Supporting information

Gold(I) catalysed regio- and stereoselective intermolecular hydroamination of internal alkynes: towards functionalized azoles.

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I) General Remarks.

All reactions were carried out under air atmosphere and were repeated at least twice. All experiments under microwave irradiations were performed on a CEM Discover SP. Analytical grade solvents were used when needed. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV_{254} plates. Flash chromatography was carried out with Macherey silica gel (Kielselgel 60). ^{1}H (300, 600 and 900 MHz) and ^{13}C (75 and 126 MHz) spectra were acquired on Bruker Avance II, II HD, III, III HD and NEO spectrometers. Assignment was accomplished using 1D and 2D NMR techniques: 1D-^{1}H quantitative, 2D-^{1}H-NOESY (T_m = 0.3-0.4 s), 2D-^{13}C-HSQC, 2D-^{13}C-HSQC-TOCSY (T_m = 50 ms), 2D-^{13}C-HMBC (J_{app} = 10 Hz), 2D-^{15}N-HMBC (J_{app} = 8 Hz), 1D-^{1}H-NOESY (T_m = 0.5 s) selective if necessary, 1D-^{1}H-TOCSY (T_m=100 ms) selective if necessary. The definition of the (*Z*)/(*E*) (cis/trans) isomerism of pure or mixed isomers was established according the observed and non-observed NOEs profiles after full assignment of $^{1}H/^{13}C/^{15}N$ chemical shifts. Chemical shifts (δ) are reported downfield of Me_4Si in ppm and coupling constants are expressed in Hz. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. Gas chromatography analyses were done on GC Shimadzu 2010+with FID detectors using Supelco SPB-5 column (30 m, 0.25 mm, 0.25 μm) and with nitrogen as gas carrier. GC-MS analyses were performed on a Shimadzu QP2010+ (EI mode) using Supelco column SLBTM-5ms (30m, 0.25mm, 0.25μm). HRMS-ESI analyses were performed at PSM-EA 7365 GRITA-Pharm. Dept.-University of Lille. All reagents, e.g. alkynes and heterocycles, were used as received without any purification. [Au(IPr)(OH)] **1a**,[1a] [Au(IPr)][NTf_2] **1b**[1b,c] and [{Au(IPr)}$_2$(μ-OH)][BF_4] **1c**[1d] were synthesized according to previous reports.[1]

II) <u>General Procedures for the catalyses:</u>

Synthetic procedure by heating with a sand bath - method A:

All reactions were performed in screw-capped vials containing a stirring bar. To a mixture of [{Au(IPr)}$_2$(μ-OH)][BF_4] (0.5 mol%), tetrabutylammonium triflate (5 mol%) and heterocycle (1 eq., 0.22 mmol) was added the alkyne reagent (1.3 eq., 0.29 mmol). The reaction mixture was stirred in a sand bath at 100°C for 72 hours. After cooling, the completion of the reaction was checked by GC analysis and the reaction mixture was purified by flash chromatography or preparative TLC using mixtures of petroleum ether and ethylacetate (70/30 to 95/5) to afford the corresponding product.

Synthetic procedure by heating with microwave irradiations - method B:

All reactions were performed in capped closed tubes containing a stirring bar under monomode microwave at 150 °C for 45 minutes. To a mixture of [{Au(IPr)}$_2$(μ-OH)][BF_4] (0.5 mol%), tetrabutylammonium triflate (5 mol%) and heterocycle (1 eq., 0.22 mmol) was added the alkyne reagent (1.3 eq., 0.29 mmol). The reaction mixture was the stirred at 150°C for 45 minutes. After cooling, the completion of the reaction was checked by GC analysis and the reaction mixture was purified by flash chromatography or preparative TLC using mixtures of petroleum ether and ethylacetate (70/30 to 95/5) to afford the corresponding product.

Synthetic procedure for the hydrogenation of enamines at atmospheric pressure (e.g. 1 bar) – method C:

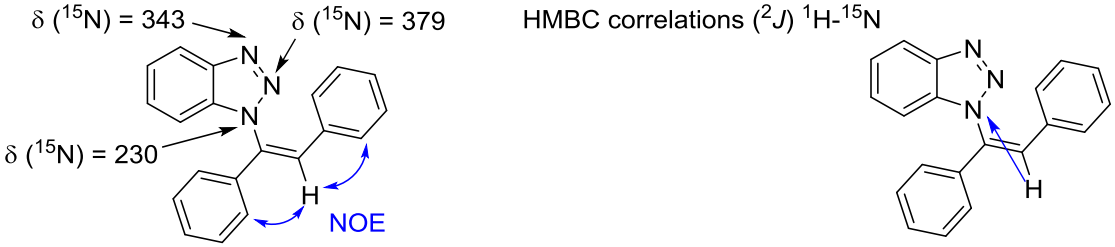
In a Schlenk tube connected to a 3 ways stopcock were placed enamine substrate (50 mg), palladium on carbon at 5% (1 mol%) and ethyl acetate (3 mL). The reaction mixture was then connected to a hydrogen balloon, purged 3 times through vacuum-hydrogen cycles and finally heated at the desired temperature for 15 hours. After cooling, the crude reaction mixture was filtered over a pad of Celite™ which was then washed with ethyl acetate (2 * 10 mL) and the completion of the reaction was checked by GC analysis. When necessary, the reaction mixture was purified by flash chromatography or preparative TLC using mixtures of petroleum ether and ethyl acetate (70/30 to 95/5) to afford the corresponding product.

Synthetic procedure for the hydrogenation of enamines at subatmospheric pressure (e.g. >1 bar) – method D:

In a stainless steel autoclave were placed enamine substrate (50 mg), palladium on carbon at 5% (1 mol%) and ethylacetate (3 mL). The autoclave was then connected to hydrogen gas, purged 3 times through vacuum-hydrogen cycles and finally pressurized at the chosen pressure. Heating (water bath) and stirring (magnetic stirring plate) were started and the reaction time was counted since the desired temperature was reached. The reactions were run at 60 or 80°C for 15 to 120 hours depending on the enamine to hydrogenate. After cooling (1 hour), the autoclave was degassed and subsequently opened. The crude reaction mixture was filtered over a pad of Celite™ which was then washed with ethyl acetate (2 * 10 mL) and the completion of the reaction was checked by GC analysis. When necessary, the reaction mixture was purified by flash chromatography or preparative TLC using mixtures of petroleum ether and ethylacetate (70/30 to 95/5) to afford the corresponding product.

III) <u>Characterization of compounds.</u>

4aa (*Z*)-1-(1,2-diphenylvinyl)-1H-benzo[d][1,2,3]triazole[2]

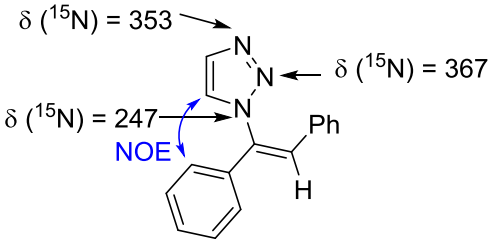


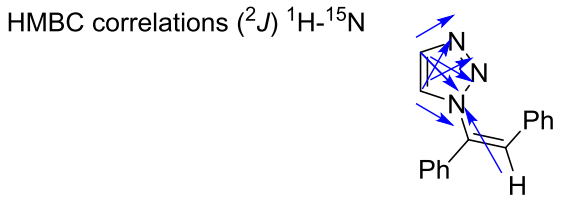
White solid (from 0.022 mmol of benzotriazole using method A, 0.043 g, 66% yield) or (from 1 mmol of benzotriazole using method B, 0.285 g, 96% yield), Rf = 0.3, petroleum ether and ethyl acetate solvent mixture (9:1).

^{1}H NMR ($CDCl_3$): δ 8.05 (d, 1H, J = 6.7), 7.25 (m, 6H), 7.10 (m, 2H), 7.00 (m, 4H), 6.65 (d, 2H, J = 6.7).

^{13}C NMR ($CDCl_3$): δ 145.9 (C), 136.8 (C), 133.7 (C), 133.6 (C), 133.3 (C), 129.4 (1CH), 129.0 (2CH), 128.7 (4CH), 128.2 (1CH), 127.8 (1CH), 126.1 (2CH), 124.3 (1CH), 120.1 (1CH), 110.6 (1CH).

4ab (*Z*)-1-(1,2-diphenylvinyl)-1H-1,2,3-triazole





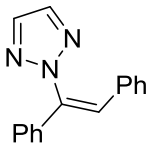
White solid. (0.017 g, 31 % yield using method A) or (from 1.1 mmol triazole using method B, 0.155 g, 57% yield), Rf = 0.4, petroleum ether and ethyl acetate solvent mixture (8:2).

^{1}H NMR ($CDCl_3$): δ 7.85 (d, 1H, *J* = 1.0), 7.55 (d, 1H, *J* = 1.0), 7.37 (m, 3H), 7.21 (m, 6H), 6.79 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 136.5 (C), 134.9 (C), 134.3 (CH), 133.3 (C), 129.5 (CH), 129.0 (2CH), 128.9 (CH), 128.8 (4CH), 127.0 (CH), 125.9 (CH), 125.8 (2CH).

HRMS (ESI+): m/z calcd for $C_{16}H_{14}N_3$ [MH^+] 248.11822, found 248.11777.

4ac (*Z*)-2-(1,2-diphenylvinyl)-2H-1,2,3-triazole

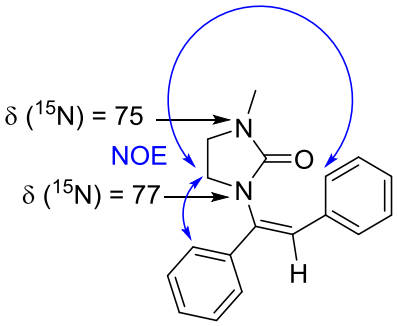


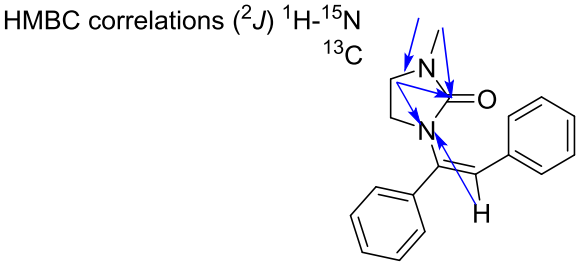
White solid (0.008 g, 15 % yield using method A) or (from 1.1 mmol triazole using method B, 0.058 g, 21% yield using method B), Rf = 0.7, petroleum ether and ethyl acetate solvent mixture (8:2).

^{1}H NMR ($CDCl_3$): δ 7.85 (s, 2H), 7.35 (m, 3H), 7.19 (m, 6H), 6.73 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 138.2 (C), 136.9 (C), 135.6 (2CH), 133.9 (C), 129.2 (CH), 128.9 (2CH), 128.8 (2CH), 128.6 (CH), 128.5 (2CH), 127.2 (CH), 126.1 (2CH).

4ad (*Z*,*E*)-1-(1,2-diphenylvinyl)-3-methylimidazolidin-2-one





Mixture of (*Z*)/(*E*) isomers (68/32)

yellow oil (0.051 g, 83% yield using method A), Rf = 0.5, petroleum ether and ethyl acetate solvent mixture with 5% triethylamine (70:25:5).

major (*Z*)-4ad:

^{1}H NMR ($CDCl_3$): δ 7.36 (d, 4H, *J* = 7.8), 7.28 (m, 6H), 6.62 (s, 1H), 3.39 (m, 4H), 2.77 (s, 3H, Me).

^{13}C NMR ($CDCl_3$): δ 159.2 (CO), 138.0 (C), 136.7 (C), 136.2 (C), 129.1 (CH), 128.6 (CH), 128.5 (4CH), 128.3 (CH), 127.6 (CH) 125.5 (CH), 45.7 (CH_2), 42.9 (CH_2), 31.7 (CH_3).

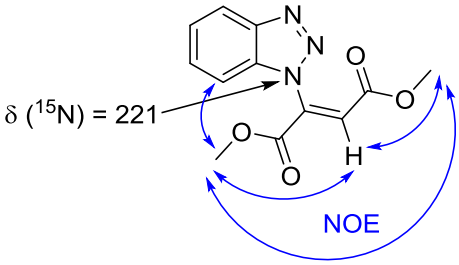
minor (*E*)-4ad:

^{1}H NMR ($CDCl_3$): δ 7.28 (m, 5H), 6.95 (m, 3H), 6.82 (d, 2H, J = 8.1), 6.54 (s, 1H), 3.26 (m, 4H), 2.76 (s, 3H, Me).

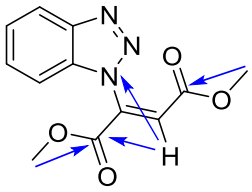
^{13}C NMR ($CDCl_3$): δ 158.7 (CO), 138.2 (C), 136.2 (C), 135.7 (C), 129.7 (CH), 128.6 (2CH), 128.3 (CH), 127.8 (CH), 126.2 (2CH), 125.9 (CH), 118.4 (CH), 44.5 (CH_2), 43.6 (CH_2), 31.4 (CH_3).

HRMS (ESI+): m/z calcd for $C_{18}H_{19}N_2O$ [MH^+] 279.14919, found 279.14798.

4ba (*Z*)-dimethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)fumarate[3]



HMBC correlations (^2J) ^{1}H-^{15}N ^{13}C

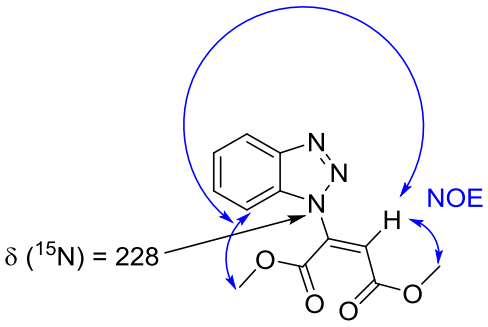


White solid (0.040 g, 69% yield of (*Z*) and (*E*) isomers (1/1) using method A with only 6 hours of reaction), Rf = 0.7, petroleum ether and ethyl acetate solvent mixture (7:3).

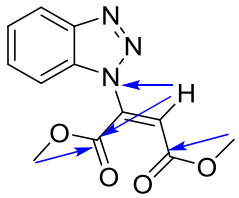
^{1}H NMR ($CDCl_3$): δ 8.07 (d, 1H, J = 8.3), 7.52 (t, 1H, J = 8.2), 7.42 (m, 2H), 7.34 (s, 1H), 3.89 (s, 3H), 3.57 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 162.9 (C), 162.2 (C), 145.7 (C), 134.2 (C), 133.7 (C), 128.7 (CH), 128.6 (CH), 124.5 (CH), 120.3 (CH), 110.4 (CH), 53.9 (CH_3), 52.6 (CH_3).

4ba (*E*)-dimethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)maleate[3]



HMBC correlations (^2J) ^{1}H-^{15}N ^{13}C

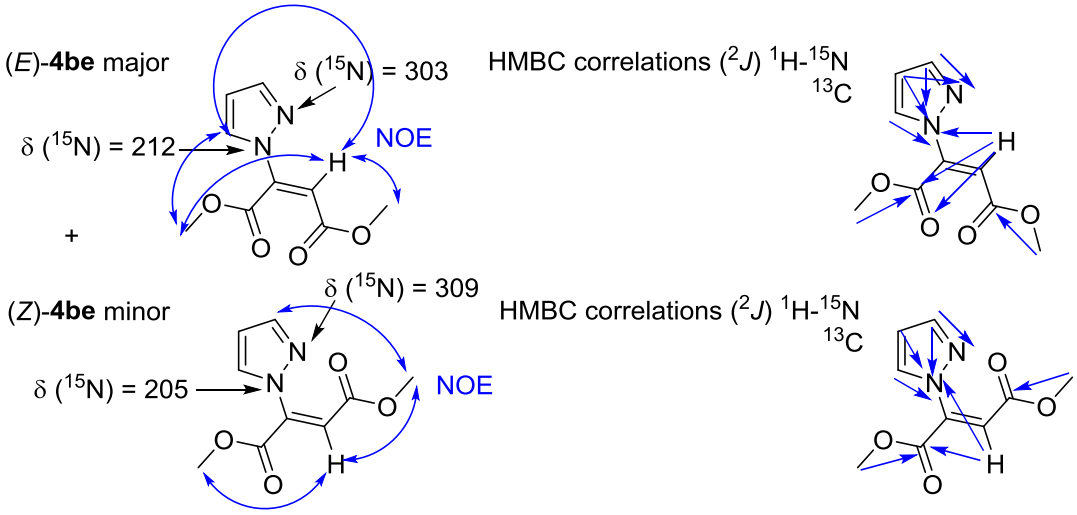


White solid (0.040 g, 69% yield) of (*Z*) and (*E*) isomers (1/1) using method A with only 6 hours of reaction), Rf = 0.5, petroleum ether and ethyl acetate solvent mixture (7:3).

^{1}H NMR ($CDCl_3$): δ 8.14 (d, 1H, J = 7.4), 7.62 (m, 2H), 7.51 (m, 1H), 6.89 (s, 1H), 4.06 (s, 3H), 3.87 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 164.7 (C), 162.4 (C), 146.7 (C), 140.4 (C), 131.2 (C), 129.9 (2CH), 125.7 (2CH), 121.1 (CH), 110.9 (CH), 109.9 (CH), 53.8 (CH), 52.6 (CH).

4be (*Z*,*E*)-dimethyl 2-(1H-pyrazol-1-yl)maleate[4]



mixture of (*Z*)/(*E*) isomers (1/9).

Colorless oil (0.026 g, 56% yield using method A) or (from 1.1 mmol pyrazole using method B, 0.150 g, 65% yield), Rf = 0.3, petroleum ether and triethylamine solvent mixture (95:5).

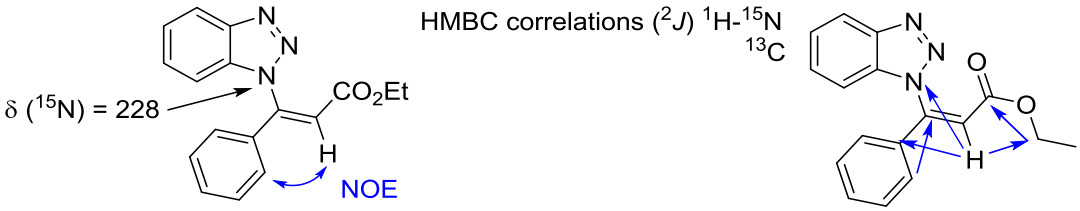
Major (*Z*)-4be isomer: ^{1}H NMR ($CDCl_3$): δ 7.72 (d, 1H, *J* = 1.6), 7.63 (d, 1H, *J* = 2.7), 6.45 (dd, 1H, *J* = 2.7, *J* = 1.6), 6.39 (s, 1H), 4.00 (s, 3H), 3.77 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 165.5 (CO), 163.4 (CO), 143.7 (CH), 143.6 (C), 128.6 (CH), 109.7 (CH), 104.5 (CH), 53.7 (CH_3), 52.3 (CH_3).

Minor (*E*)-4be isomer: ^{1}H NMR ($CDCl_3$): δ 7.82 (d, 1H, *J* = 1.6), 7.64 (d, 1H, *J* = 2.7), 6.83 (s, 1H), 6.40 (m, 1H), 3.88 (s, 3H, Me), 3.70 (s, 3H, Me).

^{13}C NMR ($CDCl_3$): δ 165.5 (CO), 163.4 (CO), 149.4 (C), 141.6 (CH), 131.9 (CH), 122.1 (CH), 107.5 (CH), 53.6 (CH_3), 52.4 (CH_3).

4ca (*Z*)-ethyl-3-(1H-benzo[d][1,2,3]triazol-1-yl)-3-phenylacrylate[5]

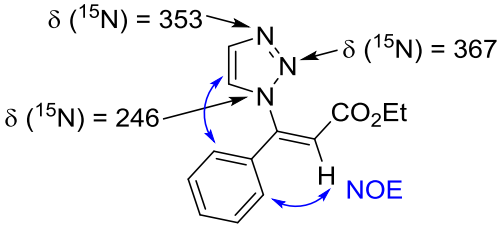


Colorless oil (0.054 g, 88% yield using method A) or (from 1.1 mmol benzotriazole using method B, 0.162 g, 50% yield), Rf = 0.6, petroleum ether and ethyl acetate solvent mixture (8:2).

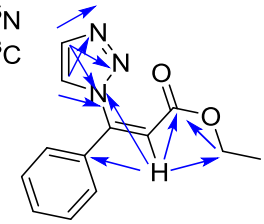
^{1}H NMR ($CDCl_3$): δ 8.07 (dd, 1H, *J* = 6.8), 7.34 (m, 5H), 7.18 (dd, 2H, *J* = 7.1), 7.05 (dd, 1H, *J* = 6.8), 6.55 (s, 1H), 3.89 (q, 2H, *J* = 7.2), 0.85 (t, 3H, *J* = 7.2).

^{13}C NMR ($CDCl_3$): δ 163.7 (CO), 145.8 (C), 144.8 (C), 134.2 (C), 133.9 (C), 131.6 (CH), 129.3 (CH), 128.3 (CH), 127.4 (CH), 124.4 (CH), 120.3 (CH), 116.6 (CH), 110.5 (CH), 61.0 (CH_2), 13.8 (CH_3).

4cb (*Z*)-ethyl-3-phenyl-3-(1H-1,2,3-triazol-1-yl)acrylate



HMBC correlations (^2J) ^{1}H-^{15}N ^{13}C



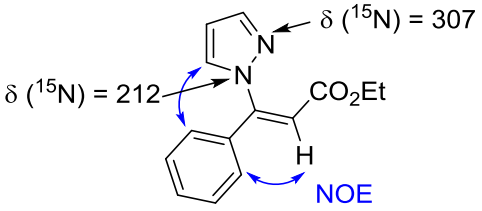
Orange solid (0.038 g, 70% yield using method A) or (from 1 mmol triazole using method B, 0.188 g, 70% yield), Rf = 0.3, petroleum ether and ethyl acetate solvent mixture (8:2).

^{1}H NMR ($CDCl_3$): δ 7.76 (bs, 1H), 7.66 (bs, 1H), 7.40 (t, 1H, J = 7.2), 7.32 (t, 2H, J = 7.4), 7.14 (d, 2H, J = 7.2), 6.42 (s, 1H), 4.03 (q, 2H, J = 7.2), 1.09 (t, 3H, J = 7.1).

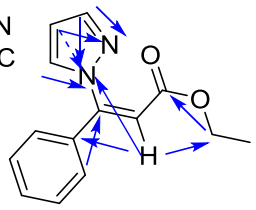
^{13}C NMR ($CDCl_3$): δ 163.5 (CO), 145.4 (C), 134.4 (C), 133.5 (CH), 131.6 (CH), 129.2 (2CH), 127.2 (2CH), 125.9 (CH), 116.0 (CH), 61.2 (CH_2), 14.1 (CH_3).

HRMS (ESI+): m/z calcd for $C_{13}H_{14}N_3O_2$ [MH^+] 244.10805, found 244.10744.

4ce (*Z*)-ethyl-3-phenyl-3-(1H-pyrazol-1-yl)acrylate[6]



HMBC correlations (^2J) ^{1}H-^{15}N ^{13}C

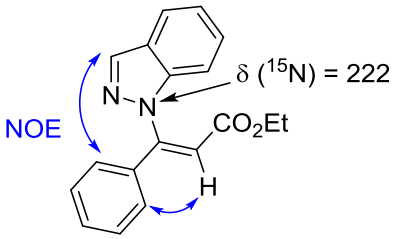


Colorless oil (0.033 g, 62% yield using method A) or (from 1.1 mmol pyrazole using method B, 0.198 g, 74% yield), Rf = 0.7, petroleum ether and ethyl acetate solvent mixture with 5% triethylamine (90:5:5).

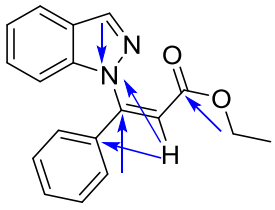
^{1}H NMR ($CDCl_3$): δ 7.65 (d, 1H, J = 1.5), 7.56 (d, 1H, J = 2.4), 7.33 (m, 3H), 7.19 (d*, 2H, J = 6.9), 6.37 (t*, 1H, J = 2.1), 6.10 (s, 1H), 4.08 (q, 2H, J = 7.2), 1.13 (t, 3H, J = 7.1).

^{13}C NMR ($CDCl_3$): δ 164.6 (CO), 149.0 (C), 141.5 (CH), 135.9 (C), 132.5 (CH), 131.0 (CH), 128.8 (2CH), 128.2 (2CH), 112.2 (CH), 106.8 (CH), 60.8 (CH_2), 14.2 (CH_3).

4cf (*Z*)-ethyl-3-(1H-indazol-1-yl)-3-phenylacrylate



HMBC correlations (^2J) ^{1}H-^{15}N ^{13}C



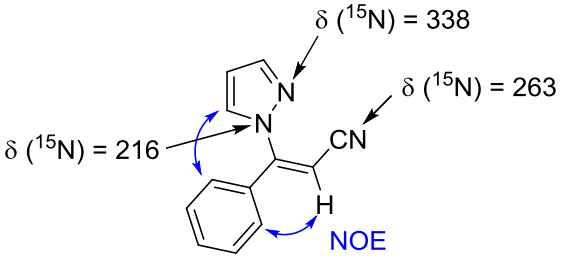
Colorless oil (0.042 g, 65% yield using method A), Rf = 0.4, petroleum ether and ethyl acetate solvent mixture (8:2).

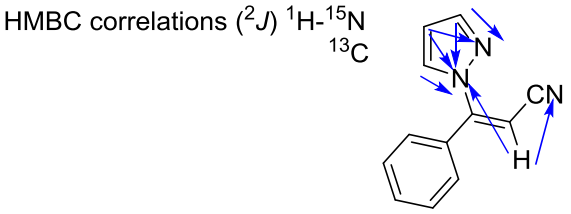
^{1}H NMR ($CDCl_3$): δ 8.05 (d, 1H, J = 0.9), 7.64 (dd, 2H, J = 8.5), 7.29 (m, 4H), 7.16 (m, 3H), 7.05 (dd, 1H, J = 6.7), 6.39 (s, 1H), 3.98 (q, 2H, J = 7.2), 0.95 (t, 3H, J = 7.2).

^{13}C NMR ($CDCl_3$): δ 164.2 (CO), 149.7 (C), 149.3 (C), 135.4 (C), 131.2 (CH), 129.0 (2CH), 127.7 (2CH), 127.1 (CH), 126.0 (CH), 122.7 (CH), 121.9 (C), 120.7 (CH), 118.3 (CH), 115.0 (CH), 60.9 (CH_2), 14.0 (CH_3).

HRMS (ESI+): m/z calcd for $C_{18}H_{17}N_2O_2$ [MH^+] 293.12845, found 293.12799.

4de (*Z*)-3-phenyl-3-(1H-pyrazol-1-yl)acrylonitrile[7]



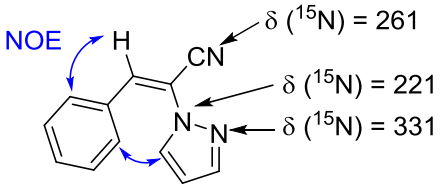


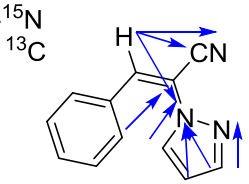
Colorless oil (0.039 g, 91% yield using method A) or (from 0.44 mmol pyrazole using method B, 0.058 g, 67% yield), Rf = 0.7, petroleum ether and ethyl acetate solvent mixture (8:2).

^{1}H NMR ($CDCl_3$): δ 7.84 (d, 1H, *J* = 1.5), 7.73 (d, 1H, *J* = 2.6), 7.54 (t, 1H, *J* = 7.5), 7.45 (t, 2H, *J* = 7.5), 7.36 (d, 2H, *J* = 7.1), 6.50 (t, 1H, *J* = 2.2), 5.35 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 154.4 (C), 143.1 (CH), 133.9 (C), 131.8 (CH), 131.6 (CH), 129.1 (2CH), 128.9 (2CH), 116.3 (C), 108.7 (CH), 85.9 (CH).

5de (*Z*)-3-phenyl-2-(1H-pyrazol-1-yl)acrylonitrile[8]



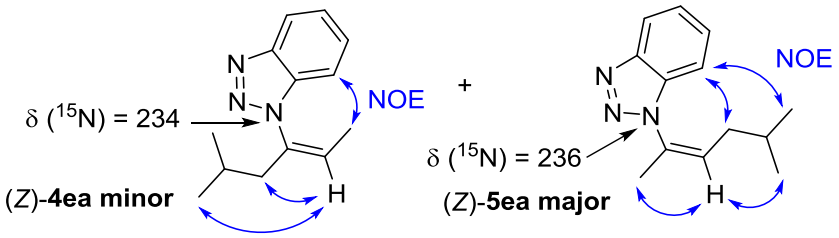


Colorless oil (0.004 g, 10% yield using method A) or (from 0.440 mmol pyrazole using method B, 0.012 g, 14% yield), Rf = 0.8, petroleum ether and ethyl acetate solvent mixture (8:2).

^{1}H NMR ($CDCl_3$): δ 7.71 (bs, 1H), 7.48 (m, 5H), 7.21 (t, 1H, *J* = 2.4), 6.34 (t, 1H, *J* = 1.8), 6.17 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 155.1 (C), 143.8 (CH), 131.6 (CH), 131.1 (C), 130.9 (CH), 129.7 (2CH), 129.2 (2CH), 117.2 (C), 109.2 (CH), 85.6 (CH).

4ea (*Z*)-1-(5-methylhex-2-en-3-yl)-1H-benzo[d][1,2,3]triazole and 5ea (*Z*)-1-(5-methylhex-2-en-2-yl)-1H-benzo[d][1,2,3]triazole



Mixture of **4ea** and **5ea** with a ratio of (23/77)

Colorless oil (0.036 g, 75% yield using method A), Rf = 0.8, petroleum ether and ethyl acetate solvent mixture (8:2).

Minor product (*Z*)-4ea:

^{1}H NMR ($CDCl_3$): δ 8.02 (d, 1H, *J* = 8.2), 7.42 (t, 1H, *J* = 7.5), 7.18 (m, 2H), 5.79 (m, 1H), 2.21 (d*, 3H, *J* = 1.2), 1.62 (m, 2H), 1.55 (m, 1H), 0.72 (d, 6H, *J* = 6.5).

^{13}C NMR ($CDCl_3$): δ 145.5 (C), 132.9 (C), 131.5 (C), 129.1 (CH), 127.6 (CH), 124.0 (CH), 120.1 (CH), 110.3 (CH), 36.6 (CH_2), 28.3 (CH), 22.3 ($2CH_3$), 22.2 (CH_3).

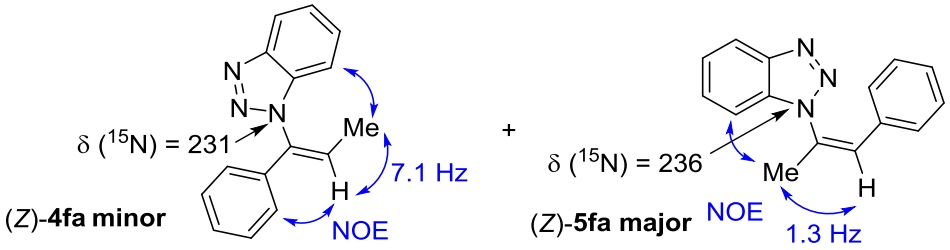
Major product (*Z*)-5ea:

^{1}H NMR ($CDCl_3$): δ 8.02 (d, 1H, *J* = 8.2), 7.42 (t, 1H, *J* = 7.5), 7.18 (m, 2H), 5.79 (m, 1H), 2.46 (d, 2H, *J* = 7.1), 1.45 (d, 3H, *J* = 7.0), 1.29 (m, 1H), 0.79 (d, 6H, *J* = 6.6).

^{13}C NMR ($CDCl_3$): δ 145.4 (C), 135.5 (C), 131.7 (C), 127.7 (CH), 124.4 (CH), 123.9 (CH), 120.2 (CH), 110.4 (CH), 45.7 (CH_2), 25.8 (CH), 22.5 ($2CH_3$), 13.4 (CH_3).

HRMS (ESI+): m/z calcd for $C_{13}H_{18}N_3$ [MH^+] 216.14952, found 216.14925.

4fa (*Z*)-1-(1-phenylprop-1-en-2-yl)-1H-benzo[d][1,2,3]triazole and 5fa (*Z*)-1-(1-phenylprop-1-en-2-yl)-1H-benzo[d][1,2,3]triazole[2]



Mixture of **4fa** and **5fa** with a ratio of (3/7)

Pale yellow oil (0.045 g, 88% yield using method A), Rf = 0.5, petroleum ether and ethyl acetate solvent mixture (8:2).

Minor product (*Z*)-4fa:

^{1}H NMR ($CDCl_3$): δ 8.03 (d, 1H, *J* = 7.3), 7.23 (m, 2H), 7.00 (m, 4H), 6.74 (bd, 1H, *J* = 1.3), 6.68 (d, 2H, *J* = 7.5), 2.49 (d, 3H, *J* = 1.5).

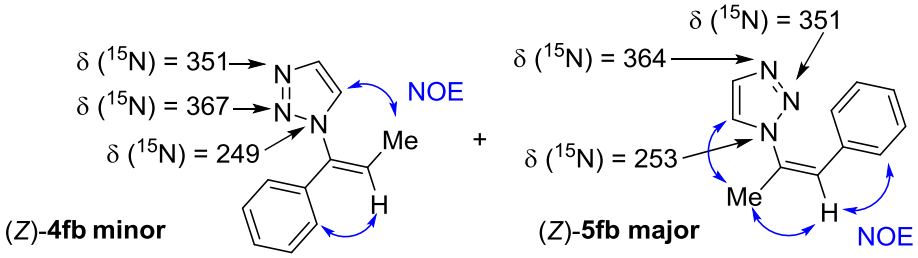
^{13}C NMR ($CDCl_3$): δ 145.8 (C), 136.1 (C), 133.8 (C), 131.4 (C), 128.8 (CH), 128.5 (2CH), 128.1 (2CH), 127.9 (CH), 126.0 (CH), 124.0 (CH), 119.9 (CH), 110.8 (CH), 23.7 (CH_3).

Major product (*Z*)-5fa:

^{1}H NMR ($CDCl_3$): δ 8.13 (d, 1H, *J* = 6.8), 7.39 (m, 2H), 7.23 (m, 5H), 7.08 (m, 1H), 6.59 (q, 1H, *J* = 7.1), 1.76 (d, 3H, *J* = 7.1).

^{13}C NMR ($CDCl_3$): δ 145.7 (C), 135.8 (C), 133.7 (C), 131.7 (C), 128.7 (CH), 128.5 (CH), 128.1 (2CH), 128.0 (CH), 127.6 (CH), 125.5 (CH), 124.2 (CH), 120.2 (CH), 110.5 (CH), 14.0 (CH_3).

4fb (*Z*)-1-(1-phenylprop-1-en-2-yl)-1H-1,2,3-triazole and 5fb *(Z)*-1-(1-phenylprop-1-en-2-yl)-1H-1,2,3-triazole



Mixture of **4fb** and **5fb** with a ratio of (23/77).

white solid (0.031 g, 76% yield using method A), Rf = 0.2, petroleum ether and ethyl acetate solvent mixture (8:2).

Minor product (*Z*)-4fb:

^{1}H NMR ($CDCl_3$): δ 7.61 (bd, 1H, *J* = 1.0), 7.28 (m, 1H), 7.19 (m, 3H), 6.81 (m, 2H), 6.53 (bd, 1H, *J* = 1.2), 2.44 (d, 3H, *J* = 1.0).

^{13}C NMR ($CDCl_3$): δ 133.7 (C), 132.8 (C), 133.5 (CH), 128.7 (2CH), 128.4 (2CH), 128.1 (CH), 125.5 (CH), 124.3 (CH), 23.4 (CH_3).

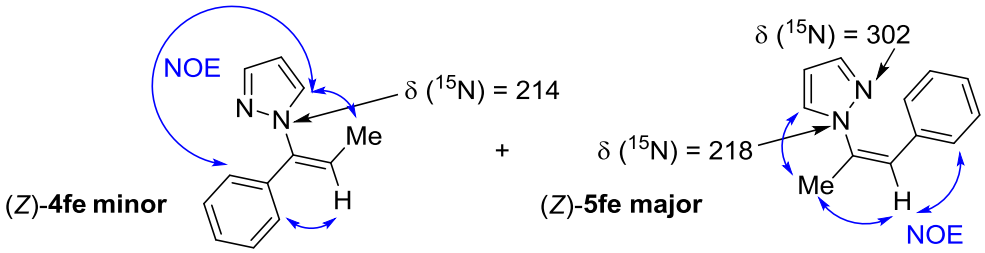
Major product (*Z*)-5fb:

^{1}H NMR ($CDCl_3$): δ 7.77 (bd, 1H, *J* = 1.1), 7.57 (bd, 1H, *J* = 1.1), 7.28 (m, 3H), 7.08 (m, 2H), 6.43 (q, 1H, *J* = 7.0), 1.72 (d, 3H, *J* = 7.2).

^{13}C NMR ($CDCl_3$): δ 137.6 (C), 136.4 (C), 128.9 (2CH), 128.4 (2CH), 128.1 (CH), 125.3 (CH), 124.9 (CH), 124.4 (CH), 13.8 (CH_3).

HRMS (ESI+): m/z calcd for $C_{11}H_{12}N_3$ [MH^+] 186.10257, found 186.10220.

4fe (*Z*)-1-(1-phenylprop-1-en-2-yl)-1H-pyrazole and 5fe *(Z)*-1-(1-phenylprop-1-en-1-yl)-1H-pyrazole[9]



Mixture **4fe** and **5fe** with a ratio of (2/8)

Colorless oil (0.034 g, 83% yield using method A), Rf = 0.3, petroleum ether and ethyl acetate solvent mixture (9:1).

Minor product (*Z*)-4fe:

^{1}H NMR ($CDCl_3$): δ 7.56 (d, 1H, *J* = 1.5), 7.08 (m, 4H), 6.74 (dd, 2H, *J* = 7.7), 6.25 (bs, 1H), 6.11 (t, 1H, *J* = 2.1), 2.34 (bd, 3H, *J* = 1.2).

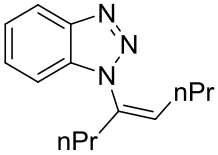
^{13}C NMR ($CDCl_3$): δ 140.1 (CH), 135.8 (C), 134.9 (C), 130.4 (CH), 128.5 (2CH), 128.4 (2CH), 127.3 (CH), 121.6 (CH), 106.1 (CH), 23.0 (CH_3).

Major product (*Z*)-5fe:

^{1}H NMR ($CDCl_3$): δ 7.63 (d, 1H, *J* = 1.5), 7.39 (d, 1H, *J* = 2.3), 7.18 (m, 3H), 7.02 (m, 2H), 6.33 (t, 1H, *J* = 2.1), 6.15 (q*, 1H, *J* = 7.1), 1.67 (d, 3H, *J* = 6.9).

^{13}C NMR ($CDCl_3$): δ 140.1 (CH), 140.0 (C), 137.7 (C), 131.4 (CH), 128.6 (2CH), 128.3 (2CH), 125.8 (CH), 122.4 (CH), 105.9 (CH), 13.7 (CH_3).

4ga (*Z*)-1-(oct-4-en-4-yl)-1H-benzo[d][1,2,3]triazole[2]

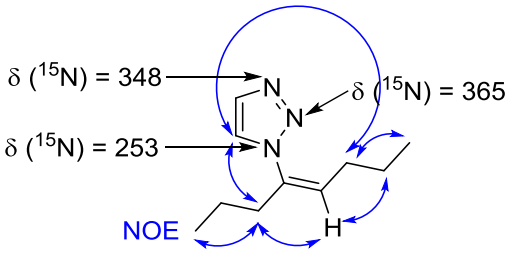


Pale yellow oil (0.035 g, 70% yield using method A) or (from 1.1 mmol benzotriazole using method B, 0.201 g, 80% yield), Rf = 0.9, petroleum ether and ethyl acetate solvent mixture with 5% triethylamine (70:25:5).

