Supplementary Information for

Transfer hydrogenation promoted by N-heterocyclic carbene and water

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Experimental Section

General

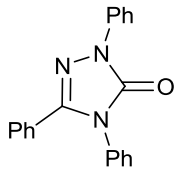
All reactions were performed under nitrogen atmosphere. Microwave irradiation experiments were carried out in a Biotage Initiator microwave reactor. The reaction temperature was measured by a surface sensor. NHC precursors were prepared according to the previous literatures (**2a**[1], **2b**[1], **2c**[2], **2d**[2], **2e**[3], **2f**[4], **2g**[4], **2h**[4], **2i**[5], **2j**[6]). Dibutyl fumarate, dibutyl maleate, *n*-butyl alcohol, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *N*,*N*-diisopropylethylamine (DIPEA), 1,2-dimethoxyethane (DME),and *N*,*N*-dimethylformamide (DMF) were distilled from CaH_2 under reduced pressure before use. Anhydrous toluene and ethanol were purchased from KANTO CHEMICAL CO., INC. Deuterium oxide (99.9 atom D%) was purchased from SIGMA-ALDRICH. Thiamine hydrochloride (**2k**), *trans*-1,2-dibenzoylethylene(**1j**), *N*-phenylmaleimide (**1k**), 2-methyl-*N*-phenylmaleimide(**1m**), *N*,*N*'-dicyclohexylcarbodiimide (DCC, **1p**), diisopropyl azodicarboxylate (DIAD, **1q**), and other reagents were used as received. Several substrates shown in Table 2 were prepared according to the previous literatures (**1c**[7], **1f**[8], **1h**[9], **1i**[10], **1n**[11], **1o**[12]). Kugelrohr distillations were carried out under reduced pressure (2.0 mmHg) at 110 °C ~ 220 °C. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III HD (400 MHz for ^{1}H, 100 MHz for ^{13}C) or JEOL JNM-ECA700 (700 MHz for ^{1}H, 176 Hz for ^{13}C) NMR spectrometers. Chemical shift values in ^{1}H and ^{13}C NMR spectra are relative to the internal TMS standard (0.0 ppm for ^{1}H) or $CDCl_3$ resonance (77.16 ppm for ^{13}C). Electrospray ionization mass spectrometry (ESI-MS) was performed in methanol solutions on a Waters Synapt G2 HDMS tandem quadrupole orthogonal acceleration time-of-flight instrument equipped with a Z-spray nanoelectrospray ionization source. Infrared spectra were obtained on a JASCO FT/IR-460 Plus spectrometer. Thin layer chromatography was performed on TLC Silica gel 60 F_{254} Merck KGaA.

Experimental Procedure and Compound Characterization Data

The transfer hydrogenation of dibutyl fumarate (1a) (Table 1, Entry 1)

In a two-necked flask equipped with a three way stopcock, NHC precursor **2b** (100 mg, 0.30 mmol) was heated at 100 °C for 12 h under vacuum to generate NHC **2a**. To this flask, 1,2-dimethoxyethane (1.0 mL) and H_2O (16.0 mg, 0.90 mmol) were added. After the stirring for 3 min at room temperature, dibutyl fumarate (57.0 mg, 0.25 mmol) was added and the mixture was transferred by a microsyringe into a 2.0 mL microwave vial. The vial was then sealed and heated with microwave irradiation at 150 °C for 2 h. The precipitated **4a** was removed by filtration and washed with hexane. The filtrate was subjected to Kugelrohr distillation under reduced pressure to give dibutyl succinate **3a** (54.1 mg, 0.24 mmol, transparent liquid) in 94% yield. For the ^{1}H and ^{13}C NMR data of **3a**, see ref 13. In the case of the isolation of **4a**, the crude reaction mixture was subjected to the silica gel column chromatography using dichloromethane as the eluent (R_f = 0.6) to give **4a** (73 mg, 0.24 mmol, white solid) in 78% yield.

1,3,4-triphenyl-1H-1,2,4-triazol-5(4*H*)-one (4a)



mp = 213-214 °C.

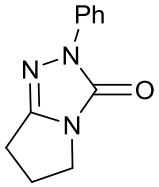
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.48 (m, 13H, *Ph*), 8.11 (d, *J* = 7.8 Hz, 2H, *Ph*).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 119.0, 125.6, 126.4, 127.4, 128.1, 128.7, 128.9, 129.1, 129.6, 133.6, 138.0, 145.3, 151.9.

HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{15}N_3O$ $[M+Na]^+$ 336.1113, found 336.1112.

IR (KBr, cm^{-1}): 3392, 3045, 2922, 2857, 1703, 1592, 1491, 1375, 1151, 966, 756, 693.

2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)-one (4c) (Table 1, Entry 7)



16 mg, 0.077 mmol, 26% isolated yield, white solid, purified by silica gel column chromatography (ethyl acetate: hexane = 3: 1, R_f = 0.3).

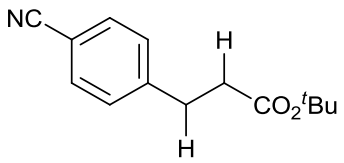
mp = 108-109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.56 (m, 2H, -CH_2-CH_2-CH_2-), 2.90 (t, *J* = 7.6 Hz, 2H, =C-CH_2-CH_2-), 3.84 (t, *J* = 7.0 Hz, 2H, N-CH_2-CH_2-), 7.18 (t, *J* = 7.5 Hz, 1H, *Ph*), 7.40 (t, *J* = 7.9 Hz, 2H, *Ph*), 7.91 (d, *J* = 7.7 Hz, 2H, *Ph*).
^{13}C NMR (100 MHz, $CDCl_3$); δ: 22.7, 26.3, 41.9, 118.7, 125.1, 129.0, 138.7, 150.5, 153.3.
HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{11}N_3O$ $[M+Na]^+$ 224.0799, found 224.0808.
IR (KBr, cm^{-1}): 3417, 2922, 2852, 1703, 1615, 1596, 1501, 1362, 1335, 1101, 757, 727, 690.

The transfer hydrogenation of (*E*)-*tert*-butyl 3-(4-cyanophenyl)propenoate (1h) (Table 2, Entry 7)

NHC **2b** (100 mg, 0.30 mmol), H_2O (16 mg, 0.90 mmol) and 1,2-dimethoxyethane (1.0 mL) were added into a 2.0 mL microwave vial. The mixture was stirred for 3 min at room temperature and (*E*)-*tert*-butyl 3-(4-cyanophenyl)propenoate **1h** (58 mg, 0.25 mmol) was added. The vial was then sealed and heated with microwave irradiation at 150 °C for 2 h. The precipitated **4a** was removed by filtration and washed with hexane. The filtrate was purified by silica gel column chromatography (ethyl acetate : hexane = 1 : 10, R_f = 0.3) to give **3h** (43 mg, 0.19 mmol, white solid) in 74% yield.

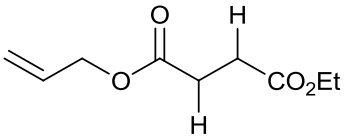
***tert*-butyl 3-(4-cyanophenyl)propanoate (3h)**



^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.40 (s, 9H, -CH_3), 2.56 (t, *J* = 7.5 Hz, 2H, Ph-CH_2-), 2.97 (t, *J* = 7.5 Hz, 2H, -CH_2-CO-), 7.31 (d, *J* = 8.4 Hz, 2H, *Ar*), 7.68 (d, *J* = 8.4 Hz, 2H, *Ar*).
^{13}C NMR (100 MHz, $CDCl_3$); δ: 28.1, 31.2, 36.2, 80.9, 110.2, 119.0, 129.3, 132.3, 146.5, 171.6.
HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{17}NO_2$ $[M+Na]^+$ 254.1157, found 254.1167.
IR (KBr, cm^{-1}): 3429, 2923, 2853, 2226, 1725, 1608, 1509, 1371, 1154, 948, 825, 760.

diethyl 2-methylsuccinate (3c)[14]; purified by Kugelrohr distillation to give 31 mg of the crude mixture. The yield was estimated by ^{1}H NMR spectroscopy; the mixture of unreacted **1c** (19%), the *E*-isomer of **1c** (11%), and product **3c** (36%) were obtained.

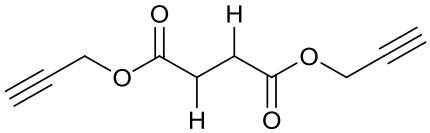
allyl ethyl succinate (3d)



41 mg, 0.22 mmol, 85% isolated yield, transparent liquid, purified by Kugelrohr distillation.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (t, *J* = 7.2 Hz, 3H, C*H*$_3$), 2.61-2.67 (m, 4H, -C(=O)-C*H*$_2$-), 4.14 (q, *J* = 7.2 Hz, 2H, -C*H*$_2$-CH$_3$), 4.59 (dt, *J* = 5.7 Hz, *J* = 1.5 Hz, 2H, =CH-C*H*$_2$-), 5.22 (dq, *J* = 10.5 Hz, *J* = 1.5 Hz, 1H, C*H*$_2$=), 5.31 (dq, *J* = 17.3 Hz, *J* = 1.5 Hz, 1H, C*H*$_2$=), 5.9 (m, 1H, C*H*=).
^{13}C NMR (100 MHz, $CDCl_3$); δ: 14.3, 29.2, 29.3, 60.8, 65.5, 118.4, 132.2, 172.2, 172.4.
HRMS (ESI) *m*/*z*: calcd for $C_9H_{14}O_4$ $[M+Na]^+$ 209.0789, found 209.0805.
IR (NaCl, cm^{-1}): 3087, 2984, 2938, 1736, 1415, 1375, 1211, 1159, 1025, 992, 933, 857.

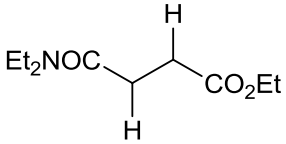
dipropyn-2-yl succinate (3e)



33 mg, 0.17 mmol, 68% isolated yield, transparent liquid, purified by Kugelrohr distillation
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (t, *J* = 2.5 Hz, C*H*), 2.70 (s, 4H, -C(=O)-C*H*$_2$-), 4.67 (d, *J* = 2.5 Hz, 4H, O-C*H*$_2$-).
^{13}C NMR (100 MHz, $CDCl_3$); δ: 28.8, 52.4, 75.1, 171.4.
HRMS (ESI) *m*/*z*: calcd for $C_{10}H_{10}O_4$ $[M+Na]^+$ 217.0476, found 217.0485.
IR (KBr, cm^{-1}): 3291, 2945, 2130, 1741, 1437, 1382, 1348, 1271, 1209, 1154, 1026, 995, 652.

***tert*-butyl 4-oxopentanoate (3f)**[15]; 28 mg, 0.17 mmol, 65% isolated yield, transparent liquid, purified by Kugelrohr distillation.

ethyl 4-(diethylamino)-4-oxobutanoate (3g)



40 mg, 0.20 mmol, 79% isolated yield, transparent liquid, purified by Kugelrohr distillation.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11 (t, *J* = 7.1 Hz, 3H, -N-CH$_2$-C*H*$_3$), 1.20 (t, *J* = 7.1 Hz, 3H, -N-CH$_2$-C*H*$_3$), 1.26 (t, *J* = 7.2 Hz, 3H, -O-CH$_2$-C*H*$_3$), 2.60-2.69 (m, 4H, -CO-C*H*$_2$-C*H*$_2$-CO-), 3.34 (q, 2H, -N-C*H*$_2$-), 3.37 (q, 2H, -N-C*H*$_2$-), 4.15 (q, *J* = 7.1 Hz, 2H, -O-C*H*$_2$-).
^{13}C NMR (100 MHz, $CDCl_3$); δ: 13.1, 14.2, 27.8, 29.5, 40.3, 41.8, 60.5, 170.3, 173.3.
HRMS (ESI) *m*/*z*: calcd for $C_{10}H_{19}NO_3$ $[M+Na]^+$ 224.1262 , found 254.1264.
IR (NaCl, cm^{-1}): 2978, 2934, 1736, 1646, 1482, 1434, 1376, 1177, 1141, 1028.

***tert*-butyl 3-(4-acetylphenyl)propanoate (3i)**; purified by silica gel column chromatography (ethyl acetate : hexane = 1 : 10, R_f = 0.3) to give 26 mg of the crude mixture. Yields were estimated by ^{1}H

NMR. The unreacted 1i (13%) and the product 3i (24%) were obtained.

1,4-diphenylbutane-1,4-dione (3j)[16]; 41 mg, 0.17 mmol, 68% isolated yield, white solid, purified by silica gel column chromatography (dichloromethane, R_f = 0.6)

1-butylpyrrolidine-2,5-dione (3k)[17]; 20 mg, 0.13 mmol, 51% isolated yield, transparent liquid, purified by Kugelrohr distillation.

1-phenylpyrrolidine-2,5-dione (3l)[18]; 24 mg, 0.14 mmol, 55% isolated yield, white solid, purified by silica gel column chromatography (ethyl acetate : hexane = 2 : 3, R_f = 0.3).

3-methyl-1-phenylpyrrolidine-2,5-dione (3m)[19]; 34 mg, 0.18 mmol, 72% isolated yield, yellow solid, purified by silica gel column chromatography (ethyl acetate : hexane = 2 : 3, R_f = 0.3).

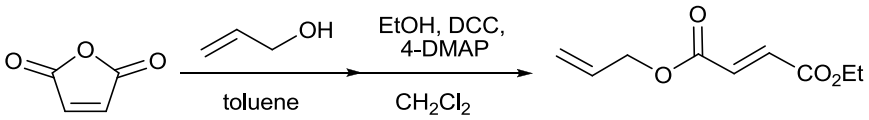
4-((phenylamino)methyl)benzonitrile (3n)[20]; 42 mg, 0.20 mmol, 80% isolated yield, pale yellow solid, purified by silica gel column chromatography (ethyl acetate : hexane = 3 : 1, R_f = 0.4).

methyl 4-((phenylamino)methyl)benzoate (3o)[21]; 41 mg, 0.17 mmol, 68% isolated yield, pale yellow solid, purified by silica gel column chromatography (ethyl acetate : hexane = 3 : 1, R_f = 0.5).

(*E*)-*N*,*N*'-dicyclohexylformimidamide (3p)[22]; 44 mg, 0.21 mmol, 70% isolated yield, white solid, purified by Kugelrohr distillation. 1.0 equivalent of NHC **2b** was used.

diisopropyl hydrazine-1,2-dicarboxylate (3q)[23]; 45 mg, 0.22 mmol, 88% isolated yield, white solid, purified by silica gel column chromatography (ethyl acetate : hexane = 2 : 3, R_f = 0.6).

Synthesis of allyl ethyl fumarate (1d)



To a two-necked 30 mL flask equipped with a three way stopcock, maleic anhydride (0.70 g, 7.0 mmol), toluene (3.0 mL), and allyl alcohol (0.57 g, 9.8 mmol) were added and heated at 90 °C for 8 h. After the volatiles were removed under reduced pressure, 4-dimethylaminopyridine (86 mg, 0.70 mmol), anhydrous ethanol (2.5 g, 54.8 mmol), dichloromethane (4.0 mL), and *N*,*N*'-dicyclohexylcarbodiimide (1.8 g, 8.7 mmol) were added and then stirred at room temperature for 48 h. The reaction mixture was filtered and washed with dichloromethane, and the filtrate was subjected to silica gel column chromatography (ethyl acetate : hexane = 1 : 3, R_f = 0.3) to give **1d** (0.13 g, 0.69 mmol, transparent liquid) in 10% yield.

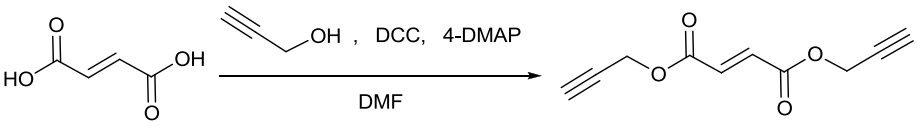
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 4.25 (q, *J* = 7.1 Hz, 2H, -C*H*$_2$-CH$_3$), 4.69 (dt, *J* = 5.8 Hz, *J* = 1.3 Hz, 2H, =CH-C*H*$_2$-), 5.28 (dq, *J* = 10.4 Hz, *J* = 1.3 Hz, 1H, C*H*$_2$=CH-), 5.30 (dq, *J* = 17.1 Hz, *J* = 1.5 Hz, 1H, C*H*$_2$=CH-), 5.94 (m, 1H, CH$_2$-C*H*=), 6.87 (s, 2H, -C*H*=C*H*-).

^{13}C NMR (100 MHz, $CDCl_3$); δ: 14.2, 61.4, 66.0, 118.9, 131.6, 133.3, 134.1, 164.8, 165.0.

HRMS (ESI) *m*/*z*: calcd for $C_9H_{12}O_4$ $[M+Na]^+$ 207.0633, found 207.0635.

IR (NaCl, cm^{-1}): 3439, 3084, 2985, 1724, 1647, 1448, 1368, 1300, 1259, 1154, 1033, 981, 936, 775

Synthesis of diprop-2-ynyl fumarate (1e)



In a two-necked 30 mL flask equipped with a three way stopcock, fumaric acid (0.50 g, 4.3 mmol), 4-dimethylaminopyridine (52 mg, 0.43 mmol), 2-propyn-1-ol (1.0 g, 18 mmol), DMF (4.0 mL), and *N*,*N*'-dicyclohexylcarbodiimide (2.3 g, 11 mmol) were added and then stirred at room temperature for 48 h. The reaction mixture was filtered and washed with dichloromethane, and the filtrate was subjected to silica gel column chromatography (ethyl acetate: hexane = 1:3, R_f = 0.3). Compound **1d** (0.18 g, 0.93 mmol, white solid) was obtained in 22% yield.

mp=79.9-80.6 °C.

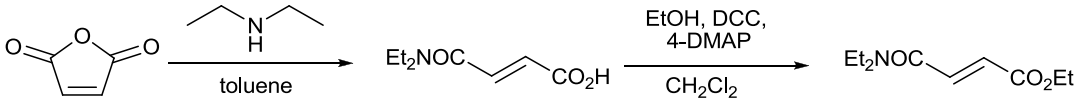
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.25 (t, *J* = 2.4 Hz, 2H, C*H*), 4.80 (d, *J* = 2.5 Hz, 4H, C*H*$_2$), 6.93 (s, 2H, -C*H*=).

^{13}C NMR (100 MHz, $CDCl_3$); δ: 53.0, 75.7, 77.0, 133.7, 164.0.

HRMS (ESI) *m*/*z*: calcd for $C_{10}H_8O_4$ $[M+Na]^+$ 215.0320, found 215.0317.

IR (neat, cm^{-1}): 3278, 3087, 2943, 2131, 1723, 1359, 1296, 1159, 1032, 771, 711, 656.

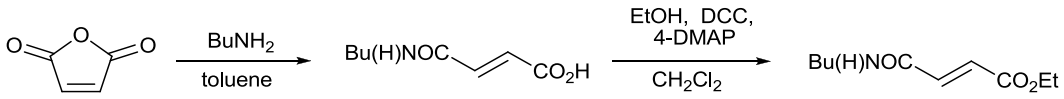
Synthesis of (*E*)-ethyl 4-(diethylamino)-4-oxobut-2-enoate (1g)



In a two-necked 50 mL flask equipped with a three way stopcock, maleic anhydride (1.0 g, 10 mmol), toluene (3.0 mL),and diethylamine (0.75 g, 10 mmol) were added and stirred at 50 °C for 8 h. Dichloromethane (30 mL) was added to reaction mixture and washed with 1M HCl aq. The organic layer was dried over $MgSO_4$, followed by the filtration and consentration to yield (*E*)-4-(diethylamino)-4-oxobut-2-enoic acid [24] (1.0 g, 5.8 mmol) in 58% yield.

In a two-necked 30 mL flask equipped with a three way stopcock, (*E*)-4-(diethylamino)-4-oxobut-2-enoic acid (1.0 g, 5.8 mmol), 4-dimethylaminopyridine (71 mg, 0.58 mmol), anhydrous ethanol (3.2 g, 69 mmol), dichloromethane (5.0 mL), and *N*,*N*'-dicyclohexylcarbodiimide (1.4 g, 7.0 mmol) were added and stirred at room temperature for 48 h. The reaction mixture was filtered and washed with dichloromethane (5 mL), and the filtrate was subjected to silica gel column chromatography (ethyl acetate: hexane = 1:1, R_f = 0.4) to give **1g** (0.25 g, 1.3 mmol, transparent liquid) in 22% yield. For the ^{1}H NMR spectrum data of **1g**, see ref 25.

Synthesis of (*E*)-ethyl 4-(butylamino)-4-oxobut-2-enoate (1k)



In a two-necked 50 mL flask equipped with a three way stopcock, maleic anhydride (1.0 g, 10 mmol), toluene (3.0 mL), and *N*-butyl amine (0.82 g, 11 mmol) were added and stirred at 70 °C for 8 h. Dichloromethane (30 mL) was added to reaction mixture and washed with 1M HCl aq. The organic layer was dried over $MgSO_4$, followed by the filtration and consentration to yield (*E*)-4-(butylamino)-4-oxobut-2-enoic acid[26] (1.1 g, 6.4 mmol) in 64% yield.

In a two-necked 30 mL flask equipped with a three way stopcock, (*E*)-4-(butylamino)-4-oxobut-2-enoic acid (1.1 g, 6.4 mmol), 4-dimethylaminopyridine (78 mg, 0.64 mmol), anhydrous ethanol (3.2g, 69 mmol), and *N*,*N*'-dicyclohexylcarbodiimide (1.6 g, 0.75 mmol) were added and stirred at room temperature for 48 h. The reaction mixture was filtered and washed with dichloromethane, and the filtrate was subjected to silica gel column chromatography (ethyl acetate : hexane = 1 : 1, R_f = 0.6) to give **1k** (0.36 g, 1.8 mmol) in 28% yield. For the ^{1}H and ^{13}C NMR data of **1k**, see ref 27.

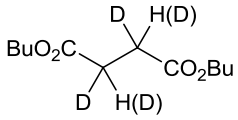
The transfer hydrogenation of dibutyl fumarate by an equimolar amount of D_2O (Scheme 1)

To the mixture of D_2O (5.0 mg, 0.25 mmol) and 1,2-dimethoxyethane (1.0 mL) in a 2.0

mL microwave vial, NHC **2a** (91 mg, 0.30 mmol) was added. After the mixture was stirred for 3 min, dibutyl fumarate (57.0 mg, 0.25 mmol) was added at room temperature. The vial was then sealed and heated with microwave irradiation at 120 °C for 6 h. The resulting mixture was cooled to room temperature, and the precipitate was removed by filtration. Kugelrohr distillation of the filtrate under reduced pressure gave **3r** (55.1 mg, 0.24 mmol) in 95% yield.

Compound **3s** (28 mg, 0.16 mmol, 65% yield) was also obtained from **1f** by a similar procedure. In the case of **1m** as a substrate, the reaction mixture was filtered, and washed with hexane, The filtrate was purified by using column chromatography (ethyl acetate: hexane = 2: 3, R_f= 0.3) to give **3t** (13 mg, 0.07 mmol) in 28% yield. In addition, the precipitate was washed with ethyl acetate three times to give **5t** (34 mg, 0.07mmol) in 28% yield.

Compound 3r



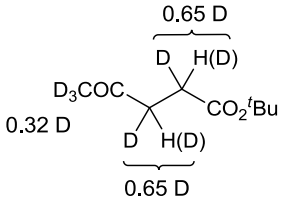
Total 2.0 D

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, 6.0H), 1.34-1.36 (m, 4.0H), 1.58-1.62 (m, 4.0H), 2.59 (m, 2.0H), 4.08 (t, J = 6.6 Hz, 4.0H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 19.2, 28.7, 28.8, 28.9, 29.0, 29.1, 29.2, 29.3, 30.7, 64.7, 172.5.

HRMS (ESI) *m/z*: calcd for $C_{12}H_{21}DO_4$ $[M+Na]^+$ 254.1478 , found 254.1474, calcd for $C_{12}H_{20}D_2O_4$ $[M+Na]^+$ 255.1541 , found 255.1542, calcd for $C_{12}H_{19}D_3O_4$ $[M+Na]^+$ 256.1604, found 256.1595.

Compound 3s

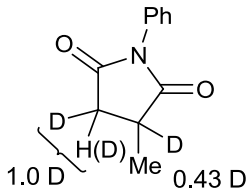


^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (s, 9.0H), 2.17-2.19 (m, 2.68 H), 2.49-2.55 (m, 1.3H), 2.67-2.71 (m, 1.3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.1, 29.2, 30.0, 37.9, 38.0, 38.1, 80.6, 172.0, 206.9.

HRMS (ESI) *m/z*: calcd for $C_9H_{16}O_3$ $[M+Na]^+$ 195.0997, found 195.0996, calcd for $C_9H_{15}DO_3$ $[M+Na]^+$ 196.1059, found 196.1054; calcd for $C_9H_{14}D_2O_3$ $[M+Na]^+$ 197.1122, found 197.1115; calcd for $C_9H_{13}D_3O_3$ $[M+Na]^+$ 198.1185, found 198.1177.

Compound 3t

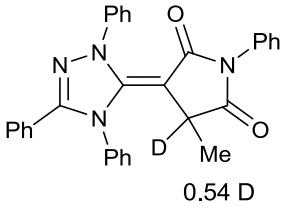


^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (m, 3.0H), 2.48-2.52 (m, 0.57H), 3.03-3.11 (m, 1.0H), 7.27-7.29 (m, 2.0H), 7.36-7.41 (m, 1.0H), 7.45-7.49 (m, 2.0H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.8, 15.9, 33.7, 33.8, 33.9, 35.5, 35.6, 125.4, 127.6, 128.1, 130.9, 174.4, 178.5.

HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{10}DNO_2$ $[M+Na]^+$ 213.0750, found 213.0748; calcd for $C_{11}H_9D_2NO_2$ $[M+Na]^+$ 214.081, found 214.0807; calcd for $C_{11}H_8D_3NO_2$ $[M+Na]^+$ 215.0875, found 215.0859.

Compound 5t



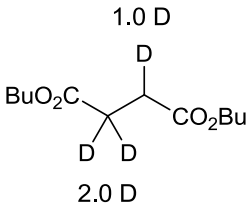
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (m, 3.0H), 2.81 (q, *J* = 7.1 Hz, 0.46H), 7.11-7.68 (m, 20H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.4, 18.5, 39.0, 70.4, 70.5, 123.4, 124.5, 126.7, 127.0, 128.2, 128.2, 128.7, 129.2, 129.3, 130.0, 130.1, 133.6, 135.1, 139.3, 150.3, 151.2, 164.7, 164.7, 177.8.

The transfer hydrogenation of dibutyl fumarate in the presence of an excess amount of D_2O (Scheme 2)

The same procedure as mentioned above for Table 1 was performed using an excess amount of D_2O (150 mg, 7.5 mmol) in place of H_2O. Consequently, **3u** (47 mg, 0.24 mmol, 80% yield) was obtained by Kugelrohr distillation.

Compound 3u



^{1}H NMR (700 MHz, $CDCl_3$) δ: 0.93 (t, *J* = 7.3 Hz, 6.0H), 1.35-1.40 (m, 4.0H), 1.59-1.63 (m, 4.0H),

2.60 (brs, 1.0H), 4.09 (t, *J* = 6.9 Hz, 4.0H).

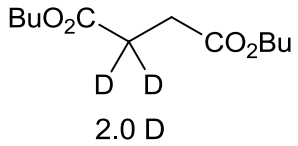
^{13}C NMR (176 MHz, $CDCl_3$) δ: 13.8, 19.2, 28.9 (t, *J* = 20 Hz), 30.7, 64.7, 172.5.

HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{19}D_3O_4$ $[M+Na]^+$ 256.1604, found 256.1601.

The transfer hydrogenation of dibutyl fumarate in the presence of an excess amount of D_2O through the deoxy-Breslow intermediate (Scheme 2)

To the solution of **2a** (90 mg, 0.30 mmol) in 1,2-dimethoxyethane (1.0 mL), dibutyl fumarate (57 mg, 0.25 mmol) was added at 80 °C and stirred at 80 °C for 10 min. The reaction mixture was cooled to room temperature and a small aliquot was subjected to ^{1}H NMR analysis to confirm the complete consumption of dibutyl fumarate. Afterwards,D_2O (150 mg, 7.5 mmol) was added,. This mixture stirred for 1 min at room temperature was transferred to a 2.0 mL microwave vial, which was then sealed and heated under microwave irradiation at 150 °C for 4 h. The resulting mixture was cooled to room temperature, and the precipitate was removed by filtration. Kugelrohr distillation of the filtrate under reduced pressure gave **3v** (47 mg, 0.24 mmol) in 80% yield.

Compound 3v

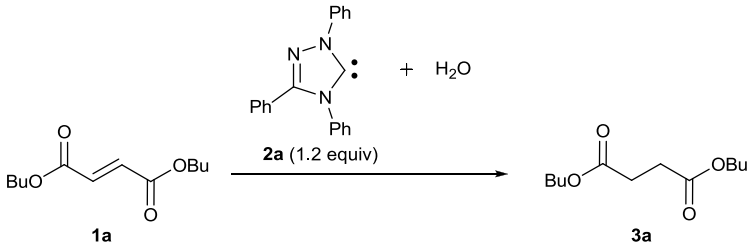


^{1}H NMR (700 MHz, $CDCl_3$) δ: 0.93 (t, *J* = 7.3 Hz, 6.0H), 1.35-1.41 (m, 4.0H), 1.59-1.63 (m, 4.0H), 2.61 (brs, 2.0H), 4.09 (t, *J* = 6.6 Hz, 4.0H).

^{13}C NMR (176 MHz, $CDCl_3$) δ: 13.8, 19.2, 28.8 (quin, *J* = 21 Hz), 29.2, 30.7, 64.7, 172.5.

HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{20}D_2O_4$ $[M+Na]^+$ 255.1541, found 255.1539.

Table S1. Transfer hydrogenation of dibutyl fumarate by NHC and water.



Entry	NHC	Proton Source (eq.)	Base[a]	Temp (°C)	Time (h)	Heating Method[b]	Yield[c] (%)
1	**2b**	H_2O (3.6)	-	100	2	MW	65
2	**2b**	H_2O (20)	-	150	2	MW	94
3	**2c**	H_2O (3.6)	K_2CO_3	120	2	MW	34
4	**2a**	H_2O (3.6)	DBU	120	4	MW	59
5	**2a**	H_2O (3.6)	DIEA	120	4	MW	83
6	**2b**	Aniline (3.6)	-	150	2	MW	0
7	**2b**	Benzoic acid (3.6)	-	150	2	MW	0
8	**2b**	H_2O (3.6)	-	120	2	OB	91
9	**2b**	H_2O (3.6)	-	80	12	OB	81

[a] 2.0 equivalent relative to NHC.

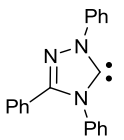
[b] MW: microwave irradiation, OB: oil bath heating.

[c] isolated yield.

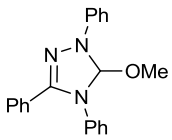
DBU:1,8-diazabicyclo[5.4.0]undec-7-ene,

DIPEA: *N*,*N*-diisopropylethylamine,

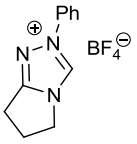
DME: 1,2-dimethoxyethane



2a



2b



2c

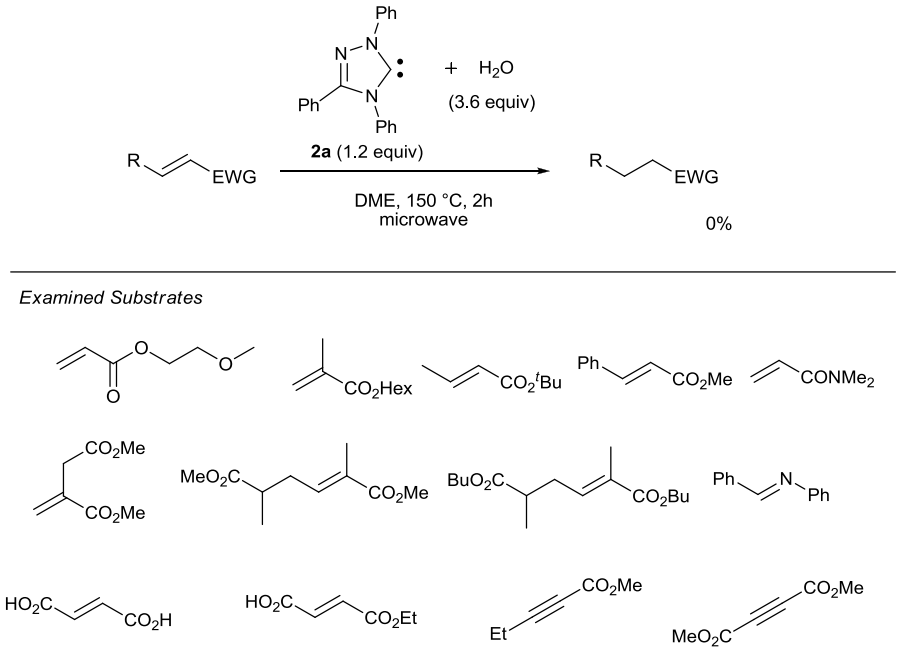
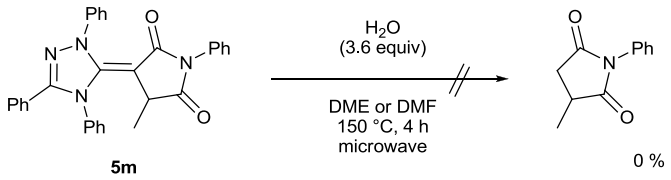


Figure S1. Substrates that did not undergo the transfer hydrogenation.



Scheme S1. The attempted reaction of the deoxy-Breslow intermediate 5m with H_2O.

Compound 5m was prepared according to the previous literature (ref. 28).

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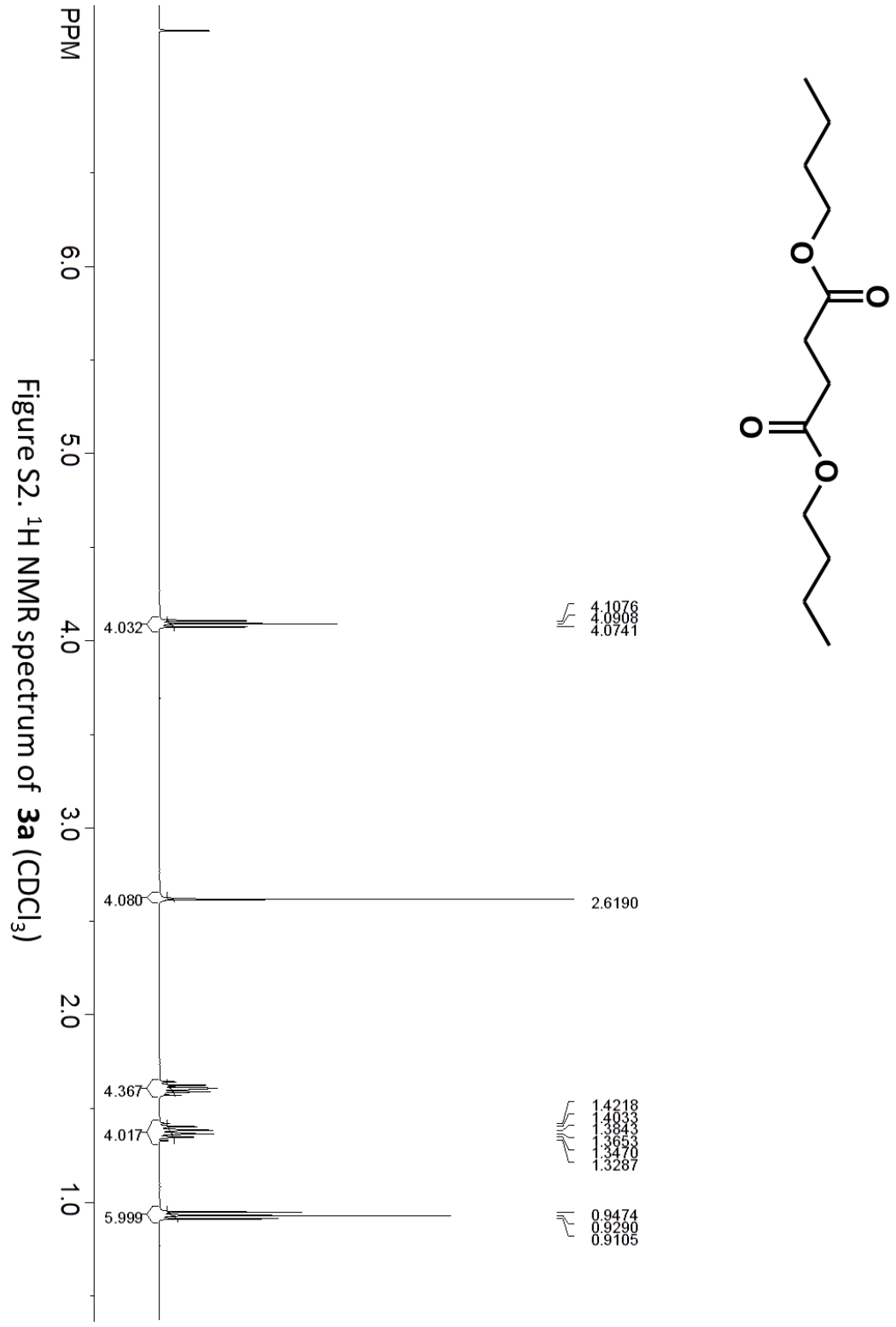

Figure S2. ^{1}H NMR spectrum of **3a** ($CDCl_3$)

Figure S3. ^{13}C NMR spectrum of **3a** ($CDCl_3$)

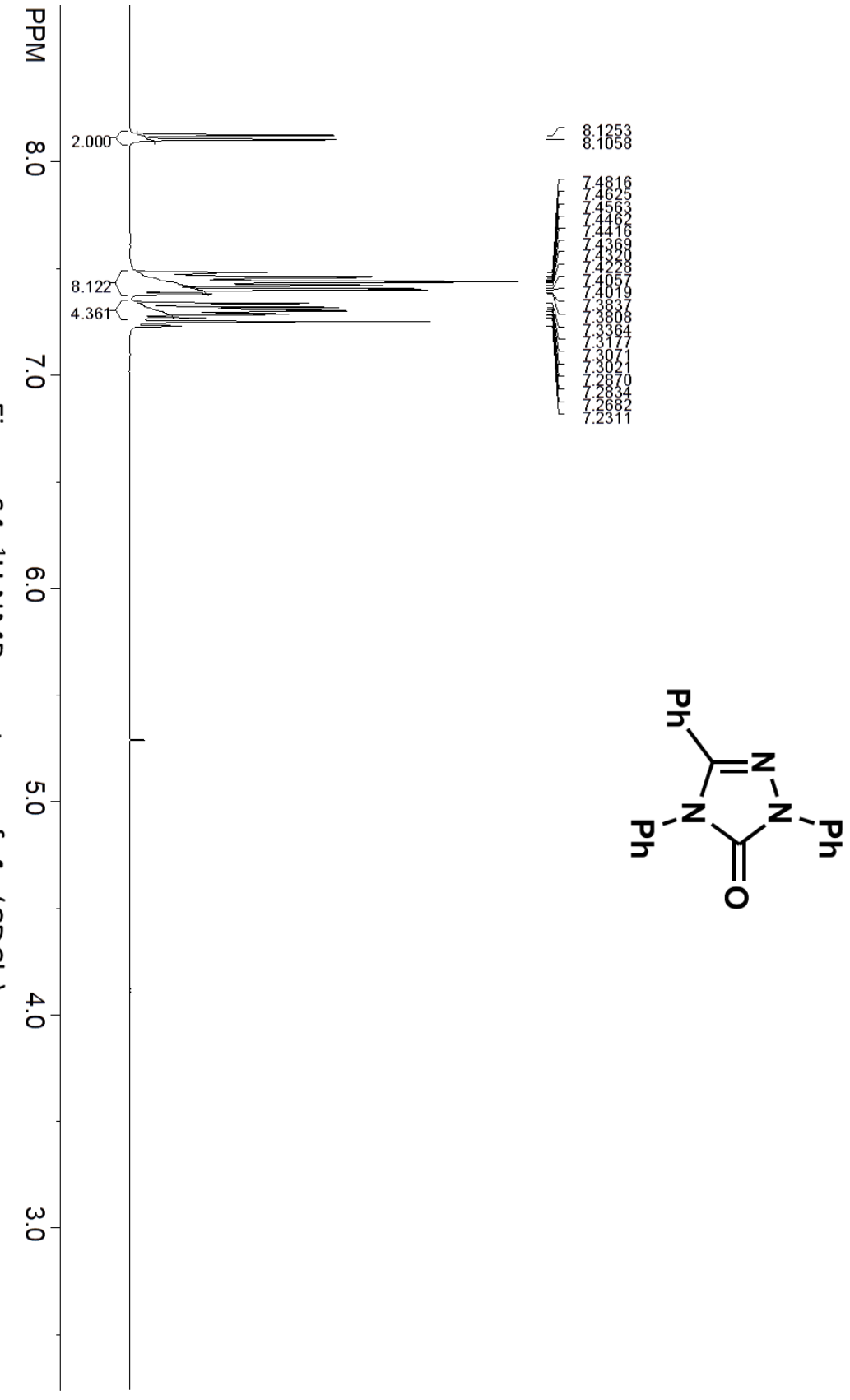

Figure S4. ^{1}H NMR spectrum of **4c** ($CDCl_3$)

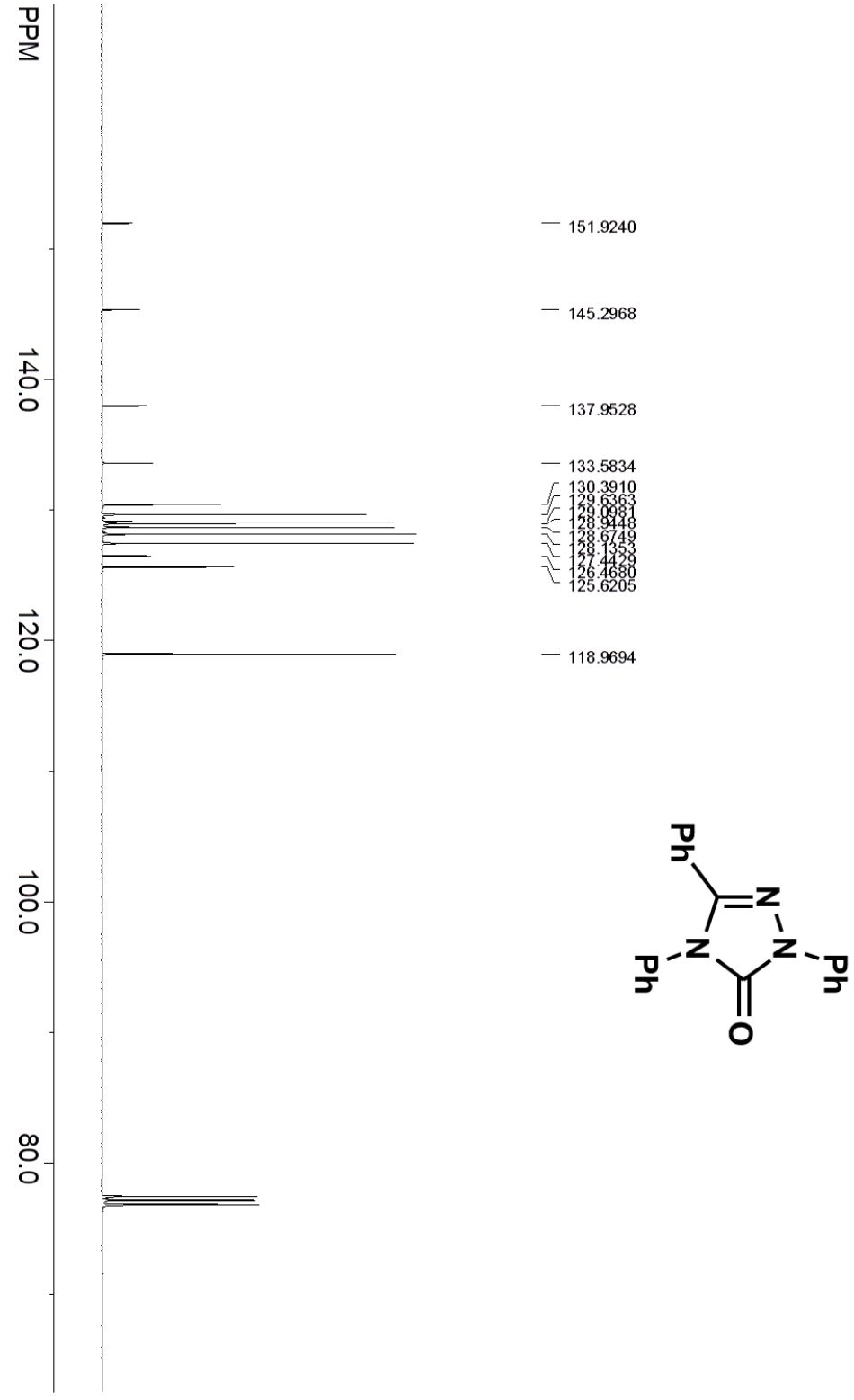

Figure S5. ^{13}C NMR spectrum of **4c** ($CDCl_3$)

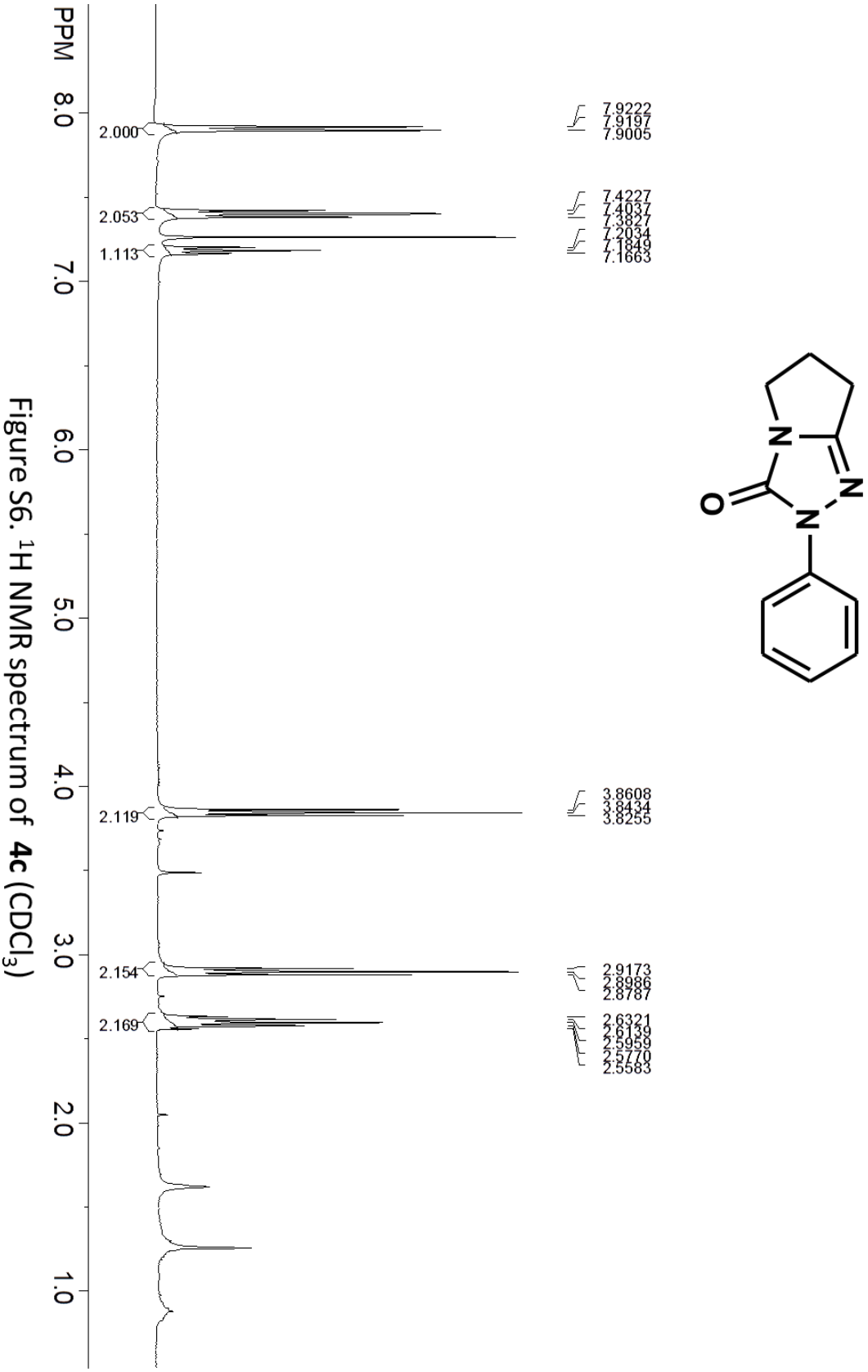

Figure S6. ^{1}H NMR spectrum of **4c** ($CDCl_3$)

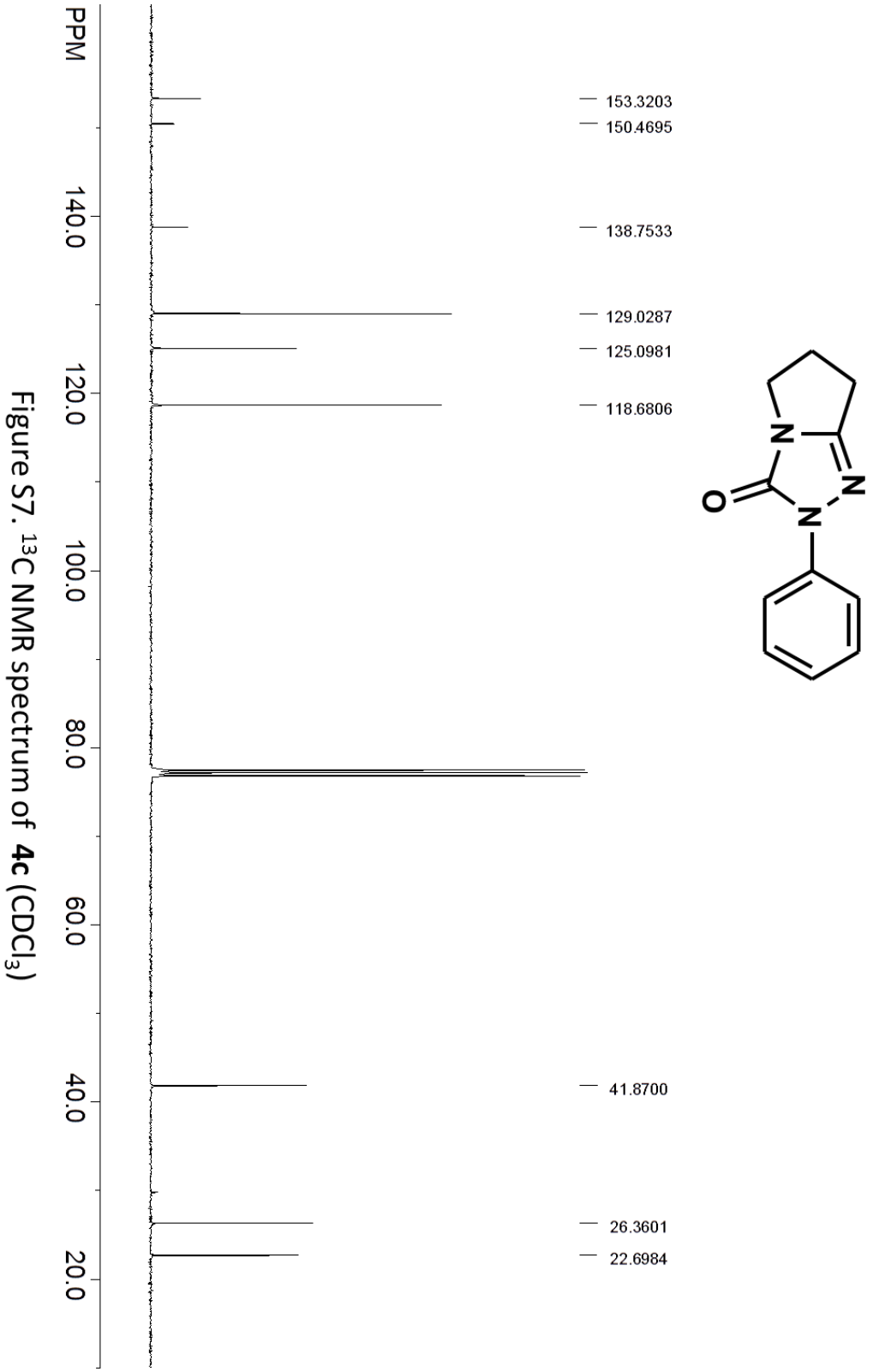

Figure S7. ^{13}C NMR spectrum of **4c** ($CDCl_3$)

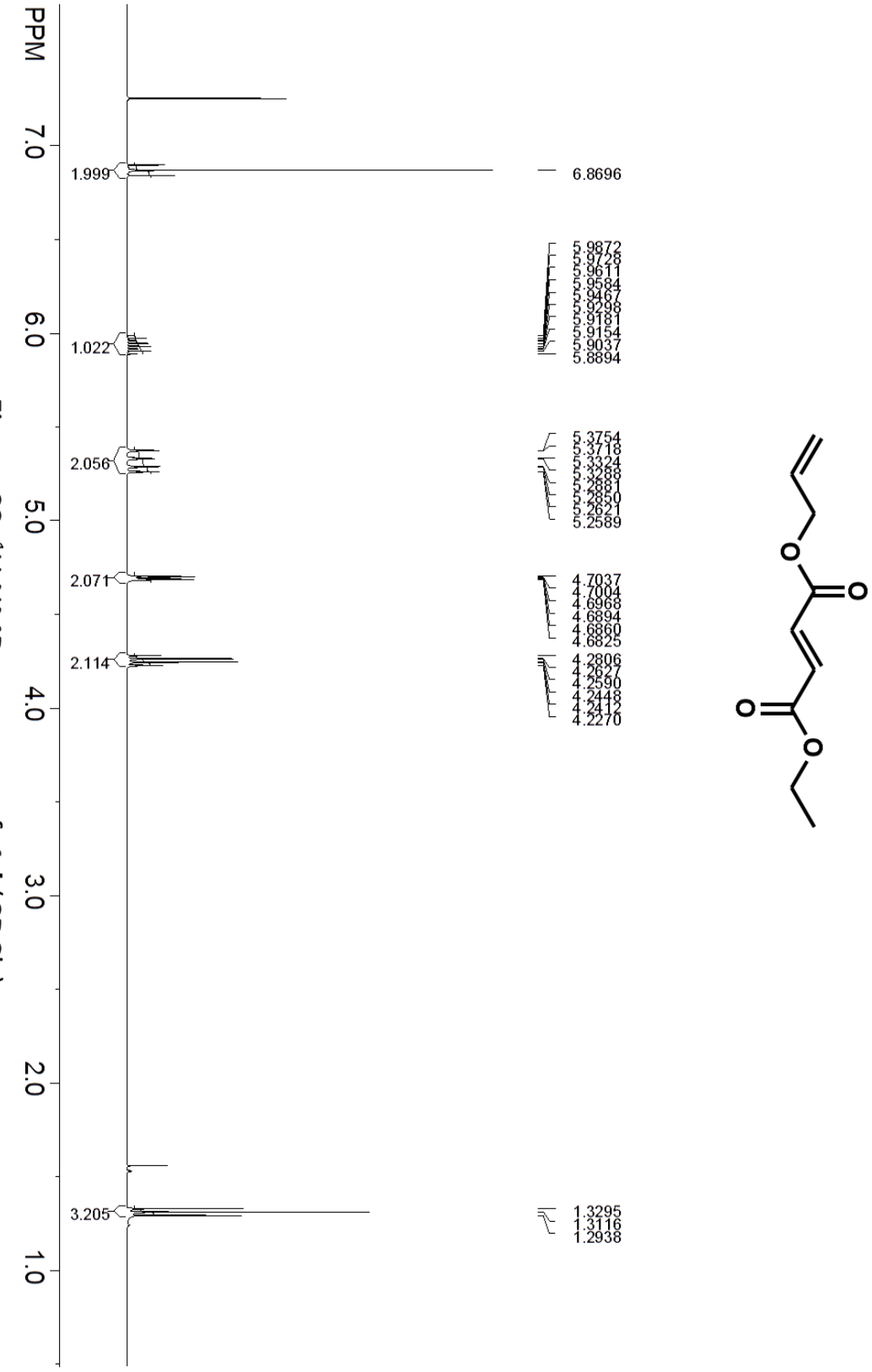

Figure S8. ^{1}H NMR spectrum of **1d** ($CDCl_3$)

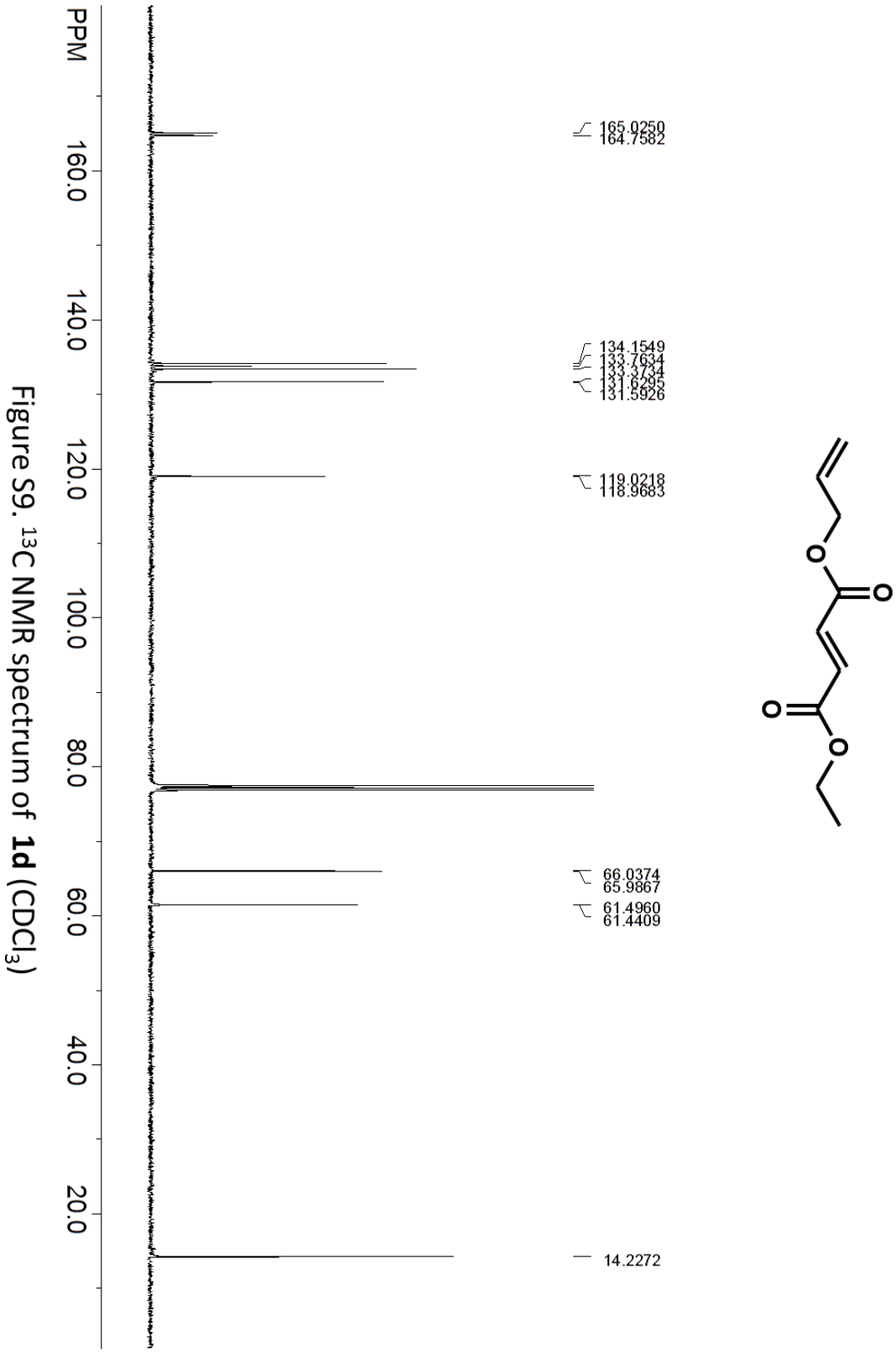

Figure S9. ^{13}C NMR spectrum of **1d** ($CDCl_3$)

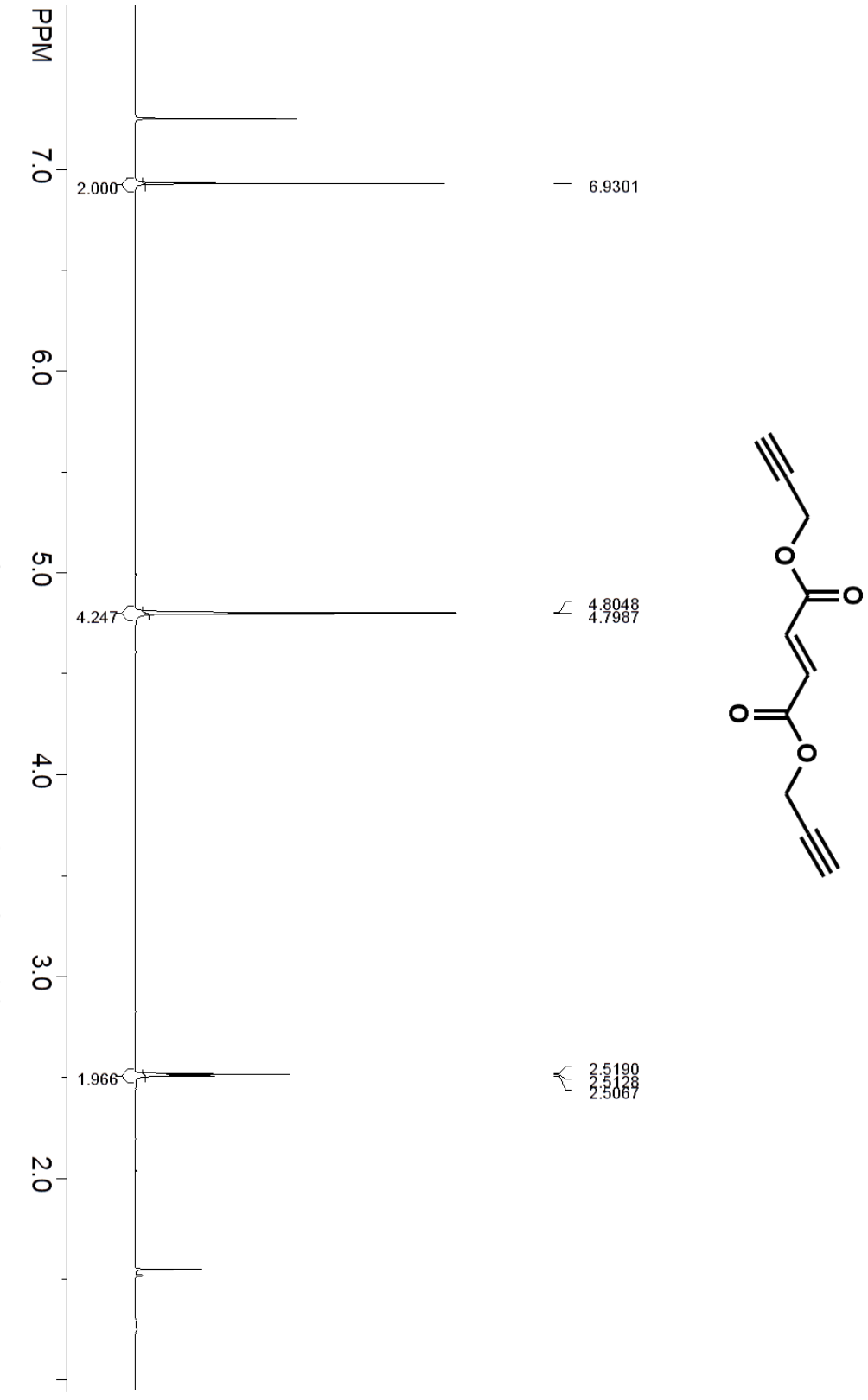

Figure S10. ^{1}H NMR spectrum of **1e** ($CDCl_3$)

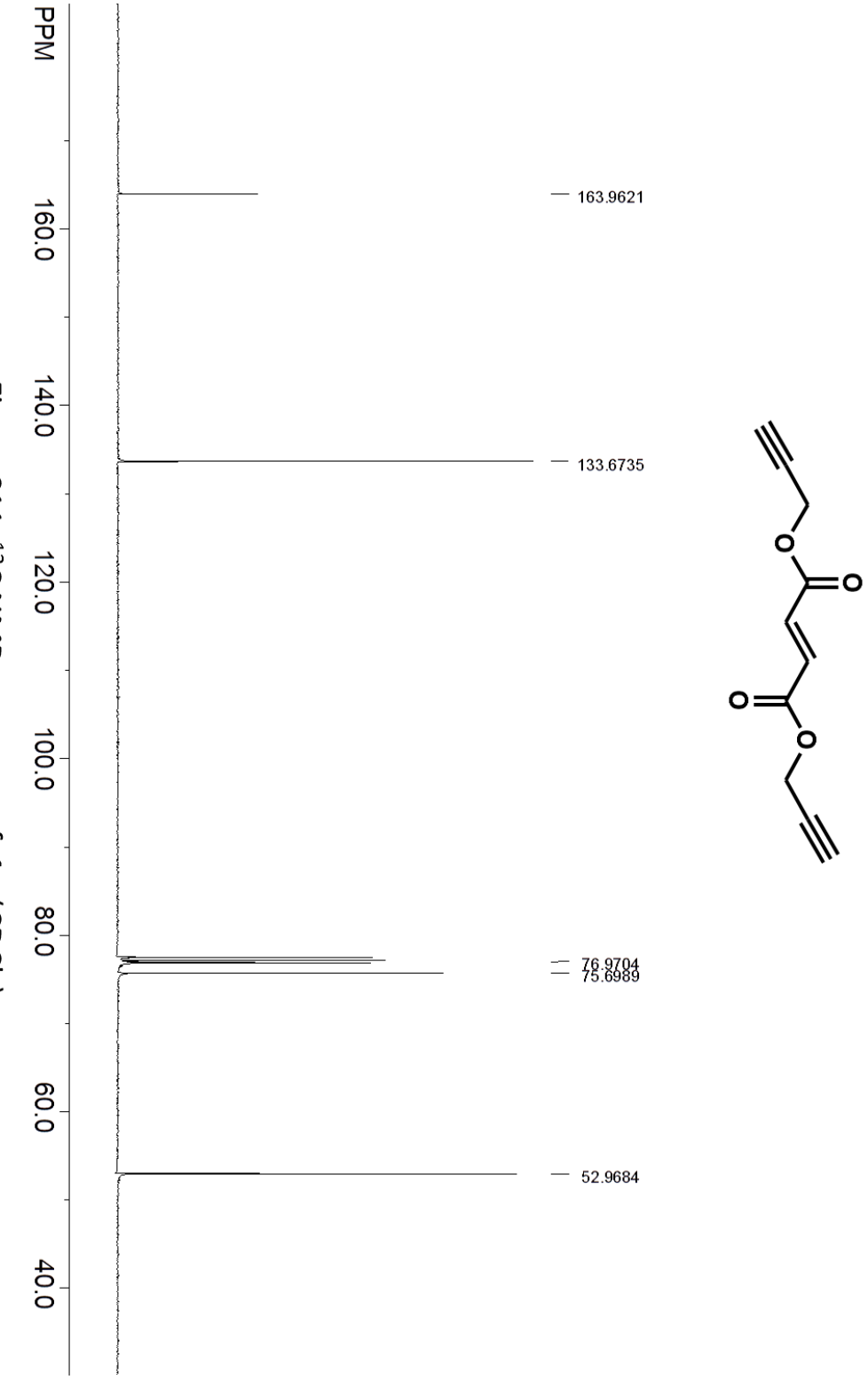

Figure S11. ^{13}C NMR spectrum of **1e** ($CDCl_3$)

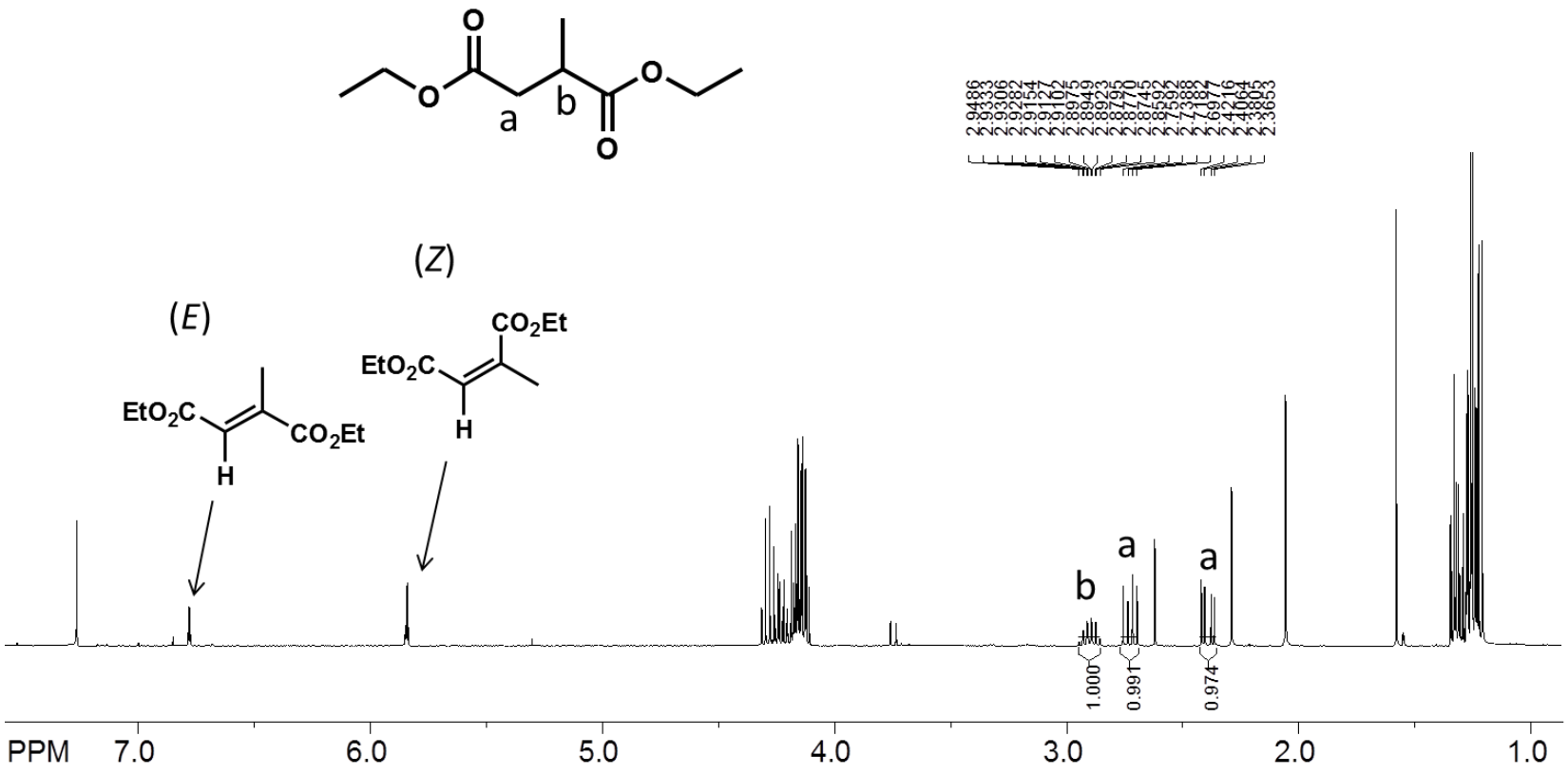

Figure S12. ^{1}H NMR spectrum of **3c** ($CDCl_3$)

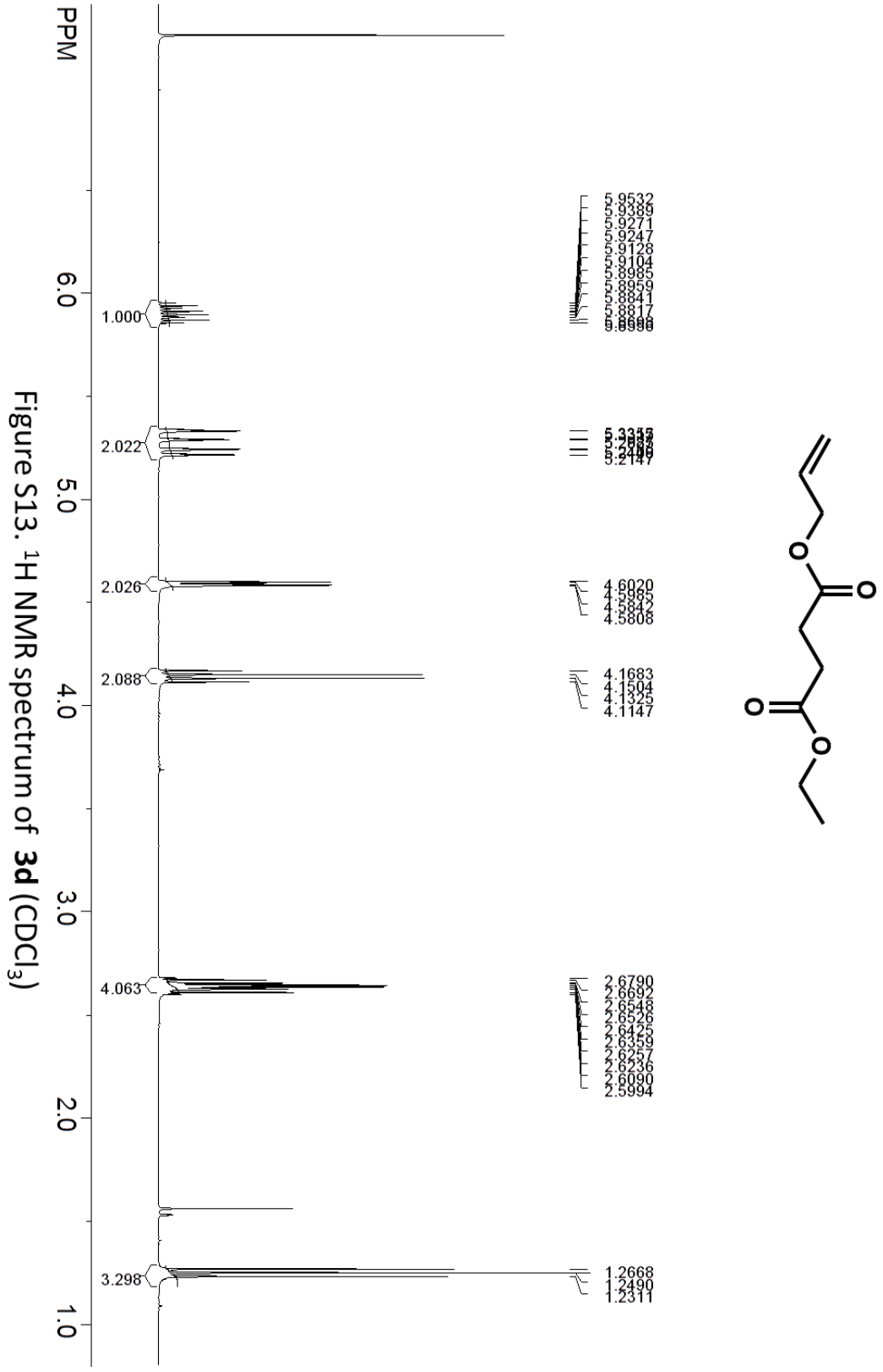

Figure S13. ^{1}H NMR spectrum of **3d** ($CDCl_3$)

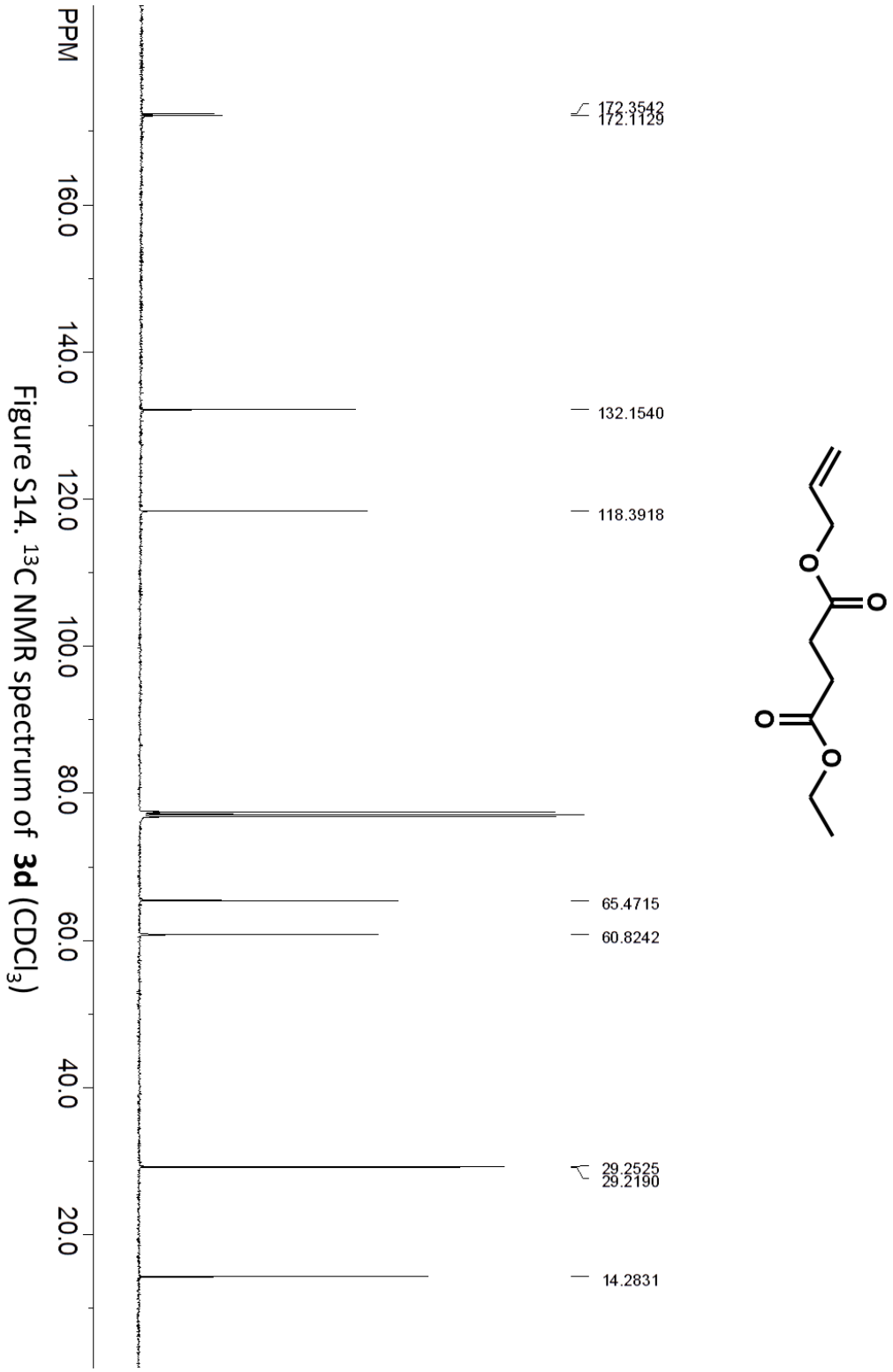

Figure S14. ^{13}C NMR spectrum of **3d** ($CDCl_3$)

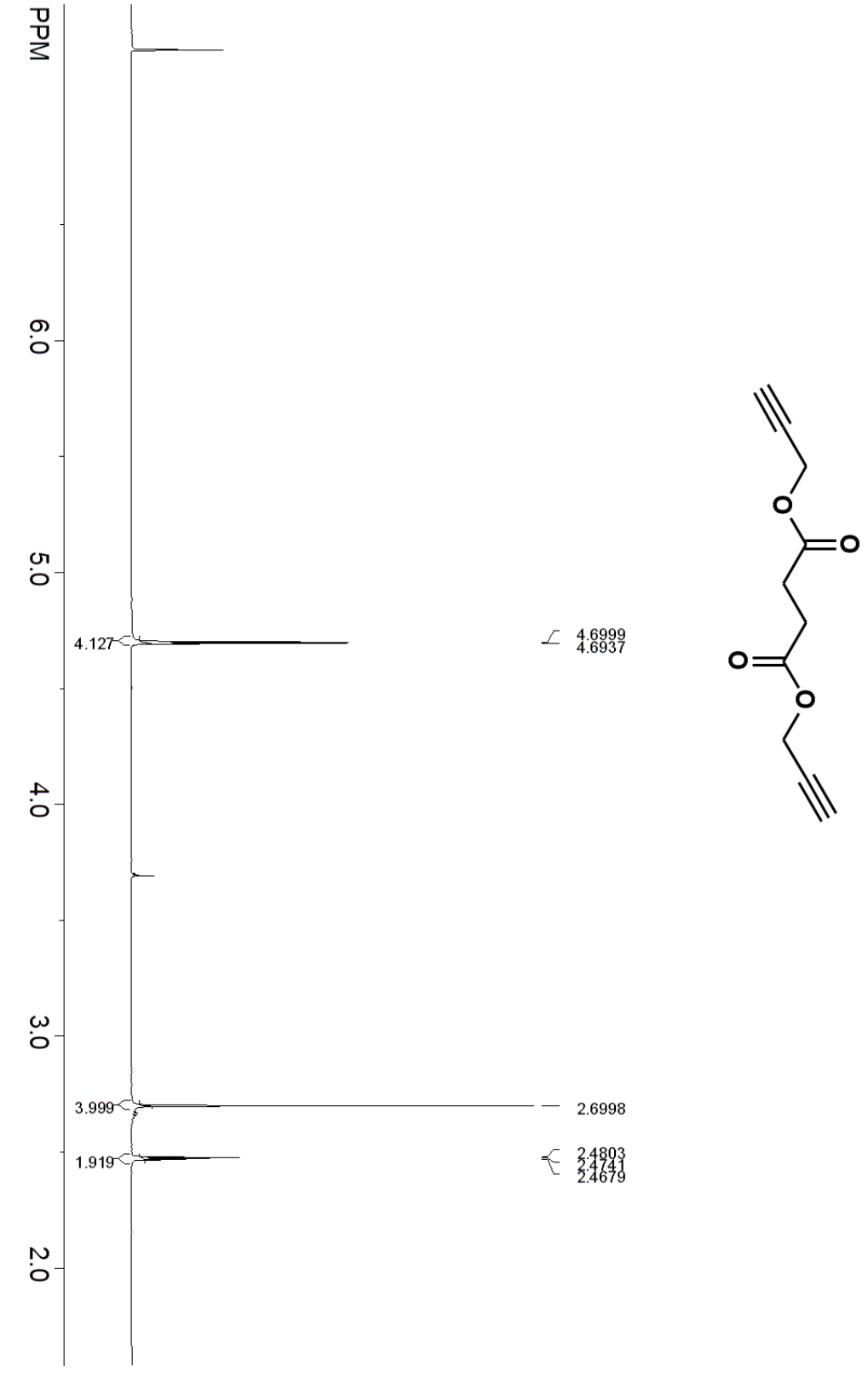

Figure S15. ^{1}H NMR spectrum of **3e** ($CDCl_3$)

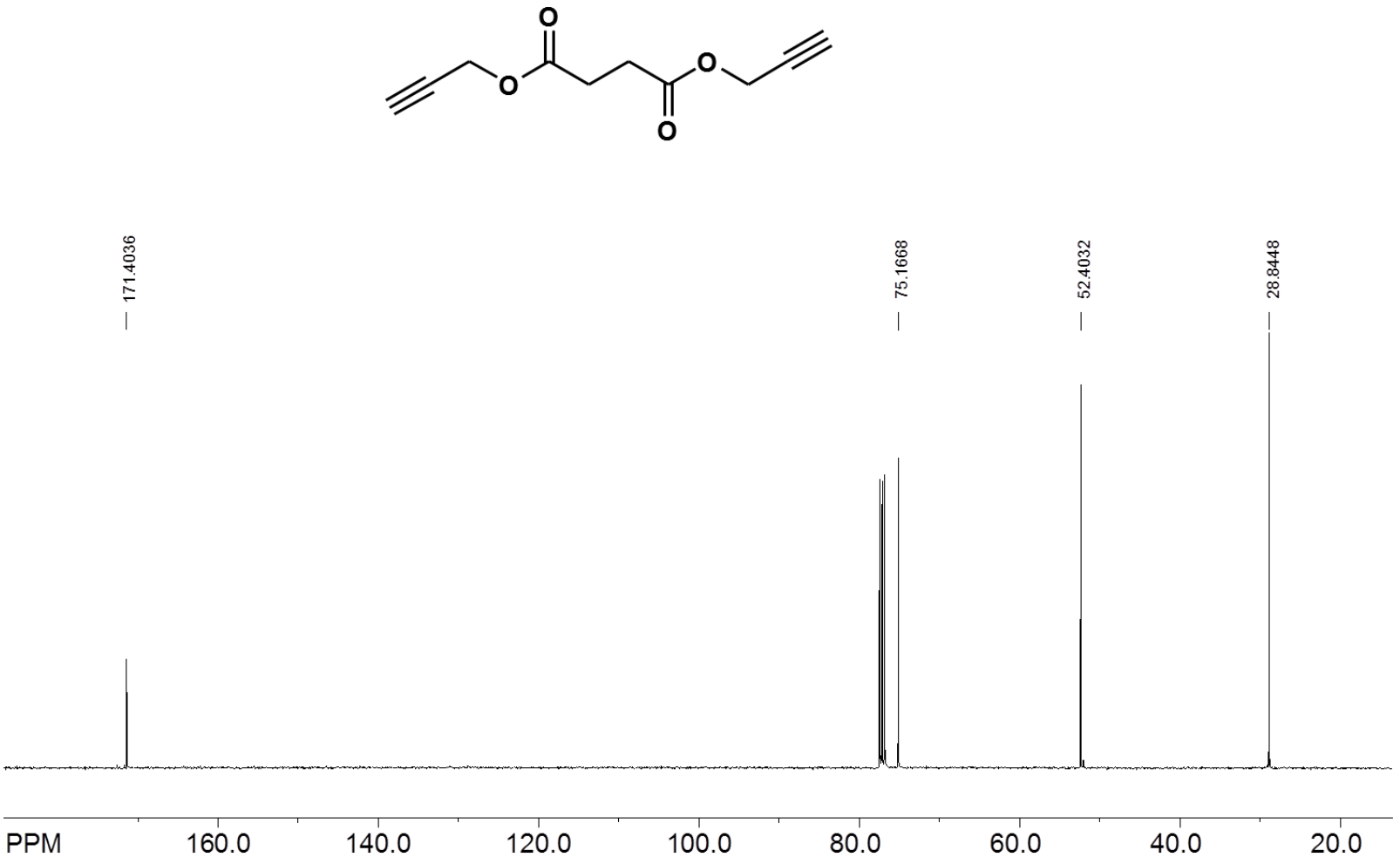

Figure S16. ^{13}C NMR spectrum of **3e** ($CDCl_3$)

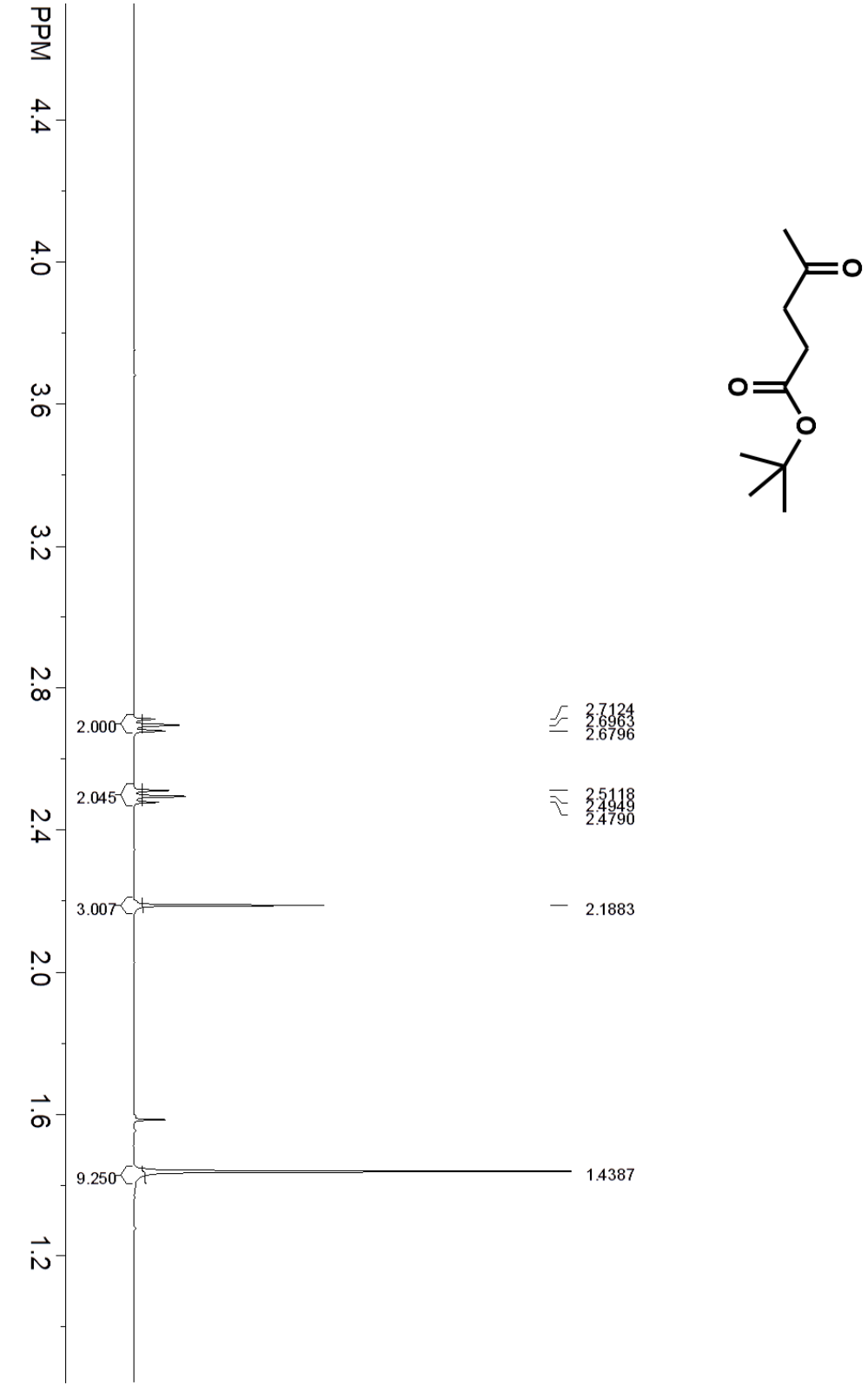

Figure S17. ^{1}H NMR spectrum of **3f** ($CDCl_3$)

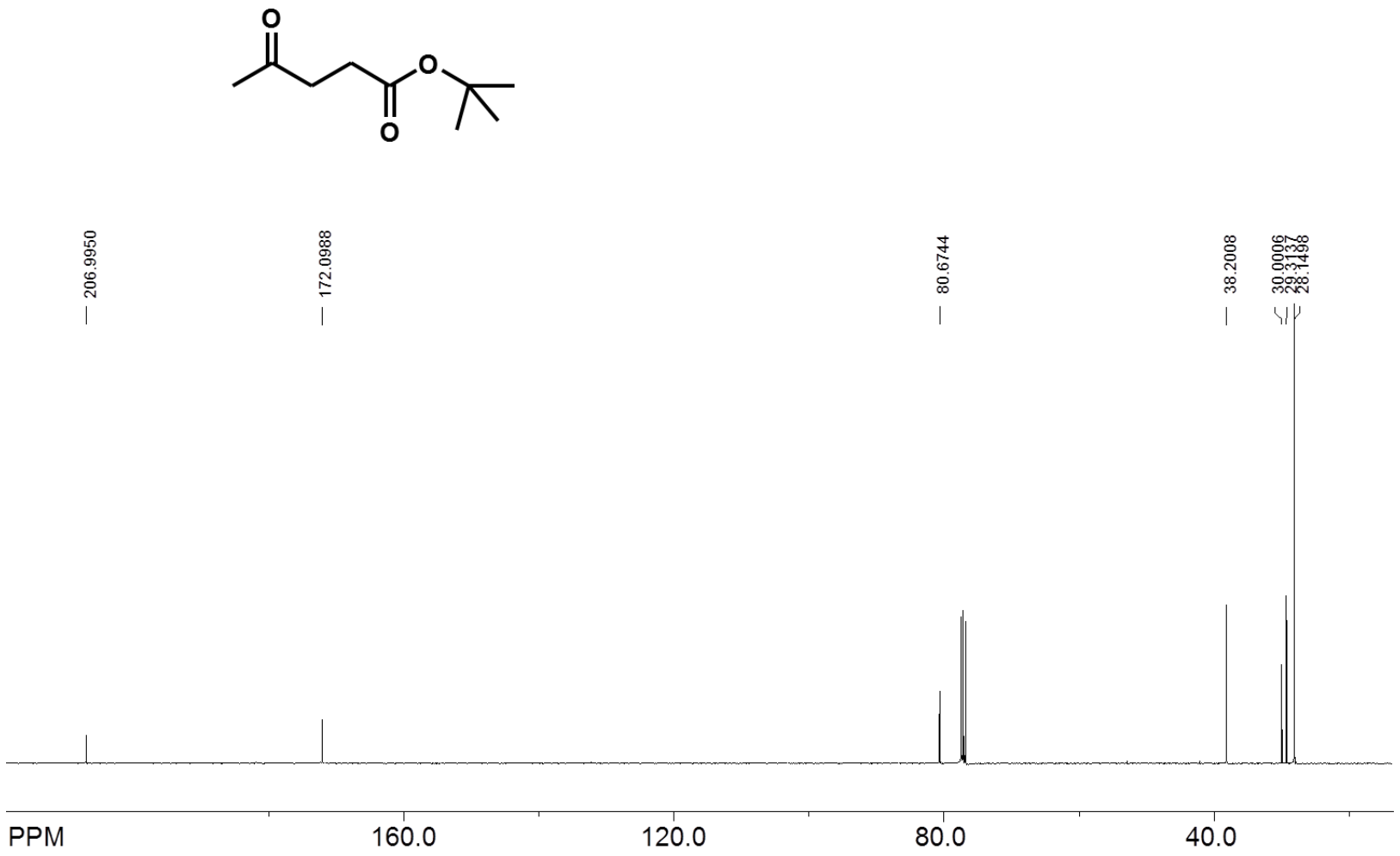

Figure S18. ^{13}C NMR spectrum of **3f** ($CDCl_3$)

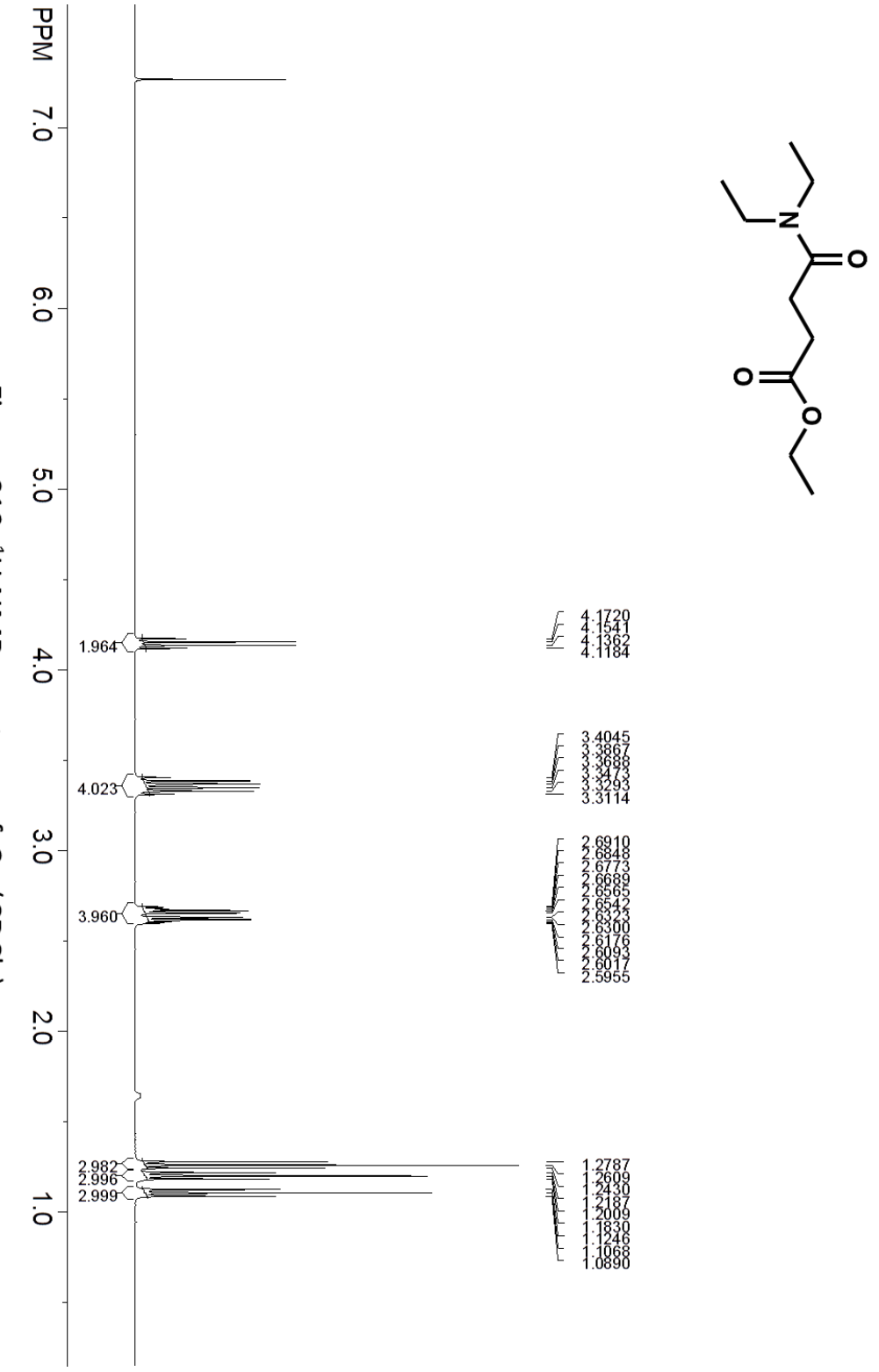

Figure S19. ^{1}H NMR spectrum of **3g** ($CDCl_3$)

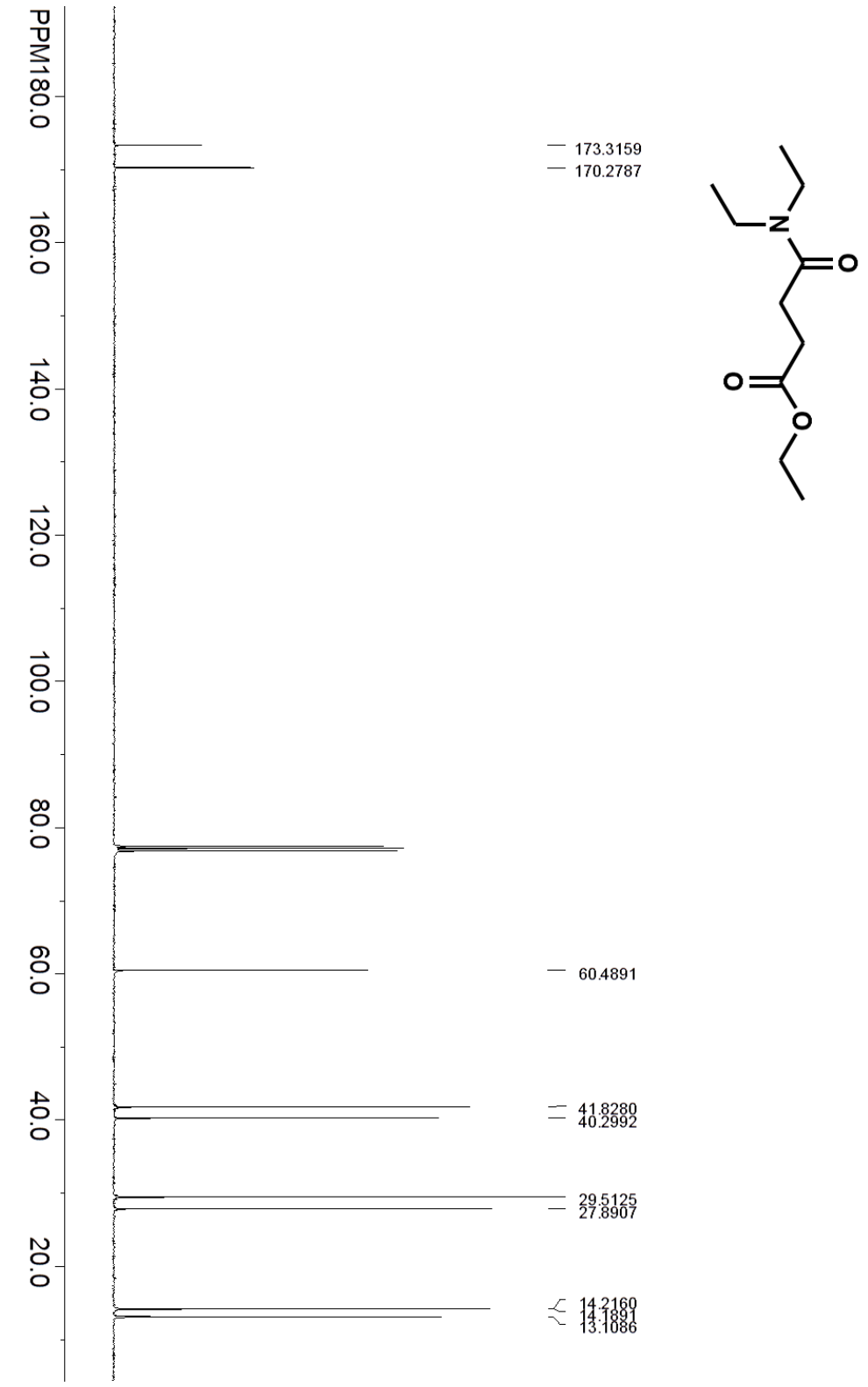

Figure S20. ^{13}C NMR spectrum of **3g** ($CDCl_3$)

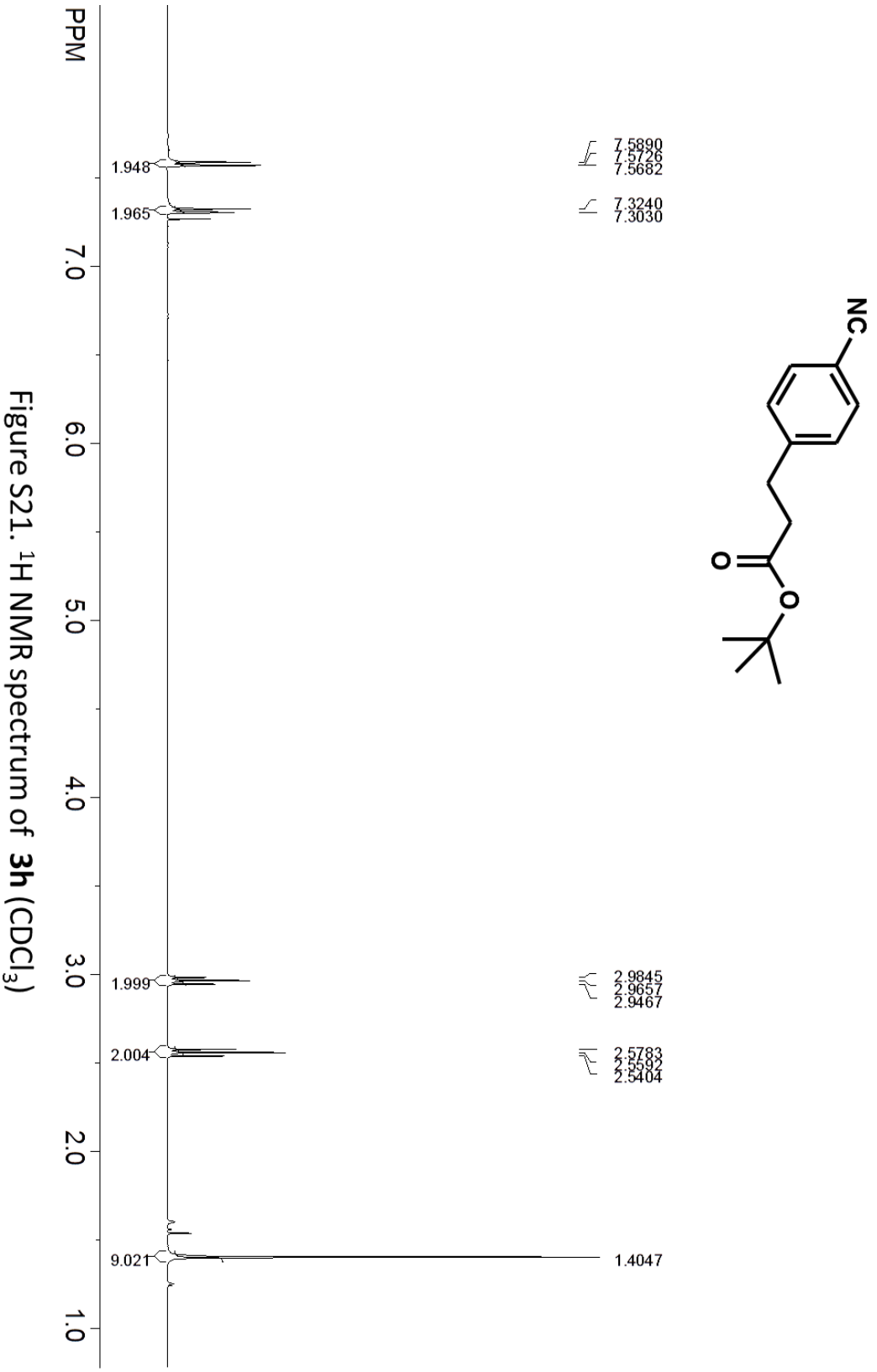

Figure S21. ^{1}H NMR spectrum of **3h** ($CDCl_3$)

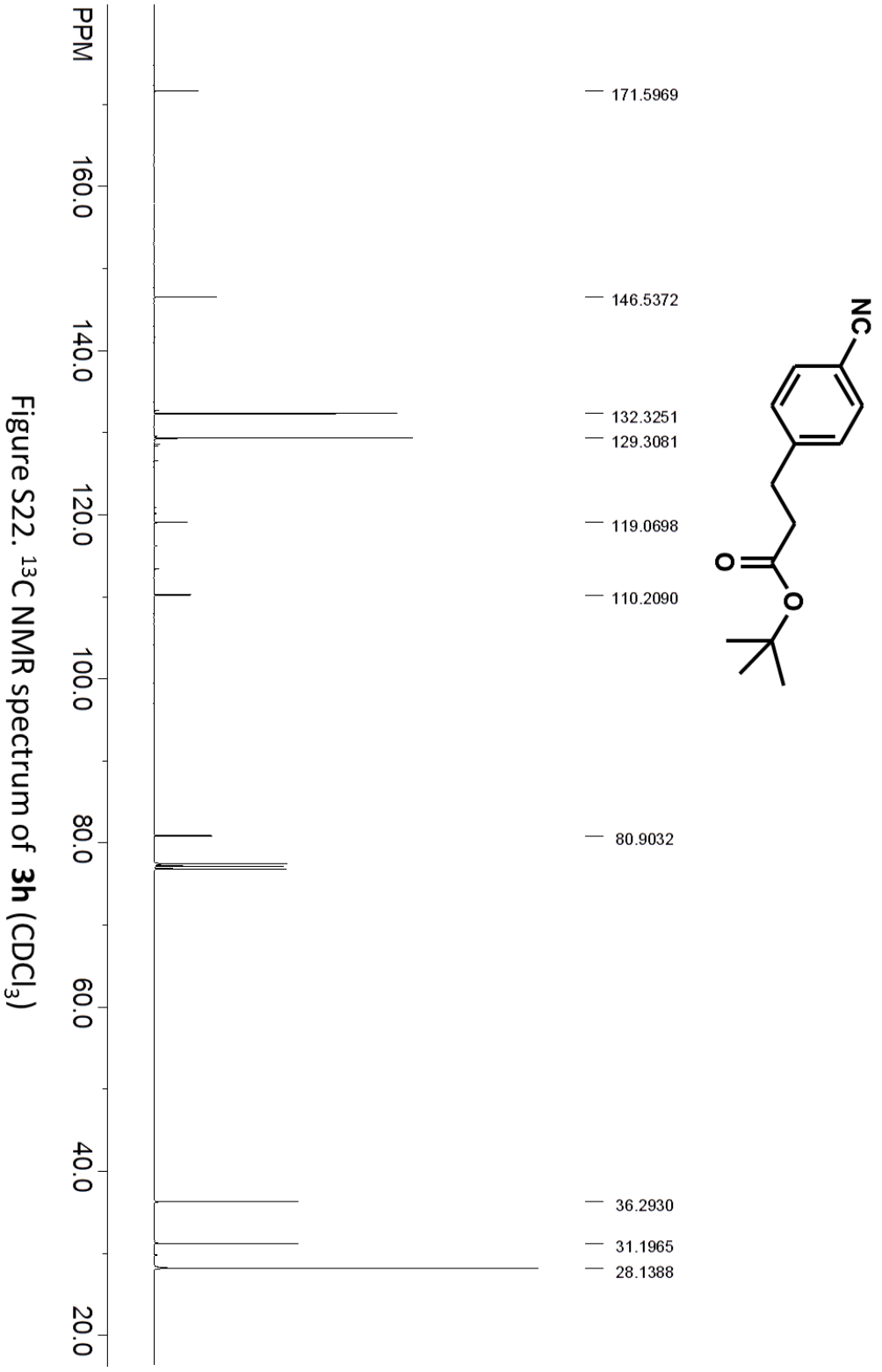

Figure S22. ^{13}C NMR spectrum of **3h** ($CDCl_3$)

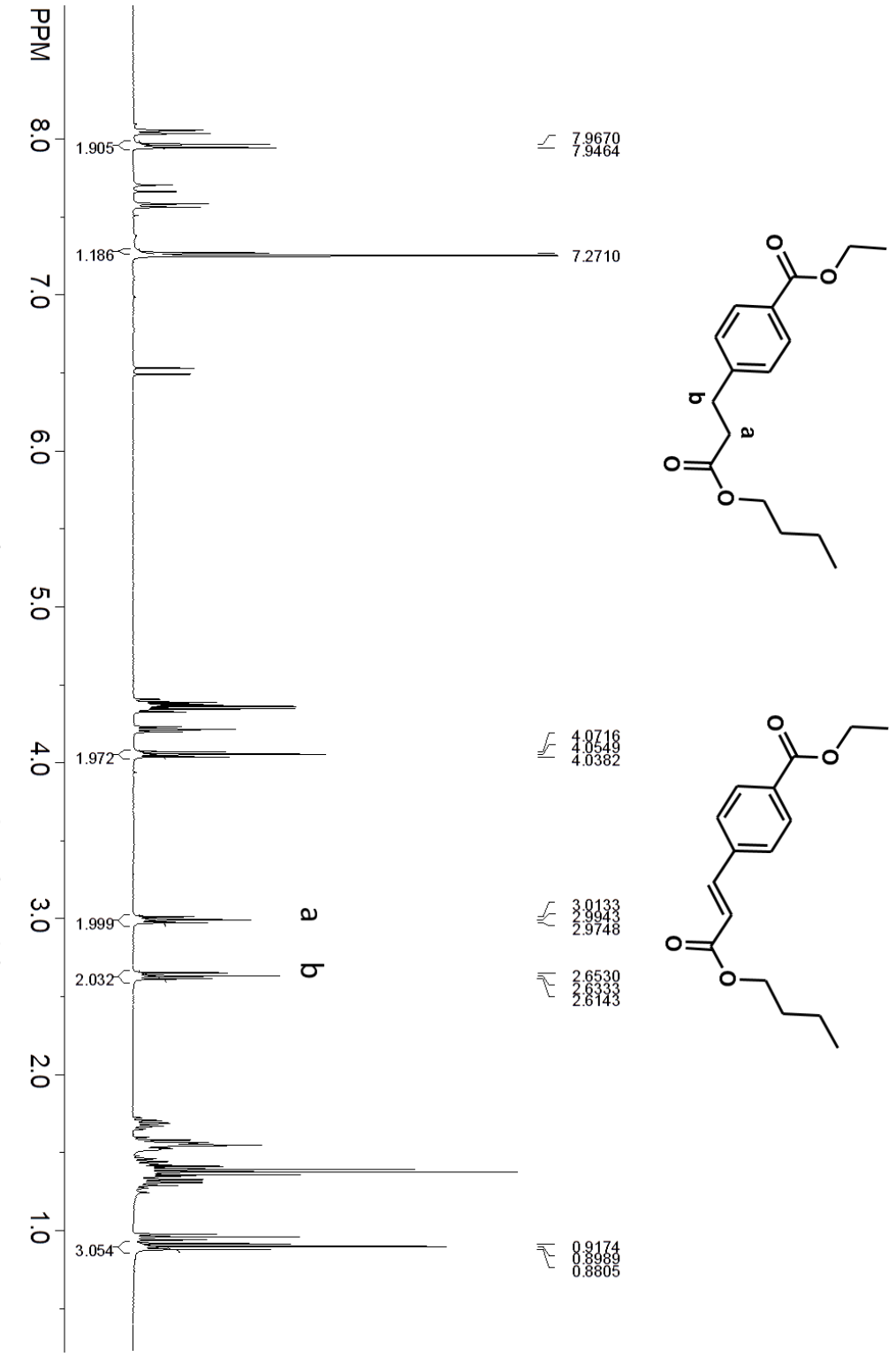

Figure S23. ^{1}H NMR spectrum of **3i** ($CDCl_3$)

Figure S24. ^{1}H NMR spectrum of **3j** ($CDCl_3$)

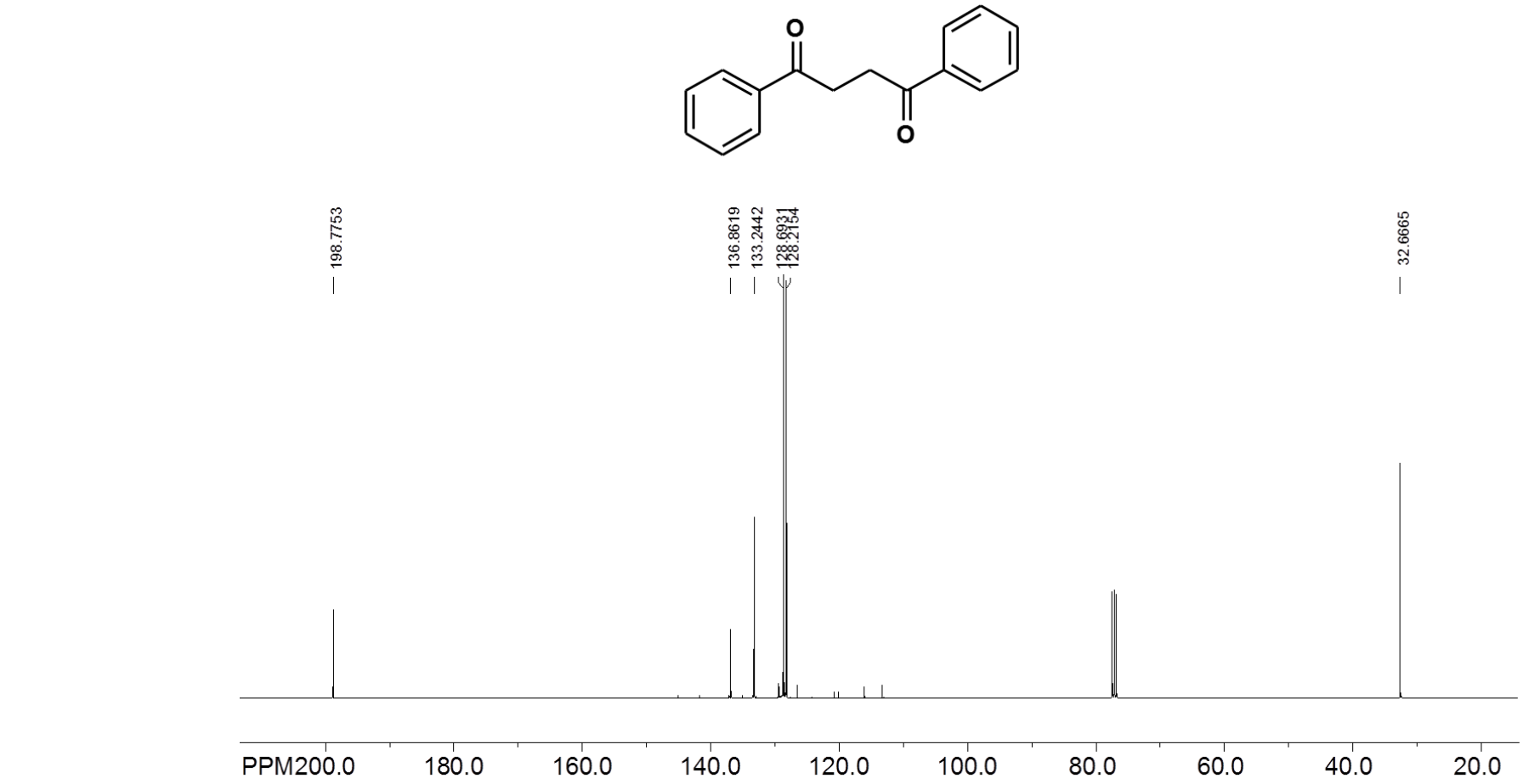

Figure S25. ^{13}C NMR spectrum of **3j** ($CDCl_3$)

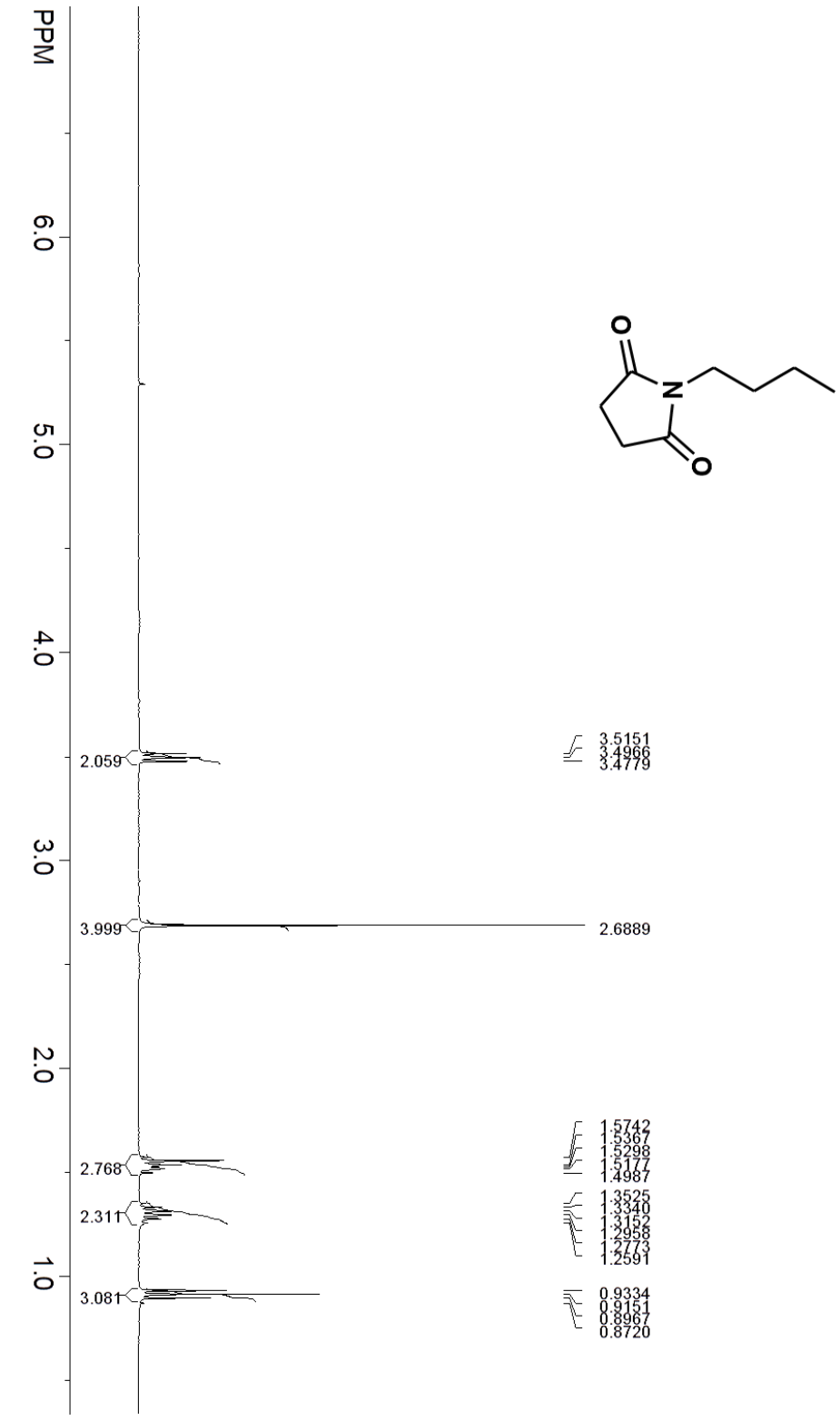

Figure S26. ^{1}H NMR spectrum of **3k** ($CDCl_3$)

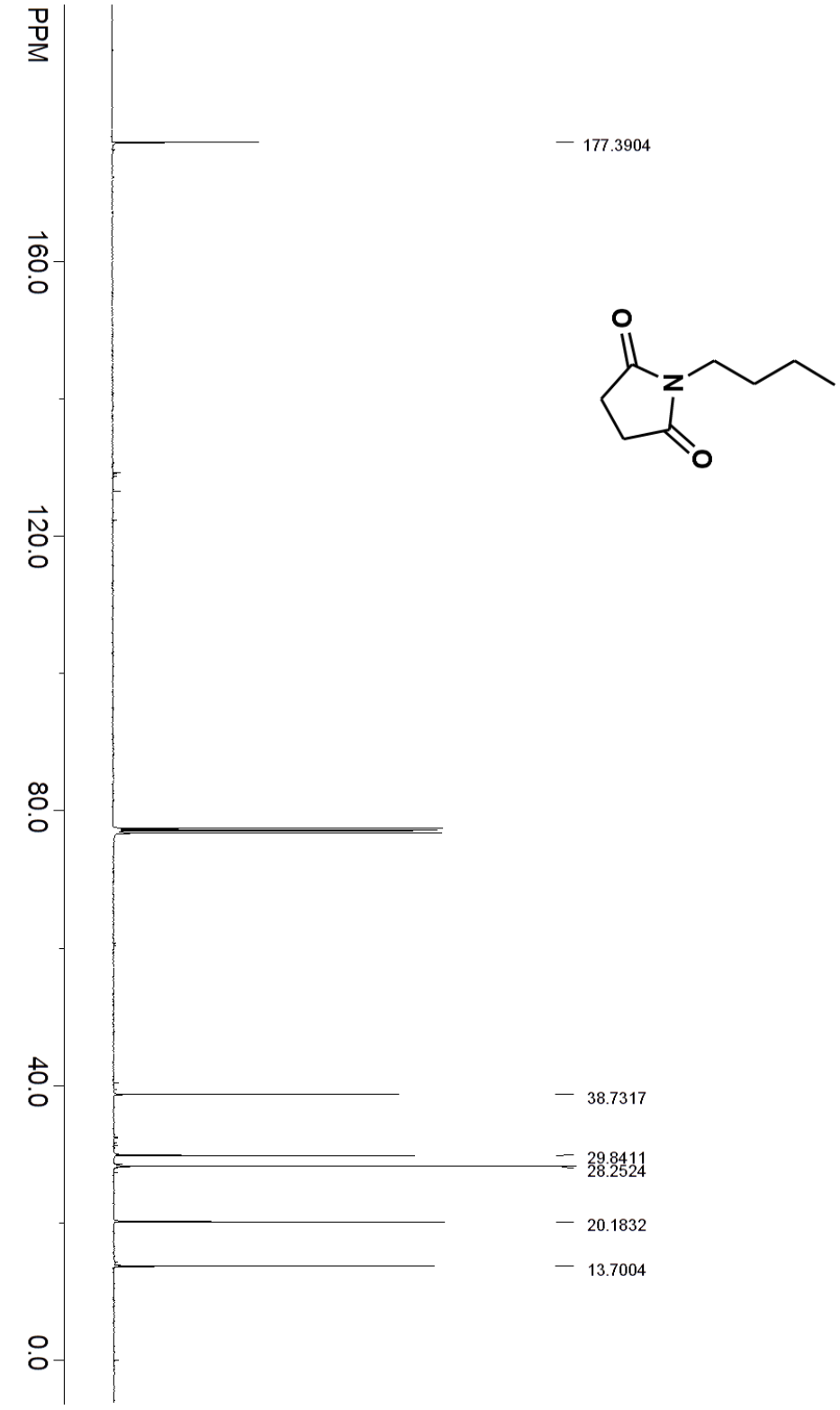

Figure S27. ^{1}H NMR spectrum of **3k** ($CDCl_3$)

Figure S28. ^{1}H NMR spectrum of **3l** ($CDCl_3$)

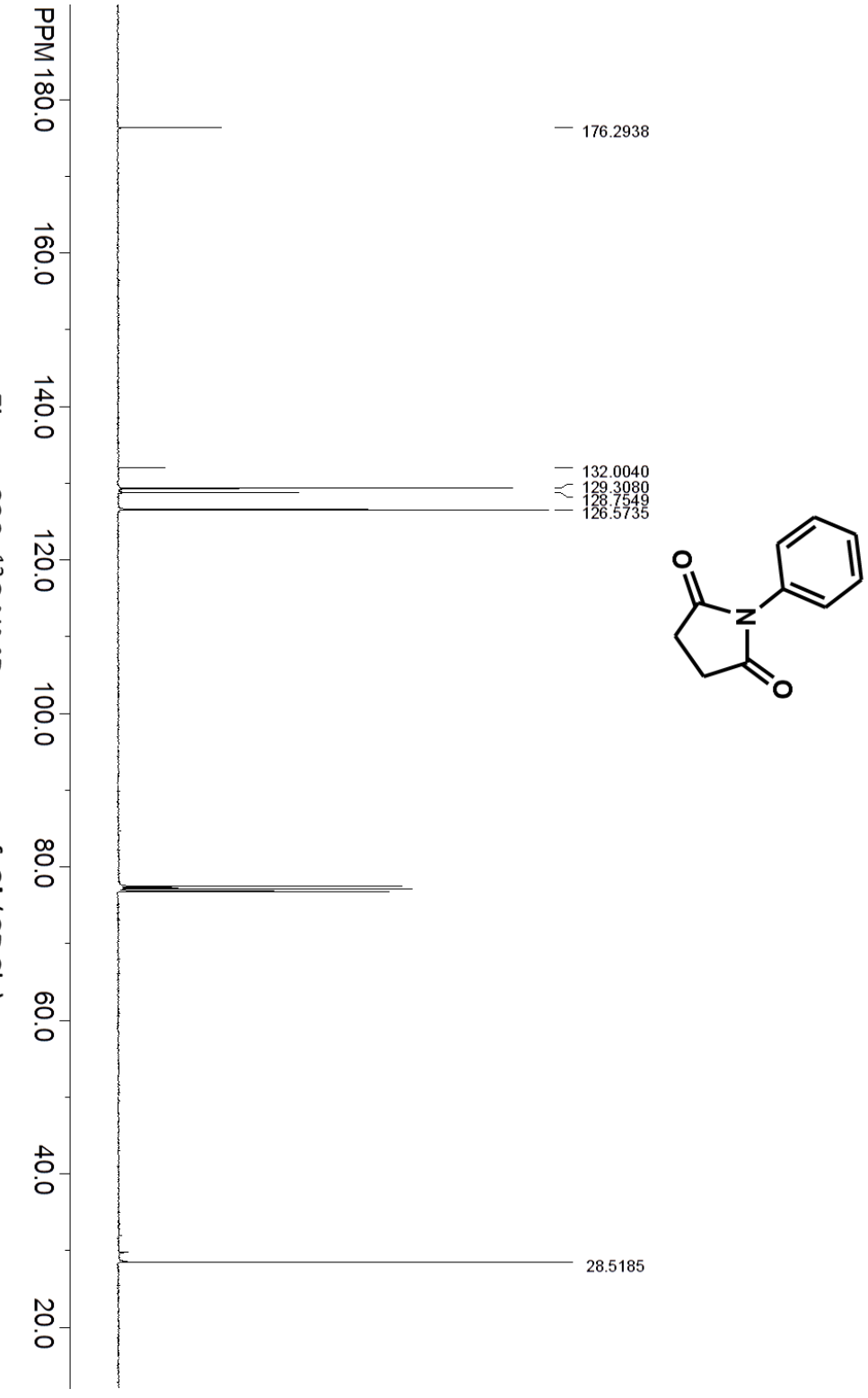

Figure S29. ^{13}C NMR spectrum of **3l** ($CDCl_3$)

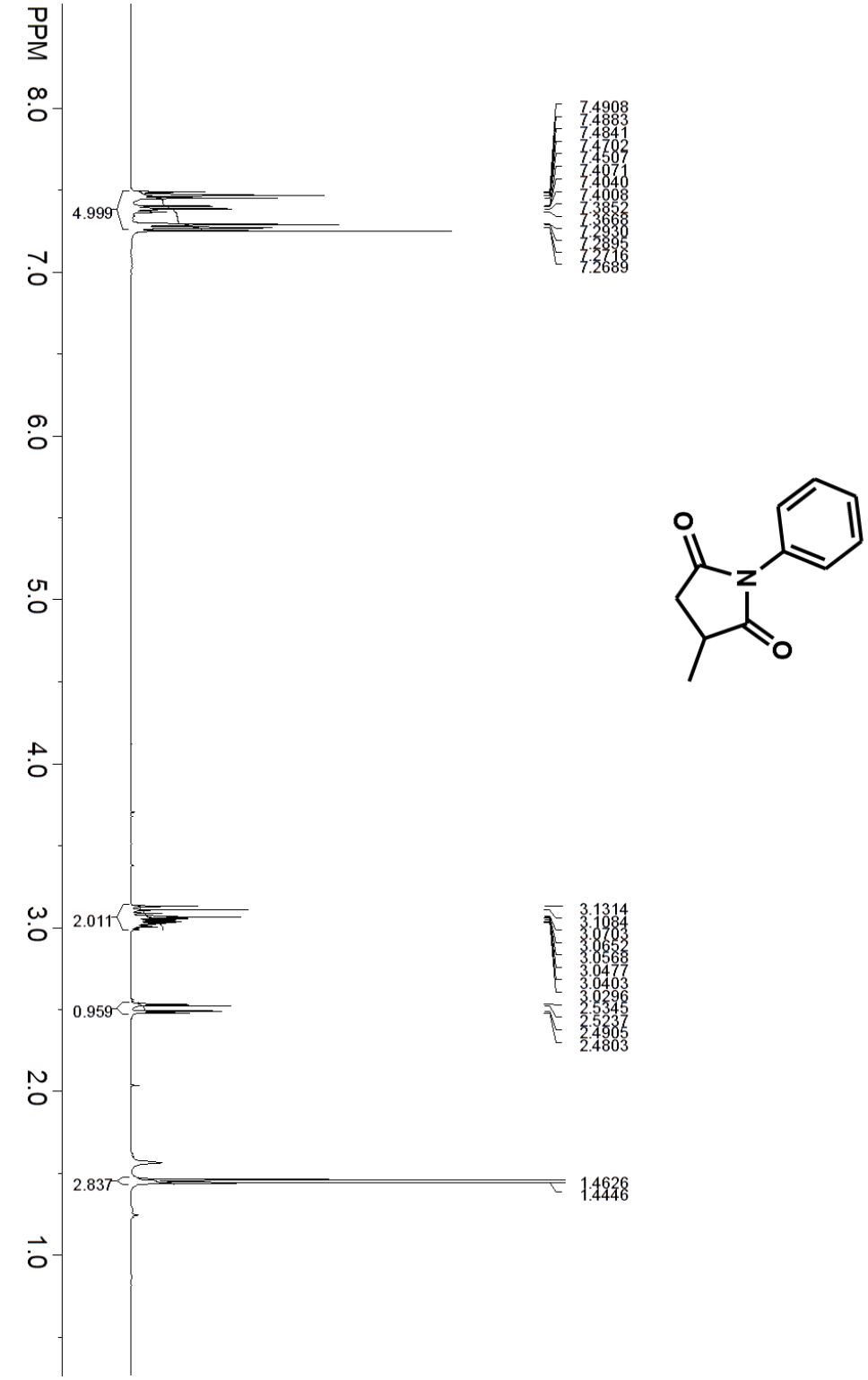

Figure S30. ^{1}H NMR spectrum of **3m** ($CDCl_3$)

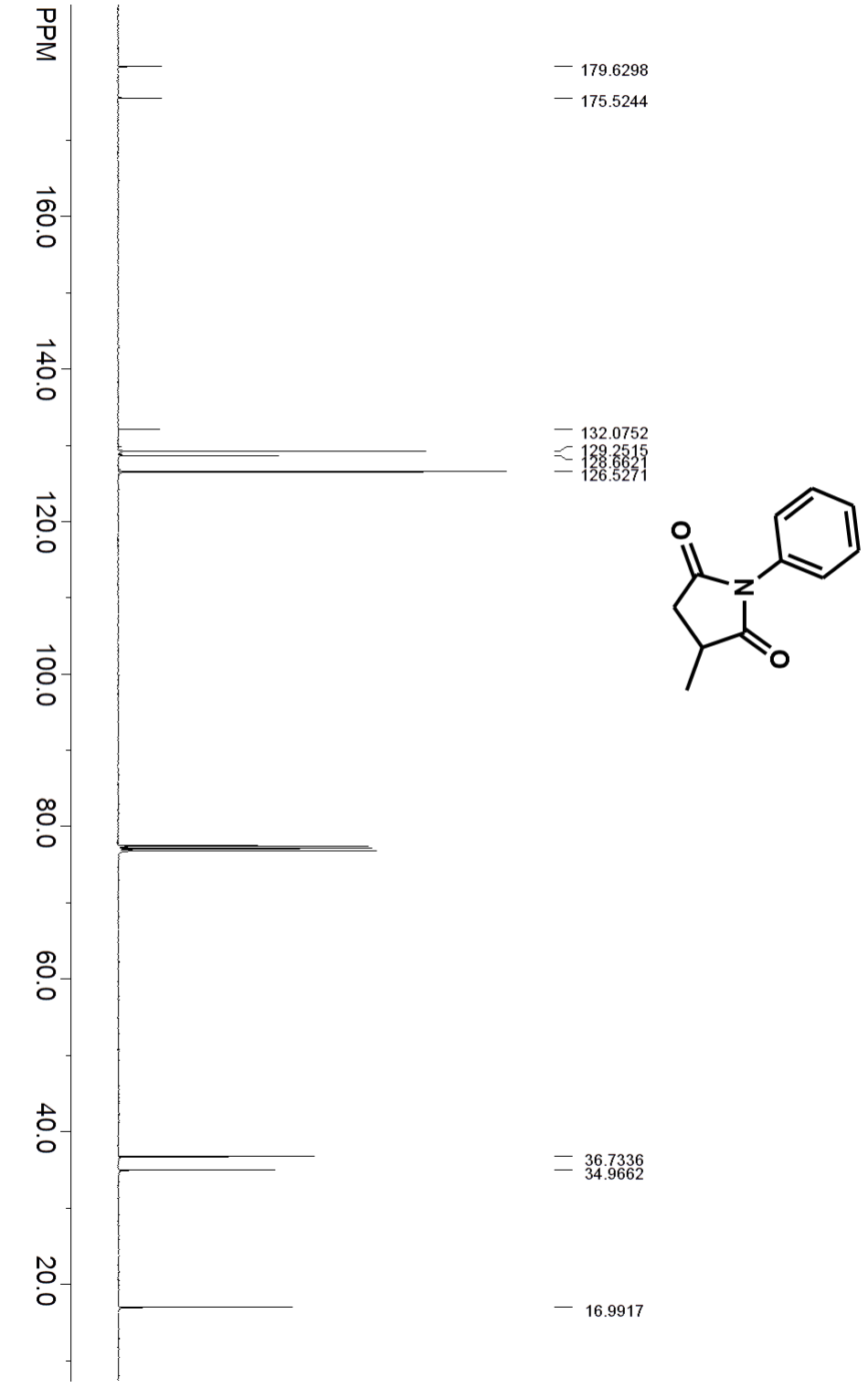

Figure S31. ^{13}C NMR spectrum of **3m** ($CDCl_3$)

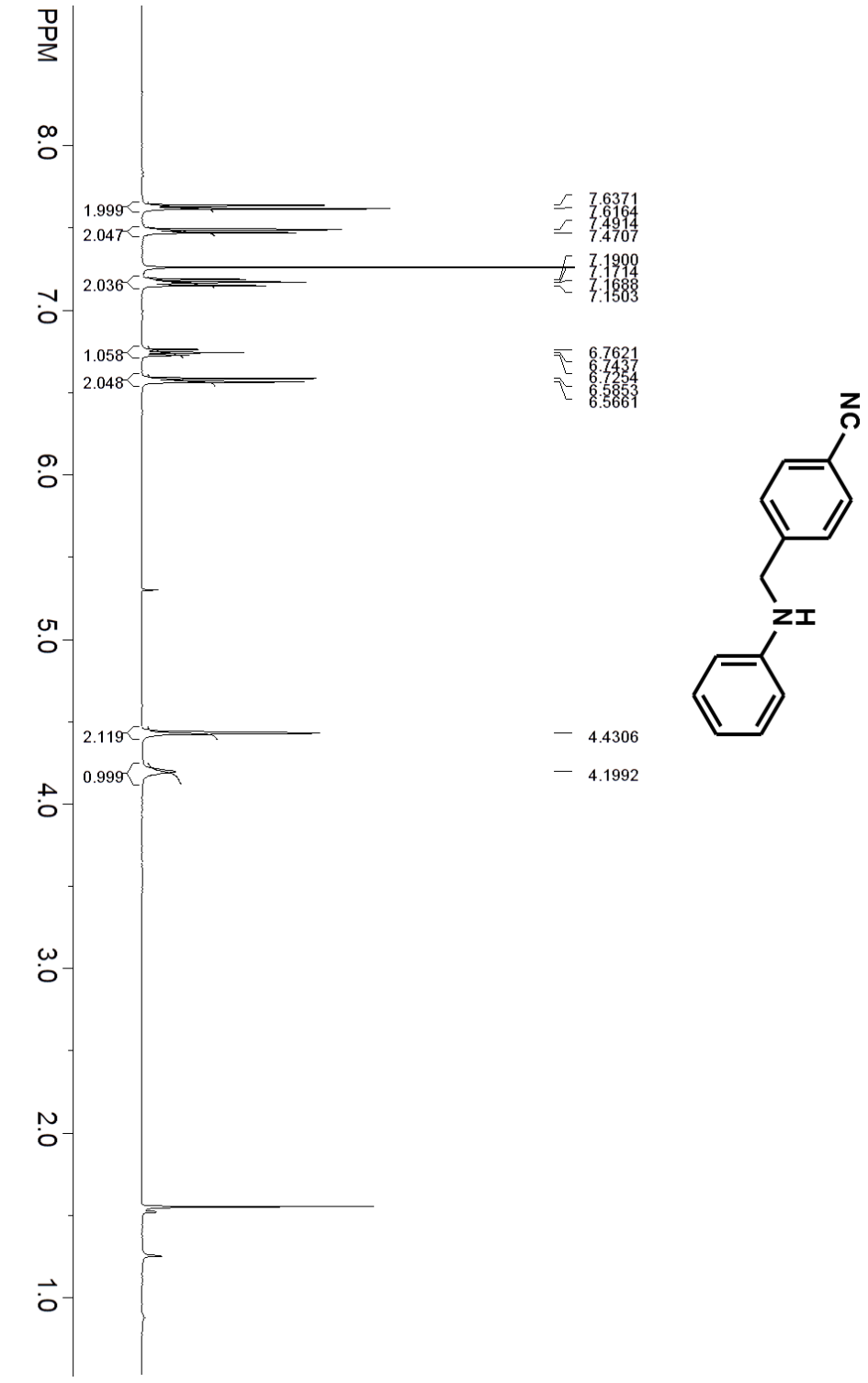

Figure S32. ^{1}H NMR spectrum of **3n** ($CDCl_3$)

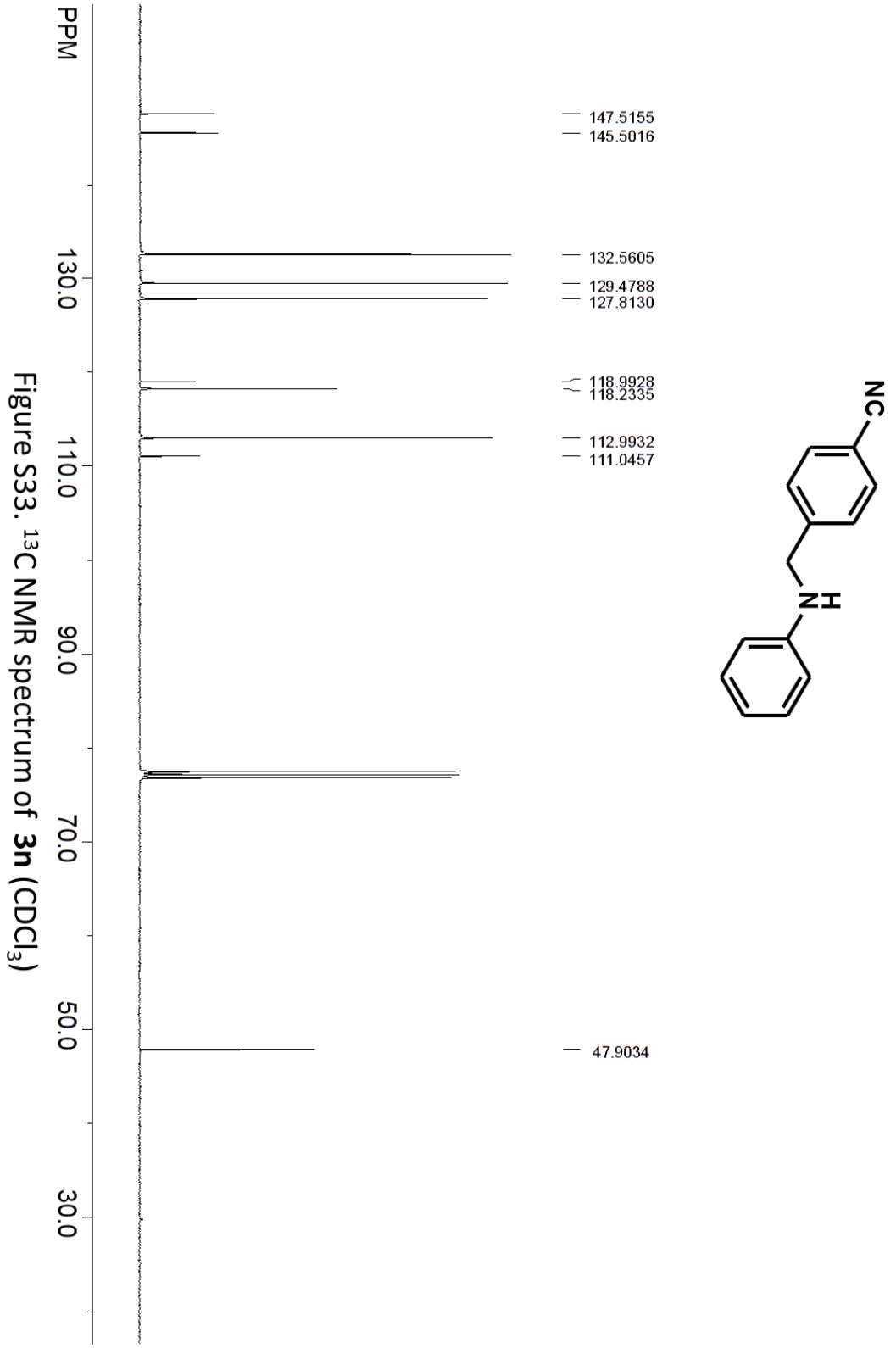

Figure S33. ^{13}C NMR spectrum of **3n** ($CDCl_3$)

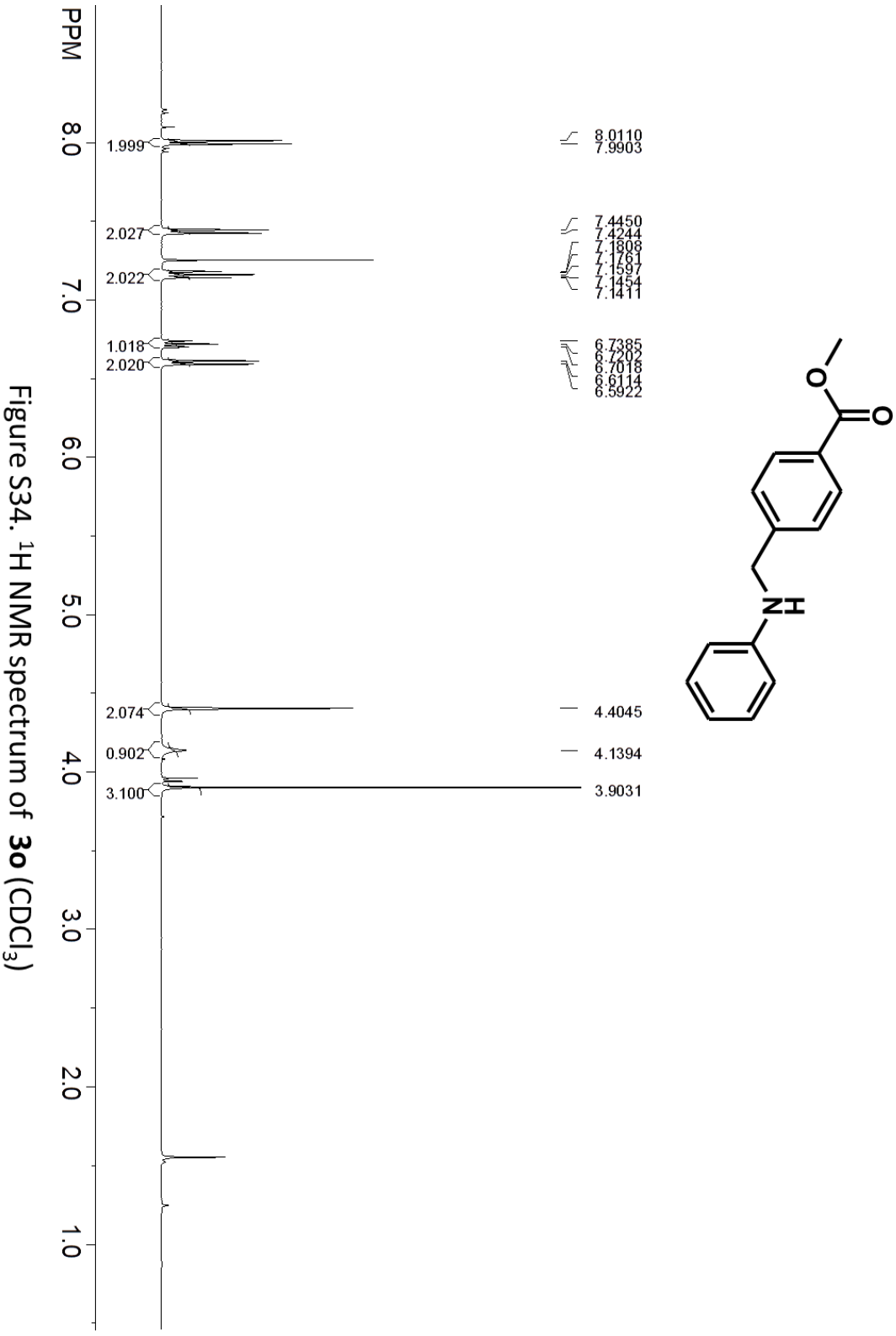

Figure S34. ^{1}H NMR spectrum of **3o** ($CDCl_3$)

Figure S35. ^{13}C NMR spectrum of **3o** ($CDCl_3$)

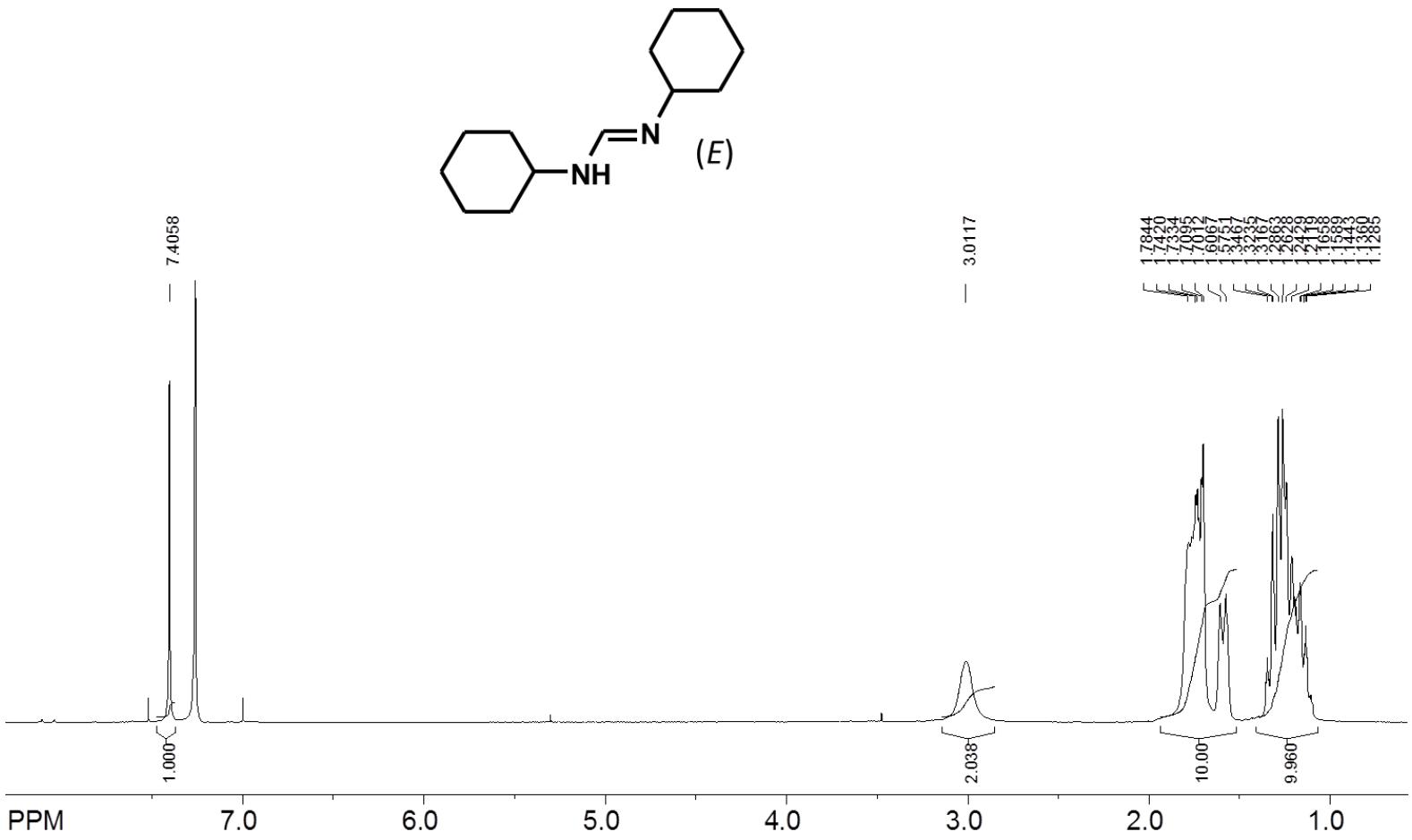

Figure S36. ^{13}C NMR spectrum of **3p** ($CDCl_3$)

Figure S37. ^{13}C NMR spectrum of **3p** ($CDCl_3$)

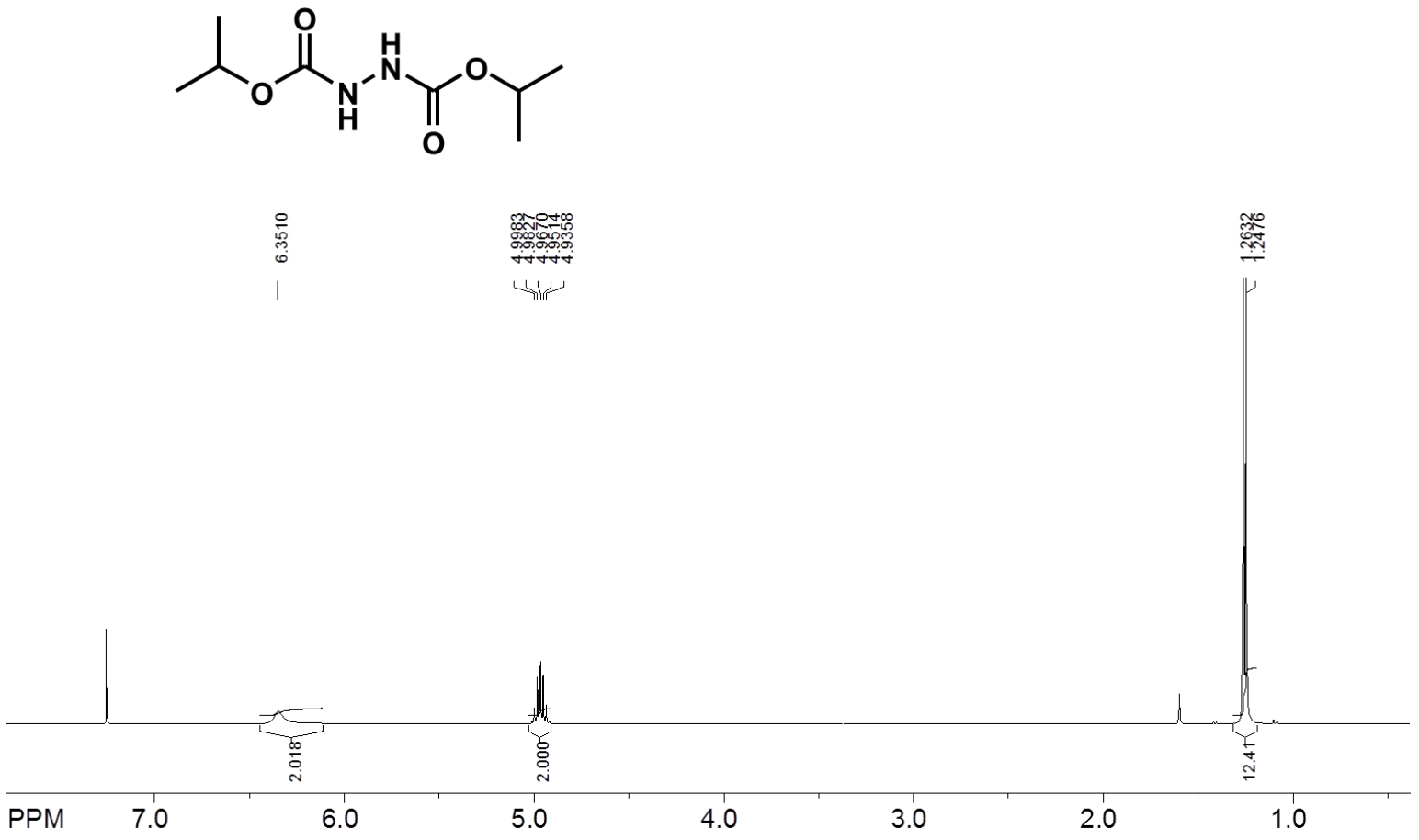

Figure S38. ^{1}H NMR spectrum of **3q** ($CDCl_3$)

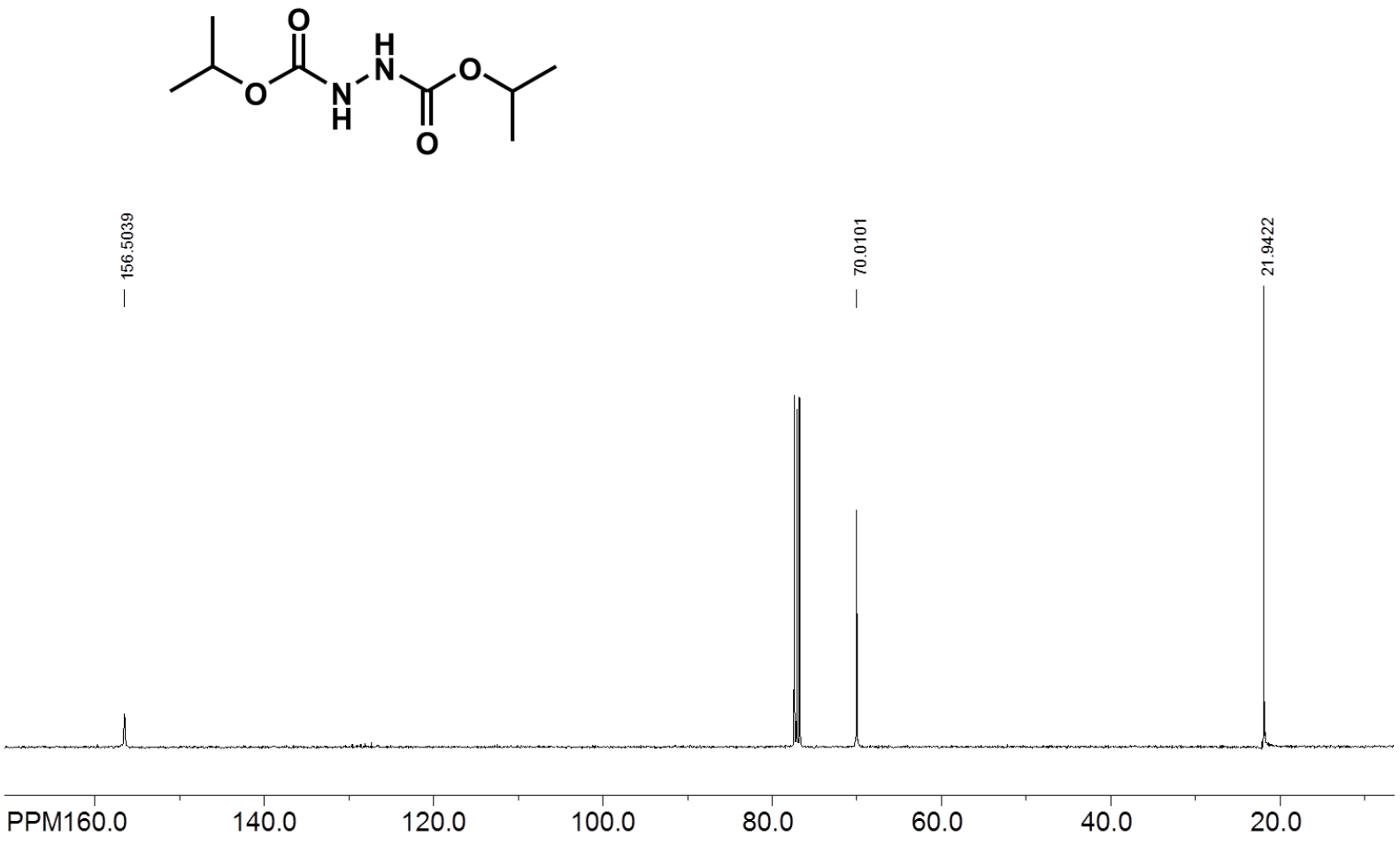

Figure S39. ^{13}C NMR spectrum of **3q** ($CDCl_3$)

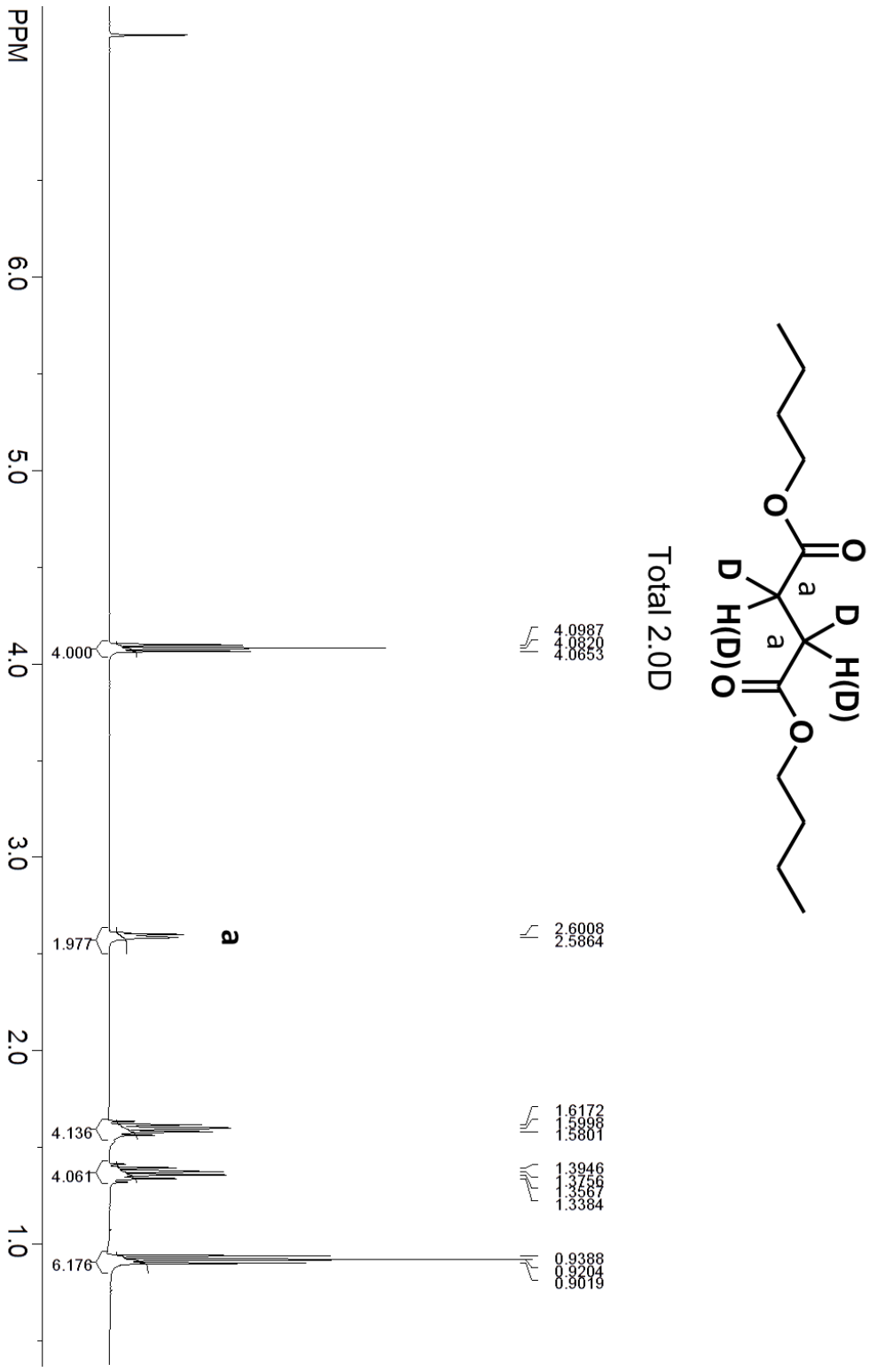

Figure S40. ^{1}H NMR spectrum of **3r** ($CDCl_3$)

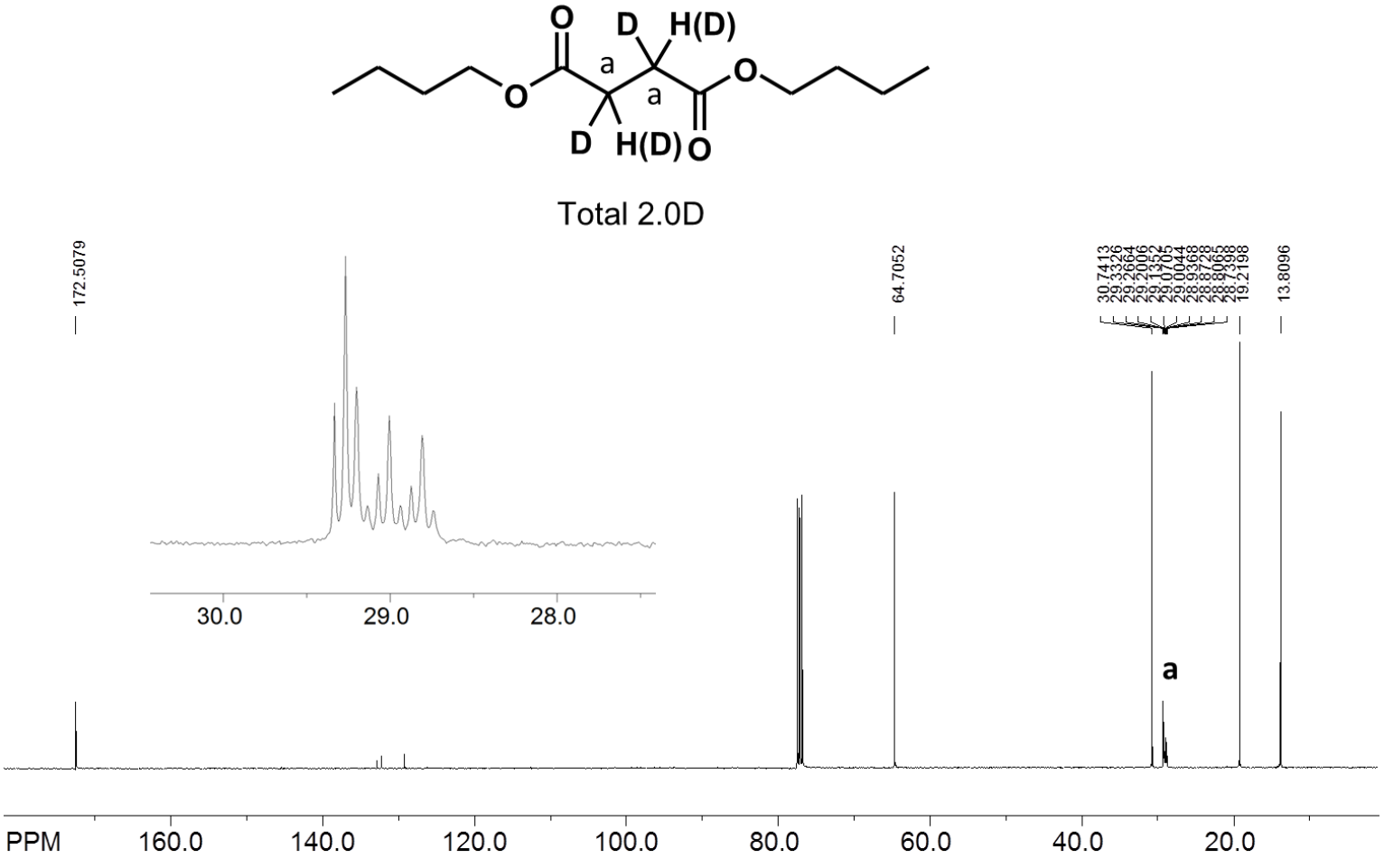

Figure S41. ^{13}C NMR spectrum of **3r** ($CDCl_3$)

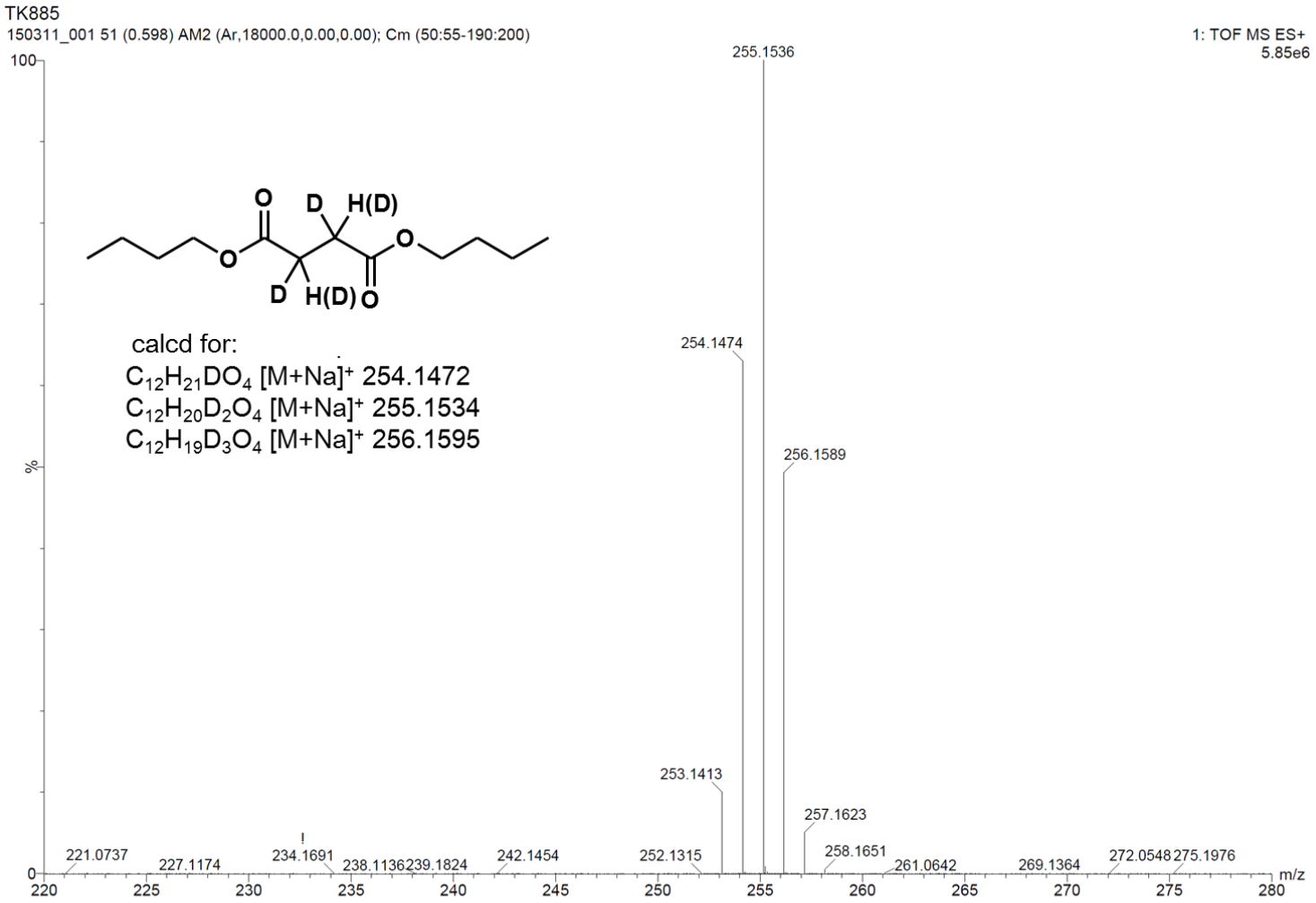

Figure S42. ESI-MS spectrum of **3r**

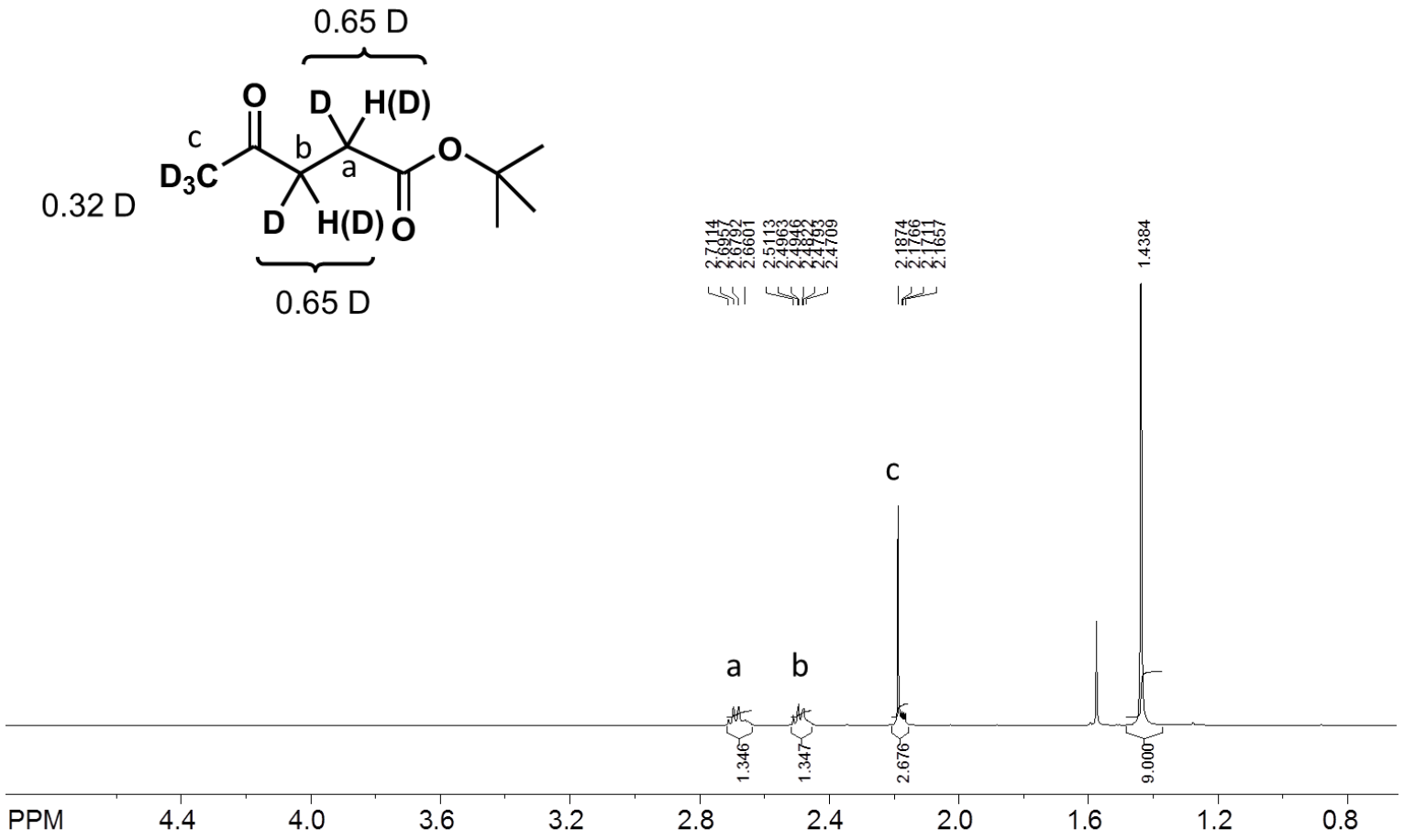

Figure S43. ^{1}H NMR spectrum of **3s** ($CDCl_3$)

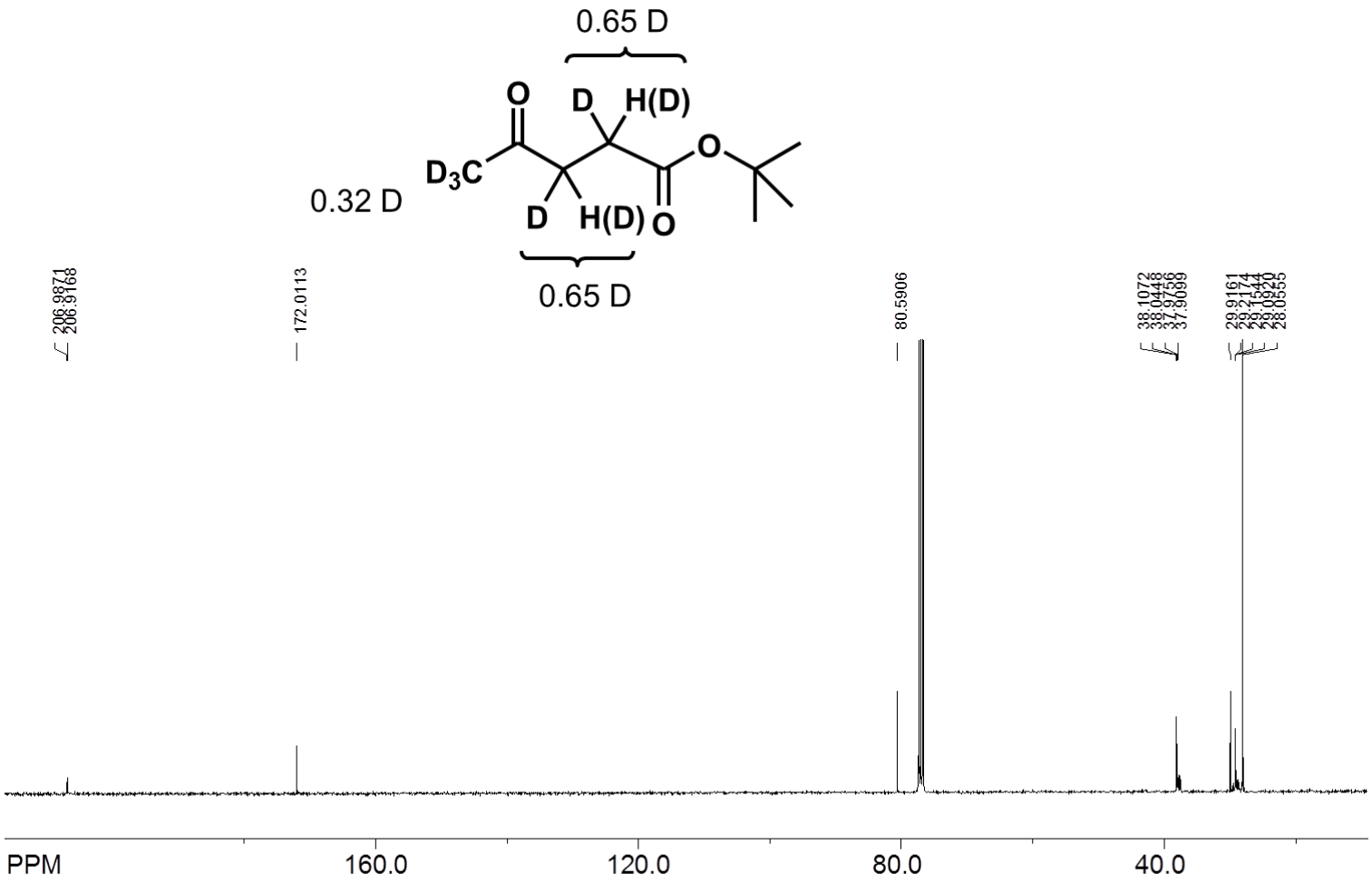

Figure S44. ^{13}C NMR spectrum of **3s** ($CDCl_3$)

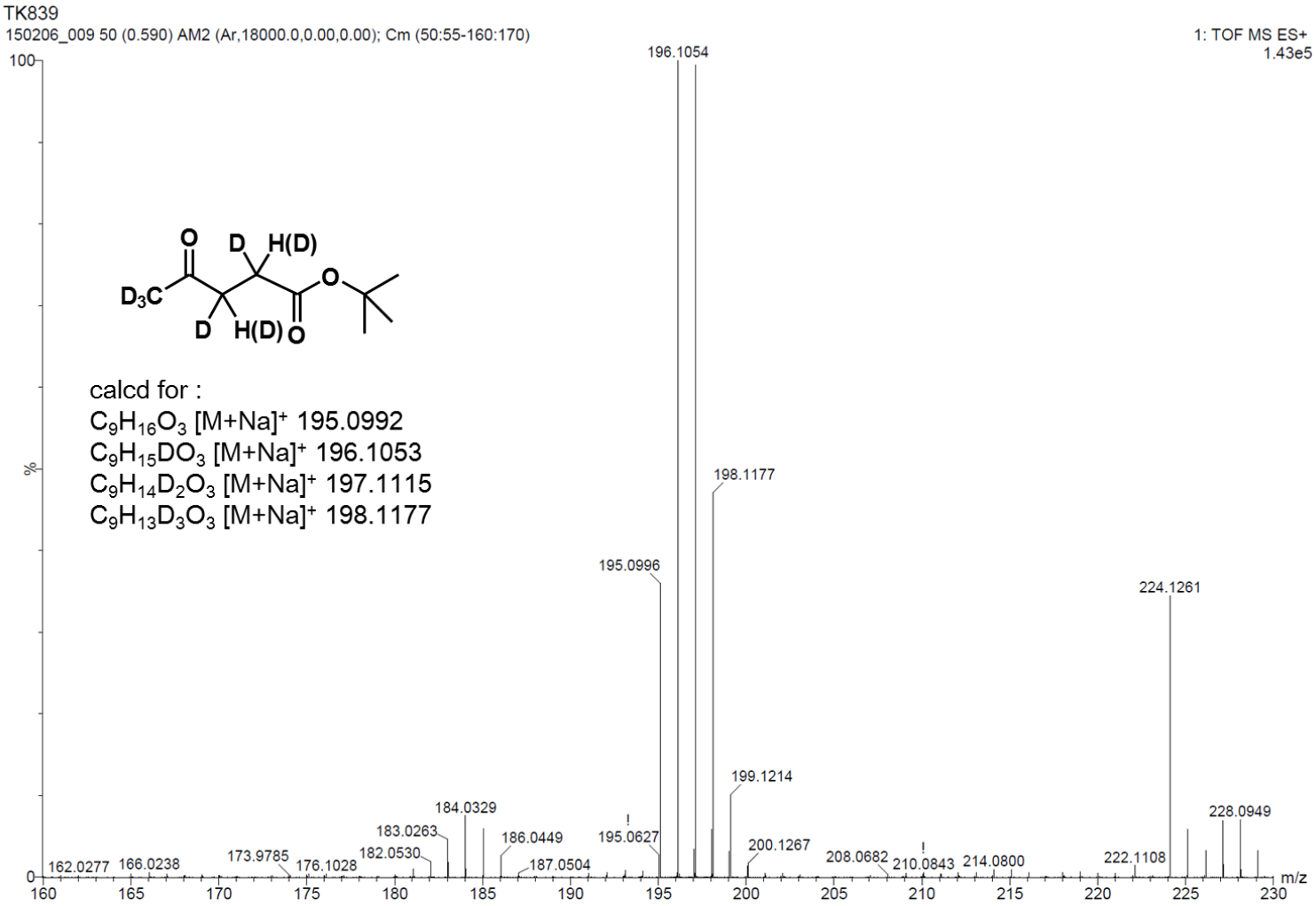

Figure S45. ESI-MS spectrum of **3s**

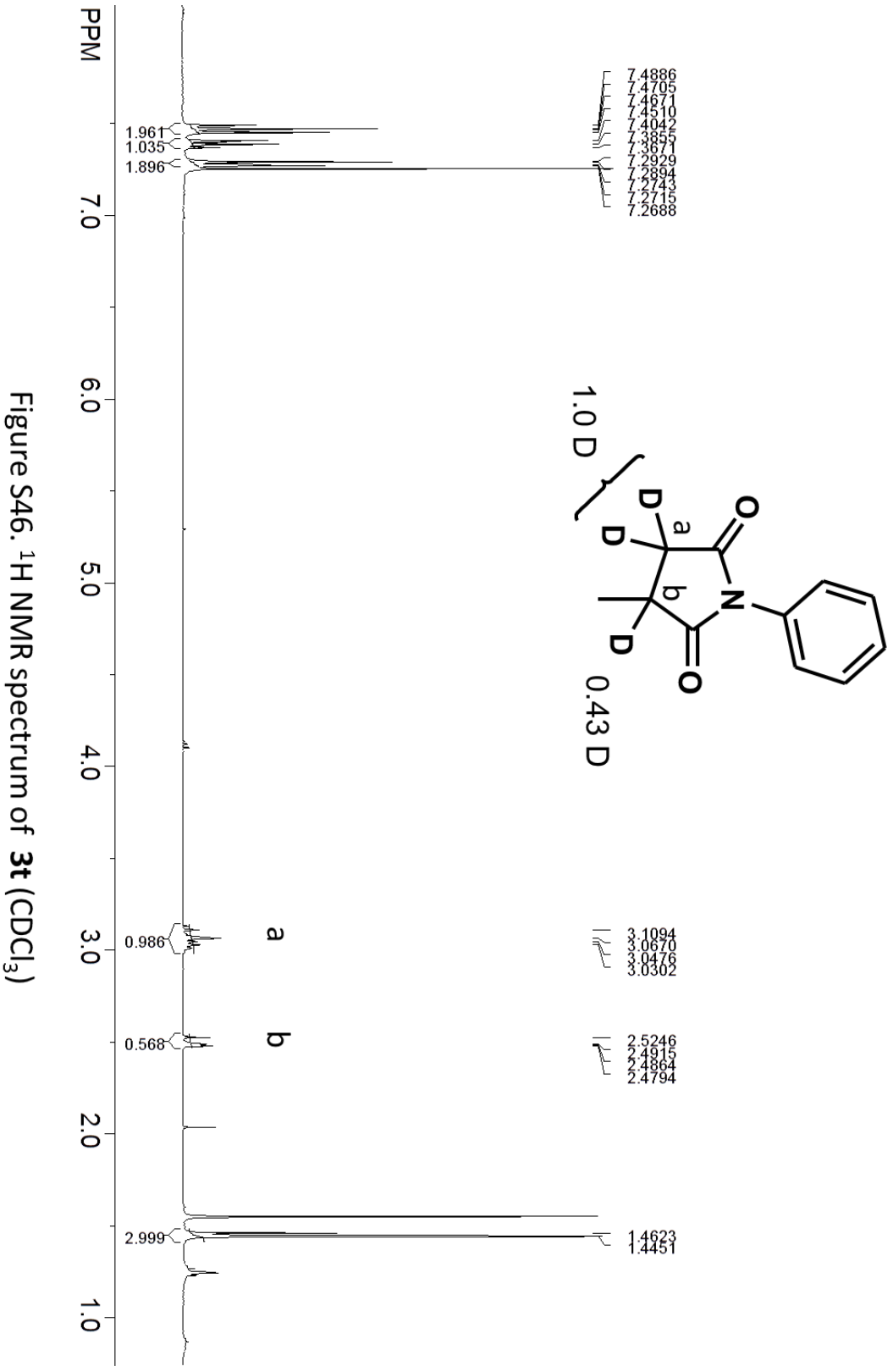

Figure S46. ^{1}H NMR spectrum of **3t** ($CDCl_3$)

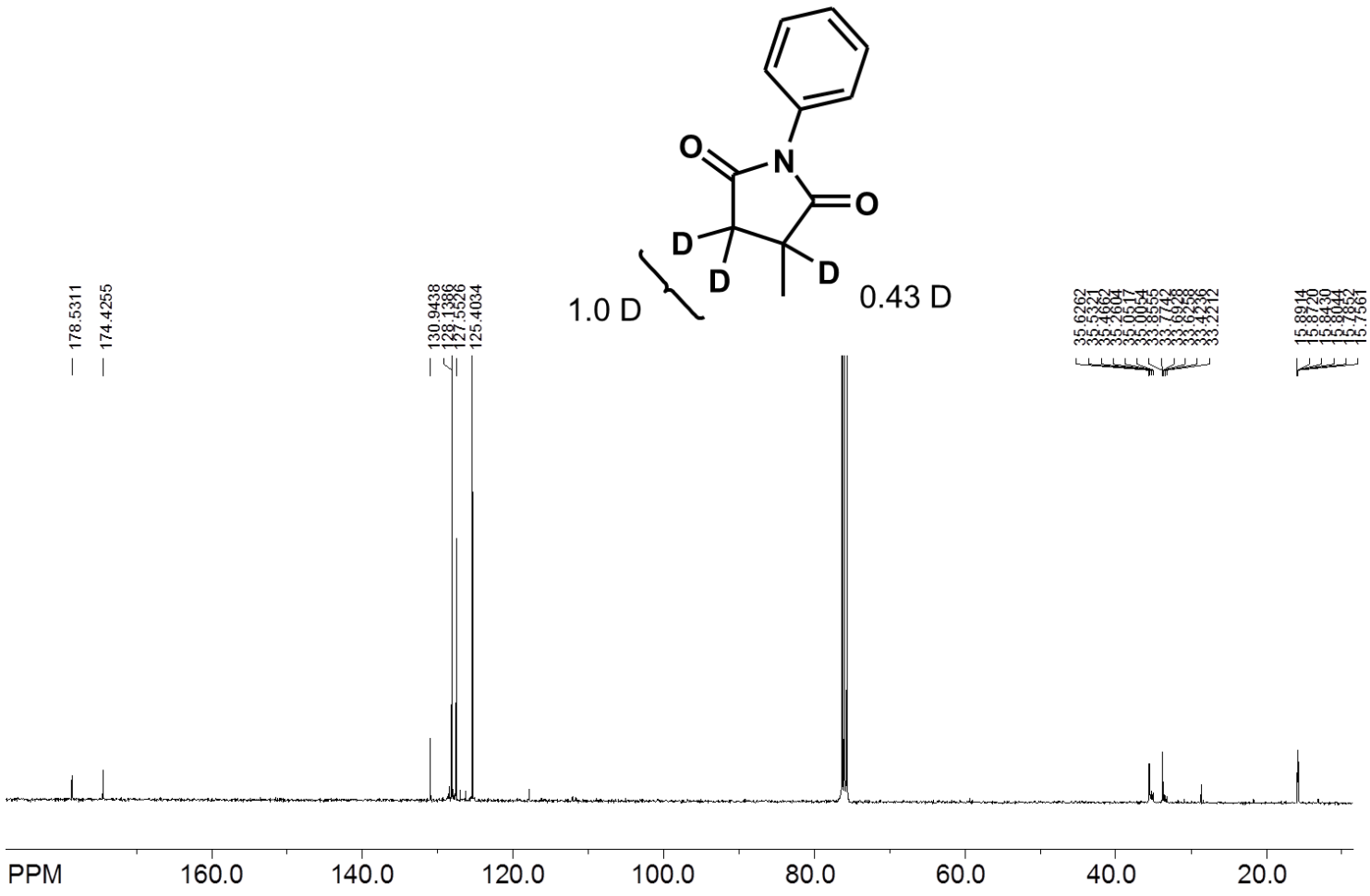

Figure S47. ^{13}C NMR spectrum of **3t** ($CDCl_3$)

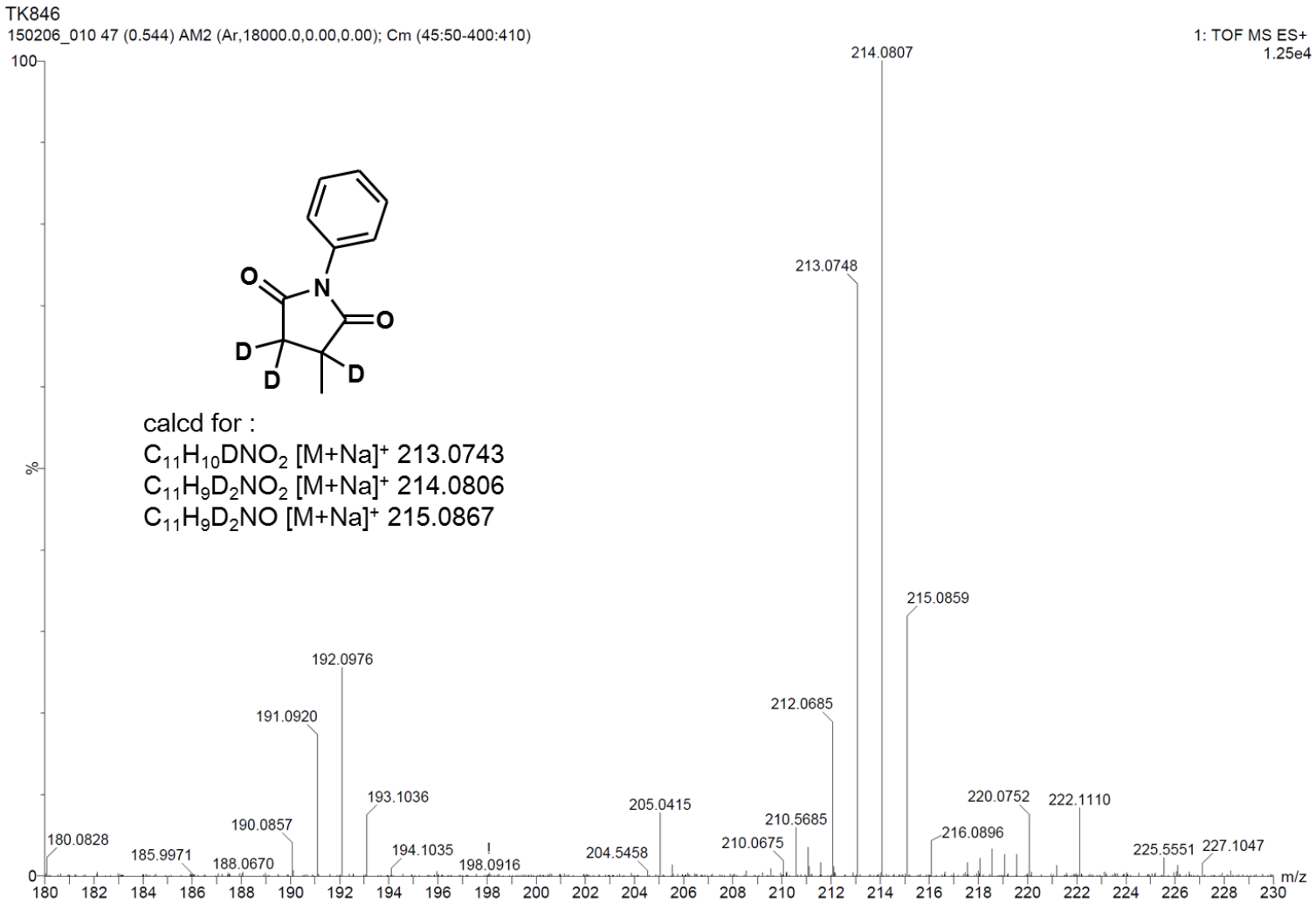

Figure S48. ESI-MS spectrum of **3t**

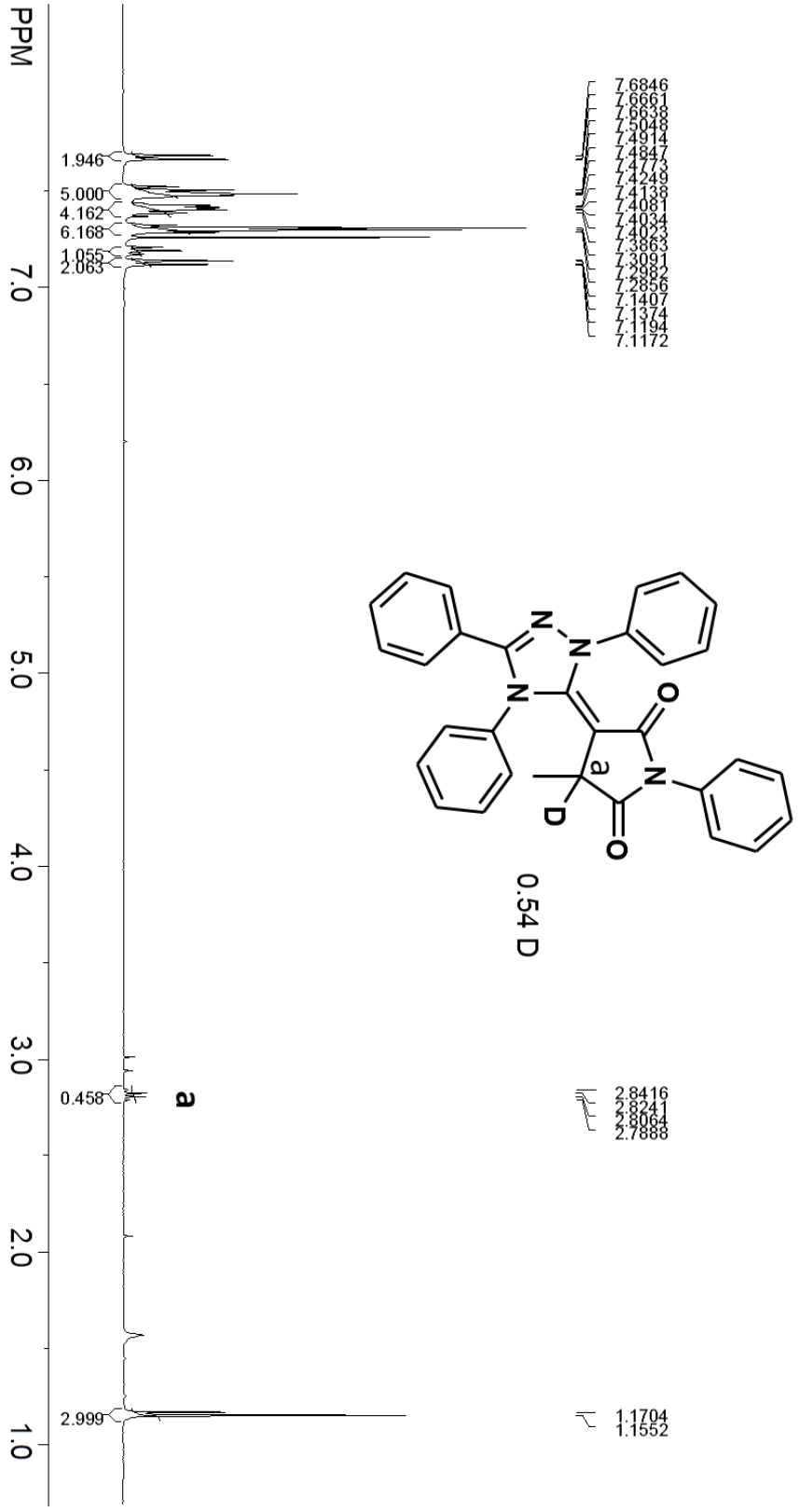

Figure S49. ^{1}H NMR spectrum of **5t** ($CDCl_3$)

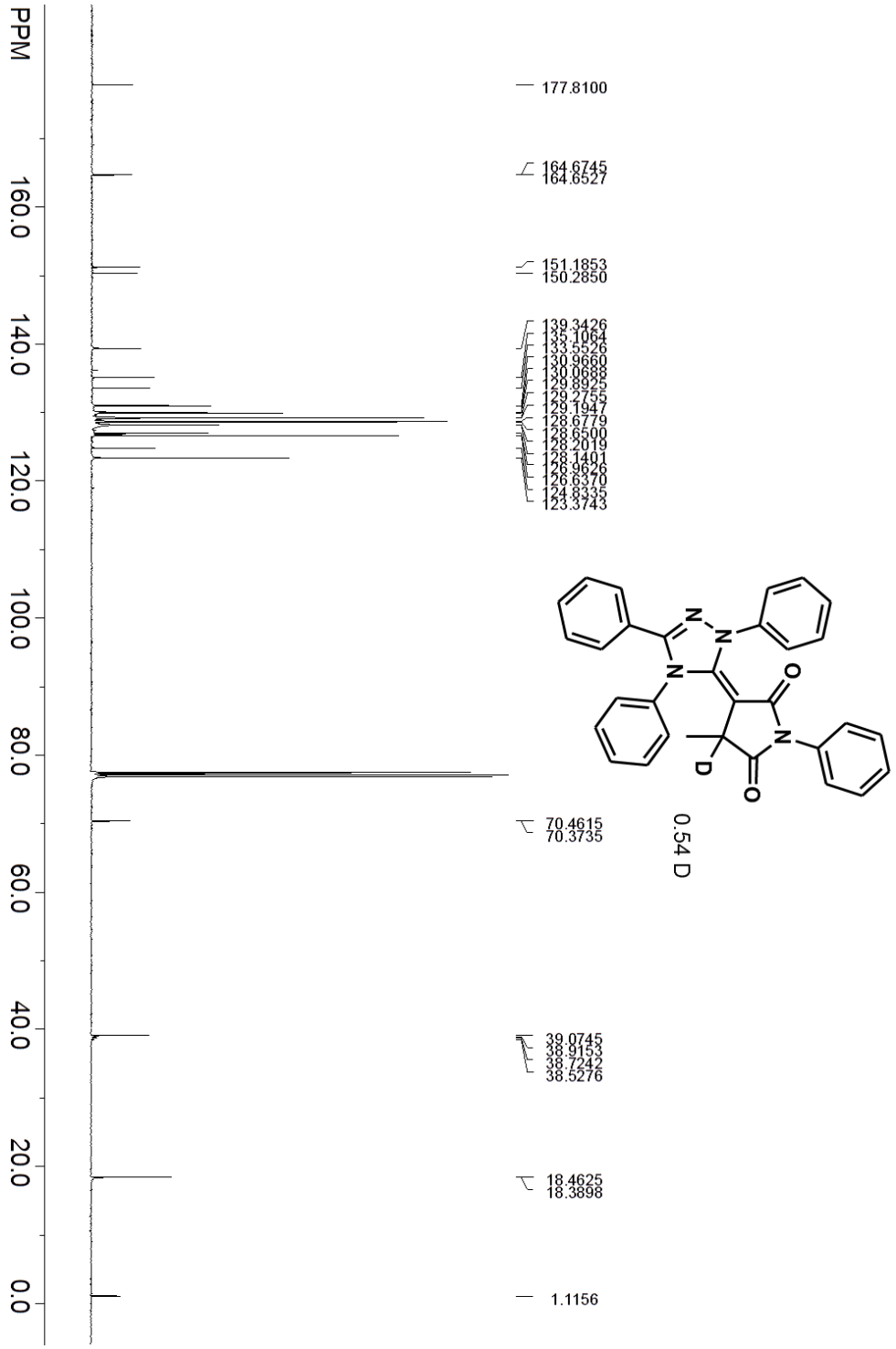

Figure S50. ^{13}C NMR spectrum of **5t** ($CDCl_3$)

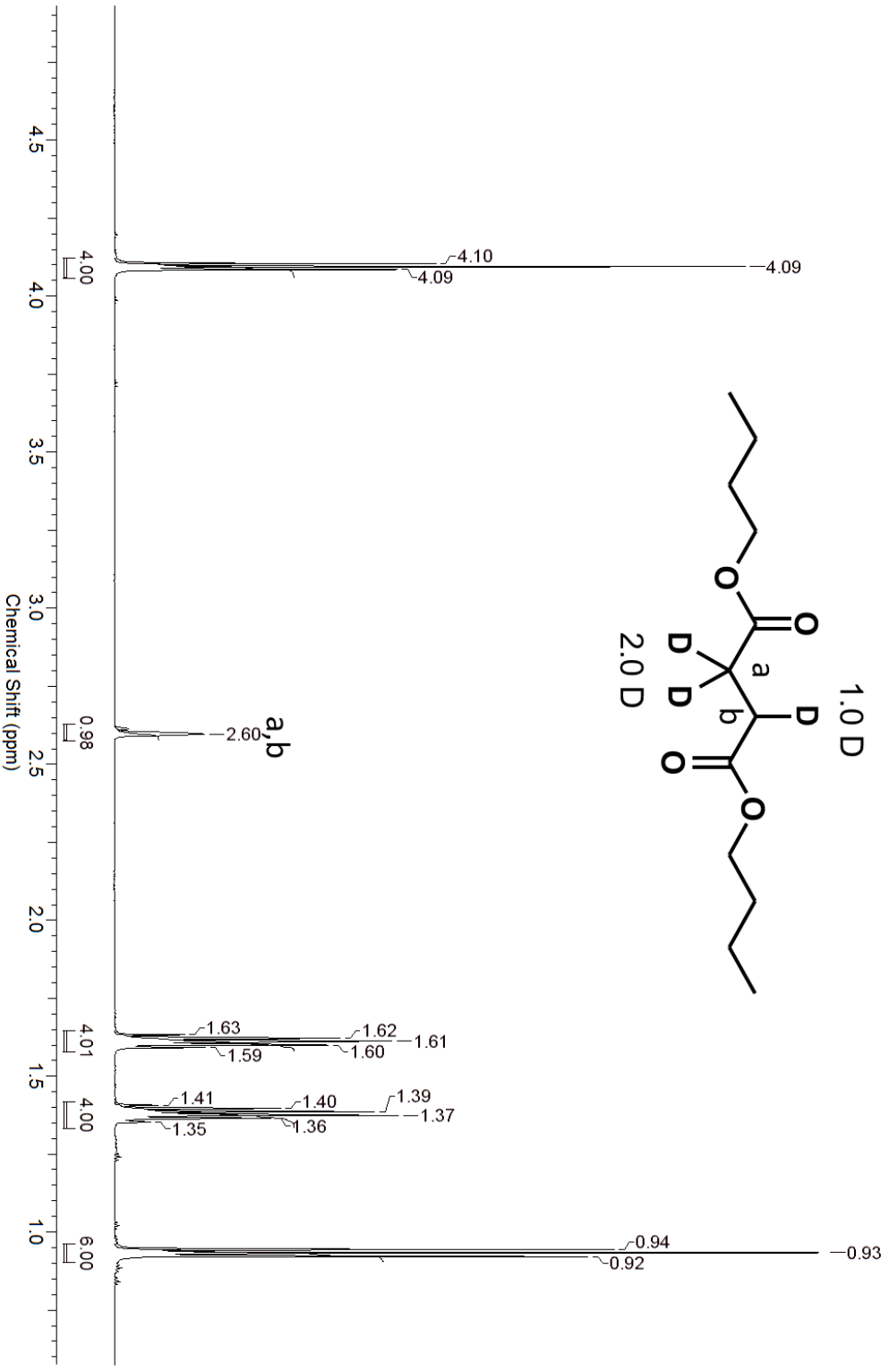

Figure S51. ^{1}H NMR spectrum of **3u** ($CDCl_3$, 700MHz)

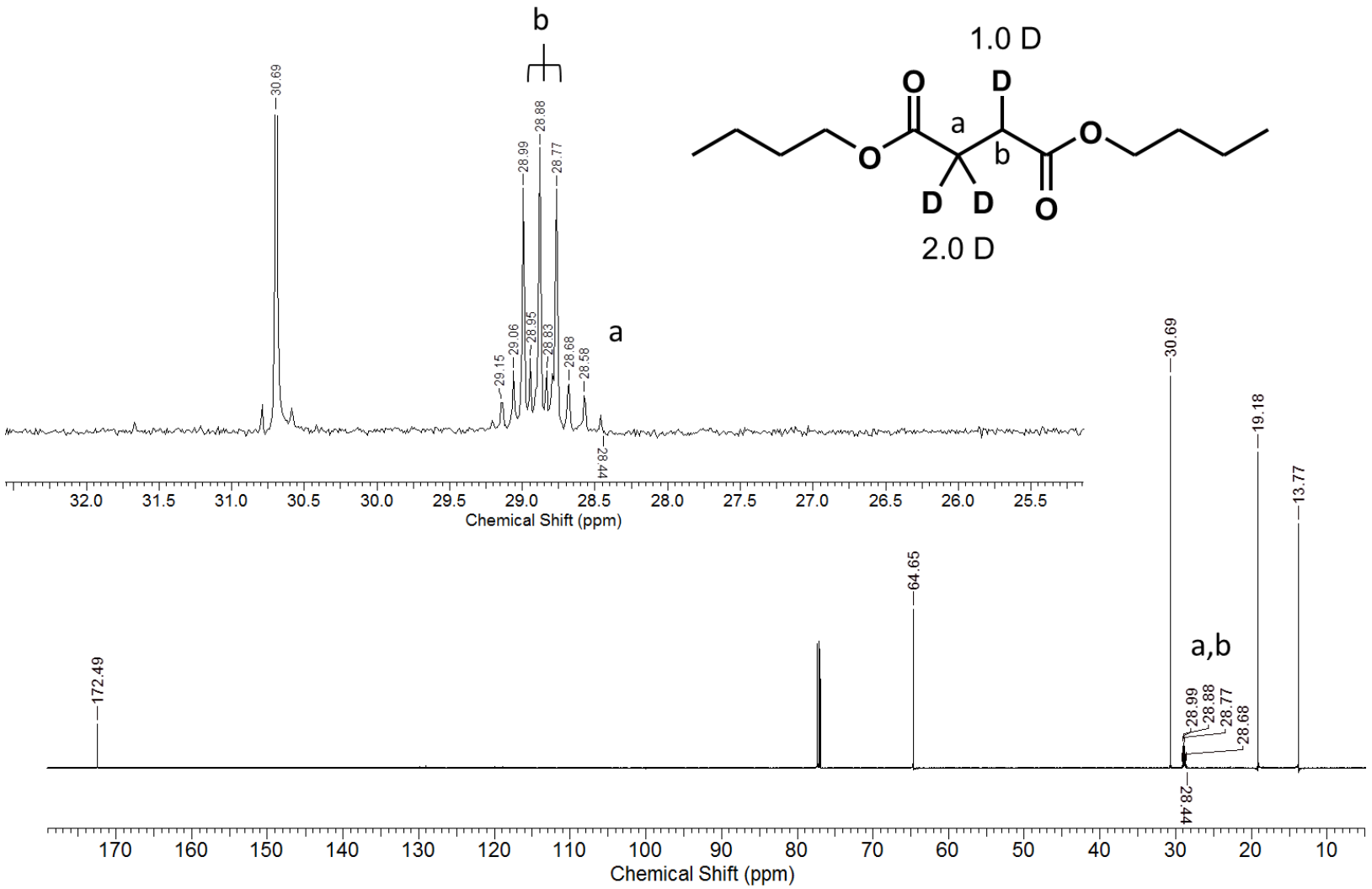

Figure S52. ^{13}C NMR spectrum of **3u** ($CDCl_3$, 176MHz)

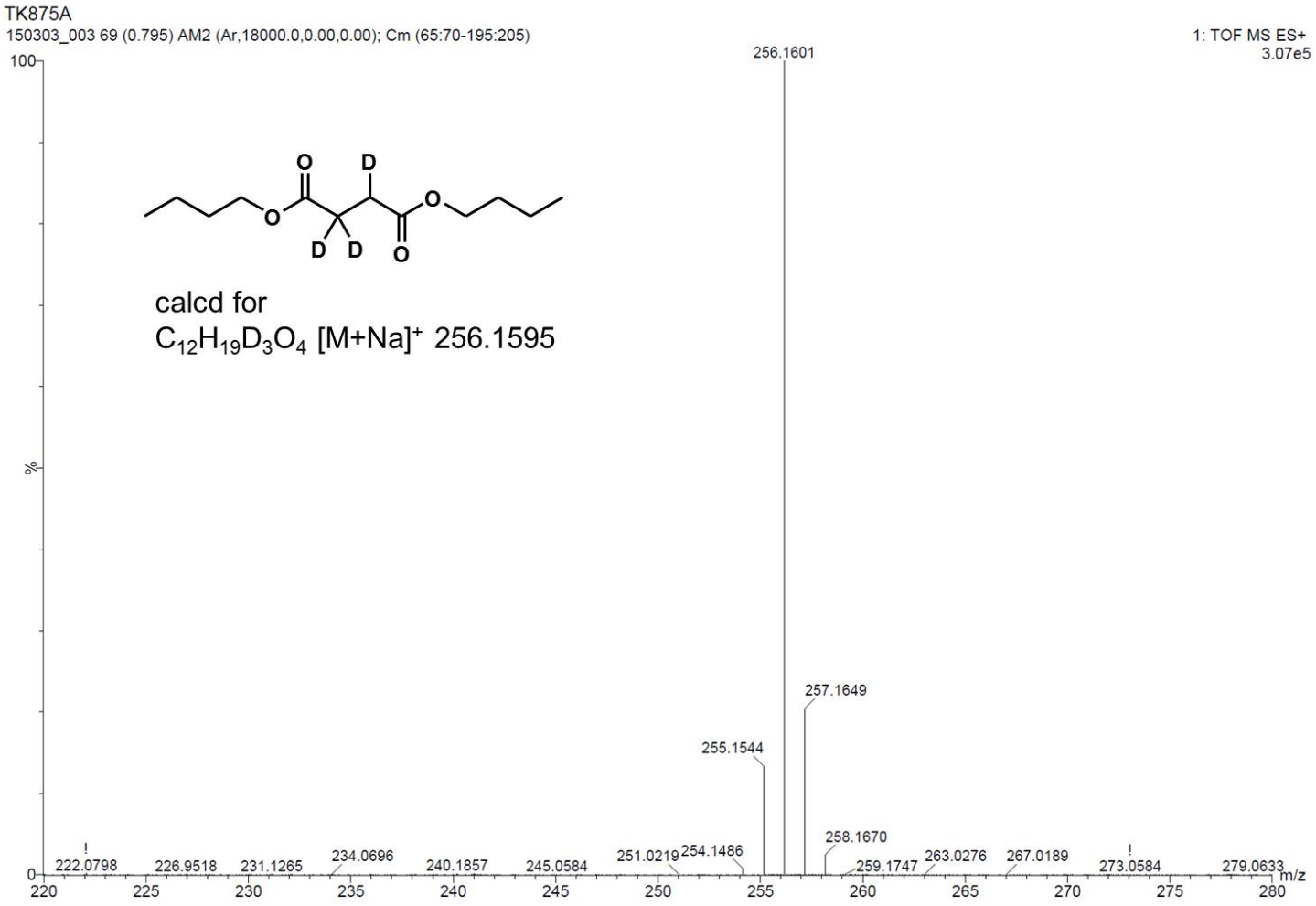

Figure S53. ESI-MS Spectrum of **3u**

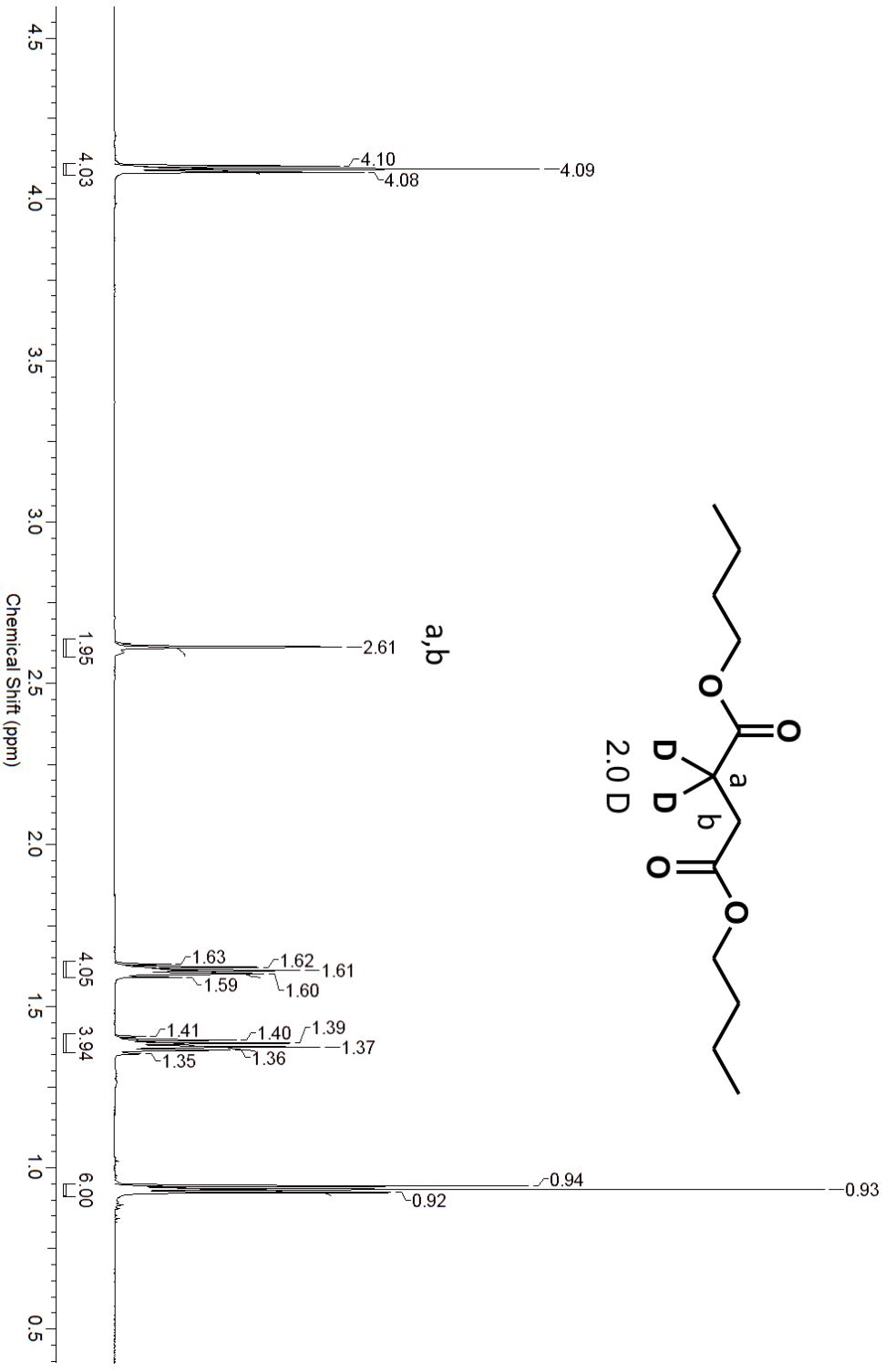

Figure S54. ^{1}H NMR spectrum of **3v** ($CDCl_3$, 700MHz)

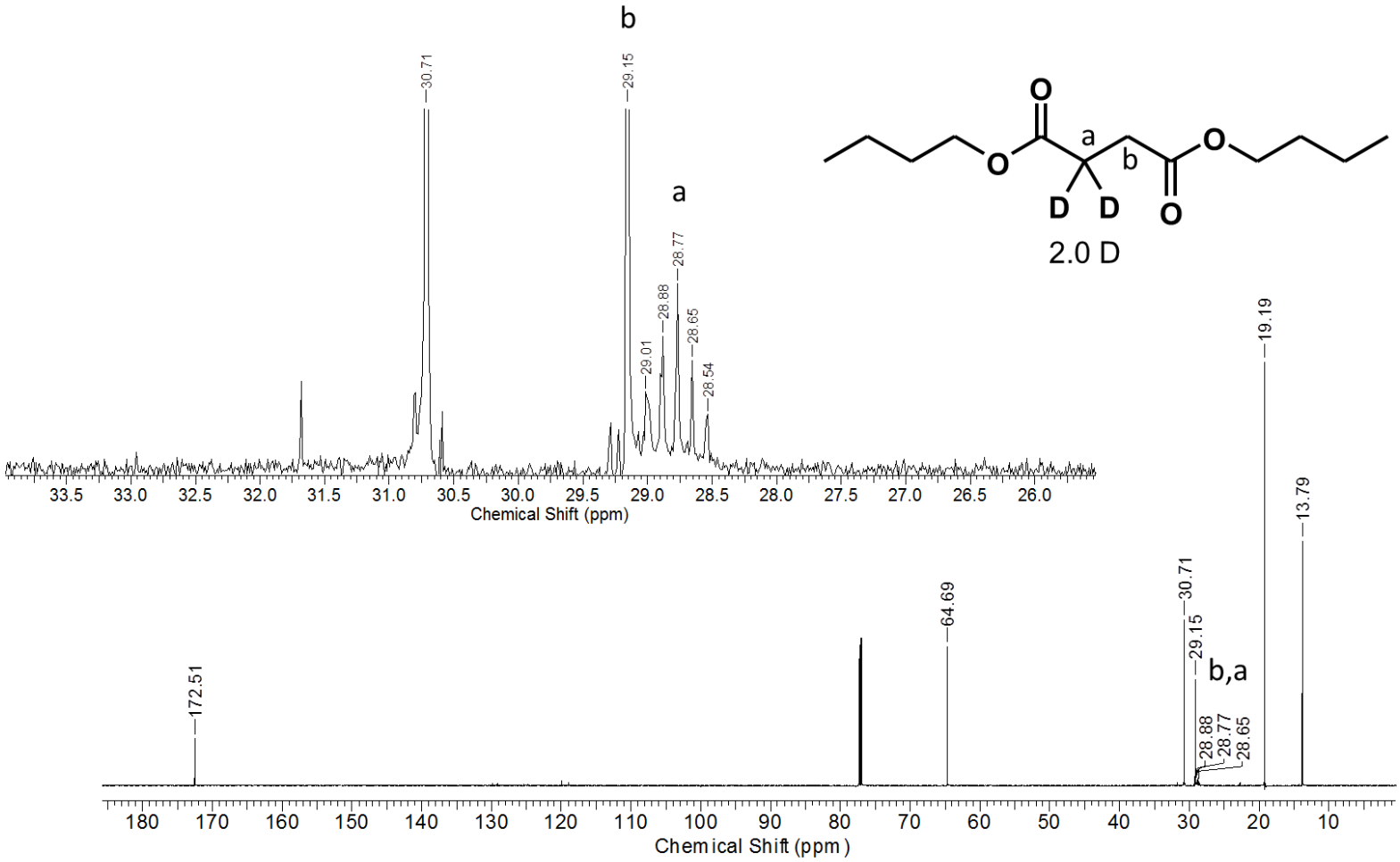

Figure S55. ^{13}C NMR spectrum of **3v** ($CDCl_3$, 176MHz)

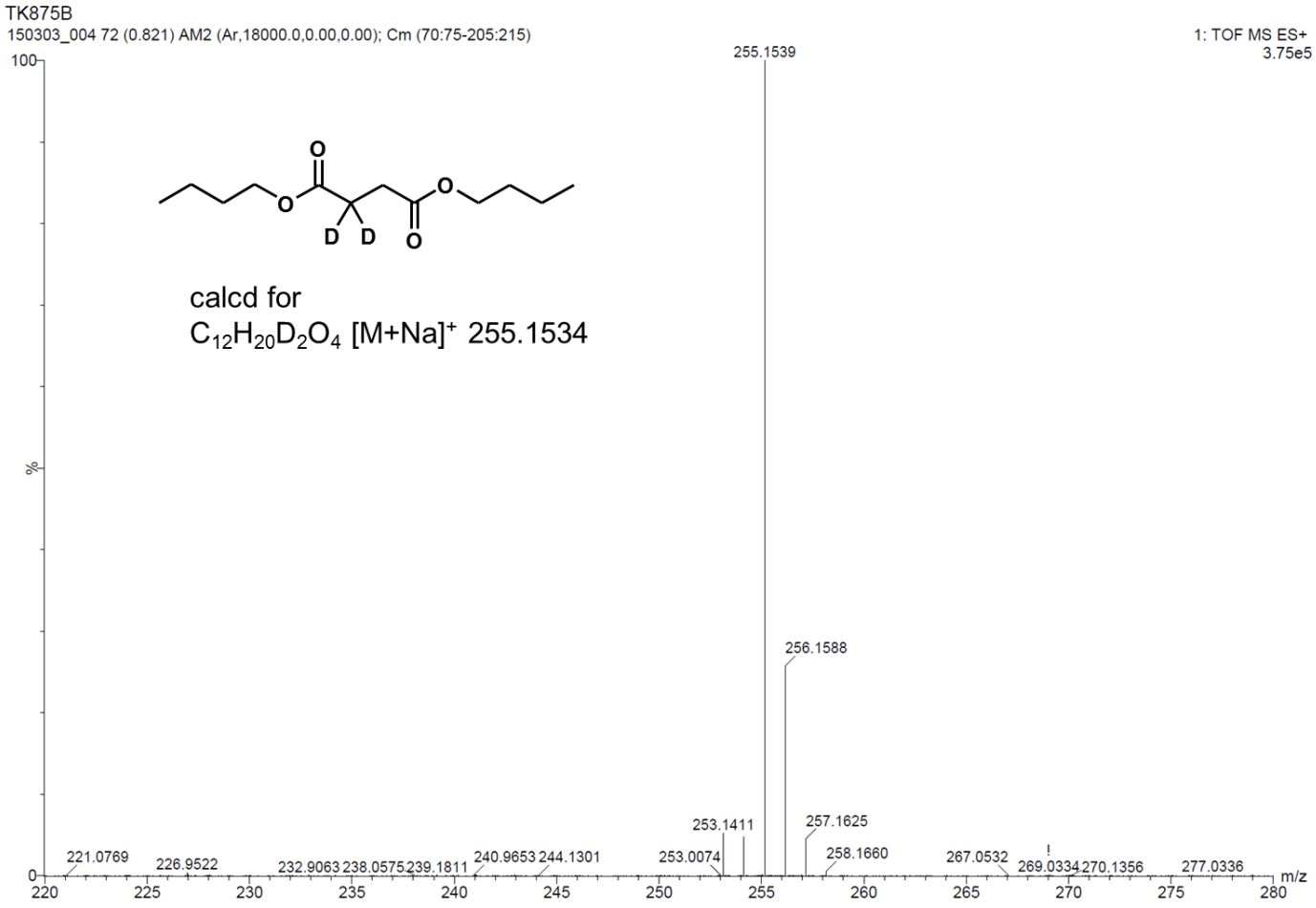

Figure S56. ESI-MS Spectrum of **3v**