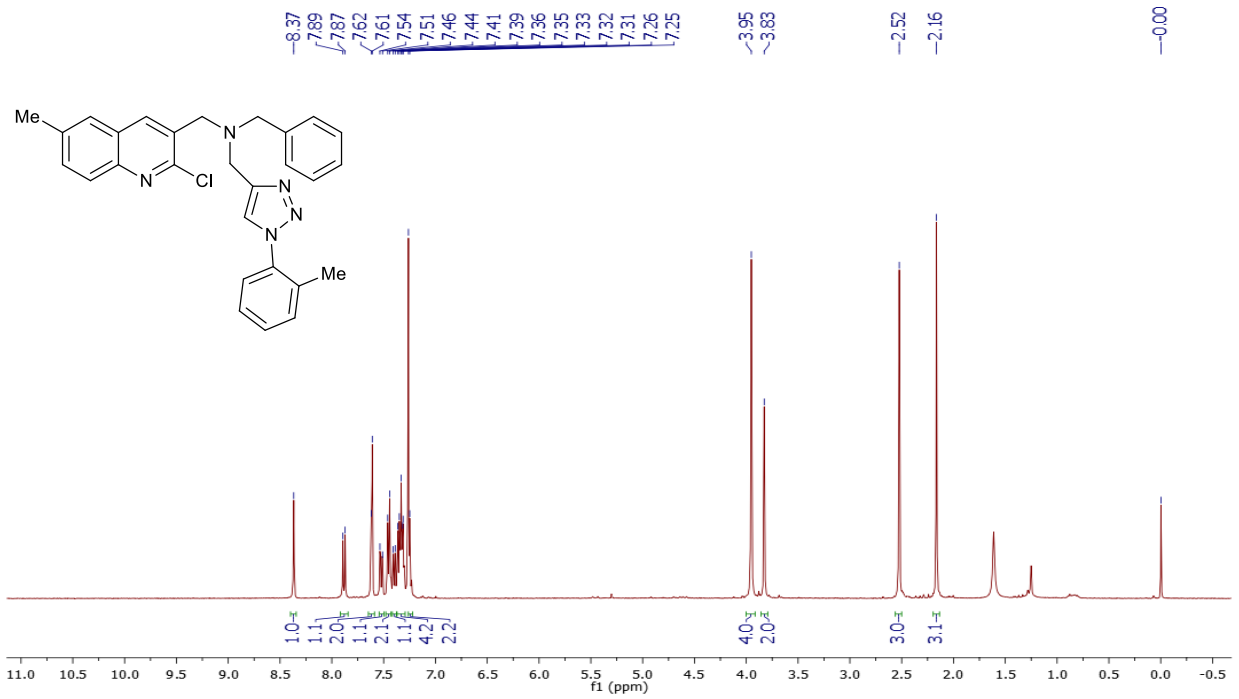
58.5
56.5
55.4
53.9
21.4
Cl
N
O
Me
Me
f1 (ppm)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7.35
7.33
7.32
7.31
7.26
7.25
3.95
3.83
2.52
2.16
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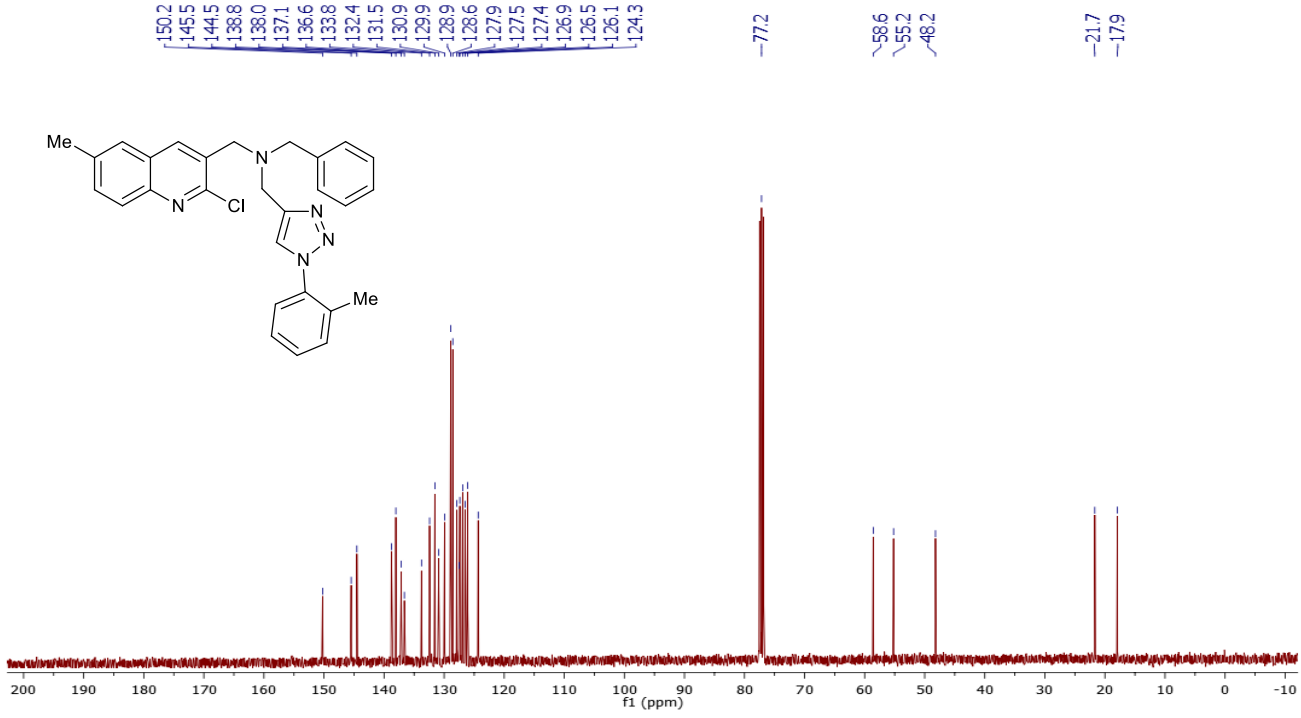
Me
N
Cl
N
N
N
Me
1.0
1.1
2.0
1.1
2.1
1.1
4.2
2.2
4.0
2.0
3.0
3.1
f1 (ppm)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138.8
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137.1
136.6
133.8
132.4
131.5
130.9
129.9
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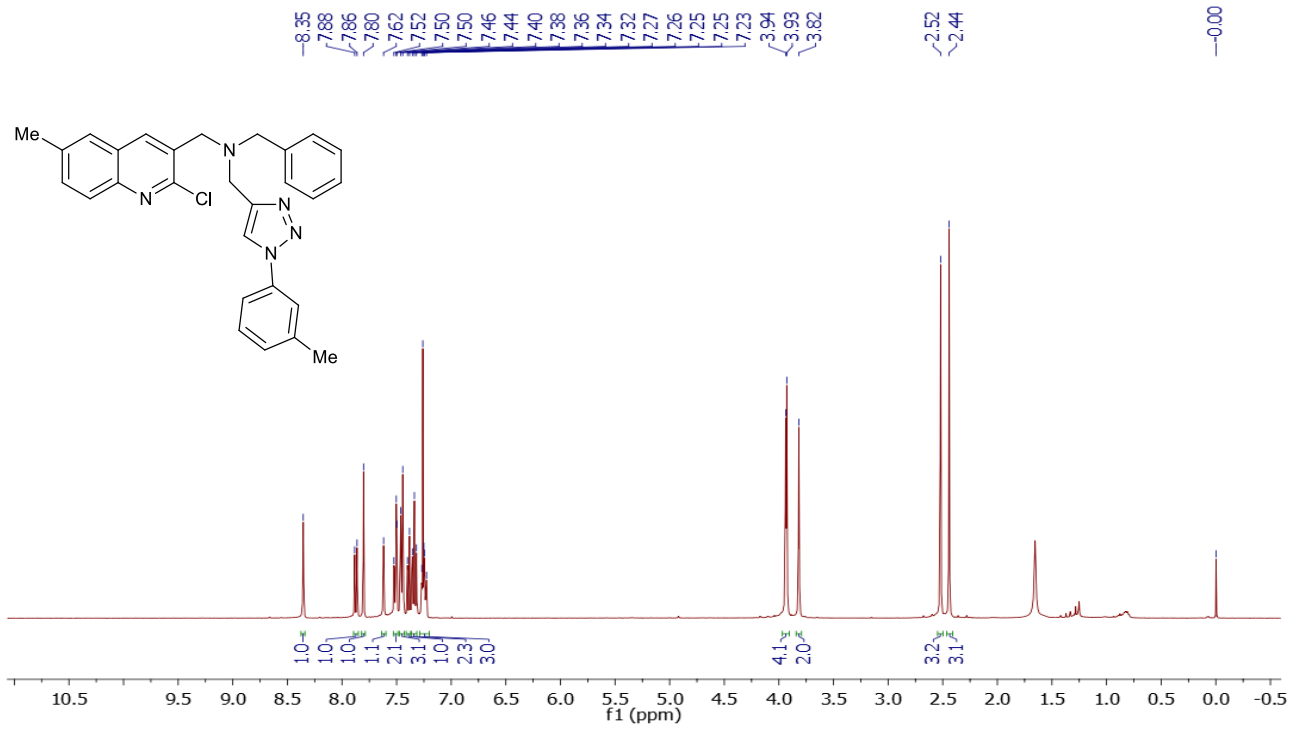
128.6
127.9
127.5
127.4
126.9
126.5
126.1
124.3
77.2
58.6
55.2
48.2
21.7
17.9
Me
N
Cl
N
N
N
Me
f1 (ppm)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7.36
7.34
7.32
7.27
7.26
7.25
7.25
7.23
3.94
3.93
3.82
2.52
2.44
0.00
Me
N
Cl
N
N
N
Me
1.0
1.0
1.0
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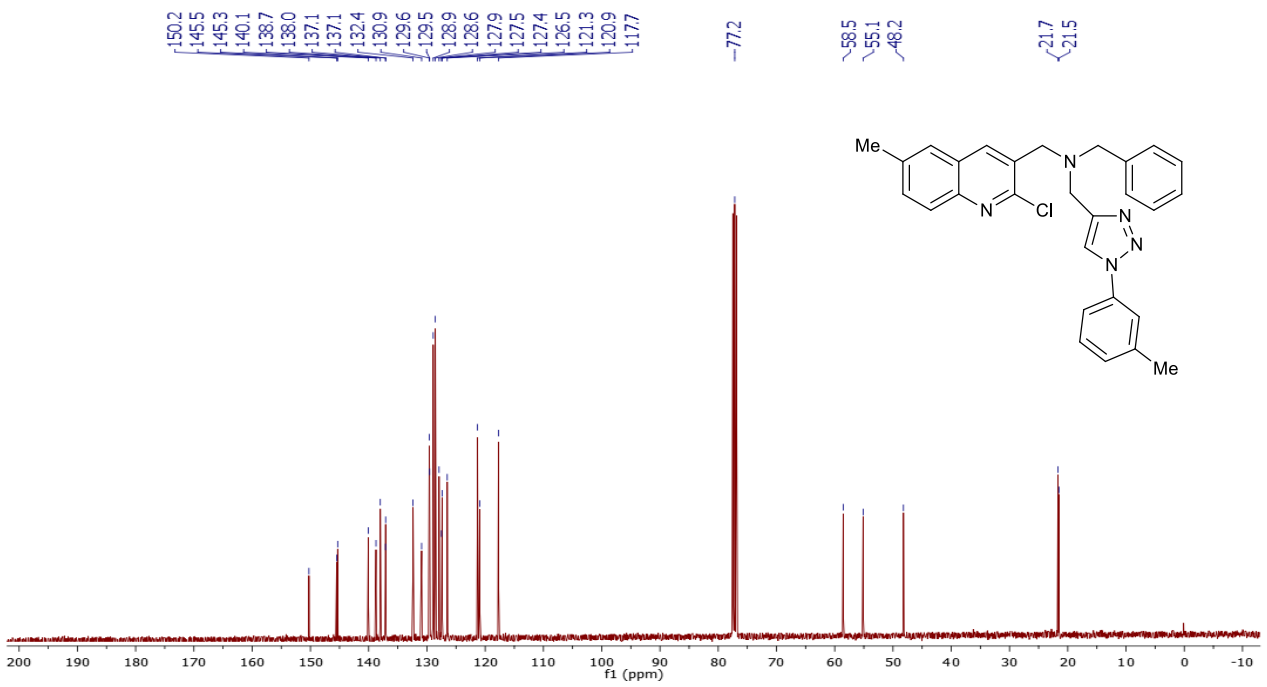
3.1
1.0
2.3
3.0
4.1
2.0
3.2
3.1
f1 (ppm)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129.6
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128.9
128.6
127.9
127.5
127.4
126.5
121.3
120.9
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77.2
58.5
55.1
48.2
21.7
21.5
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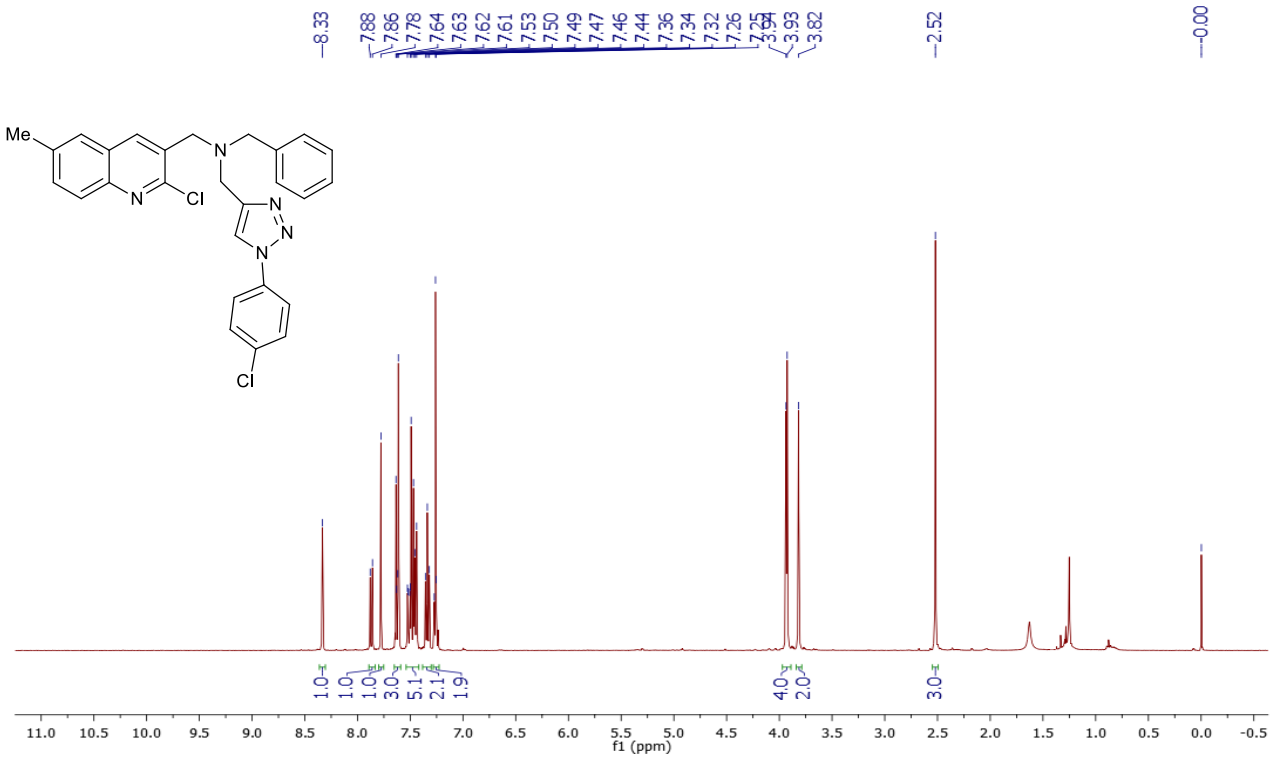
N
Cl
N
N
N
Me
f1 (ppm)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7.44
7.36
7.34
7.32
7.26
3.94
3.93
3.82
2.52
0.00
Me
N
Cl
N
N
N
Cl
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1.0
1.0
3.0
5.1
2.1
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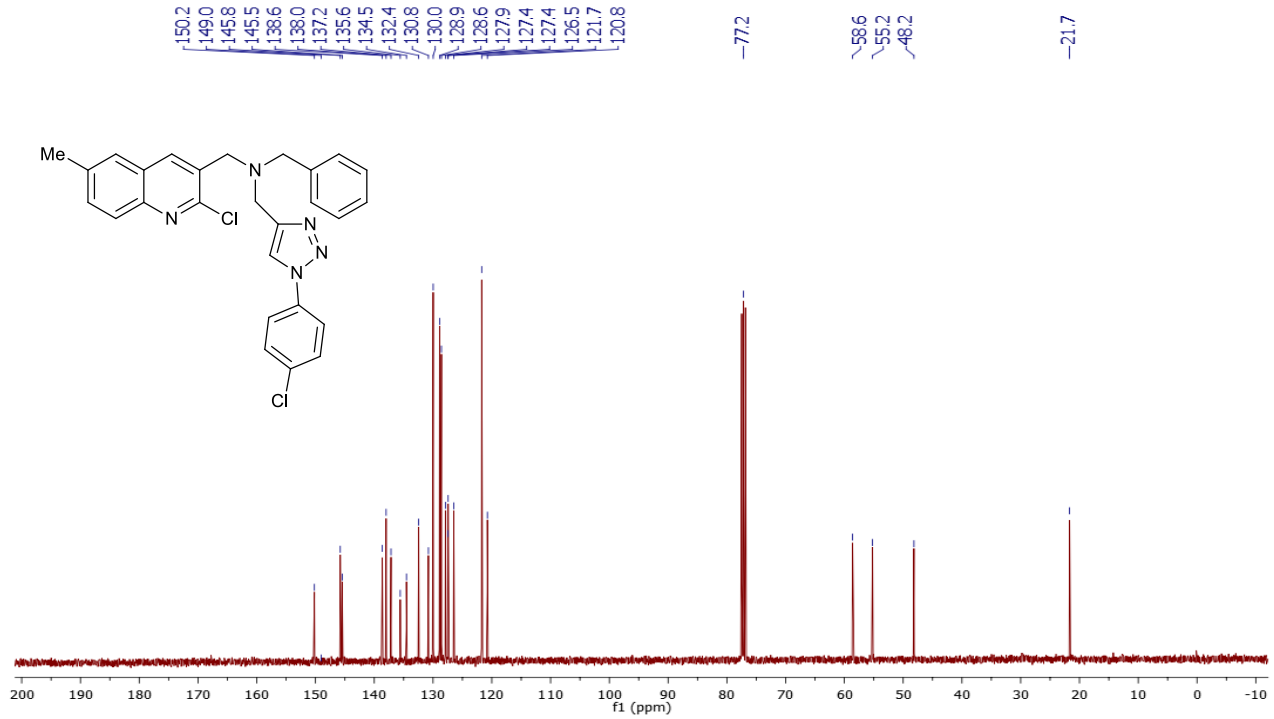
4.0
2.0
3.0
f1 (ppm)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145.5
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138.0
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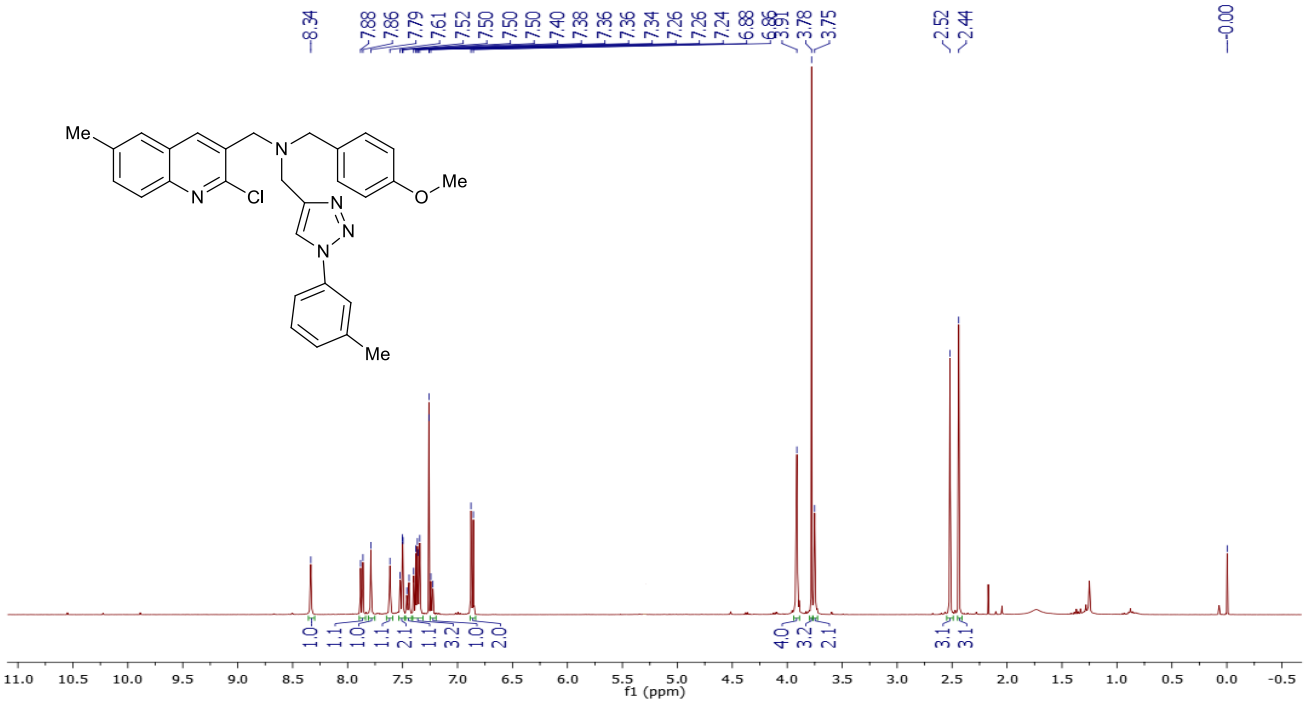
132.4
130.8
130.0
128.9
128.6
127.9
127.4
127.4
126.5
121.7
120.8
77.2
58.6
55.2
48.2
21.7
Me
N
Cl
N
N
N
Cl
f1 (ppm)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Cl
N
O
Me
N
N
N
Me
1.0
1.1
1.0
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3.2
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6.5
6.0
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5.0
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0.5
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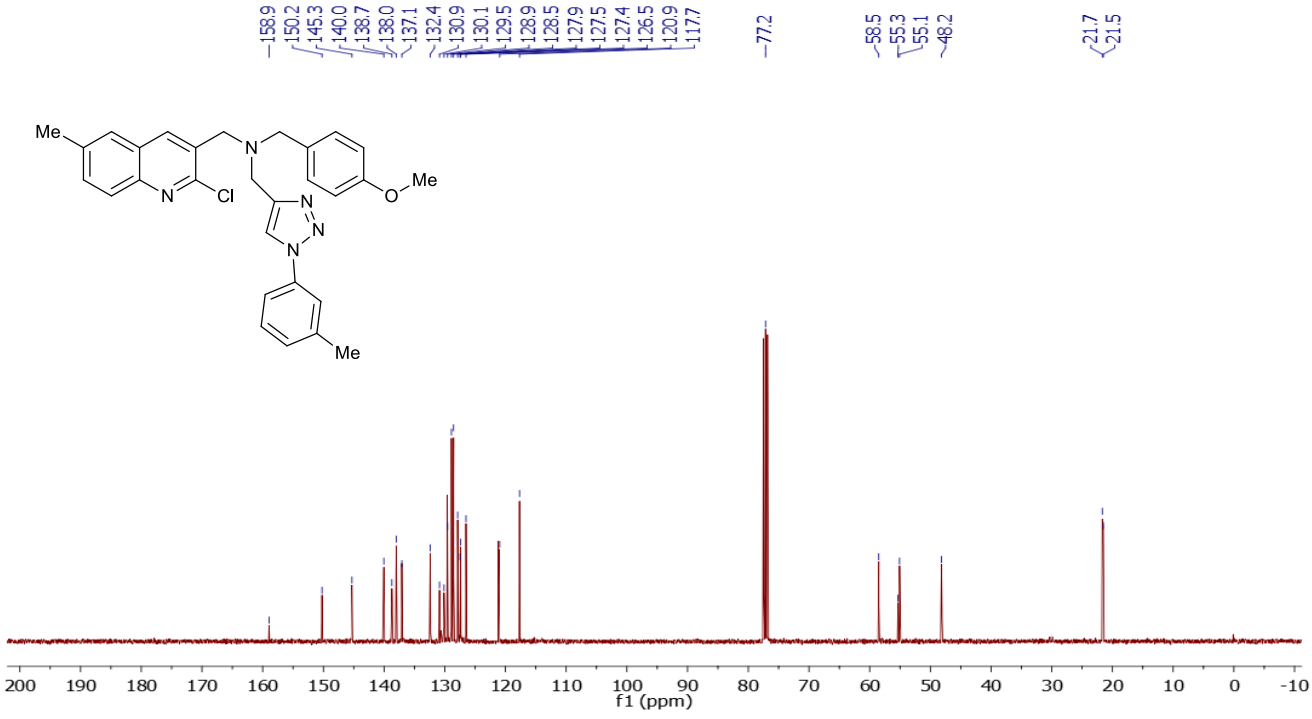
f1 (ppm)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127.5
127.4
126.5
120.9
