Supporting Information

First Stereoselective Addition of Grignard Reagents to *P*-Chirogenic *N*-Phosphinoylimines

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1. General.

All the solvents used were dried and freshly distilled in argon atmosphere. Tetrahydrofuran and diethyl ether were distilled under sodium and benzophenone, toluene and heptane were distilled over sodium, dichloromethane and 1,2-dichloroethane were dried with calcium hydride and fractionally distilled. Chlorobenzene was simply dried with activated Linde 4Å molecular sieves.

Benzaldehyde, triethylamine and benzylamine were distilled just before use. Palladium on carbon (10%, 50% wet with water for safety) was purchased from Acros and stored in a drying device. Titanium tetrachloride was used like a 1 M solution in dichloromethane. Alkyl- and aryl- magnesium halides solutions were purchased from Aldrich and Acros or prepared just by adding a solution of corresponding organohalide on the activated magnesium and refluxing the resulting solutions for 2h.

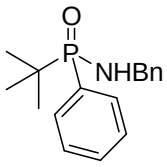
All the reactions were performed under argon atmosphere and in flamed under high vacuum flasks. Thin-layer chromatography (TLC) was carried out on aluminum plates silica gel 60 F_{254} purchased from Merck. Chromatography columns were performed with Merck silica gel Si 60 (40-63μm). All hydrogenation reactions were carried out in a 75 ml standard stainless steel autoclave.

Compounds **4** and **5** were prepared according to literature procedure[1].
^{1}H,^{13}C and large band decoupled ^{31}P nuclear magnetic resonance (NMR) spectra were recorded at 300, 75 and 162 MHz, respectively. Chemical shifts are reported in δ units, parts per million (ppm) from tetramethylsilane and were measured relative to the signals for residual chloroform (7.26 ppm for proton and 77.00 for carbon NMR spectra). Coupling constants *J* are given in Hz. Coupling patterns are abbreviated as, for example, br (broad) s (singlet), d (doublet), t (triplet) and m (multiplet).
Mass spectra were recorded by HRMS by electrospray ionization method obtained with a microTOF LC Brucker Daltonics microTOF LC from Brucker Daltonics apparatus.
Melting ranges (m.p.) given were found to be reproducible after resolidification.

[1] Haynes, R. K.; Au-Yeung, T-L.; Chan, W-K.; Lam, W-L.; Li, Z-Y.; Yeung, L-L.; Chan, A. S. C.; Li, P.; Koen, M.; Mitchell, C. R.; Vonwiller, S. C. *Eur. J. Org. Chem.*, **2000**, 3205-3216, and cited references.

2. Preparation of substrates.

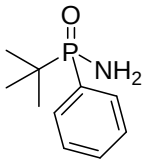
(±)-6



To a solution of triethylamine (0.39 mL, 2.8 mmol) and bromide **5** (0.326 g, 1.25 mmol) in Et_2O (10 mL) was added benzylamine (0.687 mL, 6.25 mmol) at room temperature. The mixture was stirred for 16 h and the white precipitate of ammonium bromide was filtered off. The filtrate was then poured into a saturated NH_4Cl solution (15 mL). The aqueous layer was extracted with Et_2O (3x15 mL) and the combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. Silica gel column chromatography (EtOAc/cyclohexane 4:1) of the crude mixture afforded pure **3** (261 mg, 0.91 mmol, 73% yield) as a white solid. (mp = 148.7-151.3 °C) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.896-7.271(m, 10H, C-*H* arom.), 4.192 (ABd, J_{AB} = 79.3 Hz, $^3J_{P\text{-}H}$ = 3 Hz, 2H, O=P-*CH*$_2$-NH-Ph), 2.967 (br s, 1H, O=P-*NH*-CH_2-Ph), 1.169 (d, $^3J_{P\text{-}H}$ = 15 Hz, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.934 (d, $^3J_{P\text{-}C}$ = 7.75 Hz, *C* quat. arom.), 133.792 (d, $^2J_{P\text{-}C}$ = 8.32 Hz, 2 *C*-H arom.), 131.760 (d, $^4J_{P\text{-}C}$ = 2.4 Hz, *C*-H arom.), 128.751 (d, $^1J_{P\text{-}C}$ = 58.72 Hz, *C* quat. arom.),128.582 (s, 2 *C*-H arom.), 128.209 (d, $^3J_{P\text{-}C}$ = 11.62 Hz, 2 *C*-H arom), 127.662 (s, 1 *C*-H arom.), 127.325 (s, 2 *C*-H arom.), 44.376 (d, $^2J_{P\text{-}C}$ = 2.7 Hz, -*C*H_2-) , 32.165 (d, $^1J_{P\text{-}C}$ = 89.1 Hz, *C* quat. *t*-Bu.), 24.944 (s, 3 –*C*H_3, *t*-Bu); ^{31}P NMR(162 MHz, $CDCl_3$) δ 43.2849. HMRS calculated for $C_{17}H_{22}NNaOP$ 310.1331, found 310.1306.

(*R*)-(-)-**6**: $[\alpha]_D^{20}$ = -7.4° (c 1, MeOH).

(±)-7

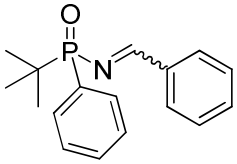


Compound **6** (200 mg, 0.7 mmol), Pd/C (20 mg) and EtOH (5 mL) were placed in the autoclave and flushed three times with hydrogen before pressuring up to 20 Bar. The mixture was stirred at room temperature for 24 h and then depressurized. The solution was filtered through a Celite pad that was thoroughly rinsed with ethanol. The solvent was removed *in vacuo* affording pure phosphinamide **7** (0.135 g, 0.69 mmol, 98 % yield) as a colorless needles. (mp = 128.1-133.5) ^{1}H NMR (300 MHz,

$CDCl_3$) δ 7.873-7.413 (m, 5H, C-*H* arom.), 2.897 (br s, 2H, -NH_2) 1.134 (d, $^3J_{P\text{-}H}$ = 15.3 Hz, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.191 (d, $^2J_{P\text{-}C}$ = 8.32 Hz, 2 *C*-H arom.), 131.842 (d, $^4J_{P\text{-}C}$ = 2.48 Hz, *C*-H arom.), 130.04 (d, $^1J_{P\text{-}C}$ = 115.09 Hz, *C* quat. arom.), 128.079 (d, $^3J_{P\text{-}C}$ = 11.55 Hz, 2 *C*-H arom), 32.304 (d, $^1J_{P\text{-}C}$ = 92.25 Hz, *C* quat. *t*-Bu.), 24.672 (s, 3 –CH_3, *t*-Bu); ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.5063. HMRS calculated for $C_{10}H_{16}NNaOP$ 220.0862, found 220.0850.

(*R*)-(-)-**7**: $[\alpha]_D^{20}$ = -12.6 (c 1, $CHCl_3$).

(±)-1



To a solution of benzaldehyde (0.08 ml, 0.76 mmol), P-*t*-butyl-P-phenyl phosphinamide (0.150 mg, 0.76 mmol) and triethylamine (0.32 ml, 2.28 mmol) in dichloromethane at 0°C was added $TiCl_4$ (0.38 ml, 0.38 mmol) dropwise. The reaction mixture was allowed to stir for 2 h before the solvent was removed *in vacuo*. The yellow oily solid was diluted with ethyl acetate and the precipitate filtered through Celite. The filtrate was concentrated *in vacuo*. Crude imine was purified by flash-chromatography (EtOAc 100%) affording pure phosphinoyl benzaldimine **1** (162 mg, 75% yield) that was isolated as one single isomer. White solid (mp = 176.3-177.7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.21 (d, $^3J_{P\text{-}H}$ = 29.7 Hz, 1H, N=C-*H*), 8.01-7.44 (m, 10H, C-*H* arom), 1.19 (d, $^3J_{P\text{-}H}$ = 15.3 Hz, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.251 (d, $^2J_{P\text{-}C}$ = 8.1 Hz, N=*C*-H), 136.032 (d, $^3J_{P\text{-}C}$ = 23.25 Hz, *C* quat. arom.), 133.193 (d, $^2J_{P\text{-}C}$ = 14.77 Hz, 2 *C*-H arom.), 132.994 (s, 2 *C*-H arom.), 131.645 (d, $^4J_{P\text{-}C}$ = 2.62 Hz, *C*-H arom.), 130.141 (d, $^1J_{P\text{-}C}$ = 113.02 Hz, *C* quat. arom.), 129.901(s, 1 *C*-H arom.), 128.871 (s, 2 *C*-H arom.), 127.968 (d, $^3J_{P\text{-}C}$ = 11.17 Hz, 2 *C*-H arom), 32.893 (d, $^1J_{P\text{-}C}$ = 88.35 Hz, *C* quat. *t*-Bu.) , 24.428 (s, 3 –*C*H_3, *t*-Bu); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.0214. HMRS calculated for $C_{17}H_{20}NNaOP$ 308.1175 found 308.1154.

(*R*)-(+)-**1**: $[\alpha]_D^{20}$ = +84.9° (c 1.88, Acetone).

3. 1, 2 Grignard additions to P-*tert*-butyl-P-phenyl-N-phosphinoyl benzaldimine (1)

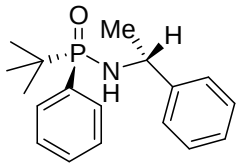
3.1 General experimental procedure.

A representative experimental procedure is shown by the synthesis of **2a** and **3a** adducts. Methyl magnesium bromide (3 M solution in diethyl ether, 3 equiv., 0.6 mmol, 200 μL) was added dropwise at

0°C to a solution of **1** (1equiv., 0.2 mmol, 57 mg) in dichloromethane (1.5 mL). The mixture was stirred at room temperature for 3h, then cooled to 0°C, quenched with aqueous $KHSO_4$ (0.5 M, 10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic phases were washed once with brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The slightly yellow oily solid was purified by flash chromatography (EtOAc 100%) affording the two diastereoisomers (major/minor = 85 : 15) **2a** and **3a** as colorless solid with 70 and 9% yield respectively.

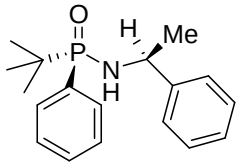
3.2 Characterization data of compunds 2 and 3a-l.

(*R*P,*R*)-(+)-**2a** (Major)



Colorless solid (mp = 164.1-167.6°C). $[\alpha]_D^{20}$ = +42.8 (c = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.672-7.206 (m, 10H, C-*H* arom.), 4.274 (brm, 1H, C-*H*), 2.86 (brm, 1H, N-*H*), 1.587 (d, *J* = 6.9 Hz, 1H, H-C-*CH*$_3$), 1.141 (d, $^3J_{PH}$ = 14.7 Hz, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.362 (d, $^3J_{P\text{-}C}$ = 7.12 Hz, *C* quat. arom.), 134.024 (d, $^2J_{P\text{-}C}$ = 8.47 Hz, 2 *C*-H arom.), 131.574 (d, $^4J_{P\text{-}C}$ = 2.4 Hz, *C*-H arom.), 129.952 (d, $^1J_{P\text{-}C}$ = 48.37 Hz, *C* quat. arom.), 128.525 (s, 2 *C*-H arom.), 127.869 (d, $^3J_{P\text{-}C}$ = 11.85 Hz, 2 *C*-H arom), 126.971 (s, 1 *C*-H arom.), 125.765(s, 2 *C*-H arom.), 50.712 (d, $^2J_{P\text{-}C}$ = 2.55 Hz, HN-*C*H-), , 32.089 (d, $^1J_{P\text{-}C}$ = 88.72 Hz, *C* quat. *t*-Bu.), 24.950 (s, 3 –*C*H$_3$, *t*-Bu); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.30. HMRS calculated for $C_{18}H_{24}NNaOP$ 324.1488, found 324.1456.

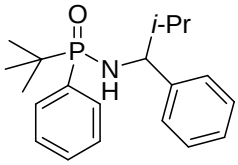
(*R*$_P$,*S*)-(-)-**3a** (Minor)



Colorless solid (mp = 151.4-153.8°C). $[\alpha]_D^{20}$= -39.8° (c = 1.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.21 (m, 10H, C-*H* arom.), 4.512 (sestet, $^2J_{PH}$ = $^3J_{H\text{-}C\text{-}N\text{-}H}$ = $J_{H\text{-}C\text{-}Me}$ = 7.2 Hz, 1H, C-*H*), 2.855 (t, $^2J_{PH}$ = $^3J_{H\text{-}C\text{-}N\text{-}H}$ = 8.7 Hz, 1H, N-*H*), 1.402 (d, *J*= 6.6 Hz, 1H, H-C-*CH*$_3$), 1.085 (d, $^3J_{PH}$= 15 Hz, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.514 (d, $^3J_{P\text{-}C}$ = 4.27 Hz, *C* quat. arom.), 133.447 (d, $^2J_{P\text{-}C}$ = 8.45 Hz, 2 *C*-H arom.), 131.484 (d, $^4J_{P\text{-}C}$ = 2.49 Hz, *C*-H arom.) , 131.026 (d, $^1J_{P\text{-}C}$ = 115.87 Hz, *C* quat. arom.), 128.492 (s, 2 *C*-H arom.), 127.963 (d, $^3J_{P\text{-}C}$ = 11.55 Hz, 2 *C*-H arom), 126.996 (s, 1 *C*-H arom.),

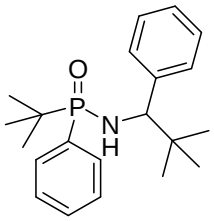
126.185 (s, 2 *C*-H arom.), 49.871(d, $^{2}J_{P\text{-}C}$ = 2.41 Hz, HN-*C*H-), 32.448 (d, $^{1}J_{P\text{-}C}$ = 88.72 Hz, *C* quat. *t*-Bu.), 24.948 (d, $^{3}J_{P\text{-}C}$ = 4.27 Hz, HC-*C*H_3), 24.835; ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.5. HMRS calculated for $C_{18}H_{24}NNaOP$ 324.1488, found 324.1461.

Addition of *i*-PrMgBr: **2b-2b'/3b-3b'**



Major/minor = 75 : 25. 98% Yield, white solid (mp = 178.3-182.1°C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.868-7.00 (m, 10H, C-*H* arom. minor + major), 4.126 (brm, 1H, C-*H* major), 3.859 (brm, 1H, C-*H* minor), 3.147 (brm, 1H, N-*H* minor), 3.019 (brm, 1H, N-*H* major), 2.039 (m, 1H, *H*-C$(CH_3)_2$ minor), 1.935(m, 1H, *H*-C$(CH_3)_2$ major),1.143 (d, $^{3}J_{PH}$= 15 Hz, 9H, *t*-Bu minor), 1.02 (d, J = 6.9 Hz, 3H, H-C-*CH_3* minor), 1.015 (d, $^{3}J_{PH}$= 15 Hz, 9H, *t*-Bu major) 0.874 (d, J = 6.9 Hz, 3H, *H*-C-*CH_3* major), 0.814 (d, J = 7.8 Hz, 3H, *H*-C-*CH_3* minor) 0.79 (d, J = 6.6 Hz, 3H, H-C-*CH_3* major); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.268, 134.139, 134.021, 132.987, 132.878, 131.457, 131.421, 128.061, 128.018, 127.920, 127.543, 127.386, 127.081, 126.968, 126.757, 60.357, 60.322, 35.913, 35.889, 35.833, 35.667, 35.596, 33.700, 32.498, 24.949, 24.833, 19.288, 19.132, 18.975; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.68 (minor), 40.32 (major). HMRS calculated for $C_{20}H_{28}NNaOP$ 352.1801, found 352.1774.

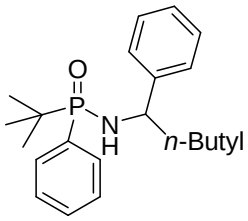
Addition of *t*-BuMgBr: **2c-2c'/3c-3c'**



Major/minor = 65 : 35. 90% Yield, pale yellow solid (mp = 198.7-205.7°C). ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.834-6.924 (m, 10H, C-*H* arom. minor + major), 4.068 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.9 Hz, 1H, C-*H* major), 3.782 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 11.1 Hz, 1H, C-*H* minor), 3.221 (brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 10.8 Hz, 1H, N-*H* minor), 3.063 (brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.3 Hz, 1H, N-*H* major), 1.078 (d, $^{3}J_{PH}$ = 6.6 Hz, 9H, HC-*tBu* major), 0.859 (m, 27H, 2 *t*-Bu [major + minor] + HC-*tBu* minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.319, 142.293, 142.253, 142.128, 142.102, 134.164, 134.046, 132.607, 132.500, 131.376, 131.343, 131.124, 131.094, 129.714, 129.679, 128.245, 128.092, 127.944, 127.510, 127.487, 127.328, 127.171,

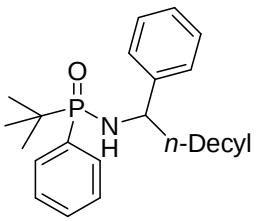
126.703, 126.544, 63.239, 63.200, 62.710, 62.669, 35.677, 35.610, 35.580, 35.544, 34.032, 32.817, 31.491, 31.053, 29.679, 26.940, 24.999, 24.777; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.31 (minor), 40.28 (major). HMRS calculated for $C_{21}H_{31}NOP$ 344.2138, found 344.2141.

Addition of *n*-BuMgBr: **2d-2d'/3d-3d'**



Major/minor = 70: 30. 93% Yield, white solid, (mp = 142.1-146.7 °C). ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.90-7.08 (m, 10H, C-*H* arom. minor + major), 4.293 (m, 1H, C-*H* major), 4.06 (m, 1H, C-*H* minor), 2.903 (brs, 1H, N-*H* minor + major), 1.845 (m, 4H, H-C-*CH_2*-*CH_2*- major + minor), 1.239 (m, 2H, -*CH_2*-CH_3 major + minor), 1.124 (d, $^3J_{PH}$= 15 Hz, *9H*, *t*-Bu minor), 1.046 (d, $^3J_{PH}$= 15 Hz, 9H, *t*-Bu major), 0.798 (t, *J* = 7.5 Hz, 3H, -*CH_3* minor), 0.75 (t, *J* = 7.2 Hz, 3H, -*CH_3* major); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.418, 144.371, 144.264, 144.187, 134.128, 134.011, 133.250, 133.139, 131.850, 131.836, 131.455, 131.421, 131.354, 131.319, 130.308, 128.433, 128.369, 128.016, 127.864, 127.690, 127.534, 126.938, 126.865, 126.594, 126.386, 55.083, 55.046, 54.838, 54.805, 39.791, 39.764, 38.925, 38.862, 33.225, 32.607, 32.035, 31.423, 28.126, 28.075, 24.923, 24.836, 22.463, 22.379, 13.906, 13.810; ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.41 (major), 40.07 (minor). HMRS calculated for $C_{21}H_{30}NNaOP$ 366.1957, found 366.1938.

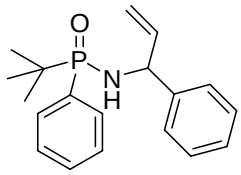
Addition of *n*-Decyl MgBr: **2e-2e'/3e-3e'**



Major/minor = 70 : 30. 91% Yield, white solid, (mp = 237.6-238.9°C). ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.895-7.075 (m, 10H, C-*H* arom. minor + major), 4.296 (quintet, $^2J_{PH}$ = $^3J_{H\text{-}C\text{-}N\text{-}H}$ = $J_{H\text{-}C\text{-}CH2}$ = 8.1 Hz, 1H, C-*H* major) , 4.053 (quintet, $^2J_{PH}$ = $^3J_{H\text{-}C\text{-}N\text{-}H}$ = $J_{H\text{-}C\text{-}CH2}$ = 9.3 Hz, 1H, C-*H* minor), 2.925 (brt, $^2J_{PH}$ = $^3J_{H\text{-}C\text{-}N\text{-}H}$ = 9.3 Hz, 1H, N-*H* minor), 2.871 (brt, $^2J_{PH}$ = $^3J_{H\text{-}C\text{-}N\text{-}H}$ = 8.7 Hz, 1H, N-*H* major), 1.820 ,(m, 2H, HC-*CH_2*- minor + major), 1.181 (m, 16H, 8 -*CH_2*- minor + major), 1.113 (d, $^3J_{PH}$ = 14.7 Hz, *9H*, *t*-

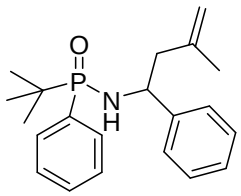
Bu minor), 1;035(d, $^{3}J_{PH}$= 14.7 Hz, 9H, *t*-Bu major), 0.859 (t, *J*= 6.6 Hz, 3H, -CH_3 major), 0.853(t, J= 6.6 Hz, 3H, -CH_3 minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.429, 144.384, 134.096, 133.979, 133.240, 133.129, 131.826, 131.386, 131.303, 131.275, 130.296, 128.403, 128.334, 127.990, 127.838, 127.659, 127.503, 126.905, 126.832, 126.563, 126.369, 55.079, 55.047, 54.817, 54.785, 40.045, 40.019, 39.185, 39.122, 33.186, 32.587, 31.996, 31.836, 31.402, 29.659, 29.493, 29.446, 29.376, 29.321, 29.279, 29.231, 25.949, 25.918, 24.901, 24.805, 22.620, 14.064; ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.28 (minor), 41.8 (major). HMRS calculated for $C_{27}H_{42}NNaOP$ 450.2896, found 450.2849.

Addition of Vinyl MgBr: **2f-2f'**/**3f-3f'**



Major/minor = 60 : 40. 67% Yield, white solid, (mp = 116.4-119.8°C).^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.905-7.161 (m, 10H, C-*H* arom. minor + major), 6.137 (m, 1H, *H*-*C*=CH_2 minor), 5.967 (m, 1H, *H*-*C*=CH_2 major), 5.154 (m, 2H, HC=CH_2 major + minor), 4.801 (m, 1H, C-*H* major + minor), 3.009 (brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.6 Hz, 1H, N-*H* minor), 2.952 (brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.6 Hz, 1H, N-*H* major), 1.156 (d, $^{3}J_{PH}$= 15 Hz, 9H, *t*-Bu minor), 1.115 (d, $^{3}J_{PH}$= 15 Hz, 9H, *t*-Bu major); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.702, 142.666, 142.311, 142.227, 140.780, 140.756, 139.822, 139.745, 133.929, 133.842, 133.729, 131.642, 131.608, 131.548, 131.515, 130.571, 129.006, 128.524, 128.492, 127.955, 127.882, 127.800, 127.727, 127.249, 127.135, 126.958, 115.389, 56.382, 56.357, 33.047, 32.960, 31.859, 31.769, 24.968, 24.904,; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.99 (minor), 41.47 (major). HMRS calculated for $C_{19}H_{24}LiNOP$ 320.1750, found 320.1736.

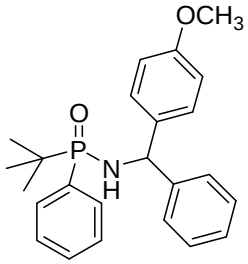
Addition of 2-Methylallyl MgBr: **2g-2g'**/**3g-3g'**



Major/minor = 75 : 25. 85% Yield, white solid, (mp = 129.7-131.2°C). ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.851-7.132 (m, 10H, C-*H* arom. minor + major), 4.85 (s, 1H, C=*C*-*H* major), 4.796 (s, 1H, C=*C*-*H* major), 4.752 (s, 1H, C=*C*-*H* minor), 4;668 (s, 1H, C=*C*-*H* minor), 4.404 (m, 1H, C-*H* major + minor),

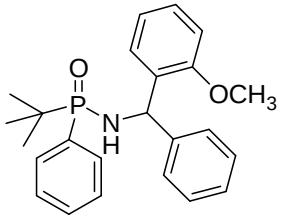
3.141(brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 7.2 Hz, 1H, N-*H* major), 3.026 (brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.6 Hz, 1H, N-*H* minor), 2.605 (m, 2H, -CH_2- major), 2.457 (m, 2H, -CH_2- minor), 1.62 (s, 3H, -CH_3 major) 1.51 (s, 3H, -CH_3 minor), 1.118 (d, $^{3}J_{PH}$= 14.7 Hz, *9H*, *t*-Bu major), 1.061(d, $^{3}J_{PH}$= 14.7 Hz, *9H*, *t*-Bu minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.150, 144.133, 143.781, 143.721, 142.597, 142.435, 133.959, 133.843, 133.198, 133.085, 131.428, 131.393, 131.145, 131.112, 129.910, 128.247, 128.099, 127.973, 127.821, 127.487, 127.330, 126.917, 126.826, 126.608, 126.541, 114.510, 114.181, 52.648, 52.616, 51.857, 51.825, 48.239, 48.160, 48.109, 48.061, 33.291, 32.867, 32.093, 31.695, 24.846, 24.766, 22.365, 22.266; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.74 (major), 40.03 (minor). HMRS calculated for $C_{21}H_{28}LiNOP$ 348.2064, found 348.2030.

Addition of *p*-Anisyl MgBr: **2h-2h'/3h-3h'**



Major/minor = 60 : 40. 97% Yield, pale yellow viscous oil. ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.694-6.783 (m, 14H, C-*H* arom. minor + major), 5.427 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.9 Hz, 1H, C-*H* major), 5.404 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.9 Hz, 1H, C-*H* minor), 3.786 (s, 3H, -OCH_3 major), 3.767(s, 3H, -OCH_3 minor), 3.266 (brt, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9 Hz, 1H, N-*H* minor + major), 1.134 (d, $^{3}J_{PH}$= 15 Hz, 9H, *t*-Bu minor + major); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.569, 144.217, 144.199, 133.910, 133.856, 133.753, 131.503, 128.968, 128.712, 128.385, 128.310, 127.825, 127.716, 127.639, 127.460, 127.007, 126.946, 113.760, 113.683, 57.026, 55.234, 32.954, 31.826, 24.939; ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.35(minor), 42.18 (major). HMRS calculated for $C_{24}H_{28}NNaOP$ 416.1750, found 416.1798.

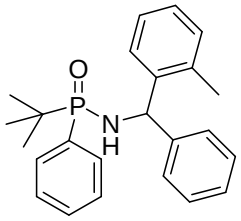
Addition of *o*-Anisyl MgBr: **2i-2i'/3i-3i'**



Major/minor = 60 : 40. 97% Yield, white solid, (mp = 148.2-156.3°C). ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.813-6.869 (m, 14H, C-*H* arom. minor + major), 5.507 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 10.2 Hz, 1H, C-*H* minor),

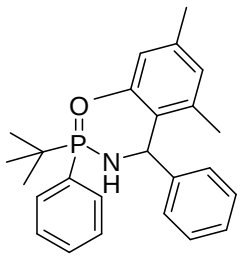
5.436 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 10.8 Hz, 1H, C-*H* major), 4.23 (m, 1H, -*NH* minor + major), 3.714 (s, 3H, -O*CH*$_3$ minor), 3.631(s, 3H, -O*CH*$_3$ major), 1.159 (d, *J* = 14.7 Hz, 9H, *t*-Bu major), 1.104 (d, $^{3}J_{PH}$= 15 Hz, 9H, *t*-Bu minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.085, 156.660, 134.123, 134.006, 133.556, 133.443, 131.862, 131.507, 131.283, 129.379, 128.956, 128.505, 128.453, 127.995, 127.928, 127.846, 127.650, 127.495, 127.046, 126.750, 126.463, 120.991, 120.783, 111.602, 111.508, 56.056, 56.030, 55.471, 55.444, 55.417, 55.372, 33.298, 32.722, 32.572, 32.104, 31.527, 24.962, 24.891; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.65(minor), 41.47 (major). HMRS calculated for $C_{24}H_{28}NNaOP$ 416.1750, found 416.1747.

Addition of *o*-Tolyl MgBr: **2j-2j'/3j-3j'**



Major/minor = 55 : 45. 95% Yield, white solid, (mp = 161.7-165.3°C). ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.796-7.023 (m, 14H, C-*H* arom. minor + major), 5.728 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.3 Hz, 1H, C-*H* minor), 5.516 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.6 Hz, 1H, C-*H* major), 3.361 (t, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.3, 1H, -*NH* minor), 3.199 (t, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.3 Hz, 1H, -*NH* major), 2.157 (s, 3H, -*CH*$_3$ minor), 1.789 (s, 3H, -*CH*$_3$ major), 1.163 (d, $^{3}J_{PH}$ = 14.7 Hz, 9H, *t*-Bu major), 1.092 (d, $^{3}J_{PH}$ = 15 Hz, 9H, *t*-Bu minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.428, 143.395, 143.315, 141.514, 141.471, 141.362, 135.447, 134.053, 133.936, 133.203, 133.091, 131.561, 131.526, 130.694, 130.352, 128.427, 128.401, 128.002, 127.932, 127.849, 127.771, 127.607, 127.106, 127.041, 127.004, 126.868, 126.501, 126.212, 126.066, 54.714, 54.688, 54.223, 54.194, 33.679, 32.752, 32.473, 31.560, 25.010, 24.872, 19.490, 19.100,; ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.00(minor), 41.33 (major). HMRS calculated for $C_{24}H_{28}NNaOP$ 400.1801, found 400.1837.

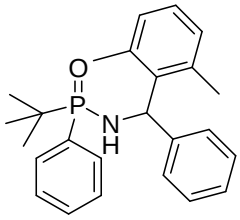
Addition of 2-Mesityl MgBr: **2k-2k'**



Major/minor = 100 : 0. 98% Yield, pale yellow viscous oil. ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.867-7.109

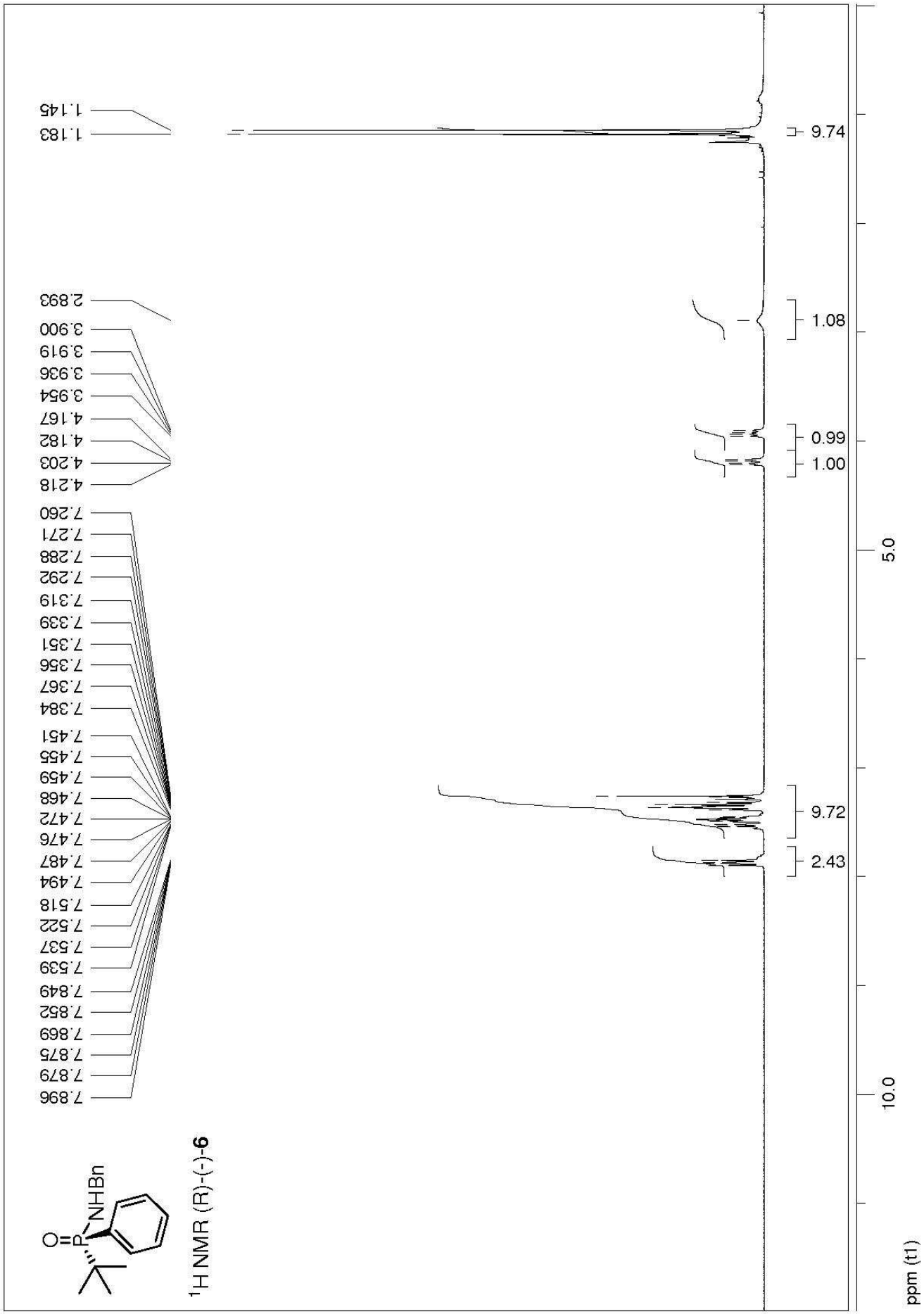
(m, 10H, C-*H* arom), 6.748 (s, 2H, C-*H* arom), 5.823 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 9.9 Hz, 1H, -*CH*), 3.361 (m, 1H, -*NH*), 2.183 (s, 3H, -CH_3), 2.074 (s, 6H, 2-CH_3), 1.04(d, $^{3}J_{PH}$ = 15 Hz, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.555, 143.455, 137.325, 136.497, 135.766, 133.119, 133.010, 131.612, 131.579, 130.733, 130.163, 129.204, 128.232, 128.093, 126.400, 126.144, 52.820, 52.793, 33.632, 32.433, 24.797, 20.850, 20.666; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.35. HMRS calculated for $C_{26}H_{32}LiNOP$ 412.2377, found 412.2339.

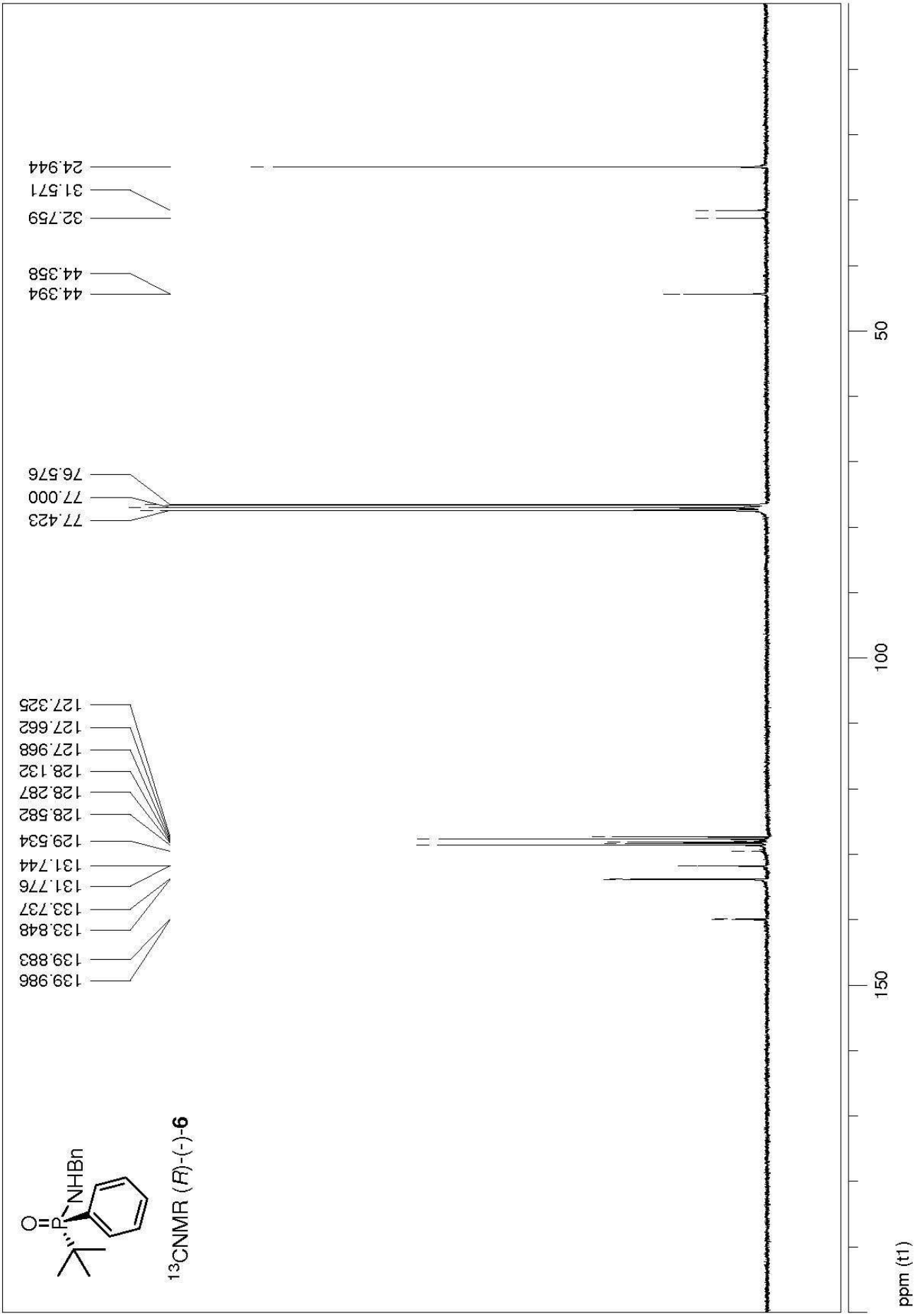
Addition of 2,6-dimethylphenyl MgBr: **2l-2l'/3l-3l'**

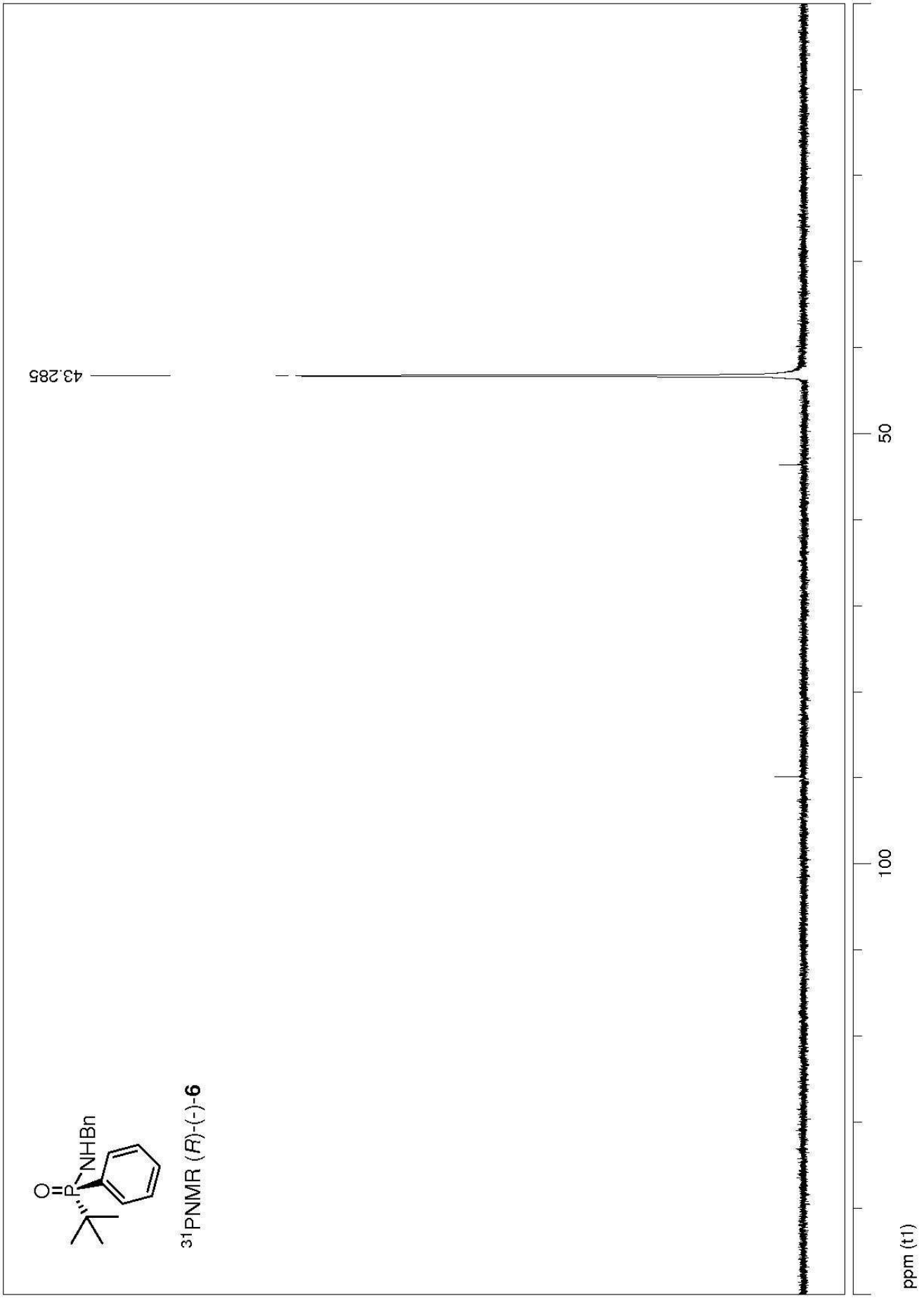


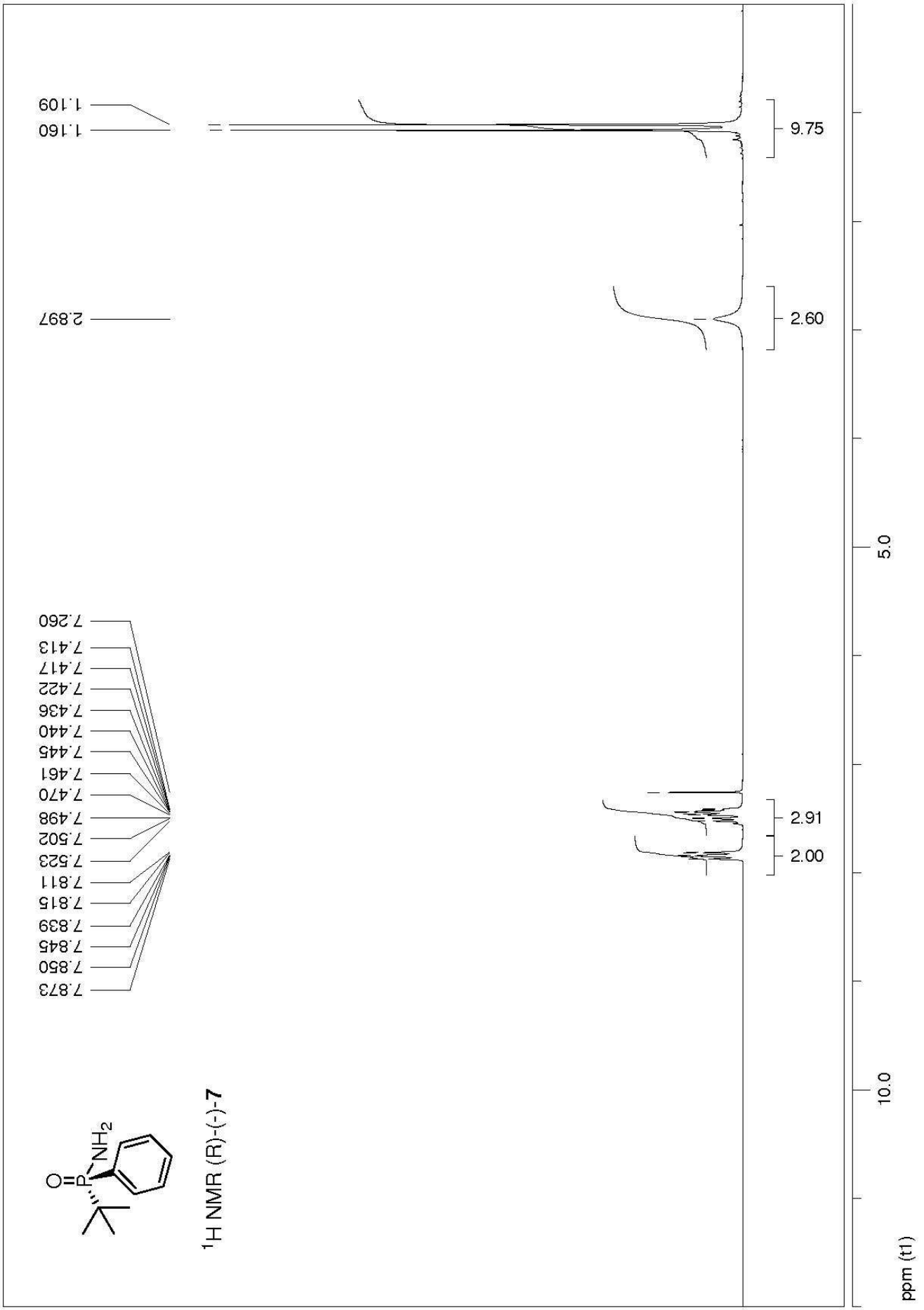
Major/minor = 85 : 15. 99% Yield, pale yellow viscous oil. ^{1}H -NMR (300 MHz, $CDCl_3$) δ 7.942-6.997 (m, 13H, C-*H* arom), 5.963 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 10.8 Hz, 1H, C-*H* major), 5.963 (t, $^{3}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 11.1 Hz, 1H, C-*H* minor) 3.625 (t, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 10.8 Hz, 1H, -*NH* minor), 3.498 (t, $^{2}J_{PH}$ = $^{3}J_{H\text{-}C\text{-}N\text{-}H}$ = 10.8 Hz, 1H, -*NH* major), 2.2 (s, 6H, 2-CH_3 major), 2.2 (s, 6H, 2-CH_3 minor), 1.206 (d, $^{3}J_{PH}$ = 14.7 Hz, 9H, *t*-Bu major), 1.078(d, $^{3}J_{PH}$ = 15 Hz, 9H, *t*-Bu minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.252, 143.154, 140.209, 135.987, 134.247, 134.128, 133.062, 132.953, 131.691, 131.657, 130.678, 129.404, 129.363, 129.155, 128.376, 128.297, 128.151, 127.702, 127.540, 127.243, 127.090, 126.772, 126.517, 126.145, 53.016, 52.990, 33.678, 32.479, 25.130, 24.745, 20.846, 20.778; ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.75 (minor), 41;64 (major). HMRS calculated for $C_{25}H_{31}NOP$ 392.2138, found 392.2154.

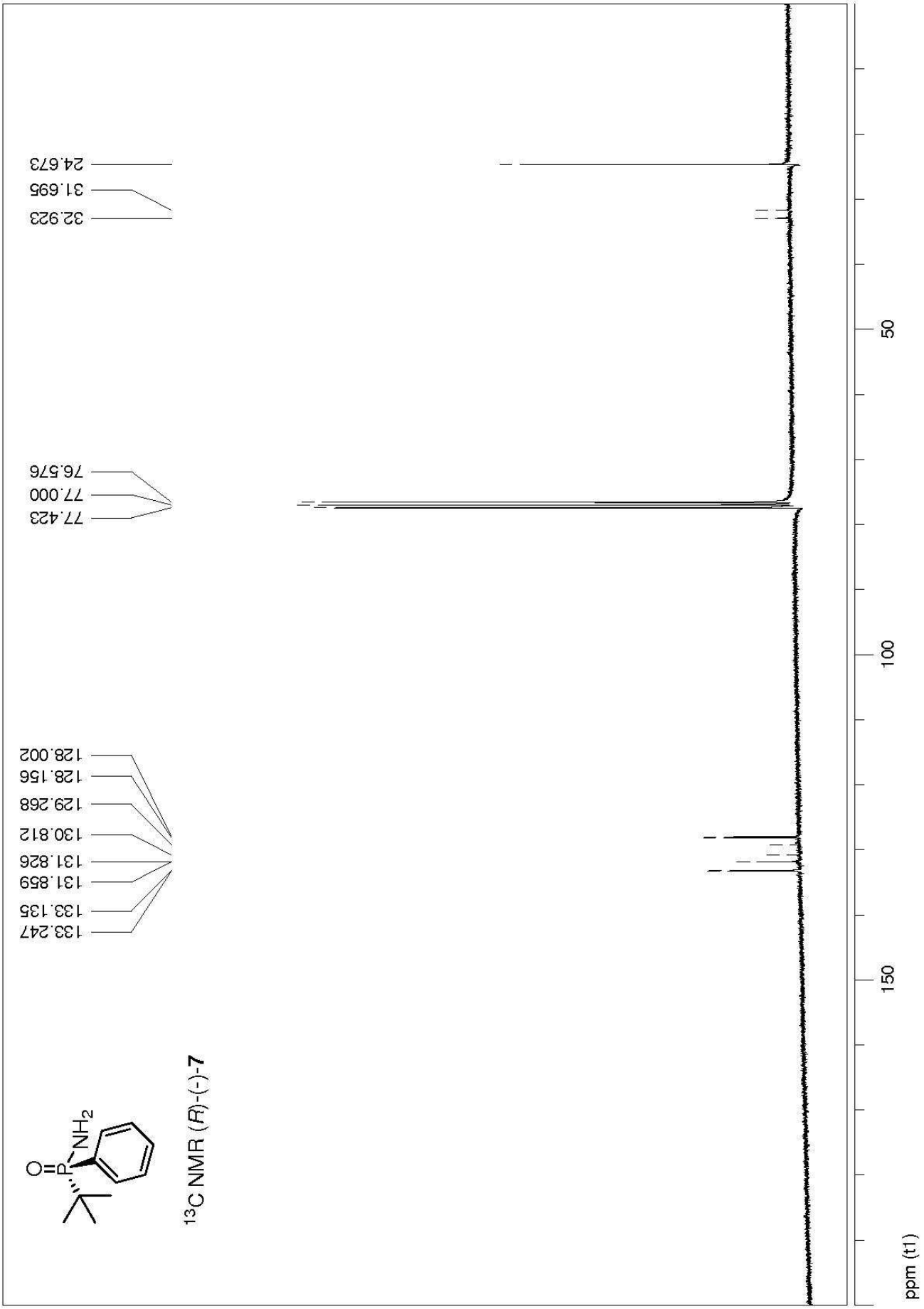
^{1}H-, ^{13}C- and ^{31}P-NMR Spectra

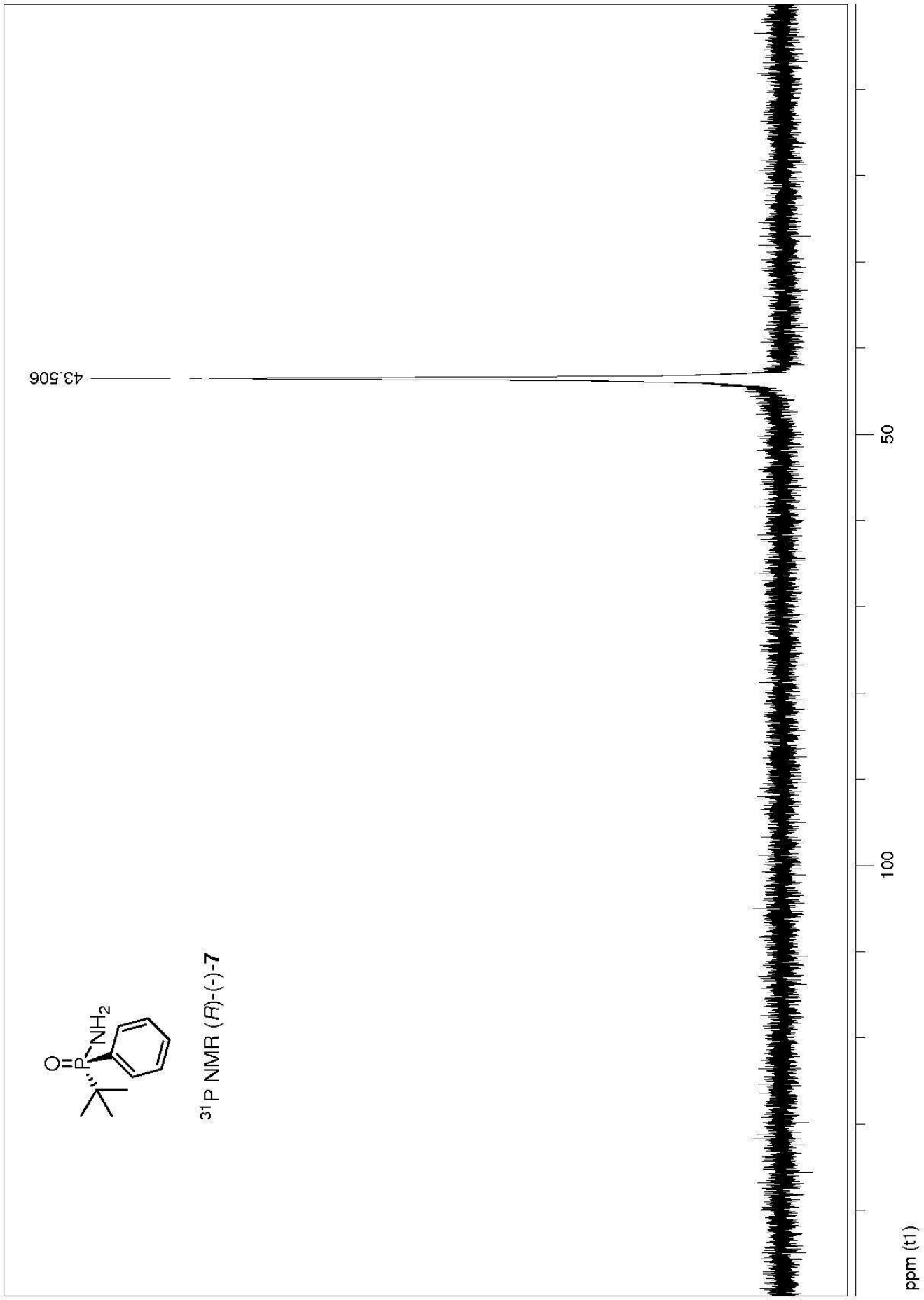

1.145
1.183
2.893
3.900
3.919
3.936
3.954
4.167
4.182
4.203
4.218
7.260
7.271
7.288
7.292
7.319
7.339
7.351
7.356
7.367
7.384
7.451
7.455
7.459
7.468
7.472
7.476
7.487
7.494
7.518
7.522
7.537
7.539
7.849
7.852
7.869
7.875
7.879
7.896
9.74
1.08
0.99
1.00
9.72
2.43
5.0
10.0
ppm (t1)
^{1}H NMR (R)-(-)-**6**
O=P
NHBn


24.944
31.571
32.759
44.358
44.394
76.576
77.000
77.423
127.325
127.662
127.968
128.132
128.287
128.582
129.534
131.744
131.776
133.737
133.848
139.883
139.986
O=P
NHBn
^{13}CNMR (*R*)-(-)-**6**
50
100
150
ppm (t1)

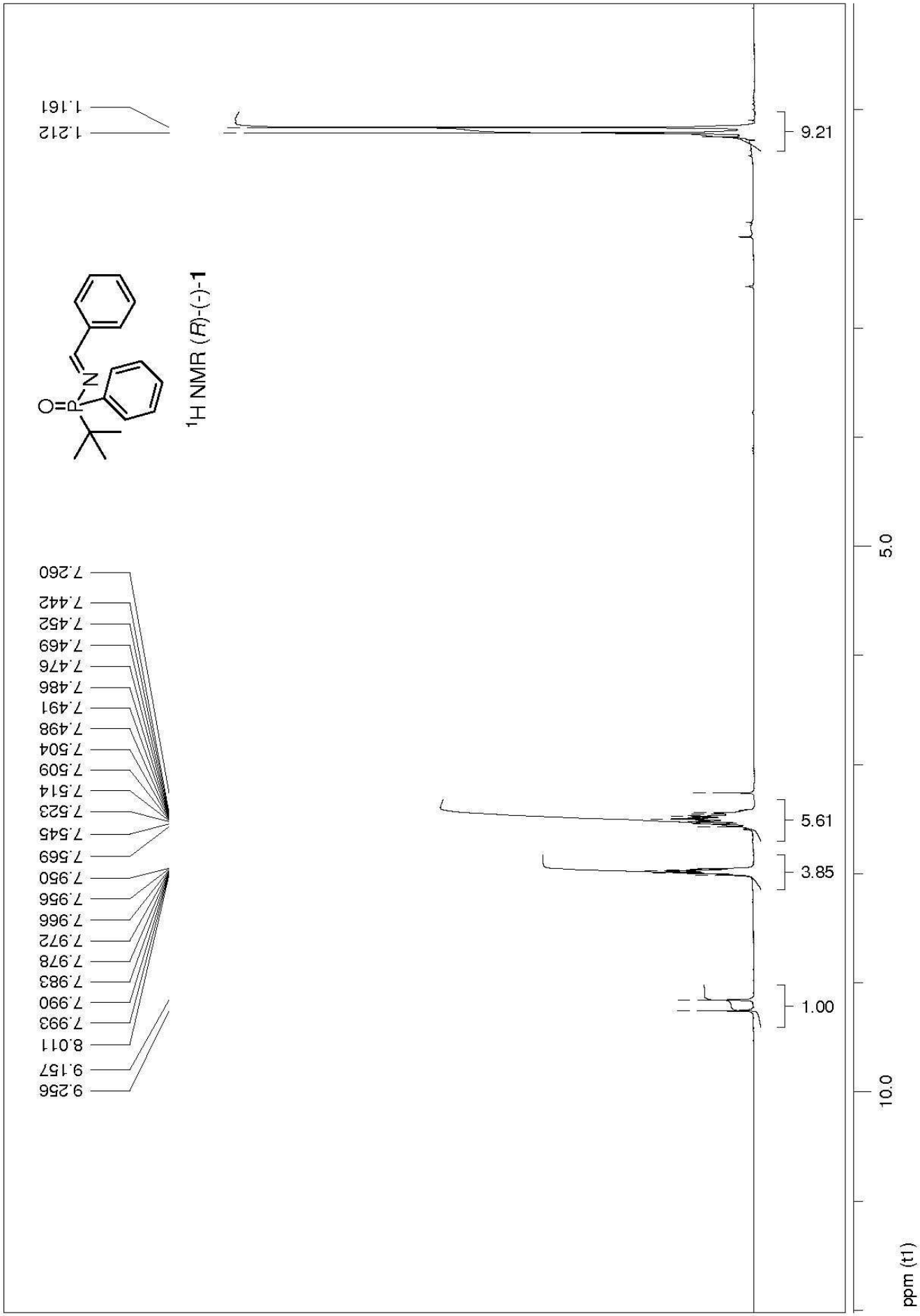

43.285
50
100
ppm (t1)
O=P
NHBn
^{31}PNMR (*R*)-(-)-**6**

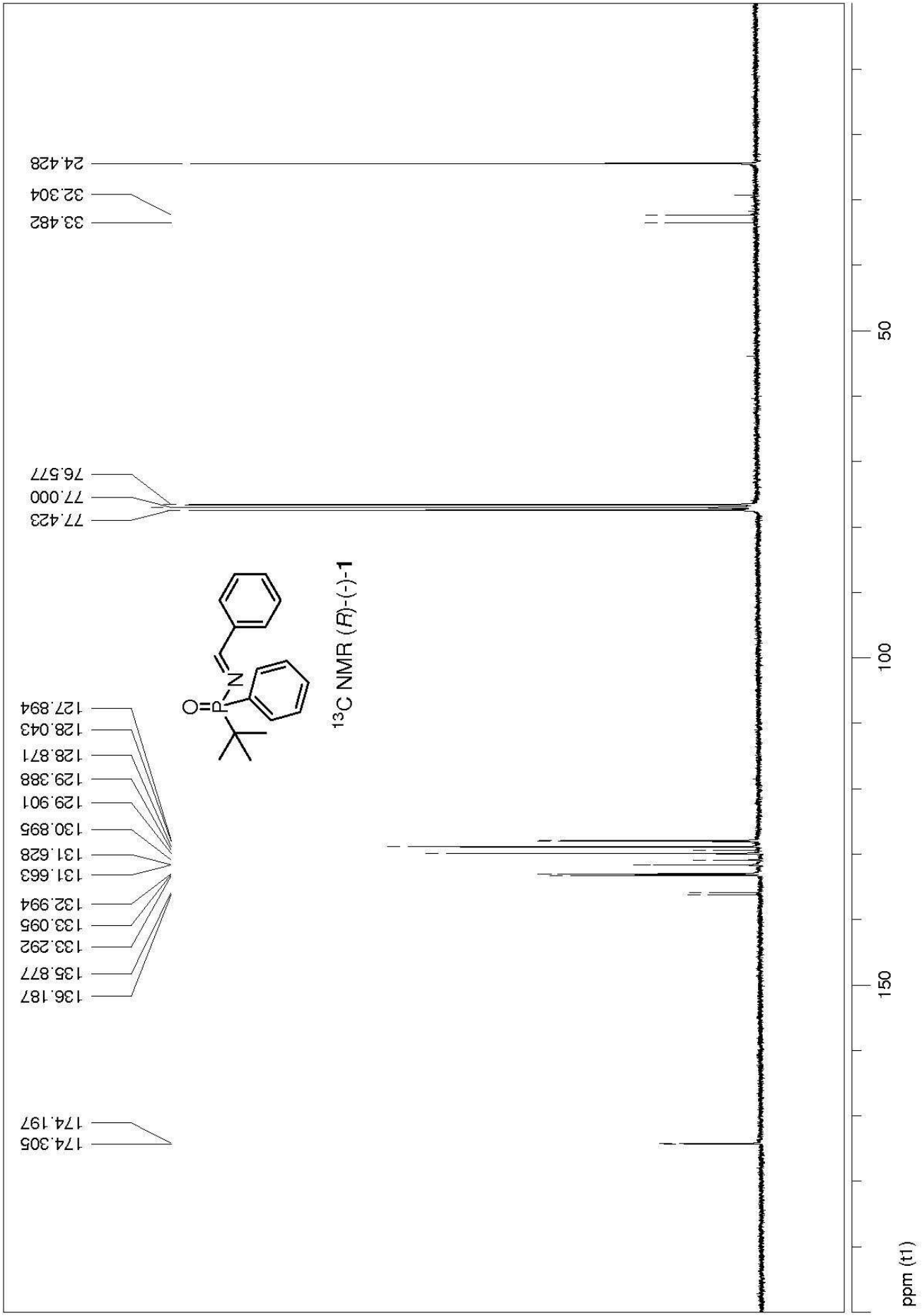

1.109
1.160
2.897
7.260
7.413
7.417
7.422
7.436
7.440
7.445
7.461
7.470
7.498
7.502
7.523
7.811
7.815
7.839
7.845
7.850
7.873
9.75
2.60
2.91
2.00
5.0
10.0
ppm (t1)
^{1}H NMR (R)-(-)-**7**
O=P
NH$_2$

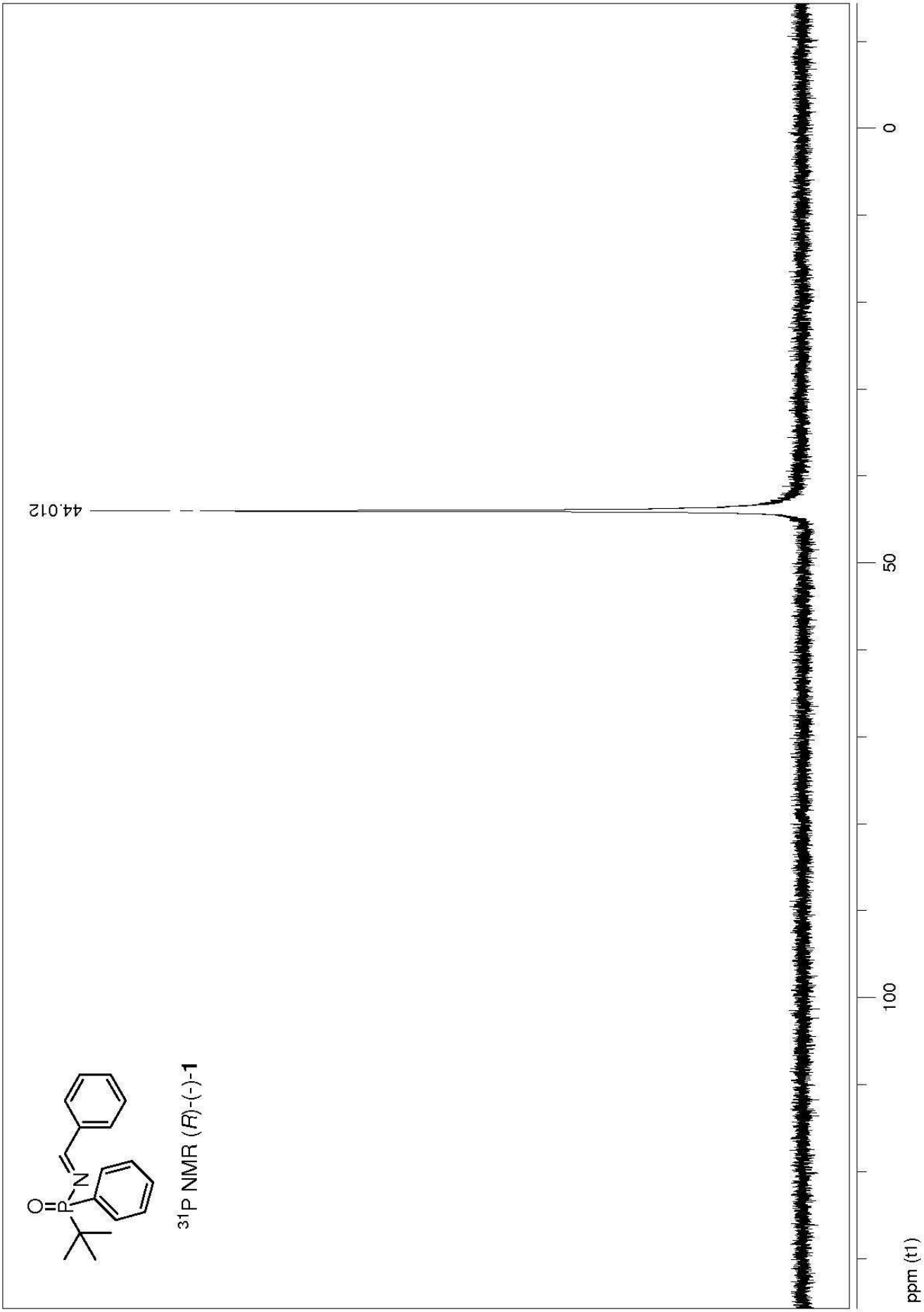

24.673
31.695
32.923
76.576
77.000
77.423
128.002
128.156
129.268
130.812
131.826
131.859
133.135
133.247
50
100
150
ppm (t1)
^{13}C NMR (*R*)-(-)-**7**
O=P
NH$_2$

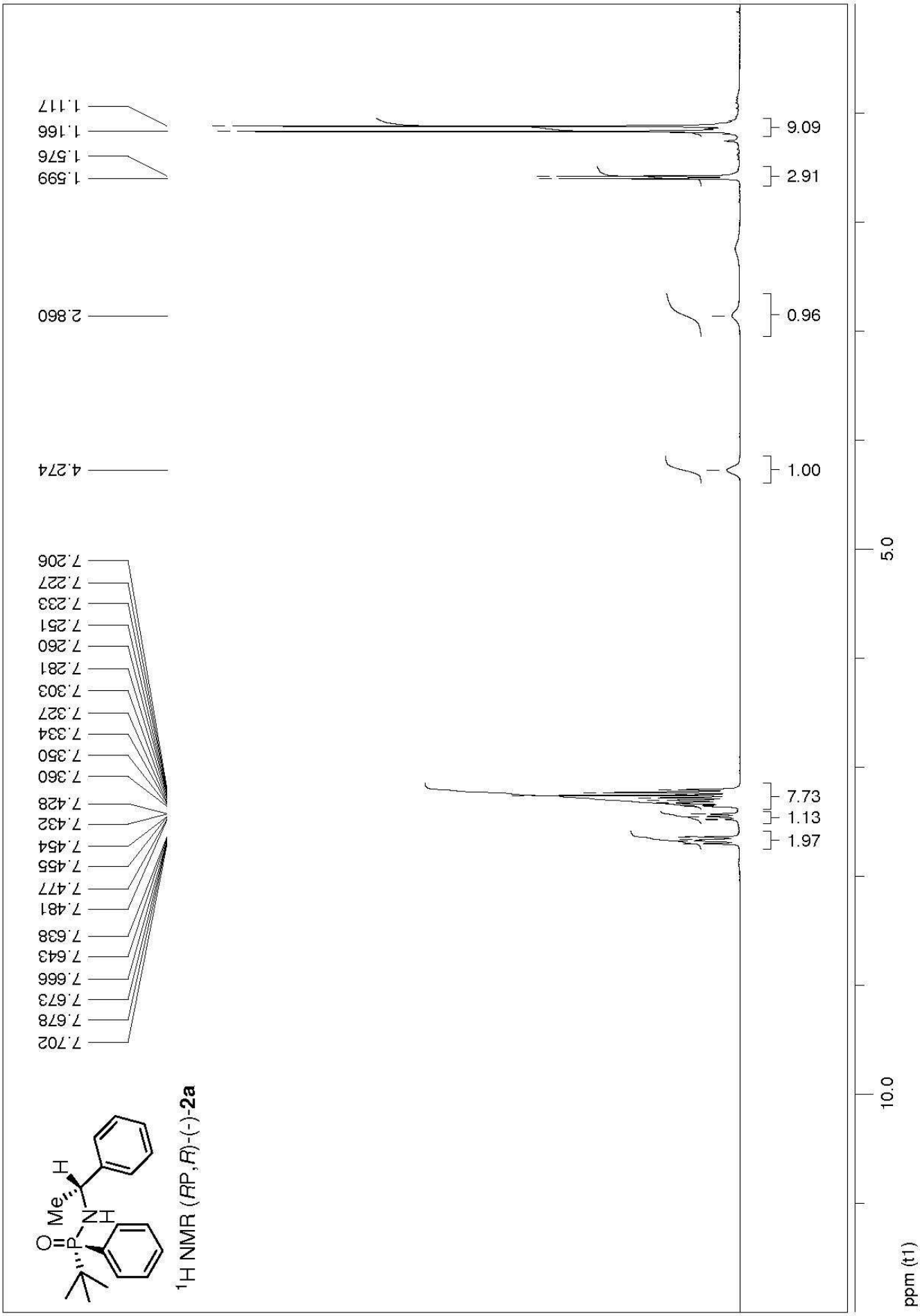


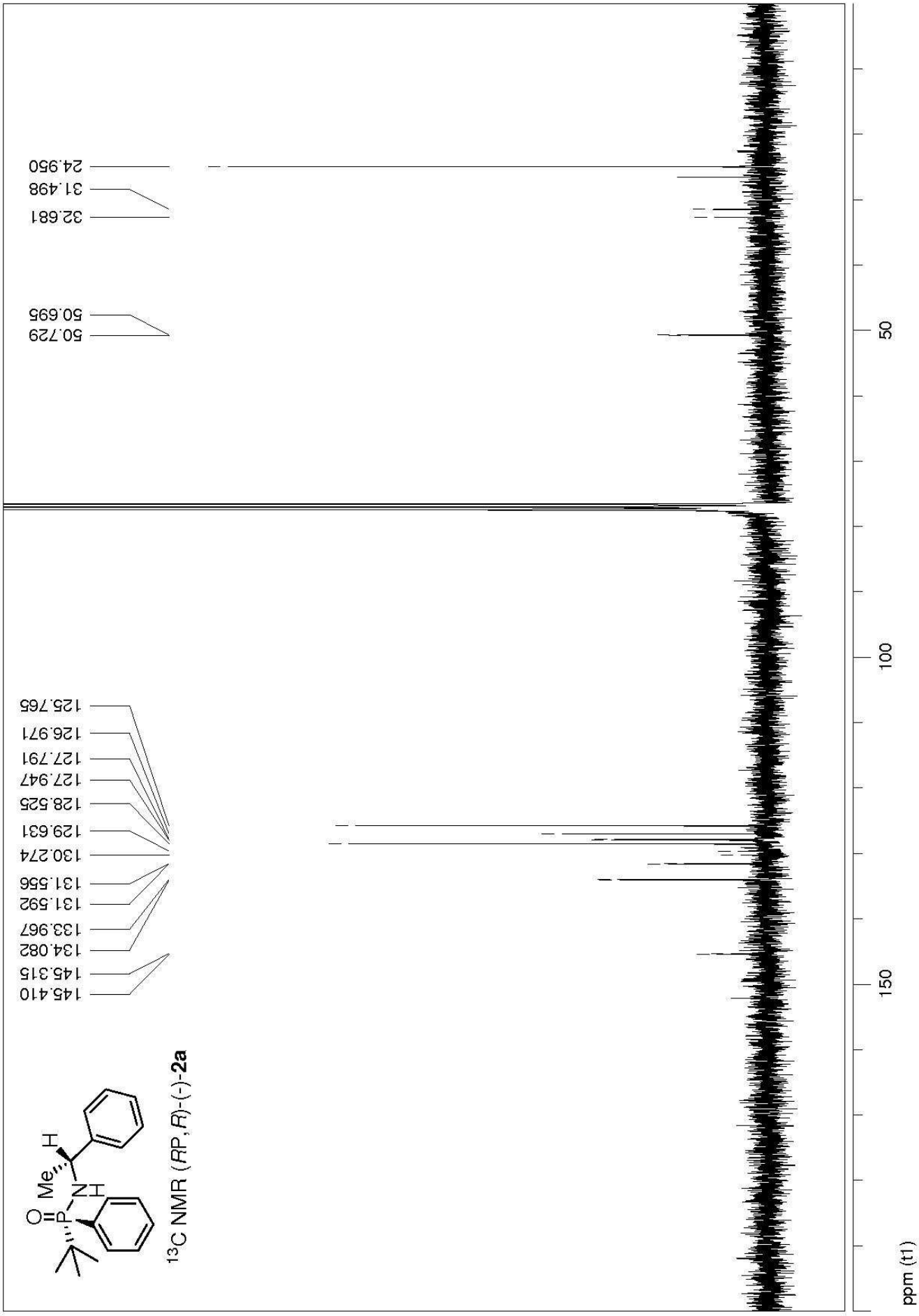
^{31}P NMR (*R*)-(-)-**7**

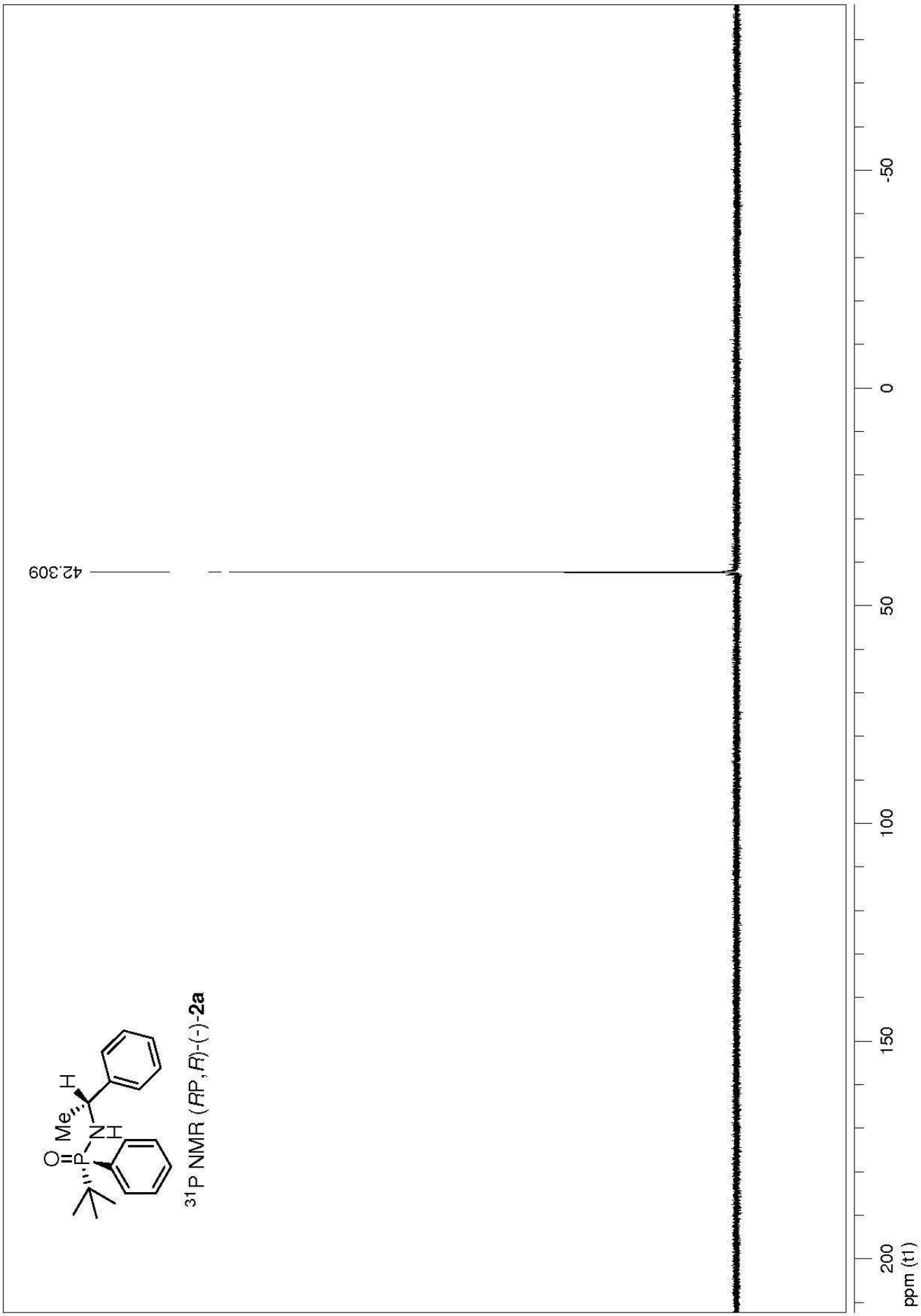

1.161
1.212
9.21
^{1}H NMR (*R*)-(-)-**1**
O=P
N
7.260
7.442
7.452
7.469
7.476
7.486
7.491
7.498
7.504
7.509
7.514
7.523
7.545
7.569
7.950
7.956
7.966
7.972
7.978
7.983
7.990
7.993
8.011
9.157
9.256
5.61
3.85
1.00
5.0
10.0
ppm (t1)

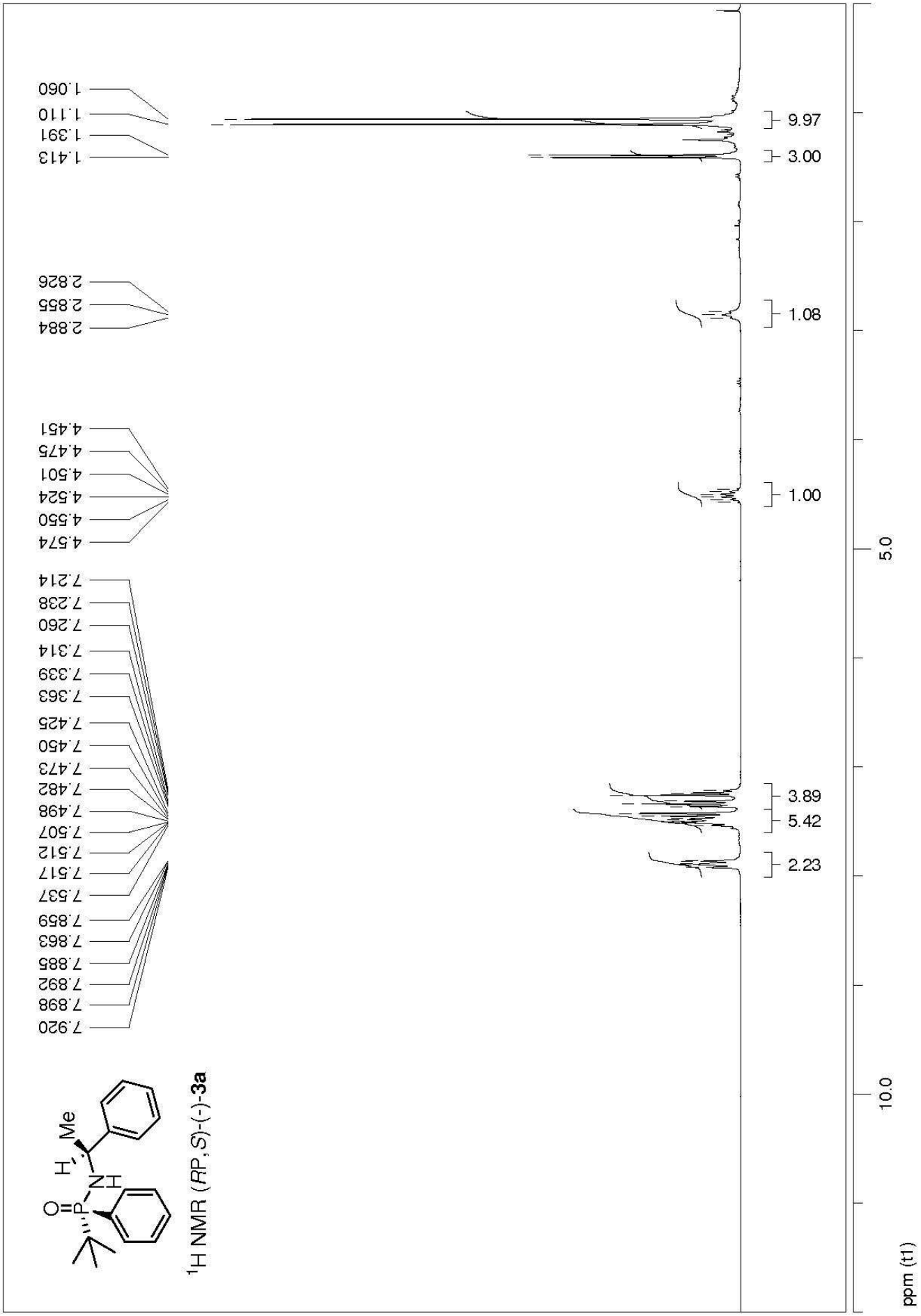

24.428
32.304
33.482
76.577
77.000
77.423
127.894
128.043
128.871
129.388
129.901
130.895
131.628
131.663
132.994
133.095
133.292
135.877
136.187
174.197
174.305
50
100
150
ppm (t1)
^{13}C NMR (*R*)-(-)-**1**
O=P
N


44.012
0
50
100
ppm (t1)
^{31}P NMR (*R*)-(-)-**1**

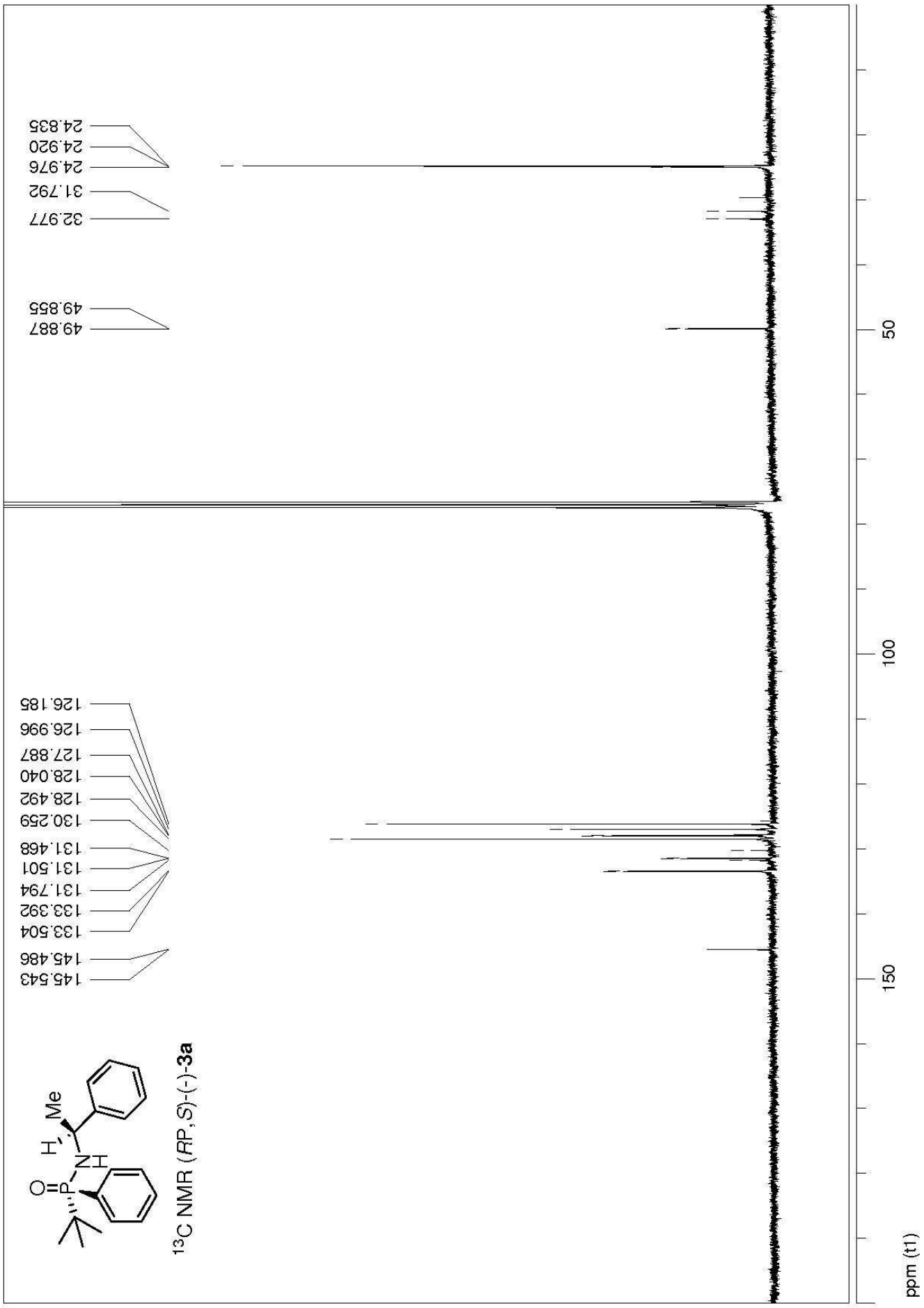

1.117
1.166
1.576
1.599
2.860
4.274
7.206
7.227
7.233
7.251
7.260
7.281
7.303
7.327
7.334
7.350
7.360
7.428
7.432
7.454
7.455
7.477
7.481
7.638
7.643
7.666
7.673
7.678
7.702
9.09
2.91
0.96
1.00
7.73
1.13
1.97
5.0
10.0
ppm (t1)
Me
H
NH
O=P
^{1}H NMR (*RP*,*R*)-(-)-**2a**


24.950
31.498
32.681
50.695
50.729
125.765
126.971
127.791
127.947
128.525
129.631
130.274
131.556
131.592
133.967
134.082
145.315
145.410
50
100
150
ppm (t1)
^{13}C NMR (*RP*,*R*)-(-)-**2a**
Me
H
N
H
O=P

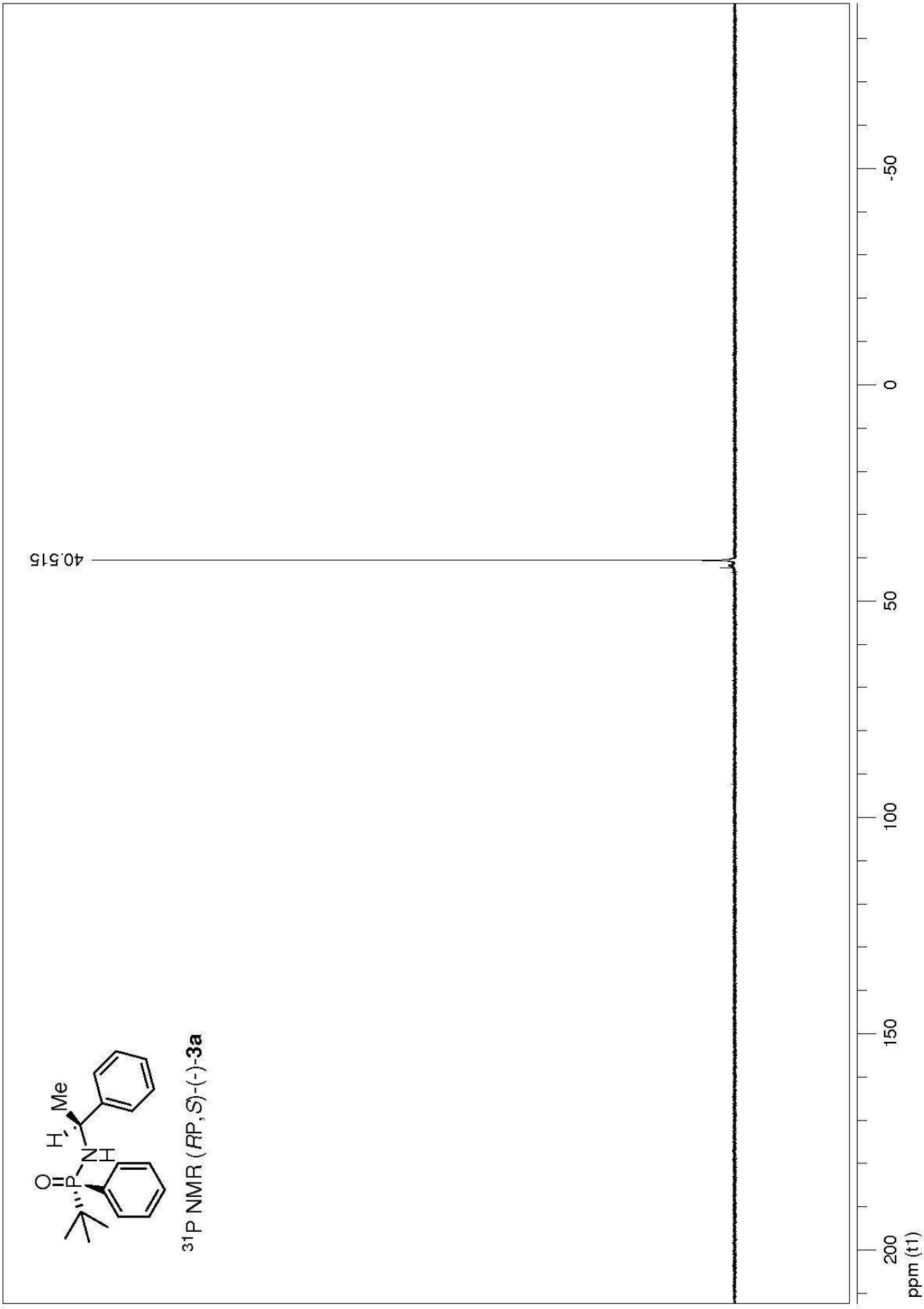

42.309
200
150
100
50
0
-50
ppm (t1)
^{31}P NMR (*RP*,*R*)-(-)-**2a**

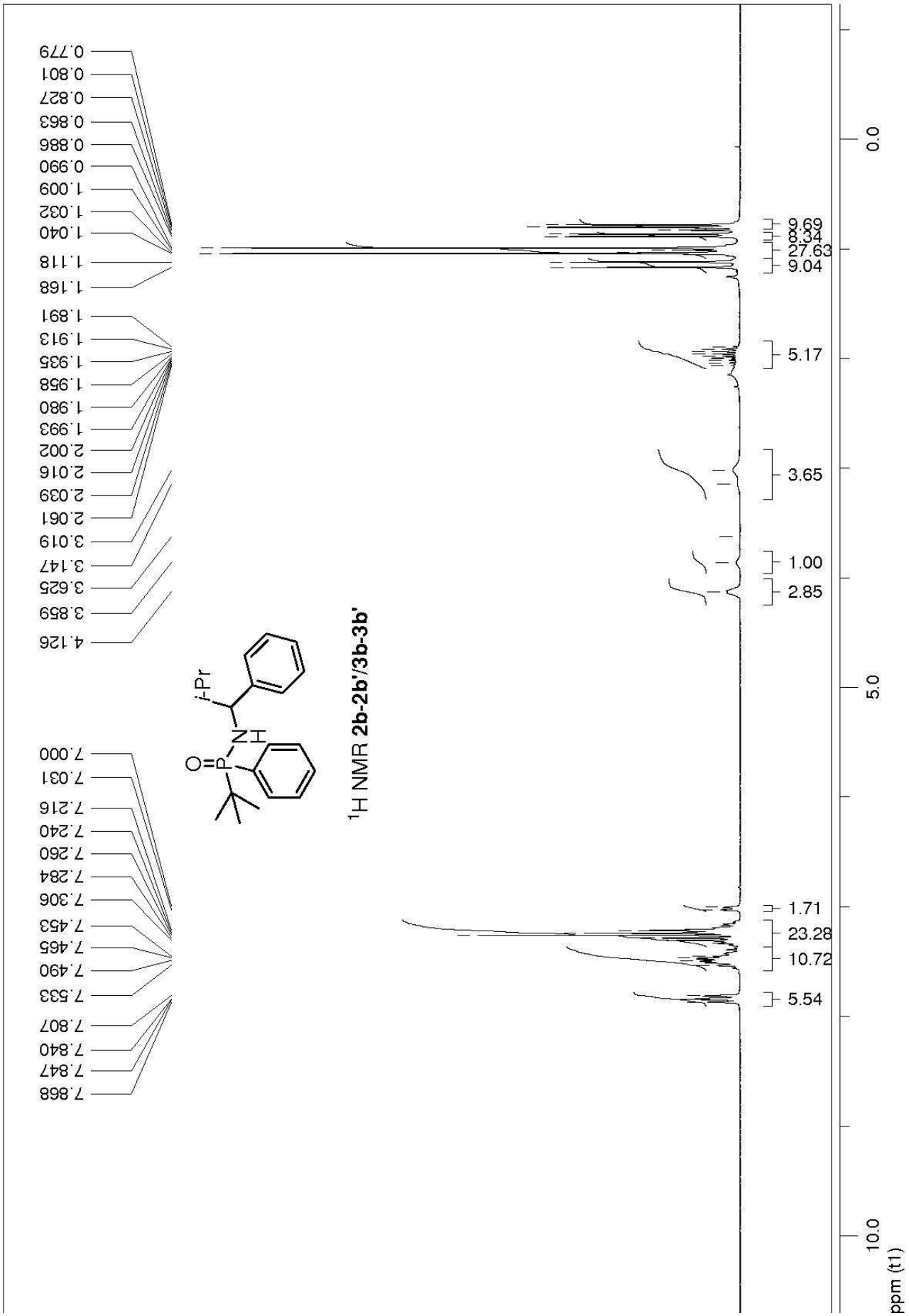

1.060
1.110
1.391
1.413
2.826
2.855
2.884
4.451
4.475
4.501
4.524
4.550
4.574
7.214
7.238
7.260
7.314
7.339
7.363
7.425
7.450
7.473
7.482
7.498
7.507
7.512
7.517
7.537
7.859
7.863
7.885
7.892
7.898
7.920
9.97
3.00
1.08
1.00
3.89
5.42
2.23
5.0
10.0
ppm (t1)
Me
H
N
H
O=P

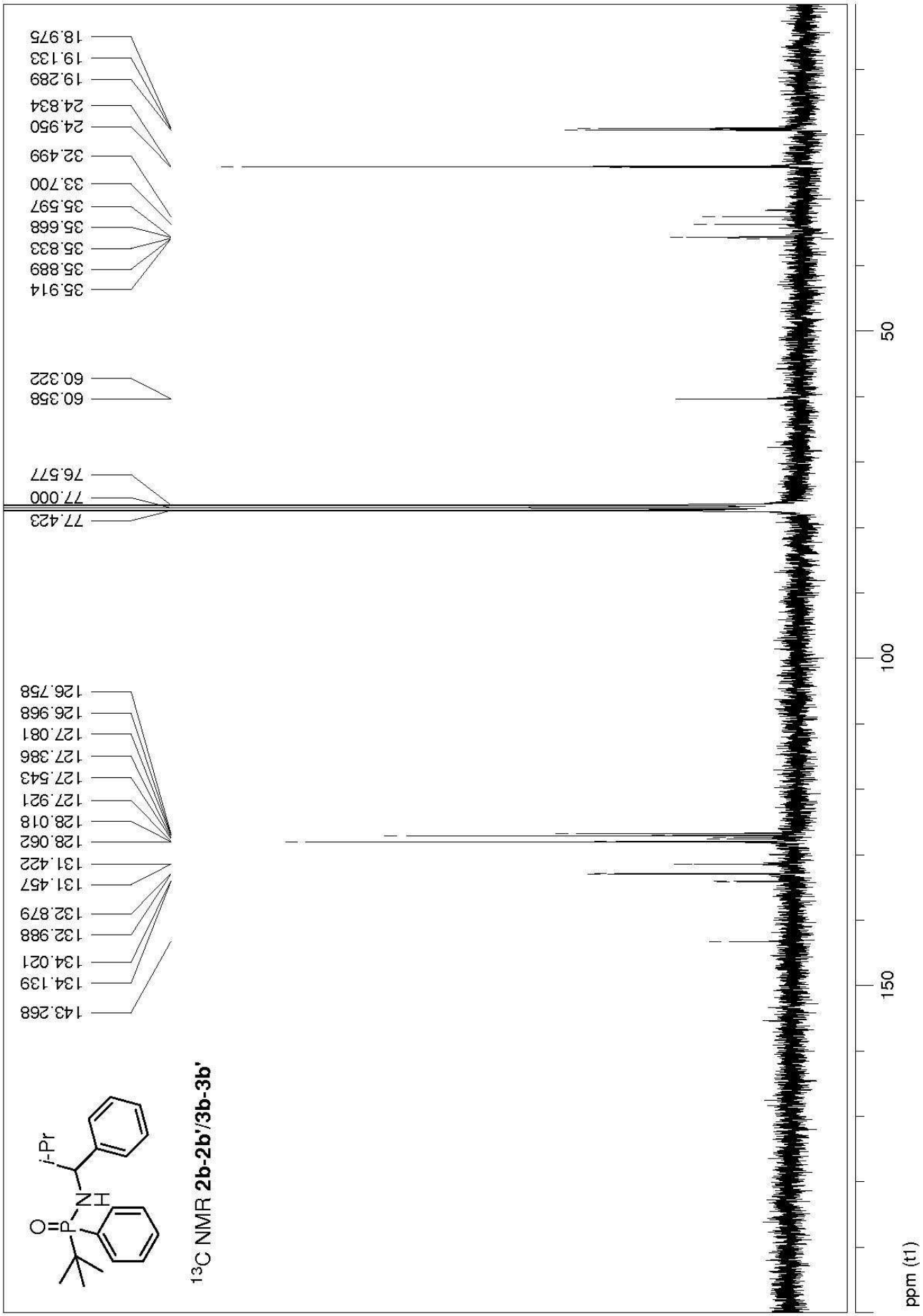
^{1}H NMR (*RP*,*S*)-(-)-**3a**

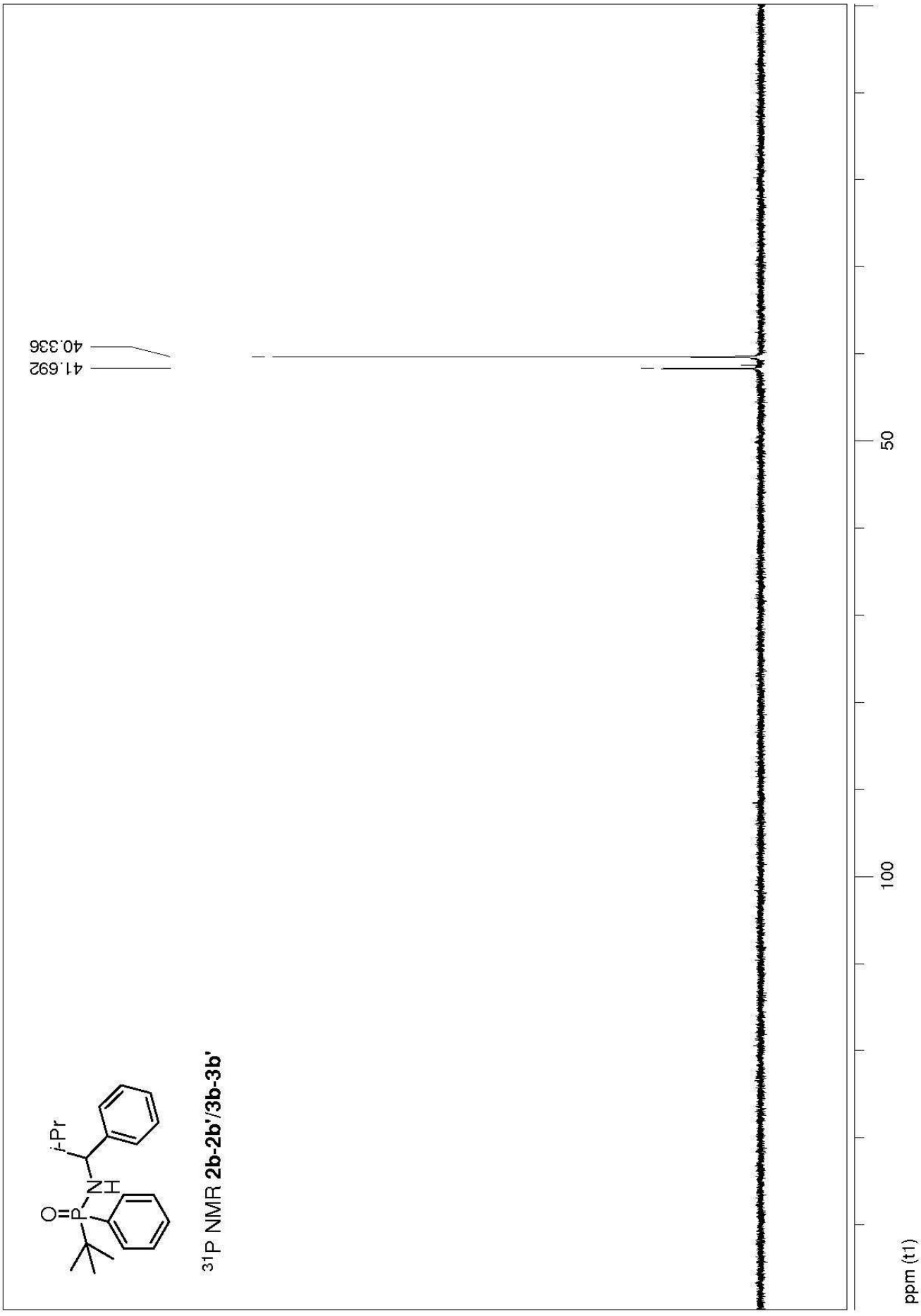


^{13}C NMR (*RP*,*S*)-(-)-**3a**

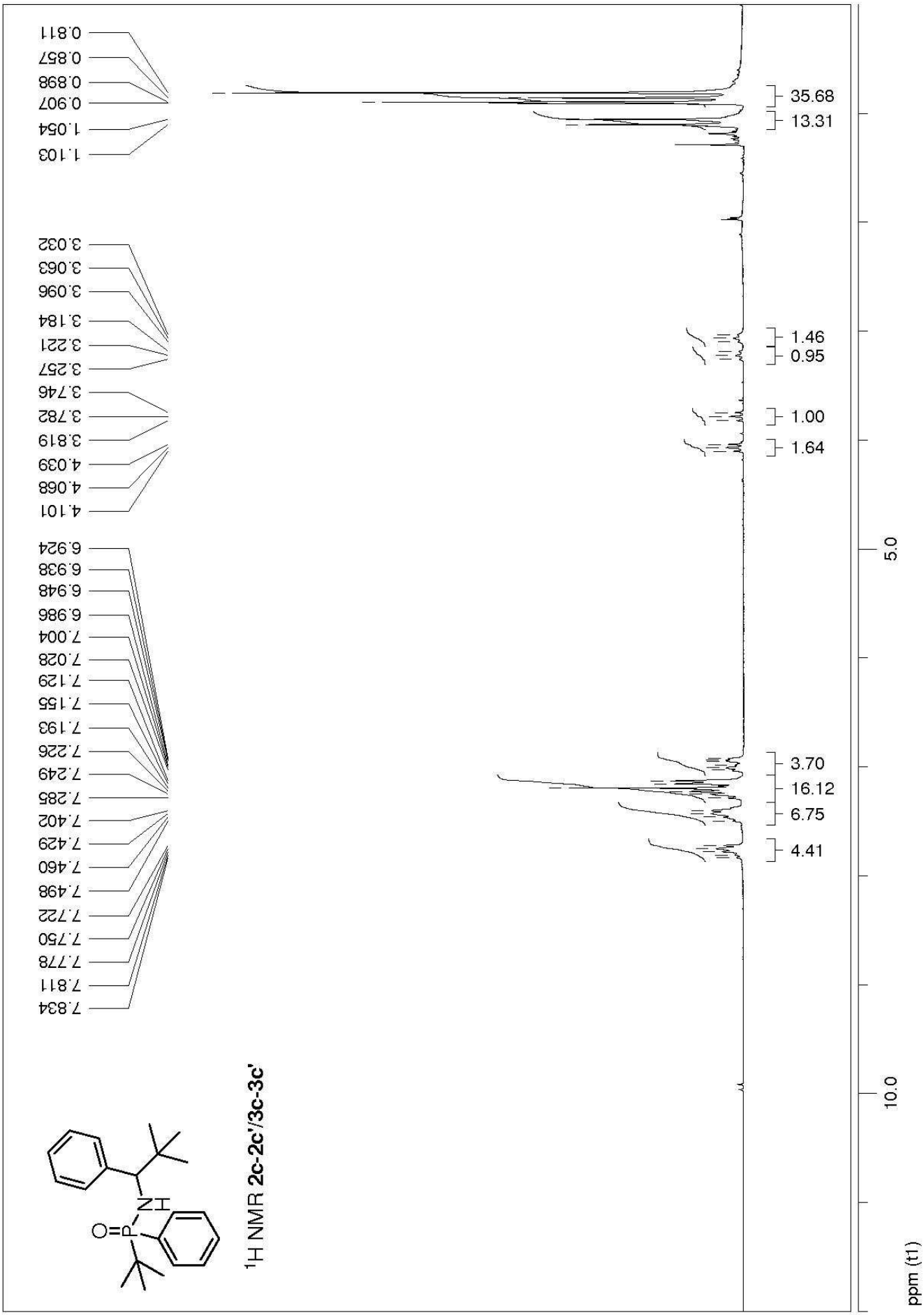

40.515
^{31}P NMR (*RP*,*S*)-(-)-**3a**
Me
H
NH
O=P
200
150
100
50
0
-50
ppm (t1)

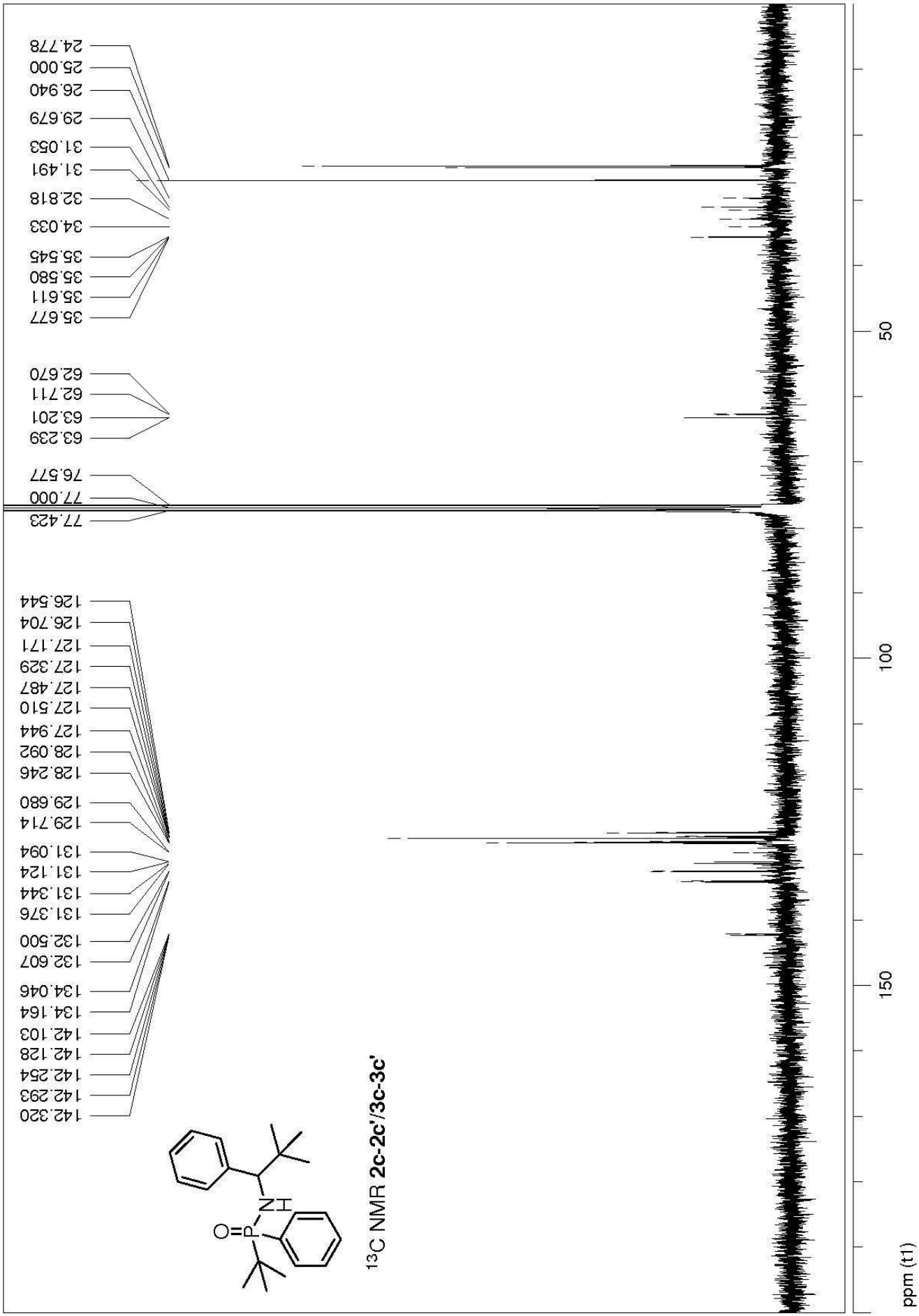

0.779
0.801
0.827
0.863
0.886
0.990
1.009
1.032
1.040
1.118
1.168
1.891
1.913
1.935
1.958
1.980
1.993
2.002
2.016
2.039
2.061
3.019
3.147
3.625
3.859
4.126
7.000
7.031
7.216
7.240
7.260
7.284
7.306
7.453
7.465
7.490
7.533
7.807
7.840
7.847
7.868
i-Pr
NH
O=P
1H NMR 2b-2b'/3b-3b'
9.69
8.34
27.63
9.04
5.17
3.65
1.00
2.85
1.71
23.28
10.72
5.54
0.0
5.0
10.0
ppm (t1)

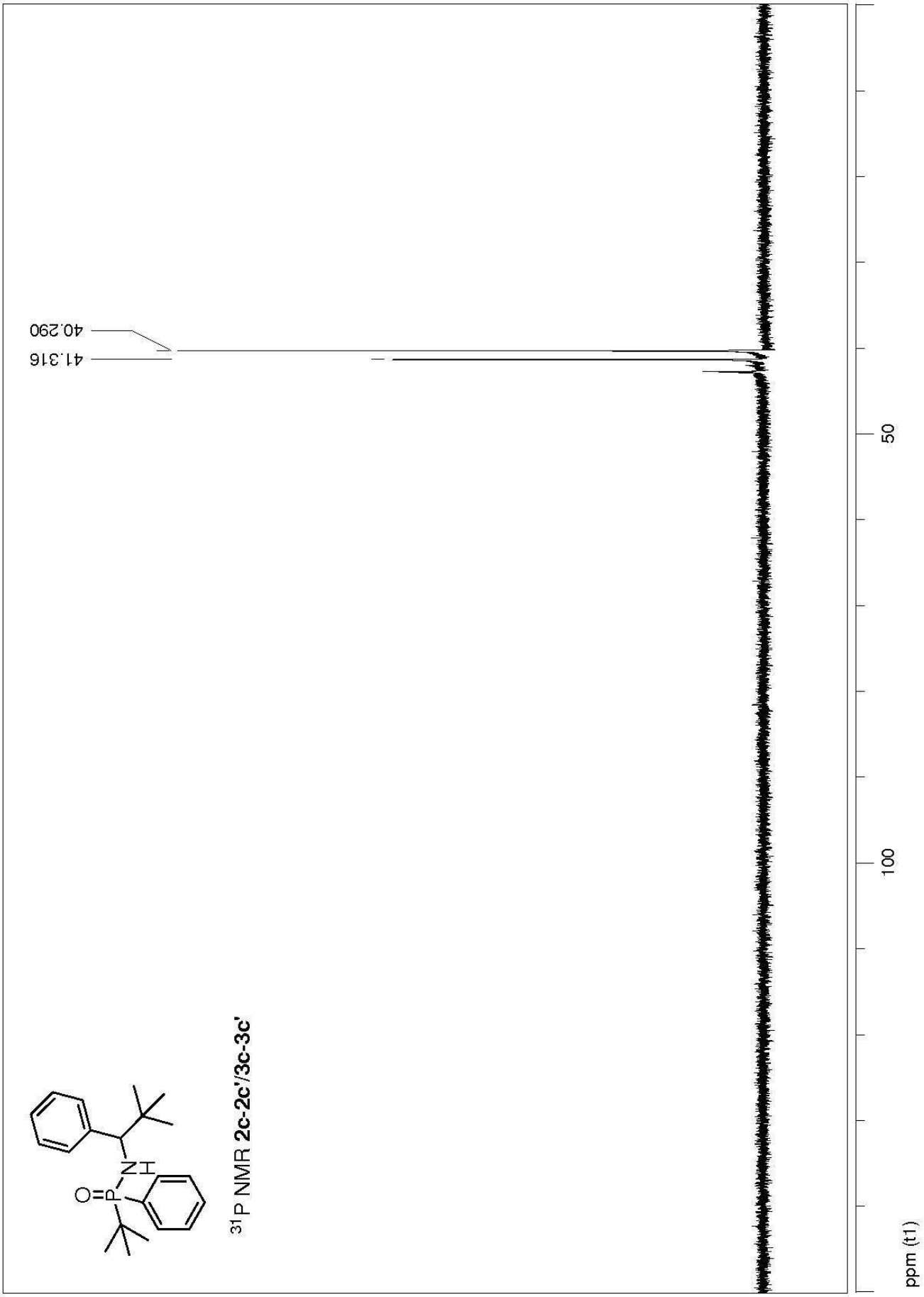

18.975
19.133
19.289
24.834
24.950
32.499
33.700
35.597
35.668
35.833
35.889
35.914
60.322
60.358
76.577
77.000
77.423
126.758
126.968
127.081
127.386
127.543
127.921
128.018
128.062
131.422
131.457
132.879
132.988
134.021
134.139
143.268
50
100
150
ppm (t1)
^{13}C NMR **2b-2b'/3b-3b'**
i-Pr
N
H
O=P

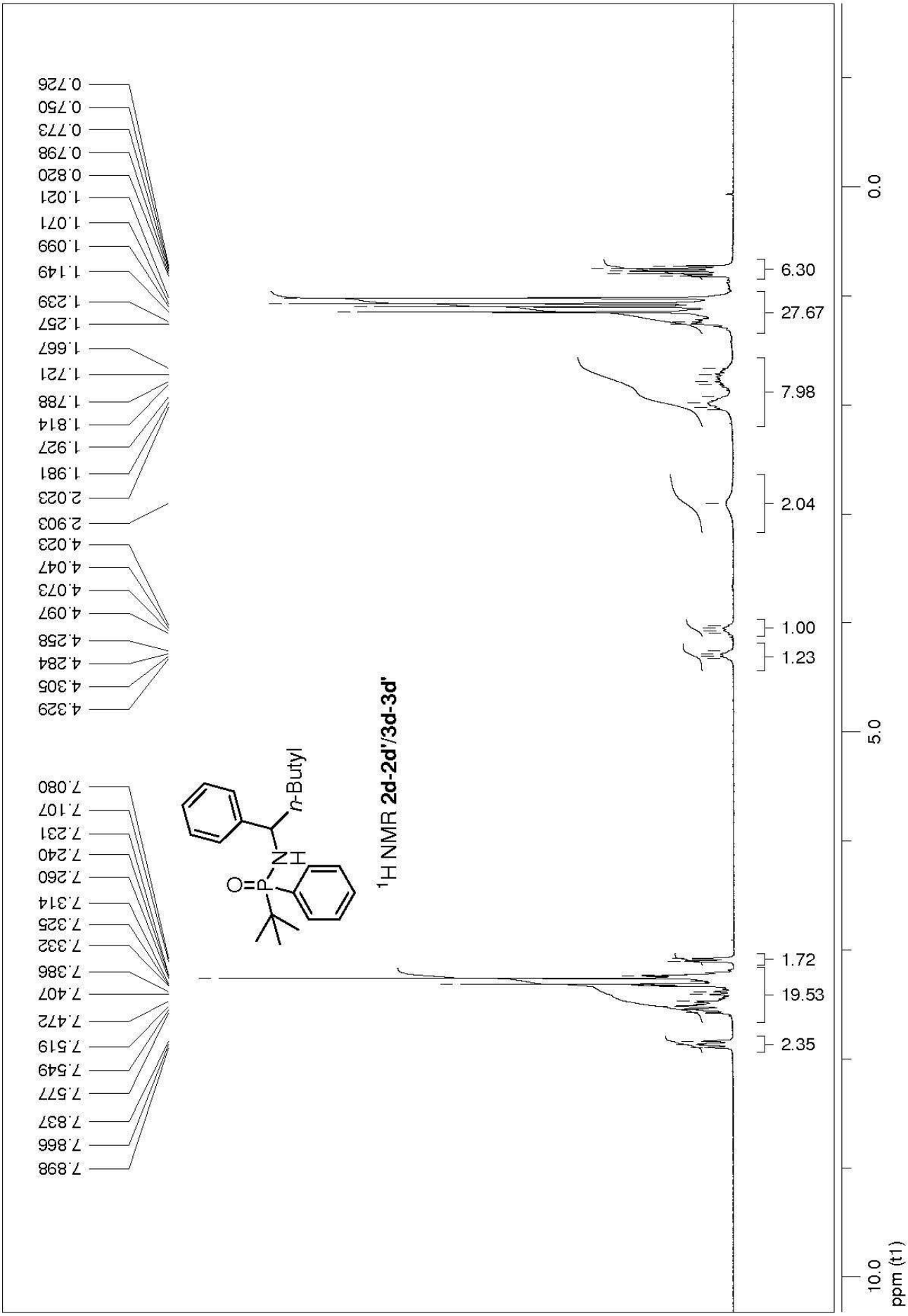


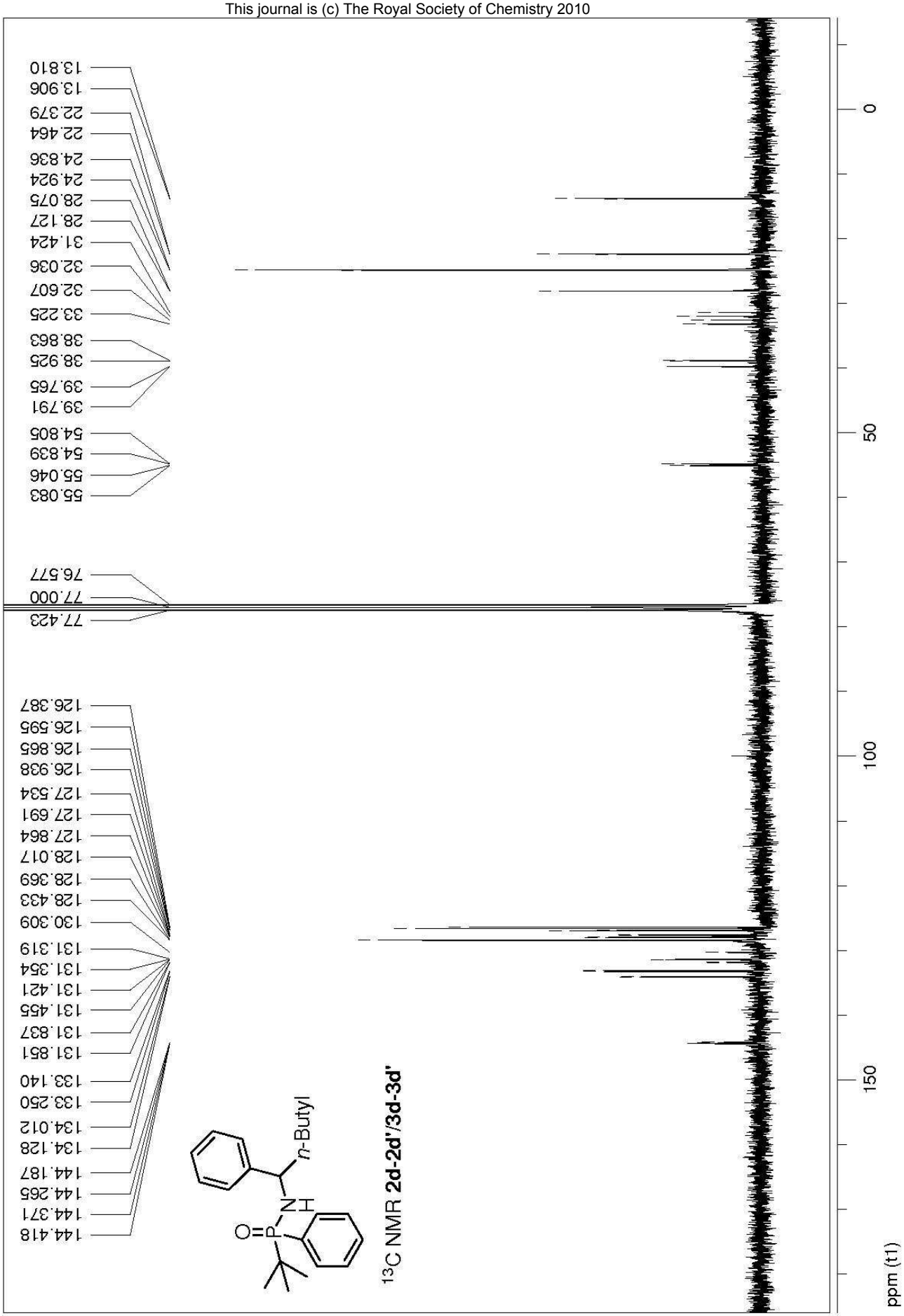
^{31}P NMR **2b-2b'/3b-3b'**

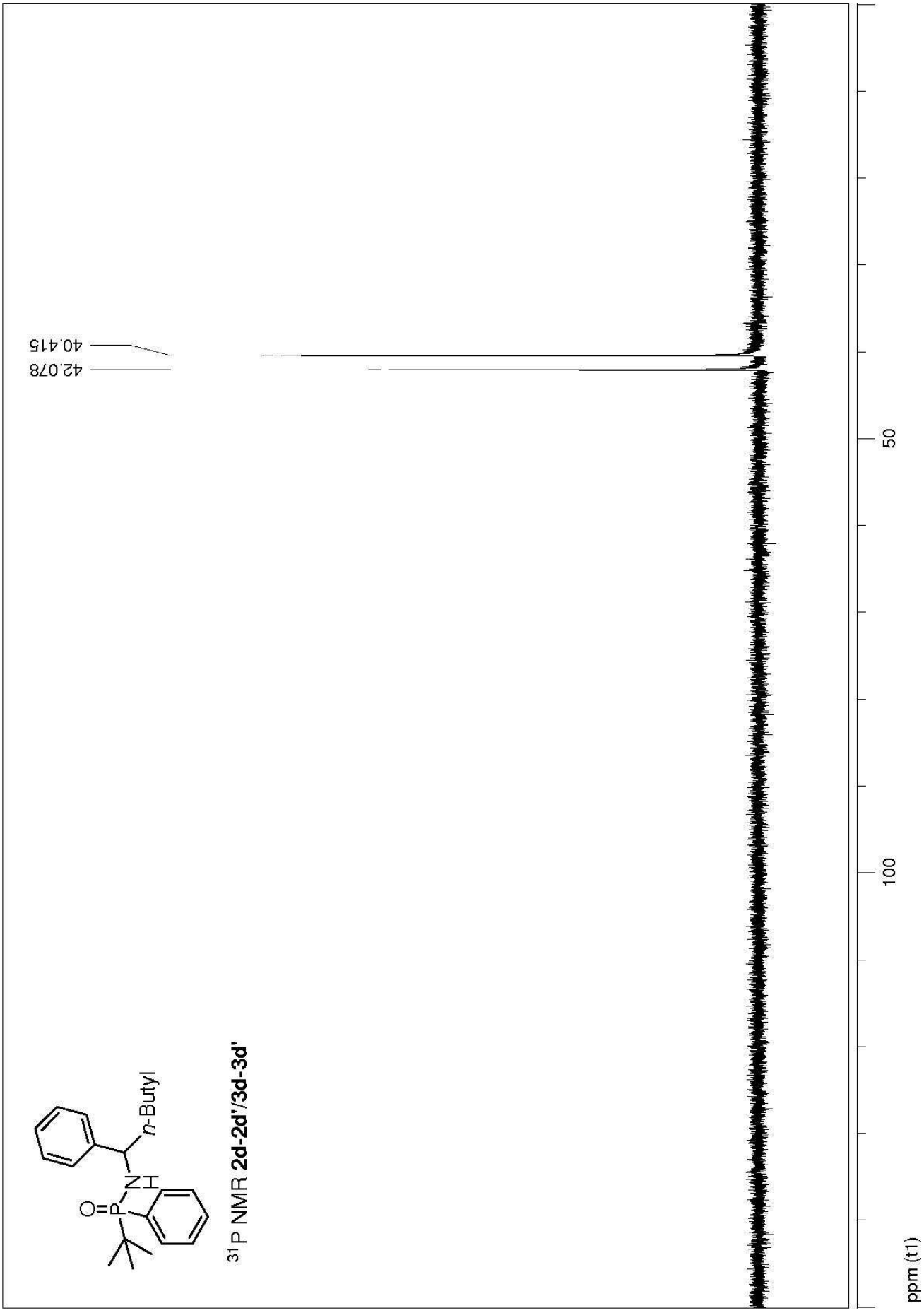

0.811
0.857
0.898
0.907
1.054
1.103
3.032
3.063
3.096
3.184
3.221
3.257
3.746
3.782
3.819
4.039
4.068
4.101
6.924
6.938
6.948
6.986
7.004
7.028
7.129
7.155
7.193
7.226
7.249
7.285
7.402
7.429
7.460
7.498
7.722
7.750
7.778
7.811
7.834
35.68
13.31
1.46
0.95
1.00
1.64
3.70
16.12
6.75
4.41
5.0
10.0
ppm (t1)
^{1}H NMR **2c-2c'/3c-3c'**
NH
O=P

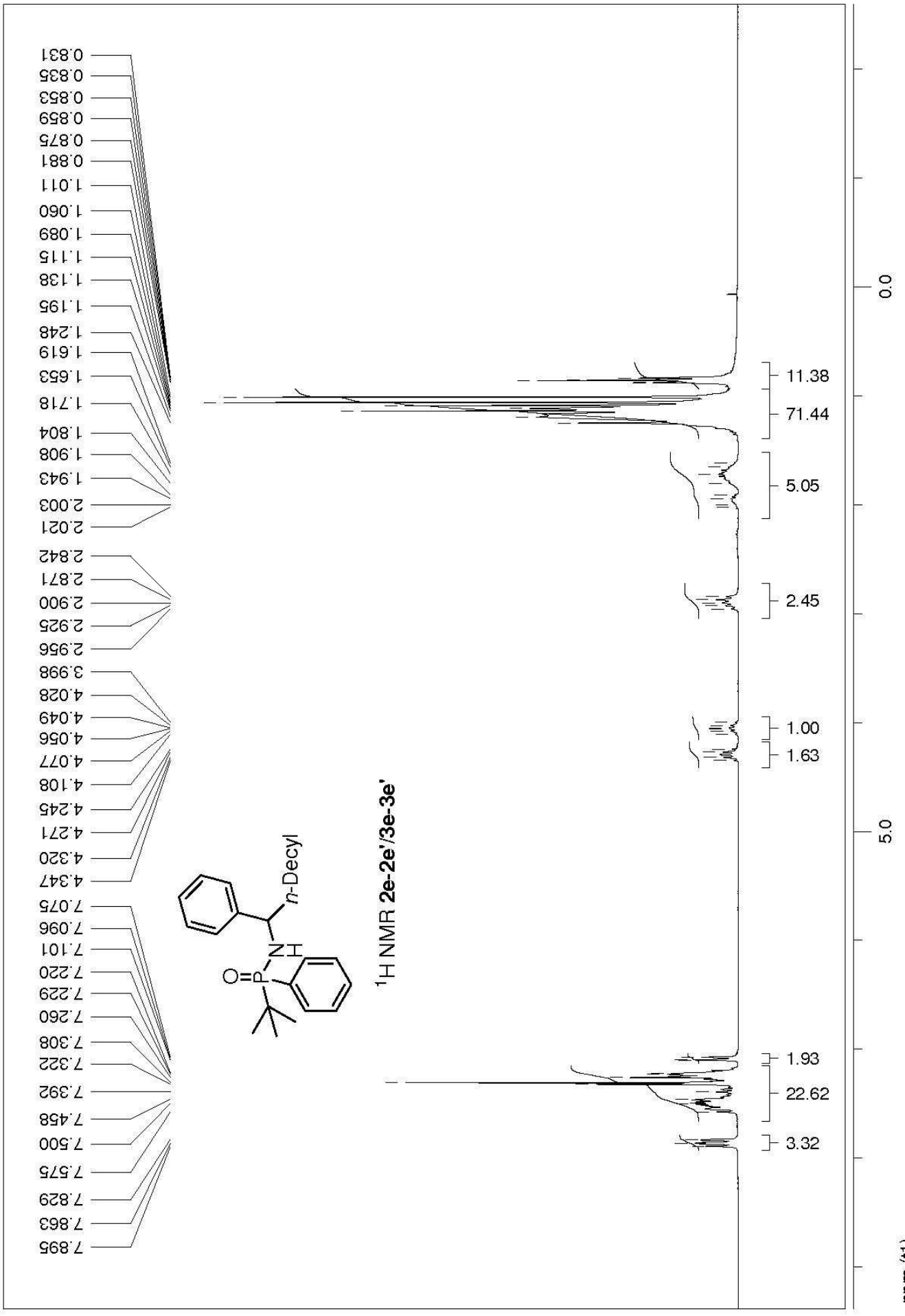

24.778
25.000
26.940
29.679
31.053
31.491
32.818
34.033
35.545
35.580
35.611
35.677
62.670
62.711
63.201
63.239
76.577
77.000
77.423
126.544
126.704
127.171
127.329
127.487
127.510
127.944
128.092
128.246
129.680
129.714
131.094
131.124
131.344
131.376
132.500
132.607
134.046
134.164
142.103
142.128
142.254
142.293
142.320
NH
O=P
^{13}C NMR **2c-2c'/3c-3c'**
50
100
150
ppm (t1)

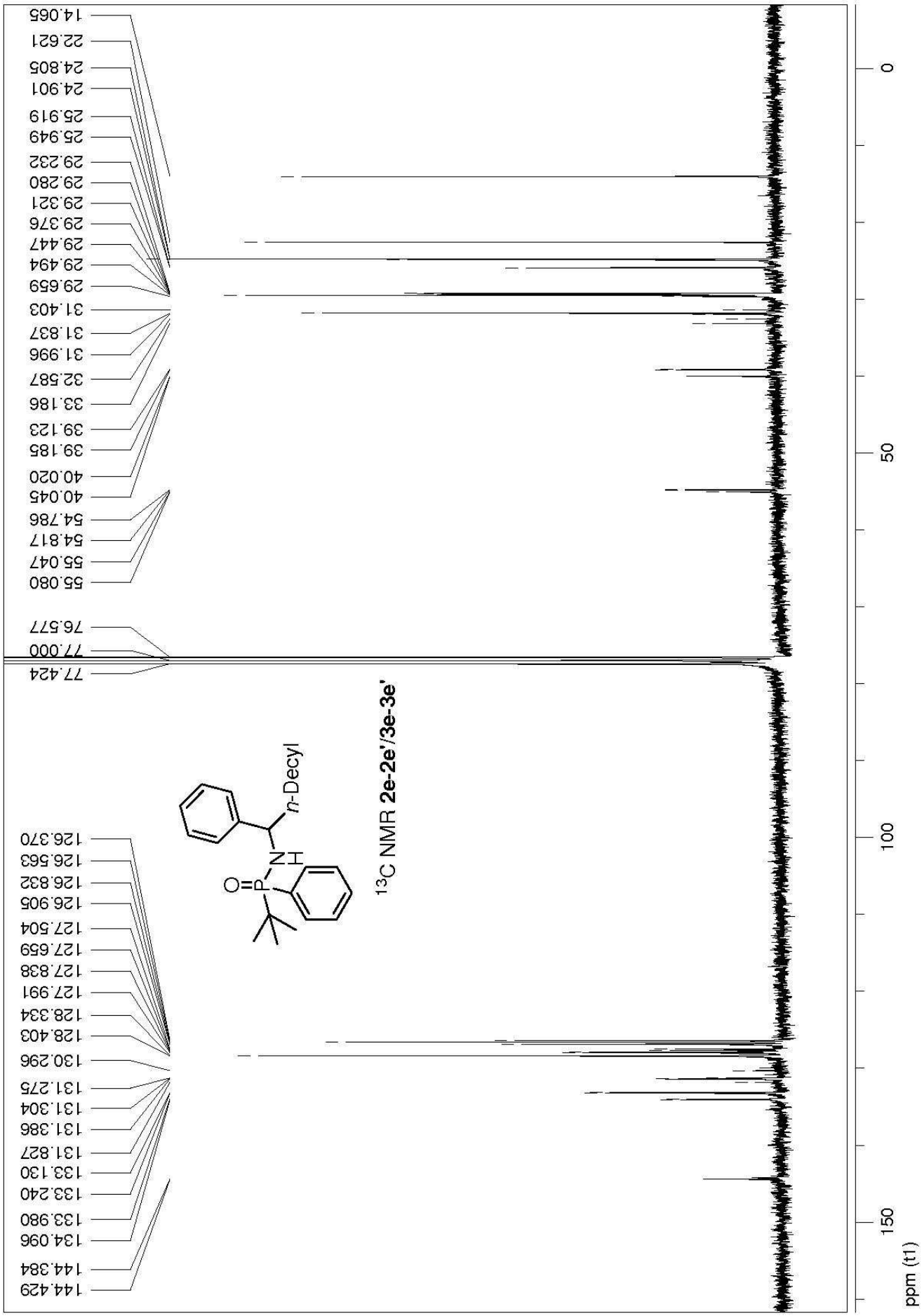

40.290
41.316
50
100
ppm (t1)
^{31}P NMR **2c-2c'/3c-3c'**
O=P
NH

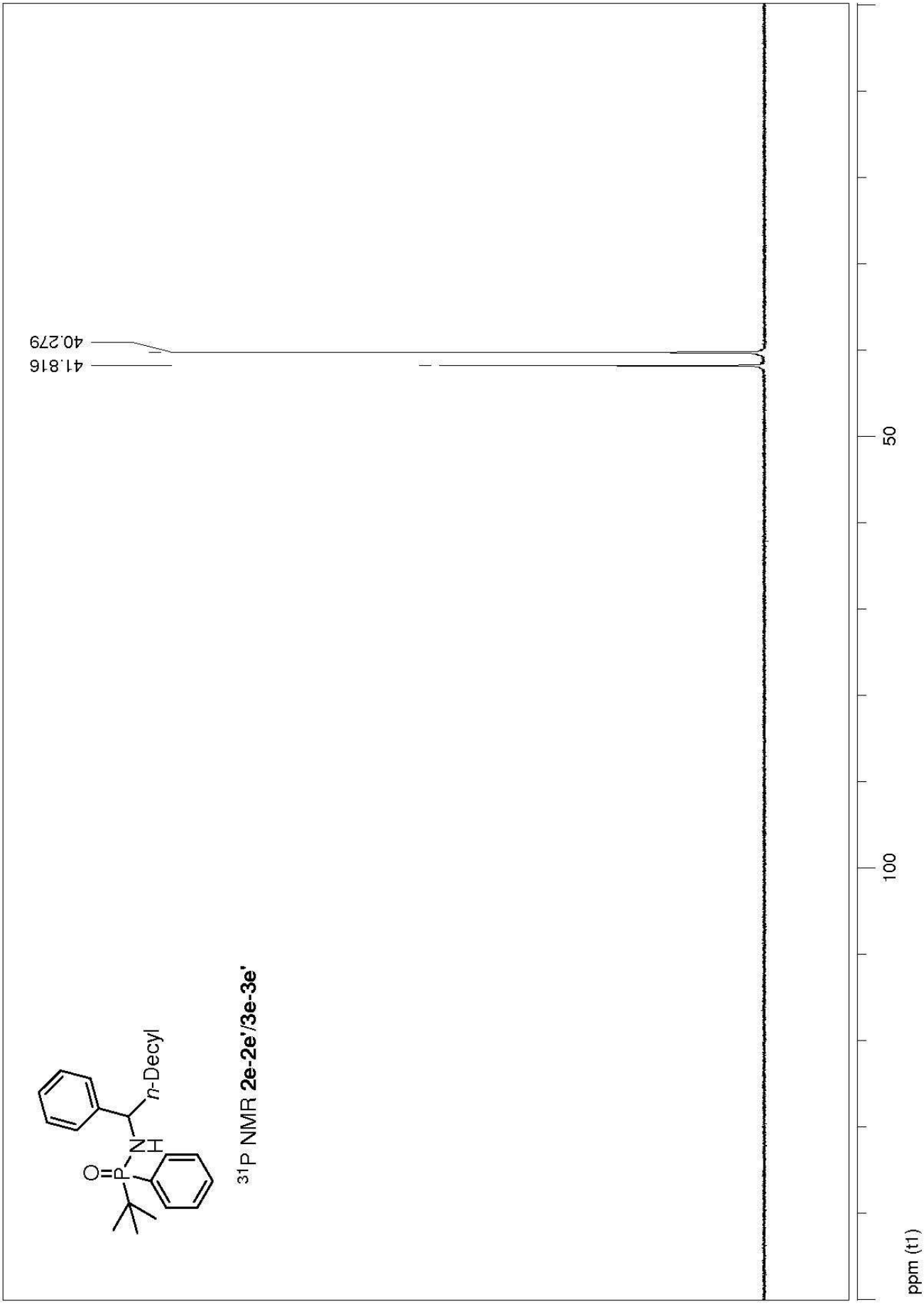

0.726
0.750
0.773
0.798
0.820
1.021
1.071
1.099
1.149
1.239
1.257
1.667
1.721
1.788
1.814
1.927
1.981
2.023
2.903
4.023
4.047
4.073
4.097
4.258
4.284
4.305
4.329
7.080
7.107
7.231
7.240
7.260
7.314
7.325
7.332
7.386
7.407
7.472
7.519
7.549
7.577
7.837
7.866
7.898
n-Butyl
N
H
O=P
1H NMR 2d-2d'/3d-3d'
6.30
27.67
7.98
2.04
1.00
1.23
1.72
19.53
2.35
0.0
5.0
10.0
ppm (t1)

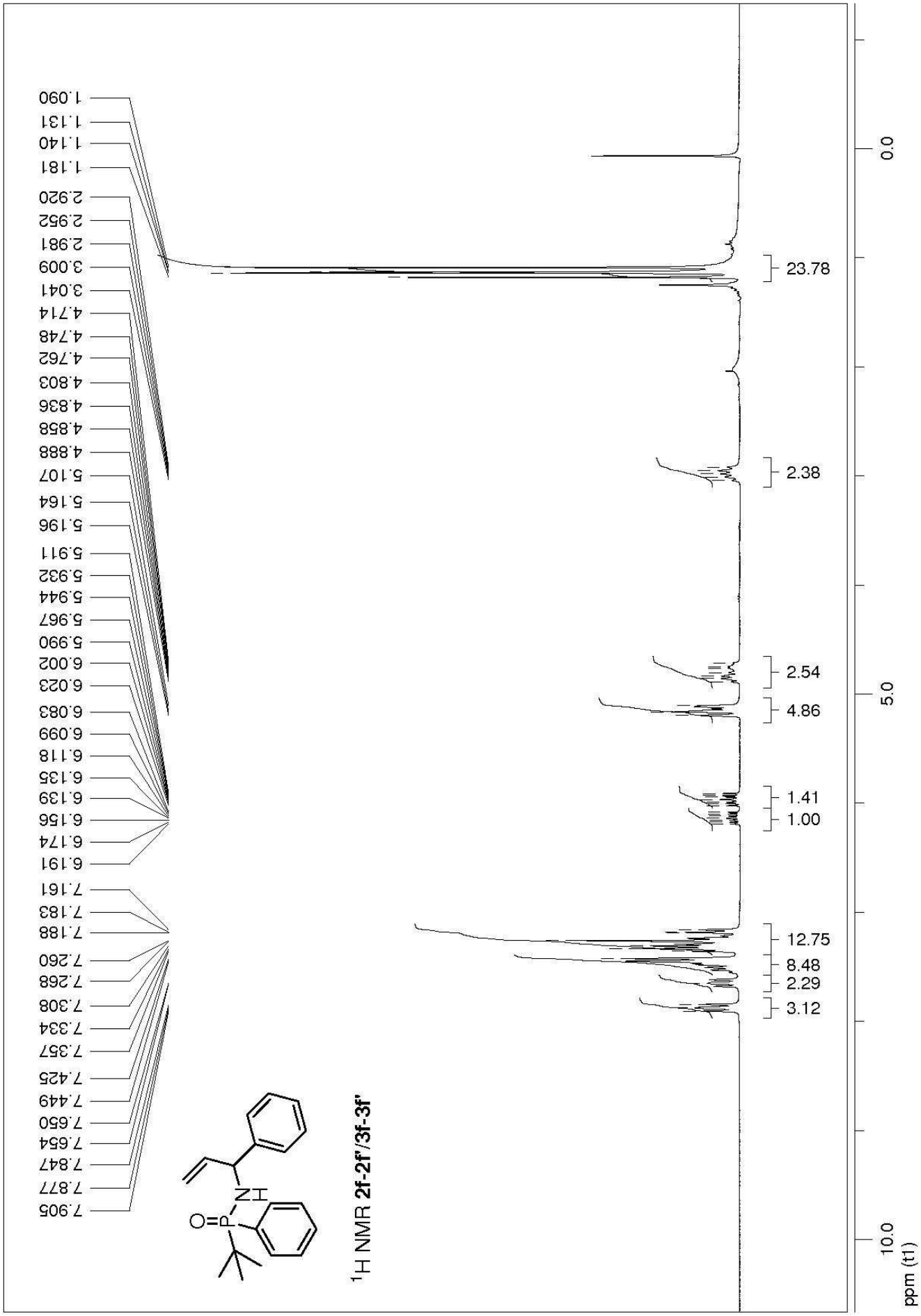

13.810
13.906
22.379
22.464
24.836
24.924
28.075
28.127
31.424
32.036
32.607
33.225
38.863
38.925
39.765
39.791
54.805
54.839
55.046
55.083
76.577
77.000
77.423
126.387
126.595
126.865
126.938
127.534
127.691
127.864
128.017
128.369
128.433
130.309
131.319
131.354
131.421
131.455
131.837
131.851
133.140
133.250
134.012
134.128
144.187
144.265
144.371
144.418
n-Butyl
NH
O=P
^{13}C NMR **2d-2d'/3d-3d'**
0
50
100
150
ppm (t1)

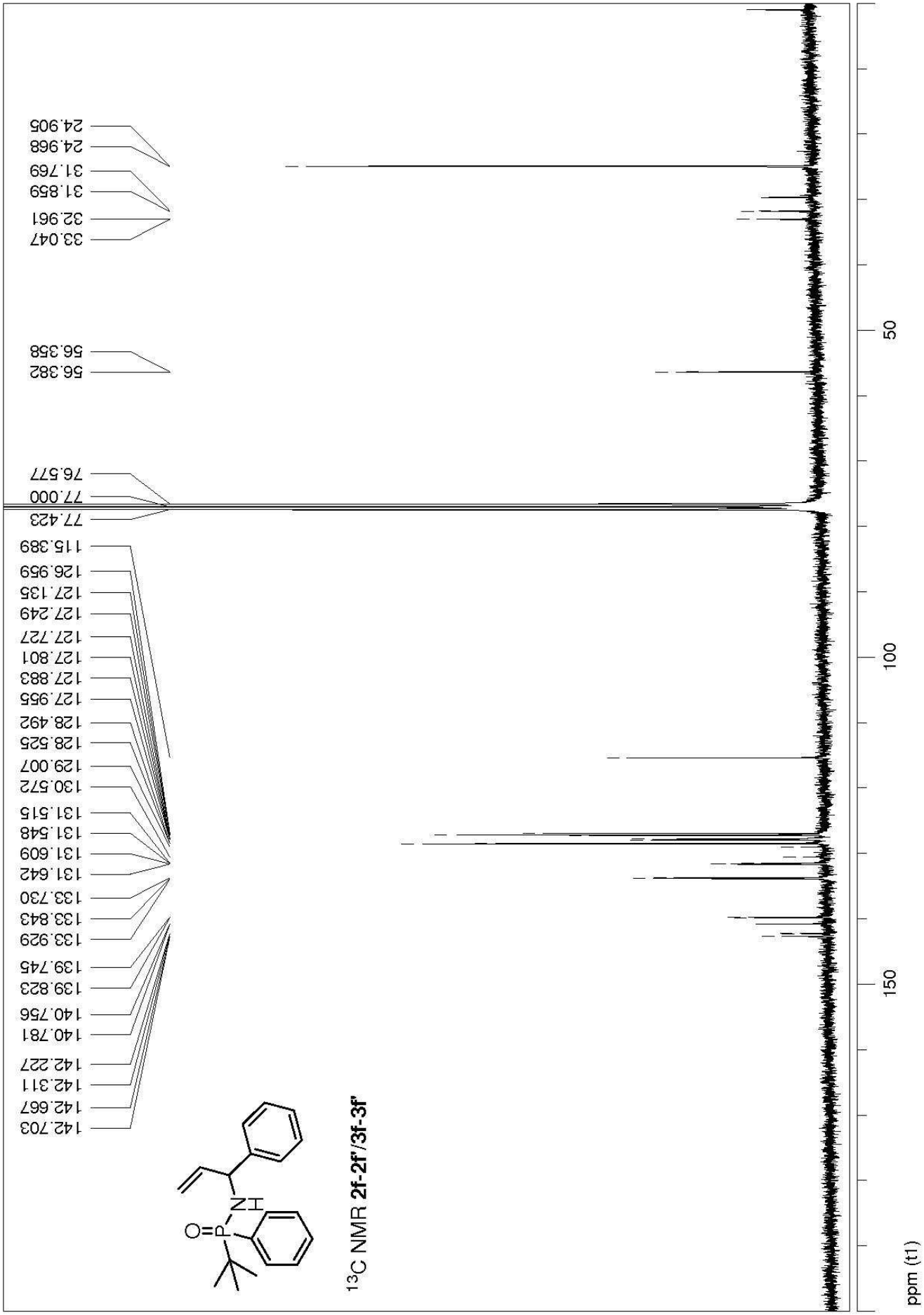

40.415
42.078
50
100
ppm (t1)
n-Butyl
O=P
N
H
31P NMR 2d-2d'/3d-3d'

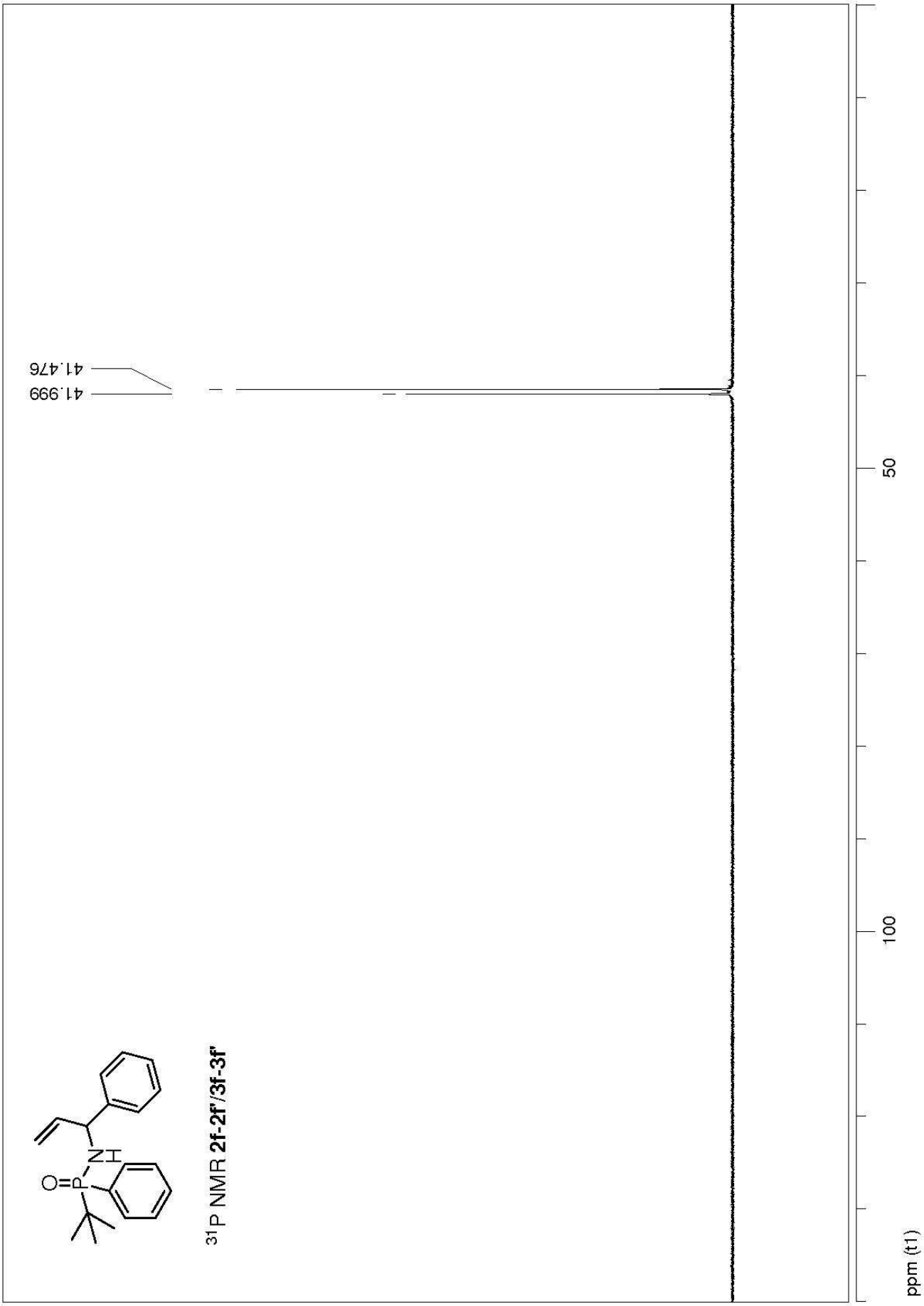

0.831
0.835
0.853
0.859
0.875
0.881
1.011
1.060
1.089
1.115
1.138
1.195
1.248
1.619
1.653
1.718
1.804
1.908
1.943
2.003
2.021
2.842
2.871
2.900
2.925
2.956
3.998
4.028
4.049
4.056
4.077
4.108
4.245
4.271
4.320
4.347
7.075
7.096
7.101
7.220
7.229
7.260
7.308
7.322
7.392
7.458
7.500
7.575
7.829
7.863
7.895
n-Decyl
O=P
NH
1H NMR 2e-2e'/3e-3e'
11.38
71.44
5.05
2.45
1.00
1.63
1.93
22.62
3.32
0.0
5.0
ppm (t1)

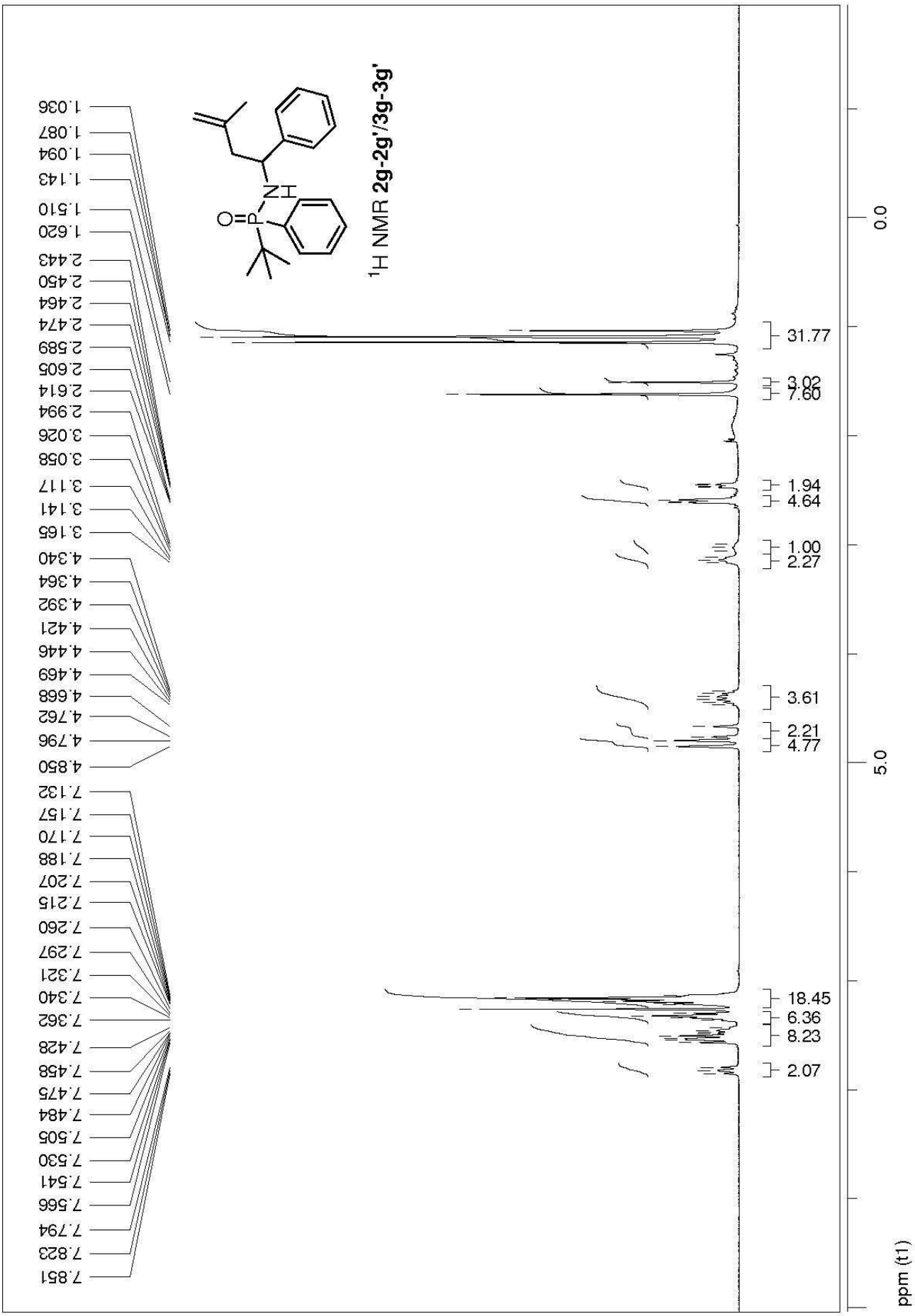

14.065
22.621
24.805
24.901
25.919
25.949
29.232
29.280
29.321
29.376
29.447
29.494
29.659
31.403
31.837
31.996
32.587
33.186
39.123
39.185
40.020
40.045
54.786
54.817
55.047
55.080
76.577
77.000
77.424
126.370
126.563
126.832
126.905
127.504
127.659
127.838
127.991
128.334
128.403
130.296
131.275
131.304
131.386
131.827
133.130
133.240
133.980
134.096
144.384
144.429
n-Decyl
NH
O=P
13C NMR 2e-2e'/3e-3e'
0
50
100
150
ppm (t1)

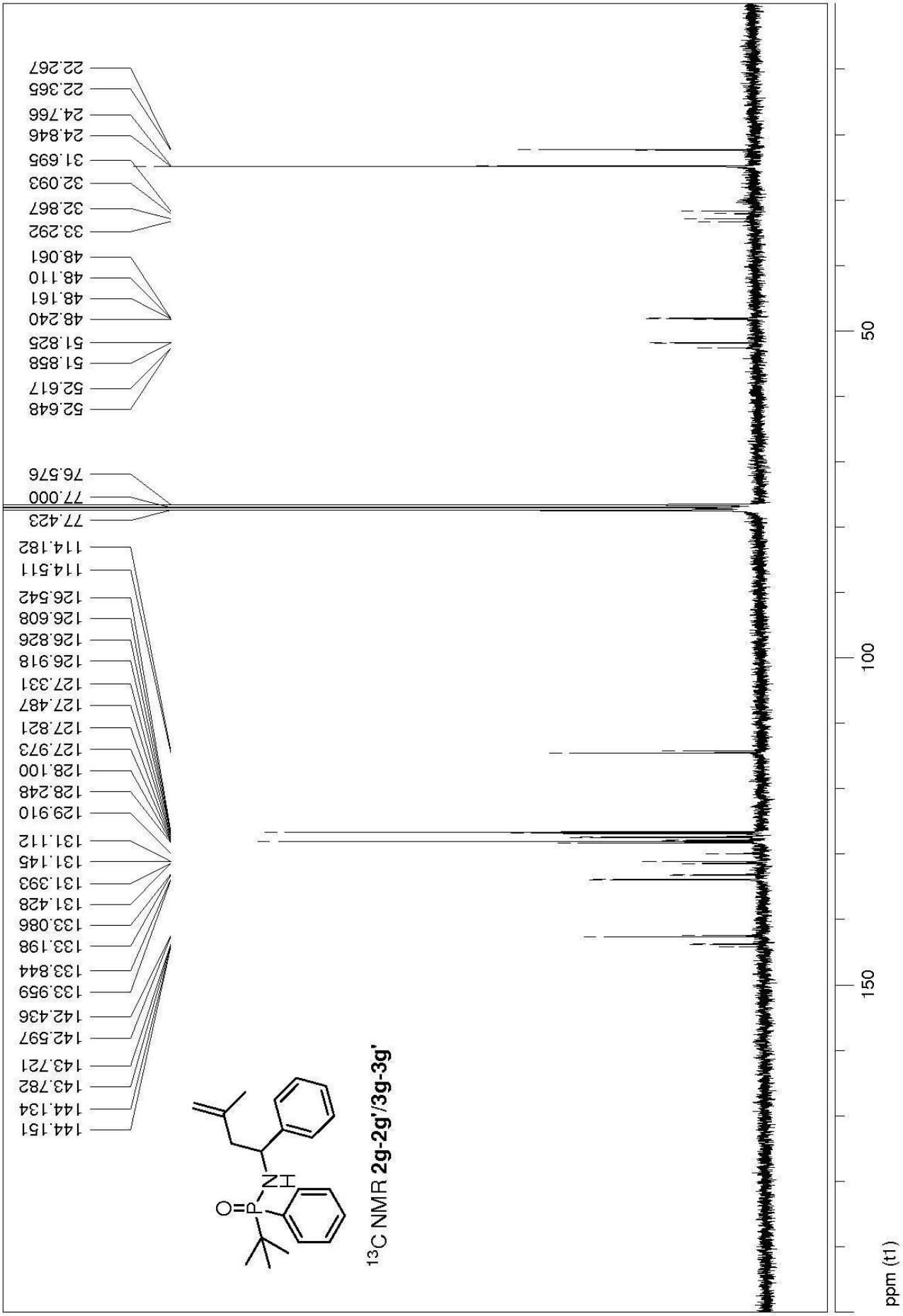

40.279
41.816
50
100
ppm (t1)
n-Decyl
NH
O=P
31P NMR 2e-2e'/3e-3e'

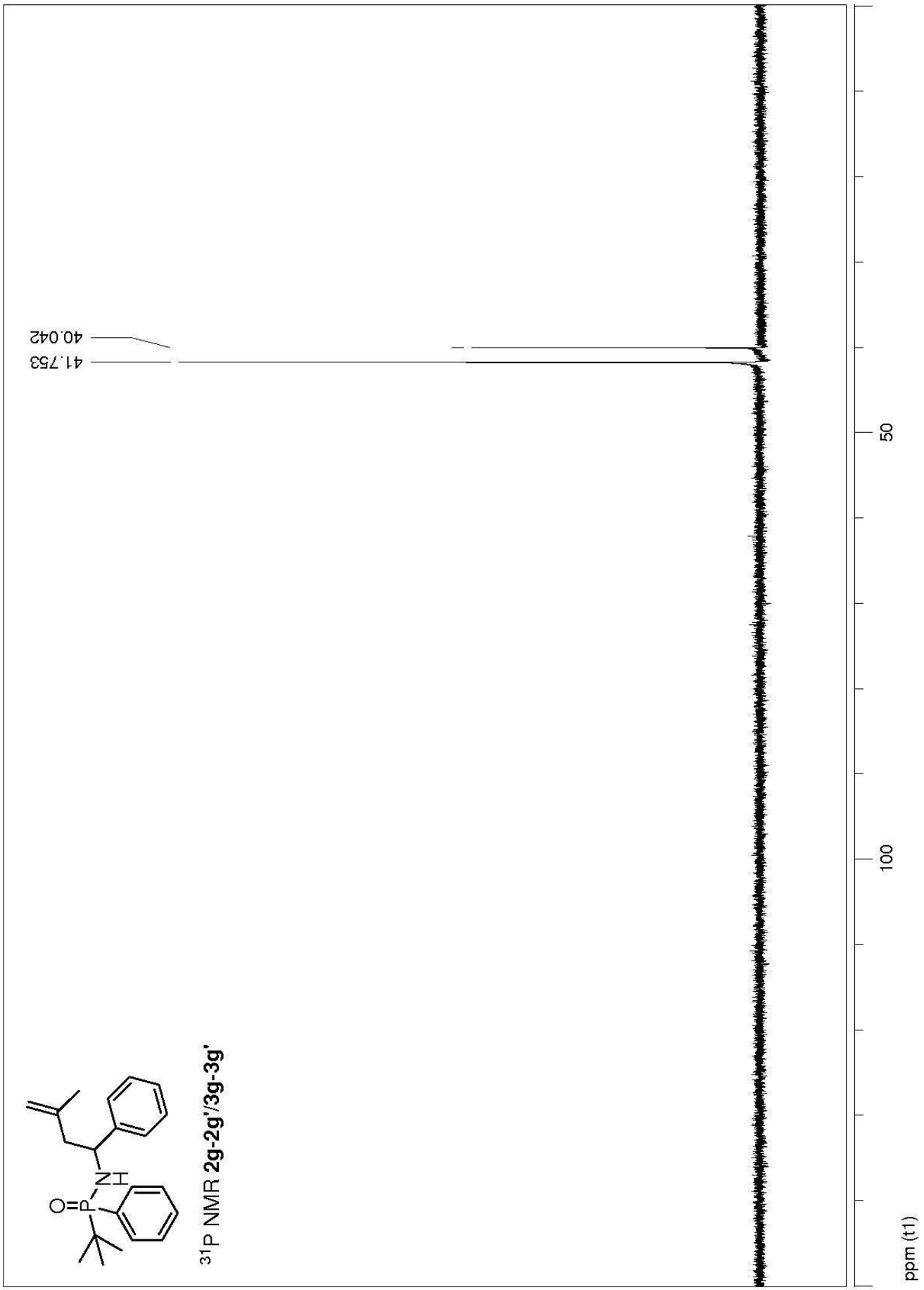

1.090
1.131
1.140
1.181
2.920
2.952
2.981
3.009
3.041
4.714
4.748
4.762
4.803
4.836
4.858
4.888
5.107
5.164
5.196
5.911
5.932
5.944
5.967
5.990
6.002
6.023
6.083
6.099
6.118
6.135
6.139
6.156
6.174
6.191
7.161
7.183
7.188
7.260
7.268
7.308
7.334
7.357
7.425
7.449
7.650
7.654
7.847
7.877
7.905
23.78
2.38
2.54
4.86
1.41
1.00
12.75
8.48
2.29
3.12
0.0
5.0
10.0
ppm (t1)
NH
O=P
^{1}H NMR **2f-2f'/3f-3f'**

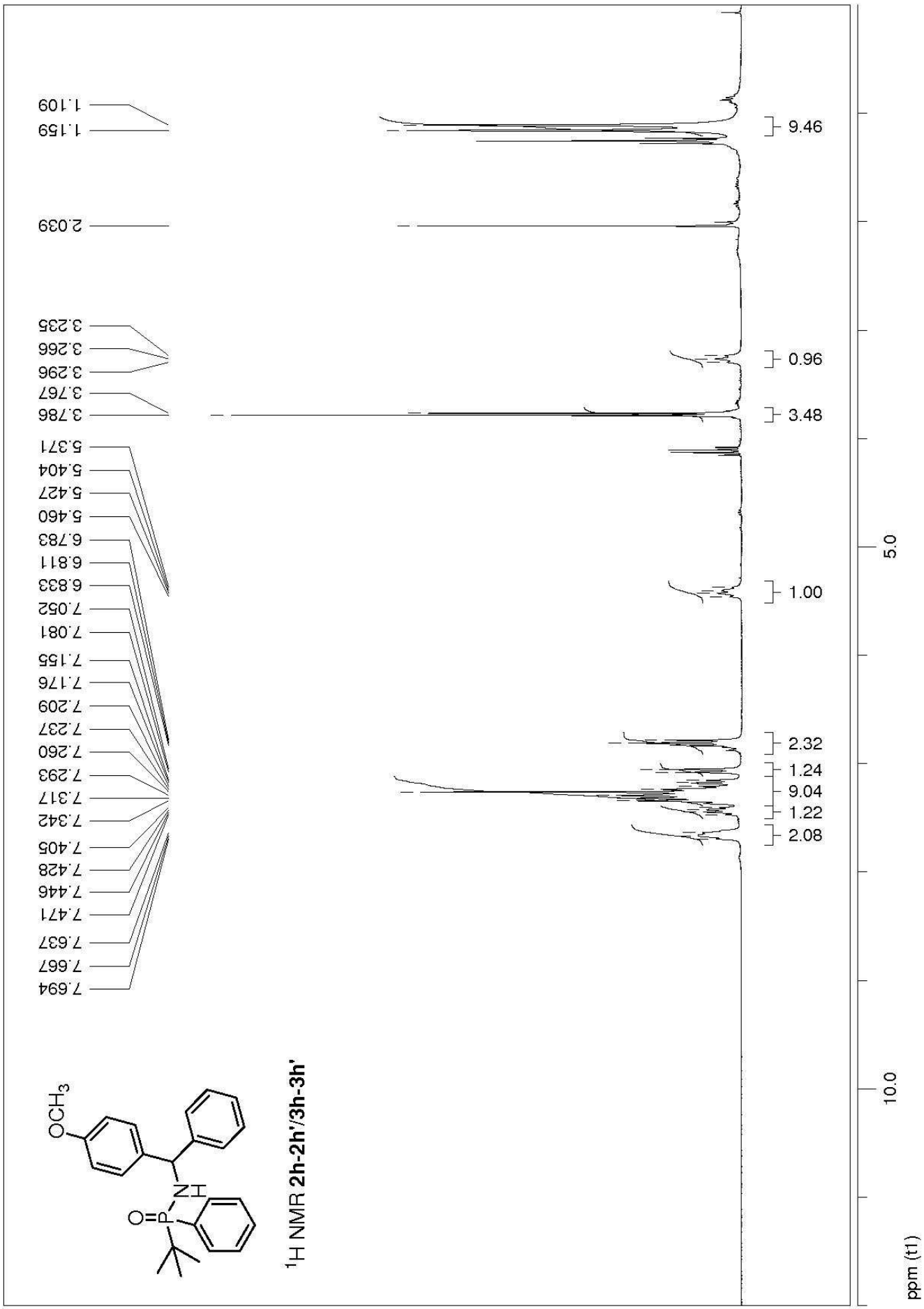

24.905
24.968
31.769
31.859
32.961
33.047
56.358
56.382
76.577
77.000
77.423
115.389
126.959
127.135
127.249
127.727
127.801
127.883
127.955
128.492
128.525
129.007
130.572
131.515
131.548
131.609
131.642
133.730
133.843
133.929
139.745
139.823
140.756
140.781
142.227
142.311
142.667
142.703
NH
O=P
^{13}C NMR **2f-2f'/3f-3f'**
50
100
150
ppm (t1)

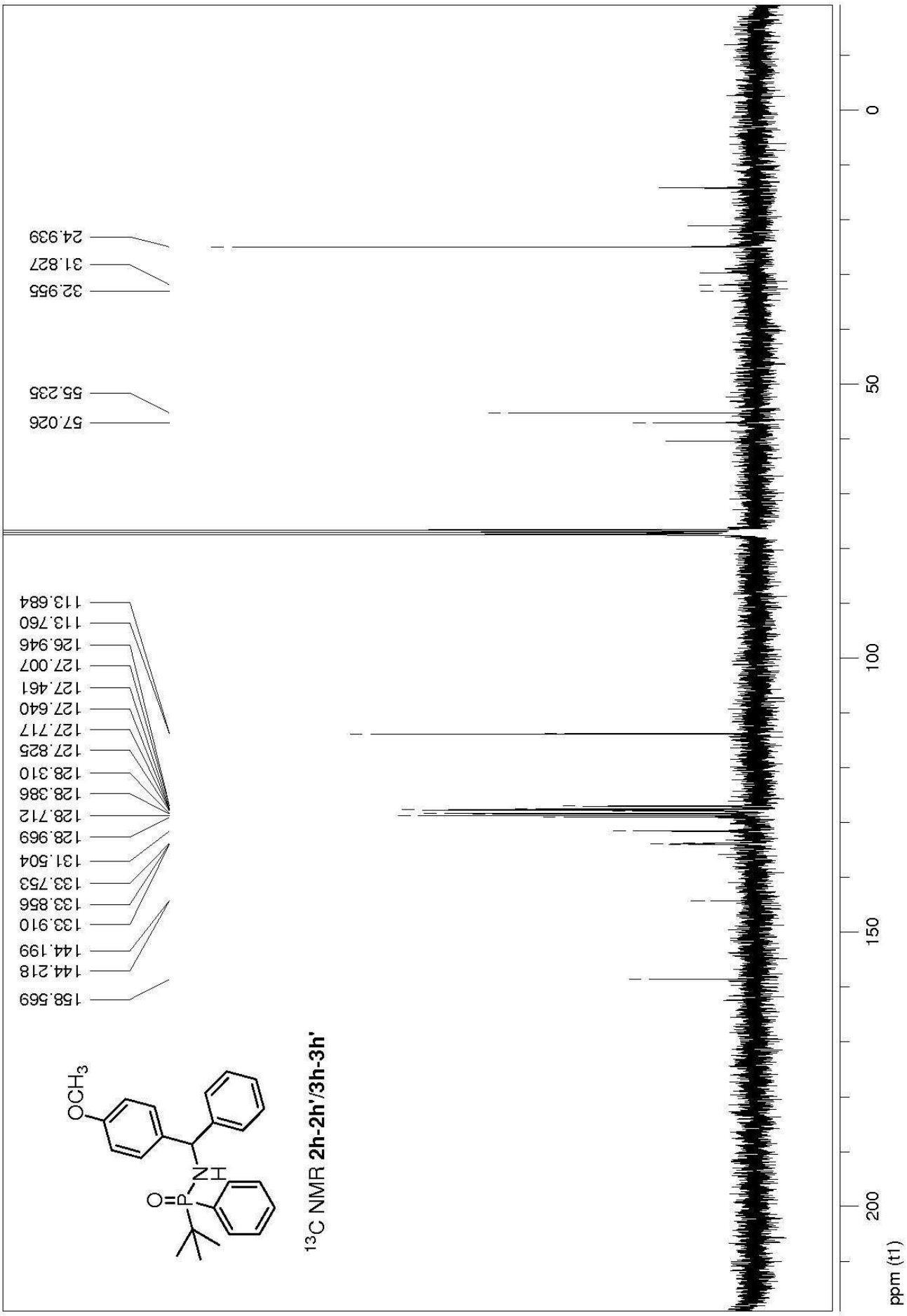

41.476
41.999
50
100
ppm (t1)
^{31}P NMR **2f-2f'/3f-3f'**
O=P
NH

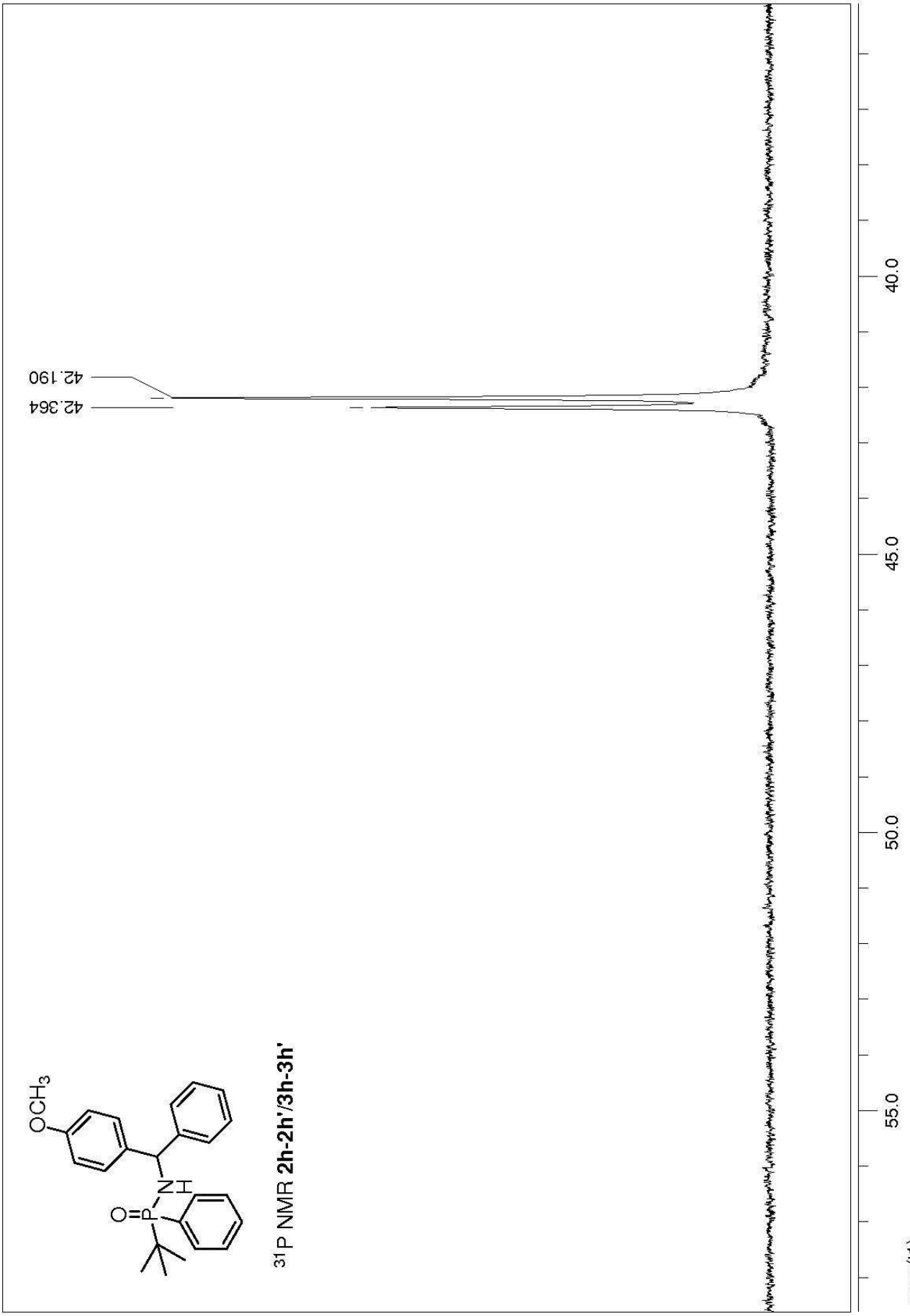

^{1}H NMR **2g-2g'/3g-3g'**
1.036
1.087
1.094
1.143
1.510
1.620
2.443
2.450
2.464
2.474
2.589
2.605
2.614
2.994
3.026
3.058
3.117
3.141
3.165
4.340
4.364
4.392
4.421
4.446
4.469
4.668
4.762
4.796
4.850
7.132
7.157
7.170
7.188
7.207
7.215
7.260
7.297
7.321
7.340
7.362
7.428
7.458
7.475
7.484
7.505
7.530
7.541
7.566
7.794
7.823
7.851
31.77
3.02
7.60
1.94
4.64
1.00
2.27
3.61
2.21
4.77
18.45
6.36
8.23
2.07
0.0
5.0
ppm (t1)

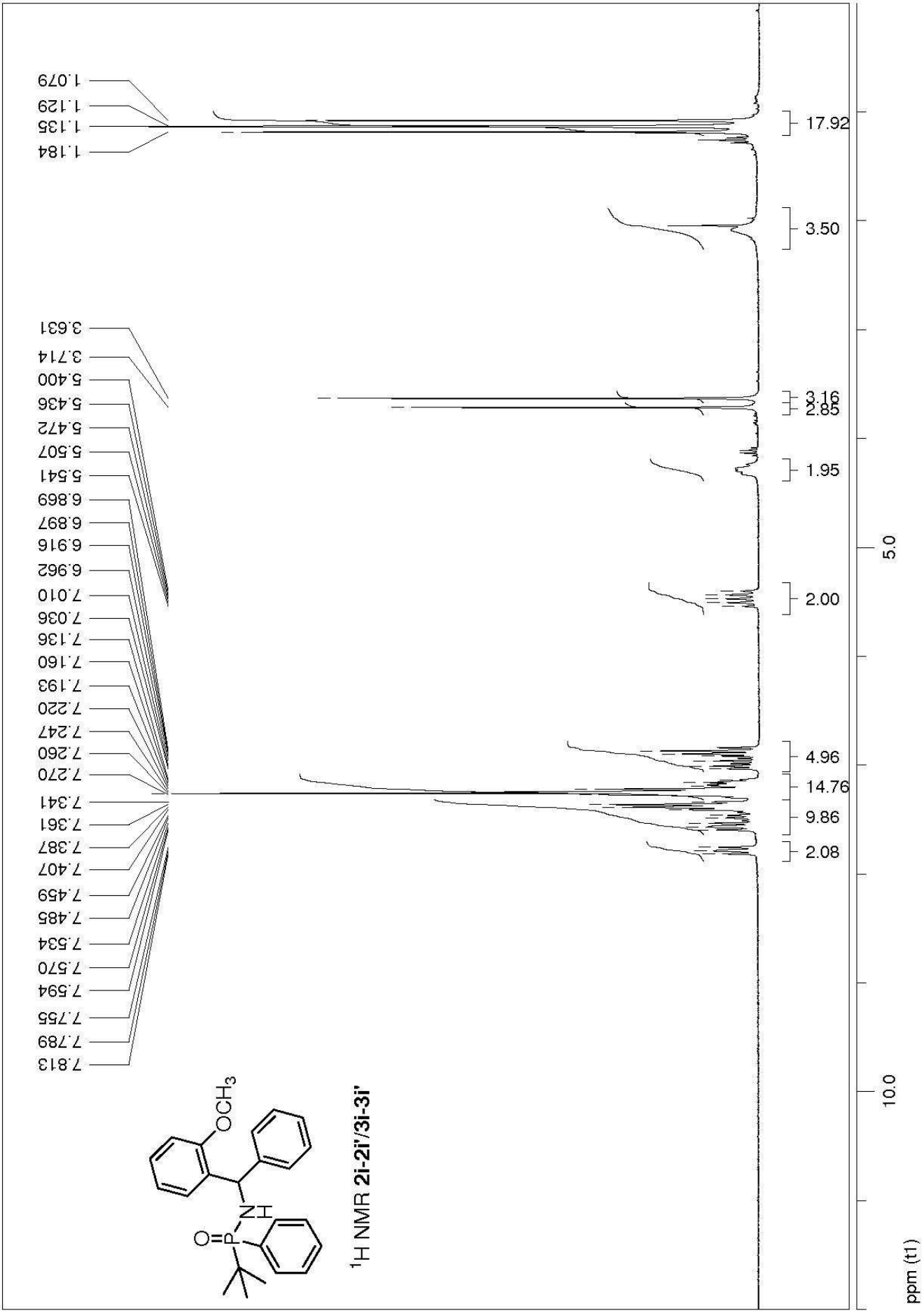

22.267
22.365
24.766
24.846
31.695
32.093
32.867
33.292
48.061
48.110
48.161
48.240
51.825
51.858
52.617
52.648
76.576
77.000
77.423
114.182
114.511
126.542
126.608
126.826
126.918
127.331
127.487
127.821
127.973
128.100
128.248
129.910
131.112
131.145
131.393
131.428
133.086
133.198
133.844
133.959
142.436
142.597
143.721
143.782
144.134
144.151
NH
O=P
^{13}C NMR **2g-2g'/3g-3g'**
50
100
150
ppm (t1)

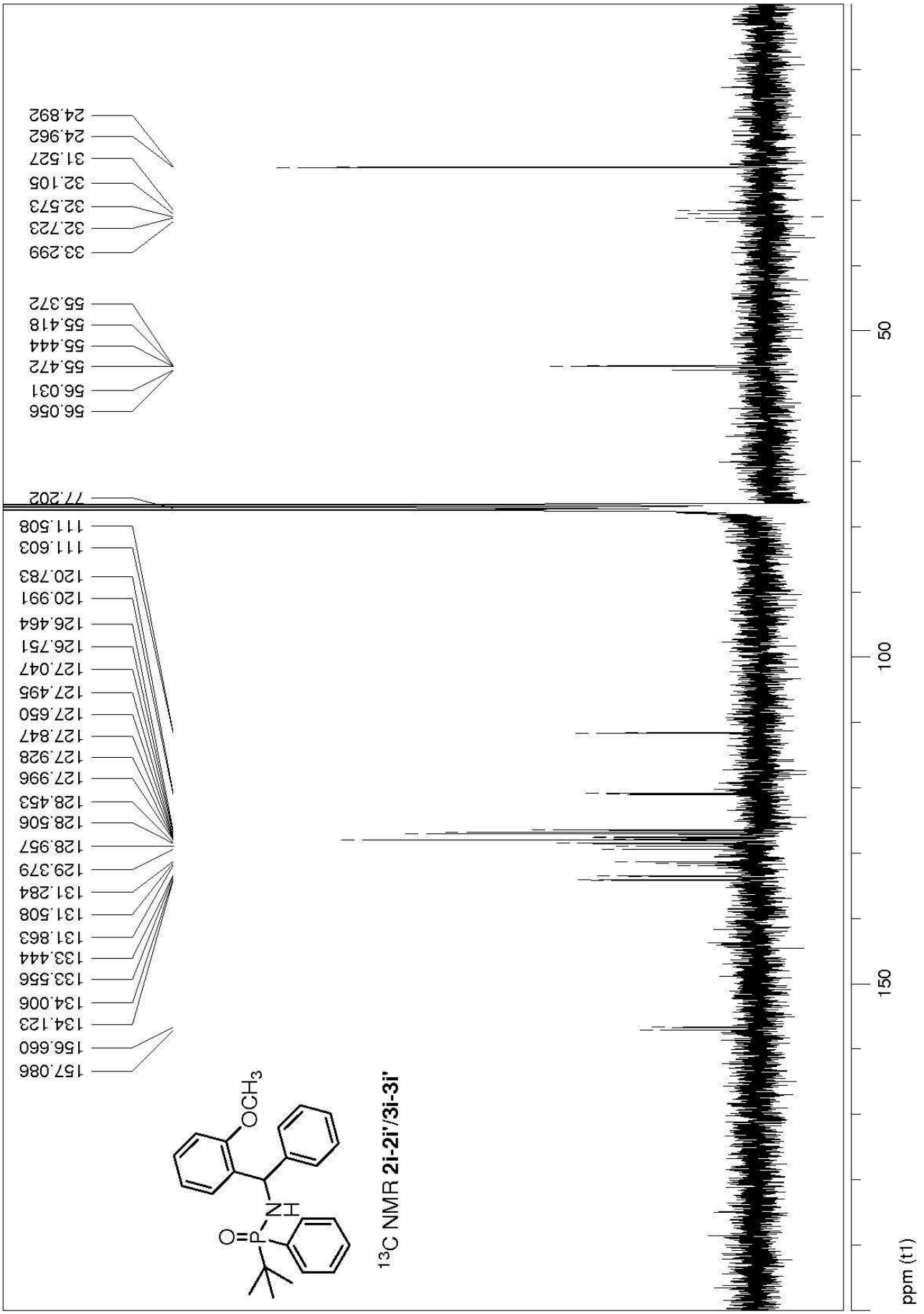

40.042
41.753
50
100
ppm (t1)
^{31}P NMR **2g-2g'/3g-3g'**
O=P
NH

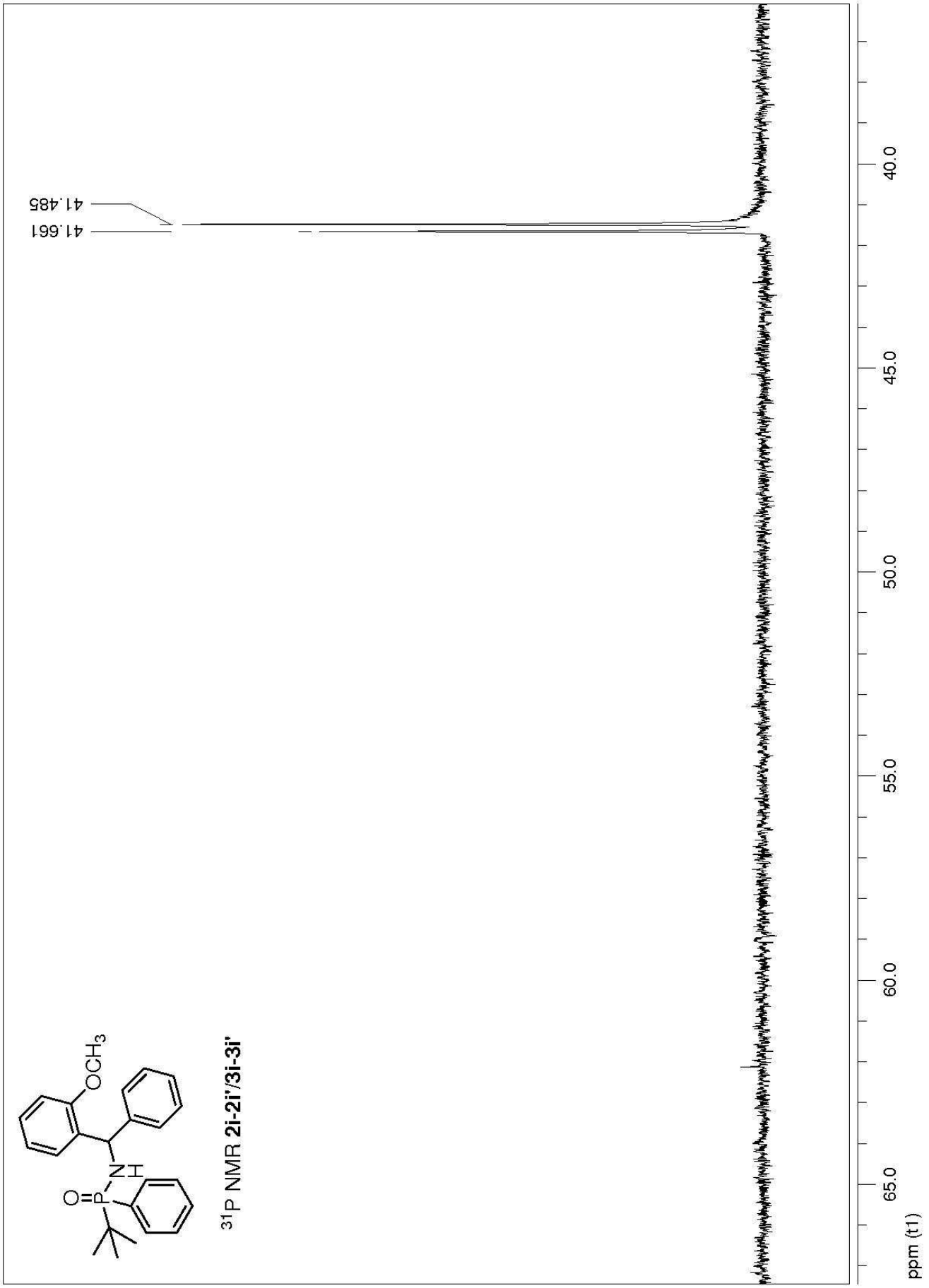

1.109
1.159
2.039
3.235
3.266
3.296
3.767
3.786
5.371
5.404
5.427
5.460
6.783
6.811
6.833
7.052
7.081
7.155
7.176
7.209
7.237
7.260
7.293
7.317
7.342
7.405
7.428
7.446
7.471
7.637
7.667
7.694
9.46
0.96
3.48
1.00
2.32
1.24
9.04
1.22
2.08
5.0
10.0
ppm (t1)
OCH3
NH
O=P
1H NMR 2h-2h'/3h-3h'

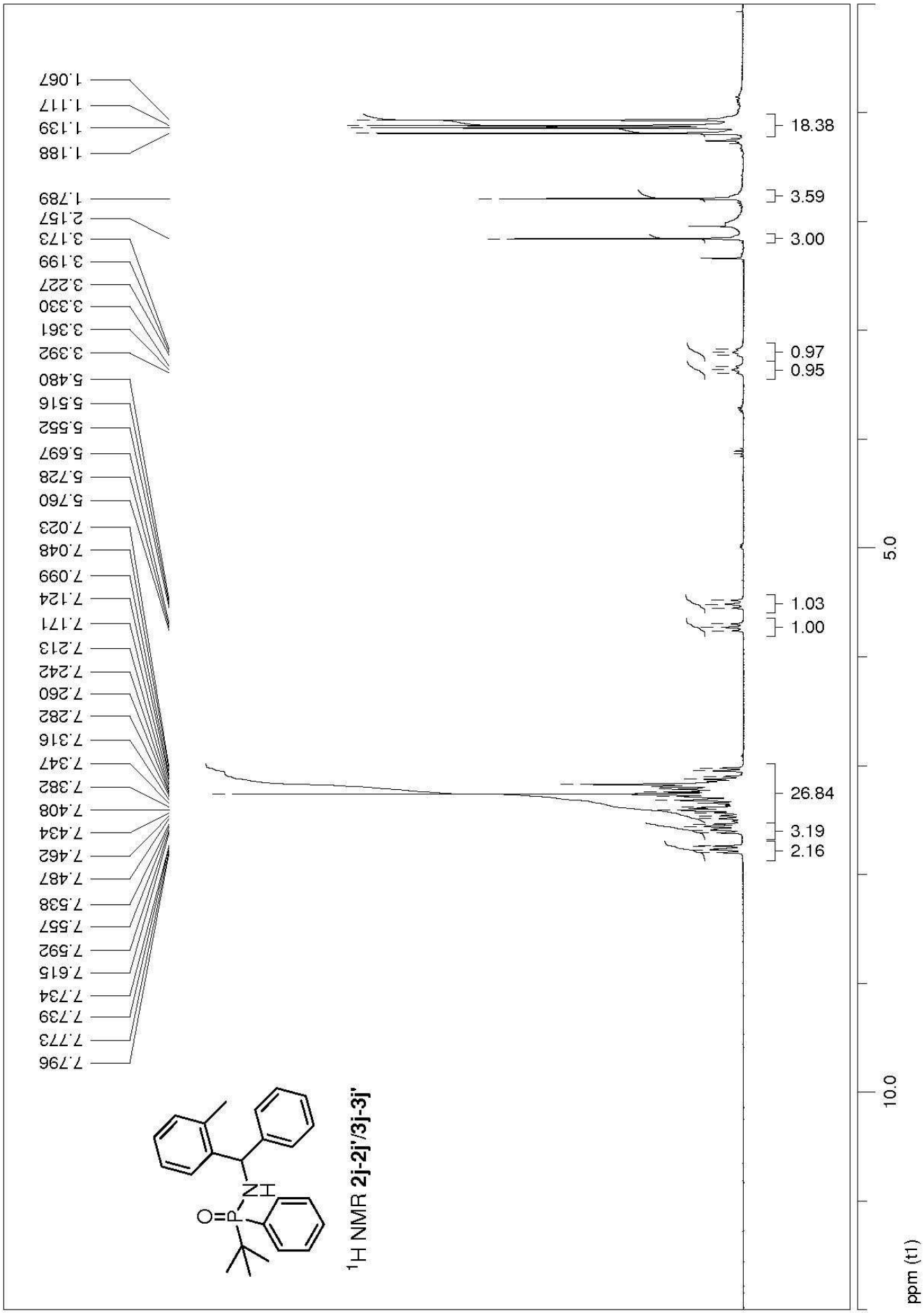

24.939
31.827
32.955
55.235
57.026
113.684
113.760
126.946
127.007
127.461
127.640
127.717
127.825
128.310
128.386
128.712
128.969
131.504
133.753
133.856
133.910
144.199
144.218
158.569
OCH3
O=P
NH
13C NMR 2h-2h'/3h-3h'
0
50
100
150
200
ppm (t1)

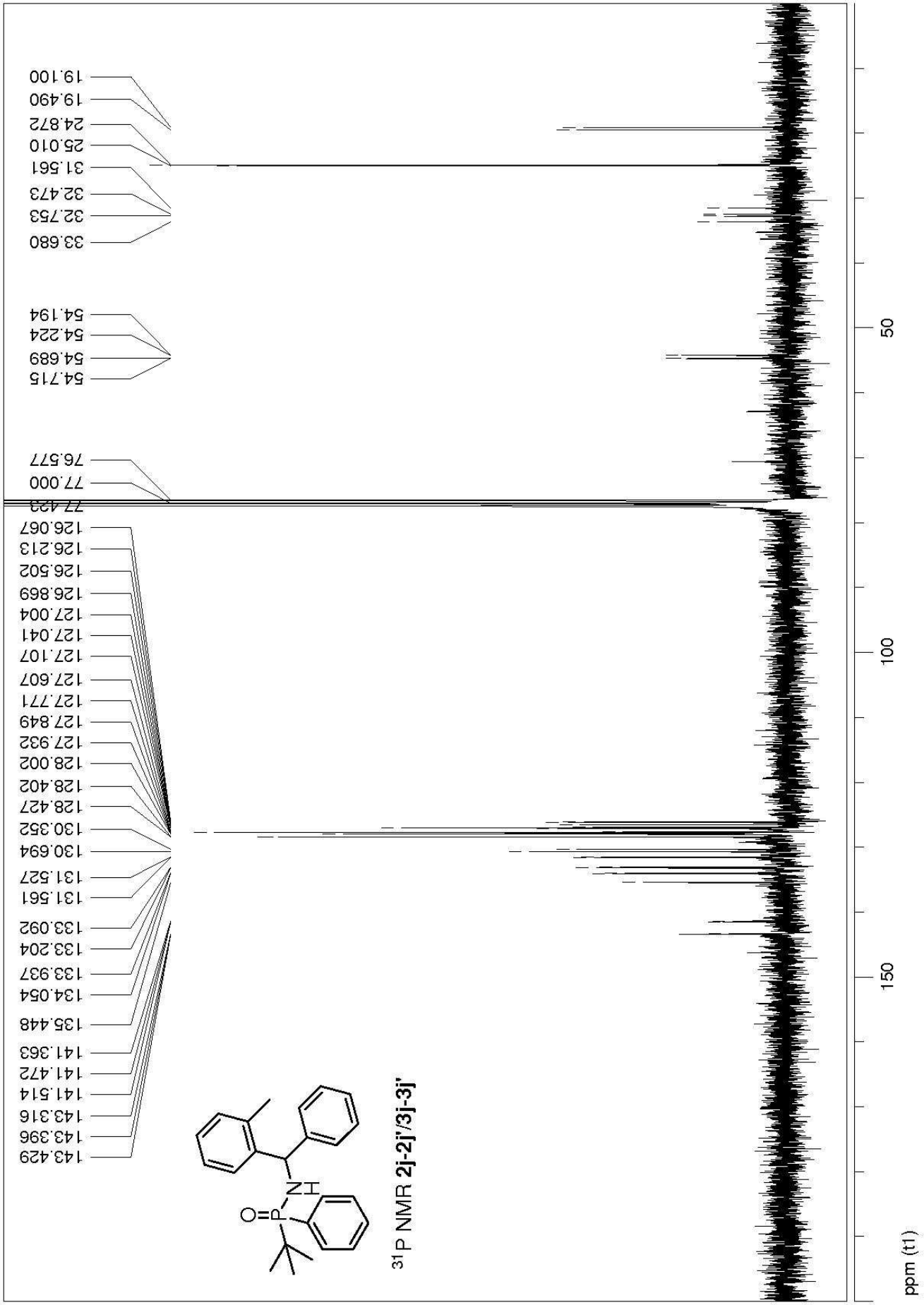

42.190
42.364
40.0
45.0
50.0
55.0
ppm (t1)
OCH3
O=P
NH
31P NMR 2h-2h'/3h-3h'

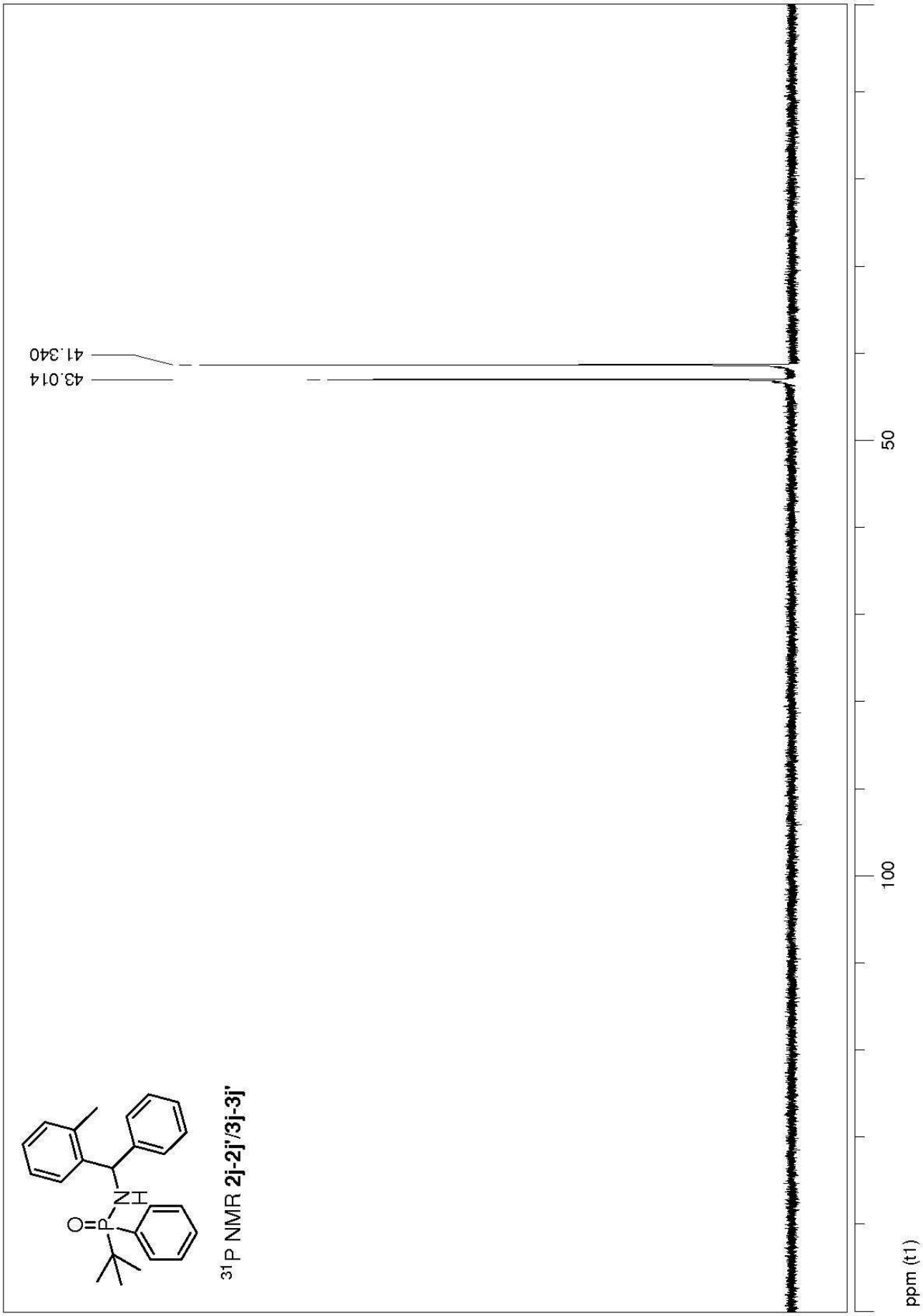

1.079
1.129
1.135
1.184
3.631
3.714
5.400
5.436
5.472
5.507
5.541
6.869
6.897
6.916
6.962
7.010
7.036
7.136
7.160
7.193
7.220
7.247
7.260
7.270
7.341
7.361
7.387
7.407
7.459
7.485
7.534
7.570
7.594
7.755
7.789
7.813
17.92
3.50
3.16
2.85
1.95
2.00
4.96
14.76
9.86
2.08
5.0
10.0
ppm (t1)
OCH3
NH
O=P
1H NMR 2i-2i'/3i-3i'

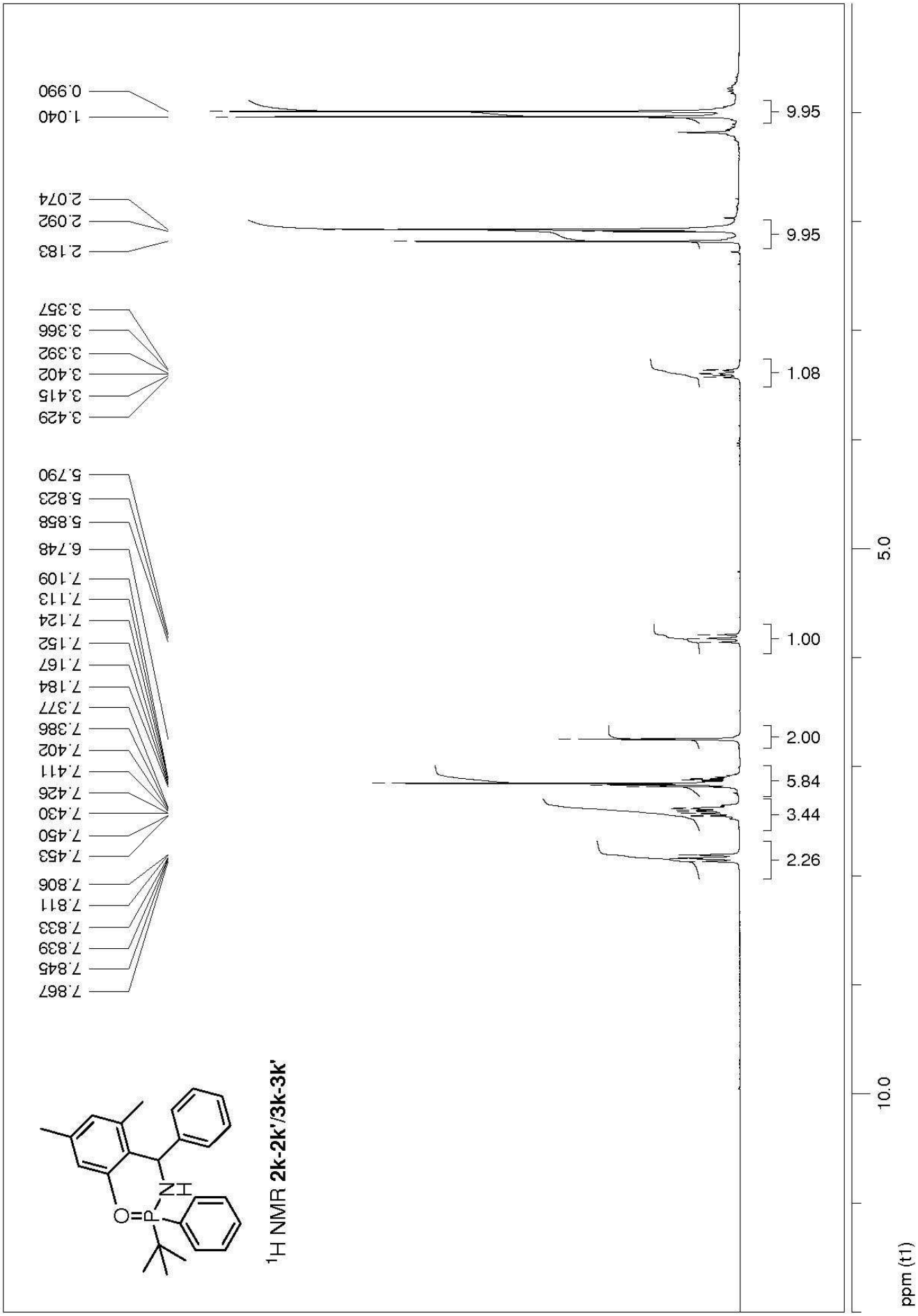

24.892
24.962
31.527
32.105
32.573
32.723
33.299
55.372
55.418
55.444
55.472
56.031
56.056
77.202
111.508
111.603
120.783
120.991
126.464
126.751
127.047
127.495
127.650
127.847
127.928
127.996
128.453
128.506
128.957
129.379
131.284
131.508
131.863
133.444
133.556
134.006
134.123
156.660
157.086
OCH3
NH
O=P
13C NMR 2i-2i'/3i-3i'
50
100
150
ppm (t1)


41.485
41.661
40.0
45.0
50.0
55.0
60.0
65.0
ppm (t1)
^{31}P NMR **2i-2i'/3i-3i'**
OCH3
NH
O=P

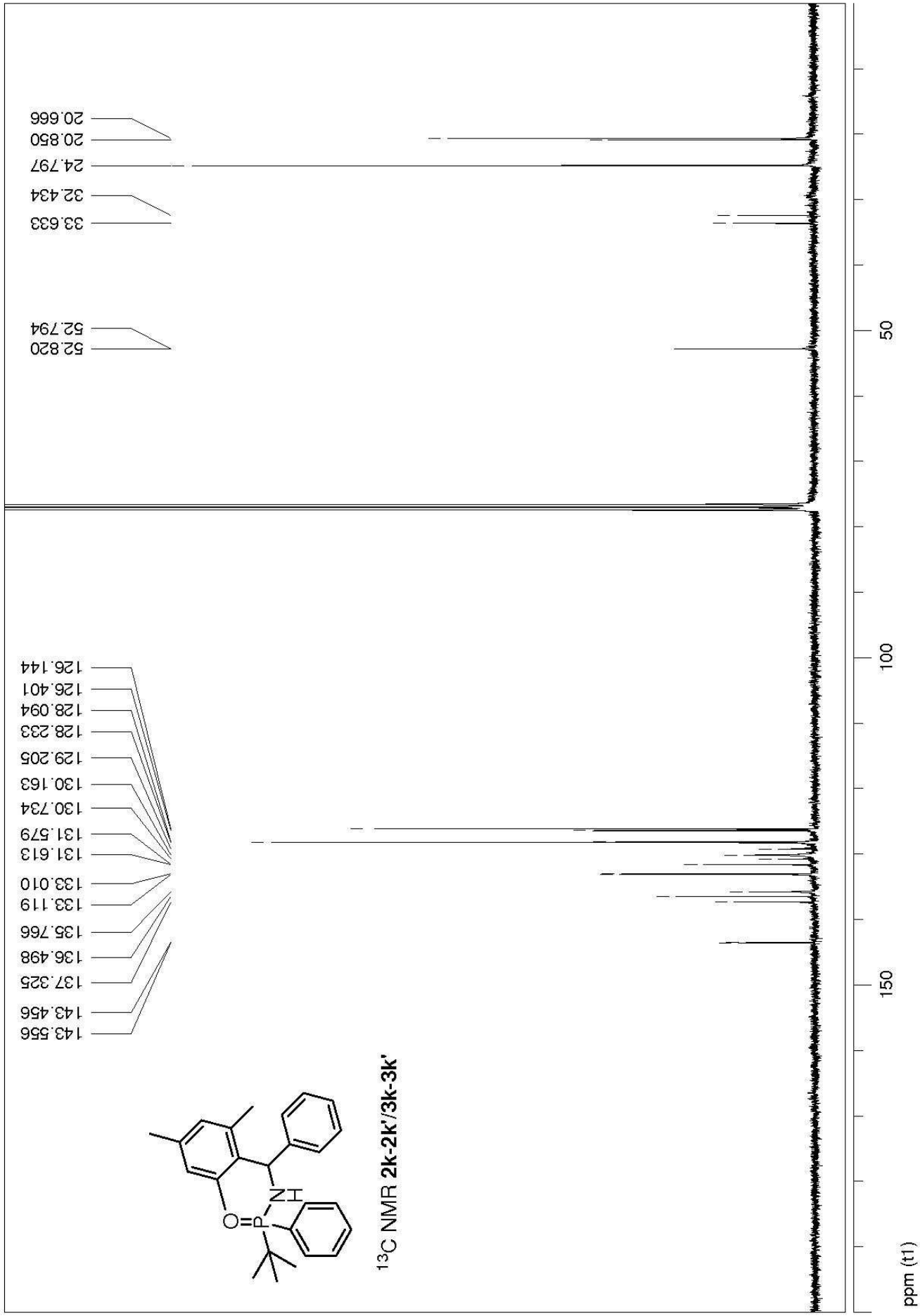

1.067
1.117
1.139
1.188
1.789
2.157
3.173
3.199
3.227
3.330
3.361
3.392
5.480
5.516
5.552
5.697
5.728
5.760
7.023
7.048
7.099
7.124
7.171
7.213
7.242
7.260
7.282
7.316
7.347
7.382
7.408
7.434
7.462
7.487
7.538
7.557
7.592
7.615
7.734
7.739
7.773
7.796
18.38
3.59
3.00
0.97
0.95
1.03
1.00
26.84
3.19
2.16
5.0
10.0
ppm (t1)
NH
O=P
^{1}H NMR **2j-2j'/3j-3j'**

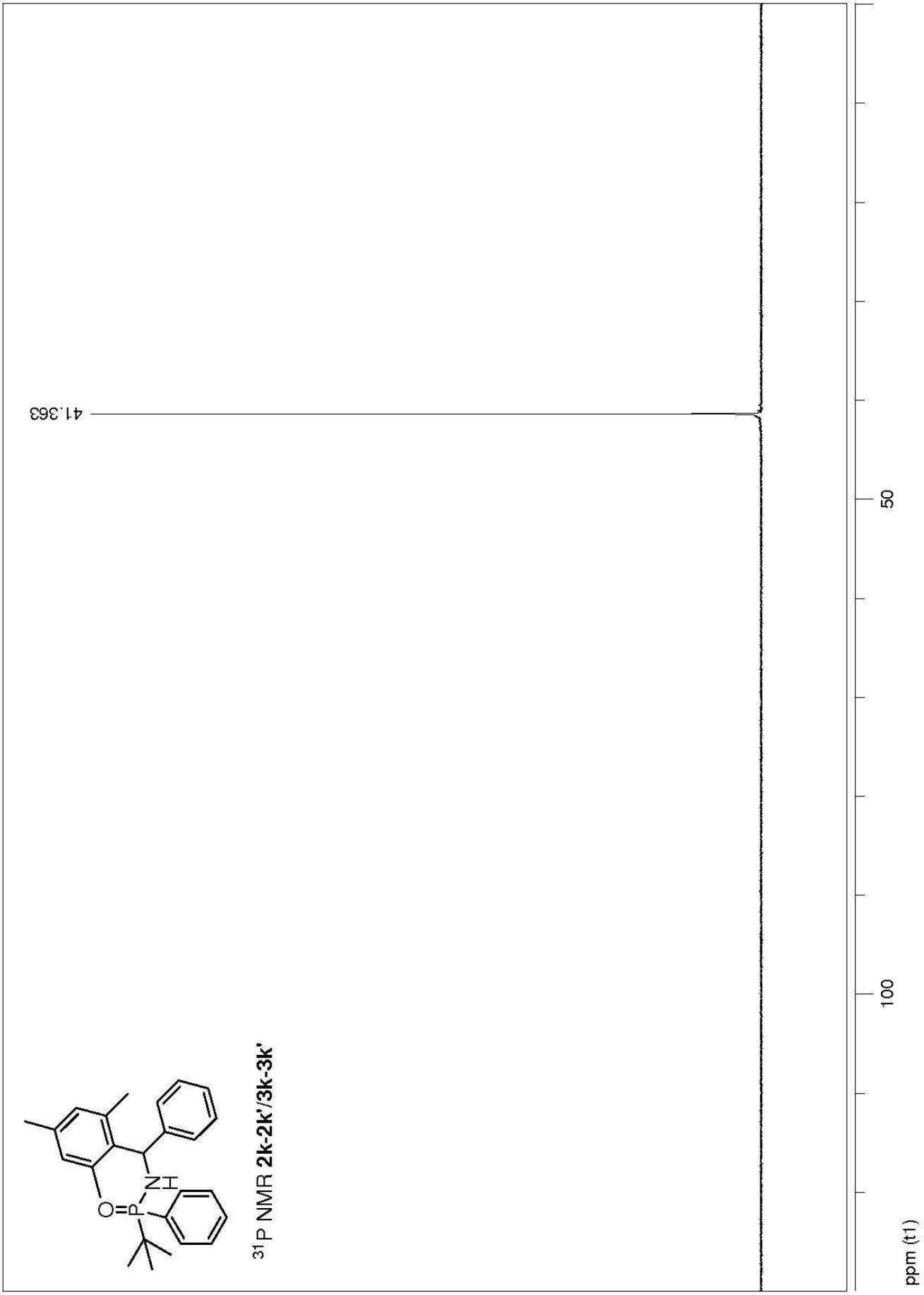

19.100
19.490
24.872
25.010
31.561
32.473
32.753
33.680
54.194
54.224
54.689
54.715
76.577
77.000
77.423
126.067
126.213
126.502
126.869
127.004
127.041
127.107
127.607
127.771
127.849
127.932
128.002
128.402
128.427
130.352
130.694
131.527
131.561
133.092
133.204
133.937
134.054
135.448
141.363
141.472
141.514
143.316
143.396
143.429
O=P
NH
^{31}P NMR **2j-2j'/3j-3j'**
50
100
150
ppm (t1)


41.340
43.014
50
100
ppm (t1)
O=P
NH
^{31}P NMR **2j-2j'/3j-3j'**

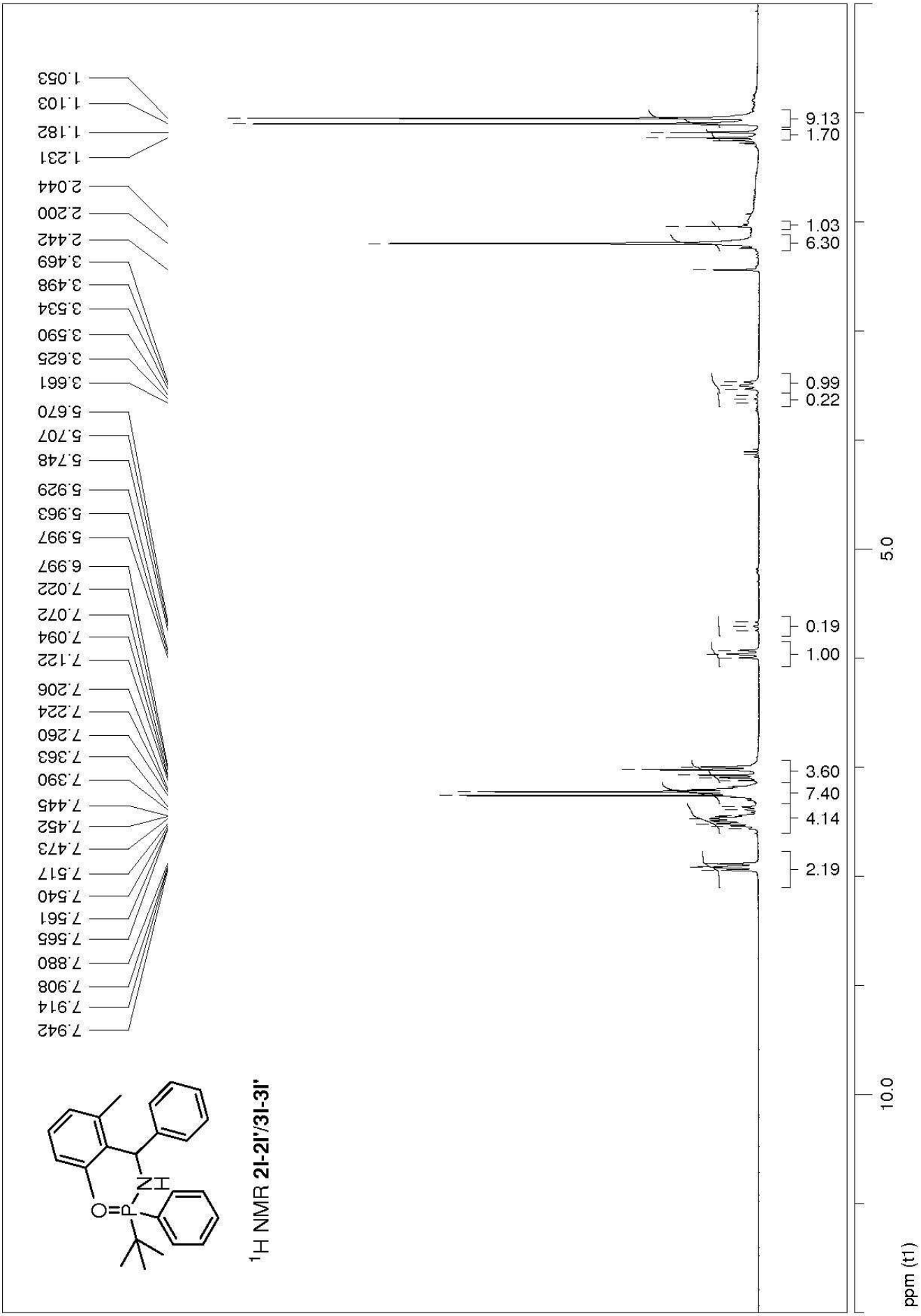


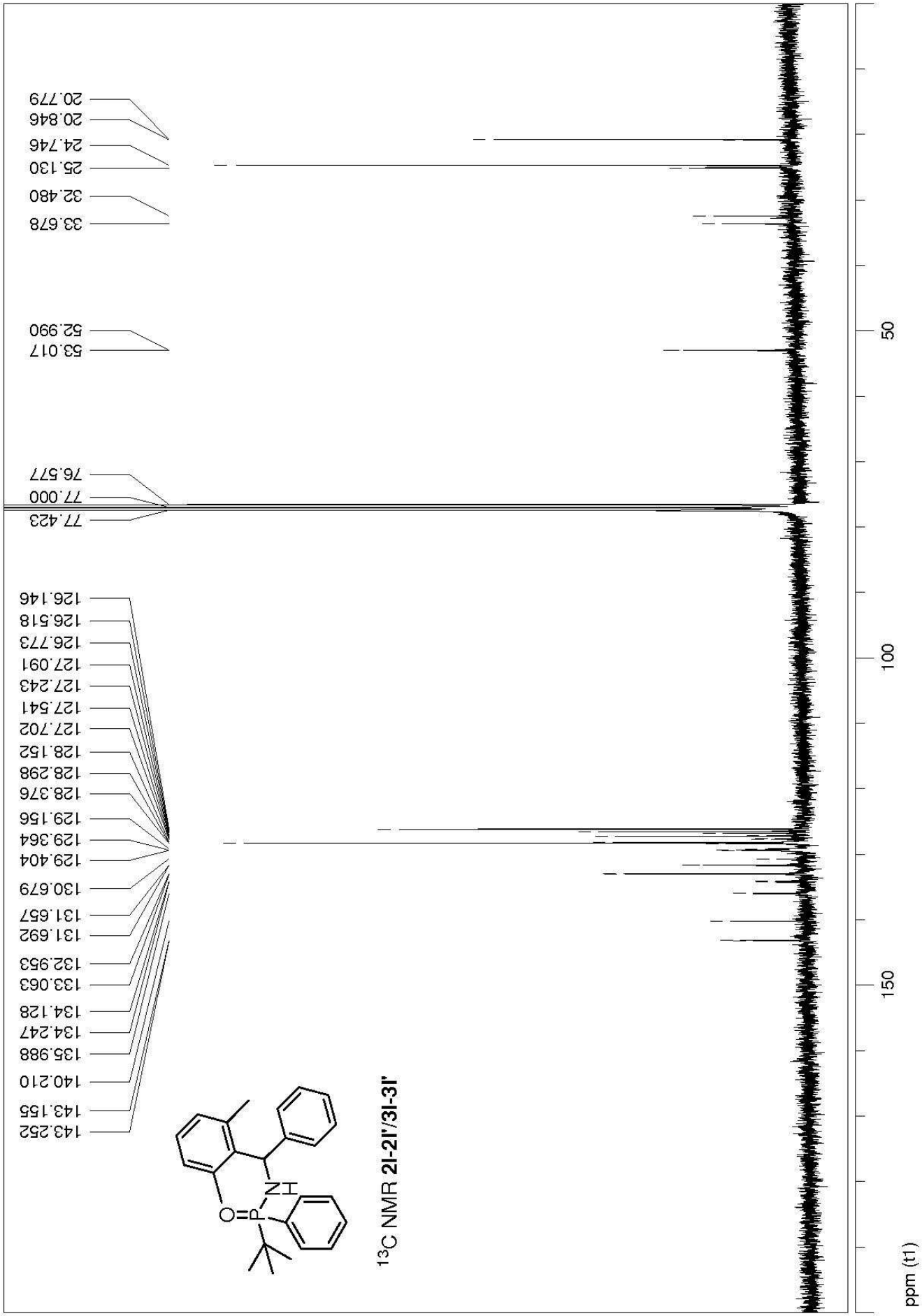
^{1}H NMR **2k-2k'/3k-3k'**

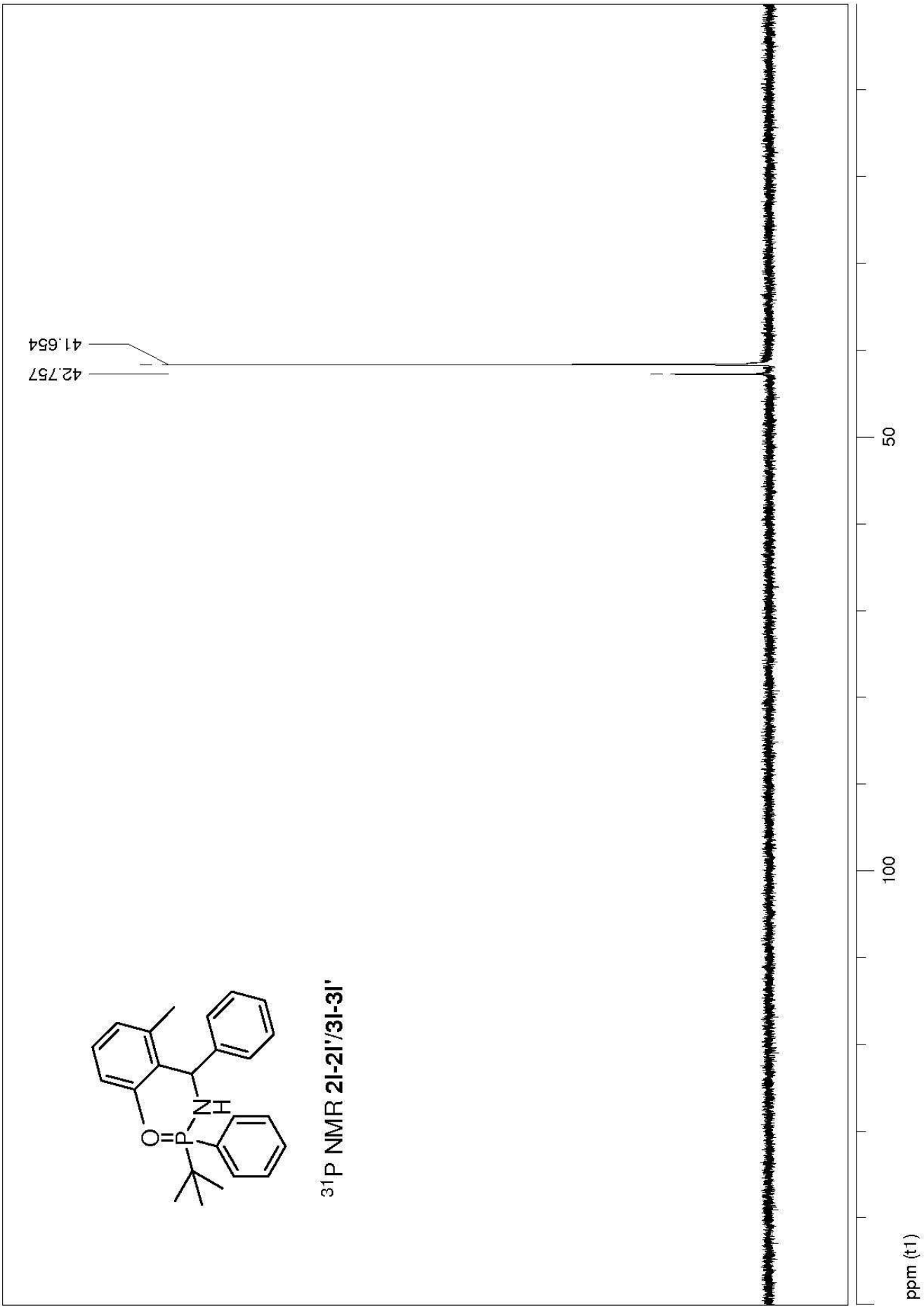

20.666
20.850
24.797
32.434
33.633
52.794
52.820
126.144
126.401
128.094
128.233
129.205
130.163
130.734
131.579
131.613
133.010
133.119
135.766
136.498
137.325
143.456
143.556
O=P
NH
^{13}C NMR **2k-2k'/3k-3k'**
50
100
150
ppm (t1)



^{31}P NMR **2k-2k'/3k-3k'**


1.053
1.103
1.182
1.231
2.044
2.200
2.442
3.469
3.498
3.534
3.590
3.625
3.661
5.670
5.707
5.748
5.929
5.963
5.997
6.997
7.022
7.072
7.094
7.122
7.206
7.224
7.260
7.363
7.390
7.445
7.452
7.473
7.517
7.540
7.561
7.565
7.880
7.908
7.914
7.942
9.13
1.70
1.03
6.30
0.99
0.22
0.19
1.00
3.60
7.40
4.14
2.19
5.0
10.0
ppm (t1)
^{1}H NMR **2I-2I'/3I-3I'**


20.779
20.846
24.746
25.130
32.480
33.678
52.990
53.017
76.577
77.000
77.423
126.146
126.518
126.773
127.091
127.243
127.541
127.702
128.152
128.298
128.376
129.156
129.364
129.404
130.679
131.657
131.692
132.953
133.063
134.128
134.247
135.988
140.210
143.155
143.252
^{13}C NMR **2I-2I'/3I-3I'**
50
100
150
ppm (t1)



^{31}P NMR **2l-2l'/3l-3l'**