

Reaction of sodium *N*-benzylideneglycinate with dialkyl chlorophosphites in the presence of water

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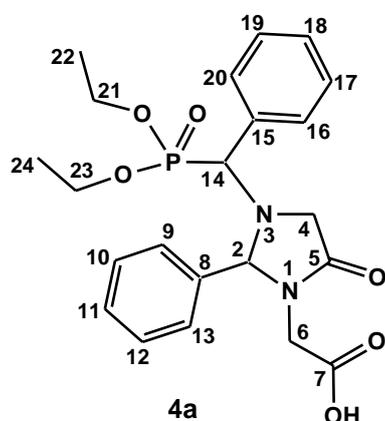
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General remarks

NMR experiments were carried out using a Bruker Avance-400 spectrometer [400.1 MHz (^1H), 162.0 MHz, (^{31}P), 100.6 MHz (^{13}C)] or Avance-600 one [600.1 MHz (^1H), 242.9 MHz, (^{31}P), 150.9 MHz (^{13}C)]. Chemical shifts are reported in δ (ppm) relative to the residual ^1H and ^{13}C signals of CHCl_3 , acetone or H_3PO_4 as the external standard for ^{31}P . IR spectra were measured on a Bruker Vector-22 spectrometer (USA) as suspensions in nujol or KBr pellet. Melting points were obtained using a Cole-Parmer Stuart digital SMP10 apparatus (USA) and were uncorrected. ESI mass spectra were recorded on a Bruker Daltonik Amazon X spectrometer (Germany) in positive and negative ions modes. MALDI mass spectra were acquired using an Ultra flex III TOF/TOF spectrometer (Bruker Daltonics, Germany). Elemental analyses for C, H and N were performed using a Euro Vector 2000 CHNS-3 analyzer (Italy). Phosphorus content (%) was determined by pyrolysis in oxygen stream. All the manipulations were performed in argon atmosphere. All the solvents were dehydrated according to standard methods.

2-{3-[α -(Diethoxyphosphoryl)benzyl]-5-oxo-2-phenylimidazolidin-1-yl}acetic acid (**4a**).



Found: C, 58.93; H, 5.91; N, 6.42; P, 7.31. Calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_6\text{P}$: C, 59.19; H, 6.10; N, 6.27; P, 6.94. ESI mass spectrum, m/z : found 445 $[\text{M} - \text{H}]^-$ (in the negative ion mode), 447 $[\text{M} + \text{H}]^+$ (in the positive ion mode), calculated 446 $[\text{M}]$. IR spectrum, cm^{-1} (pellet KBr): 3402, 2984, 2933, 1746, 1708, 1494, 1455, 1431, 1401, 1315, 1199, 1098, 1058, 1029, 984, 906, 827, 770, 734, 703, 679, 652, 628, 573, 558, 498.

^1H NMR spectrum of compound (**4a**) (400 MHz, CDCl_3 , d_1), δ ppm, J Hz: 7.47 m (C_6H_5 , 5H), 7.39 m (C_6H_5 , 5H), 5.55 o. m. c (CO_2H , 1H), 5.21 ym. c (CH^2 , 1H), 4.26 d (C^6H_B , 1H, $^2J_{\text{H}_A\text{CH}}$ 17.8), 4.10 m ($\text{C}^{21,23}\text{H}_A\text{H}_B$, 2H), 4.09 d (C^4H_B , 1H, $^2J_{\text{H}_A\text{CH}}$ 14.7), 4.01 d (C^{14}H , 1H, $^2J_{\text{PCH}}$ 25.2), 3.66 d (C^4H_A , 1H, $^2J_{\text{H}_B\text{CH}}$ 14.7), 3.62 m ($\text{C}^{21,23}\text{H}_A$, 1H, $^2J_{\text{H}_B\text{CH}}$ 9.7, $^3J_{\text{HCCH}}$ 7.2), 3.08 d (C^6H_A , 1H, $^2J_{\text{H}_A\text{CH}}$ 17.8), 3.86 d ($\text{C}^{21,23}\text{H}_B$, 1H, $^2J_{\text{H}_A\text{CH}}$ 9.7, $^3J_{\text{POCH}}$ 7.3, $^3J_{\text{HCCH}}$ 7.2), 1.30 t ($\text{C}^{22,24}\text{H}_3$, 3H, $^3J_{\text{HCCH}}$ 7.1), 0.98 t ($\text{C}^{22,24}\text{H}_3$, 3H, $^3J_{\text{HCCH}}$ 7.1).

^{13}C NMR spectrum of compound (**4a**) (100.6 MHz, CDCl_3 , d_1), δ ppm, J Hz (thereafter the view of signal in $^{13}\text{C}\{-^1\text{H}\}$ is in parentheses): 79.10 d. d. m (d) (C^2 , $^1J_{\text{HC}}$ 152.0, $^3J_{\text{PCNC}}$ 19.1), 171.68 m (c) (C^5), 50.49 br. d. d. d (c) (C^4 , $^1J_{\text{HC}}$ 153.4, $^1J_{\text{HC}}$ 124.0, $^3J_{\text{PCNC}}$ 6.3-6.4), 58.69 br. d. d. m (d) (C^{14} , $^1J_{\text{PC}}$ 167.5, $^1J_{\text{HC}}$ 130.4), 130.35 m (d) (C^{15} , $^2J_{\text{PC}^{14}\text{C}}$ 3.2), 130.98 d. d. m (d) ($\text{C}^{16,20}$, $^1J_{\text{HC}}$ 159.0, $^3J_{\text{PCCC}}$ 8.5, $^3J_{\text{HC}^{18}\text{CC}}$ 7.0, $^3J_{\text{HC}^{20,16}\text{CC}^{16,20}}$ 6.5-7.0), 129.17 d. d (s) ($\text{C}^{17,19}$, $^1J_{\text{HC}}$ 161.5, $^3J_{\text{HCCC}}$ 6.0), 128.94 d. m (d) (C^{18} , $^1J_{\text{HC}}$ 161.0, $^3J_{\text{HC}^{16,20}\text{CC}}$ 7.2, $^5J_{\text{PCCCC}}$ 1.1), 135.41 m (s) (C^8), 129.55 d. m (s) ($\text{C}^{9,13}$, $^1J_{\text{HC}}$ 159.0), 129.05 d. d (s) ($\text{C}^{10,12}$, $^1J_{\text{HC}}$ 161.5, $^3J_{\text{HC}^{12,10}\text{CC}^{10,12}}$ 6.8), 130.49 d. m (s) (C^{11} , $^1J_{\text{HC}}$ 161.5, $^3J_{\text{HC}^{9,13}\text{CC}}$ 6.5-7.0), 41.47 br. t (s) (C^6 , $^1J_{\text{HC}}$ 141.1), 171.51 br. t (br. s) (C^7 , $^2J_{\text{HC}^6\text{C}}$ 5.3-5.4), 63.16 t. m (d) ($\text{C}^{21,23}$, $^1J_{\text{HC}}$ 148.3, $^2J_{\text{POC}}$ 7.2, $^2J_{\text{HCC}}$ 4.4), 63.05 t. m (d) ($\text{C}^{21,23}$, $^1J_{\text{HC}}$ 148.0, $^2J_{\text{POC}}$ 6.9, $^2J_{\text{HCC}}$ 4.4), 16.57 q. d. t (d) ($\text{C}^{22,24}$, $^1J_{\text{HC}}$ 127.2, $^3J_{\text{POCC}}$ 6.3, $^3J_{\text{HCCC}}$ 3.0), 16.16 q. d. t (d) ($\text{C}^{22,24}$, $^1J_{\text{HC}}$ 128.2, $^3J_{\text{POCC}}$ 5.7, $^3J_{\text{HCCC}}$ 2.7).

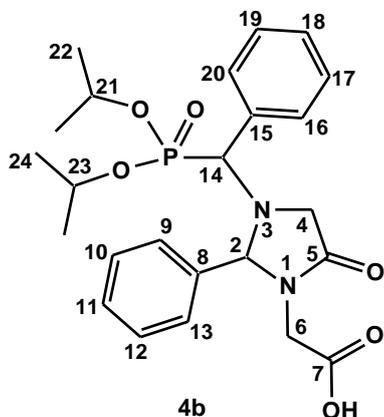
^{31}P / $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of compound (**4a**) (162.0 MHz, CDCl_3 , d_1), δ_{P} ppm, J Hz: 21.1 br. d. m (s) ($^2J_{\text{PCH}}$ 25.5, $^3J_{\text{POCH}}$ 8.0, $^3J_{\text{POCH}}$ 7.3). ^1H NMR spectrum (400 MHz, CDCl_3 , d_2), δ ppm, J Hz: 7.34 m (C_6H_5 , 5H), 7.25 m (C_6H_5 , 5H), 6.53 v. br. s (CO_2H , 1H), 5.83 br. s (CH^2 , 1H), 4.40 d (C^6H_B , 1H, $^2J_{\text{H}_A\text{CH}}$ 17.8), 4.27 br. d (C^4H_B , 1H, $^2J_{\text{H}_A\text{CH}}$ 15.7), 4.12 d (C^{14}H , 1H, $^2J_{\text{PCH}}$ 16.5), 3.83 br. d (C^4H_A , 1H, $^2J_{\text{H}_B\text{CH}}$

15.7), 4.09-4.11 m (C^{21,23}H, 2H), 3.06 d (C⁶H_A, 1H, ²J_{H_ACH} 17.8), 1.29 t (C^{22,24}H₃, 3H, ³J_{HCC} 7.1), 1.13 t (C^{22,24}H₃, 3H, ³J_{HCC} 7.1).

¹³C NMR spectrum of compound (**4a**) (100.6 MHz, CDCl₃, *d*₂), δ_C ppm, *J* Hz: 80.42 d. m (d) (C², ¹J_{HC} 152.5, ³J_{PCNC} 4.0), 171.28 m (c) (C⁵), 51.44 br. d. m (s) (C⁴, ¹J_{HC} 148.5, ¹J_{HC} 140.3, ³J_{HCCC} 4.7, ³J_{HCCC} 3.3, ³J_{PCNC} 2.6), 61.71 br. d. d. m (d) (C¹⁴, ¹J_{PC} 144.2, ¹J_{HC} 122.7), 133.95 m (d) (C¹⁵, ²J_{PC¹⁴C} 3.1), 129.68 d. d. m (d) (C^{16,20}, ¹J_{HC} 160.0, ³J_{PCCC} 7.6, ³J_{HC¹⁸CC} 7.0, ³J_{HC²⁰,¹⁶CC^{16,20}} 6.2), 128.98 d. d (s) (C^{17,19}, ¹J_{HC} 160.8, ³J_{HC¹⁹,¹⁷CC^{17,19}} 6.0), 128.36 d. m (d) (C¹⁸, ¹J_{HC} 160.7, ³J_{HC¹⁶,²⁰CC} 7.0, ⁵J_{PCCCC} 1.2), 136.83 m (s) (C⁸, ³J_{HCCC} 5.5-6.0), 129.02 d. m (s) (C^{9,13}, ¹J_{HC} 160.8, ³J_{HC¹¹CC} 7.0, ³J_{HC¹³,⁹CC^{9,13}} 6.5), 128.57 d. d (s) (C^{10,12}, ¹J_{HC} 160.4, ³J_{HC¹²,¹⁰CC^{10,12}} 7.0), 129.99 d. t (s) (C¹¹, ¹J_{HC} 163.1, ³J_{HC⁹,¹³CC} 7.0), 41.29 t (s) (C⁶, ¹J_{HC} 140.3), 170.50 br. t (br. s) (C⁷, ²J_{HC⁶C} 5.4), 63.23 t. d. q (d) (C^{21,23}, ¹J_{HC} 148.5, ²J_{POC} 7.3, ²J_{HCC} 4.0), 62.57 t. d. q (d) (C^{21,23}, ¹J_{HC} 148.1, ²J_{POC} 7.7, ²J_{HCC} 4.0), 16.37 q. d. t (d) (C^{22,24}, ¹J_{HC} 127.4, ³J_{POCC} 5.5, ³J_{HCCC} 2.8), 16.18 q. d. t (d) (C^{22,24}, ¹J_{HC} 127.3, ³J_{POCC} 5.5, ³J_{HCCC} 2.8).

³¹P / ³¹P-¹H NMR spectrum of compound (**4a**) (162.0 MHz, CDCl₃, *d*₂), δ_P ppm, *J* Hz: 22.8 br. d. m (s) (²J_{PCH} 16.5, ³J_{POCH} 7.3-8.0, ³J_{POCH} 7.3-8.0).

2-{3-[α-(Diisopropoxyphosphoryl)benzyl]-5-oxo-2-phenylimidazolidin-1-yl}acetic acid (**4b**)



MALDI mass-spectrum: 474 [M], 497 [M + Na]⁺, 513 [M + K]⁺. ESI mass spectrum, *m/z*: found 473 [M - H]⁻ (in the negative ion mode), 475 [M + H]⁺ (in the positive ion mode), calculated 474 [M]. IR spectrum, cm⁻¹ (film): 3250-3350, 2981, 2937, 1704-1740, 1535, 1494, 1451, 1386, 1316, 1180, 1103, 994, 828, 775, 703, 652, 627, 564, 512, 425.

¹H NMR spectrum of compound (**4b**) (400 MHz, CDCl₃, *d*₁ : *d*₂ = 1 : 1), δ ppm, *J* Hz: 9.58 br. s (OH), 7.0 m, 7.49-7.52 m, 7.37-7.47 m, 7.25-7.35 m, 7.20 m (C₆H₅), 5.87 d. t (H², ⁴J_{H_AC⁴NCH} 2.3-2.4, ⁴J_{H_BC⁴NCH} 2.1, ⁴J_{PCNCH} 2.1, *d*₂), 5.18 d. t (H², ⁴J_{H_AC⁴NCH} 2.1-2.2, ⁴J_{PCNCH} 1.5, *d*₁), 4.70 d. sept (OCH, ³J_{HCC} 6.2, ³J_{POCH} 6.0-7.0, *d*₁), 4.67 d. sept (OCH, ³J_{HCC} 6.2, ³J_{POCH} 6.0-7.0, *d*₂), 4.49 br. d. sept (OCH, ³J_{HCC} 6.2, ³J_{POCH} 6.0-7.0, *d*₂), 4.39 d (H⁶_A, ²J_{H_BCH} 18.0, *d*₂), 4.38 d. sept (OCH, ³J_{HCC} 6.2, ³J_{POCH} 6.0-7.0, *d*₁), 4.28 d (H⁶_A, ²J_{H_BCH} 18.0, *d*₁), 4.04 d (H¹⁴, ²J_{PCH} 17.2, *d*₂), 4.23 d. d. d (H⁴_A, ²J_{H_BCH} 14.8, ⁴J_{PCNCH} 3.8-4.0, ⁴J_{HC²NCH} 2.3-2.4, *d*₂), 4.12 br. d (H⁴_A, ²J_{H_BCH} 14.6, *d*₁), 3.93 d (H¹⁴, ²J_{PCH} 26.1, *d*₁), 3.85 d. d. d (H⁴_B, ²J_{H_ACH} 14.7, ⁴J_{HC²NCH} 2.1, ⁴J_{PCNCH} 1.3, *d*₂), 3.74 d. d. d (H⁴_B, ²J_{H_ACH} 14.6, ⁴J_{HC²NCH} 2.1, ⁴J_{PCNCH} 1.5, *d*₁), 3.02 d (H⁶_B, ²J_{H_ACH} 18.0, *d*₂), 3.0 d (H⁶_B, ²J_{H_ACH} 18.0, *d*₁), 1.31 d (Me, ³J_{POCH} 6.2, *d*₁), 1.28 d (Me, ³J_{POCH} 6.2, *d*₂), 1.25 d (Me, ³J_{HCC} 6.2, *d*₁), 1.23 d (Me, ³J_{HCC} 6.2, *d*₂), 1.20 d (Me, ³J_{HCC} 6.2, *d*₂), 1.13 d (Me, ³J_{HCC} 6.2, *d*₁), 0.84 d (Me, ³J_{HCC} 6.2, *d*₂), 0.62 d (Me, ³J_{HCC} 6.2, *d*₁).

¹H-³¹P NMR spectrum of compound (**4b**) (400 MHz, CDCl₃, *d*₁ : *d*₂ = 1 : 1), δ ppm, *J* Hz: 5.18 t (H², ⁴J_{H_AC⁴NCH} 2.1-2.2, *d*₁), 4.70 sept (OCH, ³J_{HCC} 6.2, *d*₁), 4.67 sept (OCH, ³J_{HCC} 6.2, *d*₂), 4.49 br. sept (OCH, ³J_{HCC} 6.2, *d*₂), 4.38 sept (OCH, ³J_{HCC} 6.2, *d*₁), 3.93 c (H¹⁴, *d*₁), 4.23 d. d (H⁴_A, ²J_{H_BCH} 14.8, ⁴J_{HC²NCH} 2.3-2.4, *d*₂), 4.04 s (H¹⁴, *d*₂), 3.74 d. d (H⁴_B, ²J_{H_ACH} 14.6, ⁴J_{HC²NCH} 2.1, *d*₁), 3.85 d. d (H⁴_B, ²J_{H_ACH} 14.7, ⁴J_{HC²NCH} 2.1, *d*₂).

¹³C NMR spectrum of compound (**4b**) (100.6 MHz, CDCl₃, *d*₁ : *d*₂ = 1 : 1), δ_C ppm, *J* Hz: 80.47 d. m (d) (C², ¹J_{HC} 153.0, ³J_{PCNC} 3.6, *d*₂), 79.06 d. d. m (d) (C², ¹J_{HC} 150.3, ³J_{PCNC} 19.8, *d*₁), 51.51 d. d. m

(d) (C^4 , $^1J_{HC}$ 149.3, $^1J_{HC}$ 140.4, $^3J_{PCNC}$ 2.7, d_2), 50.66 d. d. d (s) (C^4 , $^1J_{HC}$ 152.3, $^1J_{HC}$ 135.0, $^3J_{PCNC}$ 0, d_1), 171.72 m (s) (C^5 , d_1), 171.37 m (s) (C^5 , d_2), 41.46 t (s) (C^6 , $^1J_{HC}$ 140.1, d_1), 41.40 t (s) (C^6 , $^1J_{HC}$ 140.1, d_2), 170.52 t (s) (C^7 , $^2J_{HC6C}$ 5.5, d_1), 170.45 t (s) (C^7 , $^2J_{HC6C}$ 5.5, d_2), 136.77 m (s) (C^8 , d_2), 135.39 m (s) (C^8 , d_1), 129.63 d. m (s) ($C^{9,13}$, $^1J_{HC}$ 159.2, $^3J_{HC^{11}CH}$ 6.5, $^3J_{HC^{13,9}CC^{9,13}}$ 5.0, d_1 , d_2), 129.91 d. d (s) ($C^{10,12}$, $^1J_{HC}$ 160.4, $^3J_{HC^{12,10}CC^{10,12}}$ 6.0, d_1 , d_2), 130.35 d. t (s) (C^{11} , $^1J_{HC}$ 160.7, $^3J_{HC^9,13CC}$ 7.2, d_1), 129.93 d. t (s) (C^{11} , $^1J_{HC}$ 161.4, $^3J_{HC^9,13CC}$ 7.2, d_2), 60.48 d. d. m (d) (C^{14} , $^1J_{PC}$ 145.1, $^1J_{HC}$ 131.3, d_2), 59.18 d. d. m (d) (C^{14} , $^1J_{PC}$ 170.2, $^1J_{HC}$ 131.5, d_1), 134.16 m (d) (C^{15} , $^3J_{HC^{17,19}CC}$ 7.2, $^2J_{PC^{14}C}$ 3.8, d_2), 130.67 m (d) (C^{15} , $^3J_{HC^{17,19}CC}$ 7.0-7.2, $^2J_{PC^{14}C}$ 3.3, d_1), 131.04 d. d. m (d) ($C^{16,20}$, $^1J_{HC}$ 160.0, $^3J_{PCCC}$ 8.4, $^3J_{HC^{18}CC}$ 7.1, $^3J_{HC^{20,16}CC^{16,20}}$ 6.5-7.0, d_1), 129.16 d. d. m (d) ($C^{16,20}$, $^1J_{HC}$ 160.0, $^3J_{PCCC}$ 9.0, $^3J_{HC^{18}CC}$ 7.1, $^3J_{HC^{20,16}CC^{16,20}}$ 6.5-7.0, d_2), 129.06 d. d (br. s) ($C^{17,19}$, $^1J_{HC}$ 161.3, $^3J_{HC^{19,17}CC^{17,19}}$ 7.2, d_1 , d_2), 128.79 d. t (s) (C^{18} , $^1J_{HC}$ 160.0, $^3J_{HC^{16,20}CC}$ 7.1, d_1), 128.20 d. t (s) (C^{18} , $^1J_{HC}$ 160.8, $^3J_{HC^{16,20}CC}$ 7.2, d_2), 72.51 d. d. sept (d) (OCH, $^1J_{HC}$ 147.5, $^2J_{POC}$ 8.0, $^2J_{HCC}$ 4.2, d_2), 72.15 d. d. sept (d) (OCH, $^1J_{HC}$ 147.5, $^2J_{POC}$ 7.2, $^2J_{HCC}$ 4.2, d_1), 71.98 d. d. sept (d) (OCH, $^1J_{HC}$ 147.6, $^2J_{POC}$ 7.9, $^2J_{HCC}$ 4.2, d_2), 71.61 d. d. sept (d) (OCH, $^1J_{HC}$ 147.6, $^2J_{POC}$ 7.6, $^2J_{HCC}$ 4.2, d_1), 24.38 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.7, $^3J_{POCC}$ 3.0, $^3J_{HCCC}$ 3.0, d_2), 24.36 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.7, $^3J_{POCC}$ 4.4, $^3J_{HCCC}$ 3.0, d_2), 24.16 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.6, $^3J_{POCC}$ 5.9, $^3J_{HCCC}$ 3.0, d_1), 24.23 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.6, $^3J_{POCC}$ 4.9, $^3J_{HCCC}$ 3.0, d_1), 24.04 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.6, $^3J_{POCC}$ 5.2, $^3J_{HCCC}$ 3.0, d_2), 23.38 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.5, $^3J_{POCC}$ 5.5, $^3J_{HCCC}$ 3.0, d_2), 22.93 q. q. d (d) (CH_3 , $^1J_{HC}$ 126.7, $^3J_{POCC}$ 6.0, $^3J_{HCCC}$ 3.0, d_1).

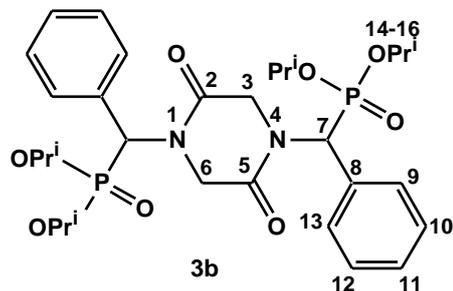
^{31}P / ^{31}P - $\{^1H\}$ NMR spectrum of compound (**4b**) (162.0 MHz, $CDCl_3$, $d_1 : d_2 = 1 : 1$), δ_P ppm, J Hz: 20.5 br. d. d. d (s) ($^2J_{PCH}$ 25.6, $^3J_{POCH}$ 6.7-7.4, d_1), 22.1 br. m (s) ($^2J_{PCH}$ 17.2, d_2).

1H NMR spectrum of compound (**4b**) (600 MHz, $CDCl_3$, $d_1 : d_2 = 2 : 1$), δ ppm, J Hz: 9.07 br. s (OH), 7.47 m, 7.43 m, 7.37 m, 7.32-7.35 m, 7.29 m, 7.25 m, 7.19 m (C_6H_5), 5.84 d. t (H^2 , $^4J_{HAC^4NCH}$ 2.4, $^4J_{HBC^4NCH}$ 2.1, $^4J_{PCNCH}$ 2.1, d_2), 5.18 br. s (H^2 , d_1), 4.71 d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_1), 4.66 d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_2), 4.50 br. d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_2), 4.38 d (H^6_A , $^2J_{H_BCH}$ 17.9, d_2), 4.37 d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_1), 4.26 d (H^6_A , $^2J_{H_BCH}$ 18.0, d_1), 4.03 d (H^{14} , $^2J_{PCH}$ 17.2, d_2), 4.21 d. d. d (H^4_A , $^2J_{H_BCH}$ 14.7, $^4J_{PCNCH}$ 4.1, $^4J_{HC^2NCH}$ 2.3, d_2), 4.11 br. d (H^4_A , $^2J_{H_BCH}$ 14.8, d_1), 3.93 d (H^{14} , $^2J_{PCH}$ 26.0, d_1), 3.84 d. d. d (H^4_B , $^2J_{H_ACH}$ 14.8, $^4J_{HC^2NCH}$ 2.3, $^4J_{PCNCH}$ 2.0, d_2), 3.74 br. d (H^4_B , $^2J_{H_ACH}$ 14.8, d_1), 3.01 d (H^6_B , $^2J_{H_ACH}$ 17.9, d_1), 2.99 d (H^6_B , $^2J_{H_ACH}$ 18.0, d_2), 1.30 d (Me, $^3J_{POCH}$ 6.2, d_1), 1.27 d (Me, $^3J_{POCH}$ 6.2, d_2), 1.25 d (Me, $^3J_{HCCH}$ 6.2, d_1), 1.23 d (Me, $^3J_{HCCH}$ 6.2, d_2), 1.19 d (Me, $^3J_{HCCH}$ 6.2, d_2), 1.13 d (Me, $^3J_{HCCH}$ 6.2, d_1), 0.87 d (Me, $^3J_{HCCH}$ 6.2, d_2), 0.64 d (Me, $^3J_{HCCH}$ 6.2, d_1).

1H NMR spectrum of compound (**4b**) (400 MHz, acetone- d_6 , $d_1 : d_2 = 2 : 1$), δ ppm, J Hz: 7.5 br. s (OH, superimposed with phenyl proton signals), 7.0 m, 7.49-7.52 m, 7.37-7.44 m, 7.26 m (C_6H_5), 5.92 d. t (H^2 , $^4J_{HAC^4NCH}$ 2.5, $^4J_{HBC^4NCH}$ 2.3, $^4J_{PCNCH}$ 2.3, d_2), 5.18 d. t (H^2 , $^4J_{HC^4NCH}$ 2.0, $^4J_{PCNCH}$ 1.6, d_1), 4.77 d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_1), 4.73 d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_2), 4.47 br. d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_2), 4.37 d. sept (OCH, $^3J_{HCCH}$ 6.2, $^3J_{POCH}$ 6.0-7.0, d_1), 4.35 d (H^6_A , $^2J_{H_BCH}$ 17.9, d_2), 4.23 d (H^6_A , $^2J_{H_BCH}$ 17.8, d_1), 4.05 d (H^{14} , $^2J_{PCH}$ 17.8, d_2), 4.27 d. d. d (H^4_A , $^2J_{H_BCH}$ 14.9, $^4J_{PCNCH}$ 4.1, $^4J_{HC^2NCH}$ 2.3, d_2), 4.06 br. d. d (H^4_A , $^2J_{H_BCH}$ 14.5, $^4J_{PCNCH}$ 1.0, d_1), 3.98 d (H^{14} , $^2J_{PCH}$ 26.0, d_1), 3.74 d. d. d (H^4_B , $^2J_{H_ACH}$ 14.5, $^4J_{HC^2NCH}$ 2.4, $^4J_{PCNCH}$ 2.1, d_2), 3.62 d. d. d (H^4_B , $^2J_{H_ACH}$ 14.6, $^4J_{HC^2NCH}$ 2.1, $^4J_{PCNCH}$ 1.7, d_1), 3.04 d (H^6_B , $^2J_{H_ACH}$ 17.8, d_2), 3.02 d (H^6_B , $^2J_{H_ACH}$ 17.8, d_1), 1.35 d (Me, $^3J_{POCH}$ 6.3, d_1), 1.33 d (Me, $^3J_{POCH}$ 6.4, d_2), 1.31 d (Me, $^3J_{HCCH}$ 6.3, d_2), 1.28 d (Me, $^3J_{HCCH}$ 6.2, d_1), 1.22 d (Me, $^3J_{HCCH}$ 6.1, d_2), 1.09 d (Me, $^3J_{HCCH}$ 6.2, d_1), 0.84 d (Me, $^3J_{HCCH}$ 6.2, d_2), 0.65 d (Me, $^3J_{HCCH}$ 6.2, d_1).

1,4-Bis[α -(diisopropoxyphosphoryl)benzyl]piperazine-2,5-dione **3b**

^1H , ^{13}C , $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of a crystalline sample isolated from one of the fractions with a 20:1 ratio of *meso* and *d,l* diastereomers



Elemental analysis: Found: C, 60.45; H, 6.21; N, 6.25; P, 6.21. Calculated for $\text{C}_{24}\text{H}_{31}\text{N}_2\text{O}_6\text{P}$: C, 60.76; H, 6.54; N, 5.90; P, 6.54.

^1H NMR spectrum (600 MHz, CDCl_3 , *meso*-pattern) of compound **3b**, δ ppm, J Hz: 7.61 m (C_6H_5 , 4H), 7.37 br. s (C_6H_5 , 6H), 6.17 d (H^7 , 2H, $^2J_{\text{PCH}}$ 22.9), 4.70 and 4.62 two d. sept (OCH, 4H, $^3J_{\text{HCCH}}$ 5.9, $^3J_{\text{POCH}}$ 6.0-7.0), 4.52 d ($\text{H}^{3,6}_A$, 2H, $^2J_{\text{H}_B\text{CH}}$ 17.2), 3.94 d ($\text{H}^{3,6}_B$, 2H, $^2J_{\text{H}_A\text{CH}}$ 17.2), 1.27 d (Me, 6H, $^3J_{\text{POCH}}$ 5.9), 1.23 d (Me, 6H, $^3J_{\text{POCH}}$ 5.9), 1.13 d (Me, 6H, $^3J_{\text{POCH}}$ 5.9), 0.98 d (Me, 6H, $^3J_{\text{POCH}}$ 5.9). ^{13}C NMR spectrum (150.9 MHz, CDCl_3 , *meso*-pattern) of compound **3b**, δ_C ppm, J Hz (the view of signal in $^{13}\text{C}\{-^1\text{H}\}$ is in parentheses): 164.55 m (d) ($\text{C}^{2,5}$, $^3J_{\text{PCNC}}$ 5.3), 47.50 d. d. d (s) ($\text{C}^{3,6}$, $^1J_{\text{HC}}$ 144.6, $^1J_{\text{HC}}$ 142.5, $^3J_{\text{HCNC}}$ 5.5, $^3J_{\text{PCNC}}$ 0), 132.31 t. d. d (d) (C^8 , $^3J_{\text{HC}^{9,12}\text{CC}}$ 7.2-7.3, $^2J_{\text{HC}^7\text{C}}$ 7.2, $^2J_{\text{PC}^7\text{C}}$ 3.9), 130.06 d. d. m (d) ($\text{C}^{9,13}$, $^1J_{\text{HC}}$ 159.4, $^3J_{\text{PCCC}}$ 8.4, $^3J_{\text{HC}^{11}\text{CC}}$ 7.0, $^3J_{\text{HC}^{13,9}\text{CC}^{9,13}}$ 6.5-7.0), 129.12 d. d (s) ($\text{C}^{10,12}$, $^1J_{\text{HC}}$ 160.9, $^3J_{\text{HCCC}}$ 7.5), 128.97 d. t (s) (C^{11} , $^1J_{\text{HC}}$ 160.9, $^3J_{\text{HC}^{9,13}\text{CC}}$ 7.4), 72.38 d. d. sept (d) (OC, $^1J_{\text{HC}}$ 147.6, $^2J_{\text{POC}}$ 7.1, $^2J_{\text{HCC}}$ 4.2), 71.92 d. d. sept (d) (OC, $^1J_{\text{HC}}$ 147.2, $^2J_{\text{POC}}$ 7.5, $^2J_{\text{HCC}}$ 4.2), 53.10 d. d. t (d) (C^7 , $^1J_{\text{PC}}$ 159.9, $^1J_{\text{HC}}$ 130.8, $^3J_{\text{HCCC}}$ 4.0), 24.32 q. q. d. d (d) (Me, $^1J_{\text{HC}}$ 126.7, $^3J_{\text{HCCC}}$ 4.5, $^3J_{\text{POCC}}$ 3.0, $^2J_{\text{HCC}}$ 1.1), 24.19 q. q. d. d (d) (Me, $^1J_{\text{HC}}$ 127.0, $^3J_{\text{POCC}}$ 3.7, $^3J_{\text{HCCC}}$ 4.2-4.4, $^2J_{\text{HCC}}$ 1.1), 23.94 q. q. d. d (d) (Me, $^1J_{\text{HC}}$ 126.7-127.0, $^3J_{\text{POCC}}$ 4.8, $^3J_{\text{HCCC}}$ 4.5-4.6, $^2J_{\text{HCC}}$ 1.1-1.2), 23.51 q. q. d. d (d) (Me, $^1J_{\text{HC}}$ 127.7, $^3J_{\text{POCC}}$ 5.4, $^3J_{\text{HCCC}}$ 4.7-4.9, $^2J_{\text{HCC}}$ 1.1-1.2). $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum (242.9 MHz, CDCl_3 , *meso*-pattern) of compound (**3b**): δ_P 17.4 ppm.

^1H NMR spectrum (600 MHz, CDCl_3 , *d,l*-pattern) of compound **3b**, δ ppm, J Hz: 7.56 m (C_6H_5), 7.33 br. m (C_6H_5), 6.21 d (H^7 , $^2J_{\text{PCH}}$ 21.4), 4.80 and 4.62 two d. sept (OCH, $^3J_{\text{HCCH}}$ 5.9, $^3J_{\text{POCH}}$ 6.0-7.0), 4.52 d ($\text{H}^{3,6}_A$, $^2J_{\text{H}_B\text{CH}}$ 17.0), 3.83 d ($\text{H}^{3,6}_B$, $^2J_{\text{H}_A\text{CH}}$ 17.0), 1.37 d (Me, $^3J_{\text{POCH}}$ 5.9), 1.35 d (Me, $^3J_{\text{POCH}}$ 5.9), 1.32 d (Me, $^3J_{\text{POCH}}$ 5.9), 1.27 d (Me, $^3J_{\text{POCH}}$ 5.9).

$^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum (150.9 MHz, CDCl_3 , *d,l*-pattern) of compound **3b**, δ_C ppm, J Hz: 164.06 d ($\text{C}^{2,5}$, $^3J_{\text{PCNC}}$ 5.4), 47.29 s ($\text{C}^{3,6}$, $^3J_{\text{PCNC}}$ 0), 131.94 d (C^8 , $^2J_{\text{PC}^7\text{C}}$ 3.7), 130.29 d ($\text{C}^{9,13}$, $^3J_{\text{PCCC}}$ 8.6), 129.06 s ($\text{C}^{10,12}$), 128.97 s (C^{11}), 72.45 d (OC, $^2J_{\text{POC}}$ 7.3), 71.97 d (OC, $^2J_{\text{POC}}$ 7.5), 53.13 d (C^7 , $^1J_{\text{PC}}$ 160.6), 24.38 d (Me, $^3J_{\text{POCC}}$ 3.0), 24.31 d (Me, $^3J_{\text{POCC}}$ 3.5), 23.23 d (Me, $^3J_{\text{POCC}}$ 3.7), 24.18 d (Me, $^3J_{\text{POCC}}$ 3.7). $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum (242.9 MHz, CDCl_3 , *d,l*-pattern) of compound **3b**: δ_P 17.4 ppm.

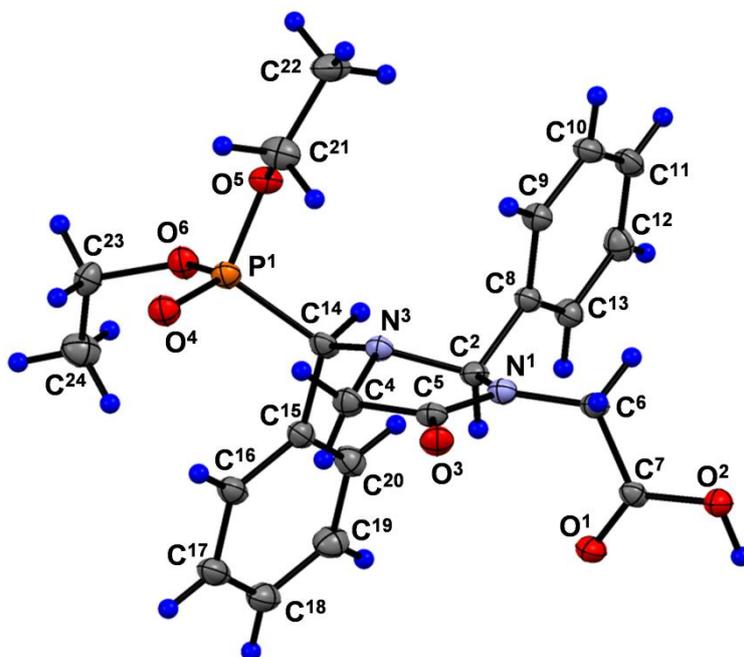


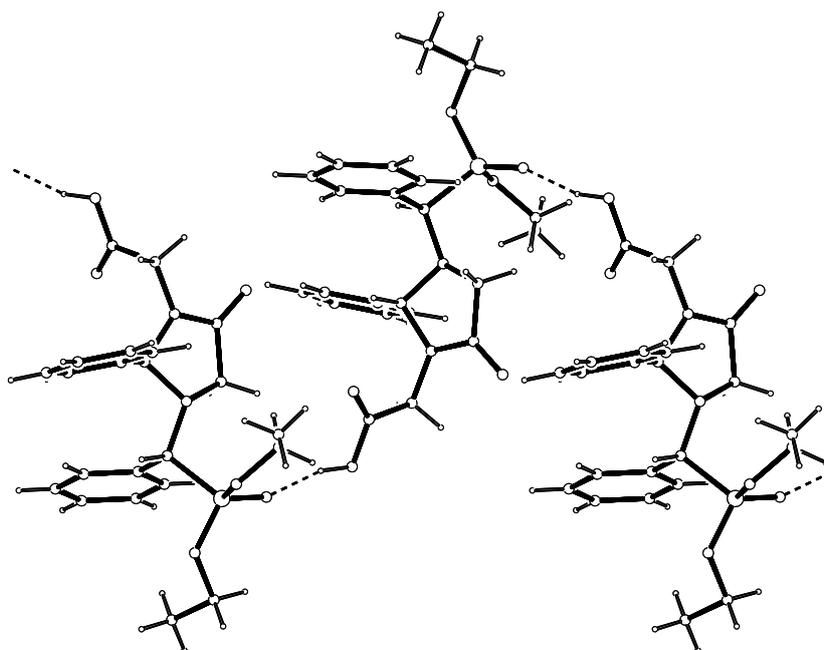
Figure S1. Geometry of the molecule **4a** in the crystal (the figure shows the geometry of the $C^2_S C^{14}_R N^3_S$ -enantiomer, conglomerate, the $C^2_S C^{14}_R N^3_S / C^2_R C^{14}_S N^3_R$ -diastereomer d_1).

Table S1. Bond length (angstrom) and bond angles (degrees) of **4a**.

Bond length	d, Å	Bond length	d, Å	Bond length	d, Å
P ¹ –O ⁴	1.467(3)	N ¹ –C ⁶	1.435(5)	C ¹¹ –C ¹²	1.379(7)
P ¹ –O ⁵	1.566(4)	N ³ –C ⁴	1.463(6)	C ¹² –C ¹³	1.397(7)
P ¹ –O ⁶	1.556(3)	N ³ –C ¹⁴	1.472(5)	C ¹⁴ –C ¹⁵	1.524(6)
P ¹ –C ¹⁴	1.816(5)	N ³ –C ²	1.476(5)	C ¹⁵ –C ¹⁶	1.396(6)
O ¹ –C ⁷	1.208(5)	C ² –C ⁸	1.510(6)	C ¹⁵ –C ²⁰	1.385(7)
O ² –C ⁷	1.312(5)	C ⁴ –C ⁵	1.497(6)	C ¹⁶ –C ¹⁷	1.395(7)
O ³ –C ⁵	1.225(5)	C ⁶ –C ⁷	1.518(6)	C ¹⁷ –C ¹⁸	1.385(9)
O ⁵ –C ²¹	1.459(6)	C ⁸ –C ¹³	1.386(6)	C ¹⁸ –C ¹⁹	1.380(8)
O ⁶ –C ²³	1.457(5)	C ⁸ –C ⁹	1.387(6)	C ¹⁹ –C ²⁰	1.397(8)
N ¹ –C ²	1.470(5)	C ⁹ –C ¹⁰	1.382(6)	C ²¹ –C ²²	1.479(8)
N ¹ –C ⁵	1.349(6)	C ¹⁰ –C ¹¹	1.380(7)	C ²³ –C ²⁴	1.479(8)
Bond angle	φ, deg.	Bond angle	φ, deg.	Bond angle	φ, deg.
O ⁴ –P ¹ –O ⁵	114.6(2)	C ² –N ¹ –C ⁵	112.0(3)	N ¹ –C ⁶ –C ⁷	113.6(3)
O ⁴ –P ¹ –O ⁶	115.0(2)	C ² –N ³ –C ⁴	106.2(3)	O ¹ –C ⁷ –O ²	125.7(4)
O ⁴ –P ¹ –C ¹⁴	114.8(2)	C ⁴ –N ³ –C ¹⁴	118.8(3)	O ¹ –C ⁷ –C ⁶	123.4(4)
O ⁵ –P ¹ –O ⁶	103.1(2)	C ² –N ³ –C ¹⁴	114.3(4)	O ² –C ⁷ –C ⁶	111.0(4)
O ⁵ –P ¹ –C ¹⁴	105.1(2)	N ¹ –C ² –N ³	99.8(3)	C ² –C ⁸ –C ¹³	120.1(4)
O ⁶ –P ¹ –C ¹⁴	102.9(2)	N ³ –C ² –C ⁸	112.1(3)	C ⁹ –C ⁸ –C ¹³	119.5(4)
P ¹ –O ⁵ –C ²¹	119.8(3)	N ¹ –C ² –C ⁸	113.0(3)	C ² –C ⁸ –C ⁹	120.4(4)
P ¹ –O ⁶ –C ²³	123.1(3)	N ³ –C ⁴ –C ⁵	102.9(3)	P ¹ –C ¹⁴ –C ¹⁵	114.0(3)
P ¹ –C ¹⁴ –N ³	107.7(3)	O ³ –C ⁵ –C ⁴	127.1(4)	N ³ –C ¹⁴ –C ¹⁵	117.2(3)
C ² –N ¹ –C ⁶	124.0(3)	N ¹ –C ⁵ –C ⁴	107.2(4)	O ⁵ –C ²¹ –C ²²	108.5(5)
C ⁵ –N ¹ –C ⁶	122.2(3)	O ³ –C ⁵ –N ¹	125.7(4)	O ⁶ –C ²³ –C ²⁴	108.8(4)

Table S2. Torsion angles (degrees) of **4a**.

Torsion angle	τ , deg.	Torsion angle	τ , deg.	Torsion angle	τ , deg.
O ⁴ –P ¹ –O ⁵ –C ²¹	30.9(4)	C ⁶ –N ¹ –C ² –N ³	–169.5(4)	C ⁴ –N ³ –C ¹⁴ –P ¹	74.1(4)
O ⁶ –P ¹ –O ⁵ –C ²¹	156.5(3)	C ⁶ –N ¹ –C ² –C ⁸	–50.3(5)	C ⁴ –N ³ –C ¹⁴ –C ¹⁵	–55.9(6)
C ¹⁴ –P ¹ –O ⁵ –C ²¹	–96.1(4)	C ² –N ¹ –C ⁵ –O ³	173.2(4)	N ¹ –C ² –C ⁸ –C ⁹	–51.3(5)
O ⁴ –P ¹ –O ⁶ –C ²³	3.8(4)	C ² –N ¹ –C ⁵ –C ⁴	–7.4(5)	N ¹ –C ² –C ⁸ –C ¹³	128.3(4)
O ⁵ –P ¹ –O ⁶ –C ²³	–121.6(3)	C ⁶ –N ¹ –C ⁵ –O ³	8.1(7)	N ³ –C ² –C ⁸ –C ⁹	60.6(5)
C ¹⁴ –P ¹ –O ⁶ –C ²³	129.3(4)	C ⁶ –N ¹ –C ⁵ –C ⁴	–172.5(4)	N ³ –C ² –C ⁸ –C ¹³	–119.9(4)
O ⁴ –P ¹ –C ¹⁴ –N ³	–64.5(3)	C ² –N ¹ –C ⁶ –C ⁷	–71.2(5)	N ³ –C ⁴ –C ⁵ –O ³	164.9(4)
O ⁴ –P ¹ –C ¹⁴ –C ¹⁵	67.3(4)	C ⁵ –N ¹ –C ⁶ –C ⁷	92.1(5)	N ³ –C ⁴ –C ⁵ –N ¹	–14.5(5)
O ⁵ –P ¹ –C ¹⁴ –N ³	62.3(3)	C ⁴ –N ³ –C ² –N ¹	–34.0(4)	N ¹ –C ⁶ –C ⁷ –O ¹	–1.2(6)
O ⁵ –P ¹ –C ¹⁴ –C ¹⁵	–165.9(3)	C ⁴ –N ³ –C ² –C ⁸	–153.8(3)	N ¹ –C ⁶ –C ⁷ –O ²	178.8(3)
O ⁶ –P ¹ –C ¹⁴ –N ³	169.9(3)	C ¹⁴ –N ³ –C ² –N ¹	–167.0(3)	C ² –C ⁸ –C ⁹ –C ¹⁰	177.8(4)
O ⁶ –P ¹ –C ¹⁴ –C ¹⁵	–58.3(4)	C ¹⁴ –N ³ –C ² –C ⁸	73.2(4)	C ¹³ –C ⁸ –C ⁹ –C ¹⁰	–1.8(6)
P ¹ –O ⁵ –C ²¹ –C ²²	171.3(3)	C ² –N ³ –C ⁴ –C ⁵	30.7(4)	P ¹ –C ¹⁴ –C ¹⁵ –C ¹⁶	–47.9(5)
P ¹ –O ⁶ –C ²³ –C ²⁴	–120.1(4)	C ¹⁴ –N ³ –C ⁴ –C ⁵	161.2(4)	P ¹ –C ¹⁴ –C ¹⁵ –C ²⁰	131.9(4)
C ⁵ –N ¹ –C ² –N ³	25.7(4)	C ² –N ³ –C ¹⁴ –P ¹	–159.2(3)	N ³ –C ¹⁴ –C ¹⁵ –C ¹⁶	79.1(5)
C ⁵ –N ¹ –C ² –C ⁸	144.9(4)	C ² –N ³ –C ¹⁴ –C ¹⁵	70.8(5)	N ³ –C ¹⁴ –C ¹⁵ –C ²⁰	–101.1(5)

**Figure S2.** Hydrogen bonds system for the molecule (**3a**) in the crystal, view along the 0x axis.**Table S3.** Hydrogen-bond geometry in the crystal of molecule (**3a**).

$D-H\cdots A$	$D-H$, Å	$H\cdots A$, Å	$D\cdots A$, Å	$D-H\cdots A$, deg.
O ² –H ² ...O ⁴ⁱ	0.97(7)	1.68(7)	2.611(4)	161.0(6)

(i) Symmetry code: $-x + 1, y - 1/2, -z + 1$.

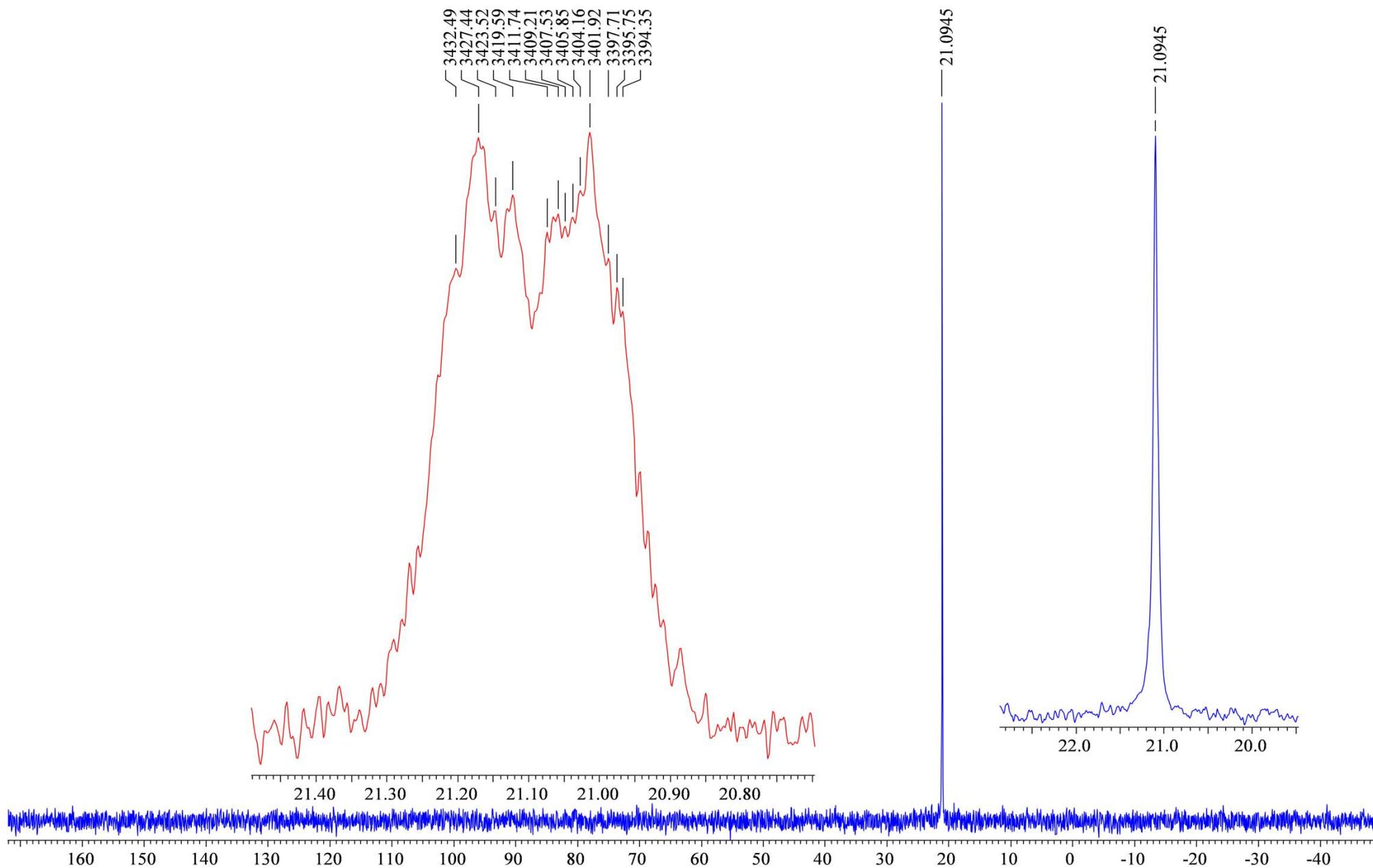


Figure S3. ^{31}P - $\{^1\text{H}\}$ and ^{31}P NMR spectra (242.9 MHz, CDCl_3) of (**4a**, d_1).

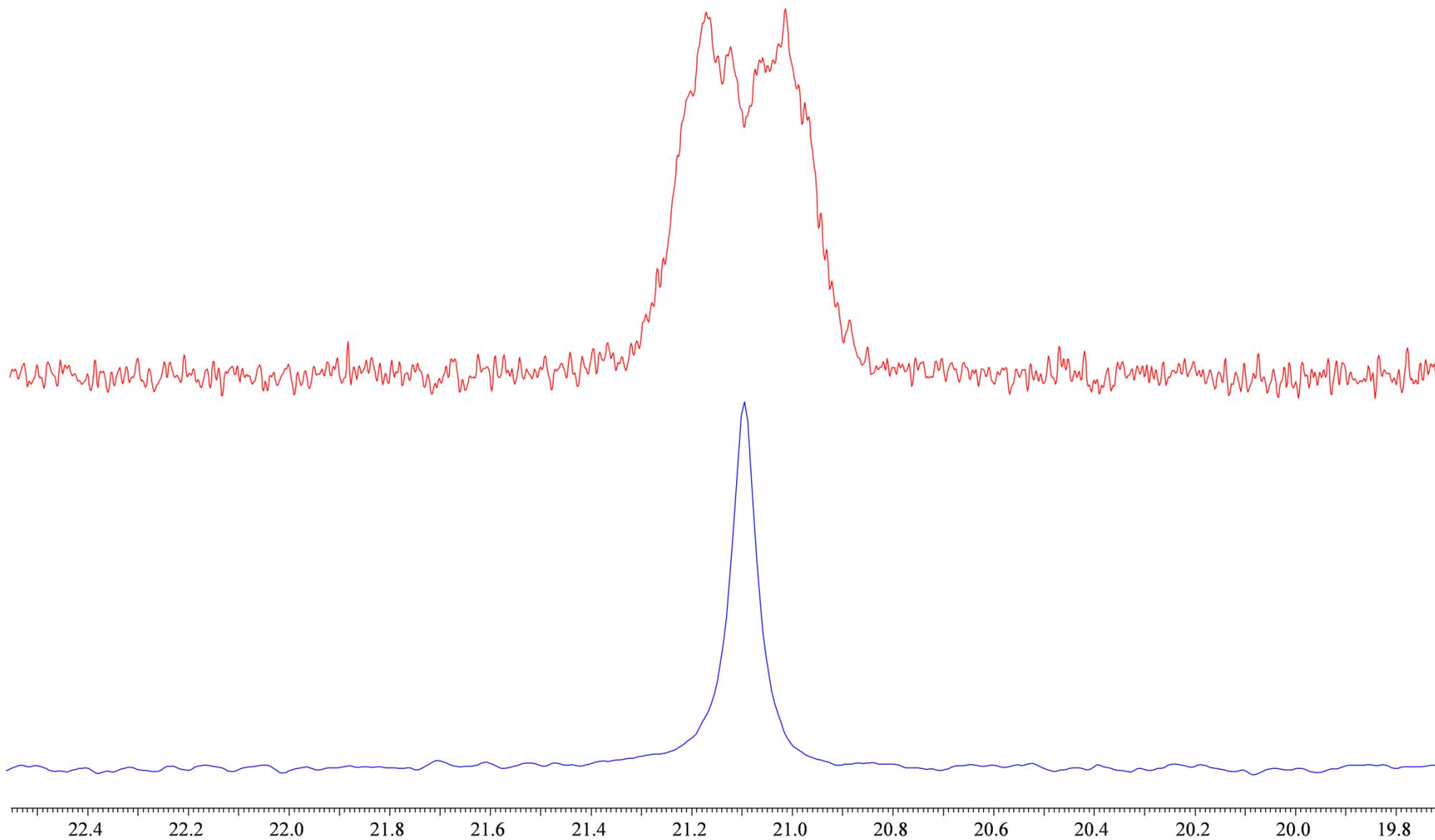


Figure S4. ^{31}P - $\{^1\text{H}\}$ and ^{31}P NMR spectra (242.9 MHz, CDCl_3) of $(4a, d_1)$.

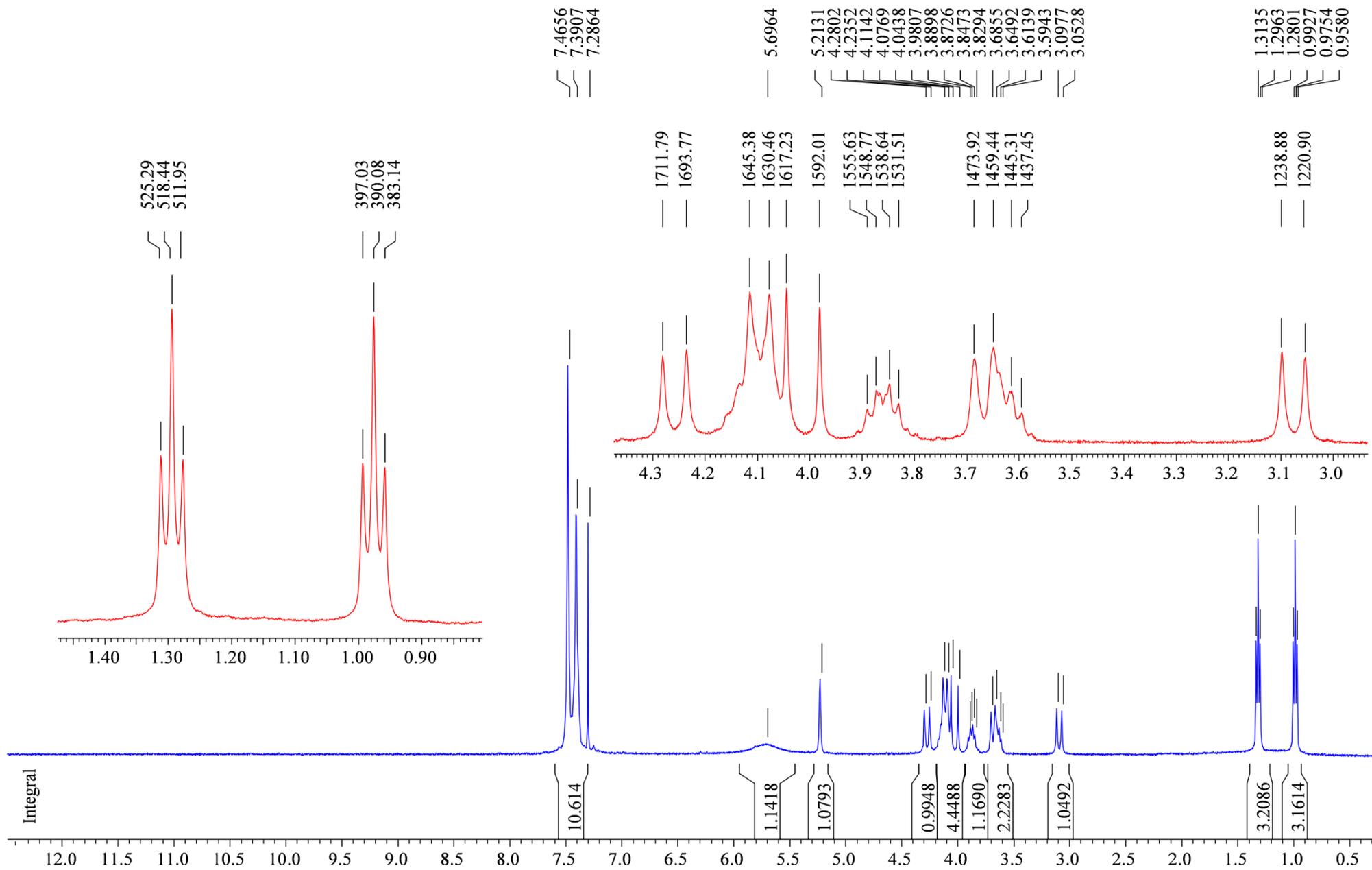


Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃) of (4a, d₁).

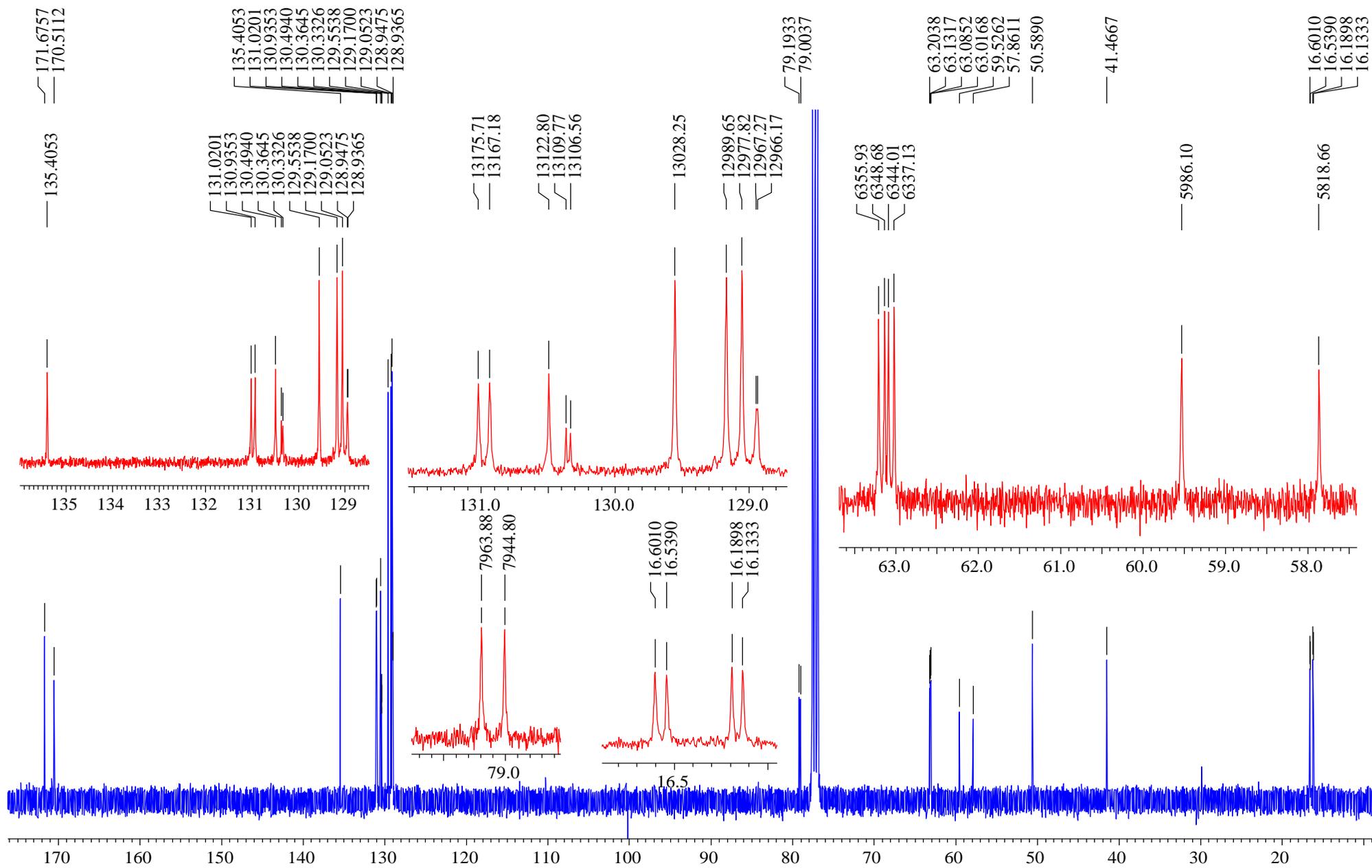


Figure S6. ^{13}C - $\{^1\text{H}\}$ NMR spectrum (100.6 MHz, CDCl_3) of (**4a**, d_1).

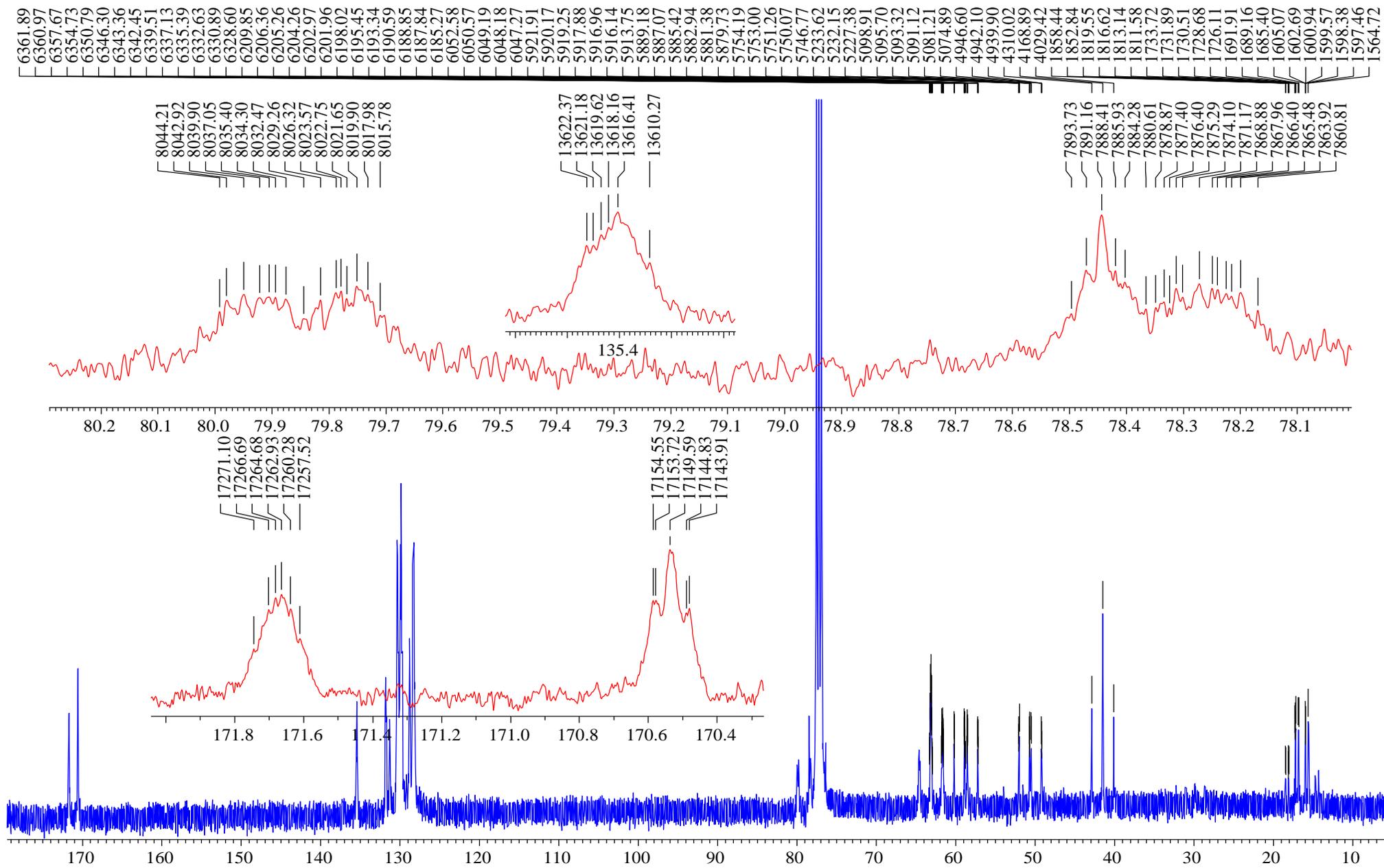


Figure S7. ^{13}C NMR spectrum (100.6 MHz, CDCl_3) of (4a, d_1).

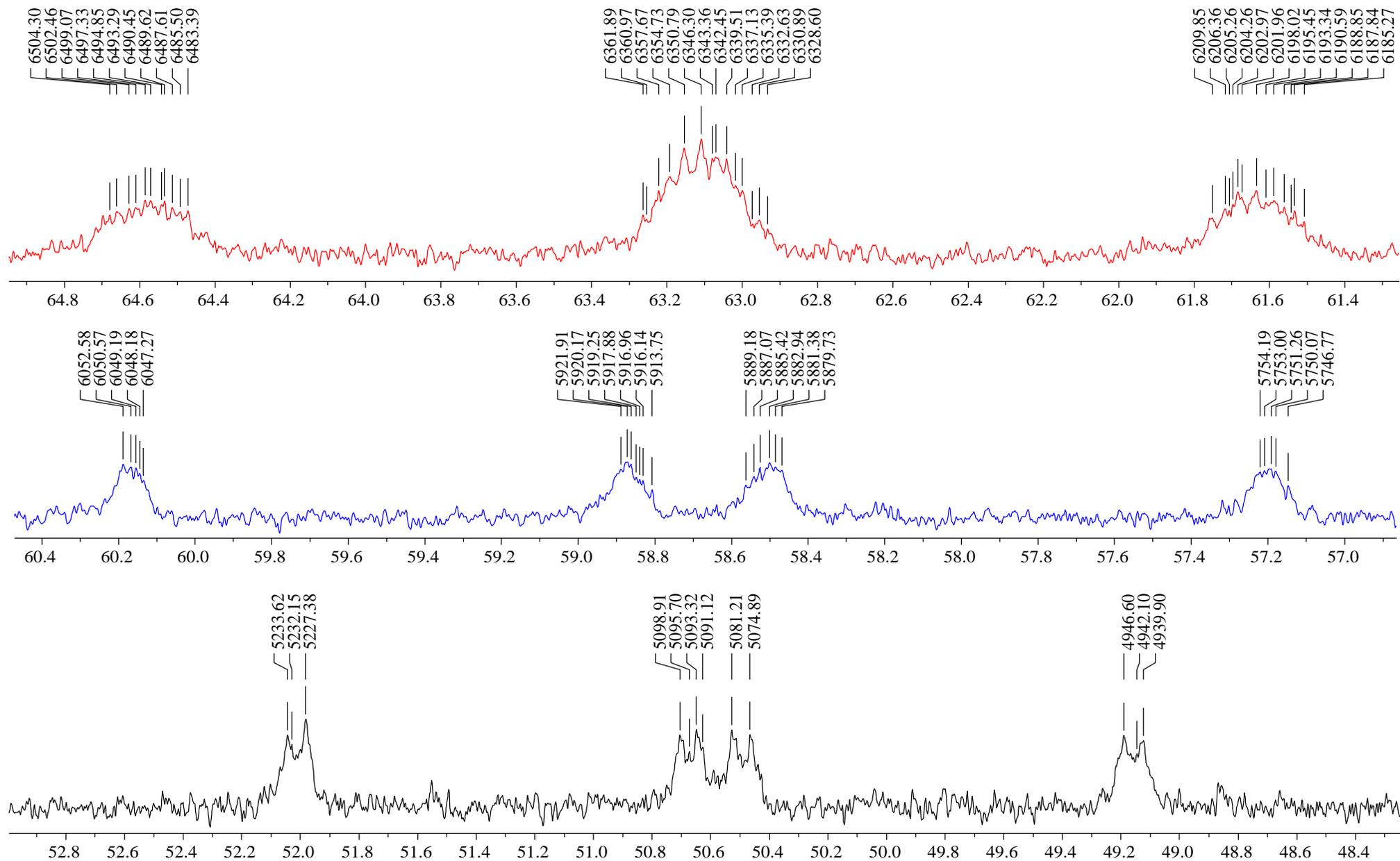


Figure S8. Fragments of ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1).

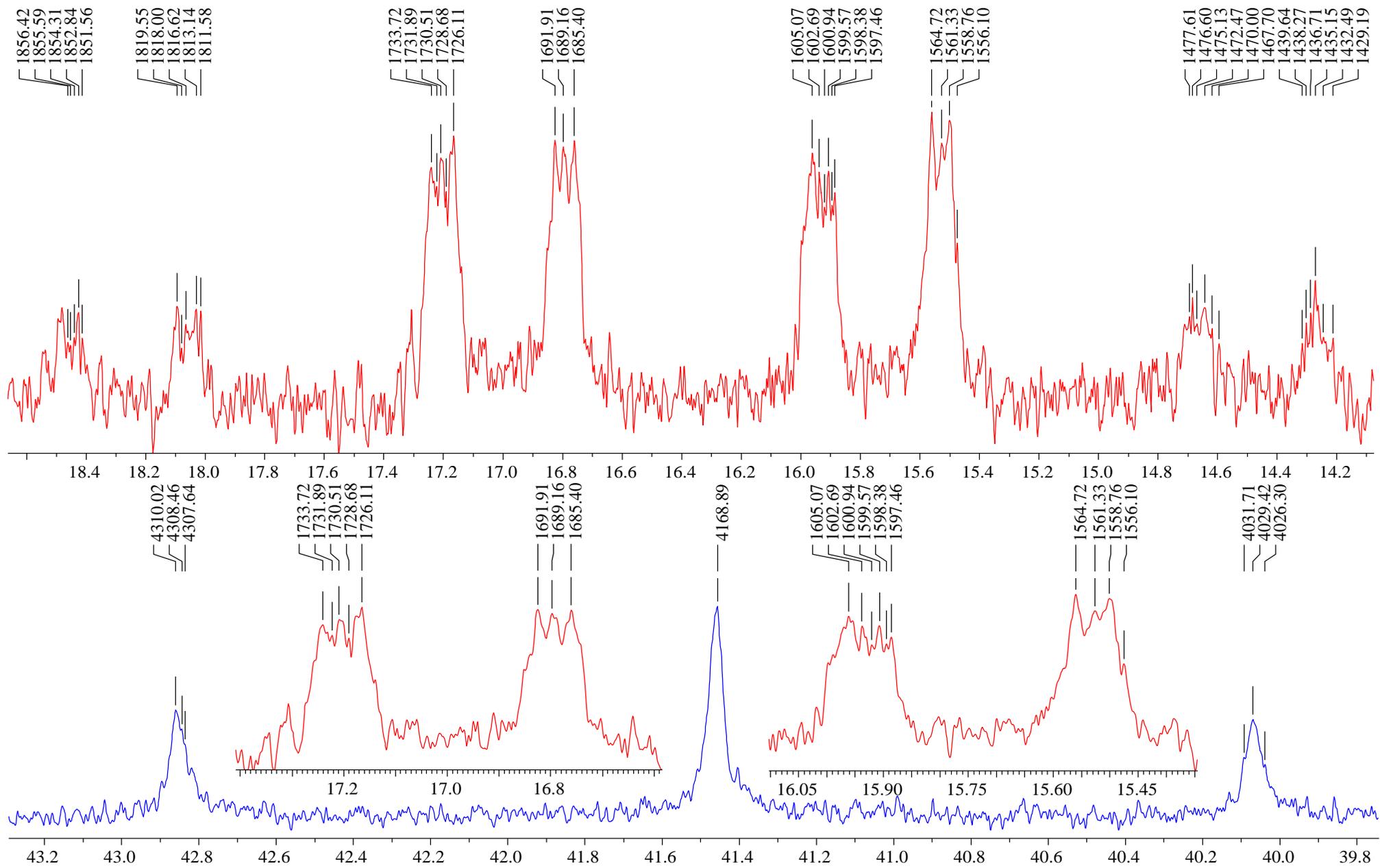


Figure S9. Fragments of ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1).

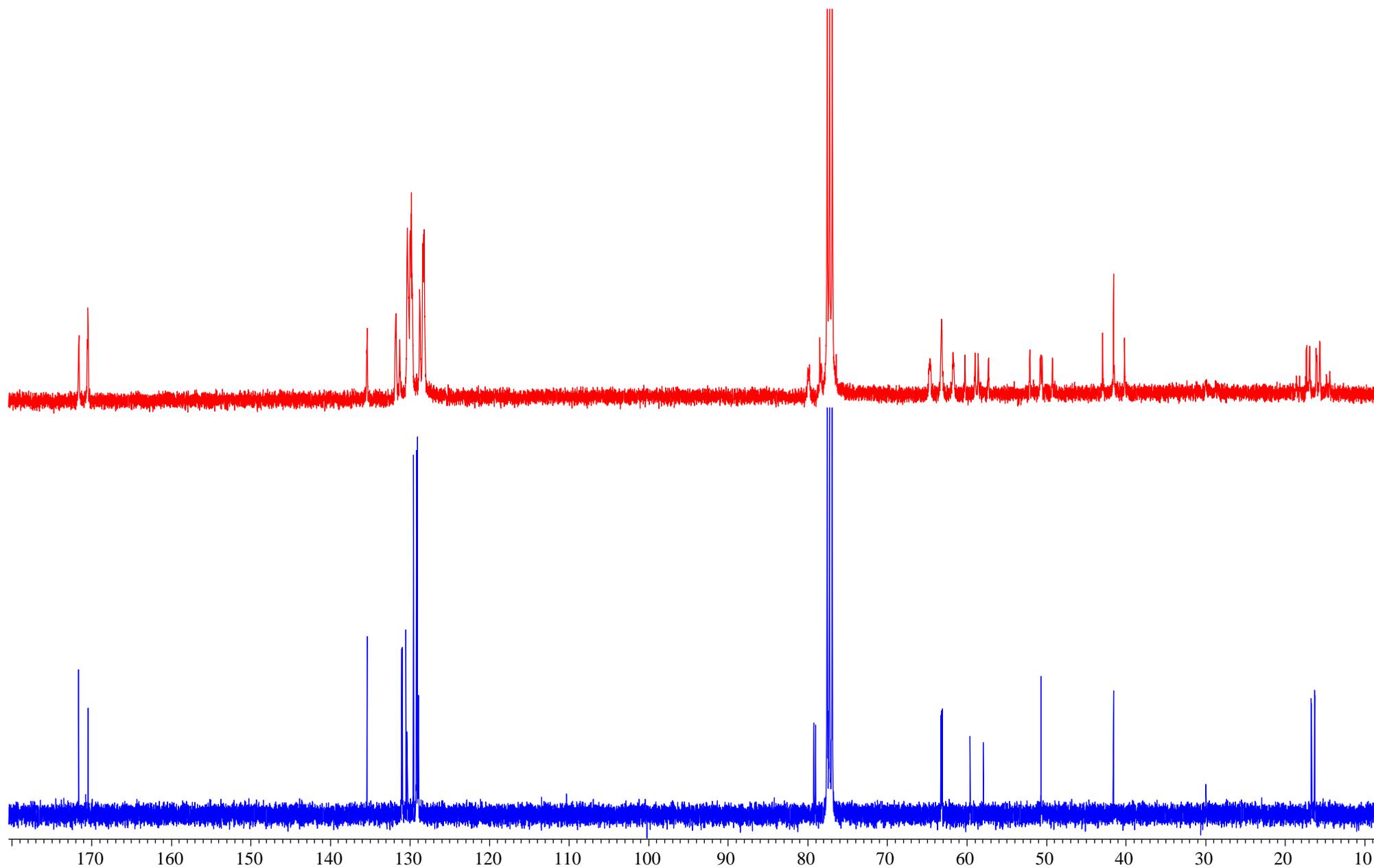


Figure S10. ¹³C-¹H and ¹³C NMR spectra (100.6 MHz, CDCl₃) of (**4a**, *d*₁).

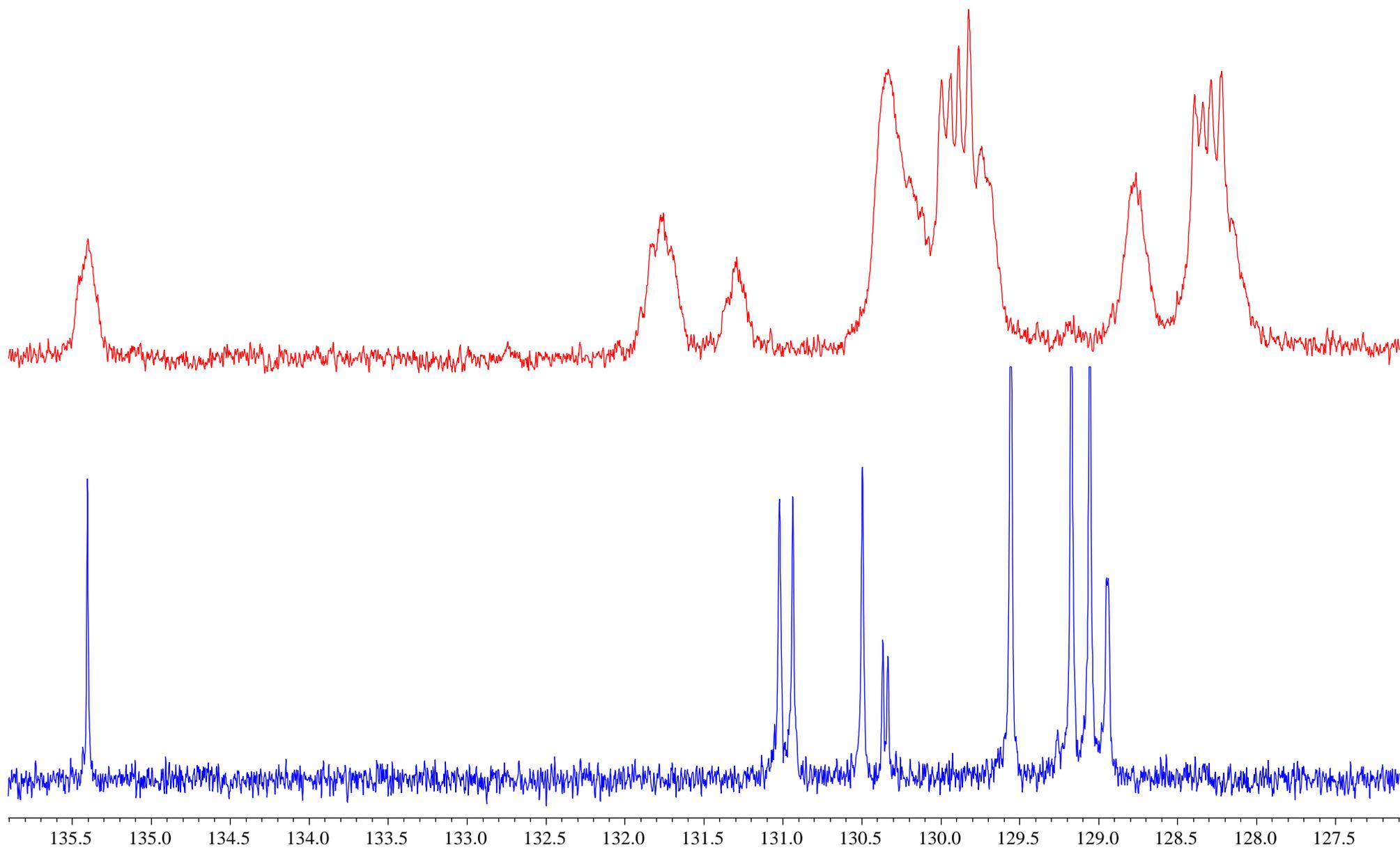


Figure S11. 127-136 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1).

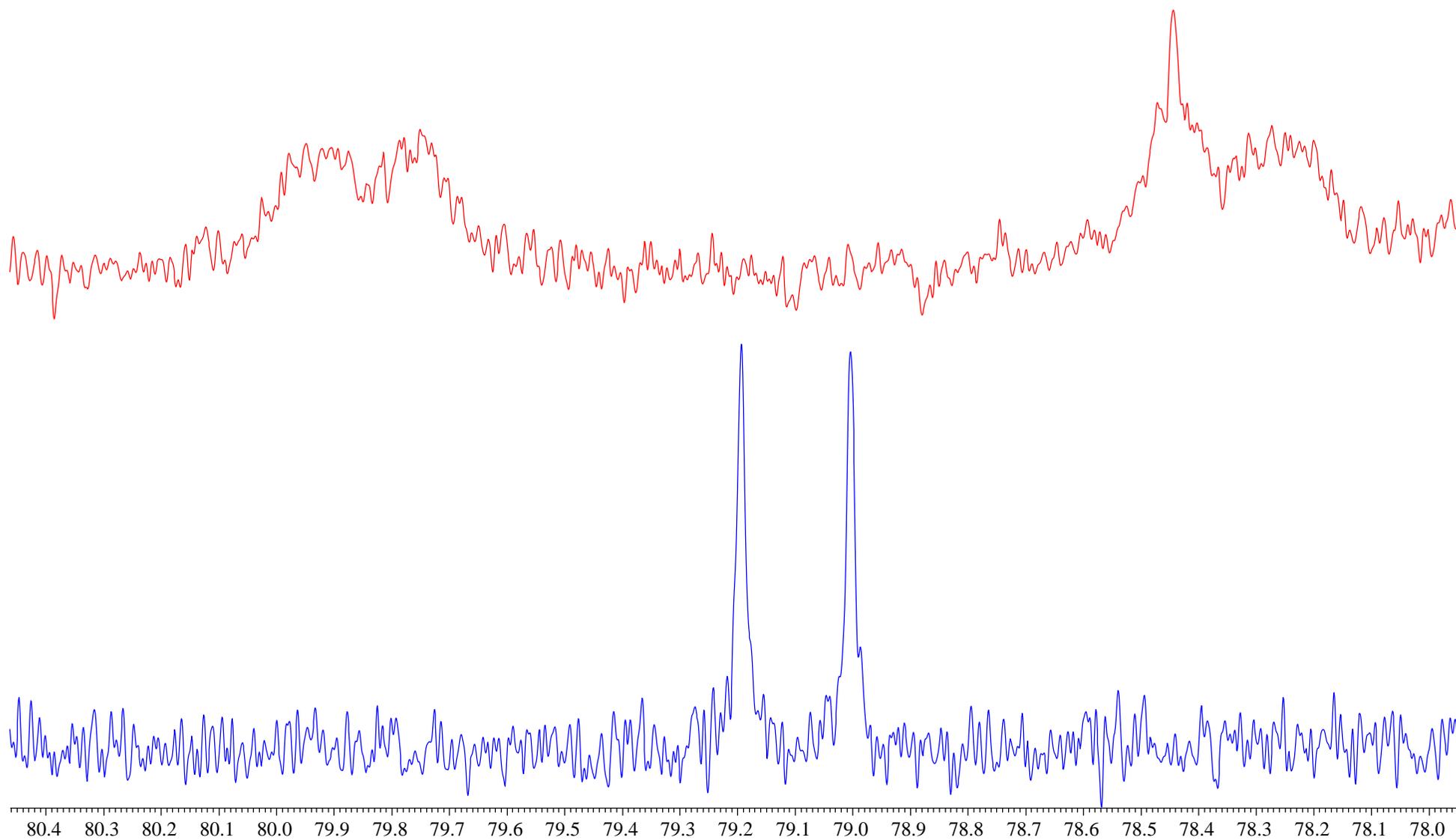


Figure S12. 79 ppm region of ¹³C-¹H and ¹³C NMR spectra (100.6 MHz, CDCl₃) of (**4a, d₁**).

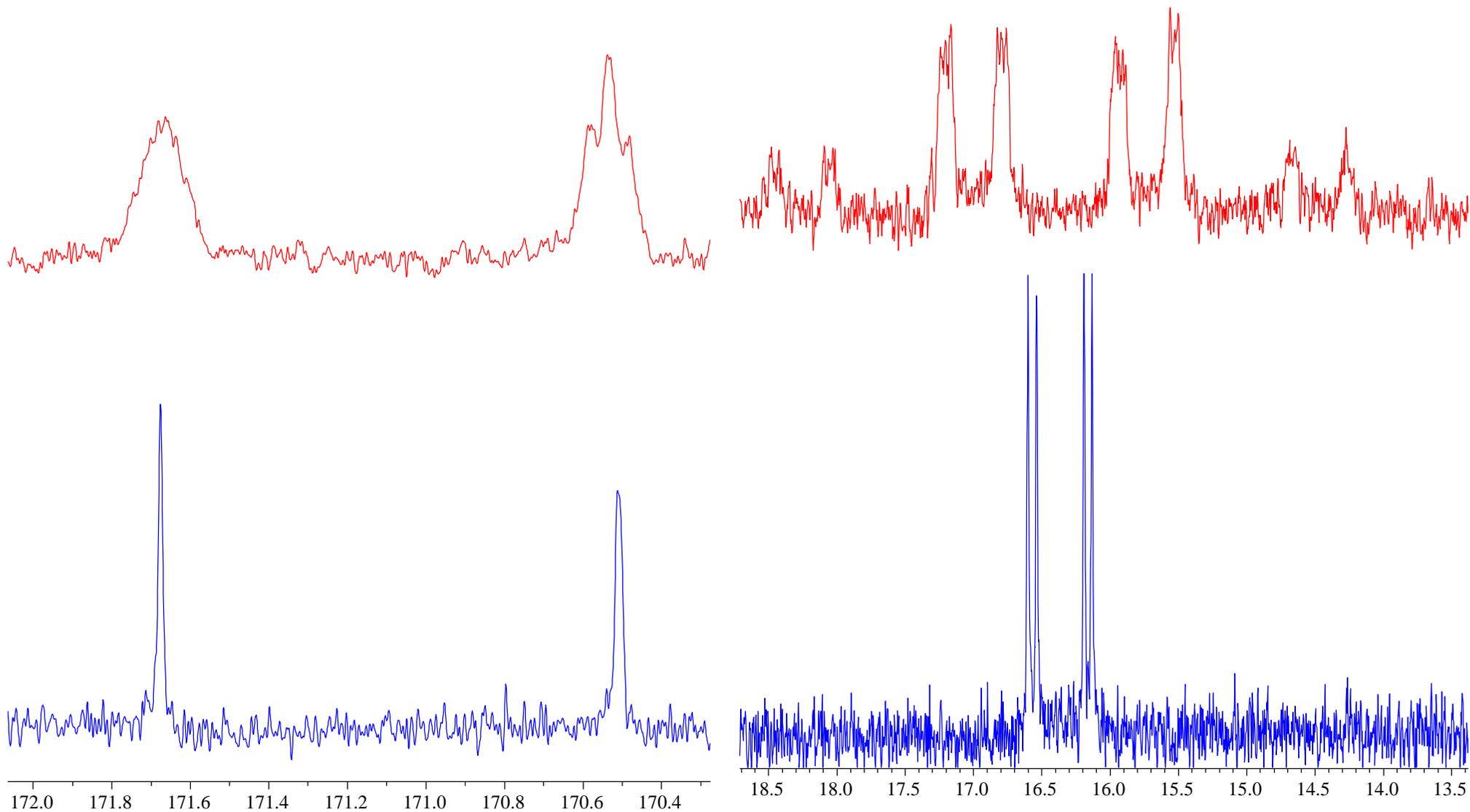


Figure S13. 170-172 and 16 ppm regions of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1).

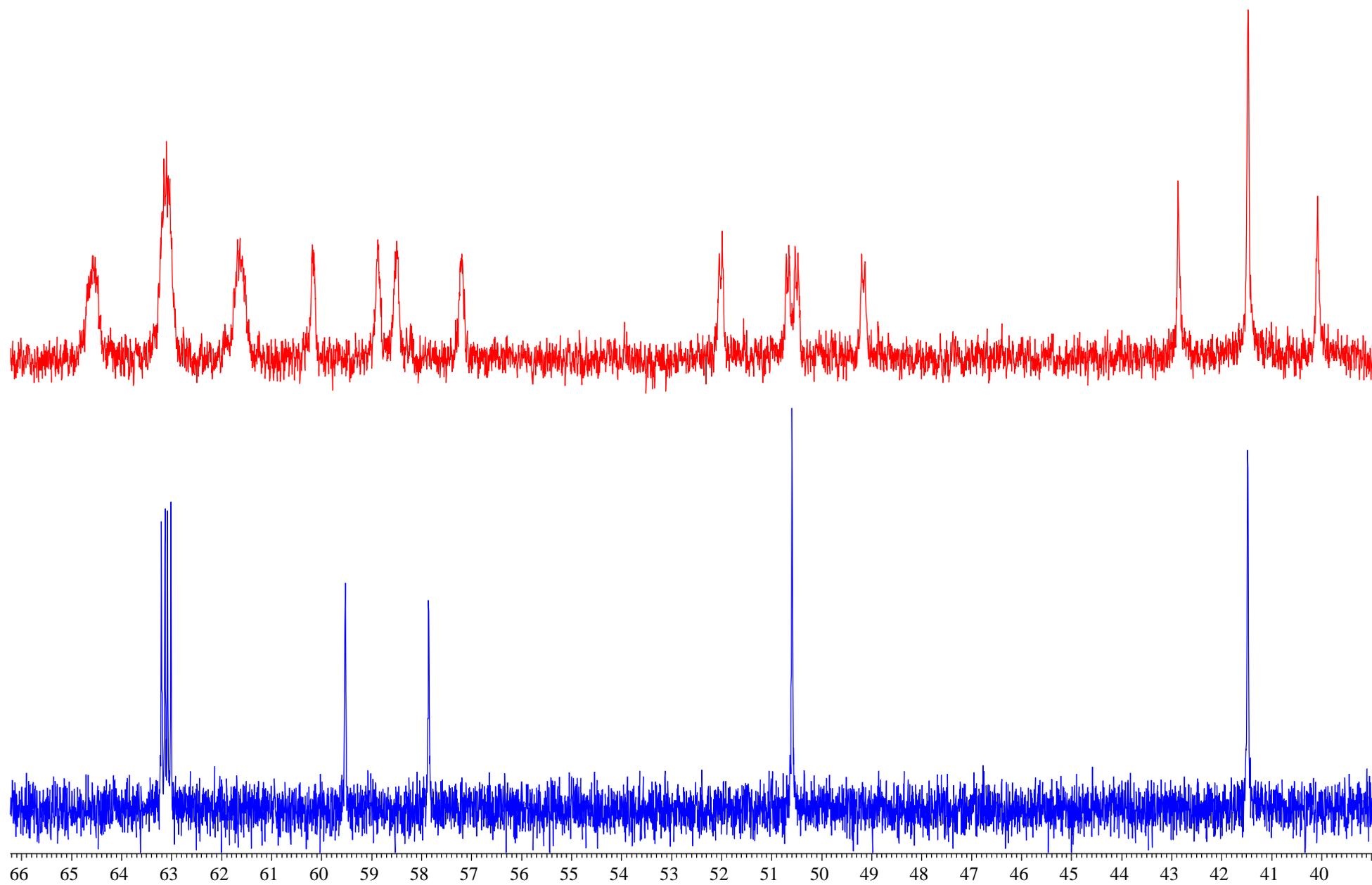


Figure S14. 40-66 ppm region of ¹³C-{¹H} and ¹³C NMR spectra (100.6 MHz, CDCl₃) of (**4a**, *d*₁).

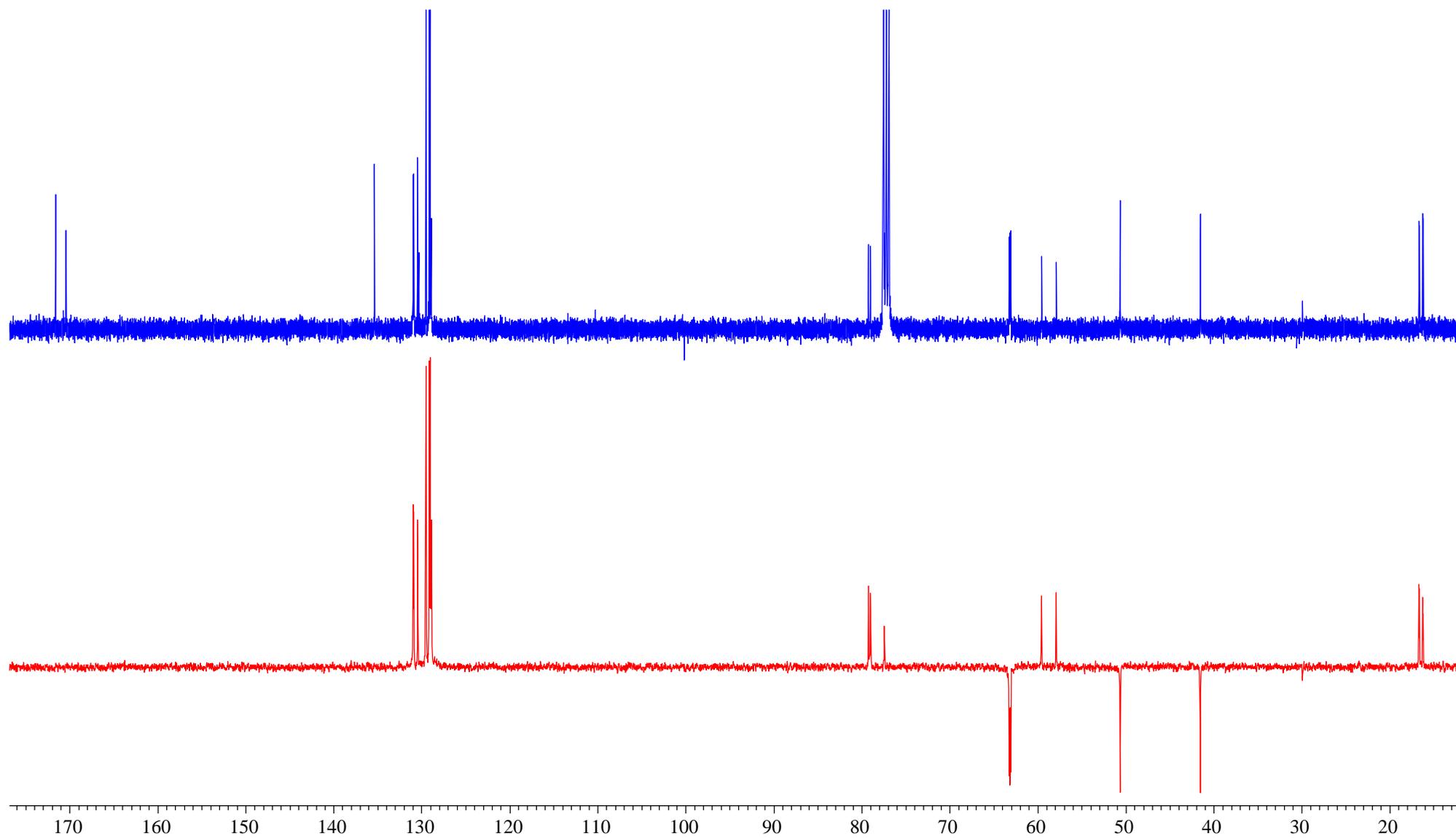


Figure S15. $^{13}\text{C}\{-^1\text{H}\}$ and $^{13}\text{C}\{-^1\text{H}\}$ -dept NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1).

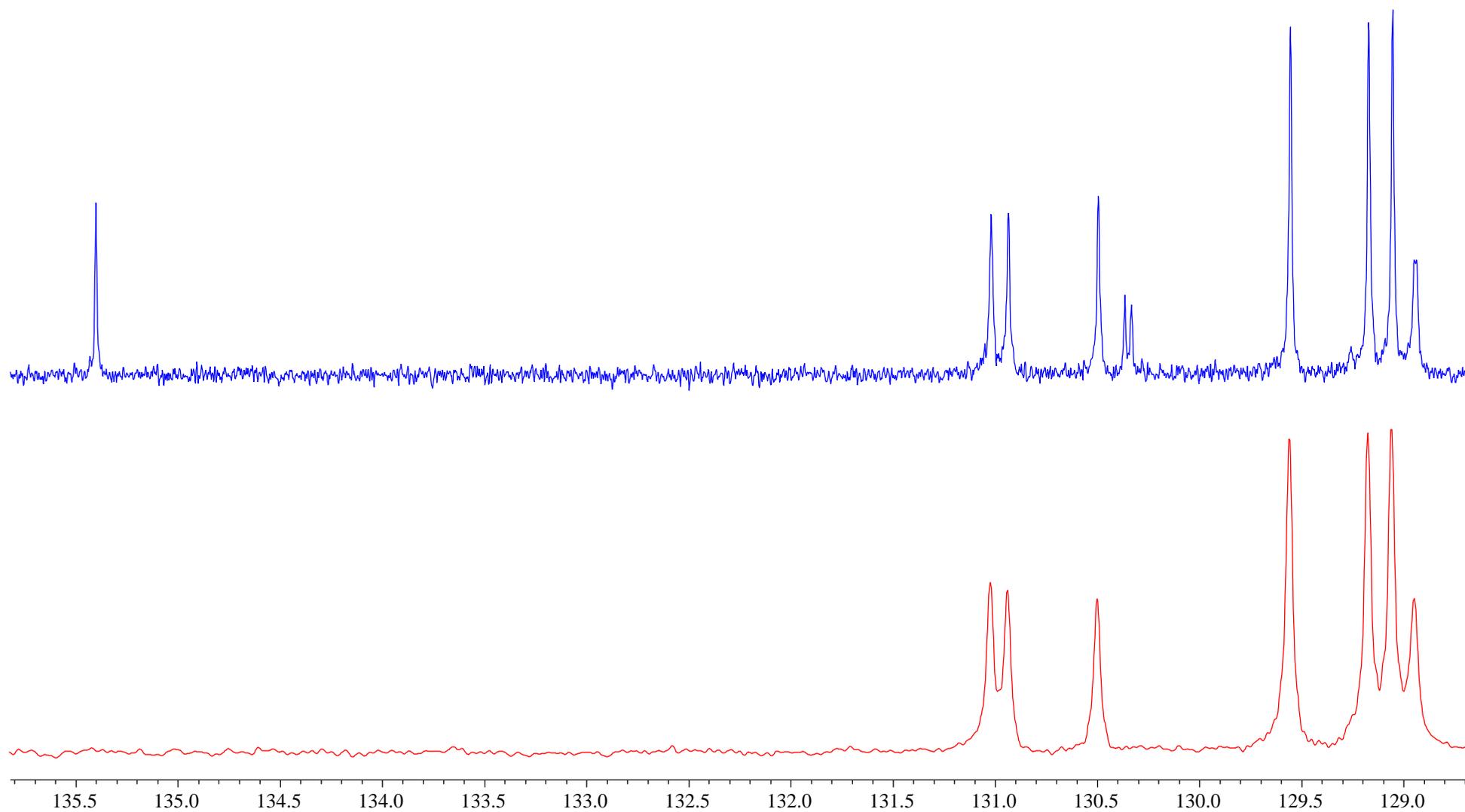


Figure S16. 128-136 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and $^{13}\text{C}\{-^1\text{H}\}$ -dept NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1).

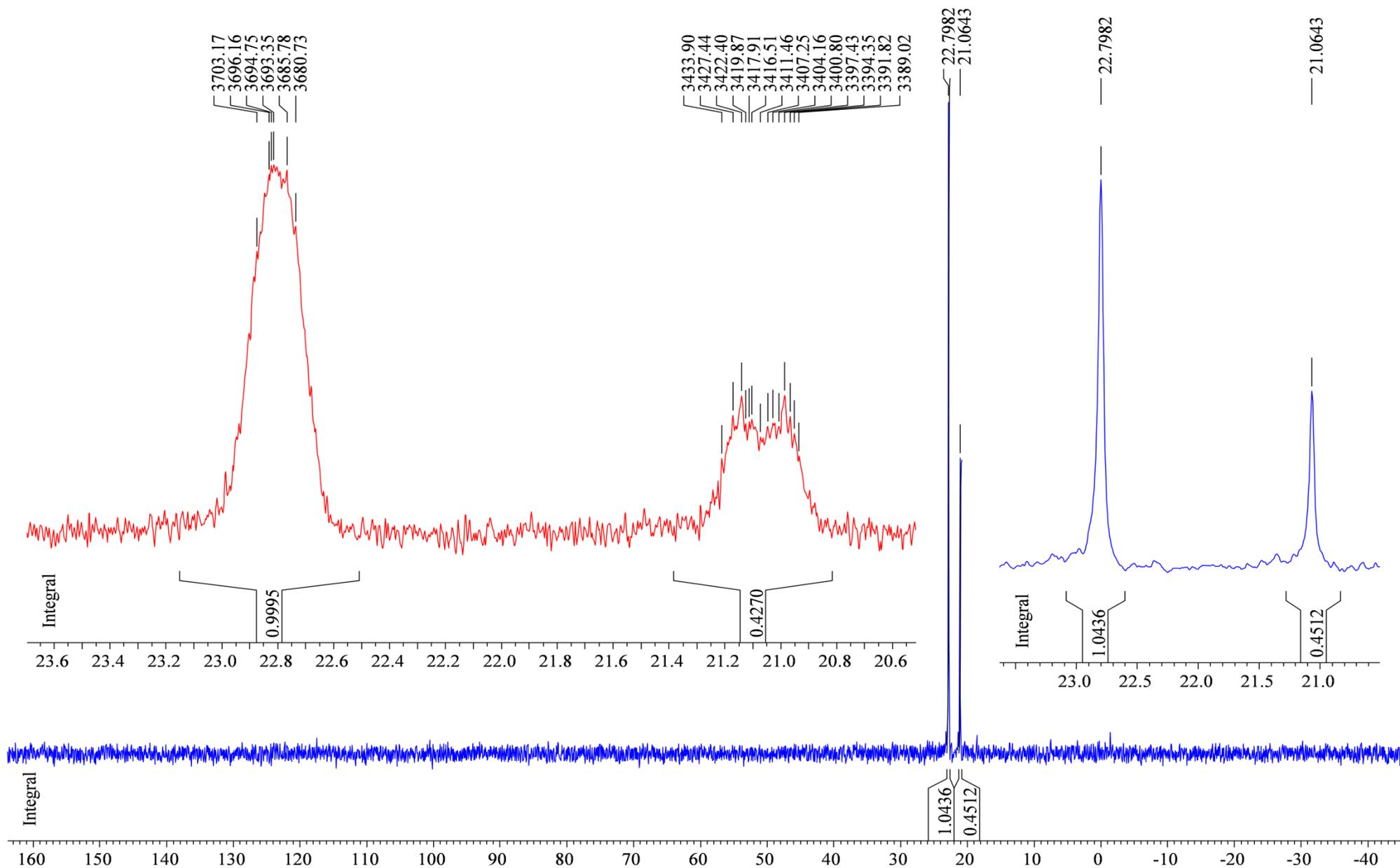


Figure S17. $^{31}\text{P}\{-^1\text{H}\}$ and ^{31}P NMR spectra (242.9 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 2).

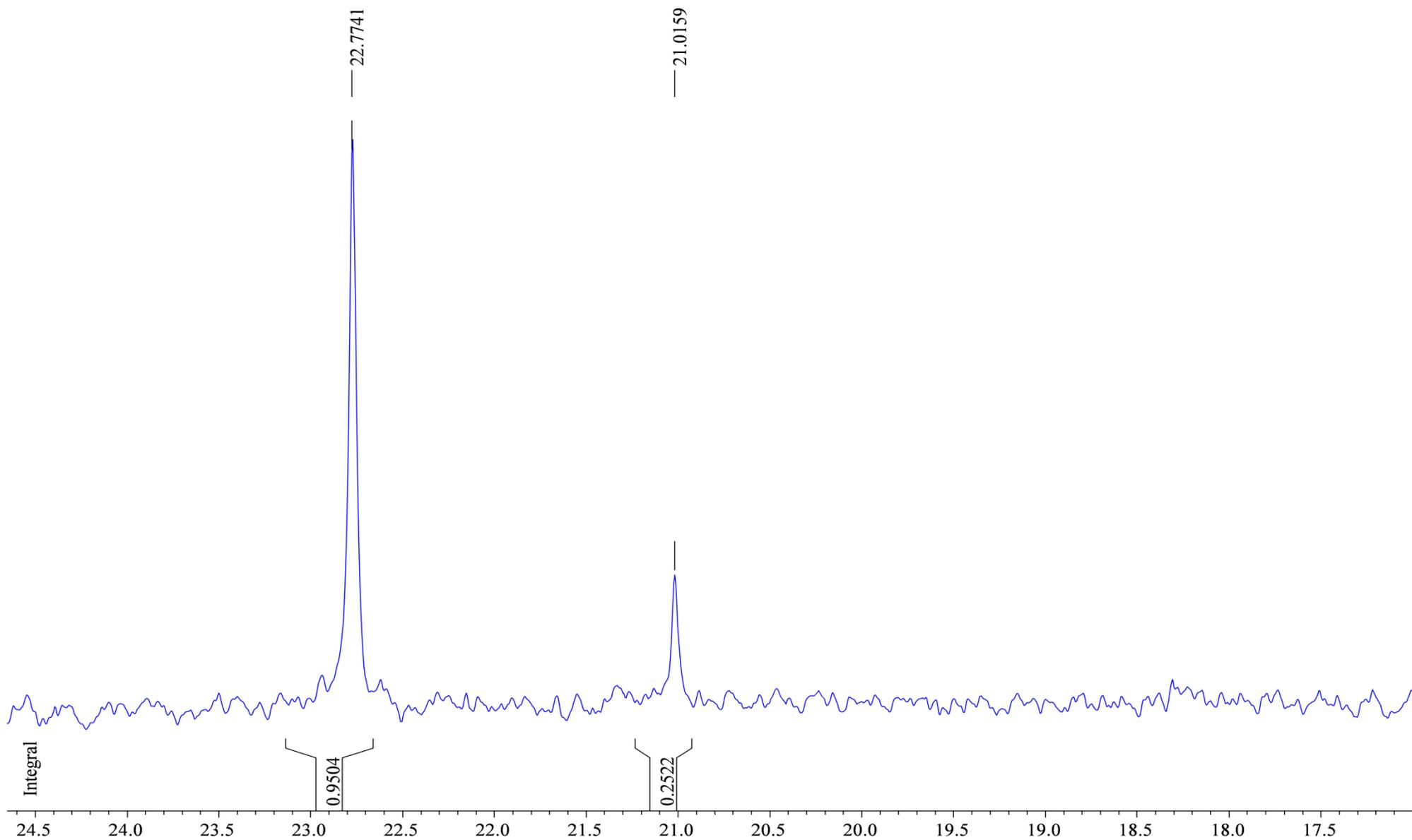


Figure S18. ^{31}P - $\{^1\text{H}\}$ and ^{31}P NMR spectra (242.9 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

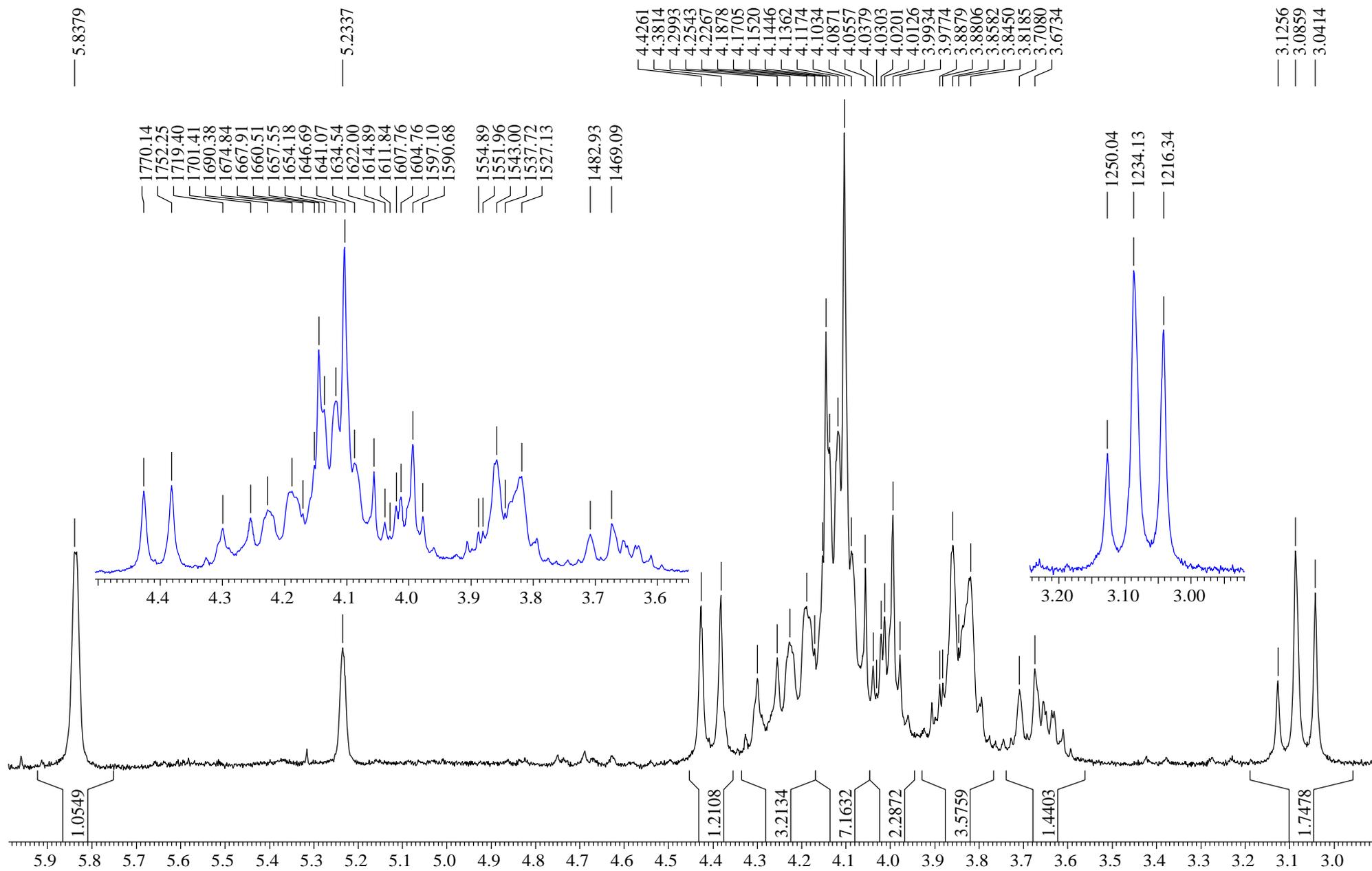


Figure S19. Fragment of ^1H NMR spectrum (400 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

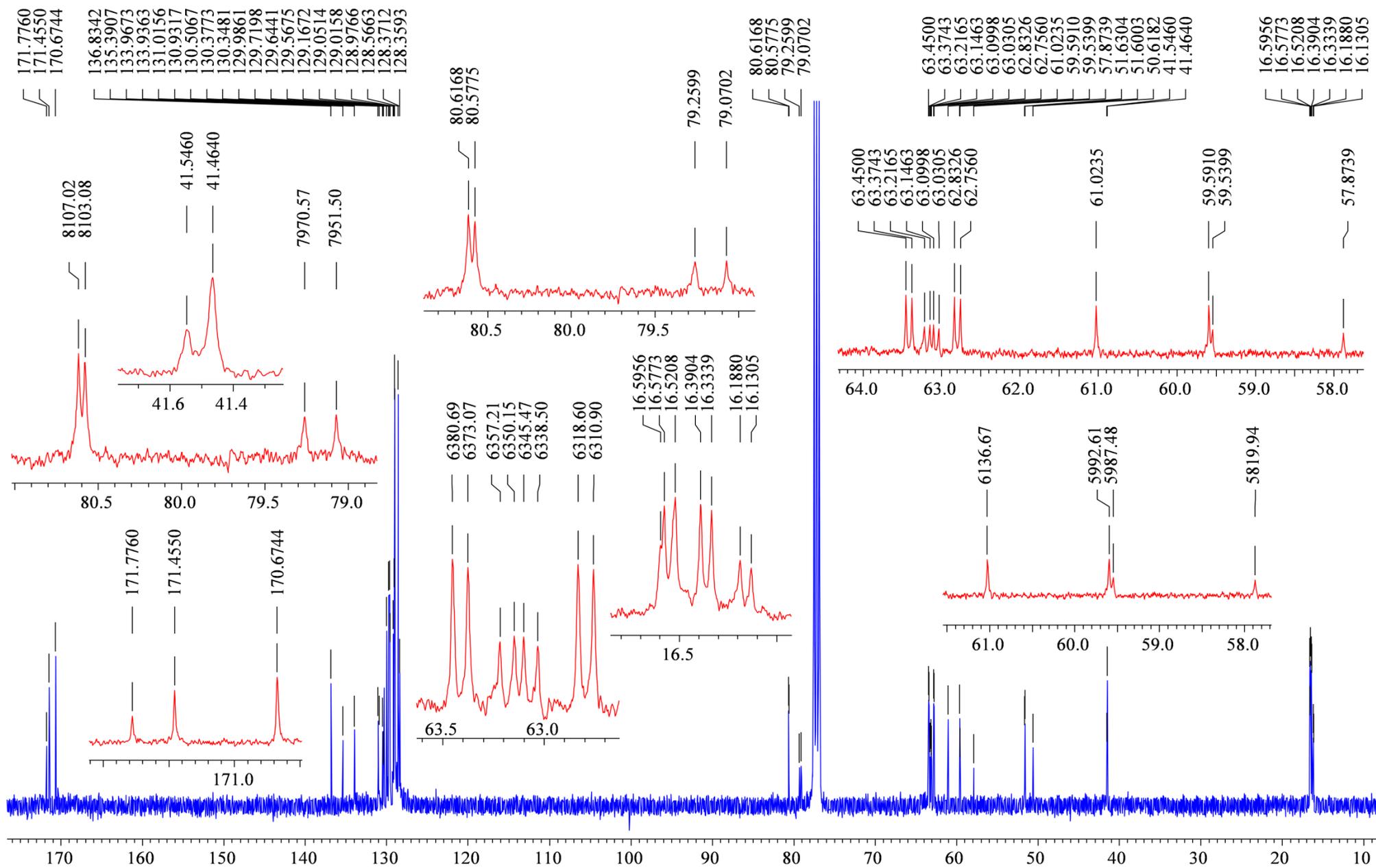


Figure S20. ^{31}C - $\{^1\text{H}\}$ NMR spectrum (100.6 MHz, CDCl_3) of diastereoisomers (**4a**) mixture (d_1 , d_2 in the ratio of 4 : 1).

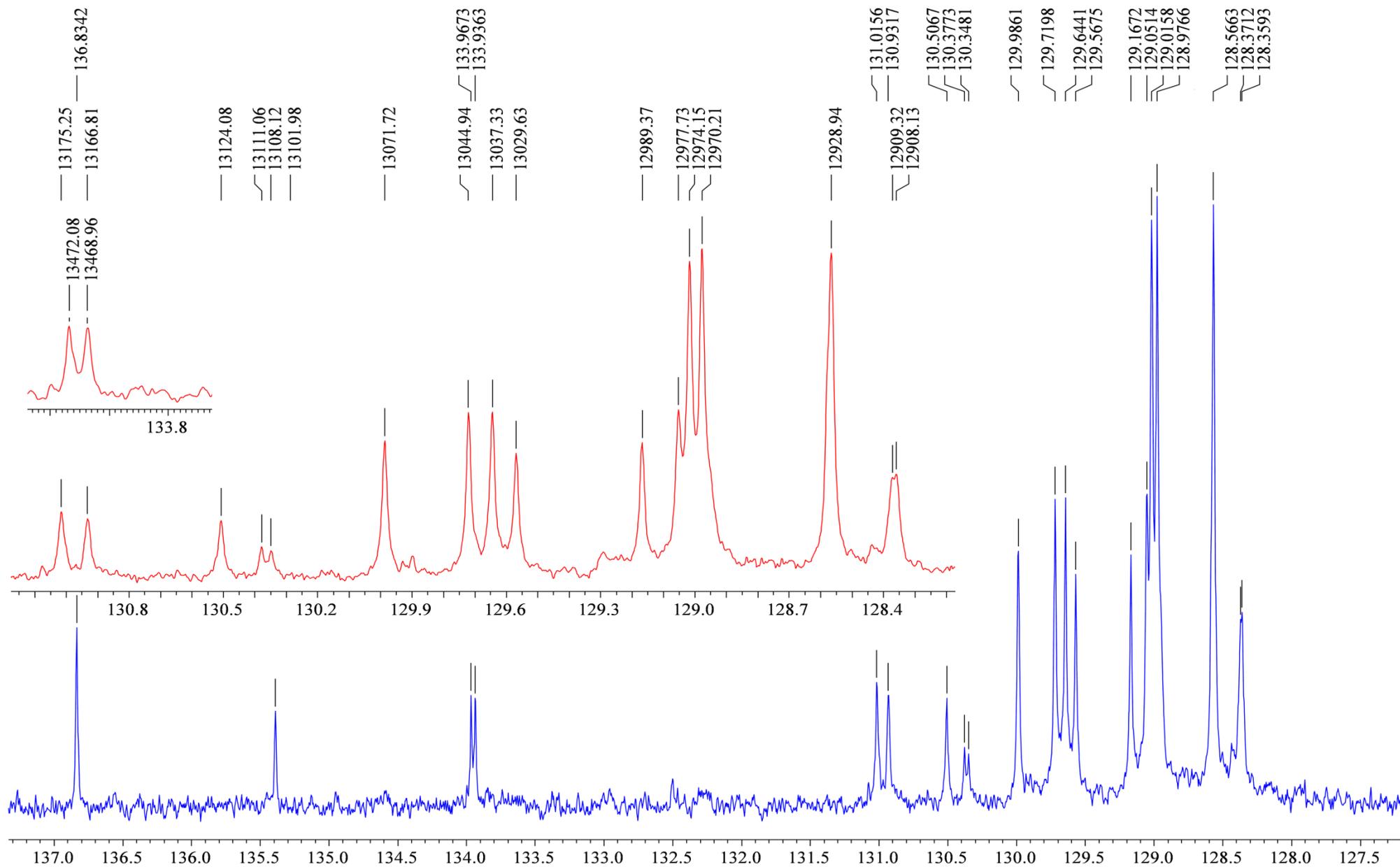


Figure S21. Fragment of ^{13}C - NMR spectrum (400 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

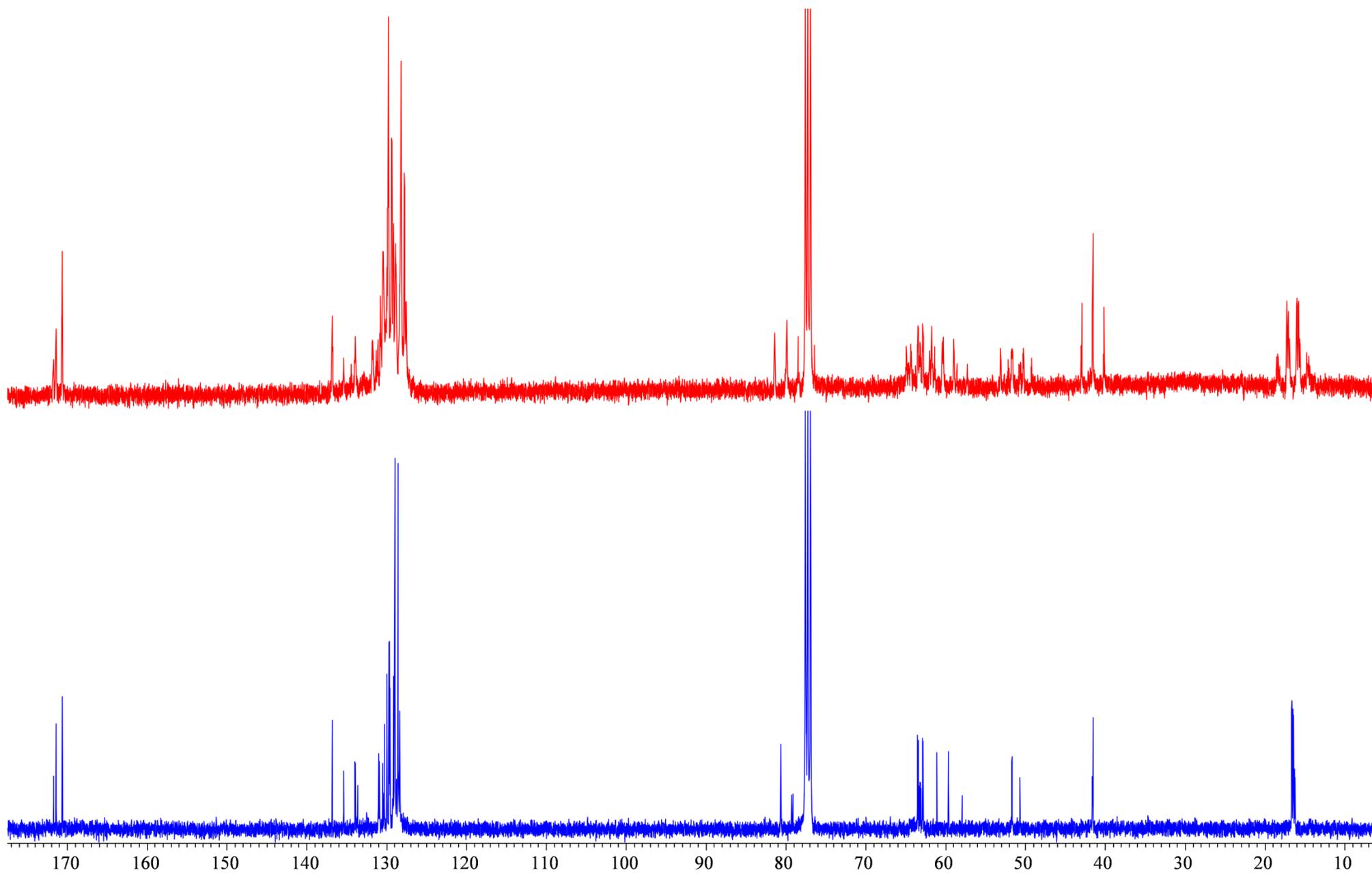


Figure S22. ^{31}C - $\{^1\text{H}\}$ and ^{31}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

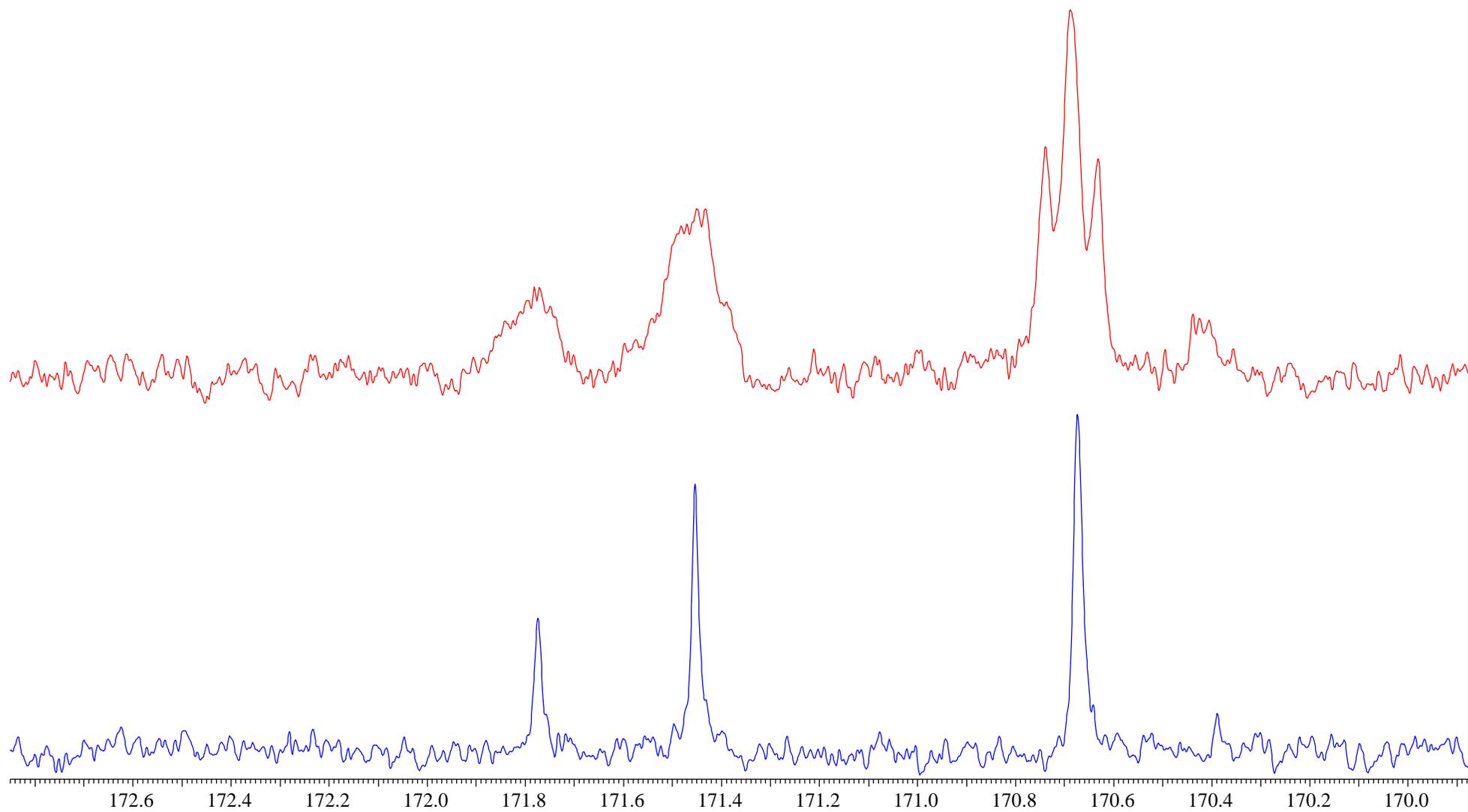


Figure S23. 170-173 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

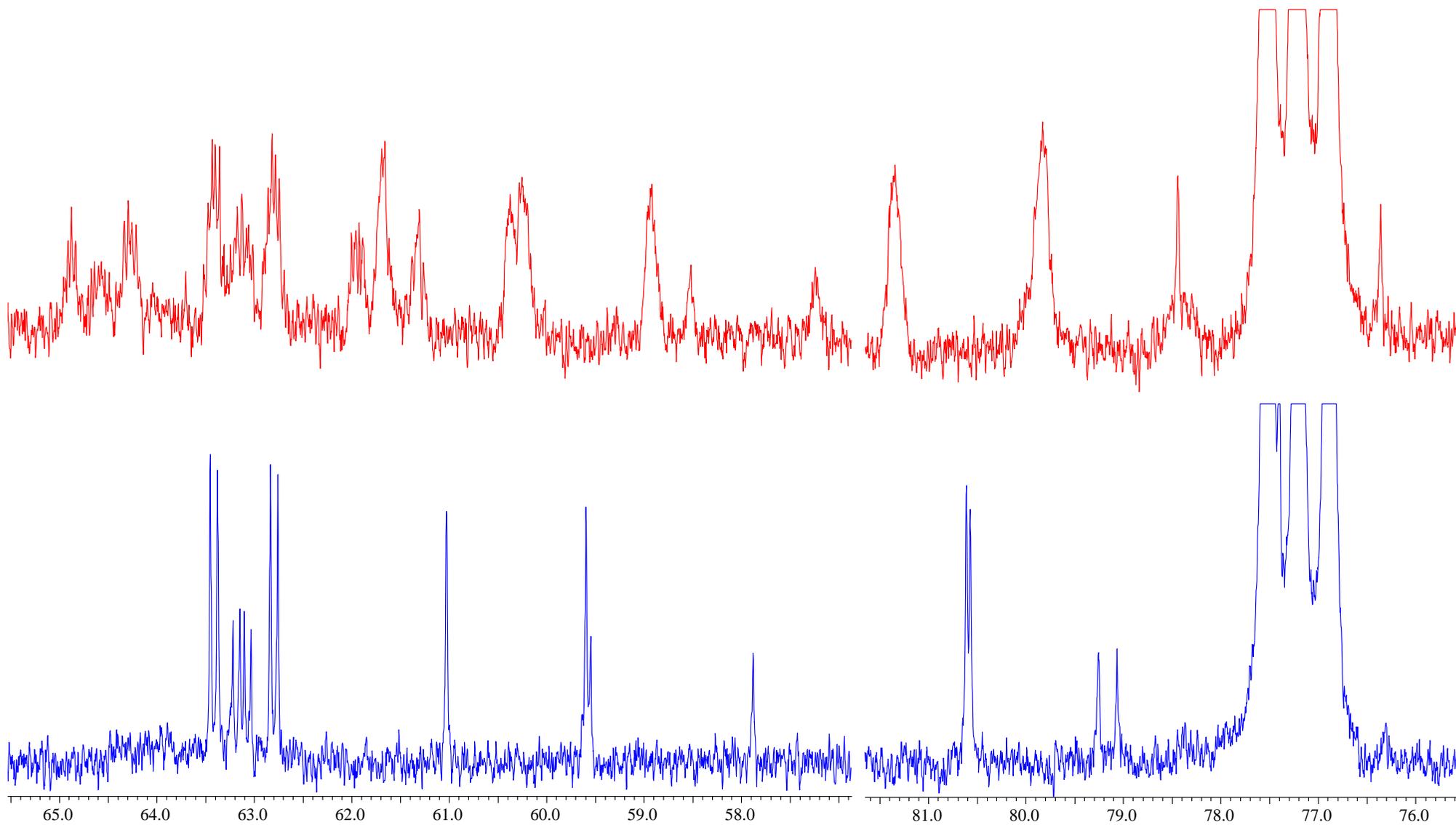


Figure S24. 65-76 ppm region of ^{13}C - $\{^1\text{H}\}$ and ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

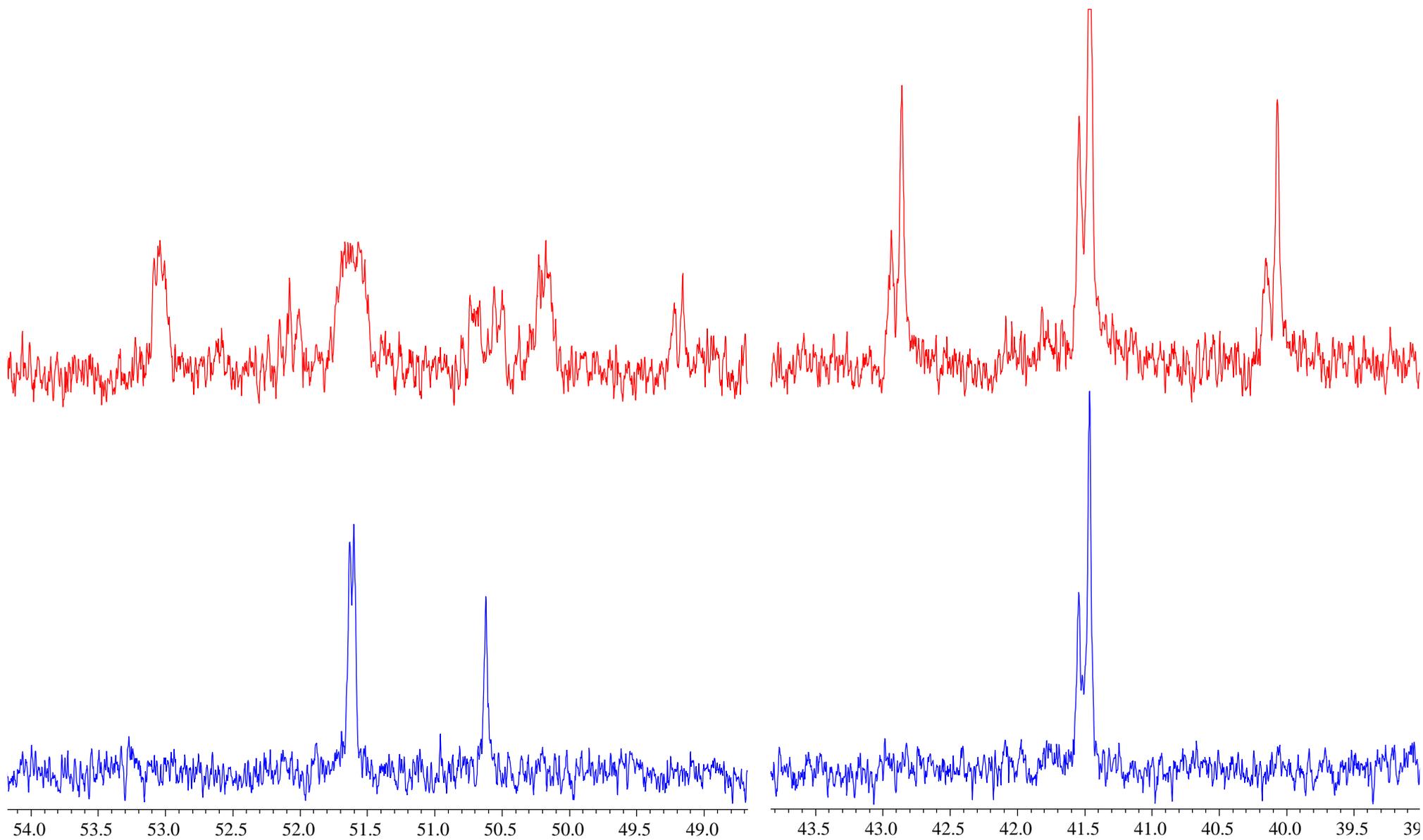


Figure S25. 50-52 and 41 ppm regions of ^{13}C - $\{^1\text{H}\}$ and ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

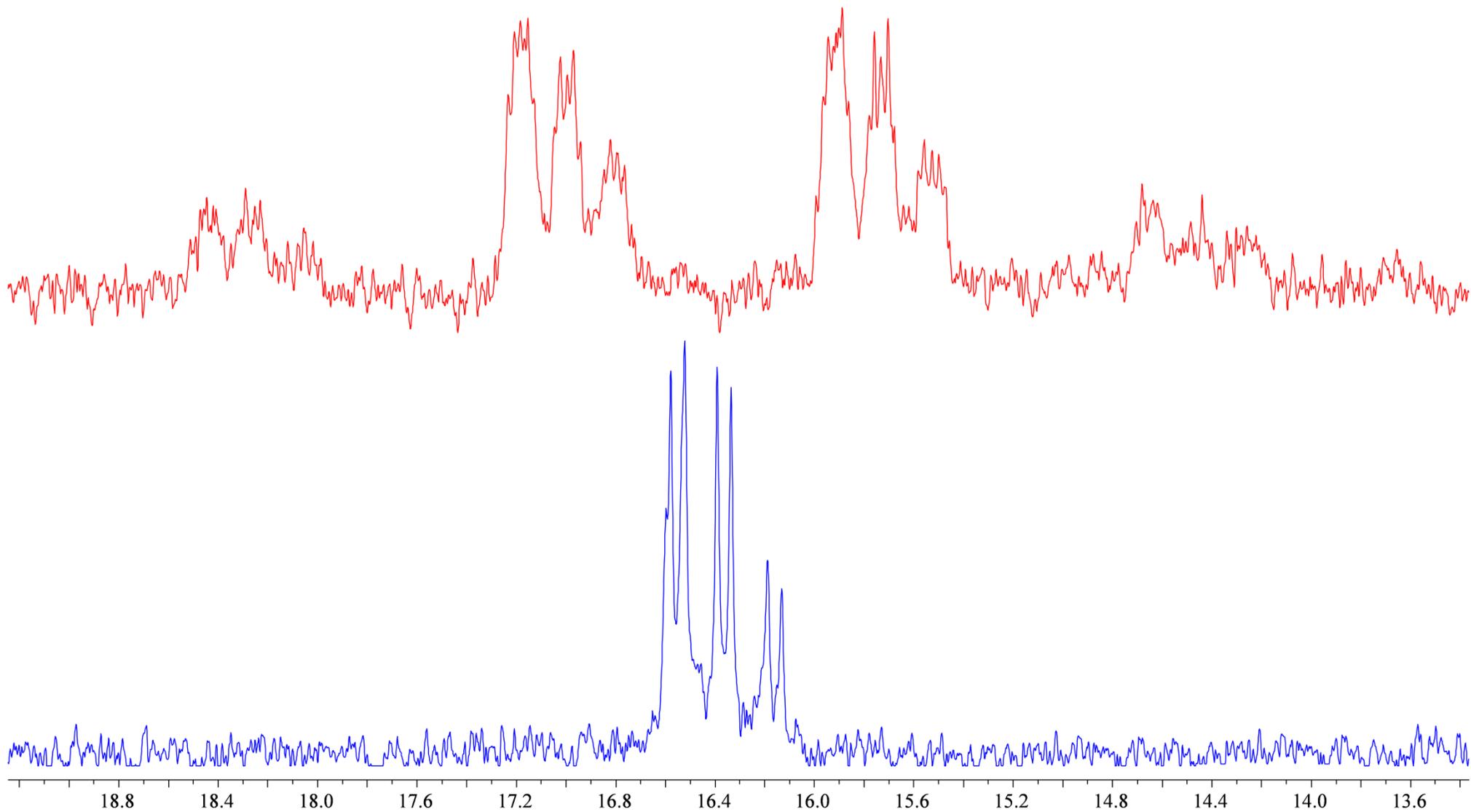


Figure S26. Up-field fragment $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 and d_2 in the ratio of 1 : 4).

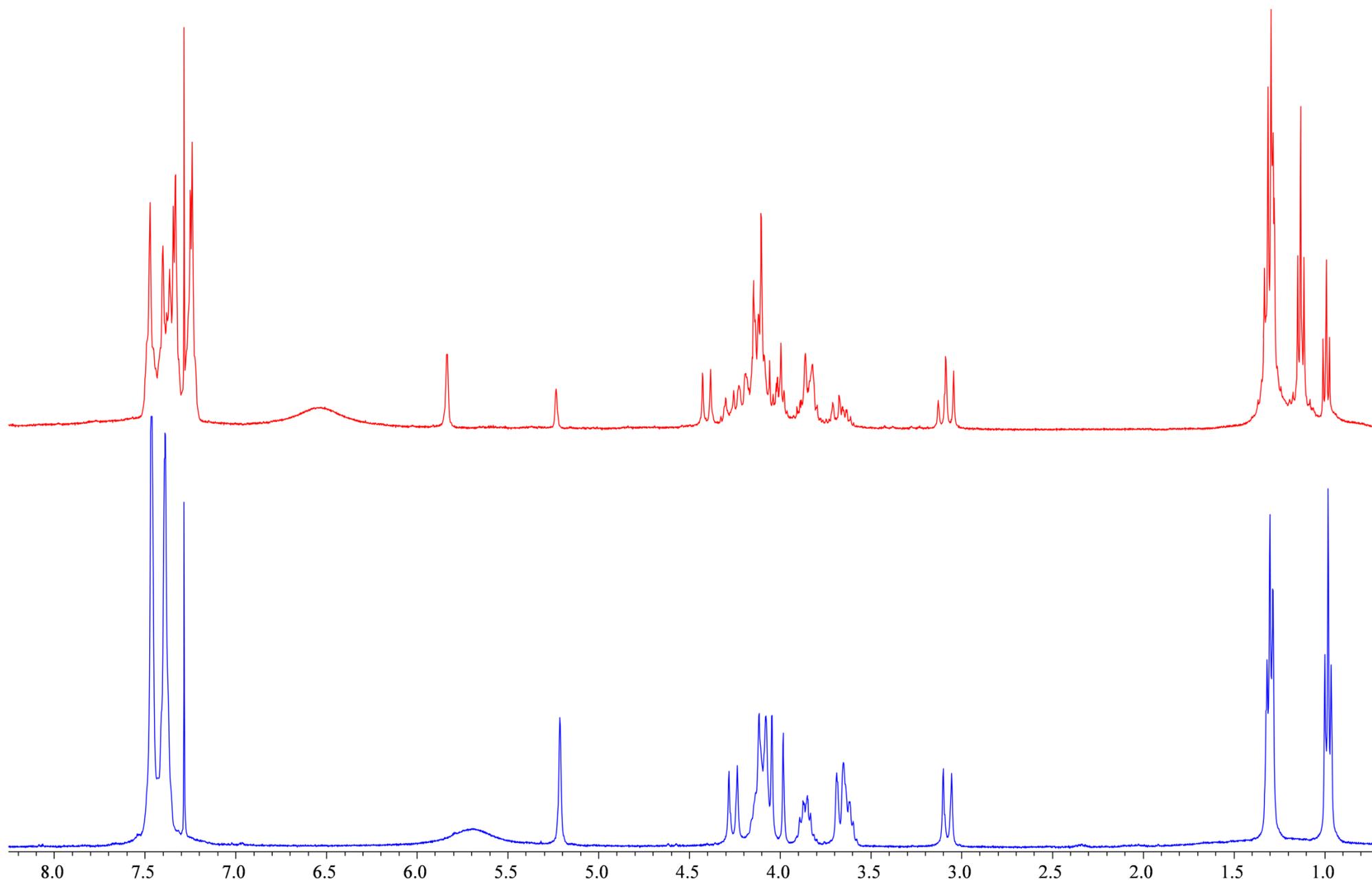


Figure S27. ^1H NMR spectra (400 MHz, CDCl_3) of (**4a**, d_1 , blue) and (**4a**, d_1 , d_2 in the ratio of 1 : 4, red).

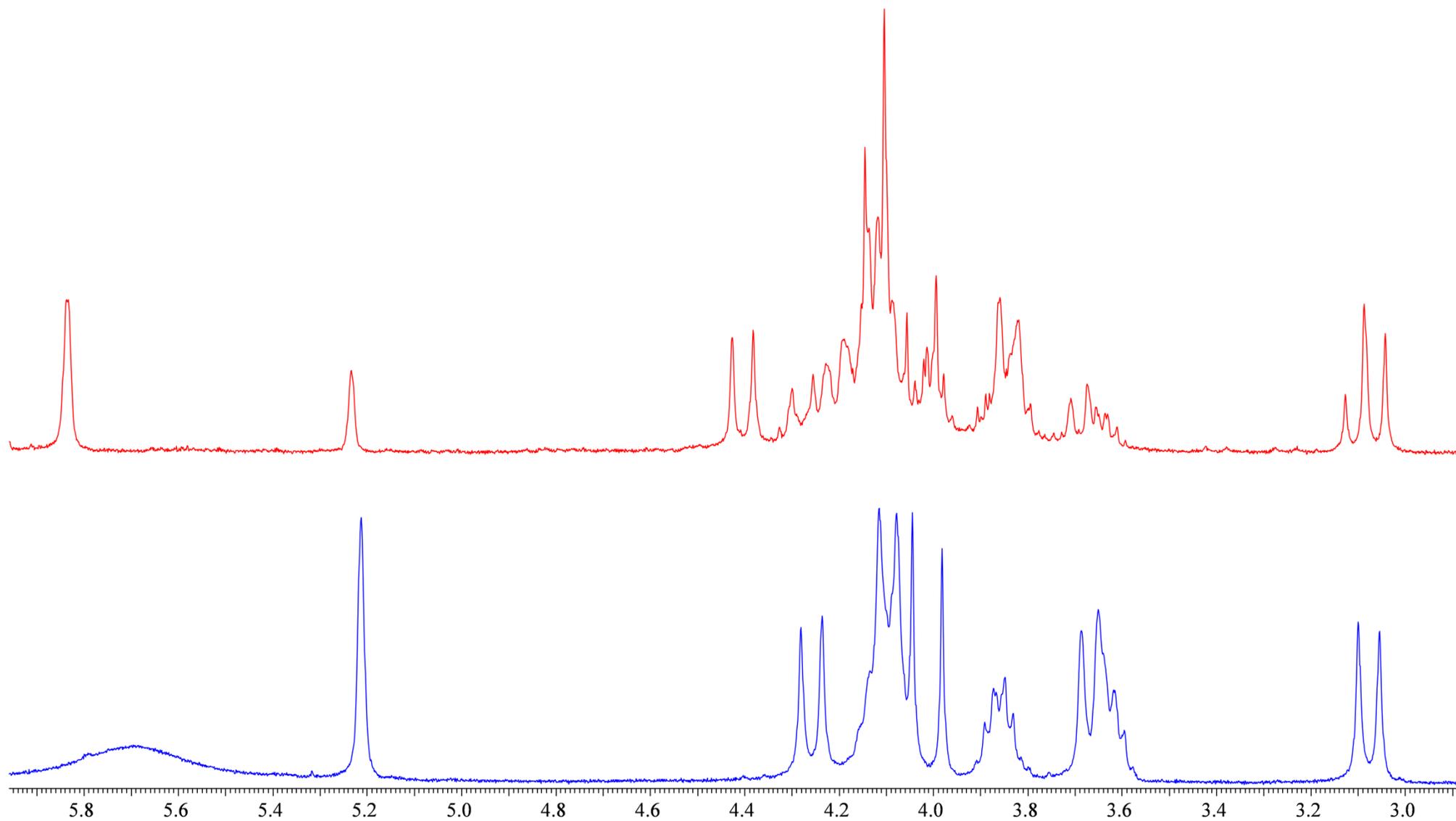


Figure S28. Fragments of ^1H NMR spectra (400 MHz, CDCl_3) of (**4a**, d_1 , blue) and (**4a**, d_1 , d_2 in the ratio of 1 : 4, red).

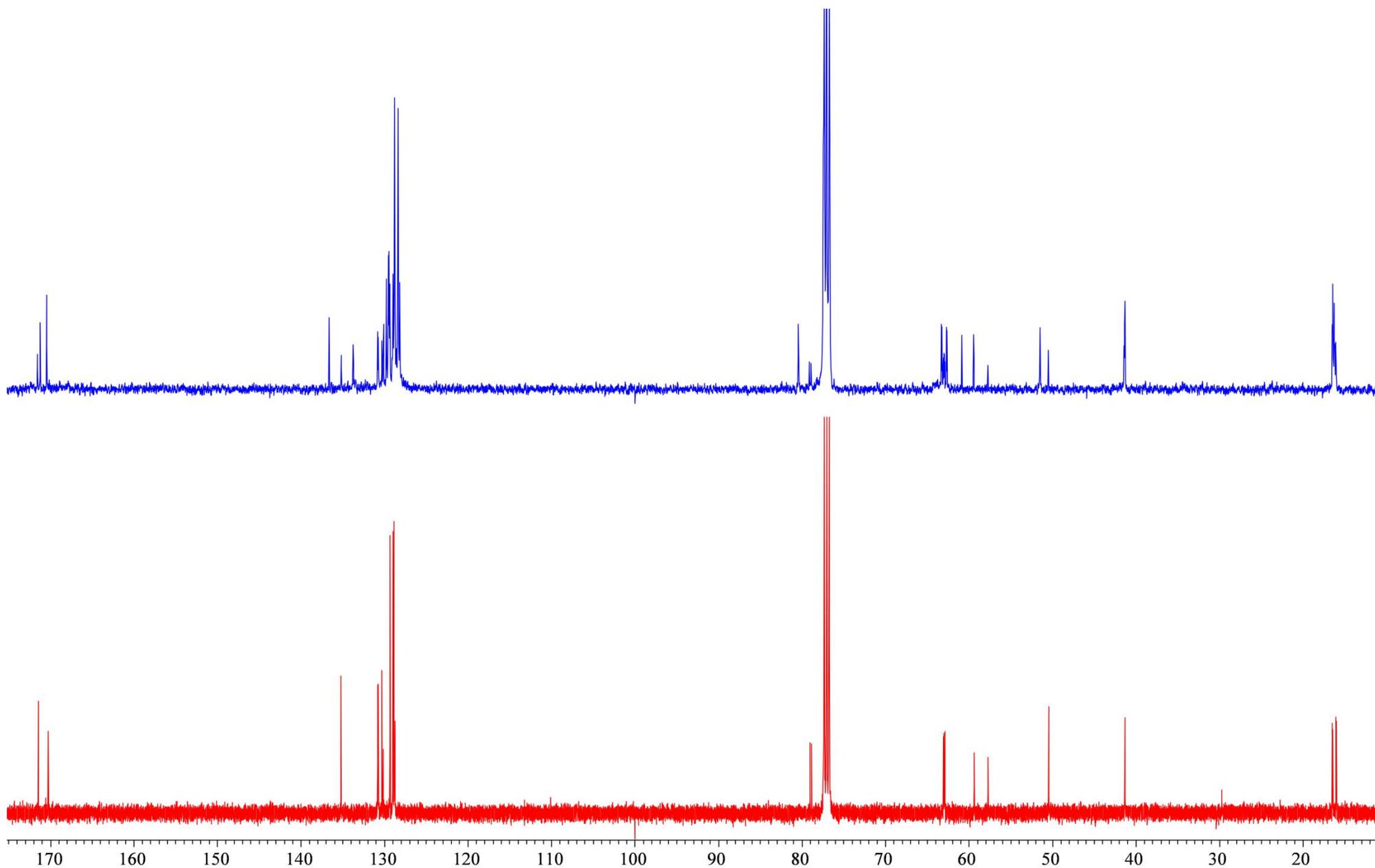


Figure S29. ^{13}C - $\{^1\text{H}\}$ NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 , red) and (**4a**, d_1 , d_2 in the ratio of 1 : 4, blue).

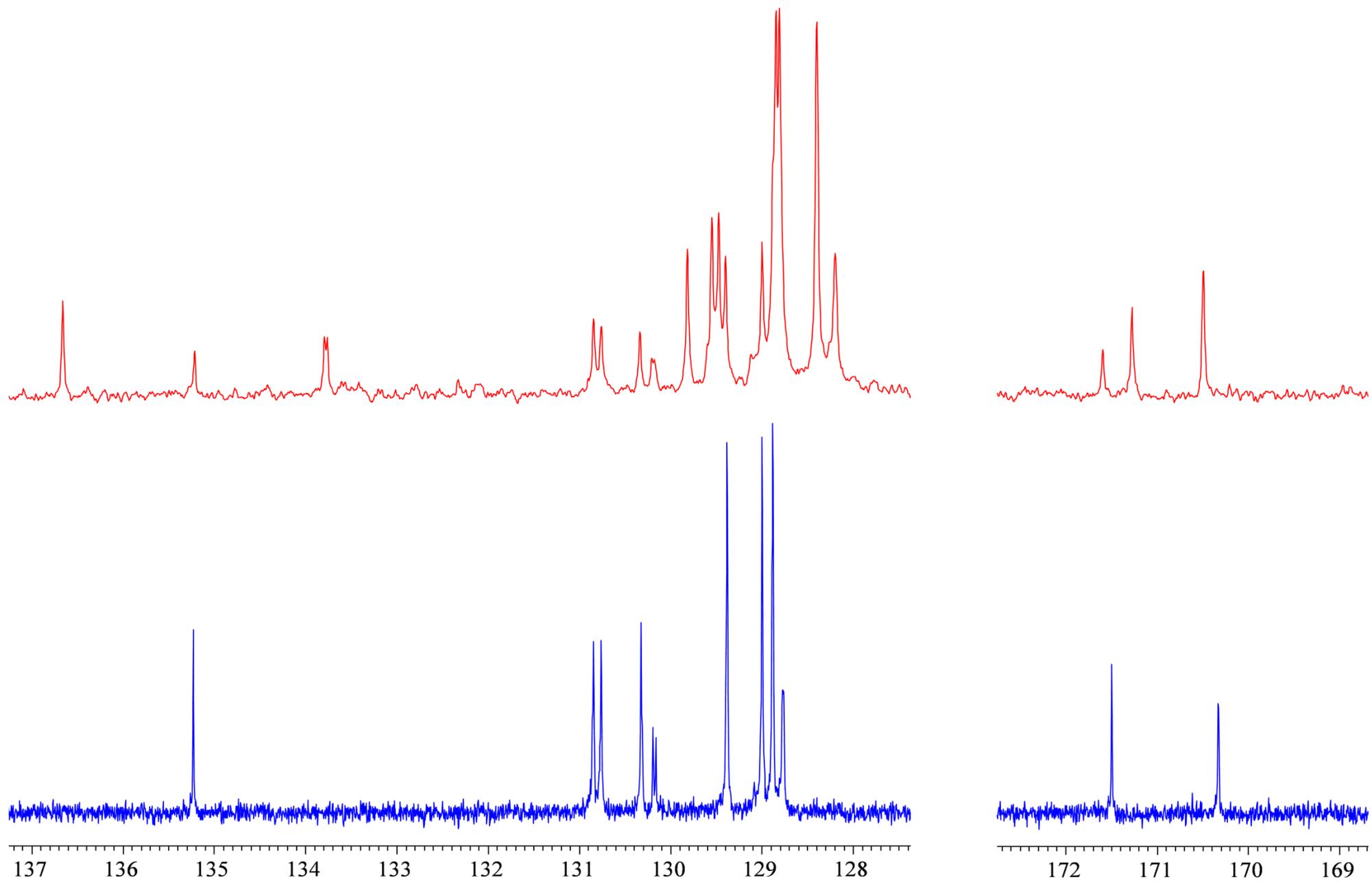


Figure S30. 128-136 and 170-172 ppm regions of ^{31}C - $\{^1\text{H}\}$ NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 , blue) and (**4a**, d_1 , d_2 in the ratio of 1 : 4, red).

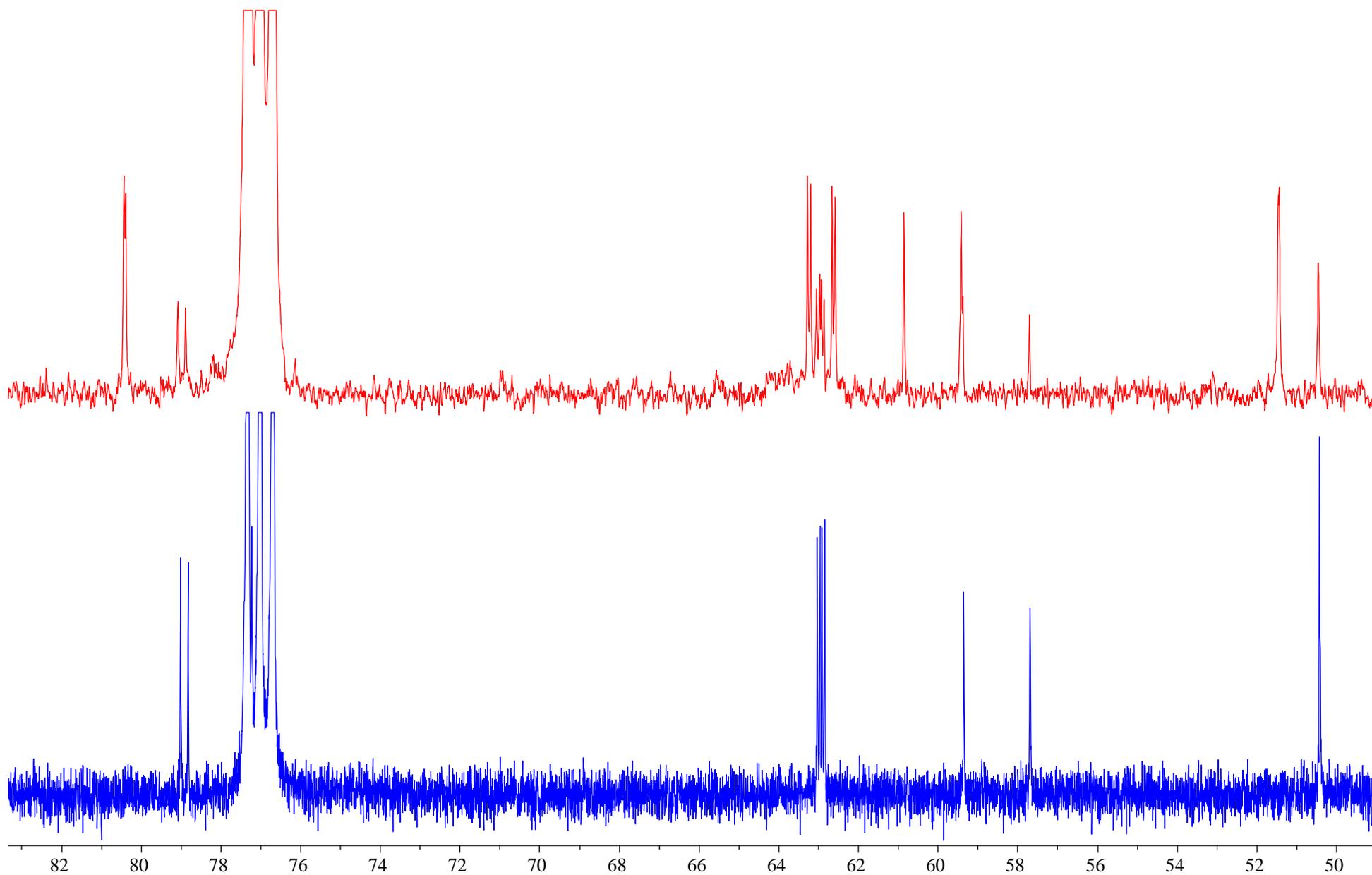


Figure S31. 50-82 ppm regions of ^{31}C - $\{^1\text{H}\}$ NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 , blue) and (**4a**, d_1 , d_2 in the ratio of 1 : 4, red).

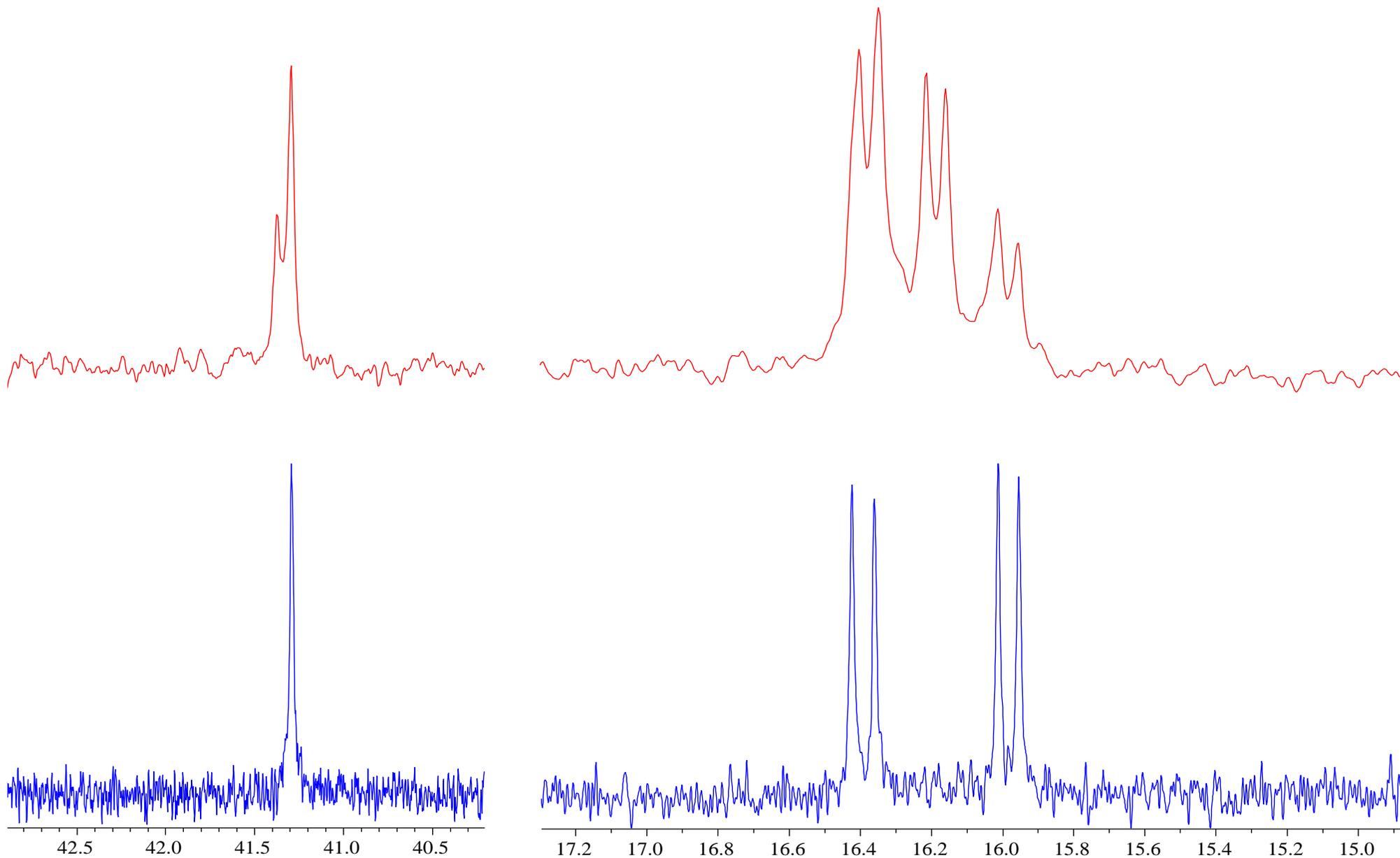


Figure S32. 15-17 and 41 ppm regions of ^{31}C - $\{^1\text{H}\}$ NMR spectra (100.6 MHz, CDCl_3) of (**4a**, d_1 , blue) and (**4a**, d_1 , d_2 in the ratio of 1 : 4, red).

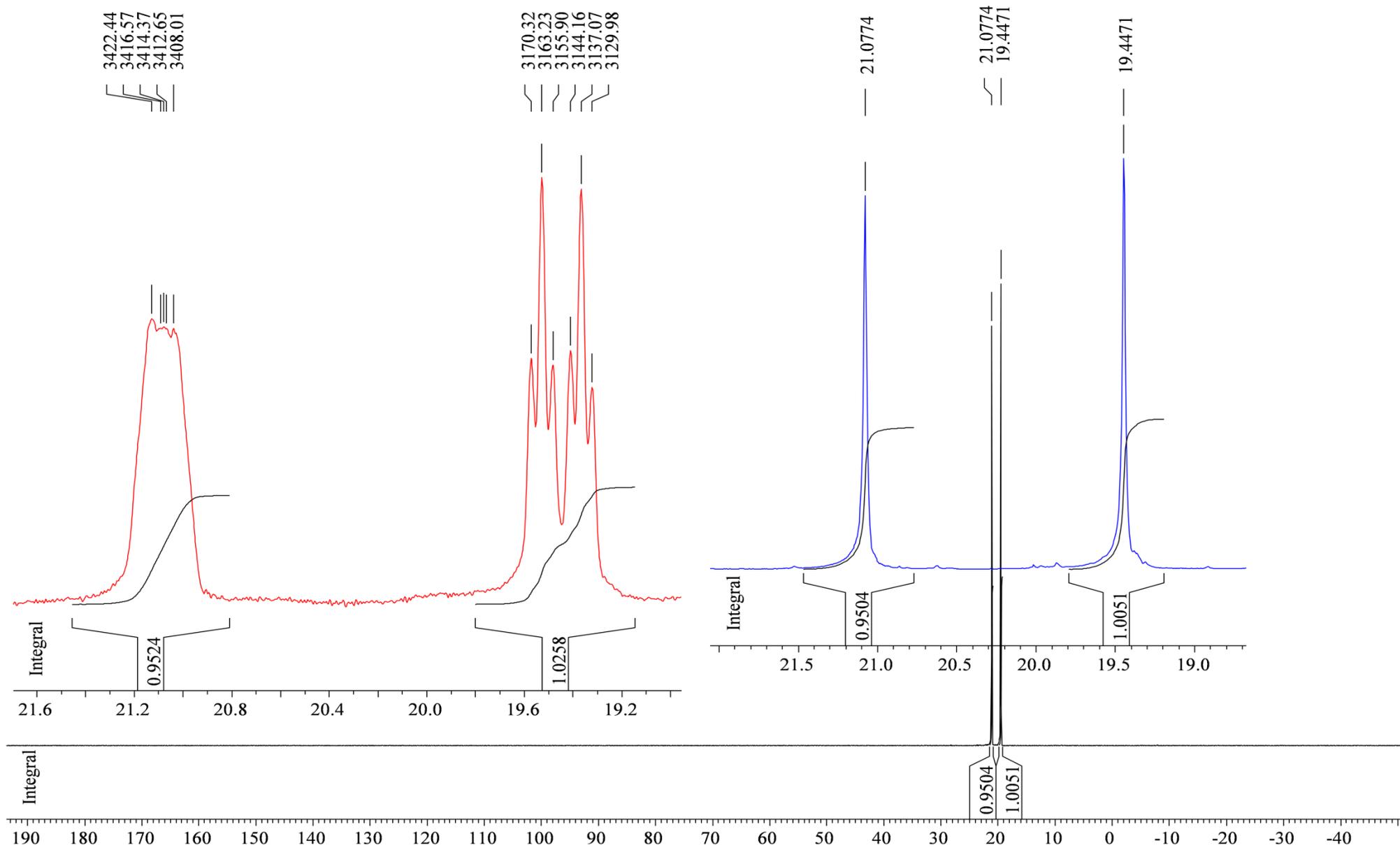


Figure S33. $^{31}\text{P}\{-^1\text{H}\}$ and ^{31}P NMR spectra (242.9 MHz, CDCl_3) of (**4b**, d_1 and d_2).

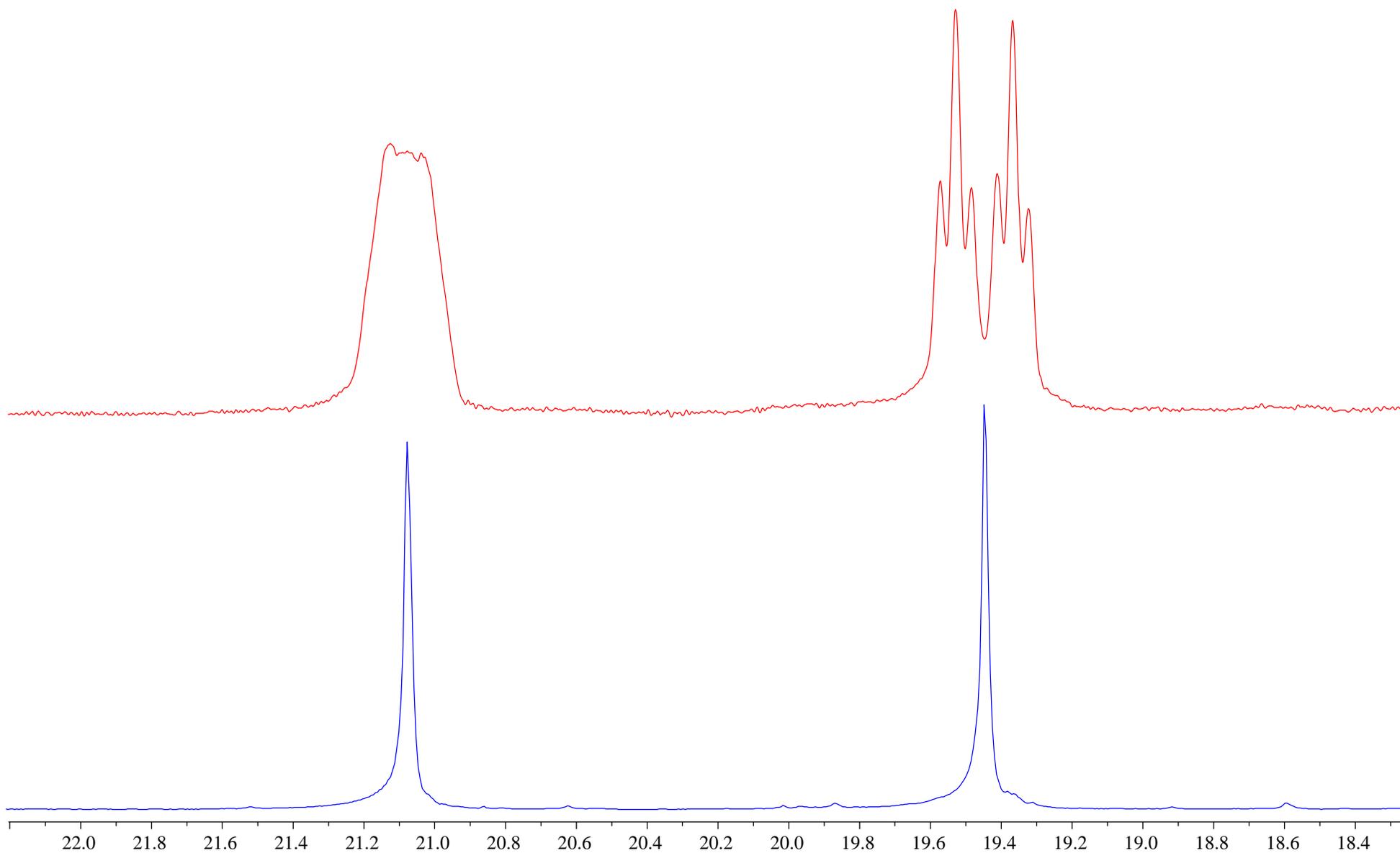


Figure S34. $^{31}\text{P}\{-^1\text{H}\}$ and ^{31}P NMR spectra (242.9 MHz, CDCl_3) of (**4b**, d_1 and d_2).

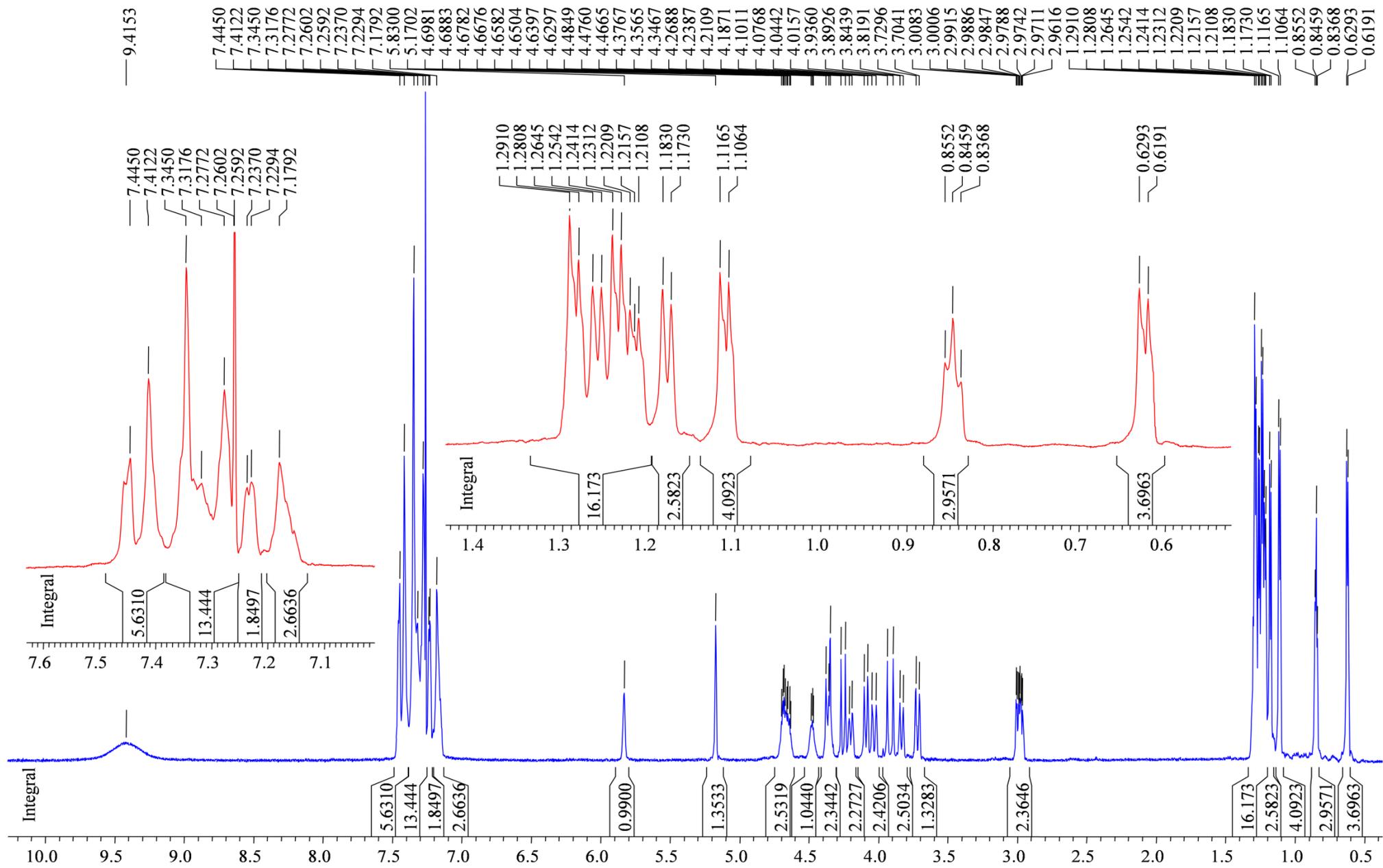


Figure S35. ^1H NMR spectrum (600 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

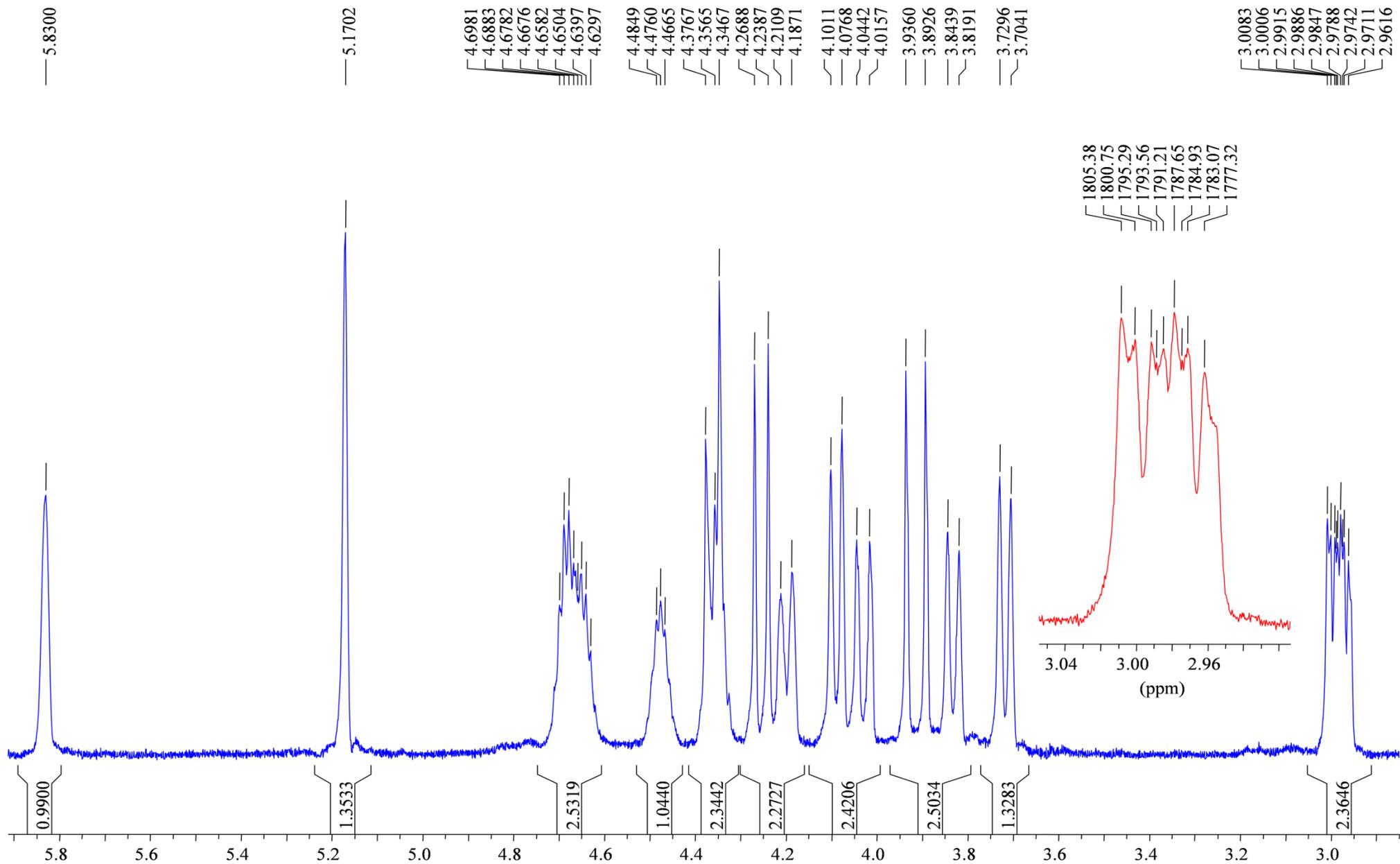


Figure S36. Fragment of ^1H NMR spectrum (600 MHz, CDCl_3) of **(4b)**, d_1 and d_2 in the ratio of 1.3 : 1).

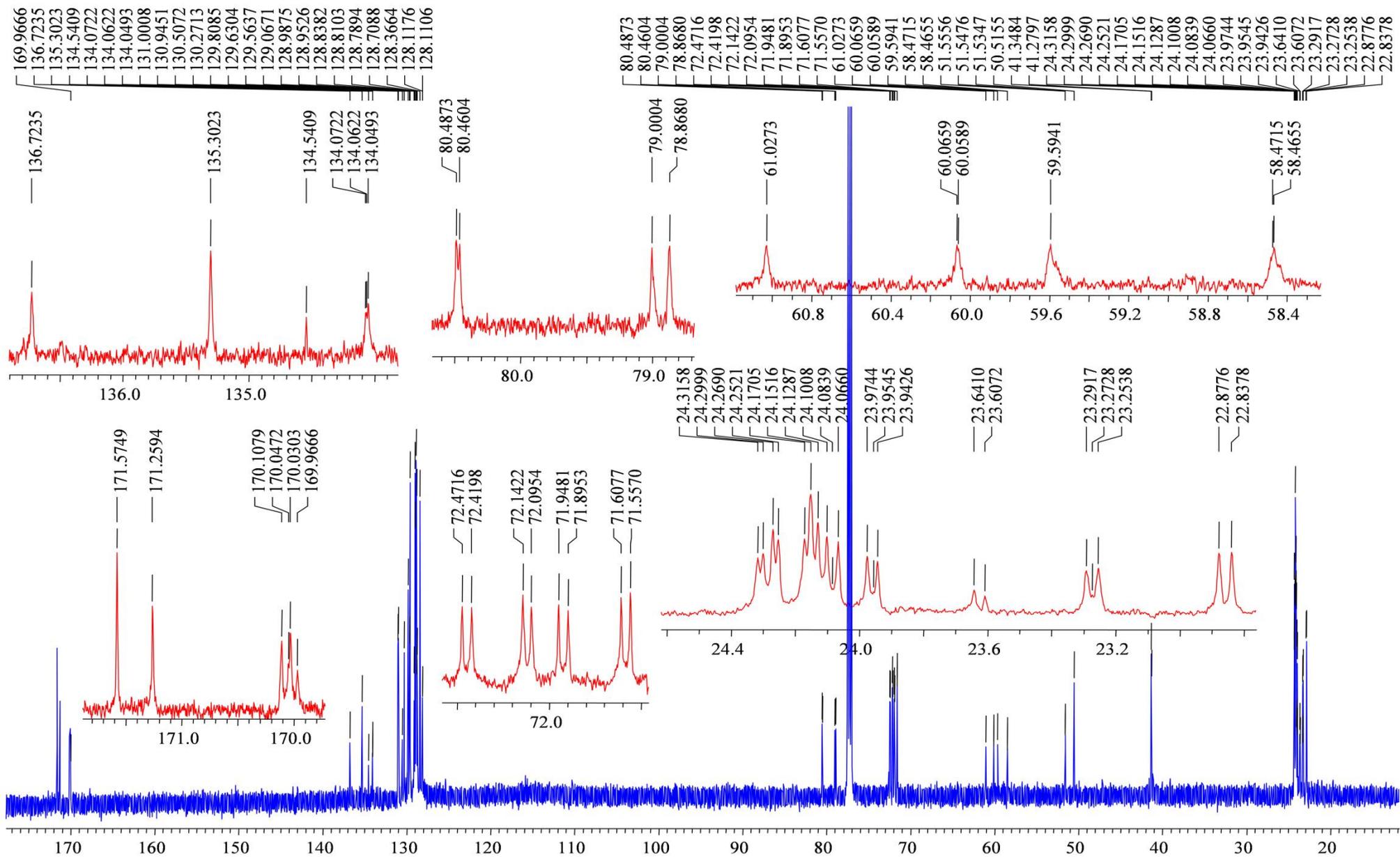


Figure S37. $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

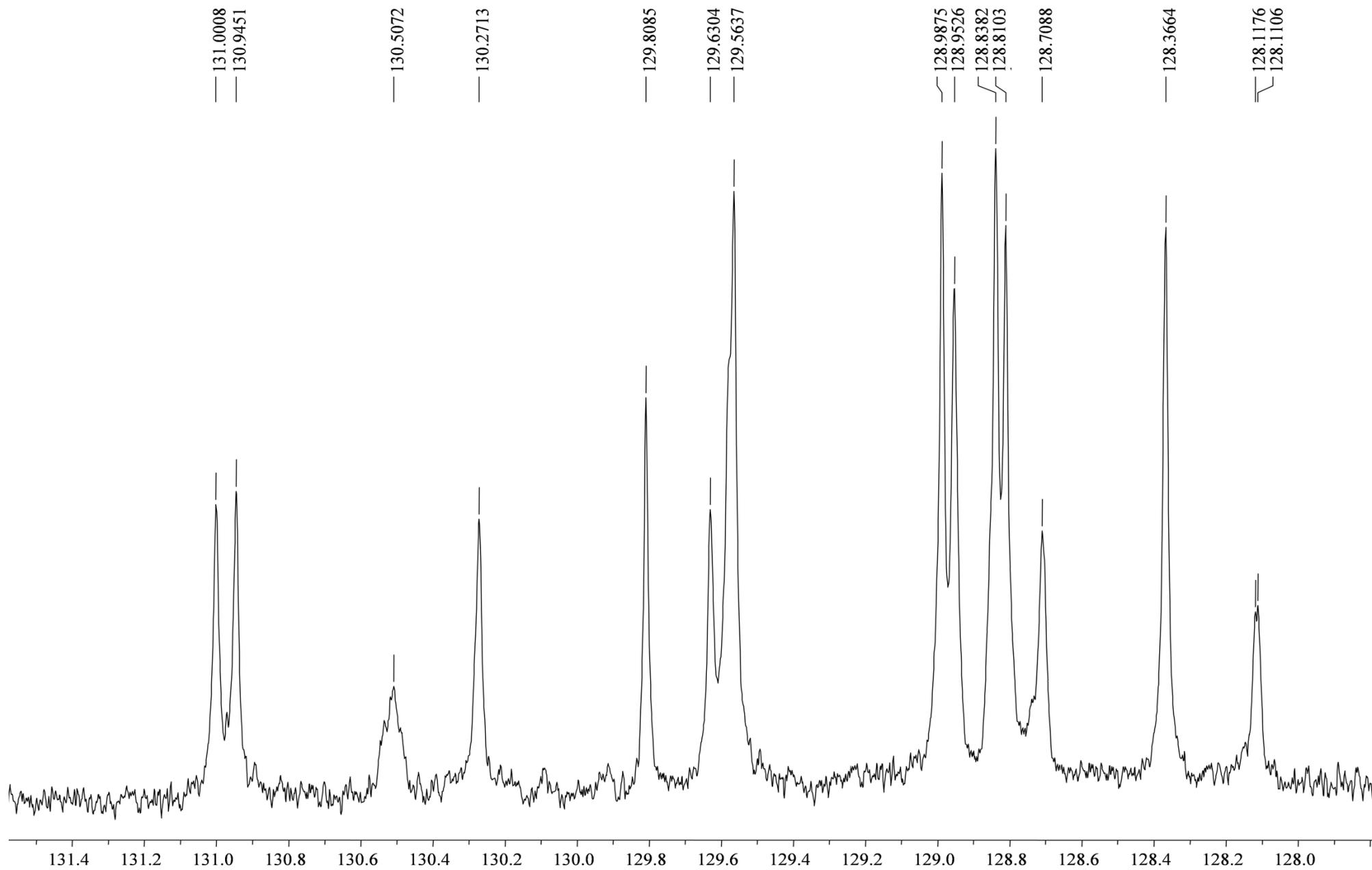


Figure S38. 128-131 region of $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

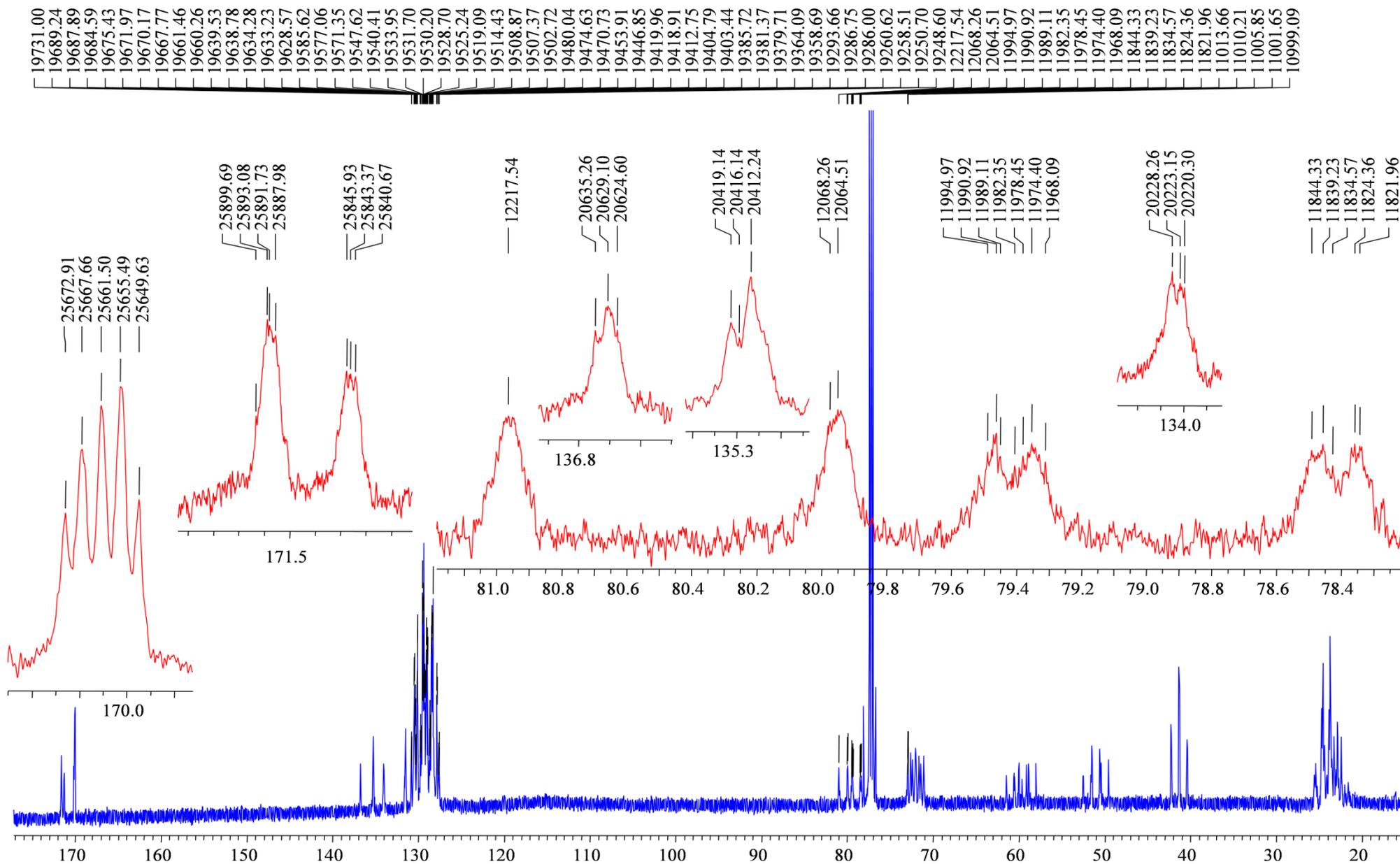


Figure S39. ^{13}C NMR spectrum (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

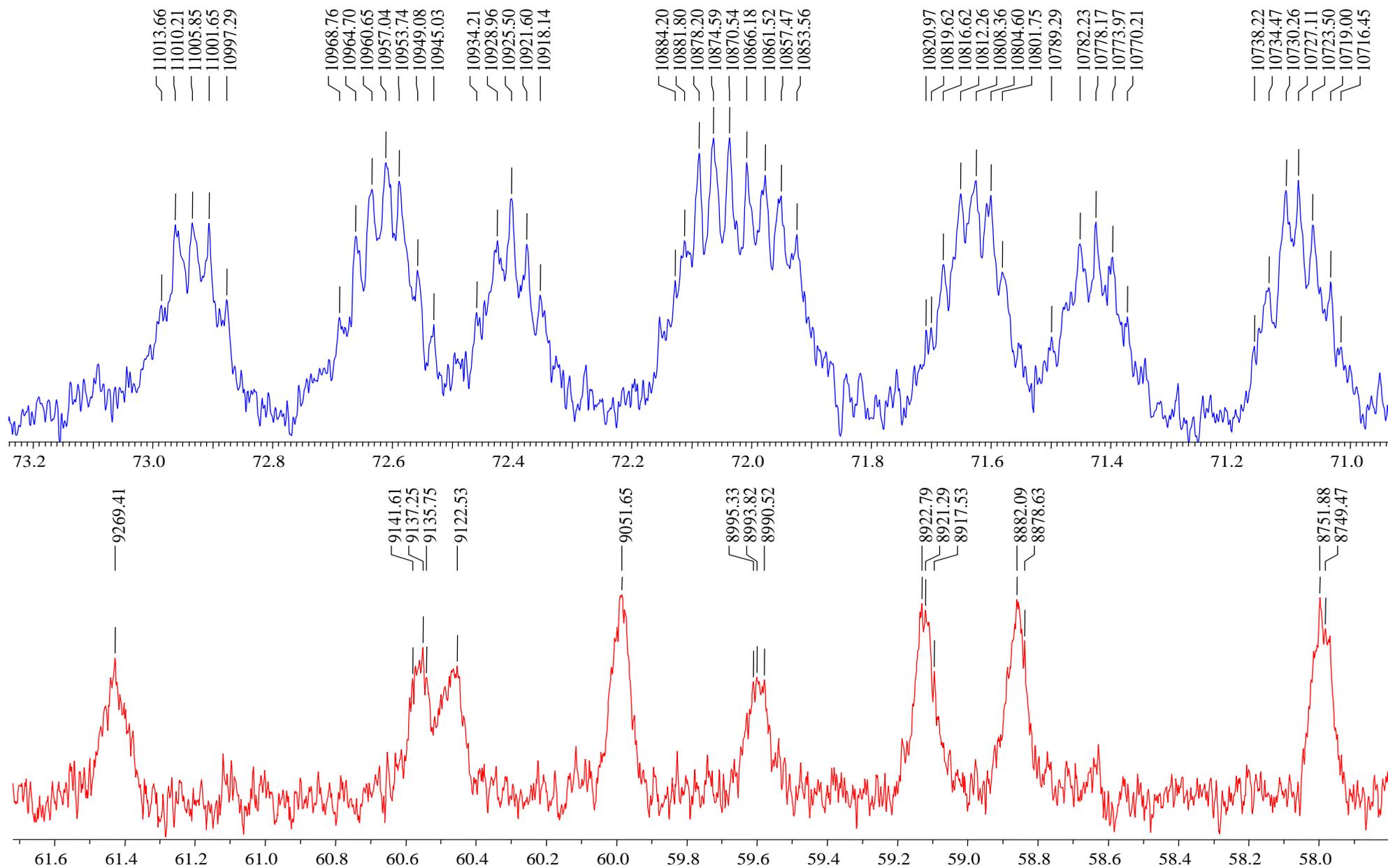


Figure S40. 71-73 and 57-62 ppm regions of ^{13}C NMR spectrum (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

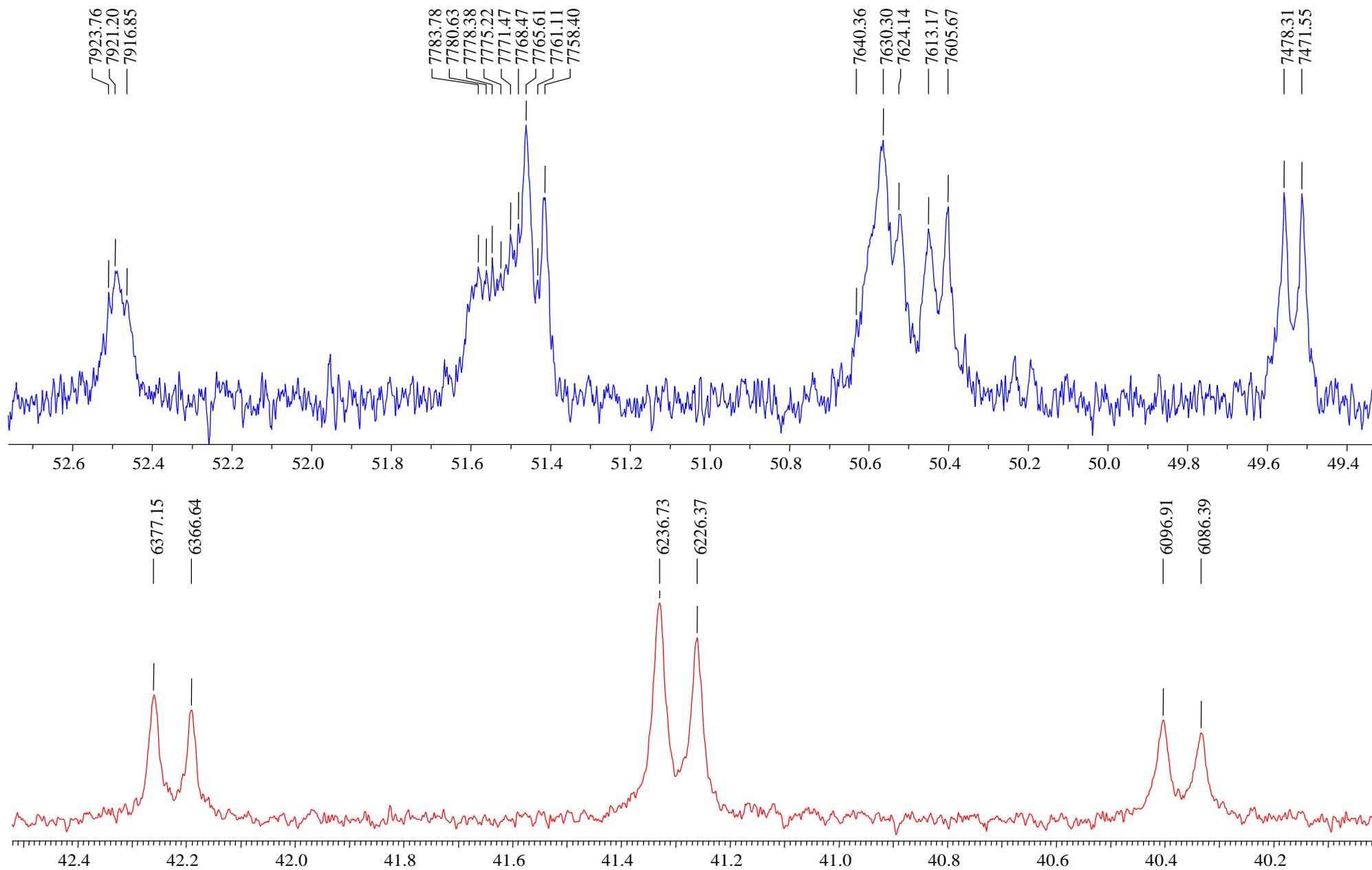


Figure S41. 49-53 and 40-42 ppm regions of ^{13}C NMR spectrum (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

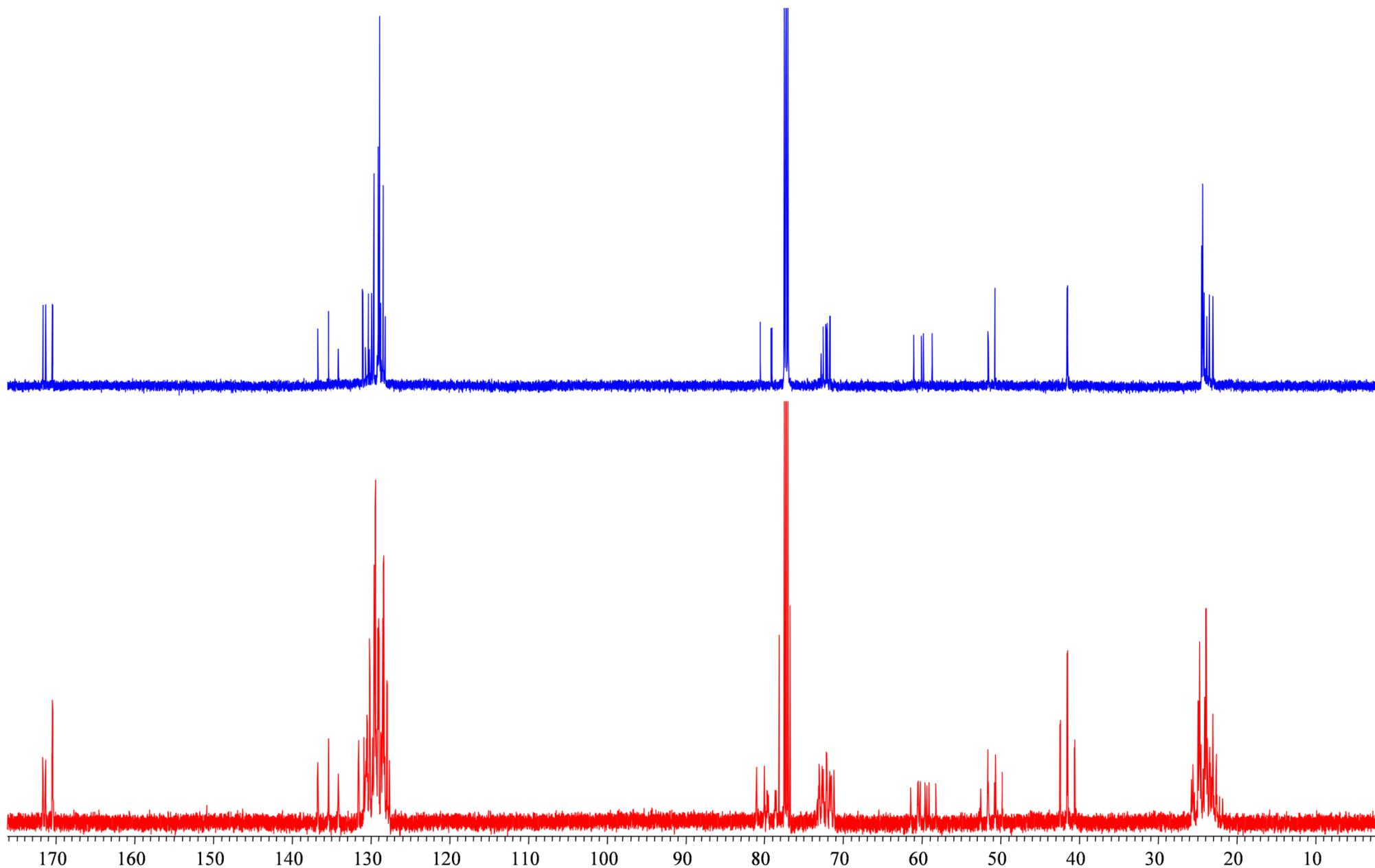


Figure S42. $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

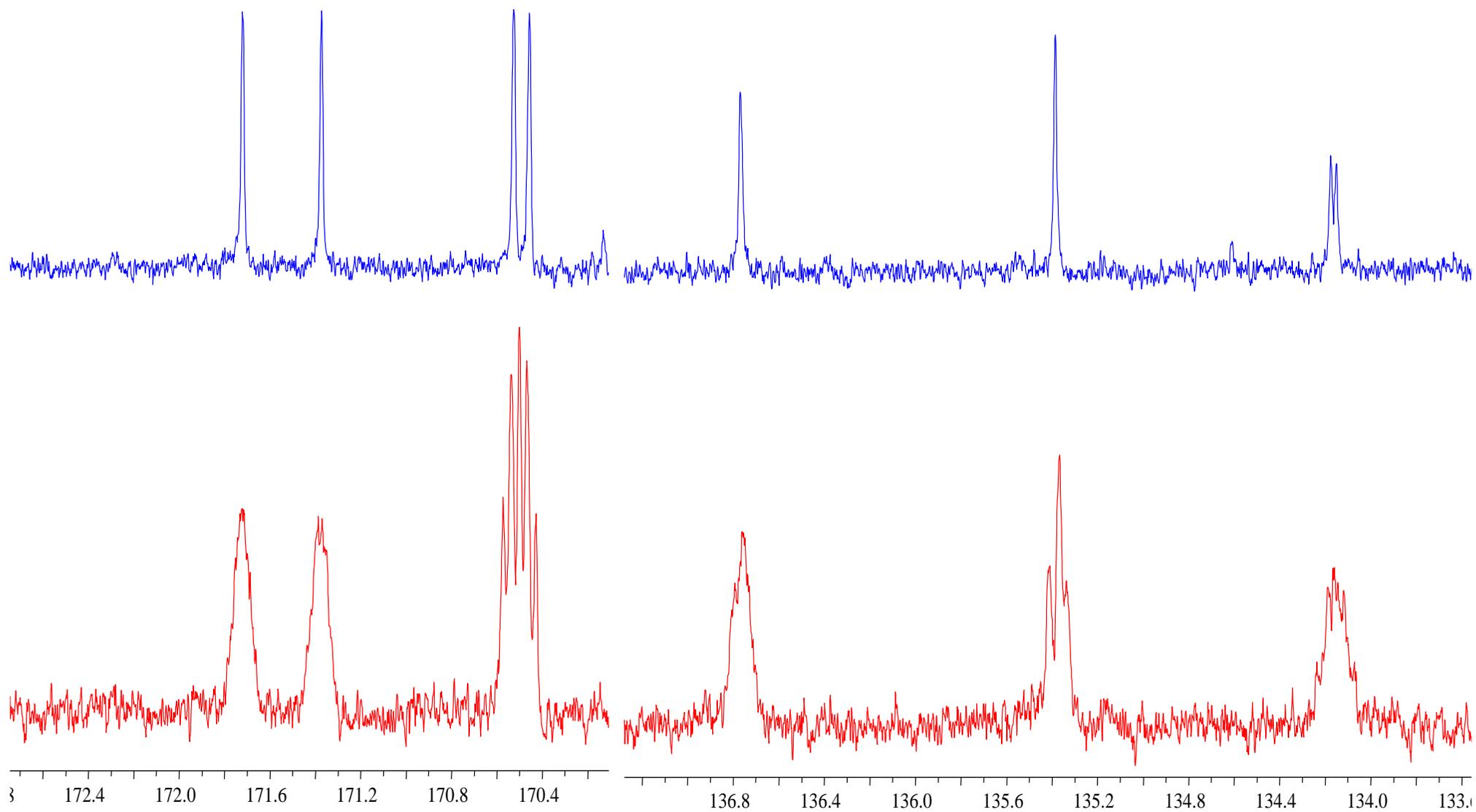


Figure S43. 133-172 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

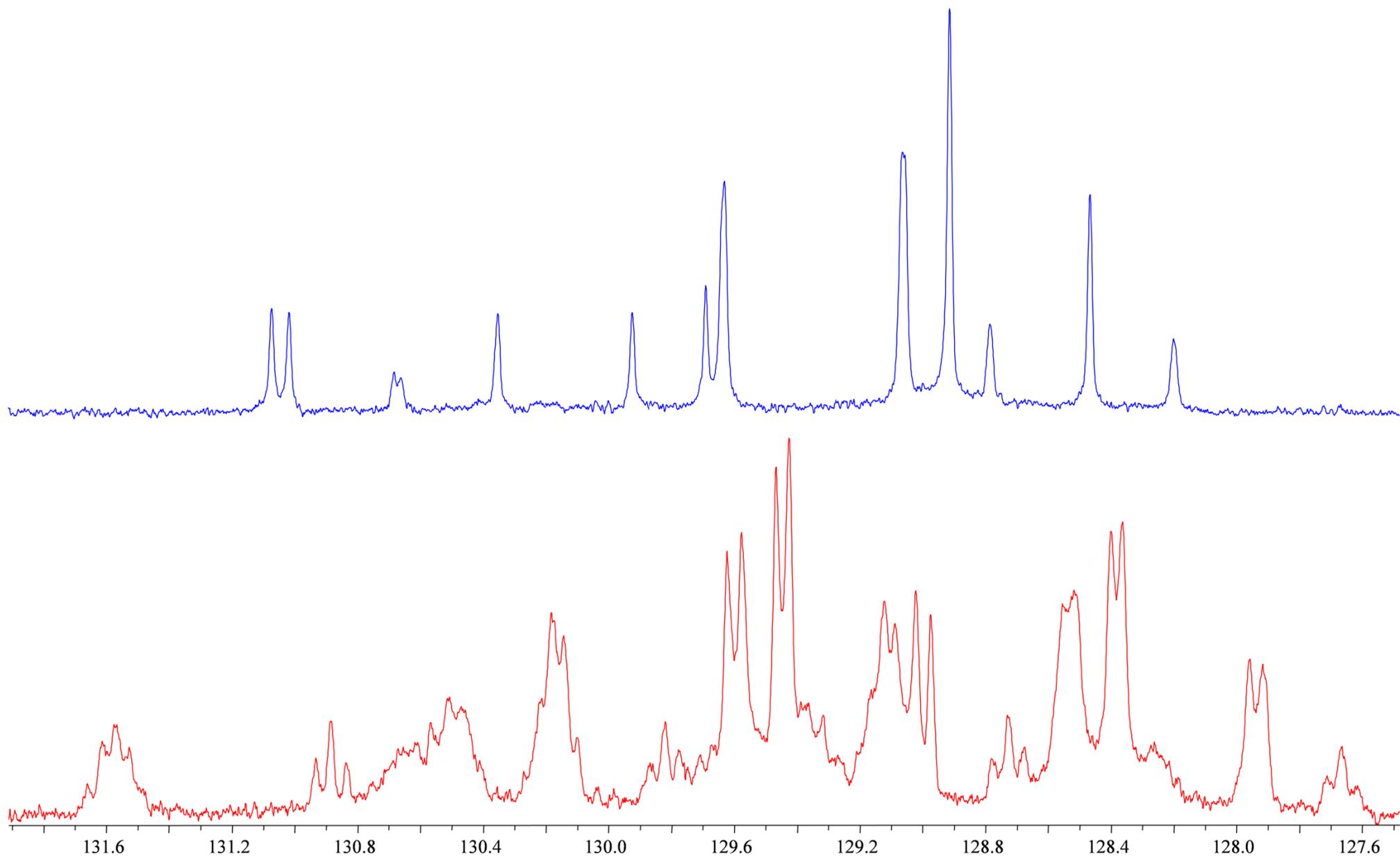


Figure S44. 132-127 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

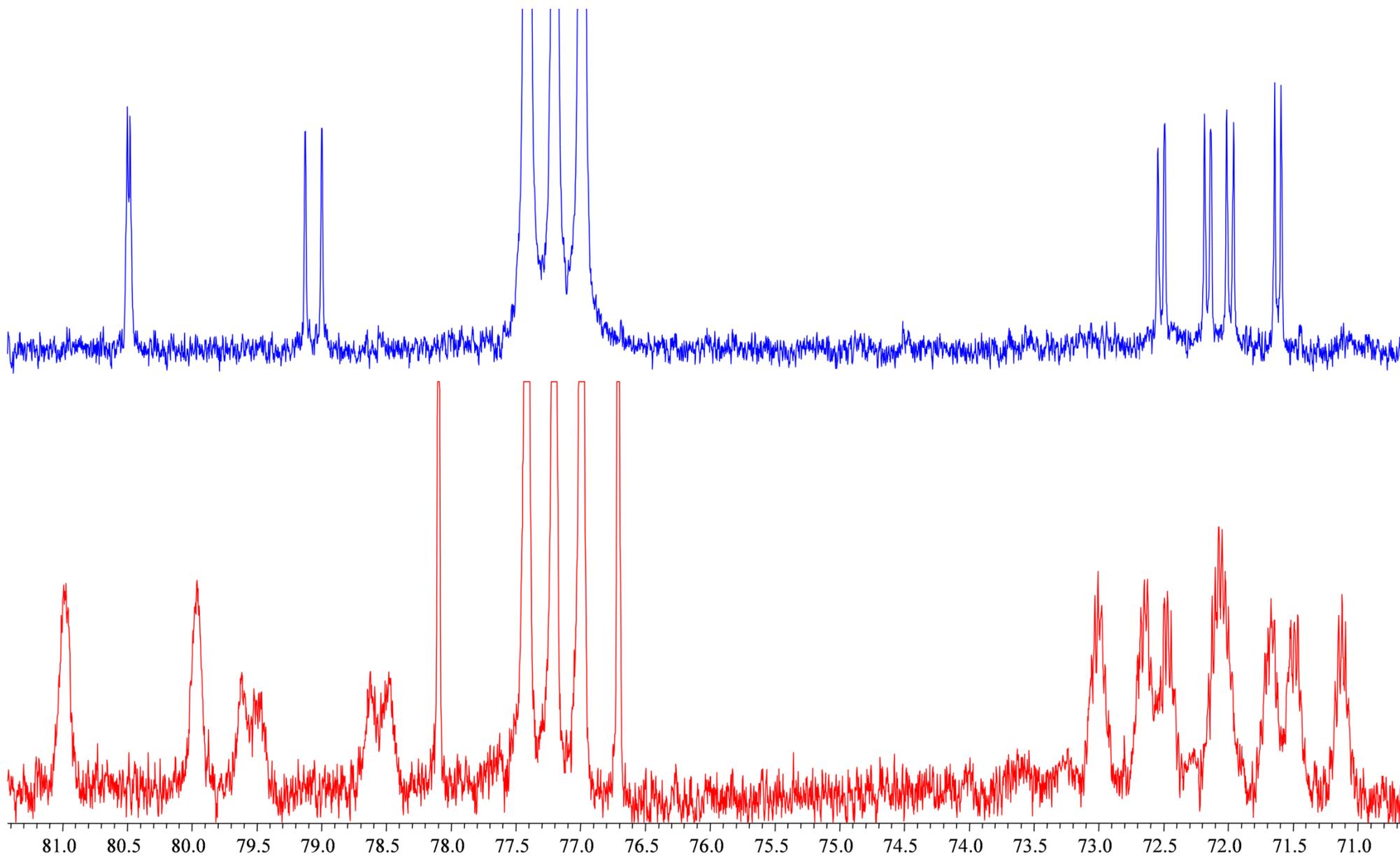


Figure S45. 71-81 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

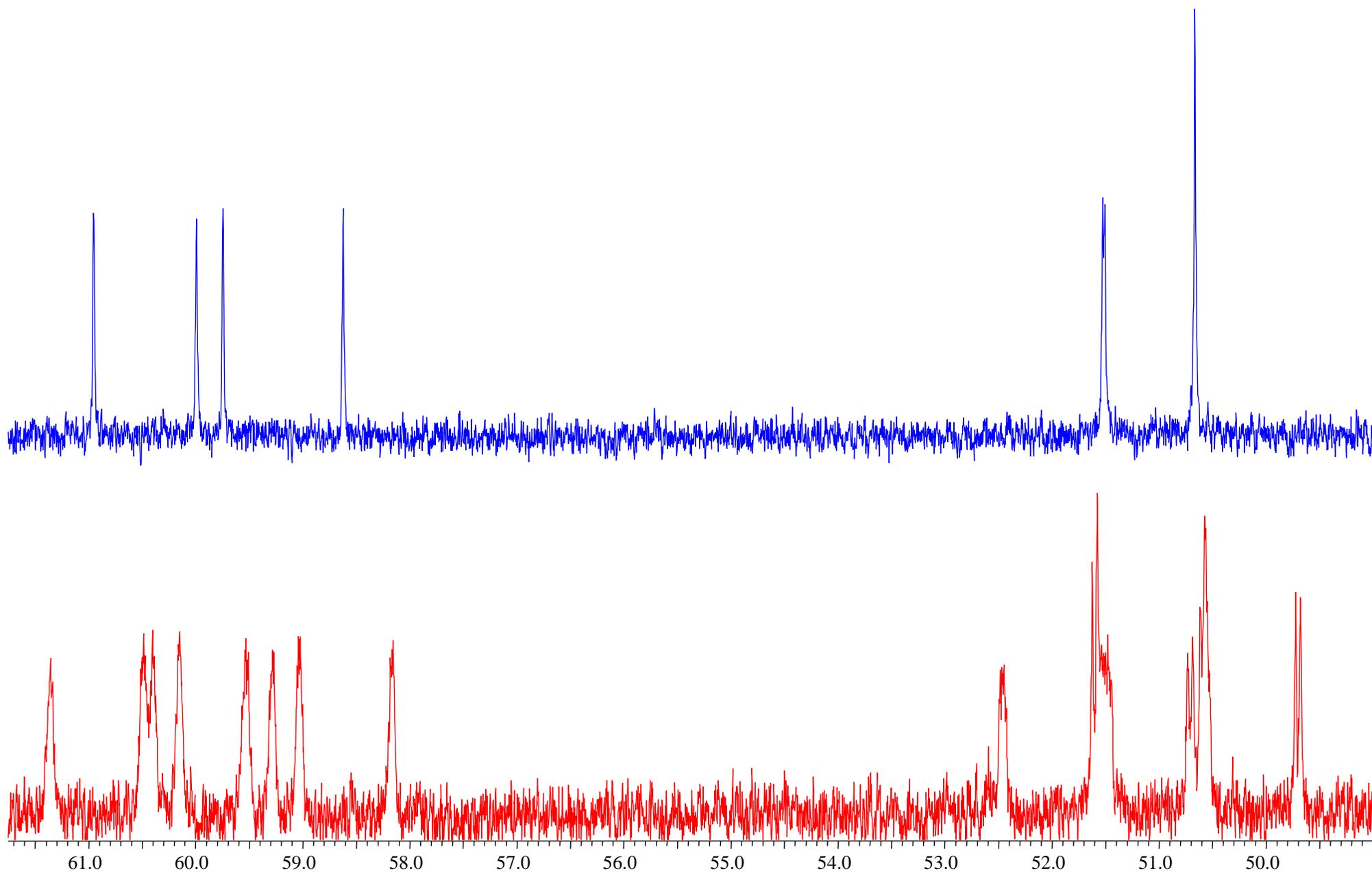


Figure S46. 49-62 ppm region of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

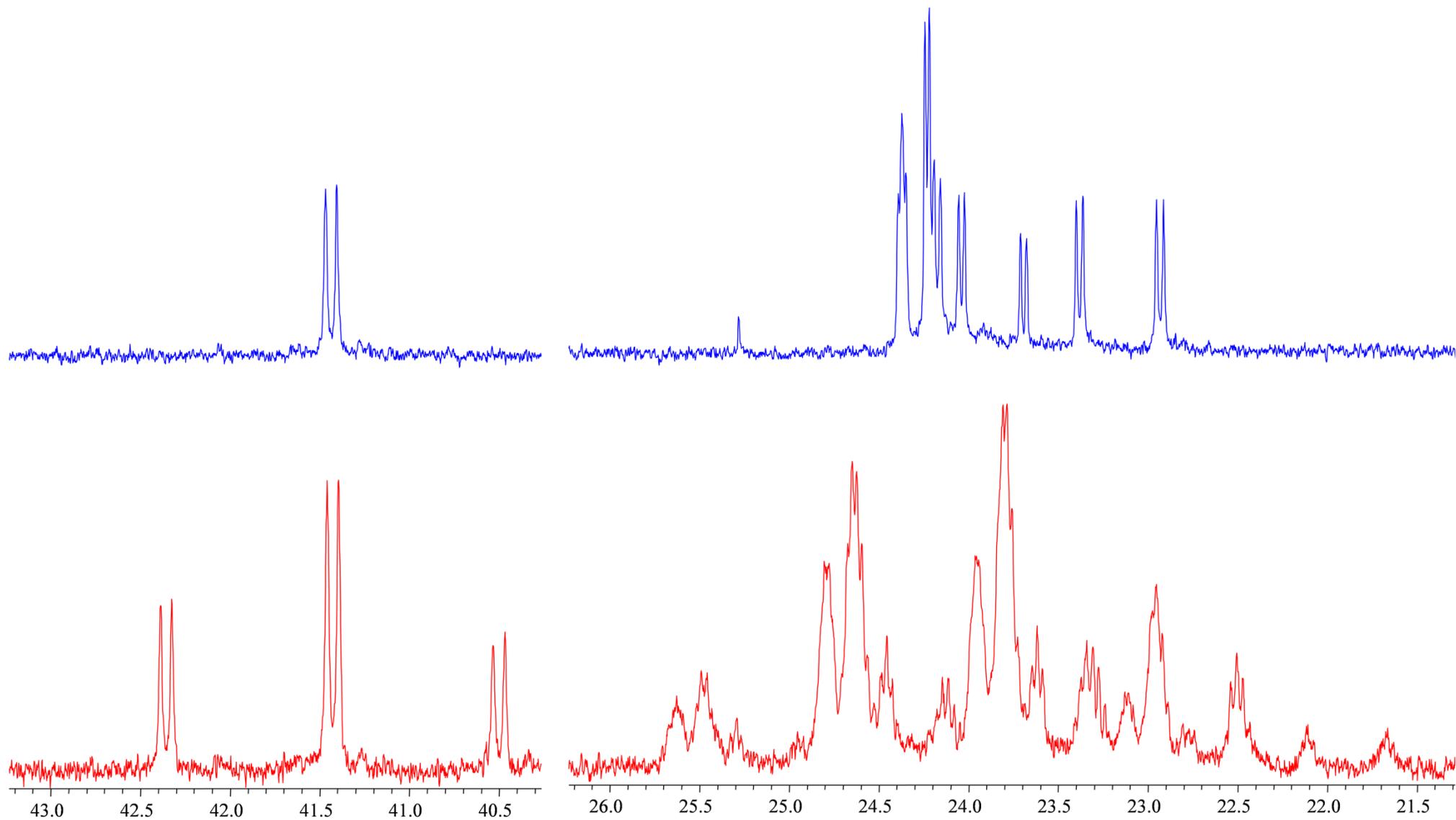


Figure S47. 41-43 and 20-26 ppm regions of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

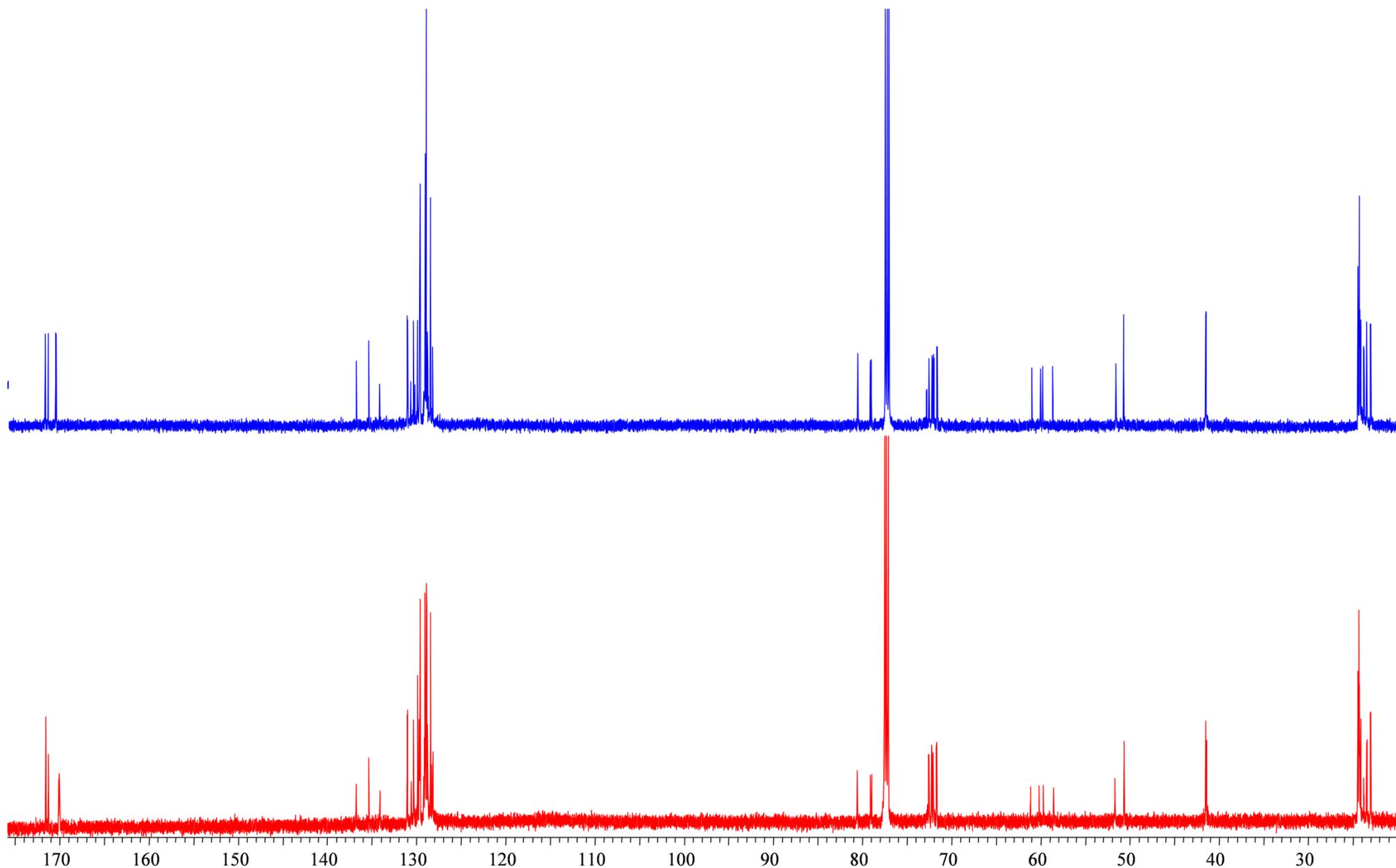


Figure S48. ^{13}C - $\{^1\text{H}\}$ NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, blue).

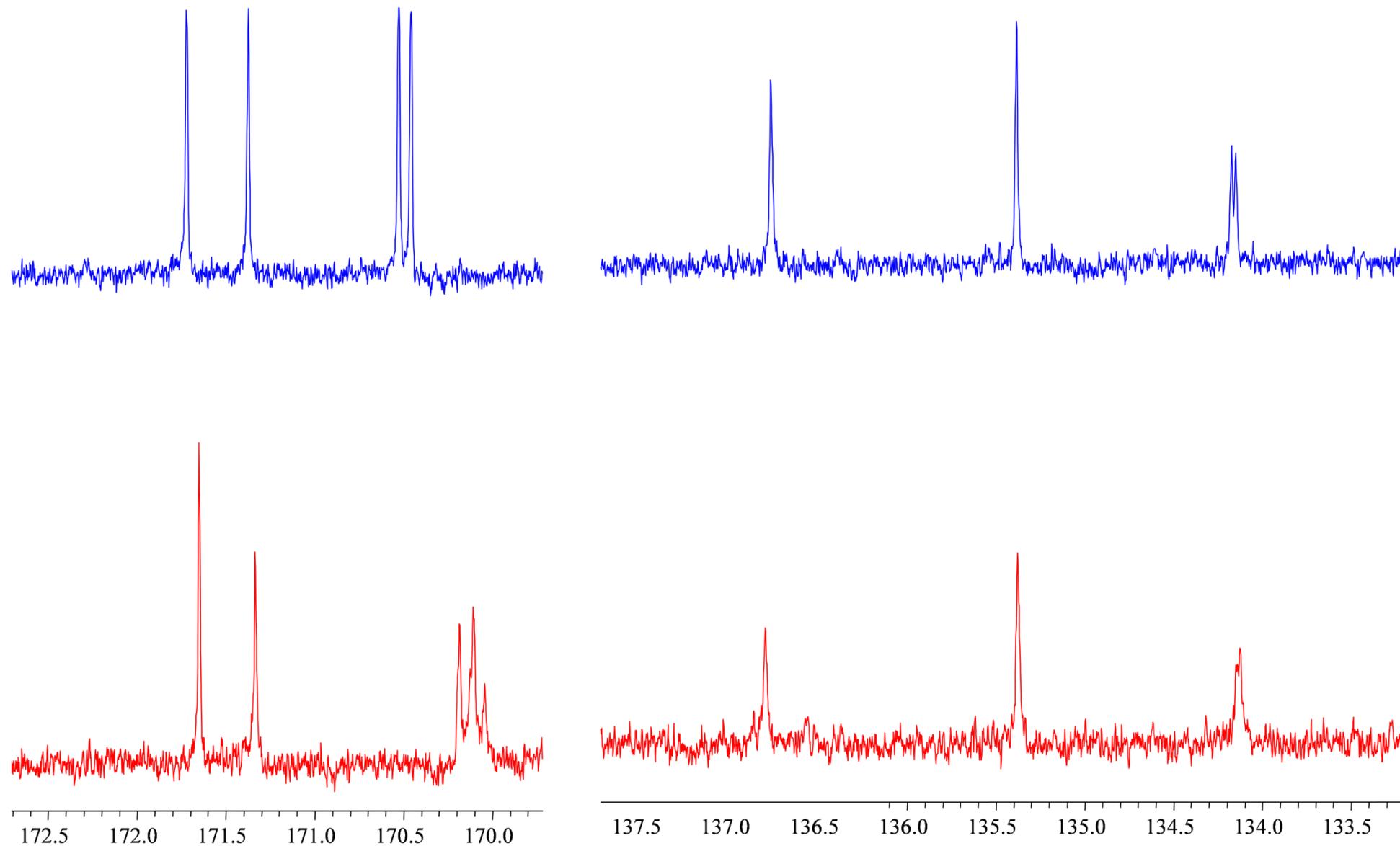


Figure S49. 170-172 and 133-137 ppm regions of ^{13}C - $\{^1\text{H}\}$ NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, blue).

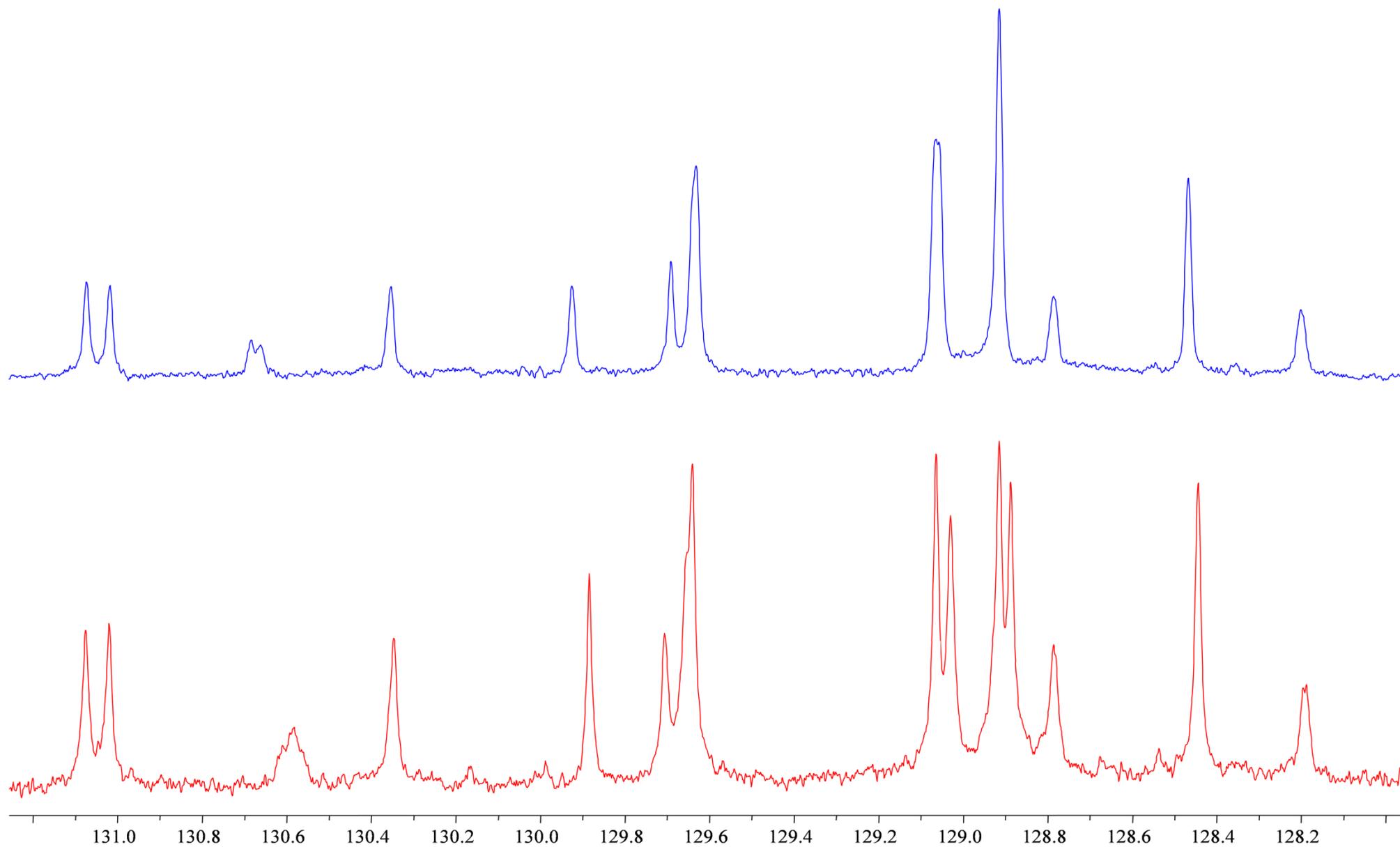


Figure S50. 128-132 ppm region of ^{13}C - $\{^1\text{H}\}$ NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, blue).

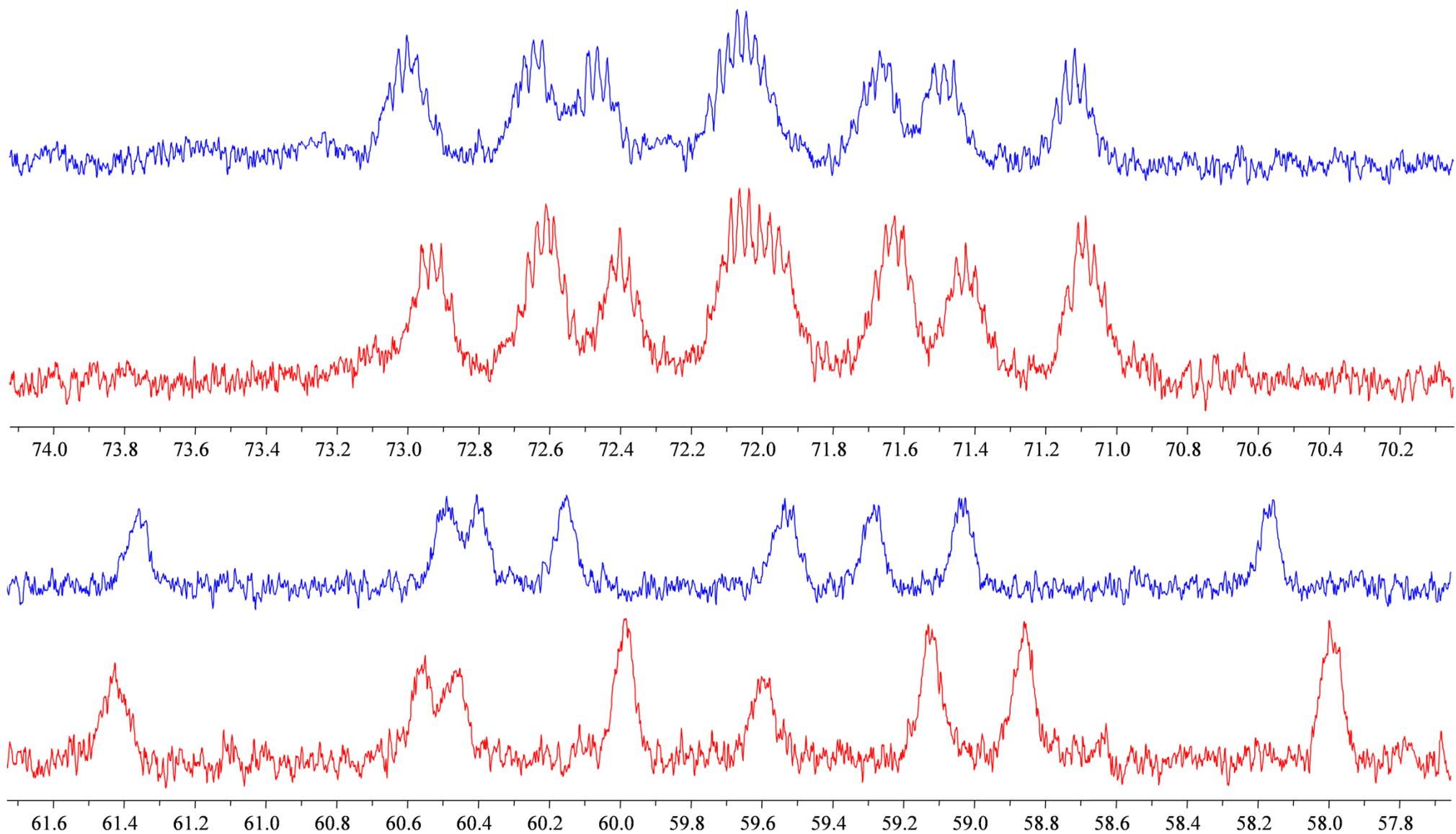


Figure S51. 57-62 and 70-74 ppm regions of ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, blue).

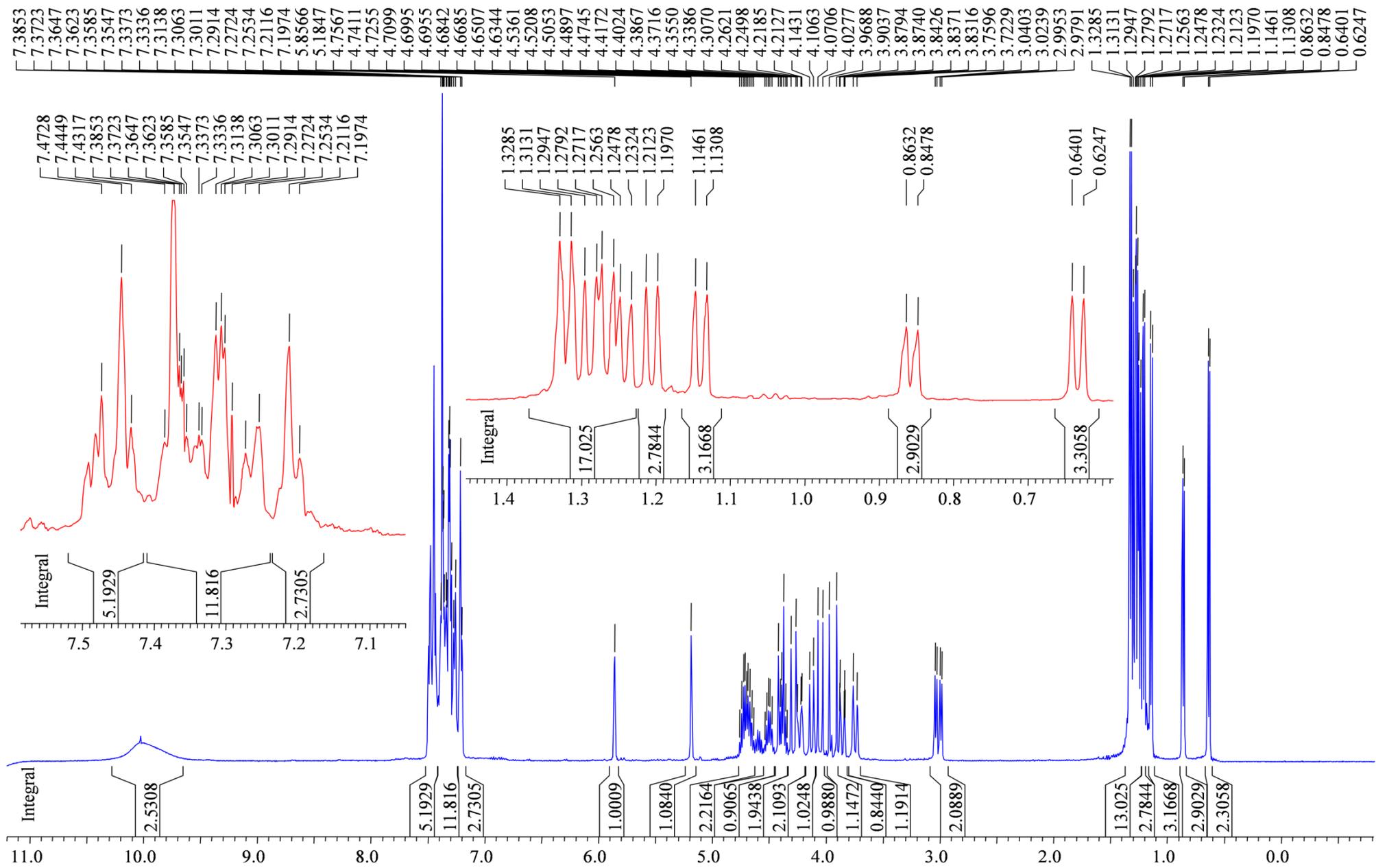


Figure S52. ^1H NMR spectra (400 MHz, CDCl_3) of **4b**, d_1 and d_2 in the ratio of 1.3 : 1).

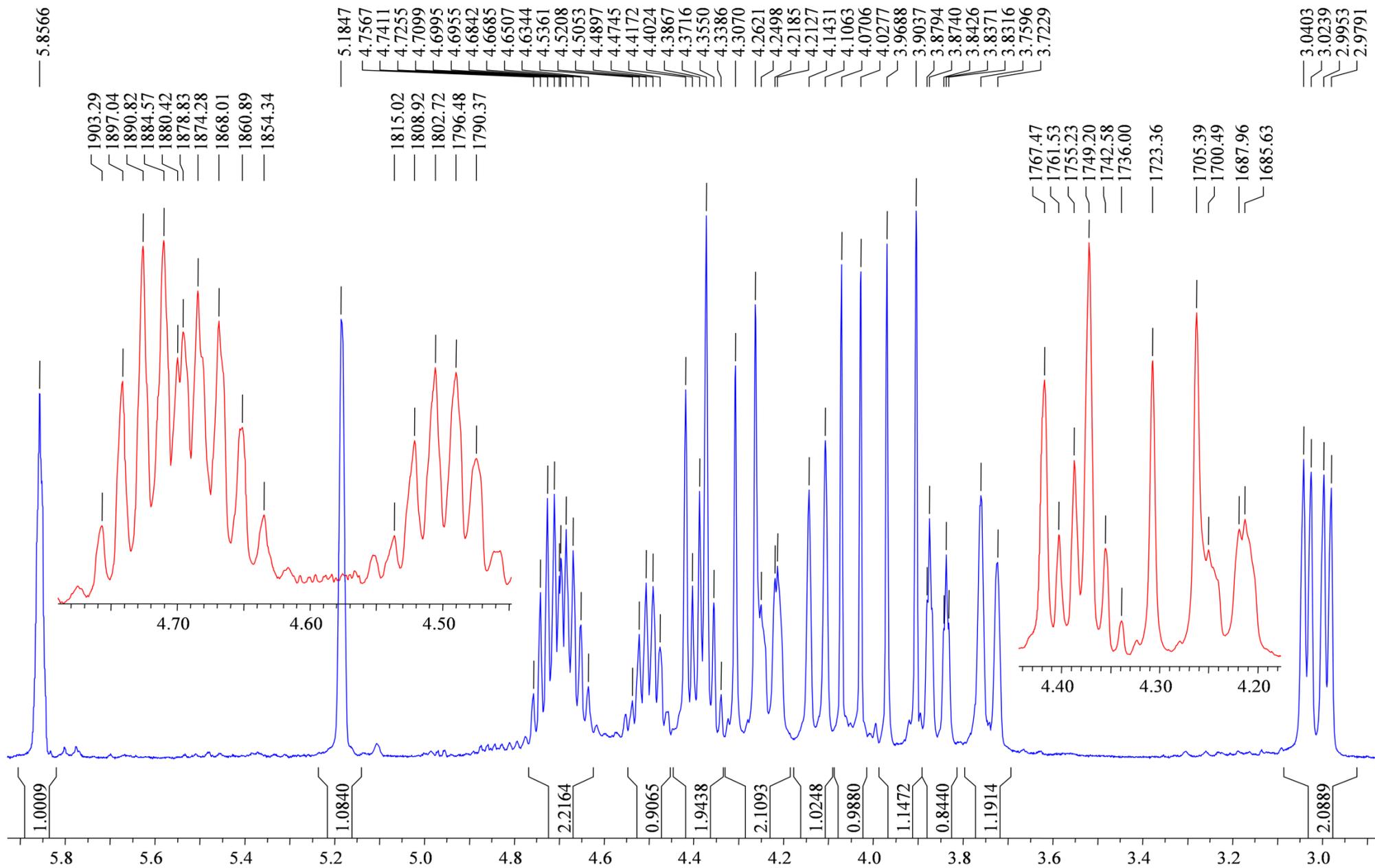


Figure S53. Fragment of ^1H NMR spectra (400 MHz, CDCl_3) of **4b**, d_1 and d_2 in the ratio of 1.3 : 1).

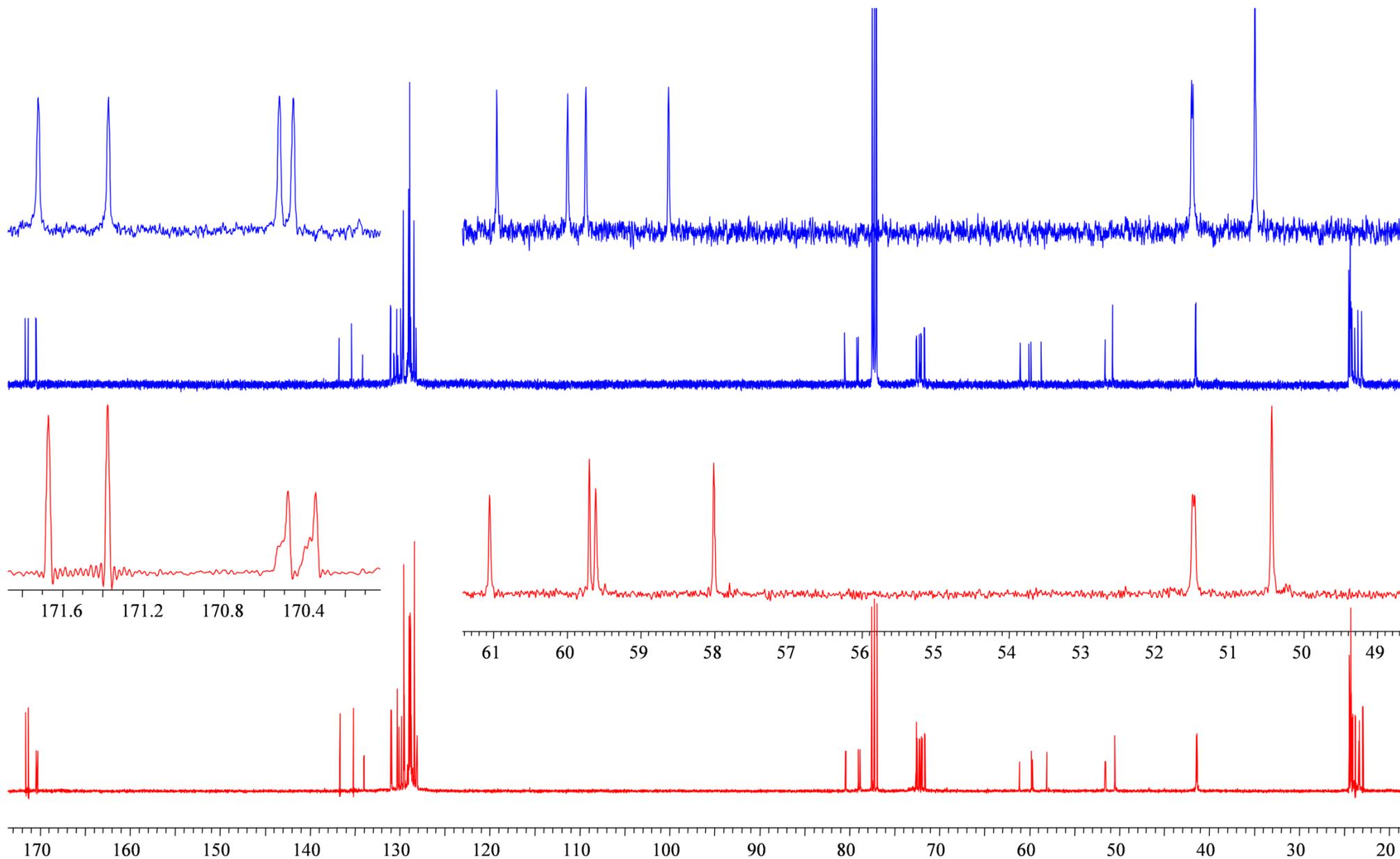


Figure S54. ^{13}C - $\{^1\text{H}\}$ NMR spectra (CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, 100.6 MHz, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, 150.9 MHz, blue).

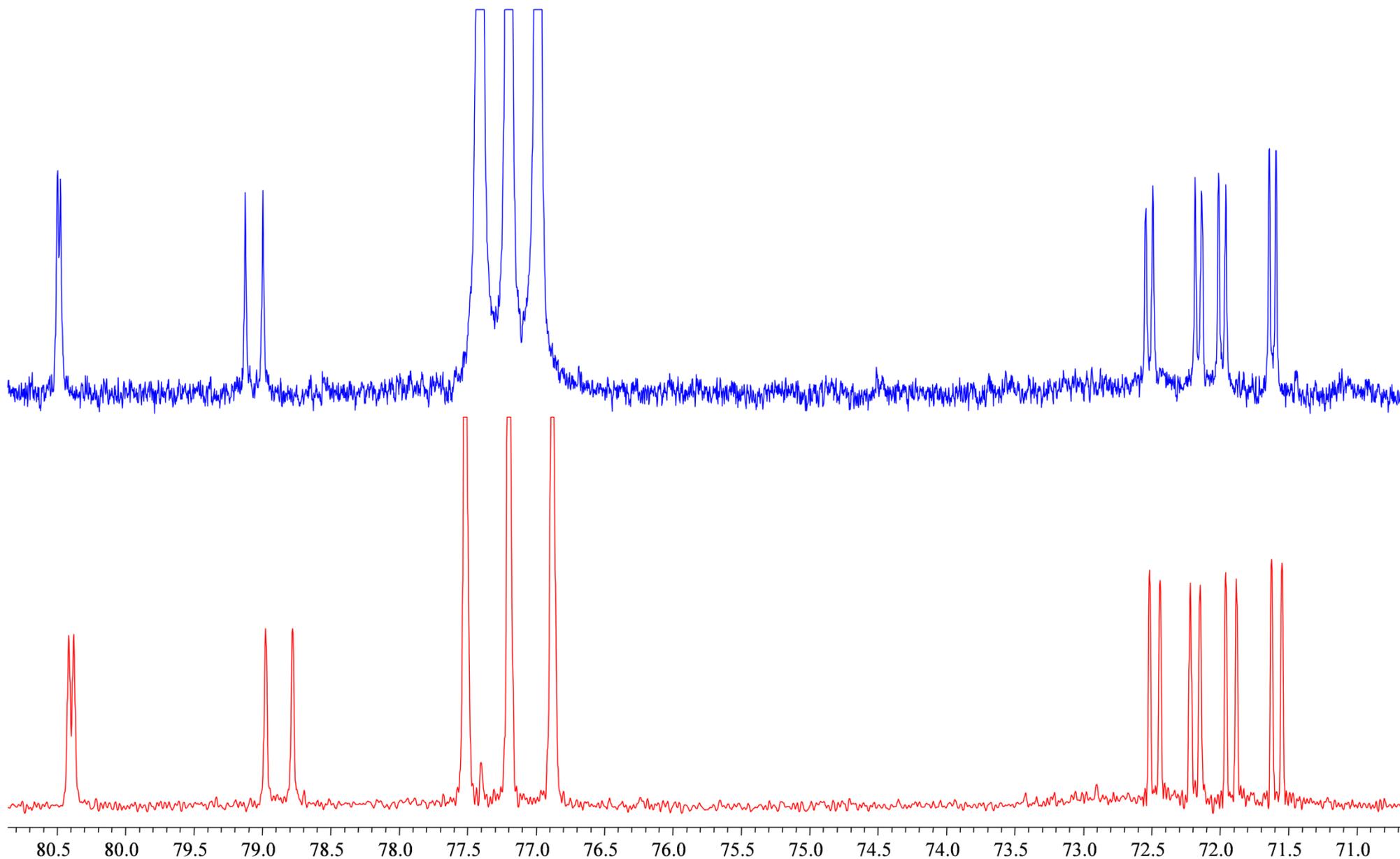


Figure S55. 71-81 ppm region of ^{13}C - $\{^1\text{H}\}$ NMR spectra (CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, 100.6 MHz, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, 150.9 MHz, blue).

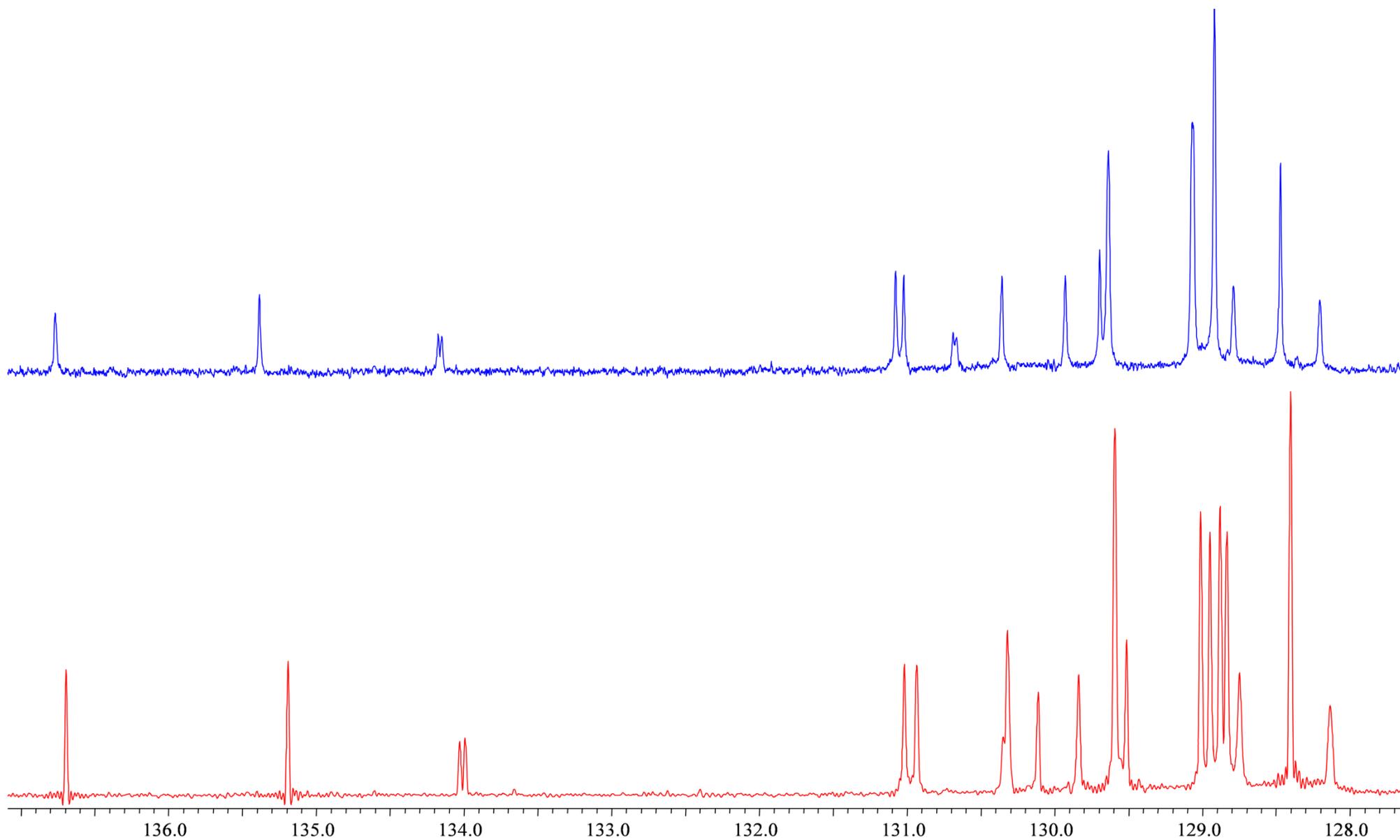


Figure S56. 128-137 ppm region of ^{13}C - $\{^1\text{H}\}$ NMR spectra (CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1, 100.6 MHz, red) and (**4b**, d_1 and d_2 in the ratio of 1 : 1, 150.9 MHz, blue).

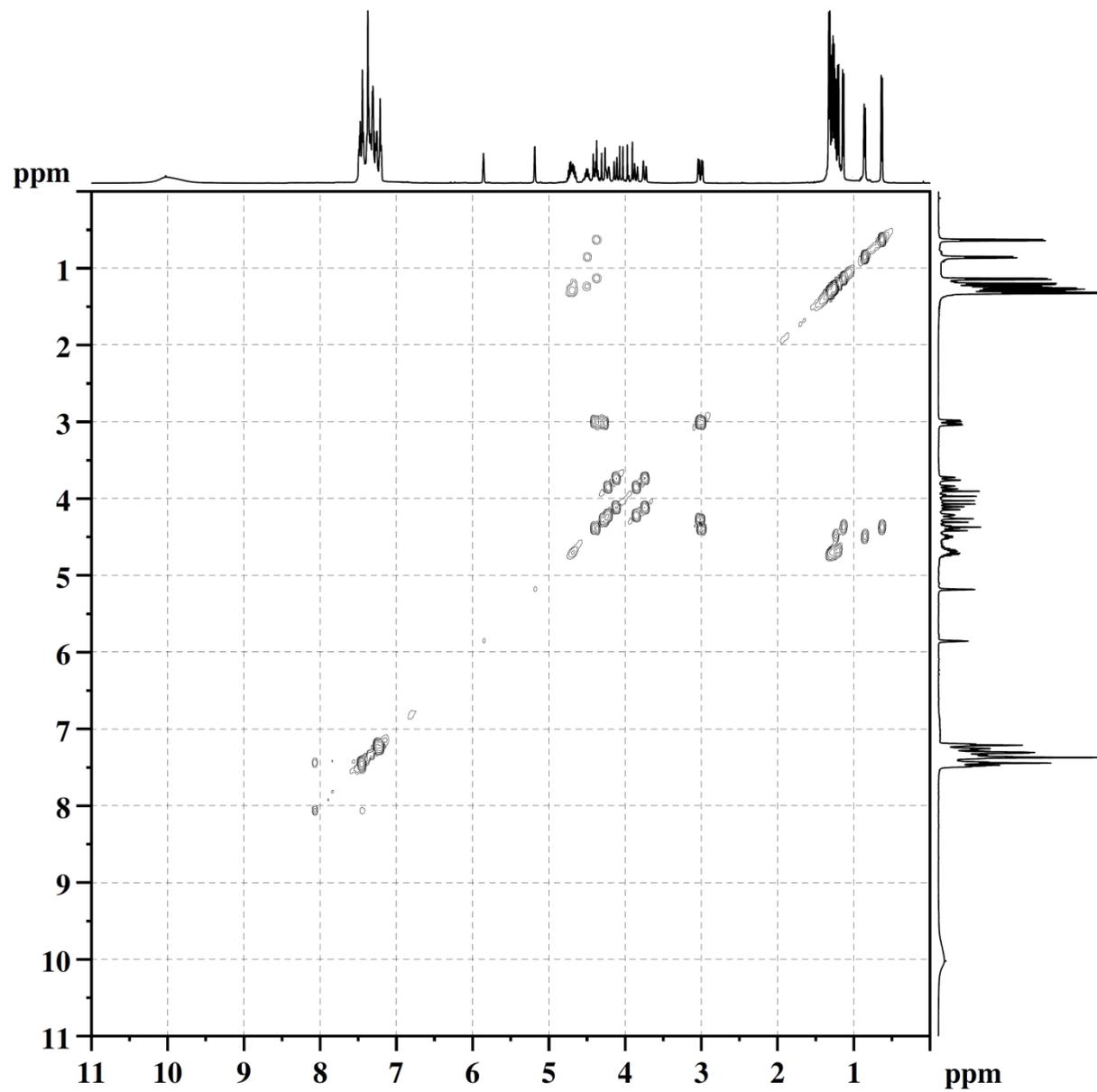


Figure S57. ^1H - ^1H -COSY spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

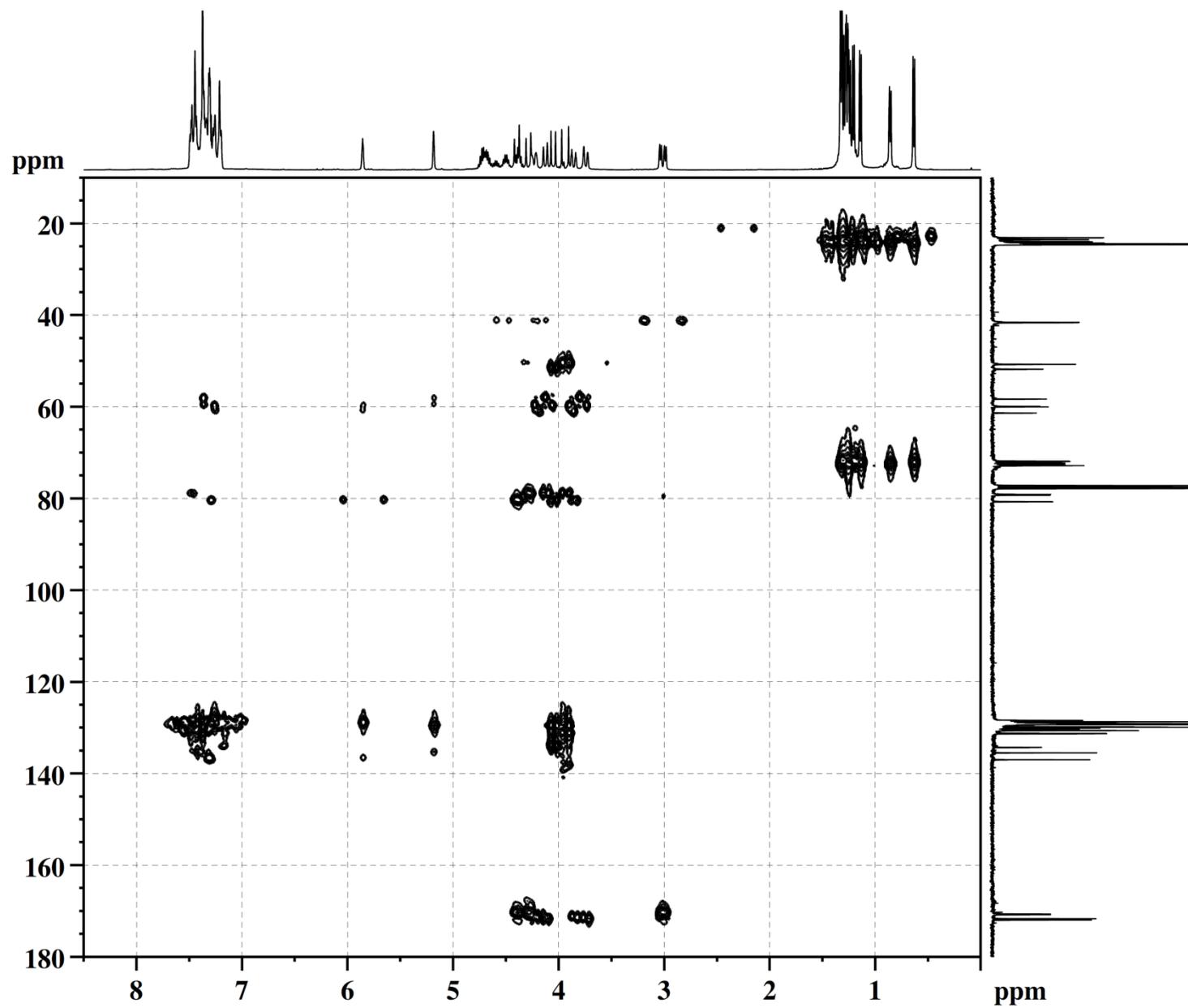


Figure S59. ^1H - ^{13}C -HMBC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

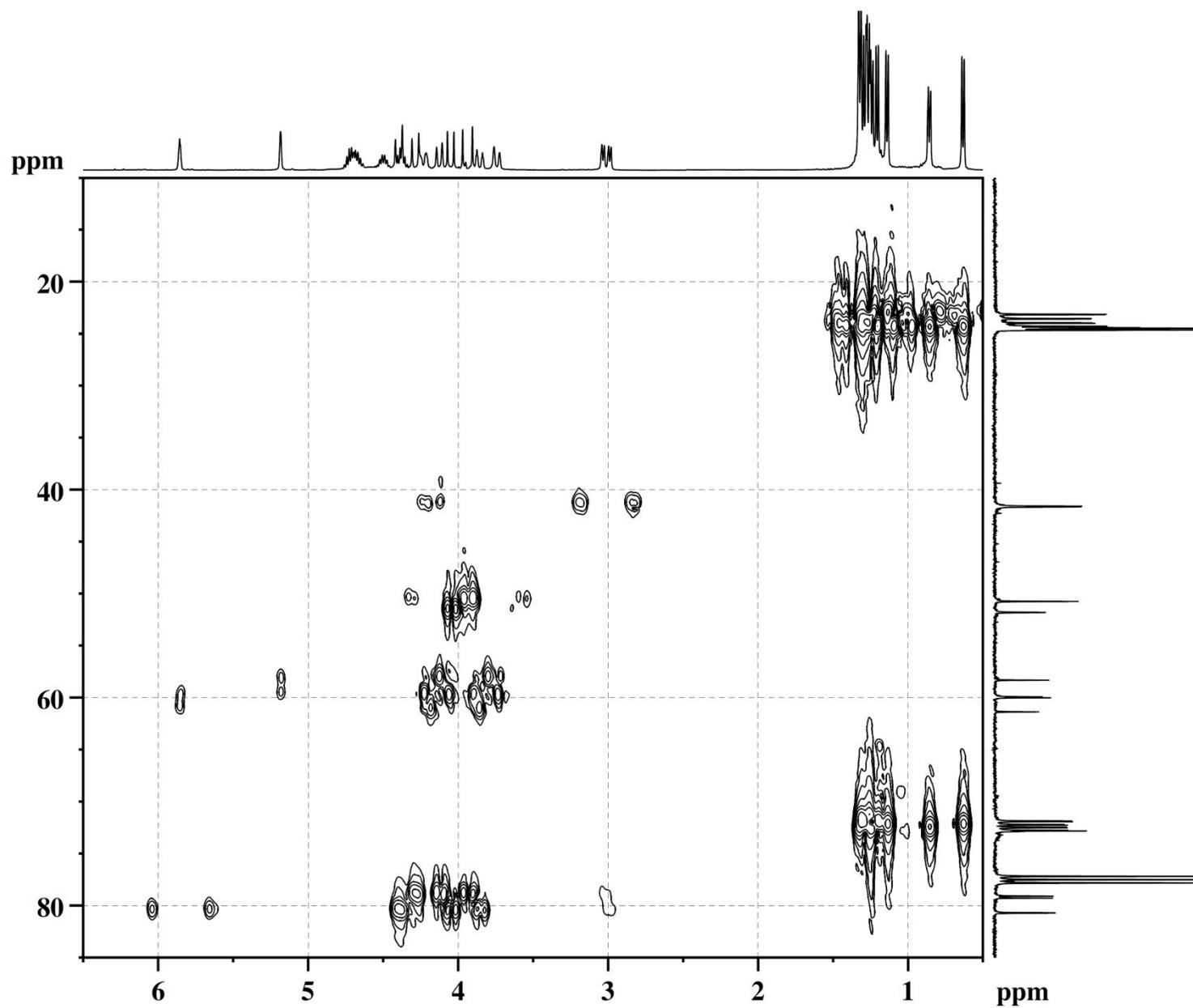


Figure S60. Fragment of ^1H - ^{13}C -HMBC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

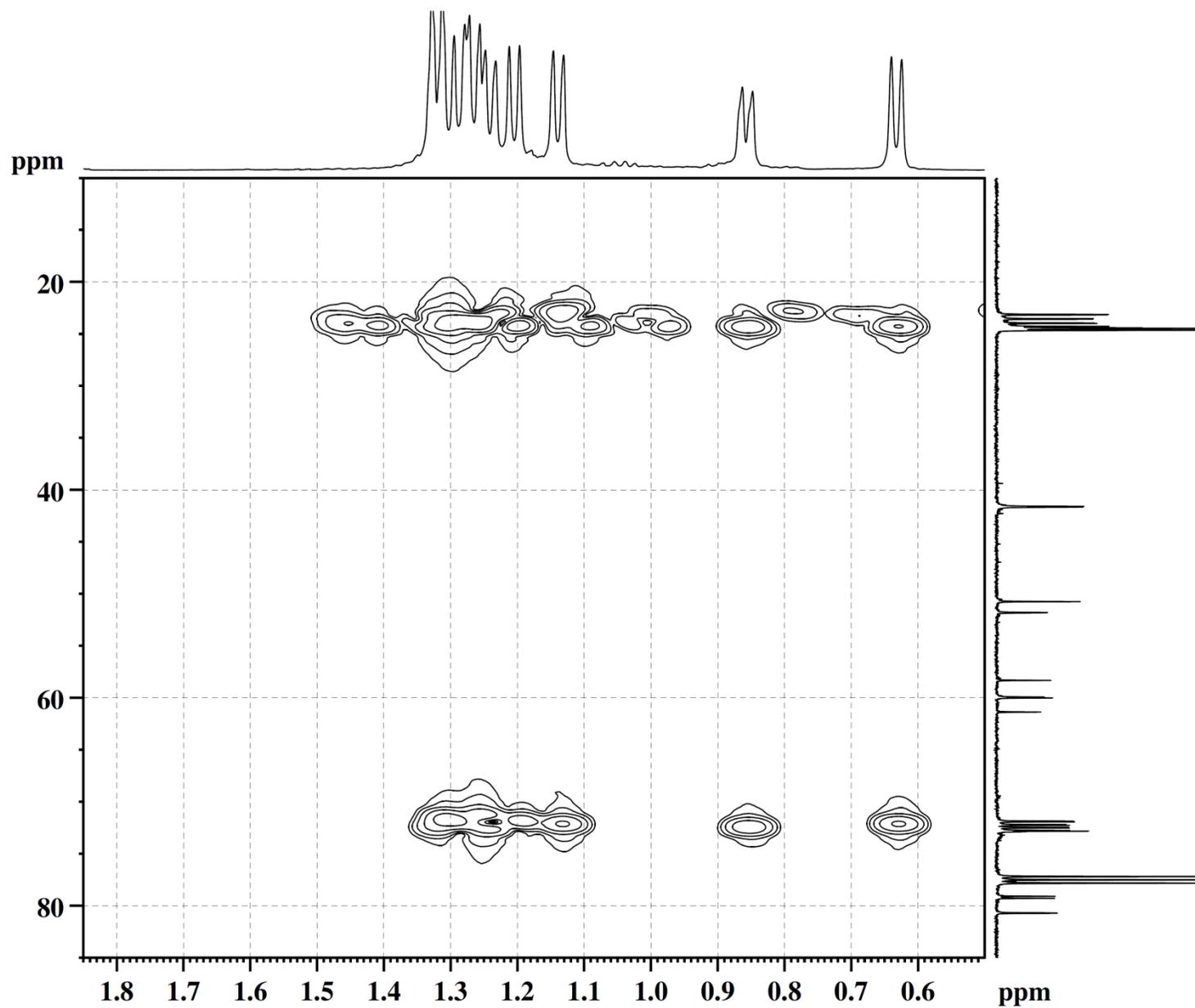


Figure S61. Up-field fragment of ^1H - ^{13}C -HMBC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

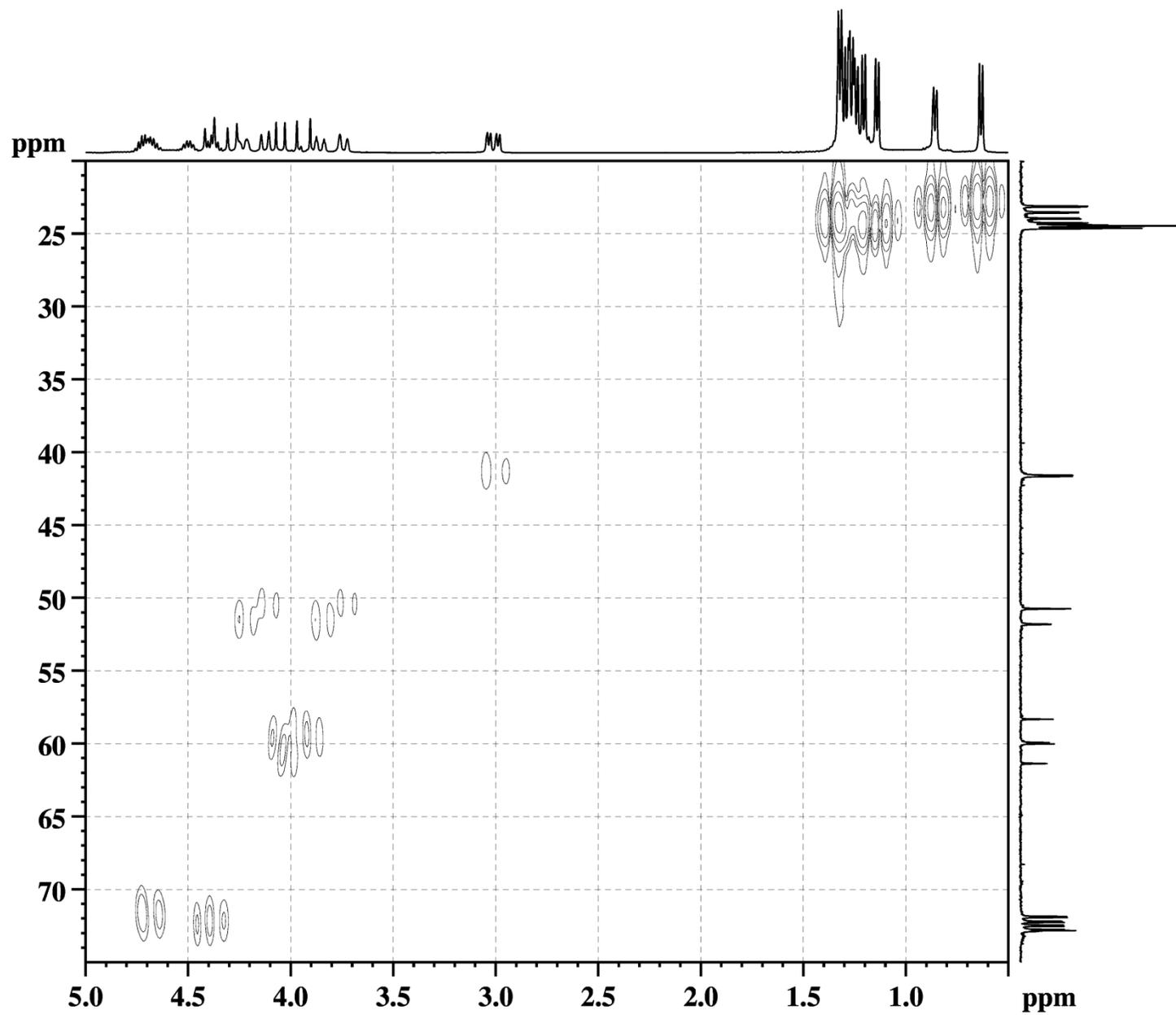


Figure S62. Fragment of ^1H - ^{13}C -HSQC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

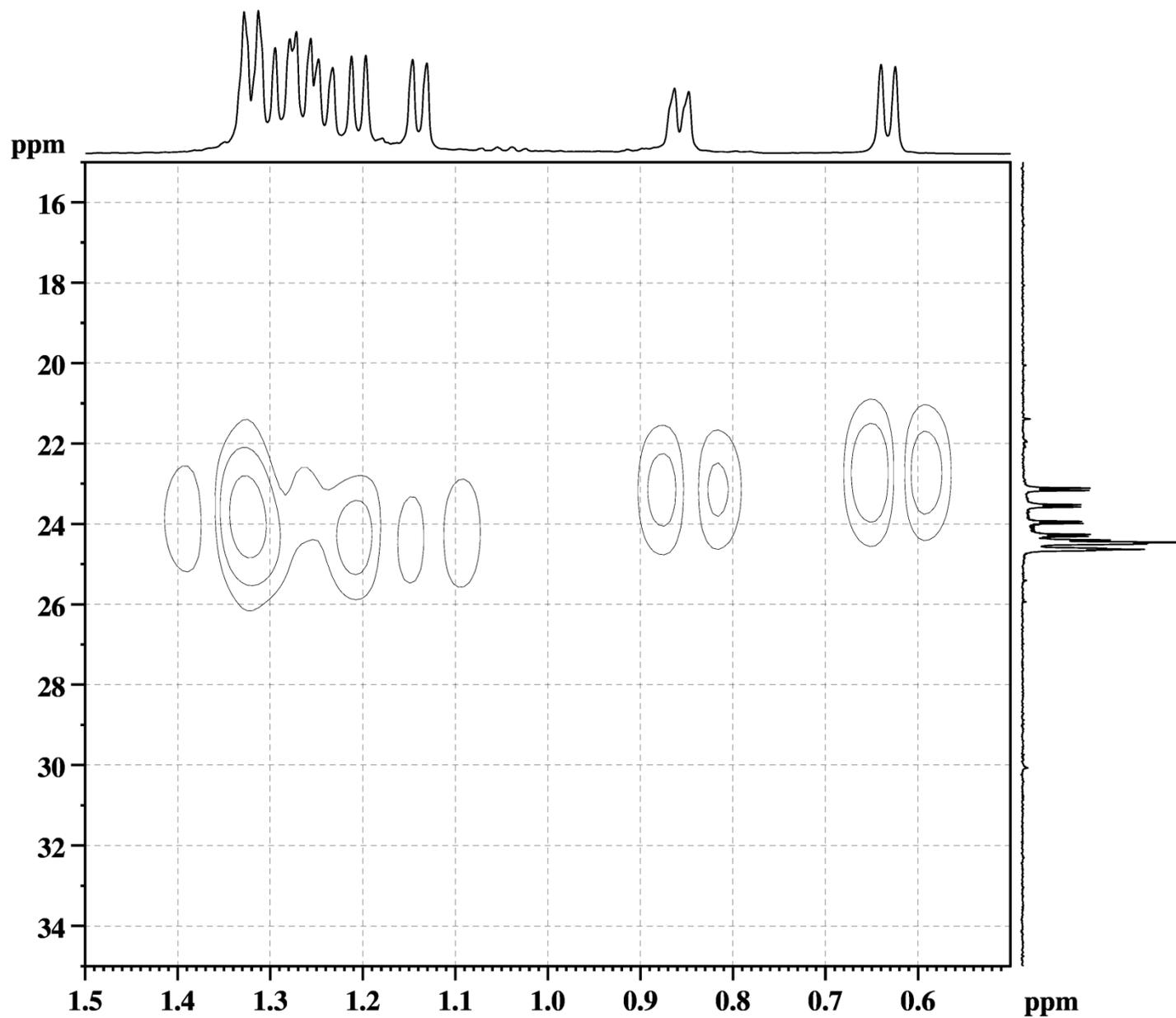


Figure S63. Up-field fragment of ^1H - ^{13}C -HSQC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

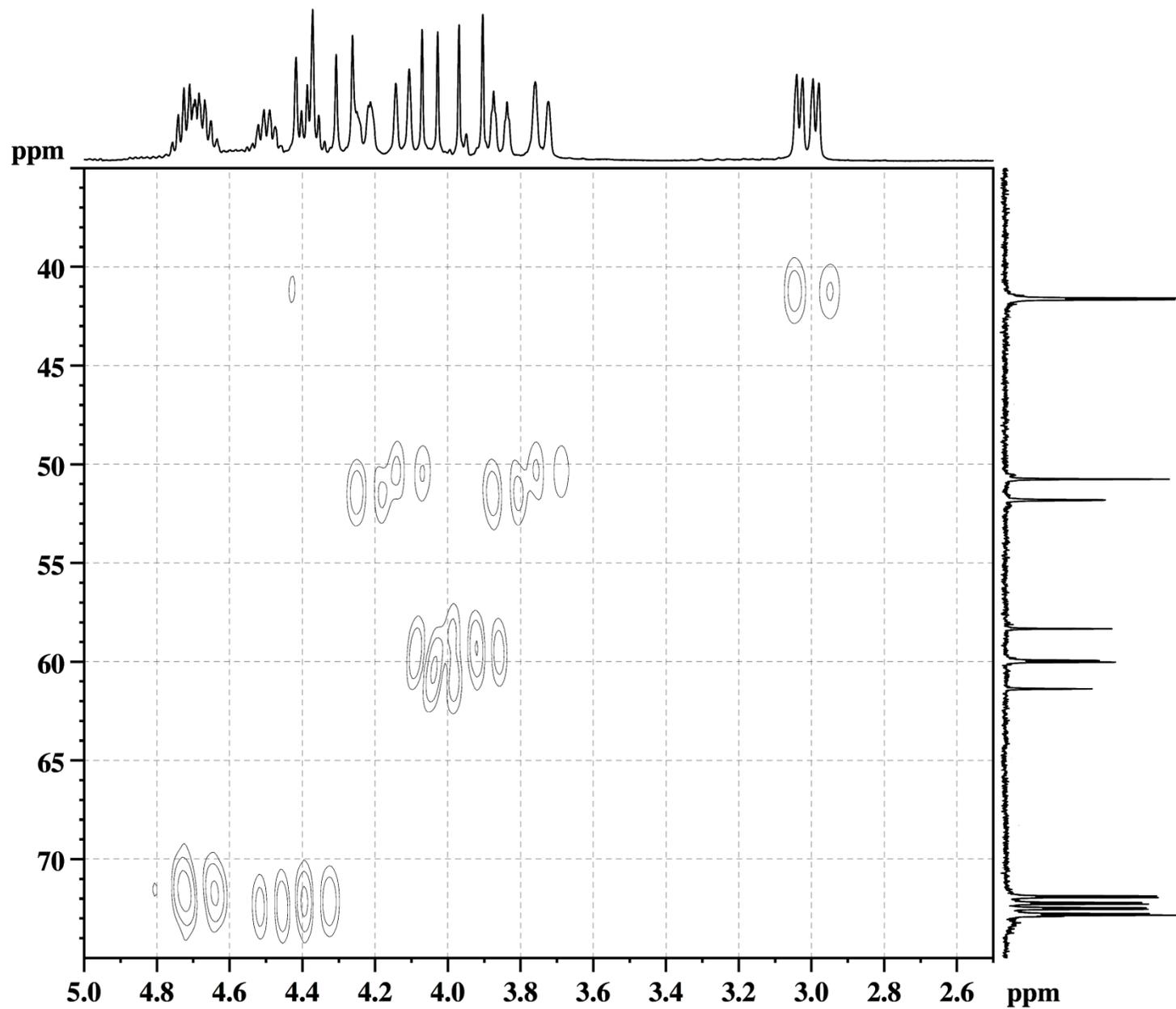


Figure S64. Down-field fragment of ^1H - ^{13}C -HSQC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

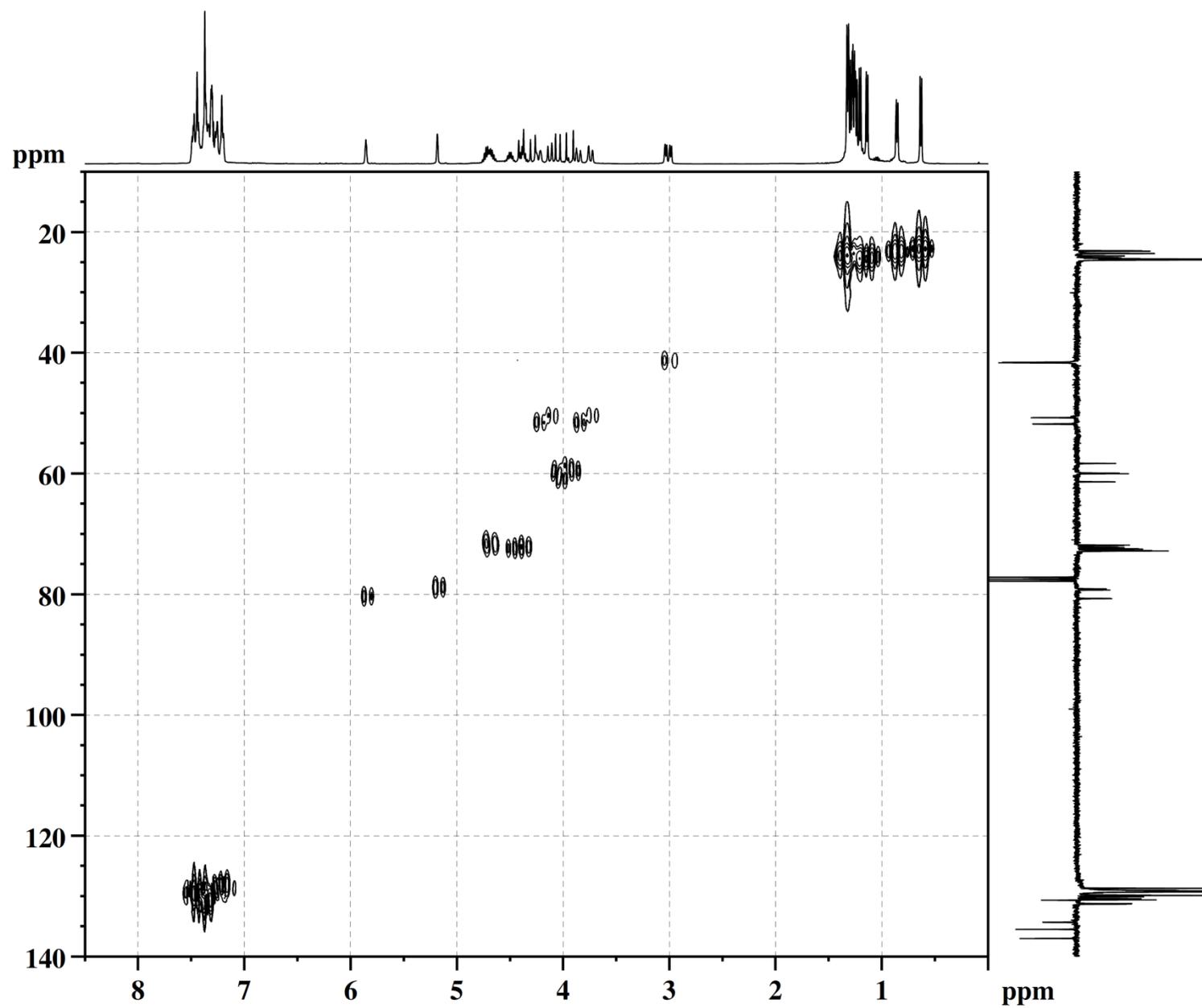


Figure S65. ^1H - ^{13}C -APT-HSQC spectrum (100.6 MHz, CDCl_3) of (**4b**, d_1 and d_2 in the ratio of 1.3 : 1).

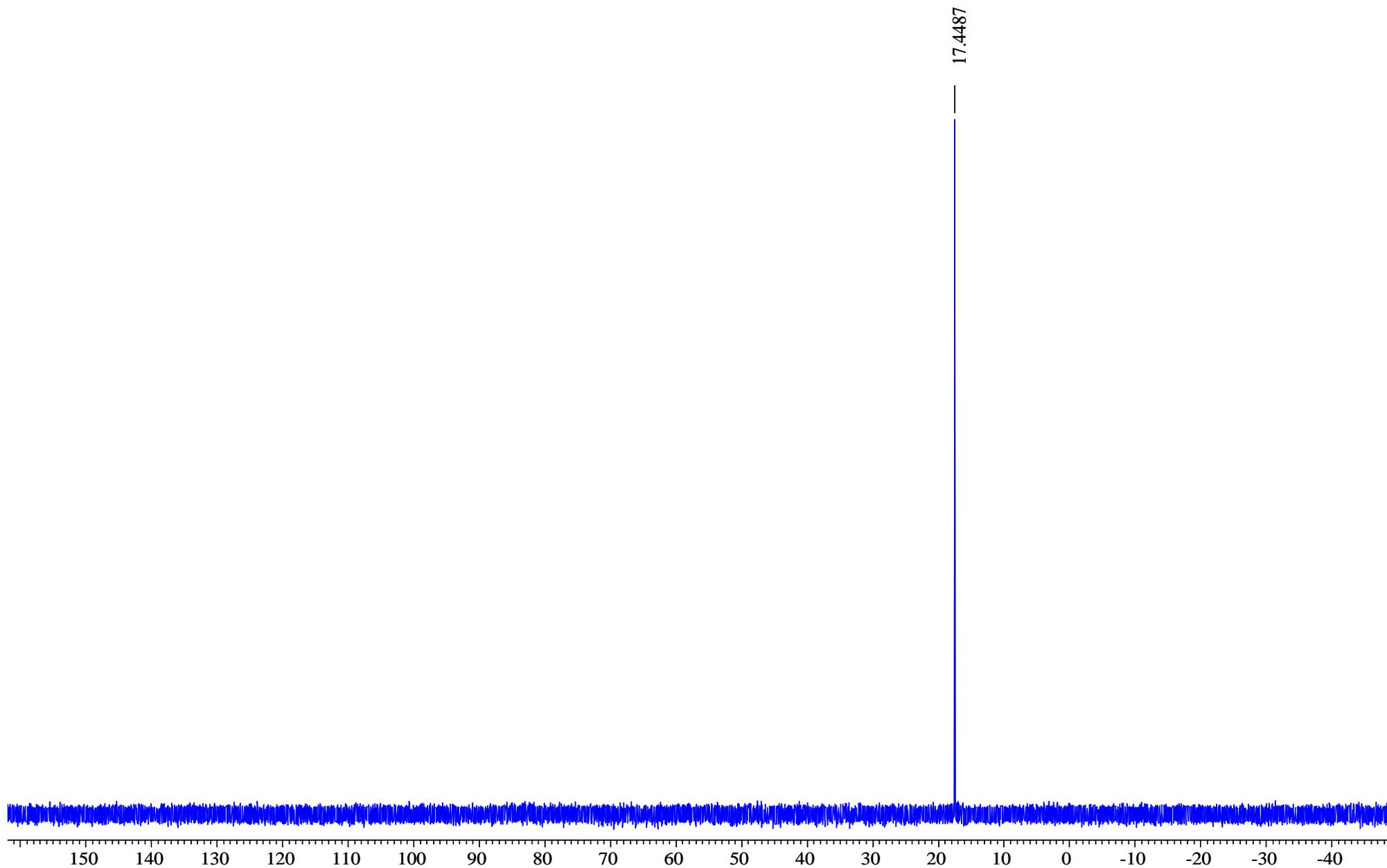


Figure S66. ^{31}P - $\{^1\text{H}\}$ NMR spectrum (242.9 MHz, CDCl_3) of **[3b]**, d_1 (*meso*) and d_2 (*d, l*) in the ratio of 20 : 1].

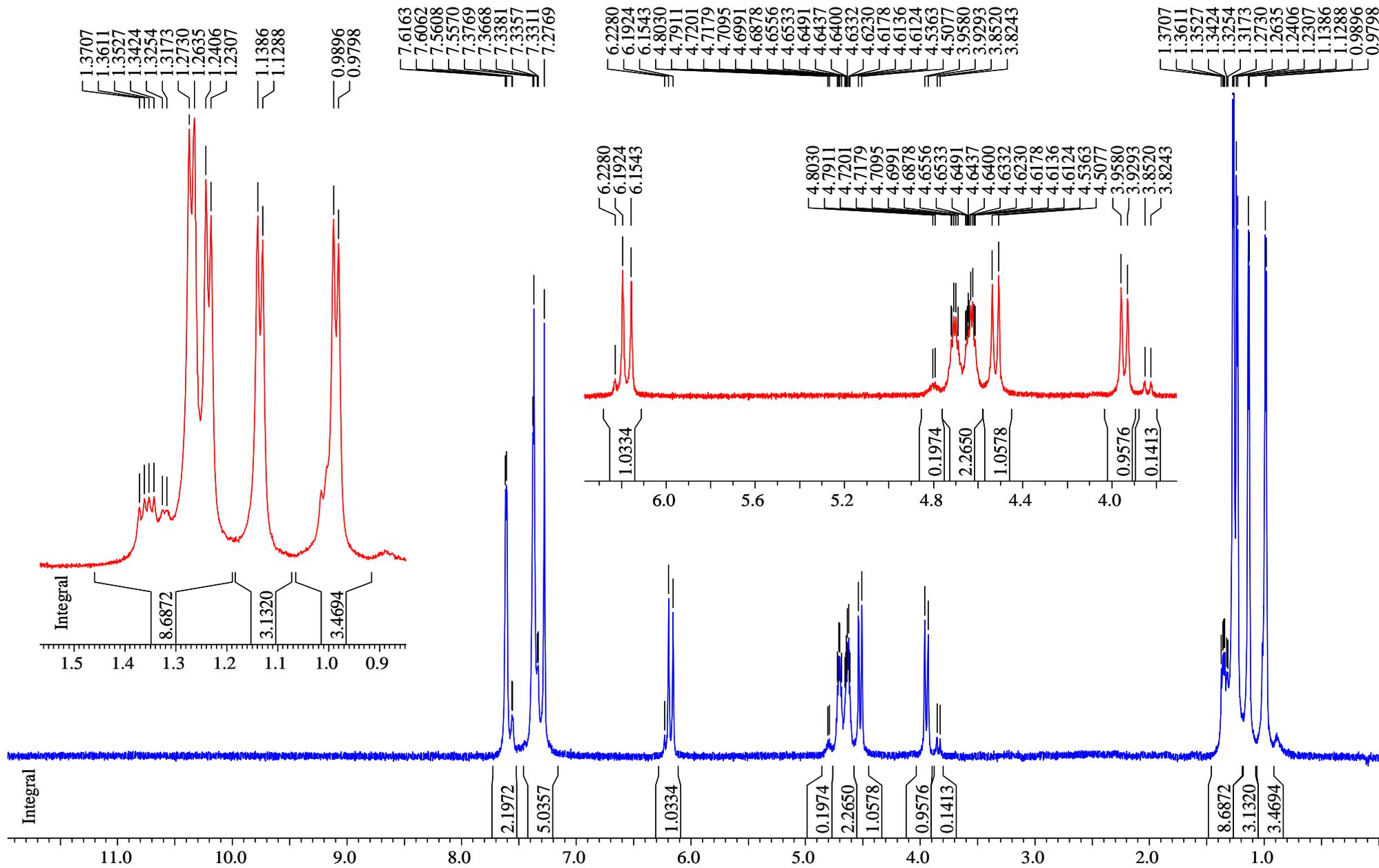


Figure S67. ^1H NMR spectrum (600 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).

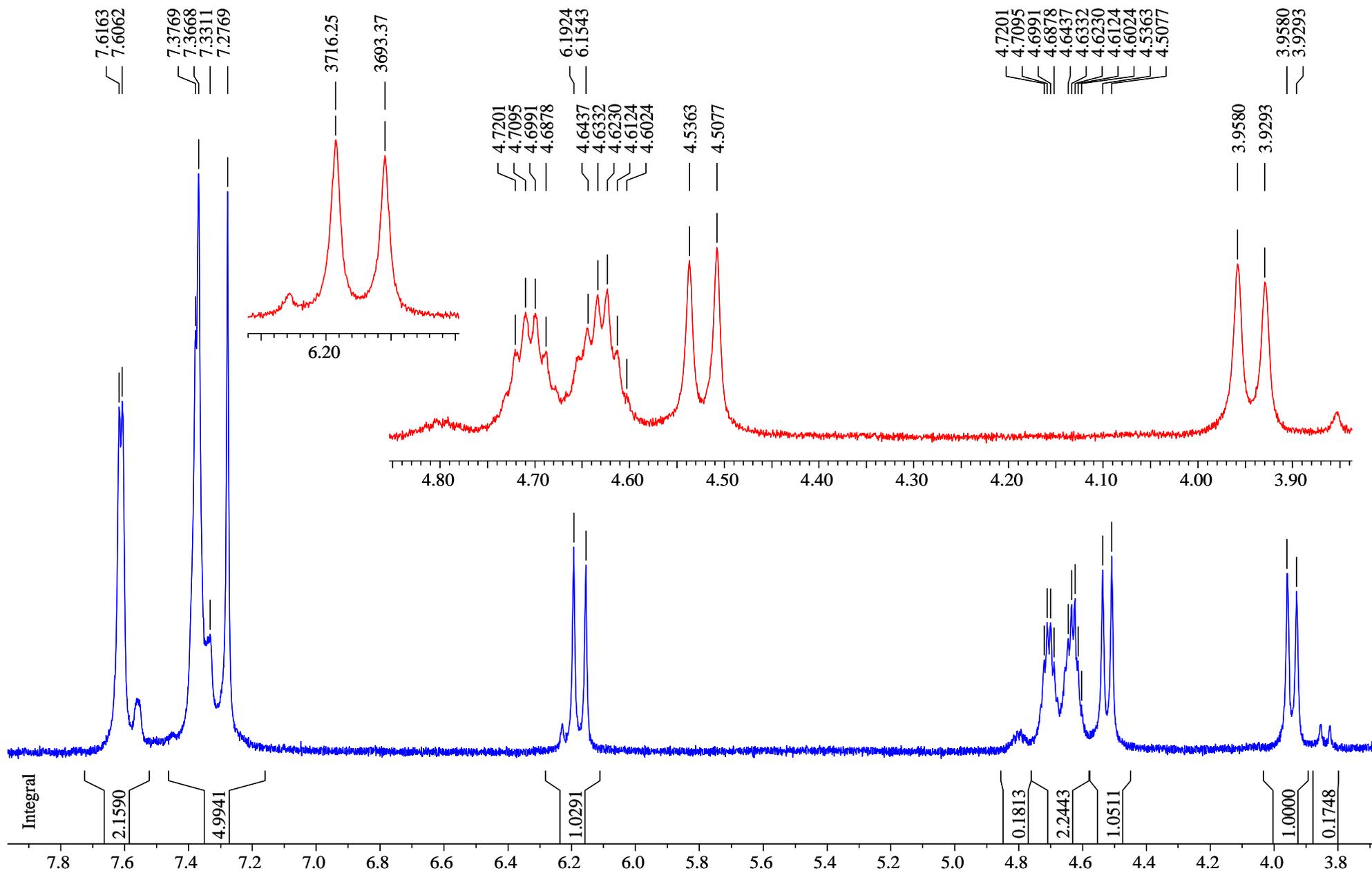


Figure S68. Fragment of ¹H NMR spectrum (600 MHz, CDCl₃) of (**3b**, *d*₁ and *d*₂ in the ratio of 20 : 1).

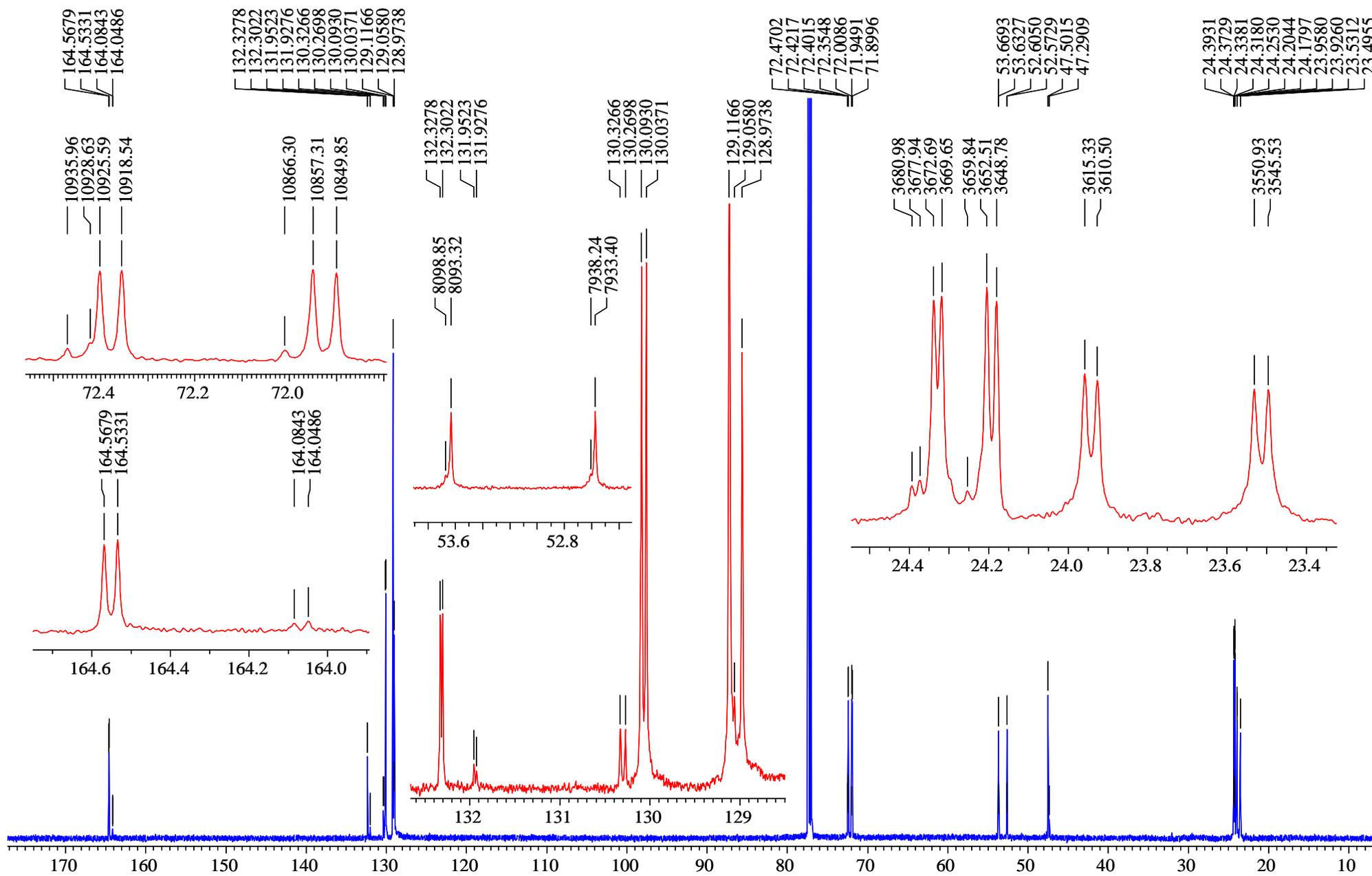


Figure S69. ¹³C-¹H NMR spectrum (150.9 MHz, CDCl₃) of (3b, *d*₁ and *d*₂ in the ratio of 20 : 1).

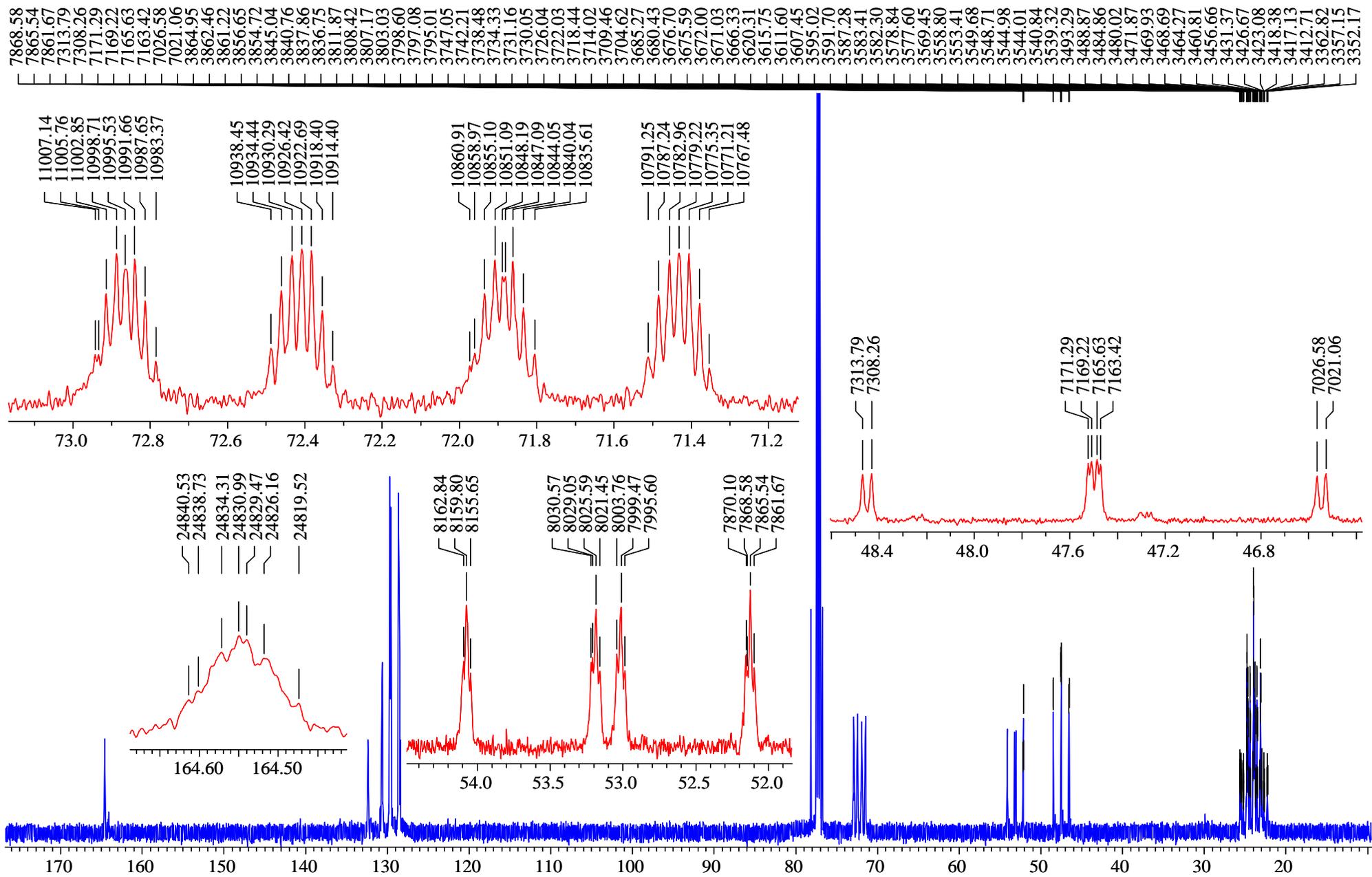


Figure S70. ^{13}C NMR spectrum (150.9 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).

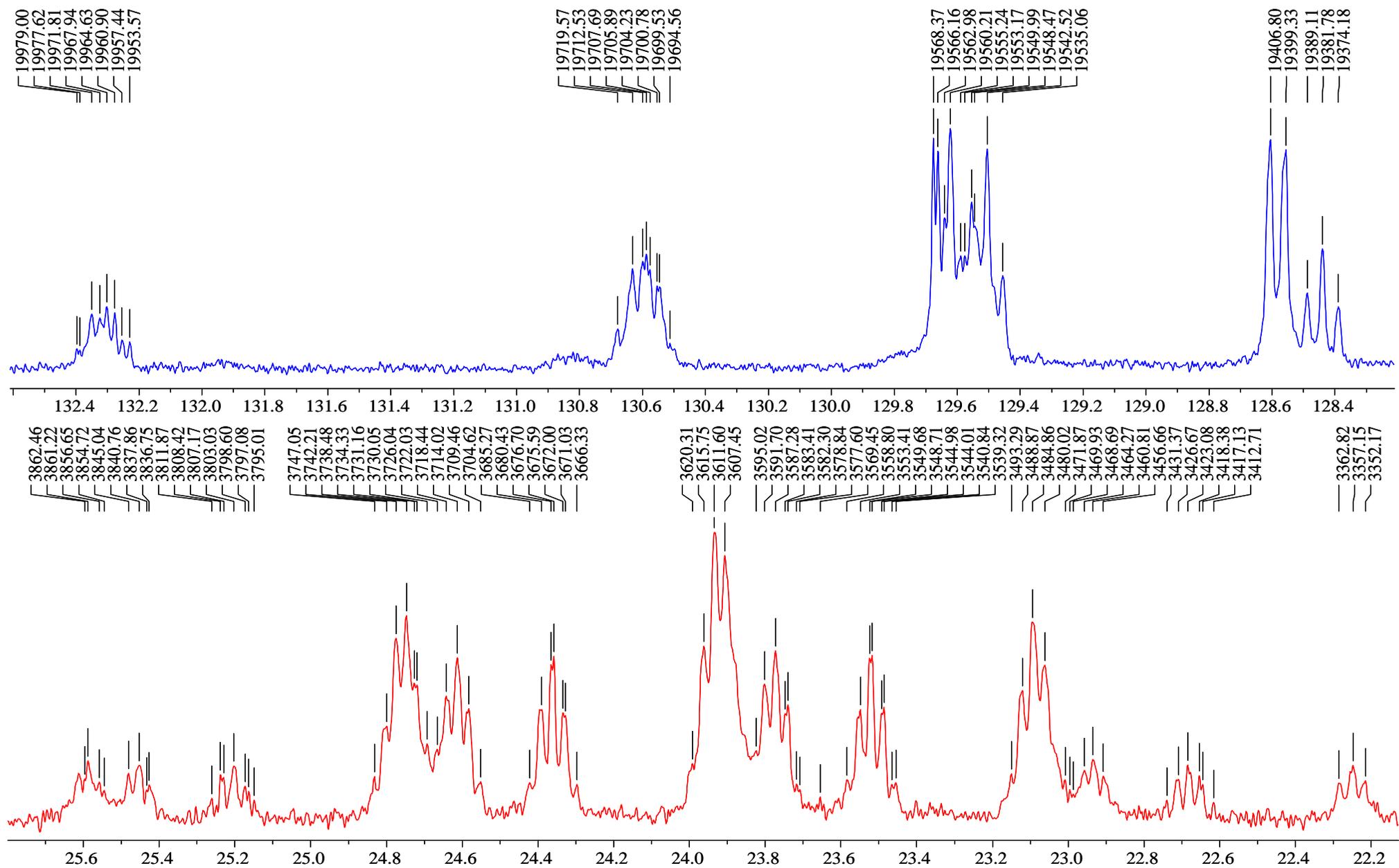


Figure S71. Fragments of ^{13}C NMR spectrum (150.9 MHz, CDCl_3) of **(3b)**, d_1 and d_2 in the ratio of 20 : 1).

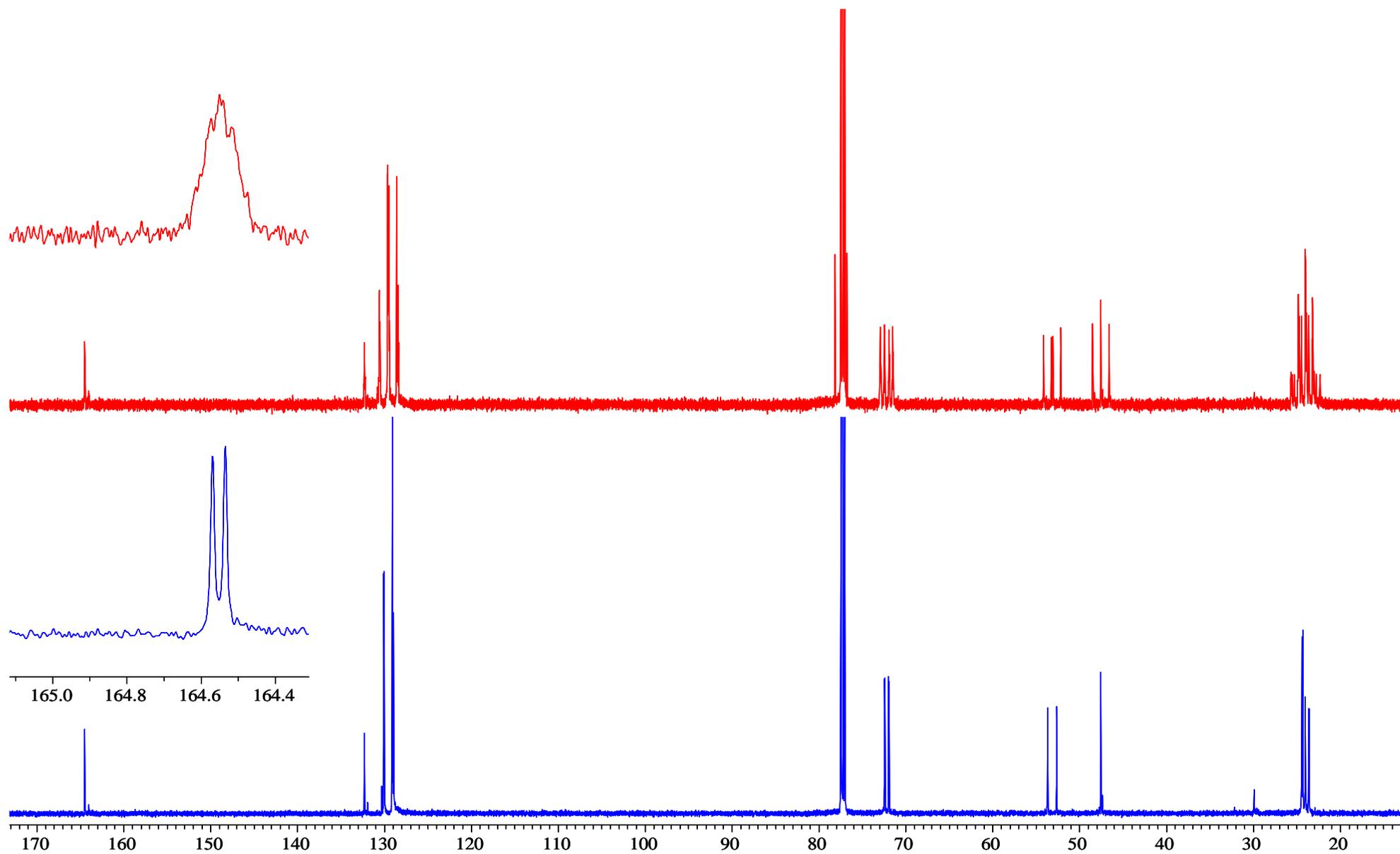


Figure S72. ^{13}C - $\{^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).

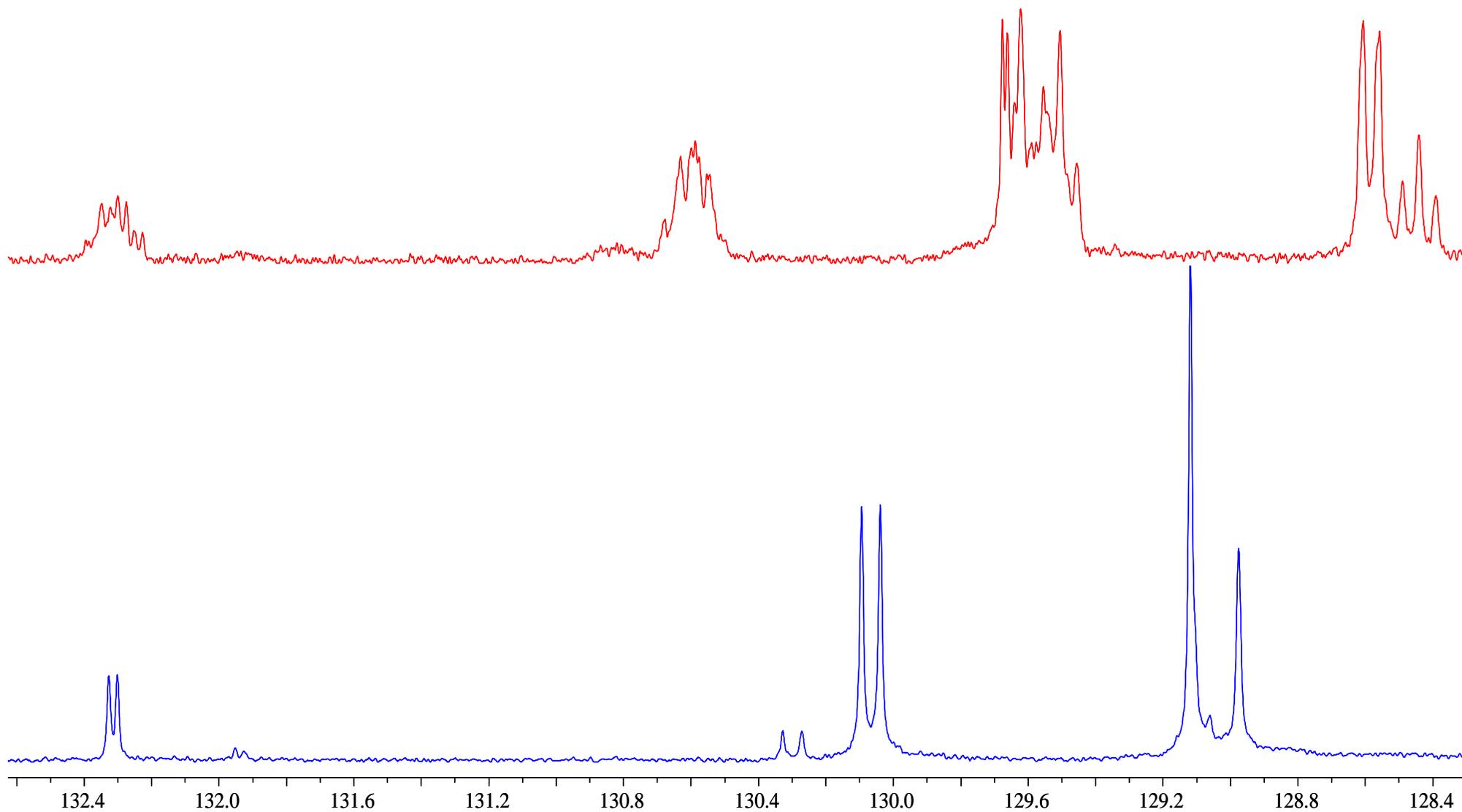


Figure S73. Fragments of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).

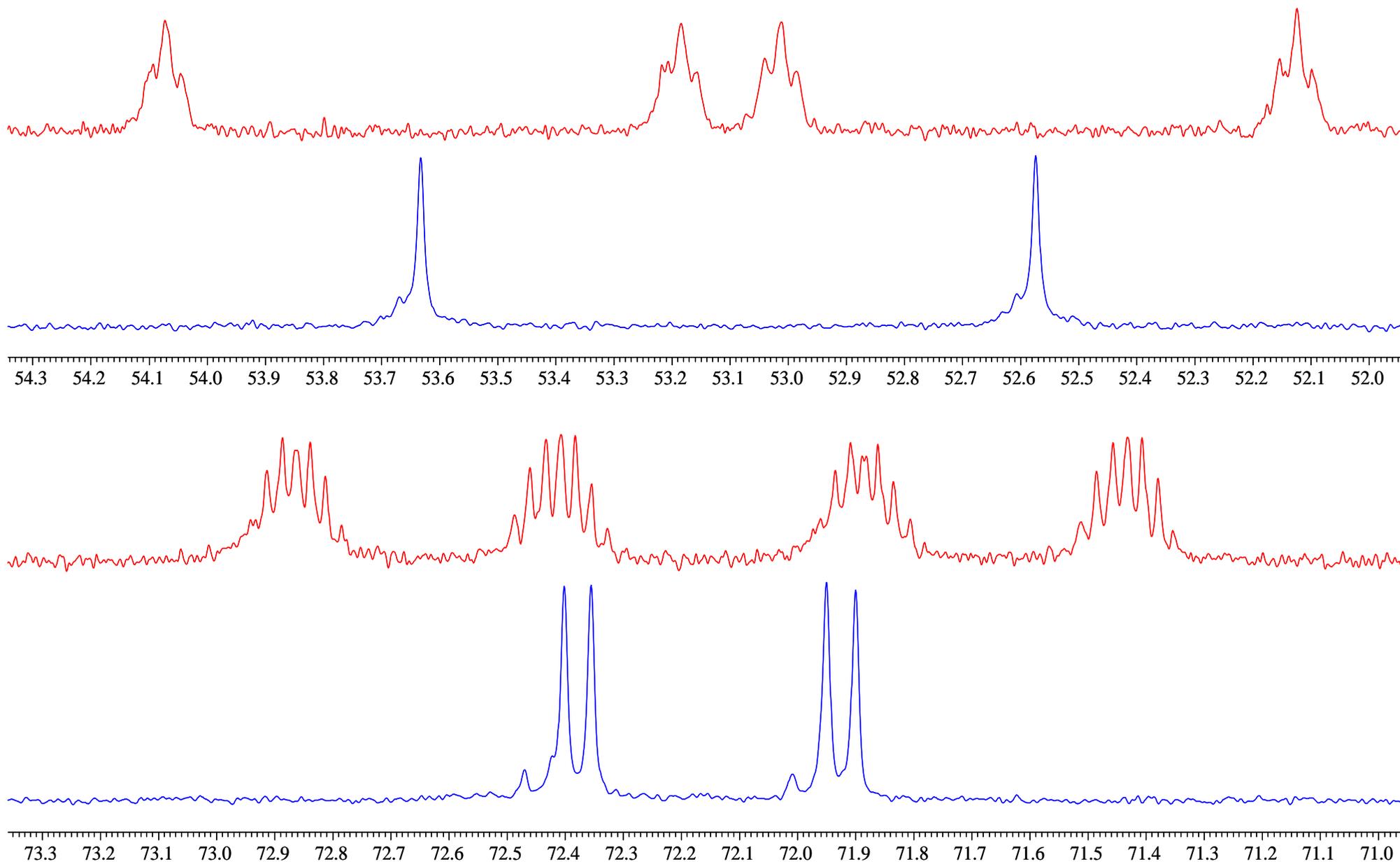


Figure S74. 52-54 and 71-74 ppm regions of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).

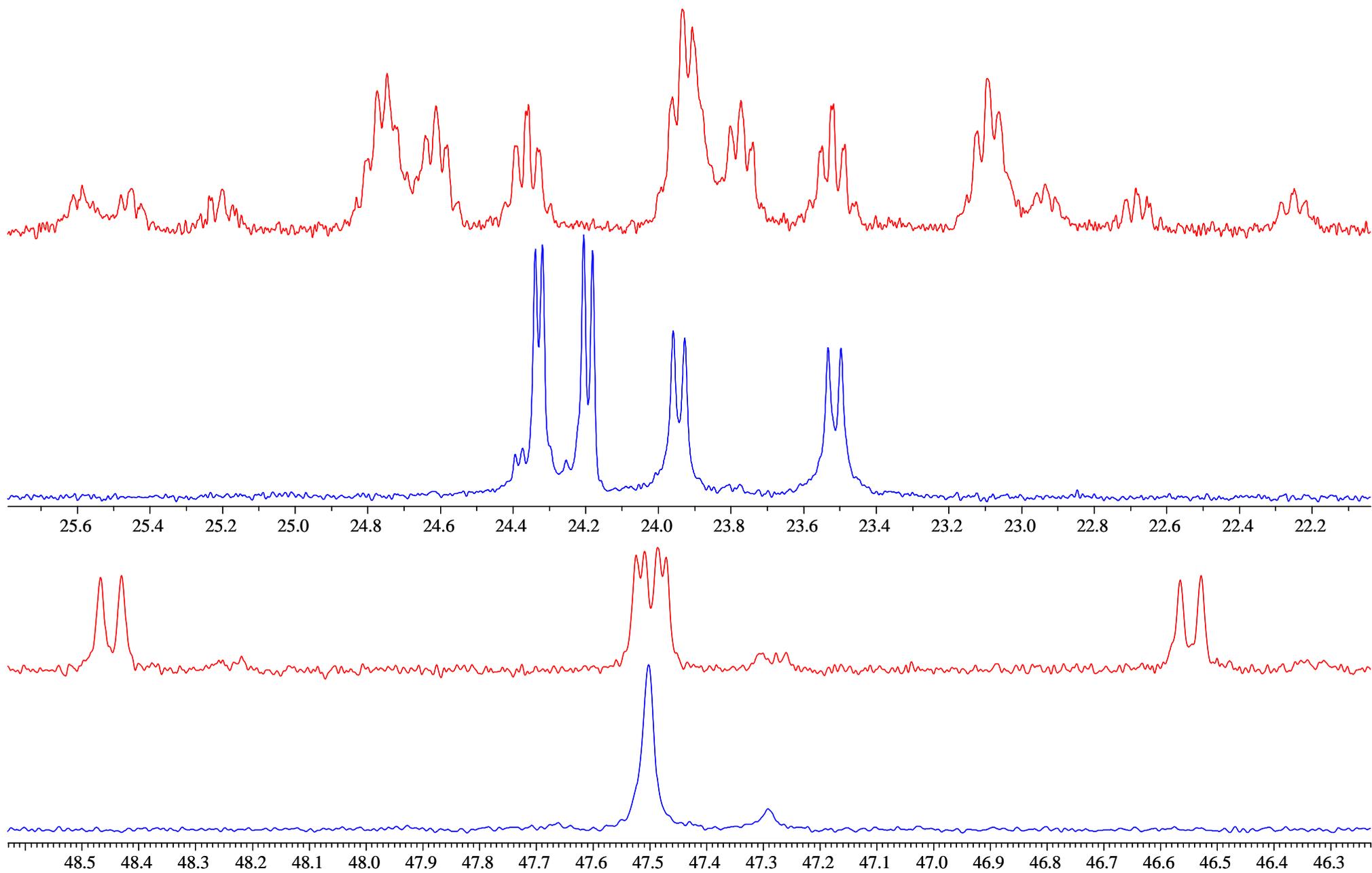


Figure S75. 22-26 and 46-49 ppm regions of $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra (150.9 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).

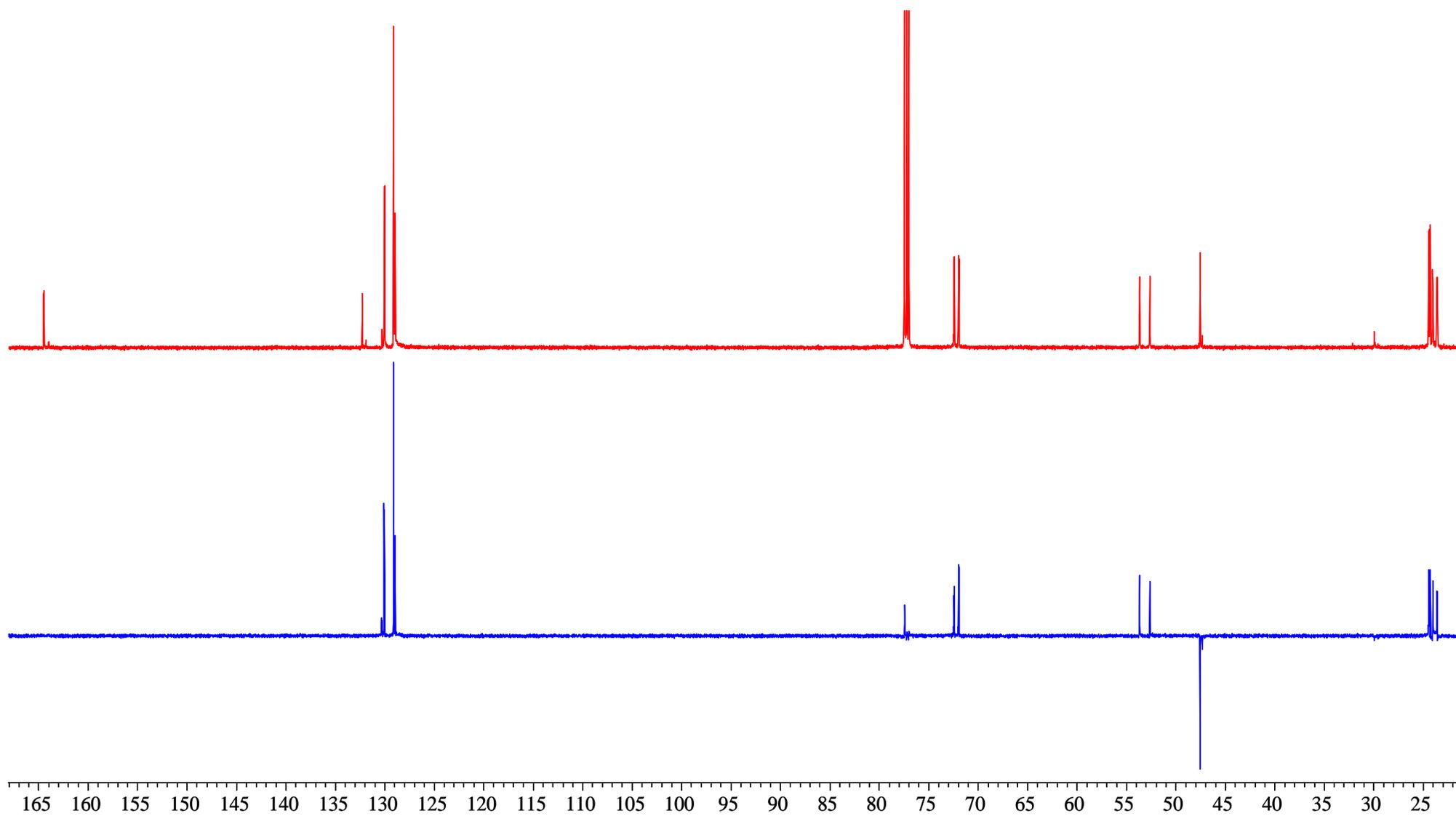


Figure S76. ^{13}C - $\{^1\text{H}\}$ and ^{13}C - $\{^1\text{H}\}$ -dept NMR spectra (150.9 MHz, CDCl_3) of (**3b**, d_1 and d_2 in the ratio of 20 : 1).