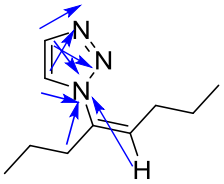
^{1}H NMR ($CDCl_3$): δ 8.01 (d, 1H, *J* = 7.1), 7.4 (t*, 1H, *J* = 6.6), 7.38 (d*+t*, 2H), 5.83 (t, 1H, *J* = 7.3), 2.59 (t, 2H, *J* = 7.5), 1.71 (q, 2H, *J* = 7.5), 1.33 (m, 4H), 0.90 (t, 3H, *J* = 7.5), 0.80 (t, 3H, *J* = 7.5).

^{13}C NMR ($CDCl_3$): δ 145.4 (C), 135.2 (C), 133.5 (C), 129.7 (CH), 127.7 (CH), 123.9 (CH), 120.1 (CH), 110.2 (CH), 38.4 (CH_2), 29.5 (CH_2), 22.4 (CH_2), 20.4 (CH_2), 13.7 (CH_3), 13.4 (CH_3).

4gb (*Z*)-1-(oct-4-en-4-yl)-1H-1,2,3-triazole



HMBC correlations (^{2}J) ^{1}H-^{15}N



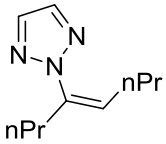
Colorless oil (0.022 g, 56% yield using method A) or (from 1.1 mmol triazole using method B, 0.088 g, 45% yield), Rf = 0.3, petroleum ether and triethylamine solvent mixture (95:5).

^{1}H NMR ($CDCl_3$): δ 7.71 (s, 1H), 7.52 (s, 1H), 5.56 (t, 1H, *J* = 7.5), 2.47 (t, 2H, *J* = 7.5), 1.85 (q, 2H, *J* = 7.5), 1.34 (m, 4H), 0.85 (m, 6H).

^{13}C NMR ($CDCl_3$): δ 136.1 (C), 133.1 (CH), 127.4 (CH), 124.3 (CH), 38.3 (CH_2), 29.2 (CH_2), 22.6 (CH_2), 20.2 (CH_2), 13.7 (CH_3), 13.3 (CH_3).

HRMS (ESI+): m/z calcd for $C_{10}H_{18}N_3$ [MH^+] 180.14886, found 180.14952.

4gc (*Z*)-2-(oct-4-en-4-yl)-2H-1,2,3-triazole

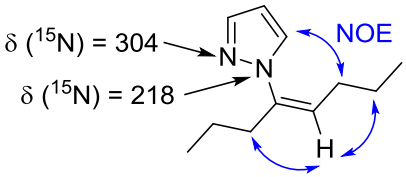


Colorless oil (0.004 g, 10% yield using method A) or (from 1.1 mmol triazole using method B, 0.047 g, 24% yield), Rf = 0.8, petroleum ether and triethylamine solvent mixture (95:5).

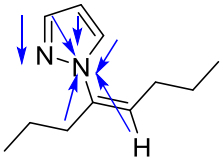
^{1}H NMR ($CDCl_3$): δ 7.69 (bs, 1H), 5.49 (t, 1H, J = 7.3), 2.58 (t, 2H, J = 7.4), 2.10 (q, 2H, J = 7.5), 1.39 (m, 4H), 0.88 (m, 6H).

^{13}C NMR ($CDCl_3$): δ 143.2 (C), 134.1 (CH), 125.6 (2CH), 37.6 (CH_2), 29.5 (CH_2), 22.7 (CH_2), 20.6 (CH_2), 13.9 (CH_3), 13.5 (CH_3).

4ge (*Z*)-1-(oct-4-en-4-yl)-1H-pyrazole



HMBC correlations (^{2}J) ^{1}H-^{15}N



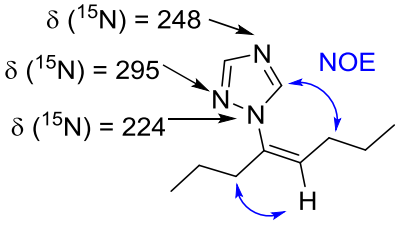
Colorless oil (0.025 g, 62% yield using method A) or (from 1.1 mmol pyrazole using method B, 0.146 g, 75% yield), Rf = 0.9, petroleum ether and ethyl acetate solvent mixture using 5% triethylamine (70:25:5).

^{1}H NMR ($CDCl_3$): δ 7.61 (d, 1H, J = 1.5), 7,39 (d, 1H, J = 2.3), 6.29 (t, 1H, J = 2.0), 5.38 (t, 1H, J = 7.3), 2.49 (t, 2H, J = 8.1), 1.95 (q, 2H, J = 7.3), 1.35 (m, 4H), 0.85 (m, 6H).

^{13}C NMR ($CDCl_3$): δ 139.6 (CH), 139.2 (C), 130.4 (CH), 124.2 (CH), 105.1 (CH), 38.2 (CH_2), 29.3 (CH_2), 22.9 (CH_2), 20.4 (CH_2), 13.9 (CH_3), 13.5 (CH_3).

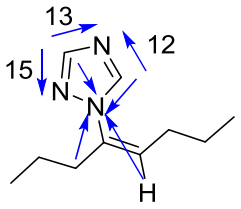
HRMS (ESI+): m/z calcd for $C_{11}H_{19}N_2$ [MH^+] 179.15428, found 179.15398.

4gg (*Z*)-1-(oct-4-en-4-yl)-1H-1,2,4-triazole



HMBC correlations (^{2}J) ^{1}H-^{15}N

^{13}C



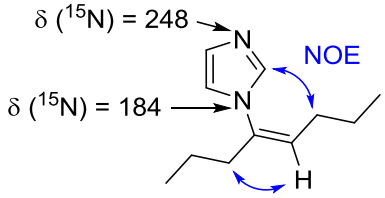
Colorless oil (volatile) (0.029 g, 74% yield using method A) or (from 1.1 mmol 1,2,4-triazole using method B, 0.124 g, 63% yield), Rf = 0.9, petroleum ether and triethylamine solvent mixture (95:5).

^{1}H NMR ($CDCl_3$): δ 8.07 (bs, 1H), 8.02 (bs, 1H), 5.53 (t, 1H, J = 7.5), 2.45 (t, 2H, J = 7.2), 1.91 (q, 2H, J = 7.5), 1.36 (m, 4H), 0.89 (m, 6H, Me).

^{13}C NMR ($CDCl_3$): δ 152.0 (CH), 136.0 (C), 126.6 (2CH), 37.7 (CH_2), 29.3 (CH_2), 22.8 (CH_2), 20.3 (CH_2), 13.8 (CH_3), 13.4 (CH_3).

HRMS (ESI+): m/z calcd for $C_{10}H_{18}N_3$ [MH^+] 180.14952, found 180.14961.

4gh (*Z*)-1-(oct-4-en-4-yl)-1H-imidazole



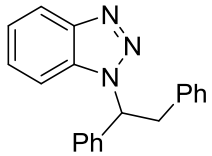
Colorless oil (0.009 g, 21% yield using method A) or (from 1.1 mmol imidazole using method B, 0.092 g, 47% yield), Rf = 0.3, petroleum ether and ethyl acetate solvent mixture (7:3).

^{1}H NMR ($CDCl_3$): δ 7.40 (s, 1H), 7.10 (s, 1H), 6.86 (s, 1H), 5.44 (t, 1H, J = 7.5), 2.31 (t, 2H, J = 7.8), 1.85 (q, 2H, J = 7.4), 1.31 (m, 4H), 0.85 (m, 6H).

^{13}C NMR ($CDCl_3$): δ 137.0 (CH), 135.6 (C), 129.1 (CH), 126.3 (CH), 119.1 (CH), 39.1 (CH_2), 29.0 (CH_2), 22.8 (CH_2), 20.3 (CH_2), 13.8 (CH_3), 13.4 (CH_3).

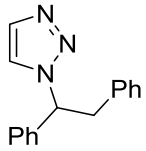
HRMS (ESI+): m/z calcd for $C_{11}H_{19}N_2$ [MH^+] 179.15428, found 179.15434.

6aa 1-(1,2-diphenylethyl)-1H-benzo[d][1,2,3]triazole[10]



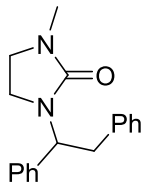
By using method C with 1 bar H_2 at 25°C during 15 h. White solid (0.037 g, 73% yield from 0.168 mmol of enamine), Rf = 0.4, petroleum ether and ethyl acetate solvent mixture (95:5).
^{1}H NMR ($CDCl_3$): δ 8.12 (bd, 1H, *J* = 6.5), 7.42 (m, 8H), 7.23 (m, 5H), 6.08 (dd, 1H, *J* = 6.7), 4.27 (dd, 1H, *J* = 8.9), 3.87 (dd, 1H, *J* = 6.5).
^{13}C NMR ($CDCl_3$): δ 146.1 (C), 138.9 (C), 137.2 (C), 133.1 (C), 129.2 (2CH), 128.9 (2CH), 128.5 (2CH), 128.4 (CH), 127.2 (CH), 127.0 (2CH), 126.9 (CH), 123.9 (CH), 120.0 (CH), 109.7 (CH), 65.4 (CH), 41.5 (CH_2).

6ab 1-(1,2-diphenylethyl)-1H-1,2,3-triazole



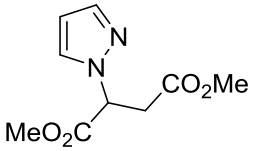
By using method D with 10 bar H_2 at 60°C during 15 h. White solid (0.049 g, 95% yield from 0.210 mmol of enamine) after filtration on Celite with ethylacetate.
^{1}H NMR ($CDCl_3$): δ 7.63 (bs, 1H), 7.43 (bs, 1H), 7.34 (m, 5H), 7.20 (m, 3H), 7.05 (m, 2H), 5.77 (dd, 1H, *J* = 6.9), 3.89 (dd, 1H, *J* = 8.9), 3.55 (dd, 1H, *J* = 6.6).
^{13}C NMR ($CDCl_3$): δ 138.6 (C), 136.8 (C), 133.6 (CH), 129.1 (2CH), 129.0 (2CH), 128.7 (CH), 128.6 (2CH), 127.2 (2CH), 127.0 (CH), 123.4 (CH), 66.9 (CH), 41.9 (CH_2).
HRMS (ESI+): m/z calcd for $C_{16}H_{16}N_3$ [MH^+] 250.13387, found 250.13365.

6ad 1-(1,2-diphenylethyl)-3-methylimidazolidin-2-one



By using method C with 1 bar H_2 at 25°C during 8 h. White solid (0.022 g, 44% yield from from 0.182 mmol of enamine), Rf = 0.3, petroleum ether and ethyl acetate solvent mixture with 5% triethylamine (80:15:5).
^{1}H NMR ($CDCl_3$): δ 7.32 (m, 4H), 7.27 (m, 5H), 7.20 (m, 1H), 5.43 (dd, 1H, *J* = 7.1), 3.31 (m, 3H), 3.16 (m, 2H), 3.07 (m, 1H), 2.72 (s, 3H).
^{13}C NMR ($CDCl_3$): δ 161.1 (C), 139.5 (C), 138.4 (C), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.9 (CH), 127.6 (CH), 126.4 (CH), 56.6 (CH), 45.3 (CH), 38.5 (CH), 36.9 (CH), 31.5 (CH).
HRMS (ESI+): m/z calcd for $C_{18}H_{21}N_2O$ [MH^+] 281.16484, found 281.16522.

6be dimethyl 2-(1H-pyrazol-1-yl)succinate[11]

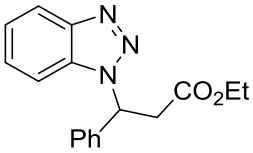


By using method C with 1 bar H_2 at 60°C during 15 h. Colorless oil (0.034 g, 67% yield from 0.236 mmol of enamine), Rf = 0.6, petroleum ether and ethyl acetate solvent mixture using 5% triethylamine (75:20:5).

^{1}H NMR ($CDCl_3$): δ 7.51 (bd, 2H, J = 2.7), 6.26 (bd, 1H, J = 1.8), 5.38 (t, 1H, J = 6.6), 3.72 (bs, 3H, Me), 3.65 (bs, 3H, Me), 3.27 (qd, 2H, J = 1.8).

^{13}C NMR ($CDCl_3$): δ 170.6 (CO), 169.1 (CO), 140.2 (CH), 130.3 (CH), 106.2 (CH), 60.1 (CH), 53.2 (CH_3), 52.3 (CH_3), 36.3 (CH_2).

6ca ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-3-phenylpropanoate



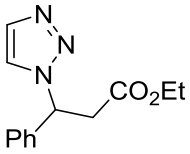
By using method D with 10 bar H_2 at 60°C during 72h. Pale yellow solid (0.024 g, 53% yield from 0.150 mmol of enamine), Rf = 0.8, petroleum ether and ethyl acetate solvent mixture (8:2).

^{1}H NMR ($CDCl_3$): δ 7.98 (d, 1H, J = 8.3), 7.25 (m, 8H), 6.21 (dd, 1H, J = 5.7), 4.01 (q, 2H, J = 7.1), 3.89 (dd, 1H, J = 9.3), 3.29 (dd, 1H, J = 5.7), 1.06 (t, 3H, J = 7.1).

^{13}C NMR ($CDCl_3$): δ 170.1 (C), 146.3 (C), 138.3 (C), 133.1 (C), 129.2 (2CH), 128.8 (CH), 127.5 (CH), 126.9 (2CH), 124.2 (CH), 120.1 (CH), 109.9 (CH), 61.2 (CH_2), 59.6 (CH), 40.5 (CH_2), 14.1 (CH_3).

HRMS (ESI+): m/z calcd for $C_{17}H_{18}N_3O_2$ [MH^+] 296.13935, found 296.13916.

6cb ethyl 3-phenyl-3-(1H-1,2,3-triazol-1-yl)propanoate



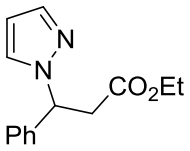
By using method C with 1 bar H_2 at 60°C during 30h. Orange solid (0.074 g, 63% yield from 0.480 mmol of enamine) after filtration over Celite with ethylacetate.

^{1}H NMR ($CDCl_3$): δ 7.64 (bd, 1H, J = 1.5), 7.51 (bs, 1H), 7.29 (5H, m), 6.04 (1H, dd, J = 6.1), 4.07 (bq, 2H, J = 6.8), 3.71 (dd, 1H, J = 9.7), 3.18 (dd, 1H, J = 5.9), 1.14 (t, 3H, J = 6.6).

^{13}C NMR ($CDCl_3$): δ 169.7 (C), 138.1 (C), 133.8 (CH), 129.2 (2CH), 128.9 (CH), 126.9 (2CH), 123.7 (CH), 61.2 (CH), 61.1 (CH_2), 40.3 (CH_2), 14.0 (CH_3).

HRMS (ESI+): m/z calcd for $C_{13}H_{16}N_3O_2$ [MH^+] 246.12370, found 246.12331.

6ce ethyl 3-phenyl-3-(1H-pyrazol-1-yl)propanoate[6]

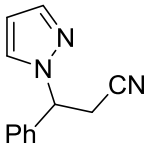


By using method C with 1 bar H_2 at 25°C during 15h. Colorless oil (0.054 g, 53% yield from 0.417 mmol of enamine) after filtration over Celite with ethylacetate.

^{1}H NMR ($CDCl_3$): δ 7.38 (d, 1H, *J* = 1.6), 7.29 (d, 1H, *J* = 2.3), 7.25 (m, 5H, H_{Ar}), 6.21 (t, 1H, *J* = 2.0), 5.80 (dd, 1H, *J* = 5.9), 4.06 (q, 2H, *J* = 7.1), 3.57 (dd, 1H, *J* = 9.2), 3.08 (dd, 1H, *J* = 5.9), 1.12 (t, 3H, *J* = 7.1).

^{13}C NMR ($CDCl_3$): δ 171.5 (C), 139.8 (C), 139.5 (CH), 129.2 (CH), 128.9 (2CH), 128.3 (CH), 126.8 (2CH), 105.7 (CH), 61.9 (CH), 60.9 (CH_2), 40.6 (CH_2), 14.1 (CH_3).

6de 3-phenyl-3-(1H-pyrazol-1-yl)propanenitrile



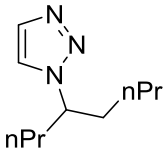
By using method D with 50 bar H_2 at 80°C during 15h. Colorless oil (0.049 g, 85% yield, from 0.294 mmol of enamine) after filtration over Celite with ethylacetate.

^{1}H NMR ($CDCl_3$): δ 7.62 (d, 1H, *J* = 1.5), 7.37 (m, 4H), 7.29 (m, 2H), 6.30 (t, 1H, *J* = 2.1), 5.60 (t, 1H, *J* = 7.2), 3.58 (dd, 1H, *J* = 7.8), 3.26 (dd, 1H, *J* = 6.7).

^{13}C NMR ($CDCl_3$): δ 140.3 (CH), 137.6 (C), 129.6 (CH), 129.3 (CH), 126.8 (CH), 116.9 (C, CN), 106.6 (CH), 61.7 (CH), 24.7 (CH_2).

HRMS (ESI+): m/z calcd for $C_{12}H_{12}N_3$ [MH^+] 198.10257, found 198.10239.

6gc 1-(octan-4-yl)-1H-1,2,3-triazole



By using method D with 50 bar H_2 at 80°C during 72 h. Colorless oil (volatile) (0.074 g, 84% yield from 0.490 mmol of enamine) after filtration over Celite with ethylacetate.

^{1}H NMR ($CDCl_3$): δ 7.65 (bs, 1H), 7.47 (bs, 1H), 4.48 (m, 1H), 1.80 (m, 4H), 1.16 (m, 5H), 0.75 (m, 7H).

^{13}C NMR ($CDCl_3$): δ 133.6 (CH), 121.7 (CH), 61.9 (CH), 37.9 (CH_2), 35.5 (CH_2), 28.1 (CH_2), 22.2 (CH_2), 19.2 (CH_2), 13.8 (CH_3), 13.6 (CH_3).

HRMS (ESI+): m/z calcd for $C_{10}H_{20}N_3$ [MH^+] 182.16517, found 182.16536.

IV) NMR study of $^{3}J(^{1}H\text{-}^{15}N)$ coupling constants and of ^{15}N chemical shifts.

Figure S1: ^{15}N chemical shifts δ (ppm) of aza-heterocycles according the bibliography.[12,13]

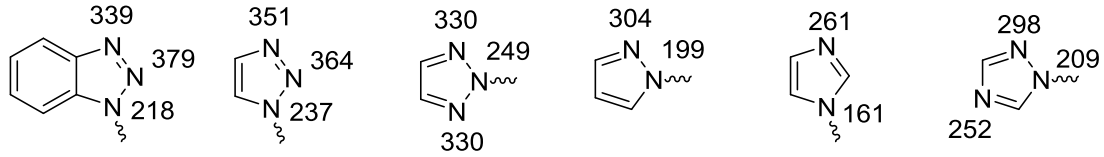
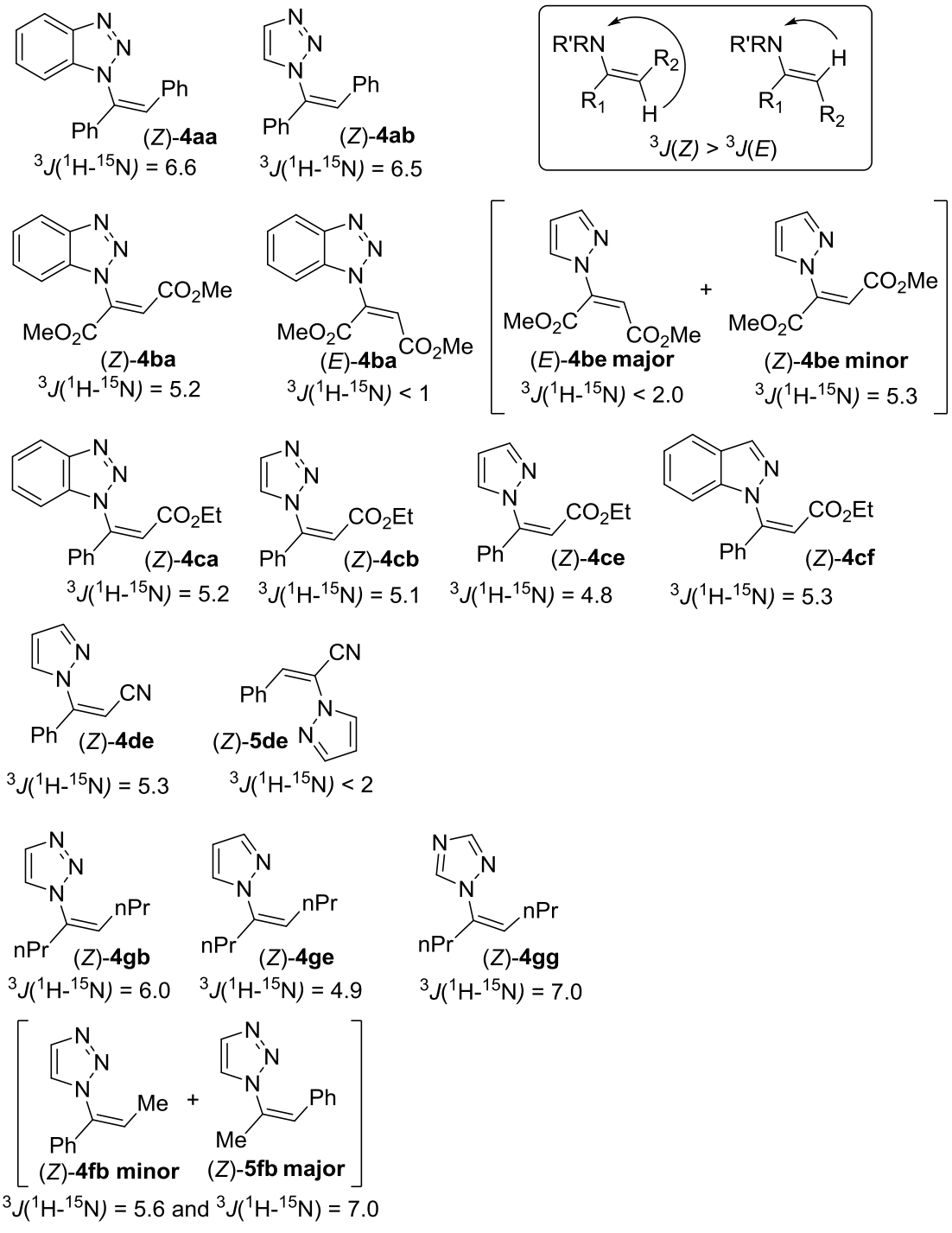
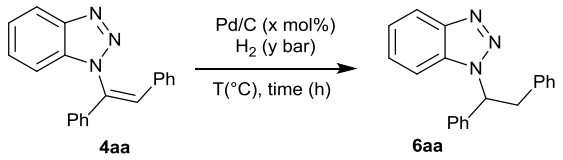


Figure S2. Study of the $^{3}J(^{1}H\text{-}^{15}N)$ coupling constants of the enamines 4 and 5.[14]



V) Hydrogenation of enamines 4: screening of the reaction conditions.

Table S1. Screening of the hydrogenation conditions of enamine 4aa.



4aa **6aa**

Entry	Solvent	Catalyst loading (mol%)	T. (°C)	H_2 (bar)	t (h)	Yield (%)[a]
1	EtOH	1.4	RT	1	3	36
2	THF	1.4	RT	1	3	26[b]
3	AcOEt	1.4	RT	1	3	35
4	AcOEt	1.4	RT	1	15	100
5	EtOH	1.4	RT	1	15	100[b]
6	AcOEt	1.4	60	5	3	42
7	AcOEt	1	RT	1	15	100
8	EtOH	1	RT	1	15	97[b]

[a] GC yield. [b] several by-products were formed.

VI) References

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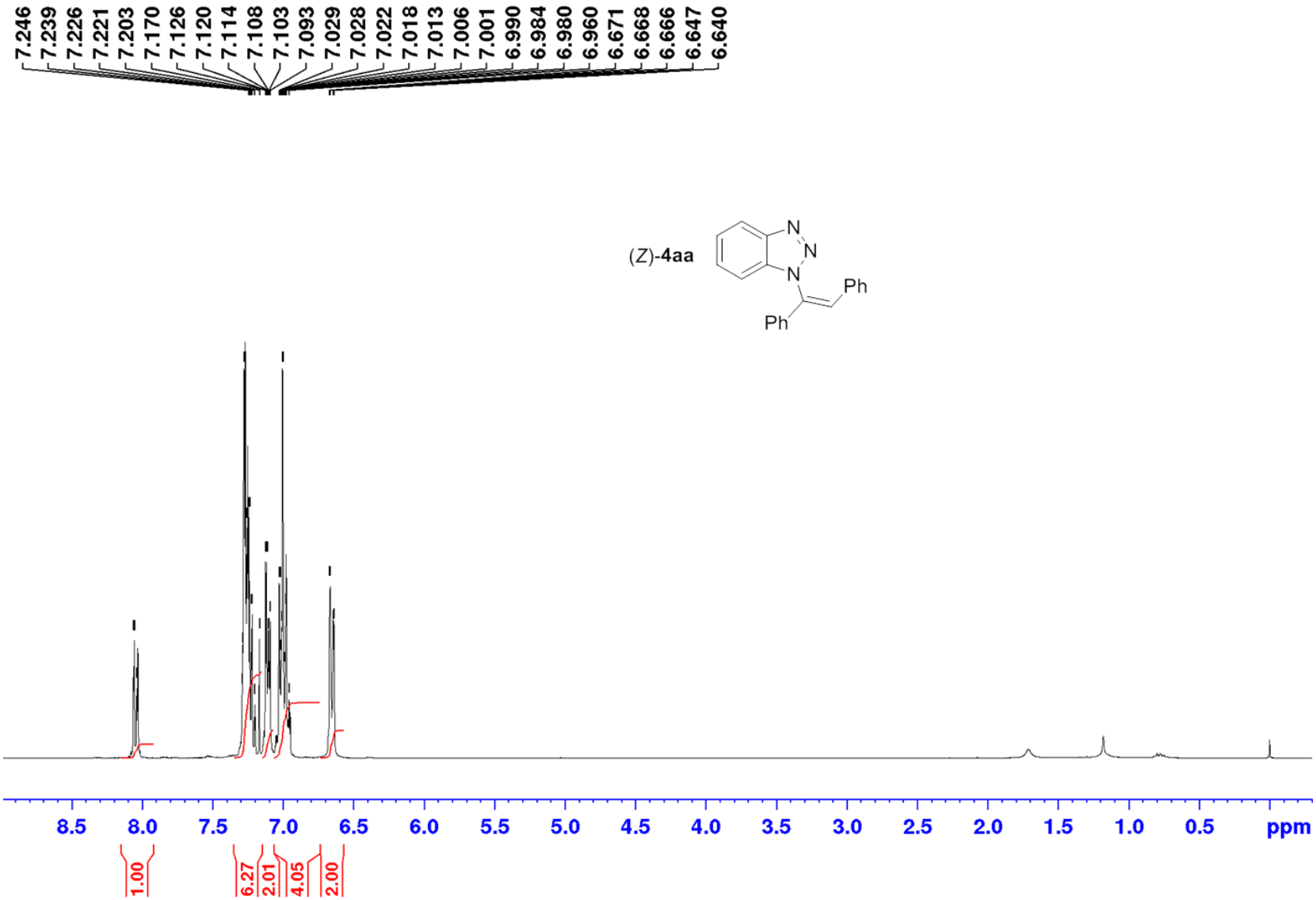
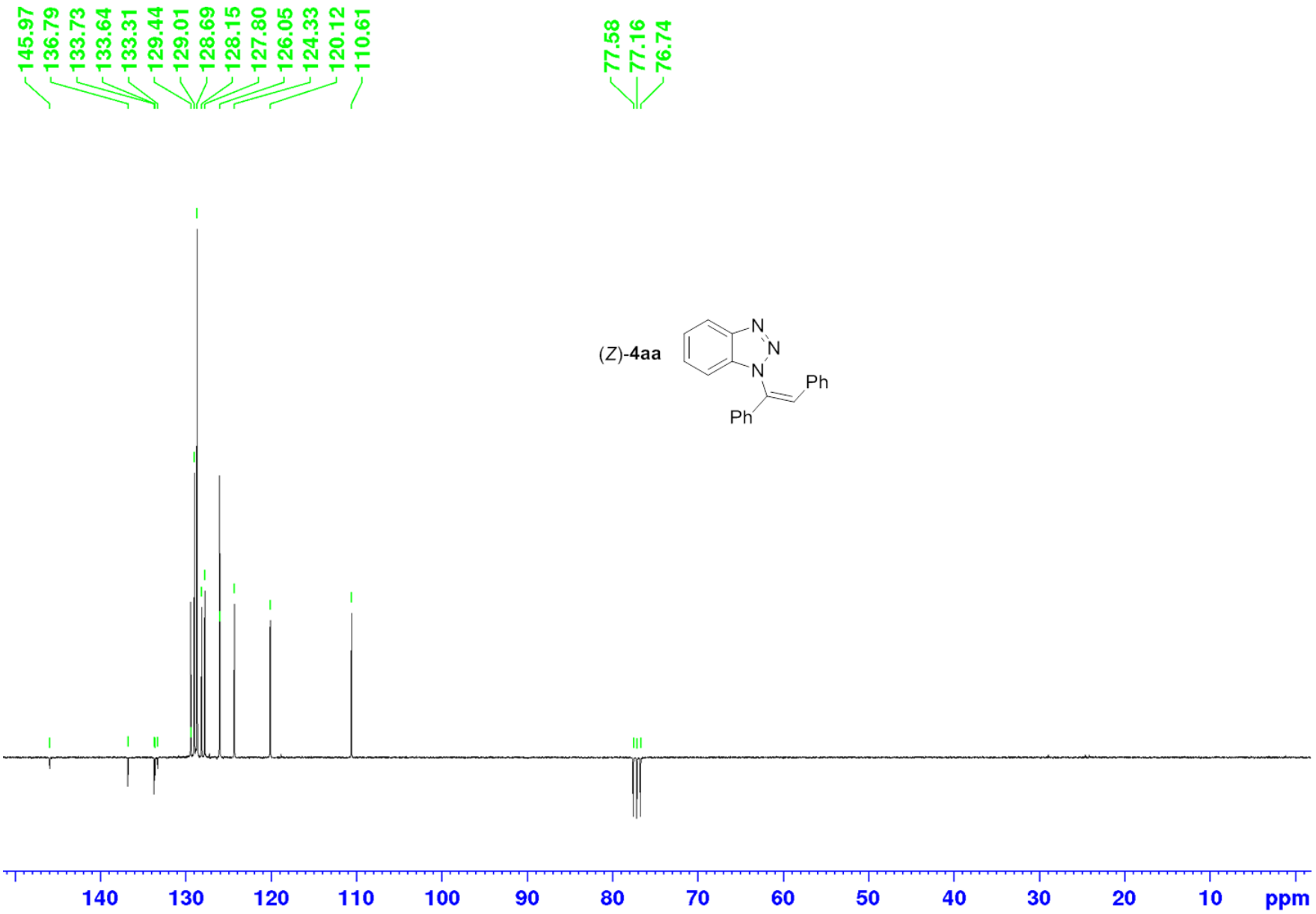
VII) ^{1}H, ^{13}C NMR spectra of isolated compounds.

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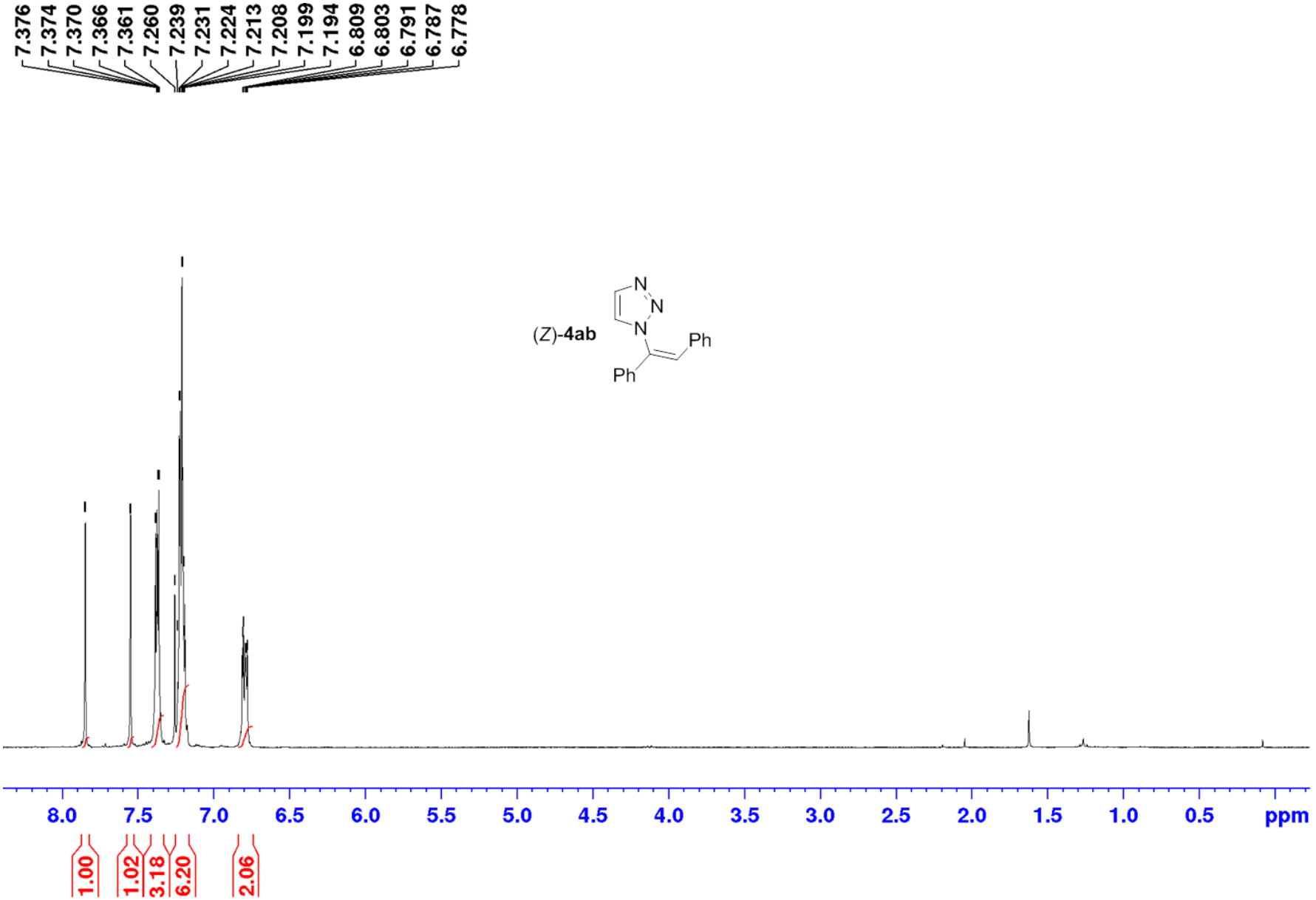
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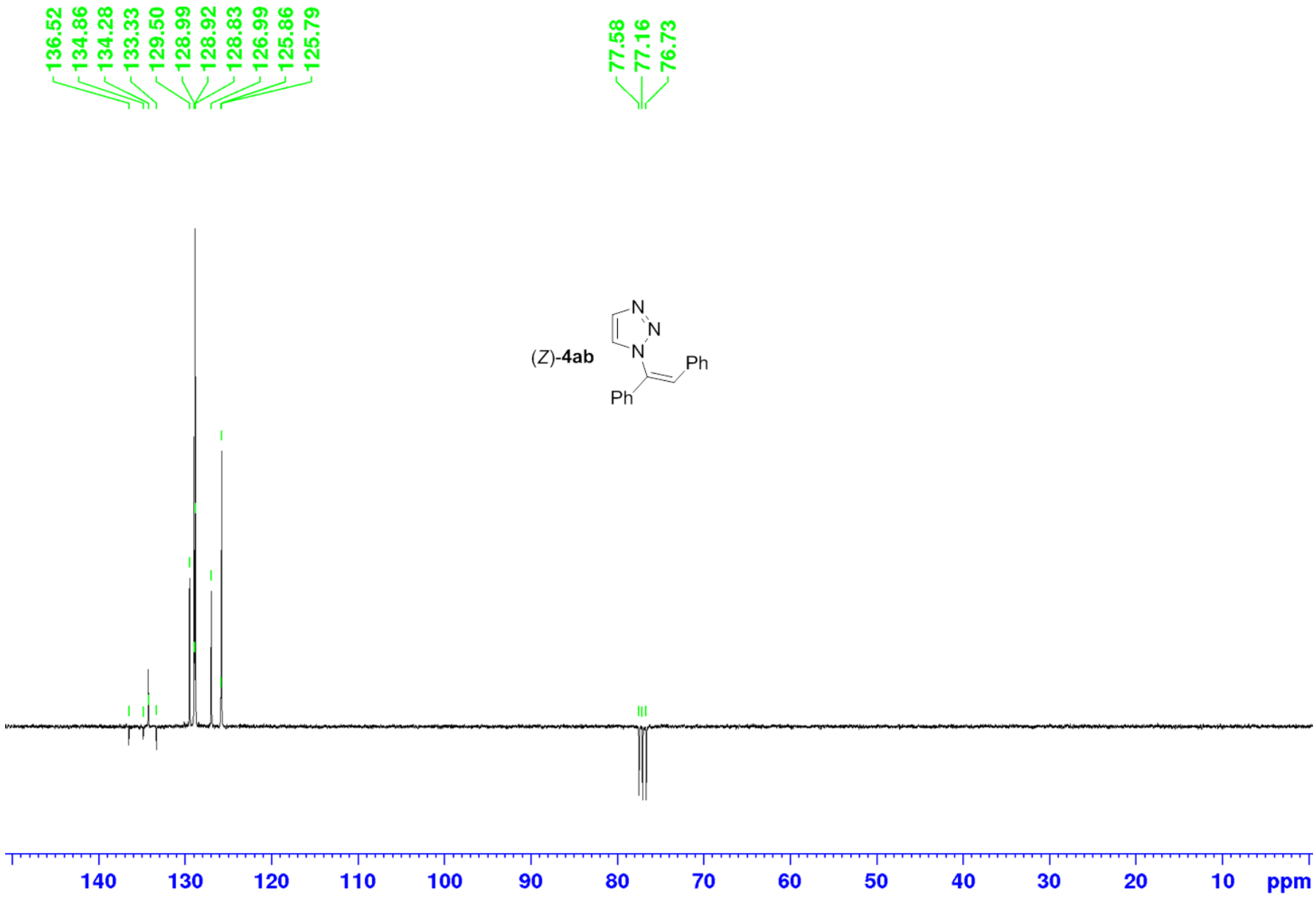
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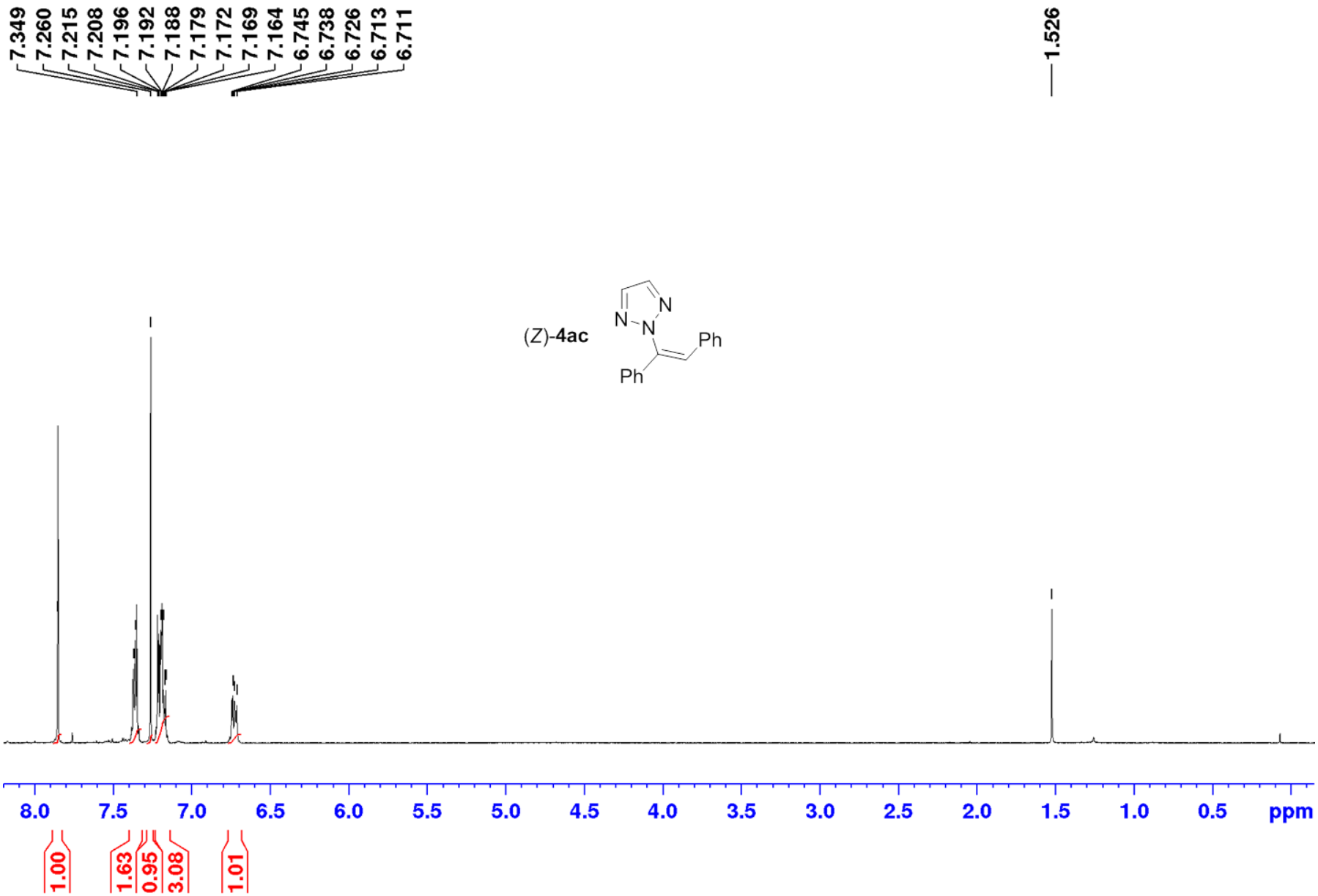
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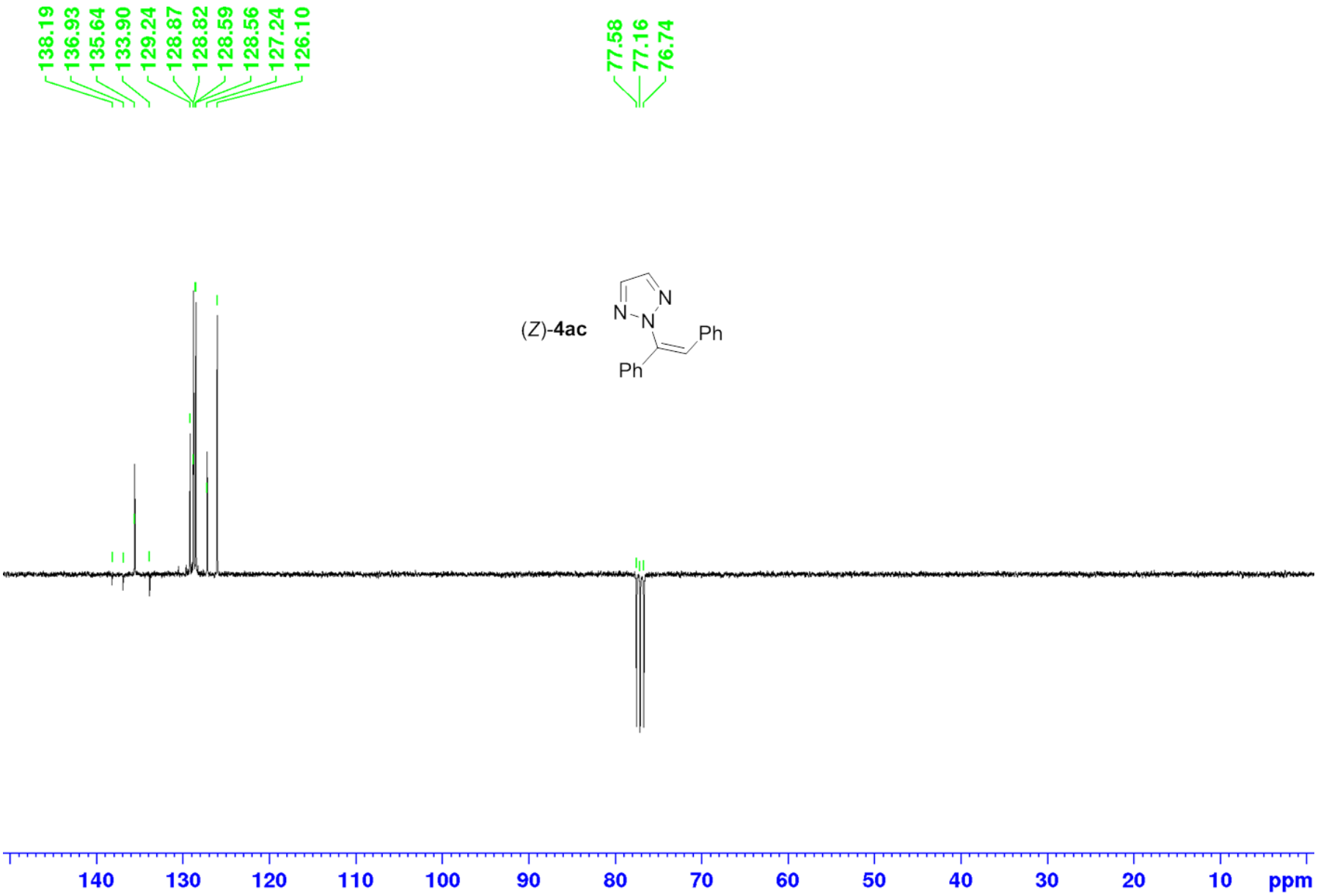
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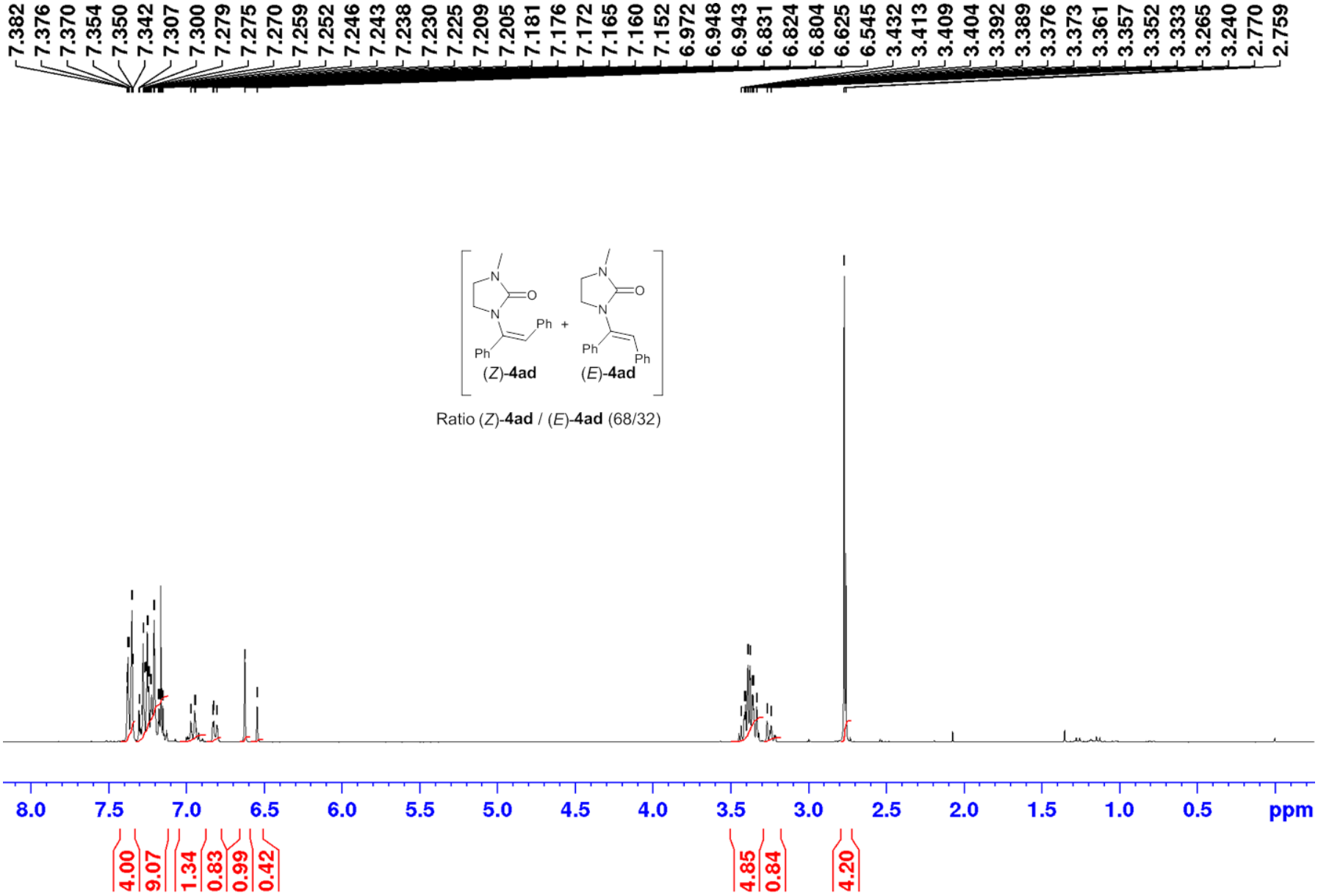
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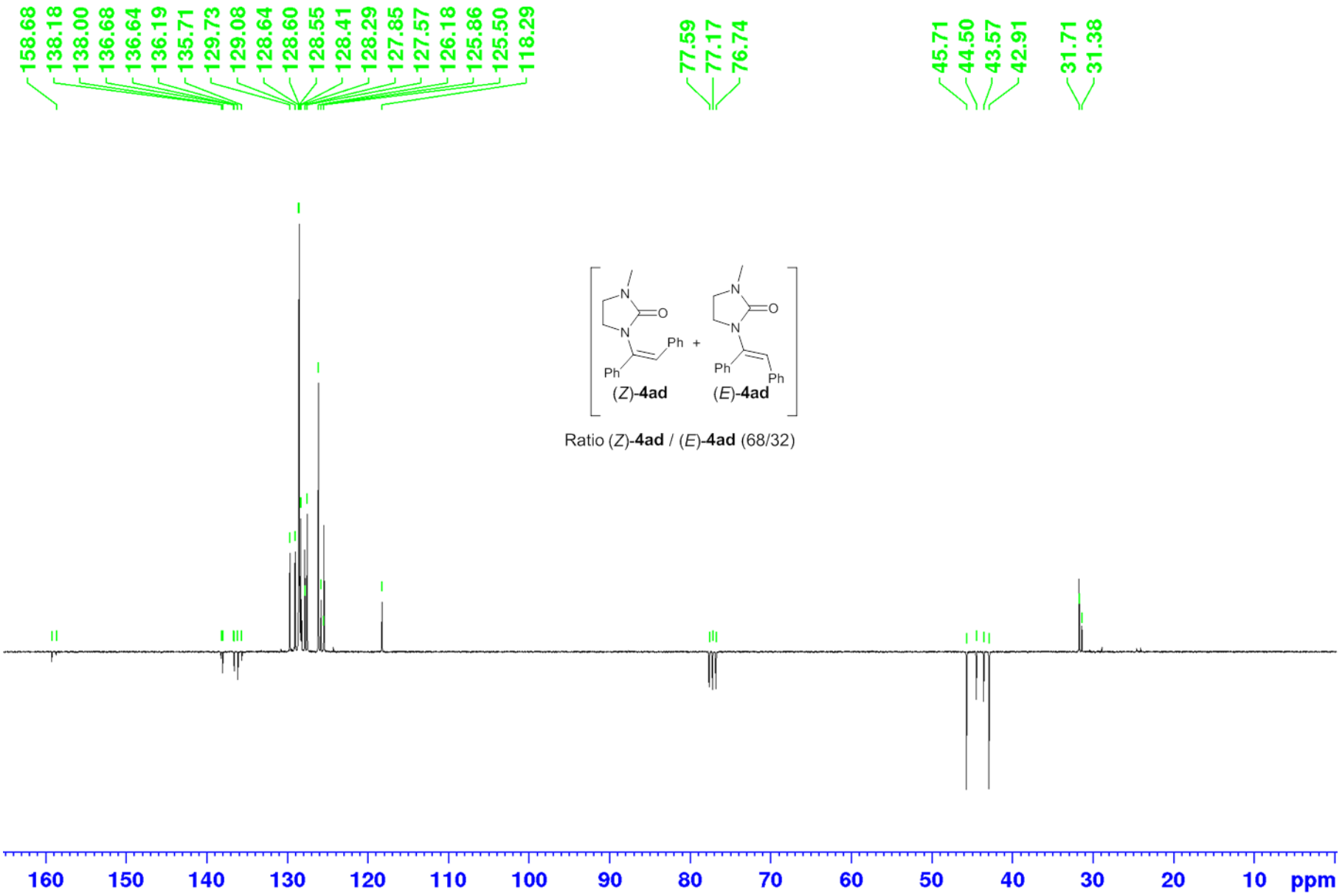
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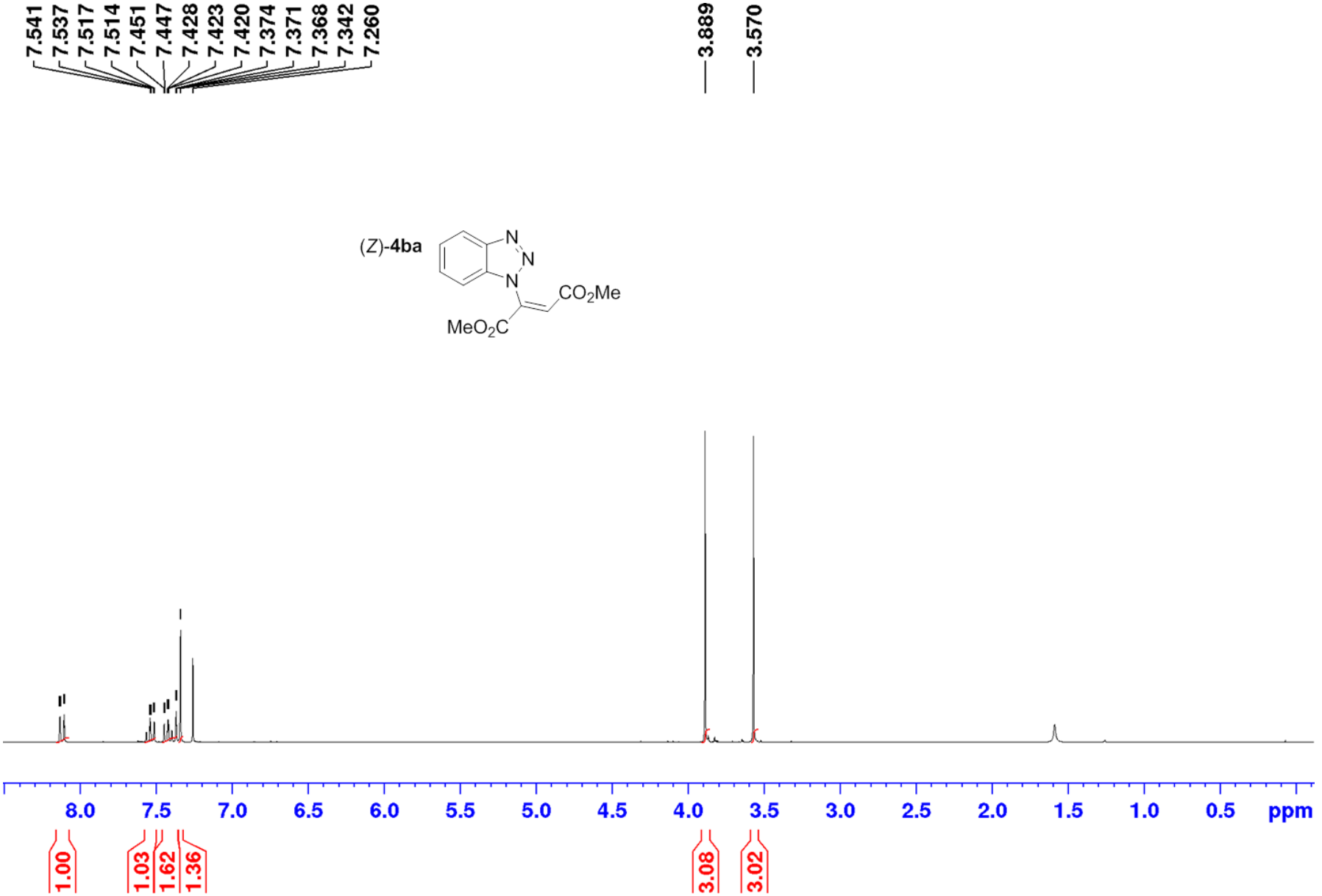
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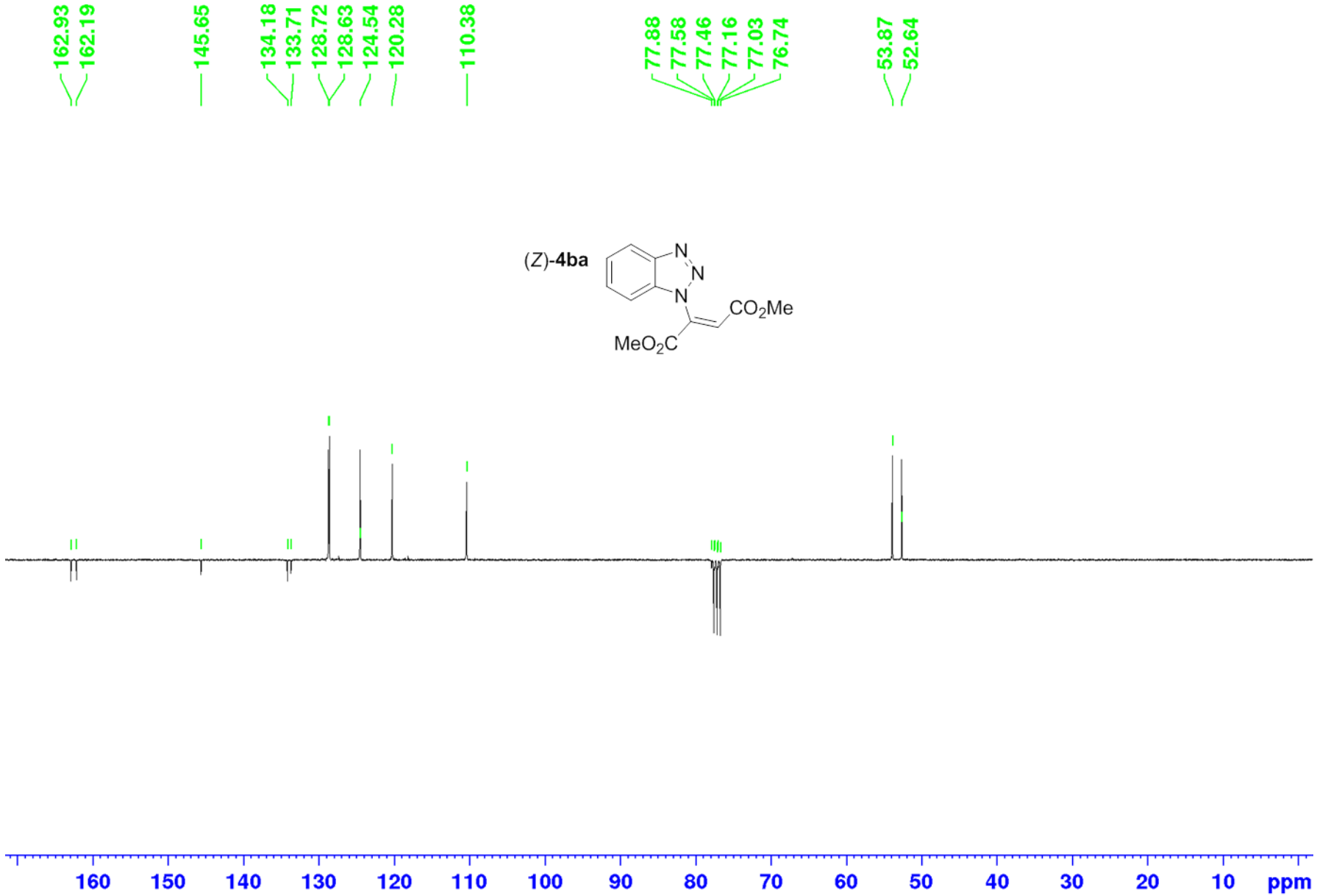
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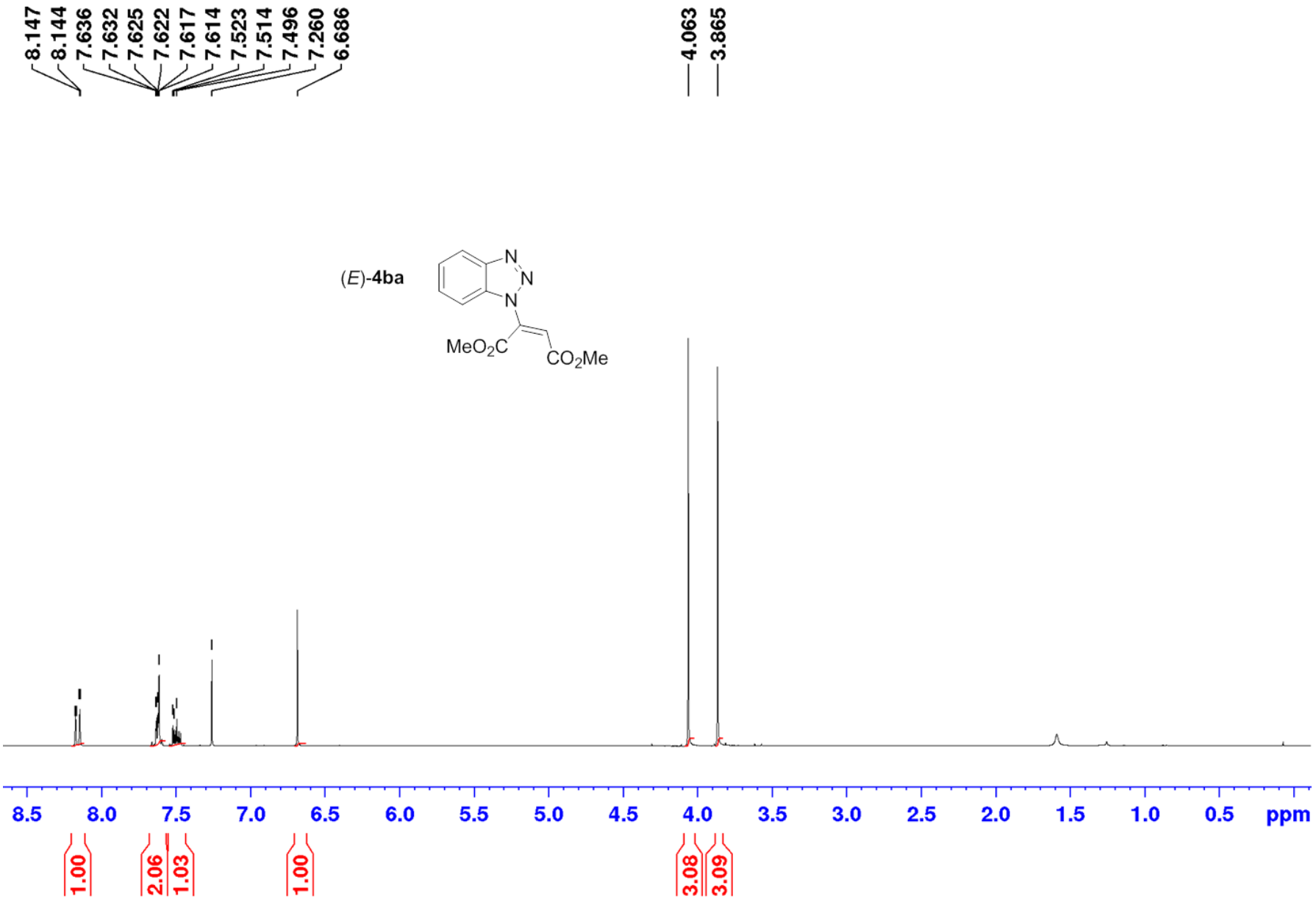
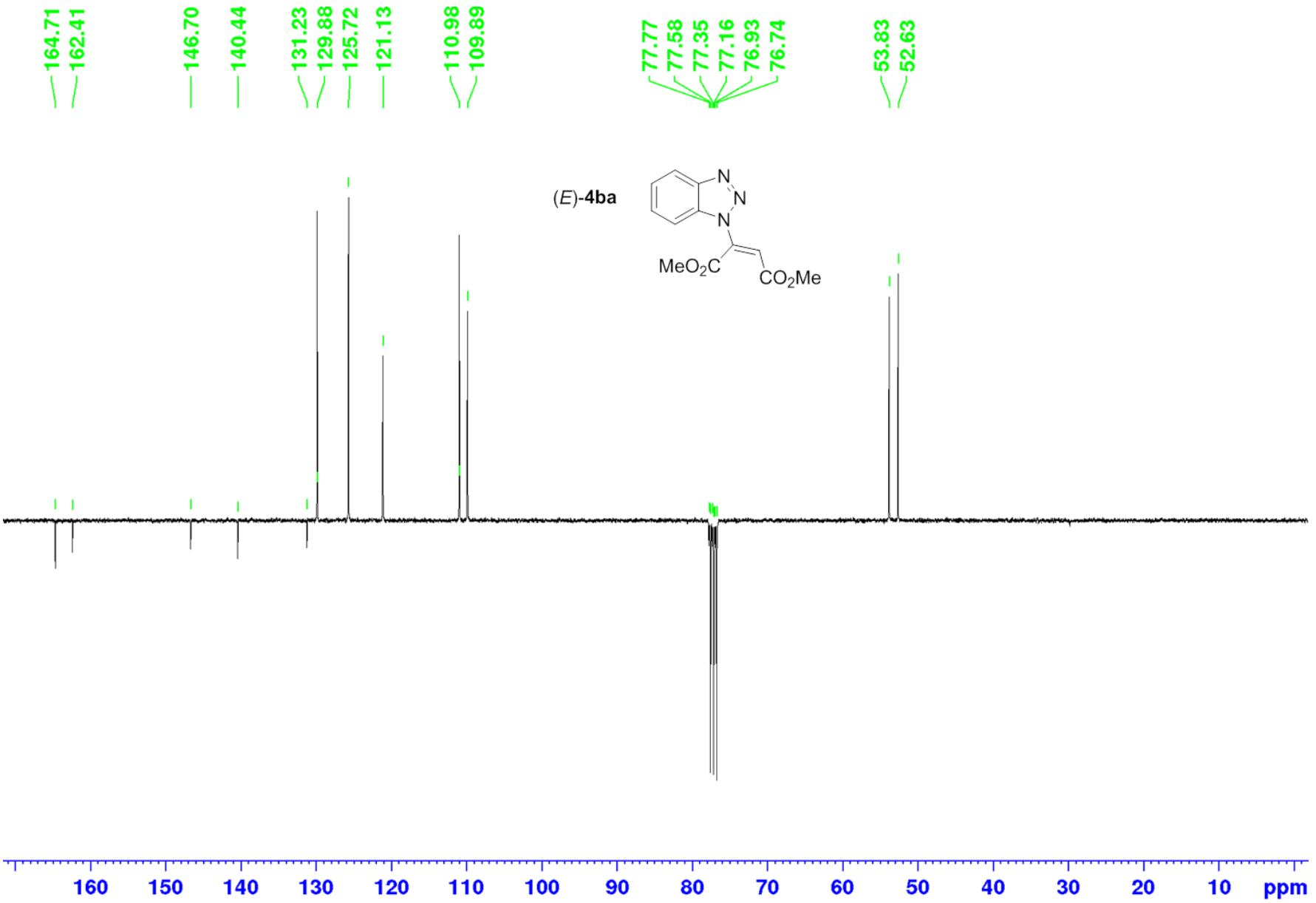
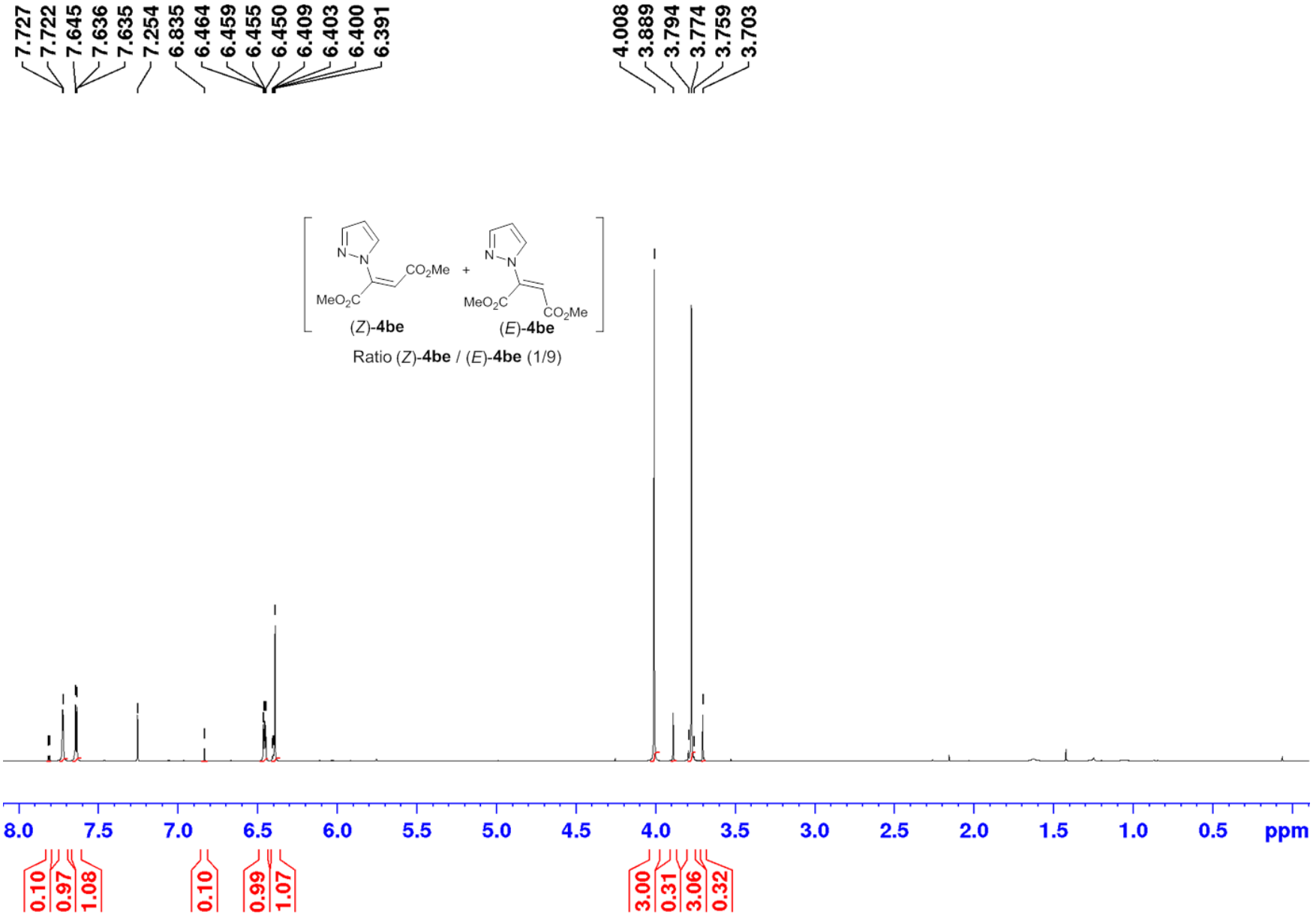
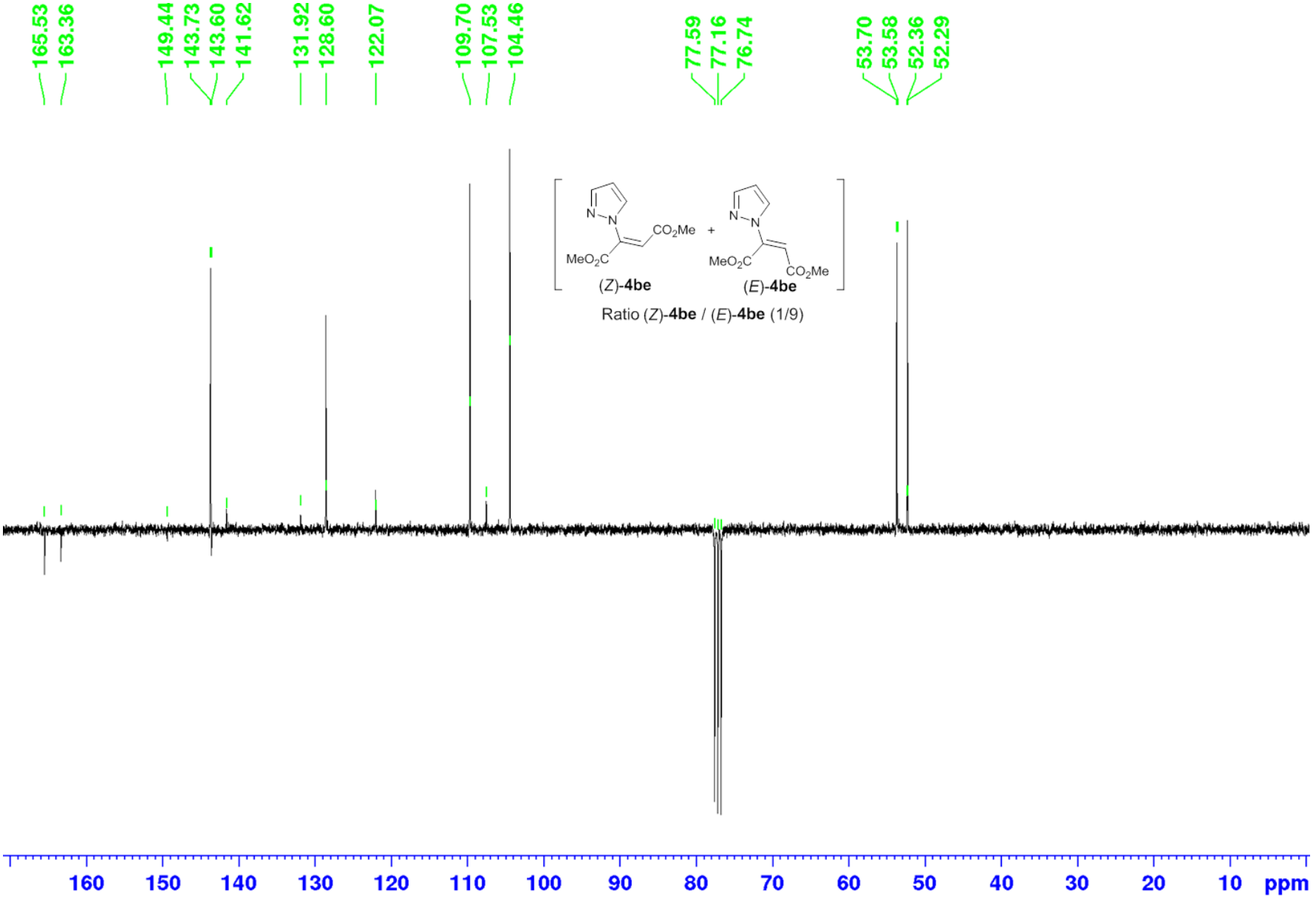
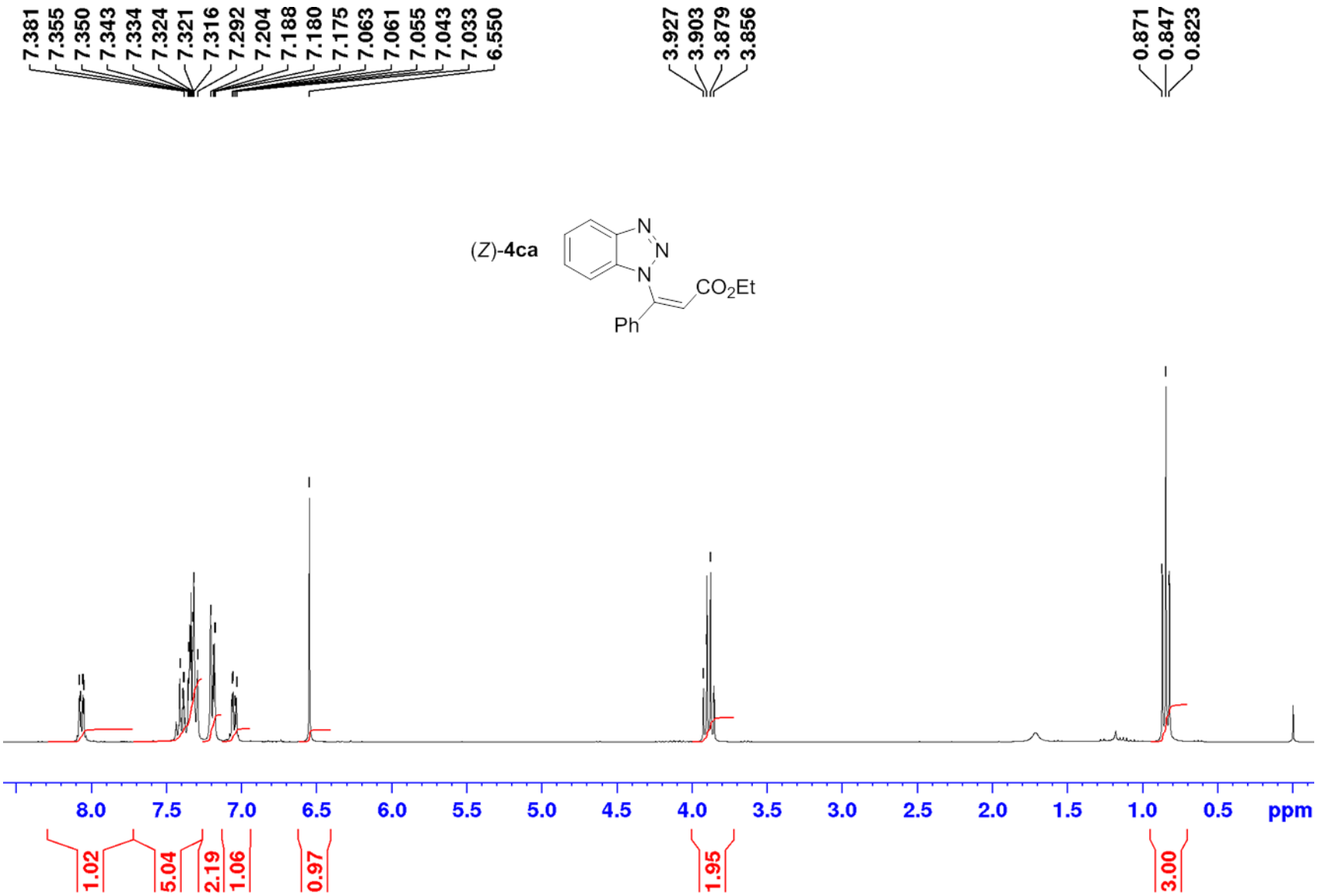
53.87
52.64
(Z)-4ba
N
N
N
CO2Me
MeO2C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