117.7
77.2
58.5
55.3
55.1
48.2
21.7
21.5
Me
N
Cl
N
O
Me
N
N
N
Me
200
190
180
170
160
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140
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120
110
100
90
80
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60
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40
30
20
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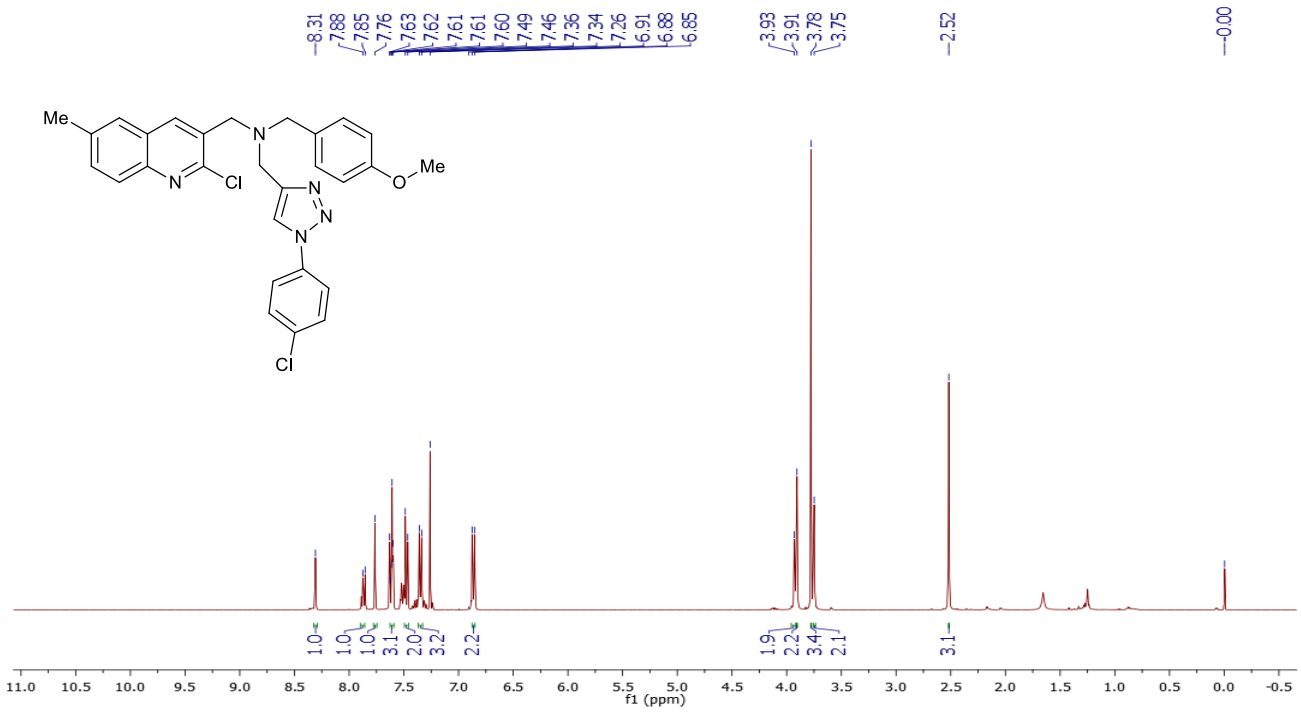
0
-10
f1 (ppm)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6.88
6.85
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3.91
3.78
3.75
2.52
0.00
Me
N
Cl
N
N
N
O
Me
Cl
1.0
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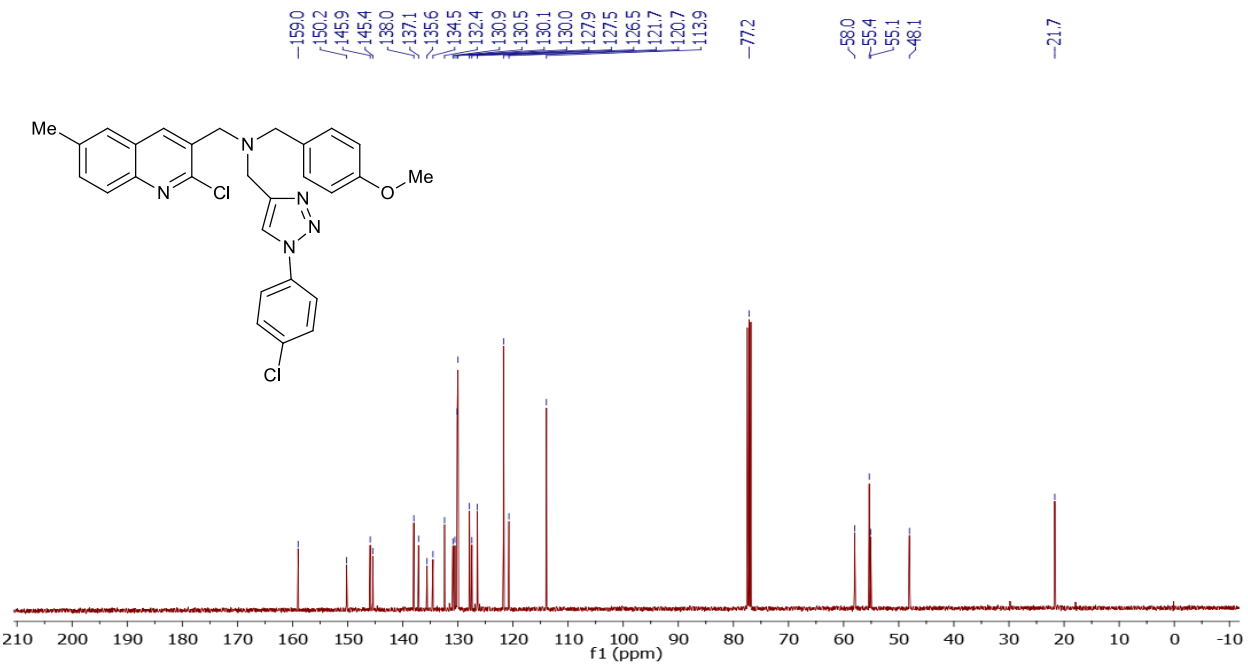
3.4
2.1
3.1
f1 (ppm)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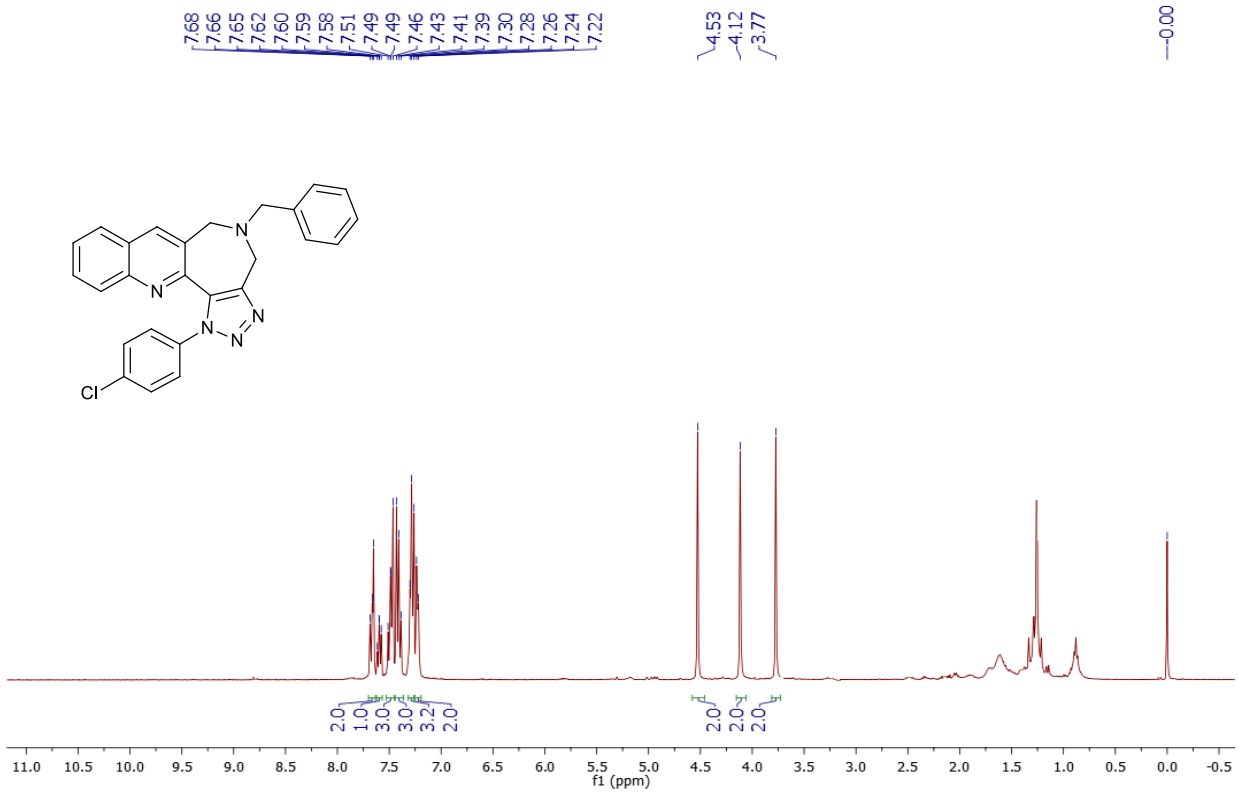
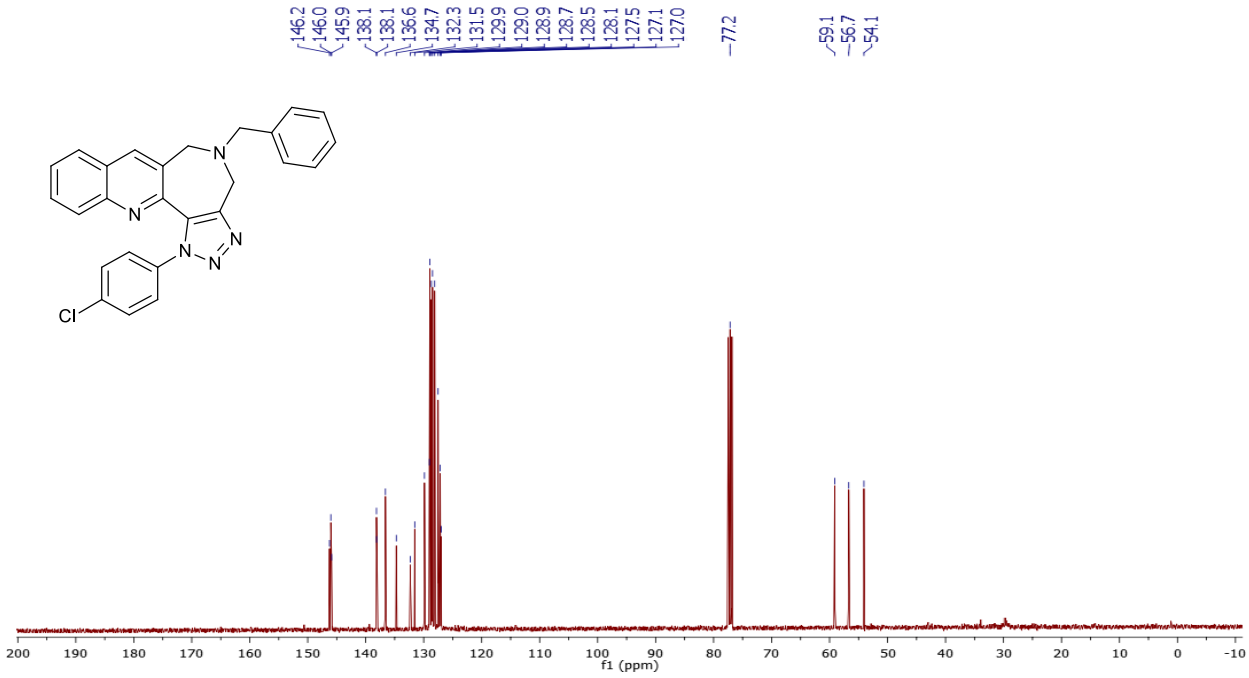
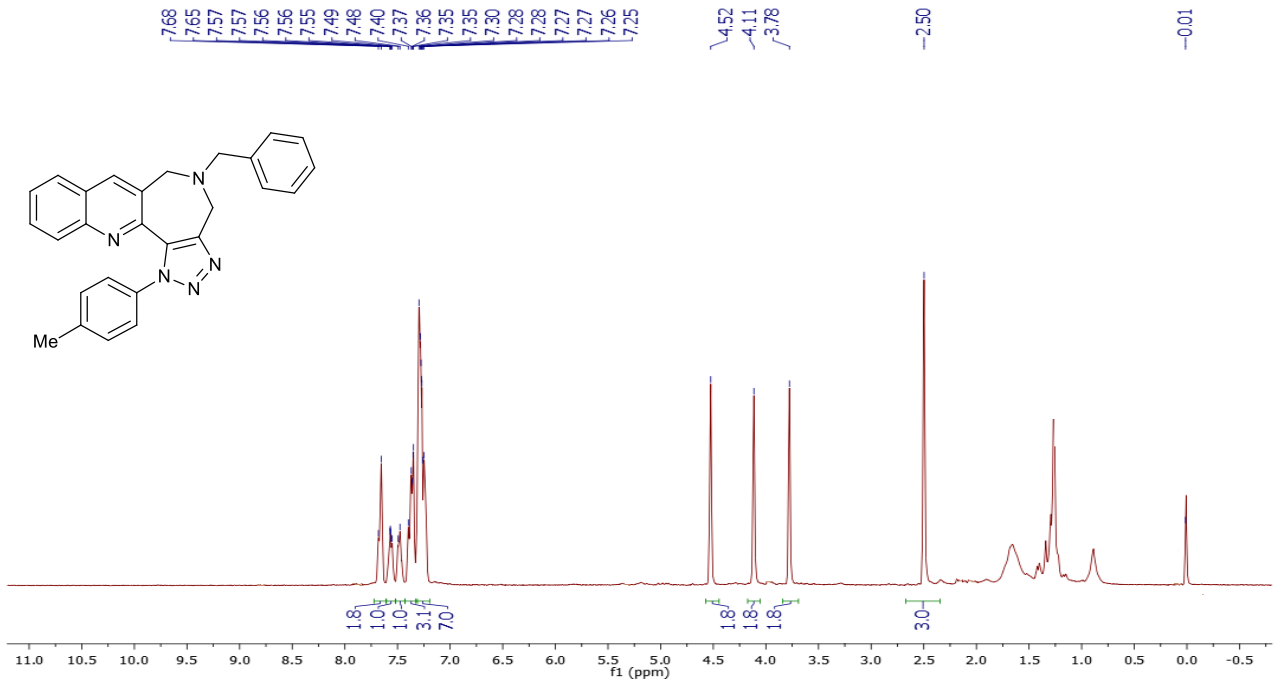
130.0
127.9
127.5
126.5
121.7
120.7
113.9
77.2
58.0
55.4
55.1
48.1
21.7
Me
N
Cl
N
N
N
O
Me
Cl
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of the compounds (6a-m)



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7.35
7.30
7.28
7.28
7.27
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7.26
7.25
4.52
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1.0
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1.8
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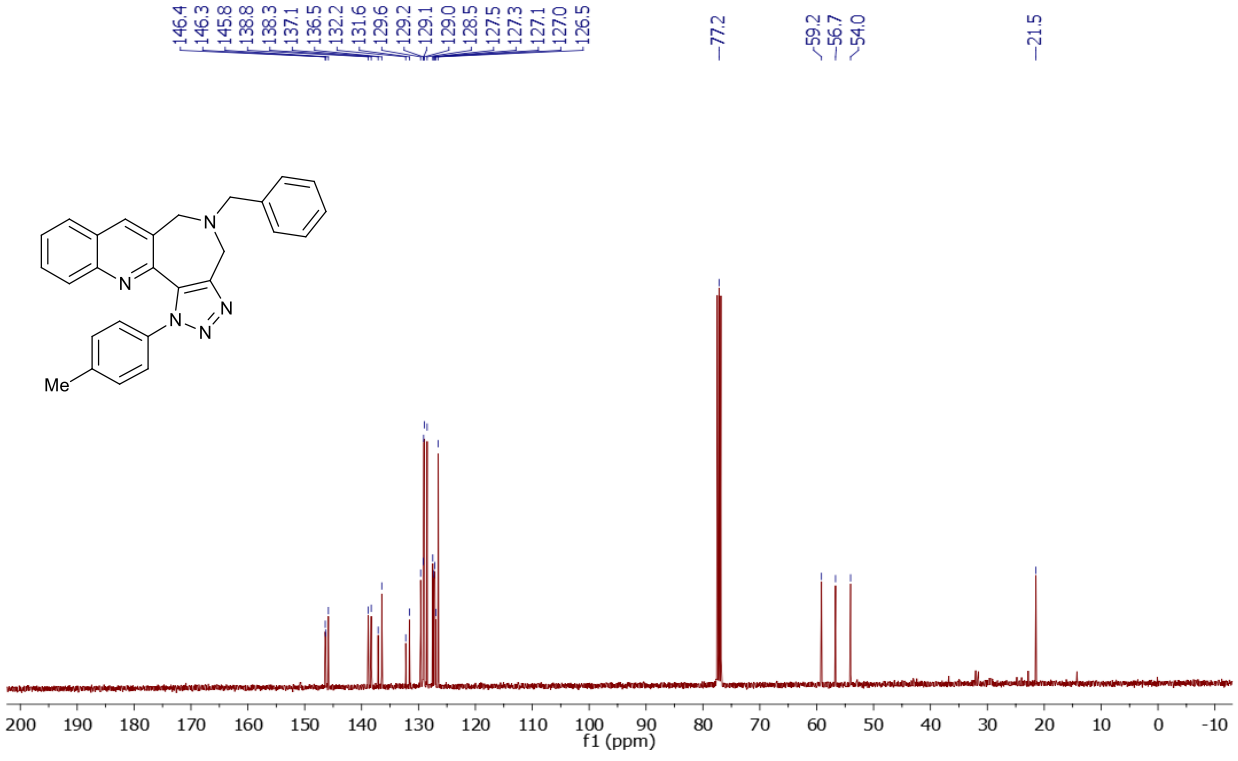
3.0
f1 (ppm)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129.0
128.5
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77.2
59.2
56.7
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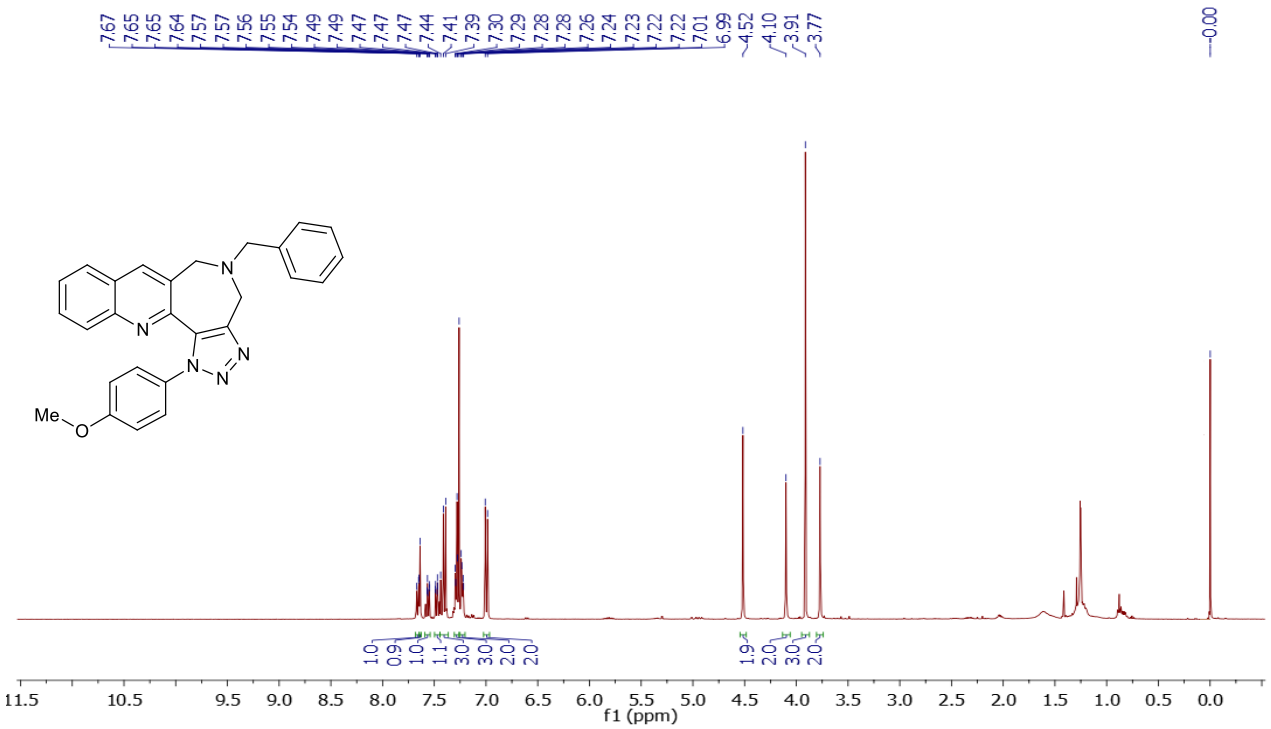
Me
f1 (ppm)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7.26
7.24
7.23
7.22
7.22
7.01
6.99
4.52
4.10
3.91
3.77
0.00
N
N
N
N
Me
O
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0.9
1.0
1.1
3.0
3.0
2.0
2.0
1.9
2.0
3.0
2.0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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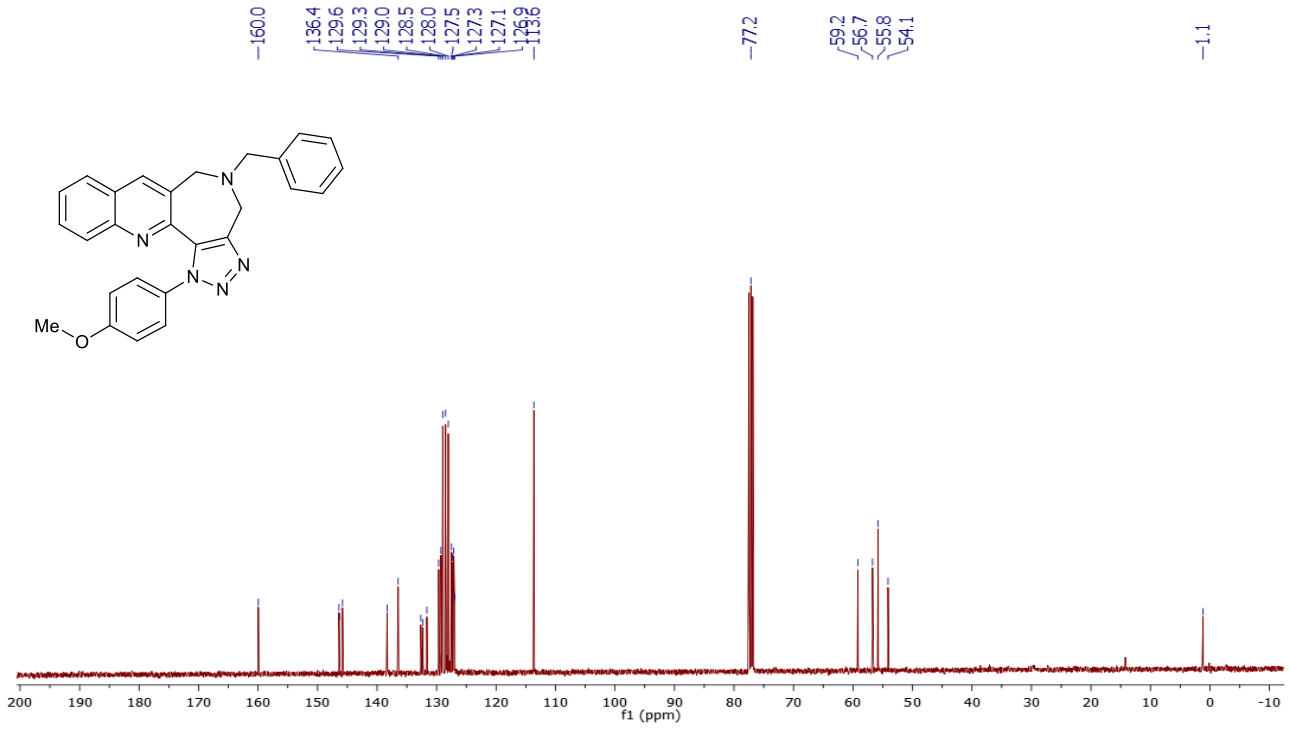
0.0
f1 (ppm)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127.1
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59.2
56.7
55.8
54.1
1.1
N
N
N
N
Me
O
200
190
180
170
160
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120
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100
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80
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40
30
