Supporting Information for

# Enamines from Terminal Epoxides and Hindered Lithium Amides

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## General Details

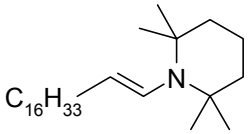
All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon. THF was distilled from benzophenone ketyl; TMP, benzene-$d_6$ and acetonitrile-$d_3$ from $CaH_2$; all other reagents were used as received unless stated otherwise. Column chromatography was carried out on Kieselgel 60 (40-63 μm). Silica was deactivated by stirring with neat $NEt_3$ for 12 h. Light petrol refers to the fraction of petroleum boiling between 30 ºC and 40 ºC. IR spectra were recorded as thin films, using a Perkin-Elmer 1750 FTIR spectrophotometer. Peak intensities are specified as strong (s), medium (m) or weak (w). $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ at 25 ºC, with Bruker DPX250, DPX400, DQX400 or AMX500 spectrometers unless otherwise stated. Chemical shifts are reported relative to $CDCl_3$ ($^1$H NMR 7.27; $^{13}$C NMR 77.0 (central signal of triplet)) unless stated otherwise. Coupling constants (*J*) are given in Hz, multiplicities are given as multiplet (m), singlet (s) (and where applicable are described as broad (b)), doublet (d), triplet (t), quartet (q) and septet (sept). Mass spectra were obtained using a Micromass GCT spectrometer or by the EPSRC National Mass Spectrometry Service Centre at the University of Swansea using a 900 XLT high resolution double focusing mass spectrometer with tandem Ion Trap.

Epoxides in Table 1 were either commercially available (1,2-Epoxyoctadecane (tech.) was recrystallized and 1,2-epoxypentane, 3-methyl-1,2-epoxybutane, 1,2-epoxy-9-decene, 1,2-epoxyhexane and 1,2,7,8-diepoxyoctane were distilled prior to use) or prepared according to: (a) Elings, J. A.; Downing, R. S.; Sheldon, R. A. *Eur. J. Org. Chem*. **1999**, 837–846 (entry 4); (b) Yang, L.; Weber, A. E.; Greenlee, W. J.; Patchett, A. A. *Tetrahedron Lett*. **1993**, *34*, 7035–7038 (entry 5); (c) Hodgson, D. M.; Reynolds, N. J.; Coote, S. J. *Tetrahedron Lett.* **2002**, *43*, 7895-7897 (entry 6); (d) 2,5,5-Trimethyl-2-(2-oxiranyl-ethyl)-[1.3]dioxane (entry 7) was synthesized from 5-hexen-2-one by a two-step

sequence: (i) $Me_2C(CH_2OH)_2$ (1.3 equiv.), benzene, Δ, 4 h, azeotrope (76%); (ii) *m*-CPBA (1.5 equiv.), $CH_2Cl_2$, $KHCO_3$ (0.5 M in $H_2O$), 16 h (38%); IR ($cm^{-1}$) 2982m, 2955s, 2968s, 1471m, 1457m, 1396m, 1373m, 1276m, 1250m, 1212m, 1191w, 1169w, 1123m, 1093s, 1040m, 1021m; $^1$H NMR (400 MHz) 3.54-3.37 (m, 4H, 2 ×OC*H*$_2$), 2.95-2.90 (m, 1H, OCH), 2.71 (dd, 1H, *J* = 5 and 5, OCH), 2.45 (dd, 1H, *J* = 5 and 3, OCH), 1.88-1.56 (m, 4H, C*H*$_2$C*H*$_2$), 1.33 (s, 3H, Me), 0.98 (s, 3H, C*Me*Me), 0.84 (s, 3H, CMe*Me*); $^{13}$C NMR (100 MHz) 98.4 ($O_2C$), 70.3 (2 × O*C*), 52.2 (O*C*H$_2$), 47.1 (O*C*H), 34.3 ($CH_2$), 29.8 (*C*Me$_2$), 26.5 (*C*H$_2$), 22.7 (C*Me*Me), 22.4 (CMe*Me*), 20.1 (Me); HRMS *m/z* (M + $H^+$) Found: 201.1493. $C_{11}H_{21}O_3$ requires 201.1490; (e) Rothberg, I.; Schneider, L.; Kirsch, S.; OFee, R. *J. Org. Chem*. **1982**, *47*, 2675-2676 (entry 8). *N*-(2-hydroxyoctadecyl)-TMP was prepared by ring opening of 1,2-epoxyoctadecane with TMP (3 equiv. $K_2CO_3$, *i*-PrOH, 100 °C (sealed tube), 16 h) in 6% yield. *N*-*tert*-Butylpinacoylamine[1] was prepared from pinacolone and *tert*-butylamine using the method described by Stowell and Padegimas in 34% yield.

**General procedure for the formation of enamines from terminal epoxides and LTMP:**

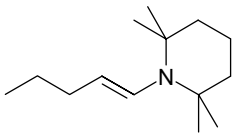
2,2,6,6-Tetramethyl-1-octadec-1-enylpiperidine **2a**




To a solution of 2,2,6,6-tetramethylpiperidine (0.50 cm³, 2.96 mmol) in THF (6 cm³) at 0 °C was added *n*-BuLi (1.6 mol $dm^{-3}$ in hexanes; 1.85 cm³, 2.96 mmol) dropwise. The solution was allowed to warm to 25 °C over 15 min. before a solution of 1,2-epoxyoctadecane (318 mg, 1.19 mmol) in THF (1.5 cm³) was added in one portion. The reaction mixture was stirred at 25 ºC for 1 h before being filtered through a pad of deactivated silica (5 cm × 5 cm). The pad was washed with 5 % $NEt_3$ in light petrol (250 $cm^3$). The solvent and amines were removed *in vacuo* (down to 0.1 mbar, 50 ºC) to give *enamine* **2a** (361 mg, 78%) as a glassy solid; IR ($cm^{-1}$) 2924s, 2853s, 1641w (C=C), 1465m, 1376w, 1382w, 1265w, 1246w, 1174w, 1131w, 1080w, 1033w; $^1$H NMR (500 MHz, $C_6D_6$) 5.79 (d, 1H, *J* = 14, NCH), 5.32 (dt, 1H, *J* = 14 and 7, =CH), 2.08 (dt, 2H, *J* = 7 and 7, =CHC*H*$_2$), 1.51-1.18 (m, 34H, 17 × $CH_2$), 1.13 (s, 12H, 2 × $NCMe_2$), 0.91 (t, 3H, *J* = 7, Me); $^{13}$C NMR (125 MHz, $C_6D_6$) 131.8 (NCH=), 126.2 (=*C*H), 53.7 (2 × *C*Me$_2$), 41.6 (2 ×

$CMe_2CH_2$), 32.4 (=$CHCH_2$), 32.1 ($CH_2$), 31.1 ($CH_2$), 30.9 ($CH_2$), 30.2-29.7 (12 × $CH_2$) 28.0 (2 × $NCMe_2$), 23.1 ($CH_2$), 18.1 ($CH_2$), 14.4 (Me). HRMS *m/z* ($M + H^+$) Found: 392.4254. $C_{27}H_{54}N$ requires 392.4251.

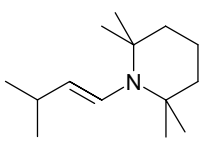
2,2,6,6-Tetramethyl-1-(pent-1-enyl)-piperidine **2b**



According to the general procedure, 1,2-epoxypentane (204 mg, 2.37 mmol) gave, following bulb-to-bulb distillation, *enamine* **2b** (371 mg, 75%) as a colorless oil; bp 60 °C / 0.06 mbar; IR ($cm^{-1}$) 2965s, 2928s, 2871m, 1662m (C=C), 1641m (C=C), 1463m, 1376m, 1362m, 1353m, 1265m, 1246w, 1174w, 1147w, 1131m, 1031w, 956s; $^1H$ NMR (400 MHz, $C_6D_6$) 5.78 (dt, 1H, *J* = 14 and 1, NCH), 5.30 (dt, 1H, *J* = 14 and 7, =CH), 2.01 (dt, 2 H, *J* = 7 and 7, =CHC*H*$_2$), 1.47-1.43 (m, 6H, 3 × ring $CH_2$), 1.38 (tq, 2H, *J* = 7 and 7, C*H*$_2$Me), 1.13 (s, 12H, 2 × $NCMe_2$), 0.91 (t, 3H, *J* = 7, $CH_2$*Me*); $^{13}C$ NMR (100 MHz, $C_6D_6$) 132.2 (NCH=), 126.0 (=CH), 53.9 (2 × *C*$Me_2$), 41.8 (2 × $CMe_2CH_2$), 33.4 (=$CHCH_2$), 28.2 (2 × $NCMe_2$), 24.2 ($CH_2$), 18.3 ($CH_2$), 14.2 (Me). HRMS *m/z* ($M + H^+$) Found: 210.2221. $C_{14}H_{28}N$ requires 210.2222.

Alternatively, to a solution of *N*-formyl-TMP (430 mg, 2.54 mmol) in $Et_2O$ (1 $cm^3$) at –15 °C was added *n*-BuMgCl (2.0 mol $dm^{-3}$ in THF; 1.00 $cm^3$, 2.00 mmol) dropwise. The solution was stirred at room temperature for 7 days. The solvent was then removed *in vacuo*, dry *n*-pentane (2 × 2.5 $cm^3$) was added and the supernatant liquid filtered (syringe filter) to give a clear solution. The solvent was removed *in vacuo* and the residue was purified by bulb-to-bulb distillation to give *enamine* **2b** (133 mg, 32%) as colorless oil. Data as above.

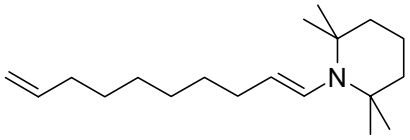
2,2,6,6-Tetramethyl-1-(3-methyl-but-1-enyl)-piperidine **2c**



According to the general procedure, 3-methyl-1,2-epoxybutane (204 mg, 2.37 mmol) gave, following removal of the solvent from the reaction mixture under a stream of argon and direct distillation of the residue, *enamine* **2c** (297 mg, 60%) as a colorless

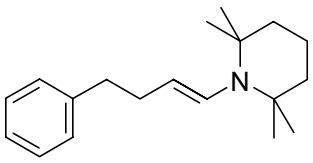
oil; bp 60 °C / 0.06 mbar; IR ($cm^{-1}$) 2964s, 2930s, 2869s, 1662w (C=C), 1641m (C=C), 1544w, 1465m, 1376m, 1362m, 1266m, 1246m, 1202w, 1174m, 1131m, 1066w, 1033m, 960m, 919w, 874w, 838w, 800w, 694w; $^1$H NMR (400 MHz, $C_6D_6$) 5.74(dd, 1H, *J* = 14 and 1, NCH), 5.26 (dd, 1H, *J* = 14 and 7, =CH), 2.30 (dsept, 1H, *J* = 14 and 7, CH), 1.50-1.35 (m, 6H, 3 × ring $CH_2$), 1.11 (s, 12H, 2 × NC*Me*$_2$), 1.02 (d, 6H, *J* = 7, CH*Me*$_2$); $^{13}$C NMR (100 MHz, $C_6D_6$) 134.0 (NCH=), 129.5 (=CH), 53.9 (2 × *C*Me$_2$), 41.8 (2 × CMe$_2$*C*H$_2$), 30.7 (=CH*C*), 28.2 (2 × NC*Me*$_2$), 24.0 (CH*Me*$_2$), 18.3 ($CH_2$); HRMS *m/z* ($M + H^+$) Found: 210.2220. $C_{14}H_{28}N$ requires 210.2222.

1-Deca-1,9-dienyl-2,2,6,6-tetramethylpiperidine **2d**



According to the general procedure, 1,2-epoxy-9-decene (154 mg, 1.00 mmol) gave *enamine* **2d** as a colorless oil (230 mg, 83%); IR ($cm^{-1}$) 3076w, 2966s, 2927s, 2854s, 1661m (C=C), 1641m (C=C), 1463m, 1376m, 1362m, 1266m, 1246m, 1201w, 1174m, 1131m, 1080w, 1033w; $^1$H NMR (500 MHz, $C_6D_6$) 5.79-5.73 (m, 2H, $CH_2$=C*H* and NCH), 5.28 (dt, 1H, *J* = 14 and 7, NCH=C*H*), 5.03-4.95 (m, 2H, =$CH_2$), 2.04-1.97 (m, 4H, 2 × =CHC*H*$_2$), 1.46-1.26 (m, 14H, 7 × $CH_2$), 1.11 (s, 12H, 2 × CMe$_2$); $^{13}$C NMR (125 MHz, $C_6D_6$) 139.6 (=$CH_2$), 132.1 (NCH), 126.5 (NCH=C*H*), 114.9 (C*H*=$CH_2$), 54.1 (2 ×*C*Me$_2$), 41.9 (2 ×CMe$_2$*C*H$_2$), 34.6 ($CH_2$), 31.4 ($CH_2$), 31.2 ($CH_2$), 29.9 ($CH_2$), 29.7 (2 × $CH_2$), 28.4 (2 × C*Me*$_2$), 18.2 (ring $CH_2$); HRMS *m/z* ($M + H^+$) Found: 278.2848. $C_{19}H_{36}N$ requires 278.2848.

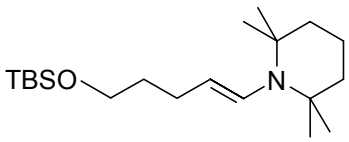
2,2,6,6-Tetramethyl-1-(4-phenyl-1-but-1-enyl)-piperidine **2e**



According to the general procedure, 1,2-epoxy-4-phenylbutane (351 mg, 2.37 mmol) gave *enamine* **2e** as a colorless oil (463 mg, 72%); IR ($cm^{-1}$) 3027m, 2966s, 2928s, 2869m, 1660w (C=C), 1641m (C=C), 1604w, 1496m, 1453m, 1376m, 1382m, 1266m, 1246m, 1200w, 1174m, 1131m, 1030w, 955m; $^1$H NMR (400 MHz, $C_6D_6$) 7.24-7.05 (m, 5H, 5 × ArH), 5.74 (dt, 1H, *J* = 14 and 1, NCH), 5.18 (dt, 1H, *J* = 14 and 7, =CH), 2.67-2.58 (m, 2H, PhC*H*$_2$), 2.32 (dt, 2H, *J* = 7 and 1, =CHC*H*$_2$), 1.49-1.38 (m, 6H, 3 × ring $CH_2$), 1.06

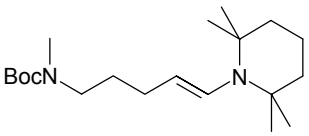
(s, 12H, 2 × $CMe_2$); $^{13}C$ NMR (100 MHz, $C_6D_6$) 142.5 (ArC), 132.6 (N*C*H), 129.0 (ArC-H), 128.7(ArC-H), 126.2 (NCH=*C*H), 123.4 (ArC-H), 53.9 (2 × *C*$Me_2$), 41.7 (2 × $CMe_2$*C*$H_2$), 37.5 and 33.3 (Ph*C*$H_2$ and =CH*C*$H_2$), 28.0 (2 × C*Me*$_2$), 18.2 ($CH_2$); HRMS *m/z* ($M + H^+$) Found: 272.2383. $C_{19}H_{30}N$ requires 272.2378.

1-[5-(*tert*-Butyldimethylsilanyloxy)-pent-1-enyl]-2,2,6,6-tetramethylpiperidine **2f**




According to the general procedure, 1-*tert*-butyldimethylsilyoxy-4,5-epoxypentane (513 mg, 2.37 mmol) gave *enamine* **2f** as a colorless oil (620 mg, 77%), IR ($cm^{-1}$) 2978s, 2857s, 1731w, 1661m (C=C), 1641m (C=C), 1471s, 1376s, 1362w, 1255s, 1175m, 1131s, 1099 (C–O), 1035m, 1006m; $^1H$ NMR (500 MHz, $C_6D_6$) 5.79 (dt, 1H, *J* = 14 and 1, NCH), 5.24 (dt, 1H, *J* = 14 and 7, =C*H*), 3.60 (t, 2H, *J* = 7, $OCH_2$), 2.12 (dt, 2H, *J* = 7 and 7, =CHC*H*$_2$), 1.64-1.41 (m, 8H, 4 × $CH_2$), 1.10 (s, 12H, 2 × $CMe_2$), 0.96 (s, 9H, $CMe_3$), 0.01 (s, 6H, $SiMe_2$); $^{13}C$ NMR (125 MHz, $C_6D_6$) 132.1 (NCH), 124.8 (=CH), 62.8 ($OCH_2$), 53.7 (2 ×*C*$Me_2$), 41.6 (2 × $CMe_2$*C*$H_2$), 34.0 (=CH*C*$H_2$), 28.0 (2 × C*Me*$_2$), 27.3 (chain $CH_2$), 26.2 (C*Me*$_3$), 18.6 (ring $CH_2$), 18.1 (Si*C*$Me_3$), –5.0 (SiMe), –5.1 (SiMe); HRMS *m/z* ($M + H^+$) Found: 340.3035. $C_{20}H_{42}NOSi$ requires 340.3036.

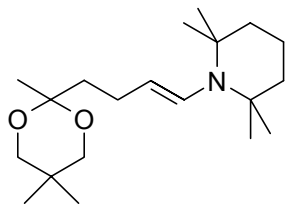
1-(5-*N*-Boc-*N*-methylamino-pent-1-enyl)-2,2,6,6-tetramethylpiperidine **2g**




According to the general procedure, 5-(*N*-Boc-*N*-methylamino)-1,2-epoxypentane (210 mg, 0.98 mmol) gave *enamine* **2g** as a light yellow oil (209 mg, 63%); IR ($cm^{-1}$) 3380w, 2927s, 1693s (C=O), 1640m (C=C), 1452s, 1391s, 1375s, 1364s, 1305s, 1265s, 1246s, 1221s, 1173s, 1094m, 1080w, 1061m, 1035m, 955s; $^1H$ NMR (250 MHz, $C_6D_6$, 60 °C) 5.77 (dt, 1H, *J* = 14 and 1, NC*H*), 5.17 (dt, 1H, *J* = 14 and 7, =CH), 3.15 (bt, 2H, *J* = 7, $NCH_2$), 2.67 (bs, 3H, NMe), 1.95 (dt, 2H, *J* = 7 and 7, =CHC*H*$_2$), 1.67-1.37 (m, 17H, 4 × C*H*$_2$ and C*Me*$_3$), 1.10 (s, 12H, 2 × $CMe_2$); $^{13}C$ NMR (62.5 MHz, $C_6D_6$, 60 °C) 155.6 (C=O),

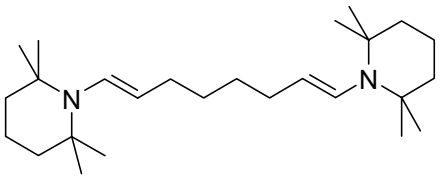
132.4 (N*C*H), 123.4 (=*C*H), 78.7 (O*C*Me$_3$), 54.0 (2 ×*C*Me$_2$), 41.8, 34.2, 29.3, 28.7, 28.7, 28.5, 28.1, 18.1 (ring CH$_2$); HRMS *m/z* (M + H$^+$) Found: 339.3012. $C_{20}H_{39}N_2O_2$ requires 339.3011.

2,2,6,6-Tetramethyl-1-[4-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-but-1-enyl]-piperidine **2h**



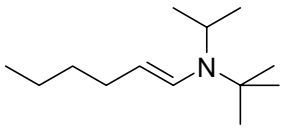
According to the general procedure, 2,5,5-trimethyl-2-(2-oxiranyl-ethyl)-[1.3]dioxane (238 mg, 1.19 mmol) gave *enamine* **2h** as a colorless oil (292 mg, 76%); IR (cm$^{-1}$) 2928s, 2867s, 2361w, 2341w, 1729w, 1661w (C=C), 1641m (C=C), 1453m, 1394m, 1375s, 1362s, 1265s, 1247s, 1212s, 1190m, 1175m, 1130s, 1091s, 1042m, 1022m; $^1$H NMR (250 MHz, $C_6D_6$) 5.81 (dt, 1H, *J* = 14 and 1, NC*H*), 5.34 (dt, 1H, *J* = 14 and 7, NCH=C*H*), 3.40-3.25(m, 4H, 2 × OCH$_2$), 2.47-2.29 (m, 2H, O$_2$CC*H*$_2$), 1.96-1.82 (m, 2H, =CHC*H*$_2$), 1.51-1.33 (m, 6H, 3 × C*H*$_2$), 1.30 (s, 3H, *Me*), 1.08 (s, 12H, 2 ×C*Me*$_2$), 0.91 (s, 3H, *Me*), 0.60 (s, 3H, Me); $^{13}$C NMR (62.5 MHz, $C_6D_6$) 131.7 (N*C*H), 126.2 (NCH=*C*H), 98.9 (O$_2$C), 70.5 (2 × OCH$_2$), 53.8 (2 × *C*Me$_2$), 41.7 (2 × NCMe$_2$*C*H$_2$), 40.6, 30.0, 28.1 (2 × NC*Me*$_2$), 25.4, 23.1, 22.6, 20.2, 18.2; HRMS *m/z* (M + H$^+$) Found: 324.2893. $C_{20}H_{38}NO_2$ requires 324.2903.

1,8-Bis-(2,2,6,6-tetramethyl-piperidin-1-yl)-1,7-octadiene **2i**



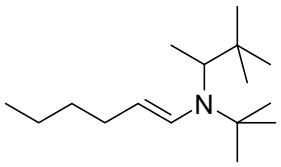
According to the general procedure, except employing 5.0 equiv. of LTMP, 1,2,7,8-diepoxyoctane (337 mg, 2.37 mmol) gave *enamine* **2j** as a colorless oil (634 mg, 69%); IR (cm$^{-1}$) 2965s, 2926s, 1661m (C=C), 1641m (C=C), 1461m, 1376s, 1362s, 1353m, 1265s, 1246s, 1201w, 1175s, 1131s, 1033m, 955s; $^1$H NMR (400 MHz, $C_6D_6$) 5.77(dt, 2H, *J* = 14 and 1, 2 × NCH), 5.31 (dt, 2H, *J* = 14 and 7, 2 × NCH=C*H*), 2.17-1.99 (m, 4H, 2 × =CHC*H*$_2$), 1.51-1.38 (m, 16H, 6 × ring CH$_2$ and 2 × chain CH$_2$), 1.12 (24H, s, 4 × C*Me*$_2$); $^{13}$C NMR (100 MHz, $C_6D_6$) 131.0 (2 × NCH=), 126.6 (2 × NCH=*C*H), 53.8 (4 × *C*Me$_2$), 41.6 (4 × CMe$_2$*C*H$_2$), 30.9 and 30.4 (2 × chain CH$_2$ and 2 × =CH*C*), 29.0 (4 × C*Me*$_2$), 18.3 (2 × ring CH$_2$); HRMS *m/z* (M + H$^+$) Found: 389.3884. $C_{26}H_{49}N_2$ requires 389.3896.

*tert*-Butyl-hex-1-enyl-isopropylamine **3a**



To a solution of *N-tert*-butylisopropylamine (1.50 cm³, 9.46 mmol) in THF (15 cm³) at –78 °C was added *n*-BuLi (1.6 mol $dm^{-3}$ in hexanes; 5.91 cm³, 9.46 mmol) dropwise. The solution was allowed to warm to 25 °C over 15 min. before a solution of 1,2-epoxyhexane (378 mg, 3.78 mmol) in THF (5 cm³) was added in one portion. The reaction was stirred at room temperature for 1 h before being filtered through a pad of celite (5 $cm^2$ × 5 cm). The pad was washed with $Et_2O$ (250 $cm^3$). The solvent was removed *in vacuo,* and the residue purified by bulb-to-bulb distillation to give *enamine* **3a** (314 mg, 42%) as a colourless oil; bp 90 °C / 0.1 mbar; IR ($cm^{-1}$) 2970s, 2925s, 2873s, 1645s (C=C), 1465w, 1377m, 1363m, 1302m, 1220m; $^1$H NMR (400 MHz) 5.93 (dt, 1H, *J* = 14 and 1, NCH=), 4.48 (dt, 1H, *J* = 14 and 7, =CH), 3.56 (dsept, 1H, *J* = 14 and 1, C*H*$Me_2$), 1.99-1.93 (m, 2H, =CHC$H_2$), 1.35-1.30 (m, 4H, 2 × C$H_2$), 1.23-1.18 (m, 15H, C$Me_3$ and C$Me_2$), 0.91 (t, 3H, *J* = 7, Me); $^{13}$C NMR (100 MHz) 129.9 (NCH=), 105.3 (=*C*H), 55.5 (NC), 46.1 (NC), 33.8 ($CH_2$), 31.5 ($CH_2$), 29.0 (C$Me_3$), 22.1 ($CH_2$), 20.9 (C$Me_2$), 14.0 (Me); HRMS *m/z* ($M + H^+$) Found: 198.2228. $C_{13}H_{28}N$ requires 198.2222.

*tert*-Butyl-(hex-1-enyl)-(1,2,2-trimethyl-propyl)-amine **3b**

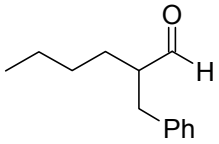


To a solution of *N-tert*-butylpinacoylamine (1.00 g, 6.37 mmol) in THF (15 cm³) at –78 °C was added *n*-BuLi (1.6 mol $dm^{-3}$ in hexanes; 3.98 cm³, 6.37 mmol) dropwise. The solution was allowed to warm to 25 °C over 15 min. before a solution of 1,2-epoxyhexane (255 mg, 2.55 mmol) in THF (5 cm³) was added in one portion. The reaction was stirred at room temperature for 1 h before being filtered through a pad (5 $cm^2$ × 5 cm) of celite. The pad was washed with $Et_2O$ (250 $cm^3$). The solvent was removed *in vacuo,* and the residue purified by bulb-to-bulb distillation to give *enamine* **3a** (353 mg, 58%) as a colourless oil; bp 125 °C / 0.03 mbar; IR ($cm^{-1}$) 2957s, 2924s, 1646 (C=C), 1457m, 1370m, 1259w, 1195w; $^1$H NMR (500 MHz, $C_6D_6$) 5.83 (dt, 1H, *J* = 14 and 1, NCH=), 4.94 (dt, 1H, *J* = 14 and 7, =CH), 2.92 (q, 1H, *J* = 7, C*H*Me), 2.05 (dt, 2H, *J* = 7 and 7, =CHC$H_2$), 1.42-1.35 (m, 4H, 2 × $CH_2$), 1.15 (s, 9H, $NCMe_3$), 1.05 (d,

3H, $J$ = 7, CH*Me*), 0.96 (s, 9H, CHC*Me*$_3$), 0.91(t, 3H, $J$ = 7, Me); $^{13}$C NMR 133.0 (NCH=), 117.3 (=CH), 58.6 (NCH), 55.5 (NC), 36.3 (CH*C*Me$_3$), 33.5 (=CH*C*H$_2$), 31.5 (CH$_2$), 29.3 (CMe$_3$), 28.6 (CMe$_3$), 22.7 (CH$_2$), 14.2 (Me), 14.2 (Me); HRMS *m/z* (M + H$^+$) Found: 240.2692. $C_{16}H_{34}N$ requires 240.2691.

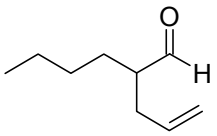
**General procedure for enamine alkylation:**

2-Benzylhexanal[2] **4a**



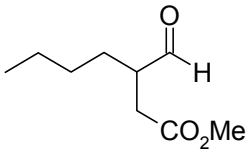

A solution of enamine **3a** (227 mg, 1.15 mmol) and BnBr (273 μL, 2.30 mmol) in MeCN-d$_3$ (1.0 cm³) was allowed to stand (with occasional shaking) at 15 °C in a NMR tube fitted with a PTFE valve,[3] until consumption of enamine **3a** was judged complete by $^1$H NMR spectroscopy (18 h). Acidic buffer solution (made up of AcOH (0.5 g), AcONa (0.5g) and water (1.0 g)) (0.5 cm³) was added and the mixture was allowed to stand at the same temperature as before, for 1 h with occasional shaking before being separated between $H_2O$ (10 cm³) and $Et_2O$ (10 cm³). The aqueous phase was washed with $Et_2O$ (10 cm³) and the combined organic layers were washed with brine (20 cm³), dried ($MgSO_4$), filtered and the solvent removed *in vacuo.* Purification by column chromatography ($SiO_2$, 5% $Et_2O$/light petrol) gave 2-benzylhexanal **4a** (217 mg, quant.) as a colorless oil; $R_f$ 0.26 (5% $Et_2O$/light petrol); IR (cm$^{-1}$) 3086w, 3063w, 3028m, 2957s, 2931s, 2859s, 2711m, 2360w, 2340w, 1725s (C=O), 1604w, 1496m, 1466m, 1454s, 1392w, 1379w, 1030w; $^1$H NMR (400 MHz) 9.67 (d, 1H, $J$ = 3, CHO), 7.33-7.26 (m, 2H, 2 × ArC-H), 7.25-7.15 (m, 3H, 3 × ArC-H), 2.99 and 2.73 (AB-part of ABX, 2H, $J_{AX}$ = 7, $J_{BX}$ = 7, $J_{AB}$ = 14, C*H*$_2$Ph), 2.67-2.58 (m, 1H, C*H*CHO), 1.72-1.22 (m, 6H, (C*H*$_2$)$_3$Me), 0.89 (t, 3H, $J$ = 7, Me); $^{13}$C NMR (100 MHz) 204.8 (CHO), 138.9 (ArC), 129.0 (2 × ArC-H), 128.5 (2 × ArC-H), 126.3 (ArC-H) 53.4 (*C*HCHO), 35.0 (*C*H$_2$Ph), 29.1 (CH$_2$), 28.3 (CH$_2$) 22.7 (CH$_2$), 13.8 (Me).

2-Allylhexanal[4] **4b**



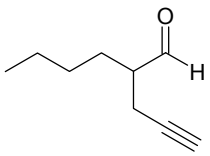
According to the general procedure, a solution of enamine **3a** (219 mg, 1.11 mmol) and allyl bromide (192 μL, 2.22 mmol) gave 2-allylhexanal **4b** as a colorless oil (149mg, 96%); $R_f$ 0.23 (5% $Et_2O$/light petrol); IR ($cm^{-1}$) 3080w, 2959s, 2931s, 2861m, 2708w, 1728s (C=O), 1642w, 1457w, 1440w; $^1H$ NMR (400 MHz) 9.61 (d, 1H, $J$ = 3, CHO), 5.79-5.68 (m, 1H, =CH), 5.10-5.03 (m, 2H, $=CH_2$), 2.43-2.31 (m, 2H, $=CHCH_2$), 2.28-2.18 (m, 1H, C*H*CHO), 1.69-1.24 (m, 6H, $(CH_2)_3Me$), 0.91 (t, 3H, $J$ = 7, Me); $^{13}C$ NMR (100 MHz) 204.9 (CHO), 135.0 (=CH), 117.0 ($=CH_2$), 51.2 (*C*HCHO), 33.0 (=CH*C*H2), 29.0 ($CH_2$), 28.0 ($CH_2$), 22.7 ($CH_2$), 13.9 (Me).

Methyl-3-formylheptanoate[5] **4c**



According to the general procedure, a solution of enamine **3a** (212 mg, 1.07 mmol) and α-bromo methyl acetate (198 μL, 2.14 mmol) at 15 °C for 16 h gave methyl-3-formylheptanoate **4c** (167mg, 91%) as a colorless oil; $R_f$ 0.20 (15% $Et_2O$/light petrol); IR ($cm^{-1}$) 2957s, 2233s, 2862s, 2722w, 1738bs (C=O), 1460m, 1438s, 1414m, 1394m, 1365m, 1206s, 1174s, 1111w, 1018m; $^1H$ NMR (400 MHz) 9.70 (d, 1H, $J$ = 1, C*H*O), 3.67 (s, 3H, OMe), 2.86-2.77 (m, 1H, C*H*CHO), 2.69 and 2.39 (AB-part of ABX, 2H, $J_{AX}$ = 5, $J_{BX}$ = 8, $J_{AB}$ = 16, $CH_2CO_2$), 1.79-1.66 (m, 1H, C*H*(H)CH), 1.53-1.40 (m, 1H, CH(*H*)CH), 1.39-1.25 (m, 4H, $(CH_2)_2Me$), 0.89 (t, 3H, $J$ = 7, Me); $^{13}C$ NMR (100 MHz) 202.9 (CHO), 172.4 ($CO_2$), 51.8 (*C*HCHO), 47.6 ($CH_2CO_2Me$), 32.7 ($CH_2$), 28.8 ($CH_2$), 28.2 ($CH_2$), 22.6 ($CH_2$), 13.8 (Me).

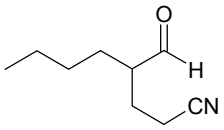
2-Prop-2-ynylhexanal[6] **4d**



According to the general procedure, a solution of enamine **3a** (140 mg, 0.71 mmol) and propargyl bromide (80% in toluene) (157 μL, 1.42 mmol) at 15 °C for 15 h gave 2-prop-2-ynyl-hexanal **4d** (99 mg, quant.) as a colorless oil; $R_f$ 0.15 (1% $Et_2O$/light petrol); IR ($cm^{-1}$) 3294m (≡CH), 2959m, 2933m, 2861m, 2728w, 2360w, 2341w, 2146w (C≡C), 1727s (C=O), 1467w, 1380w; $^1H$ NMR (400 MHz) 9.68 (d, 1H, $J$ = 1, CHO), 2.52-2.36 (m, 3H, C*H*CHO and

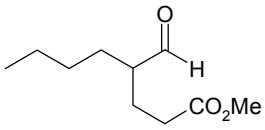
C$H_2$C≡CH), 2.01-1.98 (t, 1H, *J* = 3, C≡CH), 1.84-1.71 (m, 1H, C*H*(H)CH), 1.69-1.56 (m, 1H, CH(*H*)CH), 1.40-1.26 (m, 4H, (C$H_2$)$_2$Me), 0.90 (t, 3H, *J* = 7, Me); $^{13}$C NMR (100 MHz) 203.2 (CHO), 80.9 (*C*≡CH), 70.2 (C≡*C*H), 50.0 (C*H*CHO), 28.6 ($CH_2$), 27.6 (*C*$H_2$C≡), 22.6 ($CH_2$), 17.7 ($CH_2$), 13.8 (Me).

4-Formyl-octanenitrile **4e**



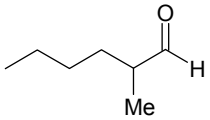

According to the general procedure, a solution of enamine **3a** (239 mg, 1.21 mmol) and acrylonitrile (160 μL, 2.42 mmol) at 82 °C for 19 h gave *4-formyl-octanenitrile* **4e** (169 mg, 91 %) as a colorless oil; $R_f$ 0.32 (30% $Et_2O$/light petrol); IR (cm$^{-1}$) 2958s, 2933s, 2861s, 2723m (*C*HO), 2246m (C≡N), 1723s (C=O), 1457m, 1428m,1379w, 1139w; $^1$H NMR (400 MHz) 9.64 (d, 1H, *J* = 1, CHO), 2.52-2.32 (m, 3H, C*H*CHO and $CH_2$C≡N), 2.07-1.95 (m, 1H, 1 of (C$H_2$)$_2$CH) 1.79-1.65 (m, 2H, 2 of (C$H_2$)$_2$CH), 1.56-1.44 (m, 1H, 1 of (C$H_2$)$_2$CH), 1.39-1.25 (m, 4H, (C$H_2$)$_2$Me), 0.90 (t, 3H, *J* = 7, Me); $^{13}$C NMR (100 MHz) 203.1 (CHO), 119.1 (CN), 50.1 (*C*HCHO), 28.7 ($CH_2$), 28.2 ($CH_2$), 23.8 ($CH_2$), 22.6 ($CH_2$), 15.1 (*C*$H_2$CN), 13.7 (Me); HRMS *m/z* (M + $NH^+$) Found: 171.1504. $C_9H_{19}N_2O$ requires 171.1497.

Methyl-4-formyloctanoate **4f**



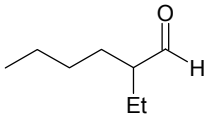

According to the general procedure, a solution of enamine **3a** (210 mg, 1.06 mmol) and methyl acrylate (192 μL, 2.12 mmol) at 82 °C for 22 h gave *methyl-4-formyloctanoate* **4f** (139 mg, 70%) as a colorless oil; $R_f$ 0.24 (15% $Et_2O$/light petrol); IR (cm$^{-1}$) 2986s, 2932s, 2861s, 2716m (CHO), 1738s (C=O), 1437s, 1375m, 1198s, 1171s, 1115w, 1011w; $^1$H NMR (400 MHz) 9.56 (d, 1H, *J* = 3, CHO), 3.63 (s, 3H, OMe), 2.38-2.22 (3H, m, C*H*CHO and C$H_2CO_2$), 1.99-1.18 (m, 8H, 4 × $CH_2$), 0.86 (t, 3H, *J* = 7, Me); $^{13}$C NMR (100 MHz) 204.3 (CHO), 173.4 ($CO_2$), 51.6 (OMe), 51.0 (*C*HCHO), 31.3 ($CH_2$), 28.9 ($CH_2$), 28.4 ($CH_2$), 23.5 ($CH_2$), 22.6 ($CH_2$), 13.8 (Me); HRMS *m/z* (M + $NH_4^+$) Found: 204.1599. $C_{10}H_{22}NO_3$ requires 204.1600.

2-Methylhexanal[7] **4g**



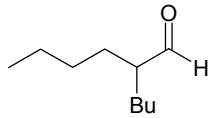

According to the general procedure, a solution of enamine **3a** (227 mg, 1.15 mmol) and MeI (143 μL, 2.30 mmol) at 15 °C for 16 h gave 2-methylhexanal **4g** as a colourless oil (113mg, 86%); $R_f$ 0.34 (5% $Et_2O$/light petrol); IR ($cm^{-1}$) 2960s, 2932s, 2860m, 2706w, 2360w, 1728s (C=O), 1460m, 1379w; $^1$H NMR (400 MHz) 9.61 (d, 1H, *J* = 2, CHO), 2.37-2.28 (m, 1H, C*H*Me), 1.75-1.66 (m, 1H, C*H*(H)*n*-Pr), 1.43-1.23 (m, 5H, (C$H_2$)$_2$Me and CH(*H*)*n*-Pr), 1.08 (d, 3H, *J* = 7, CH*Me*), 0.90 (t, 3H, *J* = 7, Me); $^{13}$C NMR (100 MHz) 205.4 (CHO), 46.3 (*C*HMe), 30.2 ($CH_2$), 29.1 ($CH_2$), 22.7 ($CH_2$), 13.9 (Me), 13.3 (Me).

2-Ethylhexanal[3] **4h**




According to the general procedure, a solution of enamine **3a** (204 mg, 1.03 mmol) and EtI (165 μL, 2.06 mmol) at 50 °C for 18 h gave 2-ethylhexanal **4h** (131 mg, quant.) as a colorless oil; $R_f$ 0.24 (5% $Et_2O$/light petrol); IR ($cm^{-1}$) 2961s, 2932s, 2874m, 2861m, 2703w, 1727s (C=O), 1461m, 1381m; $^1$H NMR (400 MHz) 9.55 (d, 1H, *J* = 3, CHO), 2.21-2.11 (m, 1H, C*H*Et), 1.70-1.38 (m, 4H, 2 × $CH_2$), 1.37-1.19 (m, 4H, 2 × $CH_2$), 0.93-0.86 (m, 6H, 2 × Me); $^{13}$C NMR (100 MHz) 205.7 (CHO), 53.4 (*C*HEt), 29.1 ($CH_2$), 28.1 ($CH_2$) 22.7 ($CH_2$), 21.8 ($CH_2$), 13.8 (Me), 11.4 (Me).

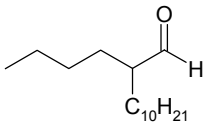
2-n-Butylhexanal[3] **4i**




According to the general procedure, a solution of enamine **3a** (144 mg, 0.73 mmol) and n-BuI (166 μL, 1.46 mmol) at 75 °C for 23 h gave 2-n-butylhexanal **4i** (110 mg, 97%.) as a colorless oil; $R_f$ 0.21 (1% $Et_2O$/light petrol); IR ($cm^{-1}$) 2958s, 2931s, 2873s, 2860s, 2693w, 1727s (C=O), 1467m, 1379w; $^1$H NMR (400 MHz) 9.54 (d, 1H, *J* = 3, CHO), 2.26-2.16 (m, 1H, C*H*Bu$_2$), 1.66-1.55 (m, 2H, 2 × C*H*(H)*n*-Pr), 1.48-1.37 (m, 2H, 2 × CH(*H*)*n*-Pr), 1.36-1.19 (m, 8H, 2 × (C$H_2$)$_2$Me), 0.88 (t, 6H, *J* = 7, 2 × Me); $^{13}$C NMR (100 MHz) 205.6 (CHO), 51.9 (*C*HBu$_2$), 29.2 (2 × $CH_2$), 28.6 (2 × $CH_2$) 22.7 (2 × $CH_2$), 13.8 (2 × Me).

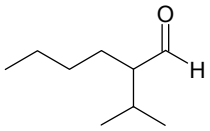
Similarly, a solution of enamine **3b** (119 mg, 0.50 mmol) and *n*-BuI (113 μL, 1.00 mmol) at 82 °C for 96 h gave 2-*n*-butylhexanal **4i** (65 mg, 84%) as a colorless oil; data as above.

2-Butyldodecanal **4j**




According to the general procedure (except that the reaction was performed in a sealed tube and vigorously stirred), a solution of enamine **3a** (212 mg, 1.07 mmol) and 1-iododecane (458 μL, 2.14 mmol) at 82 °C for 22 h gave *2-n-butyldodecanal* **4j** as a colorless oil (244 mg, 95%); $R_f$ 0.29 (2% $Et_2O$/light petrol); IR ($cm^{-1}$) 3434w, 2926s, 2855s, 2692m (CHO), 1728s (C=O), 1466s, 1378m, 1239m, 1143w, 1016w; $^1$H NMR (400 MHz) 9.54 (d, 1H, $J$ = 3, CHO), 2.26-2.16 (m, 1H, C*H*CHO), 1.67-1.16 (m, 24H, 12 × $CH_2$), 0.92-0.83 (m, 6H, 2 × Me); $^{13}$C NMR (100 MHz) 205.7 (CHO), 51.9 (*C*HCHO), 31.9 ($CH_2$), 29.7 ($CH_2$), 29.6 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.2 ($CH_2$), 28.9 ($CH_2$), 28.6 ($CH_2$), 27.0 ($CH_2$), 22.7 ($CH_2$), 22.6 ($CH_2$), 14.0 (Me), 13.8 (Me); HRMS *m/z* ($M + NH_4^+$) Found: 258.2801. $C_{16}H_{36}NO$ requires 258.2797.

2-Isopropylhexanal[8] **4k**




A solution of enamine **3a** (136 mg, 0.69 mmol) and *i*-PrI (135 μL, 1.38 mmol) in MeCN-$d_3$ (1.0 $cm^3$) at 82 °C for 40 h gave 2-isopropylhexanal **4k** as a colorless oil (79 mg, 80%); $R_f$ 0.29 (2% $Et_2O$/light petrol); IR ($cm^{-1}$) 2961s, 2873s, 1725s (C=O), 1466w, 1371w, 1264w, 1128w, 1066w; $^1$H NMR (400 MHz) 9.61 (d, 1H, $J$ = 3, CHO), 2.06-1.91 (m, 2H, C*H*CHO and C*H*$Me_2$), 1.69-1.57 (m, 1H, C*H*(H)*n*-Pr), 1.51-1.40 (m, 1H, CH(*H*)*n*-Pr), 1.37-1.13 (m, 4H, (C$H_2$)$_2$Me), 0.96 (d, 6H, $J$ = 7, CH*Me*$_2$), 0.89 (t, 3H, $J$ = 7, Me); $^{13}$C NMR (100 MHz) 206.1 (CHO), 58.3 (*C*HCHO), 29.8 ($CH_2$), 28.3 (*C*$Me_2$), 25.8 ($CH_2$), 22.8 ($CH_2$), 20.2 (C*Me*(Me)), 19.8 (CMe(*Me*)), 13.9 (Me); HRMS *m/z* ($M + NH_4^+$) Found: 160.1700. $C_9H_2NO$ requires 160.1701.

Similarly, a solution of enamine **3b** (198 mg, 0.83 mmol) and *i*-PrI (248 μL, 2.49 mmol) at 82 °C for 96 h gave *2-isopropylhexanal* **4k** as a colorless oil (58 mg, 49%); data as above.

## References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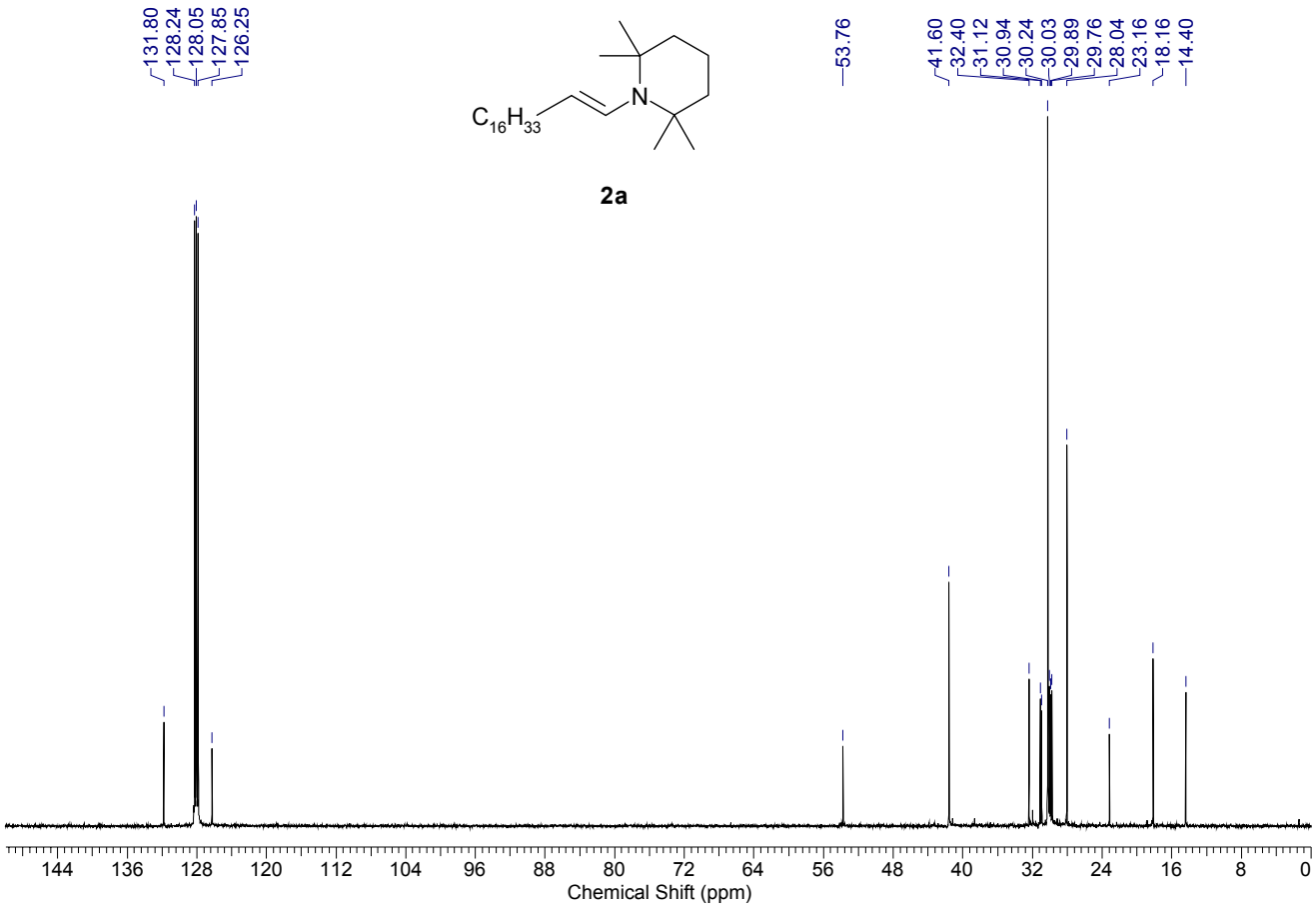
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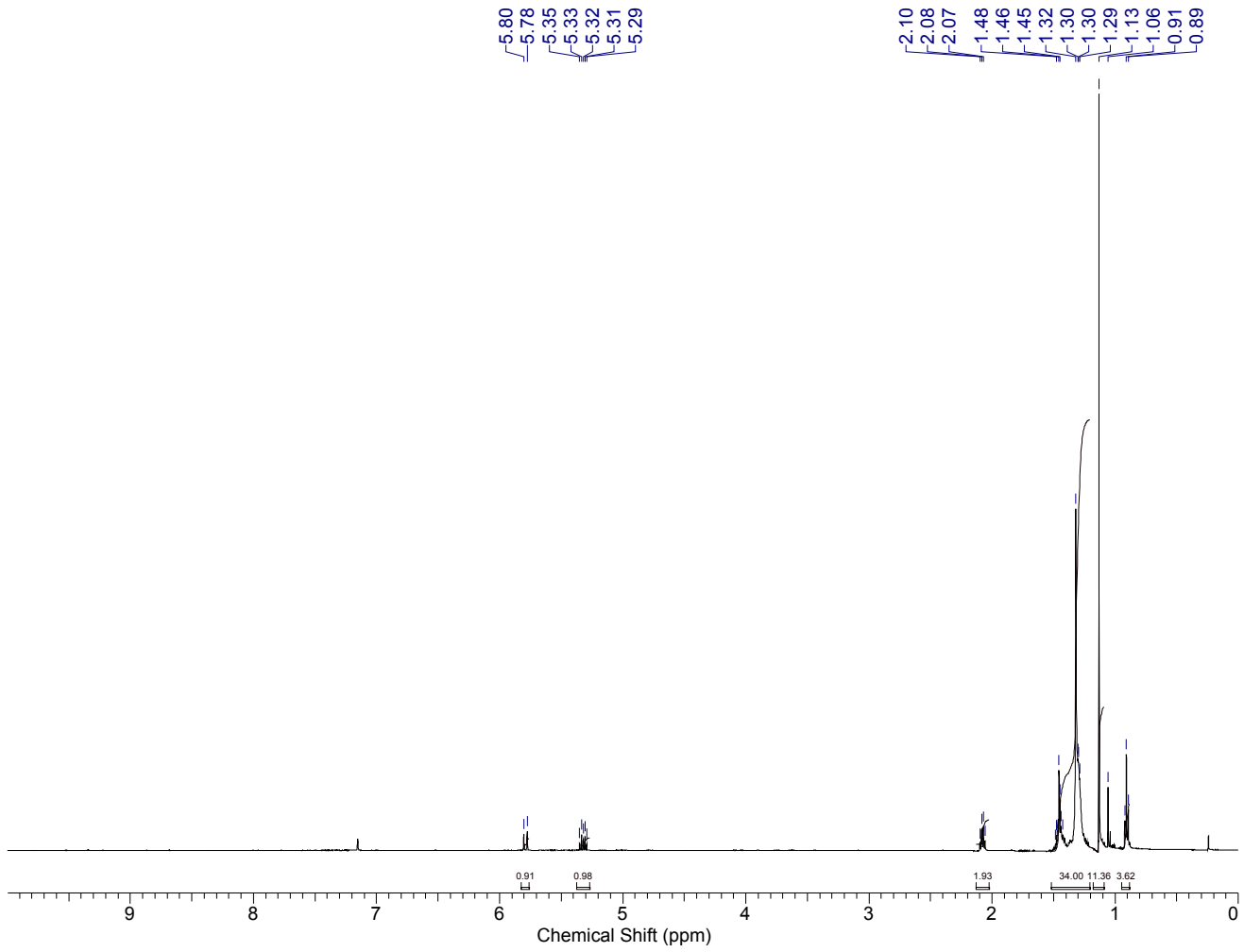
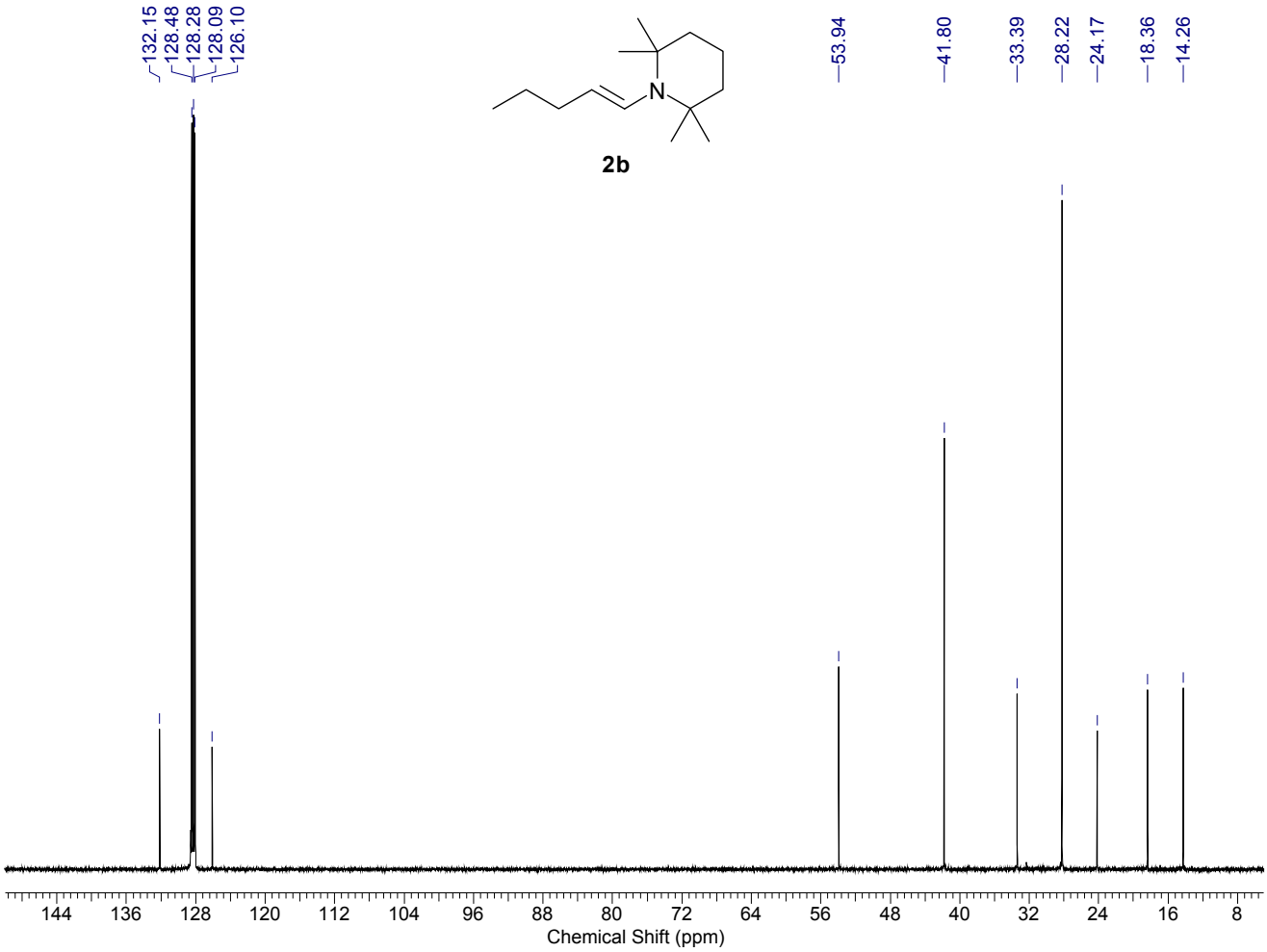
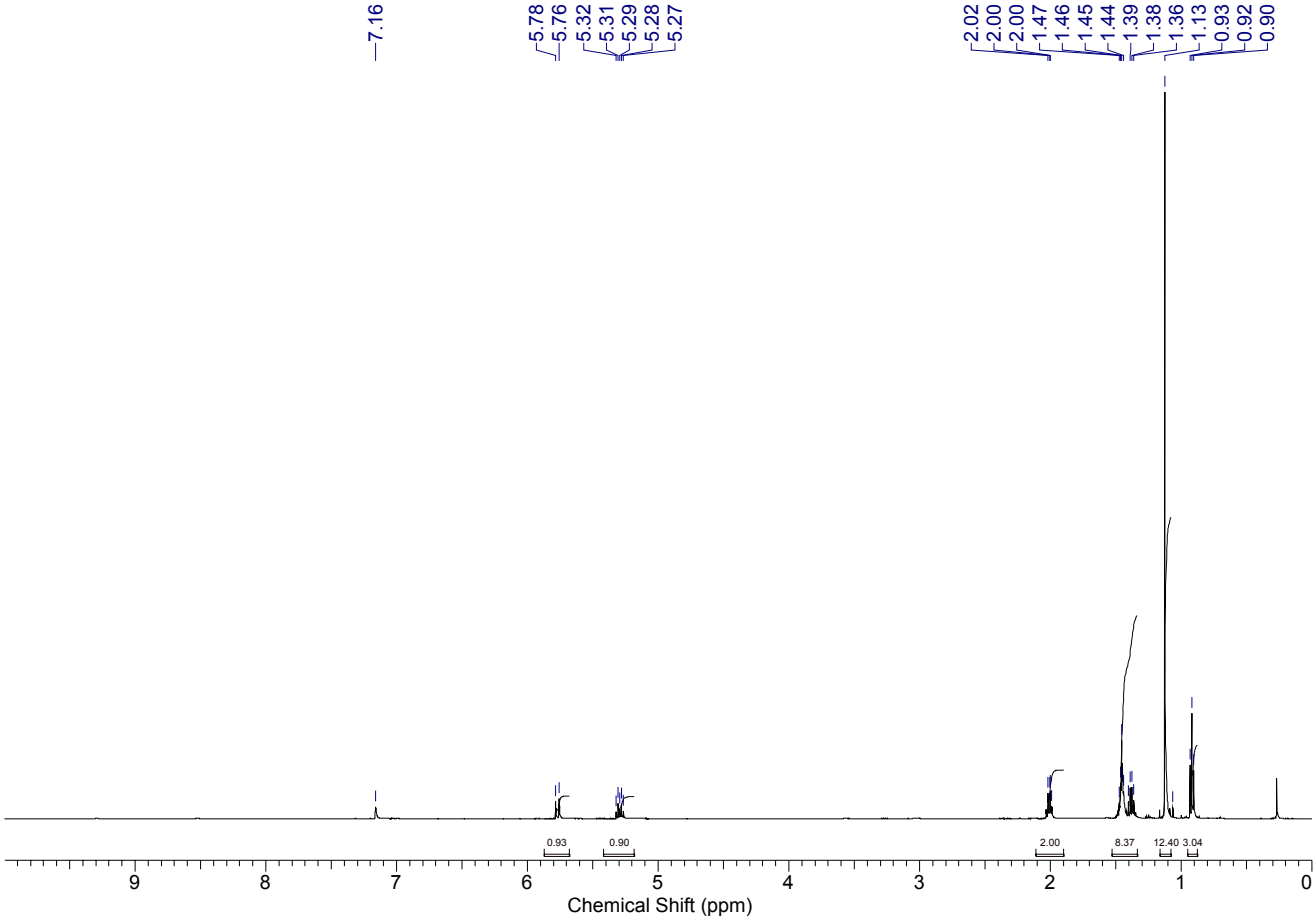
128.24
128.05
127.85
126.25
53.76
41.60
32.40
31.12
30.94
30.24
30.03
29.89
29.76
28.04
23.16
18.16
14.40
N
C16H33
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

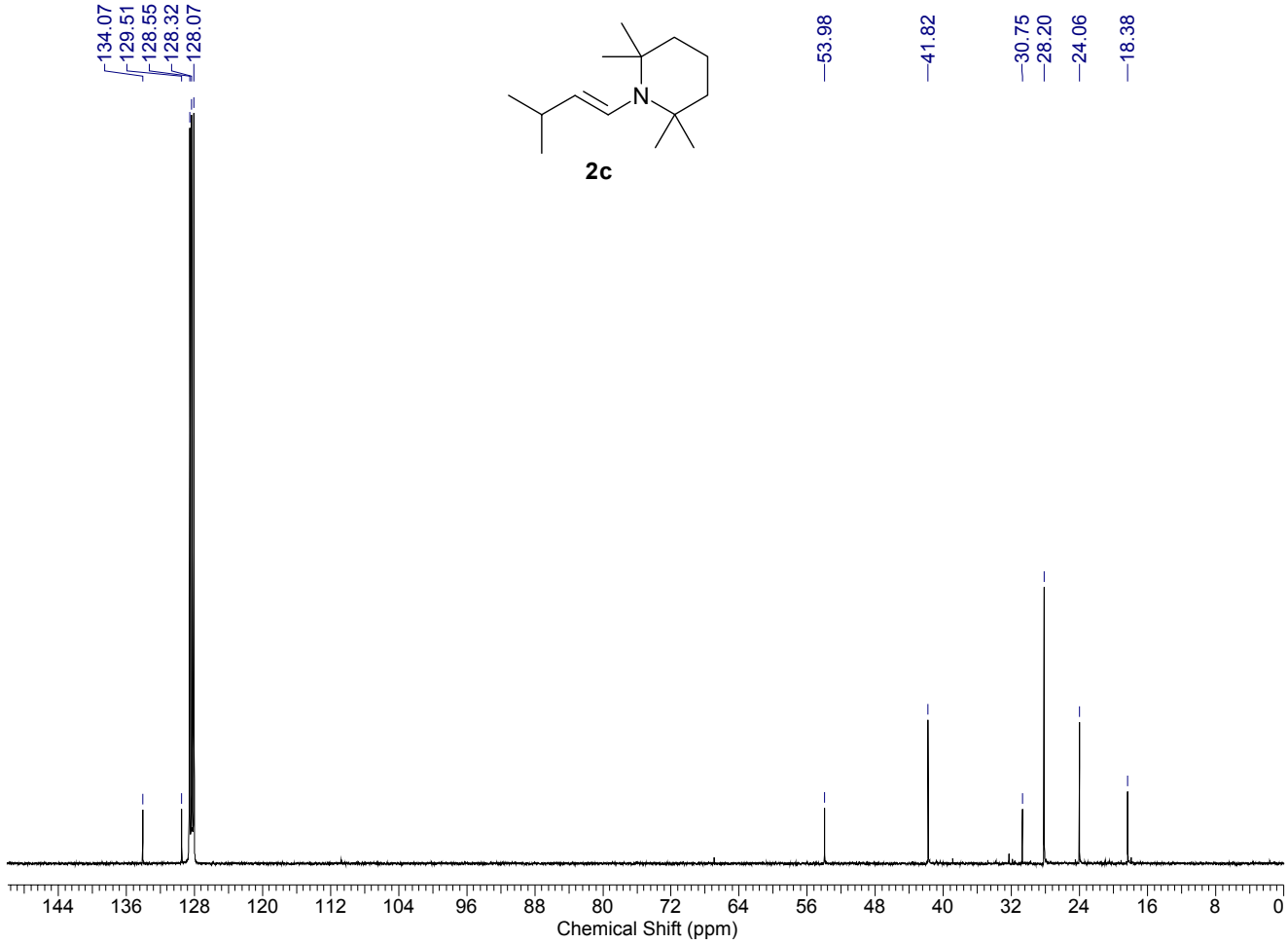
**2a**


5.80
5.78
5.35
5.33
5.32
5.31
5.29
2.10
2.08
2.07
1.48
1.46
1.45
1.32
1.30
1.30
1.29
1.13
1.06
0.91
0.89
0.91
0.98
1.93
34.00
11.36
3.62
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

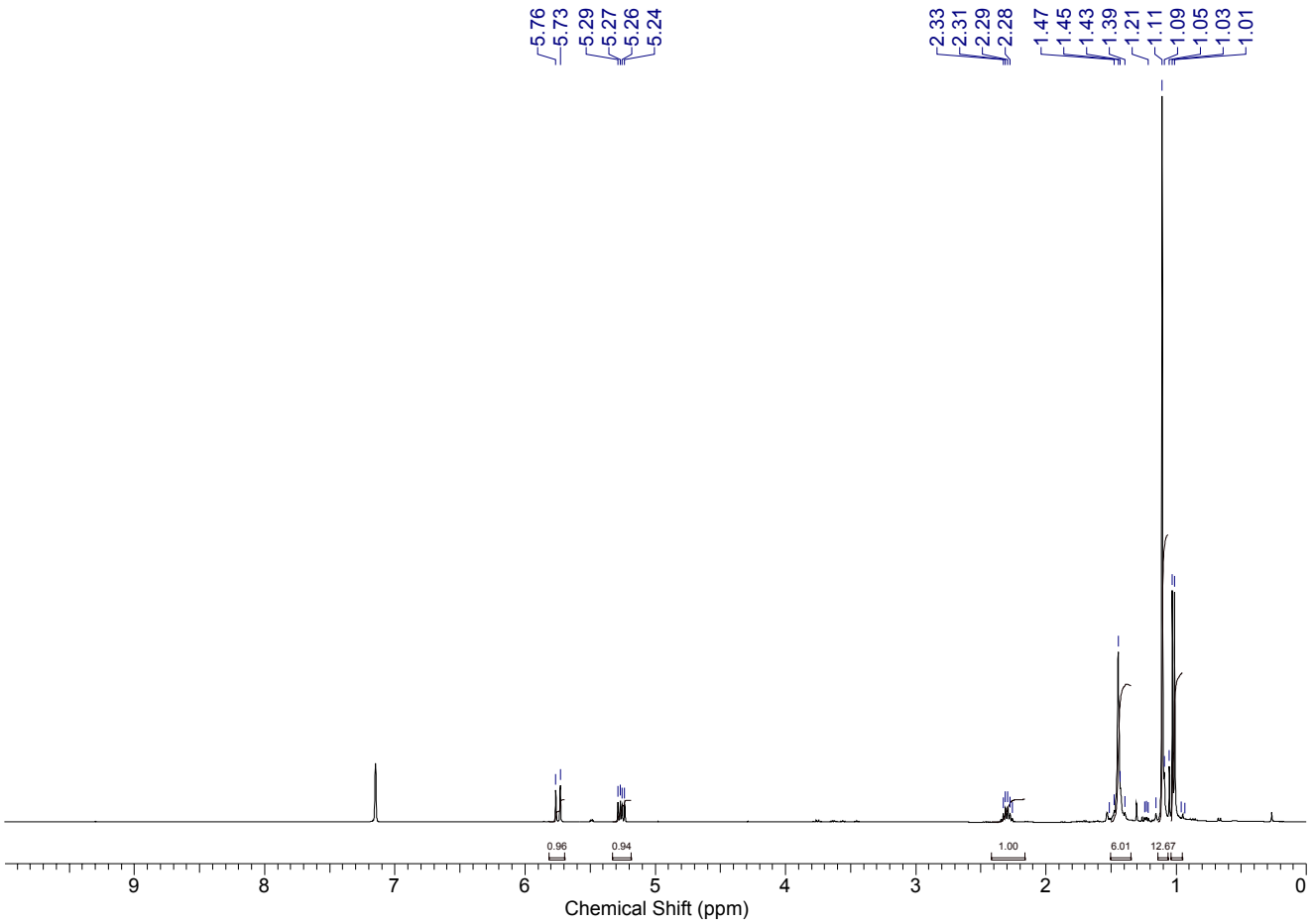

132.15
128.48
128.28
128.09
126.10
53.94
41.80
33.39
28.22
24.17
18.36
14.26
N
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

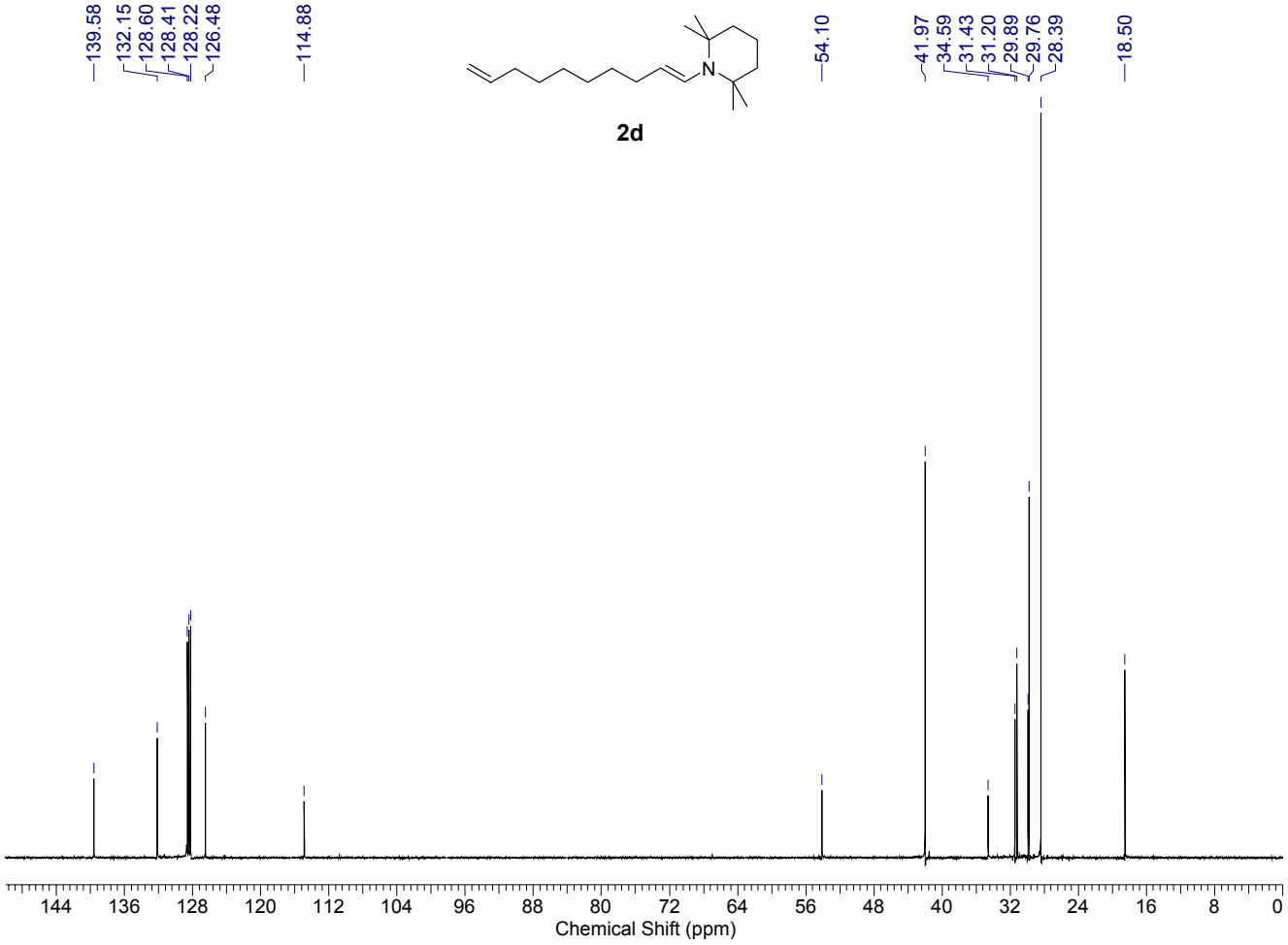
**2b**


7.16
5.78
5.76
5.32
5.31
5.29
5.28
5.27
2.02
2.00
2.00
1.47
1.46
1.45
1.44
1.39
1.38
1.36
1.13
0.93
0.92
0.90
0.93
0.90
2.00
8.37
12.40
3.04
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

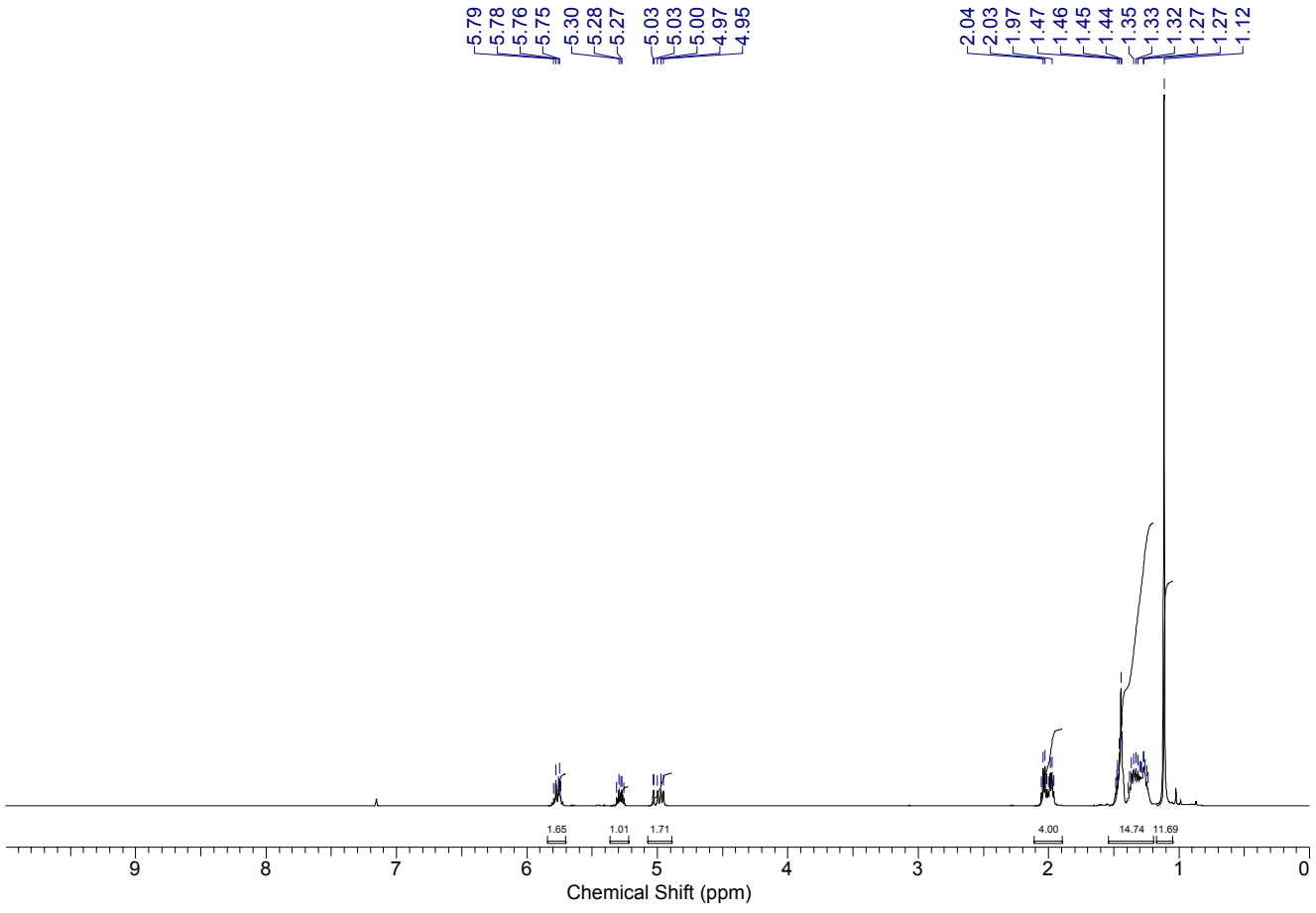

134.07
129.51
128.55
128.32
128.07
53.98
41.82
30.75
28.20
24.06
18.38
N
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

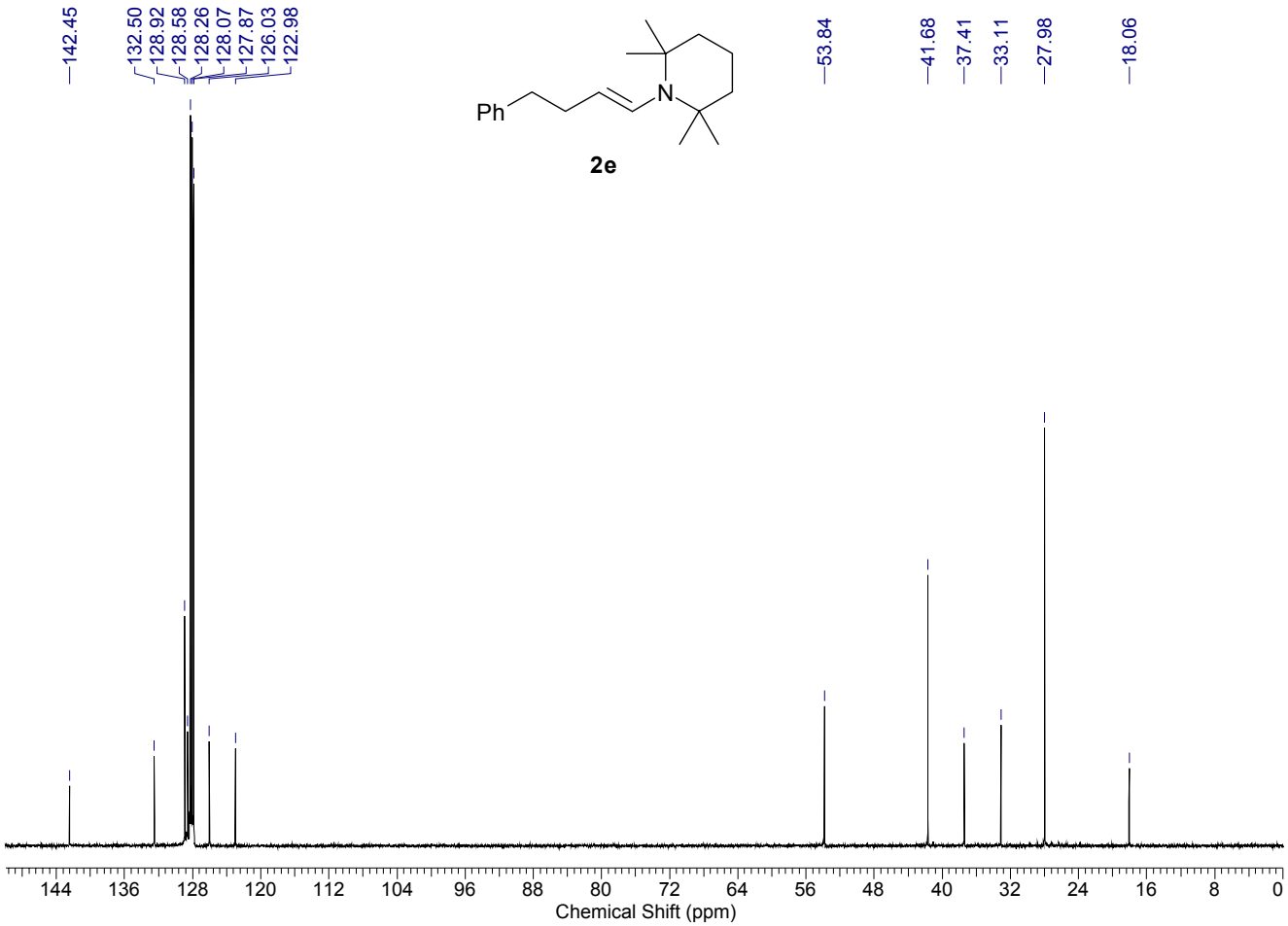
**2c**


5.76
5.73
5.29
5.27
5.26
5.24
2.33
2.31
2.29
2.28
1.47
1.45
1.43
1.39
1.21
1.11
1.09
1.05
1.03
1.01
0.96
0.94
1.00
6.01
12.67
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

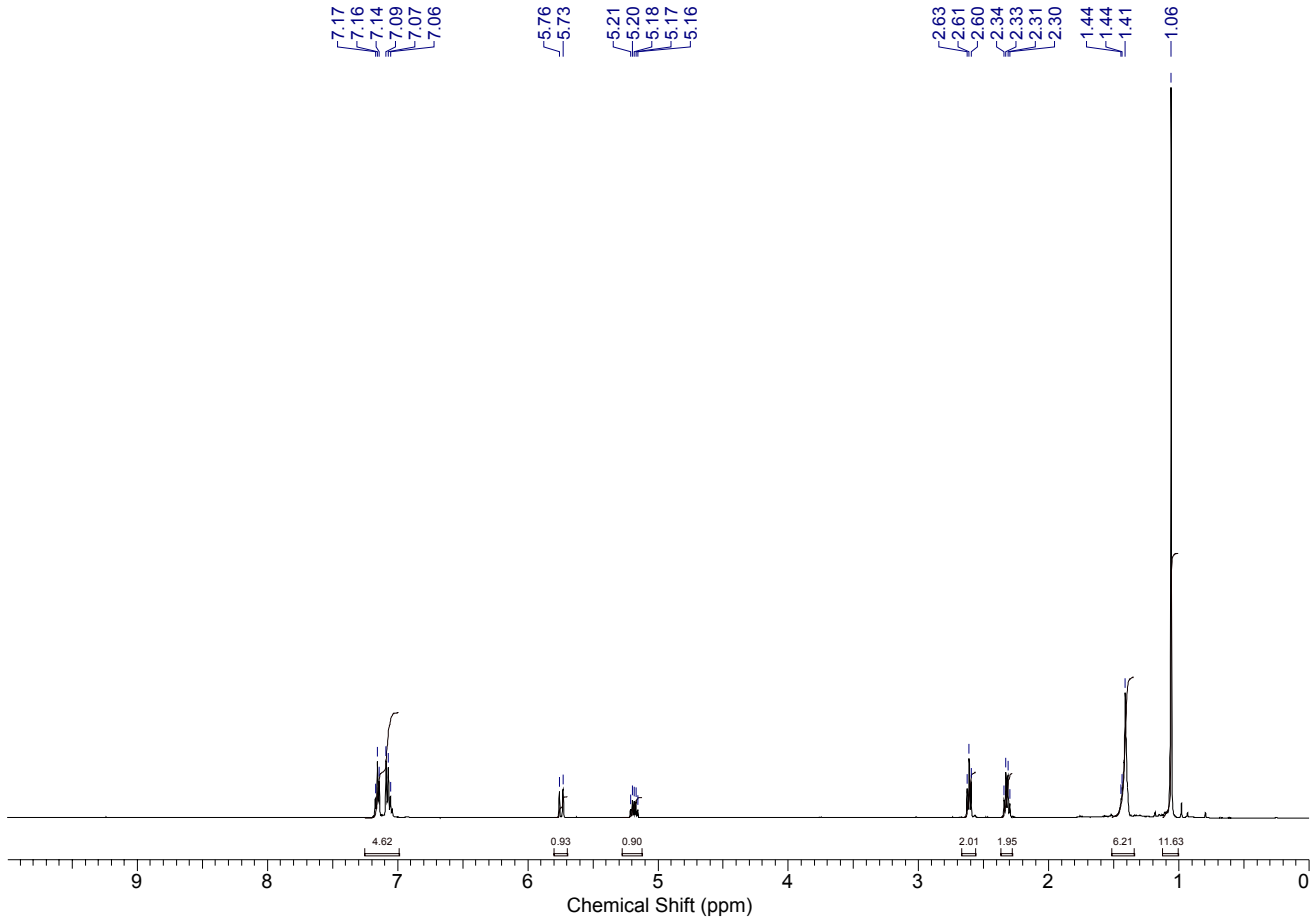

139.58
132.15
128.60
128.41
128.22
126.48
114.88
54.10
41.97
34.59
31.43
31.20
29.89
29.76
28.39
18.50
N
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

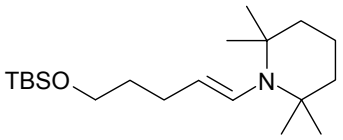
**2d**


5.79
5.78
5.76
5.75
5.30
5.28
5.27
5.03
5.03
5.00
4.97
4.95
2.04
2.03
1.97
1.47
1.46
1.45
1.44
1.35
1.33
1.32
1.27
1.27
1.12
1.65
1.01
1.71
4.00
14.74
11.69
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


142.45
132.50
128.92
128.58
128.26
128.07
127.87
126.03
122.98
53.84
41.68
37.41
33.11
27.98
18.06
Ph
N
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

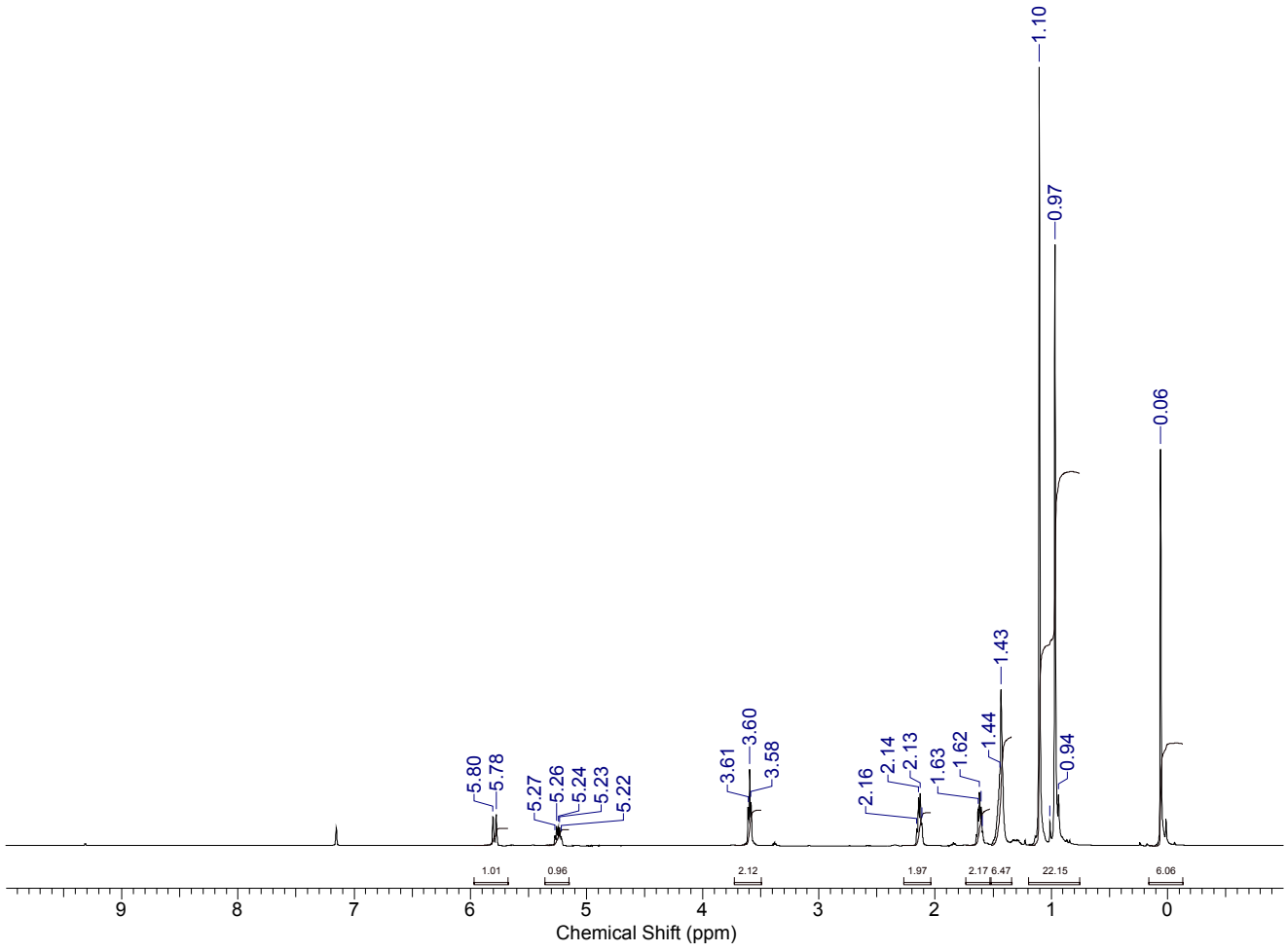
**2e**

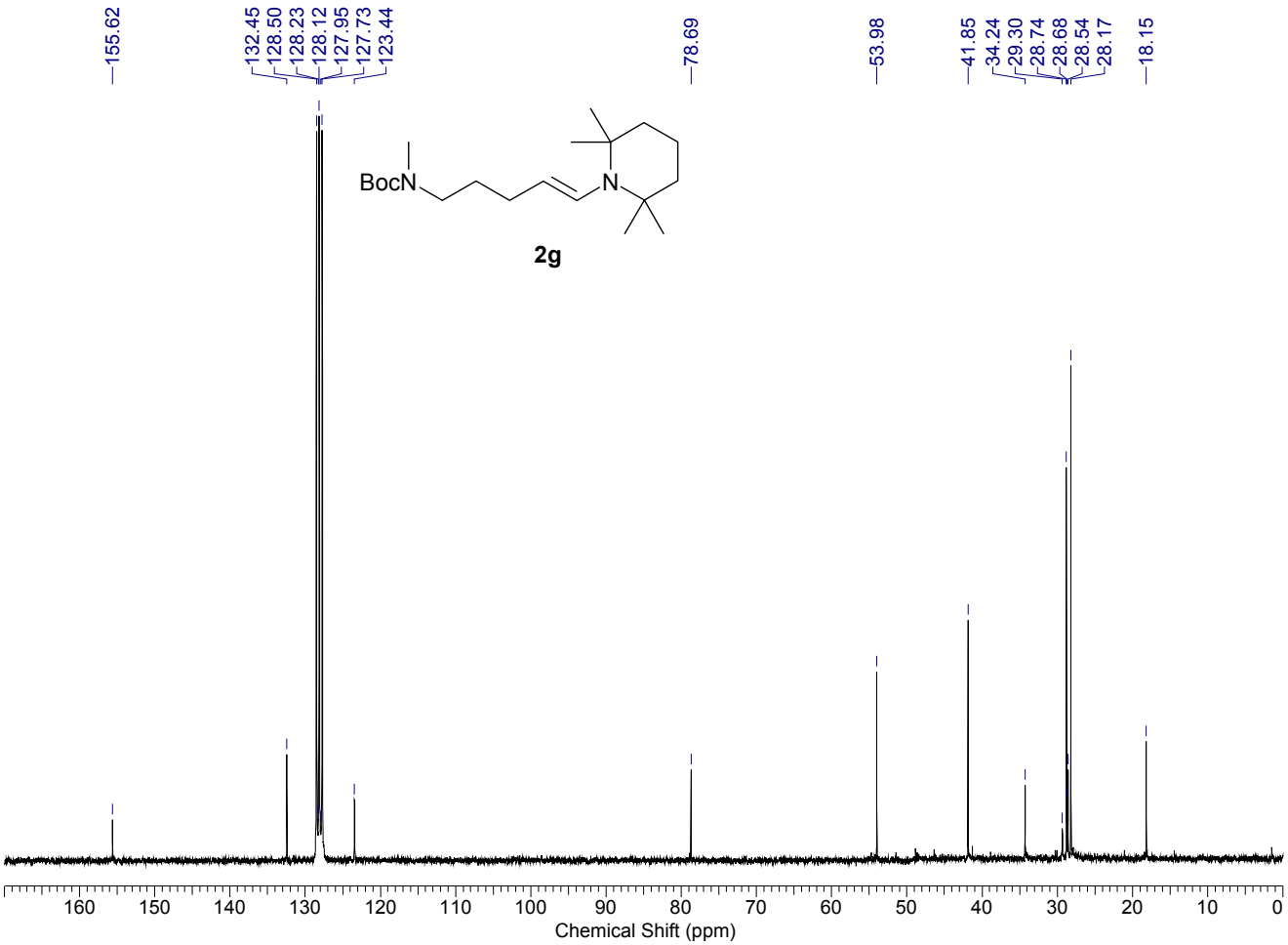

7.17
7.16
7.14
7.09
7.07
7.06
5.76
5.73
5.21
5.20
5.18
5.17
5.16
2.63
2.61
2.60
2.34
2.33
2.31
2.30
1.44
1.44
1.41
1.06
4.62
0.93
0.90
2.01
1.95
6.21
11.63
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

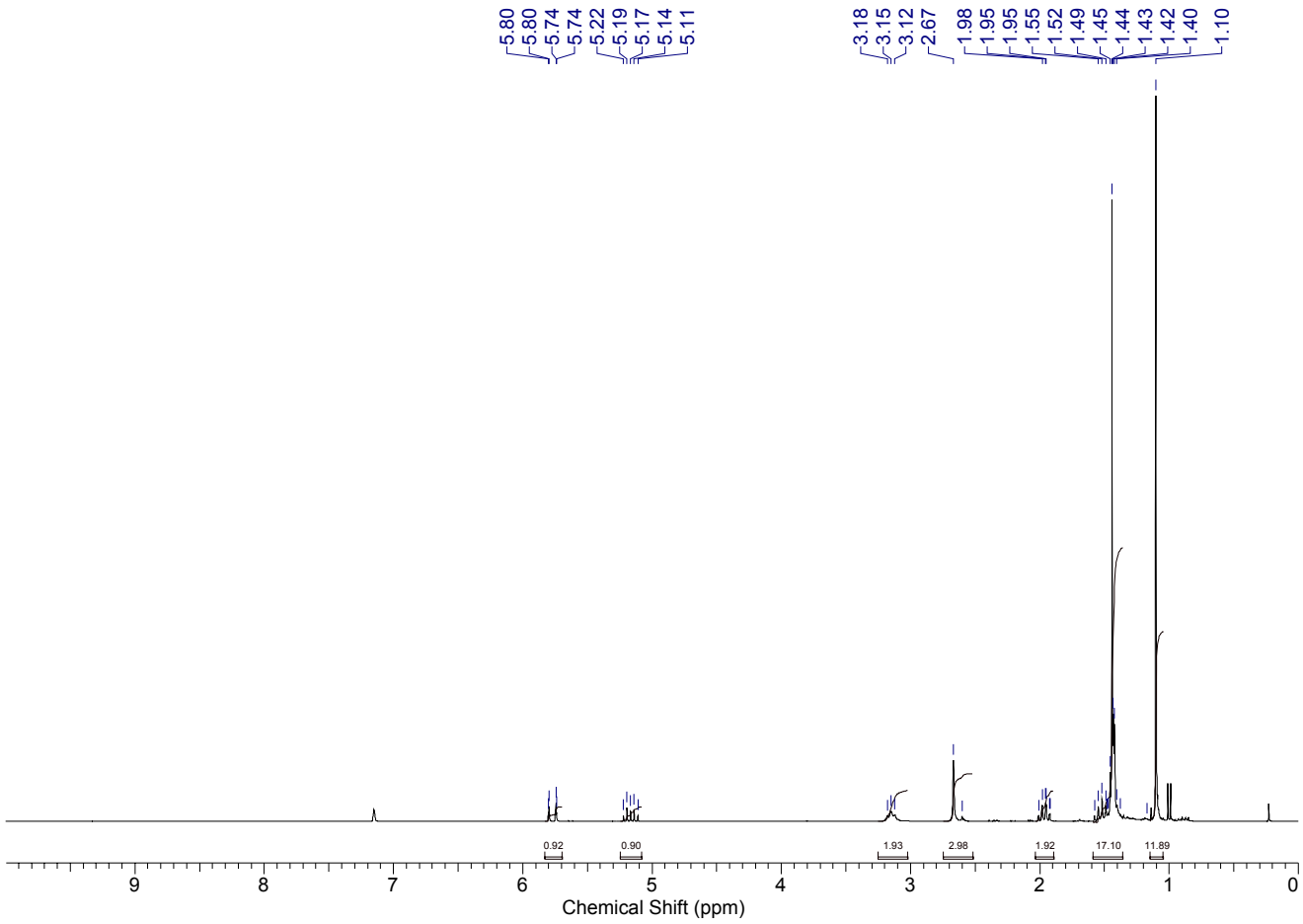

TBSO
N

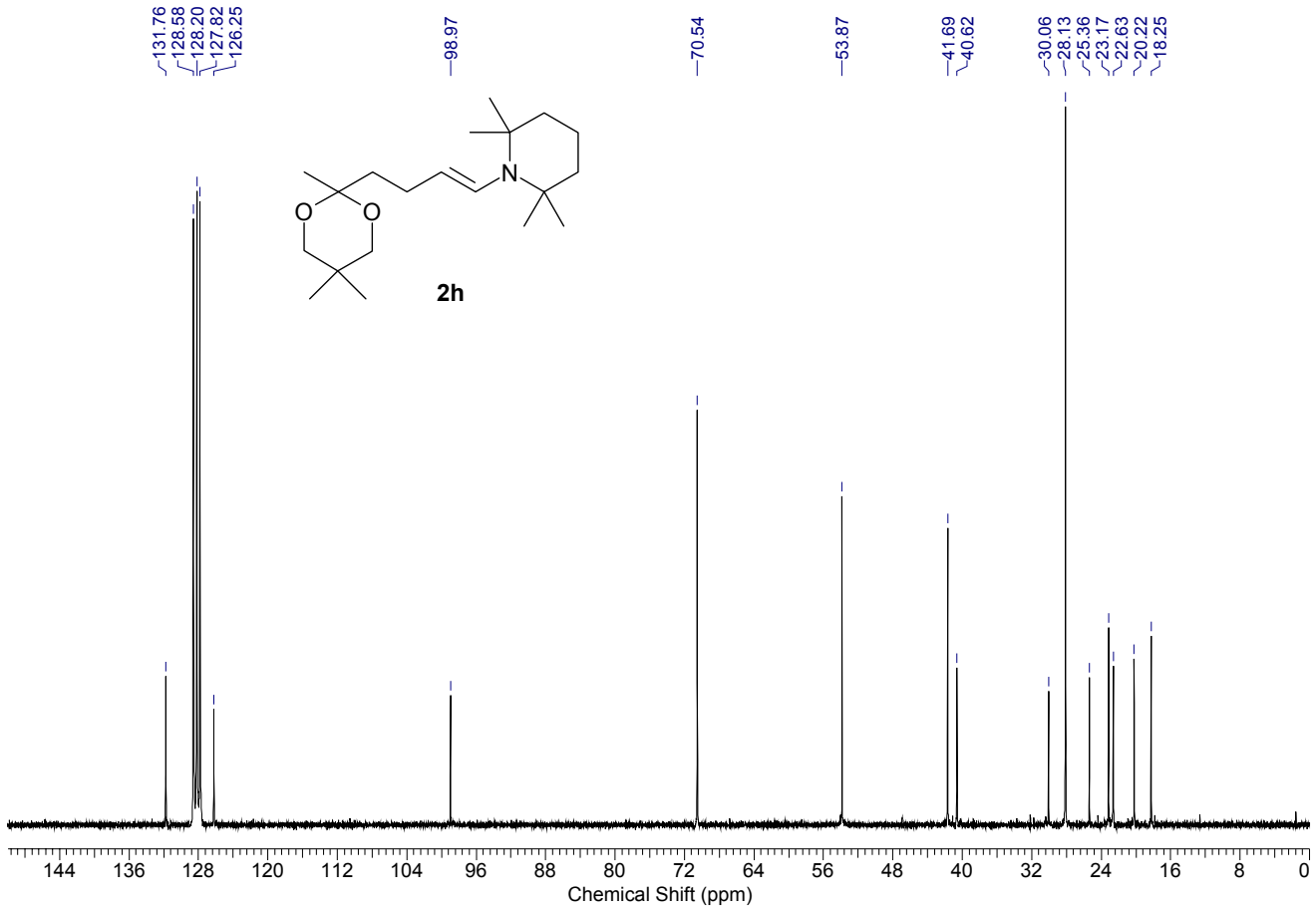
**2f**

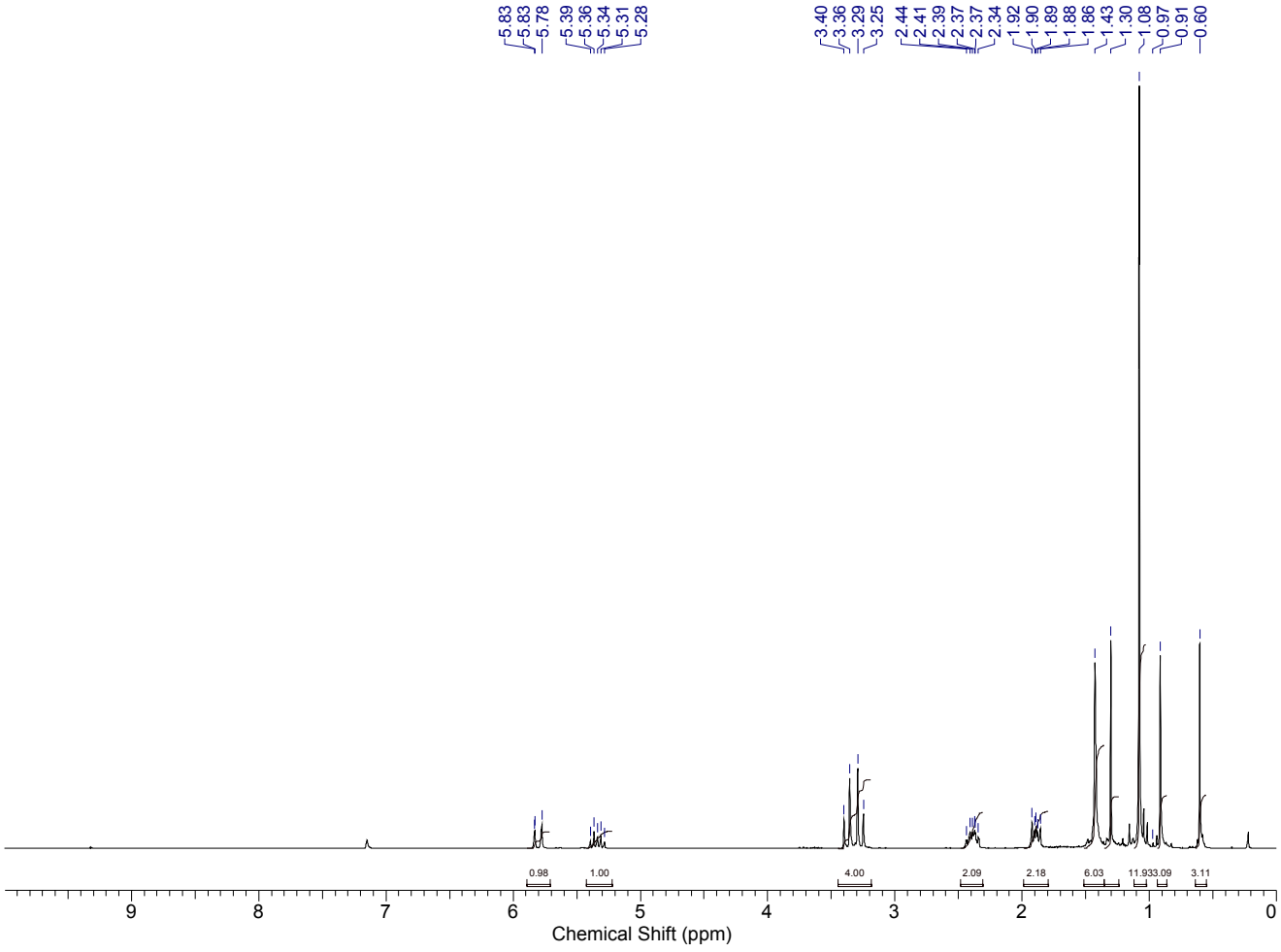

128.24
128.05
127.85
132.14
124.80
62.79
53.77
41.62
34.03
28.01
26.25
18.58
18.11
-5.07
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

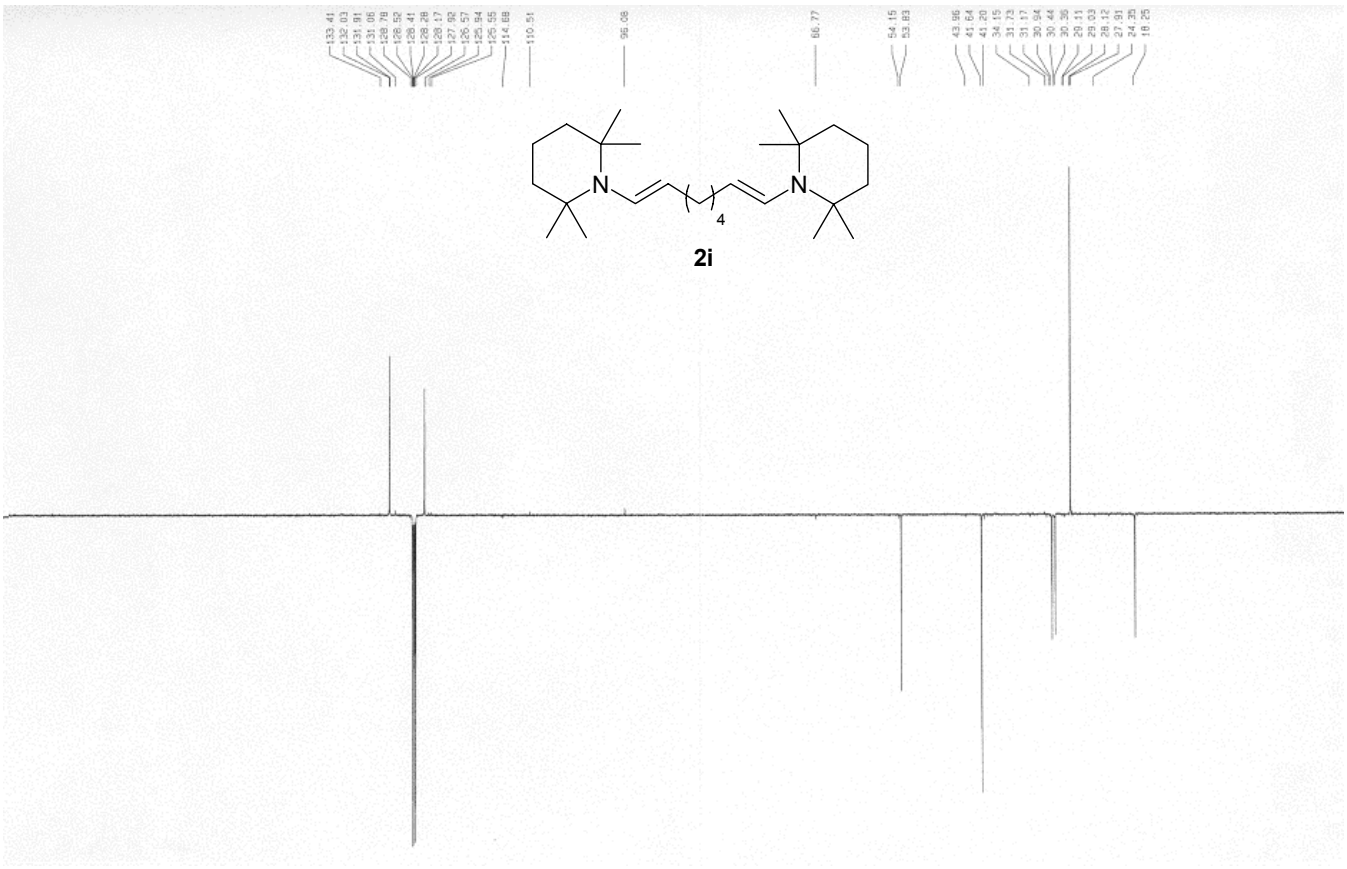

1.10
0.97
0.06
1.43
0.94
5.80
5.78
5.27
5.26
5.24
5.23
5.22
3.61
3.60
3.58
2.16
2.14
2.13
1.63
1.62
1.44
1.01
0.96
2.12
1.97
2.17
6.47
22.15
6.06
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


155.62
132.45
128.50
128.23
128.12
127.95
127.73
123.44
78.69
53.98
41.85
34.24
29.30
28.74
28.68
28.54
28.17
18.15
BocN
N
2g
Chemical Shift (ppm)

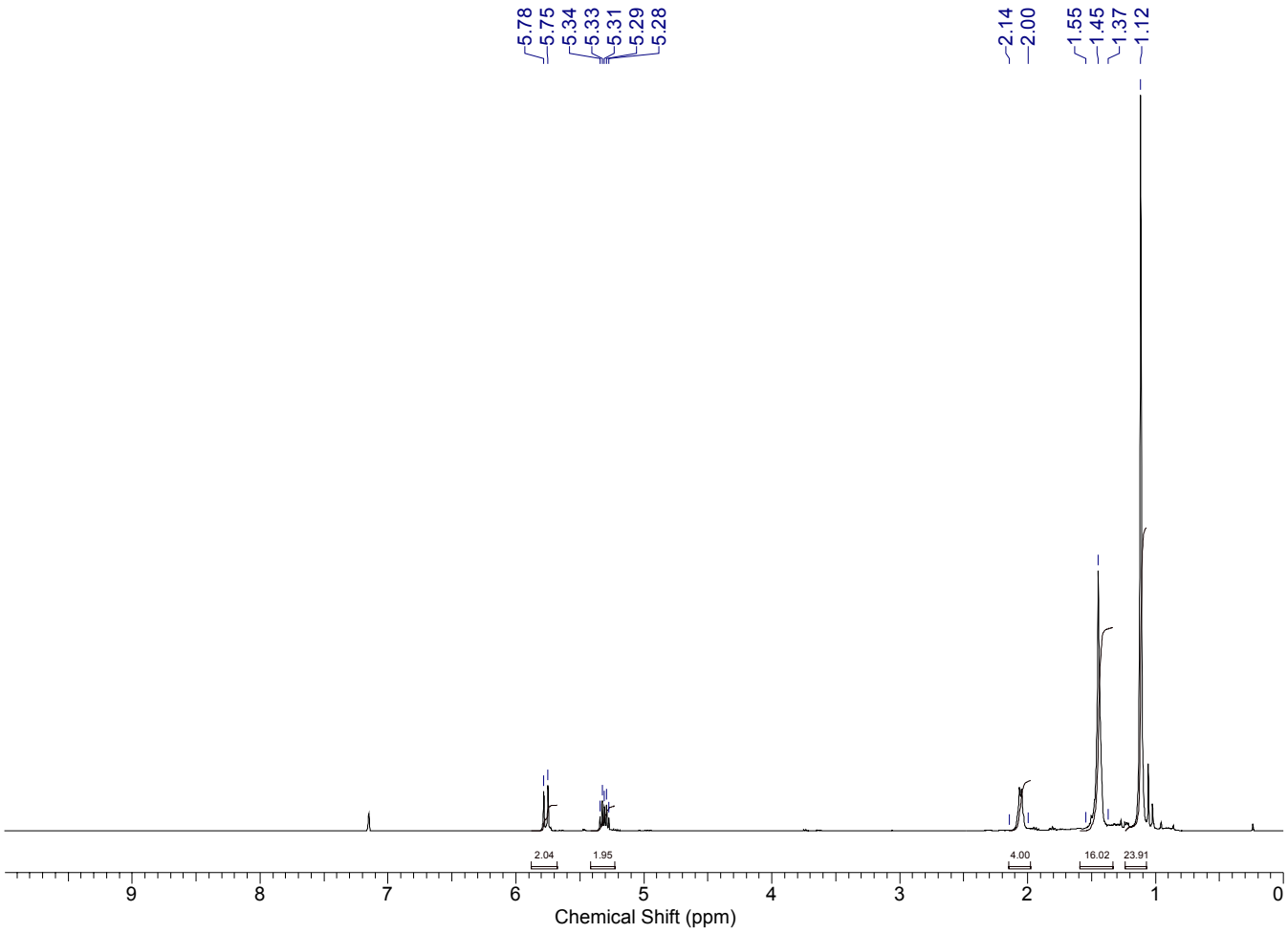

5.80
5.80
5.74
5.74
5.22
5.19
5.17
5.14
5.11
3.18
3.15
3.12
2.67
1.98
1.95
1.95
1.55
1.52
1.49
1.45
1.44
1.43
1.42
1.40
1.10
0.92
0.90
1.93
2.98
1.92
17.10
11.89
Chemical Shift (ppm)

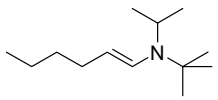

131.76
128.58
128.20
127.82
126.25
98.97
70.54
53.87
41.69
40.62
30.06
28.13
25.36
23.17
22.63
20.22
18.25
O
O
N
2h
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


5.83
5.83
5.78
5.39
5.36
5.34
5.31
5.28
3.40
3.36
3.29
3.25
2.44
2.41
2.39
2.37
2.37
2.34
1.92
1.90
1.89
1.88
1.86
1.43
1.30
1.08
0.97
0.91
0.60
0.98
1.00
4.00
2.09
2.18
6.03
11.93
3.09
3.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


133.41
132.03
131.91
131.06
128.79
128.52
128.41
128.28
128.17
127.92
126.57
125.94
125.55
114.88
110.51
96.06
66.77
54.15
53.83
43.96
41.64
41.20
34.15
31.73
31.17
30.94
30.44
30.36
29.11
29.03
28.12
27.91
24.39
18.25
N
N
4

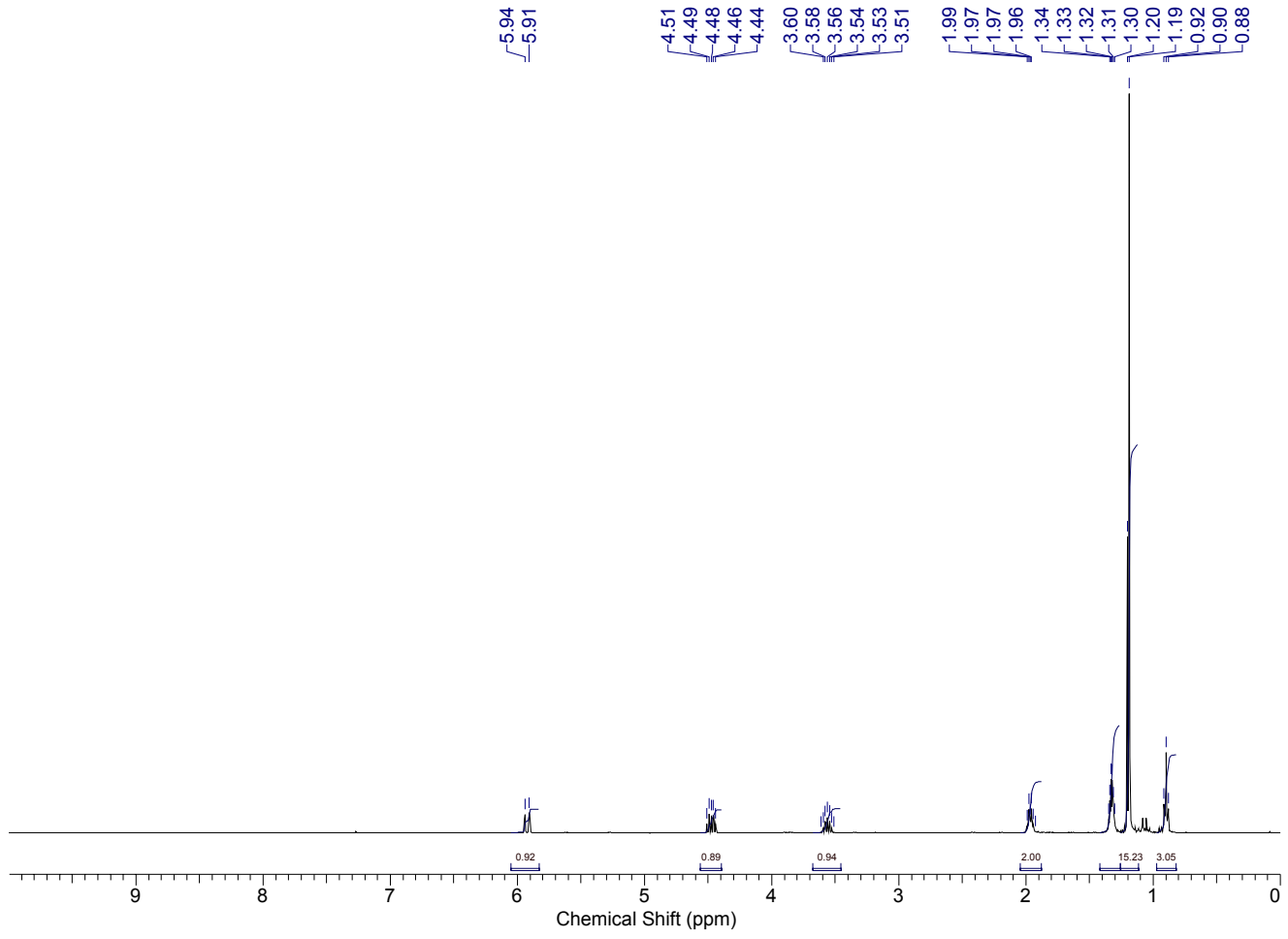
**2i**

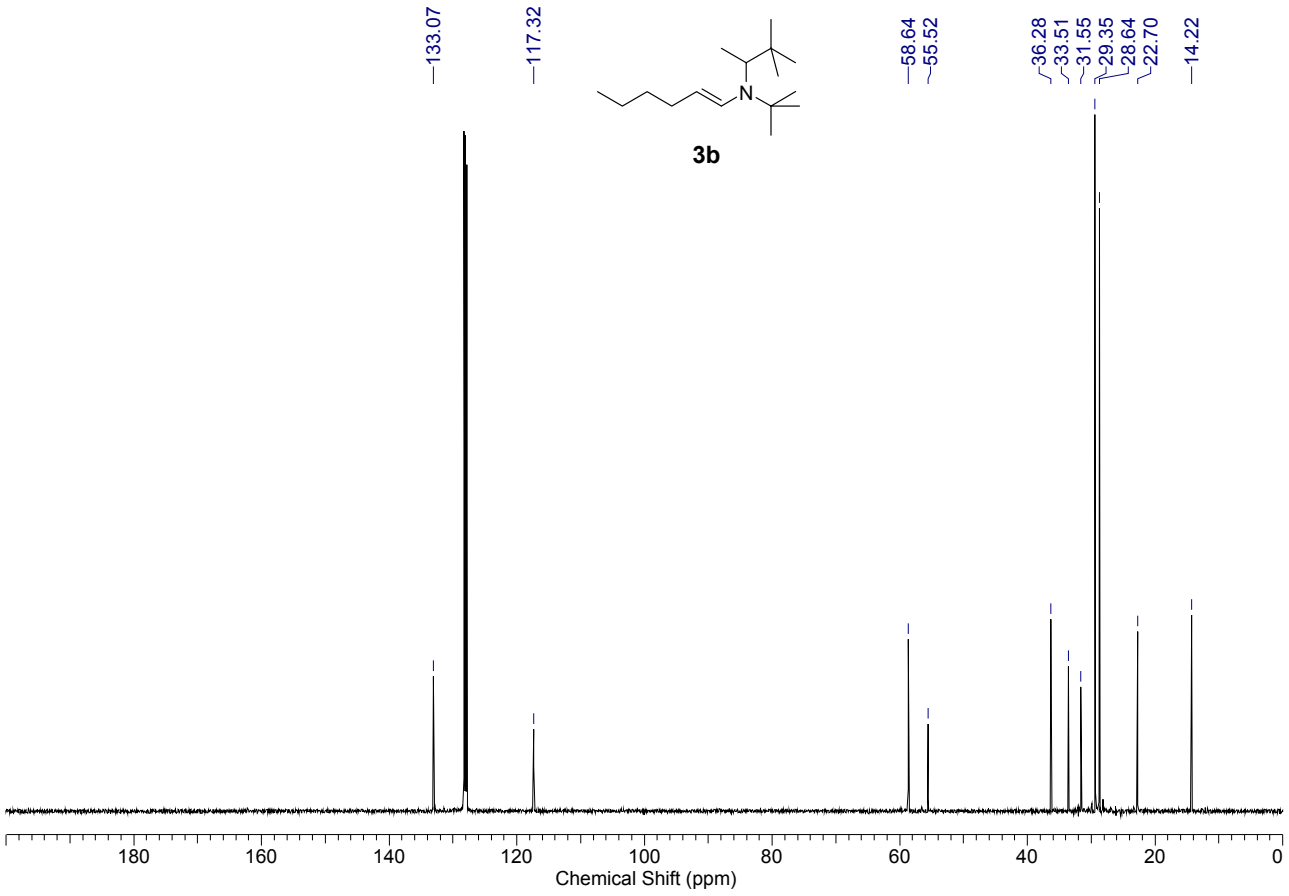

5.78
5.75
5.34
5.33
5.31
5.29
5.28
2.14
2.00
1.55
1.45
1.37
1.12
2.04
1.95
4.00
16.02
23.91
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

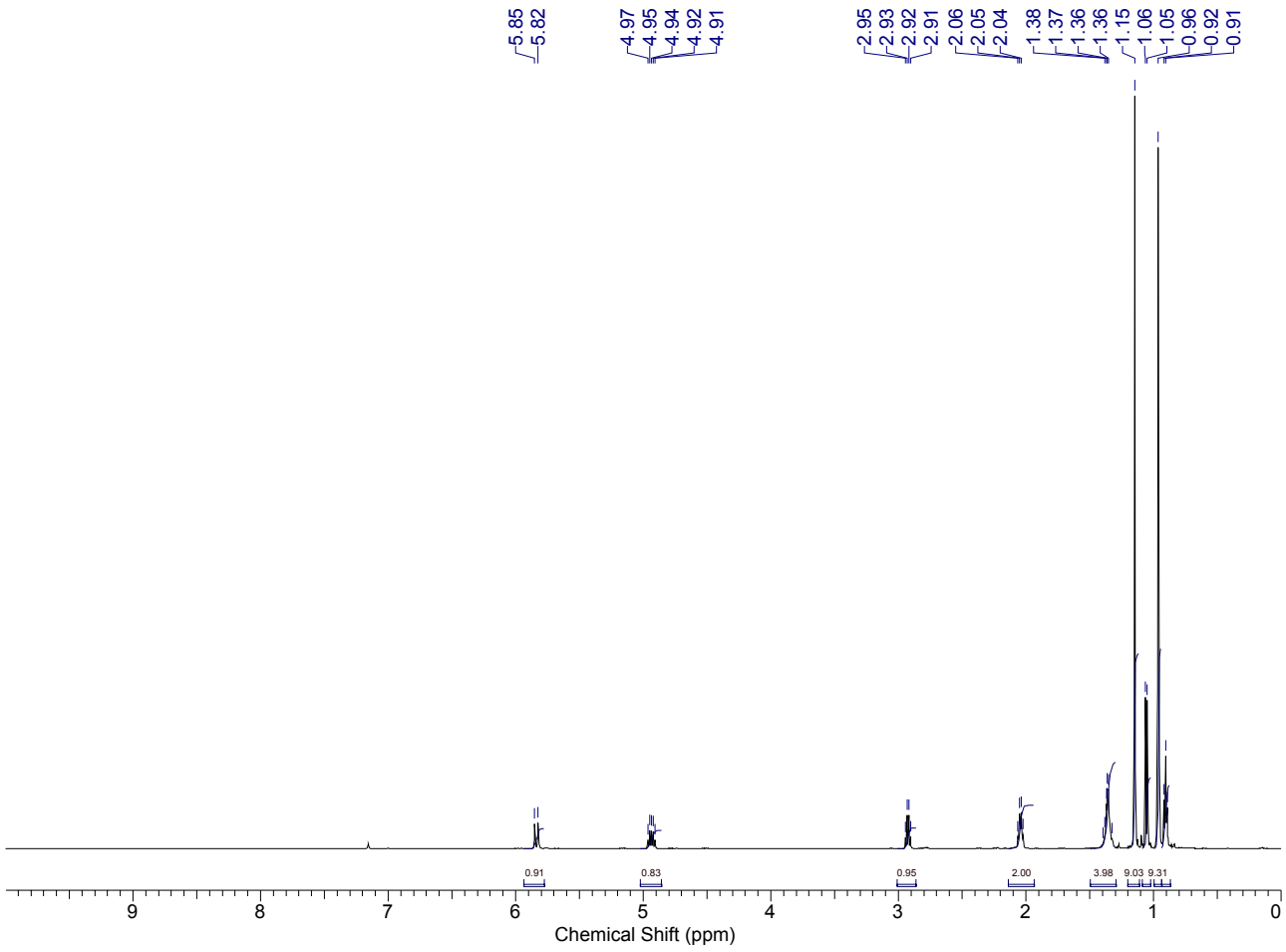


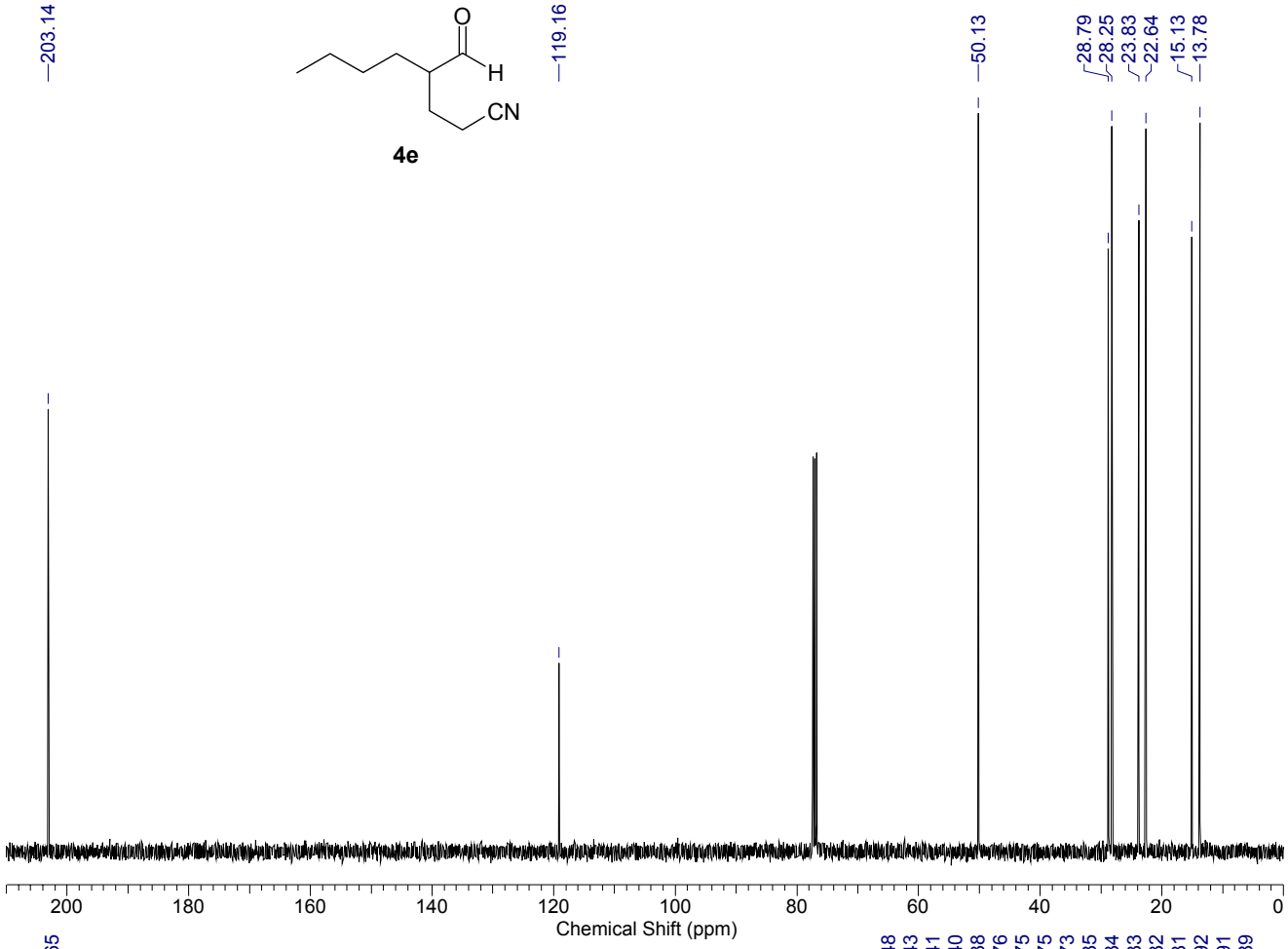
**3a**

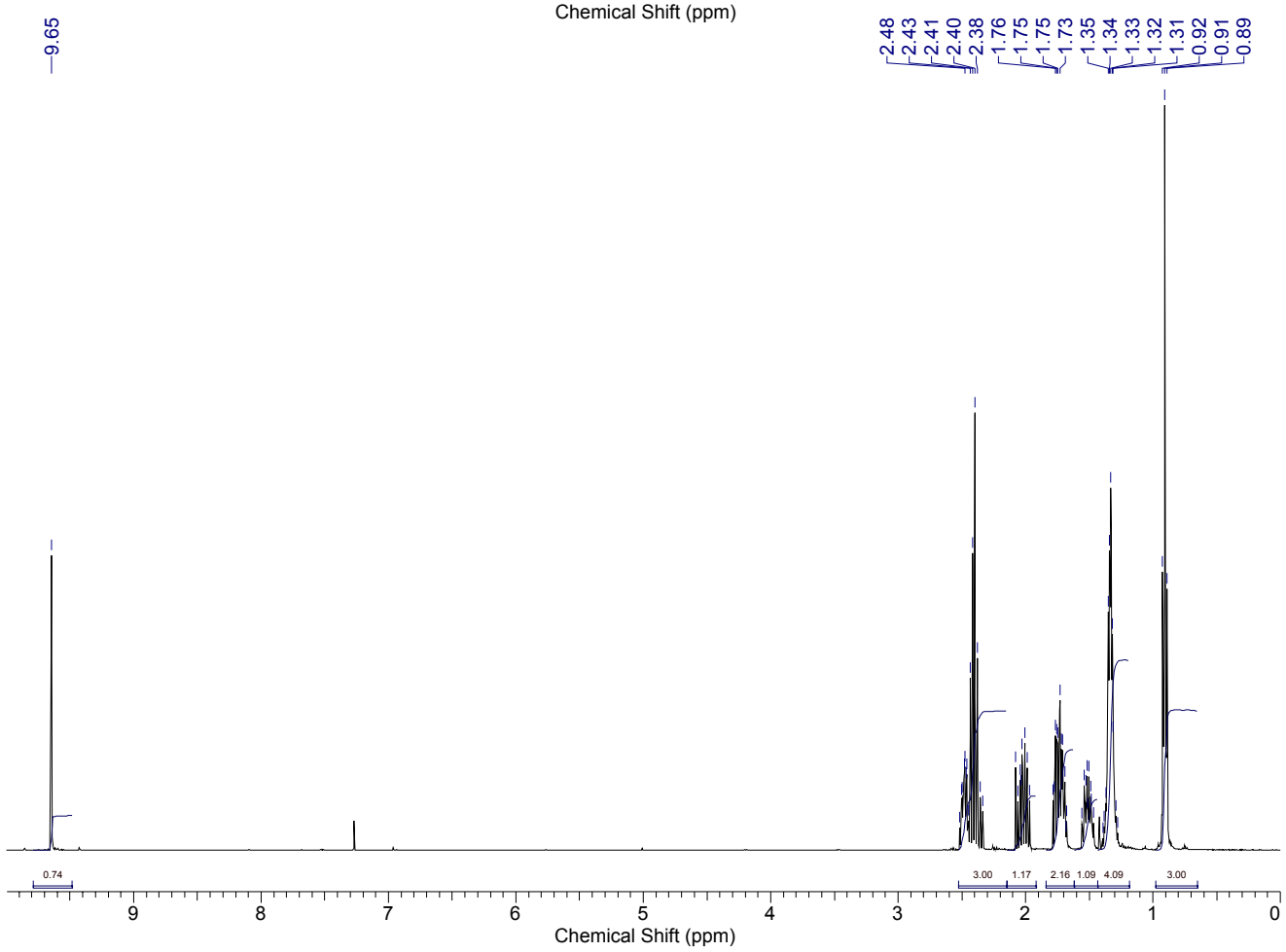

129.93
105.21
46.13
29.10
20.96
14.03
55.52
33.85
31.59
22.17
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

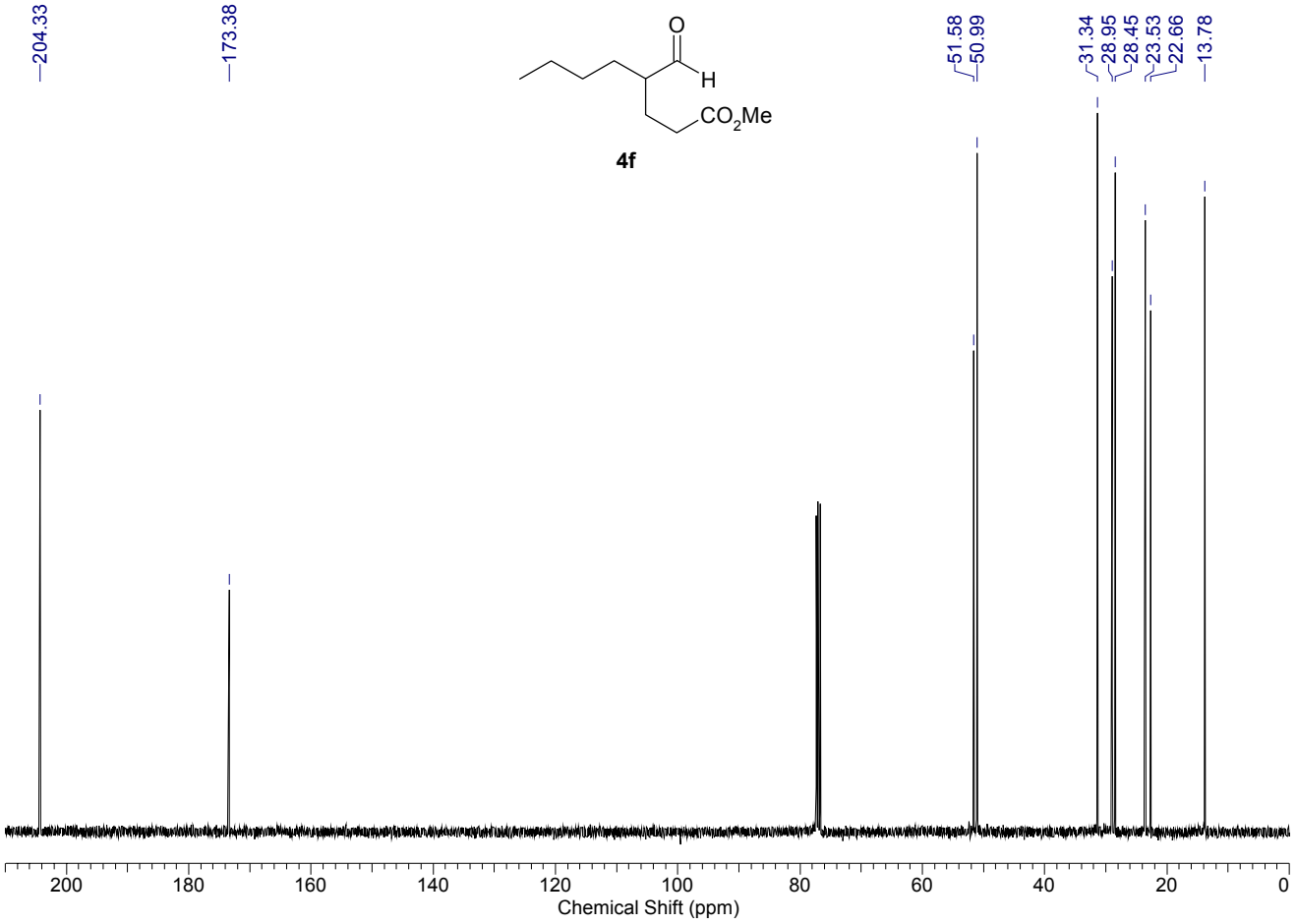

5.94
5.91
4.51
4.49
4.48
4.46
4.44
3.60
3.58
3.56
3.54
3.53
3.51
1.99
1.97
1.97
1.96
1.34
1.33
1.32
1.31
1.30
1.20
1.19
0.92
0.90
0.88
0.92
0.89
0.94
2.00
15.23
3.05
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

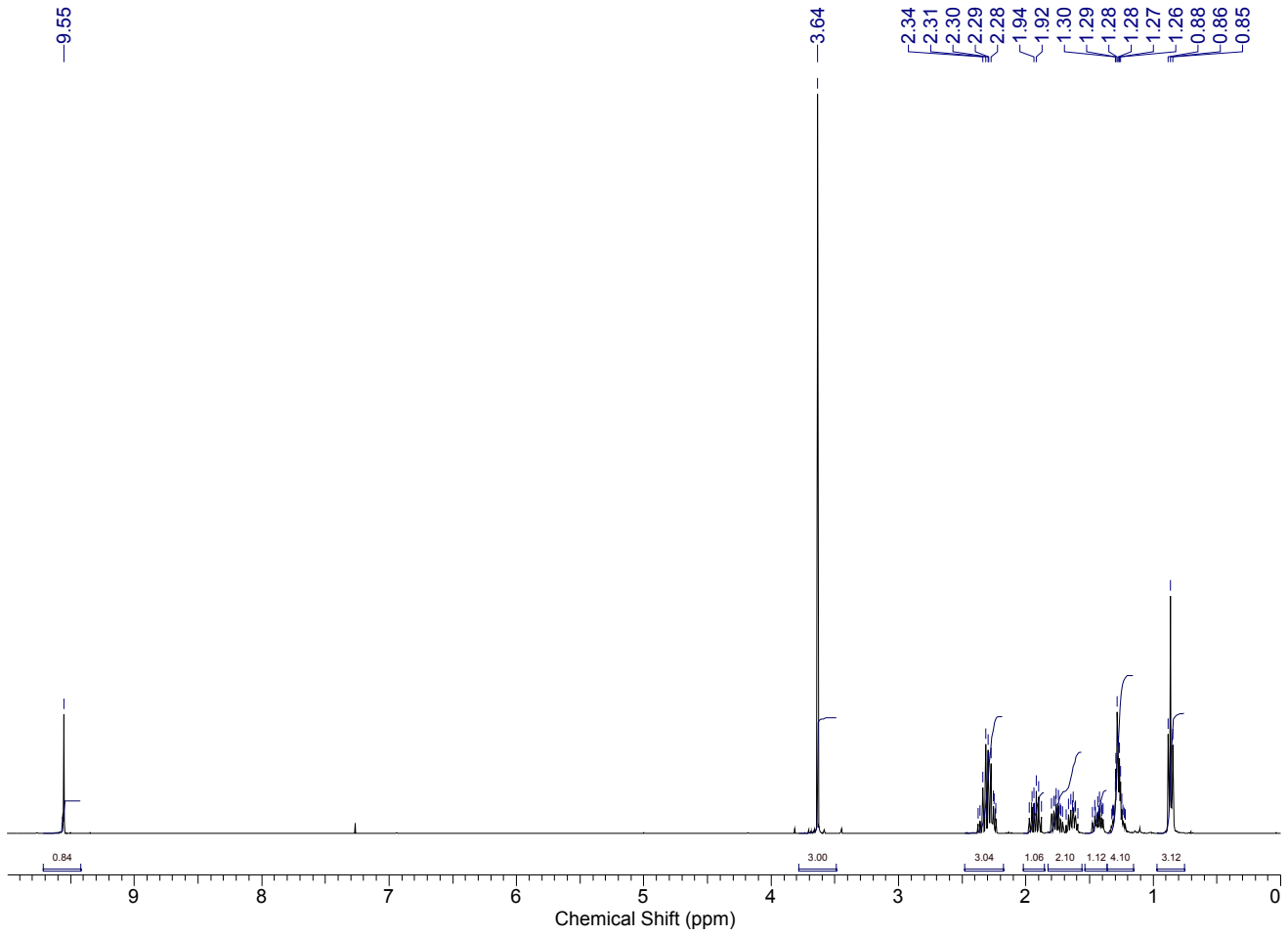

133.07
117.32
58.64
55.52
36.28
33.51
31.55
29.35
28.64
22.70
14.22
N
3b
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

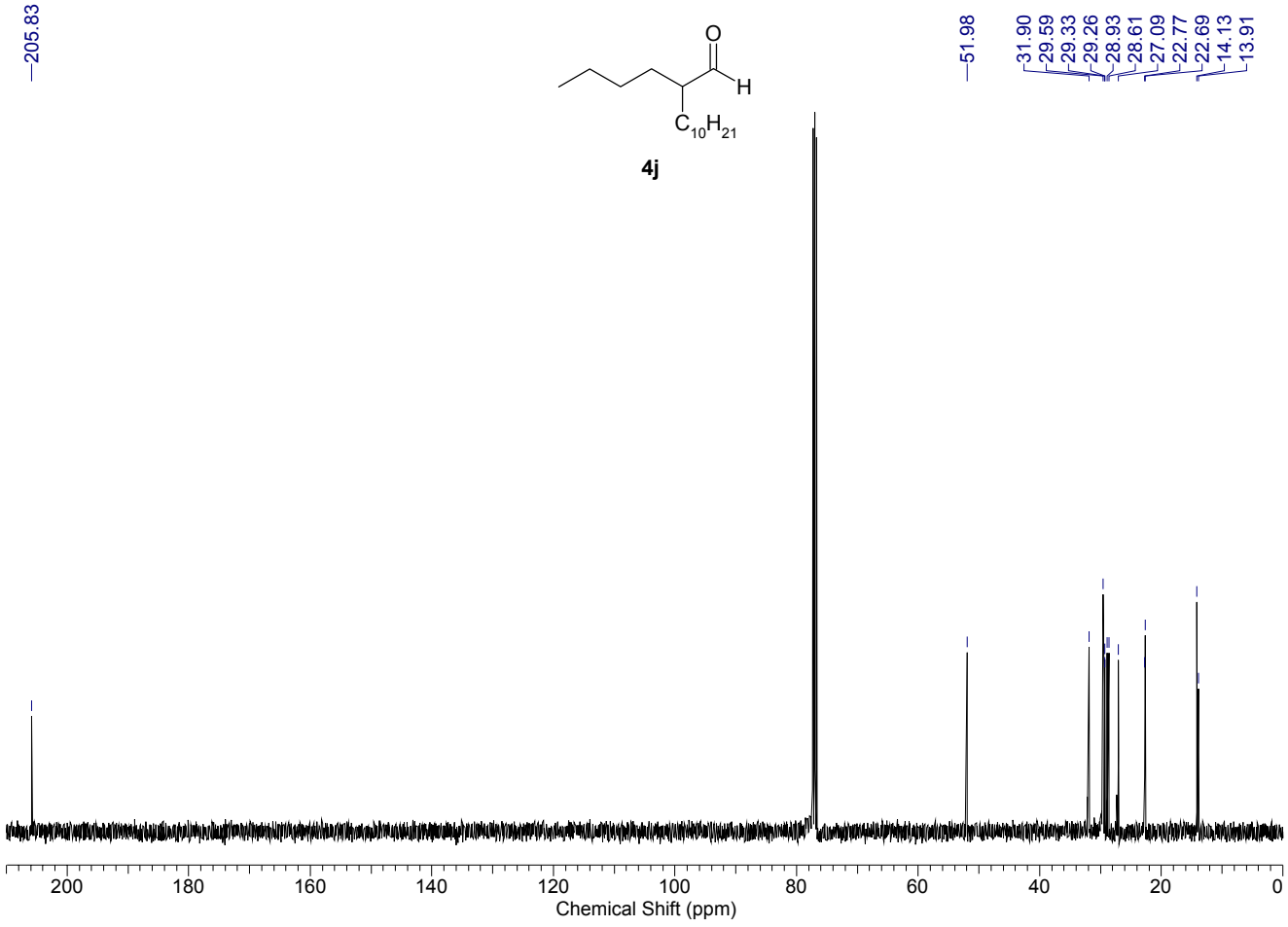

5.85
5.82
4.97
4.95
4.94
4.92
4.91
2.95
2.93
2.92
2.91
2.06
2.05
2.04
1.38
1.37
1.36
1.36
1.15
1.06
1.05
0.96
0.92
0.91
0.91
0.83
0.95
2.00
3.98
9.03
9.31
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


203.14
119.16
50.13
28.79
28.25
23.83
22.64
15.13
13.78
O
H
CN
4e
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

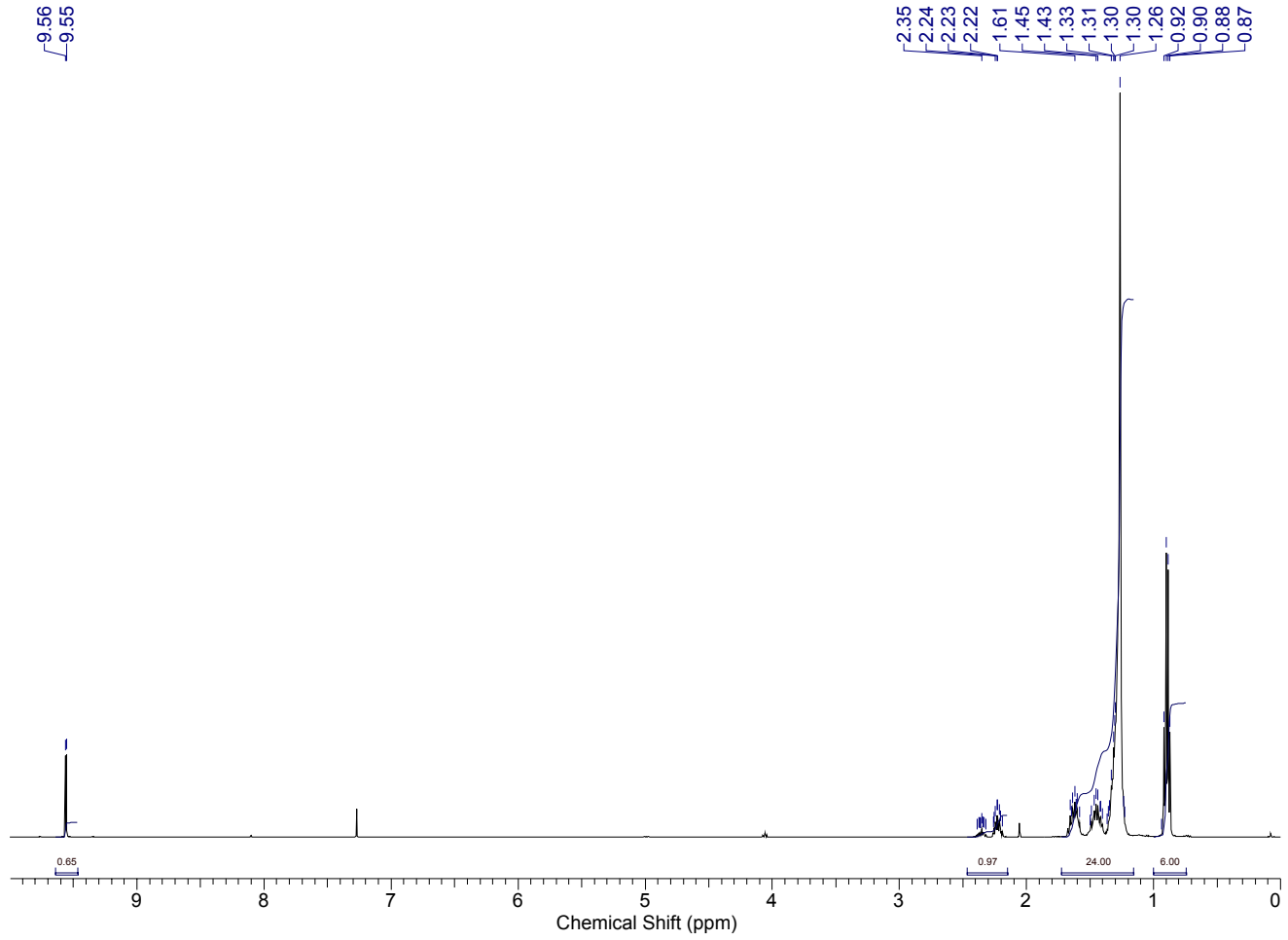

9.65
2.48
2.43
2.41
2.40
2.38
1.76
1.75
1.75
1.73
1.35
1.34
1.33
1.32
1.31
0.92
0.91
0.89
0.74
3.00
1.17
2.16
1.09
4.09
3.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


204.33
173.38
51.58
50.99
31.34
28.95
28.45
23.53
22.66
13.78
O
H
CO2Me
4f
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


9.55
3.64
2.34
2.31
2.30
2.29
2.28
1.94
1.92
1.30
1.29
1.28
1.28
1.27
1.26
0.88
0.86
0.85
0.84
3.00
3.04
1.06
2.10
1.12
4.10
3.12
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


205.83
51.98
31.90
29.59
29.33
29.26
28.93
28.61
27.09
22.77
22.69
14.13
13.91
O
H
C10H21
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

**4j**


9.56
9.55
2.35
2.24
2.23
2.22
1.61
1.45
1.43
1.33
1.31
1.30
1.30
1.26
0.92
0.90
0.88
0.87
0.65
0.97
24.00
6.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

$^{7}$Li NMR of the reaction mixture when 1,2-epoxypentane was added to *n*-BuLi (1.95 equiv. THF, 25 °C, 1h) (above), and when 1,2-epoxypentane was added to LTMP (1.95 equiv. THF, 25 °C, 1h) (below)