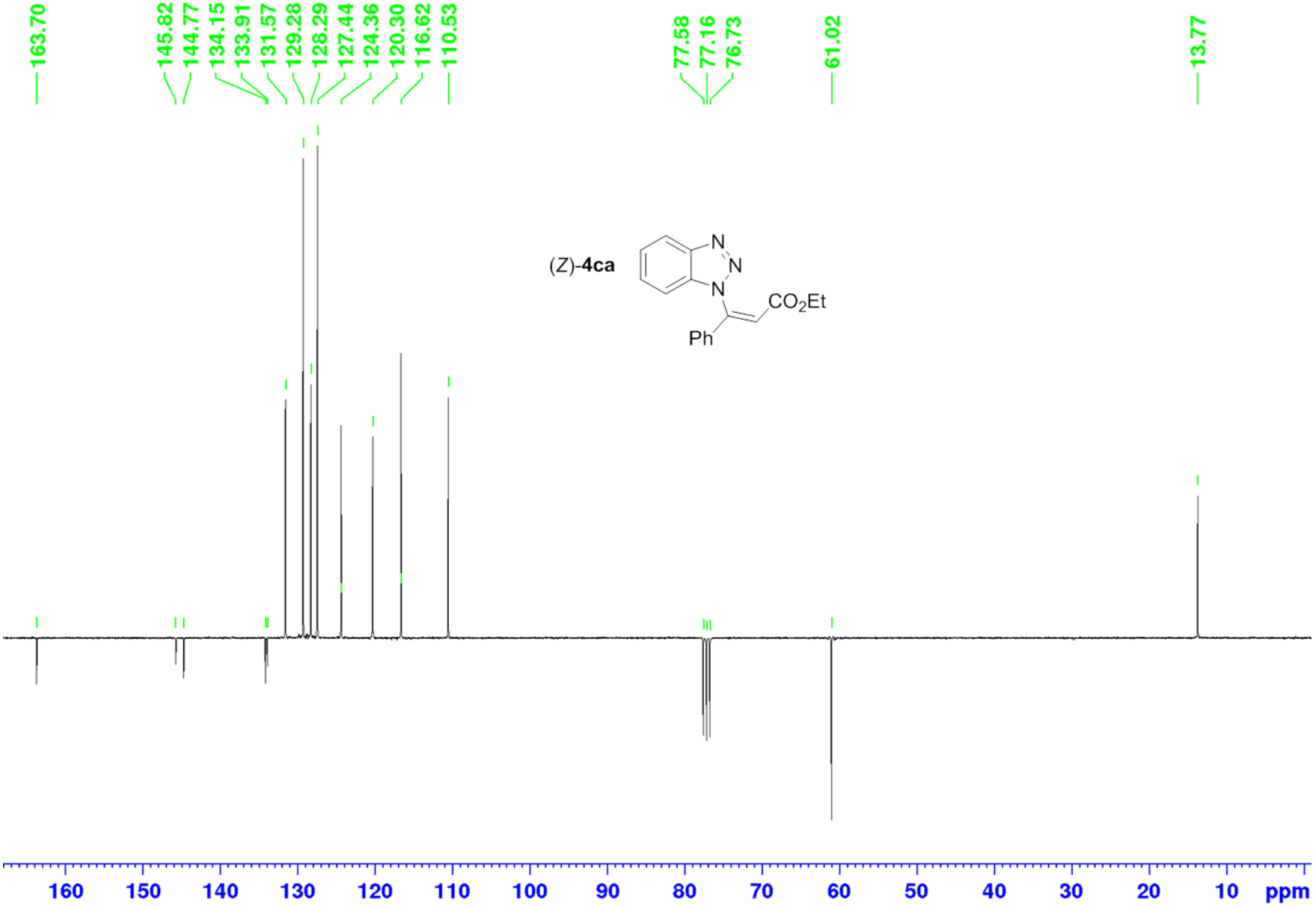

8.147
8.144
7.636
7.632
7.625
7.622
7.617
7.614
7.523
7.514
7.496
7.260
6.686
4.063
3.865
(E)-4ba
N
N
N
MeO2C
CO2Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.06
1.03
1.00
3.08
3.09

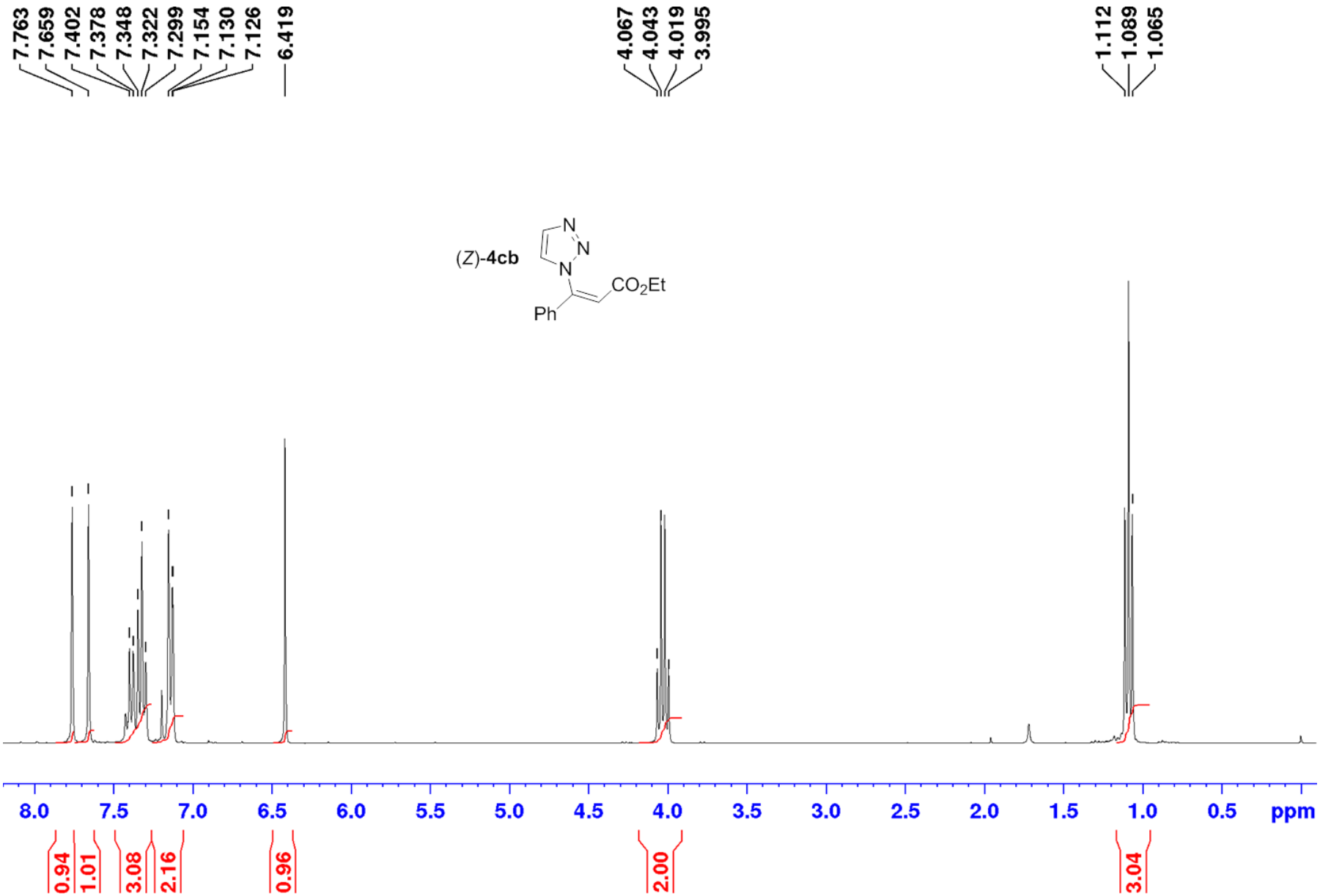

164.71
162.41
146.70
140.44
131.23
129.88
125.72
121.13
110.98
109.89
77.77
77.58
77.35
77.16
76.93
76.74
53.83
52.63
(E)-4ba
N
N
N
MeO2C
CO2Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

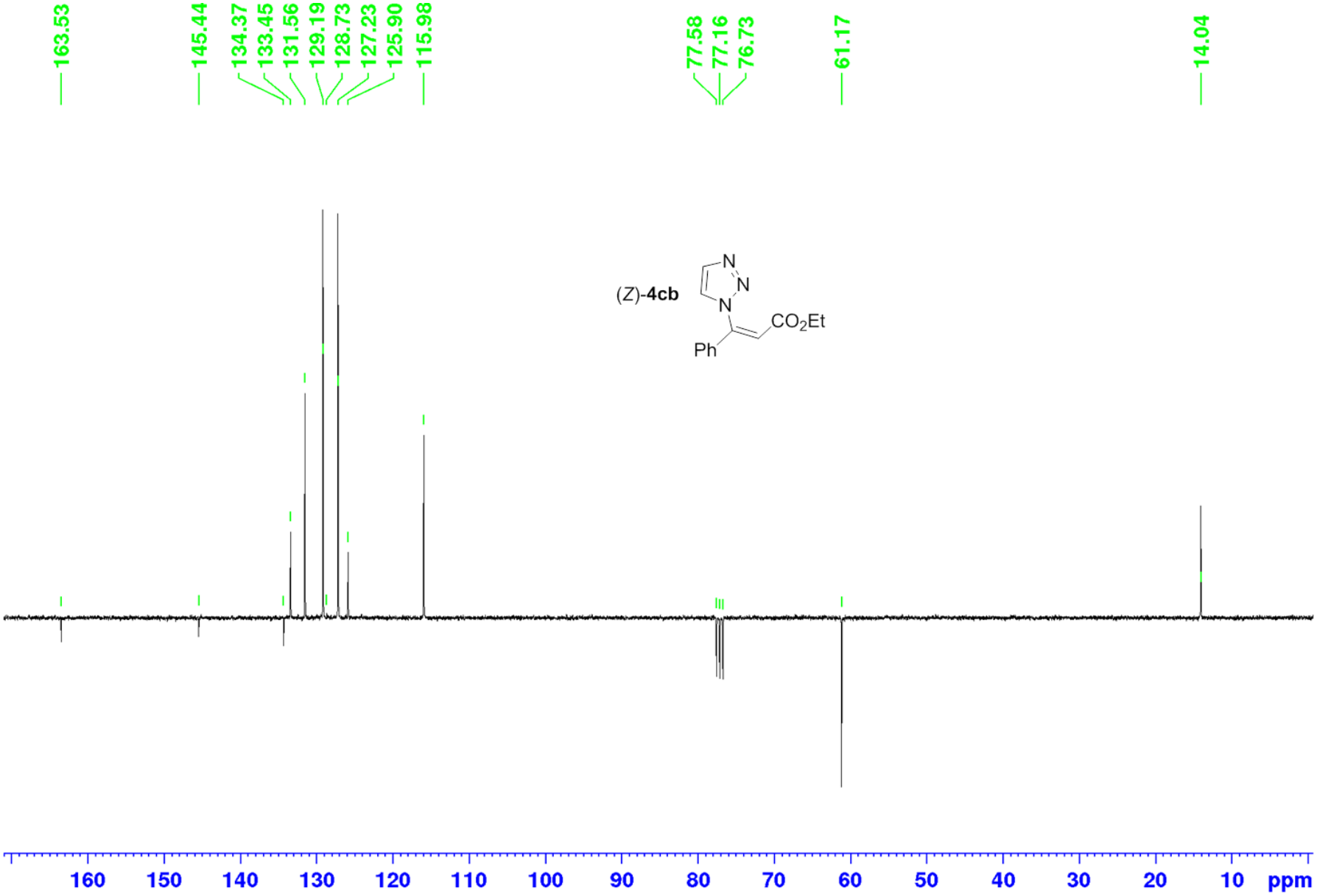

7.727
7.722
7.645
7.636
7.635
7.254
6.835
6.464
6.459
6.455
6.450
6.409
6.403
6.400
6.391
4.008
3.889
3.794
3.774
3.759
3.703
(Z)-4be
(E)-4be
Ratio (Z)-4be / (E)-4be (1/9)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.10
0.97
1.08
0.10
0.99
1.07
3.00
0.31
3.06
0.32

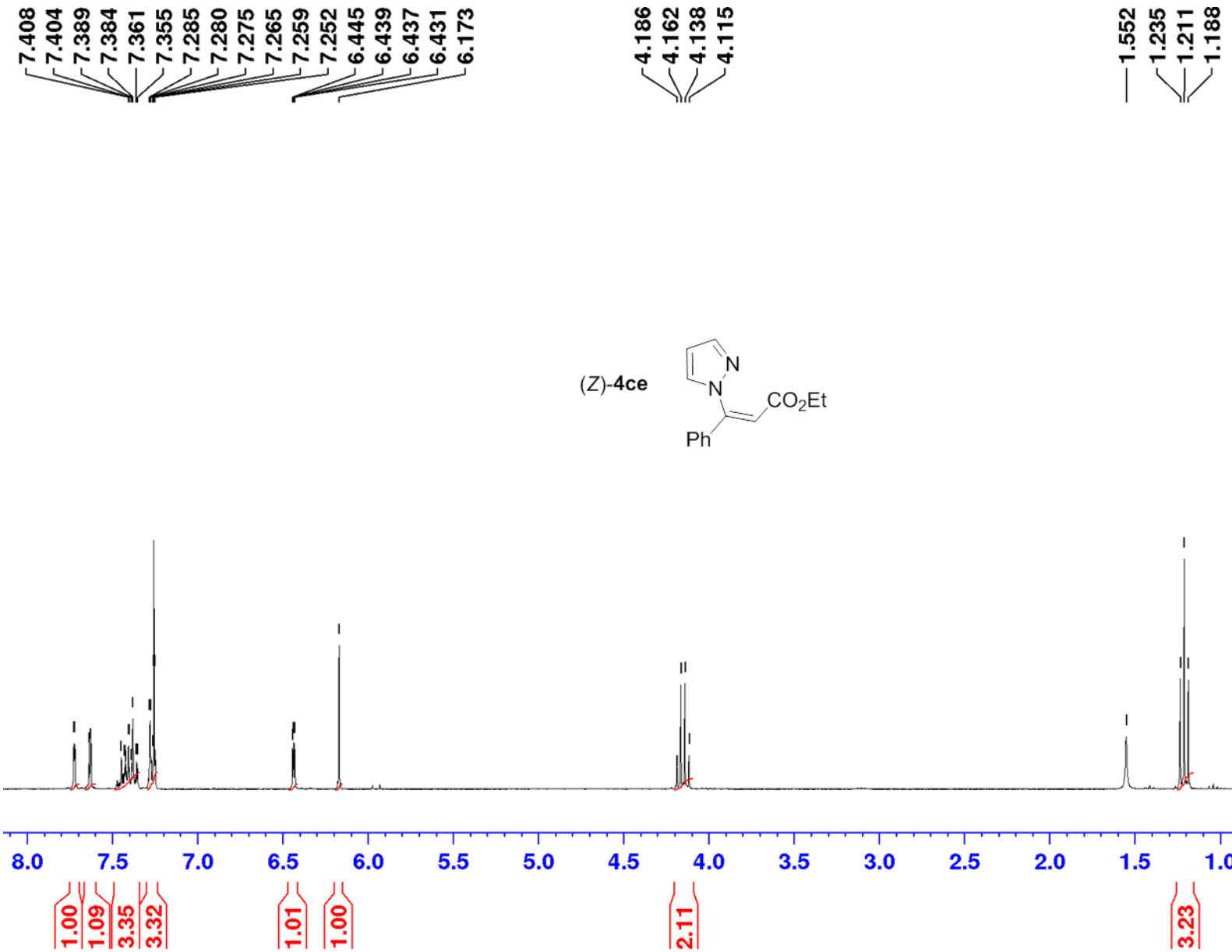

165.53
163.36
149.44
143.73
143.60
141.62
131.92
128.60
122.07
109.70
107.53
104.46
77.59
77.16
76.74
53.70
53.58
52.36
52.29
CO2Me
MeO2C
(Z)-4be
(E)-4be
Ratio (Z)-4be / (E)-4be (1/9)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

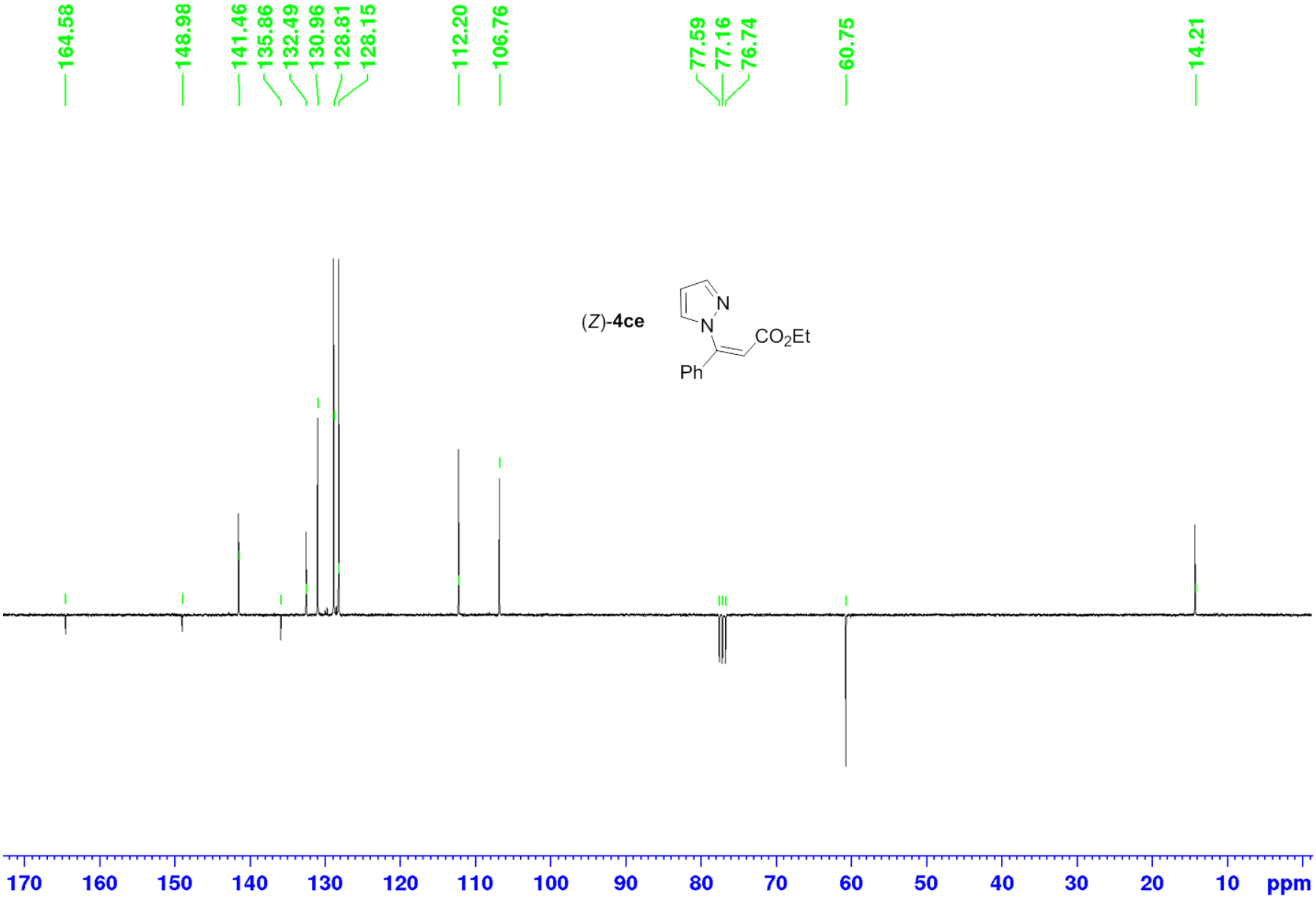

7.381
7.355
7.350
7.343
7.334
7.324
7.321
7.316
7.292
7.204
7.188
7.180
7.175
7.063
7.061
7.055
7.043
7.033
6.550
3.927
3.903
3.879
3.856
0.871
0.847
0.823
(Z)-4ca
N
N
N
CO2Et
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
5.04
2.19
1.06
0.97
1.95
3.00

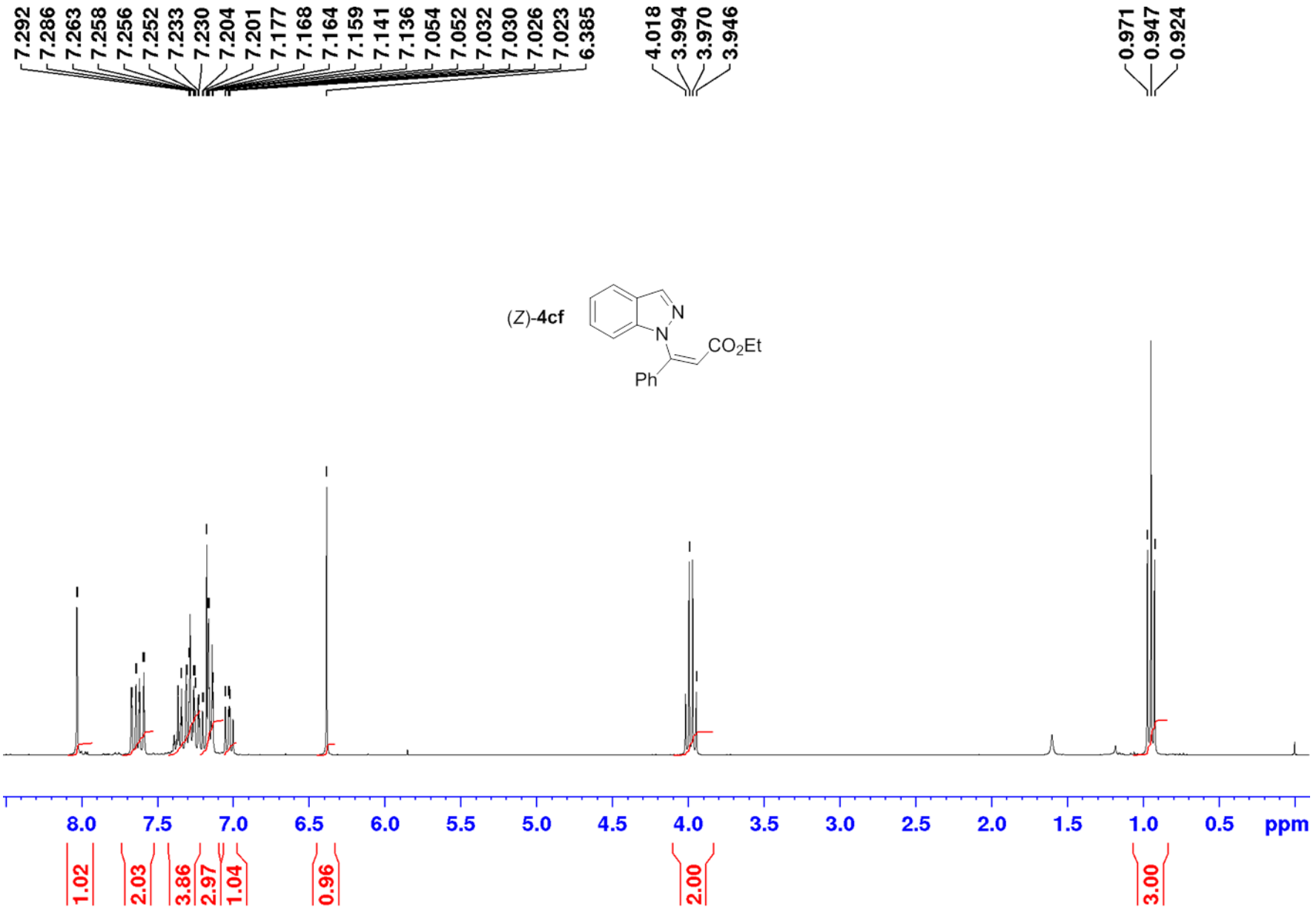

163.70
145.82
144.77
134.15
133.91
131.57
129.28
128.29
127.44
124.36
120.30
116.62
110.53
77.58
77.16
76.73
61.02
13.77
(Z)-4ca
N
N
N
CO2Et
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

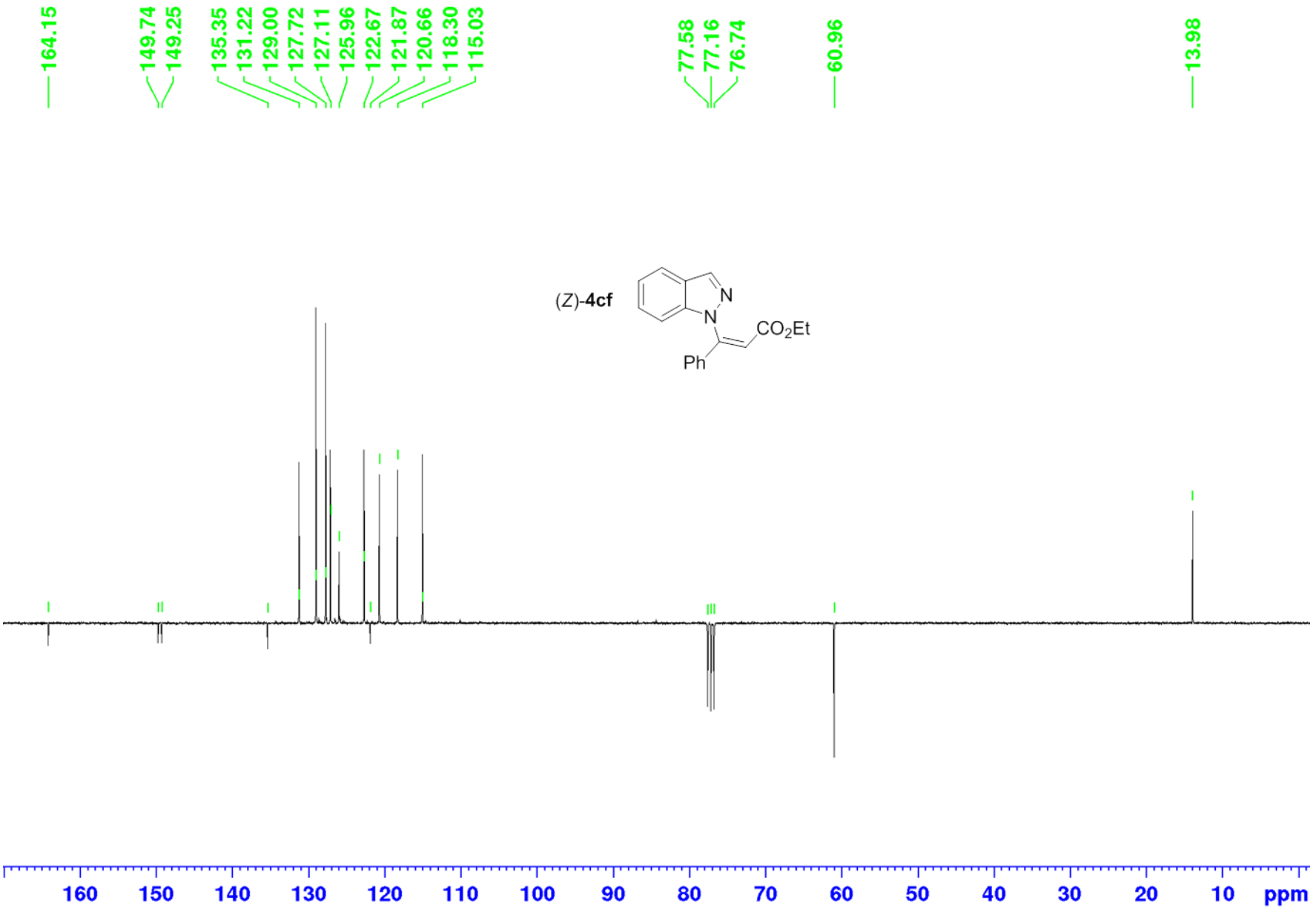

7.763
7.659
7.402
7.378
7.348
7.322
7.299
7.154
7.130
7.126
6.419
4.067
4.043
4.019
3.995
1.112
1.089
1.065
(Z)-4cb
N
N
N
CO2Et
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.94
1.01
3.08
2.16
0.96
2.00
3.04

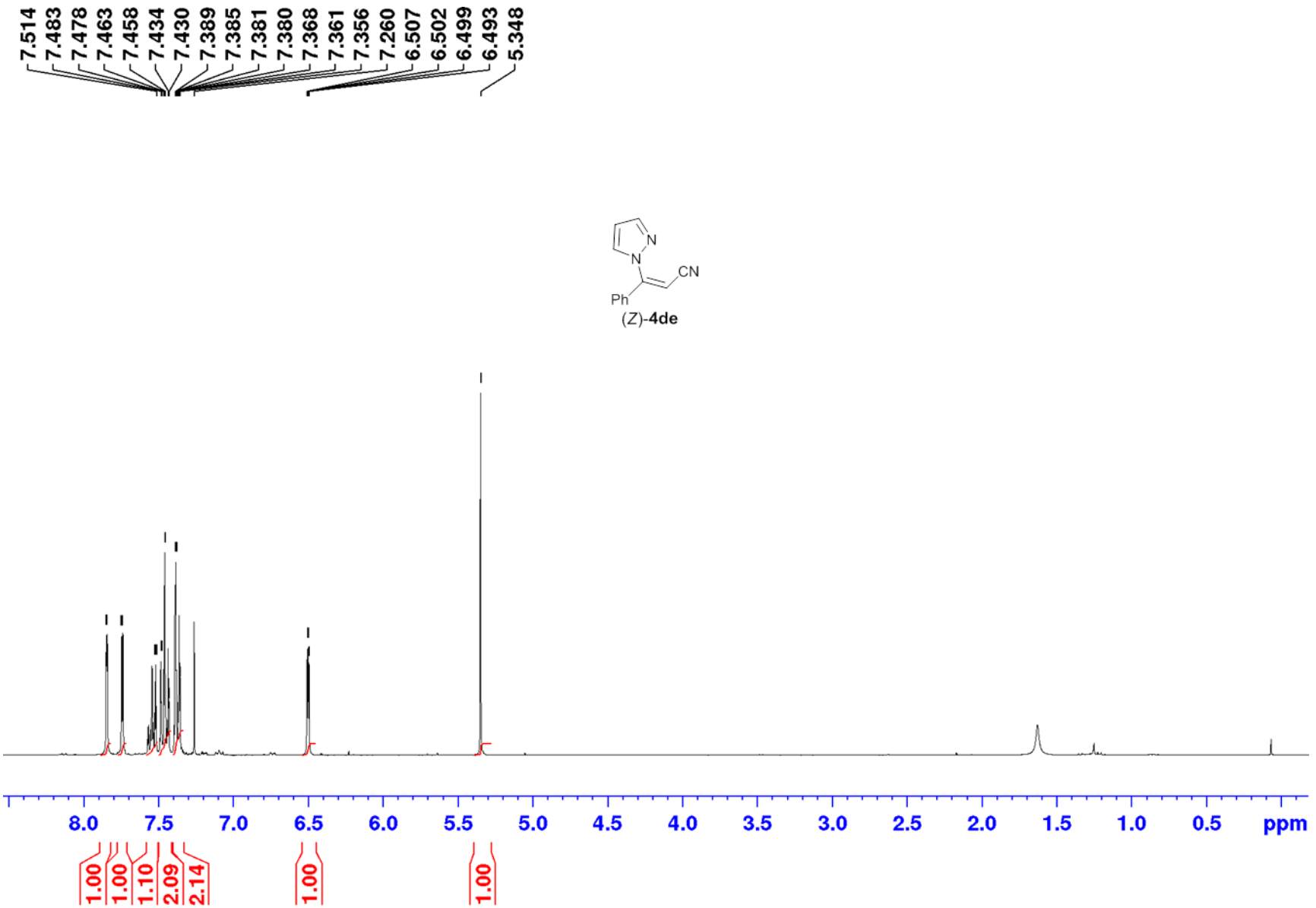

163.53
145.44
134.37
133.45
131.56
129.19
128.73
127.23
125.90
115.98
77.58
77.16
76.73
61.17
14.04
(Z)-4cb
N
N
N
CO2Et
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

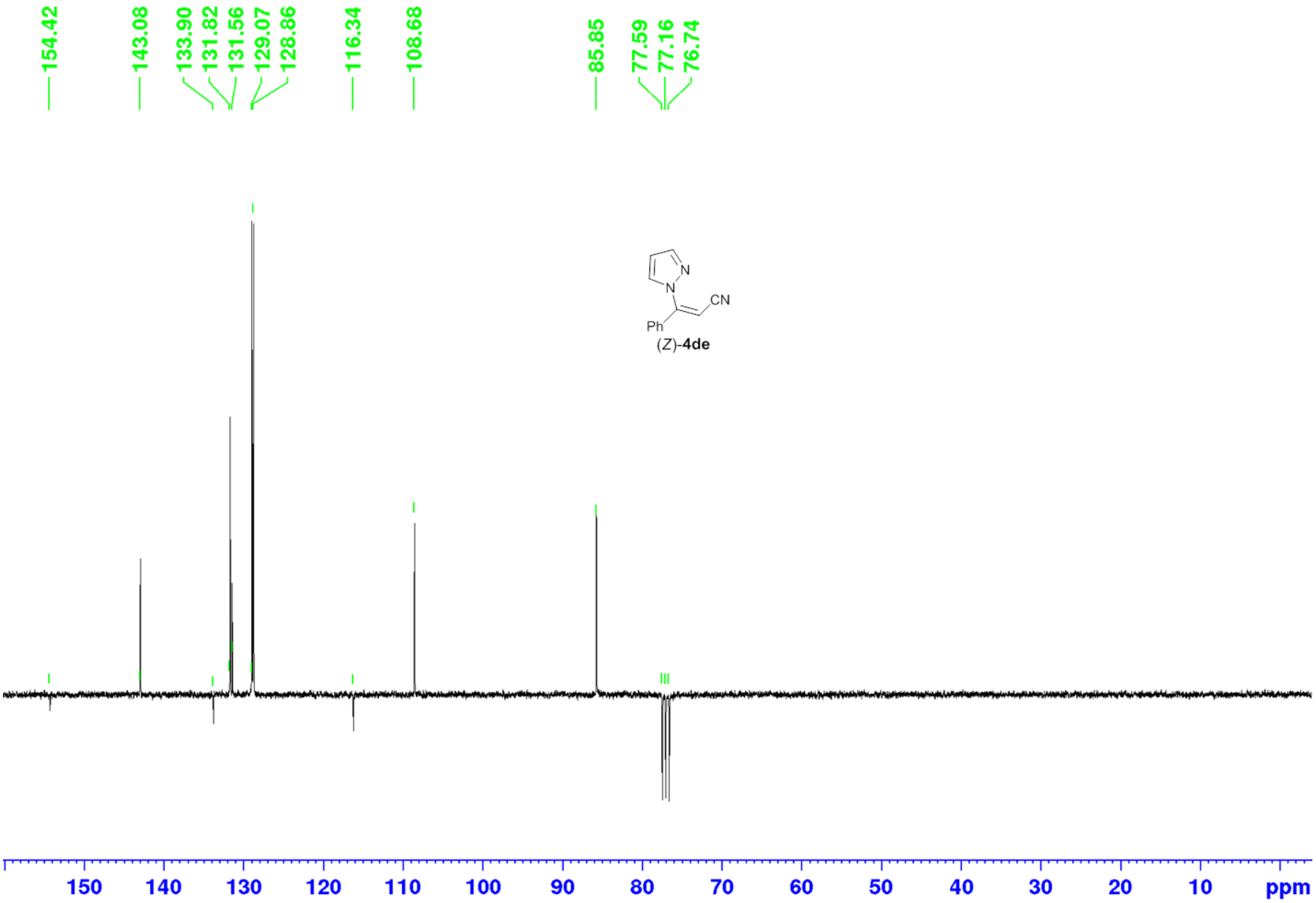

7.408
7.404
7.389
7.384
7.361
7.355
7.285
7.280
7.275
7.265
7.259
7.252
6.445
6.439
6.437
6.431
6.173
4.186
4.162
4.138
4.115
1.552
1.235
1.211
1.188
(Z)-4ce
N
N
CO2Et
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.09
3.35
3.32
1.01
1.00
2.11
3.23

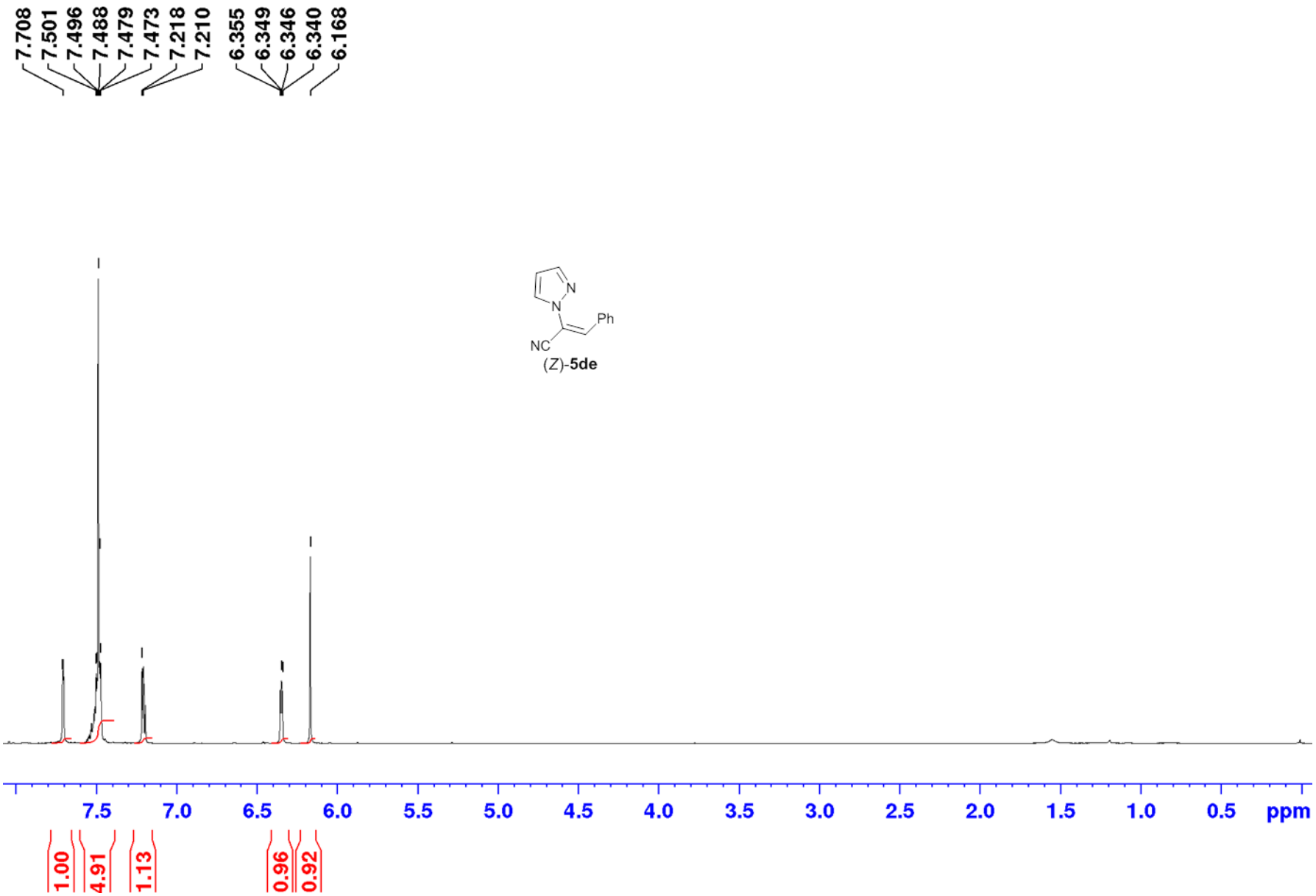

164.58
148.98
141.46
135.86
132.49
130.96
128.81
128.15
112.20
106.76
77.59
77.16
76.74
60.75
14.21
(Z)-4ce
N
N
CO2Et
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

