Electronic Supplementary Material (ESI) for Chemical Science.

Pyridine-Enabled Copper-Promoted Cross Dehydrogenative Coupling of C(sp^2)-H and C(sp^3)-H Bonds

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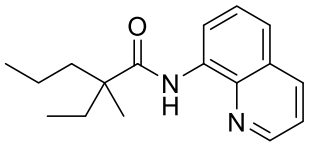
Table of Contents

General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 500 MHz NMR Fourier transform spectrometer (500 MHz and 125 MHz, respectively) using tetramethylsilane as an internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. Infrared spectra were obtained using a Thermo Nicolet IR 330 spectrometer. Mass (MS) analysis were abtained using Agilent 1100 series LC/MSD system with Electrospray Ionization (ESI). All the solvents and commercially available reagents were purchased from commercial sources and used directly.

Starting materials **1a-d**, **1f-n**, [D_3]-**1b** and **4-7** were prepared according to literature procedures.[1,2] **1e** were prepared from **1b** based on reported reaction protocol.[2]

Structures of Starting Materials



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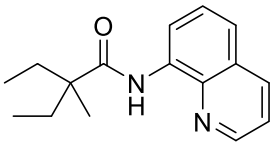

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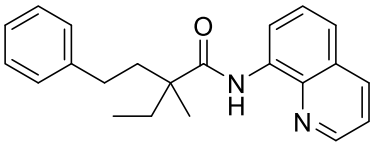

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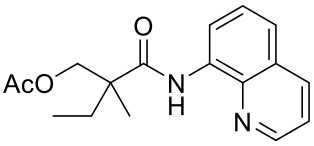

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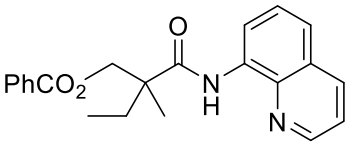

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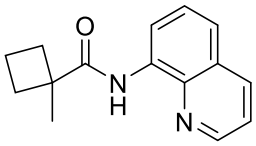

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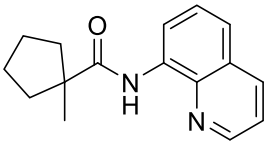

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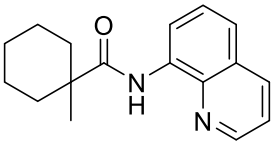

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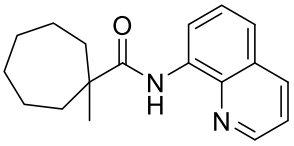

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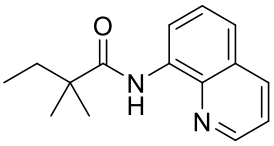

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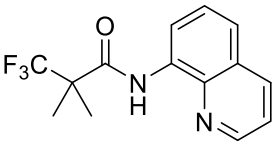

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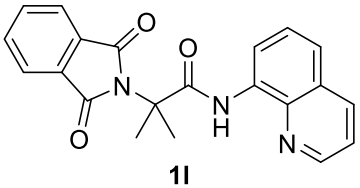

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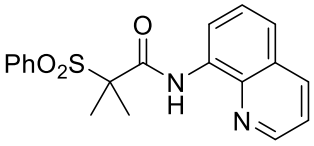

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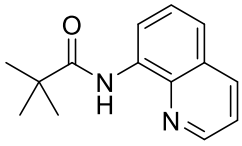

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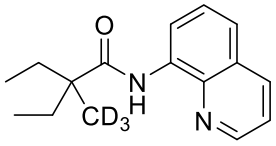
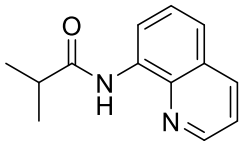


[D3]-**1b**



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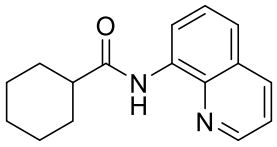

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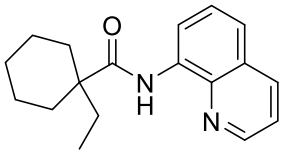

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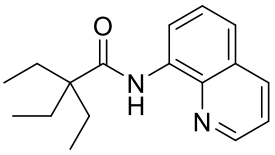
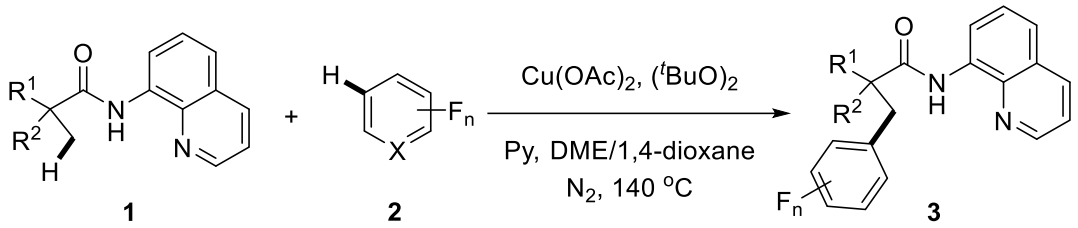


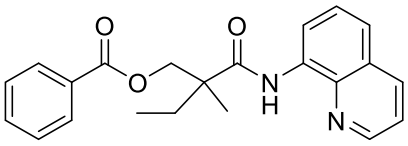
7

General Procedure for Copper-Promoted Cross Dehydrogenative Coupling of Amides



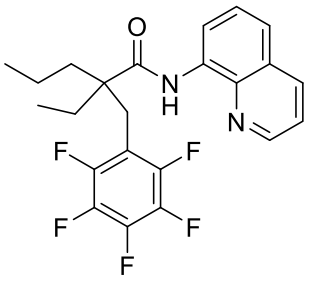
A 50 mL Schlenk tube was charged with amide (**1**, 0.30 mmol), $Cu(OAc)_2$ (54.5 mg, 0.30 mmol), DME/1,4-dioxane (7:3, v/v, 1.0 mL), pyridine (72 μL, 71 mg, 0.90 mmol), *tert*-butyl peroxide (138 μL, 110 mg, 0.75 mmol) and fluoroarene (0.60 mmol) in sequence under N_2 atmosphere. The tube was capped with a Teflon screw cap, and stirred at 140 °C for 16h. Then the reaction mixture was cooled to room temperature, diluted with EtOAc (30 mL). The organic layer was washed with 5% aqueous NaOH (10 mL), water (20 mL), brine (10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with CH_2Cl_2/Hexane (1:2 ~ 3:1, v/v), to afford corresponding product **3**.

Analytical Data



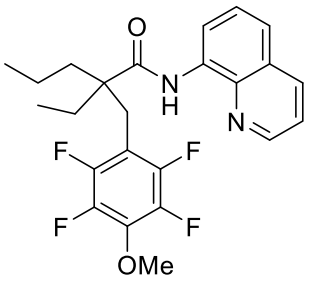
1e

Compound **1e**, colorless oil, R_f = 0.33 (hexane/EtOAc 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (brs, 1H), 8.83 (dd, J = 7.4, 1.5 Hz, 1H), 8.57 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.6 Hz, 1H), 8.08 (dd, J = 8.3, 1.2 Hz, 2H), 7.56 – 7.49 (m, 3H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 4.58 (d, J = 11.2 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.88 – 1.78 (m, 1H), 1.53 (s, 3H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 166.5, 148.3, 138.9, 136.4, 134.7, 133.1, 130.1, 130.0, 128.4, 128.1, 127.6, 121.7 (2C), 116.7, 69.9, 47.9, 29.5, 19.7, 8.8; IR (neat) ν 3359, 2968, 1722, 1682, 1529, 1487, 1424, 1384, 1325, 1270, 1111, 826, 791, 711; Ms (ESI): m/z = 363.2 $[M+H]^+$.



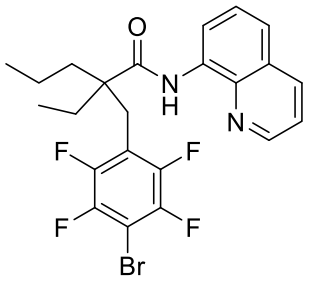
3a

Compound **3a**, colorless oil, yield: 92%, R_f = 0.55 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (brs, 1H), 8.76 – 8.71 (m, 2H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55 – 7.40 (m, 3H), 3.11 – 3.03 (m, 2H), 1.97 – 1.88 (m, 1H), 1.87 – 1.79 (m, 2H), 1.76 – 1.68 (m, 1H), 1.50 – 1.39 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 148.2, 145.9 (dm, *J* = 244.9 Hz), 140.0 (dm, *J* = 250.8 Hz), 138.8, 137.4 (dm, *J* = 249.0 Hz), 136.4, 134.3, 128.0, 127.6, 121.6, 121.5, 116.6, 111.7 (m), 51.7, 36.4, 29.6, 27.1, 17.6, 14.7, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.6 (dd, *J* = 22.6, 7.5 Hz, 2F), -156.7 (t, *J* = 20.9 Hz, 1F), -163.2 (m, 2F); IR (neat) *v* 3357, 2964, 2875, 1683, 1520, 1424, 1385, 1325, 1263, 1124, 1022, 959, 908, 826, 791, 737; Ms (ESI): *m*/*z* = 437.2 $[M+H]^+$.



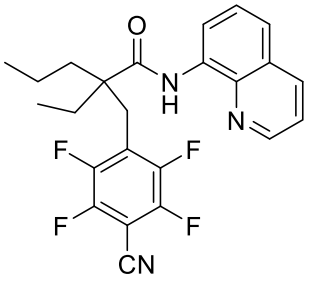
3b

Compound **3b**, white solid, yield: 71%, R_f = 0.45 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (brs, 1H), 8.76 – 8.72 (m, 2H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.48 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.95 (t, *J* = 1.1 Hz, 3H), 3.12 – 3.02 (m, 2H), 1.95 – 1.87 (m, 1H), 1.85 – 1.77 (m, 2H), 1.74 – 1.66 (m, 1H), 1.50 – 1.40 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 148.2, 146.2 (dm, *J* = 243.0 Hz), 140.8 (dm, *J* = 244.9 Hz), 138.8, 137.0 (m), 136.4, 134.5, 128.0, 127.7, 121.6, 121.4, 116.6, 109.9 (m), 62.1, 51.7, 36.7, 29.5, 27.2, 17.7, 14.8, 8.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -141.3 (dd, *J* = 21.7, 8.3 Hz, 2F), -159.0 (dd, *J* = 21.7, 8.3 Hz, 2F); IR (neat) *v* 3357, 2963, 2874, 1682, 1529, 1489, 1385, 1325, 1131, 1015, 960, 826, 792, 733; Ms (ESI): *m*/*z* = 449.2 $[M+H]^+$.



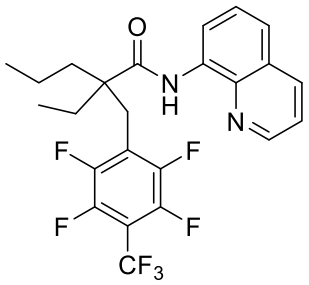
3c

Compound **3c**, colorless oil, yield: 80%, R_f = 0.55 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (brs, 1H), 8.73 – 8.70 (m, 2H), 8.15 (dd, J = 8.3, 1.6 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 3.14 – 3.06 (m, 2H), 1.97 – 1.89 (m, 1H), 1.87 – 1.79 (m, 2H), 1.77 – 1.69 (m, 1H), 1.50 – 1.39 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 148.3, 146.0 (dm, J = 246.8 Hz), 144.8 (dm, J = 245.0 Hz), 138.8, 136.7 (m), 136.4, 134.3, 128.0, 127.6, 121.7, 121.5, 166.6, 98.1 (m), 51.8, 36.5, 30.2, 27.2, 17.7, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -134.6 (m, 2F), -138.2 (dd, J = 21.5, 8.6 Hz, 2F); IR (neat) ν 3356, 2964, 2874, 1678, 1529, 1485, 1385, 1325, 1261, 1142, 948, 909, 826, 791, 733; Ms (ESI): m/z = 497.1 $[M+H]^+$.



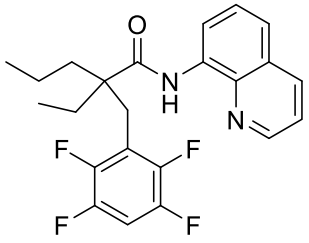
3d

Compound **3d**, colorless oil, yield: 85%, R_f = 0.36 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (brs, 1H), 8.75 (dd, J = 4.2, 1.7 Hz, 1H), 8.68 (dd, J = 7.0, 1.9 Hz, 1H), 8.18 (dd, J = 8.3, 1.6 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.48 (dd, J = 8.3, 4.2 Hz, 1H), 3.18 – 3.10 (m, 2H), 2.00 – 1.91 (m, 1H), 1.90 – 1.81 (m, 2H), 1.78 – 1.71 (m, 1H), 1.52 – 1.36 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H), 1.02 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 147.3, 146.9 (dm, J = 259.8 Hz), 145.7 (dm, J = 247.0 Hz), 138.8, 136.6, 134.1, 128.0, 127.7, 124.9 (m), 121.8 (2C), 116.7, 107.7, 92.7 (m), 52.2, 36.4, 31.0, 27.1, 17.7, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -133.7 (m, 2F), -136.4 (m, 2F); IR (neat) ν 3361, 2965, 2875, 2246, 1675, 1530, 1491, 1385, 1325, 1298, 956, 826, 792, 738; Ms (ESI): m/z = 444.2 $[M+H]^+$.



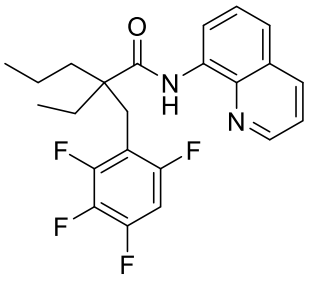
3e

Compound **3e**, colorless oil, yield: 94%, R_f = 0.54 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (brs, 1H), 8.73 – 8.70 (m, 2H), 8.16 (dd, J = 8.3, 1.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 3.18 – 3.10 (m, 2H), 1.99 – 1.90 (m, 1H), 1.89 – 1.81 (m, 2H), 1.78 – 1.71 (m, 1H), 1.52 – 1.39 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 148.3, 146.1 (dm, J = 246.1 Hz), 143.9 (dm, J = 257.4 Hz), 138.8, 136.5, 134.2, 128.0, 127.6, 122.0 (m), 121.7, 121.6, 120.9 (q, J = 269.6 Hz), 116.6, 108.6 (m), 52.0, 36.5, 30.4, 27.2, 17.7, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -56.3 (t, J = 21.4 Hz, 3F), -137.77 (m, 2F), -141.9 (m, 2F); IR (neat) ν 3357, 2965, 2876, 1683, 1530, 1492, 1331, 1147, 960, 826, 792, 715; Ms (ESI): m/z = 487.1 $[M+H]^+$.



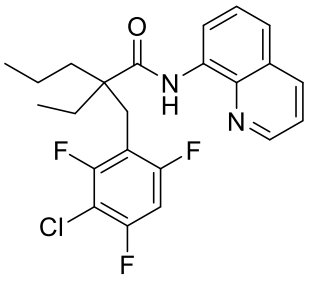
3f

Compound **3f**, colorless oil, yield: 88%, R_f = 0.52 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (brs, 1H), 8.76 – 8.72 (m, 2H), 8.14 (dd, J = 8.3, 1.6 Hz, 1H), 7.56 – 7.41 (m, 3H), 6.90 – 6.82 (m, 1H), 3.18 – 3.10 (m, 2H), 1.96 – 1.88 (m, 1H), 1.87 – 1.78 (m, 2H), 1.76 – 1.68 (m, 1H), 1.50 – 1.41 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 148.2, 145.7 (dm, J = 246.6 Hz), 138.9, 136.4, 134.5, 128.0, 127.7, 121.6, 121.4, 117.7 (m), 116.6, 104.5 (m), 51.8, 36.8, 29.9, 27.3, 17.7, 14.8, 8.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -140.1 (m, 4F); IR (neat) ν 3357, 3054, 2964, 2875, 1683, 1505, 1386, 1325, 1253, 1171, 938, 826, 792, 738; Ms (ESI): m/z = 419.2 $[M+H]^+$.



3g

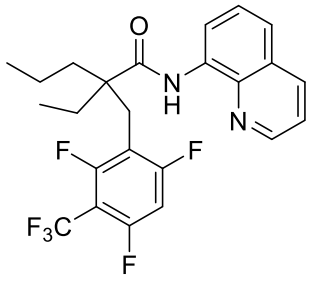
Compound **3g**, colorless oil, yield: 84%, R_f = 0.52 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (brs, 1H), 8.75 – 8.71 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.62 – 6.55 (m, 1H), 3.09 – 3.00 (m, 2H), 1.95 – 1.87 (m, 1H), 1.85 – 1.77 (m, 2H), 1.74 – 1.67 (m, 1H), 1.48 – 1.39 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 156.3 (dm, *J* = 244.0 Hz), 150.8 (dm, *J* = 247.6 Hz), 149.4 (dm, *J* = 248.0 Hz), 148.2, 138.8, 137.2 (dm, *J* = 246.3 Hz), 136.4, 134.5, 128.0, 127.6, 121.6, 121.4, 116.5, 111.6 (m), 100.3 (m), 51.6, 36.5, 29.5, 27.1, 17.6, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.6 (t, *J* = 10.0 Hz, 1F), -132.2 (d, *J* = 18.9 Hz, 1F), -134.8 (m, 1F), -165.7 (m, 1F); IR (neat) *v* 3357, 3052, 2964, 2874, 1678, 1528, 1385, 1325, 1254, 1114, 1052, 909, 826, 791, 734; Ms (ESI): *m*/*z* = 419.2 $[M+H]^+$.



3h

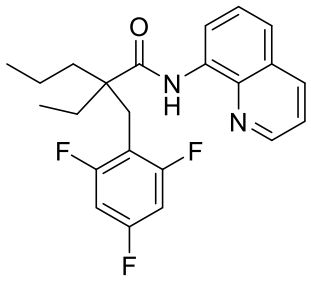
Compound **3h**, colorless oil, yield: 73%, R_f = 0.50 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (brs, 1H), 8.74 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.69 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.40 (m, 3H), 6.63 – 6.57 (m, 1H), 3.08 – 2.98 (m, 2H), 1.96 – 1.86 (m, 1H), 1.85 – 1.77 (m, 2H), 1.75 – 1.67 (m, 1H), 1.49 – 1.39 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 159.9 (dm, *J* = 247.1 Hz), 158.2 (dm, *J* = 248.1 Hz), 157.3 (dm, *J* = 248.1 Hz), 148.2, 138.8, 136.4, 134.5, 128.0, 127.6, 121.6, 121.4, 116.5, 111.4 (m), 105.9 (m), 100.4 (m), 51.7, 36.4, 29.8, 27.0, 17.6, 14.9, 8.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.0 (m, 2F), -113.1 (m, 1F); IR (neat) *v* 3357, 3053, 2963,

2874, 1682, 1527, 1486, 1436, 1385, 1149, 1047, 909, 826, 791, 736; Ms (ESI): *m*/*z* = 435.1 $[M+H]^+$.



3i

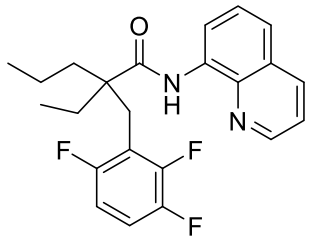
Compound **3i**, colorless oil, yield: 92%, R_f = 0.51 (hexane/EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (brs, 1H), 8.73 – 8.68 (m, 2H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.63 – 6.57 (m, 1H), 3.06 – 2.98 (m, 2H), 1.97 – 1.88 (m, 1H), 1.87 – 1.78 (m, 2H), 1.75 – 1.68 (m, 1H), 1.50 – 1.38 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 164.0 (dm, *J* = 253.1 Hz), 159.8 (dm, *J* = 257.0 Hz), 159.0 (dm, *J* = 257.8 Hz), 148.2, 138.8, 136.4, 134.4, 128.0, 127.6, 121.6, 121.5 (q, *J* = 272.1 Hz), 121.5, 116.5, 112.0 (m), 104.4 (m), 101.0 (m), 51.7, 36.2, 29.6, 26.9, 17.6, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -56.5 (t, *J* = 22.8 Hz, 3F), -101.3 (q, *J* = 9.1 Hz, 1F), -107.95 (m, 1F), -110.7 (m, 1F); IR (neat) *v* 3357, 2964, 2875, 1676, 1634, 1530, 1487, 1450, 1307, 1139, 1054, 910, 826, 792, 735; Ms (ESI): *m*/*z* = 469.2 $[M+H]^+$.



3j

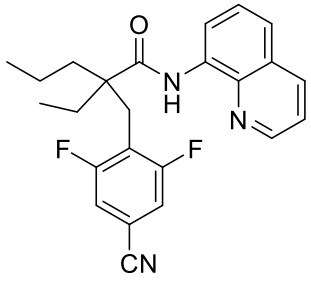
Compound **3j**, colorless oil, yield: 81%, R_f = 0.48 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (brs, 1H), 8.76 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.71 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.52 – 6.46 (m, 2H), 3.07 – 2.98 (m, 2H), 1.95 – 1.86 (m, 1H), 1.85 – 1.77 (m, 2H), 1.73 – 1.66 (m, 1H), 1.48 – 1.39 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H),

0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 162.3 (ddd, J = 248.4, 14.8, 11.6 Hz), 161.5 (dt, J = 247.8, 15.9 Hz). 148.2, 138.8, 136.3, 134.7, 128.0, 127.6, 121.6, 121.2, 116.4, 110.1 (m), 99.9 (m), 51.6, 36.5, 29.1, 27.1, 17.6, 14.8, 8.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.2 (t, J = 6.8 Hz, 2F), -110.6 (m, 1F); IR (neat) v 3359, 3053, 2963, 2874, 1683, 1624, 1538, 1488, 1385, 1325, 1117, 1042, 1000, 840, 791, 736; Ms (ESI): m/z = 401.2 $[M+H]^+$.



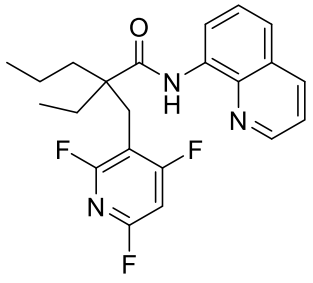
3k

Compound **3k**, colorless oil, yield: 80%, R_f = 0.47 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (brs, 1H), 8.76 (dd, J = 7.6, 1.3 Hz, 1H), 8.72 (dd, J = 4.2, 1.7 Hz, 1H), 8.13 (dd, J = 8.3, 1.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.48 (dd, J = 8.3, 1.3 Hz, 1H), 7.41 (dd, J = 8.2, 4.2 Hz, 1H), 6.94 – 6.87 (m, 1H), 6.67 – 6.62 (m, 1H), 3.15 – 3.07 (m, 2H), 1.96 – 1.87 (m, 1H), 1.86 – 1.77 (m, 2H), 1.75 – 1.66 (m, 1H), 1.50 – 1.41 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 157.5 (dm, J = 242.5 Hz), 149.9 (dm, J = 247.4 Hz), 148.2, 147.2 (dm, J = 242.4 Hz), 138.9, 136.3, 134.6, 128.0, 127.6, 121.6, 121.3, 116.5, 116.2 (dd, J = 22.5, 16.9 Hz), 115.1 (dd, J = 18.9, 9.7 Hz), 110.18 (m), 51.8, 36.8, 29.6, 27.4, 17.7, 14.8, 8.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.2 (m, 1F), -134.3 (dd, J = 21.1, 8.5 Hz, 1F), -142.9 (m, 1F); IR (neat) v 3359, 2963, 2874, 1679, 1529, 1493, 1385, 1325, 1243, 1145, 1029, 942, 825, 791, 737; Ms (ESI): m/z = 401.2 $[M+H]^+$.



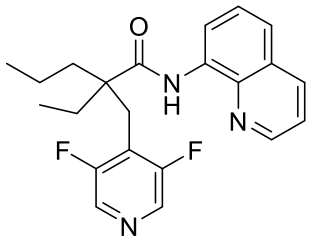
3l

Compound **3l**, colorless oil, yield: 77%, R_f = 0.45 (hexane/EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (brs, 1H), 8.72 (dd, *J* = 9.0, 2.7 Hz, 2H), 8.15 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.05 – 7.00 (m, 2H), 3.13 – 3.05 (m, 2H), 1.96 – 1.89 (m, 1H), 1.88 – 1.79 (m, 2H), 1.76 – 1.68 (m, 1H), 1.50 – 1.36 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 162.1 (d, *J* = 249.9 Hz), 162.0 (d, *J* = 249.9 Hz), 148.2, 138.8, 136.4, 134.4, 128.0, 127.6, 121.7, 121.5, 121.0 (t, *J* = 20.1 Hz), 116.8 (t, *J* = 3.4 Hz), 116.5, 115.2 (d, *J* = 22.8 Hz), 115.1 (d, *J* = 22.6 Hz), 111.8 (t, *J* = 12.3 Hz), 51.9, 36.4, 30.0, 27.1, 17.6, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.0 (d, J = 6.0 Hz, 2F); IR (neat) *v* 3358, 3065, 2963, 2874, 2232, 1675, 1526, 1487, 1423, 1385, 1325, 1138, 1043, 972, 861, 826, 792, 736; Ms (ESI): *m*/*z* = 408.2 $[M+H]^+$.



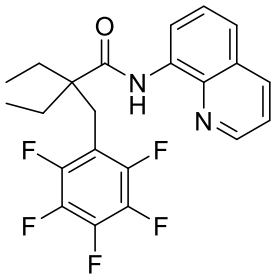
3m

Compound **3m**, pale yellow oil, yield: 79%, R_f = 0.38 (hexane/EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (brs, 1H), 8.75 – 8.71 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.40 (dd, *J* = 8.0, 2.1 Hz, 1H), 3.04 – 2.96 (m, 2H), 1.95 – 1.87 (m, 1H), 1.85 – 1.77 (m, 2H), 1.74 – 1.66 (m, 1H), 1.49 – 1.39 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 172.0 (dm, *J* = 261.3 Hz), 161.4 (dm, *J* = 242.1 Hz), 160.7 (dm, *J* = 241.9 Hz), 148.3, 138.9, 136.5, 134.4, 128.0, 127.7, 121.7, 121.5, 116.6, 105.9 (m), 95.0 (m), 51.7, 36.5, 29.0, 27.1, 17.6, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.3 (m, 1F), -67.7 (dd, *J* = 19.7, 13.4 Hz, 1F), -92.56 (m, 1F); IR (neat) *v* 3357, 2963, 2874, 1675, 1616, 1528, 1472, 1414, 1385, 1142, 1018, 826, 792, 733; Ms (ESI): *m*/*z* = 402.2 $[M+H]^+$.



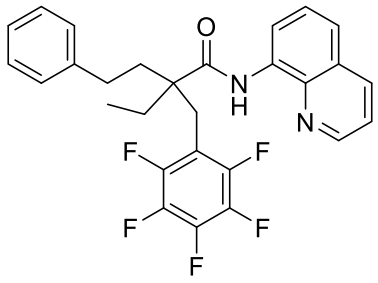
3n

Compound **3n**, pale yellow oil, yield: 83%, R_f = 0.33 (hexane/EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (brs, 1H), 8.75 – 8.70 (m, 2H), 8.17 (s, 2H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.17 – 3.09 (m, 2H), 1.94 – 1.86 (m, 1H), 1.85 – 1.76 (m, 2H), 1.75 – 1.67 (m, 1H), 1.50 – 1.40 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 158.8 (d, *J* = 257.9 Hz), 158.7 (d, *J* = 258.0 Hz), 148.3, 138.8, 136.4, 134.4, 134.0 (d, *J* = 24.6 Hz), 133.9 (d, *J* = 24.8 Hz), 128.0, 127.6, 122.8 (t, *J* = 17.3 Hz), 121.7, 121.5, 116.5, 51.8, 36.9, 28.9, 27.5, 17.6, 14.8, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -126.3 (2F); IR (neat) *v* 3357, 3049， 2963, 2874, 1682, 1527, 1486, 1421, 1385, 1325, 1140, 1040, 909, 826, 791, 733; Ms (ESI): *m*/*z* = 384.2 $[M+H]^+$.



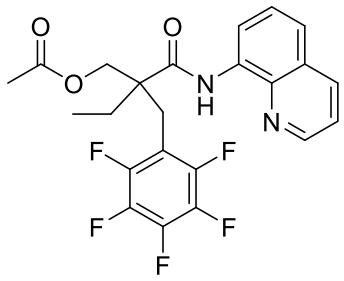
3o

Compound **3o**, colorless oil, yield: 93%, R_f = 0.53 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (brs, 1H), 8.75 – 8.71 (m, 2H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55 – 7.41 (m, 3H), 3.07 (s, 2H), 1.98 – 1.89 (m, 2H), 1.86 – 1.77 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 148.2, 146.0 (dm, *J* = 244.8 Hz), 140.0 (dm, *J* = 250.8 Hz), 138.8, 138.4 (dm, *J* = 245.5 Hz), 136.4, 134.3, 128.0, 127.6, 121.6, 121.5, 116.6, 111.7 (m), 51.9, 29.4, 26.6, 8.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.3 (dd, *J* = 22.6, 7.7 Hz, 2F), -156.7 (t, *J* = 20.9 Hz, 1F), -163.2 (m, 2F); IR (neat) *v* 3358, 3051, 2927, 2883, 1683, 1505, 1385, 1325, 1003, 949, 826, 792, 736; Ms (ESI): *m*/*z* = 423.1 $[M+H]^+$.



3p

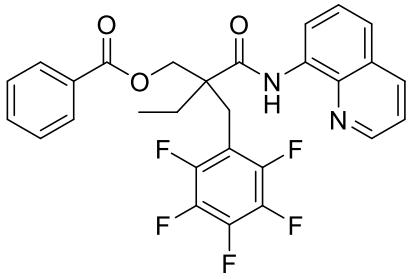
Compound **3p**, pale yellow oil, yield: 84%, R_f = 0.51 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (brs, 1H), 8.76 – 8.73 (m, 2H), 8.17 (dd, J = 8.3, 1.6 Hz, 1H), 7.58 – 7.44 (m, 3H), 7.31 – 7.24 (m, 4H), 7.21 – 7.17 (m, 1H), 3.15 (dd, J = 32.0, 14.1 Hz, 2H), 2.79 – 2.66 (m, 2H), 2.19 – 2.12 (m, 1H), 2.08 – 1.97 (m, 2H), 1.95 – 1.87 (m, 1H), 1.14 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 148.3, 146.0 (dm, J = 245.4 Hz), 141.9, 140.1 (dm, J = 251.4 Hz), 138.8, 137.5 (dm, J = 246.0 Hz), 136.5, 134.3, 128.6, 128.5, 128.1, 127.7, 126.2, 121.8, 121.7, 116.8, 111.4 (m), 51.7, 36.8, 30.9, 29.5, 27.1, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.2 (dd, J = 22.6, 7.6 Hz, 2F), -156.2 (t, J = 20.9 Hz, 1F), -162.8 (m, 2F); IR (neat) ν 3357, 2942, 1682, 1521, 1503, 1424, 1385, 1325, 1124, 987, 826, 792, 757, 738, 699; Ms (ESI): m/z = 499.2 $[M+H]^+$.



3q

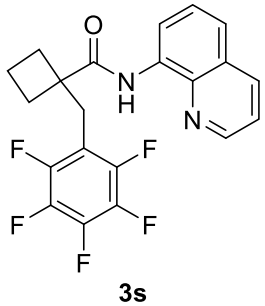
Compound **3q**, white solid, yield: 71%, R_f = 0.44 (hexane/EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (brs, 1H), 8.76 – 8.73 (m, 2H), 8.18 (dd, J = 8.3, 1.6 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 4.43 (d, J = 11.9 Hz, 1H), 4.33 (d, J = 11.9 Hz, 1H), 3.29 (d, J = 14.2 Hz, 1H), 3.17 (d, J = 14.2 Hz, 1H), 2.23 (s, 3H), 2.05 – 1.96 (m, 1H), 1.80 – 1.72 (m, 1H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.7, 148.3, 146.0 (dm, J = 248.1 Hz), 140.3 (dm, J = 255.9 Hz), 138.9, 137.6 (dm, J = 245.9 Hz), 136.6, 134.4, 128.1, 127.7, 122.0, 121.8, 117.1, 110.7 (m), 65.8, 51.3, 28.1, 26.9, 21.0, 8.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.5 (dd, J = 22.4, 7.6 Hz, 2F), -155.6 (t, J = 20.9 Hz, 1F), -162.4 (m, 2F); IR (neat)

v 3327, 2924, 2361, 1750, 1683, 1522, 1503, 1382, 1227, 1123, 998, 969, 826, 792, 748; Ms (ESI): *m*/*z* = 467.1 $[M+H]^+$.



3r

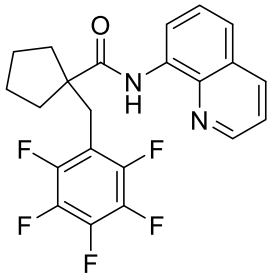
Compound **3r**, white solid, yield: 55%, R_f = 0.47 (hexane/EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (brs, 1H), 8.76 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.36 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.15 – 8.09 (m, 3H), 7.60 – 7.51 (m, 3H), 7.45 – 7.41 (m, 2H), 7.37 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 3.38 (d, *J* = 14.2 Hz, 1H), 3.29 (d, *J* = 14.2 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.94 – 1.85 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 166.3, 148.2, 146.0 (dm, *J* = 244.6 Hz), 140.5 (dm, *J* = 252.8 Hz), 138.8, 137.6 (dm, *J* = 244.4 Hz), 136.4, 134.3, 133.4, 130.0, 129.8, 128.6, 128.0, 127.6, 122.0, 121.7, 117.0, 110.7 (m), 66.2, 51.7, 28.5, 27.2, 9.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.4 (dd, *J* = 22.5, 7.7 Hz, 2F), -155.6 (t, *J* = 20.9 Hz, 1F), -162.3 (m, 2F); IR (neat) ν 3342, 2925, 2361, 1723, 1683, 1522, 1504, 1266, 1122, 984, 913, 826, 792, 743, 711; Ms (ESI): *m*/*z* = 529.2 $[M+H]^+$.



3s

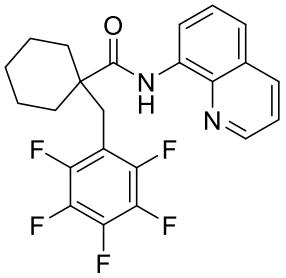
Compound **3s**, colorless oil, yield: 80%, R_f = 0.48 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75 (brs, 1H), 8.72 – 8.69 (m, 2H), 8.16 (dd, *J* = 8.3, 1.6 Hz,

1H), 7.57 – 7.49 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.31 (s, 2H), 2.67 – 2.60 (m, 2H), 2.29 – 2.22 (m, 2H), 2.11 – 2.02 (m, 1H), 2.00 – 1.91 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 148.2, 145.6 (dm, *J* = 247.0 Hz), 140.1 (dm, *J* = 251.0 Hz), 138.6, 137.5 (dm, *J* = 250.9 Hz), 136.5, 134.2, 128.0, 127.6, 121.7 (2C), 116.6, 111.4 (m), 50.7, 31.2, 30.2, 15.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -140.9 (dd, *J* = 22.7, 8.0 Hz, 2F), -156.3 (t, *J* = 20.9 Hz, 1F), -162.6 (m, 2F); IR (neat) *v* 3349, 2925, 2853, 1684, 1521, 1502, 1486, 1424, 1324, 1123, 986, 826, 792, 734; Ms (ESI): *m*/*z* = 407.1 $[M+H]^+$.



3t

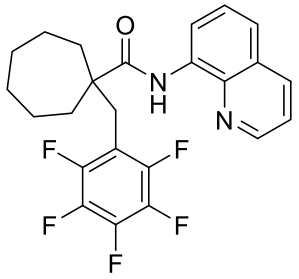
Compound **3t**, colorless oil, yield: 91%, R_f = 0.52 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (brs, 1H), 8.73 – 8.69 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.42 (m, 3H), 3.16 (s, 2H), 2.40 – 2.28 (m, 2H), 1.90 – 1.77 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 148.2, 145.7 (dm, *J* = 245.0 Hz), 140.1 (dm, *J* = 250.9 Hz), 138.6, 137.5 (dm, *J* = 251.1 Hz), 136.5, 134.4, 128.0, 127.6, 121.7, 121.6, 116.6, 111.9 (m), 57.5, 35.0, 31.1, 23.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -140.4 (dd, *J* = 22.7, 7.9 Hz, 2F), -156.6 (t, *J* = 20.9 Hz, 1F), -162.9 (m, 2F); IR (neat) *v* 3354, 3050, 2961, 2878, 1682, 1521, 1424, 1385, 1324, 1123, 1022, 964, 826, 792, 757, 737; Ms (ESI): *m*/*z* = 421.1 $[M+H]^+$.



3u

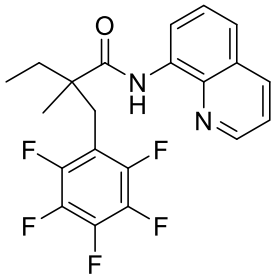
Compound **3u**, colorless oil, yield: 62%, R_f = 0.53 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (brs, 1H), 8.75 – 8.71 (m, 2H), 8.17 (dd, *J* = 8.3, 1.6 Hz,

1H), 7.58 – 7.50 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.99 (s, 2H), 2.42 – 2.32 (m, 2H), 1.80 – 1.72 (m, 2H), 1.70 – 1.63 (m, 1H), 1.54 – 1.45 (m, 4H), 1.34 – 1.27 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 148.3, 145.8 (dm, *J* = 237.4 Hz), 140.0 (dm, *J* = 250.9 Hz), 138.8, 137.4 (dm, *J* = 244.0 Hz), 136.5, 134.4, 128.0, 127.7, 121.7, 121.6, 116.8, 111.1 (m), 49.8, 38.9, 34.4, 25.8, 23.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.6 (dd, *J* = 22.7, 7.8 Hz, 2F), -156.6 (t, *J* = 20.9 Hz, 1F), -163.1 (m, 2F); IR (neat) *v* 3358, 2932, 2861, 1727, 1683, 1521, 1503, 1423, 1386, 1324, 1124, 976, 945, 826, 791, 756; Ms (ESI): *m*/*z* = 435.1 $[M+H]^+$.



3v

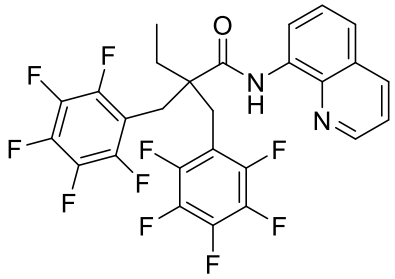
Compound **3v**, colorless oil, yield: 83%, R_f = 0.53 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (brs, 1H), 8.75 – 8.70 (m, 2H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.57 – 7.42 (m, 3H), 3.03 (s, 2H), 2.41 – 2.35 (m, 2H), 1.80 – 1.71 (m, 4H), 1.70 – 1.57 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 148.2, 145.8 (dm, *J* = 247.3 Hz), 140.1 (dm, *J* = 250.8 Hz), 138.8, 137.4 (dm, *J* = 250.5 Hz), 136.5, 134.5, 128.0, 127.7, 121.7, 121.5, 116.7, 111.5 (m), 52.2, 35.9, 34.5, 29.7, 23.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.7 (dd, *J* = 22.7, 7.8 Hz, 2F), -156.6 (t, *J* = 20.9 Hz, 1F), -163.1 (m, 2F); IR (neat) *v* 3357, 2929, 2858, 1683, 1521, 1502, 1385, 1326, 1124, 989, 925, 826, 792, 736; Ms (ESI): *m*/*z* = 449.2 $[M+H]^+$.



3w1

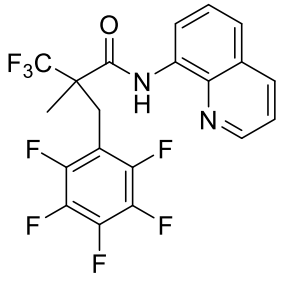
Compound **3w1**, white solid, yield: 73%, R_f = 0.50 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (brs, 1H), 8.78 – 8.75 (m, 2H), 8.17 (dd, *J* = 8.3, 1.6 Hz,

1H), 7.57 – 7.43 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.16 – 3.08 (m, 2H), 2.14 – 2.06 (m, 1H), 1.60 – 1.52 (m, 1H), 1.42 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 148.4, 145.8 (dm, *J* = 244.8 Hz), 140.1 (dm, *J* = 251.0 Hz), 138.9, 137.5 (dm, *J* = 252.4 Hz), 136.5, 134.4, 128.1, 127.6, 121.8, 121.7, 116.6, 111.6 (m), 48.8, 32.8, 31.8, 20.4, 9.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.3 (dd, *J* = 22.6, 7.8 Hz, 2F), -156.4 (t, *J* = 20.9 Hz, 1F), -162.8 (m, 2F); IR (neat) *v* 3360, 2971, 1683, 1521, 1502, 1424, 1385, 1324, 1123, 981, 826, 791, 756; Ms (ESI): *m*/*z* = 409.1 $[M+H]^+$.



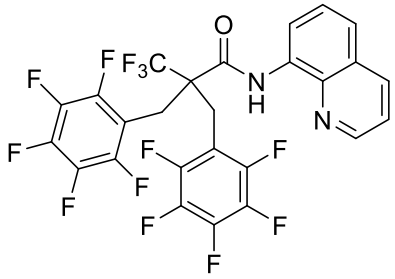
3w2

Compound **3w2**, white solid, yield: 12%, R_f = 0.54 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (brs, 1H), 8.73 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.53 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59 – 7.451 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.28 (d, *J* = 14.2 Hz, 2H), 3.19 (d, *J* = 14.2 Hz, 2H), 1.78 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 148.0, 146.1 (dm, *J* = 248.0 Hz), 140.4 (dm, *J* = 251.9 Hz), 138.4, 137.7 (dm, *J* = 250.9 Hz), 136.6, 133.7, 128.0, 127.7, 122.0, 121.8, 116.7, 110.9 (m), 52.9, 28.7, 25.9, 9.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -138.3 (dd, *J* = 22.4, 7.3 Hz, 4F), -155.4 (t, *J* = 20.9 Hz, 2F), -162.4 (m, 4F); IR (neat) *v* 3346, 3052, 2981, 2946, 1683, 1505, 1424, 1386, 1325, 1122, 1096, 1009, 890, 826, 792, 739; Ms (ESI): *m*/*z* = 575.1 $[M+H]^+$.



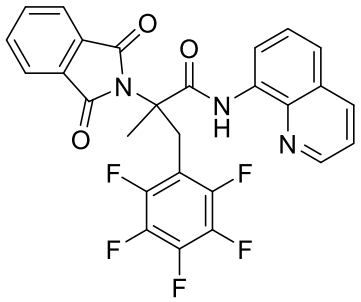
3x1

Compound **3x1**, colorless oil, yield: 54%, R_f = 0.55 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.58 (brs, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 – 8.68 (m, 1H), 8.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.52 (d, *J* = 14.5 Hz, 1H), 3.39 (d, *J* = 14.5 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 148.6, 146.0 (dm, *J* = 246.5 Hz), 140.8 (dm, *J* = 252.9 Hz), 138.8, 137.6 (dm, *J* = 251.5 Hz), 136.5, 133.9, 128.0, 127.5, 126.8 (q, *J* = 281.9 Hz), 122.6, 121.9, 117.1, 109.1 (m), 53.6 (q, *J* = 24.3 Hz), 26.7, 16.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -71.9 (s, 3F), -139.1 (m, 2F), -154.4 (t, *J* = 20.9 Hz, 1F), -161.9 (m, 2F); IR (neat) *v* 3344, 1695, 1522, 1505, 1328, 1266, 1183, 1099, 992, 976, 826, 791, 756; Ms (ESI): *m*/*z* = 449.1 $[M+H]^+$.



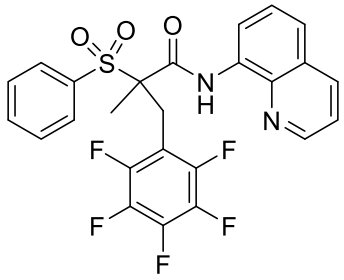
3x2

Compound **3x2**, colorless oil, yield: 36%, R_f = 0.57 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.34 (brs, 1H), 8.73 – 8.68 (m, 1H), 8.62 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.60 – 3.52 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 148.4, 146.2 (dm, *J* = 250.1 Hz), 141.0 (dm, *J* = 253.5 Hz), 138.7, 137.7 (dm, *J* = 250.4 Hz), 136.5, 133.6, 128.0, 127.5, 126.4 (q, *J* = 282.5 Hz), 122.9, 122.0, 117.6, 109.1 (m), 57.1 (q, *J* = 22.6 Hz), 26.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.5 (s, 3F), -138.1 (dd, *J* = 14.9, 5.8 Hz, 4F), -154.2 (t, *J* = 20.9 Hz, 2F), -162.2 (m, 4F); IR (neat) *v* 3336, 2929, 1694, 1506, 1426, 1388, 1267, 1180, 1068, 955, 827, 792, 741; Ms (ESI): *m*/*z* = 615.1 $[M+H]^+$.



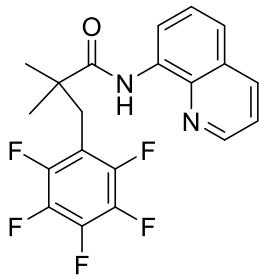
3y

Compound **3y**, white solid, yield: 67%, R_f = 0.38 (hexane/EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (brs, 1H), 8.72 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.43 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.78 – 7.74 (m, 2H), 7.59 – 7.49 (m, 2H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.92 (d, *J* = 14.5 Hz, 1H), 3.76 (d, *J* = 14.4 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 168.9, 148.3, 146.1 (dm, *J* = 246.9 Hz), 140.5 (dm, *J* = 252.6 Hz), 138.7, 137.6 (dm, *J* = 251.0 Hz), 136.5, 134.6, 134.0, 131.6, 128.0, 127.5, 123.6, 122.0, 121.7, 116.8, 110.2 (m), 65.2, 28.3, 22.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -140.6 (dd, *J* = 21.8, 6.4 Hz, 2F), -154.4 (t, *J* = 20.9 Hz, 1F), -161.7 (m, 2F); IR (neat) *v* 3338, 2924, 1716, 1696, 1522, 1502, 1321, 1124, 987, 909, 825, 792, 721; Ms (ESI): *m*/*z* = 526.1 $[M+H]^+$.



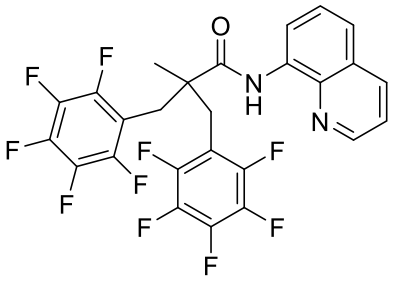
3z

Compound **3z**, yellow solid, yield: 76%, R_f = 0.49 (hexane/EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.64 (brs, 1H), 8.98 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.53 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.55 – 7.50 (m, 2H), 7.47 – 7.43 (m, 2H), 3.97 (d, *J* = 14.2 Hz, 1H), 3.74 (d, *J* = 14.2 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 149.1, 145.9 (dm, *J* = 251.4 Hz), 140.9 (dm, *J* = 253.1 Hz), 137.7 (dm, *J* = 251.9 Hz), 139.3, 136.4, 135.1, 134.8, 134.2, 130.7, 129.4, 128.2, 127.3, 122.8, 122.0, 117.4, 108.5 (m), 72.4, 26.6, 17.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -138.4 (dd, *J* = 21.8, 6.7 Hz, 2F), -153.8 (t, *J* = 20.9 Hz, 1F), -161.4 (m, 2F); IR (neat) *v* 3273, 2964, 1684, 1522, 1505, 1325, 1308, 1146, 991, 912, 827, 792, 738; Ms (ESI): *m*/*z* = 521.1 $[M+H]^+$.



3aa1

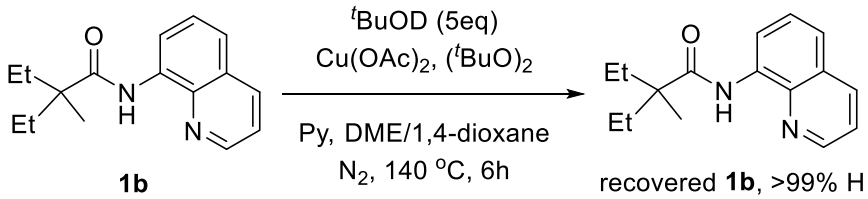
Compound **3aa1**, white solid, yield: 62%, R_f = 0.47 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (brs, 1H), 8.78 – 8.74 (m, 2H), 8.17 (dd, J = 8.3, 1.5 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.46 (dd, J = 8.2, 4.2 Hz, 1H), 3.14 (s, 2H), 1.45 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 148.4, 145.8 (dm, J = 242.9 Hz), 140.1 (dm, J = 251.1 Hz), 138.9, 137.6 (dm, J = 244.3 Hz), 136.5, 134.4, 128.1, 127.6, 121.8, 121.7, 116.6, 111.6 (m), 44.9, 33.1, 24.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.6 (dd, J = 22.6, 7.7 Hz, 2F), -156.2 (t, J = 20.8 Hz, 1F), -162.7 (m, 2F); IR (neat) v 3360, 2971, 1683, 1521, 1504, 1424, 1385, 1325, 1123, 977, 917, 826, 792, 733; Ms (ESI): m/z = 395.1 $[M+H]^+$.



3aa2

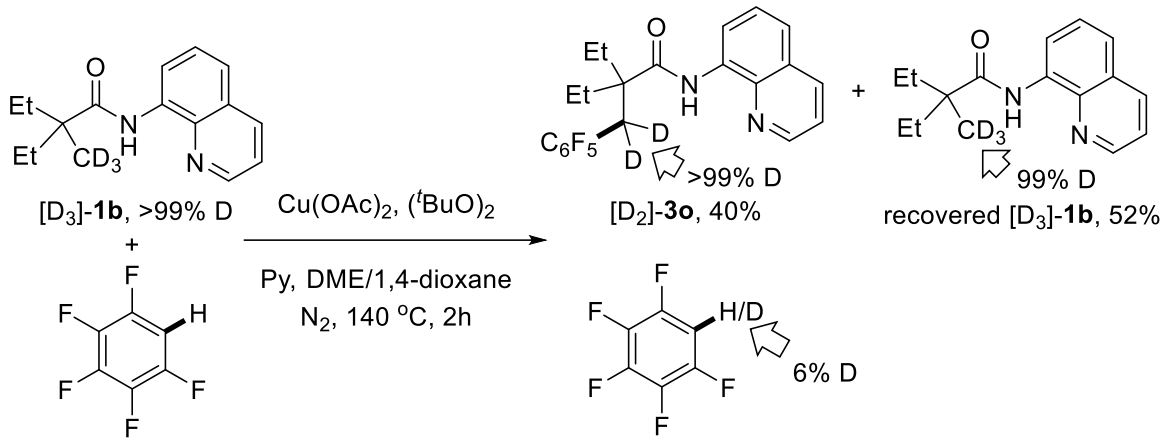
Compound **3aa2**, colorless oil, yield: 30%, R_f = 0.51 (hexane/EtOAc 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (brs, 1H), 8.73 (dd, J = 7.2, 1.7 Hz, 1H), 8.65 (dd, J = 4.2, 1.6 Hz, 1H), 8.17 (dd, J = 8.3, 1.6 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 3.36 (d, J = 14.0 Hz, 2H), 3.17 (d, J = 14.0 Hz, 2H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 148.3, 145.8 (dm, J = 248.1 Hz), 140.4 (dm, J = 251.6 Hz), 138.7, 137.7 (dm, J = 249.9 Hz), 136.6, 133.8, 128.0, 127.6, 122.2, 121.8, 117.0, 110.9 (m), 49.0, 31.9, 19.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -138.8 (dd, J = 22.4, 7.5 Hz, 4F), -155.2 (t, J = 20.9 Hz, 2F), -162.0 (m, 4F); IR (neat) v 3355, 2976, 1684, 1522, 1503, 1424, 1386, 1325, 1121, 985, 944, 826, 792, 736; Ms (ESI): m/z = 561.1 $[M+H]^+$.

Deuterium Labeling Experiment



A 50 mL Schlenk tube was charged with amide **1b** (76.8 mg, 0.30 mmol), $Cu(OAc)_2$ (54.5 mg, 0.30 mmol), DME/1,4-dioxane (7:3, v/v, 1.0 mL), pyridine (72 μL, 71 mg, 0.90 mmol), *tert*-butyl peroxide (138 μL, 110 mg, 0.75 mmol) and *tert*-butan(ol-*d*) (99% D, 143 μL, 113 mg, 1.5 mmol) in sequence under N_2 atmosphere. The tube was capped with a Teflon screw cap, and stirred at 140 °C for 6h. Then the reaction mixture was cooled to room temperature, diluted with EtOAc (30 mL), filtered through a celite pad, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/Hexane (1:30, v/v), to afford recovered **1b** (72.4 mg, 94% yield).

Recovered **1b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (brs, 1H), 8.84 – 8.81 (m, 2H), 8.15 (dd, J = 8.3, 1.7 Hz, 1H), 7.55 – 7.42 (m, 3H), 1.93 – 1.85 (m, 2H), 1.67 – 1.59 (m, 2H), 1.35 (s, **3H**), 0.94 (t, J = 7.5 Hz, 6H).



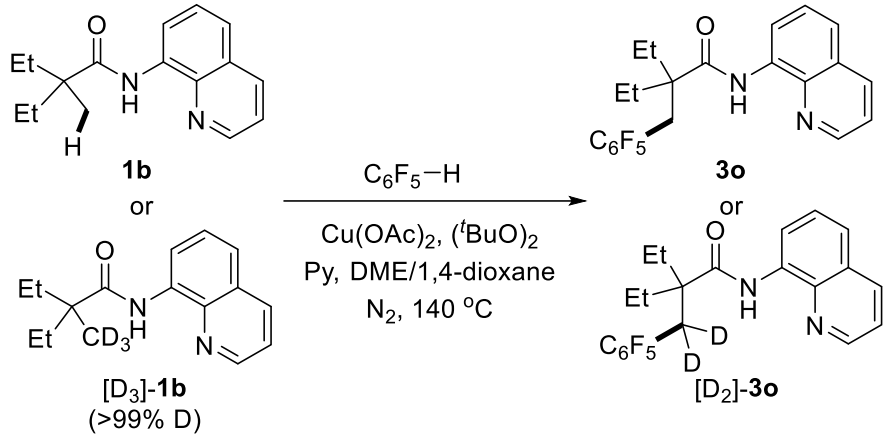
A 50 mL Schlenk tube was charged with [D_3]-**1b** (77.7 mg, 0.30 mmol), $Cu(OAc)_2$ (54.5 mg, 0.30 mmol), DME/1,4-dioxane (7:3, v/v, 1.0 mL), pyridine (72 μL, 71 mg, 0.90 mmol), *tert*-butyl peroxide (138 μL, 110 mg, 0.75 mmol) and pentafluorobenzene (67 μL, 101 mg, 0.60 mmol) in sequence under N_2 atmosphere. The tube was capped with a Teflon screw cap, and stirred at 140 °C for 2h. Then the reaction mixture was cooled to room temperature, and analyzed by GC-MS to obtain the rate of H/D exchange of pentafluorobenzene. The resultant mixture was diluted with EtOAc (30 mL), filtered through a celite pad, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with CH_2Cl_2/Hexane (1:2, v/v), to afford [D_2]-**3o** (50.9 mg, 40% yield) and recovered [D_3]-**1b** (40.4 mg, 52% yield).

[D_2]-**3o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (brs, 1H), 8.74 – 8.71 (m, 2H), 8.16 (dd, J = 8.3, 1.6 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 (dd, J = 8.3, 4.2 Hz, 1H), 1.97 – 1.89 (m, 2H), 1.85 – 1.77 (m, 2H), 1.04 (t, J = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 148.2, 146.0 (dm, J = 244.8 Hz), 140.0 (dm, J = 250.6 Hz), 138.8,

137.4 (dm, J = 242.9 Hz), 136.5, 134.4, 128.0, 127.7, 121.7, 121.6, 116.7, 111.6 (m), 51.8, 26.6, 8.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -139.4 (dd, J = 22.6, 7.9 Hz, 2F), -156.6 (t, J = 20.9 Hz, 1F), -163.1 (m, 2F); IR (neat) ν 3361, 2971, 1683, 1521, 1496, 1424, 1385, 1325, 1009, 922, 826, 791, 757; Ms (ESI): m/z = 425.2 $[M+H]^+$.

Recovered [D_3]-**1b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (brs, 1H), 8.84 – 8.81 (m, 2H), 8.15 (dd, J = 8.3, 1.6 Hz, 1H), 7.55 – 7.41 (m, 3H), 1.93 – 1.85 (m, 2H), 1.67 – 1.59 (m, 2H), 1.32 – 1.28 (m, **0.04H**), 0.94 (t, J = 7.5 Hz, 6H).

Parallel KIE Experiment

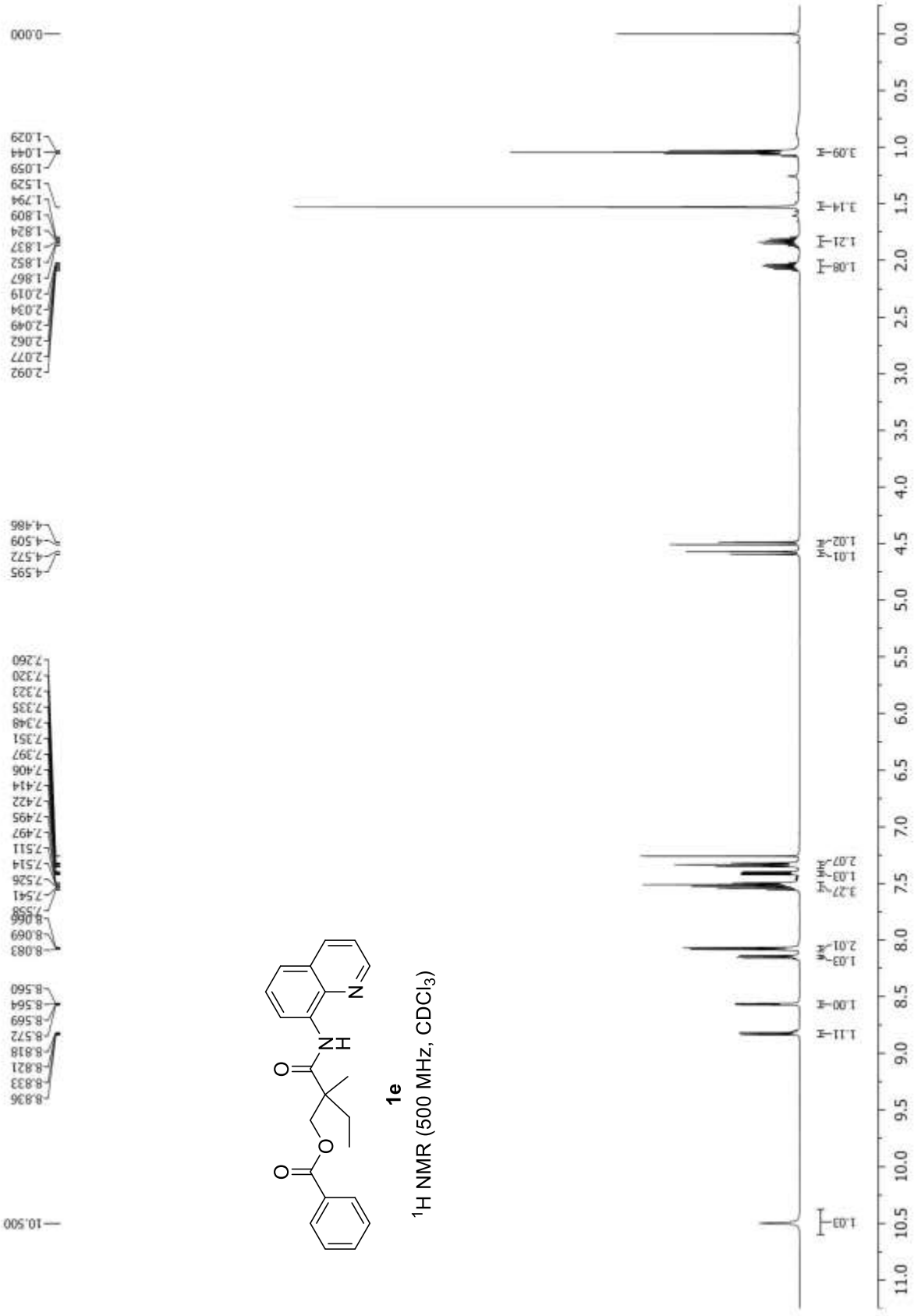


A 50 mL Schlenk tube was charged with **1b** (76.8 mg, 0.30 mmol) or [D_3]-**1b** (77.7 mg, 0.30 mmol), $Cu(OAc)_2$ (54.5 mg, 0.30 mmol), DME/1,4-dioxane (7:3, v/v, 1.0 mL), pyridine (72 μL, 71 mg, 0.90 mmol), *tert*-butyl peroxide (138 μL, 110 mg, 0.75 mmol) and pentafluorobenzene (67 μL, 101 mg, 0.60 mmol) in sequence under N_2 atmosphere. The tube was capped with a Teflon screw cap, and stirred at 140 °C for 2h. The reaction was stopped by rapid cooling in the indicated reaction period, and analyzed by GC using benzophenone as the internal standard. The average GC yield was calculated after calibrating the response of GC based on five runs of each reaction. The KIE value determined from two parallel reactions is 1.1.

Time (min)	10	20	30	40	50	60	70	80	90
Yield of **3o** (%)	0.1	0.8	3.3	6.8	8.2	14.8	20.9	28.5	48.0
Yield of [D_2]-**3o** (%)	0.1	1.1	2.2	4.2	10.2	12.6	19.5	32.0	38.5

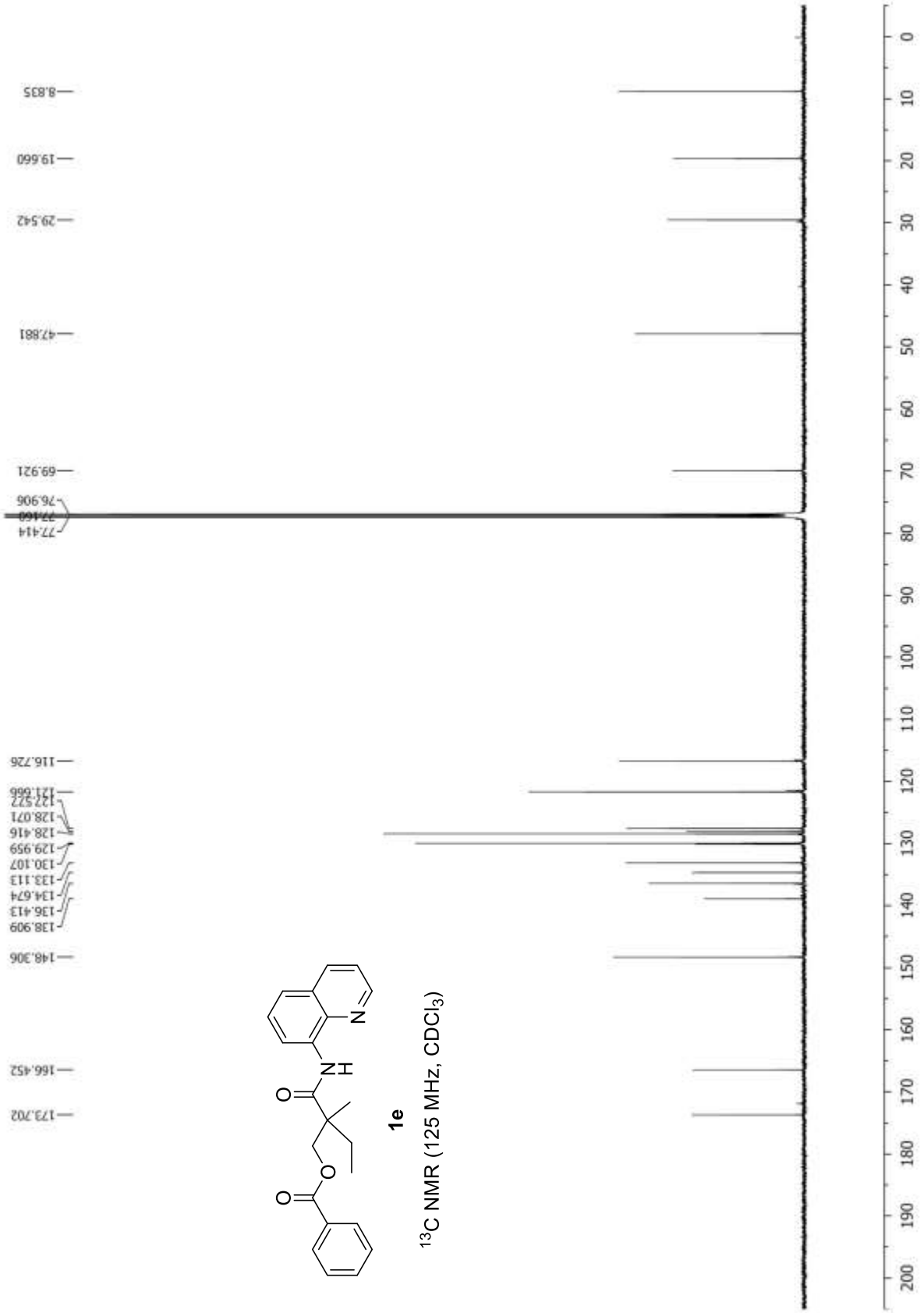
References

1. (a) Tran, L. D.; Daugulis, O. *Angew. Chem. Int. Ed.* **2012**, *51*, 5188. (b) Shang, R.; Ilies, L.; Matsumoto, A.; Nakamura, E. *J. Am. Chem. Soc.* **2013**, *135*, 6030. (c) Wu, X.; Zhao, Y.; Ge, H. *J. Am. Chem. Soc.* **2014**, *136*, 1789. (d) Wu, X.; Zhao, Y.; Zhang, G.; Ge, H. *Angew. Chem. Int. Ed.* **2014**, *53*, 3706. (e) Wu, X.; Zhao, Y.; Ge, H. *Chem. Eur. J.* **2014**, *20*, 9530. (f) Wu, X.; Yang, K.; Zhao, Y.; Sun, H.; Li, G.; Ge, H. *Nat. Commun*. **2015**, *6*, 6462.
2. Wu, X.; Zhao, Y.; Ge, H. *Chem. Asian J*. **2014**, *9*, 2736.



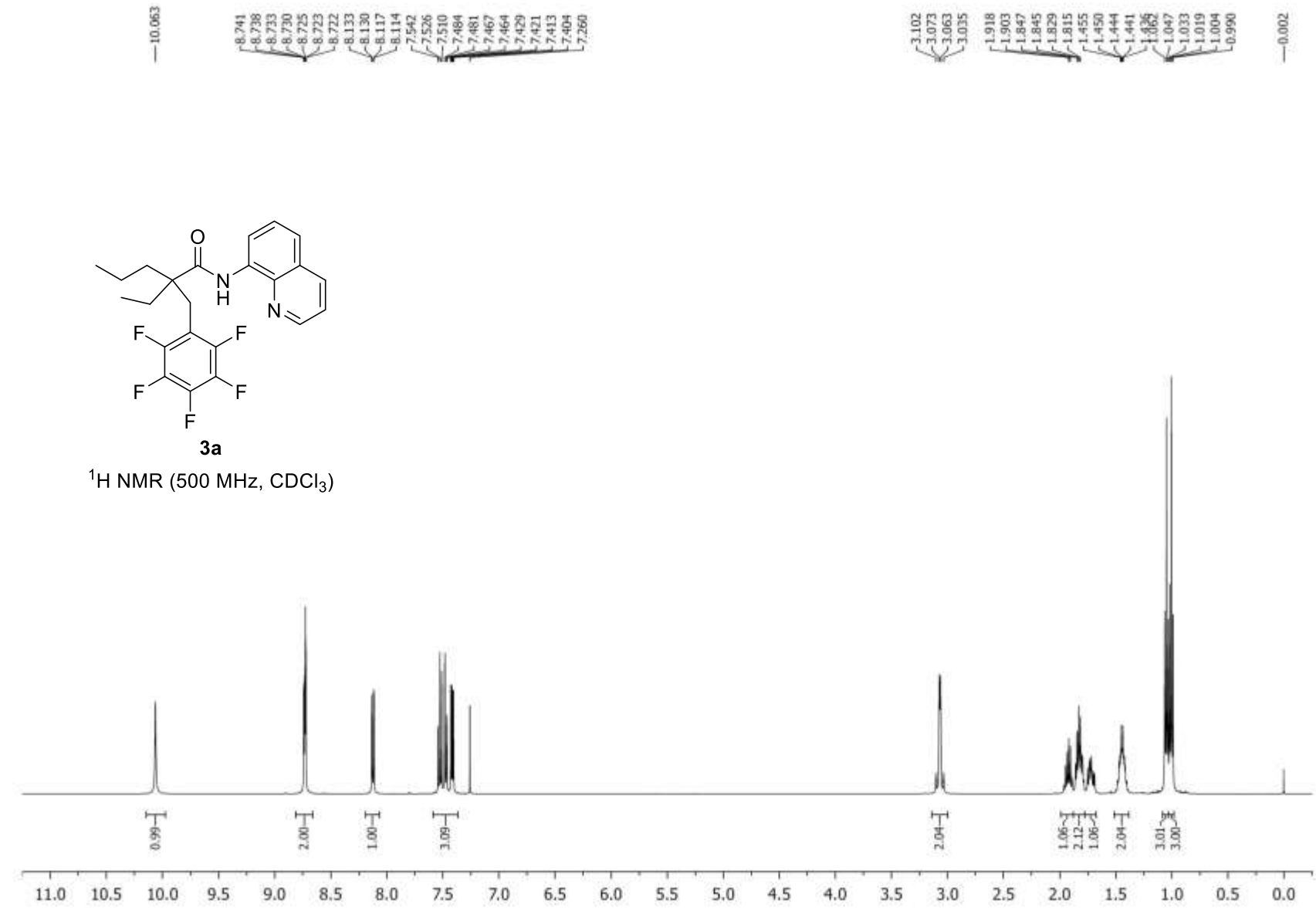
1e

^{1}H NMR (500 MHz, $CDCl_3$)



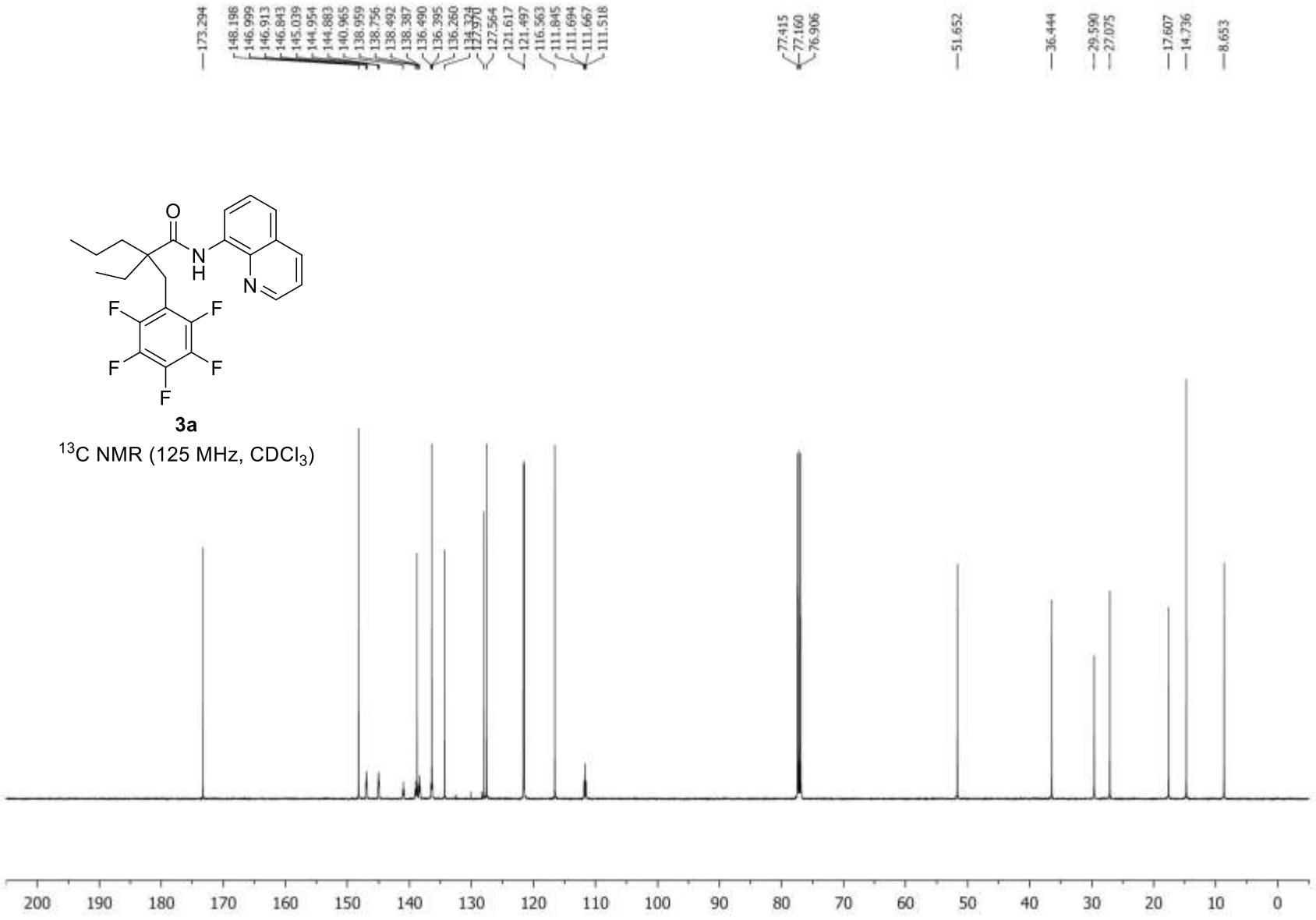
1e

^{13}C NMR (125 MHz, $CDCl_3$)



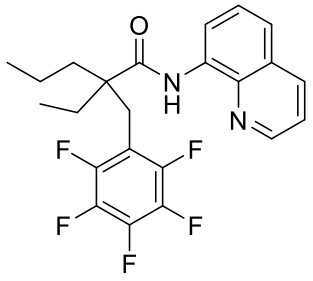
3a

^{1}H NMR (500 MHz, $CDCl_3$)



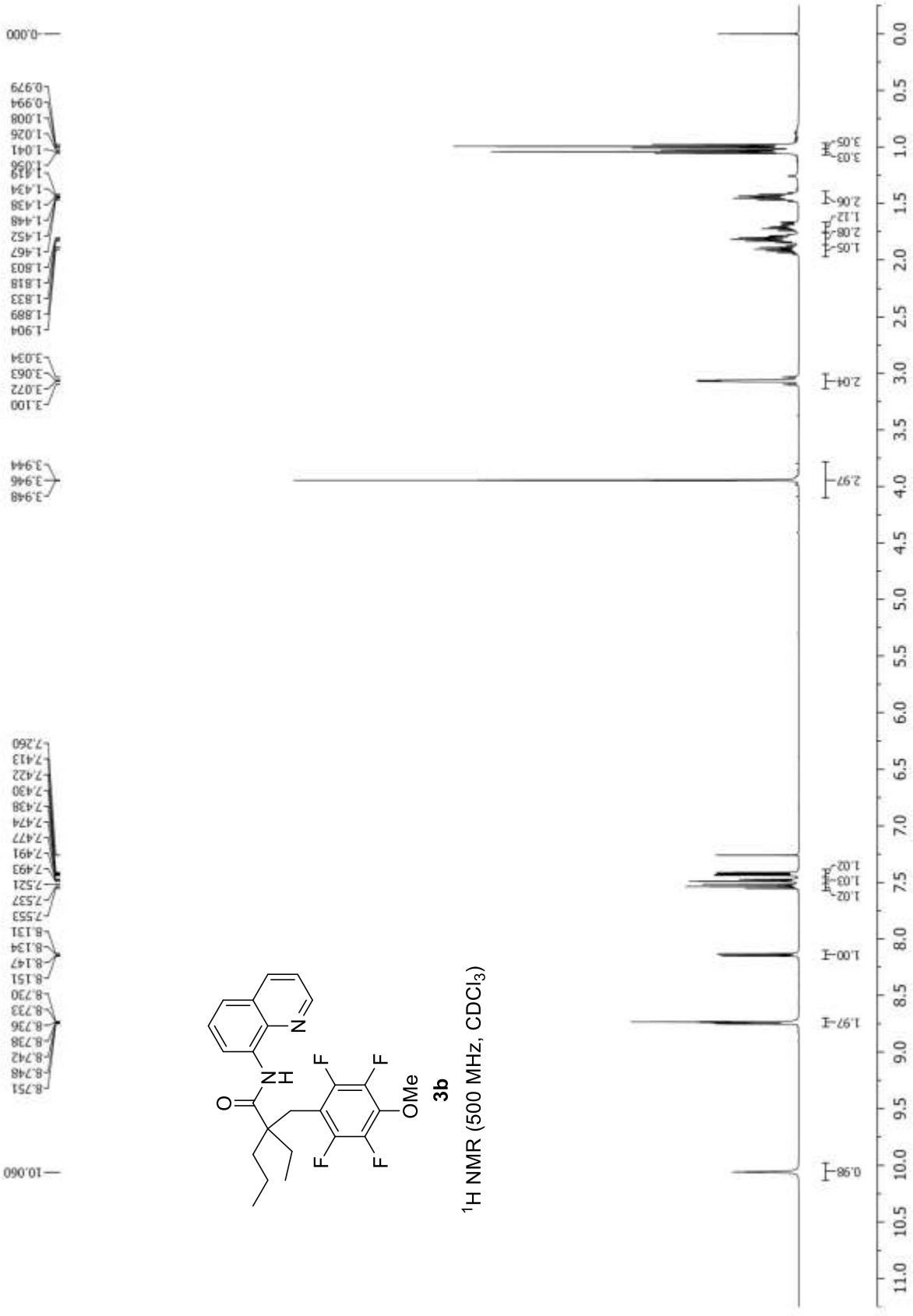
3a

^{13}C NMR (125 MHz, $CDCl_3$)



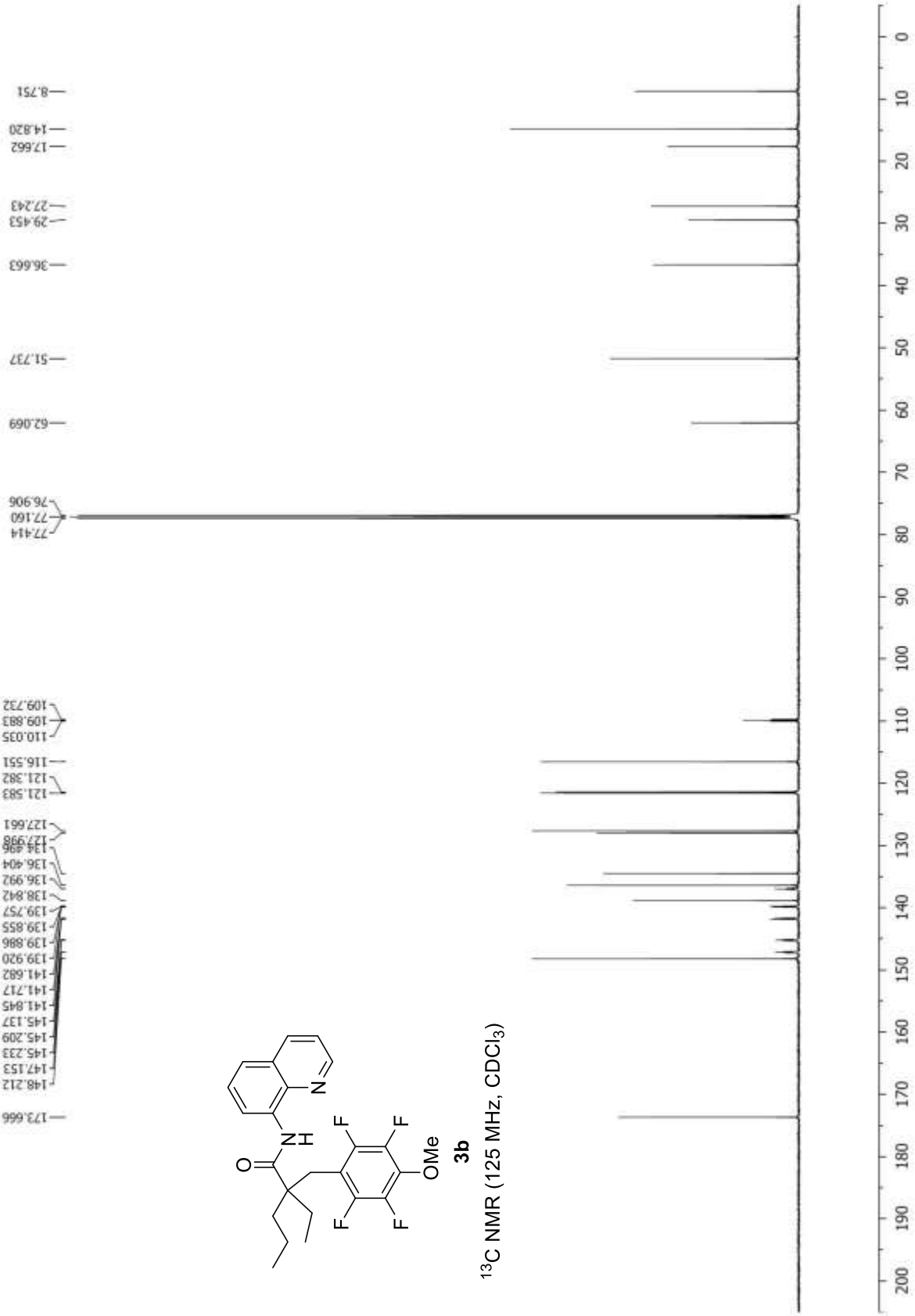
3a

^{19}F NMR (471 MHz, $CDCl_3$)



3b

^{1}H NMR (500 MHz, $CDCl_3$)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121.382
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127.998
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136.404
136.992
138.842
139.757
139.855
139.886
139.920
141.682
141.717
141.845
145.137
145.209
145.233
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F
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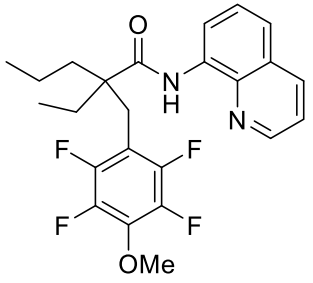
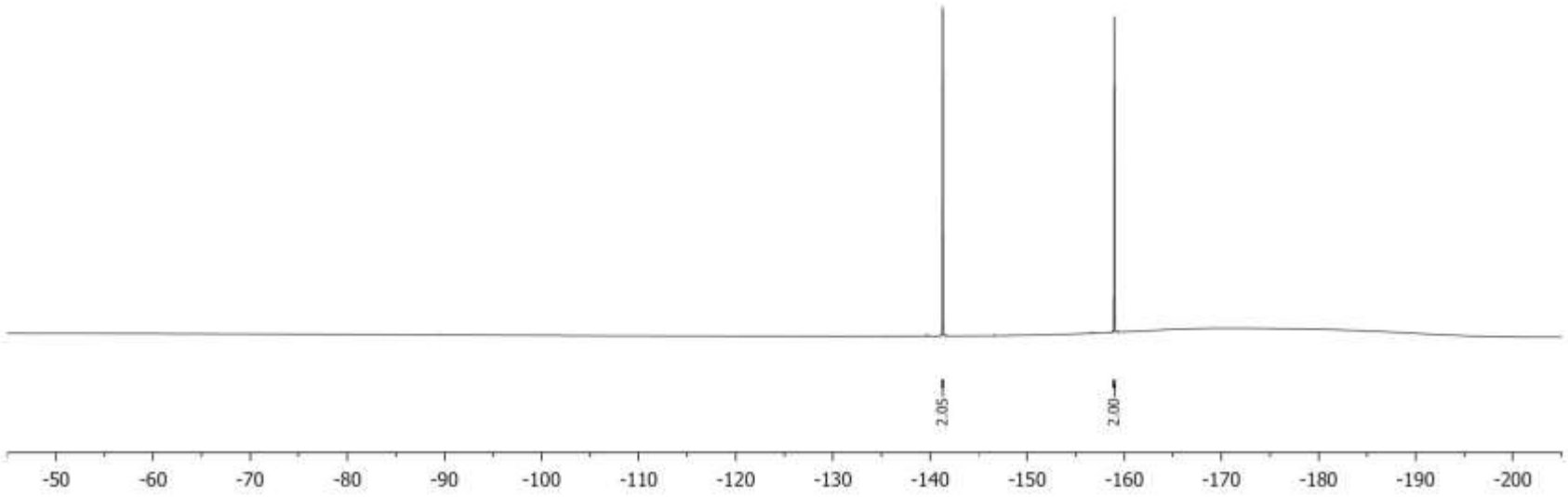
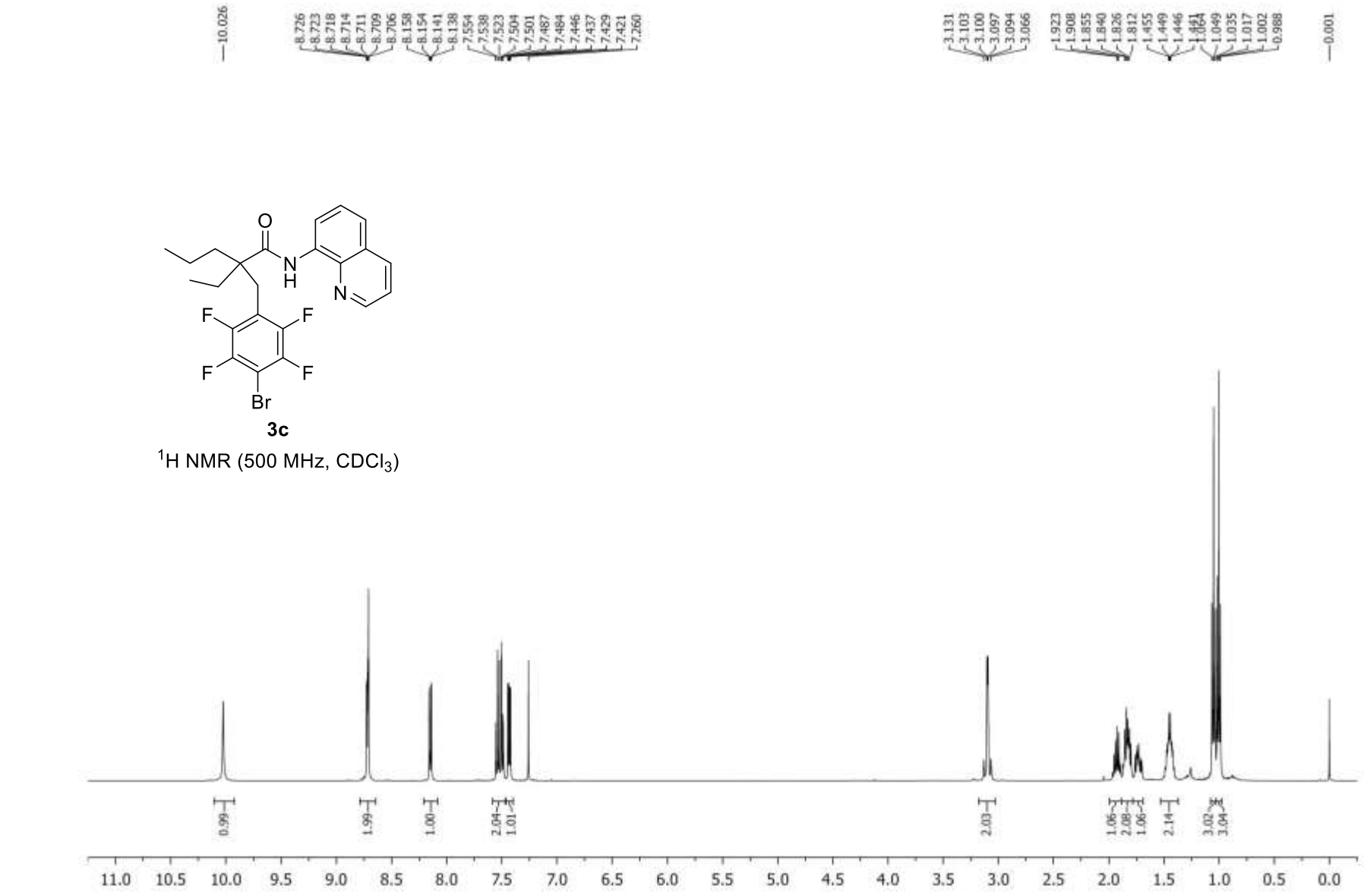
O
N
H
N
OMe
3b
^{13}C NMR (125 MHz, CDCl$_3$)



3b

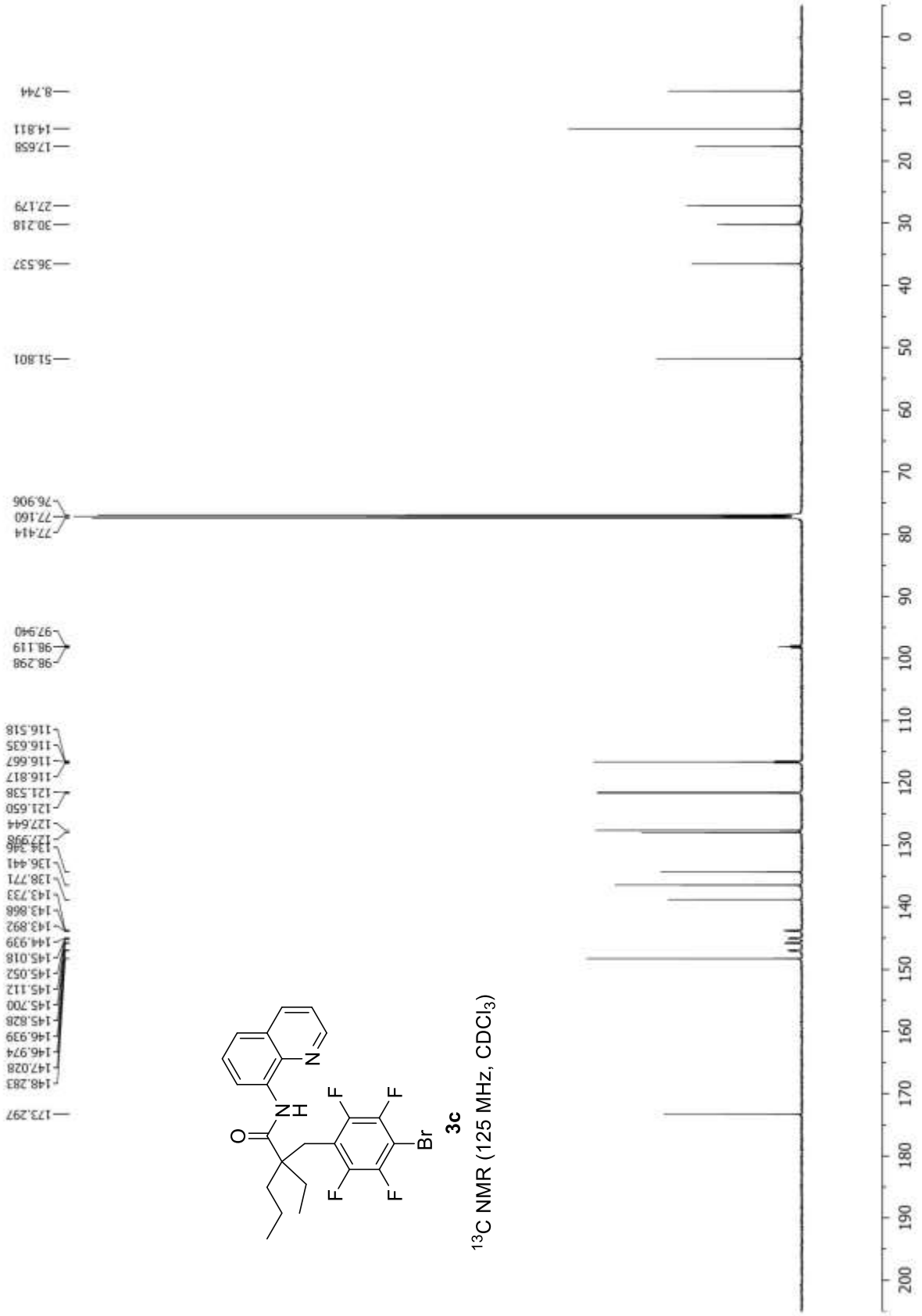
^{19}F NMR (471 MHz, $CDCl_3$)





3c

^{1}H NMR (500 MHz, $CDCl_3$)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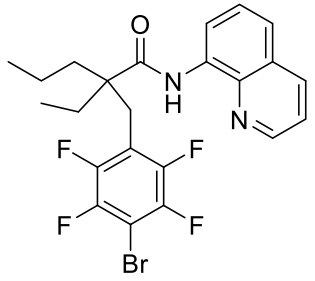
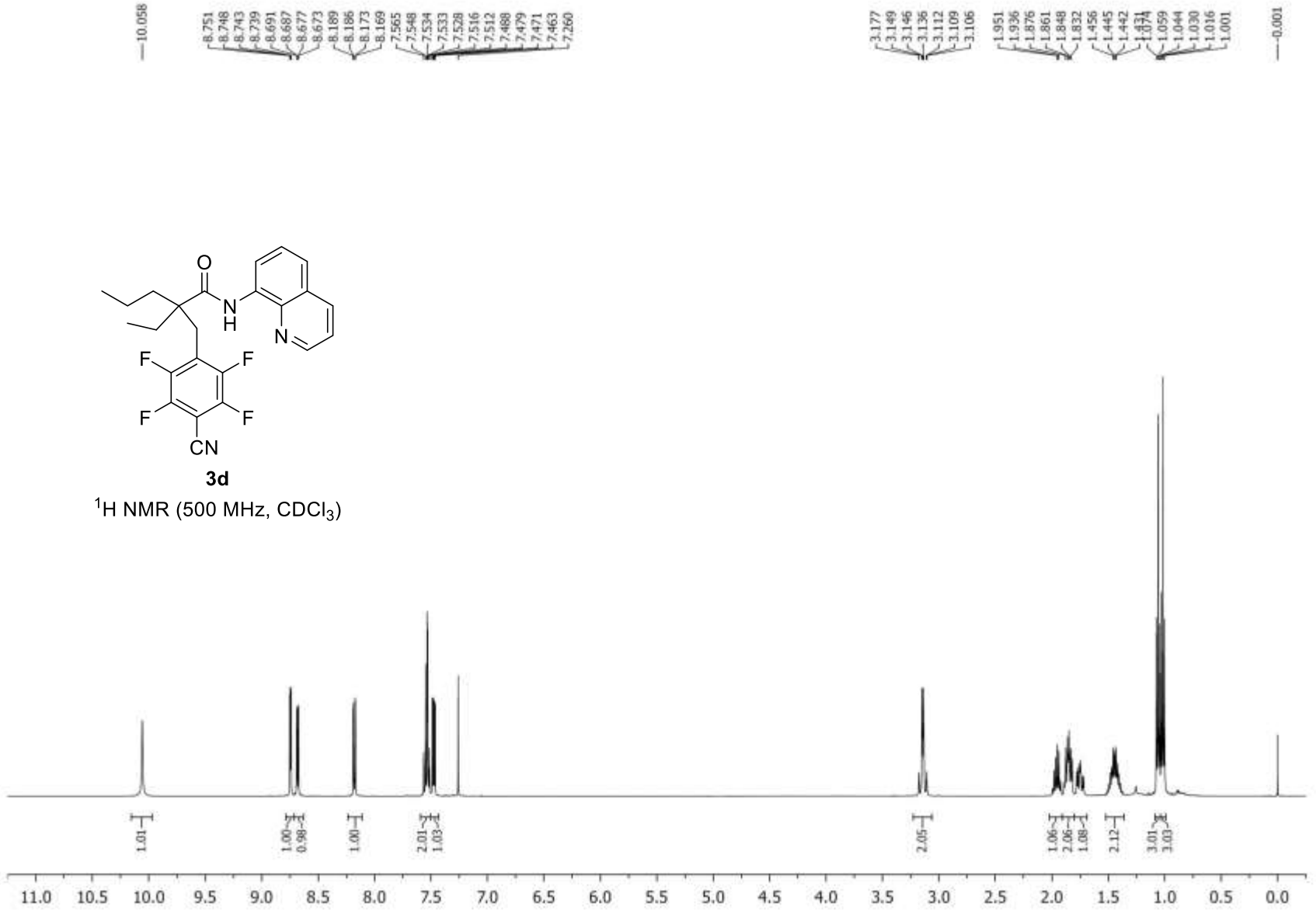
98.298
116.518
116.635
116.667
116.817
121.538
121.650
127.644
127.998
134.346
136.441
138.771
143.733
143.868
143.892
144.939
145.018
145.052
145.112
145.700
145.828
146.939
146.974
147.028
148.283
173.297
F
F
F
F
Br
O
N
H
N
3c
^{13}C NMR (125 MHz, CDCl$_3$)



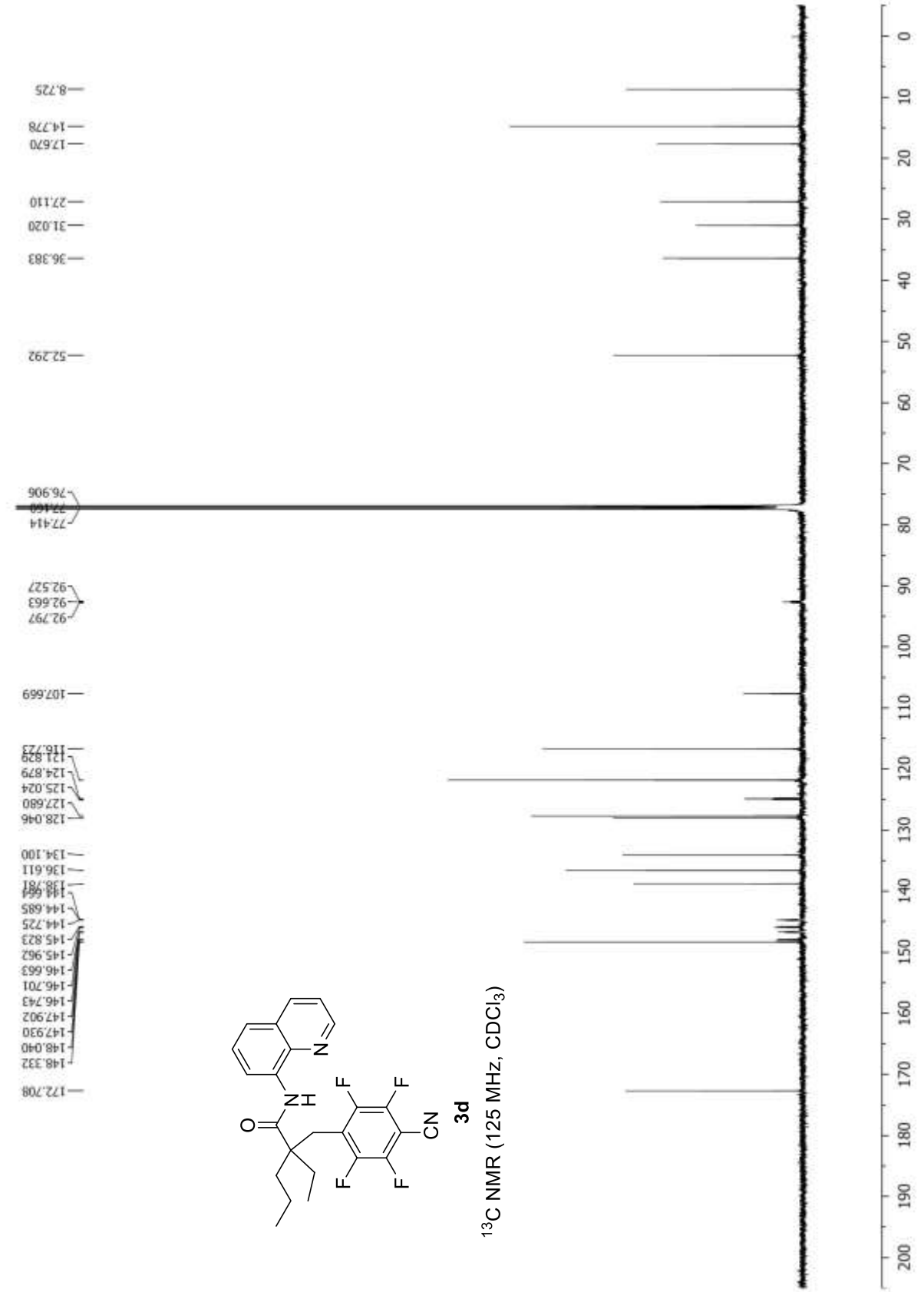
3c

^{19}F NMR (471 MHz, $CDCl_3$)



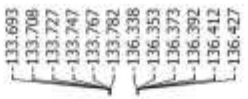
3d

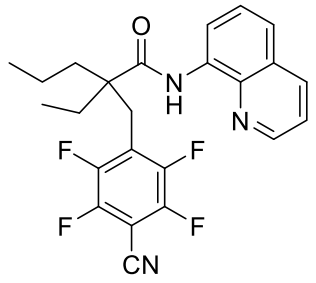
^{1}H NMR (500 MHz, $CDCl_3$)



3d

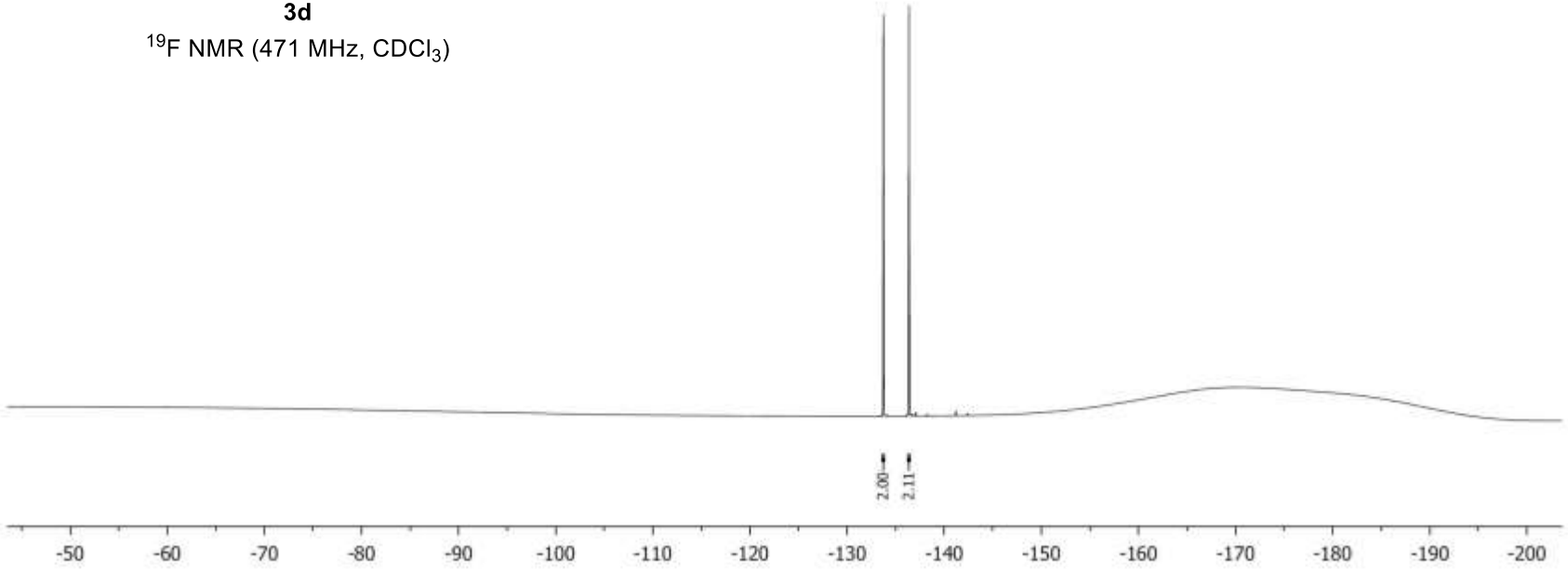
^{13}C NMR (125 MHz, $CDCl_3$)

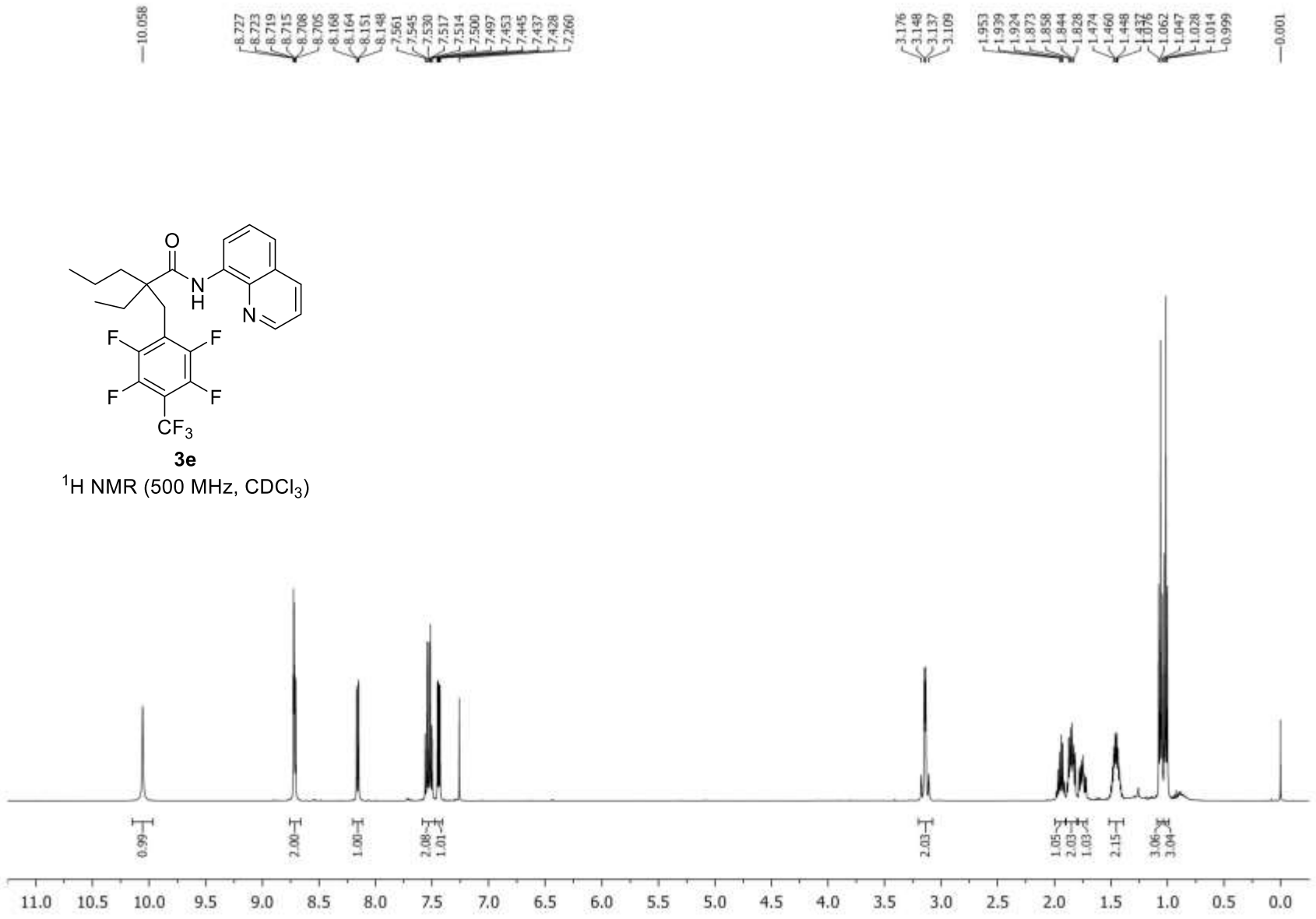




3d

^{19}F NMR (471 MHz, $CDCl_3$)





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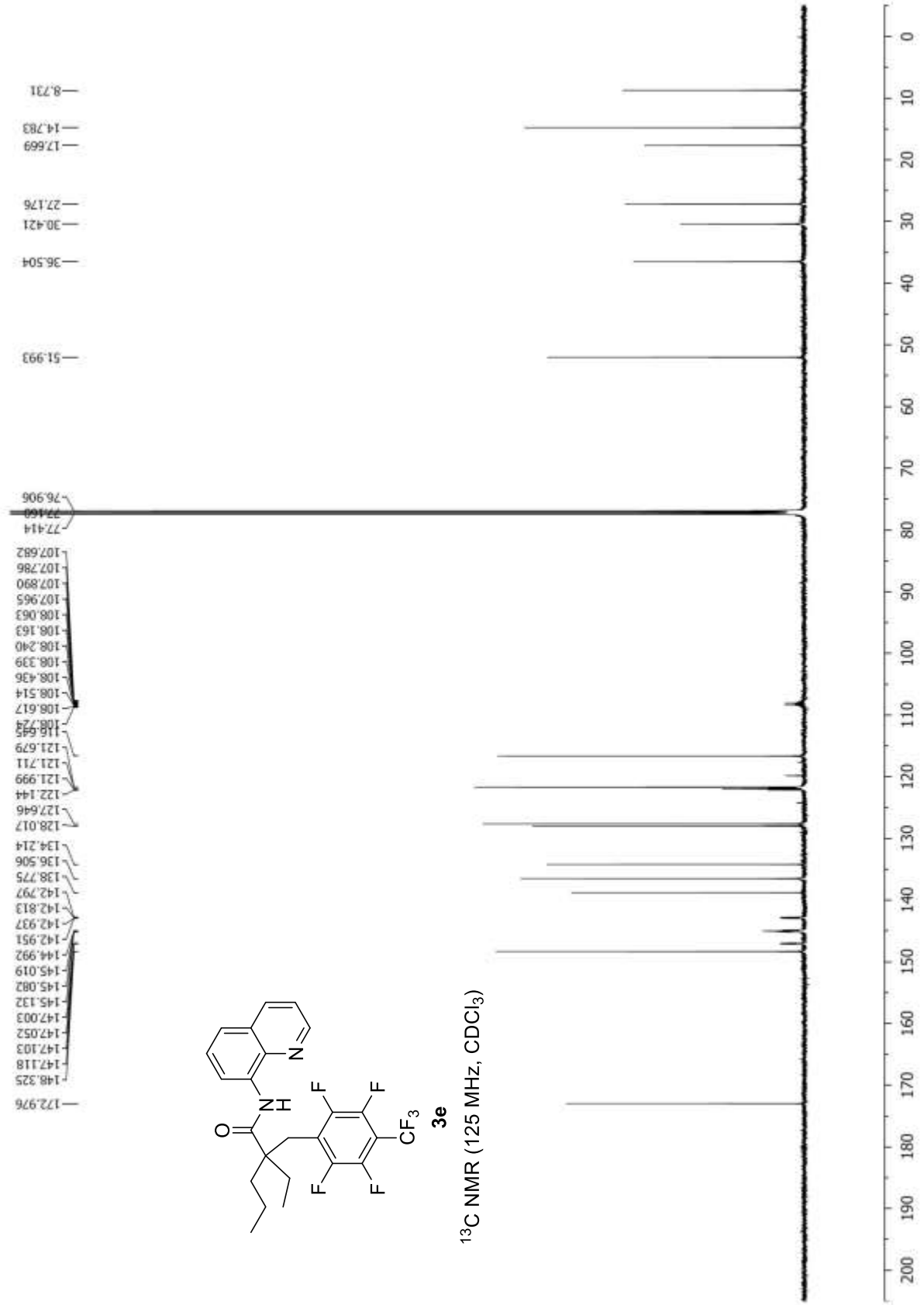

3e

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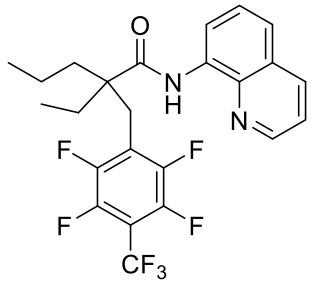

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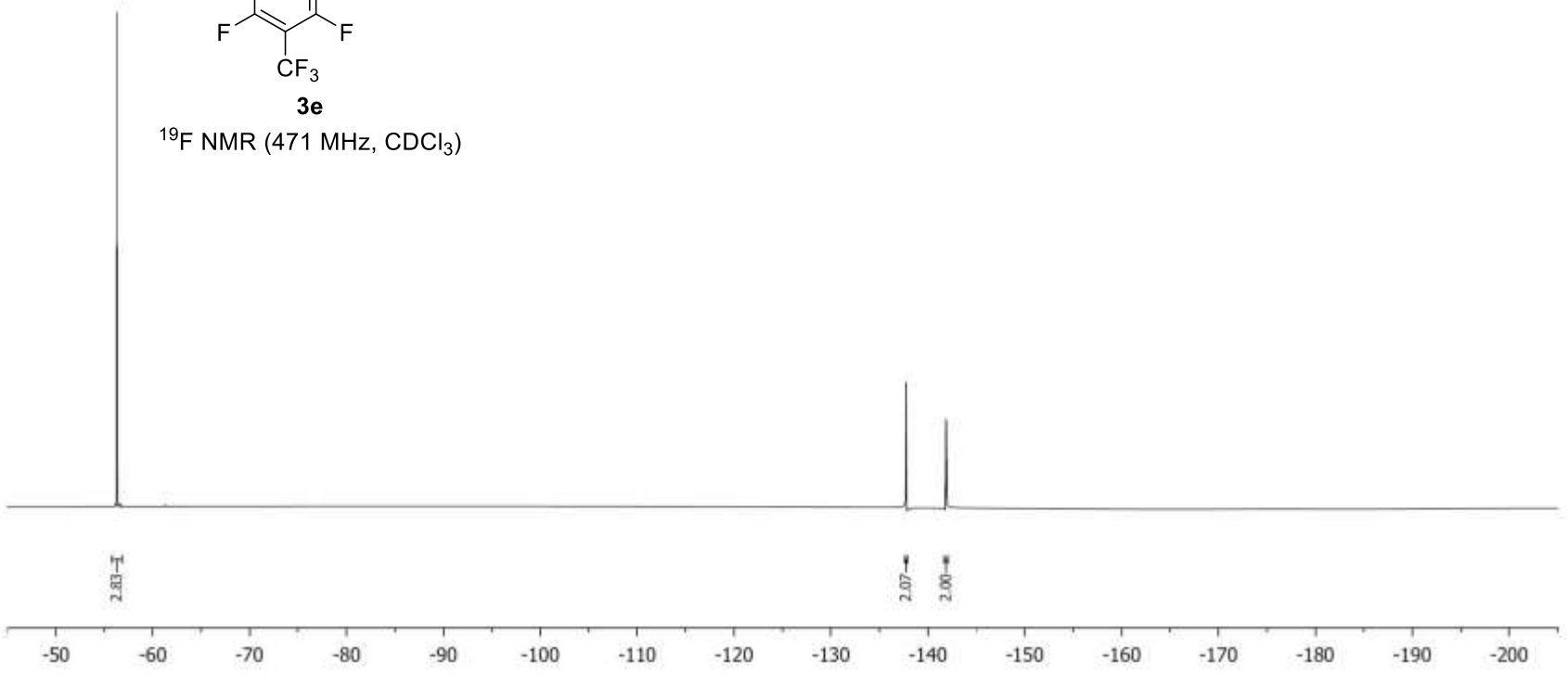

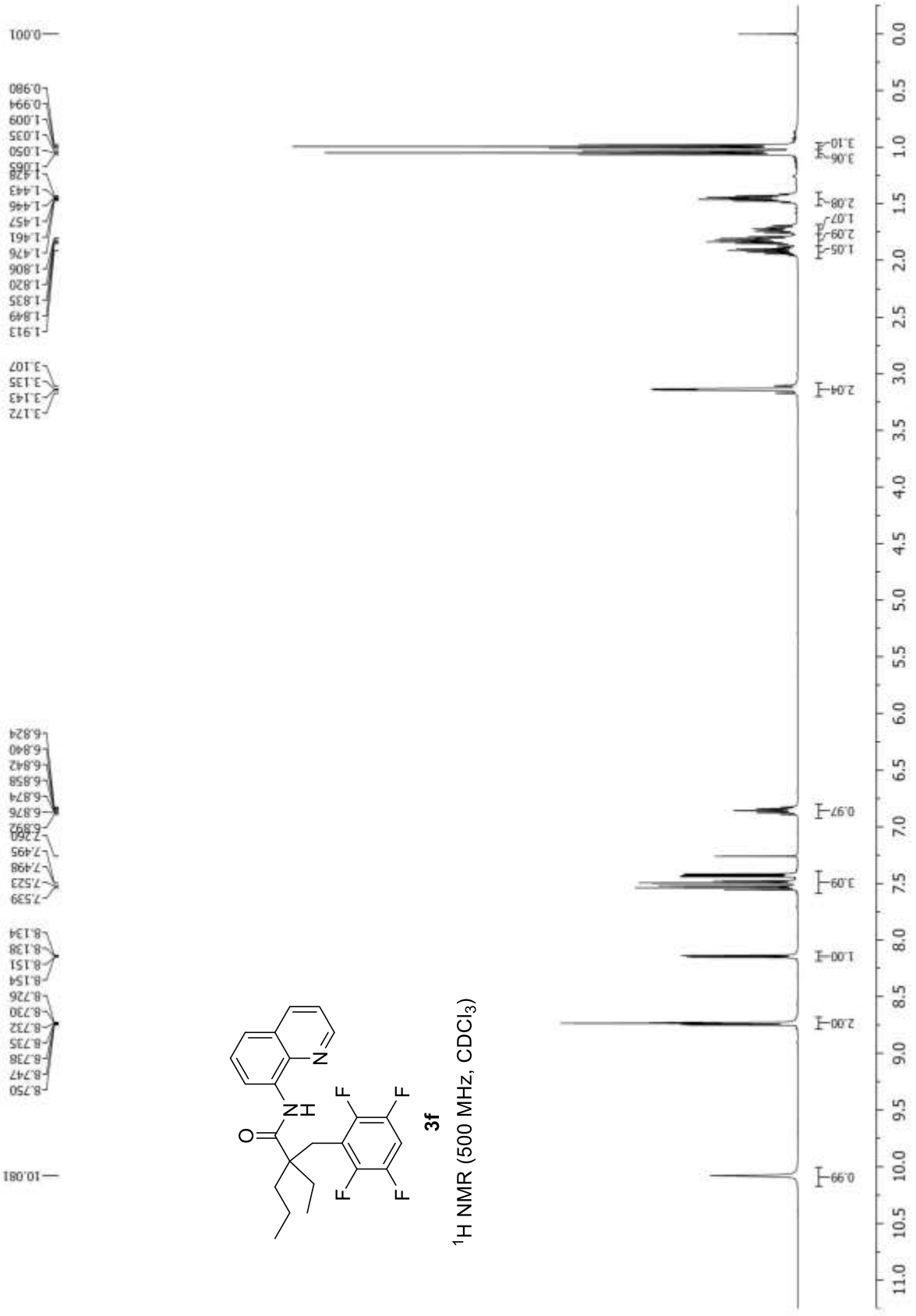
3f
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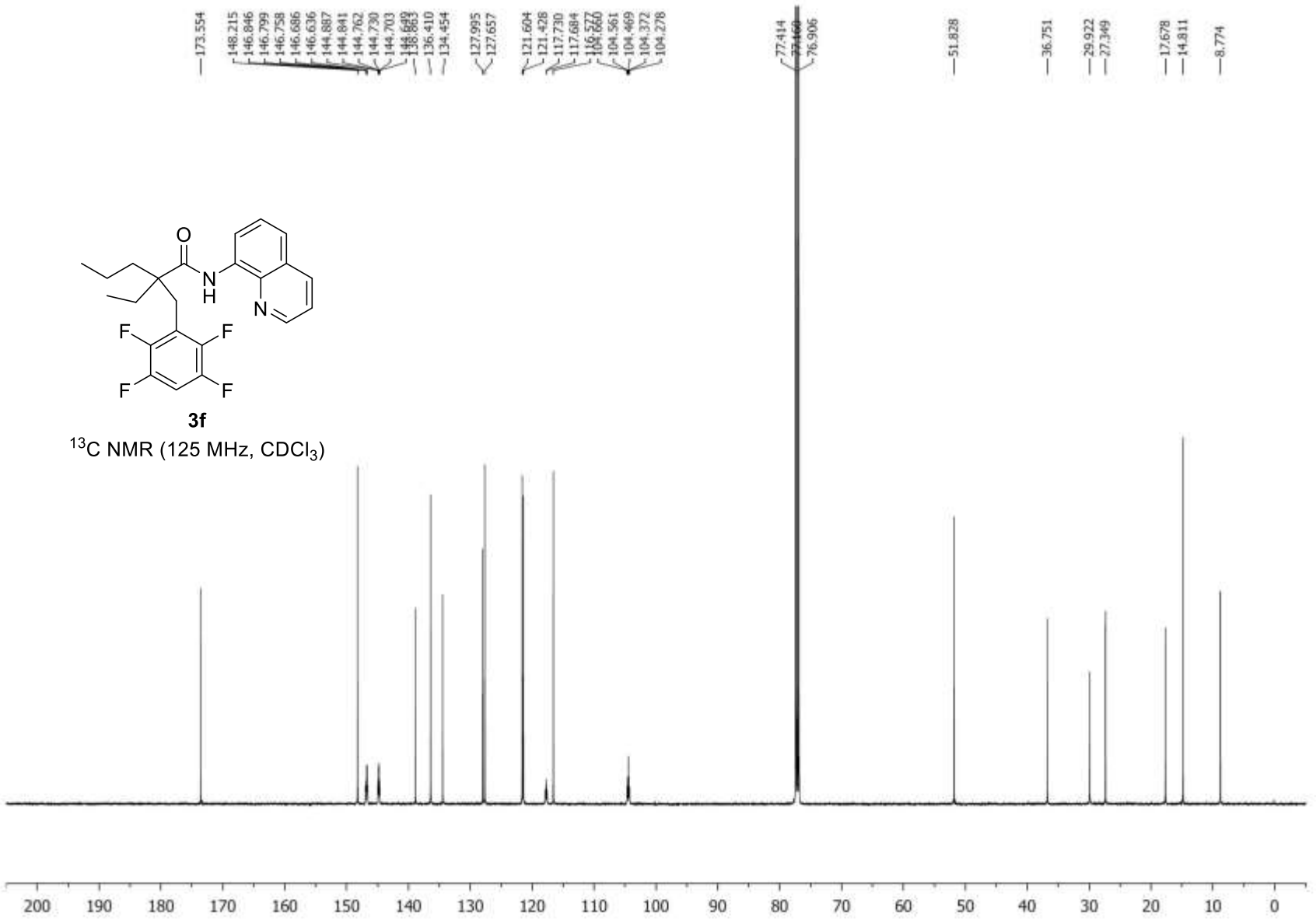

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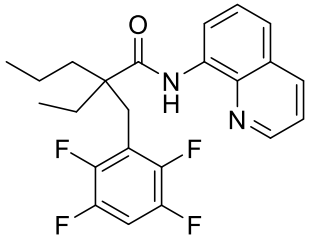

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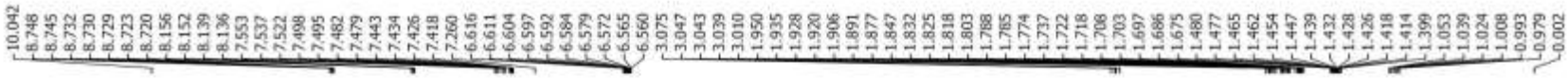

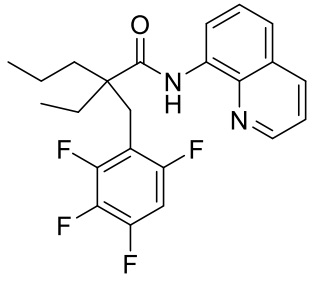

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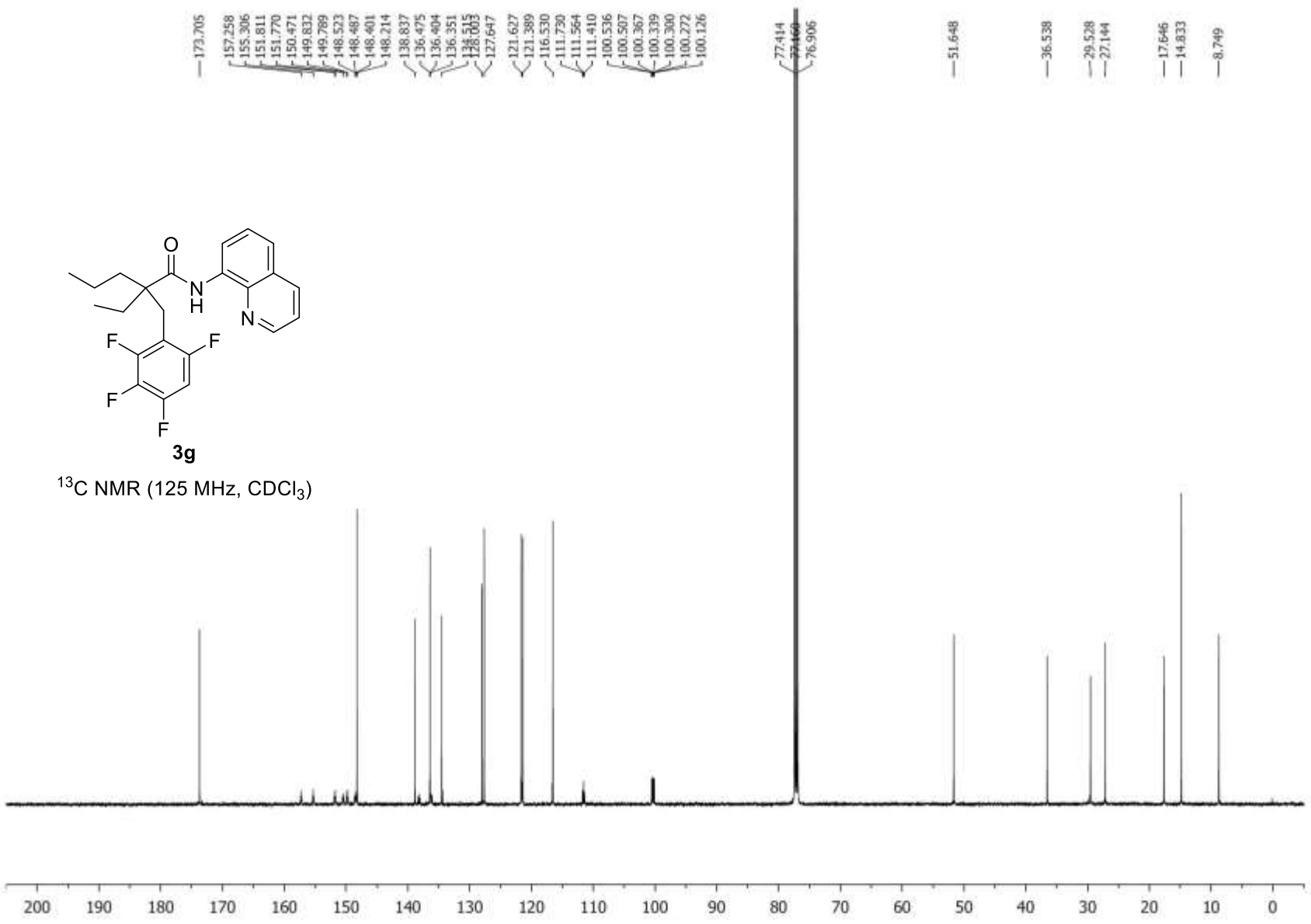

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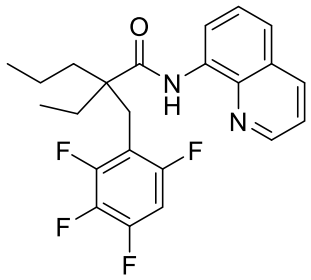

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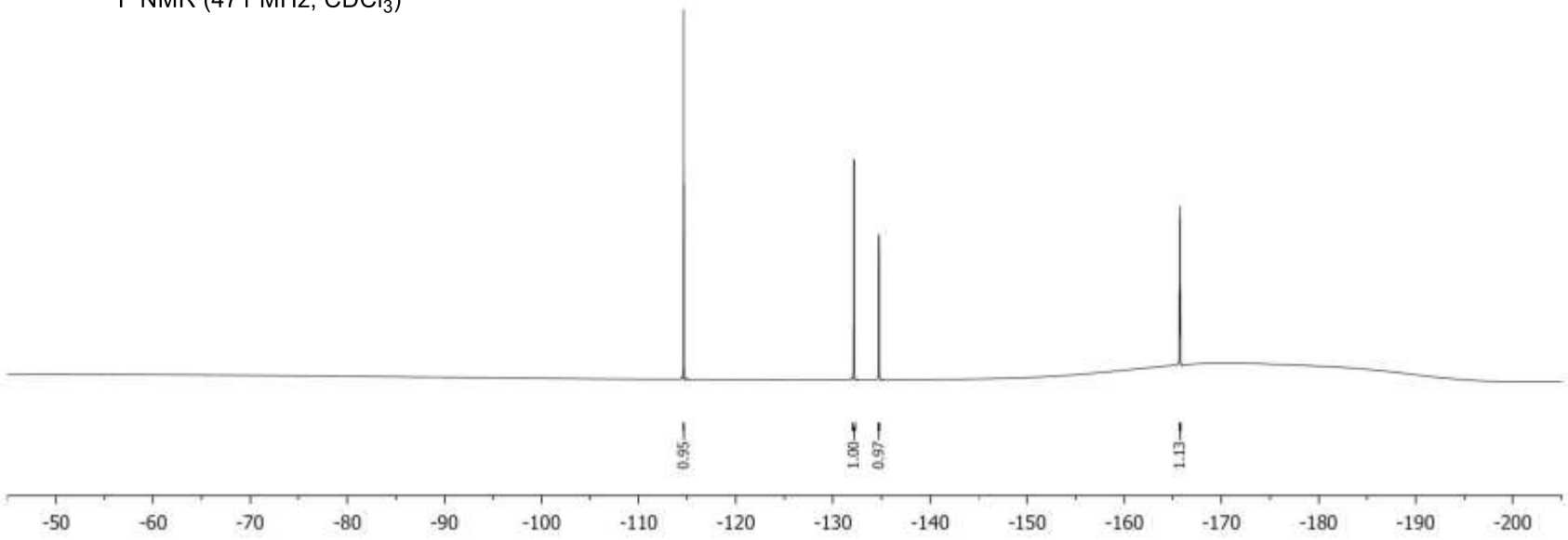

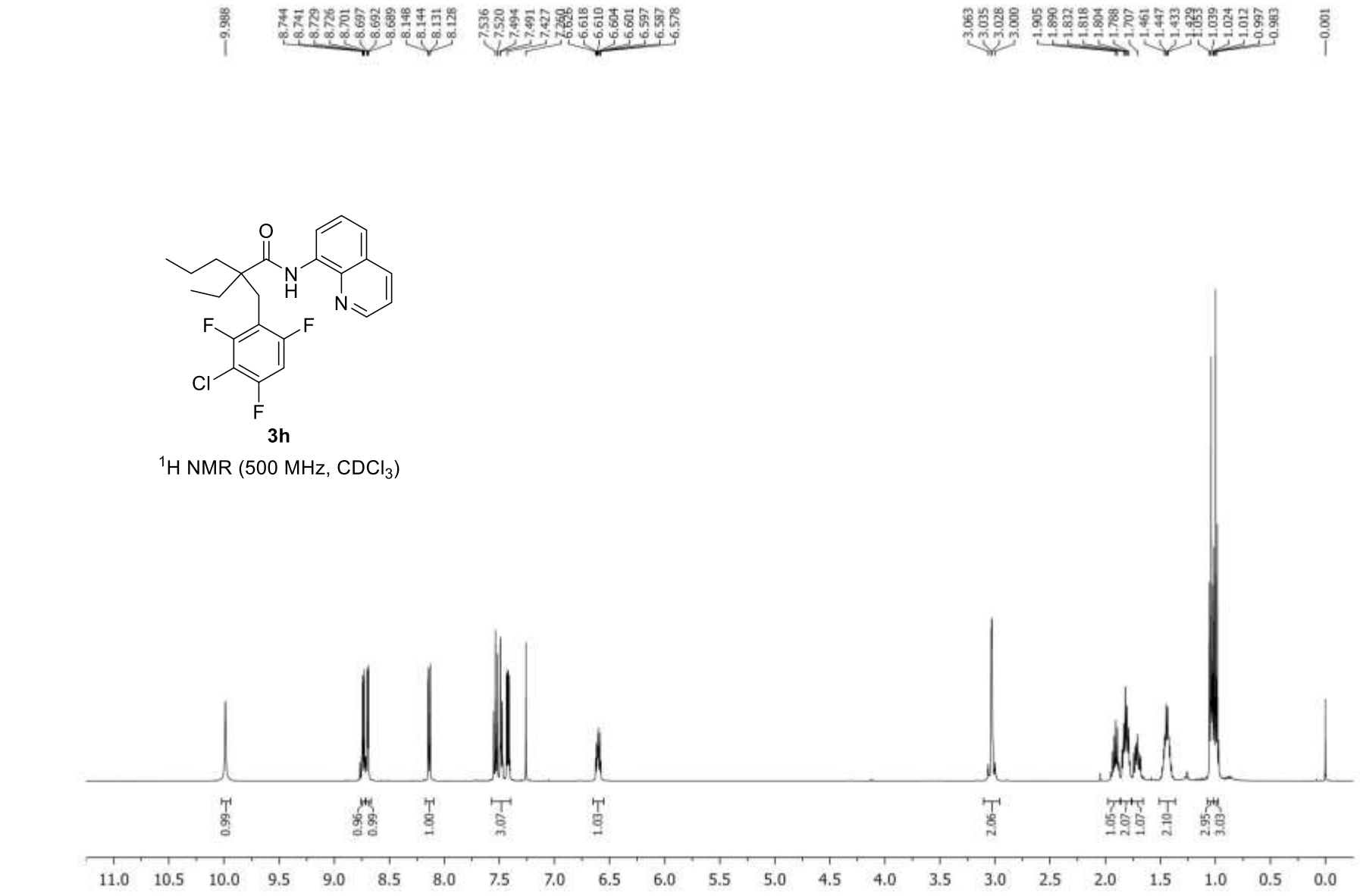

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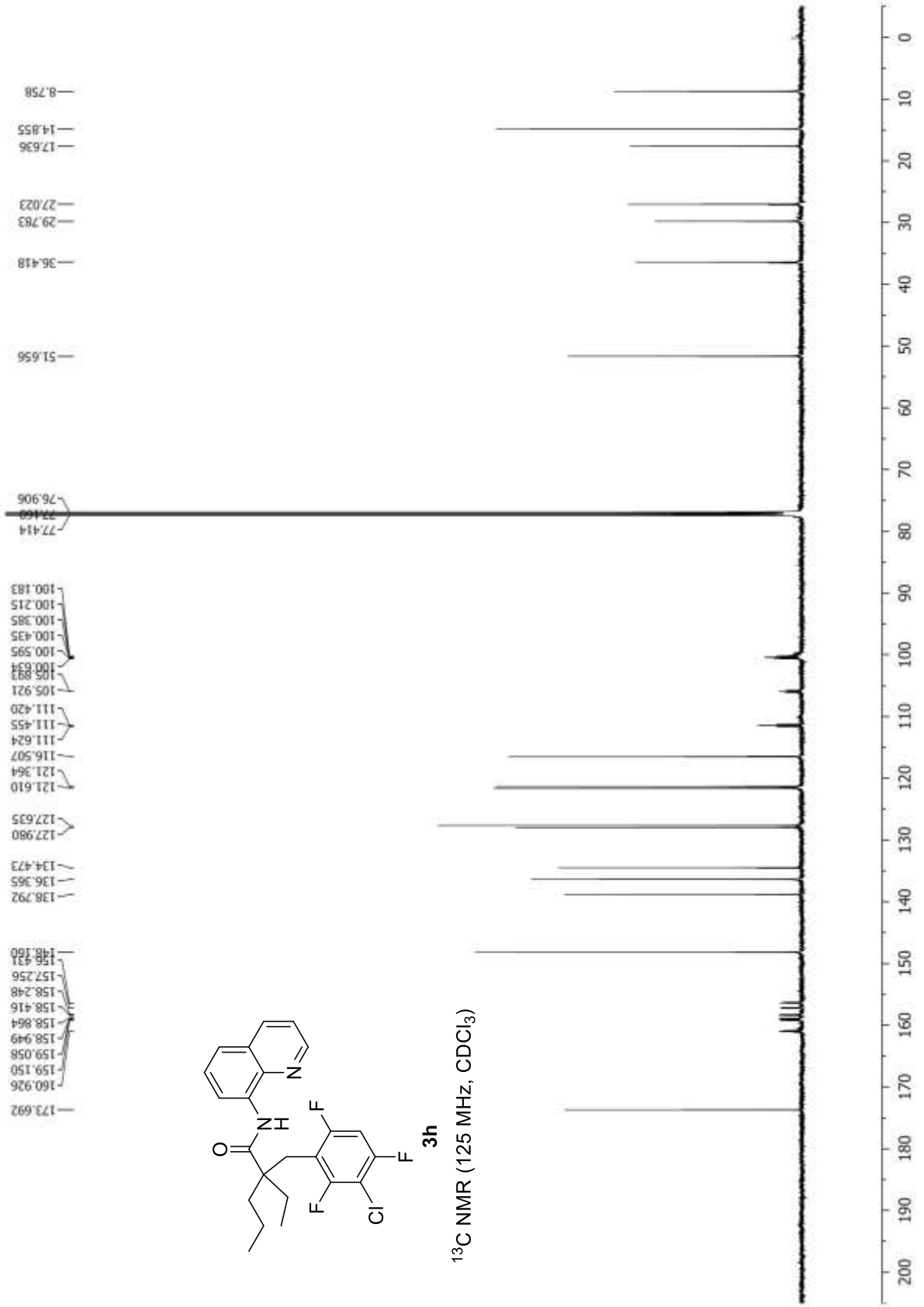
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Cl
N
3h
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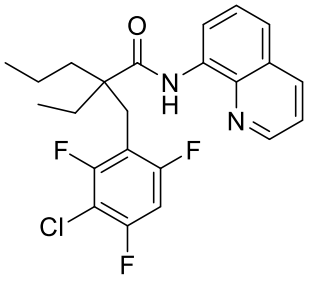

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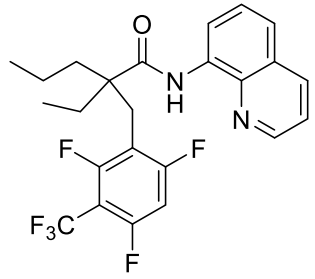
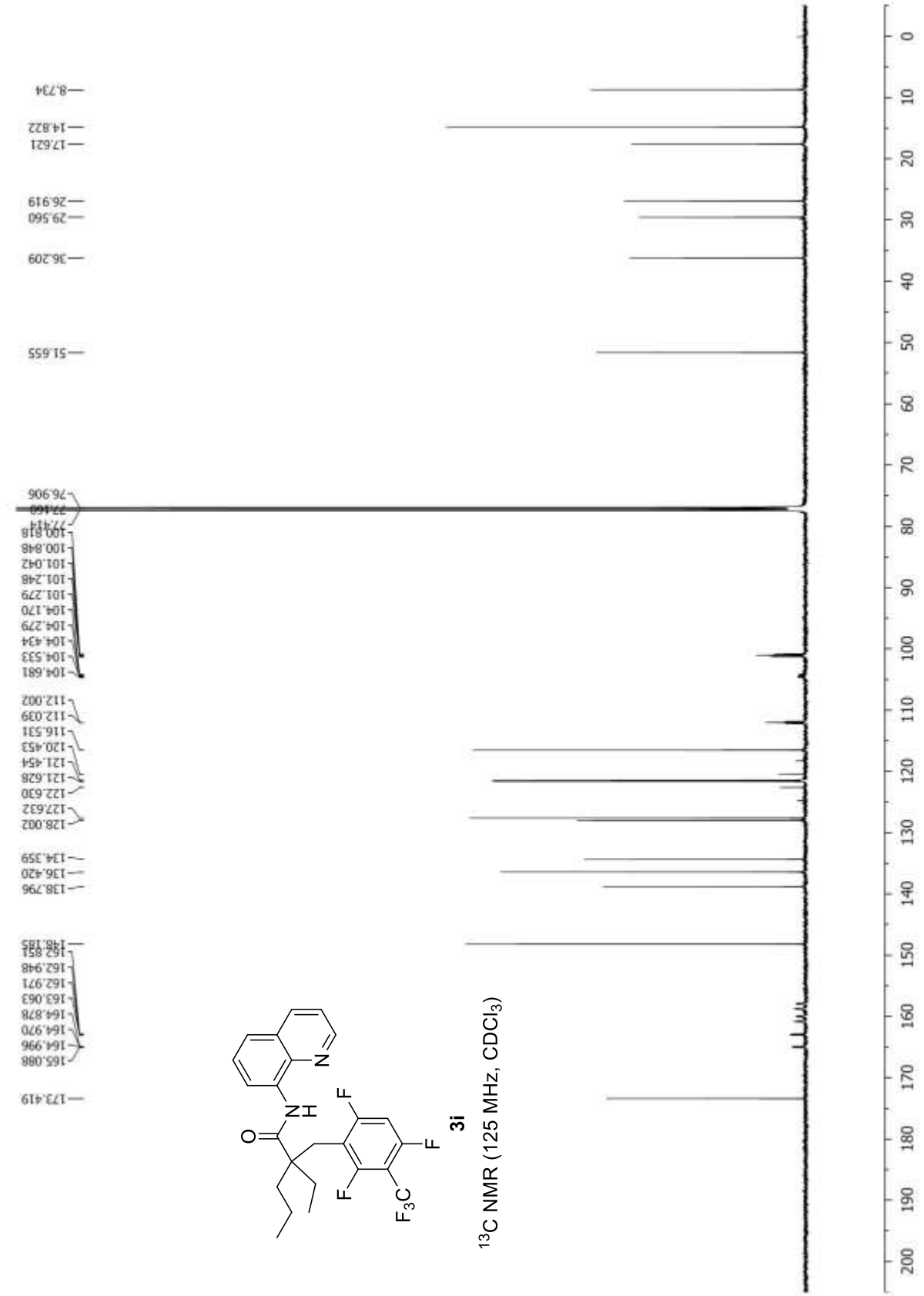


3i

^{1}H NMR (500 MHz, $CDCl_3$)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104.533
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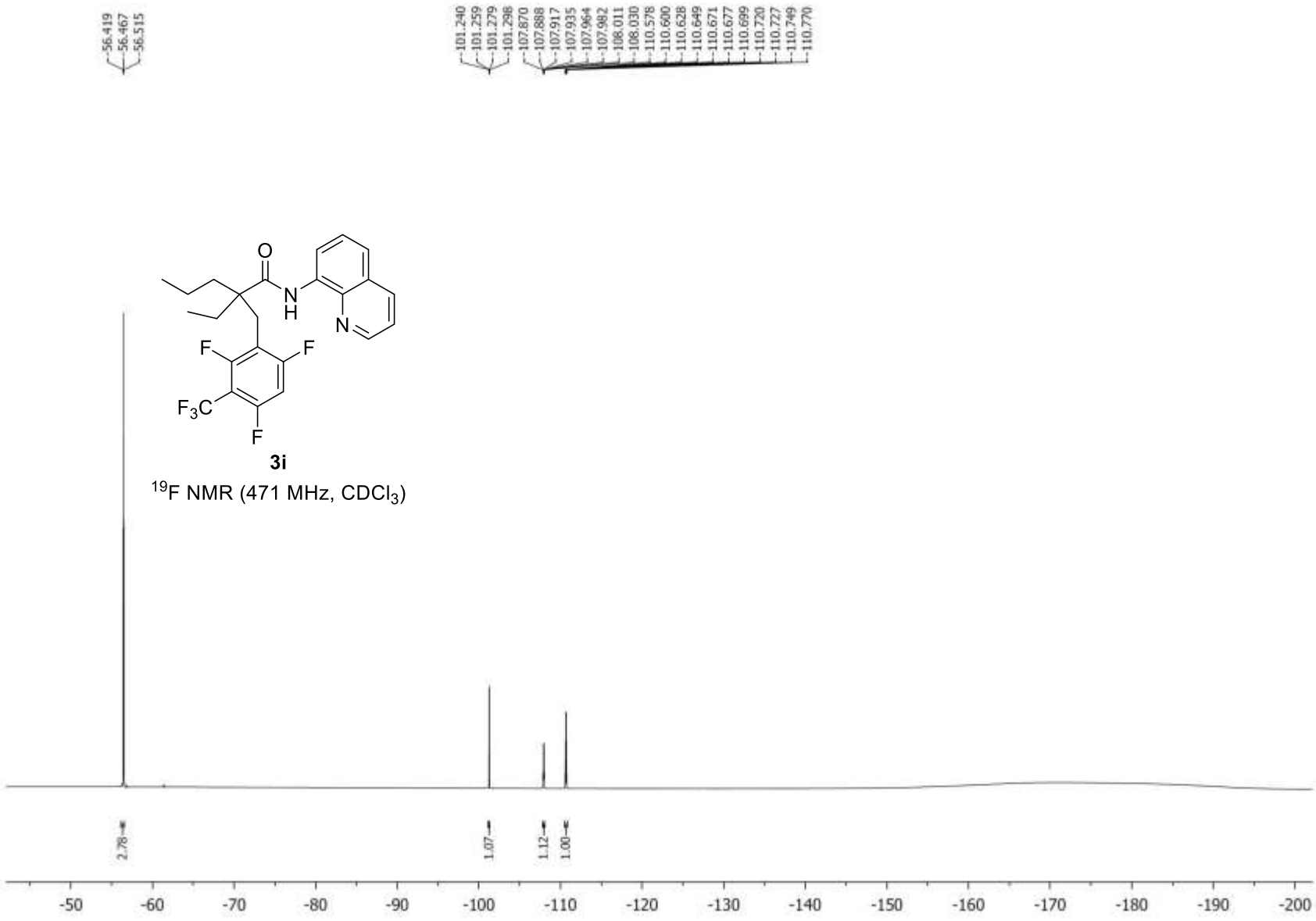
F
F
F3C
3i
13C NMR (125 MHz, CDCl3)



3i

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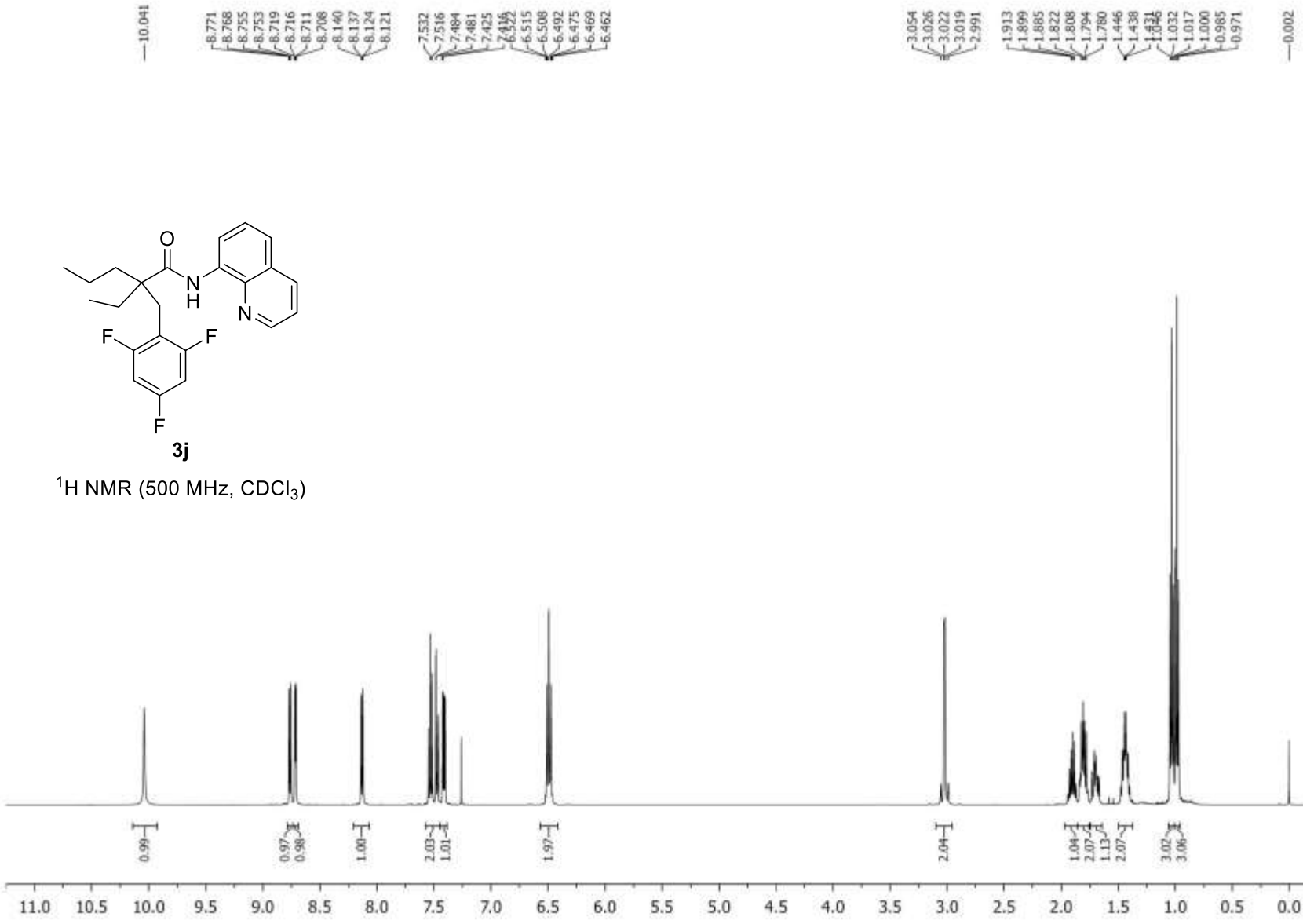
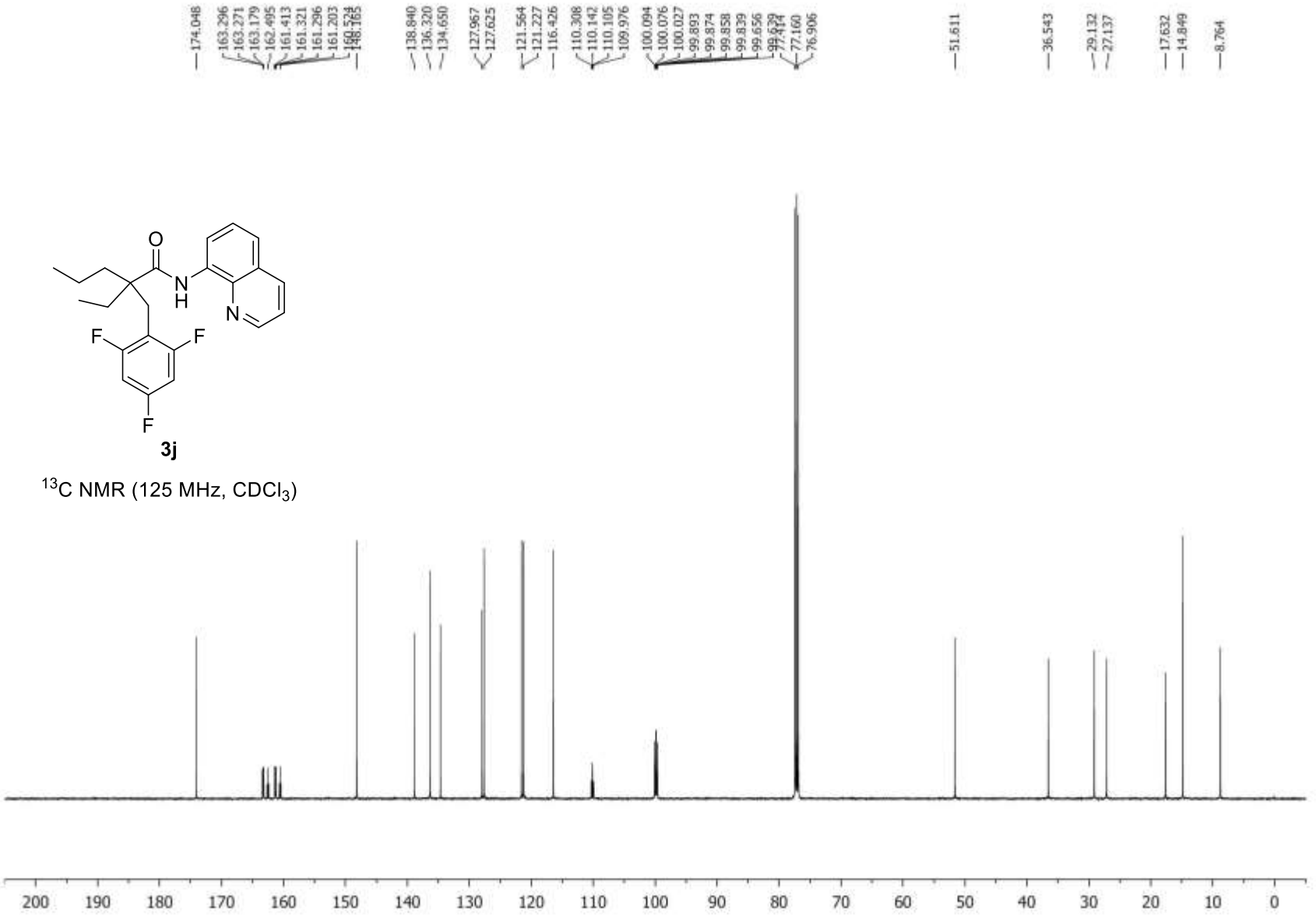


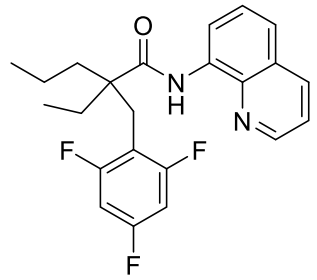
3j

^{1}H NMR (500 MHz, $CDCl_3$)



3j

^{13}C NMR (125 MHz, $CDCl_3$)



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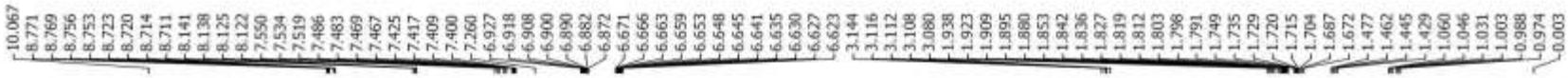
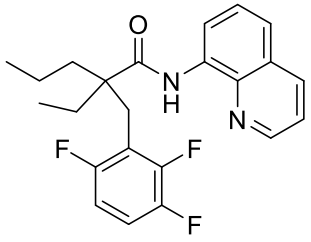
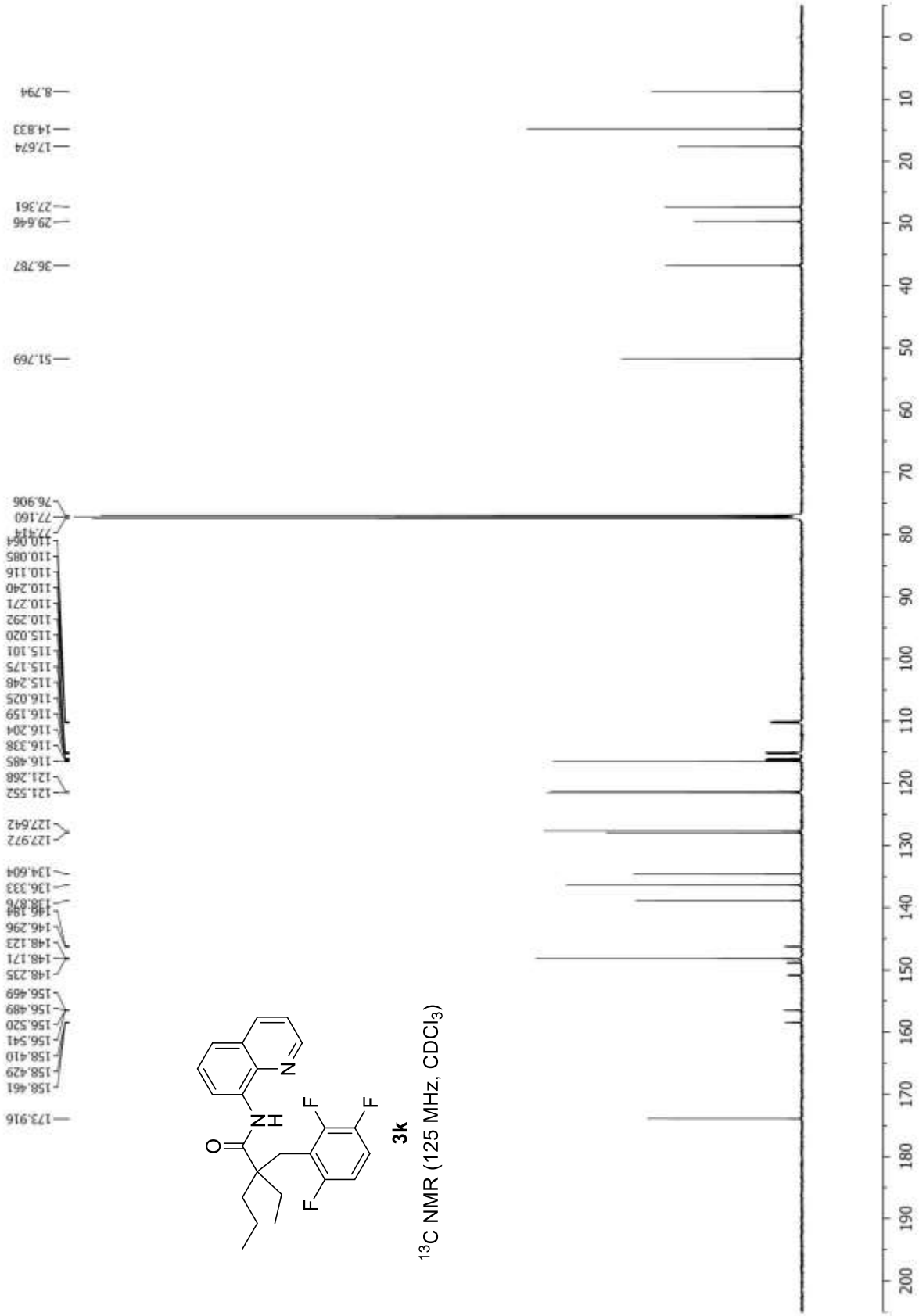
^{19}F NMR (471 MHz, $CDCl_3$)

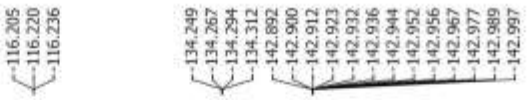


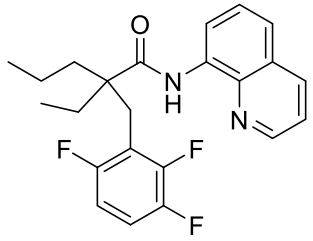


3k

^{1}H NMR (500 MHz, $CDCl_3$)

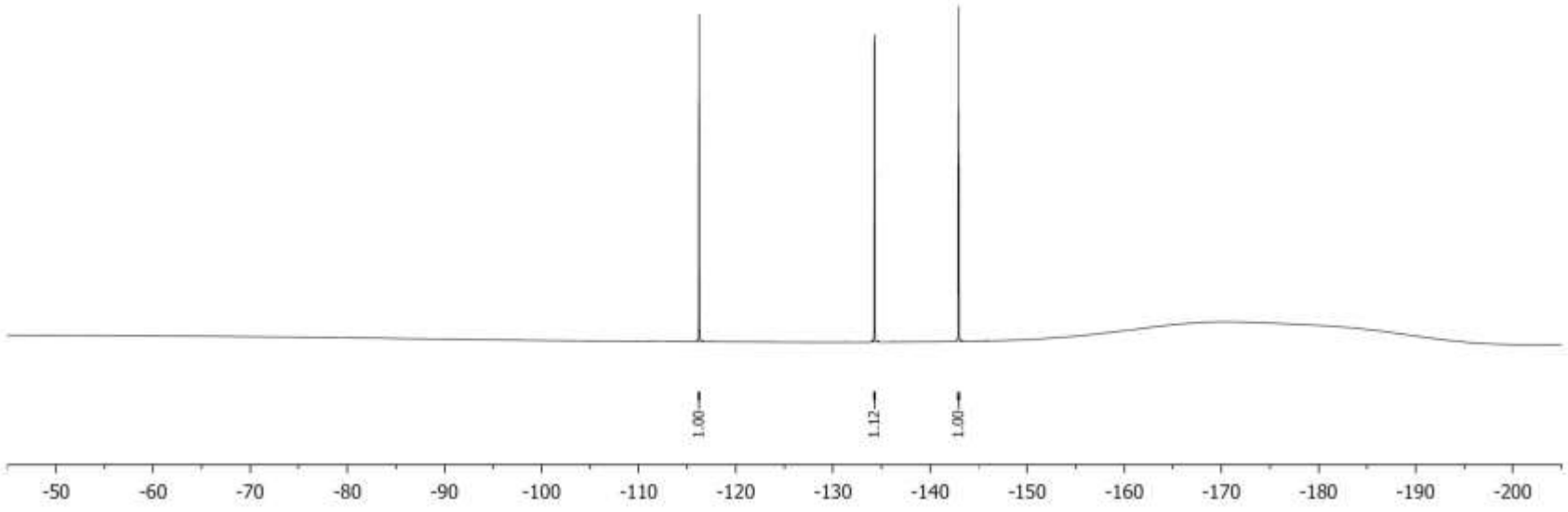

8.794
14.833
17.674
27.361
29.646
36.787
51.769
76.906
77.160
110.064
110.085
110.116
110.240
110.271
110.292
115.020
115.101
115.175
115.248
116.025
116.159
116.204
116.338
116.485
121.268
121.552
127.642
127.972
134.604
136.333
138.876
146.194
146.296
148.123
148.171
148.235
156.469
156.489
156.520
156.541
158.410
158.429
158.461
173.916
O
N
H
F
F
N
3k
^{13}C NMR (125 MHz, $CDCl_3$)

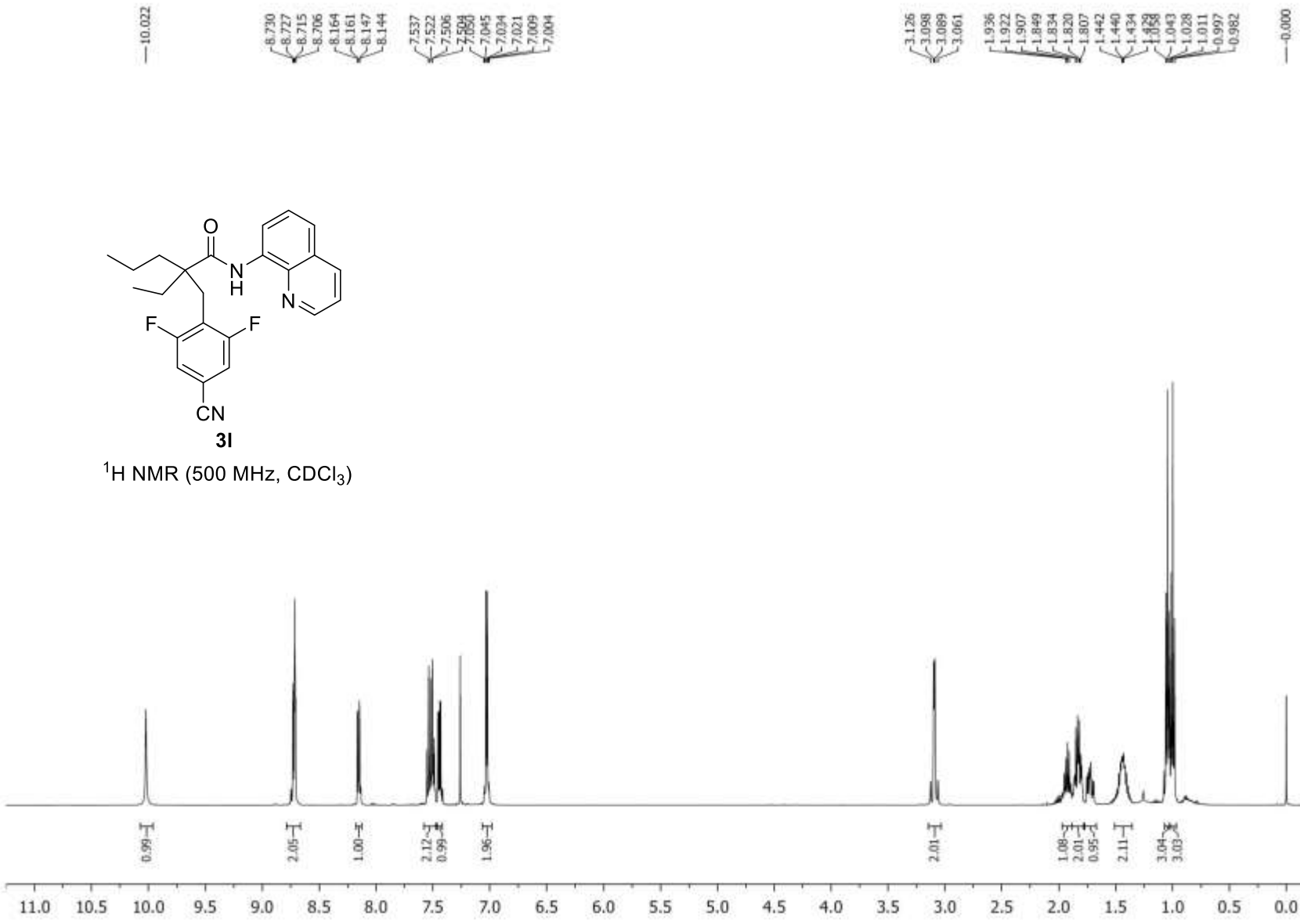




3k

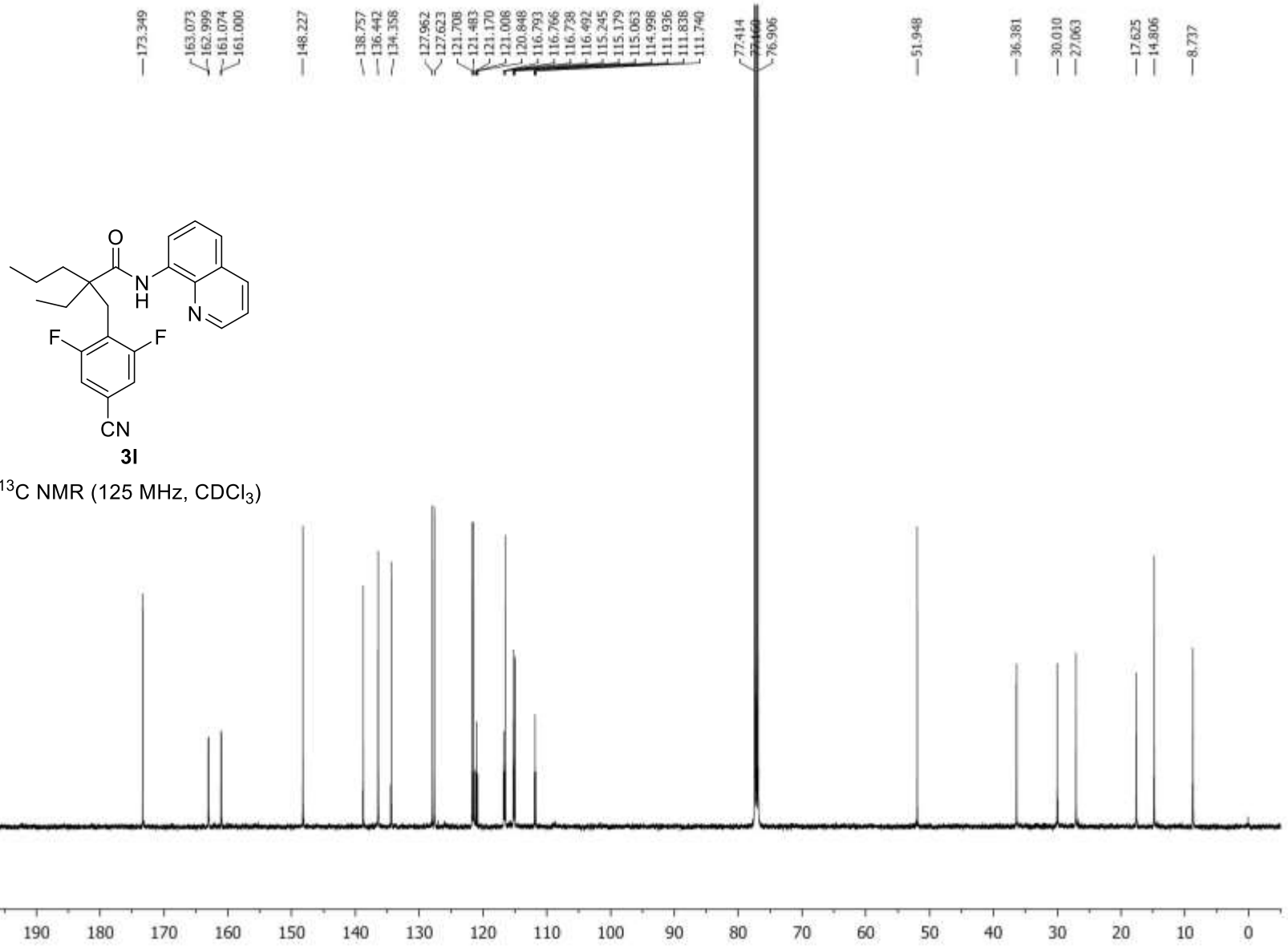
^{19}F NMR (471 MHz, $CDCl_3$)





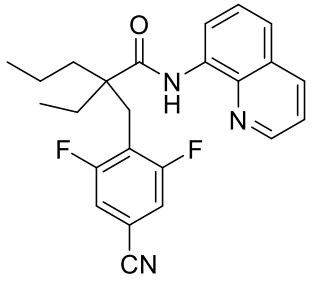
3l

^{1}H NMR (500 MHz, $CDCl_3$)



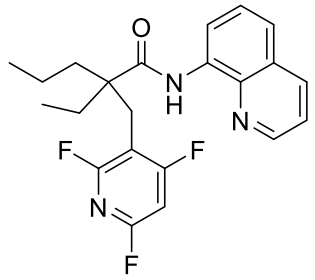
3l

^{13}C NMR (125 MHz, $CDCl_3$)



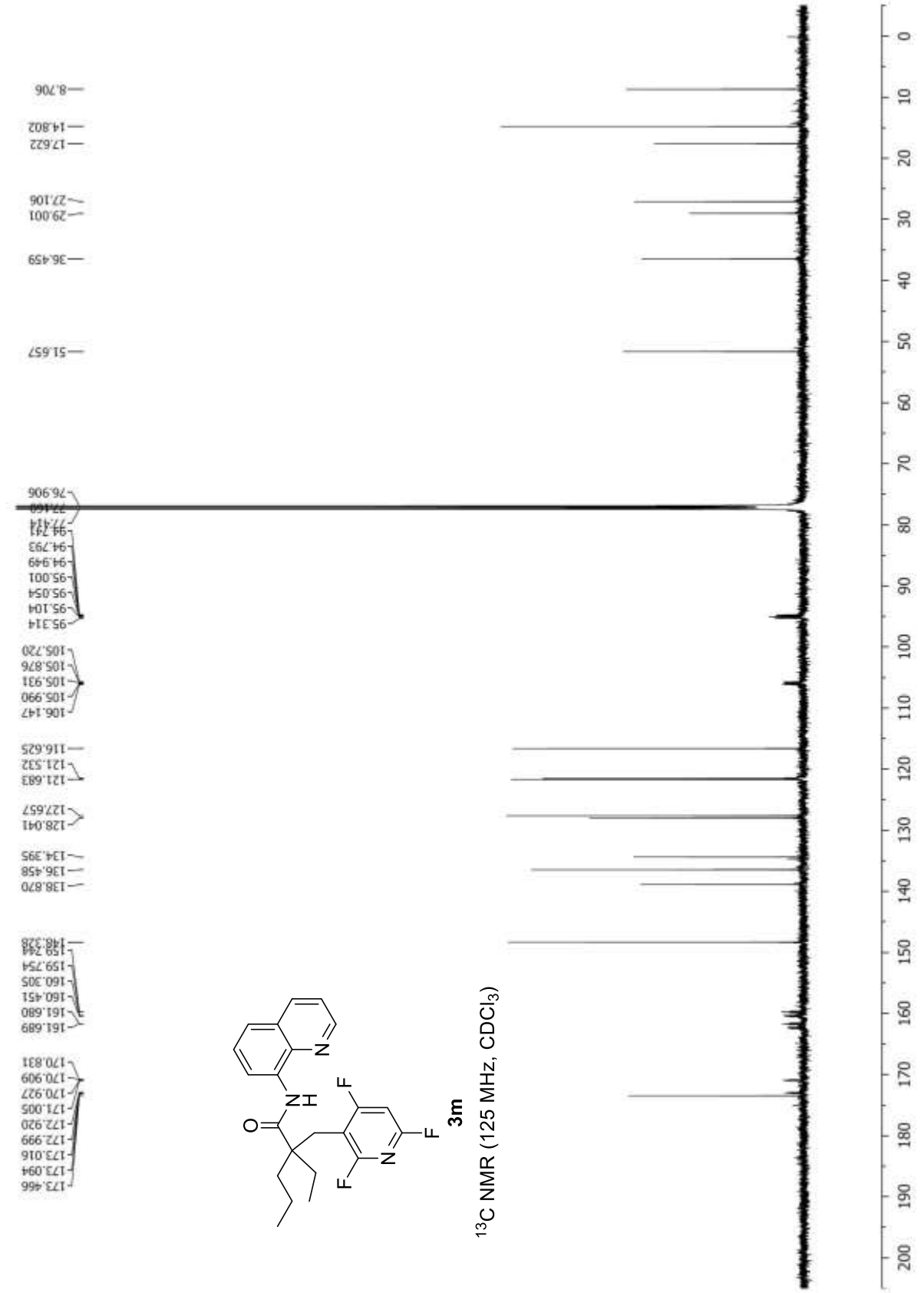
3l

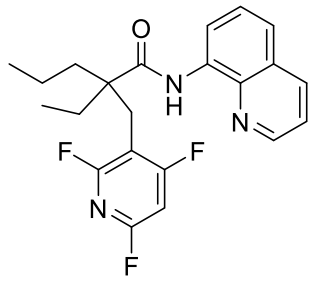
^{19}F NMR (471 MHz, $CDCl_3$)



3m

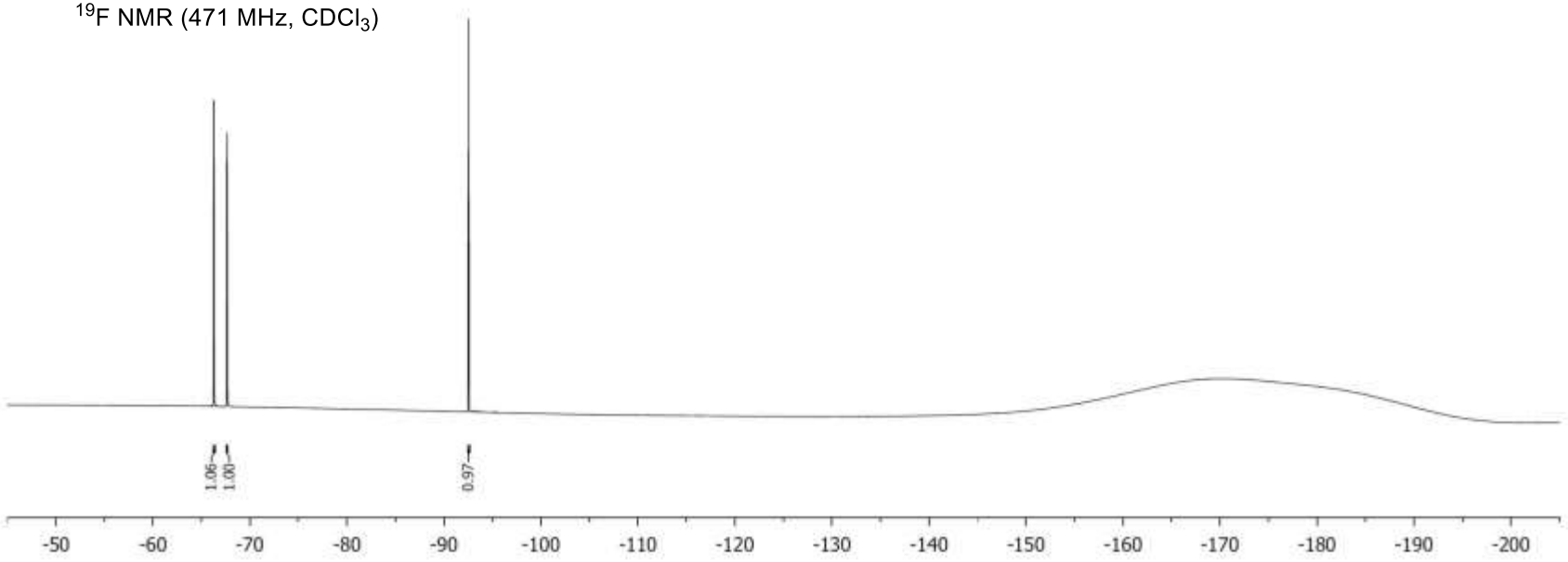
^{1}H NMR (500 MHz, $CDCl_3$)

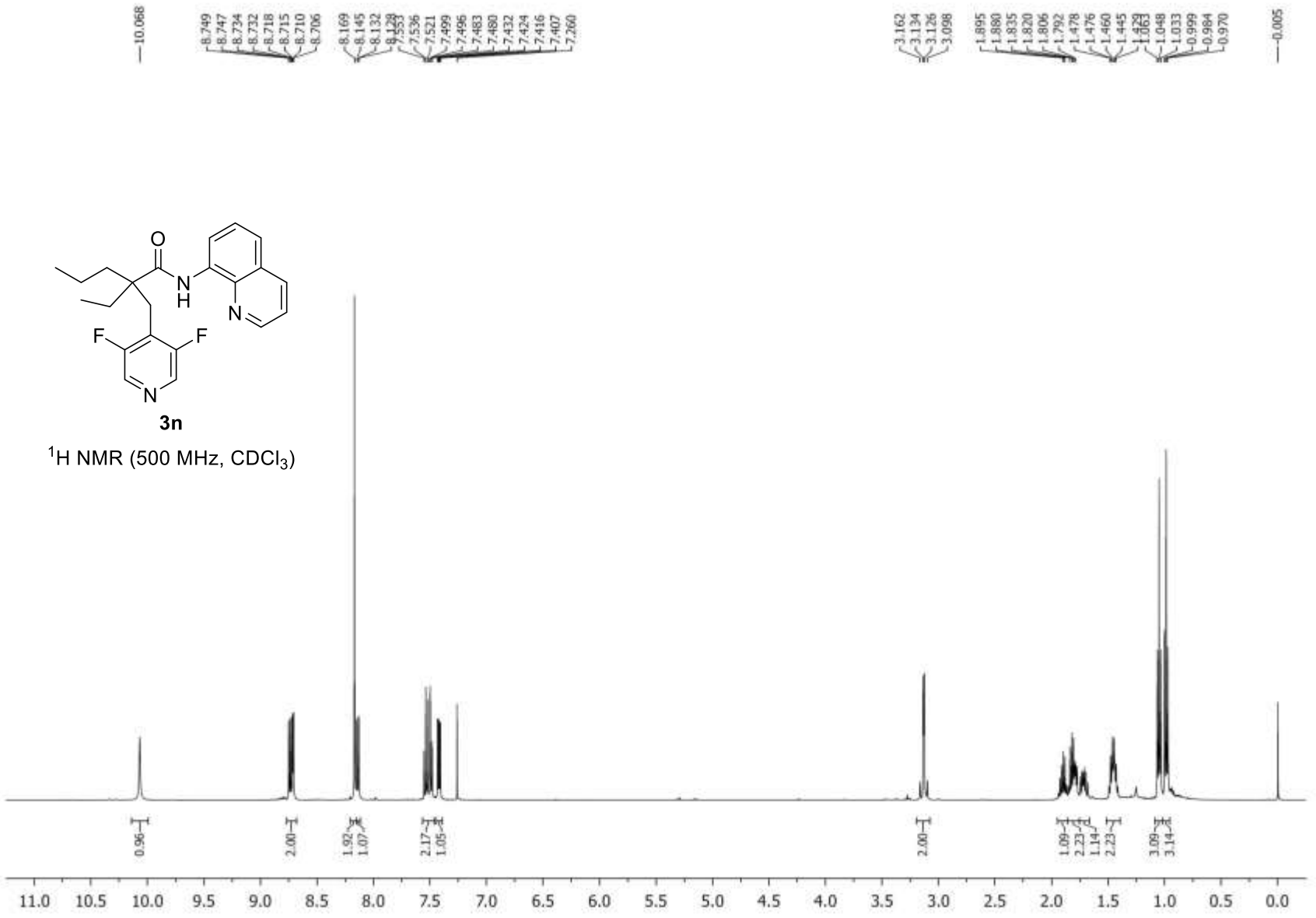

3m
^{13}C NMR (125 MHz, CDCl$_3$)



3m

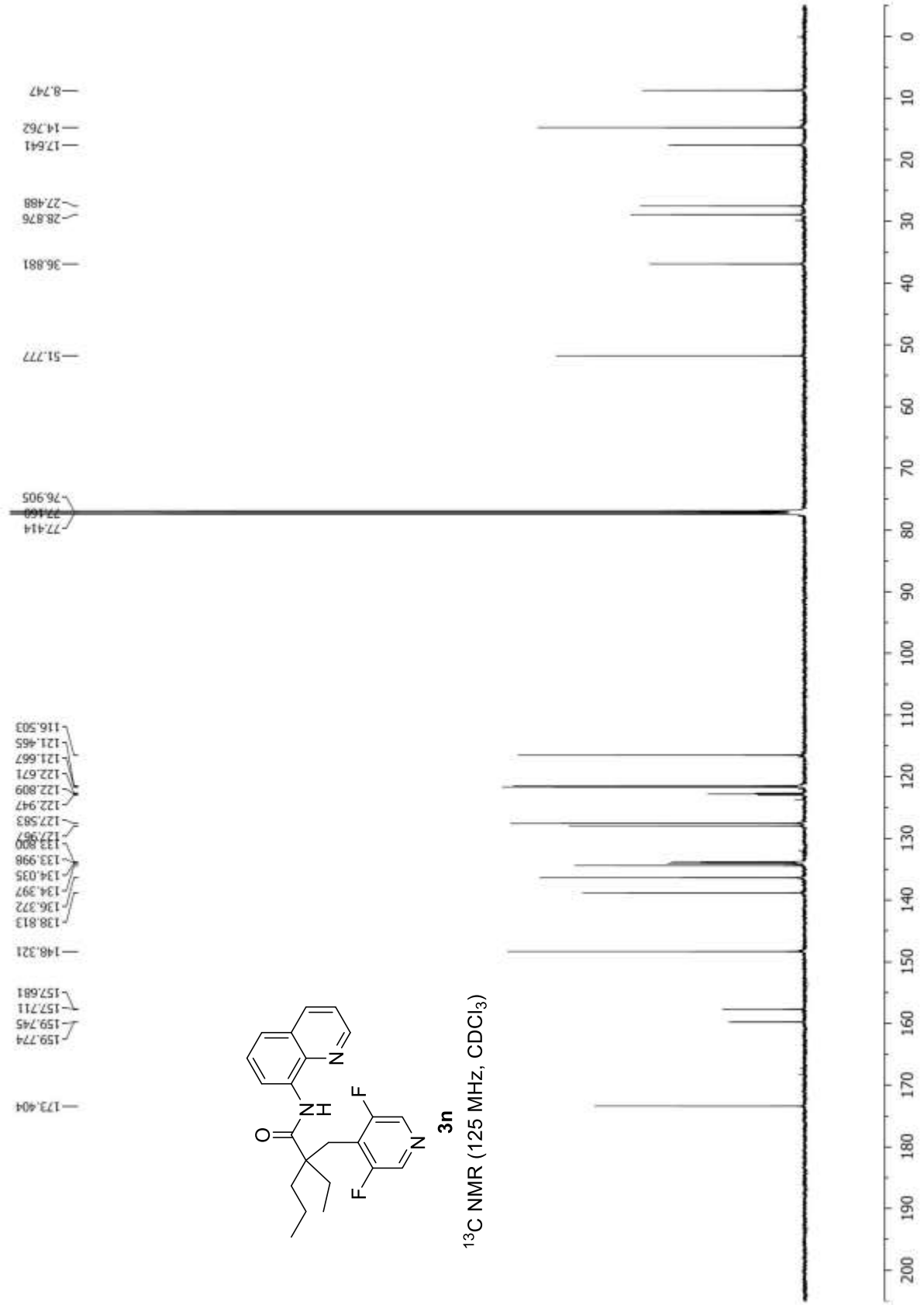
^{19}F NMR (471 MHz, $CDCl_3$)

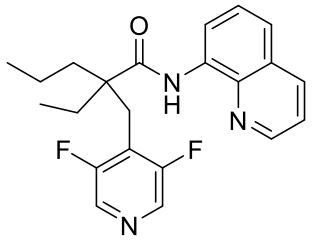




3n

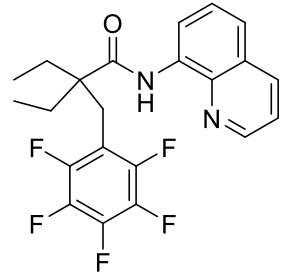
^{1}H NMR (500 MHz, $CDCl_3$)


8.747
14.762
17.641
27.488
28.876
36.881
51.777
76.905
77.160
77.414
116.503
121.465
121.667
122.671
122.809
122.947
127.583
127.967
133.800
133.998
134.035
134.397
136.372
138.813
148.321
157.681
157.711
159.745
159.774
173.404
O
NH
N
F
F
N
3n
^{13}C NMR (125 MHz, $CDCl_3$)



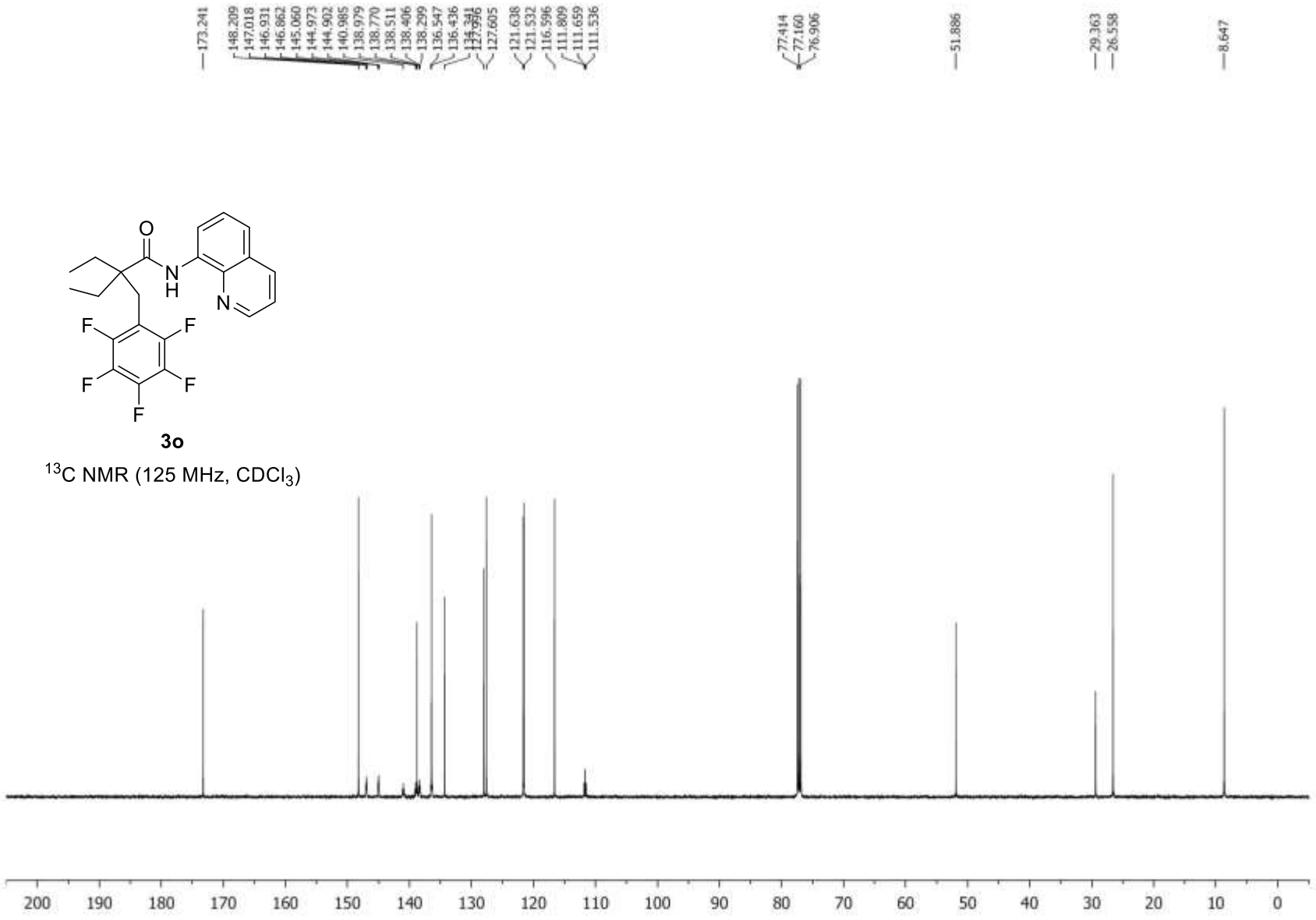
3n

^{19}F NMR (471 MHz, $CDCl_3$)



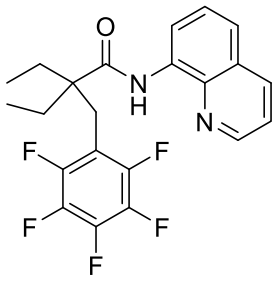
3o

^{1}H NMR (500 MHz, $CDCl_3$)



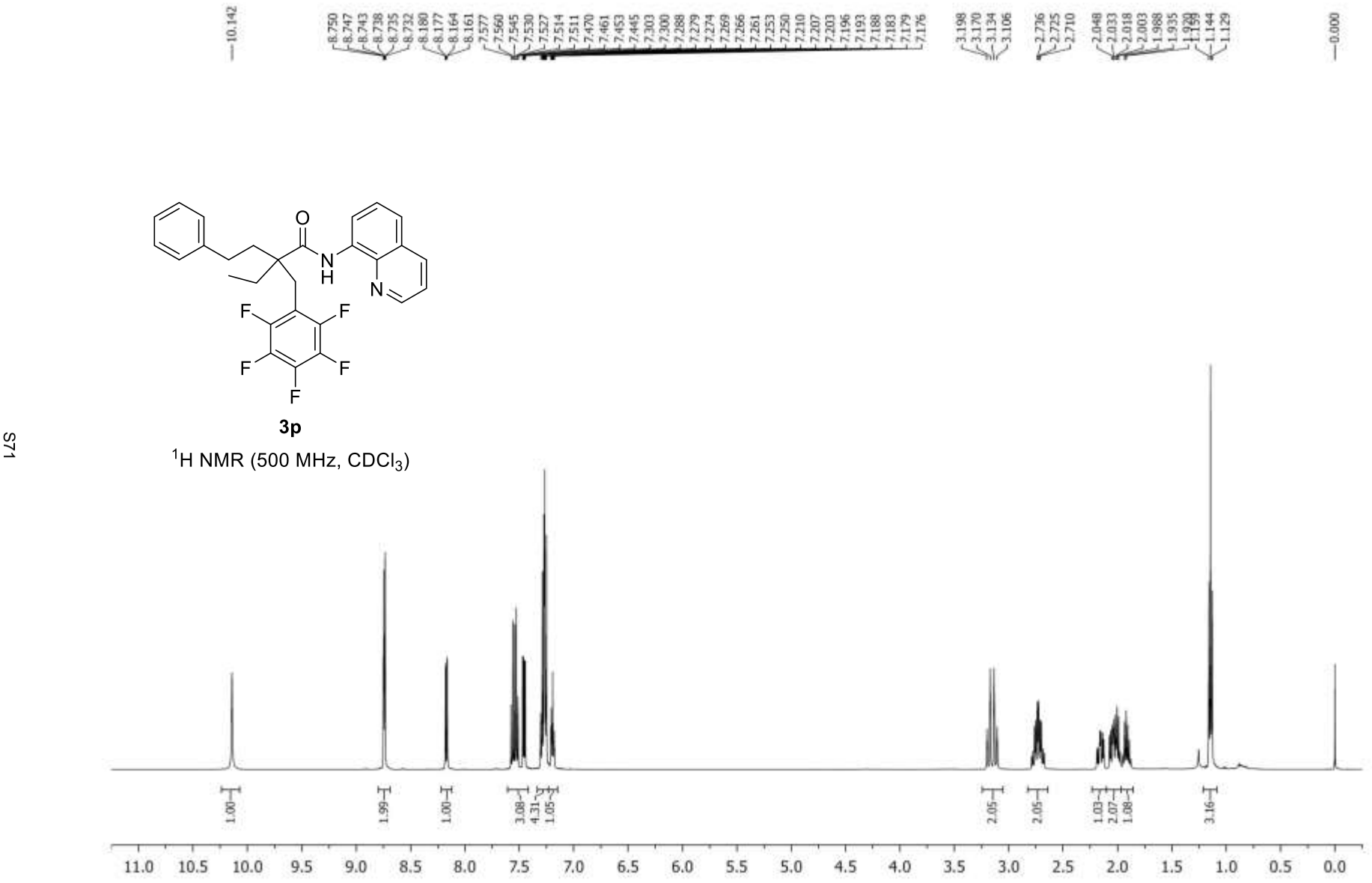
3o

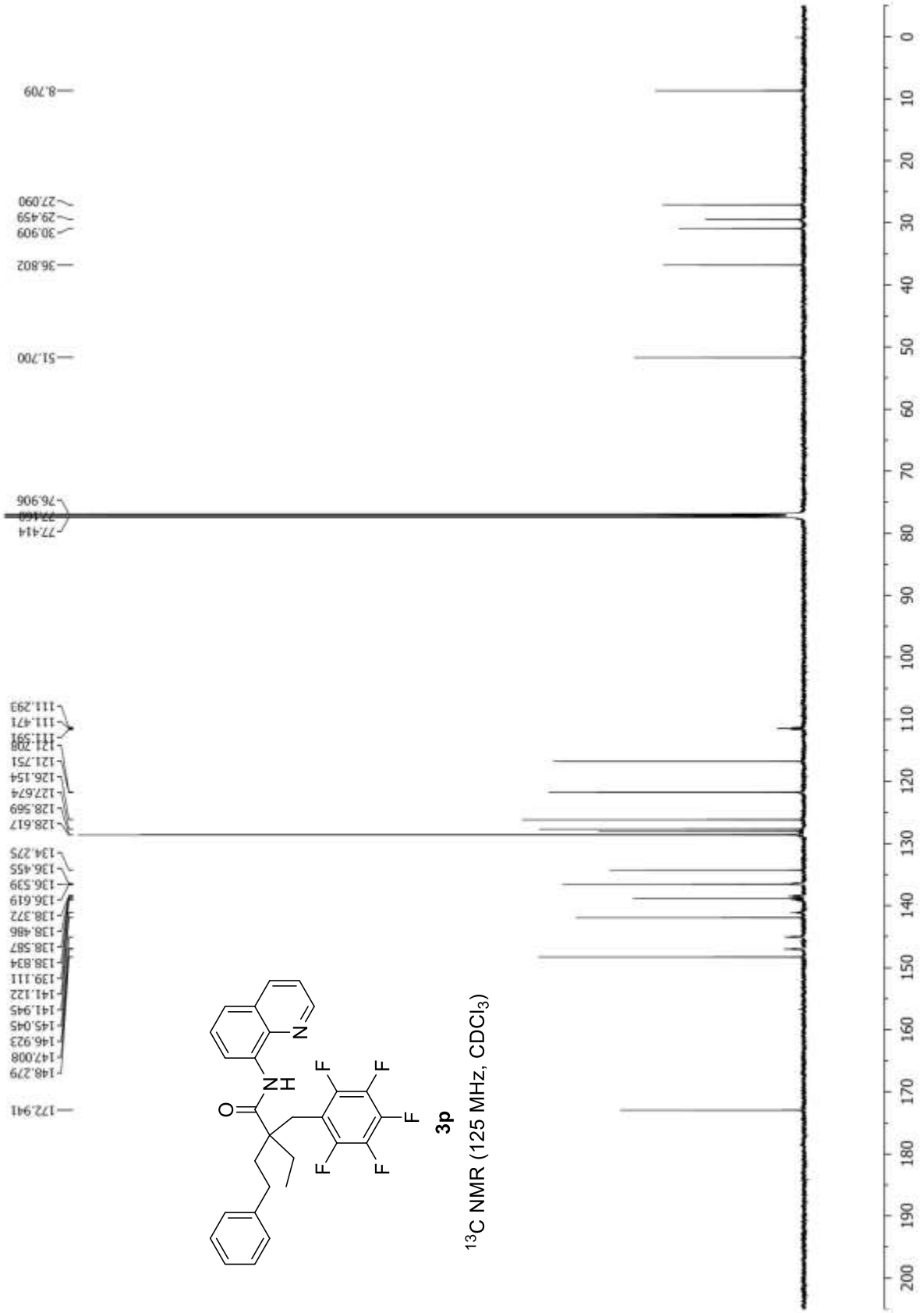
^{13}C NMR (125 MHz, $CDCl_3$)



3o

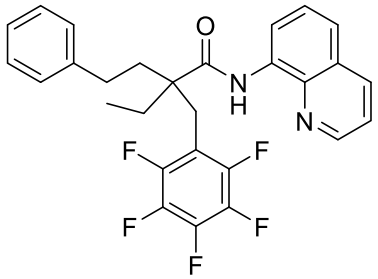
^{19}F NMR (471 MHz, $CDCl_3$)


10.142
8.750
8.747
8.743
8.738
8.735
8.732
8.180
8.177
8.164
8.161
7.577
7.560
7.545
7.530
7.527
7.514
7.511
7.470
7.461
7.453
7.445
7.303
7.300
7.288
7.279
7.274
7.269
7.266
7.261
7.253
7.250
7.210
7.207
7.203
7.196
7.193
7.188
7.183
7.179
7.176
3.198
3.170
3.134
3.106
2.736
2.725
2.710
2.048
2.033
2.018
2.003
1.988
1.935
1.144
1.129
0.000
O
N
H
N
F
F
F
F
F
3p
1H NMR (500 MHz, CDCl3)
1.00
1.99
1.00
3.08
4.31
1.05
2.05
2.05
1.03
2.07
1.08
3.16
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



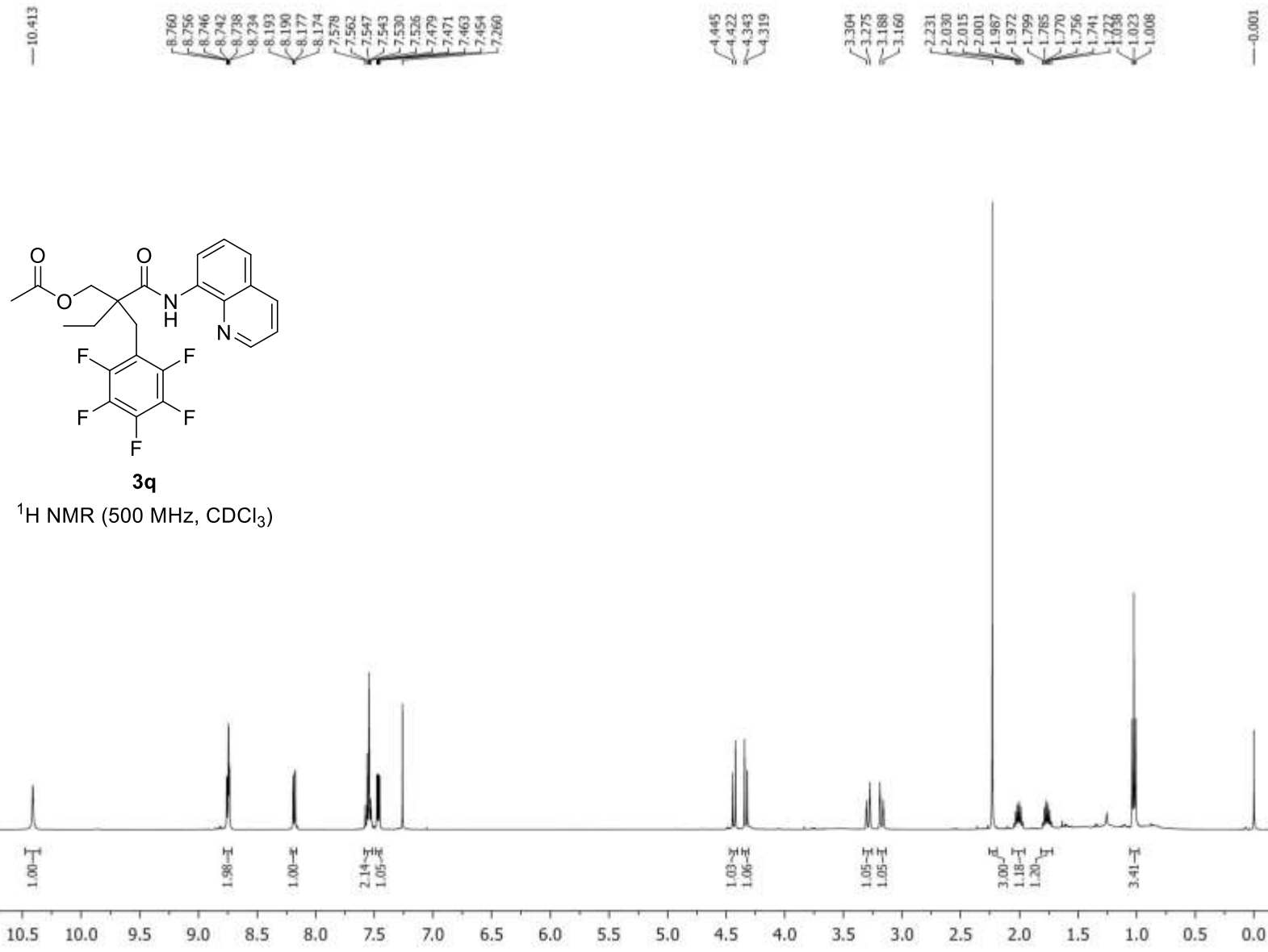
3p

^{13}C NMR (125 MHz, $CDCl_3$)



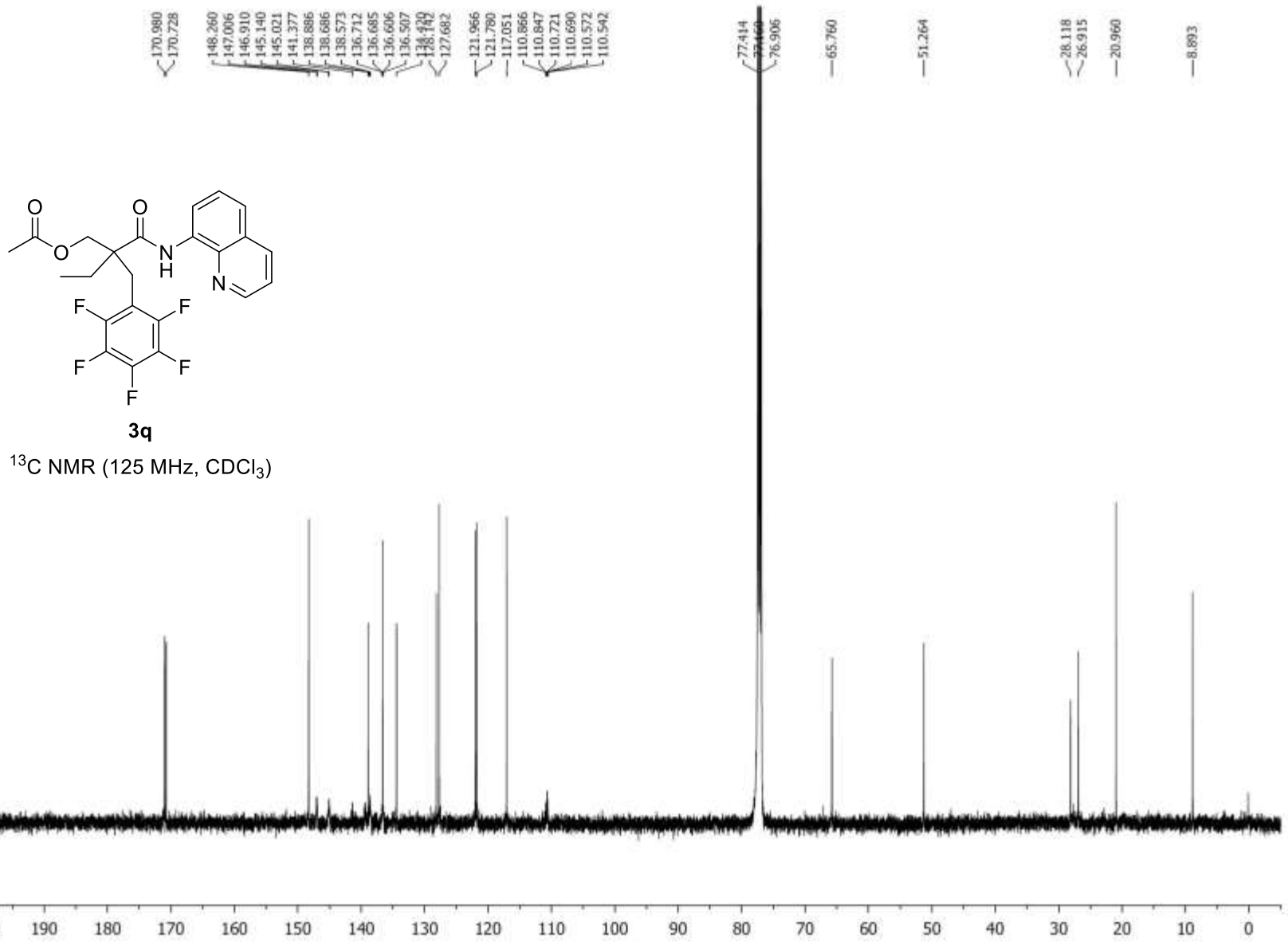
3p

^{19}F NMR (471 MHz, $CDCl_3$)



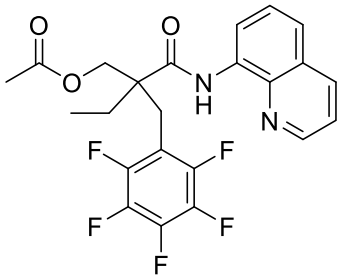
3q

^{1}H NMR (500 MHz, $CDCl_3$)



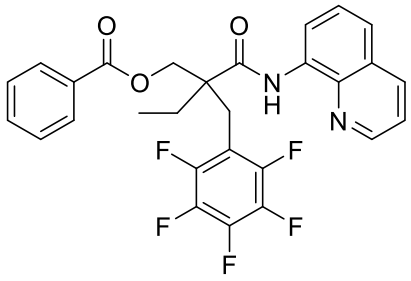
3q

^{13}C NMR (125 MHz, $CDCl_3$)



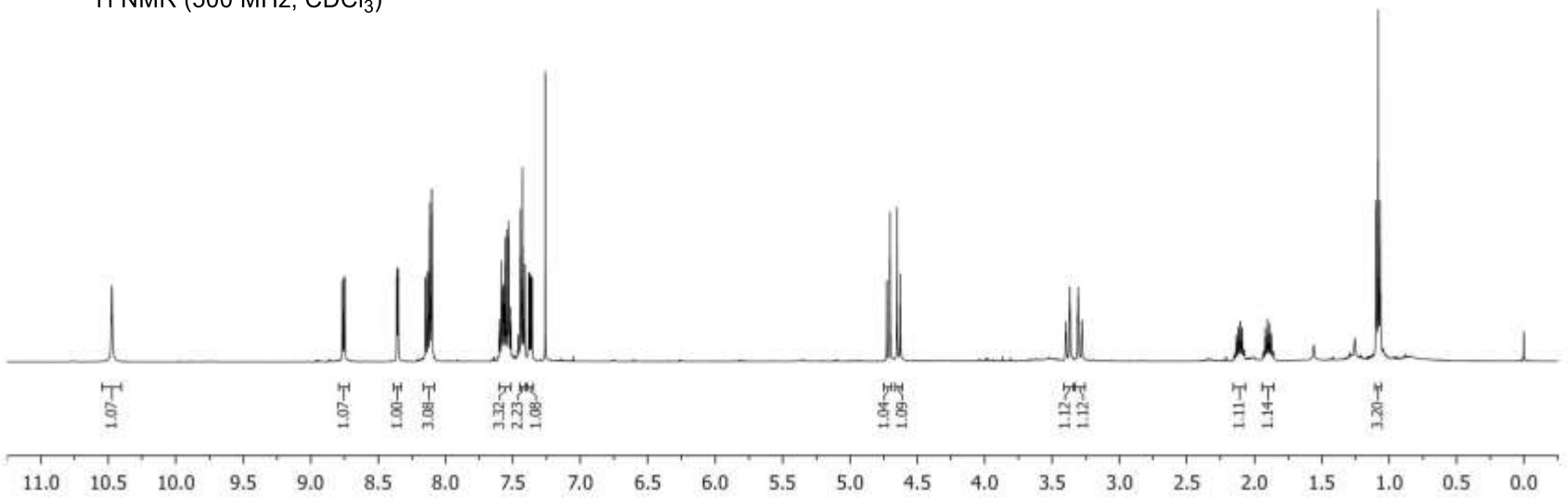
3q

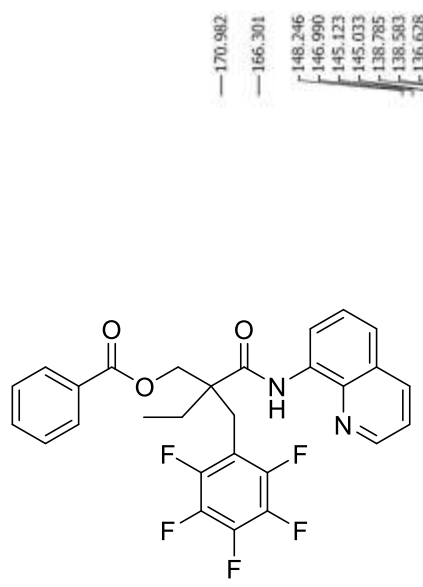
^{19}F NMR (471 MHz, $CDCl_3$)



3r

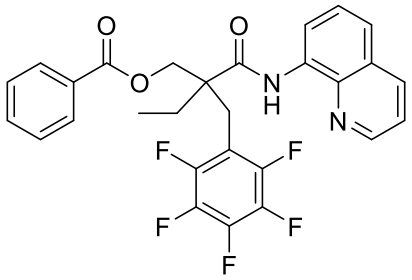
^{1}H NMR (500 MHz, $CDCl_3$)





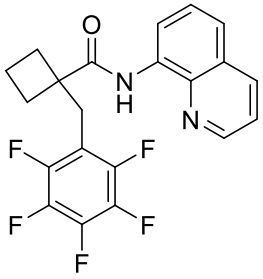
3r

^{13}C NMR (125 MHz, $CDCl_3$)



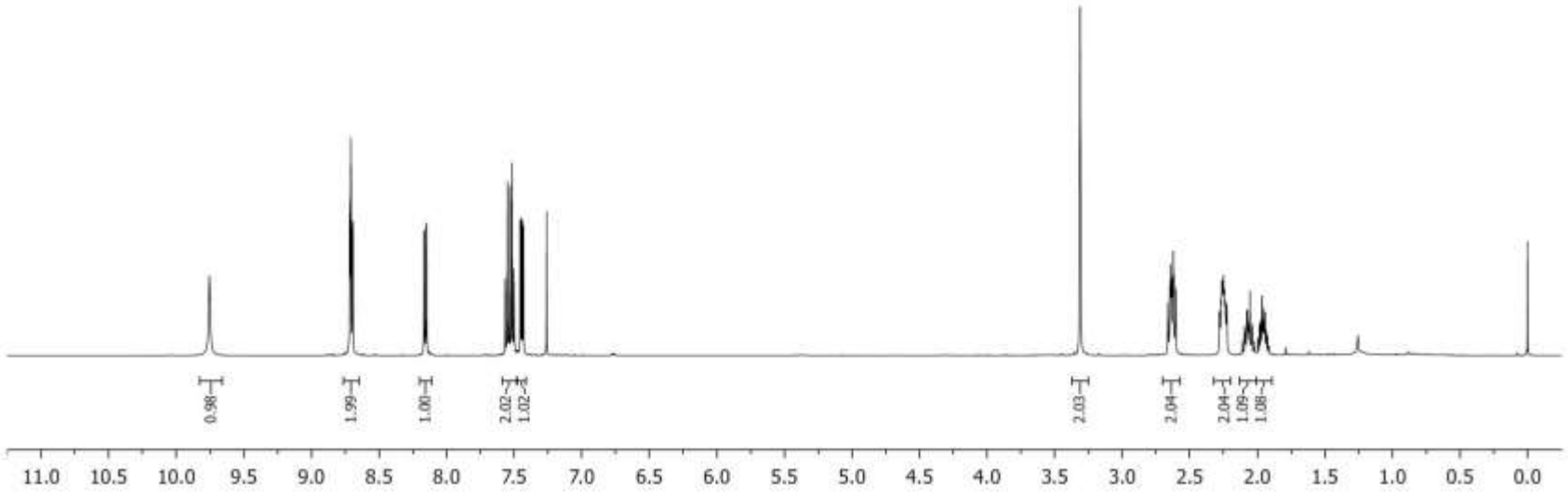
3r

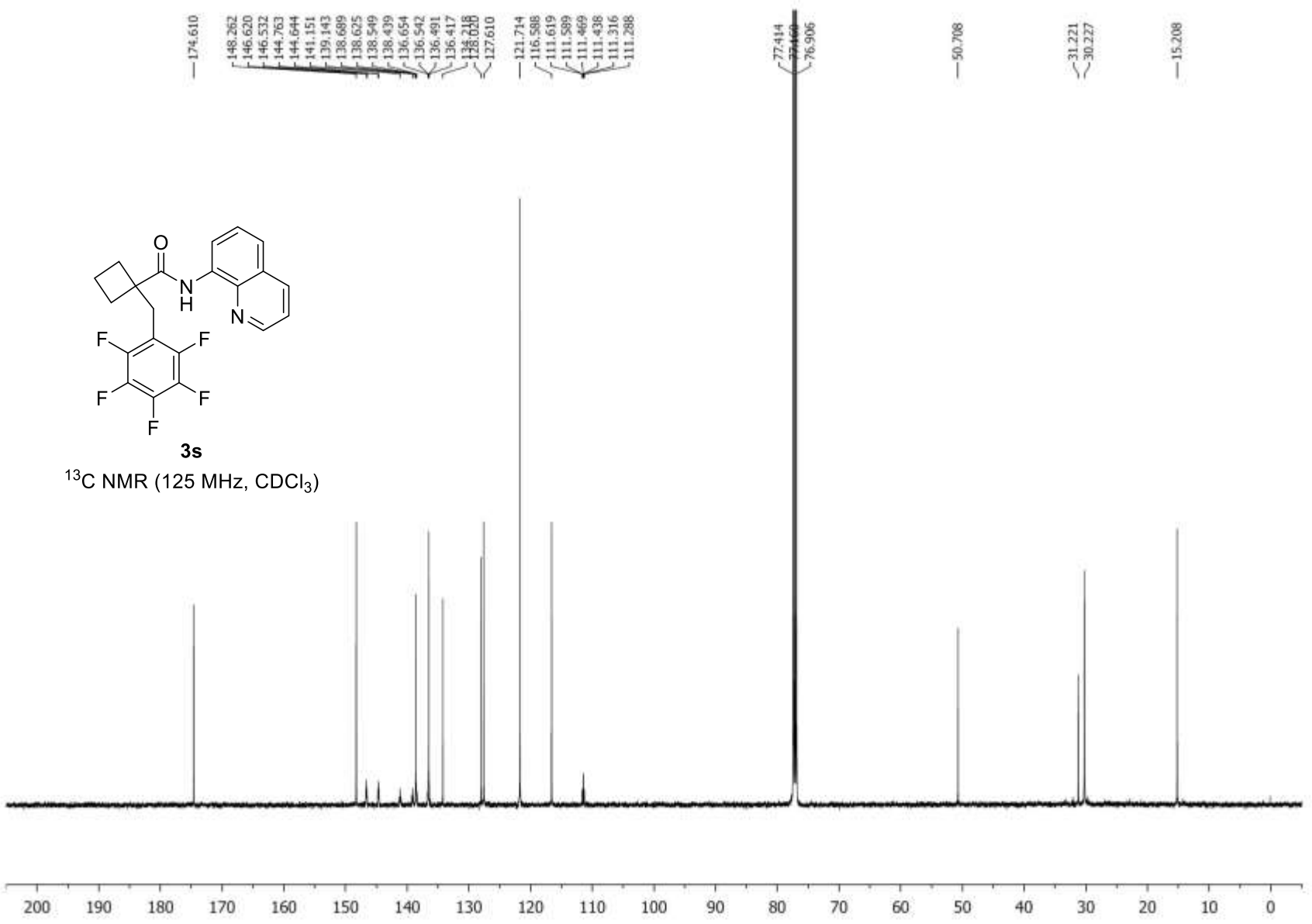
^{19}F NMR (471 MHz, $CDCl_3$)



3s

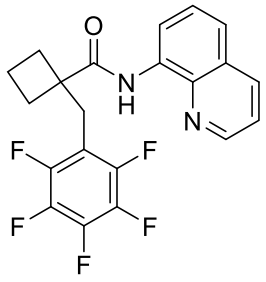
^{1}H NMR (500 MHz, $CDCl_3$)





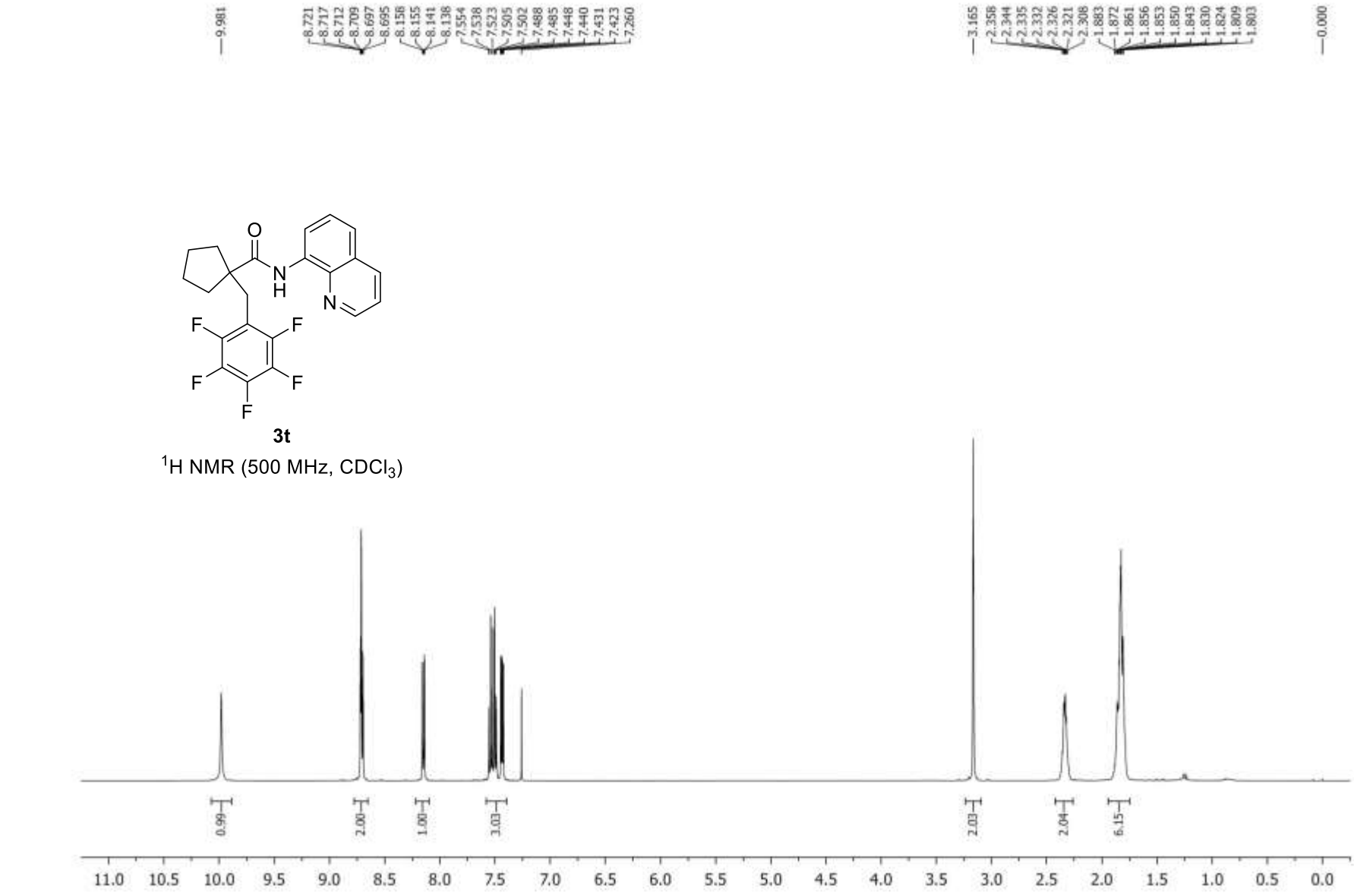
3s

^{13}C NMR (125 MHz, $CDCl_3$)



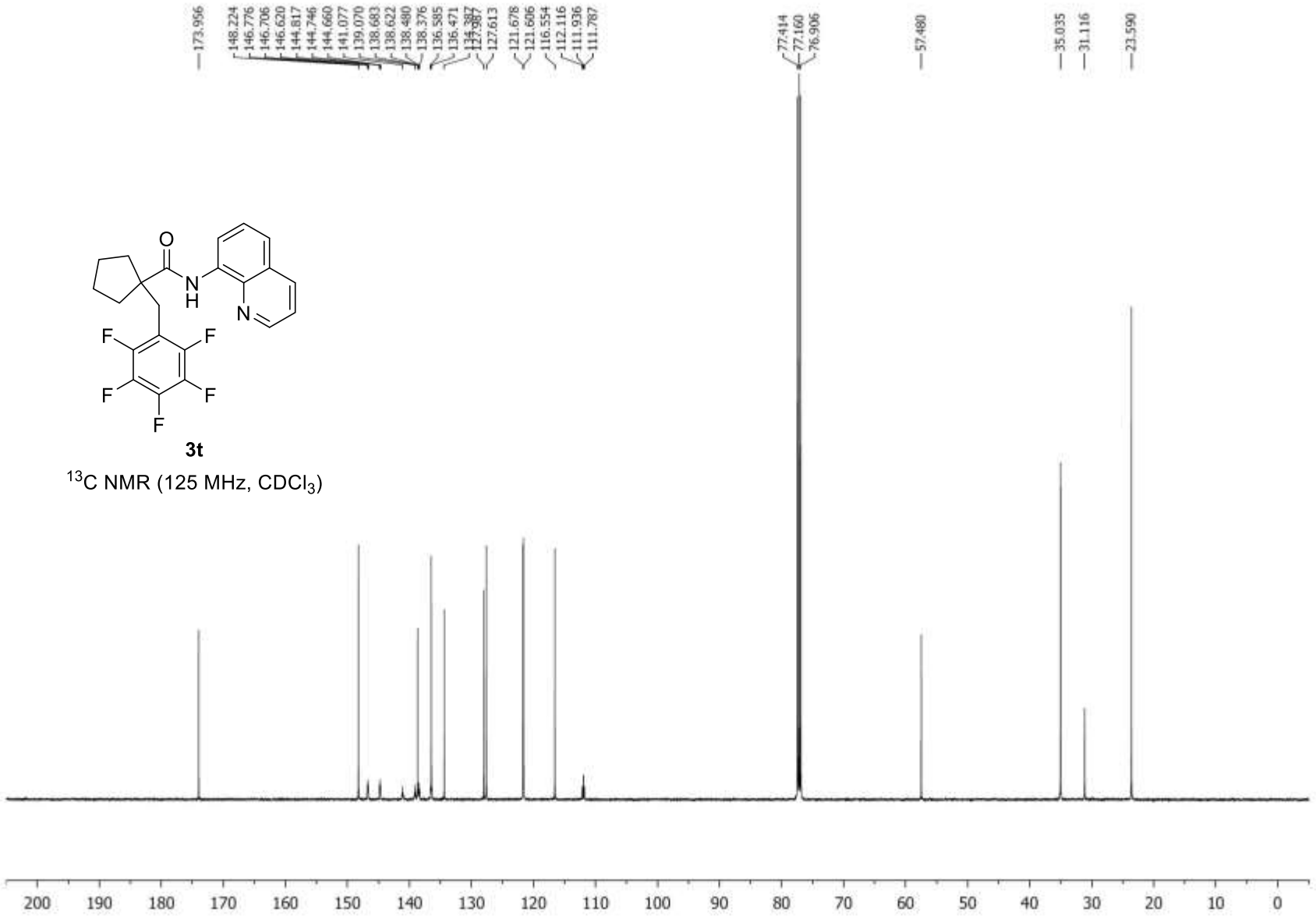
3s

^{19}F NMR (471 MHz, $CDCl_3$)



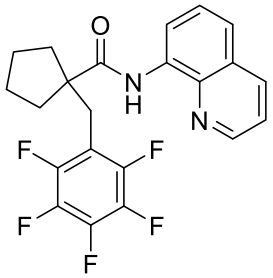
3t

^{1}H NMR (500 MHz, $CDCl_3$)



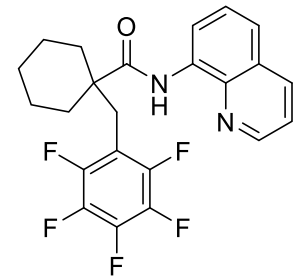
3t

^{13}C NMR (125 MHz, $CDCl_3$)



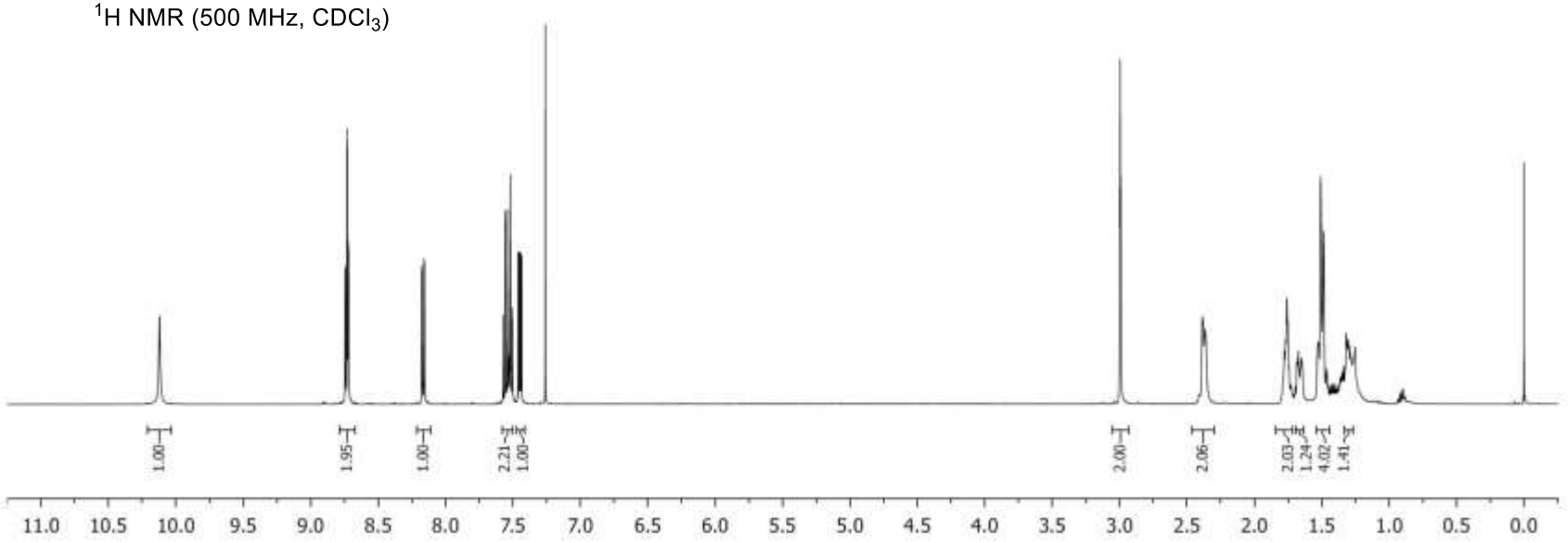
3t

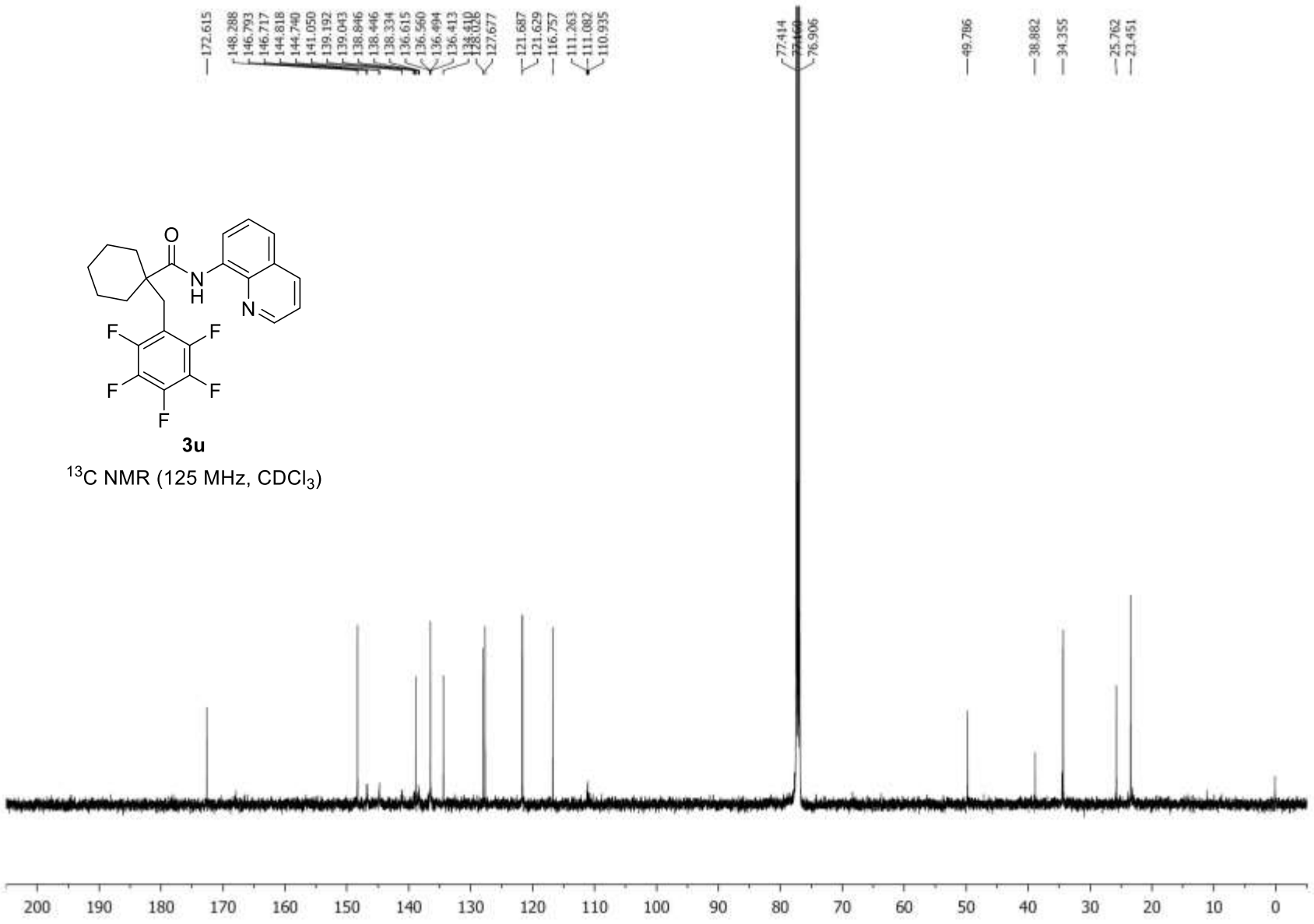
^{19}F NMR (471 MHz, $CDCl_3$)



3u

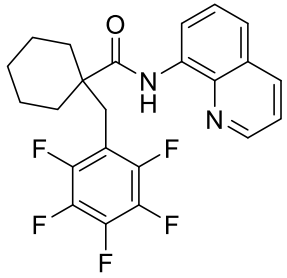
^{1}H NMR (500 MHz, $CDCl_3$)





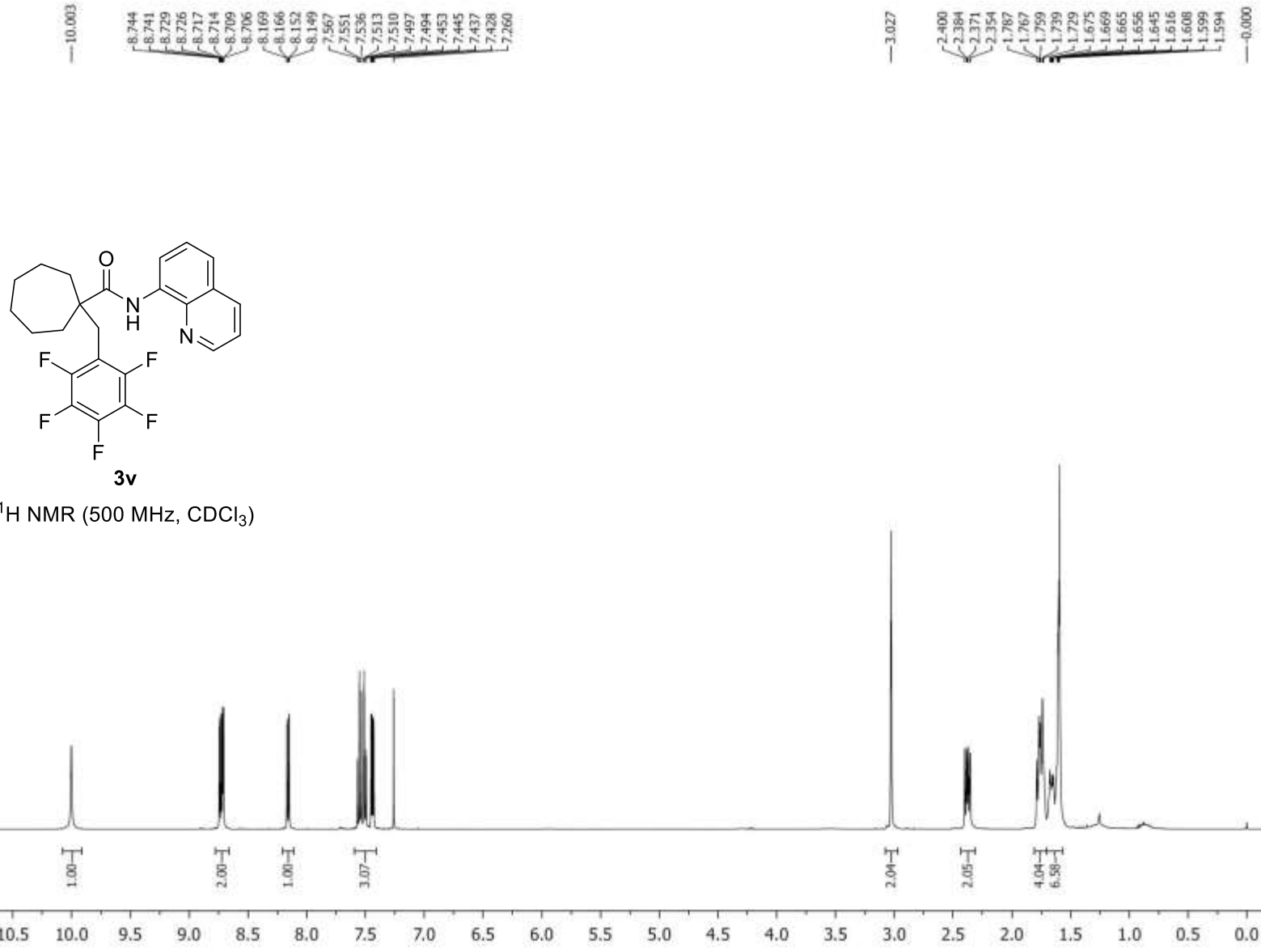
3u

^{13}C NMR (125 MHz, $CDCl_3$)



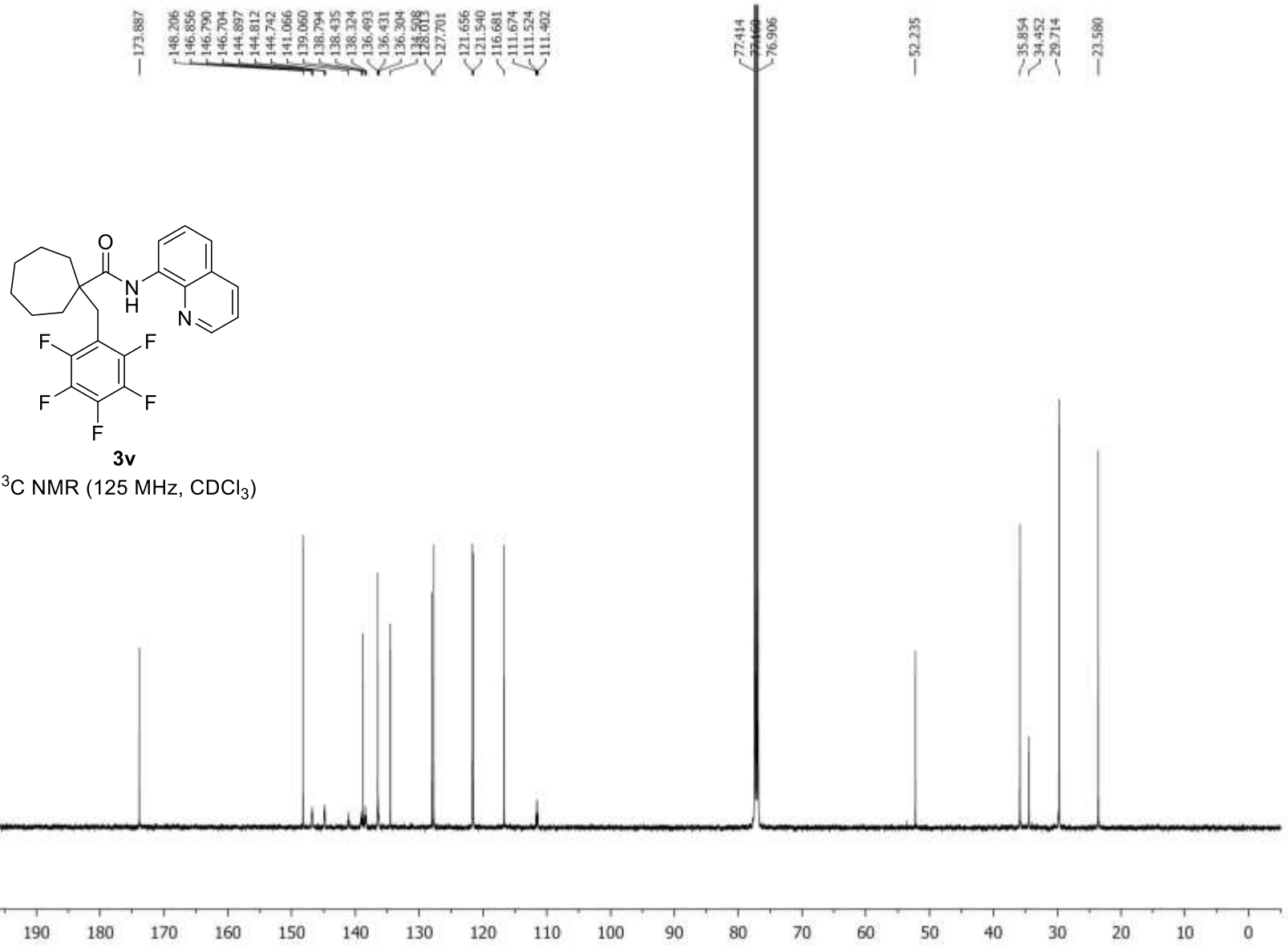
3u

^{19}F NMR (471 MHz, $CDCl_3$)



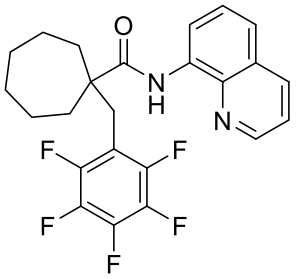
3v

^{1}H NMR (500 MHz, $CDCl_3$)



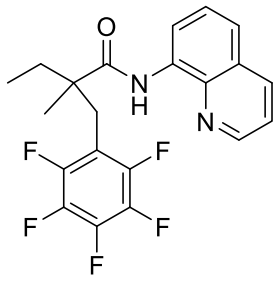
3v

^{13}C NMR (125 MHz, $CDCl_3$)



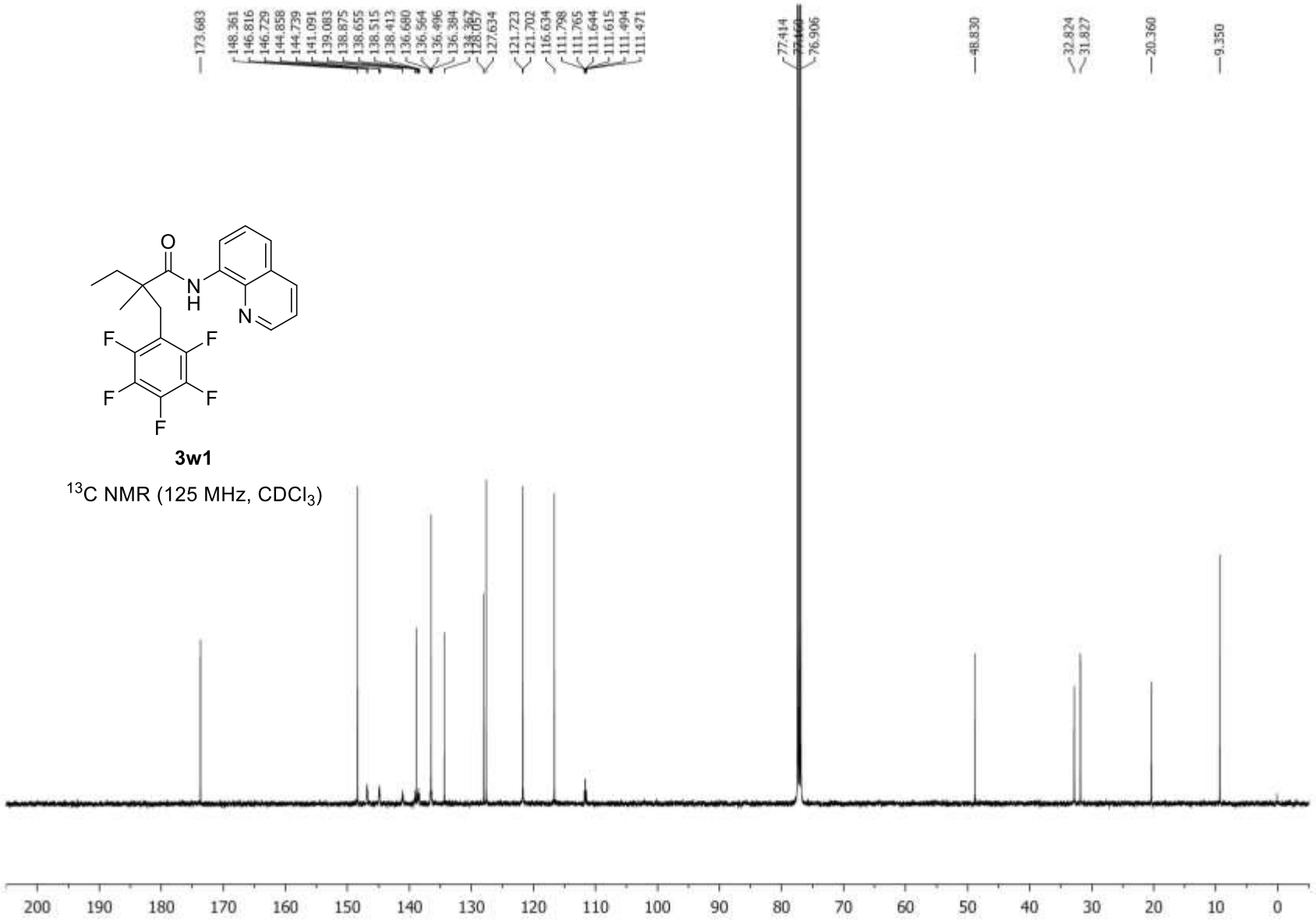
3v

^{19}F NMR (471 MHz, $CDCl_3$)



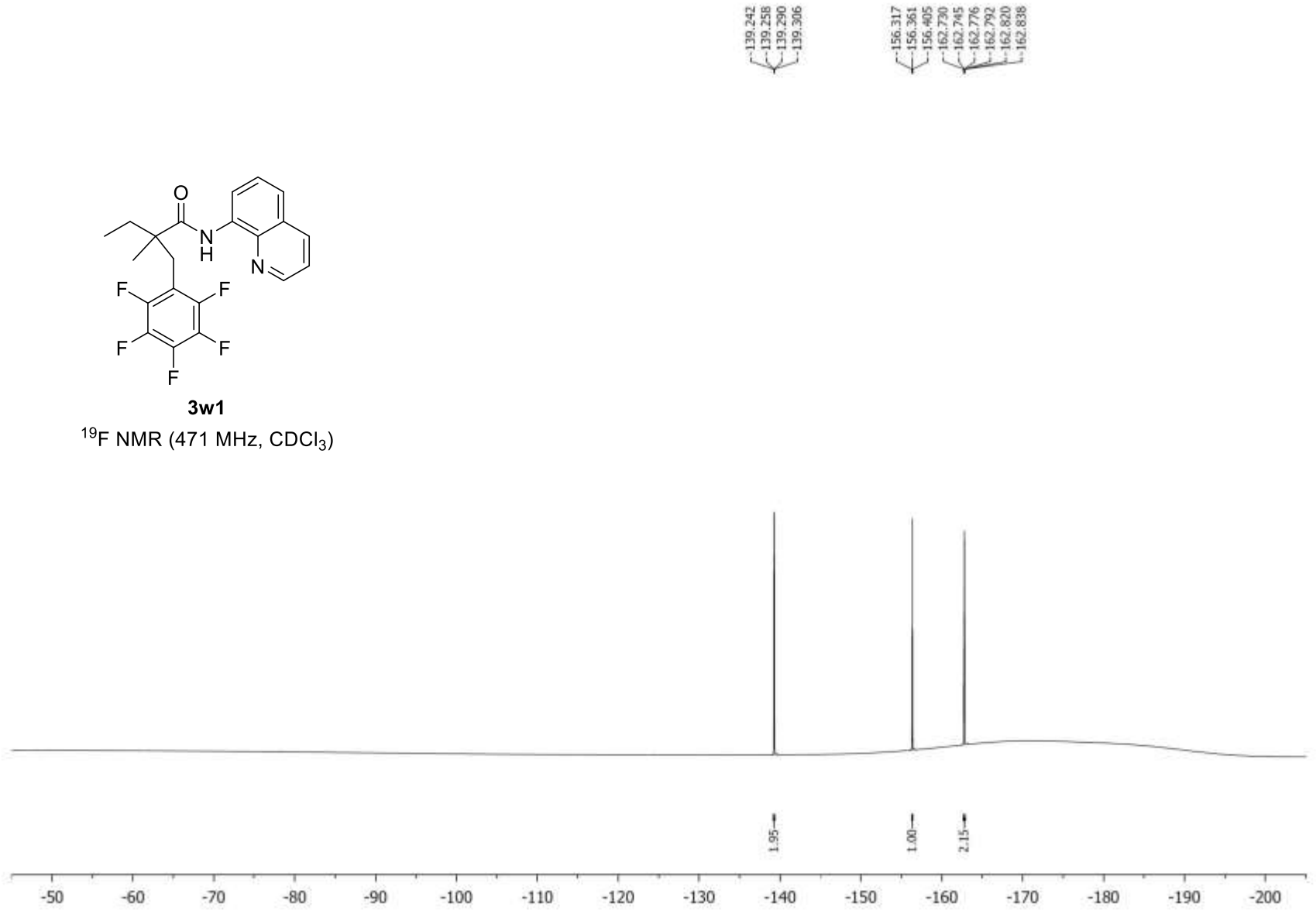
3w1

^{1}H NMR (500 MHz, $CDCl_3$)



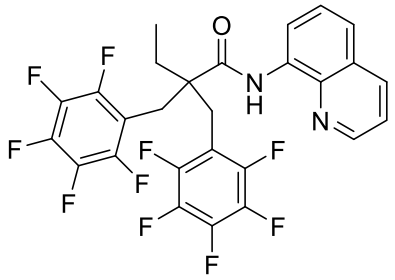
3w1

^{13}C NMR (125 MHz, $CDCl_3$)



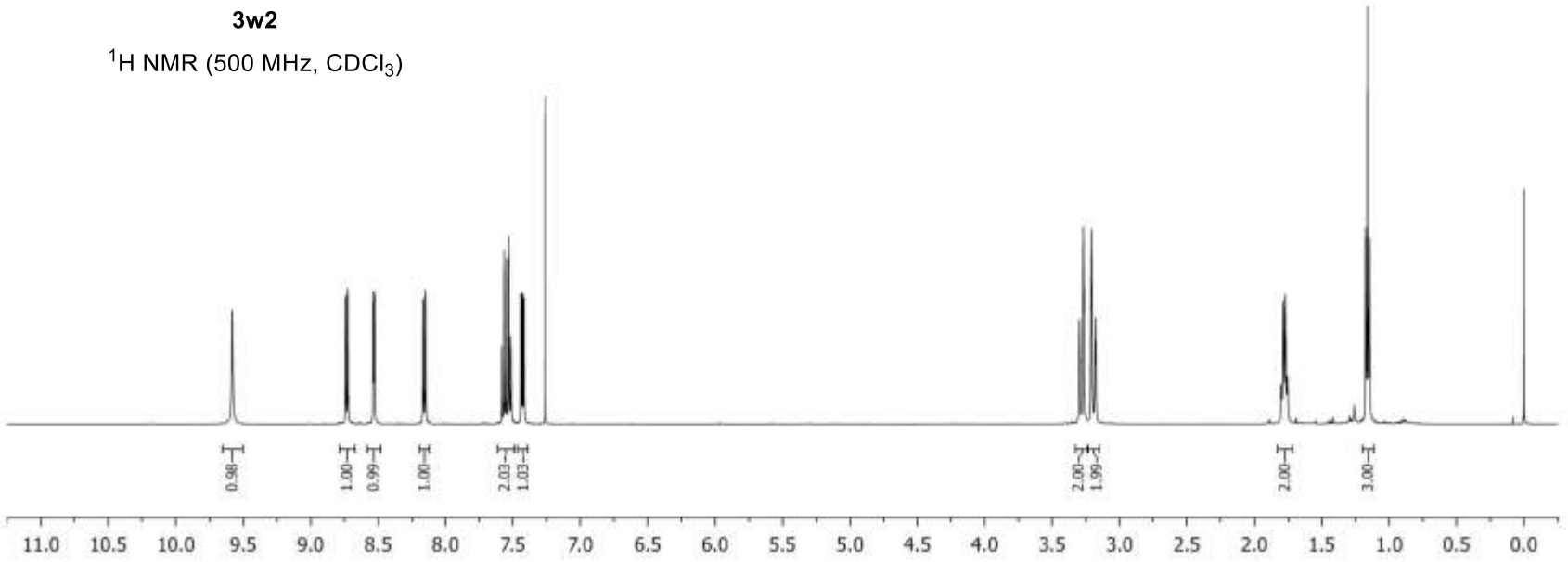
3w1

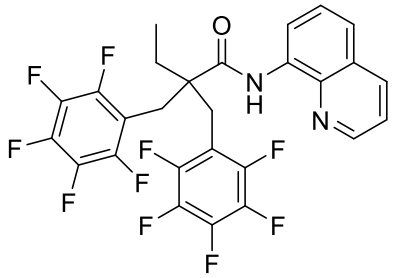
^{19}F NMR (471 MHz, $CDCl_3$)



3w2

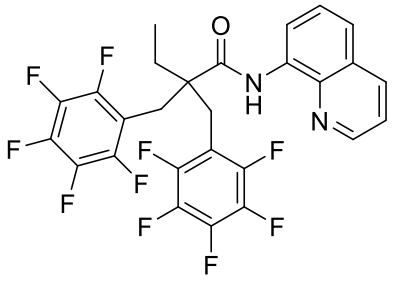
^{1}H NMR (500 MHz, $CDCl_3$)





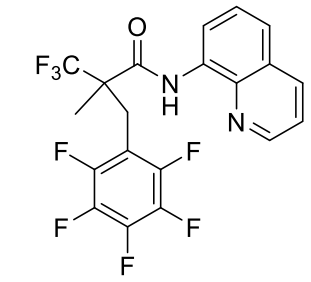
3w2

^{13}C NMR (125 MHz, $CDCl_3$)



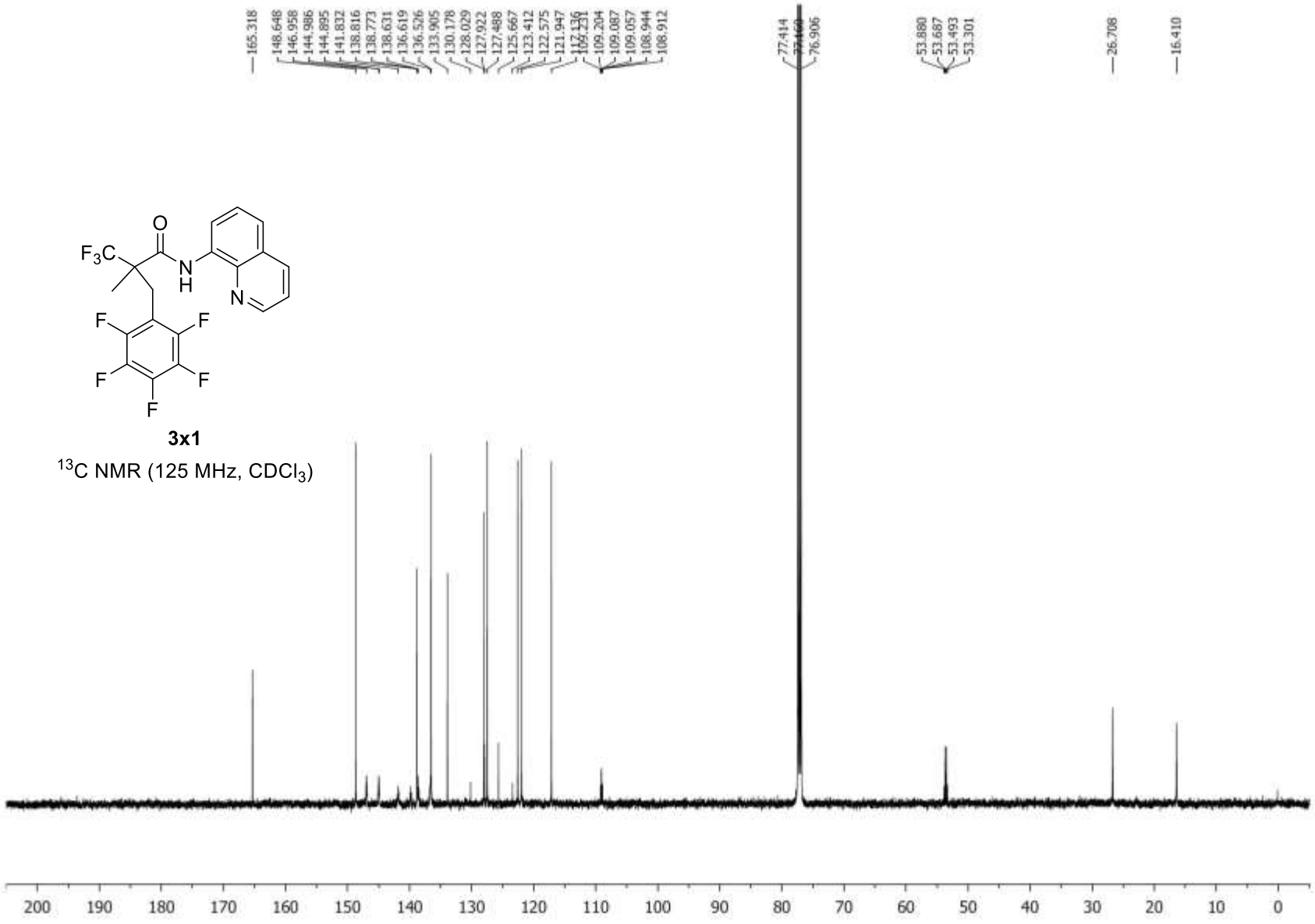
3w2

^{19}F NMR (471 MHz, $CDCl_3$)



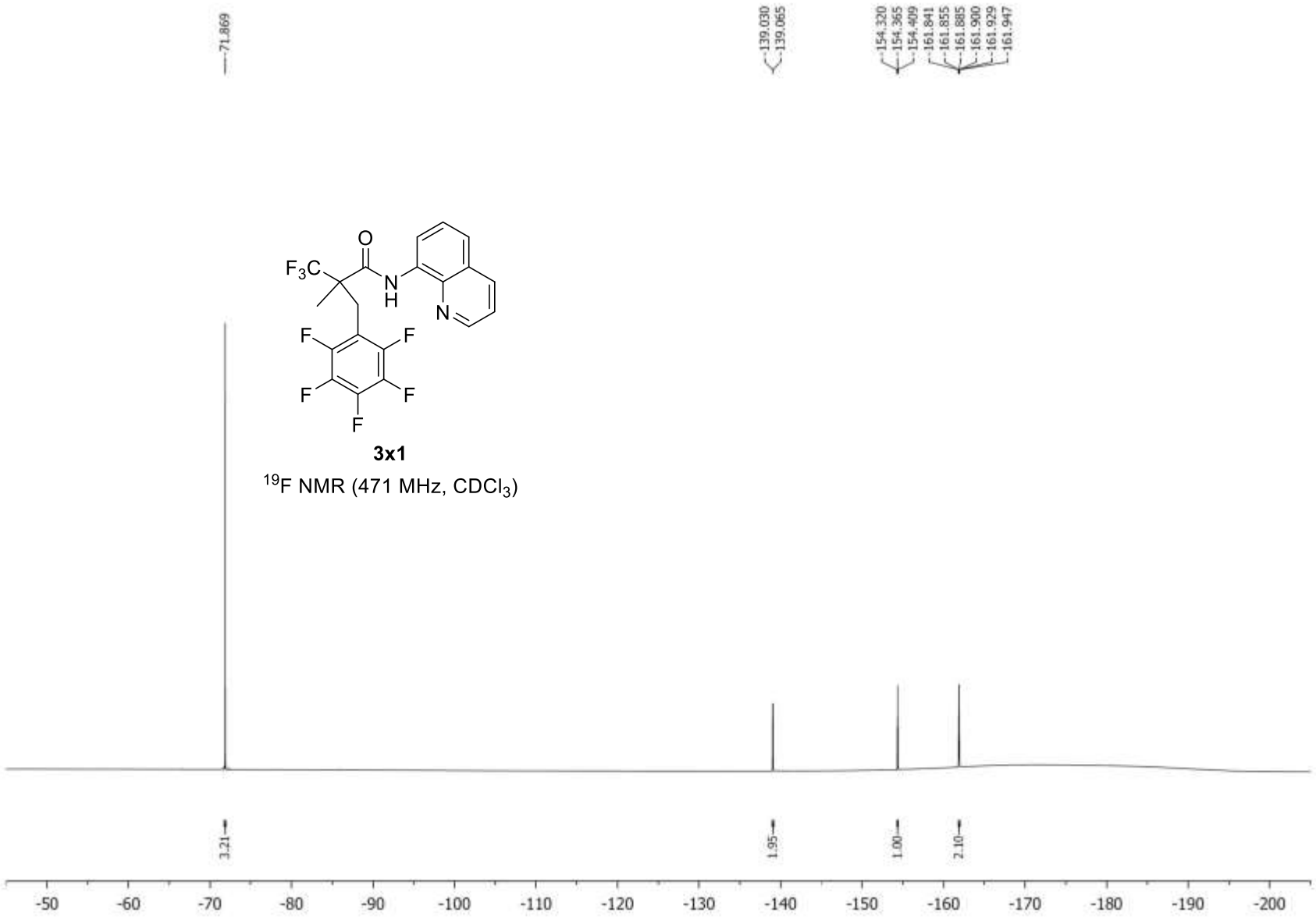
3x1

^{1}H NMR (500 MHz, $CDCl_3$)



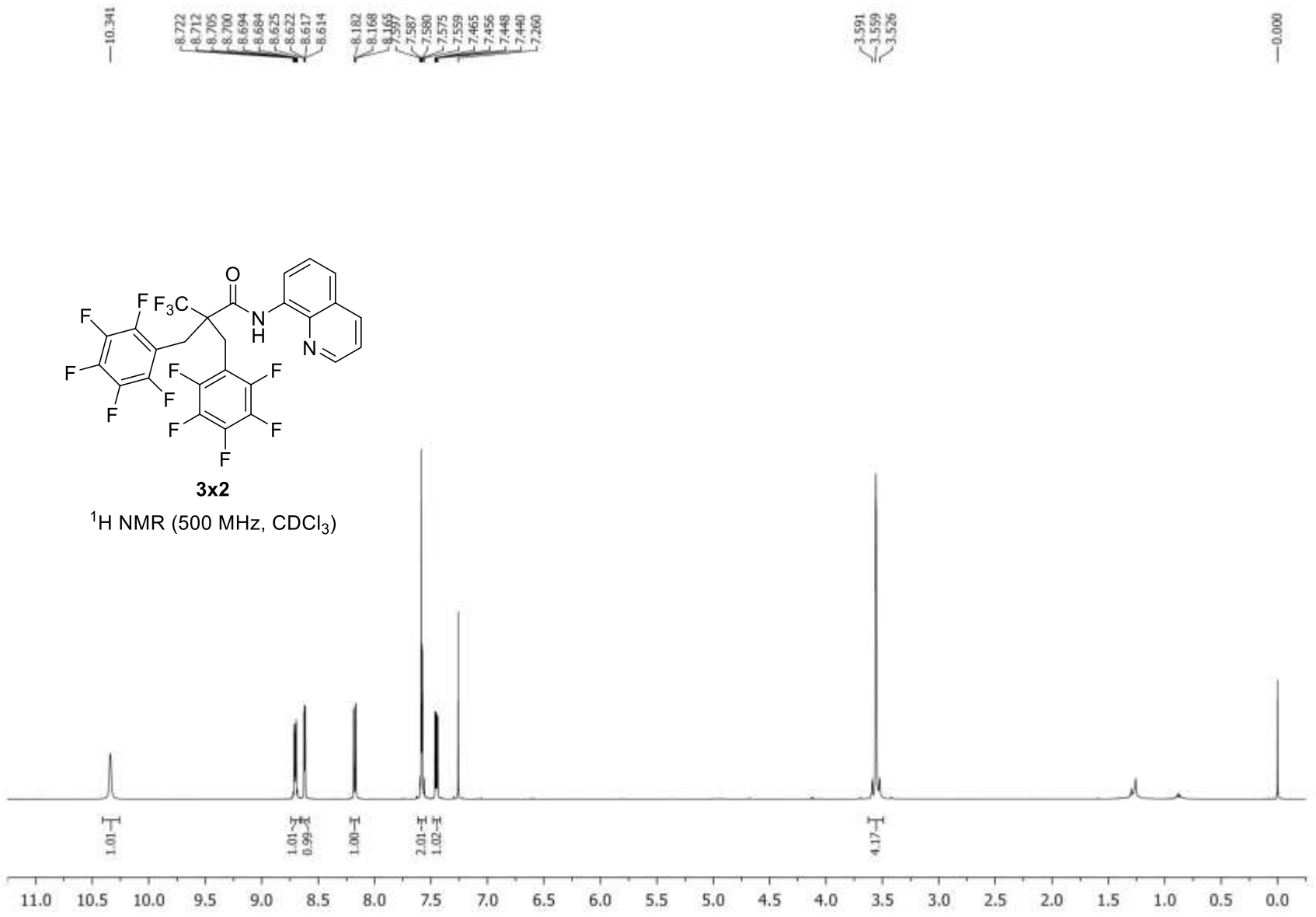
3x1

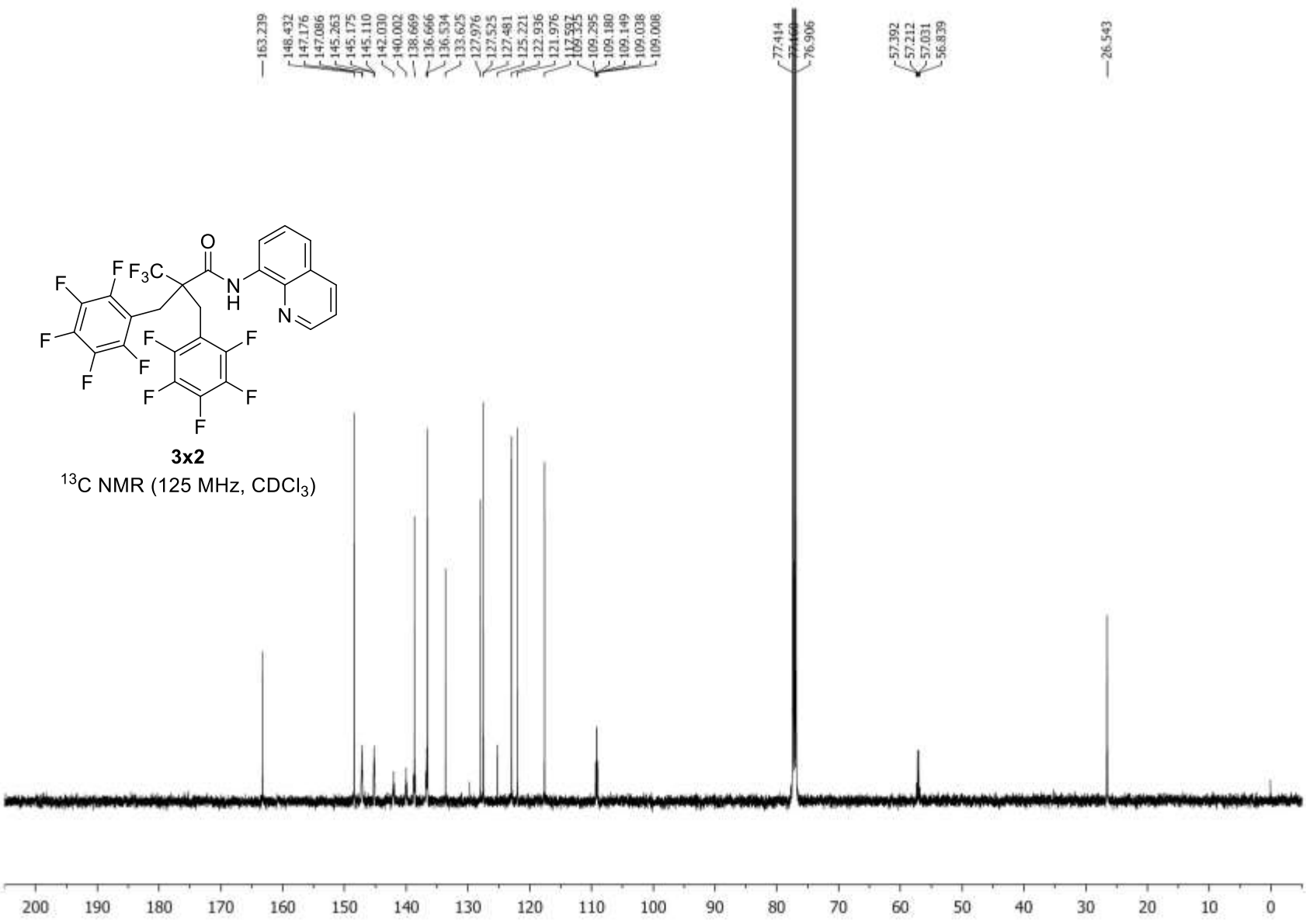
^{13}C NMR (125 MHz, $CDCl_3$)



3x1

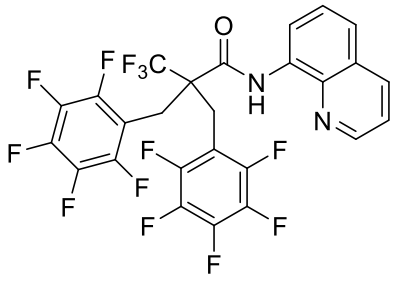
^{19}F NMR (471 MHz, $CDCl_3$)


10.341
8.722
8.712
8.705
8.700
8.694
8.684
8.625
8.622
8.617
8.614
8.182
8.168
8.165
7.597
7.587
7.580
7.575
7.559
7.465
7.456
7.448
7.440
7.260
3.591
3.559
3.526
0.000
O
F
F3C
N
H
N
F
F
F
F
F
F
F
F
F
3x2
1H NMR (500 MHz, CDCl3)
1.01
1.01
0.99
1.00
2.01
1.02
4.17
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



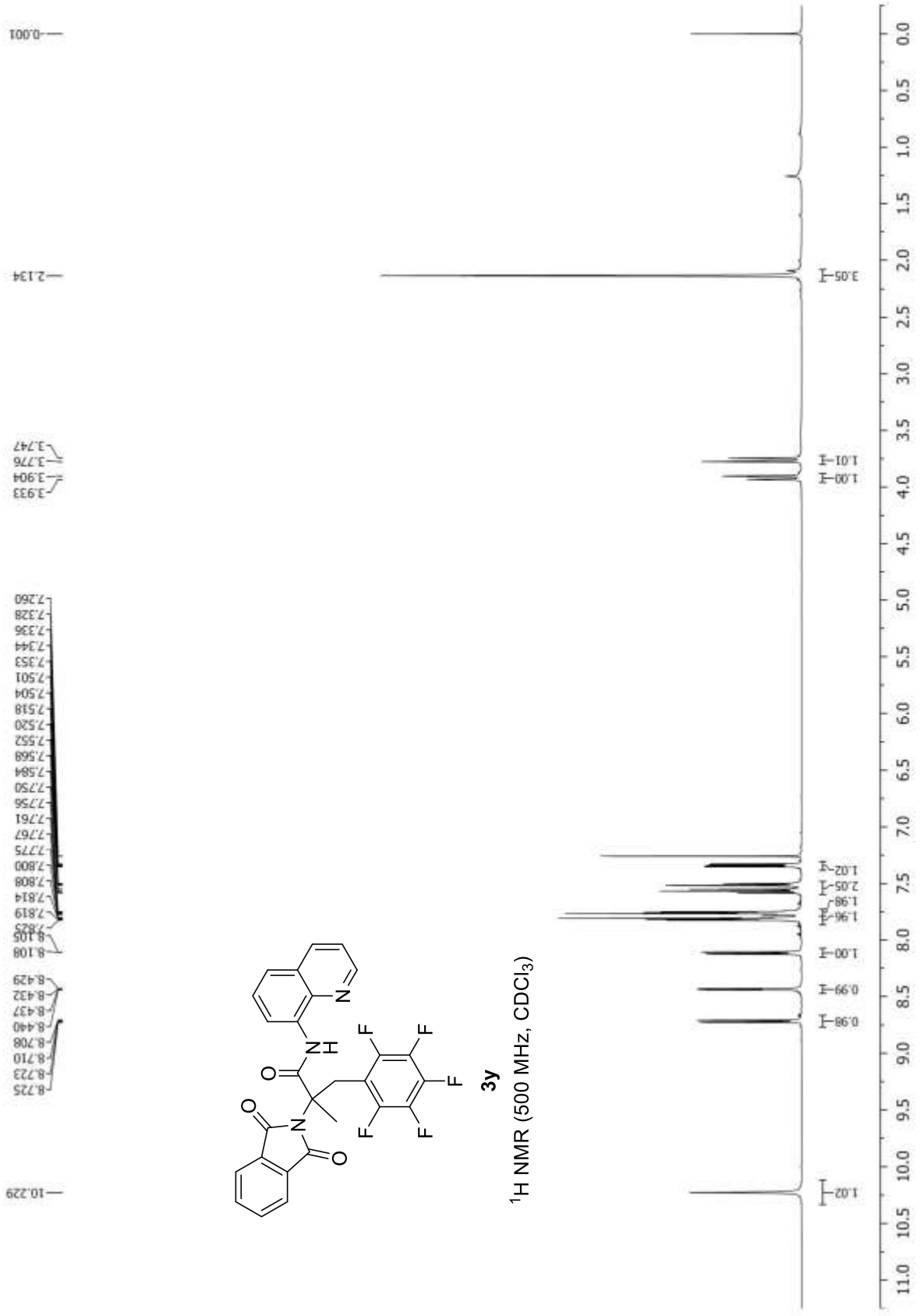
3x2

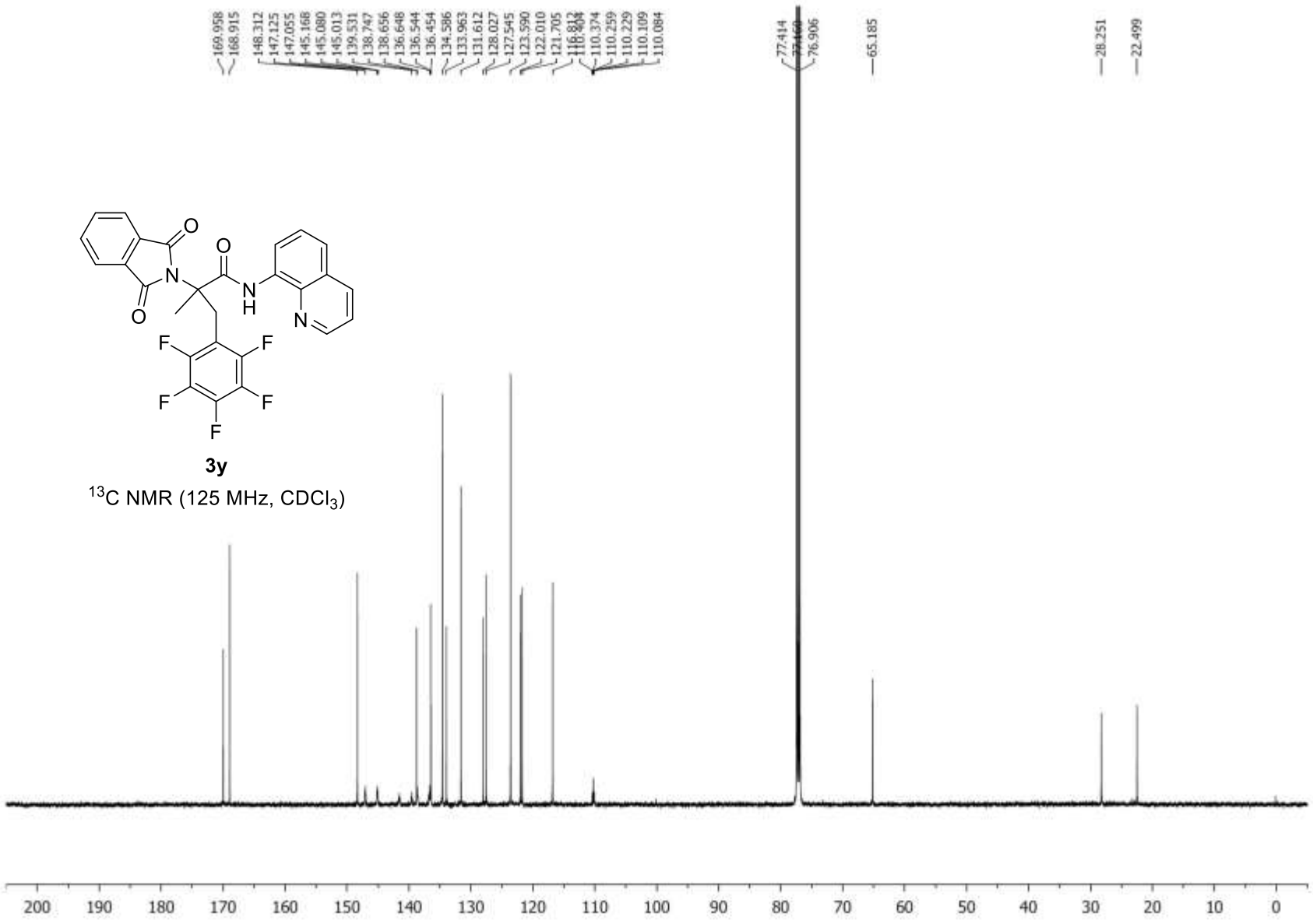
^{13}C NMR (125 MHz, $CDCl_3$)



3x2

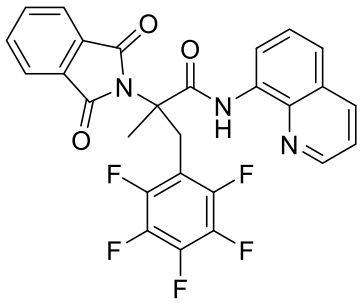
^{19}F NMR (471 MHz, $CDCl_3$)


3y
^{1}H NMR (500 MHz, CDCl$_3$)



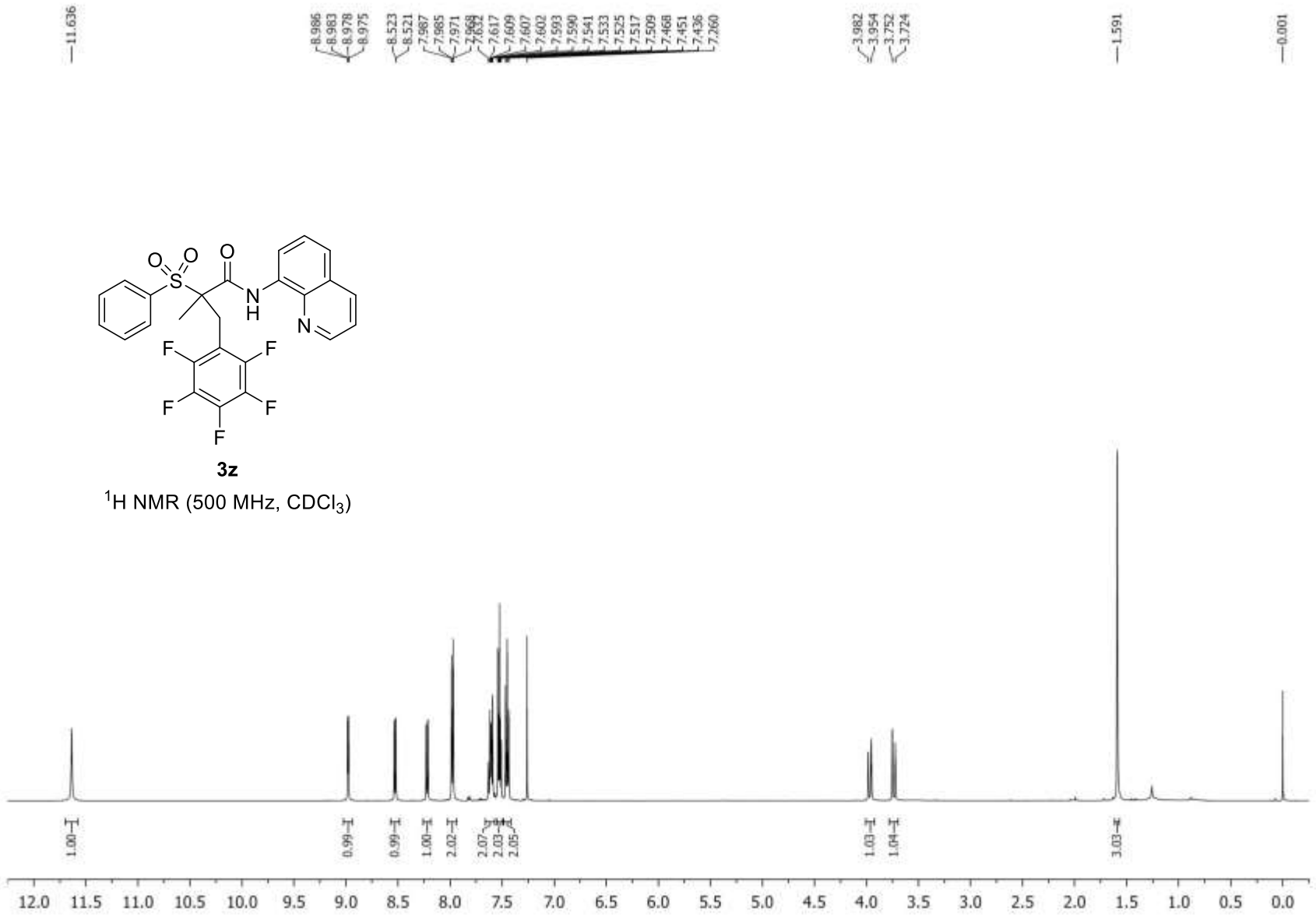
3y

^{13}C NMR (125 MHz, $CDCl_3$)



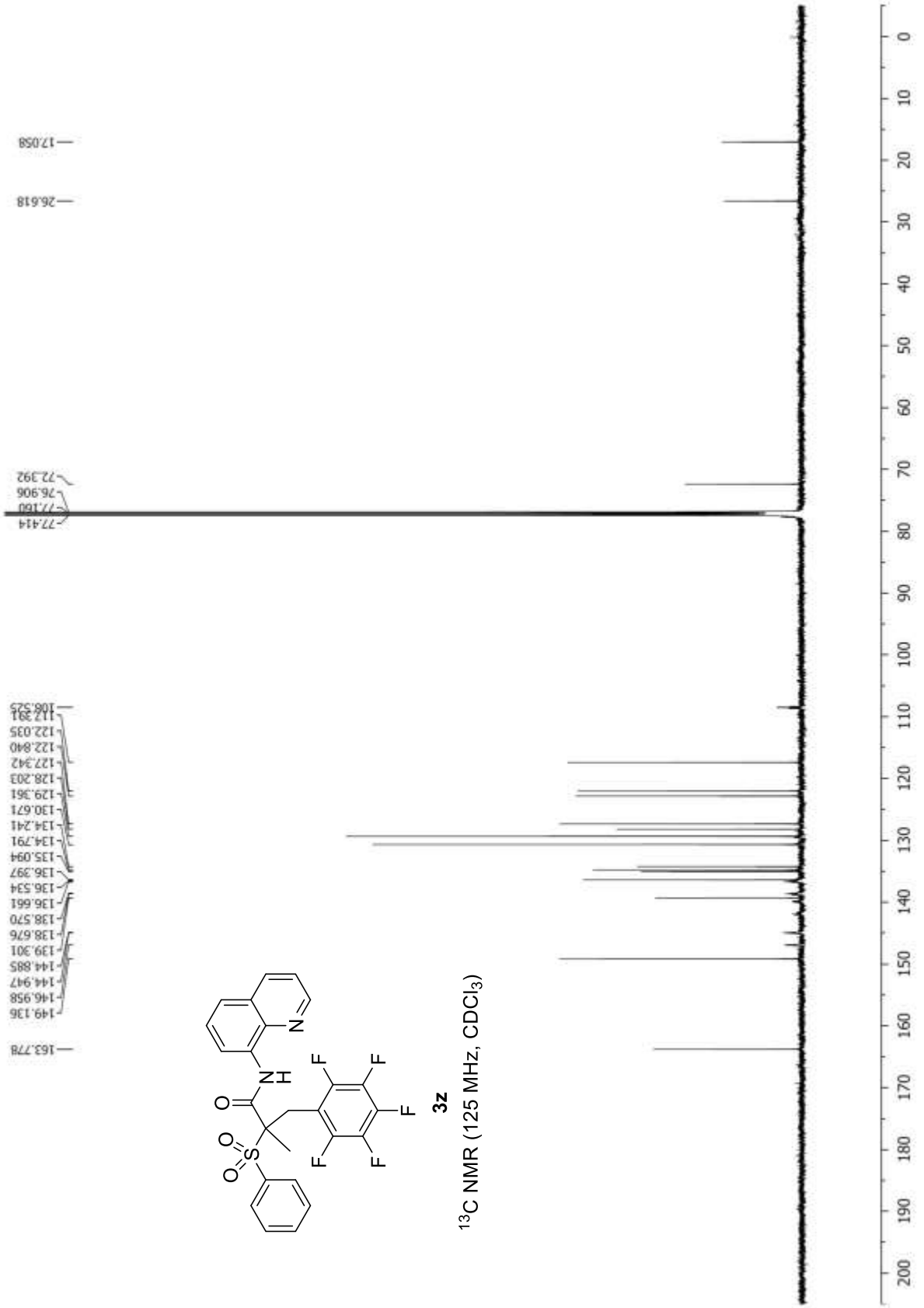
3y

^{19}F NMR (471 MHz, $CDCl_3$)



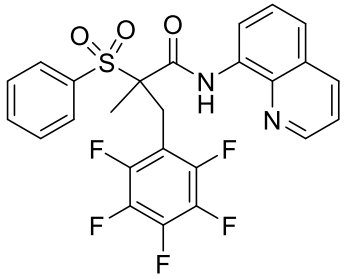
3z

^{1}H NMR (500 MHz, $CDCl_3$)



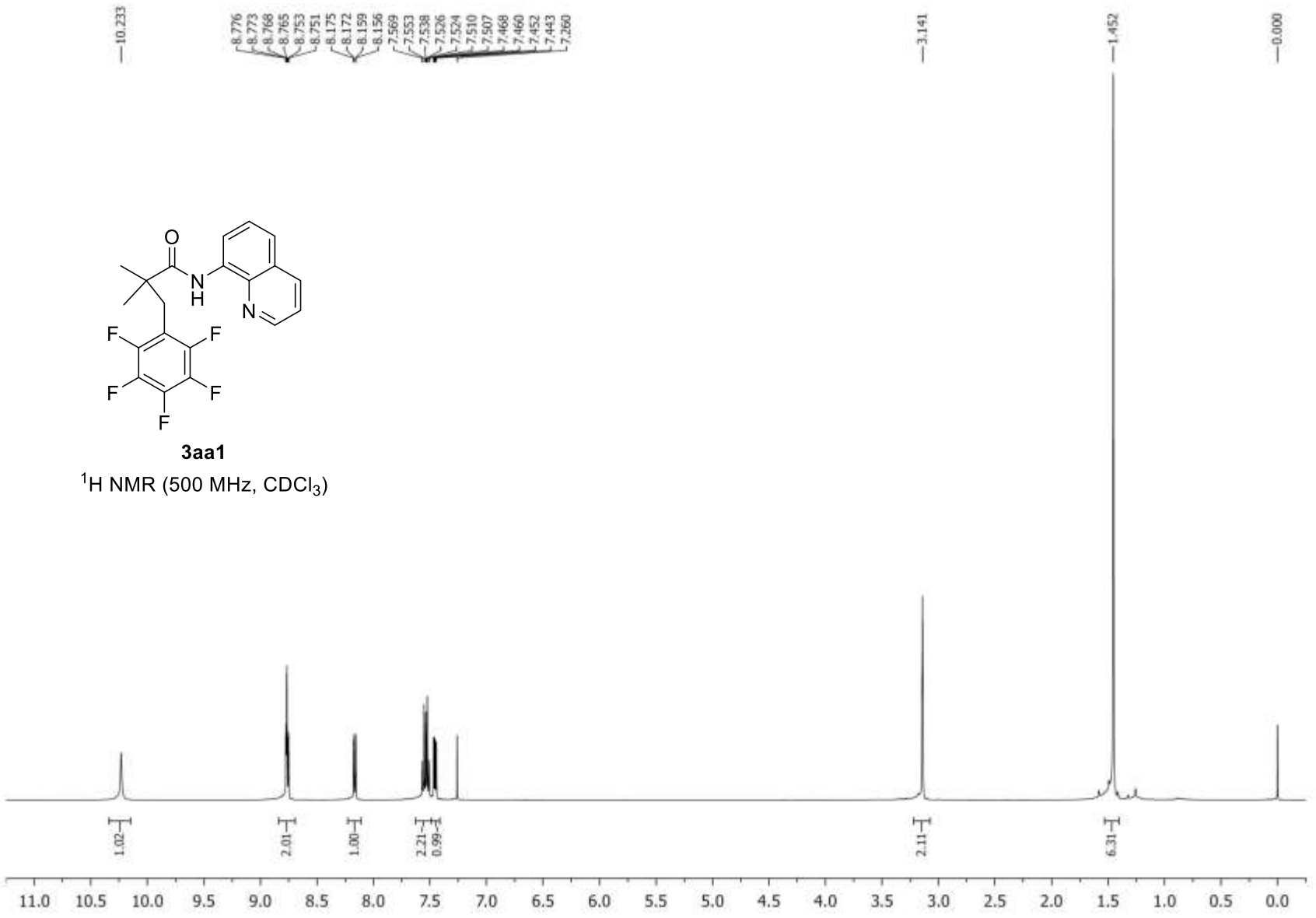
3z

^{13}C NMR (125 MHz, $CDCl_3$)



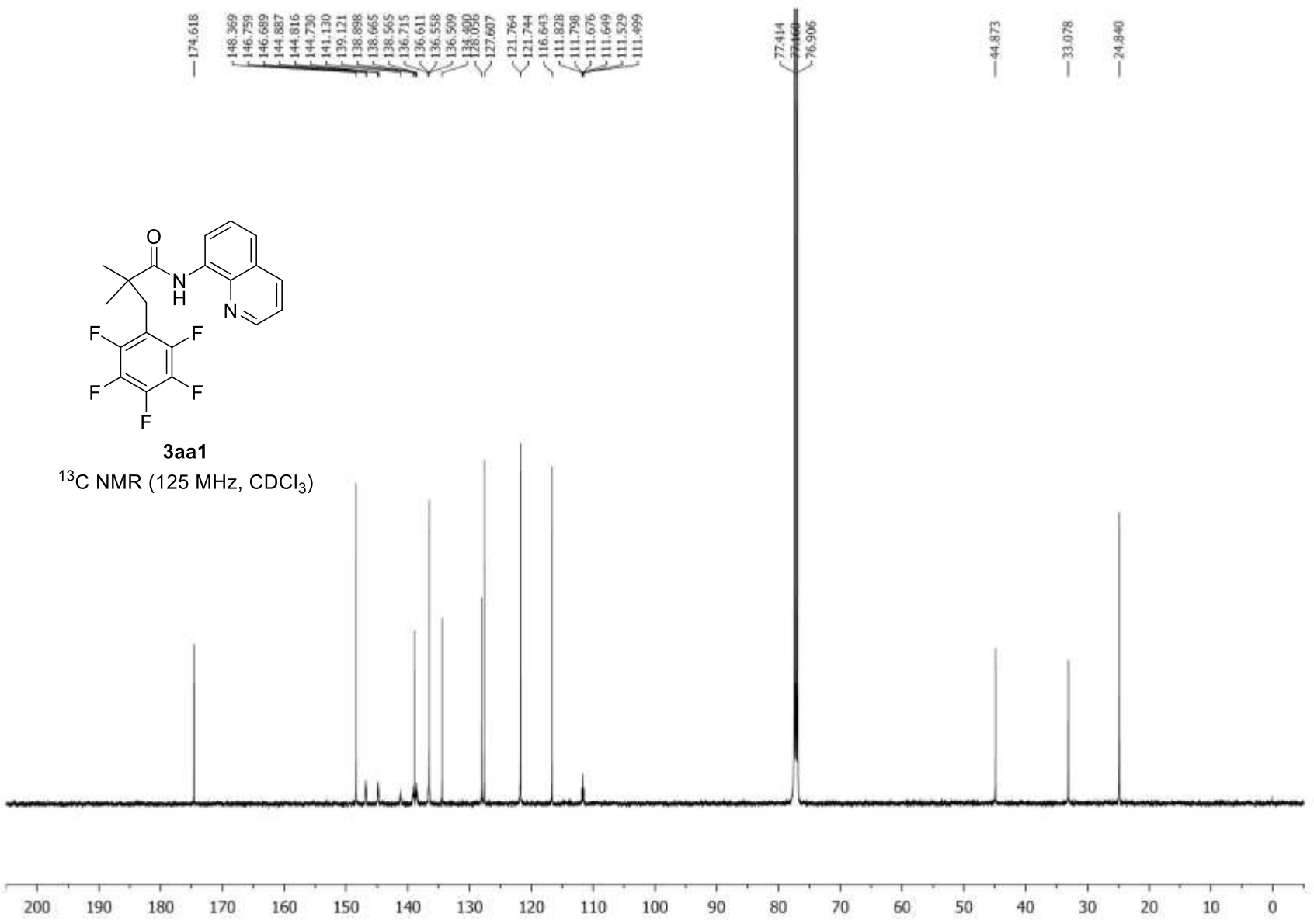
3z

^{19}F NMR (471 MHz, $CDCl_3$)



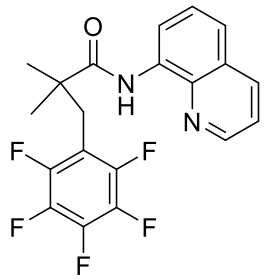
3aa1

^{1}H NMR (500 MHz, $CDCl_3$)



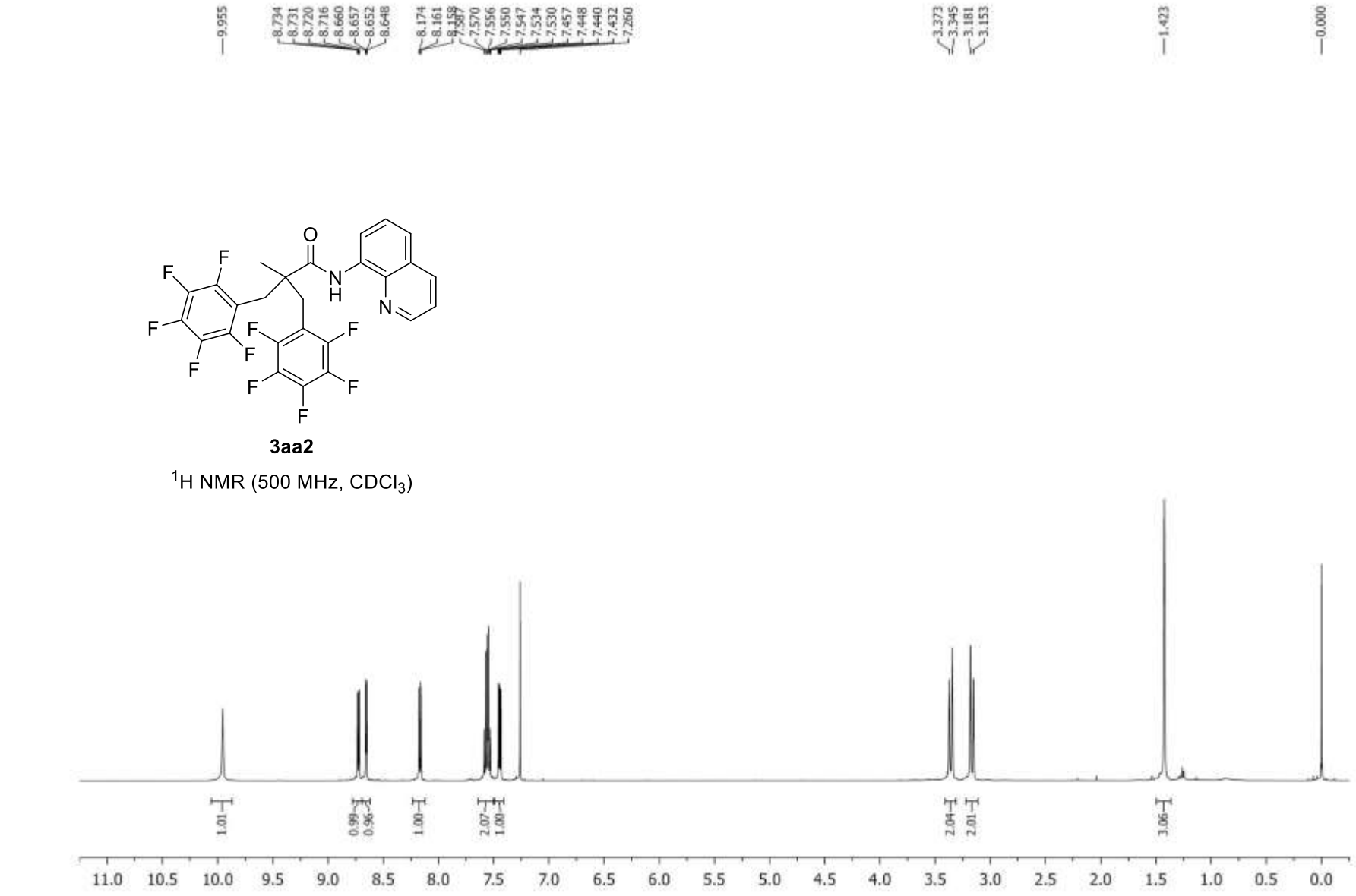
3aa1

^{13}C NMR (125 MHz, $CDCl_3$)



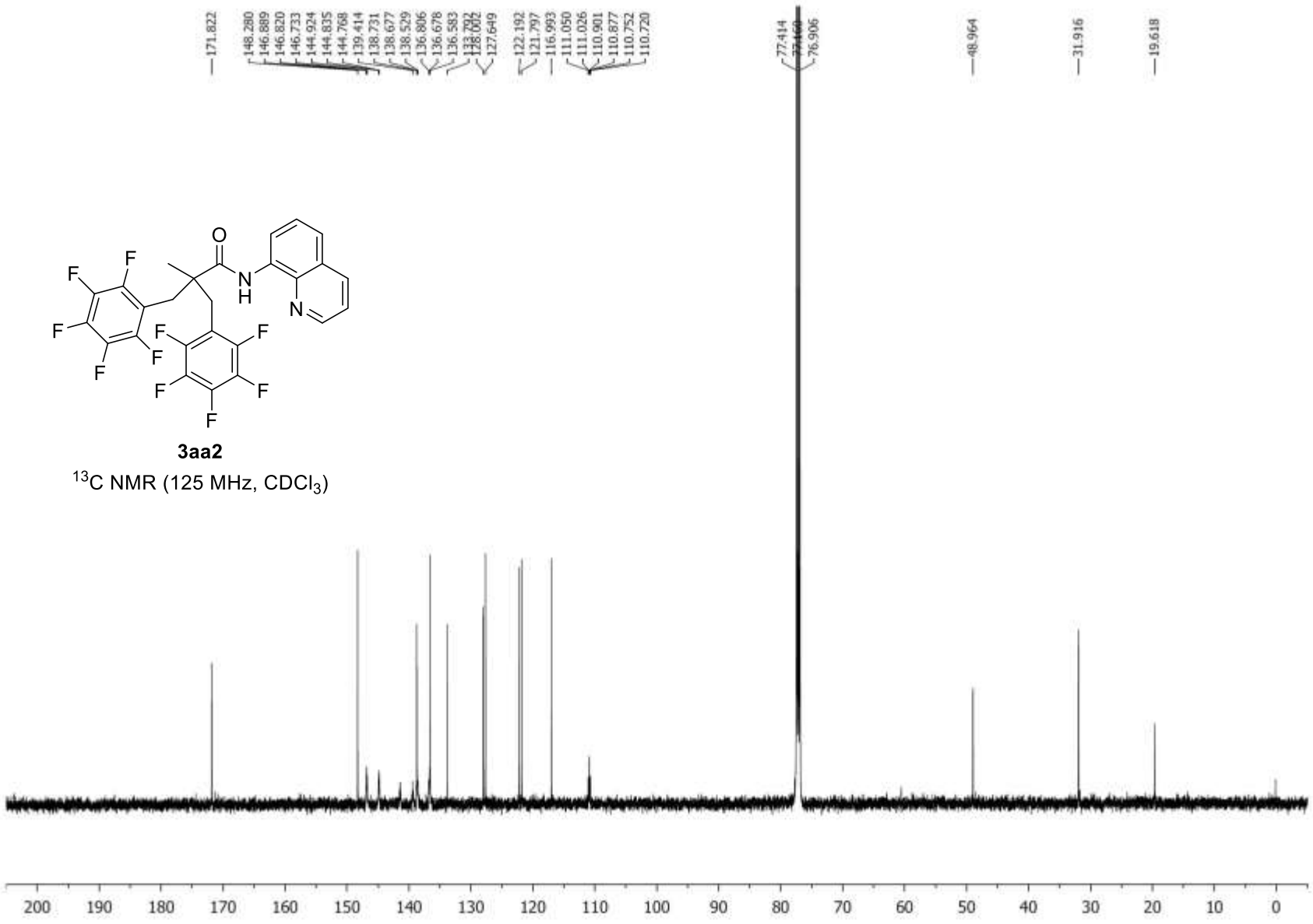
3aa1

^{19}F NMR (471 MHz, $CDCl_3$)



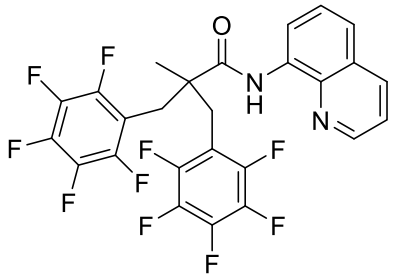
3aa2

^{1}H NMR (500 MHz, $CDCl_3$)



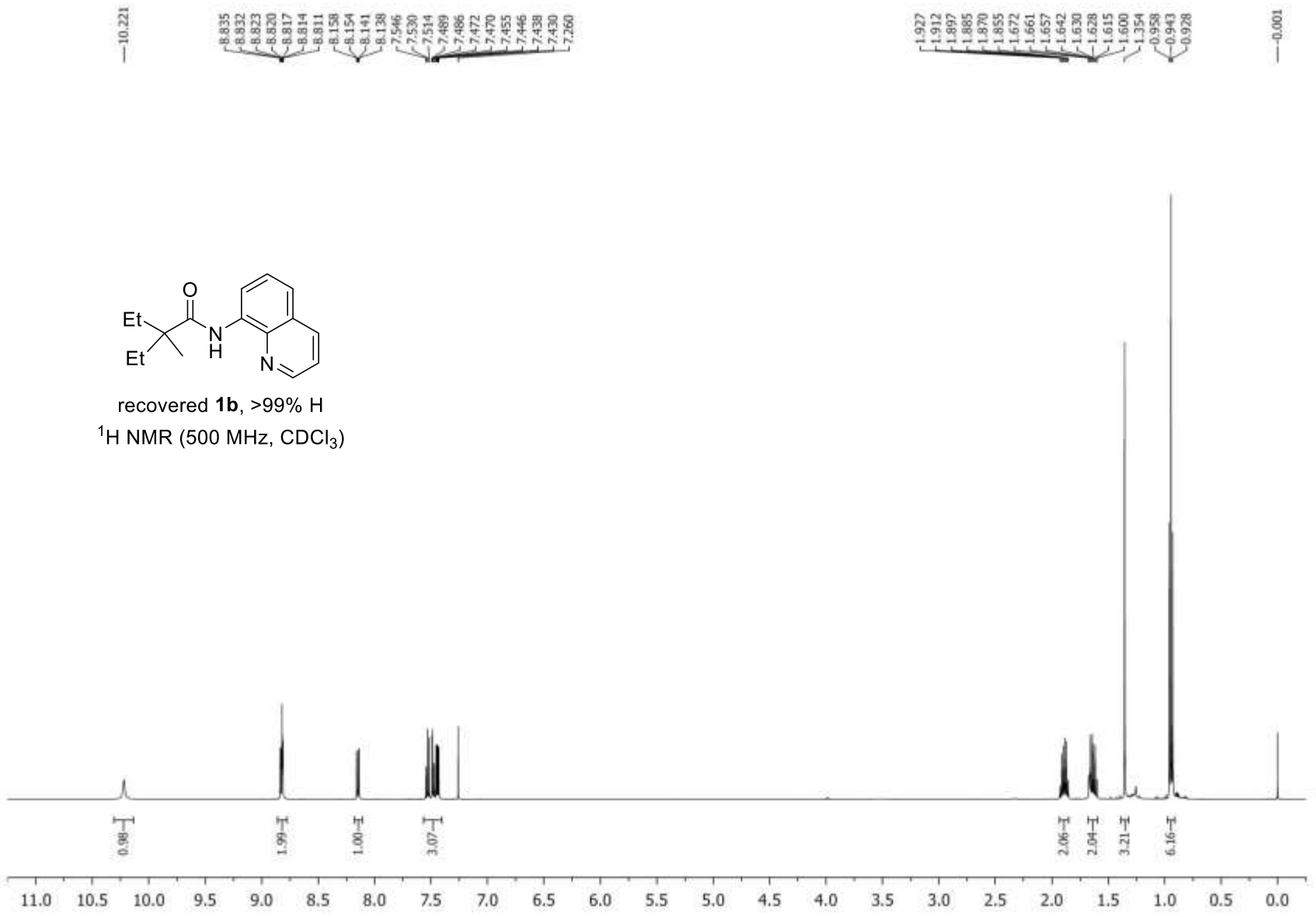
3aa2

^{13}C NMR (125 MHz, $CDCl_3$)



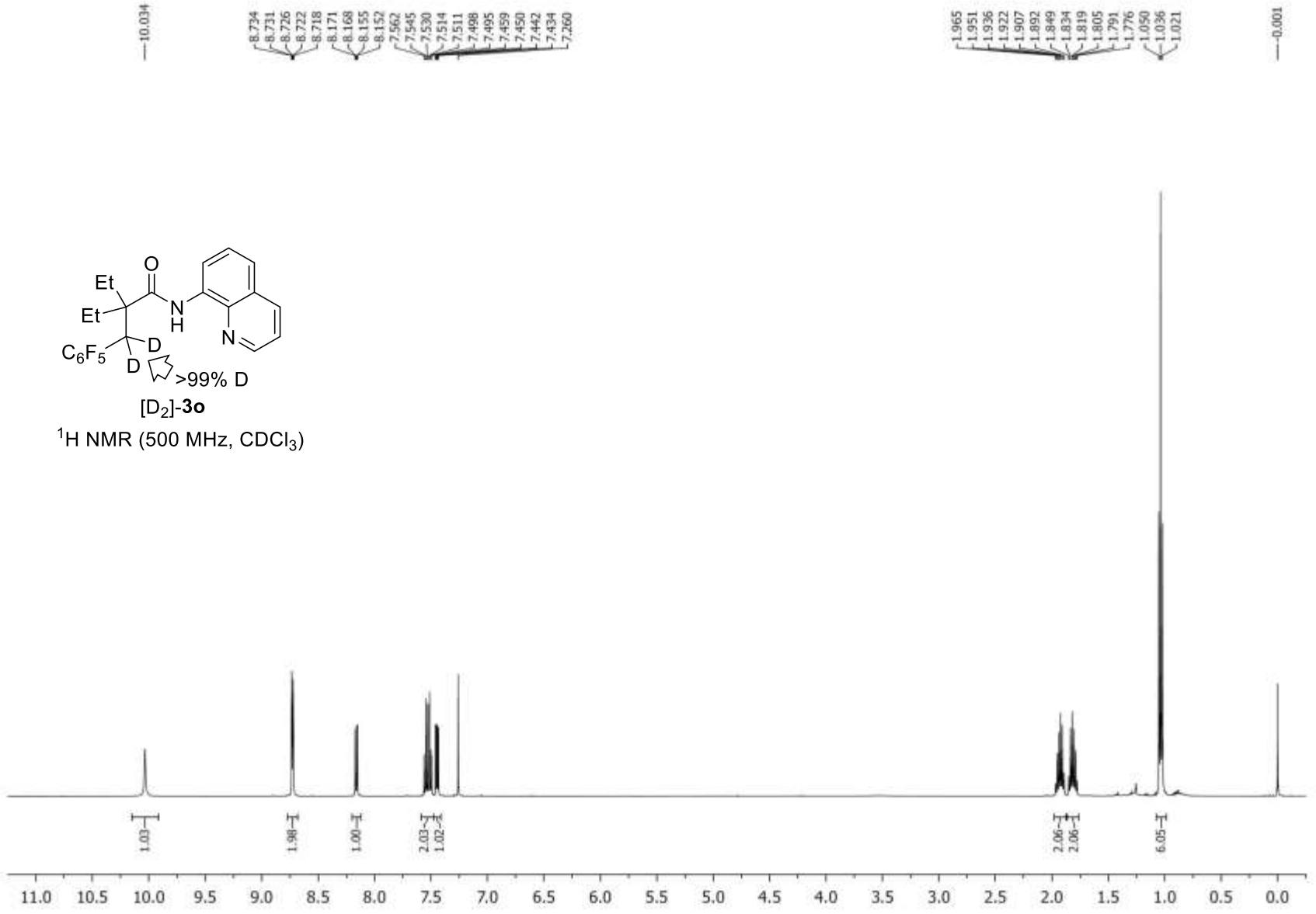
3aa2

^{19}F NMR (471 MHz, $CDCl_3$)



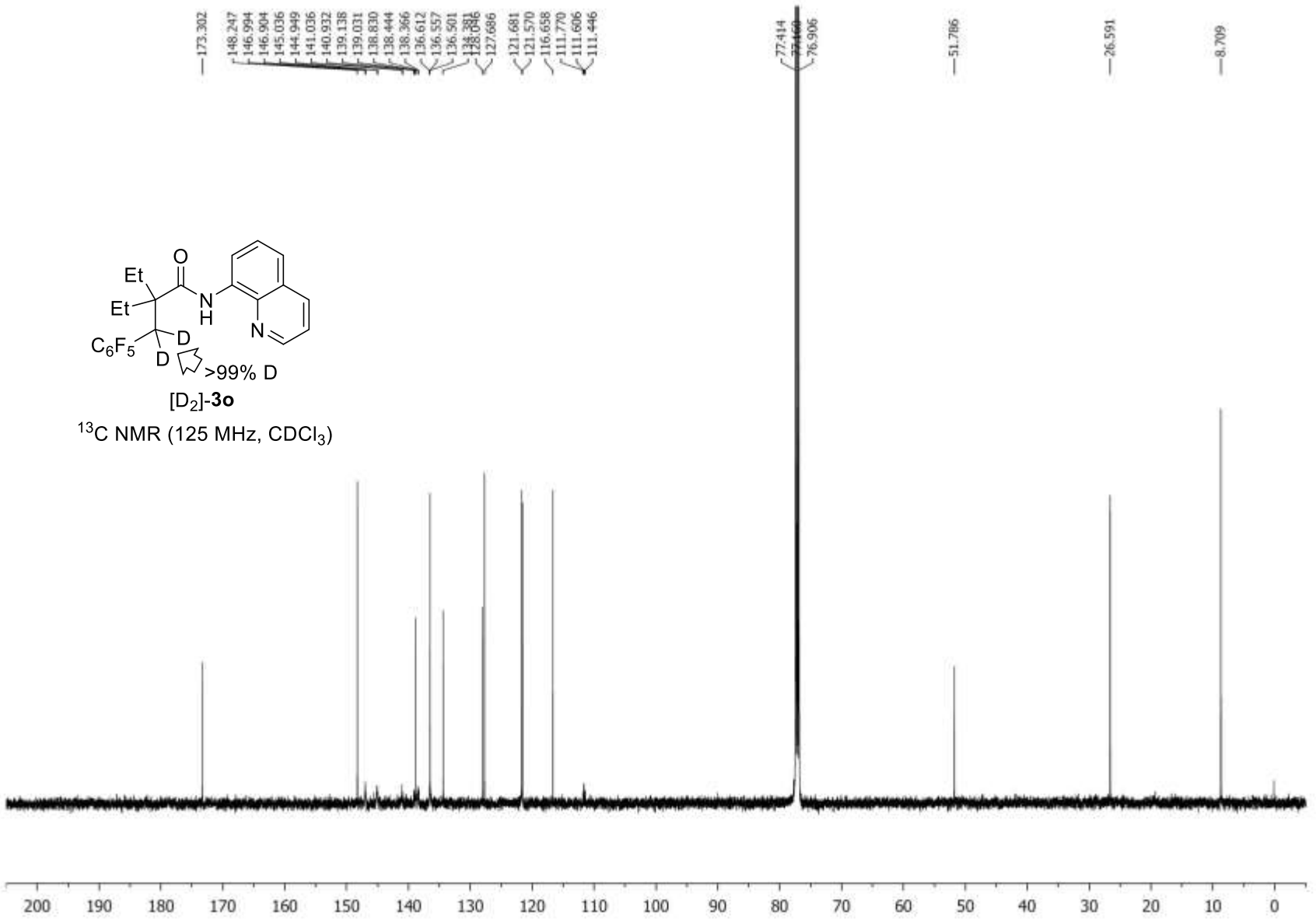
recovered **1b**, >99% H

^{1}H NMR (500 MHz, $CDCl_3$)



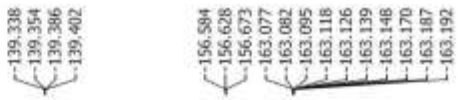
[D_2]-**3o**

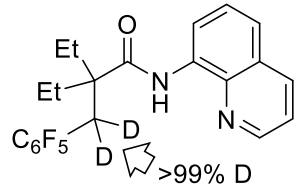
^{1}H NMR (500 MHz, $CDCl_3$)



$[D_2]$-**3o**

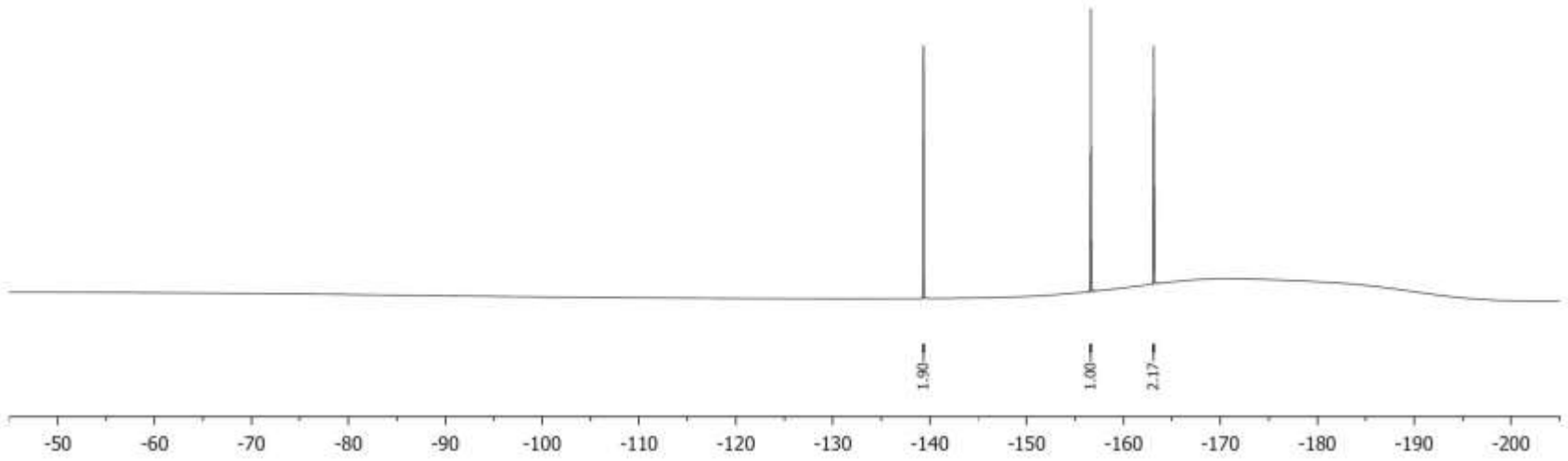
^{13}C NMR (125 MHz, $CDCl_3$)

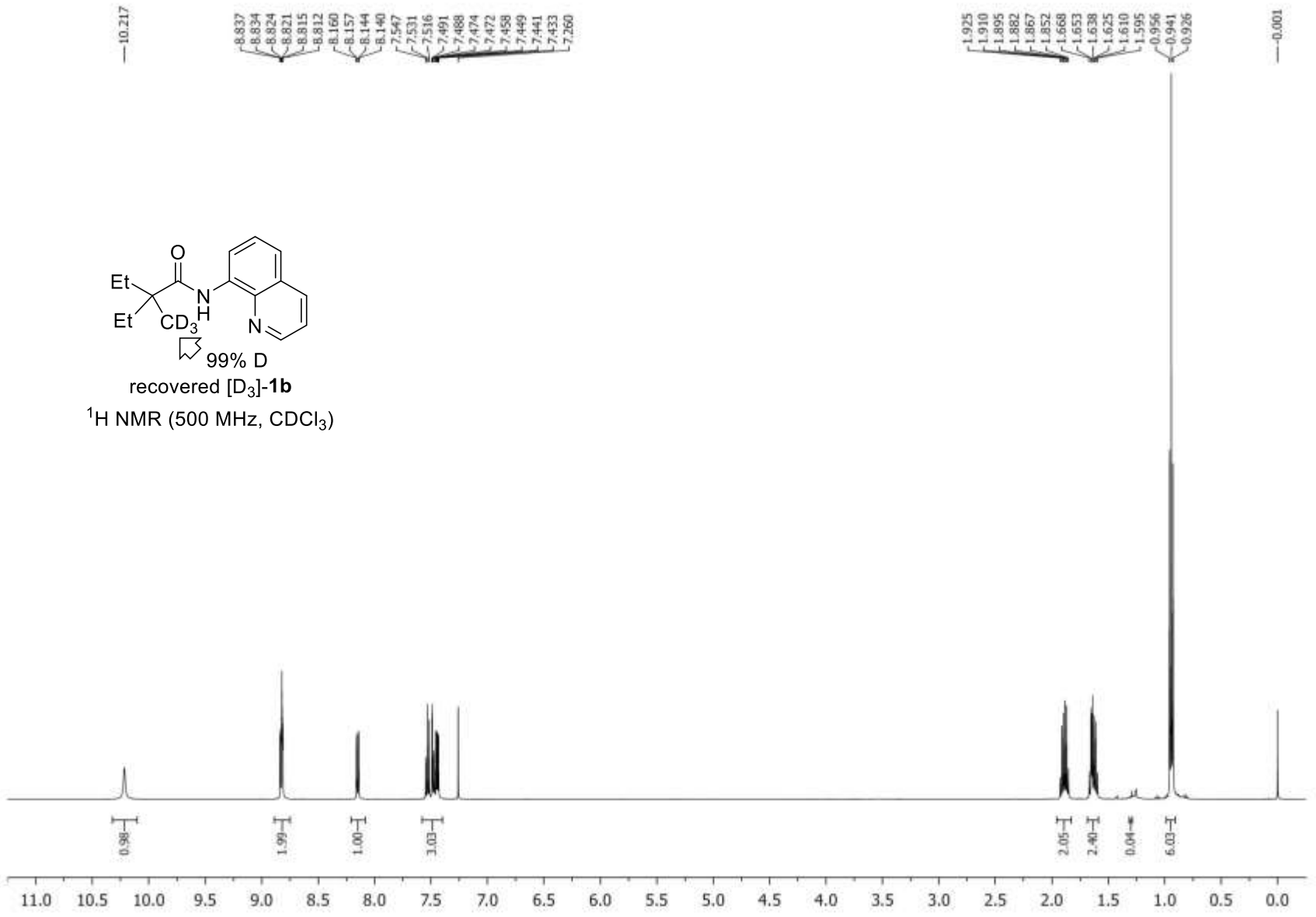




[D_2]-**3o**

^{19}F NMR (471 MHz, $CDCl_3$)





recovered [D_3]-**1b**

^{1}H NMR (500 MHz, $CDCl_3$)