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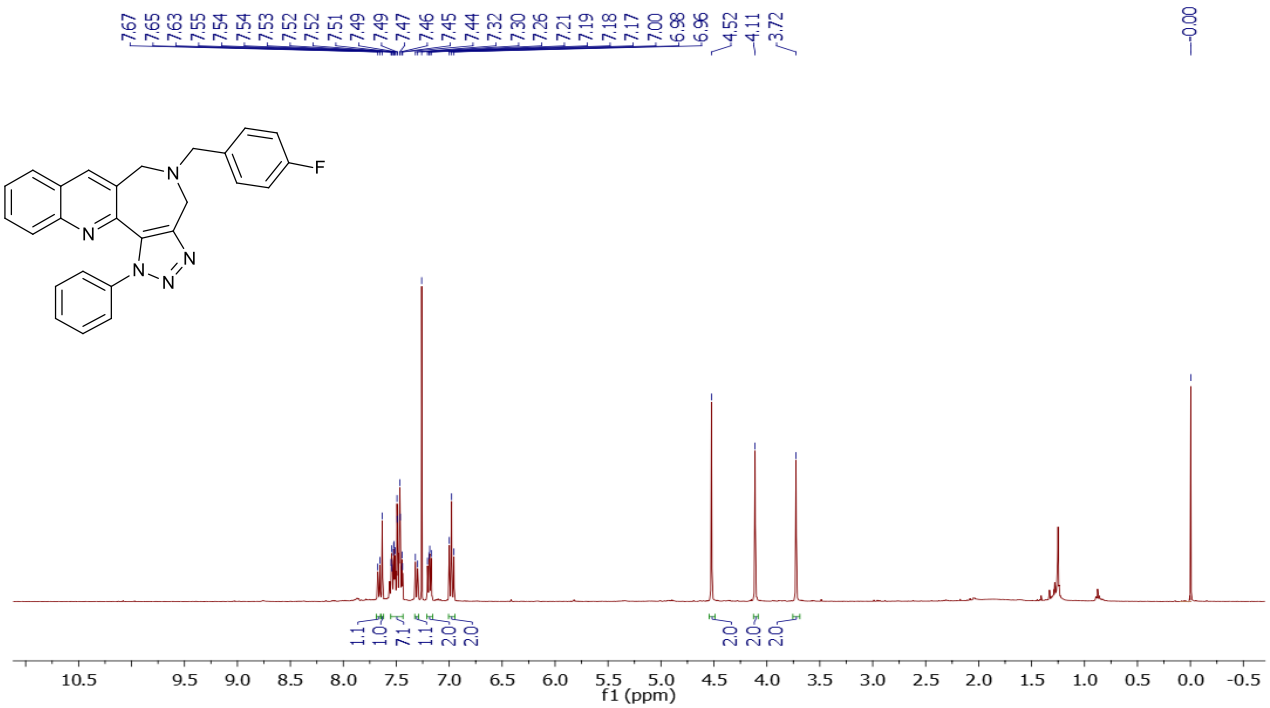
-10
f1 (ppm)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7.47
7.46
7.45
7.44
7.32
7.30
7.26
7.21
7.19
7.18
7.17
7.00
6.98
6.96
4.52
4.11
3.72
0.00
F
N
N
N
N
1.1
1.0
7.1
1.1
2.0
2.0
2.0
2.0
2.0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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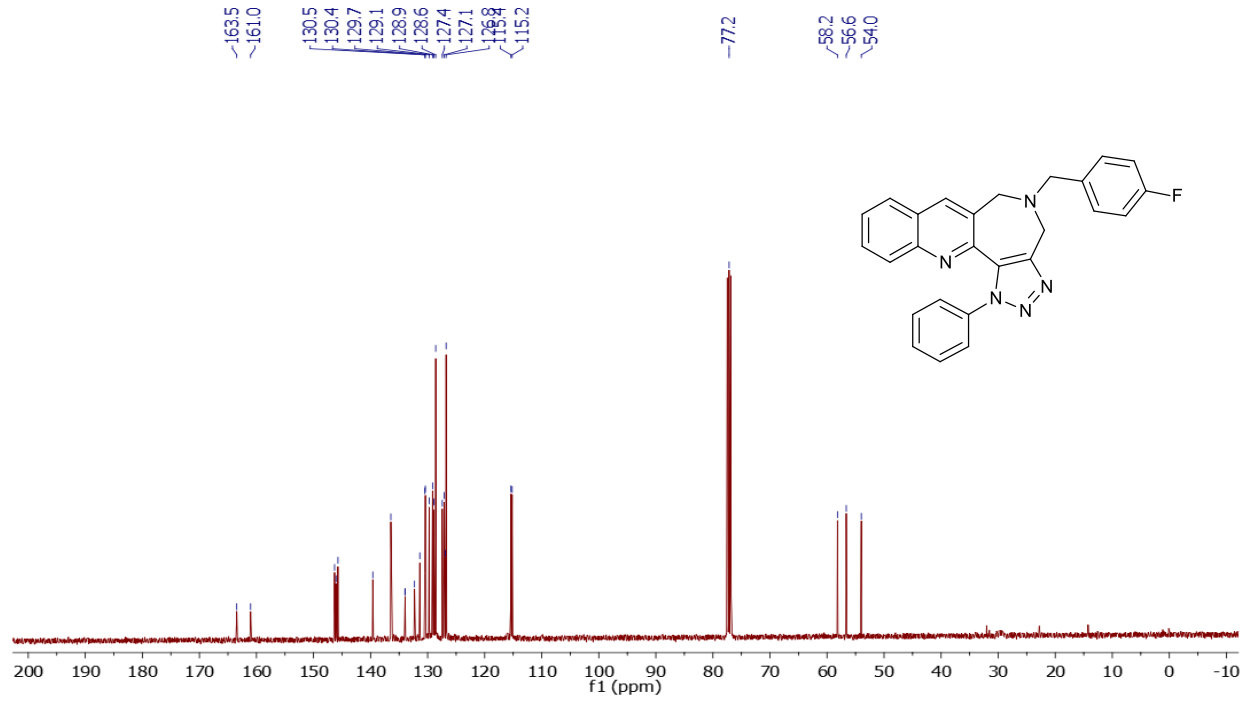
-0.5
f1 (ppm)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127.1
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77.2
58.2
56.6
54.0
F
N
N
N
N
200
190
180
170
160
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140
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120
110
100
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80
70
60
50
40
30
20
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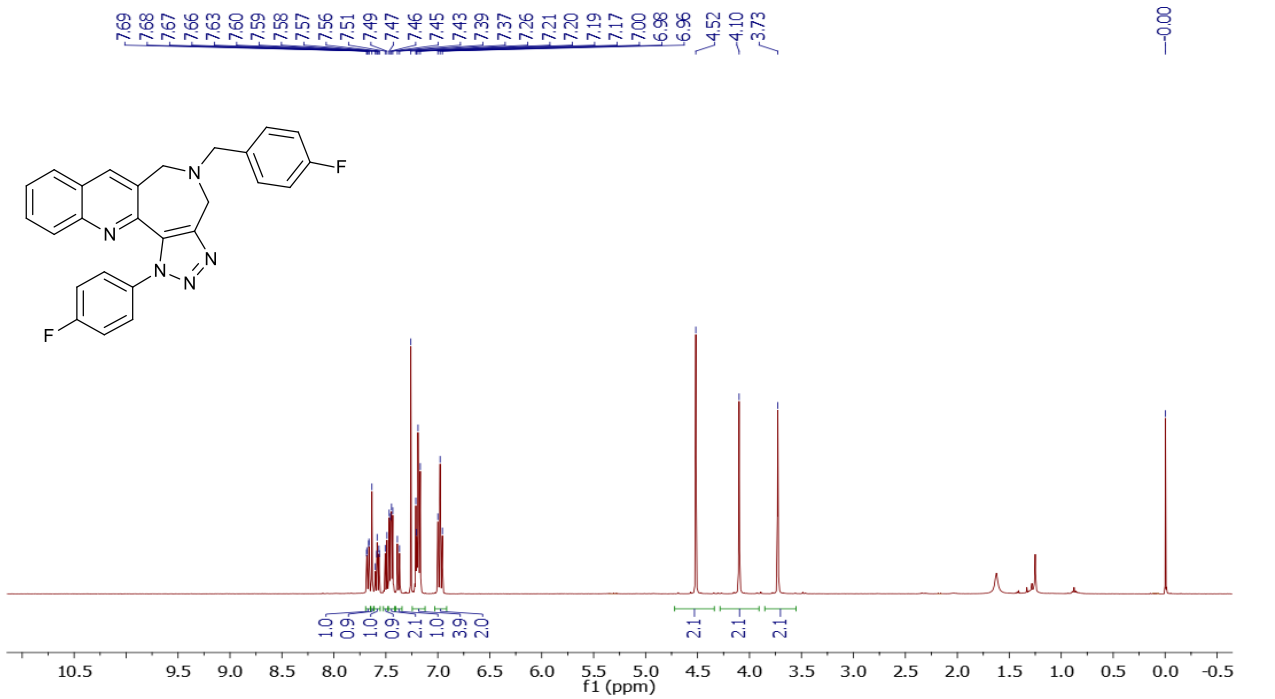
0
-10
f1 (ppm)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7.49
7.47
7.46
7.45
7.43
7.39
7.37
7.26
7.21
7.20
7.19
7.17
7.00
6.98
6.96
4.52
4.10
3.73
0.00
F
N
N
N
N
F
1.0
0.9
1.0
0.9
2.1
1.0
3.9
2.0
2.1
2.1
2.1
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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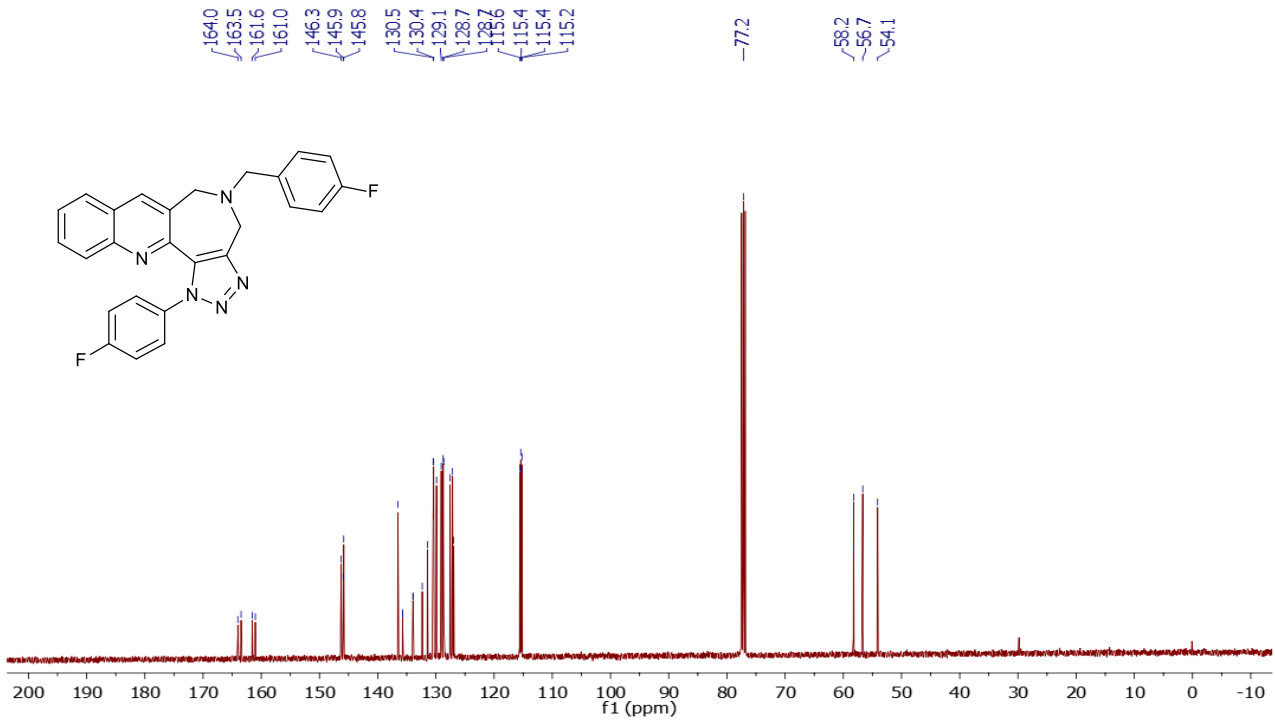
0.0
-0.5
f1 (ppm)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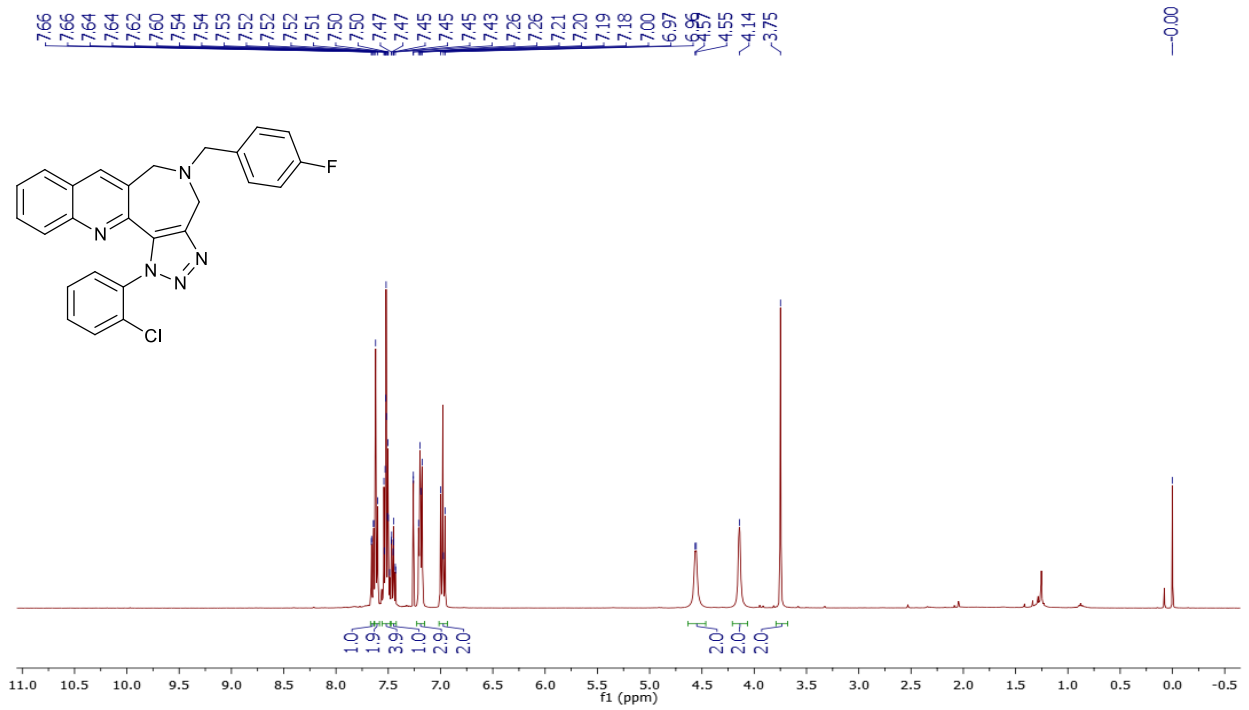
129.1
128.7
128.7
115.6
115.4
115.4
115.2
77.2
58.2
56.7
54.1
F
N
N
N
N
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.52
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7.52
7.51
7.50
7.50
7.47
7.47
7.45
7.45
7.45
7.43
7.26
7.26
7.21
7.20
7.19
7.18
7.00
6.97
4.55
4.14
3.75
0.00
F
N
N
N
N
Cl
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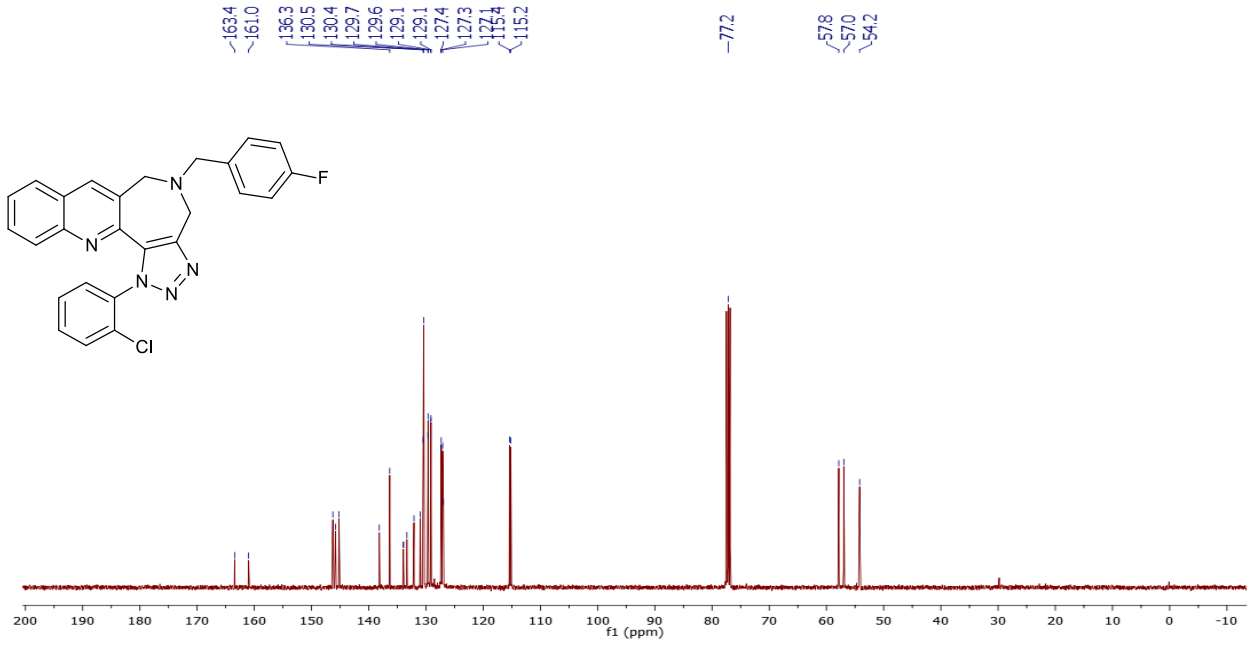
1.9
3.9
1.0
2.9
2.0
2.0
2.0
2.0
f1 (ppm)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129.1
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127.3
77.2
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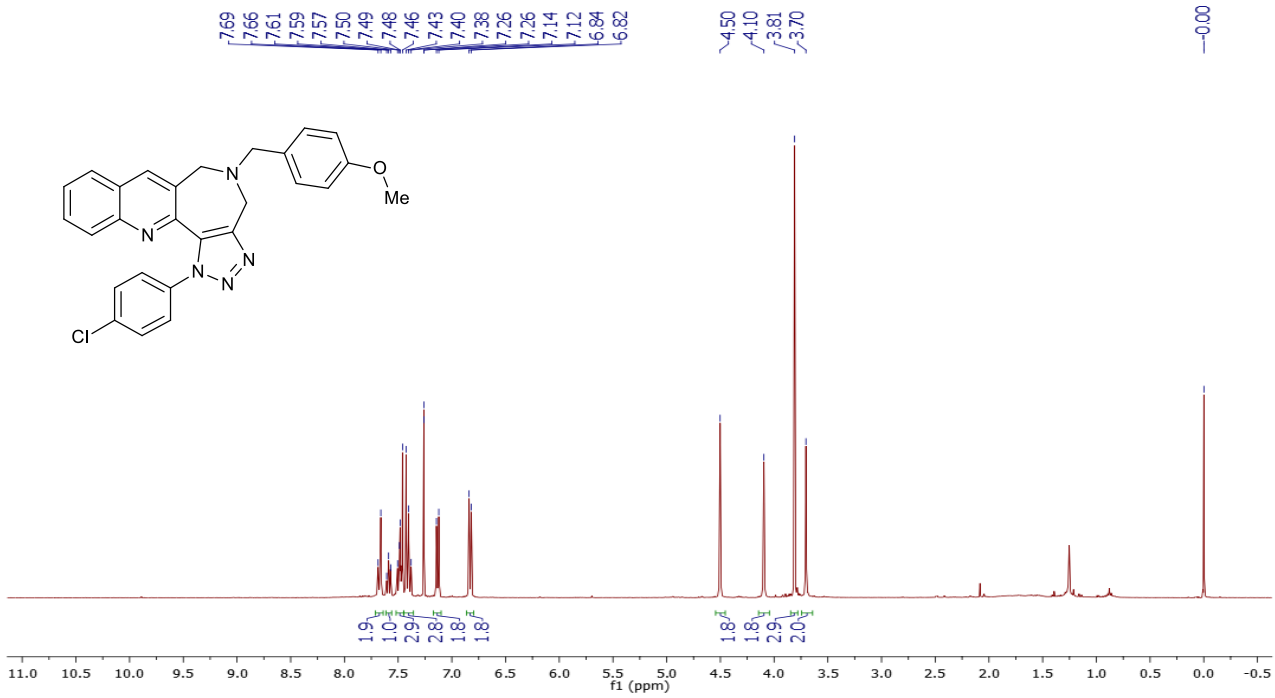
57.0
54.2
F
N
N
N
N
Cl
f1 (ppm)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7.46
7.43
7.40
7.38
7.26
7.25
7.14
7.12
6.84
6.82
4.50
4.10
3.81
3.70
0.00
O
Me
N
N
N
N
Cl
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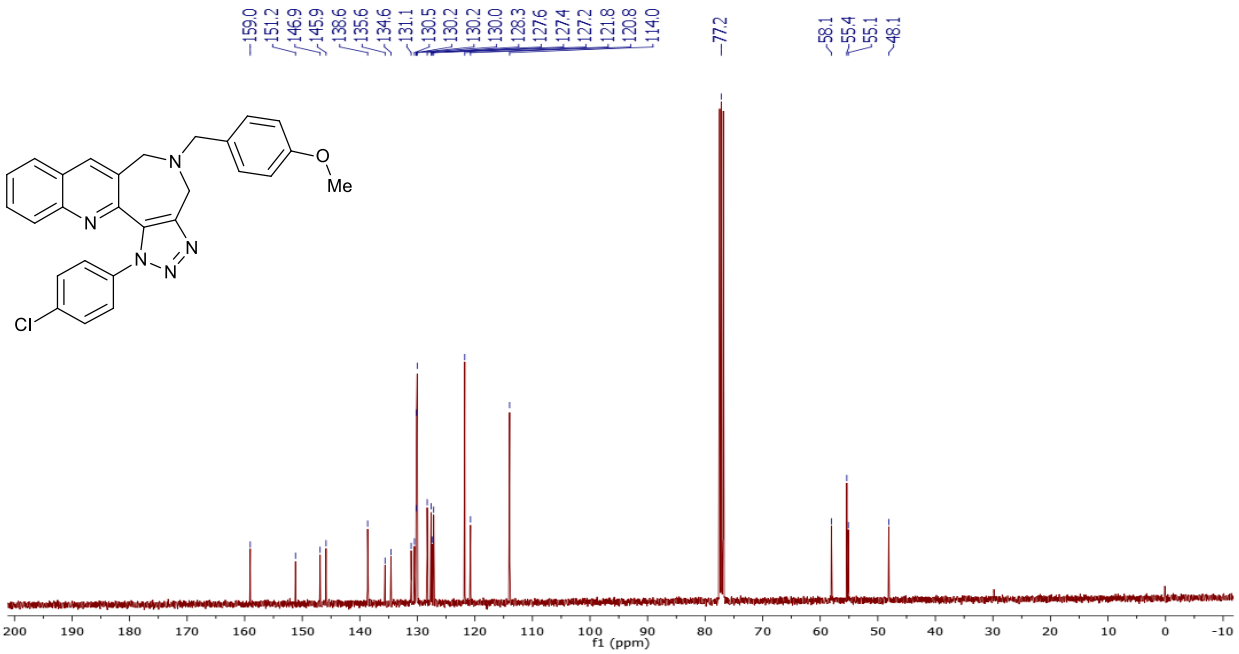
2.9
2.8
1.8
1.8
1.8
1.8
2.9
2.0
f1 (ppm)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145.9
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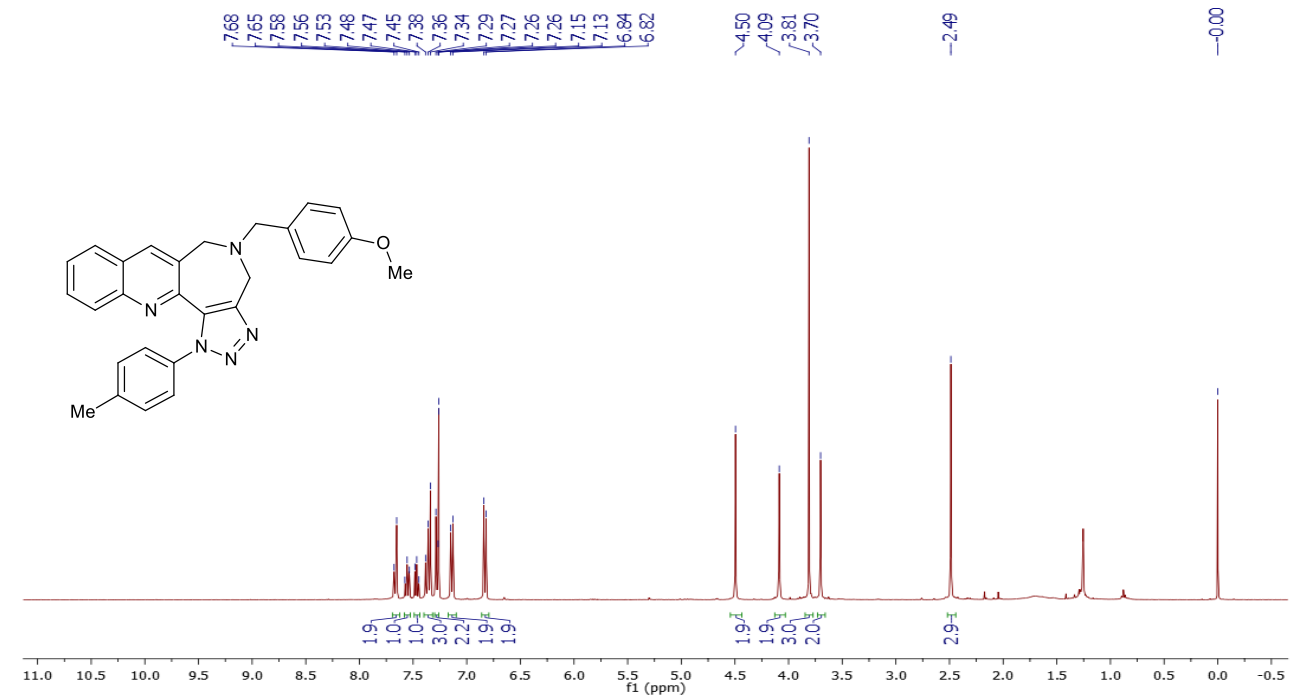
130.2
130.2
130.0
128.3
127.6
127.4
127.2
121.8
120.8
114.0
77.2
58.1
55.4
55.1
48.1
O
Me
N
N
N
N
Cl
f1 (ppm)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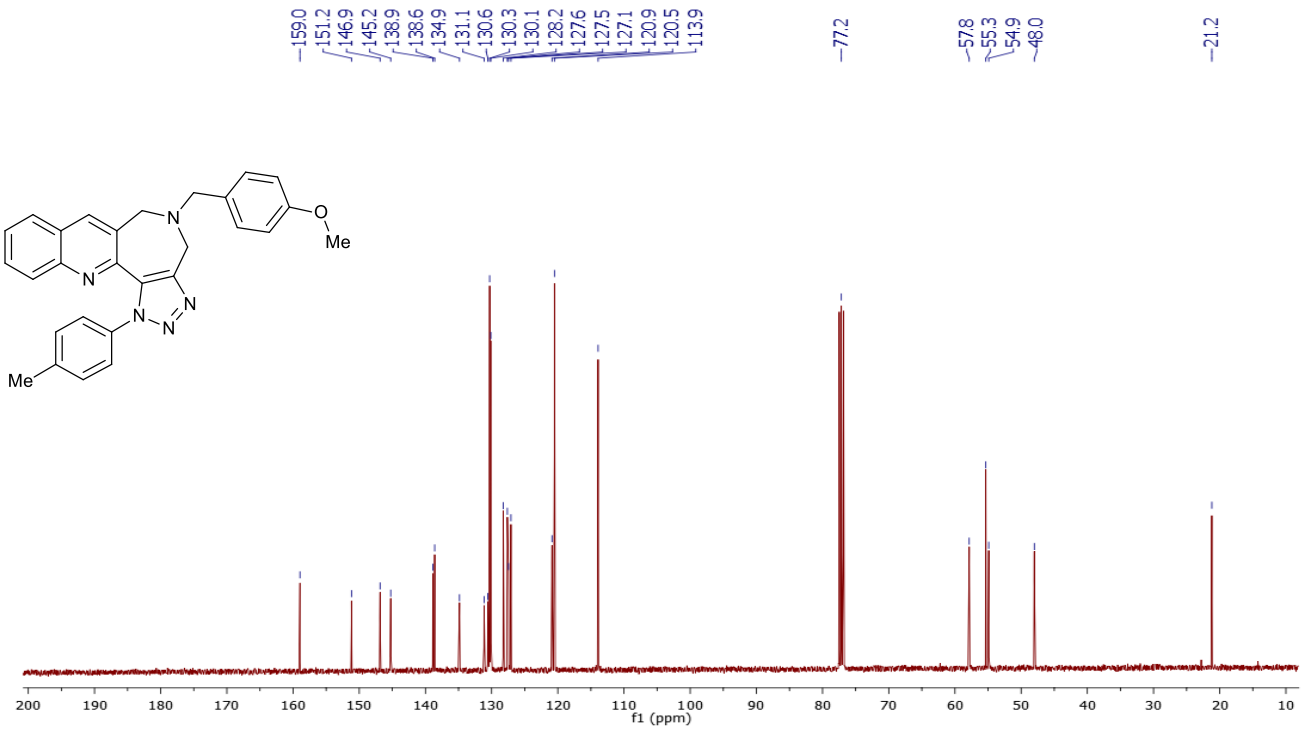
7.29
7.27
7.26
7.26
7.15
7.13
6.84
6.82
4.50
4.09
3.81
3.70
2.49
0.00
Me
Me
1.9
1.0
1.0
3.0
2.2
1.9
1.9
1.9
1.9
3.0
2.0
2.9
f1 (ppm)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145.2
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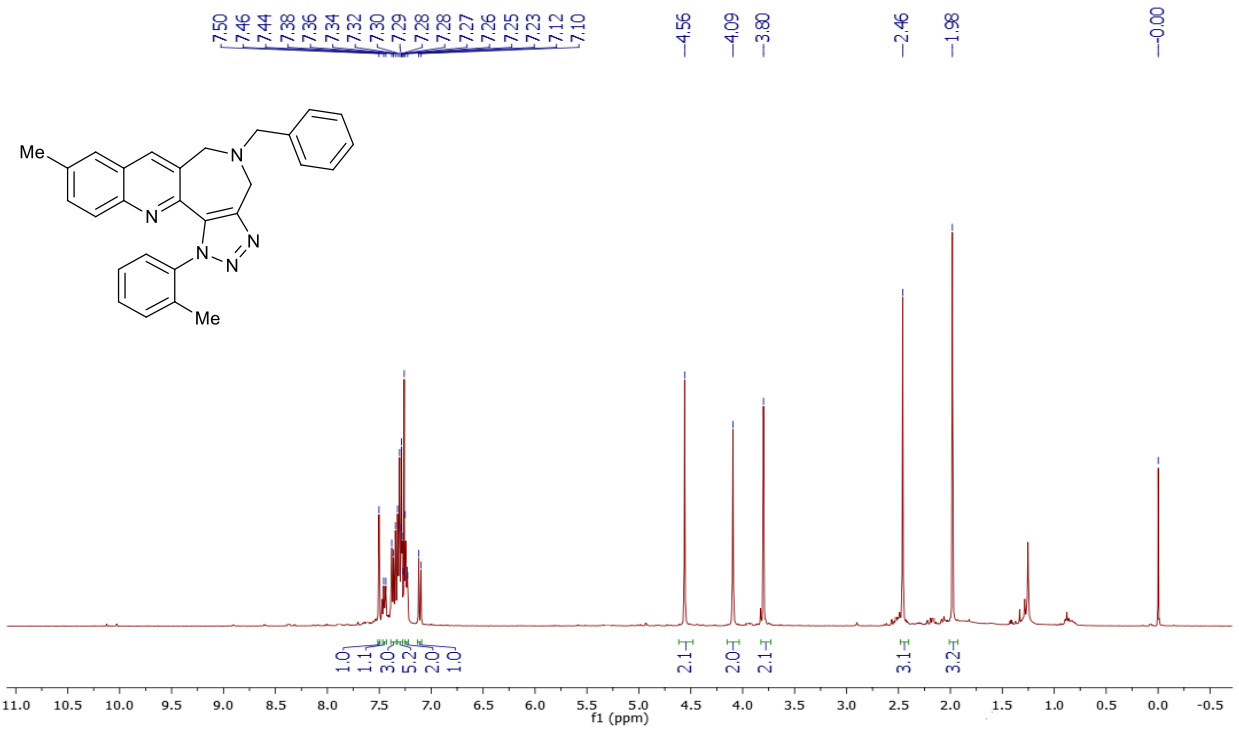
138.6
134.9
131.1
130.6
130.3
130.1
128.2
127.6
127.5
127.1
120.9
120.5
113.9
77.2
57.8
55.3
54.9
48.0
21.2
Me
Me
f1 (ppm)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7.32
7.30
7.29
7.28
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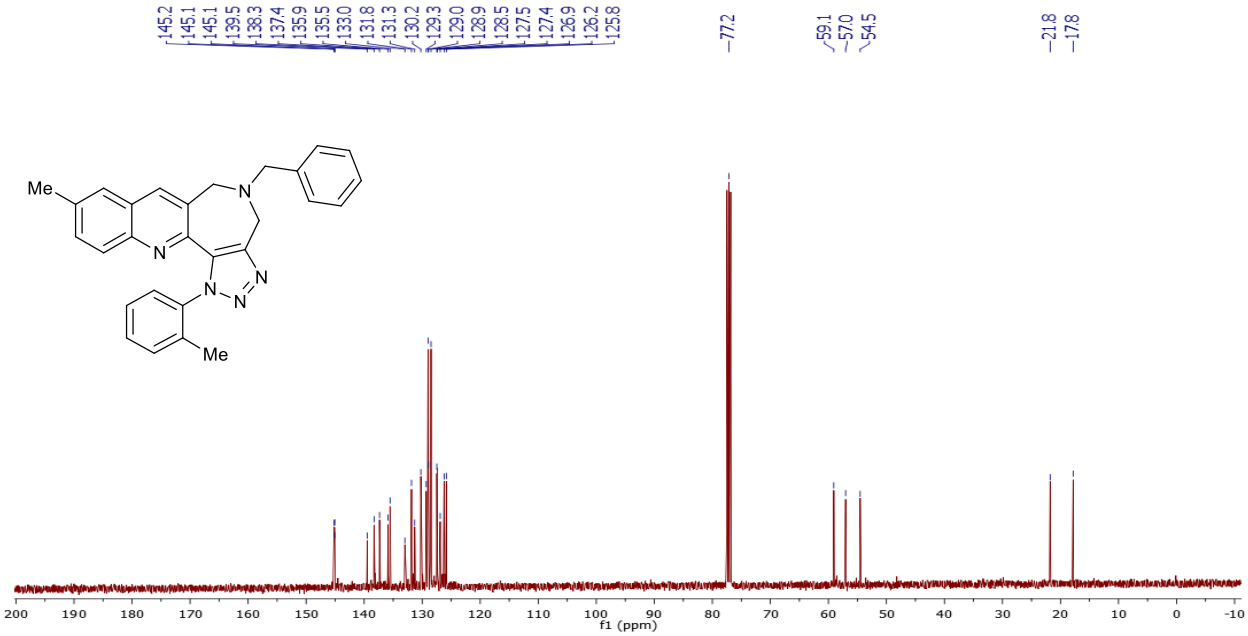
7.27
7.26
7.25
7.23
7.12
7.10
4.56
4.09
3.80
2.46
1.98
0.00
Me
N
N
N
N
Me
1.0
1.1
3.0
5.2
2.0
1.0
2.1
2.0
2.1
3.1
3.2
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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145.1
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135.5
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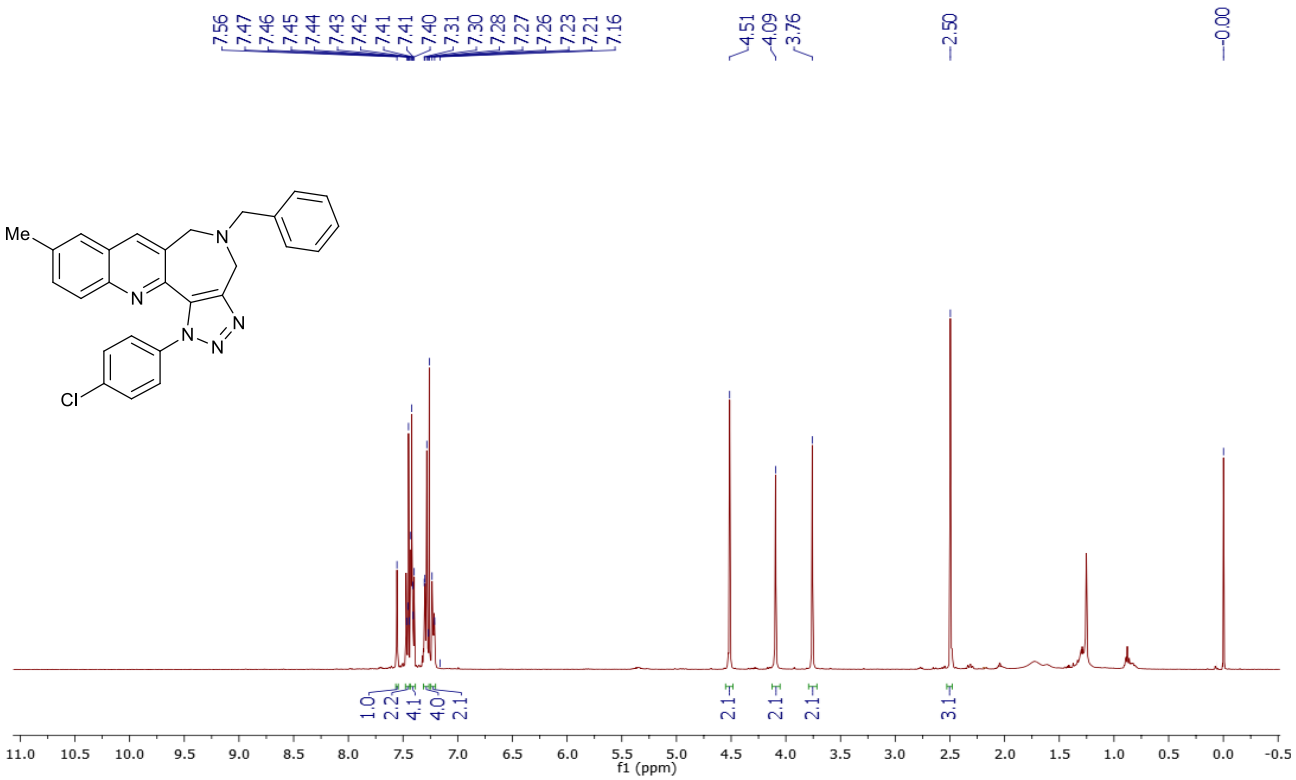
131.8
131.3
130.2
129.3
129.0
128.9
128.5
127.5
127.4
126.9
126.2
125.8
77.2
59.1
57.0
54.5
21.8
17.8
Me
N
N
N
N
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.42
7.41
7.41
7.40
7.31
7.30
7.28
7.27
7.26
7.23
7.21
7.16
4.51
4.09
3.76
2.50
0.00
Me
N
N
N
N
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Cl
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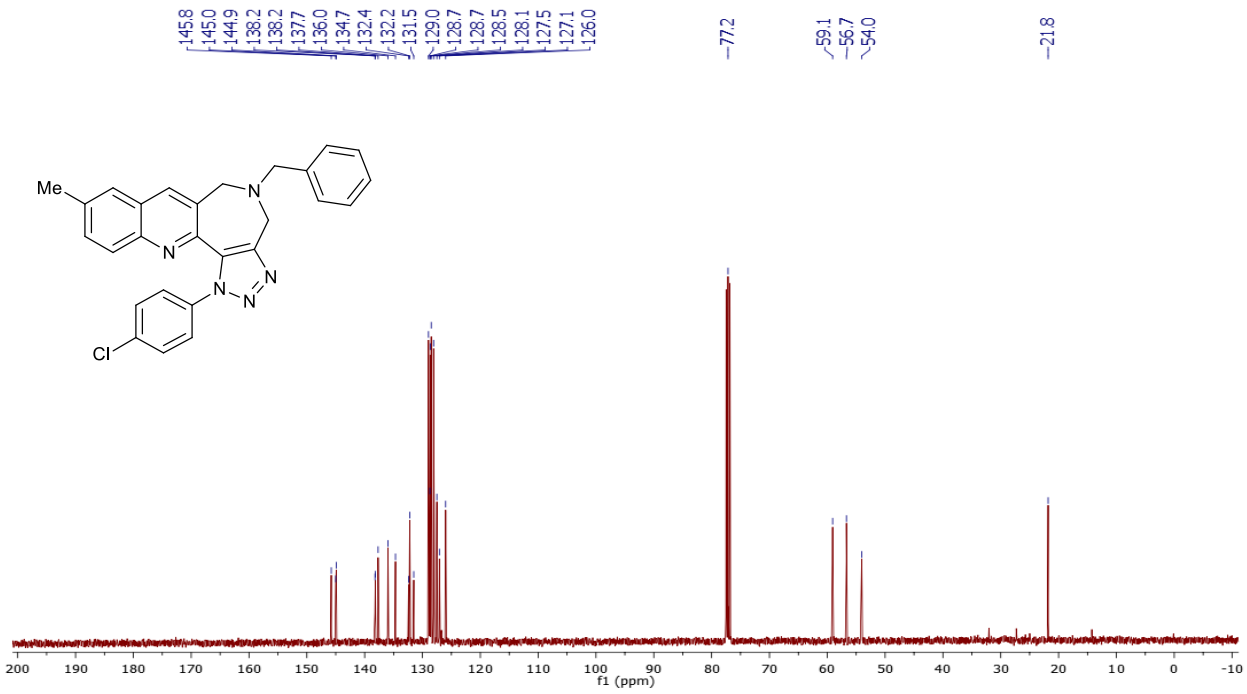
2.2
4.1
4.0
2.1
2.1
2.1
2.1
3.1
f1 (ppm)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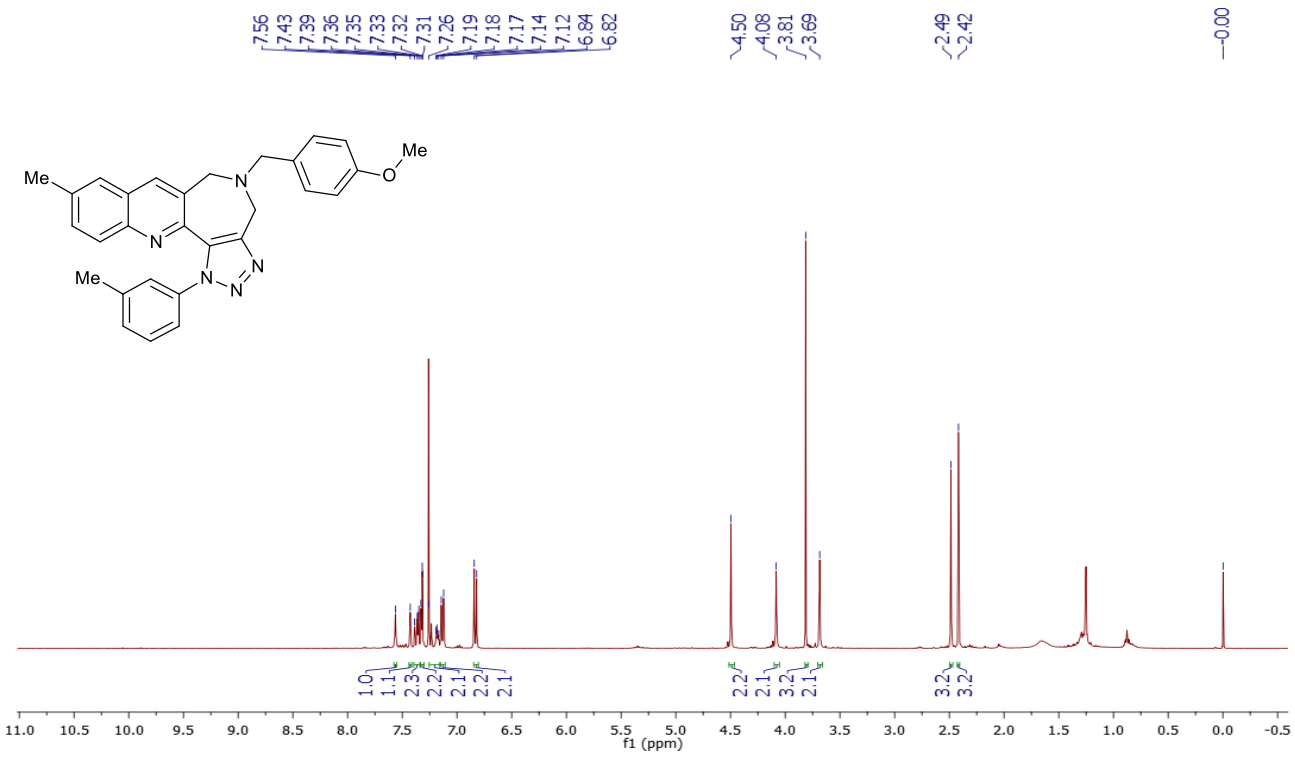
144.9
138.2
138.2
137.7
136.0
134.7
132.4
132.2
131.5
129.0
128.7
128.7
128.5
128.1
127.5
127.1
126.0
77.2
59.1
56.7
54.0
21.8
Me
N
N
N
N
N
Cl
f1 (ppm)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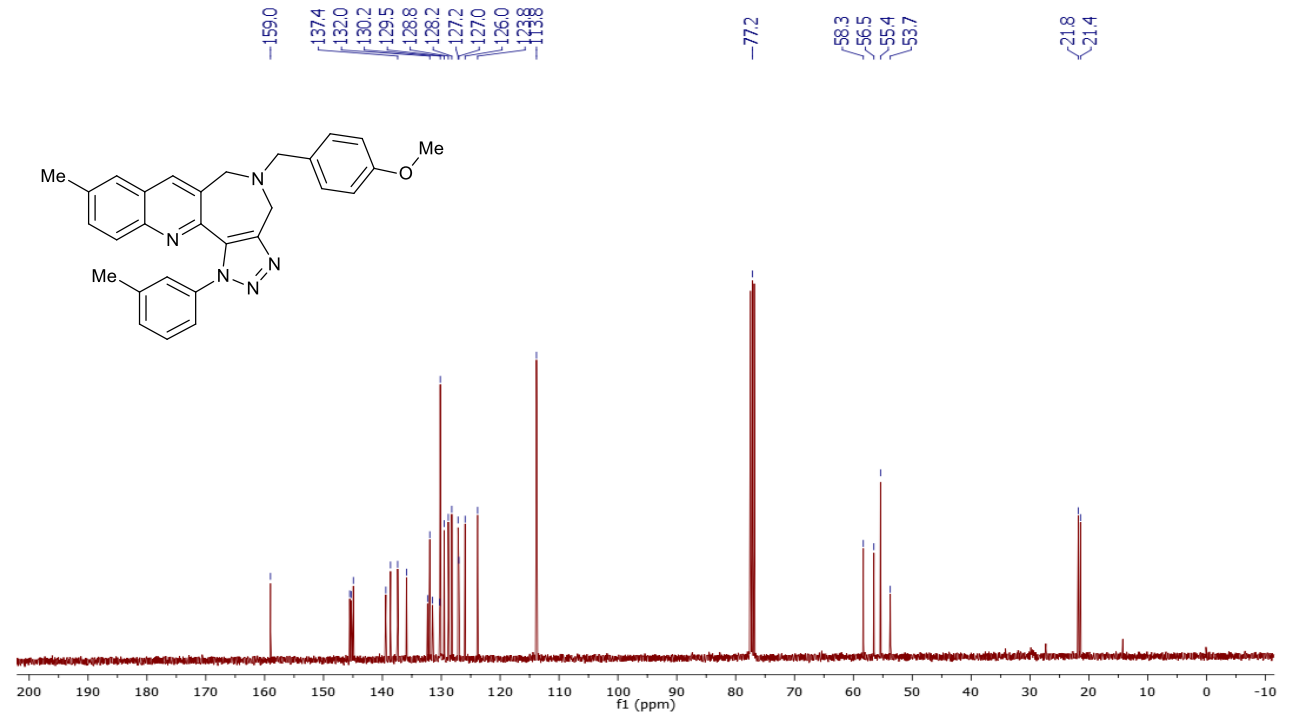
7.14
7.12
6.84
6.82
4.50
4.08
3.81
3.69
2.49
2.42
0.00
Me
Me
Me
N
O
N
N
N
N
1.0
1.1
2.3
2.2
2.1
2.2
2.1
2.2
2.1
3.2
2.1
3.2
3.2
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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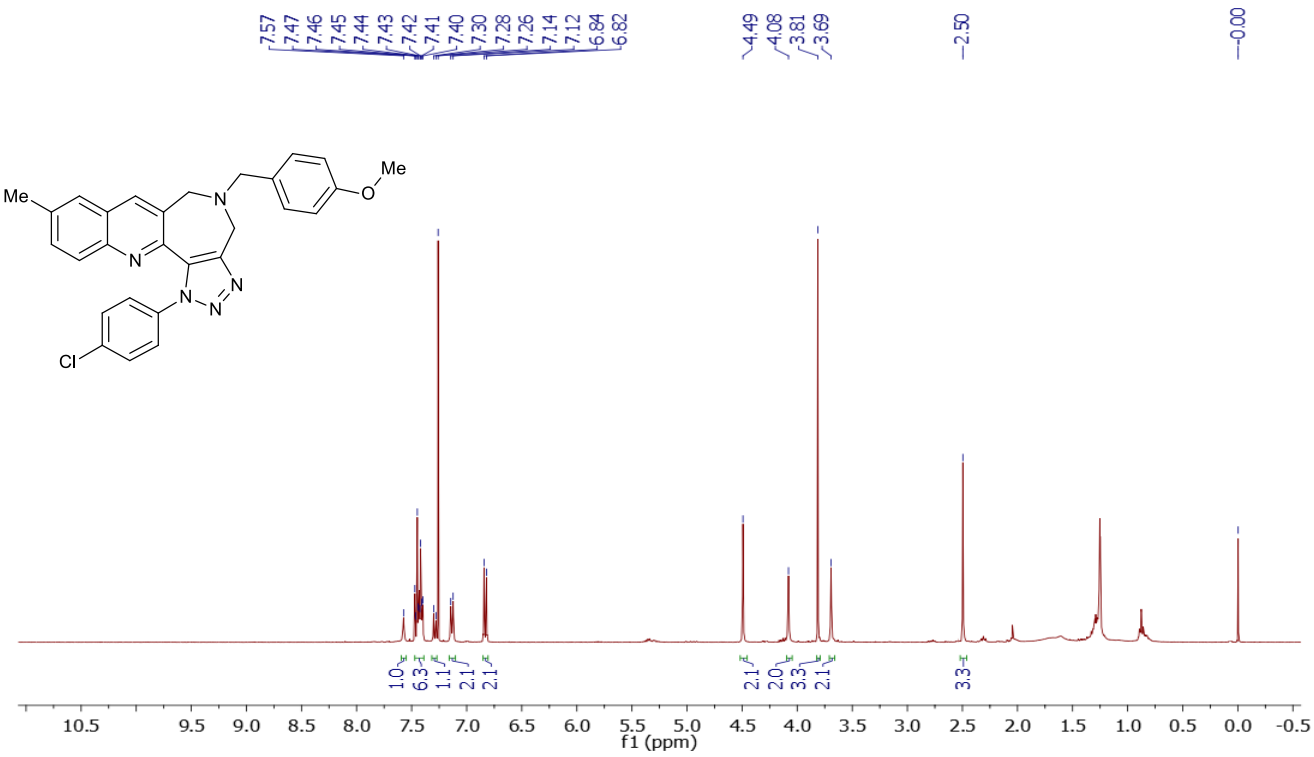
129.5
128.8
128.2
127.2
127.0
126.0
123.8
113.8
77.2
58.3
56.5
55.4
53.7
21.8
21.4
Me
Me
Me
N
O
N
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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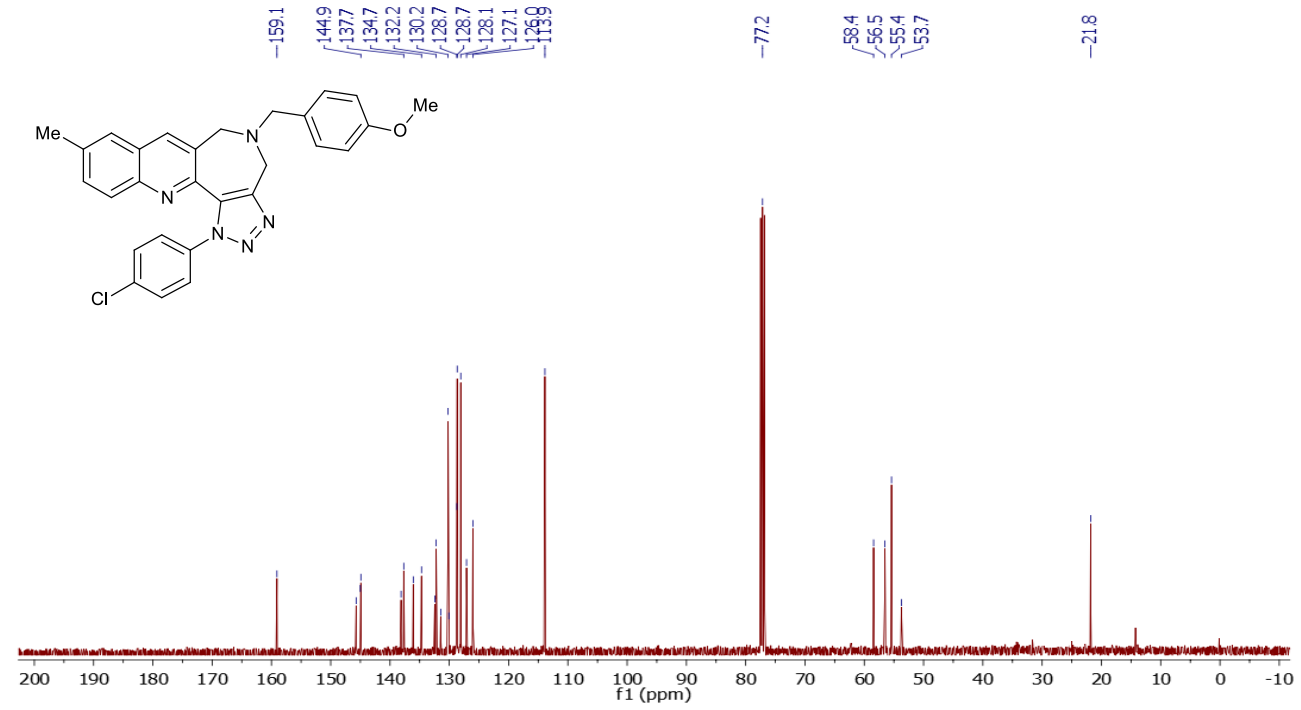
7.30
7.28
7.26
7.14
7.12
6.84
6.82
4.49
4.08
3.81
3.69
2.50
0.00
Me
O
Me
N
N
N
N
Cl
1.0
6.3
1.1
2.1
2.1
2.1
2.0
3.3
2.1
3.3
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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130.2
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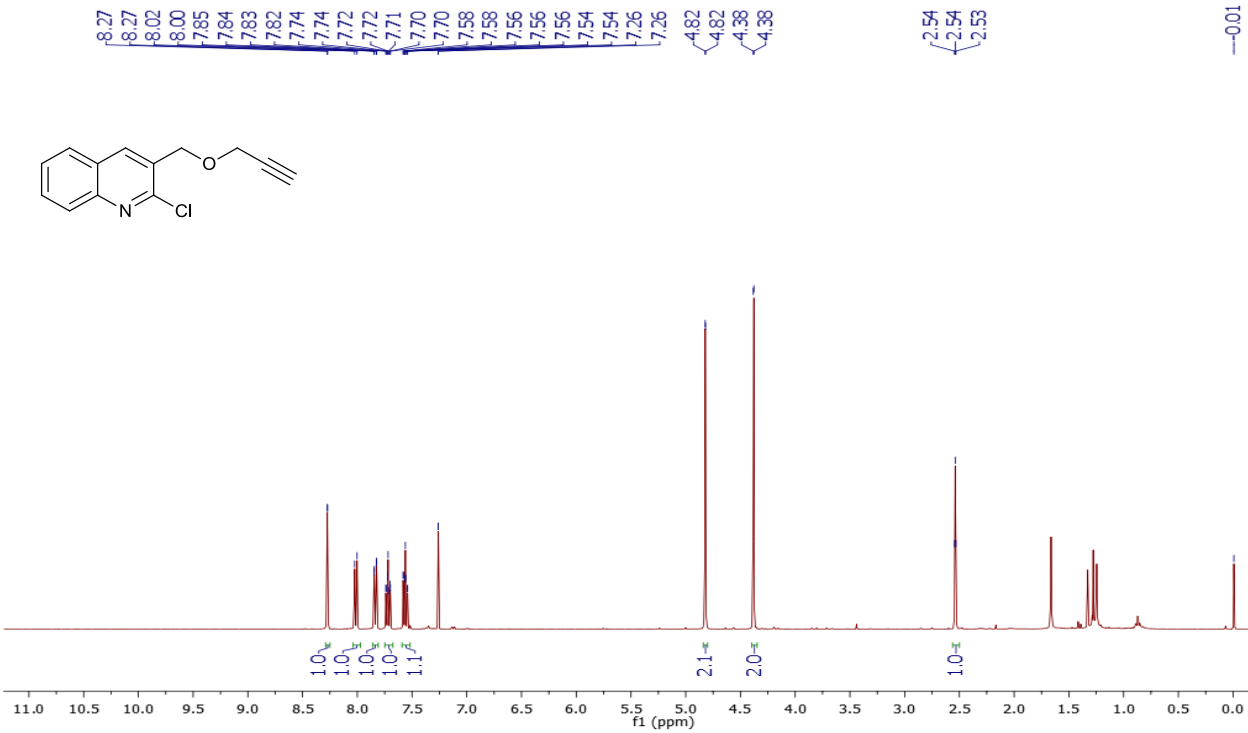
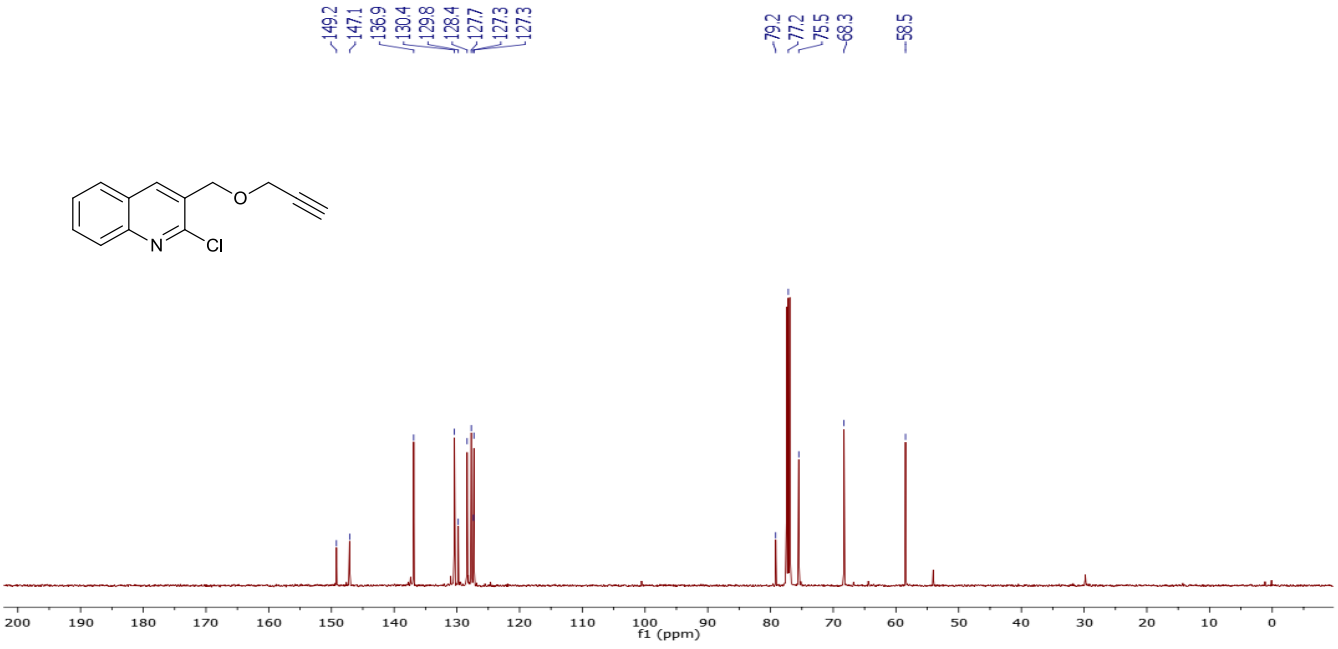
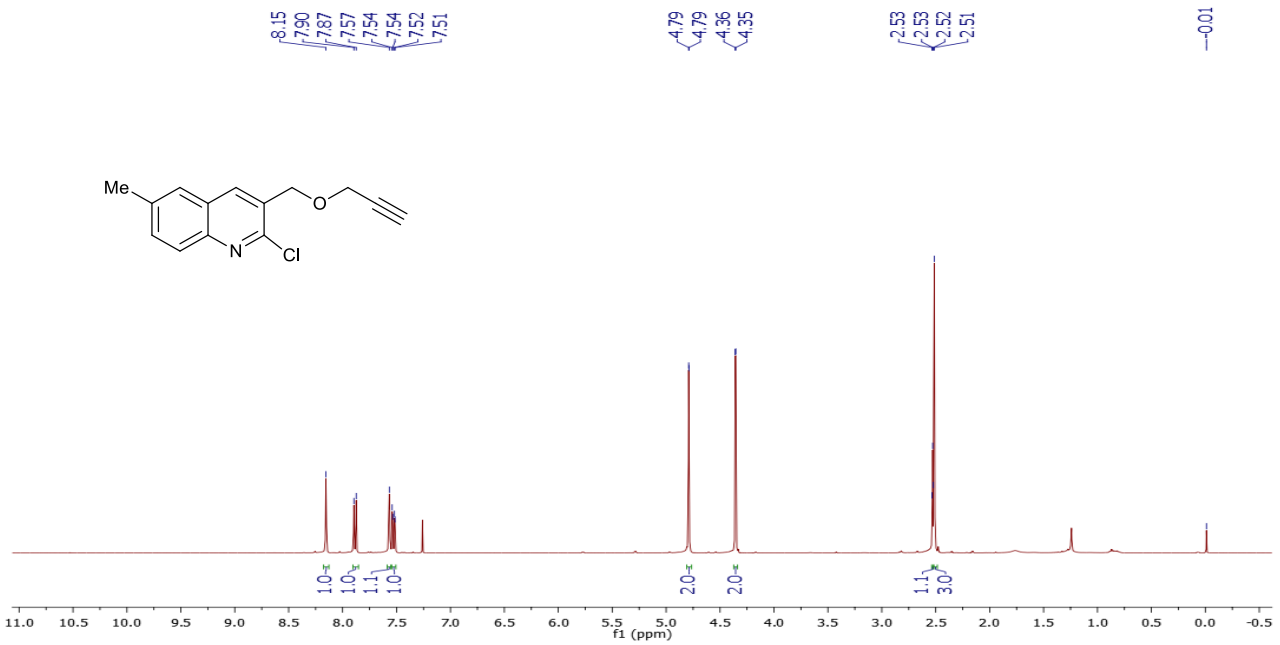
128.7
128.1
127.1
126.0
113.9
77.2
58.4
56.5
55.4
53.7
21.8
Me
O
Me
N
N
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of the compounds (3a-d)



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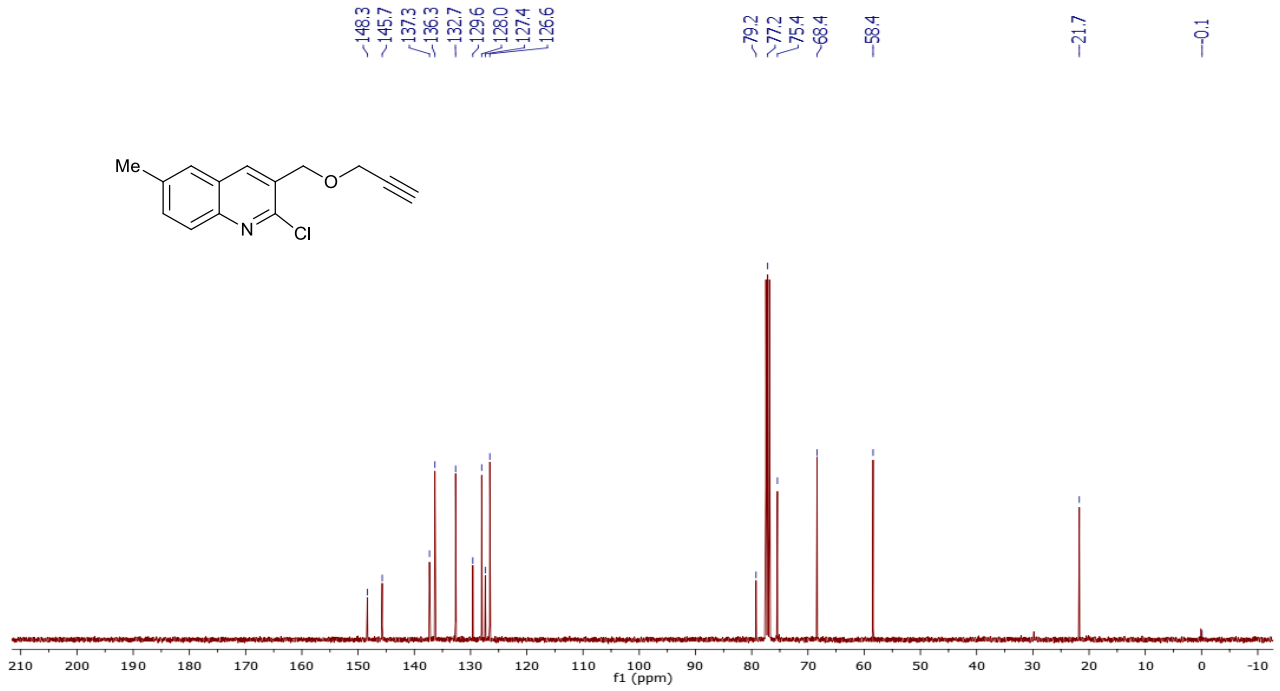
7.51
4.79
4.79
4.36
4.35
2.53
2.53
2.52
2.51
0.01
Me
O
N
Cl
1.0
1.0
1.1
1.0
2.0
2.0
1.1
3.0
f1 (ppm)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145.7
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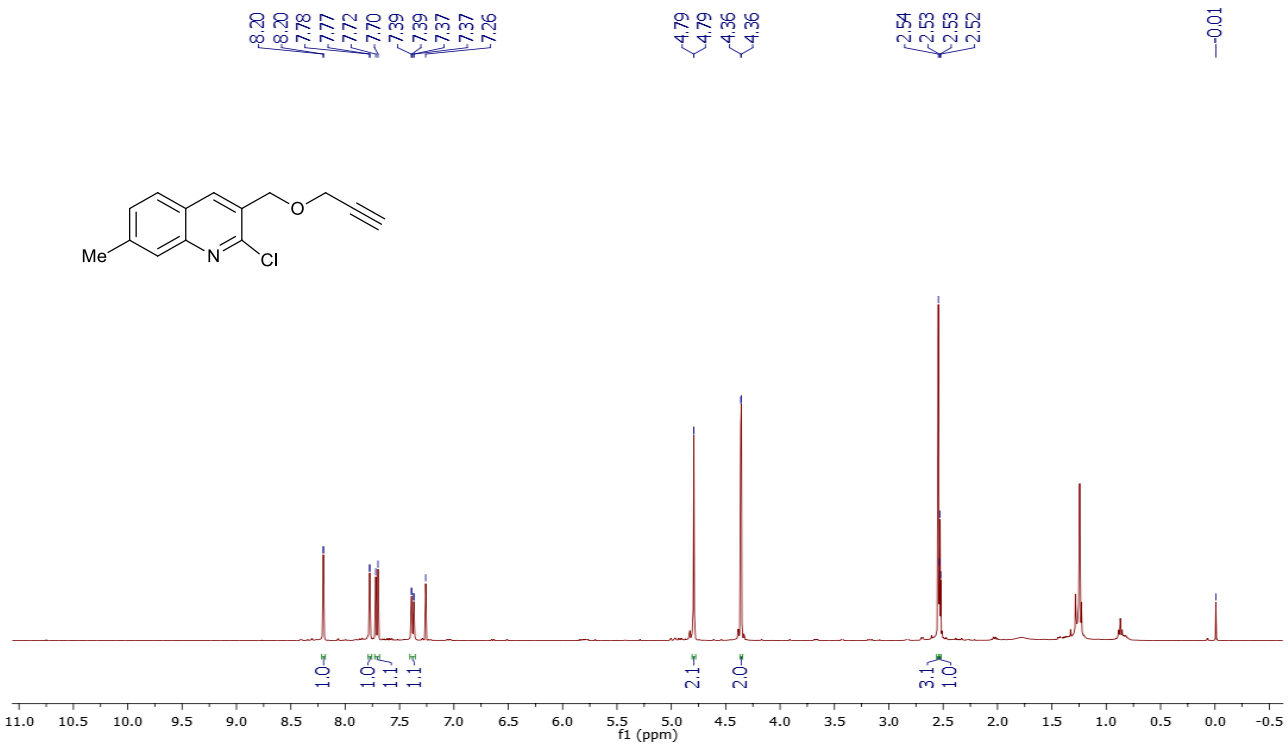
136.3
132.7
129.6
128.0
127.4
126.6
79.2
77.2
75.4
68.4
58.4
21.7
0.1
Me
O
N
Cl
f1 (ppm)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7.39
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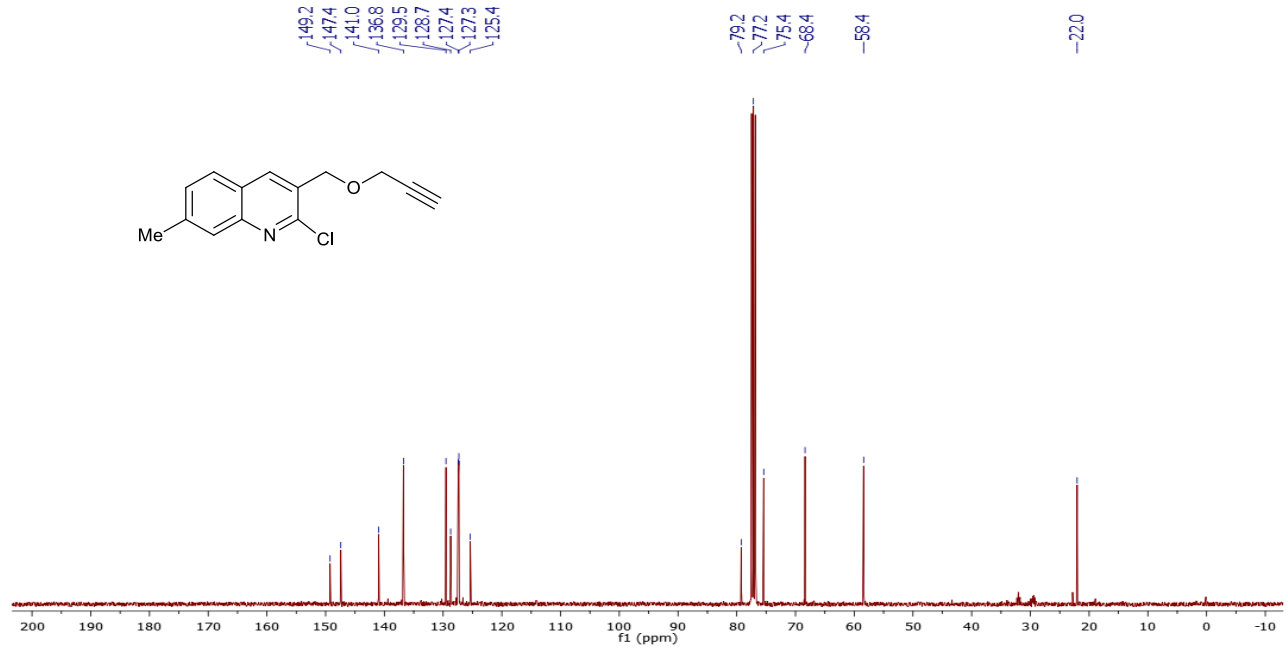
7.37
7.26
4.79
4.79
4.36
4.36
2.54
2.53
2.53
2.52
0.01
Me
N
Cl
O
1.0
1.0
1.1
1.1
2.1
2.0
3.1
1.0
f1 (ppm)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136.8
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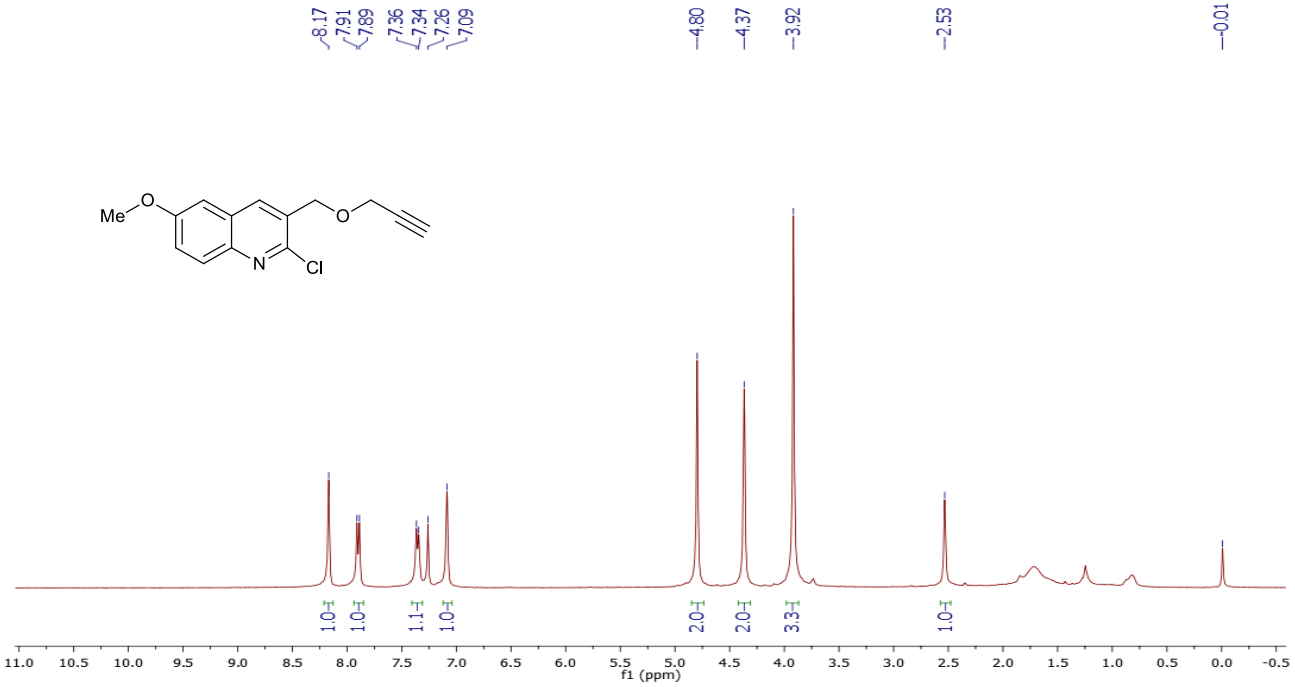
128.7
127.4
127.3
125.4
79.2
77.2
75.4
68.4
58.4
22.0
Me
N
Cl
O
f1 (ppm)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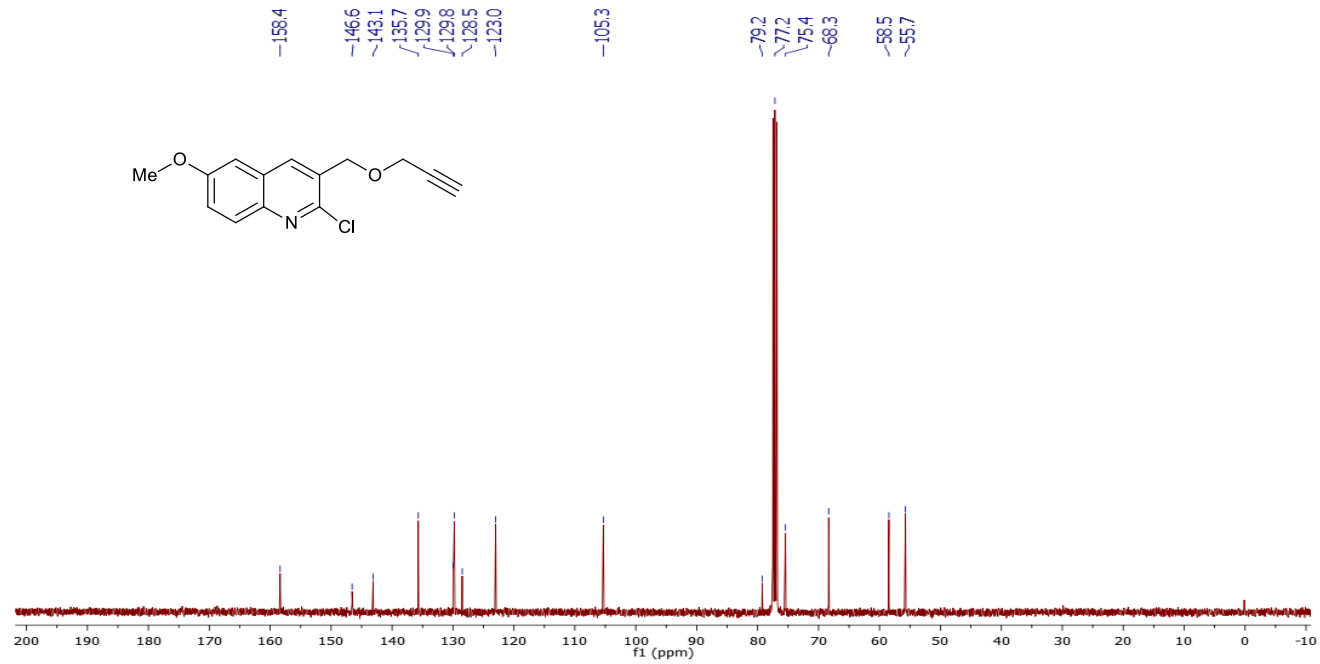
7.26
7.09
4.80
4.37
3.92
2.53
0.01
Me
O
O
N
Cl
1.0
1.0
1.1
1.0
2.0
2.0
3.3
1.0
f1 (ppm)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143.1
135.7
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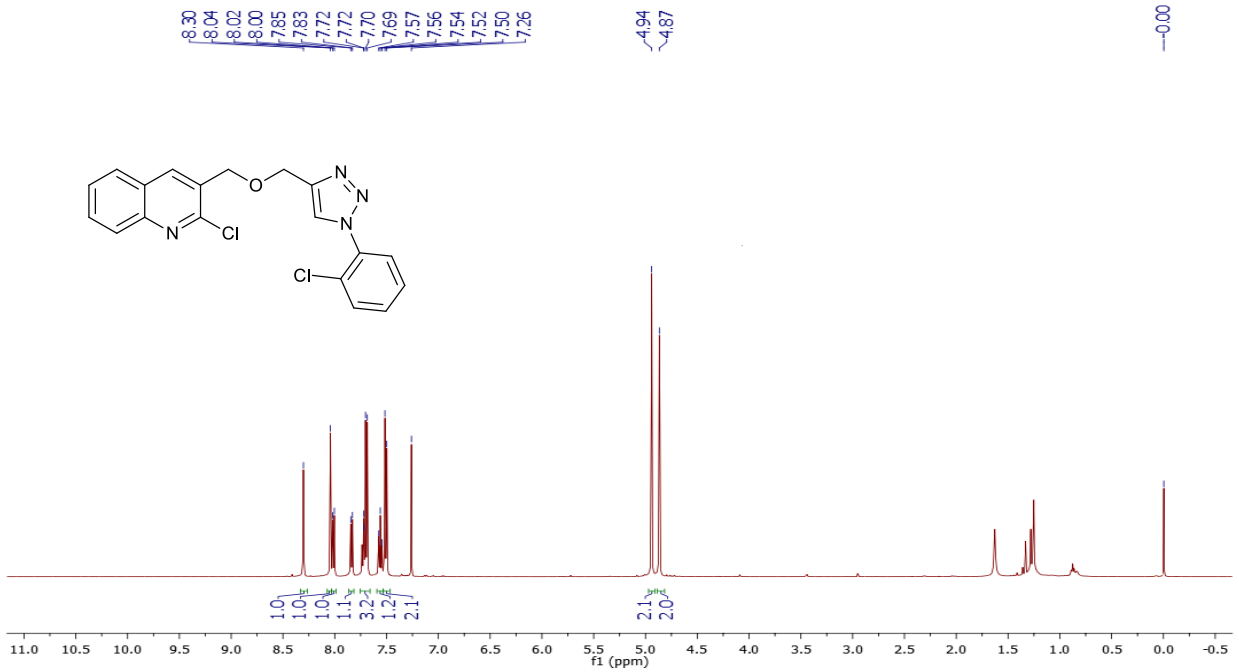
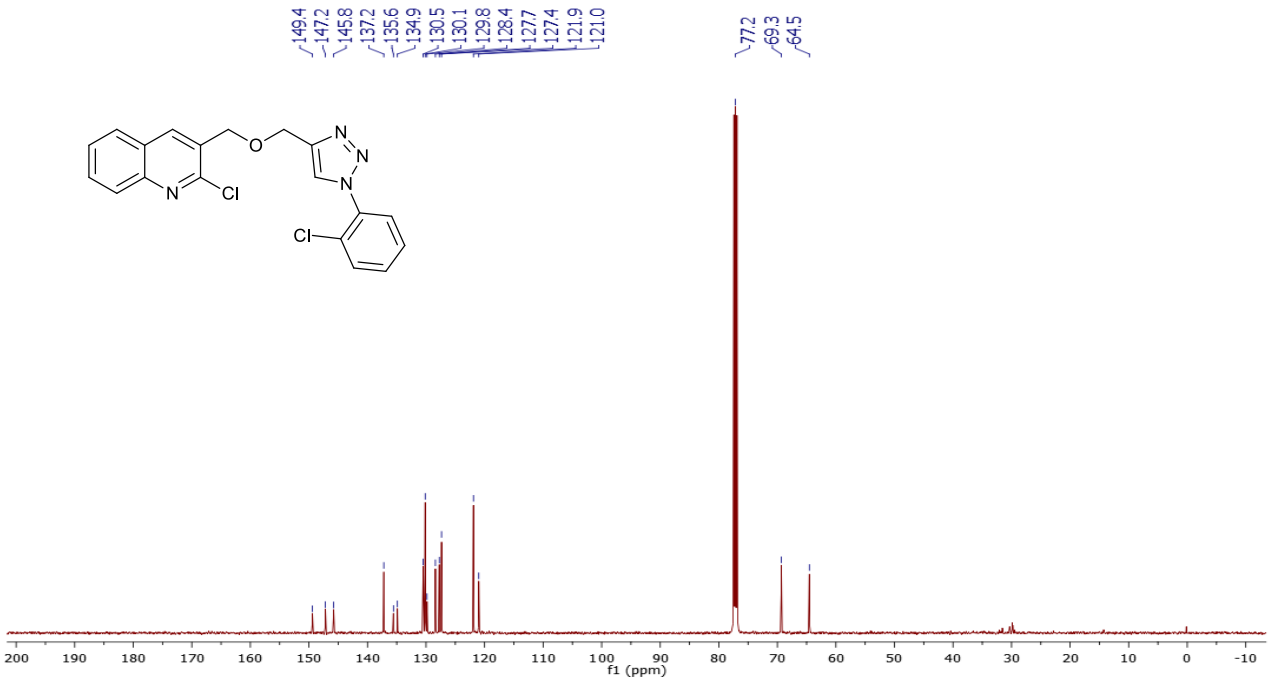
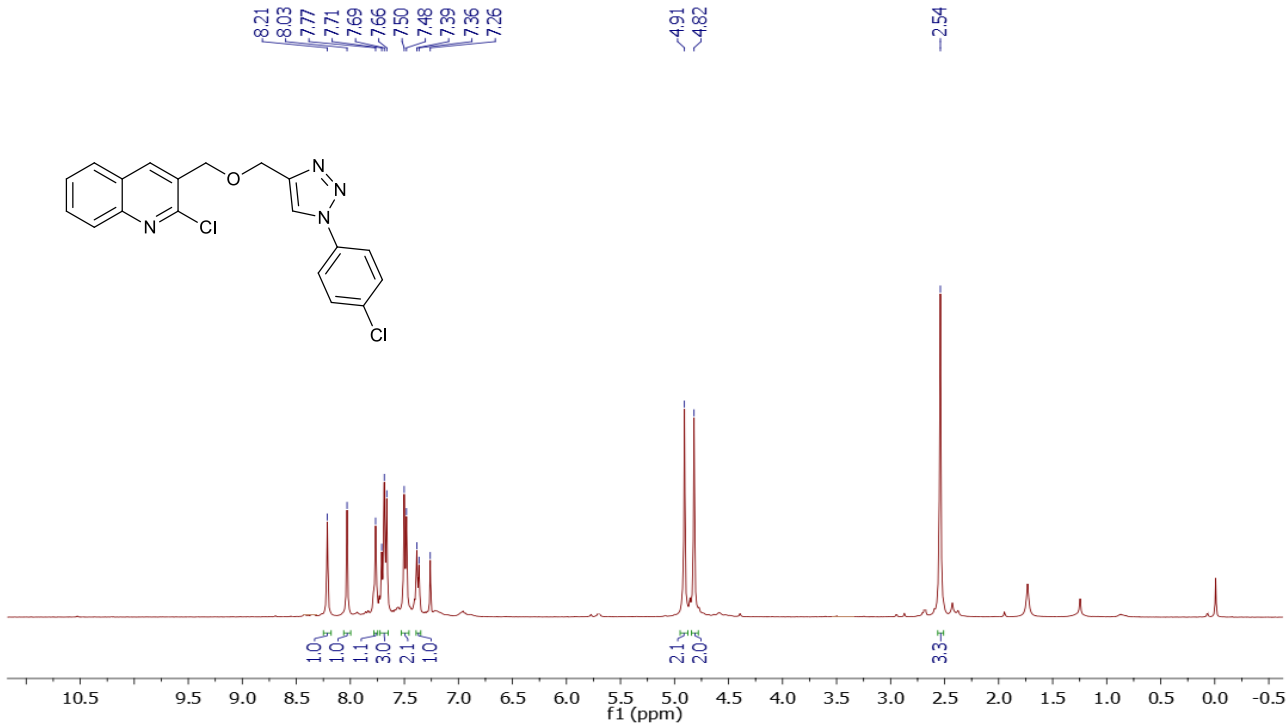
129.8
128.5
123.0
105.3
79.2
77.2
75.4
68.3
58.5
55.7
Me
O
O
N
Cl
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of the compounds (5a-h)



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7.69
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7.48
7.39
7.36
7.26
4.91
4.82
2.54
N
N
N
O
N
Cl
Cl
1.0
1.0
1.1
3.0
2.1
1.0
2.1
2.0
3.3
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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0.5
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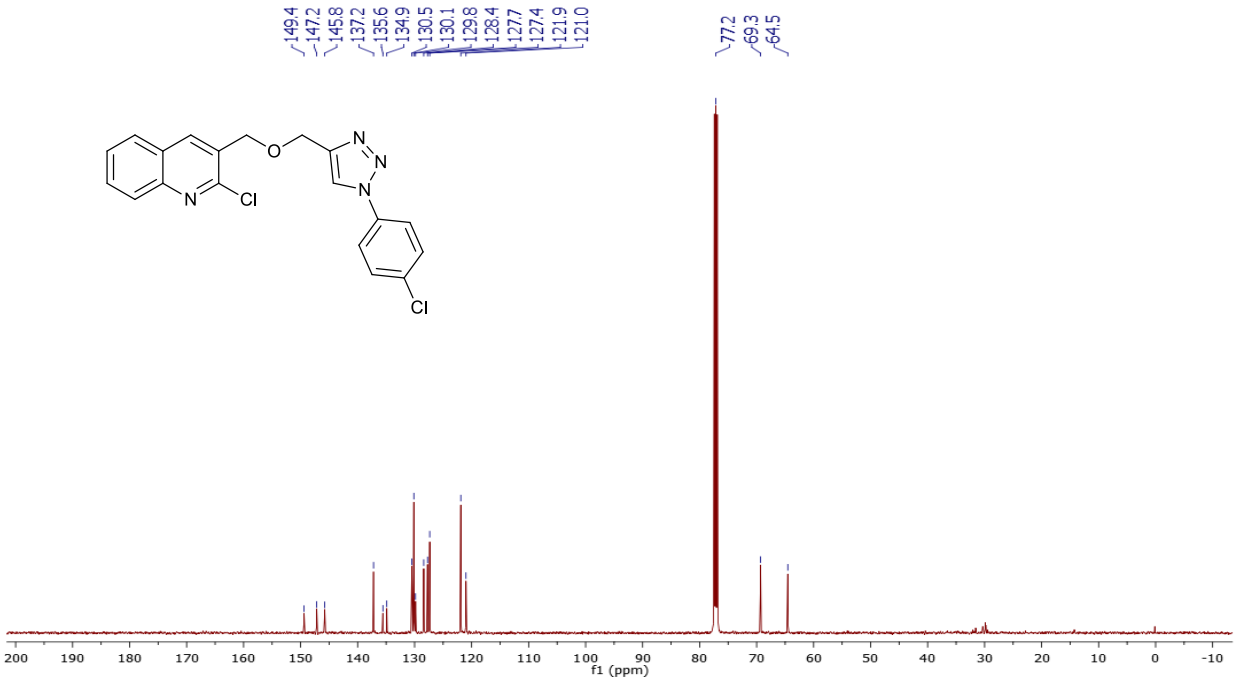
-0.5
f1 (ppm)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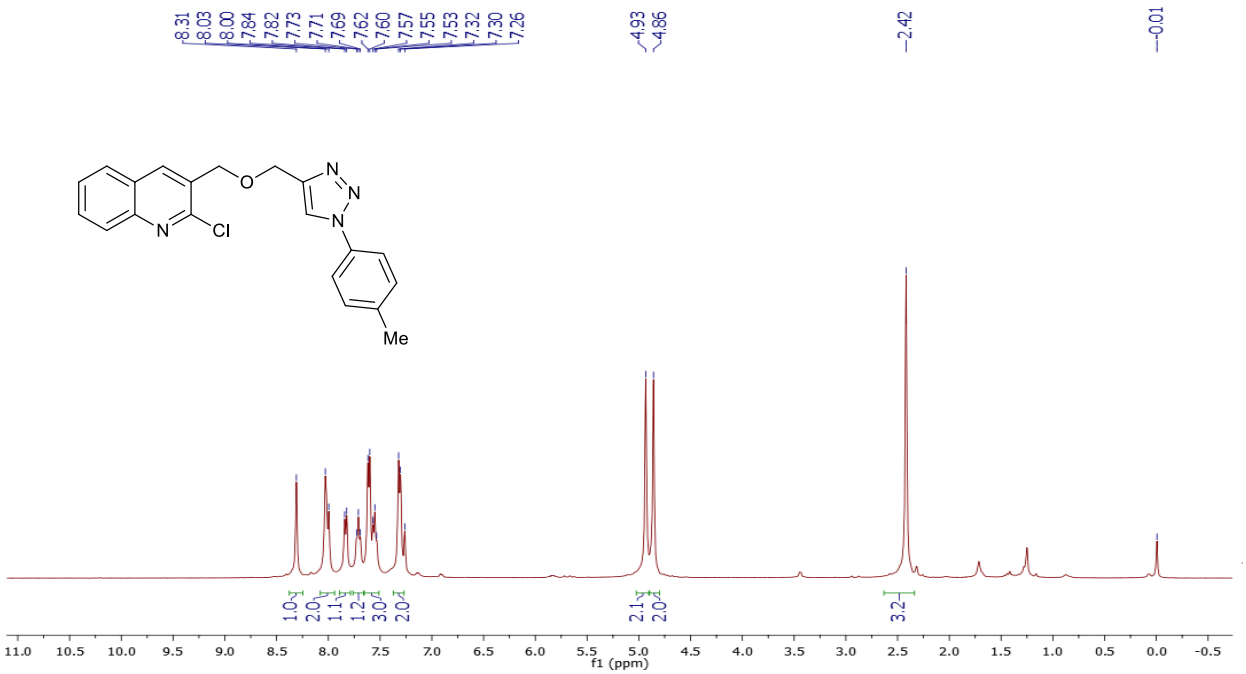
130.5
130.1
129.8
128.4
127.7
127.4
121.9
121.0
77.2
69.3
64.5
N
N
N
O
N
Cl
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.55
7.53
7.32
7.30
7.26
4.93
4.86
2.42
0.01
N
N
N
O
Cl
Me
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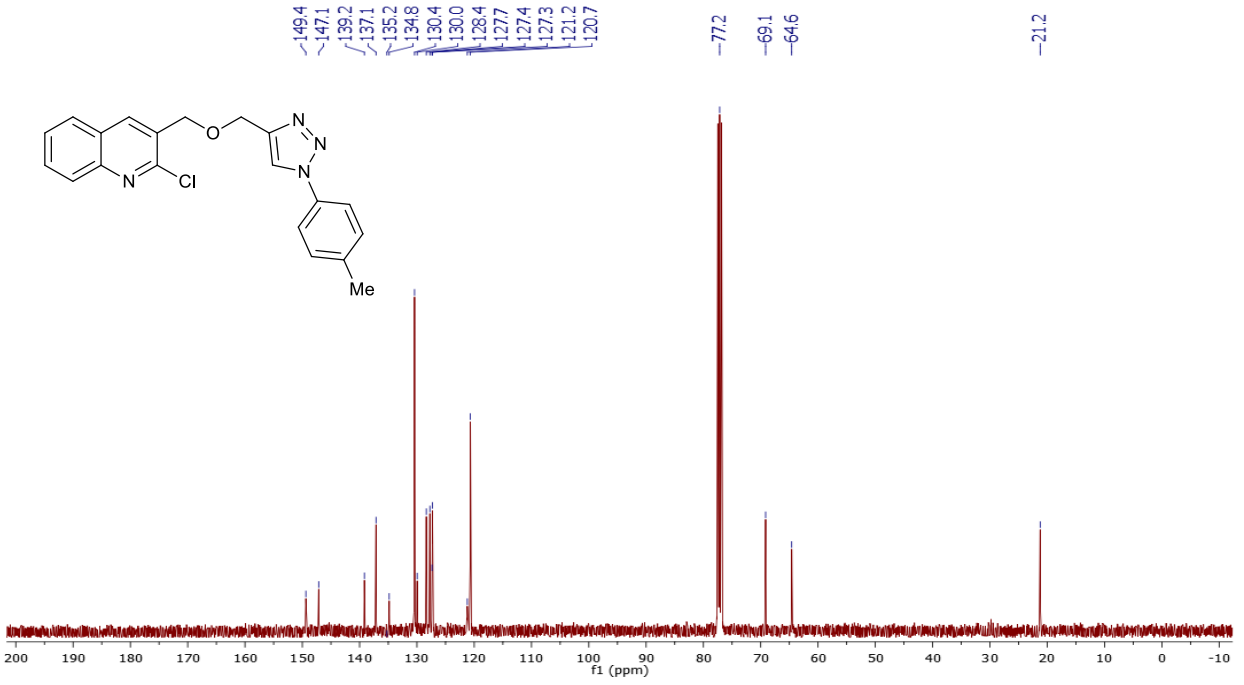
2.0
1.1
1.2
3.0
2.0
2.1
2.0
3.2
f1 (ppm)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137.1
135.2
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130.4
130.0
128.4
127.7
127.4
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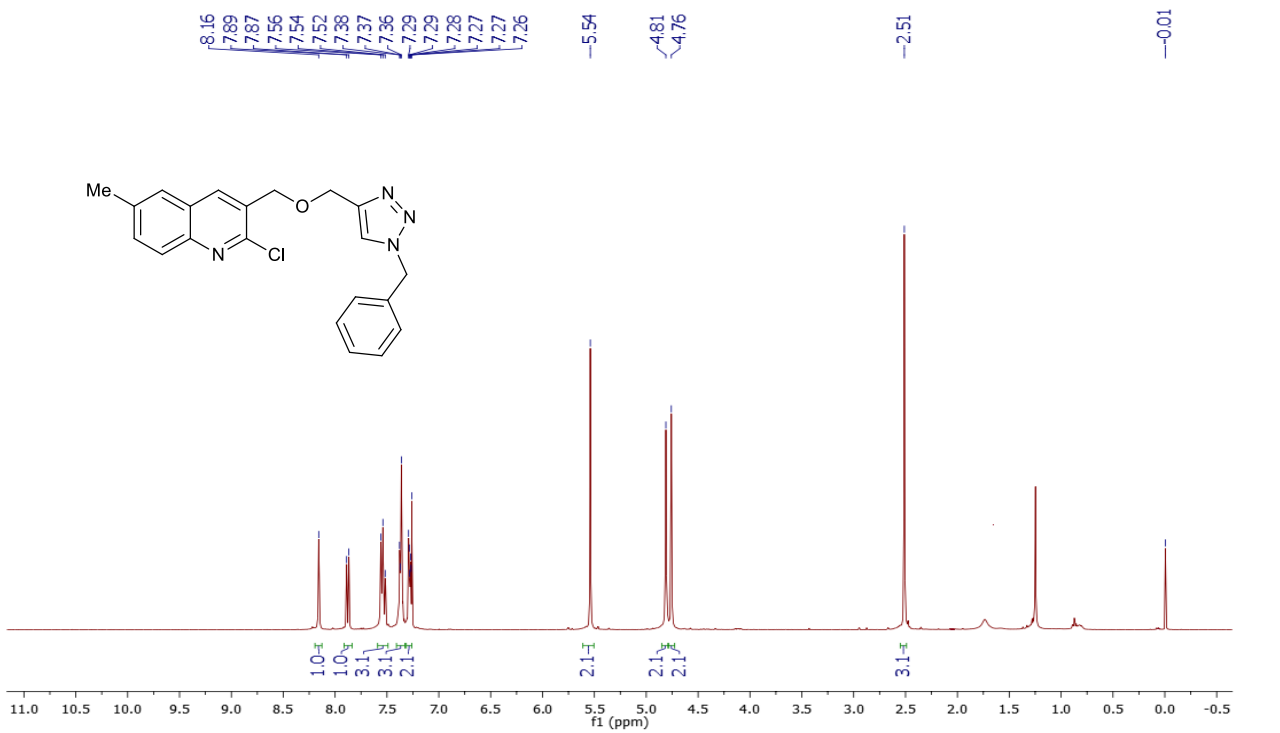
121.2
120.7
77.2
69.1
64.6
21.2
N
N
N
O
Cl
Me
f1 (ppm)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7.29
7.28
7.27
7.27
7.26
5.54
4.81
4.76
2.51
0.01
Me
O
N
N
N
Cl
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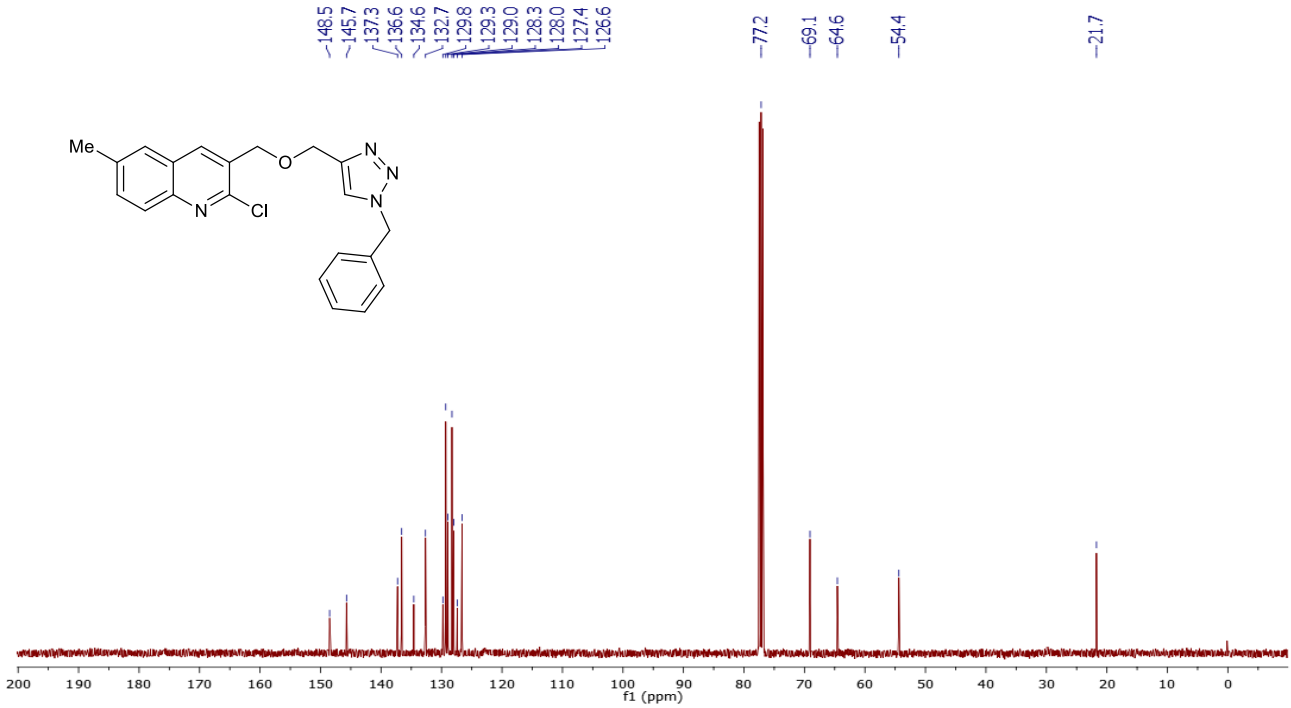
1.0
3.1
3.1
2.1
2.1
2.1
2.1
3.1
f1 (ppm)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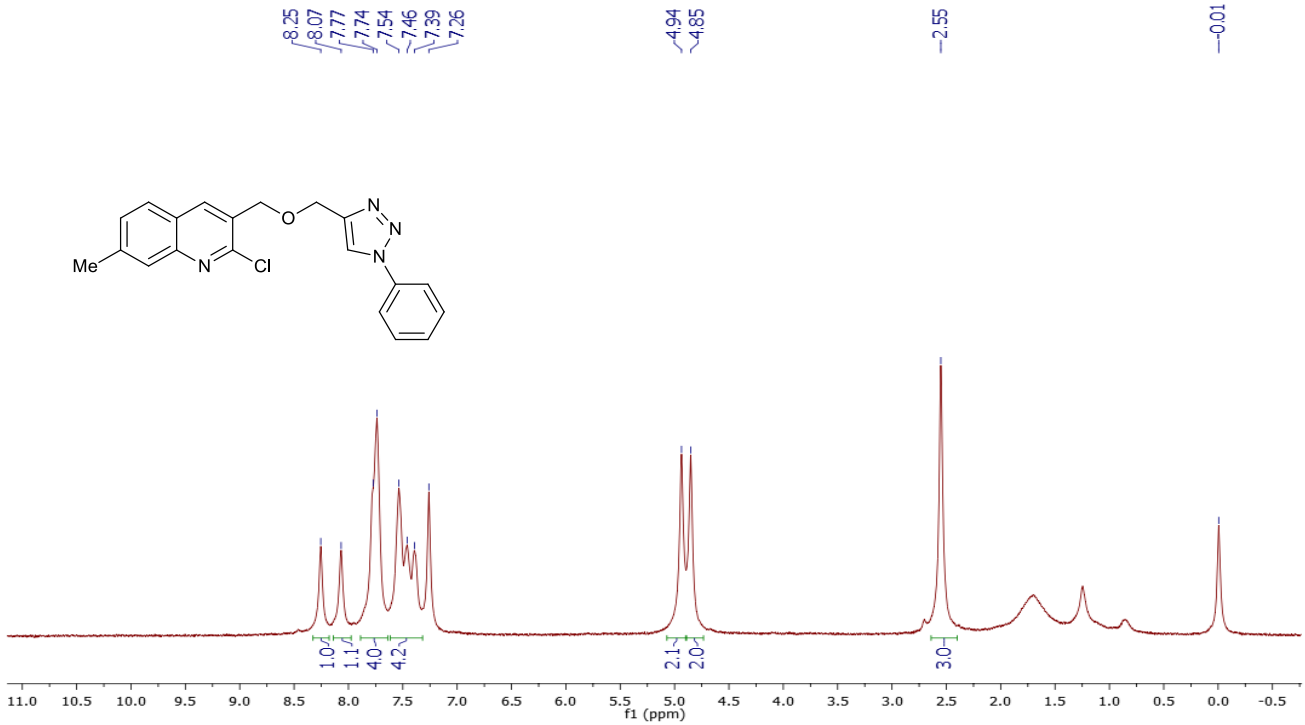
137.3
136.6
134.6
132.7
129.8
129.3
129.0
128.3
128.0
127.4
126.6
77.2
69.1
64.6
54.4
21.7
Me
O
N
N
N
Cl
f1 (ppm)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7.46
7.39
7.26
4.94
4.85
2.55
0.01
Me
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Cl
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N
N
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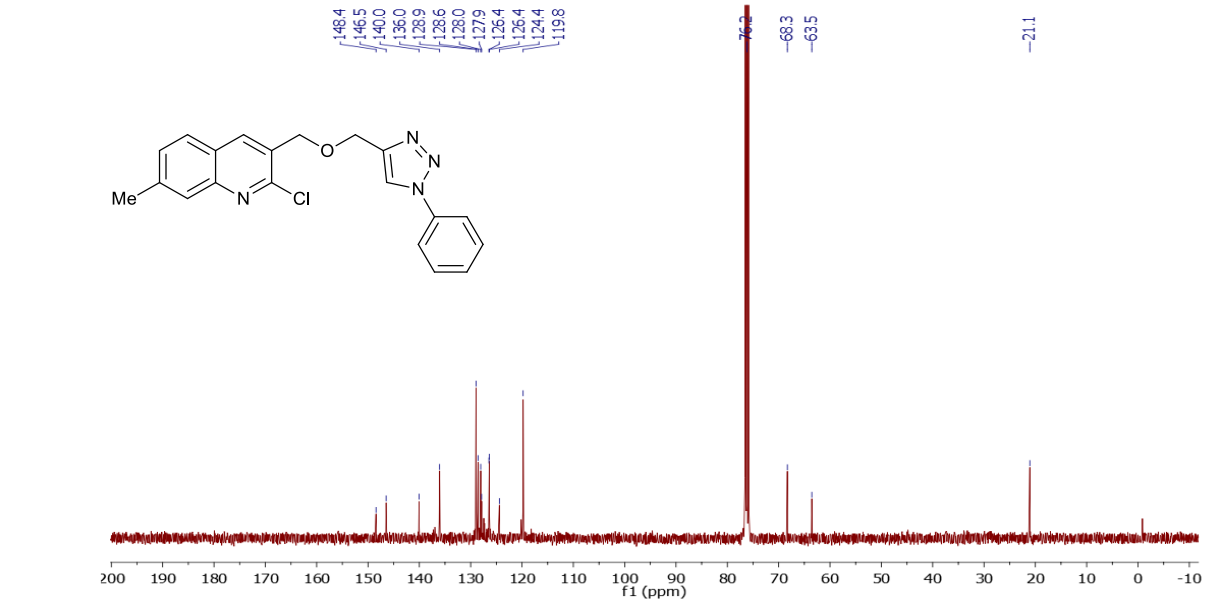
1.1
4.0
4.2
2.1
2.0
3.0
f1 (ppm)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140.0
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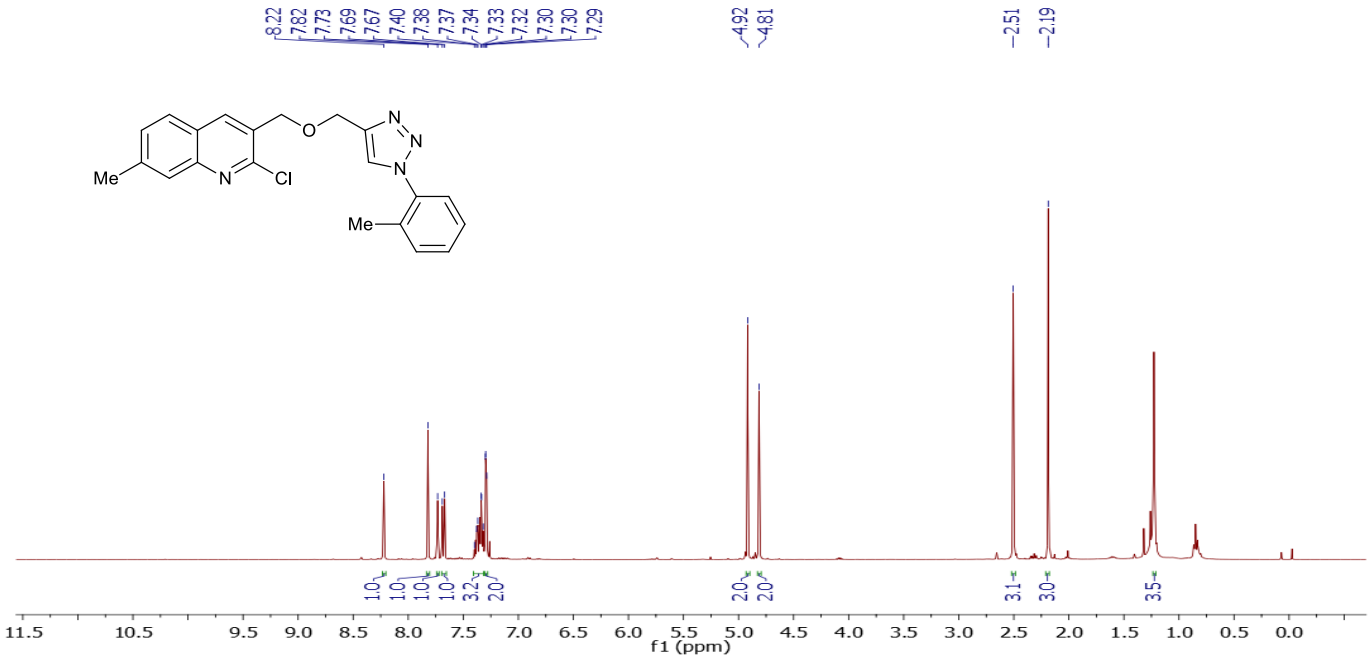
128.9
128.6
128.0
127.9
126.4
126.4
124.4
119.8
76.0
68.3
63.5
21.1
Me
N
Cl
O
N
N
N
f1 (ppm)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7.37
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7.33
7.32
7.30
7.30
7.29
4.92
4.81
2.51
2.19
Me
N
Cl
O
N
N
N
Me
1.0
1.0
1.0
1.0
3.2
2.0
2.0
2.0
3.1
3.0
3.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
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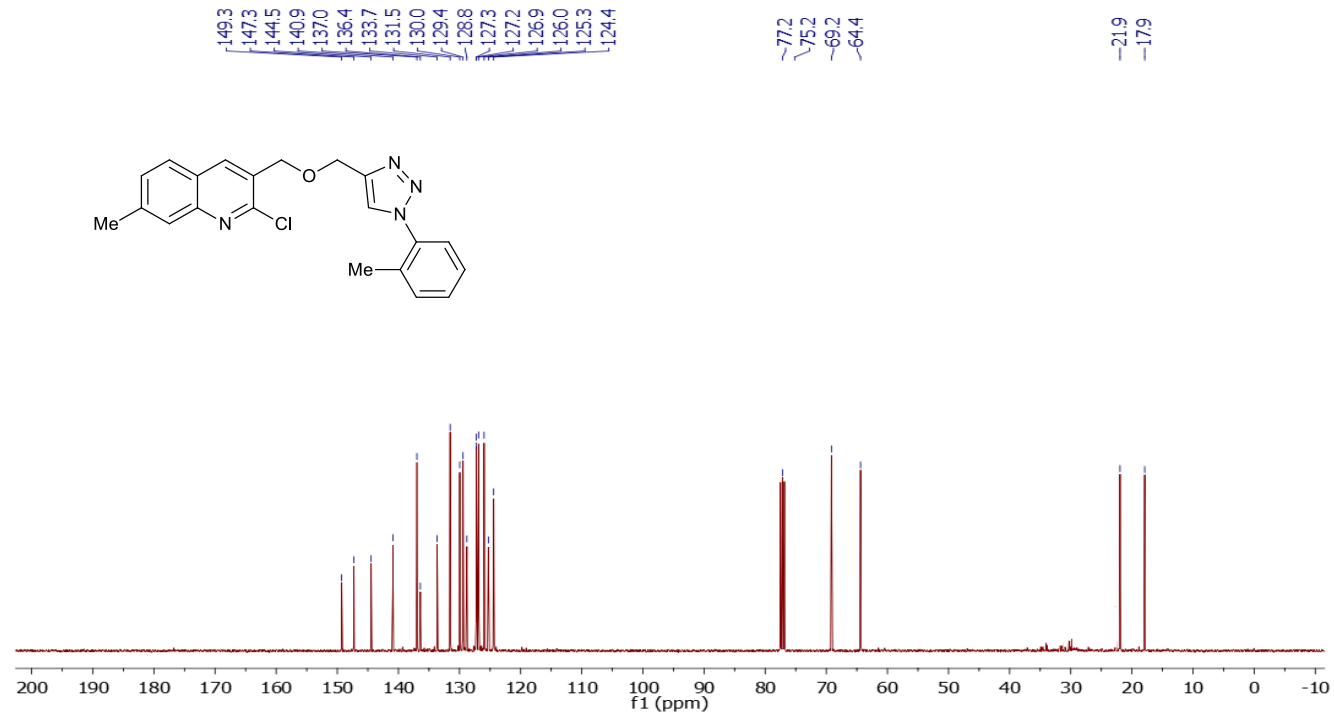
0.0
f1 (ppm)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144.5
140.9
137.0
136.4
133.7
131.5
130.0
129.4
128.8
127.3
127.2
126.9
126.0
125.3
124.4
77.2
75.2
69.2
64.4
21.9
17.9
Me
N
Cl
O
N
N
N
Me
200
190
180
170
160
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140
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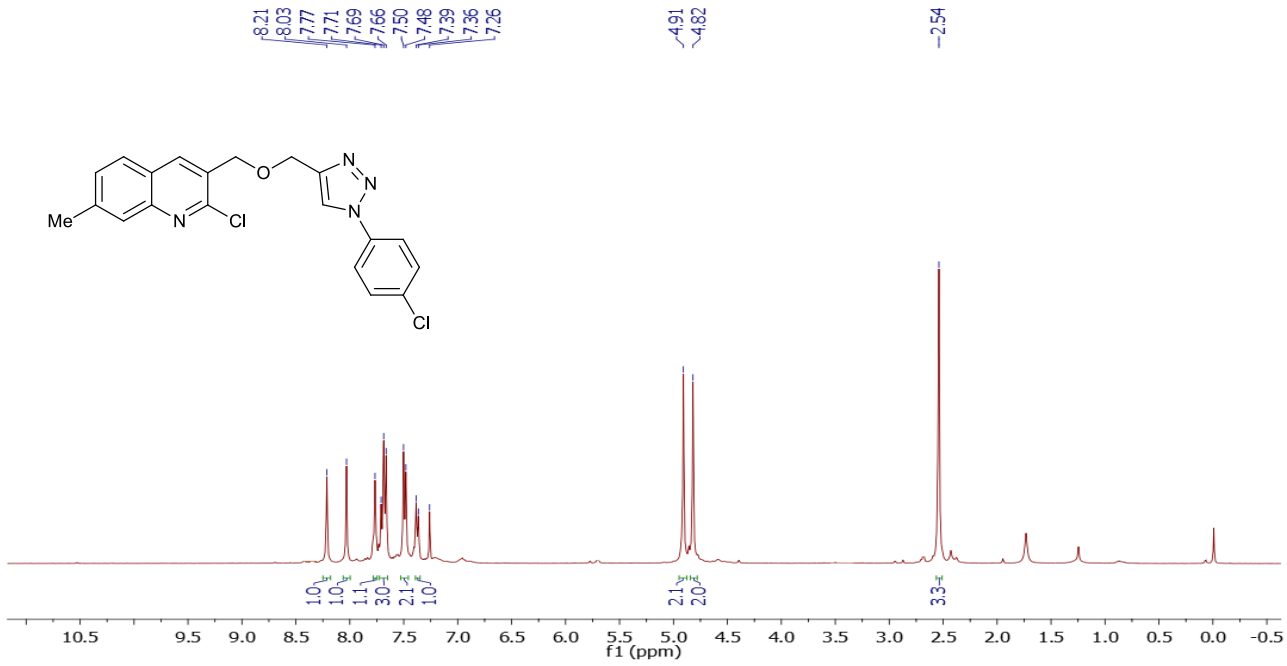
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.39
7.36
7.26
4.91
4.82
2.54
Me
N
Cl
O
N
N
N
Cl
1.0
1.0
1.1
3.0
2.1
1.0
2.1
2.0
3.3
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
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0.5
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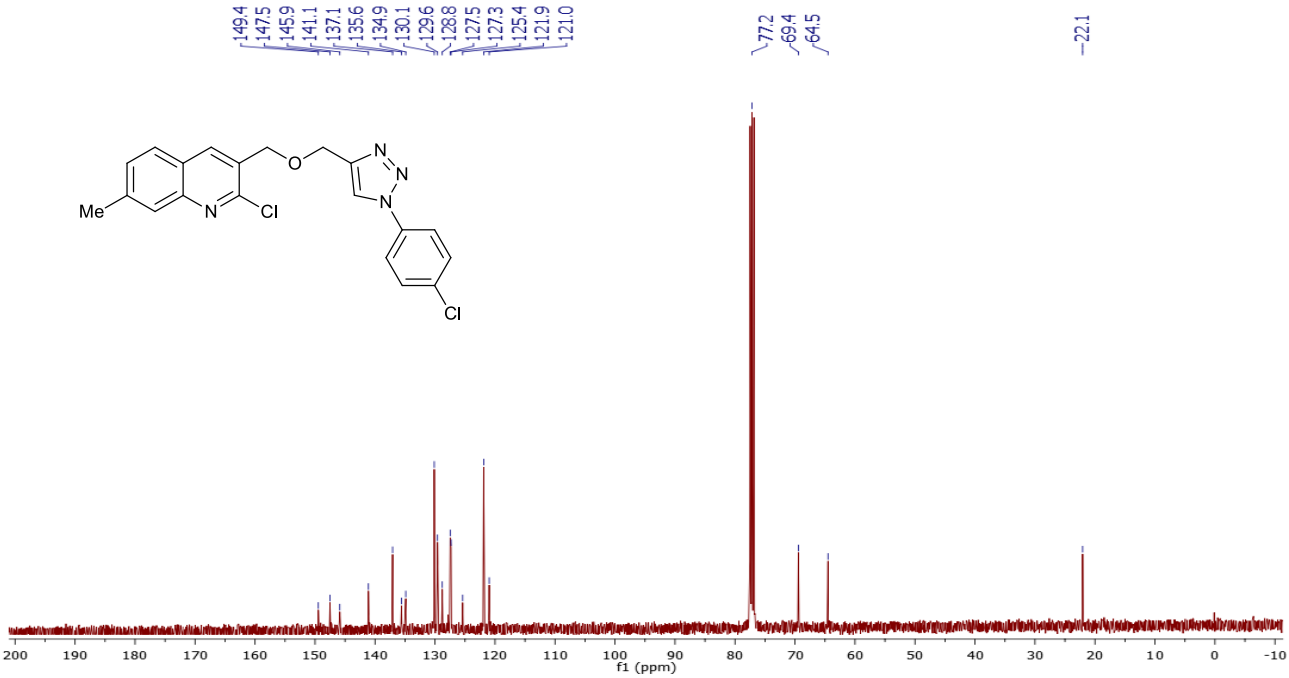
f1 (ppm)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127.3
125.4
121.9
121.0
77.2
69.4
64.5
22.1
Me
N
Cl
O
N
N
N
Cl
200
190
180
170
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120
110
100
90
80
70
60
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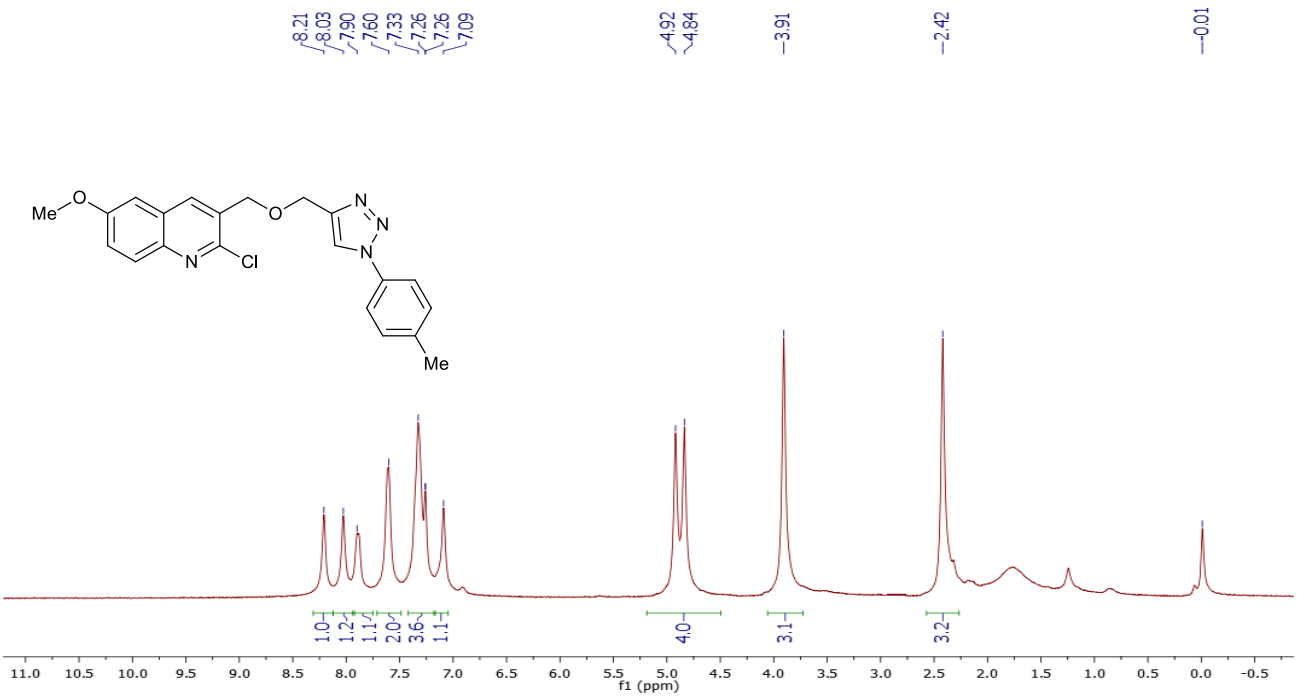
40
30
20
10
0
-10
f1 (ppm)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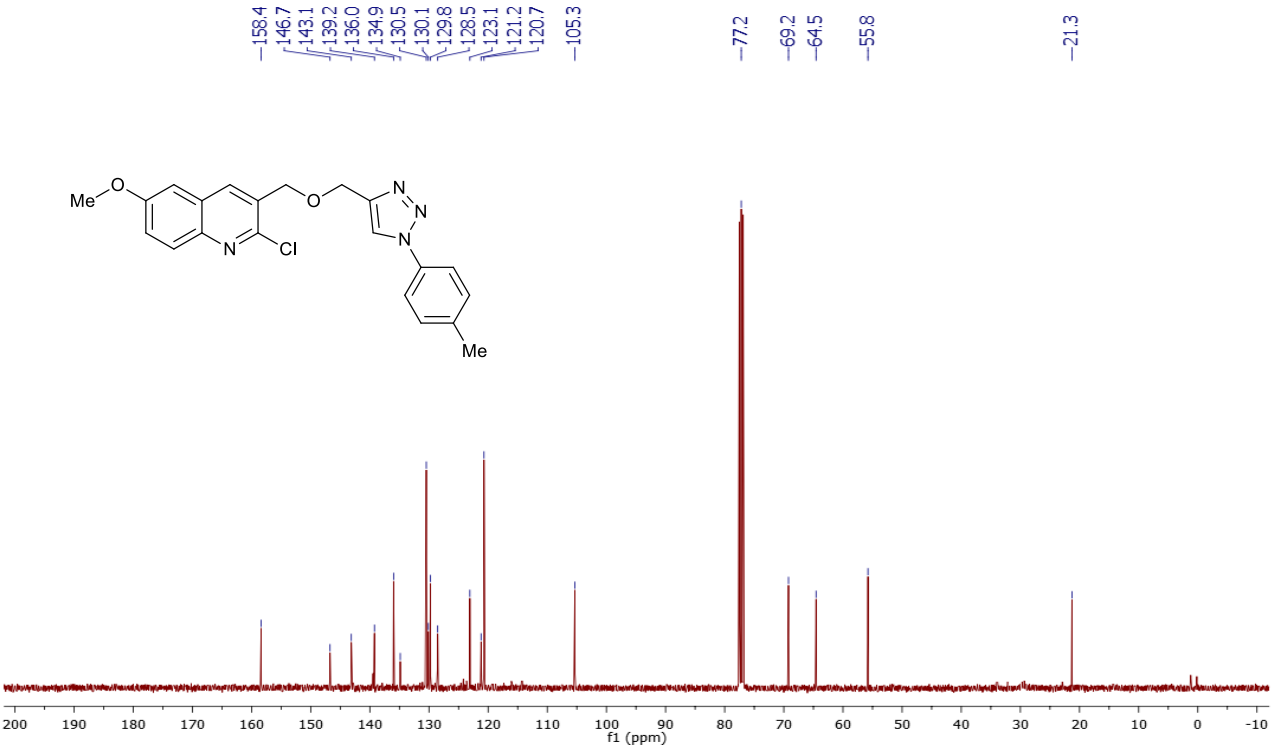
7.26
7.26
7.09
4.92
4.84
3.91
2.42
0.01
Me
O
N
Cl
O
N
N
N
Me
1.0
1.2
1.1
2.0
3.6
1.1
4.0
3.1
3.2
f1 (ppm)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130.1
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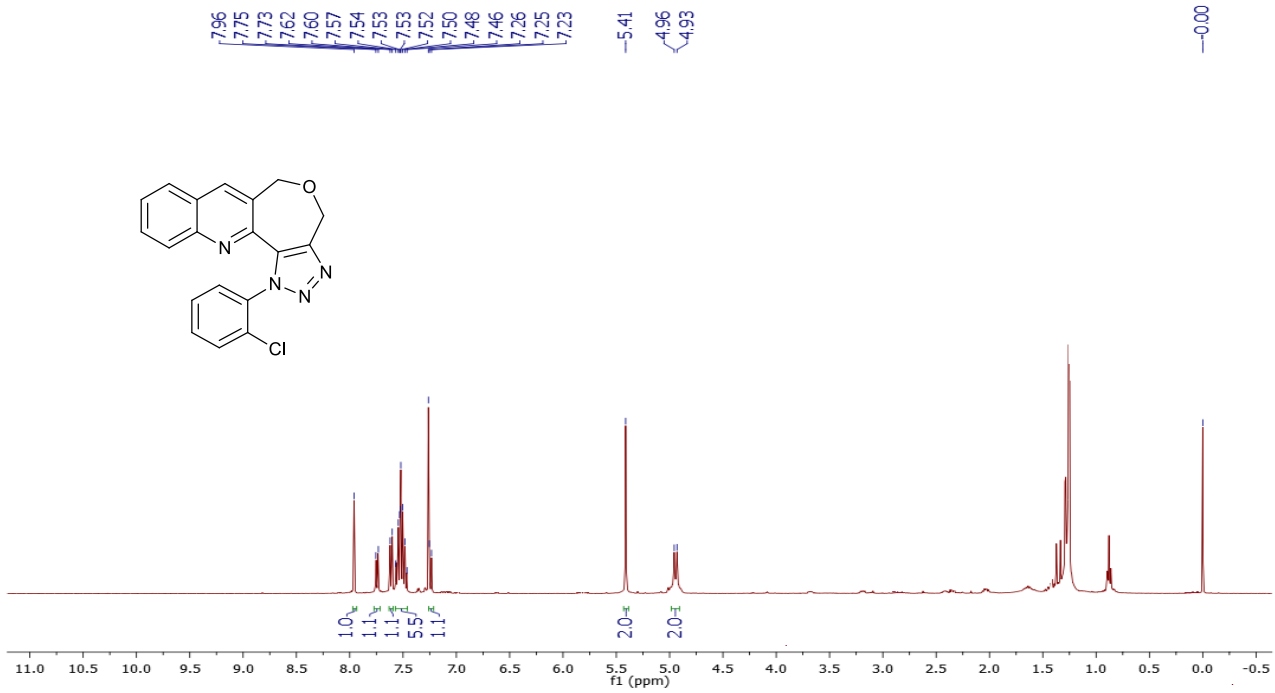
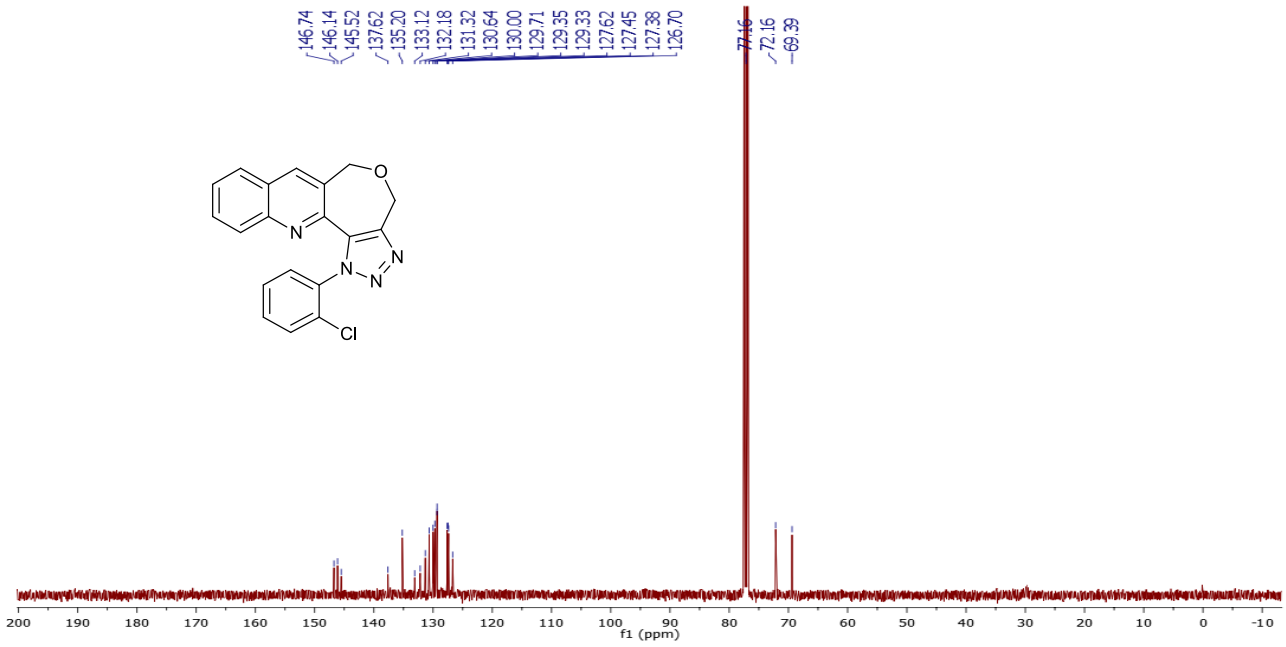
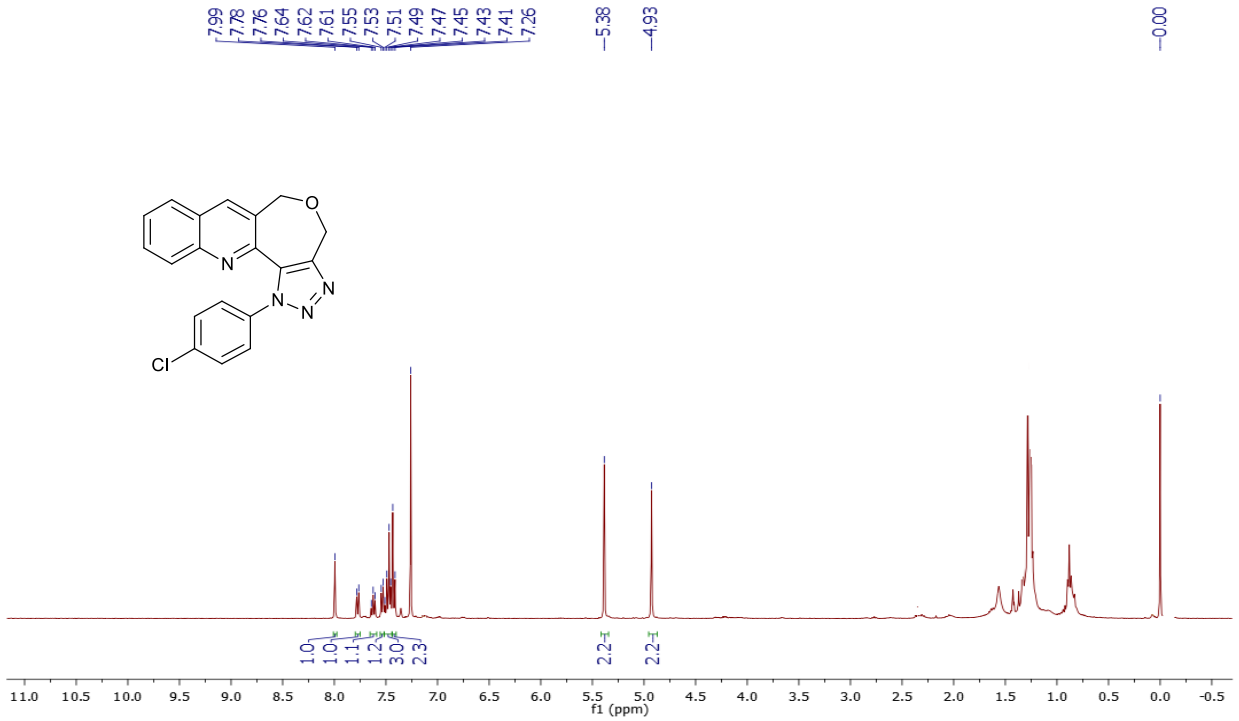
128.5
123.1
121.2
120.7
105.3
77.2
69.2
64.5
55.8
21.3
Me
O
N
Cl
O
N
N
N
Me
f1 (ppm)

^{1}H-NMR and ^{13}C-NMR spectra of the compounds (7a-h)



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7.41
7.26
5.38
4.93
0.00
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N
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Cl
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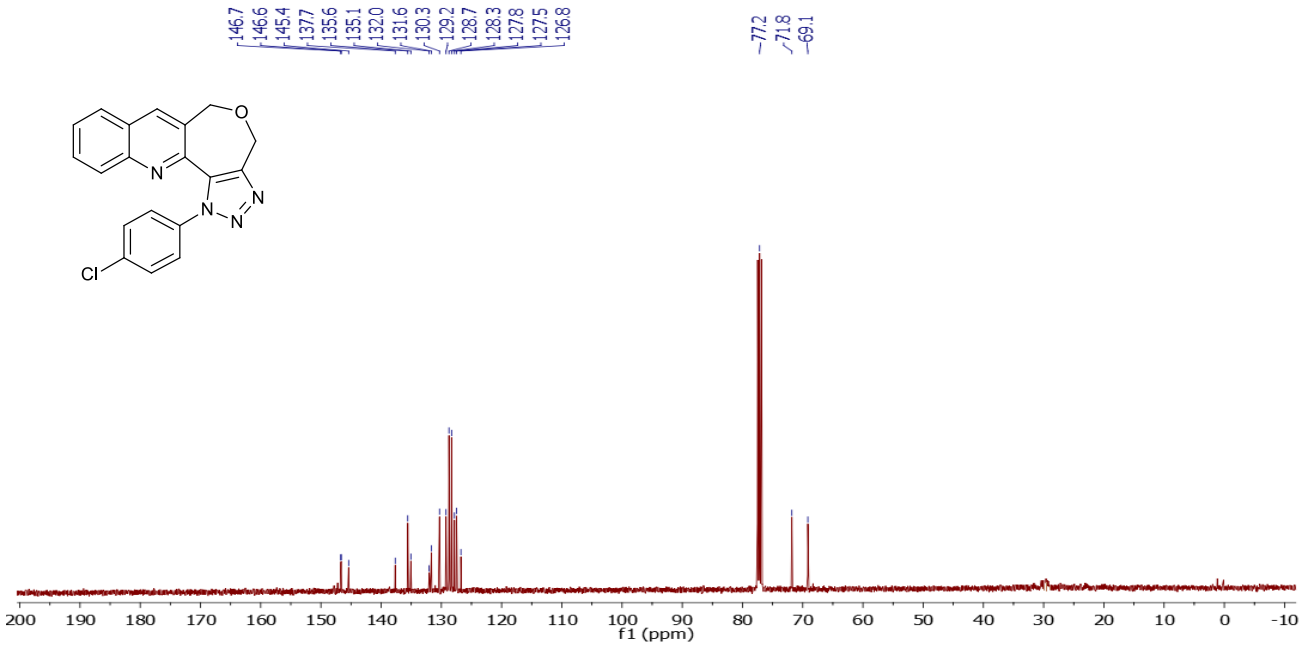
1.0
1.1
1.2
3.0
2.3
2.2
2.2
f1 (ppm)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135.1
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131.6
130.3
129.2
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127.5
126.8
77.2
71.8
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O
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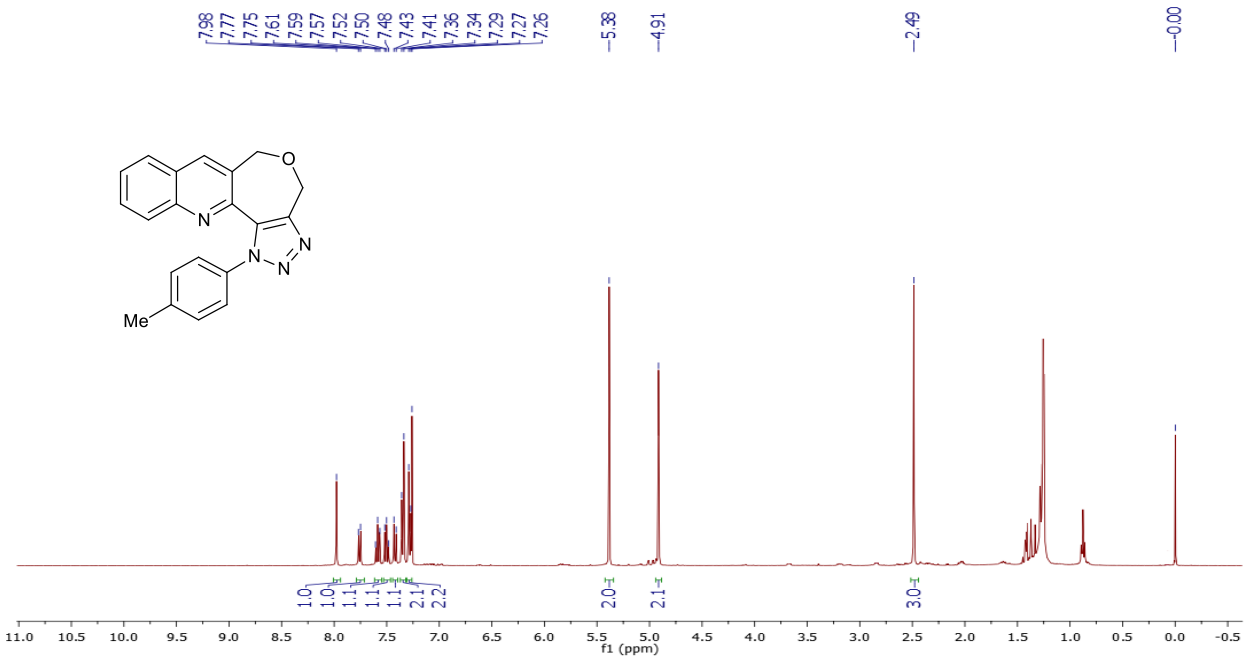
N
N
Cl
f1 (ppm)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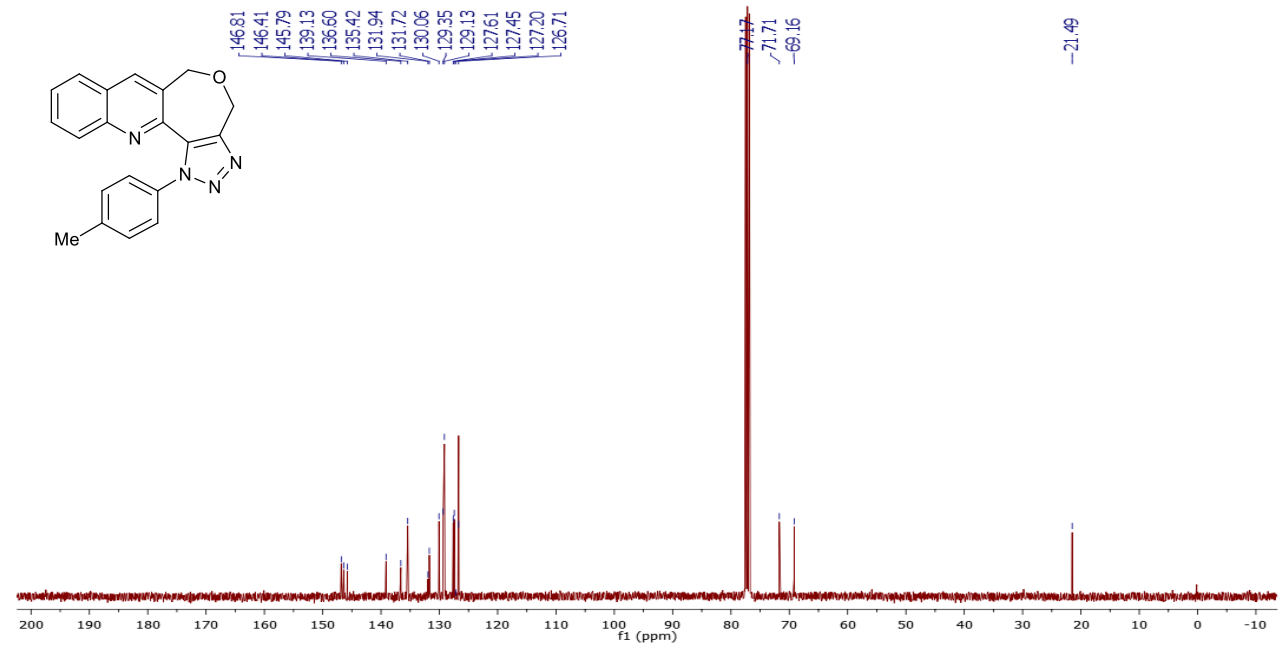
7.50
7.48
7.43
7.41
7.36
7.34
7.29
7.27
7.26
5.38
4.91
2.49
0.00
O
N
N
N
N
Me
1.0
1.0
1.1
1.1
1.1
2.1
2.2
2.0
2.1
3.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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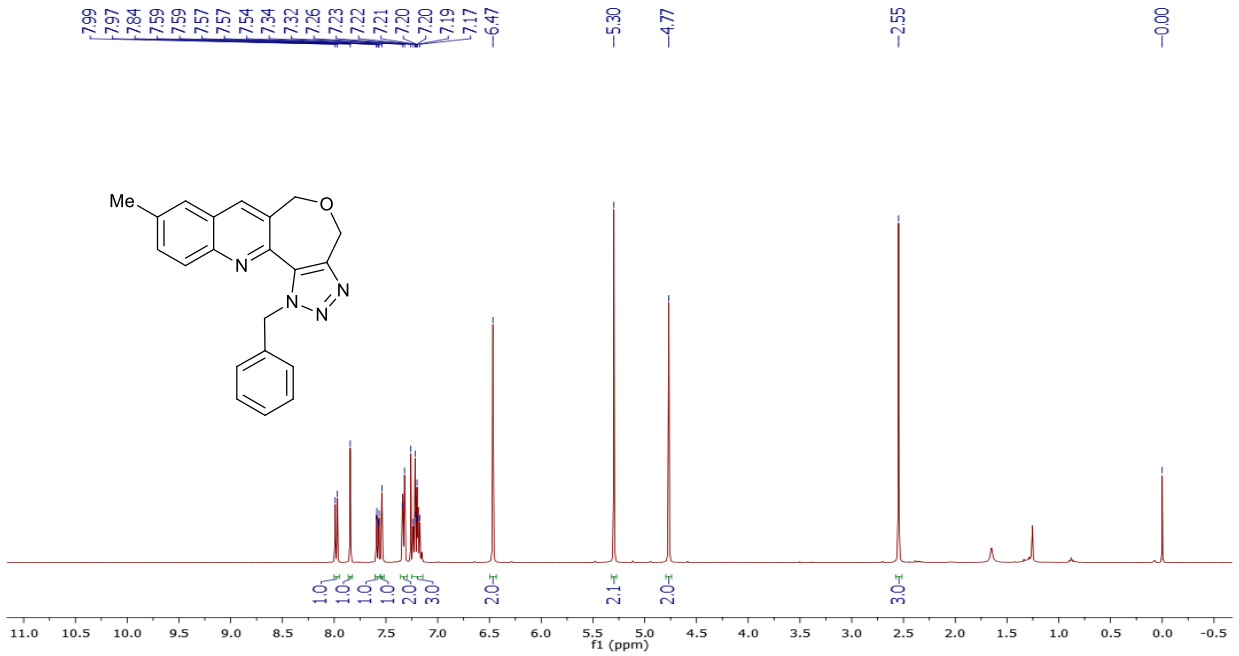
135.42
131.94
131.72
130.06
129.35
129.13
127.61
127.45
127.20
126.71
77.17
71.71
69.16
21.49
O
N
N
N
N
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.59
7.57
7.57
7.54
7.34
7.32
7.26
7.23
7.22
7.21
7.20
7.20
7.19
7.17
6.47
5.30
4.77
2.55
0.00
Me
O
N
N
N
N
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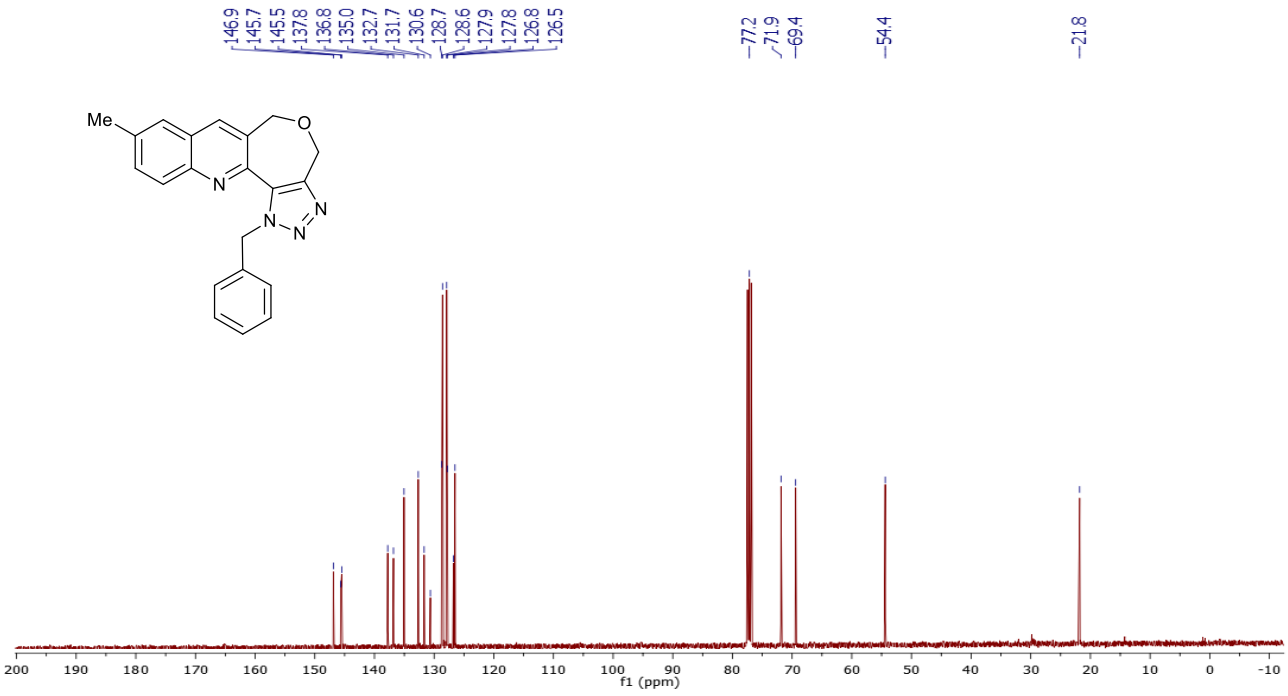
1.0
1.0
1.0
2.0
3.0
2.0
2.1
2.0
3.0
f1 (ppm)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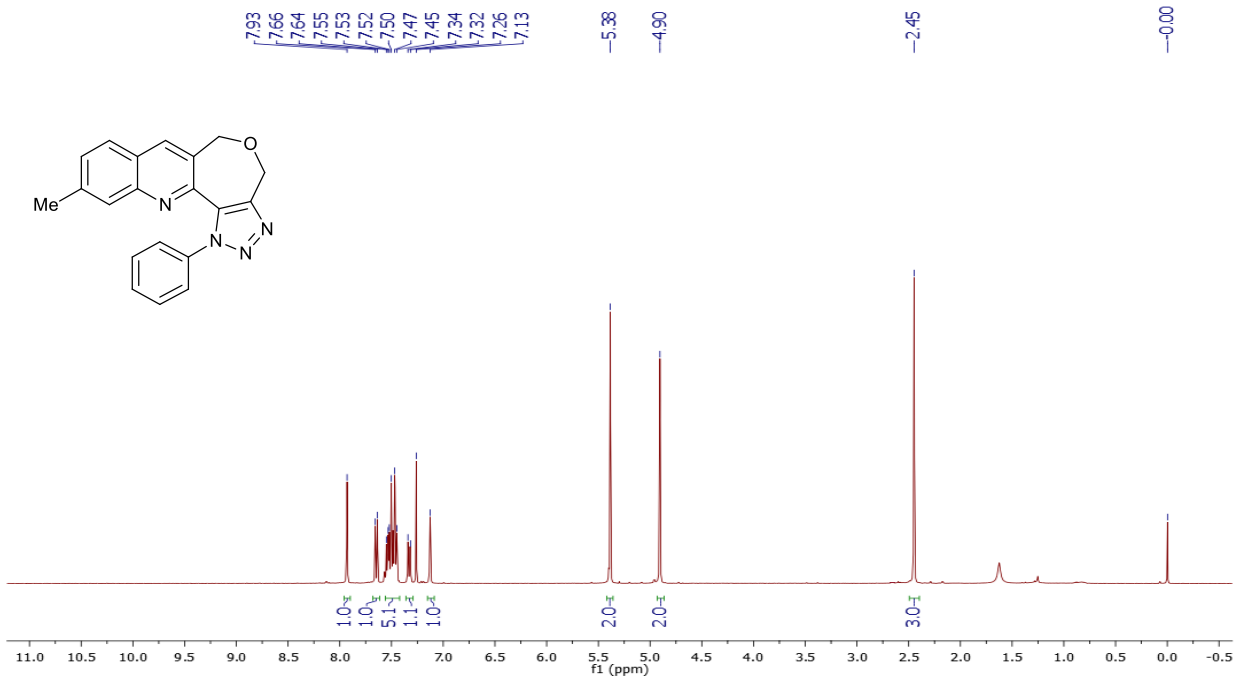
132.7
131.7
130.6
128.7
128.6
127.9
127.8
126.8
126.5
77.2
71.9
69.4
54.4
21.8
Me
O
N
N
N
N
f1 (ppm)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7.47
7.45
7.34
7.32
7.26
7.13
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4.90
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0.00
Me
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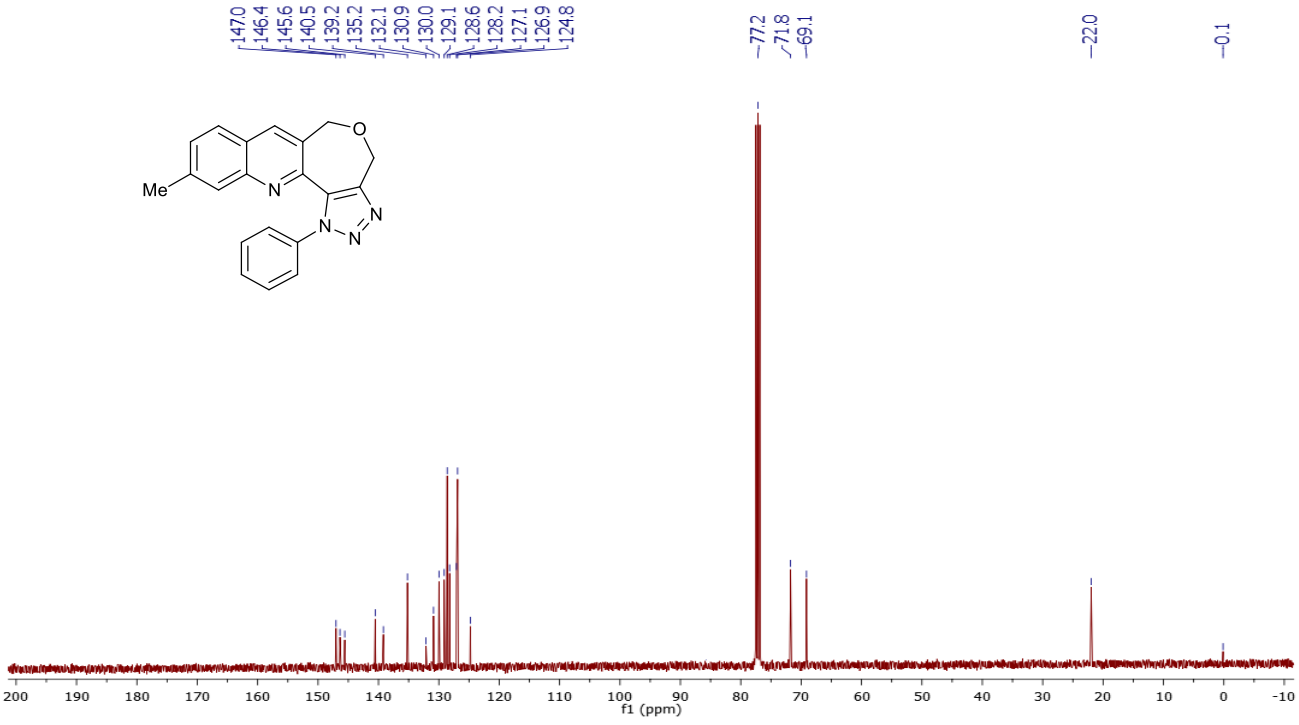
1.0
5.1
1.1
1.0
2.0
2.0
3.0
f1 (ppm)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140.5
139.2
135.2
132.1
130.9
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128.6
128.2
127.1
126.9
124.8
77.2
71.8
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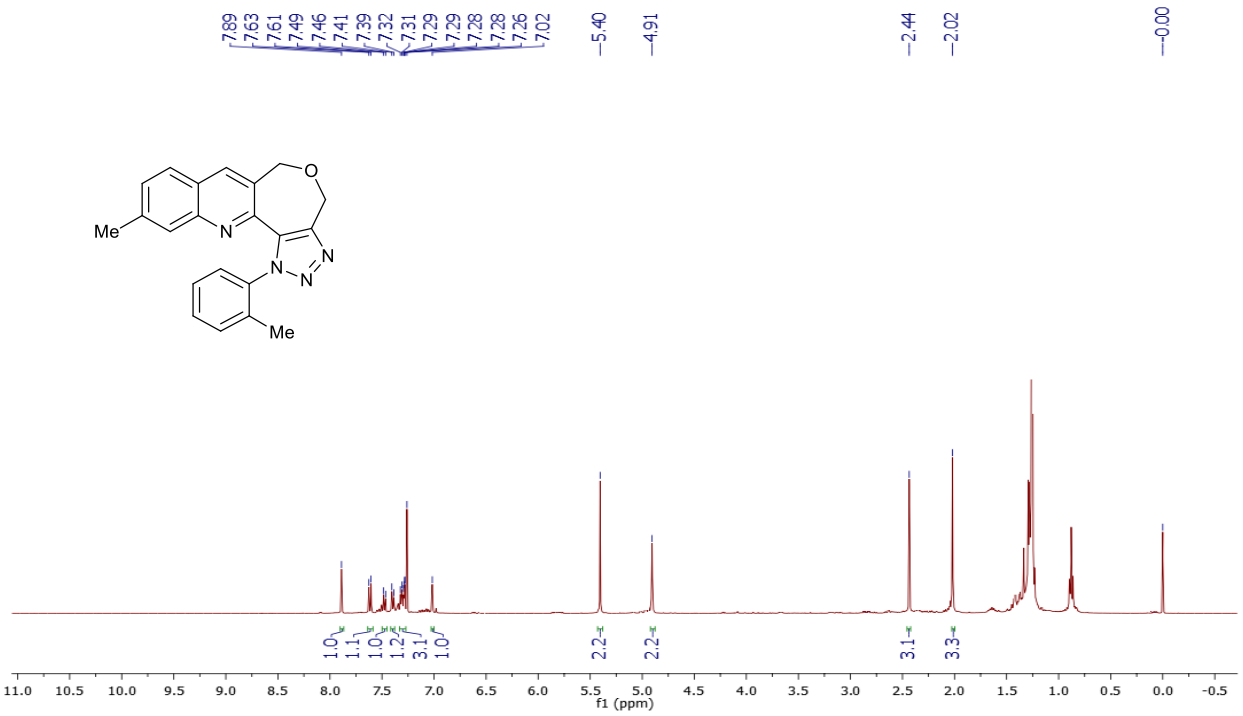
22.0
0.1
Me
O
N
N
N
N
f1 (ppm)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7.29
7.28
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7.26
7.02
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2.02
0.00
Me
N
O
N
N
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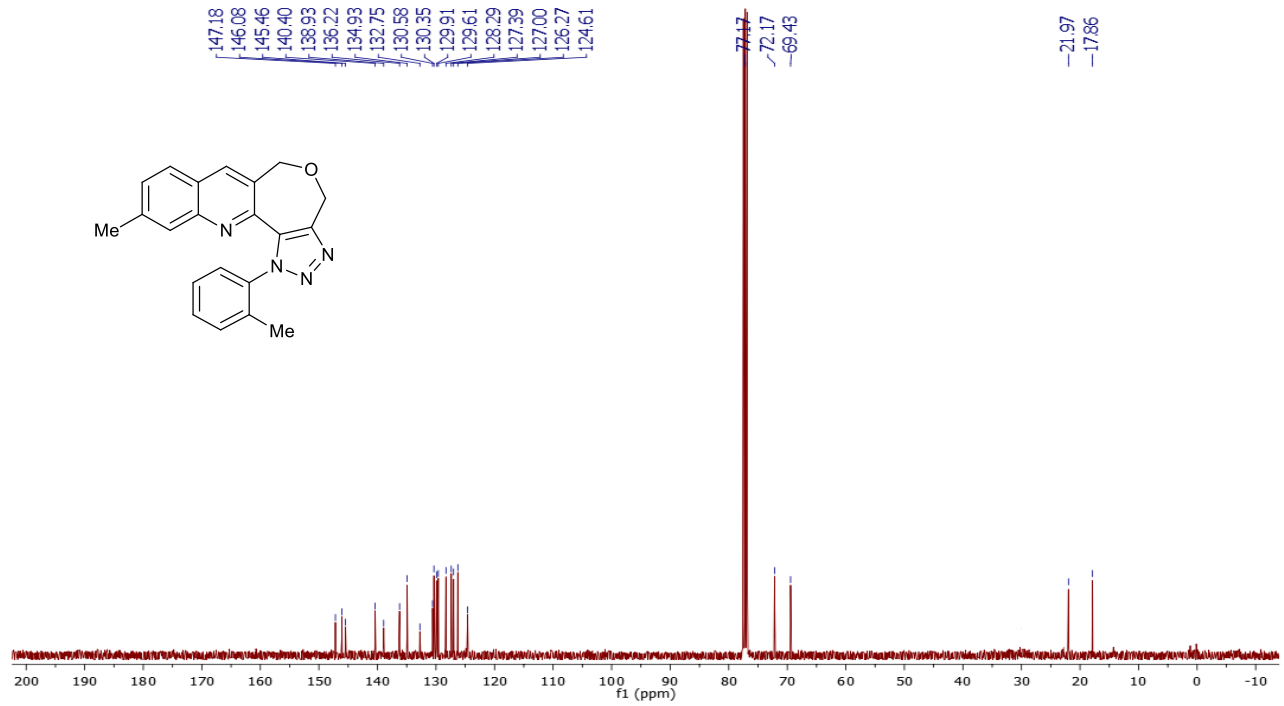
1.0
1.2
3.1
1.0
2.2
2.2
3.1
3.3
f1 (ppm)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129.91
129.61
128.29
127.39
127.00
126.27
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72.17
69.43
21.97
17.86
Me
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O
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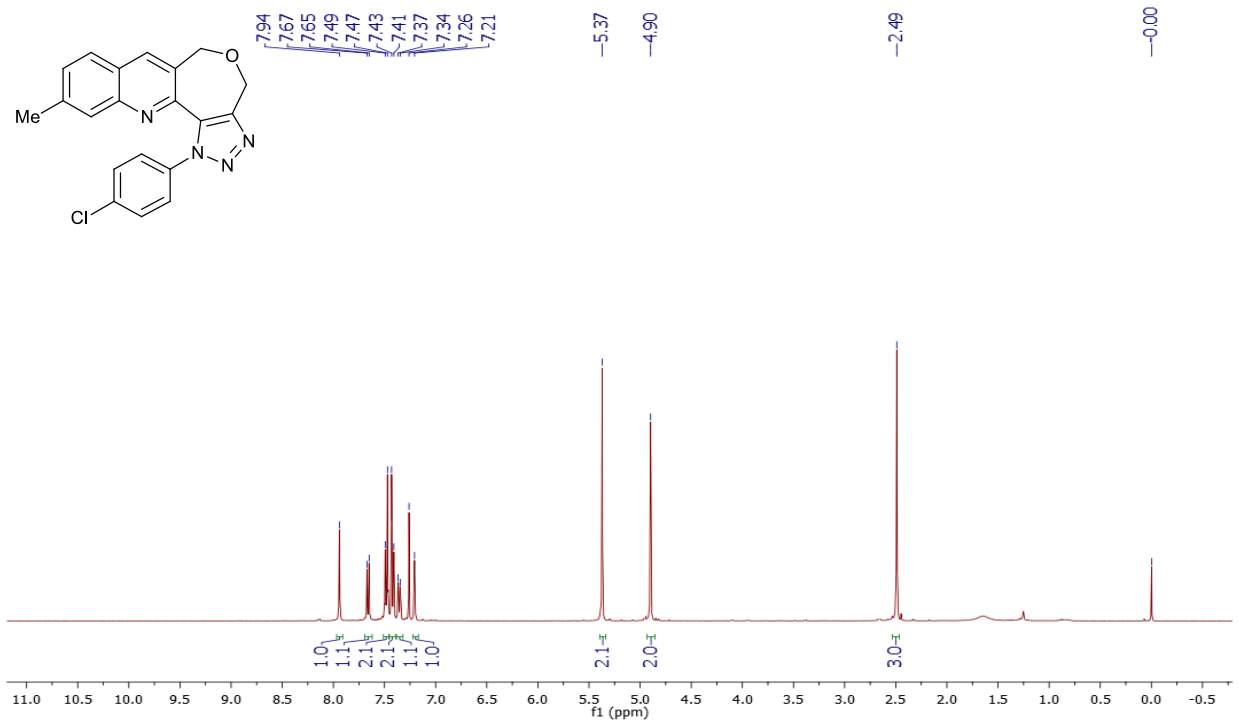
N
N
Me
f1 (ppm)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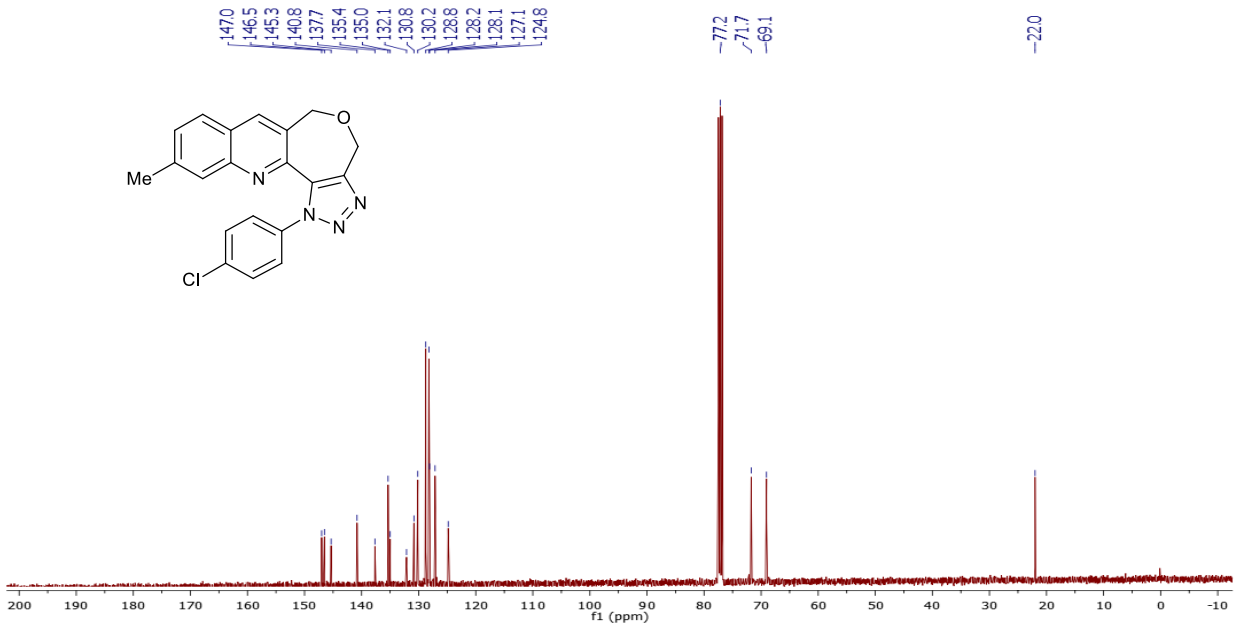
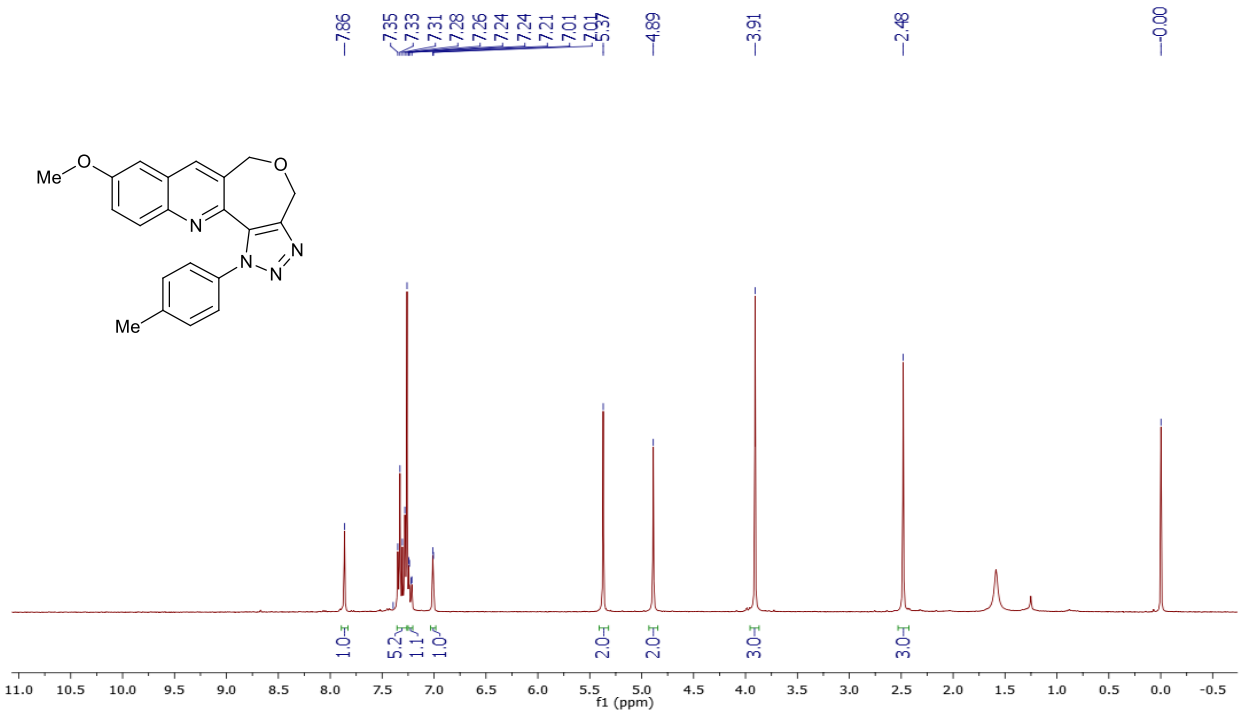
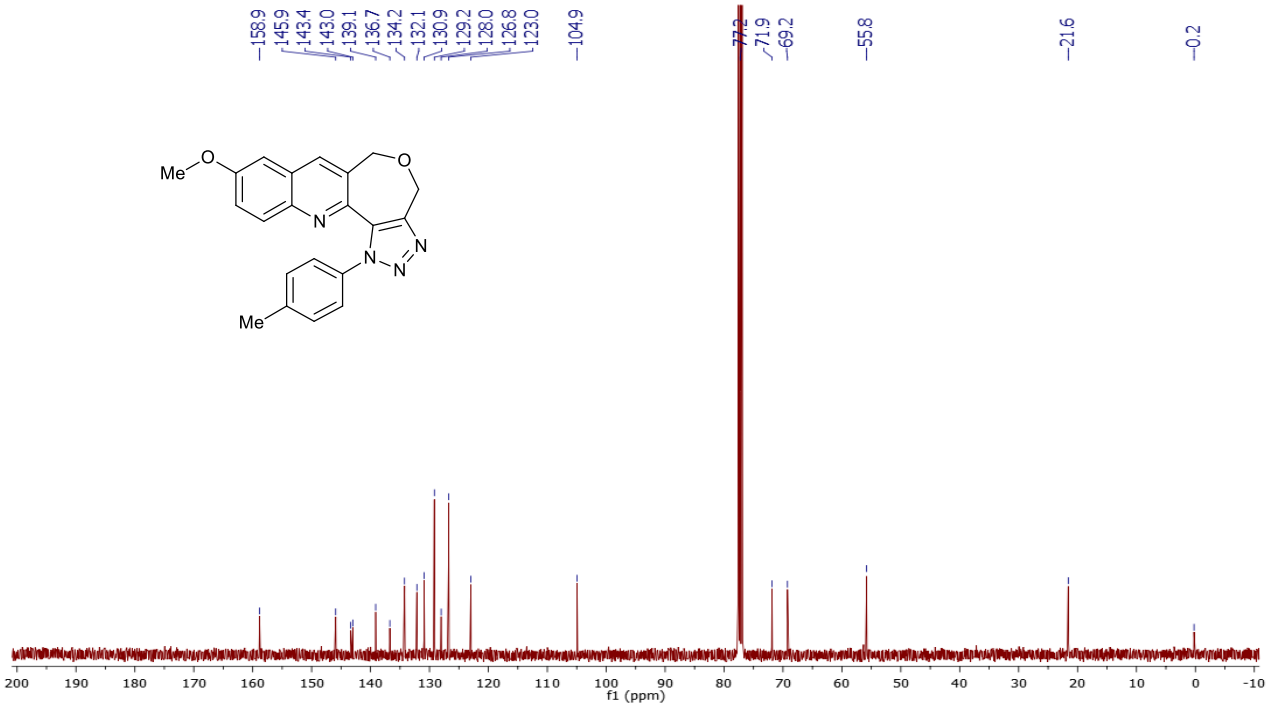
7.47
7.43
7.41
7.37
7.34
7.26
7.21
5.37
4.90
2.49
0.00
Me
N
O
N
N
N
Cl
1.0
1.1
2.1
2.1
1.1
1.0
2.1
2.0
3.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


147.0
146.5
145.3
140.8
137.7
135.4
135.0
132.1
130.8
130.2
128.8
128.2
128.1
127.1
124.8
77.2
71.7
69.1
22.0
Me
N
O
N
N
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.86
7.35
7.33
7.31
7.28
7.26
7.24
7.24
7.21
7.01
7.01
5.37
4.89
3.91
2.48
0.00
Me
O
O
N
N
N
N
Me
1.0
5.2
1.1
1.0
2.0
2.0
3.0
3.0
f1 (ppm)


158.9
145.9
143.4
143.0
139.1
136.7
134.2
132.1
130.9
129.2
128.0
126.8
123.0
104.9
77.2
71.9
69.2
55.8
21.6
0.2
Me
O
O
N
N
N
N
Me
f1 (ppm)