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Study on 1,4-hydride shift triggered spirocyclization of arylidene imidazolones: substituent control on formation of indane or tetrahydrobenzazepine systems

Amir M. Al Mufti, Viktoria A. Ikonnikova, Alexander Yu. Smirnov, Vladislav A. Lushpa, Pavel N. Solyev, Mohamad Nurul Azmi, Mikhail S. Baranov and Andrey A. Mikhaylov

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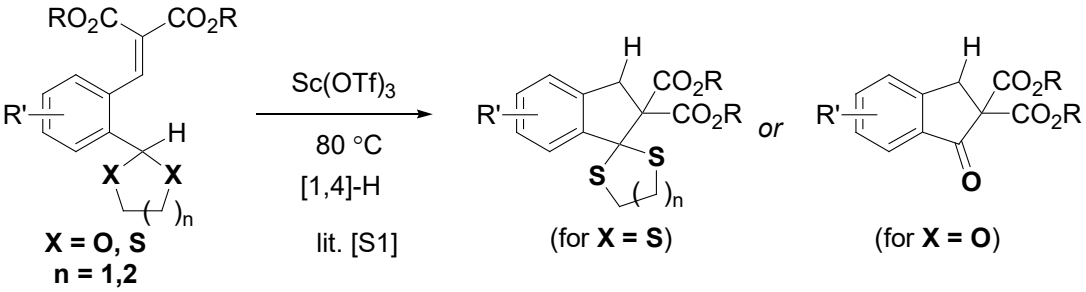
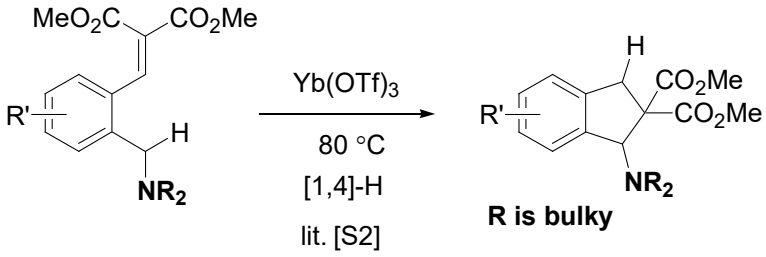
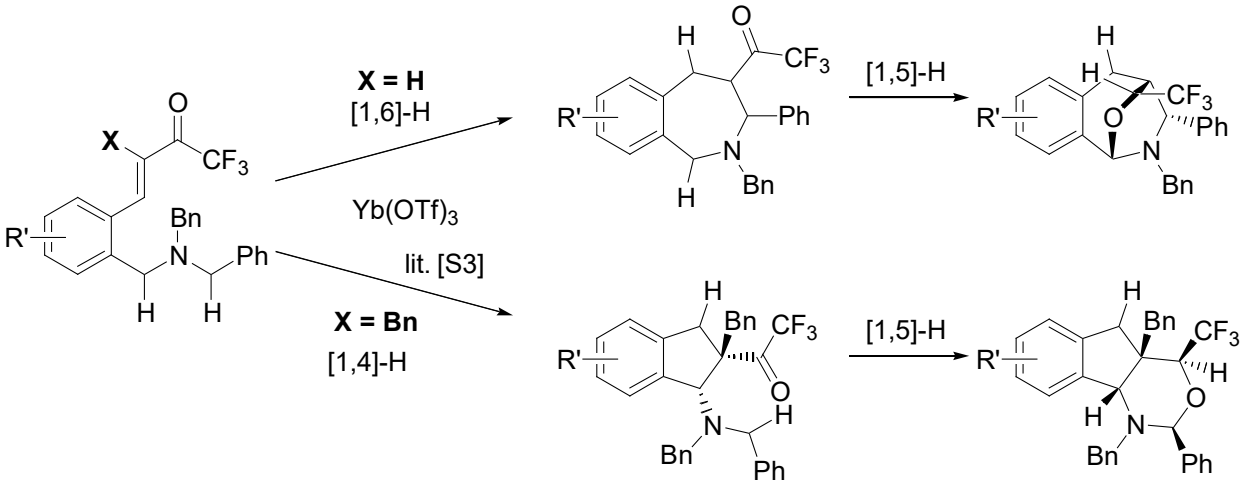
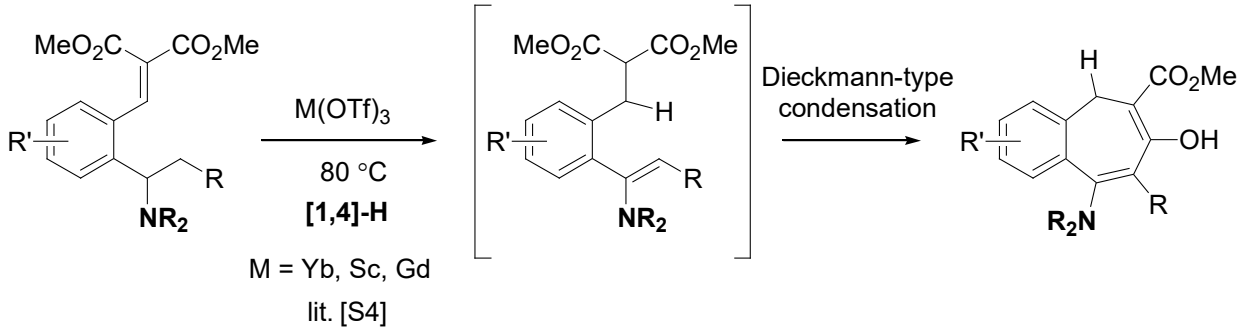
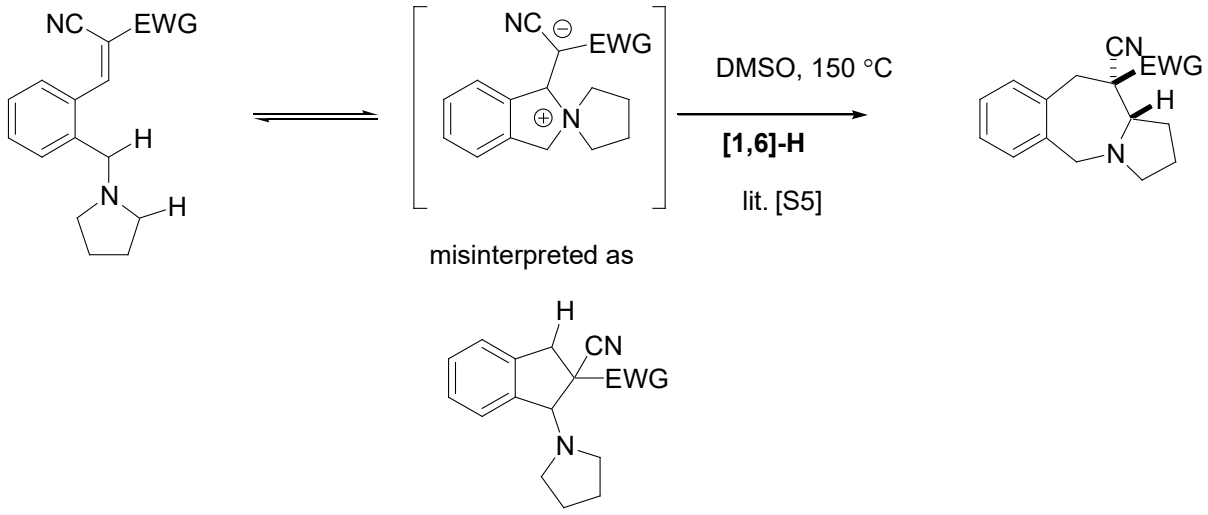
Literature reports on 1,4-Hydride-Shift-Triggered Cyclization



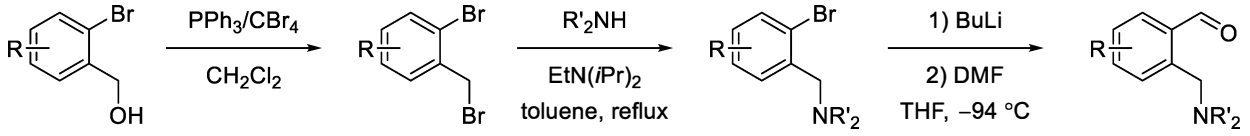







NC
EWG
H
N
H
NC
EWG
N
DMSO, 150 °C
[1,6]-H
lit. [S5]
CN
EWG
H
N
misinterpreted as
H
CN
EWG
N

General route for synthesis of starting aldehydes



Details described in the supporting information in ref [S2]

General Experimentation

Reagents and methods: All reactions were performed in pre-dried at 180 °C glassware. Solvents and reagents were distilled over indicated drying agents prior use: $CHCl_3$, dichloroethane (CaH_2), ethyl acetate (K_2CO_3).

Analytical thin-layer chromatography (TLC) was performed using aluminum plates pre-coated with silica gel (silica gel 60 F_{254}, Merck). TLC plates were visualized by exposure to 254 nm ultraviolet light (UV) or were stained by submersion in acidic ethanolic solution of vanillin followed by brief heating (vanillin). Flash-column chromatography was carried out on silica gel (60 Å, 230–400 mesh, Sigma-Aldrich).

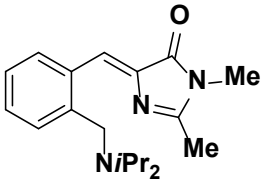
Nuclear magnetic resonance spectra were recorded using Bruker Furier 300, Bruker Avance III 700 and Bruker Avance II 800 instruments at indicated temperature. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant (J) in Hertz, integration. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvents ($CHCl_3$, δ 7.26 ppm). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonances of the NMR solvents ($CDCl_3$, δ 77.16 ppm).

High-resolution mass spectra were recorded on a Bruker micrOTOF-Q II mass spectrometer using electrospray ionization (ESI–TOF). Melting points were determined on Kofler melting point apparatus and are uncorrected.

Starting materials

General procedure: Substituted benzaldehyde (2 mmol, 1 equiv.) was dissolved in $CHCl_3$ (5 ml), then 35% solution of $MeNH_2$ in Pr^iOH (1 mL, excess) along with anhydrous Na_2SO_4 (1 g). The mixture was vigorously stirred overnight. The obtained solution was filtered from inorganics through cotton wool. Solid was washed excessively with $CHCl_3$. Combined filtrate was evaporated to dryness. To the residue ethyl 2-[(1-methoxyethylidene)amino]acetate **2** (0.38 g, 2.4 mmol, 1.2 equiv.) was added. The obtained solution was left with occasional shaking for 48 h and evaporated. The product **1** was purified by flash chromatography using hexane/EtOAc 1/1→0/1 as eluent.

***(Z)*-5-[2-(Diisopropylaminomethyl)benzylidene]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1a**



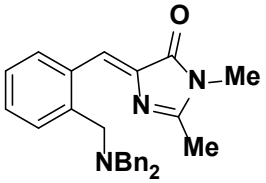
Yield 455 mg (1.45 mmol, 73%). Yellowish crystals, mp = 106-108 °C, R_f = 0.36 (SiO_2, EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.58–8.41 (m, 1H), 7.82 (s, 1H), 7.59–7.38 (m, 1H), 7.36–7.14 (m, 2H), 3.82 (s, 2H), 3.17 (s, 3H), 3.01 (hept, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 1.03 (d, *J* = 6.9 Hz, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300K): δ = 170.8, 162.4, 142.8, 138.3, 132.9, 132.2, 129.8, 129.6, 126.8, 125.5, 47.7 (×2), 47.6, 26.6, 20.6 (×4), 15.7.

HRMS (ESI+) m/z: calctd for $C_{19}H_{28}N_3O$ [M+H$^+$] 314.2227, found 314.2235.

***(Z)*-5-[2-(Dibenzylaminomethyl)benzylidene]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1b**



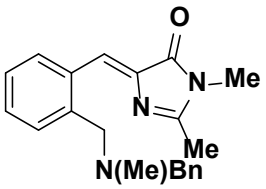
Yield 605 mg (1.48 mmol, 74%). Beige crystals, mp = 114-116 °C, R_f = 0.45 (SiO_2, EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.66–8.39 (m, 1H), 7.77 (s, 1H), 7.59–7.46 (m, 1H), 7.41 (d, *J* = 7.2 Hz, 4H), 7.34–7.27 (m, 6H), 7.21 (t, *J* = 7.3 Hz, 2H), 3.71 (s, 2H), 3.54 (s, 4H), 3.23 (s, 3H), 2.37 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300K): δ = 170.7, 162.7, 140.1, 139.2 (×2), 138.8, 133.4, 132.5, 130.4, 129.7, 129.0 (×4), 128.4 (×4), 127.4, 126.9 (×2), 125.1, 58.5 (×2), 56.9, 26.7, 15.8.

HRMS (ESI+) m/z: calctd for $C_{27}H_{28}N_3O$ [M+H$^+$] 410.2227, found 410.2231.

***(Z)*-5-[2-(*N*-Benzyl-*N*-methylaminomethyl)benzylidene]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1c**



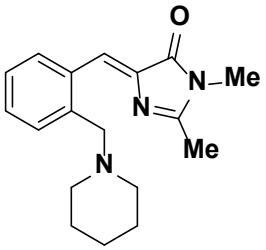
Yield 546 mg (1.64 mmol, 82%). Yellowish crystals, mp = 68-70 °C, R_f = 0.37 (SiO_2, EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.61 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.47–7.11 (m, 8H), 3.67 (s, 2H), 3.56 (s, 2H), 3.21 (s, 3H), 2.38 (s, 3H), 2.10 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.7, 162.7, 140.1, 139.1, 138.6, 133.5, 132.5, 130.5, 129.6, 129.2 (×2), 128.3 (×2), 127.6, 127.0, 125.2, 62.5, 60.6, 41.8, 26.6, 15.8.

HRMS (ESI+) m/z: calctd for $C_{21}H_{24}N_3O$ [M+H$^+$] 334.1914, found 334.1908.

***(Z)*-2,3-Dimethyl-5-[2-(piperidin-1-ylmethyl)benzylidene]-3,5-dihydro-4*H*-imidazol-4-one 1d**



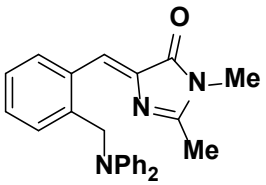
Yield 518 mg (1.74 mmol, 87%). Yellowish crystals, mp = 130-132 °C, R_f = 0.31 (SiO_2, EtOAc).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = δ 8.57 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.73 (s, 1H), 7.42–7.11 (m, 3H), 3.57 (s, 2H), 3.18 (s, 3H), 2.45–2.20 (m, 7H), 1.52 (p, *J* = 5.4 Hz, 4H), 1.40 (q, *J* = 6.5 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.7, 162.5, 140.0, 138.3, 133.5, 132.3, 130.3, 129.4, 127.3, 125.3, 61.6, 54.5 (×2), 26.6, 26.1 (×2), 24.5, 15.7.

HRMS (ESI+) m/z: calctd for $C_{18}H_{24}N_3O$ [M+H$^+$] 298.1914, found 298.1920.

***(Z)*-5-[2-(Diphenylaminomethyl)benzylidene]-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1e**



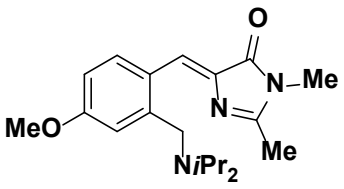
Yield 495 mg (1.30 mmol, 65%). Yellowish crystals, mp = 181-183 °C, R_f = 0.21 (SiO_2, EtOAc).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.53 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.51 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.39 (s, 1H), 7.36–7.20 (m, 6H), 7.07 (d, *J* = 7.6 Hz, 4H), 6.95 (t, *J* = 7.3 Hz, 2H), 5.20 (s, 2H), 3.19 (s, 3H), 2.38 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.5, 163.6, 147.9 (×2), 139.4, 139.0, 132.4, 131.4, 130.2, 129.4 (×4), 127.1, 126.9, 122.7, 121.6 (×2), 120.7 (×4), 54.6, 26.7, 15.8.

HRMS (ESI+) m/z: calctd for $C_{25}H_{24}N_3O$ [M+H$^+$] 382.1914, found 382.1922.

***(Z)*-5-(2-Diisopropylaminomethyl-4-methoxybenzylidene)-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1f**



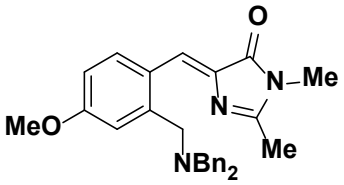
Yield 467 mg (1.36 mmol, 68%). Yellowish crystals, mp = 118-120 °C, R_f = 0.32 (SiO_2, EtOAc).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.61 (d, *J* = 8.7 Hz, 1H), 7.67 (s, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 2H), 3.15 (s, 3H), 3.02 (hept, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 1.03 (d, *J* = 6.6 Hz, 12H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.9, 161.2, 161.1, 145.9, 136.8, 134.2, 125.4, 124.6, 114.8, 112.2, 55.2, 48.1 (×2), 47.3, 26.6, 20.7 (×4), 15.7.

HRMS (ESI+) m/z: calctd for $C_{20}H_{30}N_3O_2$ [M+H$^+$] 344.2333, found 344.2334.

***(Z)*-5-(2-Dibenzylaminomethyl-4-methoxybenzylidene)-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1g**



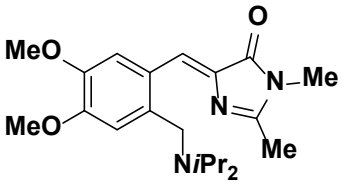
Yield 526 mg (1.20 mmol, 60%). Beige crystals, mp = 120-122 °C, R_f = 0.37 (SiO_2, EtOAc).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.71 (d, *J* = 8.7 Hz, 1H), 7.69 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 4H), 7.32 (t, *J* = 7.4 Hz, 4H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.87 (dd, J = 8.7, 2.8 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 2H), 3.58 (s, 4H), 3.19 (s, 2H), 2.34 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.8, 161.5, 160.9, 142.7, 139.2 (×2), 137.2, 134.5, 128.9 (×4), 128.4 (×4), 127.0 (×2), 126.0, 124.5, 115.5, 112.9, 58.6 (×2), 56.6, 55.3, 26.6, 15.7.

HRMS (ESI+) m/z: calctd for $C_{28}H_{30}N_3O_2$ [M+H$^+$] 440.2333, found 344.2333.

***(Z)*-5-(2-Diisopropylaminomethyl-4,5-dimethoxybenzylidene)-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1h**



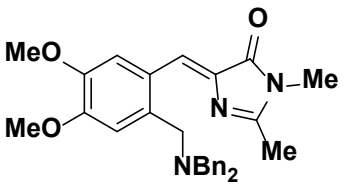
Yield 535 mg (1.43 mmol, 72%). Yellowish crystals, mp = 147-149 °C, R_f = 0.25 (SiO_2, EtOAc).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.44 (s, 1H), 7.66 (d, *J* = 2.6 Hz, 1H), 7.19 (d, J = 2.6Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.79 (s, 2H), 3.15 (s, 3H), 3.01 (hept, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 1.02 (d, *J* = 6.6 Hz, 12H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.9, 161.0, 150.7, 147.3, 138.3, 136.7, 125.0, 124.3, 114.9, 112.2, 56.0, 55.9, 48.0 (×2), 46.5, 26.6, 20.8, 15.8 (×4).

HRMS (ESI+) m/z: calctd for $C_{21}H_{32}N_3O_3$ [M+H$^+$] 374.2438, found 374.2448.

***(Z)*-5-(2-Dibenzylaminomethyl-4,5-dimethoxybenzylidene)-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1i**



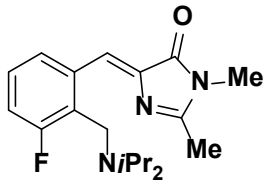
Yield 480 mg (1.30 mmol, 65%). Beige crystals, mp = 146-148 °C, R_f = 0.37 (SiO_2, hexane/EtOAc, 1/1).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.53 (d, *J* = 1.4 Hz, 1H), 7.68 (s, 1H), 7.42 (d, *J* = 7.5 Hz, 4H), 7.32 (t, *J* = 7.4 Hz, 4H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 1.4 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.71 (s, 2H), 3.57 (s, 4H), 3.20 (s, 3H), 2.35 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.8, 161.5, 160.9, 142.7, 139.2 (×2), 137.2, 134.5, 128.9 (×4), 128.4 (×4), 127.0 (×2), 126.0, 124.5, 115.5, 112.9, 58.6 (×2), 56.6, 55.3, 26.6, 15.7.

HRMS (ESI+) m/z: calctd for $C_{29}H_{32}N_3O_3$ [M+H$^+$] 470.2438, found 470.2437.

***(Z)*-5-(2-Diisopropylaminomethyl-3-fluorobenzylidene)-2,3-dimethyl-3,5-dihydro-4*H*-imidazol-4-one 1j**



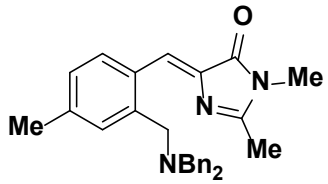
Yield 590 mg (1.84 mmol, 92%). Yellowish crystals, mp = 115-117 °C, R_f = 0.41 (SiO_2, hexane/EtOAc, 1/1).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.33 (d, *J* = 7.9 Hz, 1H), 7.95 (s, 1H), 7.27 (dt, *J* = 8.5, 6.3 Hz, 1H), 7.00 (dd, *J* = 9.7, 8.3 Hz, 1H), 3.84 (d, *J* = 1.9 Hz, 2H), 3.17 (s, 3H), 2.95 (hept, J = 6.7 Hz, 2H), 2.35 (s, 3H), 1.07 (d, *J* = 6.6 Hz, 12H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.6, 162.9, 162.1 (d, *J* = 243.8 Hz), 138.7, 136.5 (d, *J* = 3.7 Hz), 128.3 (d, J = 3.3 Hz), 128.2 (d, *J* = 9.1 Hz), 128.1 (d, *J* = 12.6 Hz), 125.4 (d, *J* = 3.3 Hz), 116.1 (d, *J* = 24.2 Hz), 47.1 (×2), 38.70 (d, *J* = 4.9 Hz), 26.6, 20.6 (×4), 15.8.

HRMS (ESI+) m/z: calctd for $C_{19}H_{27}FN_3O$ [M+H$^+$] 322.2133, found 322.2139.

***(Z)*-5-(2-Dibenzylaminomethyl-4-methylbenzylidene)-2,3-dimethyl-3,5-dihydro-*4H*-imidazol-4-one 1k**



Yield 660 mg (1.56 mmol, 78%). Yellowish crystals, mp = 104-105 °C, R_f = 0.54 (EtOAc).

^1H NMR (300 MHz, $CDCl_3$, 300K): δ = 8.44 (s, 1H), 7.82 (s, 1H), 7.51–7.31 (m, 9H), 7.25 (t, *J* = 7.4 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 2H), 3.57 (s, 4H), 3.21 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300K): δ = 170.6, 162.5, 139.2 (×2), 138.5, 137.3, 136.9, 133.2, 132.9, 130.6, 130.5, 128.9 (×4), 128.3 (×4), 126.8, 125.4, 58.4 (×2), 56.7, 26.6, 21.3, 15.7.

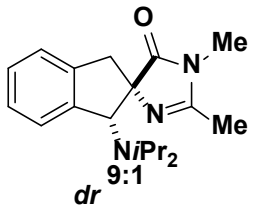
HRMS (ESI+) m/z: calctd for $C_{28}H_{30}N_3O$ [M+H$^+$] 424.2383, found 424.2384.

Cyclization products

General procedure for spirocyclization: Arylidene imidazolone **1** (0.30 mmol, 1 equiv.) was dissolved in anhydrous dichloroethane (2 ml) in a screw-cap vial (10 mL volume). The apparatus was flushed with argon. Then $AlCl_3$ (60 mg, 0.45 mmol, 1.5 equiv.) was added, the vial was sealed and immersed into preheated to 100 °C oil bath. The reaction mixture was stirred at the indicated temperature for 2-5 h. Then it was allowed to cool to room temperature and transferred into separatory funnel with EtOAc (20 mL) and saturated aqueous $NaHCO_3$ solution (10 mL). Organic layer was separated. Aqueous layer was extracted with EtOAc (10 mL). Combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness on a rotary evaporator. Column chromatography of the residue on silica gel (eluent hexane/EtOAc 1/1→2/3→0/1) provided pure indane derivative **3** or tetrahydrobenzoazepine **4**.

In case of arylidene imidazolone **1b** both products **3b** and **4b** could be isolated, indane derivative **3b** has lower R_f.

***cis*-1'-Diisopropylamino-1,2-dimethyl-1',3'-dihydrospiro[imidazole-4,2'-inden]-5(1*H*)-one 3a**



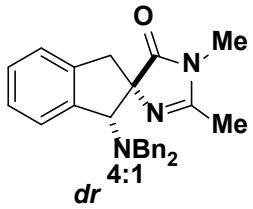
Yield 79 mg (0.25 mmol, 84%). R_f = 0.32 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 7.35–7.28 (m, 1H), 7.23–7.12 (m, 3H), 5.03 (s, 1H), 3.24 (d, *J* = 15.8 Hz, 1H), 3.15 (m, *J* = 6.5 Hz, 2H), 3.08 (s, 3H), 2.86 (d, *J* = 15.8 Hz, 1H), 2.23 (s, 3H), 1.09 (d, J = 6.5 Hz, 6H), 0.86 (d, J = 6.5 Hz, 6H), δ (for ***trans*** isomer, selected signals) = 4.67 (s, 1H), 3.37 (d, *J* = 16.0 Hz, 1H), 3.02 (s, 3H), 2.88 (d, *J* = 16.0 Hz, 1H), 2.20 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300K): δ = 185.3, 159.6, 143.1, 138.8, 127.6, 126.6, 125.2, 125.0, 82.9, 71.8, 48.4 (br), 43.3 (br), 40.7, 26.5 (br, ×2), 24.6 (br, ×2), 23.0, 16.0.

HRMS (ESI+) m/z: calctd for $C_{19}H_{28}N_3O$ [M+H$^+$] 314.2227, found 314.2222.

***cis*-1'-Dibenzylamino-1,2-dimethyl-1',3'-dihydrospiro[imidazole-4,2'-inden]-5(1*H*)-one 3b**



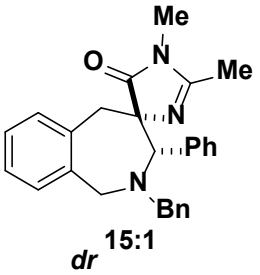
Yield 12 mg (0.03 mmol, 10%). R_f = 0.11 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (700 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 7.34–7.13 (m, 14H), 5.00 (s, 1H), 3.99 (d, *J* = 14.7 Hz, 2H), 3.79 (d, *J* = 14.7 Hz, 2H), 3.21 (d, *J* = 15.7 Hz, 1H), 3.18 (s, 3H), 2.85 (d, *J* = 15.7 Hz, 1H), 2.12 (s, 3H); δ (for ***trans*** isomer, selected signals) = 4.43 (s, 1H), 3.85 (d, J = 13.9 Hz, 2H), 3.68 (d, *J* = 13.9 Hz, 2H), 3.53 (d, *J* = 16.1 Hz, 1H), 3.20 (s, 3H), 2.94 (d, *J* = 16.1 Hz, 1H), 2.12 (s, 3H).

^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 184.4, 160.5, 141.3, 140.2, 139.3, 129.0, 128.4[4] (×4), 128.3[5] (×4), 128.2, 127.9, 127.0 (×2), 125.2, 124.7, 82.1, 72.9, 55.8 (×2), 41.2, 27.0, 15.7.

HRMS (ESI+) m/z: calctd for $C_{27}H_{28}N_3O$ [M+H$^+$] 410.2227, found 410.2216.

***cis*-2-Benzyl-1',2'-dimethyl-3-phenyl-1,2,3,5-tetrahydrospiro[benzo[*c*]azepine-4,4'-imidazol]-5'(1'*H*)-one 4b**



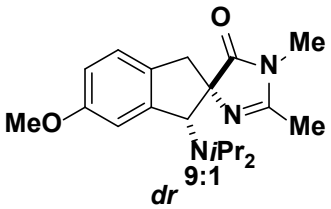
Yield 90 mg (0.22 mmol, 73%). R_f = 0.19 (SiO_2, hexane/EtOAc, 1/1), colorless foam.

^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) =7.45–7.07 (m, 13H), 6.99–6.77 (m, 1H), 4.24 (br d, *J* = 14.4 Hz, 1H), 3.95 (br s, 1H), 3.83 (d, *J* = 14.4 Hz, 1H), 3.63–3.44 (m, 2H), 3.21 (d, *J* = 14.1 Hz, 1H), 2.87 (d, *J* = 14.7 Hz, 1H), 2.53 (s, 3H), 1.96 (s, 3H).

^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 184.7, 160.7, 140.1, 138.8, 137.6, 129.9, 129.7, 129.5 (×2), 129.3, 128.8 (×2), 128.3 (×2), 127.7, 127.6, 127.2 (×2), 127.1, 126.8, 75.4, 57.2 (br), 40.6 (br), 26.1, 15.2. *One carbon signal too broad to be determined (ca. 68 ppm based on HSQC correlation).*

HRMS (ESI+) m/z: calctd for $C_{27}H_{28}N_3O$ [M+H$^+$] 410.2227, found 410.2229.

***cis*-1'-Diisopropylamino-6'-methoxy-1,2-dimethyl-1',3'-dihydrospiro[imidazole-4,2'-inden]-5(1*H*)-one 3f**



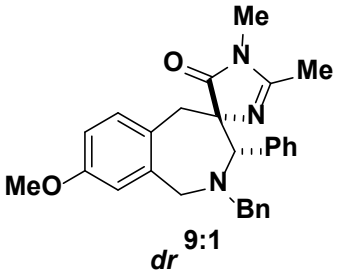
Yield 70 mg (0.20 mmol, 68%). R_f = 0.20 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (800 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 7.05 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.00 (s, 1H), 3.78 (s, 3H), 3.20–3.13 (m, 3H), 3.09 (s, 3H), 2.79 (d, *J* = 15.4 Hz, 1H), 2.24 (s, 3H), 1.19–0.65 (m, 12H); δ (for ***trans*** isomer) = 7.10 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.78 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.65 (s, 1H), 3.77 (s, 3H), 3.28 (d, *J* = 15.5 Hz, 1H), 3.20–3.13 (m, 2H), 3.02 (s, 3H), 2.83 (d, *J* = 15.5 Hz, 1H), 2.21 (s, 3H), 1.19–0.65 (m, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 185.2, 159.6, 159.2, 144.9, 130.8, 125.4, 113.6, 111.0, 83.4, 71.6, 55.6, 48.9 (br), 43.2 (br), 40.0, 26.6, 24.6 (br, ×2), 23.1 (br, ×2), 16.0; δ (for ***trans*** isomer) = 182.6, 159.1, 159.0, 144.2, 132.6, 125.4, 114.0, 111.5, 81.9, 72.2, 55.6, 39.7, 26.4, 15.6. – *Broad signals could not be identified for minor isomer.*

HRMS (ESI+) m/z: calctd for $C_{20}H_{30}N_3O_2$ [M+H$^+$] 344.2227, found 344.2231.

***cis*-2-Benzyl-8-methoxy-1',2'-dimethyl-3-phenyl-1,2,3,5-tetrahydrospiro[benzo[*c*]azepine-4,4'-imidazol]-5'(1'*H*)-one 4g**



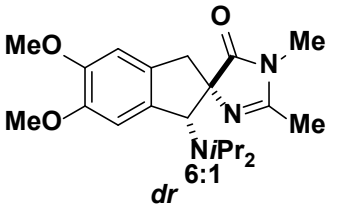
Yield 72 mg (0.16 mmol, 55%). R_f = 0.31 (SiO_2, hexane/EtOAc, 1/1), colorless oil.

^{1}H NMR (800 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 7.35 (d, *J* = 6.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.18–7.13 (m, 3H), 7.06 (br d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.8 Hz, 1H), 6.51 (br d, *J* = 2.8 Hz, 1H), 4.17 (br s, 1H), 3.98 (br s, 1H), 3.77 (s, 3H), 3.60 (br d, *J* = 14.2 Hz, 1H), 3.48 (br s, 1H), 3.25 (d, *J* = 14.2 Hz, 1H), 2.78 (br s, 1H), 2.70 (br s, 1H), 2.53 (s, 3H), 1.97 (s, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 184.7, 160.6, 158.7, 140.1, 138.8, 130.6, 129.6, 129.5 (×2), 128.8 (×2), 128.4, 128.3 (×2), 127.7, 127.3 (×2), 126.9, 115.5, 112.1, 75.5 (br), 57.1 (br), 55.4, 39.9 (br), 29.8 (br), 26.1, 15.2. *One carbon signal too broad to be determined.*

HRMS (ESI+) m/z: calctd for $C_{28}H_{30}N_3O_2$ [M+H$^+$] 440.2333, found 440.2330.

***cis*-1'-Diisopropylamino-5',6'-dimethoxy-1,2-dimethyl-1',3'-dihydrospiro[imidazole-4,2'-inden]-5(1*H*)-one 3h**



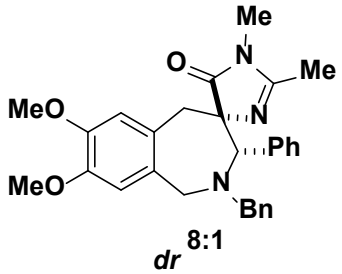
Yield 66 mg (0.18 mmol, 59%). R_f = 0.16 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (800 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 6.84 (s, 1H), 6.70 (s, 1H), 4.98 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.18 (d, *J* = 15.6 Hz, 1H), 3.19–3.13 (m, 2H), 3.09 (s, 3H), 2.81 (d, *J* = 15.6 Hz, 1H), 2.25 (s, 3H), 1.11 (br s, 6H), 0.97–0.67 (br m, 6H); δ (for ***trans*** isomer) = 6.81 (s, 1H), 6.73 (s, 1H), 4.58 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.34 (d, J = 15.8 Hz, 1H), 3.19–3.13 (m, 2H), 3.03 (s, 3H), 2.79 (d, *J* = 15.8 Hz, 1H), 2.21 (s, 3H), 1.11 (br s, 6H), 0.97–0.67 (br m, 6H);

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 185.4, 159.6, 149.3, 148.5, 134.7, 130.5, 108.7, 108.1, 82.9, 71.8, 56.2, 56.2, 48.6 (br), 43.3 (br), 40.6, 29.8, 26.6, 24.6 (br, ×2), 23.2 (br, ×2), 16.0.

HRMS (ESI+) m/z: calctd for $C_{21}H_{32}N_3O_3$ [M+H$^+$] 374.2438, found 374.2432.

***cis*-2-Benzyl-7,8-dimethoxy-1',2'-dimethyl-3-phenyl-1,2,3,5-tetrahydrospiro[benzo[*c*]azepine-4,4'-imidazol]-5'(1'*H*)-one 4i**



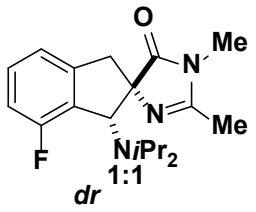
Yield 65 mg (0.14 mmol, 46%). R_f = 0.64 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (800 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 7.35 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.18–7.12 (m, 3H), 6.67 (br s, 1H), 6.45 (br s, 1H), 4.12 (br s, 1H), 4.02 (br s, 1H), 3.87 (s, 3H), 3.84–3.75 (m, 4H), 3.61 (br d, J = 14.2 Hz, 1H), 3.50 (br s, 1H), 3.26 (d, *J* = 14.2 Hz, 1H), 2.54 (s, 3H), 1.97 (s, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 184.6, 160.6, 147.9, 147.5, 140.2, 138.8, 129.6, 129.5 (×2), 128.7 (×2), 128.4, 128.2 (×2), 127.7, 127.2 (×2), 126.8, 113.5, 113.1, 75.6, 57.1 (br), 56.2 (br), 56.1, 56.0, 40.4 (br), 29.8 (br), 26.1, 15.2.

HRMS (ESI+) m/z: calctd for $C_{29}H_{32}N_3O_3$ [M+H$^+$] 470.2430, found 470.2438.

1'-Diisopropylamino-1,2-dimethyl-7'-fluoro-1',3'-dihydrospiro[imidazole-4,2'-inden]-5(1*H*)-one 3j



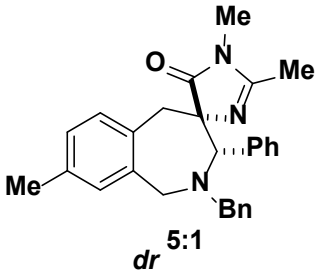
Yield 73 mg (0.22 mmol, 74%). R_f = 0.30 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300K): δ (for ***both*** isomers, without attribution) = 7.25–7.11 (m, 1H), 6.99 (d, *J* = 7.5 Hz, 0.5H), 6.93 (d, *J* = 7.5 Hz, 0.5H), 6.83 (td, J = 8.4, 3.3 Hz, 1H), 5.09 (s, 0.5H), 4.65 (s, 0.5H), 3.50 (d, *J* = 18.0 Hz, 0.5H), 3.21 (hept, *J* = 6.6 Hz, 1H), 3.11 (s, 1H), 3.05 (s, 1.5H), 3.03 (s, 1.5H), 2.74 (d, *J* = 16.4 Hz, 0.5H), 2.66 (hept, *J* = 6.5 Hz, 0.5H), 2.23 (s, 1.5H), 2.20 (s, 1.5H), 1.26–0.62 (br m, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300K): δ (for ***both*** isomers, without attribution) = 186.0, 180.9, 159.9 (d, *J* = 249.7 Hz, for both isomers), 159.8, 159.2, 144.6 (d, *J* = 5.4 Hz), 143.0 (d, *J* = 5.3 Hz), 130.2 (d, *J* = 7.7 Hz), 129.7 (d, *J* = 8.0 Hz), 129.4 (d, *J* = 13.9 Hz), 128.8 (d, *J* = 16.6 Hz), 120.7 (d, *J* = 3.3 Hz), 120.5 (d, *J* = 3.4 Hz), 114.2 (d, *J* = 16.8 Hz), 113.9 (d, *J* = 16.0 Hz), 81.2, 80.3, 69.8, 69.0, 48.7, 44.1, 41.4, 40.9, 26.5 (for both isomers), 23.8, 22.5, 21.8[3], 21.7[5], 21.2, 15.9, 15.7. *Isopropyl signals too broad to be determined for second isomer.*

HRMS (ESI+) m/z: calctd for $C_{19}H_{27}FN_3O$ [M+H$^+$] 332.2133, found 332.2137.

***cis*-2-Benzyl-1',2',8-trimethyl-3-phenyl-1,2,3,5-tetrahydrospiro[benzo[*c*]azepine-4,4'-imidazol]-5'(1'*H*)-one 4k**



Yield 74 mg (0.17 mmol, 58%). R_f = 0.20 (SiO_2, EtOAc), colorless oil.

^{1}H NMR (800 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 7.42–7.31 (m, 2H), 7.31–7.24 (m, 4H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.17–7.08 (m, 3H), 7.01 (br d, *J* = 7.4 Hz, 1H), 6.96 (br s, 1H), 6.84 (br d, *J* = 7.4 Hz, 1H), 4.17 (br s, 1H), 3.96 (br s, 1H), 3.80 (br d, *J* = 14.4 Hz, 1H), 3.63–3.34 (m, 2H), 3.21 (d, *J* = 14.2 Hz, 1H), 2.79 (br s, 1H), 2.53 (s, 3H), 2.33 (s, 3H), 1.97 (s, 3H).

^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$, 300K): δ (for ***cis*** isomer) = 184.7, 160.6, 140.2, 138.9, 137.4, 137.1, 130.6, 129.6 (×2), 129.2, 128.8 (×2), 128.4, 128.2 (×2), 127.7^2, 127.6^9, 127.2 (×2), 126.8, 75.5 (br), 57.1 (br), 40.7 (br), 29.8 (br), 26.1, 21.3, 15.2. *One carbon signal too broad to be determined.*

HRMS (ESI+) m/z: calctd for $C_{28}H_{30}N_3O$ [M+H$^+$] 424.2383, found 424.2379.

References

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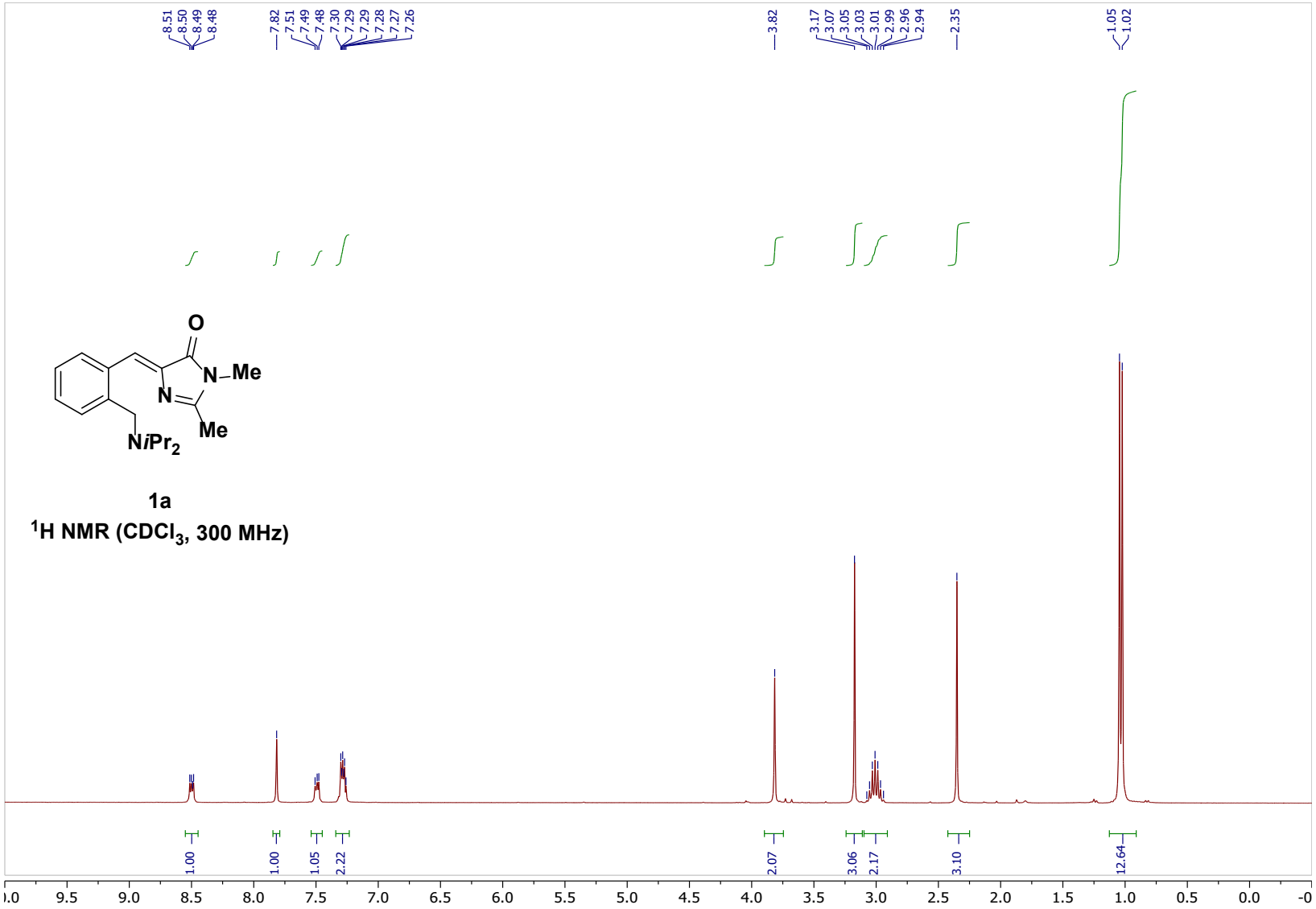
S2. K. Mori, K. Kurihara and T. Akiyama, *Chem. Commun.,* 2014, **50**, 3729; https://doi.org/10.1039/c4cc00894d.

S3. K. Mori, K. Kurihara, S. Yabe, M. Yamanaka and T. Akiyama, *J. Am. Chem. Soc.,* 2014, **136**, 3744; https://doi.org/10.1021/ja412706d.

S4. J. Nagaki, T. Kawasaki-Takasuka and K. Mori, *Synlett,* 2024; https://doi.org/10.1055/a-2287-9391.

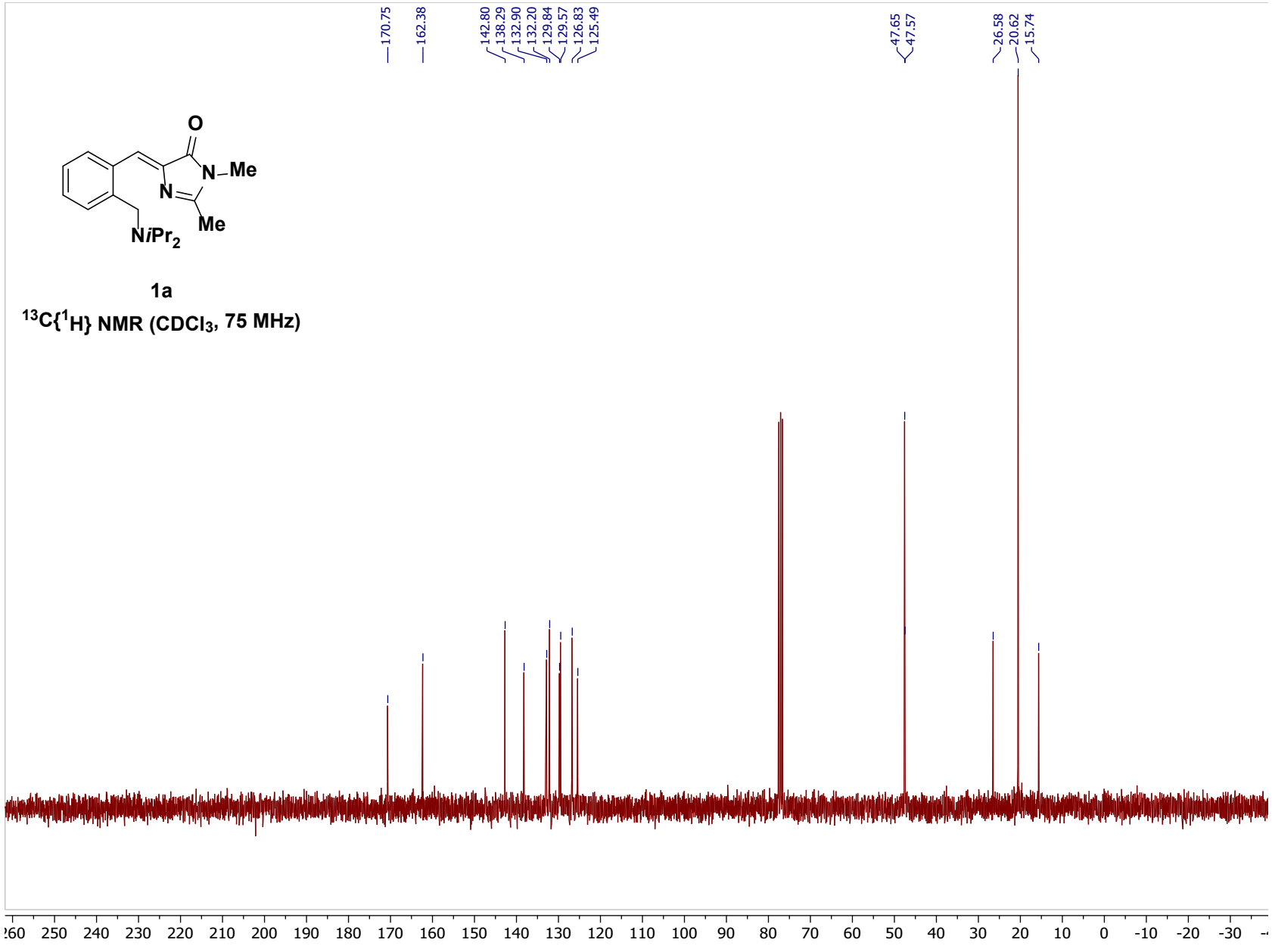
S5. A. P. Gorulya, A. V. Tverdokhlebov, A. A. Tolmachev, O. V. Shishkin and S. V. Shishkina, *Tetrahedron,* 2011, **67**, 1030; https://doi.org/10.1016/j.tet.2010.11.101.

Copies of NMR spectra



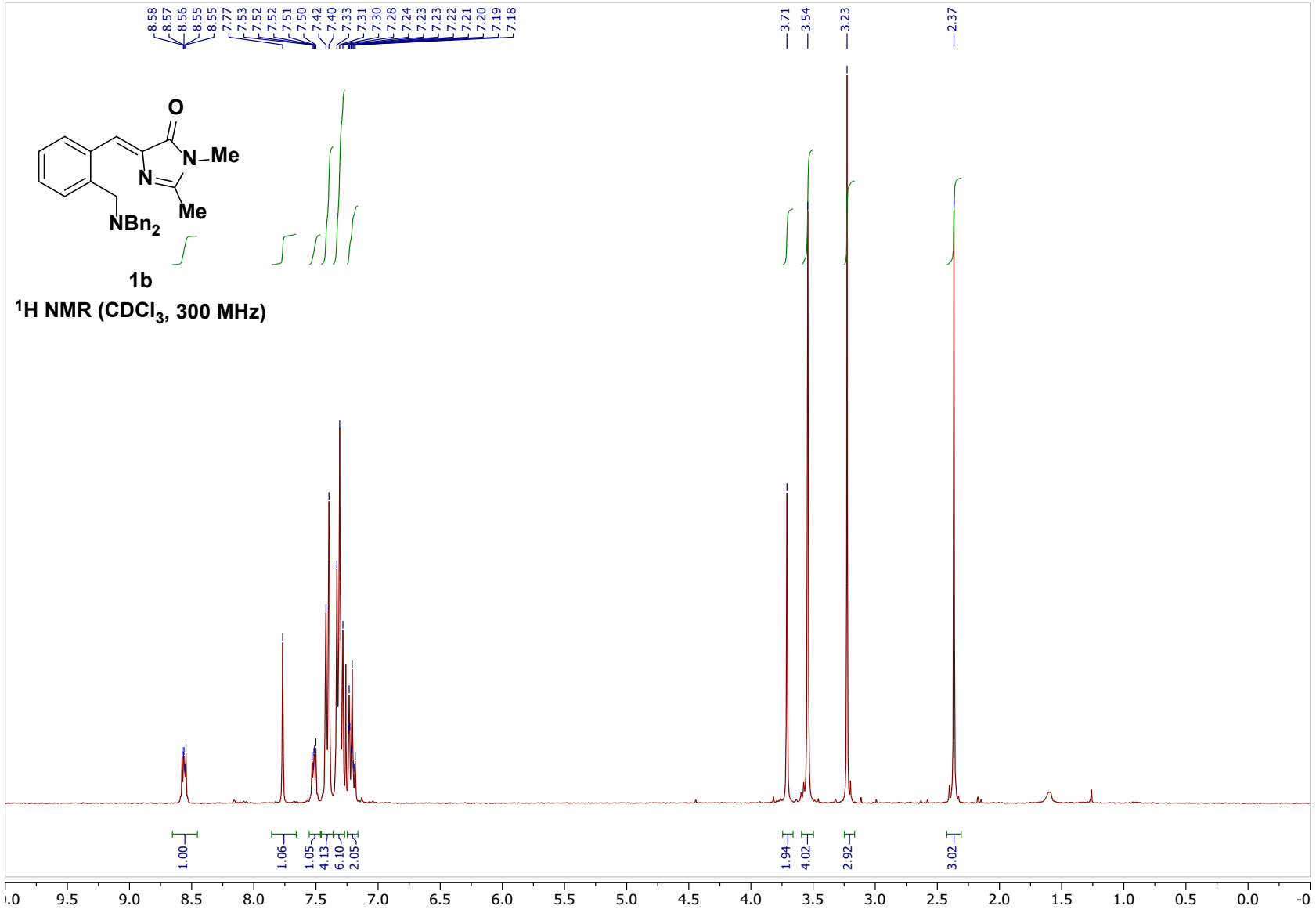
1a

^{1}H NMR ($CDCl_3$, 300 MHz)