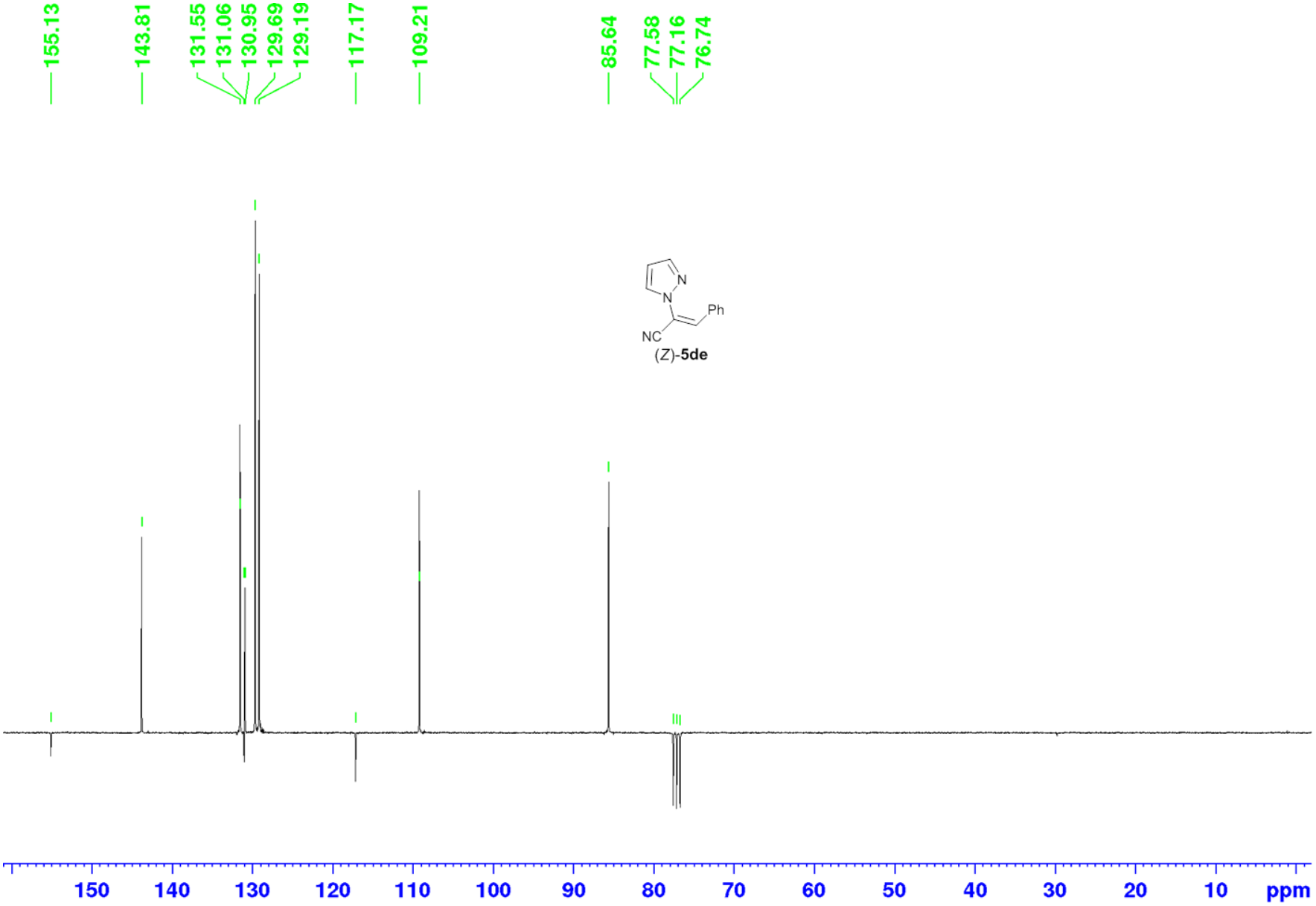

7.292
7.286
7.263
7.258
7.256
7.252
7.233
7.230
7.204
7.201
7.177
7.168
7.164
7.159
7.141
7.136
7.054
7.052
7.032
7.030
7.026
7.023
6.385
4.018
3.994
3.970
3.946
0.971
0.947
0.924
(Z)-4cf
N
N
CO2Et
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
2.03
3.86
2.97
1.04
0.96
2.00
3.00

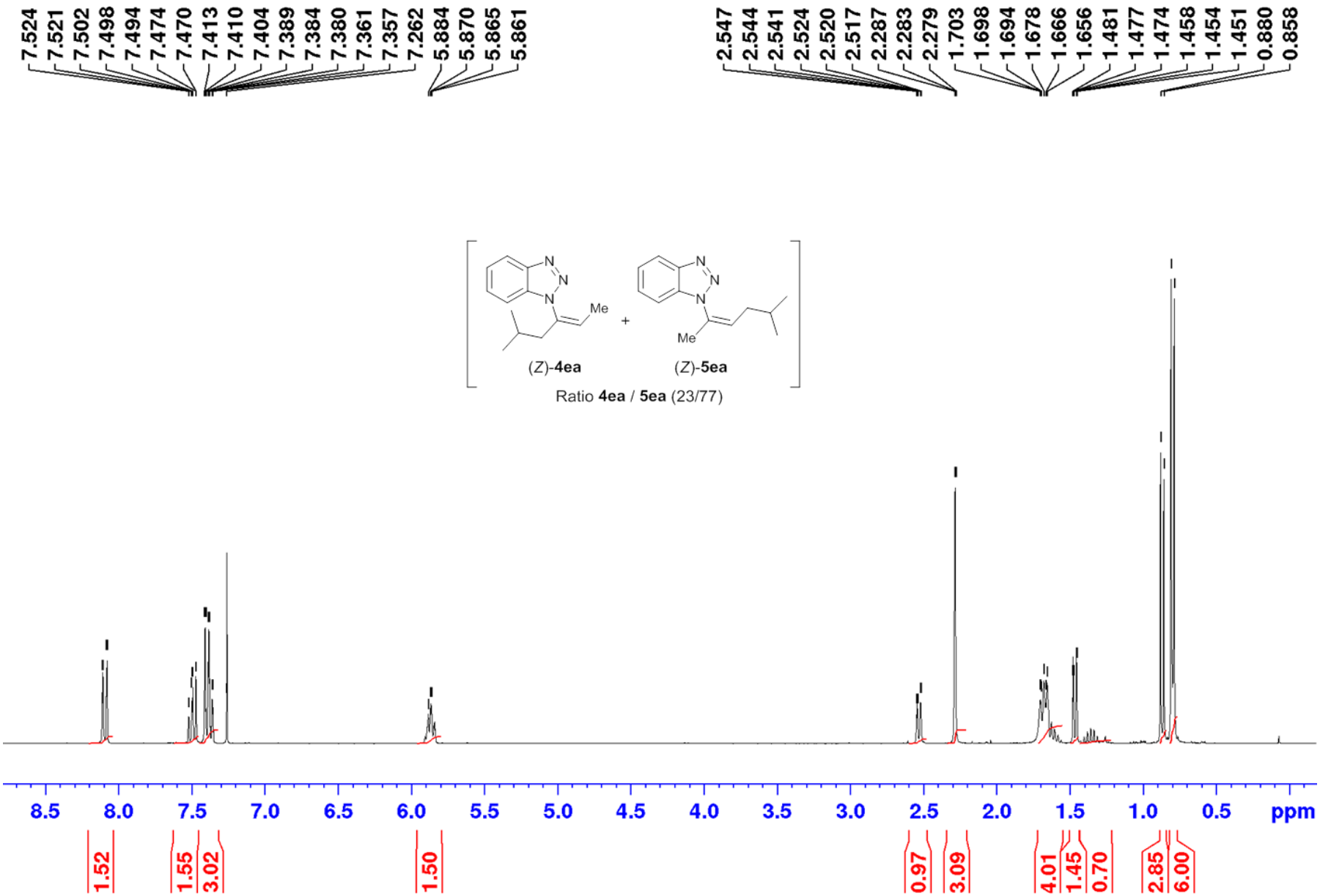

164.15
149.74
149.25
135.35
131.22
129.00
127.72
127.11
125.96
122.67
121.87
120.66
118.30
115.03
77.58
77.16
76.74
60.96
13.98
(Z)-4cf
N
N
CO2Et
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

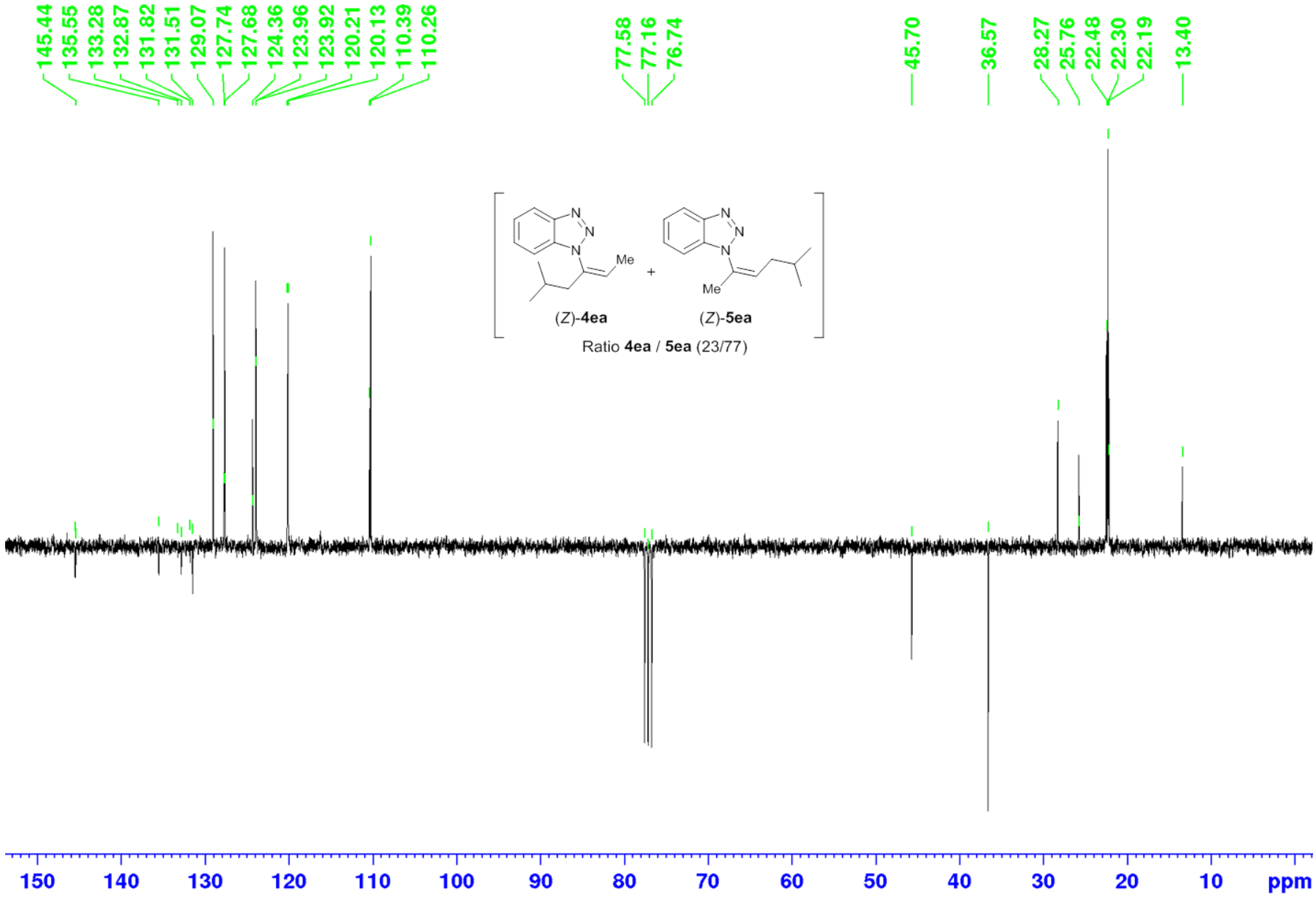

7.514
7.483
7.478
7.463
7.458
7.434
7.430
7.389
7.385
7.381
7.380
7.368
7.361
7.356
7.260
6.507
6.502
6.499
6.493
5.348
N
N
CN
Ph
(Z)-4de
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.00
1.10
2.09
2.14
1.00
1.00

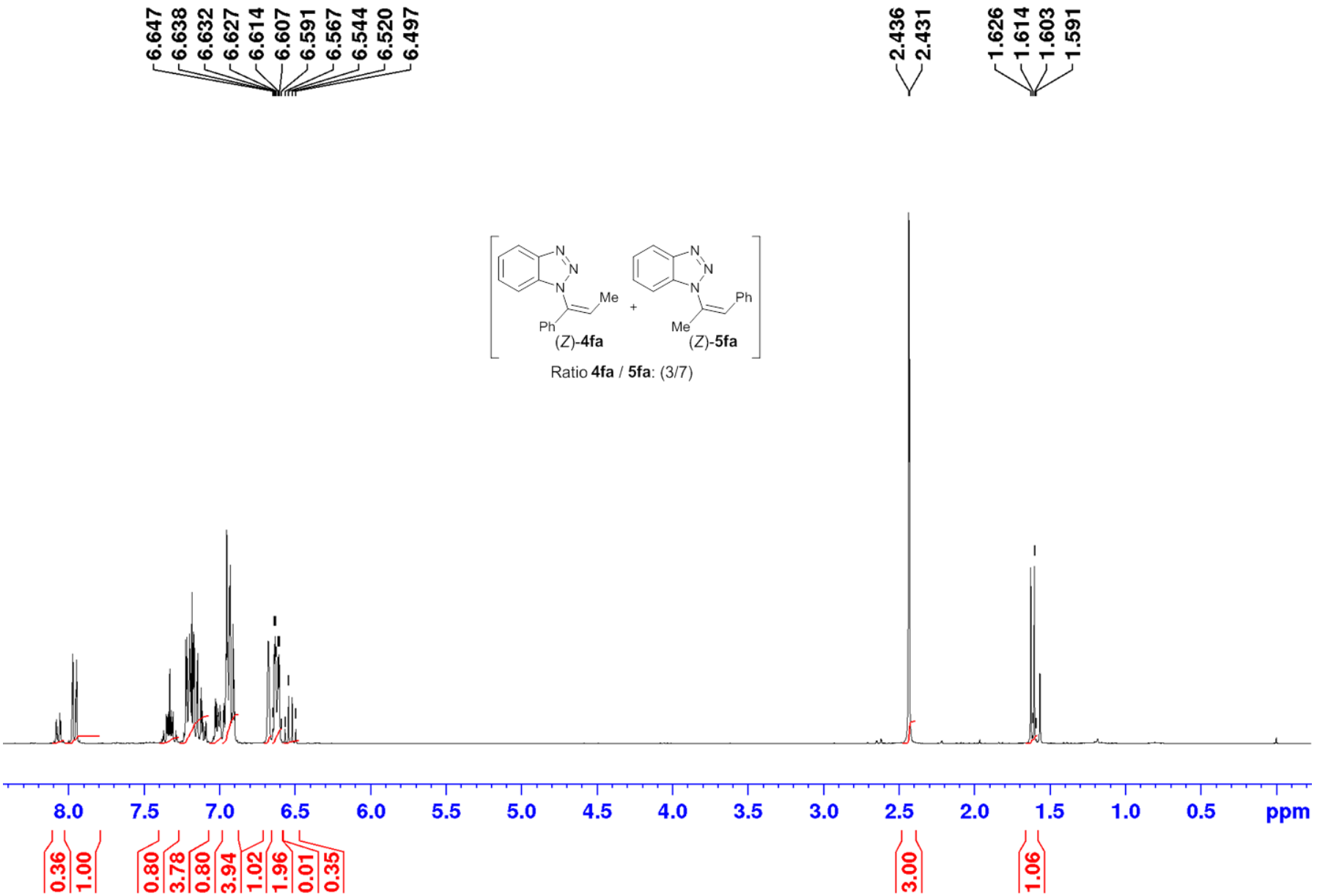

154.42
143.08
133.90
131.82
131.56
129.07
128.86
116.34
108.68
85.85
77.59
77.16
76.74
N
N
CN
Ph
(Z)-4de
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

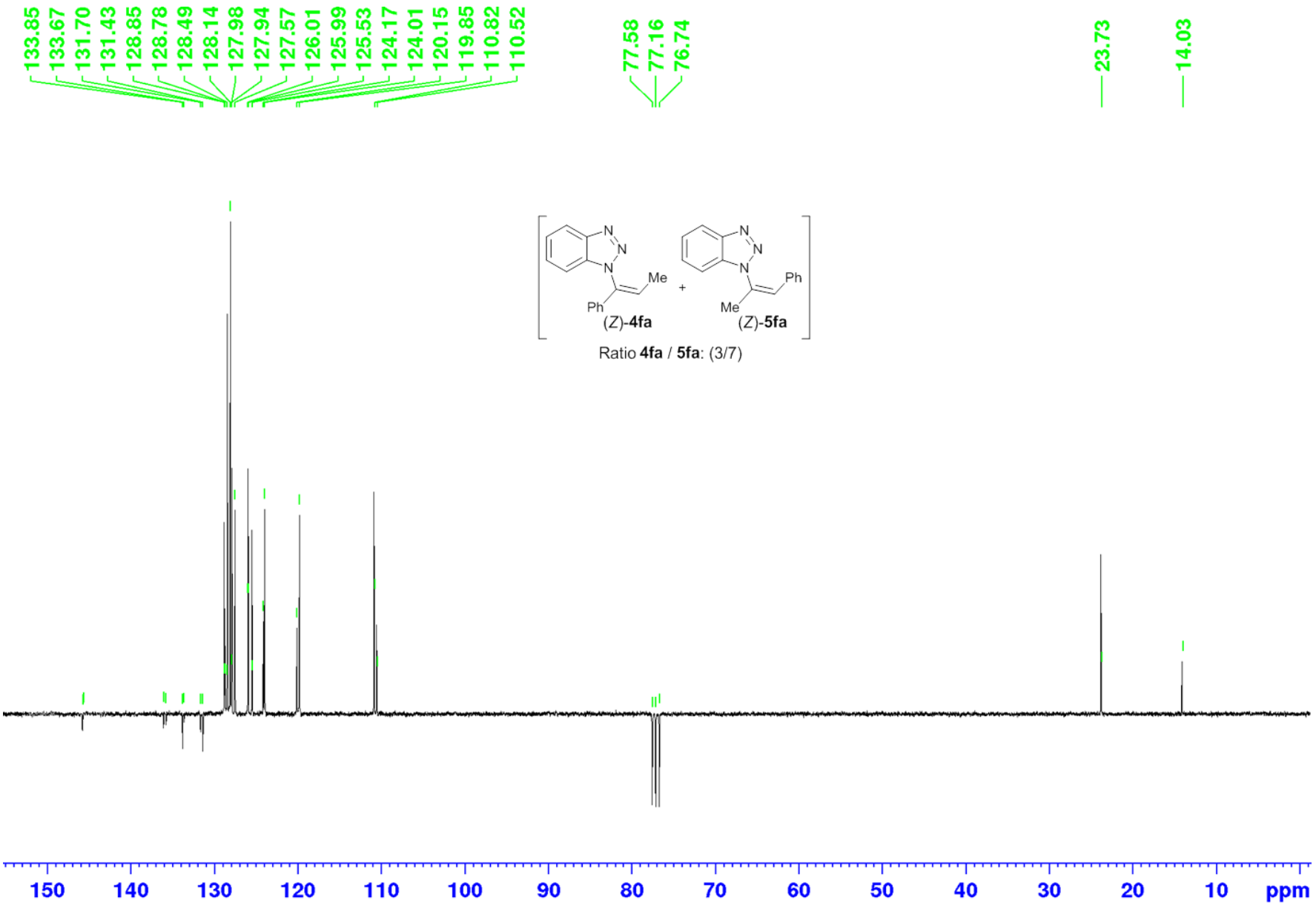

7.708
7.501
7.496
7.488
7.479
7.473
7.218
7.210
6.355
6.349
6.346
6.340
6.168
N
N
Ph
NC
(Z)-5de
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
4.91
1.13
0.96
0.92

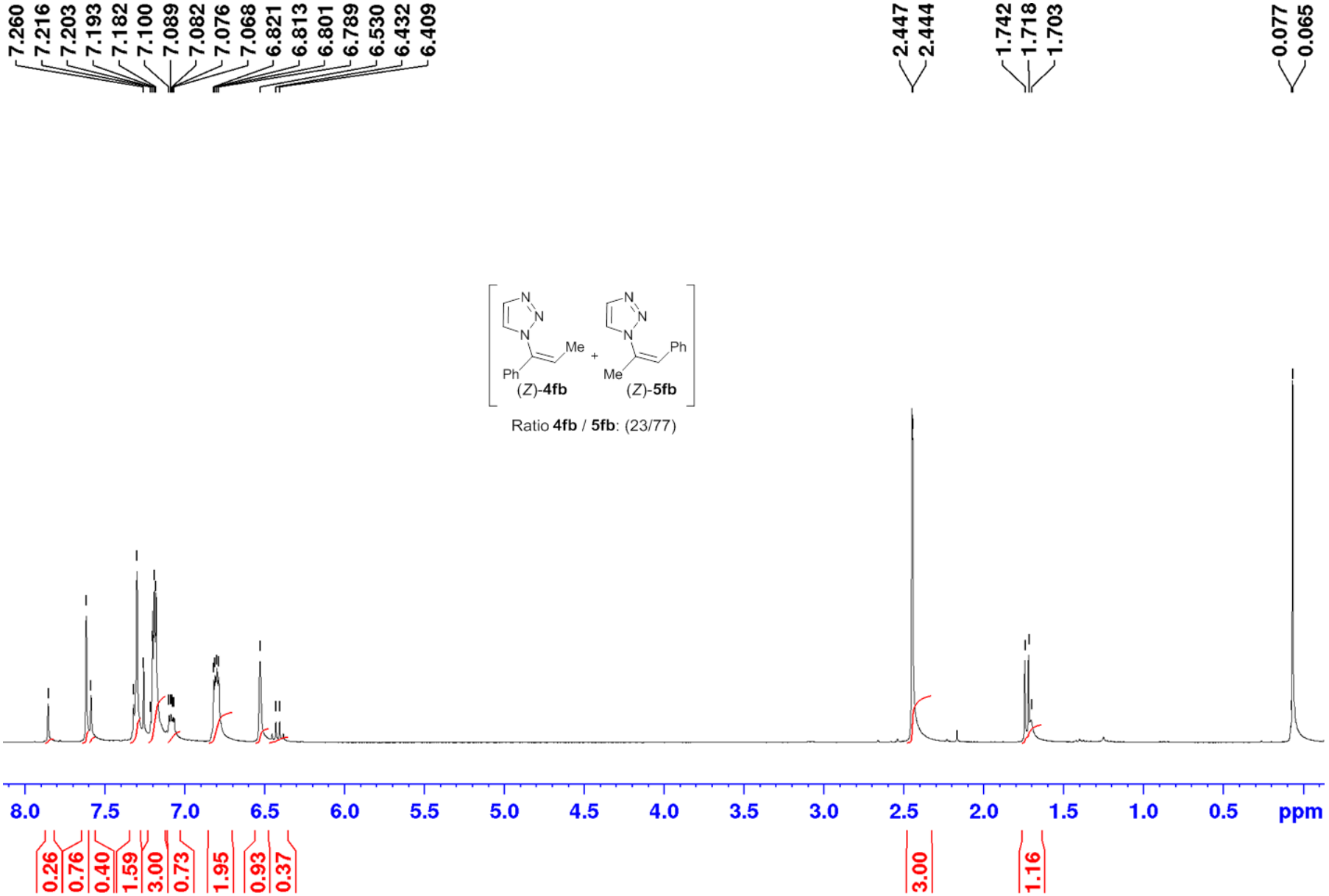

155.13
143.81
131.55
131.06
130.95
129.69
129.19
117.17
109.21
85.64
77.58
77.16
76.74
N
N
Ph
NC
(Z)-5de
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

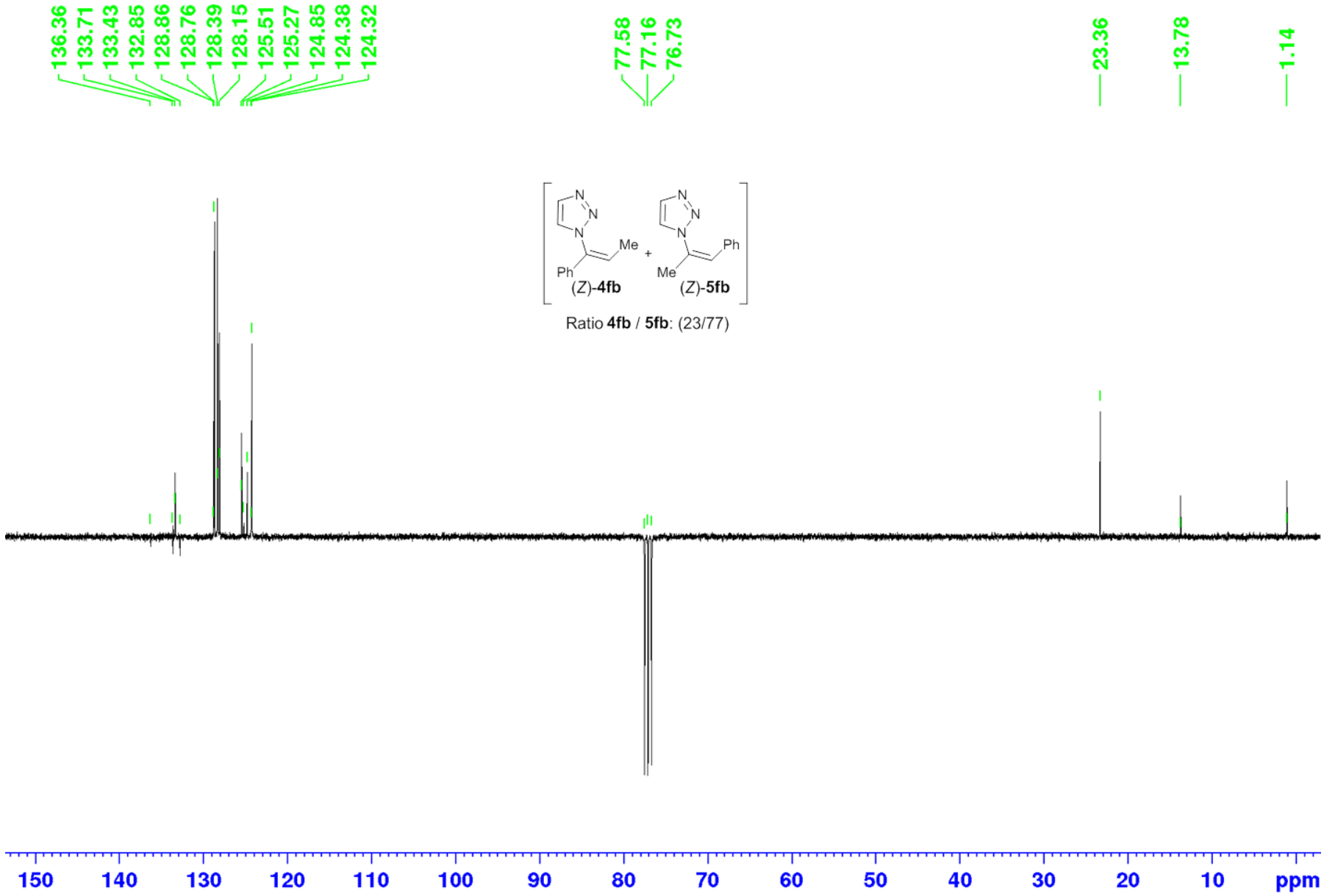

7.524
7.521
7.502
7.498
7.494
7.474
7.470
7.413
7.410
7.404
7.389
7.384
7.380
7.361
7.357
7.262
5.884
5.870
5.865
5.861
2.547
2.544
2.541
2.524
2.520
2.517
2.287
2.283
2.279
1.703
1.698
1.694
1.678
1.666
1.656
1.481
1.477
1.474
1.458
1.454
1.451
0.880
0.858
Me
+
Me
(Z)-4ea
(Z)-5ea
Ratio 4ea / 5ea (23/77)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.52
1.55
3.02
1.50
0.97
3.09
4.01
1.45
0.70
2.85
6.00

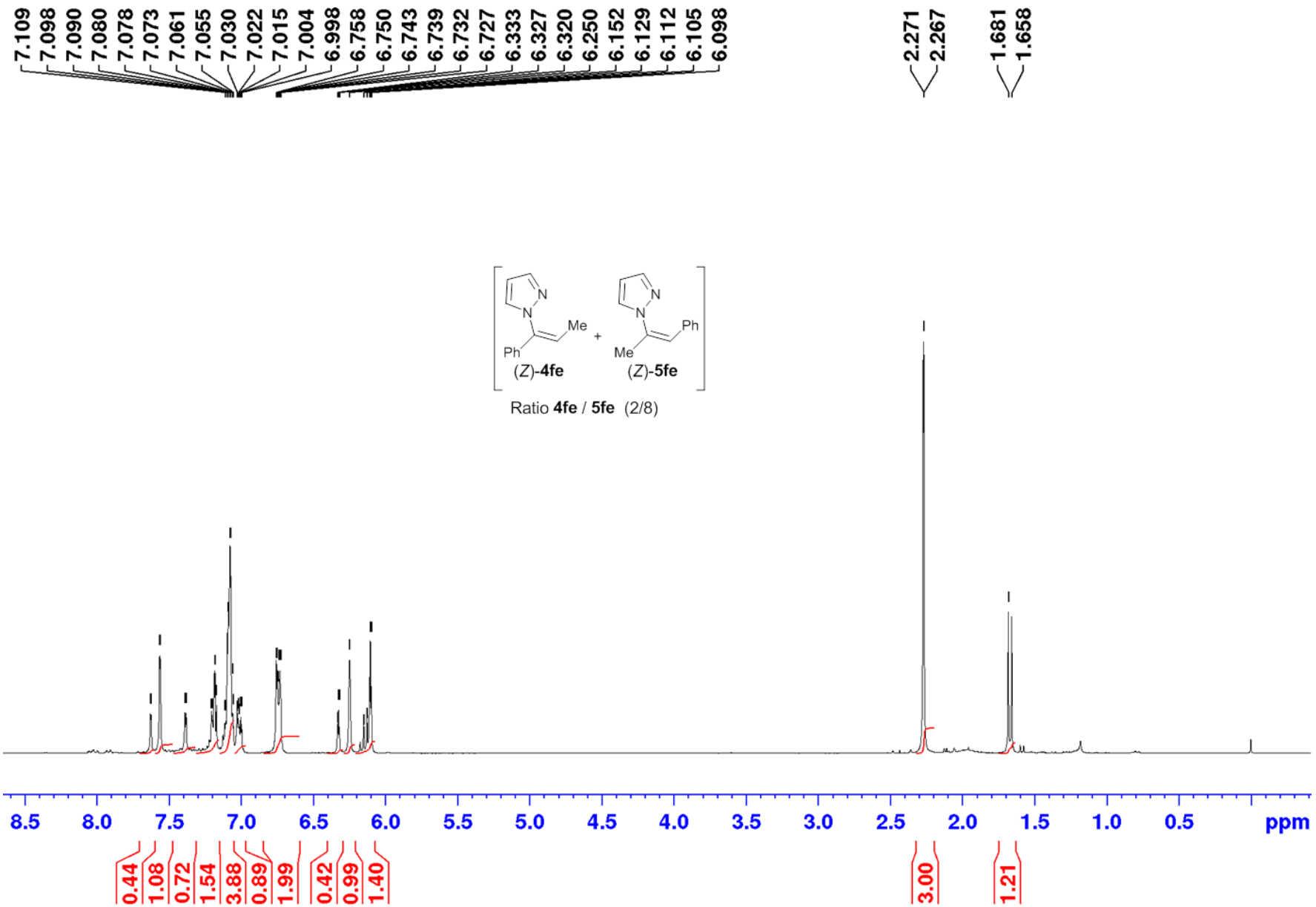

145.44
135.55
133.28
132.87
131.82
131.51
129.07
127.74
127.68
124.36
123.96
123.92
120.21
120.13
110.39
110.26
77.58
77.16
76.74
45.70
36.57
28.27
25.76
22.48
22.30
22.19
13.40
Me
+
Me
(Z)-4ea
(Z)-5ea
Ratio 4ea / 5ea (23/77)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

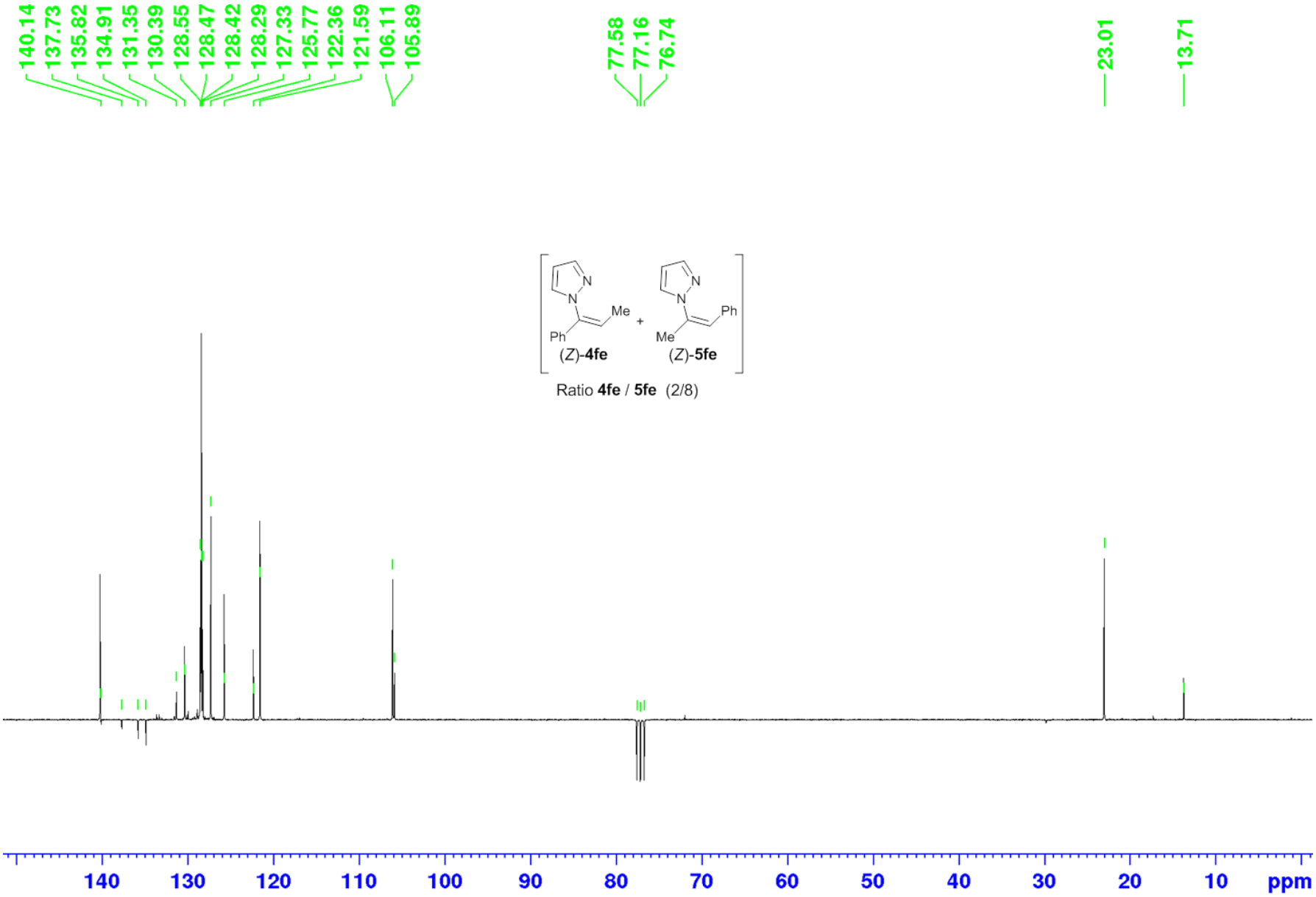

6.647
6.638
6.632
6.627
6.614
6.607
6.591
6.567
6.544
6.520
6.497
2.436
2.431
1.626
1.614
1.603
1.591
Me
Ph
(Z)-4fa
+
Ph
Me
(Z)-5fa
Ratio 4fa / 5fa: (3/7)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.36
1.00
0.80
3.78
0.80
3.94
1.02
1.96
0.01
0.35
3.00
1.06


133.85
133.67
131.70
131.43
128.85
128.78
128.49
128.14
127.98
127.94
127.57
126.01
125.99
125.53
124.17
124.01
120.15
119.85
110.82
110.52
77.58
77.16
76.74
23.73
14.03
Me
Ph
(Z)-4fa
+
Ph
Me
(Z)-5fa
Ratio 4fa / 5fa: (3/7)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.260
7.216
7.203
7.193
7.182
7.100
7.089
7.082
7.076
7.068
6.821
6.813
6.801
6.789
6.530
6.432
6.409
2.447
2.444
1.742
1.718
1.703
0.077
0.065
(Z)-4fb
(Z)-5fb
Ratio 4fb / 5fb: (23/77)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.26
0.76
0.40
1.59
3.00
0.73
1.95
0.93
0.37
3.00
1.16


136.36
133.71
133.43
132.85
128.86
128.76
128.39
128.15
125.51
125.27
124.85
124.38
124.32
77.58
77.16
76.73
23.36
13.78
1.14
Me
Ph
(Z)-4fb
Ph
Me
(Z)-5fb
Ratio 4fb / 5fb: (23/77)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.109
7.098
7.090
7.080
7.078
7.073
7.061
7.055
7.030
7.022
7.015
7.004
6.998
6.758
6.750
6.743
6.739
6.732
6.727
6.333
6.327
6.320
6.250
6.152
6.129
6.112
6.105
6.098
2.271
2.267
1.681
1.658
Me
Ph
(Z)-4fe
Ph
Me
(Z)-5fe
Ratio 4fe / 5fe (2/8)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.44
1.08
0.72
1.54
3.88
0.89
1.99
0.42
0.99
1.40
3.00
1.21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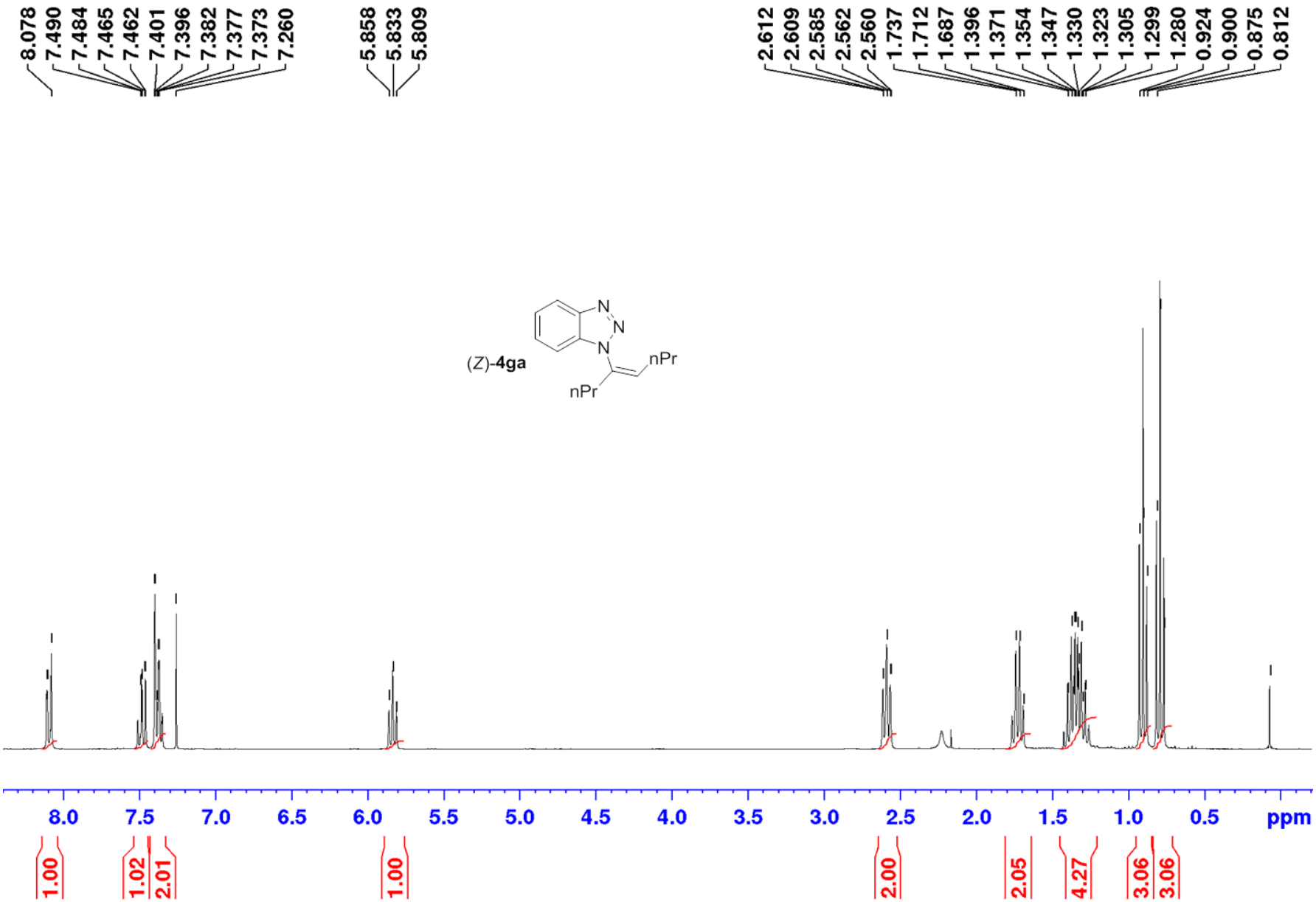
137.73
135.82
134.91
131.35
130.39
128.55
128.47
128.42
128.29
127.33
125.77
122.36
121.59
106.11
105.89
77.58
77.16
76.74
23.01
13.71
Me
Ph
(Z)-4fe
Ph
Me
(Z)-5fe
Ratio 4fe / 5fe (2/8)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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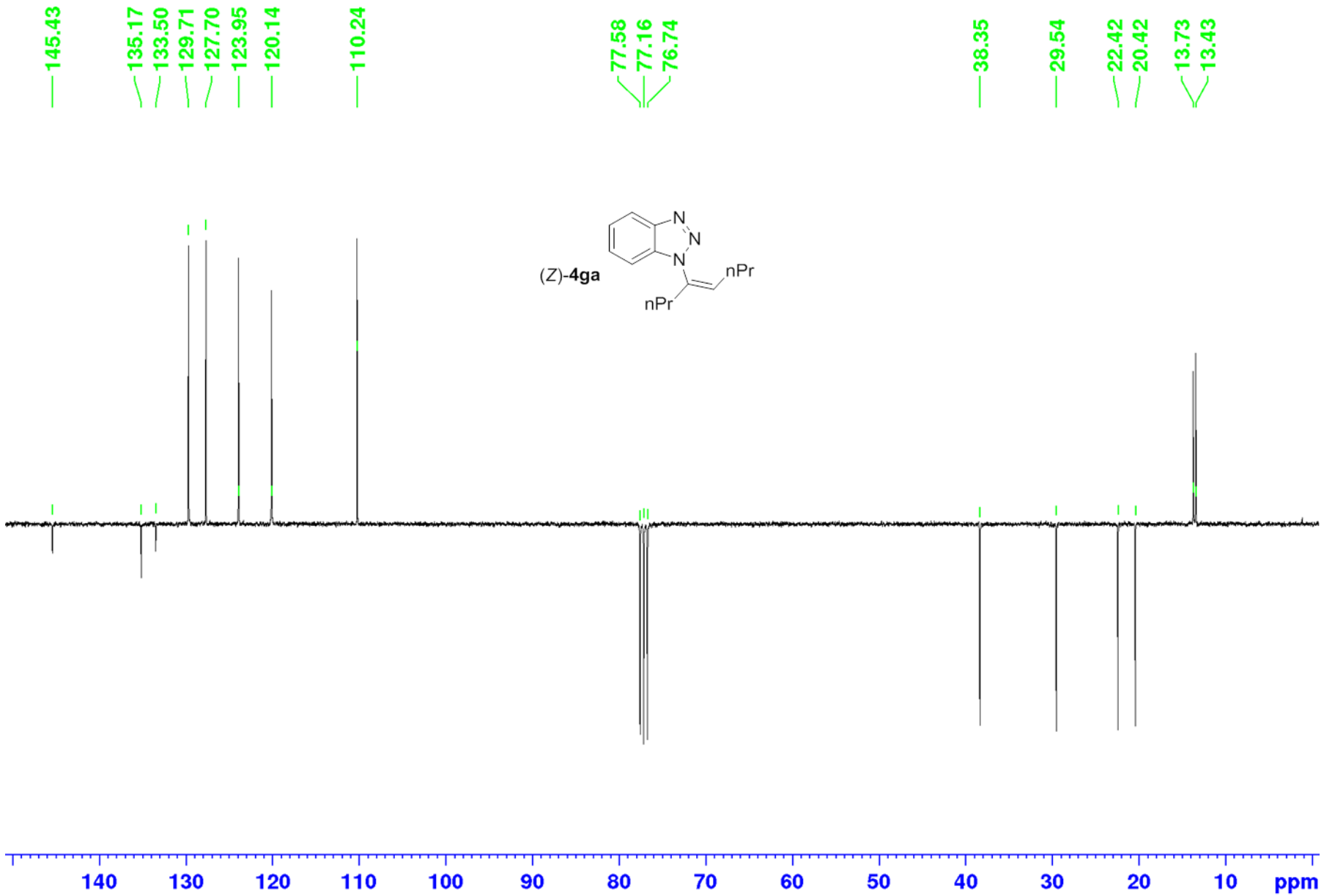
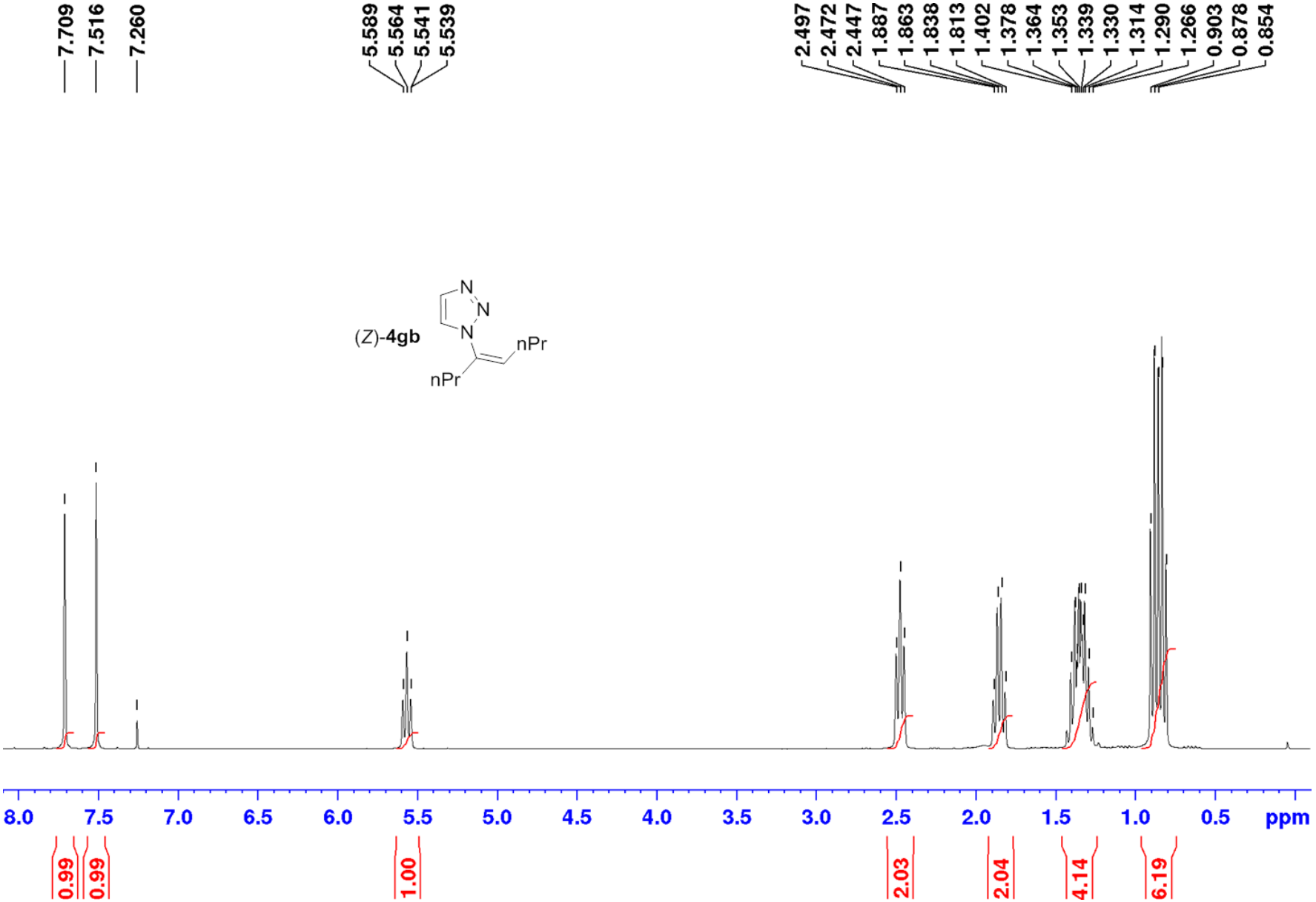
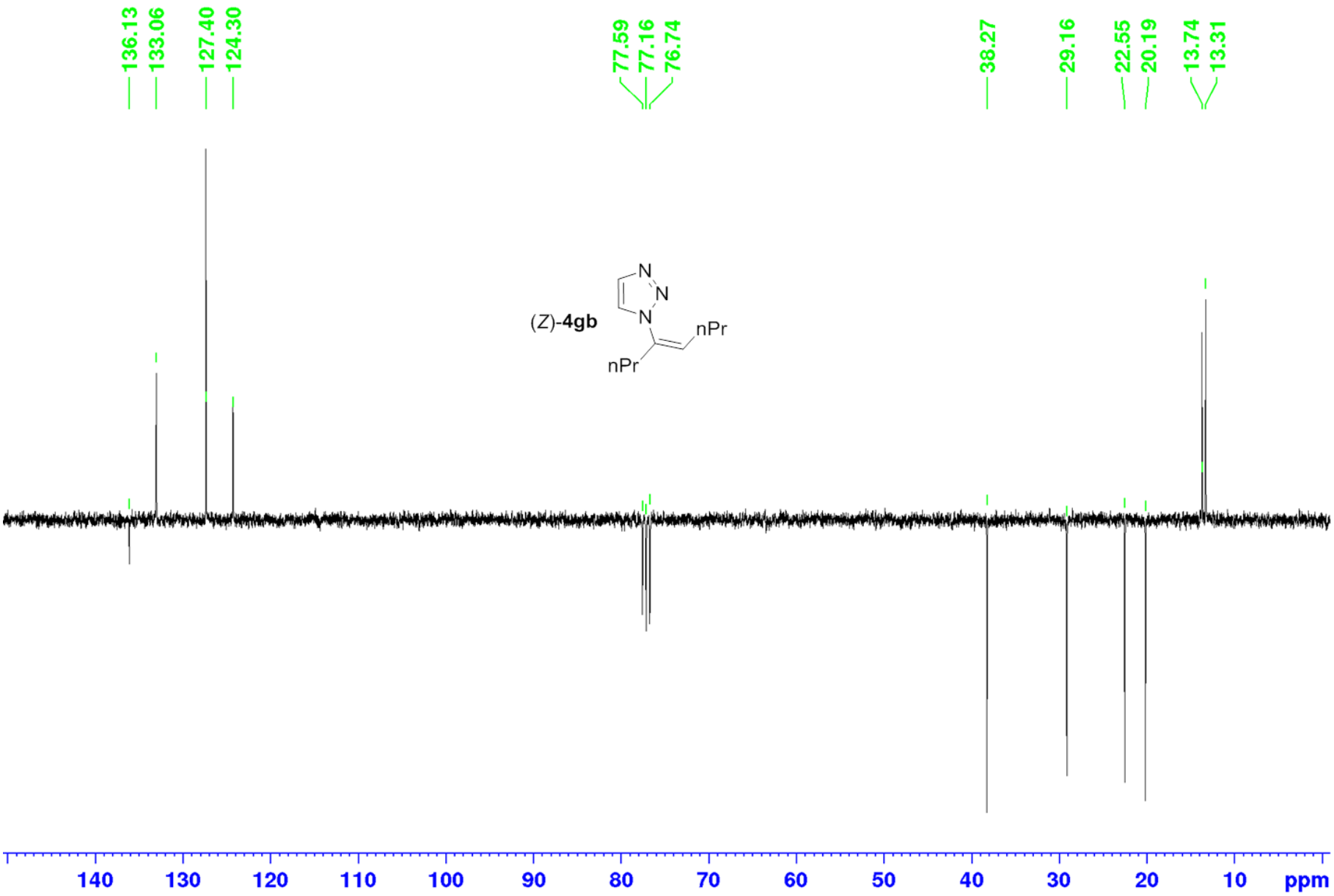
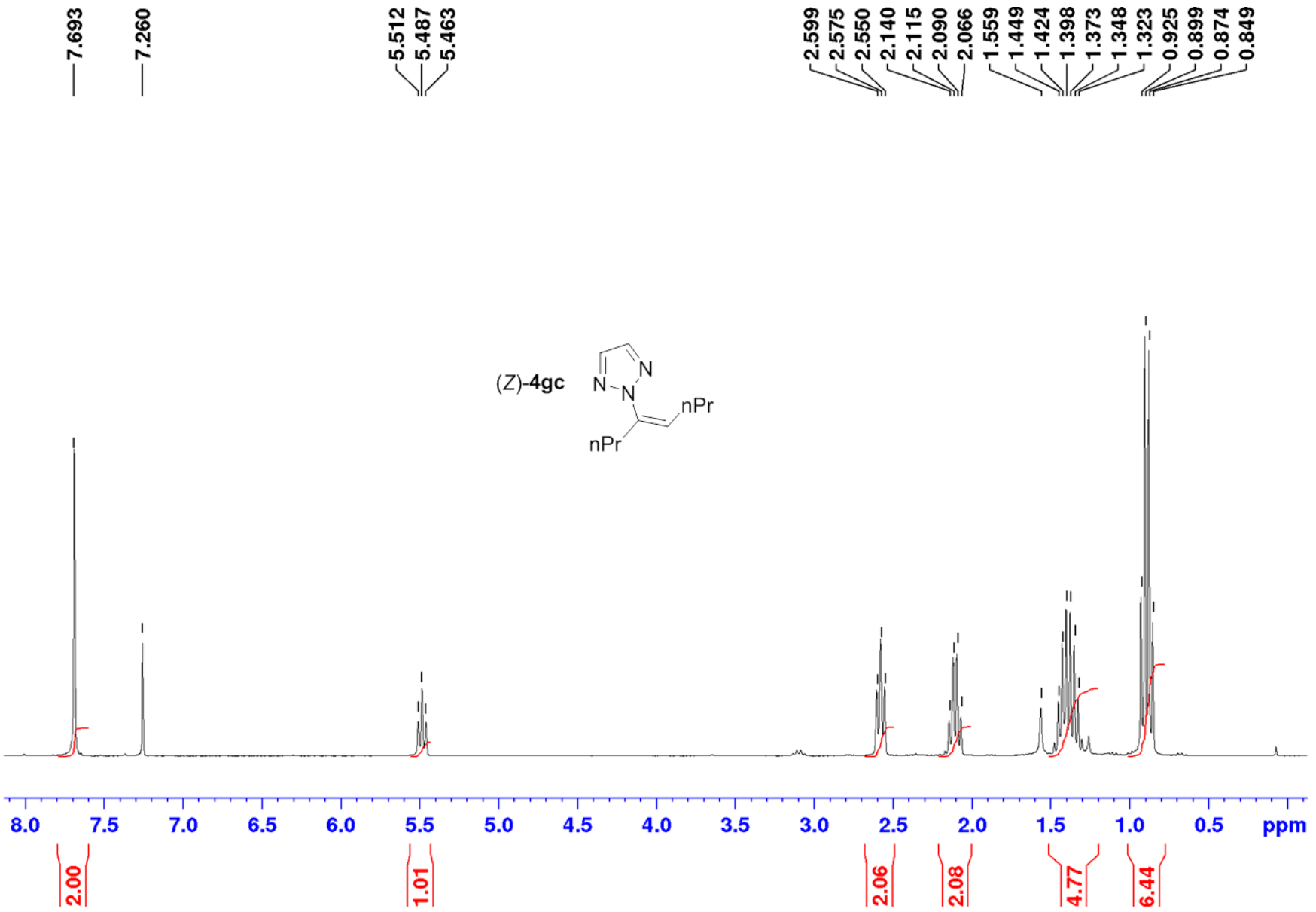
7.490
7.484
7.465
7.462
7.401
7.396
7.382
7.377
7.373
7.260
5.858
5.833
5.809
2.612
2.609
2.585
2.562
2.560
1.737
1.712
1.687
1.396
1.371
1.354
1.347
1.330
1.323
1.305
1.299
1.280
0.924
0.900
0.875
0.812
(Z)-4ga
N
N
N
nPr
nPr
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.02
2.01
1.00
2.00
2.05
4.27
3.06
3.06


145.43
135.17
133.50
129.71
127.70
123.95
120.14
110.24
77.58
77.16
76.74
38.35
29.54
22.42
20.42
13.73
13.43
(Z)-4ga
N
N
N
nPr
nPr
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.709
7.516
7.260
5.589
5.564
5.541
5.539
2.497
2.472
2.447
1.887
1.863
1.838
1.813
1.402
1.378
1.364
1.353
1.339
1.330
1.314
1.290
1.266
0.903
0.878
0.854
(Z)-4gb
N
N
N
nPr
nPr
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.99
0.99
1.00
2.03
2.04
4.14
6.19


136.13
133.06
127.40
124.30
77.59
77.16
76.74
38.27
29.16
22.55
20.19
13.74
13.31
(Z)-4gb
N
N
N
nPr
nPr
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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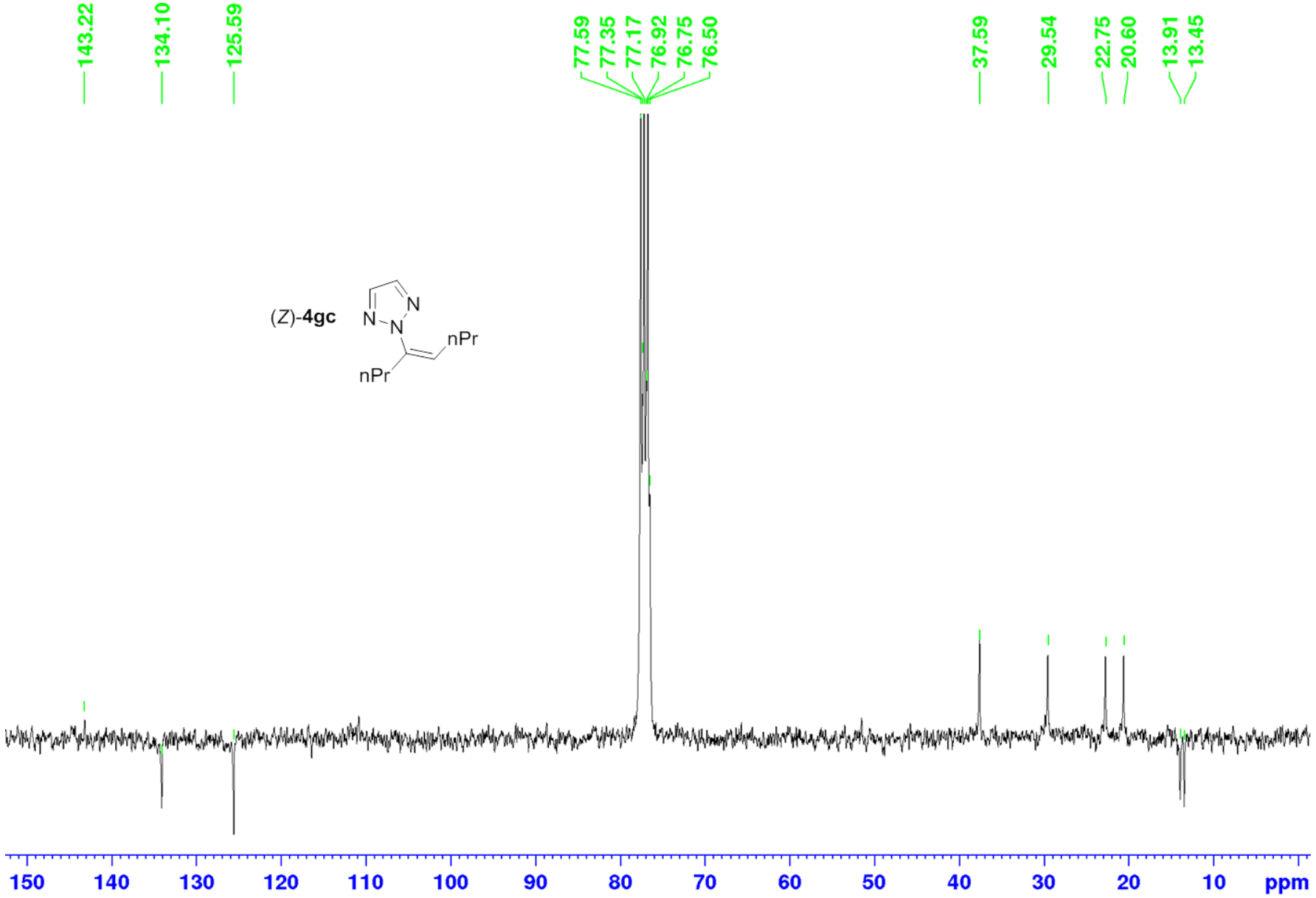
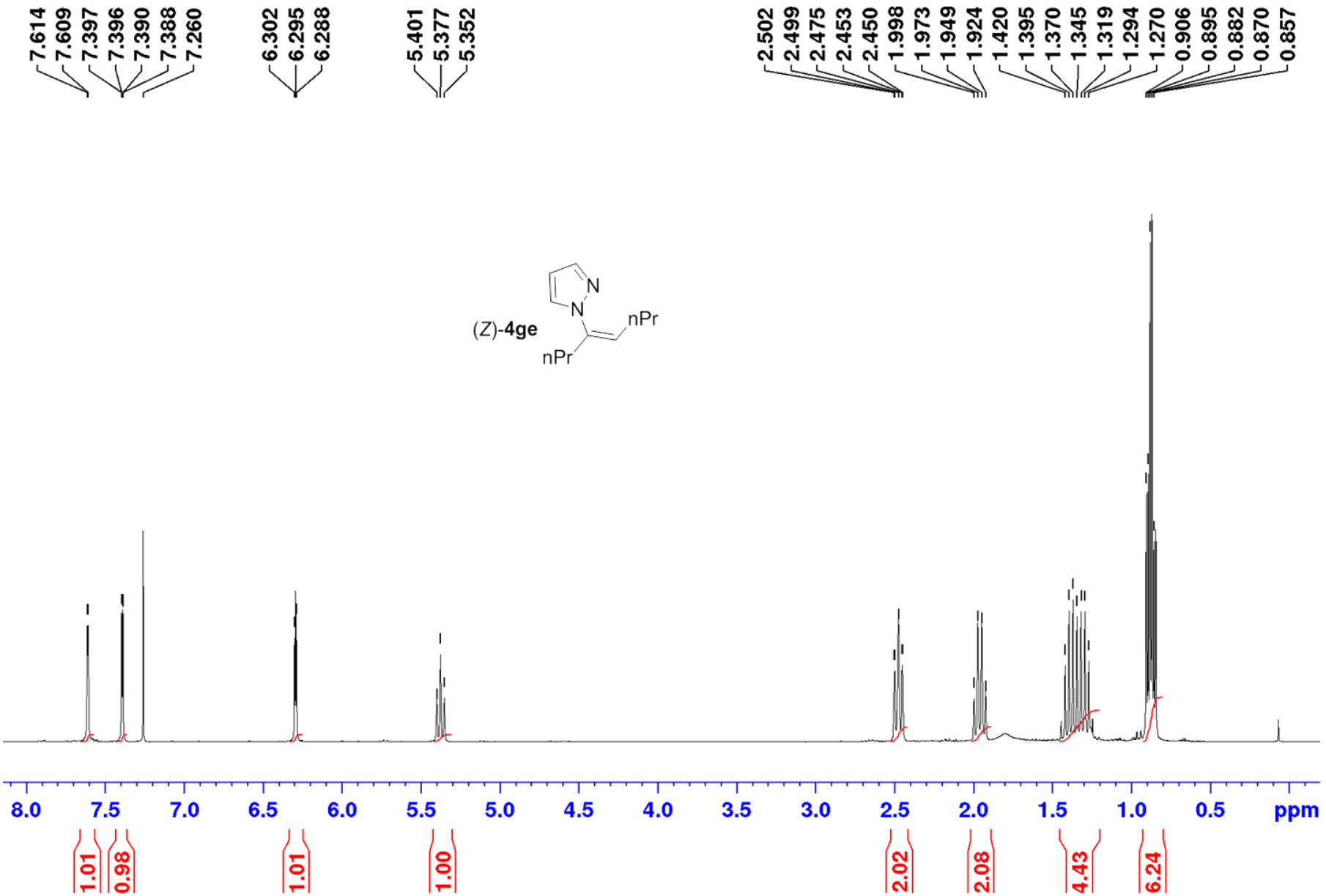
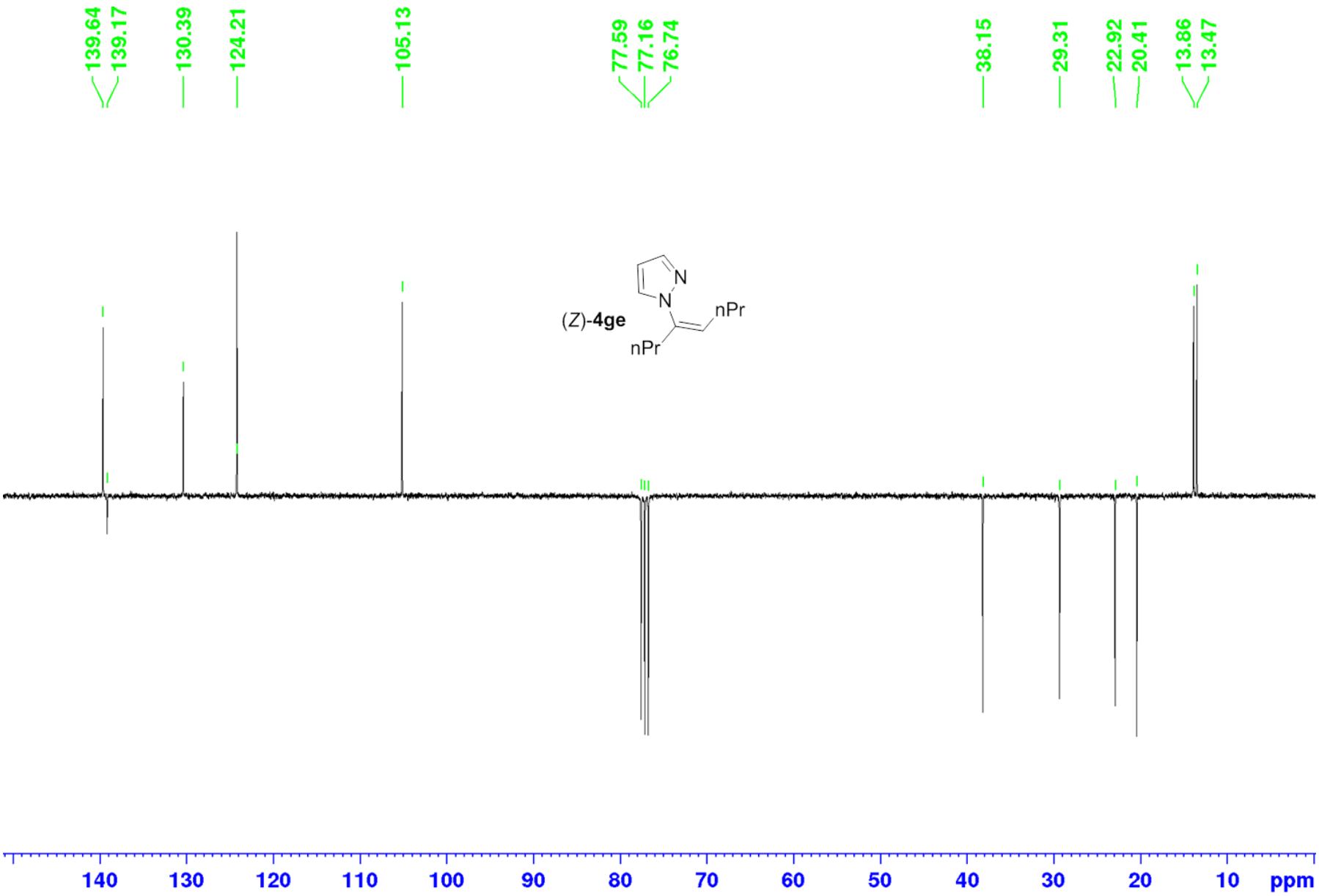
7.260
5.512
5.487
5.463
2.599
2.575
2.550
2.140
2.115
2.090
2.066
1.559
1.449
1.424
1.398
1.373
1.348
1.323
0.925
0.899
0.874
0.849
(Z)-4gc
N
N
N
nPr
nPr
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.01
2.06
2.08
4.77
6.44


143.22
134.10
125.59
77.59
77.35
77.17
76.92
76.75
76.50
37.59
29.54
22.75
20.60
13.91
13.45
(Z)-4gc
N
N
N
nPr
nPr
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.614
7.609
7.397
7.396
7.390
7.388
7.260
6.302
6.295
6.288
5.401
5.377
5.352
2.502
2.499
2.475
2.453
2.450
1.998
1.973
1.949
1.924
1.420
1.395
1.370
1.345
1.319
1.294
1.270
0.906
0.895
0.882
0.870
0.857
(Z)-4ge
N
N
nPr
nPr
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
0.98
1.01
1.00
2.02
2.08
4.43
6.24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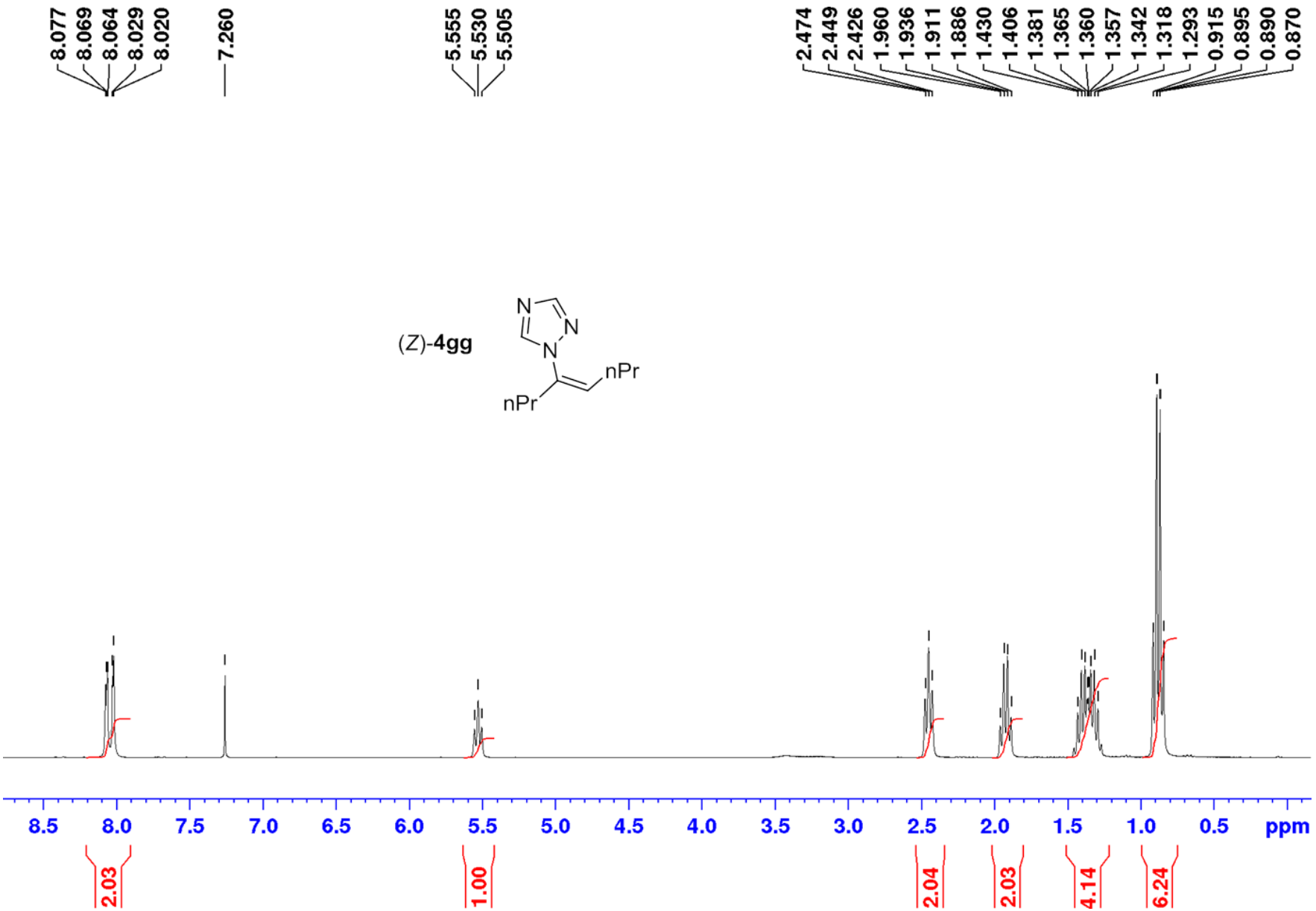
139.17
130.39
124.21
105.13
77.59
77.16
76.74
38.15
29.31
22.92
20.41
13.86
13.47
(Z)-4ge
N
N
nPr
nPr
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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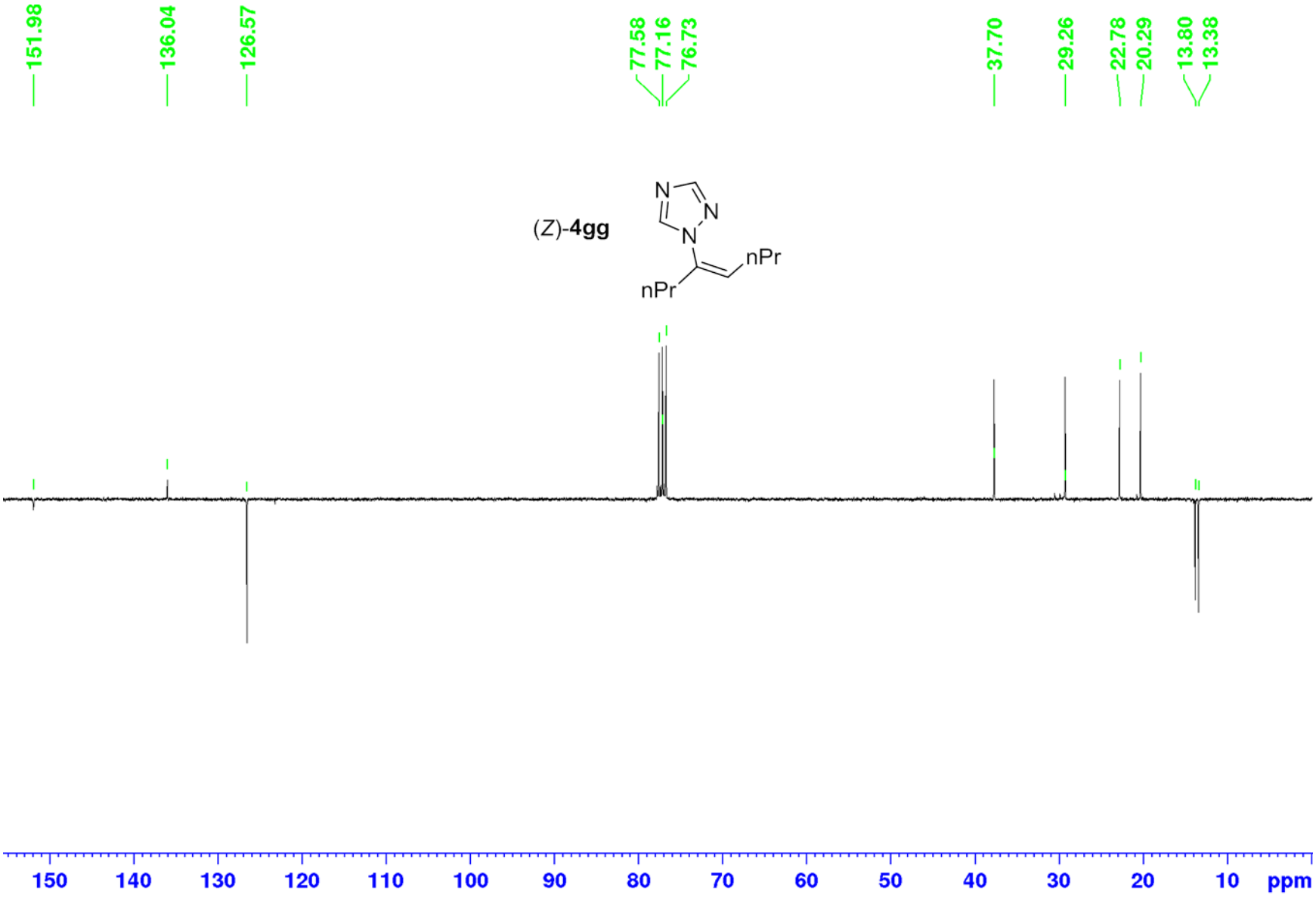
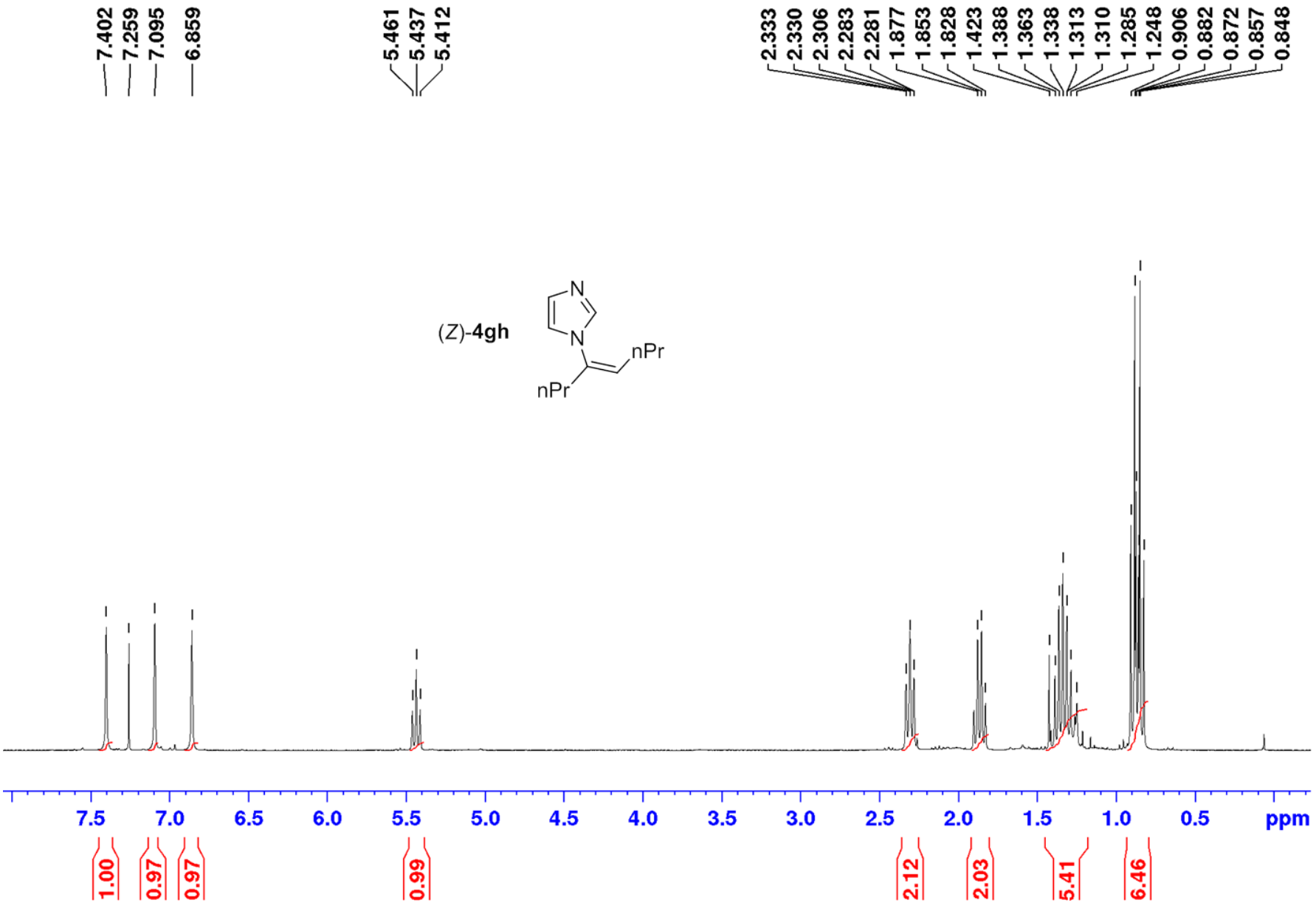
8.069
8.064
8.029
8.020
7.260
5.555
5.530
5.505
2.474
2.449
2.426
1.960
1.936
1.911
1.886
1.430
1.406
1.381
1.365
1.360
1.357
1.342
1.318
1.293
0.915
0.895
0.890
0.870
(Z)-4gg
N
N
N
nPr
nPr
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
1.00
2.04
2.03
4.14
6.24


151.98
136.04
126.57
77.58
77.16
76.73
37.70
29.26
22.78
20.29
13.80
13.38
(Z)-4gg
N
N
N
nPr
nPr
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.402
7.259
7.095
6.859
5.461
5.437
5.412
2.333
2.330
2.306
2.283
2.281
1.877
1.853
1.828
1.423
1.388
1.363
1.338
1.313
1.310
1.285
1.248
0.906
0.882
0.872
0.857
0.848
(Z)-4gh
N
N
nPr
nPr
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
ppm
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0.97
0.99
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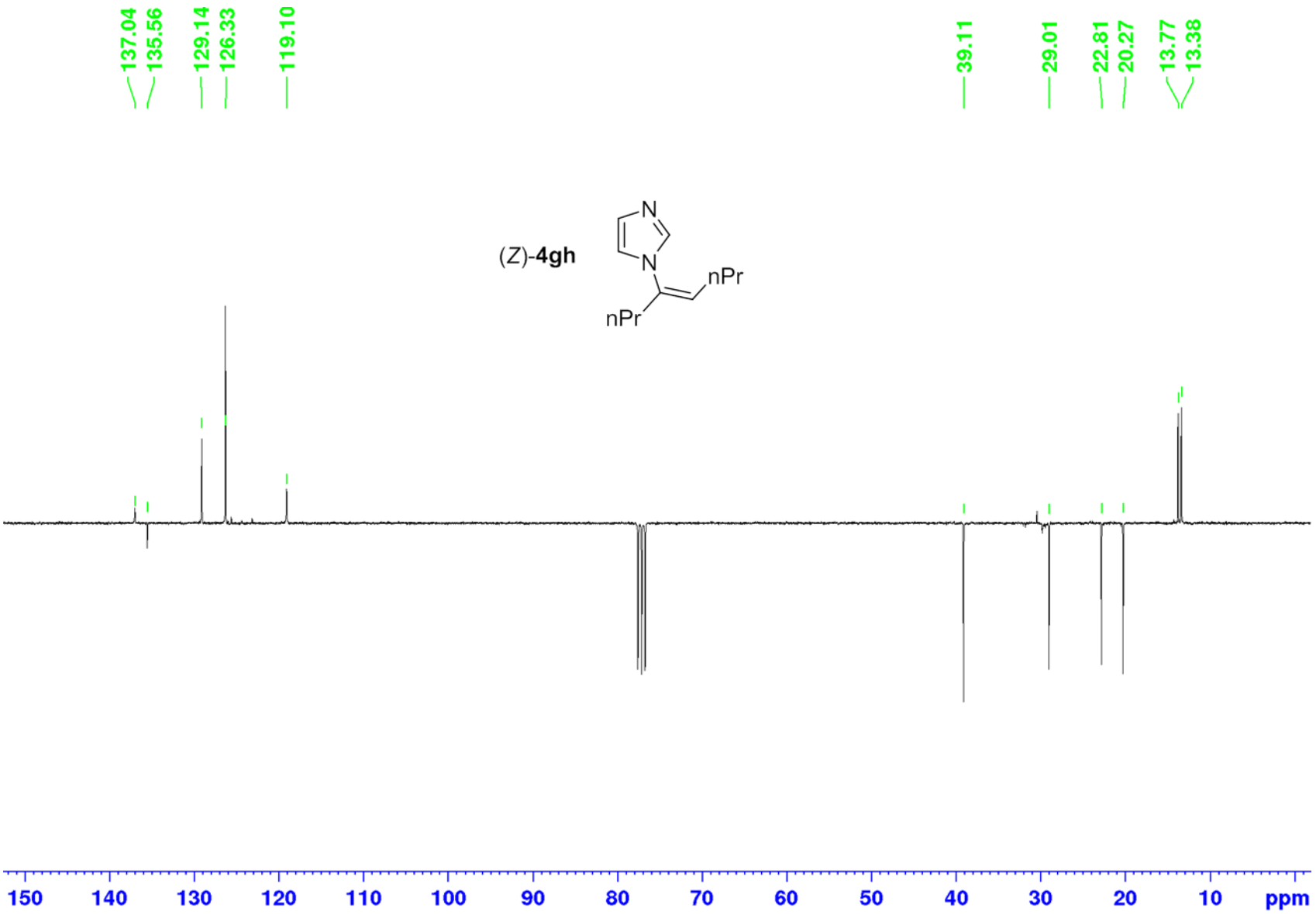
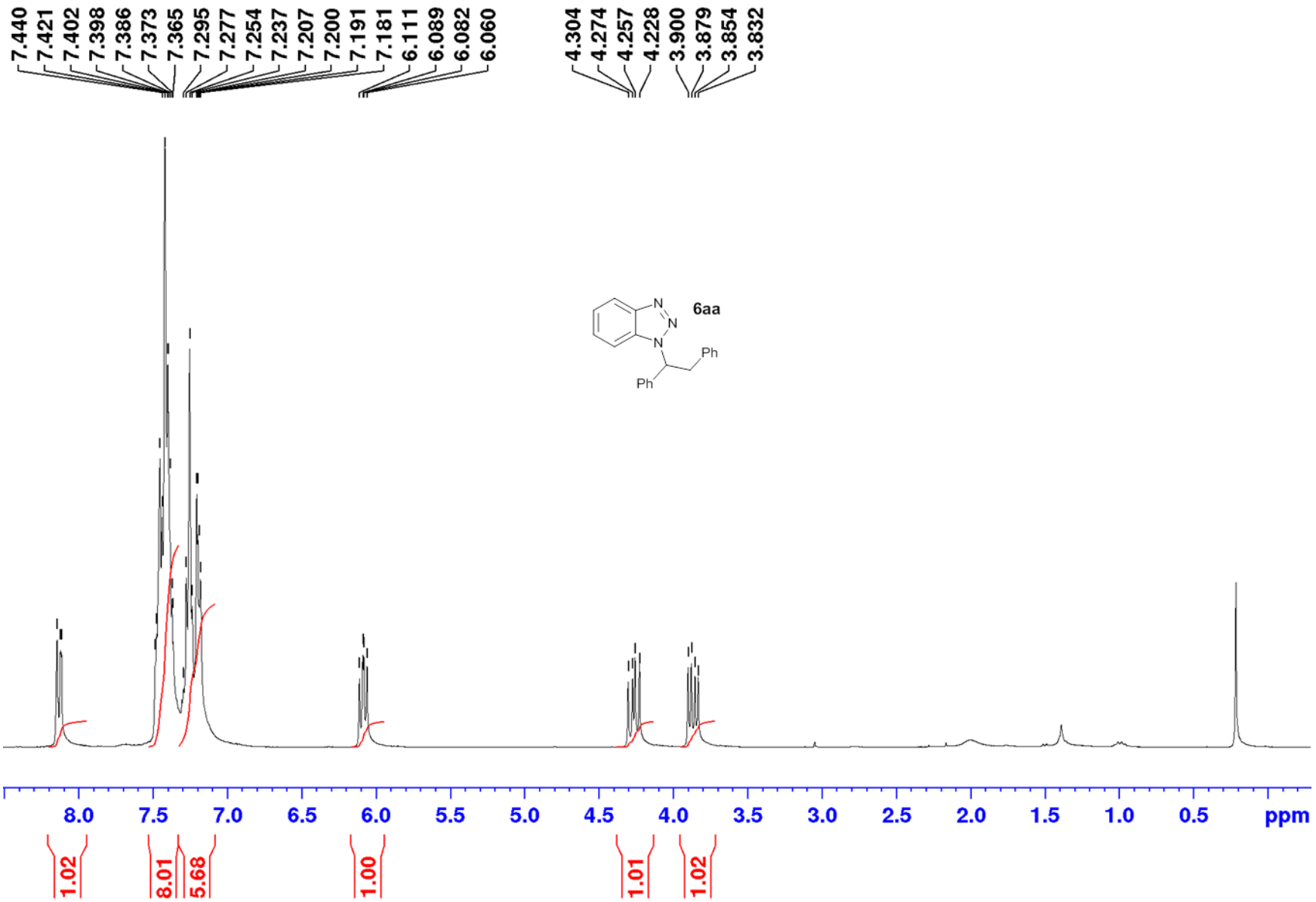
2.03
5.41
6.46


137.04
135.56
129.14
126.33
119.10
39.11
29.01
22.81
20.27
13.77
13.38
(Z)-4gh
N
N
nPr
nPr
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.421
7.402
7.398
7.386
7.373
7.365
7.295
7.277
7.254
7.237
7.207
7.200
7.191
7.181
6.111
6.089
6.082
6.060
4.304
4.274
4.257
4.228
3.900
3.879
3.854
3.832
6aa
N
N
N
Ph
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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1.02
8.01
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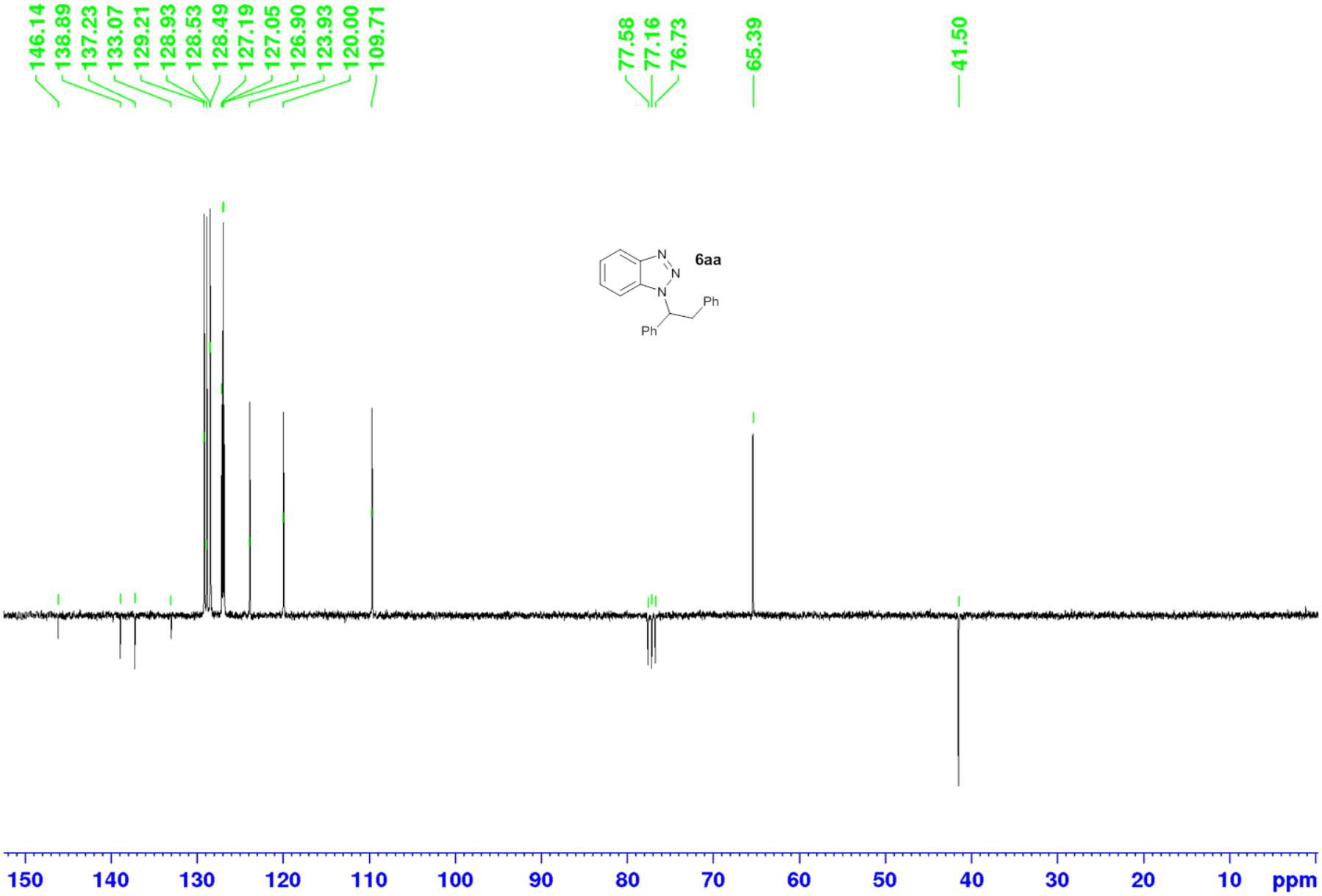
1.00
1.01
1.02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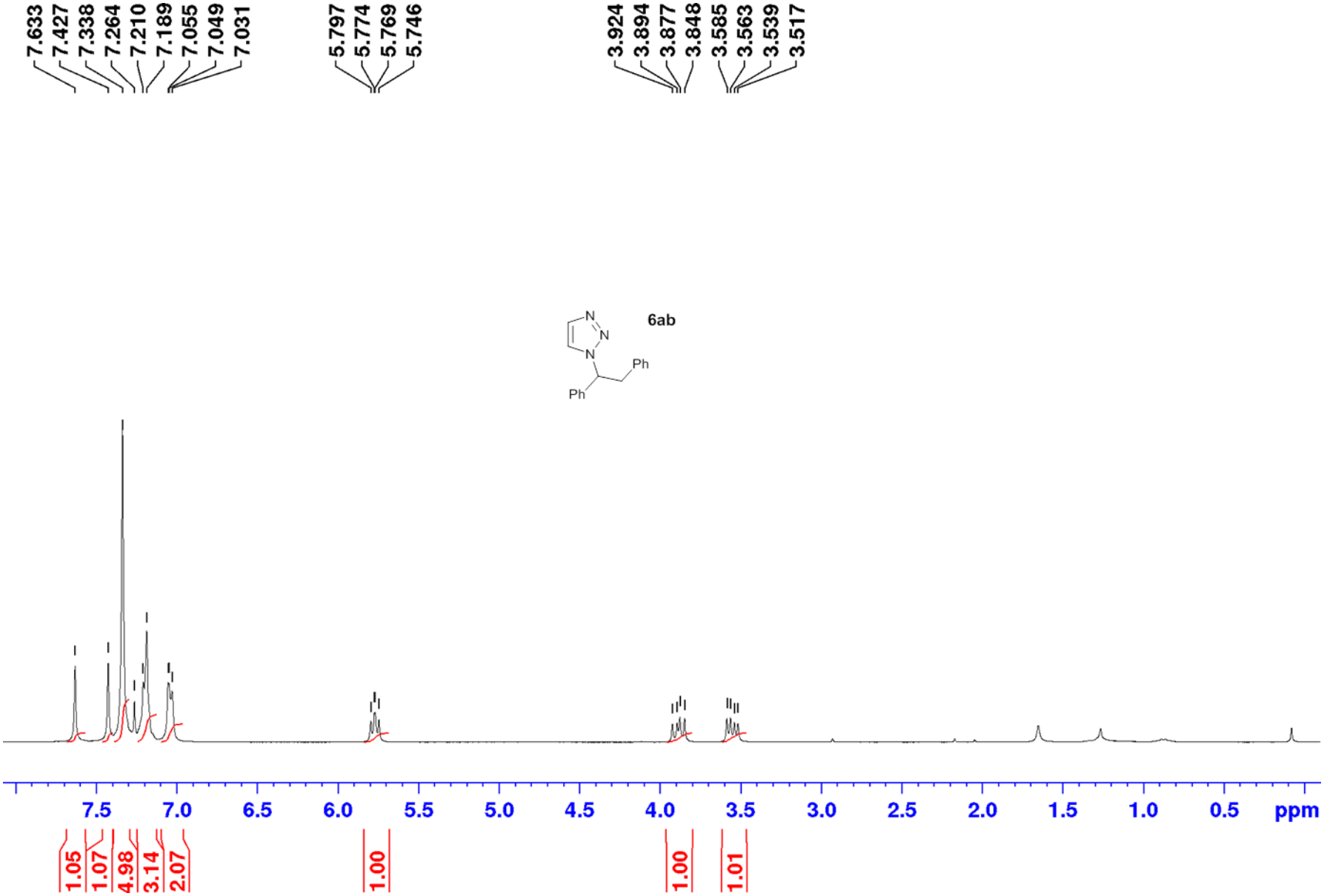
137.23
133.07
129.21
128.93
128.53
128.49
127.19
127.05
126.90
123.93
120.00
109.71
77.58
77.16
76.73
65.39
41.50
6aa
N
N
N
Ph
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.427
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7.264
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7.049
7.031
5.797
5.774
5.769
5.746
3.924
3.894
3.877
3.848
3.585
3.563
3.539
3.517
6ab
N
N
N
Ph
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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1.07
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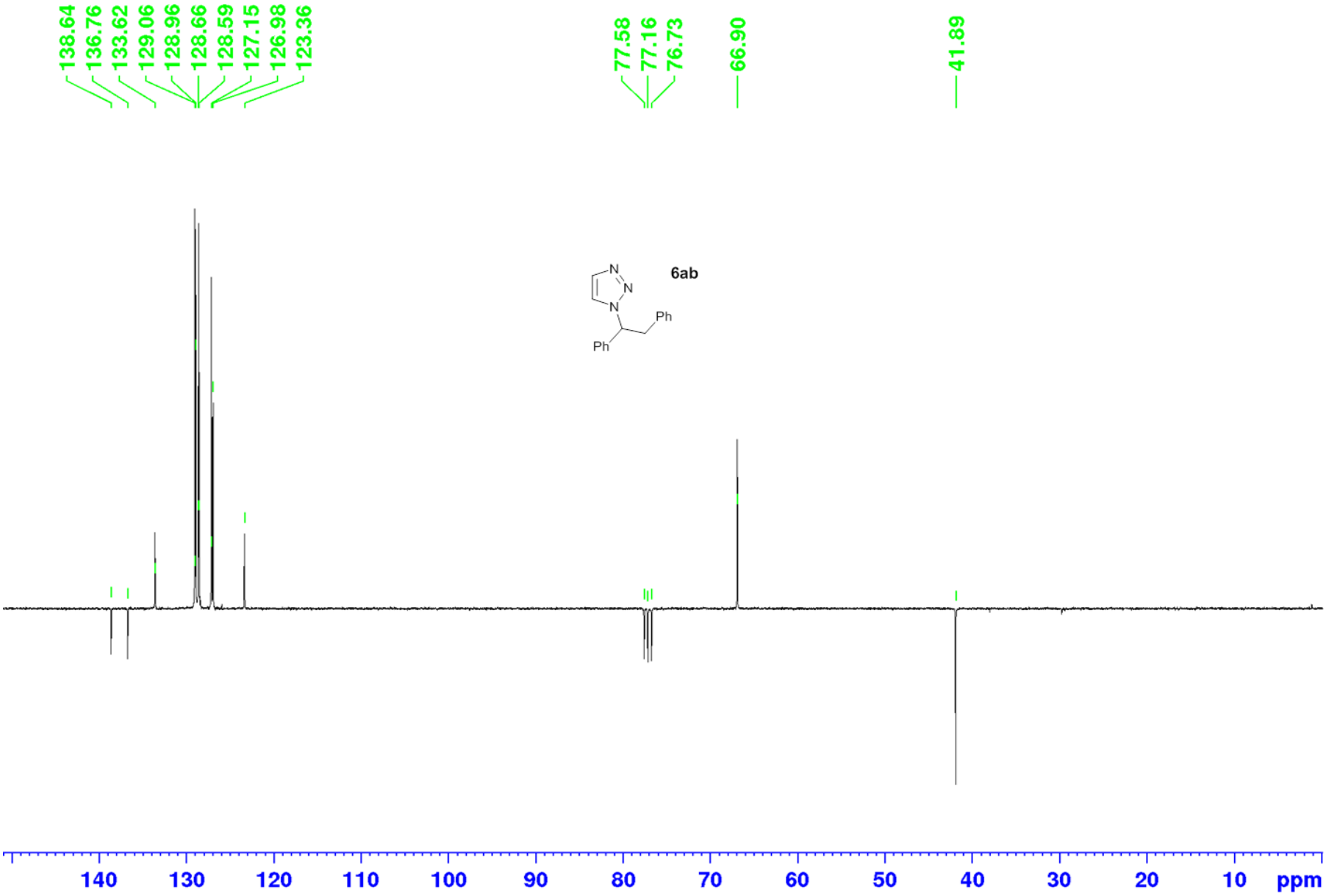
3.14
2.07
1.00
1.00
1.01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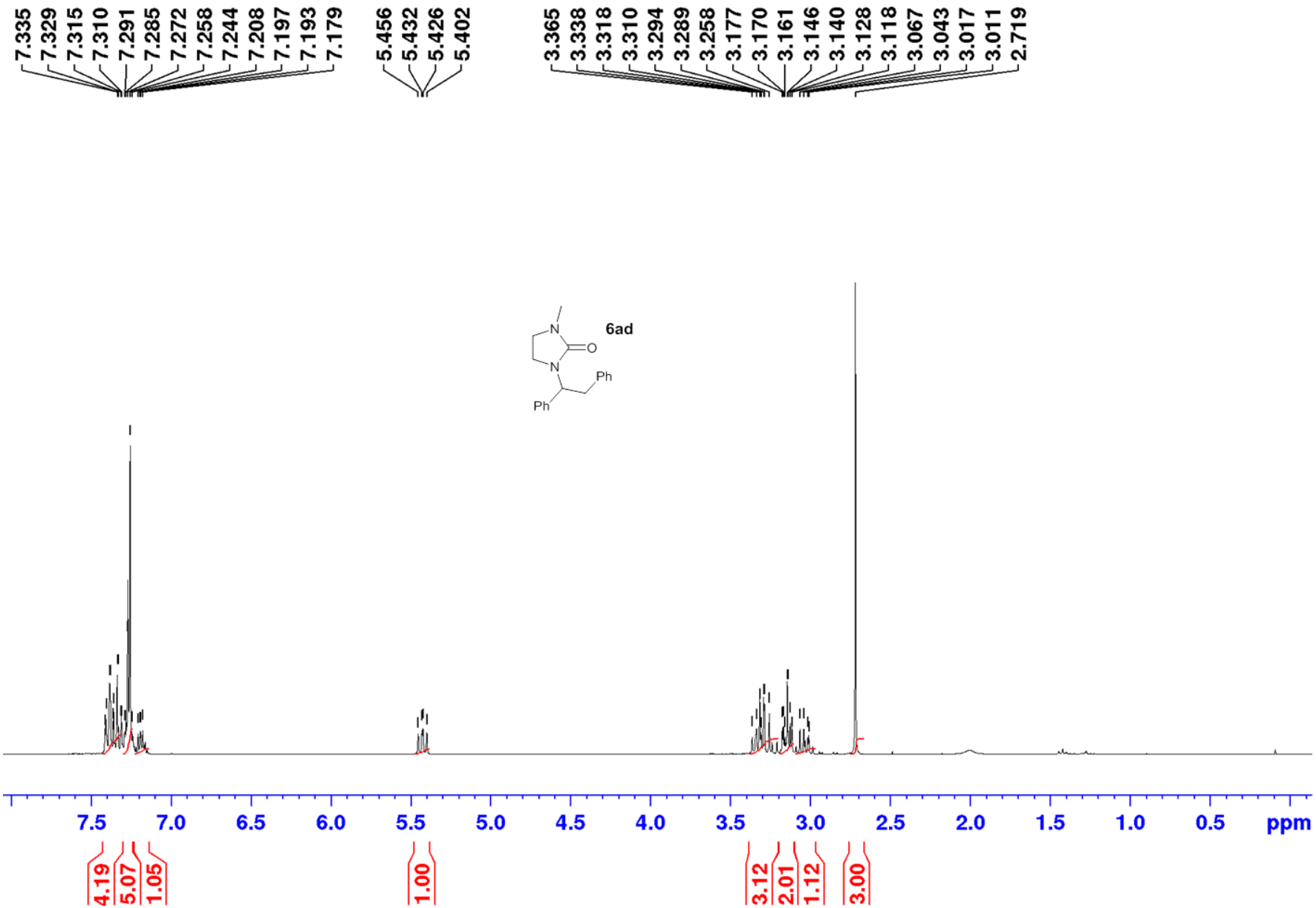
128.96
128.66
128.59
127.15
126.98
123.36
77.58
77.16
76.73
66.90
41.89
6ab
N
N
N
Ph
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.310
7.291
7.285
7.272
7.258
7.244
7.208
7.197
7.193
7.179
5.456
5.432
5.426
5.402
3.365
3.338
3.318
3.310
3.294
3.289
3.258
3.177
3.170
3.161
3.146
3.140
3.128
3.118
3.067
3.043
3.017
3.011
2.719
6ad
N
O
N
Ph
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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5.07
1.05
1.00
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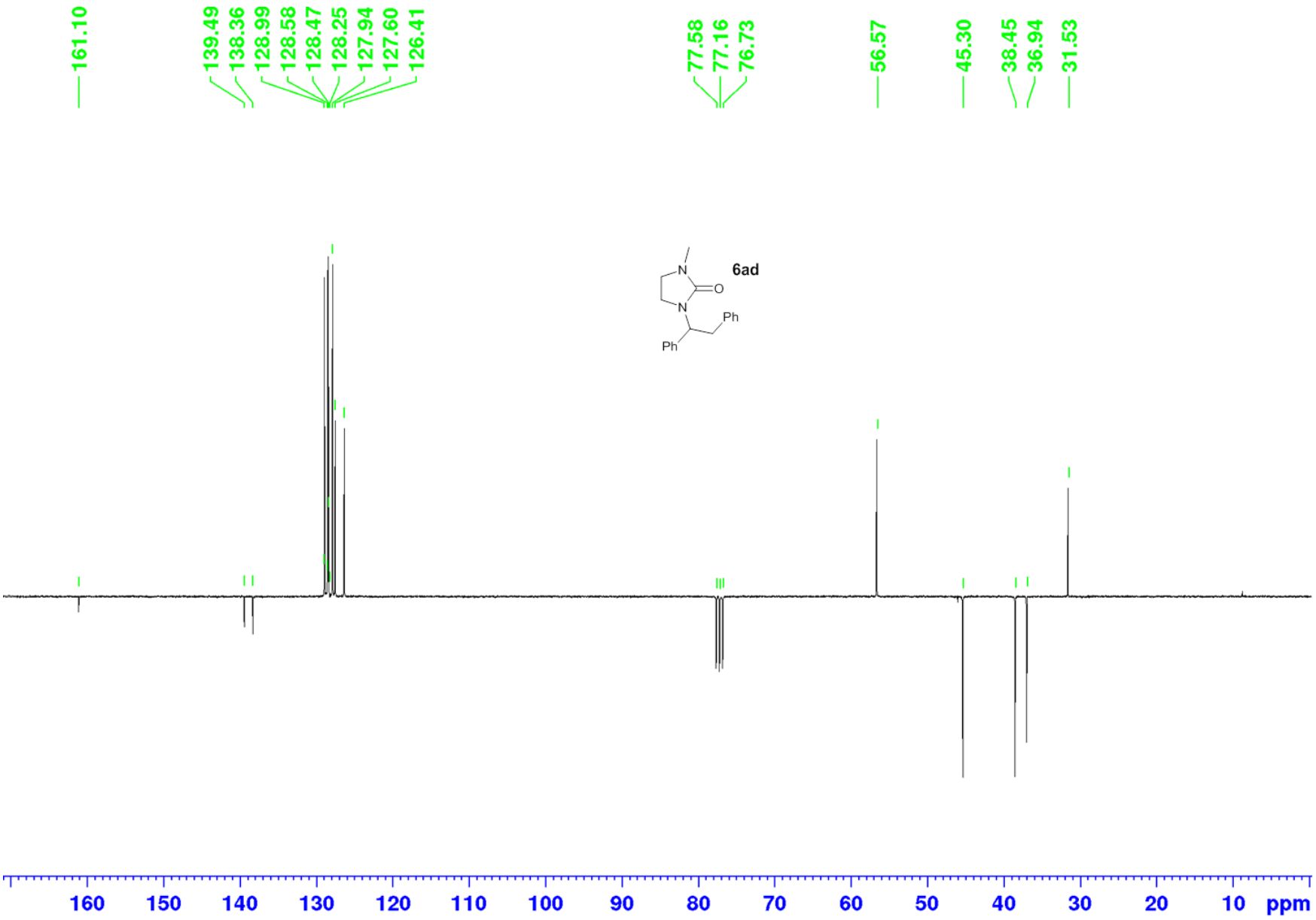
2.01
1.12
3.00


161.10
139.49
138.36
128.99
128.58
128.47
128.25
127.94
127.60
126.41
77.58
77.16
76.73
56.57
45.30
38.45
36.94
31.53
6ad
N
O
N
Ph
Ph
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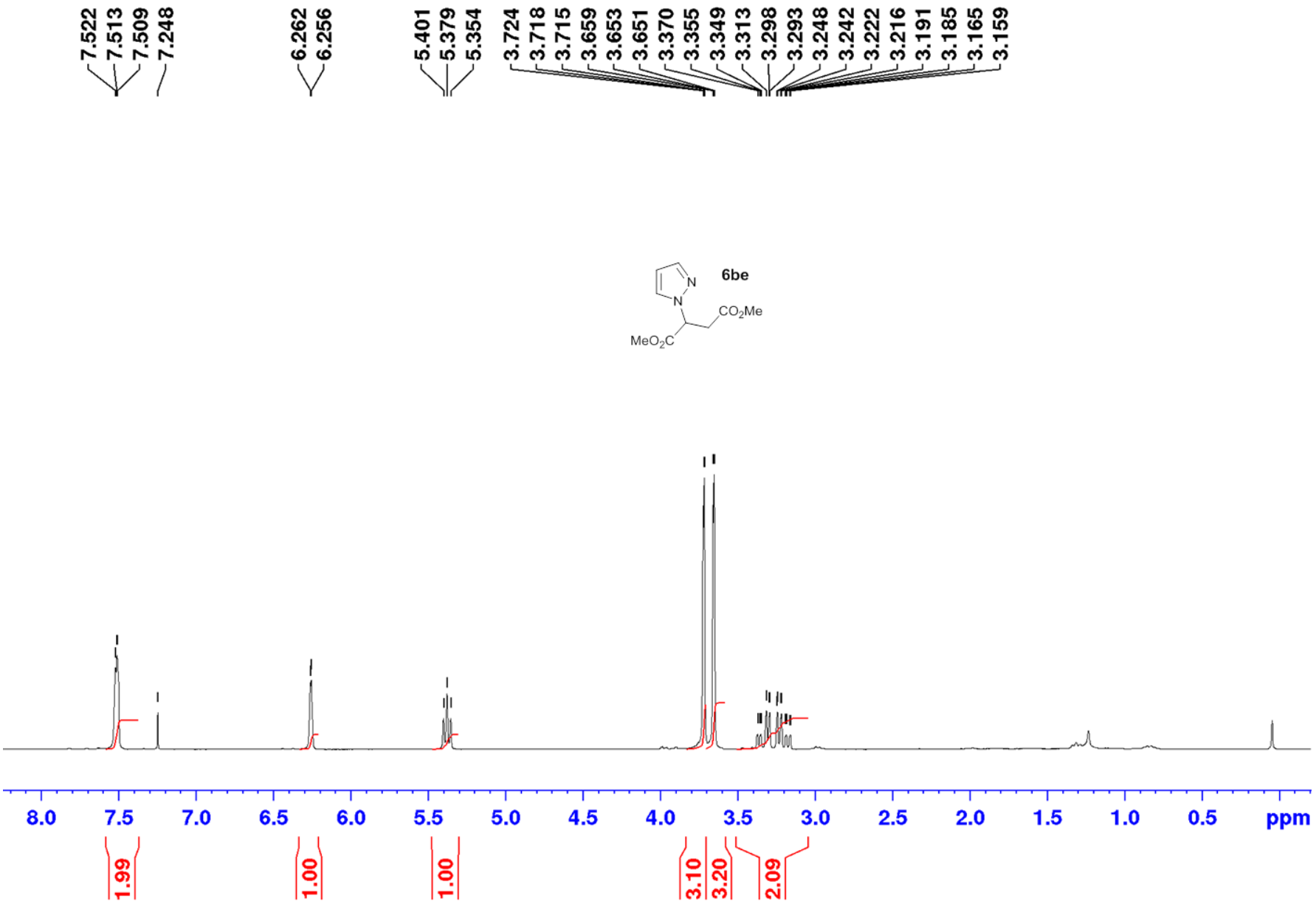
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.513
7.509
7.248
6.262
6.256
5.401
5.379
5.354
3.724
3.718
3.715
3.659
3.653
3.651
3.370
3.355
3.349
3.313
3.298
3.293
3.248
3.242
3.222
3.216
3.191
3.185
3.165
3.159
6be
N
N
CO2Me
MeO2C
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
0.5
ppm
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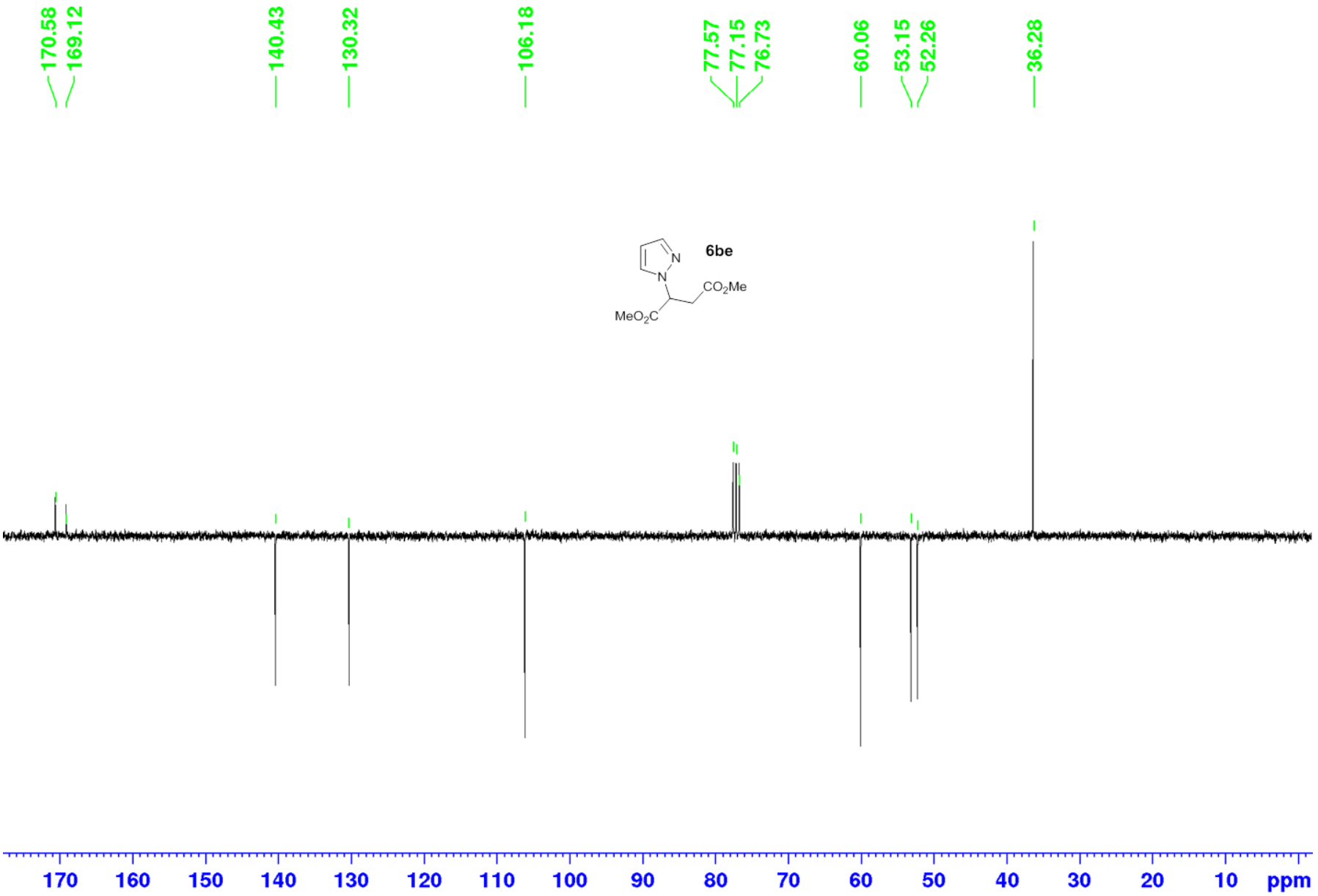
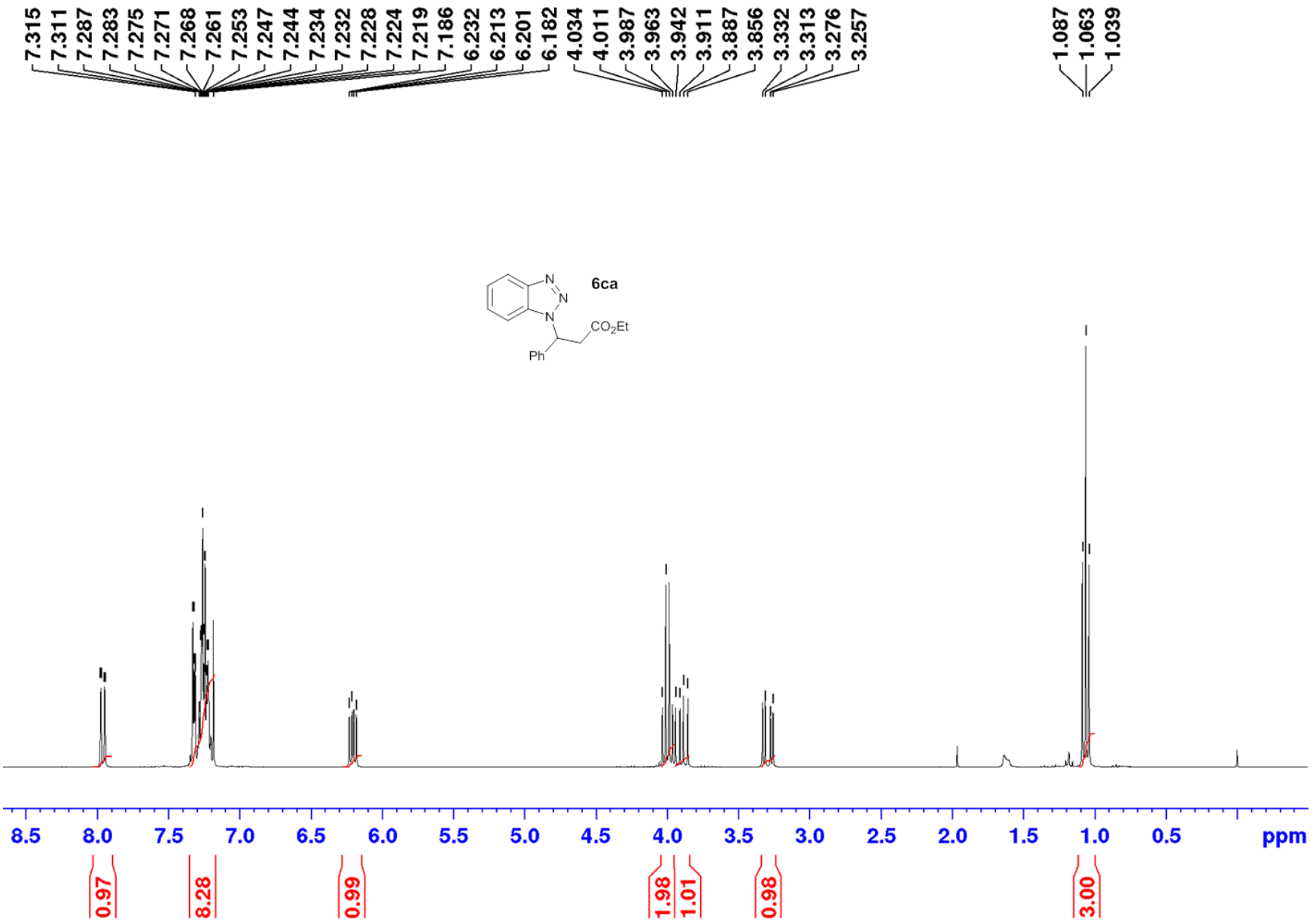
1.00
1.00
3.10
3.20
2.09


