Ni-Catalyzed Regioselective Hydroalkoxylation of Branched 1,3-Dienes

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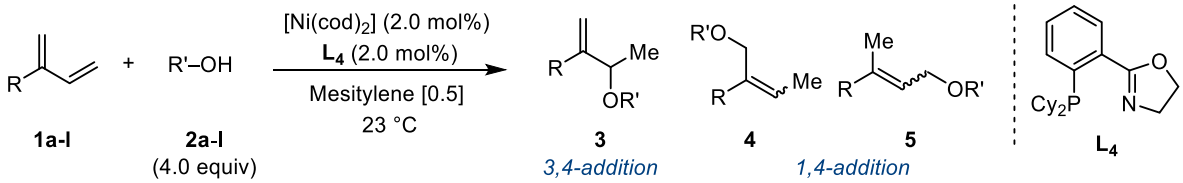
1. General Information

Unless otherwise noted, all reactions were carried out under air. All liquid alcohols were distilled over CaO and degassed by three successive "fr*ee*ze-pump-thaw" cycles, followed by drying over activated 4Å MS. THF was degassed by N_2 bubbling and dried over activated alumina columns. Mesitylene was dried and distilled over CaH_2 and degassed by thr*ee* successive "fr*ee*ze-pump-thaw" cycles. $Ni(cod)_2$ was dissolved in toluene (*ca*. 1 g/20 mL), filtered over Celite, and recrystallized at −78 °C. All the dienes were prepared according to reported literature procedures.[1] Ligand **L_4** was prepared accorded to reported literature procedures.[2] NMR spectra were recorded on AMX−400 and AMX−500 Bruker Avance spectrometers at 298 K. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. ^1H NMR spectra were referenced to $CHCl_3$ (δ = 7.26 ppm), $^{13}C\{^1H\}$ NMR spectra were referenced to $CDCl_3$ (δ = 77.16 ppm), $^{19}F\{^1H\}$ NMR chemical shifts are reported in ppm relative to $CFCl_3$. ^1H and ^{13}C assignments were made based on 2D NMR data (COSY, HSQC, HMBC, NOESY). Infrared spectra were obtained on a Perkin−Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. HRMS were obtained on a Xevo G2 Tof spectrometer (Ionization mode: ESI positive polarity; Mobile phase: MeOH 100 µl/min). Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution). Melting points were recorded on a Büchi M-565 apparatus. SFC analyses were performed on a Waters Acquity UPC2 with columns OD-3, OJ-3, OZ-3, OB-H, AZ-3, AD, AS-3, AY-H. Retention times (t_R) are given in minutes. The first enantiomer to elute was arbitrarily referenced as the first isomer in the enantiomeric ratio *er*. Thin layer chromatography (TLC) was performed on plates of silica precoated with 0.25 mm Kieselgel 60 F_{254} from *Merck*. Flash chromatography was performed using silica gel SiliaFlash® P60 (230-400 mesh) from *Silicycle*.

2. General Procedure



1a-l **2a-l** (4.0 equiv) **3** *3,4-addition* **4** **5** *1,4-addition* **L_4**

In a N_2-filled glovebox, $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%) and (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) were charged in a 5 mL Schlenk tube and dissolved in anhydrous mesitylene (1.0 mL, 0.50 M). After stirring at room temperature for 5 min, the appropriate diene **1** (0.50 mmol, 1.0 equiv) and the appropriate alcohol **2** (2.00 mmol, 4.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and the reaction mixture was stirred at room temperature. After complete consumption of diene **1** (determined by TLC), the reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (5 mL) and concentrated under vacuum to afford the crude mixture. The conversion and regioisomeric ratio were determined by ^1H NMR analysis of the crude reaction mixture using *p*-methoxytoluene as an internal standard. The residue was purified by silica gel column chromatography to afford the analytically pure hydroalkoxylation product **3**.

3. Substrate scope

3.1. Scope in diene

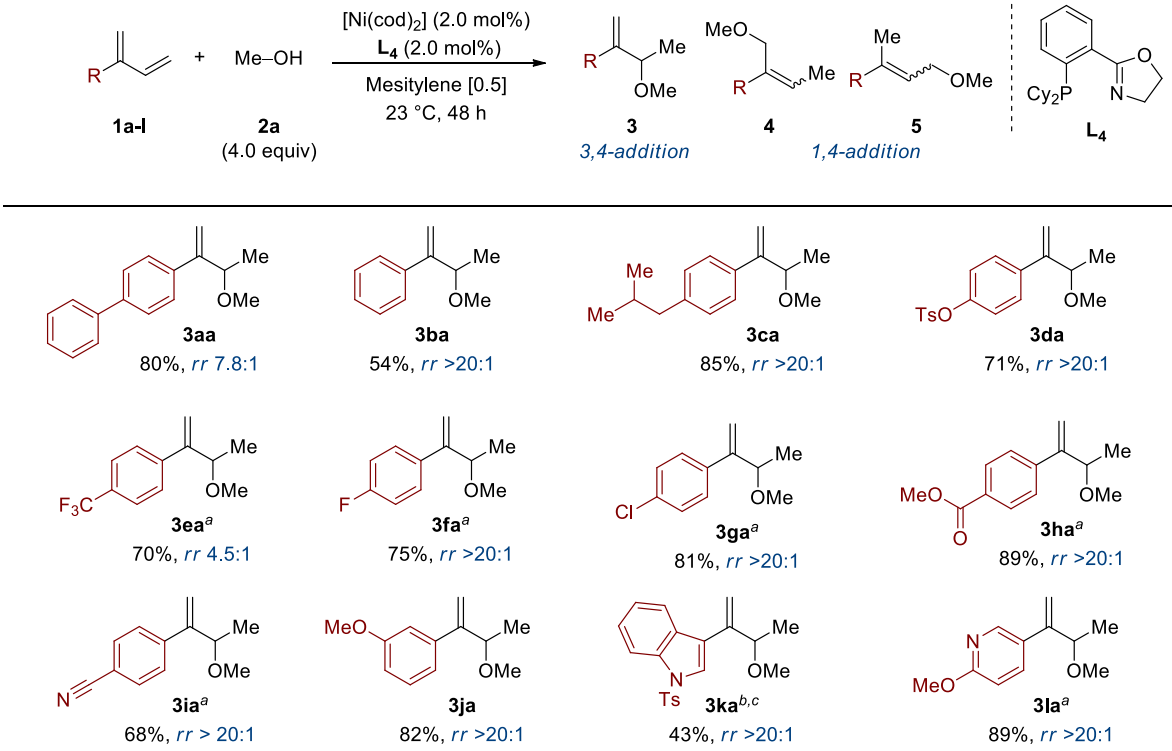
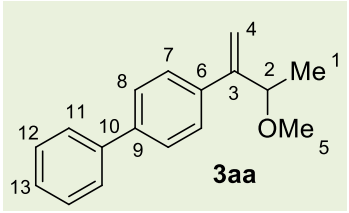


Figure S1. Scope of the Ni-catalyzed hydroalkoxylation of 2-substituted 1,3-dienes - Variation of the diene component. 0.50 mmol scale. Yields of 3,4-addition product after purification. Regioselectivity expressed as the ratio between 3,4- and 1,4-addition products as determined by ^{1}H NMR using *p*-methoxytoluene as an internal standard (**3**:[**4**+**5**]). [a] 10 °C. [b] 70 h. [c] 6 mol% catalyst.

4-(3-Methoxybut-1-en-2-yl)-1,1'-biphenyl 3aa



3aa

Synthesized at room temperature for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: >95%, conversion of **3aa**: 86%, *rr* = 7.8:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 19:1) afforded the desired product as a colorless oil (95 mg, 0.40 mmol, 80% yield).

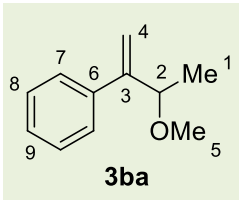
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.69 – 7.51 (m, 6H, *H*-7, *H*-8, *H*-11), 7.48 – 7.41 (m, 2H, *H*-12), 7.38 – 7.32 (m, 1H, *H*-13), 5.44 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.34 – 5.29 (m, 1H, *H*-4), 4.24 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.7 Hz, 1H, *H*-2), 3.40 (s, 3H, *H*-5), 1.33 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 148.9 (*C*-3), 1 40.9 (*C*-10), 140.5 (*C*-9), 138.8 (*C*-6), 128.9 (*C*H-12), 127.5 (*C*H-7), 127.4 (*C*H-13), 127.1 (*C*H-8), 127.1 (*C*H-11), 114.2 (CH_2-4), 80.1 (*C*H-2), 56.3 (CH_3-5), 21.3 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{17}H_{19}O^+$: 239.1436; found: 239.1422.

IR (neat) ν (cm^{-1}): 3029, 2978, 2819, 1626, 1486, 1446, 1371, 1203, 115, 1091, 1005, 909, 844, 769, 740, 695.

(3-Methoxybut-1-en-2-yl)benzene 3ba



3ba

Synthesized at room temperature for 48 h following the general procedure using buta-1,3-dien-2-ylbenzene **1b** (66 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1b**: >95%, conversion of **3ba**: 82%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 32:1) afforded the desired product as a colorless oil (44 mg, 0.27 mmol, 54% yield, CAUTION: volatile).

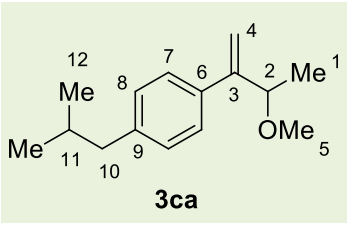
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.45 – 7.41 (m, 2H, *H*-7), 7.37 – 7.30 (m, 2H, *H*-8), 7.33 – 7.25 (m, 1H, *H*-9), 5.37 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.29 (s, 1H, *H*-4), 4.19 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.39 (s, 3H, *H*-5), 1.28 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.3 (*C*-3), 139.9 (*C*-6), 128.4 (*C*H-7), 127.6 (*C*H-9), 127.1 (*C*H-8), 114.2 (CH_2-4), 80.1 (*C*H-2), 56.3 (CH_3-5), 21.2 (CH_3-1).

HRMS (ESI$^+$): calculated $[M-MeO]^+$ for $C_{10}H_{11}$: 131.0856; found: 131.0838.

IR (neat) ν (cm^{-1}): 3081, 2979, 2929, 2820, 1629, 199, 1573, 1493, 1443, 1372, 1204, 1117, 1091, 1017, 909, 838, 778, 697.

1-Isobutyl-4-(3-methoxybut-1-en-2-yl)benzene 3ca



3ca

Synthesized at room temperature for 48 h following the general procedure using 1-(but-1-en-2-yl)-4-isobutylbenzene **1c** (93 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), Ni(cod)$_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L$_4$** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1c**: >95%, conversion of **3ca**: 86%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et$_2$O = 49:1) afforded the desired product as a colorless oil (92 mg, 0.39 mmol, 85% yield).

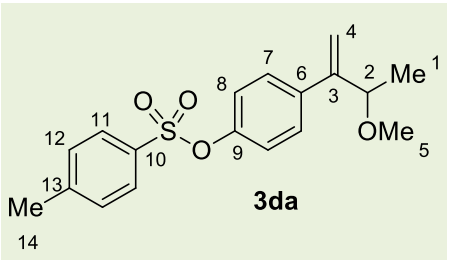
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.37 – 7.30 (m, 2H, *H*-7), 7.10 (d, *J* = 8.1 Hz, 2H, *H*-8), 5.36 (d, $^2J_{HH}$ = 1.5 Hz, 1H, *H*-4), 5.30 – 5.19 (m, 1H, *H*-4), 4.19 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.6 Hz, *H*-2), 3.38 (s, 3H, *H*-5), 2.47 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *H*-10), 1.87 (dh$_{app}$, $^3J_{HH}$ = 13.6, 6.6 Hz, 1H, *H*-11), 1.29 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1), 0.91 (d, $^3J_{HH}$ = 6.6 Hz, 6H, *H*-12).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.3 (*C*-3), 141.2 (*C*-9), 137.2 (*C*-6), 129.1 (*C*H-8), 126.7 (*C*H-7), 113.3 (CH_2-4), 80.1 (*C*H-2), 56.3 (CH_3-5), 45.2 (CH_2-10), 30.3 (*C*H-11), 22.5 (CH_3-12), 21.4 (CH_3-1).

HRMS (ESI$^+$): calculated [M+H]$^+$ for $C_{15}H_{23}O$: 219.1744; found: 219.1741.

IR (neat) ν (cm^{-1}): 2955, 2869, 1627, 1511, 1463, 1370, 1204, 1118, 1092, 1017, 907, 848, 801.

4-(3-Methoxybut-1-en-2-yl)phenyl 4-methylbenzenesulfonate 3da



3da

Synthesized at room temperature for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)phenyl 4-methylbenzenesulfonate **1d** (150 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), Ni(cod)$_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L$_4$** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1d**: 90%, conversion of **3da**: 75%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et$_2$O = 5.5:1) afforded the desired product as a white solid (118 mg, 0.35 mmol, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.77 – 7.61 (m, 2H, *H*-11), 7.36 – 7.29 (m, 4H, *H*-7, *H*-12), 6.96 – 6.87 (m, 2H, *H*-8), 5.33 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.30 – 5.27 (m, 1H, *H*-4), 4.11

(qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.7 Hz, 1H, *H*-2), 3.34 (s, 3H, *H*-5), 2.45 (s, 3H, *H*-14), 1.23 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

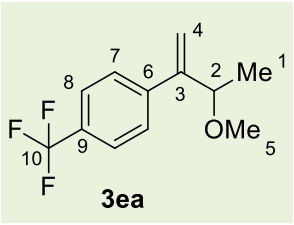
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.1 (*C*-9), 148.1 (*C*-3), 145.5 (*C*-13), 138.7 (*C*-6), 132.7 (*C*-10), 129.9 (*C*H-7), 128.7 (*C*H-11), 128.4 (*C*H-12), 122.2 (*C*H-8), 115.3 (CH_2-4), 80.2 (*C*H-2), 56.3 (CH_3-5), 21.9 (CH_3-14), 21.0 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{18}H_{21}O_4S$: 333.1156; found: 333.1142.

IR (neat) ν (cm^{-1}): 2980, 2929, 1631, 1597, 1500, 1449, 1369, 1296, 1199, 1177, 1154, 1121, 1091, 1016, 859, 814, 764.

m.p. (°C): 46-47.

1-(3-Methoxybut-1-en-2-yl)-4-(trifluoromethyl)benzene 3ea



3ea

Synthesized at 10 °C for 48 h following the general procedure using 1-(buta-1,3-dien-2-yl)-4-(trifluoromethyl)benzene **1e** (99 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L$_4$** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1e**: >95%, conversion of **3ea**: 77%, *rr* = 4.5:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 39:1) afforded the desired product as a colorless oil (81 mg, 0.35 mmol, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.58 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*-8), 7.54 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*-7), 5.42 (d, $^2J_{HH}$ = 1.2 Hz, 1H, *H*-4), 5.38 – 5.36 (m, 1H, *H*-4), 4.18 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.8 Hz, 1H, *H*-2), 3.38 (s, 3H, *H*-5), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

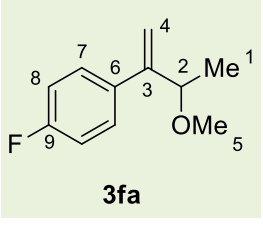
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 148.3 (*C*-3), 143.4 (*C*-6), 129.7 (q, $^2J_{CF}$ = 33 Hz, *C*-9), 127.5 (*C*H-7), 125.3 (q, $^3J_{CF}$ = 4 Hz, *C*H-8), 124.3 (q, $^1J_{CF}$ = 272 Hz, *C*-10), 116.3 (CH_2-4), 80.1 (*C*H-2), 56.3 (CH_3-5), 20.9 (CH_3-1).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ (ppm) = -62.56.

HRMS (ESI$^+$): calculated $[M+NH_4]^+$ for $C_{12}H_{17}F_3NO$: 248.1262; found: 248.1263.

IR (neat) ν (cm^{-1}): 2981, 2932, 1616, 1451, 1405, 1373, 1321, 1163, 1122, 1063, 1015, 919, 848.

1-Fluoro-4-(3-methoxybut-1-en-2-yl)benzene 3fa



3fa

Synthesized at 10 °C for 48 h following the general procedure using 1-(buta-1,3-dien-2-yl)-4-fluorobenzene **1f** (74 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L$_4$** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1f**: >95%, conversion of

3fa: 78%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 49:1) afforded the desired product as a colorless oil (68 mg, 0.38 mmol, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.44 – 7.34 (m, 2H, *H*-7), 7.03 – 6.98 (m, 2H, *H*-8), 5.32 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.30 – 5.20 (m, 1H, *H*-4), 4.14 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.8 Hz, 1H, *H*-2), 3.37 (s, 3H, *H*-5), 1.26 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

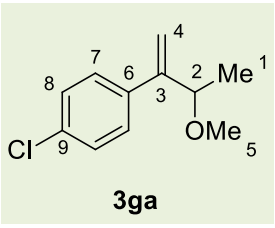
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 162.5 (d, $^1J_{CF}$ = 246 Hz, *C*-9), 148.3 (*C*-3), 135.8 (d, $^4J_{CF}$ = 4 Hz, *C*-6), 128.8 (d, $^3J_{CF}$ = 8 Hz, *C*H-7), 115.2 (d, $^2J_{CF}$ = 21 Hz, *C*H-8), 114.5 (*C*H_2-4), 80.4 (*C*H-2), 56.3 (*C*H_3-5), 21.0 (*C*H_3-1).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ (ppm) = -155.15.

HRMS (ESI$^+$): calculated $[M+NH_4]^+$ for $C_{11}H_{18}FNO$: 198.1289; found: 198.1258.

IR (neat) ν (cm^{-1}): 2981, 2931, 1629, 1603, 1507, 1451, 133, 1224, 1161, 1121, 1089, 1014, 913, 839, 812.

1-Chloro-4-(3-methoxybut-1-en-2-yl)benzene 3ga



3ga

Synthesized at 10 °C for 48 h following the general procedure using 1-(buta-1,3-dien-2-yl)-4-chlorobenzene **1g** (82 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1g**: >95%, conversion of **3ga**: 91%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 99:1) afforded the desired product as a colorless oil (80 mg, 0.41 mmol, 81% yield).

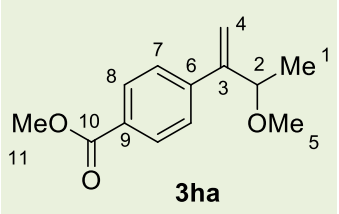
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.34 (m, 2H, *H*-8), 7.32 – 7.27 (m, 2H, *H*-7), 5.35 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.30 – 5.28 (m, 1H, *H*-4), 4.14 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.8 Hz, 1H, *H*-2), 3.36 (s, 3H, *H*-5), 1.26 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 148.2 (*C*-3), 138.2 (*C*-6), 133.5 (*C*-9), 128.52 (*C*H-7 or *C*H-8), 128.51 (*C*H-7 or *C*H-8), 115.0 (*C*H_2-4), 80.2 (*C*H-2), 56.3 (*C*H_3-5), 21.0 (*C*H_3-1).

HRMS (ESI$^+$): calculated $[M-MeO]^+$ for $C_{10}H_{10}Cl$: 165.0466; found: 165.0475.

IR (neat) ν (cm^{-1}): 3081, 2980, 2930, 2820, 1629, 1594, 1490, 1450, 1373, 1204, 1117, 1089, 1012, 913, 833.

Methyl 4-(3-methoxybut-1-en-2-yl)benzoate 3ha



3ha

Synthesized at 10 °C for 48 h following the general procedure using methyl 4-(buta-1,3-dien-2-yl)benzoate **1h** (94 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg,

0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1h**: >95%, conversion of **3ha**: 90%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 9:1) afforded the desired product as a colorless oil (98 mg, 0.45 mmol, 89% yield).

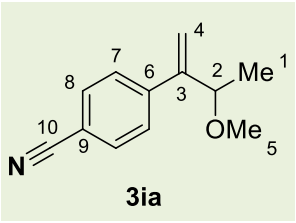
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.99 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *H*-8), 7.49 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *H*-7), 5.44 (s, 1H, *H*-4), 5.37 (s, 1H, *H*-4), 4.19 (q, $^3J_{HH}$ = 6.4 Hz, 1H, *H*-2), 3.92 (s, 3H, *H*-11), 3.37 (s, 3H, *H*-5), 1.27 (d, $^3J_{HH}$ = 6.4 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 167.1 (*C*-10), 148.7 (*C*-3), 144.5 (*C*-6), 129.7 (*C*H-8), 129.3 (*C*-9), 127.1 (*C*H-7), 115.9 (CH_2-4), 80.0 (*C*H-2), 56.3 (CH_3-5), 52.2 (CH_3-11), 21.0 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{13}H_{17}O_3$: 221.1173; found: 221.1165.

IR (neat) ν (cm^{-1}): 3060, 3029, 297, 2929, 2863, 1625, 1600, 1518, 1486, 1451, 1391, 1369, 1311, 1204, 1077, 1025, 908, 843, 770, 732, 694.

4-(3-Methoxybut-1-en-2-yl)benzonitrile 3ia



3ia

Synthesized at 10 °C for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)benzonitrile **1i** (78 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1i**: >95%, conversion of **3ia**: 70%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 19:1) afforded the desired product as a colorless oil (64 mg, 0.34 mmol, 68% yield).

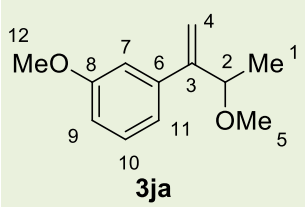
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.59 (m, 2H, *H*-8), 7.58 – 7.51 (m, 2H, *H*-7), 5.45 (d, $^3J_{HH}$ = 1.0 Hz, 1H, *H*-4), 5.41 – 5.38 (m, 1H, *H*-4), 4.17 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.7 Hz, 1H, *H*-2), 3.36 (s, 3H, *H*-5), 1.26 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 147.9 (*C*-3), 144.4 (*C*-6), 132.2 (*C*H-8), 127.9 (*C*H-7), 119.0 (*C*-10), 117.2 (CH_2-4), 111.3 (*C*-9), 80.0 (*C*H-2), 56.3 (CH_3-5), 20.8 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{12}H_{14}NO$: 188.1070; found: 188.1066.

IR (neat) ν (cm^{-1}): 2980, 2930, 2822, 2228, 1605, 1503, 1449, 1403, 1373, 1204, 1117, 1088, 1016, 921, 847, 750.

1-Methoxy-3-(3-methoxybut-1-en-2-yl)benzene 3ja



3ja

Synthesized at rt for 48 h following the general procedure using 1-(buta-1,3-dien-2-yl)-3-methoxybenzene **1j** (93 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2

mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **j** >95%, conversion of **3ja**: 80%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 19:1) afforded the desired product as a colorless oil (79 mg, 0.41 mmol, 82% yield).

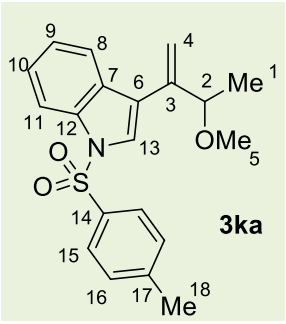
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.25 (t, $^3J_{HH}$ = 7.9 Hz, 1H, *H*-10), 7.01 (ddd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.5, 1.0 Hz, 1H, *H*-11), 6.99 – 6.96 (m, 1H, *H*-7), 6.84 (ddd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.6, 0.9 Hz, 1H, *H*-9), 5.37 (d, $^2J_{HH}$ = 1.5 Hz, 1H, *H*-4), 5.32 – 5.24 (m, 1H, *H*-4), 4.17 (qd, $^3J_{HH}$ = 6.4, $^4J_{HH}$ = 0.8 Hz, 1H, *H*-2), 3.82 (s, 3H, *H*-12), 3.38 (s, 3H, *H*-5), 1.28 (d, $^3J_{HH}$ = 6.4 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 159.6 (*C*-8), 149.3 (*C*-3), 141.5 (*C*-6), 129.3 (*C*H-10), 119.6 (*C*H-11), 114.2 (CH_2-4), 113.0 (*C*H-7 or *C*H-9), 112.8 (*C*H-7 or *C*H-9), 80.0 (*C*H-2), 56.3 (CH_3-5), 55.4 (CH_3-12), 21.2 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{12}H_{17}O_2$: 193.1223; found: 193.1221.

IR (neat) ν (cm^{-1}): 2978, 2932, 1598, 1575, 1487, 1462, 1427, 1286, 1223, 1116, 1090, 1045, 911, 871, 784.

3-(3-Methoxybut-1-en-2-yl)-1-tosyl-1*H*-indole 3ka



Synthesized at rt for 70 h following the general procedure using 3-(buta-1,3-dien-2-yl)-1-tosyl-1*H*-indole **1k** (161 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (8.2 mg, 0.01 mmol, 6 mol%), (Cy)-Phox **L_4** (10.3 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1k** = 69%, conversion of **3ka**: 43%, *rr* >20:1. Purification by flash chromatography over silica gel (CH_2Cl_2) afforded the desired product as a white solid (76 mg, 0.21 mmol, 43% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.01 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*-11), 7.77 (d, $^3J_{HH}$ = 8.4 Hz, 2H, *H*-15), 7.75 – 7.68 (m, 2H, *H*-8, *H*-13), 7.34 – 7.30 (m, 1H, *H*-10), 7.27 – 7.19 (m, 3H, *H*-9, *H*-16), 5.56 – 5.54 (m, 1H, *H*-4), 5.48 (s, 1H, *H*-4), 4.10 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.39 (s, 3H, *H*-5), 2.34 (s, 3H, *H*-18), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

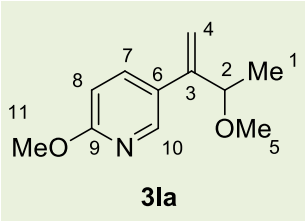
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 145.1 (*C*-17), 141.3 (*C*-3), 135.36 (*C*-12 or *C*-14), 135.31 (*C*-12 or *C*-14), 130.2 (*C*-7), 130.0 (*C*H-16), 127.0 (*C*H-15), 124.8 (*C*H-10), 123.9 (*C*H-13), 123.5 (*C*H-9), 120.9 (*C*H-8), 120.2 (*C*-6), 115.7 (CH_2-4), 113.9 (*C*H-11), 81.5 (*C*H-2), 56.3 (CH_3-5), 21.7 (CH_3-18), 21.0 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{20}H_{22}NO_3S$: 356.115; found: 356.1301.

IR (neat) ν (cm^{-1}): 3146, 2978, 2928, 1631, 1594, 1446, 1366, 1303, 1272, 1252, 1171, 1115, 1089, 1013, 959, 812, 751, 661.

m.p. (°C): 81-83.

2-Methoxy-5-(3-methoxybut-1-en-2-yl)pyridine 3la



3la

Synthesized at 10 °C for 48 h following the general procedure using 5-(buta-1,3-dien-2-yl)-2-methoxypyridine **1l** (74 mg, 0.50 mmol, 1.0 equiv), methanol **2a** (82 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (8.2 mg, 0.01 mmol, 6 mol%), (Cy)-Phox $\mathbf{L_4}$ (10.3 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1l** > 95%, conversion of **3la**: 90%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 49:1) afforded the desired product as a clear colorless oil (86 mg, 0.44 mmol, 89% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.25 – 8.19 (m, 1H, *H*-10), 7.67 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.5 Hz, 1H, *H*-7), 6.70 (dd, $^3J_{HH}$ = 8.7, $^5J_{HH}$ = 0.7 Hz, 1H, *H*-8), 5.32 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.28 – 5.23 (m, 1H, *H*-4), 4.12 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ 0.6 Hz, 1H, *H*-2), 3.94 (s, 3H, *H*-11), 3.35 (s, H5), 1.26 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) = 163.7 (*C*-9), 146.0 (*C*-3), 145.2 (*C*H-10), 137.6 (*C*H-7), 128.5 (*C*-6), 114.6 (CH_2-4), 110.4 (*C*H-8), 80.4 (*C*H-2), 56.2 (CH_3-5), 53.6 (CH_3-11), 20.9 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{11}H_{16}NO_2$: 194.1176; found: 194.1183.

IR (neat) ν (cm^{-1}): 2979, 2936, 1625, 1600, 1562, 1491, 1460, 1369, 1282, 1250, 1119, 1090, 1021, 909, 833.

3.2. Scope in alcohols

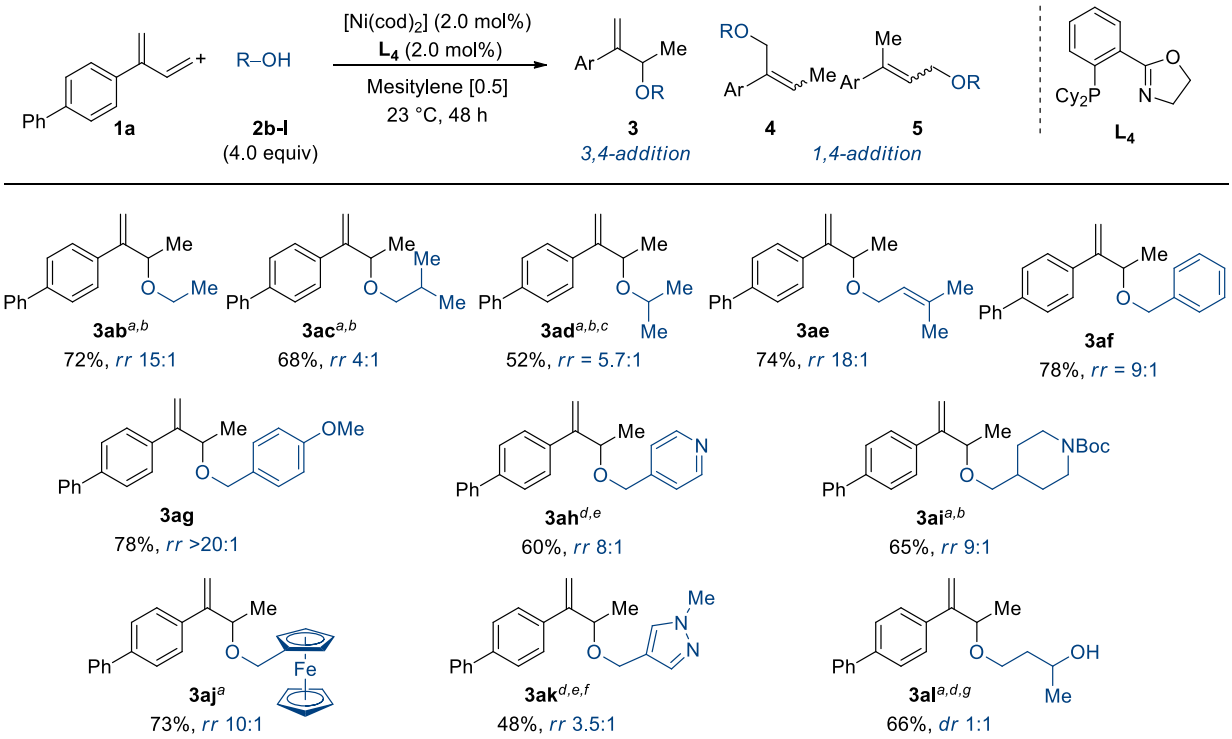
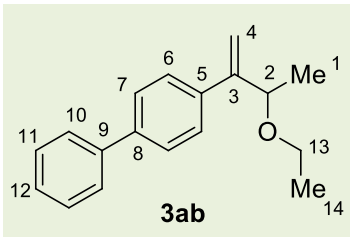


Figure S2. Scope of the Ni-catalyzed hydroalkoxylation of 2-substituted 1,3-dienes - Variation of the alcohol component. 0.10-0.50 mmol scale. Yields of 3,4-addition product after purification. Regioselectivity expressed as the ratio between 3,4- and 1,4-addition products as determined by ^{1}H NMR using *p*-methoxytoluene as an internal standard (**3**:[**4**+**5**]). [a] 40°C. [b] 24 h. [c] 10 mol% catalyst. [d] THF used as solvent. [e] 6 mol% catalyst. [f] 96 h. [g] 70 h.

4-(3-Ethoxybut-1-en-2-yl)-1,1'-biphenyl 3ab



Synthesized at 40 °C for 24 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), ethanol **2b** (116 µL, 2.00 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: 88%, conversion of **3ab**: 75%, *rr* = 15:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 19:1) afforded the desired product as a colorless oil (92 mg, 0.36 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.49 (m, 6H, *H*-6, *H*-7, *H*-10), 7.45 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *H*-11), 7.35 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *H*-12), 5.41 (d, $^2J_{HH}$ = 1.3 Hz, 1H, *H*-4), 5.33 (s, 1H, *H*-4), 4.34 (q, $^3J_{HH}$ = 6.4 Hz, 1H, *H*-2), 3.73 – 3.56 (m, 1H, *H*-13), 3.58 – 3.38 (m, 1H, *H*-13), 1.33 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1), 1.27 (t, $^3J_{HH}$ = 7.0 Hz, 3H, *H*-14).

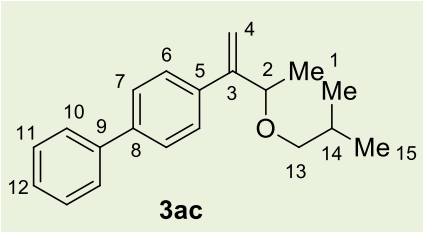
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.5 (*C*-3), 140.9 (*C*-8), 140.4 (*C*-9), 138.9 (*C*-5), 128.9 (*C*H-11), 127.5 (*C*H-7), 127.4 (*C*H-12), 127.14 (*C*H-6 or *C*H-10), 127.07 (*C*H-6 or *C*H-10), 113.8 (CH_2-4), 78.3 (*C*H-2), 63.9 (CH_2-13), 21.7 (CH_3-1), 15.6 (CH_3-14).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{18}H_{21}O$: 253.1587; found: 253.1582.

IR (neat) ν (cm^{-1}): 3029, 2974, 2867, 1626, 1600, 1486, 1445, 1399, 1370, 1322, 1157, 1120, 1083, 908, 845, 769, 740, 695.

.

4-(3-Isobutoxybut-1-en-2-yl)-1,1'-biphenyl 3ac



3ac

Synthesized at 40 °C for 24 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (21 mg, 0.1 mmol, 1.0 equiv), isobutyl alcohol **2c** (37 µL, 0.40 mmol, 4.0 equiv), $Ni(cod)_2$ (0.6 mg, 0.002 mmol, 2 mol%), (Cy)-Phox **L_4** (0.7 mg, 0.002 mmol, 2 mol%) and mesitylene (0.20 mL, 0.50 M). Consumption of **1a**: >95%, conversion of **3ac**: 70%, *rr* = 5.7:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 32:1) afforded the desired product as a colorless oil (19 mg, 0.068 mmol, 68% yield).

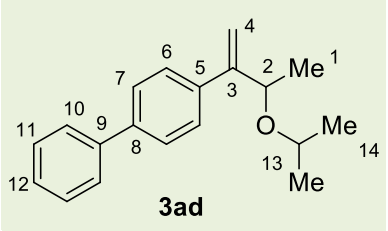
^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.59 (m, 2H, *H*-10), 7.60 – 7.51 (m, 4H, *H*-6, *H*-7), 7.49 – 7.38 (m, 2H, *H*-11), 7.35 (tt, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 1.2 Hz, 1H, *H*-12), 5.42 (d, $^2J_{HH}$ = 1.5 Hz, 1H, *H*-4), 5.33 (s, 1H, *H*-4), 4.31 (q, $^2J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.36 (dd, $^2J_{HH}$ = 9.0, $^3J_{HH}$ = 7.1 Hz, 1H, *H*-13), 3.19 (dd, $^2J_{HH}$ = 9.0, $^3J_{HH}$ = 6.4 Hz, 1H, *H*-13), 1.93 (dh, $^3J_{HH}$ = 13.3, 6.7 Hz, 1H, *H*-14), 1.33 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1), 0.97 – 0.95 (m, 6H, *H*-15).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.5 (*C*-3), 140.9 (*C*-8), 140.3 (*C*-9), 138.9 (*C*-5), 128.9 (*C*H-11), 127.4 (*C*H-7), 127.4 (*C*H-12), 127.1 (*C*H-6 or *C*H-10), 127.0 (*C*H-6 or *C*H-10), 113.8 (CH_2-4), 78.5 (*C*H-2), 75.7 (CH_2-13), 28.8 (*C*H-14), 21.5 (CH_3-1), 19.8 (CH_3-15), 19.7 (CH_3-15).

HRMS (ESI$^+$): calculated $[M\text{-}O\textit{i}Bu]^+$ for $C_{16}H_{15}$: 207.1169; found: 207.1165.

IR (neat) ν (cm^{-1}): 3030, 2956, 2929, 2870, 1626, 1601, 1519, 1487, 1470, 1448, 1400, 1367, 1328, 1081, 1008, 907, 843, 770, 741, 696.

4-(3-Isopropoxybut-1-en-2-yl)-1,1'-biphenyl 3ad



3ad

Synthesized at 40 °C for 24 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.5 mmol, 1.0 equiv), isopropanol **2d** (153 µL, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%), (Cy)-Phox **L_4** (17.2 mg, 0.05 mmol, 10 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: 85%, conversion of **3ad**: 53%, *rr* = 6:1. Purification by flash

chromatography over silica gel (pentane:Et_2O = 65:1) afforded the desired product as a colorless oil (69 mg, 0.26 mmol, 52% yield).

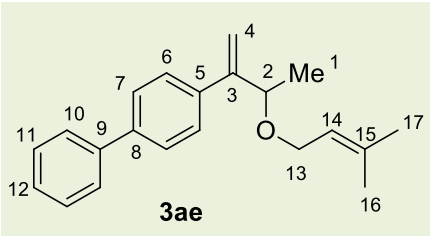
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.50 (m, 6H, *H*-6, *H*-7, *H*-10), 7.48 – 7.41 (m, 2H, *H*-11), 7.40 – 7.29 (m, 1H, *H*-12), 5.39 (d, $^2J_{HH}$ = 1.6 Hz, 1H, *H*-4), 5.35 (s, 1H, *H*-4), 4.46 (q, $^3J_{HH}$ = 6.4 Hz, 1H, *H*-2), 3.77 (hept, $^3J_{HH}$ = 6.0 Hz, 1H, *H*-13), 1.30 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1), 1.21 (dd_{app}, *J* = 6.1, 1.8 Hz, 6H, *H*-14).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 150.3 (*C*-3), 140.9 (*C*-8 or *C*-9), 140.4 (*C*-8 or *C*-9), 139.1 (*C*-5), 128.9 (*C*H-11), 127.5 (*C*H-6, *C*H-7 or *C*H-10) 127.42 (*C*H-5), 127.14 (*C*H-6, *C*H-7 or *C*H-10), 127.06 (*C*H-6, *C*H-7 or *C*H-10), 113.5 (CH_2-4), 75.1 (*C*H-2), 68.8 (*C*H-13), 23.4 (CH_3-14), 22.3 (CH_3-1), 21.7 (CH_3-14).

GCMS (EI^+): calculated $[M+Na]^+$ for $C_{19}H_{22}ONa$: 289.1569; found: 289.1561.

IR (neat) ν (cm^{-1}): 3030, 2972, 1625, 100, 1487, 1447, 1369, 1316, 1121, 1077, 981, 907, 843, 769, 741, 695.

4-(3-((3-Methylbut-2-en-1-yl)oxy)but-1-en-2-yl)-1,1'-biphenyl 3ae



3ae

Synthesized at rt for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), 3-methylbut-2-en-1-ol **2e** (203 µL, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: >95%, conversion of **3ae**: 80%, *rr* = 18:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 32:1) afforded the desired product as a colorless oil (108 mg, 0.37 mmol, 74% yield).

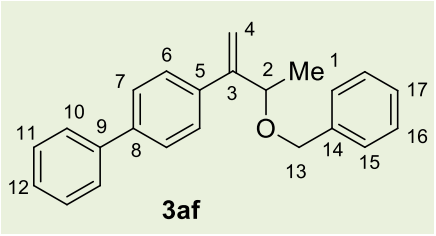
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.66 – 7.50 (m, *H*-6, *H*-7, *H*-10), 7.49 – 7.41 (m, 2H, *H*-11), 7.38 – 7.31 (m, 1H, *H*-12), 5.49 – 5.39 (m, 2H, *H*-4, *H*-14), 5.34 (s, 1H, *H*-4), 4.38 (q, $^3J_{HH}$ = 6.4 Hz, 1H, *H*-2), 4.13 (dd, $^2J_{HH}$ = 11.3, $^3J_{HH}$ = 6.7 Hz, 1H, *H*-13), 3.95 (dd, $^2J_{HH}$ = 11.2, $^3J_{HH}$ = 7.3 Hz, 1H, *H*-13), 1.77 (s, 3H, *H*-16 or *H*-17), 1.67 (s, 3H, *H*-16 *or H*-17), 1.34 (d, *J* = 6.4 Hz, 2H, *H*-1).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 149.5 (*C*-3), 140.9 (*C*-8), 140.4 (*C*-9), 138.9 (*C*-5), 137.0 (*C*-15), 128.9 (*C*H-11), 127.5 (*C*H-7), 127.4 (*C*H-12), 127.14 (*C*H-6 or *C*H-10), 127.08 (*C*H-6 or *C*H-10), 121.5 (*C*H-14), 114.0 (CH_2-4), 77.6 (*C*H-2), 65.0 (CH_2-13), 26.0 (CH_3-16 or CH_3-17), 21.8 (CH_3-1), 18.2 (CH_3-16 or CH_3-17).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{21}H_{21}NaO$: 315.1725; found: 315.1741.

IR (neat) ν (cm^{-1}): 3030, 2977, 2929, 2861, 1675, 1625, 1600, 1487, 1445, 132, 1313, 1200, 1078, 1052, 1008, 908, 843, 76, 741, 695.

4-(3-(Benzyloxy)but-1-en-2-yl)-1,1'-biphenyl 3af



3af

Synthesized at rt for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), benzyl alcohol **2f** (213 µL, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: >95%, conversion of **3ae**: 79%, *rr* = 9:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 32:1) afforded the desired product as a colorless oil (124 mg, 0.39 mmol, 78% yield).

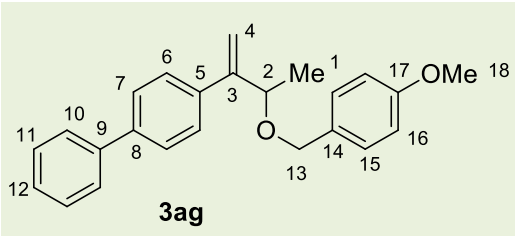
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.58 (m, 2H, *H*-10), 7.60 – 7.51 (m, 4H, *H*-7, *H*-15), 7.48 – 7.41 (m, 2H, *H*-11), 7.41 – 7.33 (m, 5H, *H*-6, *H*-12, *H*-16), 7.32 – 7.28 (m, 1H, *H*-17), 5.49 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.42 – 5.39 (m, 1H, *H*-4), 4.71 (d, $^2J_{HH}$ = 11.8 Hz, 1H, *H*-13), 4.49 (d, $^2J_{HH}$ = 11.8 Hz, 1H, *H*-13), 4.45 (qd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 0.7 Hz, 1H, *H*-2), 1.38 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 149.1 (*C*-3), 140.9 (*C*-8 or *C*-9), 140.5 (*C*-8 or *C*-9), 138.8 (*C*-5 or *C*-14), 138.7 (*C*-5 or *C*-14), 128.9 (*C*H -11), 128.6 (*C*H -Ar), 127.9 (*C*H -Ar), 127.7 (*C*H -12 or *C*H -17) 127.5 (*C*H -Ar), 127.4 (*C*H -12 or *C*H -17), 127.14 (*C*H -Ar), 127.12 (*C*H-Ar), 114.4 (CH_2-4), 77.8 (*C*H-2), 70.3 (CH_2-13), 21.6 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{23}H_{23}O$: 315.1744; found: 315.1736.

IR (neat) ν (cm^{-1}): 3060, 3029, 297, 2929, 2863, 1625, 1600, 1518, 1486, 1451, 1391, 1369, 1311, 1204, 1077, 1025, 908, 843, 770, 732, 694.

4-(3-((4-Methoxybenzyl)oxy)but-1-en-2-yl)-1,1'-biphenyl 3ag



3ag

Synthesized at rt for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), (4-methoxyphenyl)methanol **2g** (248 µL, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: >95%, conversion of **3ag**: 80%, *rr* >20:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 13:1) afforded the desired product as a colorless oil (135 mg, 0.39 mmol, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.63 – 7.60 (m, 2H, *H*-10), 7.59 – 7.53 (m, 4H, *H*-6, *H*-7), 7.48 – 7.42 (m, 2H, *H*-11), 7.37 – 7.33 (m, 1H, *H*-12), 7.32 – 7.28 (m, 2H, *H*-15), 6.92 – 5.88 (m, 2H, *H*-16), 5.49 (d, $^2J_{HH}$ = 1.5 Hz, 1H, *H*-4), 5.39 (s, 1H, *H*-4), 4.64 (d, $^2J_{HH}$ = 11.4

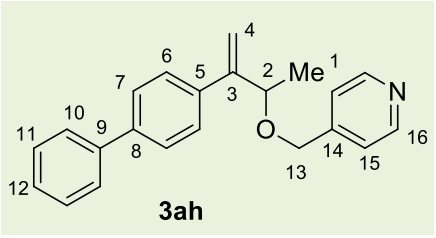
Hz, 1H, *H*-13), 4.47 – 4.39 (m, 2H, *H*-13, *H*-2), 3.82 (s, 3H, *H*-18), 1.36 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 159.3 (*C*-17), 149.2 (*C*-3), 140.9 (*C*-8), 140.5 (*C*-9), 138.8 (*C*-5), 130.9 (*C*-14), 129.5 (*C*H-15), 128.9 (*C*H-11), 127.5 (*C*H-7), 127.4 (*C*H-12), 127.14 (*C*H-6 or *C*H-10), 127.10 (*C*H-6 or *C*H-10), 114.3 (CH_2-4), 114.0 (*C*H-16), 77.4 (*C*H-2), 70.0 (CH_2-13), 55.4 (CH_3-18), 21.7 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+Na]^+$ for $C_{24}H_{24}O_2Na$: 367.1669; found: 367.1655.

IR (neat) ν (cm^{-1}): 3052, 2932, 2860, 1611, 1582, 1511, 1489, 1442, 1300, 1246, 1171, 1103, 1079, 1028, 904, 846, 825, 773, 742, 699.

4-(((3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)oxy)methyl)pyridine 3ah



3ah

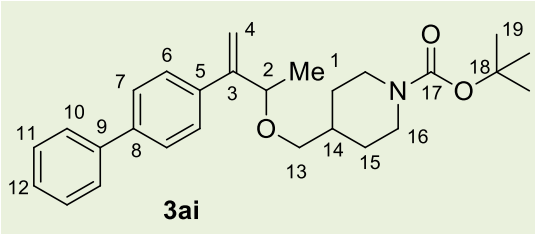
Synthesized at rt for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), pyridin-4-ylmethanol **2h** (218 mg, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (8.2 mg, 0.03 mmol, 6 mol%), (Cy)-Phox **L_4** (10.3 mg, 0.01 mmol, 6 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: 85%, conversion of **3ah**: 63%, *rr* > 8:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 2:3) afforded the desired product as a colorless oil (95 mg, 0.30 mmol, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.59 (d, $^{3}J_{HH}$ = 5.5 Hz, 1H, *H*-16), 7.63 – 7.49 (m, 6H, *H*-6, *H*-7, *H*-10), 7.48 – 7.41 (m, 2H, *H*-11), 7.39 – 7.29 (m, 3H, *H*-12, *H*-15), 5.50 (d, $^{2}J_{HH}$ = 1.2 Hz, 1H, *H*-4), 5.37 (s, 1H, *H*-4), 4.71 (d, $^{2}J_{HH}$ = 13.6 Hz, 1H, *H*-13), 4.54 – 4.40 (m, 2H, *H*-2, *H*-13), 1.42 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 149.8 (*C*-16), 148.7 (*C*-3), 148.2 (*C*-14), 140.75 (*C*-8 or *C*-9), 140.71 (*C*-8 or *C*-9), 138.3 (*C*-5), 128.9 (*C*H-11), 127.5 (*C*H-12), 127.4 (*C*H-6 or *C*H-7 or *C*H-10), 127.2 (*C*H-6 or *C*H-7 or *C*H-10), 127.1 (*C*H-6 or *C*H-7 or *C*H-10), 122.0 (*C*H-15), 114.6 (CH_2-4), 78.6 (*C*H-2), 68.6 (CH_2-13), 21.5 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{22}H_{22}NO$: 316.1701; found: 316.1694.

IR (neat) ν (cm^{-1}): 3028, 2979, 1603, 1561, 1487, 1447, 1414, 1370, 114, 1219, 1099, 1079, 1007, 910, 844, 796, 770, 741, 696.



3ai

***Tert*-butyl 4-(((3-([1,1'-biphenyl]-4-yl)but-3-en-2-yl)oxy)methyl)piperidine-1-carboxylate 3ai**

Synthesized at 40 °C for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51 mg, 0.25 mmol, 1.0 equiv),

tert-butyl 4-(hydroxymethyl)piperidine-1-carboxylate **2i** (215 mg, 1.0 mmol, 4.0 equiv), $Ni(cod)_2$ (1.4 mg, 0.005 mmol, 2 mol%), (Cy)-Phox **L_4** (1.7 mg, 0.005 mmol,2 mol%) and mesitylene (0.5 mL, 0.50 M). Consumption of **1a**: 85%, conversion of **3ai**: 68%, *rr* = 9:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 6:1) afforded the desired product as a colorless oil (68 mg, 0.16 mmol, 65% yield).

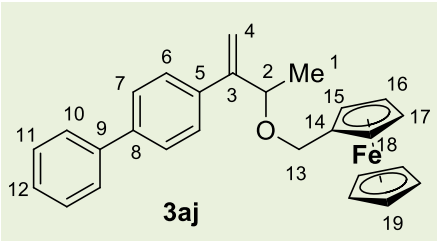
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.63 – 7.57 (m, 2H, *H*-10), 7.59 – 7.53 (m, 2H, *H*-7), 7.54 – 7.48 (m, 2H, *H*-6), 7.48 – 7.41 (m, 2H, *H*-6), 7.38 – 7.31 (m, 1H, *H*-11), 5.41 (d, $^2J_{HH}$ = 1.5 Hz, 1H, *H*-12), 5.30 (s, 1H, *H*-4), 4.29 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-4), 4.11 (d, J_{HH} = 11.1 Hz, 1H, *H*-16), 3.43 (dd, $^2J_{HH}$ = 9.0, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-13), 3.25 (dd, $^2J_{HH}$ = 9.0, $^3J_{HH}$ = 5.9 Hz, 1H, *H*-13), 2.71 (t, J_{HH} = 12.4 Hz, 2H, *H*-16), 1.83 – 1.70 (m, 3H, *H*-14, *H*-15), 1.45 (s, 9H, *H*-19), 1.32 (d, $^3J_{HH}$ = 6.5 Hz, 2H, *H*-1), 1.10 –1.21 (m, 2H, *H*-15).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 155.0 (*C*-17), 149.4 (*C*-3), 140.8 (*C*-8 or *C*-9), 140.5 (*C*-8 or *C*-9), 138.7 (*C*-5), 128.9 (*C*H-11), 127.45 (*C*H-12), 127.40 (*C*H-6), 127.13 (*C*H-10), 127.08 (*C*H-7), 113.8 (CH_2-4), 79.4 (*C*-18), 78.7 (*C*H-2), 73.5 (CH_2-13), 43.9 (CH_2-16), 36.9 (*C*H-14), 29.42 (CH_2-15), 29.34 (CH_2-15), 28.6 (CH_3-19), 21.4 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{27}H_{36}NO_3$: 422.2695; found: 422.2673.

IR (neat) ν (cm^{-1}): 29878, 2925, 2886, 1684, 1485, 1422, 1366, 1274, 1247, 1172, 1150, 1080, 1007, 967, 907, 844, 730, 696.

4-(3-(Ferrocenyl)but-1-en-2-yl)-1,1'-biphenyl 3aj



3aj

Synthesized at 40 °C for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), 1-(Hydroxymethyl)-ferrocene **2j** (432 mg, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.01 mmol, 2 mol%) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: >95%, conversion of **3aj**: 76%, *rr* = 10:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 19:1) afforded the desired product as an orange solid (155 mg, 0.37 mmol, 73% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.51 (m, 6H, *H*-6, *H*-7, *H*-10), 7.45 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *H*-11), 7.35 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *H*-12), 5.48 (d, $^2J_{HH}$ = 1.1 Hz, 1H, *H*-4), 5.36 (s, 1H, *H*-4), 4.46 – 4.36 (m, 2H, *H*-2, *H*-13), 4.32 – 4.11 (m, 9H, *H*-13, *H*-14, *H*-15, *H*-16, *H*-17, *H*-18, *H*-19), 1.29 (d, $^3J_{HH}$ = 6.4 Hz, 3H, *H*-1).

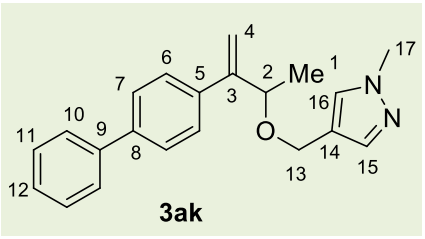
^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 140.9 (*C*-3), 140.5 (*C*-8 or *C*-9), 138.7 (*C*-8 or *C*-9), 128.9 (*C*-5), 127.5 (*C*H-6, *C*H-7 or *C*H-11), 127.4 (*C*H-12), 127.2 (*C*H-6, *C*H-7 or *C*H-11), 127.1 (*C*H-6, *C*H-7 or *C*H-11), 114.1 (CH_2-4), 84.3 (*C*-14), 77.3 (*C*H-2), 69.8 (*C*H-Fc, broad), 68.9 (*C*H-Fc, broad), 66.5 (CH_2-13), 21.7 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{27}H_{27}FeO$: 422.1333; found: 422.1328.

IR (neat) ν (cm^{-1}): 3084, 3030, 2976, 2859, 1623, 1600, 1518, 1486, 1446, 1403, 1372, 1316, 1235, 1104, 1078, 1041, 1003, 908, 842, 816, 769, 741, 695.

m.p. (°C): 70-71.

4-(((3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)oxy)methyl)-1-methyl-1H-pyrazole 3ak



3ak

Synthesized at rt for 96 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), (1-methyl-1*H*-pyrazol-4-yl)methanol **2k** (432 mg, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (8.2 mg, 0.03 mmol, 6 mol%), (Cy)-Phox **L_4** (10.3 mg, 0.03 mmol, 6 mol%) and THF (1.0 mL, 0.50 M). Consumption of **1a**: 93%, conversion of **3aj**: 50%, *rr* = 3.5:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) afforded the desired product as an pale yellow oil (76 mg, 0.23 mmol, 48% yield).

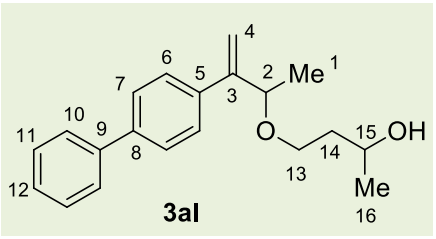
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.51 (m, 6H, *H*-6, *H*-7, *H*-10), 7.49 – 7.41 (m, 2H, *H*-11, *H*-15), 7.39 – 7.32 (m, 2H, *H*-12, *H*-16), 5.48 (d, $^2J_{HH}$ = 1.4 Hz, 1H, *H*-4), 5.37 (d, $^2J_{HH}$ = 1.1 Hz, 1H, *H*-4), 4.56 (d, $^2J_{HH}$ = 11.6 Hz, 1H, *H*-13), 4.43 (q, $^3J_{HH}$ = 6.3 Hz, 1H, *H*-2), 4.37 (d, $^2J_{HH}$ = 11.6 Hz, 1H, *H*-13), 3.88 (s, 3H, *H*-17), 1.34 (d, $^3J_{HH}$ = 6.3 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 149.1 (*C*-3), 140.8 (*C*-8 or *C*-9), 140.5 (*C*-8 or *C*-9), 139.4 (*C*H-15), 138.7 (*C*-5), 129.8 (*C*H-16), 128.9 (*C*H-11), 127.5 (*C*H-6 and *C*H-12), 127.14 (*C*H-7 or *C*H-10), 127.12 (*C*H-7 or *C*H-10), 119.0 (*C*-14), 114.3 (CH_2-4), 77.4 (*C*H-2), 61.1 (CH_2-13), 39.1 (CH_3-17), 21.7 (CH_3-1).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{21}H_{23}N_2O$: 319.1805; found: 319.1808.

IR (neat) ν (cm^{-1}): 3031, 2977, 1624, 1599, 1571, 1486, 1447, 1402, 1370, 1313, 1164, 1078, 1006, 983, 908, 844, 771, 741, 696.

4-((3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)oxy)butan-2-ol 3al



3al

Synthesized at rt for 70 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), butane-1,3-diol **2l** (178 μL, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (2.8 mg, 0.03 mmol, 2 mol%), (Cy)-Phox **L_4** (3.4 mg, 0.03 mmol, 6 mol%) and THF (1.0 mL, 0.50 M). Consumption of **1a**: 77%, conversion of **3al**: 67%. Purification by flash chromatography over silica gel (pentane:Et_2O = 1:1) led a 1:1 diastereomeric mixture of the desired products as an pale yellow oil (97 mg, 0.33 mmol, 66% yield).

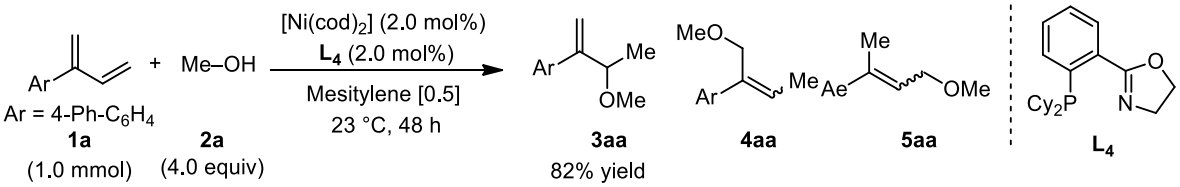
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.39 (m, 8H, *H*-6, *H*-7, *H*-10, *H*-11), 7.41 – 7.29 (m, 1H, *H*-12), 5.43 (d, $^2J_{HH}$ = 1.1 Hz, 1H, *H*-4), 5.33 (s, 1H, *H*-4), 4.36 (qd_{app}, *J* = 6.4, 3.3 Hz, 1H, *H*-2), 4.12 – 3.94 (m, 1H, *H*-15), 3.91 – 3.78 (m, 0.5H, *H*-13, *diastereoisomer 1*), 3.83 – 3.70 (m, 0.5H, *H*-13, *diastereoisomer 2*), 3.72 – 3.58 (m, 0.5H, H13, *diastereoisomer 2*), 3.63 – 3.51 (m, 0.5H, *H*-13, *diastereoisomer 1*), 2.94 (s, 1H, -O*H*, broad), 1.88 – 1.64 (m, 2H, *H*-14), 1.35 (dd_{app}, *J* = 6.5, 1.5 Hz, 3H, *H*-1), 1.21 (d, $^3J_{HH}$ = 6.2 Hz, 3H, *H*-16).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 149.3 (*C*-3), 149.0 (*C*-3), 140.8 (*C*-8), 140.59 (*C*-9), 140.58 (*C*-9), 138.7 (*C*-5), 138.5 (*C*-5), 128.9 (*C*H-11), 127.5 (*C*H-6, *C*H-7, *C*H-10 or *C*H-12), 127.41 (*C*H-6, *C*H-7, *C*H-10 or *C*H-12), 127.36 (*C*H-6, *C*H-7, *C*H-10 or *C*H-12), 127.16 (*C*H-6, *C*H-7, *C*H-10 or *C*H-12), 127.14 (*C*H-6, *C*H-7, *C*H-10 or *C*H-12), 114.1 (CH_2-4), 113.9 (CH_2-4), 79.0 (*C*H-2), 78.8 (*C*H-2), 68.1 (CH_2-13), 67.82 (*C*H-15), 67.78 (CH_2-13), 67.4 (*C*H-15), 38.5 (CH_2-14), 38.4 (CH_2-14), 23.6 (CH_3-16), 23.5 (CH_3-16), 21.6 (CH_3-1), 21.5 (CH_3-1).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{20}H_{24}O_2Na$: 319.1669; found: 319.1662.

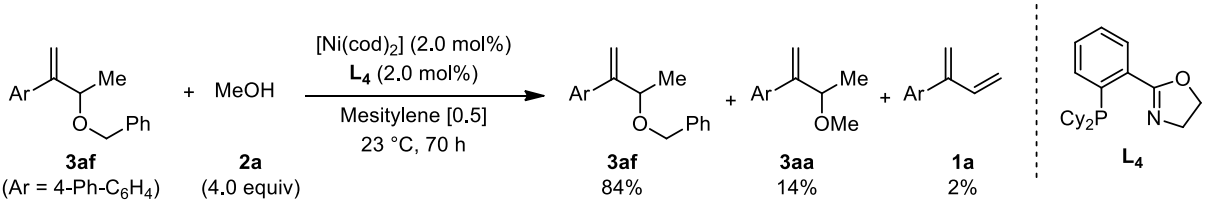
IR (neat) ν (cm^{-1}): 3425, 3030, 2970, 2928, 2868, 1817, 1626, 1600, 1486, 1447, 1401, 1371, 1321, 1078, 1038, 909, 844, 770, 741.

3.3. 1 Mmol scale experiment



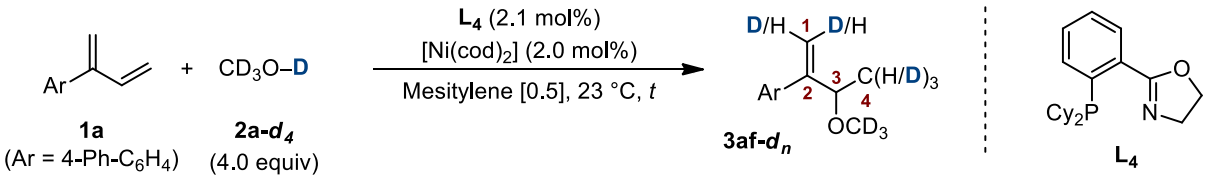
In a N_2-filled glovebox, $Ni(cod)_2$ (5.5 mg, 0.02 mmol, 2 mol%) and (Cy)-Phox **L$_4$** (6.9 mg, 0.02 mmol, 2 mol%) were charged in a 5 mL Schlenk tube and dissolved in anhydrous mesitylene (2.0 mL, 0.50 M). After stirring at room temperature for 5 min, diene **1a** (206 mg, 1.0 mmol, 1.0 equiv) and methanol **2a** (162 μL, 4.0 mmol, 4.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (5 mL) and concentrated under vacuum to afford the crude mixture. Consumption of **1a**: >95%, conversion of **3aa**: 83%, *rr* = 7:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 19:1) afforded the desired product **3aa** as a colorless oil (195 mg, 0.82 mmol, 82% yield).

4. Alcohol exchange experiment



In a N_2-filled glovebox, $Ni(cod)_2$ (0.6 mg, 0.002 mmol, 2 mol%) and (Cy)-Phox **L_4** (0.7 mg, 0.002 mmol, 2 mol%) were charged in a 5 mL Schlenk tube and dissolved in anhydrous mesitylene (0.20 mL, 0.50 M). After stirring at room temperature for 5 min, allylic ether **3af** (31 mg, 0.10 mmol, 1.0 equiv) and methanol **2a** (16 μL, 0.4 mmol, 4.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and the reaction mixture was stirred at room temperature for 70 h. The reaction mixture was then filtered over a short pad of silica gel, washed with ethyl acetate (5 mL) and concentrated under vacuum to afford the crude mixture. The conversions were determined by ^1H NMR analysis of the crude reaction mixture using *p*-methoxytoluene as an internal standard.

5. Deuterium labeling experiment



1a (Ar = 4-Ph-C_6H_4)

2a-d_4 (4.0 equiv)

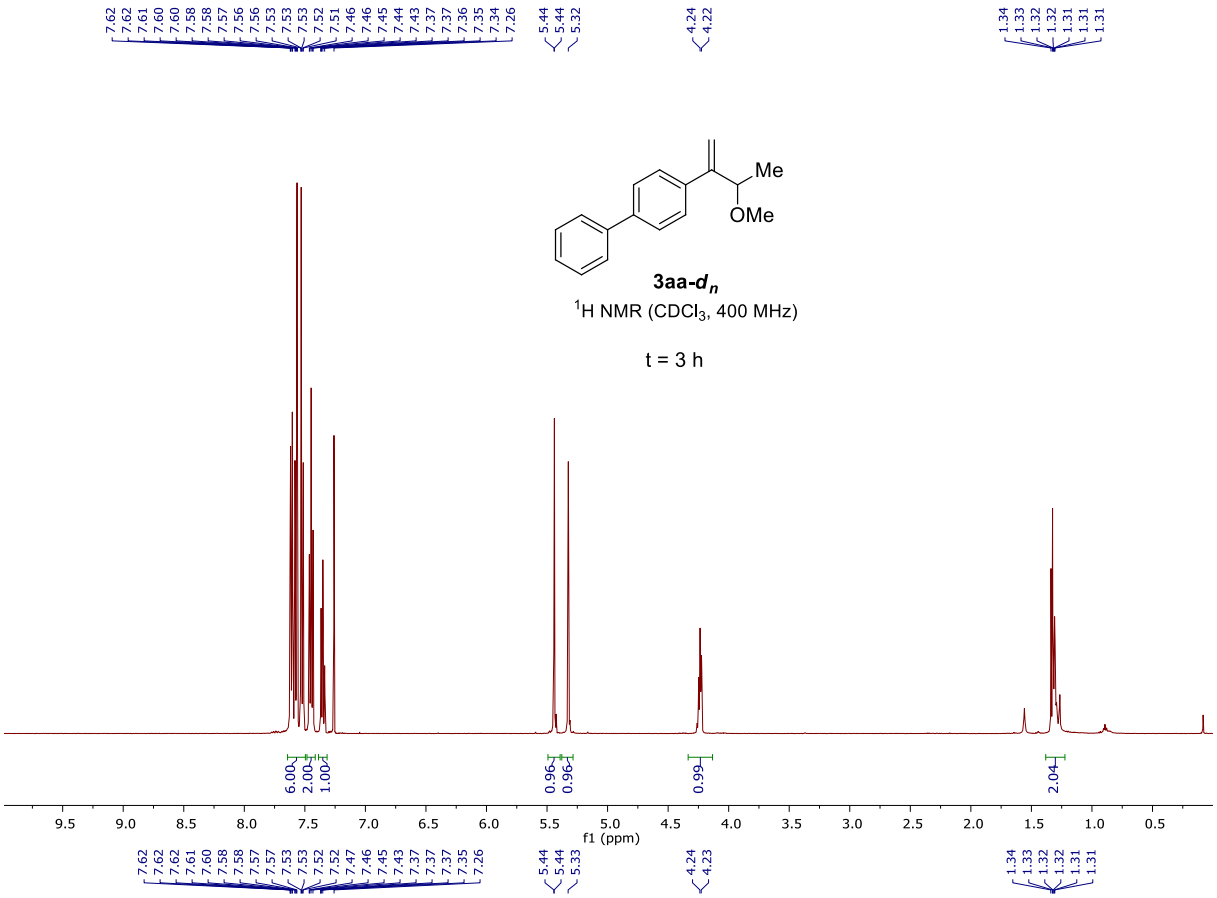
3af-d_n

L_4

	D incorporation (1a-d_n)		
***t* (h)**	**C1/C4**	**C2**	**C3**
3	28%	-	4%
6	39%	-	11%
24	18%	-	9%

		D incorporation (3af-d_n)			
***t* (h)**	**Conv. (%)**	**C1**	**C2**	**C3**	**C4**
3	58	5%	-	-	32%
6	81	4%	-	-	34%
24	86	9%	-	-	43%

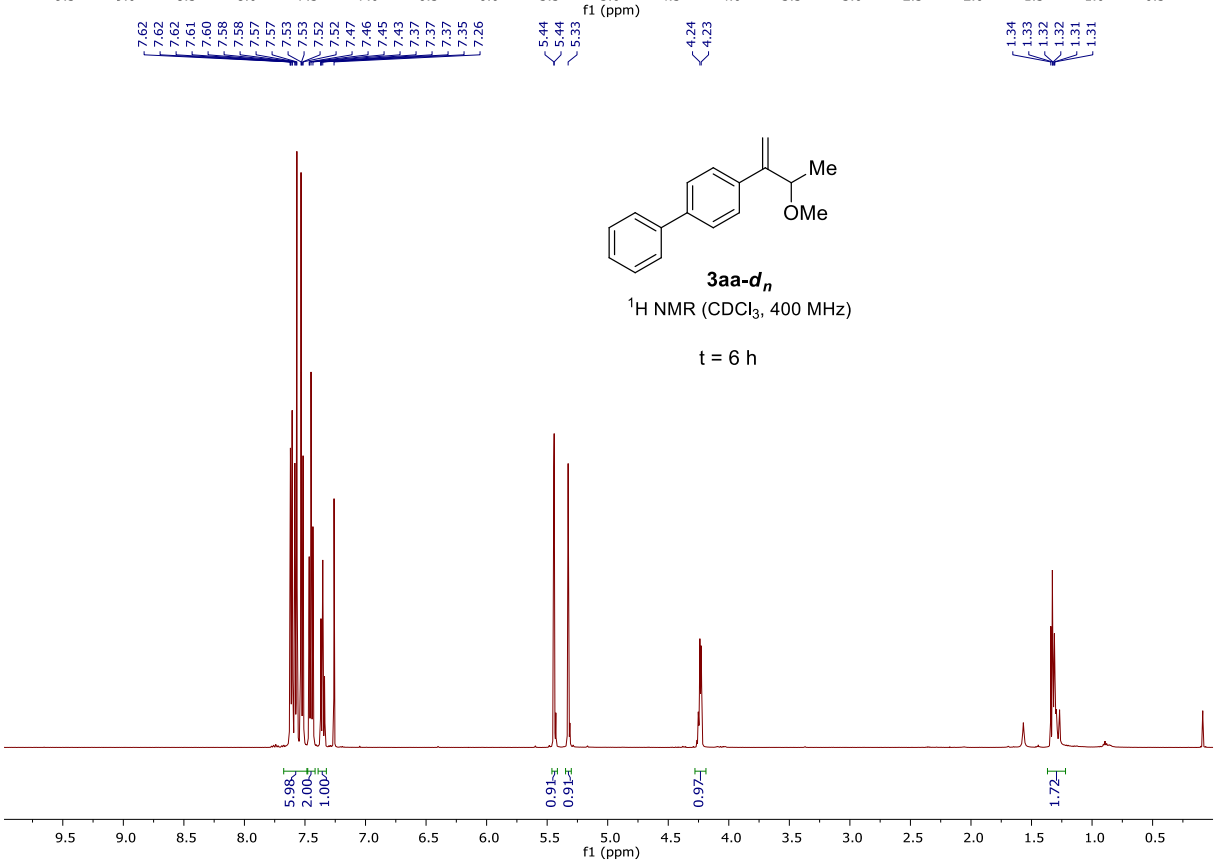
In a N_2-filled glovebox, $Ni(cod)_2$ (2.2 mg, 0.008 mmol, 2 mol%) and (Cy)-Phox **L_4** (2.8 mg, 0.008 mmol, 2 mol%) were charged in a 5 mL vial and dissolved in anhydrous mesitylene (0.80 mL, 0.50 M). After stirring at room temperature for 5 min, diene **1a** (84 mg, 0.40 mmol, 1.0 equiv) and methanol-d_4 **2a-d_4** (58 mg, 1.6 mmol, 4.0 equiv) were added sequentially. The reaction mixture solution was stirred for 5 min. Subsequently, 0.2 mL of the resulting solution was introduced in three different Schlenk tubes. The tubes were sealed, taken out of the glovebox and the reaction mixtures were stirred at room temperature before being worked up at different times (t = 3, 6 and 24 h). The reaction mixtures were filtered over a short pad of silica gel, washed with ethyl acetate (5 mL) and concentrated under vacuum to afford the crude mixture. Each crude reaction mixture was purified by flash chromatography over silica gel (pentane:Et_2O = 1:0 to 31:1) to give, by order of elution, unreacted diene **1a-d_n** and the desired product **3aa-d_n**. ^2H incorporation was determined by ^1H NMR using the purified compounds and using the aromatic protons as internal reference.



3aa-*d*$_n$

^{1}H NMR ($CDCl_3$, 400 MHz)

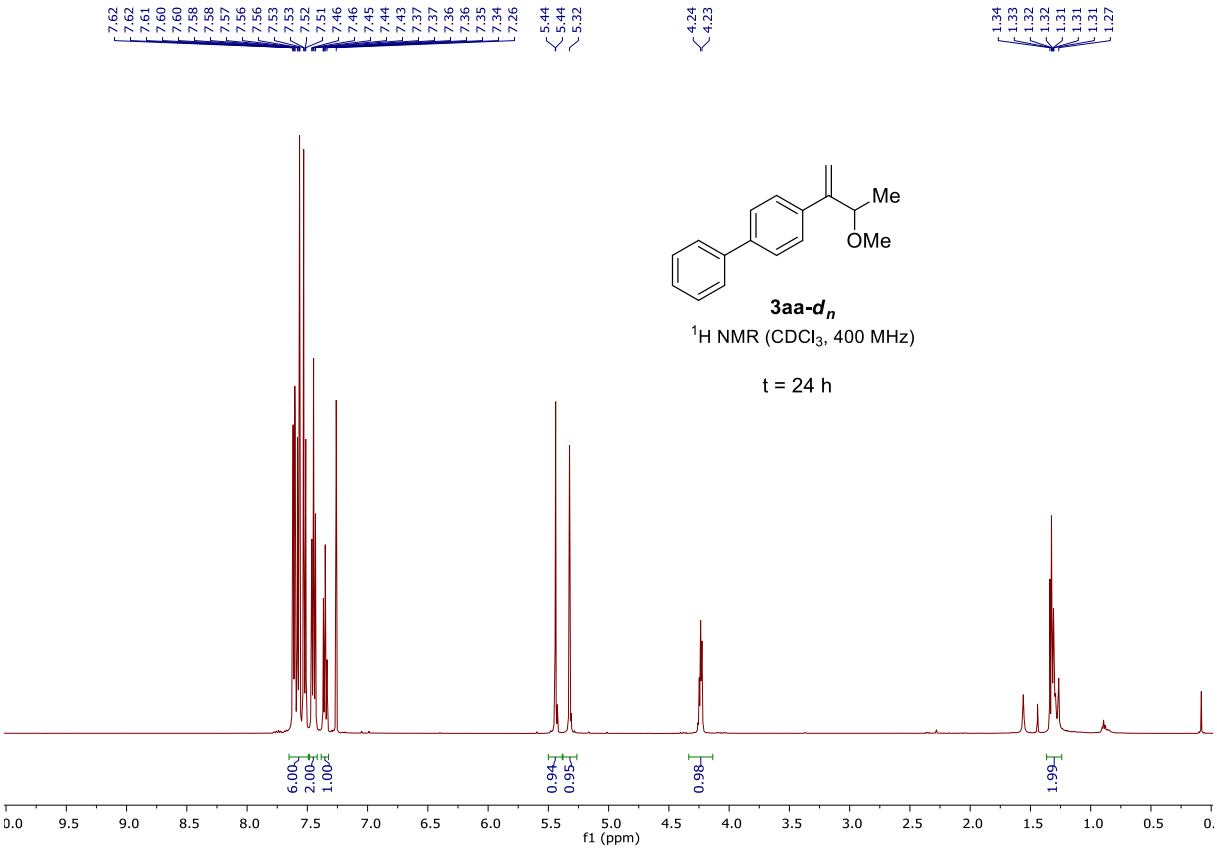
t = 3 h



3aa-*d*$_n$

^{1}H NMR ($CDCl_3$, 400 MHz)

t = 6 h


7.62
7.62
7.61
7.60
7.60
7.58
7.58
7.57
7.56
7.56
7.53
7.53
7.52
7.51
7.46
7.46
7.45
7.44
7.43
7.37
7.37
7.36
7.36
7.35
7.34
7.26
5.44
5.44
5.32
4.24
4.23
1.34
1.33
1.32
1.32
1.31
1.31
1.31
1.27
Me
OMe
3aa-d_n
1H NMR (CDCl3, 400 MHz)
t = 24 h
6.00
2.00
1.00
0.94
0.95
0.98
1.99
f1 (ppm)

6. Enantioselective conditions

6.1. Selected Ligand screening

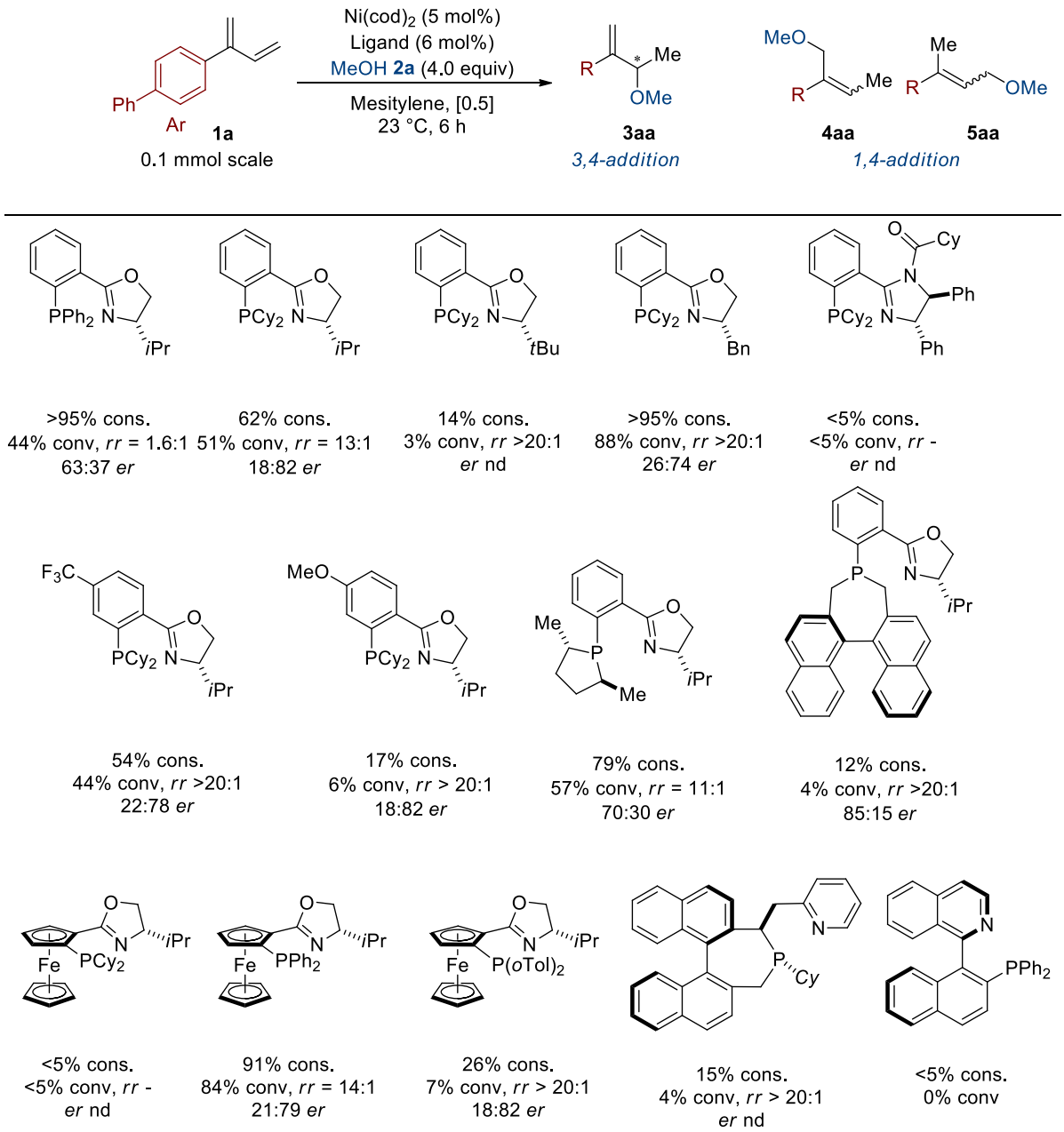
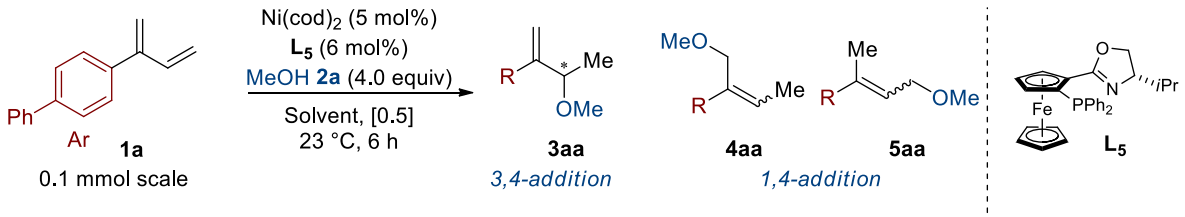


Figure S3: **Ligand screening.** Reaction conditions: all reactions were performed with diene **1a** (0.10 mmol, 1.0 equiv), MeOH **2a** (0.40 mmol, 4.0 equiv), $Ni(cod)_2$ (0.005 mmol, 5 mol%), ligand (0.006 mmol, 6 mol%), in mesitylene (0.20 mL, 0.50 M) at room temperature. Consumption of **1a**, conversions of **3aa**, **4aa** and **5aa** were assessed by ^1H NMR of the crude reaction mixture using an internal standard. nd = not determined. *er* were determined by SFC from the purified reaction mixtures.

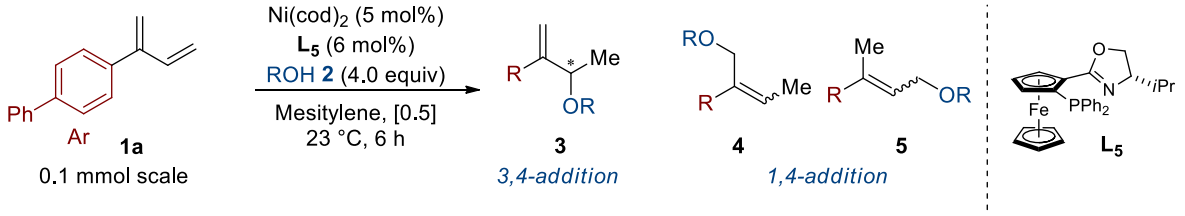
6.2. Selected Solvent screening



Mesitylene	Toluene	$PhCF_3$	THF	CH_2Cl_2
91% cons. 84% conv, *rr* = 14:1 21:79 *er*	>95% cons. 73% conv, *rr* = 12:1 23:77 *er*	>17% cons. 5% conv, *rr* > 20:1 14:86 *er*	80% cons. 58% conv, *rr* = 8:1 76:24 *er*	<5 cons. 0% conv, *rr* - – *er*

Figure S4: **Solvent screening.** Reaction conditions: all reactions were performed with diene **1a** (0.10 mmol, 1.0 equiv), ROH **2** (0.40 mmol, 4.0 equiv), $Ni(cod)_2$ (0.005 mmol, 5 mol%), ligand $\mathbf{L_5}$ (0.006 mmol, 6 mol%), in the indicated solvent (0.20 mL, 0.50 M) at room temperature. Consumption of **1a**, conversions of **3**, **4** and **5** were assessed by ^{1}H NMR of the crude reaction mixture using an internal standard. nd = not determined. *er* were determined by SFC from the crude reaction mixtures.

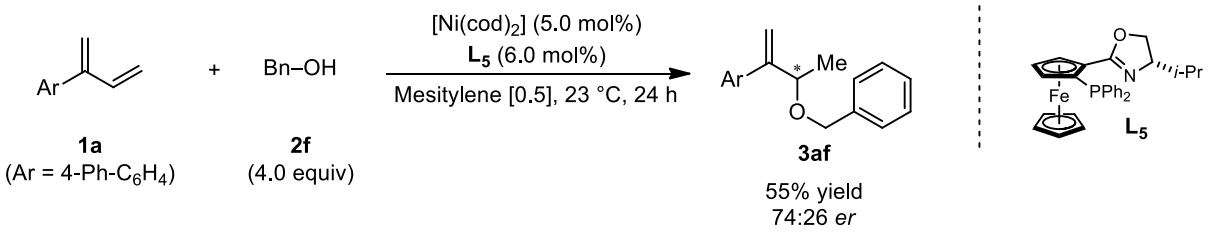
6.3. Selected Alcohol screening



MeOH	*i*PrOH	*i*BuOH	BnOH
91% cons. 84% conv, *rr* = 14:1 21:79 *er*	30% cons. 6% conv, *rr* >20:1 88:12 *er*	88% cons. 62% conv, *rr* = 2.3:1 73:27 *er*	38% cons. 24% conv, *rr* > 20:1 87:13 *er*

Figure S5: **Alcohol screening.** Reaction conditions: all reactions were performed with diene **1a** (0.10 mmol, 1.0 equiv), ROH **2** (0.40 mmol, 4.0 equiv), $Ni(cod)_2$ (0.005 mmol, 5 mol%), ligand $\mathbf{L_5}$ (0.006 mmol, 6 mol%), in mesitylene (0.20 mL, 0.50 M) at room temperature. Consumption of **1a**, conversions of **3**, **4** and **5** were assessed by ^{1}H NMR of the crude reaction mixture using an internal standard. n.d. = not determined. *er* were determined by SFC from the purified reaction mixtures.

6.4. Extended reaction time with L_5 and BnOH



1a
(Ar = 4-Ph-C_6H_4)

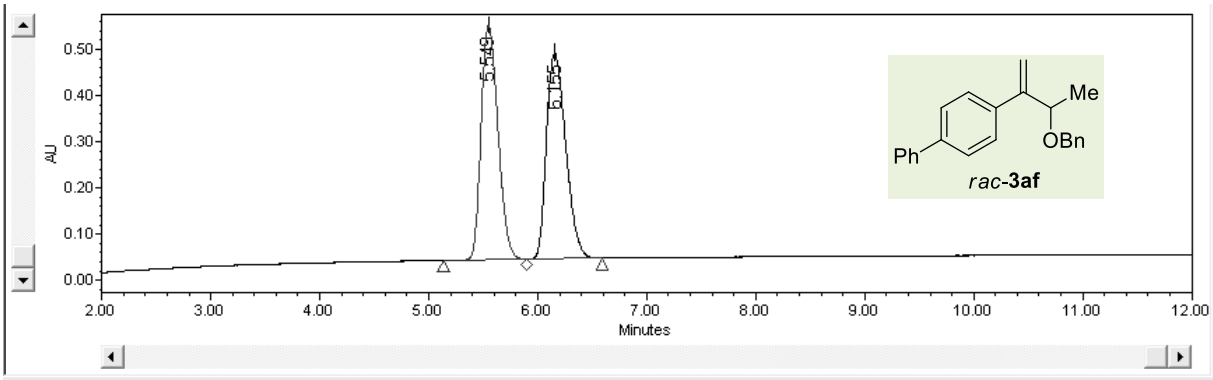
2f
(4.0 equiv)

3af
55% yield
74:26 *er*

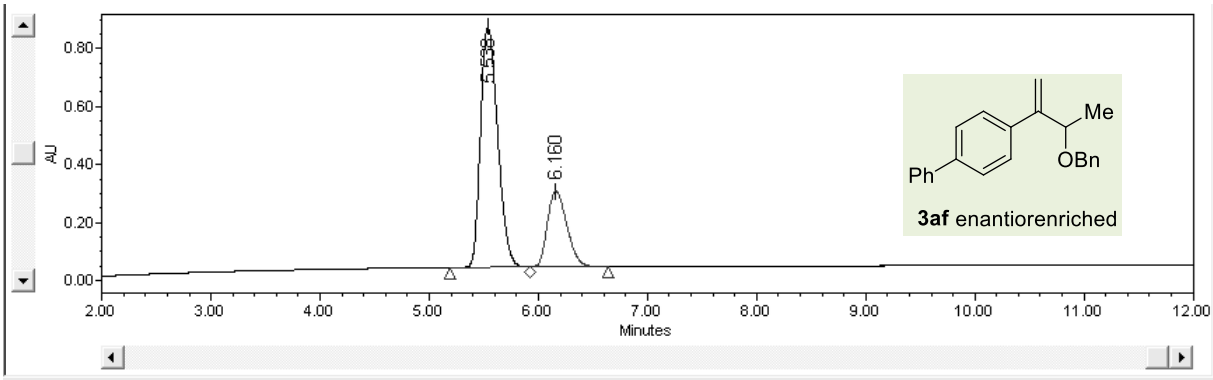
L_5

In a N_2-filled glovebox, $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5 mol%) and ligand **L_5** (5.8 mg, 0.012 mmol, 6 mol%) were charged in a 5 mL Schlenk tube and dissolved in anhydrous mesitylene (0.50 mL, 0.50 M). After stirring at room temperature for 5 min, diene **1a** (42 mg, 0.20 mmol, 1.0 equiv) and benzyl alcohol **2f** (82 μL, 0.80 mmol, 4.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (5 mL) and concentrated under vacuum to afford the crude mixture. The conversion and regioisomeric ratio were determined by ^1H NMR analysis of the crude reaction mixture using *p*-methoxytoluene as an internal standard. Consumption of **1a**: 94%, conversion of **3af**: 63%, *rr* = 4:1. Purification by flash chromatography over silica gel (pentane:Et_2O = 32:1) afforded the desired product as a colorless oil (34 mg, 0.11 mmol, 55% yield).

SFC: 74:26 *er*, chiral stationary phase: AD column, gradient elution from 2% to 30% MeOH (12 min), 3 ml/min, 210 nm, t_R (major) = 5.5 min, t_R (minor) = 6.2 min.

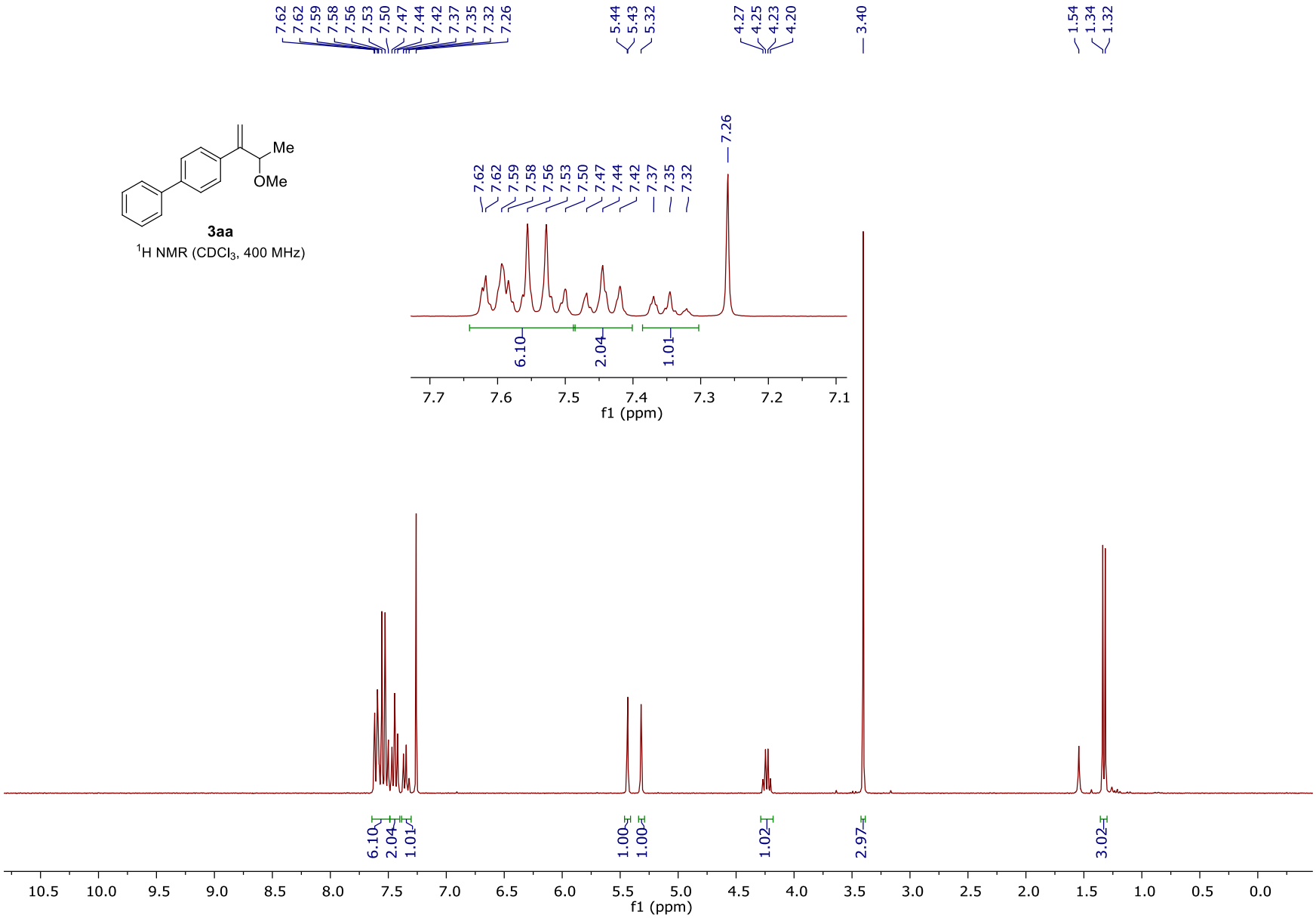


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes	A_RTsec	GradientSpec	GradientStdDevPassFail	Gradie
1		5.549	5457026	49.90	506698	bv			Unknown		332.942963	SD RT < or = 1.0sec		
2		6.155	5479036	50.10	445917	vb			Unknown		369.272638	SD RT < or = 1.0sec		



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes	A_RTsec	GradientSpec	GradientStdDevPassFail	Gradie
1		5.538	9031565	73.69	828073	bV			Unknown		332.292626	SD RT < or = 1.0sec		
2		6.160	3224615	26.31	262824	Vb			Unknown		369.592513	SD RT < or = 1.0sec		

7. NMR Spectra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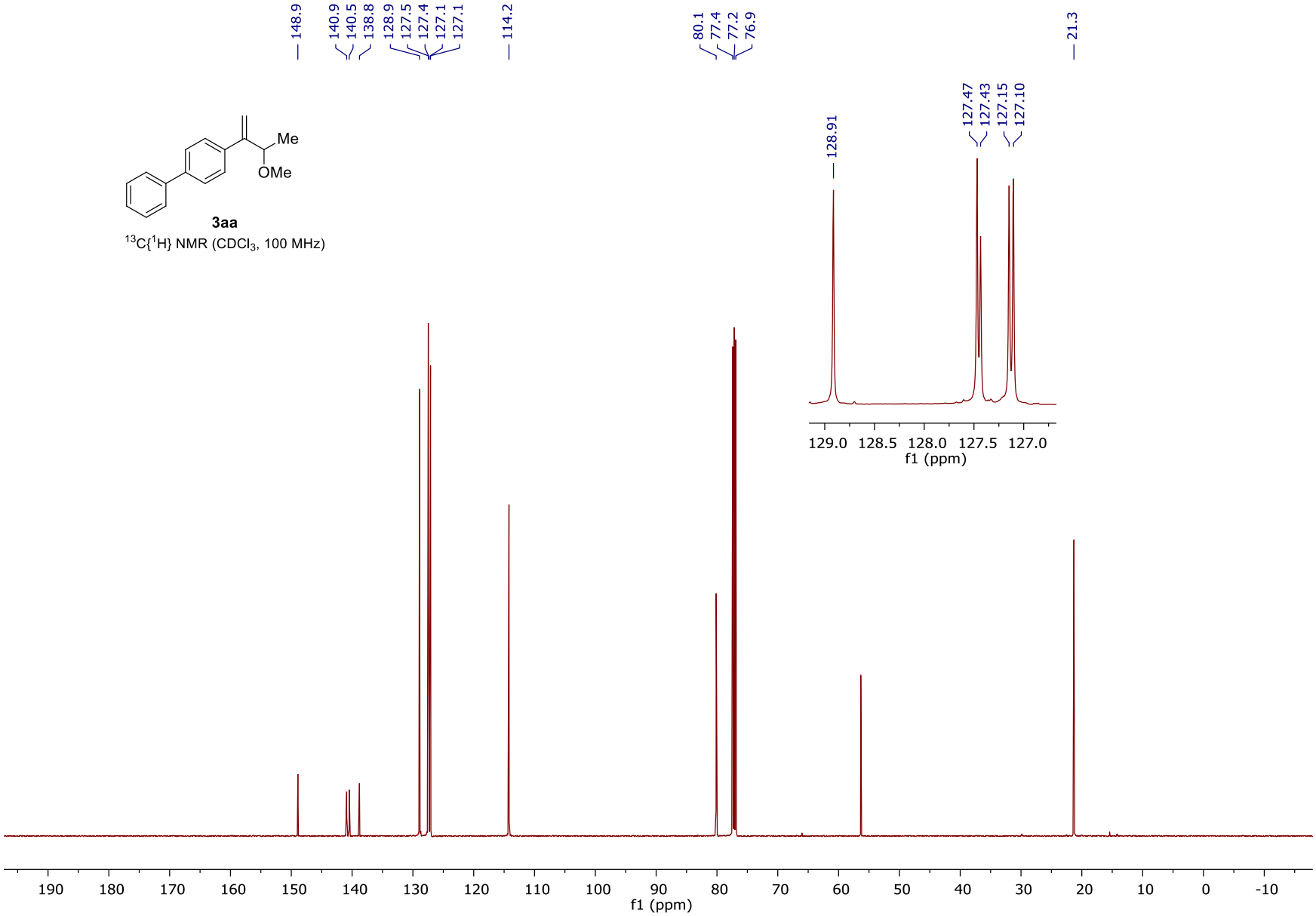
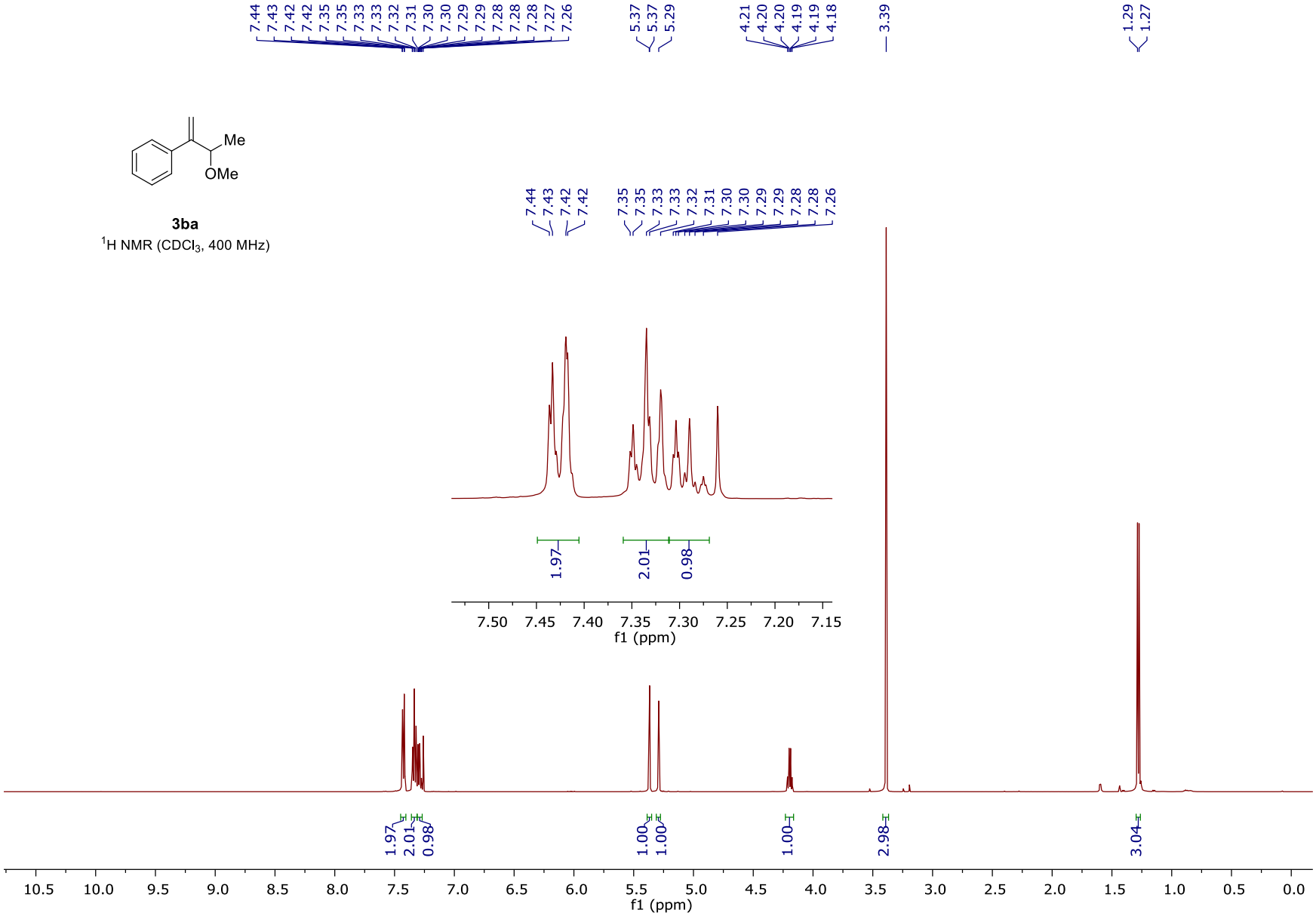
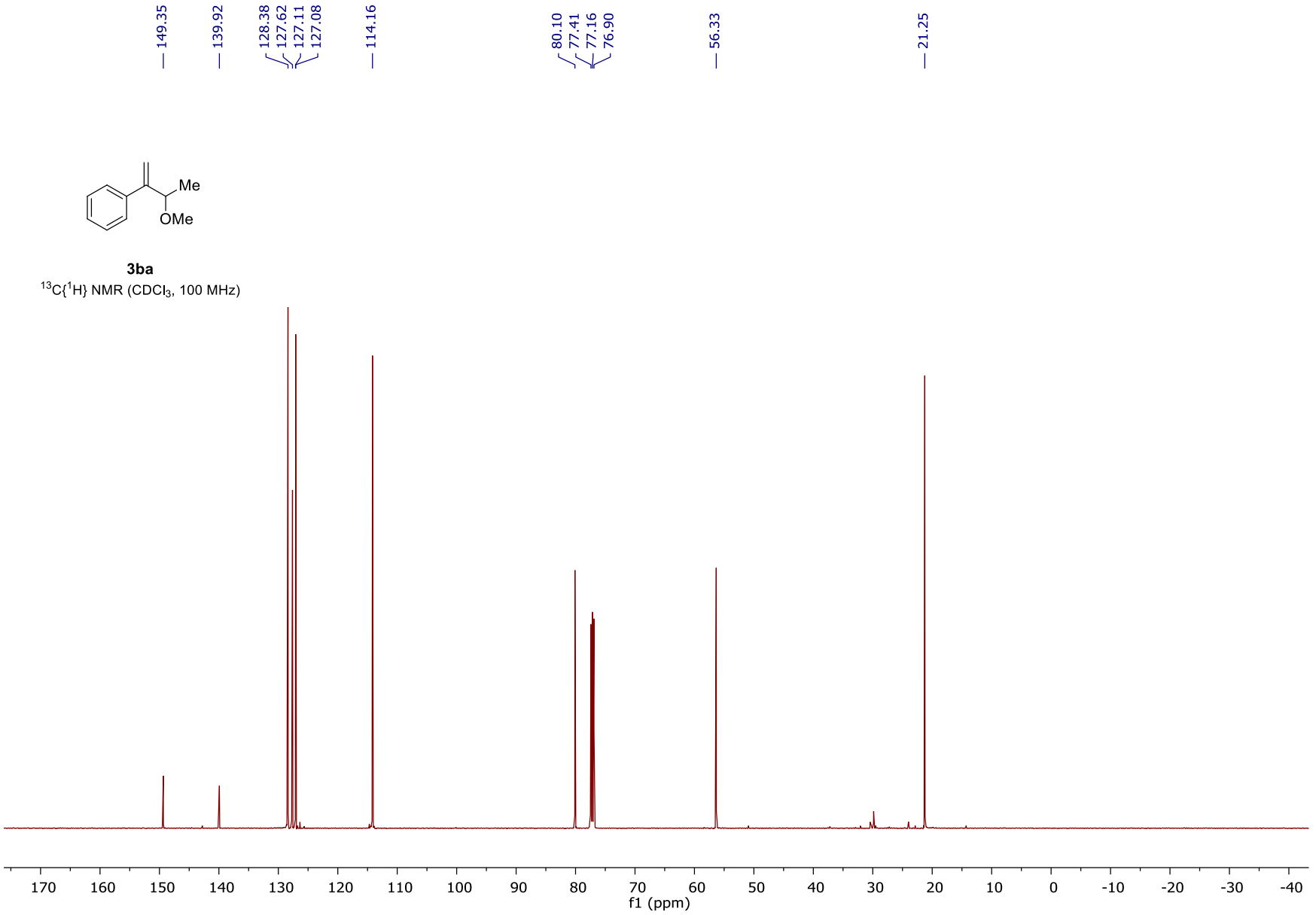
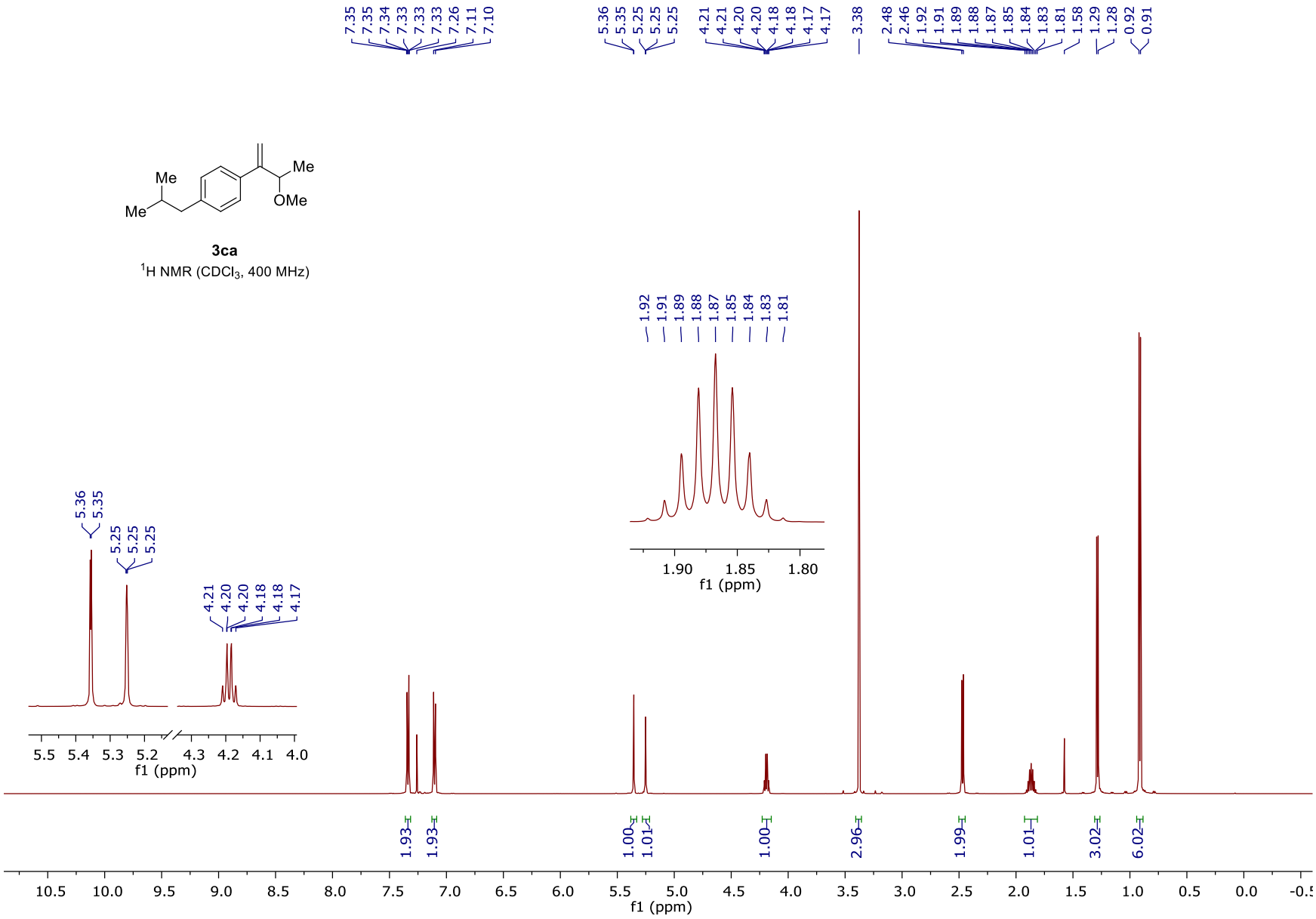
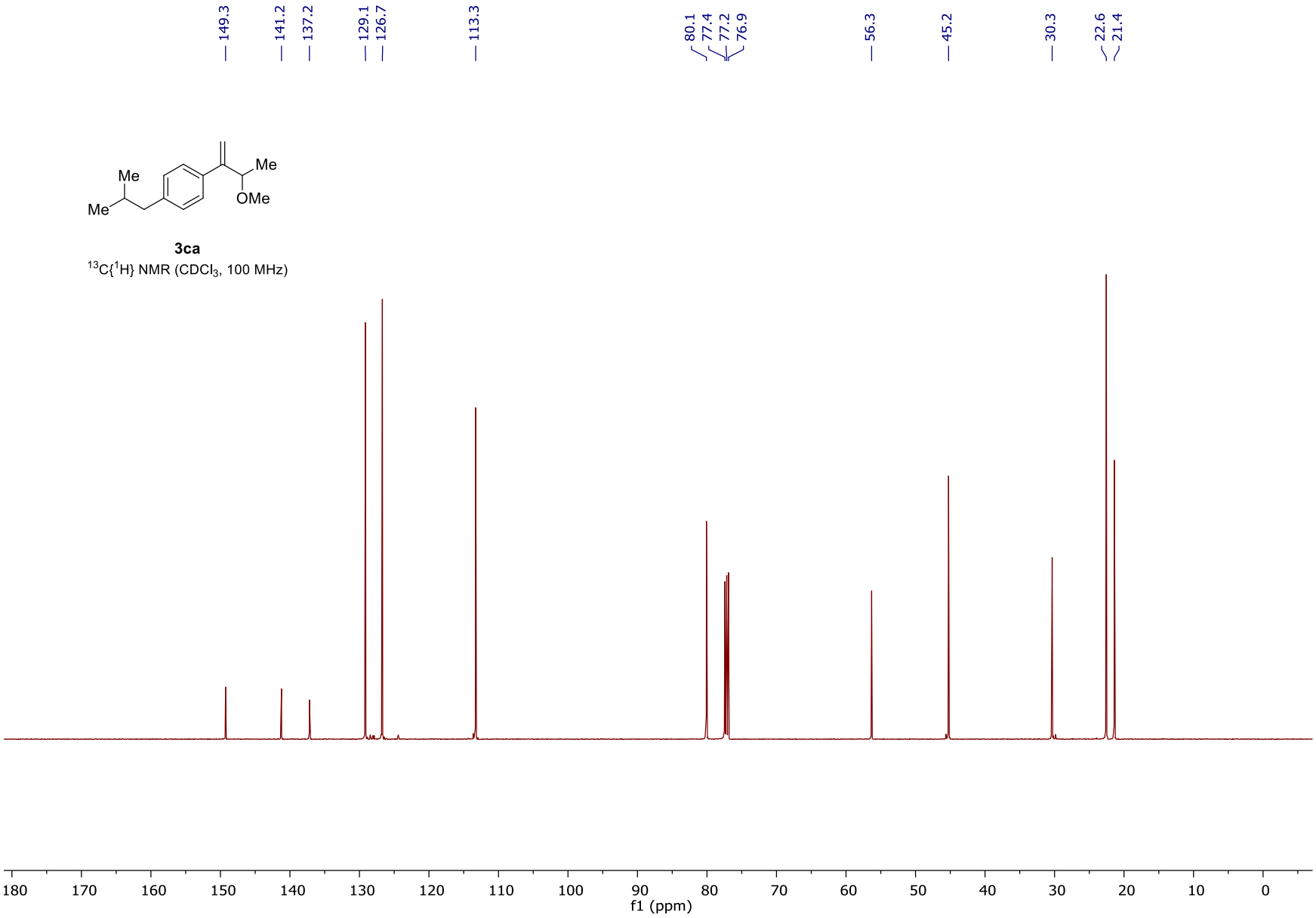
7.62
7.59
7.58
7.56
7.53
7.50
7.47
7.44
7.42
7.37
7.35
7.32
7.26
5.44
5.43
5.32
4.27
4.25
4.23
4.20
3.40
1.54
1.34
1.32
Me
OMe
3aa
1H NMR (CDCl3, 400 MHz)
6.10
2.04
1.01
f1 (ppm)
1.00
1.00
1.02
2.97
3.02

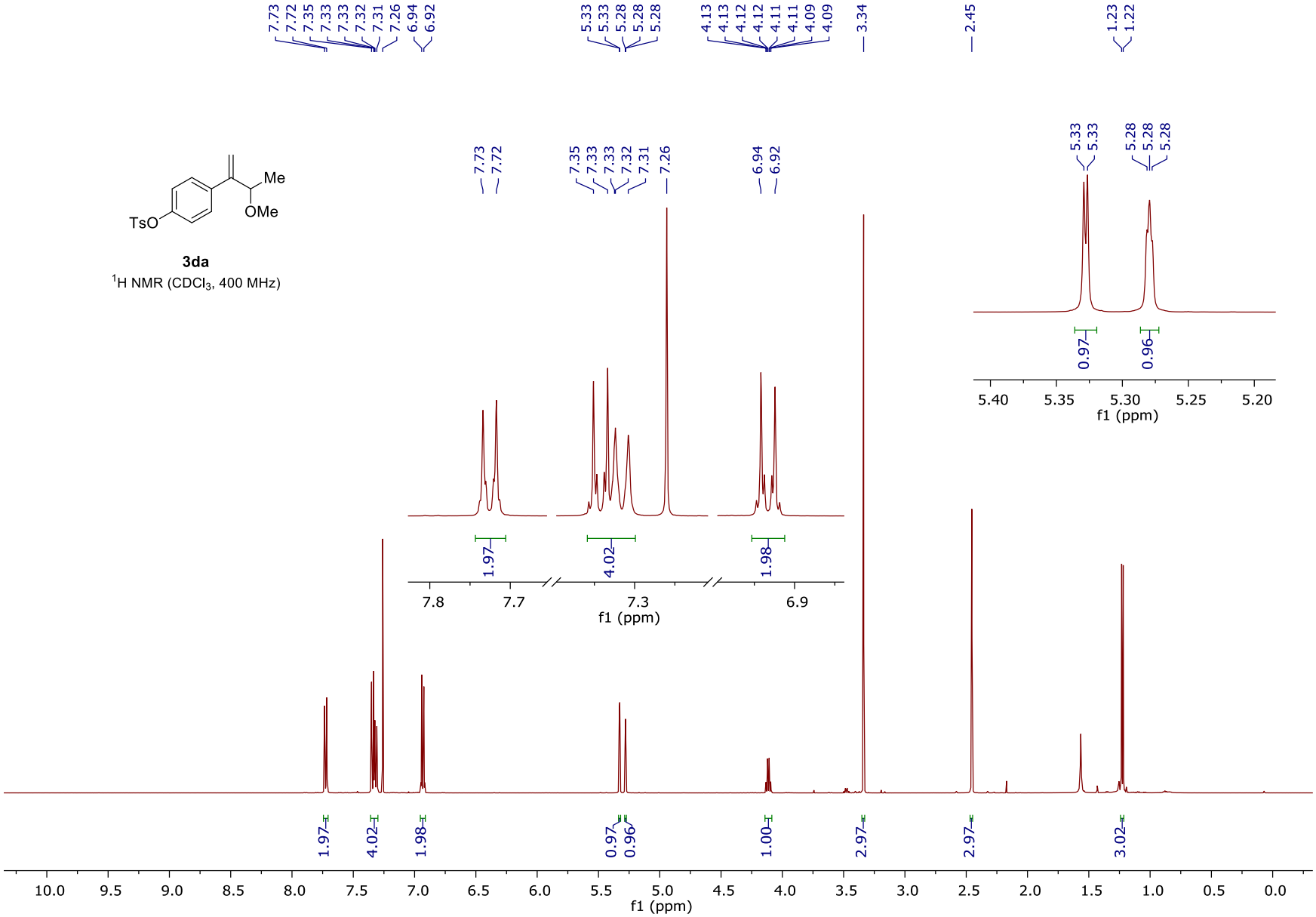

148.9
140.9
140.5
138.8
128.9
127.5
127.4
127.1
127.1
114.2
80.1
77.4
77.2
76.9
21.3
Me
OMe
3aa
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)
128.91
127.47
127.43
127.15
127.10
129.0 128.5 128.0 127.5 127.0
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

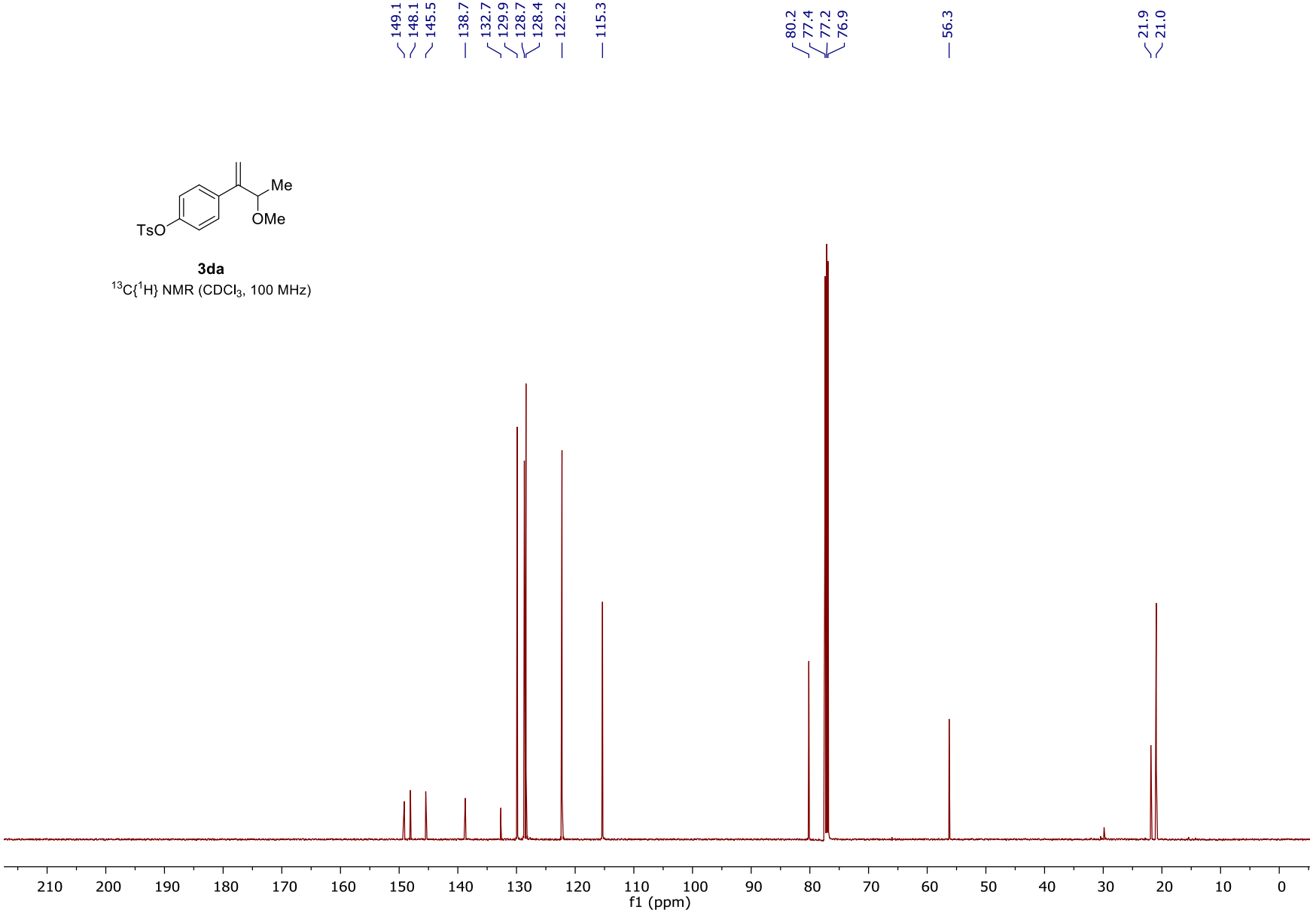

Me
OMe
3ba
1H NMR (CDCl3, 400 MHz)
f1 (ppm)


149.35
139.92
128.38
127.62
127.11
127.08
114.16
80.10
77.41
77.16
76.90
56.33
21.25
Me
OMe
3ba
13C{1H} NMR (CDCl3, 100 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


Me
Me
Me
OMe
3ca
1H NMR (CDCl3, 400 MHz)
f1 (ppm)


149.3
141.2
137.2
129.1
126.7
113.3
80.1
77.4
77.2
76.9
56.3
45.2
30.3
22.6
21.4
Me
Me
Me
OMe
3ca
13C{1H} NMR (CDCl3, 100 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.73
7.72
7.35
7.33
7.33
7.32
7.31
7.26
6.94
6.92
5.33
5.33
5.28
5.28
5.28
4.13
4.13
4.12
4.12
4.11
4.11
4.09
4.09
3.34
2.45
1.23
1.22
Me
OMe
TsO
3da
1H NMR (CDCl3, 400 MHz)
1.97
4.02
1.98
0.97
0.96
1.00
2.97
2.97
3.02
f1 (ppm)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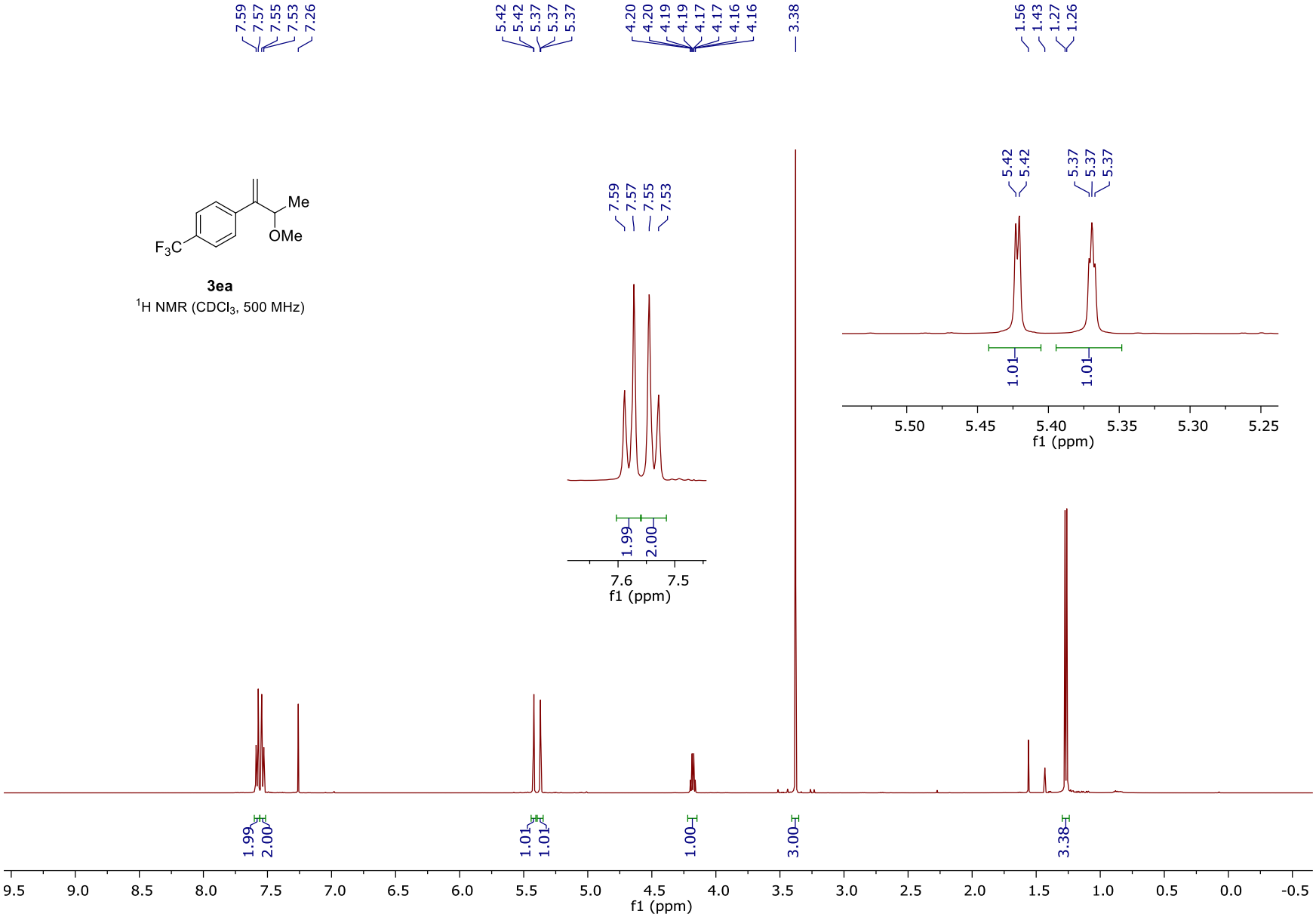
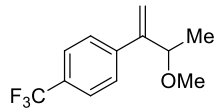
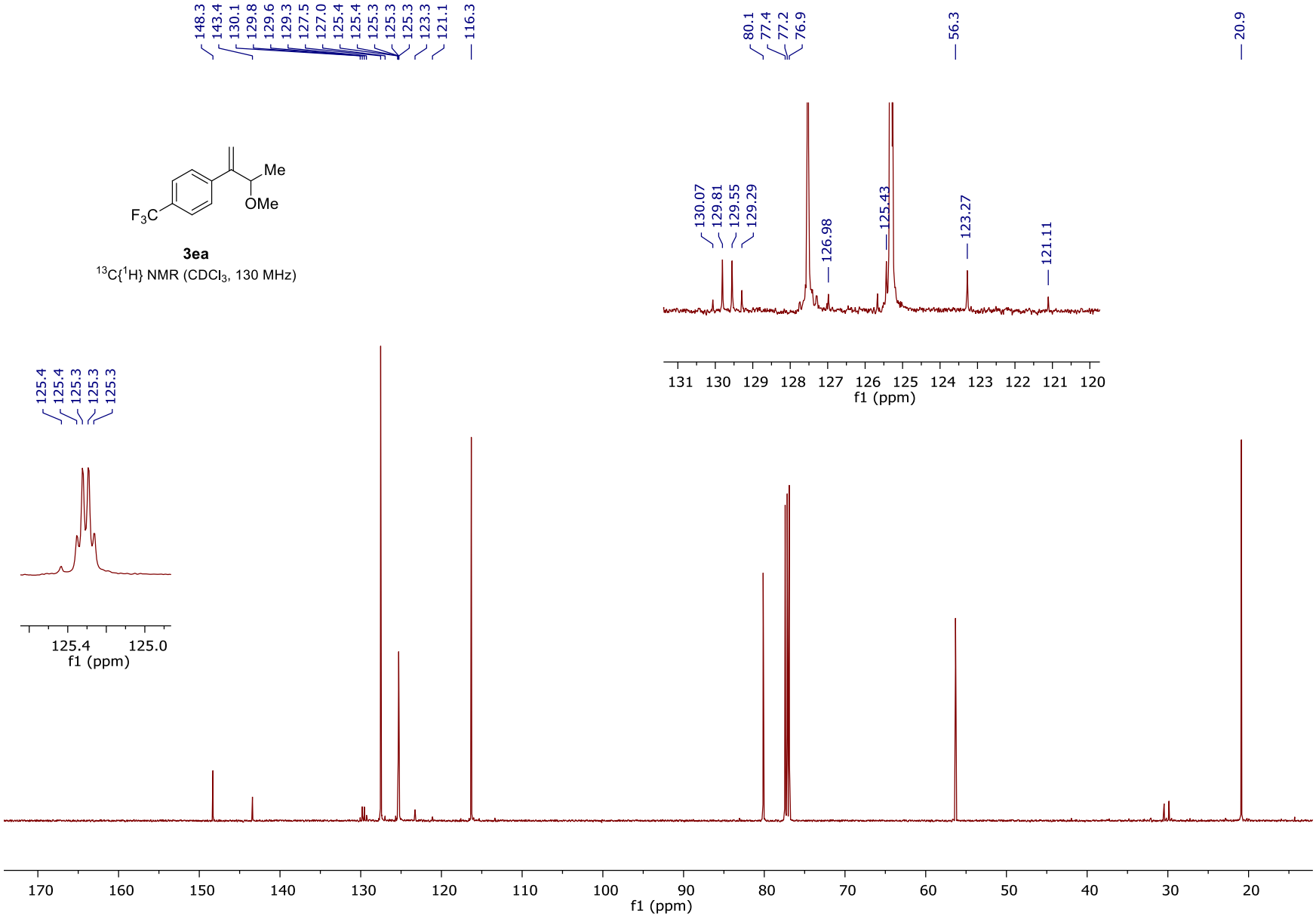
148.1
145.5
138.7
132.7
129.9
128.7
128.4
122.2
115.3
80.2
77.4
77.2
76.9
56.3
21.9
21.0
Me
OMe
TsO
3da
13C{1H} NMR (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

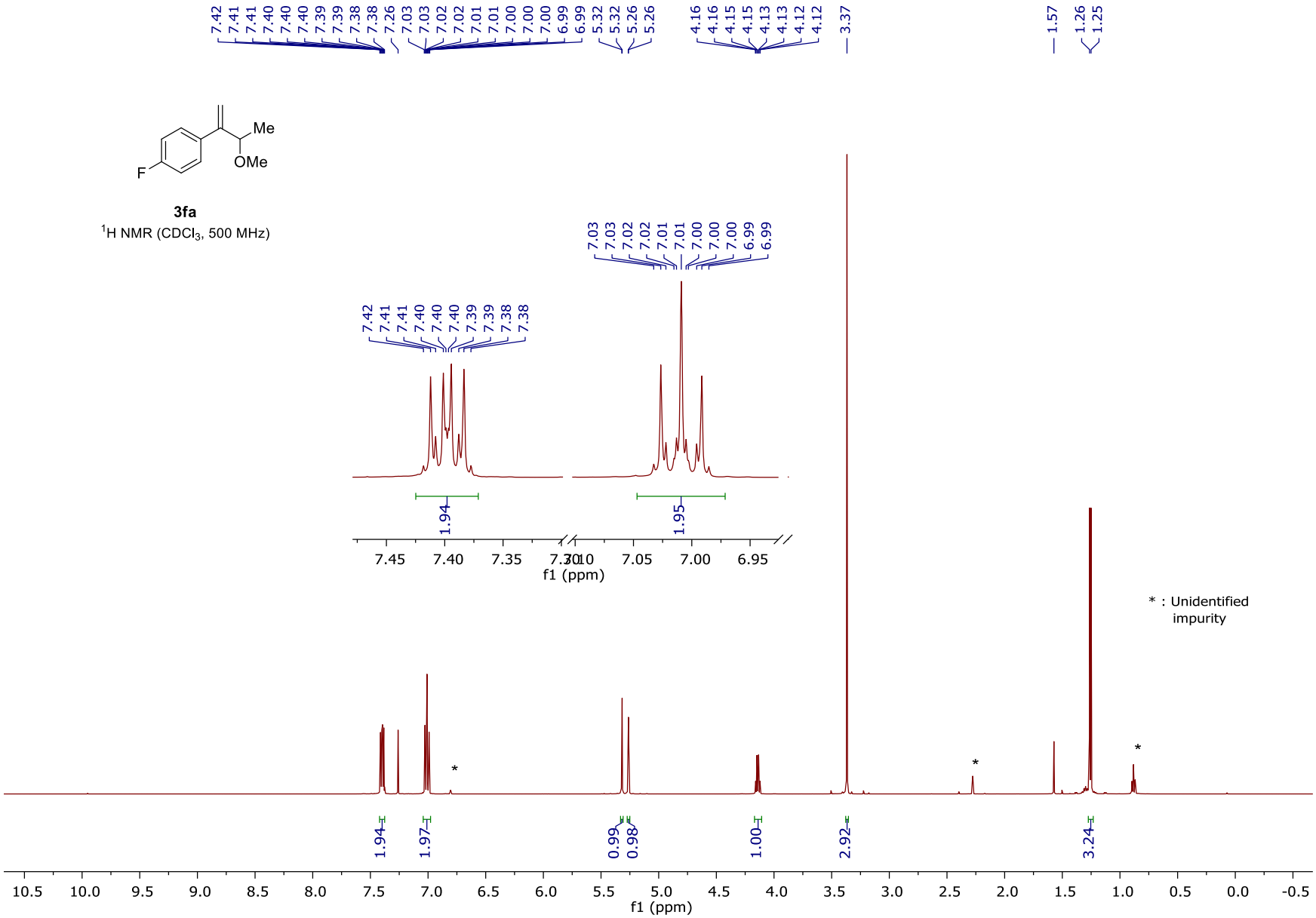

7.59
7.57
7.55
7.53
7.26
5.42
5.42
5.37
5.37
5.37
4.20
4.20
4.19
4.19
4.17
4.17
4.16
4.16
3.38
1.56
1.43
1.27
1.26
Me
OMe
F3C
3ea
1H NMR (CDCl3, 500 MHz)
1.99
2.00
1.01
1.01
1.00
3.00
3.38
f1 (ppm)

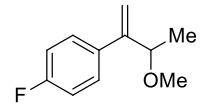


3ea

$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz)

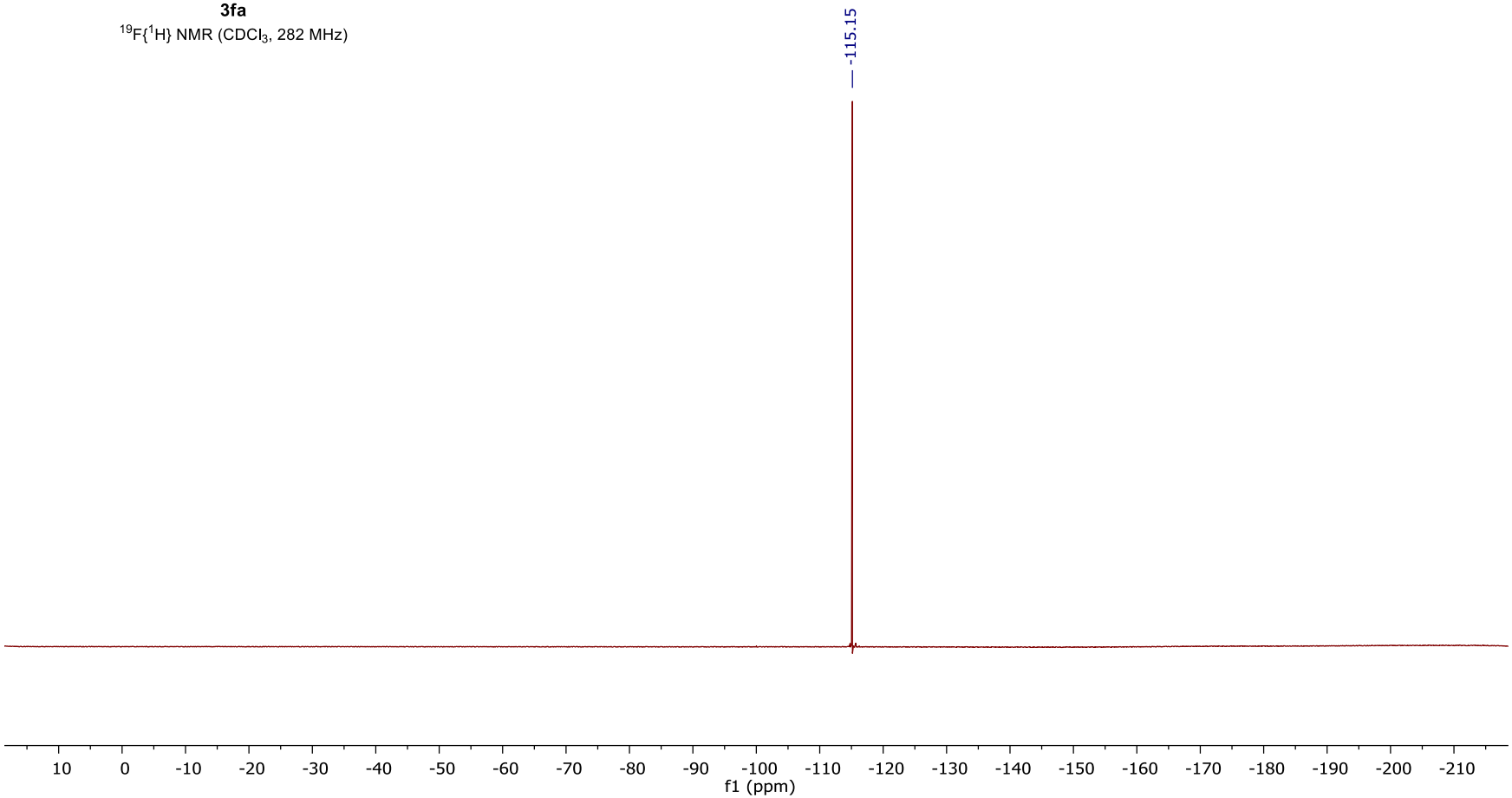

148.3
143.4
130.1
129.8
129.6
129.3
127.5
127.0
125.4
125.4
125.3
125.3
123.3
121.1
116.3
80.1
77.4
77.2
76.9
56.3
20.9
Me
OMe
F3C
3ea
13C{1H} NMR (CDCl3, 130 MHz)
130.07
129.81
129.55
129.29
126.98
125.43
123.27
121.11
131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
125.4
125.4
125.3
125.3
125.3
125.4 125.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

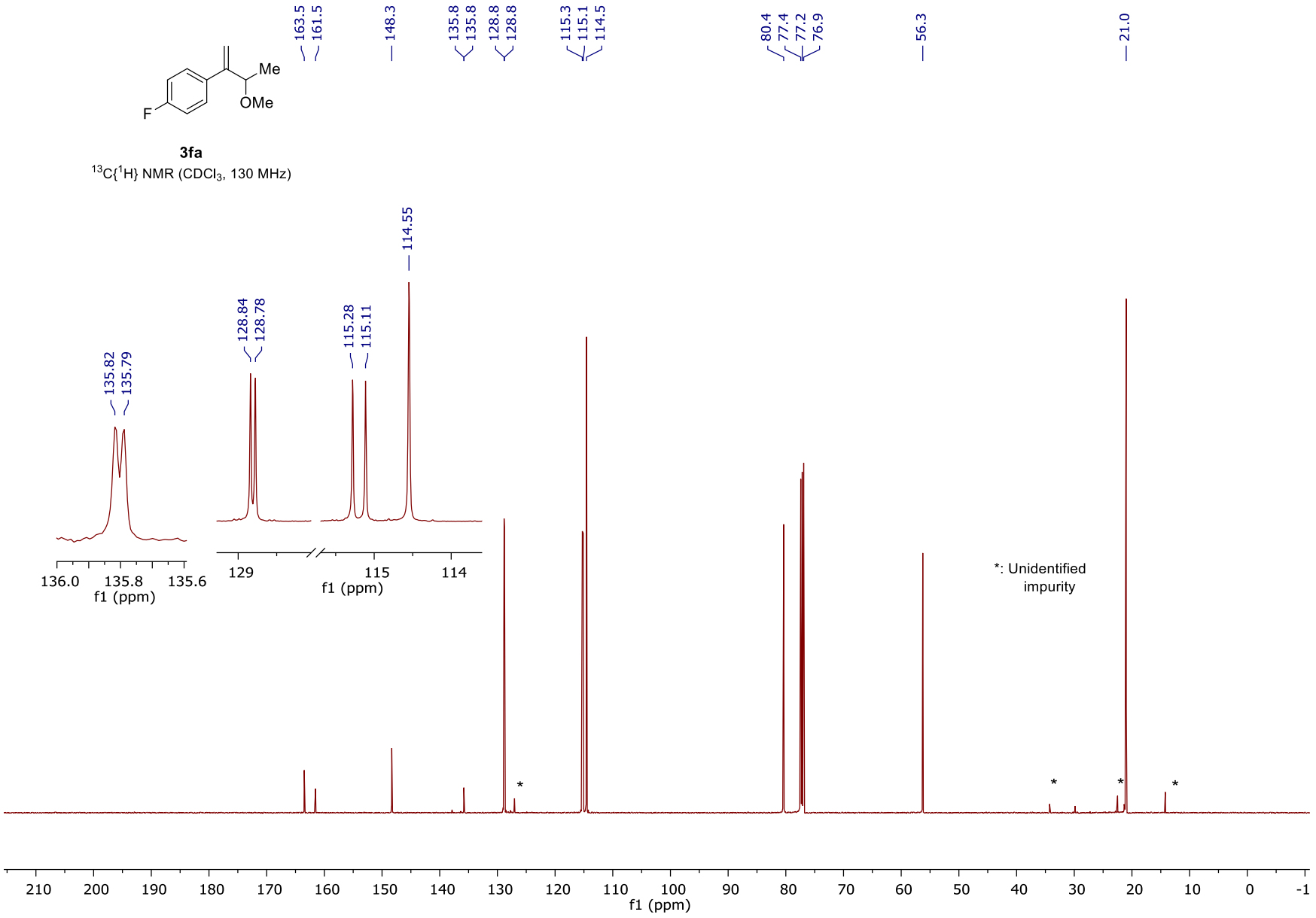

7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.26 7.03 7.03 7.02 7.02 7.01 7.01 7.00 7.00 7.00 6.99 5.32 5.32 5.26 5.26 4.16 4.16 4.15 4.15 4.13 4.13 4.12 4.12 3.37 1.57 1.26 1.25
Me
OMe
F
3fa
1H NMR (CDCl3, 500 MHz)
7.03 7.03 7.02 7.02 7.01 7.01 7.00 7.00 7.00 6.99 6.99
7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38
1.94
1.95
7.45 7.40 7.35 7.30 7.10 7.05 7.00 6.95
f1 (ppm)
* : Unidentified impurity
1.94 1.97 0.99 0.98 1.00 2.92 3.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

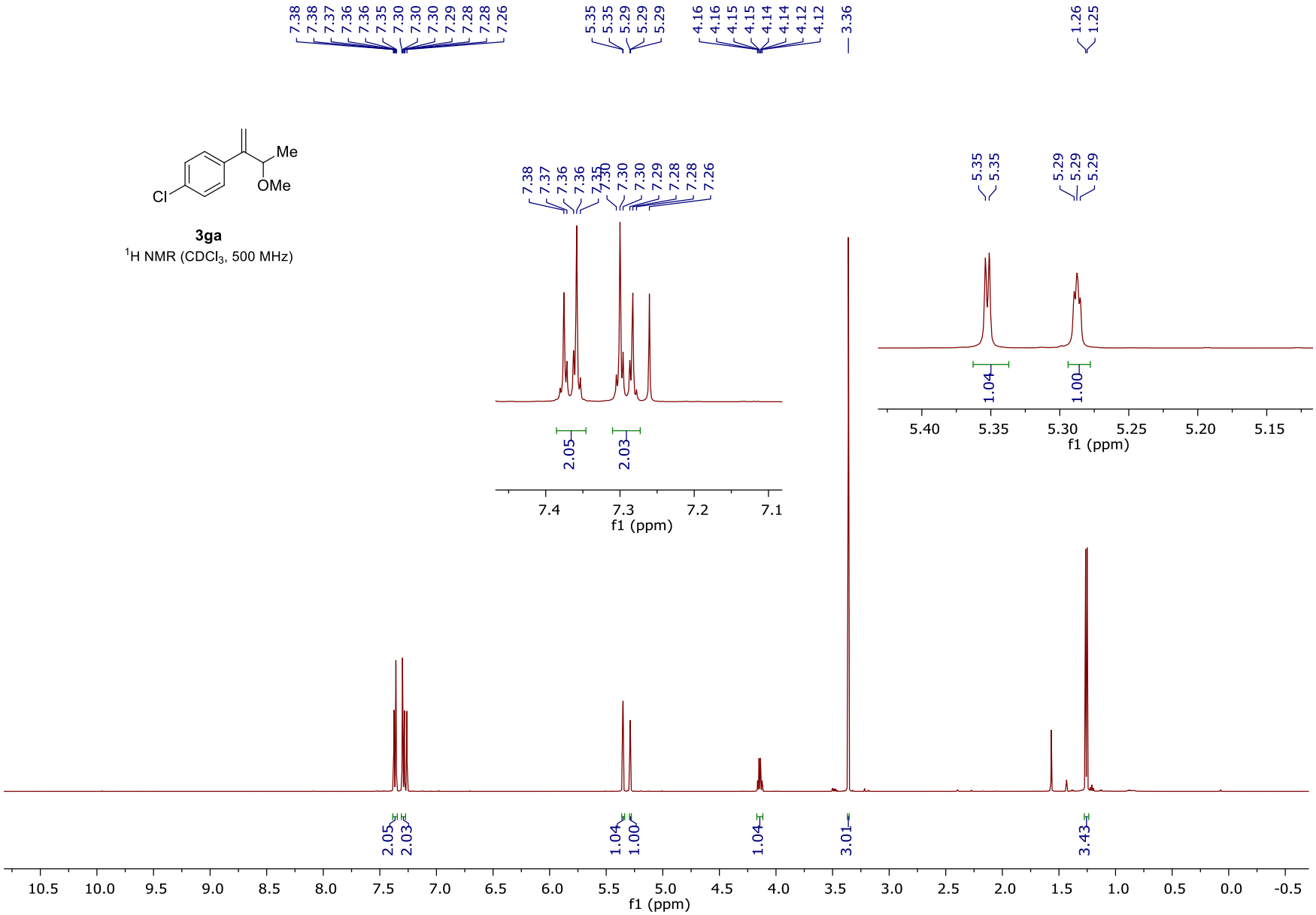


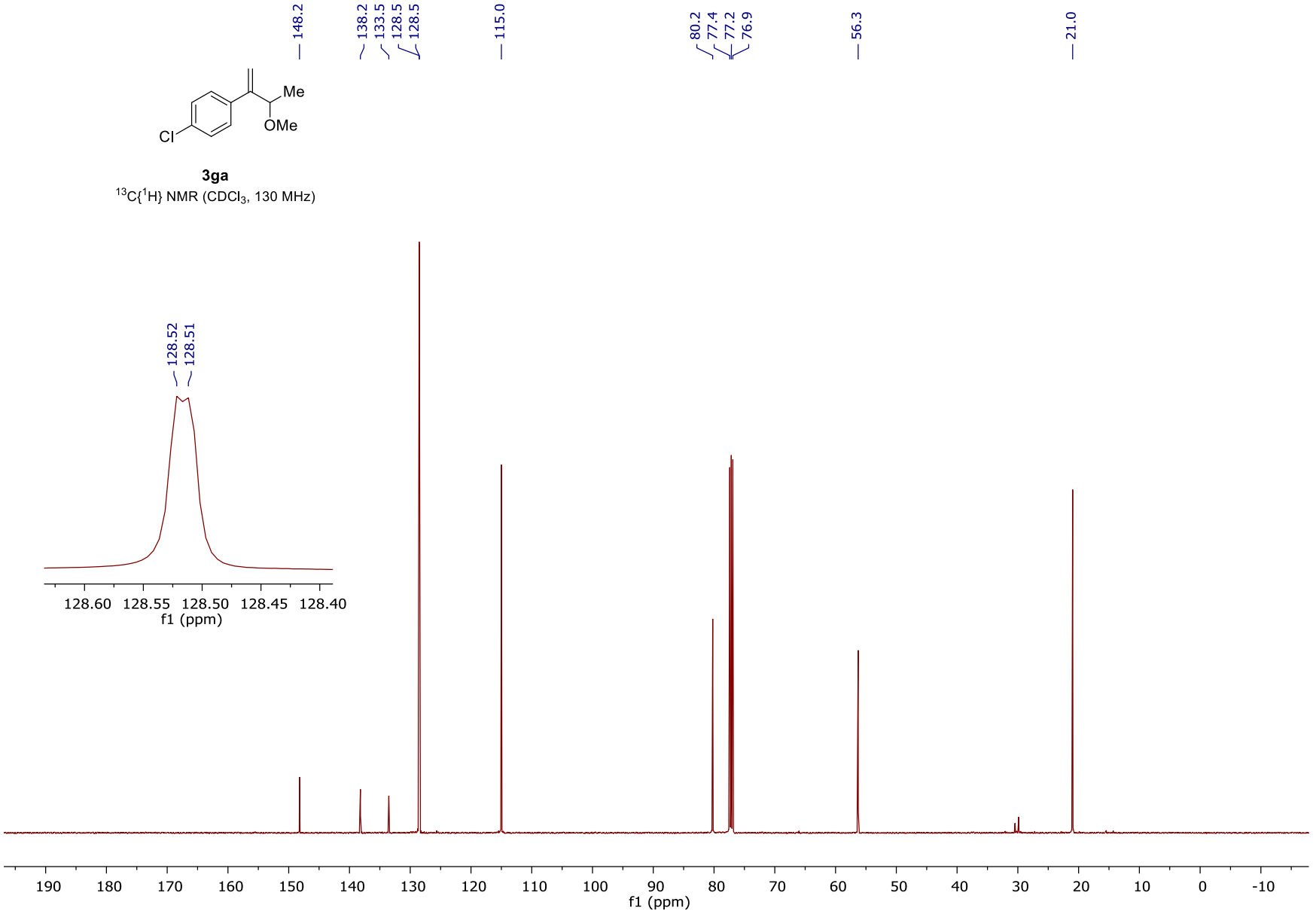
3fa

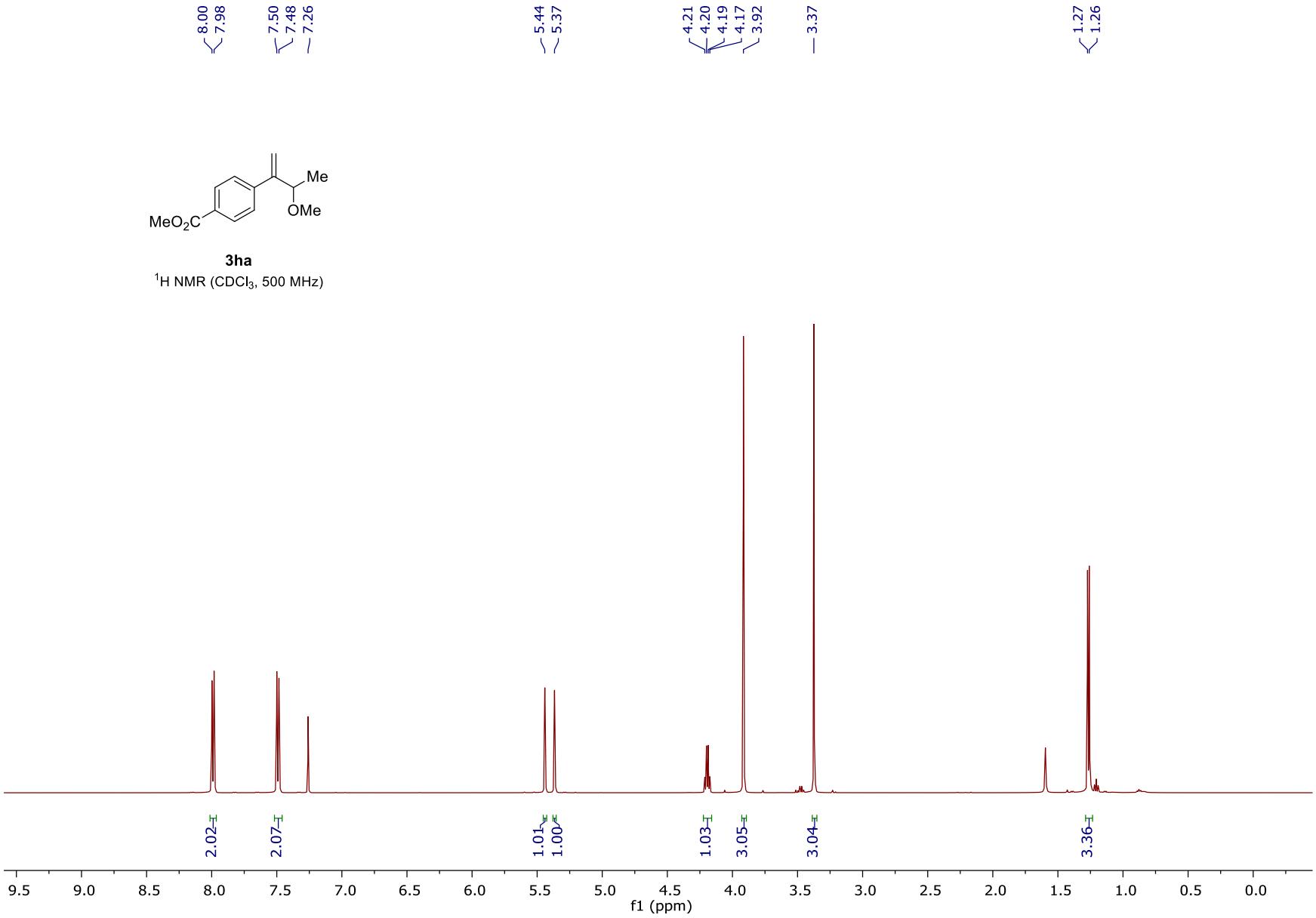
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz)




163.5
161.5
148.3
135.8
135.8
128.8
128.8
115.3
115.1
114.5
80.4
77.4
77.2
76.9
56.3
21.0
Me
OMe
F
3fa
13C{1H} NMR (CDCl3, 130 MHz)
114.55
128.84
128.78
115.28
115.11
135.82
135.79
136.0
135.8
135.6
f1 (ppm)
129
115
114
f1 (ppm)
*: Unidentified impurity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

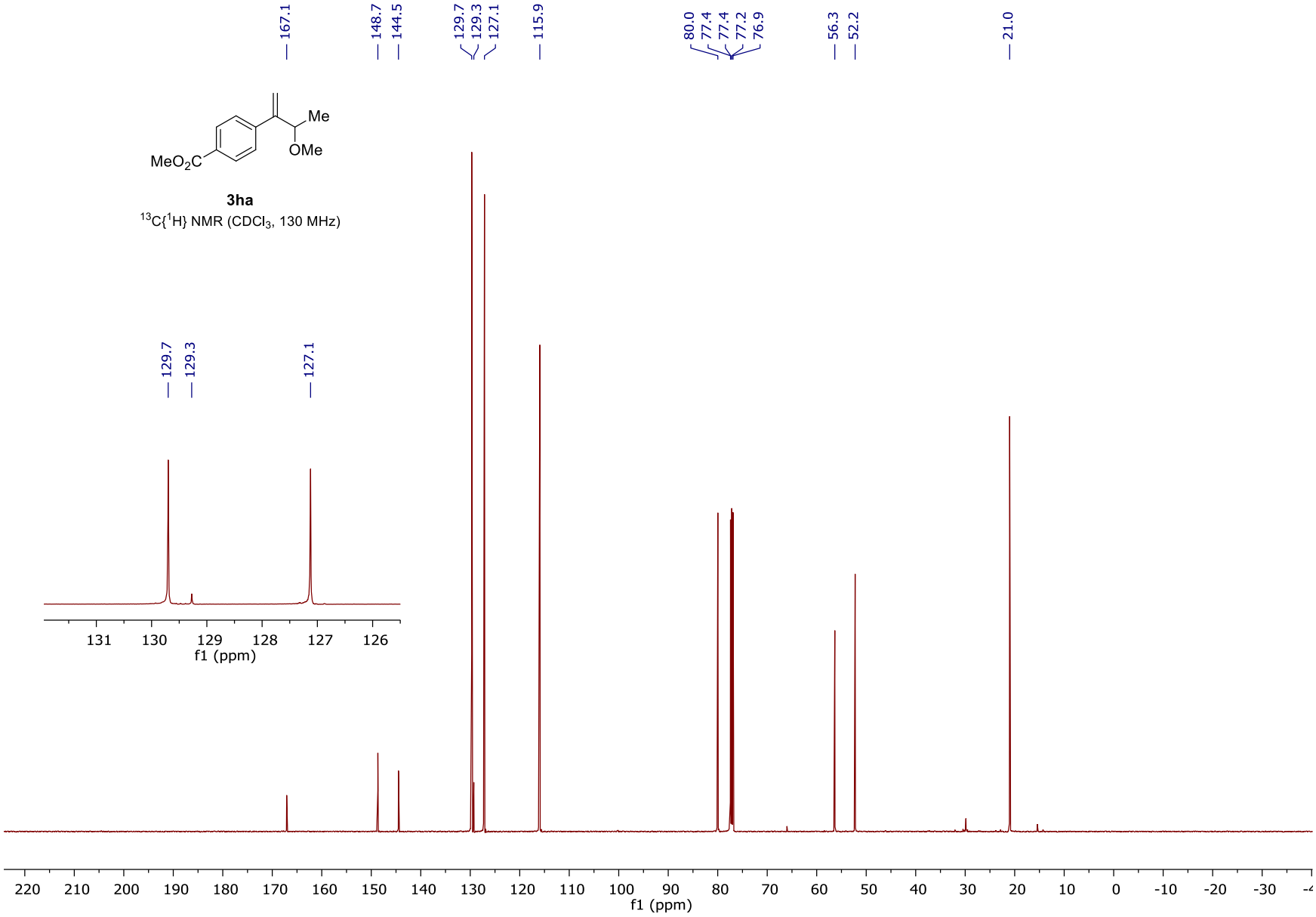

7.38
7.38
7.37
7.36
7.36
7.35
7.30
7.30
7.30
7.29
7.28
7.28
7.26
5.35
5.35
5.29
5.29
5.29
4.16
4.16
4.15
4.15
4.14
4.14
4.12
4.12
3.36
1.26
1.25
Me
OMe
Cl
3ga
1H NMR (CDCl3, 500 MHz)
2.05
2.03
1.04
1.00
1.04
3.01
3.43
f1 (ppm)

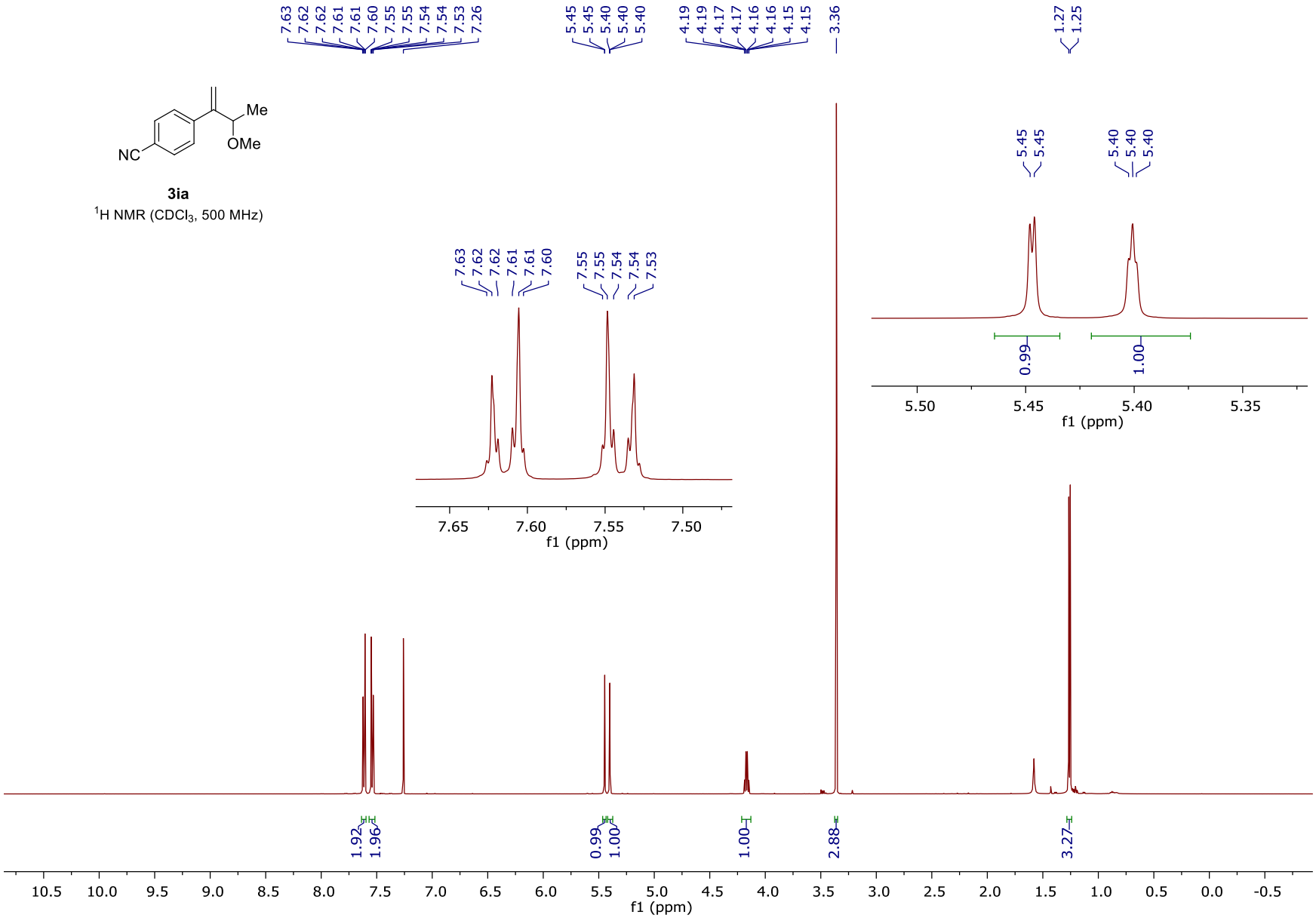

148.2
138.2
133.5
128.5
128.5
115.0
80.2
77.4
77.2
76.9
56.3
21.0
Me
OMe
Cl
3ga
13C{1H} NMR (CDCl3, 130 MHz)
128.52
128.51
128.60 128.55 128.50 128.45 128.40
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

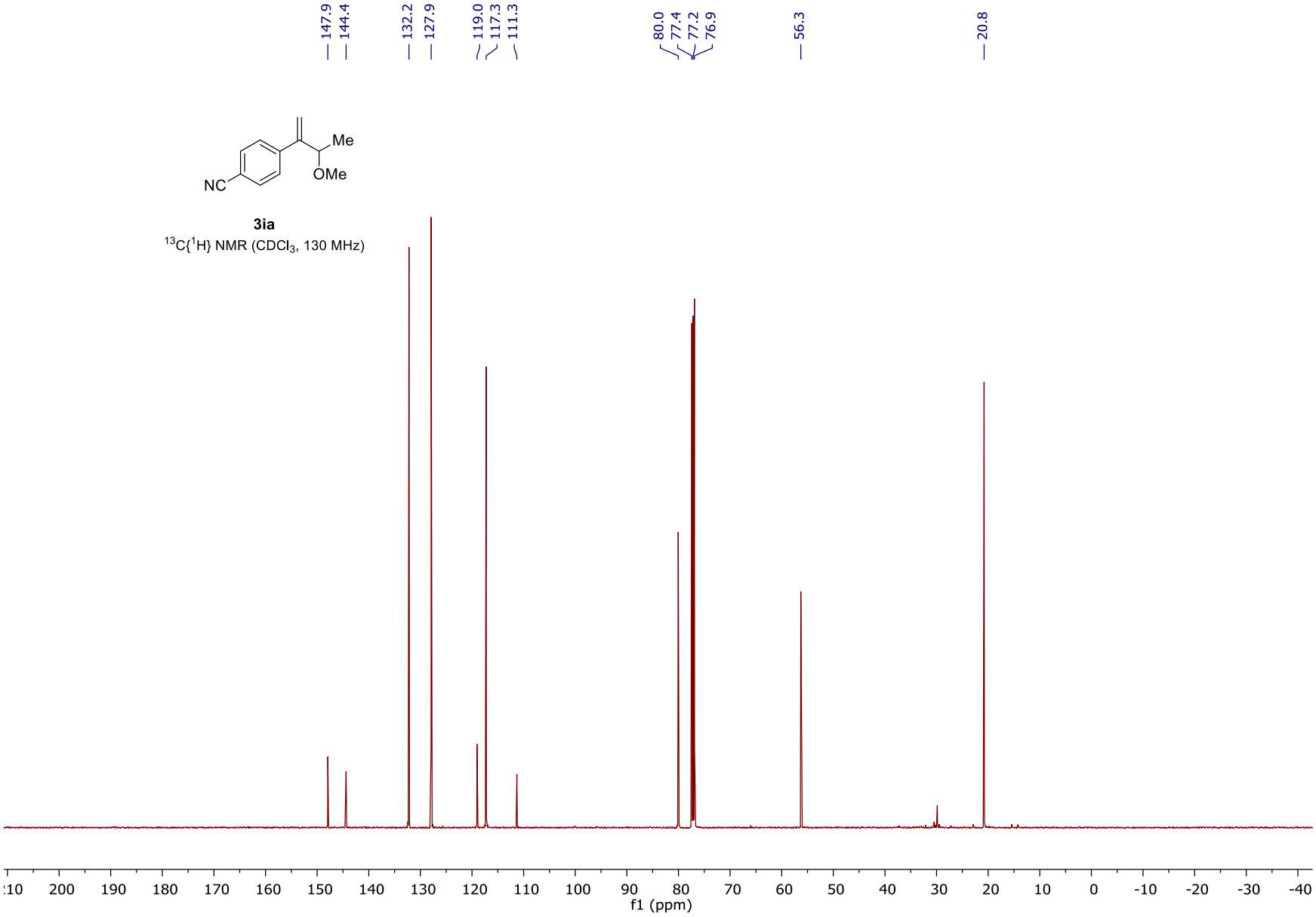


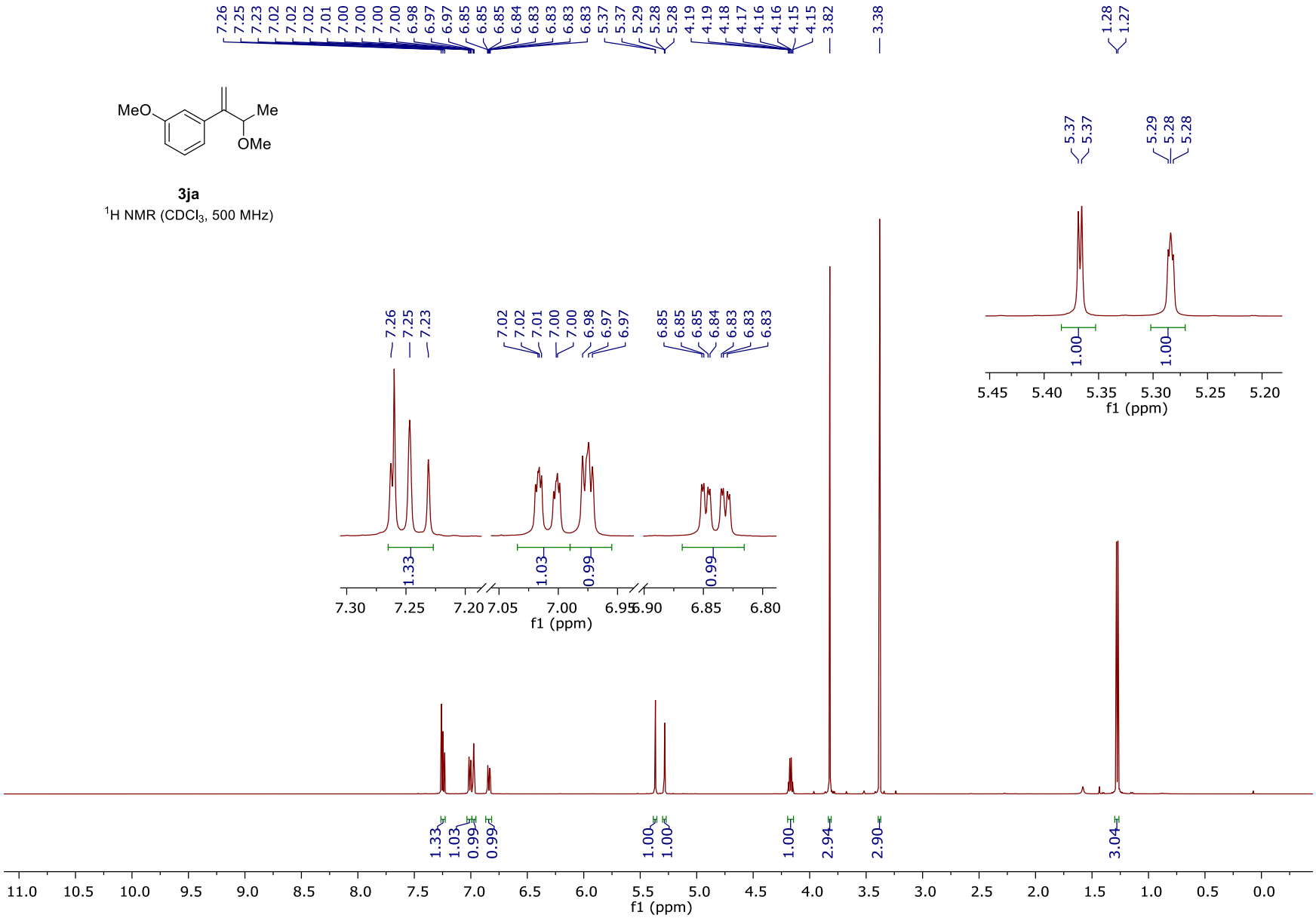
3ha

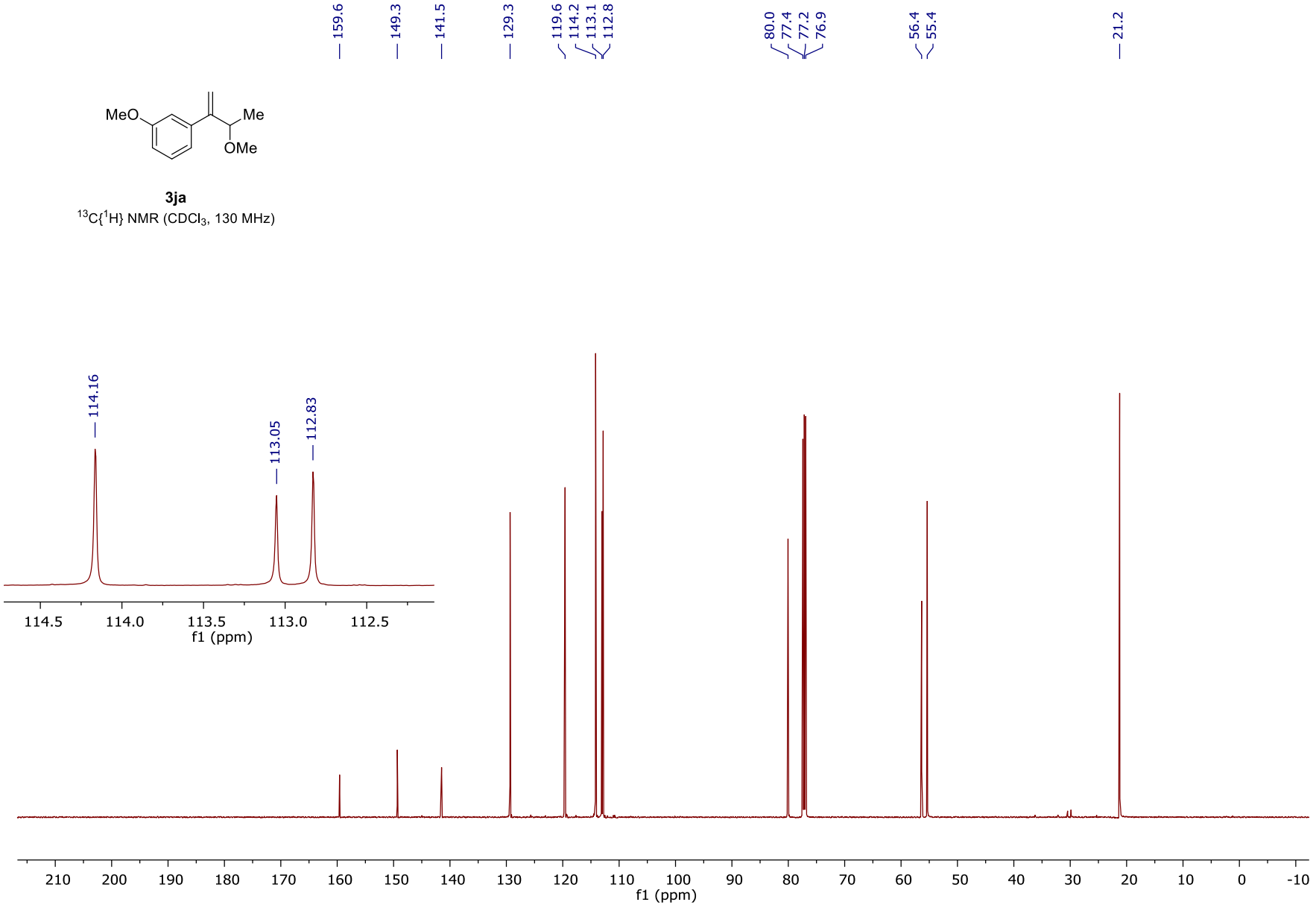
^{1}H NMR ($CDCl_3$, 500 MHz)

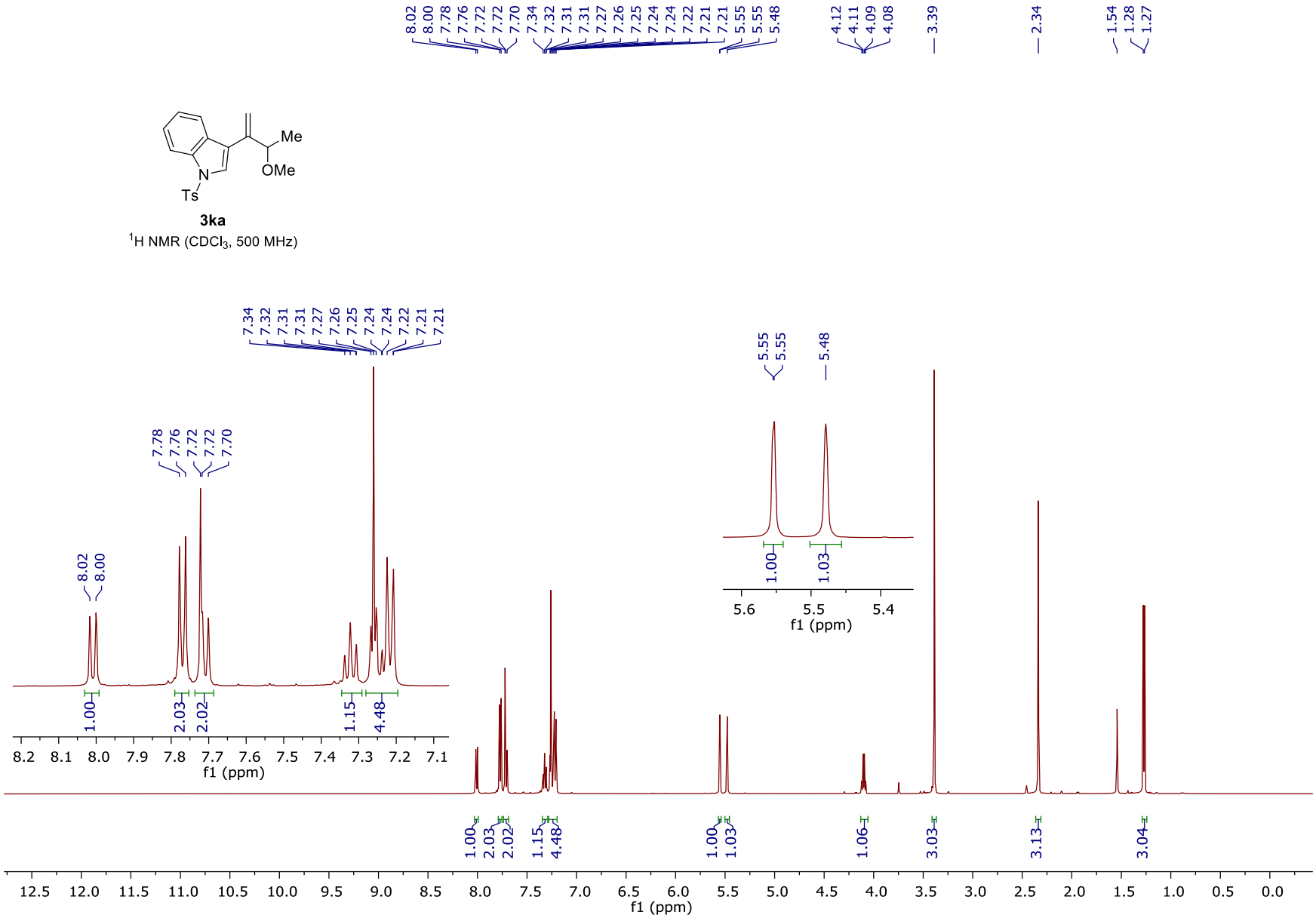

167.1
148.7
144.5
129.7
129.3
127.1
115.9
80.0
77.4
77.4
77.2
76.9
56.3
52.2
21.0
Me
OMe
MeO2C
3ha
13C{1H} NMR (CDCl3, 130 MHz)
129.7
129.3
127.1
131
130
129
128
127
126
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

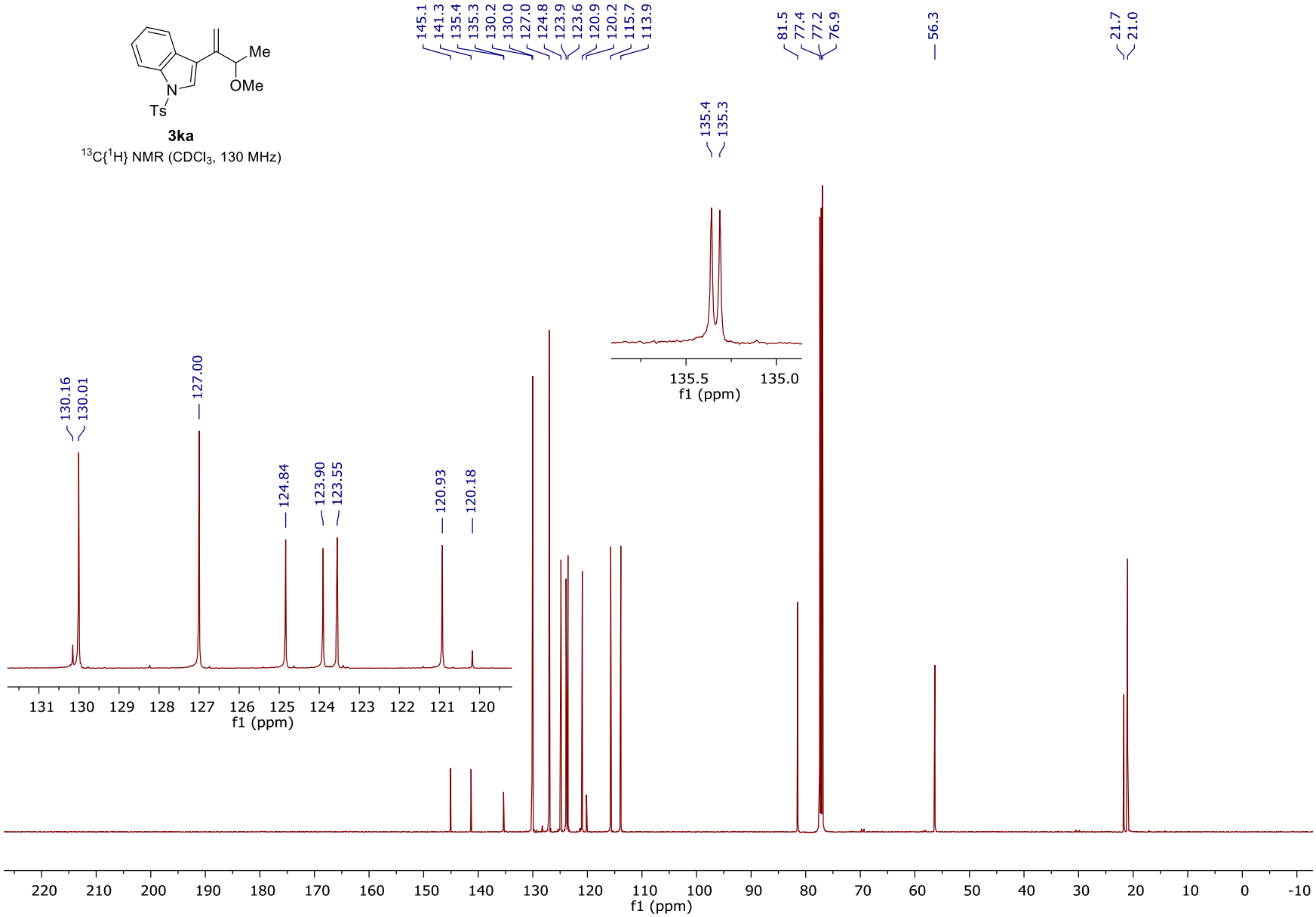

7.63
7.62
7.62
7.61
7.61
7.60
7.55
7.55
7.54
7.54
7.53
7.26
5.45
5.45
5.40
5.40
5.40
4.19
4.19
4.17
4.17
4.16
4.16
4.15
4.15
3.36
1.27
1.25
Me
OMe
NC
3ia
1H NMR (CDCl3, 500 MHz)
0.99
1.00
5.50
5.45
5.40
5.35
f1 (ppm)
7.65
7.60
7.55
7.50
f1 (ppm)
1.92
1.96
0.99
1.00
1.00
2.88
3.27
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

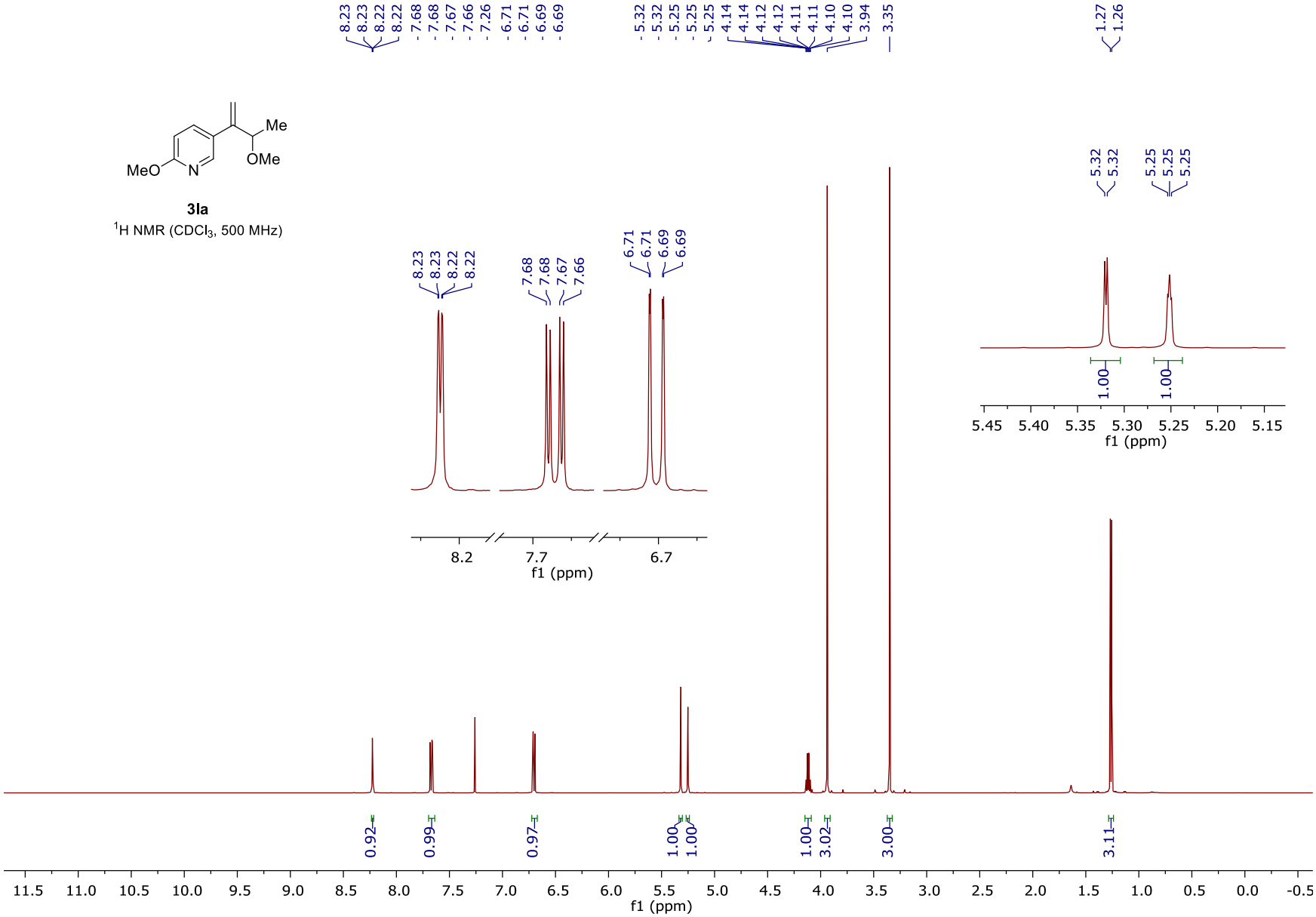

147.9
144.4
132.2
127.9
119.0
117.3
111.3
80.0
77.4
77.2
76.9
56.3
20.8
Me
OMe
NC
3ia
13C{1H} NMR (CDCl3, 130 MHz)
f1 (ppm)

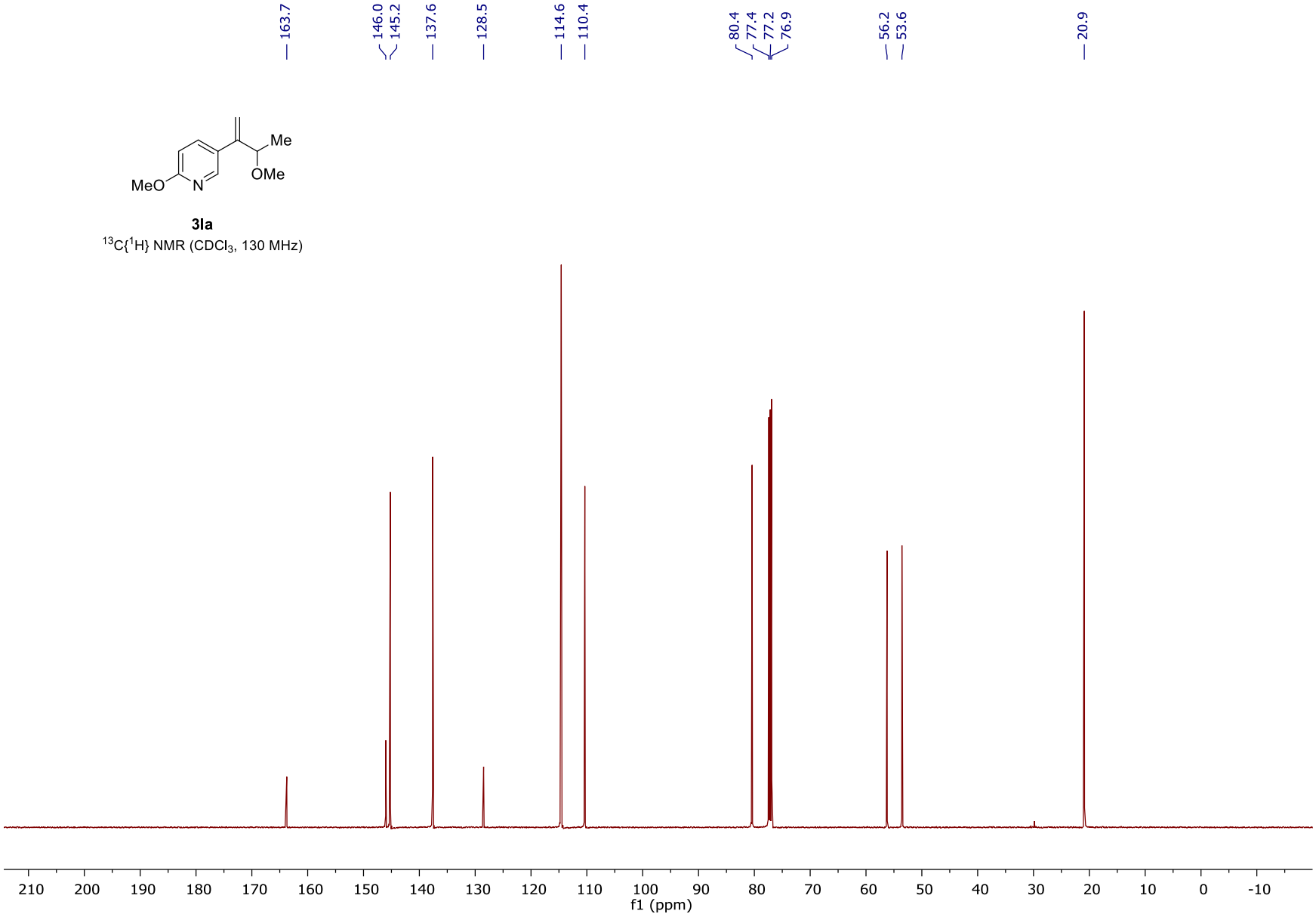

MeO
Me
OMe
3ja
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

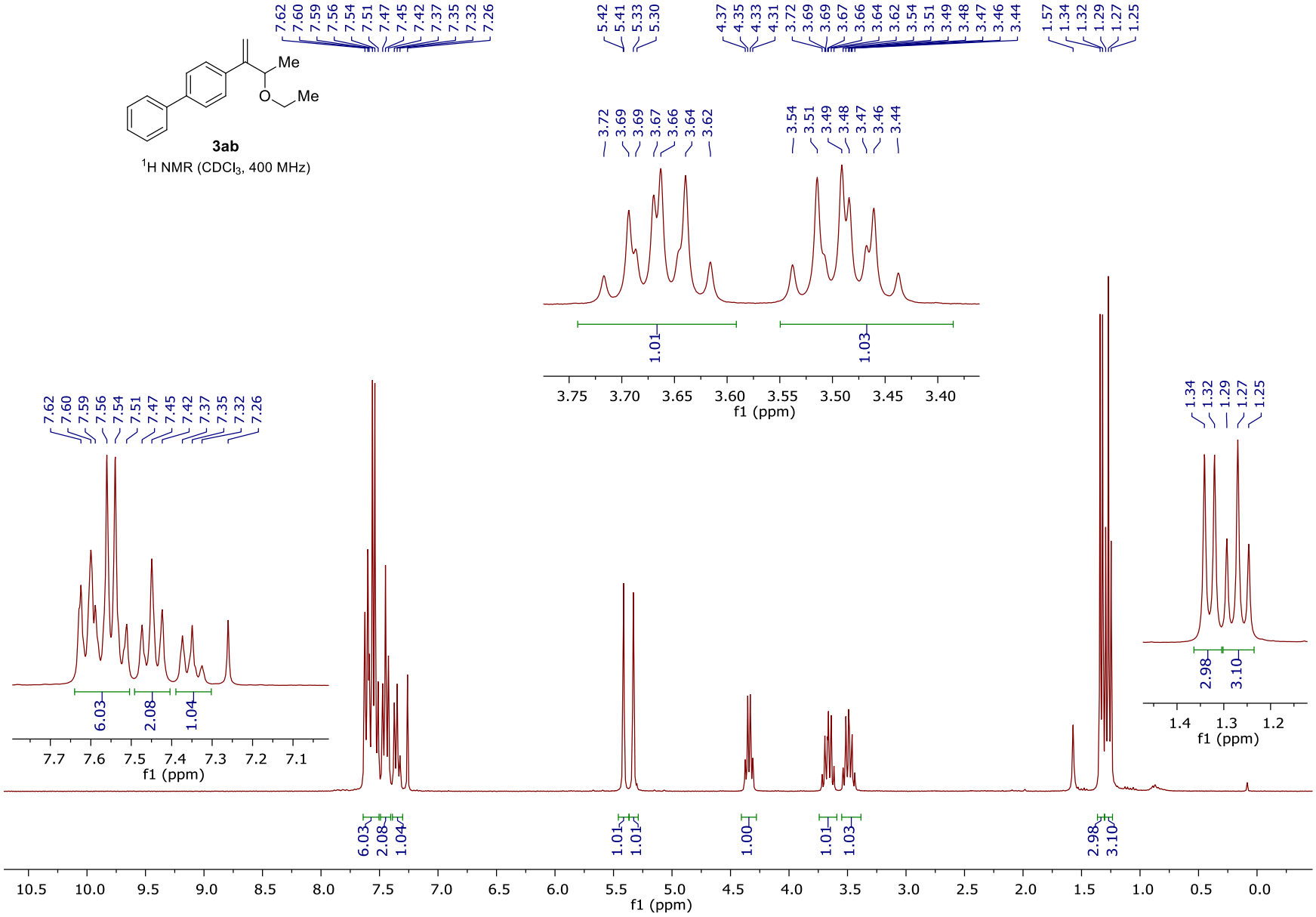

159.6
149.3
141.5
129.3
119.6
114.2
113.1
112.8
80.0
77.4
77.2
76.9
56.4
55.4
21.2
MeO
Me
OMe
3ja
13C{1H} NMR (CDCl3, 130 MHz)
114.16
113.05
112.83
114.5
114.0
113.5
113.0
112.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

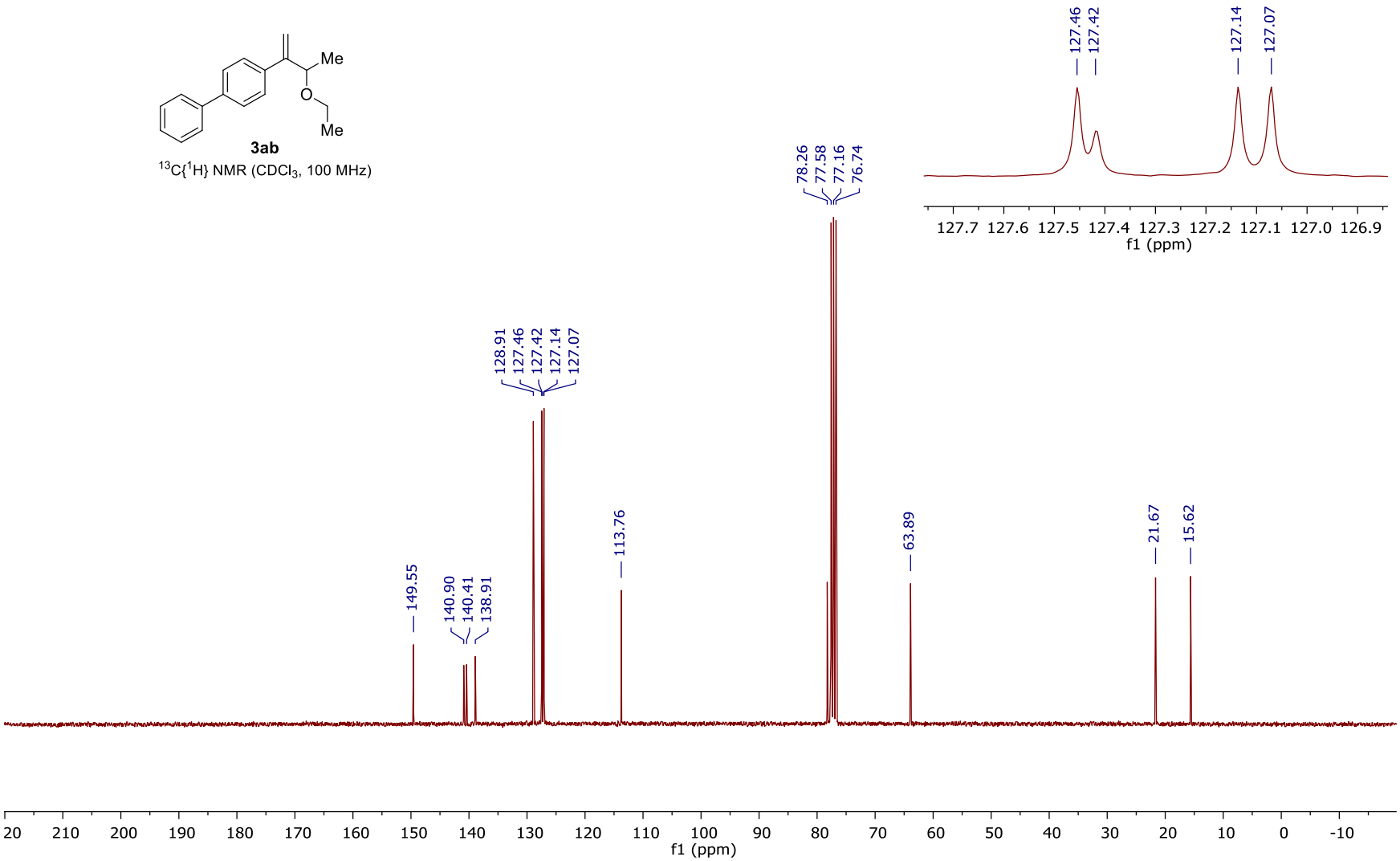

8.02
8.00
7.78
7.76
7.72
7.72
7.70
7.34
7.32
7.31
7.31
7.27
7.26
7.25
7.24
7.24
7.22
7.21
7.21
5.55
5.55
5.48
4.12
4.11
4.09
4.08
3.39
2.34
1.54
1.28
1.27
Me
OMe
N
Ts
3ka
1H NMR (CDCl3, 500 MHz)
1.00
2.03
2.02
1.15
4.48
1.00
1.03
1.06
3.03
3.13
3.04
f1 (ppm)

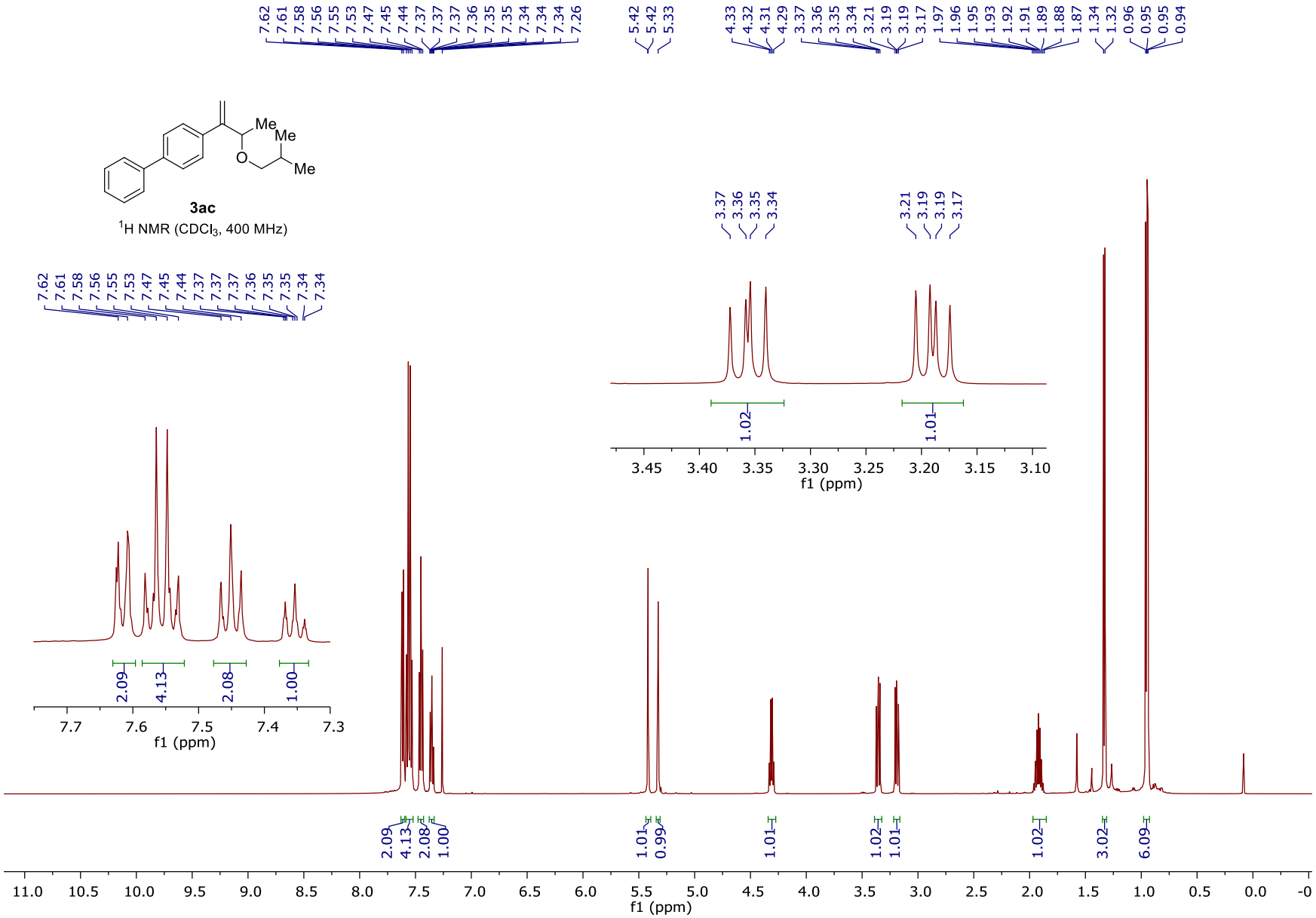

Me
OMe
N
Ts
3ka
13C{1H} NMR (CDCl3, 130 MHz)
145.1
141.3
135.4
135.3
130.2
130.0
127.0
124.8
123.9
123.6
120.9
120.2
115.7
113.9
81.5
77.4
77.2
76.9
56.3
21.7
21.0
135.4
135.3
135.5
135.0
f1 (ppm)
130.16
130.01
127.00
124.84
123.90
123.55
120.93
120.18
131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
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)

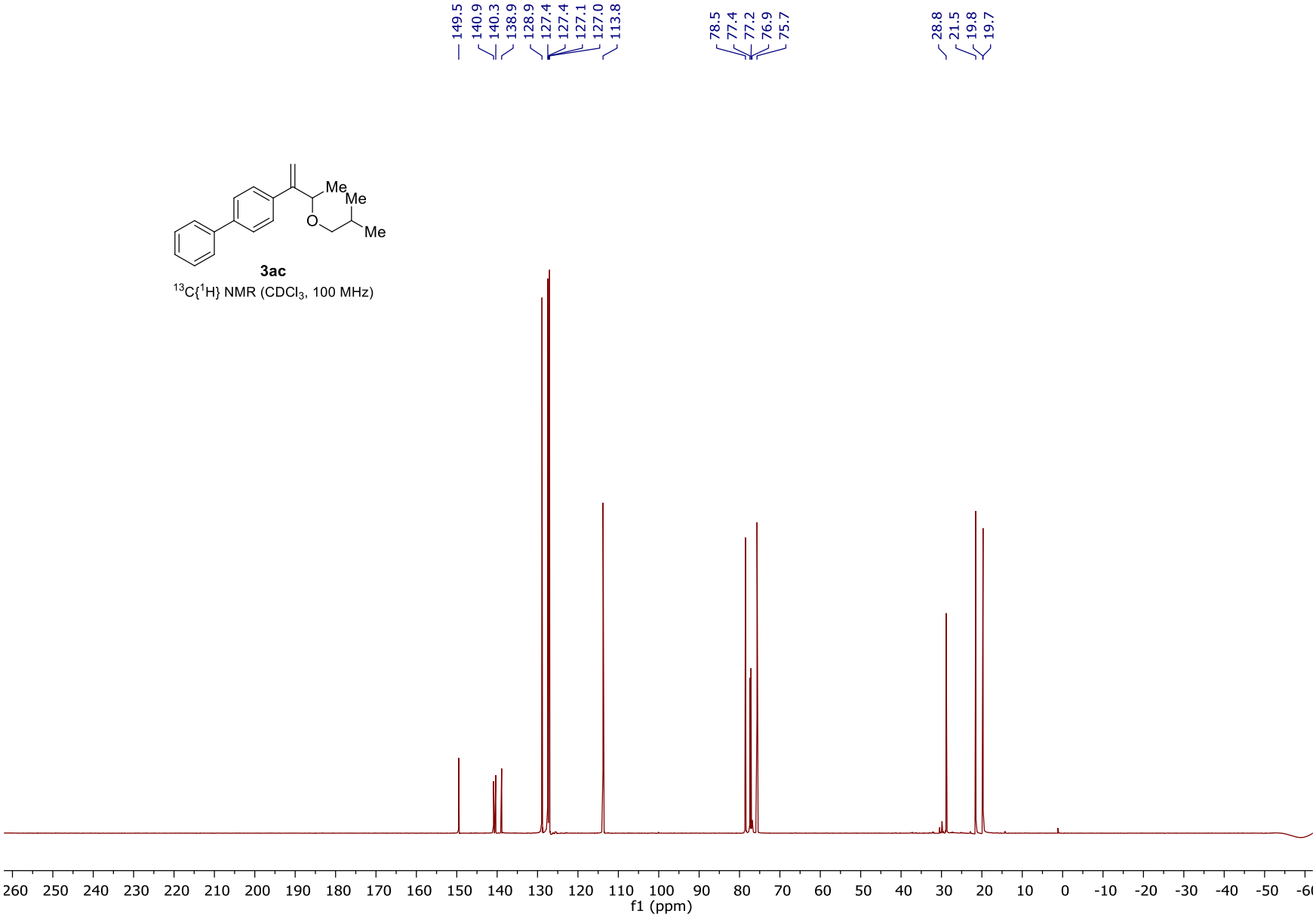

MeO
N
Me
OMe
3la
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

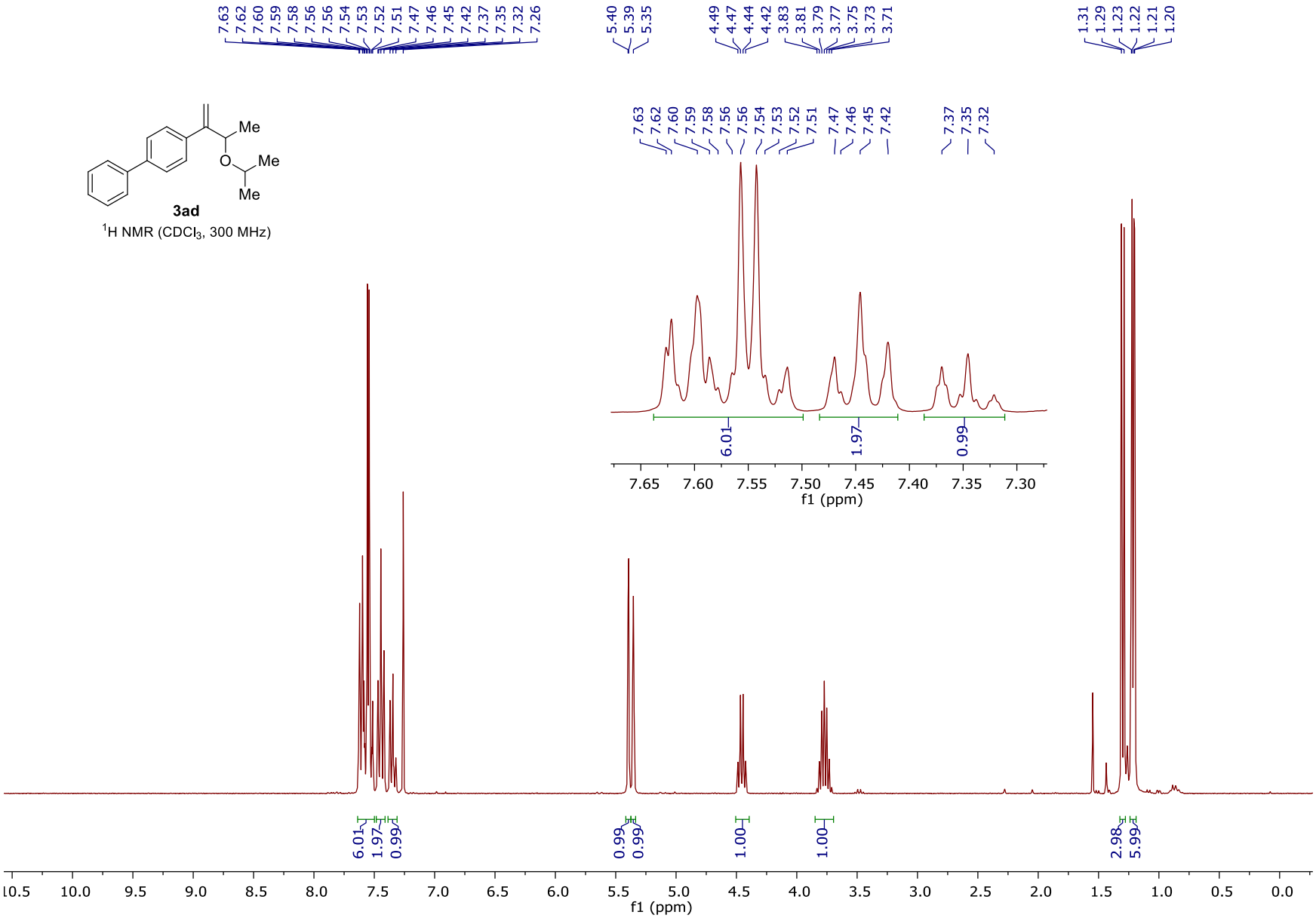

163.7
146.0
145.2
137.6
128.5
114.6
110.4
80.4
77.4
77.2
76.9
56.2
53.6
20.9
Me
OMe
MeO
N
3Ia
13C{1H} NMR (CDCl3, 130 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

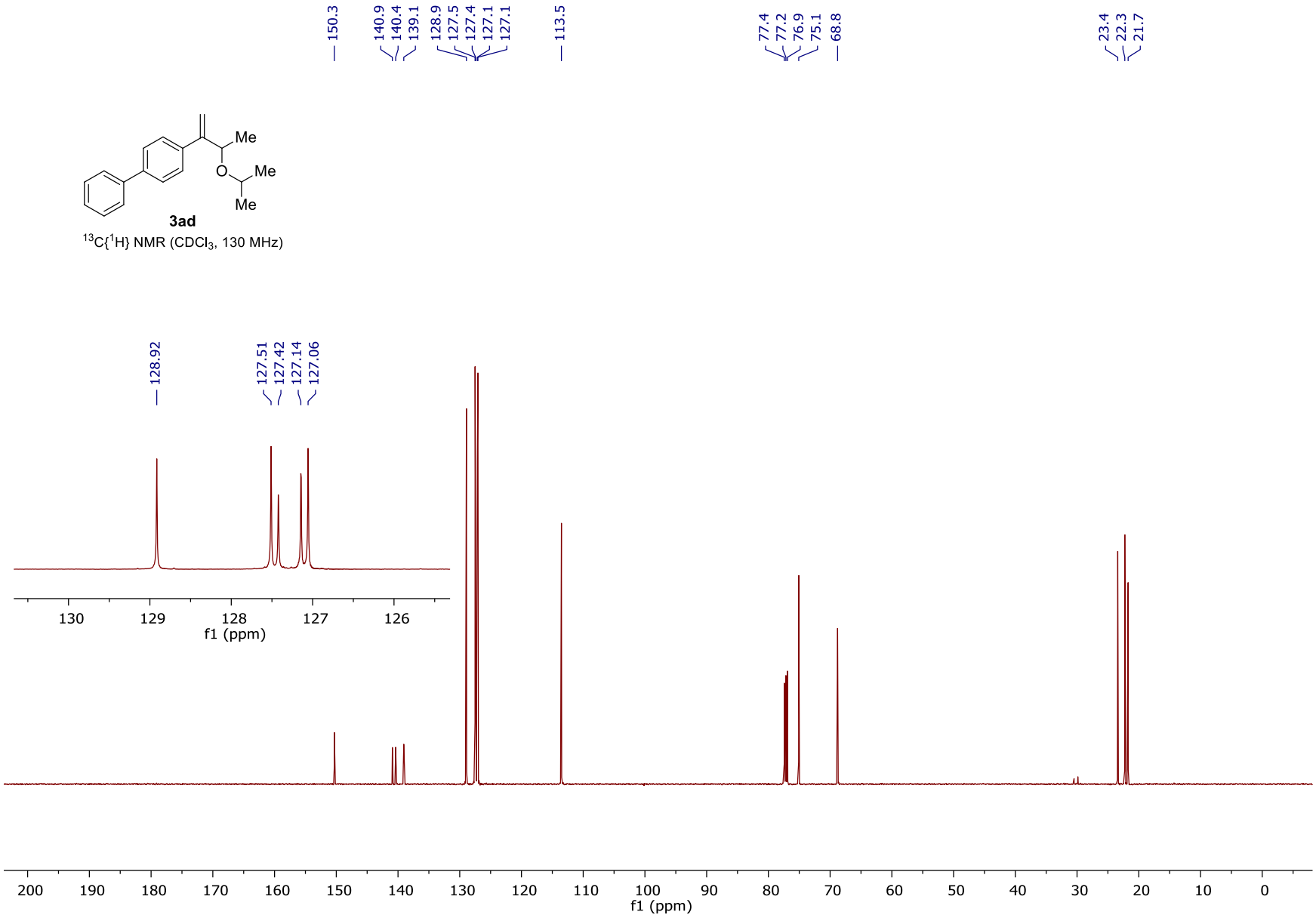

Me
O
Me
3ab
1H NMR (CDCl3, 400 MHz)
f1 (ppm)

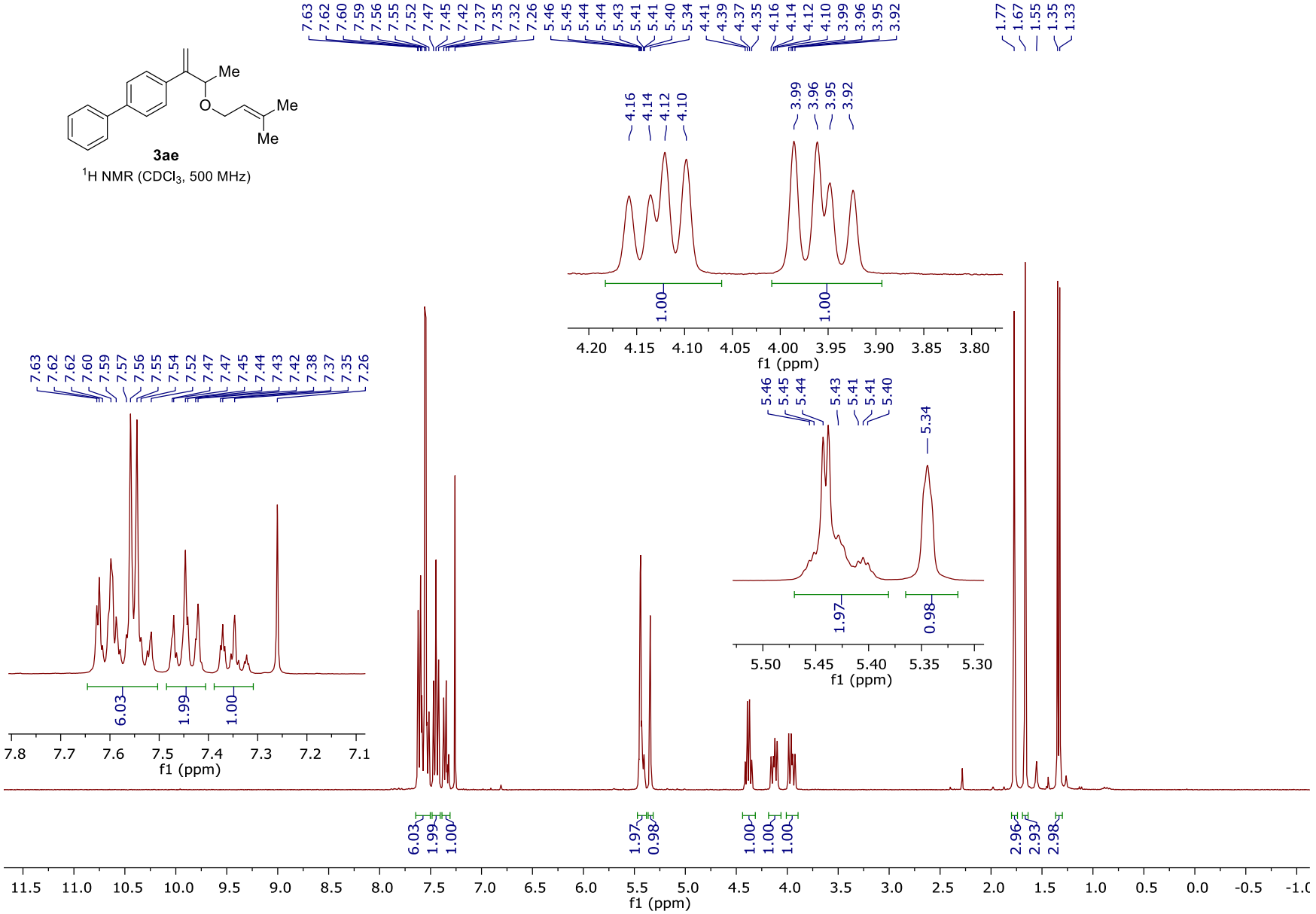

Me
O
Me
3ab
13C{1H} NMR (CDCl3, 100 MHz)
127.46
127.42
127.14
127.07
127.7 127.6 127.5 127.4 127.3 127.2 127.1 127.0 126.9
f1 (ppm)
78.26
77.58
77.16
76.74
128.91
127.46
127.42
127.14
127.07
149.55
140.90
140.41
138.91
113.76
63.89
21.67
15.62
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

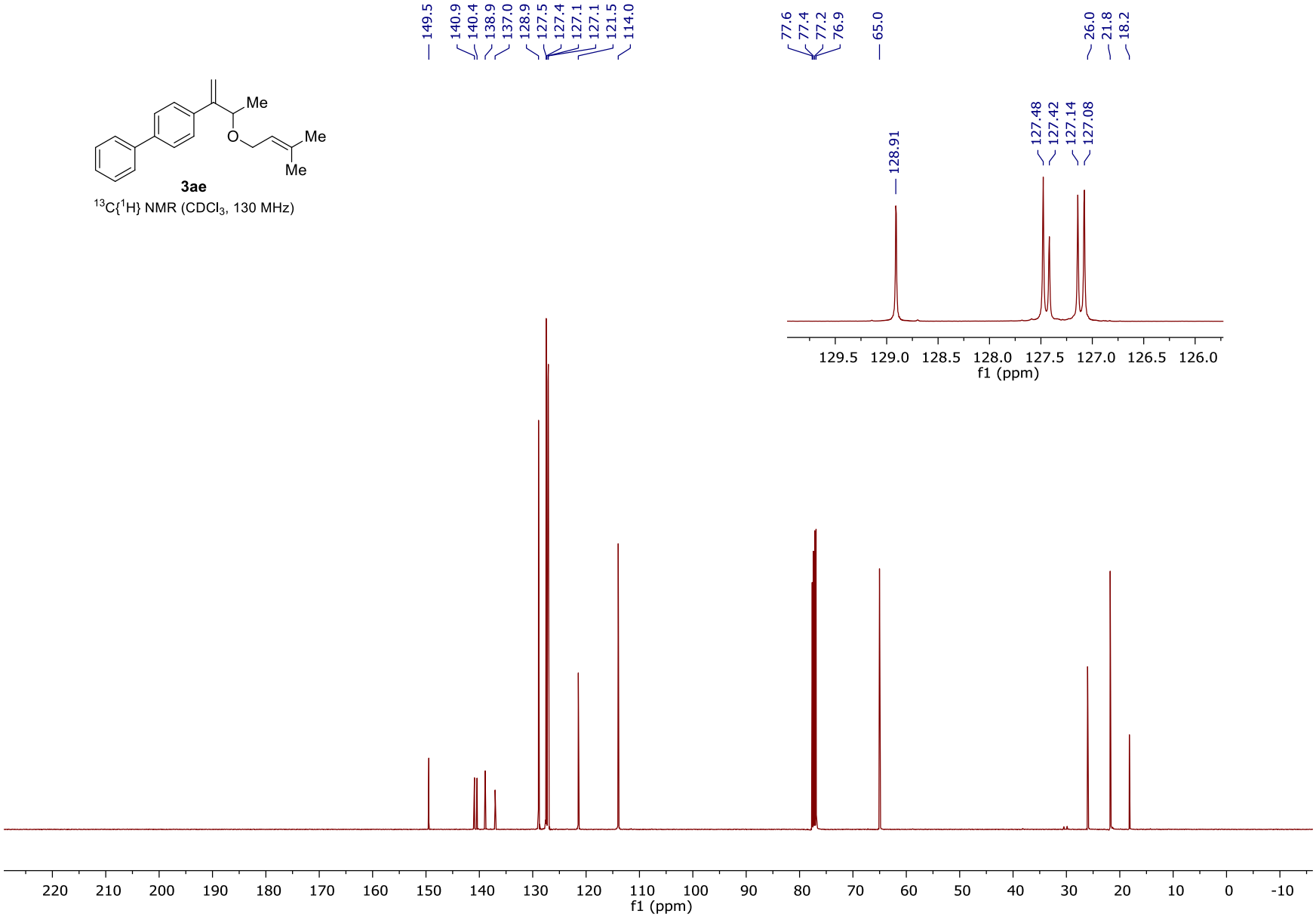

Me
Me
O
Me
3ac
1H NMR (CDCl3, 400 MHz)
f1 (ppm)

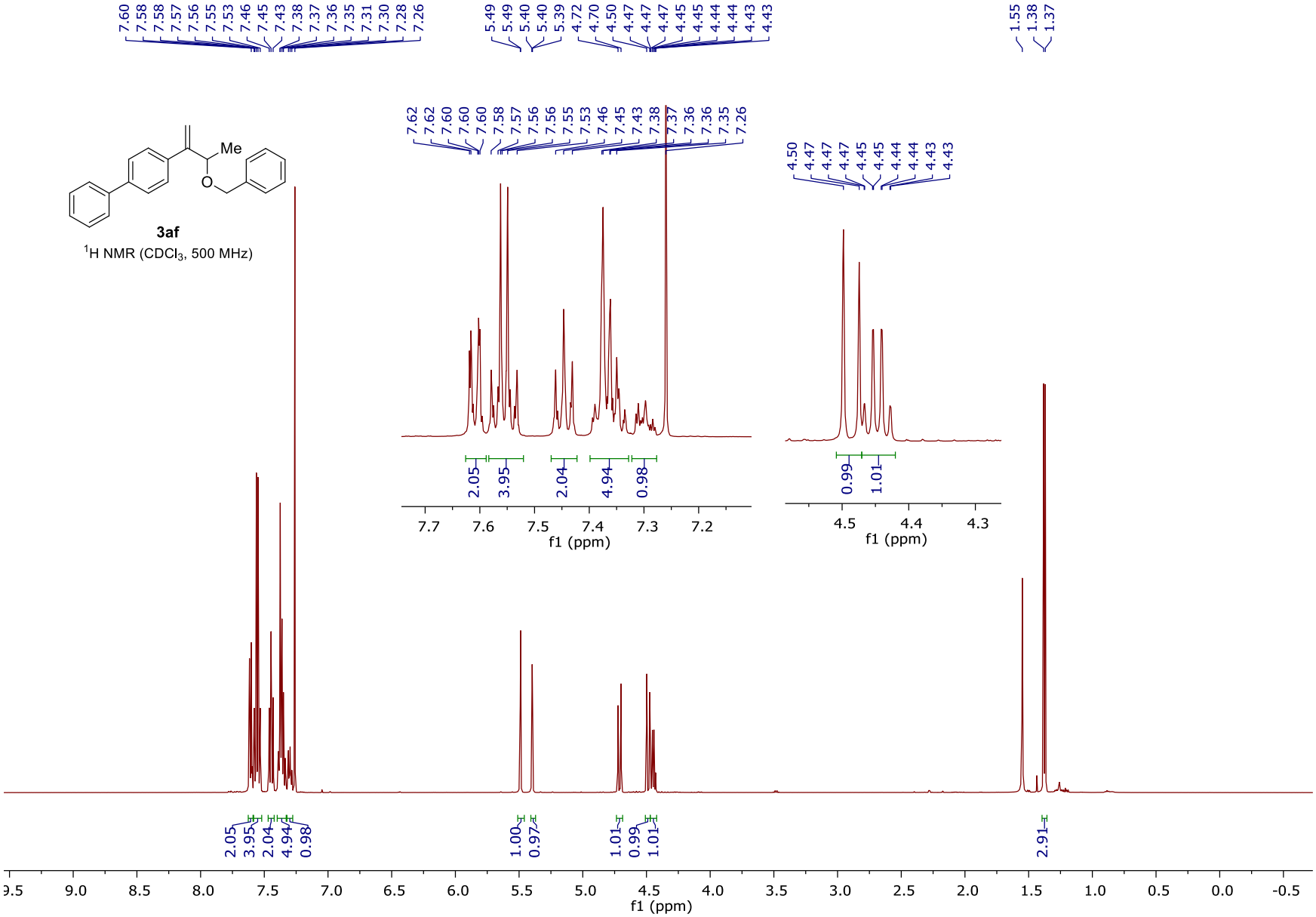

149.5
140.9
140.3
138.9
128.9
127.4
127.4
127.1
127.0
113.8
78.5
77.4
77.2
76.9
75.7
28.8
21.5
19.8
19.7
Me
Me
O
Me
3ac
13C{1H} NMR (CDCl3, 100 MHz)
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

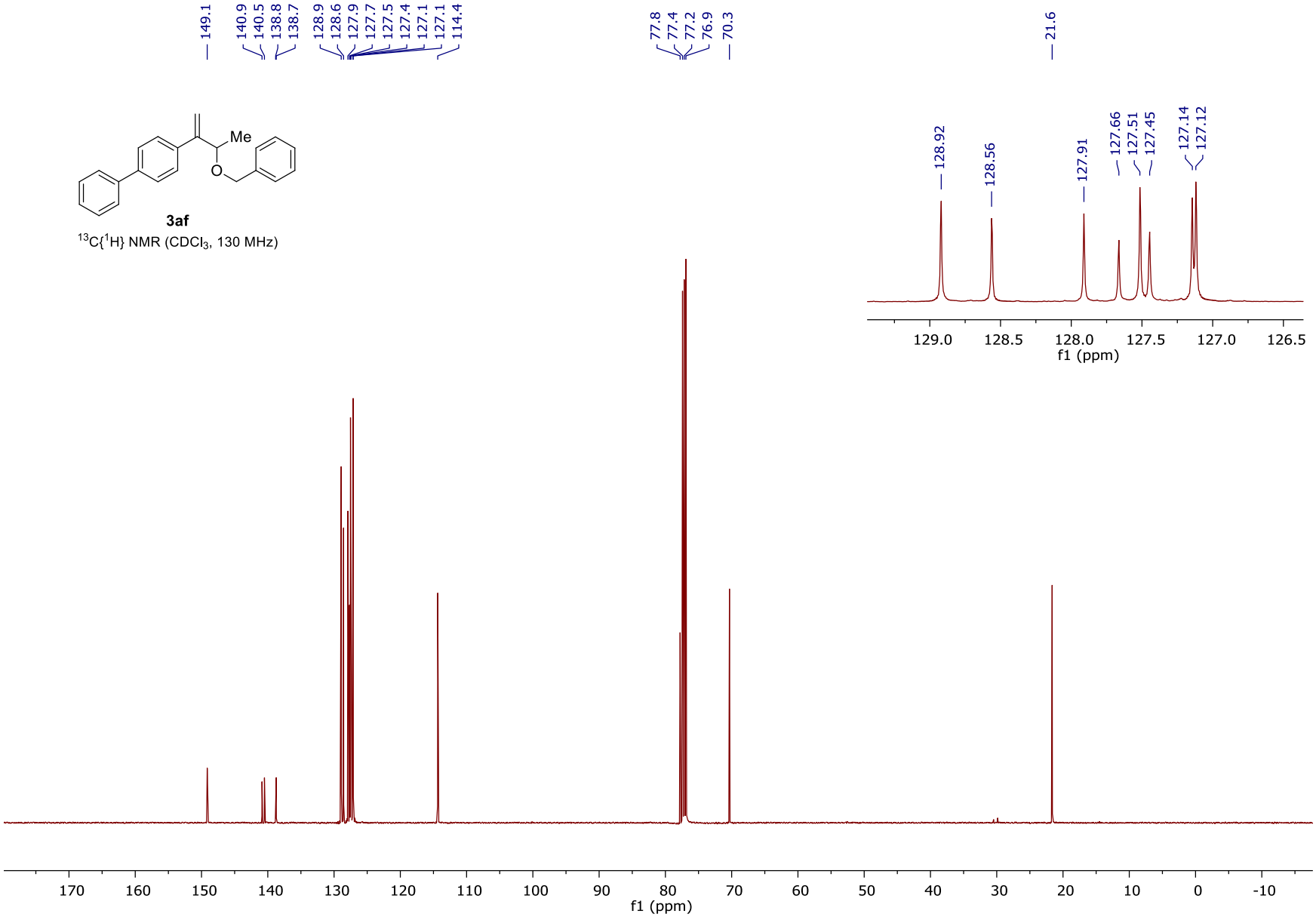

7.63
7.62
7.60
7.59
7.58
7.56
7.56
7.54
7.53
7.52
7.51
7.47
7.46
7.45
7.42
7.37
7.35
7.32
7.26
5.40
5.39
5.35
4.49
4.47
4.44
4.42
3.83
3.81
3.79
3.77
3.75
3.73
3.71
1.31
1.29
1.23
1.22
1.21
1.20
Me
O
Me
Me
3ad
1H NMR (CDCl3, 300 MHz)
6.01
1.97
0.99
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
f1 (ppm)
6.01
1.97
0.99
0.99
0.99
1.00
1.00
2.98
5.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

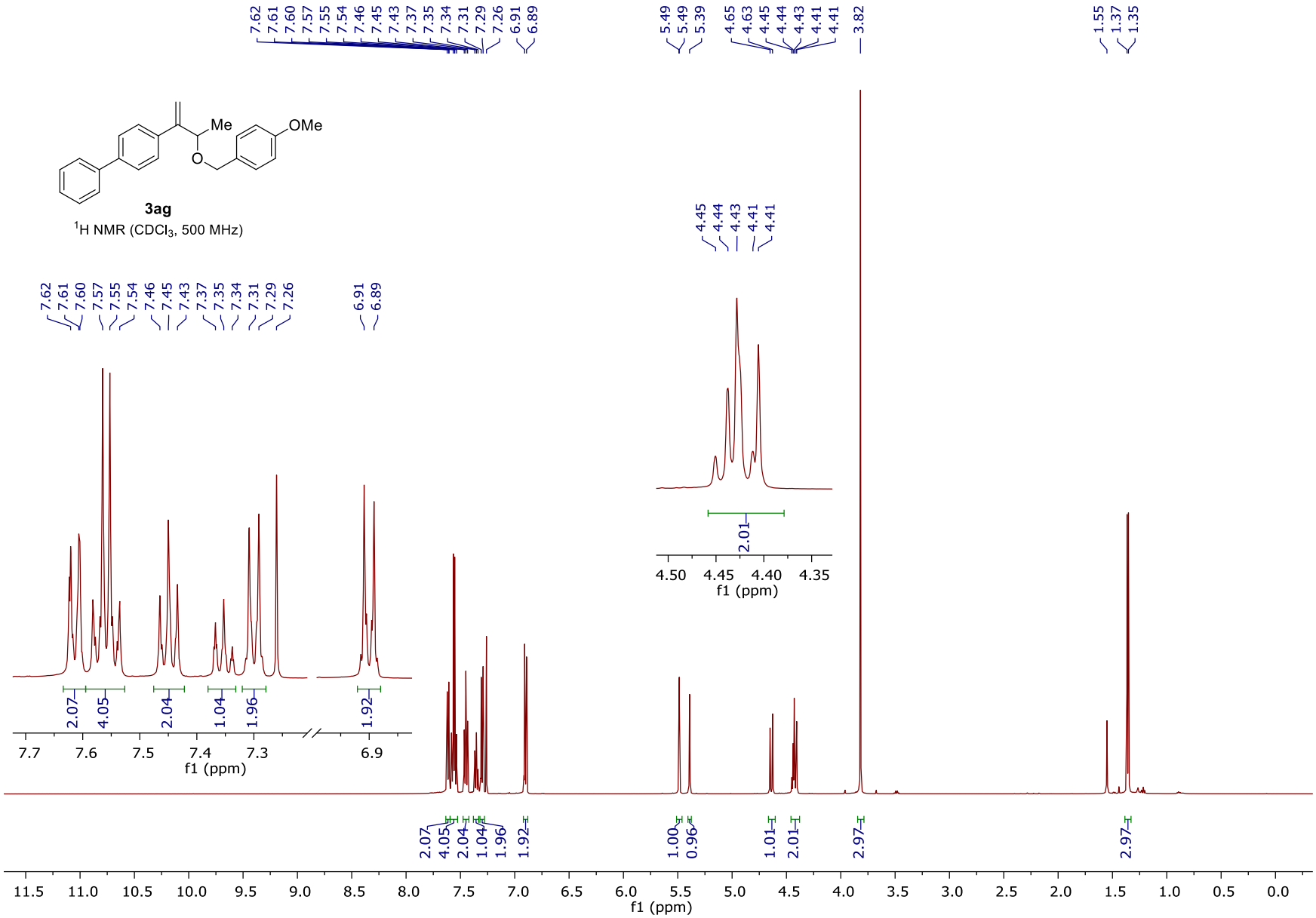

150.3
140.9
140.4
139.1
128.9
127.5
127.4
127.1
127.1
113.5
77.4
77.2
76.9
75.1
68.8
23.4
22.3
21.7
Me
O
Me
Me
3ad
13C{1H} NMR (CDCl3, 130 MHz)
128.92
127.51
127.42
127.14
127.06
130
129
128
127
126
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

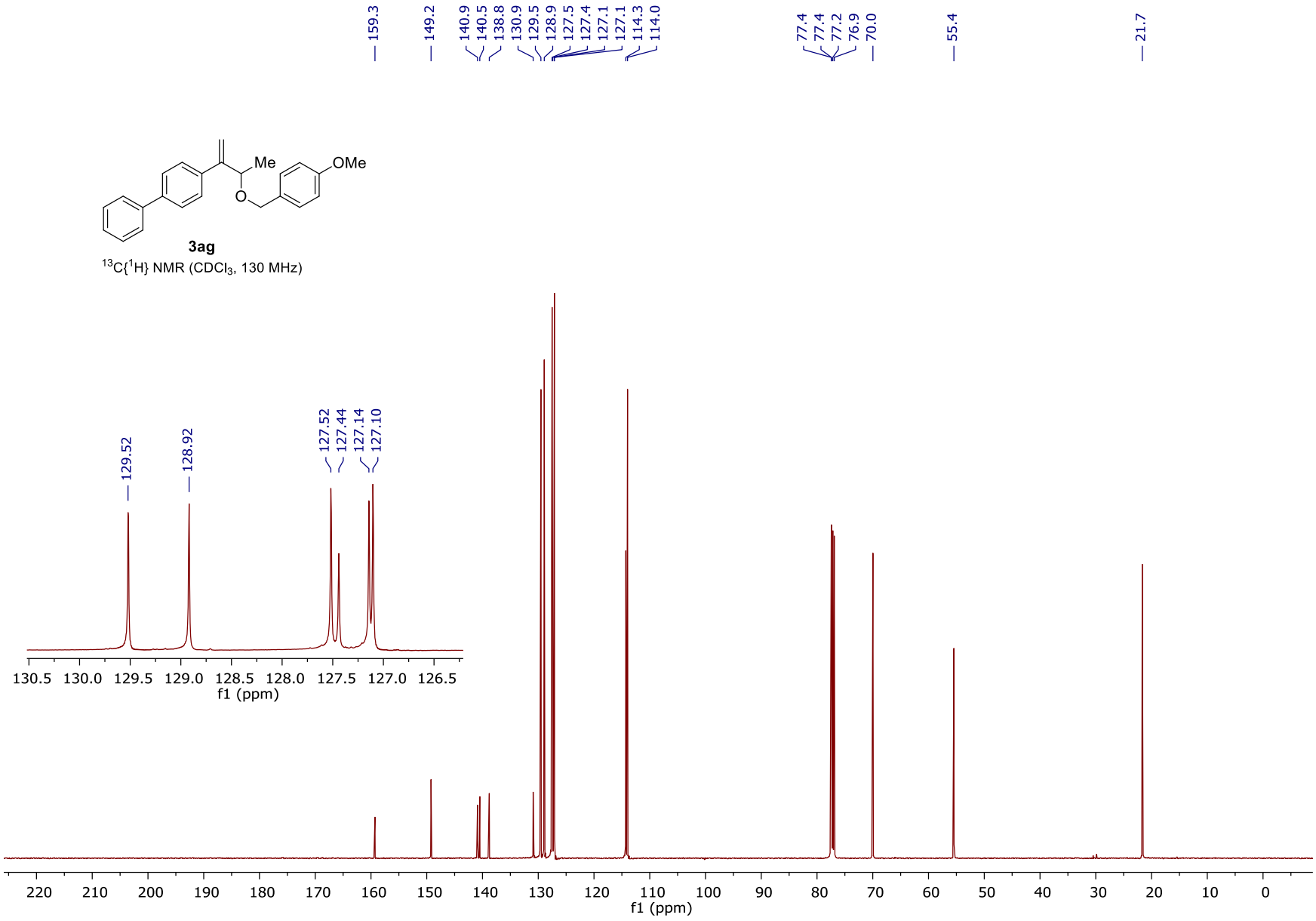

Me
O
Me
Me
3ae
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

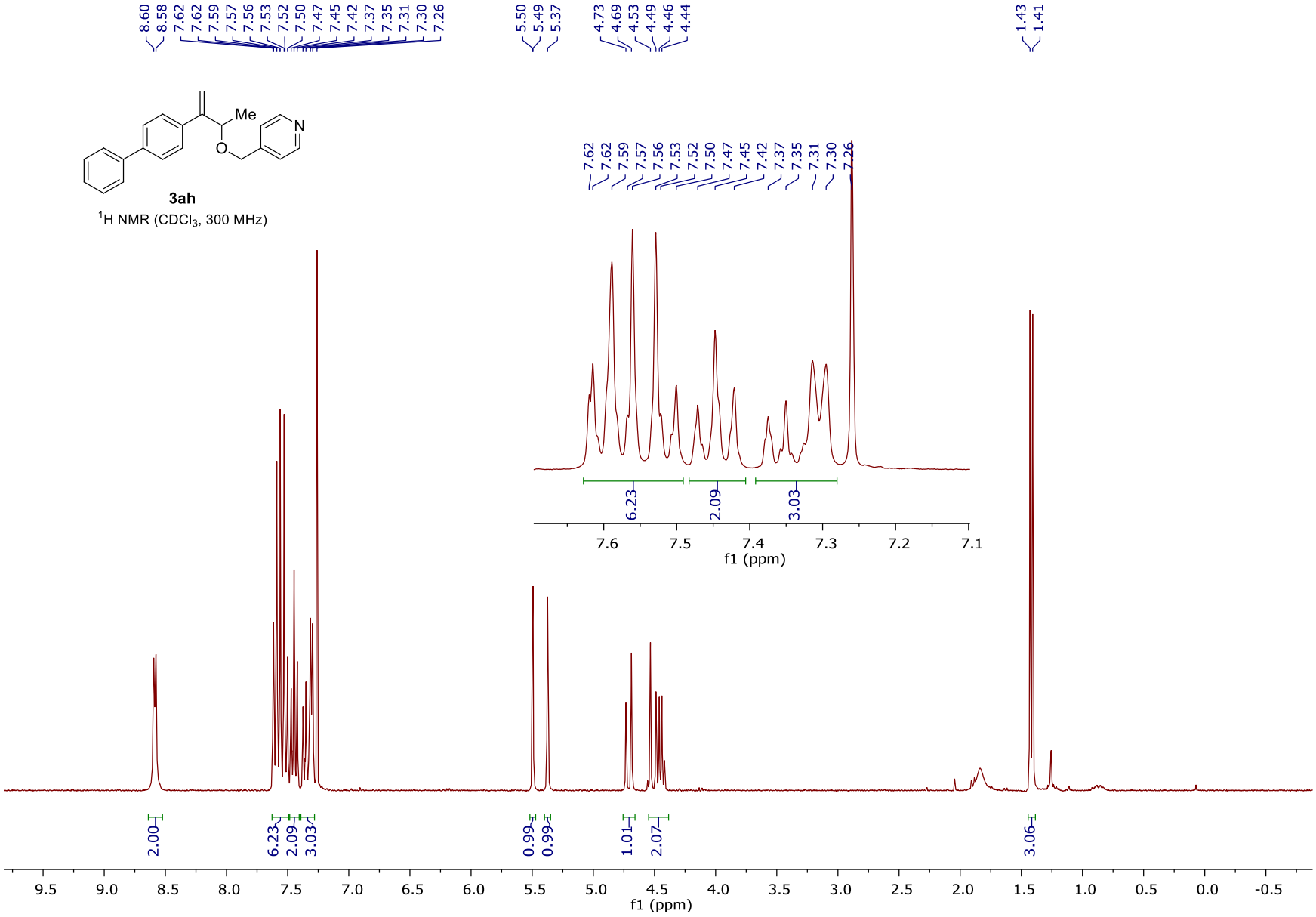

149.5
140.9
140.4
138.9
137.0
128.9
127.5
127.4
127.1
127.1
121.5
114.0
77.6
77.4
77.2
76.9
65.0
26.0
21.8
18.2
128.91
127.48
127.42
127.14
127.08
Me
O
Me
Me
3ae
13C{1H} NMR (CDCl3, 130 MHz)
129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

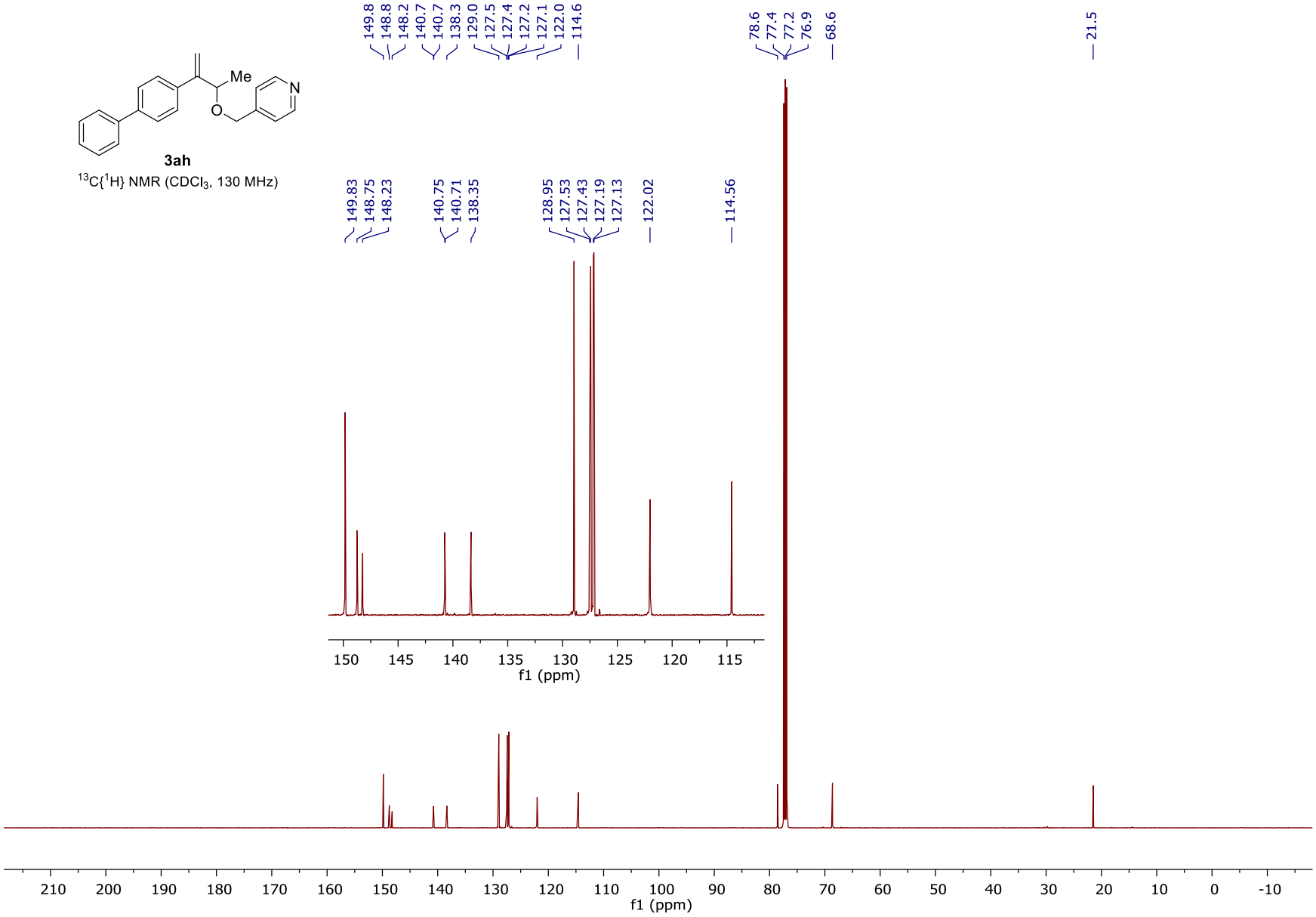

Me
O
3af
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

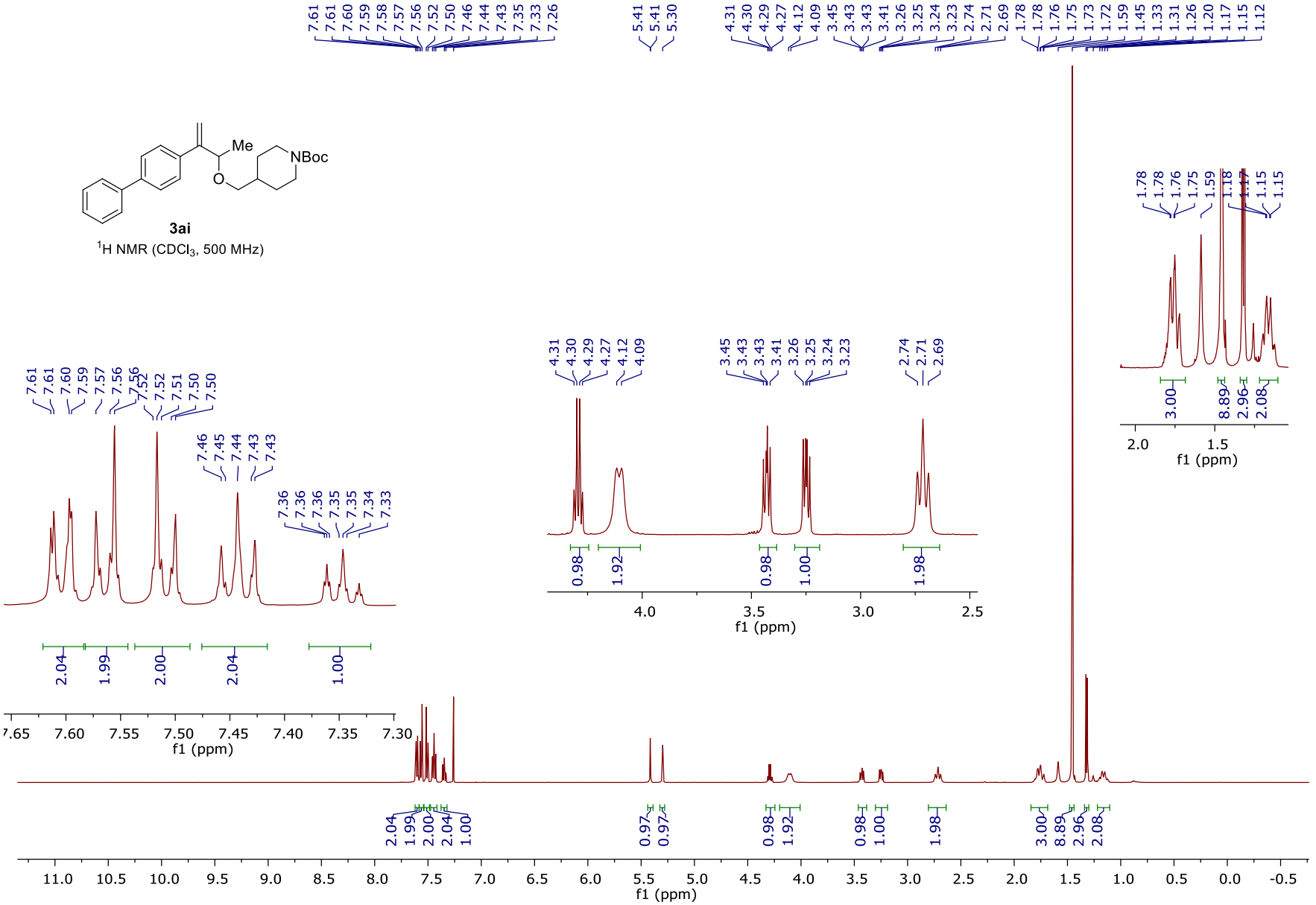

149.1
140.9
140.5
138.8
138.7
128.9
128.6
127.9
127.7
127.5
127.4
127.1
127.1
114.4
77.8
77.4
77.2
76.9
70.3
21.6
Me
O
3af
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 130 MHz)
128.92
128.56
127.91
127.66
127.51
127.45
127.14
127.12
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

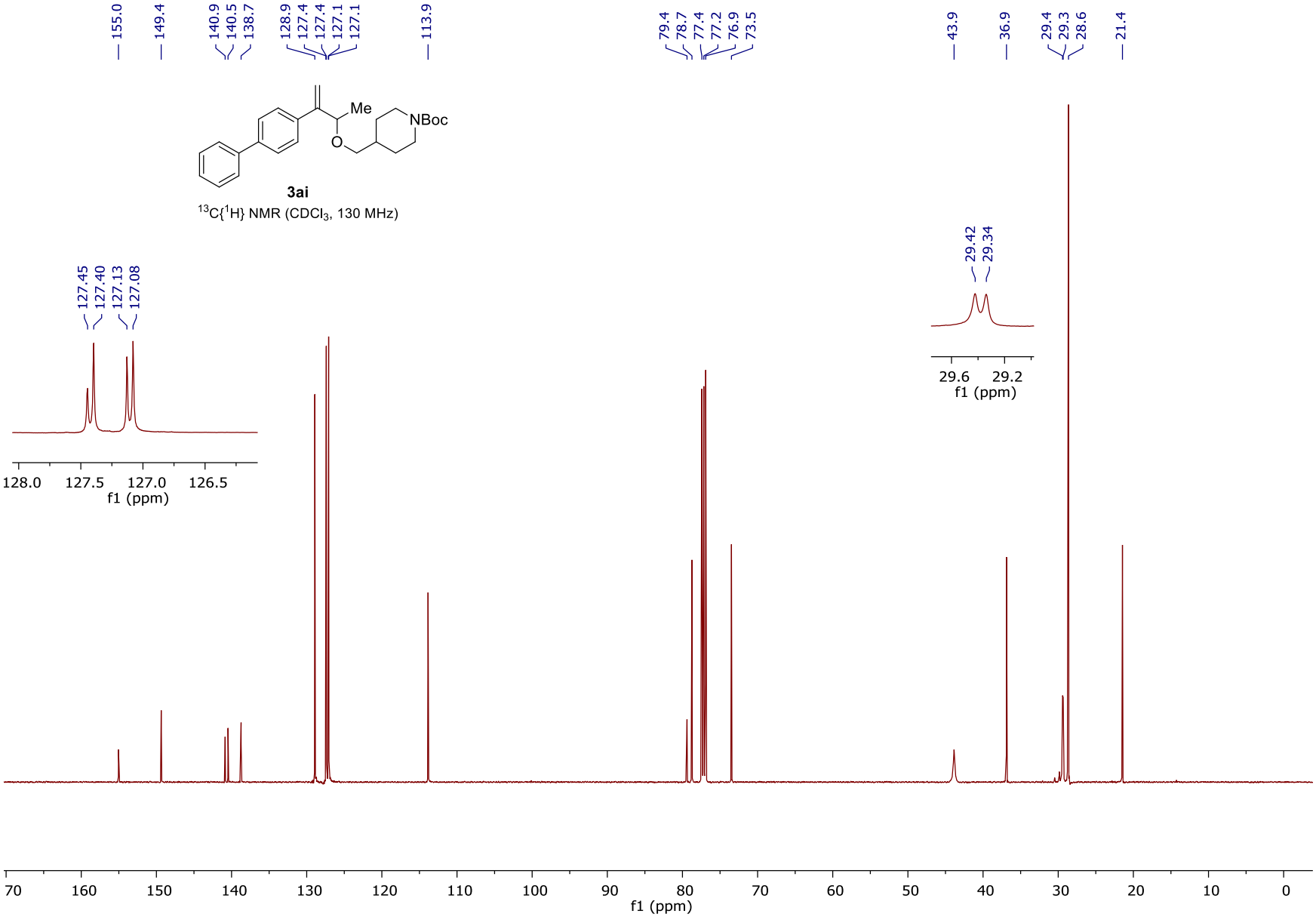

Me
OMe
O
3ag
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

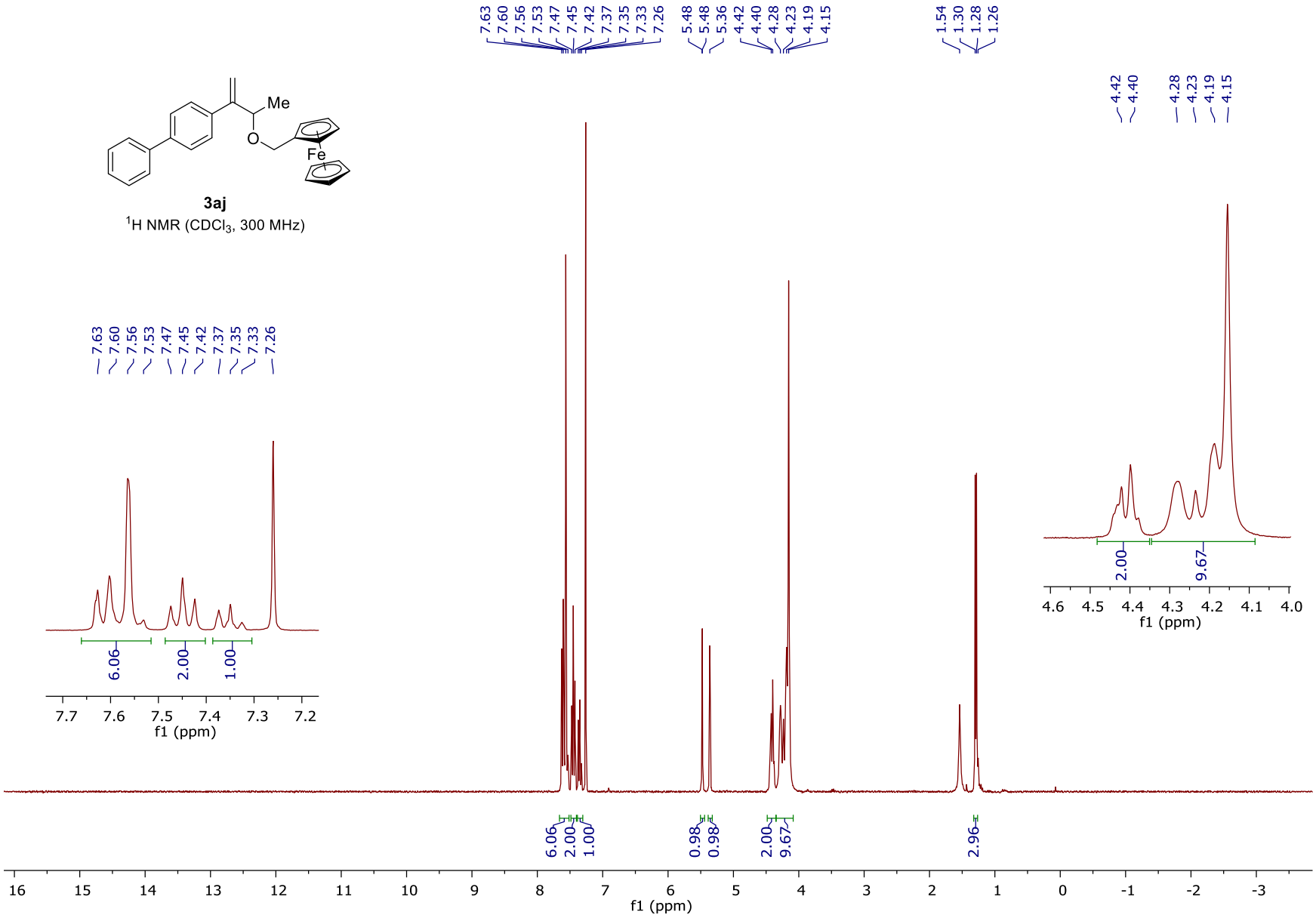

159.3
149.2
140.9
140.5
138.8
130.9
129.5
128.9
127.5
127.4
127.1
127.1
114.3
114.0
77.4
77.4
77.2
76.9
70.0
55.4
21.7
Me
OMe
O
3ag
13C{1H} NMR (CDCl3, 130 MHz)
129.52
128.92
127.52
127.44
127.14
127.10
130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

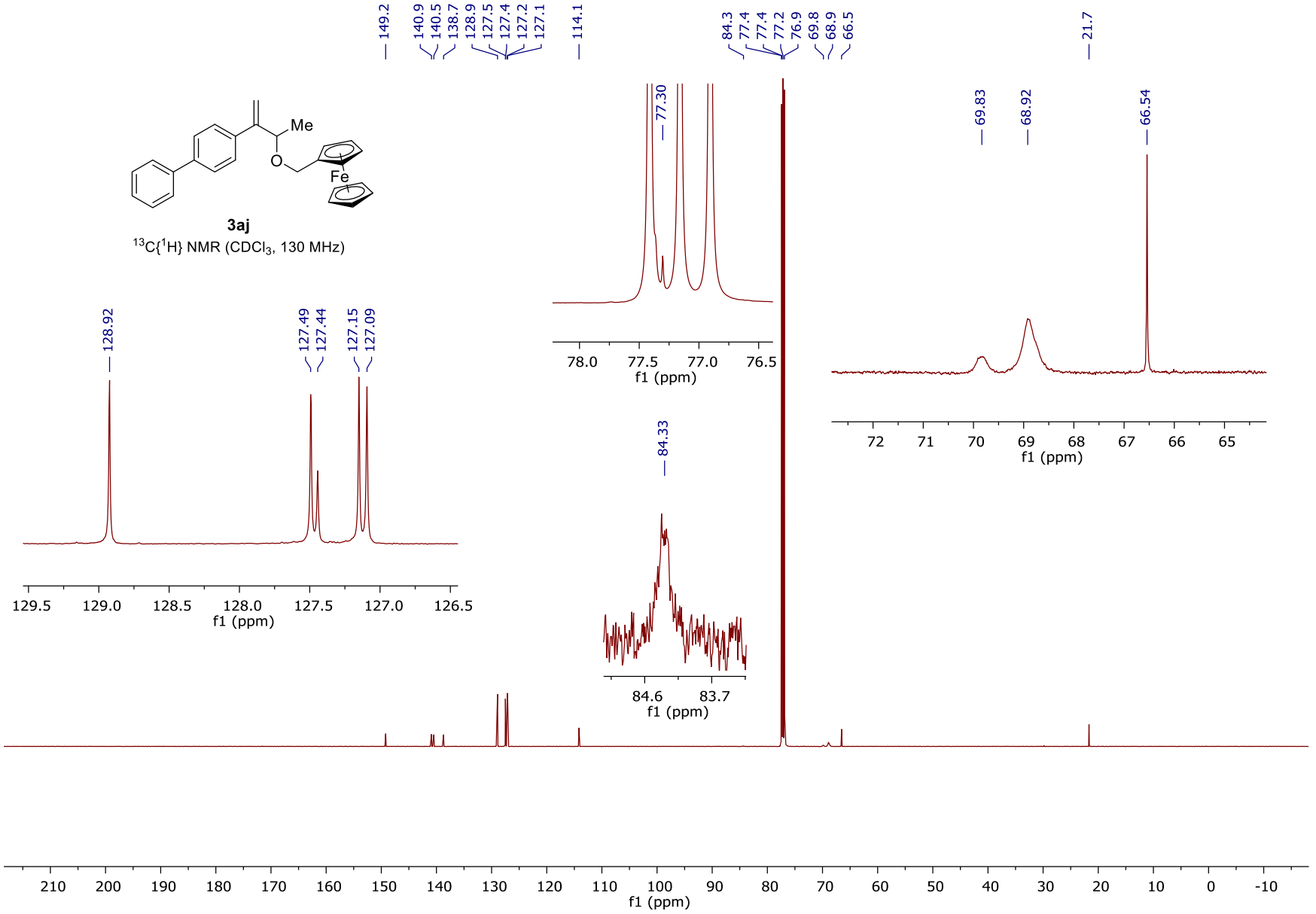

8.60
8.58
7.62
7.62
7.59
7.57
7.56
7.53
7.52
7.50
7.47
7.45
7.42
7.37
7.35
7.31
7.30
7.26
5.50
5.49
5.37
4.73
4.69
4.53
4.49
4.46
4.44
1.43
1.41
Me
O
N
3ah
1H NMR (CDCl3, 300 MHz)
6.23
2.09
3.03
f1 (ppm)
2.00
6.23
2.09
3.03
0.99
0.99
1.01
2.07
3.06
f1 (ppm)

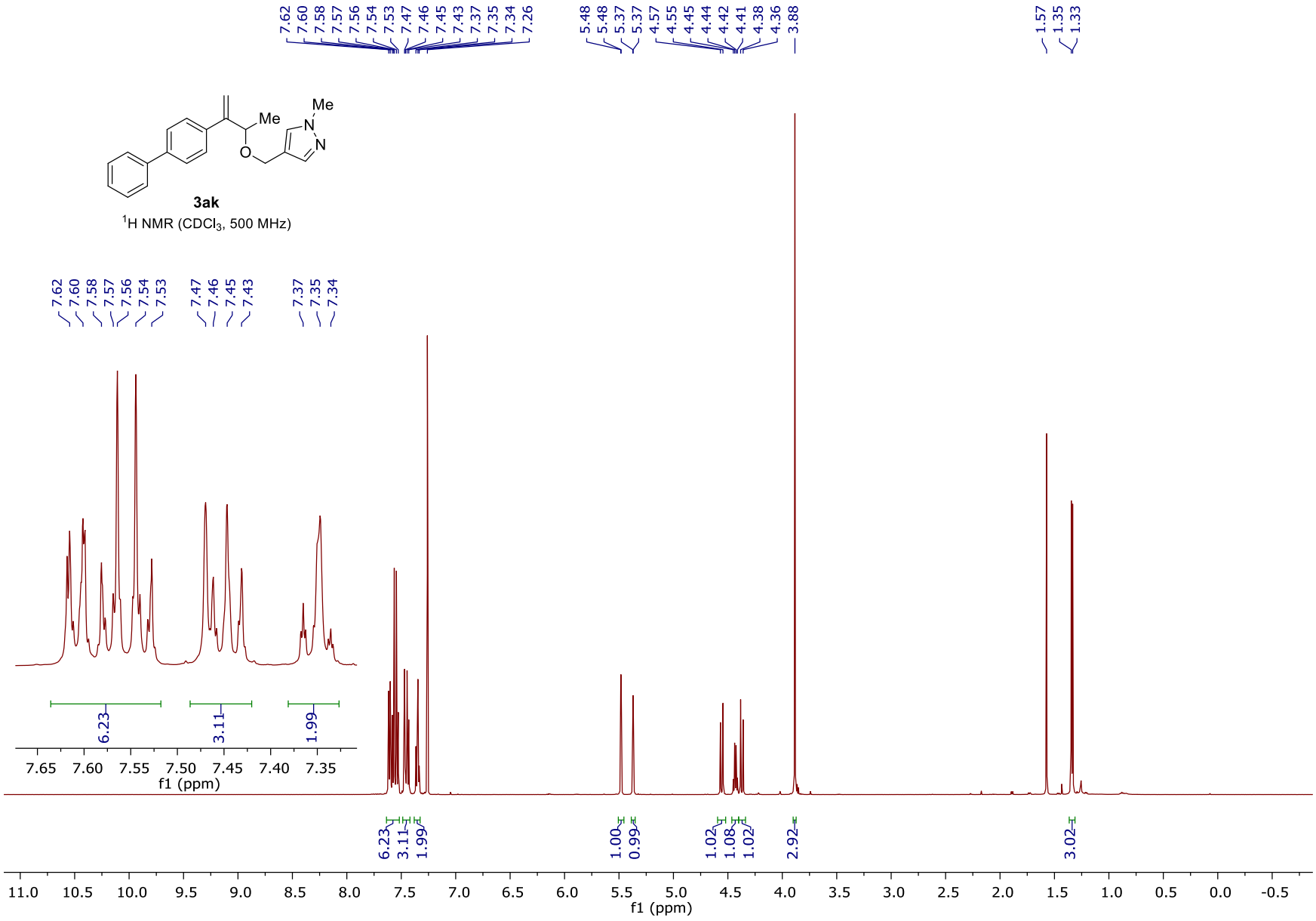

Me
O
N
3ah
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 130 MHz)
149.8
148.8
148.2
140.7
140.7
138.3
129.0
127.5
127.4
127.2
127.1
122.0
114.6
78.6
77.4
77.2
76.9
68.6
21.5
149.83
148.75
148.23
140.75
140.71
138.35
128.95
127.53
127.43
127.19
127.13
122.02
114.56
150 145 140 135 130 125 120 115
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

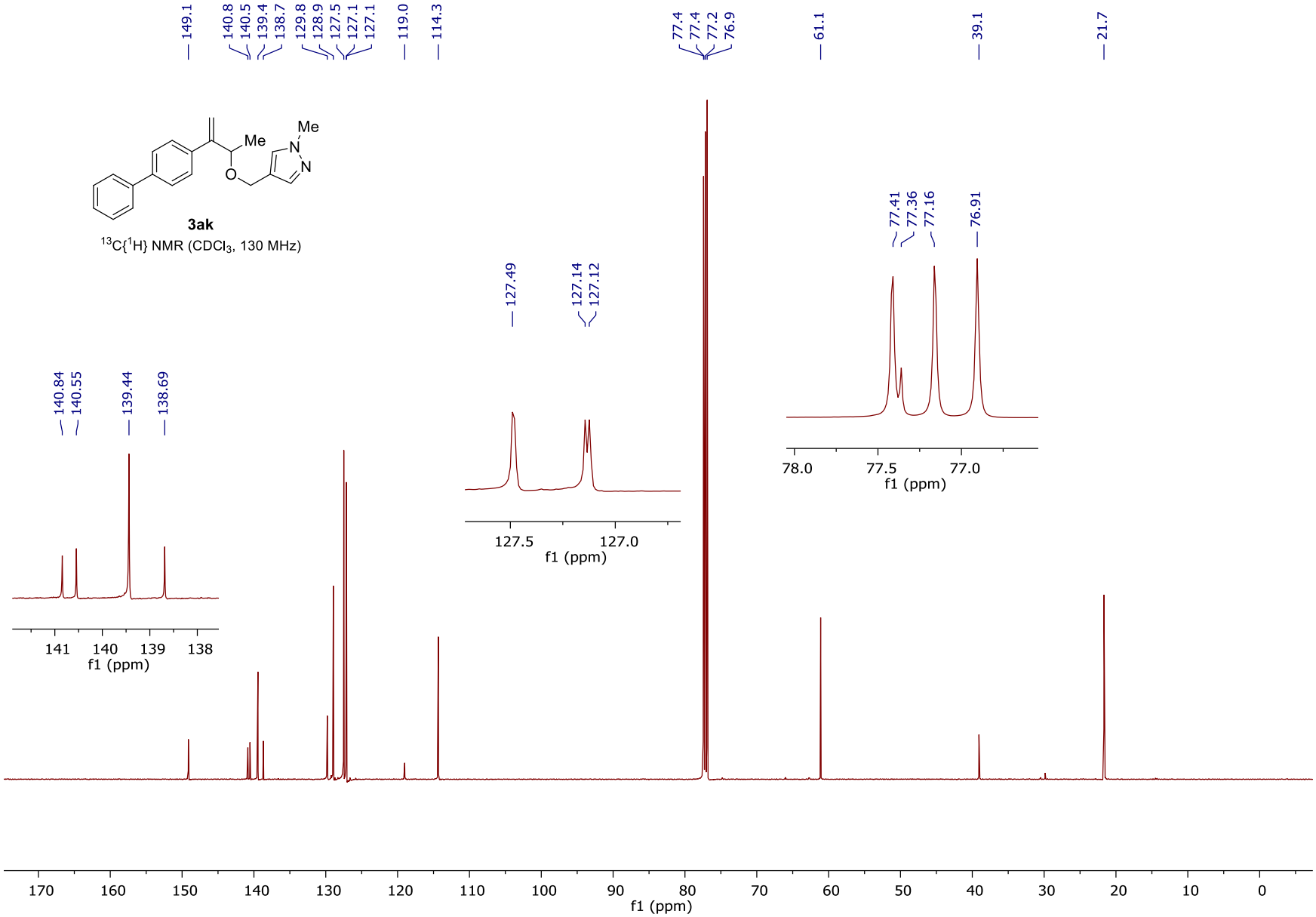

Me
NBoc
O
3ai
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

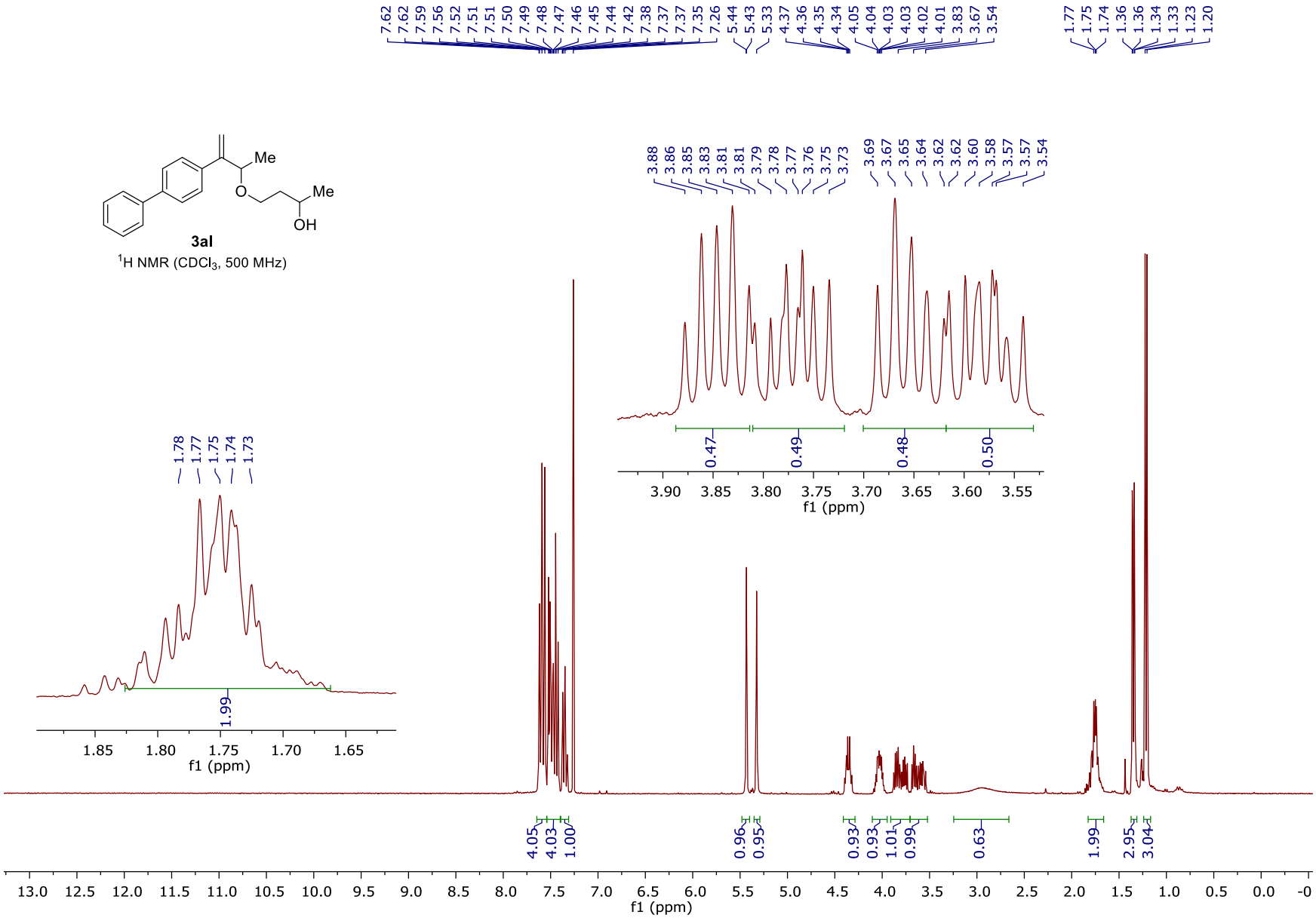

155.0
149.4
140.9
140.5
138.7
128.9
127.4
127.4
127.1
127.1
113.9
79.4
78.7
77.4
77.2
76.9
73.5
43.9
36.9
29.4
29.3
28.6
21.4
Me
NBoc
O
3ai
13C{1H} NMR (CDCl3, 130 MHz)
127.45
127.40
127.13
127.08
128.0
127.5
127.0
126.5
f1 (ppm)
29.42
29.34
29.6
29.2
f1 (ppm)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

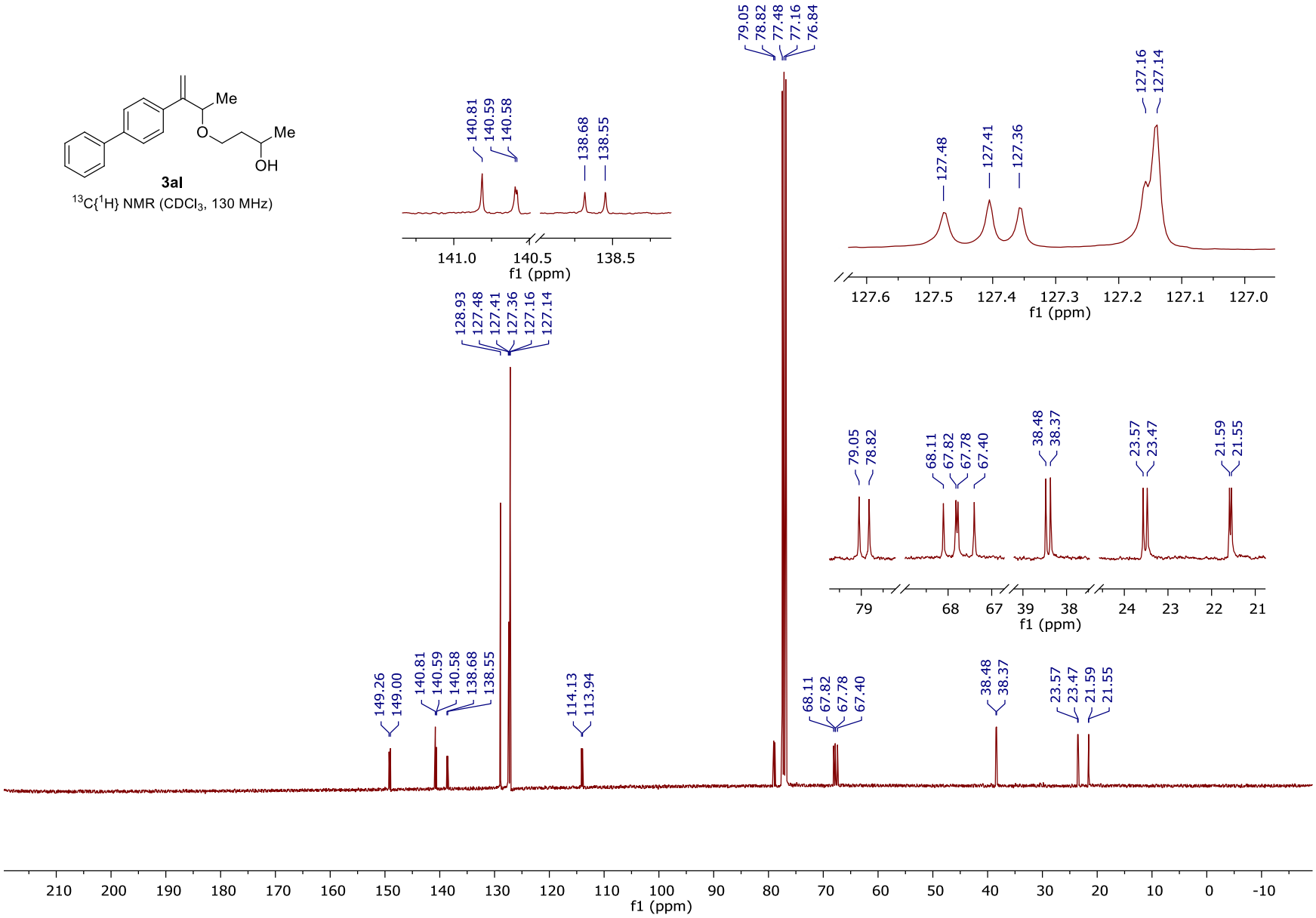

Me
O
Fe
3aj
1H NMR (CDCl3, 300 MHz)
7.63
7.60
7.56
7.53
7.47
7.45
7.42
7.37
7.35
7.33
7.26
5.48
5.48
5.36
4.42
4.40
4.28
4.23
4.19
4.15
1.54
1.30
1.28
1.26
6.06
2.00
1.00
0.98
0.98
2.00
9.67
2.96
f1 (ppm)


Me
O
Fe
3aj
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 130 MHz)
149.2
140.9
140.5
138.7
128.9
127.5
127.4
127.2
127.1
114.1
84.3
77.4
77.4
77.2
76.9
69.8
68.9
66.5
21.7
77.30
69.83
68.92
66.54
128.92
127.49
127.44
127.15
127.09
84.33
f1 (ppm)


7.62
7.60
7.58
7.57
7.56
7.54
7.53
7.47
7.46
7.45
7.43
7.37
7.35
7.34
7.26
5.48
5.48
5.37
5.37
4.57
4.55
4.45
4.44
4.42
4.41
4.38
4.36
3.88
1.57
1.35
1.33
Me
Me
N
N
O
3ak
1H NMR (CDCl3, 500 MHz)
6.23
3.11
1.99
7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
6.23
3.11
1.99
1.00
0.99
1.02
1.08
1.02
2.92
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


149.1
140.8
140.5
139.4
138.7
129.8
128.9
127.5
127.1
127.1
119.0
114.3
77.4
77.4
77.2
76.9
61.1
39.1
21.7
Me
Me
N
N
O
3ak
13C{1H} NMR (CDCl3, 130 MHz)
140.84
140.55
139.44
138.69
141
140
139
138
f1 (ppm)
127.49
127.14
127.12
127.5
127.0
f1 (ppm)
77.41
77.36
77.16
76.91
78.0
77.5
77.0
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
Me
OH
3al
1H NMR (CDCl3, 500 MHz)
f1 (ppm)


Me
O
Me
OH
3al
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 130 MHz)
79.05
78.82
77.48
77.16
76.84
140.81
140.59
140.58
138.68
138.55
127.16
127.14
127.48
127.41
127.36
128.93
127.48
127.41
127.36
127.16
127.14
79.05
78.82
68.11
67.82
67.78
67.40
38.48
38.37
23.57
23.47
21.59
21.55
149.26
149.00
140.81
140.59
140.58
138.68
138.55
114.13
113.94
68.11
67.82
67.78
67.40
38.48
38.37
23.57
23.47
21.59
21.55
f1 (ppm)

8. References

[1] Fiorito, D.; Folliet, S.; Liu, Y.; Mazet, C. A General Nickel-Catalyzed Kumada Vinylation for the Preparation of 2-Substituted 1,3-Dienes *ACS Catal.* **2018**, *8*, 1392.

[2] Wüstenberg, B.; Pfaltz, A. Homogeneous Hydrogenation of Tri- and Tetrasubstituted Olefins: Comparison of Iridium-Phospinooxazoline [Ir-PHOX] Complexes and Crabtree Catalysts with Hexafluorophosphate (PF_6) and Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr_F) as Counterions. *Adv. Synth. Catal.* **2008**, *350*, 174.