1a

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)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7.23
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7.21
7.20
7.19
7.18
3.71
3.54
3.23
2.37
O
N–Me
N
Me
NBn2
1b
1H NMR (CDCl3, 300 MHz)
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1.05
4.13
6.10
2.05
1.94
4.02
2.92
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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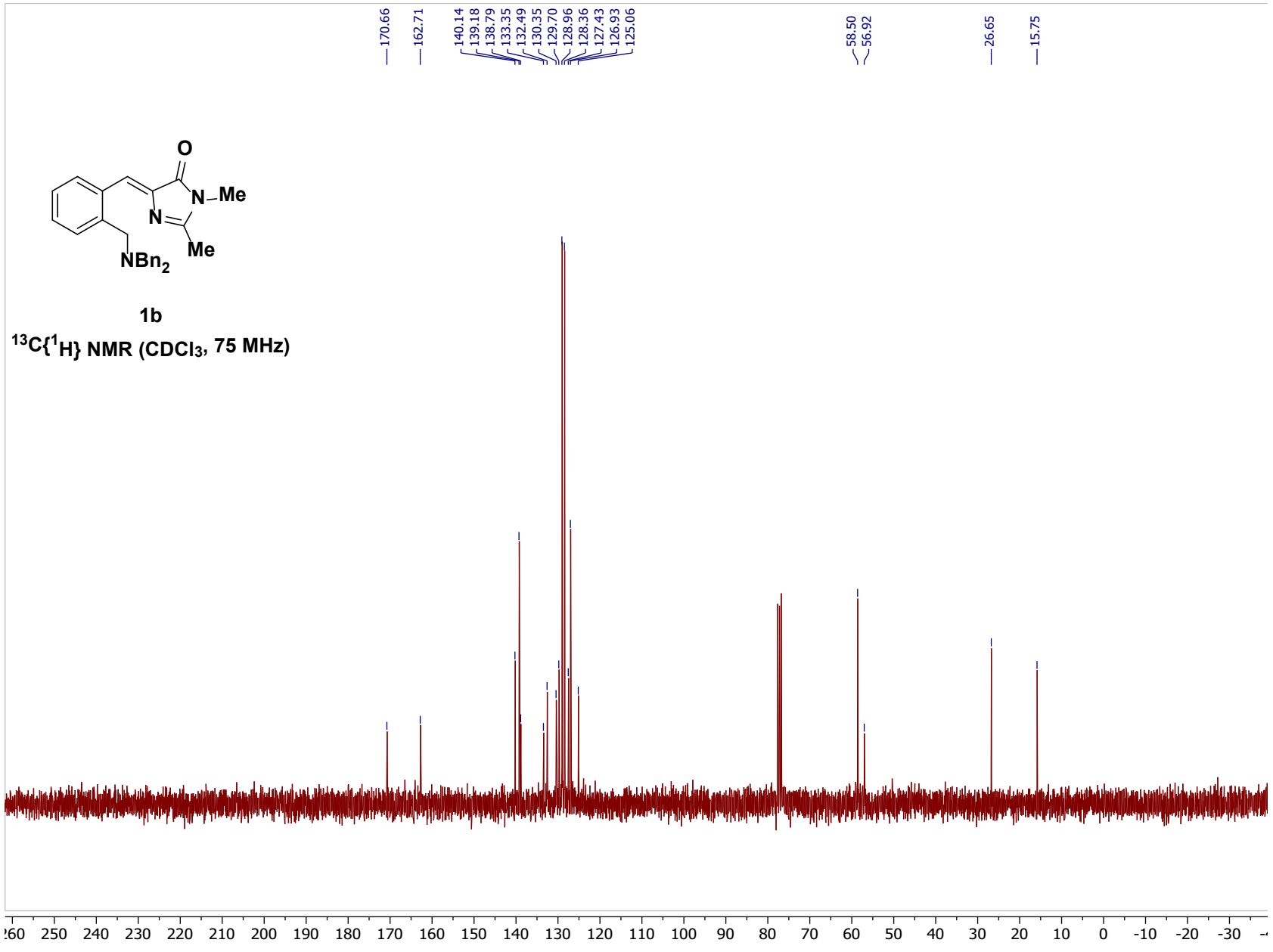
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N
Me
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1b
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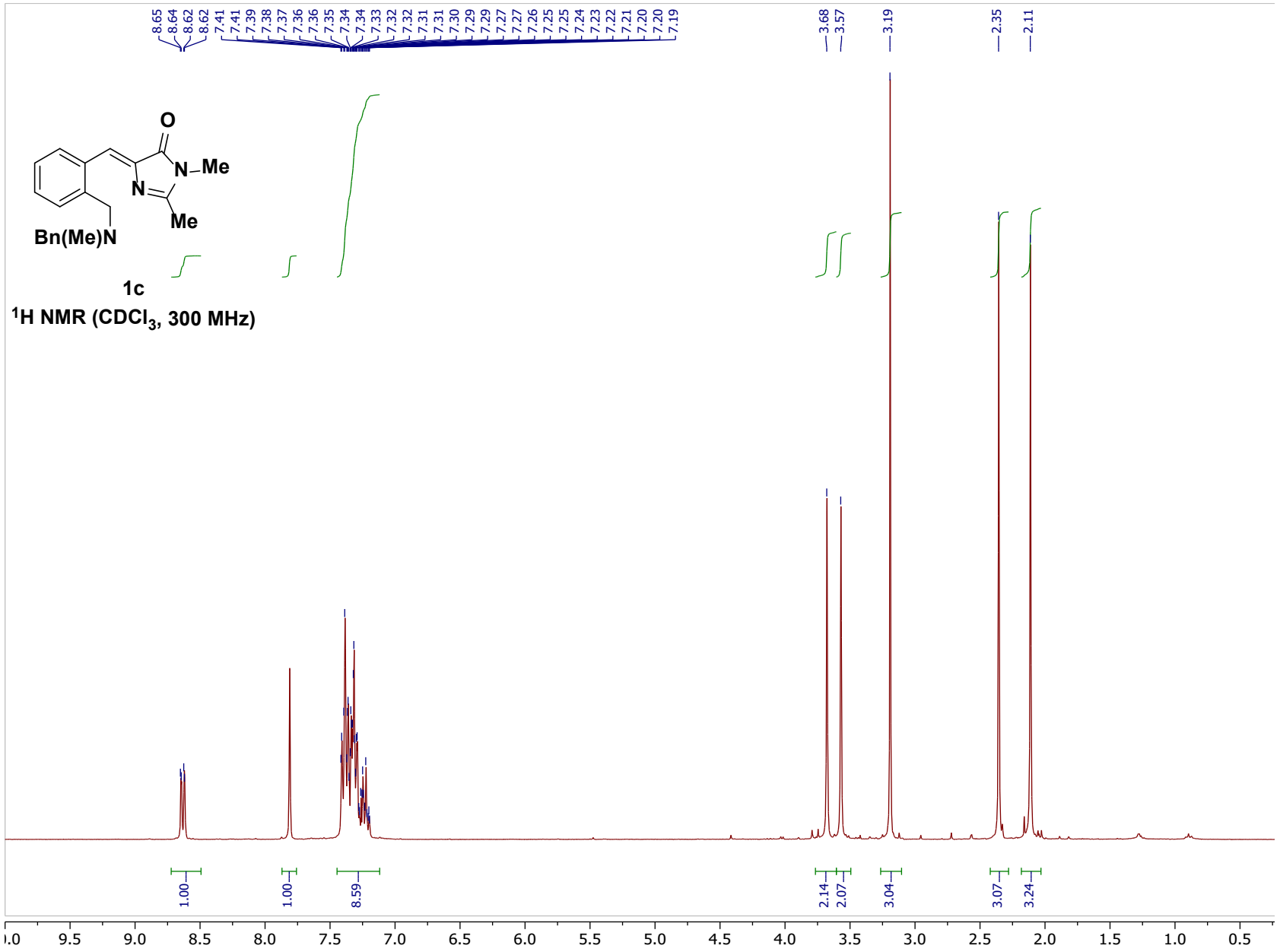
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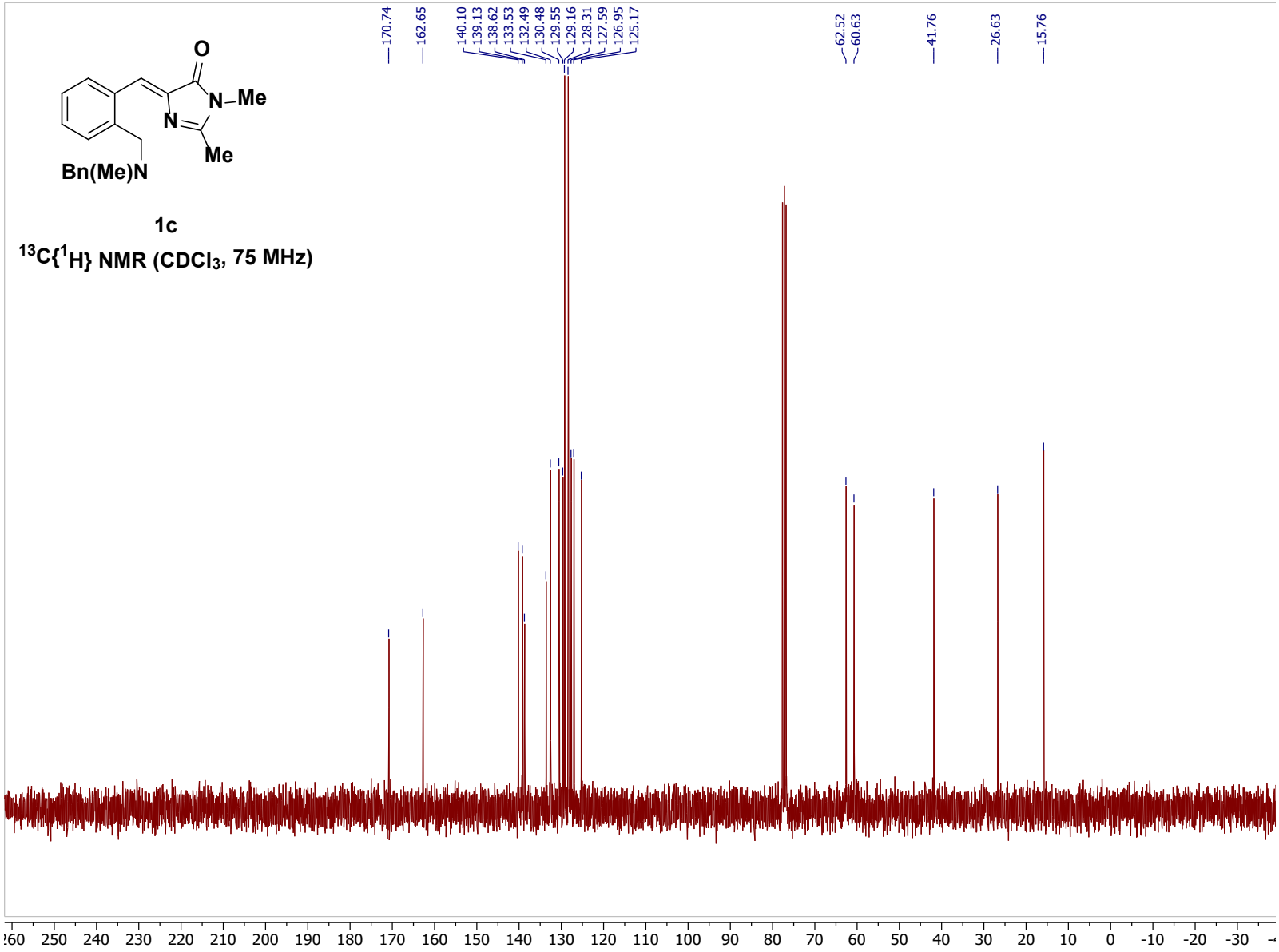
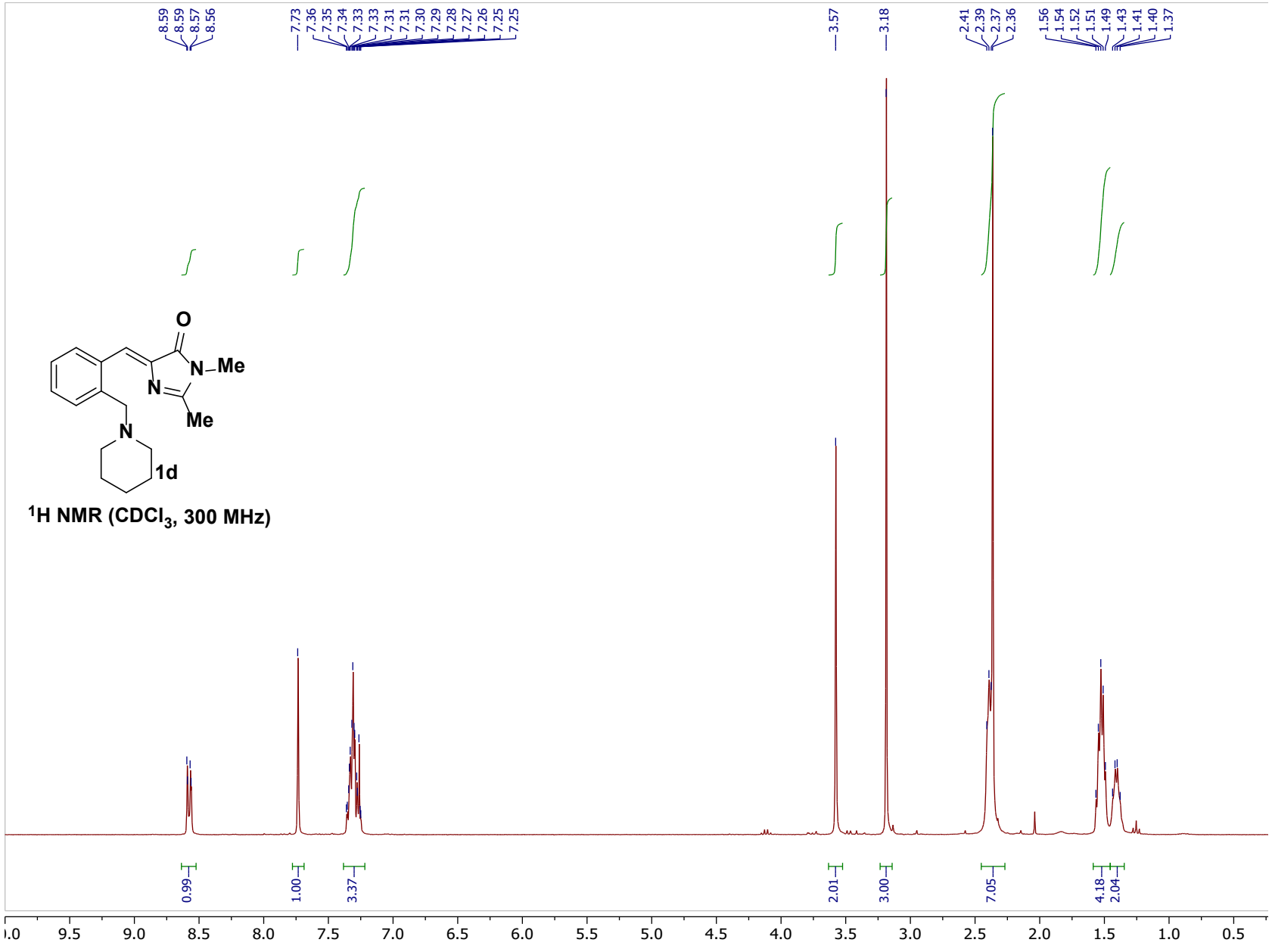
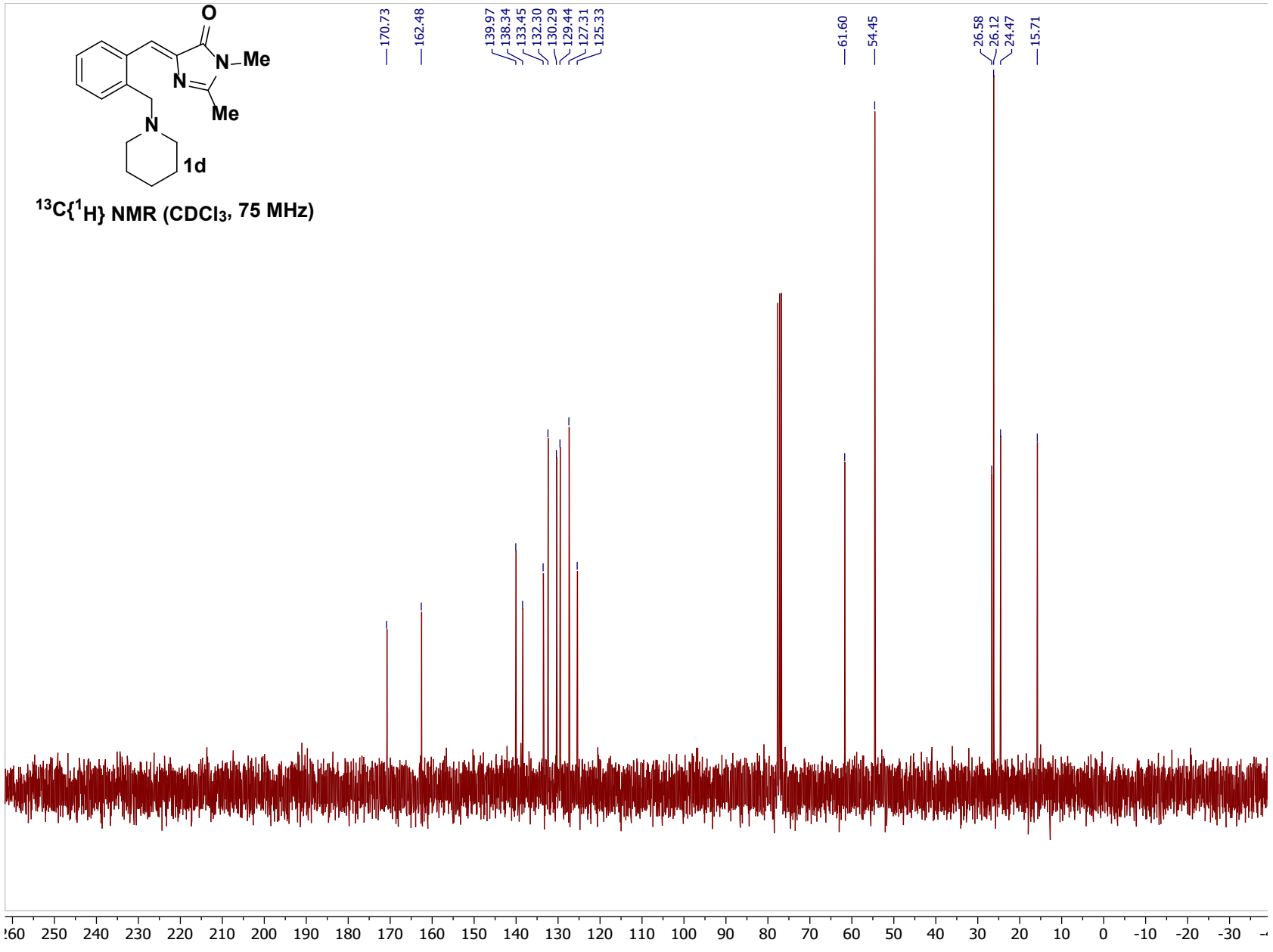
2.5
2.0
1.5
1.0
0.5

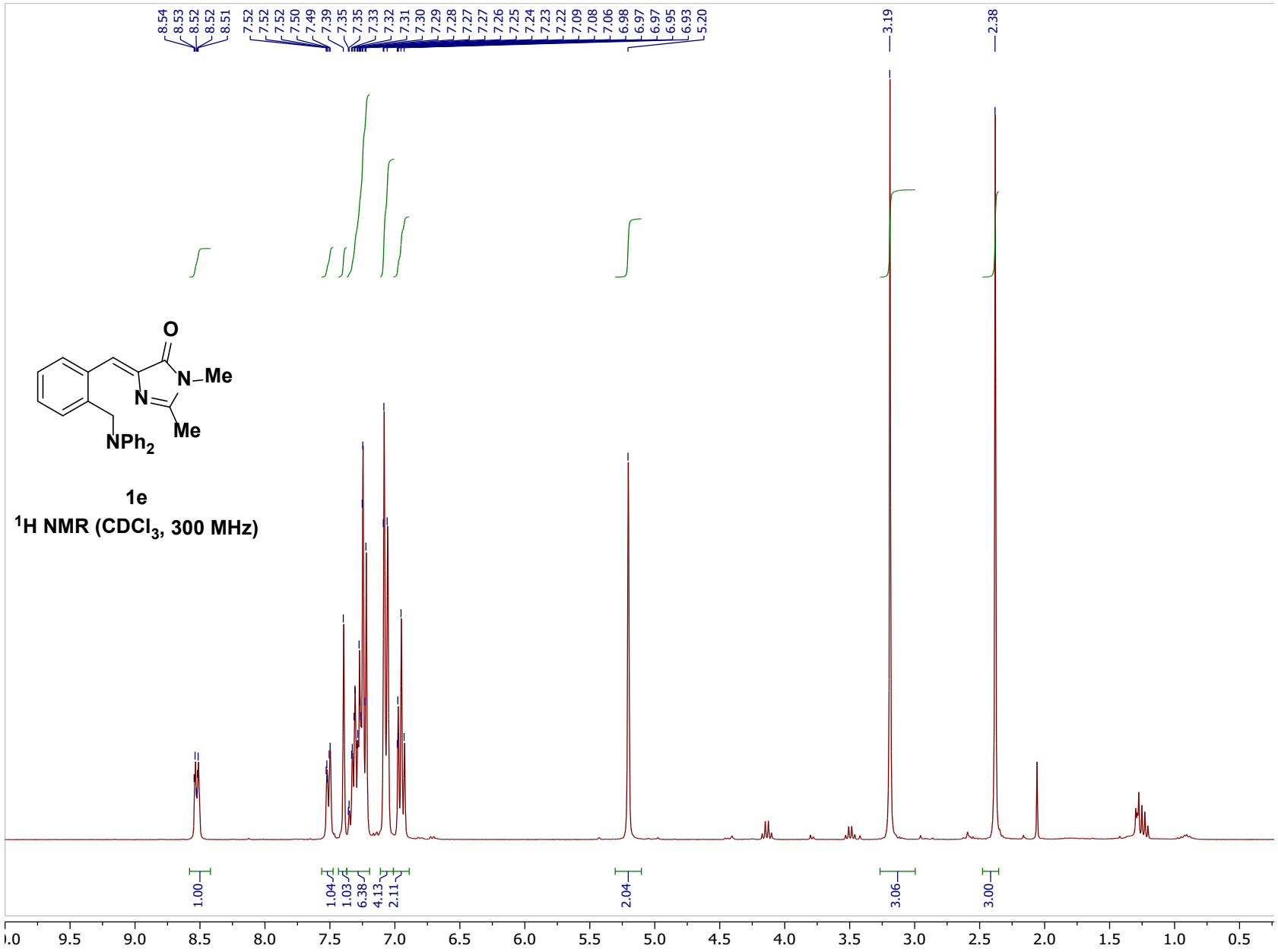

O
N–Me
N
Me
Bn(Me)N
1c
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)
170.74
162.65
140.10
139.13
138.62
133.53
132.49
130.48
129.55
129.16
128.31
127.59
126.95
125.17
62.52
60.63
41.76
26.63
15.76
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30

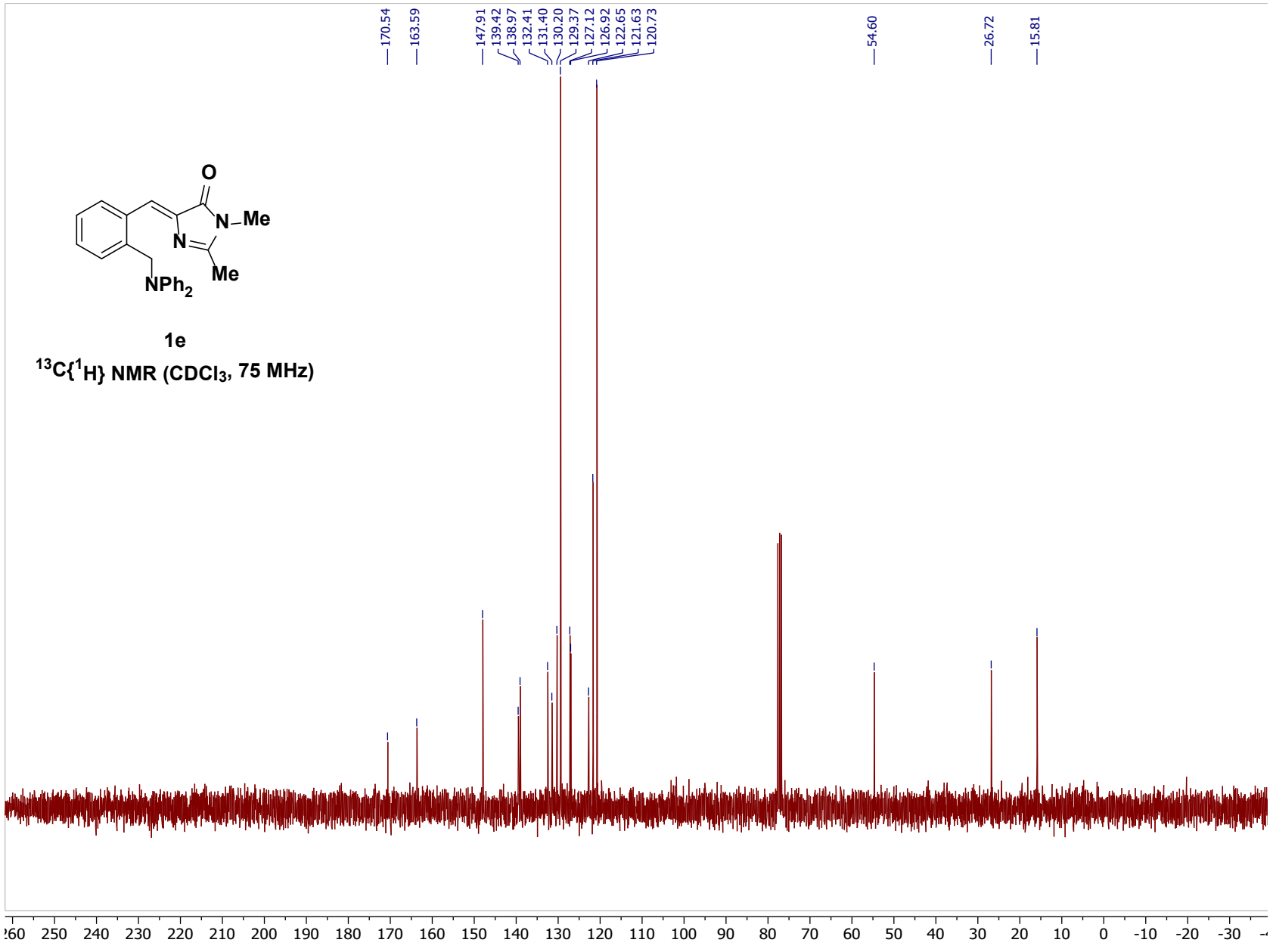


^{1}H NMR ($CDCl_3$, 300 MHz)



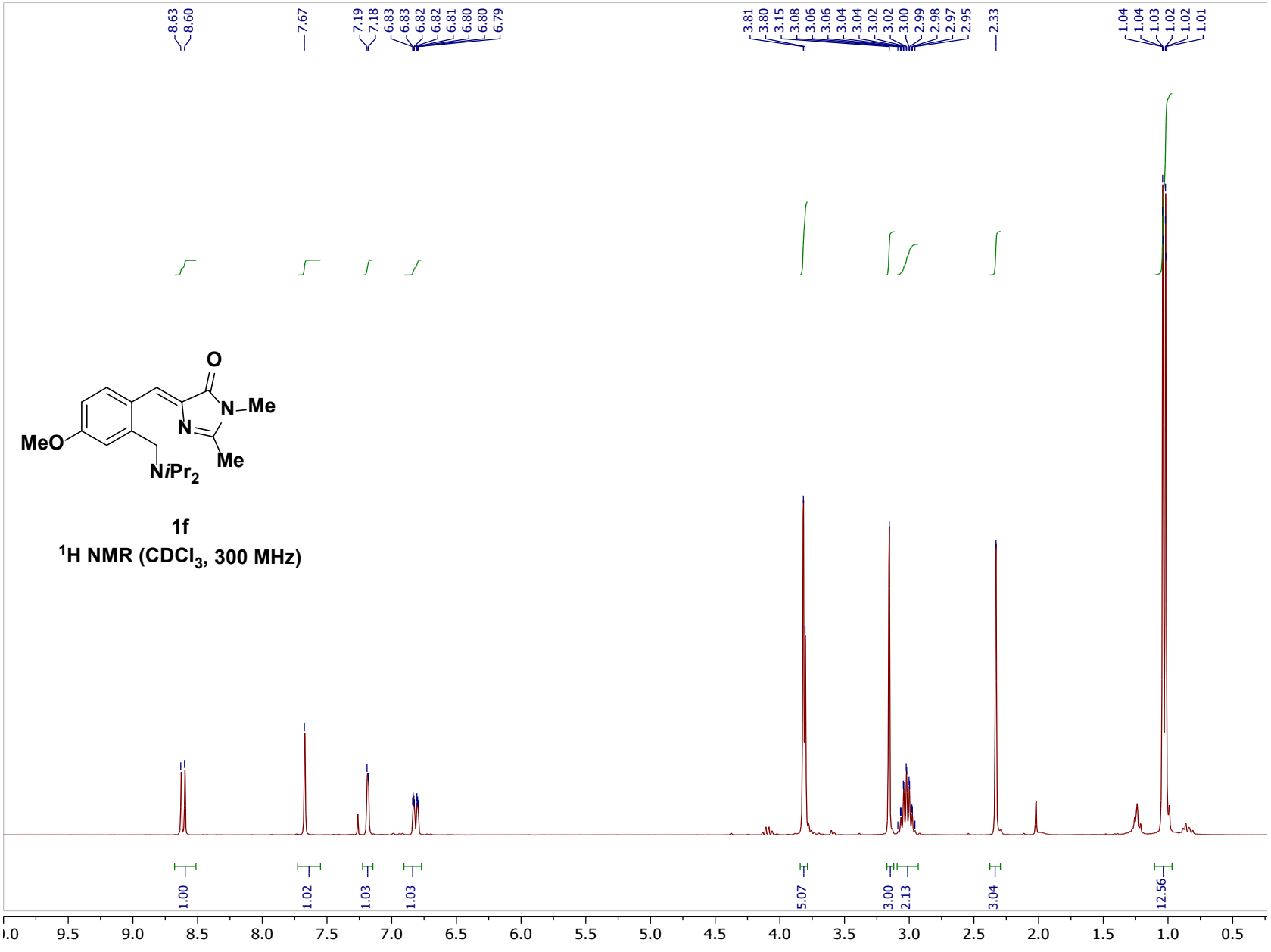
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)


8.54
8.53
8.52
8.52
8.51
7.52
7.52
7.52
7.50
7.49
7.39
7.35
7.35
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.22
7.09
7.08
7.06
6.98
6.97
6.97
6.95
6.93
5.20
3.19
2.38
O
N–Me
N
Me
NPh2
1e
1H NMR (CDCl3, 300 MHz)
1.00
1.04
1.03
6.38
4.13
2.11
2.04
3.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



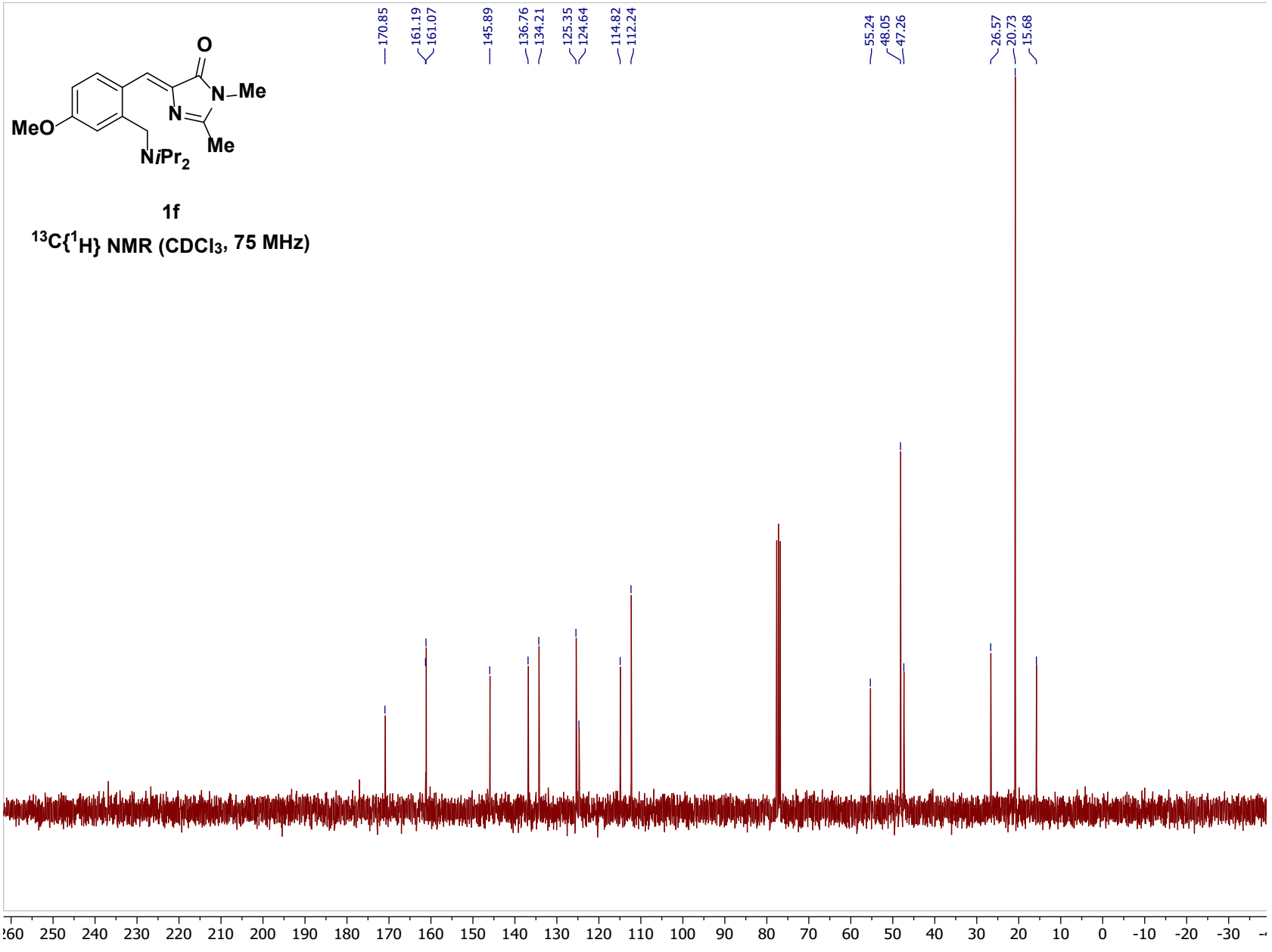
1e

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)



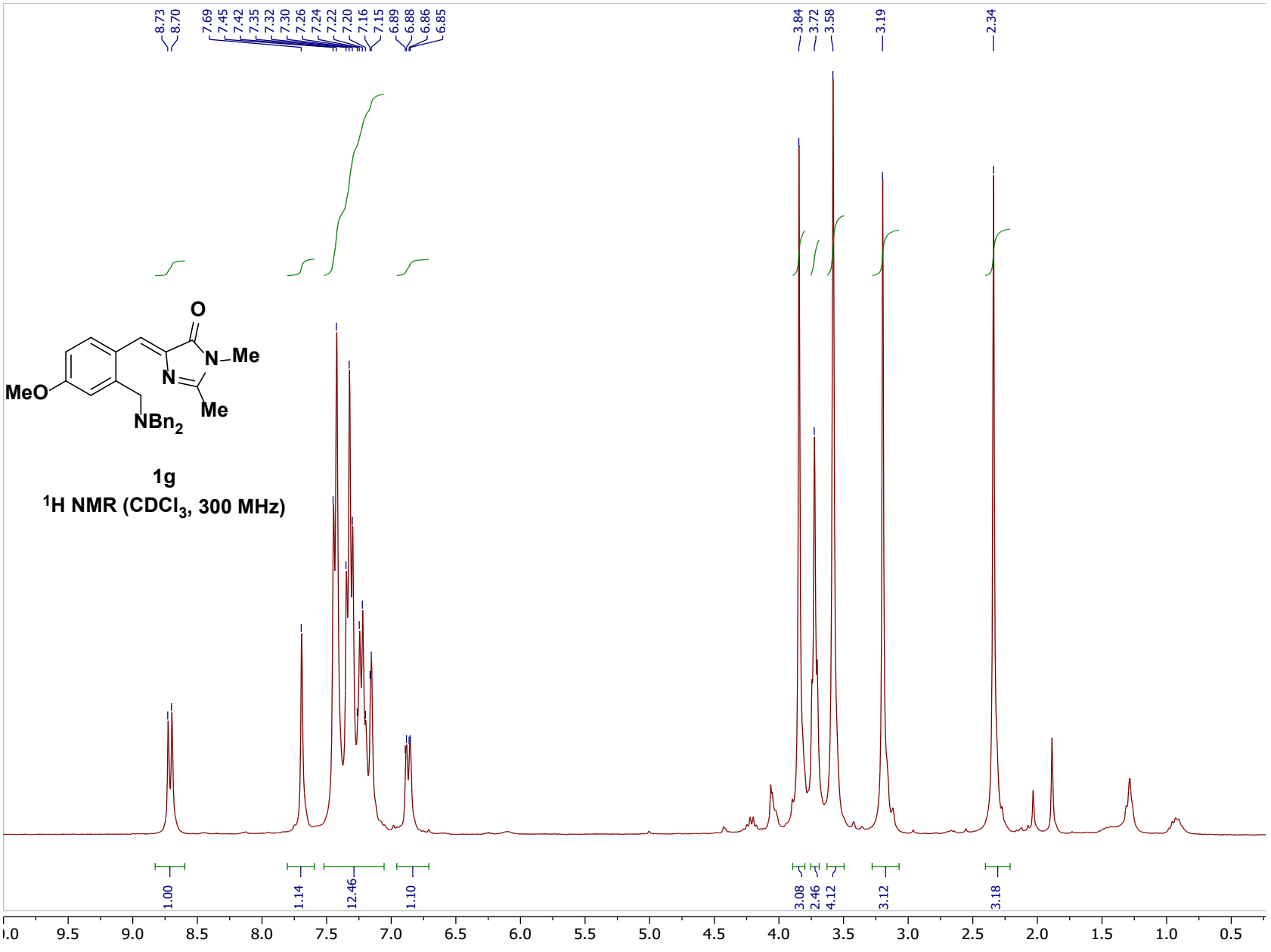
1f

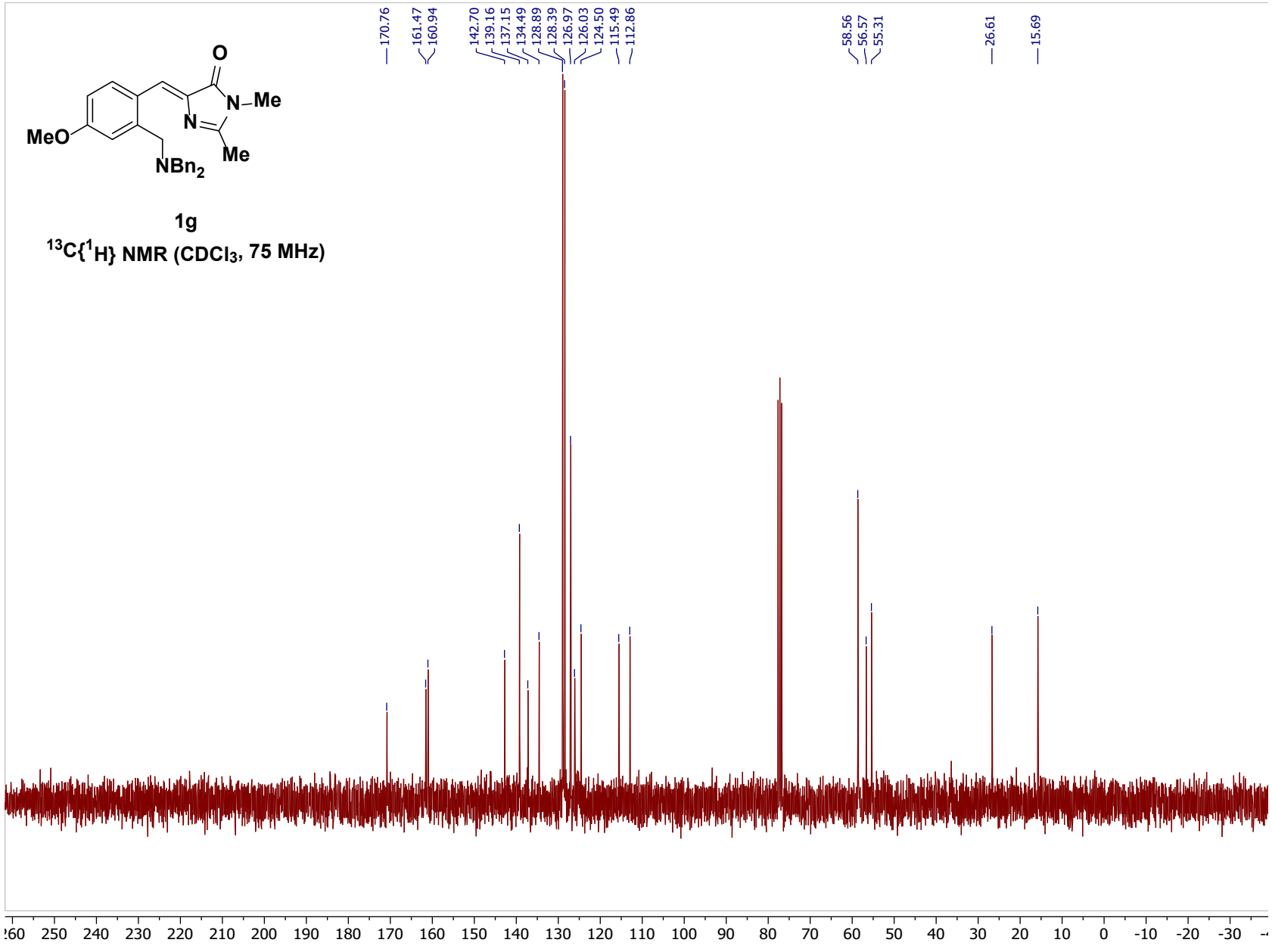
^{1}H NMR ($CDCl_3$, 300 MHz)

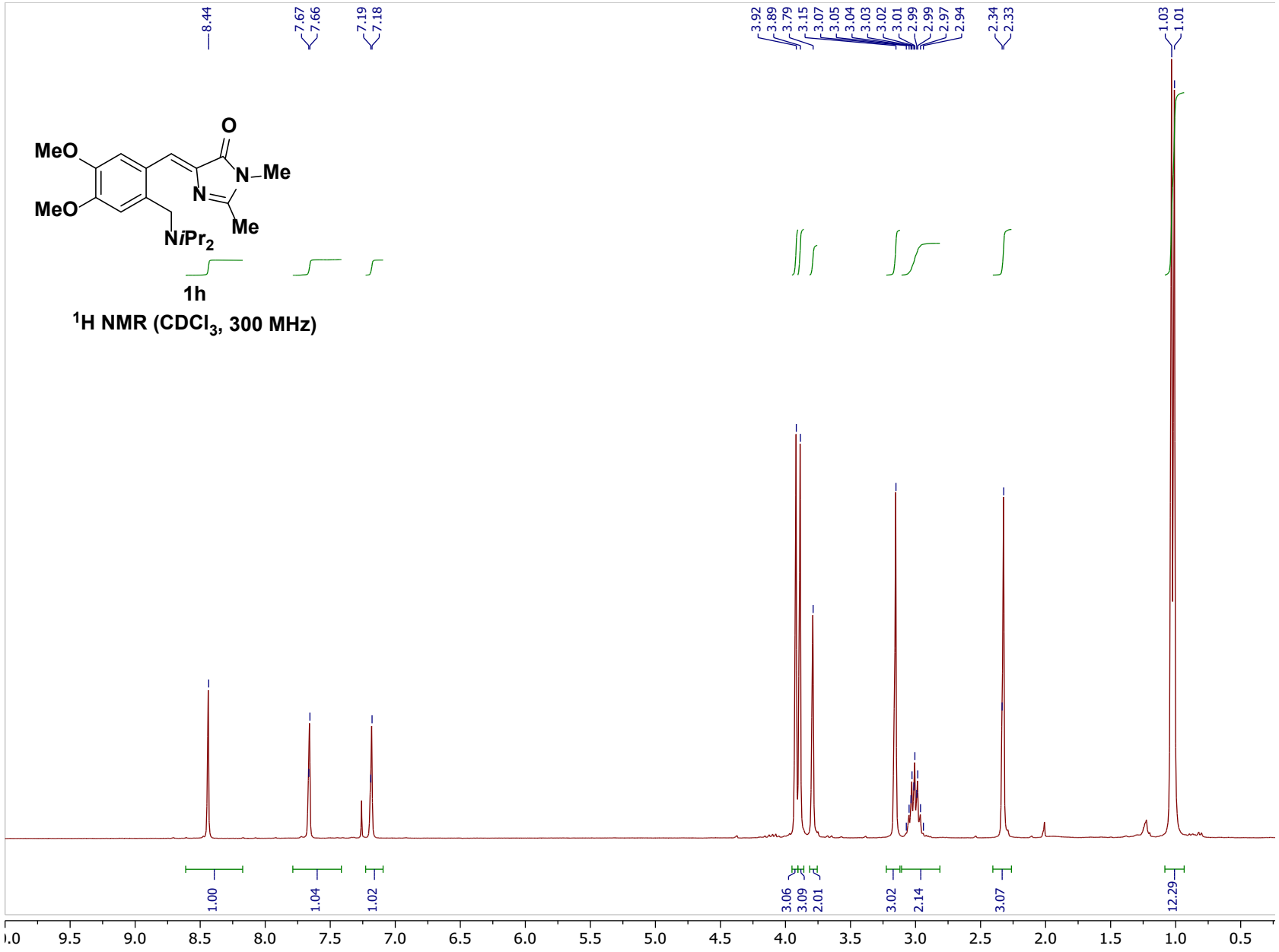


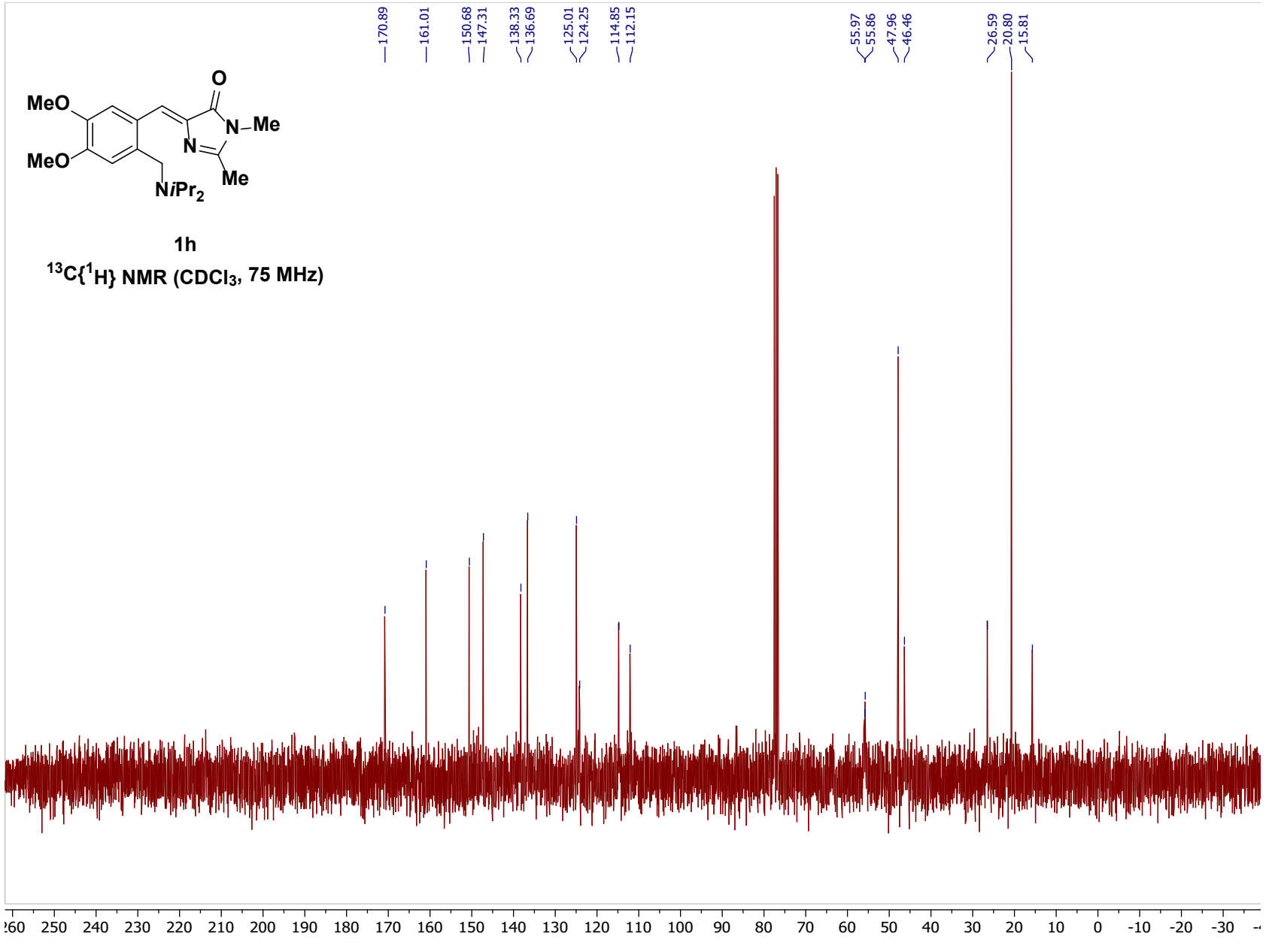
1f

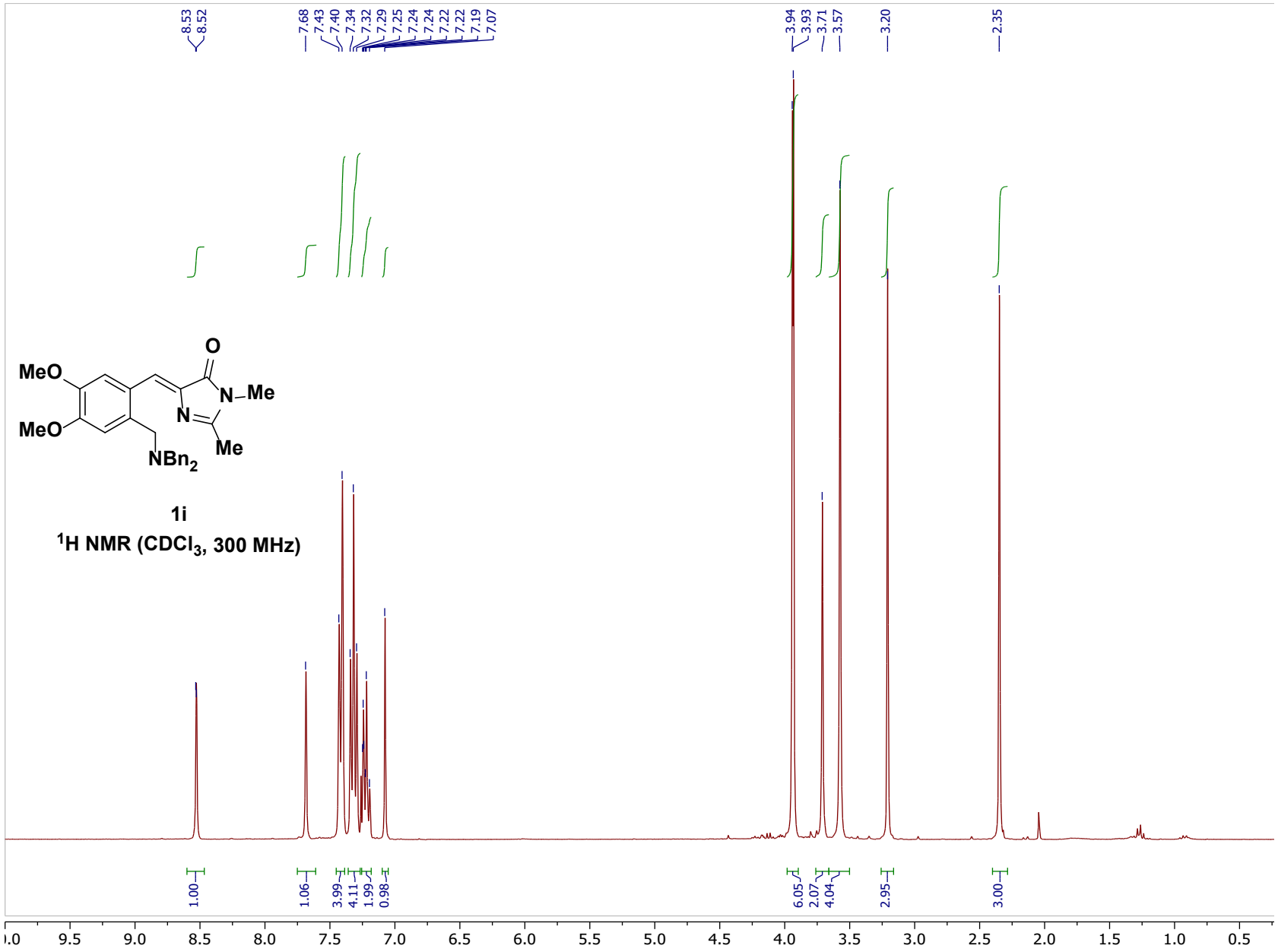
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)

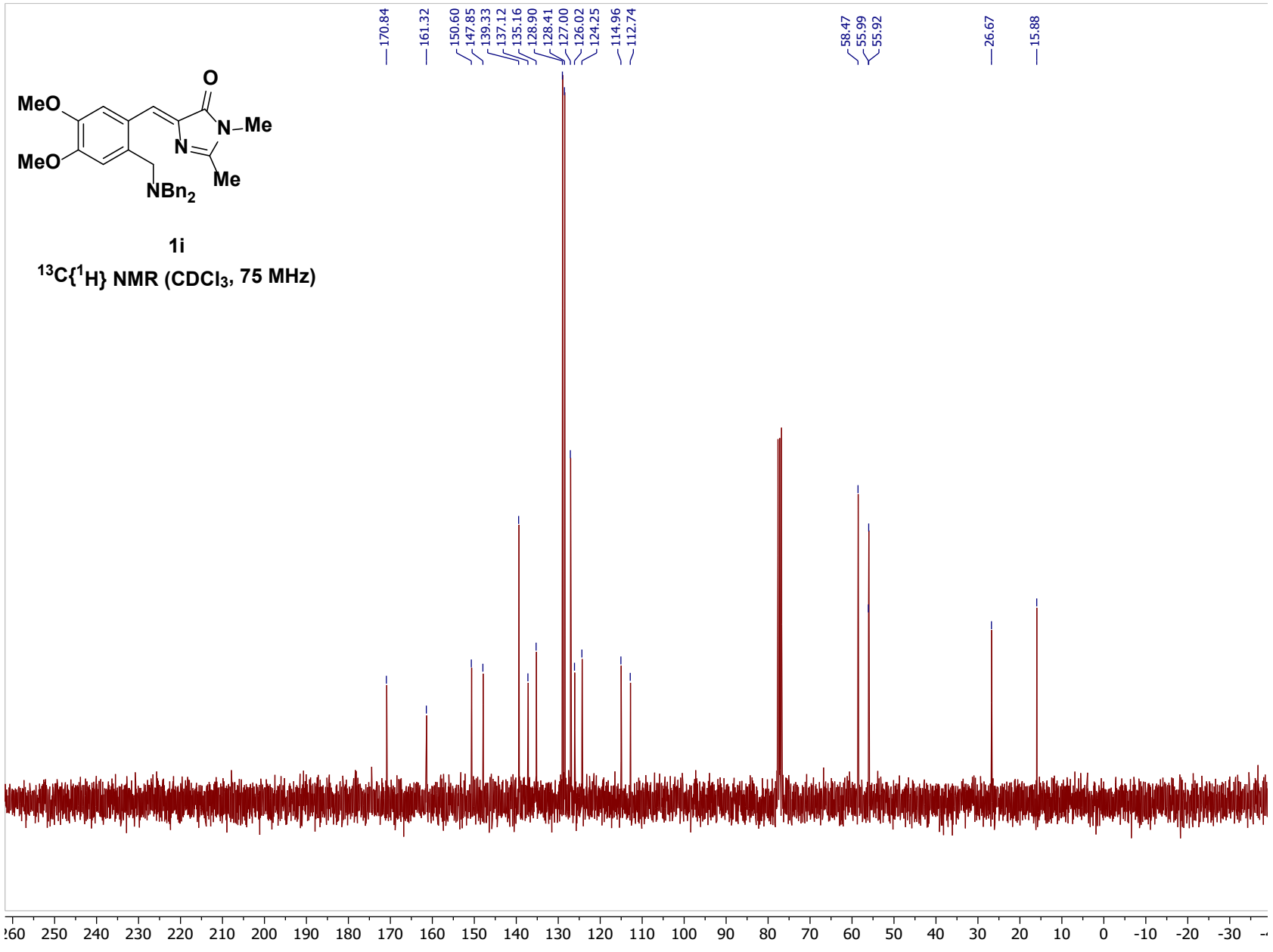

8.73
8.70
7.69
7.45
7.42
7.35
7.32
7.30
7.26
7.24
7.22
7.20
7.16
7.15
6.89
6.88
6.86
6.85
3.84
3.72
3.58
3.19
2.34
O
N–Me
N
Me
MeO
NBn2
1g
1H NMR (CDCl3, 300 MHz)
1.00
1.14
12.46
1.10
3.08
2.46
4.12
3.12
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

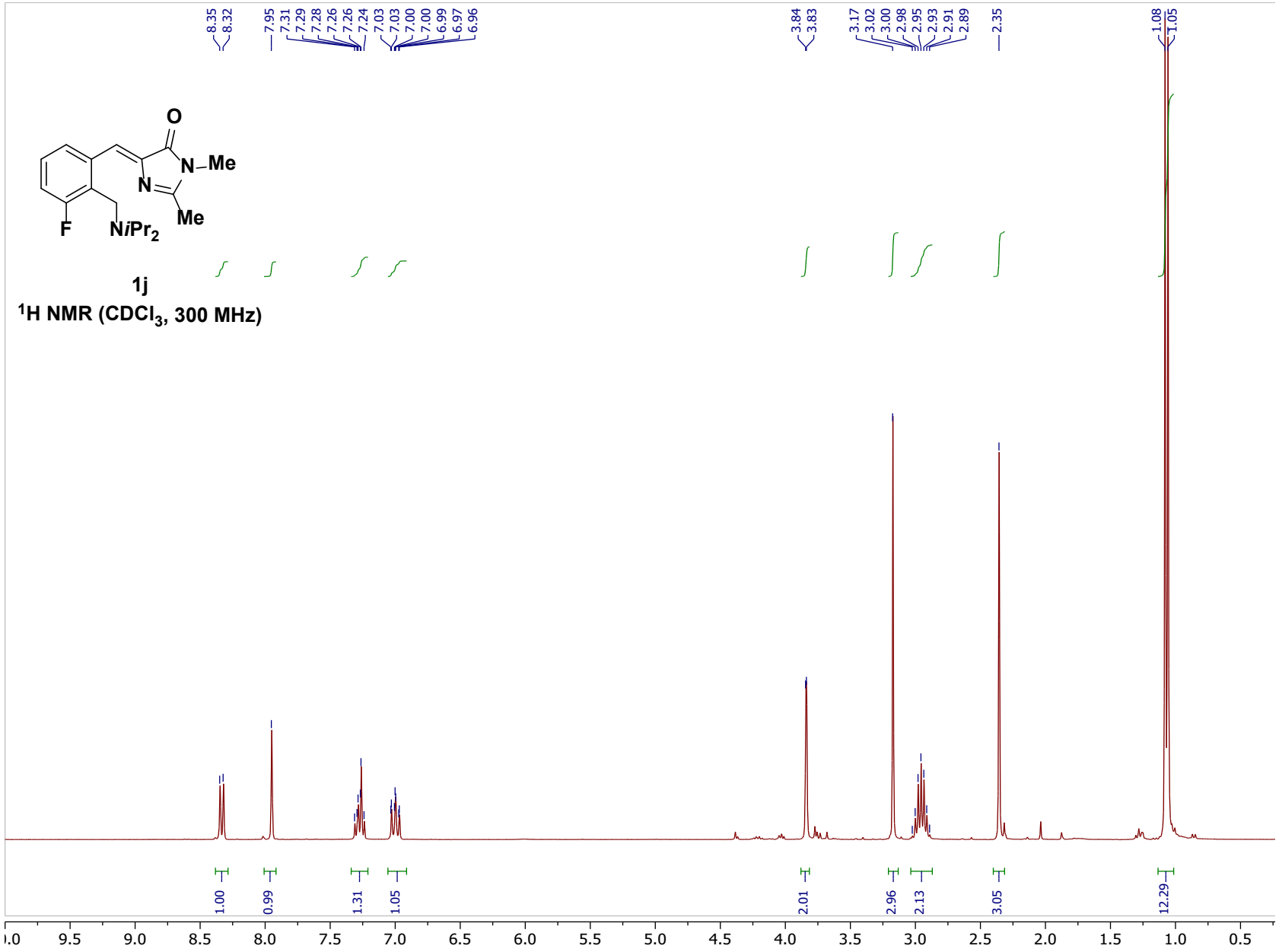

170.76
161.47
160.94
142.70
139.16
137.15
134.49
128.89
128.39
126.97
126.03
124.50
115.49
112.86
58.56
56.57
55.31
26.61
15.69
O
N–Me
N
Me
MeO
NBn2
1g
13C{1H} NMR (CDCl3, 75 MHz)
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30


8.44
7.67
7.66
7.19
7.18
3.92
3.89
3.79
3.15
3.07
3.05
3.04
3.03
3.02
3.01
2.99
2.99
2.97
2.94
2.34
2.33
1.03
1.01
MeO
MeO
O
N–Me
N
Me
NiPr2
1h
1H NMR (CDCl3, 300 MHz)
1.00
1.04
1.02
3.06
3.09
2.01
3.02
2.14
3.07
12.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


170.89
161.01
150.68
147.31
138.33
136.69
125.01
124.25
114.85
112.15
55.97
55.86
47.96
46.46
26.59
20.80
15.81
MeO
MeO
O
N–Me
N
Me
NiPr2
1h
13C{1H} NMR (CDCl3, 75 MHz)
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30

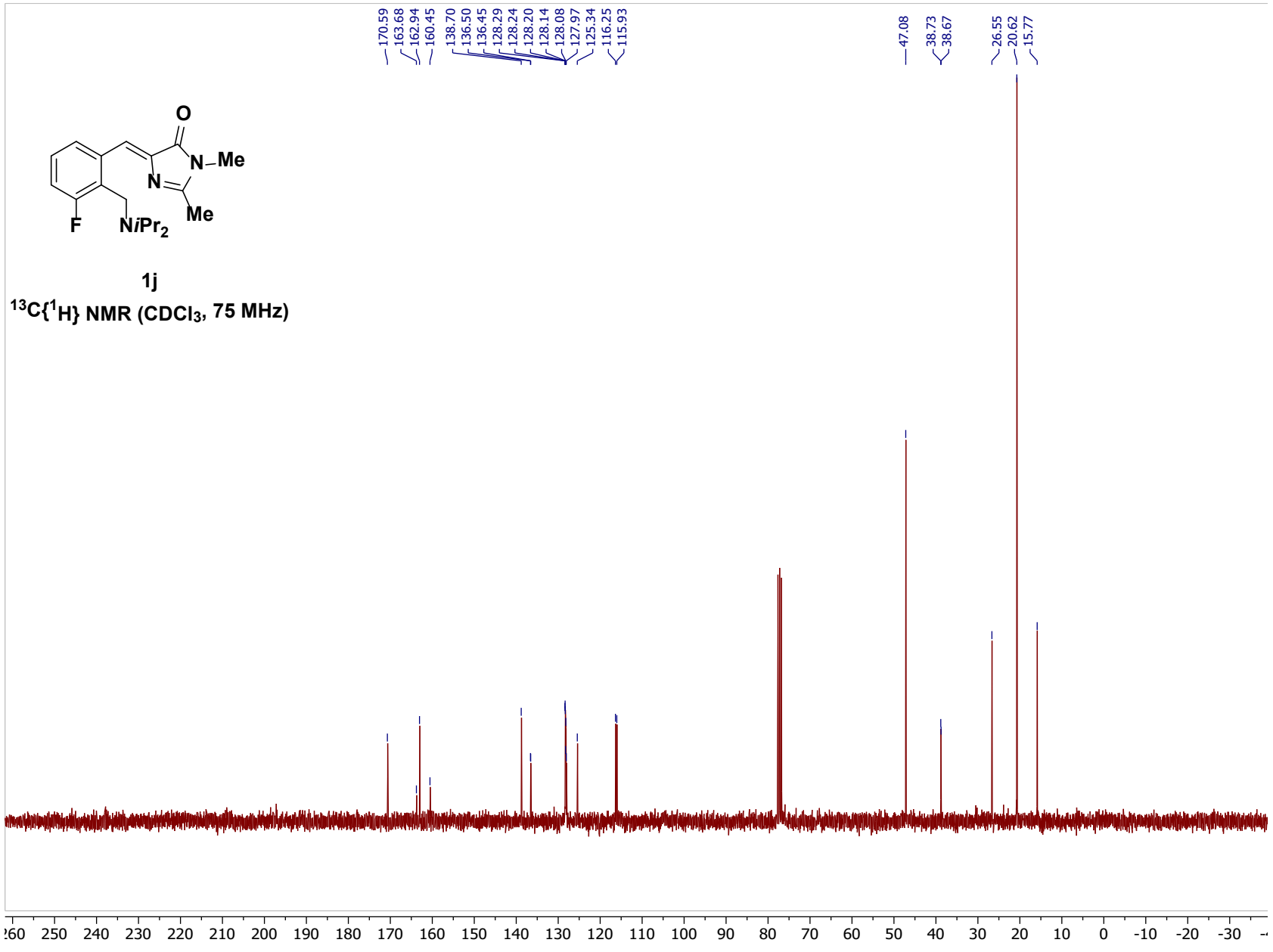

8.53
8.52
7.68
7.43
7.40
7.34
7.32
7.29
7.25
7.24
7.24
7.22
7.22
7.19
7.07
3.94
3.93
3.71
3.57
3.20
2.35
MeO
MeO
O
N–Me
N
Me
NBn2
1i
1H NMR (CDCl3, 300 MHz)
1.00
1.06
3.99
4.11
1.99
0.98
6.05
2.07
4.04
2.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


170.84
161.32
150.60
147.85
139.33
137.12
135.16
128.90
128.41
127.00
126.02
124.25
114.96
112.74
58.47
55.99
55.92
26.67
15.88
MeO
MeO
O
N–Me
N
Me
NBn2
1i
13C{1H} NMR (CDCl3, 75 MHz)
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30



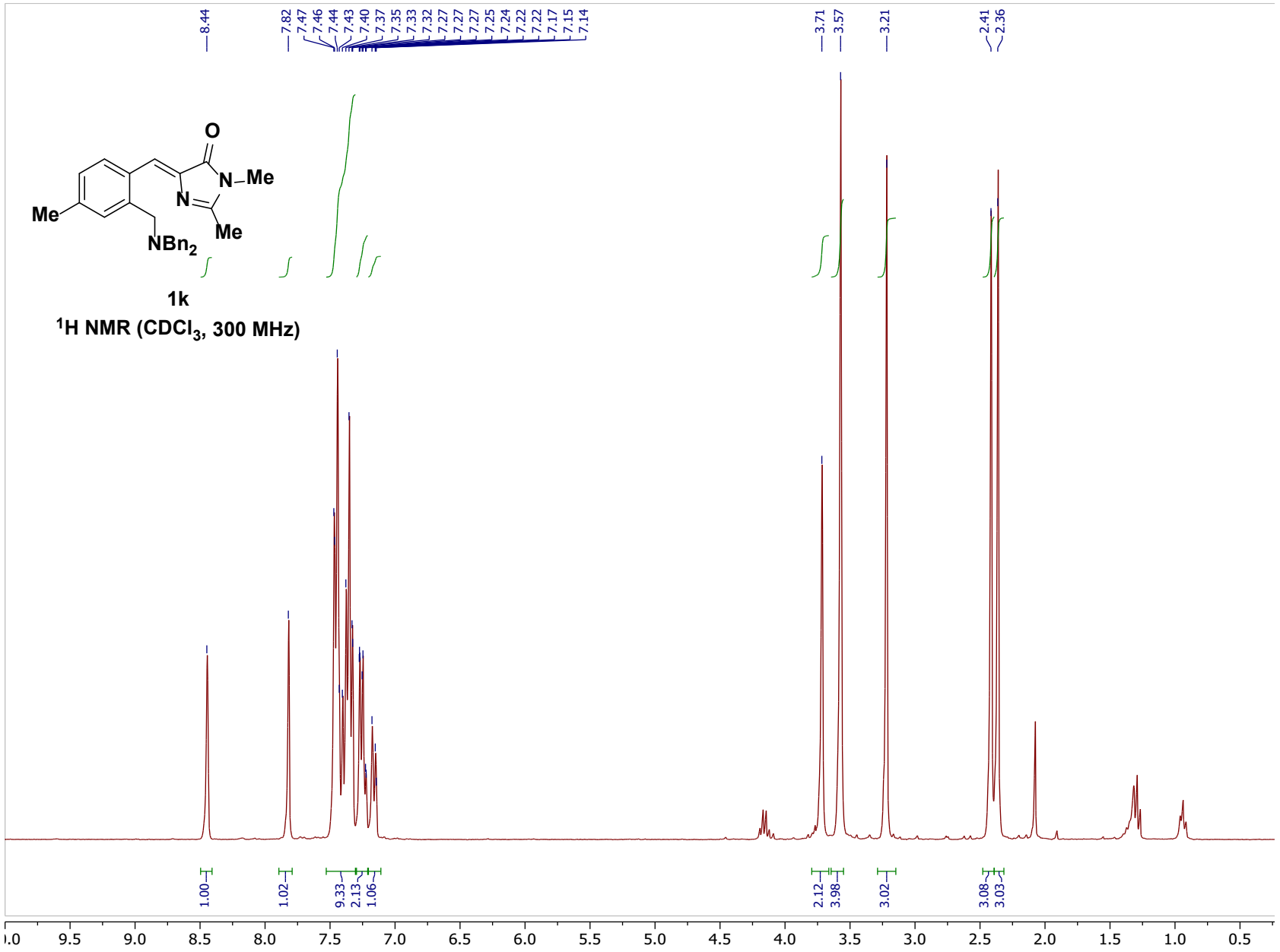
1j

^{1}H NMR ($CDCl_3$, 300 MHz)



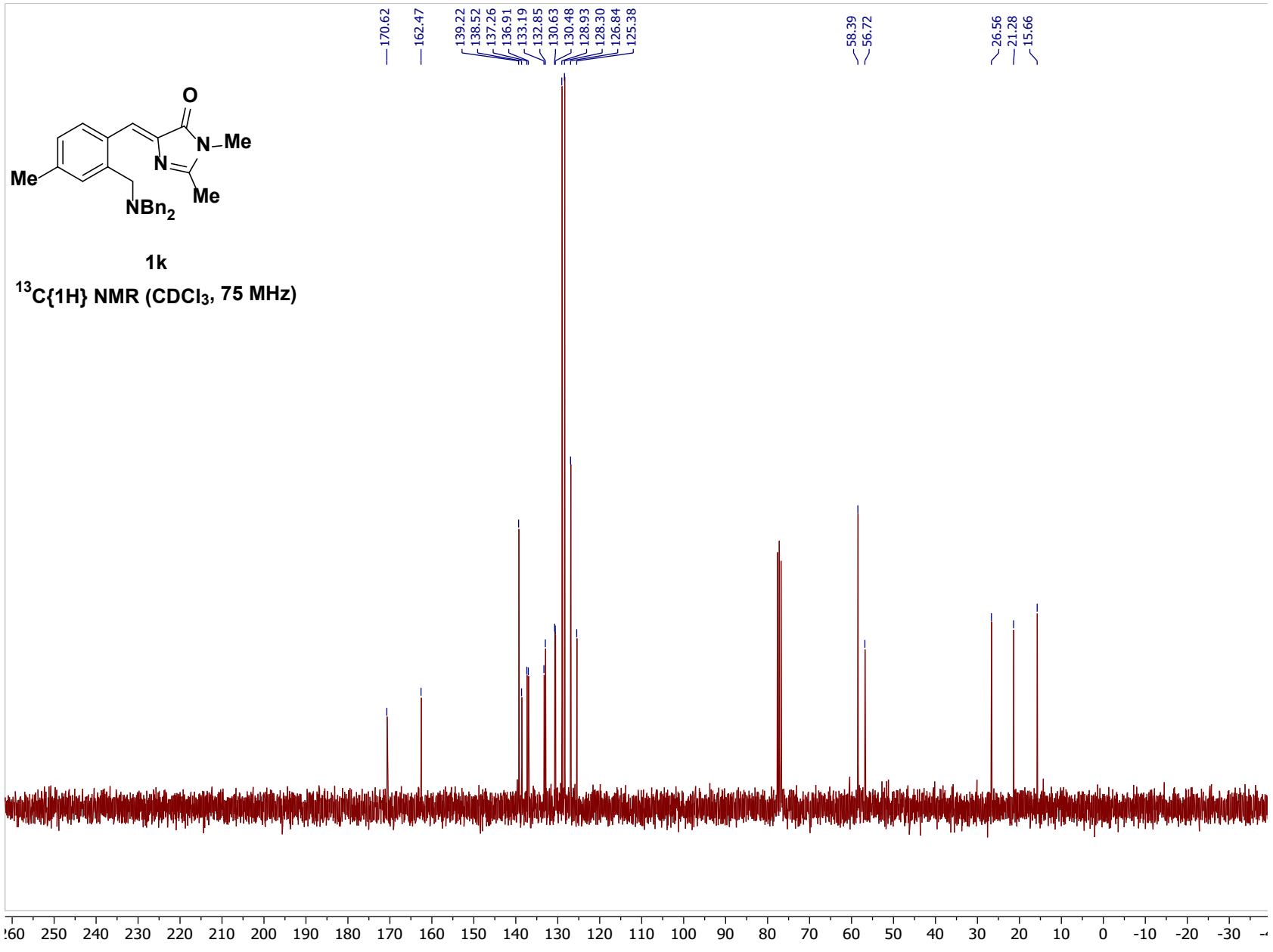
1j

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)



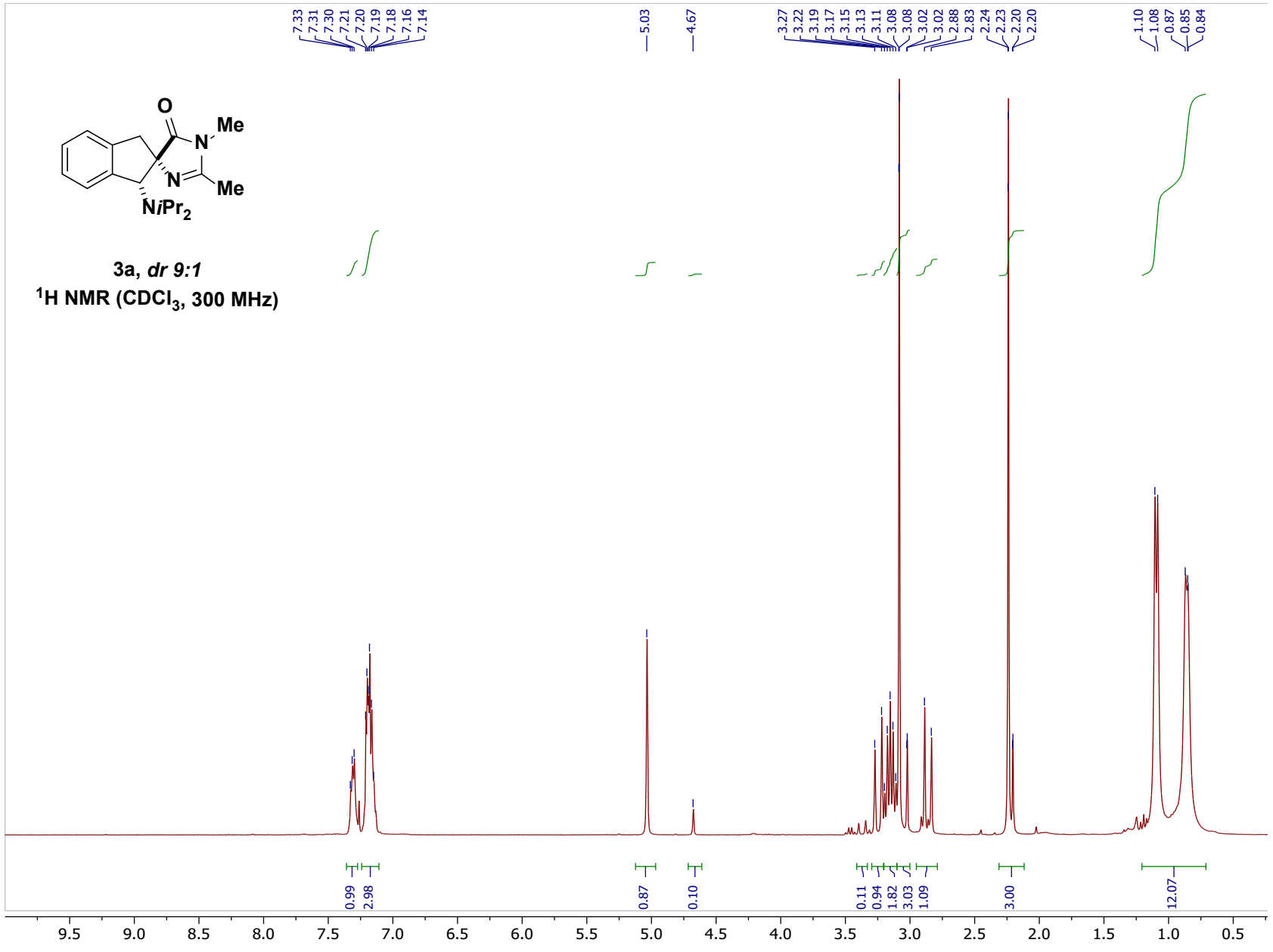
1k

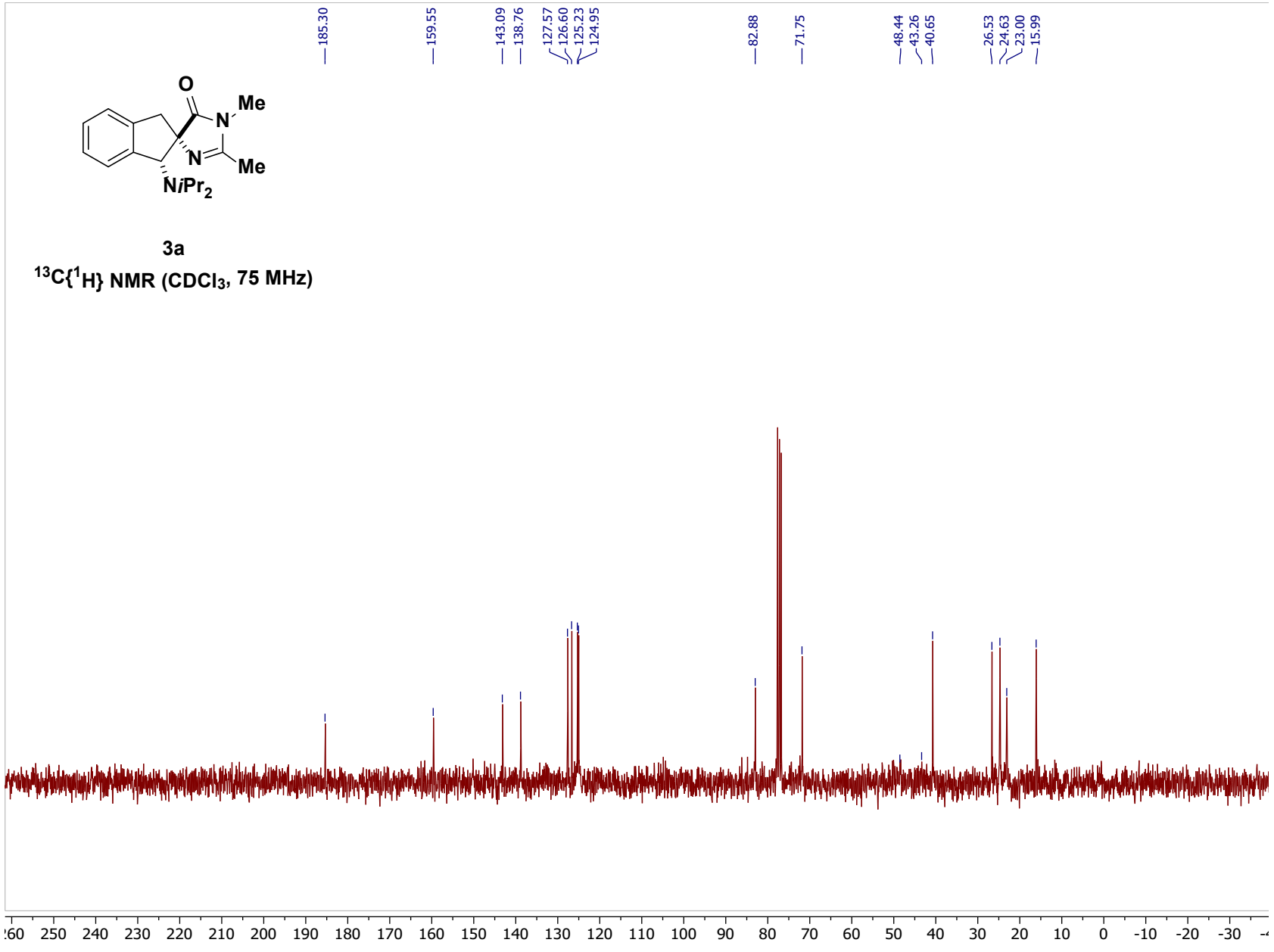
^{1}H NMR ($CDCl_3$, 300 MHz)



1k

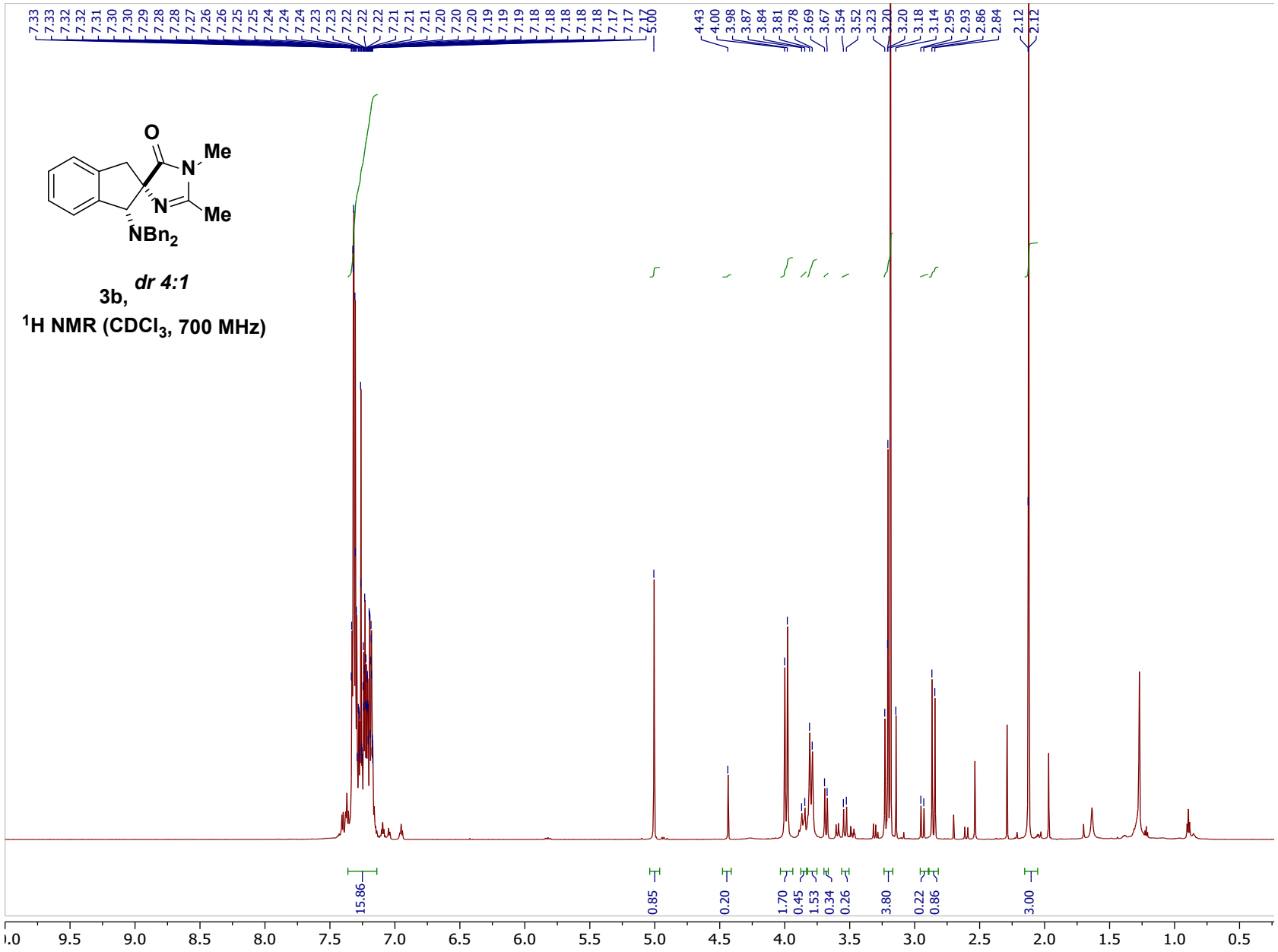
$^{13}C\{1H\}$ NMR ($CDCl_3$, 75 MHz)

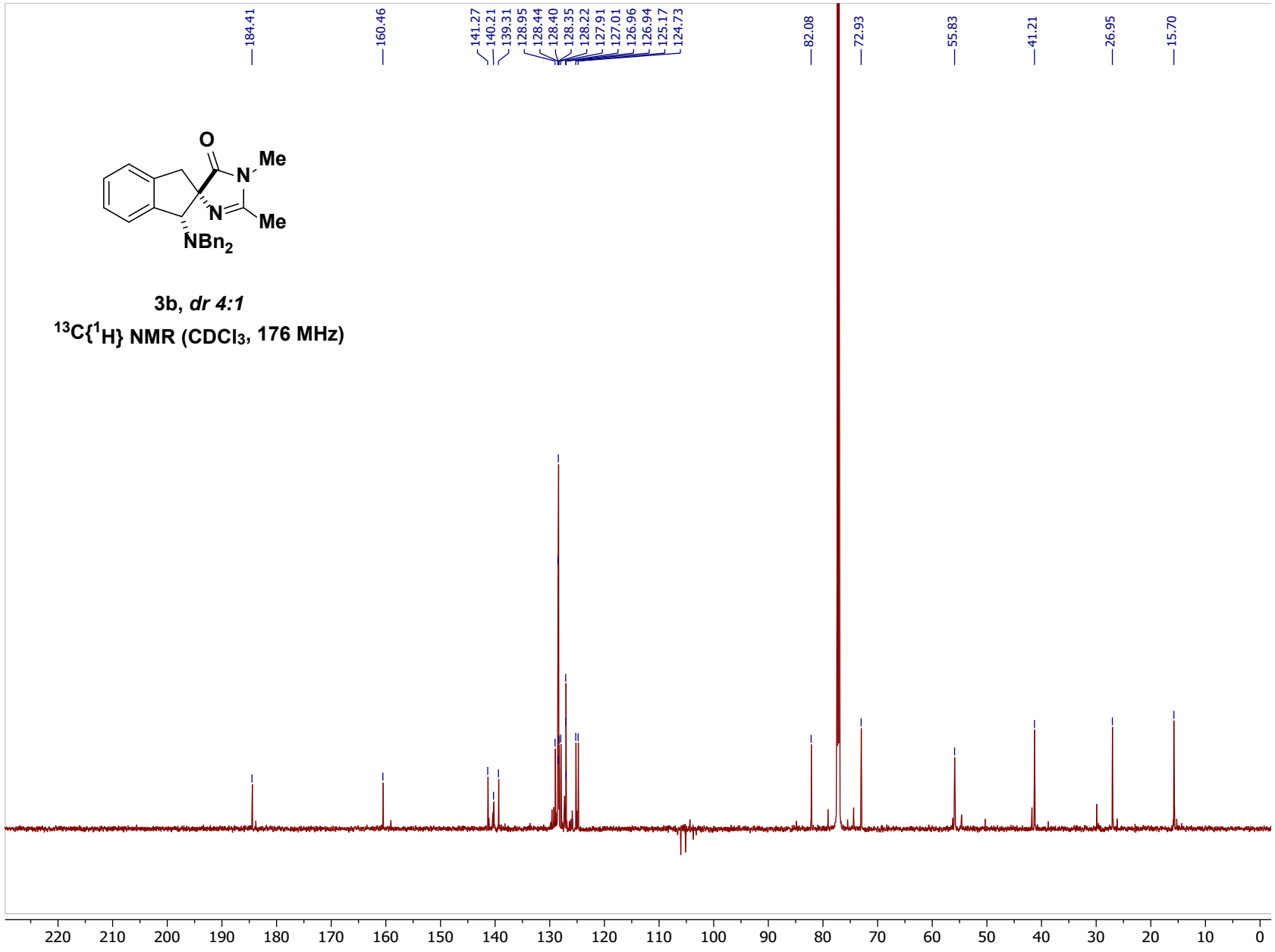

7.33
7.31
7.30
7.21
7.20
7.19
7.18
7.16
7.14
5.03
4.67
3.27
3.22
3.19
3.17
3.15
3.13
3.11
3.08
3.08
3.02
3.02
2.88
2.83
2.24
2.23
2.20
2.20
1.10
1.08
0.87
0.85
0.84
O
Me
N
N
Me
NiPr2
3a, dr 9:1
1H NMR (CDCl3, 300 MHz)
0.99
2.98
0.87
0.10
0.11
0.94
1.82
3.03
1.09
3.00
12.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



3a

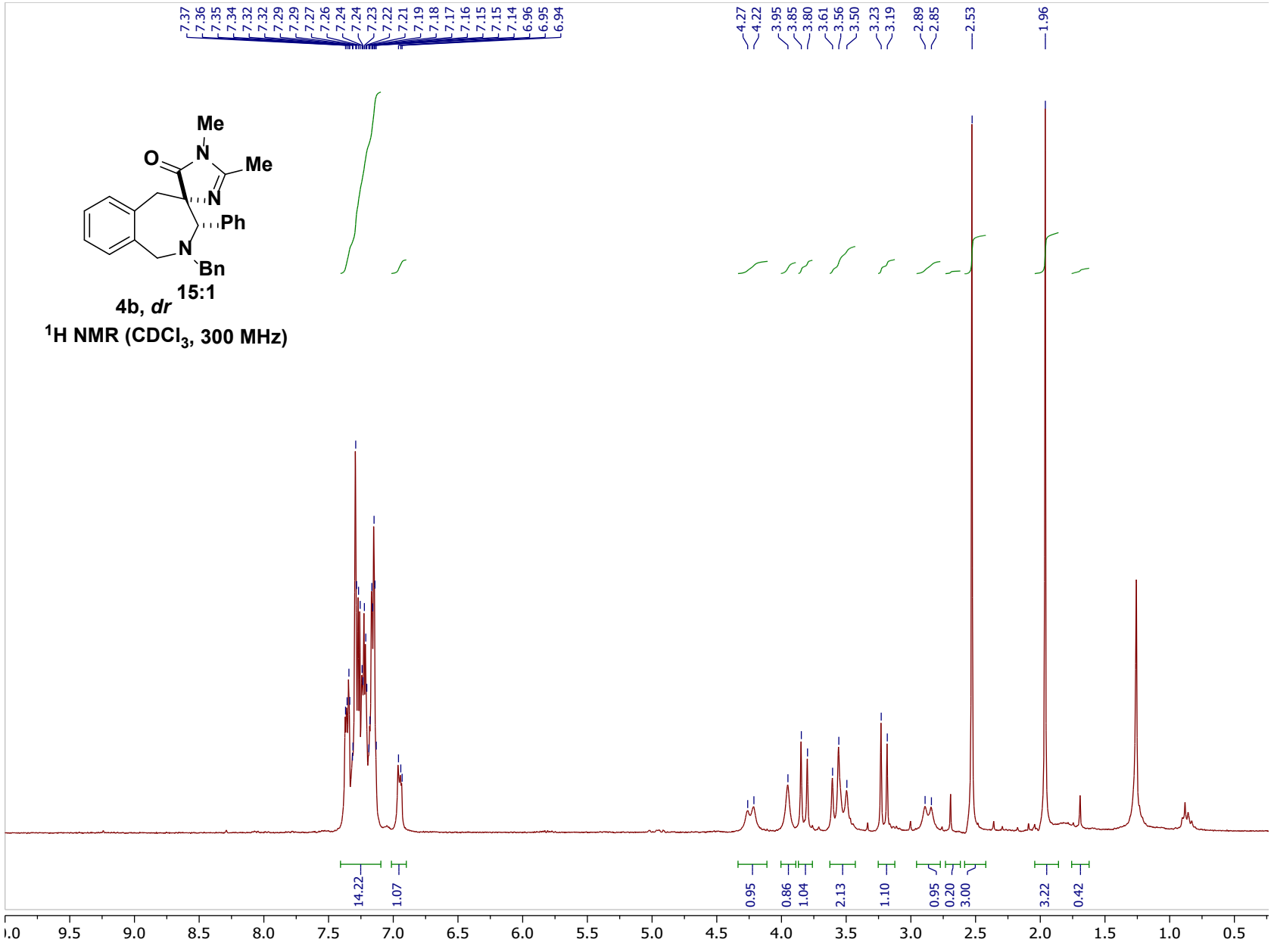
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz)

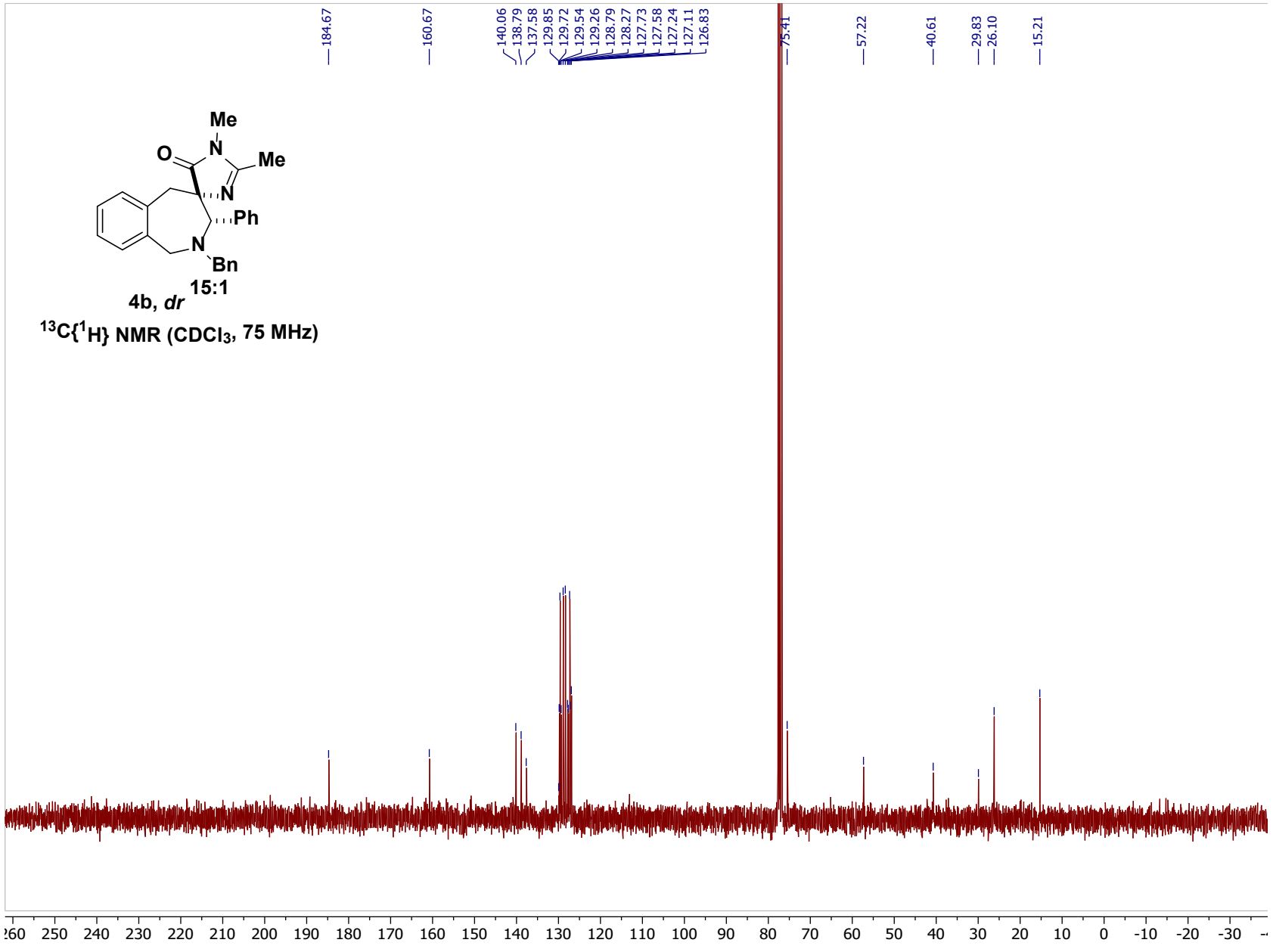

O
Me
N
N
Me
NBn2
3b, dr 4:1
1H NMR (CDCl3, 700 MHz)

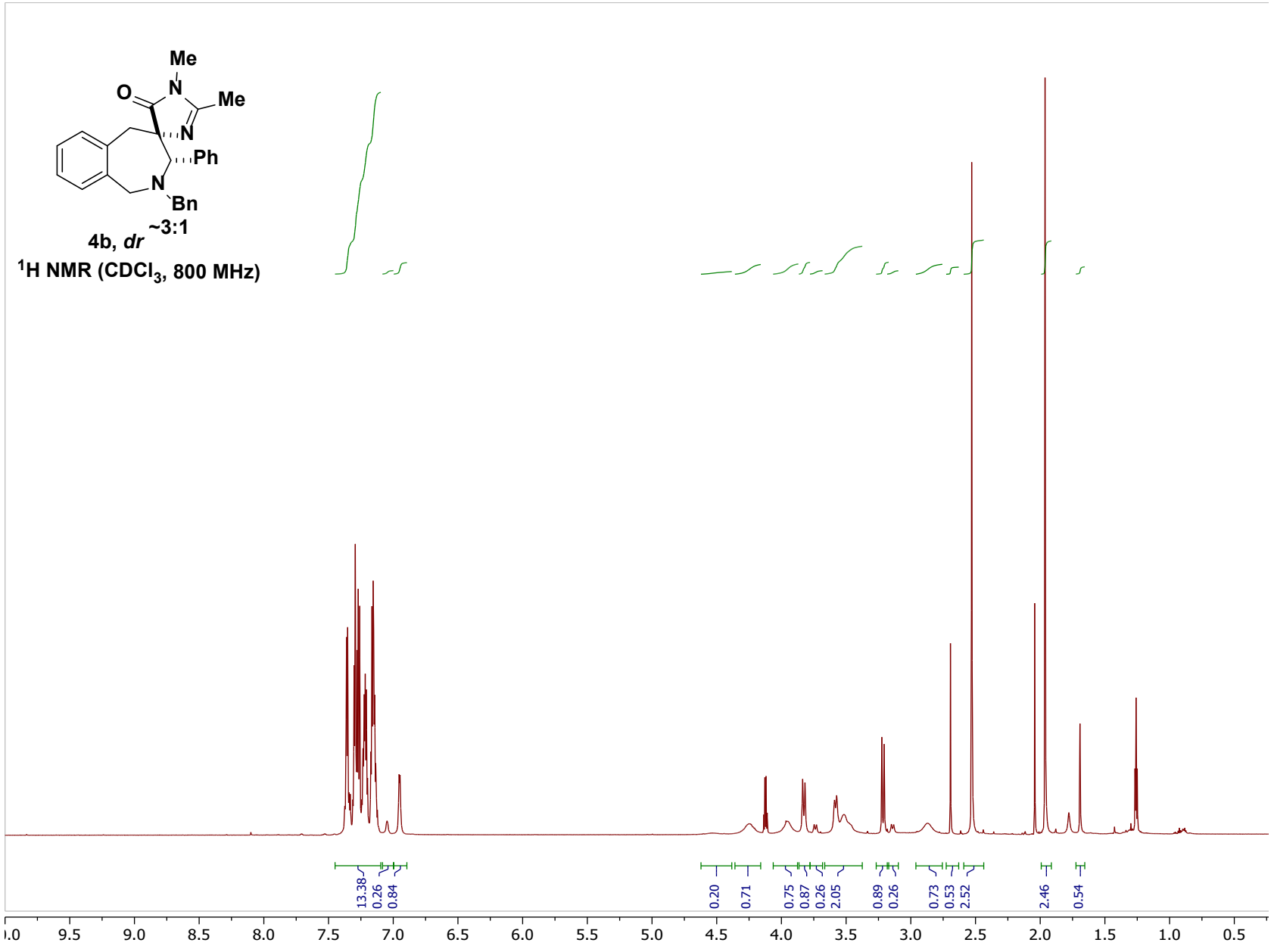


3b, *dr 4:1*

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 176 MHz)

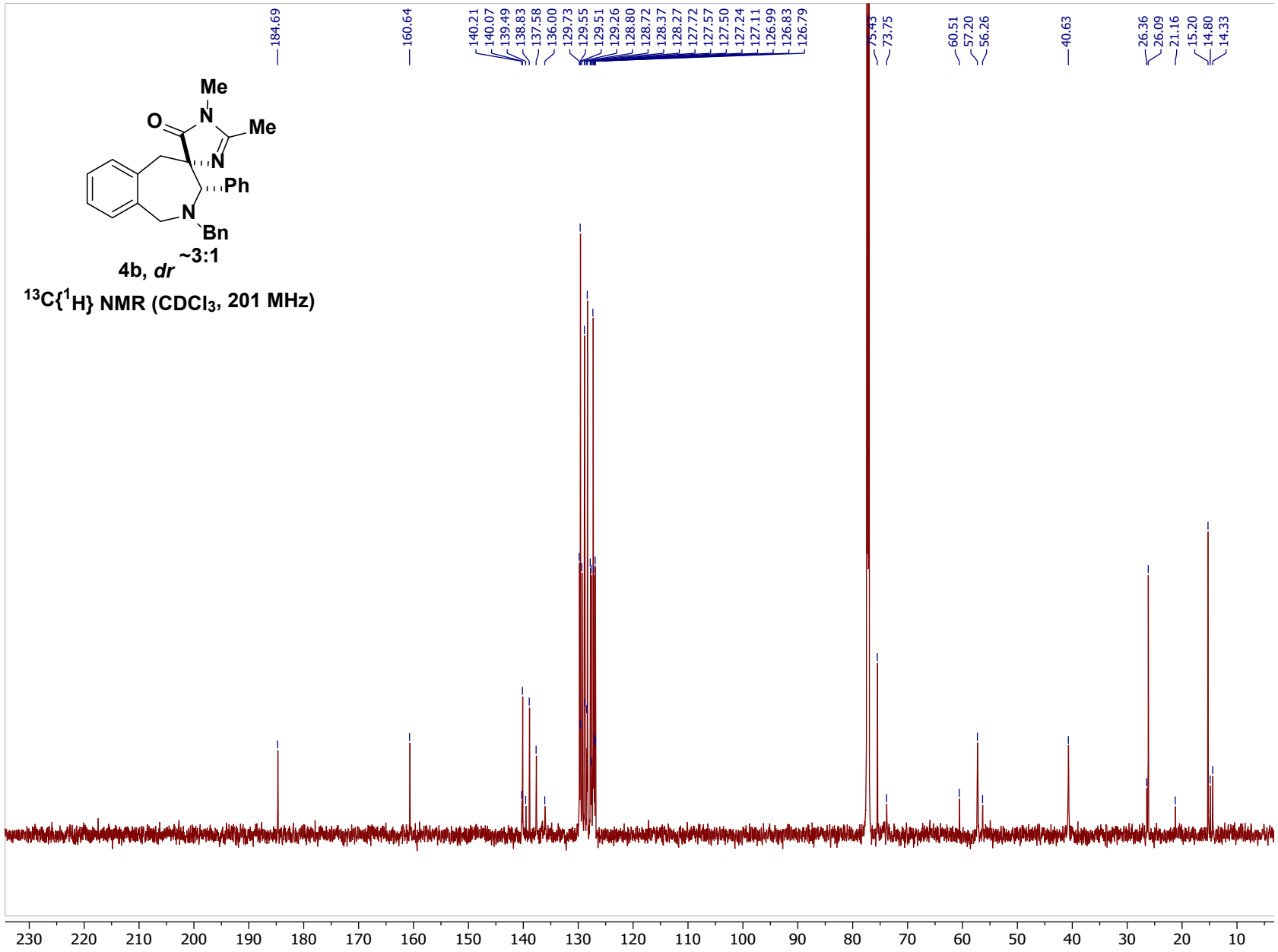

7.37
7.36
7.35
7.34
7.32
7.32
7.29
7.29
7.27
7.26
7.24
7.24
7.23
7.22
7.21
7.19
7.18
7.17
7.16
7.15
7.15
7.14
6.96
6.95
6.94
4.27
4.22
3.95
3.85
3.80
3.61
3.56
3.50
3.23
3.19
2.89
2.85
2.53
1.96
Me
N
O
Me
N
Ph
N
Bn
15:1
4b, dr
1H NMR (CDCl3, 300 MHz)
14.22
1.07
0.95
0.86
1.04
2.13
1.10
0.95
0.20
3.00
3.22
0.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

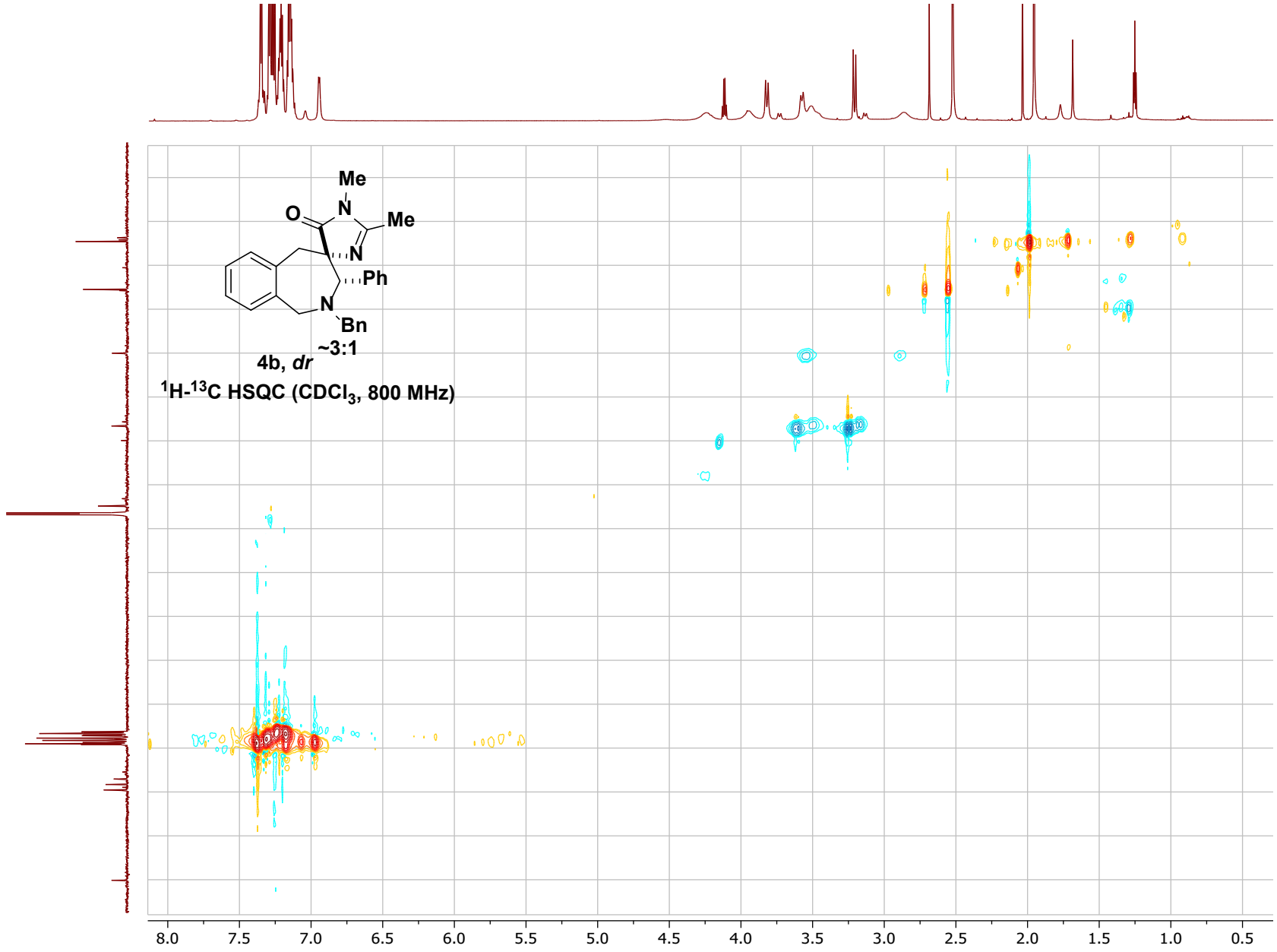

184.67
160.67
140.06
138.79
137.58
129.85
129.72
129.54
129.26
128.79
128.27
127.73
127.58
127.24
127.11
126.83
75.41
57.22
40.61
29.83
26.10
15.21
Me
N
O
Me
N
Ph
N
Bn
15:1
4b, dr
13C{1H} NMR (CDCl3, 75 MHz)
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30

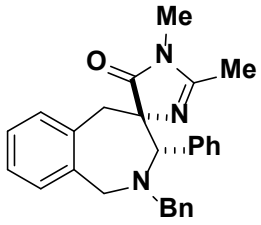


4b, *dr* ~3:1

^{1}H NMR ($CDCl_3$, 800 MHz)


184.69
160.64
140.21
140.07
139.49
138.83
137.58
136.00
129.73
129.55
129.51
129.26
128.80
128.72
128.37
128.27
127.72
127.57
127.50
127.24
127.11
126.99
126.83
126.79
75.43
73.75
60.51
57.20
56.26
40.63
26.36
26.09
21.16
15.20
14.80
14.33
Me
N
O
Me
N
Ph
N
Bn
~3:1
4b, dr
13C{1H} NMR (CDCl3, 201 MHz)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

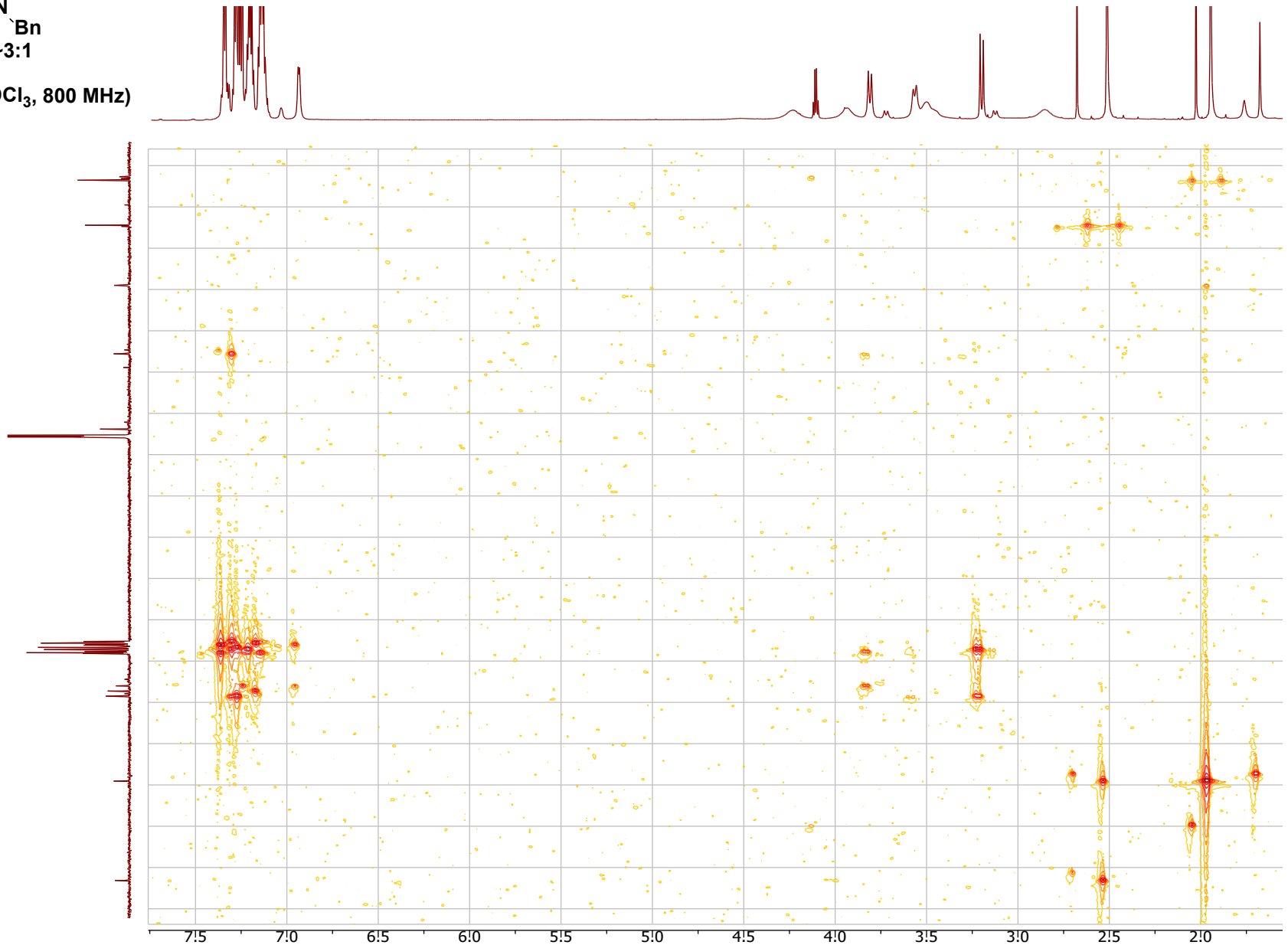

Me
O
N
Me
N
Ph
N
Bn
~3:1
4b, dr
1H-13C HSQC (CDCl3, 800 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

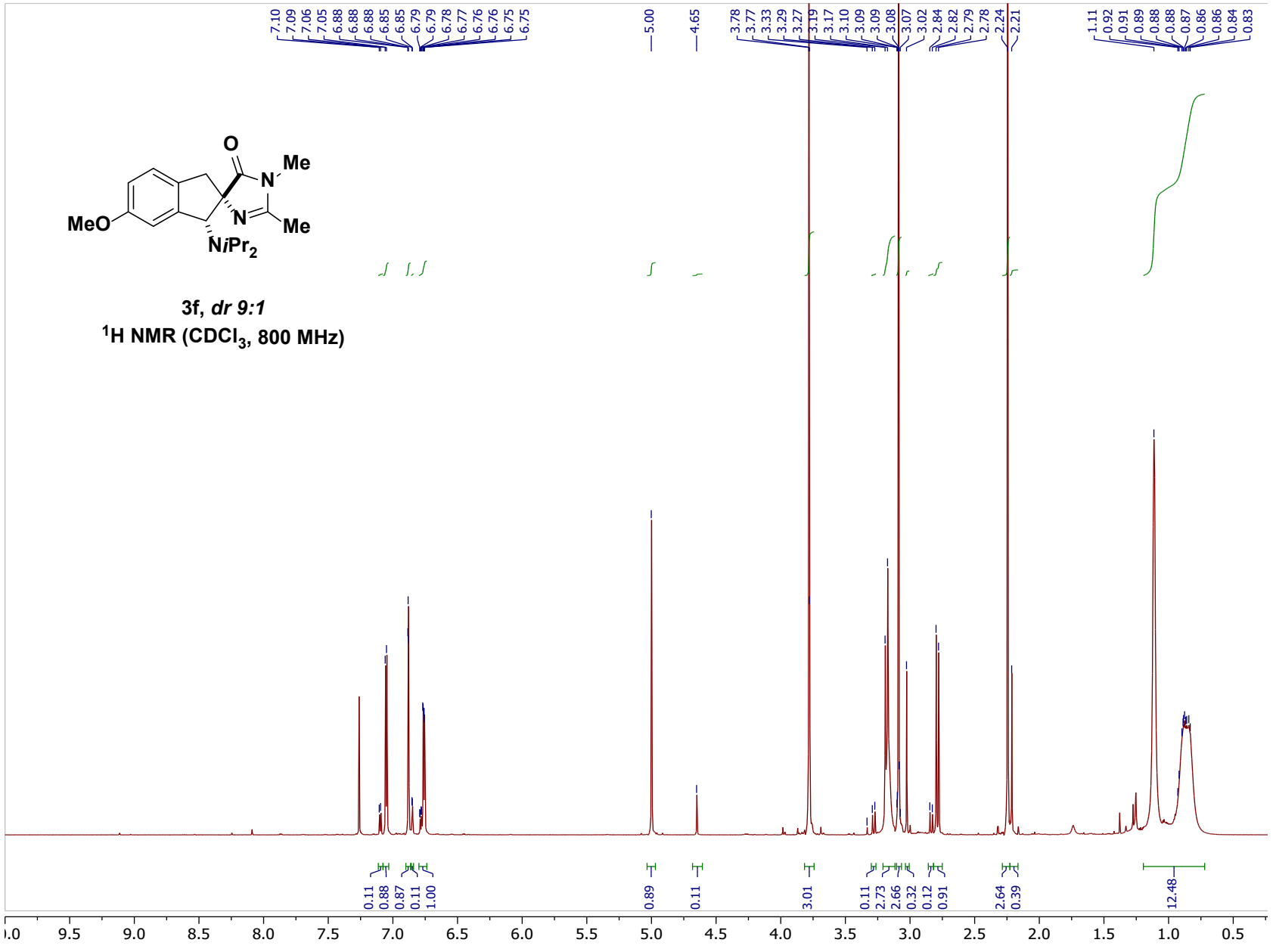


~3:1

4b, *dr*

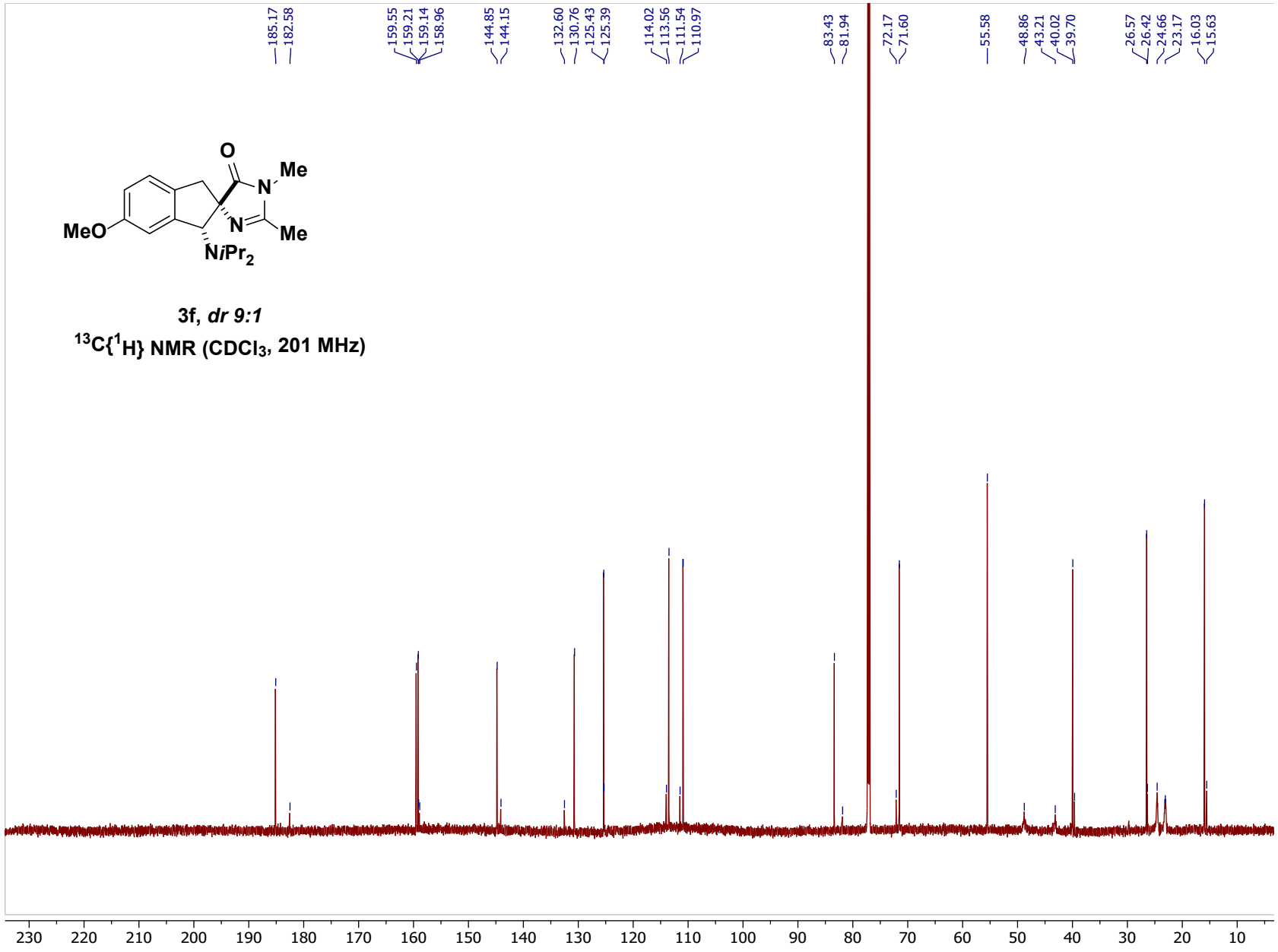
^{1}H-^{13}C HMBC ($CDCl_3$, 800 MHz)





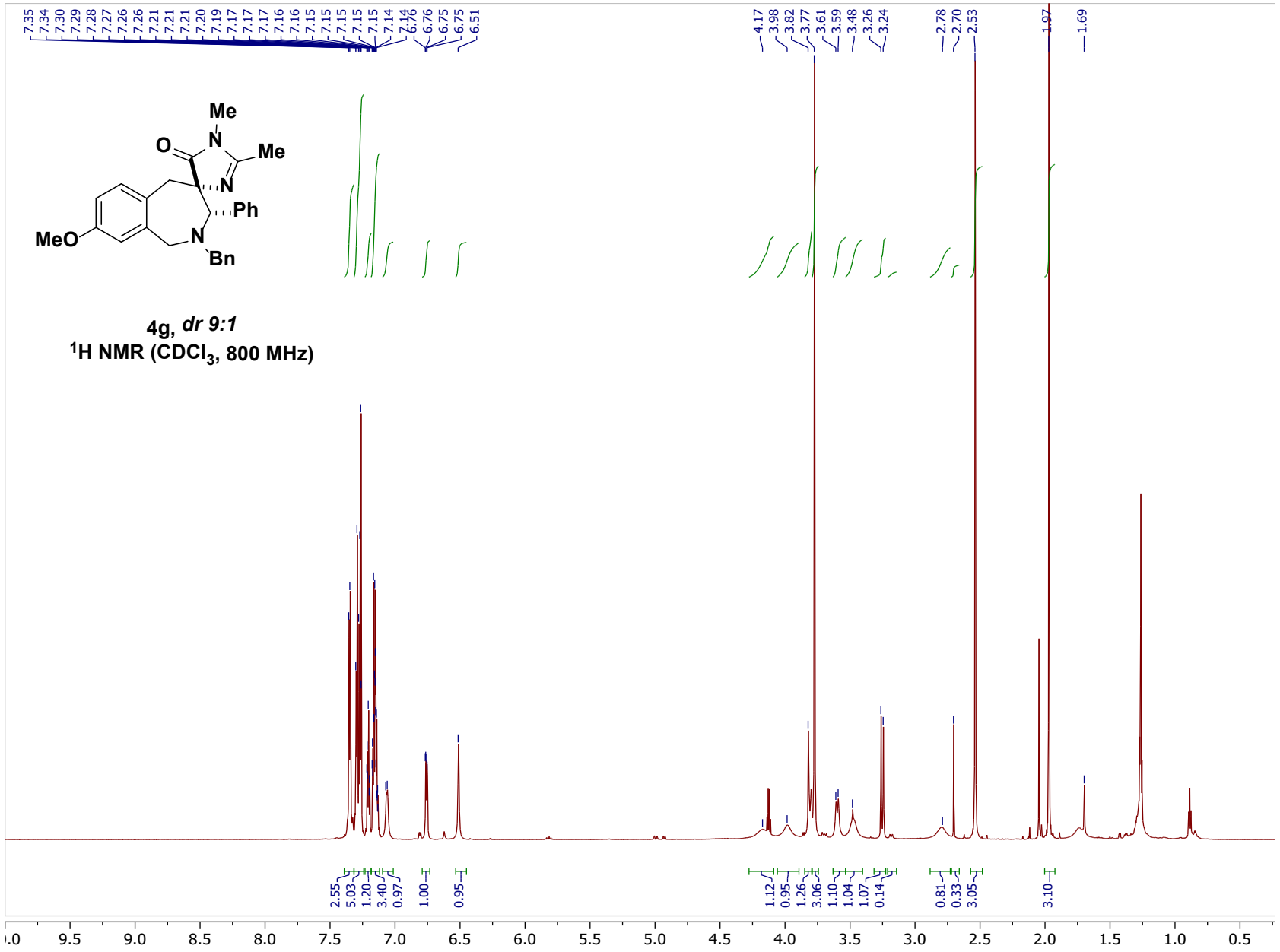
3f, *dr 9:1*

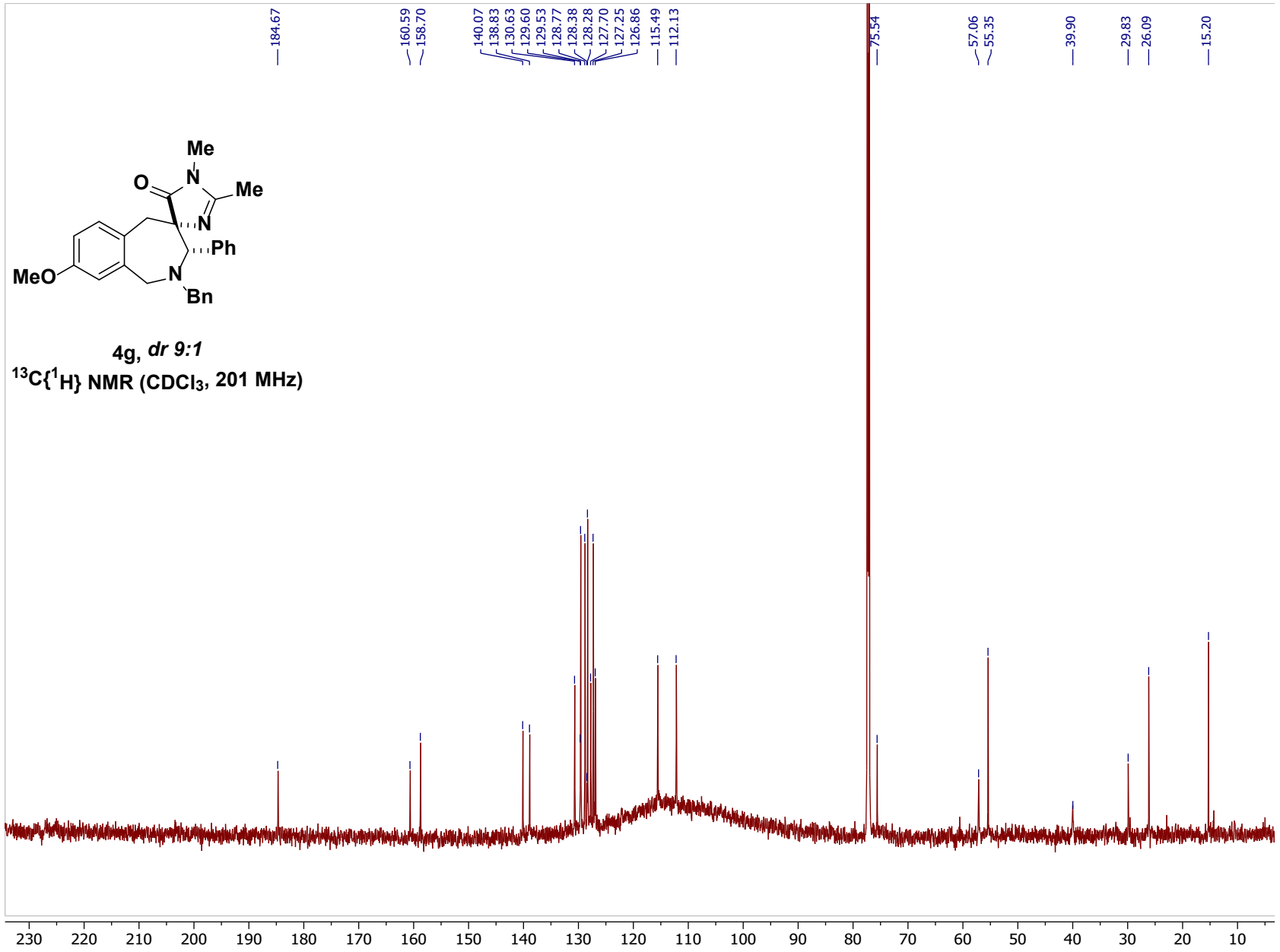
^{1}H NMR ($CDCl_3$, 800 MHz)

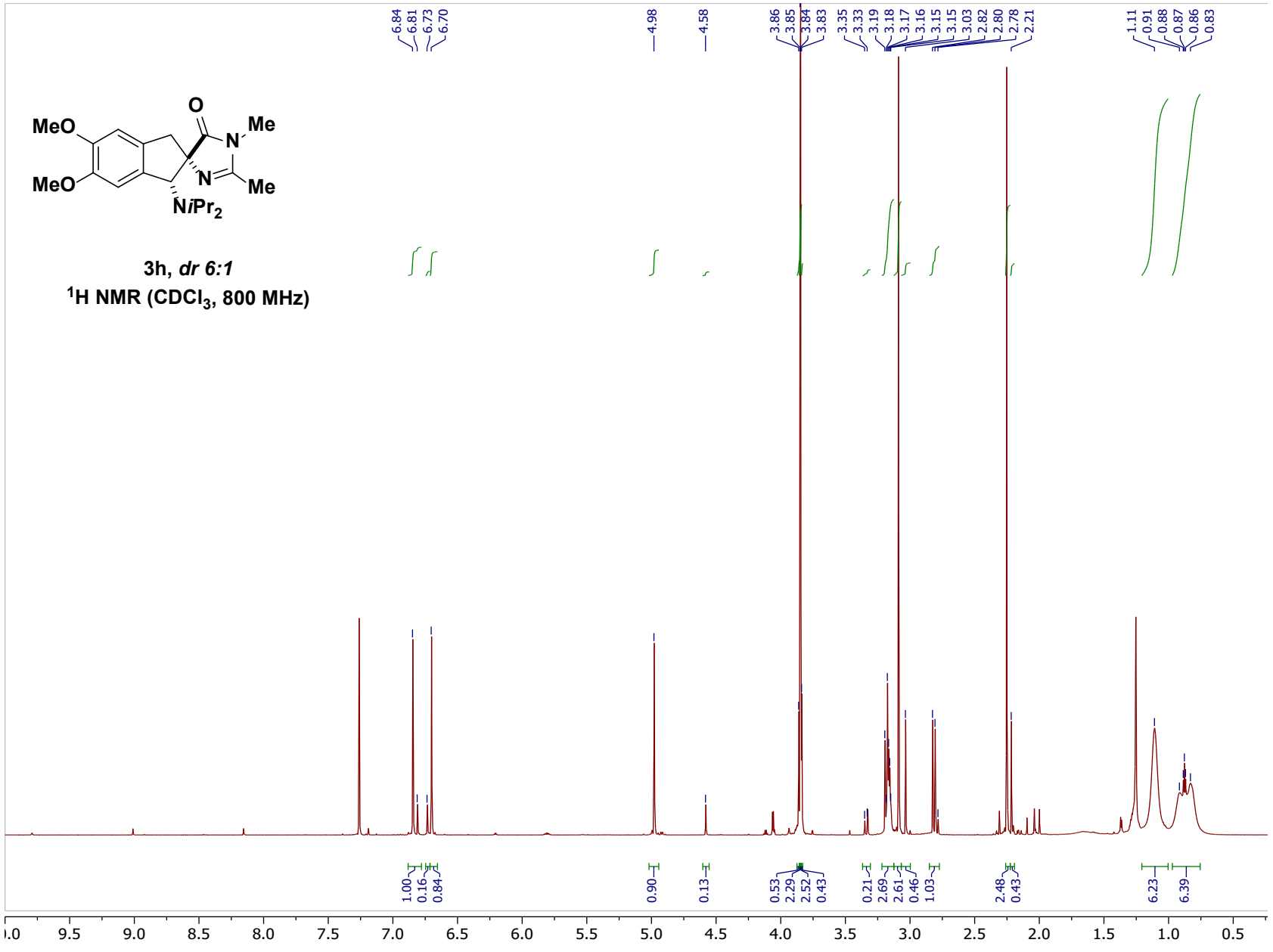


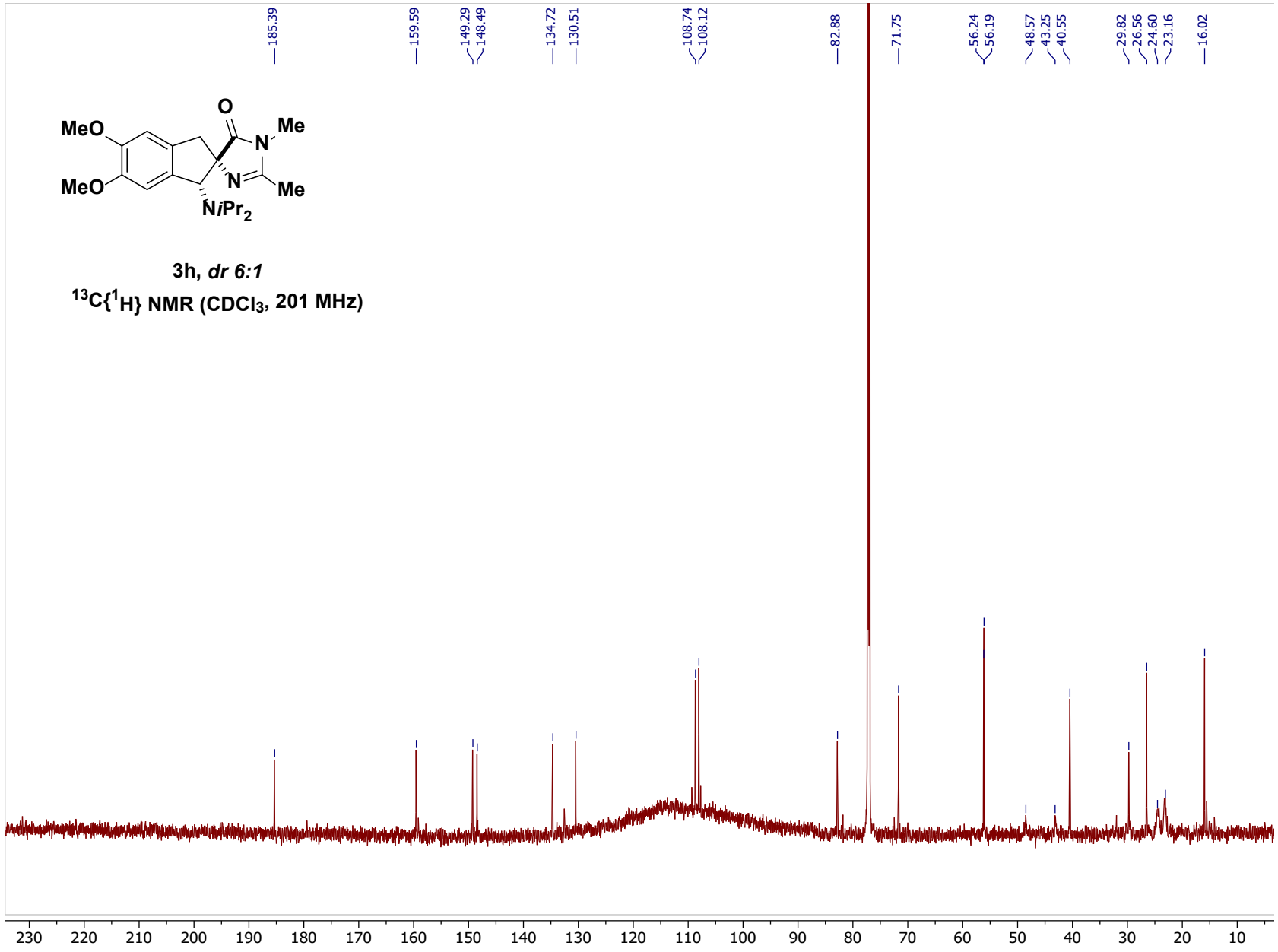
3f, *dr 9:1*

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 201 MHz)


Me
O
N
Me
N
Ph
MeO
N
Bn
4g, dr 9:1
1H NMR (CDCl3, 800 MHz)

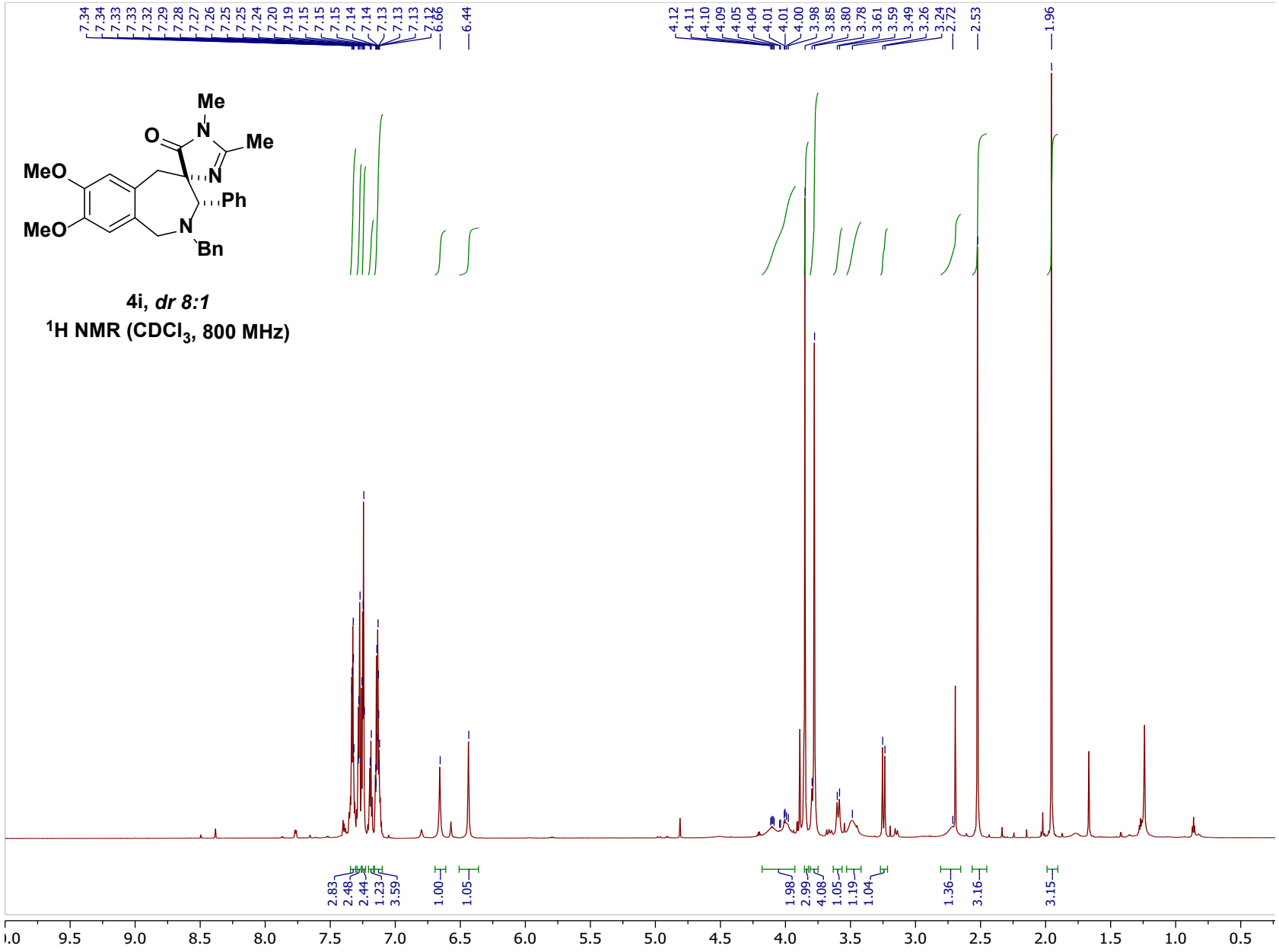

184.67
160.59
158.70
140.07
138.83
130.63
129.60
129.53
128.77
128.38
128.28
127.70
127.25
126.86
115.49
112.13
75.54
57.06
55.35
39.90
29.83
26.09
15.20
Me
O
N
Me
N
Ph
MeO
N
Bn
4g, dr 9:1
13C{1H} NMR (CDCl3, 201 MHz)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

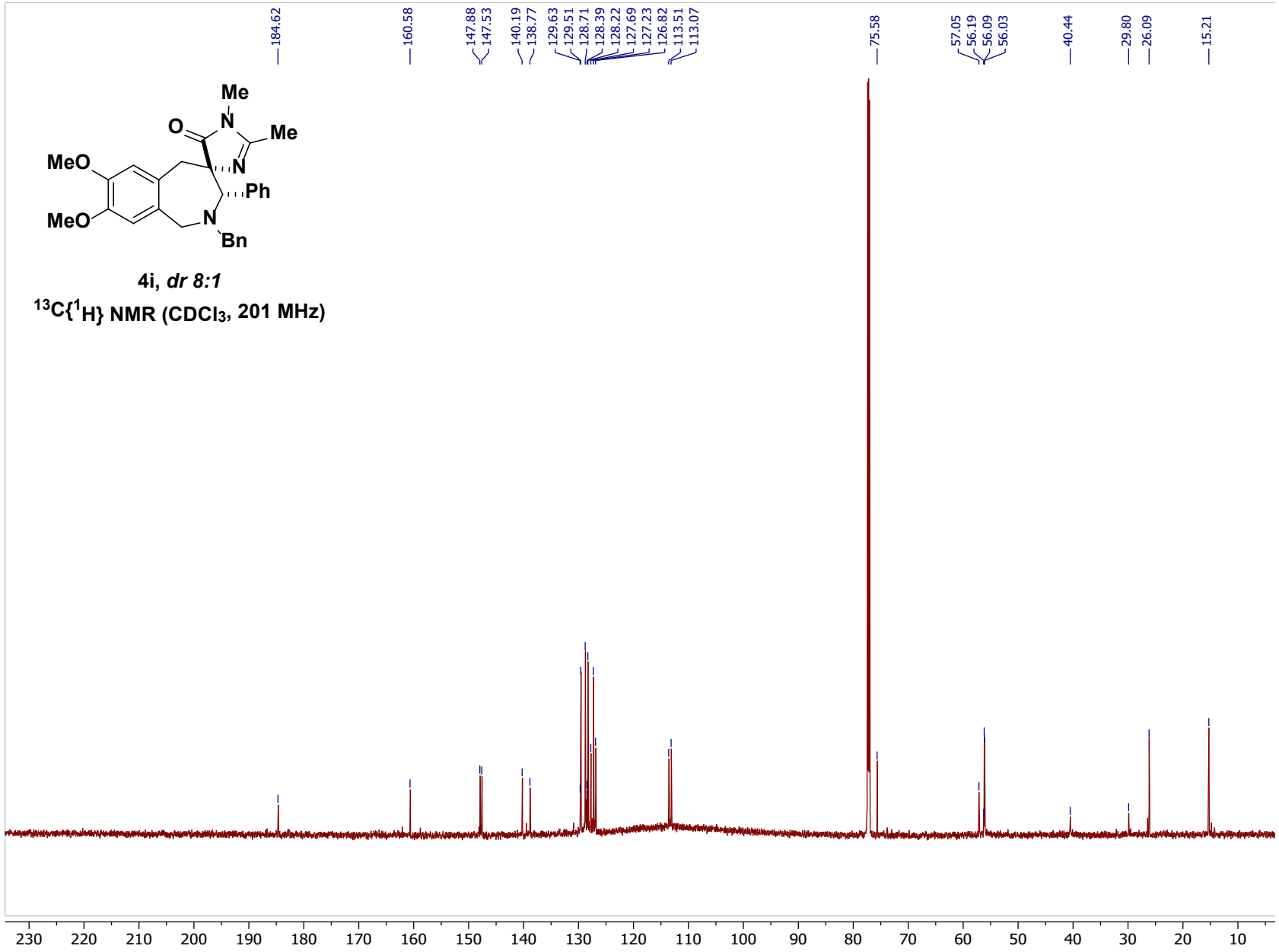

MeO
MeO
O
N
Me
N
Me
NiPr2
3h, dr 6:1
1H NMR (CDCl3, 800 MHz)
6.84
6.81
6.73
6.70
4.98
4.58
3.86
3.85
3.84
3.83
3.35
3.33
3.19
3.18
3.17
3.16
3.15
3.15
3.03
2.82
2.80
2.78
2.21
1.11
0.91
0.88
0.87
0.86
0.83
1.00
0.16
0.84
0.90
0.13
0.53
2.29
2.52
0.43
0.21
2.69
2.61
0.46
1.03
2.48
0.43
6.23
6.39
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

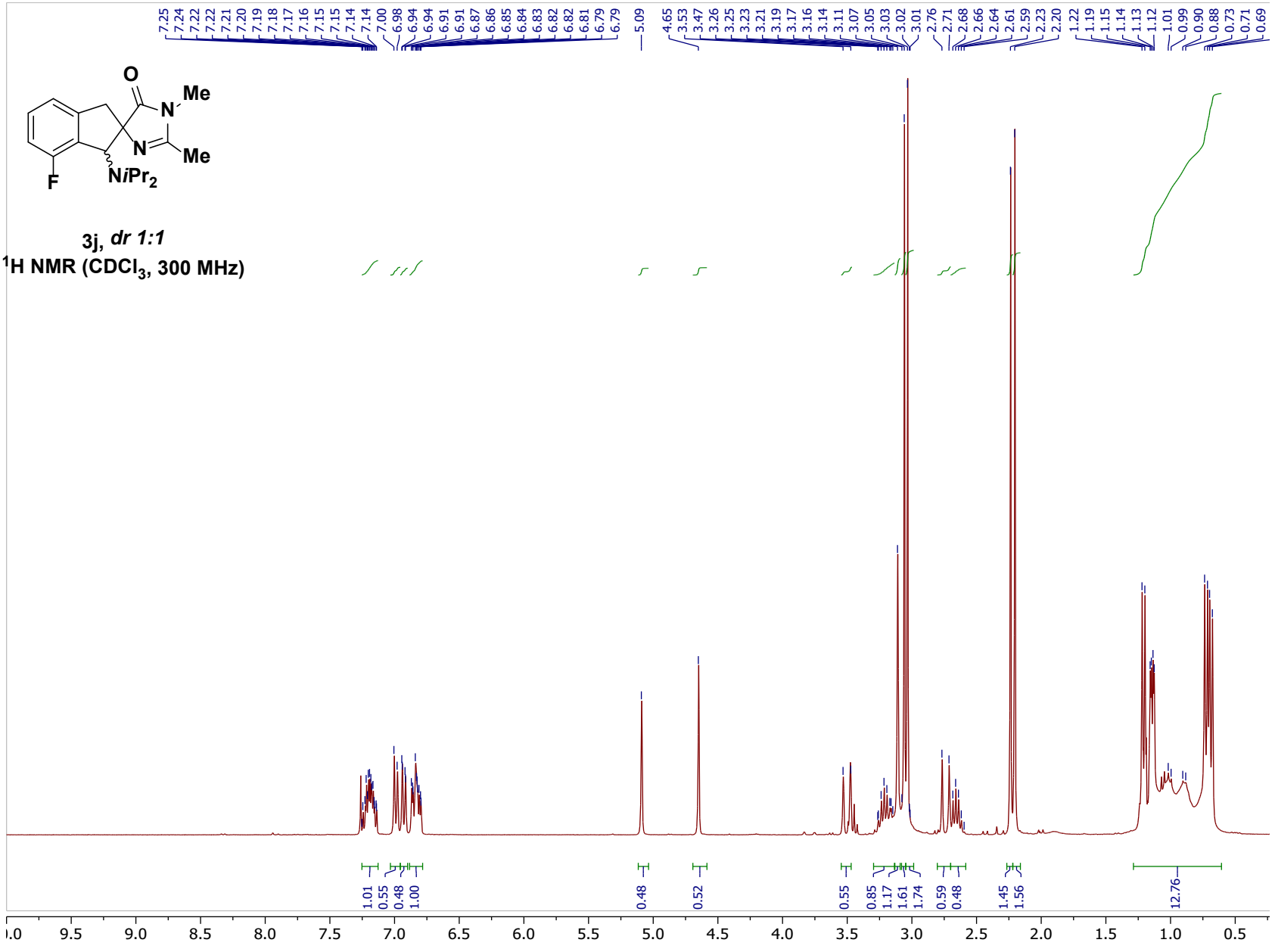


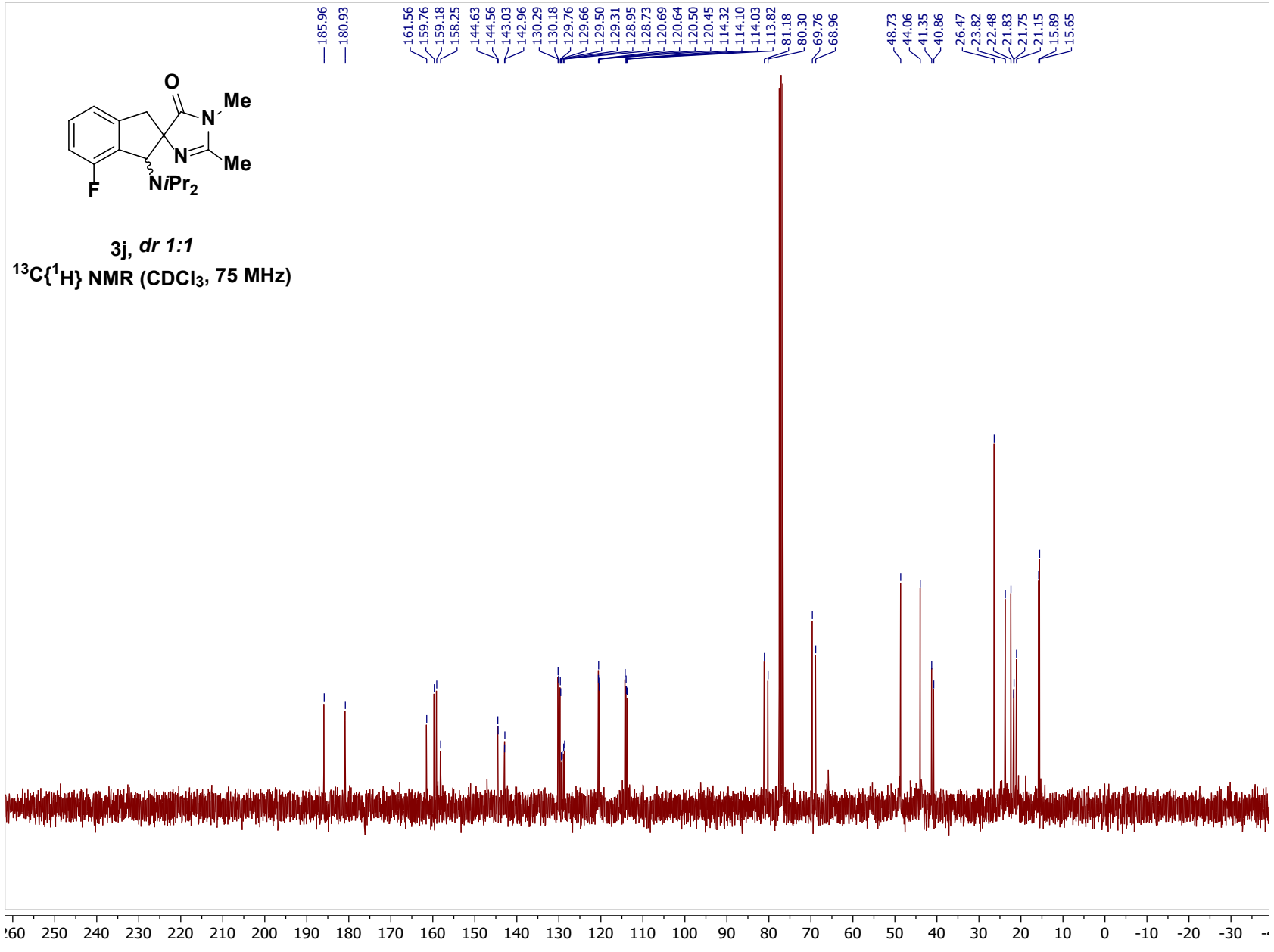
3h, *dr 6:1*

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 201 MHz)


Me
N
O
Me
MeO
N
Ph
MeO
N
Bn
4i, dr 8:1
1H NMR (CDCl3, 800 MHz)

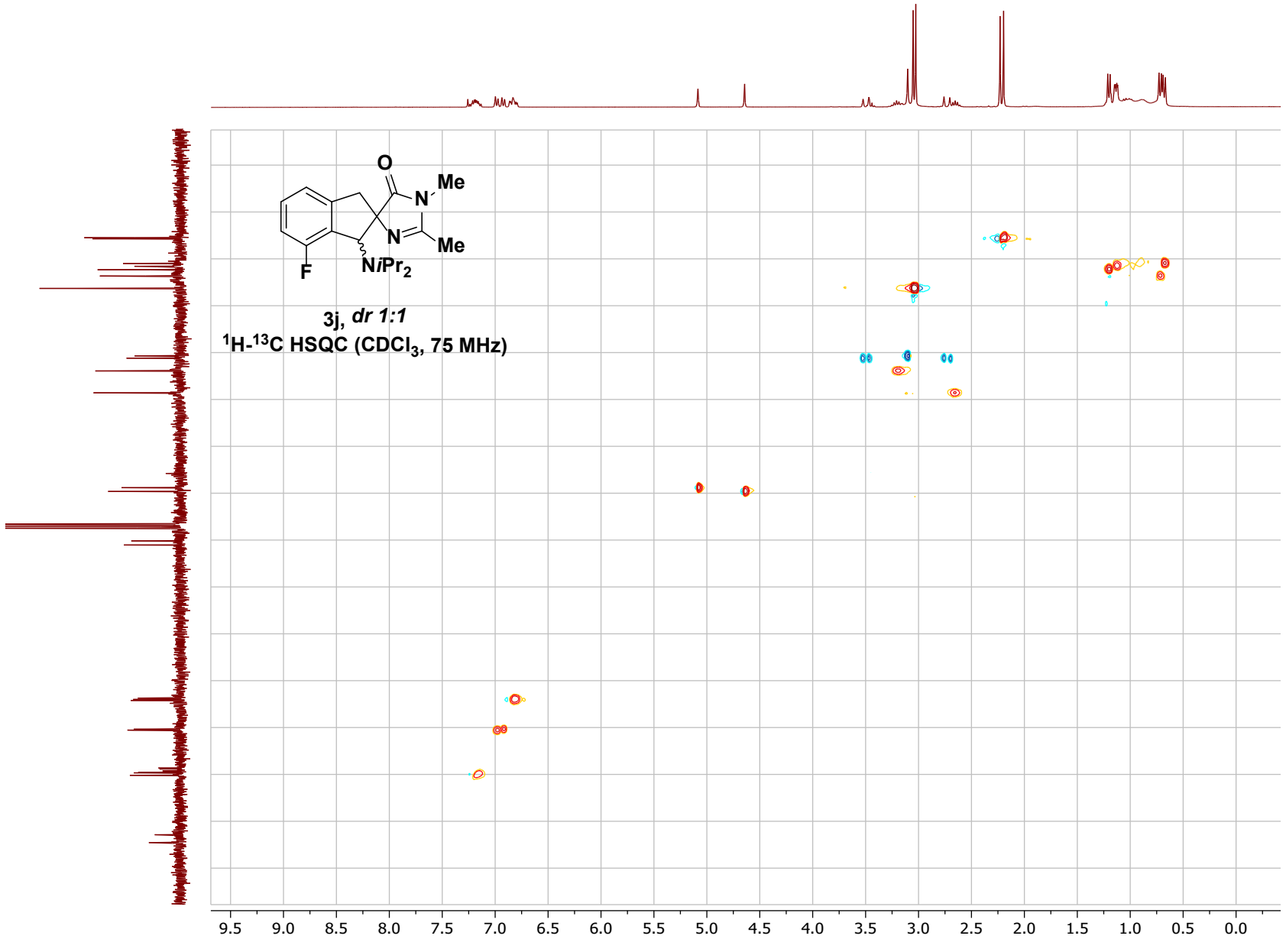

184.62
160.58
147.88
147.53
140.19
138.77
129.63
129.51
128.71
128.39
128.22
127.69
127.23
126.82
113.51
113.07
75.58
57.05
56.19
56.09
56.03
40.44
29.80
26.09
15.21
Me
N
O
Me
MeO
N
Ph
MeO
N
Bn
4i, dr 8:1
13C{1H} NMR (CDCl3, 201 MHz)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

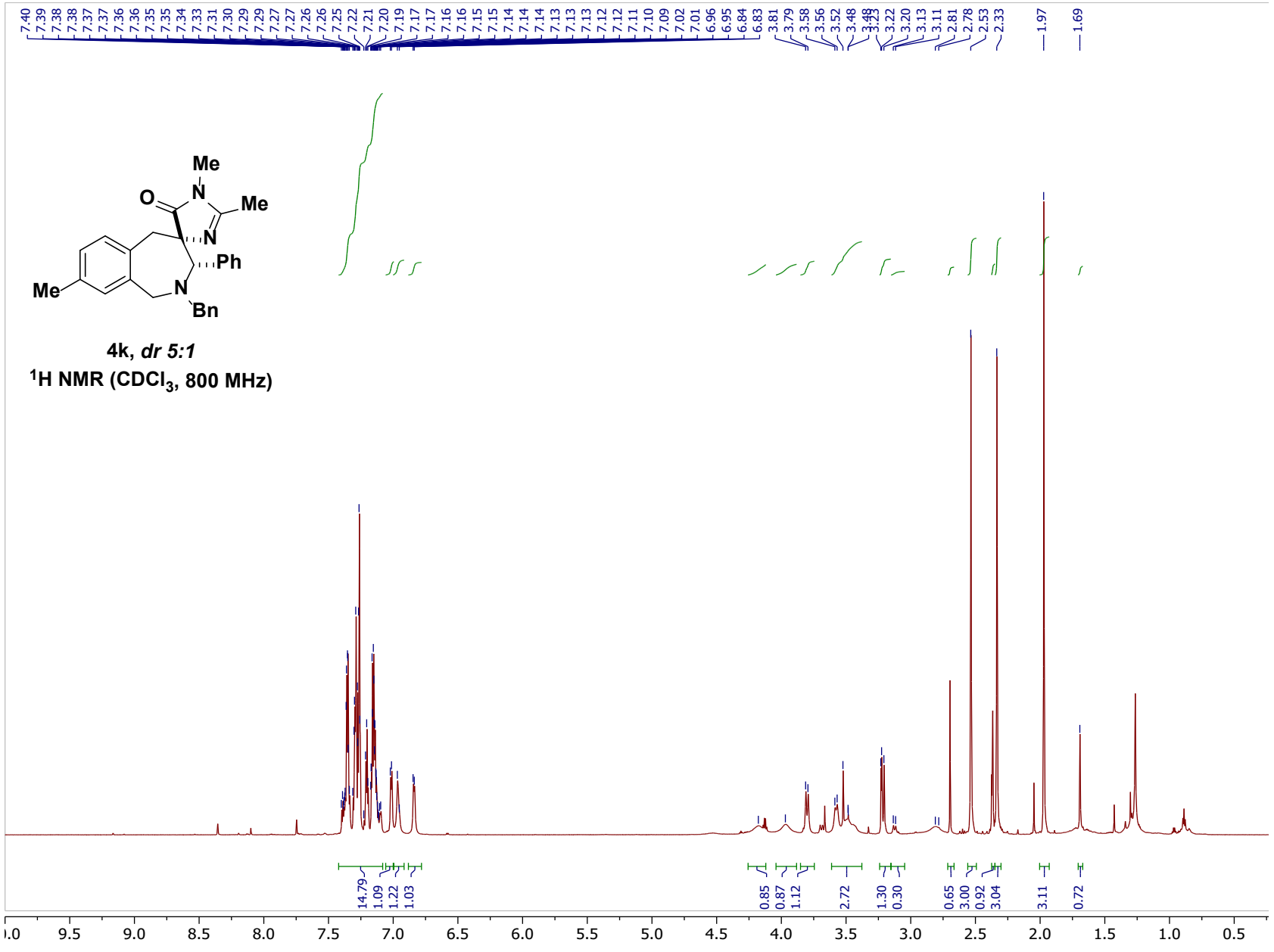

7.25 7.24 7.22 7.22 7.21 7.20 7.19 7.18 7.17 7.16 7.15 7.15 7.14 7.14 7.00 6.98 6.94 6.94 6.91 6.91 6.87 6.86 6.85 6.84 6.83 6.82 6.82 6.81 6.79 6.79
5.09
4.65 3.53 3.47 3.26 3.25 3.23 3.21 3.19 3.17 3.16 3.14 3.11 3.07 3.05 3.03 3.02 3.01 2.76 2.71 2.68 2.66 2.64 2.61 2.59 2.23 2.20 1.22 1.19 1.15 1.14 1.13 1.12 1.01 0.99 0.90 0.88 0.73 0.71 0.69
O
N
Me
N
Me
F
NiPr2
3j, dr 1:1
1H NMR (CDCl3, 300 MHz)
1.01 0.55 0.48 1.00 0.48 0.52 0.55 0.85 1.17 1.61 1.74 0.59 0.48 1.45 1.56 12.76
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

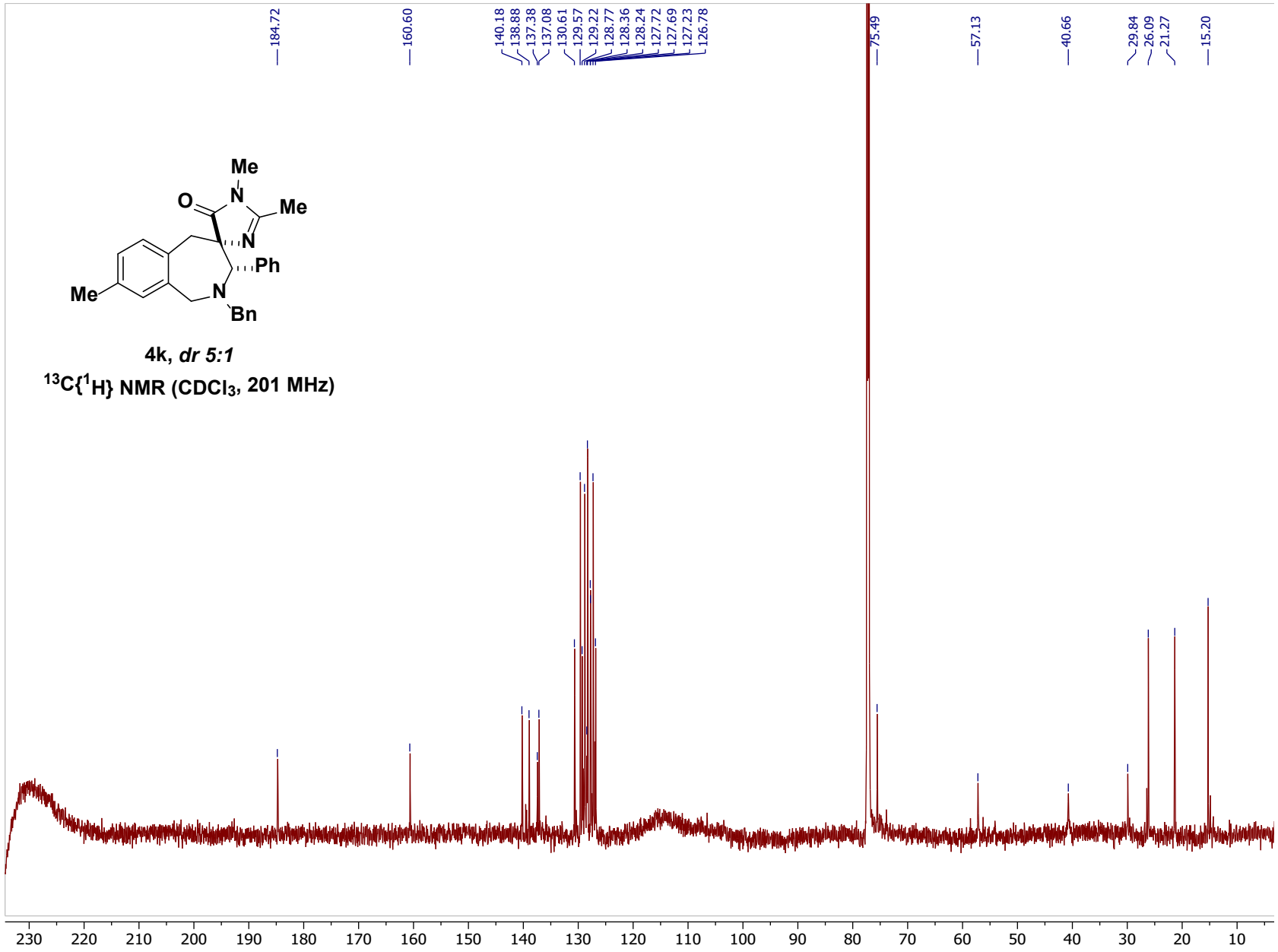


3j, ***dr 1:1***

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz)


O
Me
N
N
Me
F
NiPr2
3j, dr 1:1
1H-13C HSQC (CDCl3, 75 MHz)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Me
N
O
Me
N
Ph
Me
N
Bn
4k, dr 5:1
1H NMR (CDCl3, 800 MHz)



4k, *dr 5:1*

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 201 MHz)