Electronic Supplementary Information

A Method for the Synthesis of Pyridines from Aldehydes, Alkynes and NH_4OAc Involving Rh-Catalyzed Hydroacylation and N-Annulation

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Contents

1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel and column chromatography was monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60F-254) using UV light as a visualizing agent, *p*-anisaldehyde, ninhydrin and $KMnO_4$ solution as staining solutions, and heat as developing agent. Gas chromatographic analyses were performed on Agilent 7890A instrument with FID detector and an Agilent HP-5 capillary column. Mass chromatography analyses were performed on Agilent 5975C instrument and an Agilent HP-5MS column. IR spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. ^1H NMR and ^{13}C NMR were recorded on a Bruker Advance II/DPX 400(400 MHz ^1H, 100 MHz ^{13}C) spectrometers with chemical shifts reported relative to residual deuterated solvent peaks. ^1H NMR spectra were referenced to $CDCl_3$ (for ^1H, δ = 7.26) as internal standard, and are reported as follows: chemical shift multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (for ^{13}C, δ = 77.26) as internal standard]. High-resolution Mass spectra were provided by NCIRF Seoul national university.

2. Materials

Most commercially available reagent grade chemicals (**2a-c**, **3a**, **3b**, **5**, **9a-9j**, **10a-c**, **12** and **13**) were purchased from Aldrich Chemical Company, TCI, and Burdick and Jackson, and used as received without further purification unless otherwise stated. Toluene (purchased from Duksan Chemical) was distilled from sodium/benzophenone under nitrogen atmosphere prior to use. Complexes $[Cp^*RhCl_2]_2$ (**4**)[1] and $(Ph_3P)_3RhCl$ (**11**)[2] were prepared according to the literature procedure and stored in a refrigerator under N_2 atmosphere.

[1] J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.* 1969, **91**, 5970.

[2] J. A. Osborn and G. Wilkinson, *Inorg. Synth.* 1990, **28**, 77.

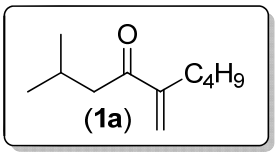
3. Experimental

- A typical procedure for Stepwise synthesis of pyridines through chelation-assisted hydroacylation of 1-alkynes with aldehydes (Table 2)

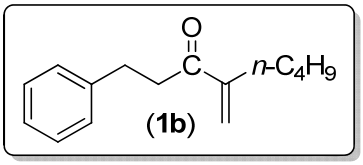
a. Chelation-assisted hydroacylation of 1-alkynes with aldehydes (entry 1): To a 1 ml screw-capped pressure vial (1 ml) was added isovaleraldehyde (**9a**, 17.2 mg, 0.20 mmol), 1-hexyne (**10a**, 32.9 mg, 0.40 mmol), $(Ph_3P)_3RhCl$ (**11**, 9.3 mg, 0.01 mmol), 2-amino-3-picoline (**12**, 8.7 mg, 0.08 mmol), benzoic acid (**13**, 4.9 mg, 0.04 mmol) and toluene (200 mg). The mixture was heated at 110 ^oC for 4 h with stirring. After cooling the vessel to room temperature, the crude mixture was purified by column chromatography (*n*-hexane:Et_2O = 15:1) on silica gel to give 2-methyl-5-methylenenonan-4-one (**1a**, 25.9 mg, 77 %) as a pale yellow oil.

b. N-Annulation of α,β-enone with internal alkyne: To a MeOH solution (0.2 mL) of 2-methyl-5-methylenenonan-4-one (**1a**) (33.7 mg, 0.20 mmol) and 4-octyne (**2a**) (44.1 mg, 0.40 mmol) were added $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) and $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol), NH_4OAc (30.8 mg, 0.40 mmol), and the reaction mixture was stirred at 130 ^oC under a nitrogen atmosphere for 6 h. After cooling to room temperature, the solvent was removed *in vacuo*, and the resulting crude mixture was subject to flash column chromatography (*n*-hexane:ethyl acetate = 90 : 1) to afford 3-butyl-2-isobutyl-5,6-dipropylpyridine (**6a**, 51.8 mg, 0.188 mmol) in 94% yield.

- Characterization data for compounds *meso*-α,β-enone (1a-g), linear α,β-enone (15a-f), and pyridines (6a-k)



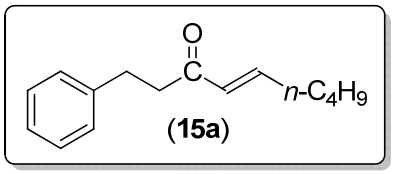
2-Methyl-5-methylenenonan-4-one (1a) ^1H NMR (400 MHz, $CDCl_3$) δ 5.92(s, 1H), 5.67 (s, 1H), 2.52 (d, *J* = 6.9 Hz, 2H), 2.24 (t, *J* = 6.6 Hz, 2H), 2.17-2.11 (m, 1H), 1.39-1.25 (m, 4H), 0.91-0.86 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 149.8, 123.5, 47.0, 30.92, 30.89, 25.7, 22.9, 22.7, 14.2; IR spectrum ($CDCl_3$) 3087, 3028, 2925, 2854, 1680, 1410, 1223, 748 cm^{-1}; HR-MS(EI+) calcd for $C_{11}H_{20}O$ $[M]^+$ 168.1514; found 168.1507.



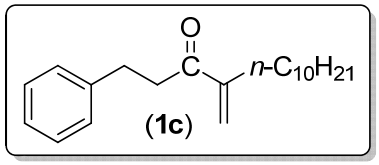
4-Methylene-1-phenyloctan-3-one (1b) ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.17 (m, 5H), 5.96 (s, 1H), 5.70 (s, 1H), 3.03-2.92 (m, 4H), 2.27 (t, *J* = 6.7 Hz, 2H), 1.41-1.26 (m, 4H), 0.90 (t, *J* = 7.0, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 201.3, 149.3, 141.7, 128.7, 128.6, 126.3, 123.9, 39.9, 30.9, 30.7, 22.7, 14.2; IR spectrum ($CDCl_3$) 3028, 2957, 2930, 2871, 1678, 1454, 1109, 749 cm^{-1}; HR-MS(EI+) calcd for $C_{15}H_{20}O$ $[M]^+$ 216.1514; found 216.1513.

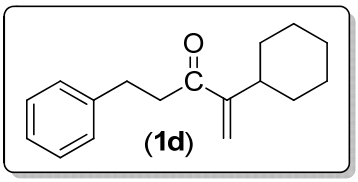
1-Phenylnon-4-en-3-one (15a) [CAS No. 90729-79-6] ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.16 (m, 5H), 6.85-6.78 (m, 1H), 6.09 (d, *J* = 16 Hz, 1H), 2.95-2.84 (m, 4H), 2.19 (d, *J* = 13.0 Hz, 2H), 1.46-1.39 (m, 2H), 1.37-1.28 (m, 2H), 0.90 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 148.0, 141.5, 130.5, 128.6, 128.5, 126.2, 41.8, 32.3, 30.4, 30.3, 22.4, 14.0.



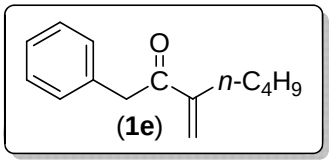
4-Methylene-1-phenyltetradecan-3-one (1c) ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 5H), 5.95 (s, 1H), 5.69 (s, 1H), 3.00-2.93 (m, 4H), 2.25 (t, *J* = 6.8 Hz, 2H), 1.38-1.25 (m, 16H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 149.3, 128.7, 128.6, 126.3, 123.8, 39.9, 32.1, 31.1, 30.6, 29.8, 29.7, 29.6, 29.5, 28.7, 22.9, 14.3; IR spectrum ($CDCl_3$) 3076, 2942, 2852, 1643, 1441, 1214, 1182 cm^{-1}; HR-MS(EI+) calcd for $C_{21}H_{32}O$ $[M]^+$ 300.2453; found 300.2447.



2-Cyclohexyl-5-phenylpent-1-en-3-one (1d) ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.17 (m, 5H), 5.93 (s, 1H), 5.63 (s, 1H), 3.01-2.91 (m, 4H), 2.57 (t, *J* = 11.6 Hz, 1H), 1.76-1.67 (m, 2H), 1.39-1.01 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 154.7, 141.7, 128.7, 128.64, 126.2, 121.7, 40.3, 37.8, 32.9, 30.7, 26.9, 26.5; IR spectrum ($CDCl_3$) 3086, 2925, 2851, 1679, 1450, 1376, 1067, 748 cm^{-1}; HR-MS(EI+) calcd for $C_{17}H_{22}O$ $[M]^+$ 242.1617; found 242.1670.

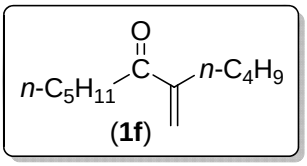


3-Methylene-1-phenylheptan-2-one (1e) ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 6.08 (s, 1H), 5.78 (s, 1H), 3.99 (s, 2H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.36-1.27 (m, 4H), 0.86 (t, *J* = 6.8, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 135.2, 134.3, 129.5, 128.8, 127.0, 125.0, 45.1, 31.0, 30.7, 22.6, 14.1; IR spectrum ($CDCl_3$) 3087, 2957, 2860, 1709, 1626, 1495, 1134, 734 cm^{-1};



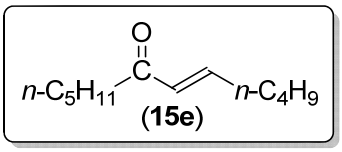
HR-MS(EI+) calcd for $C_{14}H_{18}O$ $[M]^+$ 202.1358; found 202.1362.

5-Methyleneundecan-6-one (1f) [CAS No. 101074-49-1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.9 (s, 1H), 5.6 (s, 1H), 2.6 (t, J = 7.4 Hz, 2H), 2.2 (t, J = 6.6 Hz, 2H), 1.6 (m, 2H) 1.4-1.2 (m, 8H), 0.9 (t, J = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 149.3, 123.4, 40.0, 31.7, 30.8, 24.5, 22.7, 22.6, 14.1, 14.0.



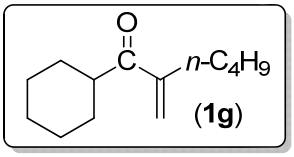
(1f)

Dodec-7-en-6-one (15e) [CAS No. 81791-67-5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.8 (m, 1H), 6.1 (m, 1H), 2.5 (t, J = 7.3 Hz, 2H), 2.2 (m, 2H), 1.6 (m, 2H), 1.5-1.2 (m, 8H), 0.9 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 147.3, 130.0, 40.1, 32.1, 31.5, 30.2, 24.0, 22.4, 22.2, 13.9, 13.8.



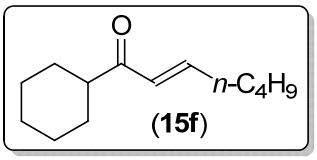
(15e)

1-Cyclohexyl-2-methylenehexan-1-one (1g) [CAS No. 473835-74-4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.9 (s, 1H,), 5.7 (s, 1H), 3.0-2.9 (m, 1H), 2.3 (t, J = 6.7 Hz, 2H), 1.8-1.6 (m, 4H), 1.5-1.2 (m, 10H), 0.9 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 148.3,122.4, 45.0, 31.0, 30.7, 29.7, 25.9, 25.8, 22.4, 13.9.



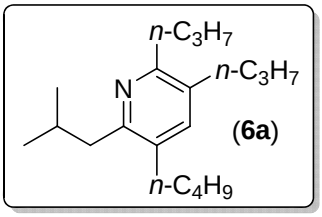
(1g)

1-Cyclohexylhept-2-en-1-one (15f) [CAS No. 111036-53-4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.9-6.8 (m, 1H), 6.1 (d, J = 15.7 Hz, 1H), 2.6-2.5 (m, 1H), 2.2 -2.1 (m, 2H), 1.8-1.7 (m, 4H), 1.5-1.2 (m, 10H), 0.9 (t, J = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 147.1, 128.6, 48.6, 32.1, 30.3, 28.7, 25.9, 25.8, 22.2, 13.8.



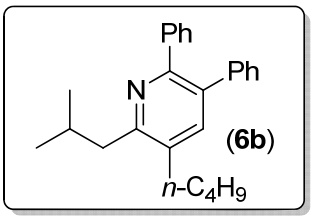
(15f)

3-Butyl-2-isobutyl-5,6-dipropylpyridine (6a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 2.69 (t, J = 7.6 Hz, 2H), 2.61 (d, J = 7.2 Hz, 2H), 2.55-2.50 (m, 4H), 2.18-2.08 (m, 1H), 1.74-1.65 (m, 2H), 1.63-1.48 (m, 4H), 1.42-1.33 (m, 2H), 0.99-0.94 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 156.0, 137.6, 132.9, 132.1, 43.3, 36.7, 34.2, 33.3, 31.8, 29.2, 24.2, 23.4, 23.0, 22.8, 14.4, 14.3, 14.2; IR spectrum ($CDCl_3$) 2957, 2869, 1557, 1449, 1379, 1365, 1169 cm^{-1}; HR-MS(EI+) calcd for $C_{19}H_{33}N$ $[M]^+$ 275.2613; found 275.2611.

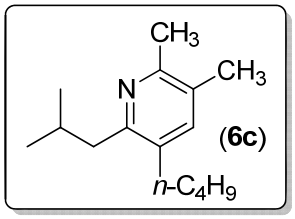


(6a)

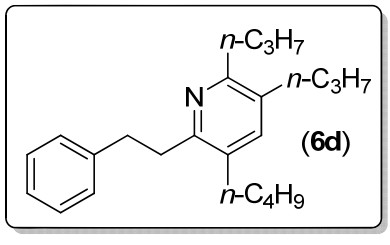
3-Butyl-2-isobutyl-5,6-diphenylpyridine (6b) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.35-7.34 (m, 2H), 7.25-7.16 (m, 8H), 2.78 (d, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.38-2.28 (m, 1H), 1.67-1.60 (m, 2H), 1.50-1.41 (m, 2H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.98 (t, *J* = 7.6 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 153.7, 140.8, 140.6, 139.3, 134.6, 133.2, 130.3, 129.9, 128.4, 128.0, 127.5, 127.0, 43.4, 33.1, 31.9, 29.1, 23.0, 14.2; IR spectrum ($CDCl_3$) 3083, 2955, 2868, 1877, 1494, 1449, 699 cm^{-1}; HR-MS(EI+) calcd for $C_{25}H_{29}N$ $[M]^+$ 343.2300; found 343.2298.



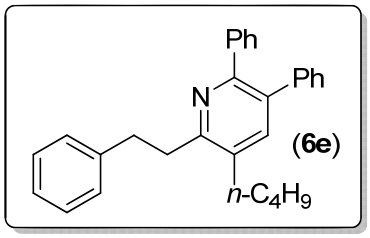
3-Butyl-2-isobutyl-5,6-dimethylpyridine (6c) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 2.60 (d, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.20 (s, 3H), 2.14-2.07 (m, 1H), 1.55-1.47 (m, 2H), 1.42-1.33 (m, 2H), 0.95-0.94 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.5, 138.3, 133.3, 128.3, 43.2, 33.4, 31.7, 29.5, 22.9, 22.8, 22.3, 18.9, 14.2; IR spectrum ($CDCl_3$) 2956, 2928, 2867, 1737, 1461, 1380, 726 cm^{-1}; HR-MS(EI+) calcd for $C_{15}H_{25}N$ $[M]^+$ 219.1987; found 219.1985.



3-Butyl-2-phenethyl-5,6-dipropylpyridine (6d) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 7.16 (s, 1H), 3.06 (br s, 4H), 2.77 (t, *J* = 4.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 1.80-1.73 (m, 2H), 1.68-1.61 (m, 2H), 1.53-1.47 (m, 2H), 1.41-1.29 (m, 2H), 1.06-1.05 (m, 6H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.7, 142.7, 138.0, 132.7, 128.8, 128.4, 126.0, 66.1, 36.8, 36.5, 36.2, 34.2, 33.2, 31.8, 24.2, 15.5, 14.3, 14.2; IR spectrum ($CDCl_3$) 3026, 2958, 2930, 2870, 1558, 1495, 1377, 749 cm^{-1}; HR-MS(EI+) calcd for $C_{23}H_{33}N$ $[M]^+$ 323.2613; found 323.2614.

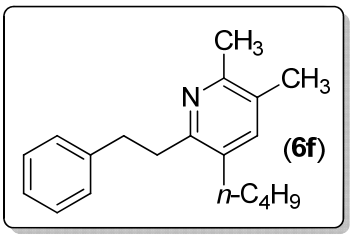


3-Butyl-2-phenethyl-5,6-diphenylpyridine (6e) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.37-7.16 (m, 15H), 3.18 (br s, 4H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.60-1.55 (m, 2H), 1.46-1.38 (m, 2H), 0.95 (t, *J* = 7.2 Hz,

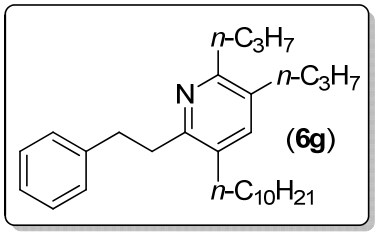


3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.9, 142.6, 140.6, 140.6, 139.5, 134.3, 133.7, 130.3, 129.8, 128.8, 128.6, 128.4, 128.0, 127.7, 127.1, 126.1, 36.7, 35.8, 33.0, 31.8, 23.0, 14.2; IR spectrum ($CDCl_3$) 3026, 2956, 2929, 2859, 1601, 1427, 621 cm^{-1}; HR-MS(EI+) calcd for $C_{29}H_{29}N$ $[M]^+$ 391.2300; found 391.2307.

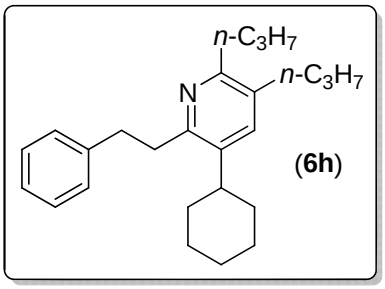
3-Butyl-5,6-dimethyl-2-phenethylpyridine (6f) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.17 (m, 5H), 7.13 (s, 1H), 3.00 (br s, 4H), 2.49-2.45 (m, 5H), 2.22 (s, 3H), 1.51-1.43 (m, 2H), 1.39-1.30 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 153.9, 142.6, 138.5, 133.0, 128.8, 128.7, 128.6, 126.0, 36.7, 36.5, 33.3, 31.7, 22.9, 22.3, 19.0, 14.2; IR spectrum ($CDCl_3$) 2957, 2929, 2870, 1714, 1454, 1071, 699 cm^{-1}; HR-MS(EI+) calcd for $C_{19}H_{25}N$ $[M]^+$ 267.1987; found 267.1991.



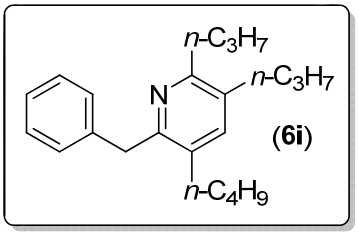
3-Decyl-2-phenethyl-5,6-dipropylpyridine (6g) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (m, 5H), 7.11 (s, 1H), 3.01 (br s, 4H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.45 (t, *J* = 7.5 Hz, 2H), 1.75-1.70 (m, 2H), 1.68-1.57 (m, 2H), 1.48 (m, 2H), 1.30-1.21 (m, 14H), 1.02-0.95 (m, 6H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.7, 142.7, 138.0, 132.7, 132.6, 128.8, 128.7, 128.6, 128.5, 126.0, 36.8, 36.6, 36.2, 34.1, 32.1, 32.0, 31.8, 31.0, 29.8, 29.7, 29.6, 24.2, 23.5, 22.93, 22.91, 14.5, 14.4; IR spectrum ($CDCl_3$) 3062, 3027, 2956, 2854, 1715, 1672, 1561, 1453, 1261 cm^{-1}; HR-MS(EI+) calcd for $C_{29}H_{45}N$ $[M]^+$ 407.3552; found 407.3546.



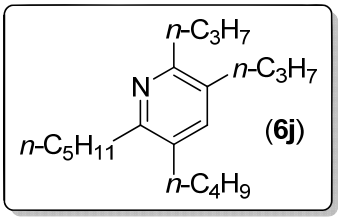
3-Cyclohexyl-2-phenethyl-5,6-dipropylpyridine (6h) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (m, 6H), 3.07-3.00 (m, 4H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.2Hz, 2H), 1.79-1.57 (m, 10H), 1.32-1.25 (m, 4H), 1.01-0.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.0, 142.6, 137.7, 134.8, 132.8, 128.8, 128.5, 126.0, 39.3, 36.8, 36.7, 36.5, 34.4, 34.3, 27.3, 26.4, 24.3, 23.5, 14.6, 14.3; IR spectrum ($CDCl_3$)



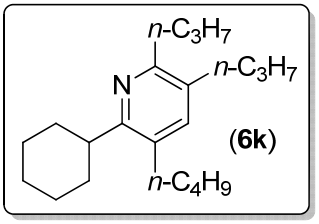
3084, 3026, 2957, 2852, 1799, 1450, 699 cm^{-1}; HR-MS(EI+) calcd for $C_{25}H_{35}N$ $[M]^+$ 349.2769; found 349.2772.



2-Benzyl-3-butyl-5,6-dipropylpyridine (6i) ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.12 (m, 6H), 4.15 (s, 2H), 2.76-2.72 (m, 2H), 2.56-2.45 (m, 4H), 1.78-1.67 (m, 4H), 1.43-1.29 (m, 4H), 1.01-0.93 (m, 6H), 0.86 (t, J = 7.2 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 154.8, 140.6, 138.2, 133.4, 133.2, 128.8, 128.4, 126.0, 41.6, 36.8, 34.1, 32.9, 31.7, 24.2, 23.5, 22.9, 14.5, 14.4, 14.2; IR spectrum ($CDCl_3$) 3027, 2958, 2930, 2871, 1734, 1562, 1454, 1378, 1246 cm^{-1}; HR-MS(EI+) calcd for $C_{22}H_{31}N$ $[M]^+$ 309.2456; found 309.2455.

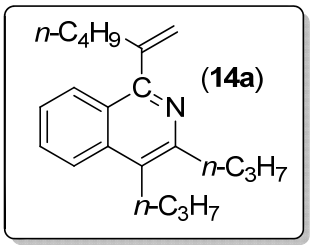


3-Butyl-2-pentyl-5,6-dipropylpyridine (6j) ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 2.73-2.67 (m, 4H), 2.55-2.50 (m, 4H), 1.74-1.50 (m, 8H), 1.43-1.29 (m, 6H), 1.00-0.88 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.9, 137.8, 132.4, 132.2, 36.9, 35.0, 34.2, 33.4, 32.3, 31.8, 30.1, 24.2, 23.6, 23.0, 22.9, 14.5, 14.4, 14.3, 14.2; IR spectrum ($CDCl_3$) 2958, 2871, 1597, 1453, 1339, 1170, 728 cm^{-1}; HR-MS(EI+) calcd for $C_{20}H_{35}N$ $[M]^+$ 289.2769; found 289.2762.

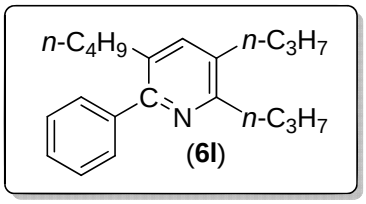


3-Butyl-2-cyclohexyl-5,6-dipropylpyridine (6k) ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 2.79-2.74 (m, 1H), 2.68 (t, J = 7.4 Hz, 2H), 2.56-2.48 (m, 4H), 1.84-1.62 (m, 10H), 1.60-1.47 (m, 4H), 1.43-1.32 (m, 4H), 0.99-0.93 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 156.5, 137.6, 131.7, 131.2, 41.5, 36.6, 34.2, 33.9, 32.7, 31.7, 27.1, 26.4, 24.1, 22.9, 22.6, 14.5, 14.4, 14.2; IR spectrum ($CDCl_3$) 2957, 2928, 2869, 2857, 1557, 1448, 1377, 1141 cm^{-1}; HR-MS(EI+) calcd for $C_{21}H_{35}N$ $[M]^+$ 301.2769; found 301.2763.

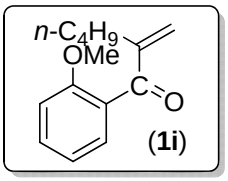
- Characterization data in Scheme 3 (14a-b and 6l-n)



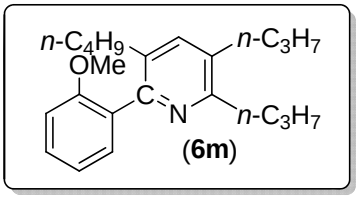
1-(Hex-1-en-2-yl)-3,4-dipropylisoquinoline (14a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 6.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 5.53 (s, 1H), 5.16 (s, 1H), 3.03-2.91 (m, 4H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.84-1.68 (m, 4H), 1.58-1.34 (m, 4H) 1.10 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 152.0, 148.5, 136.2, 129.6, 128.8, 128.3, 128.0, 126.8, 125.2, 123.4, 116.4, 37.6, 37.3, 30.19, 30.17, 24.3, 23.8, 22.8, 14.9, 14.5, 14.2; IR spectrum ($CDCl_3$) 3029, 2958, 2871, 1729, 1689, 1502, 1378, 1276, 1164 cm^{-1}; HR-MS(EI+) calcd for $C_{21}H_{29}N$ $C_{21}H_{30}N$ $[M]^+$ 296.2378; found 296.2375.



3-Butyl-2-phenyl-5,6-dipropylpyridine (6l) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.34 (m, 5H), 7.30 (s, 1H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.55 (t, *J* = 8.0 Hz, 2H), 1.77-1.71 (m, 2H), 1.68-1.61 (m, 2H), 1.48-1.42 (m, 2H), 1.27-1.21 (m, 2H), 1.04-0.98 (m, 6H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 155.7, 141.3, 138.3, 133.8, 132.7, 129.3, 128.3, 127.6, 36.9, 34.2, 33.5, 31.9, 24.2, 23.5, 22.7, 14.5, 14.4, 14.1; IR spectrum ($CDCl_3$) 3058, 3027, 2958, 2930, 2870, 1551, 1377, 1072, 759 cm^{-1}; HR-MS(EI+) calcd for $C_{21}H_{29}N$ $C_{21}H_{30}N$ $[M]^+$ 296.2378; found 296.2376.



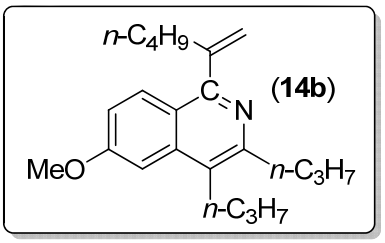
1-(2-Methoxyphenyl)-2-methylenehexan-1-one (1i) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 4H), 5.90 (s, 1H), 5.58 (s, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.54-1.47 (m, 2H), 1.43-1.30 (m, 2H), 0.94 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 149.9, 139.4, 136.3, 130.9, 129.9, 129.1, 128.1, 125.2, 30.7, 30.6, 22.7, 19.9, 14.2; IR spectrum ($CDCl_3$) 2957, 2931, 2871, 2838, 1712, 1377, 1247, 792 cm^{-1}; HR-MS(EI+) calcd for $C_{14}H_{18}O_2$ $[M]^+$ 219.1385; found 219.1389.



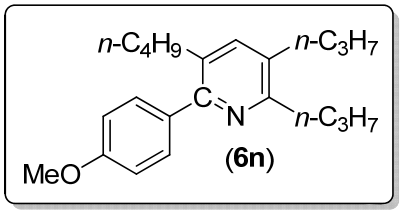
3-Butyl-2-(2-methoxyphenyl)-5,6-dipropylpyridine (6m) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.20 (d, *J* = 7.36 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H) 3.73 (s, 3H), 2.76 (t, *J* = 8.0

Hz, 2H), 2.61 (t, *J* = 6.9 Hz, 2H), 2.35 (br, 2H), 1.72-1.64 (m, 4H), 1.43-1.37 (m, 2H), 1.20-1.15 (m, 2H), 1.05-0.97 (m, 6H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 156.9, 153.5, 137.3, 134.1, 133.7, 131.2, 130.5, 129.2, 120.9, 111.0, 55.6, 37.0, 34.3, 32.7, 31.6, 24.2, 23.7, 22.7, 14.54, 14.52, 14.0; IR spectrum ($CDCl_3$) 3037, 2958, 2930, 2870, 1610, 1512, 1377, 1247, 1126 cm^{-1}; HR-MS(EI+) calcd for $C_{22}H_{31}NO$ $[M]^+$ 325.2407; found 325.2406.

1-(Hex-1-en-2-yl)-6-methoxy-3,4-dipropylisoquinoline (14b) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.2 Hz, 1H), 7.19 (s, 1H), 7.08 (d, *J* = 9.2 Hz, 1H), 5.50 (s, 1H), 5.13 (s, 1H), 3.95 (s, 3H), 2.97-2.89 (m, 4H), 2.62 (t, *J* = 6.8 Hz, 2H), 1.81-1.67 (m, 4H), 1.44-1.29 (m, 4H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 152.6, 148.7, 138.2, 129.9, 125.8, 121.0, 117.4, 116.2, 102.1, 55.5, 37.7, 37.3, 30.3, 30.2, 23.7, 22.8, 14.9, 14.5, 14.1; IR spectrum ($CDCl_3$) 3077, 2957, 2930, 2871, 1652, 1463, 1312, 1220, 1165 cm^{-1}; HR-MS(EI+) calcd for $C_{22}H_{31}NO$ $[M]^+$ 325.2406; found 325.2400.



3-Butyl-2-(4-methoxyphenyl)-5,6-dipropylpyridine (6n) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.61-2.54 (m, 4H), 1.75-1.73 (m, 2H), 1.67-1.63 (m, 2H), 1.51-1.45 (m, 2H), 1.30-1.26 (m, 2H), 1.23-1.20 (m, 6H), 0.98 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.2, 155.3, 138.2, 134.0, 133.5, 132.7, 130.5, 113.7, 55.5, 36.9, 34.2, 33.6, 32.0, 24.2, 23.5, 22.8, 14.5, 14.4, 14.1; IR spectrum ($CDCl_3$) 3037, 2958, 2930, 2870, 1610, 1512, 1377, 1247, 1126 cm^{-1}; HR-MS(EI+) calcd for $C_{22}H_{31}NO$ $[M]^+$ 325.2406; found 325.2411.

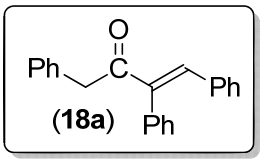


- A typical procedure for stepwise synthesis of pyridines through chelation-assisted hydroacylation of internal alkynes with aldehydes (Table 3)

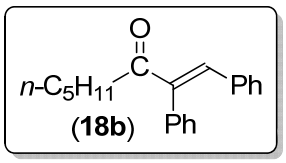
a. Chelation-assisted hydroacylation of internal alkynes with aldehydes: A screw-capped pressure vial (1.0 mL) was charged with 2-phenylacetaldehyde (**9c**, 26.8 mg (0.2 mmol)), 1,2-diphenylethyne (**2b**, 71.2 mg (0.4 mmol)), $(Ph_3P)_3RhCl$ (**11**, 9.3 mg (0.01 mmol)), 2-amino-3-picoline (**12**, 21.6 mg (0.2 mmol)), benzoic acid (**13**, 4.9 mg (0.04 mmol)) in toluene (200 μl). The solution was stirred at 150 ^oC for 4 h. After the reaction, the reaction mixture was filtered through silica gel pad, washed thoroughly with ethyl acetate. The reaction progress was monitored by gas chromatography (GC). The reaction mixture was purified by column chromatograph (*n*-hexane : ethyl acetate = 10 : 1) to give 50 mg (84%) of 1,3,4-triphenylbut-3-en-2-one (**18a**).

- Characterization data for α,β-enones (18a-d)

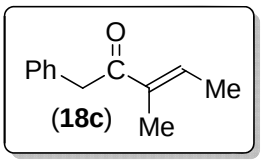
1,3,4-Triphenylbut-3-en-2-one (18a) [CAS No. 128753-25-3] 84% yield, yellow powder, ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), δ 7.39-7.38 (m, 3H), δ 7.27-7.18 (m, 4H), 7.16-7.12 (m, 4H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 140.5, 139.3, 136.9, 134.9, 134.7, 131.1, 129.9, 129.6, 129.5, 129.2, 128.6, 128.4, 128.2, 126.9,46.9.



1,2-Diphenyloct-1-en-3-one (18b) 77% yield, yellow oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.29 (m, 10H), δ 6.97 (s, 1H), δ 2.45 (t, *J* = 7.2 Hz, 2H), δ 1.60-1.53 (m, 3H), δ 1.21-1.13 (m, 3H), δ 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 144.1, 137.4, 136.0, 129.1, 129.0, 128.8, 128.4, 126.6, 44.0, 31.2, 23.4, 22.5, 14.0; IR spectrum ($CDCl_3$) 3081, 3058, 3025, 2956, 2929, 2870, 1695, 1494, 1448 cm^{-1}; HR-MS(CI+) calcd for $C_{20}H_{23}O$ $[M+H]^+$ 279.1743; found 279.1749.

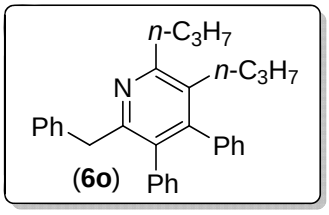


3-Methyl-1-phenylpent-3-en-2-one (18c) [CAS No. 408524-72-1] 88% yield, yellow oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), δ 7.23-7.18 (m, 3H), δ 6.87 (q, *J* = 6.8 Hz, 1H), δ 3.96 (s, 2H), δ 1.85 (d, *J* = 6.8 Hz, 3H), δ 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 138.8, 138.2, 135.7, 129.4, 128.7, 126.7, 44.3, 15.1, 11.4.

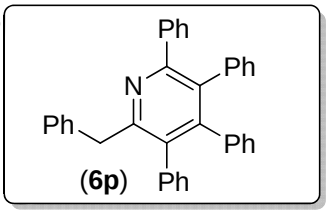


b. N-Annulation of α,β-enone with internal alkyne: A screw-capped pressure vial (1.0 mL) was charged with (*E*)-1,3,4-triphenylbut-3-en-2-one (**17a**, 59.6 mg (0.2 mmol)), oct-4-yne (**2a**, 44 mg (0.4 mmol)), NH_4OAc (**3**, 30.8 mg (0.4 mmol)), $[Cp^*RhCl_2]_2$ (**4**, 6.2 mg (0.01 mmol)), $Cu(OAc)_2{\cdot}H_2O$ (**5**, 80.0 mg (0.4 mmol)), in MeOH (158.4mg (5.0 mmol)). The solution was stirred at 150 ^oC for 6 h. After the reaction, the reaction mixture was filtered through silica gel pad, washed thoroughly with ethyl acetate. The reaction progress was monitored by gas chromatography (GC). The reaction mixture was purified by column chromatograph (*n*-hexane : ethyl acetate = 5 : 1) to give 62 mg (77%) of 2-benzyl-3,4-diphenyl-5,6-dipropylpyridine (**6o**).

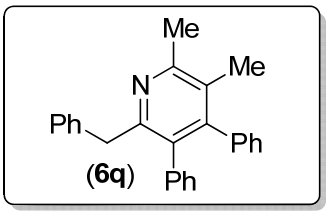
- Characterization data for pyridines (6o-v)



2-Benzyl-3,4-diphenyl-5,6-dipropylpyridine (6o). 77% yield, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.05 (m, 9H), δ 6.97 (d, *J* = 7.2 Hz, 2H), δ 6.89 (d, *J* = 6.4 Hz, 2H), δ 6.79-6.78 (m, 2H), δ 3.93 (s, 2H), δ 2.87 (t, *J* = 8.0 Hz, 2H), δ 2.35 (t, *J* = 8.0 Hz, 2H), δ 1.92-1.86 (m, 2H), δ 1.39-1.33 (m, 2H), δ 1.08 (t, *J* = 7.2 Hz, 3H), δ 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 154.6, 140.6, 139.0, 138.8, 134.0, 131.3, 130.6, 129.4, 129.2, 128.0, 127.6, 127.5, 126.6, 126.5, 125.8, 42.4, 37.5, 31.9, 24.4, 23.4, 14.8, 14.7; IR spectrum ($CDCl_3$) 3059, 3027, 2959, 2870, 1602, 1576, 1555, 1494, 1454 cm^{-1}; HR-MS(CI+) calcd for $C_{30}H_{32}N$ $[M+H]^+$ 406.2535; found 406.2539.



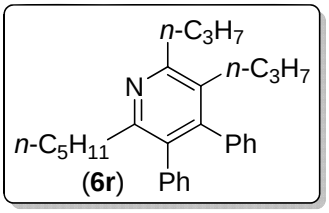
2-Benzyl-3,4,5,6-tetraphenylpyridine (6p) [CAS No. 352667-98-2] 51% yield, yellow powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.34 (m, 2H), δ 7.18-7.13 (m, 9H), δ 7.08-7.07 (m, 2H), δ 6.96-6.92 (m, 5H), δ 6.85-6.82 (m, 5H), δ 6.69-6.68 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 156.3, 150.1, 140.2, 138.5, 138.4, 138.3, 135.0, 133.1, 131.5, 130.8, 130.4, 130.3, 129.4, 128.1, 127.9, 127.8, 127.6, 127.5, 127.0, 126.9, 126.3, 126.2, 126.0, 42.6.



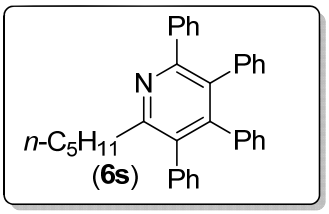
2-Benzyl-5,6-dimethyl-3,4-diphenylpyridine (6q) 80% yield, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.05 (m, 9H), δ 6.96 (d, *J* = 6.8 Hz,

2H), δ 6.87 (d, *J* = 6.8 Hz, 2H), δ 6.79-6.78 (m, 2H), δ 3.96 (s, 2H), δ 2.62 (s, 3H), δ 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 154.5, 149.8, 140.6, 139.1, 138.7, 134.2, 130.6, 129.4, 129.0, 128.1, 127.8, 127.6, 127.2, 126.7, 126.6, 125.8, 42.3, 23.6, 16.8; IR spectrum ($CDCl_3$) 3081, 3058, 3027, 2975, 2921, 2866, 1601, 1558, 1493, 1441, 1409 cm^{-1}; HR-MS(CI+) calcd for $C_{26}H_{24}N$ $[M+H]^+$ 350.1903; found 350.1904.

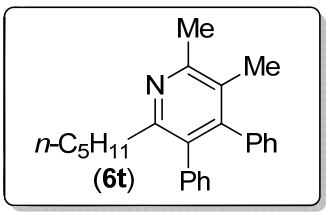
2-Pentyl-3,4-diphenyl-5,6-dipropylpyridine (6r) 71% yield, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.04 (m, 6H), δ 6.94-6.90 (m, 4H), δ 2.83 (t, *J* = 8.0 Hz, 2H), δ 2.51 (t, *J* = 8.0 Hz, 2H), δ 2.35 (t, *J* = 8.0 Hz, 2H), δ 1.90-1.82 (m, 2H), δ 1.58-1.57 (m, 2H), δ 1.39-1.33 (m, 2H), δ 1.15-1.06 (m, 7H), δ 0.79-0.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 156.7, 149.6, 139.3, 139.2, 133.5, 130.6, 130.4, 129.5, 127.6, 127.5, 126.5, 126.3, 37.6, 36.2, 32.0, 31.9, 30.0, 24.4, 23.8, 22.6, 14.8, 14.7, 14.1; IR spectrum ($CDCl_3$) 3058, 3025, 2958, 2929, 2870, 1552, 1442, 1403, 1377 cm^{-1}; HR-MS(CI+) calcd for $C_{28}H_{36}N$ $[M+H]^+$ 386.2848; found 386.2848.



2-Pentyl-3,4,5,6-tetraphenylpyridine (6s) [CAS No. 198758-19-9] 73% yield, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 2H), δ 7.17-7.12 (m, 6H), δ 7.06-7.04 (m, 2H), δ 6.95-6.94 (m, 3H), δ 6.87-6.83 (m, 5H), δ 6.73-6.71 (m, 2H), δ 2.72 (t, *J* = 7.2Hz, 2H), δ 1.75-1.68 (m, 2H), δ 1.25-1.21 (m, 4H), δ 0.83-0.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 156.2, 149.6, 141.3, 138.8, 138.7, 138.5, 134.6, 132.4, 131.6, 130.5, 130.4, 130.2, 127.8, 127.7, 127.5, 127.4, 127.0, 126.7, 126.3, 126.2, 36.4, 32.0, 29.6, 22.6, 14.2.

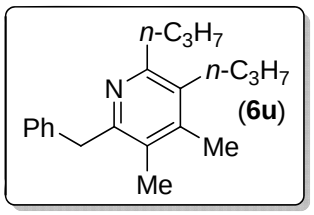


2,3-Dimethyl-6-pentyl-4,5-diphenylpyridine (6t) 85% yield, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.06 (m, 6H), δ 6.94 (d, *J* = 6.8 Hz, 2H), δ 6.89 (d, *J* = 6.8 Hz, 2H), δ 2.60 (s, 3H), δ 2.53 (t, *J* = 8.0 Hz, 2H), δ 2.00 (s, 3H), δ 1.58-1.55 (m, 2H), δ 1.16-1.15 (m, 4H), δ 0.77 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.7, 149.4, 139.3, 139.1, 133.6, 130.4, 129.4, 127.7, 127.6, 126.7, 126.4, 36.2, 32.0, 30.2, 23.5, 22.5, 16.7, 14.1; IR

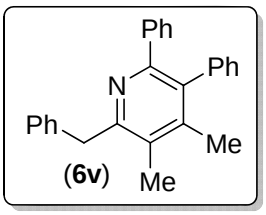


spectrum ($CDCl_3$) 3058, 3026, 2927, 2858, 2735, 1602, 1555, 1494, 1409, 1378 cm^{-1}; HR-MS(CI+) calcd for $C_{24}H_{28}N$ $[M+H]^+$ 330.2222; found 330.2225.

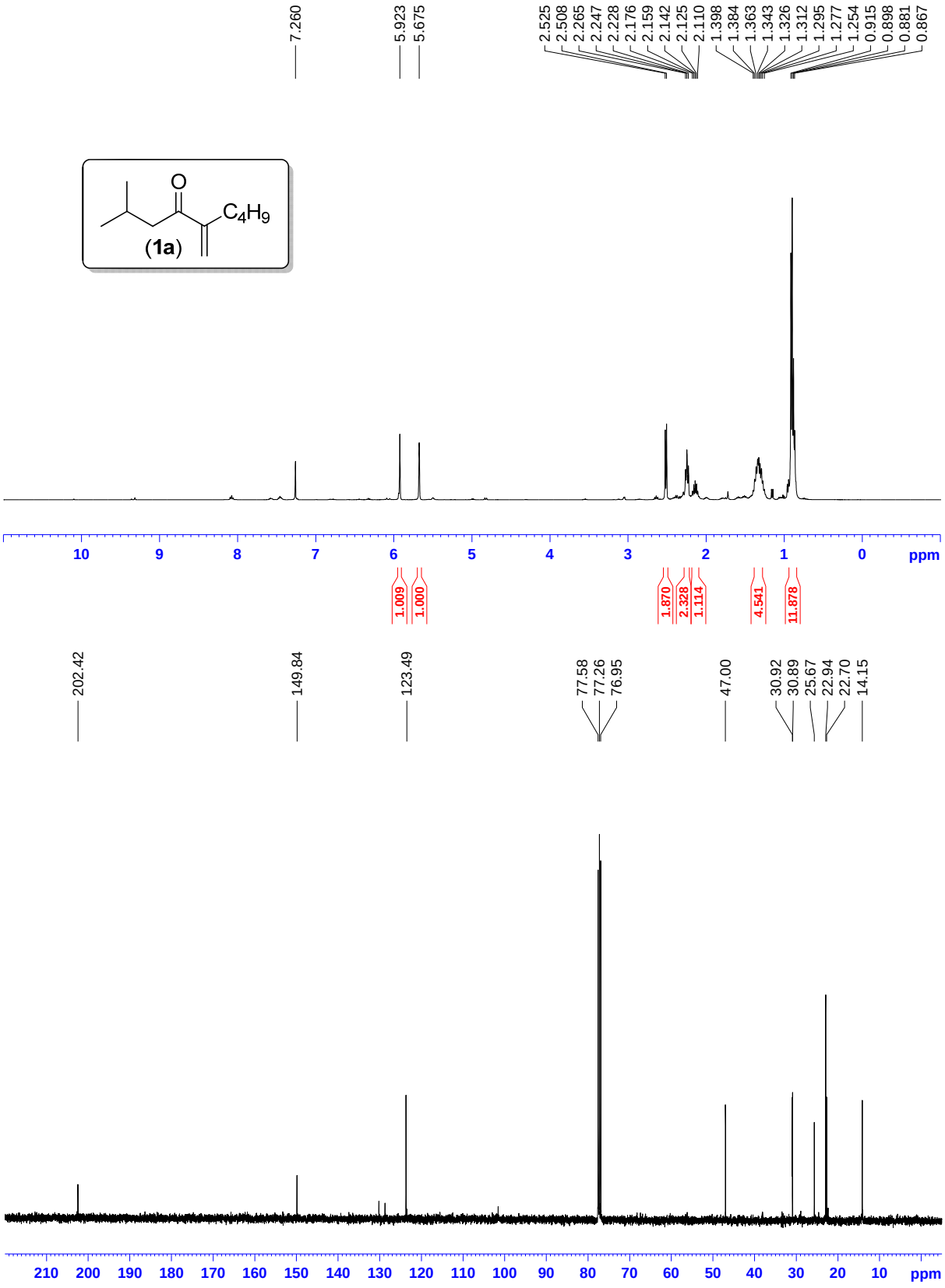
2-Benzyl-3,4-dimethyl-5,6-dipropylpyridine (6u) 60% yield, yellow oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.11 (m, 5H), δ 4.16 (s, 2H), δ 2.75(t, *J* = 7.6 Hz, 2H), δ 2.59 (t, *J* = 7.6 Hz, 2H), δ 2.16 (s, 3H), δ 2.08 (s, 3H), δ 1.76-1.71 (m, 2H), δ 1.52-1.46 (m, 2H), δ 1.01-1.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.6, 144.6, 140.3, 132.0, 128.7, 128.4, 128.0, 125.9, 43.0, 37.7, 31.4, 23.8, 23.7, 15.8, 15.5, 14.8, 14.6; IR spectrum ($CDCl_3$) 3060, 3026, 2960, 2870, 1663, 1565, 1490, 1455, 1381 cm^{-1}; HR-MS(CI+) calcd for $C_{20}H_{28}N$ $[M+H]^+$ 282.2222; found 282.2215.

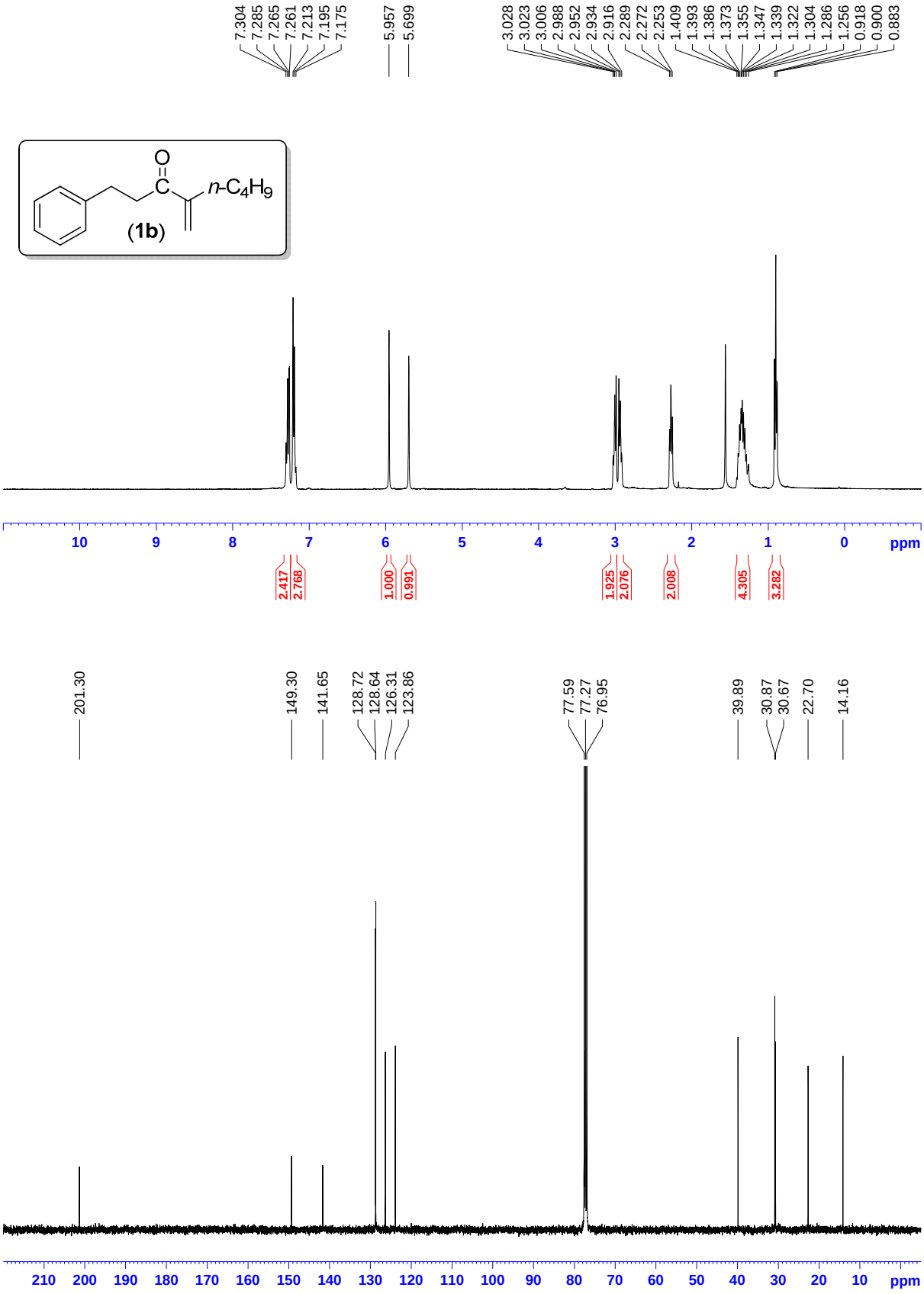


2-Benzyl-3,4-dimethyl-5,6-diphenylpyridine (6v) 41% yield, yellow oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.19 (m, 10H), δ 7.14-7.13 (m, 3H), δ 7.05-7.03 (m, 2H), δ 4.34 (s, 2H), δ 2.25 (s, 3H), δ 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 154.4, 145.3, 141.4, 140.0, 139.5, 134.5, 130.8, 130.1, 129.4, 128.9, 128.5, 128.2, 127.6, 127.1, 126.9, 126.2, 43.2, 17.8, 15.6; IR spectrum ($CDCl_3$) 3059, 3027, 2974, 2927, 2866, 1601, 1552, 1494, 1444, 1402 cm^{-1}; HR-MS(CI+) calcd for $C_{26}H_{24}N$ $[M+H]^+$ 350.1909; found 350.1909.



^{1}H and ^{13}C NMR spectra of new compounds

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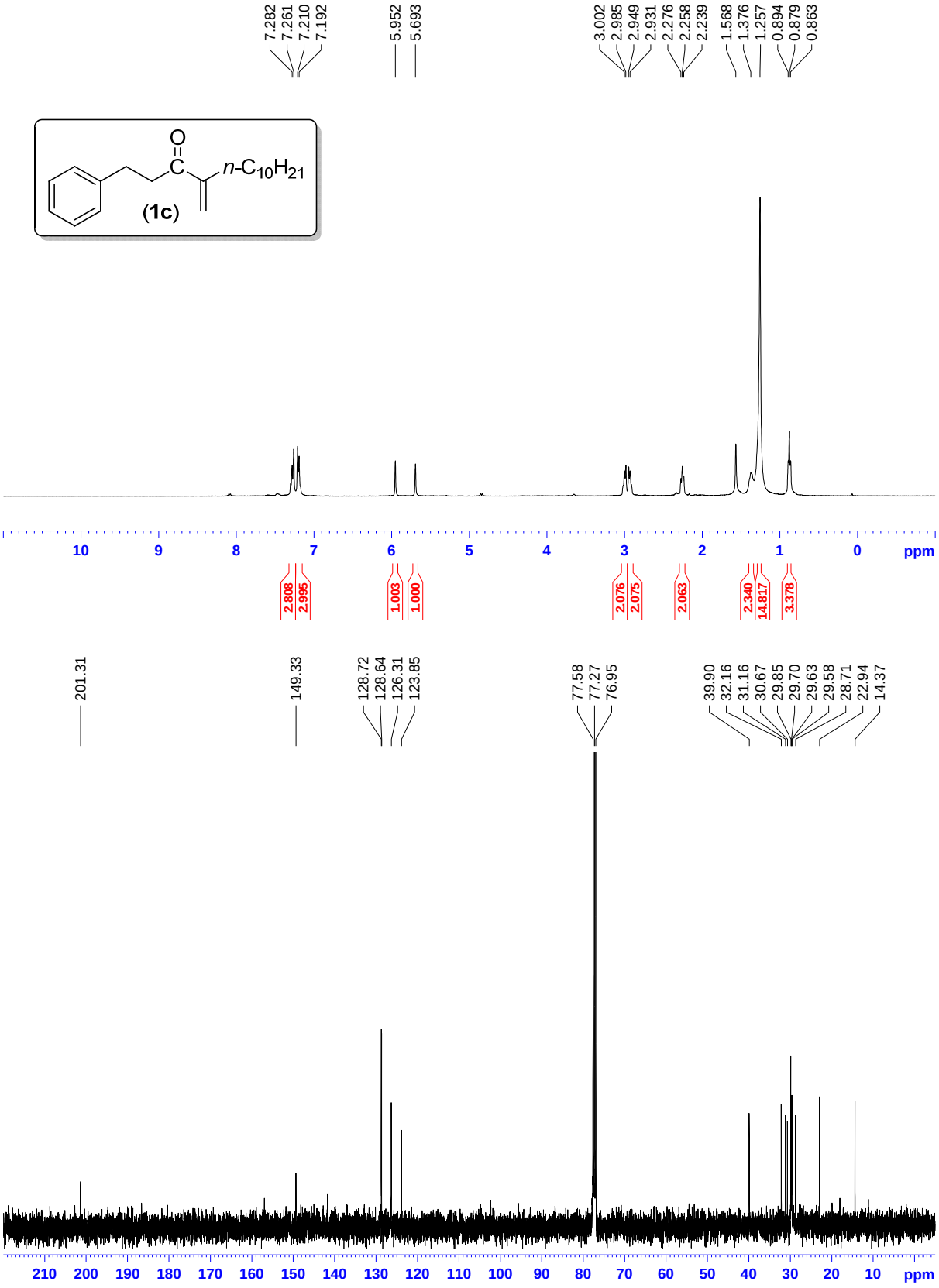
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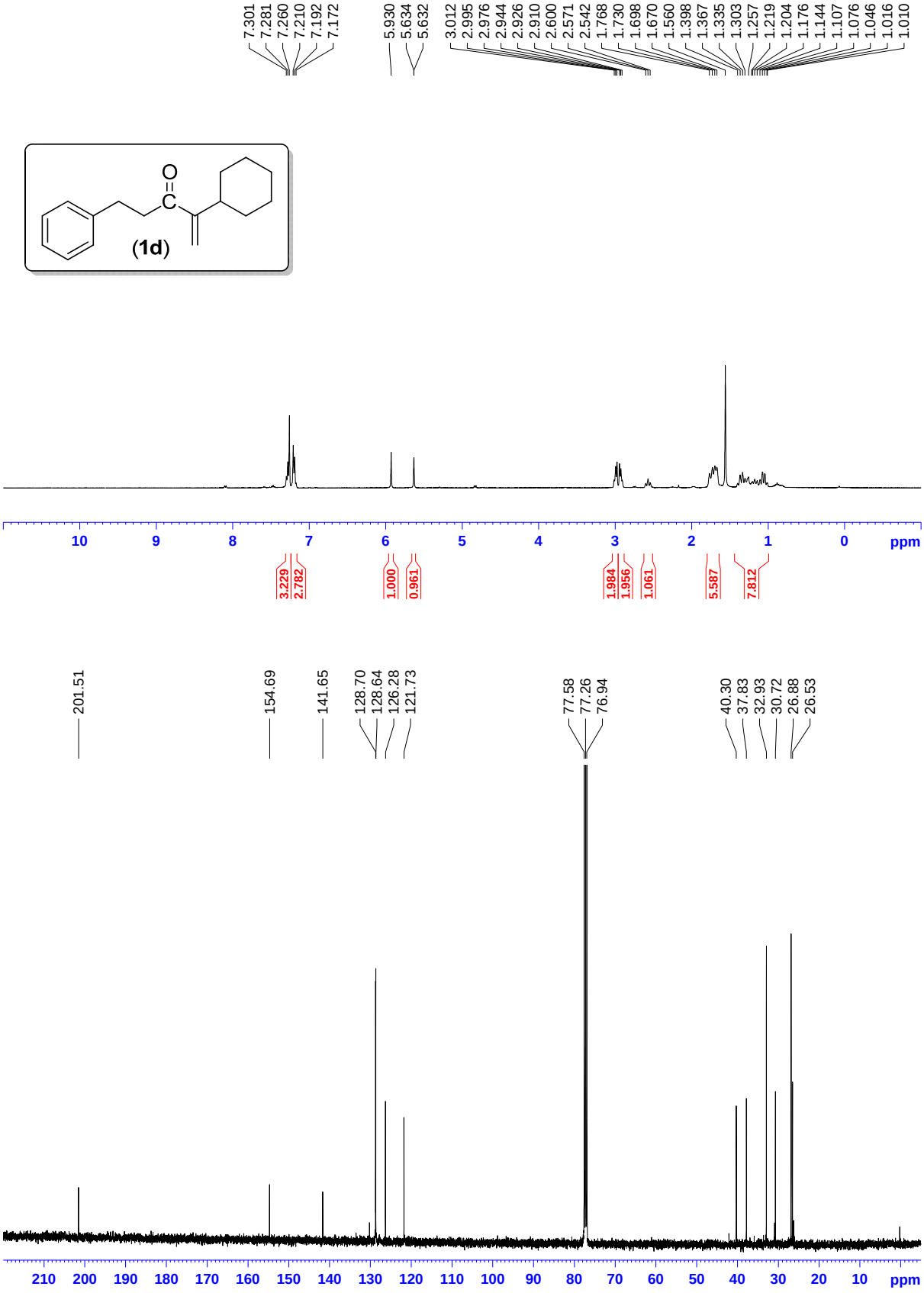
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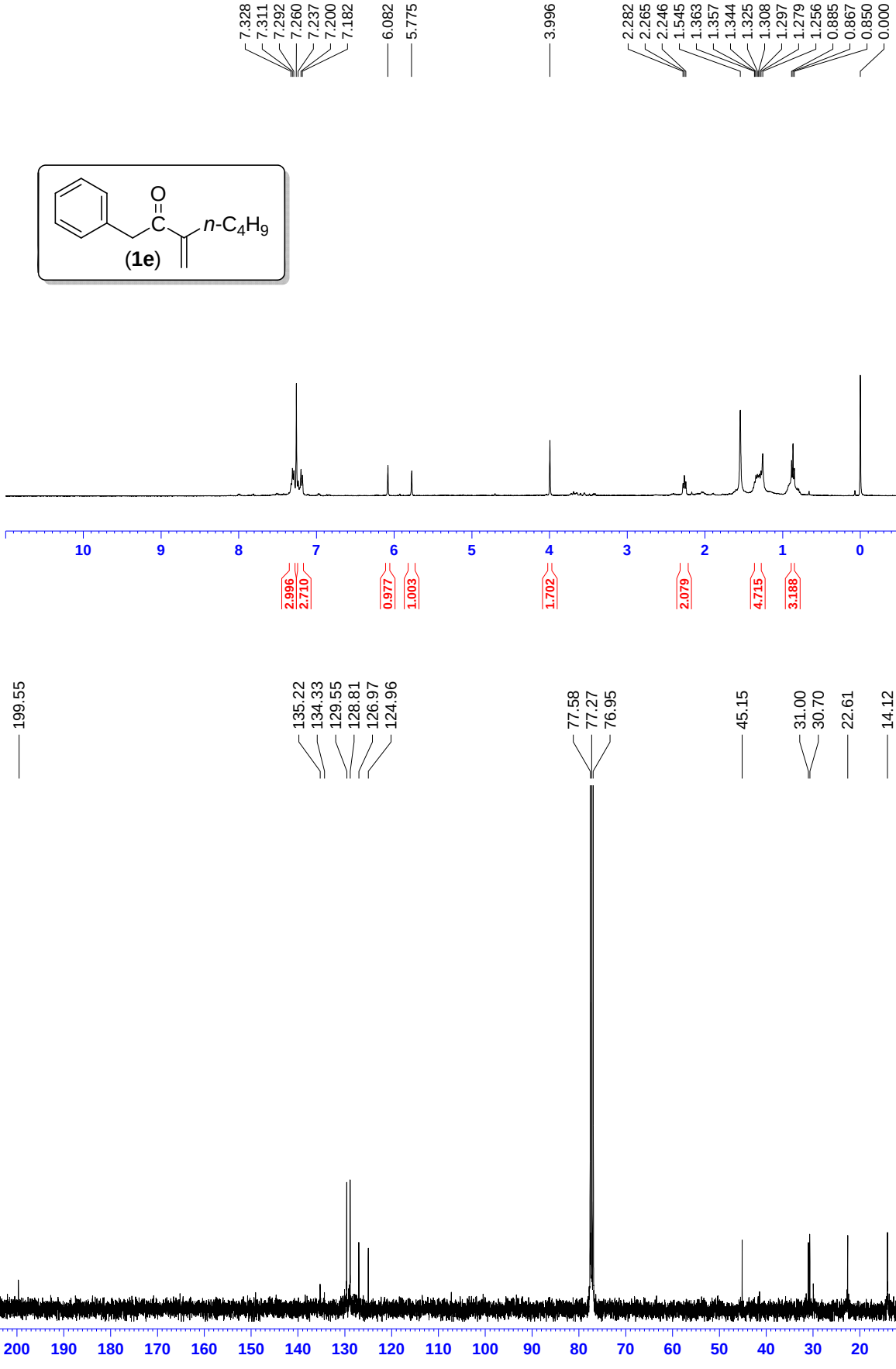
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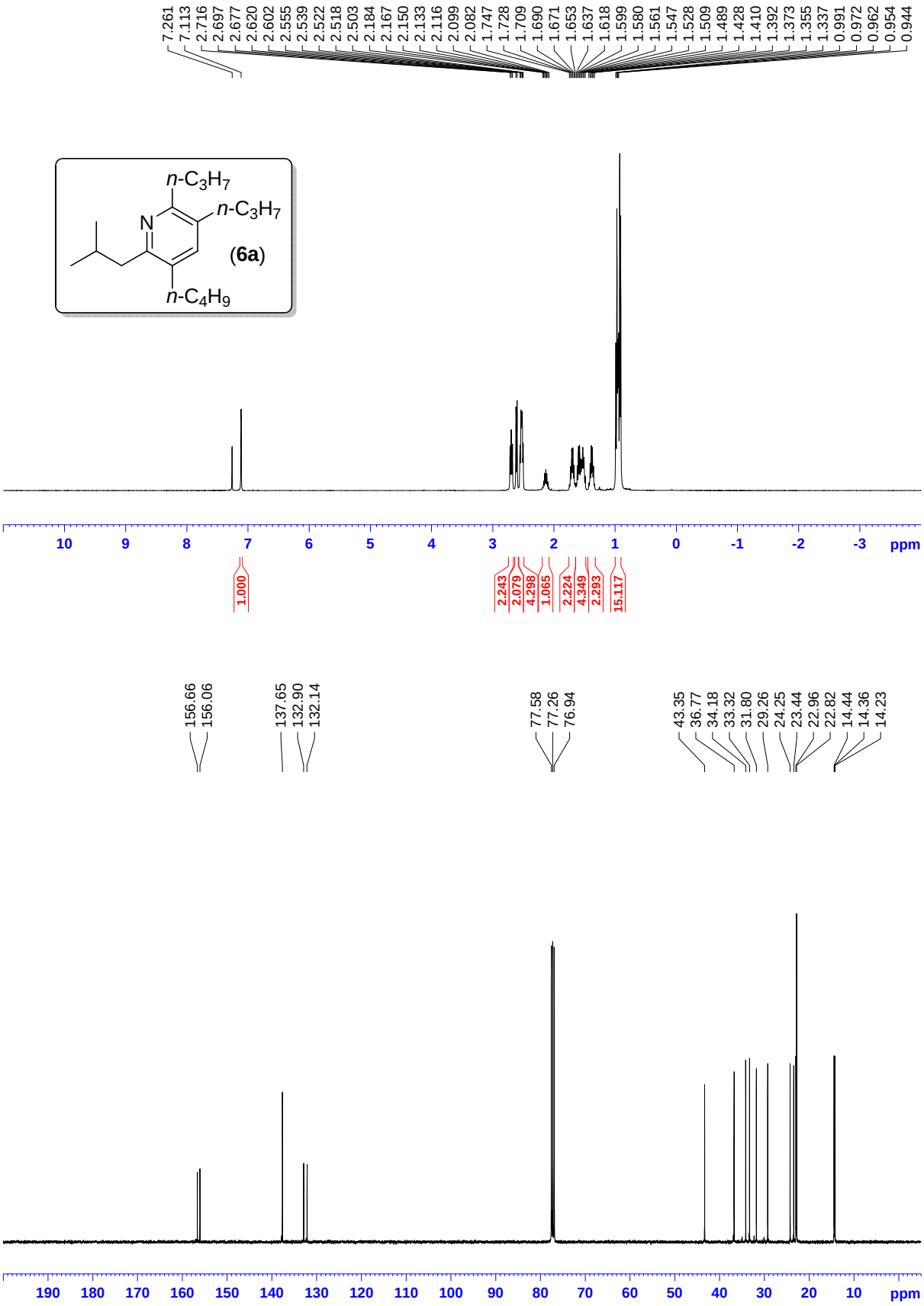
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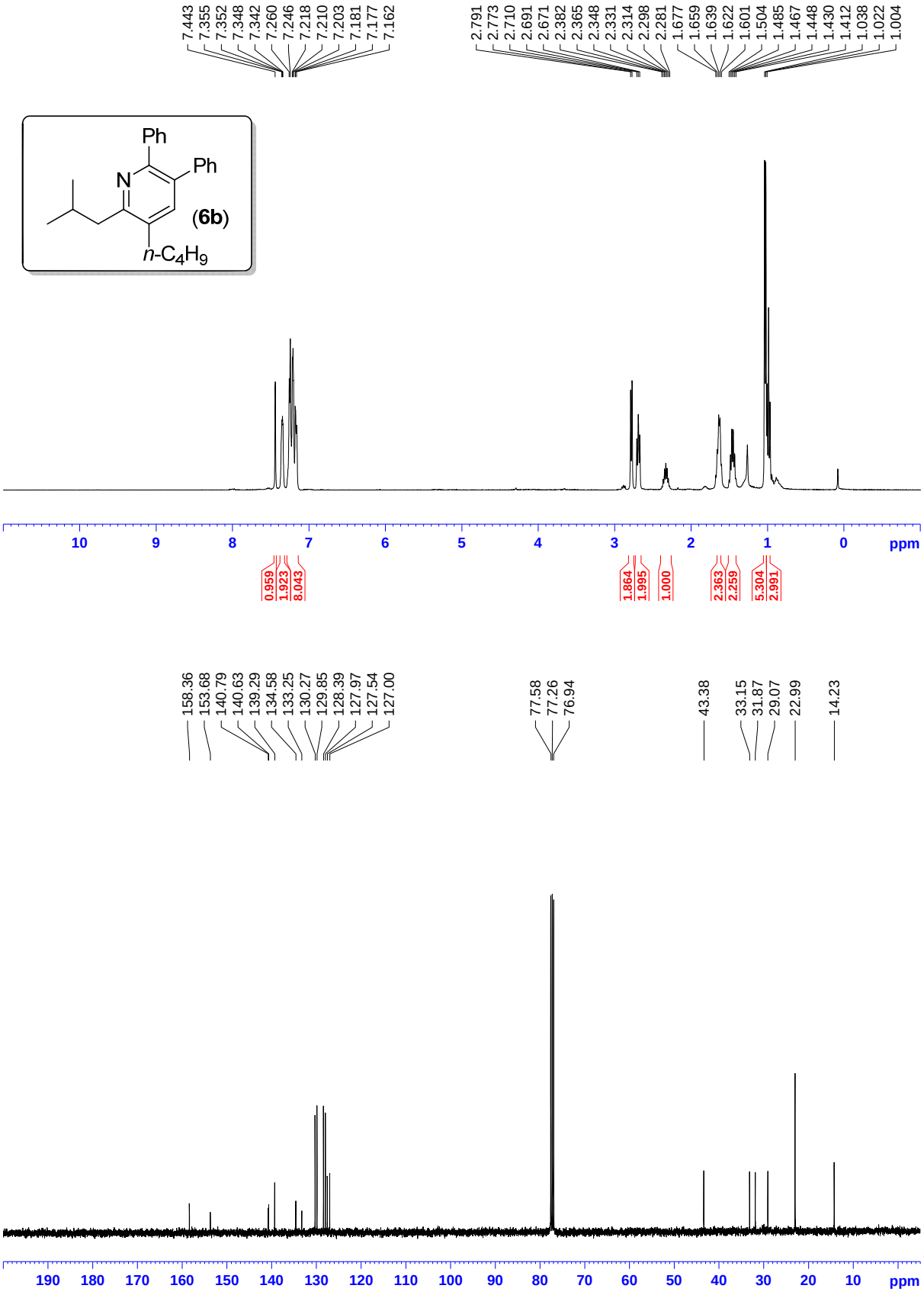
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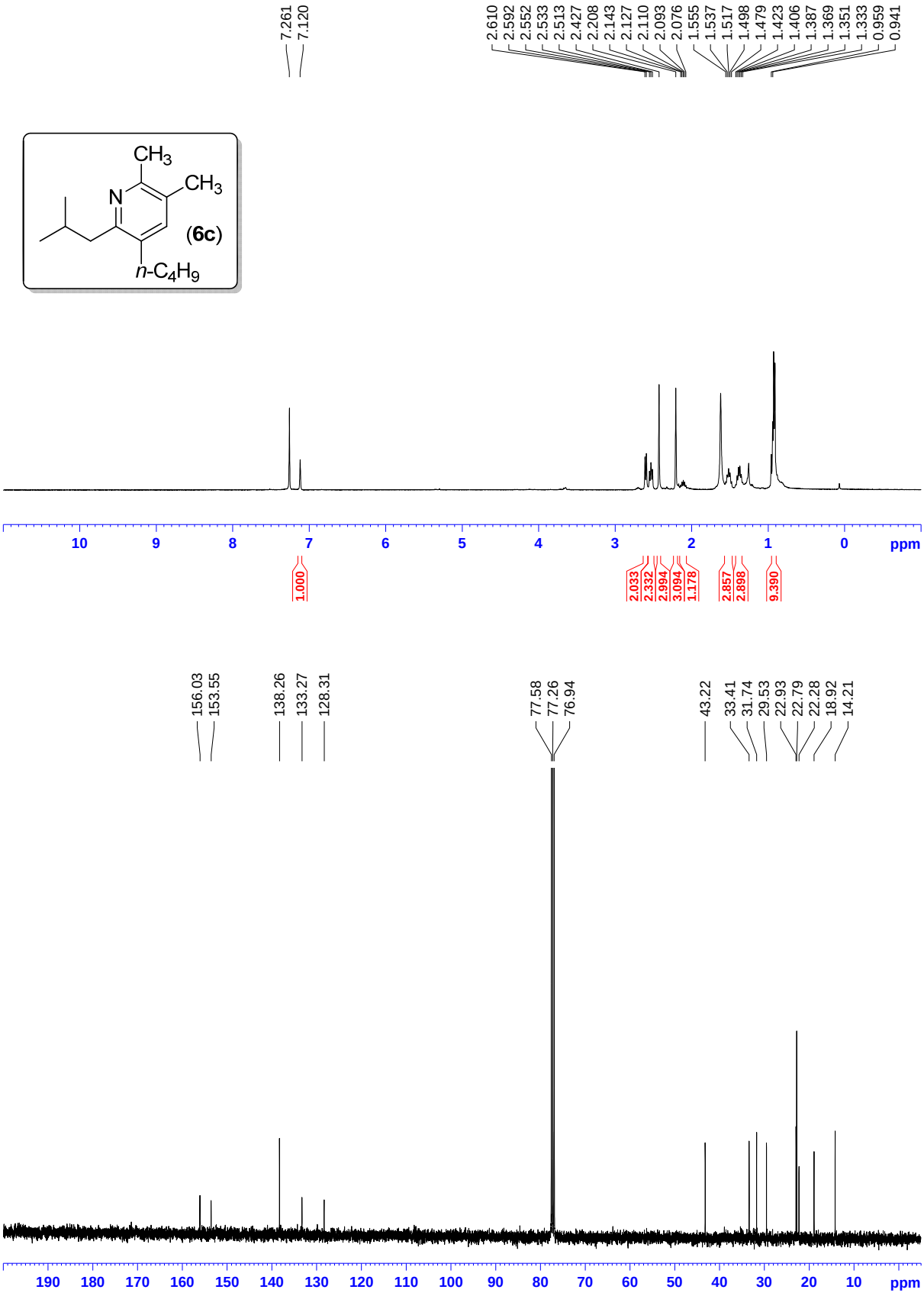
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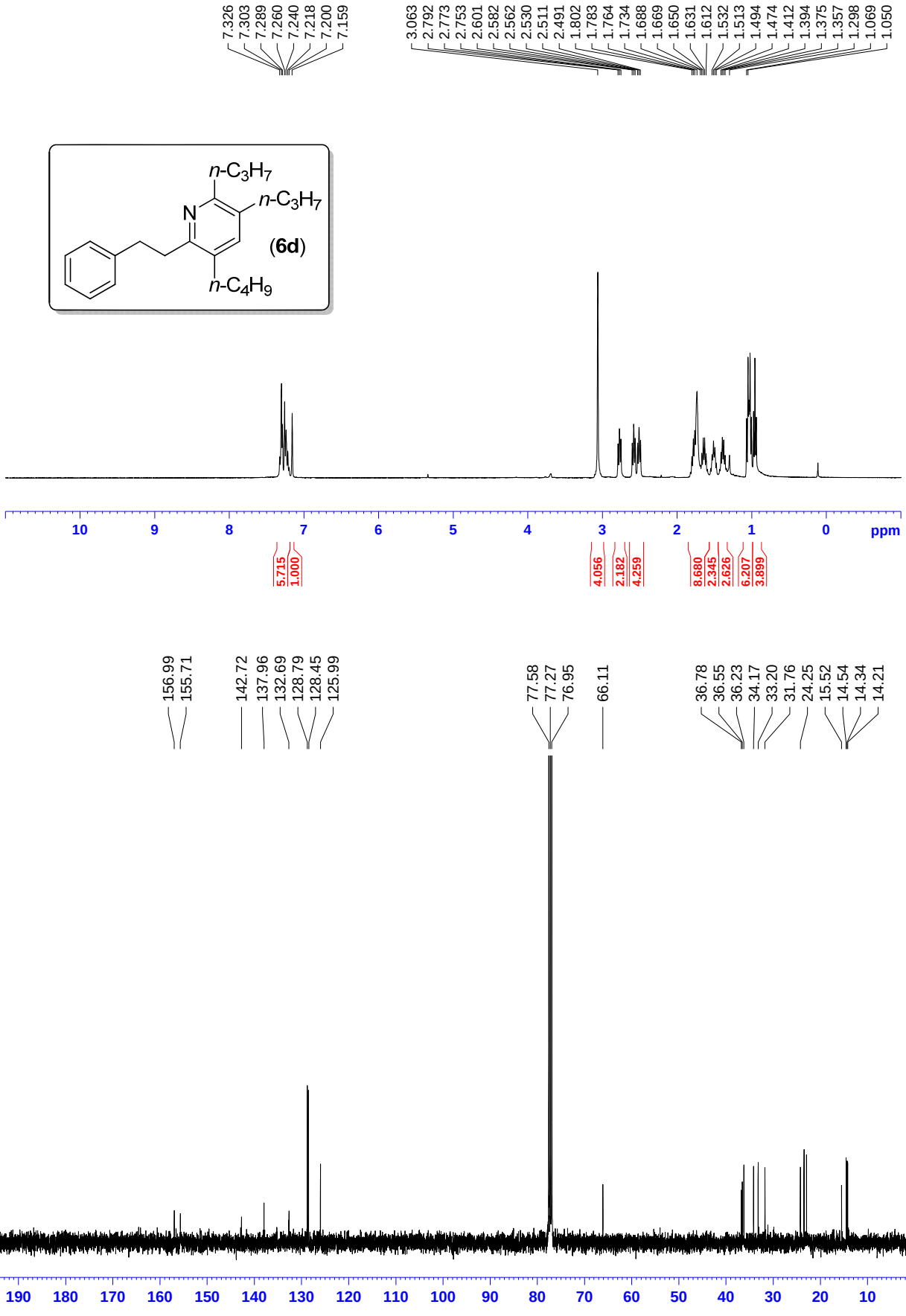
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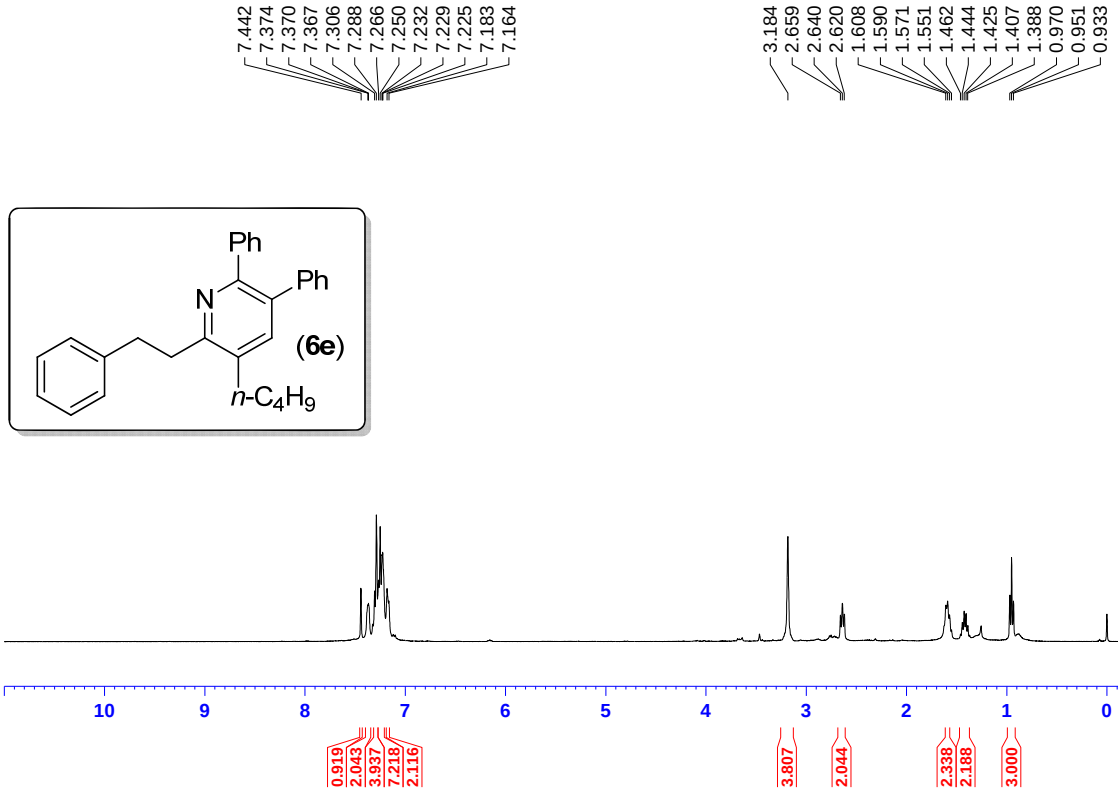
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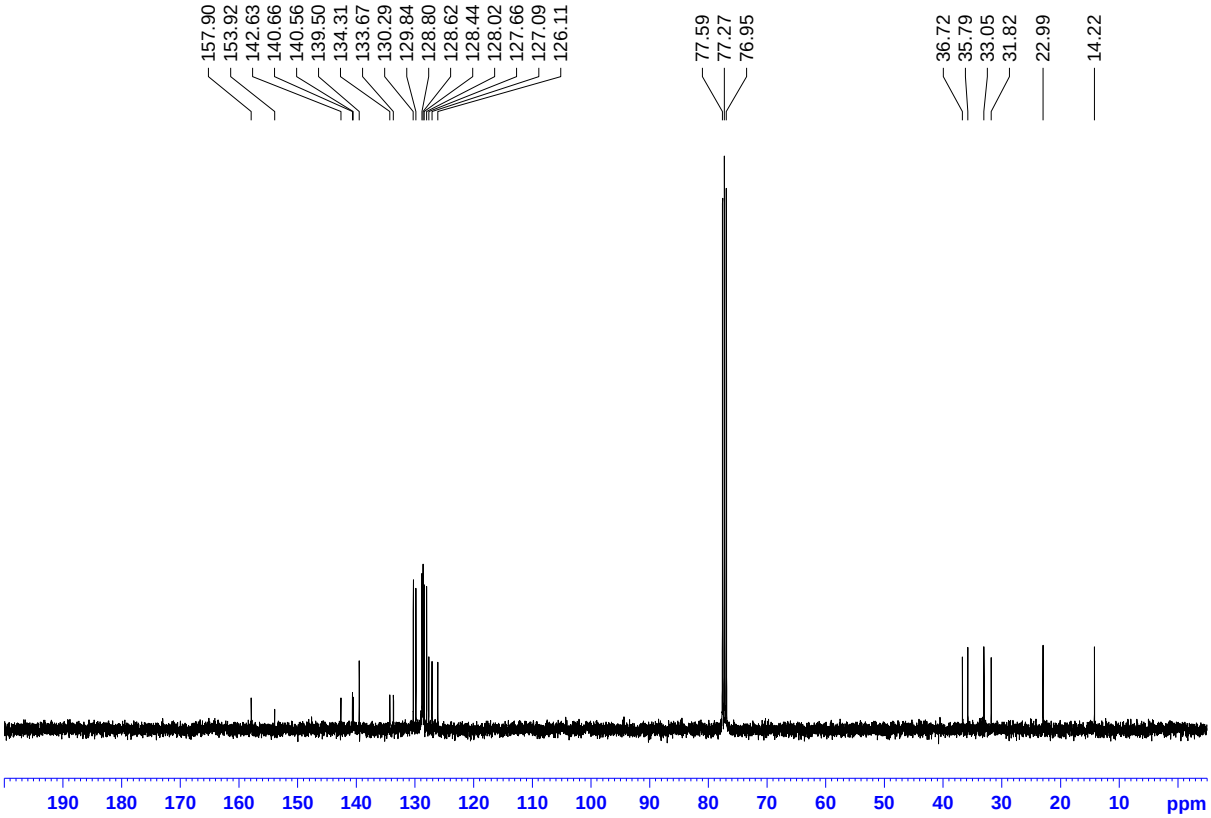
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153.92
142.63
140.66
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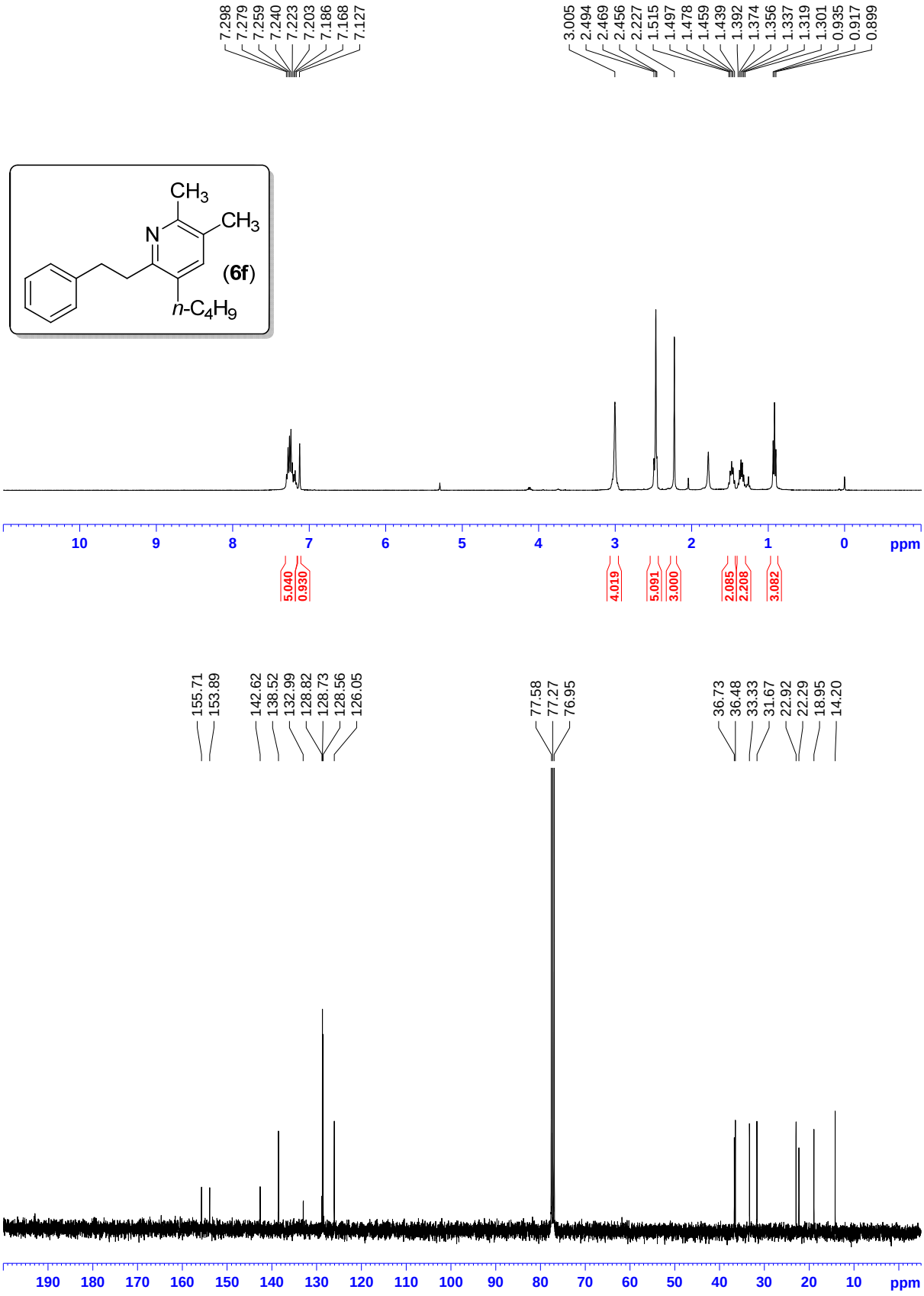
139.50
134.31
133.67
130.29
129.84
128.80
128.62
128.44
128.02
127.66
127.09
126.11
77.59
77.27
76.95
36.72
35.79
33.05
31.82
22.99
14.22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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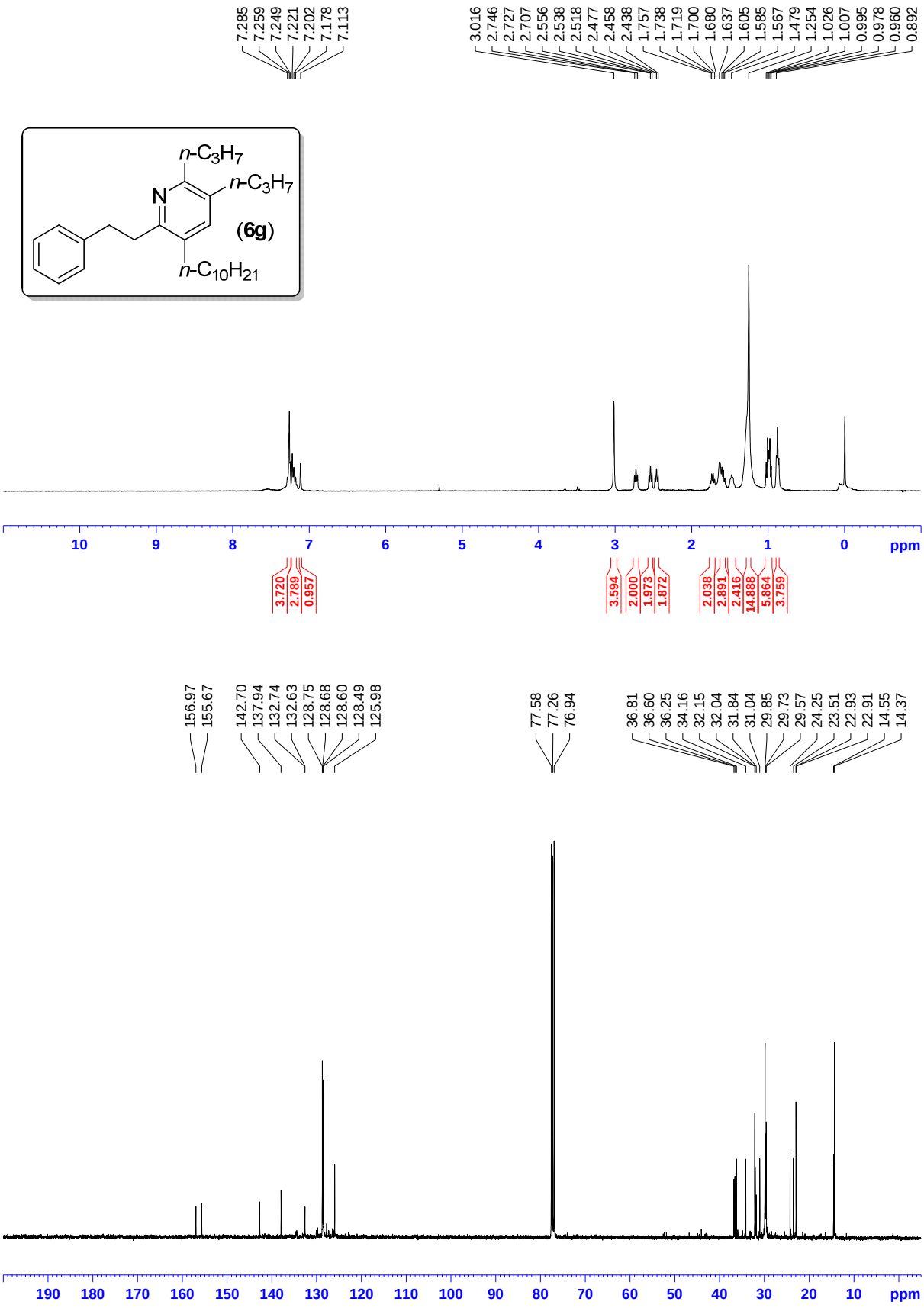
7.279
7.259
7.240
7.223
7.203
7.186
7.168
7.127
3.005
2.494
2.469
2.456
2.227
1.515
1.497
1.478
1.459
1.439
1.392
1.374
1.356
1.337
1.319
1.301
0.935
0.917
0.899
CH3
CH3
N
(6f)
n-C4H9
10
9
8
7
6
5
4
3
2
1
0
ppm
5.040
0.930
4.019
5.091
3.000
2.085
2.208
3.082
155.71
153.89
142.62
138.52
132.99
128.82
128.73
128.56
126.05
77.58
77.27
76.95
36.73
36.48
33.33
31.67
22.92
22.29
18.95
14.20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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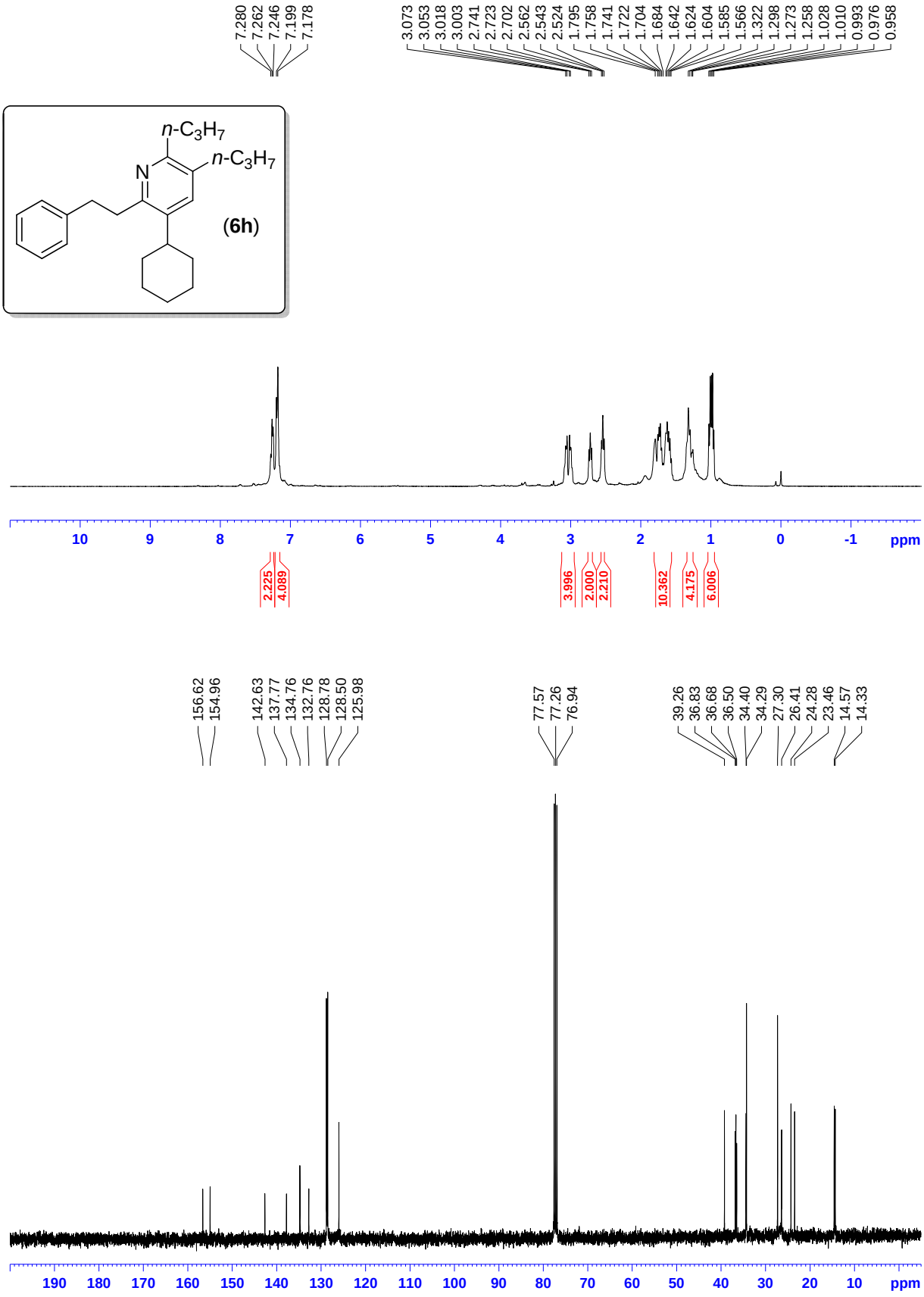
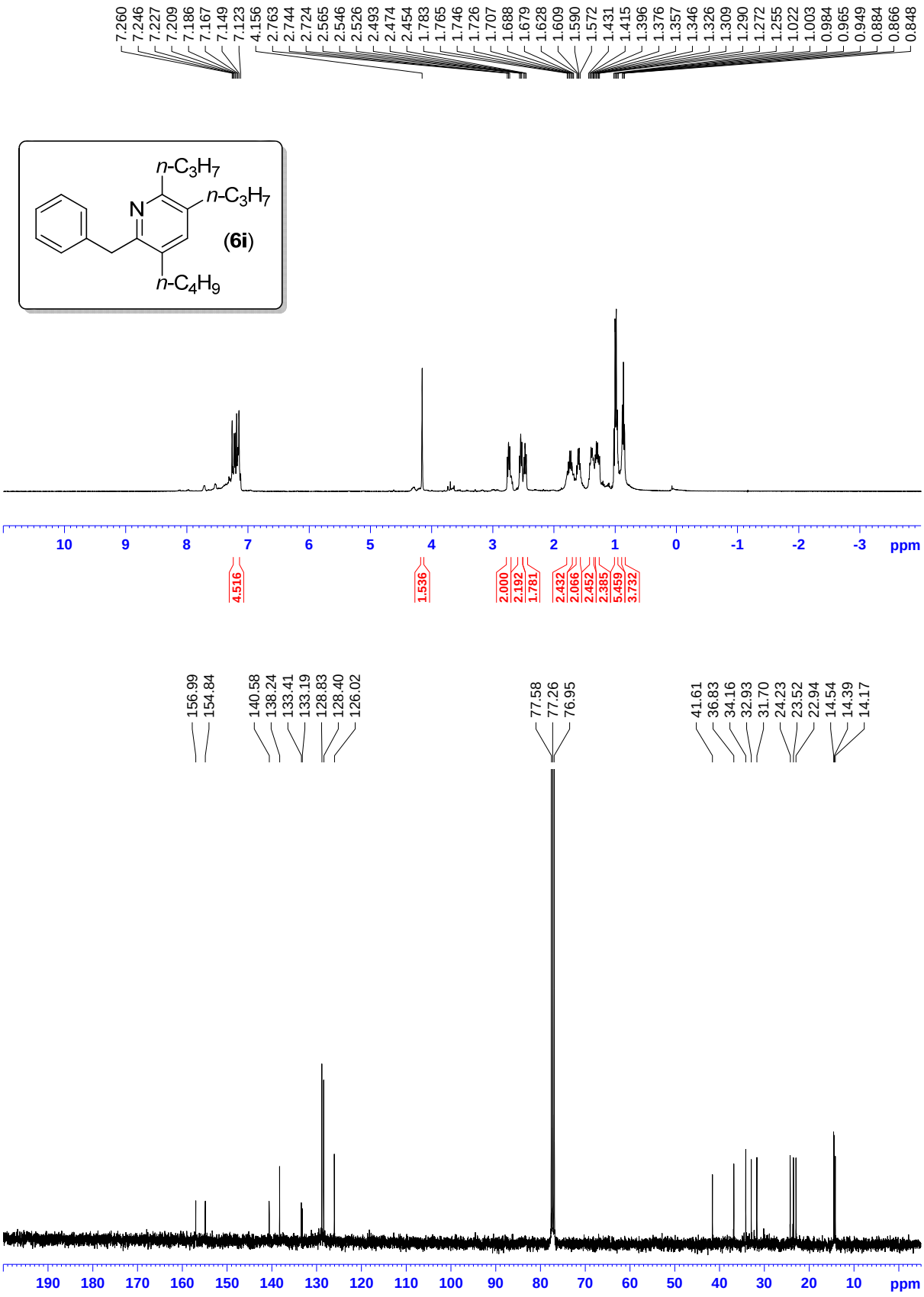
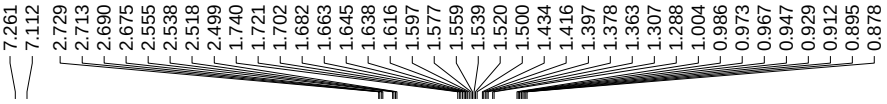
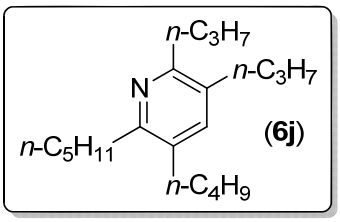
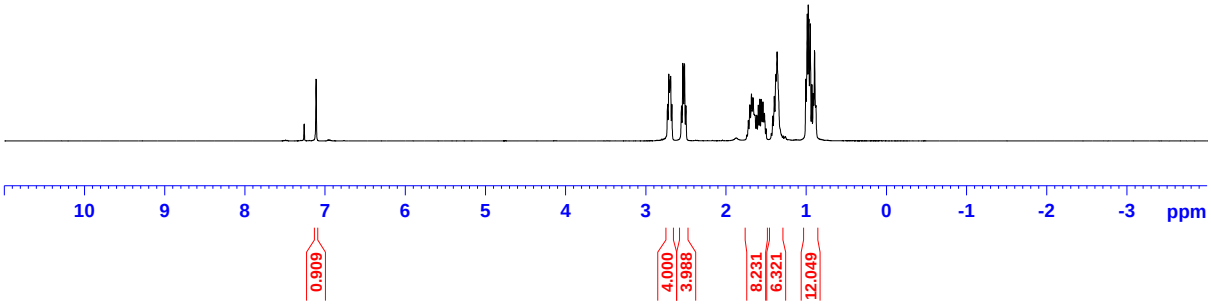
7.259
7.249
7.221
7.202
7.178
7.113
3.016
2.746
2.727
2.707
2.556
2.538
2.518
2.477
2.458
2.438
1.757
1.738
1.719
1.700
1.680
1.637
1.605
1.585
1.567
1.479
1.254
1.026
1.007
0.995
0.978
0.960
0.892
n-C3H7
n-C3H7
N
(6g)
n-C10H21
10
9
8
7
6
5
4
3
2
1
0
ppm
3.720
2.789
0.957
3.594
2.000
1.973
1.872
2.038
2.891
2.416
14.888
5.864
3.759
156.97
155.67
142.70
137.94
132.74
132.63
128.75
128.68
128.60
128.49
125.98
77.58
77.26
76.94
36.81
36.60
36.25
34.16
32.15
32.04
31.84
31.04
29.85
29.73
29.57
24.25
23.51
22.93
22.91
14.55
14.37
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

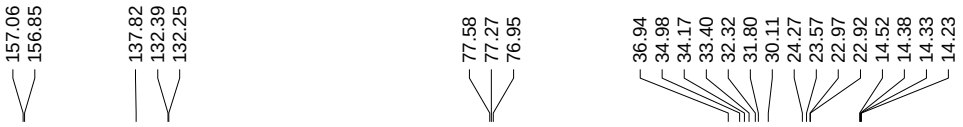

7.280
7.262
7.246
7.199
7.178
3.073
3.053
3.018
3.003
2.741
2.723
2.702
2.562
2.543
2.524
1.795
1.758
1.741
1.722
1.704
1.684
1.642
1.624
1.604
1.585
1.566
1.322
1.298
1.273
1.258
1.028
1.010
0.993
0.976
0.958
n-C3H7
n-C3H7
N
(6h)
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.225
4.089
3.996
2.000
2.210
10.362
4.175
6.006
156.62
154.96
142.63
137.77
134.76
132.76
128.78
128.50
125.98
77.57
77.26
76.94
39.26
36.83
36.68
36.50
34.40
34.29
27.30
26.41
24.28
23.46
14.57
14.33
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

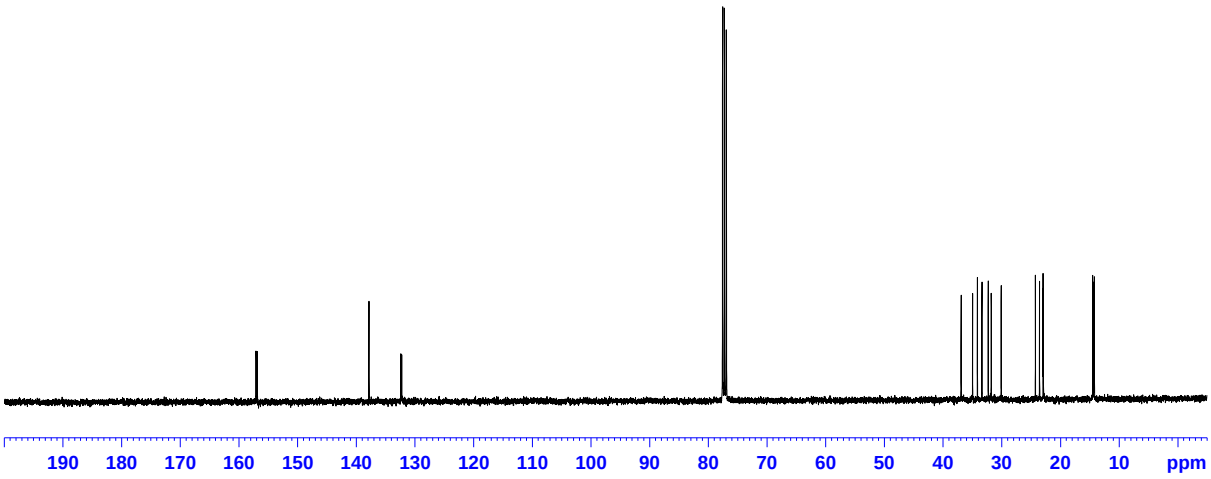

7.260
7.246
7.227
7.209
7.186
7.167
7.149
7.123
4.156
2.763
2.744
2.724
2.565
2.546
2.526
2.493
2.474
2.454
1.783
1.765
1.746
1.726
1.707
1.688
1.679
1.628
1.609
1.590
1.572
1.431
1.415
1.396
1.376
1.357
1.346
1.326
1.309
1.290
1.272
1.255
1.022
1.003
0.984
0.965
0.949
0.884
0.866
0.848
n-C3H7
n-C3H7
N
(6i)
n-C4H9
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
4.516
1.536
2.000
2.192
1.781
2.432
2.066
2.452
2.385
5.459
3.732
156.99
154.84
140.58
138.24
133.41
133.19
128.83
128.40
126.02
77.58
77.26
76.95
41.61
36.83
34.16
32.93
31.70
24.23
23.52
22.94
14.54
14.39
14.17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

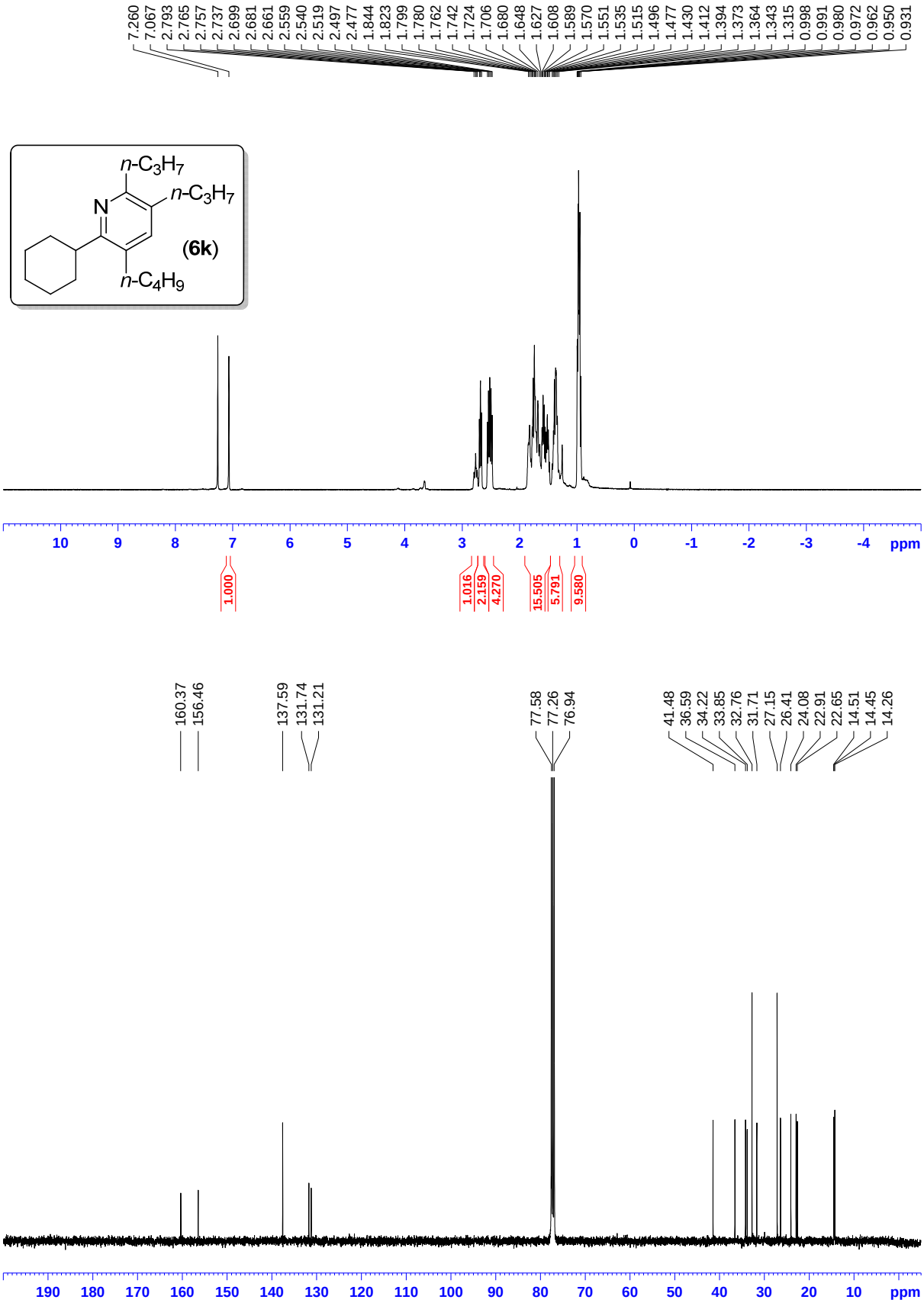

7.261
7.112
2.729
2.713
2.690
2.675
2.555
2.538
2.518
2.499
1.740
1.721
1.702
1.682
1.663
1.645
1.638
1.616
1.597
1.577
1.559
1.539
1.520
1.500
1.434
1.416
1.397
1.378
1.363
1.307
1.288
1.004
0.986
0.973
0.967
0.947
0.929
0.912
0.895
0.878

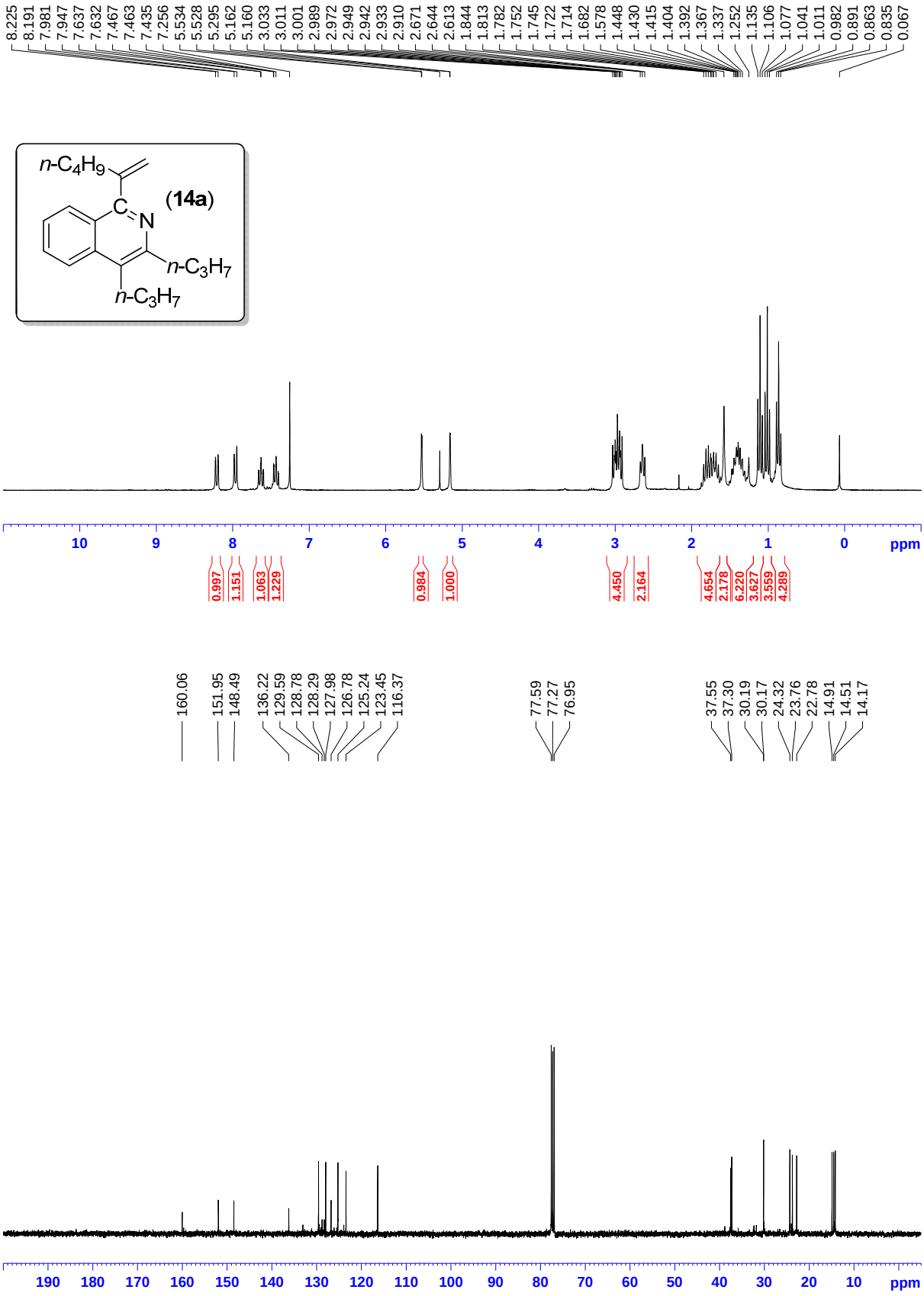

n-C3H7
n-C3H7
N
n-C5H11
n-C4H9
(6j)

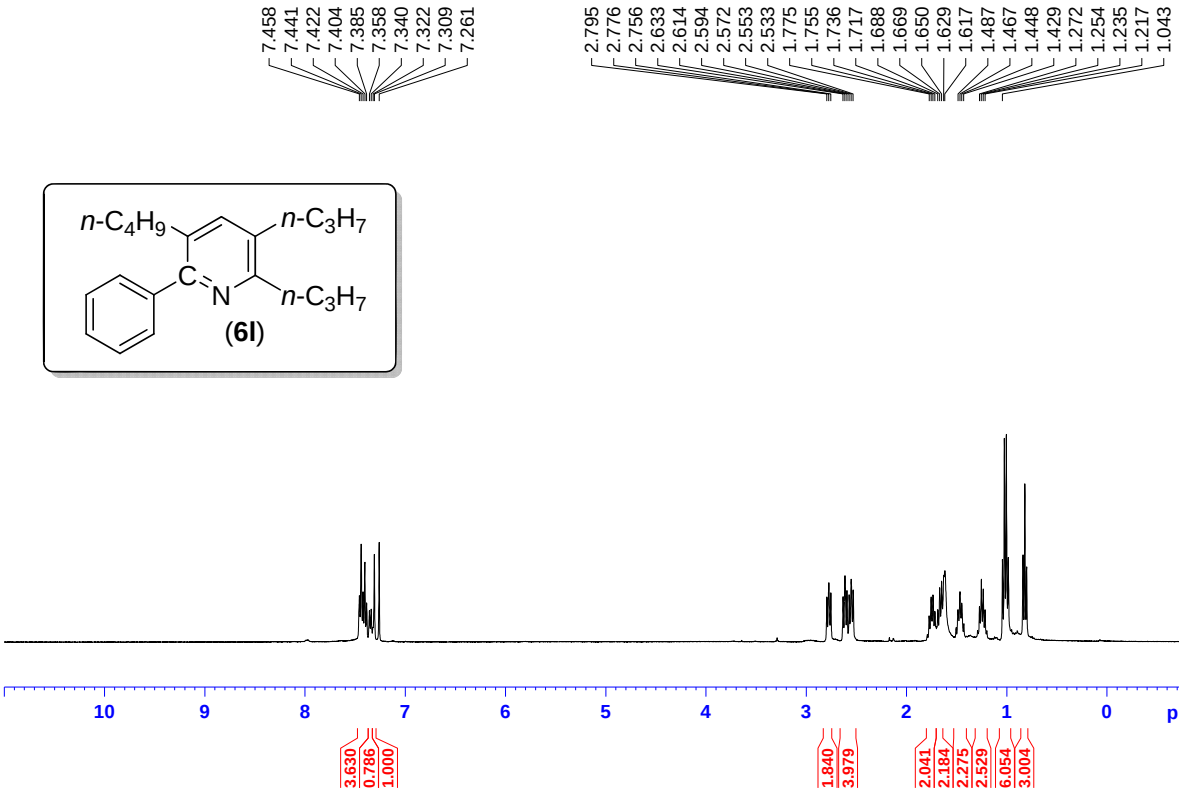

10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
0.909
4.000
3.988
8.231
6.321
12.049


157.06
156.85
137.82
132.39
132.25
77.58
77.27
76.95
36.94
34.98
34.17
33.40
32.32
31.80
30.11
24.27
23.57
22.97
22.92
14.52
14.38
14.33
14.23

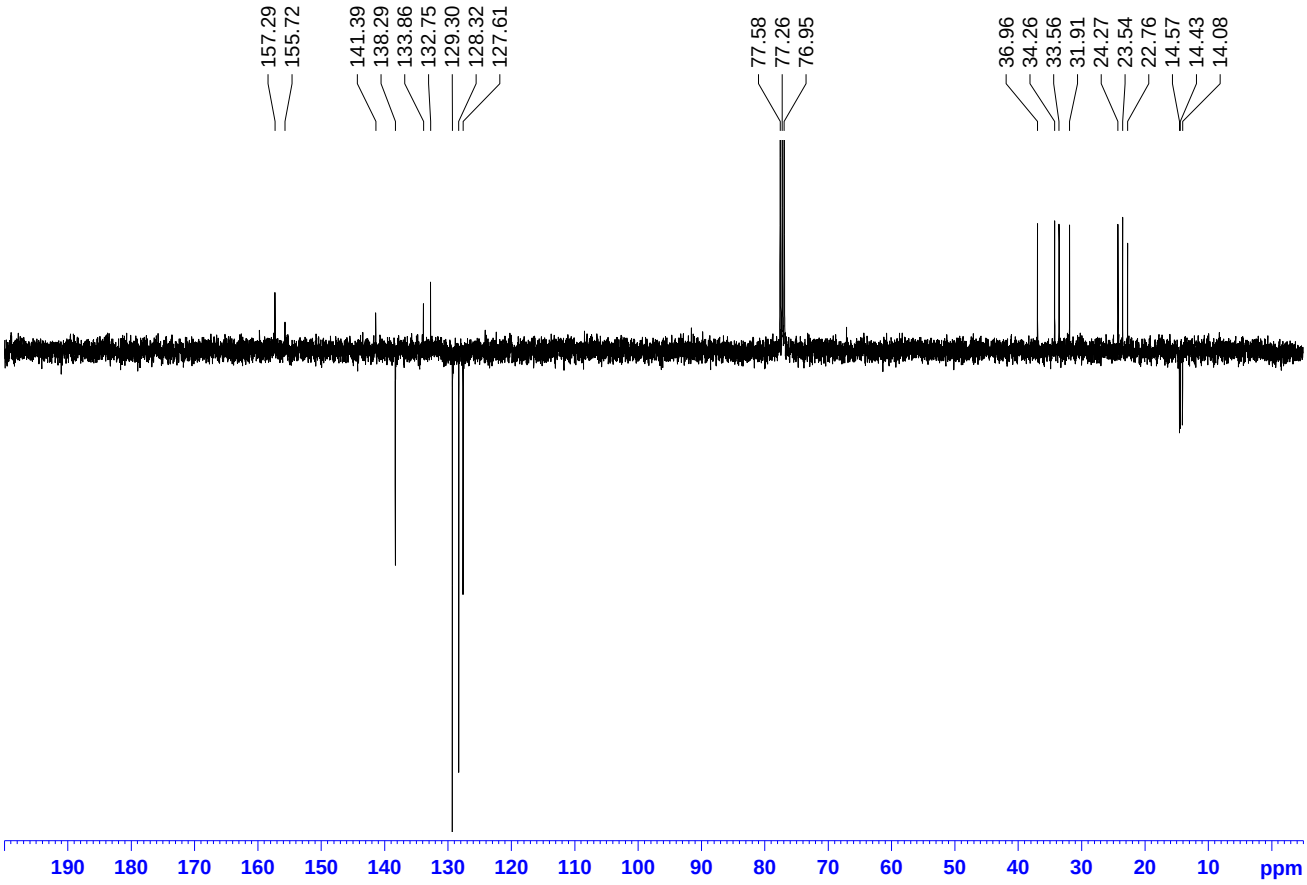

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

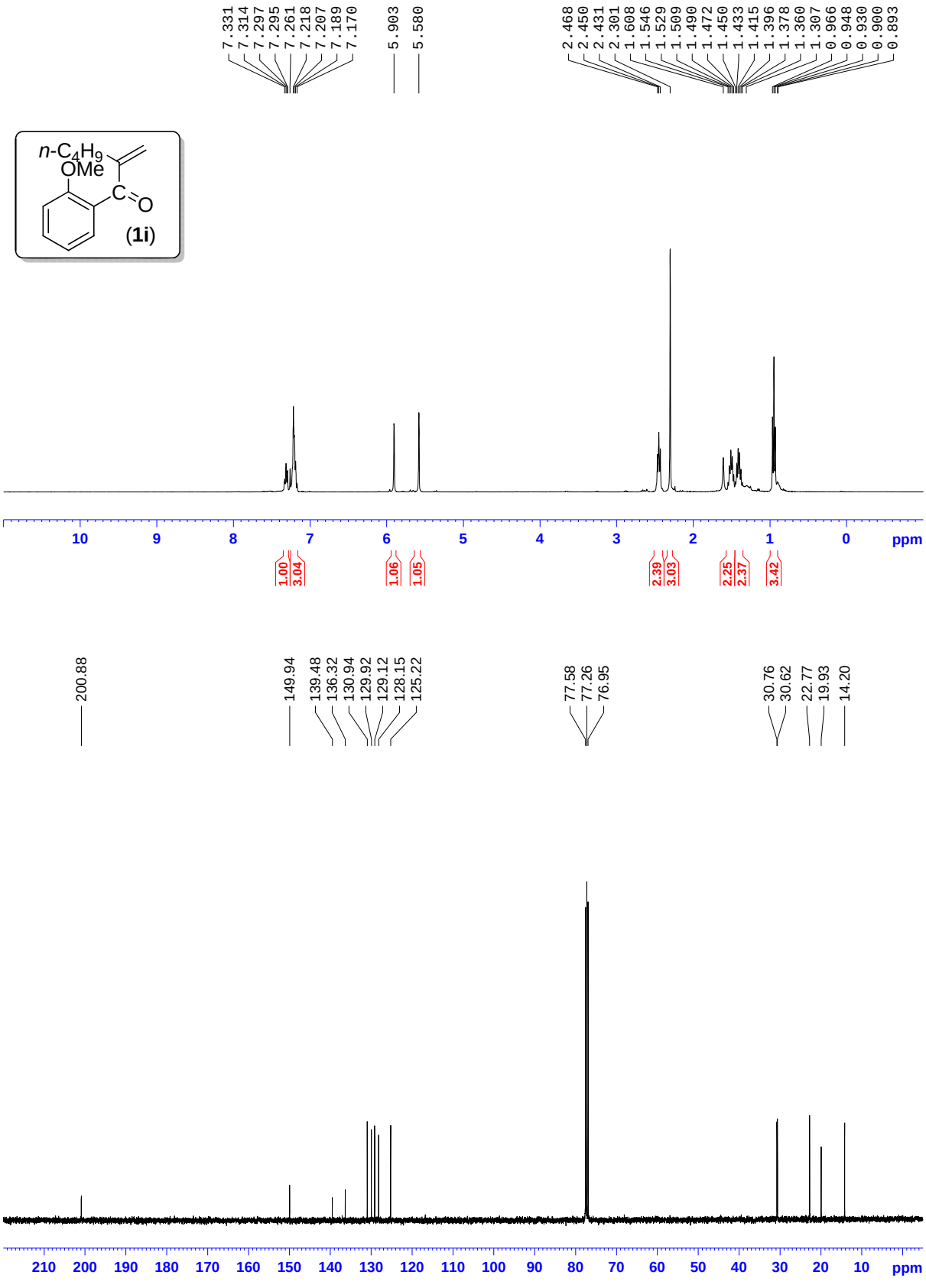

7.260
7.067
2.793
2.765
2.757
2.737
2.699
2.681
2.661
2.559
2.540
2.519
2.497
2.477
1.844
1.823
1.799
1.780
1.762
1.742
1.724
1.706
1.680
1.648
1.627
1.608
1.589
1.570
1.551
1.535
1.515
1.496
1.477
1.430
1.412
1.394
1.373
1.364
1.343
1.315
0.998
0.991
0.980
0.972
0.962
0.950
0.931
n-C3H7
n-C3H7
N
(6k)
n-C4H9
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 ppm
1.000
1.016
2.159
4.270
15.505
5.791
9.580
160.37
156.46
137.59
131.74
131.21
77.58
77.26
76.94
41.48
36.59
34.22
33.85
32.76
31.71
27.15
26.41
24.08
22.91
22.65
14.51
14.45
14.26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

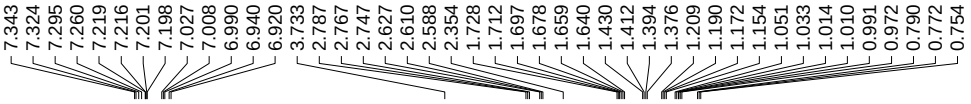

8.225
8.191
7.981
7.947
7.637
7.632
7.467
7.463
7.435
7.256
5.534
5.528
5.295
5.162
5.160
3.033
3.011
3.001
2.989
2.972
2.949
2.942
2.933
2.910
2.671
2.644
2.613
1.844
1.813
1.782
1.752
1.745
1.722
1.714
1.682
1.578
1.448
1.430
1.415
1.404
1.392
1.367
1.337
1.252
1.135
1.106
1.077
1.041
1.011
0.982
0.891
0.863
0.835
0.067
n-C4H9
(14a)
C
N
n-C3H7
n-C3H7
10
9
8
7
6
5
4
3
2
1
0
ppm
0.997
1.151
1.063
1.229
0.984
1.000
4.450
2.164
4.654
2.178
6.220
3.627
3.559
4.289
160.06
151.95
148.49
136.22
129.59
128.78
128.29
127.98
126.78
125.24
123.45
116.37
77.59
77.27
76.95
37.55
37.30
30.19
30.17
24.32
23.76
22.78
14.91
14.51
14.17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

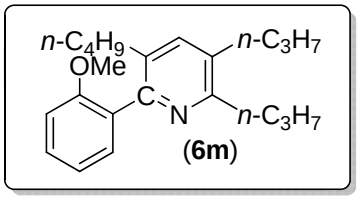


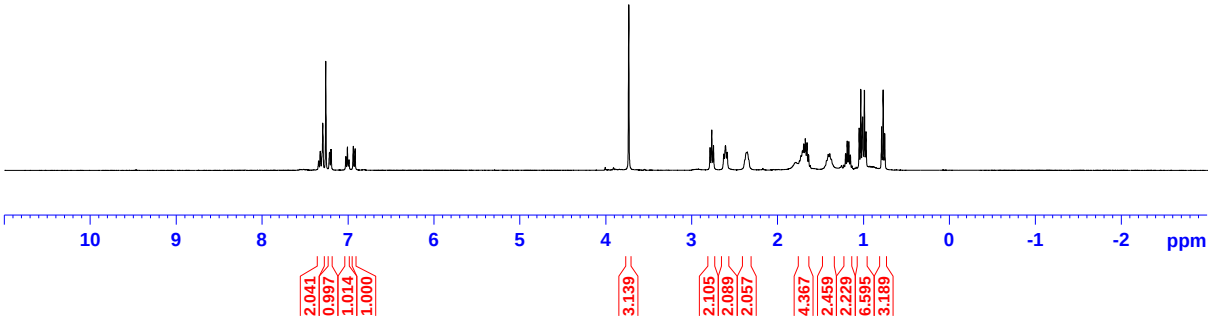
Measured by ^{13}C APT

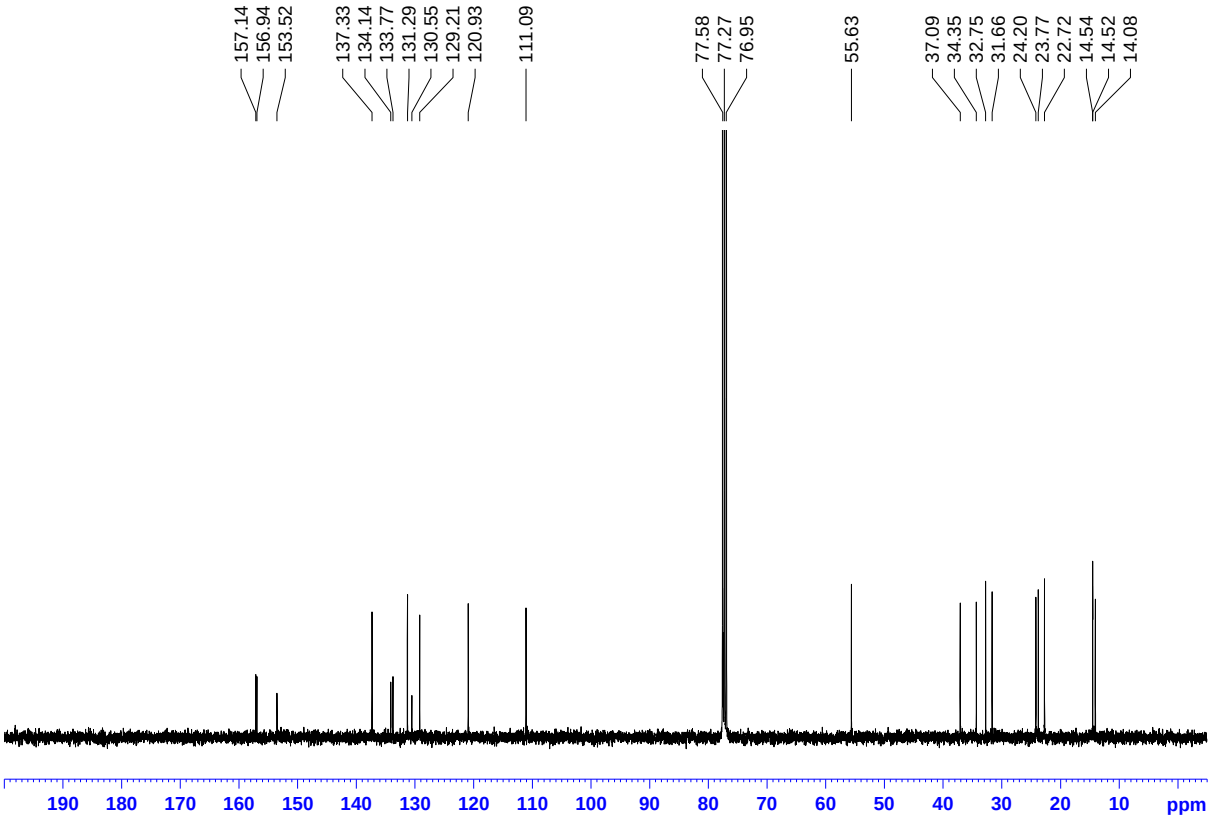


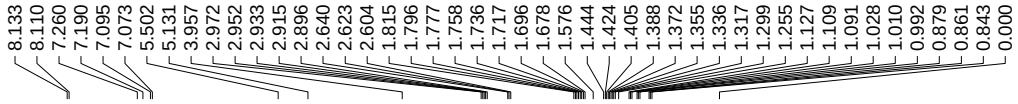

7.331
7.314
7.297
7.295
7.261
7.218
7.207
7.189
7.170
5.903
5.580
2.468
2.450
2.431
2.301
1.608
1.546
1.529
1.509
1.490
1.472
1.450
1.433
1.415
1.396
1.378
1.360
1.307
0.966
0.948
0.930
0.900
0.893
n-C4H9
OMe
C
O
(1i)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.04
1.06
1.05
2.39
3.03
2.25
2.37
3.42
200.88
149.94
139.48
136.32
130.94
129.92
129.12
128.15
125.22
77.58
77.26
76.95
30.76
30.62
22.77
19.93
14.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

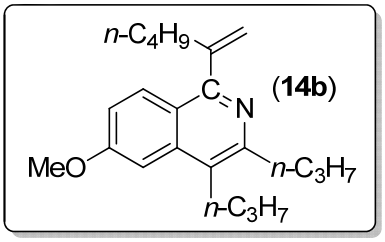

7.343
7.324
7.295
7.260
7.219
7.216
7.201
7.198
7.027
7.008
6.990
6.940
6.920
3.733
2.787
2.767
2.747
2.627
2.610
2.588
2.354
1.728
1.712
1.697
1.678
1.659
1.640
1.430
1.412
1.394
1.376
1.209
1.190
1.172
1.154
1.051
1.033
1.014
1.010
0.991
0.972
0.790
0.772
0.754

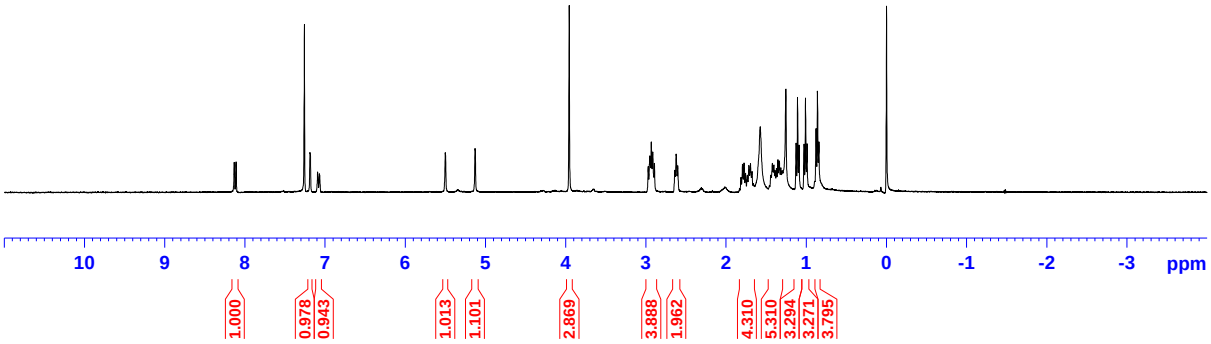

n-C4H9
OMe
n-C3H7
C
N
n-C3H7
(6m)

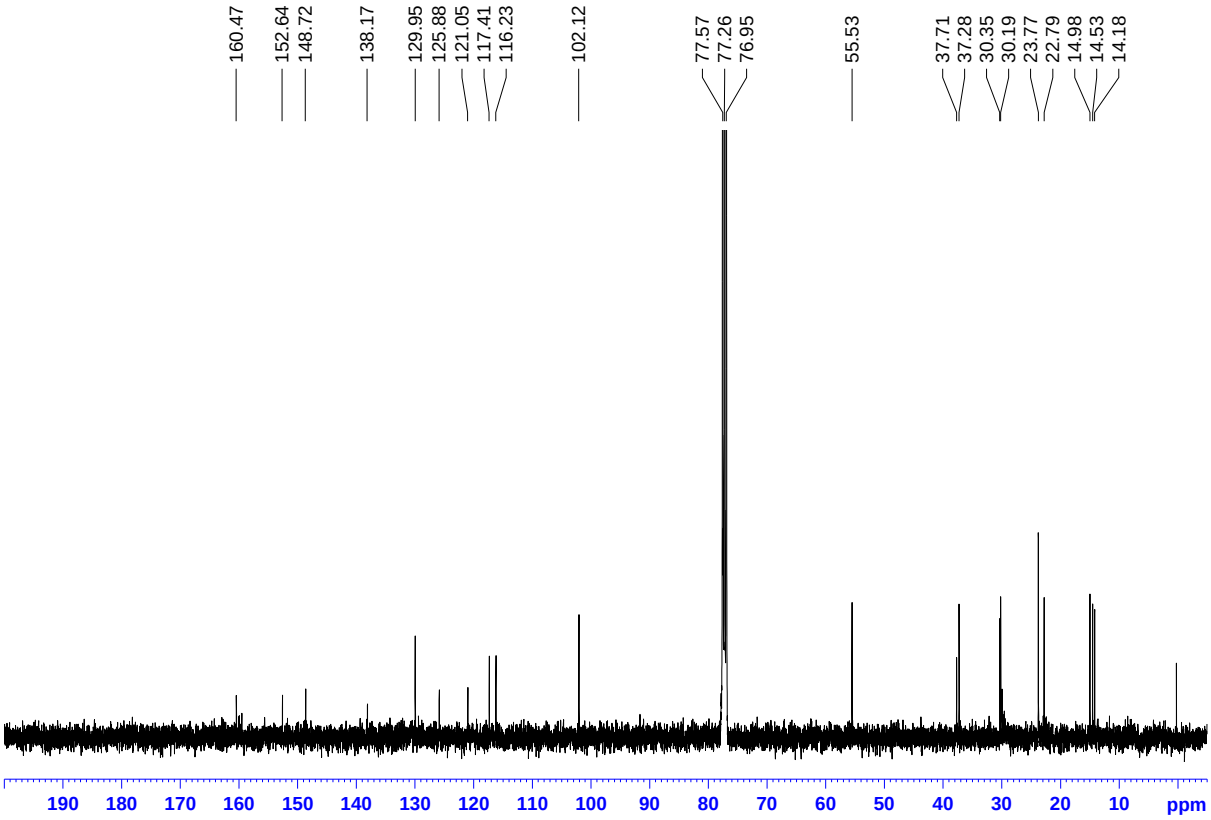

10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
2.041
0.997
1.014
1.000
3.139
2.105
2.089
2.057
4.367
2.459
2.229
6.595
3.189

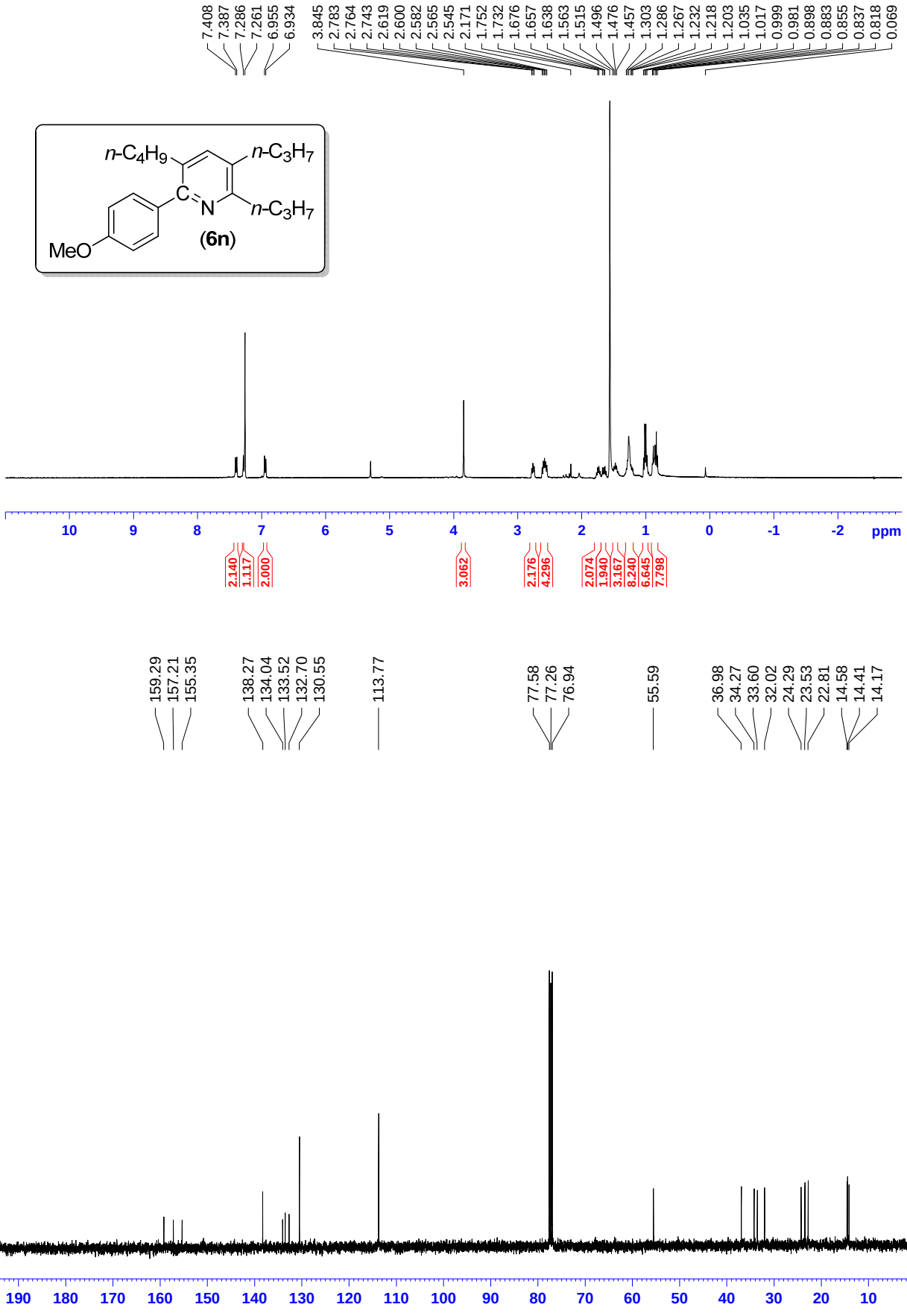

157.14
156.94
153.52
137.33
134.14
133.77
131.29
130.55
129.21
120.93
111.09
77.58
77.27
76.95
55.63
37.09
34.35
32.75
31.66
24.20
23.77
22.72
14.54
14.52
14.08
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.133
8.110
7.260
7.190
7.095
7.073
5.502
5.131
3.957
2.972
2.952
2.933
2.915
2.896
2.640
2.623
2.604
1.815
1.796
1.777
1.758
1.736
1.717
1.696
1.678
1.576
1.444
1.424
1.405
1.388
1.372
1.355
1.336
1.317
1.299
1.255
1.127
1.109
1.091
1.028
1.010
0.992
0.879
0.861
0.843
0.000


n-C4H9
C
N
(14b)
MeO
n-C3H7
n-C3H7


10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
1.000
0.978
0.943
1.013
1.101
2.869
3.888
1.962
4.310
5.310
3.294
3.271
3.795


160.47
152.64
148.72
138.17
129.95
125.88
121.05
117.41
116.23
102.12
77.57
77.26
76.95
55.53
37.71
37.28
30.35
30.19
23.77
22.79
14.98
14.53
14.18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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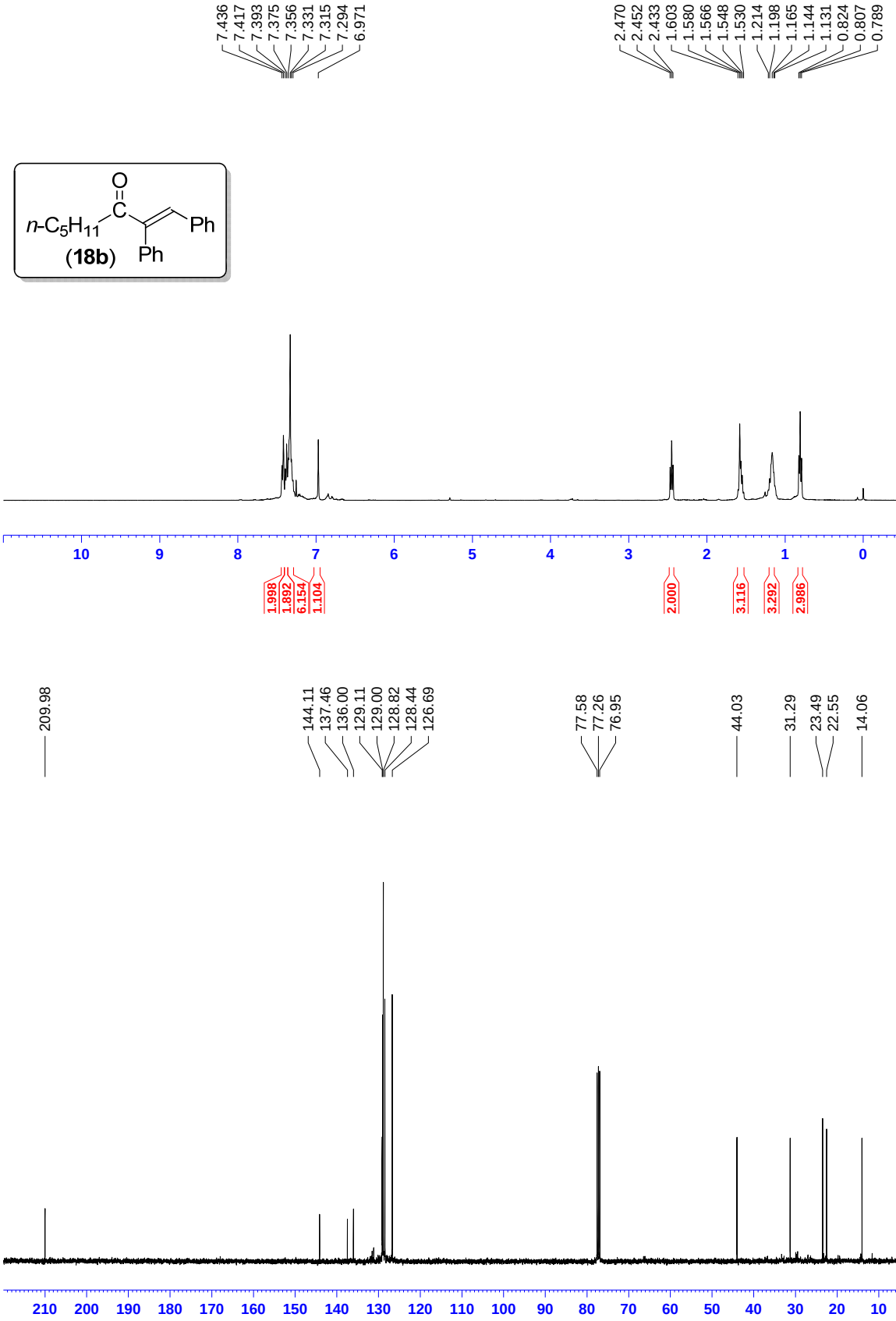
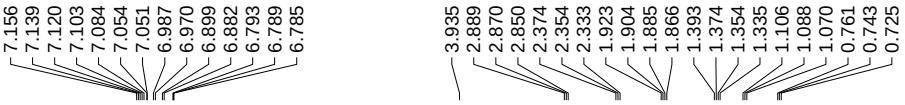
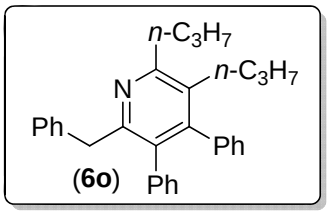
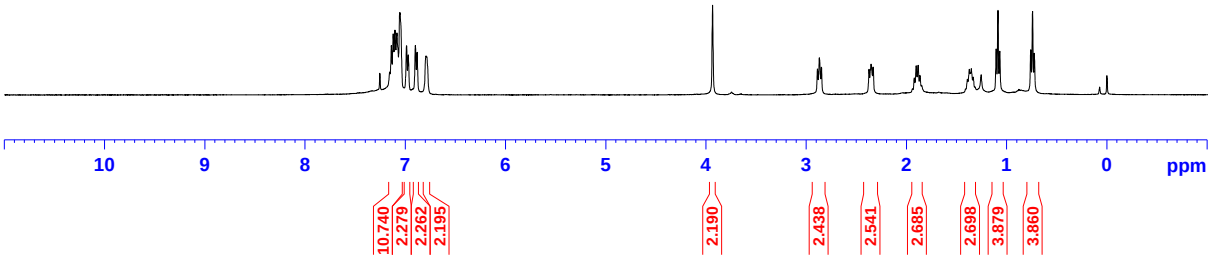
7.387
7.286
7.261
6.955
6.934
3.845
2.783
2.764
2.743
2.619
2.600
2.582
2.565
2.545
2.171
1.752
1.732
1.676
1.657
1.638
1.563
1.515
1.496
1.476
1.457
1.303
1.286
1.267
1.232
1.218
1.203
1.035
1.017
0.999
0.981
0.898
0.883
0.855
0.837
0.818
0.069
n-C4H9
n-C3H7
C
N
n-C3H7
MeO
(6n)
10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
2.140
1.117
2.000
3.062
2.176
4.296
2.074
1.940
3.167
8.240
6.645
7.798
159.29
157.21
155.35
138.27
134.04
133.52
132.70
130.55
113.77
77.58
77.26
76.94
55.59
36.98
34.27
33.60
32.02
24.29
23.53
22.81
14.58
14.41
14.17
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

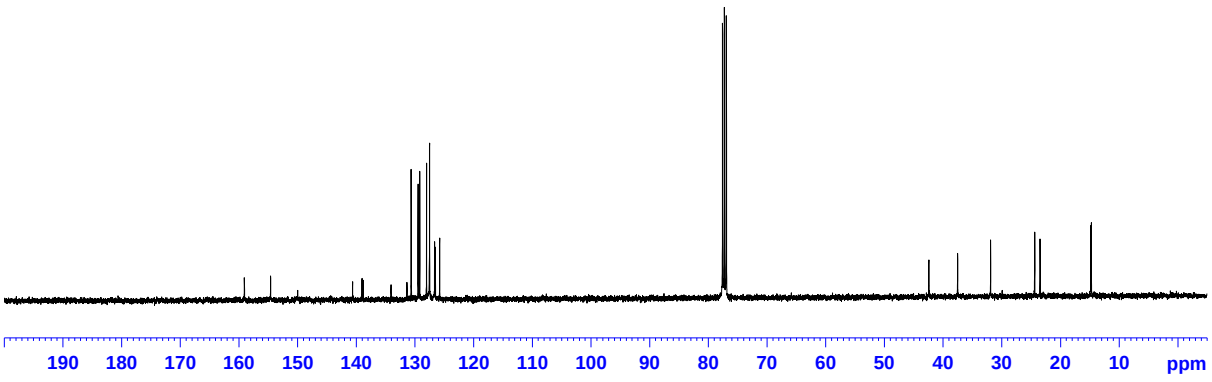

7.436
7.417
7.393
7.375
7.356
7.331
7.315
7.294
6.971
2.470
2.452
2.433
1.603
1.580
1.566
1.548
1.530
1.214
1.198
1.165
1.144
1.131
0.824
0.807
0.789
n-C5H11
O
C
Ph
Ph
(18b)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.998
1.892
6.154
1.104
2.000
3.116
3.292
2.986
209.98
144.11
137.46
136.00
129.11
129.00
128.82
128.44
126.69
77.58
77.26
76.95
44.03
31.29
23.49
22.55
14.06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

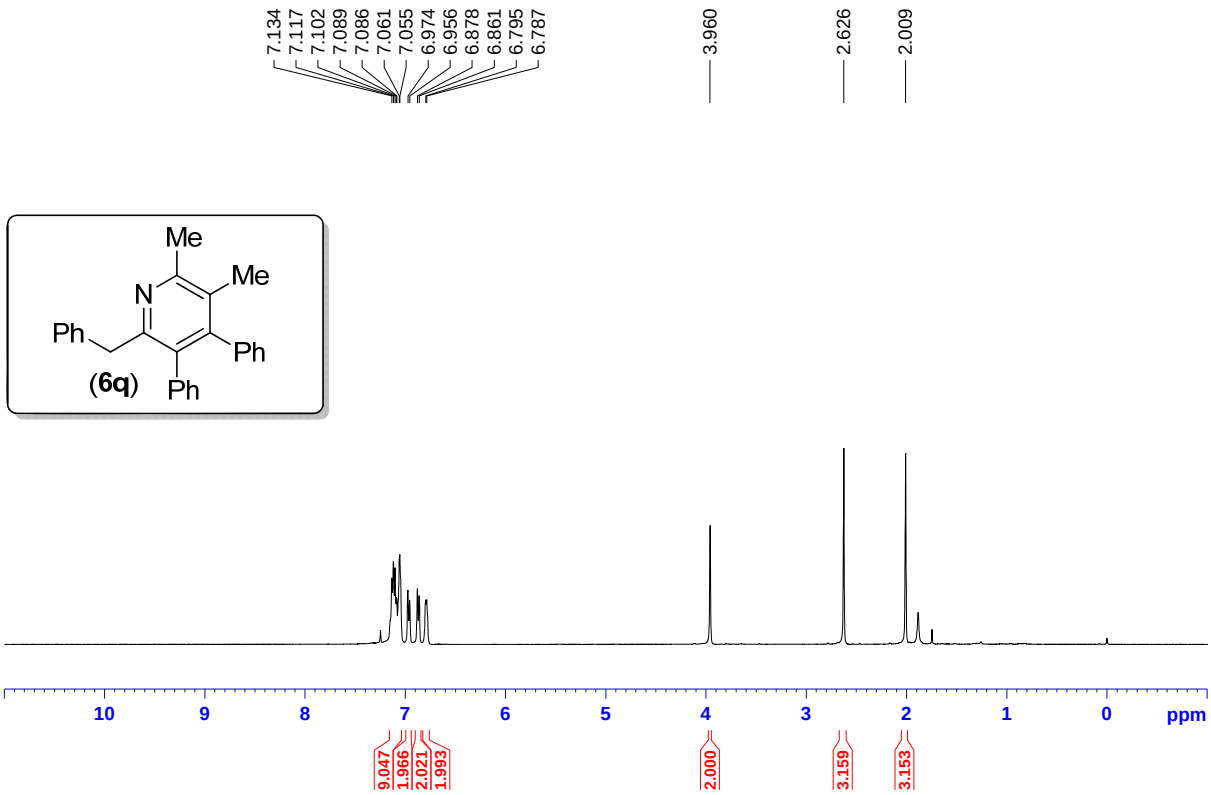

7.156
7.139
7.120
7.103
7.084
7.054
7.051
6.987
6.970
6.899
6.882
6.793
6.789
6.785
3.935
2.889
2.870
2.850
2.374
2.354
2.333
1.923
1.904
1.885
1.866
1.393
1.374
1.354
1.335
1.106
1.088
1.070
0.761
0.743
0.725

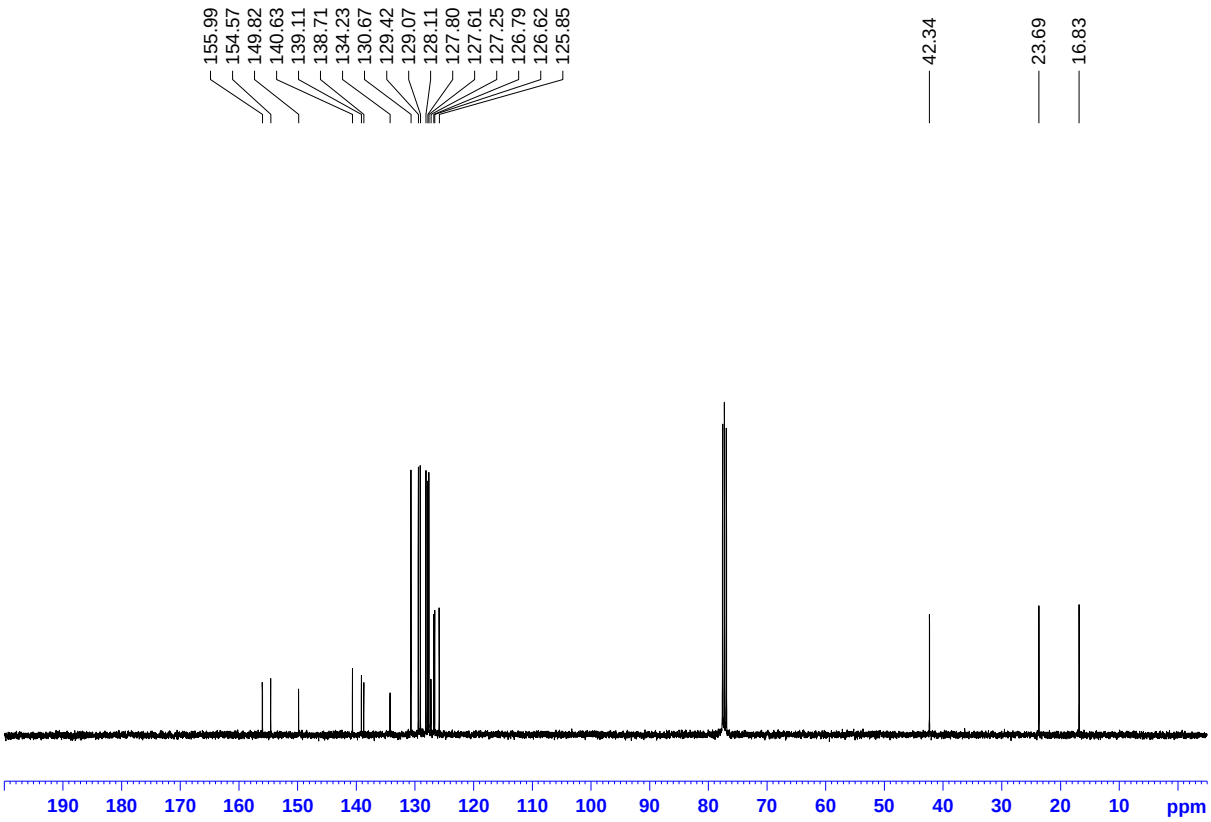

n-C3H7
n-C3H7
N
Ph
Ph
Ph
(6o)

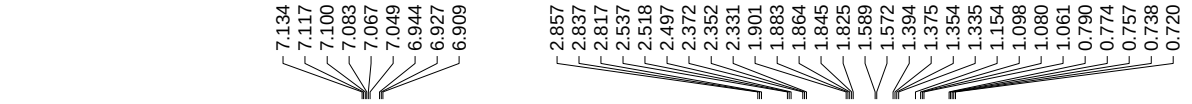

10
9
8
7
6
5
4
3
2
1
0
ppm
10.740
2.279
2.262
2.195
2.190
2.438
2.541
2.685
2.698
3.879
3.860

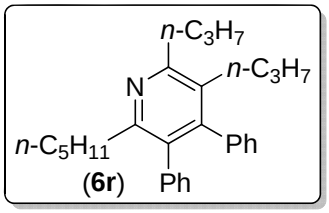

159.11
154.62
140.63
139.04
138.82
134.09
131.37
130.65
129.48
129.20
128.04
127.53
127.52
126.67
126.53
125.80
42.44
37.53
31.91
24.41
23.49
14.84
14.75

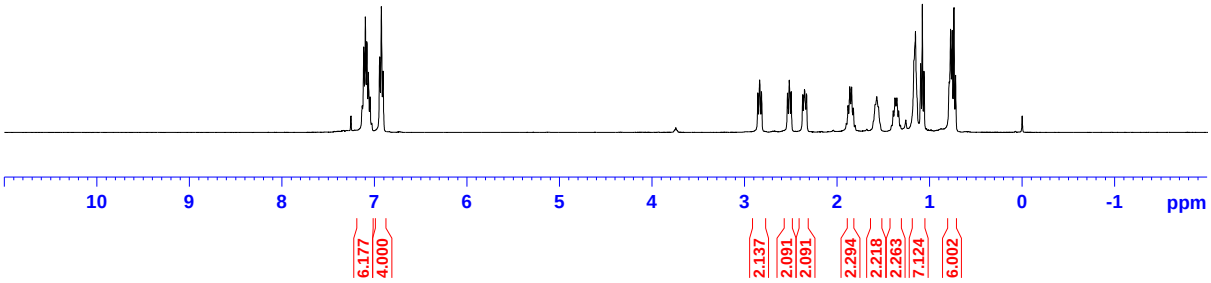

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

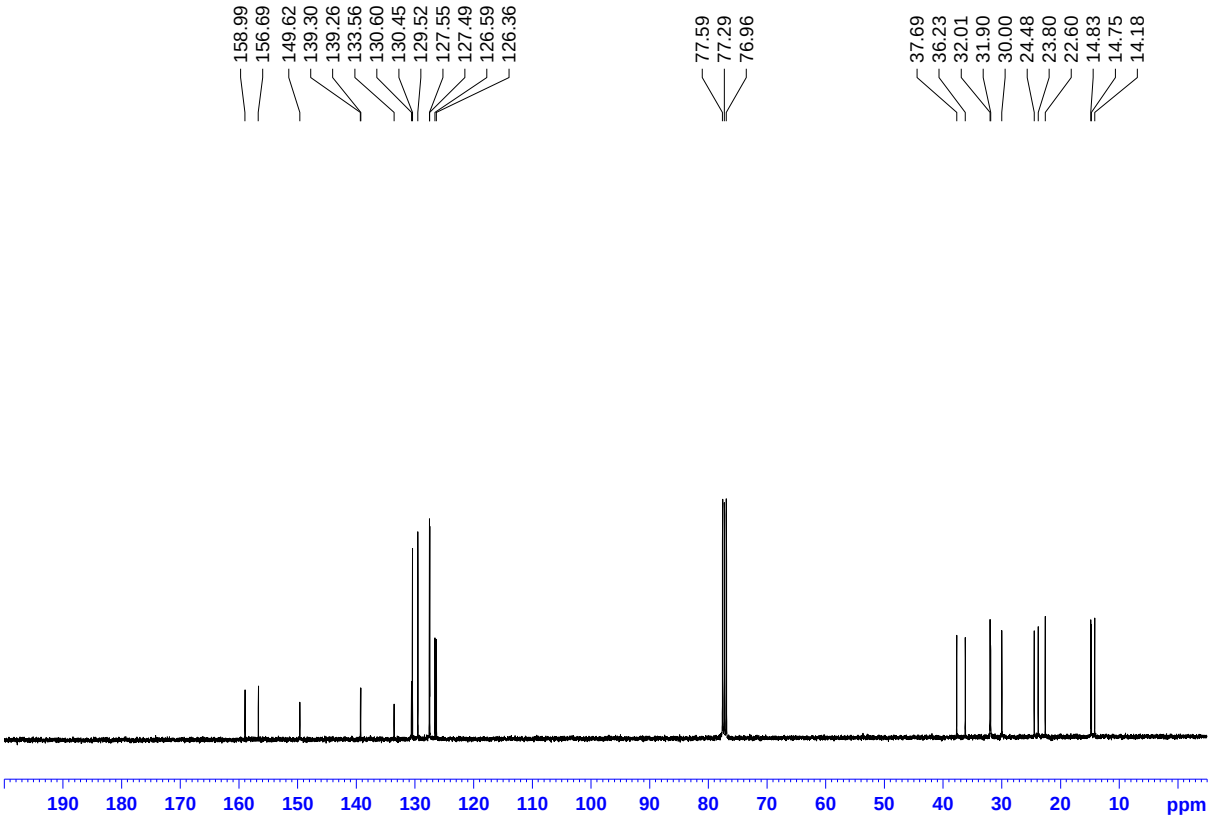

7.134
7.117
7.102
7.089
7.086
7.061
7.055
6.974
6.956
6.878
6.861
6.795
6.787
3.960
2.626
2.009
Me
Me
N
Ph
Ph
(6q)
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
9.047
1.966
2.021
1.993
2.000
3.159
3.153

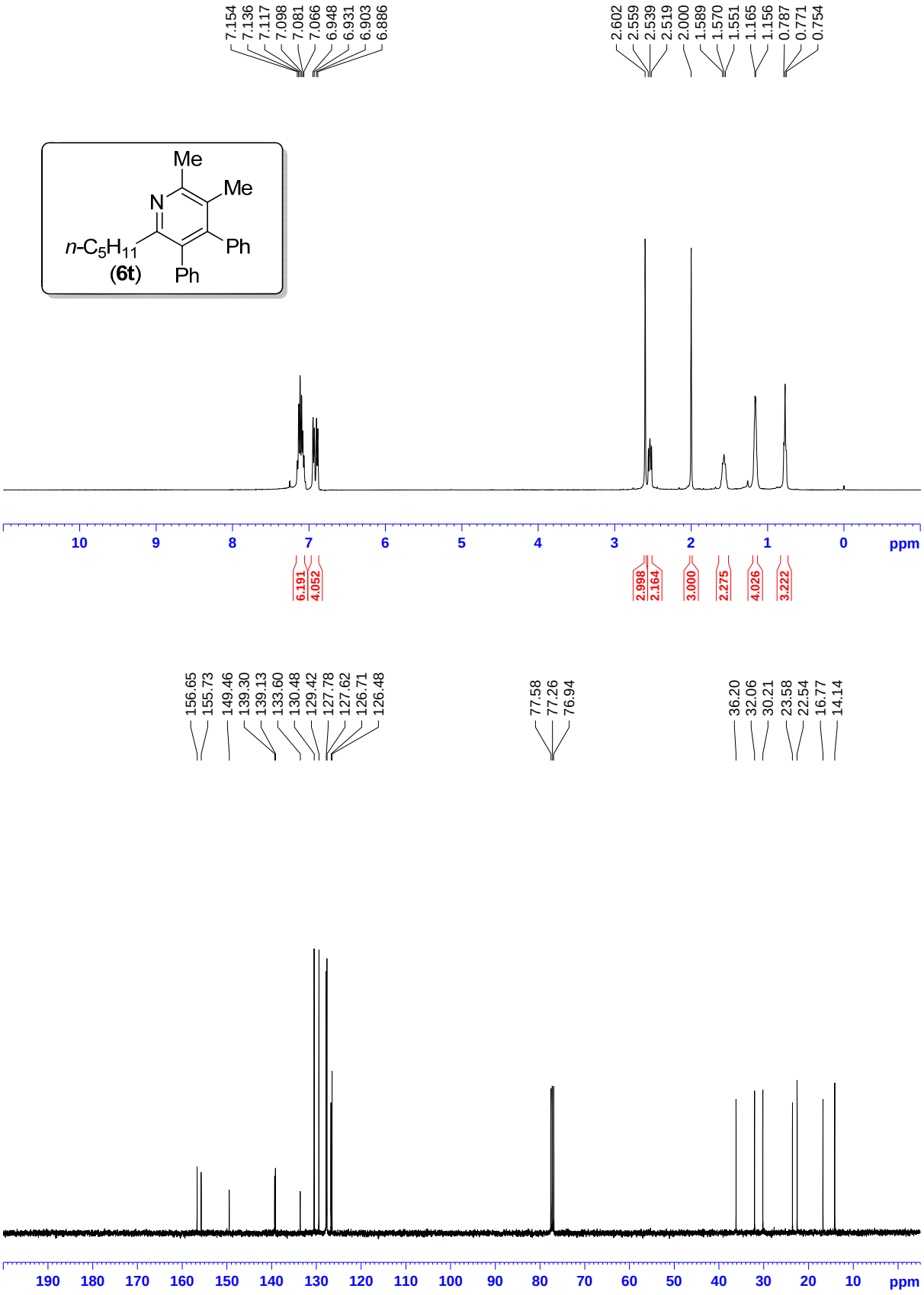

155.99
154.57
149.82
140.63
139.11
138.71
134.23
130.67
129.42
129.07
128.11
127.80
127.61
127.25
126.79
126.62
125.85
42.34
23.69
16.83
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

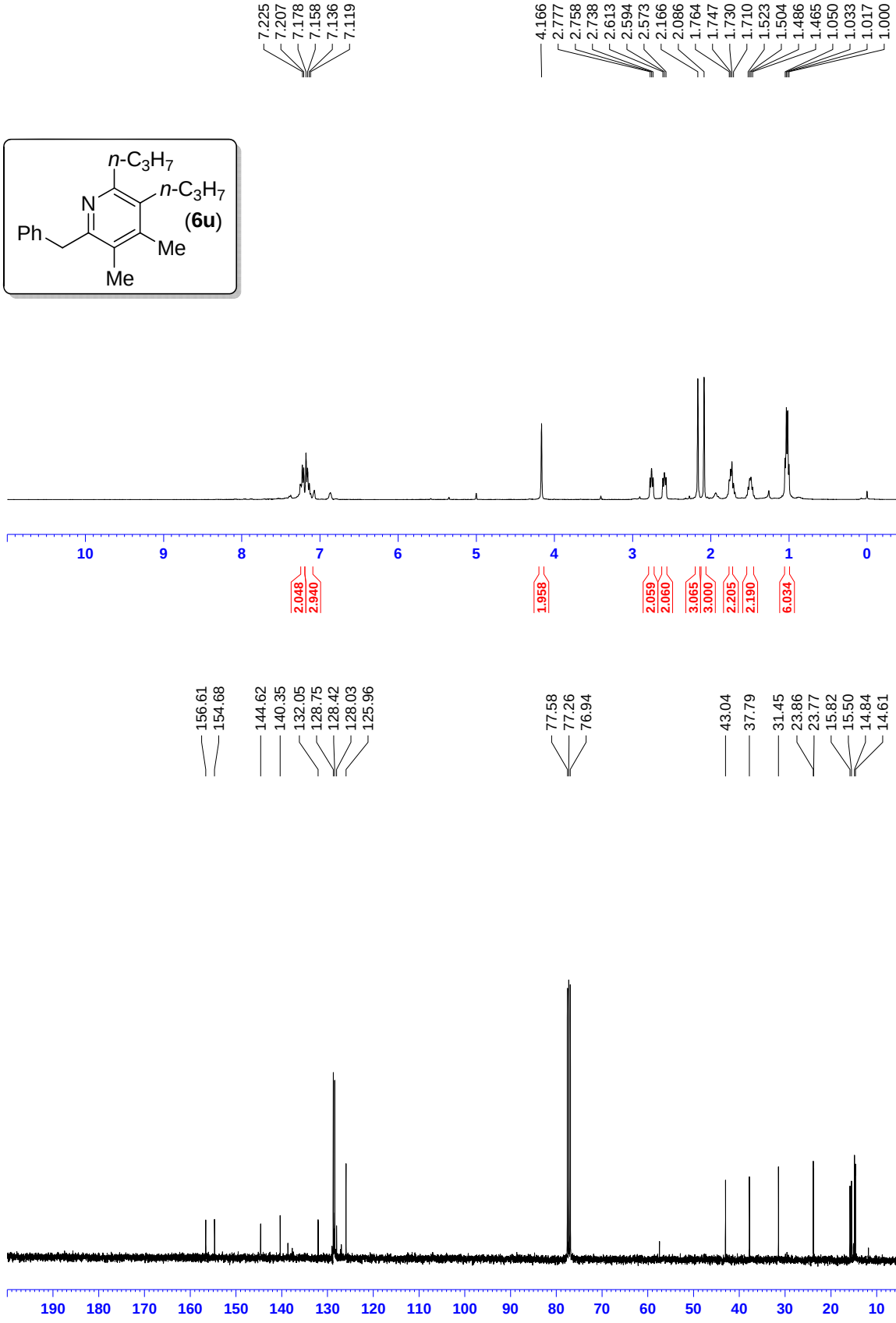

7.134
7.117
7.100
7.083
7.067
7.049
6.944
6.927
6.909
2.857
2.837
2.817
2.537
2.518
2.497
2.372
2.352
2.331
1.901
1.883
1.864
1.845
1.825
1.589
1.572
1.394
1.375
1.354
1.335
1.154
1.098
1.080
1.061
0.790
0.774
0.757
0.738
0.720

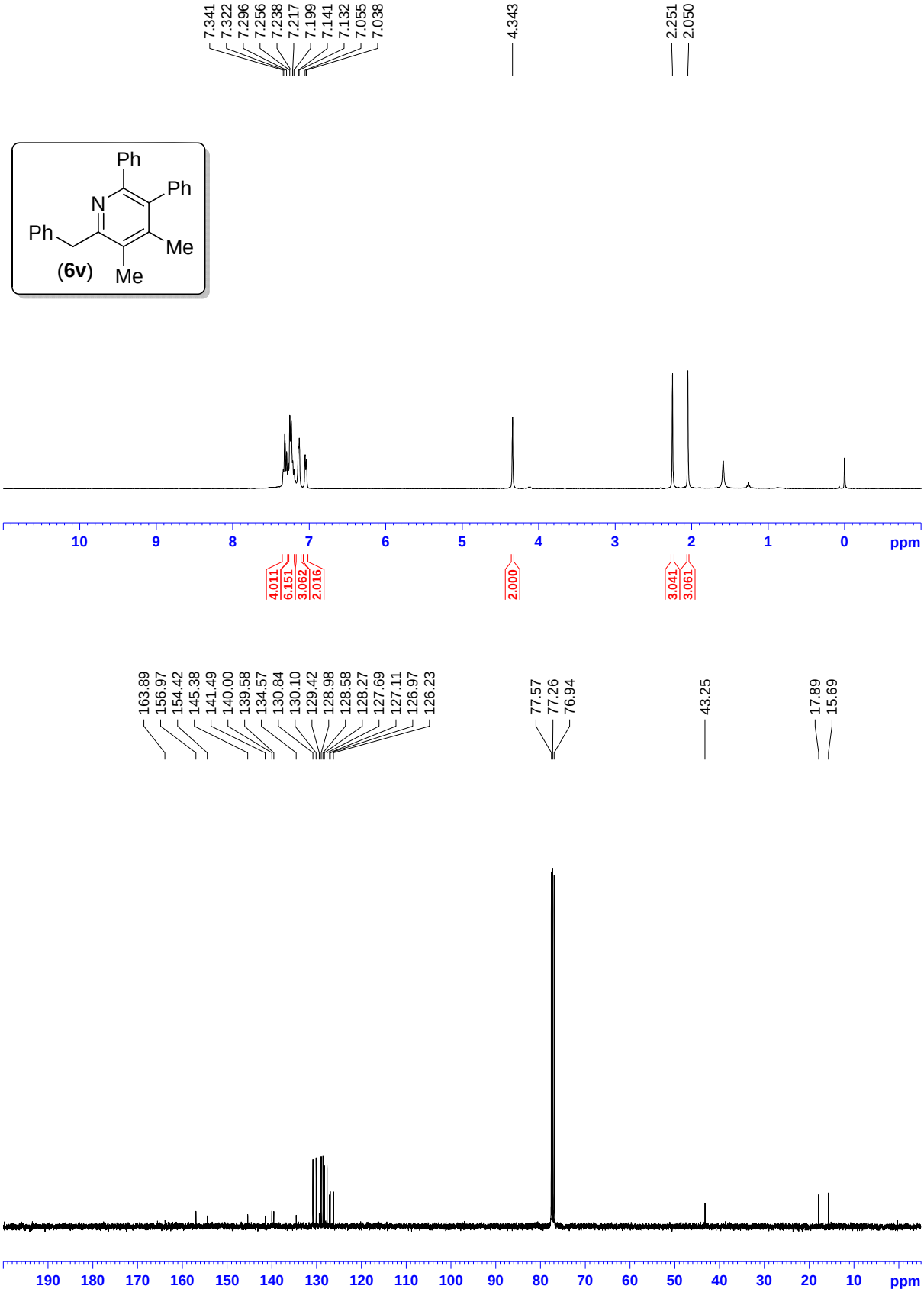

n-C3H7
n-C3H7
N
n-C5H11
Ph
(6r)
Ph


10
9
8
7
6
5
4
3
2
1
0
-1
ppm
6.177
4.000
2.137
2.091
2.091
2.294
2.218
2.263
7.124
6.002


158.99
156.69
149.62
139.30
139.26
133.56
130.60
130.45
129.52
127.55
127.49
126.59
126.36
77.59
77.29
76.96
37.69
36.23
32.01
31.90
30.00
24.48
23.80
22.60
14.83
14.75
14.18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.154
7.136
7.117
7.098
7.081
7.066
6.948
6.931
6.903
6.886
2.602
2.559
2.539
2.519
2.000
1.589
1.570
1.551
1.165
1.156
0.787
0.771
0.754
Me
Me
N
n-C5H11
Ph
Ph
(6t)
10
9
8
7
6
5
4
3
2
1
0
ppm
6.191
4.052
2.998
2.164
3.000
2.275
4.026
3.222
156.65
155.73
149.46
139.30
139.13
133.60
130.48
129.42
127.78
127.62
126.71
126.48
77.58
77.26
76.94
36.20
32.06
30.21
23.58
22.54
16.77
14.14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.225
7.207
7.178
7.158
7.136
7.119
4.166
2.777
2.758
2.738
2.613
2.594
2.573
2.166
2.086
1.764
1.747
1.730
1.710
1.523
1.504
1.486
1.465
1.050
1.033
1.017
1.000
n-C3H7
n-C3H7
N
Ph
Me
Me
(6u)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.048
2.940
1.958
2.059
2.060
3.065
3.000
2.205
2.190
6.034
156.61
154.68
144.62
140.35
132.05
128.75
128.42
128.03
125.96
77.58
77.26
76.94
43.04
37.79
31.45
23.86
23.77
15.82
15.50
14.84
14.61
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.341
7.322
7.296
7.256
7.238
7.217
7.199
7.141
7.132
7.055
7.038
4.343
2.251
2.050
Ph
Ph
N
Ph
Me
(6v)
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
4.011
6.151
3.062
2.016
2.000
3.041
3.061
163.89
156.97
154.42
145.38
141.49
140.00
139.58
134.57
130.84
130.10
129.42
128.98
128.58
128.27
127.69
127.11
126.97
126.23
77.57
77.26
76.94
43.25
17.89
15.69
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm