Electronic Supplementary Material (ESI) for Chemical Communications

Formal hydration of non-activated terminal olefins using tandem catalysts

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Supporting Information

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General information:

All olefin oxidation and hydration reactions were carried out under a nitrogen atmosphere in a Vacuum Atmospheres Glovebox. $PdCl_2(MeCN)_2$ was prepared following literature procedures.[1] *p*-benzoquinone from TCI was recrystallized from *i*-PrOH prior to usage. Commercial Shvo's catalyst [1-Hydroxytetraphenyl-cyclopentadienyl(tetraphenyl-2,4-cyclopentadien-1-one)-μ-hydrotetracarbonyldiruthenium(II)] from Aldrich was used as received. Deionized H_2O was distilled under N_2. Anhydrous MeOH and *i*-PrOH were freeze-pump-thawed three times under N_2 before use. All liquid olefins were filtered through a plug of basic alumina prior to usage, except for 1-octene, which was distilled over CaH_2 before being filtered through a plug of basic alumina. 4-pentenoic acid was filtered through a plug of neutral alumina. Tridecane was distilled over CaH_2 and stored under N_2 for usage.

^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer.

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatography system equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). Instrument conditions-inlet temperature: 250 ^oC; detector temperature: 250 ^oC; hydrogen flow: 30 ml/min; air flow: 400 ml/min.; constant col + makeup flow: 25 ml/min. Method: 50^oC for 2 min., followed by a temperature increase of 10 ^oC/min. to 115^oC, hold for 0.5 min., another temperature increase of 1^oC/min. to 125 ^oC, hold for 0.5 min., then a temperature increase of 5 ^oC/min. to 140 ^oC, hold 0.5 min. and a final temperature increase of 60 ^oC/min. to 300 ^oC and hold at 300 ^oC for 5 min. (total run time = 30.67 min.). Response factors were collected for styrene, phenylacetaldehyde, acetophenone, 2-phenylethanol, 1-phenylethanol, ethylbenzene, 1-octene, octanal, 2-octanone, 1-octanol, 2-octanol, n-octane, 4-phenyl-1-butene, 4-phenyl-2-butanone, 4-phenyl-2-butanol and 4-phenyl-1-butanol following literature procedures.[2]

GC sample preparation:

Tridecane (0.00123 mmol, 3 μl) was added to the reaction mixture as an internal standard. The mixture was then diluted with diethyl ether (2 ml) and *ca.* 0.5 ml of the resultant mixture was filtered through a plug of basic alumina followed by flushing with ethyl acetate (*ca.* 1 ml). GC retention times (min) were as follows: styrene (5.53), phenylacetaldehyde (8.08), acetophenone (8.46), 2-phenylethanol (9.25), 1-phenylethanol (8.35), ethylbenzene (5.04), 1-octene (3.91), octanal (7.38), 2-octanone (7.18), 1-octanol (8.45), 2-octanol (7.31) and tridecane (13.86).

HPLC sample preparation:

High pressure liquid chromatography (HPLC) data was obtained using the Daicel Chiralcel OD-H column. Instrument conditions were as follows: column temperature: 25 ^{o}C; UV detector: 250 nm; pressure limit: min = 0.00 bar, max. = 600.00 bar; sampler draw speed: 200 μl/min; sampler eject speed: 200 μl/min. HPLC method for separation of 4-phenyl-2-butanol was as follows: flow rate: 1.000 mL/min; solvent: 2% isopropyl alcohol, 98% hexane; injection volume: 10.00 μl; stop time: 35.00 min; post time: 10.00 min. Retention times (min) obtained were as follows: (*S*)-4-phenyl-2-butanol (28.02), (*R*)-4-phenyl-2-butanol (18.25).

Typical procedure for hydration of styrene-related substrates 1a-1m:

In a 20 ml glass vial containing $PdCl_2(MeCN)_2$ (1.6 mg, 0.006 mmol), Shvo's catalyst (6.5 mg, 0.006 mmol) and *p*-benzoquinone (0.0973 g, 0.9 mmol). *i*-PrOH (2.17 ml) was added followed by H_2O (0.72 ml) and olefin (0.60 mmol). The mixture was stirred at at 85^{o}C for 36 hours.

Typical procedure for hydration of olefin substrates 2a-2m:

In a 20 ml glass vial containing $PdCl_2(MeCN)_2$ (1.6 mg, 0.006 mmol), Shvo's catalyst (6.5 mg, 0.006 mmol) and *p*-benzoquinone (0.0973 g, 0.9 mmol). *i*-PrOH (2.17 ml) was added followed by H_2O (0.72 ml) and olefin (0.60 mmol). The mixture was stirred at 85 °C for 48 hours.

Typical procedure for hydration of 4-phenyl-1-butene 3f:

In a 20 ml glass vial containing $PdCl_2(MeCN)_2$ (3.2 mg, 0.012 mmol), Shvo's catalyst (6.5 mg, 0.006 mmol) and *p*-benzoquinone (0.0973 g, 0.9 mmol). *i*-PrOH (2.17 ml) was added followed by H_2O (0.72 ml) and 4-phenyl-1-butene (91 µl, 0.60 mmol). The mixture was stirred at 85 °C for 48 hours.

Typical procedure for isolation of alcohols:

Mesitylene (0.216 mmol, 30 µl) was added upon solvent removal under vacuum. A crude ^1H NMR spectrum is collected to determine the selectivity (markovnikov: anti-markovnikov) before the material is being purified by flash column chromatography using ratio ethyl acetate in hexane.

NMR data of products

The ^{1}H NMR data matched that reported in literatures.[3-13]

1-phenylethan-1-ol (Table 4, entry 1): Light yellow oil; Yield: 66%; R_f = 0.51 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (d, J = 6.30 Hz, 3H), 1.87 (br, s, 1H), 4.90 (q, J = 6.60 Hz, 1H), 7.25-7.40 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.8 (C), 128.5 (2CH), 127.5 (CH), 125.4 (CH), 70.4 (CH), 25.1 (CH_3) ppm.

1-(p-tolyl)ethan-1-ol (Table 4, entry 2): Light yellow oil; Yield: 68%; R_f = 0.45 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (d, J = 6.30 Hz, 3H), 1.83 (br, s, 1H), 2.35 (s, 3H), 4.87 (q, J = 6.30 Hz, 1H), 7.13-7.29 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.8 (C), 137.1 (C), 129.1 (2CH), 125.3 (2CH), 70.2 (CH), 25.0 (CH_3), 21.1 (CH_3) ppm.

1-(o-tolyl)ethan-1-ol (Table 4, entry 3): Light yellow oil; Yield: 54%; R_f = 0.49 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (d, J = 6.60 Hz, 3H), 1.71 (br, s, 1H), 2.35 (s, 3H), 5.14 (q, J = 6.30 Hz, 1H), 7.12-7.53 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8 (C), 134.2 (C), 130.4 (CH), 127.2 (CH), 126.4 (CH), 124.4 (CH), 66.8 (CH), 23.9 (CH_3), 18.9 (CH_3) ppm.

1-(m-tolyl)ethan-1-ol (Table 4, entry 4): Light yellow oil; Yield: 59%; R_f = 0.49 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (d, J = 6.30 Hz, 3H), 1.82 (br, s, 1H), 2.37 (s, 3H), 4.87 (q, J = 6.30 Hz, 1H), 7.08-7.27 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.8 (C), 138.1 (C), 128.4 (CH), 128.2 (CH), 126.1 (CH), 122.4 (CH), 70.4 (CH), 25.1 (CH_3), 21.4 (CH_3) ppm.

1-(4-(tert-butyl)phenyl)ethan-1-ol (Table 4, entry 5): Colorless oil; Yield: 58%; R_f = 0.45 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (s, 9H), 1.50 (d, J = 6.60 Hz, 3H), 1.88 (br, s, 1H), 4.87 (q, J = 6.30 Hz, 1H), 7.26-7.40 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2 (C), 150.4 (C), 142.8 (C), 125.4 (2CH), 125.1 (2CH), 70.1 (CH), 31.3 (3 CH_3), 24.9 (CH_3) ppm.

1-(4-chlorophenyl)ethan-1-ol (Table 4, entry 6): Colorless oil; Yield: 83%; R_f = 0.39 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (d, J = 6.30 Hz, 3H), 2.09 (br, s, 1H), 4.85 (q, J = 6.30 Hz, 1H), 7.26-7.33 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2 (C), 133.0 (C), 128.5 (2CH), 126.8 (2CH), 69.7 (CH), 25.2 (CH_3) ppm.

1-(4-methoxyphenyl)ethan-1-ol (Table 4, entry 7): Colorless oil; Yield: 49%; R_f = 0.47 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (d, J = 6.6 Hz, 2H), 3.20 (s, 3H), 3.81 (s, 3H), 4.25 (q, J = 6.6 Hz, 1H), 6.94 (d, J = 7.4 Hz, 2H), 7.15 (d, J = 7.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0 (C), 135.5 (C), 127.4 (CH), 113.7 (2CH), 79.1 (CH), 56.2 (CH), 55.2 (CH_3), 23.7 (CH_3) ppm.

methyl 4-(1-hydroxyethyl)benzoate (Table 4, entry 8): Colorless oil; Yield: 56%; R_f = 0.33 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (d, J = 6.60 Hz, 3H), 2.05 (br, s, 1H), 3.90 (s, 3H), 4.93 (q, J = 6.60 Hz, 1H), 7.41-7.43 (m, 2H), 7.97-8.01 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0 (C), 150.9 (C), 129.8 (2CH), 129.0 (C), 125.3 (2CH), 69.9 (CH), 52.1 (CH_3), 25.3 (CH_3) ppm.

1-(4-(trifluoromethyl)phenyl)ethan-1-ol (Table 4, entry 9): Colorless oil; Yield: 55%; R_f = 0.41 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (d, J = 6.30 Hz, 3H), 1.81 (br, s, 1H), 4.96 (q, J = 6.60 Hz, 1H), 7.47-7.62 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.6 (C), 125.5.0 (C), 125.5 (CH), 125.4 (2CH), 125.4 (2CH), 69.8 (CH), 25.4 (CH_3) ppm.

4-(1-hydroxyethyl)benzoic acid (Table 4, entry 10): White solid; Yield: 33%; R_f = 0.11 (Ethyl acetate/hexane 2:1); ^{1}H NMR (300 MHz, MeOD): δ 1.44 (d, J = 6.6 Hz, 3H), 7.47 (d, J = 20 Hz, 2H), 7.99 (d, J = 20 Hz, 2H) ppm; ^{13}C NMR (75 MHz, MeOD): δ 169.9 (C), 153.0 (C), 130.8 (2CH), 126.5 (C), 70.4 (CH), 25.6 (CH_3) ppm.

1-(4-nitrophenyl)ethan-1-ol (Table 4, entry 11, 3k): Light yellow oil; Yield: 33%; R_f = 0.50 (Ethyl acetate/hexane 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (d, J = 6.6 Hz, 3H), 2.05 (br, s, 1H), 5.02 (q, J = 6.6 Hz, 1H), 7.54 (d, J = 8.7 Hz, 2H), 8.20 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1 (C), 147.2 (C), 126.1 (2CH), 123.8 (2CH), 69.5 (CH), 25.4 (CH_3) ppm.

2-(4-nitrophenyl)ethan-1-ol (Table 4, entry 11, 4k): Yellow oil; Yield: 51%; R_f = 0.37 (Ethyl acetate/hexane 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.98 (t, J = 6.3 Hz, 2H), 3.92 (t, J = 6.3 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7 (C), 129.8 (2CH), 123.7 (2CH), 62.9 (CH), 38.8 (CH_3) ppm.

1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol (Table 4, entry 12, 3l): White solid; Yield: 24%; R_f = 0.46 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (d, J = 6.6 Hz, 3H),

2.1 (br, s, 1H), 5.04 (q, J = 6.6 Hz, 1H), 7.78-7.84 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.2 (C), 131.9 (C), 125.6 (CH), 125.1 (CH), 121.2 (C), 69.2 (CH), 25.6 (CH_3) ppm.

2-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol (Table 4, entry 12, 4l): White solid; Yield: 56%; R_f = 0.24 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.99 (t, J = 6.3 Hz, 2H), 3.93 (t, J = 6.3 Hz, 2H), 7.71 (s, 2H), 7.75 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.4, 131.6 (q, J = 32.9 Hz), 129.2 (d, J = 2.7 Hz), 125.2, 121.5, 120.4-120.6 (m), 62.7, 38.5 ppm.

1-(naphthalen-2-yl)ethan-1-ol (Table 4, entry 13): White solid; Yield: 72%; R_f = 0.36 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58 (d, J = 6.30 Hz, 3H), 2.11 (br, s, 1H), 5.05 (q, J = 6.30 Hz, 1H), 7.45-7.85 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.1 (C), 133.3 (C), 132.9 (C), 128.2 (CH), 127.9 (CH), 125.6 (CH), 126.1 (CH), 125.7 (CH), 123.8 (CH), 123.8 (CH), 70.4 (CH), 25.1 (CH_3) ppm.

octan-2-ol (Table 5, entry 1): Colorless oil; Yield: 59%; R_f = 0.46 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.46 (t, J = 6.30 Hz, 3H), 1.17 (d, J = 6.3 Hz, 3H), 1.22-1.38 (m, 8H), 1.40-1.44 (m, 2H), 3.72-3.89 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.1 (CH), 39.4 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 25.8 (CH_3), 23.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3) ppm.

dodecan-2-ol (Table 5, entry 2): Colorless oil; Yield: 63%; R_f = 0.46 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6.60 Hz, 2H), 1.17 (d, J = 6.00 Hz, 3H), 1.24-1.51 (m, 18H), 3.74-3.80 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.1 (CH), 39.3 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.6 ($3CH_2$), 29.3 (CH_2), 25.8 (CH_2), 23.4 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm.

5-hydroxyhexanoic acid (Table 5, entry 3): Colorless oil; NMR yield: 59%.

ethyl 6-hydroxyheptanoate (Table 5, entry 4): Colorless oil; Yield: 85%; R_f = 0.17 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (d, J = 6.30 Hz, 3H), 1.40 (t, J = 2.7 Hz, 3H), 1.42-1.47 (m, 4H), 1.60-1.66 (m, 2H), 2.29 (t, J = 7.5 Hz, 2H), 3.75-3.81 (m, 1H), 4.10 (dd, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.7 (C), 67.7 (CH), 60.2 (CH_2), 38.8 (CH_2), 34.2 (CH_2), 25.2 (CH_3), 24.8 (CH_2), 23.4 (CH_2), 14.2 (CH_3) ppm.

8-hydroxynonyl acetate (Table 5, entry 5): Colorless oil; Yield: 82%; R_f = 0.14 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6.9Hz, 2H), 1.17 (d, J = 6.30 Hz, 3H), 1.24-1.62 (m, 12H), 3.73-3.82 (m, 1H), 4.04 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3 (C), 68.1 (CH), 64.6 (CH_2), 39.2 (CH_2), 29.5 (CH_2), 29.2 (CH_2), 28.5 (CH_2), 25.8 (CH_2), 25.6 (CH_2), 23.5 (CH_2), 14.2 (CH_3) ppm.

but-3-en-1-ylbenzene (Table 5, entry 6): Colorless oil; Yield: 64%; R_f = 0.36 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (d, J = 6.60 Hz, 3H), 1.74-1.83 (m, 2H), 2.63-2.82 (m, 2H), 3.79-3.89 (m, 1H), 7.17 -7.33 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0 (C), 128.3 (4CH), 125.8 (CH), 67.43 (CH), 40.78 (CH_2), 32.1 (CH_2), 23.5 (CH_3) ppm.

2-(cyclohex-3-en-1-yl)ethan-1-ol (Table 5, entry 7): Colorless oil; Yield: 42%; R_f = 0.24 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26-1.33 (m, 2H), 1.53-1.59 (m, 2H), 1.67-1.72 (m, 3H), 2.02-2.14 (m, 2H), 3.72 (t, J = 6.9 Hz, 2H), 5.64-5.66 (m, 2H) ppm; ^{13}C NMR (75

MHz, $CDCl_3$): δ 127.0 (CH), 126.2 (CH), 60.8 (CH_2), 39.5 (CH), 31.8 (CH_2), 30.1 (CH_2), 28.8 (CH_2), 25.0 (CH_2) ppm.

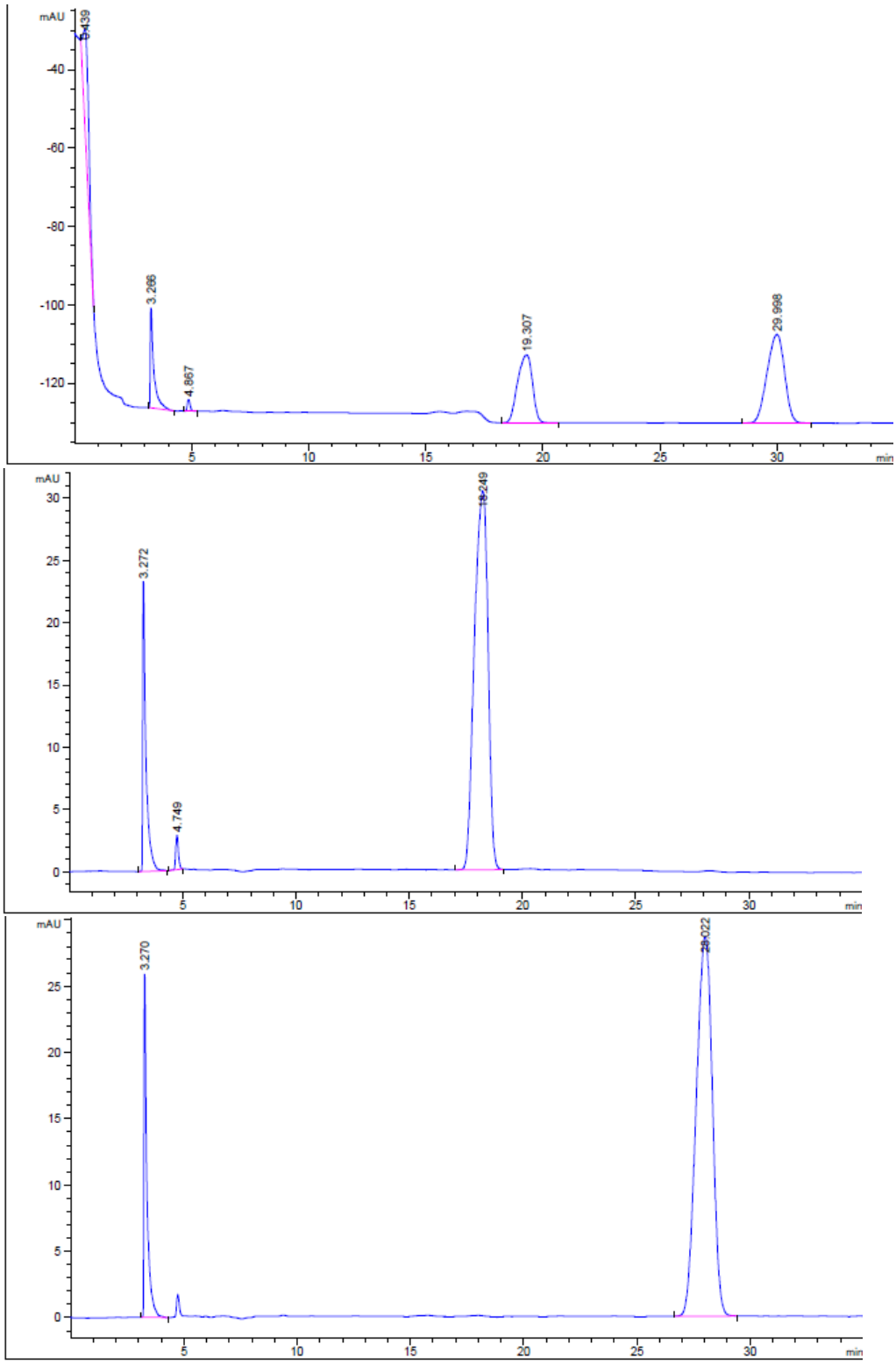
6-chlorohexan-2-one (Table 5, entry 8): Colorless oil; Yield: 40%; R_f = 0.46 (Ethyl acetate/hexane 1:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67-1.79 (m, 4H), 2.13 (s, 3H), 3.52 (t, J = 6.30 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.3 (C), 44.6 (CH_2), 42.6 (CH_2), 31.8 (CH_2), 29.8 (CH_2), 21.0 (CH_3) ppm.

butane-1,3-diol (Table 5, entry 9): Light yellow oil; Yield: 52%; R_f = 0.12 (Ethyl acetate/hexane 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (d, J = 6.30 Hz, 3H), 1.68 (q, J = 6.6 Hz, 2H), 3.80 (t, J = 6.30 Hz, 2H), 4.03-4.09 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.2 (CH), 61.6 (CH_2), 39.9 (CH_2), 23.7 (CH_3) ppm.

hexane-1,5-diol (Table 5, entry 10): Light yellow oil; Yield: 58%; R_f = 0.10 (Ethyl acetate/hexane 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (d, J = 6.30 Hz, 3H), 1.39-1.48 (m, 4H), 1.50-1.60 (m, 2H), 2.70 (br, s, 2H), 3.62 (t, J = 6.30 Hz, 2H), 3.76-3.82 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 76.8 (CH), 62.4 (CH_2), 38.6 (CH_2), 32.3 (CH_2), 23.4 (CH_2), 21.8 (CH_3) ppm.

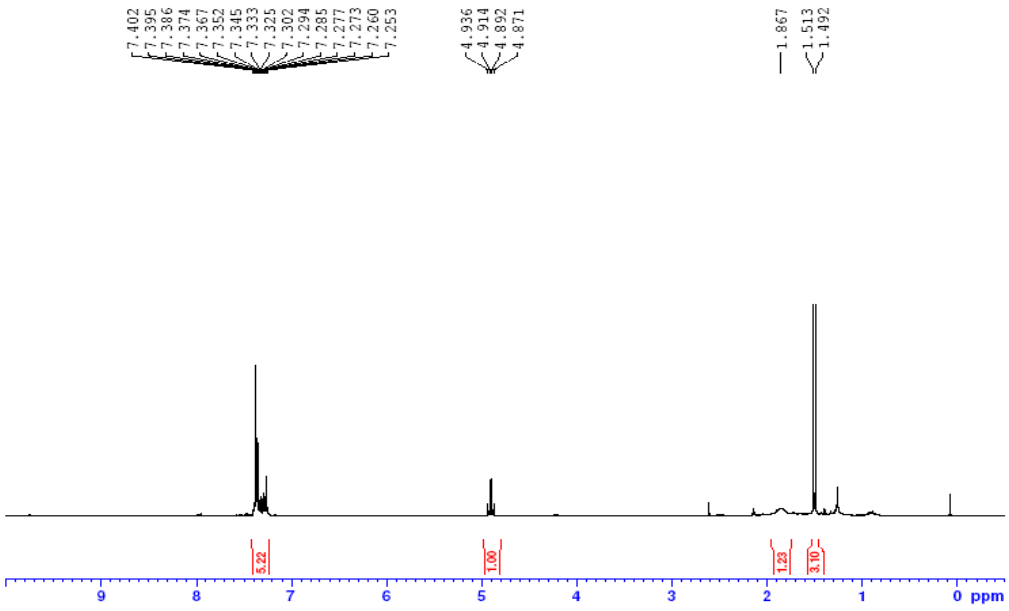
2-(2-hydroxypropyl)cyclohexan-1-ol (Table 5, entry 11): Light yellow oil; Yield: 34%; R_f = 0.27 (Ethyl acetate/hexane 2:1).

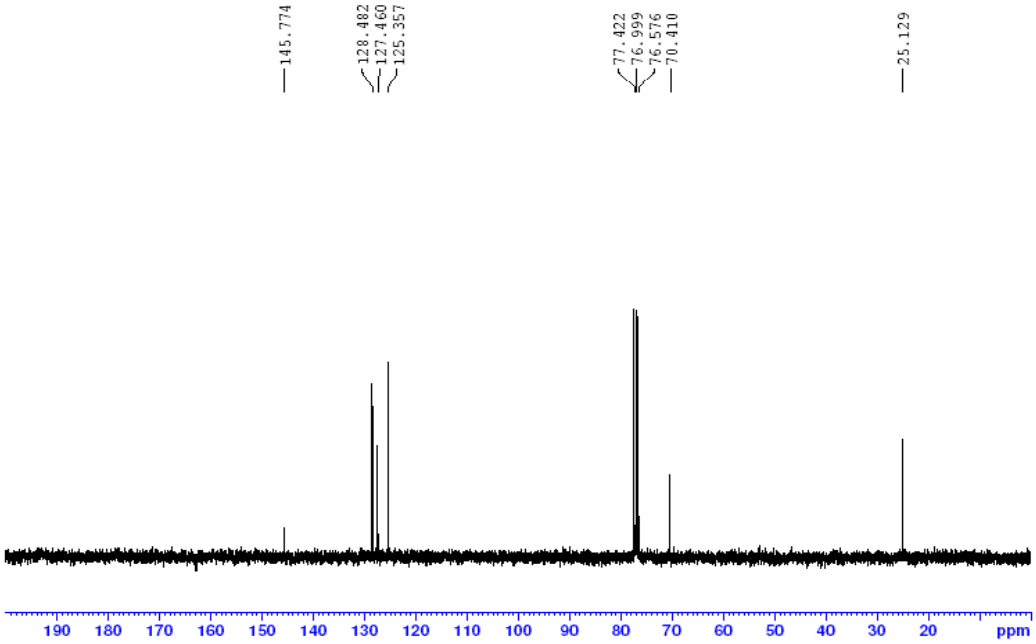
HPLC Chromatogram of isolated 4-phenyl-2-butanol (top); (*S*)-4-phenyl-2-butanol authentic sample (28.02) (bottom) and (*R*)-4-phenyl-2-butanol authentic sample (18.25) (middle):



NMR spectrum of products

3a





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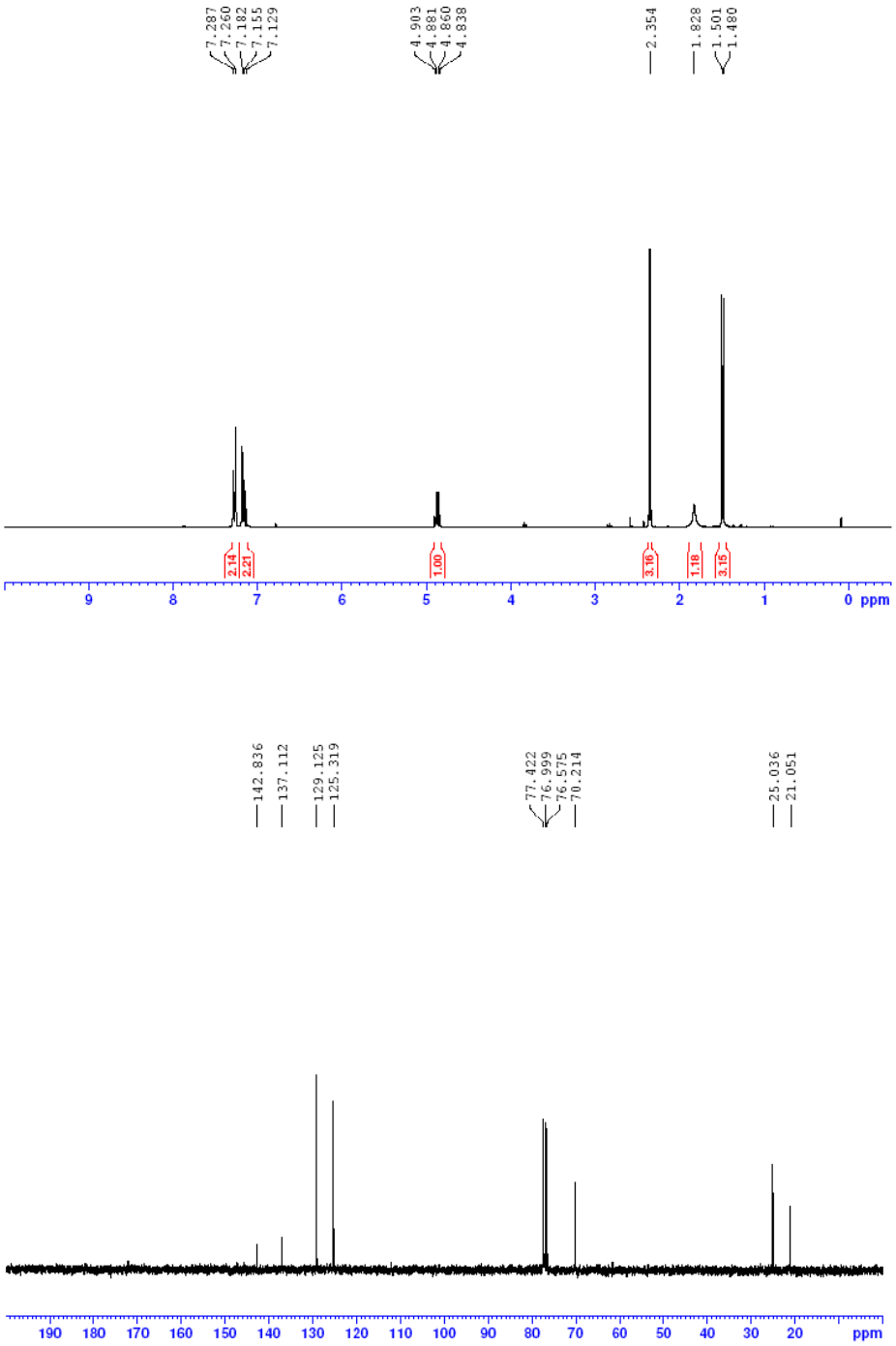
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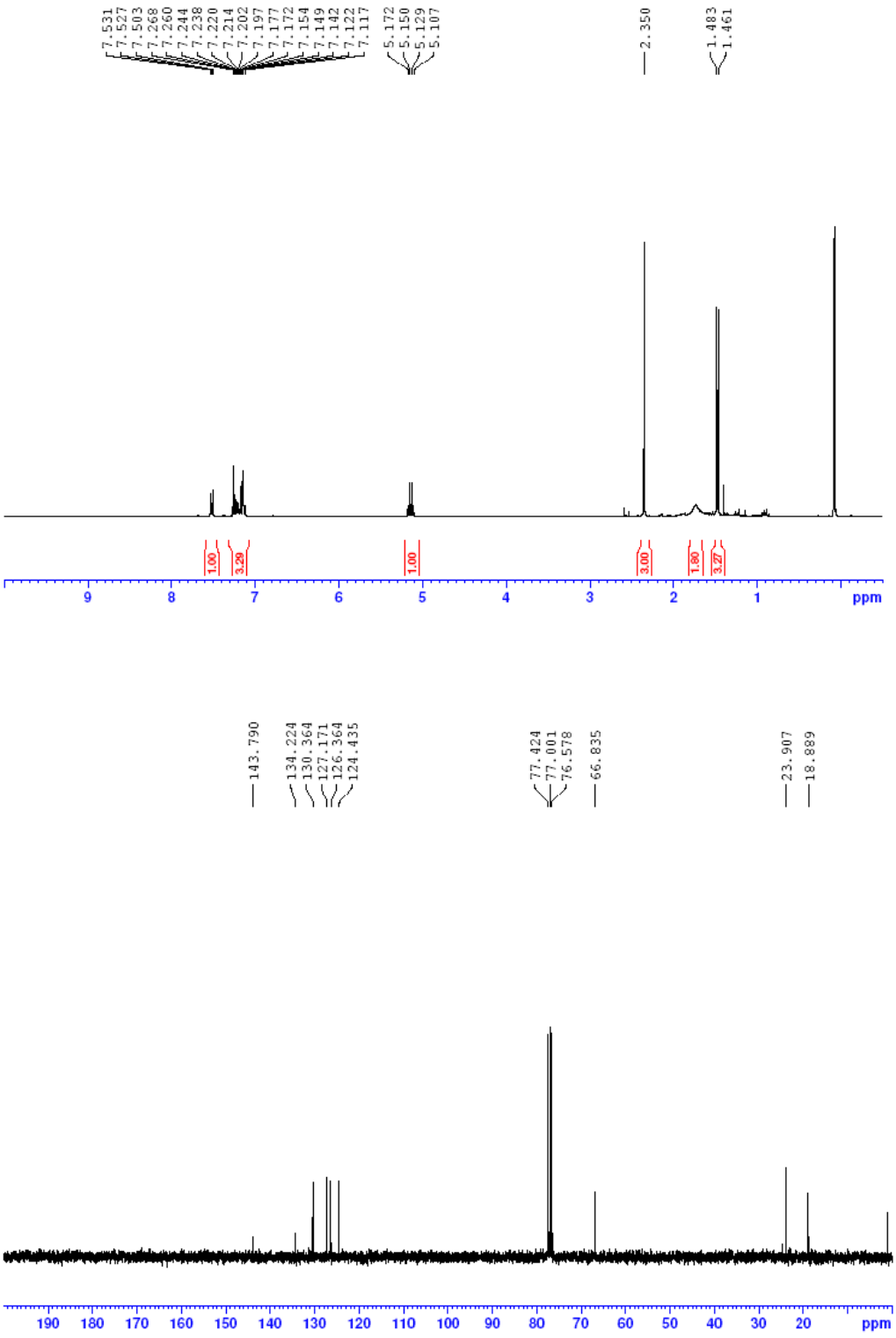
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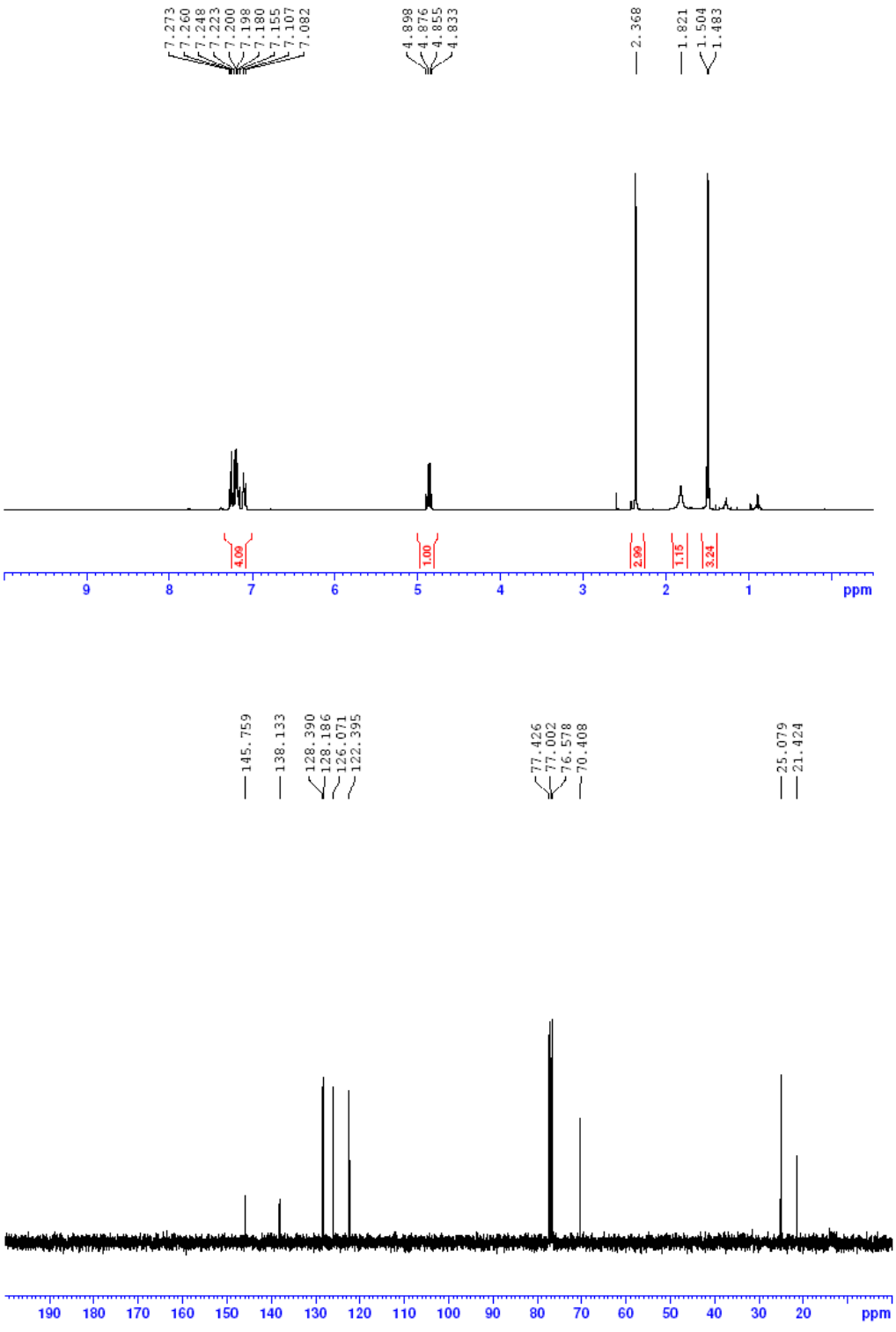
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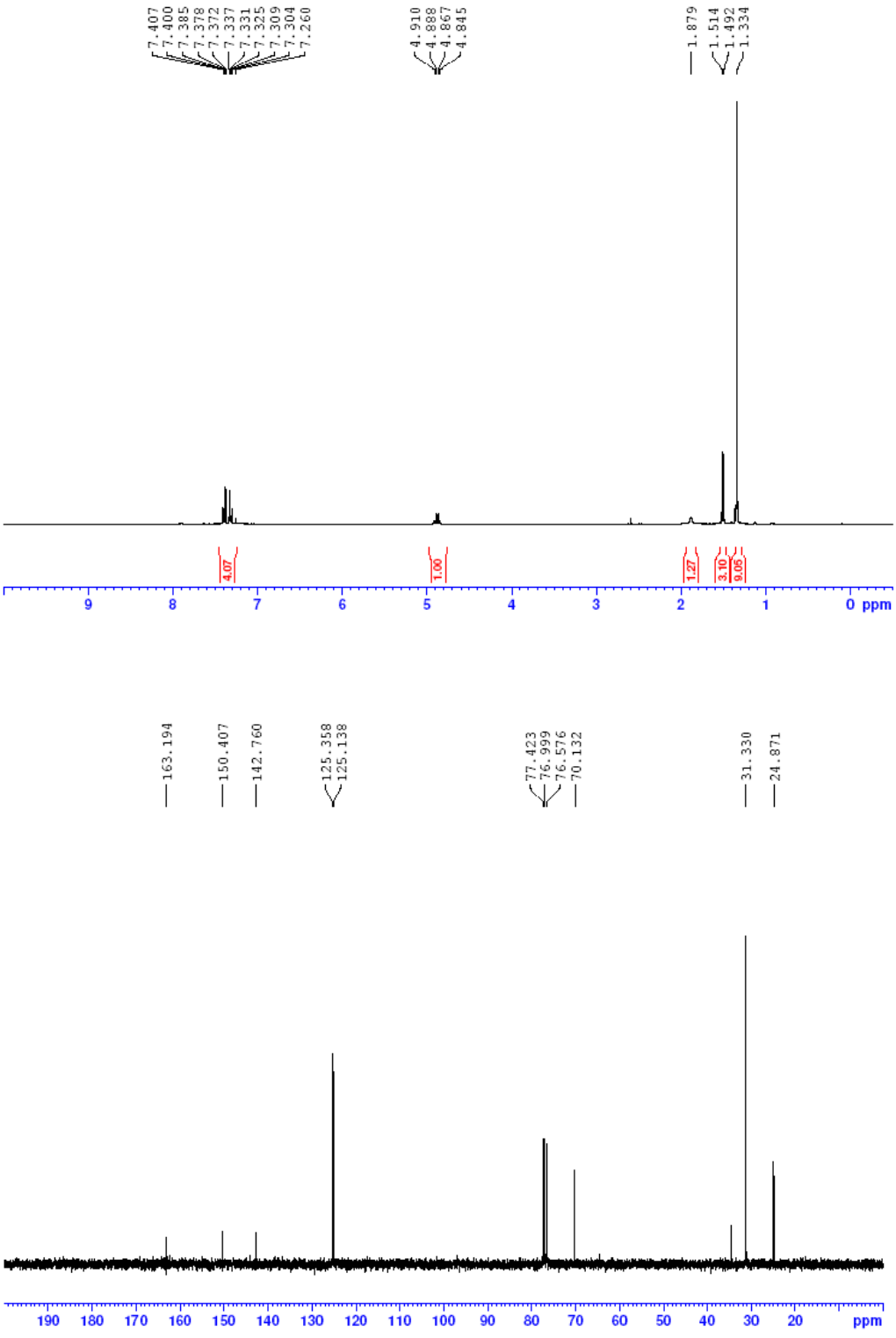
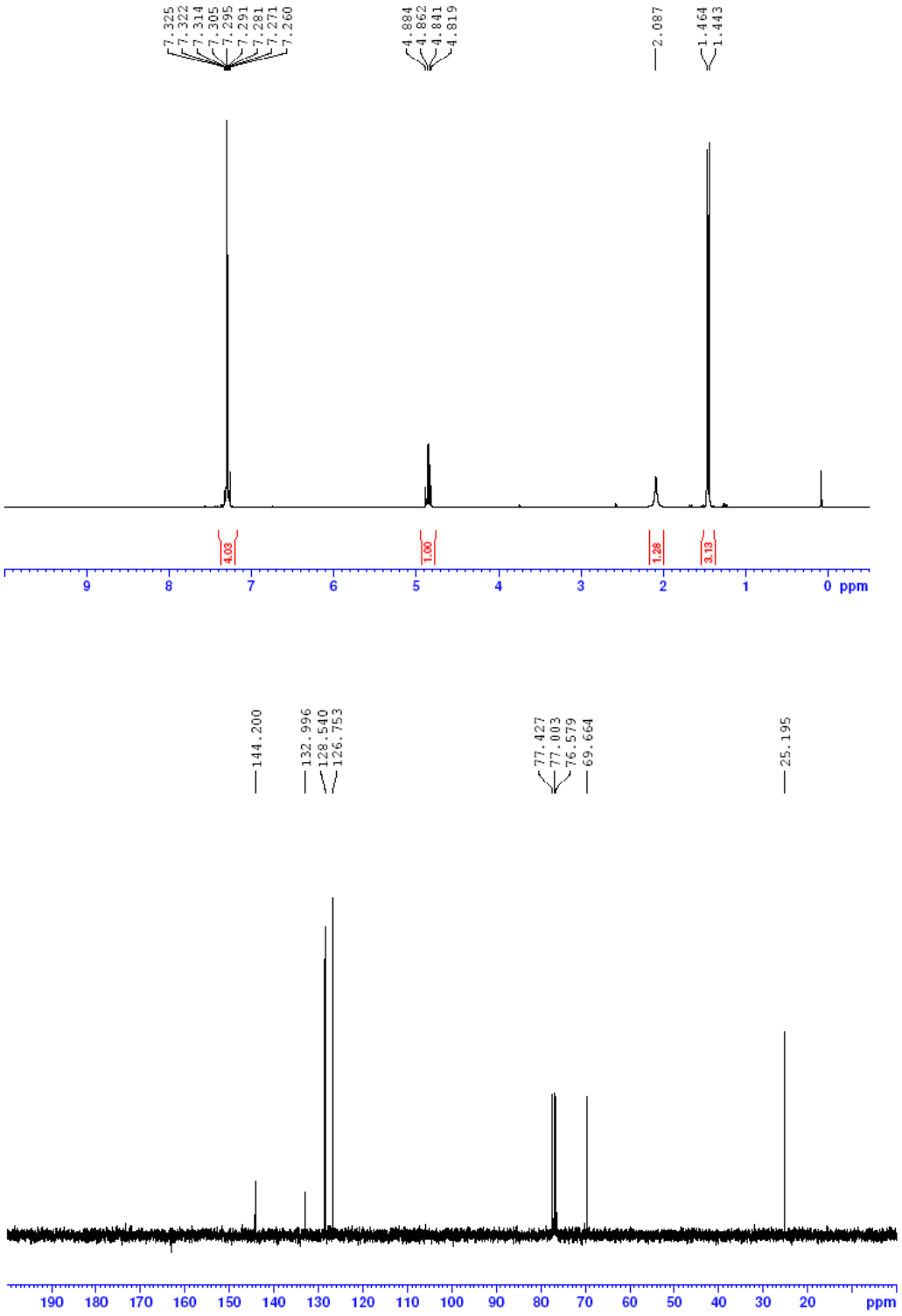
128.186
126.071
122.395
77.426
77.002
76.578
70.408
25.079
21.424
ppm

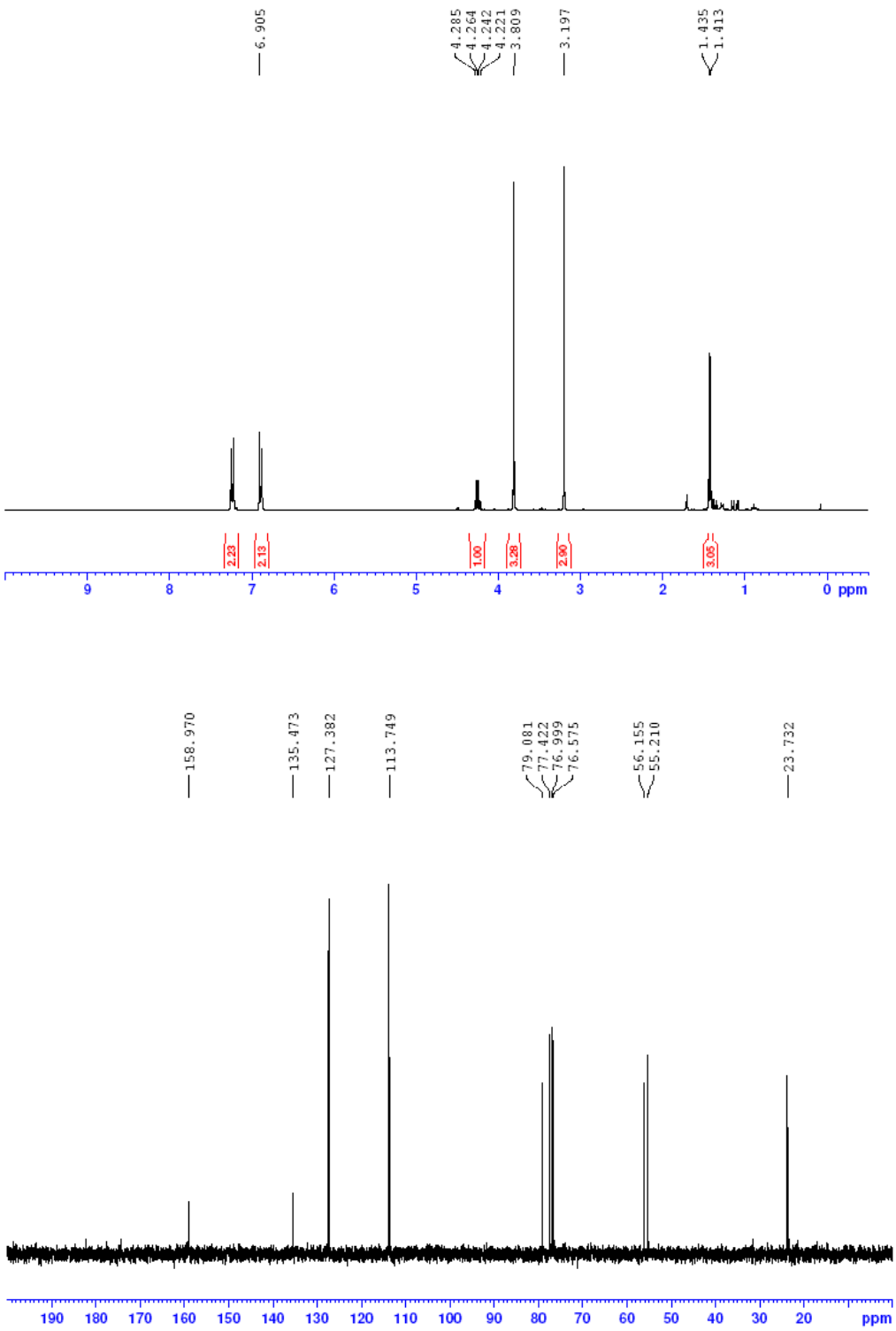
3e


7.407
7.400
7.385
7.378
7.372
7.337
7.331
7.325
7.309
7.304
7.260
4.910
4.888
4.867
4.845
1.879
1.514
1.492
1.334
4.07
1.00
1.27
3.10
9.05
9
8
7
6
5
4
3
2
1
0 ppm
163.194
150.407
142.760
125.358
125.138
77.423
76.999
76.576
70.132
31.330
24.871
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

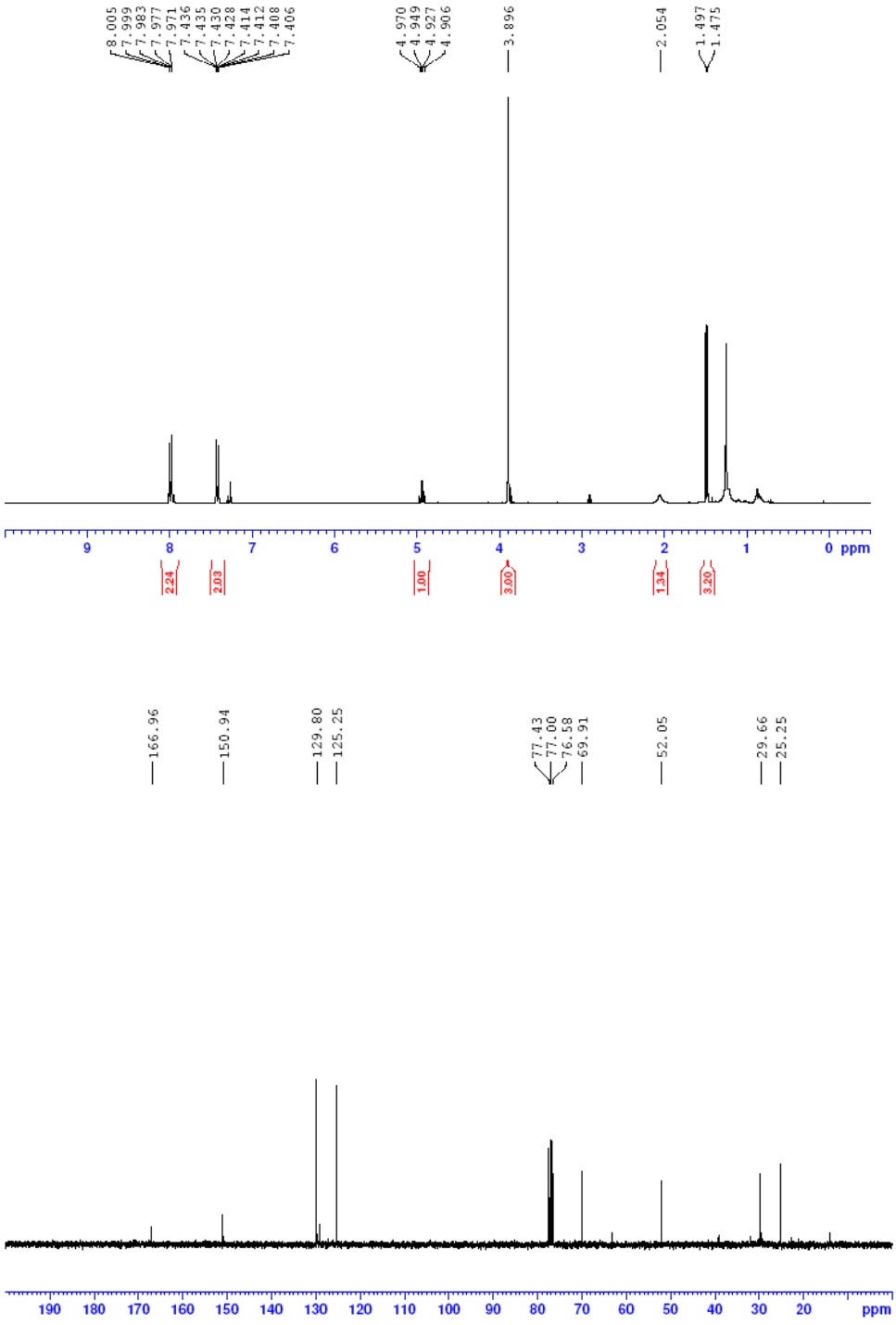
3f


7.325
7.322
7.314
7.305
7.295
7.291
7.281
7.271
7.260
4.884
4.862
4.841
4.819
2.087
1.464
1.443
4.03
1.00
1.08
3.13
9
8
7
6
5
4
3
2
1
0 ppm
144.200
132.996
128.540
126.753
77.427
77.003
76.579
69.664
25.195
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

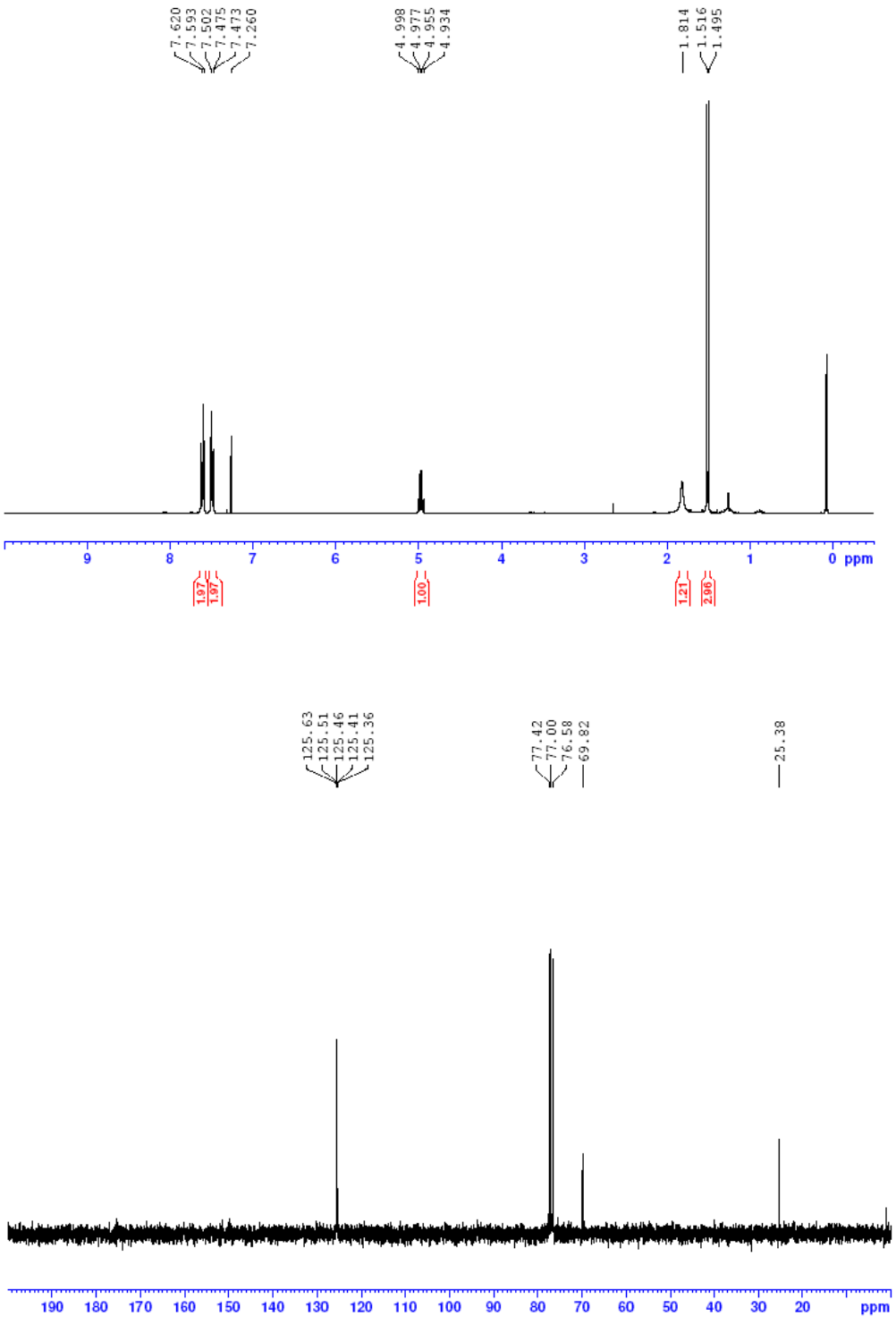
3g


6.905
4.285
4.264
4.242
4.221
3.809
3.197
1.435
1.413
2.23
2.13
1.00
3.28
2.00
3.05
9
8
7
6
5
4
3
2
1
0 ppm
158.970
135.473
127.382
113.749
79.081
77.422
76.999
76.575
56.155
55.210
23.732
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

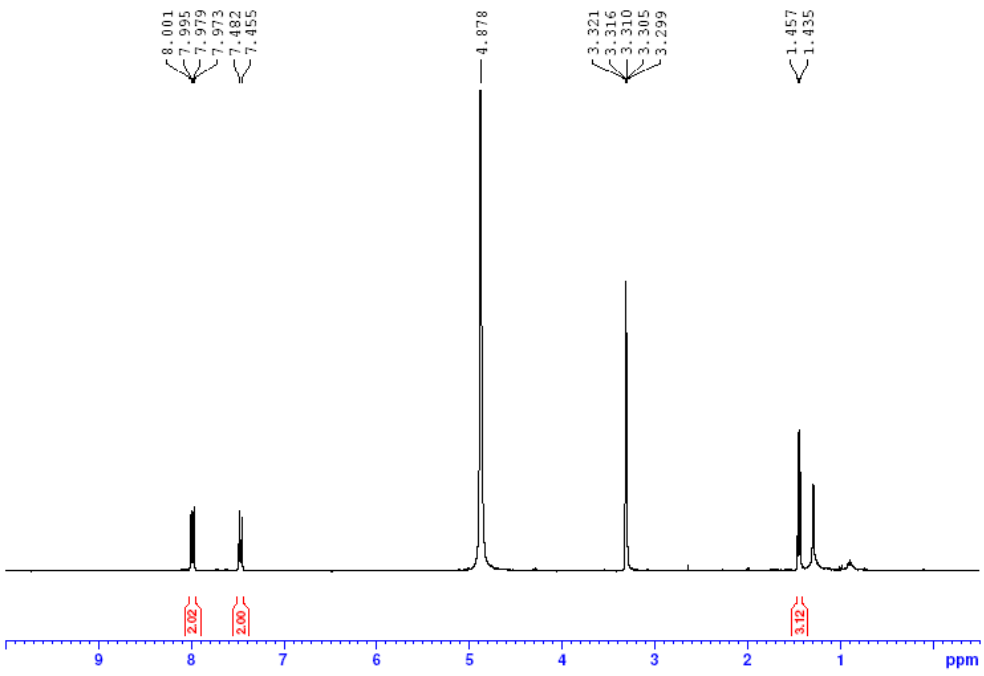
3h

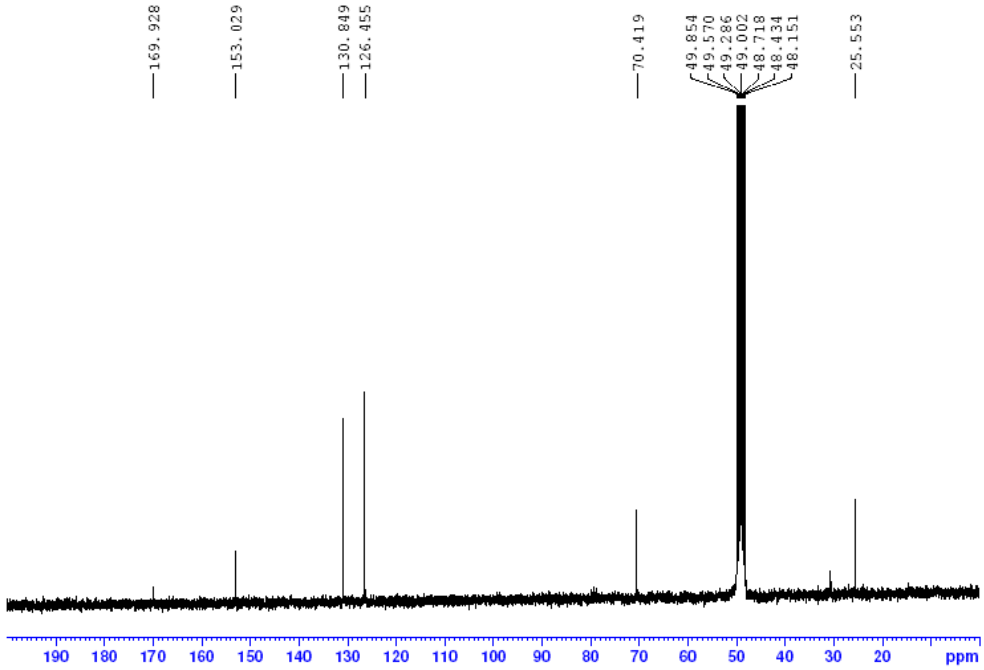

8.005
7.999
7.983
7.977
7.971
7.436
7.435
7.430
7.428
7.414
7.412
7.408
7.406
4.970
4.949
4.927
4.906
3.896
2.054
1.497
1.475
9
8
7
6
5
4
3
2
1
0 ppm
2.24
2.03
1.00
3.00
1.34
3.20
166.96
150.94
129.80
125.25
77.43
77.00
76.58
69.91
52.05
29.66
25.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3i

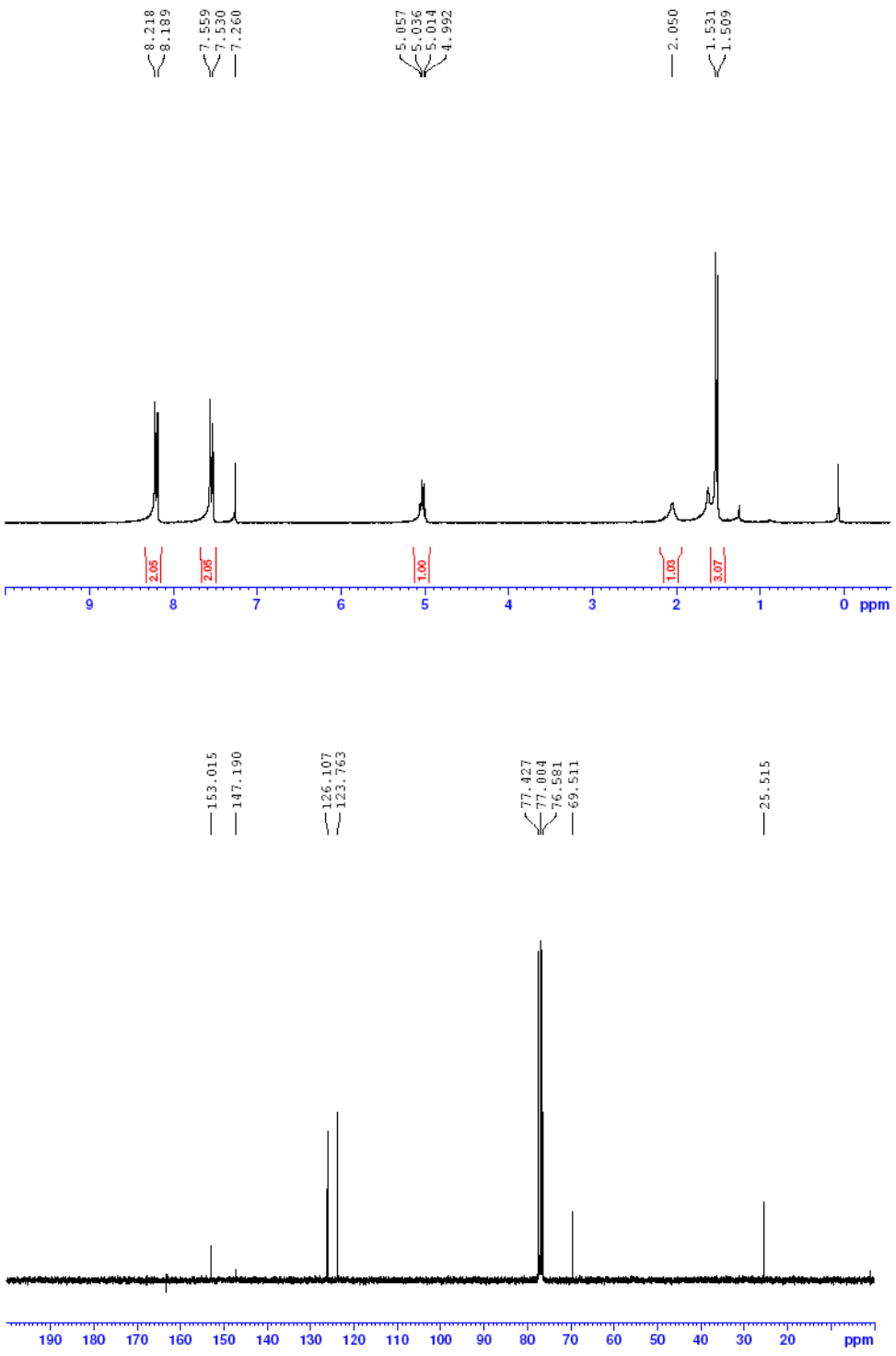

7.620
7.593
7.502
7.475
7.473
7.260
4.998
4.977
4.955
4.934
1.814
1.516
1.495
9
8
7
6
5
4
3
2
1
0 ppm
1.97
1.97
1.00
1.21
2.96
125.63
125.51
125.46
125.41
125.36
77.42
77.00
76.58
69.82
25.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3j

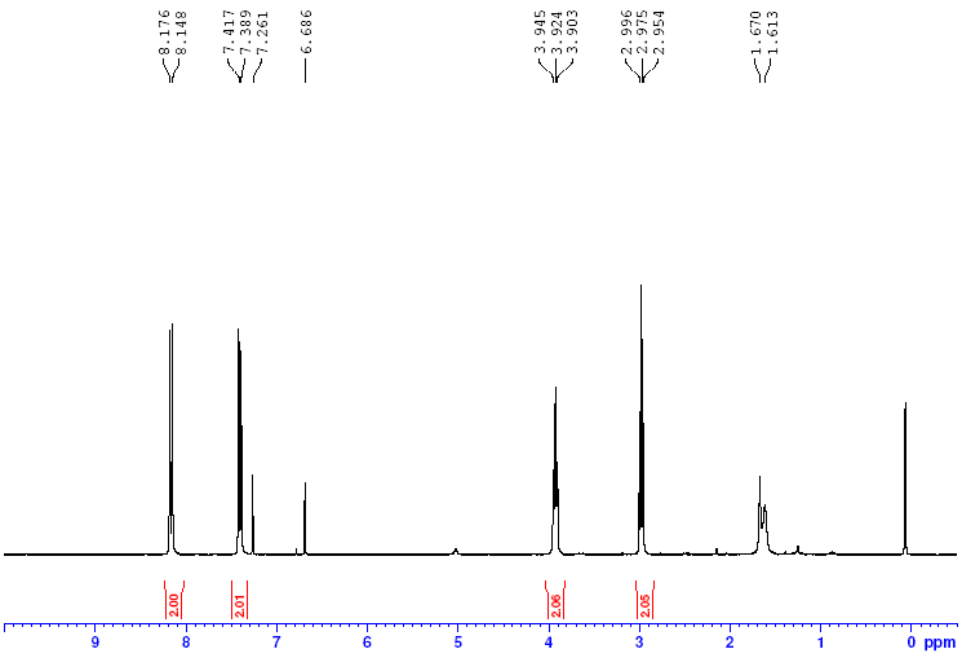

8.001
7.995
7.979
7.973
7.482
7.455
4.878
3.321
3.316
3.310
3.305
3.299
1.457
1.435
2.02
2.00
3.12
9
8
7
6
5
4
3
2
1
ppm

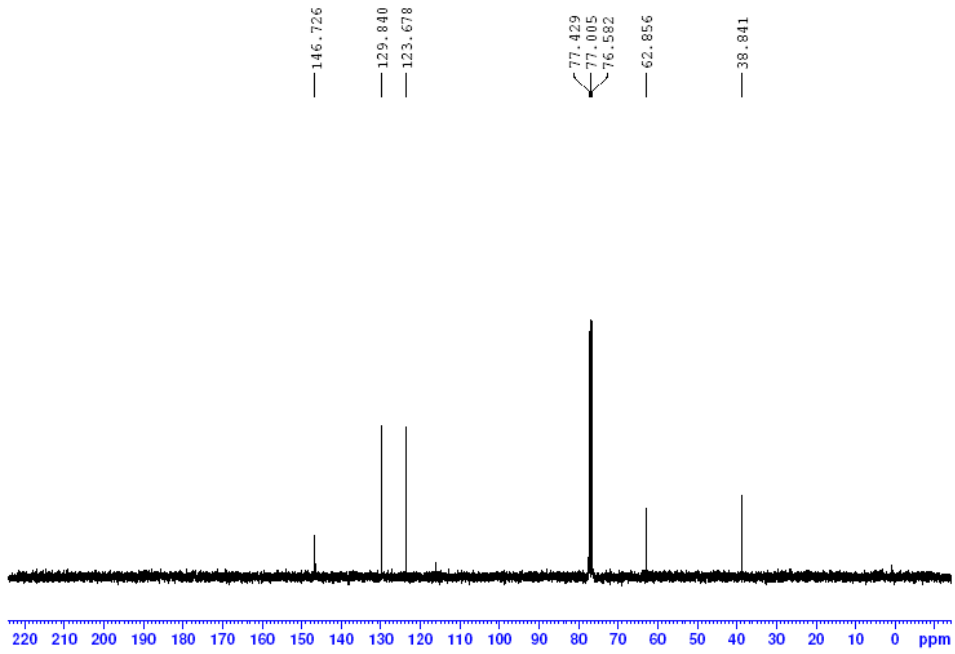

169.928
153.029
130.849
126.455
70.419
49.854
49.570
49.286
49.002
48.718
48.434
48.151
25.553
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3k

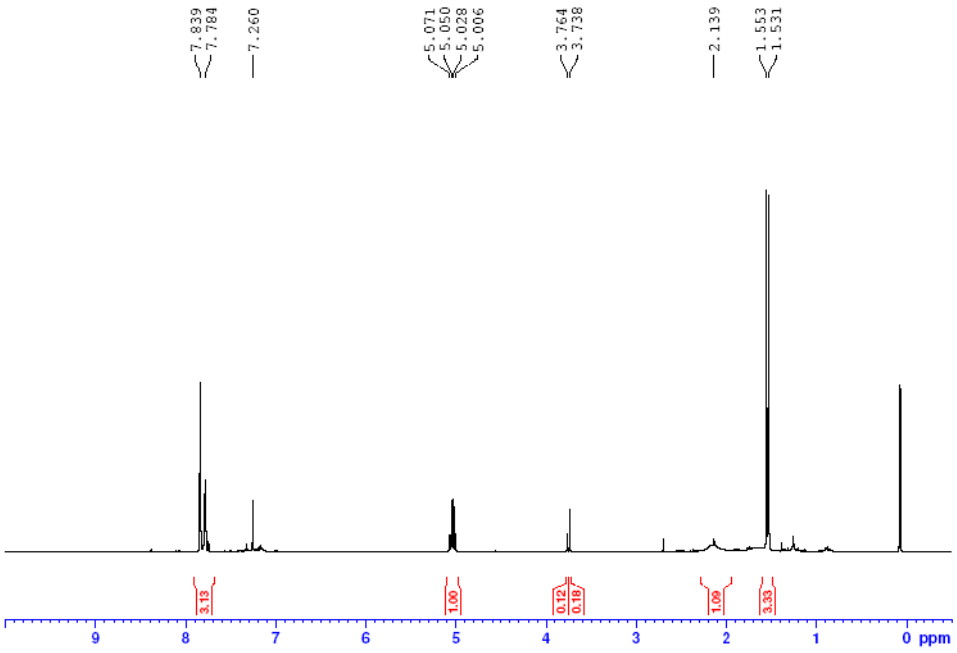

8.218
8.189
7.559
7.530
7.260
5.057
5.036
5.014
4.992
2.050
1.531
1.509
2.05
2.06
1.00
1.08
3.07
9
8
7
6
5
4
3
2
1
0 ppm
153.015
147.190
126.107
123.763
77.427
77.004
76.581
69.511
25.515
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

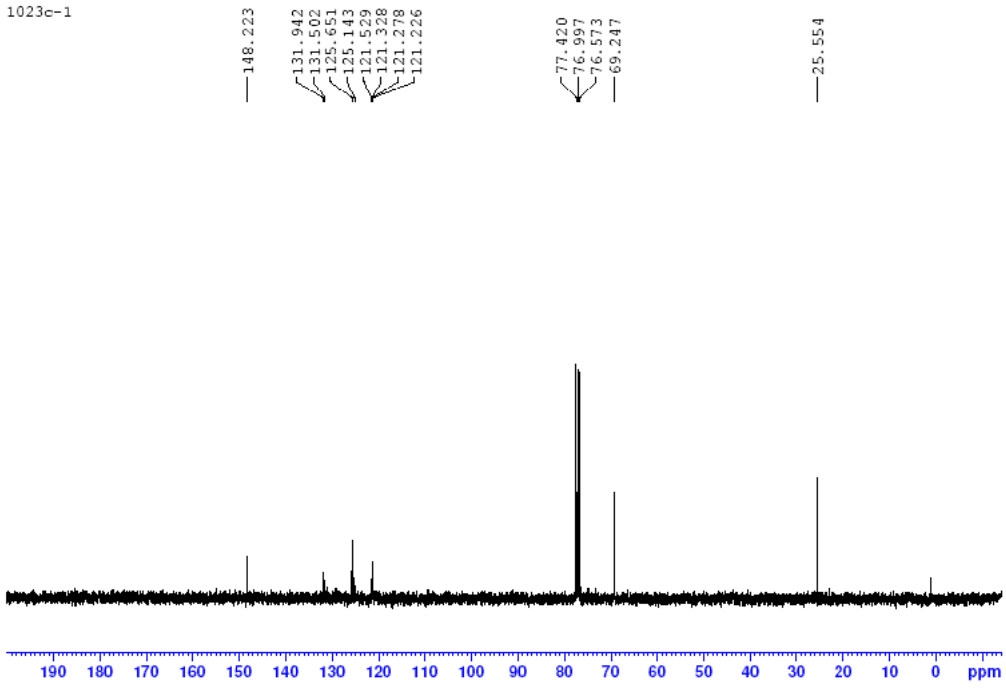
4k


8.176
8.148
7.417
7.389
7.261
6.686
3.945
3.924
3.903
2.996
2.975
2.954
1.670
1.613
2.00
2.01
2.06
2.05
9
8
7
6
5
4
3
2
1
0 ppm

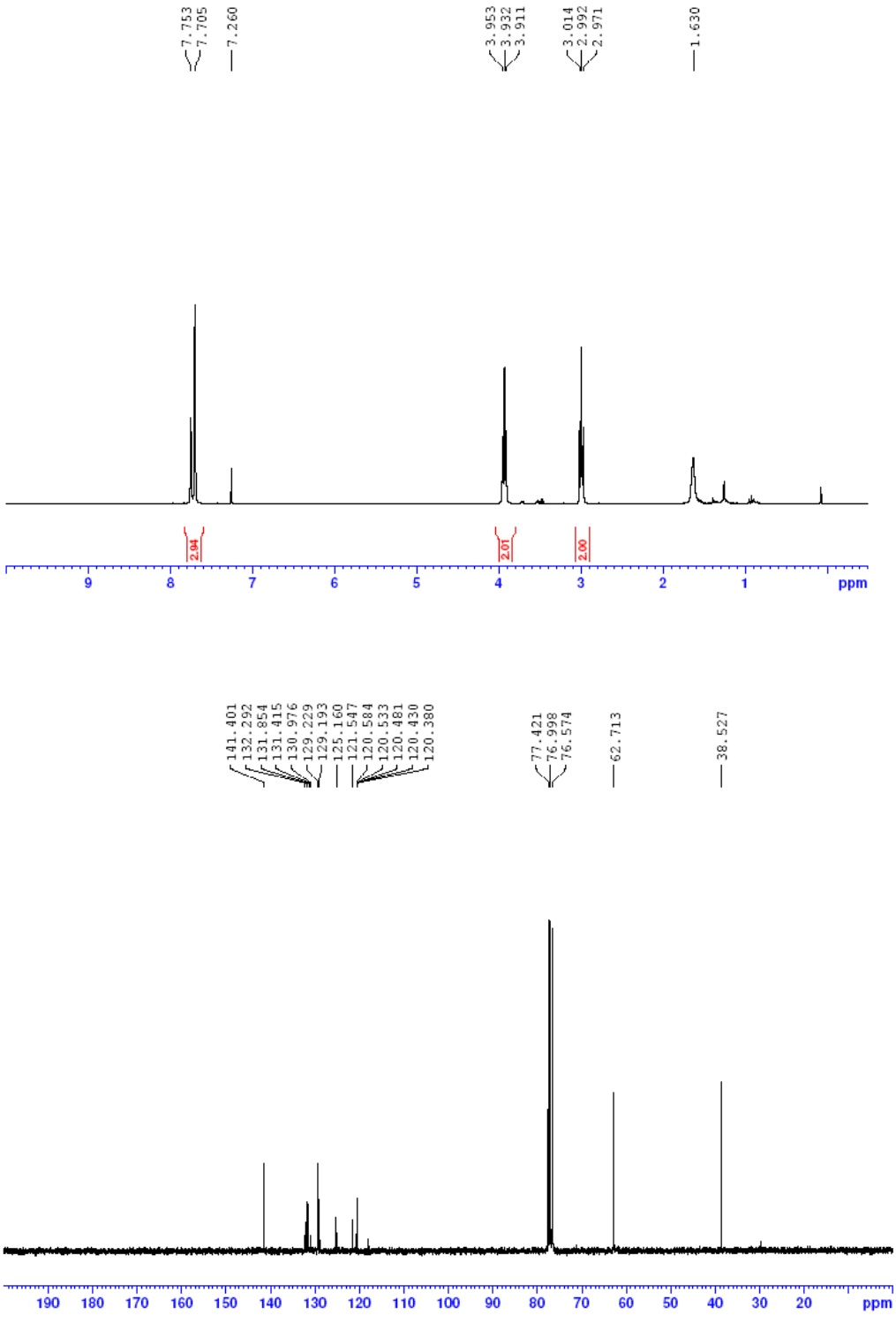

146.726
129.840
123.678
77.429
77.005
76.582
62.856
38.841
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3l

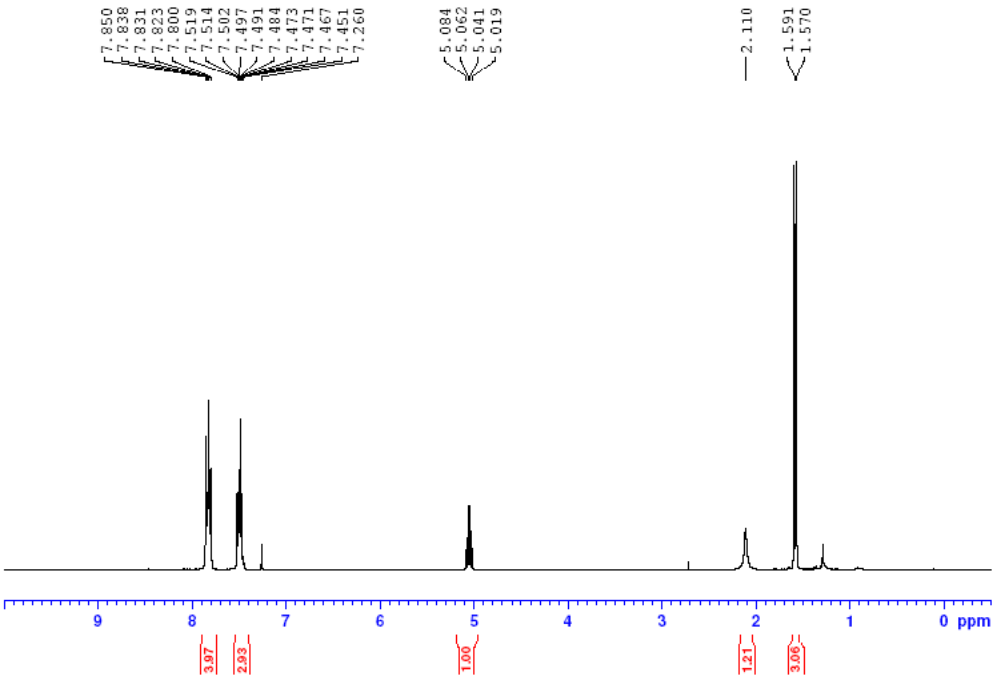

7.839
7.784
7.260
5.071
5.050
5.028
5.006
3.764
3.738
2.139
1.553
1.531
3.13
1.00
0.12
0.18
1.09
3.33
9
8
7
6
5
4
3
2
1
0 ppm

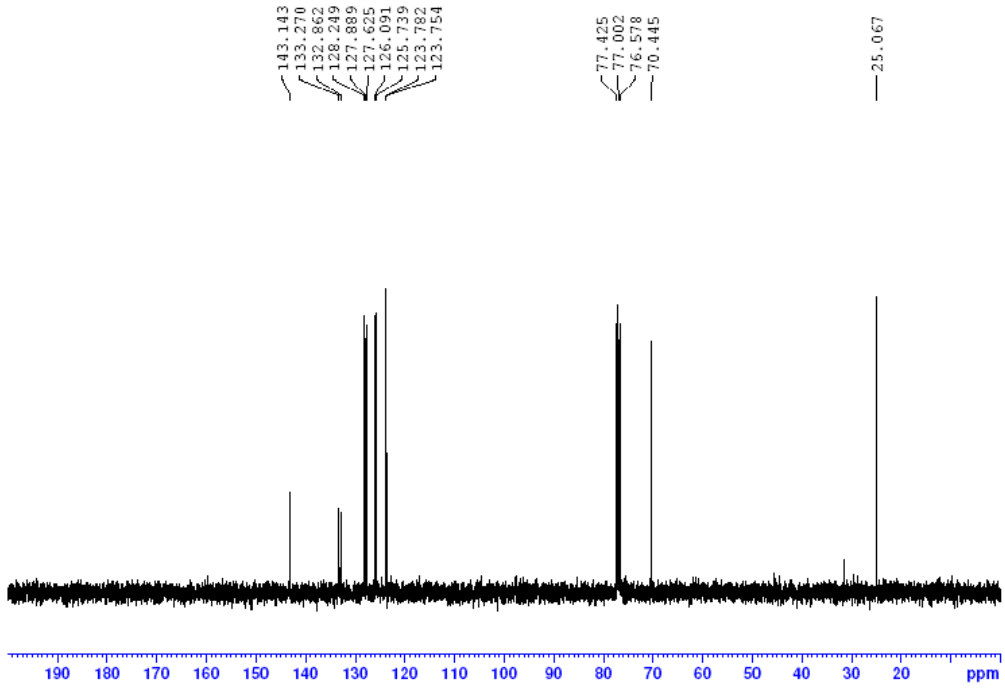

1023c-1
148.223
131.942
131.502
125.651
125.143
121.529
121.328
121.278
121.226
77.420
76.997
76.573
69.247
25.554
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4l

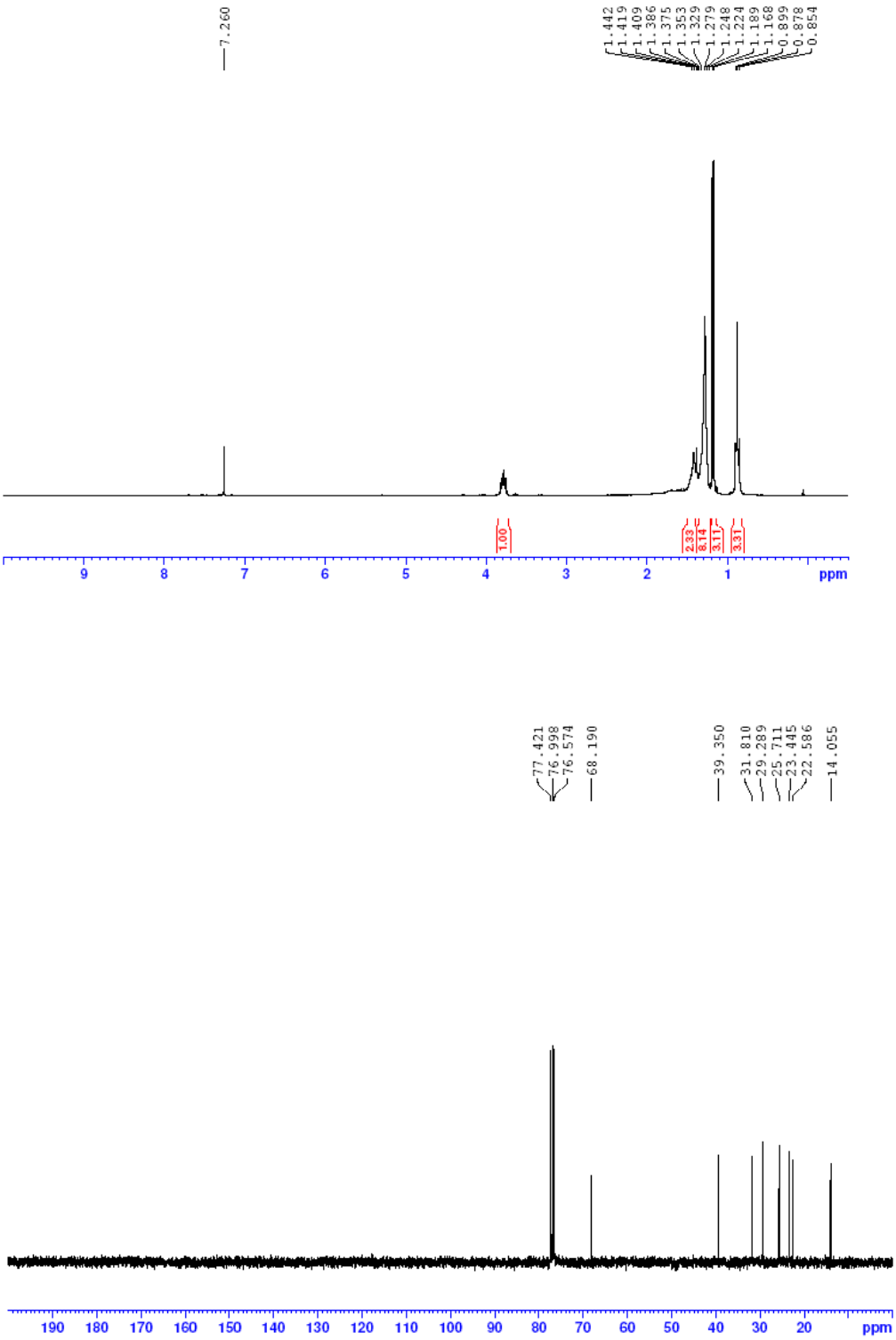

7.753
7.705
7.260
3.953
3.932
3.911
3.014
2.992
2.971
1.630
2.04
2.01
2.00
9
8
7
6
5
4
3
2
1
ppm
141.401
132.292
131.854
131.415
130.976
129.229
129.193
125.160
121.547
120.584
120.533
120.481
120.430
120.380
77.421
76.998
76.574
62.713
38.527
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3m

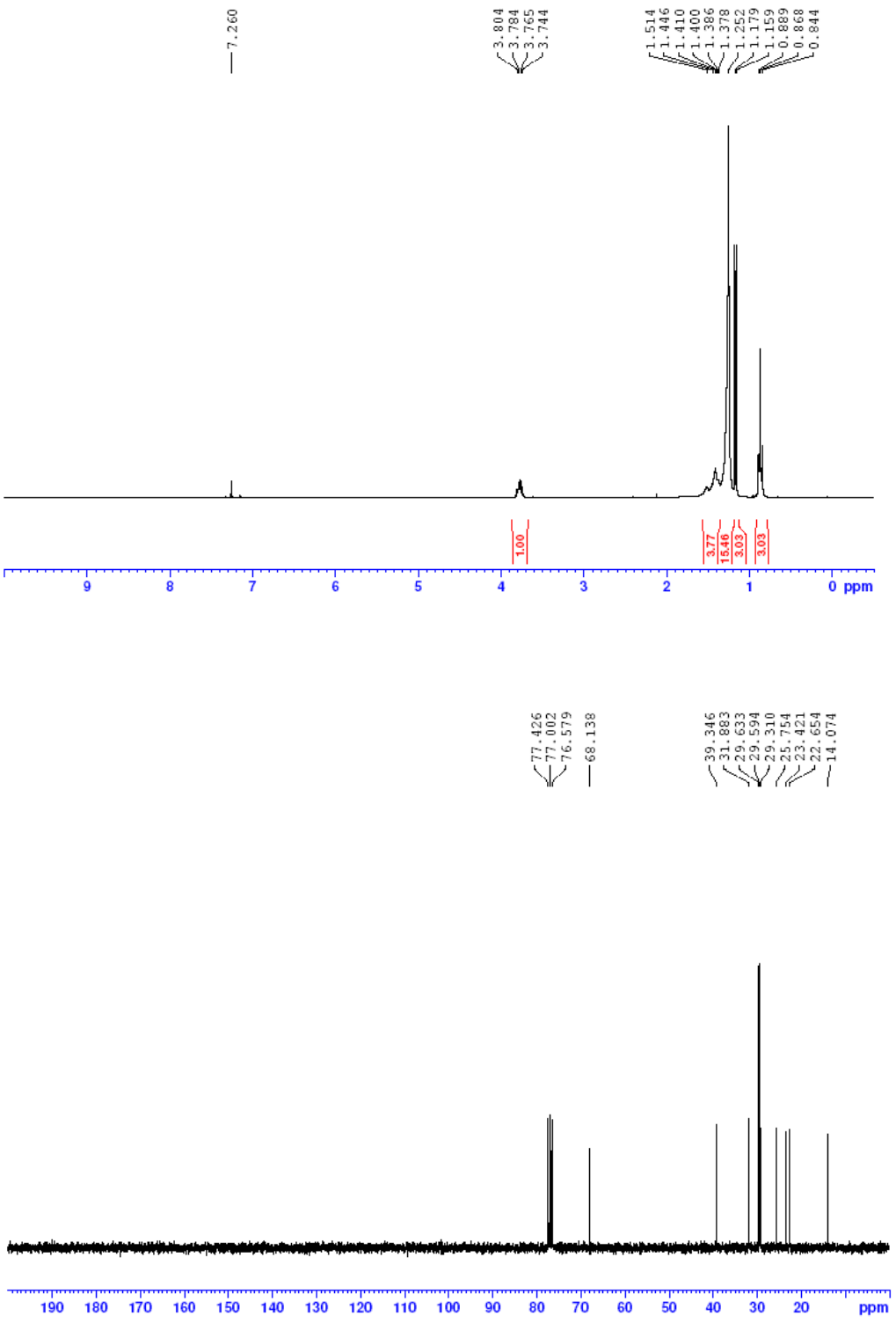

7.850
7.838
7.831
7.823
7.800
7.519
7.514
7.502
7.497
7.491
7.484
7.473
7.471
7.467
7.451
7.260
5.084
5.062
5.041
5.019
2.110
1.591
1.570
9
8
7
6
5
4
3
2
1
0 ppm
3.97
2.93
1.00
1.21
3.06


143.143
133.270
132.862
128.249
127.889
127.625
126.091
125.739
123.782
123.754
77.425
77.002
76.578
70.445
25.067
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

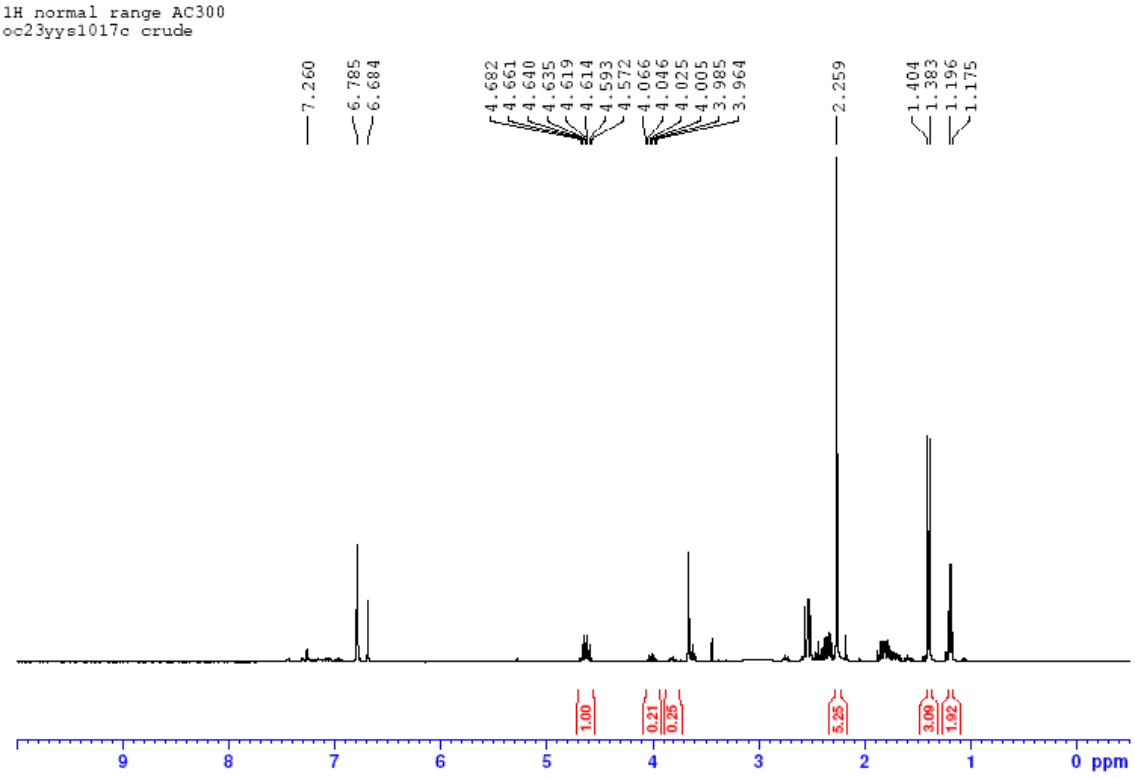
3aa


7.260
1.442
1.419
1.409
1.386
1.375
1.353
1.329
1.279
1.248
1.224
1.189
1.168
0.899
0.878
0.854
1.00
2.33
8.14
3.11
3.31
9
8
7
6
5
4
3
2
1
ppm
77.421
76.998
76.574
68.190
39.350
31.810
29.289
25.711
23.445
22.586
14.055
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

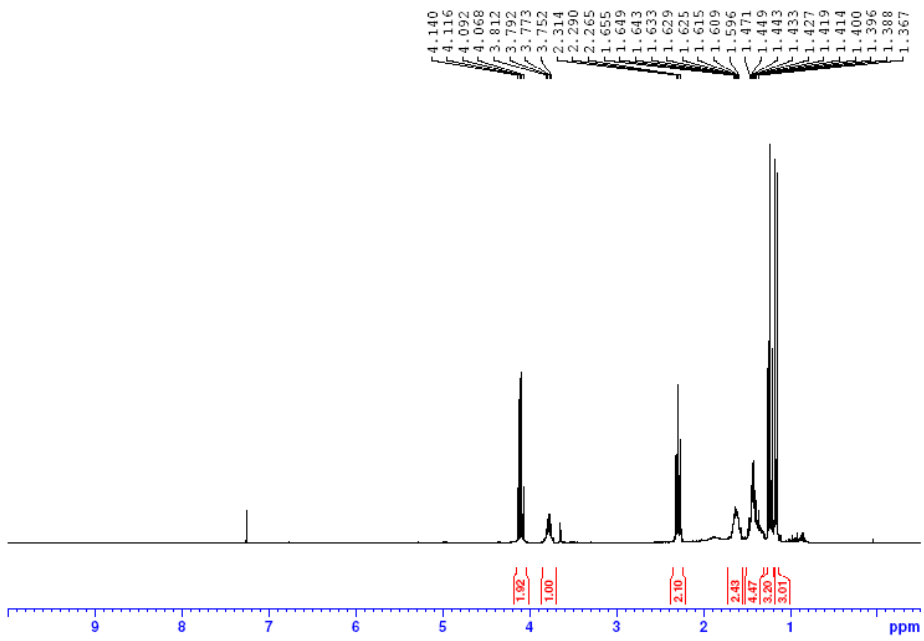
3bb

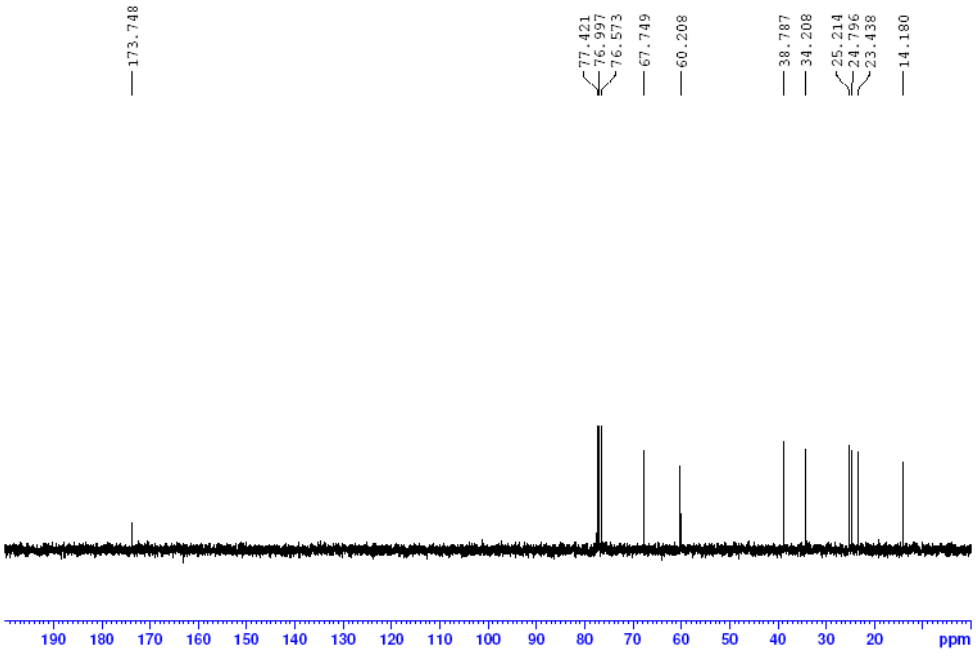

7.260
3.804
3.784
3.765
3.744
1.514
1.446
1.410
1.400
1.386
1.378
1.252
1.179
1.159
0.889
0.868
0.844
1.00
3.77
15.46
3.03
3.03
9 8 7 6 5 4 3 2 1 0 ppm
77.426
77.002
76.579
68.138
39.346
31.883
29.633
29.594
29.310
25.754
23.421
22.654
14.074
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

3cc
Crude NMR

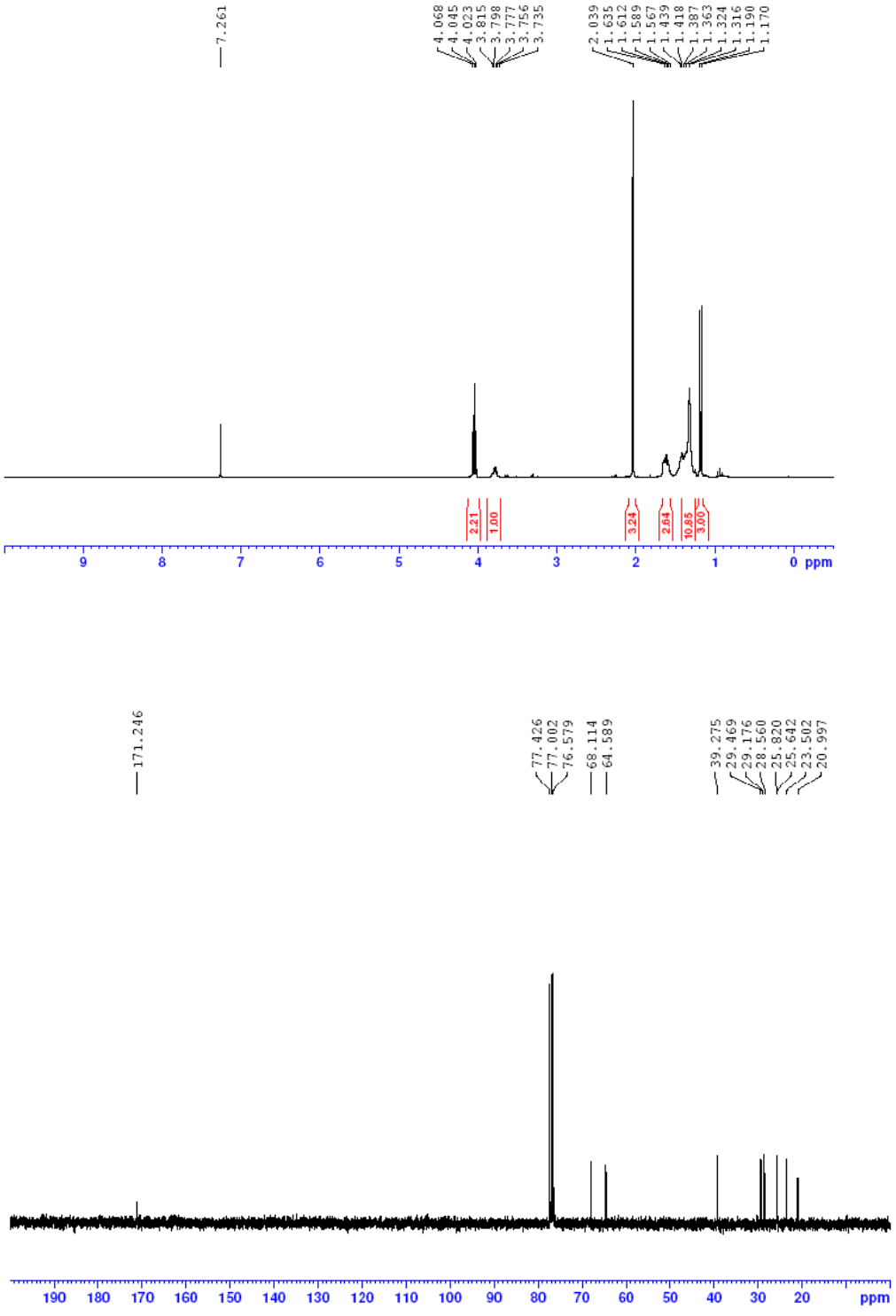


3dd

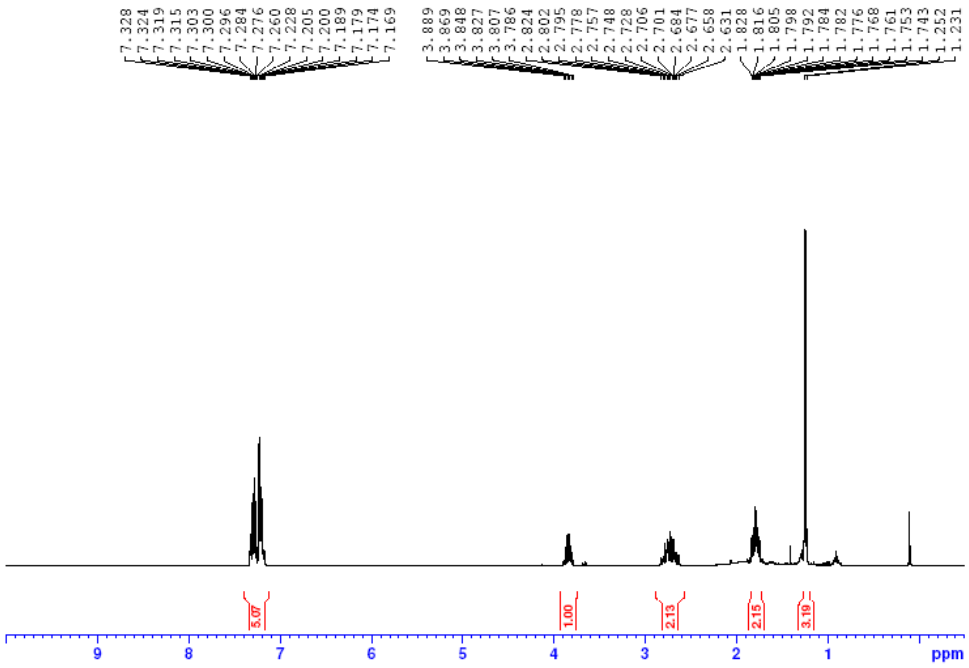

4.140
4.116
4.092
4.068
3.812
3.792
3.773
3.752
2.314
2.290
2.265
1.655
1.649
1.643
1.633
1.629
1.625
1.615
1.609
1.596
1.471
1.449
1.443
1.433
1.427
1.419
1.414
1.400
1.396
1.388
1.367
1.02
1.00
2.10
2.43
4.47
3.20
3.01
9
8
7
6
5
4
3
2
1
ppm

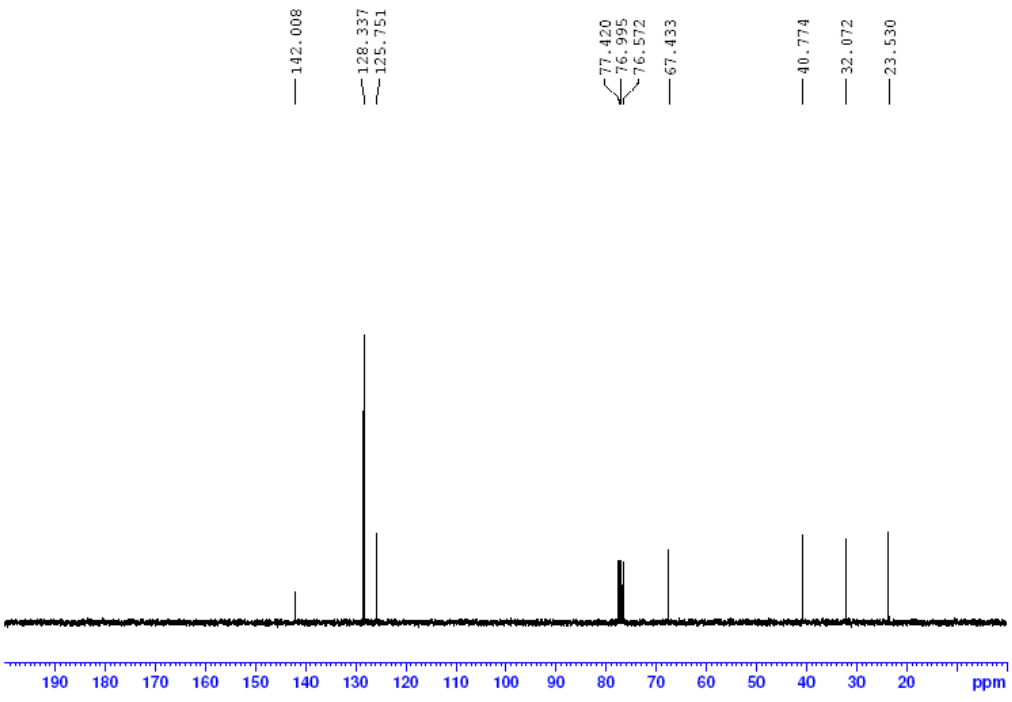

173.748
77.421
76.997
76.573
67.749
60.208
38.787
34.208
25.214
24.796
23.438
14.180
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3ee

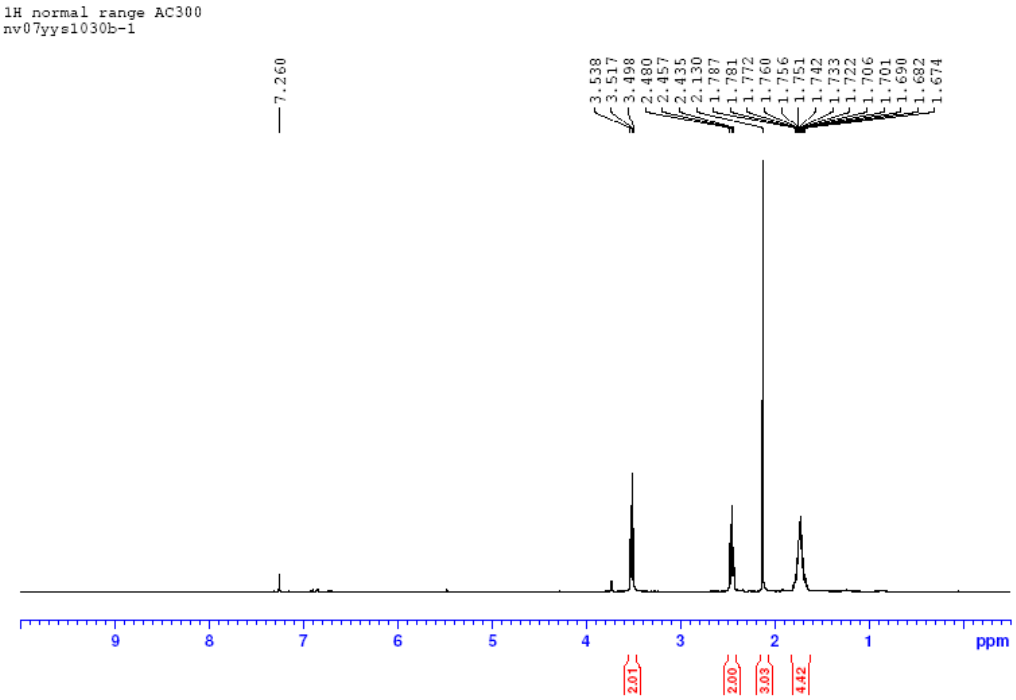

7.261
4.068
4.045
4.023
3.815
3.798
3.777
3.756
3.735
2.039
1.635
1.612
1.589
1.567
1.439
1.418
1.387
1.363
1.324
1.316
1.190
1.170
2.21
1.00
3.24
2.64
10.85
3.00
9 8 7 6 5 4 3 2 1 0 ppm
171.246
77.426
77.002
76.579
68.114
64.589
39.275
29.469
29.176
28.560
25.820
25.642
23.502
20.997
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

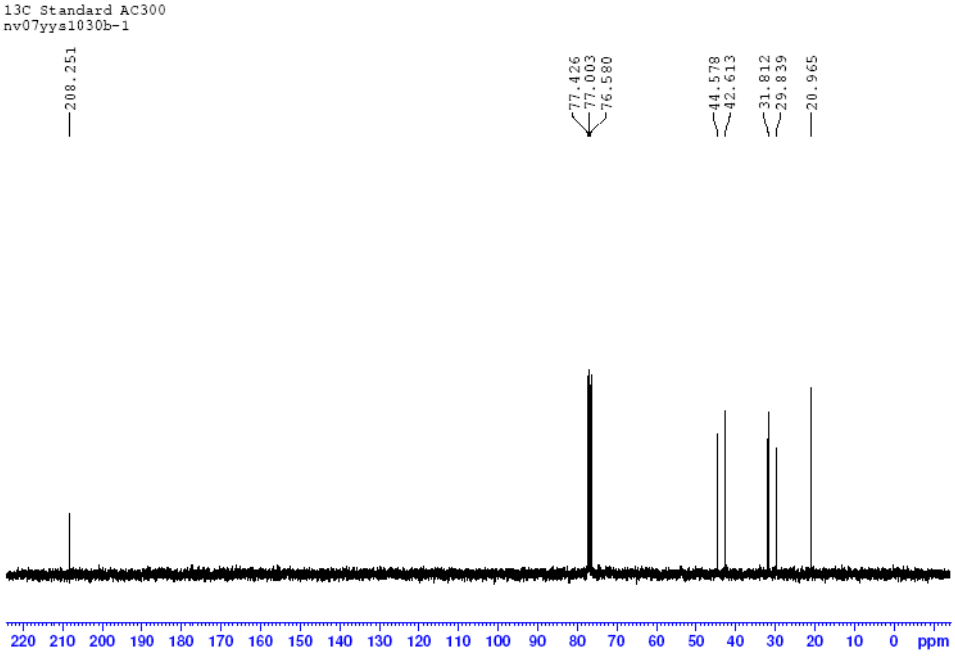
3ff


7.328
7.324
7.319
7.315
7.303
7.300
7.296
7.284
7.276
7.260
7.228
7.205
7.200
7.189
7.179
7.174
7.169
3.889
3.869
3.848
3.827
3.807
3.786
2.824
2.802
2.795
2.778
2.757
2.748
2.728
2.706
2.701
2.684
2.677
2.658
2.631
1.828
1.816
1.805
1.798
1.792
1.784
1.782
1.776
1.768
1.761
1.753
1.743
1.252
1.231
5.07
1.00
2.13
2.15
3.10
9
8
7
6
5
4
3
2
1
ppm

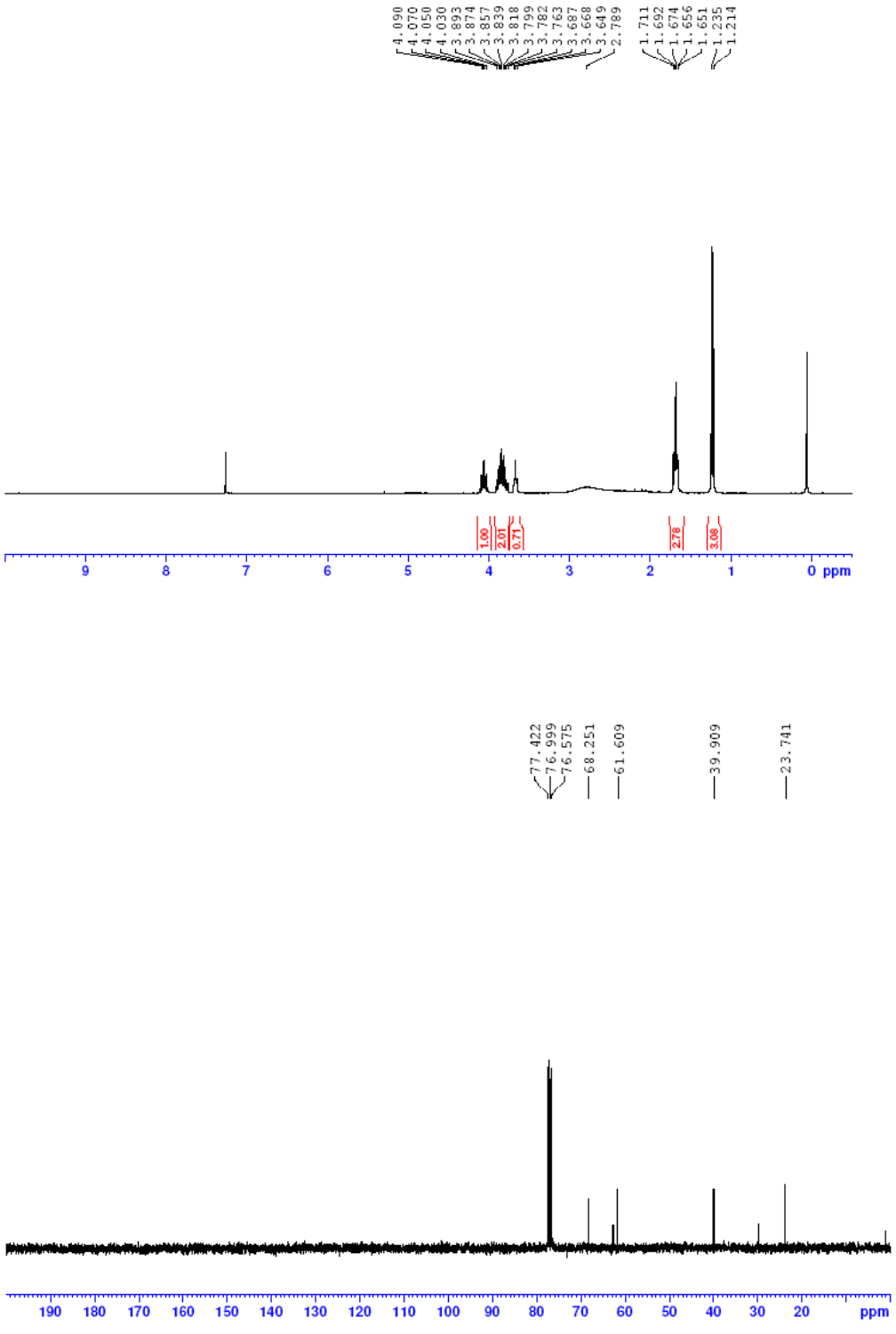

142.008
128.337
125.751
77.420
76.995
76.572
67.433
40.774
32.072
23.530
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

4hh

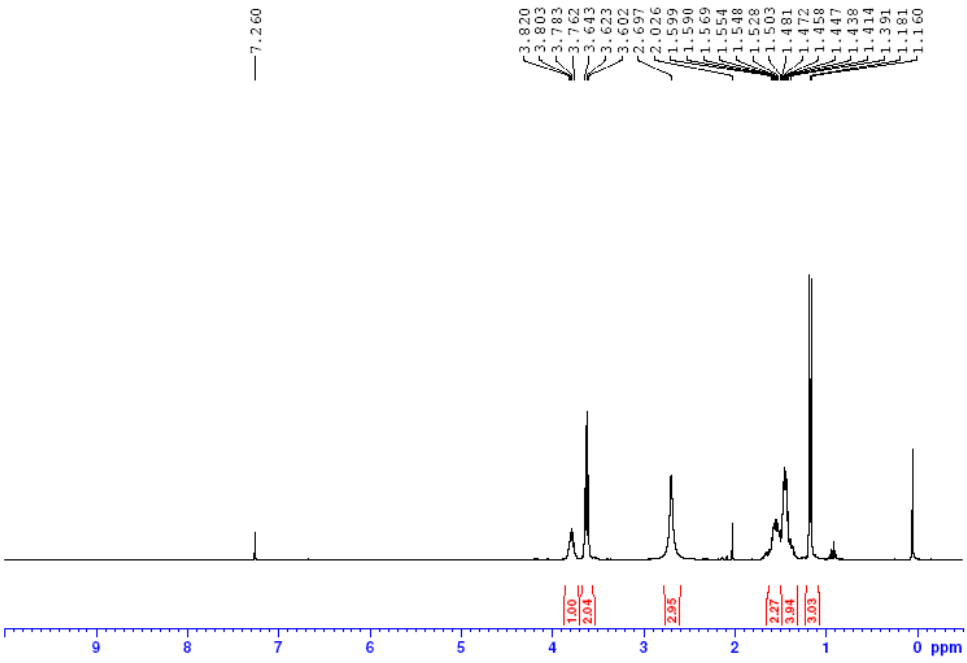

1H normal range AC300
nv07yys1030b-1
7.260
3.538
3.517
3.498
2.480
2.457
2.435
2.130
1.787
1.781
1.772
1.760
1.756
1.751
1.742
1.733
1.722
1.706
1.701
1.690
1.682
1.674
9
8
7
6
5
4
3
2
1
ppm
2.01
2.00
3.03
4.42

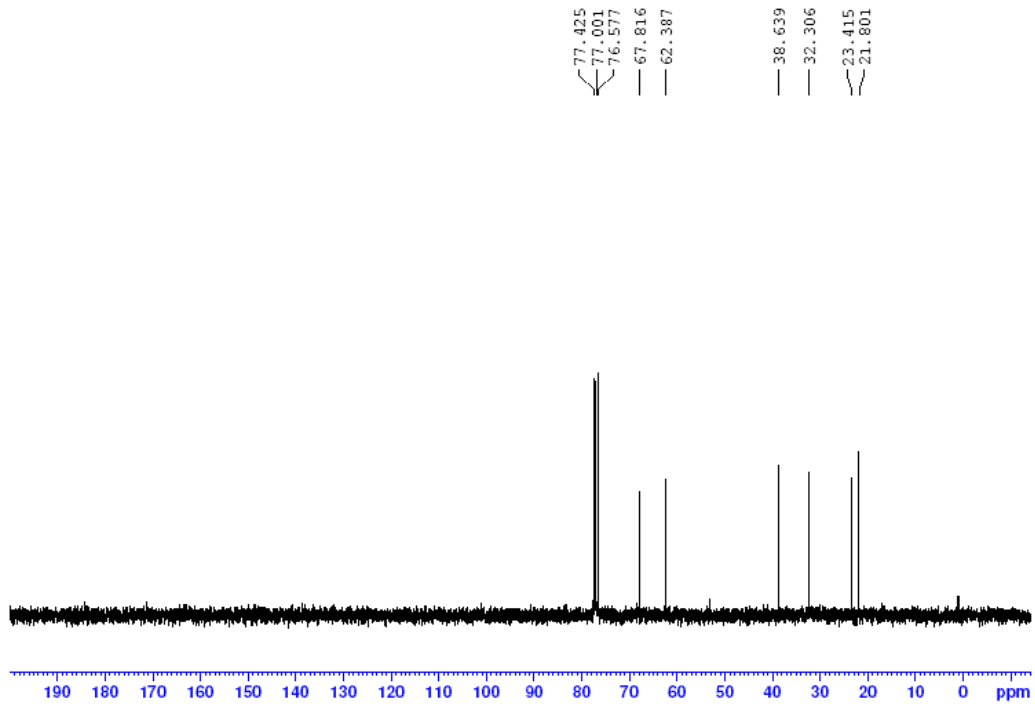

13C Standard AC300
nv07yys1030b-1
208.251
77.426
77.003
76.580
44.578
42.613
31.812
29.839
20.965
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3ii

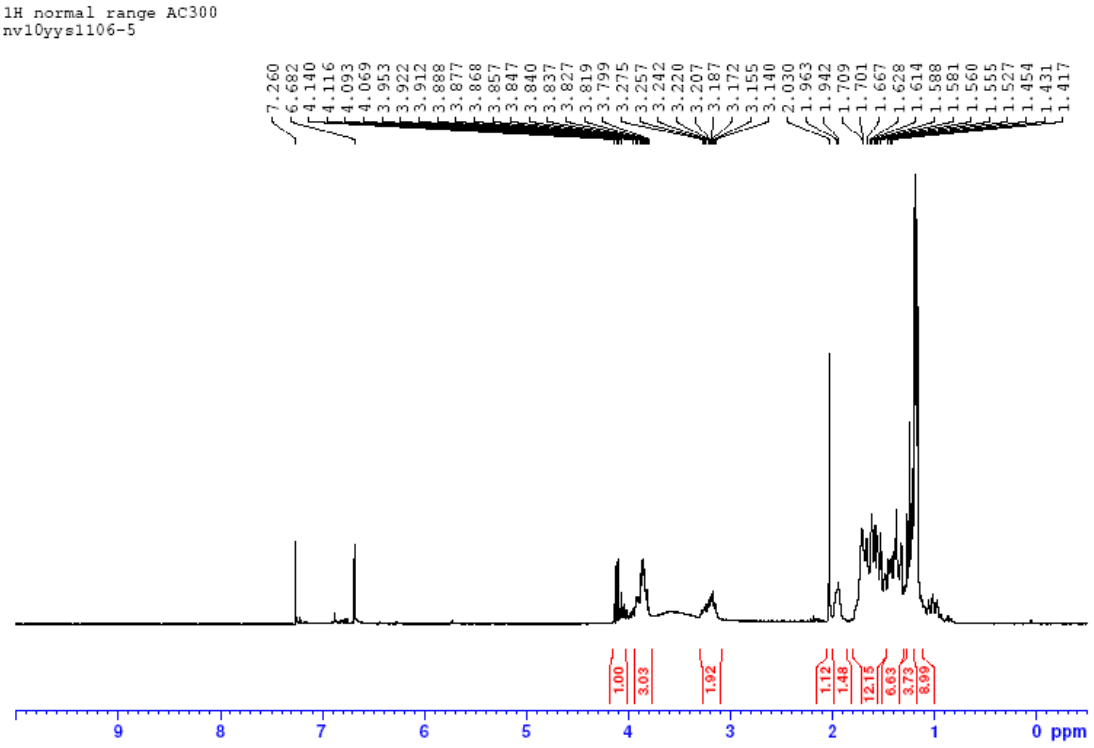

4.090
4.070
4.050
4.030
3.893
3.874
3.857
3.839
3.818
3.799
3.782
3.763
3.687
3.668
3.649
2.789
1.711
1.692
1.674
1.656
1.651
1.235
1.214
1.00
2.01
0.71
2.76
3.06
9
8
7
6
5
4
3
2
1
0 ppm
77.422
76.999
76.575
68.251
61.609
39.909
23.741
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3jj


7.260
3.820
3.803
3.783
3.762
3.643
3.623
3.602
2.697
2.026
1.599
1.590
1.569
1.554
1.548
1.528
1.503
1.481
1.472
1.458
1.447
1.438
1.414
1.391
1.181
1.160
1.00
2.04
2.05
2.27
3.94
3.03
9
8
7
6
5
4
3
2
1
0 ppm


77.425
77.001
76.577
67.816
62.387
38.639
32.306
23.415
21.801
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3kk


1H normal range AC300
nv10yys1106-5
7.260
6.682
4.140
4.116
4.093
4.069
3.953
3.922
3.912
3.888
3.877
3.868
3.857
3.847
3.840
3.837
3.827
3.819
3.799
3.275
3.257
3.242
3.220
3.207
3.187
3.172
3.155
3.140
2.030
1.963
1.942
1.709
1.701
1.667
1.628
1.614
1.588
1.581
1.560
1.555
1.527
1.454
1.431
1.417
1.00
3.03
1.92
1.12
1.48
12.15
6.63
3.73
8.99
9
8
7
6
5
4
3
2
1
0 ppm

References:

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