Supplementary Material (ESI) for *Chemical Communications*

Supporting Information

Catalytic Intramolecular Aromatic C–H Alkenylation of Arenes with Non-Activated Ketones: Synthesis of 4-Alkylene Quinolin-2-ones

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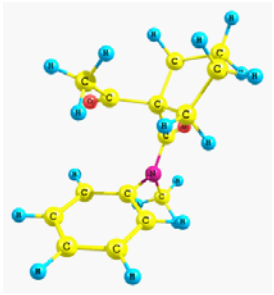
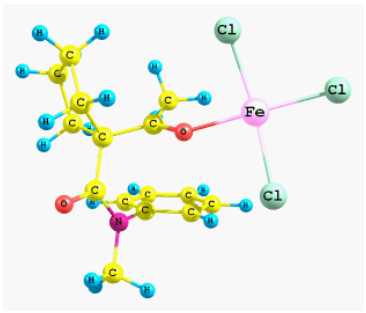
I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25°C at 500 MHz and 125 MHz, respectively, with TMS as internal standard. IR spectra (KBr) were recorded on FTIR-spectrophotometer in the range of 400-4000 cm^{-1}. Mass spectra were recorded on LCMsD mass spectrometer.

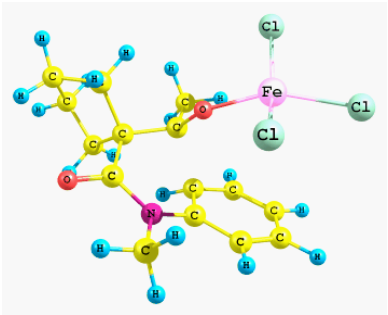
II. DFT theoretical study on the intramolecular alkenylation of acetoacetanilide 1a1



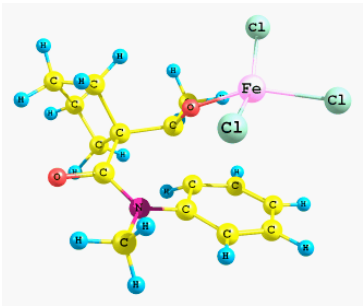
Acetoacetanilide 1a1



Coordinated Complex



Transition State



Ring-Closing Product

Figure S1 The optimized structures of acetoacetanilide 1a1, and three coordinated complexes in closing-ring process.

	$Energy_{total}$	Distance C1-C2)	Charge (C1)	Charge (C2)	Distance (Fe-O)
1a1	-788.0272	3.158	0.369	-0.090	
Coordinated Complex	-3432.3119	3.183	0.489	-0.108	1.960
Transition State	-3432.2778	1.840	0.320	-0.322	1.852
Ring-Closing Product	-3432.2780	1.63	0.320	-0.303	1.807

Table S1 Total energies (.au), Distances (Å) between C1 and C2, Bond lengths of Fe-O (or Fe-C) and charge densities of C1,C2 atoms of all complexes and intermediates, transition states in closing-ring process. **Note**: C1 is the alpha-carbon atom of the ketone carbonyl, and C2 is the ortho-C of aryl amine fragment.

Computational details

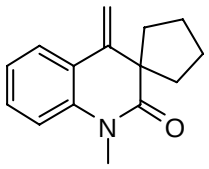
DFT calculations reported in this work have been carried out using the B3LYP composite exchange-correlation functional and the 6-31G basis set as implemented in the Gaussian 98 suite of programs. Naturally, Density functional theory (DFT) has been applied to Three-coordinate or **Four-Coordinate Fe(III) complexes** and give rational results. A large number of experimental and theoretical studies support the contention that high-spin configurations are lowest in energy for various **Four-Coordinate Fe(III) complexes**.

For each coordinated types under consideration, a full geometry optimization reactants, intermediates, transition states with high-spin configurations has been performed using unrestricted open-shell DFT without symmetry constraints. Analytical Hessians were computed to determine the nature of stationary points (one and zero imaginary frequencies for TSs and minima, respectively).

The final structures of the metal complexes are shown in Figure S1, and the electronic energy and some important geometric parameters corresponding to these complexes are summarized in Table S1.

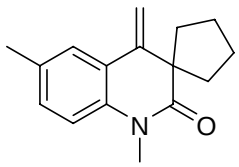
III. Synthesis and analytical data of compounds 2 - 3

Typical procedure for the preparation of 2 (with 2a as an example): Compound 1a (1 mmol, 0.245 g) and $FeCl_3$ (0.1 mmol, 0.162 g) were added to CH_3CN (2.0 mL) under stirring. The mixture was warmed to 60 ℃ and was stirred for 0.5 h. After the staring material was consumed (monitored by TLC), the reaction mixture was poured into saturated sodium chloride aqueous (20 mL). The mixture was extracted with dichloromethane (3 × 20 mL), the combined organic phase was washed with water (3 × 20 mL), dried over $MgSO_4$, filtered and concentrated in vacuum. The crude product was purified by flash chromatography (silica gel, petroleum ether: diethyl ether = 10 : 1) to give 2a as a colorless liquid (186 mg, 82%).



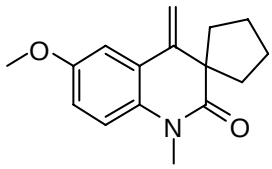
1'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2a)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.68-1.71 (m, 2H), 1.77-1.84 (m, 4H), 2.13-2.18 (m, 2H), 3.37 (s, 3H), 5.18 (s, 1H), 5.40 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.04-7.07 (m, 1H), 7.30-7.33 (m, 1H), 7.46 (d, *J* = 8.0 Hz , 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.34, 30.25, 34.25, 55.39, 110.18, 114.18, 122.79, 125.57, 126.19, 128.90, 138.44, 144.97, 173.57; IR (KBr, cm^{-1}) 3040, 2954, 2871, 1652, 1598, 1499, 1459, 1357, 1269, 1156, 1129, 1089, 1044, 898, 752, 670; MS m/z Calcd: 227.1; Found: 228.1 [$(M+1)^+$].



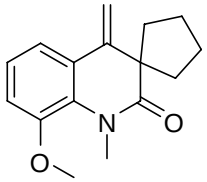
1',6'-dimethyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2b)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.66-1.82 (m, 6H), 2.15 (t, *J* = 6.5 Hz, 2H), 2.34 (s, 3H), 3.36 (s, 3H), 5.16 (s, 1H), 5.38 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 1H) , 7.27 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.65, 24.34, 30.25, 34.25, 55.42, 109.92, 114.13, 125.99, 126.16, 129.43, 132.22, 136.14, 145.13, 173.45 ; IR (KBr, cm^{-1}) 3455, 2955, 2870, 1663, 1583, 1500, 1349, 1275, 1139, 810, 621, 469; MS m/z Calcd: 241.2; Found: 242.2 [$(M+1)^+$].



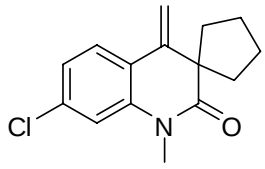
6'-methoxy-1'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2c)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.67-1.70 (m, 2H), 1.77-1.82 (m, 4H), 2.12-2.17 (m, 2H), 3.34 (s, 3H), 3.82 (s, 3H), 5.18 (s, 1H), 5.39 (s, 1H), 6.85 (dd, *J* = 3.0, 9.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 7.00 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.31, 30.35, 34.21, 55.30, 55.48, 110.39, 111.22, 113.75, 115.20, 127.39. 132.22. 145.15. 155.30. 173.06; IR (KBr, cm^{-1}) 2954, 2385, 1661, 1584, 1499, 1355, 1294, 1227, 1134, 1042, 898, 809, 636, 614; MS *m/z* Calcd: 257.1; Found: 258.1 [$(M+1)^{+}$].



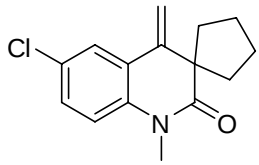
8'-methoxy-1'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2d)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.63-1.66 (m, 2H), 1.71-1.77 (m, 4H), 2.10-2.13 (m, 2H), 3.37 (s, 3H), 3.86 (s, 3H), 5.20 (s, 1H), 5.41 (s, 1H), 6.91 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.02-7.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.25, 33.58, 35.20, 55.45, 55.98, 110.19, 112.93, 118.24, 124.37, 130.97, 145.70, 149.14, 174.60; IR (KBr, cm^{-1}) 3426, 2955, 2870, 1670, 1521, 1458, 1349, 1255, 111.6, 1056, 902, 744, 640; MS m/z Calcd: 257.1; Found: 258.1 [$(M+1)^{+}$].



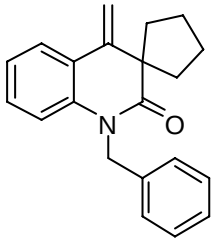
7'-chloro-1'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2e)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.68-1.75 (m, 2H), 1.79-1.87 (m, 4H), 2.12-2.16 (m, 2H), 3.35 (s, 3H), 5.20 (s, 2H), 5.37 (s, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 7.02 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.35, 30.30, 34.33, 55.32, 109.72, 110.66, 114.51, 122.65, 124.57, 126.63, 139.53, 143.98, 173.42; IR (KBr, cm^{-1}) 2955, 2871, 1678, 1595, 1424, 1330, 1257, 1088, 849, 816; MS m/z Calcd: 261.1; Found: 262.1 [$(M+1)^{+}$].



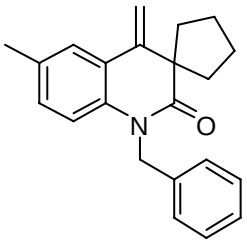
6'-chloro-1'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2f)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.66-1.67 (m, 2H), 1.76-1.79 (m, 4H), 2.10-2.12 (m, 2H), 3.32 (s, 3H), 5.20 (s, 2H), 5.37 (s, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 7.23 (dd, *J* = 2.0, 8.5Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 26.94, 30.14, 36.73, 63.72, 116.33, 121.34, 127.52, 128.57, 135.20, 141.73, 174.09; IR (KBr, cm^{-1}) 3447, 2954, 2870, 1665, 1598, 1468, 1425, 1342, 1107, 816, 732, 555; MS m/z Calcd: 261.1; Found: 262.1 [$(M+1)^{+}$].



1'-benzyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2g)

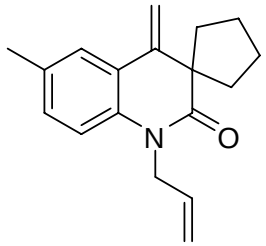
White semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.73-1.76 (m, 2H), 1.81-1.84 (m, 2H), 1.90-1.95 (m, 2H), 2.24-2.28 (m, 2H), 5.16 (s, 2H), 5.24 (s, 1H), 5.44 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.00-7.03 (m, 1H), 7.14-7.18 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.22-7.25 (m, 1H), 7.29-7.32 (m, 2H), 7.47 (dd, *J* = 1.0, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.22, 34.20, 46.90, 55.61, 110.47, 115.01, 122.96, 125.67, 126.09, 126.34, 126.96, 128.72, 128.92, 137.26, 137.90, 144.79, 173.67; IR (KBr, cm^{-1}) 3063, 3032, 2955, 2871, 1677, 1599, 1458, 1370, 1269, 1227, 1187, 901, 752, 730, 697; MS m/z Calcd: 303.2; Found: 304.2 [$(M+1)^{+}$].



1'-benzyl-6'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2h)

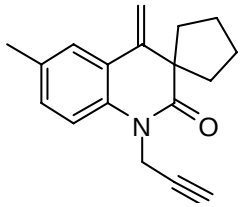
White solid; mp 110-112℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.73-1.75 (m, 2H), 1.77-1.82 (m, 2H), 1.90-1.93 (m, 2H), 2.23-2.27 (m, 2H), 2.29 (s, 3H), 5.14 (s, 2H), 5.22 (s, 1H), 5.42 (s, 1H), 6.74(d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.25 (s, 1H), 7.28-7.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.67, 24.26, 34.23, 46.84,

55.64, 110.22, 114.97, 126.12, 126.26, 126.94, 128.72, 129.50, 132.40, 135.54, 137.38, 144.95, 173.56; IR (KBr, cm^{-1}) 3058, 3037, 1665, 1629, 1501, 1428, 1371, 897, 803, 723. MS m/z Calcd: 317.2; Found: 318.2 [$(M+1)^+$].



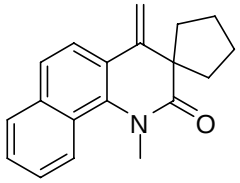
1'-allyl-6'-methyl-4'-methylene-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2i)

Colorless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ = 1.70-1.74 (m, 2H), 1.79-1.83 (m, 2H), 1.84-1.86 (m, 2H), 2.15-2.19 (m, 2H), 2.33 (s, 3H), 4.52 (d, *J* = 2.0 Hz, 2H), 5.12 (t, *J* = 13.0 Hz, 2H), 5.18 (s, 1H)), 5.40 (s, 1H), 5.85-5.92 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.64, 24.20, 34.10, 45.48, 55.48, 109.99, 114.75, 115.63, 126.11, 126.20, 129.41, 132.27, 132.60, 135.37, 145.00, 173.02; IR (KBr, cm^{-1}) 3446, 2953, 2869, 1664, 1616, 1501, 1432, 1366, 1227, 915, 813, 733; MS m/z Calcd: 267.2; Found: 268.4 [$(M+1)^+$].



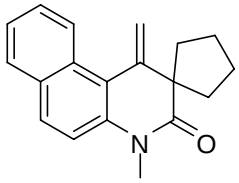
6'-methyl-4'-methylene-1'-(prop-2-ynyl)-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2j)

Colorless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ = 1.68-1.72 (m, 2H), 1.81-1.83 (m, 4H), 2.15-2.16 (m, 2H), 2.19 (s, 1H), 2.35 (s, 3H), 4.68 (s, 2H), 5.18 (s, 1H), 5.40 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.72, 24.45, 32.48, 34.13, 55.30, 71.55, 78.81, 110.30, 114.46, 126.13, 126.40, 129.51, 132.72, 134.44, 144.61, 172.83; IR (KBr, cm^{-1}) 3295, 2954, 2869, 1670, 1501, 1430, 1365, 1272, 812, 740; MS m/z Calcd: 256.2; Found: 257.2 [$(M+1)^+$].



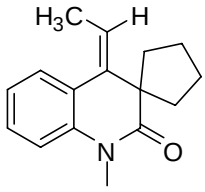
1-methyl-4-methylene-1H-spiro[benzo[h]quinoline-3,1'-cyclopentan]-2(4H)-one (2k)

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.66-1.80 (m, 6H), 2.16-2.20 (m, 2H), 3.52 (s, 3H), 5.36 (s, 1H), 5.60 (s, 1H), 7.45-7.51 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.84 (dd, *J* =2.0, 7.5 Hz, 1H), 7.96 (dd, *J* =2.0, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.35, 33.70, 38.71, 55.88, 110.95, 123.18, 124.24, 124.68, 125.06, 125.54, 125.74, 126.34, 128.64, 134.87, 136.28, 145.89, 176.31; IR (KBr, cm^{-1}) 3730, 2958, 1674, 1386, 1306, 863, 818, 752; MS m/z Calcd: 277.2; Found: 278.2 [$(M+1)^{+}$].



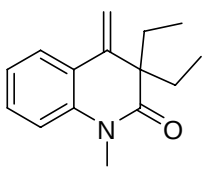
4-methyl-1-methylene-1H-spiro[benzo[f]quinoline-2,1'-cyclopentan]-3(4H)-one (2l)

Yellow solid：mp 146-147℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.73-2.09 (m, 8H), 3.47 (s, 3H), 5.50 (s, 1H), 5.73 (s, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 7.38-7.41 (m, 1H), 7.47-7.50 (m, 1H), 7.80 (dd, *J* = 7.5, 15.0 Hz, 2H), 8.30 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.21, 30.70, 33.12, 55.97, 114.74, 115.46, 121.80, 124.38, 127.88, 126.98, 128.30, 128.64, 130.48, 130.54, 135.62, 141.96, 174.56; IR (KBr, cm^{-1}) 3408, 2954, 2924, 2868, 1672, 1511, 1352, 1067, 810; MS m/z Calcd: 277.2; Found: 278.2 [$(M+1)^{+}$].



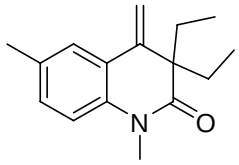
(E)-4'-ethylidene-1',6'-dimethyl-1'H-spiro[cyclopentane-1,3'-quinolin]-2'(4'H)-one (2m)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.64-1.75 (m, 6H), 1.88 (d, *J* = 7.0 Hz, 3H), 1.95-2.02 (m, 2H), 3.35 (s, 3H), 5.77 (dd, *J* = 7.0, 14.0 Hz, 1H)), 7.01 (d, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 7.28-7.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.97, 23.92, 30.28, 33.32, 55.85, 114.39, 120.47, 121.92, 125.66, 127.82, 128.46, 135.02, 139.44, 174.36; IR (KBr, cm^{-1}) 3441, 1673, 1645, 1343, 1127, 753; MS m/z Calcd: 255.2; Found: 256.2 [$(M+1)^{+}$].



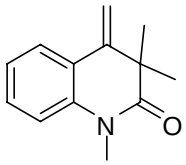
3,3-diethyl-1-methyl-4-methylene-3,4-dihydroquinolin-2(1H)-one (3a)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.84 (t, *J* = 6.0 Hz, 6H), 1.66-1.73 (m, 2H), 1.85-1.92 (m, 2H), 3.37 (s, 3H), 5.12 (s, 1H), 5.72 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.04-7.07 (m,1H), 7.28-7.31 (m, 1H), 7.55 (dd, *J* = 1.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 8.67, 29.61, 29.77, 53.22, 112.34, 113.92, 122.92, 124.67, 125.25, 128.99, 137.72, 141.78, 173.01; IR (KBr, cm^{-1}) 2968, 2931, 1670, 1598, 1464, 1358, 752; MS m/z Calcd: 229.2; Found: 230.2 [(M+1) $^{+}$].



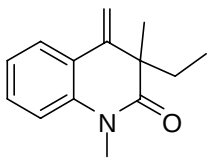
3,3-diethyl-1,6-dimethyl-4-methylene-3,4-dihydroquinolin-2(1H)-one (3b)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.84 (t, *J* = 7.5 Hz, 6H), 1.69 (q, *J* = 7.5 Hz, 2H), 1.88 (q, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 3.35 (s, 3H), 5.10 (s, 1H), 5.71 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.04 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 8.46, 20.40, 29.45, 53.00, 65.28, 111.77, 113.65, 124.22, 125.51, 129.34, 132.06, 135.22, 141.71, 172.67; IR (KBr, cm^{-1}) 3439, 2967, 2880, 1662, 1502, 1273, 1116, 755; MS m/z Calcd: 243.2; Found: 244.2 [(M+1) $^{+}$].



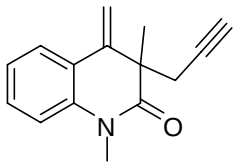
1,3,3-trimethyl-4-methylene-3,4-dihydroquinolin-2(1H)-one (3c)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.35 (s, 6H), 3.38 (s, 3H), 5.24 (s, 1H), 5.39 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.06-7.09 (m, 1H), 7.31-7.34 (m, 1H), 7.49 (dd, *J* = 1.0, 8.0 Hz,, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.41, 30.15, 44.08, 110.21, 114.12, 123.01, 125.52, 125.61, 129.02, 138.02, 147.22, 173.90; IR (KBr, cm^{-1}) 2927, 1675, 1465, 1346, 1314, 751; MS m/z Calcd: 201.1; Found: 202.1 [(M+1) $^{+}$].



3-ethyl-1,3-dimethyl-4-methylene-3,4-dihydroquinolin-2(1H)-one (3d)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.74 (t, *J* = 7.5 Hz, 3H), 1.42 (s, 3H), 1.47-1.55 (m, 2H), 3.37 (s, 3H), 5.20 (s, 1H), 5.48 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.05-7.08 (m, 1H), 7.30-7.33 (m, 1H), 7.47 (d, *J* = 8.0 Hz,, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 8.03, 18.08, 29.77, 30.52, 47.89, 111.54, 113.67, 122.69, 125.10, 125.21, 128.67, 137.82, 144.92, 173.35; IR (KBr, cm^{-1}) 3451, 1647, 1547, 1531, 1463, 674, 415; MS m/z Calcd: 215.1; Found: 216.1 [$(M+1)^{+}$].

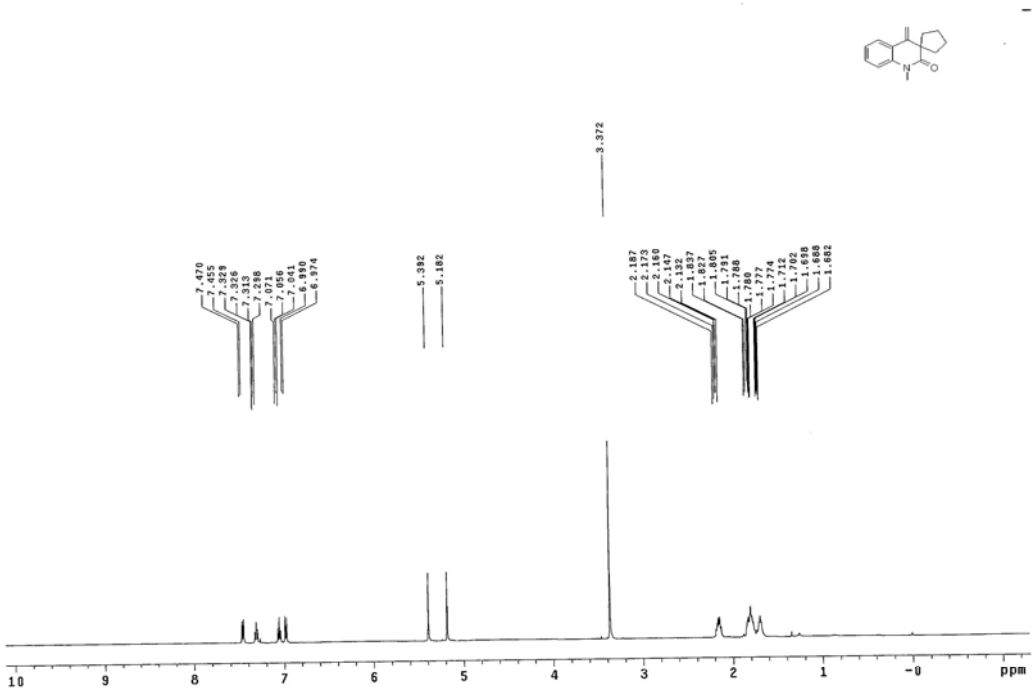


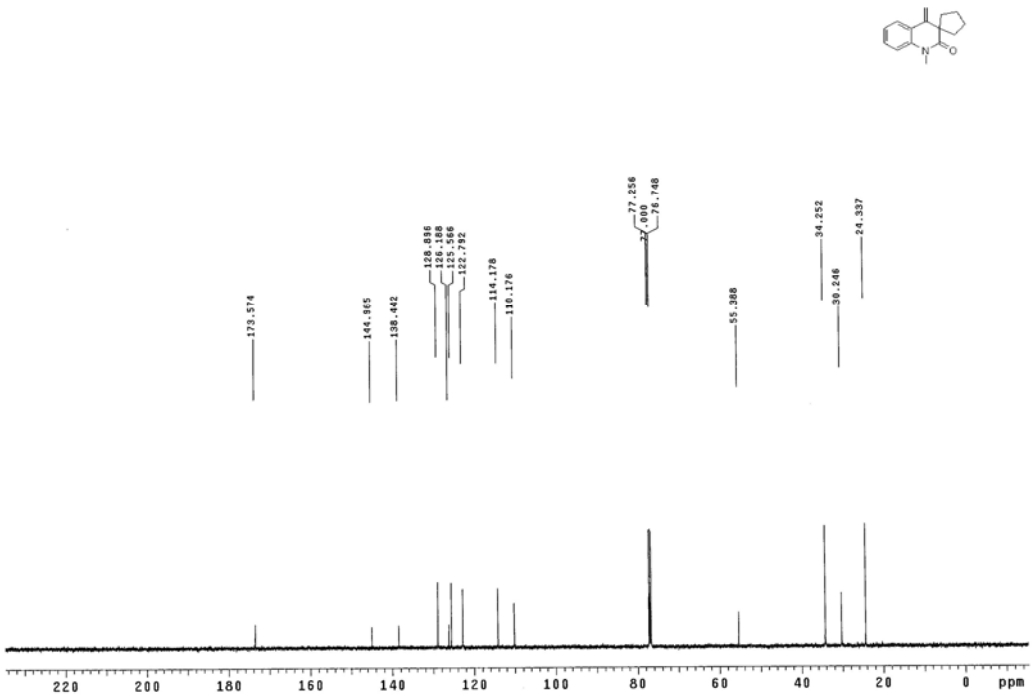
1,3-dimethyl-4-methylene-3-(prop-2-ynyl)-3,4-dihydroquinolin-2(1H)-one (3e)

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.46 (s, 3H), 2.02 (t, *J* = 2.5 Hz, 1H), 2.54-2.63 (m, 2H), 3.39 (s, 3H), 5.38 (s, 1H), 5.55 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.08-7.15 (m, 1H), 7.32-7.36 (m, 1H), 7.51 (dd, *J* = 2.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.12, 27.19, 30.24, 47.31, 71.10, 80.07, 112.71, 114.14, 123.28, 124.84, 125.77, 129.14, 137.63, 143.63, 171.78; IR (KBr, cm^{-1}) 3730, 1673, 1464, 1357, 674; MS m/z Calcd: 225.1; Found: 226.1 [$(M+1)^{+}$]

IV. Copies of NMR spectra of compounds 2-3

2a

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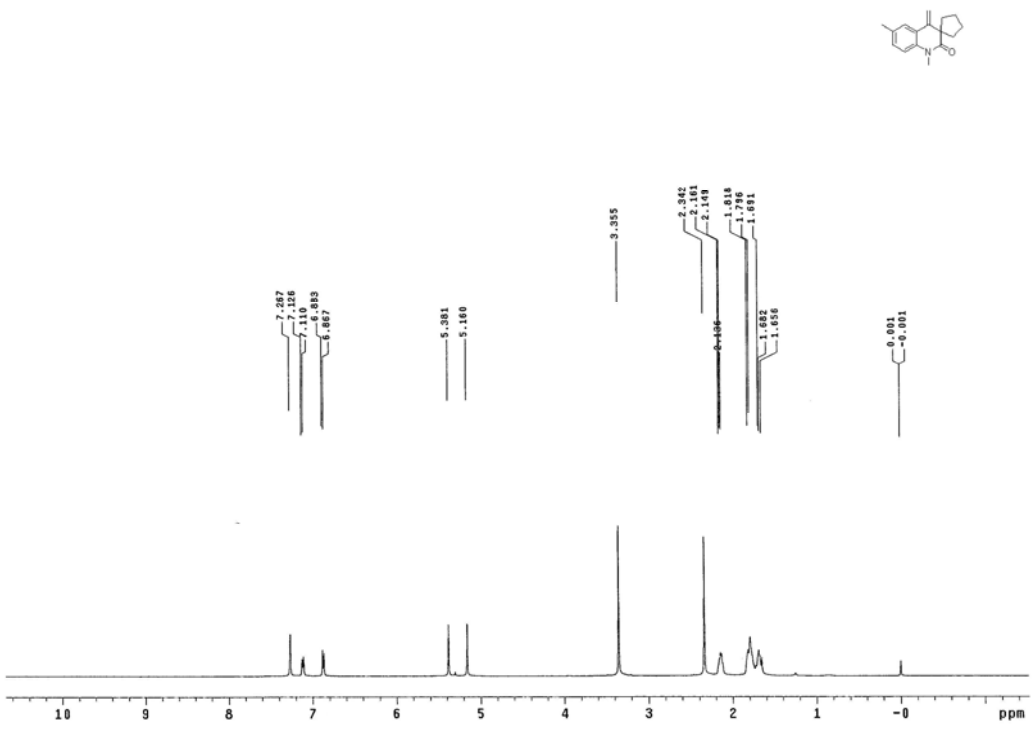
108.886
126.188
125.566
122.792
114.178
110.176
77.256
77.000
76.748
55.388
34.252
30.246
24.337
220
200
180
160
140
120
100
80
60
40
20
0
ppm