170.58
169.12
140.43
130.32
106.18
77.57
77.15
76.73
60.06
53.15
52.26
36.28
6be
N
N
CO2Me
MeO2C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.283
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7.271
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7.261
7.253
7.247
7.244
7.234
7.232
7.228
7.224
7.219
7.186
6.232
6.213
6.201
6.182
4.034
4.011
3.987
3.963
3.942
3.911
3.887
3.856
3.332
3.313
3.276
3.257
1.087
1.063
1.039
6ca
N
N
N
CO2Et
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
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1.98
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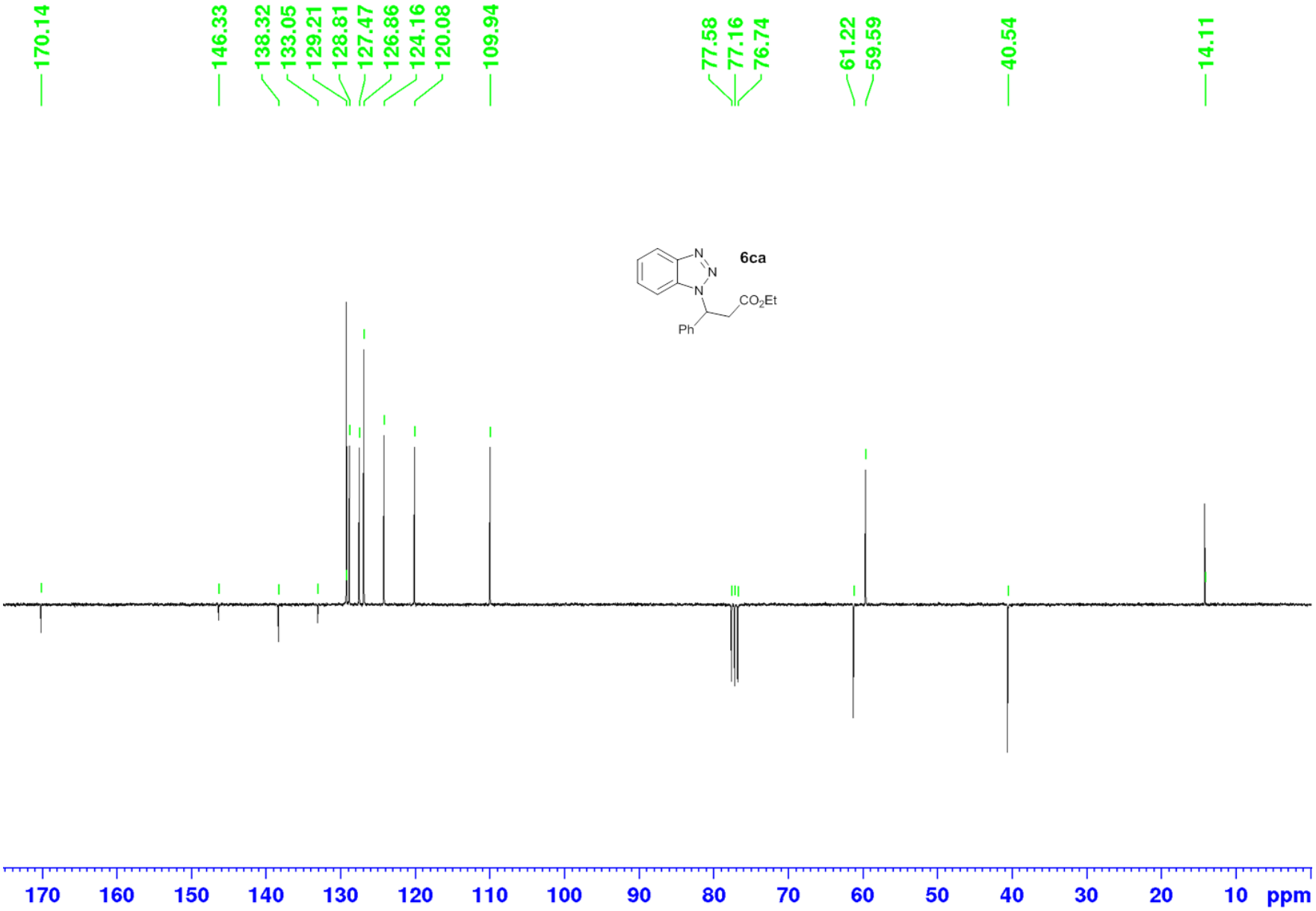
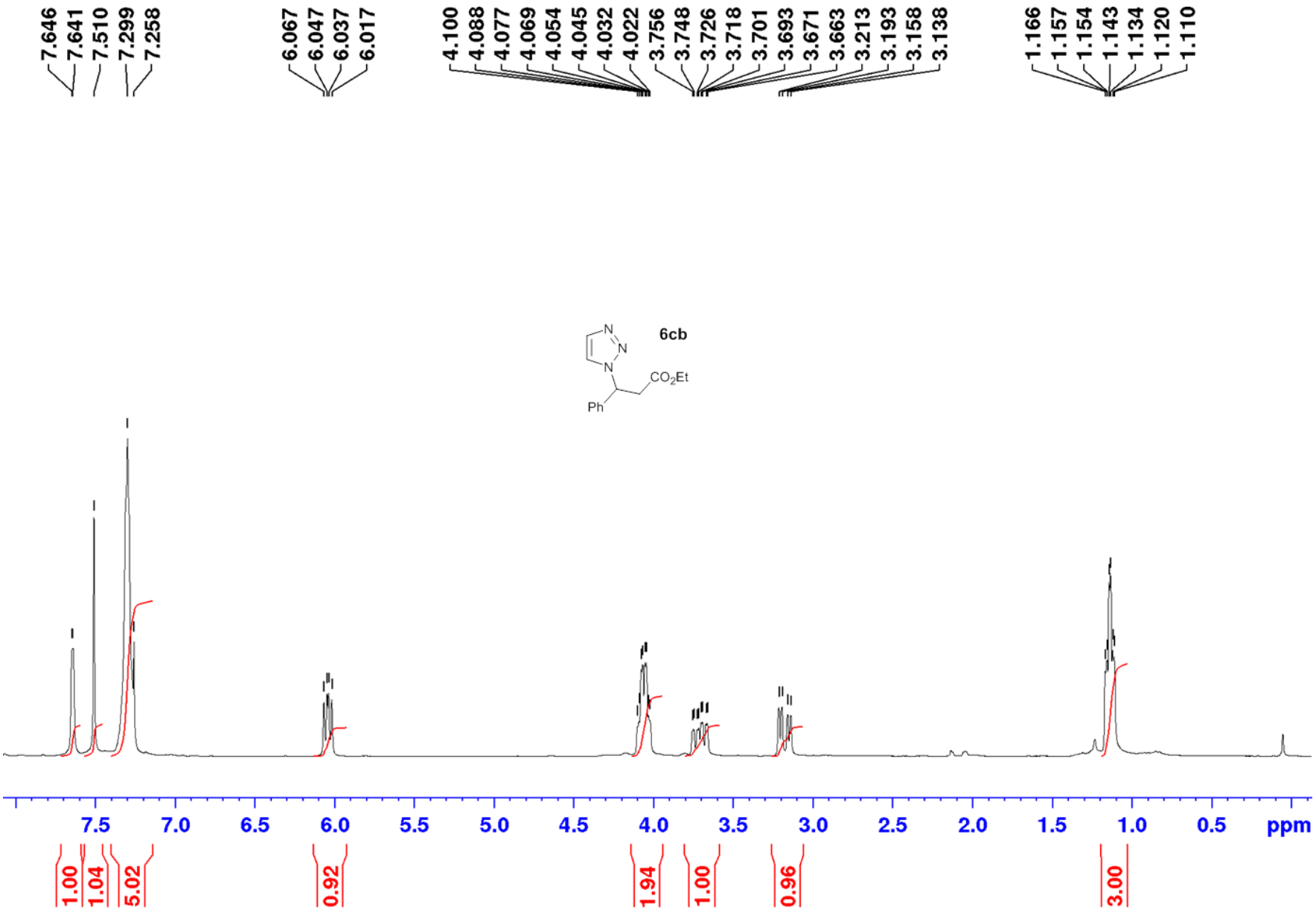
0.98
3.00


170.14
146.33
138.32
133.05
129.21
128.81
127.47
126.86
124.16
120.08
109.94
77.58
77.16
76.74
61.22
59.59
40.54
14.11
6ca
N
N
N
CO2Et
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.646
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7.510
7.299
7.258
6.067
6.047
6.037
6.017
4.100
4.088
4.077
4.069
4.054
4.045
4.032
4.022
3.756
3.748
3.726
3.718
3.701
3.693
3.671
3.663
3.213
3.193
3.158
3.138
1.166
1.157
1.154
1.143
1.134
1.120
1.110
6cb
N
N
N
CO2Et
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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5.02
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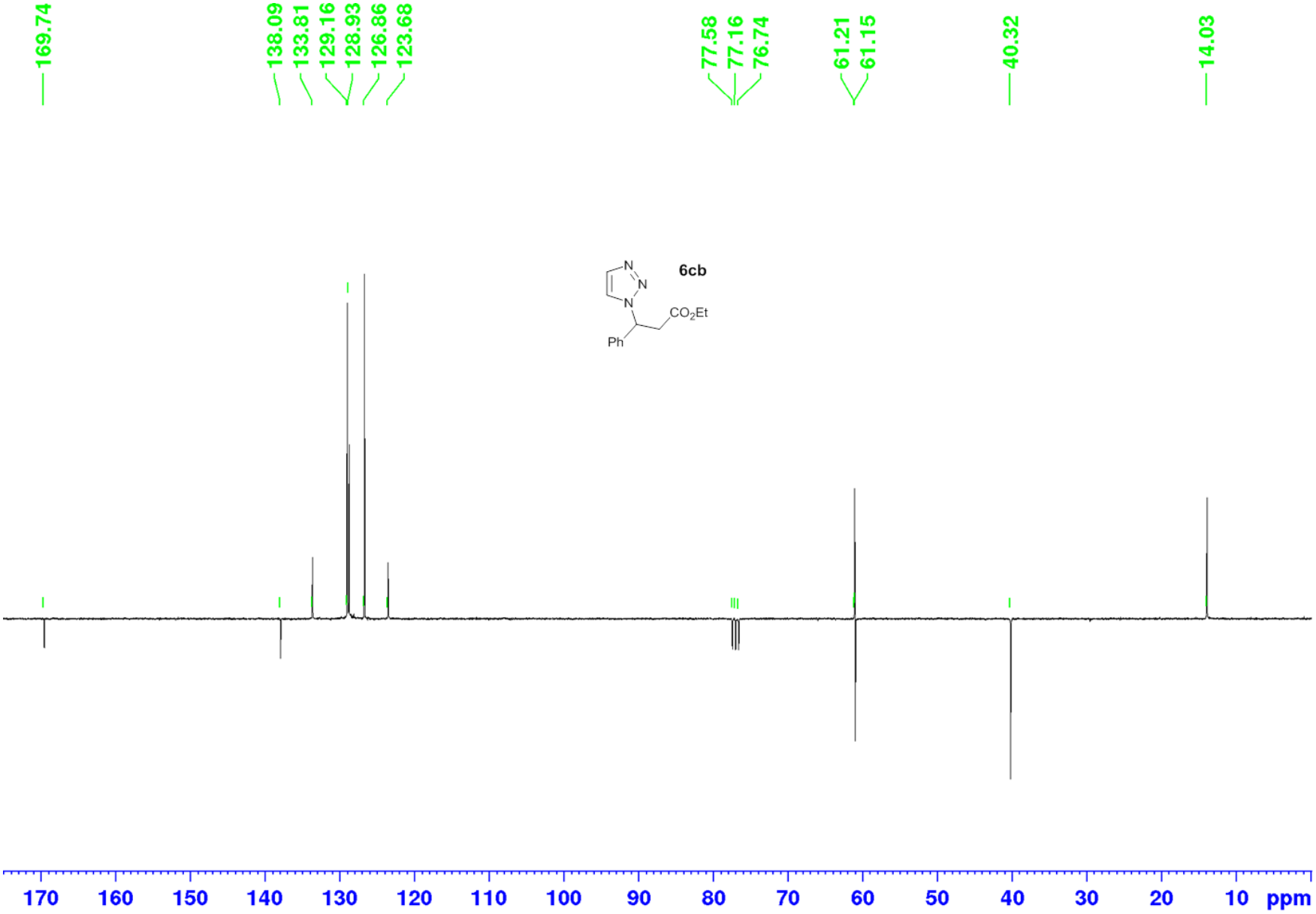
3.00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138.09
133.81
129.16
128.93
126.86
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77.58
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61.21
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40.32
14.03
6cb
N
N
N
CO2Et
Ph
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90
80
70
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30
20
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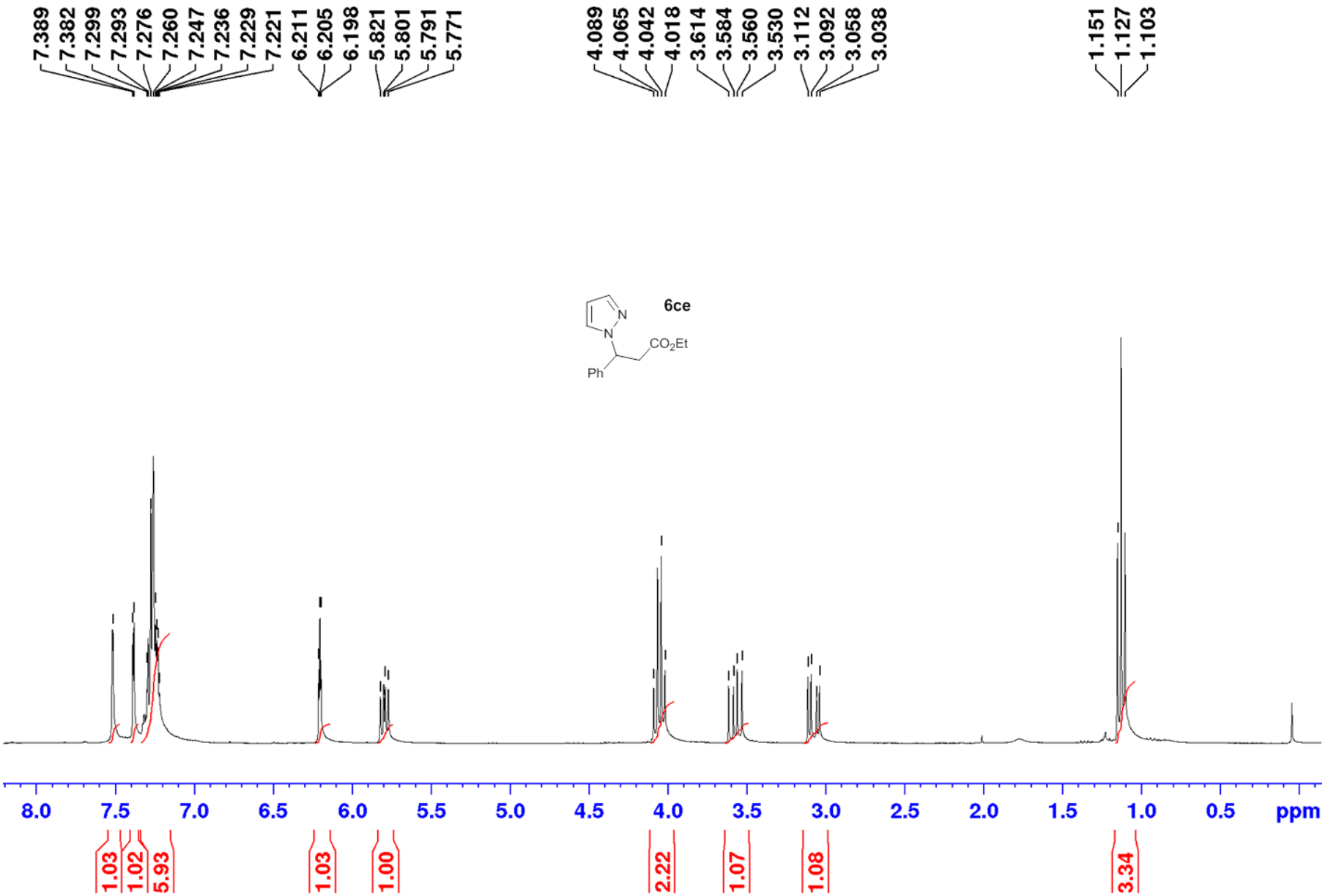
ppm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7.382
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7.221
6.211
6.205
6.198
5.821
5.801
5.791
5.771
4.089
4.065
4.042
4.018
3.614
3.584
3.560
3.530
3.112
3.092
3.058
3.038
1.151
1.127
1.103
6ce
N
N
CO2Et
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.00
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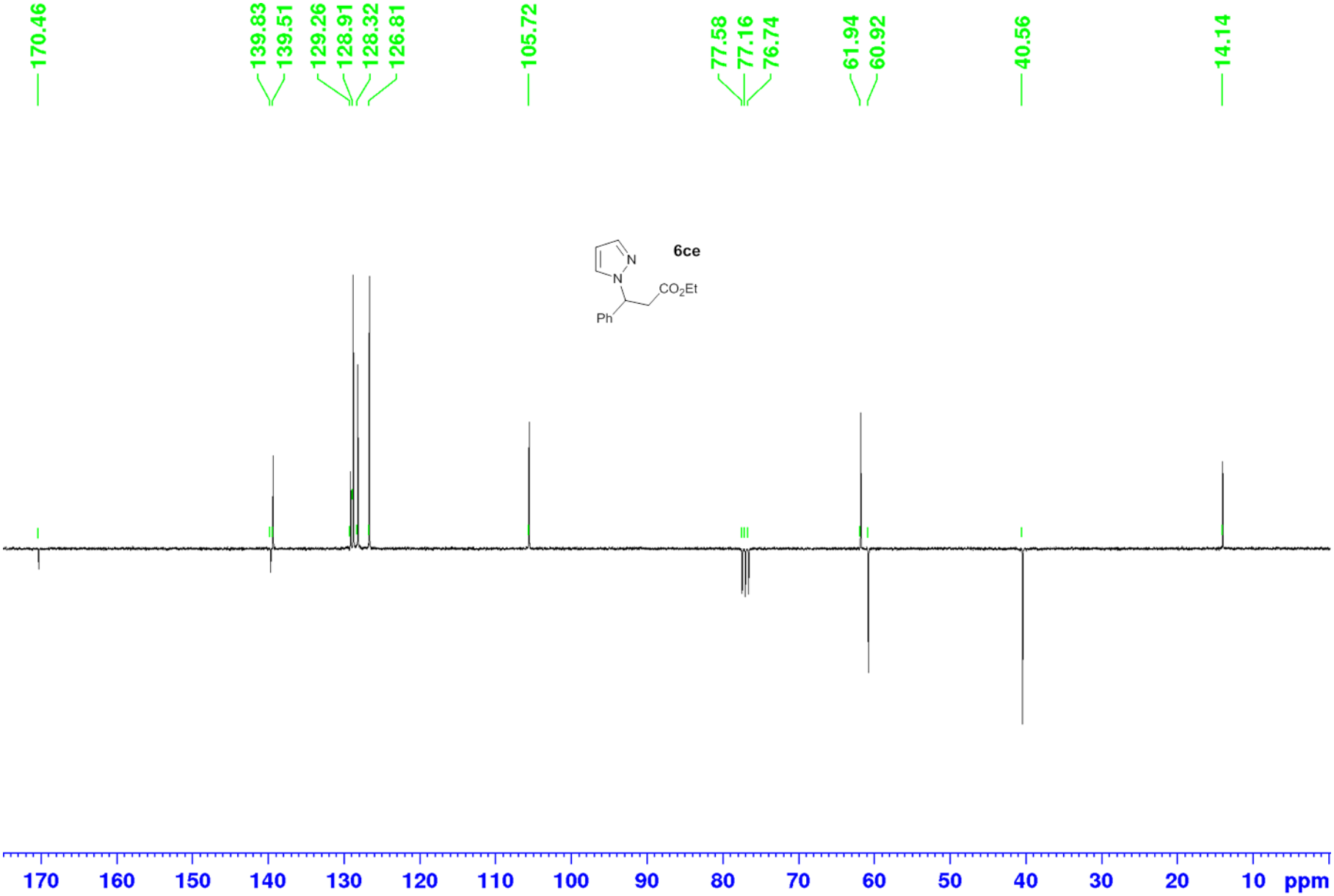
3.34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139.83
139.51
129.26
128.91
128.32
126.81
105.72
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77.16
76.74
61.94
60.92
40.56
14.14
6ce
N
N
CO2Et
Ph
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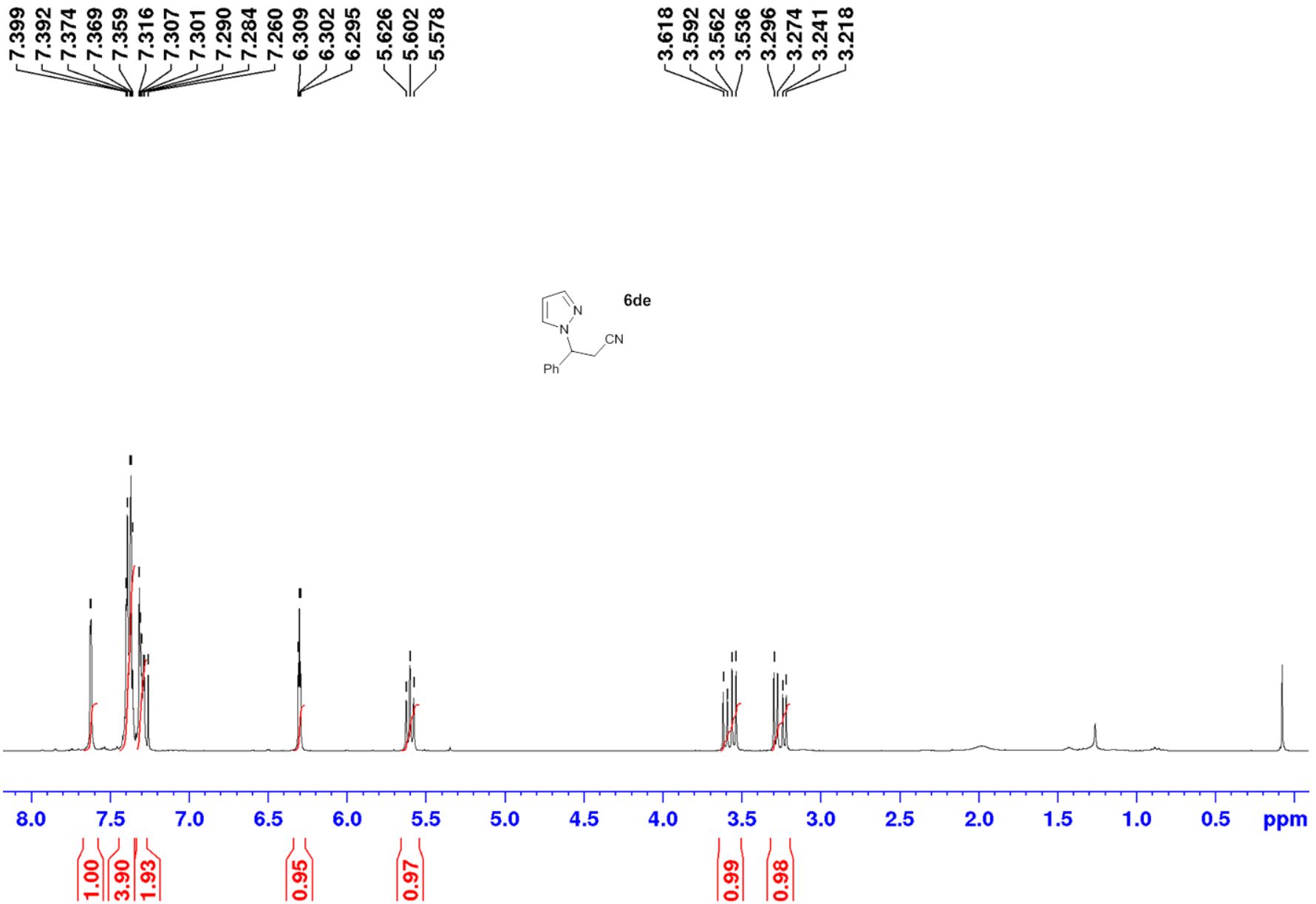
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.374
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7.316
7.307
7.301
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7.284
7.260
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6.302
6.295
5.626
5.602
5.578
3.618
3.592
3.562
3.536
3.296
3.274
3.241
3.218
6de
N
N
CN
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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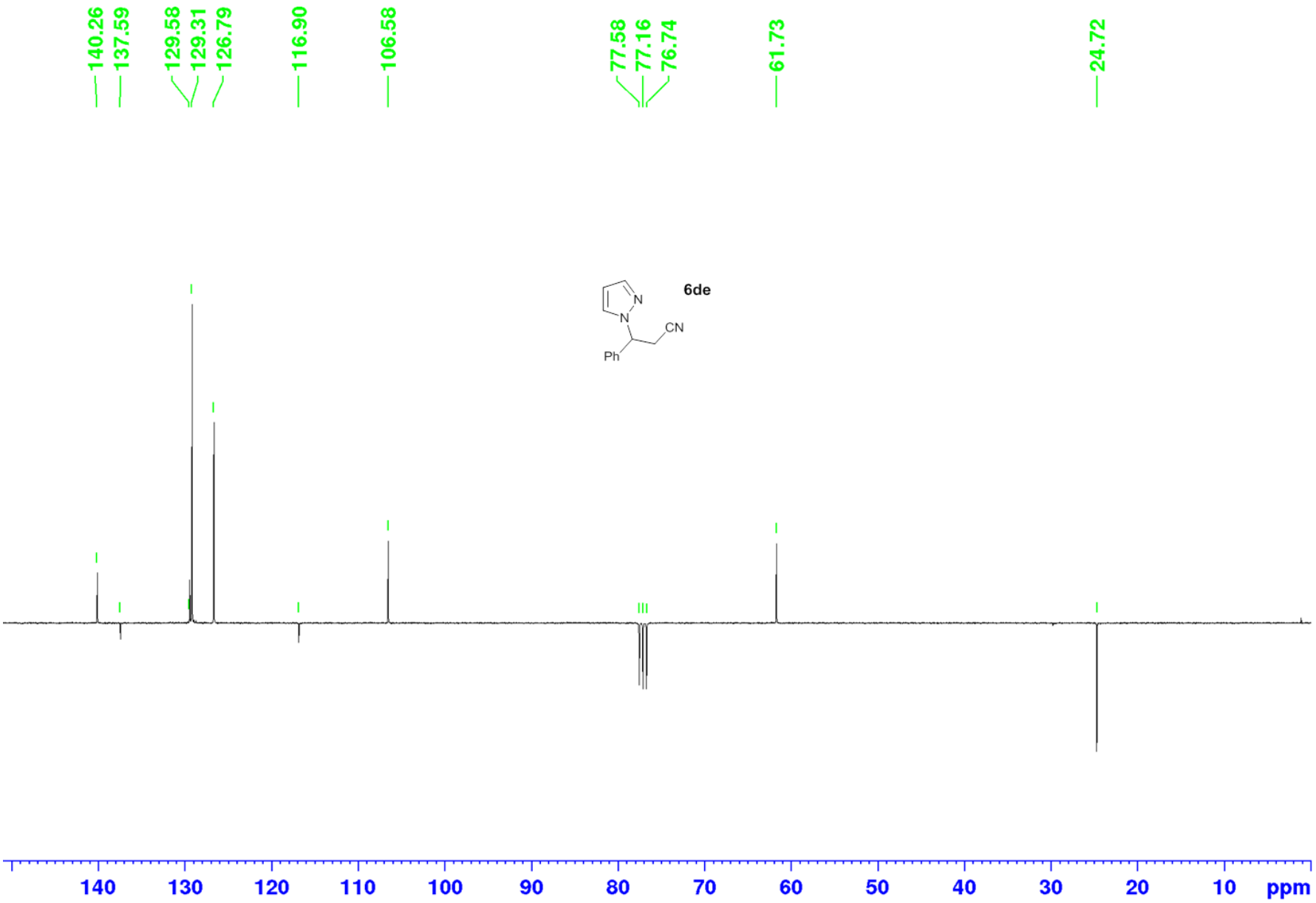
1.93
0.95
0.97
0.99
0.98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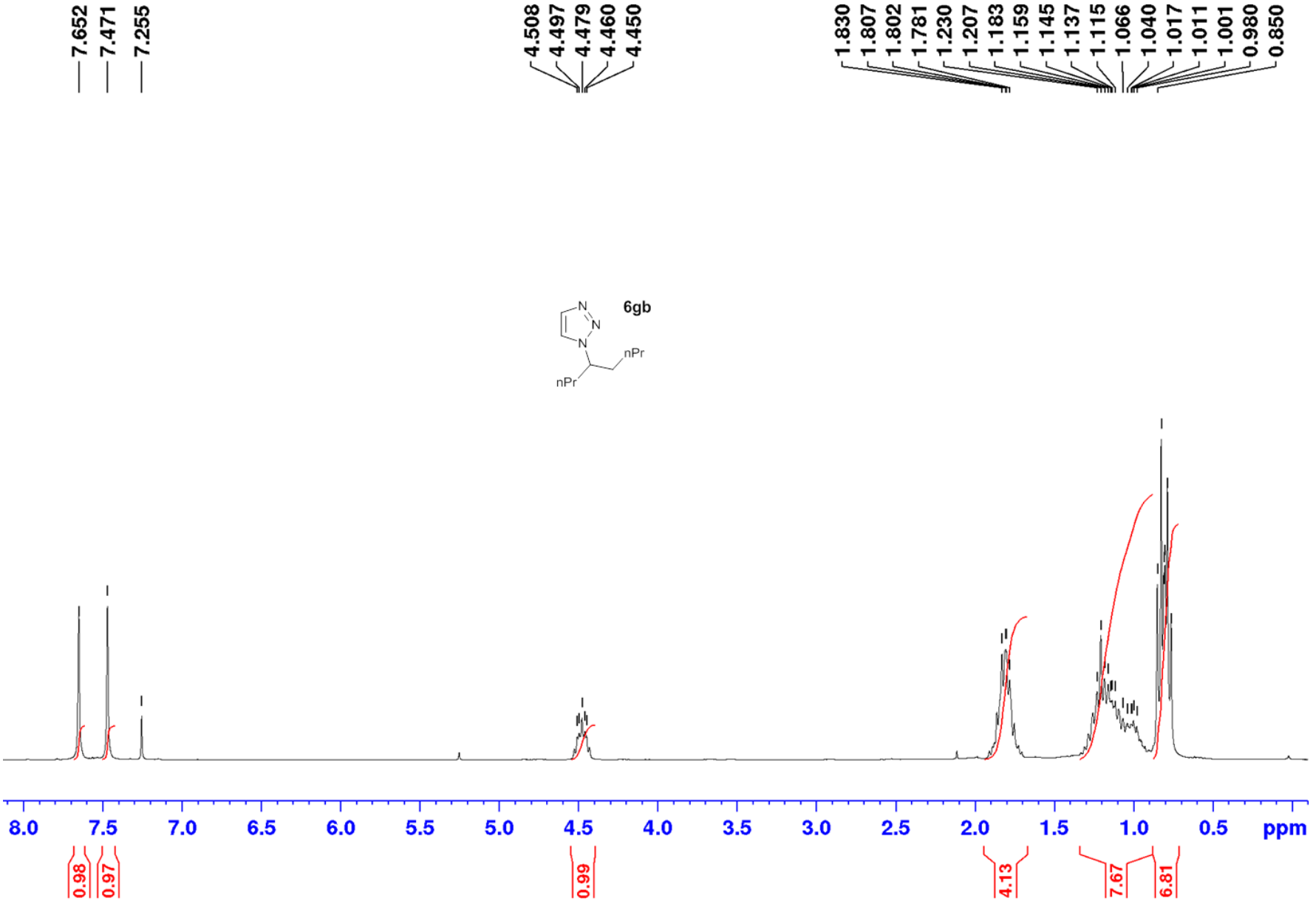
129.58
129.31
126.79
116.90
106.58
77.58
77.16
76.74
61.73
24.72
6de
N
N
CN
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.471
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4.479
4.460
4.450
1.830
1.807
1.802
1.781
1.230
1.207
1.183
1.159
1.145
1.137
1.115
1.066
1.040
1.017
1.011
1.001
0.980
0.850
6gb
nPr
nPr
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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ppm
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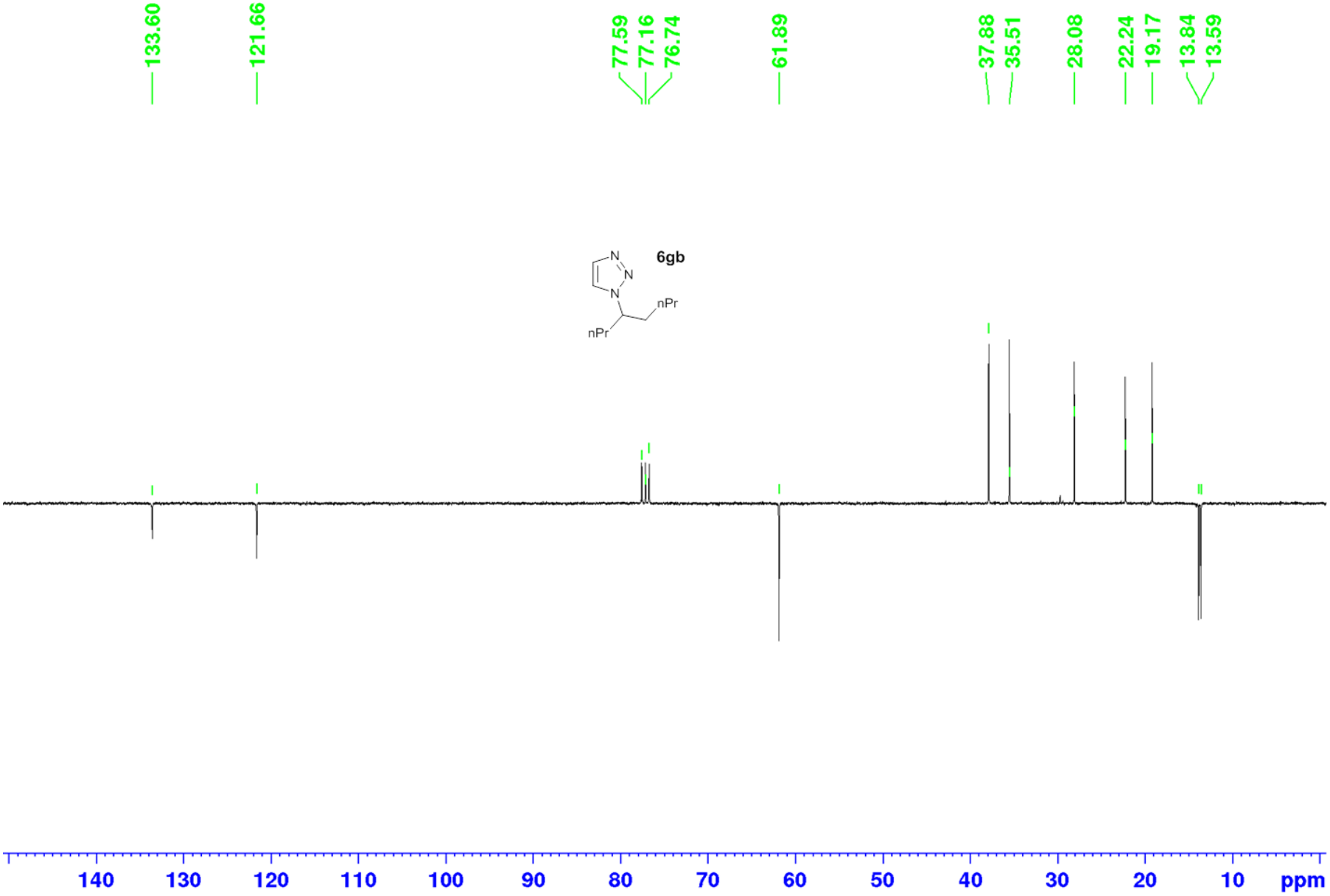
6.81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77.16
76.74
61.89
37.88
35.51
28.08
22.24
19.17
13.84
13.59
6gb
N
N
N
nPr
nPr
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm