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ORGANIC CHEMISTRY
FRONTIERS

Supporting Information

Trisannulation of Benzamides and Cyclohexadienone-Tethered 1,1-Disubstituted Allenes Initiated by Cp*Rh(III)-Catalyzed C-H Activation

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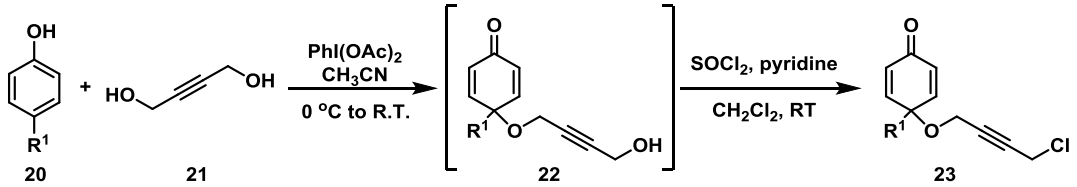
1. GENERALINFORMATION

All solvents were dried before use. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification.All reactions used standard Schlenk techniques and the mixtures were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light. Nuclear Magnetic Resonance (NMR) spectrawas acquired on Agilent400or Bruker 400 instrumentoperating at 400MHz for ^{1}H,and 100MHz for^{13}C. $CDCl_3$(δ = 7.26 ppm for ^{1}H and δ = 77.10 ppm for ^{13}C) was used as the solvent. IR spectra were recorded on a Nicolet iN 10 MX. ESI mass spectra were recorded on an Agilent1200/G6100A.

2.SUBSTRATE PREPARATION

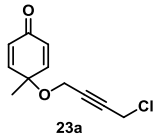
1.1 General Procedures for the Preparation of Cyclohexadienone-tethered Alkynes



20 21 22 23

A well-stirred solution of substituted phenol **20** (100.0 mmol, 1.0 equiv) and 2-Butyne-1,4-diol **21** (400.0 mmol, 4.0 equiv) in 200 mLacetonitrilewere cooled to 0^{o} Cand treated withphenyliodine (III) diacetate (PIDA, 48.3 g, 150.0 mmol, 1.5 equiv) in several portions. The resulting mixturewas warmed to room temperature and stirred for 20-40min. Then it was diluted with water (300 mL) andextracted with EtOAc (400 mL). The organic phases were washed with water (300 mL×4), dried over anhydrous $Na_2SO_4$and concentrated under reduced pressure. The residue was purified by flashcolumn chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to afford the crude intermediateproduct **22**. Subsequently, the solution of **22** (0.5 M in DCM) was treated with pyridine (1.8 equiv based on **22**), and $SOCl_2$ (1.5 equiv based on **22**) was added by drop at r.t. After 12h, the reaction mixture was concentratedunder reduced pressure, and the residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure substrates **23**.

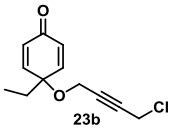
4-((4-Chlorobut-2-yn-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (23a)



23a

R_f = 0.5 (PE/EA = 3/1). Yellow oil. 756.1 mg, 31.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.82 (d, J = 10.2 Hz, 2H), 6.31 (d, J = 10.1 Hz, 2H), 4.15 (t, J = 2.0 Hz, 2H), 4.04 (t, J = 2.0 Hz, 2H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.8, 150.5, 130.5, 83.0, 81.5, 73.2, 53.8, 30.2, 26.2; ESI-MS: $[M+H]^{\oplus}$ 211.0; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{11}H_{12}O_2Cl^{\oplus}$211.0520, found 211.0519; IR (KBr) ν (cm^{-1}) 2983.5, 1674.3, 1631.8, 1383.0, 1265.7, 862.2.

4-((4-Chlorobut-2-yn-1-yl)oxy)-4-ethylcyclohexa-2,5-dien-1-one (23b)

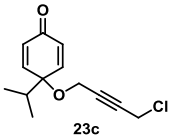


23b

R_f = 0.5 (PE/EA = 3/1). Yellow oil. 1.4 g, 17.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.73 (dd, J = 10.2, 1.6 Hz, 2H), 6.33 (dd, J = 10.3, 2.0 Hz, 2H), 4.12 (q, J = 1.9 Hz, 2H), 4.03 (q, J = 2.0 Hz, 2H), 1.78 (qd, J = 7.6, 1.9 Hz, 2H), 0.79 (td, J = 7.6, 1.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.2, 149.7, 131.7, 83.2, 81.4, 77.4, 53.7, 32.1, 30.3, 7.7; ESI-MS: $[M+H]^{\oplus}$ 225.1; HRMS (ESI):

$[M+H]^{\oplus}$calcd for $C_{12}H_{14}O_2Cl^{\oplus}$225.0667, found 225.0676; IR (KBr) ν (cm^{-1}) 2971.6, 1669.9, 1393.3, 1365.1, 1053.9, 859.5.

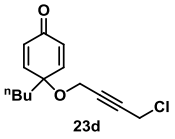
4-((4-Chlorobut-2-yn-1-yl)oxy)-4-isopropylcyclohexa-2,5-dien-1-one (23c)



23c

R_f = 0.6 (PE/EA = 2/1). Yellow oil. 252.4 mg, 4.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.77 (d, J = 10.3 Hz, 2H), 6.41 (d, J = 10.3 Hz, 2H), 4.16 (t, J = 2.0 Hz, 2H), 4.06 (t, J = 2.0 Hz, 2H), 2.05 (p, J = 6.9 Hz, 1H), 0.95 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.2, 148.8, 132.3, 83.4, 81.2, 78.9, 53.6, 36.4, 30.3, 16.9; DART-MS: $[M+H]^{\oplus}$ 239.1; HRMS (DART): $[M+H]^{\oplus}$calcd for $C_{13}H_{16}O_2Cl^{\oplus}$239.0833, found 239.0833; IR (KBr) ν (cm^{-1}) 2965.9, 1669.4, 1629.9, 1385.0, 1049.0, 854.7.

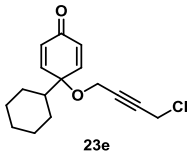
4-Butyl-4-((4-chlorobut-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one (23d)



23d

R_f = 0.5 (PE/EA = 3/1). Yellow oil. 940.0 mg, 9.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.77 (d, J = 10.2 Hz, 2H), 6.35 (d, J = 10.2 Hz, 2H), 4.15 (t, J = 2.0 Hz, 2H), 4.05 (t, J = 2.0 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.36 – 1.13 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.2, 150.0, 131.5, 83.2, 81.4, 76.4, 53.6, 39.0, 30.3, 25.4, 22.7, 13.7; ESI-MS: $[M+H]^{\oplus}$ 252.2; HRMS (ESI): $[M+Na]^{\oplus}$calcd for $C_{14}H_{17}O_2ClNa^{\oplus}$275.0809, found 275.0805; IR (KBr) ν (cm^{-1}) 2937.0, 1697.8, 1627.8, 1389.1, 1265.7, 1025.4, 878.1, 702.4.

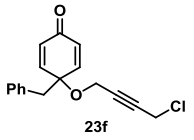
1-((4-Chlorobut-2-yn-1-yl)oxy)-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (23e)



23e

R_f = 0.5 (PE/EA = 5/1). Yellow oil. 926.0 mg, 7.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.78 (d, J = 10.3 Hz, 2H), 6.38 (d, J = 10.3 Hz, 2H), 4.15 (t, J = 2.0 Hz, 2H), 4.04 (t, J = 2.0 Hz, 2H), 1.89 (d, J = 12.8 Hz, 2H), 1.80 – 1.63 (m, 4H), 1.28 – 1.14 (m, 3H), 0.94 (td, J = 12.5, 3.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 185.4, 149.3, 132.0, 83.4, 81.2, 78.6, 53.4, 46.4, 30.3, 27.2, 26.3, 26.3; ESI-MS: $[M+H]^{\oplus}$ 279.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{16}H_{20}O_2Cl^{\oplus}$279.1146, found 279.1148; IR (KBr) ν (cm^{-1}) 2929.2, 2854.4, 1670.4, 1630.3, 1451.0, 1265.2, 1054.6.

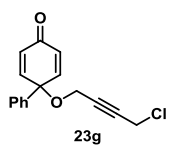
4-Benzyl-4-((4-chlorobut-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one (23f)



23f

R_f = 0.5 (PE/EA = 4/1). Yellow oil. 1.8 g, 21.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.28 – 7.21 (m, 3H), 7.16 – 7.13 (m, 2H), 6.78 (d, J = 10.3 Hz, 2H), 6.28 (d, J = 10.3 Hz, 2H), 4.14 (t, J = 2.0 Hz, 2H), 4.06 (t, J = 2.0 Hz, 2H), 3.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.9, 149.4, 134.3, 131.4, 130.6, 128.0, 127.1, 83.2, 81.5, 76.2, 53.9, 46.1, 30.3; ESI-MS: $[M+H]^{\oplus}$ 287.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{17}H_{16}O_2Cl^{\oplus}$287.0833, found 287.0831; IR (KBr) ν (cm^{-1}) 2859.0, 1670.4, 1459.2, 1264.8, 1050.6, 861.0.

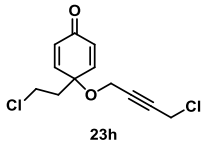
1-((4-Chlorobut-2-yn-1-yl)oxy)-[1,1'-biphenyl]-4(1*H*)-one (23g)



23g

R_f = 0.8 (PE/EA = 5/1). Yellow oil. 215 mg, 2.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.49 – 7.44 (m, 2H), 7.40 – 7.29 (m, 3H), 6.88 (d, J = 10.2 Hz, 2H), 6.41 (d, J = 10.1 Hz, 2H), 4.30 (t, J = 2.0 Hz, 2H), 4.18 (t, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.3, 149.4, 137.4, 130.0, 128.8, 128.5, 125.7, 83.2, 81.7, 76.9, 53.6, 30.3; ESI-MS: $[M+H]^{\oplus}$ 273.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{16}H_{14}O_2Cl^{\oplus}$273.0677, found 273.0679; IR (KBr) ν (cm^{-1}) 1653.8, 1487.8, 1265.1, 1141.6, 976.0, 680.4.

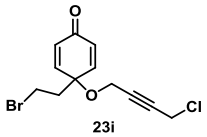
4-((4-Chlorobut-2-yn-1-yl)oxy)-4-(2-chloroethyl)cyclohexa-2,5-dien-1-one (23h)



23h

R_f = 0.4 (PE/EA = 4/1). Yellow oil. 924.0 mg, 4.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.80 (d, J = 10.2 Hz, 2H), 6.39 (d, J = 10.3 Hz, 2H), 4.13 (t, J = 2.0 Hz, 2H), 4.03 (t, J = 2.0 Hz, 2H), 3.10 – 3.04 (m, 2H), 2.40 – 2.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.5, 148.3, 132.1, 82.8, 81.8, 76.5, 53.8, 44.0, 30.2; ESI-MS: $[M+H]^{\oplus}$ 259.0; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{12}H_{13}O_2Cl_2^{\oplus}$259.0287, found 259.0286; IR (KBr) ν (cm^{-1}) 1671.3, 1631.1, 1382.0, 1264.3, 1058.5, 861.2.

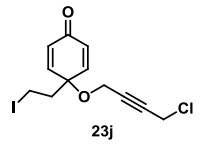
4-(2-Bromoethyl)-4-((4-chlorobut-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one (23i)



23i

R_f = 0.2 (PE/EA = 5/1). Yellow oil. 1.3g, 9.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)6.83 (d, J = 10.2 Hz, 2H), 6.41 (d, J = 10.2 Hz, 2H), 4.15 (t, J = 2.0 Hz, 2H), 4.06 (t, J = 2.0 Hz, 2H), 3.41 – 3.32 (m, 2H), 2.43 – 2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)184.5, 148.3, 132.0, 82.8, 81.8, 75.5, 53.7, 42.7, 30.2, 25.3; ESI-MS: $[M+H]^{\oplus}$302.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{12}H_{13}O_2ClBr^{\oplus}$302.9782, found 302.9784; IR (KBr) ν (cm^{-1}) 1671.4, 1630.7, 1381.9, 1264.2, 1055.3, 861.4.

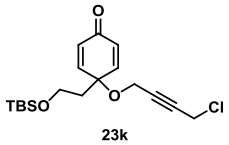
4-((4-Chlorobut-2-yn-1-yl)oxy)-4-(2-iodoethyl)cyclohexa-2,5-dien-1-one (23j)



23j

R_f = 0.6 (PE/EA = 4/1). Yellow oil. 2.5 g, 8.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.82 (d, J = 10.2 Hz, 2H), 6.37 (d, J = 10.2 Hz, 2H), 4.13 (t, J = 2.0 Hz, 2H), 4.03 (t, J = 2.0 Hz, 2H), 3.52 (t, J = 7.6 Hz, 2H), 2.23 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.6, 148.5, 131.8, 82.8, 81.8, 74.8, 53.6, 42.4, 38.4, 30.2; ESI-MS: $[M+H]^{\oplus}$ 250.9; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{12}H_{13}O_2ClI^{\oplus}$350.9643, found 350.9640; IR (KBr) ν (cm^{-1}) 1670.1, 1630.6, 1433.1, 1262.9, 1181.0, 1052.1, 860.6.

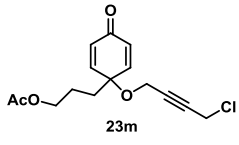
4-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-4-((4-chlorobut-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one (23k)



23k

R_f = 0.8 (PE/EA = 4/1). Yellow oil. 201mg, 6.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.85 (d, J = 10.2 Hz, 2H), 6.31 (d, J = 10.2 Hz, 2H), 4.13 (t, J = 2.0 Hz, 2H), 4.03 (t, J = 2.0 Hz, 2H), 3.67 (t, J = 6.0 Hz, 2H), 1.98 (t, J = 6.1 Hz, 2H), 0.84 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.2, 149.9, 130.8, 83.2, 81.4, 75.0, 57.7, 53.4, 42.7, 30.2, 25.7, 18.0, -5.5; ESI-MS: $[M+H]^{\oplus}$355.2; HRMS (ESI): $[M+Na]^{\oplus}$calcd for $C_{18}H_{27}O_3ClNaSi^{\oplus}$377.1310, found 377.1305; IR (KBr) ν (cm^{-1}) 3481.7, 2971.2, 1669.1, 1632.1, 1380.6, 1053.2, 859.9.

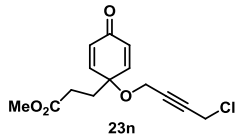
3-(1-((4-Chlorobut-2-yn-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propyl acetate (23m)



23m

R_f = 0.2 (PE/EA = 5/1). Yellow oil. 4.1 g, 9.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.79 (d, J = 10.2 Hz, 2H), 6.38 (d, J = 10.2 Hz, 2H), 4.15 (t, J = 2.0 Hz, 2H), 4.06 (t, J = 2.0 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 2.03 (s, 3H), 1.86 – 1.80 (m, 2H), 1.66 – 1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.8, 170.8, 149.3, 131.7, 83.0, 81.5, 75.8, 63.7, 53.6, 35.7, 30.2, 22.8, 20.8; ESI-MS: $[M+Na]^{\oplus}$319.0; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{15}H_{18}O_4Cl^{\oplus}$297.0883, found 297.0886; IR (KBr) ν (cm^{-1}) 2956.9, 1736.3, 1670.6, 1383.8, 1239.5, 1056.5, 826.3.

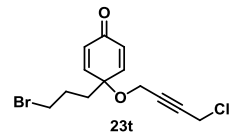
Ethyl 3-(1-((4-chlorobut-2-yn-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propanoate (23n)



23n

R_f = 0.5 (PE/EA = 4/1). Yellow oil. 485 mg, 4.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.76 (d, J = 10.2 Hz, 2H), 6.35 (d, J = 10.2 Hz, 2H), 4.12 (t, J = 2.0 Hz, 2H), 4.03 (t, J = 2.0 Hz, 2H), 3.62 (s, 3H), 2.30 (dd, J = 8.5, 7.1 Hz, 2H), 2.11 (dd, J = 8.6, 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.7, 172.7, 148.8, 131.9, 82.9, 81.6, 75.4, 53.8, 51.7, 34.0, 30.2, 28.3; DATR-MS: $[M+H]^{\oplus}$283.1; HRMS (DATR): $[M+H]^{\oplus}$calcd for $C_{14}H_{16}O_4Cl^{\oplus}$283.0732, found 283.0733; IR (KBr) ν (cm^{-1}) 2952.6, 1736.3, 1671.4, 1437.2, 1265.1, 1059.9, 862.2.

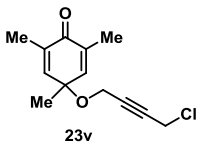
4-(3-Bromopropyl)-4-((4-chlorobut-2-yn-1-yl)oxy)cyclohexa-2,5-dien-1-one (23t)



23t

R_f = 0.6 (PE/EA = 4/1). Yellow oil. 9.0 g, 7.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.79 (d, J = 10.1 Hz, 2H), 6.37 (d, J = 10.2 Hz, 2H), 4.14 (t, J = 2.0 Hz, 2H), 4.06 (t, J = 2.0 Hz, 2H), 3.51 (t, J = 6.3 Hz, 1H), 3.37 (t, J = 6.2 Hz, 1H), 1.96 – 1.89 (m, 2H), 1.88 – 1.81 (m, 1H), 1.81 – 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.8, 149.3, 131.8, 83.0, 81.6, 75.7,53.7, 44.5, 37.9, 36.7, 32.9, 30.2, 26.7; DART-MS: $[M+H]^{\oplus}$316.0; HRMS (DART): $[M+H]^{\oplus}$calcd for $C_{13}H_{15}O_2BrCl^{\oplus}$316.9938, found 316.9940; IR (KBr) ν (cm^{-1}) 2958.1, 1670.0, 1630.4, 1382.4, 1056.1.

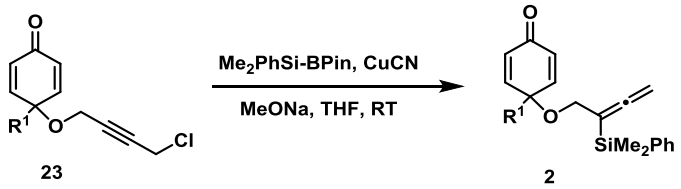
4-((4-Chlorobut-2-yn-1-yl)oxy)-2,4,6-trimethylcyclohexa-2,5-dien-1-one (23v)



23v

R_f = 0.8 (PE/EA = 5/1). Yellow oil. 450 mg, 4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.54 (s, 2H), 4.16 (s, 2H), 4.00 (s, 2H), 1.92 (s, 6H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 186.5, 145.6, 137.0, 83.8, 81.2, 73.3, 53.4, 30.4, 26.6, 16.0; EI-MS: $[M–Cl]^{\oplus}$203; HRMS (DART): $[M+H]^{\oplus}$calcd for $C_{13}H_{16}O_2Cl^{\oplus}$239.0833, found 239.0833; IR (KBr) ν (cm^{-1}) 2979.7, 1674.0, 1642.4, 1371.2, 1070.8, 905.

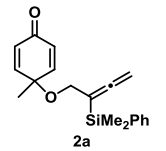
1.2 General Procedures for the Preparation of Cyclohexadienone-tethered 1,1-Disubstituted Allenes



23 2

A dried Schlenk flask was charged with CuCN (45.0 mg, 0.5 mmol, 0.5 equiv), MeONa (108.0 mg, 2.0 equiv), Me_2PhSi-BPin (314 mg, 1.2mmol, 1.2 equiv) and dry THF (5.0 mL) under argon atmosphere. After the mixture was stirred at roomtemperature for 5 min, a solution of substrate **23** (1.0 mmol) in dry THF (5.0 mL) was added, theresulting mixture was stirred at roomtemperature for 4 to 10 hours. Then the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by flash silica gel (300–400 mesh) chromatography to afford the desired product **2**.

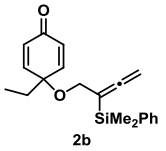
4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (2a)



2a

R_f = 0.8 (PE/EA = 3/1). Yellow oil. 2.5 g, 81.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.55 (dd, J = 7.3, 2.3 Hz, 2H), 7.42 – 7.31 (m, 3H), 6.46 (d, J = 10.2 Hz, 2H), 6.14 (d, J = 10.2 Hz, 2H), 4.50 (t, J = 2.5 Hz, 2H), 3.84 (t, J = 2.5 Hz, 2H), 1.31 (s, 3H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.1, 151.7, 137.4, 133.9, 129.8, 129.2, 127.7, 92.9, 72.4, 70.1, 65.7, 26.1, -2.5; ESI-MS: $[M+Na]^{\oplus}$333.0; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{19}H_{23}O_2Si^{\oplus}$311.1462, found 311.1460; IR (KBr) ν (cm^{-1}) 2966.5, 1931.9, 1669.3, 1249.9, 1058.9, 859.4.

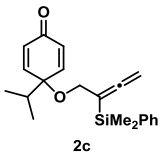
4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-ethylcyclohexa-2,5-dien-1-one (2b)



2b

R_f = 0.5 (PE/EA = 4/1). Yellow oil. 255 mg, 79.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.58 – 7.50 (m, 2H), 7.42 – 7.31 (m, 3H), 6.42 (d, J = 10.2 Hz, 2H), 6.21 (d, J = 10.3 Hz, 2H), 4.49 (t, J = 2.6 Hz, 2H), 3.87 (t, J = 2.6 Hz, 2H), 1.67 (q, J = 7.6 Hz, 2H), 0.75 (t, J = 7.6 Hz, 3H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.4, 151.0, 137.4, 133.9, 131.0, 129.2, 127.7, 92.9, 76.1, 70.1, 65.6, 32.1, 7.8, -2.4; ESI-MS: $[M+Na]^{\oplus}$347.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{20}H_{25}O_2Si^{\oplus}$325.1618, found 325.1617; IR (KBr) ν (cm^{-1}) 2965.9, 1932.1, 1669.6, 1427.9, 1249.8, 812.7.

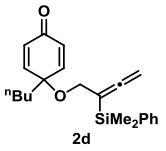
4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-isopropylcyclohexa-2,5-dien-1-one (2c)



2c

R_f = 0.8 (PE/EA = 5/1). Yellow oil. 262mg, 79.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.55 – 7.51 (m, 2H), 7.40 – 7.32 (m, 3H), 6.46 (d, J = 10.3 Hz, 2H), 6.24 (d, J = 10.3 Hz, 2H), 4.49 (t, J = 2.6 Hz, 2H), 3.85 (t, J = 2.6 Hz, 2H), 1.89 (p, J = 6.9 Hz, 1H), 0.84 (d, J = 6.9 Hz, 6H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.5, 150.1, 137.4, 133.9, 131.7, 129.2, 127.7, 93.0, 78.2, 70.1, 65.4, 36.5, 17.0, -2.4; ESI-MS: $[M+Na]^{\oplus}$361.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{21}H_{27}O_2Si^{\oplus}$339.1775, found 339.1773; IR (KBr) ν (cm^{-1}) 2962.7, 1931.6, 1669.9, 1427.7, 1248.4, 1049.3.

4-Butyl-4-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2d)

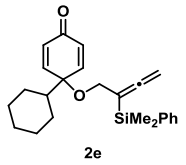


2d

R_f = 0.8 (PE/EA = 10/1). Yellow oil. 327 mg, 93.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57 – 7.51 (m, 2H), 7.41 – 7.32 (m, 3H), 6.44 (d, J = 10.2 Hz, 2H), 6.19 (d, J = 10.2 Hz, 2H), 4.49 (t, J = 2.6 Hz, 2H), 3.86 (t, J = 2.6 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.24 (q, J = 7.3 Hz, 2H), 1.16 – 1.06 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H),

0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.4, 151.2, 137.4, 133.9, 130.7, 129.2, 127.7, 92.9, 75.6, 70.1, 65.5, 39.0, 25.4, 22.8, 13.8, -2.5; ESI-MS: $[M+H]^{\oplus}$353.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{22}H_{29}O_2Si^{\oplus}$353.1931, found 353.1928; IR (KBr) ν (cm^{-1}) 2957.5, 1932.4, 1671.0, 1248.0, 1050.2, 815.3.

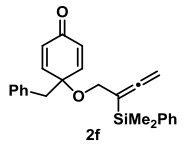
1-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (2e)



2e

R_f = 0.8 (PE/EA = 5/1). Yellow oil. 303.5 mg, 80.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.56 – 7.51 (m, 2H), 7.39 – 7.31 (m, 3H), 6.49 (d, J = 10.3 Hz, 2H), 6.22 (d, J = 10.3 Hz, 2H), 4.49 (t, J = 2.6 Hz, 2H), 3.85 (t, J = 2.6 Hz, 2H), 1.72 (t, J = 15.5 Hz, 4H), 1.63 (d, J = 12.2 Hz, 1H), 1.52 (dt, J = 12.4, 3.0 Hz, 1H), 1.19 – 0.99 (m, 3H), 0.87 – 0.72 (m, 2H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.3, 185.7, 150.6, 137.5, 133.9, 131.3, 129.1, 127.7, 93.0, 77.9, 70.0, 65.1, 46.5, 27.2, 26.41, 26.37, -2.54; ESI-MS: $[M+H]^{\oplus}$379.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{24}H_{31}O_2Si^{\oplus}$379.2088, found 379.2083; IR (KBr) ν (cm^{-1}) 2928.0, 1931.0, 1670.5, 1248.1, 1059.9, 815.3.

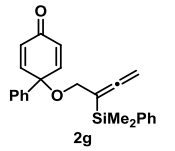
4-Benzyl-4-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2f)



2f

R_f = 0.6 (PE/EA = 4/1). Yellow oil. 335.0mg, 84.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.55 – 7.50 (m, 2H), 7.41 – 7.33 (m, 3H), 7.23 – 7.20 (m, 3H), 7.09 – 7.05 (m, 2H), 6.46 (d, J = 10.2 Hz, 2H), 6.13 (d, J = 10.2 Hz, 2H), 4.51 (t, J = 2.6 Hz, 2H), 3.86 (t, J = 2.6 Hz, 2H), 2.90 (s, 2H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.4, 185.1, 150.7, 137.4, 134.6, 133.9, 130.7, 130.7, 129.2, 127.8, 127.7, 126.9, 92.8, 75.5, 70.1, 65.7, 46.2, -2.5; ESI-MS: $[M+H]^{\oplus}$387.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{25}H_{27}O_2Si^{\oplus}$387.1775, found 387.1771; IR (KBr) ν (cm^{-1}) 2956.2, 1930.9, 1670.4, 1629.4, 1248.0, 1054.7, 815.2.

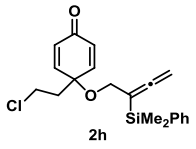
1-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-[1,1'-biphenyl]-4(1H)-one (2g)



2g

R_f = 0.8 (PE/EA = 5/1). Yellow oil. 317.9mg, 85.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.55 (dd, J = 7.7, 1.7 Hz, 2H), 7.35 (qd, J = 8.5, 7.7, 3.6 Hz, 3H), 7.28 (s, 5H), 6.57 (d, J = 10.1 Hz, 2H), 6.26 (d, J = 10.1 Hz, 2H), 4.56 (t, J = 2.5 Hz, 2H), 4.09 (t, J = 2.5 Hz, 2H), 0.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.7, 185.5, 150.5, 137.9, 137.4, 133.9, 129.5, 129.2, 128.6, 128.1, 127.8, 125.7, 92.8, 76.4, 70.3, 65.2, -2.5; ESI-MS: $[M+Na]^{\oplus}$395.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{24}H_{25}O_2Si^{\oplus}$373.1618, found 373.1621; IR (KBr) ν (cm^{-1}) 2957.8, 1931.1, 1629.2, 1488.6, 1248.8, 1057.9, 815.9.

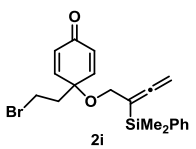
4-(2-Chloroethyl)-4-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2h)



2h

R_f = 0.8 (PE/EA = 4/1). Yellow oil. 286 mg, 80.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57 – 7.50 (m, 2H), 7.44 – 7.32 (m, 3H), 6.47 (d, J = 10.2 Hz, 2H), 6.22 (d, J = 10.2 Hz, 2H), 4.52 (t, J = 2.5 Hz, 2H), 3.85 (t, J = 2.5 Hz, 2H), 3.42 – 3.33 (m, 2H), 2.10 – 2.03 (m, 2H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.3, 184.6, 149.6, 137.4, 133.8, 131.1, 129.3, 127.8, 92.7, 74.1, 70.2, 65.4, 42.6, 38.5, -2.5; ESI-MS: $[M+Na]^{\oplus}$381.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{20}H_{24}O_2SiCl^{\oplus}$359.1229, found 359.1228; IR (KBr) ν (cm^{-1}) 2957.2, 1931.1, 1670.7, 1251.7, 1112.0, 833.4.

4-(2-Bromoethyl)-4-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2i)

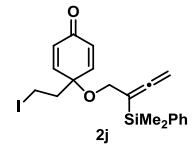


2i

R_f = 0.8 (PE/EA = 5/1). Yellow oil. 342.1 mg, 85.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57 – 7.51 (m, 2H), 7.42 – 7.35 (m, 3H), 6.46 (d, J = 10.2 Hz, 2H),

6.23 (d, *J* = 10.2 Hz, 2H), 4.52 (t, *J* = 2.5 Hz, 2H), 3.84 (t, *J* = 2.5 Hz, 2H), 3.21 – 3.16 (m, 2H), 2.18 – 2.12 (m, 2H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.3, 184.7, 149.5, 137.4, 133.8, 131.2, 127.8, 92.7, 74.7, 70.2, 65.5, 42.9, 25.6, -2.6; ESI-MS: $[M+H]^{\oplus}$403.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{20}H_{24}O_2SiBr^{\oplus}$403.0725, found 403.0723; IR (KBr) ν (cm^{-1}) 2954.0, 1967.1, 1683.7, 1255.0, 1049.9, 863.1.

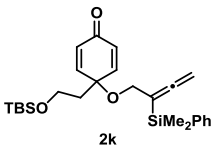
4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-(2-iodoethyl)cyclohexa-2,5-dien-1-one (2j)



2j

R_f = 0.7 (PE/EA = 4/1). Yellow oil. 360 mg, 80.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.58 – 7.48 (m, 2H), 7.45 – 7.29 (m, 3H), 6.44 (d, *J* = 10.3 Hz, 2H), 6.24 (d, *J* = 10.3 Hz, 2H), 4.51 (t, *J* = 2.5 Hz, 2H), 3.85 (t, *J* = 2.5 Hz, 2H), 2.96 – 2.88 (m, 2H), 2.23 – 2.15 (m, 2H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.3, 184.6, 149.3, 137.4, 133.8, 131.4, 129.3, 127.8, 92.7, 75.8, 70.3, 65.6, 44.2, -2.5, -3.8; ESI-MS: $[M+Na]^{\oplus}$473.0; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{20}H_{24}O_2SiI^{\oplus}$451.0585, found 451.0585; IR (KBr) ν (cm^{-1}) 2954.9, 1930.9, 1669.7, 1427.3, 1054.0, 811.3.

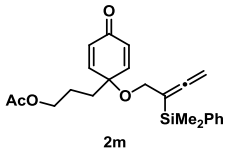
4-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-4-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2k)



2k

R_f = 0.6 (PE/EA = 10/1). Yellow oil. 130.0 mg, 71.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57 – 7.53 (m, 2H), 7.41 – 7.34 (m, 3H), 6.54 (d, *J* = 10.2 Hz, 2H), 6.18 (d, *J* = 10.2 Hz, 2H), 4.51 (t, *J* = 2.6 Hz, 2H), 3.86 (t, *J* = 2.6 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 1.86 (t, *J* = 6.3 Hz, 2H), 0.87 (s, 9H), 0.44 (s, 6H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.3, 151.0, 137.4, 133.9, 130.2, 129.2, 127.7, 92.9, 74.2, 70.1, 65.2, 57.9, 42.8, 25.8, 18.1, -2.5, -5.4; ESI-MS: $[M+H]^{\oplus}$455.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{26}H_{39}O_3Si_2^{\oplus}$455.2432, found 455.2428; IR (KBr) ν (cm^{-1}) 2955.0, 1932.8, 1672.3, 1391.0, 1251.3, 836.9.

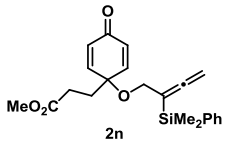
3-(1-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propyl acetate (2m)



2m

R_f = 0.5 (PE/EA = 4/1). Yellow oil. 282 mg, 48.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57 – 7.50 (m, 2H), 7.41 – 7.31 (m, 3H), 6.45 (d, *J* = 10.2 Hz, 2H), 6.21 (d, *J* = 10.2 Hz, 2H), 4.50 (t, *J* = 2.5 Hz, 2H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.86 (t, *J* = 2.5 Hz, 2H), 2.03 (s, 3H), 1.70 – 1.61 (m, 2H), 1.55 – 1.44 (m, 2H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.1, 170.9, 150.5, 137.4, 133.9, 131.0, 129.2, 127.7, 92.8, 74.9, 70.1, 65.5, 64.0, 35.8, 22.8, 20.8, -2.5; ESI-MS: $[M+H]^{\oplus}$397.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{23}H_{29}O_4Si^{\oplus}$397.1830, found 397.1827; IR (KBr) ν (cm^{-1}) 2956.0, 1931.5, 1738.6, 1670.3, 1241.1, 1055.6, 815.1.

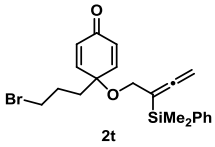
Ethyl3-(1-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propanoate (2n)



2n

R_f = 0.4 (PE/EA = 5/1). Yellow oil. 267.5 mg, 70.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.56 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 6.41 (d, *J* = 10.2 Hz, 2H), 6.20 (d, *J* = 10.2 Hz, 2H), 4.50 (t, *J* = 2.5 Hz, 2H), 3.85 (t, *J* = 2.5 Hz, 2H), 3.64 (s, 3H), 2.19 (dd, *J* = 9.0, 7.0 Hz, 2H), 1.96 (dd, *J* = 8.9, 7.0 Hz, 2H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 210.2, 184.8, 172.9, 150.0, 137.3, 133.9, 131.2, 129.2, 127.7, 92.8, 74.6, 70.1, 65.6, 51.6, 33.9, 28.2, -2.5; ESI-MS: $[M+H]^{\oplus}$ 242.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{22}H_{27}O_4Si^{\oplus}$383.1675, found 383.1673; IR (KBr) ν (cm^{-1}) 2953.6, 1931.6, 1739.3, 1671.6, 1428.1, 1075.0.

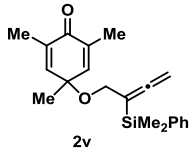
4-(3-Bromopropyl)-4-((2-(dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2t)



2t

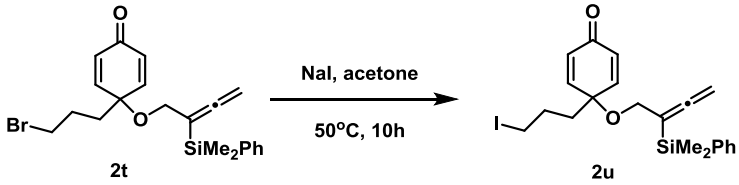
R_f = 0.7 (PE/EA = 10/1). Yellow oil. 1.8 g, 69.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.56 – 7.52 (m, 2H), 7.39 – 7.35 (m, 3H), 6.44 (dd, *J* = 10.5, 2.1 Hz, 2H), 6.21 (d, *J* = 10.3 Hz, 2H), 4.51 (t, *J* = 2.5 Hz, 2H), 3.86 (dd, *J* = 3.3, 2.1 Hz, 2H), 3.44 (t, *J* = 6.2 Hz, 1H), 3.31 (td, *J* = 4.9, 3.8, 1.4 Hz, 1H), 1.77 – 1.67 (m, 4H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 210.2, 185.0, 150.5, 137.4, 133.9, 131.0, 129.2, 127.7, 109.9, 92.8, 74.8, 70.2, 65.5, 44.7, 38.0, 36.7, 33.2, 26.7, 26.6, -2.5; ESI-MS: $[M+H]^{\oplus}$417.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{21}H_{25}BrO_2Si^{\oplus}$417.0880, found 417.0878; IR (KBr) *v* (cm^{-1}) 2957.6, 1931.4, 1670.7, 1427.5, 1070.5, 816.1.

4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-2,4,6-trimethylcyclohexa-2,5-dien-1-one (2v)



2v

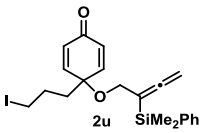
R_f = 0.8 (PE/EA = 4/1). Yellow oil. 200 mg, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.59 – 7.50 (m, 2H), 7.38 (d, *J* = 6.1 Hz, 3H), 6.16 (s, 2H), 4.48 (t, *J* = 2.3 Hz, 2H), 3.80 (t, *J* = 2.3 Hz, 2H), 1.78 (s, 6H), 1.26 (s, 3H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 210.2, 186.6, 146.9, 137.8, 136.1, 134.1, 129.3, 127.8, 93.2, 72.4, 69.9, 65.4, 26.5, 15.9, -2.4; ESI-MS: $[M+H]^{\oplus}$339.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{21}H_{27}O_2Si^{\oplus}$339.1775, found 339.1775; IR (KBr) *v* (cm^{-1}) 2957.1, 1932.3, 1644.8, 1428.1, 1070.4, 815.1.



2t 2u

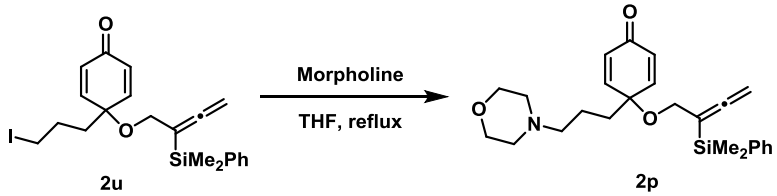
A mixture of **2t** (2.0 g, 4.4 mmol) and NaI (6.5 g, 44.0 mmol, 10 equiv) in acetone (20 mL) was stirredat 50 ^{o}C for 10h. The resulting mixture was concentrated *in vacuo* and the residue was purified by silica gel (300–400 mesh) column chromatography to afford **2u** (1.9 g, 95.0%) as yellow oil.

4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-(3-iodopropyl)cyclohexa-2,5-dien-1-one (2u)



2u

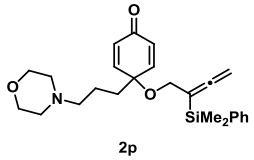
R_f = 0.7 (PE/EA = 10/1). Yellow oil. 1.9 g, 95.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57 – 7.52 (m, 2H), 7.41 – 7.34 (m, 3H), 6.42 (d, *J* = 10.2 Hz, 2H), 6.20 (d, *J* = 10.3 Hz, 2H), 4.51 (t, *J* = 2.6 Hz, 1H), 3.85 (t, *J* = 2.6 Hz, 1H), 3.10 – 3.05 (m, 2H), 1.70 – 1.64 (m, 4H), 0.42 (d, *J* = 0.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)210.2, 185.0, 150.4, 137.4, 133.9, 131.0, 129.2, 127.8, 92.8, 74.7, 70.2, 65.5, 44.7, 40.2, 36.7, 27.4, 26.6, 5.9, -2.5; ESI-MS: $[M+H]^{\oplus}$465.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{21}H_{26}O_2SiI^{\oplus}$465.0741, found 465.0738; IR (KBr) *v* (cm^{-1}) 2956.5, 1931.1, 1670.2, 1629.9, 1248.4, 1056.9815.9.



2u 2p

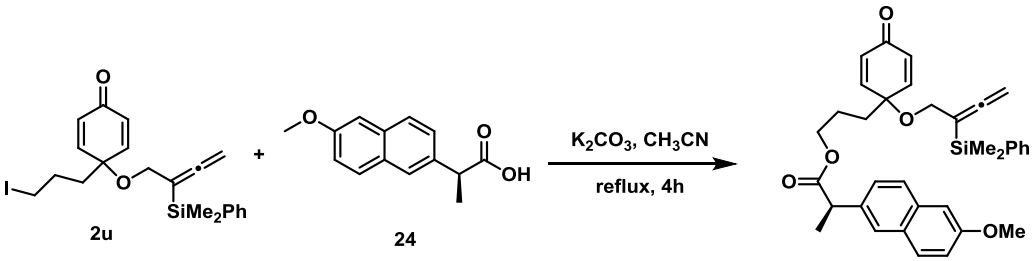
A mixture of **2u** (500.0 mg, 1.1 mmol, 1.0 equiv),morpholine (1.0 mL, 10 equiv) andTHF (5 mL) was stirredat 65^{o}C for 3h. The resulting mixture was concentrated *in vacuo* and the residue was purified by silica gel (300–400 mesh) column chromatography to afford **2p** (260.0 mg, 56.0%) as yellow oil.

4-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-(3-morpholinopropyl)cyclohexa-2,5-dien-1-one (2p)



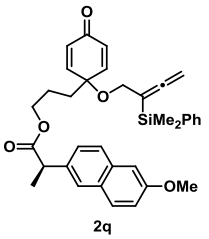
2p

R_f = 0.2 (PE/EA = 1/1). Yellow oil. 260.0mg, 56.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.52 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.39 – 7.31 (m, 2H), 6.43 (d, *J* = 10.3 Hz, 2H), 6.18 (d, *J* = 10.2 Hz, 2H), 4.48 (t, *J* = 2.5 Hz, 2H), 3.85 (t, *J* = 2.6 Hz, 2H), 3.67 (t, *J* = 4.7 Hz, 4H), 2.34 (t, *J* = 4.6 Hz, 4H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.40 – 1.28 (m, 2H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.2, 150.9, 137.4, 133.9, 130.9, 129.2 , 127.7 , 92.8, 75.3, 70.1, 66.8, 65.5, 58.5, 53.5 , 37.0, 20.5, -2.5; ESI-MS: $[M+Na]^{\oplus}$446.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{25}H_{34}O_3NSi^{\oplus}$424.2302, found 424.2302; IR (KBr) *v* (cm^{-1}) 2955.0, 1931.4, 1670.8, 1427.7, 1248.7, 1117.2, 816.1.



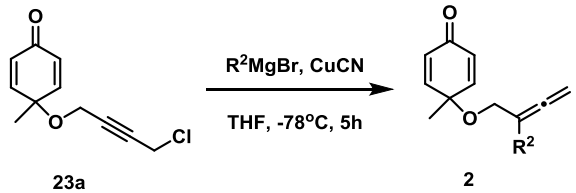
A mixture of **2u** (500.0 mg, 1.1 mmol, 1.0 equiv),(***S***)-naproxen **24** (632mg, 2.7 mmol, 2.5 equiv), K_2CO_3 (910 mg, 6.0 equiv)andCH_3CN (25 mL) was stirredat 85^o C for 4h. After cooled to room temperature, thereaction was quenched with water(30 mL) andextracted with EtOAc (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentratedunder reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the substrate **2q**.

3-(1-((2-(Dimethyl(phenyl)silyl)buta-2,3-dien-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propyl 2-(6-methoxynaphthalen-2-yl)propanoate (2q)



2q

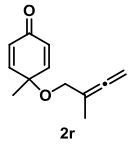
R_f = 0.5 (PE/EA = 4/1). Yellow oil. 341.0mg, 55.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.72 – 7.61 (m, 3H), 7.54 – 7.44 (m, 2H), 7.41 – 7.28 (m, 4H), 7.18 – 7.07 (m, 2H), 6.30 – 6.25 (m, 2H), 6.13 – 6.09 (m, 2H), 4.49 (t, *J* = 2.3 Hz, 2H), 4.05 – 3.93 (m, 2H), 3.91 (s, 3H), 3.85 – 3.75 (m, 3H), 1.56 (d, *J* = 7.4 Hz, 3H), 1.52 – 1.35 (m, 4H), 0.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.2, 185.0, 174.4, 157.6, 150.4(d, *J* = 4.1 Hz), 137.4, 135.5, 133.9, 133.6, 130.9, 130.9, 129.2, 129.2, 128.8, 127.7, 127.1, 126.1, 125.8, 119.0, 105.5, 92.8, 74.7, 70.1, 65.4, 64.2, 55.2, 45.4, 35.7, 22.8, 18.3, -2.5; ESI-MS: $[M+H]^{\oplus}$567.3; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{35}H_{39}O_5Si^{\oplus}$567.2561, found 567.2566; IR (KBr) *v* (cm^{-1}) 2957.4, 1931.3, 1732.0, 1670.3, 1484.7, 1176.5, 1032.7, 815.7.



Under argon atmosphere, a dried Schlenk flask was charged with **23a** (420 mg, 2 mmol, 1.0 equiv), 3 mL dry THFand stirred at -78 ^{o}C. To a suspension ofCuCN (90.0 mg, 0.5 equiv) in 2 mL dry THF was added R^2MgBr (2M in THF, 1.5 mL, 1.5 equiv) and stirred for 20 min at roomtemperature, after which the mixture was added to the Schlenk flask by drop and stirred for another 5h at -78 ^{o}C. Then the reaction

mixture was filtered and concentrated *in vacuo*. The residue was purified by flash silica gel (300–400 mesh) chromatography to afford the desired product **2**.

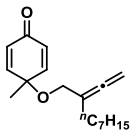
4-Methyl-4-((2-methylbuta-2,3-dien-1-yl)oxy)cyclohexa-2,5-dien-1-one (2r)



2r

R_f = 0.7 (PE/EA = 4/1). Yellow oil. 147.0mg, 37.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.81 (d, J = 10.2 Hz, 2H), 6.28 (d, J = 10.2 Hz, 2H), 4.65 (dt, J = 3.2, 2.2 Hz, 2H), 3.79 (t, J = 2.2 Hz, 2H), 1.71 (t, J = 3.2 Hz, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 207.0, 185.1, 151.8, 129.8, 96.4, 74.7, 72.5, 67.8, 26.3, 15.6; ESI-MS: $[M+H]^{\oplus}$191.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{12}H_{15}O_2^{\oplus}$191.1067, found 191.1066; IR (KBr) v (cm^{-1}) 2928.2, 1673.8, 1631.0, 1382.8, 1082.3, 861.7.

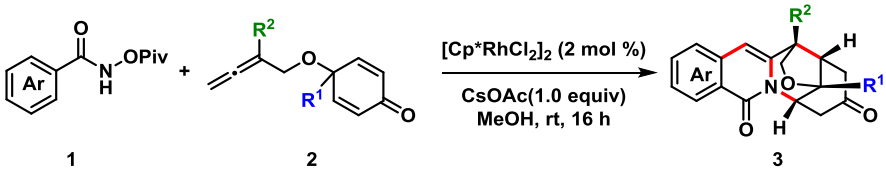
4-Methyl-4-((2-vinylidenenonyl)oxy)cyclohexa-2,5-dien-1-one (2s)



2s

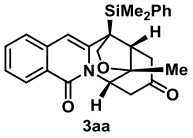
R_f = 0.8 (PE/EA = 4/1). Yellow oil. 90.0mg, 65.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.81 (d, J = 10.1 Hz, 2H), 6.28 (d, J = 10.1 Hz, 2H), 4.71 (td, J = 3.3, 1.6 Hz, 2H), 3.81 (t, J = 2.2 Hz, 2H), 1.99 (tt, J = 7.3, 3.3 Hz, 2H), 1.45 (s, 3H), 1.33 – 1.22 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.7, 185.1, 151.9, 129.8, 101.3, 75.9, 72.5, 67.0, 31.7, 29.1, 29.0, 28.9, 27.2, 26.3, 22.5, 14.0; ESI-MS: $[M+H]^{\oplus}$275.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{18}H_{27}O_2^{\oplus}$275.2006, found 275.2009; IR (KBr) v (cm^{-1}) 2965.8, 1669.3, 1629.9, 1384.9, 1267.2, 1048.8, 854.3.

3.SCOPE OF THE SUBSTRATES



GENERAL PROCEDURE: Underair atmosphere, the mixture of *N*-(pivaloyloxy)benzamide **1** (1.5 equiv, 0.3 mmol), cyclohexadienone-tethered 1,1-disubstitutedallenes **2** (1.0 equiv, 0.2 mmol), $[Cp^*RhCl_2]_2$(2.4 mg, 0.004 mmol, 2 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv) and methanol (2 mL) was stirred in a Schlenk flask at room temperature for 16h.The resulting mixture was concentrated *in vacuo* and the crude product was purified by silica gel(300−400 mesh)column chromatography using PE/EA=2/1 to afford the desired product **3**.

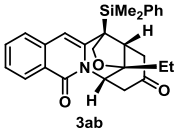
rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-*b*]isoquinoline-5,9(10*H*)-dione (3aa)



3aa

R_f = 0.3 (PE/EA = 1/1). White solid, 82.3 mg, 96.0% yield; Melting point: 215-224℃;^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 (d, *J* = 8.7 Hz, 1H), 7.64 – 7.56 (m, 3H), 7.49 – 7.40 (m, 4H), 7.38 (d, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 4.96 (dt, *J* = 4.4, 2.5 Hz, 1H), 4.17 (d, *J* = 8.1 Hz, 1H), 3.93 (d, *J* = 8.1 Hz, 1H), 2.90 (dd, *J* = 17.9, 2.8 Hz, 1H), 2.70 (d, *J* = 5.5 Hz, 2H), 2.61 (dd, *J* = 17.9, 3.8 Hz, 1H), 2.22 (dt, *J* = 5.8, 3.0 Hz, 1H), 1.53 (s, 3H), 0.67 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.7, 162.5, 141.7, 136.0, 135.0, 134.2, 132.4, 130.1, 128.4, 127.6, 126.7, 125.5, 124.9, 106.9 , 78.0, 77.2, 60.1, 44.9, 44.3, 42.5, 39.1, 22.1, -2.4, -2.7; ESI-MS: $[M+H]^{\oplus}$430.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{26}H_{28}O_3NSi^{\oplus}$430.1833, found 430.1834; IR (KBr) *v* (cm^{-1}) 2966.4, 1710.0, 1650.7, 1618.6, 1163.0, 823.1.

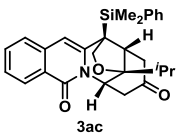
rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-ethyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-*b*]isoquinoline-5,9(10*H*)-dione (3ab)



3ab

R_f = 0.6 (PE/EA = 1/1). White solid, 84.2mg, 95.0% yield; Melting point: 210-215℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 (d, *J* = 8.1 Hz, 1H), 7.62 –7.55(m, 3H), 7.46 –7.41(m, 4H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 5.02 (dt, *J* = 4.4, 2.3 Hz, 1H), 4.11 (d, *J* = 8.1 Hz, 1H), 3.94 (d, *J* = 8.0 Hz, 1H), 2.89 (dd, *J* = 18.1, 2.7 Hz, 1H), 2.64 (d, *J* = 5.5 Hz, 2H), 2.57 (dd, *J* = 18.1, 3.9 Hz, 1H), 2.26 –2.23 (m, 1H), 1.89 (dt, *J* = 14.7, 7.3 Hz, 1H), 1.69 (dt, *J* = 14.5, 7.3 Hz, 1H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.67 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 207.1, 162.6, 142.3, 136.1, 135.1, 134.1, 132.4, 130.1, 128.3, 127.6, 126.7, 125.5, 124.9, 106.9, 79.1, 78.2, 58.7, 44.0, 42.5, 42.0, 39.0, 27.4, 7.1, -2.4, -2.8; ESI-MS: $[M+H]^{\oplus}$444.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{30}O_3NSi^{\oplus}$444.1989, found 444.1989; IR (KBr) *v* (cm^{-1}) 2964.0, 1712.3, 1645.6, 1617.8, 1396.1, 1260.4, 1019.0, 827.5.

rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-isopropyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ac)

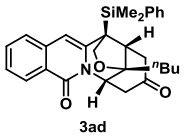


3ac

R_f = 0.2 (PE/EA = 5/1). White solid, 82.3mg, 90.0% yield; Melting point: 213-218℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.50 – 7.36 (m, 5H), 6.54 (s, 1H), 5.16 – 5.14 (m, 1H), 4.02 (d, *J* = 8.1 Hz, 1H), 3.95 (d, *J* = 8.7 Hz, 1H), 2.90 (dd, *J* = 18.3, 2.7 Hz, 1H), 2.60 – 2.55

(m, 3H), 2.44 (td, *J* = 5.6, 1.9 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.11 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.5 Hz, 3H), 0.67 (s, 3H),0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 207.3, 162.7, 142.3, 136.1, 135.1, 134.0, 132.3, 130.1, 128.3, 127.6, 126.6, 125.4, 124.9, 106.6, 80.5, 78.6, 58.2, 43.9, 41.5, 40.1, 38.8, 29.2, 16.9, 15.2, -2.5, -2.9; ESI-MS: $[M+H]^{\oplus}$458.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{28}H_{32}O_3NSi^{\oplus}$458.2146, found 458.2144; IR (KBr) *v* (cm^{-1}) 2964.8, 2876.4, 1715.8, 1648.2, 1402.0, 1061.4, 828.2.

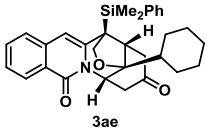
rel-(7*S*,11*R*,12*R*,16*R*)-16-Butyl-12-(dimethyl(phenyl)silyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ad)



3ad

R_f = 0.3 (PE/EA = 4/1). White solid, 88.5 mg, 94.0% yield; Melting point: 208-214℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.48 – 7.34 (m, 5H), 6.54 (s, 1H), 5.05 – 5.00 (m, 1H), 4.12 (d, *J* = 8.0 Hz, 1H), 3.93 (d, *J* = 8.1 Hz, 1H), 2.89 (dd, *J* = 18.1, 2.7 Hz, 1H), 2.68 – 2.63 (m, 2H), 2.58 (dd, *J* = 18.1, 3.9 Hz, 1H), 2.25 – 2.22 (m, 1H), 1.91 – 1.84 (m, 1H), 1.64 – 1.55 (m, 1H), 1.49 – 1.24 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.67 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 207.1, 162.7, 142.2, 136.1, 135.1, 134.1, 132.4, 130.1, 128.3, 127.6, 126.7, 125.5, 124.9, 106.9, 79.0, 78.1, 58.7, 44.0, 43.2, 42.1, 39.0, 34.5, 25.0, 22.9, 13.9, -2.4, -2.8; ESI-MS: $[M+H]^{\oplus}$472.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{29}H_{34}O_3NSi^{\oplus}$472.2302, found 472.2296; IR (KBr) *v* (cm^{-1}) 2955.1, 1708.6, 1648.0, 1596.0, 1395.8, 1022.3, 826.8.

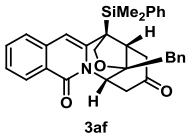
rel-(7*S*,11*R*,12*R*,16*R*)-16-Cyclohexyl-12-(dimethyl(phenyl)silyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ae)



3ae

R_f = 0.3 (PE/EA = 5/1). White solid, 89.4 mg, 90.0% yield; Melting point: 228-236℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.46 – 7.35 (m, 5H), 6.53 (s, 1H), 5.16 (dt, *J* = 4.3, 2.2 Hz, 1H), 4.01 (d, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 2.89 (dd, *J* = 18.3, 2.6 Hz, 1H), 2.62 – 2.58 (m, 2H), 2.57 – 2.51 (m, 1H), 1.98 – 1.55 (m, 6H), 1.43 – 1.10 (m, 6H), 0.66 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm)207.4, 162.7, 142.4, 136.1, 135.2, 134.0, 132.3, 130.1, 128.3, 127.6, 126.6, 125.4, 124.9, 106.6, 80.6, 78.5, 57.7, 43.7, 41.4, 39.3, 38.9, 38.8, 26.7, 26.3, 26.1, 25.9, 24.5, -2.5, -2.9; ESI-MS: $[M+H]^{\oplus}$498.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{31}H_{36}O_3NSi^{\oplus}$498.2459, found 498.2456; IR (KBr) *v* (cm^{-1}) 2961.1, 2851.8, 1720.1, 1650.0, 1595.9, 1398.4, 1259.5, 1018.4.

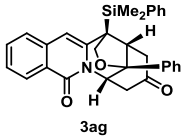
rel-(7*S*,11*R*,12*R*,16*R*)-16-Benzyl-12-(dimethyl(phenyl)silyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3af)



3af

R_f = 0.2 (PE/EA = 5/1). White solid, 91.9mg, 91.0% yield; Melting point: 244-248℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, *J* = 7.5 Hz, 1H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.46 – 7.31 (m, 7H), 7.22 – 7.13 (m, 5H), 6.51 (s, 1H), 5.00 (dt, *J* = 4.3, 2.3 Hz, 1H), 3.87 (d, *J* = 7.9 Hz, 1H), 3.81 (d, *J* = 8.0 Hz, 1H), 3.18 (d, *J* = 14.2 Hz, 1H), 3.00 – 2.87 (m, 2H), 2.76 (dd, *J* = 18.1, 3.9 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.07 – 2.02 (m, 1H), 0.58 (s, 3H), 0.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 207.2, 162.6, 142.2, 136.0, 134.7, 134.6, 133.9, 132.4, 130.1, 130.0, 128.2, 127.6, 126.9, 126.7, 125.5, 124.9, 106.9, 79.3, 78.1, 59.5, 43.6, 42.4, 41.6, 39.6, 38.9, 27.0, -2.5, -3.1; ESI-MS: $[M+H]^{\oplus}$506.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{32}H_{32}O_3NSi^{\oplus}$506.2146, found 506.2148; IR (KBr) *v* (cm^{-1}) 3062.9, 2959.1, 1715.8, 1650.7, 1397.5, 1018.2.

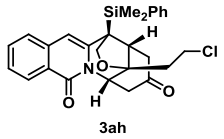
rel-(7*S*,11*R*,12*R*,16*S*)-12-(Dimethyl(phenyl)silyl)-16-phenyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ag)



3ag

R_f = 0.2 (PE/EA = 5/1). White solid, 83.1 mg, 85.0% yield; Melting point: 260-266℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.38 (d, J = 7.3 Hz, 1H), 7.68 – 7.59 (m, 3H), 7.51 – 7.34 (m, 10H), 6.65 (s, 1H), 5.41 – 5.38 (m, 1H), 4.20 (d, J = 8.2 Hz, 1H), 4.05 (d, J = 8.1 Hz, 1H), 3.01 – 2.91 (m, 2H), 2.88 – 2.72 (m, 2H), 2.14 – 2.04 (m, 1H), 0.73 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 206.7, 162.8, 142.2, 138.6, 136.1, 134.8, 134.2, 132.5, 130.2, 129.1, 129.0, 128.4, 127.7, 126.9, 125.9, 125.6, 124.9, 107.2, 80.7, 77.7, 60.1, 44.8, 41.8, 41.0, 40.0, 27.0, -2.3, -2.6; ESI-MS: $[M-H]^{\oplus}$490.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{31}H_{30}O_3NSi^{\oplus}$492.1989,found 492.1986; IR (KBr) ν (cm^{-1}) 2961.8, 2868.7, 1714.9, 1649.6, 1624.3, 1394.2, 1258.1, 1060.1, 836.0.

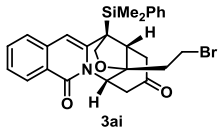
rel-(7*S*,11*R*,12*R*,16*R*)-16-(2-Chloroethyl)-12-(dimethyl(phenyl)silyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ah)



3ah

R_f = 0.6 (PE/EA = 1/1). White solid, 86.8 mg, 91.0% yield; Melting point: 235-240℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, J = 8.0 Hz, 1H), 7.64 – 7.56 (m, 3H), 7.49 – 7.36 (m, 5H), 6.54 (s, 1H), 5.02 – 4.98 (m, 1H), 4.15 (d, J = 8.1 Hz, 1H), 3.95 (d, J = 8.1 Hz, 1H), 3.74 – 3.58 (m, 2H), 2.92 (dd, J = 17.5, 1.8 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.61 (dd, J = 17.9, 3.6 Hz, 1H), 2.51 – 2.49 (m, 1H), 2.42 – 2.35 (m, 1H), 2.23 – 2.16 (mz, 1H), 0.68 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.2, 162.5, 141.6, 136.0, 134.7, 134.1, 132.5, 130.2, 128.4, 127.6, 126.8, 125.5, 124.8, 107.0, 78.6, 78.3, 59.0, 43.8, 43.0, 42.0, 38.8, 37.1, 27.0, -2.4, -2.9; ESI-MS: $[M+H]^{\oplus}$478.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{29}O_3NClSi^{\oplus}$478.1600, found 478.1600; IR (KBr) ν (cm^{-1}) 2961.1, 2866.6, 1720.1, 1651.4, 1595.9, 1399.6, 827.6.

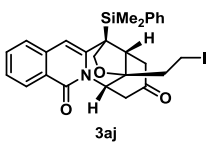
rel-(7*S*,11*R*,12*R*,16*R*)-16-(2-Bromoethyl)-12-(dimethyl(phenyl)silyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ai)



3ai

R_f = 0.3 (PE/EA = 5/1). White solid, 93.8 mg, 90.0% yield; Melting point: 240-250℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.37 – 8.31 (m, 1H), 7.65 – 7.55 (m, 3H), 7.49 – 7.36 (m, 5H), 6.54 (s, 1H), 4.99 (t, J = 2.9 Hz, 1H), 4.14 (d, J = 8.1 Hz, 1H), 3.95 (d, J = 8.1 Hz, 1H), 3.56 – 3.40 (m, 2H), 2.92 (dd, J = 17.6, 2.5 Hz, 1H), 2.78 – 2.65 (m, 2H), 2.59 (dd, J = 18.0, 3.7 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.33 – 2.23 (m, 1H), 0.65 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.0, 162.5, 141.7, 136.0, 134.7, 134.1, 132.5, 130.2, 128.4, 127.6, 126.8, 125.6, 124.8, 106.9, 78.9, 78.6, 58.8, 43.8, 42.9, 41.9, 38.8, 37.6, 25.8, -2.4, -2.8; ESI-MS: $[M+H]^{\oplus}$522.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{29}O_3NBrSi^{\oplus}$522.1095, found 522.1088; IR (KBr) ν (cm^{-1}) 2960.7, 1719.8, 1651.3, 1596.0, 1399.4, 1264.1, 1163.7, 826.8.

rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-(2-iodoethyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3aj)

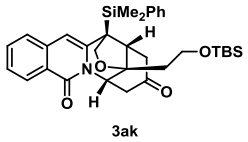


3aj

R_f = 0.7 (PE/EA = 1/1). White solid, 102.4 mg, 90.0% yield; Melting point: 244-250℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, J = 8.0 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.50 – 7.35 (m, 5H), 7.39 (d, J = 7.9 Hz, 1H), 6.54 (s, 1H), 5.00 (q, J = 2.9 Hz, 1H), 4.13 (d, J = 8.1 Hz, 1H), 3.95 (d, J = 8.1 Hz, 1H), 3.30 – 3.15 (m, 2H), 2.92 (dd, J = 18.0, 2.8 Hz, 1H), 2.70 (d, J = 6.7 Hz, 2H), 2.62 – 2.48 (m, 2H), 2.39 – 2.36 (m,1H), 2. 34 – 2. 26 (m, 1H), 0.68 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.0, 162.5, 141.7, 136.0, 134.7, 134.1, 132.5, 130.2, 128.5, 127.6, 126.8, 125.5, 124.8 , 107.0, 79.8, 78.5, 58.3, 43.9, 42.8, 41.9, 39.4, 38.8, 27.0, -2.4, -2.8; ESI-MS: $[M+H]^{\oplus}$570.0; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{29}O_3NISi^{\oplus}$570.0956, found 570.0955; IR (KBr) ν (cm^{-1}) 2931.0,

2864.1, 1714.5, 1618.1, 1559.6, 149.7, 1015.0.

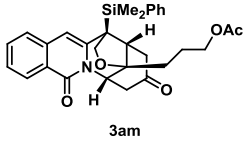
rel-(7*S*,11*R*,12*R*,16*R*)-16-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-12-(dimethyl(phenyl)silyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ak)



3ak

R_f = 0.3 (PE/EA = 1/1). White solid, 105.3mg, 92.0% yield; Melting point: 220-226℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, J = 8.0 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.47 – 7.39 (m, 4H), 7.34 (d, J = 7.9 Hz, 1H), 6.52 (s, 1H), 5.10 (q, J = 2.9 Hz, 1H), 4.16 (d, J = 8.0 Hz, 1H), 3.94 (d, J = 8.0 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.85 – 3.79 (m, 1H), 2.92 – 2.86 (m, 1H), 2.80 – 2.64 (m, 3H), 2.48 (dt, J = 8.0, 2.3 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.92 – 1.86 (m, 1H), 0.90 (s, 9H), 0.63 (d, J = 22.9 Hz, 6H), 0.66 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)207.1, 162.5, 141.9, 136.0, 135.3, 134.1, 132.3, 130.0, 128.3, 127.7, 126.6, 125.4, 124.9, 106.8, 78.6, 78.4, 59.1, 58.5, 43.8, 43.7, 42.4, 39.1, 37.5, 25.9, 18.2, -2.4, -2.7, -5.3, -5.5; ESI-MS: $[M+H]^{\oplus}$574.3; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{33}H_{44}O_4NSi_2^{\oplus}$574.2803, found 574.2801; IR (KBr) ν (cm^{-1}) 3420, 2953.8, 1717.8, 1653.9, 1399.4, 1257.6, 834.8.

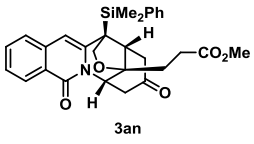
rel-3-((7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-5,9-dioxo-7,8,9,10,11,12-hexahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinolin-16-yl)propyl acetate (3am)



3am

R_f = 0.7 (PE/EA = 1/1). White solid, 92.7 mg, 90.0% yield; Melting point: 200-208℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.33 (d, J = 8.0 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.49 – 7.34 (m, 5H), 6.54 (s, 1H), 5.01 (dt, J = 4.2, 2.3 Hz, 1H), 4.13 – 3.99 (m, 3H), 3.93 (d, J = 8.1 Hz, 1H), 2.89 (dd, J = 18.2, 2.7 Hz, 1H), 2.66 (d, J = 5.5 Hz, 2H), 2.57 (dd, J = 18.1, 3.8 Hz, 1H), 2.24 (dt, J = 6.0, 3.0 Hz, 1H), 2.03 (s, 3H), 1.99 – 1.92 (m, 1H), 1.87 – 1.63 (m, 3H), 0.66 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.7, 171.0, 162.6, 142.0, 136.0, 134.9, 134.1, 132.4, 130.1, 128.4, 127.6, 126.7, 125.5, 124.8, 107.0, 78.6, 78.2, 64.1, 58.6, 44.0, 43.2, 42.0, 38.9, 31.2, 22.3, 20.9, -2.4, -2.8; ESI-MS: $[M+H]^{\oplus}$516.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{30}H_{34}O_5NSi^{\oplus}$516.2201, found 516.2199; IR (KBr) ν (cm^{-1}) 2958.6, 2858.9, 1734.7, 1650.3, 1596.1, 1242.3, 1056.8, 825.5.

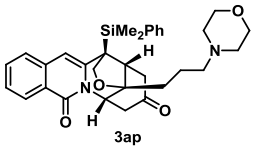
rel-Methyl3-((7*S*,11*R*,12*R*,16*R*)-12-(dimethyl(phenyl)silyl)-5,9-dioxo-7,8,9,10,11,12-hexahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinolin-16-yl)propanoate (3an)



3an

R_f = 0.4 (PE/EA = 1/1). White solid, 88.3mg, 88.0% yield; Melting point: 198-206℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.33 (d, J = 8.0 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.48 – 7.34 (m, 5H), 6.53 (s, 1H), 4.99 (q, J = 2.9 Hz, 1H), 4.08 (d, J = 8.1 Hz, 1H), 3.91 (d, J = 8.0 Hz, 1H), 3.63 (s, 3H), 2.95 – 2.86 (m, 1H), 2.77 – 2.57 (m, 3H), 2.48 – 2.42 (m, 2H), 2.26 – 2.04 (m, 3H), 0.66 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.3, 173.5, 162.5, 141.8, 136.0, 134.8, 134.1, 132.4, 130.1, 128.4, 127.6, 126.7, 125.5, 124.9, 106.9, 78.4, 78.3, 59.0, 51.8, 43.9, 42.8, 42.0, 38.8, 29.1, 27.6, -2.4, -2.8; ESI-MS: $[M+Na]^{\oplus}$524.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{29}H_{32}O_5NSi^{\oplus}$502.2044, found 502.2039; IR (KBr) ν (cm^{-1}) 2959.9, 2927.7, 1720.2, 1650.5, 1618.9, 1596.0, 1399.2, 1263.2, 1162.3, 826.1.

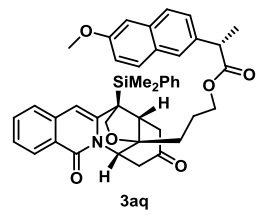
rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-(3-morpholinopropyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ap)



3ap

R_f = 0.3 (DCM/MeOH = 20/1). White solid, mg, 86.0% yield; Melting point: 234-240℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.49 – 7.34 (m, 5H), 6.54 (s, 1H), 5.02 (s, 1H), 4.10 (d, *J* = 8.1 Hz, 1H), 3.92 (d, *J* = 8.1 Hz, 1H), 3.77 – 3.67 (m, 4H), 2.88 (dd, *J* = 18.1, 2.7 Hz, 1H), 2.65 (d, *J* = 5.5 Hz, 2H), 2.57 (dd, *J* = 18.1, 3.8 Hz, 1H), 2.47 – 2.32 (m, 6H), 2.23 (dt, *J* = 5.7, 2.9 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.72 – 1.54 (m, 3H), 0.66 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.8, 162.6, 142.0, 136.0, 135.0, 134.1, 132.4, 130.1, 128.3, 127.6, 126.7, 125.5, 124.9, 106.9, 78.8, 78.2, 66.7, 58.7, 58.4, 53.4, 44.0, 43.2, 42.0, 39.0, 32.3, 19.7, -2.4, -2.8; ESI-MS: $[M+Na]^{\oplus}$565.2; HRMS (ESI): $[M+Na]^{\oplus}$calcd for $C_{32}H_{39}O_4N_2SiNa^{\oplus}$565.2493, found 565.2498; IR (KBr) *v* (cm^{-1}) 2955.5, 1719.6, 1650.1, 1618.9, 1595.4, 1398.4, 1263.9, 1115.9, 1059.6.

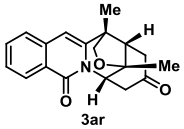
rel-3-((7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-5,9-dioxo-7,8,9,10,11,12-hexahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinolin-16-yl)propyl2-(6-methoxynaphthalen-2-yl)propanoate (3aq)



3aq

R_f = 0.6 (PE/EA = 1/1). White solid, 116.5 mg, 85.0% yield; Melting point: 246-252℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 – 8.29 (m, 1H), 7.73 – 7.64 (m, 3H), 7.62 – 7.51 (m, 3H), 7.46 – 7.31 (m, 6H), 7.14 (dt, *J* = 9.0, 3.1 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.48 (d, *J* = 4.0 Hz, 1H), 4.90 (q, *J* = 4.0, 3.2 Hz, 1H), 4.24 – 4.17 (m, 1H), 4.09 – 3.96 (m, 2H), 3.91 (s, 3H), 3.87 – 3.80 (m, 2H), 2.74 – 2.65 (m, 1H), 2.55 – 2.42 (m, 1H), 2.34 – 2.00 (m, 3H), 1.58 (dd, *J* = 7.2, 3.3 Hz, 3H), 0.59 (dd, *J* = 19.6, 8.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.1(d, *J* = 6.5 Hz), 174.4(d, *J* = 4.0 Hz), 162.5, 157.6 (d, *J* = 1.2 Hz), 141.8 (d, *J* = 3.0 Hz), 136.0, 135.7, 135.5, 135.0, 134.1, 133.6, 132.4, 130.1, 129.1 (d, *J* = 2.3 Hz), 128.8 (d, *J* = 1.5 Hz), 128.3, 127.6, 127.1 (d, *J* = 3.0 Hz), 126.7, 126.3, 126.0, 126.0, 125.8, 125.5, 124.8 (d, *J* = 1.6 Hz), 119.2 (d, *J* = 3.4 Hz), 106.8, 105.6, 78.5 (d, *J* = 1.4 Hz), 78.2, 77.3, 64.2 (d, *J* = 7.5 Hz), 58.7, 58.6, 55.2, 45.4, 43.7 (d, *J* = 3.3 Hz), 43.6, 43.4, 41.7, 38.6 (d, *J* = 10.6 Hz), 30.9, 22.3 (d, *J* = 7.6 Hz), 18.2, 18.0, -2.5 (d, *J* = 3.0 Hz), -2.8 (d, *J* = 1.4 Hz); ESI-MS: $[M+H]^{\oplus}$686.3; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{42}H_{44}O_6NSi^{\oplus}$686.2932, found 686.2934; IR (KBr) *v* (cm^{-1}) 2959.8, 2934.9, 1726.6, 1651.0, 1427.3, 1230.9, 1029.0, 823.2.

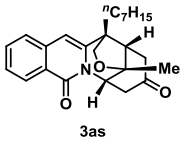
rel-(7*S*,11*S*,12*S*,16*R*)-12,16-Dimethyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ar)



3ar

R_f = 0.4 (PE/EA = 1/1). White solid, 34.6 mg, 56.0% yield; Melting point: 236-242℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, *J* = 7.4 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.49 – 7.40 (m, 2H), 6.41 (s, 1H), 5.11 (q, *J* = 2.9 Hz, 1H), 3.82 (d, *J* = 3.6 Hz, 2H), 2.91 (dt, *J* = 17.5, 2.5 Hz, 1H), 2.72 – 2.50 (m, 3H), 2.32 (dt, *J* = 7.8, 2.0 Hz, 1H), 1.71 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.2, 162.3, 142.7, 136.0, 132.4, 127.6, 126.7, 125.8, 124.9, 102.6, 80.5, 78.7, 60.7, 48.6, 47.7, 42.9, 36.9, 22.5, 16.9; ESI-MS: $[M+H]^{\oplus}$310.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{19}H_{20}O_3N^{\oplus}$310.1438, found 310.1438; IR (KBr) *v* (cm^{-1}) 2970.7, 2866.3, 1716.6, 1596.1, 1404.2, 1156.8, 1037.9.

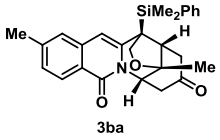
rel-(7*S*,11*S*,12*S*,16*R*)-12-Heptyl-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3as)



3as

R_f = 0.5 (PE/EA = 1/1). White solid, 53.4 mg, 68.0% yield; Melting point: 245-247℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.34 (d, J = 7.8 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.43 (dd, J = 7.9, 6.7 Hz, 2H), 6.42 (s, 1H), 5.09 (q, J = 2.8 Hz, 1H), 3.96 (d, J = 7.9 Hz, 1H), 3.70 (d, J = 7.8 Hz, 1H), 2.87 (dt, J = 17.5, 2.5 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.53 – 2.44 (m, 2H), 2.00 – 1.84 (m, 2H), 1.68 (s, 3H), 1.46 – 1.28 (m, 10H), 0.91 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.4, 162.4, 143.4, 136.1, 132.4, 127.6, 126.7, 125.9, 124.9, 102.9, 78.4, 77.8, 60.4, 50.4, 44.5, 42.8, 37.1, 31.7, 30.2, 29.2, 29.1, 24.1, 22.7, 22.6, 14.0; ESI-MS: $[M+H]^{\oplus}$394.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{25}H_{32}O_3N^{\oplus}$394.2377, found 394.2372; IR (KBr) ν (cm^{-1}) 2928.2, 2856.0, 1719.5, 1647.8, 1561.5, 1380.2, 1156.3, 1028.1.

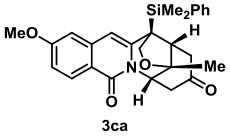
rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-2,16-dimethyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ba)



3ba

R_f = 0.5 (PE/EA = 1/1). White solid, 85.1 mg, 96.0% yield; Melting point: 275-279℃;^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.33 (d, J = 8.2 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.58 – 7.51 (m, 3H), 7.38 – 7.32 (m, 2H), 6.58 (s, 1H), 5.06 – 5.02 (m, 1H), 4.26 (d, J = 8.1 Hz, 1H), 4.01 (d, J = 8.0 Hz, 1H), 2.99 (dd, J = 18.0, 2.7 Hz, 1H), 2.78 (d, J = 5.4 Hz, 2H), 2.70 (dd, J = 17.9, 3.8 Hz, 1H), 2.55 (s, 3H), 2.29 (td, J = 5.5, 1.9 Hz, 1H), 1.62 (s, 3H), 0.76 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.8, 162.5, 143.0, 141.7, 136.2, 135.1, 134.2, 130.0, 129.1, 128.3, 127.5, 127.4, 125.2, 122.7, 106.8, 78.0, 77.2, 60.0, 44.9, 44.2, 42.6, 39.1, 22.1, 21.7, -2.4, -2.7; ESI-MS: $[M+H]^{\oplus}$444.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{30}O_3NSi^{\oplus}$444.1989, found 444.1984; IR (KBr) ν (cm^{-1}) 2964.1, 2868.3, 1713.5, 1650.6, 1596.7, 1395.6, 1060.1.

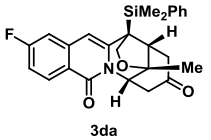
rel-(7*S*,11*R*,12*R*,16*R*)-12-(dimethyl(phenyl)silyl)-2-methoxy-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ca)



3ca

R_f = 0.3 (PE/EA = 1/1). White solid, 81.7 mg, 89.0% yield; Melting point: 248-250℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)8.26 (d, J = 8.9 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.51 – 7.39 (m, 3H), 7.01 (dd, J = 8.9, 2.5 Hz, 1H), 6.71 (d, J = 2.5 Hz, 1H), 6.46 (s, 1H), 4.93 (s, 1H), 4.15 (d, J = 8.1 Hz, 1H), 3.92 (d, J = 8.2 Hz, 1H), 3.90 (s, 3H), 2.90 (dd, J = 17.8, 2.7 Hz, 1H), 2.68 (d, J = 5.4 Hz, 2H), 2.59 (dd, J = 18.0, 3.8 Hz, 1H), 2.18 (td, J = 5.4, 1.8 Hz, 1H), 1.51 (s, 3H), 0.67 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.9, 162.8, 162.2, 142.4, 138.1, 135.0, 134.2, 130.1, 129.7, 128.4, 118.9, 116.2, 106.6, 106.3, 77.9, 77.2, 59.9, 55.5, 44.8, 44.2, 42.6, 39.1, 22.1, -2.2, -2.6; ESI-MS: $[M+H]^{\oplus}$460.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{30}O_4NSi^{\oplus}$460.1939, found 460.1932; IR (KBr) ν (cm^{-1}) 2961.4, 2861.3, 1713.5, 1650.6, 1592.9, 1257.4, 1163.2.

rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-2-fluoro-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3da)

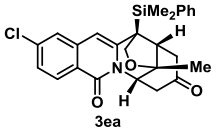


3da

R_f = 0.5 (PE/EA = 1/1). White solid, 66.1 mg, 74.0% yield; Melting point: 244-248℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.35 (dd, J = 8.9, 5.7 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.50 – 7.40 (m, 3H), 7.13 (td, J = 8.7, 2.5 Hz, 1H), 7.00 (dd, J = 9.1, 2.5 Hz, 1H), 6.47 (s, 1H), 4.97 – 4.90 (m, 1H), 4.18 (d, J = 8.1 Hz, 1H), 3.92 (d, J = 8.1 Hz, 1H), 2.89 (dd, J = 17.8, 2.8 Hz, 1H), 2.70 (d, J = 6.3 Hz, 2H), 2.61 (dd, J = 17.9, 3.7 Hz, 1H), 2.24 – 2.21 (m, 1H), 1.54 (s, 3H), 0.67 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.5, 165.3 (d, $^1J_{F-C}$= 252.8 Hz), 161.8, 143.4, 138.2 (d, $^3J_{F-C}$= 10.3 Hz), 134.9, 134.1, 130.9 (d, $^3J_{F-C}$= 10.1 Hz), 130.1, 128.4, 121.5, 115.4 (d, $^2J_{F-C}$= 23.3 Hz), 110.3 (d, $^2J_{F-C}$= 21.7 Hz), 106.2 (d, $^4J_{F-C}$= 3.2 Hz), 77.9, 77.1, 60.2, 44.9, 44.3, 42.5, 39.0, 22.0, -2.4, -2.8; ESI-MS: $[M+H]^{\oplus}$448.1;

HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{26}H_{27}O_3NFSi^{\oplus}$448.1739, found 448.1732; IR (KBr) ν (cm^{-1}) 2960.4, 2873.3, 1712.1, 1654.8, 1349.2, 1179.8, 1116.3, 869.4.

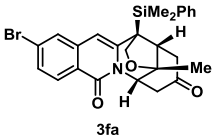
rel-(7*S*,11*R*,12*R*,16*R*)-2-Chloro-12-(dimethyl(phenyl)silyl)-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ea)



3ea

R_f = 0.3 (PE/EA = 1/1). White solid, 66.7 mg, 72.0% yield; Melting point: 240-246℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)8.27 – 8.24 (m, 1H), 7.60 – 7.55 (m, 2H), 7.46 – 7.44 (m, 3H), 7.37 – 7.34 (m, 2H), 6.45 (s, 1H), 4.92 (d, *J* = 2.6 Hz, 1H), 4.17 (d, *J* = 8.1 Hz, 1H), 3.90 (d, *J* = 8.1 Hz, 1H), 2.87 (dd, *J* = 17.8, 2.8 Hz, 1H), 2.71 – 2.67 (m, 2H), 2.60 (dd, *J* = 17.8, 3.7 Hz, 1H), 2.24 – 2.20 (m, 1H), 1.53 (s, 3H), 0.65 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.4, 161.9, 143.4, 138.8, 137.3, 134.8, 134.1, 130.2, 129.5, 128.4, 127.2, 124.7, 123.1, 105.7, 78.0, 77.1, 60.3, 44.9, 44.4, 42.4, 39.0, 22.0, -2.4, -2.8; ESI-MS: $[M+Na]^{\oplus}$486.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{26}H_{27}O_3NClSi^{\oplus}$464.1443, found 464.1442; IR (KBr) ν (cm^{-1}) 2967.1, 2866.9, 1712.8, 1648.3, 1614.9, 1555.7, 1392.5, 1159.9, 833.8.

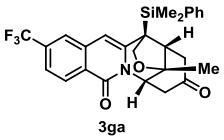
rel-(7*S*,11*R*,12*R*,16*R*)-2-Bromo-12-(dimethyl(phenyl)silyl)-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3fa)



3fa

R_f = 0.5 (PE/EA = 1/1). White solid, 71.9 mg, 71.0% yield; Melting point: 236-246℃;^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.18 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.54 – 7.49 (m, 2H), 7.49 – 7.41 (m, 3H), 6.44 (s, 1H), 4.92 (q, *J* = 2.8 Hz, 1H), 4.17 (d, *J* = 8.1 Hz, 1H), 3.91 (d, *J* = 8.1 Hz, 1H), 2.87 (dd, *J* = 17.9, 2.8 Hz, 1H), 2.71 – 2.67 (m, 2H), 2.61 (dd, *J* = 17.8, 3.7 Hz, 1H), 2.24 – 2.19 (m, 1H), 1.53 (s, 3H), 0.66 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.5, 162.1, 143.4, 137.5, 134.8, 134.1, 130.2, 129.9, 129.5, 128.4, 127.9, 127.5, 123.4, 105.6, 78.0, 77.1, 60.3, 44.9, 44.4, 42.4, 39.0, -2.4, -2.7; ESI-MS: $[M+H]^{\oplus}$508.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{26}H_{27}O_3NBrSi^{\oplus}$508.0938, found 508.0929; IR (KBr) ν (cm^{-1}) 2962.4, 2869.0, 1713.7, 1647.8, 1613.0, 1587.4, 1333.6, 1057.3.

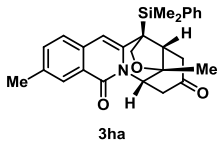
rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-methyl-2-(trifluoromethyl)-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ga)



3ga

R_f = 0.5 (PE/EA = 1/1). White solid, 69.6 mg, 70.0% yield; Melting point: 250-256℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.45 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.57 (m, 4H), 7.49 – 7.43 (m, 3H), 6.59 (s, 1H), 4.96 (q, *J* = 2.9 Hz, 1H), 4.18 (d, *J* = 8.2 Hz, 1H), 3.92 (d, *J* = 8.2 Hz, 1H), 2.88 (dd, *J* = 17.8, 2.9 Hz, 1H), 2.71 (d, *J* = 6.0 Hz, 2H), 2.63 (dd, *J* = 17.8, 3.7 Hz, 1H), 2.26 – 2.21 (m, 1H), 1.55 (s, 3H), 0.68 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.2, 161.7, 143.7, 136.0, 134.7, 134.2 (q, $^2J_{F\text{-}C}$ = 32.4 Hz), 130.2, 128.8, 128.5, 126.8,, 123.6(q, $^1J_{F\text{-}C}$= 272.1 Hz), 122.9 (q, $^3J_{F\text{-}C}$= 3.8 Hz), 122.6 (q, $^3J_{F\text{-}C}$ = 3.8 Hz), 106.2, 78.0, 77.1, 60.5, 44.9, 44.4, 42.4, 39.0, 22.0, -2.4, -2.7; ESI-MS: $[M+H]^{\oplus}$498.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{27}O_3NF_3Si^{\oplus}$498.1709, found 498.1706; IR (KBr) ν (cm^{-1}) 2960.1, 1721.8, 1631.1, 1568.8, 1317.5, 1164.7, 838.0.

rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-3,16-dimethyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ha)

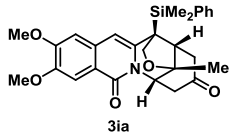


3ha

R_f = 0.5 (PE/EA = 1/1). White solid, 84.7 mg, 95.0% yield; Melting point: 248-250℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)8.15 (s, 1H), 7.60 – 7.57 (m, 2H), 7.46 – 7.41 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 4.96 (t, *J* = 1.9 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.1 Hz, 1H), 2.88 (dd, *J* = 18.0, 2.7 Hz, 1H), 2.68 (d, *J* = 5.4 Hz, 2H), 2.60 (dd, *J* = 17.9, 3.8 Hz, 1H), 2.46 (s, 3H), 2.20 (td, *J* = 5.4, 1.9 Hz, 1H), 1.52 (s, 3H), 0.66 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.8,

162.5, 140.6, 136.8, 135.1, 134.2, 133.9, 133.7, 132.6, 130.0, 128.3, 127.1, 125.5, 124.8, 124.3, 106.9, 78.0, 77.2, 60.1, 44.9, 44.1, 42.6, 39.1, 22.1, 21.4, -2.4, -2.7; ESI-MS: $[M+H]^{\oplus}$444.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{27}H_{30}O_3NSi^{\oplus}$444.1989, found 444.1984; IR (KBr) ν (cm^{-1}) 2959.6, 2873.8, 1709.4, 1651.7, 1603.4, 1346.4, 1115.9, 833.6.

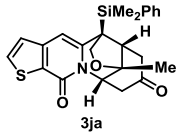
rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-2,3-dimethoxy-16-methyl-7,8,11,12-tetrahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinoline-5,9(10*H*)-dione (3ia)



3ia

R_f = 0.2 (PE/EA = 1/2). White solid, 71.3mg, 73.0% yield; Melting point: 266-270℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)7.71 (s, 1H), 7.62 – 7.54 (m, 2H), 7.48 – 7.40 (m, 3H), 6.71 (s, 1H), 6.45 (s, 1H), 4.95 (q, *J* = 2.8 Hz, 1H), 4.13 (d, *J* = 8.1 Hz, 1H), 3.97 (s, 6H), 3.90 (d, *J* = 8.0 Hz, 1H), 2.88 (dd, *J* = 17.9, 2.8 Hz, 1H), 2.67 (d, *J* = 5.4 Hz, 2H), 2.59 (dd, *J* = 17.9, 3.8 Hz, 1H), 2.16 (td, *J* = 5.3, 1.9 Hz, 1H), 1.51 (s, 3H), 0.67 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.9, 161.8, 153.6, 149.2, 140.1, 135.0, 134.2, 131.6, 130.0, 128.3, 118.9, 107.4, 106.4, 105.5, 78.0, 77.3, 60.1, 56.2, 56.1, 44.9, 44.1, 42.6, 39.1, 22.1, -2.2, -2.6; ESI-MS: $[M+H]^{\oplus}$490.2; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{28}H_{32}O_5NSi^{\oplus}$490.2044, found 490.2038; IR (KBr) ν (cm^{-1}) 2963.4, 2932.0, 1714.0, 1645.9, 1504.6, 1402.7, 1259.9, 1013.3, 881.3.

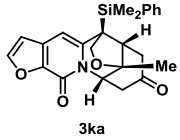
rel-(5*R*,6*R*,10*S*,13*R*)-5-(Dimethyl(phenyl)silyl)-13-methyl-6,7,9,10-tetrahydro-8*H*-6,10,5-(epimethanetriyloxymethano)thieno[3',2':4,5]pyrido[1,2-a]azocine-8,12(5*H*)-dione (3ja)



3ja

R_f = 0.2 (PE/EA = 2/1). White solid, 83.5 mg, 96.0% yield; Melting point: 246-252℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.63 (d, *J* = 5.2 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.46 – 7.39 (m, 3H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.69 (s, 1H), 4.97 (q, *J* = 2.8 Hz, 1H), 4.15 (d, *J* = 8.1 Hz, 1H), 3.88 (d, *J* = 8.2 Hz, 1H), 2.91 (dd, *J* = 17.9, 2.8 Hz, 1H), 2.70 – 2.66 (m, 2H), 2.60 (dd, *J* = 17.9, 3.8 Hz, 1H), 2.22 – 2.19 (m, 1H), 1.52 (s, 3H), 0.64 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm) 206.6, 158.7, 144.3, 143.2, 134.9, 134.2, 133.6, 130.1, 128.9, 128.4, 124.0, 103.8, 78.1, 77.1, 60.3, 44.9, 44.4, 42.6, 39.1, 22.0, -2.3, -2.7; ESI-MS: $[M+H]^{\oplus}$436.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{24}H_{26}O_3NSSi^{\oplus}$436.1397, found 436.1391; IR (KBr) ν (cm^{-1}) 2968.3, 2872.0, 1712.2, 1647.7, 1577.4, 1255.3, 1114.9, 820.7.

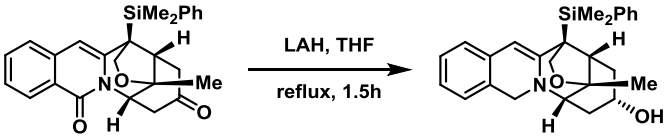
rel-(5*R*,6*R*,10*S*,13*R*)-5-(Dimethyl(phenyl)silyl)-13-methyl-6,7,9,10-tetrahydro-8*H*-6,10,5-(epimethanetriyloxymethano)furo[3',2':4,5]pyrido[1,2-a]azocine-8,12(5*H*)-dione (3ka)



3ka

R_f = 0.2 (PE/EA = 2/1). White solid, 74mg, 88% yield; Melting point: 248-250℃;^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)7.69 (t, *J* = 2.1 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.47 – 7.40 (m, 3H), 6.58 (t, *J* = 1.6 Hz, 1H), 6.50 (s, 1H), 5.03 – 5.00 (m, 1H), 4.13 (dd, *J* = 8.1, 1.4 Hz, 1H), 3.85 (dd, *J* = 8.2, 1.7 Hz, 1H), 2.90 (d, *J* = 17.8 Hz, 1H), 2.67 (d, *J* = 5.1 Hz, 2H), 2.60 (dd, *J* = 18.3, 2.8 Hz, 1H), 2.20 – 2.17 (m, 1H), 1.52 (d, *J* = 1.6 Hz, 3H), 0.64 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ (ppm)206.4, 153.5, 148.3, 142.6, 142.5, 134.8, 134.2, 131.9, 130.1, 128.4, 107.0, 100.9, 78.1, 76.9, 60.2, 45.0, 44.4, 42.7, 39.0, 21.9, -2.3, -2.7; ESI-MS: $[M+H]^{\oplus}$420.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{24}H_{26}O_4NSi^{\oplus}$420.1626, found 420.1627; IR (KBr) ν (cm^{-1}) 2921.8, 2865.5, 1713.7, 1679.2, 1586.7, 1252.4, 1188.0, 1056.6.

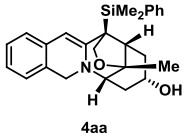
4.TRANSFORMATIONS



3aa 4aa

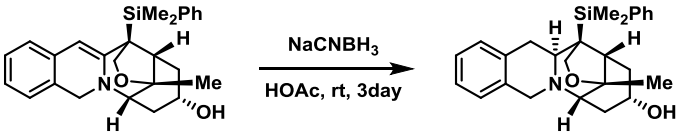
At room temperature, a well-stirred solution of **3aa** (553.0 mg, 1.3 mmol, 1.0 equiv) in 40 mL dry THF was treated with $LiAlH_4$ (296.0 mg, 7.8 mmol, 6.0 equiv) in several portions, then the mixture was stirred at 70°C for 1.5h. After cooled to room temperature, thereaction was quenched with 300 uL water, 300 uL 15% NaOH solution and another 1 mL water respectively. After drying over anhydrous Na_2SO_4, the mixture was filtered and concentratedunder reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure product **4aa**.

rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-methyl-7,8,9,10,11,12-hexahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinolin-9-ol (4aa)



4aa

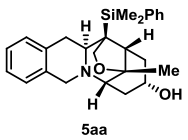
R_f = 0.1 (PE/EA = 1/1). White solid, 386.0 mg, 71.0% yield; Melting point: 254-262℃;^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.62 – 7.57 (m, 2H), 7.41 – 7.36 (m, 3H), 7.12 – 7.08 (m, 2H), 7.06 – 7.02 (m, 1H), 6.98 – 6.94 (m, 1H), 4.36 (d, *J* = 14.9 Hz, 1H), 4.14 (q, *J* = 2.6 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.71 (d, *J* = 14.9 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 2.93 – 2.83 (m, 2H), 2.66 – 2.56 (m, 1H), 2.54 – 2.45 (m, 1H), 1.89 – 1.86 (m, 1H), 1.70 – 1.63 (m, 1H), 1.30 (s, 3H), 1.08 (d, *J* = 14.1 Hz, 1H), 0.62 (s, 3H), 0.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 137.5, 134.3, 133.9, 131.2, 129.2, 127.9, 127.8, 126.0, 125.6, 125.5, 86.8, 79.8, 77.2, 72.2, 67.3, 62.0, 48.7, 45.1, 44.2, 39.2, 28.6, 23.1, 20.9, -0.9, -1.9; ESI-MS: $[M+H]^{\oplus}$418.1; HRMS (ESI): $[M+H]^{\oplus}$calcd for $C_{26}H_{32}O_2NSi^{\oplus}$418.2197, found 418.2197; IR (KBr) ν (cm^{-1}) 2931.4, 1459.7, 1376.9, 1259.3, 1070.8, 1022.0, 987.9.



4aa 5aa

To a solution of **4aa** (209.0 mg, 0.49 mmol, 1.0 equiv) in HOAc (5 mL) was added $NaCNBH_3$ (247 mg, 3.9 mmol, 8.0 equiv) and stirredat room temperature for 3 days. The reaction mixture was diluted with water (15 mL) and neutralized with10% NaOH solutionuntil the pH was approximately 7.0. The mixture wasthen extracted twice with DCM (2 × 20 mL).The combined organic solution was dried over anhydrous Na_2SO_4 and concentratedunder reduced pressure.The residue was purified by flash column chromatography (DCM/MeOH=5/1as eluent) to afford the pure product **5aa**.

rel-(7*S*,11*R*,12*R*,16*R*)-12-(Dimethyl(phenyl)silyl)-16-methyl-7,8,9,10,11,12,12a,13-octahydro-5*H*-7,11,12-(epimethanetriyloxymethano)azocino[1,2-b]isoquinolin-9-ol (5aa)

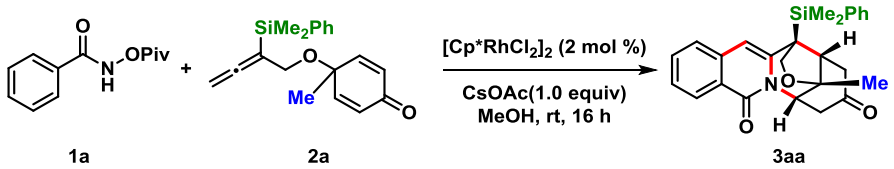


5aa

R_f = 0.5 (DCM/MeOH = 10/1). White solid, 173.0 mg, 83.0% yield; Melting point: 262-266℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.55 – 7.52 (m, 2H), 7.41 – 7.34 (m, 3H), 7.11 – 7.04 (m, 2H), 7.03 – 6.95 (m, 2H), 4.23 (d, *J* = 8.5 Hz, 1H), 4.13 (d, *J* = 14.9 Hz, 1H), 4.09 – 4.04 (m, 1H), 3.99 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.87 (d, *J* = 8.5 Hz, 1H), 3.51 (d, *J* = 14.8 Hz, 1H), 2.97 (s, 1H), 2.89 – 2.75 (m, 2H), 2.17 (d, *J* = 16.2 Hz, 1H), 2.12 – 2.04 (m, 1H), 2.01 – 1.93 (m, 1H), 1.75 – 1.69 (m, 1H), 1.63 (d, *J* = 7.6 Hz, 1H),

1.24 (s, 3H), 0.64 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 136.8, 134.4, 134.1, 133.6, 129.3, 128.4, 127.9, 125.8, 125.7, 125.4, 78.7, 69.3, 62.2, 61.6, 52.1, 51.8, 45.1, 40.1, 34.1, 30.6, 29.7, 29.6, 22.9, -2.4, -3.3; ESI-MS: $[M+H]^{\oplus}$420.2; HRMS (ESI): $[M+Na]^{\oplus}$calcd for $C_{26}H_{33}O_2NNaSi^{\oplus}$442.2173, found442.2180; IR (KBr) ν (cm^{-1}) 3393.0, 2928.8, 1426.8, 1260.4, 1109.6, 908.0.

5. GRAM-SCALEEXPERIMENT



1a 2a 3aa

According to general procedure, the mixture of *N*-(pivaloyloxy)benzamide **1a** (1.18 g, 5.34 mmol, 1.5 equiv), cyclohexadienone-tethered 1,1-disubstitutedallene **2a** (1.10 g, 3.55 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (43.8mg, 0.071 mmol, 2 mol%), CsOAc (681.2 mg, 3.55mmol, 1.0 equiv) and methanol(20 mL) was stirred at room temperature for 16h.The resulting mixture was concentrated *in vacuo* and the crude product was purified by silica gel (300−400 mesh) column chromatography using PE/EA=2/1 to afford the desired product **3aa** (1.43g, 3.33 mmol, 94.0% yield).

6. X-RayCrystal Structure

6.1 X-Ray Crystal Structure of 3aa (CCDC 1879321)

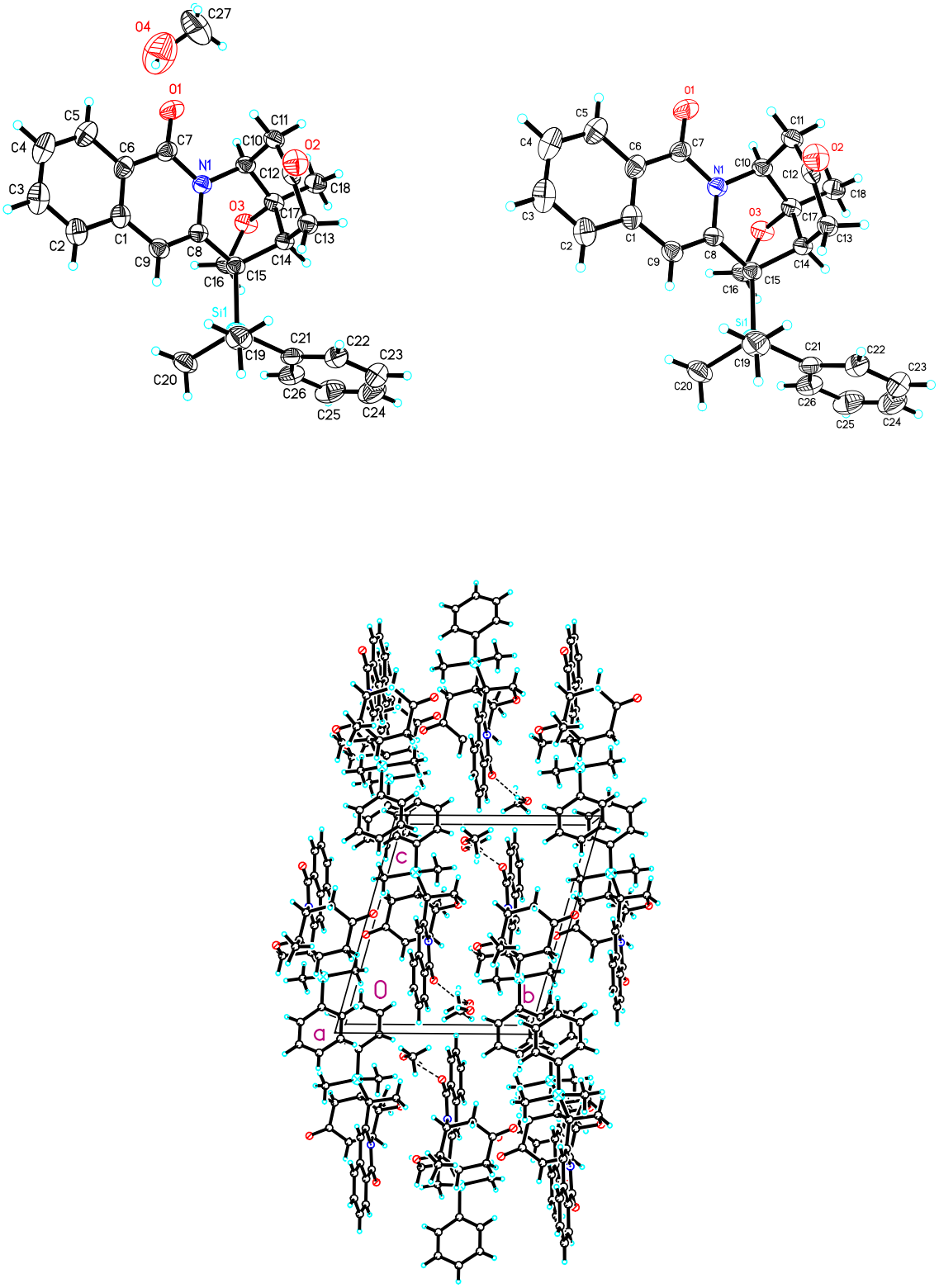


Table S1. Crystal data and structure refinement for 3aa.

Identification code	mo_d8v17709_0m	
Empirical formula	C27 H31 N O4 Si	
Formula weight	461.62	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9601(4) Å	α= 74.3930(10) °.
	b = 10.6766(3) Å	β= 85.5710(10) °.
	c = 11.8691(4) Å	γ = 88.9580(10) °.
Volume	1211.99(7) $Å^3$	
Z	2	
Density (calculated)	1.265 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	492	
Crystal size	0.180 x 0.150 x 0.140 mm^3	
Theta range for data collection	1.980 to 25.498 °.	
Index ranges	-12<=h<=12, -12<=k<=12, -14<=l<=14	
Reflections collected	20365	
Independent reflections	4491 [R(int) = 0.0322]	
Completeness to theta = 25.242 °	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6771	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4491 / 1 / 304	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0582, wR2 = 0.1647	
R indices (all data)	R1 = 0.0708, wR2 = 0.1781	
Largest diff. peak and hole	0.567 and -0.412 e.$Å^{-3}$	

6.2 X-Ray Crystal Structure of 5aa (CCDC 1879320)

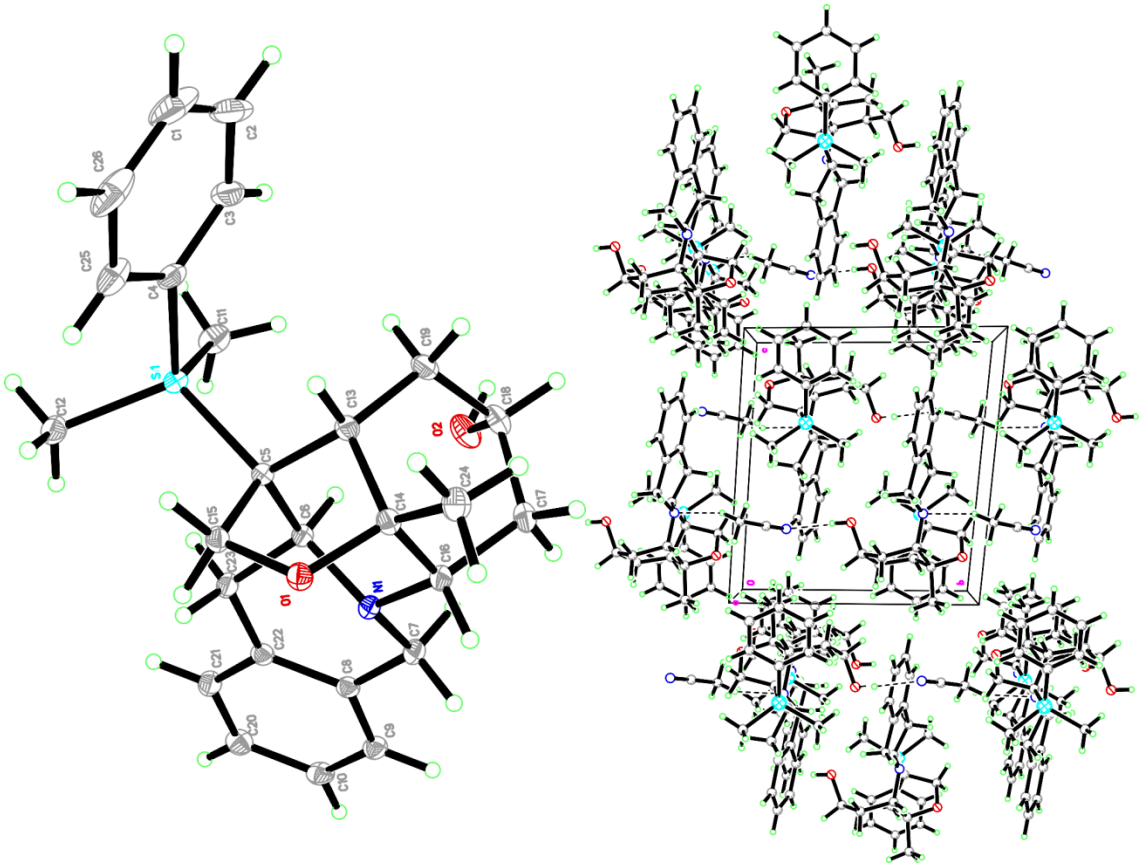
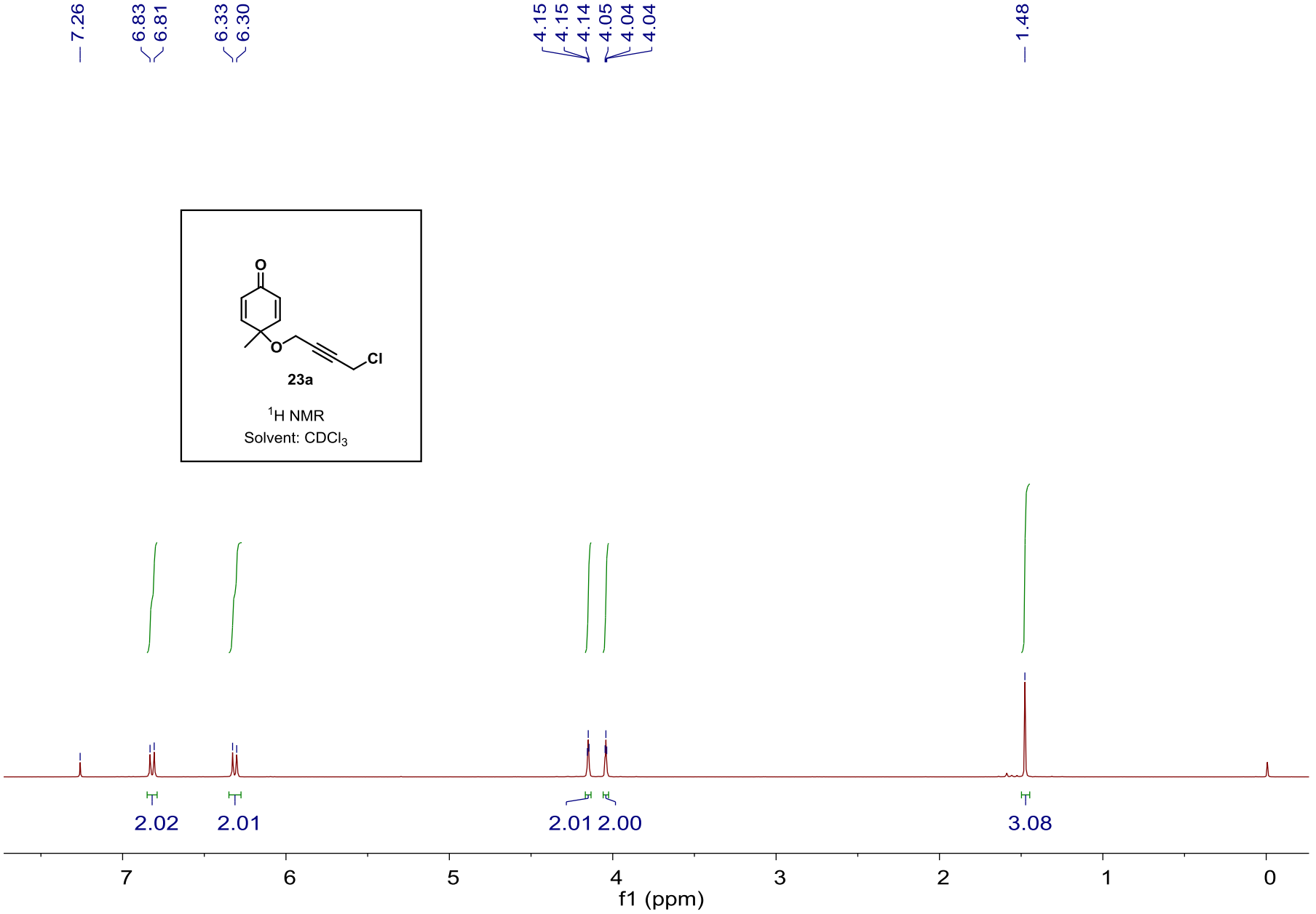


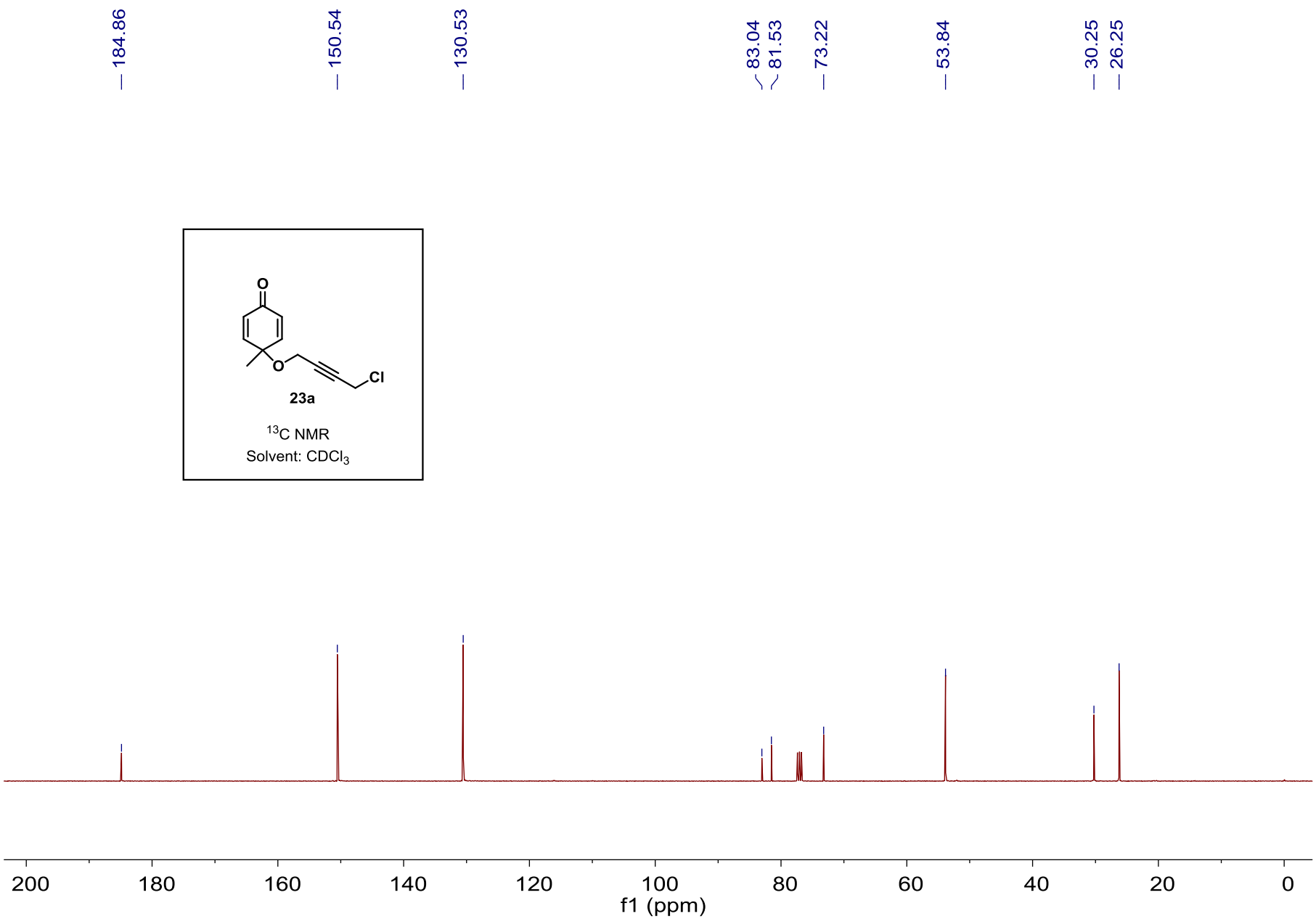
Table S2. Crystal data and structure refinement for 5aa.

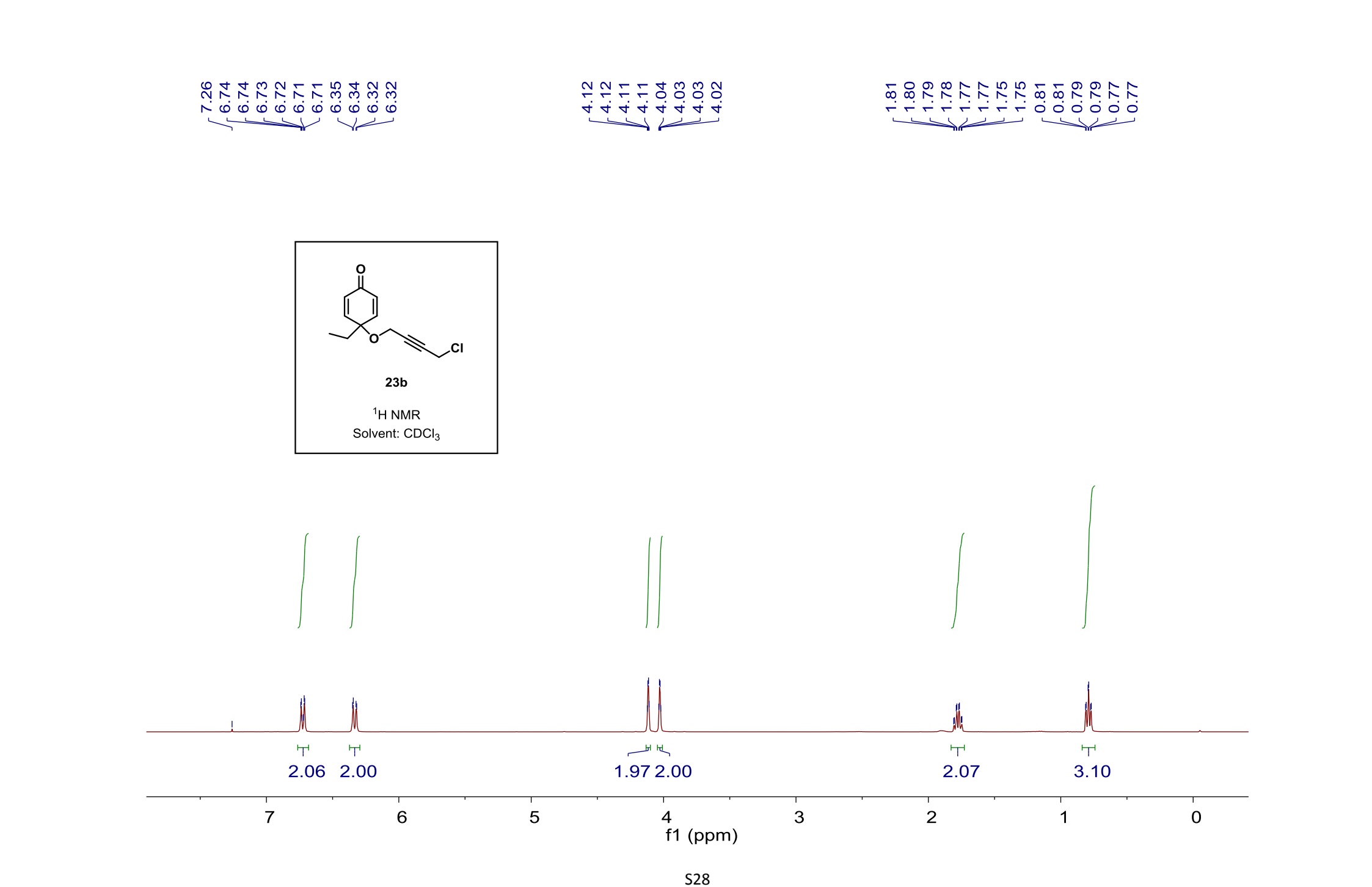
Identification code	cu_20181011kds_0m	
Empirical formula	C28 H36 N2 O2 Si	
Formula weight	460.68	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7904(3) Å	α= 83.8910(10) °.
	b = 10.7882(4) Å	β= 69.7230(10) °.
	c = 12.3517(4) Å	γ = 84.4990(10) °.
Volume	1214.36(7) $Å^3$	
Z	2	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	1.065 mm^{-1}	
F(000)	496	
Crystal size	0.170 x 0.200 x 0.300 mm^3	
Theta range for data collection	3.827 to 68.295 °.	
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=14	
Reflections collected	31749	
Independent reflections	4415 [R(int) = 0.0430]	

Completeness to theta = 67.679 °	99.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4415 / 0 / 306
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0926
R indices (all data)	R1 = 0.0370, wR2 = 0.0930
Extinction coefficient	n/a
Largest diff. peak and hole	0.376 and -0.312 e.$Å^{-3}$

7. ^{1}H NMR and ^{13}C NMR


7.26
6.83
6.81
6.33
6.30
4.15
4.15
4.14
4.05
4.04
4.04
1.48
O
O
Cl
23a
^{1}H NMR
Solvent: $CDCl_3$
2.02
2.01
2.01
2.00
3.08
7
6
5
4
3
2
1
0
f1 (ppm)


184.86
150.54
130.53
83.04
81.53
73.22
53.84
30.25
26.25
O
O
Cl
23a
13C NMR
Solvent: CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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6.74
6.74
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6.72
6.71
6.71
6.35
6.34
6.32
6.32
4.12
4.12
4.11
4.11
4.04
4.03
4.03
4.02
1.81
1.80
1.79
1.78
1.77
1.77
1.75
1.75
0.81
0.81
0.79
0.79
0.77
0.77
O
O
Cl
23b
1H NMR
Solvent: CDCl3
2.06
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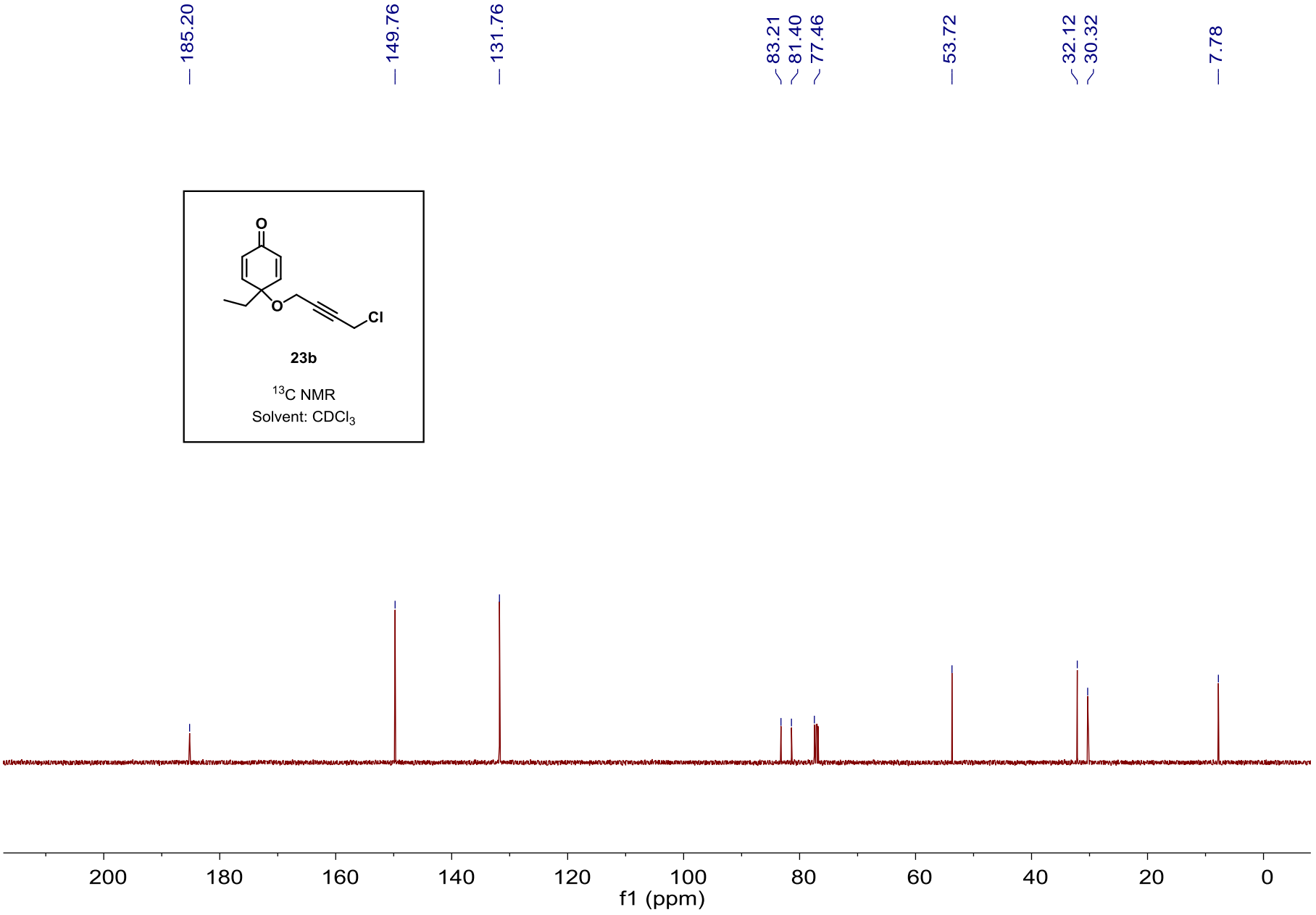
1.97
2.00
2.07
3.10
7
6
5
4
3
2
1
0
f1 (ppm)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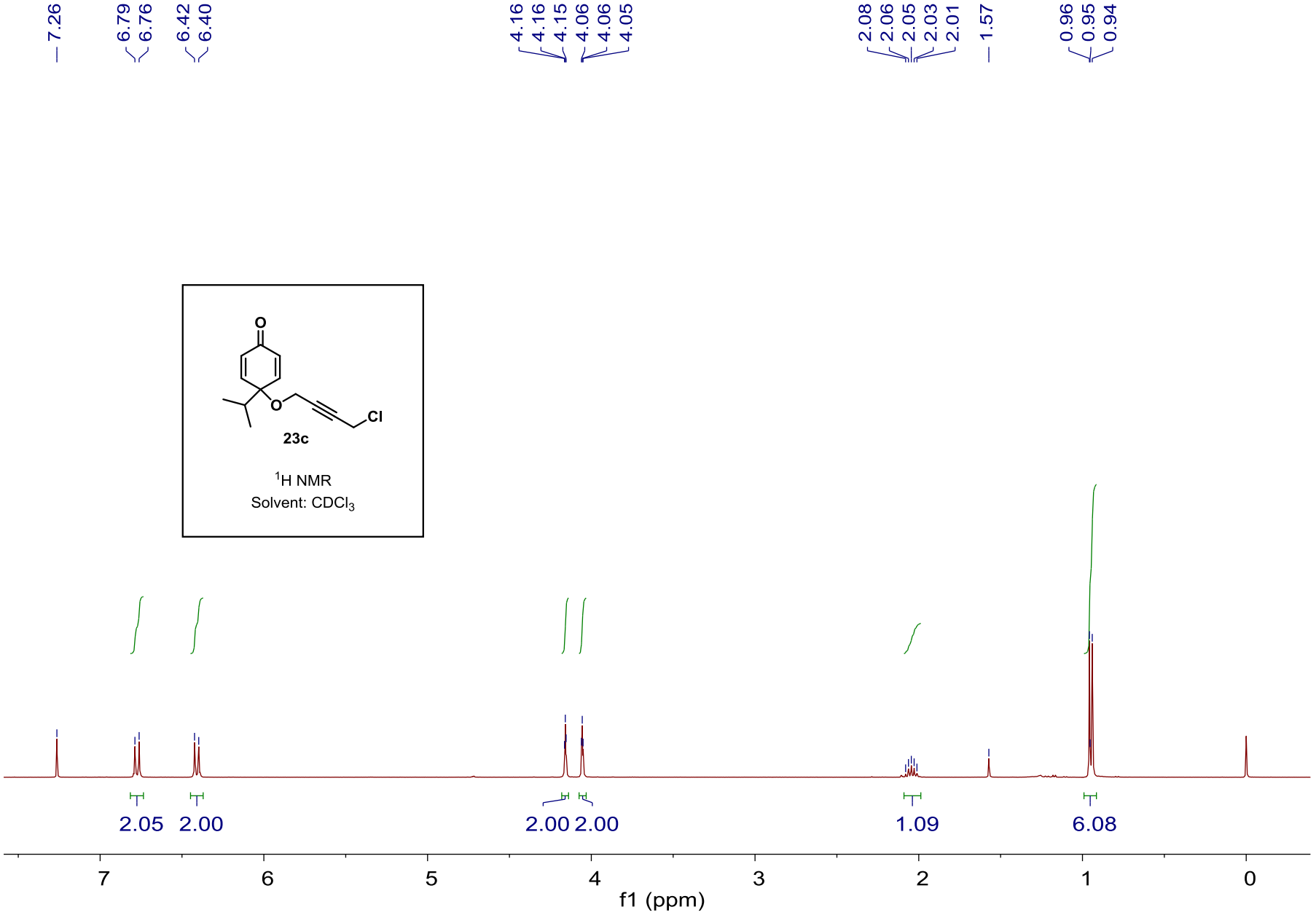
149.76
131.76
83.21
81.40
77.46
53.72
32.12
30.32
7.78
O
O
Cl
23b
^{13}C NMR
Solvent: $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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6.79
6.76
6.42
6.40
4.16
4.16
4.15
4.06
4.06
4.05
2.08
2.06
2.05
2.03
2.01
1.57
0.96
0.95
0.94
O
O
Cl
23c
1H NMR
Solvent: CDCl3
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2.00
2.00
1.09
6.08
7
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5
4
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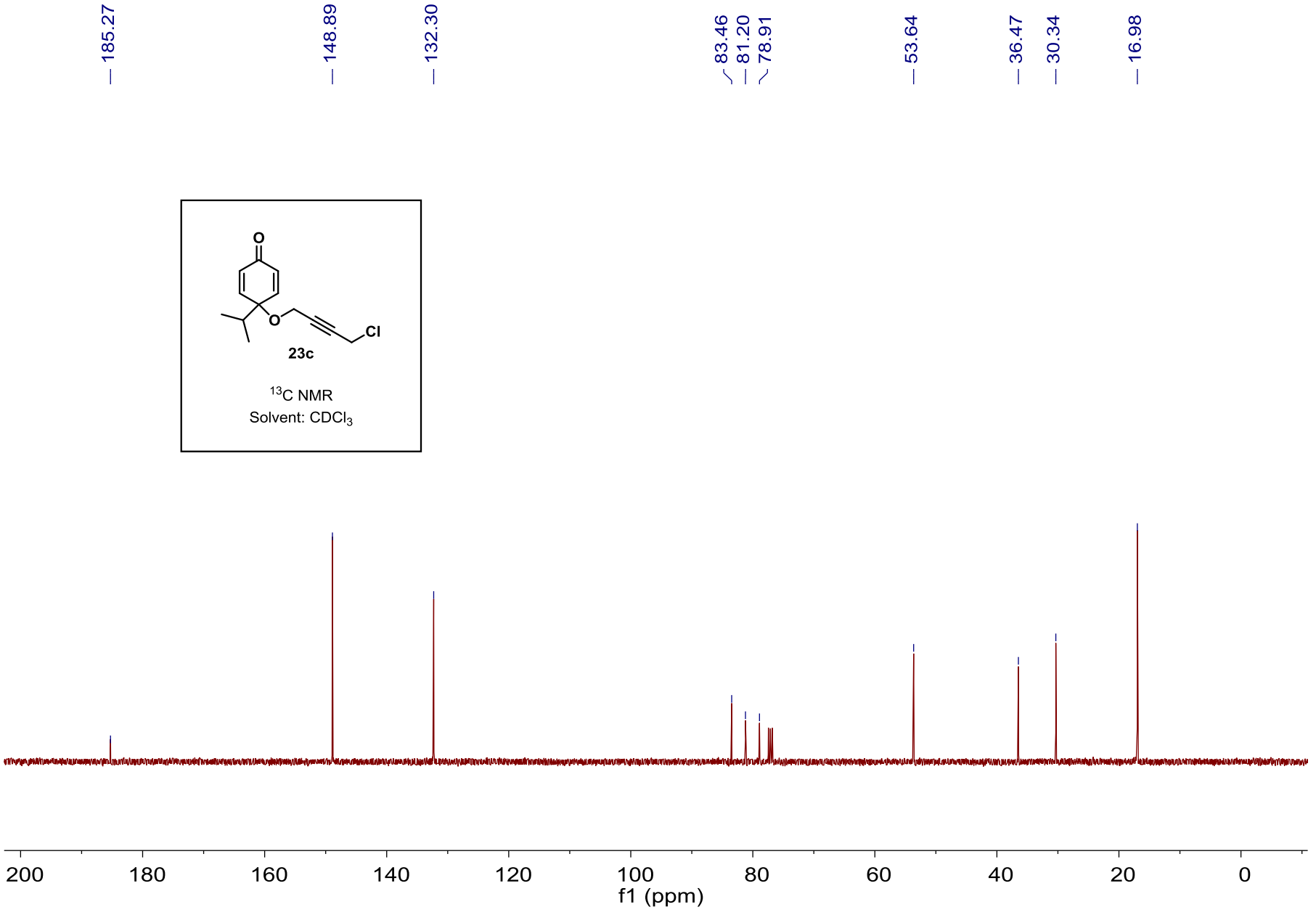
f1 (ppm)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148.89
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81.20
78.91
53.64
36.47
30.34
16.98
O
O
Cl
23c
^{13}C NMR
Solvent: $CDCl_3$
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180
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140
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100
80
60
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20
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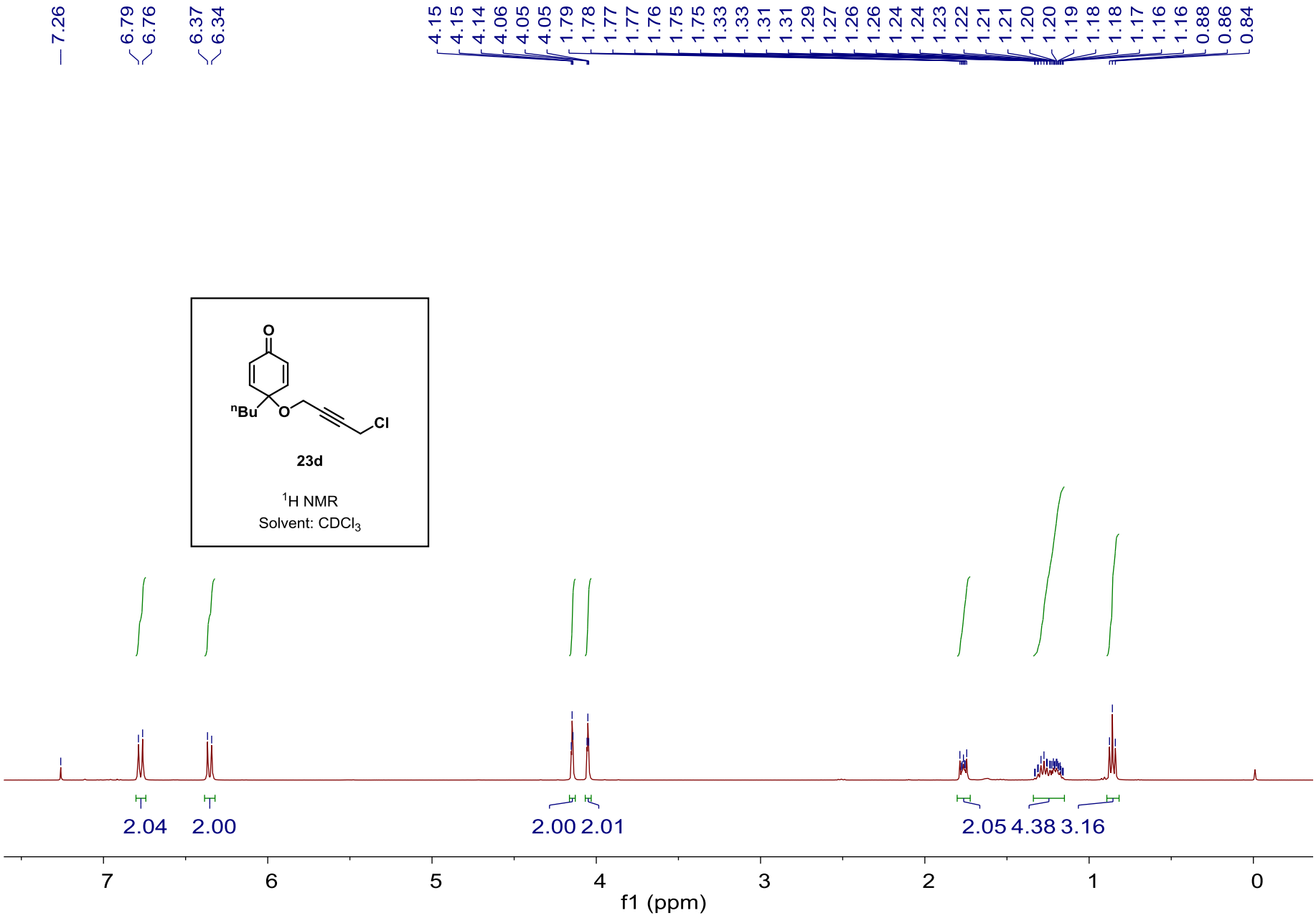
f1 (ppm)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6.79
6.76
6.37
6.34
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4.15
4.14
4.06
4.05
4.05
1.79
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1.77
1.77
1.76
1.75
1.75
1.33
1.33
1.31
1.31
1.29
1.27
1.26
1.26
1.24
1.24
1.23
1.22
1.21
1.21
1.20
1.20
1.19
1.18
1.18
1.17
1.16
1.16
0.88
0.86
0.84
O
nBu
O
Cl
23d
1H NMR
Solvent: CDCl3
2.04
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2.00
2.01
2.05
4.38
3.16
7
6
5
4
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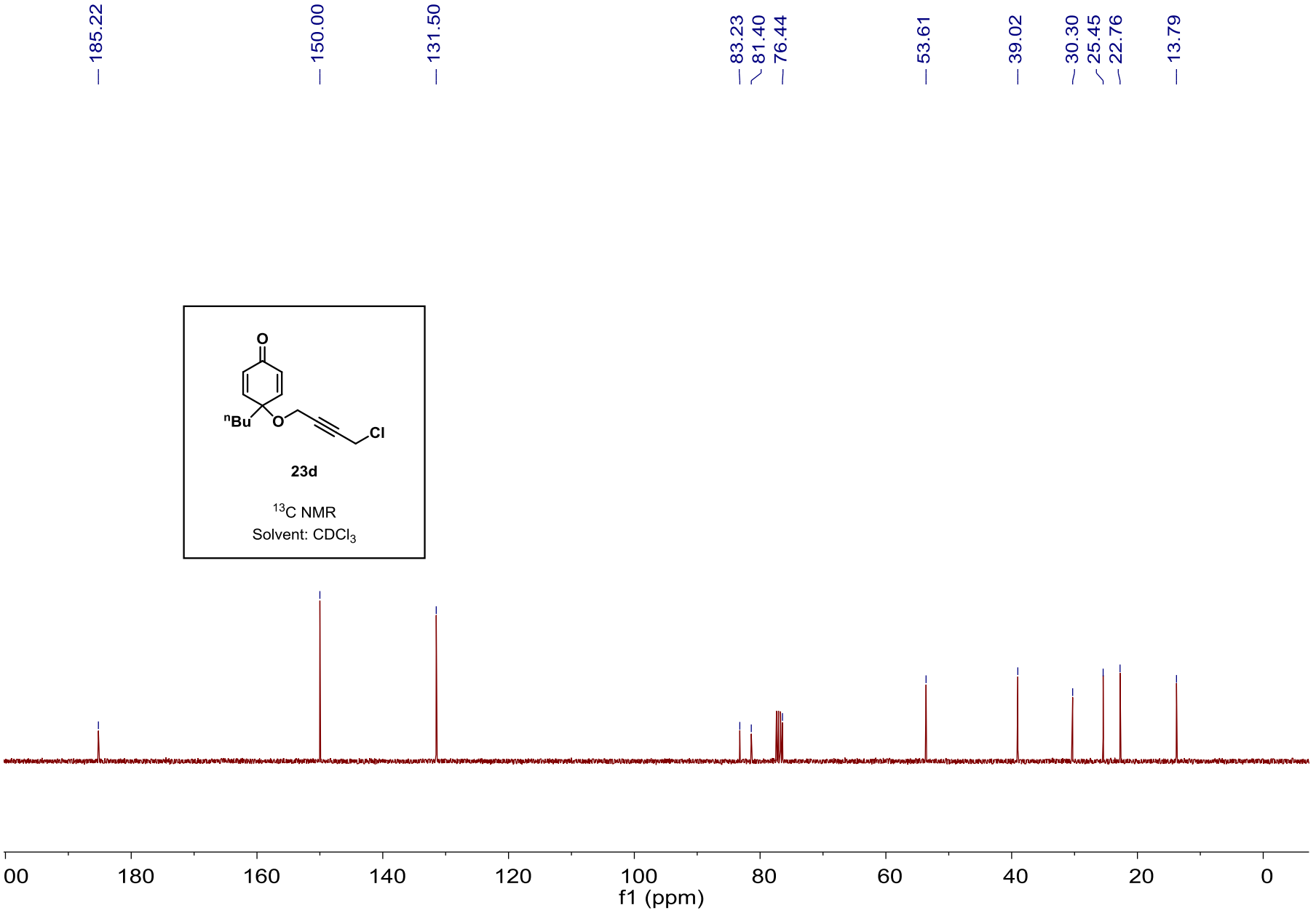
f1 (ppm)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81.40
76.44
53.61
39.02
30.30
25.45
22.76
13.79
O
nBu
O
Cl
23d
13C NMR
Solvent: CDCl3
00
180
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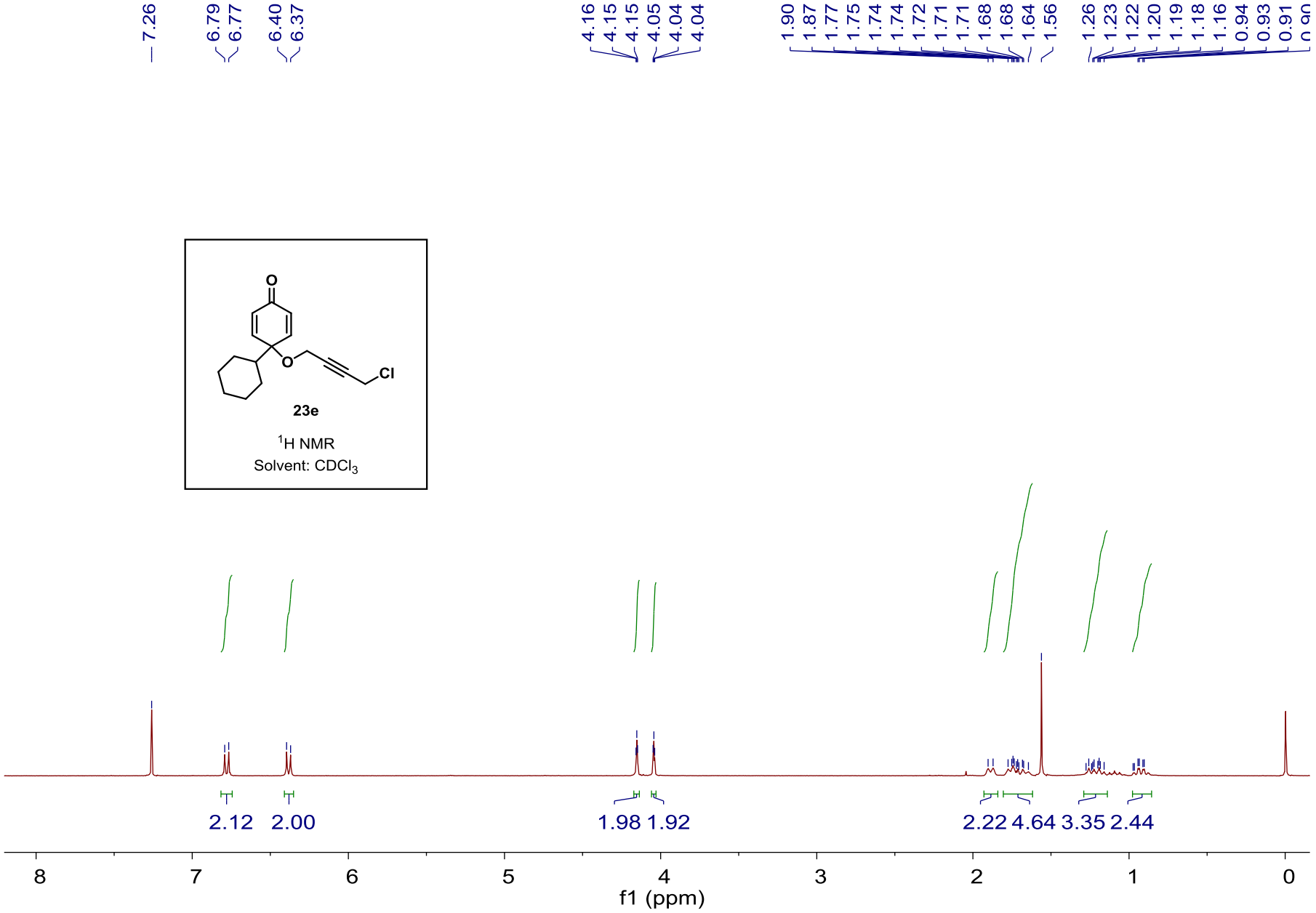
140
120
100
80
60
40
20
0
f1 (ppm)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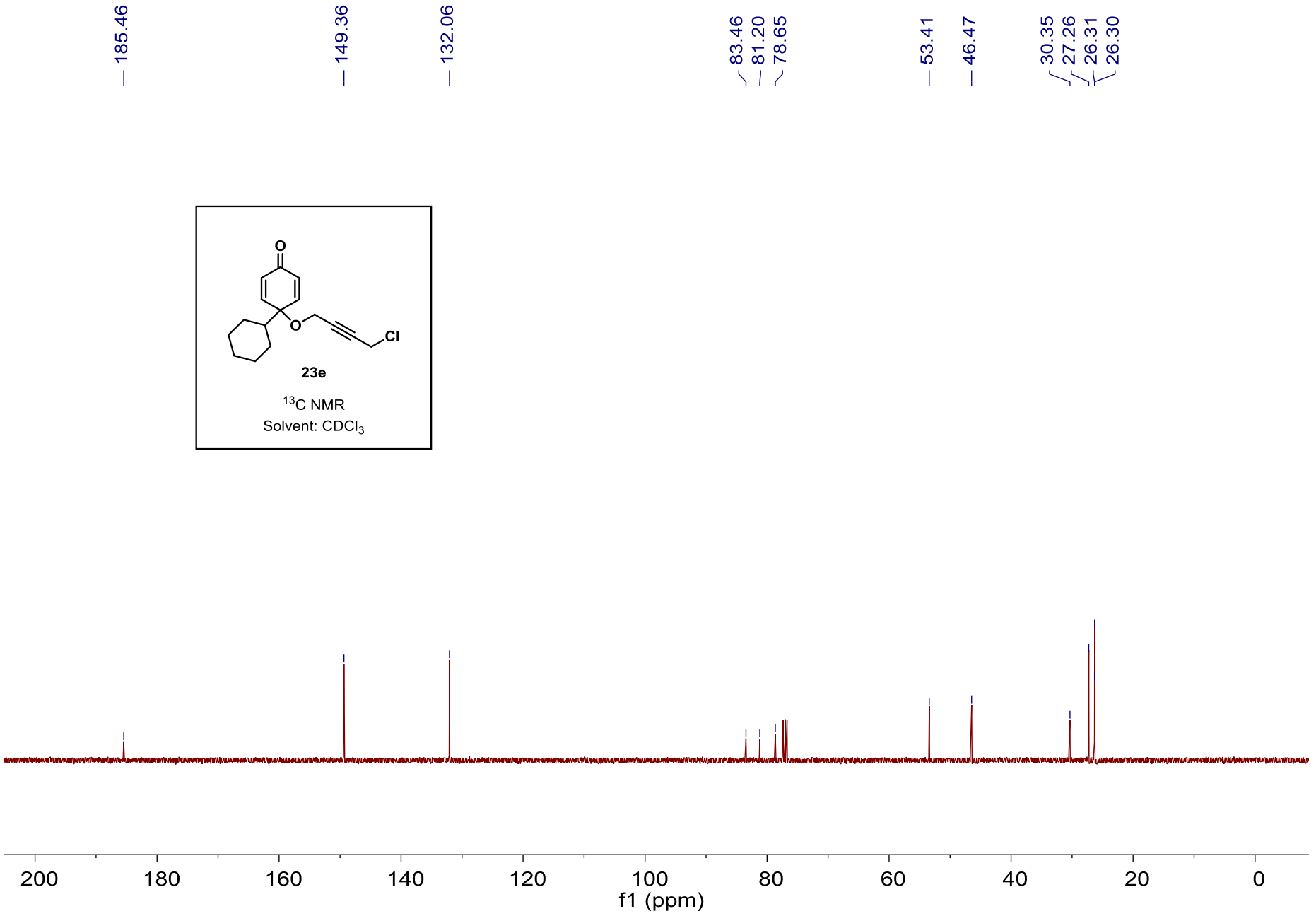
6.79
6.77
6.40
6.37
4.16
4.15
4.15
4.05
4.04
4.04
1.90
1.87
1.77
1.75
1.74
1.74
1.72
1.71
1.71
1.68
1.68
1.64
1.56
1.26
1.23
1.22
1.20
1.19
1.18
1.16
0.94
0.93
0.91
O
O
Cl
23e
1H NMR
Solvent: CDCl3
2.12
2.00
1.98
1.92
2.22
4.64
3.35
2.44
8
7
6
5
4
3
2
1
0
f1 (ppm)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149.36
132.06
83.46
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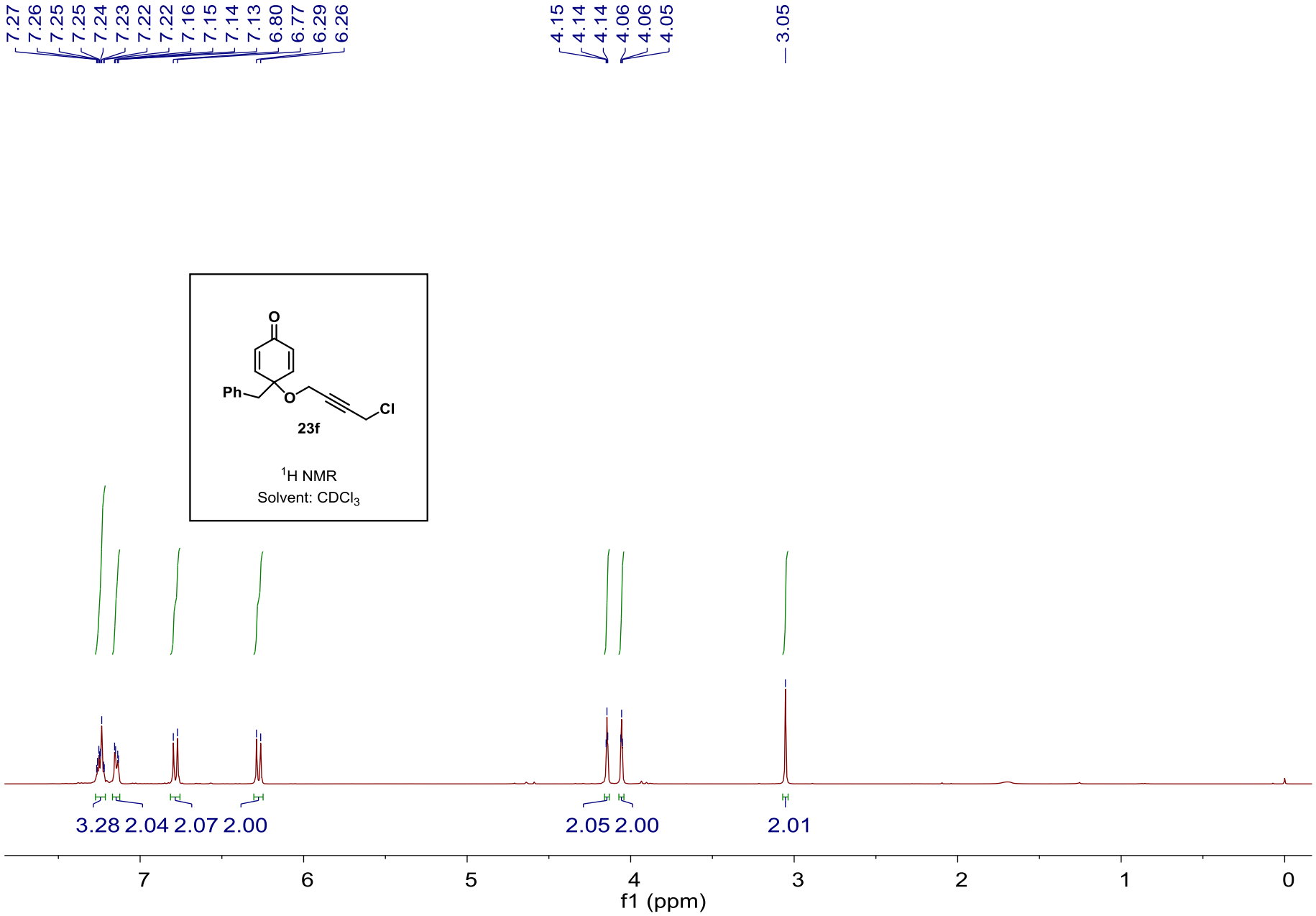
78.65
53.41
46.47
30.35
27.26
26.31
26.30
O
O
Cl
23e
13C NMR
Solvent: CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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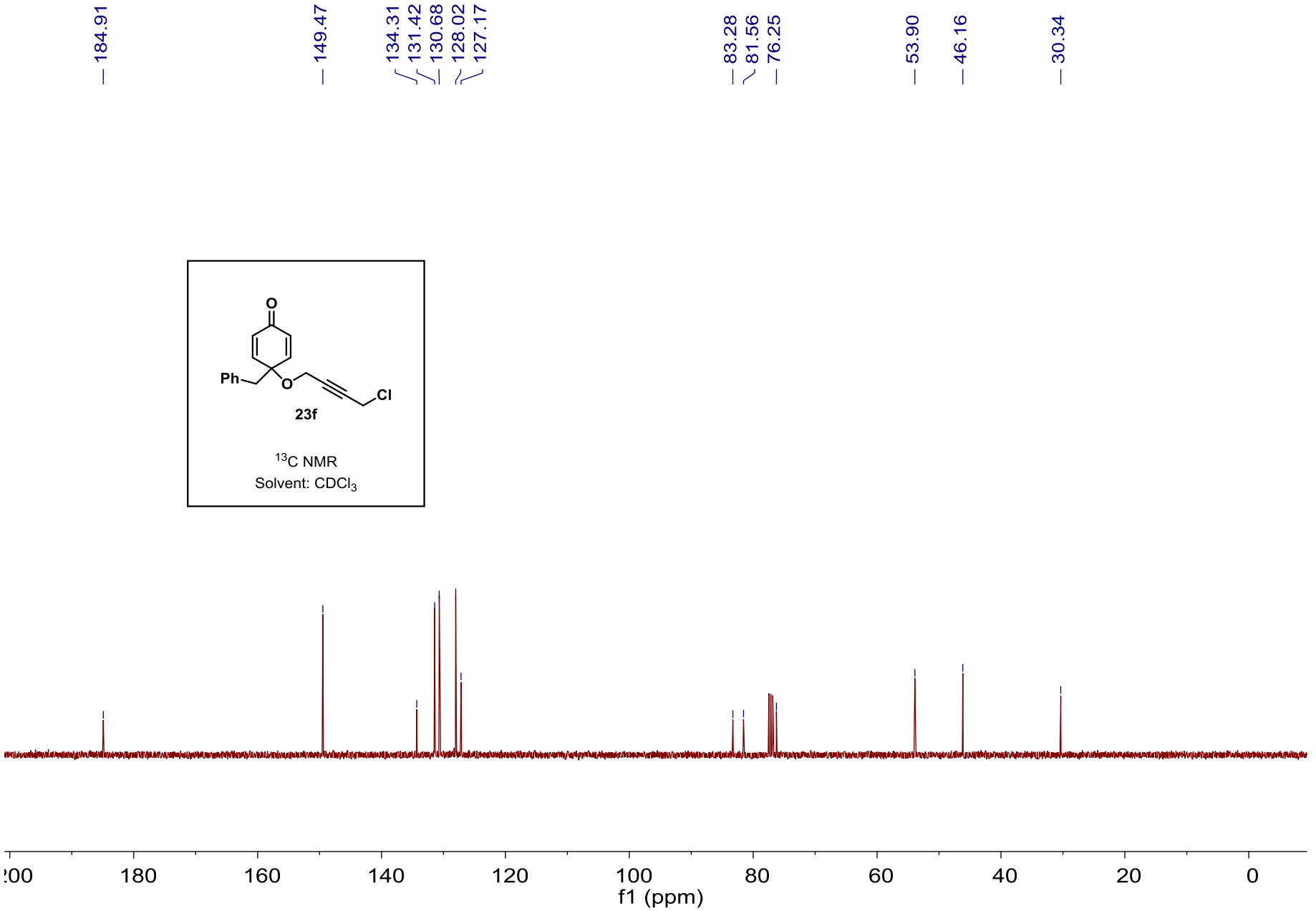
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.16
7.15
7.14
7.13
6.80
6.77
6.29
6.26
4.15
4.14
4.14
4.06
4.06
4.05
3.05
O
Ph
O
Cl
23f
1H NMR
Solvent: CDCl3
3.28 2.04 2.07 2.00
2.05 2.00
2.01
7
6
5
4
3
2
1
0
f1 (ppm)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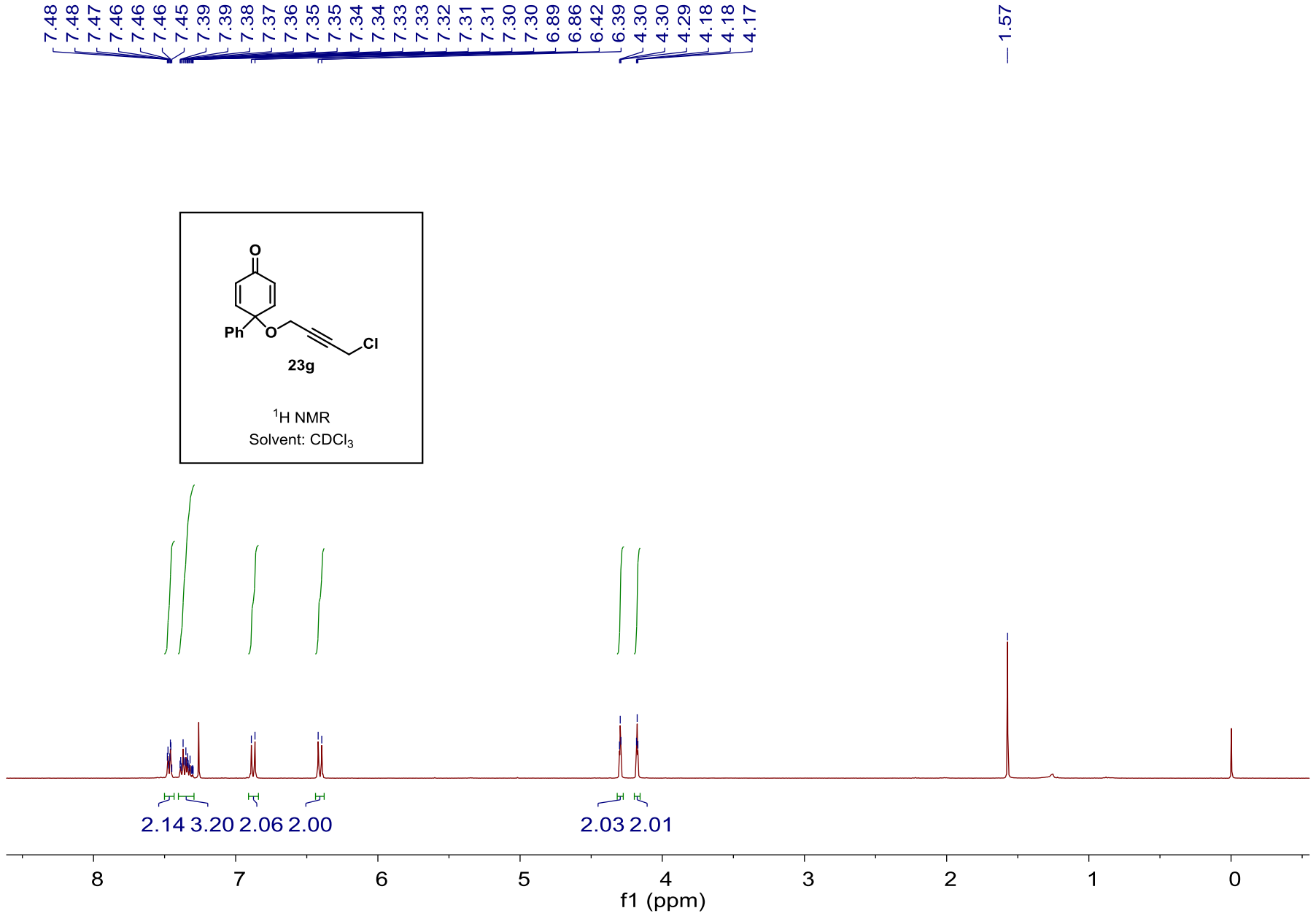
149.47
134.31
131.42
130.68
128.02
127.17
83.28
81.56
76.25
53.90
46.16
30.34
O
Ph
O
Cl
23f
13C NMR
Solvent: CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.48
7.47
7.46
7.46
7.46
7.45
7.39
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
6.89
6.86
6.42
6.39
4.30
4.30
4.29
4.18
4.18
4.17
1.57
O
Ph
O
Cl
23g
1H NMR
Solvent: CDCl3
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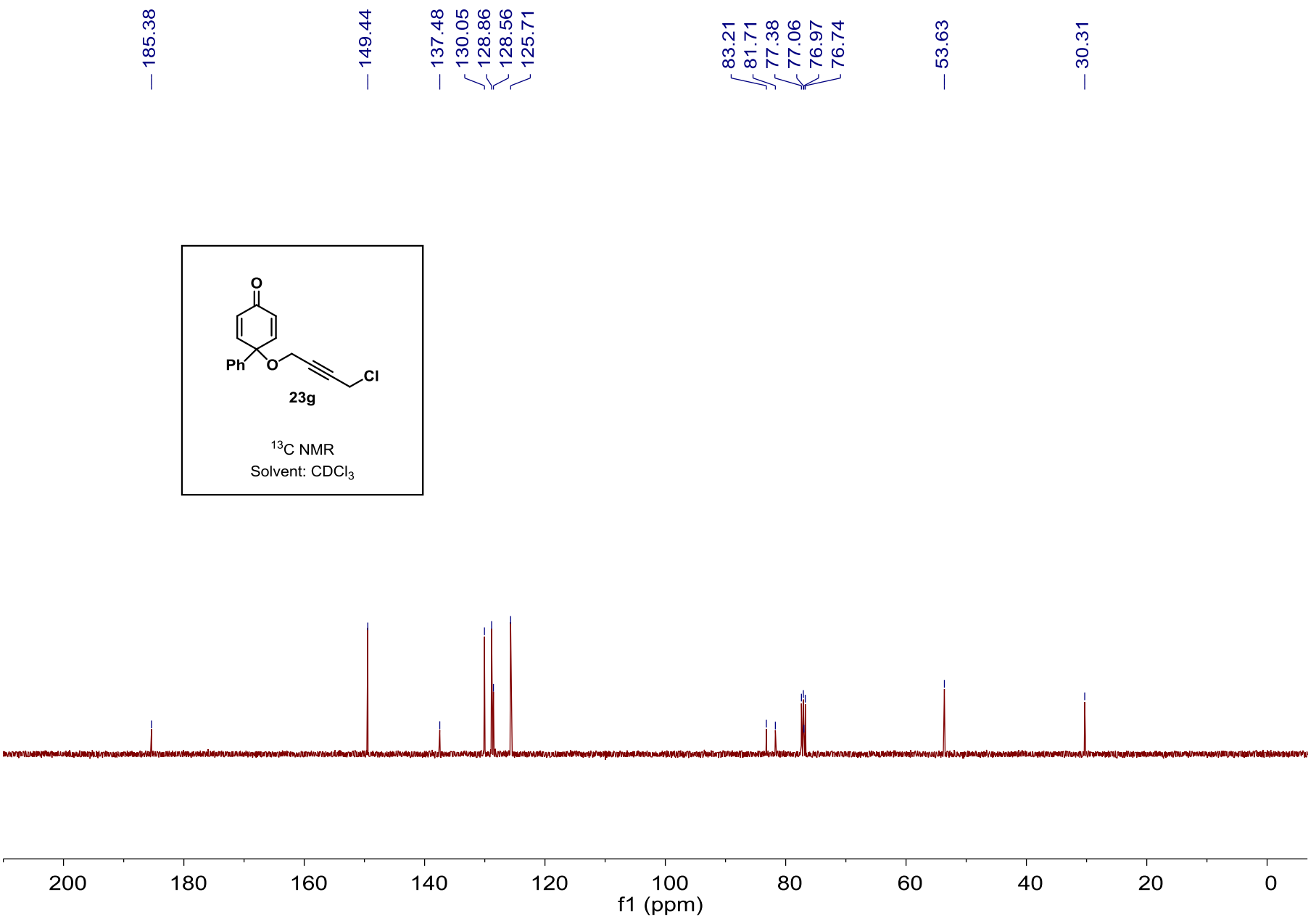
2.03 2.01
8
7
6
5
4
3
2
1
0
f1 (ppm)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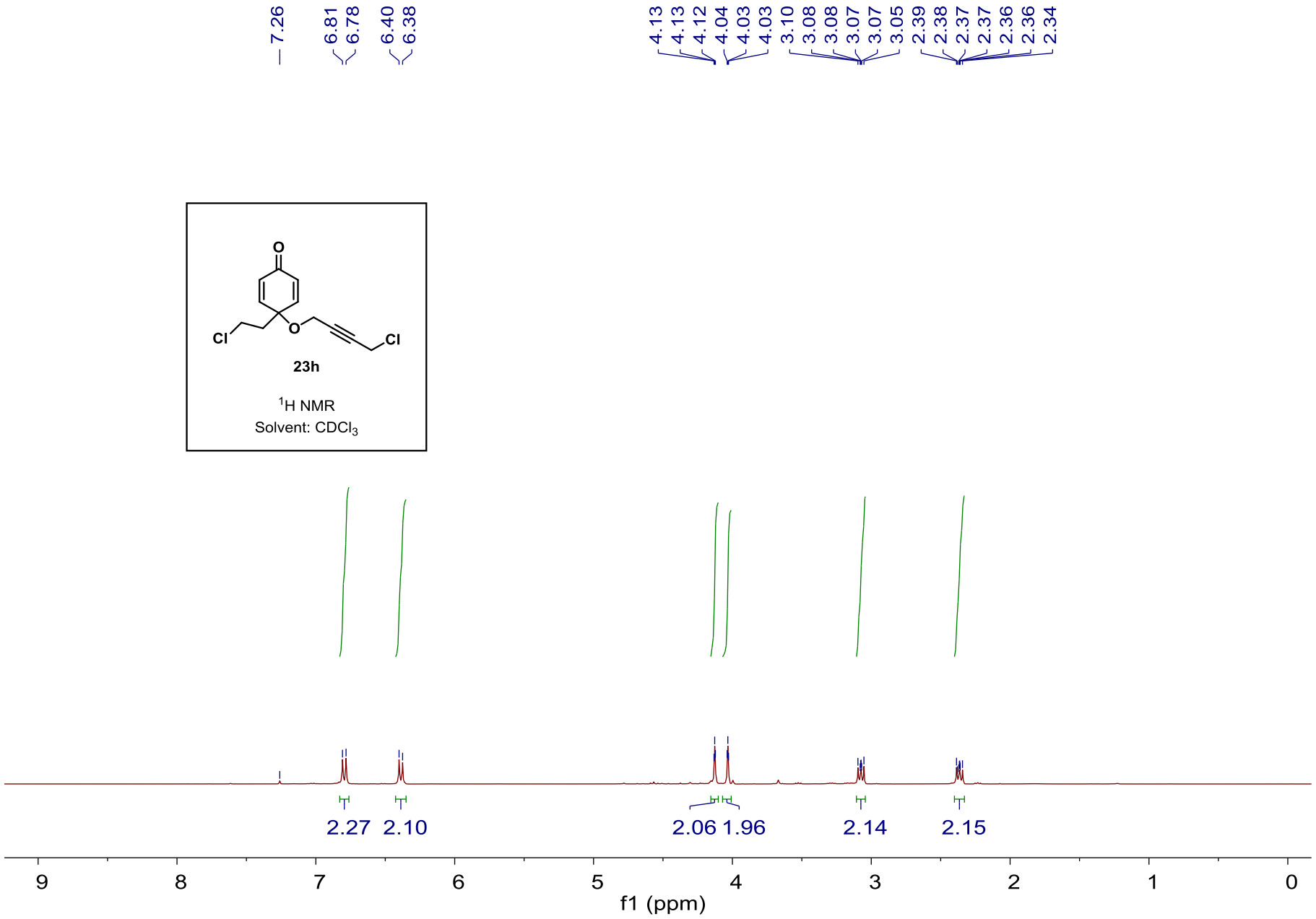
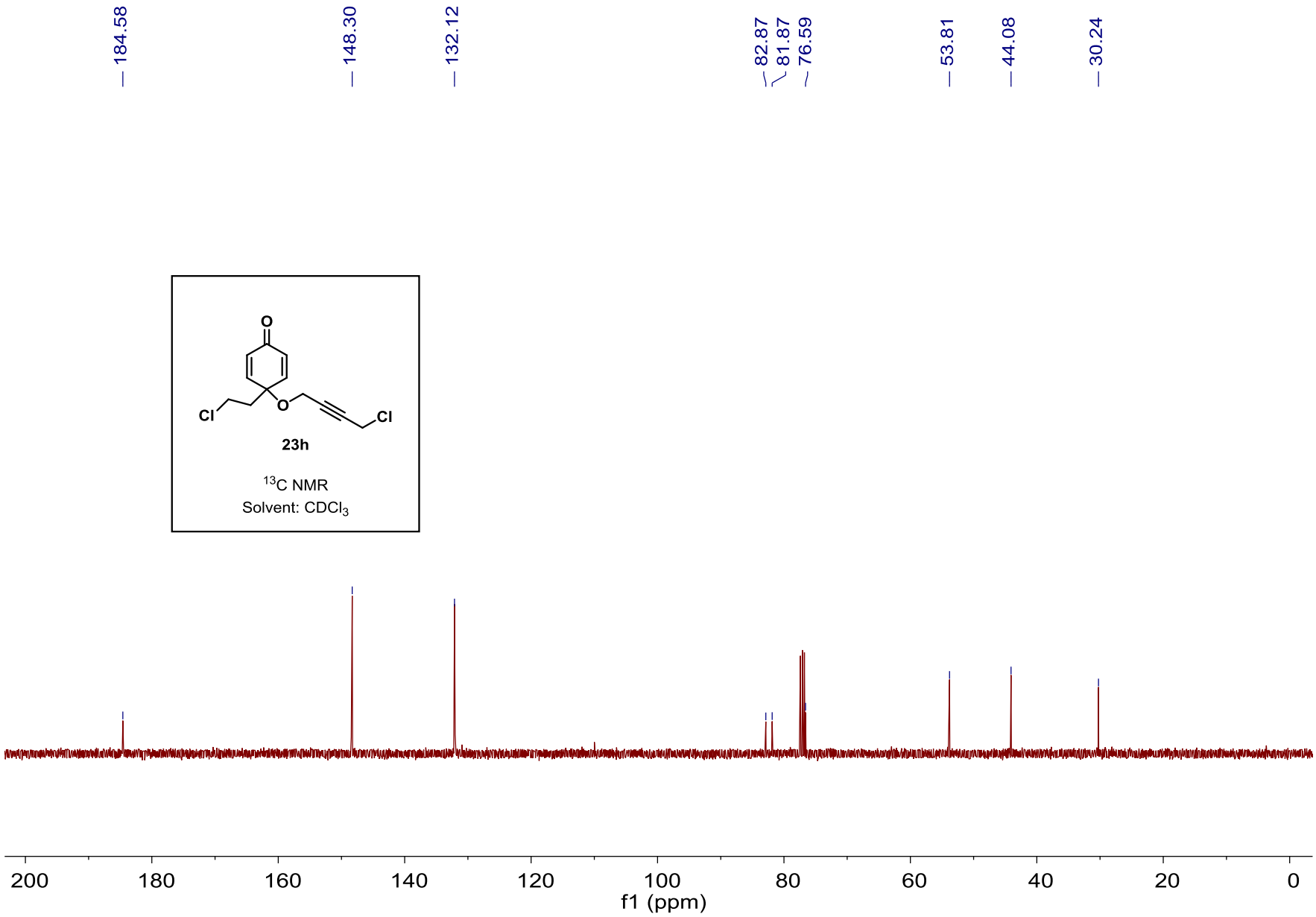
137.48
130.05
128.86
128.56
125.71
83.21
81.71
77.38
77.06
76.97
76.74
53.63
30.31
O
Ph
O
Cl
23g
13C NMR
Solvent: CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
6.81
6.78
6.40
6.38
4.13
4.13
4.12
4.04
4.03
4.03
3.10
3.08
3.08
3.07
3.07
3.05
2.39
2.38
2.37
2.37
2.36
2.36
2.34
O
Cl
O
Cl
23h
1H NMR
Solvent: CDCl3
2.27
2.10
2.06
1.96
2.14
2.15
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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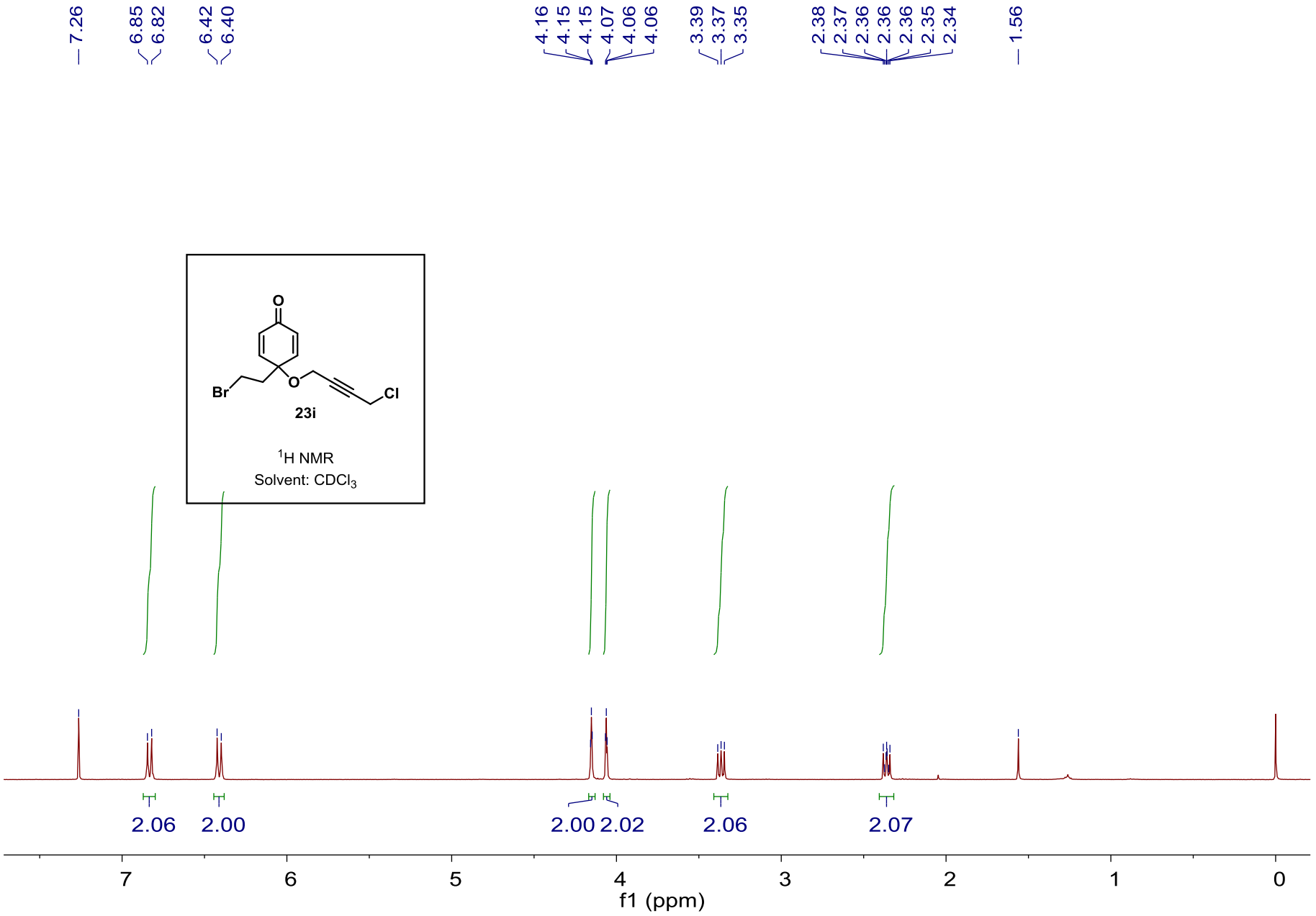
148.30
132.12
82.87
81.87
76.59
53.81
44.08
30.24
O
Cl
O
Cl
23h
^{13}C NMR
Solvent: $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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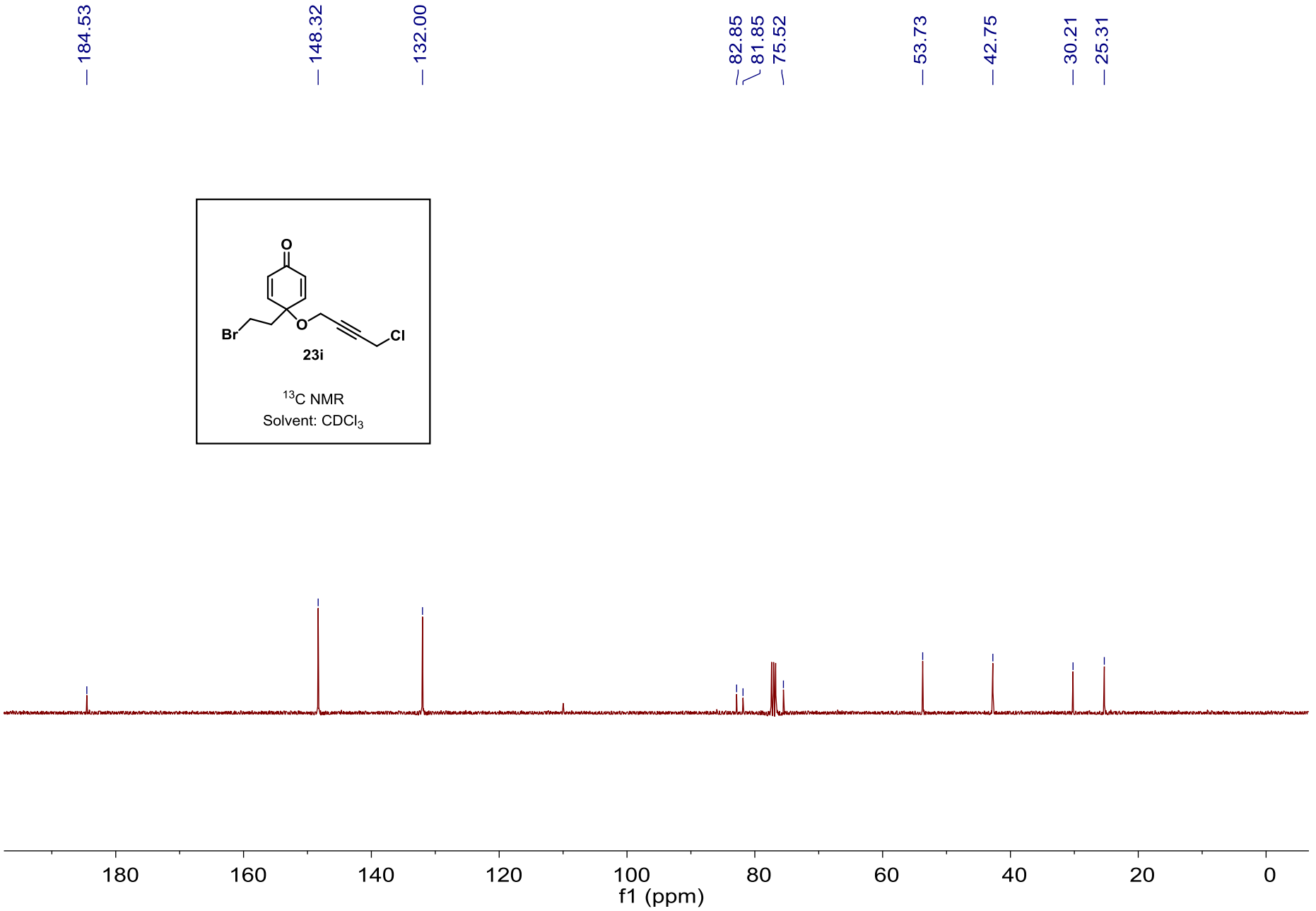
6.82
6.42
6.40
4.16
4.15
4.15
4.07
4.06
4.06
3.39
3.37
3.35
2.38
2.37
2.36
2.36
2.36
2.35
2.34
1.56
O
Br
O
Cl
23i
1H NMR
Solvent: CDCl3
2.06
2.00
2.00
2.02
2.06
2.07
7
6
5
4
3
2
1
0
f1 (ppm)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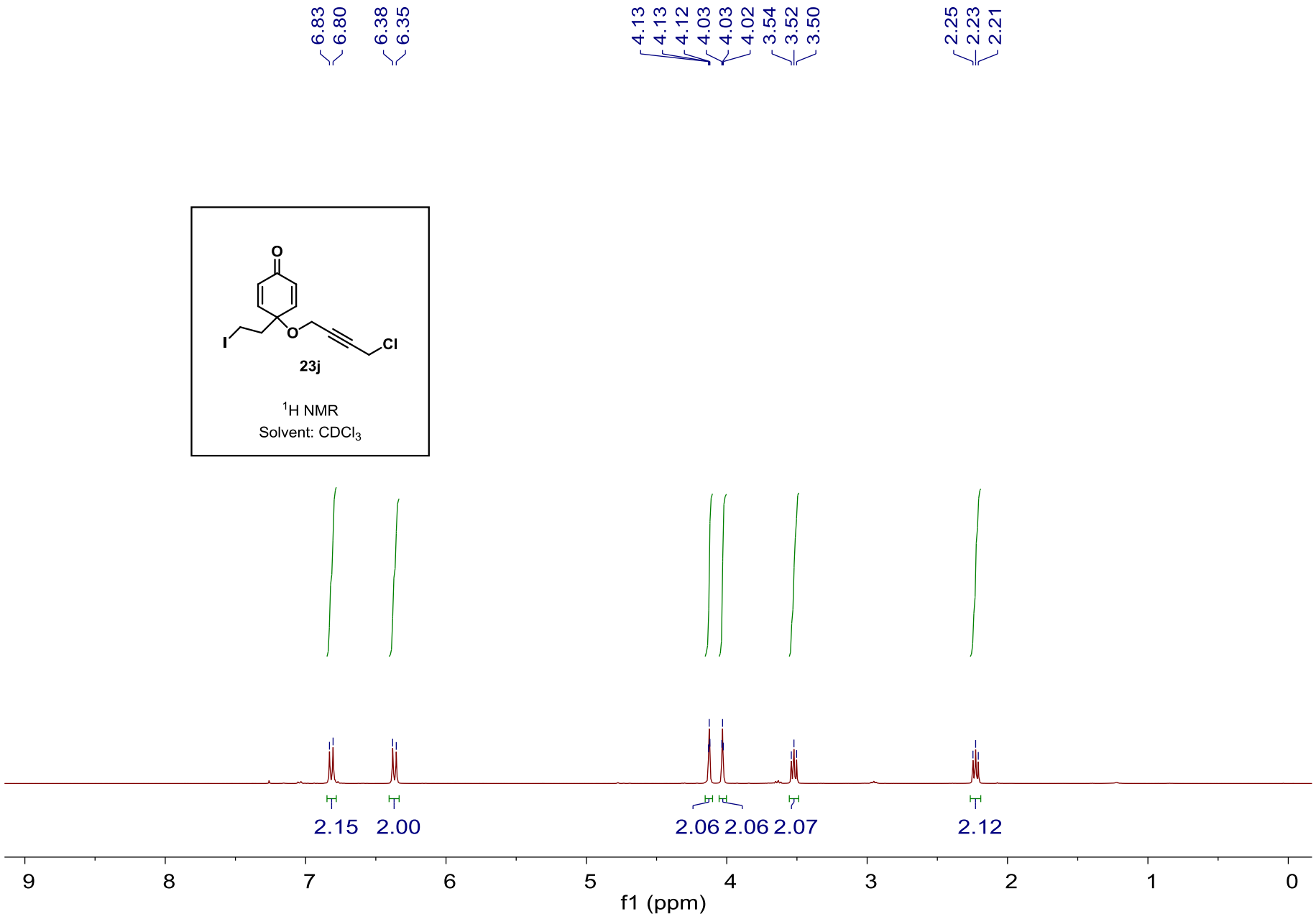
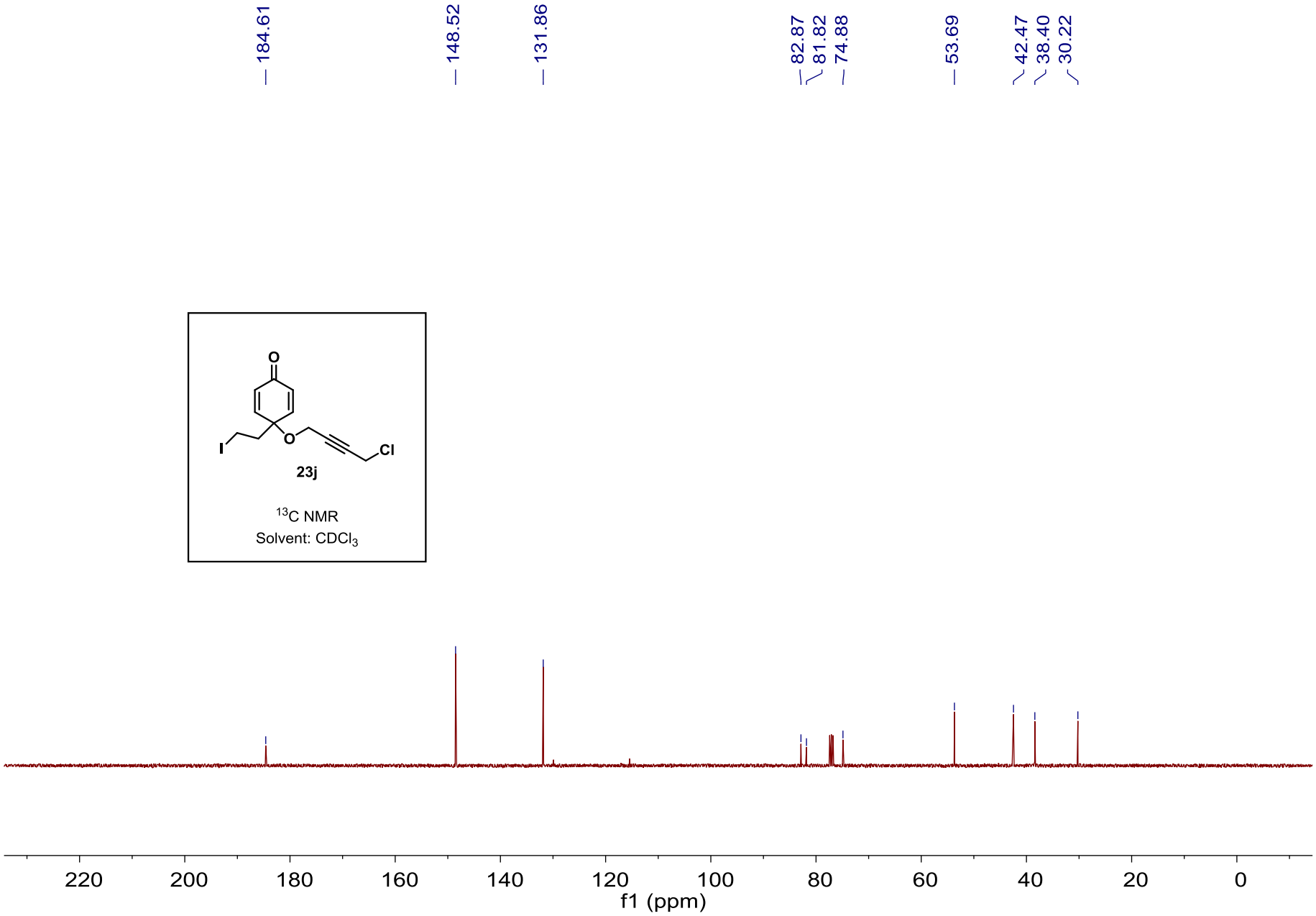
81.85
75.52
53.73
42.75
30.21
25.31
O
Br
O
Cl
23i
13C NMR
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


6.83
6.80
6.38
6.35
4.13
4.13
4.12
4.03
4.03
4.02
3.54
3.52
3.50
2.25
2.23
2.21
O
O
I
Cl
23j
1H NMR
Solvent: CDCl3
2.15
2.00
2.06
2.06
2.07
2.12
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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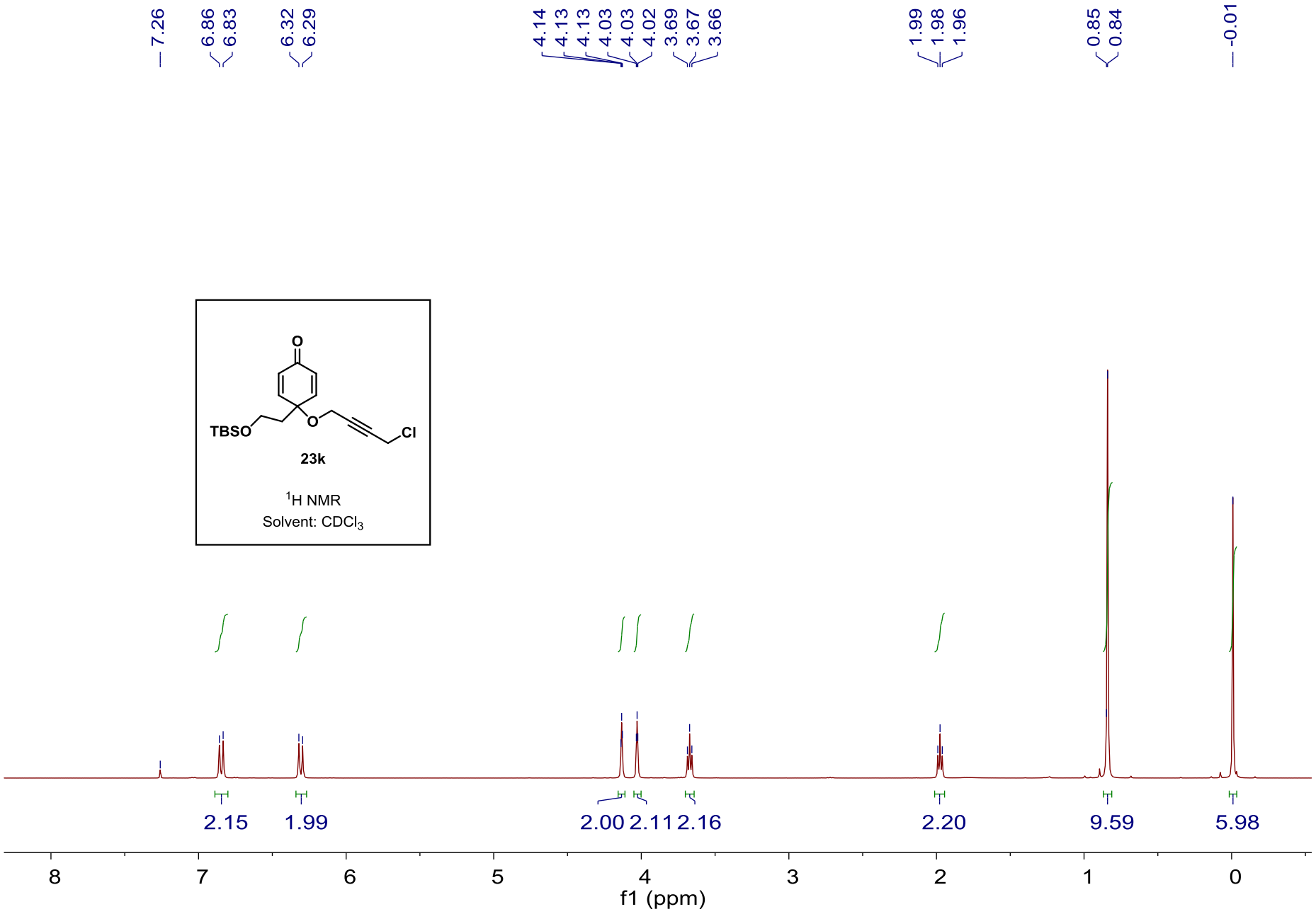
81.82
74.88
53.69
42.47
38.40
30.22
O
O
I
Cl
23j
^{13}C NMR
Solvent: $CDCl_3$
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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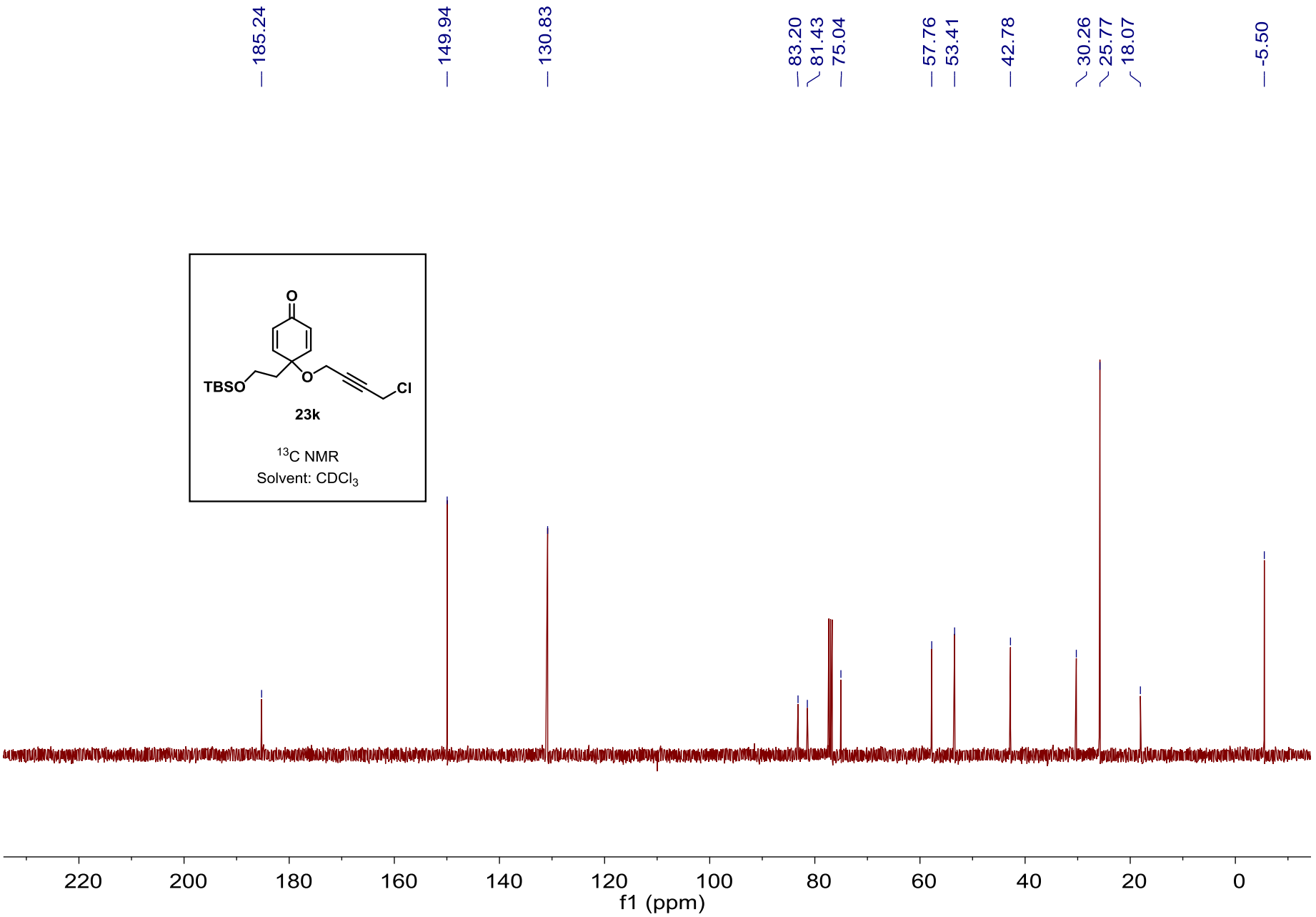
6.83
6.32
6.29
4.14
4.13
4.13
4.03
4.03
4.02
3.69
3.67
3.66
1.99
1.98
1.96
0.85
0.84
-0.01
O
TBSO
O
Cl
23k
1H NMR
Solvent: CDCl3
2.15
1.99
2.00
2.11
2.16
2.20
9.59
5.98
8
7
6
5
4
3
2
1
0
f1 (ppm)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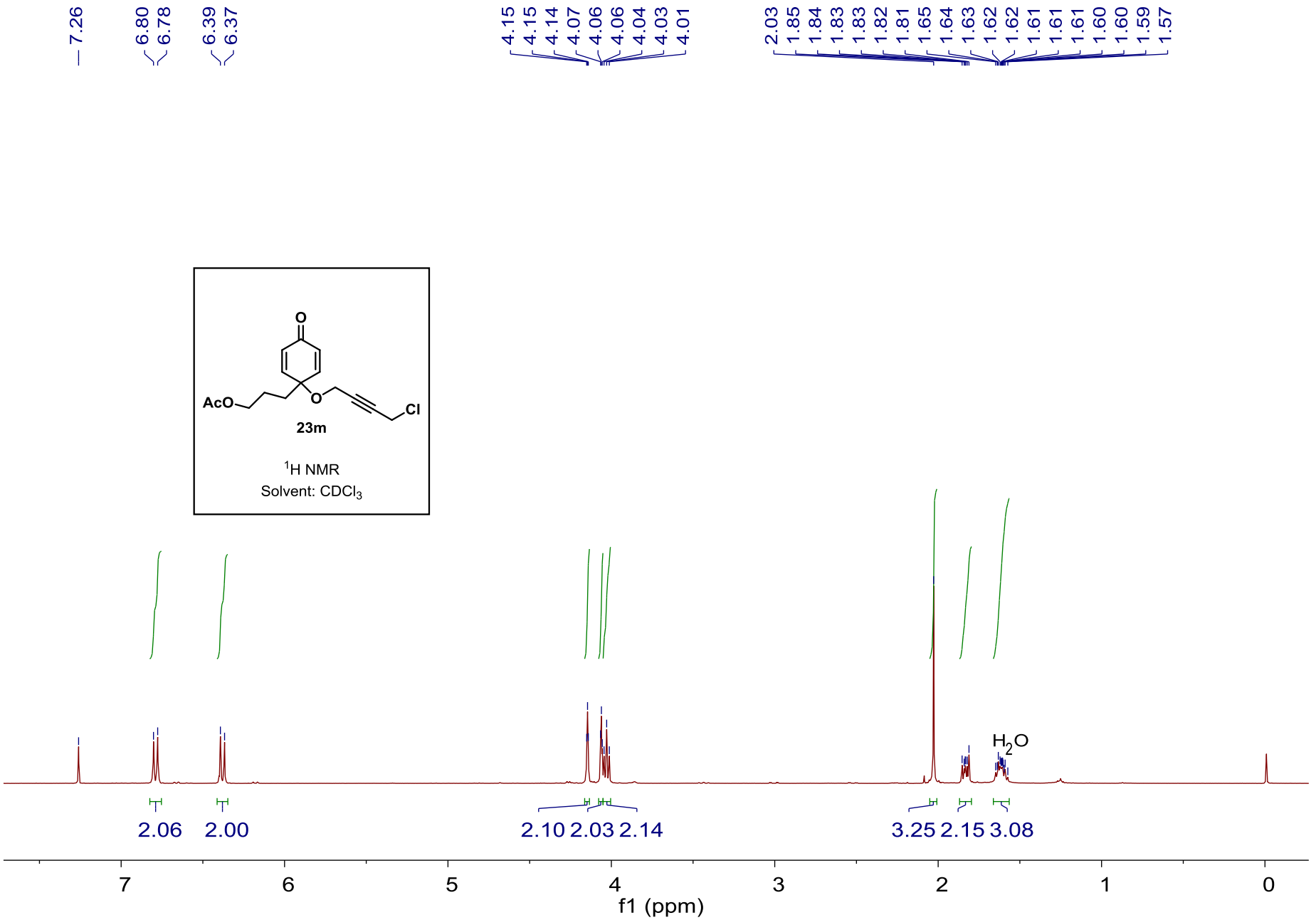
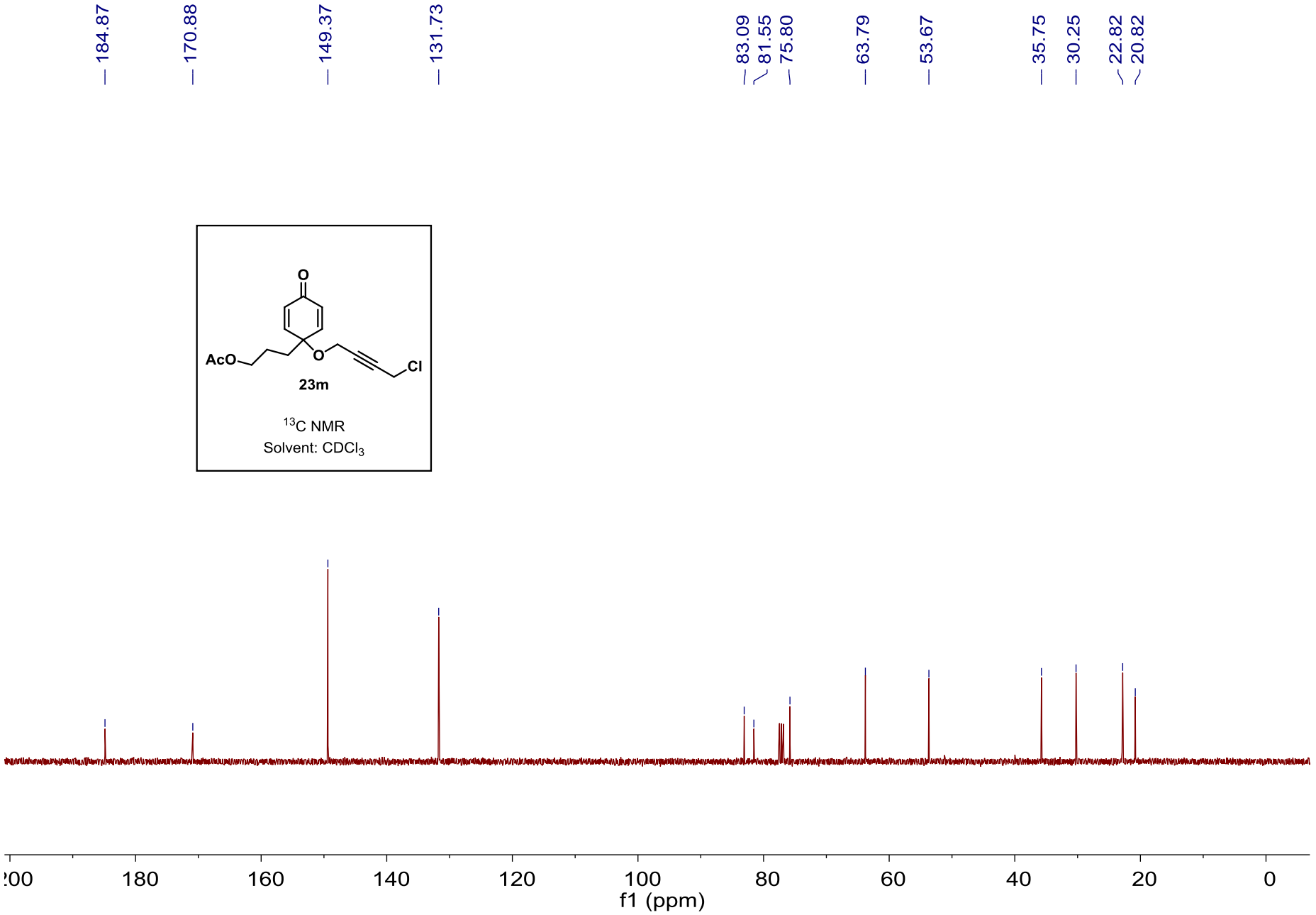
83.20
81.43
75.04
57.76
53.41
42.78
30.26
25.77
18.07
-5.50
O
TBSO
O
Cl
23k
^{13}C NMR
Solvent: $CDCl_3$
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
6.80
6.78
6.39
6.37
4.15
4.15
4.14
4.07
4.06
4.06
4.04
4.03
4.01
2.03
1.85
1.84
1.83
1.83
1.82
1.81
1.65
1.64
1.63
1.62
1.62
1.61
1.61
1.61
1.60
1.60
1.59
1.57
O
AcO
O
Cl
23m
1H NMR
Solvent: CDCl3
H2O
2.06
2.00
2.10
2.03
2.14
3.25
2.15
3.08
7
6
5
4
3
2
1
0
f1 (ppm)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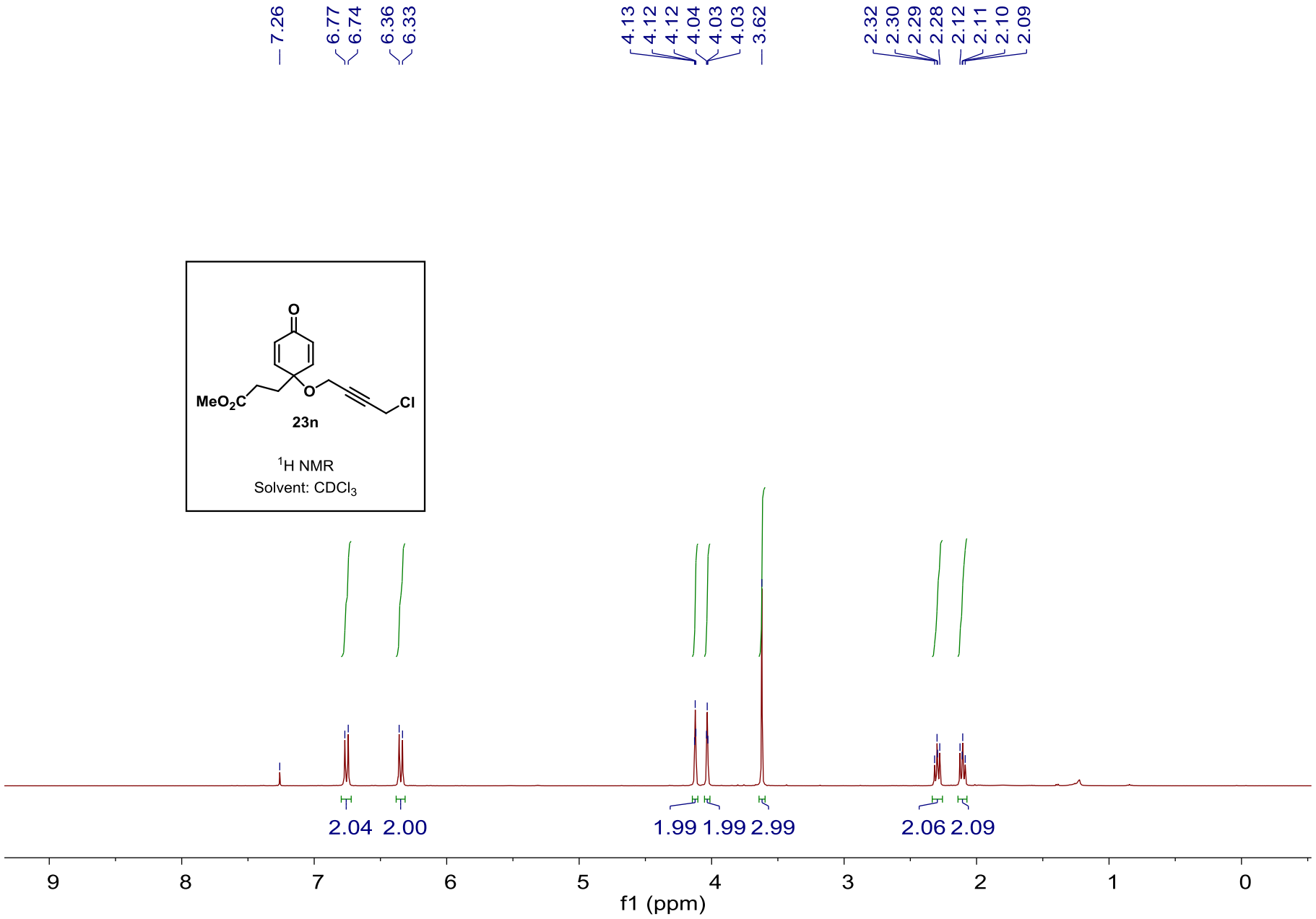
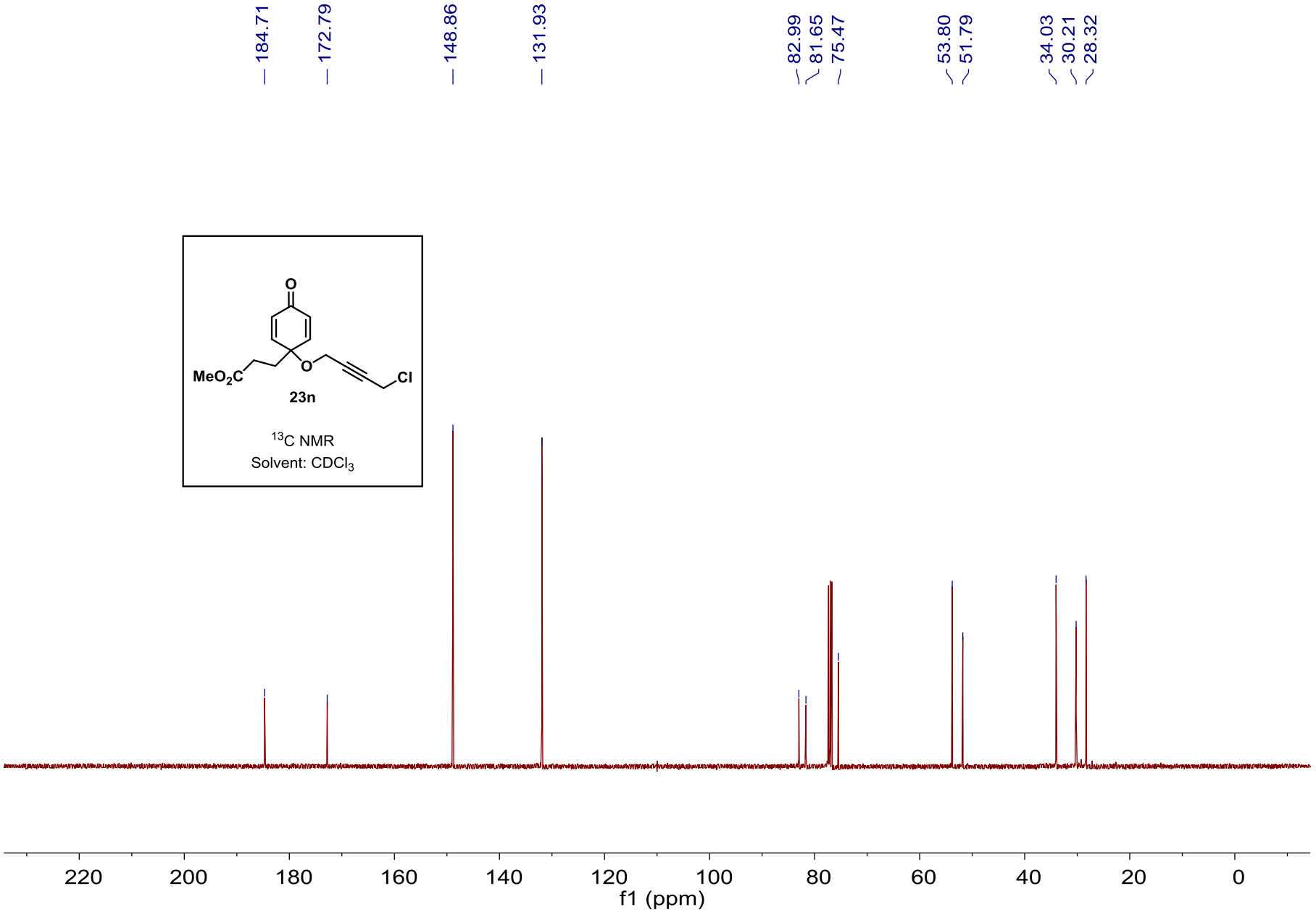
170.88
149.37
131.73
83.09
81.55
75.80
63.79
53.67
35.75
30.25
22.82
20.82
O
AcO
O
Cl
23m
13C NMR
Solvent: CDCl3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
6.77
6.74
6.36
6.33
4.13
4.12
4.12
4.04
4.03
4.03
3.62
2.32
2.30
2.29
2.28
2.12
2.11
2.10
2.09
O
MeO2C
O
Cl
23n
1H NMR
Solvent: CDCl3
2.04 2.00
1.99 1.99 2.99
2.06 2.09
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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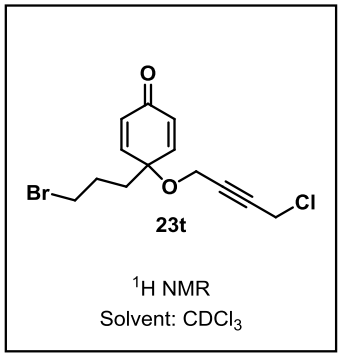
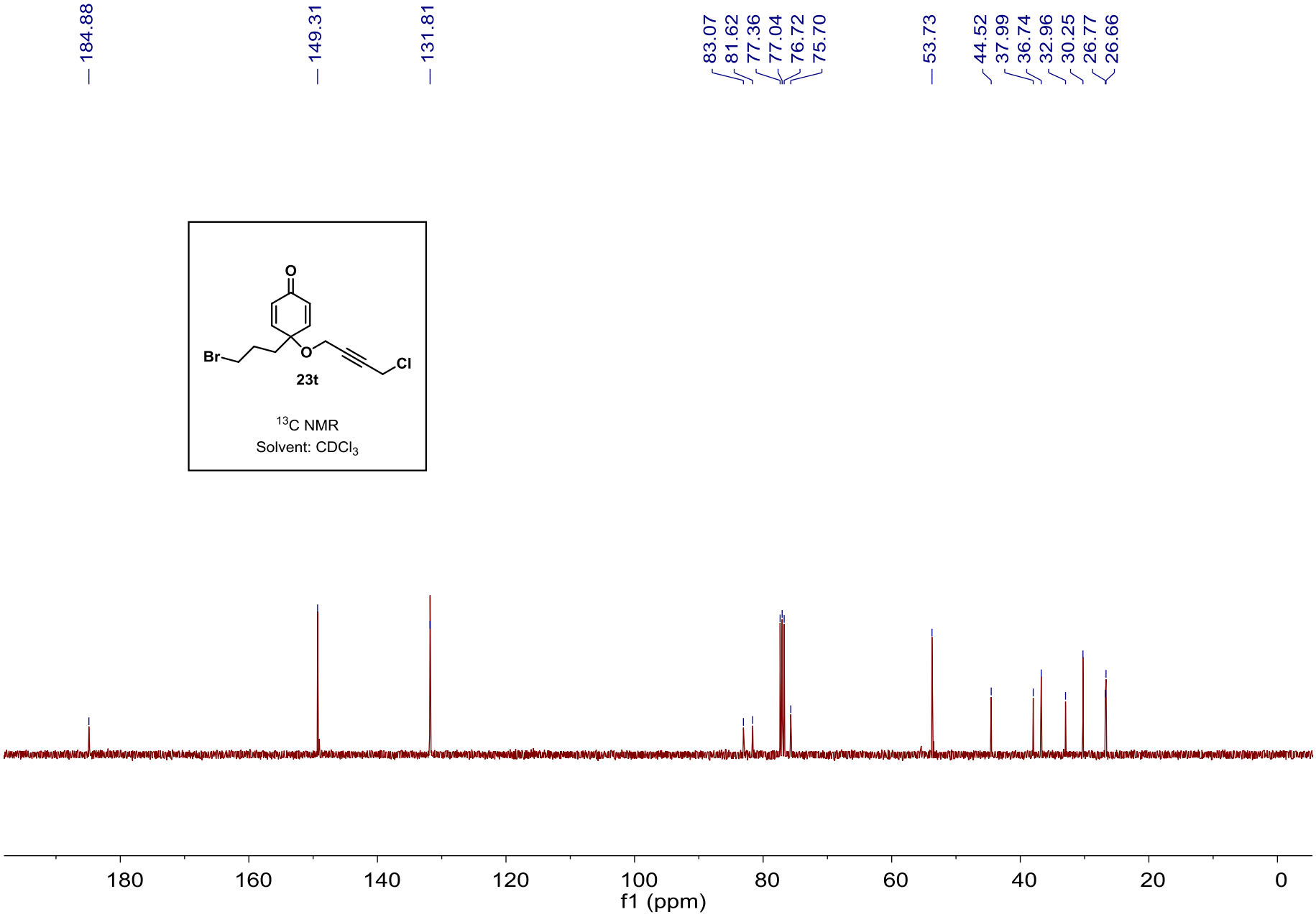
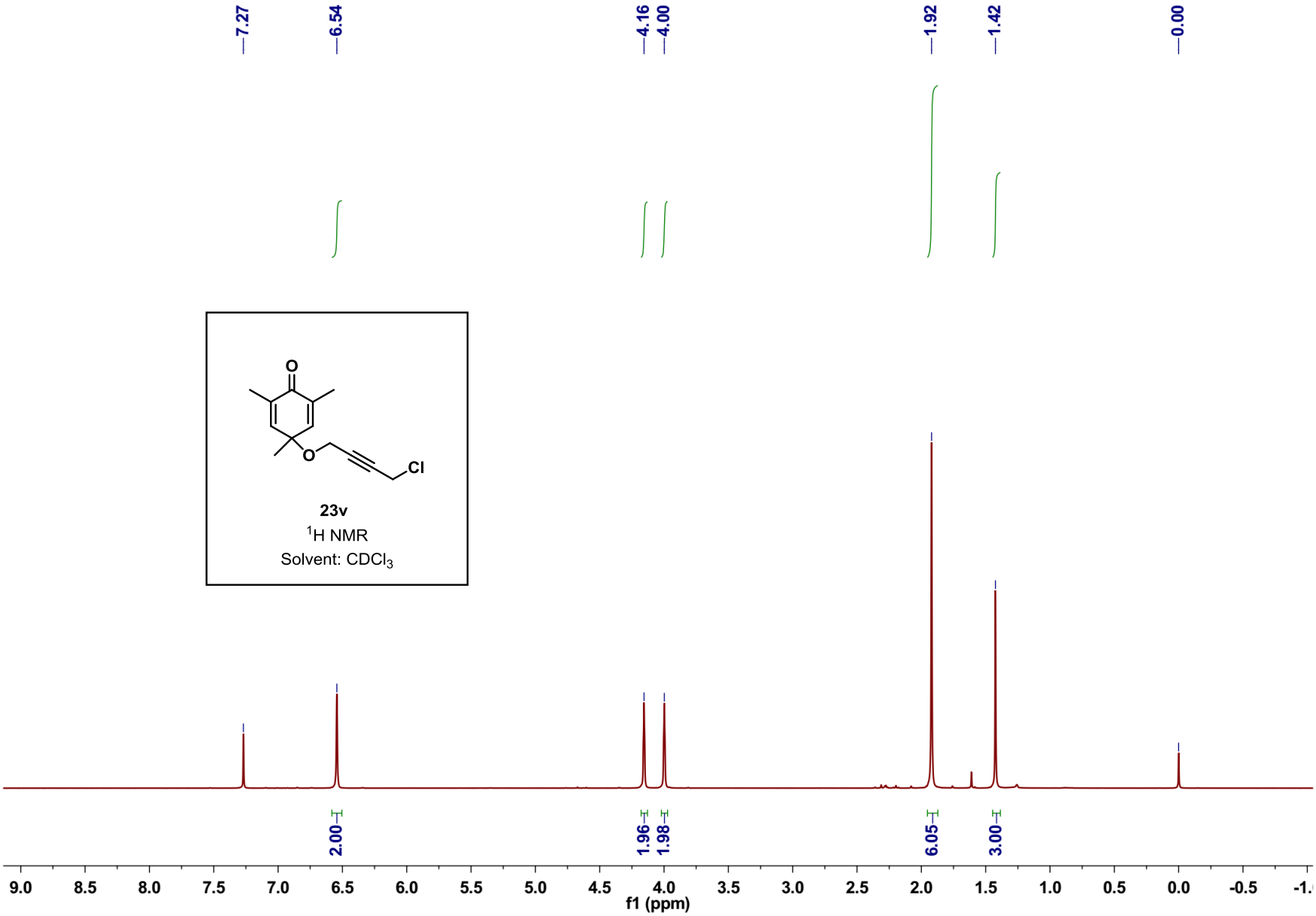
172.79
148.86
131.93
82.99
81.65
75.47
53.80
51.79
34.03
30.21
28.32
O
MeO2C
O
Cl
23n
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


O
Br
O
Cl
23t
^{1}H NMR
Solvent: $CDCl_3$

7.26
6.80
6.78
6.78
6.39
6.36
4.15
4.14
4.14
4.06
4.06
4.05
3.52
3.51
3.49
3.38
3.37
3.35
1.94
1.94
1.93
1.93
1.92
1.91
1.90
1.87
1.86
1.85
1.84
1.83
1.79
1.78
1.77
1.77
1.76
1.75
1.74
2.08 2.03
1.97 2.02 1.21 0.90
2.10 0.91 1.31
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


184.88
149.31
131.81
83.07
81.62
77.36
77.04
76.72
75.70
53.73
44.52
37.99
36.74
32.96
30.25
26.77
26.66
O
Br
O
Cl
23t
13C NMR
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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0.00
O
O
Cl
23v
1H NMR
Solvent: CDCl3
2.00
1.96
1.98
6.05
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
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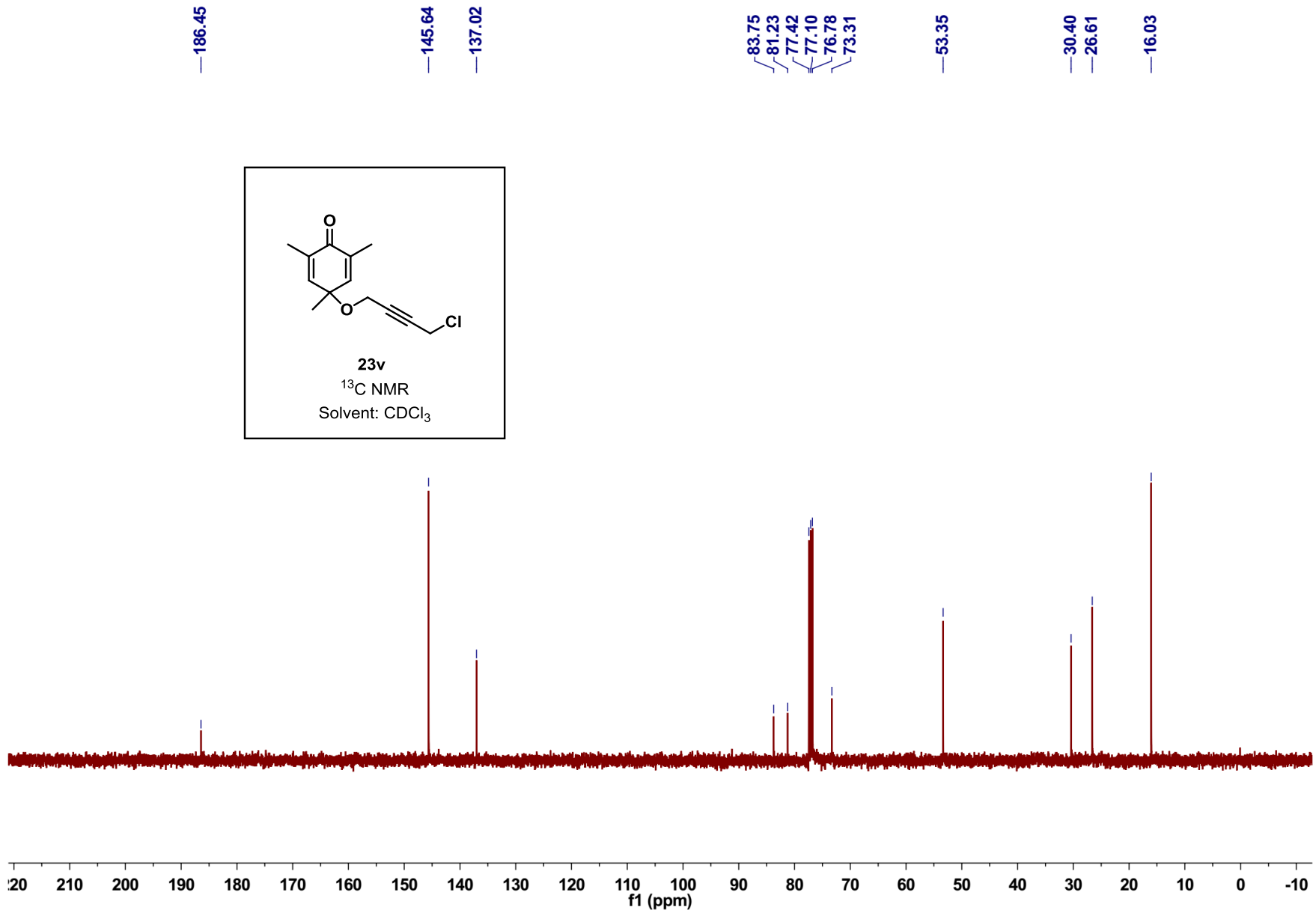
-0.5
f1 (ppm)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137.02
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77.10
76.78
73.31
53.35
30.40
26.61
16.03
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O
Cl
23v
13C NMR
Solvent: CDCl3
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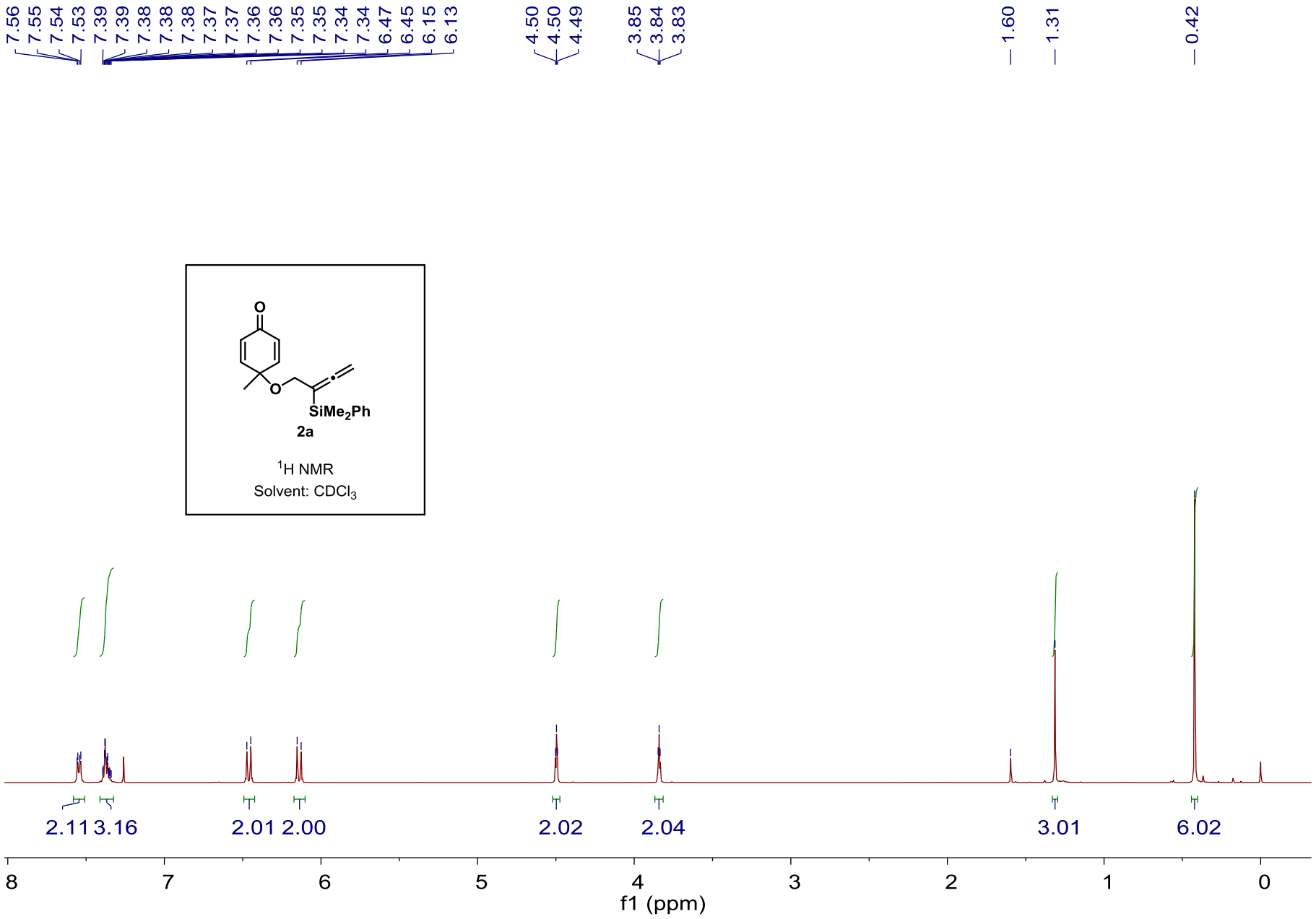
f1 (ppm)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7.34
7.34
6.47
6.45
6.15
6.13
4.50
4.50
4.49
3.85
3.84
3.83
1.60
1.31
0.42
O
O
SiMe2Ph
2a
1H NMR
Solvent: CDCl3
2.11
3.16
2.01
2.00
2.02
2.04
3.01
6.02
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5
4
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1
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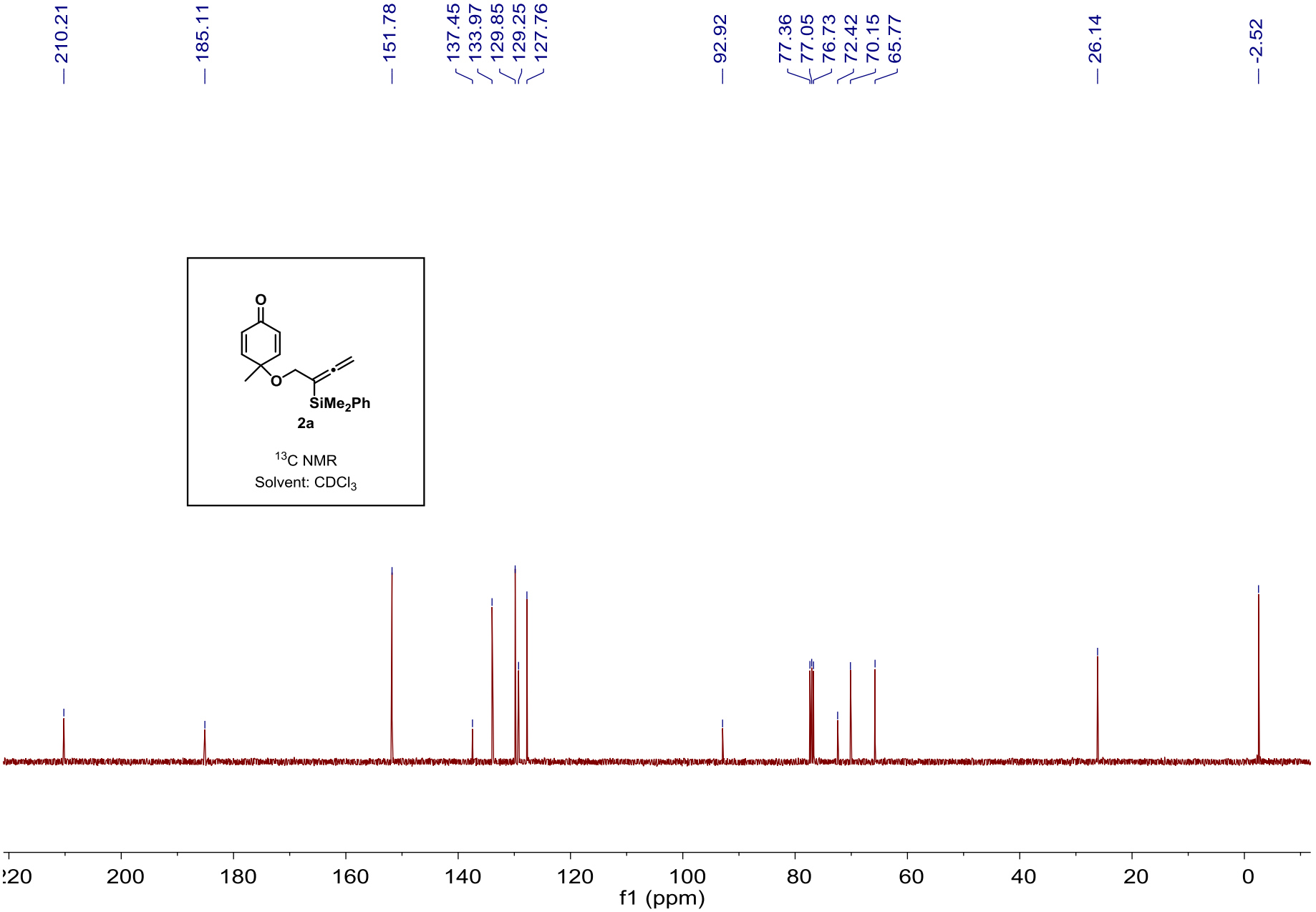
f1 (ppm)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127.76
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77.36
77.05
76.73
72.42
70.15
65.77
26.14
-2.52
O
O
SiMe2Ph
2a
13C NMR
Solvent: CDCl3
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180
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140
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100
80
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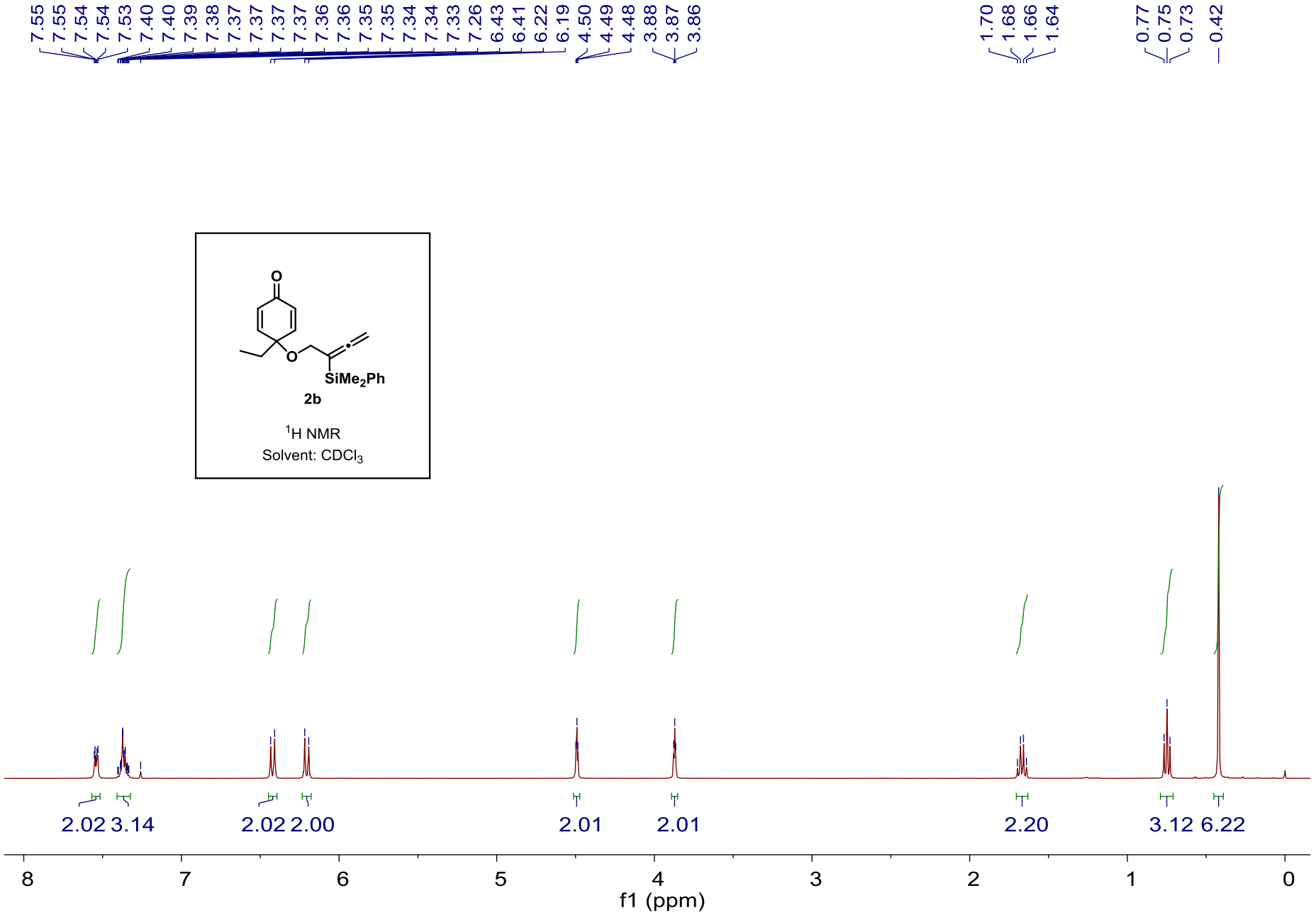
f1 (ppm)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7.33
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6.22
6.19
4.50
4.49
4.48
3.88
3.87
3.86
1.70
1.68
1.66
1.64
0.77
0.75
0.73
0.42
O
O
SiMe2Ph
2b
1H NMR
Solvent: CDCl3
2.02
3.14
2.02
2.00
2.01
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5
4
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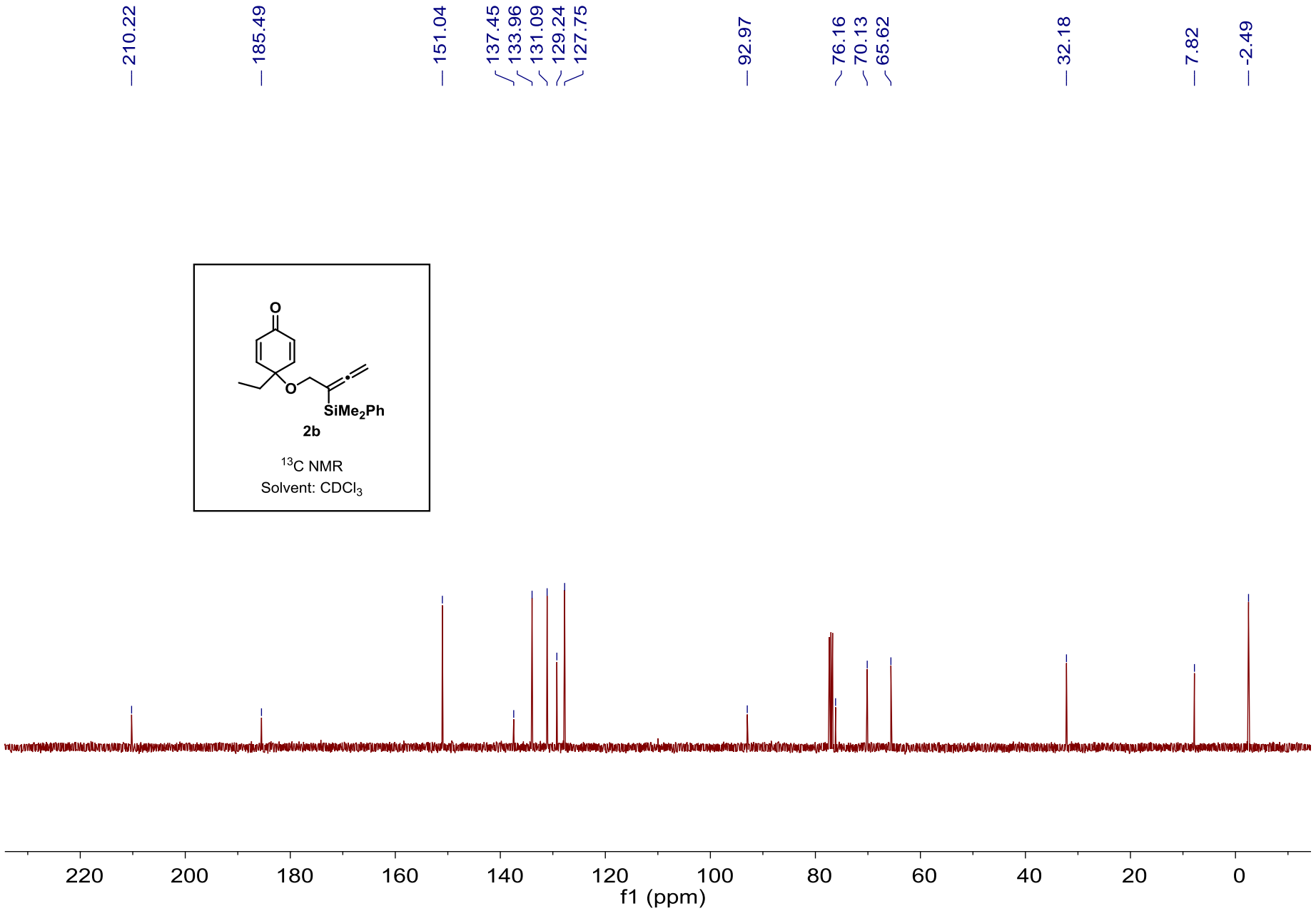
f1 (ppm)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32.18
7.82
-2.49
O
O
SiMe2Ph
2b
13C NMR
Solvent: CDCl3
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200
180
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140
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100
80
60
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20
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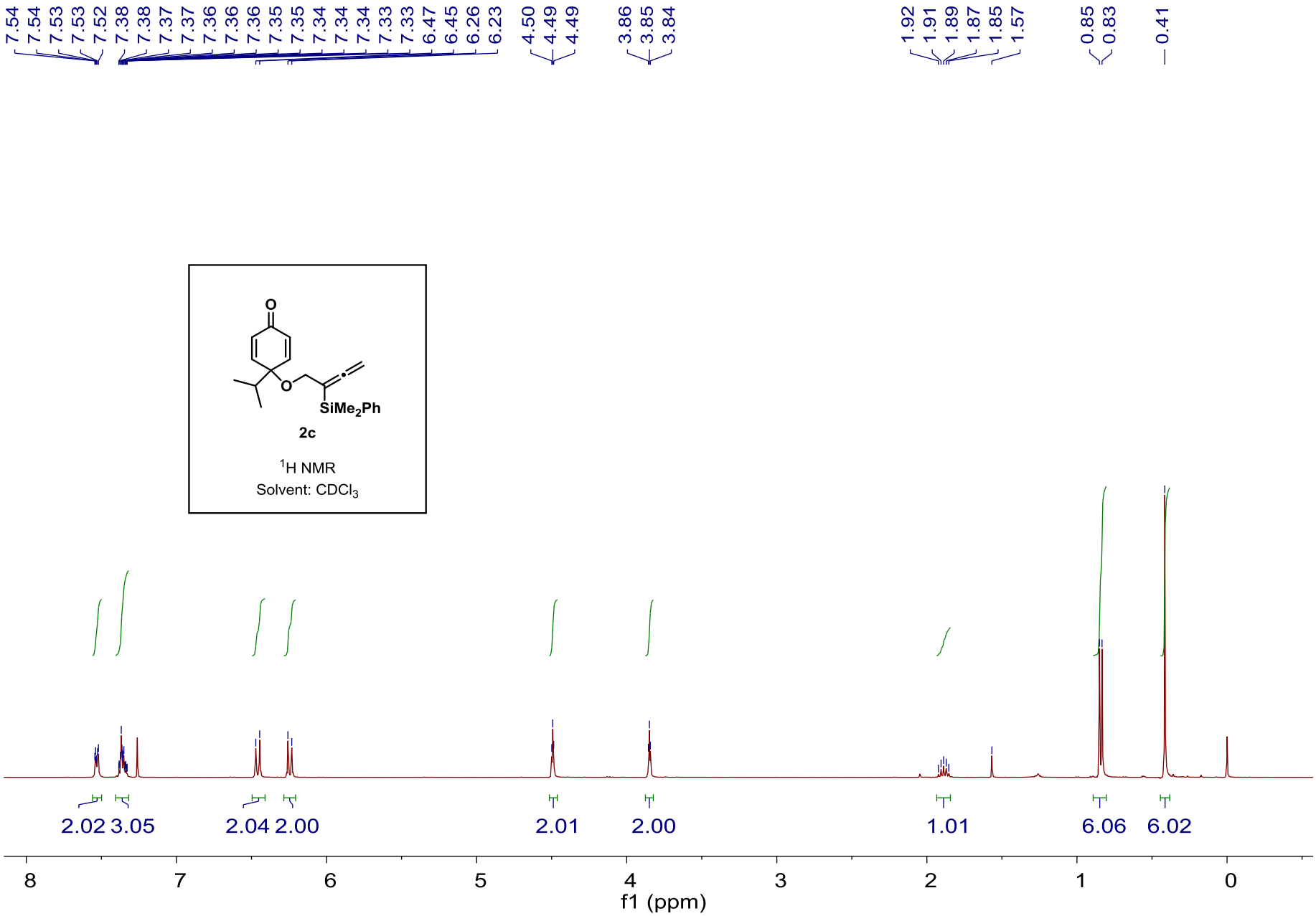
f1 (ppm)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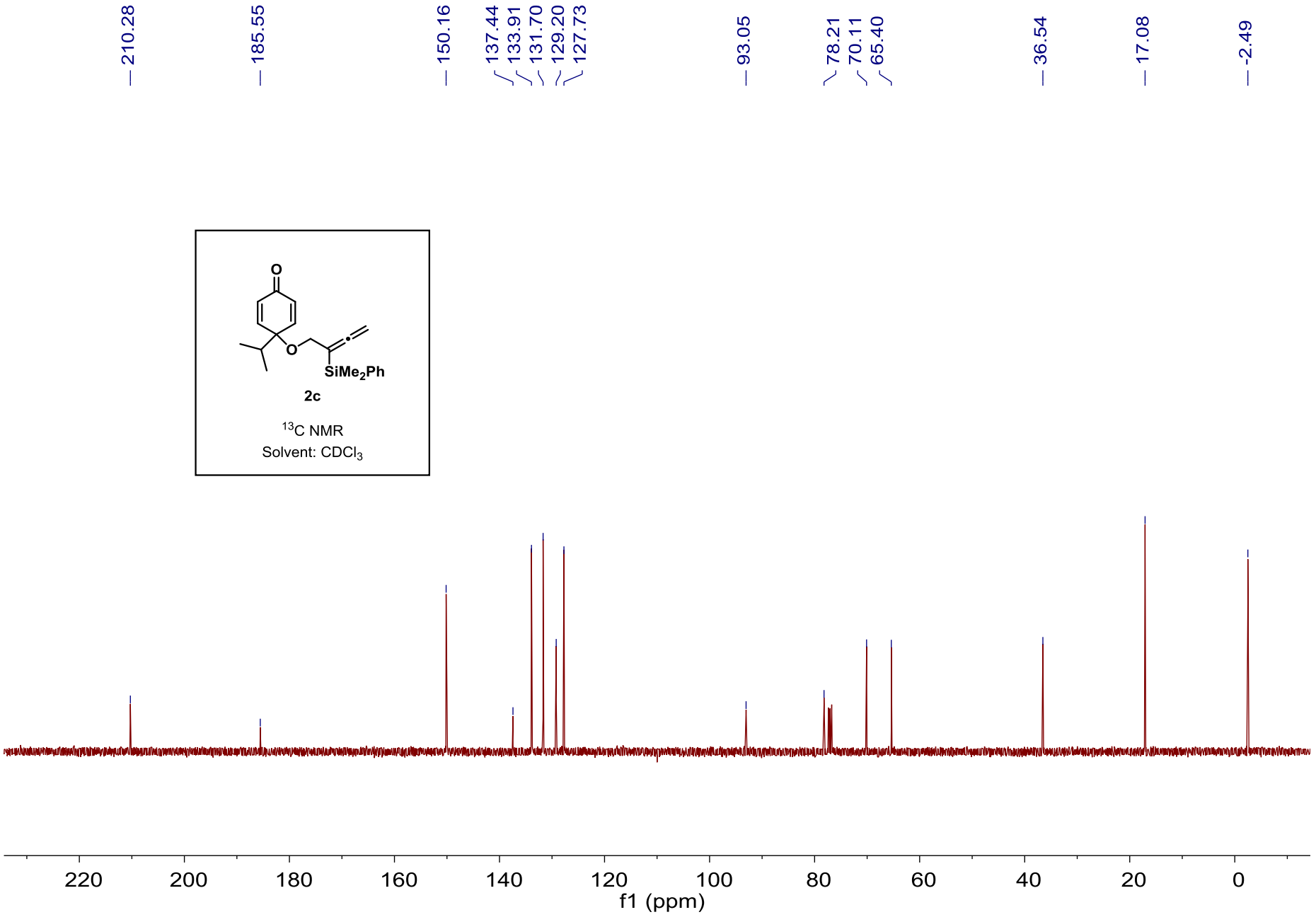
4.50 4.49 4.49
3.86 3.85 3.84
1.92 1.91 1.89 1.87 1.85 1.57
0.85 0.83
0.41
O
O
SiMe2Ph
2c
1H NMR
Solvent: CDCl3
2.02 3.05 2.04 2.00 2.01 2.00 1.01 6.06 6.02
8 7 6 5 4 3 2 1 0
f1 (ppm)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131.70
129.20
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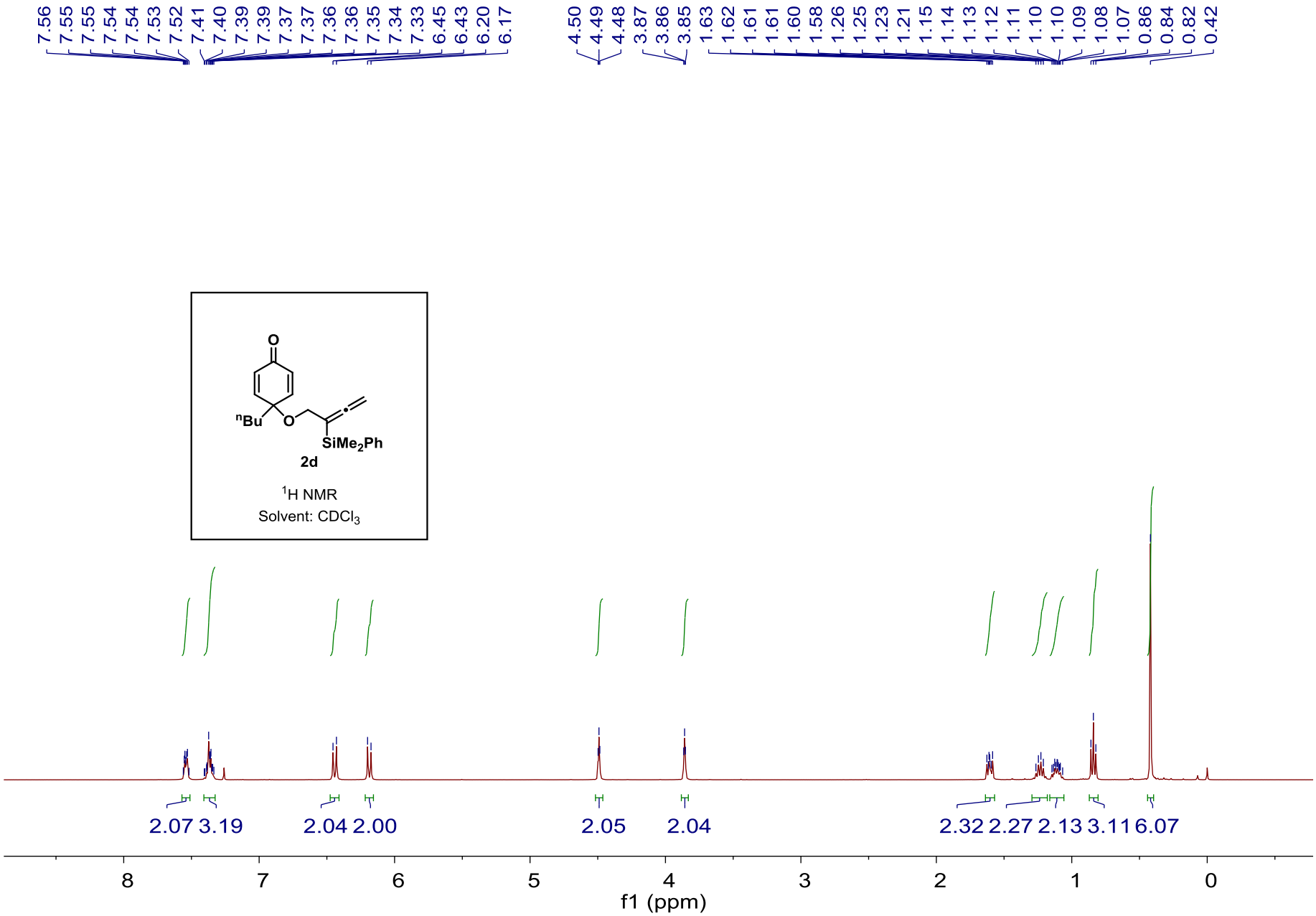
93.05
78.21
70.11
65.40
36.54
17.08
-2.49
O
O
SiMe2Ph
2c
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.50 4.49 4.48 3.87 3.86 3.85 1.63 1.62 1.61 1.61 1.60 1.58 1.26 1.25 1.23 1.21 1.15 1.14 1.13 1.12 1.11 1.10 1.10 1.09 1.08 1.07 0.86 0.84 0.82 0.42
O
nBu
O
SiMe2Ph
2d
1H NMR
Solvent: CDCl3
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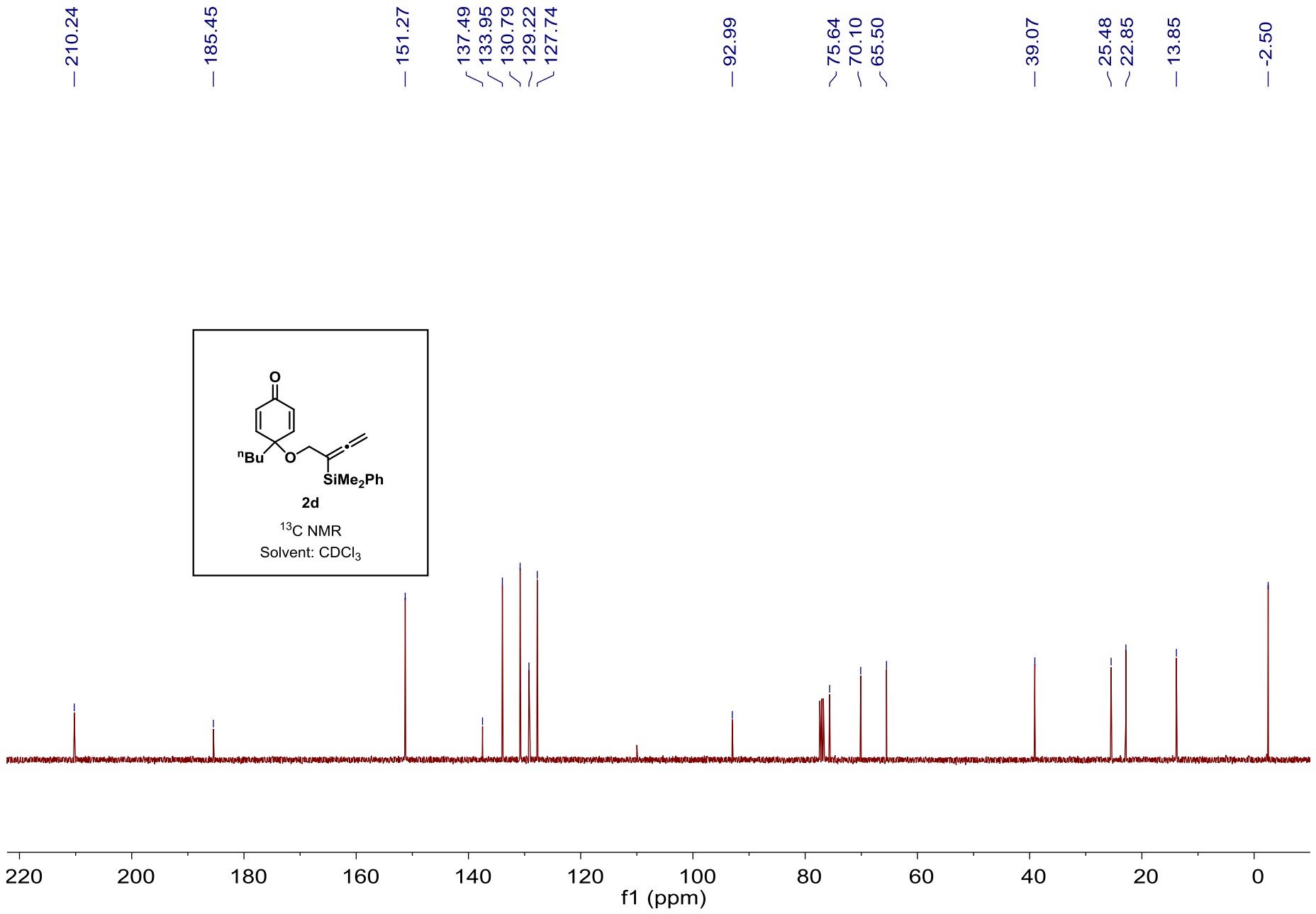
8 7 6 5 4 3 2 1 0
f1 (ppm)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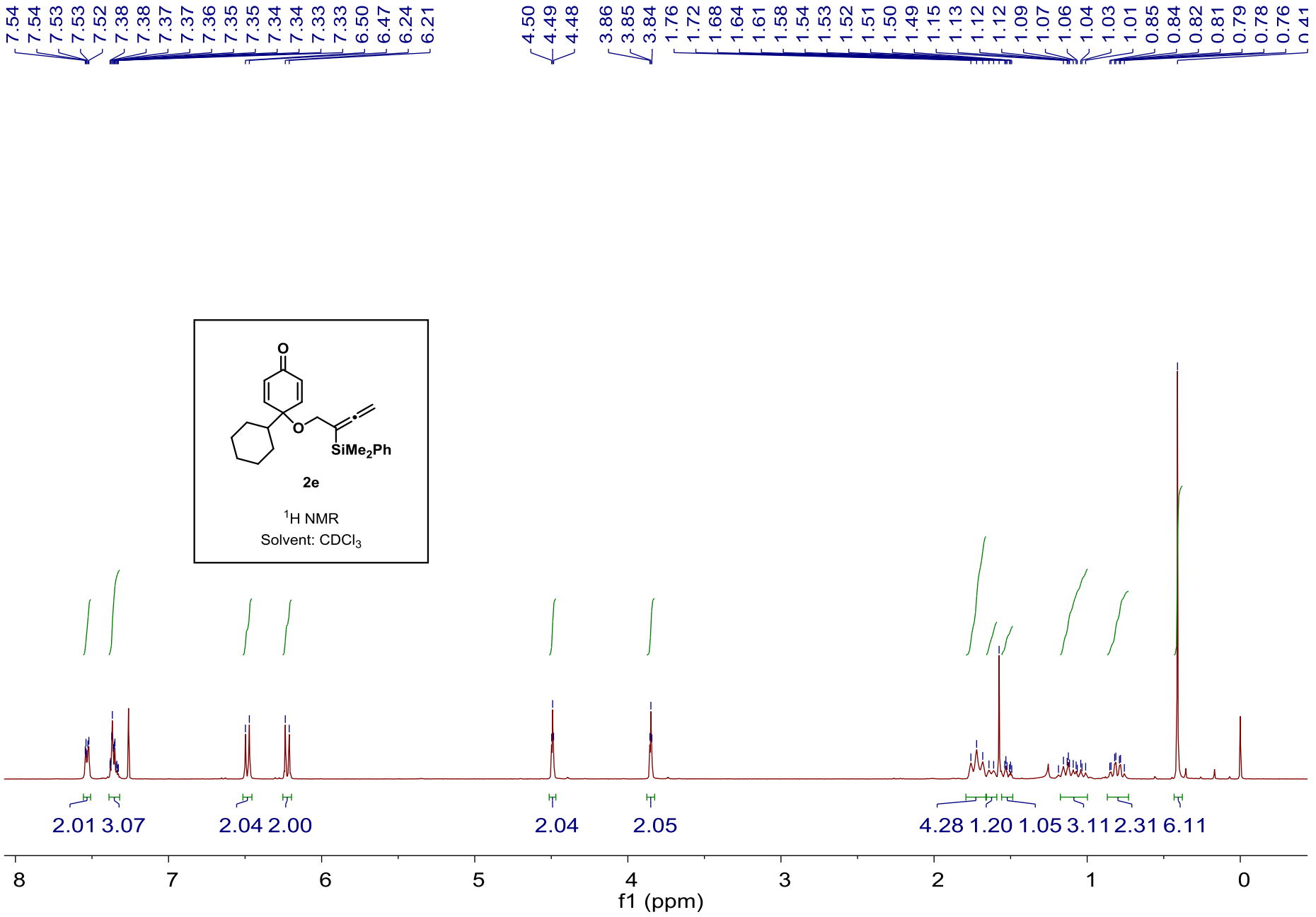
129.22
127.74
92.99
75.64
70.10
65.50
39.07
25.48
22.85
13.85
-2.50
O
nBu
O
SiMe2Ph
2d
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.50 4.49 4.48 3.86 3.85 3.84 1.76 1.72 1.68 1.64 1.61 1.58 1.54 1.53 1.52 1.51 1.50 1.49 1.15 1.13 1.12 1.12 1.09 1.07 1.06 1.04 1.03 1.01 0.85 0.84 0.82 0.81 0.79 0.78 0.76
O
O
SiMe2Ph
2e
1H NMR
Solvent: CDCl3
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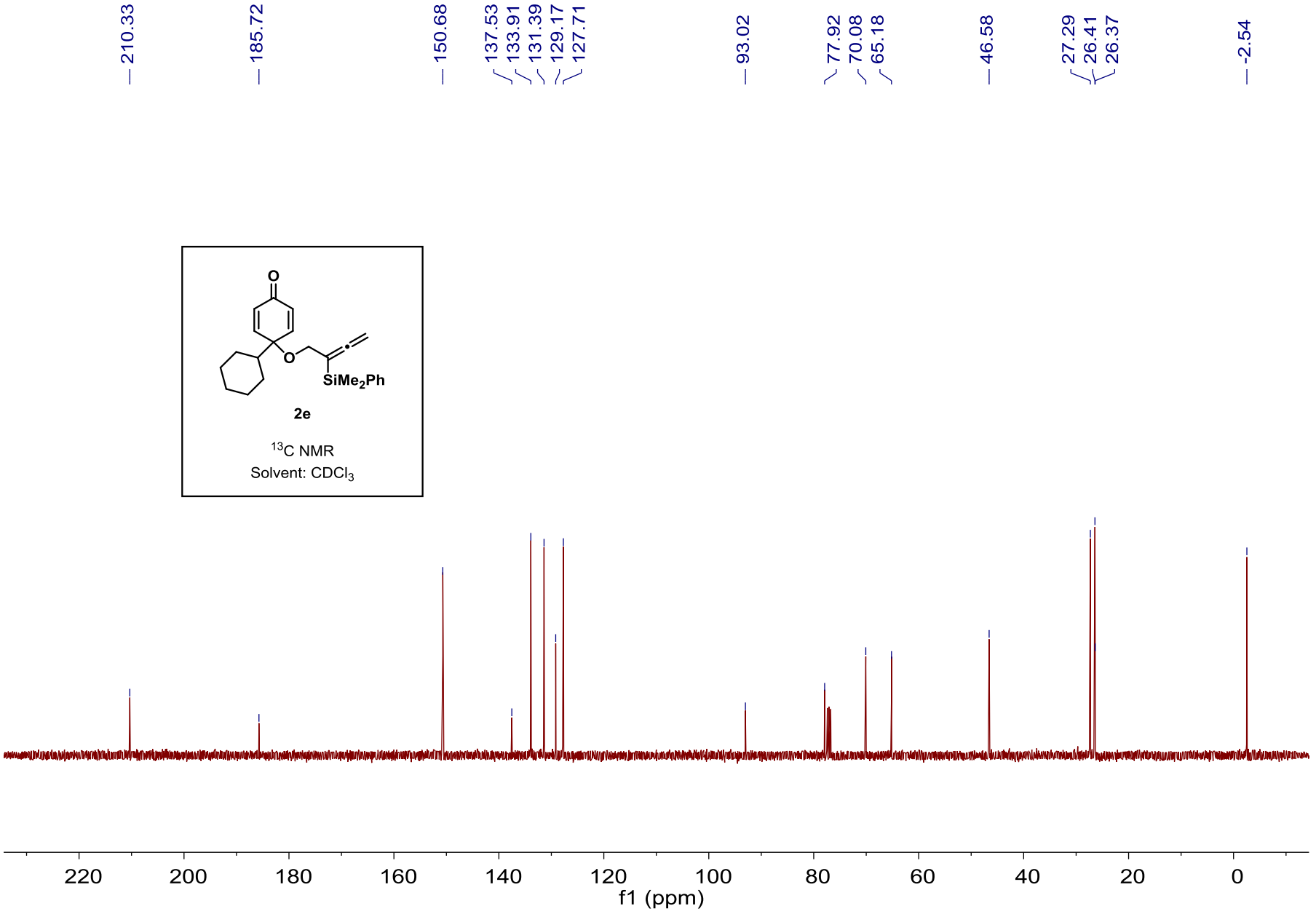
8 7 6 5 4 3 2 1 0
f1 (ppm)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77.92
70.08
65.18
46.58
27.29
26.41
26.37
-2.54
O
O
SiMe2Ph
2e
13C NMR
Solvent: CDCl3
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200
180
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140
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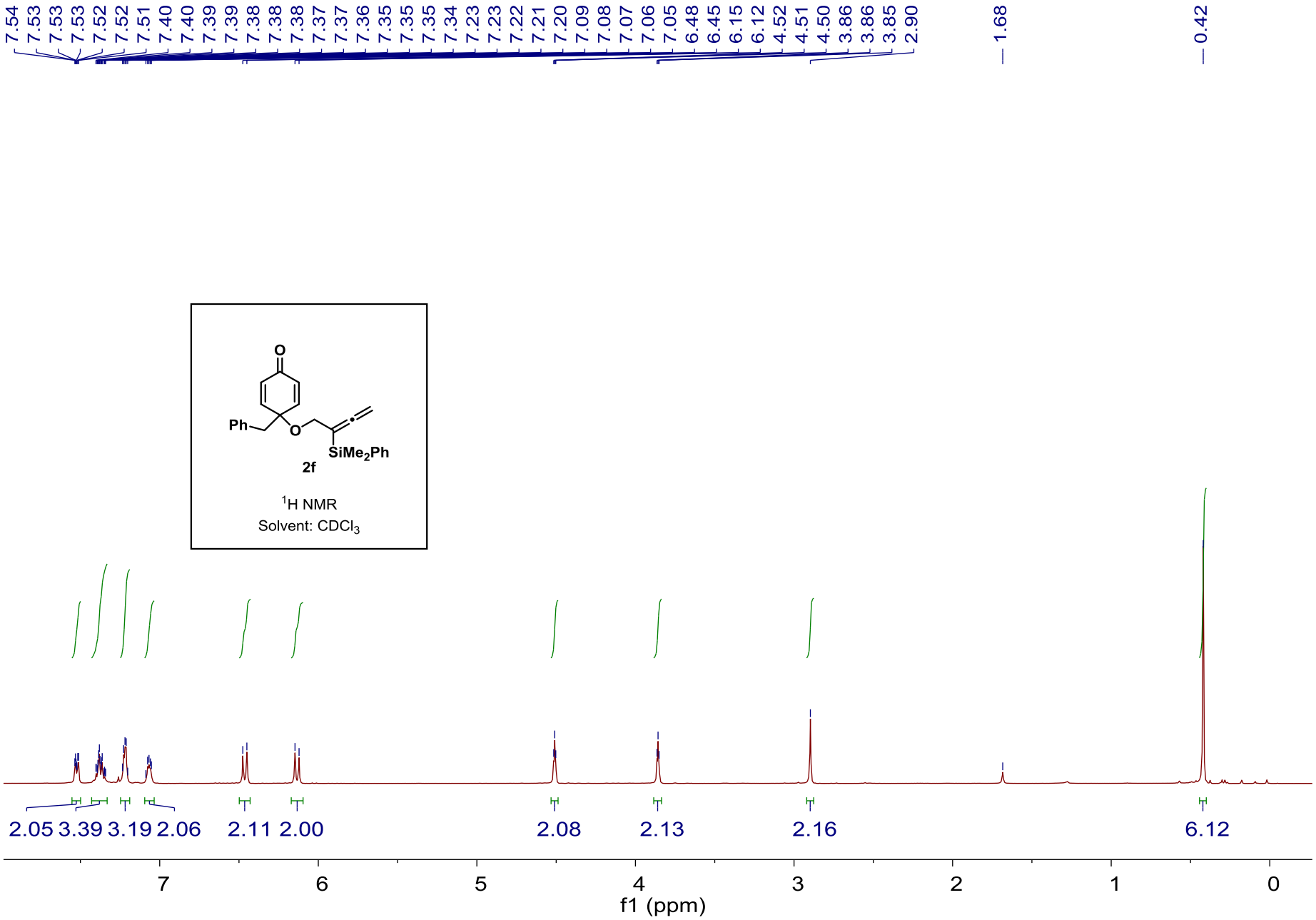
100
80
60
40
20
0
f1 (ppm)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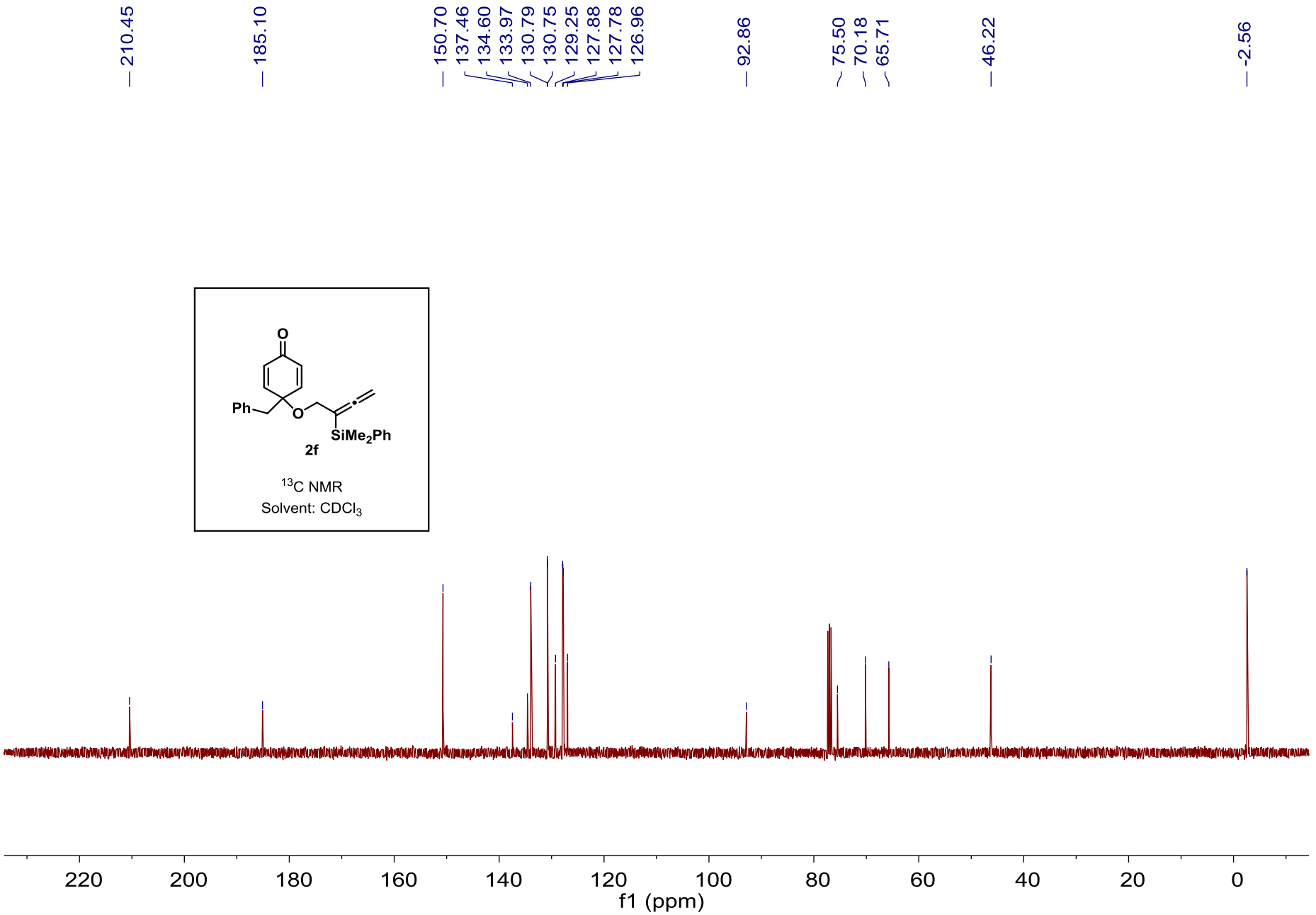
1.68
0.42
O
Ph
O
SiMe2Ph
2f
1H NMR
Solvent: CDCl3
2.05 3.39 3.19 2.06 2.11 2.00 2.08 2.13 2.16 6.12
7 6 5 4 3 2 1 0
f1 (ppm)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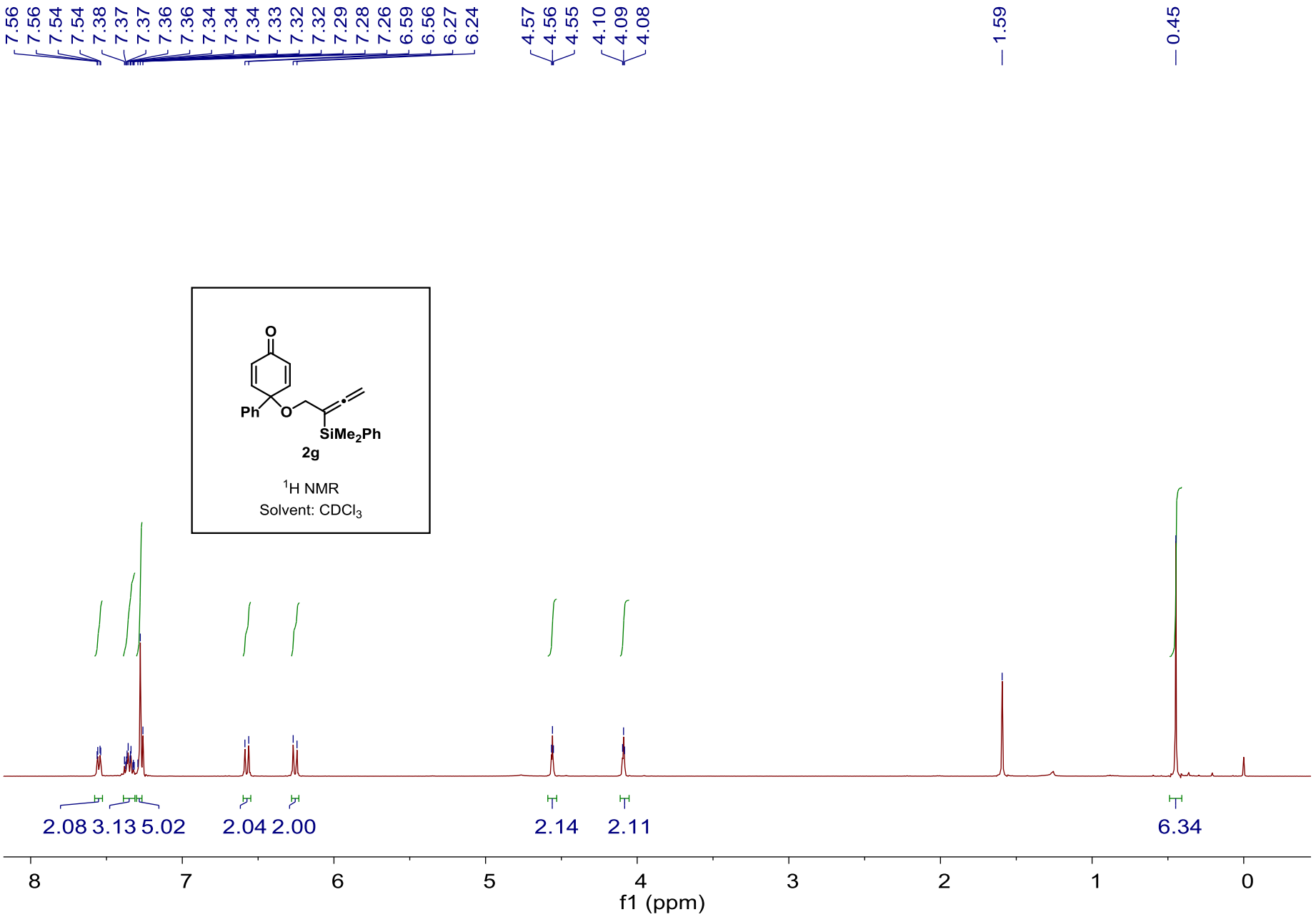
129.25
127.88
127.78
126.96
92.86
75.50
70.18
65.71
46.22
-2.56
O
Ph
O
SiMe2Ph
2f
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.32
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7.26
6.59
6.56
6.27
6.24
4.57
4.56
4.55
4.10
4.09
4.08
1.59
0.45
O
Ph
O
SiMe2Ph
2g
1H NMR
Solvent: CDCl3
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3.13
5.02
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2.14
2.11
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4
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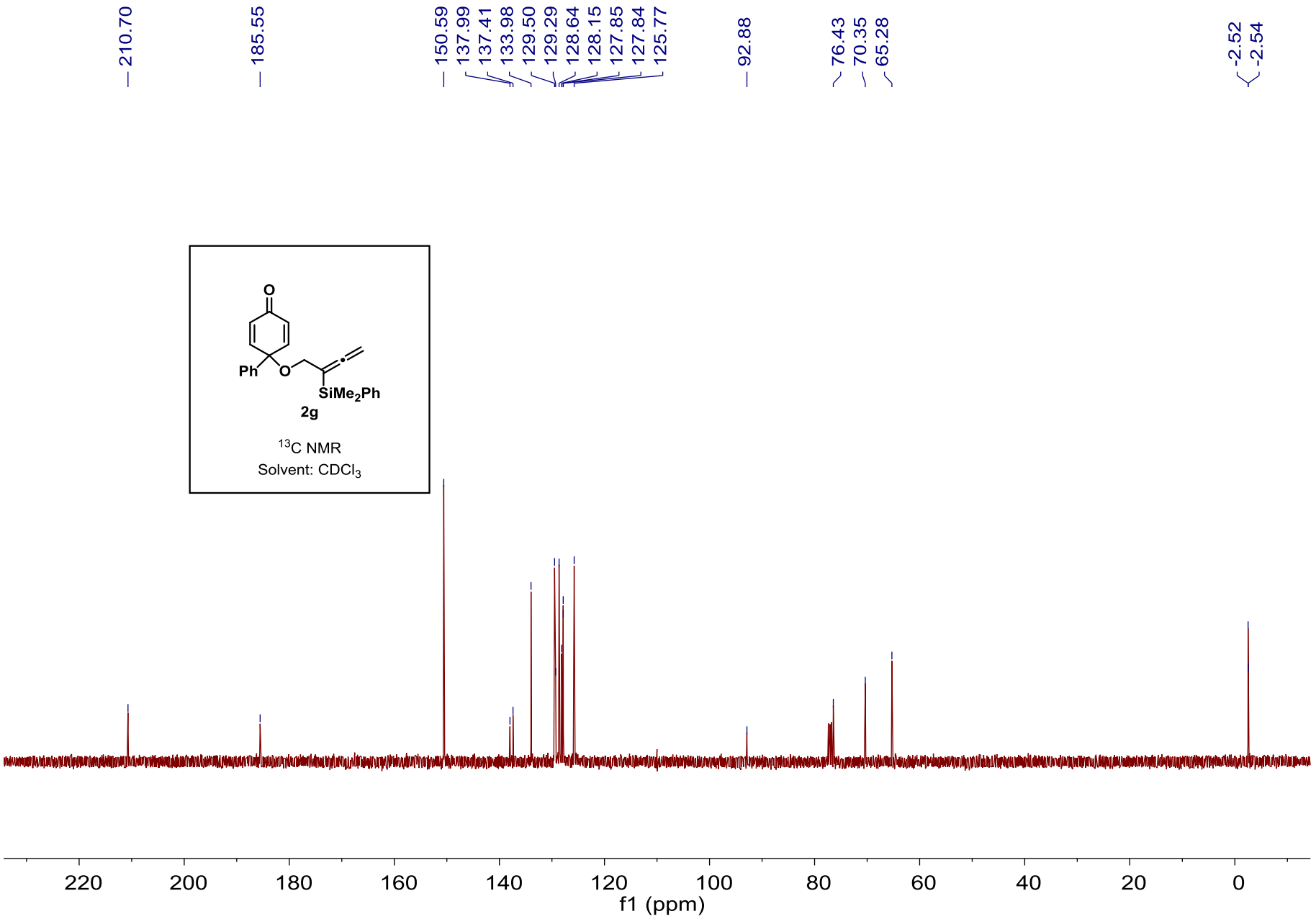
f1 (ppm)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127.85
127.84
125.77
92.88
76.43
70.35
65.28
-2.52
-2.54
O
Ph
O
SiMe2Ph
2g
13C NMR
Solvent: CDCl3
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180
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140
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100
80
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20
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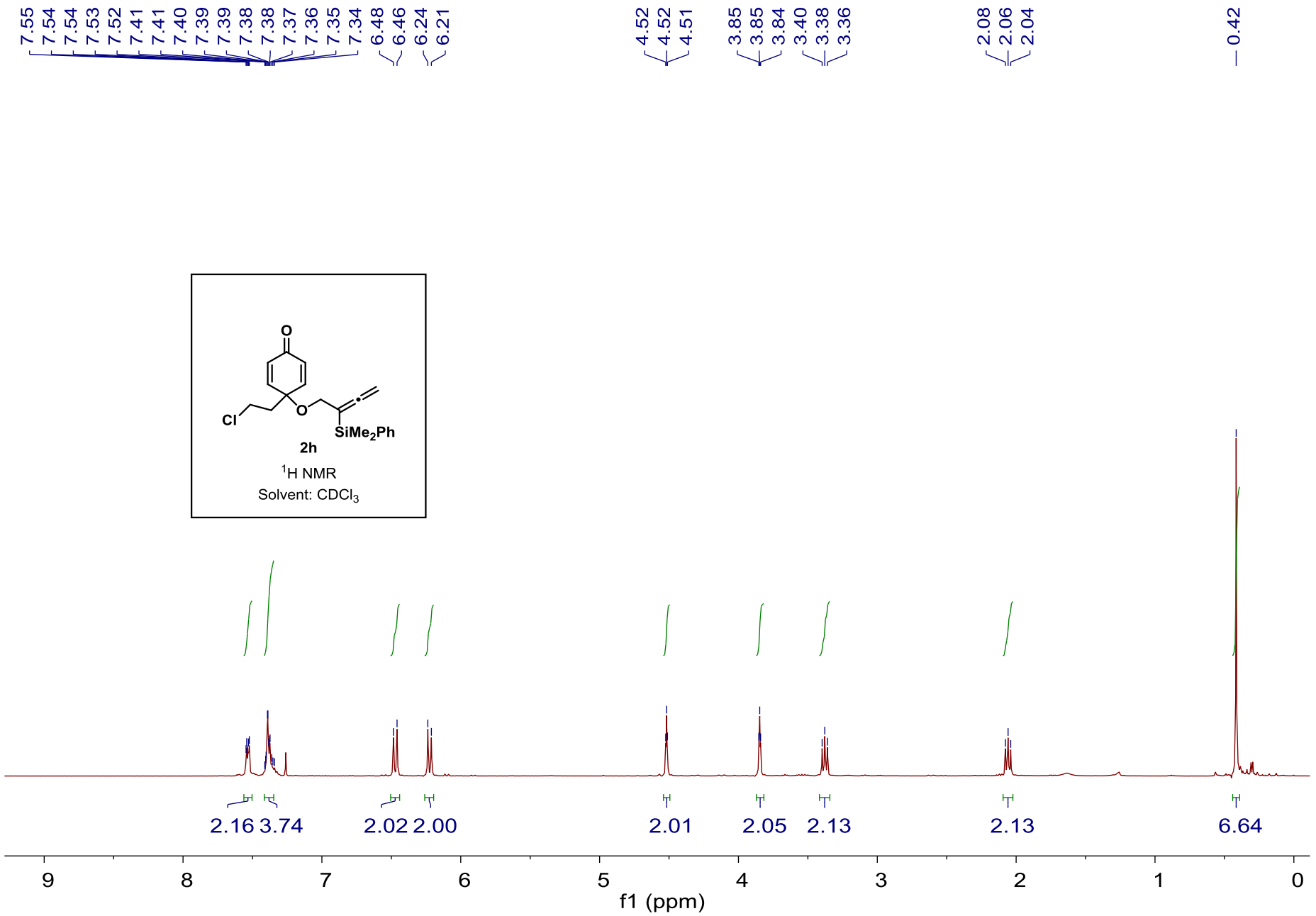
f1 (ppm)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7.37
7.36
7.35
7.34
6.48
6.46
6.24
6.21
4.52
4.52
4.51
3.85
3.85
3.84
3.40
3.38
3.36
2.08
2.06
2.04
0.42
O
Cl
O
SiMe2Ph
2h
1H NMR
Solvent: CDCl3
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3.74
2.02
2.00
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5
4
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1
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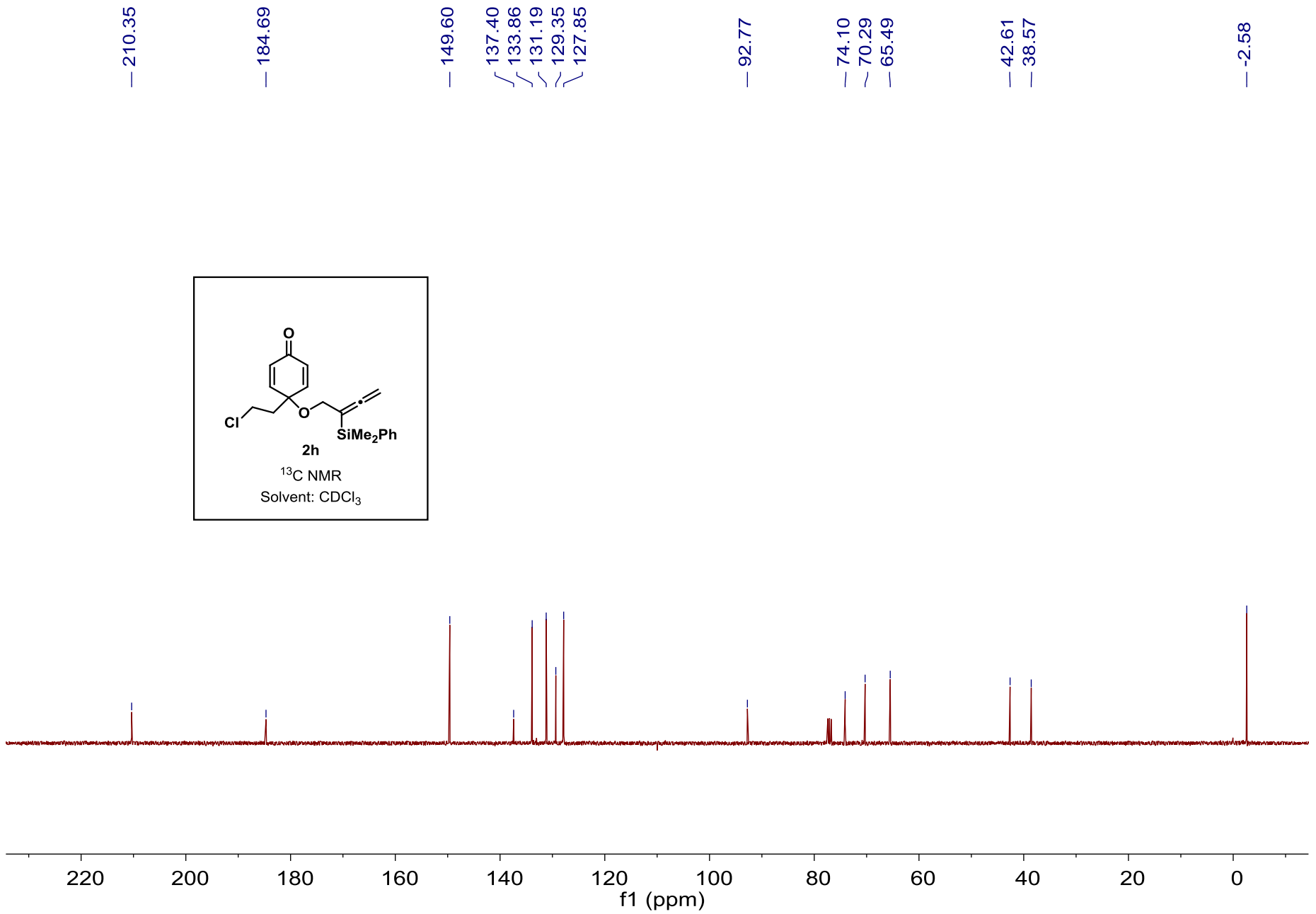
f1 (ppm)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127.85
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74.10
70.29
65.49
42.61
38.57
-2.58
O
Cl
O
SiMe2Ph
2h
13C NMR
Solvent: CDCl3
220
200
180
160
140
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100
80
60
40
20
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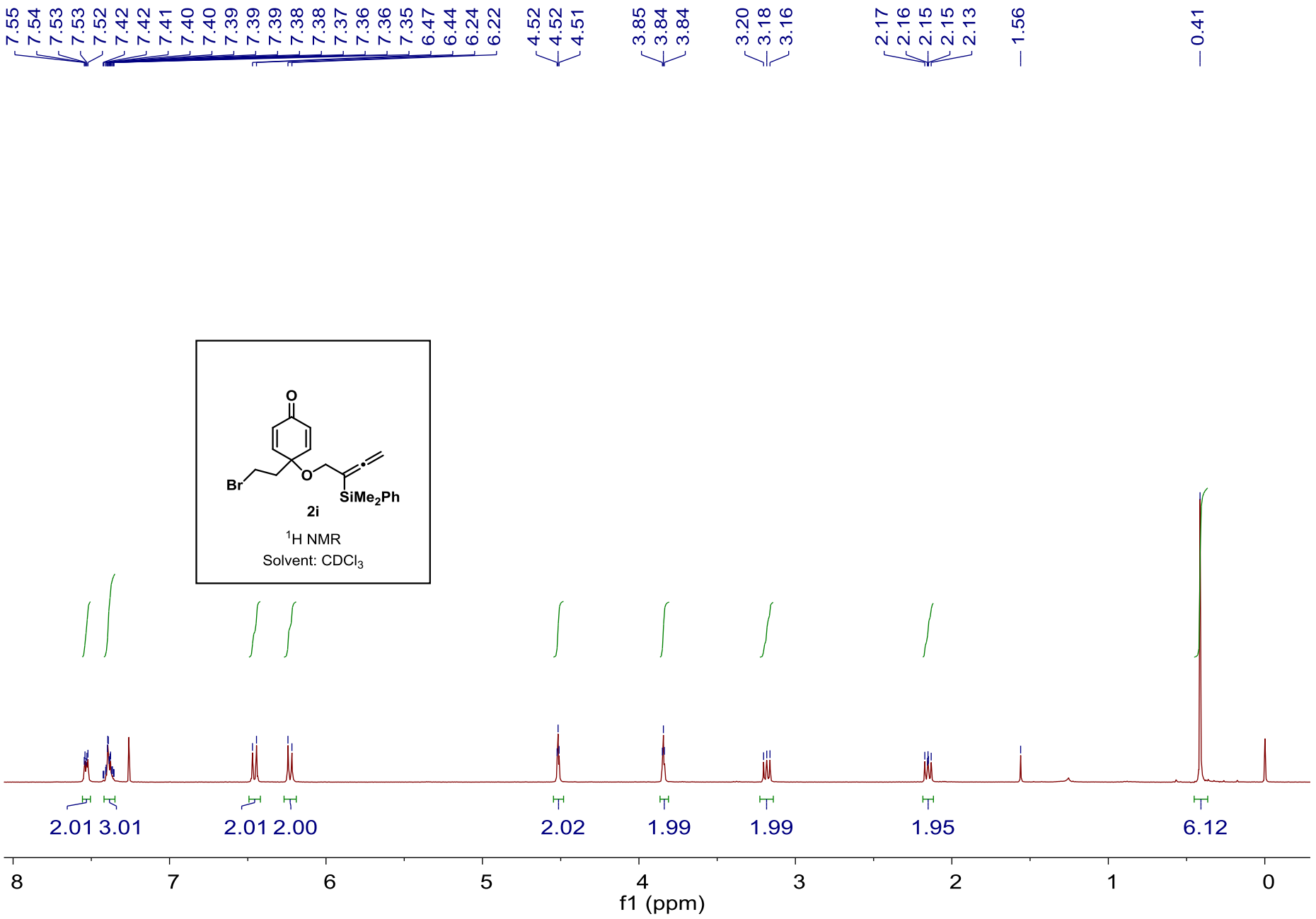
f1 (ppm)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7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
6.47
6.44
6.24
6.22
4.52
4.52
4.51
3.85
3.84
3.84
3.20
3.18
3.16
2.17
2.16
2.15
2.15
2.13
1.56
0.41
O
Br
O
SiMe2Ph
2i
1H NMR
Solvent: CDCl3
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3.01
2.01
2.00
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4
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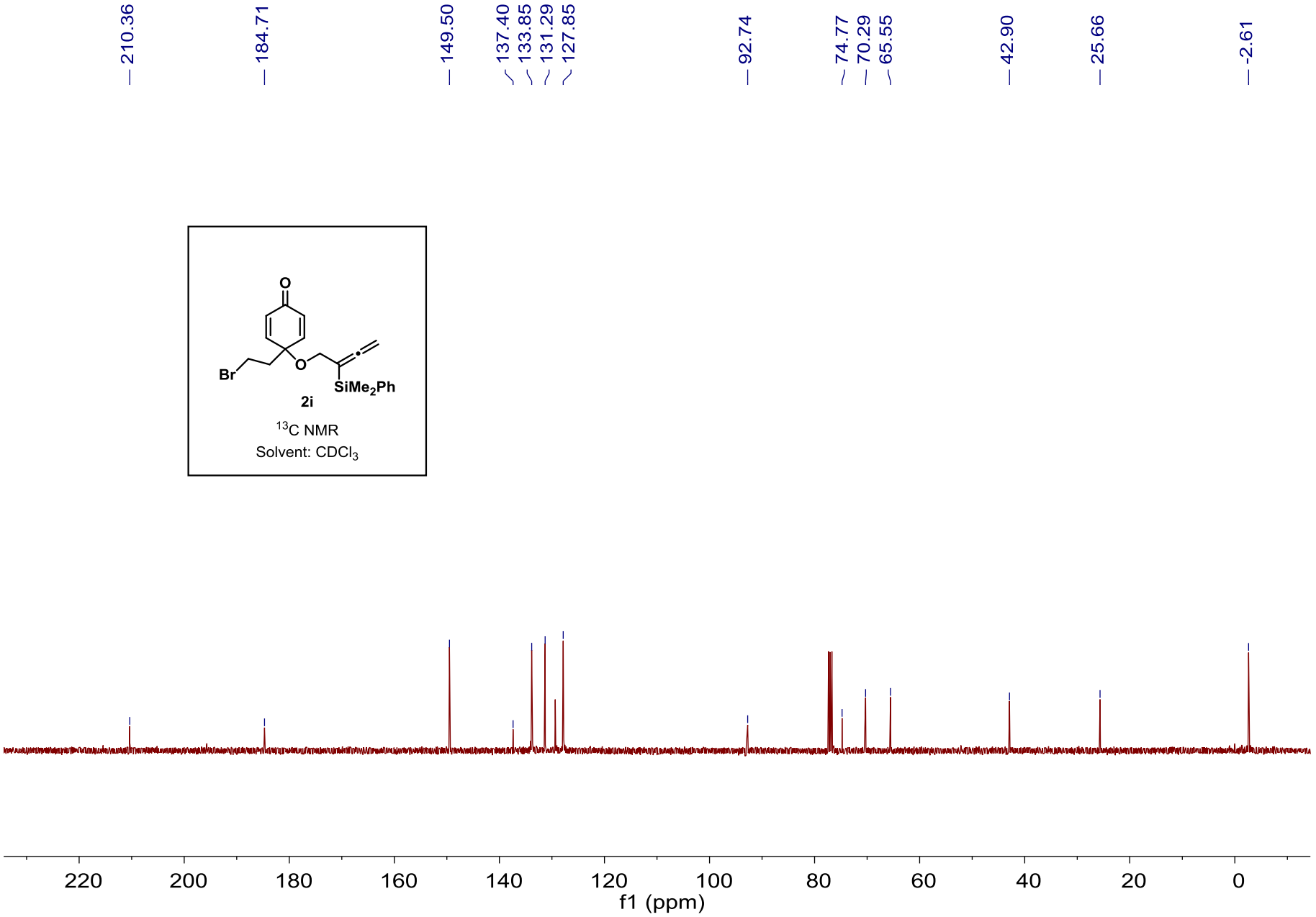
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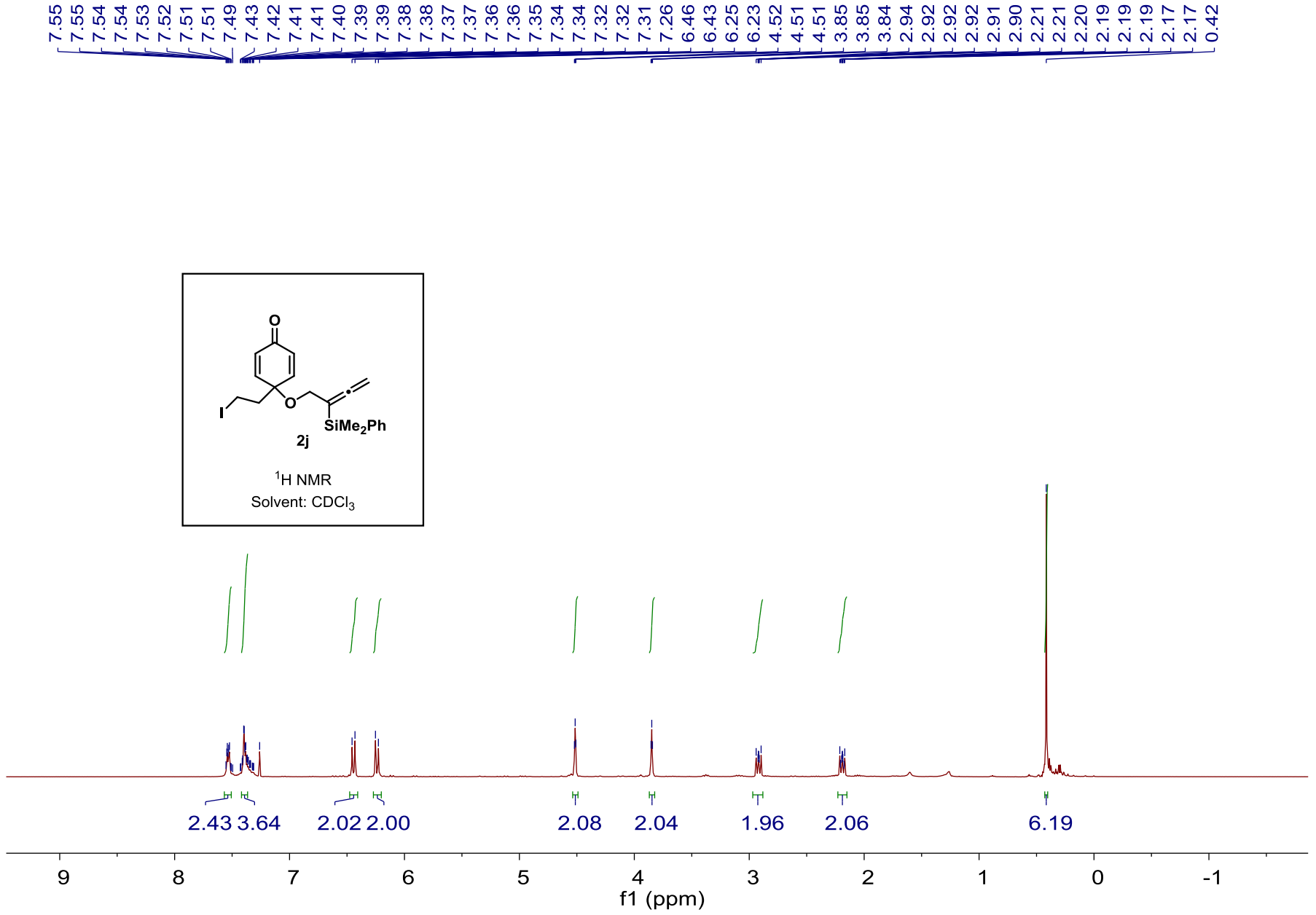
65.55
42.90
25.66
-2.61
O
Br
O
SiMe2Ph
2i
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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O
O
I
SiMe2Ph
2j
1H NMR
Solvent: CDCl3
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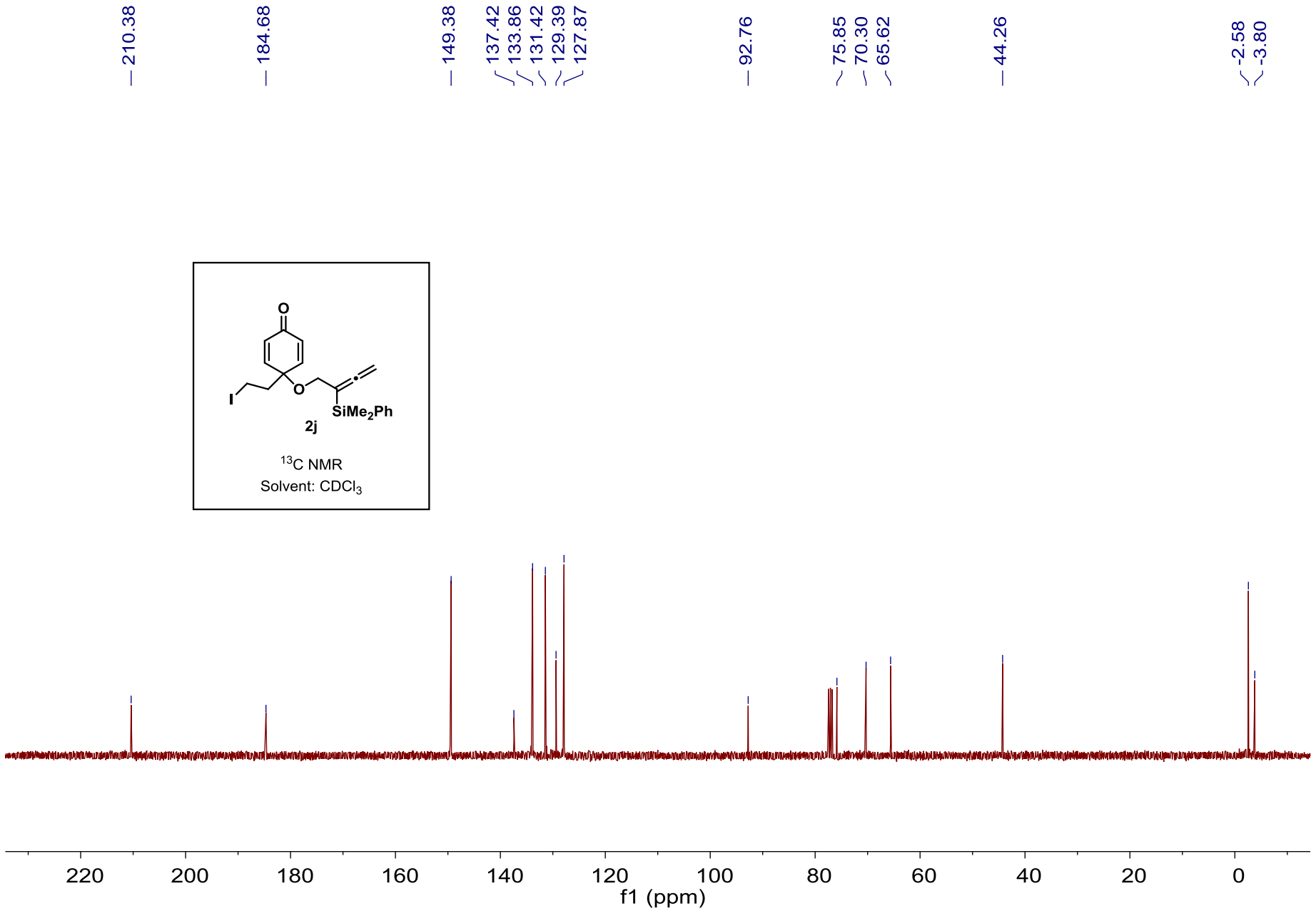
9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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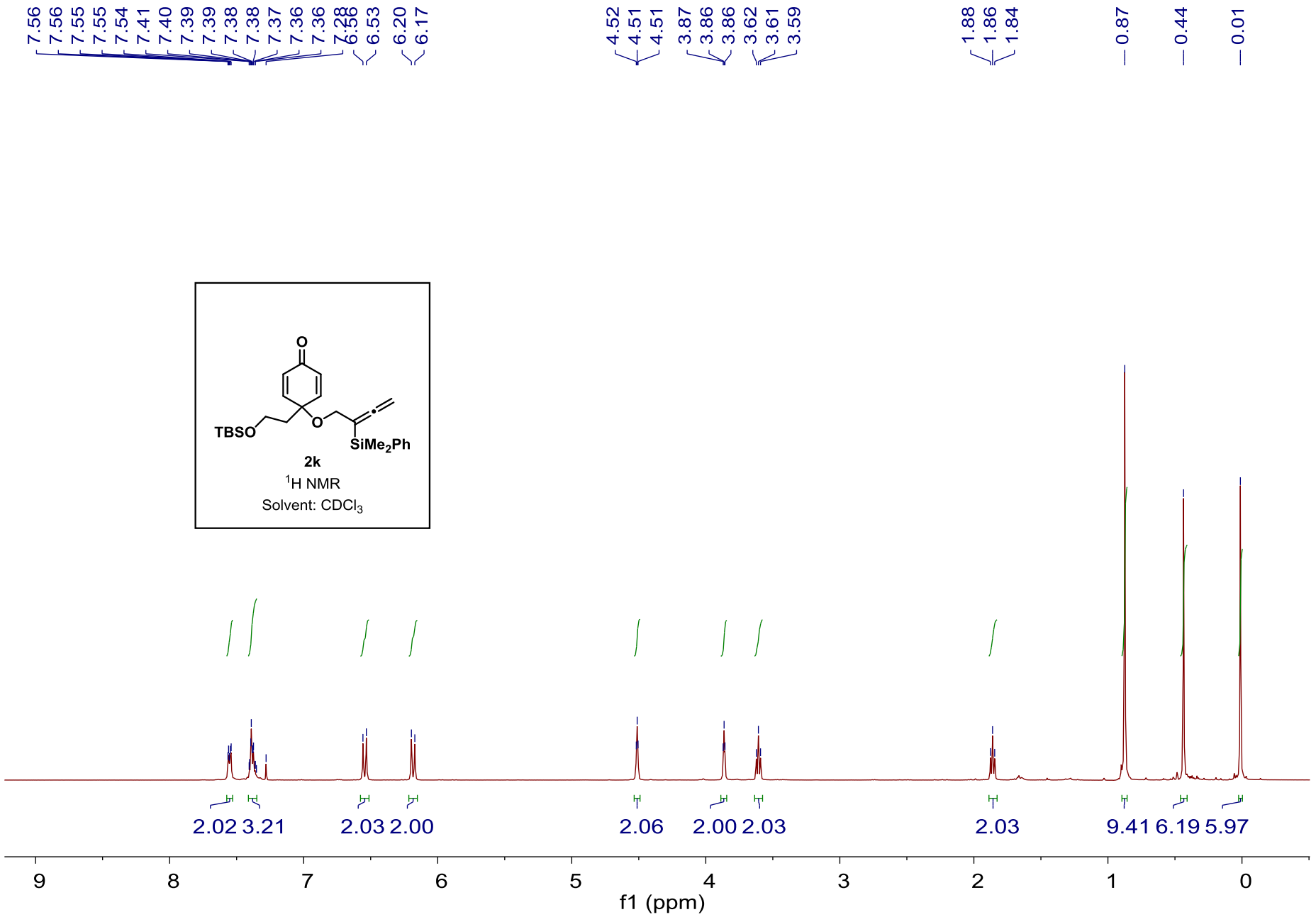
75.85
70.30
65.62
44.26
-2.58
-3.80
O
O
I
SiMe2Ph
2j
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.55
7.55
7.54
7.41
7.40
7.39
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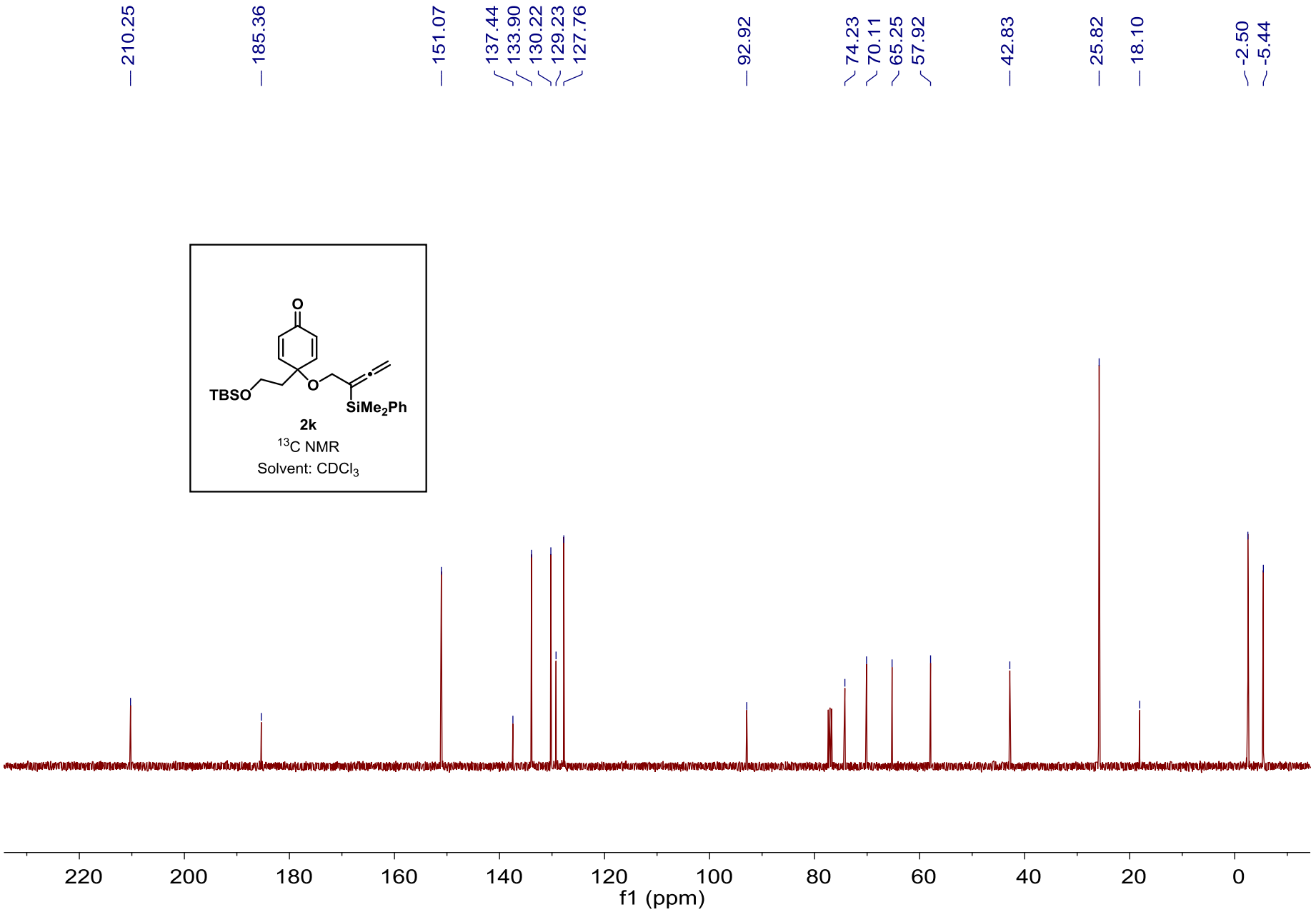
7.36
7.36
7.28
6.58
6.53
6.20
6.17
4.52
4.51
4.51
3.87
3.86
3.86
3.62
3.61
3.59
1.88
1.86
1.84
0.87
0.44
0.01
O
TBSO
O
SiMe2Ph
2k
1H NMR
Solvent: CDCl3
2.02 3.21
2.03 2.00
2.06
2.00 2.03
2.03
9.41 6.19 5.97
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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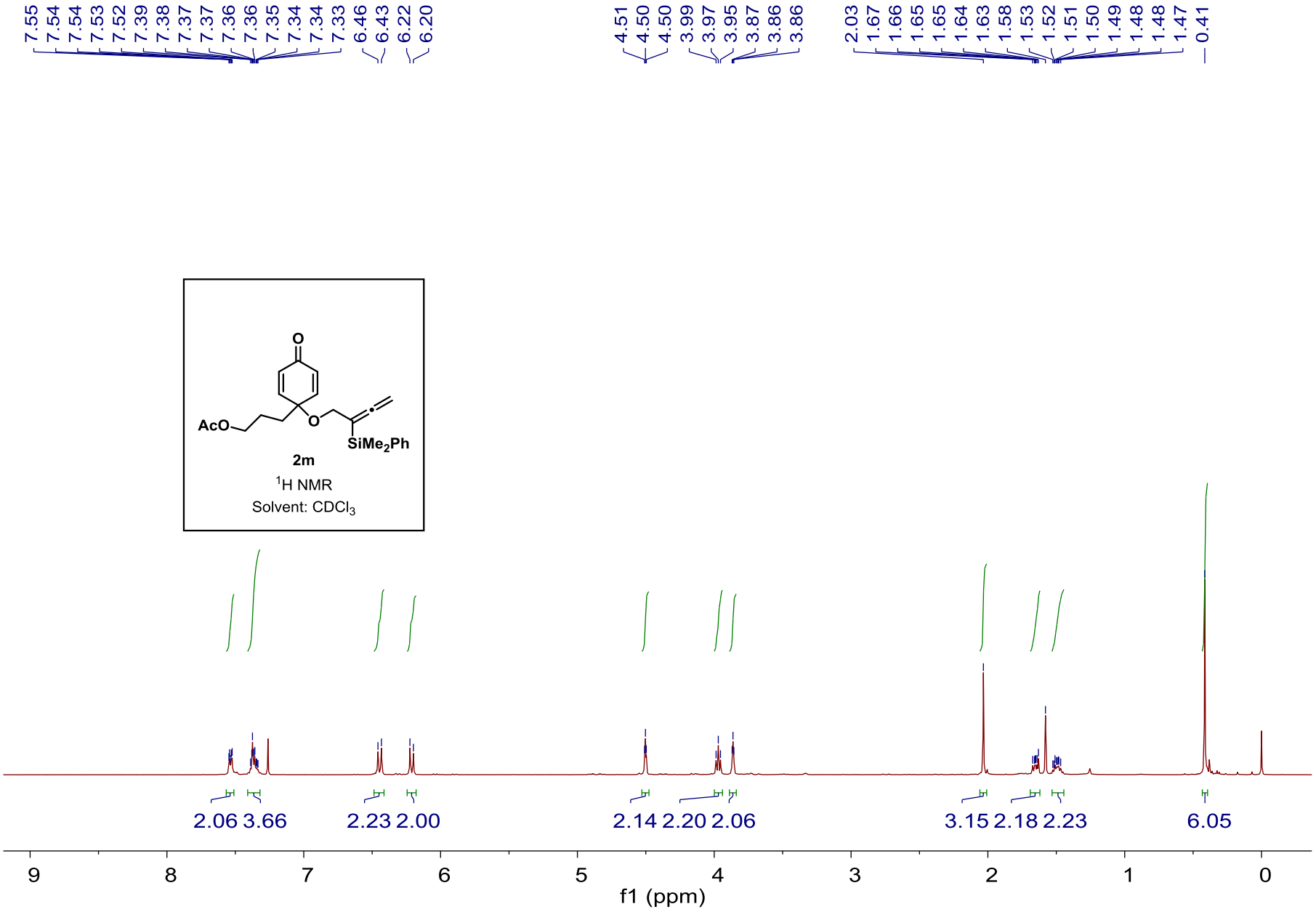
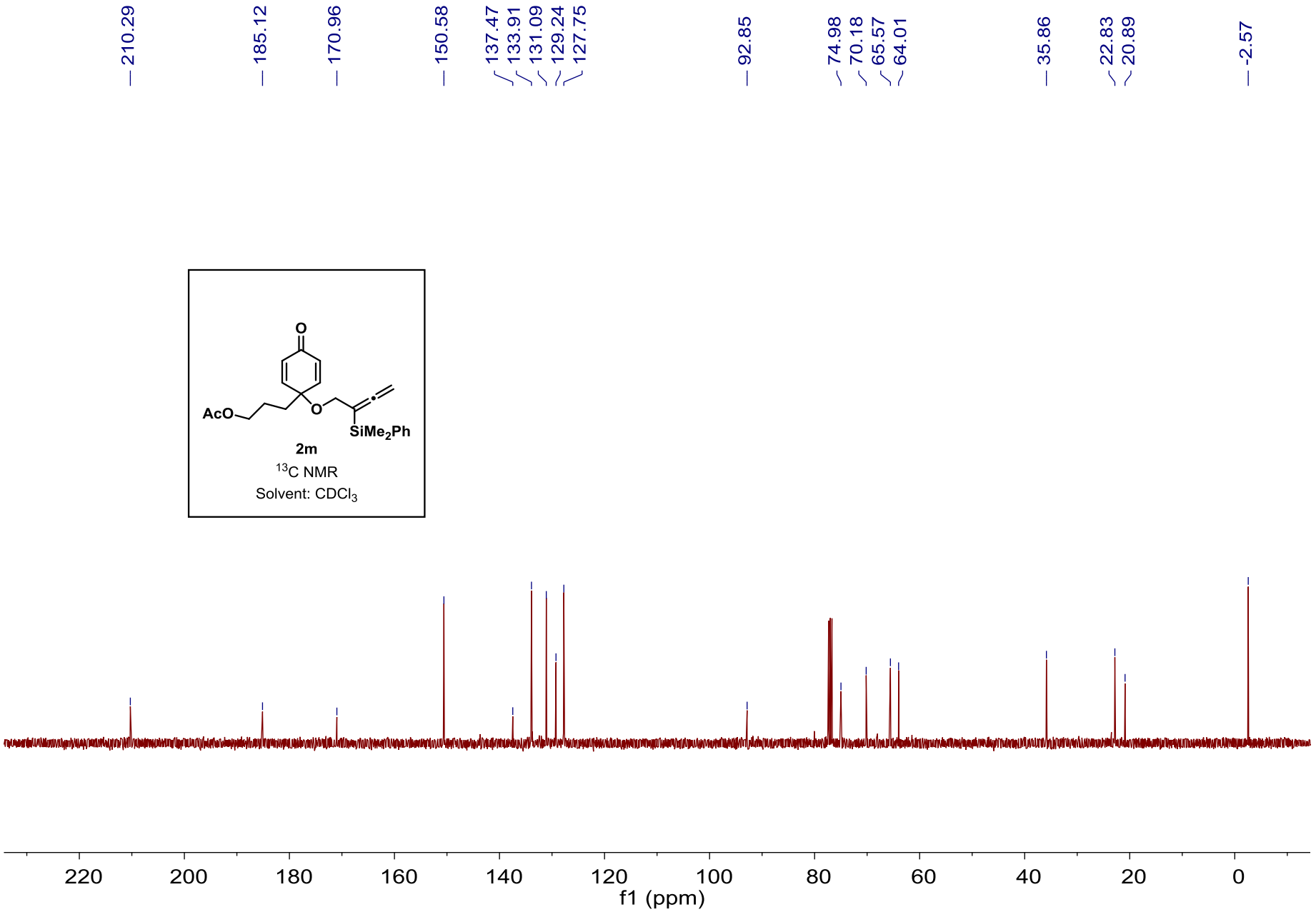
74.23
70.11
65.25
57.92
42.83
25.82
18.10
-2.50
-5.44
O
TBSO
O
SiMe2Ph
2k
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.55 7.54 7.54 7.53 7.52 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 6.46 6.43 6.22 6.20
4.51 4.50 4.50 3.99 3.97 3.95 3.87 3.86 3.86
2.03 1.67 1.66 1.65 1.65 1.64 1.63 1.58 1.53 1.52 1.51 1.50 1.49 1.48 1.48 1.47 0.41
AcO
O
O
SiMe2Ph
2m
1H NMR
Solvent: CDCl3
2.06 3.66 2.23 2.00 2.14 2.20 2.06 3.15 2.18 2.23 6.05
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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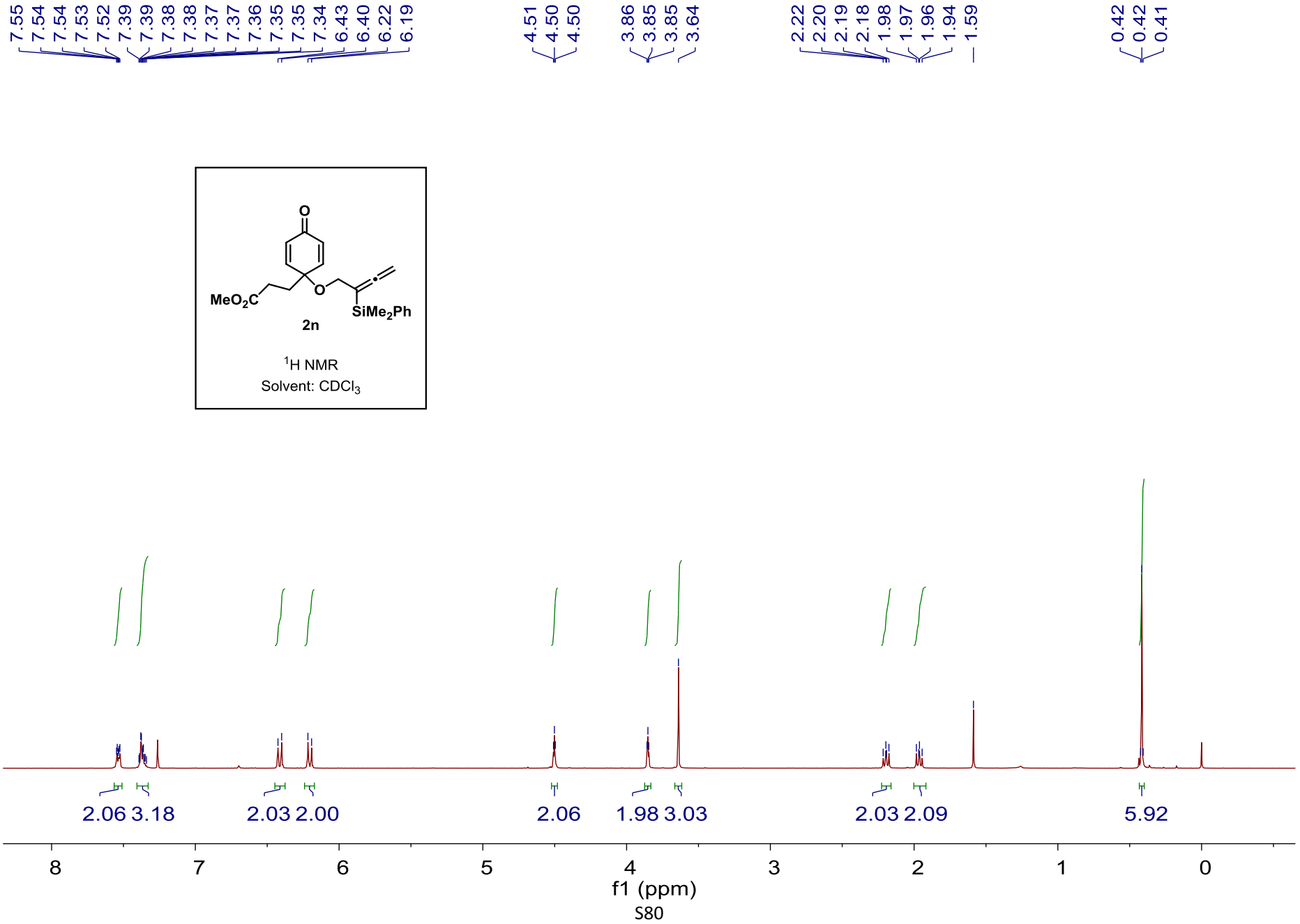
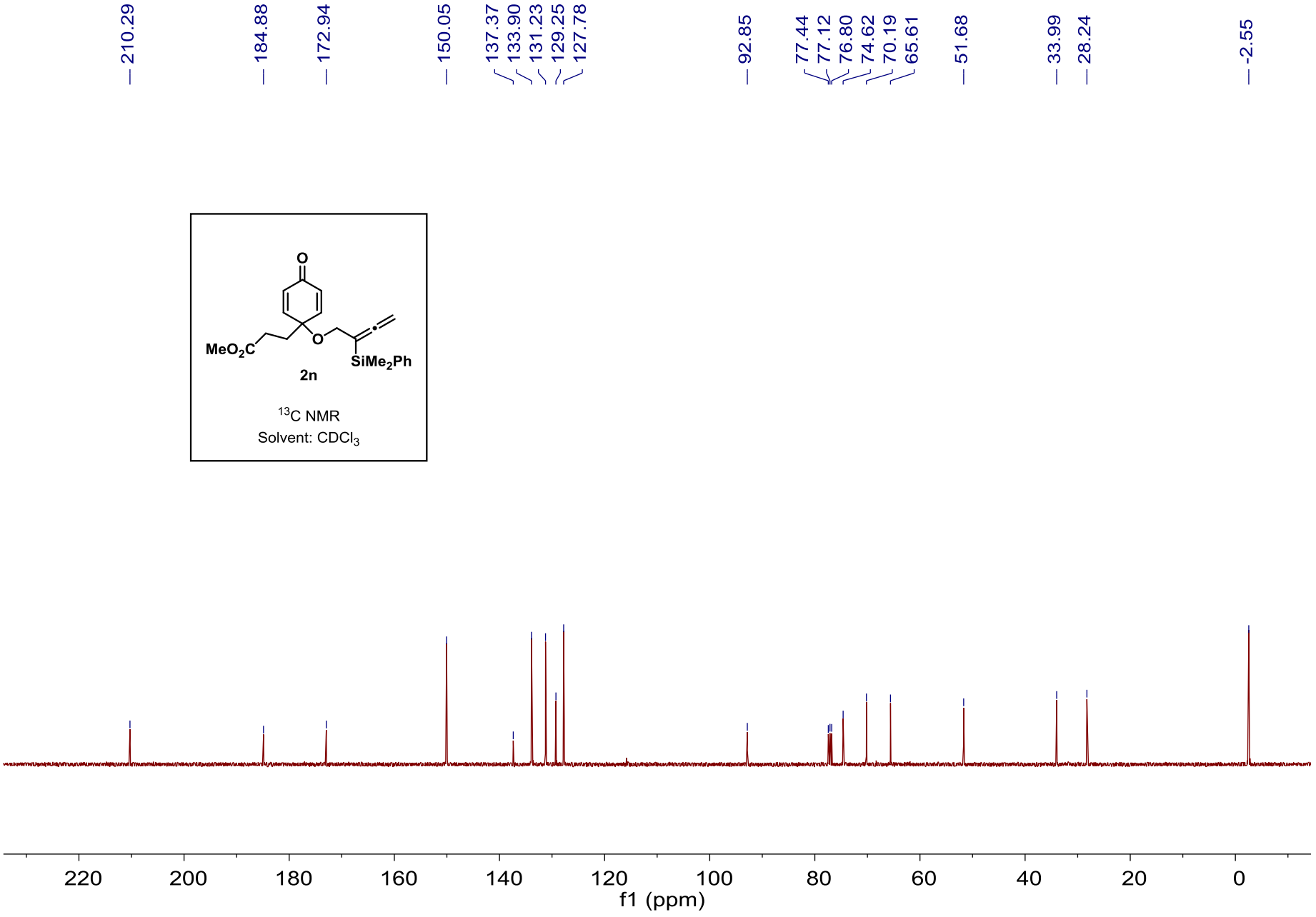
185.12
170.96
150.58
137.47
133.91
131.09
129.24
127.75
92.85
74.98
70.18
65.57
64.01
35.86
22.83
20.89
-2.57
O
AcO
O
SiMe2Ph
2m
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.55
7.54
7.54
7.53
7.52
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
6.43
6.40
6.22
6.19
4.51
4.50
4.50
3.86
3.85
3.85
3.64
2.22
2.20
2.19
2.18
1.98
1.97
1.96
1.94
1.59
0.42
0.42
0.41
O
MeO2C
O
SiMe2Ph
2n
1H NMR
Solvent: CDCl3
2.06 3.18
2.03 2.00
2.06
1.98 3.03
2.03 2.09
5.92
8
7
6
5
4
3
2
1
0
f1 (ppm)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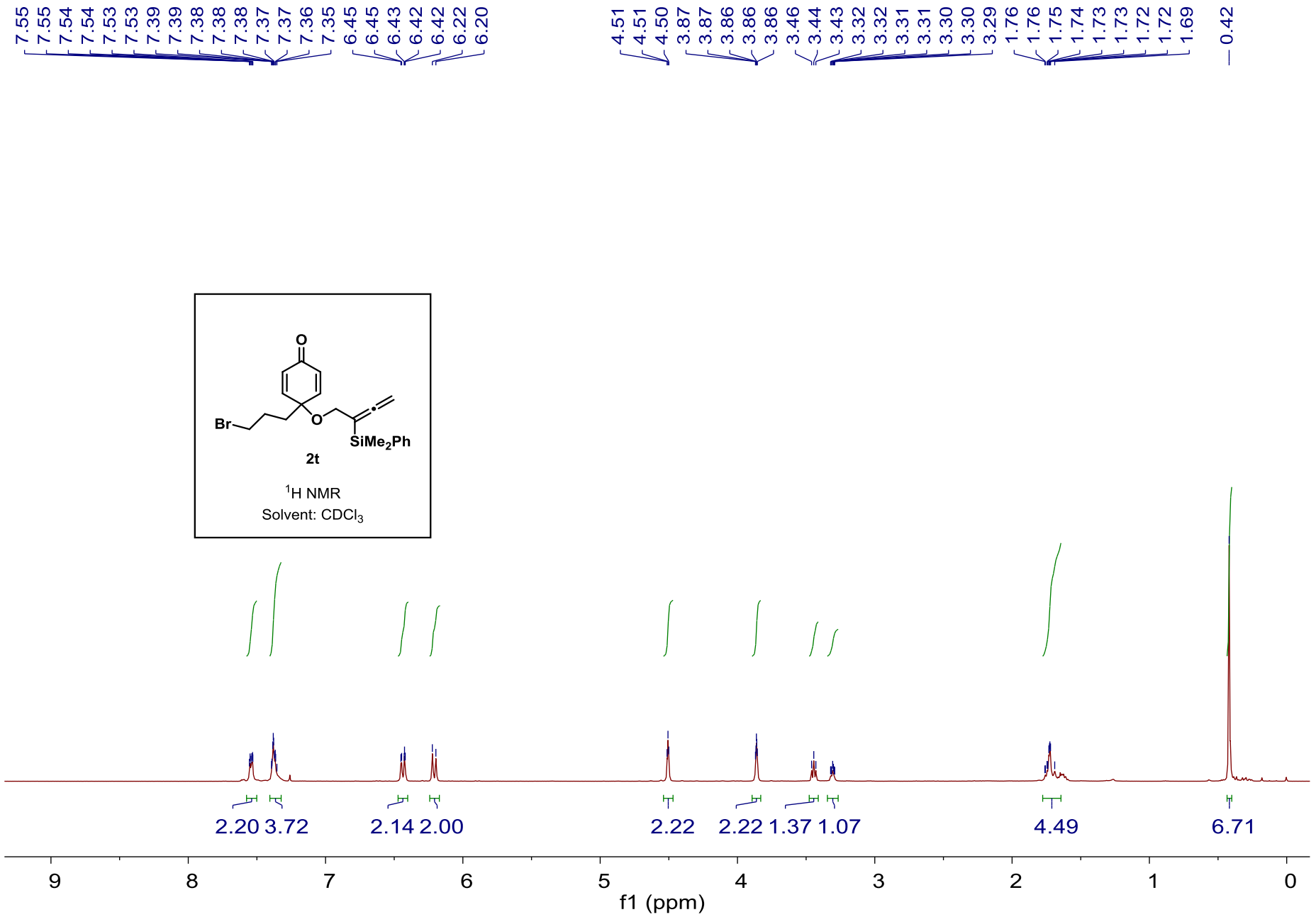
172.94
150.05
137.37
133.90
131.23
129.25
127.78
92.85
77.44
77.12
76.80
74.62
70.19
65.61
51.68
33.99
28.24
-2.55
O
O
MeO2C
SiMe2Ph
2n
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.55 7.55 7.54 7.54 7.53 7.53 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.35 6.45 6.45 6.43 6.42 6.42 6.22 6.20
4.51 4.51 4.50 3.87 3.87 3.86 3.86 3.86 3.46 3.44 3.43 3.32 3.32 3.31 3.31 3.30 3.30 3.29 1.76 1.76 1.75 1.74 1.73 1.73 1.72 1.72 1.69 0.42
Br
O
O
SiMe2Ph
2t
1H NMR
Solvent: CDCl3
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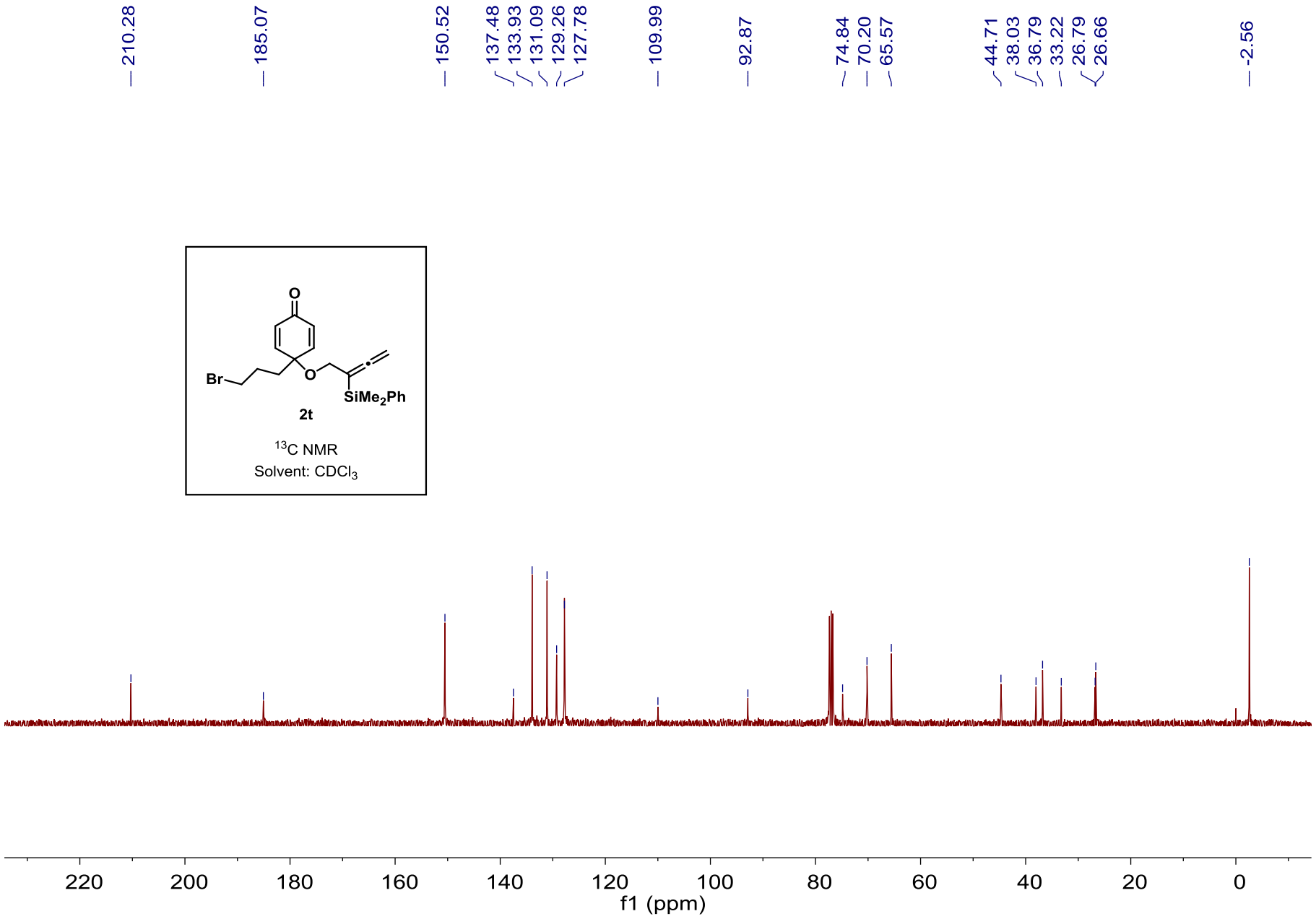
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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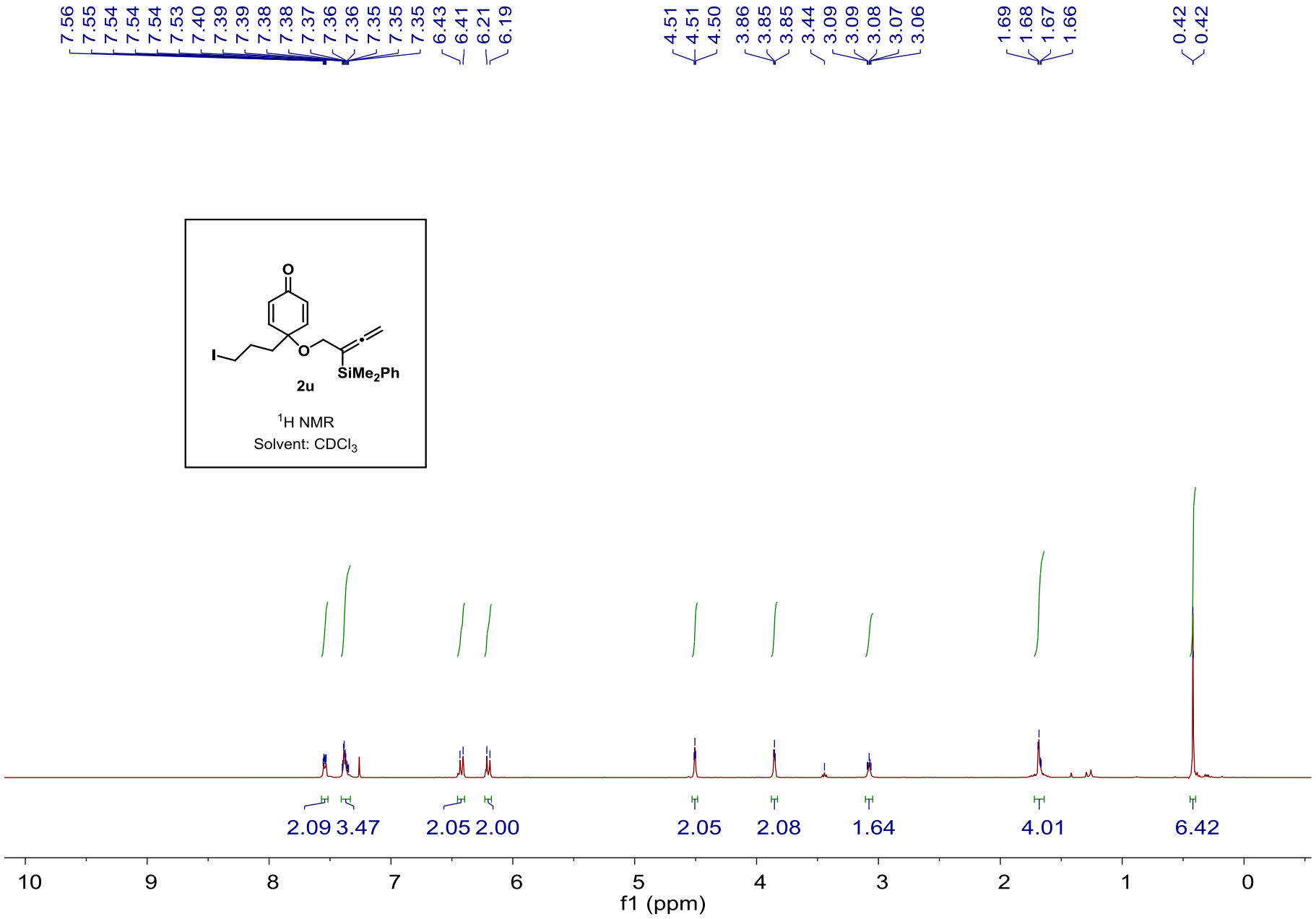
185.07
150.52
137.48
133.93
131.09
129.26
127.78
109.99
92.87
74.84
70.20
65.57
44.71
38.03
36.79
33.22
26.79
26.66
-2.56
O
Br
O
SiMe2Ph
2t
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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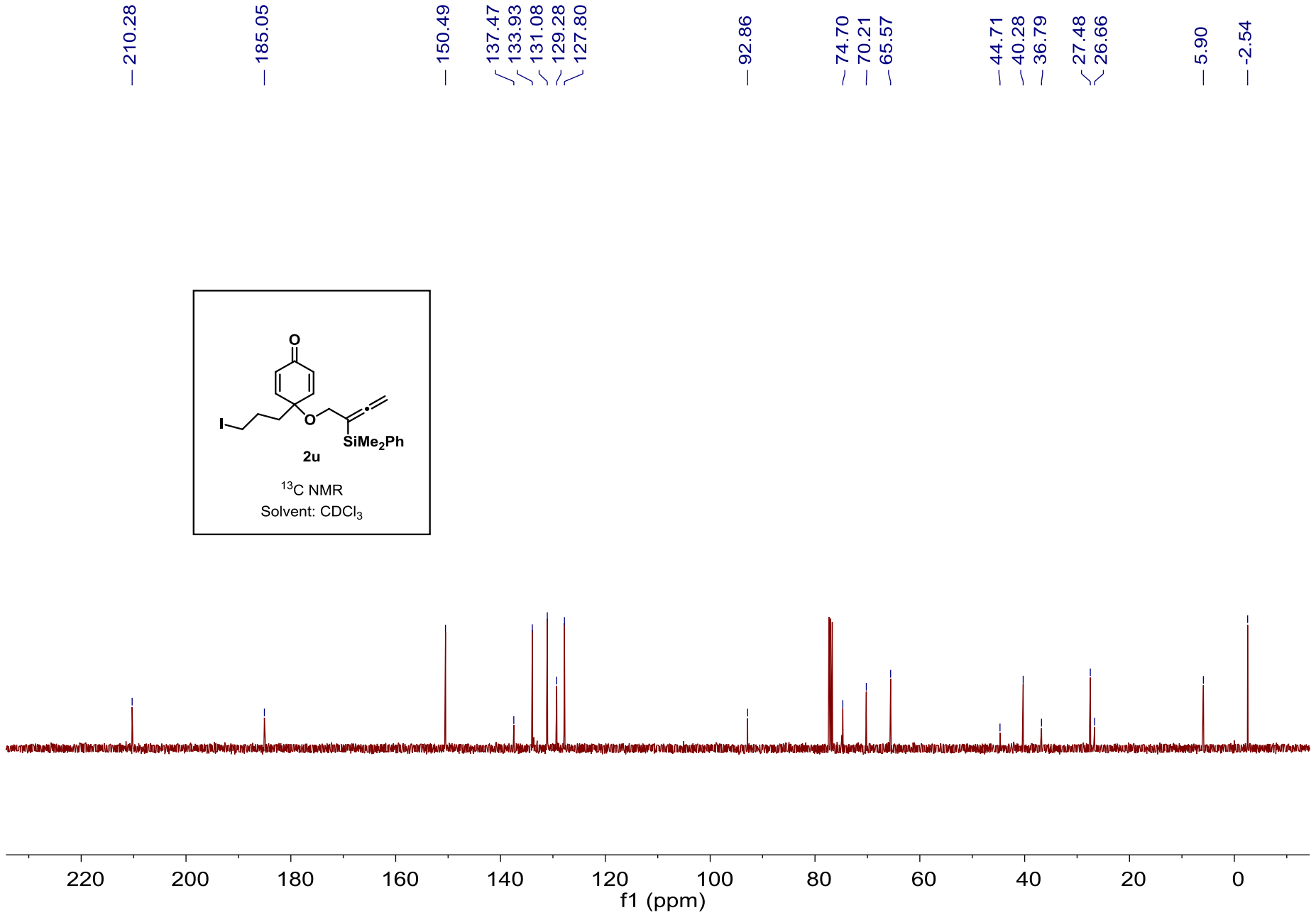
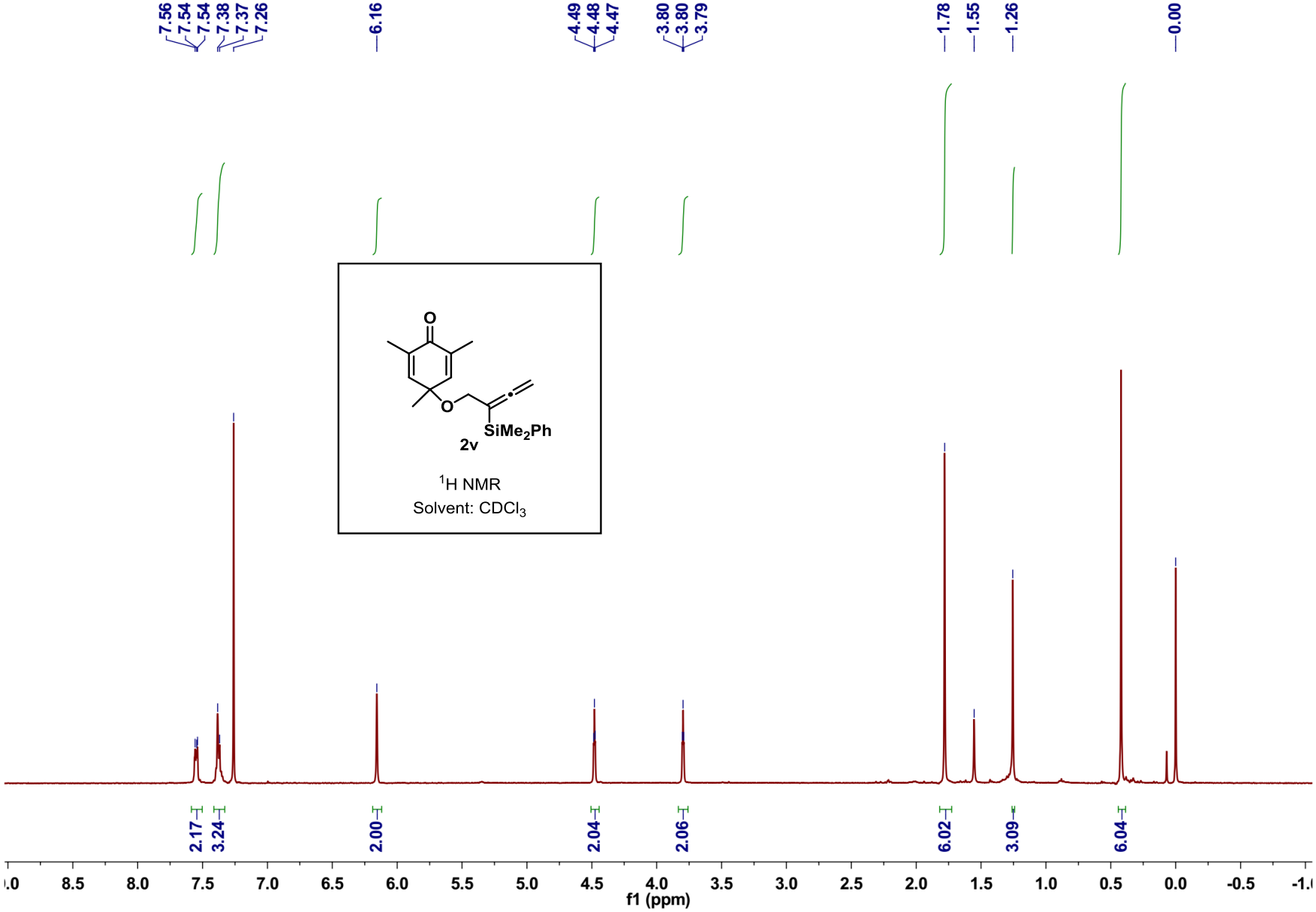
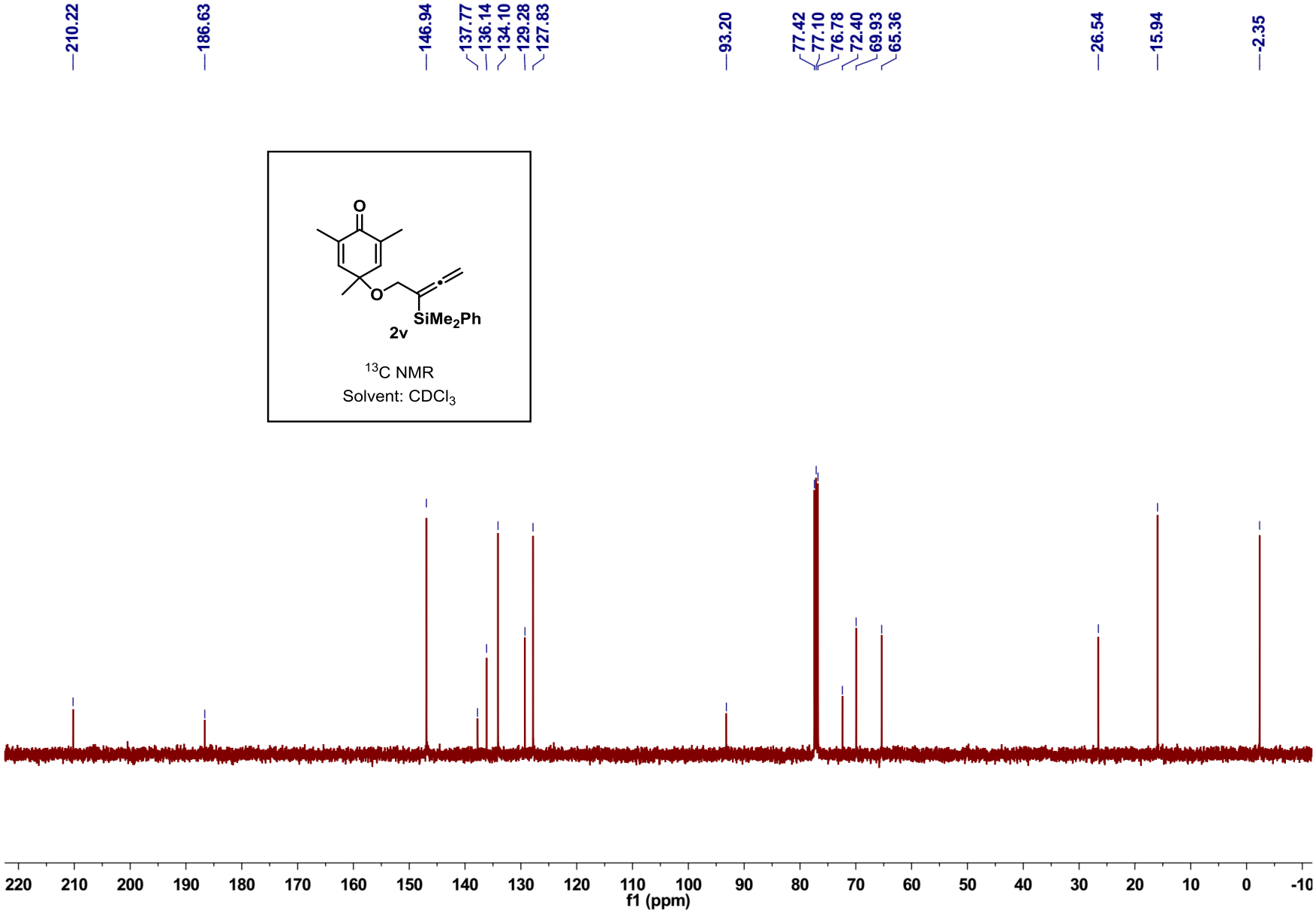
7.55
7.54
7.54
7.54
7.53
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.35
6.43
6.41
6.21
6.19
4.51
4.51
4.50
3.86
3.85
3.85
3.44
3.09
3.09
3.08
3.07
3.06
1.69
1.68
1.67
1.66
0.42
0.42
O
O
I
SiMe2Ph
2u
1H NMR
Solvent: CDCl3
2.09
3.47
2.05
2.00
2.05
2.08
1.64
4.01
6.42
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


210.28
185.05
150.49
137.47
133.93
131.08
129.28
127.80
92.86
74.70
70.21
65.57
44.71
40.28
36.79
27.48
26.66
5.90
-2.54
O
O
I
SiMe2Ph
2u
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.56
7.54
7.54
7.38
7.37
7.26
6.16
4.49
4.48
4.47
3.80
3.80
3.79
1.78
1.55
1.26
0.00
O
O
SiMe2Ph
2v
1H NMR
Solvent: CDCl3
2.17
3.24
2.00
2.04
2.06
6.02
3.09
6.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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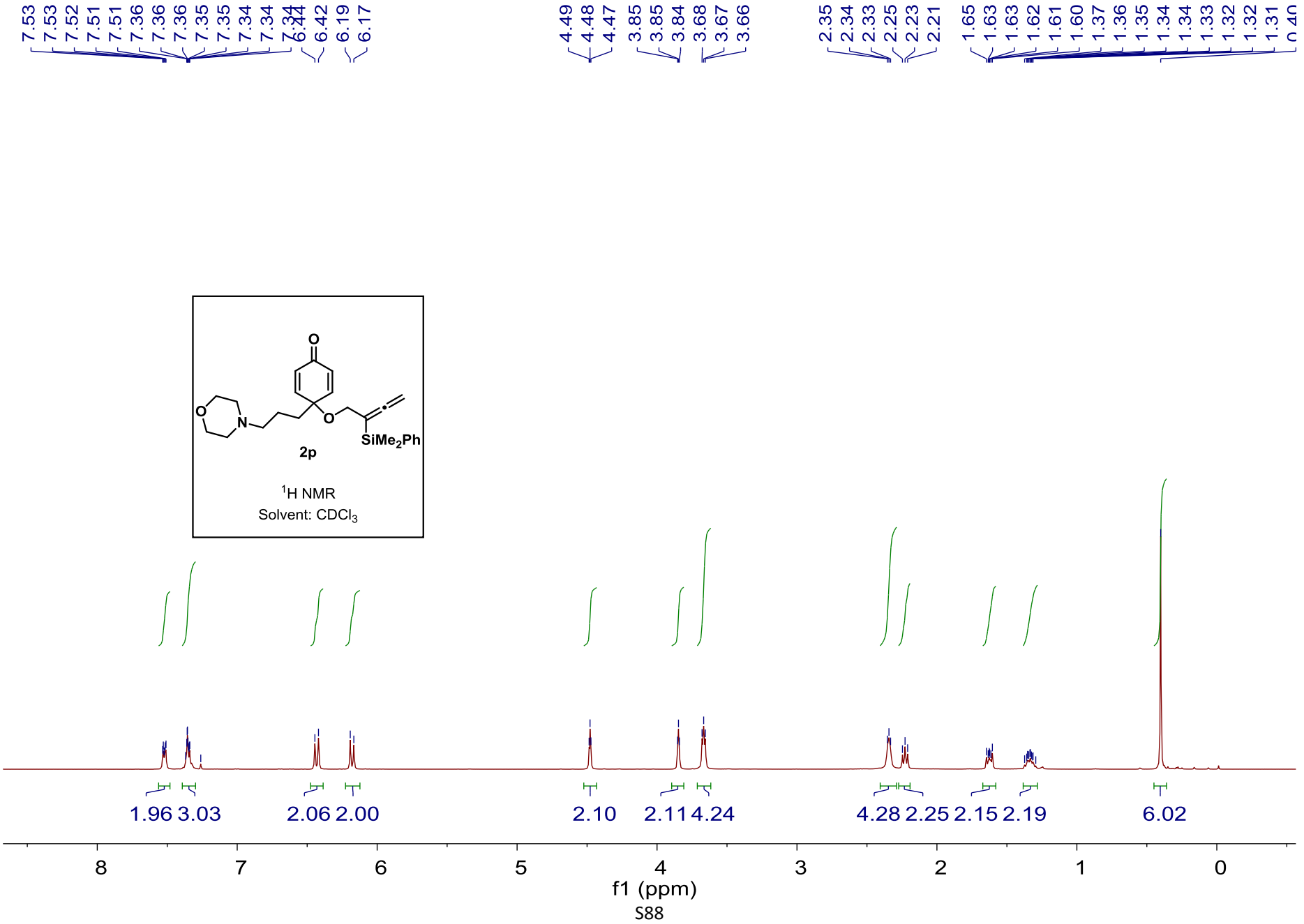
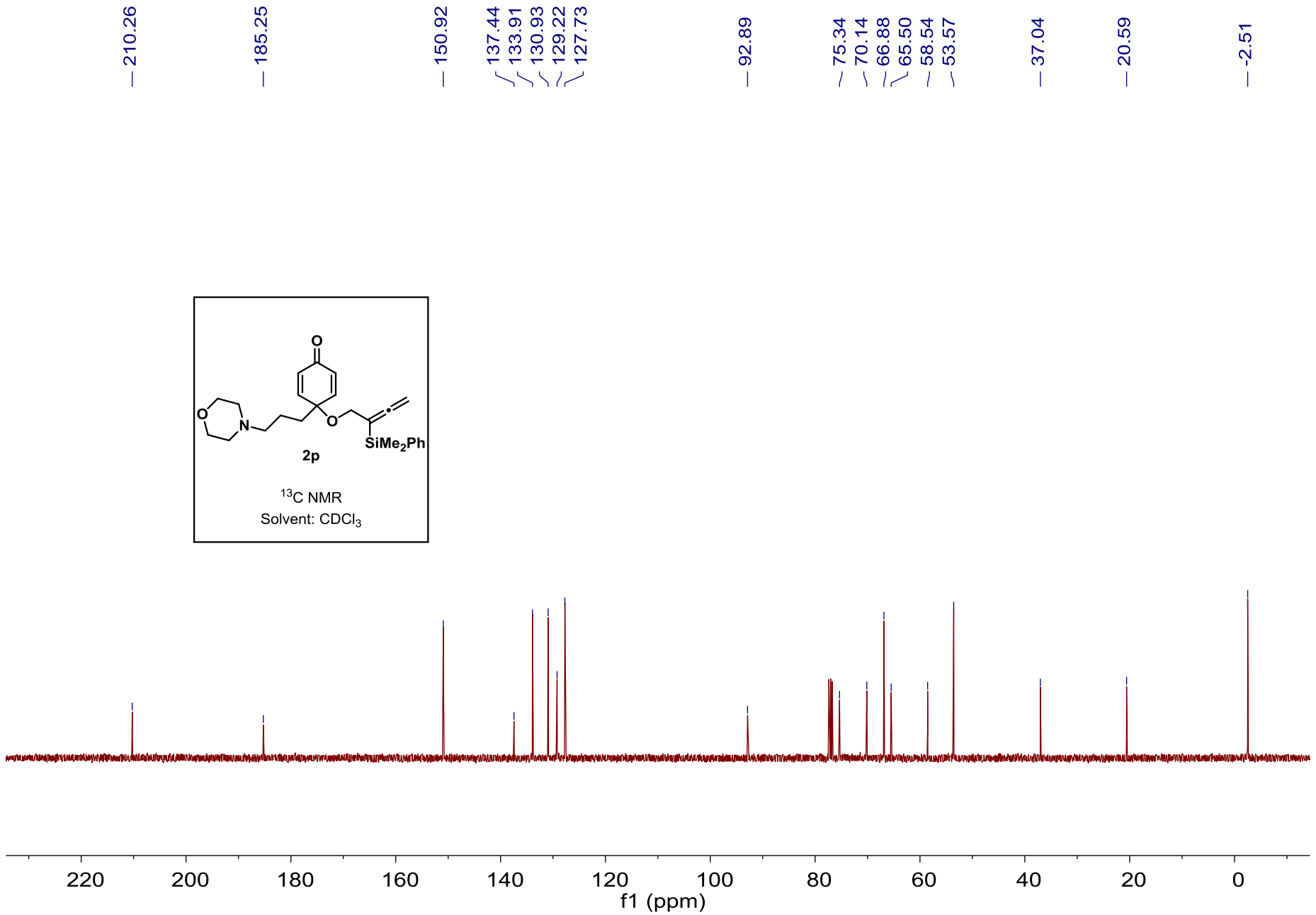
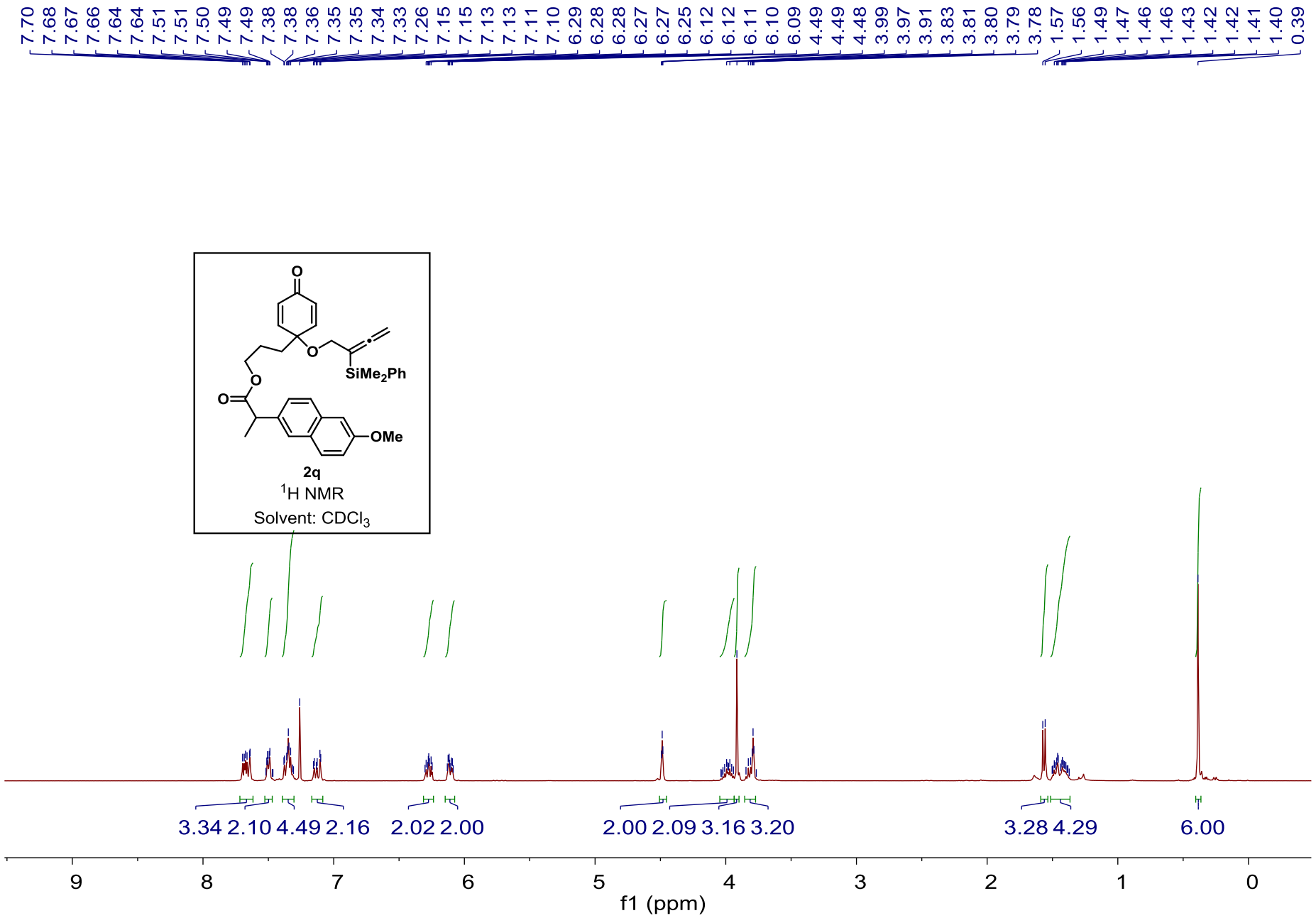
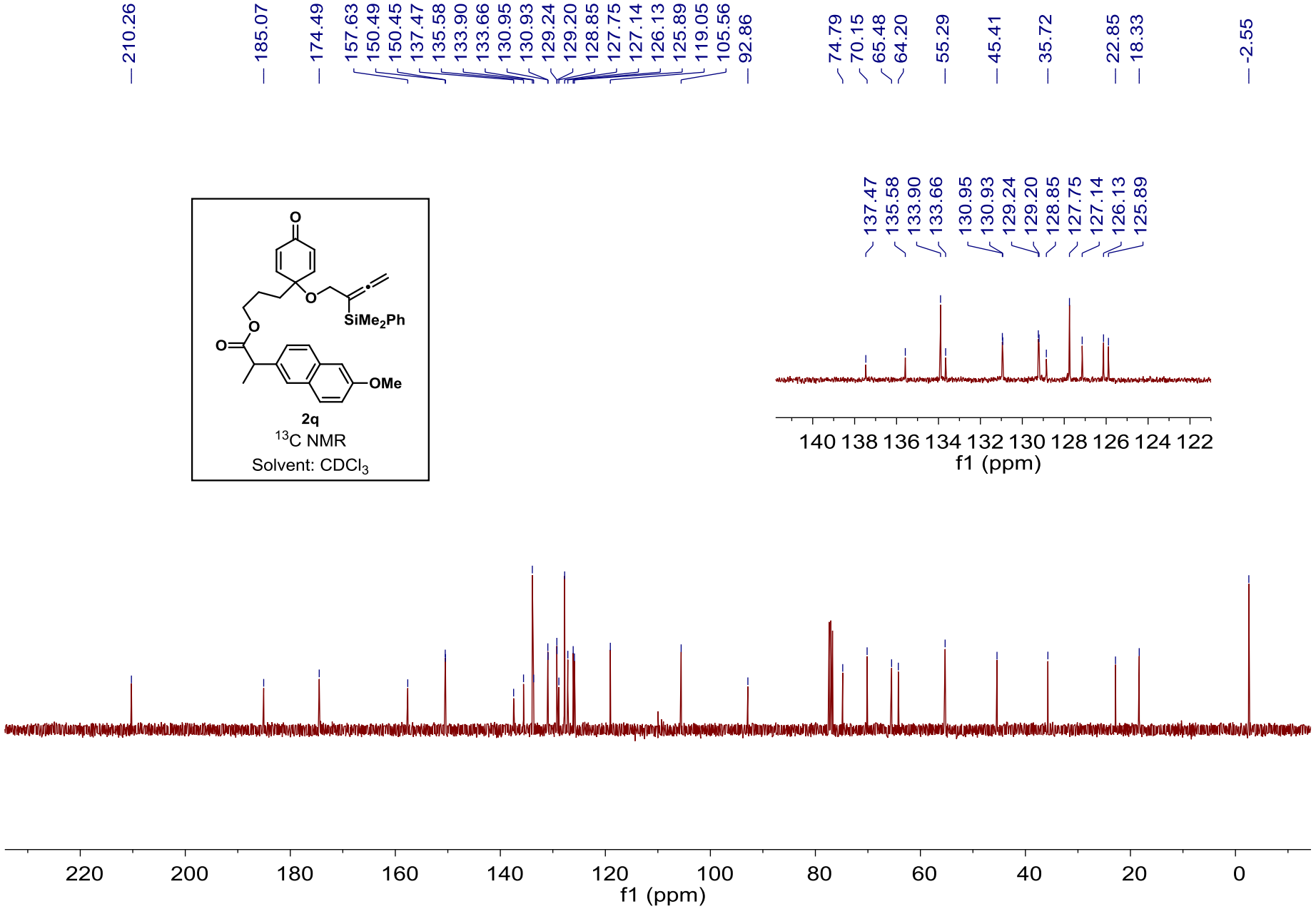
186.63
146.94
137.77
136.14
134.10
129.28
127.83
93.20
77.42
77.10
76.78
72.40
69.93
65.36
26.54
15.94
-2.35
O
O
SiMe2Ph
2v
13C NMR
Solvent: CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.53 7.53 7.52 7.51 7.51 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 6.44 6.42 6.19 6.17
4.49 4.48 4.47 3.85 3.85 3.84 3.68 3.67 3.66
2.35 2.34 2.33 2.25 2.23 2.21
1.65 1.63 1.63 1.62 1.61 1.60 1.37 1.36 1.35 1.34 1.34 1.33 1.32 1.32 1.31
O
O
N
O
SiMe2Ph
2p
1H NMR
Solvent: CDCl3
1.96 3.03 2.06 2.00 2.10 2.11 4.24 4.28 2.25 2.15 2.19 6.02
8 7 6 5 4 3 2 1 0
f1 (ppm)


210.26
185.25
150.92
137.44
133.91
130.93
129.22
127.73
92.89
75.34
70.14
66.88
65.50
58.54
53.57
37.04
20.59
-2.51
O
O
N
O
SiMe2Ph
2p
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.70 7.68 7.67 7.66 7.64 7.64 7.51 7.51 7.50 7.49 7.49 7.38 7.38 7.36 7.35 7.35 7.34 7.33 7.26 7.15 7.15 7.13 7.13 7.11 7.10 6.29 6.28 6.28 6.27 6.27 6.25 6.12 6.12 6.11 6.10 6.09 4.49 4.49 4.48 3.99 3.97 3.91 3.83 3.81 3.80 3.79 3.78 1.57 1.56 1.49 1.47 1.46 1.46 1.43 1.42 1.42 1.41 1.40 0.39
O
O
O
O
SiMe2Ph
OMe
2q
1H NMR
Solvent: CDCl3
3.34 2.10 4.49 2.16 2.02 2.00 2.00 2.09 3.16 3.20 3.28 4.29 6.00
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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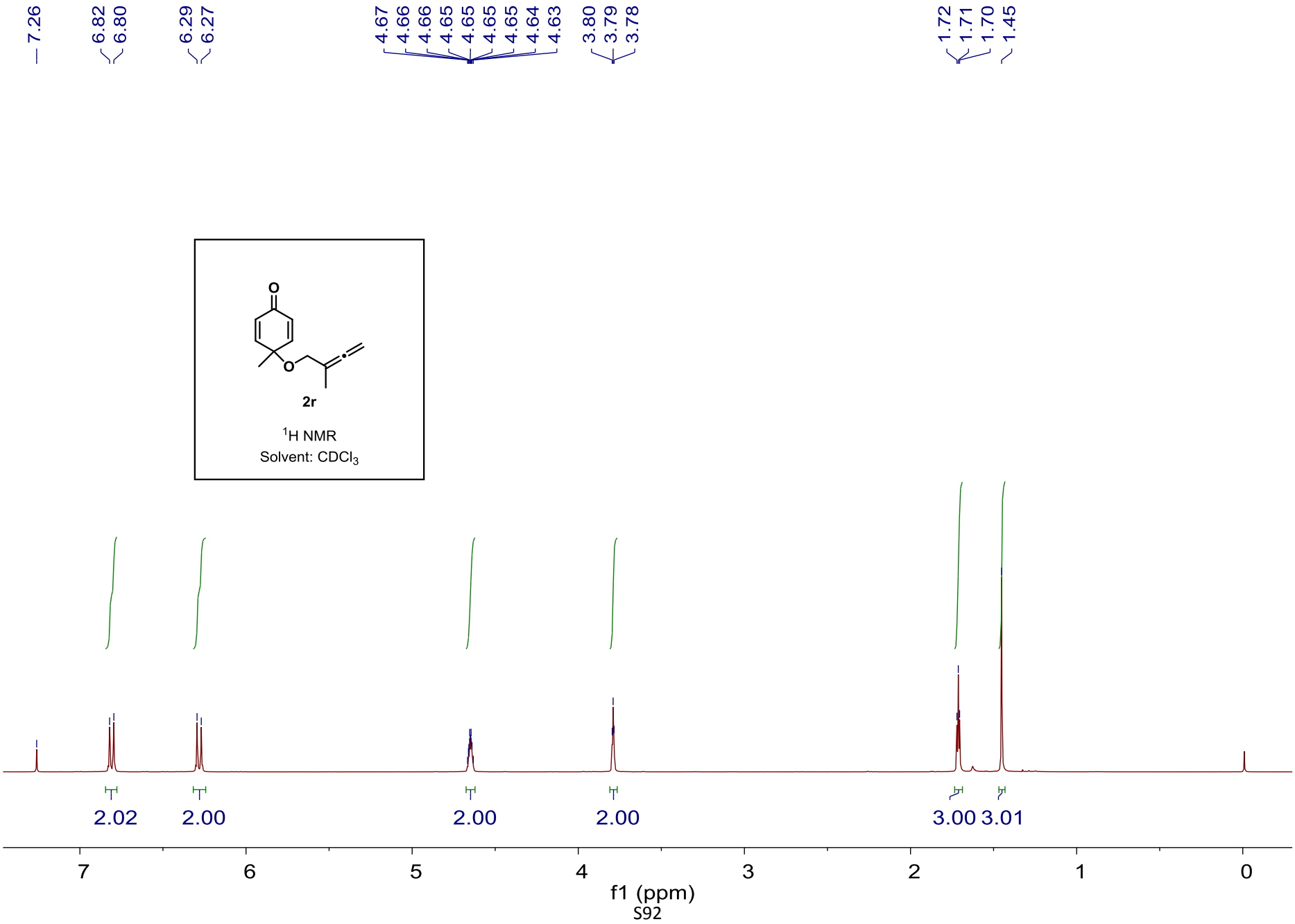
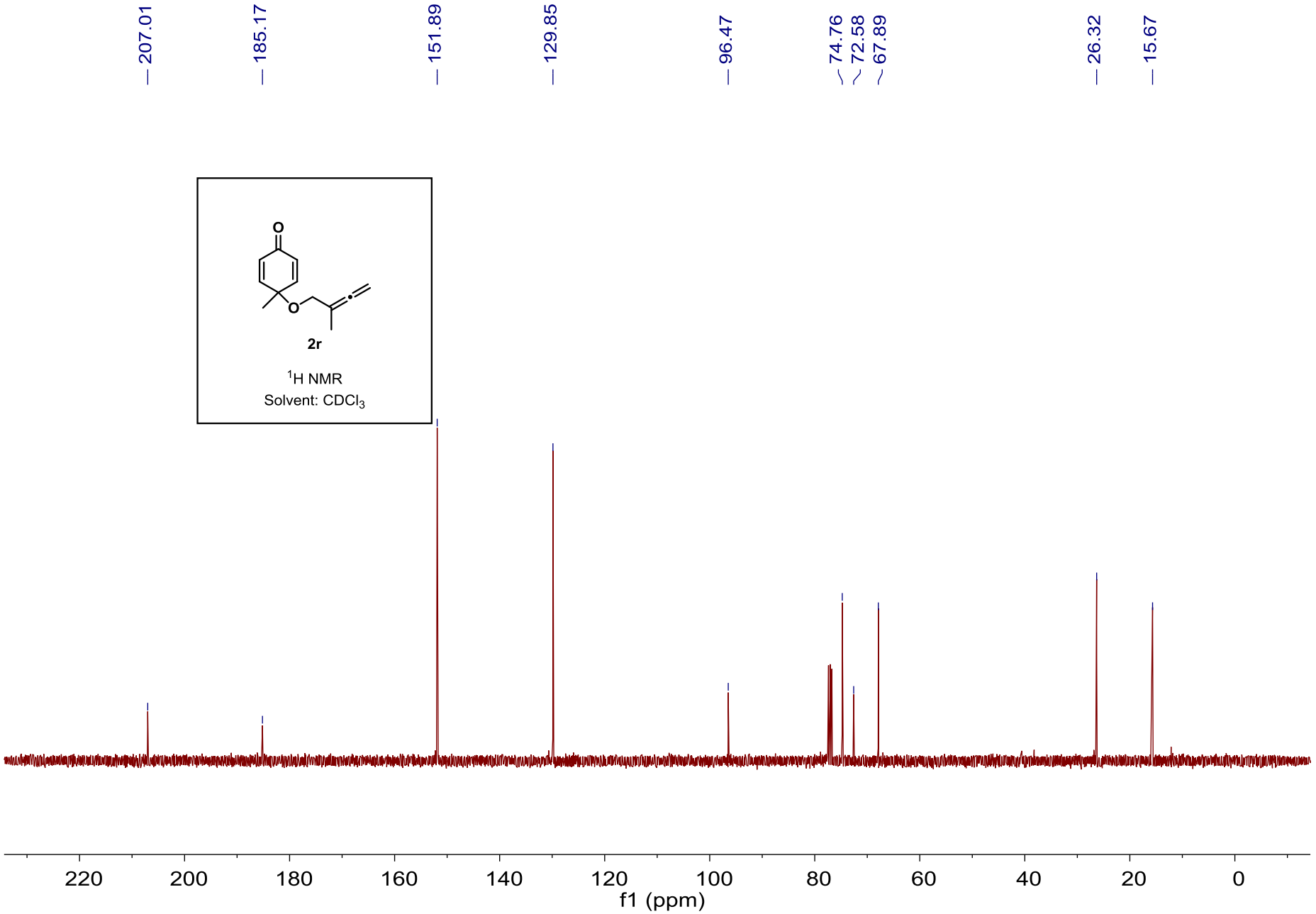
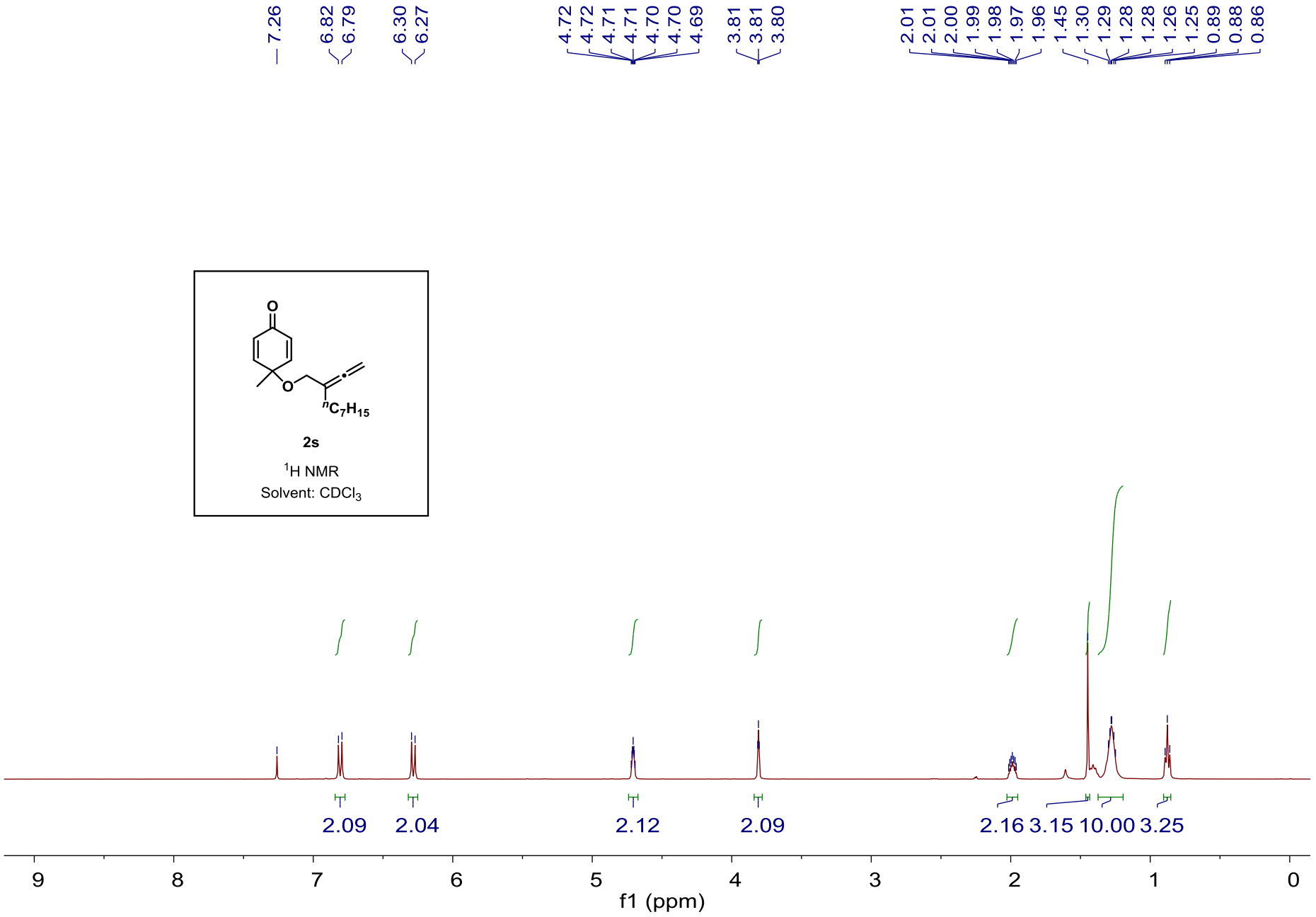
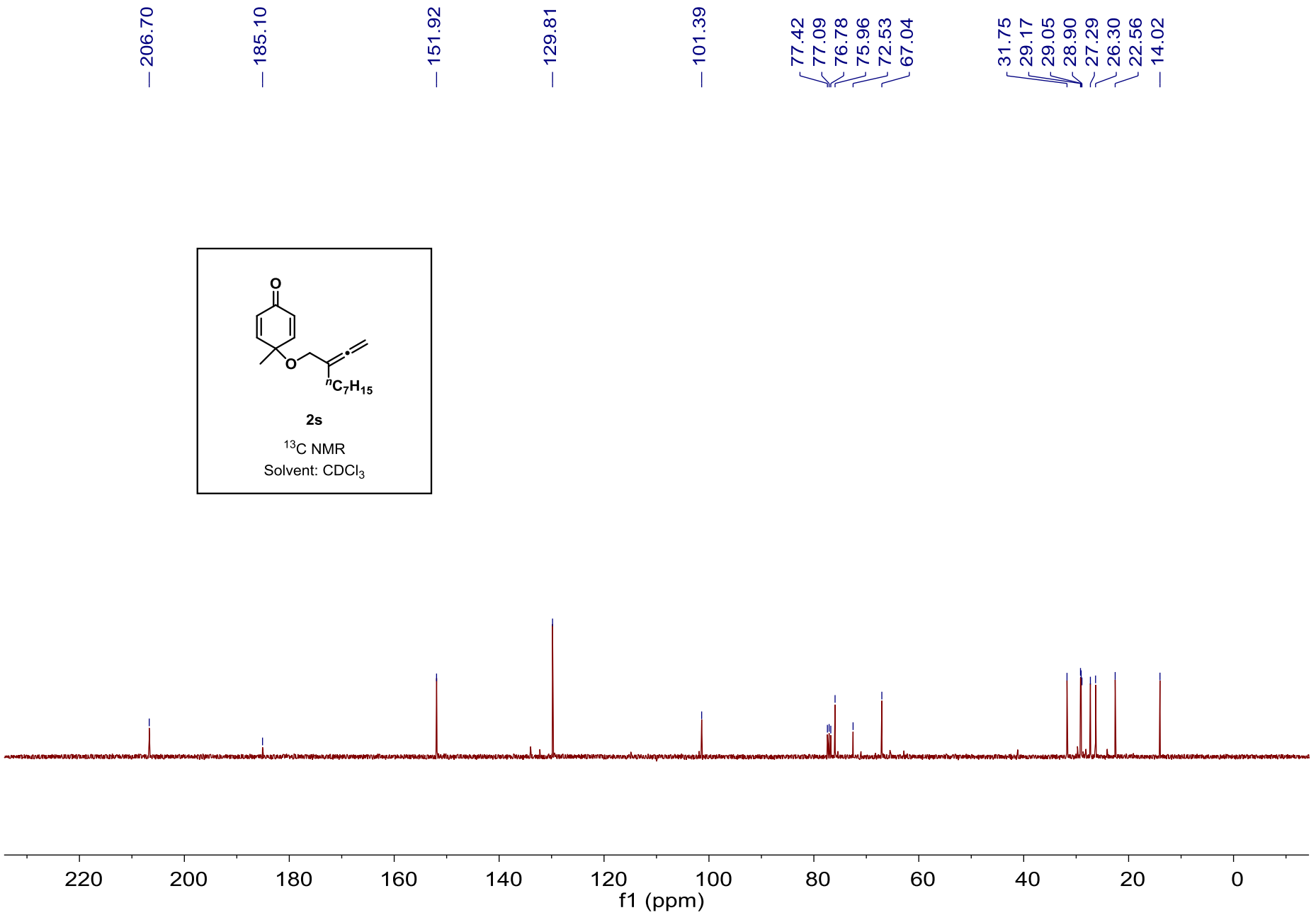
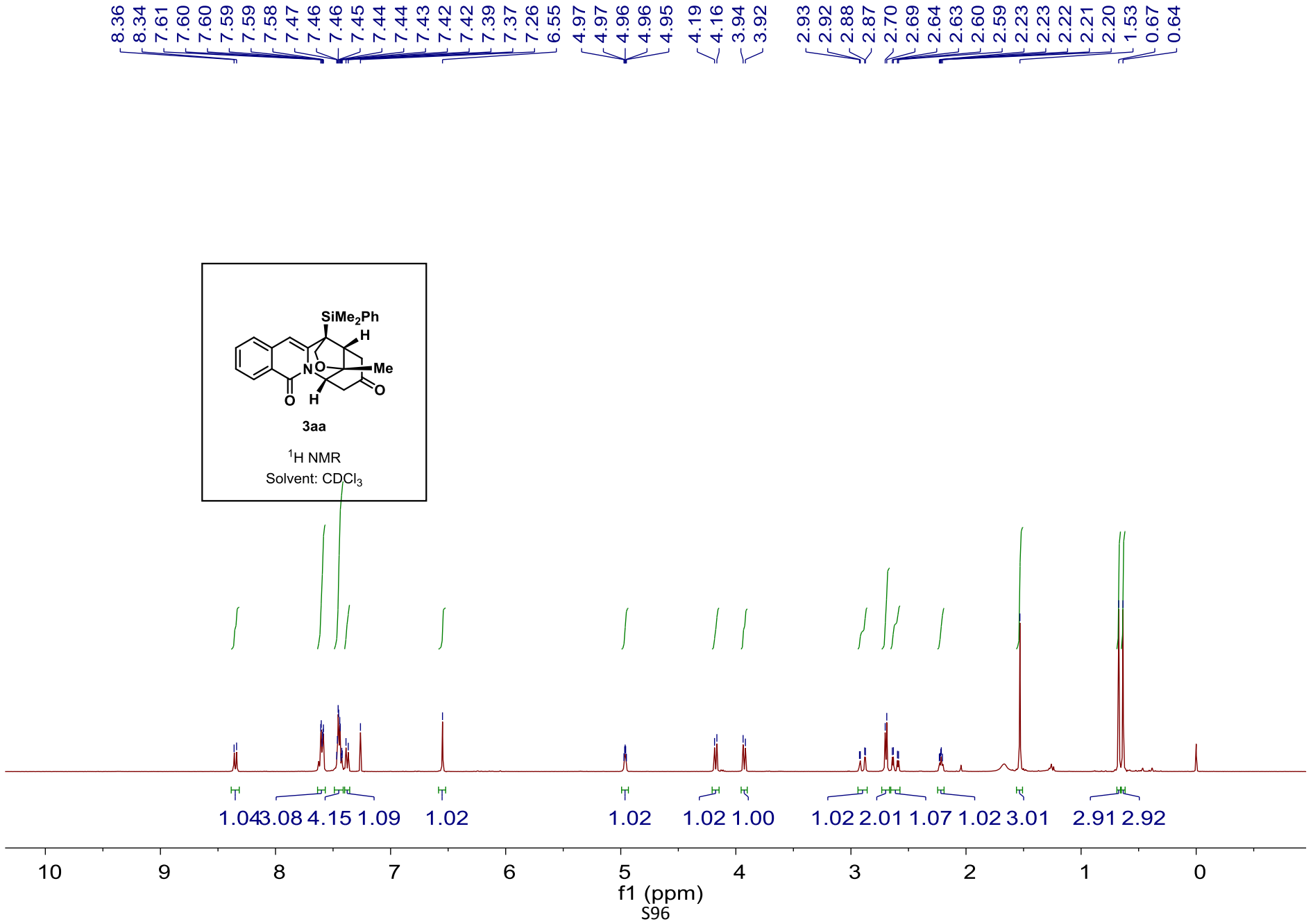
174.49
157.63
150.49
150.45
137.47
135.58
133.90
133.66
130.95
130.93
129.24
129.20
128.85
127.75
127.14
126.13
125.89
119.05
105.56
92.86
74.79
70.15
65.48
64.20
55.29
45.41
35.72
22.85
18.33
-2.55
SiMe2Ph
OMe
2q
13C NMR
Solvent: CDCl3
137.47
135.58
133.90
133.66
130.95
130.93
129.24
129.20
128.85
127.75
127.14
126.13
125.89
140 138 136 134 132 130 128 126 124 122
f1 (ppm)
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

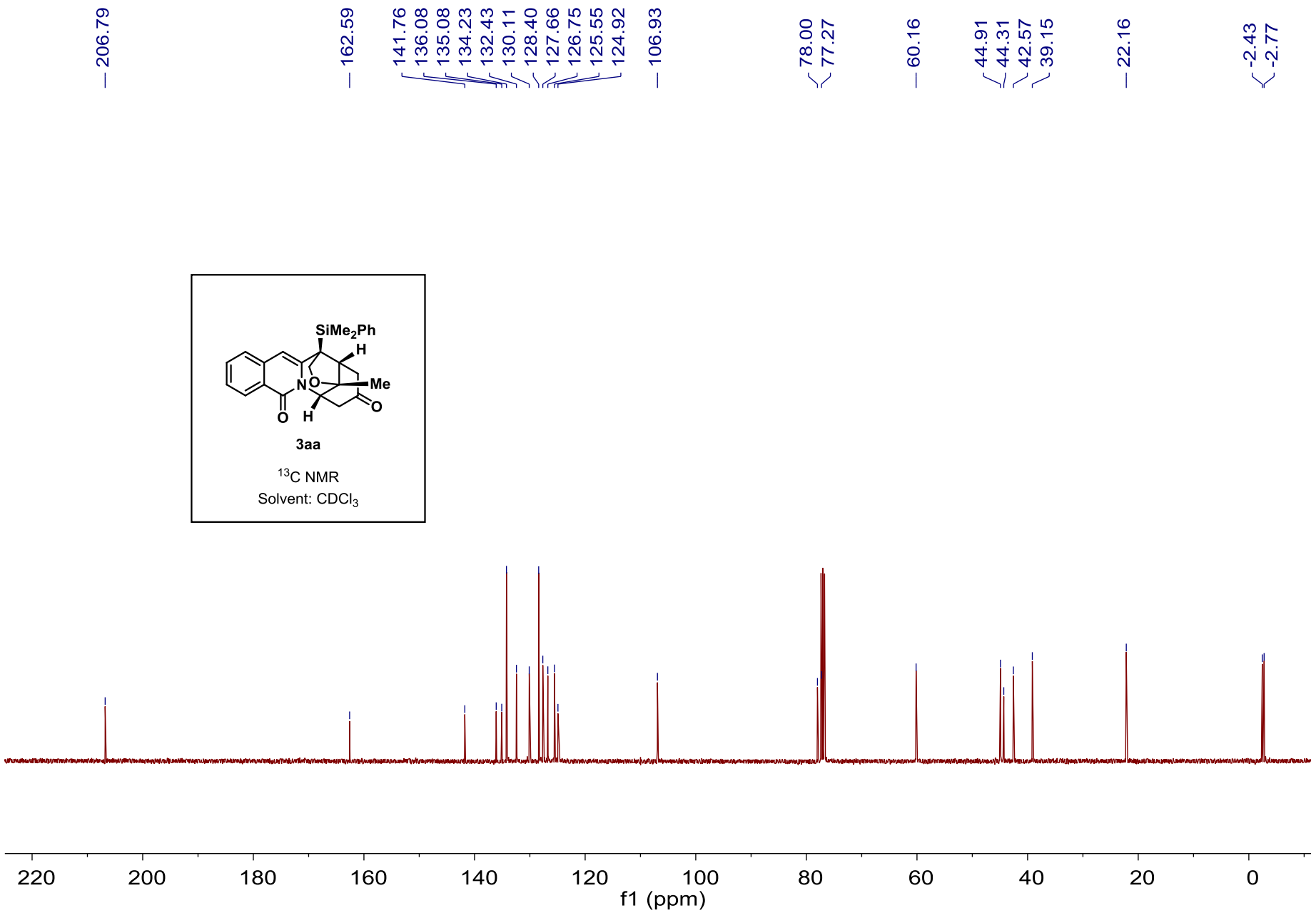

7.26
6.82
6.80
6.29
6.27
4.67
4.66
4.66
4.65
4.65
4.65
4.65
4.64
4.63
3.80
3.79
3.78
1.72
1.71
1.70
1.45
O
O
2r
1H NMR
Solvent: CDCl3
2.02
2.00
2.00
2.00
3.00
3.01
7
6
5
4
3
2
1
0
f1 (ppm)

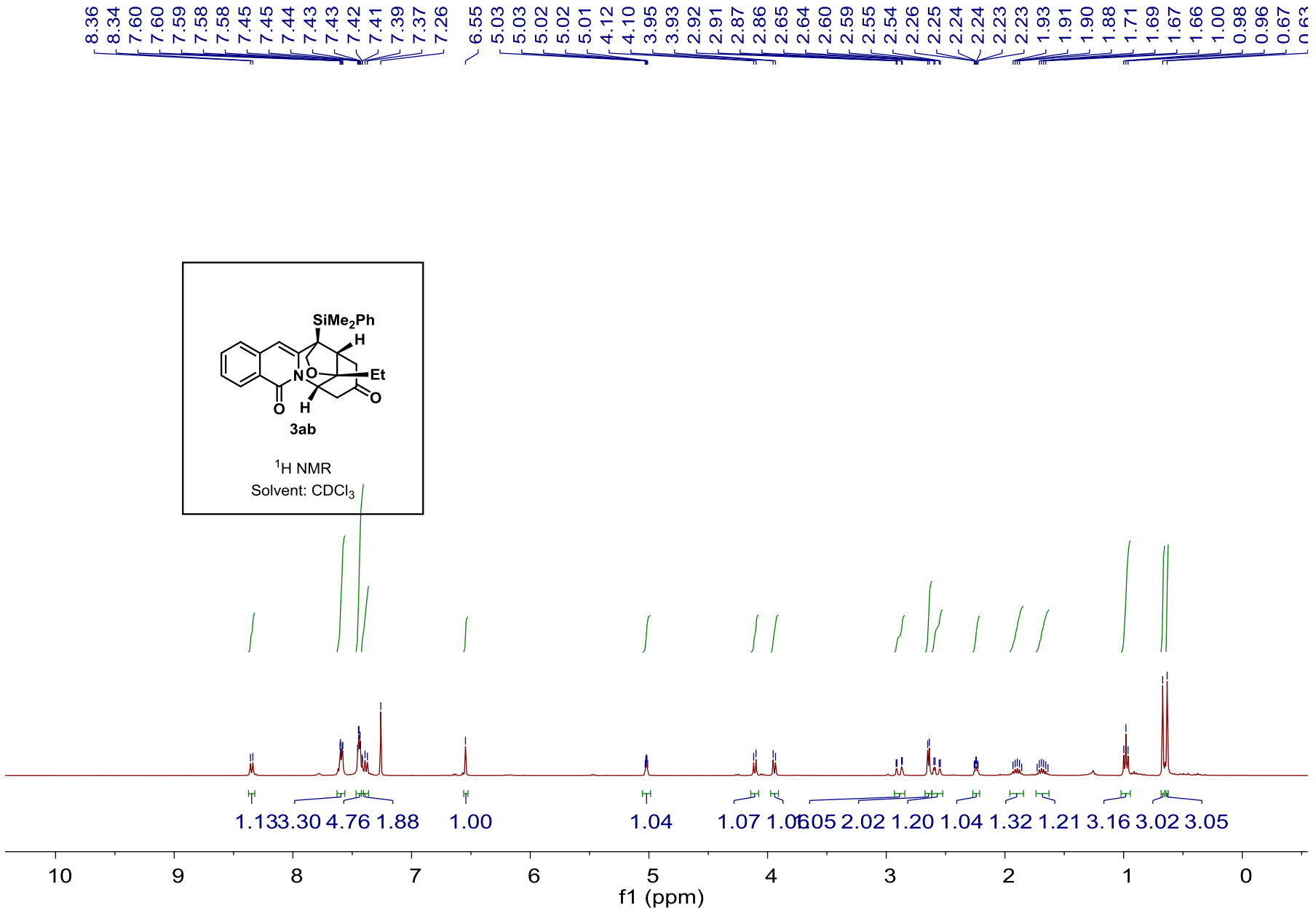

207.01
185.17
151.89
129.85
96.47
74.76
72.58
67.89
26.32
15.67
O
O
2r
1H NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

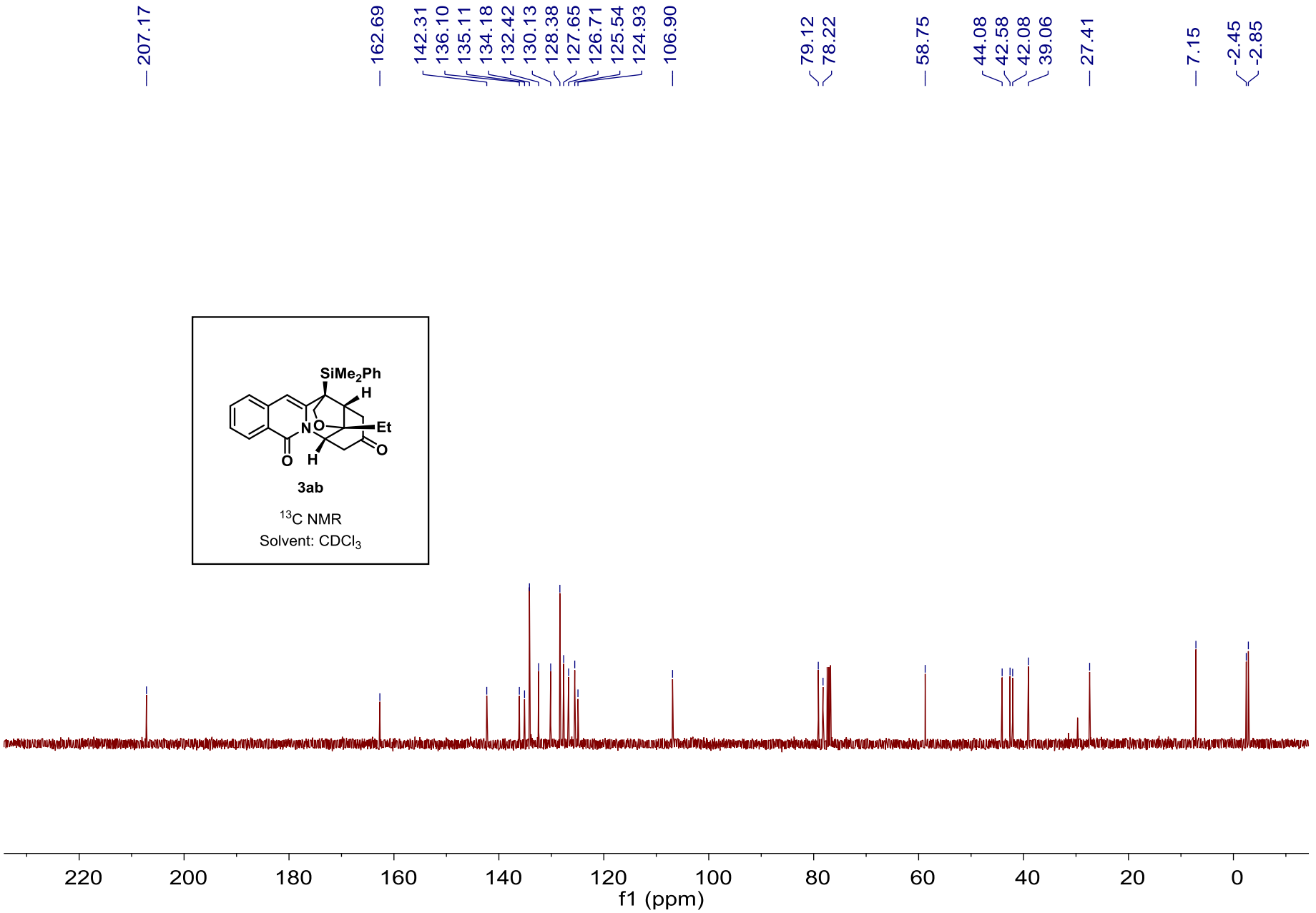

7.26
6.82
6.79
6.30
6.27
4.72
4.72
4.71
4.71
4.70
4.70
4.69
3.81
3.81
3.80
2.01
2.01
2.00
1.99
1.98
1.97
1.96
1.45
1.30
1.29
1.28
1.28
1.26
1.25
0.89
0.88
0.86
O
O
$^{n}C_7H_{15}$
2s
^{1}H NMR
Solvent: $CDCl_3$
2.09
2.04
2.12
2.09
2.16
3.15
10.00
3.25
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

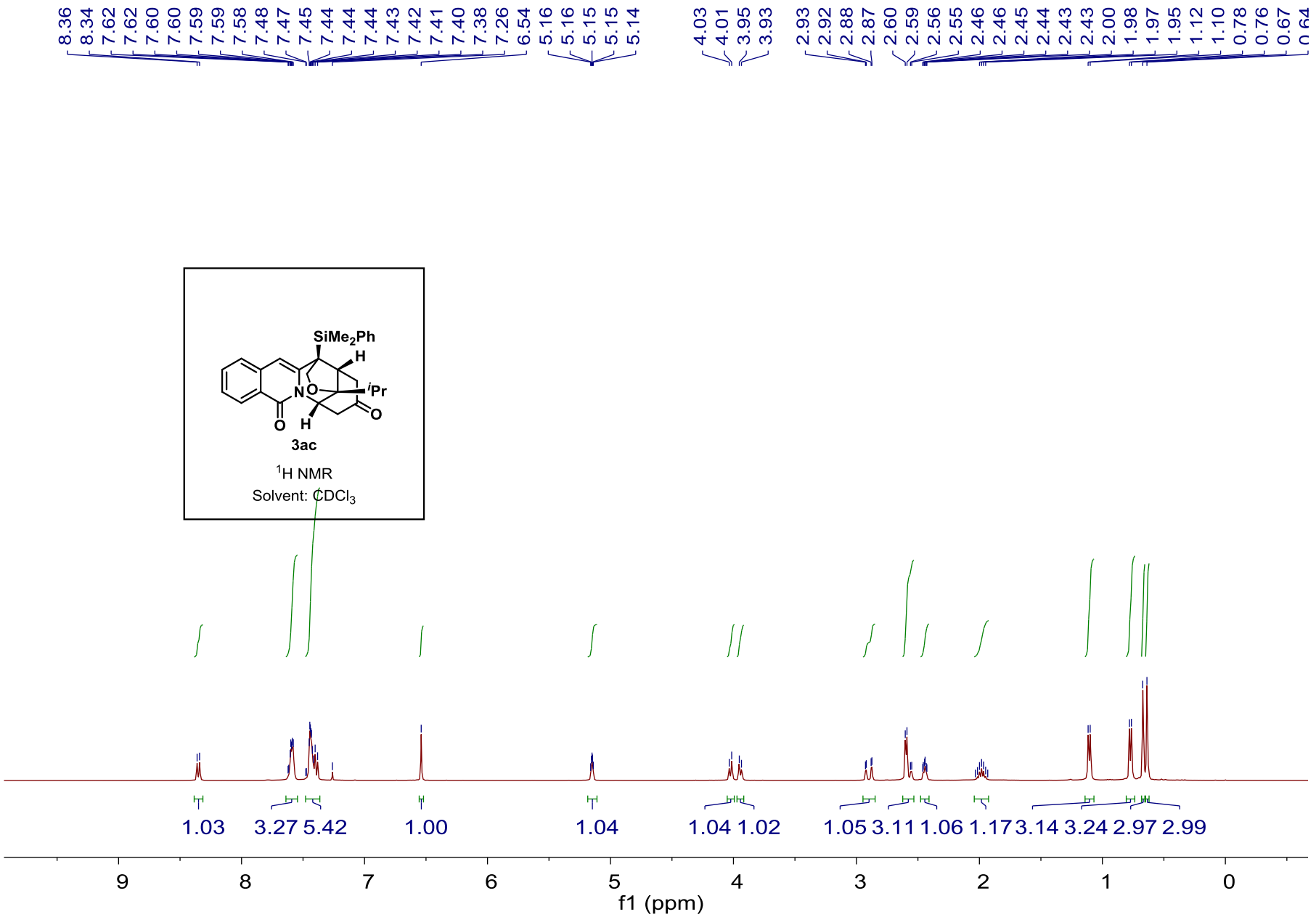

206.70
185.10
151.92
129.81
101.39
77.42
77.09
76.78
75.96
72.53
67.04
31.75
29.17
29.05
28.90
27.29
26.30
22.56
14.02
O
O
$^{n}C_7H_{15}$
2s
^{13}C NMR
Solvent: $CDCl_3$
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

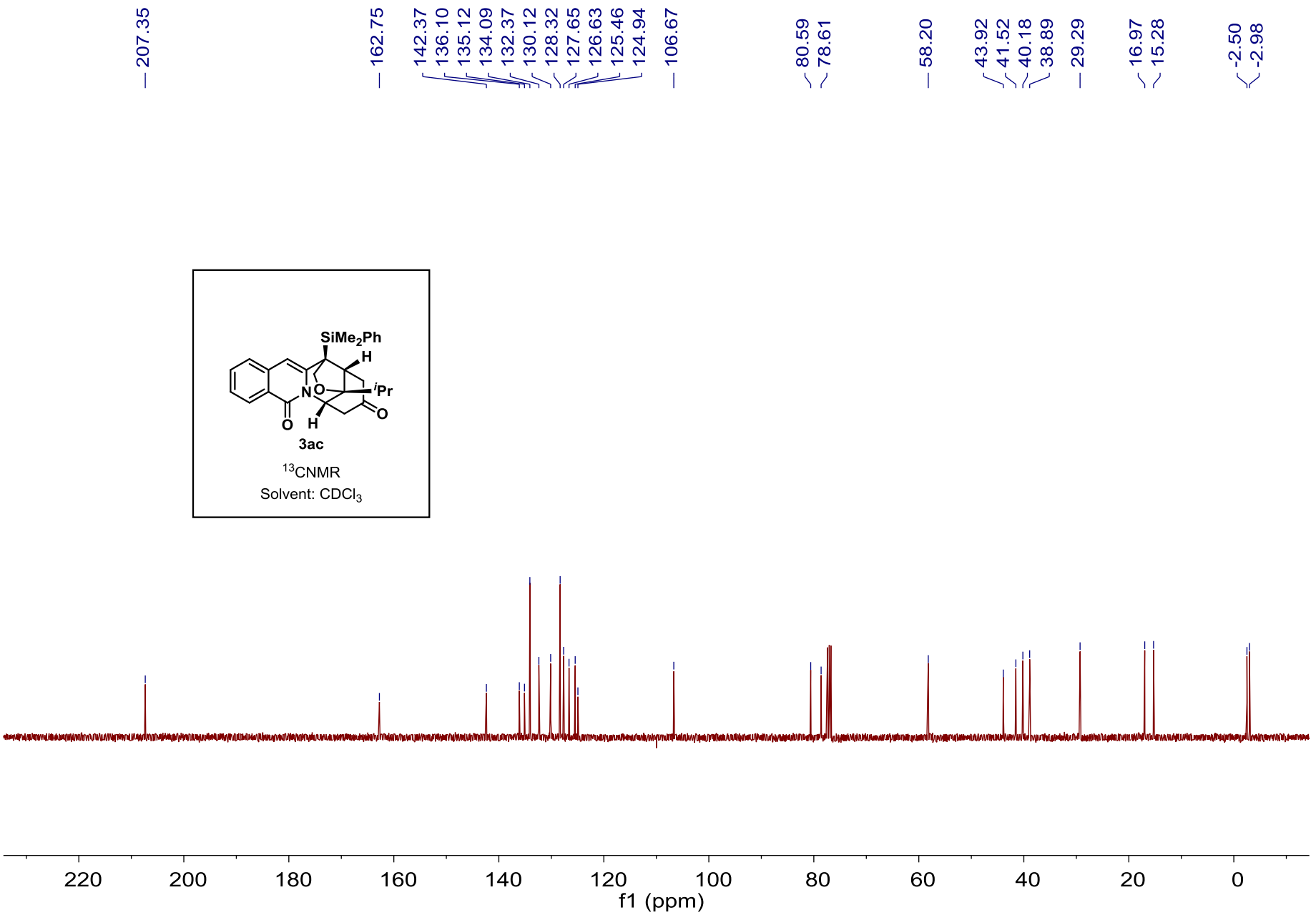

8.36 8.34 7.61 7.60 7.60 7.59 7.59 7.58 7.47 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.39 7.37 7.26 6.55
4.97 4.97 4.96 4.96 4.95
4.19 4.16 3.94 3.92
2.93 2.92 2.88 2.87 2.70 2.69 2.64 2.63 2.60 2.59 2.23 2.23 2.22 2.21 2.20 1.53 0.67 0.64
SiMe2Ph
H
N
O
Me
O
O
H
3aa
1H NMR
Solvent: CDCl3
1.04 3.08 4.15 1.09 1.02 1.02 1.02 1.00 1.02 2.01 1.07 1.02 3.01 2.91 2.92
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


206.79
162.59
141.76
136.08
135.08
134.23
132.43
130.11
128.40
127.66
126.75
125.55
124.92
106.93
78.00
77.27
60.16
44.91
44.31
42.57
39.15
22.16
-2.43
-2.77
SiMe2Ph
H
N
O
Me
O
O
H
3aa
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.36 8.34 7.60 7.60 7.59 7.58 7.58 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.39 7.37 7.26
6.55 5.03 5.03 5.02 5.02 5.01 4.12 4.10 3.95 3.93 2.92 2.91 2.87 2.86 2.65 2.64 2.60 2.59 2.55 2.54 2.26 2.25 2.24 2.24 2.23 2.23 1.93 1.91 1.90 1.88 1.71 1.69 1.67 1.66 1.00 0.98 0.96 0.67
SiMe2Ph
H
N
O
Et
O
O
H
3ab
1H NMR
Solvent: CDCl3
1.13 3.30 4.76 1.88 1.00 1.04 1.07 1.06 1.05 2.02 1.20 1.04 1.32 1.21 3.16 3.02 3.05
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


207.17
162.69
142.31
136.10
135.11
134.18
132.42
130.13
128.38
127.65
126.71
125.54
124.93
106.90
79.12
78.22
58.75
44.08
42.58
42.08
39.06
27.41
7.15
-2.45
-2.85
SiMe2Ph
H
N
O
Et
O
O
H
3ab
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.36 8.34 7.62 7.62 7.60 7.60 7.59 7.59 7.58 7.48 7.47 7.45 7.44 7.44 7.44 7.43 7.42 7.41 7.40 7.38 7.26 6.54 5.16 5.16 5.15 5.15 5.14
4.03 4.01 3.95 3.93
2.93 2.92 2.88 2.87 2.60 2.59 2.56 2.55 2.46 2.46 2.45 2.44 2.43 2.43 2.00 1.98 1.97 1.95 1.12 1.10 0.78 0.76 0.67
SiMe2Ph
H
N
O
iPr
O
O
H
3ac
1H NMR
Solvent: CDCl3
1.03 3.27 5.42 1.00 1.04 1.04 1.02 1.05 3.11 1.06 1.17 3.14 3.24 2.97 2.99
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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132.37
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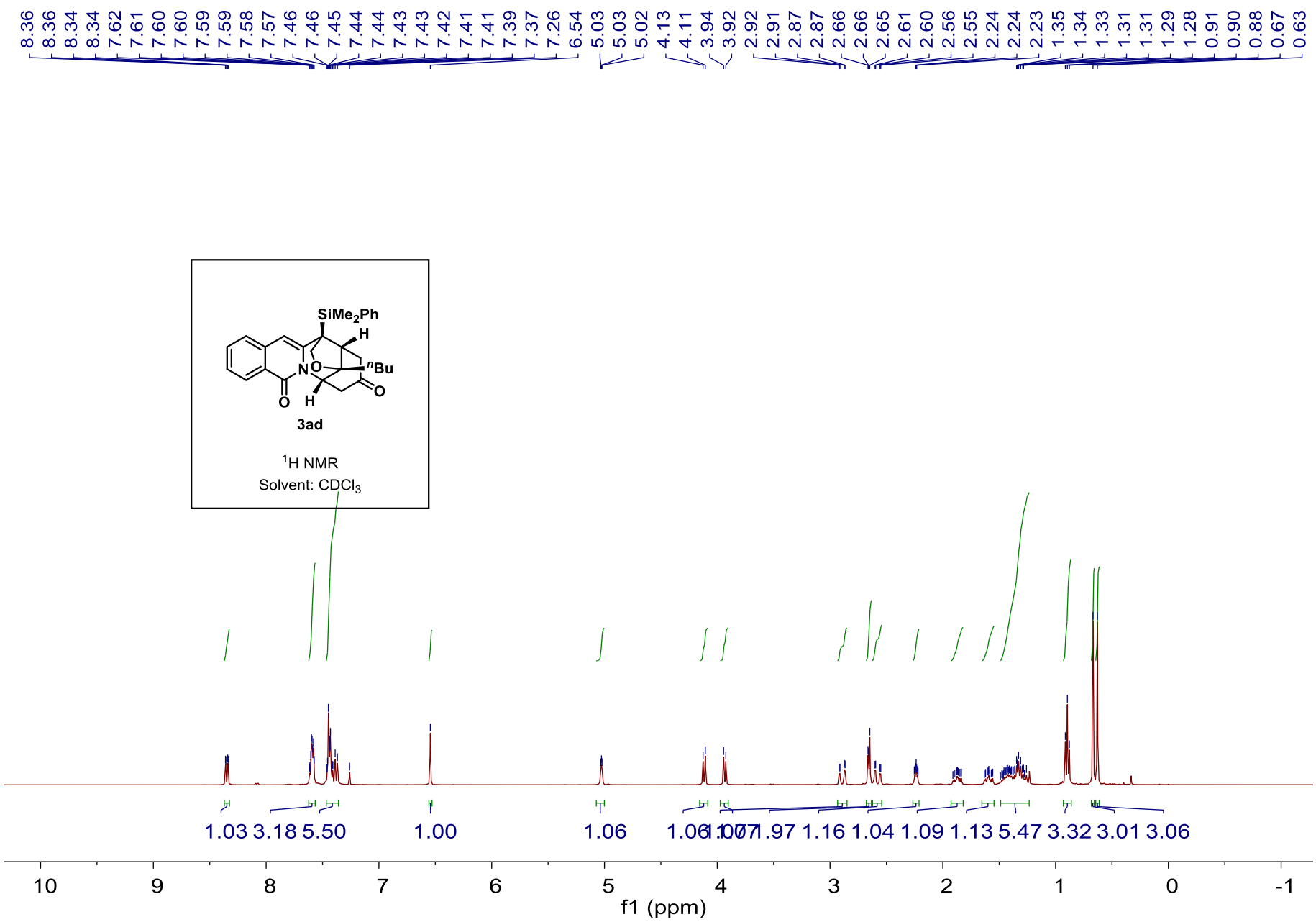
127.65
126.63
125.46
124.94
106.67
80.59
78.61
58.20
43.92
41.52
40.18
38.89
29.29
16.97
15.28
-2.50
-2.98
SiMe2Ph
H
N
O
iPr
O
O
H
3ac
13CNMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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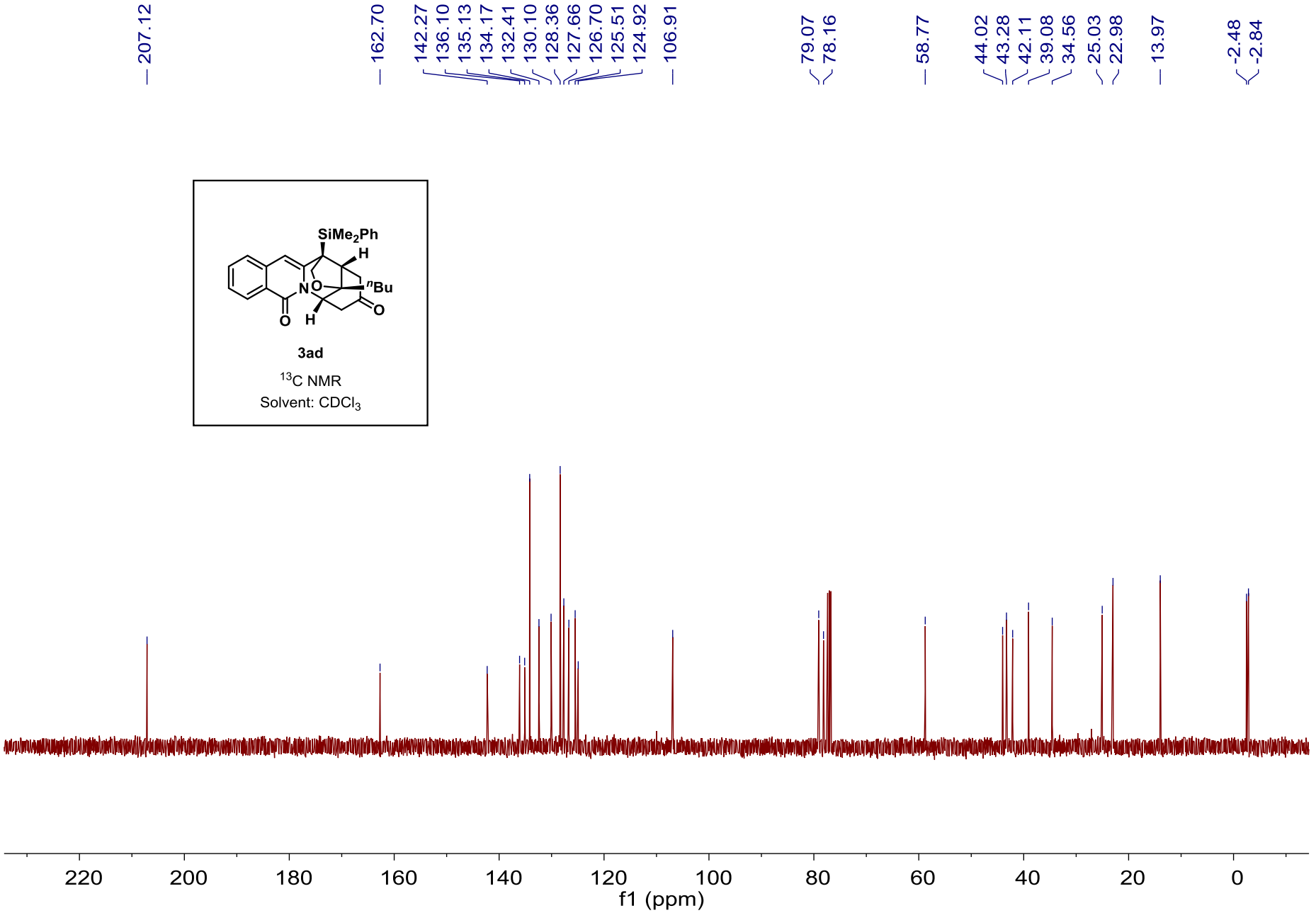
SiMe2Ph
H
N
O
nBu
O
O
H
3ad
1H NMR
Solvent: CDCl3
1.03 3.18 5.50 1.00 1.06 1.06 1.07 1.97 1.16 1.04 1.09 1.13 5.47 3.32 3.01 3.06
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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106.91
79.07
78.16
58.77
44.02
43.28
42.11
39.08
34.56
25.03
22.98
13.97
-2.48
-2.84
SiMe2Ph
H
N
O
nBu
O
O
H
3ad
13C NMR
Solvent: CDCl3
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180
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140
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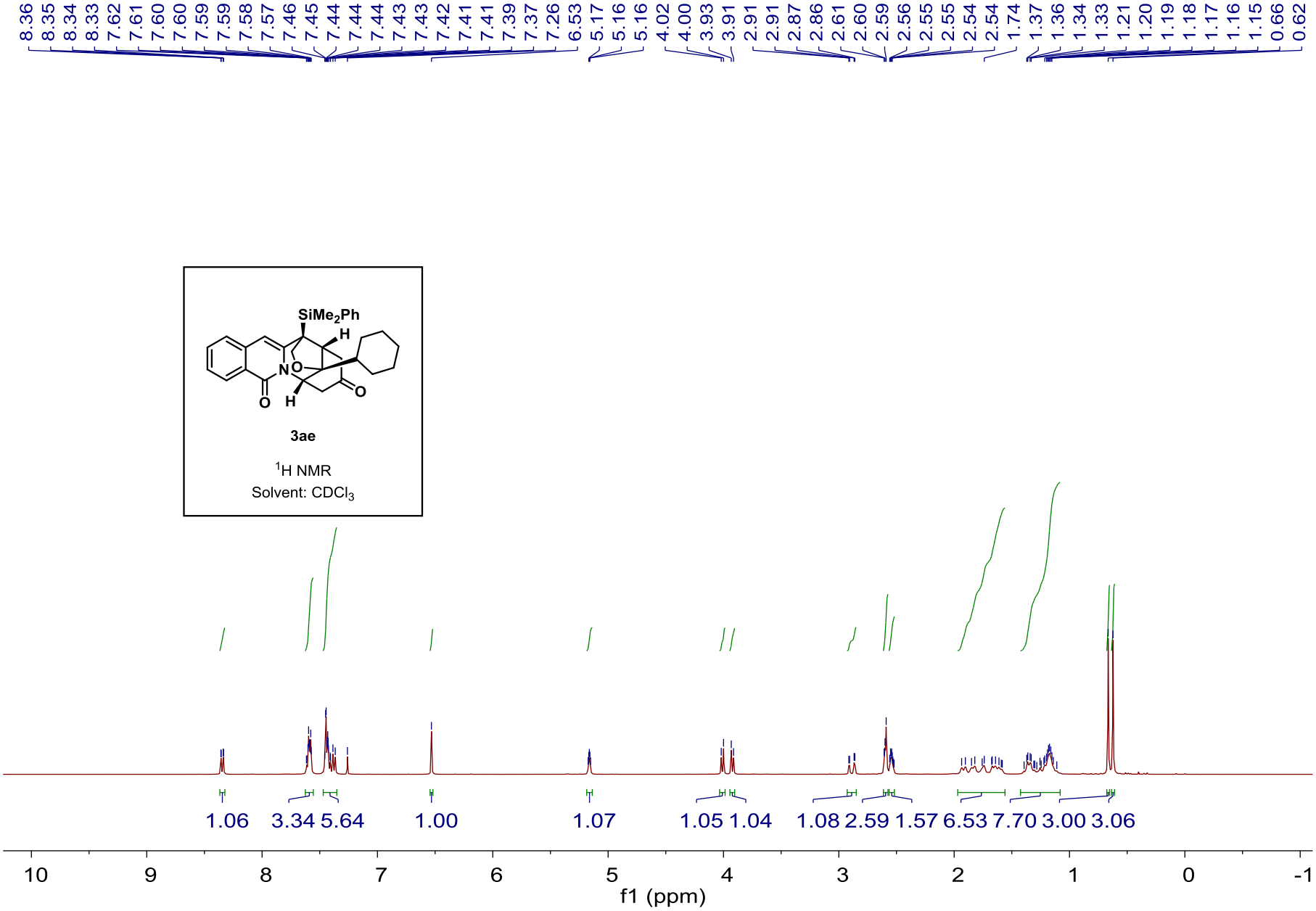
100
80
60
40
20
0
f1 (ppm)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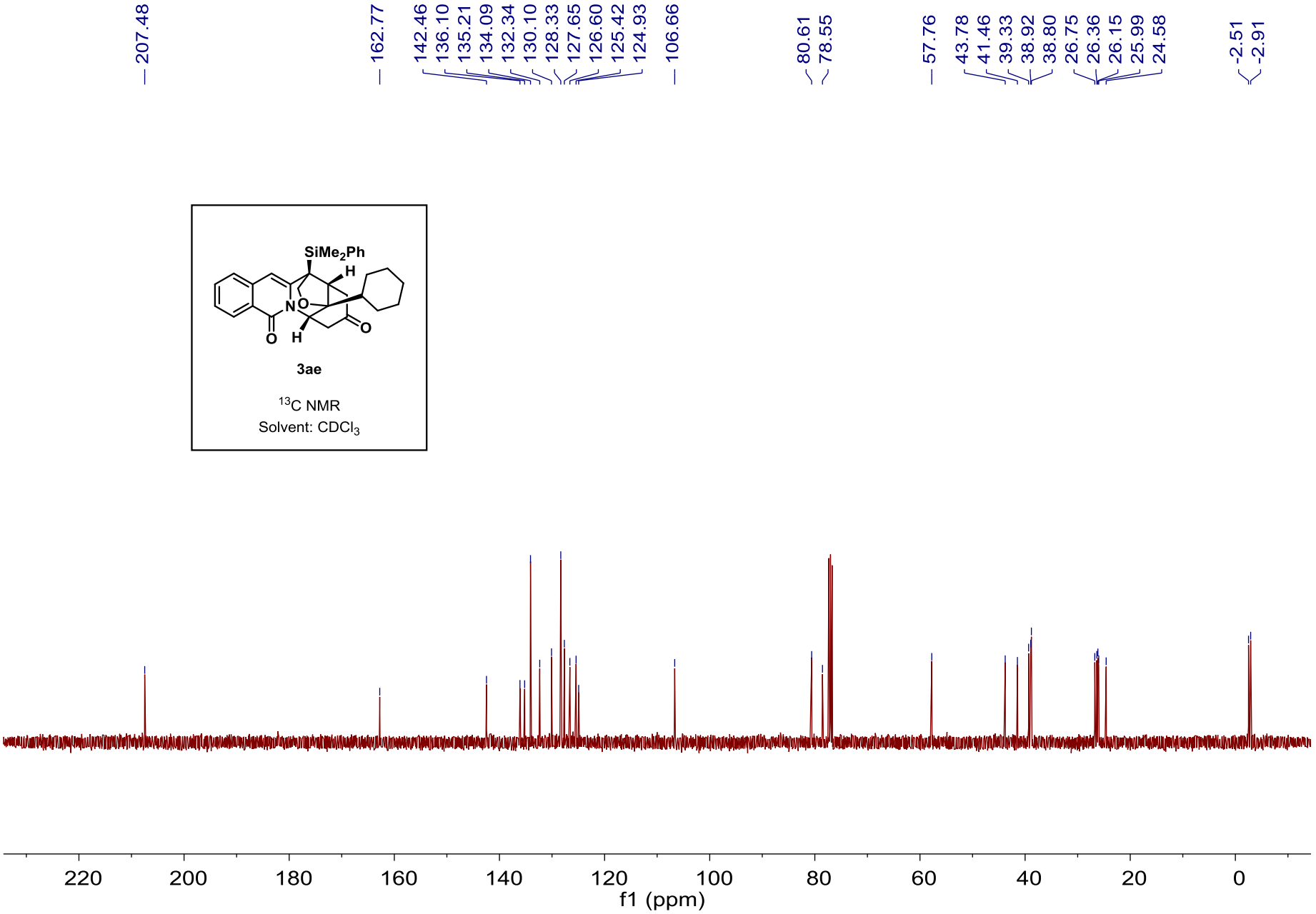
SiMe2Ph
H
N
O
O
H
O
3ae
1H NMR
Solvent: CDCl3
1.06 3.34 5.64 1.00 1.07 1.05 1.04 1.08 2.59 1.57 6.53 7.70 3.00 3.06
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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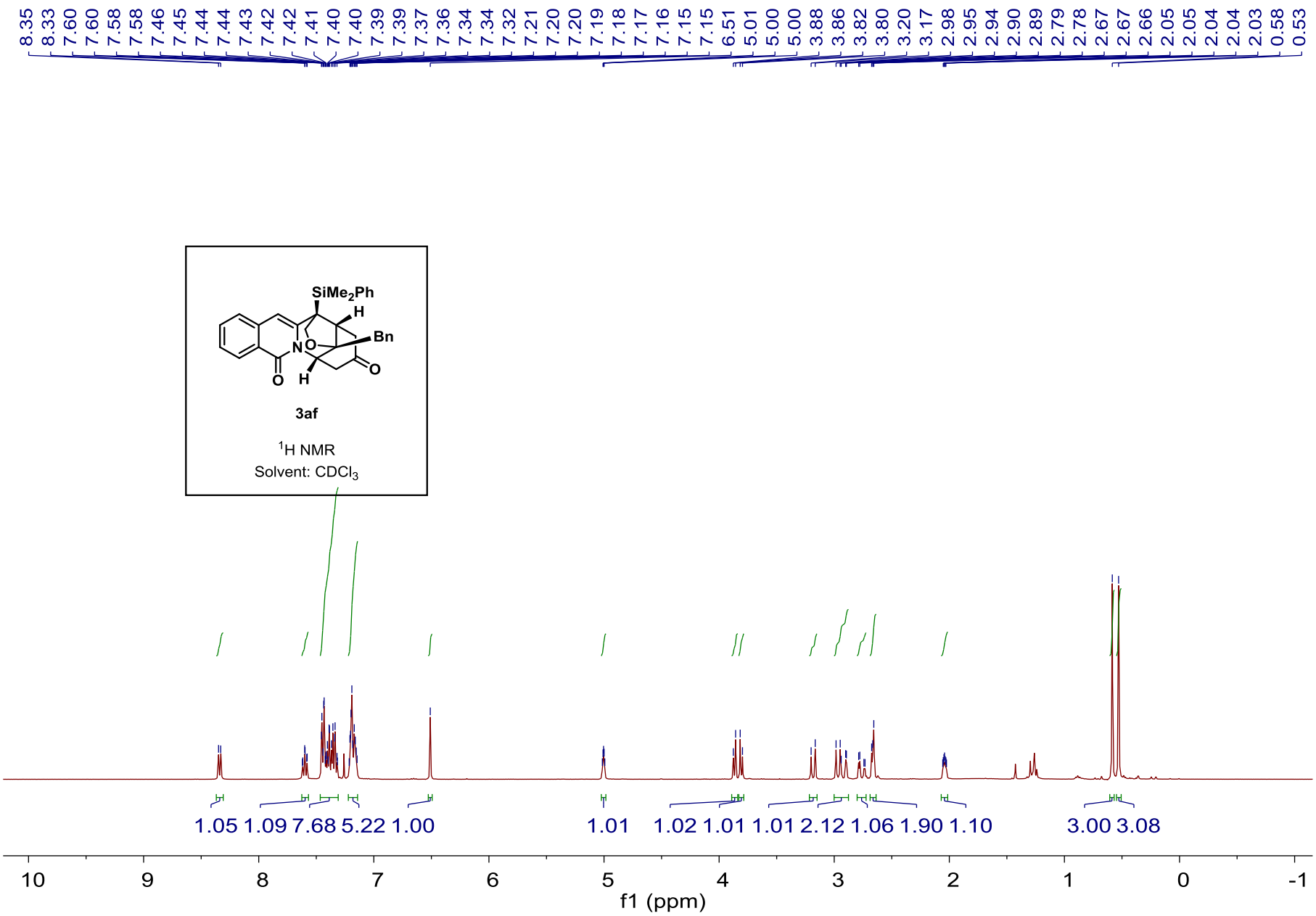
124.93
106.66
80.61
78.55
57.76
43.78
41.46
39.33
38.92
38.80
26.75
26.36
26.15
25.99
24.58
2.51
2.91
SiMe2Ph
H
N
O
O
H
O
3ae
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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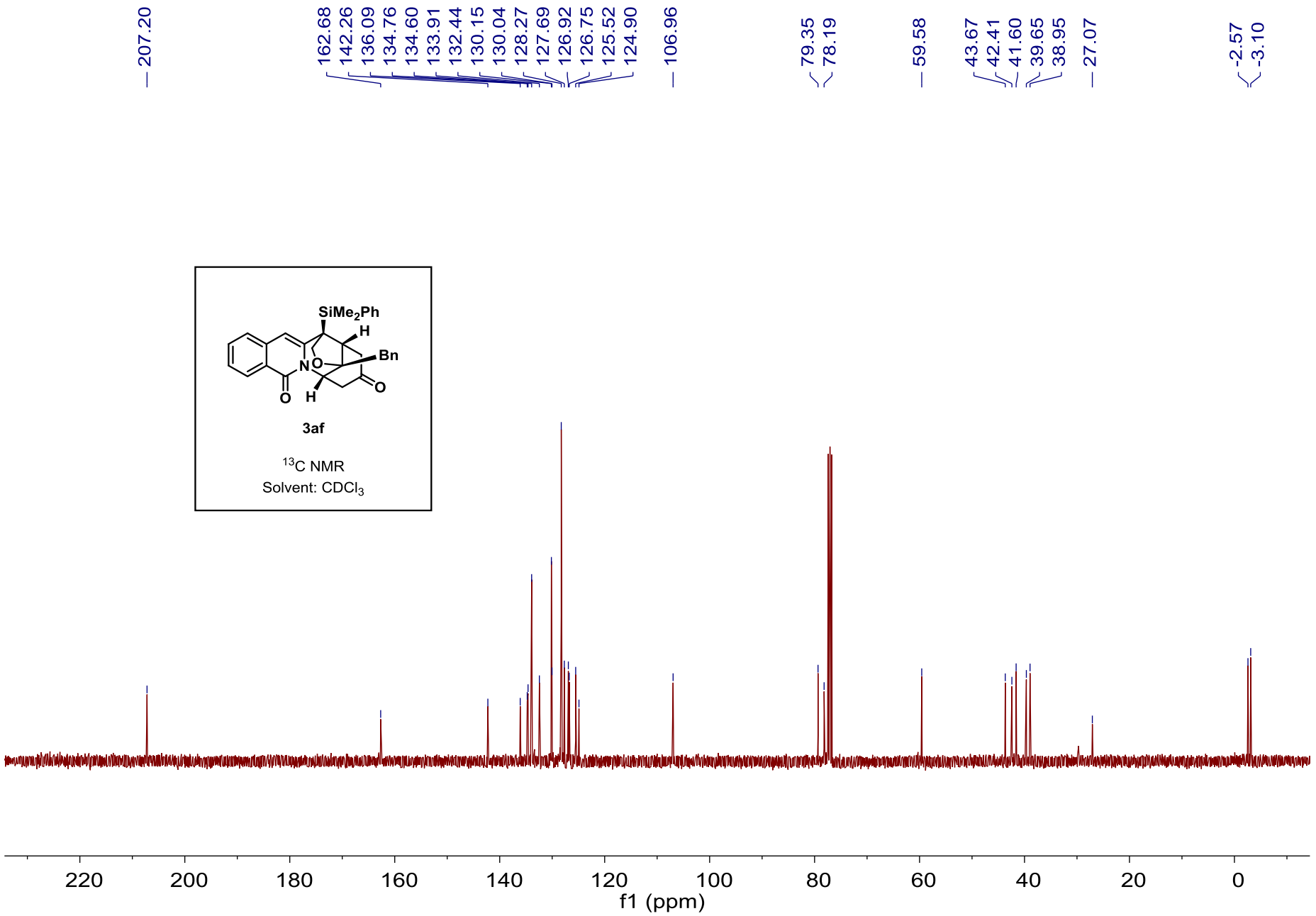
SiMe2Ph
H
Bn
N
O
O
O
H
3af
1H NMR
Solvent: CDCl3
1.05 1.09 7.68 5.22 1.00 1.01 1.02 1.01 1.01 2.12 1.06 1.90 1.10 3.00 3.08
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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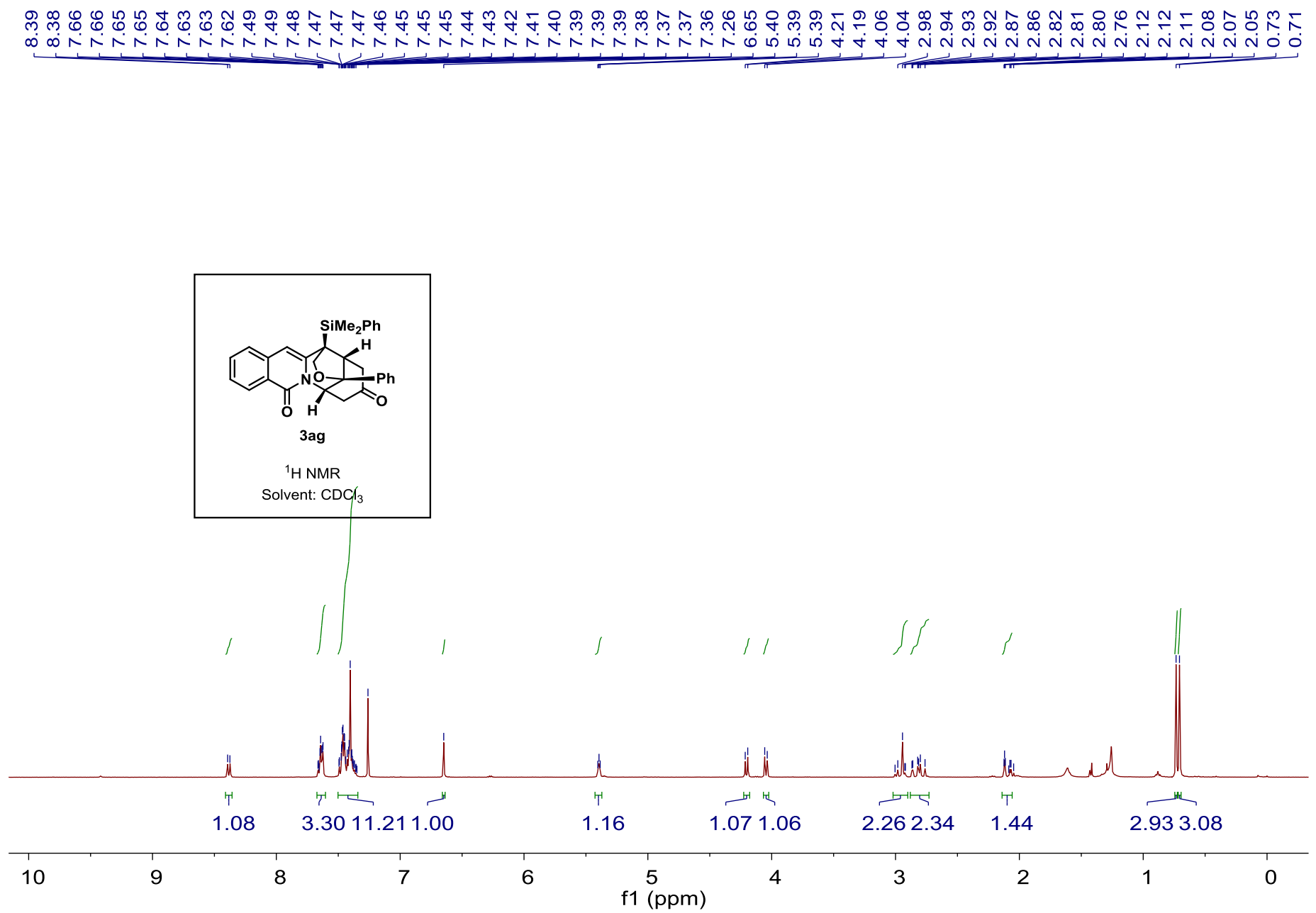
128.27
127.69
126.92
126.75
125.52
124.90
106.96
79.35
78.19
59.58
43.67
42.41
41.60
39.65
38.95
27.07
-2.57
-3.10
SiMe2Ph
H
Bn
N
O
O
O
H
3af
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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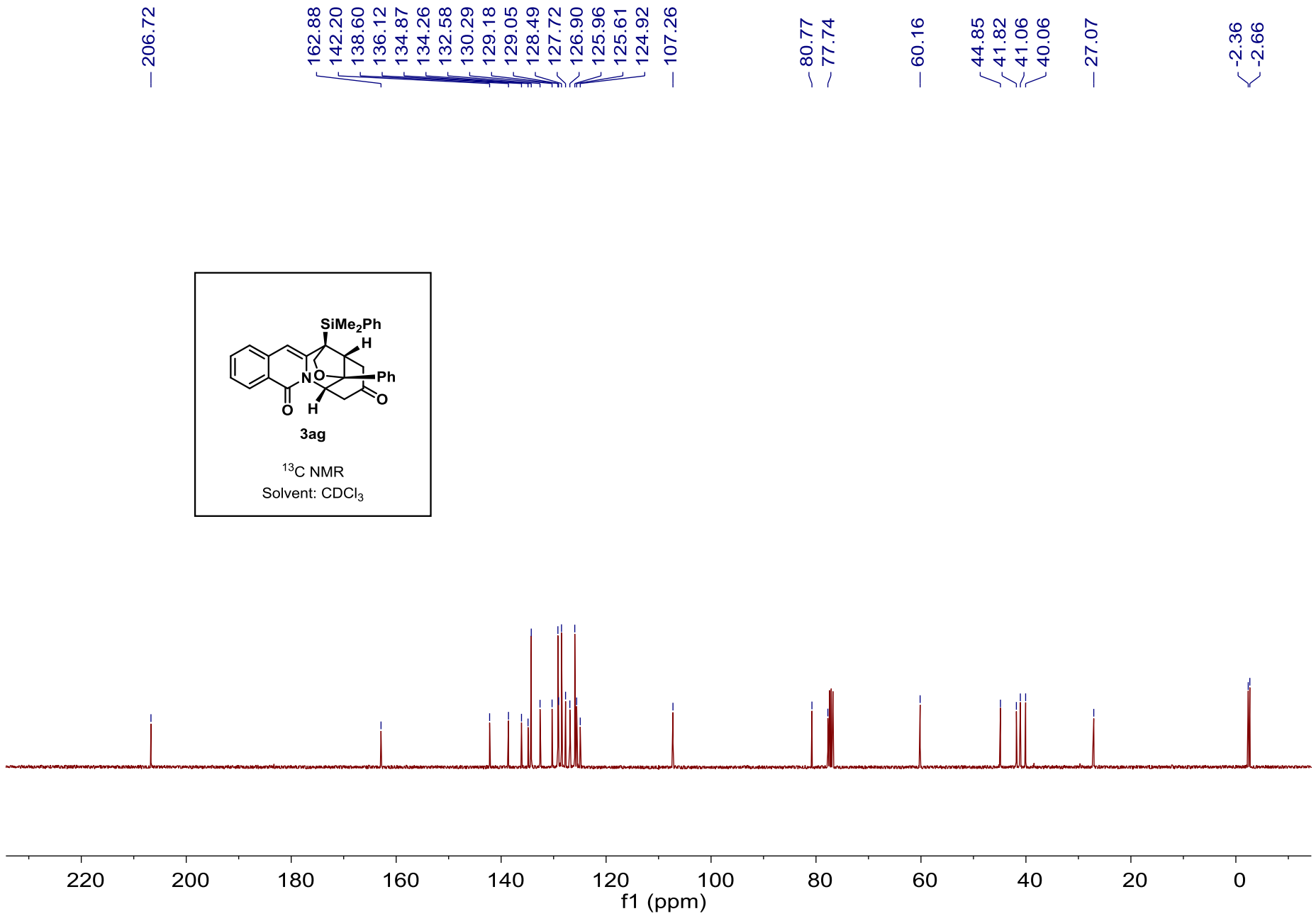
SiMe2Ph
H
N
O
Ph
O
O
H
3ag
1H NMR
Solvent: CDCl3
1.08 3.30 11.21 1.00 1.16 1.07 1.06 2.26 2.34 1.44 2.93 3.08
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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132.58
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129.18
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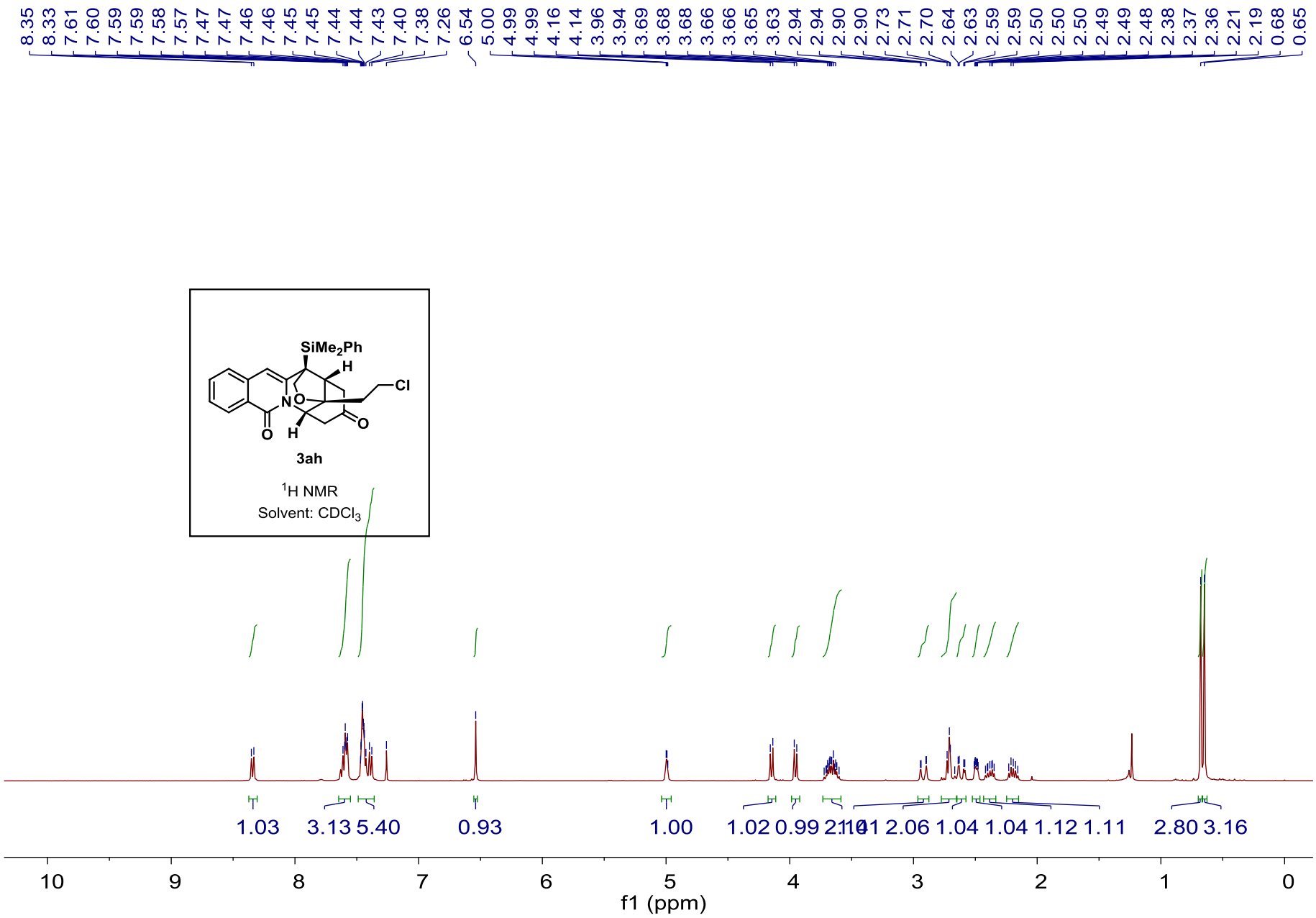
127.72
126.90
125.96
125.61
124.92
107.26
80.77
77.74
60.16
44.85
41.82
41.06
40.06
27.07
-2.36
-2.66
SiMe2Ph
H
N
O
Ph
O
O
H
3ag
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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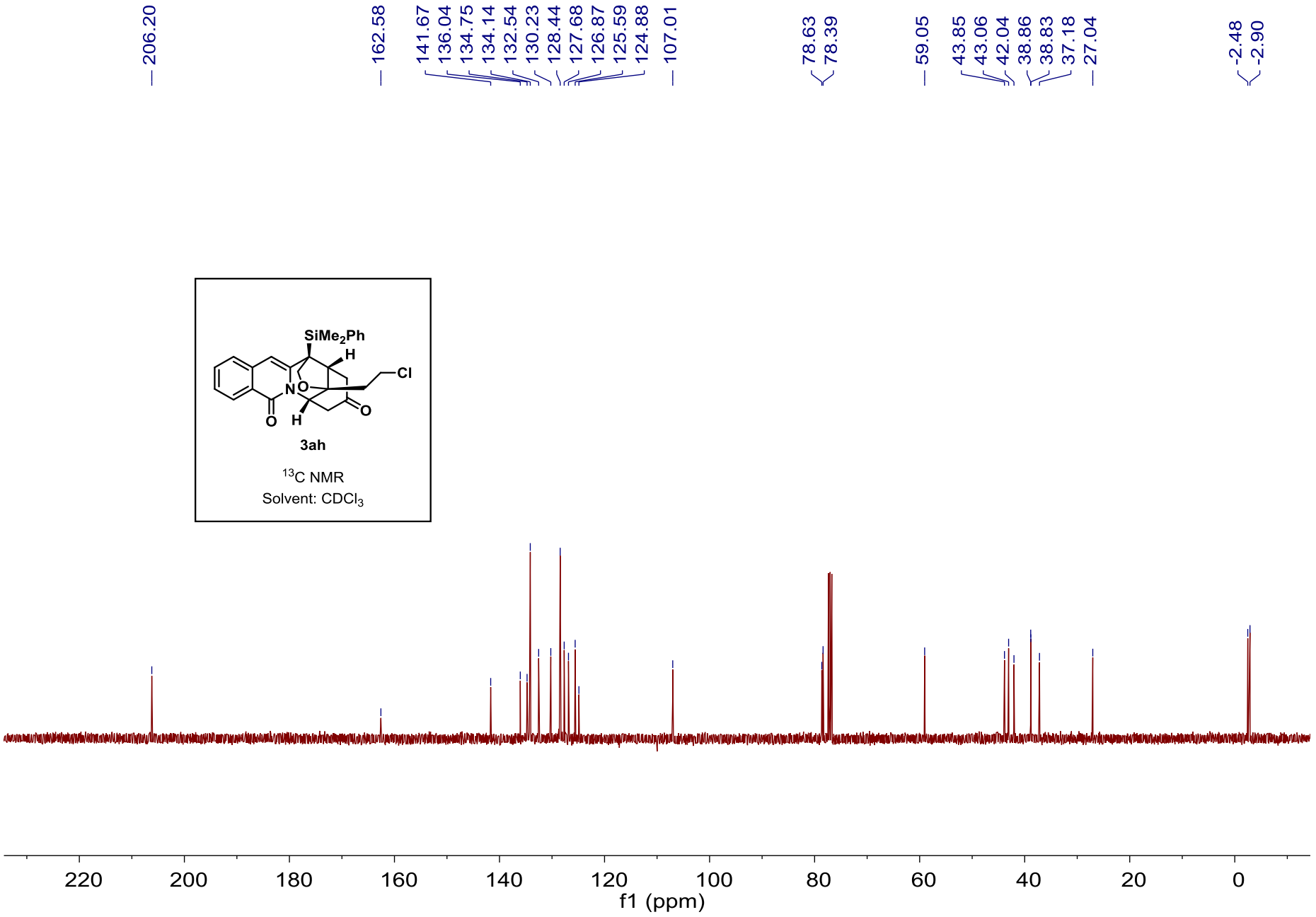
SiMe2Ph
H
Cl
N
O
O
O
H
3ah
1H NMR
Solvent: CDCl3
1.03 3.13 5.40 0.93 1.00 1.02 0.99 2.11 1.01 2.06 1.04 1.04 1.12 1.11 2.80 3.16
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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130.23
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125.59
124.88
107.01
78.63
78.39
59.05
43.85
43.06
42.04
38.86
38.83
37.18
27.04
-2.48
-2.90
SiMe2Ph
H
Cl
N
O
O
O
H
3ah
13C NMR
Solvent: CDCl3
220
200
180
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140
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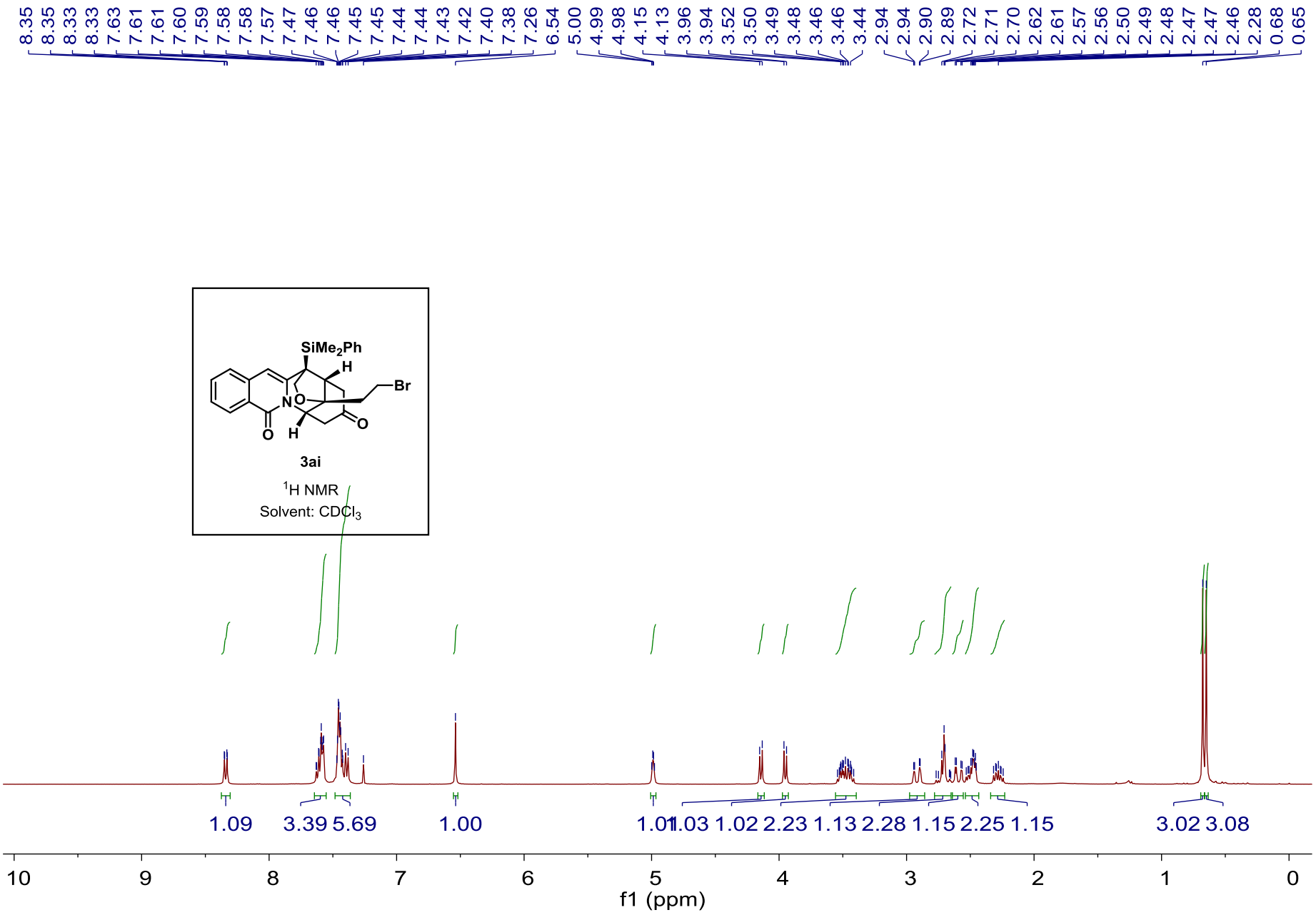
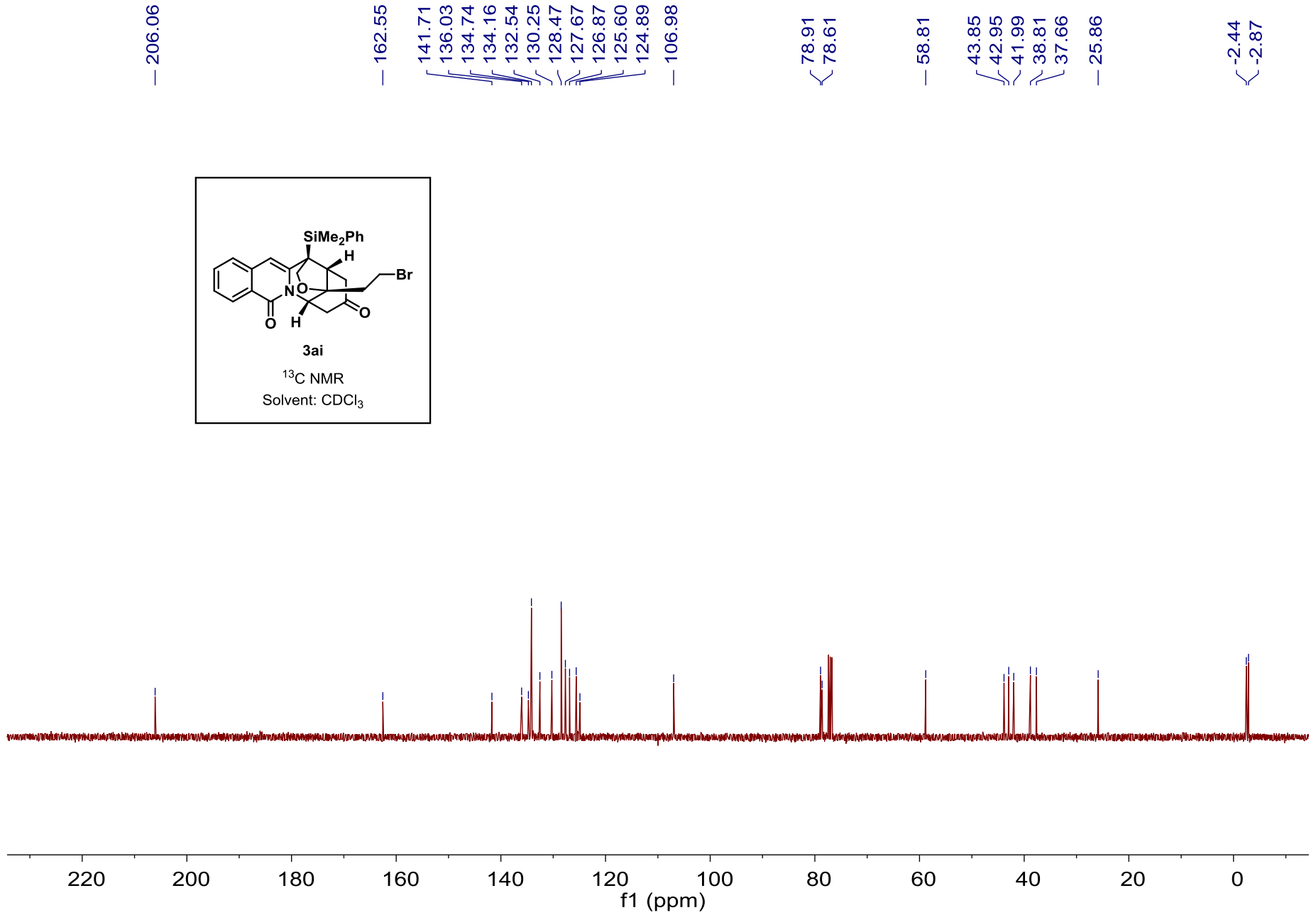
100
80
60
40
20
0
f1 (ppm)


8.35 8.35 8.33 8.33 7.63 7.61 7.61 7.60 7.59 7.58 7.58 7.57 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.40 7.38 7.26 6.54 5.00 4.99 4.98 4.15 4.13 3.96 3.94 3.52 3.50 3.49 3.48 3.46 3.46 3.44 2.94 2.94 2.90 2.89 2.72 2.71 2.70 2.62 2.61 2.57 2.56 2.50 2.49 2.48 2.47 2.47 2.46 2.28 0.68 0.65
SiMe2Ph
H
Br
N
O
O
O
H
3ai
1H NMR
Solvent: CDCl3
1.09 3.39 5.69 1.00 1.01 1.03 1.02 2.23 1.13 2.28 1.15 2.25 1.15 3.02 3.08
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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127.67
126.87
125.60
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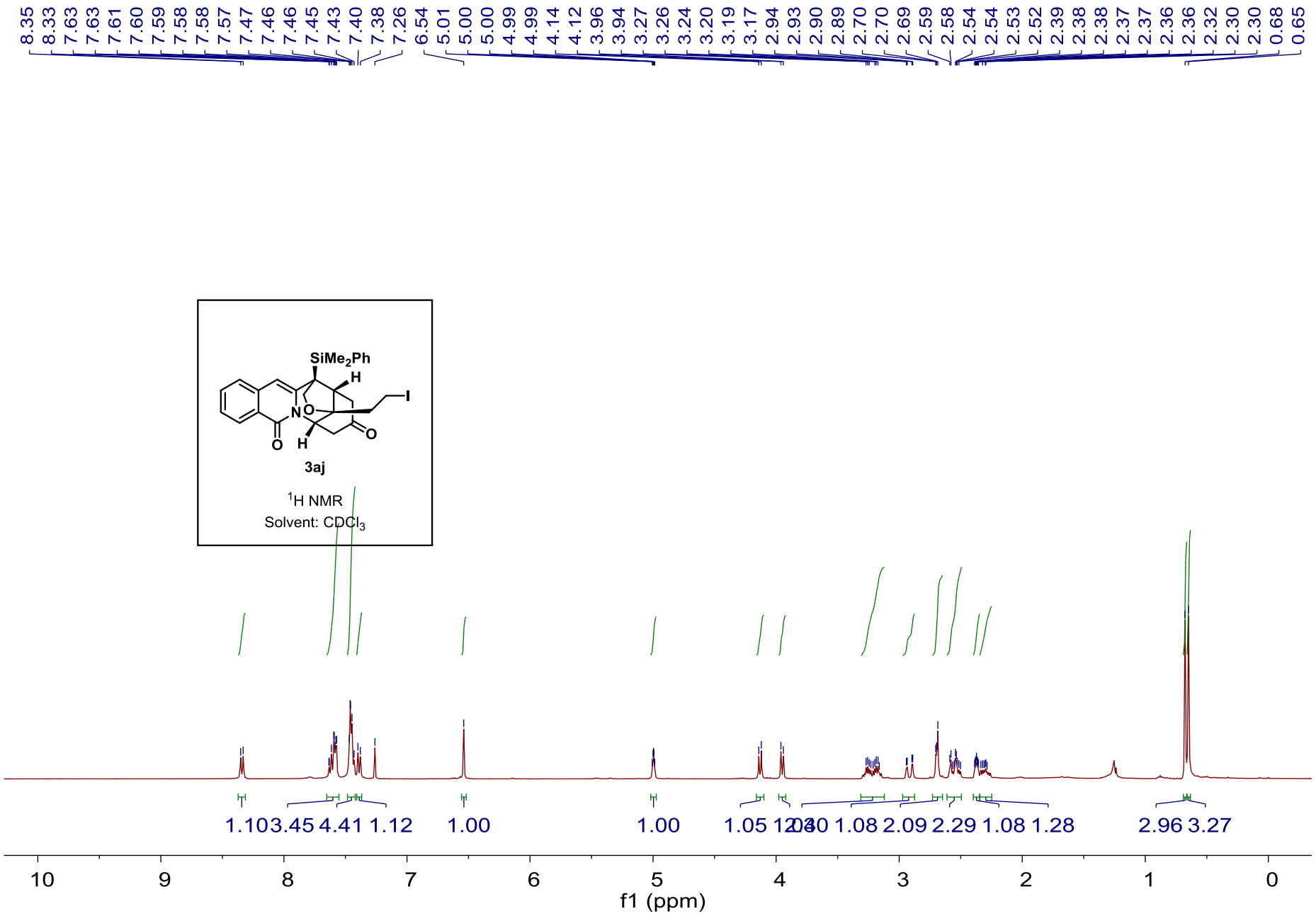
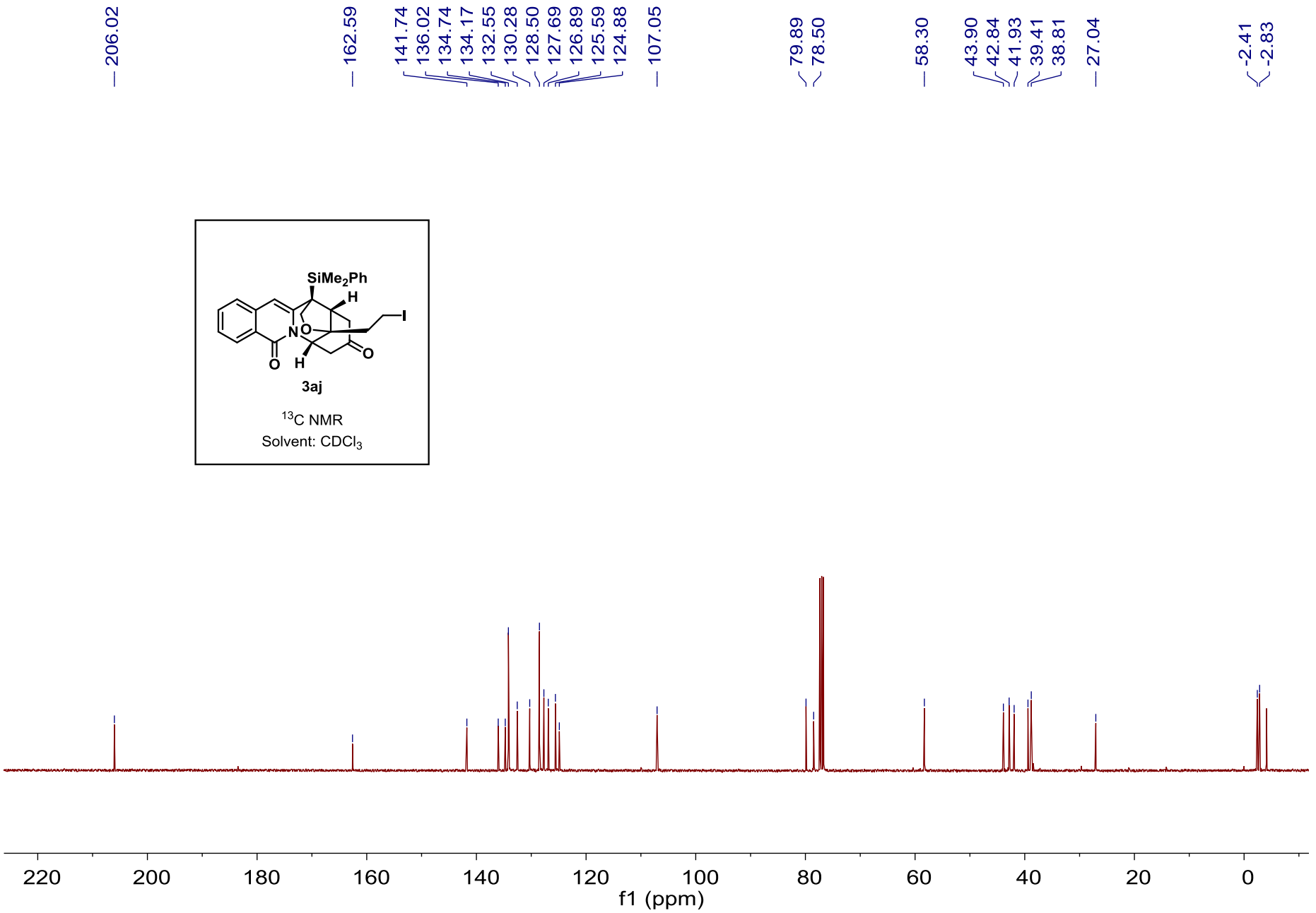
106.98
78.91
78.61
58.81
43.85
42.95
41.99
38.81
37.66
25.86
-2.44
-2.87
SiMe2Ph
H
Br
N
O
O
O
H
3ai
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.35 8.33 7.63 7.63 7.61 7.60 7.59 7.58 7.58 7.57 7.47 7.46 7.46 7.45 7.43 7.40 7.38 7.26 6.54 5.01 5.00 5.00 4.99 4.99 4.14 4.12 3.96 3.94 3.27 3.26 3.24 3.20 3.19 3.17 2.94 2.93 2.90 2.89 2.70 2.70 2.69 2.59 2.58 2.54 2.54 2.53 2.52 2.39 2.38 2.38 2.37 2.37 2.36 2.36 2.32 2.30 2.30 0.68 0.65
SiMe2Ph
H
N
O
I
O
O
H
3aj
1H NMR
Solvent: CDCl3
1.10 3.45 4.41 1.12 1.00 1.00 1.05 1.24 2.40 1.08 2.09 2.29 1.08 1.28 2.96 3.27
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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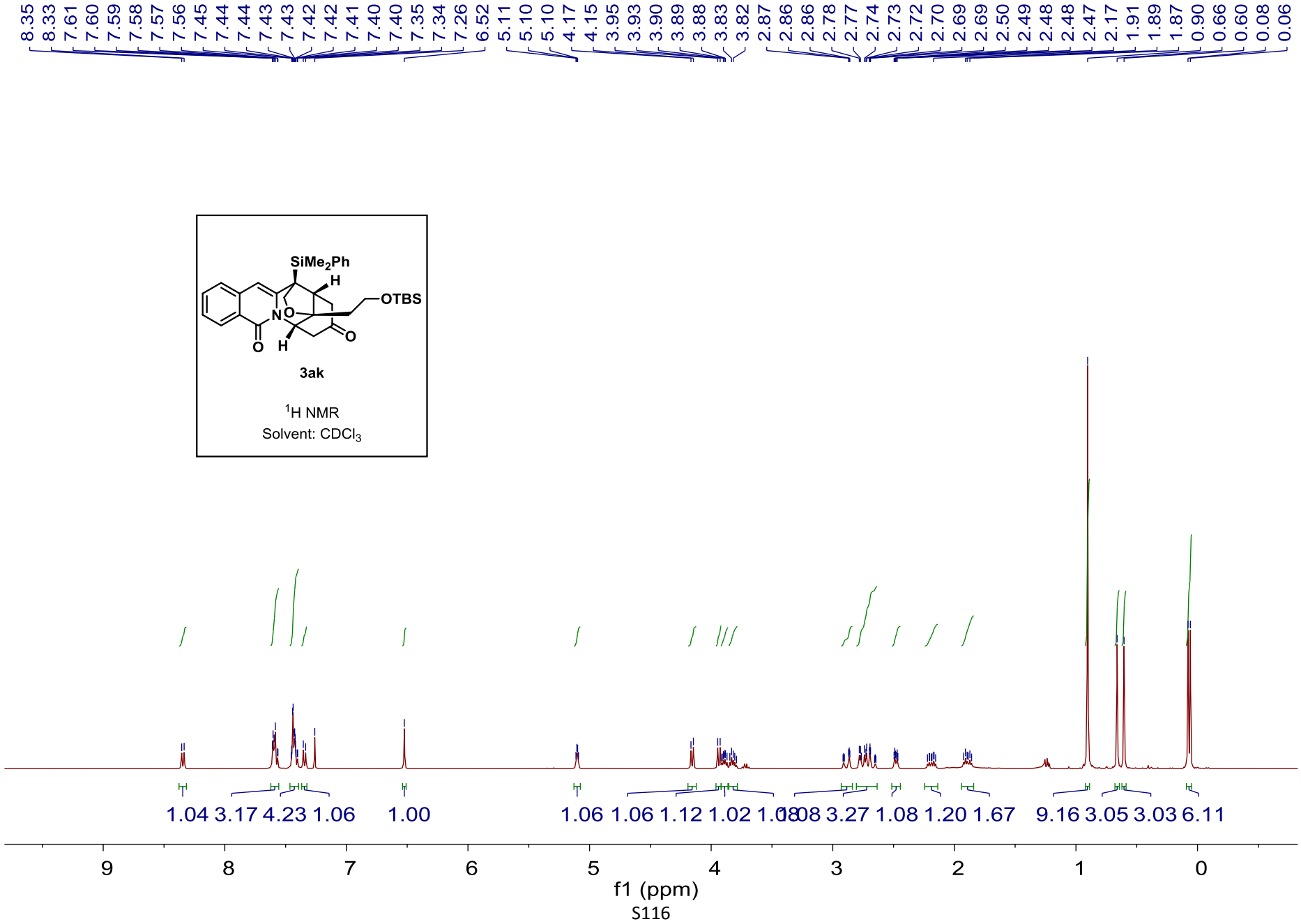
124.88
107.05
79.89
78.50
58.30
43.90
42.84
41.93
39.41
38.81
27.04
-2.41
-2.83
SiMe2Ph
H
N
O
I
O
O
H
3aj
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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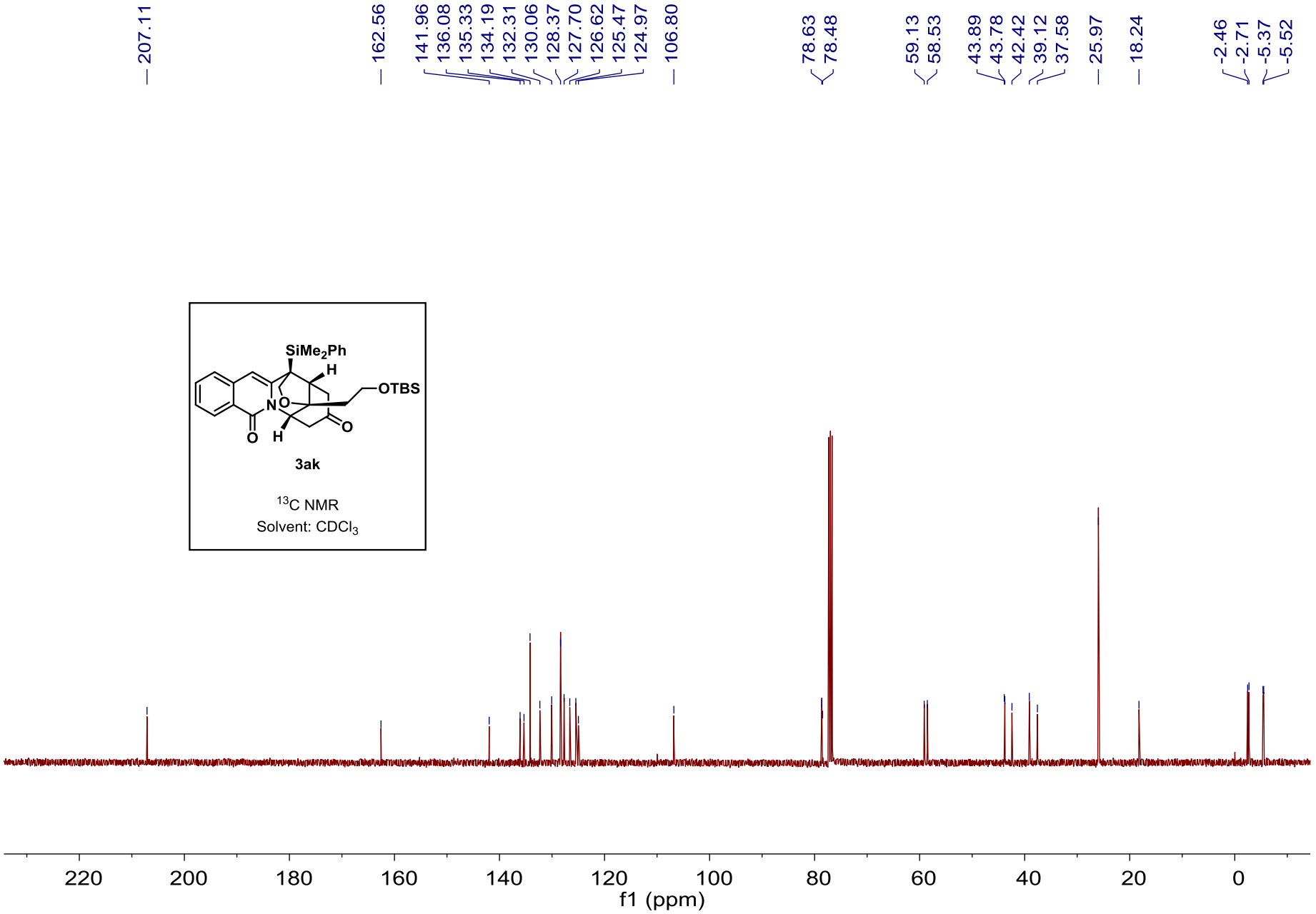
5.11 5.10 5.10 4.17 4.15 3.95 3.93 3.90 3.89 3.88 3.83 3.82
2.87 2.86 2.86 2.78 2.77 2.74 2.73 2.72 2.70 2.69 2.69 2.50 2.49 2.48 2.48 2.47 2.17 1.91 1.89 1.87 0.90 0.66 0.60 0.08 0.06
SiMe2Ph
H
OTBS
N
O
O
O
H
3ak
1H NMR
Solvent: CDCl3
1.04 3.17 4.23 1.06 1.00 1.06 1.06 1.12 1.02 1.08 3.27 1.08 1.20 1.67 9.16 3.05 3.03 6.11
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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130.06
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127.70
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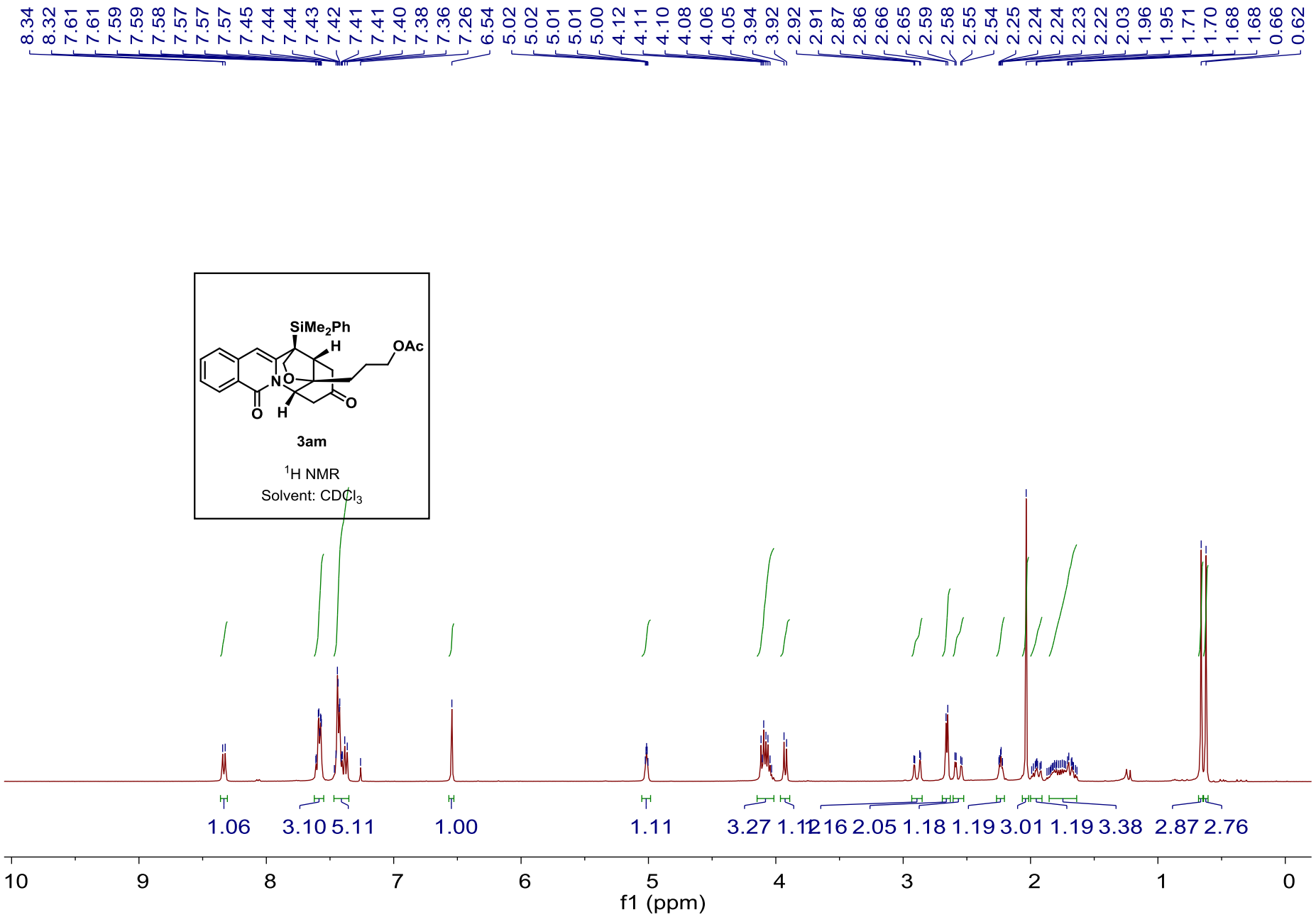
125.47
124.97
106.80
78.63
78.48
59.13
58.53
43.89
43.78
42.42
39.12
37.58
25.97
18.24
-2.46
-2.71
-5.37
-5.52
SiMe2Ph
H
OTBS
N
O
O
O
H
3ak
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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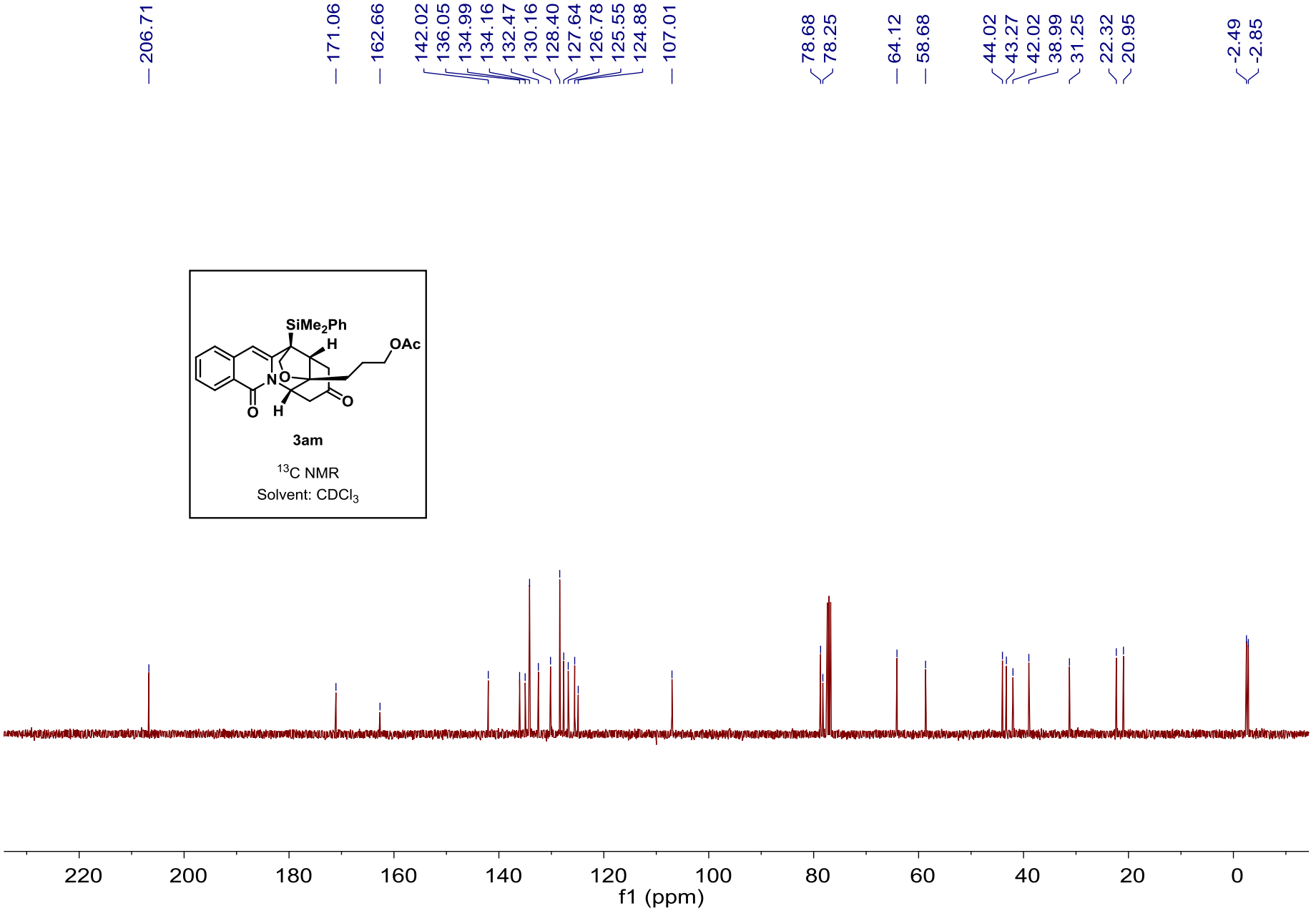
SiMe2Ph
H
OAc
N
O
O
O
H
3am
1H NMR
Solvent: CDCl3
1.06 3.10 5.11 1.00 1.11 3.27 1.12 2.16 2.05 1.18 1.19 3.01 1.19 3.38 2.87 2.76
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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171.06
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142.02
136.05
134.99
134.16
132.47
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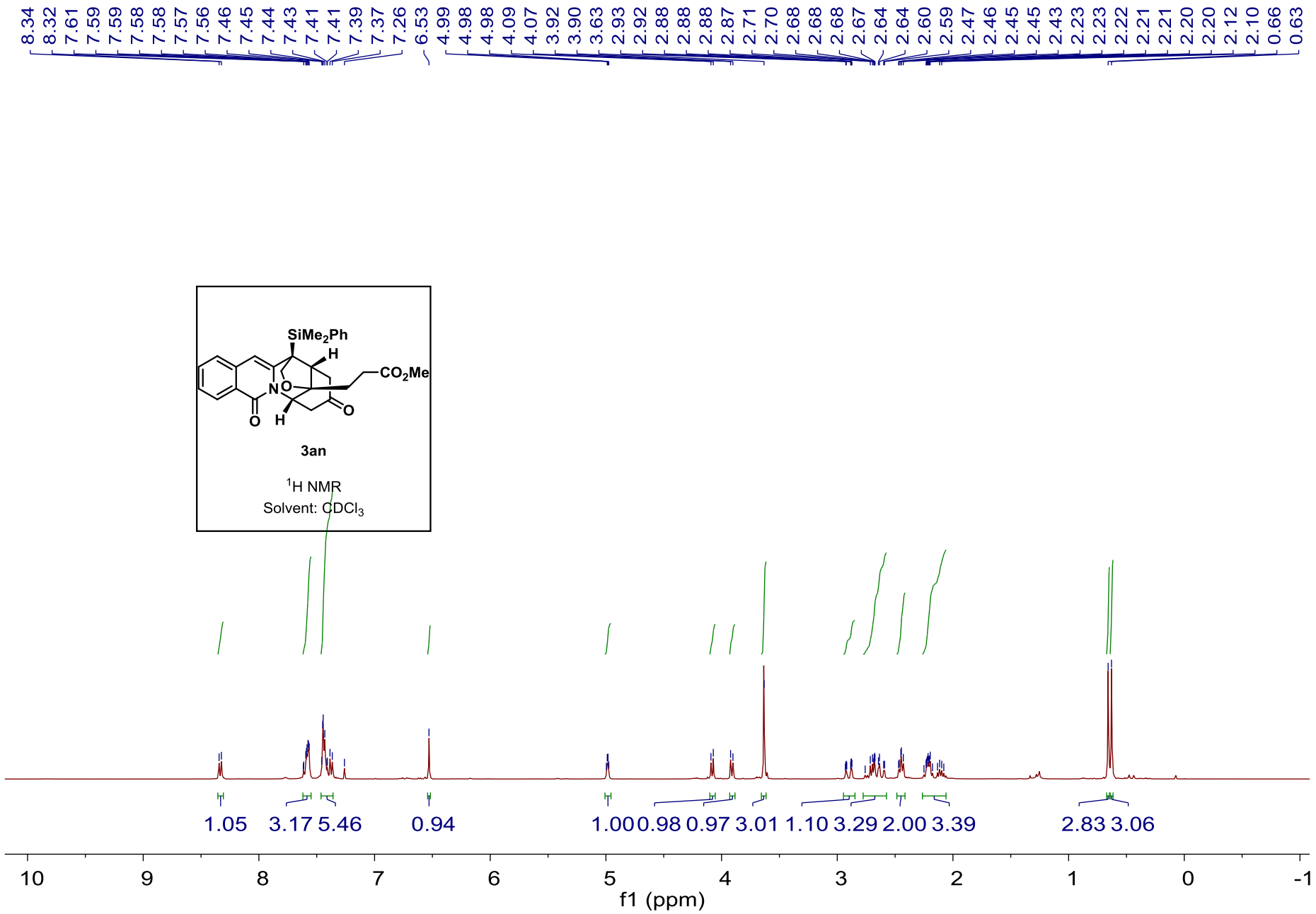
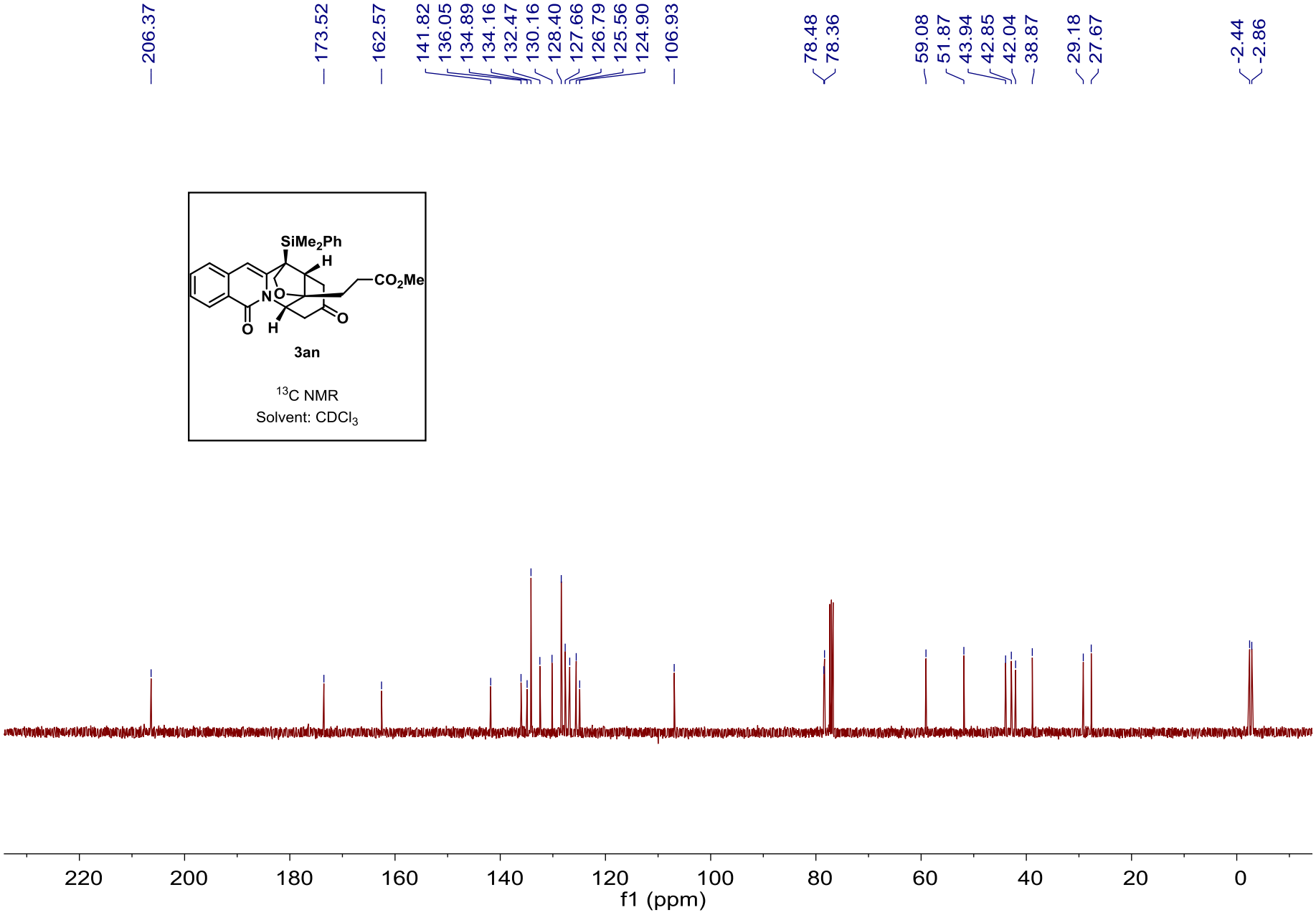
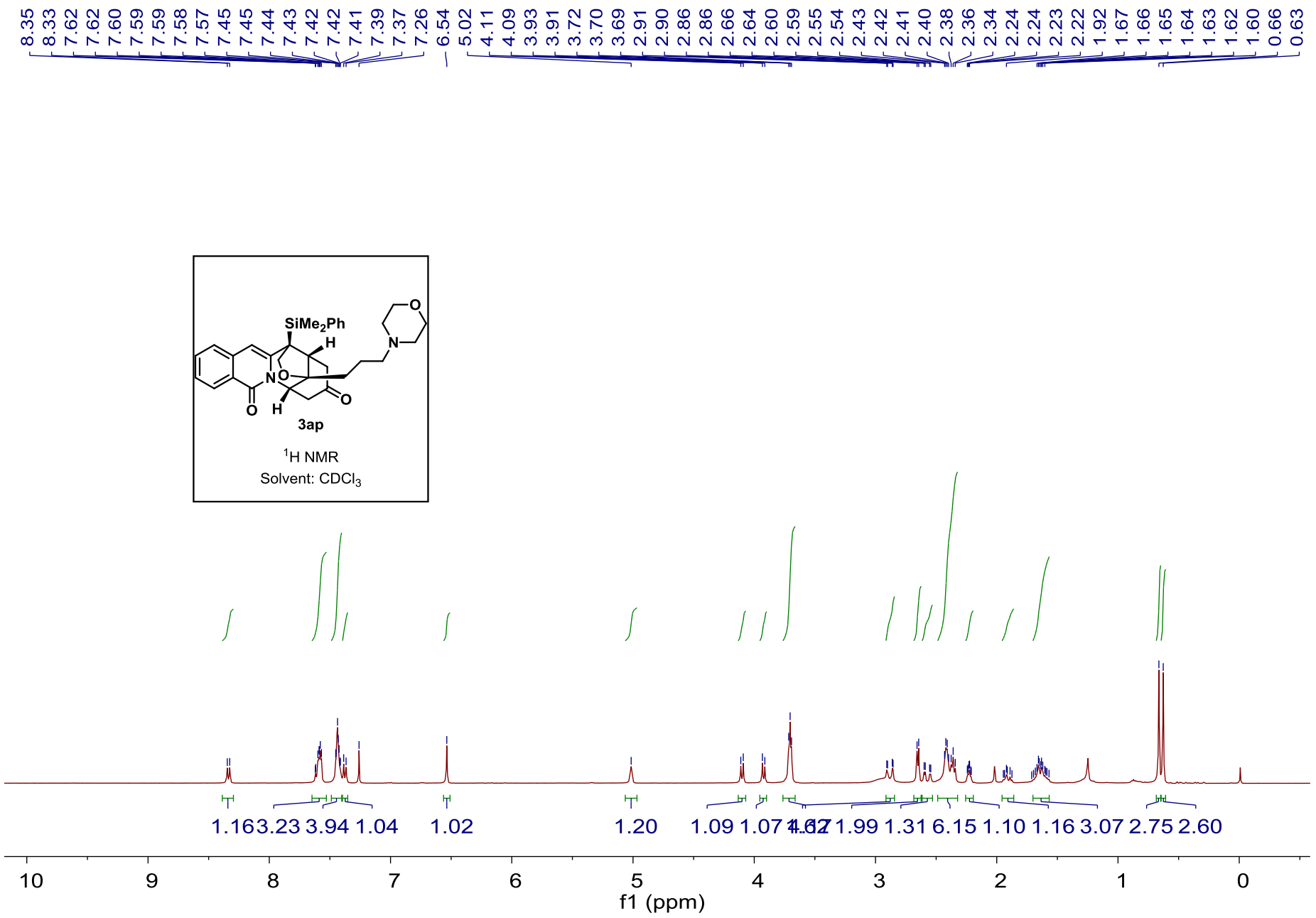
128.40
127.64
126.78
125.55
124.88
107.01
78.68
78.25
64.12
58.68
44.02
43.27
42.02
38.99
31.25
22.32
20.95
-2.49
-2.85
SiMe2Ph
H
OAc
N
O
O
O
H
3am
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.34 8.32 7.61 7.59 7.59 7.58 7.58 7.57 7.56 7.46 7.45 7.44 7.43 7.41 7.41 7.39 7.37 7.26 6.53 4.99 4.98 4.98 4.09 4.07 3.92 3.90 3.63 2.93 2.92 2.88 2.88 2.88 2.87 2.71 2.70 2.68 2.68 2.68 2.67 2.64 2.64 2.60 2.59 2.47 2.46 2.45 2.45 2.43 2.23 2.23 2.22 2.21 2.21 2.20 2.20 2.12 2.10 0.66 0.63
SiMe2Ph
H
CO2Me
N
O
O
O
H
3an
1H NMR
Solvent: CDCl3
1.05 3.17 5.46 0.94 1.00 0.98 0.97 3.01 1.10 3.29 2.00 3.39 2.83 3.06
10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


206.37
173.52
162.57
141.82
136.05
134.89
134.16
132.47
130.16
128.40
127.66
126.79
125.56
124.90
106.93
78.48
78.36
59.08
51.87
43.94
42.85
42.04
38.87
29.18
27.67
-2.44
-2.86
SiMe2Ph
H
CO2Me
N
O
O
H
O
3an
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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SiMe2Ph
H
N
O
N
O
O
H
O
3ap
1H NMR
Solvent: CDCl3
1.16 3.23 3.94 1.04 1.02 1.20 1.09 1.07 1.99 1.31 6.15 1.10 1.16 3.07 2.75 2.60
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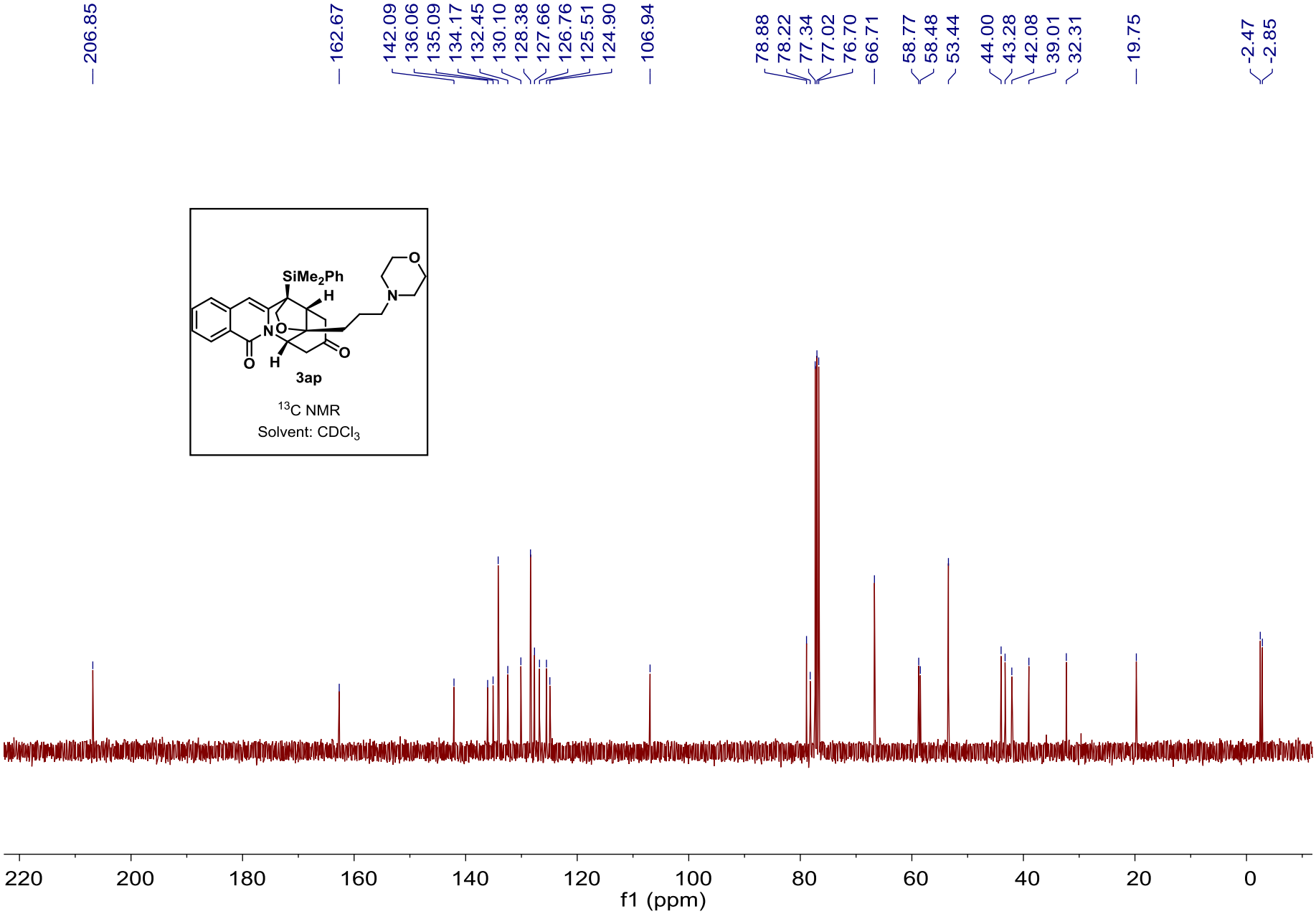
f1 (ppm)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78.88
78.22
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77.02
76.70
66.71
58.77
58.48
53.44
44.00
43.28
42.08
39.01
32.31
19.75
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SiMe2Ph
H
N
O
O
O
H
O
3ap
13C NMR
Solvent: CDCl3
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20
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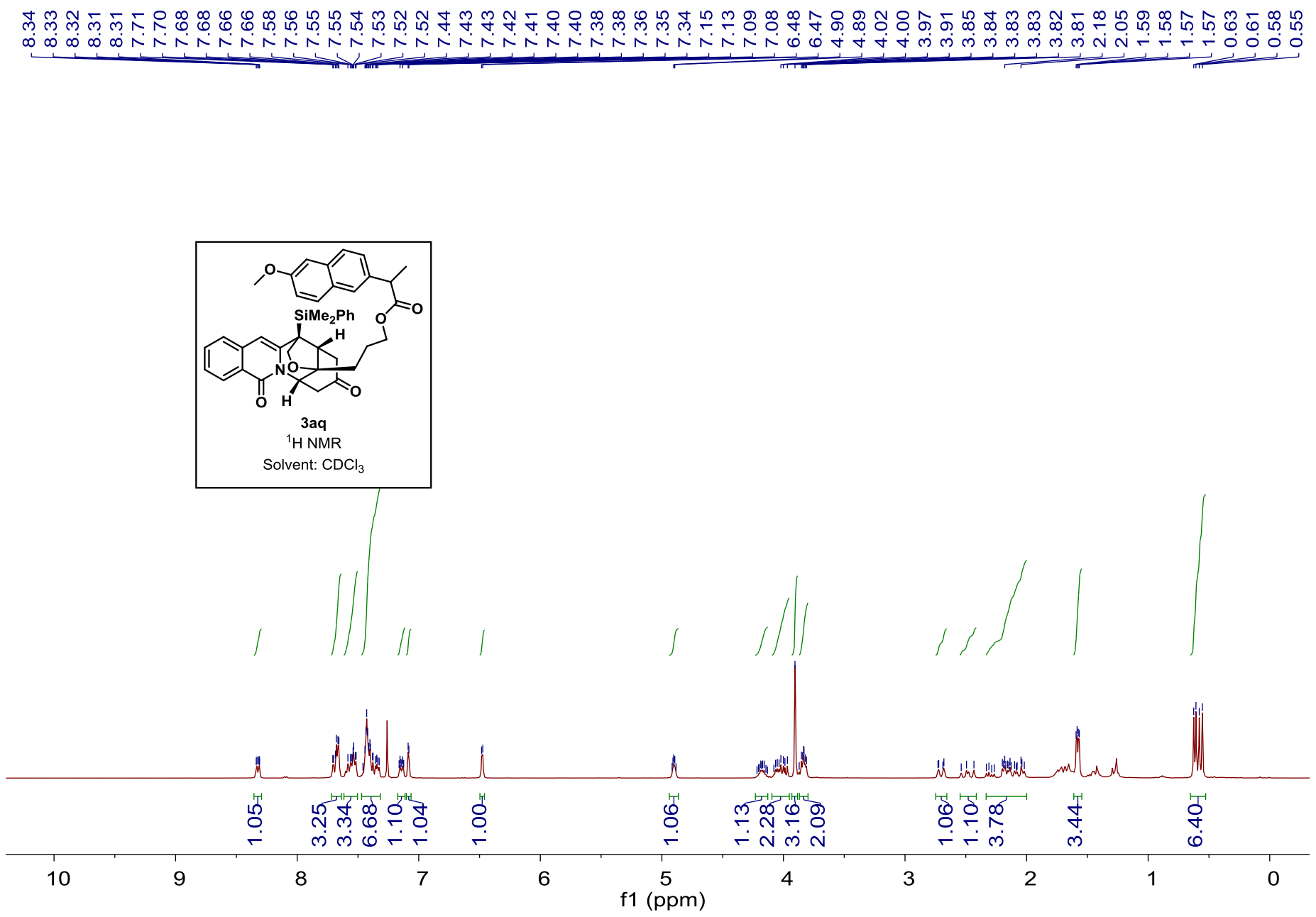
f1 (ppm)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SiMe2Ph
H
N
O
O
O
O
O
O
H
3aq
1H NMR
Solvent: CDCl3
1.05 3.25 3.34 6.68 1.10 1.04 1.00 1.06 1.13 2.28 3.16 2.09 1.06 1.10 3.78 3.44 6.40
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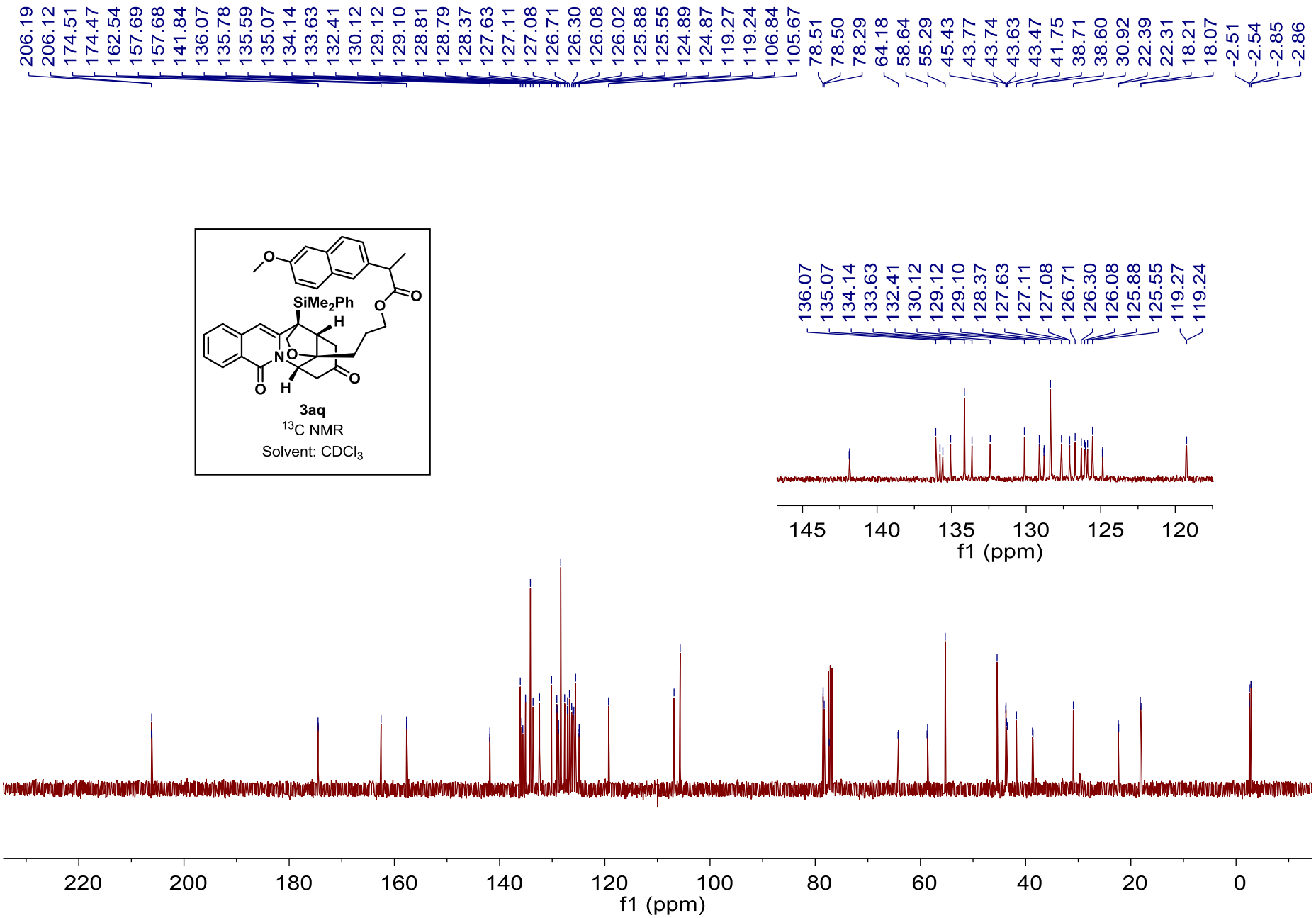
f1 (ppm)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130.12
129.12
129.10
128.81
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127.11
127.08
126.71
126.30
126.08
126.02
125.88
125.55
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124.87
119.27
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106.84
105.67
78.51
78.50
78.29
64.18
58.64
55.29
45.43
43.77
43.74
43.63
43.47
41.75
38.71
38.60
30.92
22.39
22.31
18.21
18.07
-2.51
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N
O
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O
O
H
3aq
13C NMR
Solvent: CDCl3
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126.08
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119.24
145
140
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100
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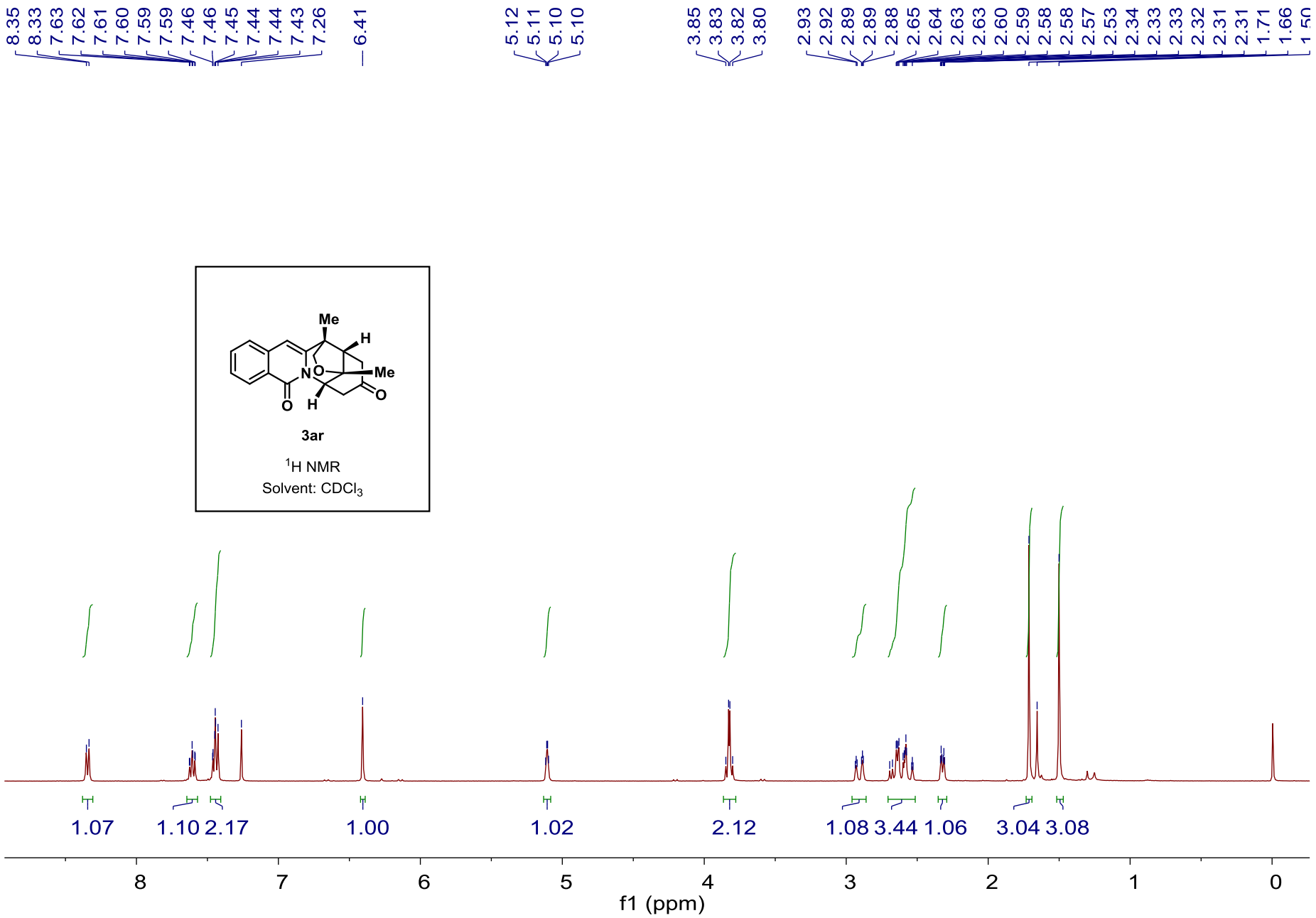
f1 (ppm)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7.44
7.43
7.26
6.41
5.12
5.11
5.10
5.10
3.85
3.83
3.82
3.80
2.93
2.92
2.89
2.89
2.88
2.65
2.64
2.63
2.63
2.60
2.59
2.58
2.58
2.57
2.53
2.34
2.33
2.33
2.32
2.31
2.31
1.71
1.66
Me
H
N
O
Me
O
O
H
3ar
1H NMR
Solvent: CDCl3
1.07
1.10
2.17
1.00
1.02
2.12
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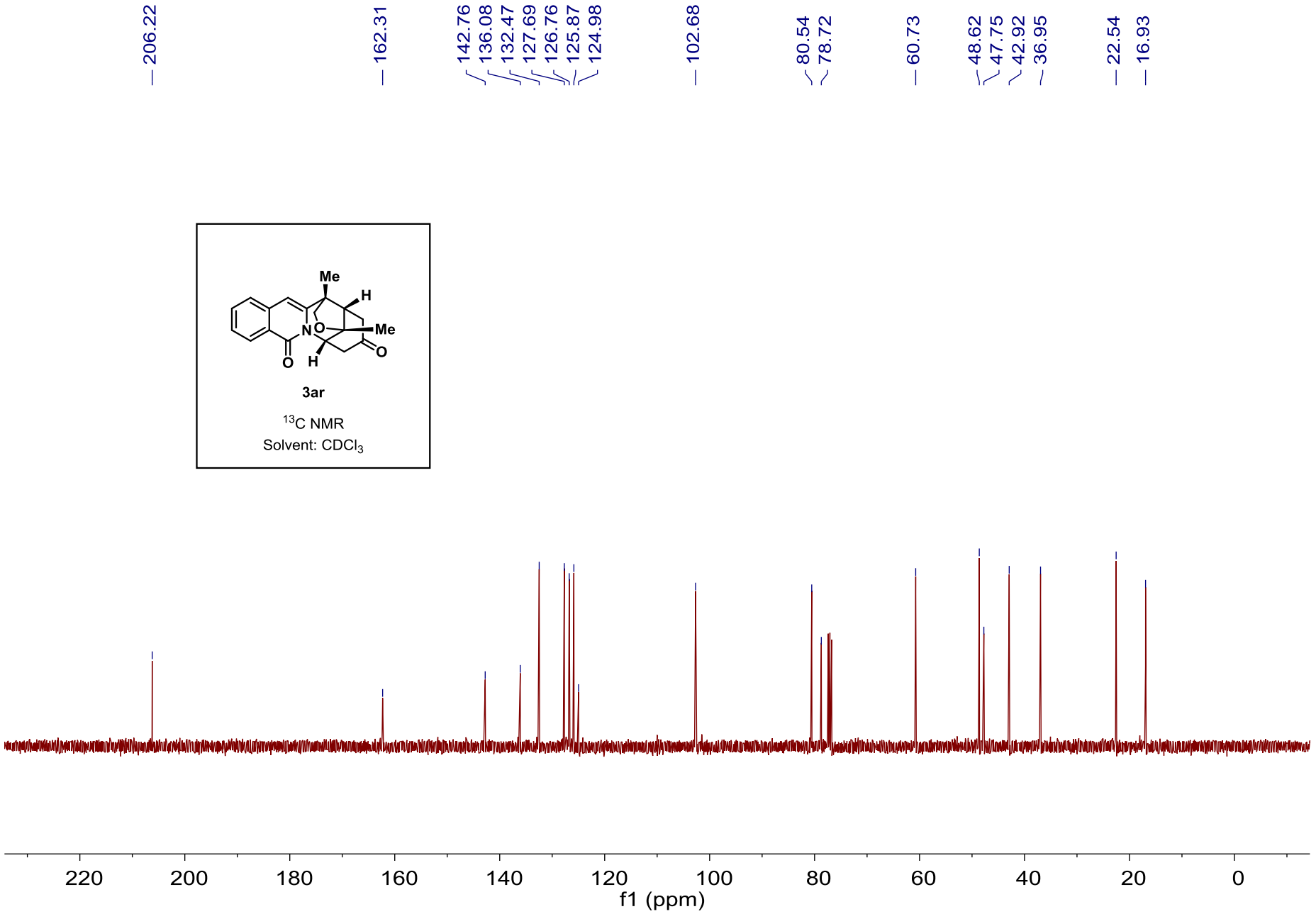
1.06
3.04
3.08
8
7
6
5
4
3
2
1
0
f1 (ppm)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60.73
48.62
47.75
42.92
36.95
22.54
16.93
Me
H
N
O
Me
O
O
H
3ar
13C NMR
Solvent: CDCl3
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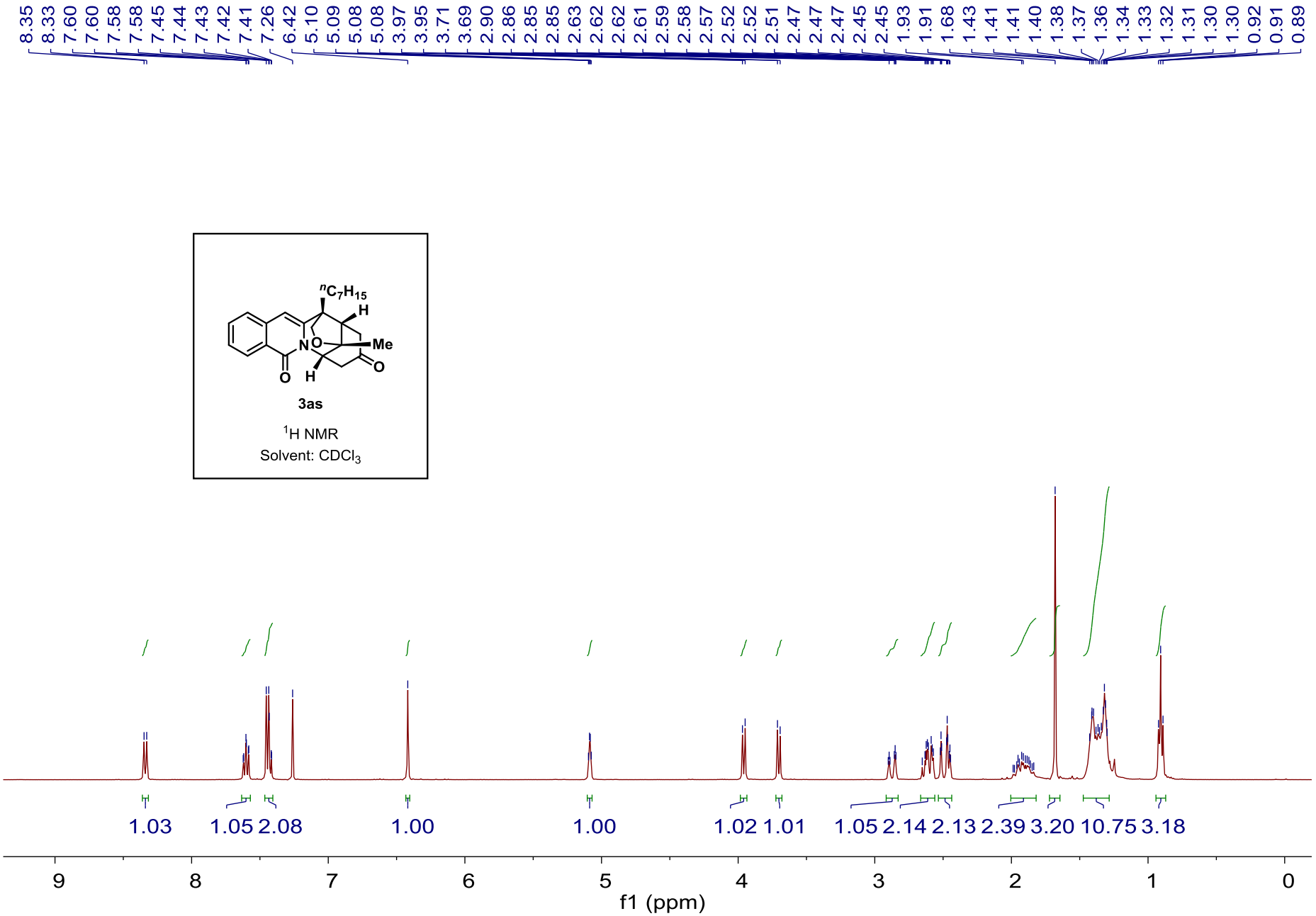
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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nC7H15
H
N
O
Me
O
O
H
3as
1H NMR
Solvent: CDCl3
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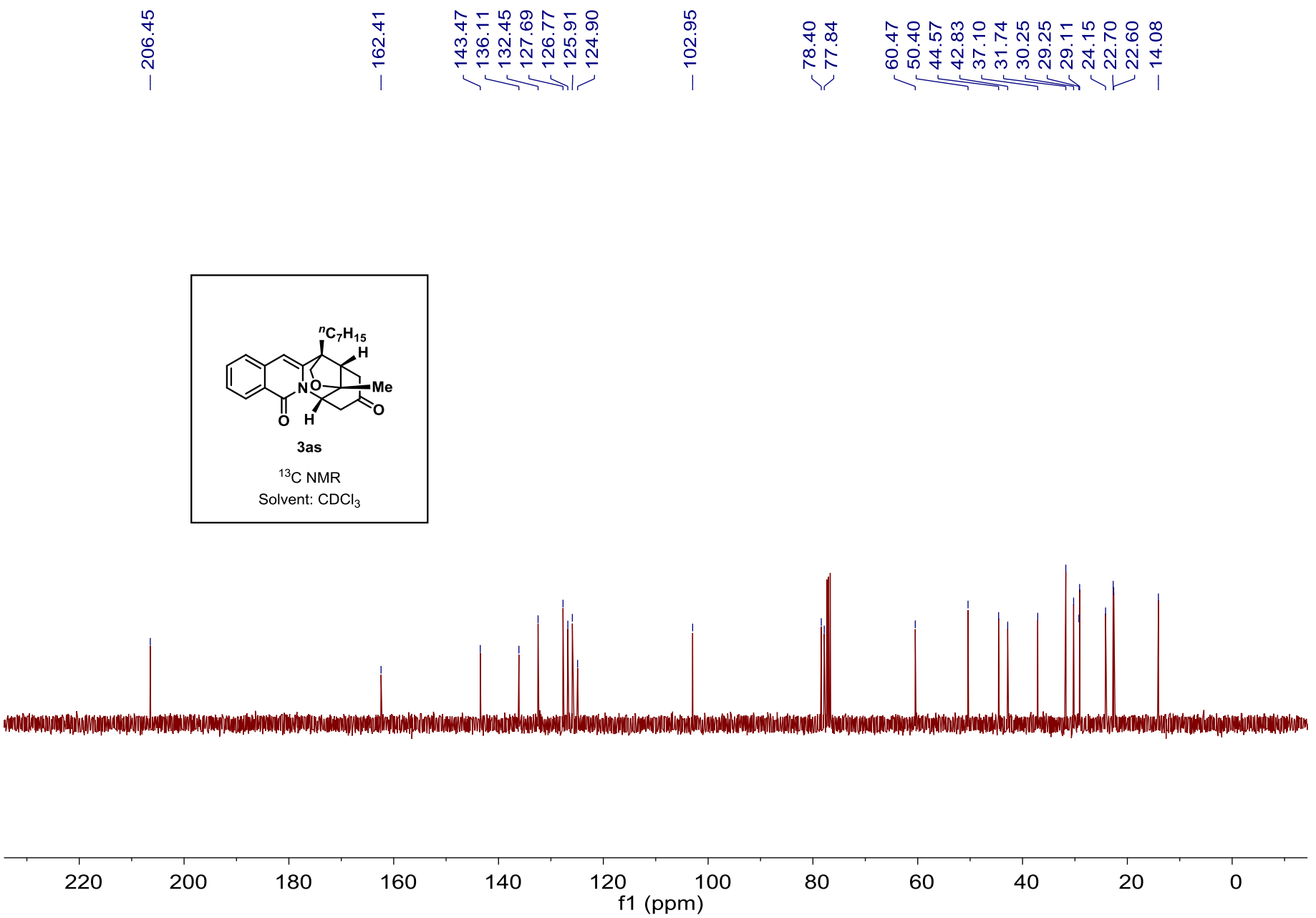
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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60.47
50.40
44.57
42.83
37.10
31.74
30.25
29.25
29.11
24.15
22.70
22.60
14.08
nC7H15
H
N
O
Me
O
O
H
3as
13C NMR
Solvent: CDCl3
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200
180
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140
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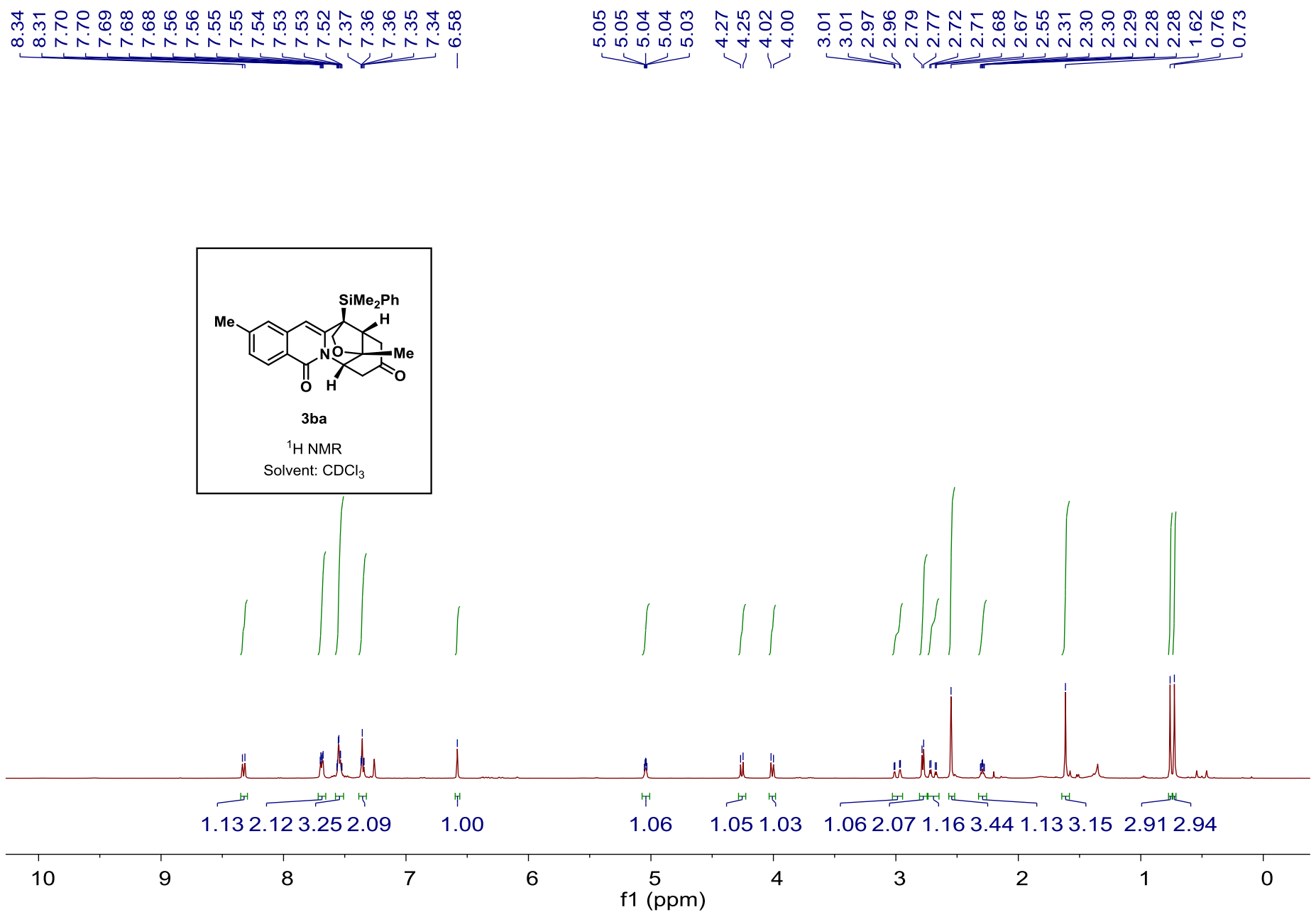
100
80
60
40
20
0
f1 (ppm)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7.52
7.37
7.36
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7.35
7.34
6.58
5.05
5.05
5.04
5.04
5.03
4.27
4.25
4.02
4.00
3.01
3.01
2.97
2.96
2.79
2.77
2.72
2.71
2.68
2.67
2.55
2.31
2.30
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2.29
2.28
2.28
1.62
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0.73
SiMe2Ph
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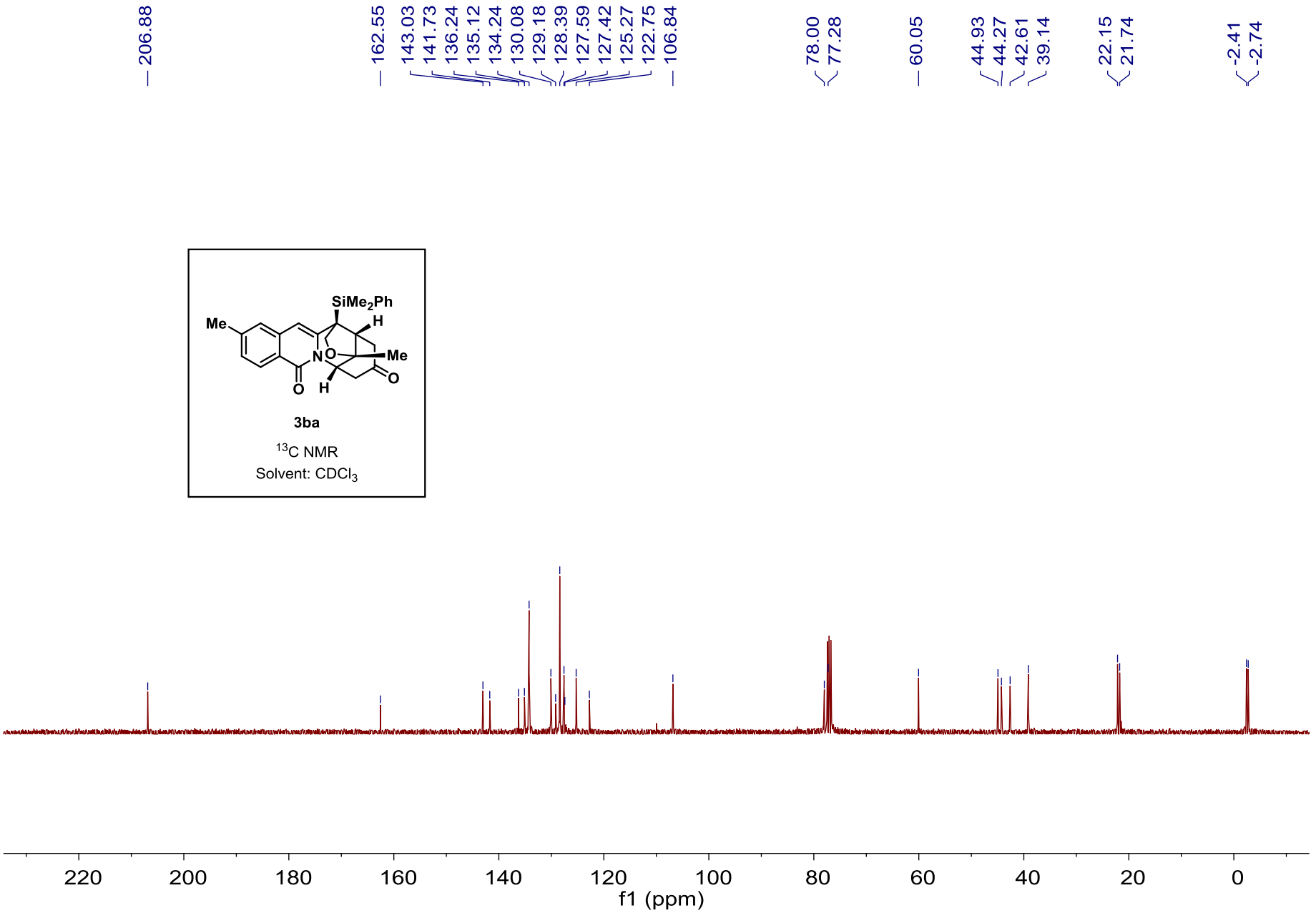
Me
N
O
Me
O
O
H
3ba
1H NMR
Solvent: CDCl3
1.13 2.12 3.25 2.09
1.00
1.06
1.05 1.03
1.06 2.07 1.16 3.44 1.13 3.15
2.91 2.94
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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78.00
77.28
60.05
44.93
44.27
42.61
39.14
22.15
21.74
-2.41
-2.74
SiMe2Ph
H
Me
N
O
Me
O
O
H
3ba
13C NMR
Solvent: CDCl3
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180
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140
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100
80
60
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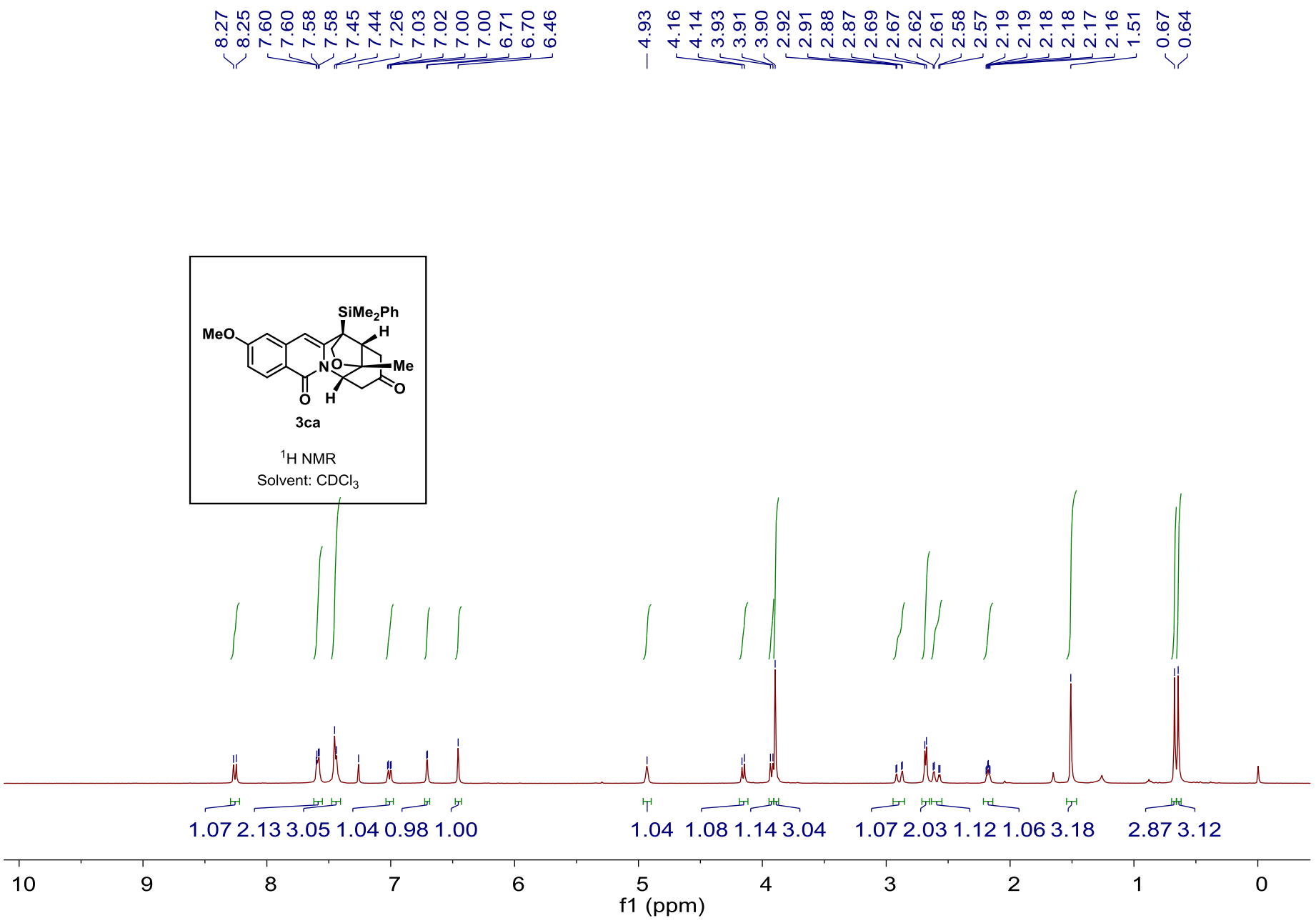
20
0
f1 (ppm)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7.03
7.02
7.00
7.00
6.71
6.70
6.46
4.93
4.16
4.14
3.93
3.91
3.90
2.92
2.91
2.88
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2.57
2.19
2.19
2.18
2.18
2.17
2.16
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0.64
SiMe2Ph
MeO
H
N
O
Me
O
O
H
3ca
1H NMR
Solvent: CDCl3
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1.04 1.08 1.14 3.04
1.07 2.03 1.12 1.06 3.18
2.87 3.12
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9
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7
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5
4
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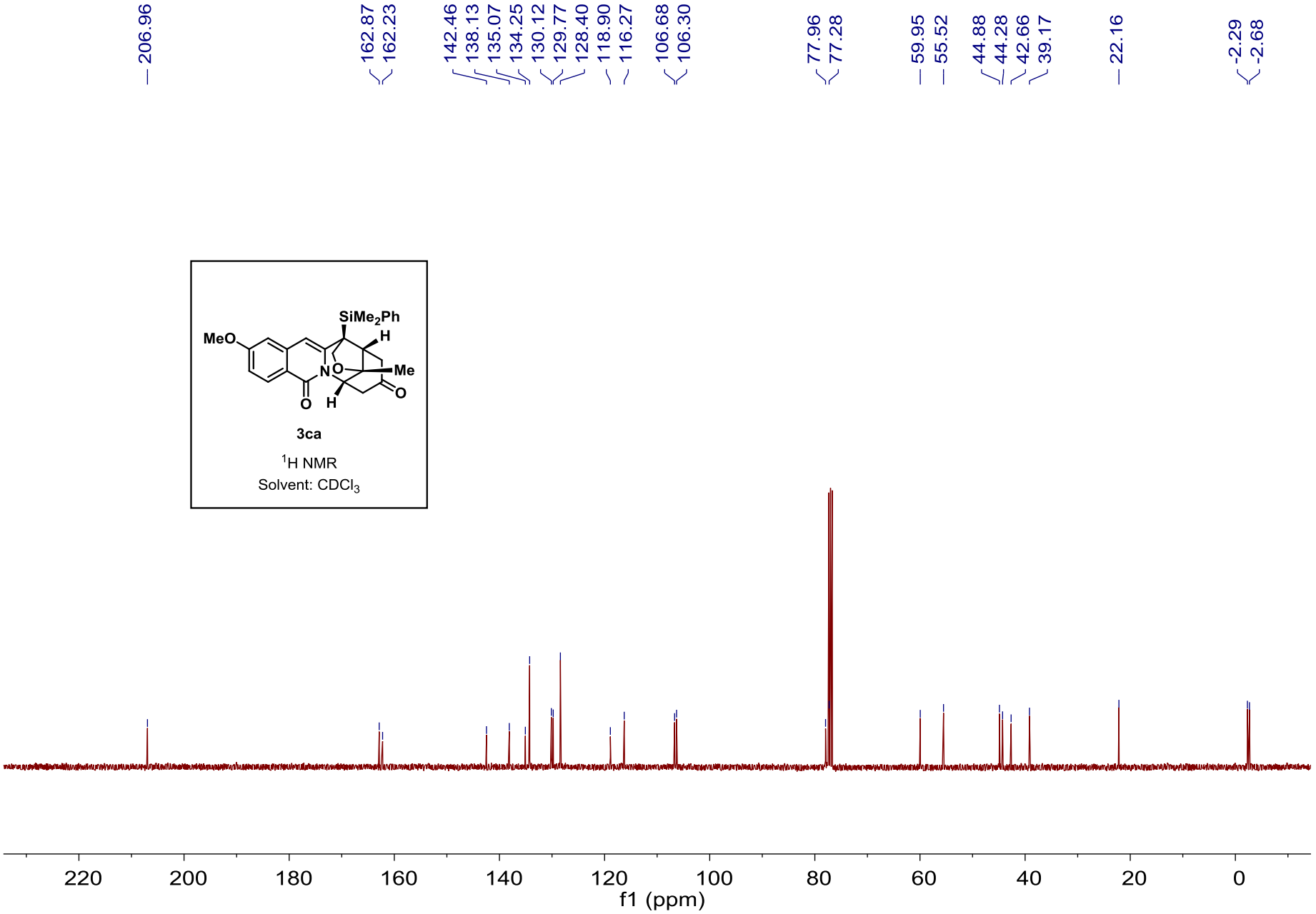
2
1
0
f1 (ppm)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106.30
77.96
77.28
59.95
55.52
44.88
44.28
42.66
39.17
22.16
-2.29
-2.68
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O
Me
O
O
H
3ca
1H NMR
Solvent: CDCl3
220
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180
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140
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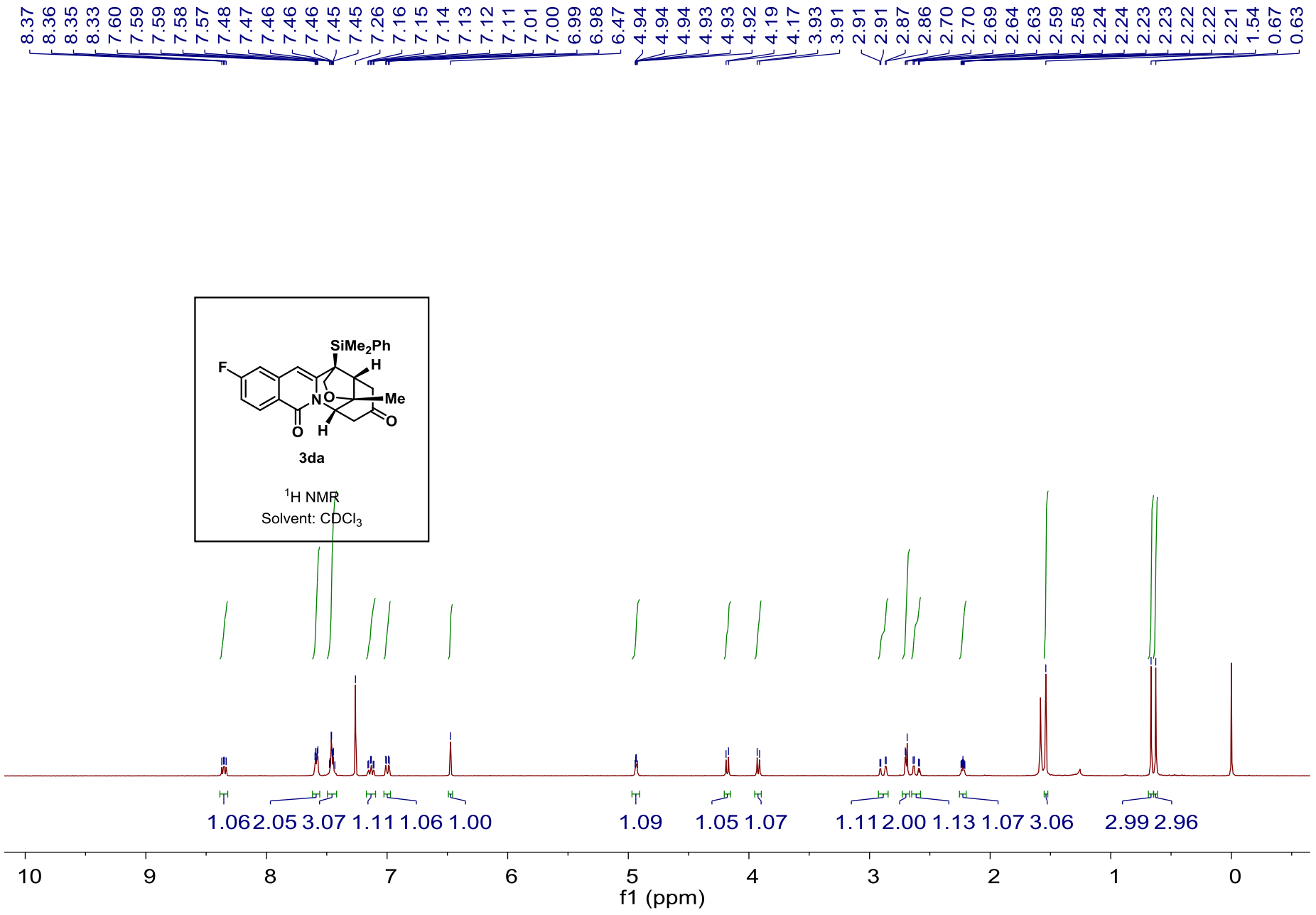
100
80
60
40
20
0
f1 (ppm)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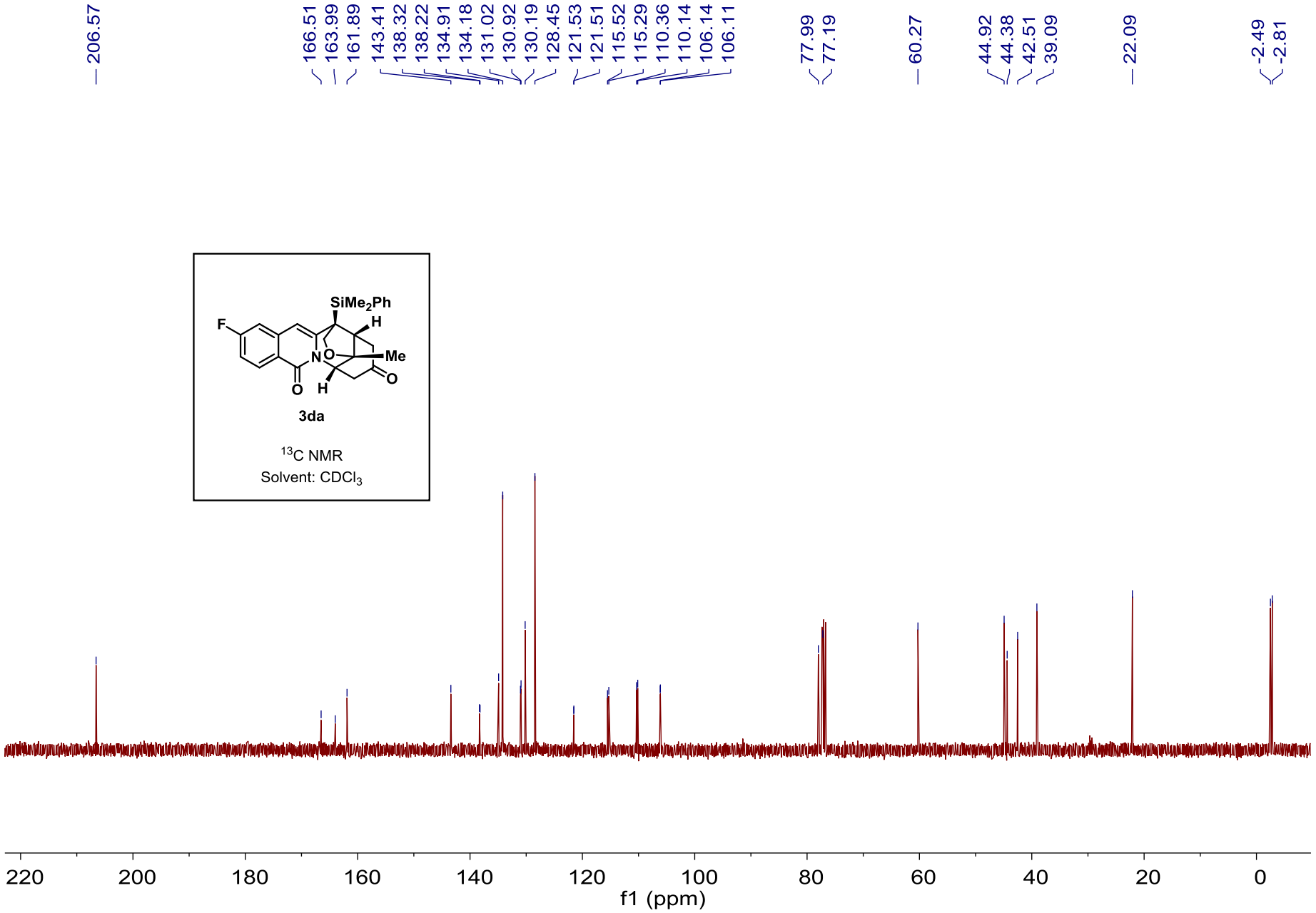
SiMe2Ph
F
H
N
O
Me
O
O
H
3da
1H NMR
Solvent: CDCl3
1.06 2.05 3.07 1.11 1.06 1.00 1.09 1.05 1.07 1.11 2.00 1.13 1.07 3.06 2.99 2.96
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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121.53
121.51
115.52
115.29
110.36
110.14
106.14
106.11
77.99
77.19
60.27
44.92
44.38
42.51
39.09
22.09
-2.49
-2.81
SiMe2Ph
F
H
N
O
Me
O
O
H
3da
13C NMR
Solvent: CDCl3
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180
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140
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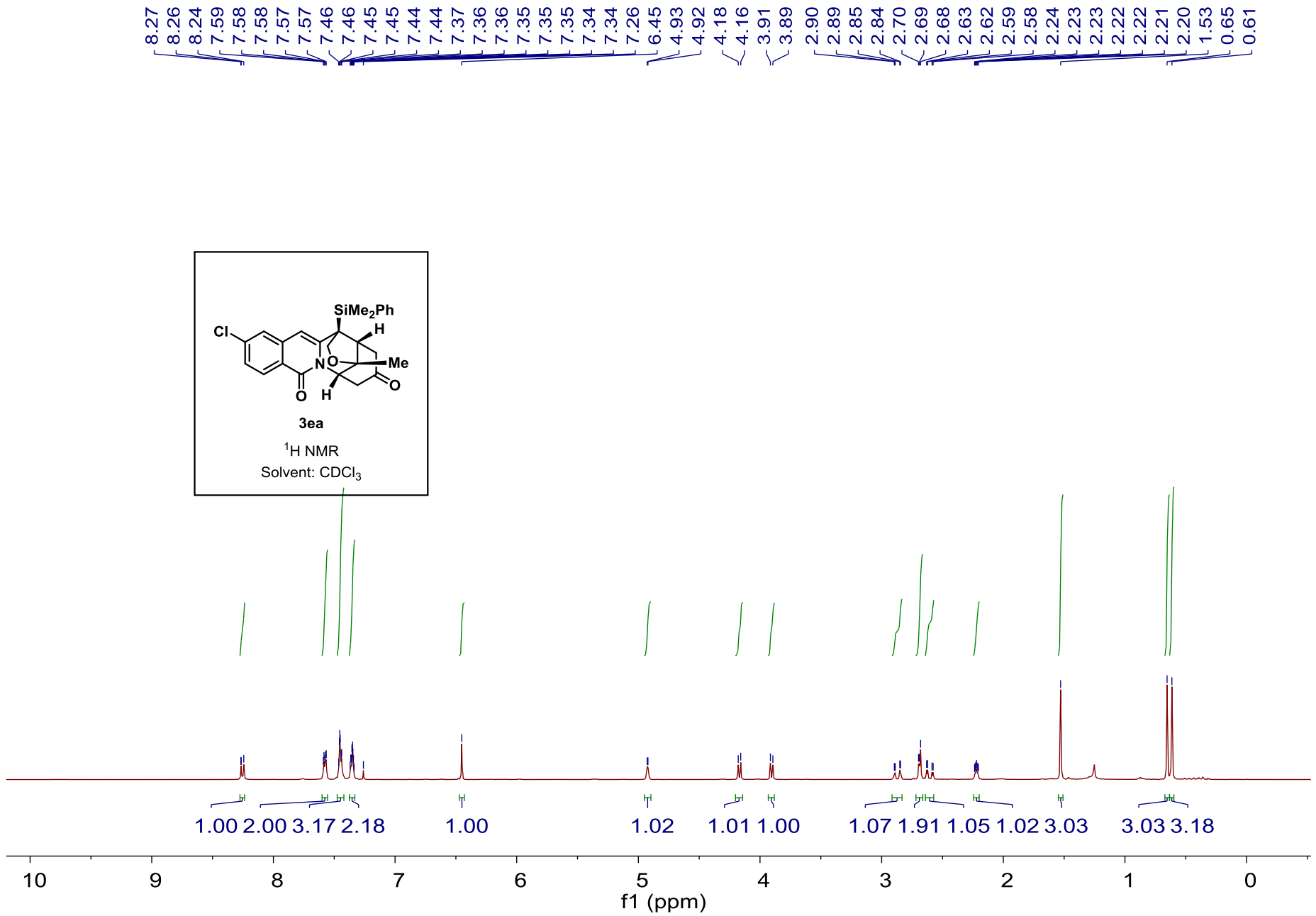
100
80
60
40
20
0
f1 (ppm)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SiMe2Ph
Cl
H
N
O
Me
O
O
H
3ea
1H NMR
Solvent: CDCl3
1.00 2.00 3.17 2.18 1.00 1.02 1.01 1.00 1.07 1.91 1.05 1.02 3.03 3.03 3.18
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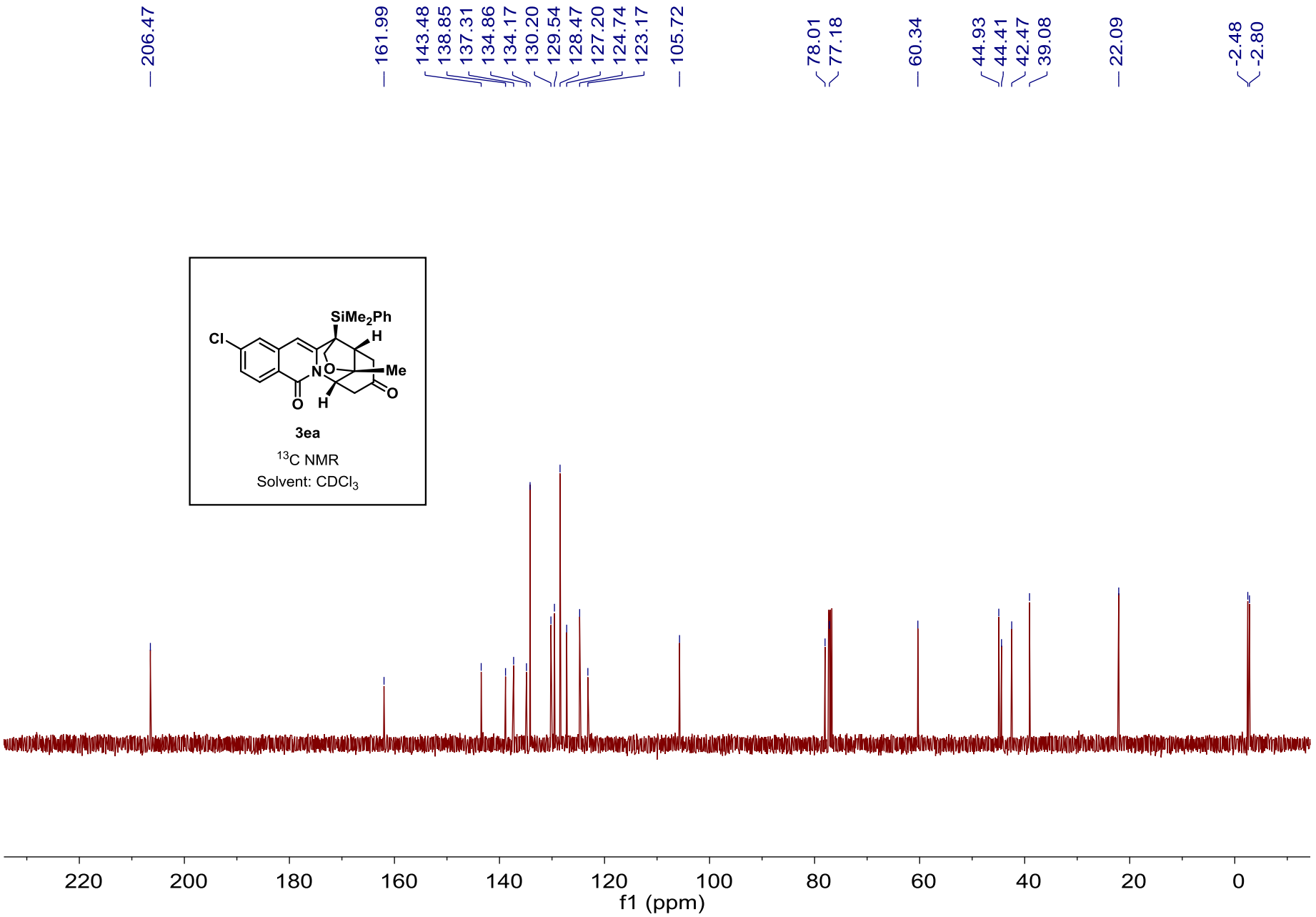
f1 (ppm)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123.17
105.72
78.01
77.18
60.34
44.93
44.41
42.47
39.08
22.09
-2.48
-2.80
SiMe2Ph
H
Cl
N
O
Me
O
O
H
3ea
13C NMR
Solvent: CDCl3
220
200
180
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140
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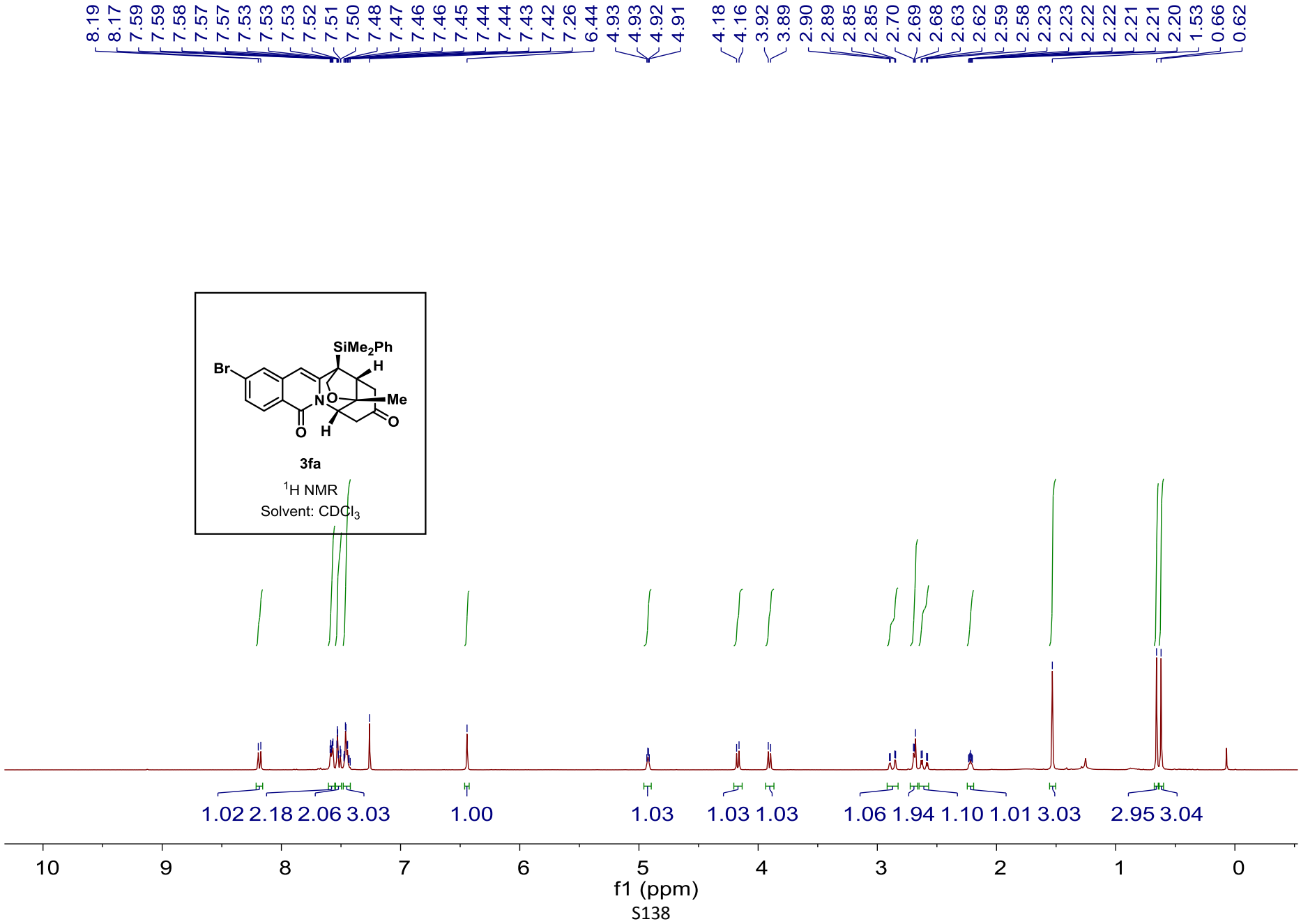
100
80
60
40
20
0
f1 (ppm)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SiMe2Ph
H
Br
N
O
Me
O
O
H
3fa
1H NMR
Solvent: CDCl3
1.02 2.18 2.06 3.03 1.00 1.03 1.03 1.03 1.06 1.94 1.10 1.01 3.03 2.95 3.04
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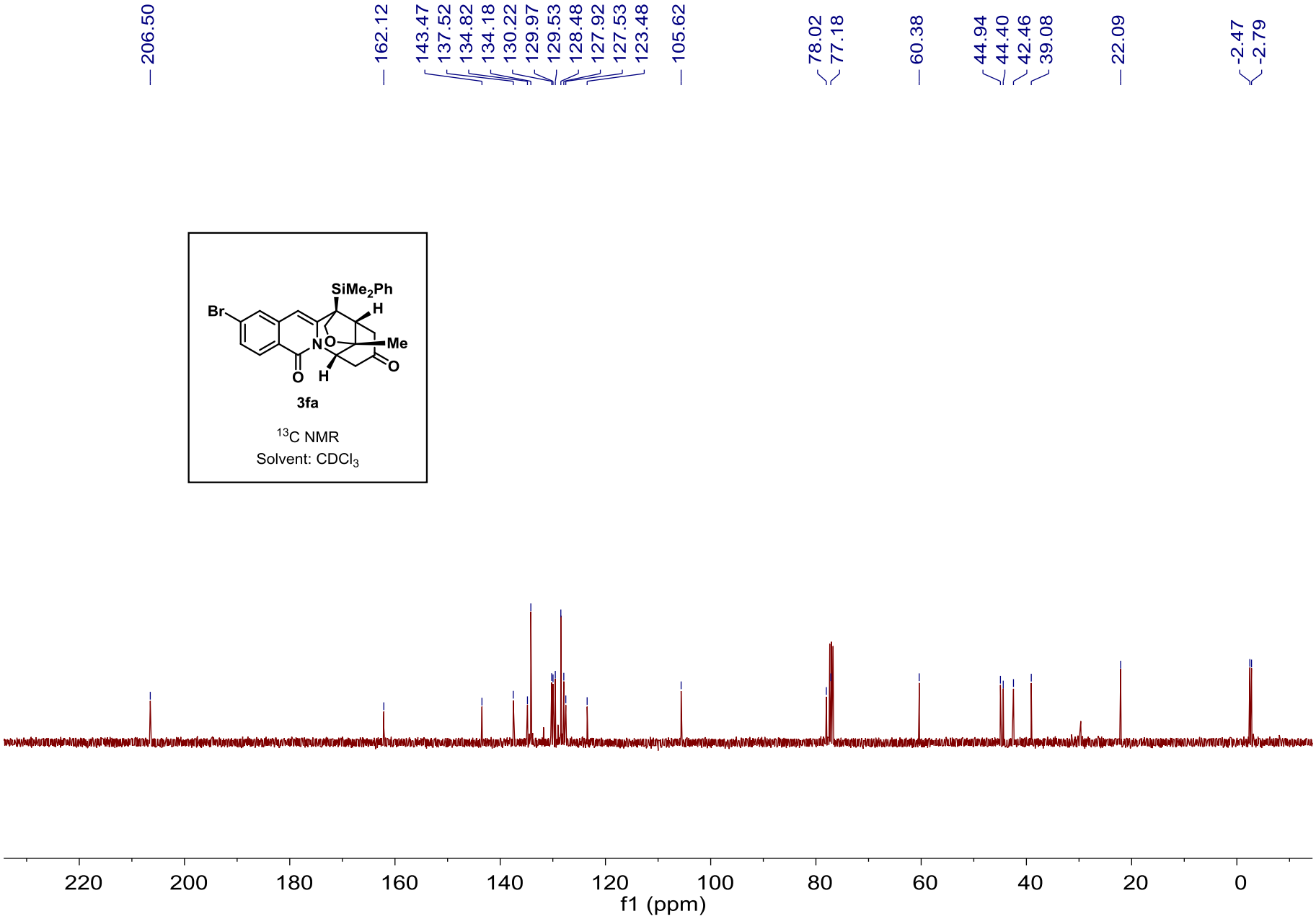
f1 (ppm)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127.53
123.48
105.62
78.02
77.18
60.38
44.94
44.40
42.46
39.08
22.09
-2.47
-2.79
SiMe2Ph
H
Br
N
O
Me
O
O
H
3fa
13C NMR
Solvent: CDCl3
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200
180
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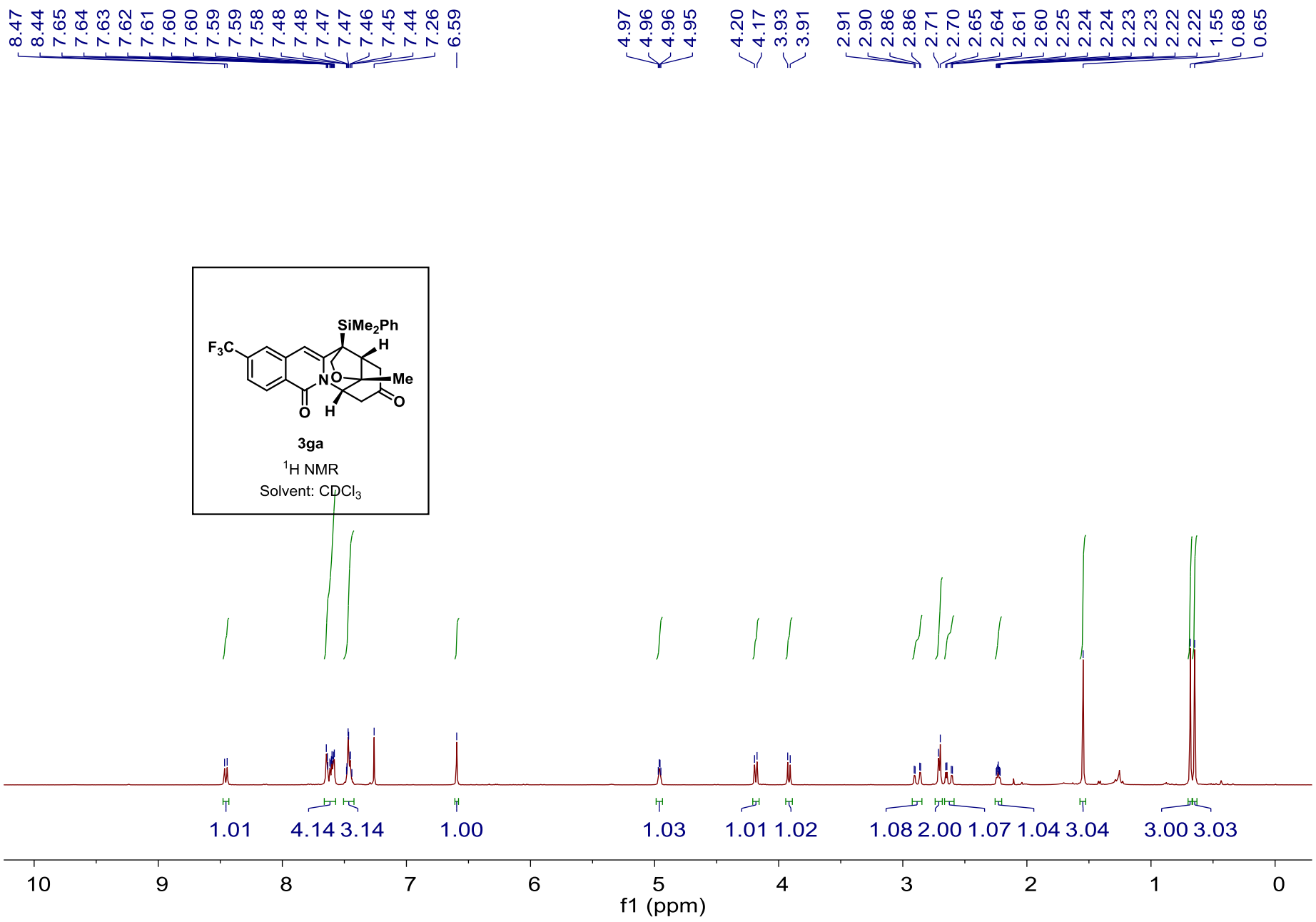
100
80
60
40
20
0
f1 (ppm)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7.48
7.47
7.47
7.46
7.45
7.44
7.26
6.59
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4.96
4.95
4.20
4.17
3.93
3.91
2.91
2.90
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2.86
2.71
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2.23
2.23
2.22
2.22
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0.65
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F3C
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Me
O
O
H
3ga
1H NMR
Solvent: CDCl3
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3.14
1.00
1.03
1.01
1.02
1.08
2.00
1.07
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3.04
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3.03
10
9
8
7
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5
4
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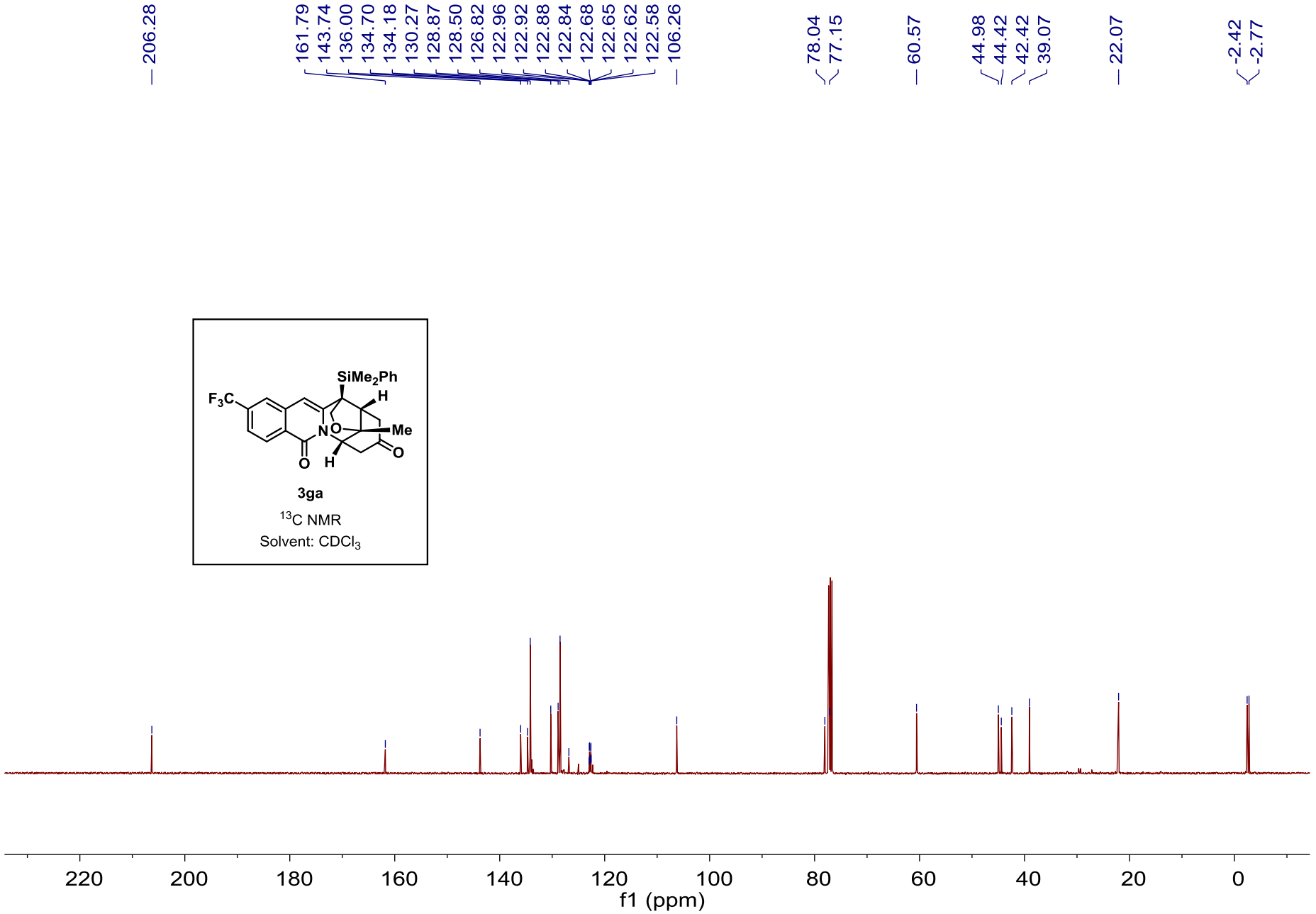
1
0
f1 (ppm)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122.62
122.58
106.26
78.04
77.15
60.57
44.98
44.42
42.42
39.07
22.07
-2.42
-2.77
SiMe2Ph
H
F3C
N
O
Me
O
O
H
3ga
13C NMR
Solvent: CDCl3
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200
180
160
140
120
100
80
60
40
20
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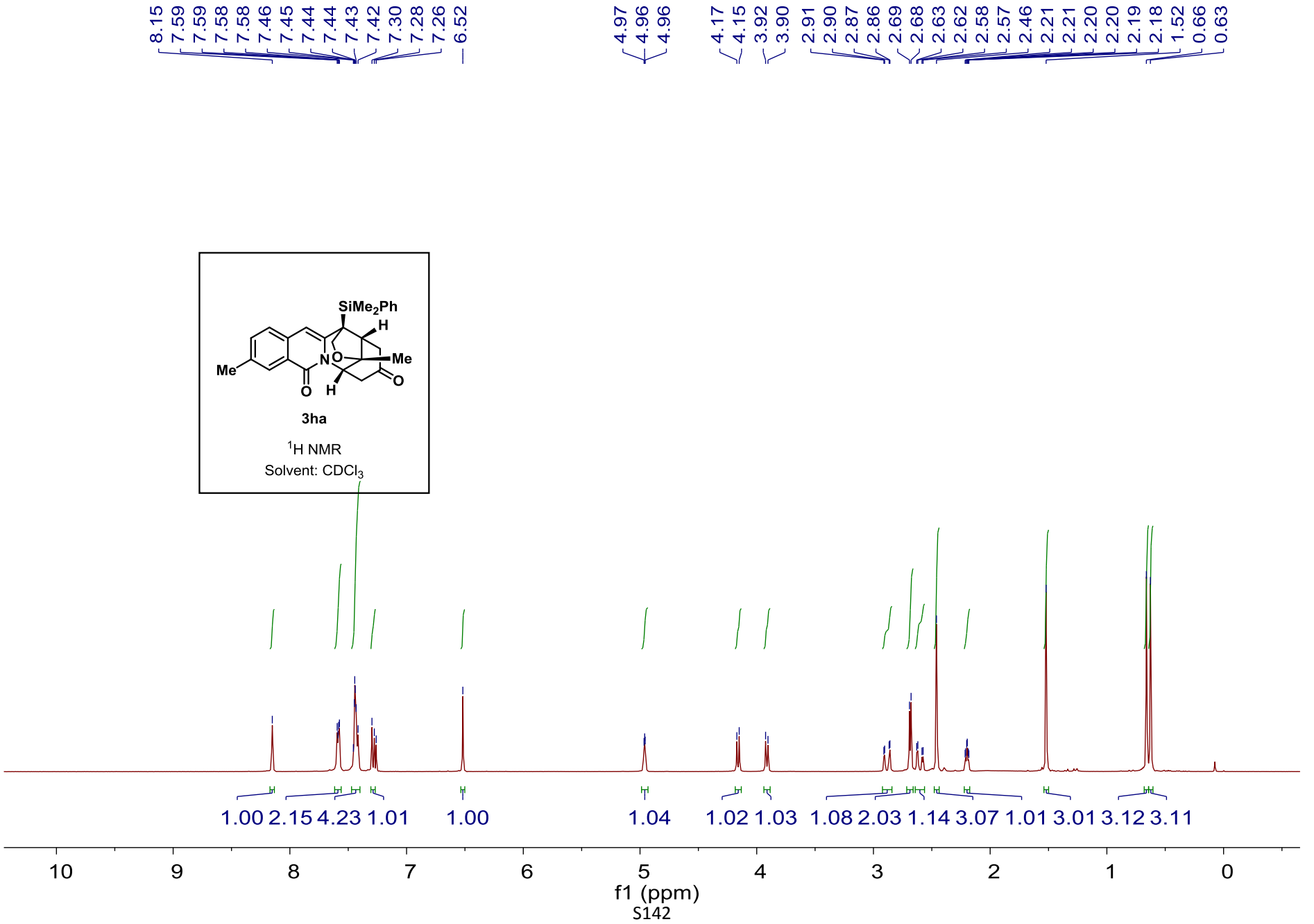
f1 (ppm)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7.59
7.58
7.58
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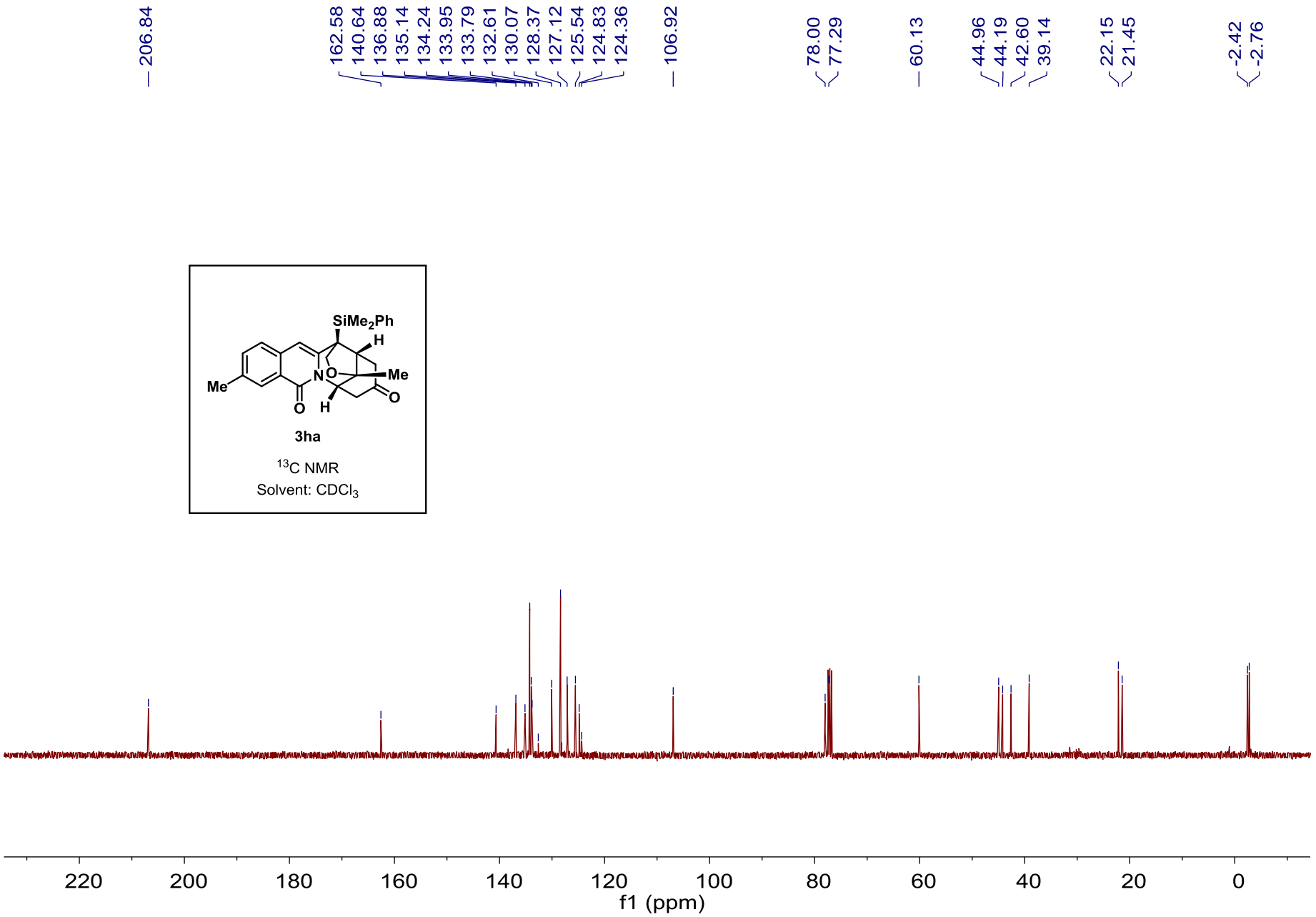
7.45
7.44
7.44
7.43
7.42
7.30
7.28
7.26
6.52
4.97
4.96
4.96
4.17
4.15
3.92
3.90
2.91
2.90
2.87
2.86
2.69
2.68
2.63
2.62
2.58
2.57
2.46
2.21
2.21
2.20
2.20
2.19
2.18
1.52
0.66
0.63
SiMe2Ph
H
N
O
Me
Me
O
O
H
3ha
1H NMR
Solvent: CDCl3
1.00 2.15 4.23 1.01 1.00 1.04 1.02 1.03 1.08 2.03 1.14 3.07 1.01 3.01 3.12 3.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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135.14
134.24
133.95
133.79
132.61
130.07
128.37
127.12
125.54
124.83
124.36
106.92
78.00
77.29
60.13
44.96
44.19
42.60
39.14
22.15
21.45
-2.42
-2.76
SiMe2Ph
H
N
O
Me
Me
O
O
H
3ha
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
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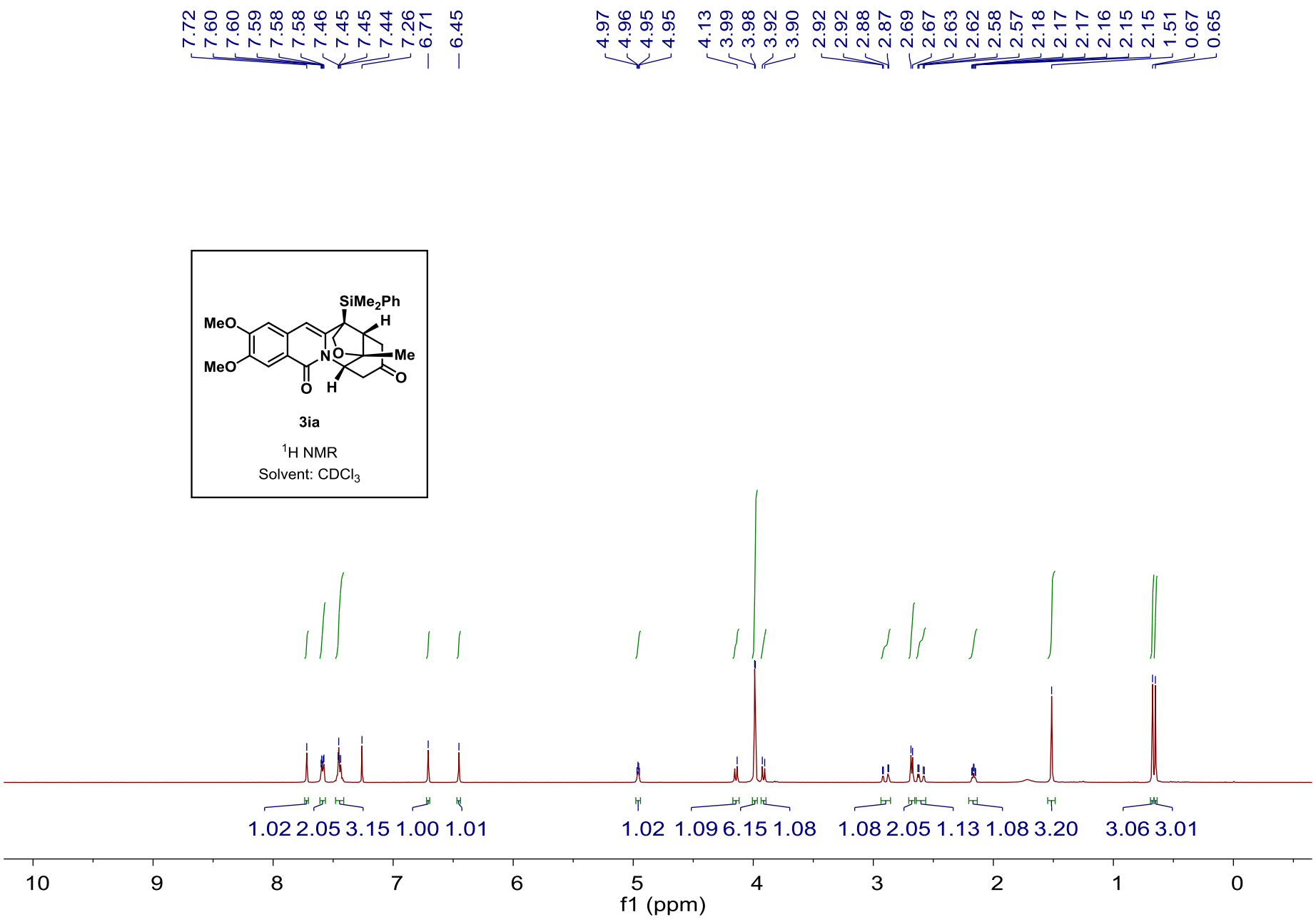
20
0
f1 (ppm)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7.60
7.60
7.59
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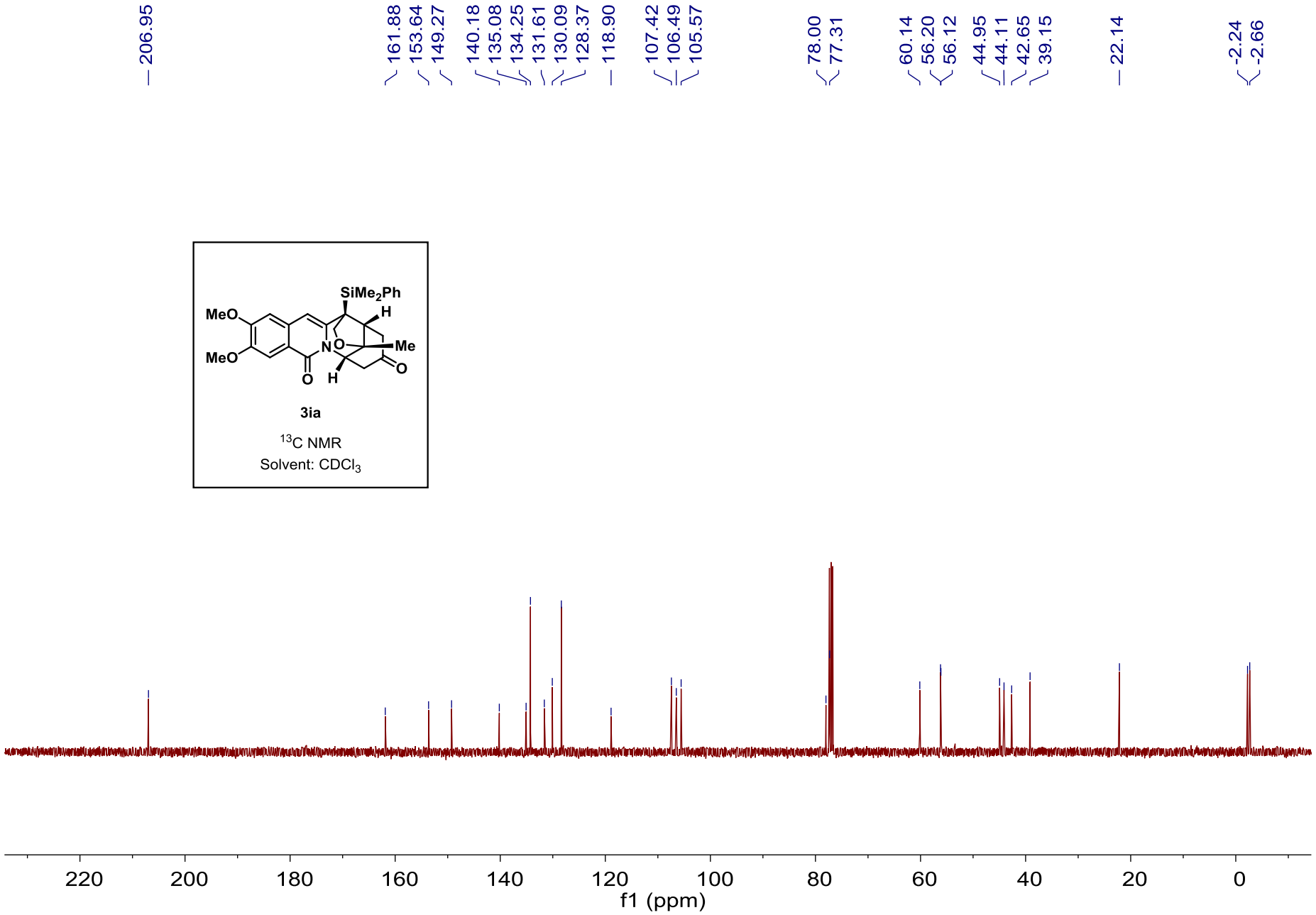
7.58
7.46
7.45
7.45
7.44
7.26
6.71
6.45
4.97
4.96
4.95
4.95
4.13
3.99
3.98
3.92
3.90
2.92
2.92
2.88
2.87
2.69
2.67
2.63
2.62
2.58
2.57
2.18
2.17
2.17
2.16
2.15
2.15
1.51
0.67
0.65
SiMe2Ph
H
MeO
MeO
N
O
Me
O
O
H
3ia
1H NMR
Solvent: CDCl3
1.02 2.05 3.15 1.00 1.01
1.02 1.09 6.15 1.08
1.08 2.05 1.13 1.08 3.20
3.06 3.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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140.18
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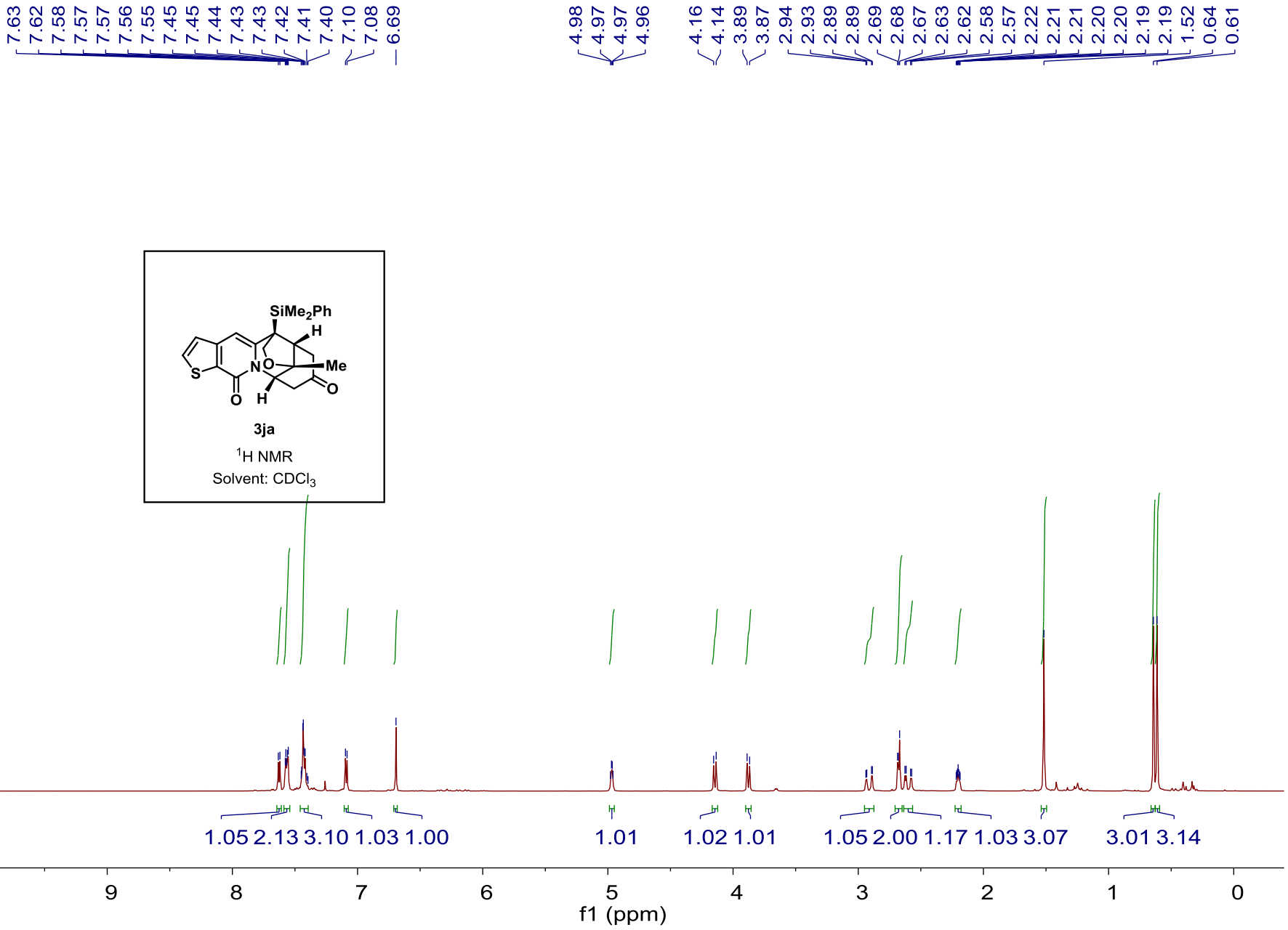
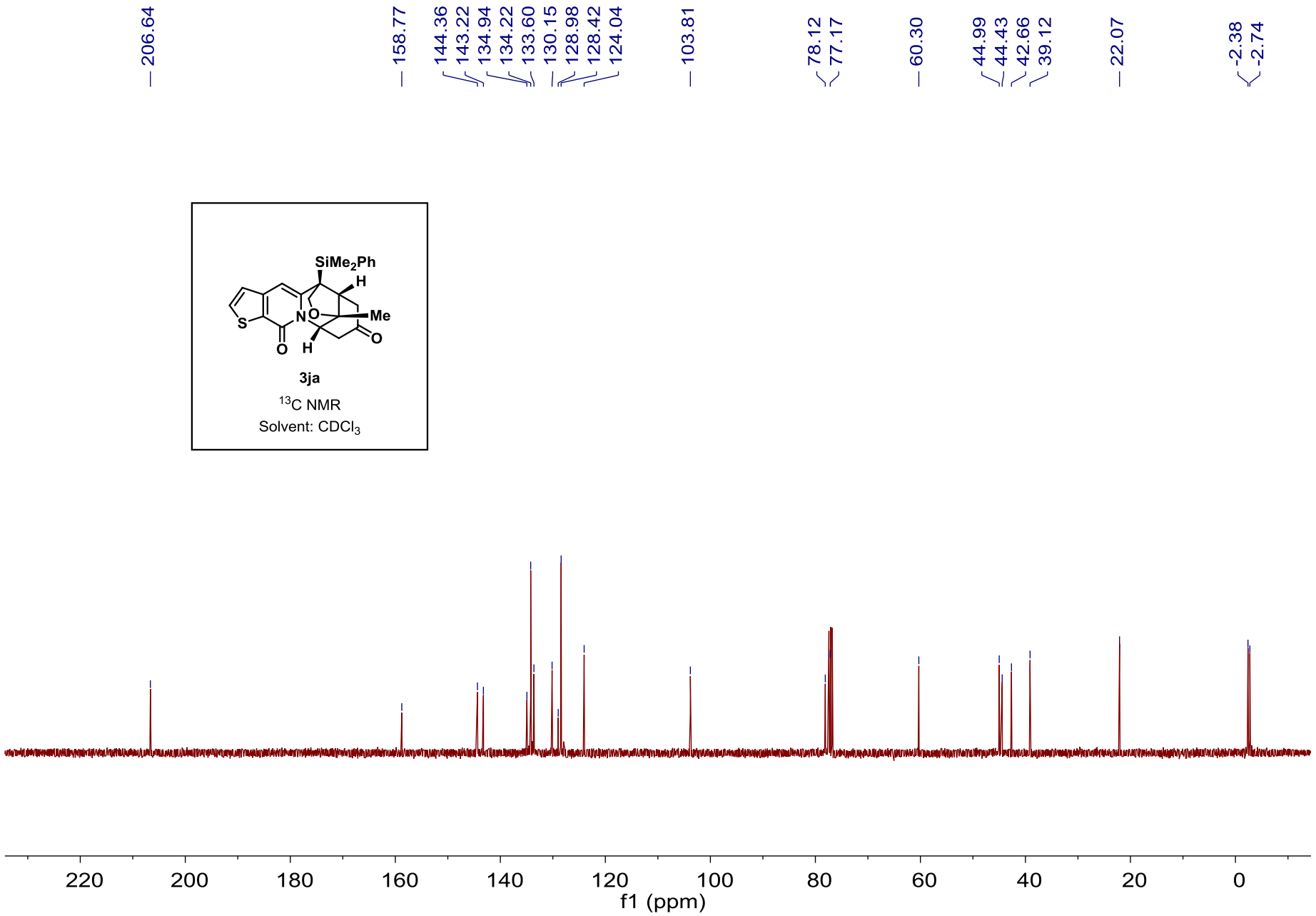
131.61
130.09
128.37
118.90
107.42
106.49
105.57
78.00
77.31
60.14
56.20
56.12
44.95
44.11
42.65
39.15
22.14
-2.24
-2.66
SiMe2Ph
H
MeO
MeO
N
O
Me
O
O
H
3ia
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.63 7.62 7.58 7.57 7.57 7.56 7.55 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.40 7.10 7.08 6.69
4.98 4.97 4.97 4.96
4.16 4.14 3.89 3.87 2.94 2.93 2.89 2.89 2.69 2.68 2.67 2.63 2.62 2.58 2.57 2.22 2.21 2.21 2.20 2.20 2.19 2.19 1.52 0.64 0.61
SiMe2Ph
H
Me
S
N
O
O
O
H
3ja
1H NMR
Solvent: CDCl3
1.05 2.13 3.10 1.03 1.00
1.01
1.02 1.01
1.05 2.00 1.17 1.03 3.07
3.01 3.14
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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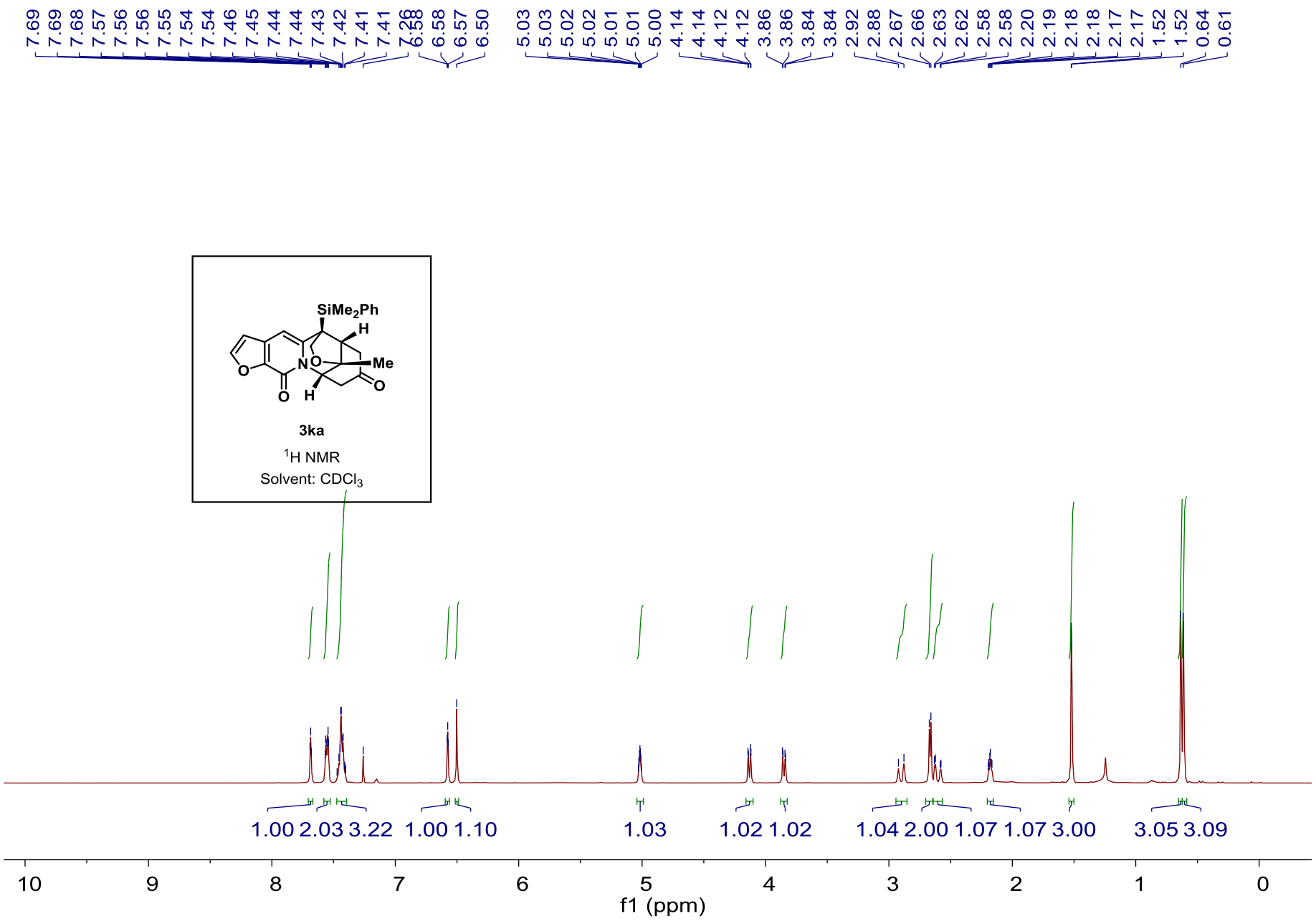
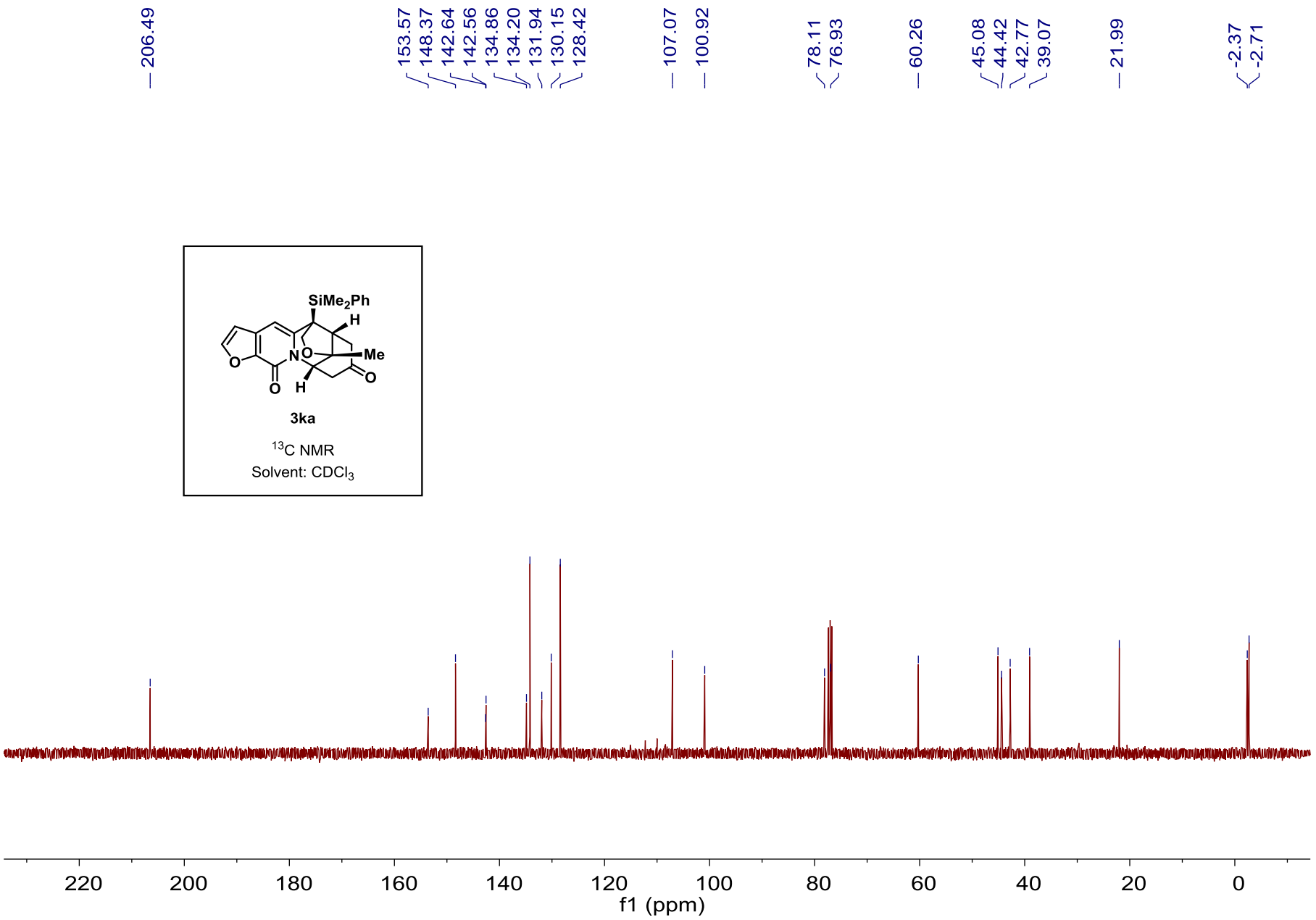
144.36
143.22
134.94
134.22
133.60
130.15
128.98
128.42
124.04
103.81
78.12
77.17
60.30
44.99
44.43
42.66
39.12
22.07
-2.38
-2.74
SiMe2Ph
H
N
O
Me
S
O
O
H
3ja
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.69 7.69 7.68 7.57 7.56 7.56 7.55 7.54 7.54 7.46 7.45 7.44 7.44 7.43 7.42 7.41 7.41 6.58 6.58 6.57 6.50
5.03 5.03 5.02 5.02 5.01 5.01 5.00 4.14 4.14 4.12 4.12 3.86 3.86 3.84 3.84 2.92 2.88 2.67 2.66 2.63 2.62 2.58 2.58 2.20 2.19 2.18 2.18 2.17 2.17 1.52 1.52 0.64 0.61
SiMe2Ph
H
N
O
Me
O
O
O
H
3ka
1H NMR
Solvent: CDCl3
1.00 2.03 3.22 1.00 1.10 1.03 1.02 1.02 1.04 2.00 1.07 1.07 3.00 3.05 3.09
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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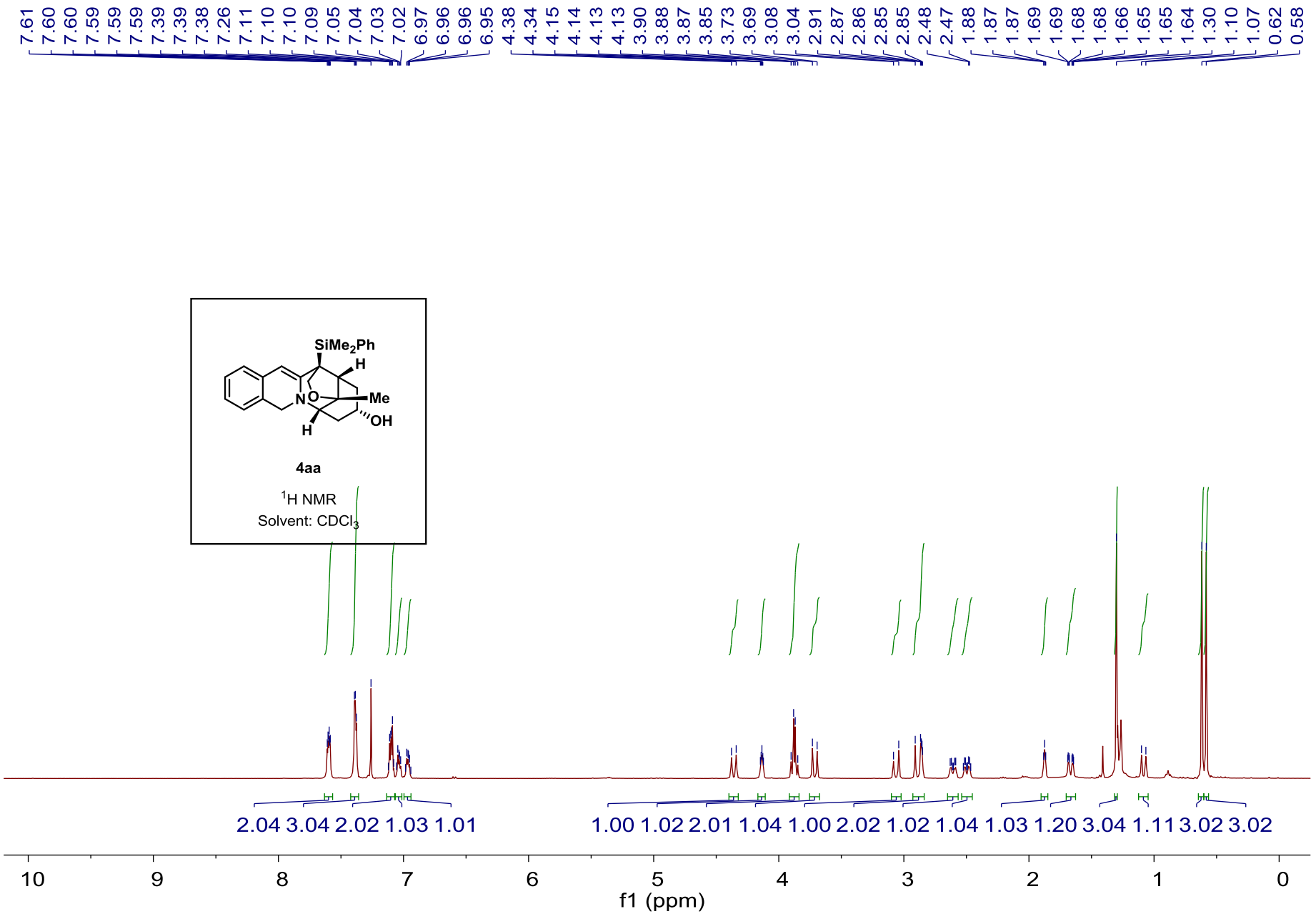
153.57
148.37
142.64
142.56
134.86
134.20
131.94
130.15
128.42
107.07
100.92
78.11
76.93
60.26
45.08
44.42
42.77
39.07
21.99
-2.37
-2.71
SiMe2Ph
H
N
O
Me
O
O
O
H
3ka
13C NMR
Solvent: CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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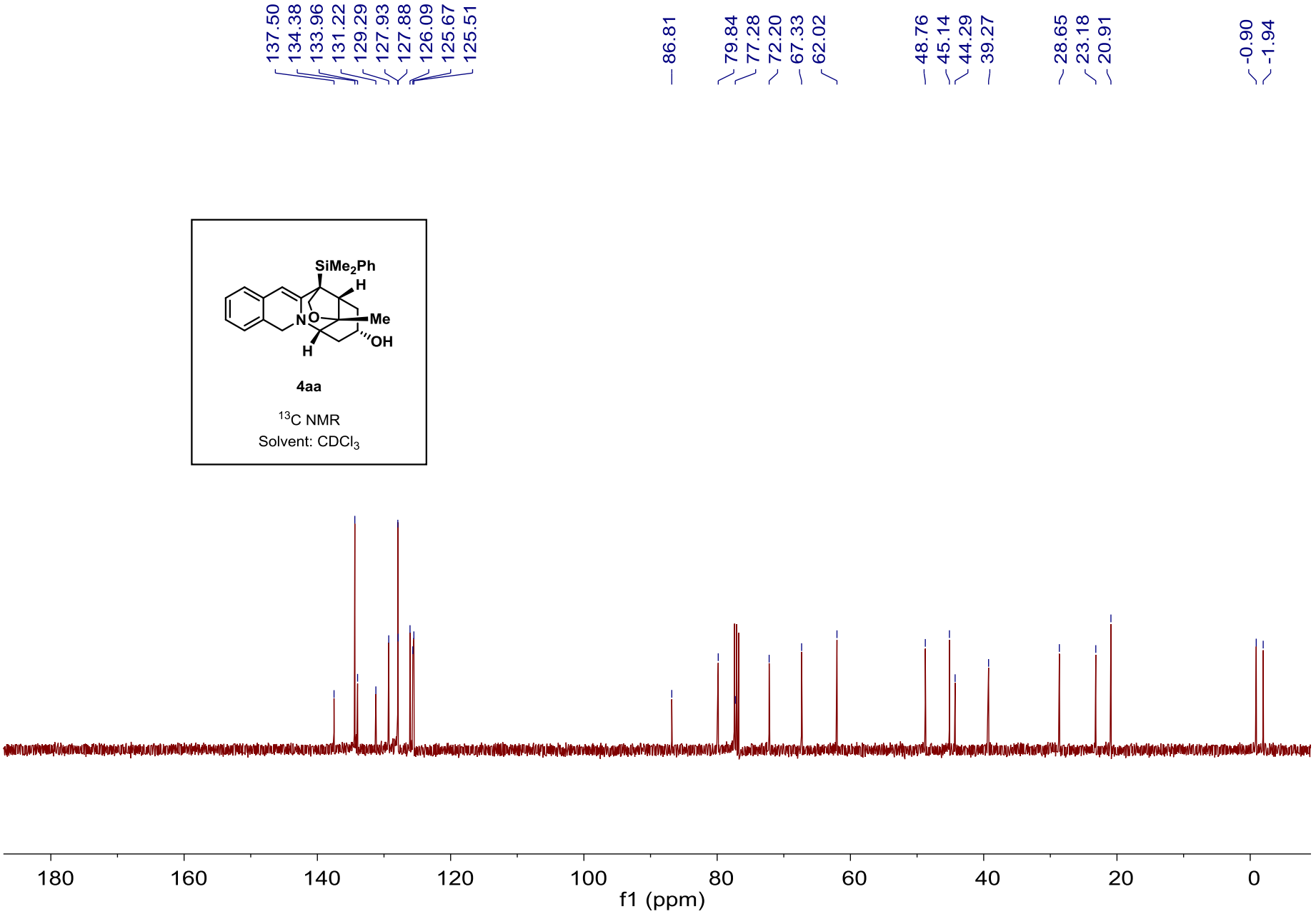
4.38 4.34 4.15 4.14 4.13 4.13 3.90 3.88 3.87 3.85 3.73 3.69 3.08 3.04 2.91 2.87 2.86 2.85 2.85 2.48 2.47 1.88 1.87 1.87 1.69 1.69 1.68 1.68 1.66 1.65 1.65 1.64 1.30 1.10 1.07 0.62 0.58
SiMe2Ph
H
N
O
Me
OH
H
4aa
1H NMR
Solvent: CDCl3
2.04 3.04 2.02 1.03 1.01
1.00 1.02 2.01 1.04 1.00 2.02 1.02 1.04 1.03 1.20 3.04 1.11 3.02 3.02
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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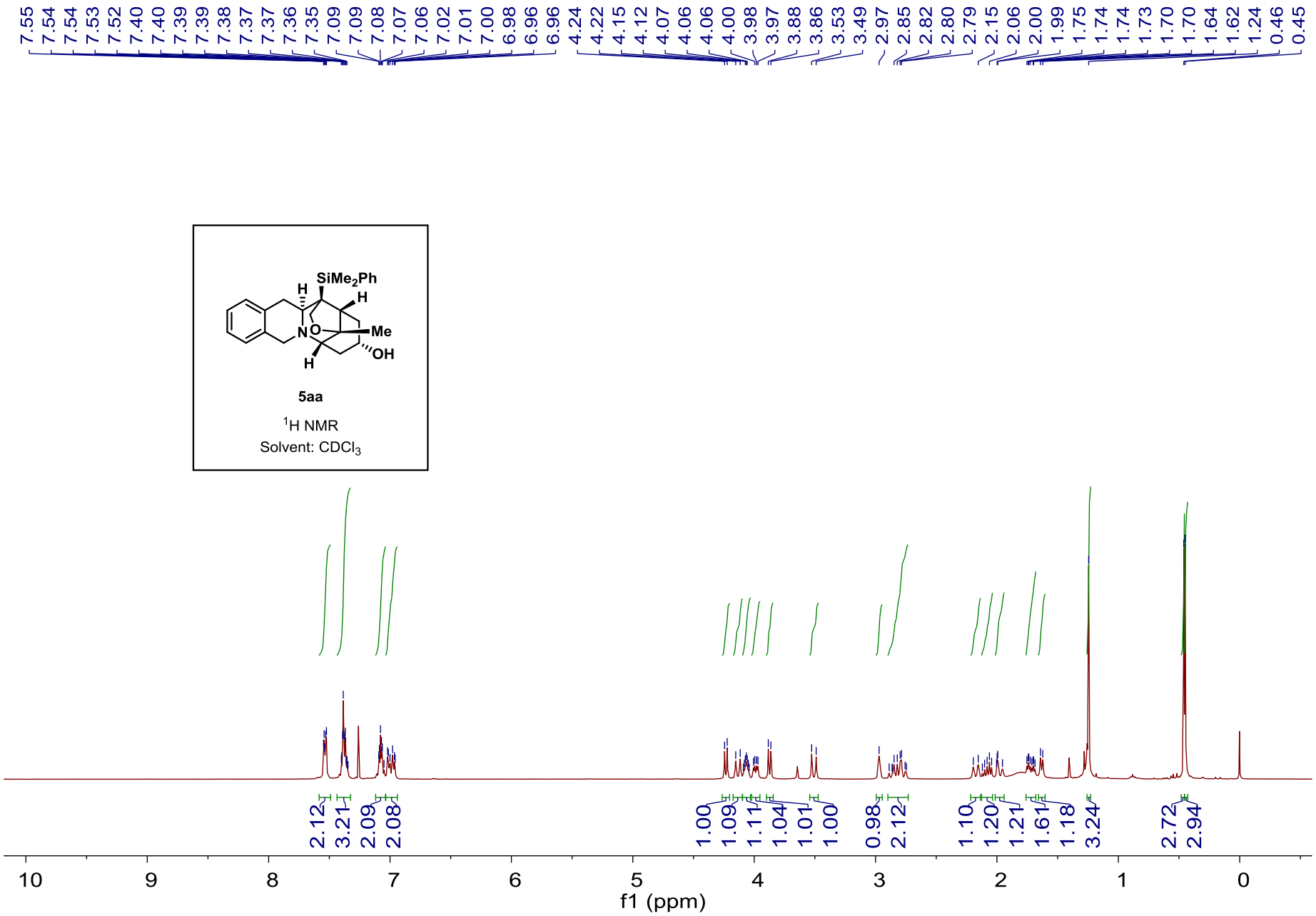
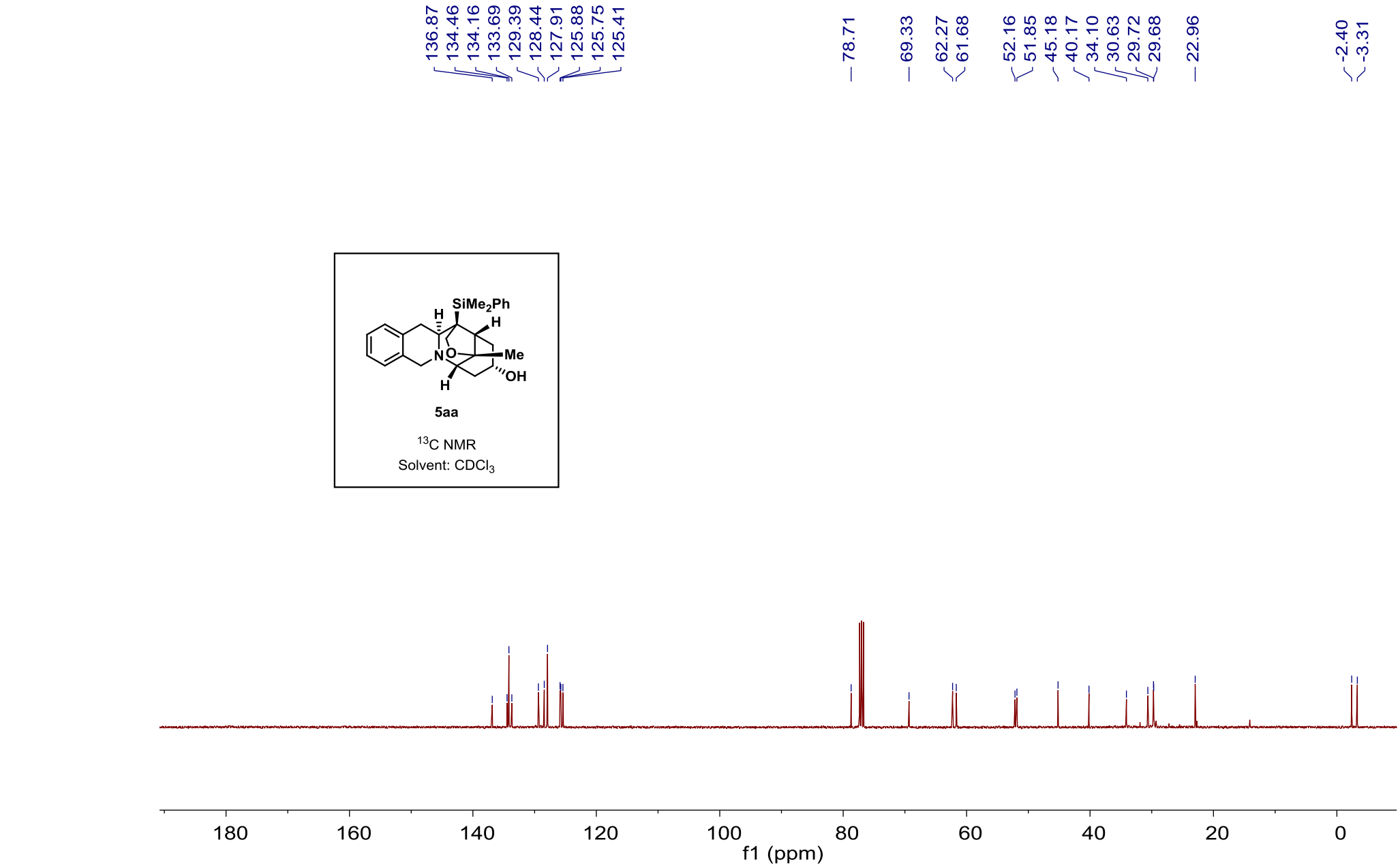
134.38
133.96
131.22
129.29
127.93
127.88
126.09
125.67
125.51
86.81
79.84
77.28
72.20
67.33
62.02
48.76
45.14
44.29
39.27
28.65
23.18
20.91
-0.90
-1.94
SiMe2Ph
H
N
O
Me
OH
H
4aa
13C NMR
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.55 7.54 7.54 7.53 7.52 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.09 7.09 7.08 7.07 7.06 7.02 7.01 7.00 6.98 6.96 6.96
4.24 4.22 4.15 4.12 4.07 4.06 4.06 4.00 3.98 3.97 3.88 3.86 3.53 3.49 2.97 2.85 2.82 2.80 2.79 2.15 2.06 2.00 1.99 1.75 1.74 1.74 1.73 1.70 1.70 1.64 1.62 1.24 0.46 0.45
SiMe2Ph
H
H
N
O
Me
OH
H
5aa
1H NMR
Solvent: CDCl3
2.12 3.21 2.09 2.08
1.00 1.09 1.11 1.04 1.01 1.00 0.98 2.12 1.10 1.20 1.21 1.61 1.18 3.24 2.72 2.94
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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134.46
134.16
133.69
129.39
128.44
127.91
125.88
125.75
125.41
78.71
69.33
62.27
61.68
52.16
51.85
45.18
40.17
34.10
30.63
29.72
29.68
22.96
-2.40
-3.31
SiMe2Ph
H
H
N
O
Me
OH
H
5aa
13C NMR
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
0
f1 (ppm)