2b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7.126
7.110
6.883
6.867
5.381
5.160
3.355
2.342
2.165
2.148
1.814
1.796
1.691
1.685
1.658
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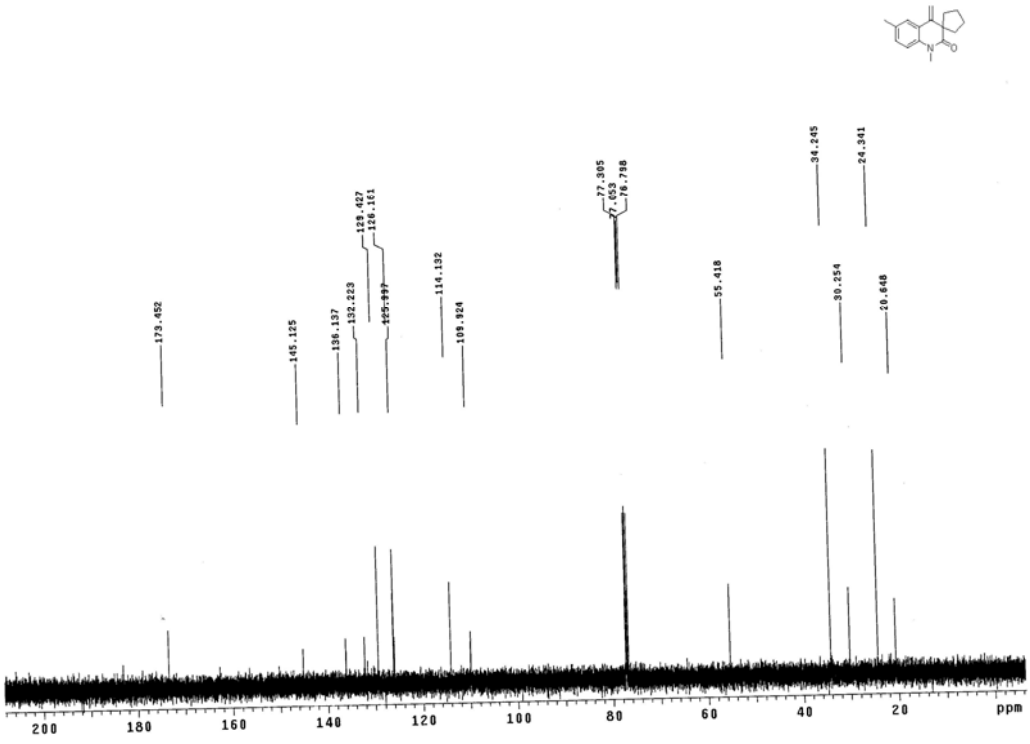
0.001
-0.001
10
9
8
7
6
5
4
3
2
1
-0
ppm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132.223
129.427
126.161
125.937
114.132
109.924
77.305
77.053
76.798
55.418
34.245
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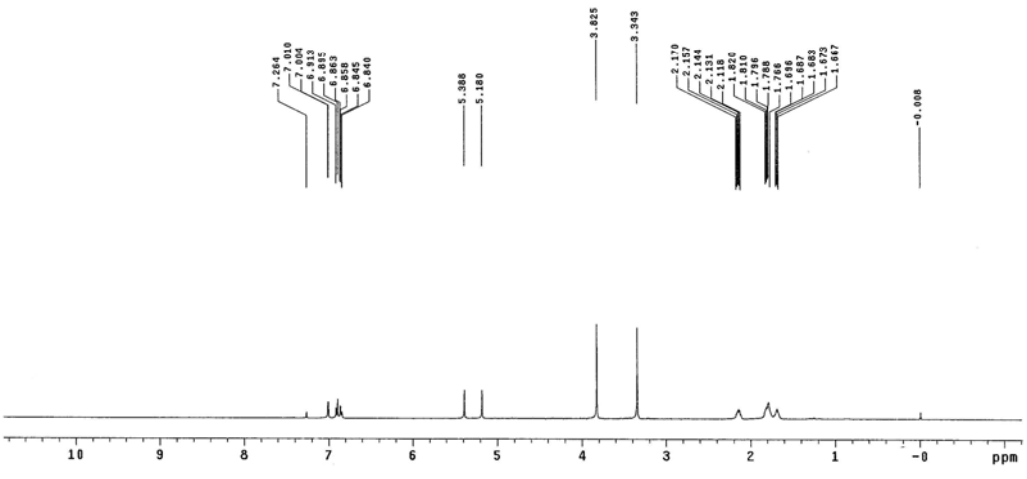
24.341
20.648
200
180
160
140
120
100
80
60
40
20
ppm

2c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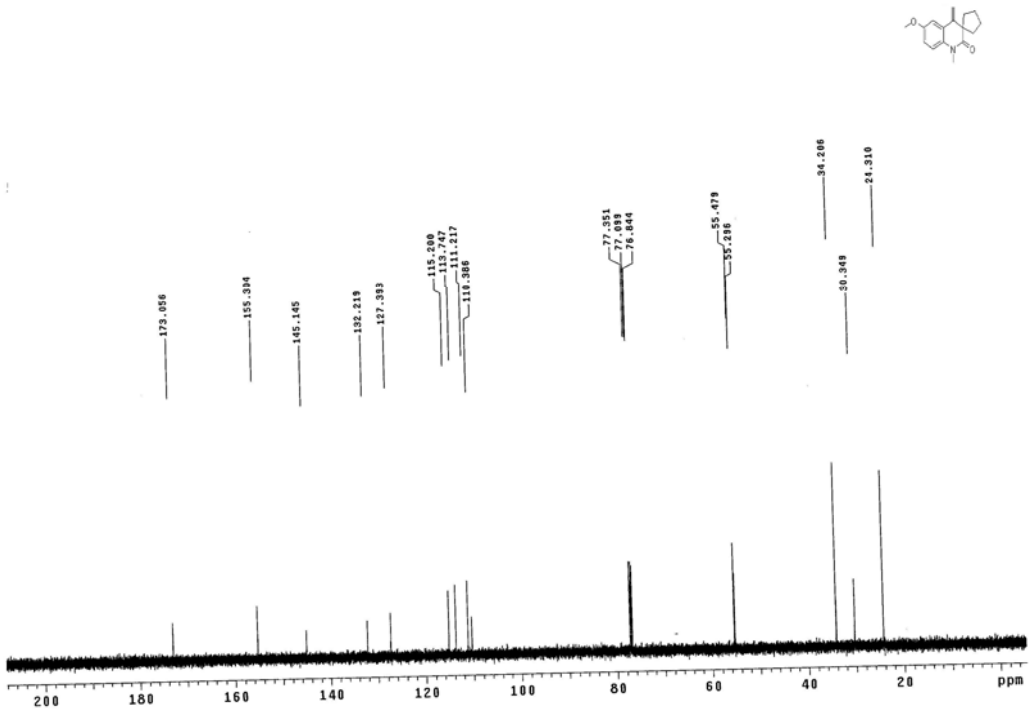
7.010
6.863
6.858
6.640
5.388
5.180
3.825
3.343
2.170
2.157
2.144
2.131
1.810
1.796
1.788
1.683
1.673
1.647
-0.008
10
9
8
7
6
5
4
3
2
1
-0
ppm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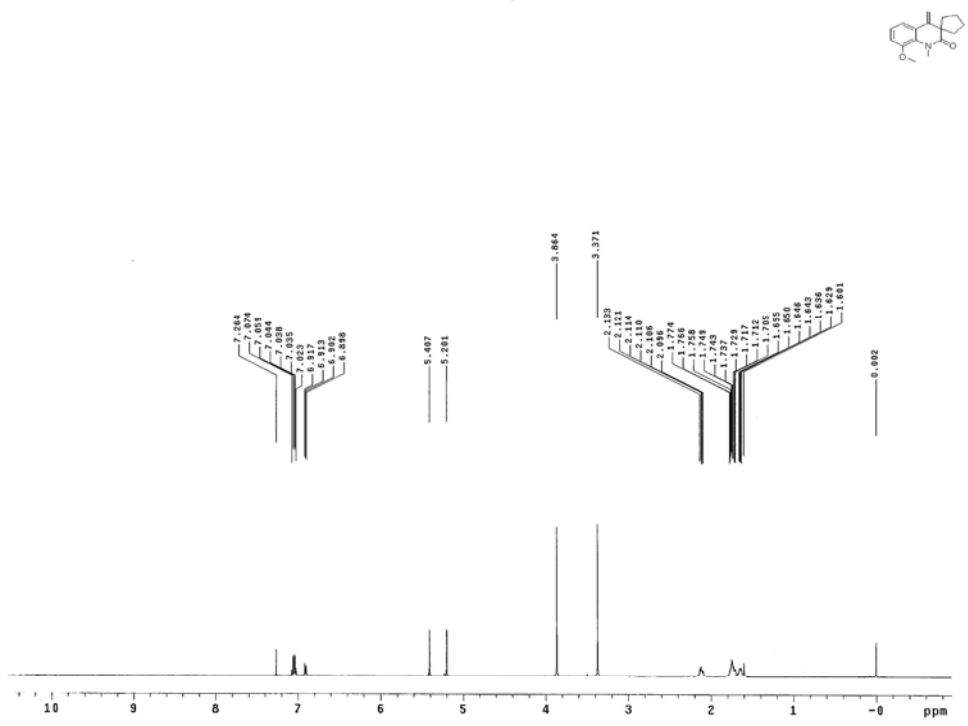
145.145
132.219
127.393
115.200
113.747
111.217
110.306
77.351
77.089
76.844
55.479
55.286
34.206
24.310
10.349
200
180
160
140
120
100
80
60
40
20
ppm

2d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0.002
10
9
8
7
6
5
4
3
2
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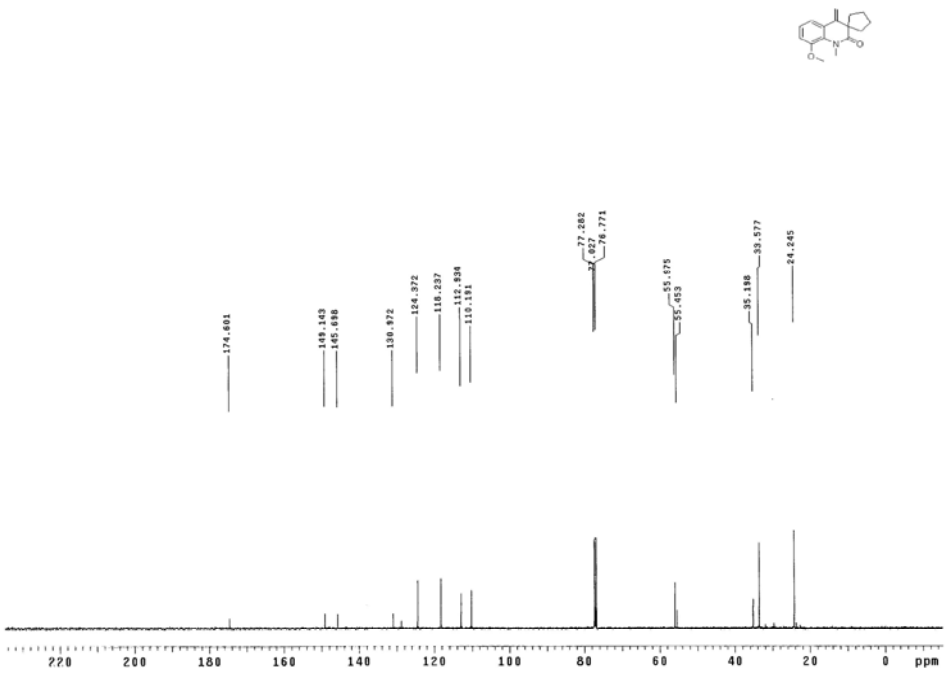
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145.698
130.972
124.372
116.237
112.834
110.191
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76.771
55.675
55.453
35.198
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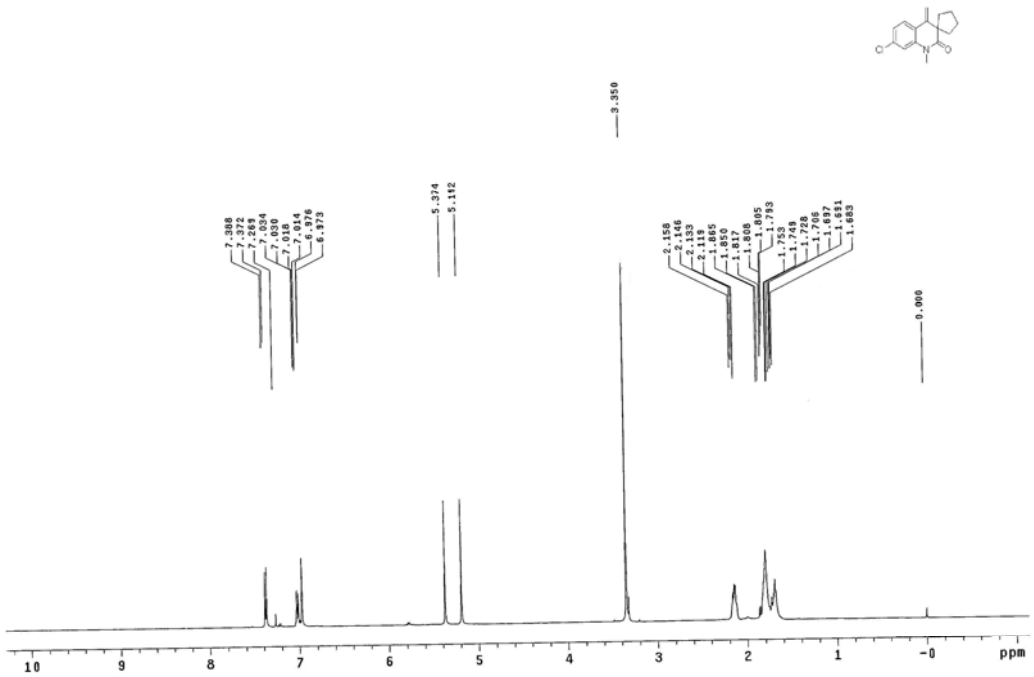
24.245
220
200
180
160
140
120
100
80
60
40
20
0
ppm

2e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7.372
7.269
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7.030
7.016
7.014
6.976
6.973
5.374
5.112
3.350
2.158
2.144
2.135
2.119
1.865
1.850
1.817
1.808
1.805
1.793
1.753
1.749
1.726
1.706
1.697
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1.683
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10
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8
7
6
5
4
3
2
1
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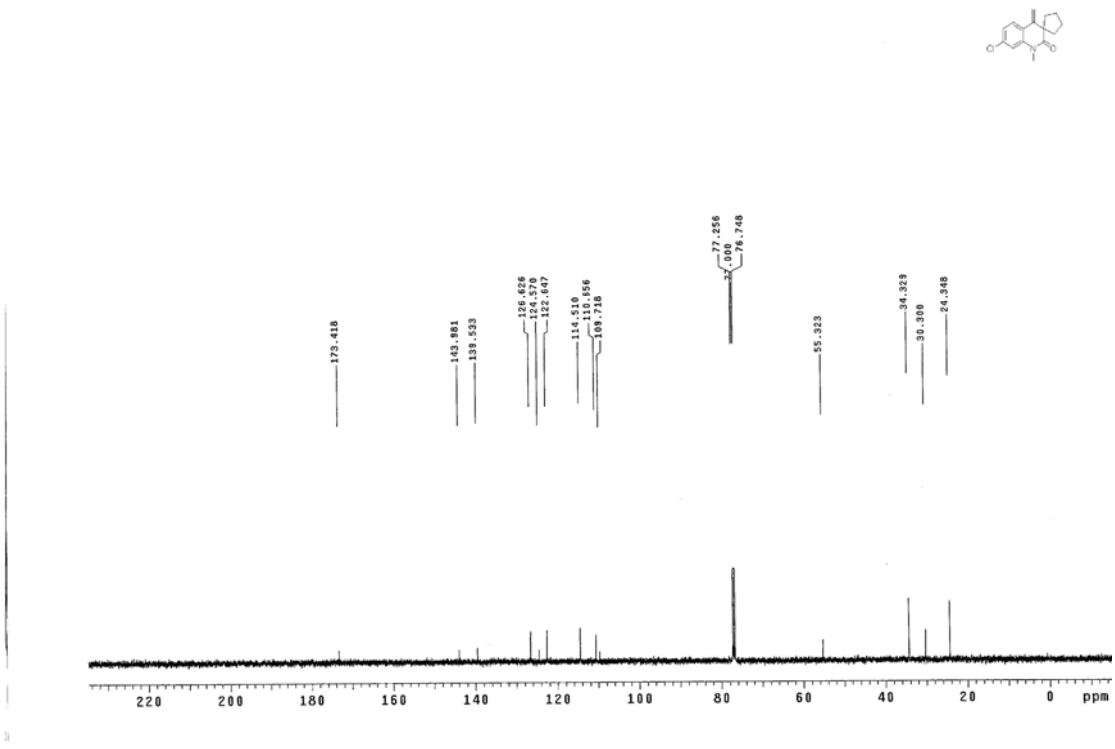
ppm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124.270
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114.510
110.656
109.718
77.256
77.000
76.748
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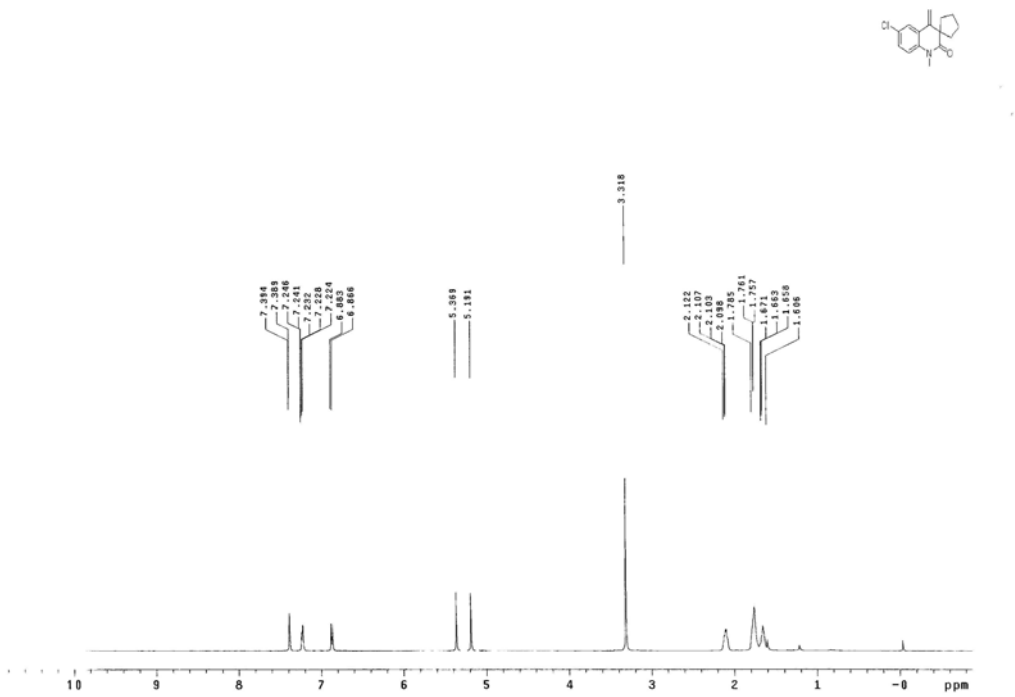
24.348
220
200
180
160
140
120
100
80
60
40
20
0
ppm

2f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7.388
7.366
7.241
7.232
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7.224
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5.191
2.122
2.107
2.103
2.098
1.785
1.761
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1.751
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1.658
1.606
10
9
8
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6
5
4
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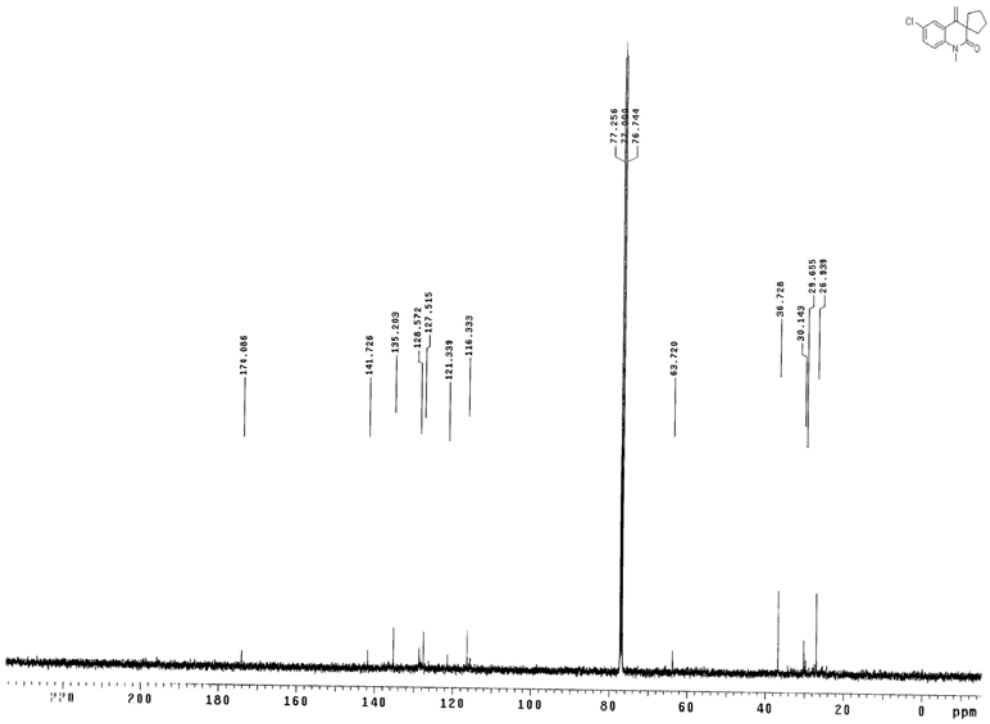
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77.256
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140
120
100
80
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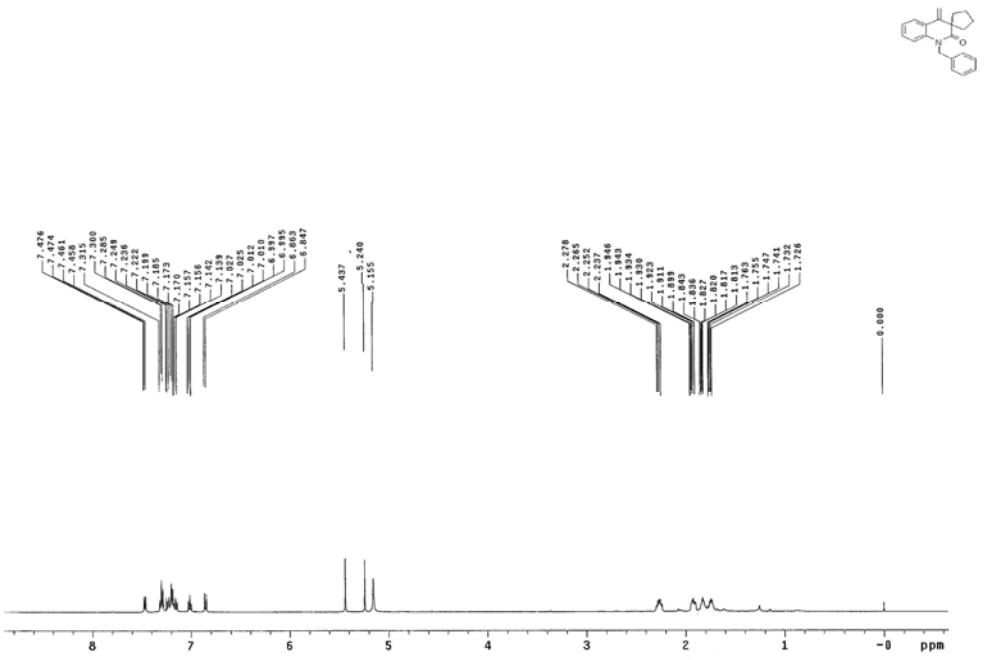
40
20
0
ppm

2g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7.458
7.315
7.300
7.285
7.240
7.236
7.222
7.219
7.185
7.173
7.170
7.157
7.156
7.142
7.139
7.027
7.025
7.012
7.010
6.897
6.895
6.863
6.847
5.437
5.240
5.155
2.278
2.265
2.252
2.237
1.946
1.940
1.934
1.930
1.923
1.911
1.899
1.843
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1.803
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6
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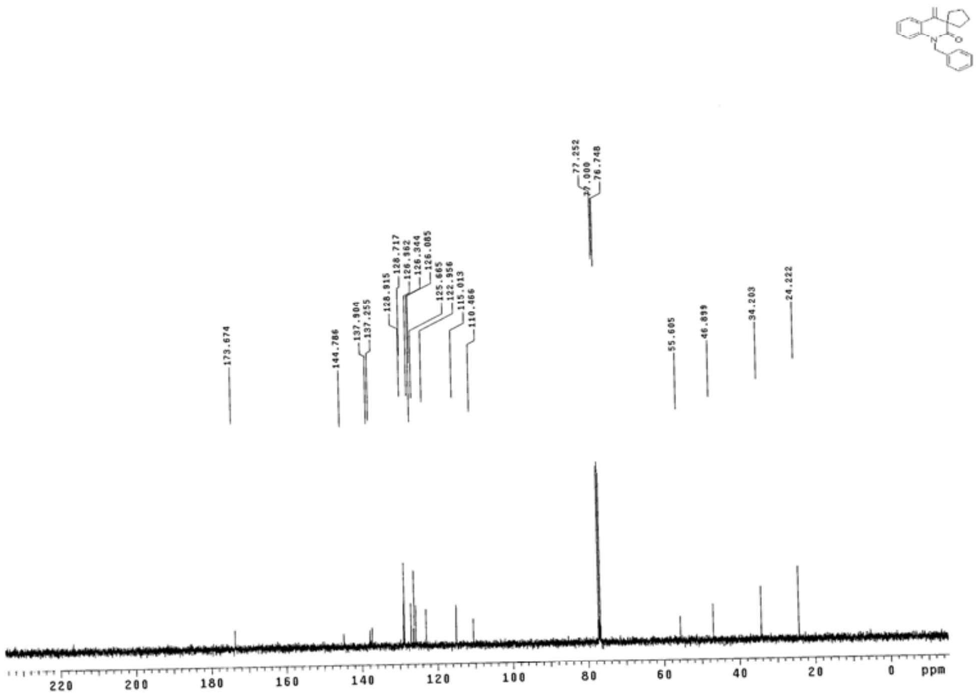
ppm



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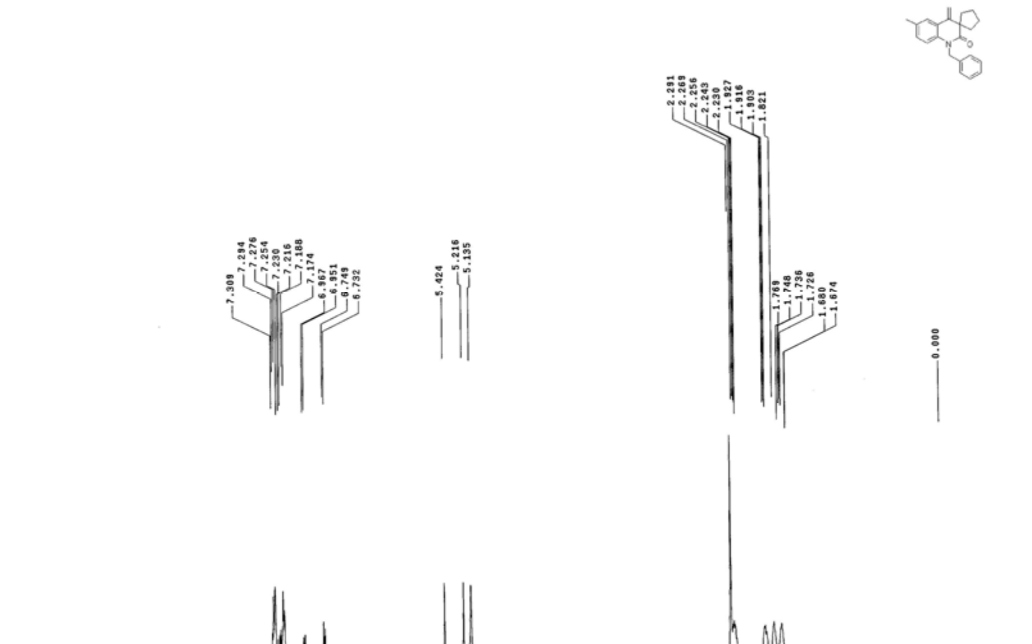

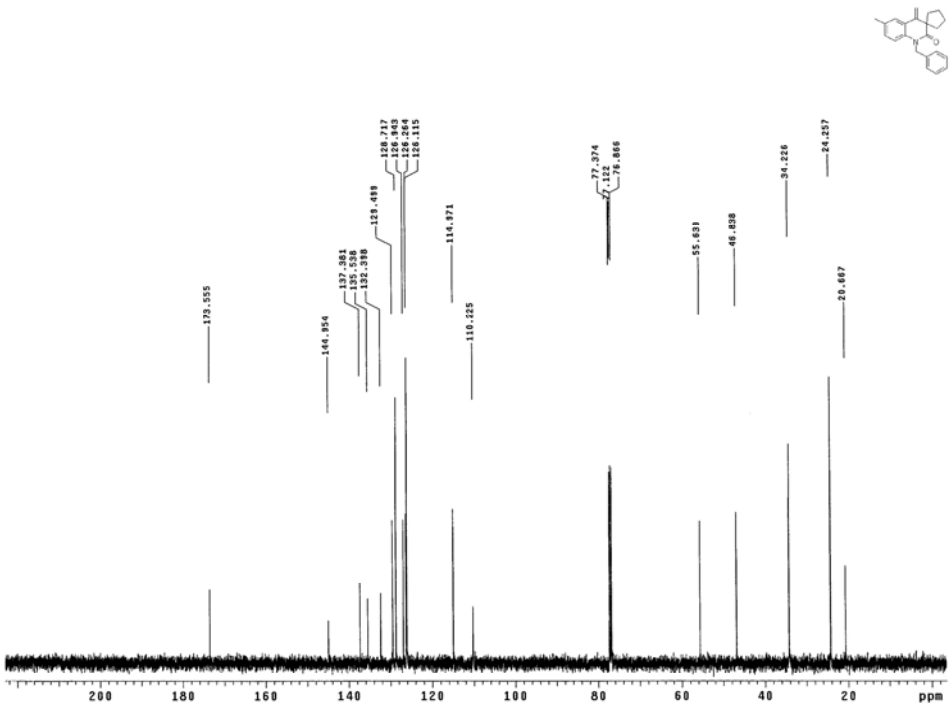
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132.398
129.489
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126.115
114.971
110.225
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24.257
20.667
200
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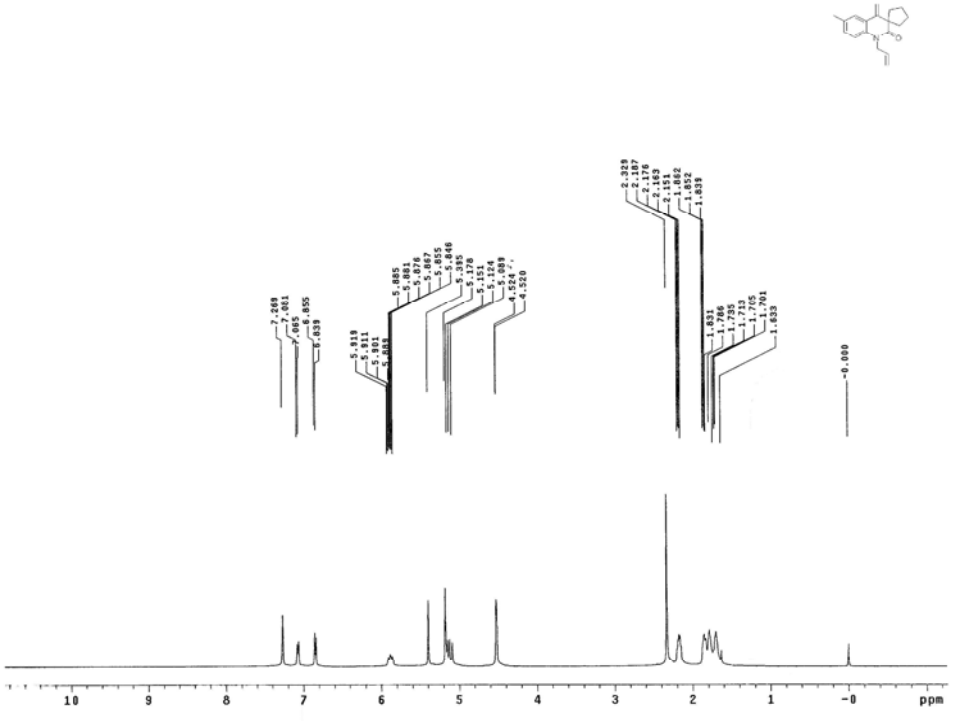
120
100
80
60
40
20
ppm

2i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7
6
5
4
3
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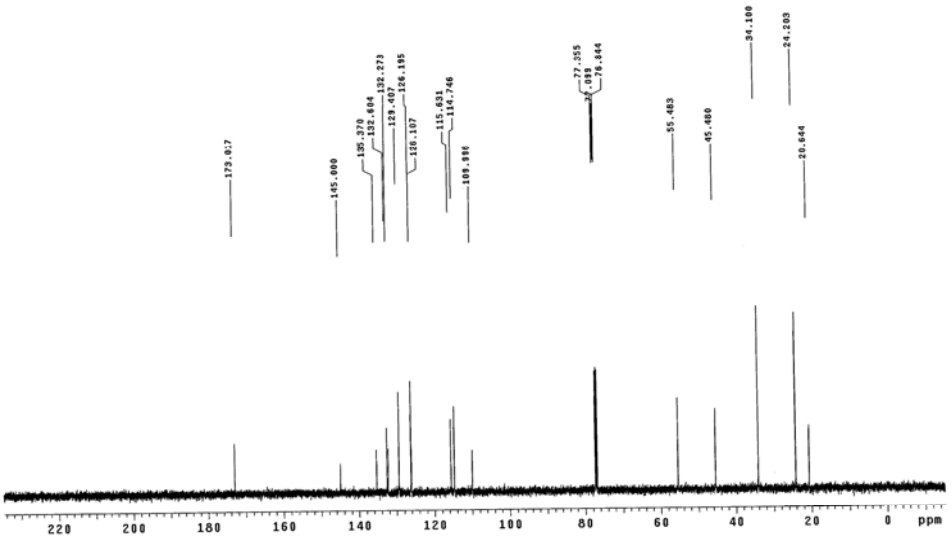
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126.107
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76.444
55.483
45.460
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100
80
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40
20
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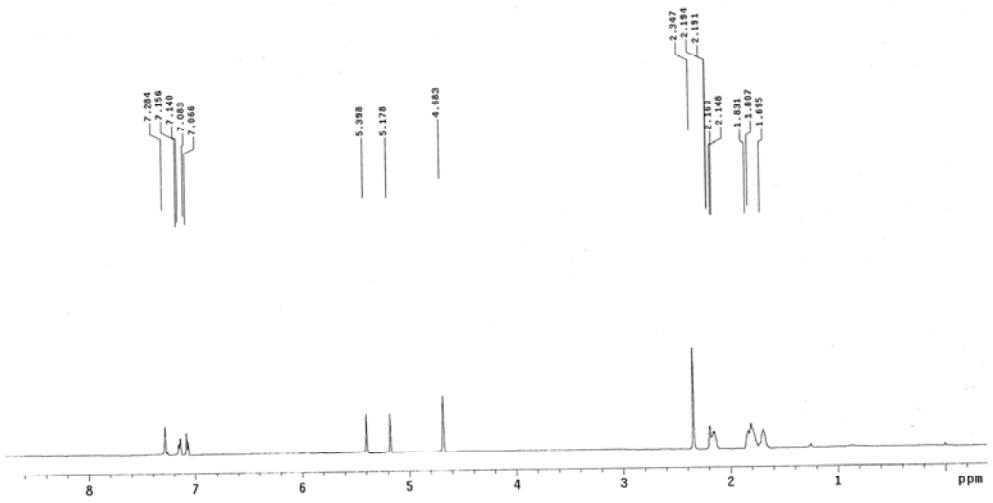
ppm

2j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4.163
2.347
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1.607
1.615
8
7
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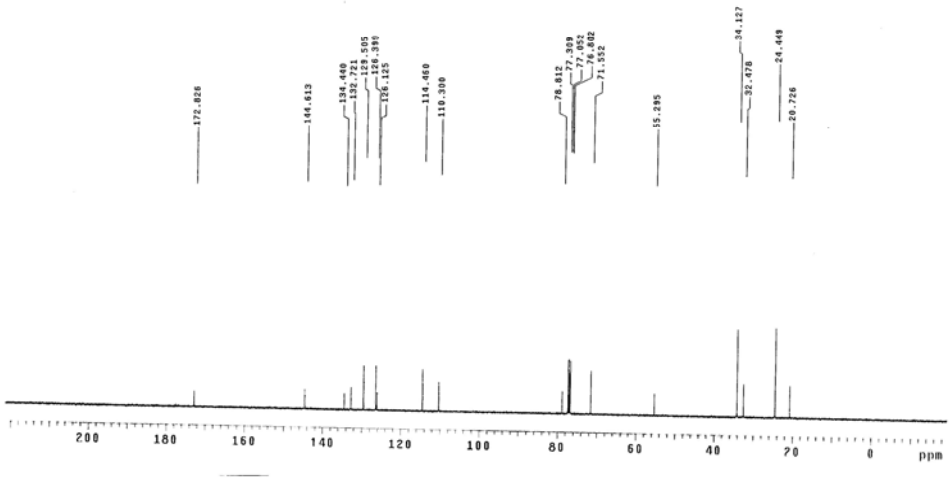
5
4
3
2
1
ppm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126.399
126.125
114.460
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78.812
77.309
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76.802
71.592
55.295
34.127
32.478
24.449
20.726
200
180
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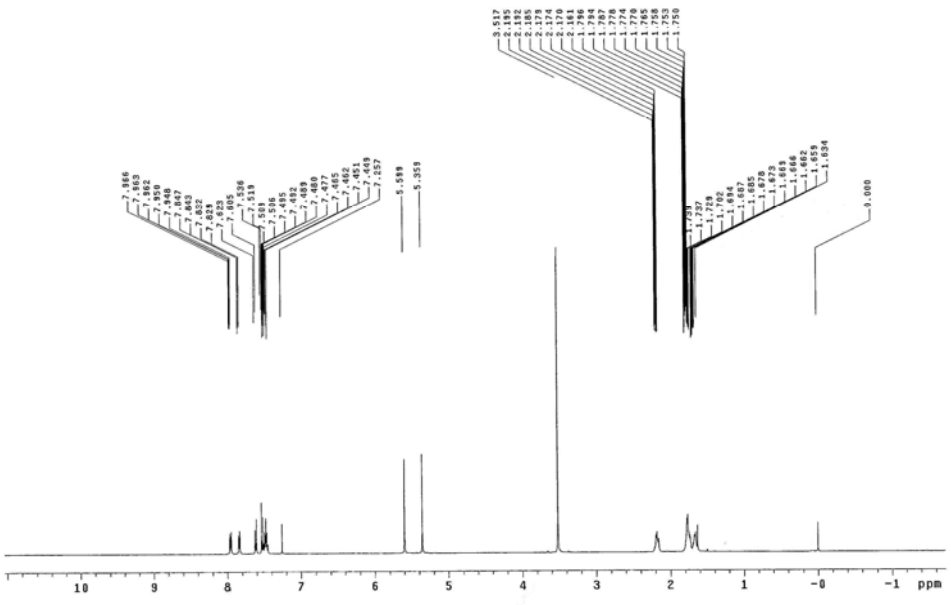
140
120
100
80
60
40
20
0
ppm

2k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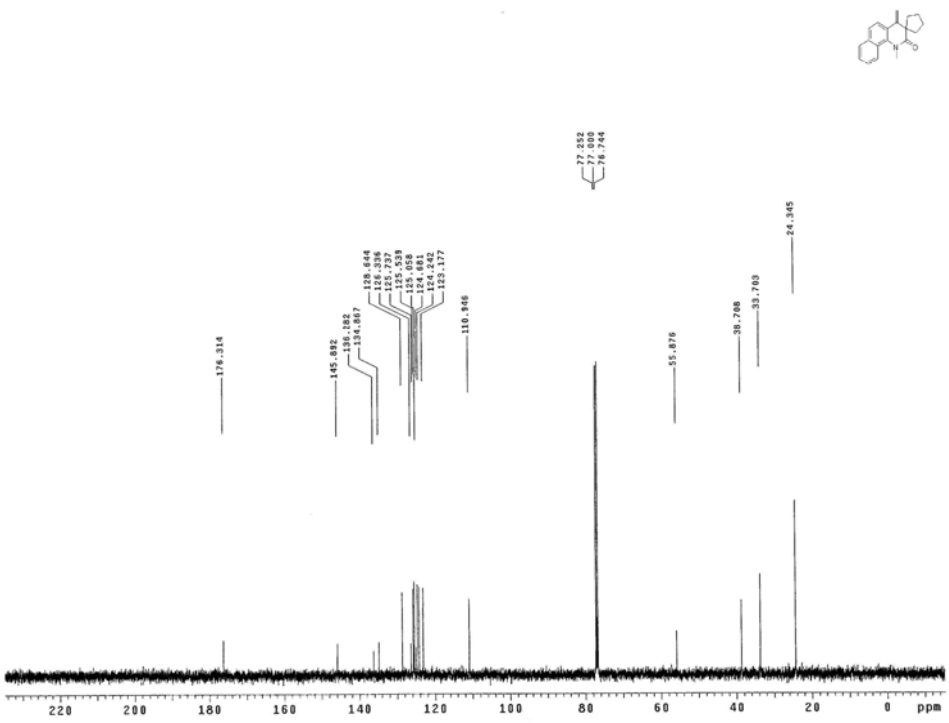
9
8
7
6
5
4
3
2
1
-0
-1
ppm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124.242
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77.252
77.000
76.744
55.876
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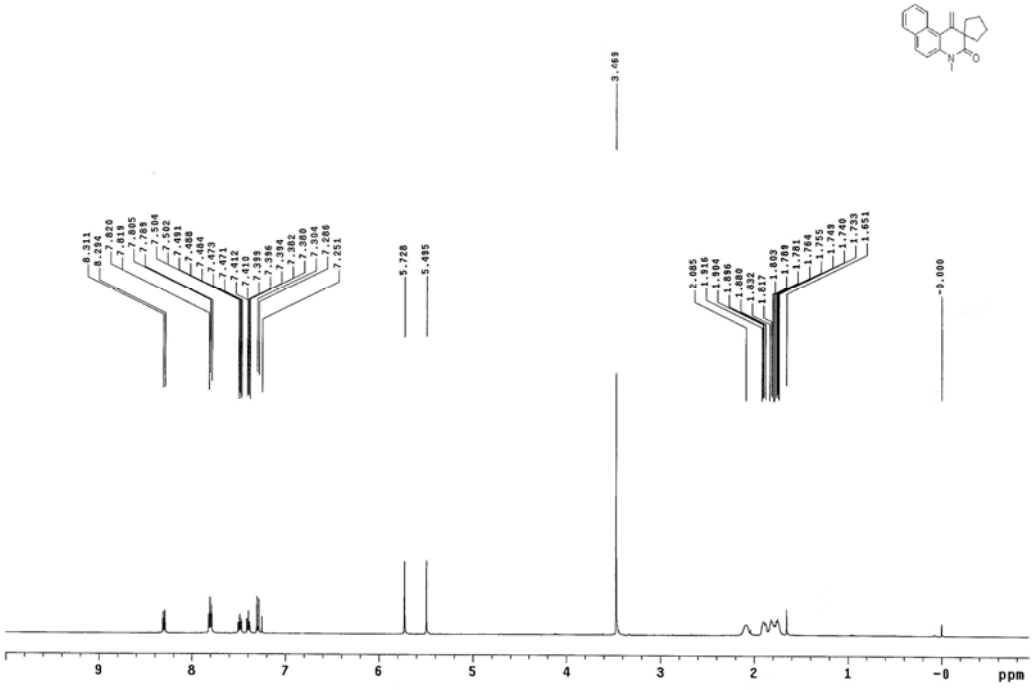
ppm

2l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7.789
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7.502
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7.412
7.410
7.399
7.396
7.394
7.382
7.380
7.304
7.286
7.251
5.728
5.485
2.085
1.916
1.904
1.896
1.880
1.832
1.817
1.803
1.788
1.784
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1.755
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5
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3
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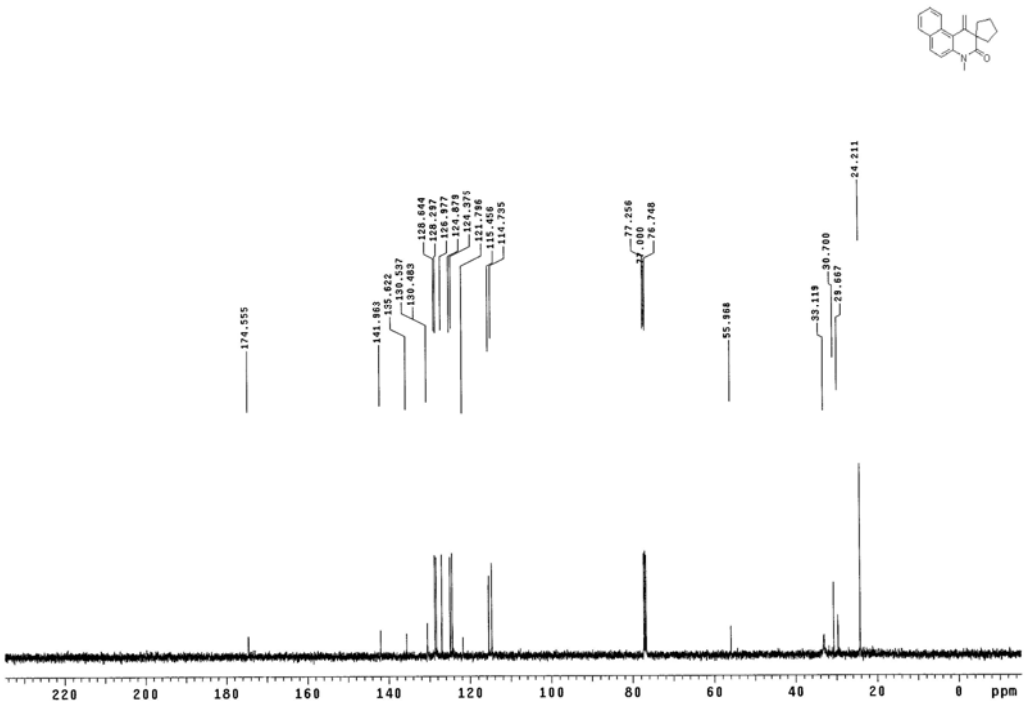
ppm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128.237
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121.786
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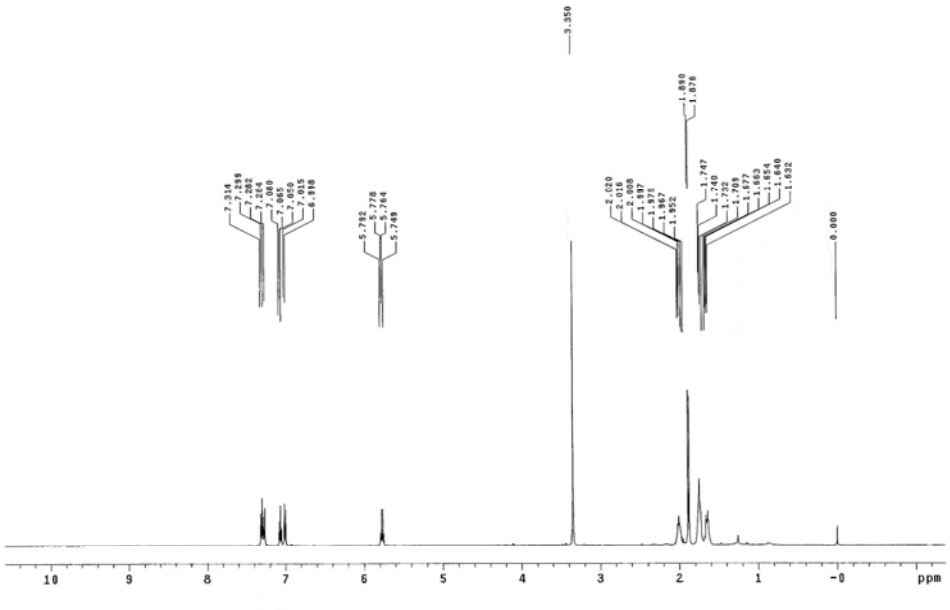
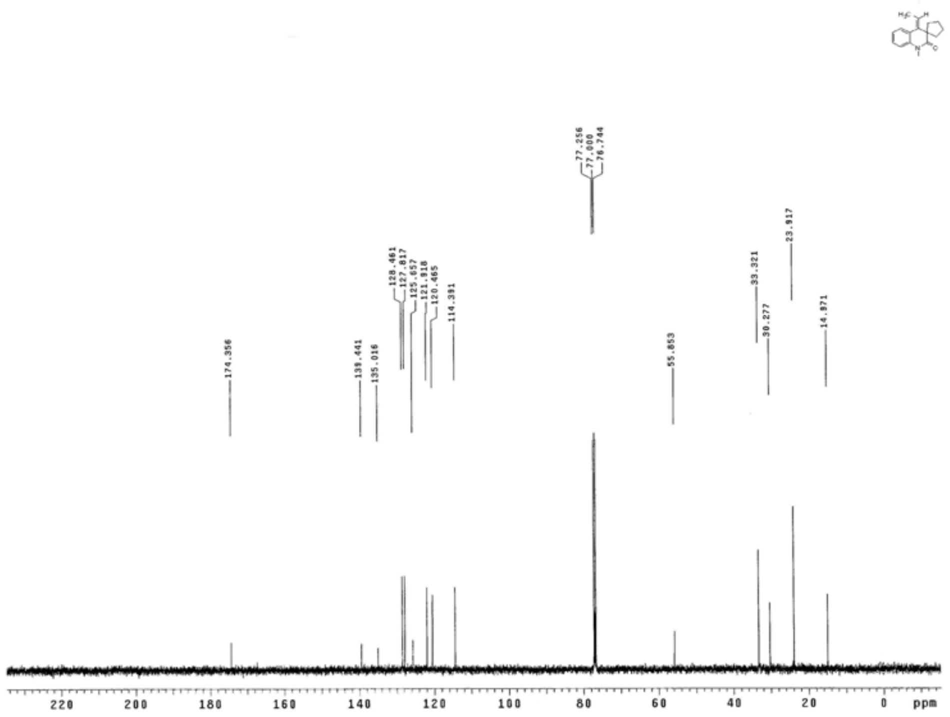
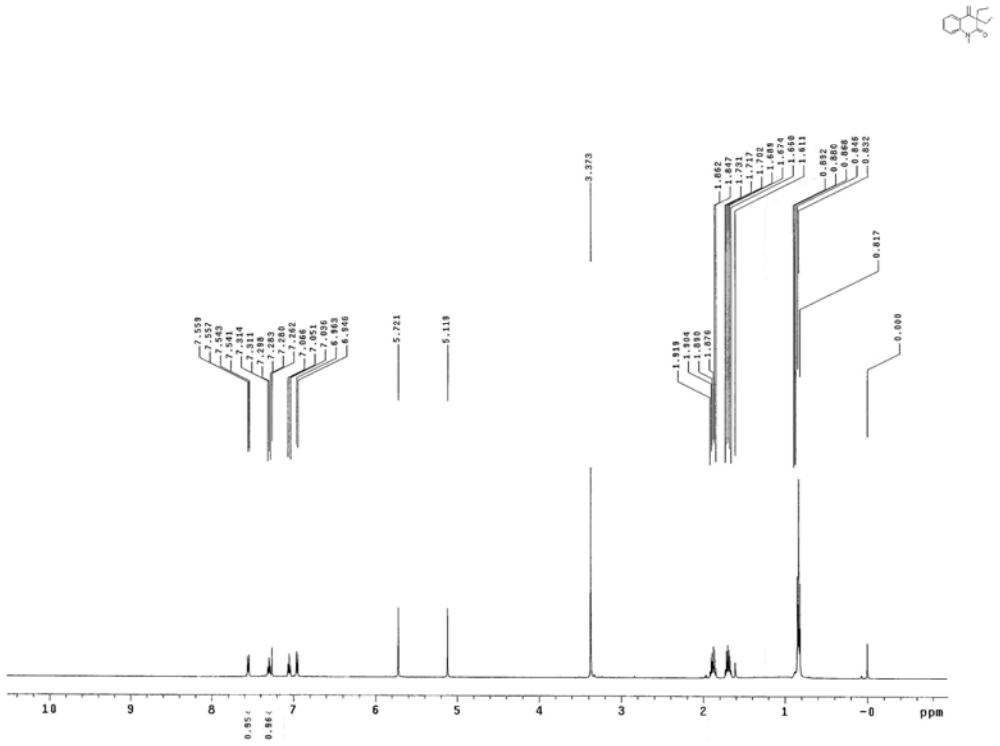
77.256
77.000
76.748
55.968
33.119
30.700
29.667
24.211
220
200
180
160
140
120
100
80
60
40
20
0
ppm

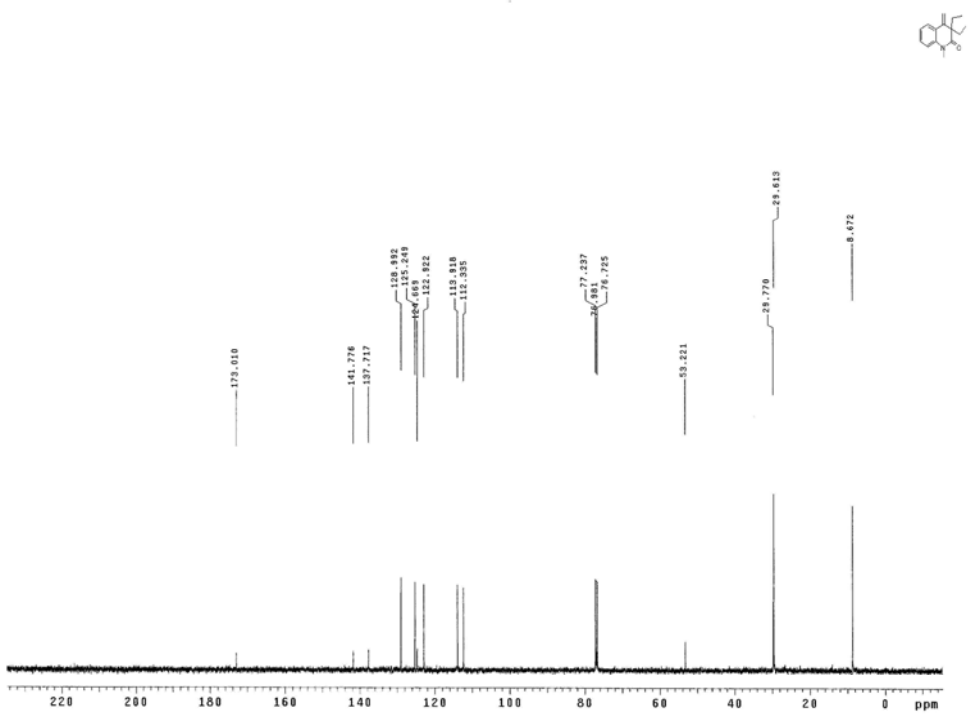
2m


7.314
7.299
7.282
7.264
7.248
7.065
7.050
7.015
6.998
5.792
5.778
5.764
5.748
3.350
2.020
2.016
2.008
1.997
1.977
1.967
1.952
1.880
1.876
1.747
1.740
1.732
1.709
1.677
1.663
1.654
1.640
1.632
0.000
10
9
8
7
6
5
4
3
2
1
-0
ppm

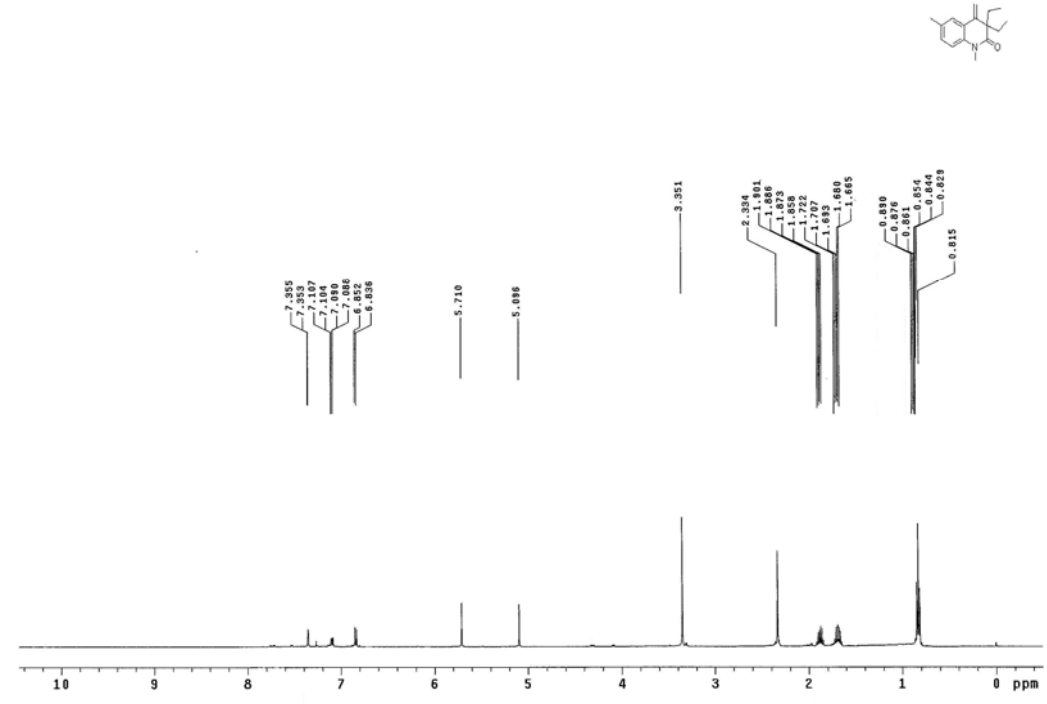


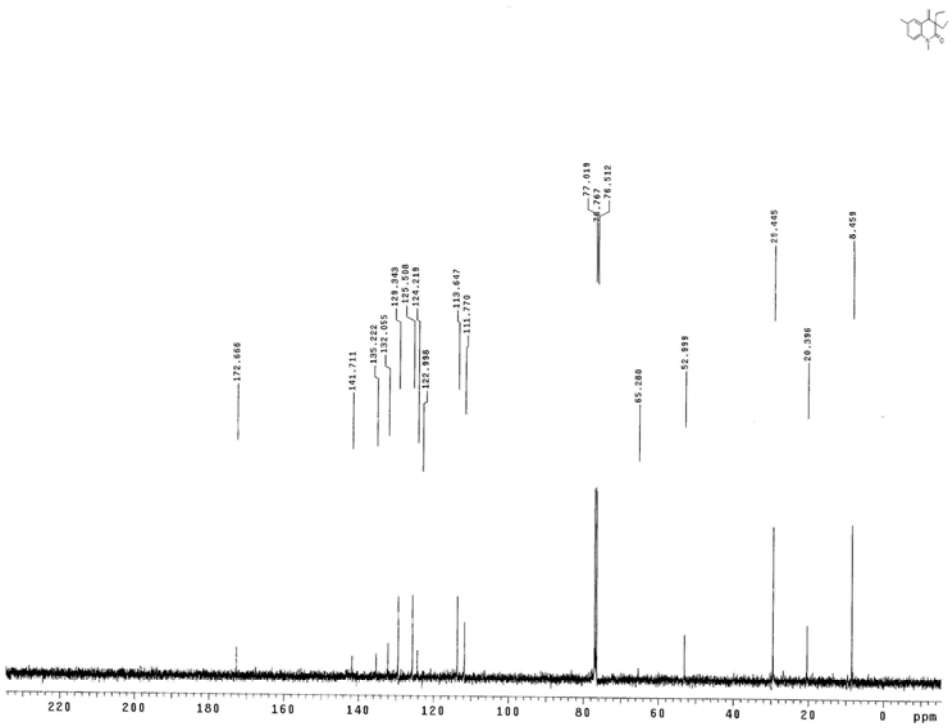
3a



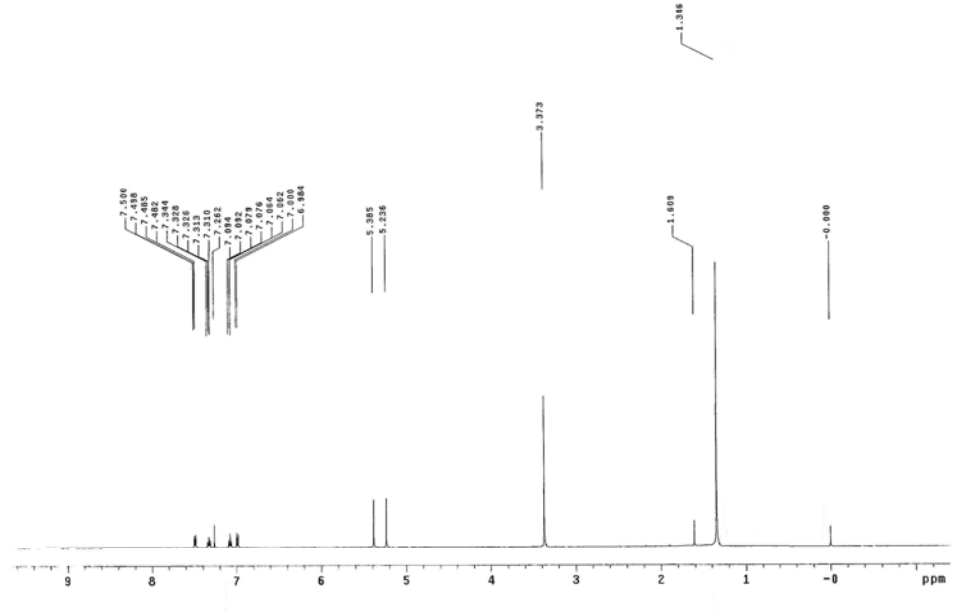

173.010
141.776
137.717
128.892
125.249
122.822
113.918
112.335
77.237
76.725
53.221
29.770
29.613
8.672
220
200
180
160
140
120
100
80
60
40
20
0
ppm

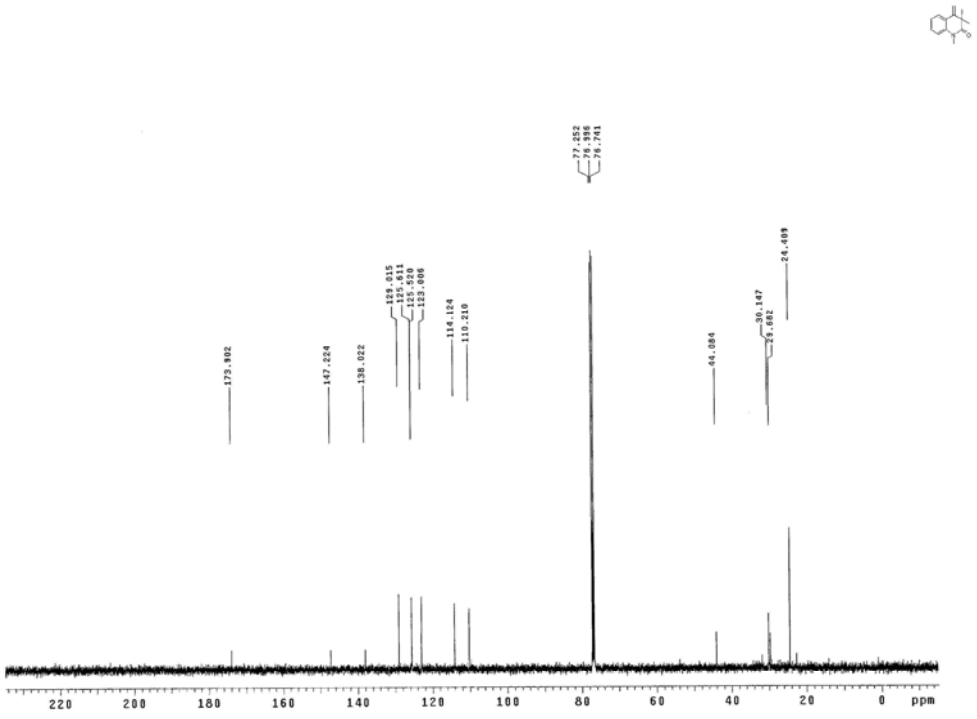
3b


7.355
7.353
7.107
7.104
7.090
7.086
6.852
6.836
5.710
5.098
3.351
2.334
1.901
1.886
1.873
1.858
1.722
1.707
1.693
1.680
1.665
0.890
0.876
0.861
0.854
0.844
0.829
0.815
10
9
8
7
6
5
4
3
2
1
0
ppm

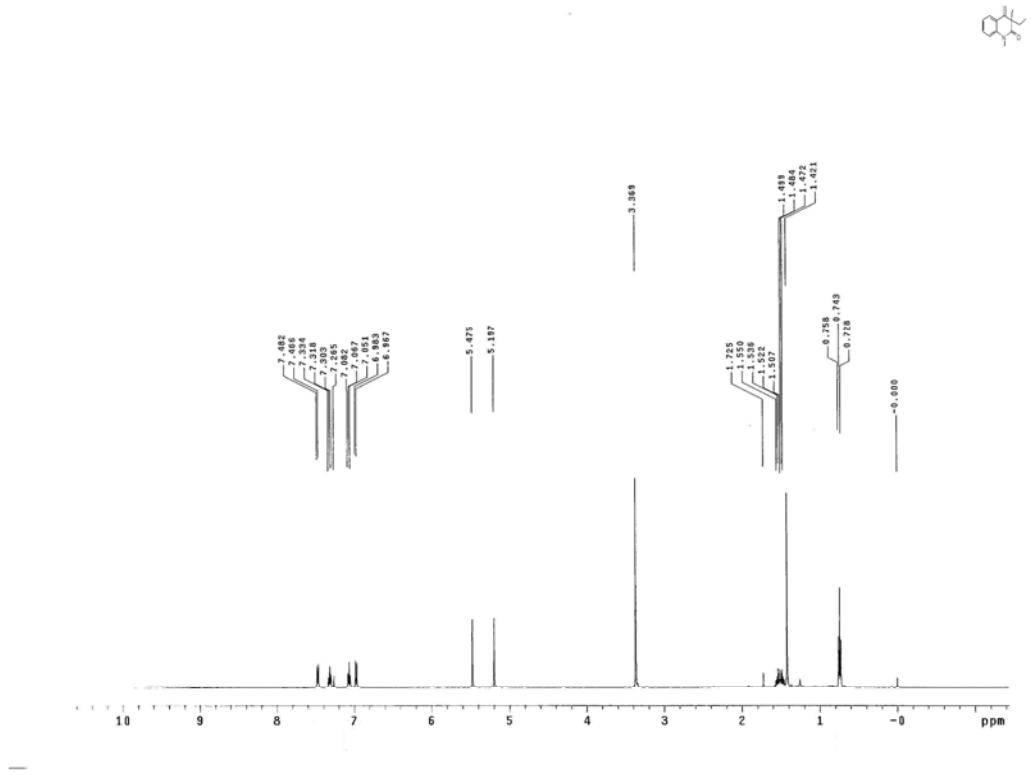


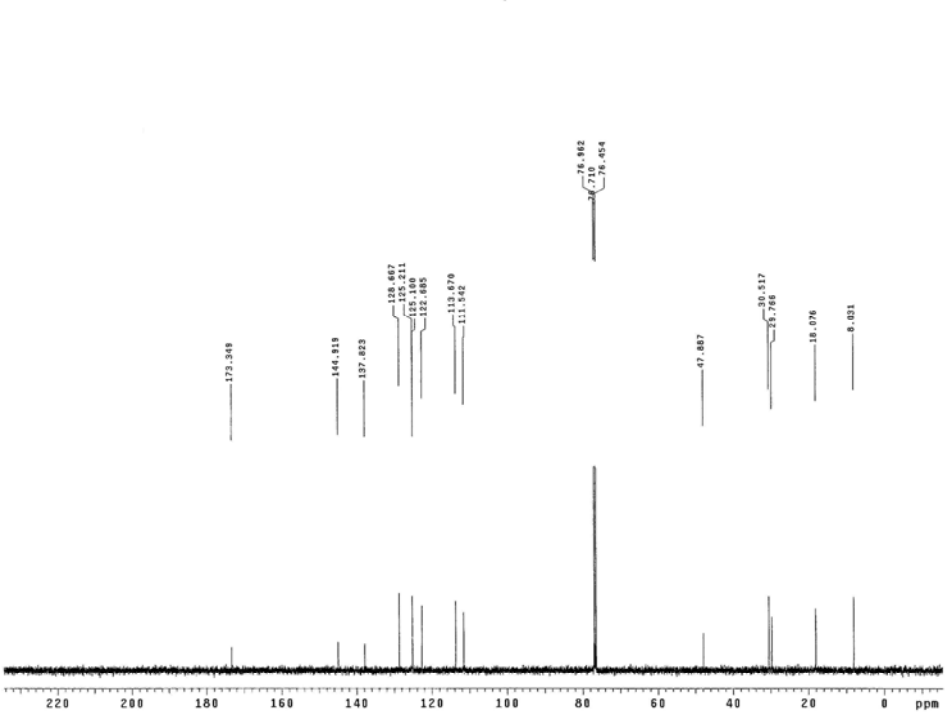
3c



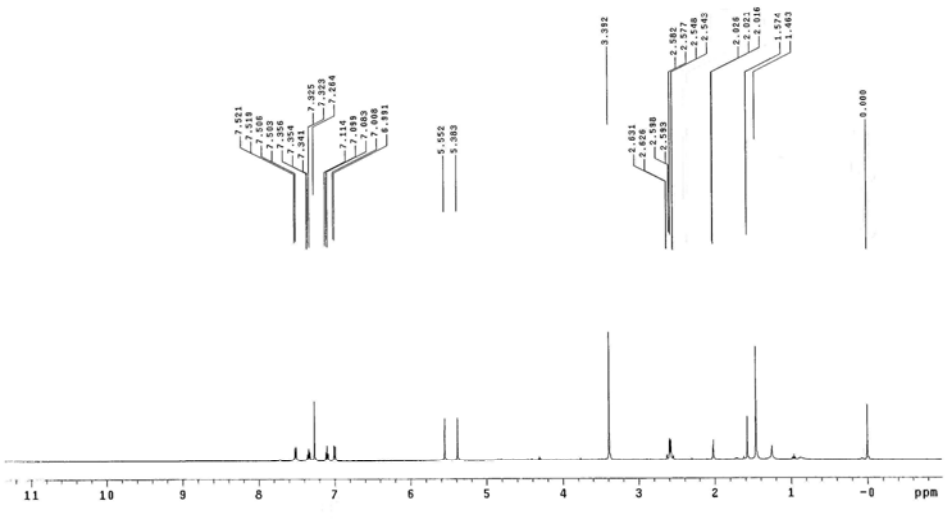

77.052
76.396
76.741
173.902
147.224
138.022
129.015
125.611
123.000
114.124
110.210
64.084
30.147
29.681
24.409
220
200
180
160
140
120
100
80
60
40
20
0
ppm

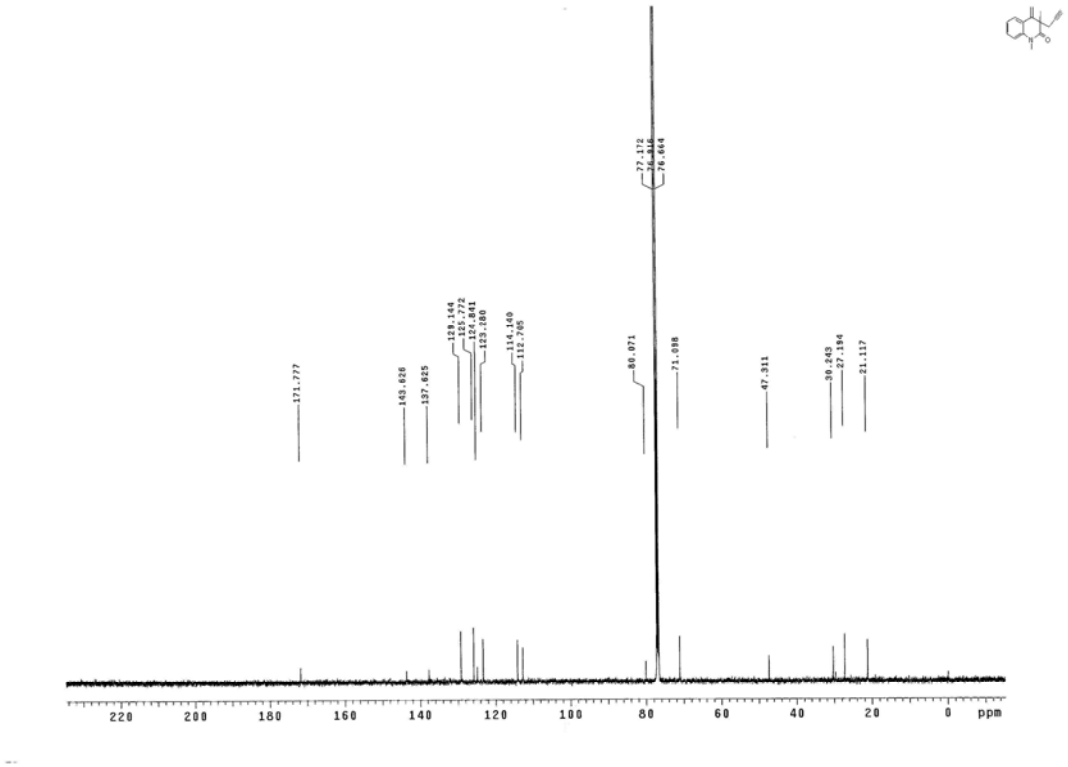
3d


3.369
1.499
1.484
1.472
1.421
5.475
5.197
0.758
0.743
0.728
-0.000
10
9
8
7
6
5
4
3
2
1
-0
ppm

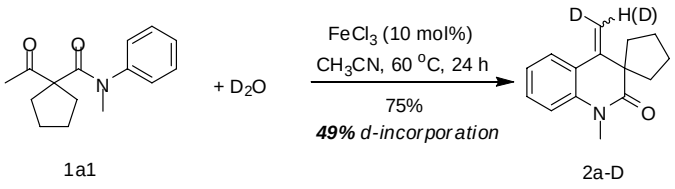

173.349
144.919
137.823
128.667
125.211
125.160
122.685
113.670
111.542
76.962
77.379
76.454
47.857
30.517
29.766
18.076
8.031
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3e

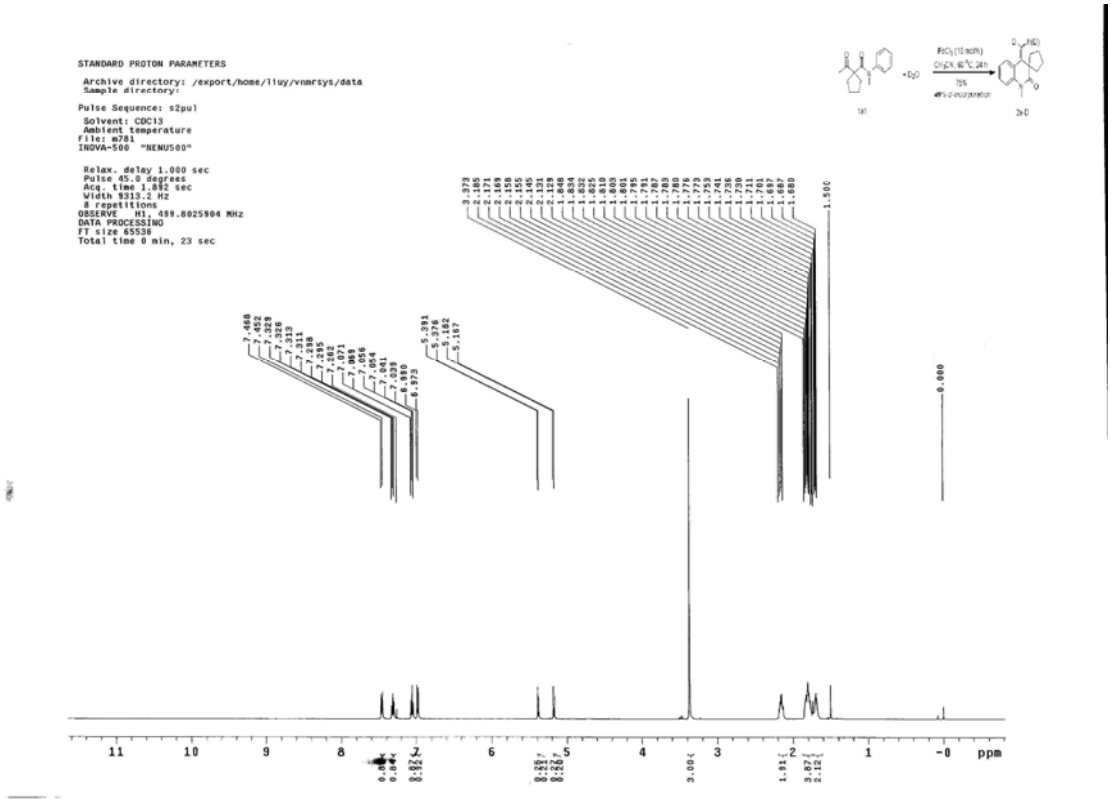

7.521
7.519
7.506
7.358
7.356
7.354
7.341
7.325
7.323
7.264
7.114
7.083
7.008
6.991
5.552
5.303
3.392
2.631
2.626
2.598
2.593
2.582
2.577
2.548
2.543
2.028
2.021
2.016
1.574
1.463
0.000
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

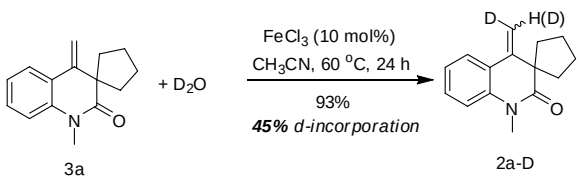


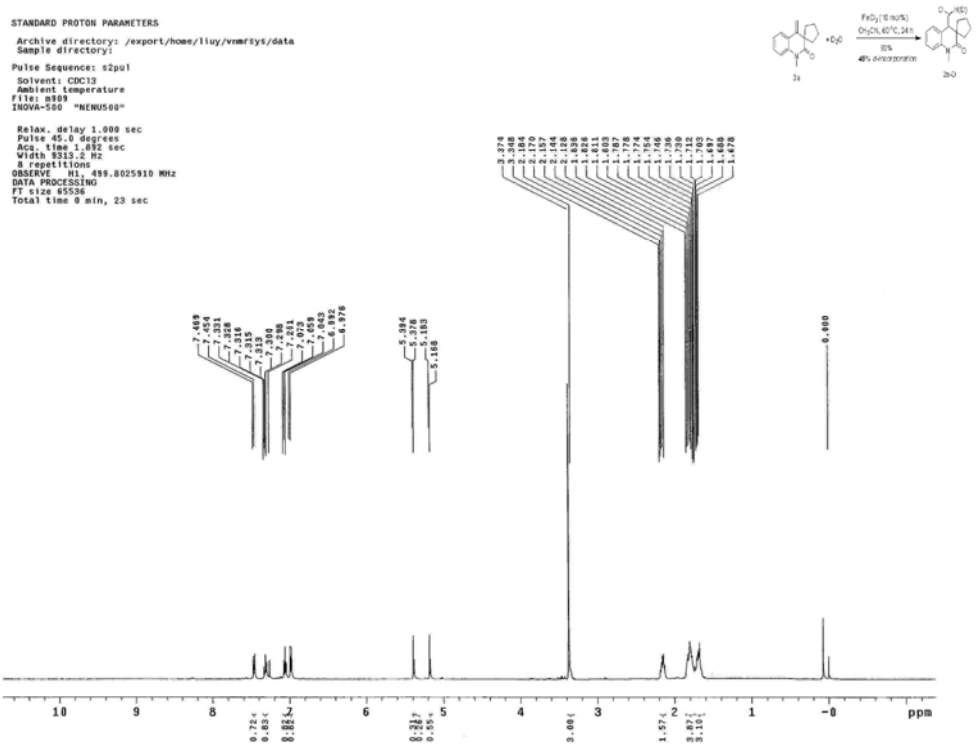
V. Copies of ^{1}H-NMR Spectra of 2a-D



1a1 2a-D


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: m781
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9313.2 Hz
8 repetitions
OBSERVE H1, 499.8025904 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
11
10
9
8
6
5
4
3
2
1
-0
ppm


FeCl3 (10 mol%)
CH3CN, 60 °C, 24 h
93%
45% d-incorporation
+ D2O
D
H(D)
N
O
3a
2a-D


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: m009
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8313.2 Hz
8 repetitions
OBSERVE H1, 499.8025910 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
ppm