Supporting Information for

α-Trideuteration of Methylarenes

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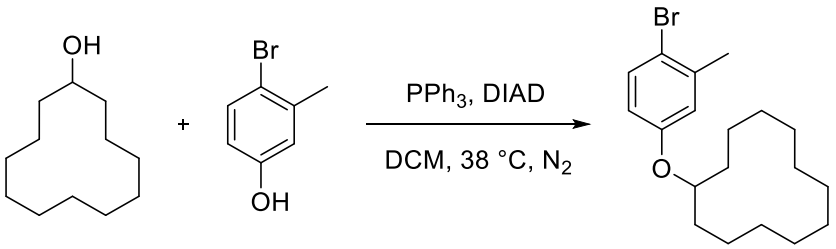
1. General information

Solvents were heated to reflux over CaH_2 (DMSO-d_6) under N_2 atmosphere and collected by distillation. All other reagents were used without purification as commercially available, such as NaOH, ^{t}BuOK, NaH and 4-Phenyltoluene. All reactions were monitored and confirmed by TLC silica gel plate. The separation yield is obtained by using analytically pure reagents through silica gel under air conditions. ^{1}H, ^{13}C{^{1}H} NMR spectra were recorded on Bruker 400/500 spectrometer. ^{2}H NMR spectra were recorded on JNM-ECZ600R/S1 600 spectrometer. Chemical shifts are reported in δ units relative to $CDCl_3$ [^{1}H δ = 7.26, ^{13}C δ = 77.36] and DMSO-d_6 [^{1}H δ = 2.50, ^{13}C δ = 39.52]. HRMS and GC were recorded by the mass spectrometry service at University of Science and Technology of China.

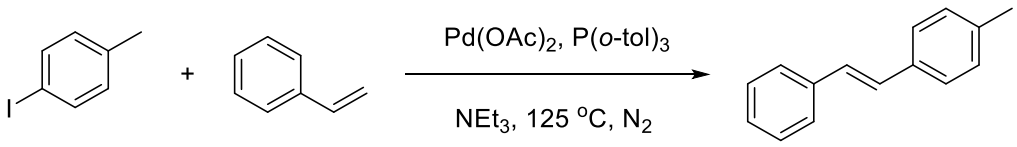
2. Experimental procedures

2.1. Preparation of Starting Materials



S1

To a solution of Cyclododecanol (55 mmol, 1.1 equiv), 4-bromo-3-methylphenol (50 mmol, 1.0 equiv) and PPh_3 (75 mmol, 1.5 equiv) in DCM (100 mL) was added DIAD (75 mmol, 1.5 equiv) under N_2 atmosphere. The mixture was stirred at 30 °C for 132 h. The resulting reaction mixture was monitored by TLC. After cooling, the reaction mixture was poured into H_2O and extracted with DCM (30 mL, three times). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation, then purified by flash column chromatography (PE/EA/DCM = 100:1:1) on silica gel to give the compound **S1** as white solid (10.4 g, 59% yield) m.p. 45-47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.72 Hz, 1H), 6.79 (d, *J* = 2.76 Hz, 1H), 6.60 (dd, *J* = 8.72, 2.88 Hz, 1H), 4.39-4.33 (m, 1H), 2.35 (s, 3H), 1.81-1.73 (m, 2H), 1.66-1.59 (m, 2H), 1.47-1.38 (m, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 138.9, 132.9, 118.9, 115.2, 114.8, 75.8, 28.7, 24.7, 24.4, 23.3, 23.3, 23.2, 20.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{29}OBr^+$ 352.1396; found 352.1393.



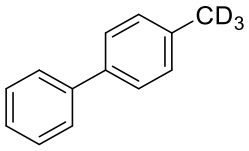
S2

To a solution of 1-iodo-4-methylbenzene (20 mmol, 1 equiv), $Pd(OAc)_2$ (1 mmol, 5 mol%), P(*o*-tol)$_3$ (4 mmol, 20 mol%), styrene (40 mmol, 2 equiv) was added NEt_3 (20 mL) under N_2 atmosphere. The mixture was stirred at 125 °C for 16 h. After cooling, the reaction mixture was poured into water and then the product was extracted with DCM (30 mL, three times). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (PE) on silica gel to afford the corresponding **S2** as white solid (2.21 g, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.75 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.55 Hz, 2H), 7.27-7.24 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.12-7.05 (m, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.7, 134.7, 129.5, 128.8, 128.8, 127.8, 127.5, 126.6, 126.5, 21.4.[1]

2.2. General procedure

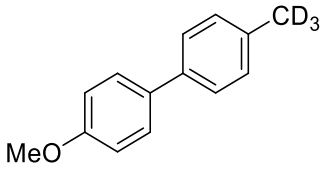
Condition A: To a Schlenk tube charged with **1a** (0.5 mmol, 1.0 equiv) and NaOH (2.0 equiv, 40.8 mg) was added solvent (1 mL) under N_2 atmosphere and the resulting reaction mixture was stirred at 110°C for 6 h (oil bath). The reaction mixture was directly prified by silica gel column to give the pure product.

Condition B: To a Schlenk tube charged with **1a** (0.5 mmol, 1.0 equiv) and ^{t}BuOK (20 mol%, 11.2 mg) was added solvent (1 mL) under N_2 atmosphere and the resulting reaction mixture was stirred at 30 °C for 6 h (oil bath). The reaction mixture was directly prified by silica gel column to give the pure product.



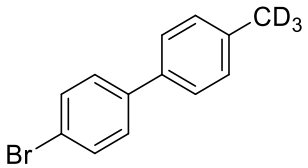
4-(methyl-*d*$_3$)-1,1'-biphenyl (1a-*d*$_3$)[2]

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 84.7 mg, 99% yield, 97% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 83.7 mg, 98% yield, 98% D-rate. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 2H, *Ar* C-H), 7.54-7.51 (m, 2H, *Ar* C-H), 7.47-7.43 (m, 2H, *Ar* C-H), 7.37-7.33 (m, 1H, *Ar* C-H), 7.29-7.26 (m, 2H, *Ar* C-H), 2.40-2.39 (m, 0.09H, 97% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.3, 138.5, 137.0, 129.6, 128.8, 127.1, 20.9-20.0 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.09.



4-methoxy-4'-(methyl-*d*$_3$)-1,1'-biphenyl (1b-*d*$_3$)

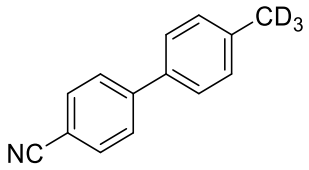
Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 92.6 mg, 92% yield, 90% D-rate. **Condition B**, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 100.3 mg, 100% yield, 97% D-rate. White solid (m.p. 94-96 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H, *Ar* C-H), 7.48-7.46 (m, 2H, *Ar* C-H), 7.26-7.24 (m, 2H, *Ar* C-H), 7.00-6.97 (m, 2H, *Ar* C-H), 3.86 (s, 3H, OC*H*$_3$), 2.39-2.36 (m, 0.08H, 97% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.0, 138.1, 136.4, 133.9, 129.6, 128.1, 126.7, 114.3, 55.5, 21.0-20.3 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.08. HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{11}D_3O^+$ 201.1228; found 201.1224.



4-bromo-4'-(methyl-*d*$_3$)-1,1'-biphenyl (1c-*d*$_3$)

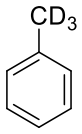
Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 115.3 mg, 92% yield, 75% D-rate.

Condition B, T = 90 ºC, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 107.5 mg, 86% yield, 97% D-rate. White solid (m.p. 115-117 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H, *Ar* C-H), 7.47-7.43 (m, 4H, *Ar* C-H),7.26-7.24 (m, 2H, *Ar* C-H), 2.37-2.36 (m, 0.09H, 97% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.2, 137.5, 137.2, 131.9, 129.8, 128.7, 126.9, 121.3, 20.6-20.3 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.09. HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_8D_3Br^+$ 249.0227; found 249.0227.



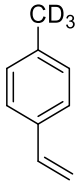
4'-(methyl-*d*$_3$)-[1,1'-biphenyl]-4-carbonitrile (1d-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 30 ºC, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 78.7 mg, 80% yield, 92% D-rate. White solid (m.p. 99-101 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.66 (m, 4H, *Ar* C-H), 7.51-7.48 (m, 2H, *Ar* C-H), 7.31-7.27 (m, 2H, *Ar* C-H), 2.39-2.38 (m, 0.25H, 92% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.7, 138.8, 136.4, 132.7, 129.9, 127.6, 127.2, 119.2, 110.6, 20.8-20.3 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.09. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9D_3N^+$ 197.1153; found 197.1151.



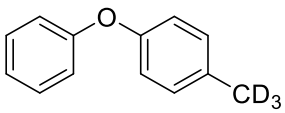
toluene-*d*$_3$ (1e-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 90 ºC, t = 6 h. Purification was performed by flash column chromatography (PE), GC: 97% yield, 97% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25 (m, 2H, *Ar* C-H), 7.21-7.15 (m, 3H, *Ar* C-H), 2.35-2.34 (m, 0.1H, 97% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.9, 129.2, 128.4, 125.5, 21.0-20.6 (m). ^{2}H NMR (92 MHz, DCM): δ 3.25. HRMS (EI) m/z: $[M]^+$ calcd for $C_7H_5D_3^+$ 95.0809; found 95.0804.



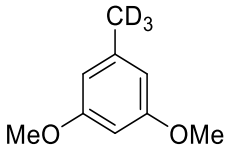
1-(methyl-*d*$_3$)-4-vinylbenzene (1f-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 30 ºC, t = 6 h. Purification was performed by flash column chromatography (PE), 59% NMR yield, 96% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H, *Ar* C-H), 7.15-7.13 (m, 2H, *Ar* C-H), 6.70 (dd, *J* = 17.6, 10.88 Hz, 1H, C=C*H*), 5.70 (dd, *J* = 17.6, 0.88 Hz, 1H, C=C*H*), 5.19 (dd, *J* = 10.88, 0.88 Hz, 1H, C=C*H*), 2.32-2.31 (m, 0.11H, 96% D, benzylic C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.6, 136.9, 135.0, 129.3, 126.2, 112.9, 20.8-20.2 (m). ^{2}H NMR (92 MHz, DCM): δ 3.24. HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_7D_3^+$ 121.0965; found 121.0965.



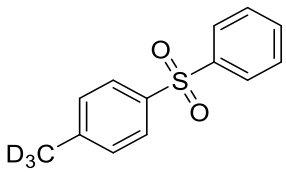
1-(methyl-*d*$_3$)-4-phenoxybenzene (1g-*d*$_3$)[2]

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 85.1 mg, 91% yield, 98% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.33 (m, 2H, *Ar* C-H), 7.25-7.21 (m, 1H, *Ar* C-H), 7.14-7.09 (m, 1H, *Ar* C-H), 7.05-7.02 (m, 2H, *Ar* C-H), 6.95-6.92 (m, 1H, *Ar* C-H), 6.86-6.83 (m, 2H, *Ar* C-H), 2.35-2.32 (m, 0.05H, 98% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.5, 157.3, 139.9, 129.8, 129.6, 124.2, 123.2, 119.7, 119.0, 116.1, 21.1-20.3 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.00.



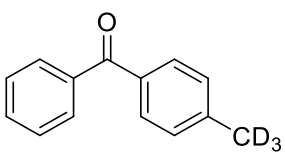
1,3-dimethoxy-5-(methyl-*d*$_3$)benzene (1h-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 75.1 mg, 97% yield, 98% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36-6.35 (m, 2H, *Ar* C-H), 6.31-6.30 (m, 1H, *Ar* C-H), 3.79 (s, 6H, OC*H*$_3$), 2.30-2.28 (m, 0.06H, 98% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8, 140.2, 107.2, 97.6, 55.3, 21.5-20.7 (m). ^{2}H NMR (92 MHz, MeCN): δ 3.97. HRMS (EI) m/z: $[M]^+$ calcd for $C_9H_9D_3O_2^+$ 155.1020; found 155.1019.



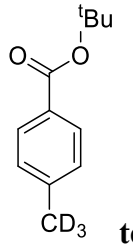
1-(methyl-*d*$_3$)-4-(phenylsulfonyl)benzene (1i-*d*$_3$)

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 5:1:1), 110.2 mg, 94% yield, 97% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 5:1:1), 112.1 mg, 95% yield, 97% D- rate. White solid (m.p. 116-118 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.91 (m, 2H, *Ar* C-H), 7.84-7.81 (m, 2H, *Ar* C-H), 7.56-7.52 (m, 1H, *Ar* C-H), 7.50-7.46 (m, 2H, *Ar* C-H), 7.30-7.28 (m, 2H, *Ar* C-H), 2.36-2.35 (m, 0.08H, 97% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.2, 142.1, 142.0, 138.8, 138.7, 133.1, 130.0, 129.9, 129.3, 129.2, 127.8, 127.6, 21.3-20.5 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.12. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_9D_3O_2S^+$ 236.0819; found 236.0822.



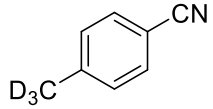
(4-(methyl-*d*$_3$)phenyl)(phenyl)methanone (1j-*d*$_3$)[2]

Prepared according to the general procedure **Condition A**, T = 30 ºC, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 91.3 mg, 92% yield, 96% D-rate. **Condition B**, T = 30 ºC, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 92.7 mg, 93% yield, 97% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.77 (m, 2H, *Ar* C-H), 7.74-7.71 (m, 2H, *Ar* C-H), 7.60-7.55 (m, 1H, *Ar* C-H), 7.50-7.45 (m, 2H, *Ar* C-H), 7.30-7.27 (m, 2H, *Ar* C-H), 2.42-2.41 (m, 0.11H, 96% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.6, 143.2, 138.0, 135.0, 132.3, 130.4, 130.0, 129.1, 128.3, 21.3-20.5 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.15.



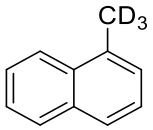
tert-butyl 4-(methyl-*d*$_3$)benzoate (1k-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 30 ºC, ^{t}BuOK (30mol%), t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 70.3 mg, 72% yield, 98% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (m, 2H, *Ar* C-H), 7.22-7.19 (m, 2H, *Ar* C-H), 2.37-2.36 (m, 0.05H, 98% D, benzylic C*H*), 1.59 (s, 9H, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.0, 143.0, 129.5, 129.4, 129.0, 80.8, 28.3, 20.9-20.3 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.11. HRMS (EI) m/z: $[M]^+$ calcd for $C_{12}H_{13}D_3O_2^+$ 195.1333; found 195.1333.



4-(methyl-*d*$_3$)benzonitrile (1l-*d*$_3$)

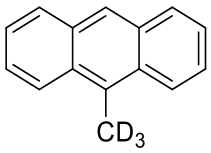
Prepared according to the general procedure **Condition A**, T = 30 ºC, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 34.3 mg, 57% yield, 98% D-rate. Yellow oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H, *Ar* C-H), 7.28-7.26 (m, 2H, *Ar* C-H), 2.40-2.38 (m, 0.06H, 98% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.7, 132.2, 130.0, 119.3, 109.5, 21.4-21.0 (m). ^{2}H NMR (92 MHz, MeCN): δ 3.37. HRMS (EI) m/z: $[M]^+$ calcd for $C_8H_4D_3N^+$ 120.0761; found 120.0761.



1-(methyl-*d*$_3$)naphthalene (1m-*d*$_3$)[3]

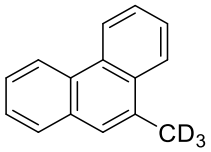
Prepared according to the general procedure **Condition A**, t = 110 ºC, T = 6 h. Purification was performed by flash column chromatography (PE), 64.7 mg, 91% yield, 98% D-rate. **Condition B**, T = 50 ºC, t = 6 h. Purification was performed by flash column chromatography (PE), 70.2 mg, 97% yield, 96% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.08 Hz, 1H, *Ar* C-H), 7.89 (d, *J* = 8.16 Hz, 1H, *Ar* C-H), 7.75 (d, *J* = 8.12 Hz, 1H, *Ar* C-H), 7.58-7.51 (m, 2H, *Ar* C-H), 7.44-7.40 (m, 1H,

Ar C-H), 7.36-7.35 (m, 1H, *Ar* C-H), 2.71-2.70 (m, 0.06H, 98% D, benzylic C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 134.3, 133.6, 132.7, 128.6, 126.7, 126.5, 125.8, 125.7, 125.7, 124.2, 18.9-18.4 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.39.



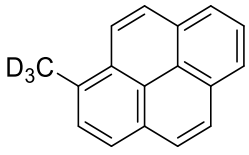
9-(methyl-*d*$_3$)anthracene (1n-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 80.2 mg, 82% yield, 98% D-rate. Yellow solid (m.p. 67-69 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H, *Ar* C-H), 8.30 (d, *J* = 8.6 Hz, 2H, *Ar* C-H), 8.02 (d, *J* = 7.88 Hz, 2H, *Ar* C-H), 7.55-7.46 (m, 4H, *Ar* C-H), 3.08-3.07 (m, 0.05H, 98% D, benzylic C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 131.6, 130.3, 130.2, 129.2, 125.4, 125.4, 124.9, 124.8, 13.6-12.9 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.80. HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_9D_3^+$ 195.1122; found 195.1119.



9-(methyl-*d*$_3$)phenanthrene (1o-*d*$_3$)

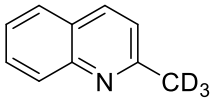
Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 96.9 mg, 99% yield, 99% D-rate. **Condition B**, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 91.7 mg, 94% yield, 98% D-rate. White solid (m.p. 82-84 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75-8.72 (m, 1H, *Ar* C-H), 8.68-8.66 (m, 1H, *Ar* C-H), 8.08-8.05 (m, 1H, *Ar* C-H), 7.83-7.81 (m, 1H, *Ar* C-H), 7.70-7.63 (m, 2H, *Ar* C-H), 7.63-7.56 (m, 3H, *Ar* C-H), 2.72-2.72 (m, 0.06H, 98% D, benzylic C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 132.5, 132.2, 132.1, 130.5, 129.8, 128.0, 126.9, 126.7, 126.6, 126.3, 125.9, 124.8, 123.1, 122.6, 19.6-19.2 (m). ^{2}H NMR (92 MHz, DCM): δ 3.65. HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_9D_3^+$ 195.1122; found 195.1118.



8-(methyl-*d*$_3$)-1,9-dihydropyrene (1p-*d*$_3$)

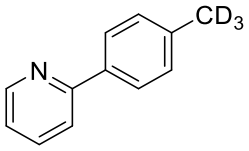
Prepared according to the general procedure **Condition B**, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 107.7 mg, 97% yield, 98% D-rate. White solid (m.p. 58-60 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.24 (m, 1H, *Ar* C-H), 8.21-8.18 (m, 1H, *Ar* C-H), 8.18-8.16 (m, 1H, *Ar* C-H), 8.13-8.09 (m, 2H, *Ar* C-H), 8.05-7.98 (m, 3H, *Ar* C-H), 7.88-7.87 (m, 1H, *Ar* C-H), 2.97-2.95 (m, 0.06H, 98% D, benzylic C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 132.3, 131.6, 131.1 129.9, 129.4, 128.0, 127.7, 127.2, 126.6, 125.9, 125.1, 125.0, 124.9, 124.9, 124.9, 124.8, 123.8. ^{2}H NMR (92 MHz,

DCM): δ 3.87. HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_9D_3^+$ 219.1122; found 219.1120.



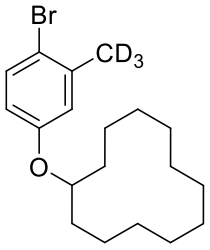
2-(methyl-*d*$_3$)quinolone (1q-*d*$_3$)[4]

Prepared according to the general procedure **Condition B**, T = 30 °C, ^{t}BuOK (5mol%), t = 3 h. Purification was performed by flash column chromatography (PE/EA/DCM = 3:1:1), 54.5 mg, 74% yield, 98% D-rate. Yellow oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-7.99 (m, 2H, *Ar* C-H), 7.76-7.74 (m, 1H, *Ar* C-H), 7.68-7.64 (m, 1H, *Ar* C-H), 7.48-7.43 (m, 1H, *Ar* C-H), 7.27-7.23 (m, 0.98H, *Ar* C-H), 2.70-2.69 (m, 0.07H, 98% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.0, 147.8, 136.2, 129.5, 128.6, 127.5, 126.5, 125.7, 122.1, 24.8-24.4 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.94.



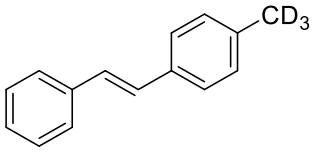
2-(4-(methyl-*d*$_3$)phenyl)pyridine (1r-*d*$_3$)

Prepared according to the general procedure **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 5:1:1), 86.7 mg, 100% yield, 97% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.67 (m, 1H, *Ar* C-H), 7.91-7.88 (m, 2H, *Ar* C-H), 7.75-7.69 (m, 2H, *Ar* C-H), 7.30-7.27 (m, 2H, *Ar* C-H), 7.22-7.19 (m, 1H, *Ar* C-H), 2.41-2.37 (m, 0.10H, 97% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.6, 149.7, 139.0, 136.8, 136.7, 129.6, 126.9, 121.9, 120.4, 21.2-20.2 (m). ^{2}H NMR (92 MHz, MeCN): δ 4.03. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_9D_3N^+$ 173.1153; found 173.1153.



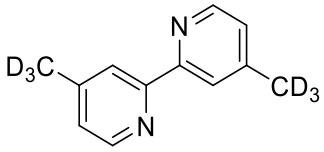
(4-bromo-3-(methyl-*d*$_3$)phenoxy)cyclododecane (1s-*d*$_3$)

Prepared according to the general procedure **Condition A**, t = 110 °C, T = 6 h. Purification was performed by flash column chromatography (PE), 178.6 mg, 100% yield, 98% D-rate. **Condition B**, T = 70 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 162.1 mg, 91% yield, 98% D-rate. White solid (m.p. 58-60 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.72 Hz, 1H, *Ar* C-H), 6.78 (d, *J* = 2.72 Hz, 1H, *Ar* C-H), 6.60 (dd, *J* = 8.64, 2.8 Hz, 1H, *Ar* C-H), 4.39-4.33 (m, 1H, C*H*), 2.32 (s, 0.07H, 98% D, benzylic C*H*), 1.81-1.72 (m, 2H, CH_2), 1.65-1.58 (m, 2H, CH_2), 1.45-1.27 (m, 18H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.6, 138.8, 132.9, 118.9, 115.2, 114.8, 75.8, 28.7, 24.7, 24.4, 23.3, 23.2, 20.8. ^{2}H NMR (92 MHz, DCM): δ 3.72. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{26}D_3OBr^+$ 355.1585; found 355.1585.



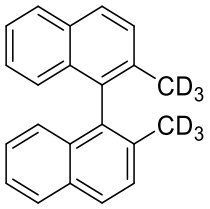
(*E*)-1-(methyl-*d*$_3$)-4-styrylbenzene (1t-*d*$_3$)

Prepared according to the general procedure **Condition A**, t = 110 °C, T = 6 h. Purification was performed by flash column chromatography (PE), 87.6 mg, 89% yield, 98% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 87.0 mg, 88% yield, 98% D-rate. White solid (m.p. 105-107 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H, *Ar* C-H), 7.47-7.42 (m, 2H, *Ar* C-H), 7.38-7.34 (m, 2H, *Ar* C-H), 7.31-7.21 (m, 1H, *Ar* C-H), 7.19-7.17 (m, 2H, *Ar* C-H), 7.13-7.04 (m, 2H, C=C*H*), 2.34 (s, 0.06H, 98% D, benzylic C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.6, 137.6, 134.7, 129.5, 128.8, 128.8, 127.8, 127.5, 126.6, 126.5. ^{2}H NMR (92 MHz, DCM): δ 4.85. HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{11}D_3^+$ 197.1278; found 197.1276.



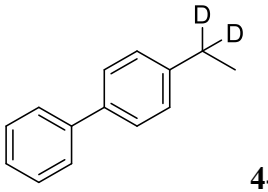
4,4'-bis(methyl-*d*$_3$)-2,2'-bipyridine (1u-*d*$_6$)[5]

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (EA), 91.0 mg, 96% yield, 96% D-rate. **Condition B**, T = 90 °C, t = 6 h. Purification was performed by flash column chromatography (EA), 88.9 mg, 93% yield, 96% D-rate. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54-8.52 (m, 2H, *Ar* C-H), 8.22-8.22 (m, 2H, *Ar* C-H), 7.13-7.12 (m, 2H, *Ar* C-H), 2.41-2.39 (m, 0.27H, 96% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.1, 149.0, 148.1, 124.8, 122.1, 20.7-20.3 (m). ^{2}H NMR (92 MHz, DCM): δ 4.09.



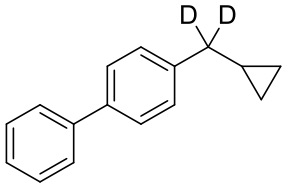
2,2'-bis(methyl-*d*$_3$)-1,1'-binaphthalene (1v-*d*$_6$)

Prepared according to the general procedure **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 144.3 mg, 100% yield, 96% D-rate. White solid (m.p. 75-77 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 4H, *Ar* C-H), 7.53-7.51 (m, 2H, *Ar* C-H), 7.42-7.38 (m, 2H, *Ar* C-H), 7.26-7.19 (m, 2H, *Ar* C-H), 7.07-7.05 (m, 2H, *Ar* C-H), 2.02-2.01 (m, 0.24H, 96% D, benzylic C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.3, 134.3, 132.9, 132.3, 128.8, 128.1, 127.6, 126.2, 125.8, 125.0, 19.8-19.0 (m). ^{2}H NMR (92 MHz, DCM): δ 2.99. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{12}D_6^+$ 288.1780; found 288.1778.



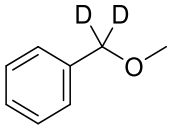
4-(ethyl-1,1-*d*$_2$)-1,1'-biphenyl (1w-*d*$_2$)[6]

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 91.6 mg, 99% yield, 86% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 92.1 mg, 100% yield, 99% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H, *Ar* C-H), 7.55-7.53 (m, 2H, *Ar* C-H), 7.46-7.42 (m, 2H, *Ar* C-H), 7.36-7.32 (m, 1H, *Ar* C-H), 7.30-7.28 (m, 2H, *Ar* C-H), 2.72-2.68 (m, 0.03H, 99% D, benzylic C*H*), 1.28 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.5, 141.3, 138.8, 128.8, 128.4, 127.2, 127.2, 127.1, 28.2-27.8 (m), 15.6. ^{2}H NMR (92 MHz, MeCN): δ 4.94.



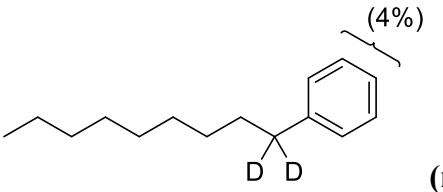
4-(cyclopropylmethyl-*d*$_2$)-1,1'-biphenyl (1x-*d*$_2$)

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 105.9 mg, 100% yield, 98% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 105.4 mg, 100% yield, 97% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.60 (m, 2H, *Ar* C-H), 7.56-7.54 (m, 2H, *Ar* C-H), 7.47-7.44 (m, 2H, *Ar* C-H), 7.37-7.33 (m, 3H, *Ar* C-H), 2.63-2.59 (m, 0.06H, 98% D, benzylic C*H*), 1.06-1.03 (m, 1H, C*H*), 0.60-0.55 (m, 2H, CH_2), 0.28-0.24 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.4, 141.3, 139.0, 128.9, 128.8, 127.2, 127.2, 127.1, 39.6-39.2 (m), 11.9, 4.8. ^{2}H NMR (92 MHz, MeCN): δ 4.93. HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{14}D_2^+$ 210.1372; found 210.1371.



(methoxymethyl-*d*$_2$)benzene (1y-*d*$_2$)

Prepared according to the general procedure **Condition B**, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 10:1:1), 34.0 mg, 55% yield (GC: 99%), 99% D- rate. Yellow oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 5H, *Ar* C-H), 4.45-4.45 (m, 0.03H, 99% D, benzylic C*H*), 3.40-3.39 (m, 3H, OCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 128.5, 127.9, 127.8, 74.3-73.6 (m), 58.1. ^{2}H NMR (92 MHz, DCM): δ 5.12. HRMS (EI) m/z: $[M]^+$ calcd for $C_8H_8D_2O^+$ 124.0852; found 124.0850.



(nonyl-1,1-*d*$_2$)benzene (1z-*d*$_2$)

Prepared according to the general procedure **Condition B**, T = 90 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 102.1 mg, 99% yield, 98% D-rate. Colorless oil liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H, *Ar* C-H), 7.19-7.15 (m, 2.88H, *Ar* C-H), 2.60-2.56 (m, 0.03H, 98% D, benzylic C*H*), 1.60-1.58 (m, 2H, CH_2), 1.32-1.26 (m, 12H, CH_2), 0.90-0.86 (m, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.0, 128.5, 128.4, 125.7, 35.8-35.2 (m), 32.1, 31.5, 29.7, 29.7, 29.5, 29.4, 22.8, 14.3. ^{2}H NMR (92 MHz, MeCN): δ 4.94. HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}D_2^+$ 206.1998; found 206.1997.

3. References

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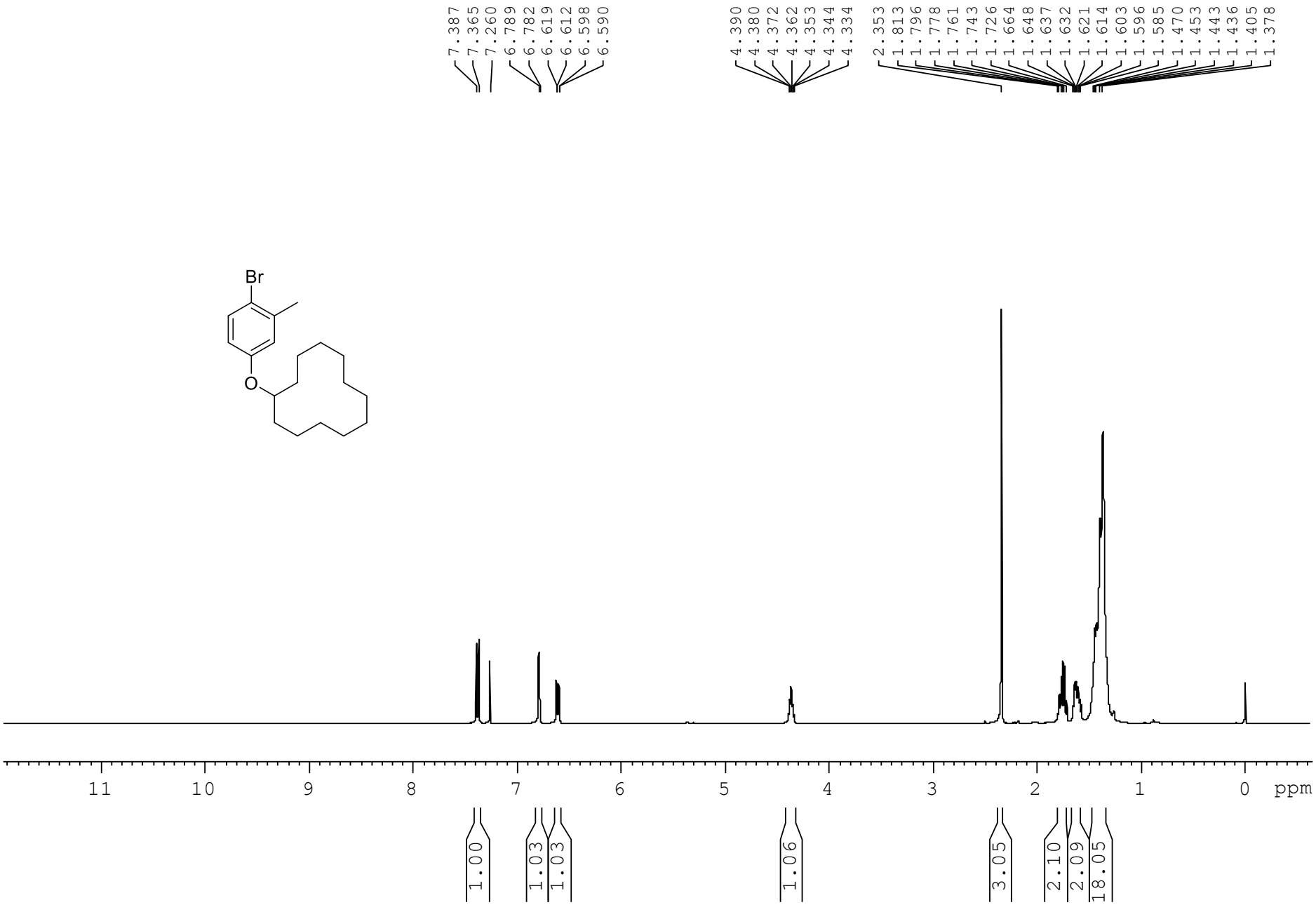

Figure S1. ^{1}H NMR spectra of **S1** ($CDCl_3$, 400 M)

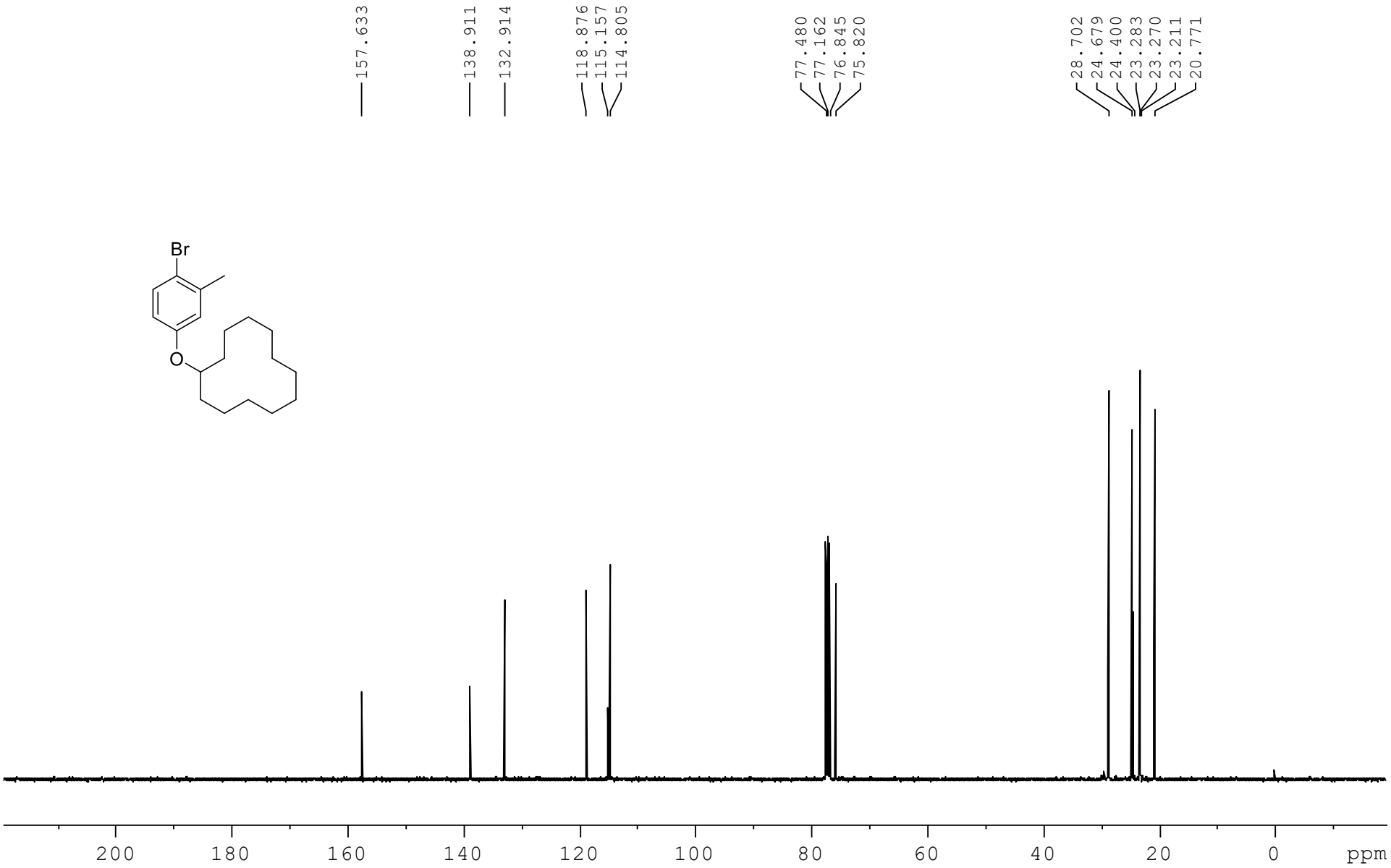

Figure S2. ^{13}C NMR spectra of **S1** ($CDCl_3$, 100 M)

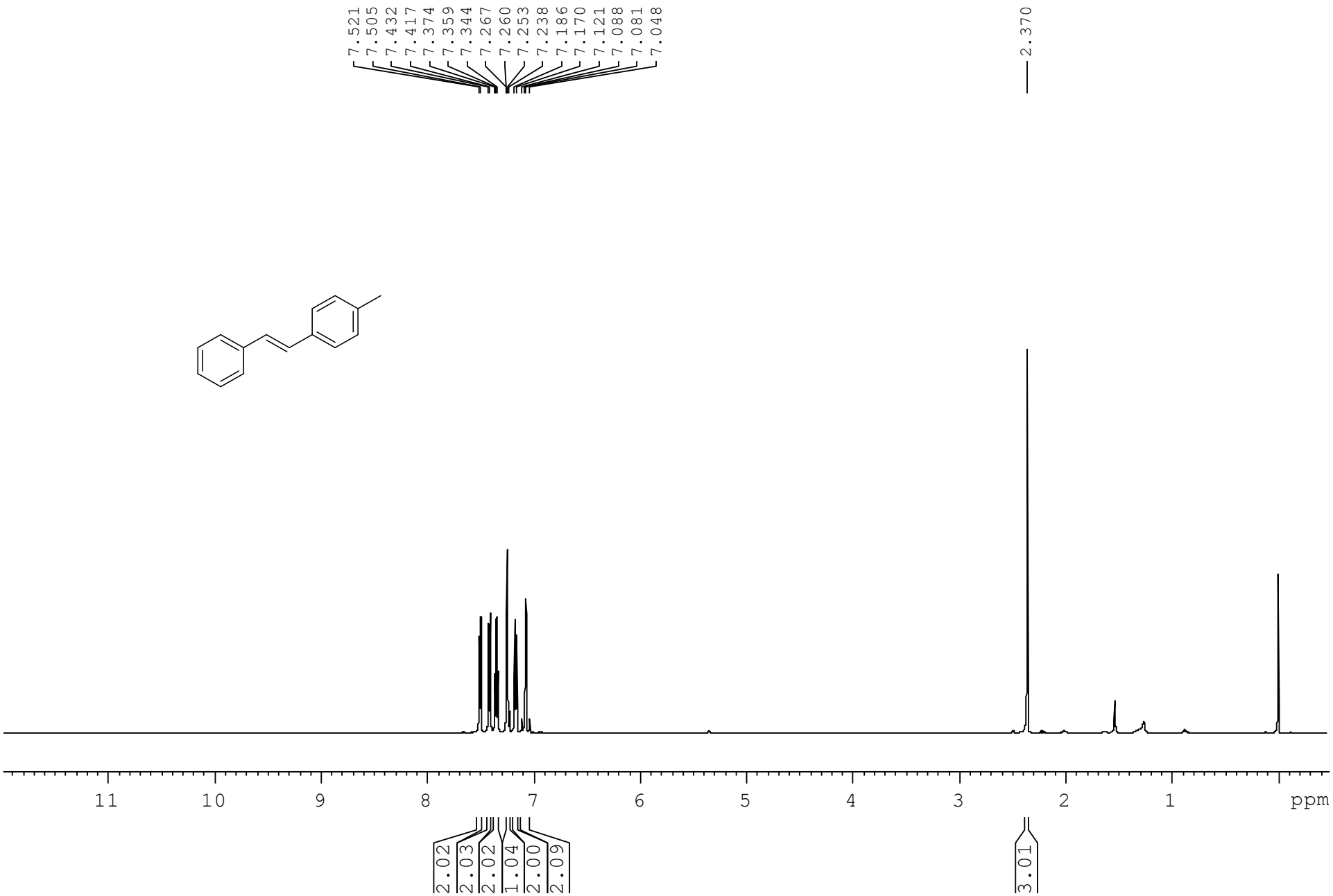

Figure S3. ^{1}H NMR spectra of **S2** ($CDCl_3$, 500 M)

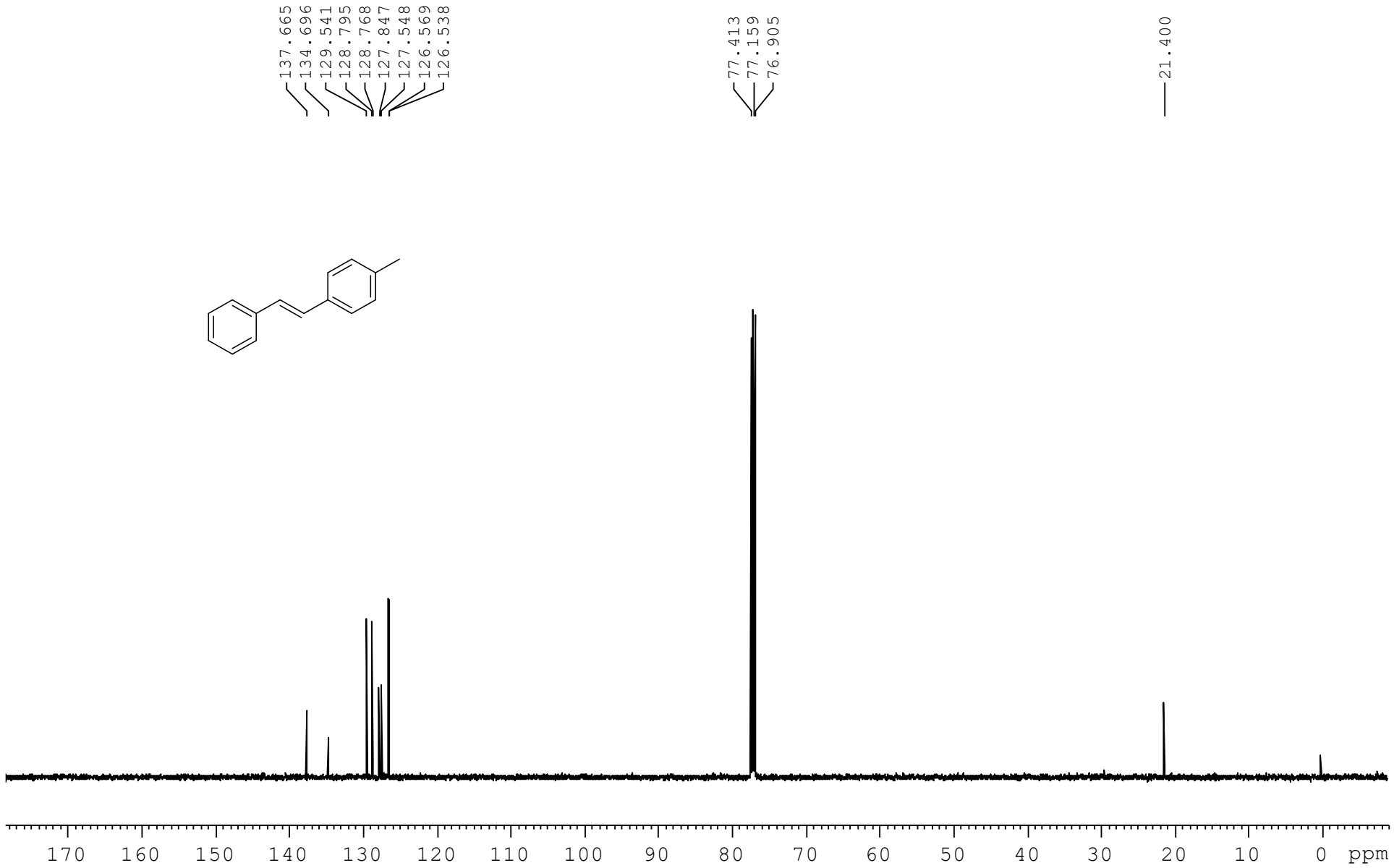

Figure S4. ^{13}C NMR spectra of **S2** ($CDCl_3$, 125 M)

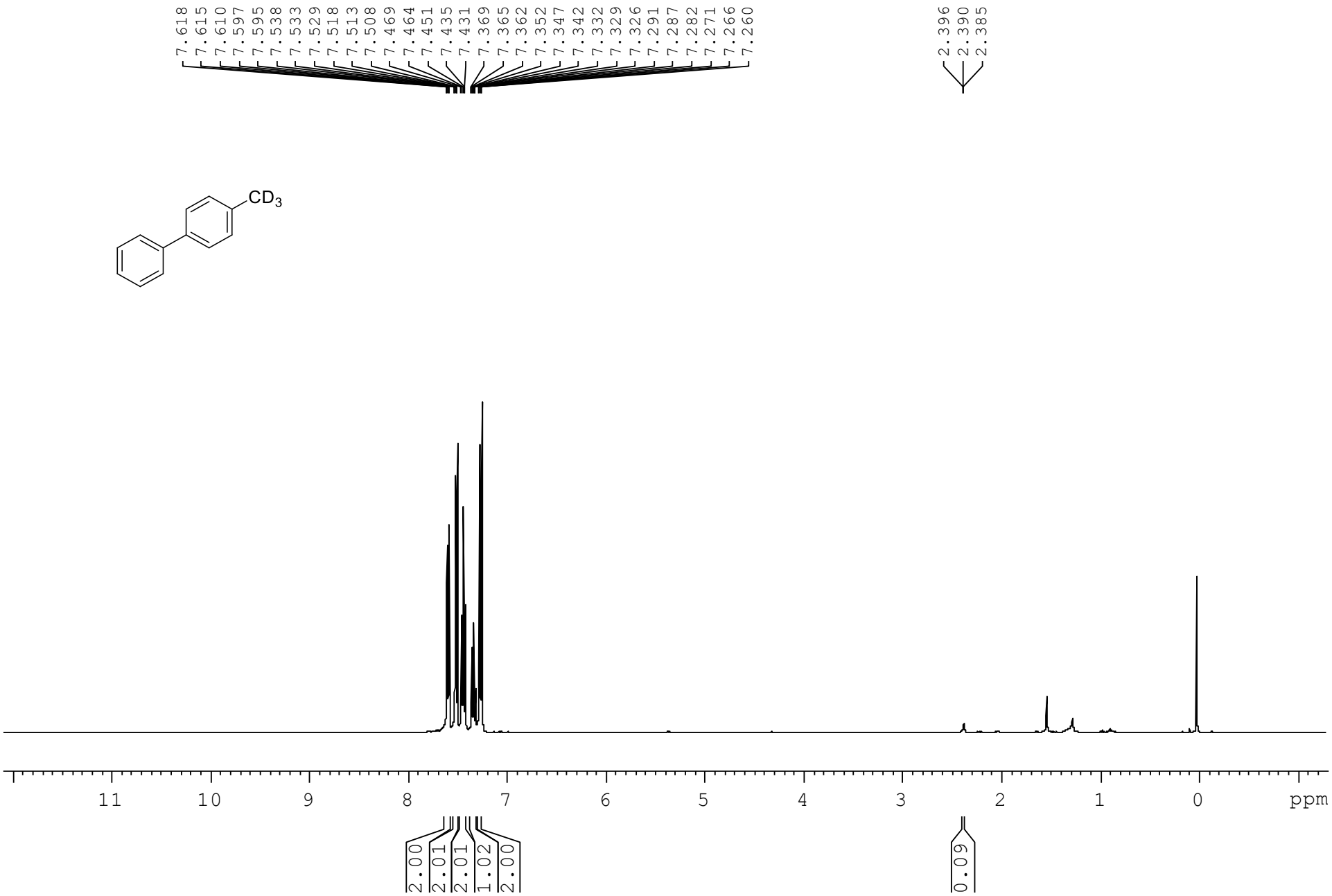

Figure S5. ^{1}H NMR spectra of **1a**-*d*$_3$ ($CDCl_3$, 400 M)

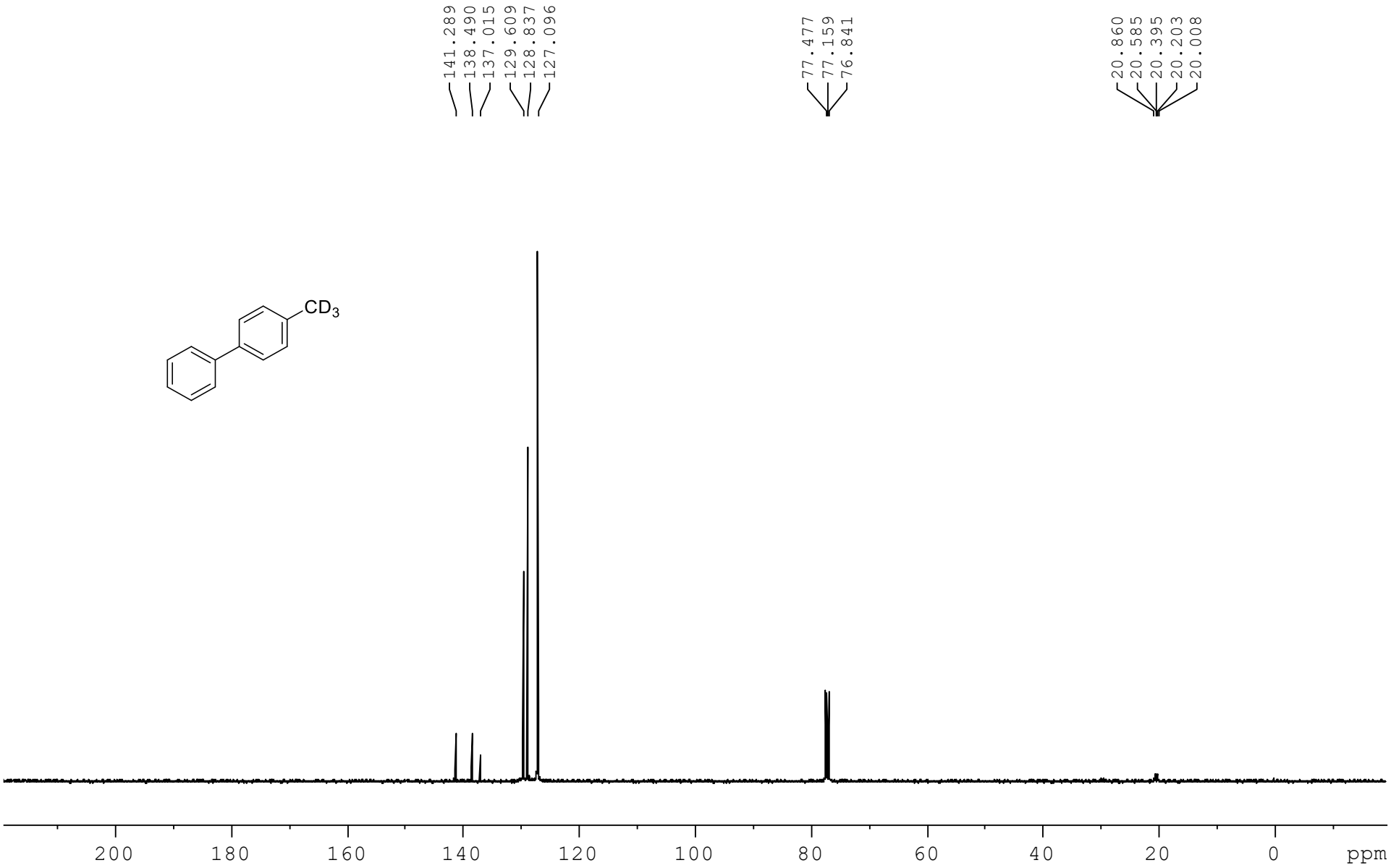

Figure S6. ^{13}C NMR spectra of **1a**-*d*$_3$ ($CDCl_3$, 100 M)

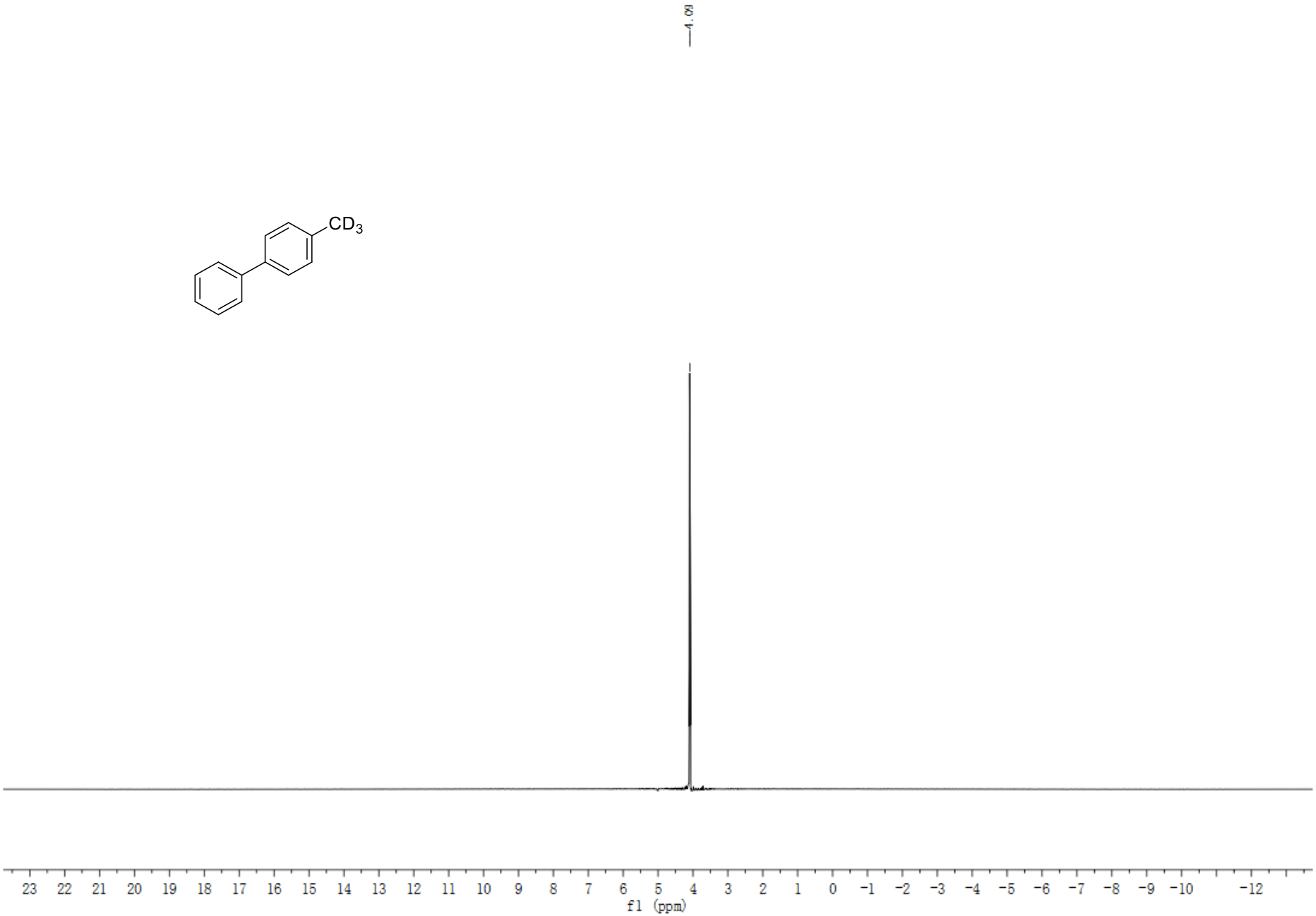

Figure S7. ^{2}H NMR spectra of **1a**-*d*$_3$ (MeCN, 92 M)

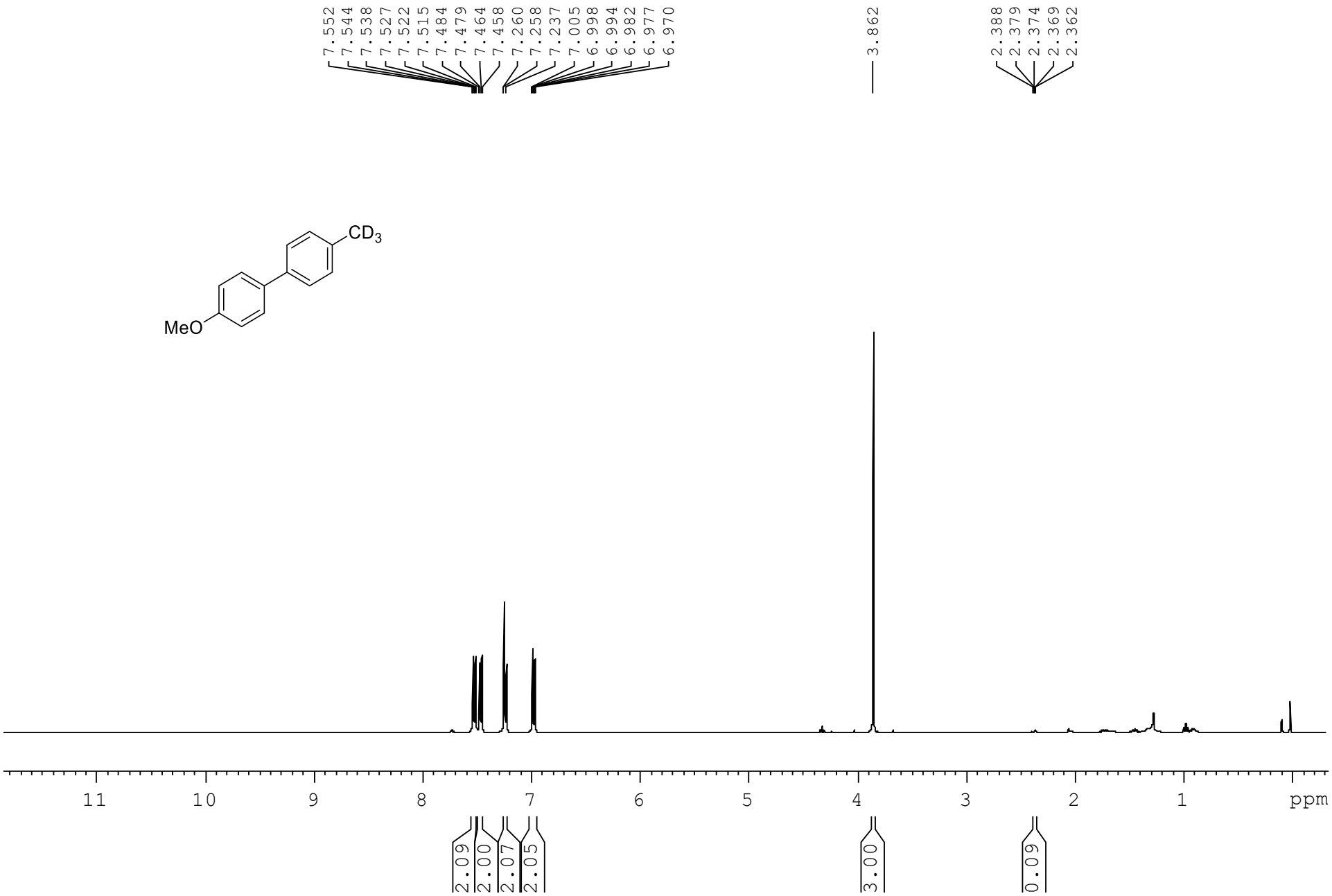

Figure S8. ^{1}H NMR spectra of **1b**-*d3* ($CDCl_3$, 400 M)

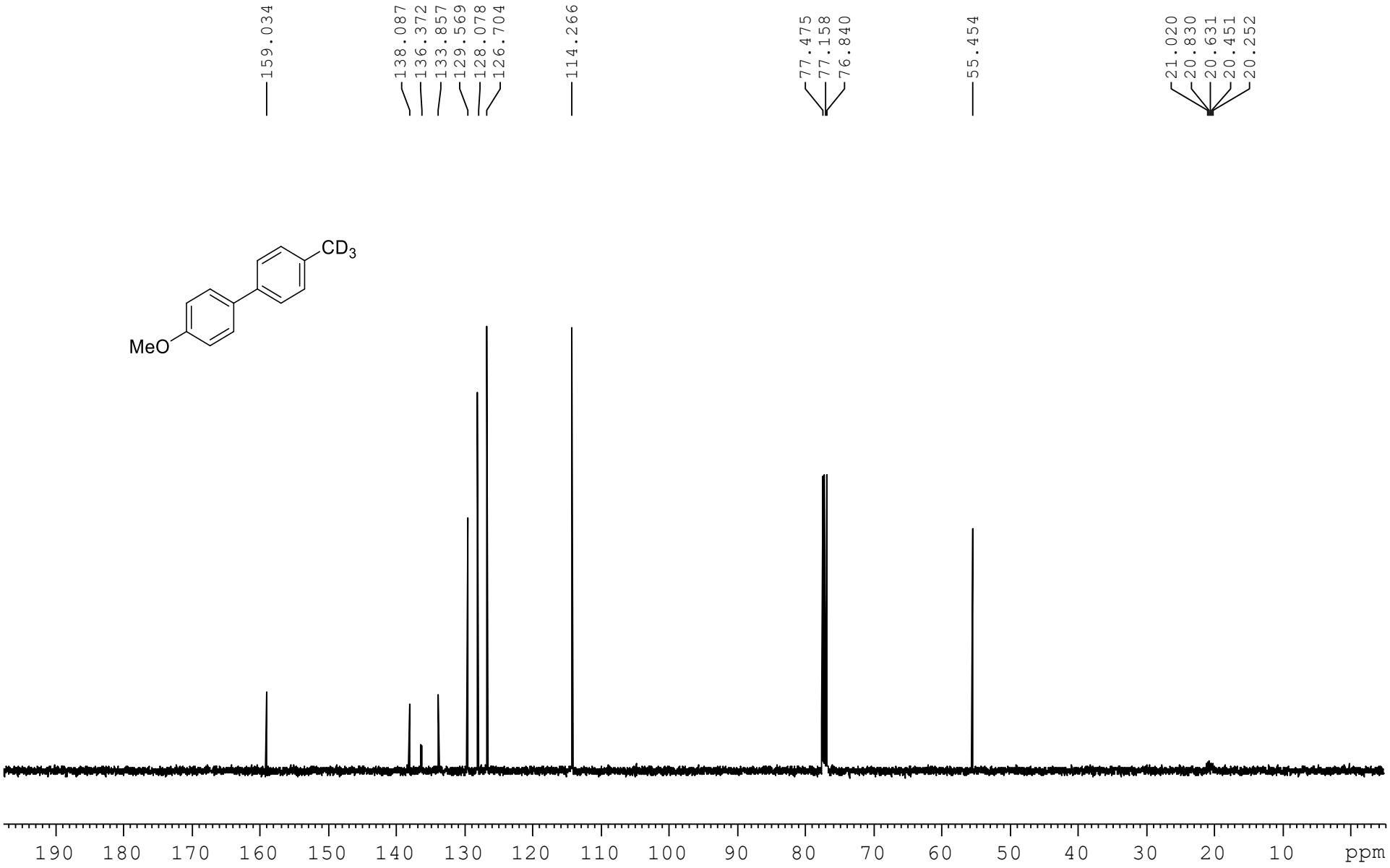

Figure S9. ^{13}C NMR spectra of **1b**-*d*$_3$ ($CDCl_3$, 100 M)

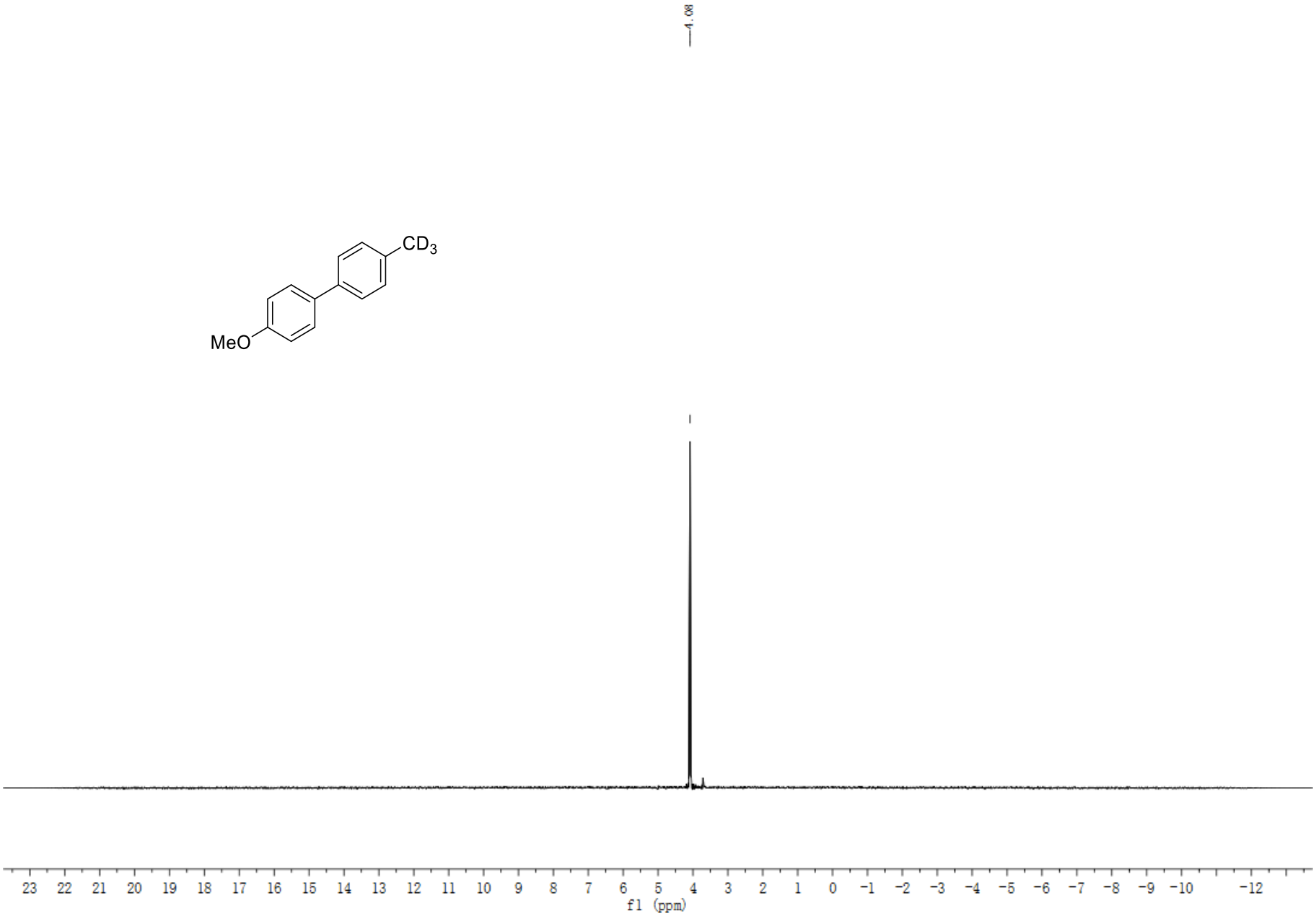

Figure S10. ^{2}H NMR spectra of **1b**-*d*$_3$ (MeCN, 92 M)

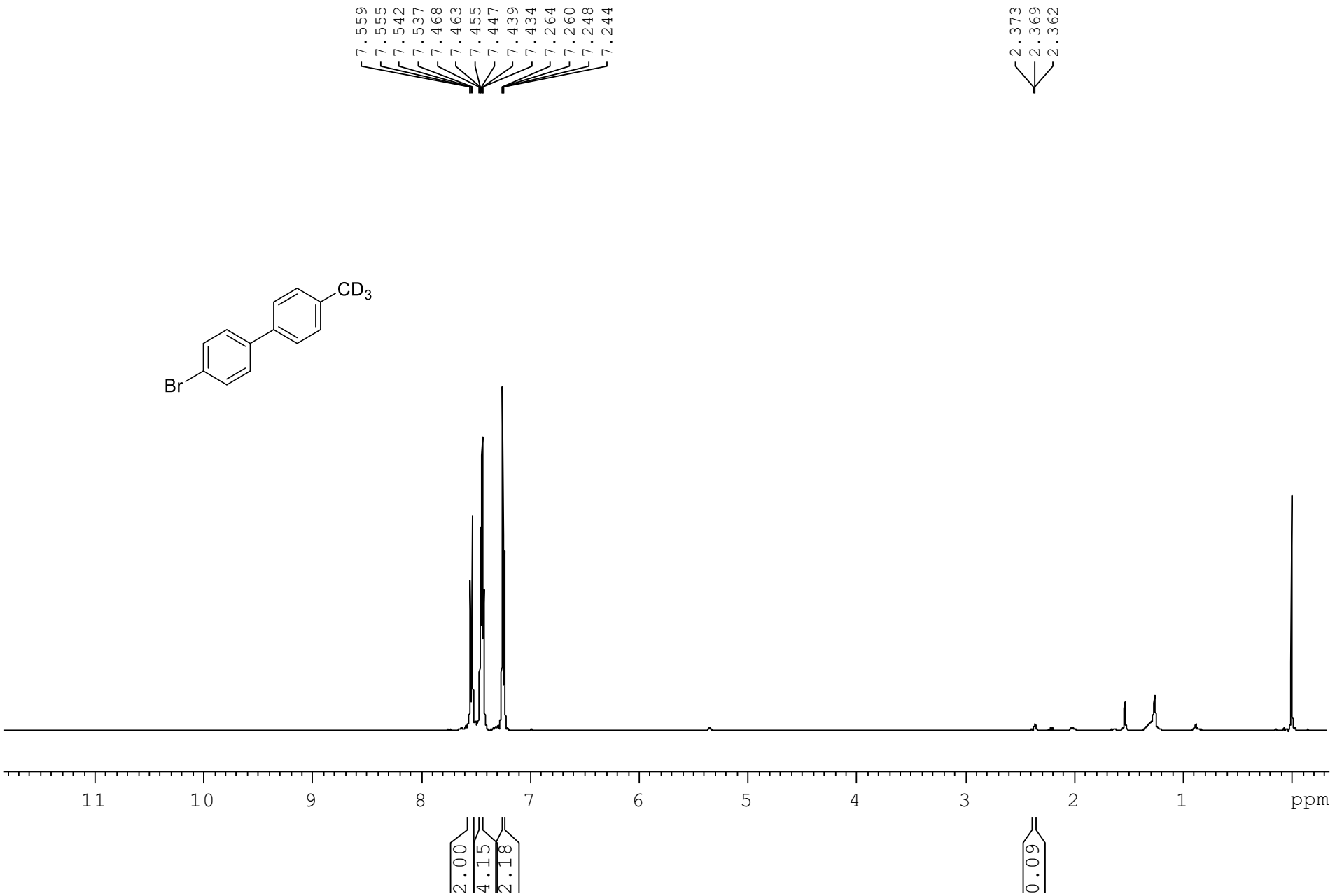

Figure S11. ^{1}H NMR spectra of **1c-*d*$_3$** ($CDCl_3$, 400 M)

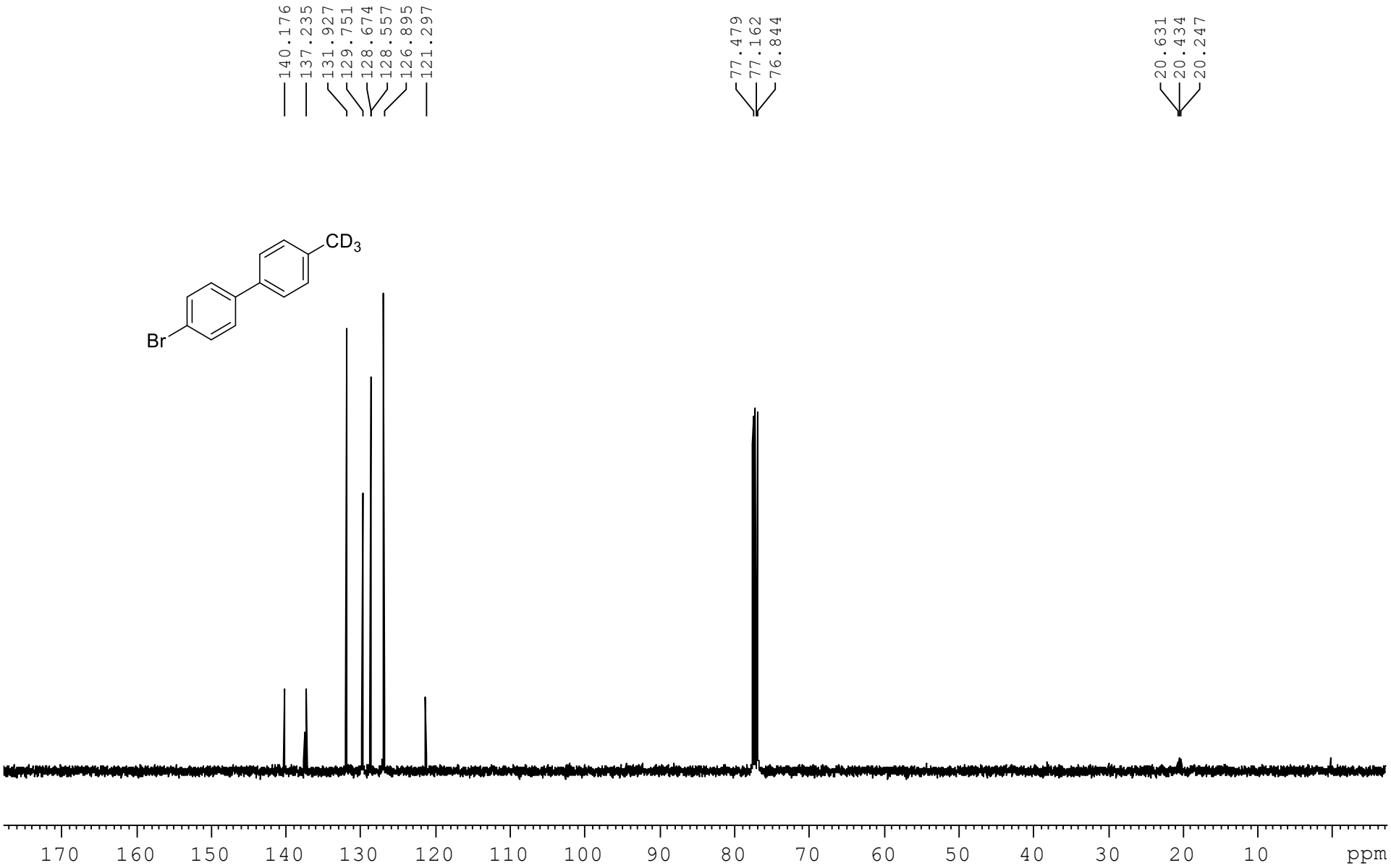

Figure S12. ^{13}C NMR spectra of **1c**-*d*$_3$ ($CDCl_3$, 100 M)

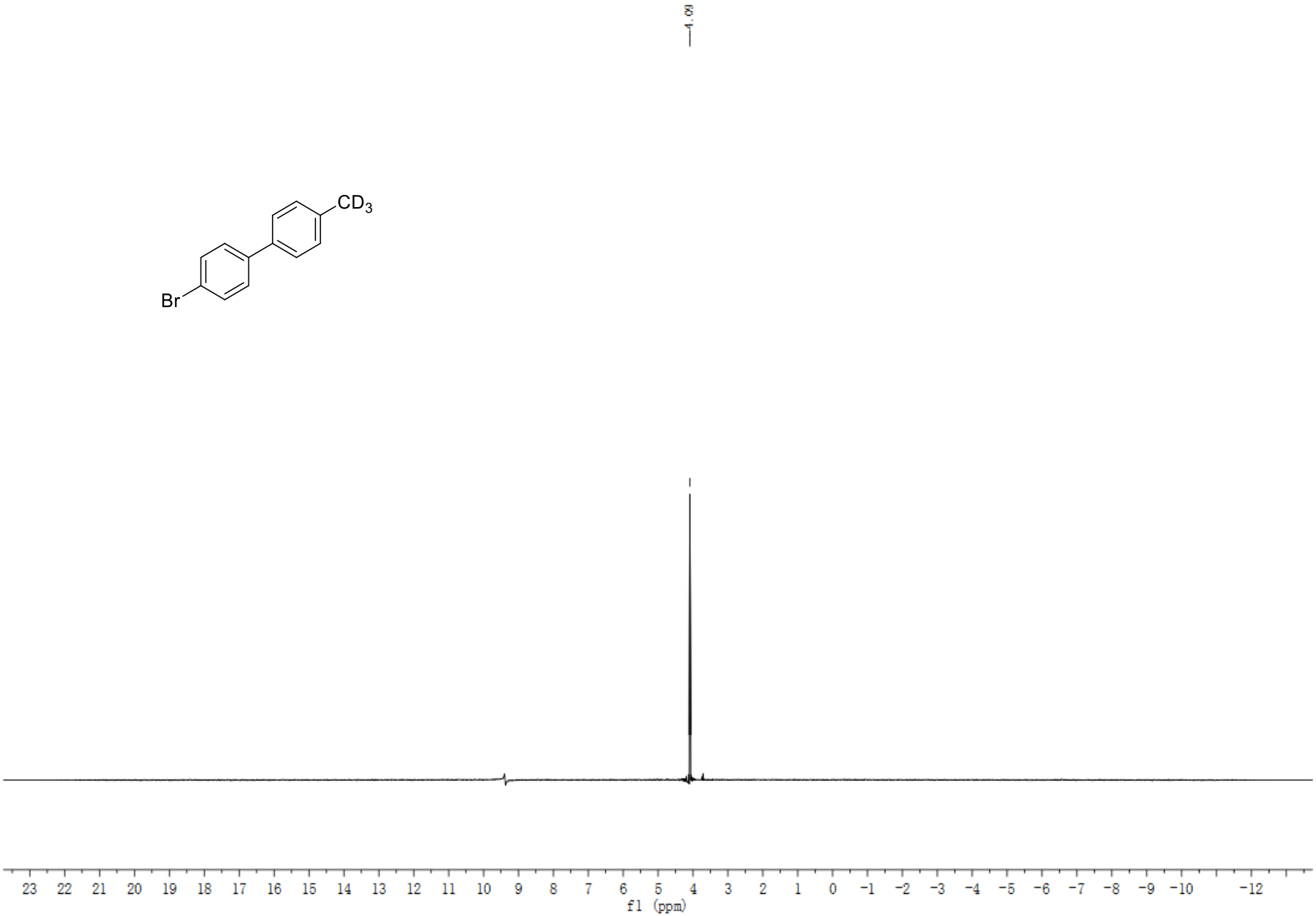

Figure S13. ^{2}H NMR spectra of **1c**-*d*$_3$ (MeCN, 92 M)

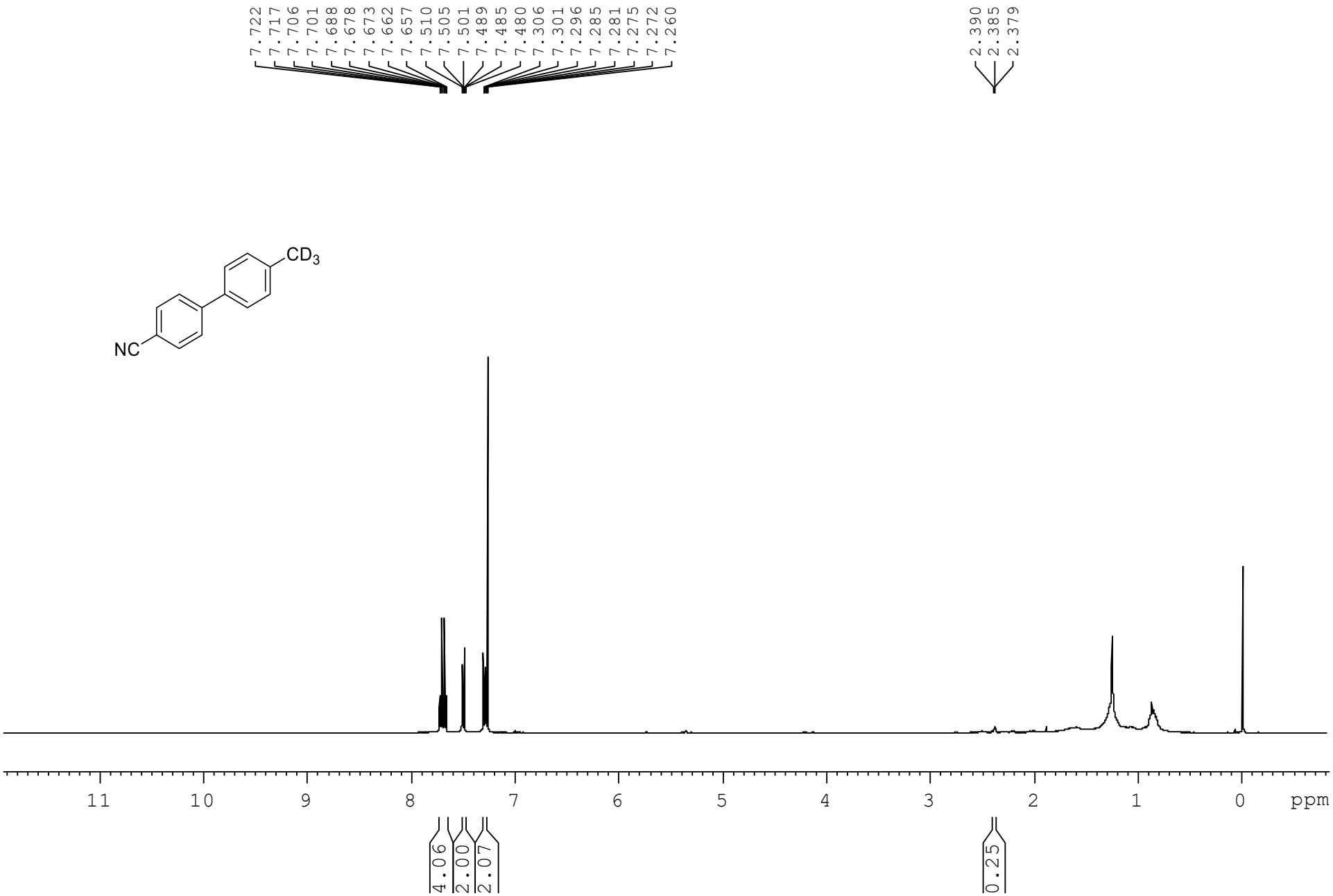

Figure S14. ^{1}H NMR spectra of **1d-*d*$_3$** ($CDCl_3$, 400 M)

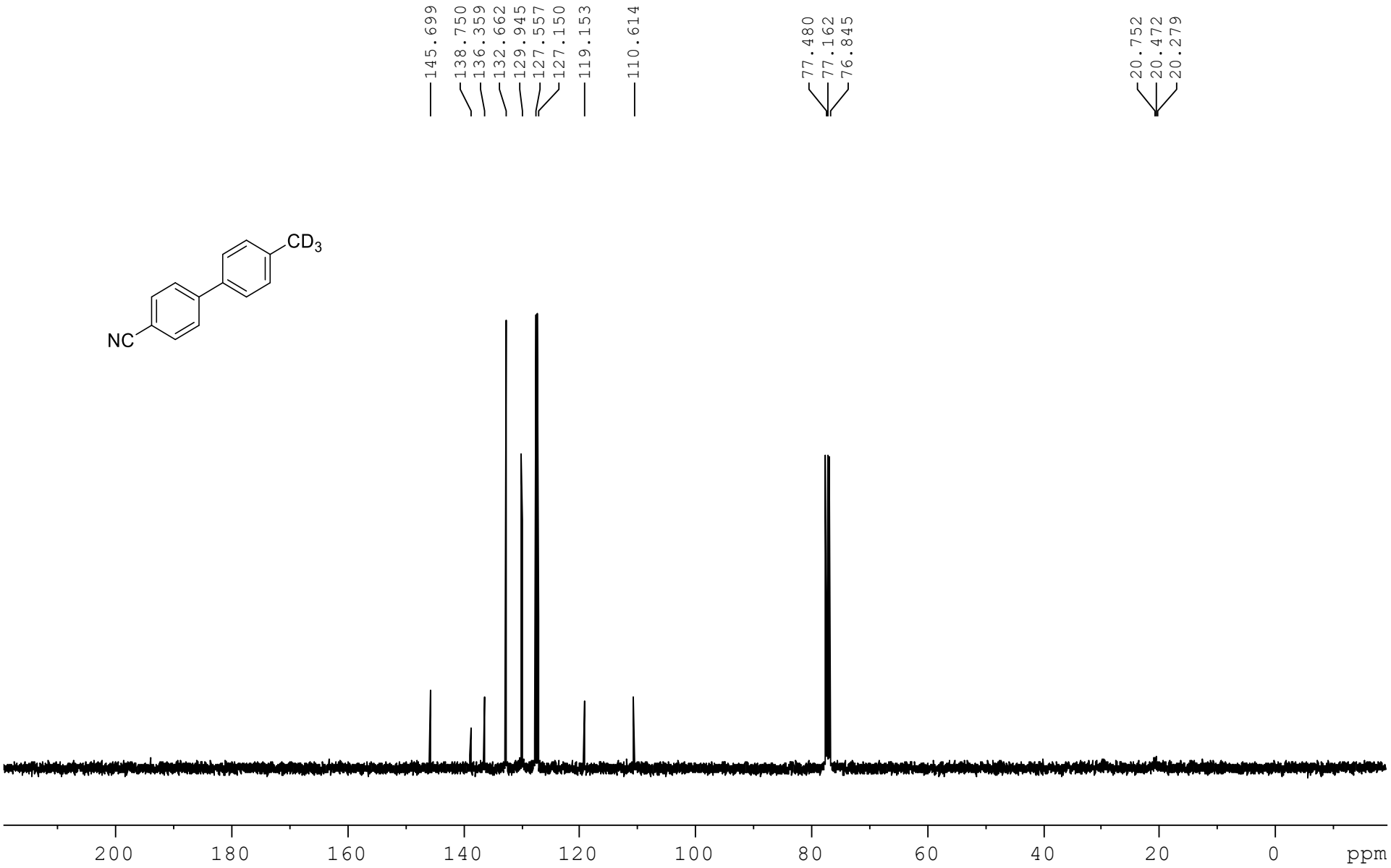

Figure S15. ^{13}C NMR spectra of **1d-*d3*** ($CDCl_3$, 100 M)

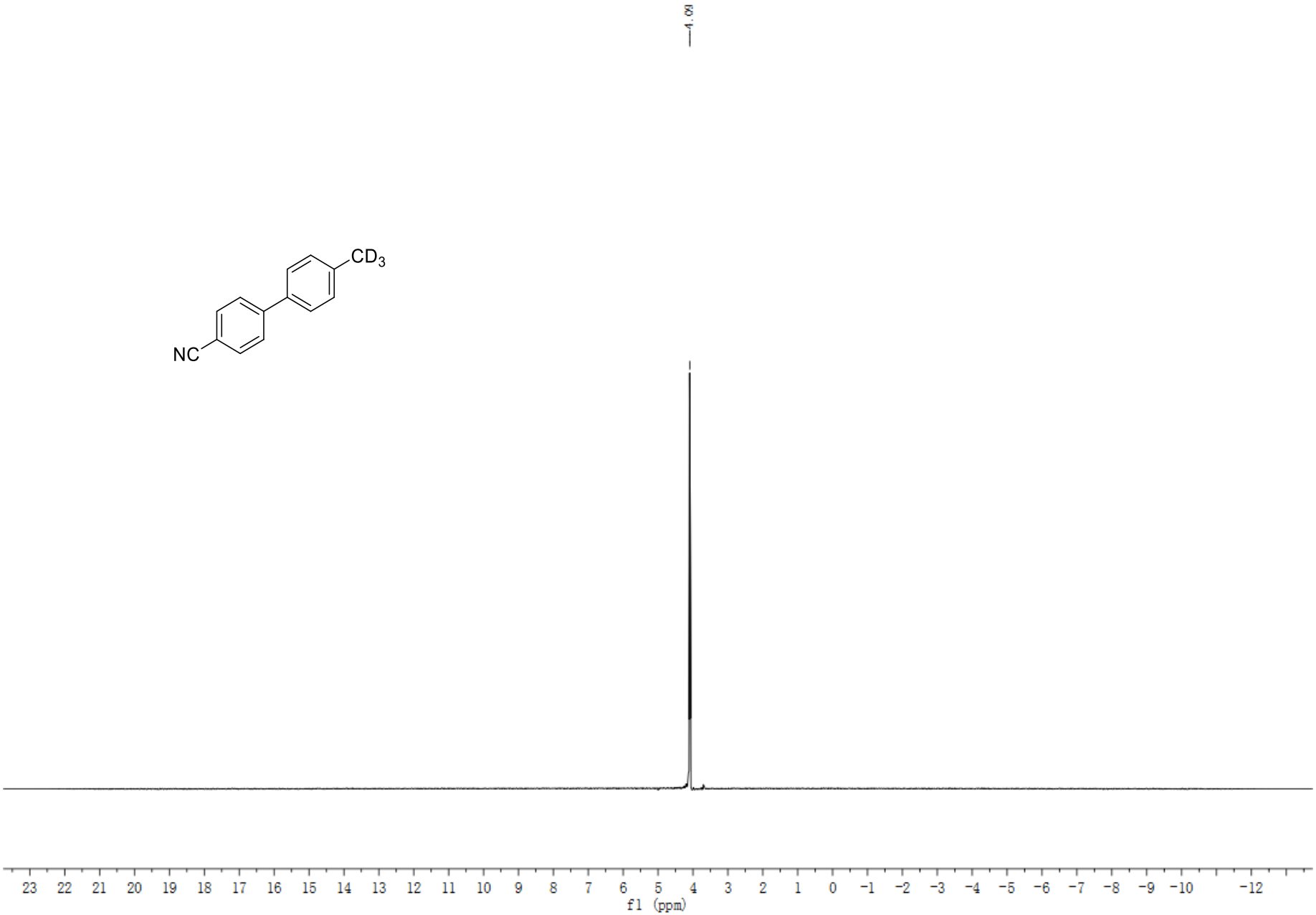

Figure S16. ^{1}H NMR spectra of **1d**-*d*$_3$ (MeCN, 92 M)

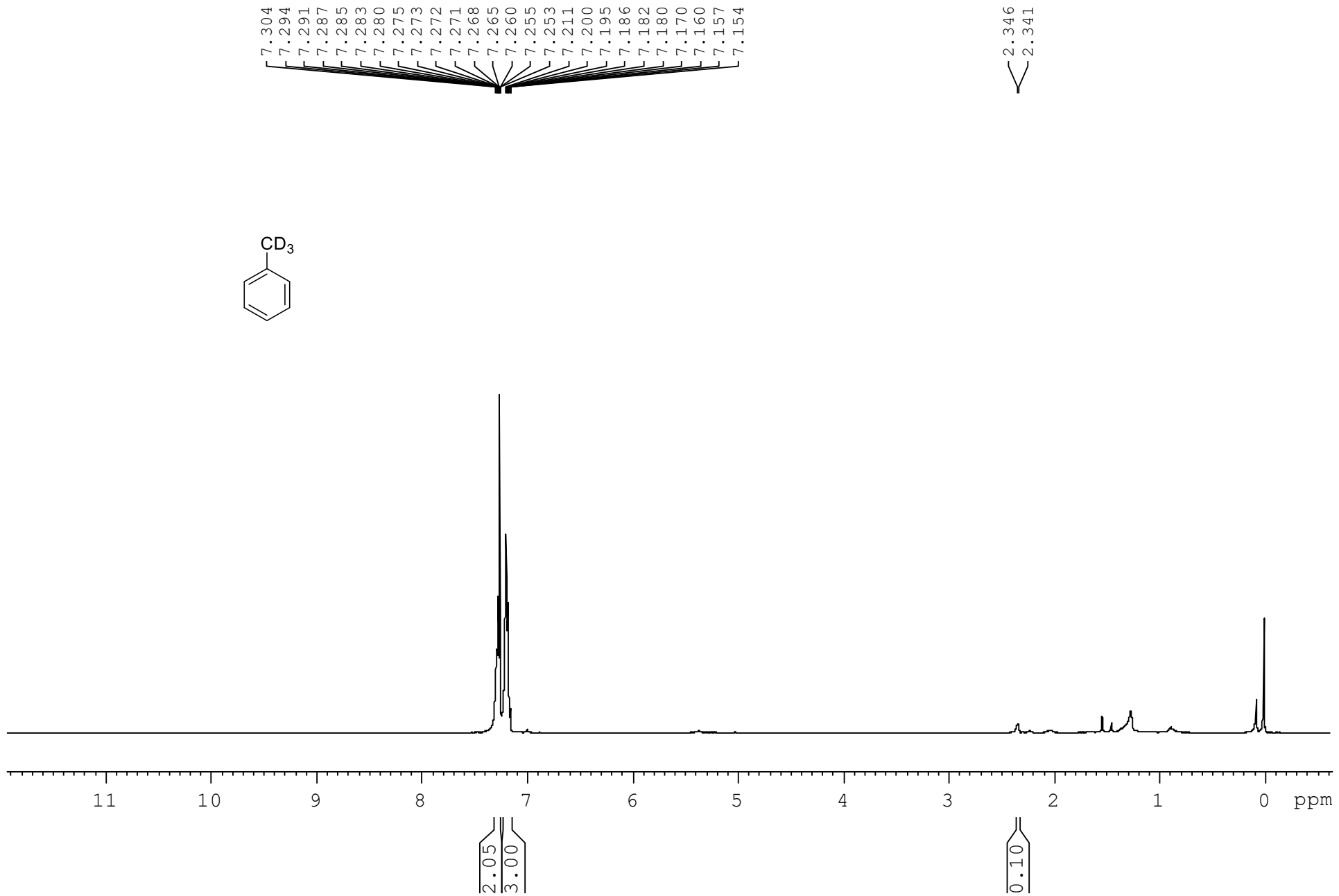

Figure S17. ^{1}H NMR spectra of **1e-*d*$_3$** ($CDCl_3$, 400 M)

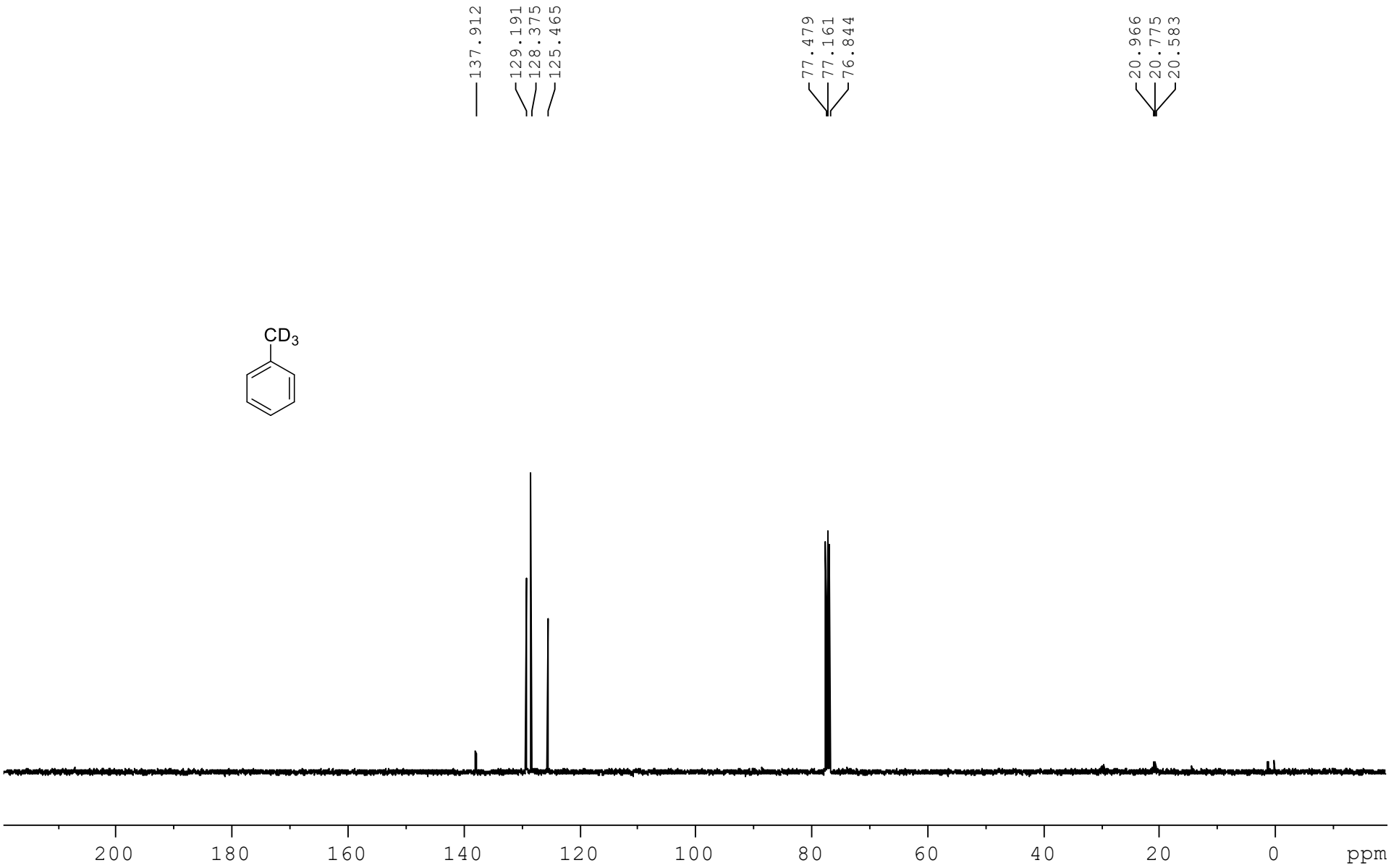

Figure S18. ^{13}C NMR spectra of **1e**-*d*$_3$ ($CDCl_3$, 100 M)

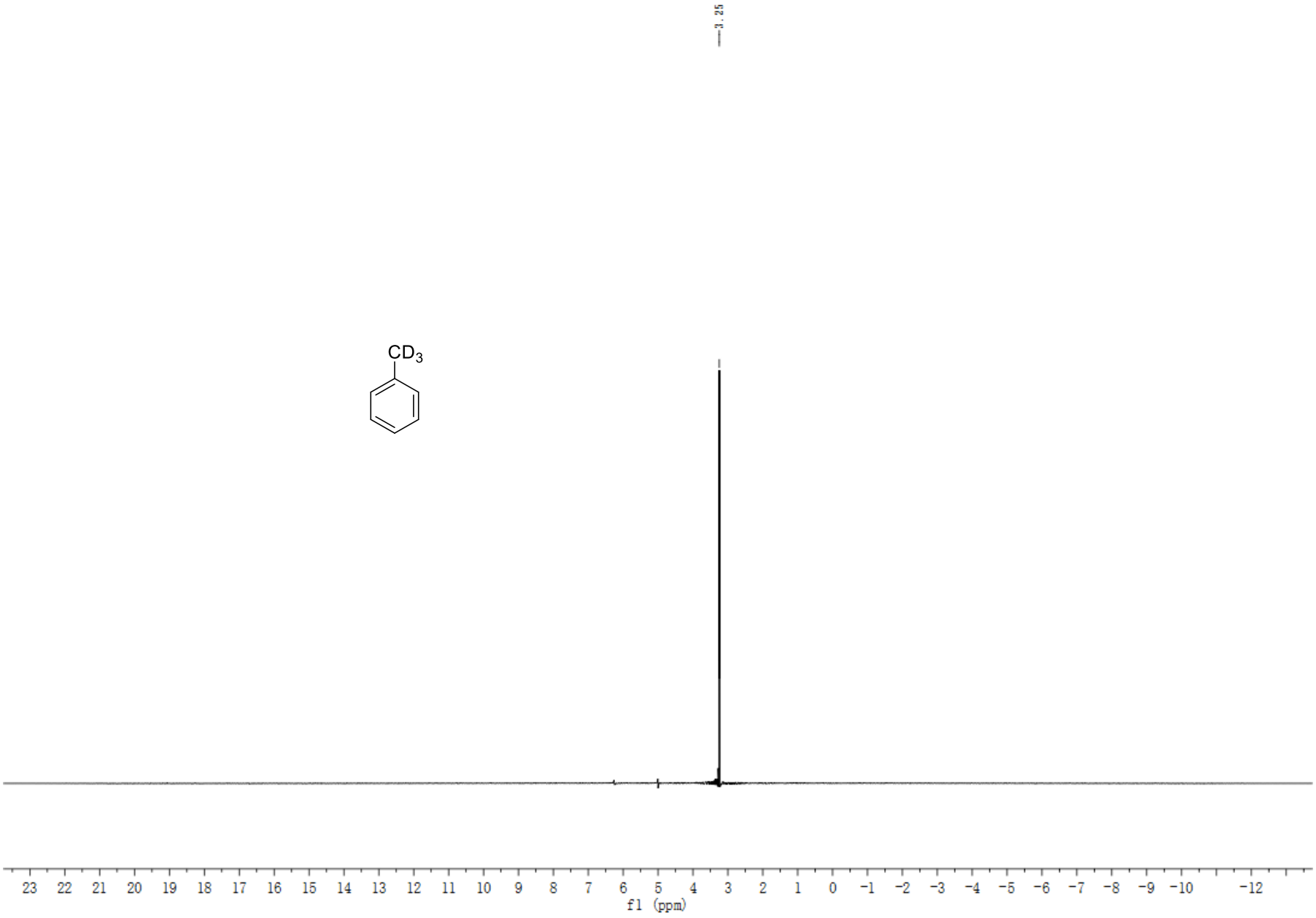

Figure S19. ^{2}H NMR spectra of **1e**-*d*$_3$ (DCM, 92 M)

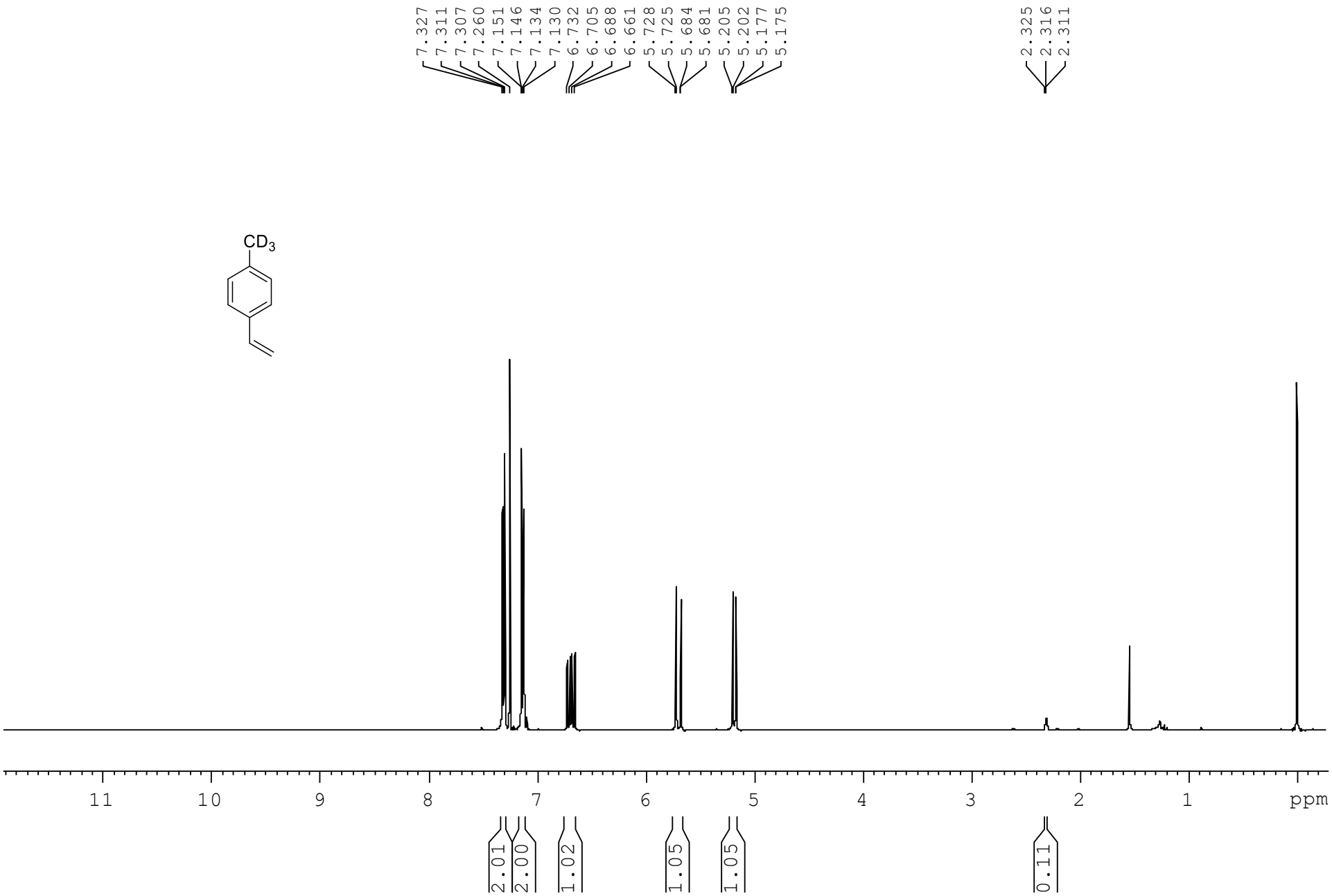

Figure S20. ^{1}H NMR spectra of **1f-*d*$_3$** ($CDCl_3$, 400 M)

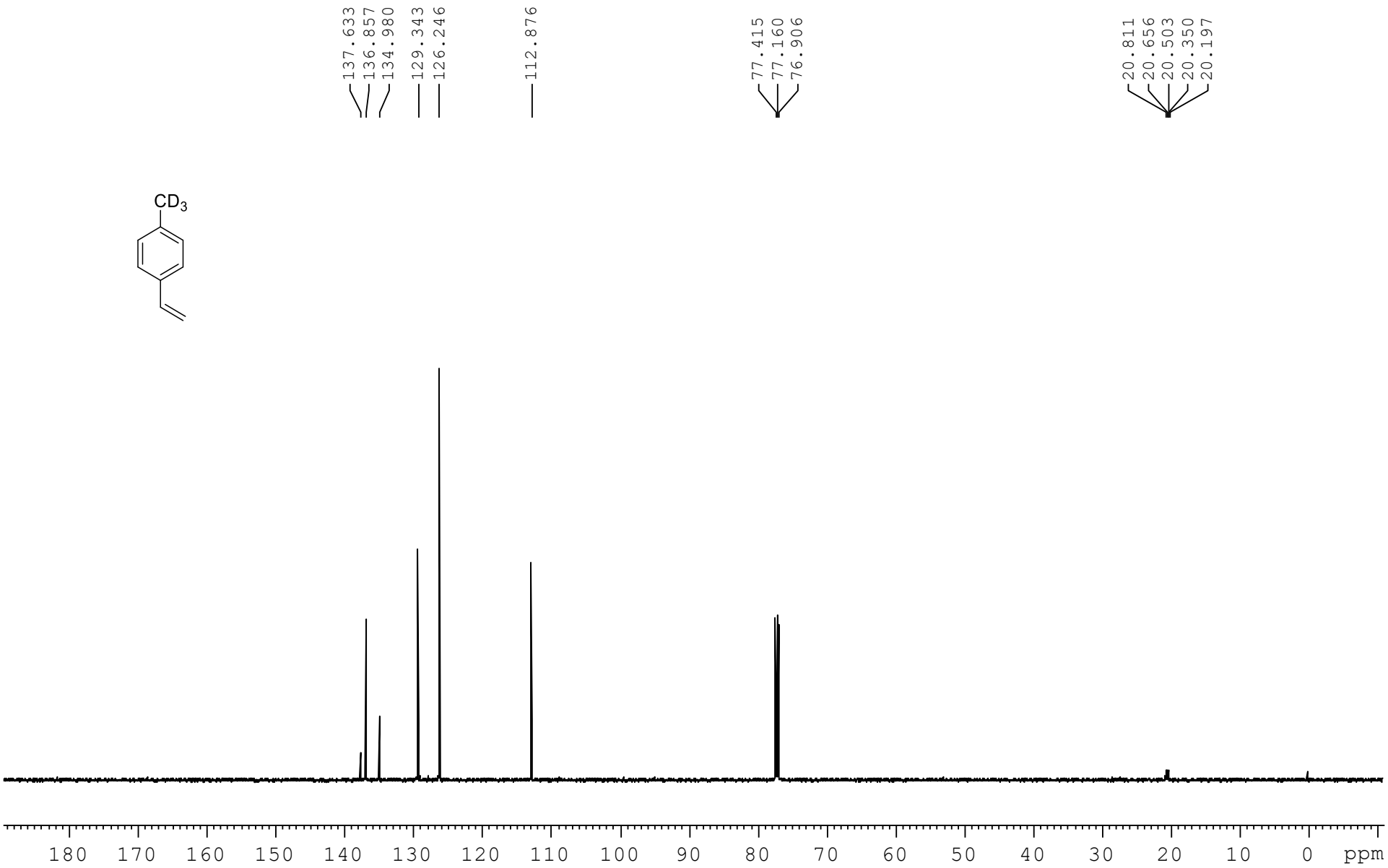

Figure S21. ^{13}C NMR spectra of **1f-*d3*** ($CDCl_3$, 125 M)

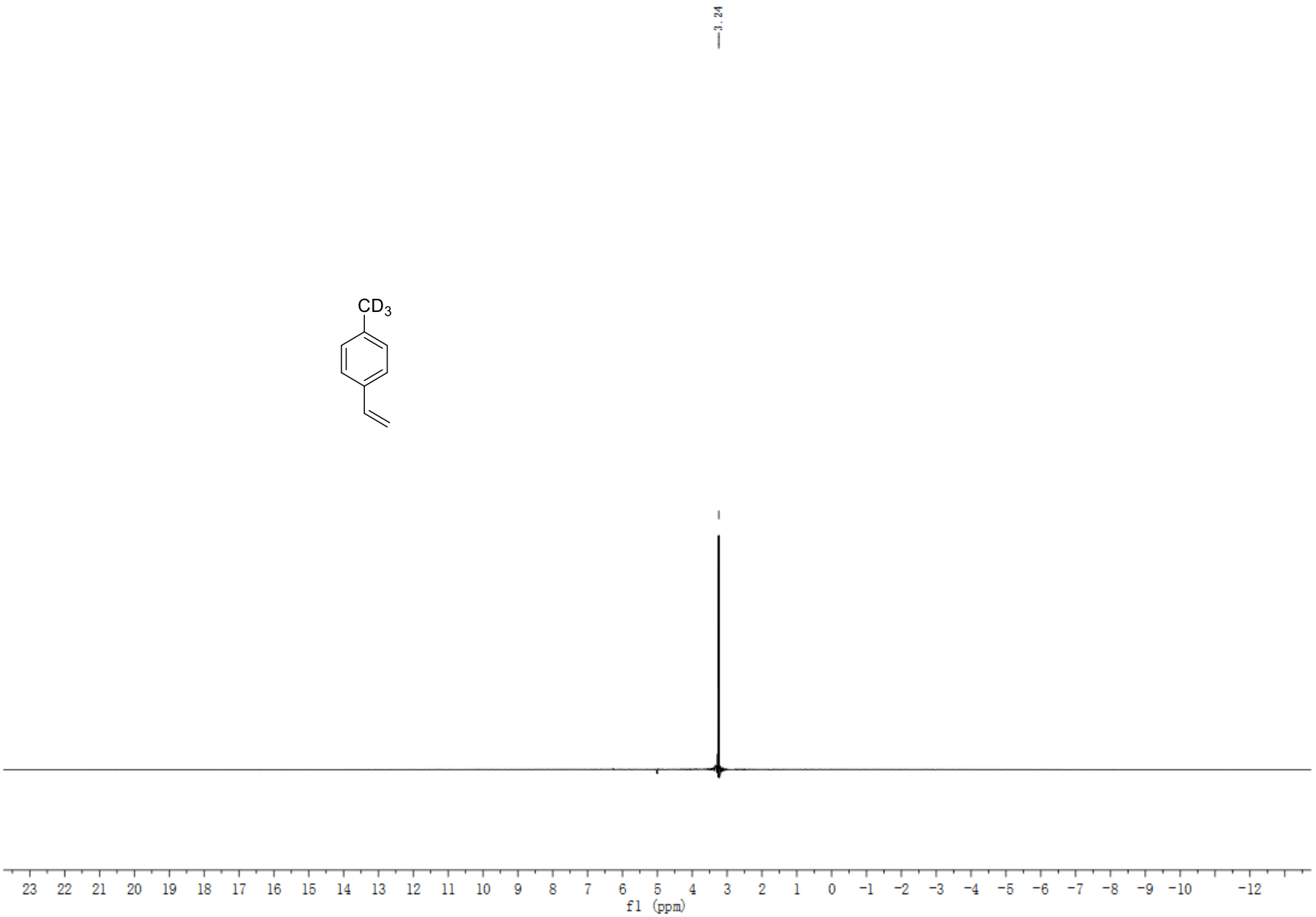

Figure S22. ^{2}H NMR spectra of **1f-*d*$_3$** (DCM, 92 M)

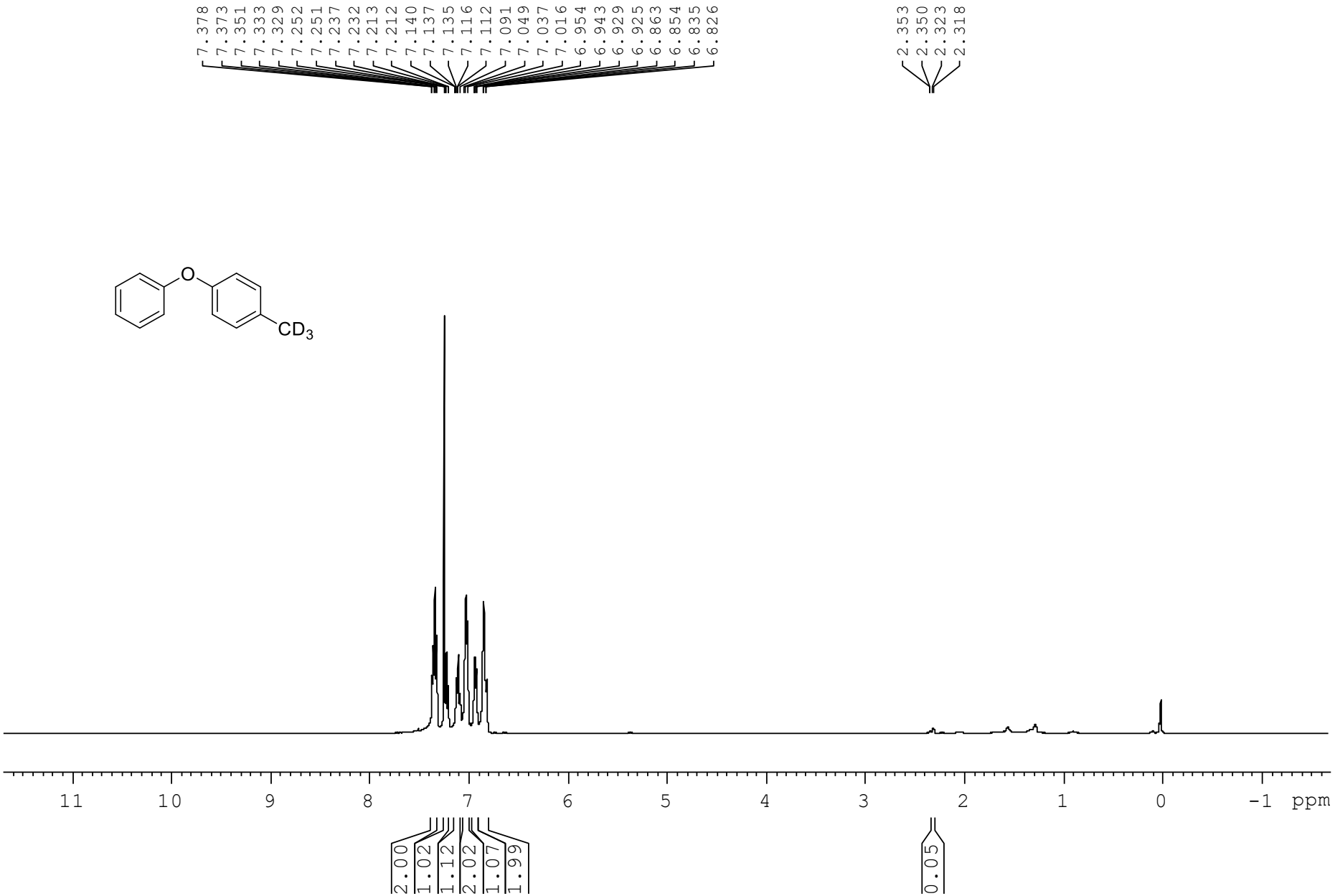

Figure S23. ^{1}H NMR spectra of **1g-*d*$_3$** ($CDCl_3$, 400 M)

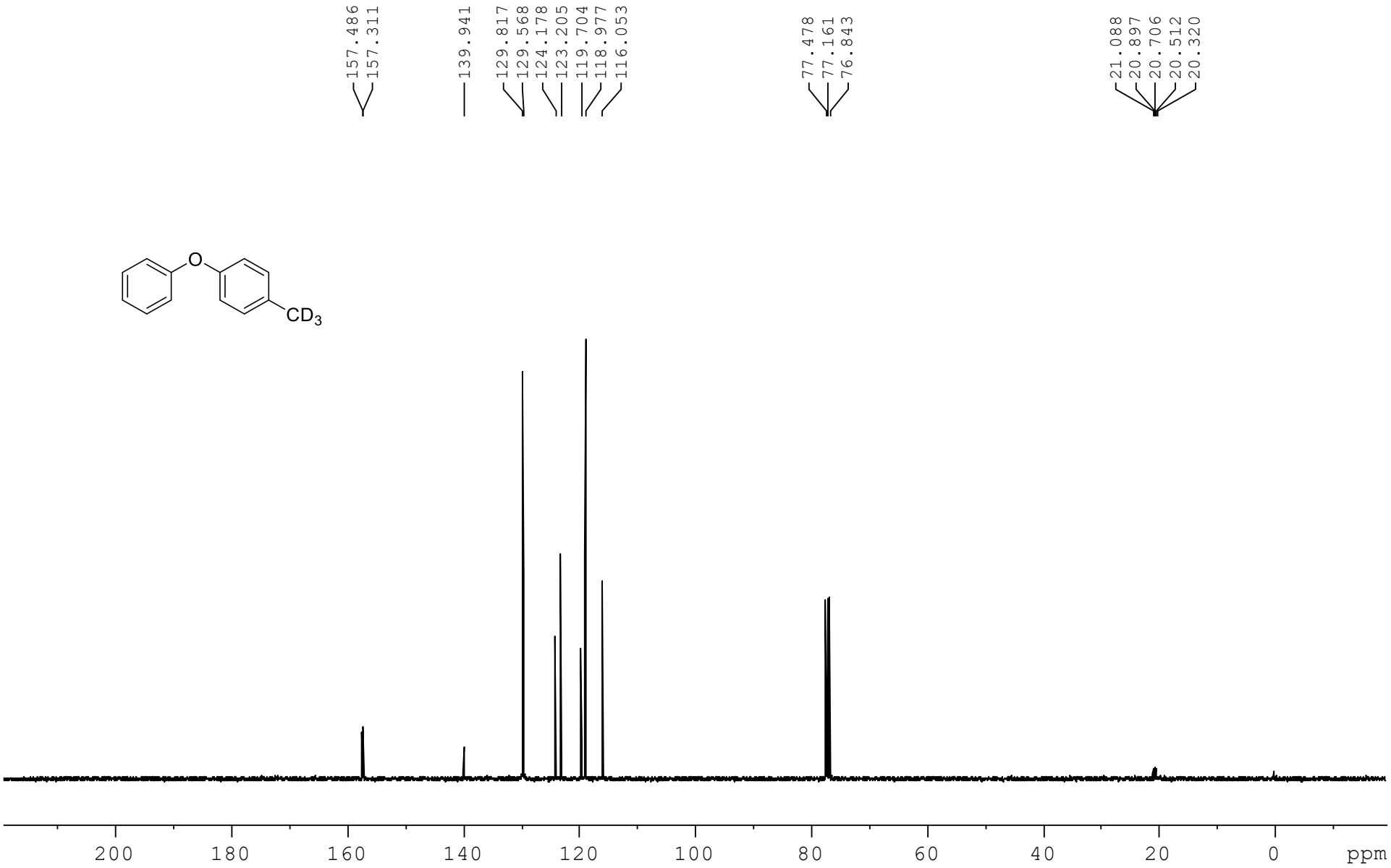

Figure S24. ^{13}C NMR spectra of **1g-*d3*** ($CDCl_3$, 100 M)

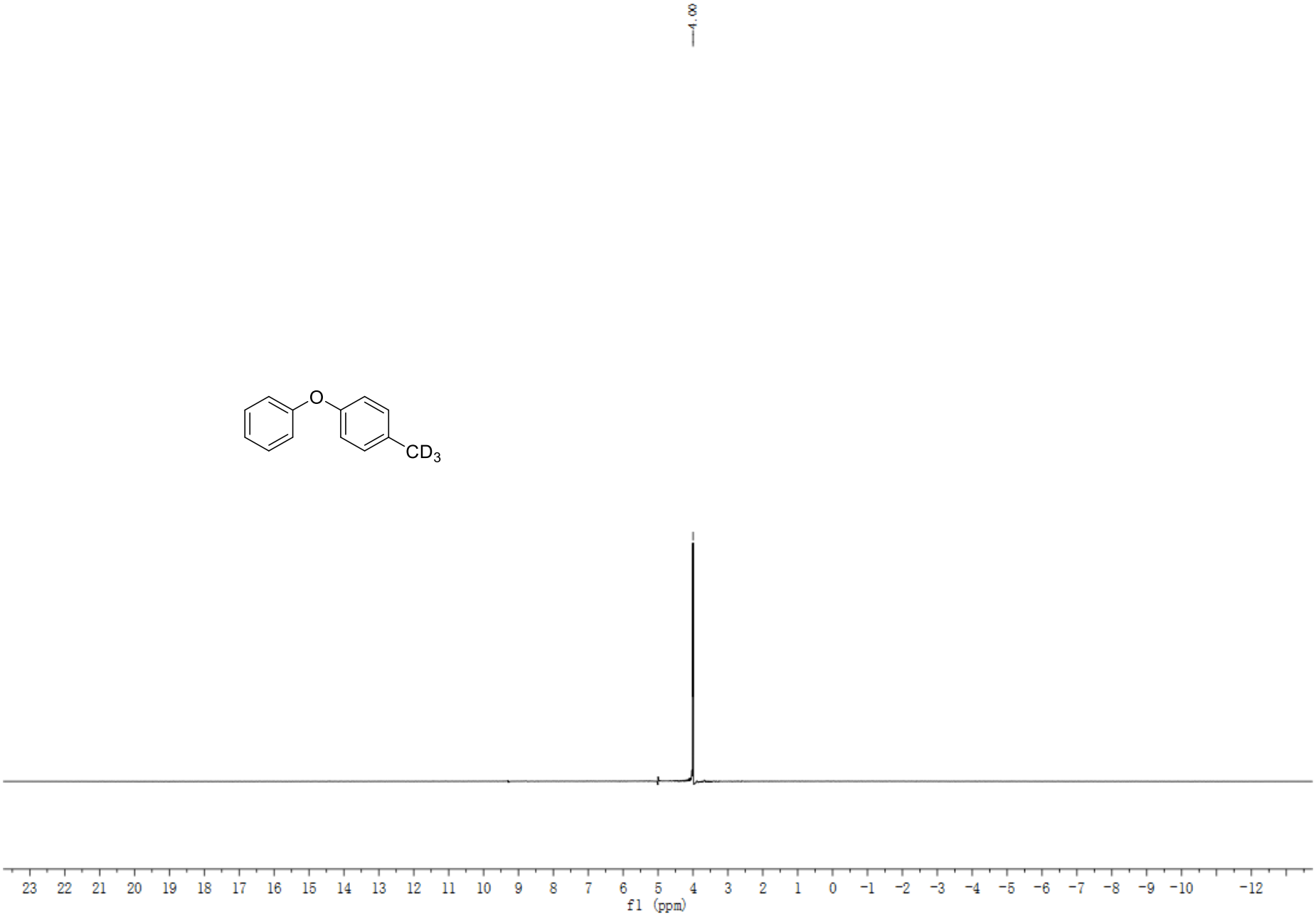

Figure S25. ^{2}H NMR spectra of **1g**-*d*$_3$ (MeCN, 92 M)

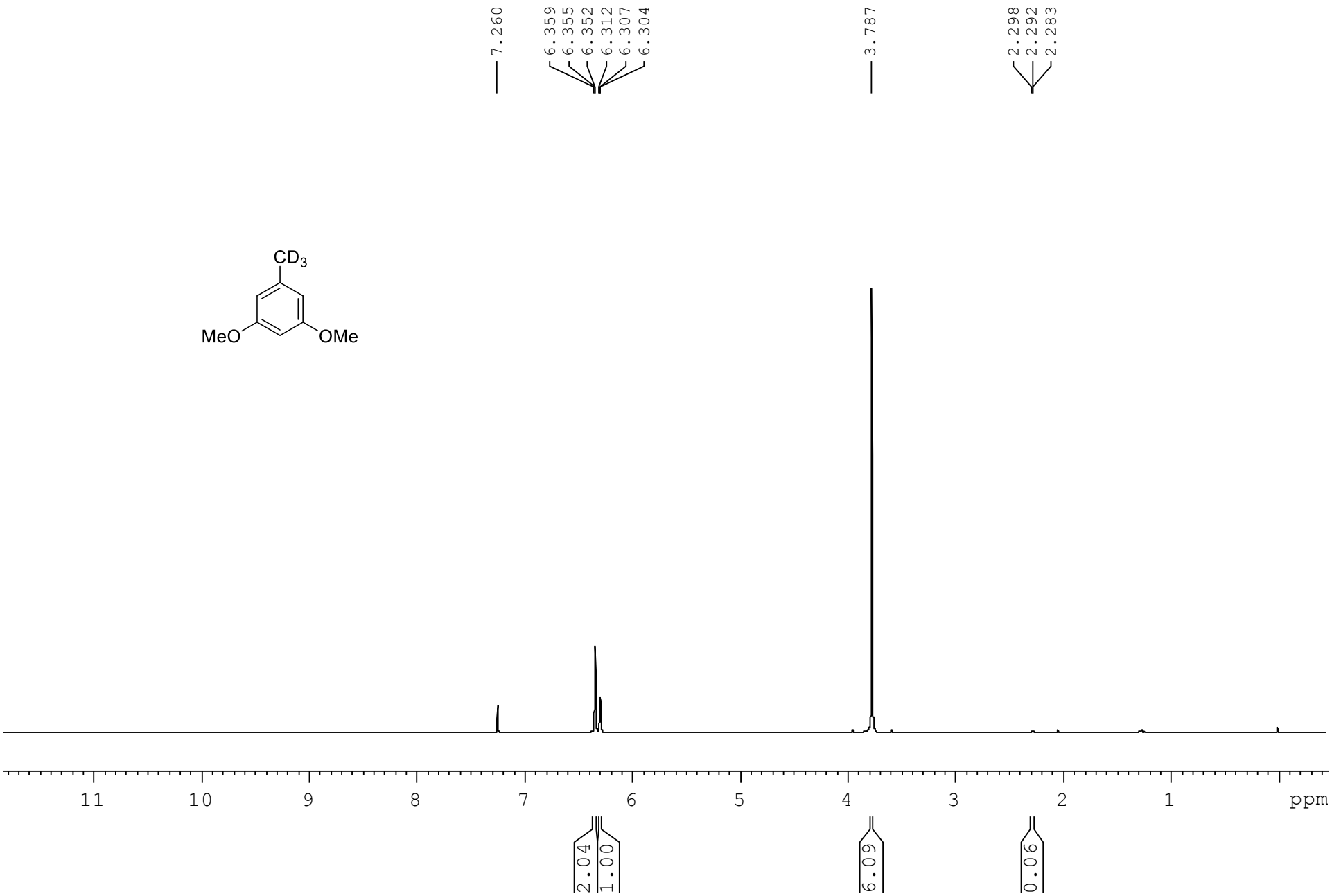

Figure S26. ^{1}H NMR spectra of **1h**-*d*$_3$ ($CDCl_3$, 400 M)

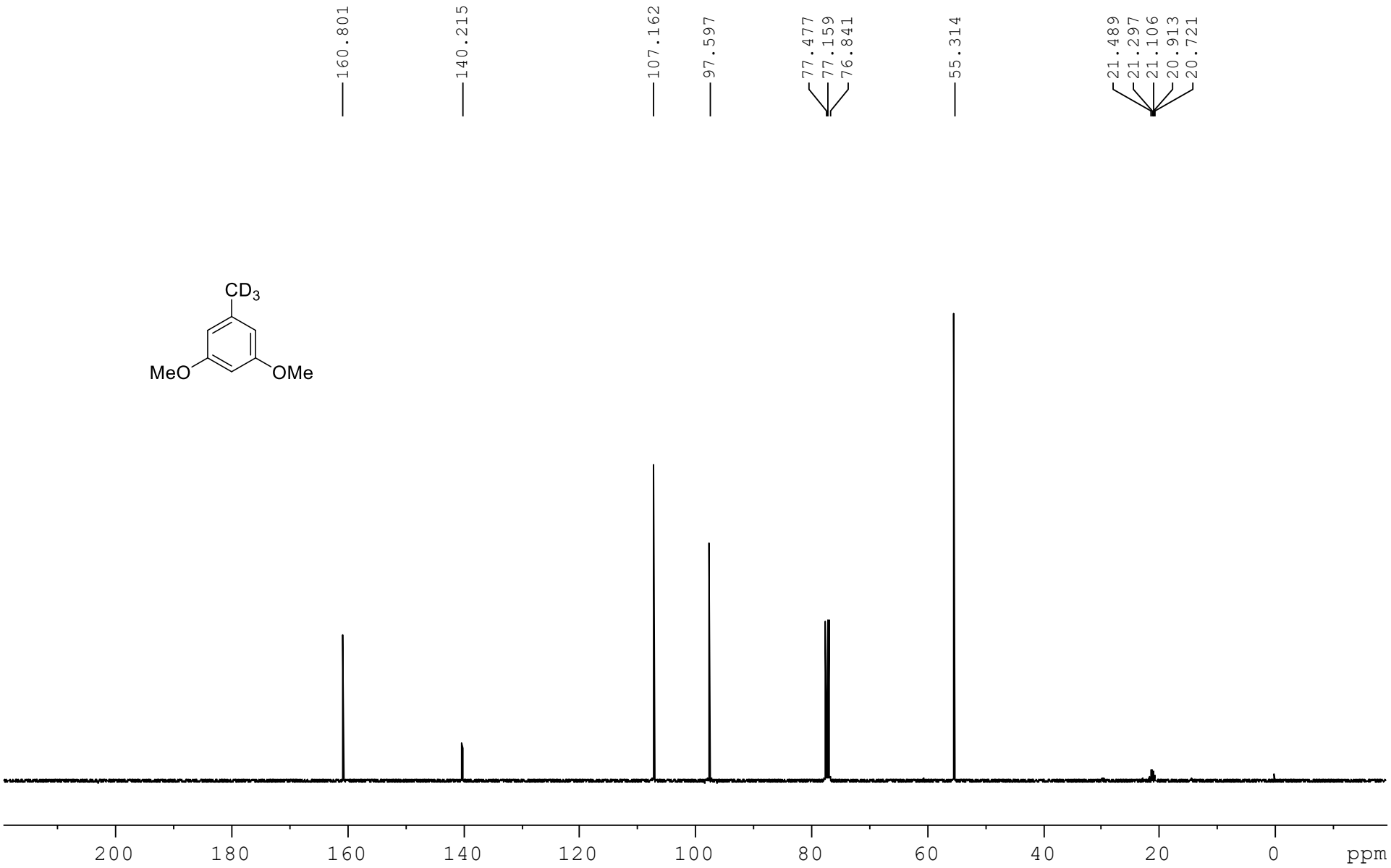

Figure S27. ^{13}C NMR spectra of **1h-*d*$_3$** ($CDCl_3$, 100 M)

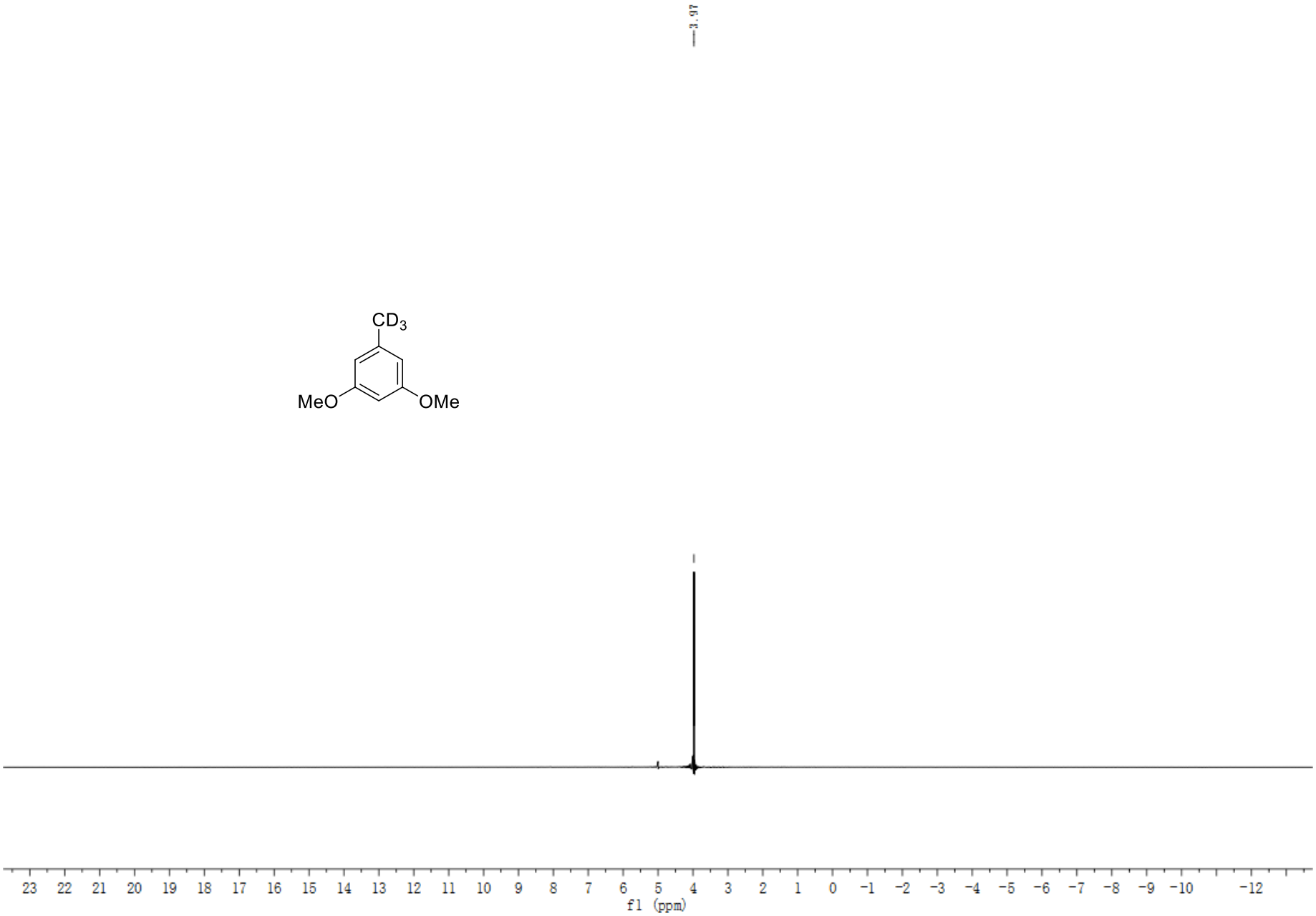

Figure S28. ^{2}H NMR spectra of **1h**-*d*$_3$ (MeCN, 92 M)

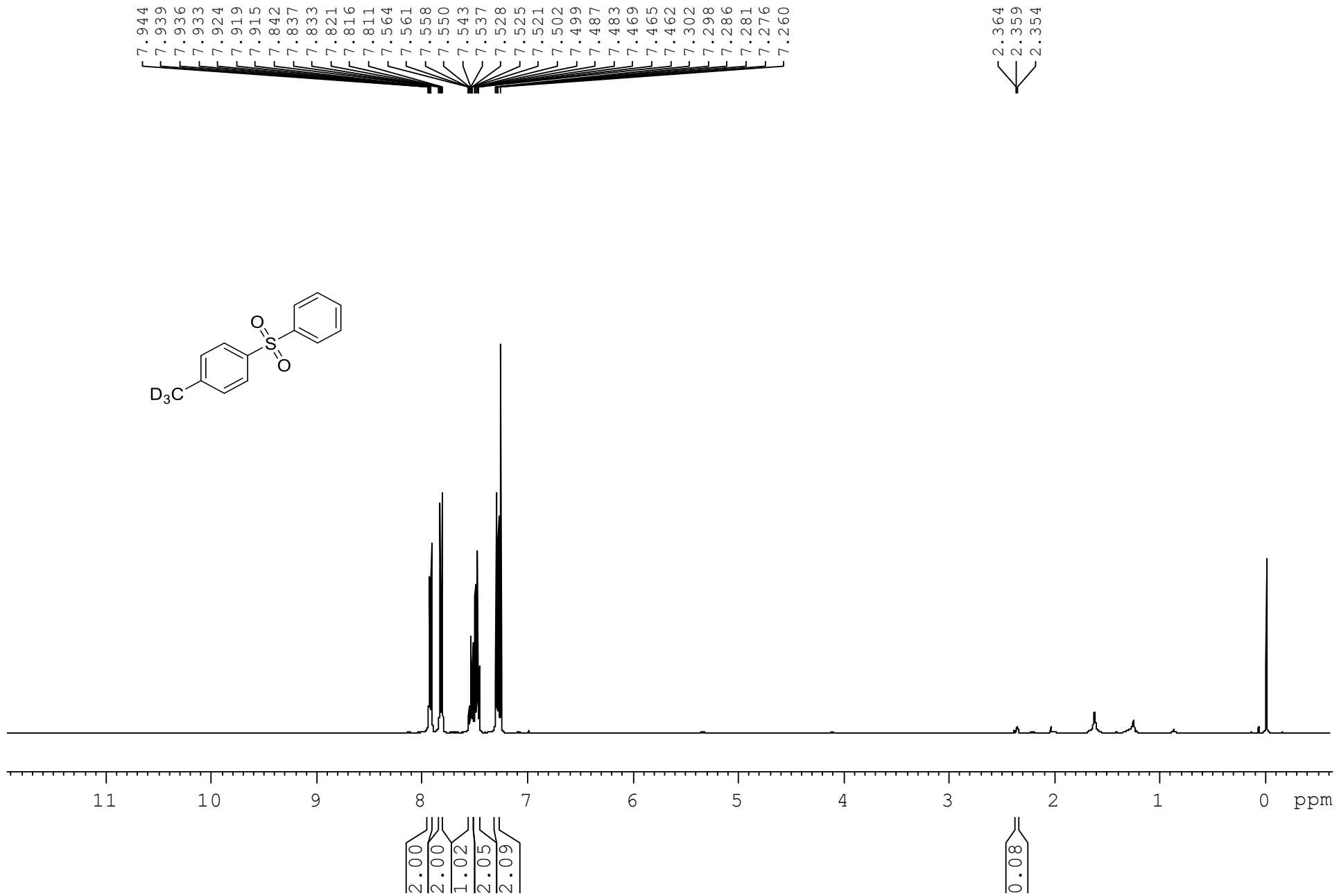

Figure S29. ^{1}H NMR spectra of **1i-*d*$_3$** ($CDCl_3$, 400 M)

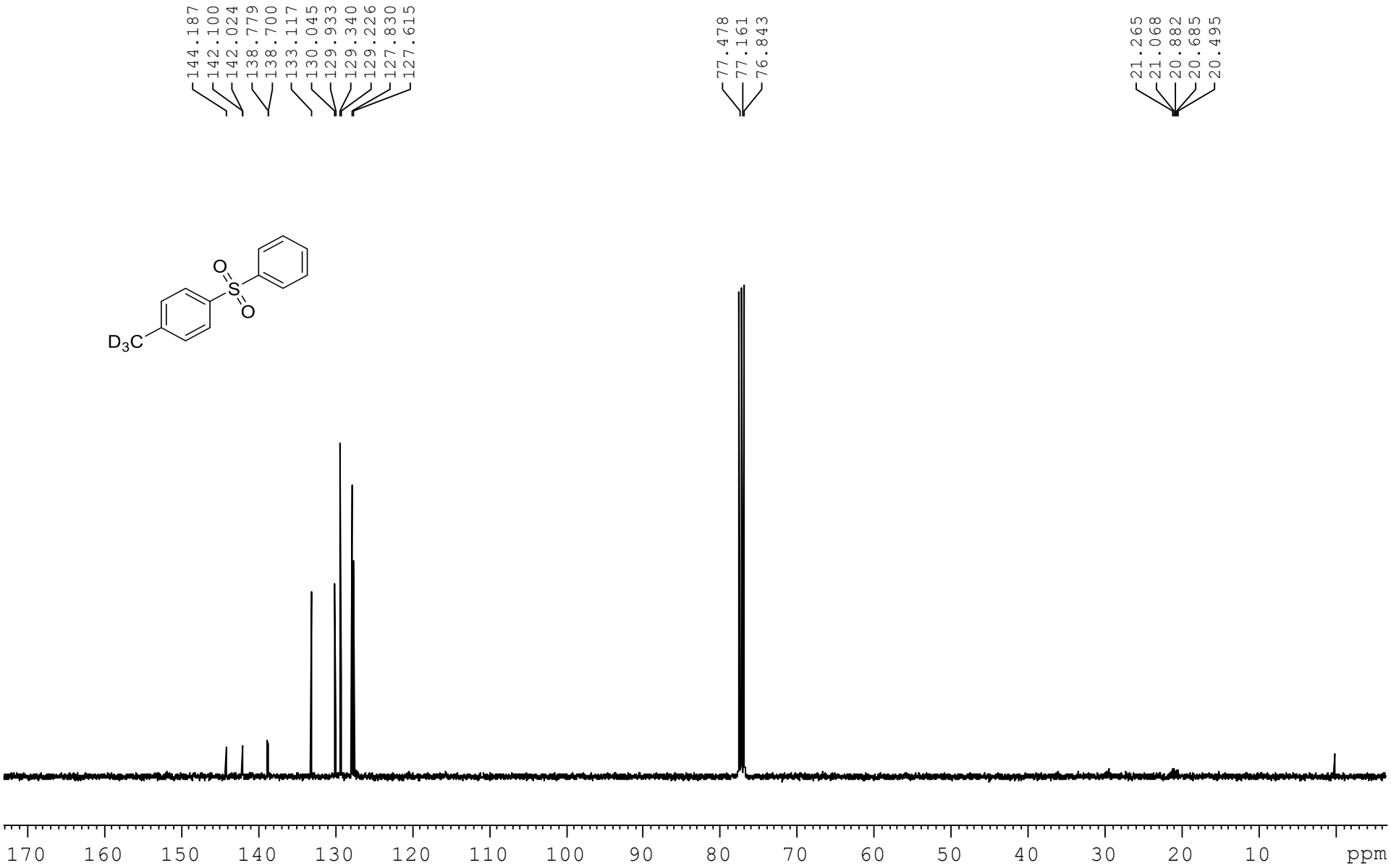

Figure S30. ^{13}C NMR spectra of **1i-*d*$_3$** ($CDCl_3$, 100 M)

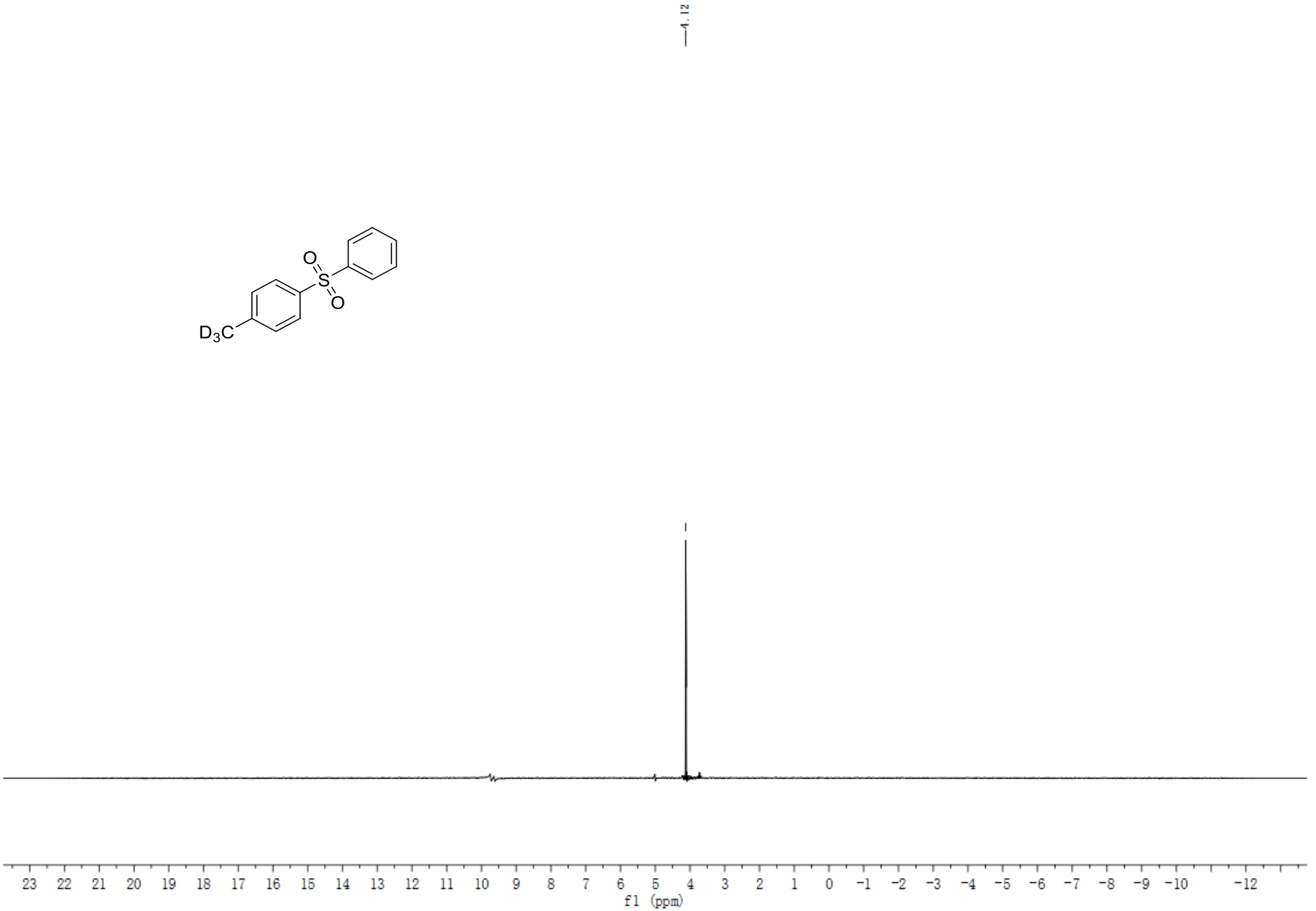

Figure S31. ^{2}H NMR spectra of **1i-*d*$_3$** (MeCN, 92 M)

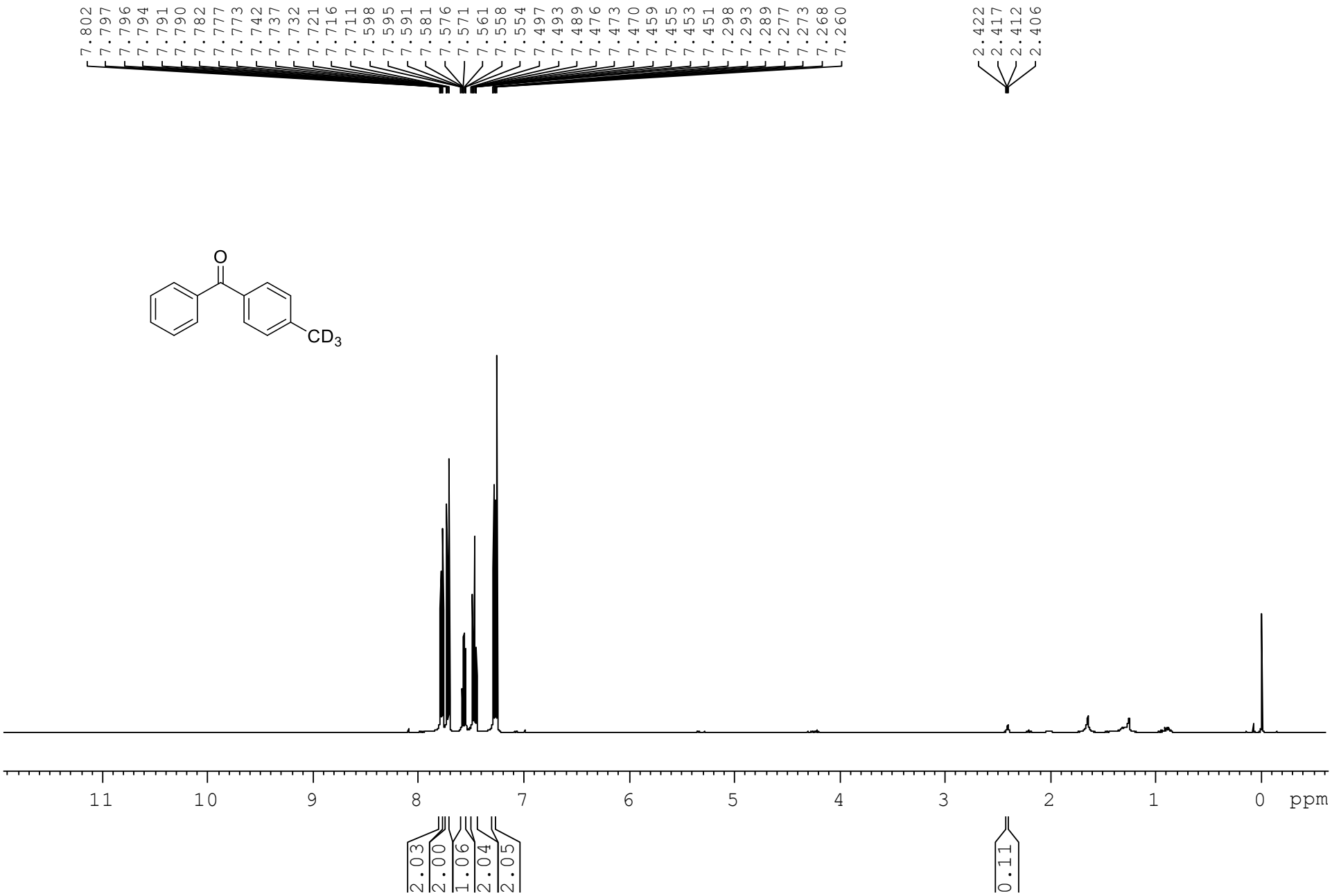

Figure S32. ^{1}H NMR spectra of **1j**-*d*$_3$ ($CDCl_3$, 400 M)

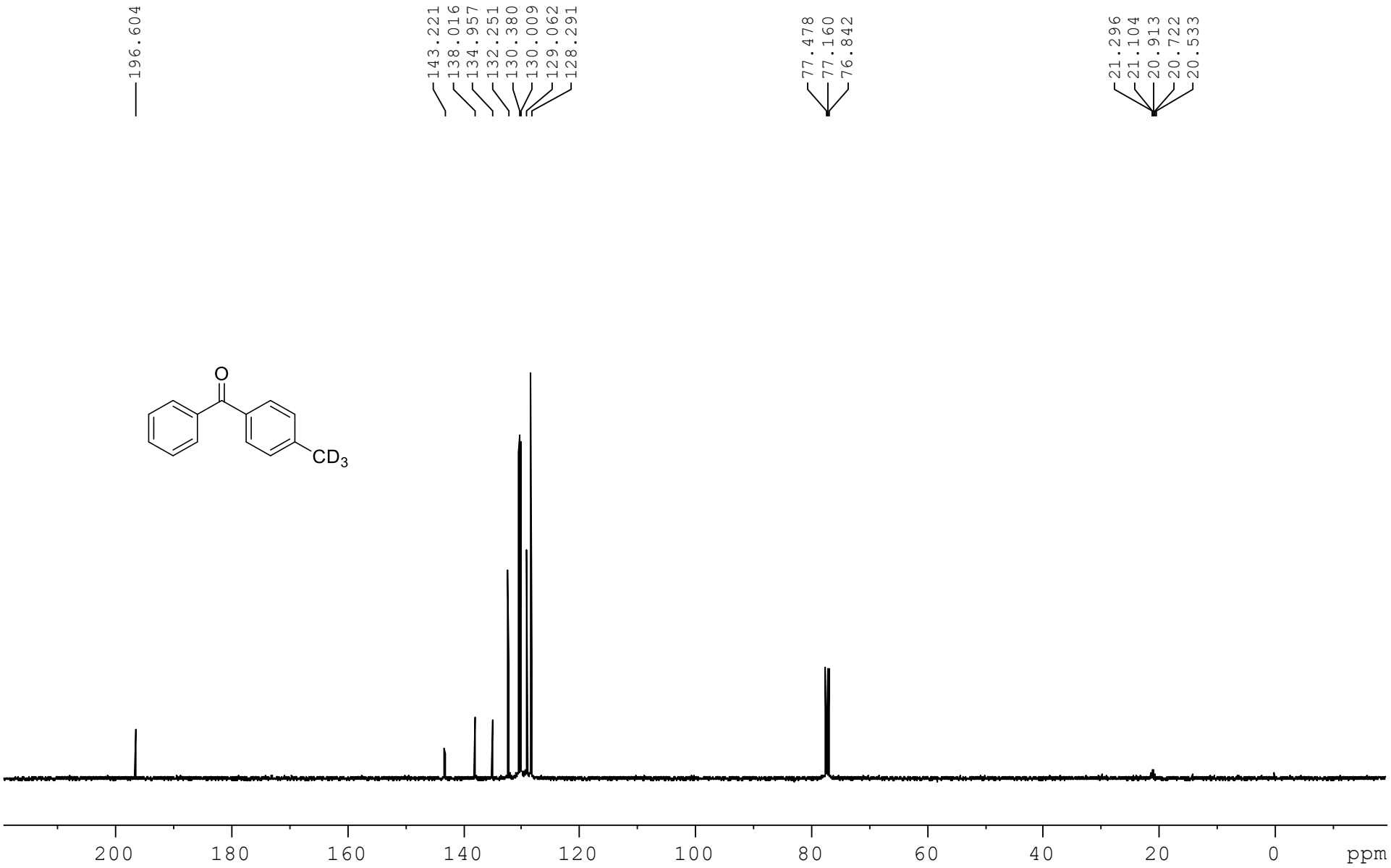

Figure S33. ^{13}C NMR spectra of **1j**-*d3* ($CDCl_3$, 100 M)

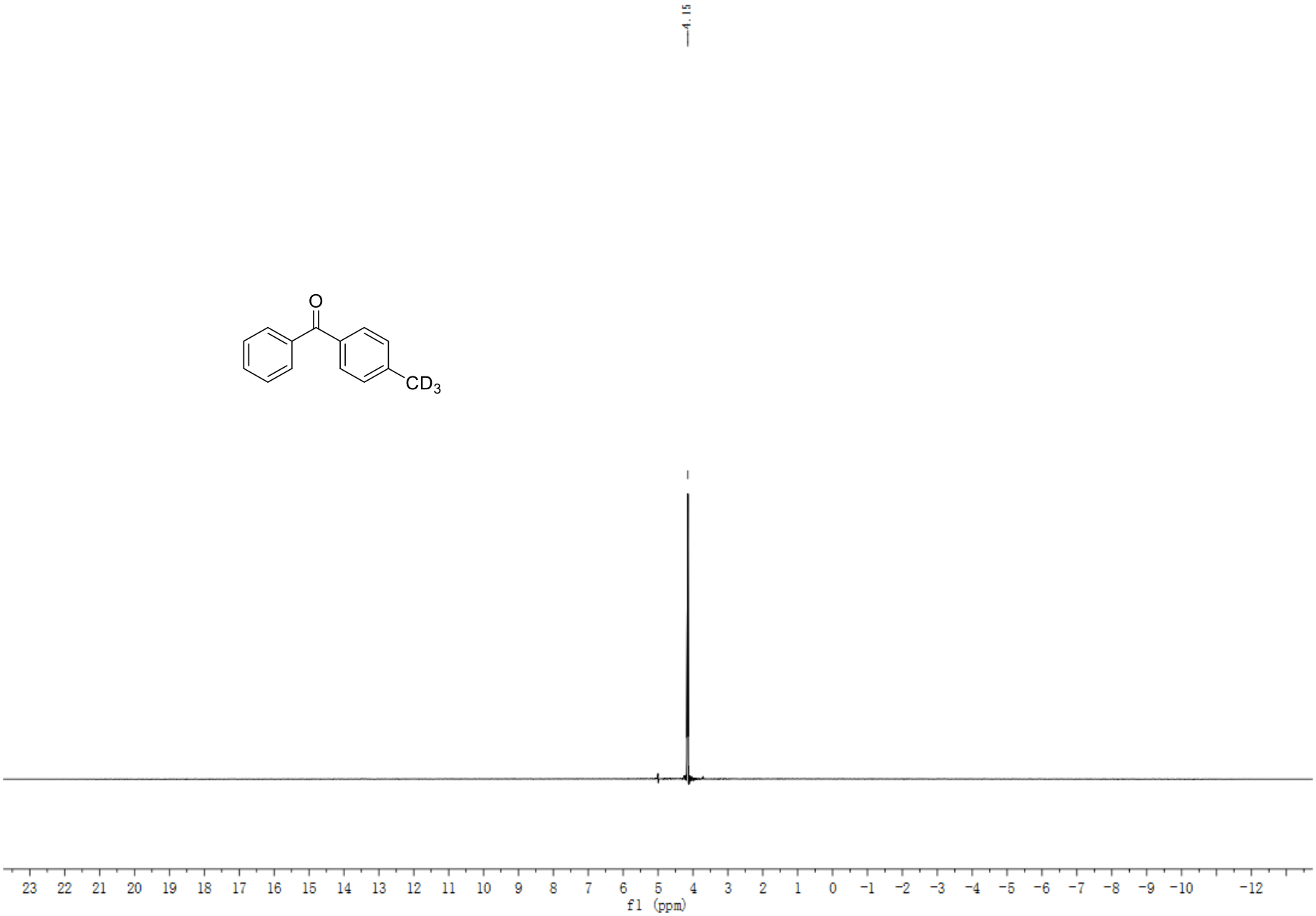

Figure S34. ^{2}H NMR spectra of **1j**-*d*$_3$ (MeCN, 92 M)

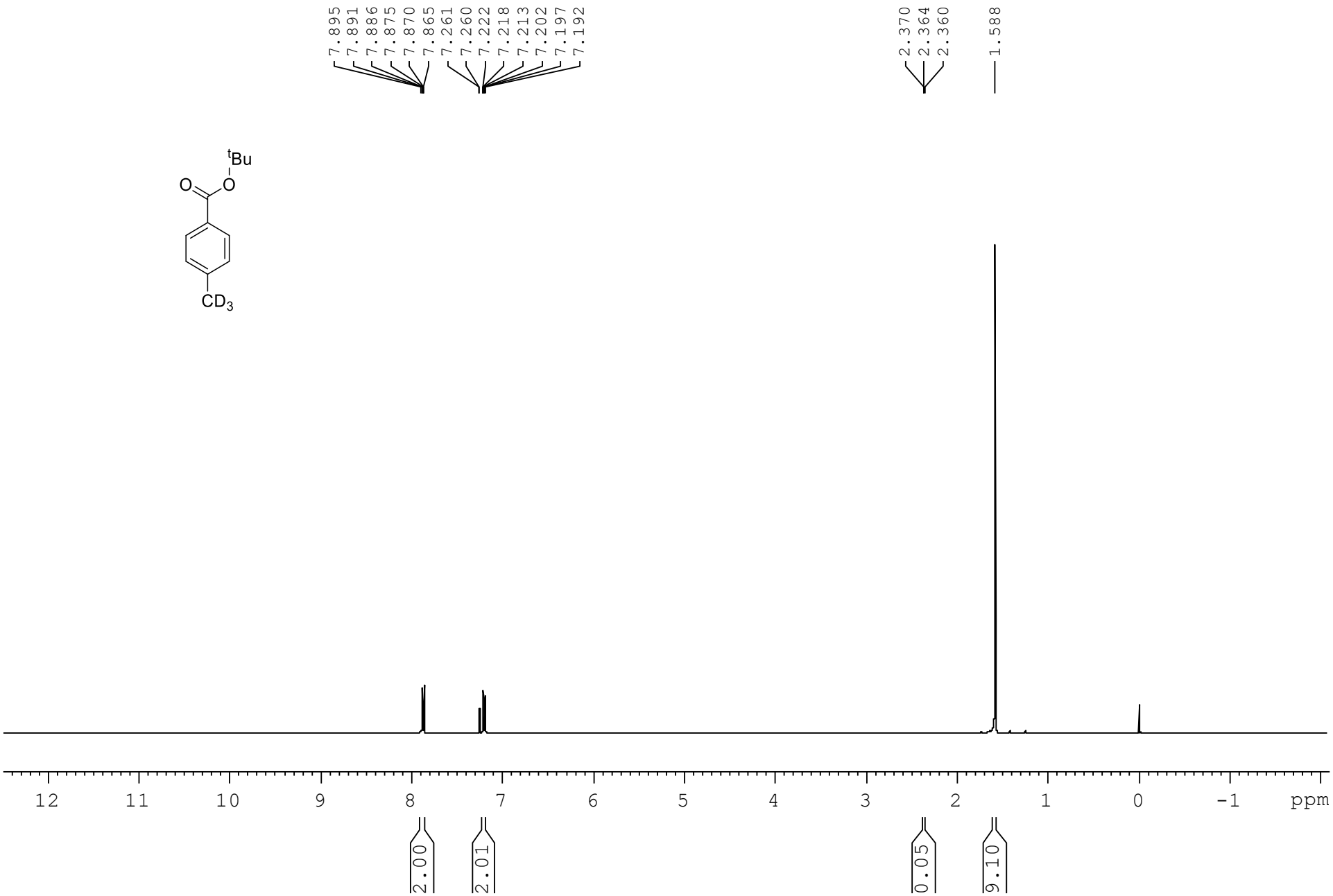

Figure S35. ^{1}H NMR spectra of **1k**-*d3* ($CDCl_3$, 400 M)

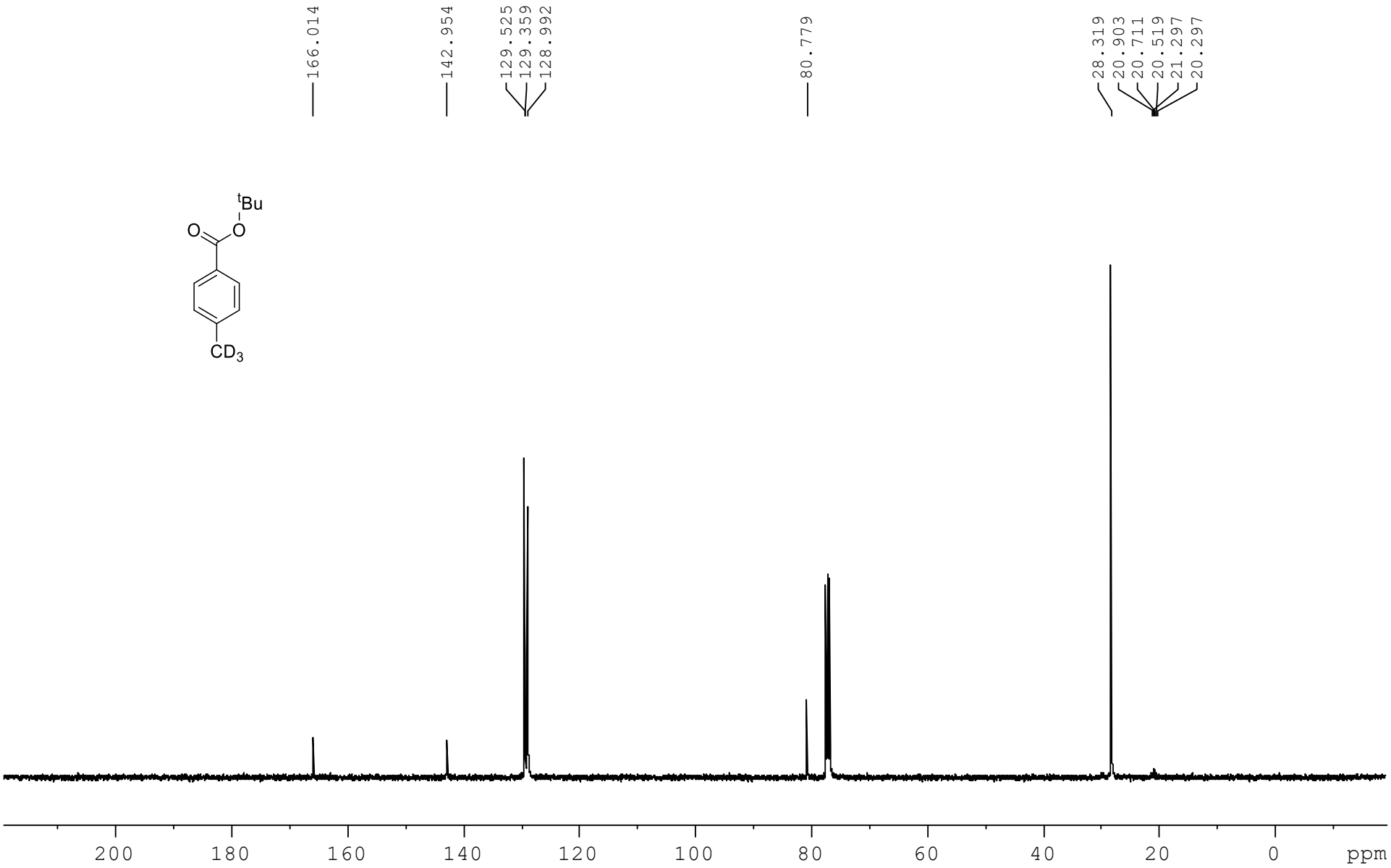

Figure S36. ^{13}C NMR spectra of **1k-*d*3** ($CDCl_3$, 100 M)

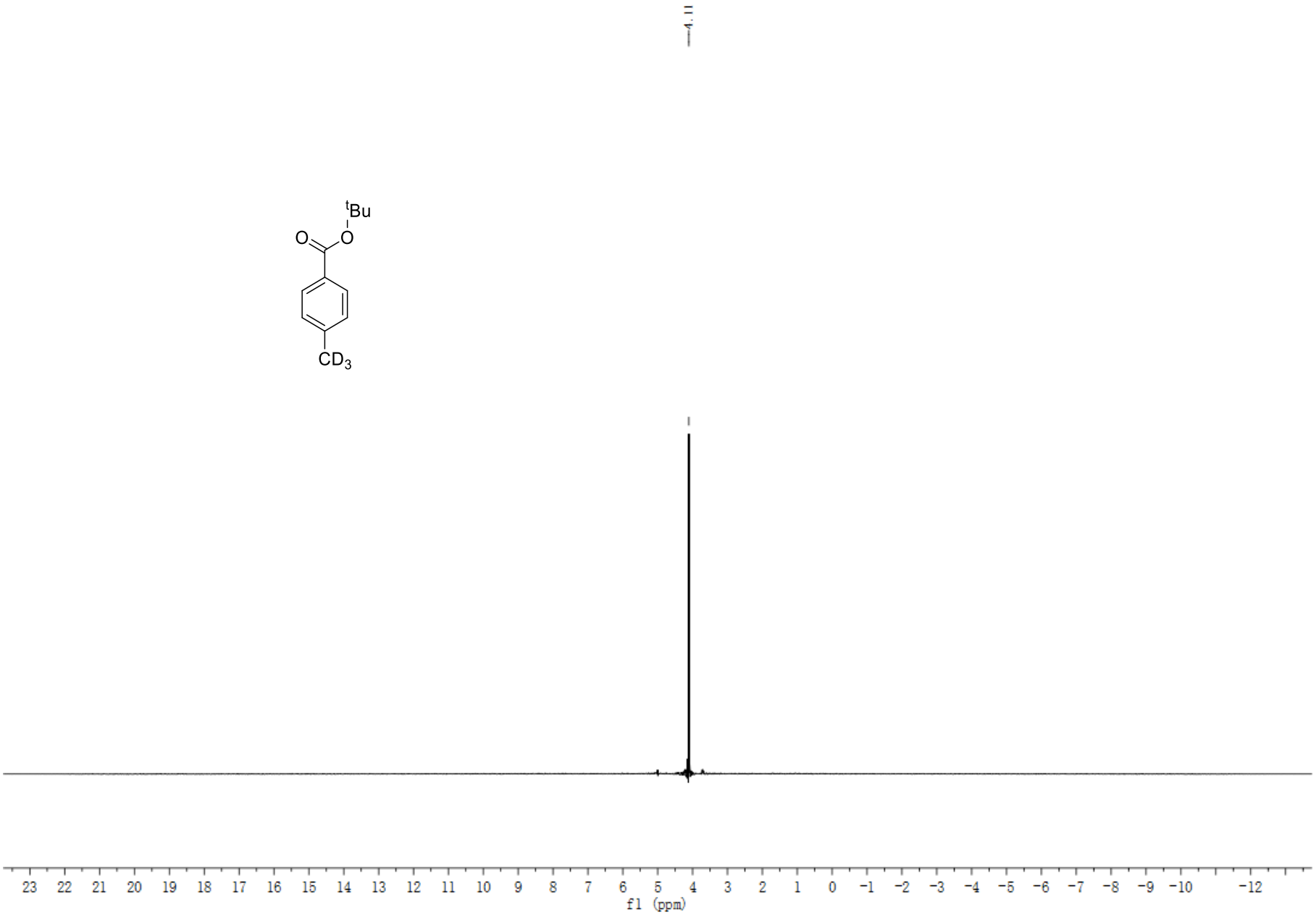

Figure S37. ^{2}H NMR spectra of **1k**-d_3 (MeCN, 92 M)

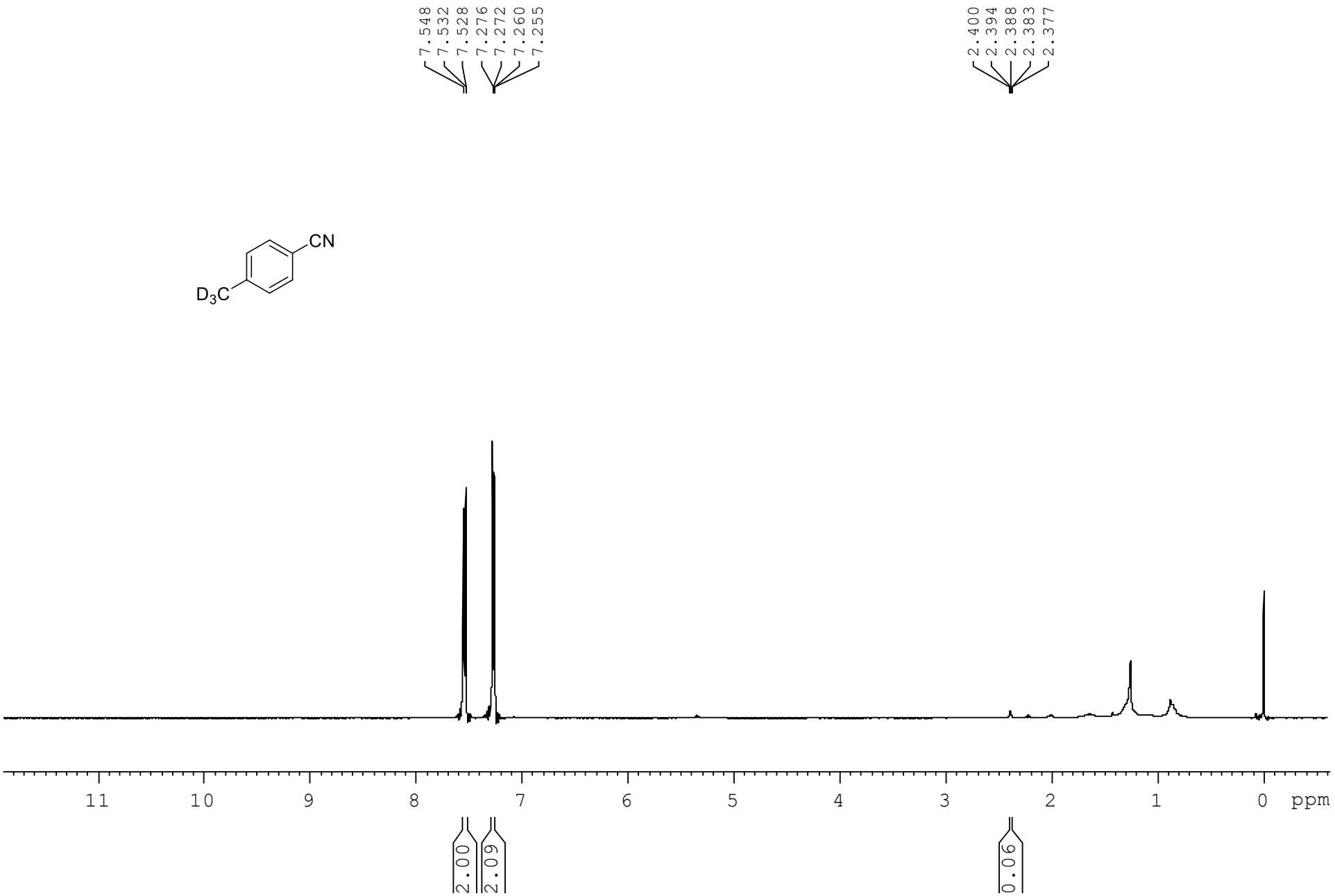

Figure S38. ^{1}H NMR spectra of **1l-*d*$_3$** ($CDCl_3$, 400 M)

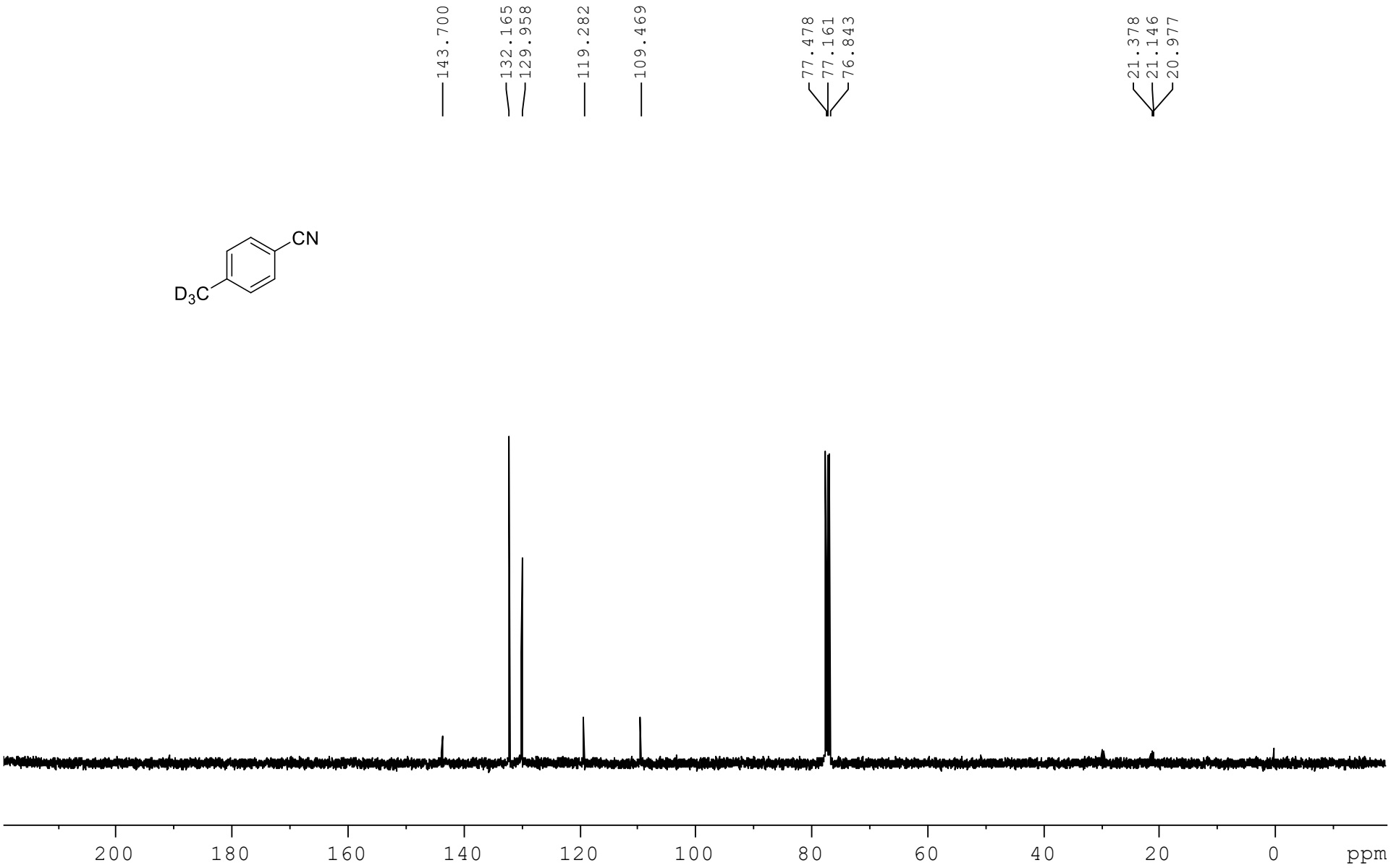

Figure S39. ^{13}C NMR spectra of **1l-*d3*** ($CDCl_3$, 100 M)

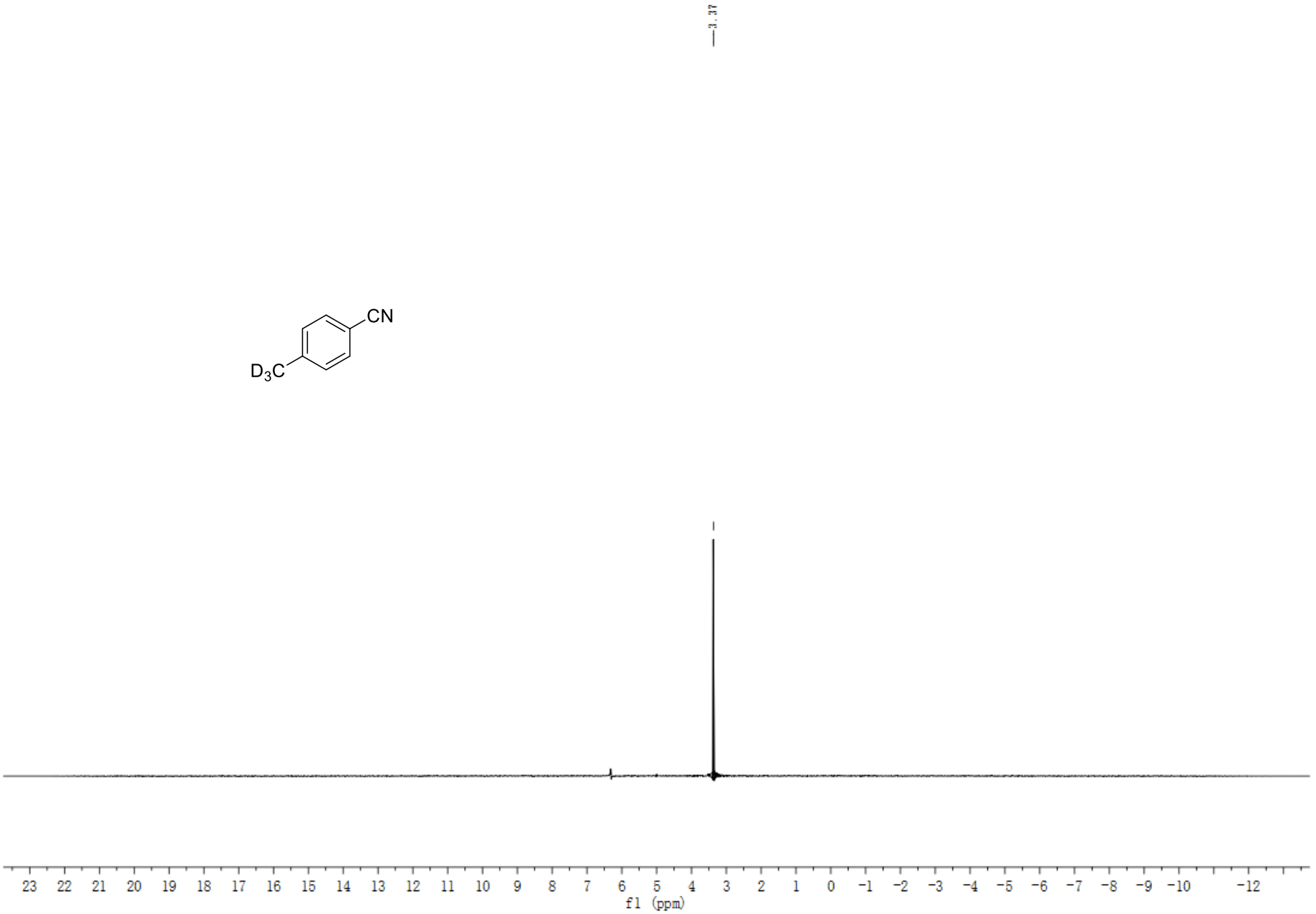

Figure S40. ^{2}H NMR spectra of **1l-*d*$_3$** (MeCN, 92 M)

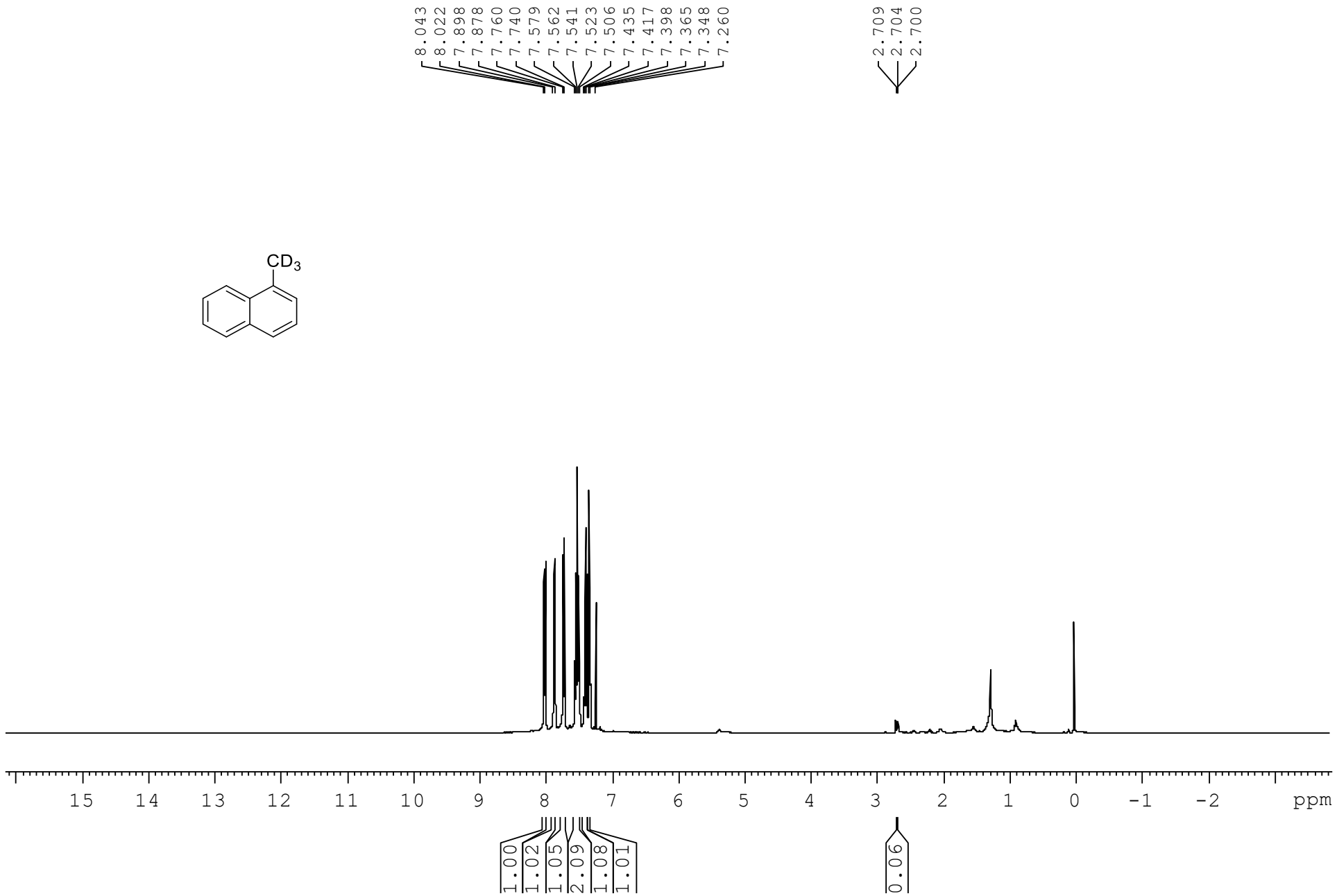

Figure S41. ^{1}H NMR spectra of **1m**-*d3* ($CDCl_3$, 400 M)

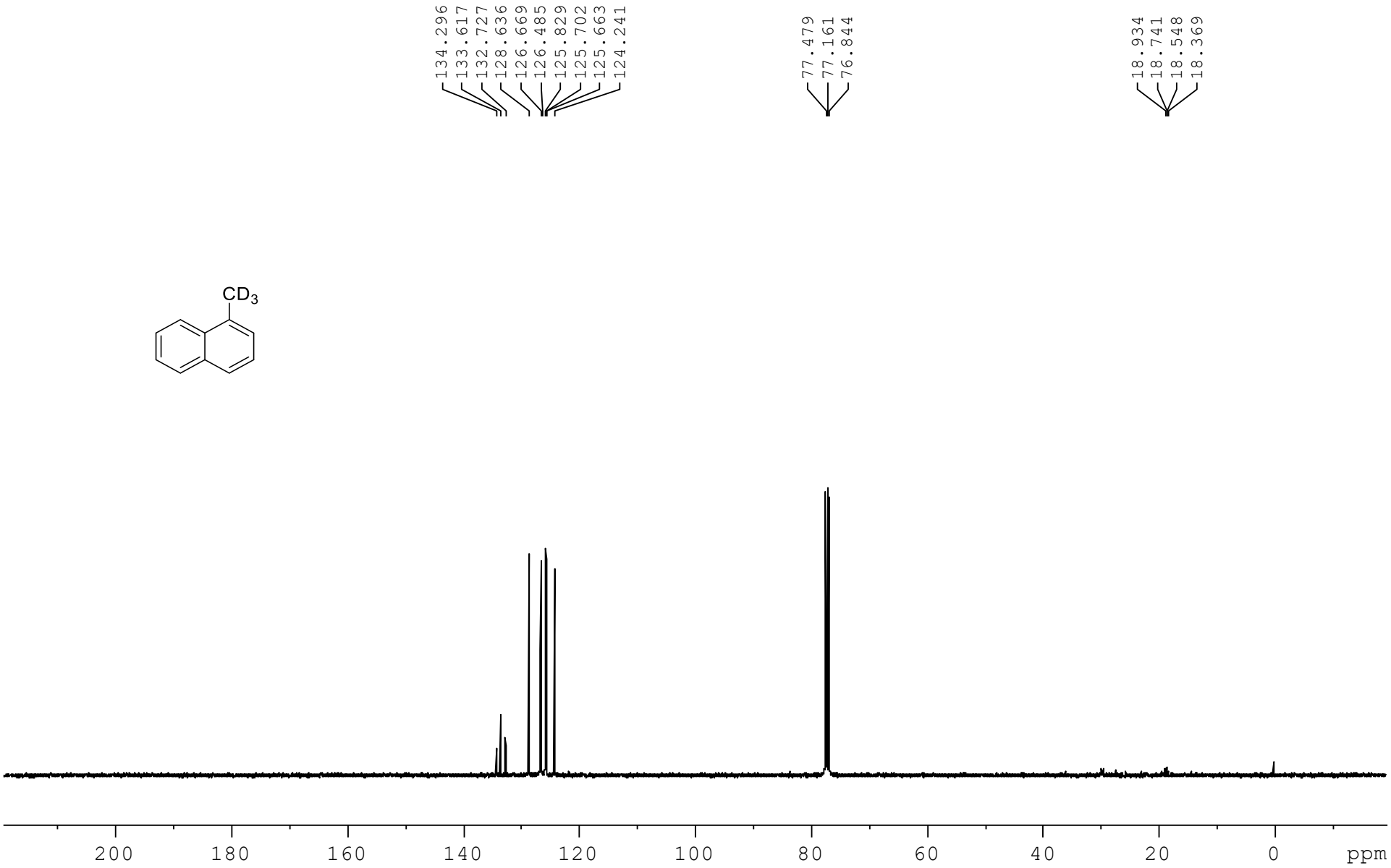

Figure S42. ^{13}C NMR spectra of **1m**-*d3* ($CDCl_3$, 100 M)

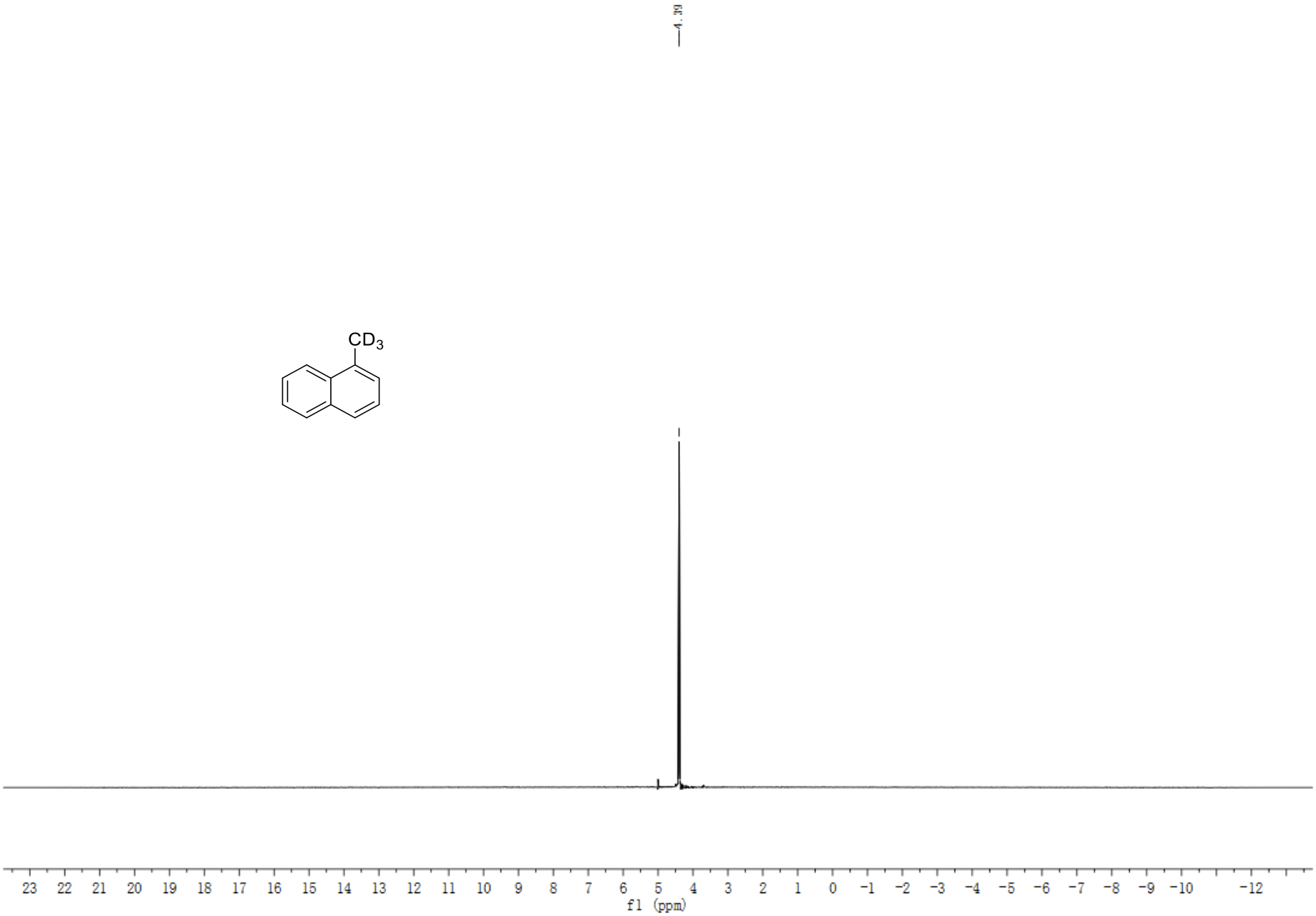

Figure S43. ^{2}H NMR spectra of **1m**-*d*$_3$ (MeCN, 92 M)

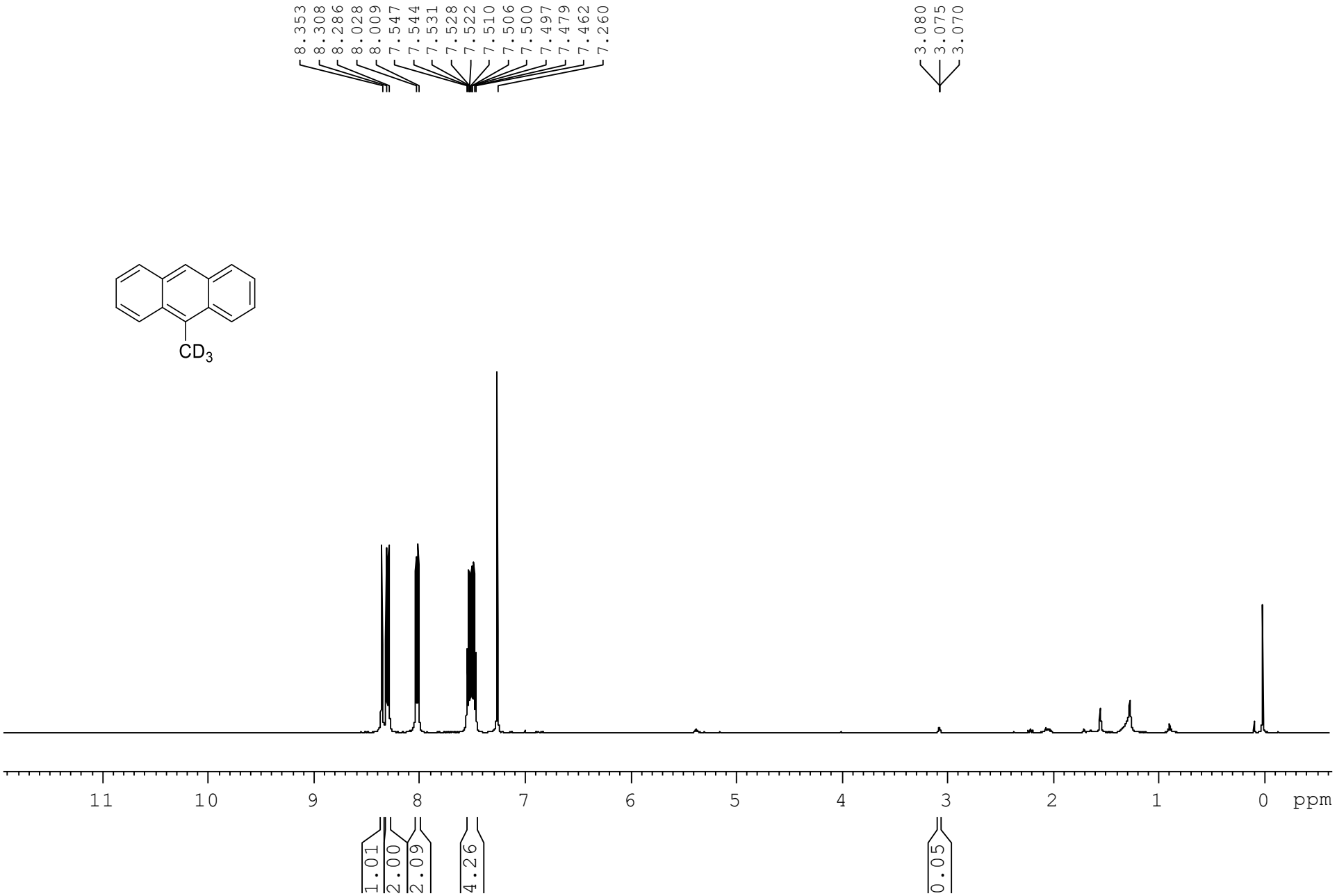

Figure S44. ^{1}H NMR spectra of **1n**-*d3* ($CDCl_3$, 400 M)

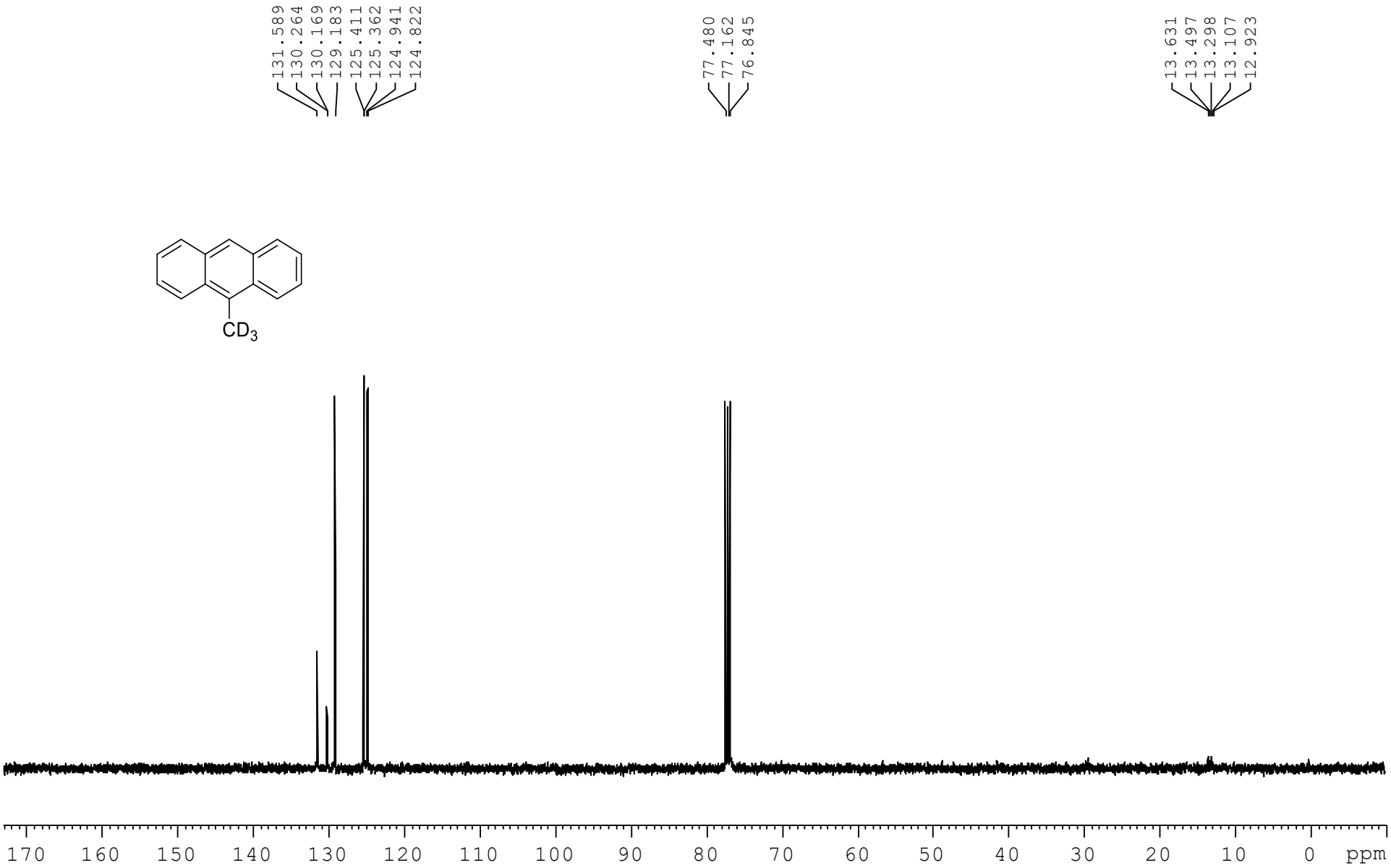

Figure S45. ^{13}C NMR spectra of **1n**-*d*$_3$ ($CDCl_3$, 100 M)

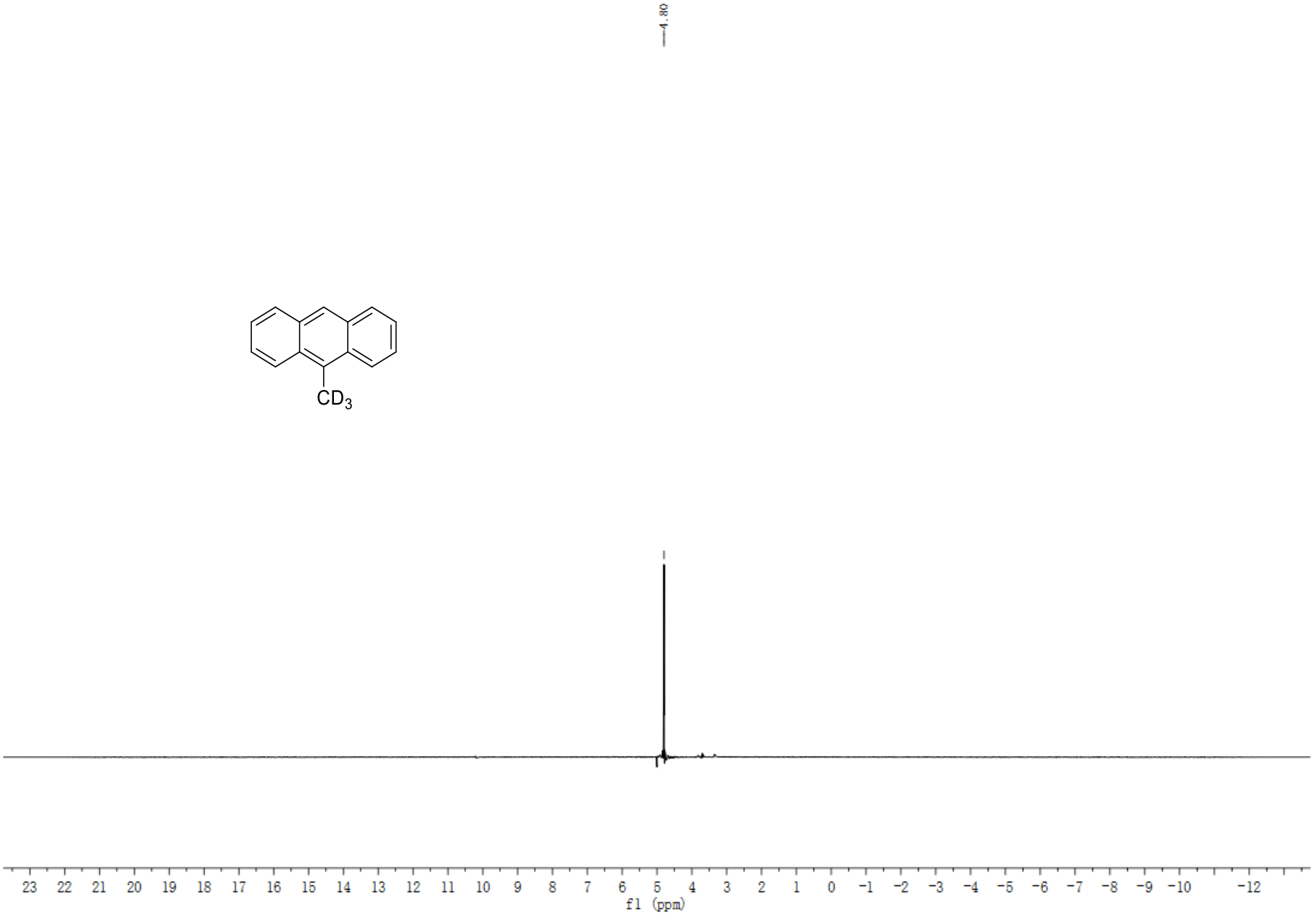

Figure S46. ^{2}H NMR spectra of **1n**-*d*$_3$ (MeCN, 92 M)

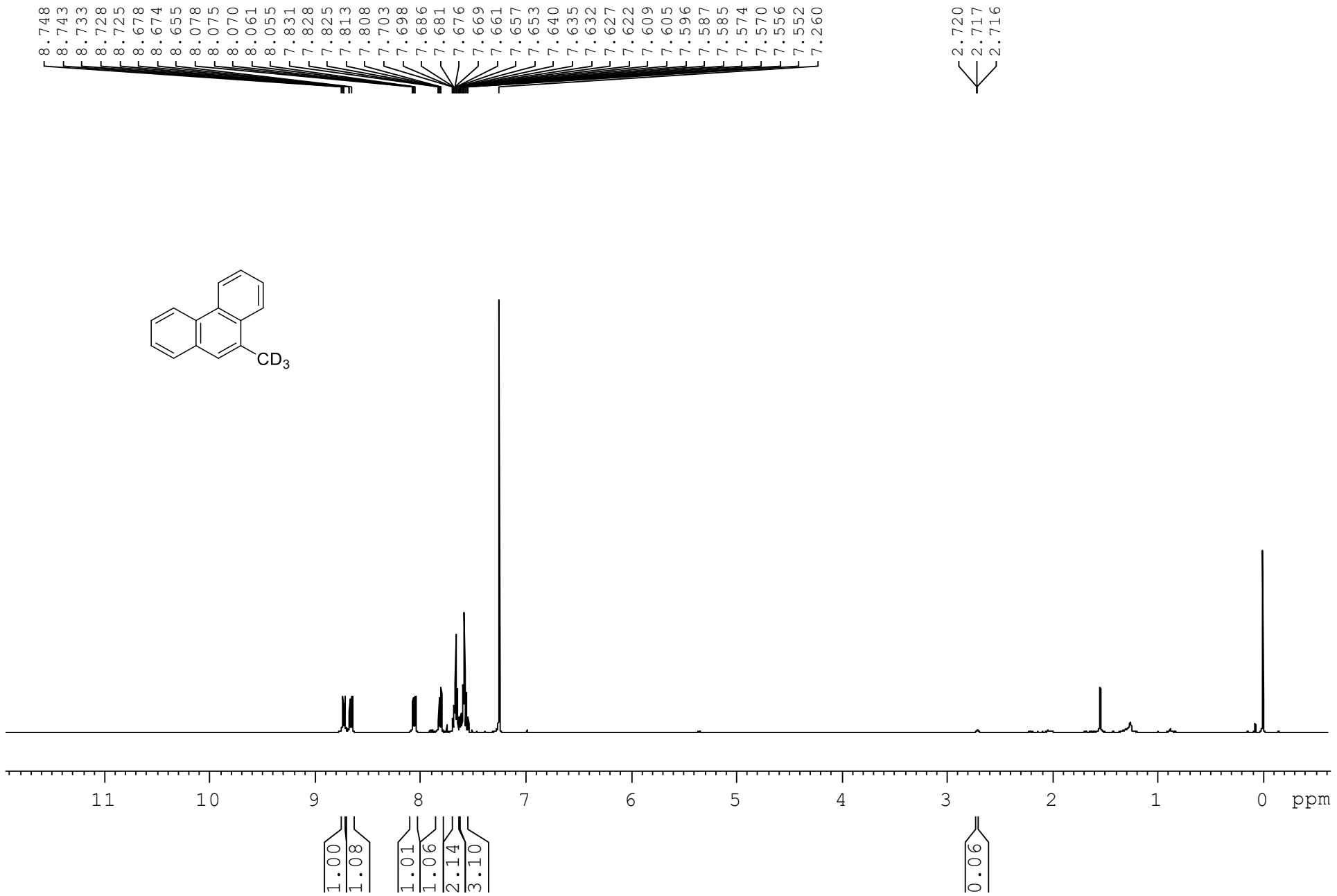

Figure S47. ^{1}H NMR spectra of **1o-*d*$_3$** ($CDCl_3$, 400 M)

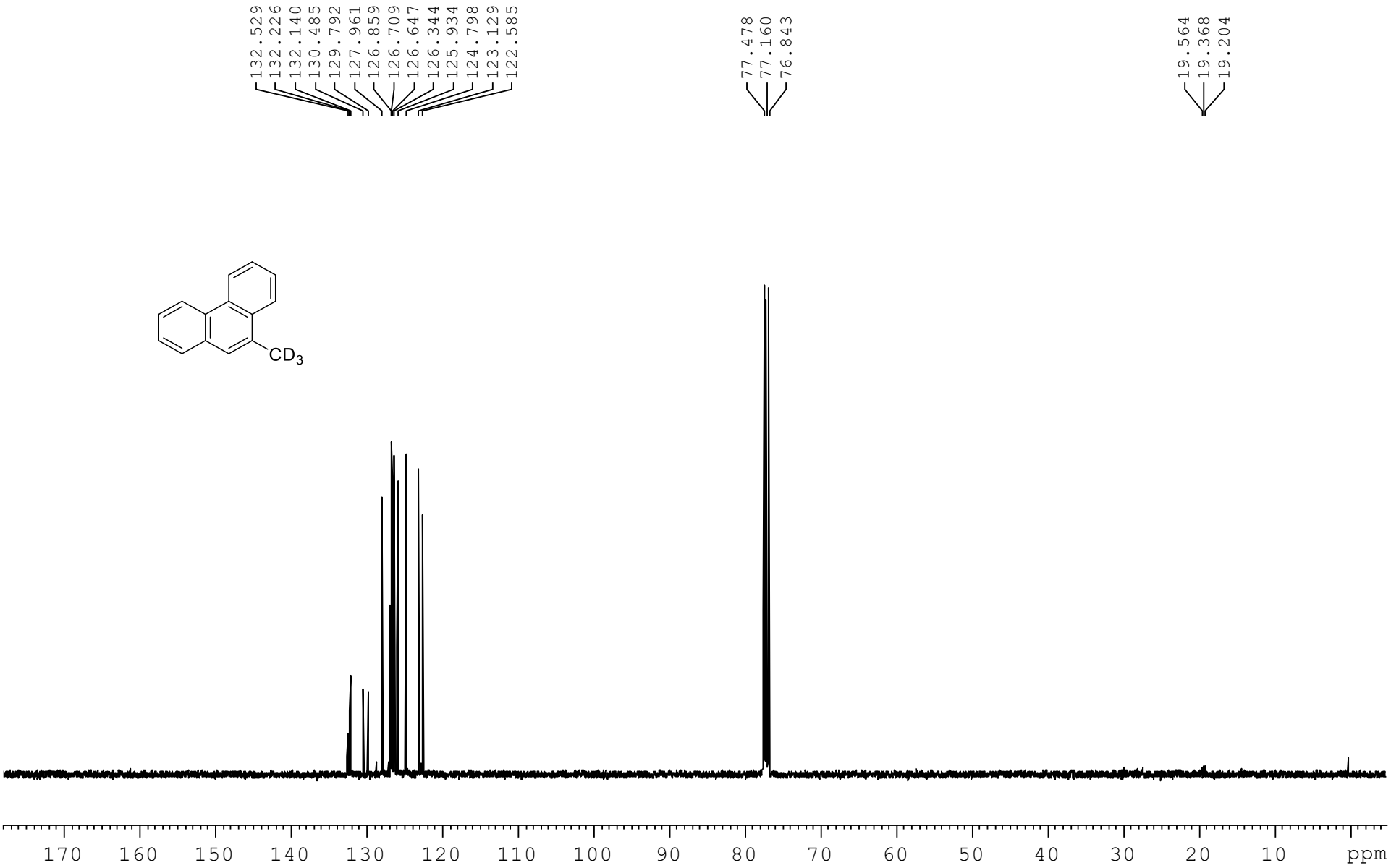

Figure S48. ^{13}C NMR spectra of **1o**-*d*$_3$ ($CDCl_3$, 100 M)

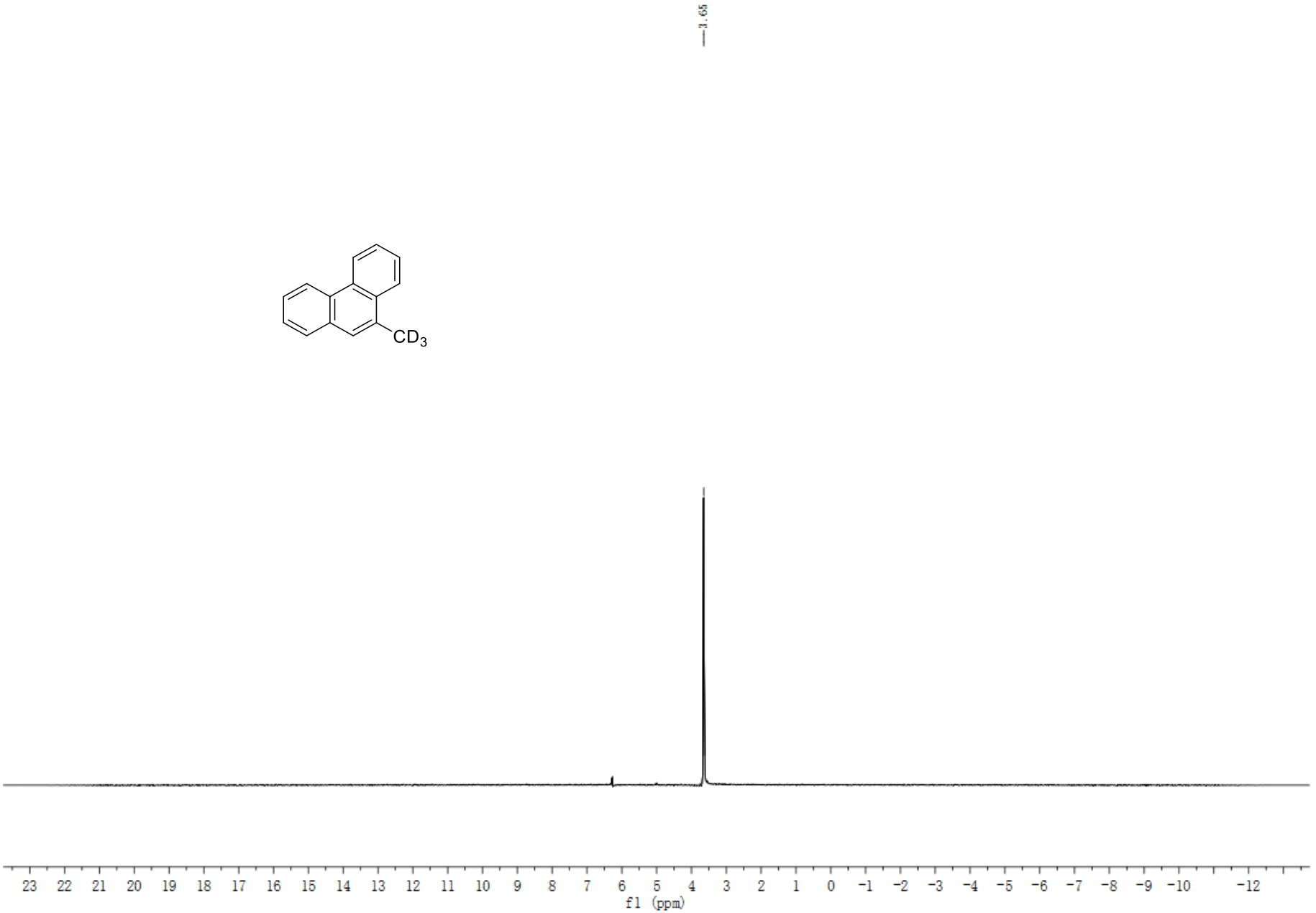

Figure S49. ^{2}H NMR spectra of **1o**-*d*$_3$ (DCM, 92 M)

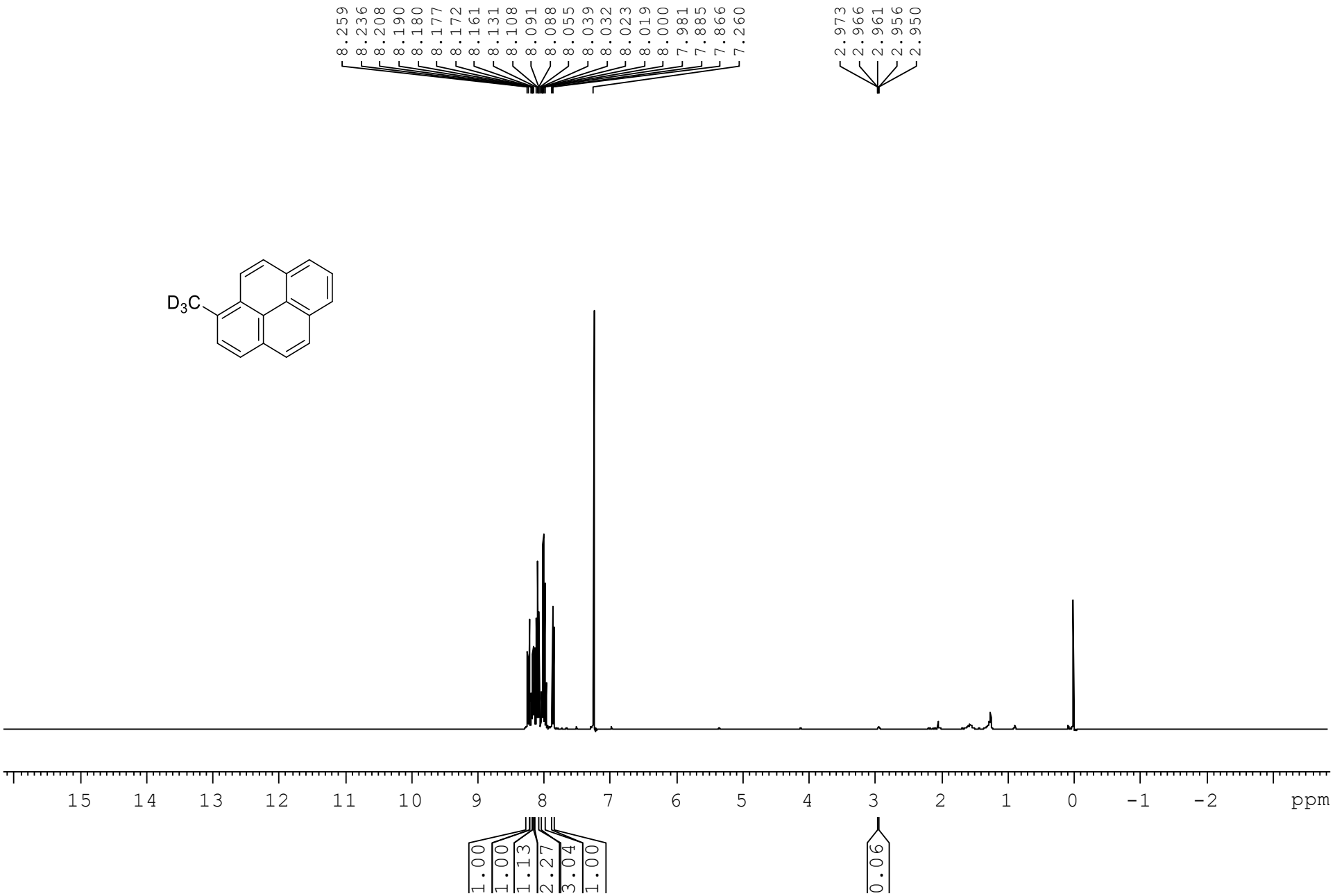

Figure S50. ^{1}H NMR spectra of **1p**-*d3* ($CDCl_3$, 400 M)

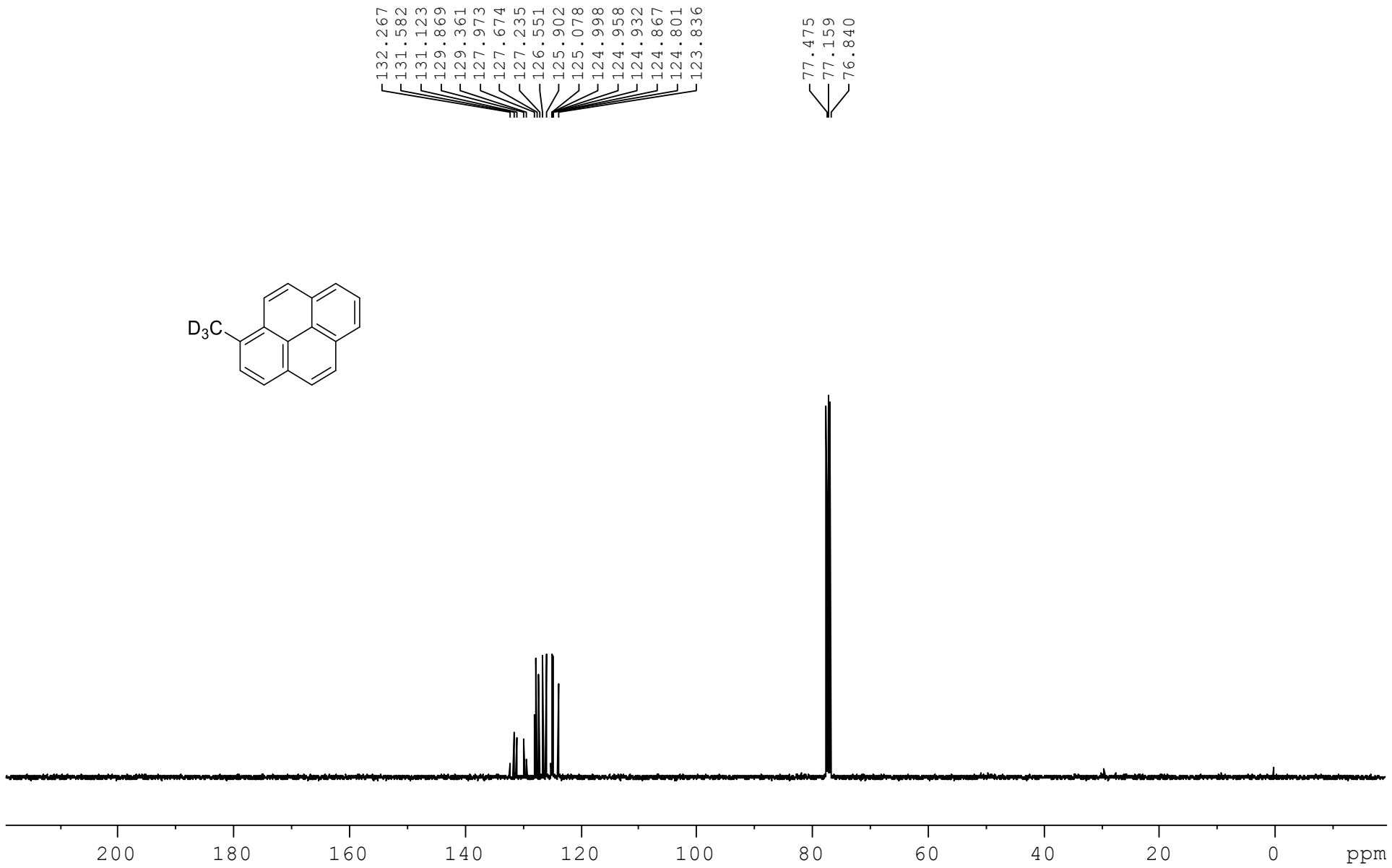

Figure S51. ^{13}C NMR spectra of **1p**-*d3* ($CDCl_3$, 100 M)

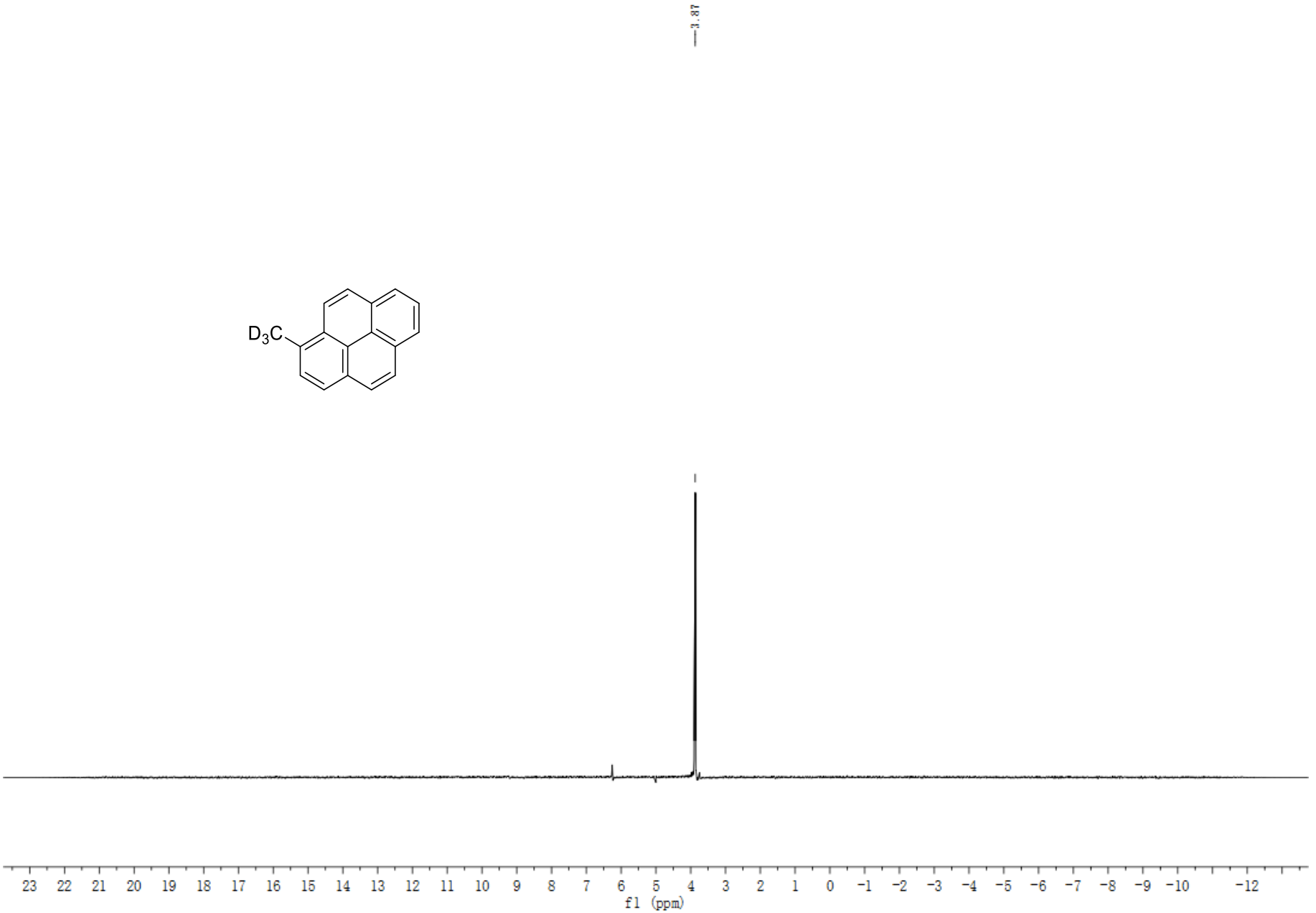

Figure S52. ^{2}H NMR spectra of **1p**-*d3* (DCM, 92 M)

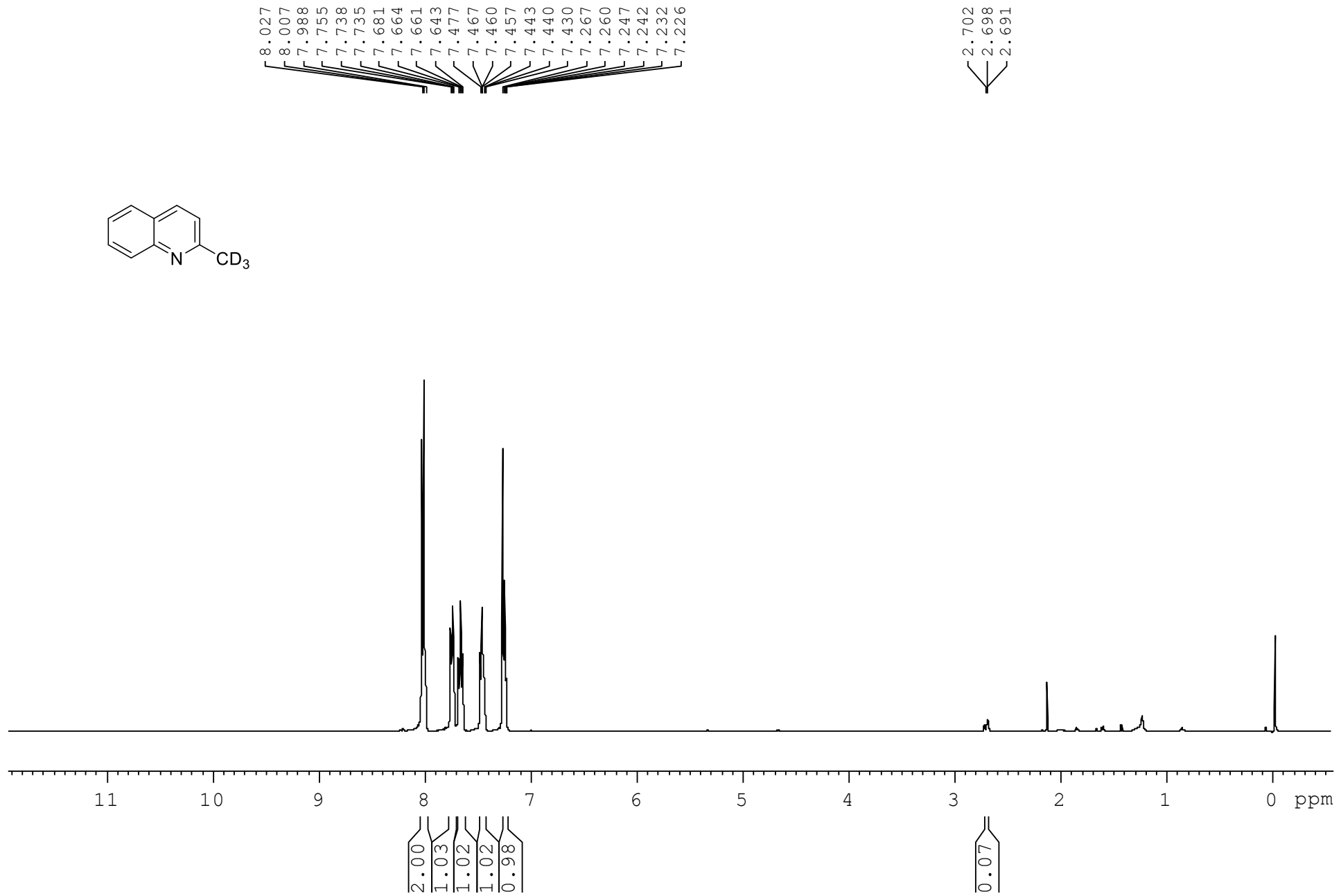

Figure S53. ^{1}H NMR spectra of **1q**-*d3* ($CDCl_3$, 400 M)

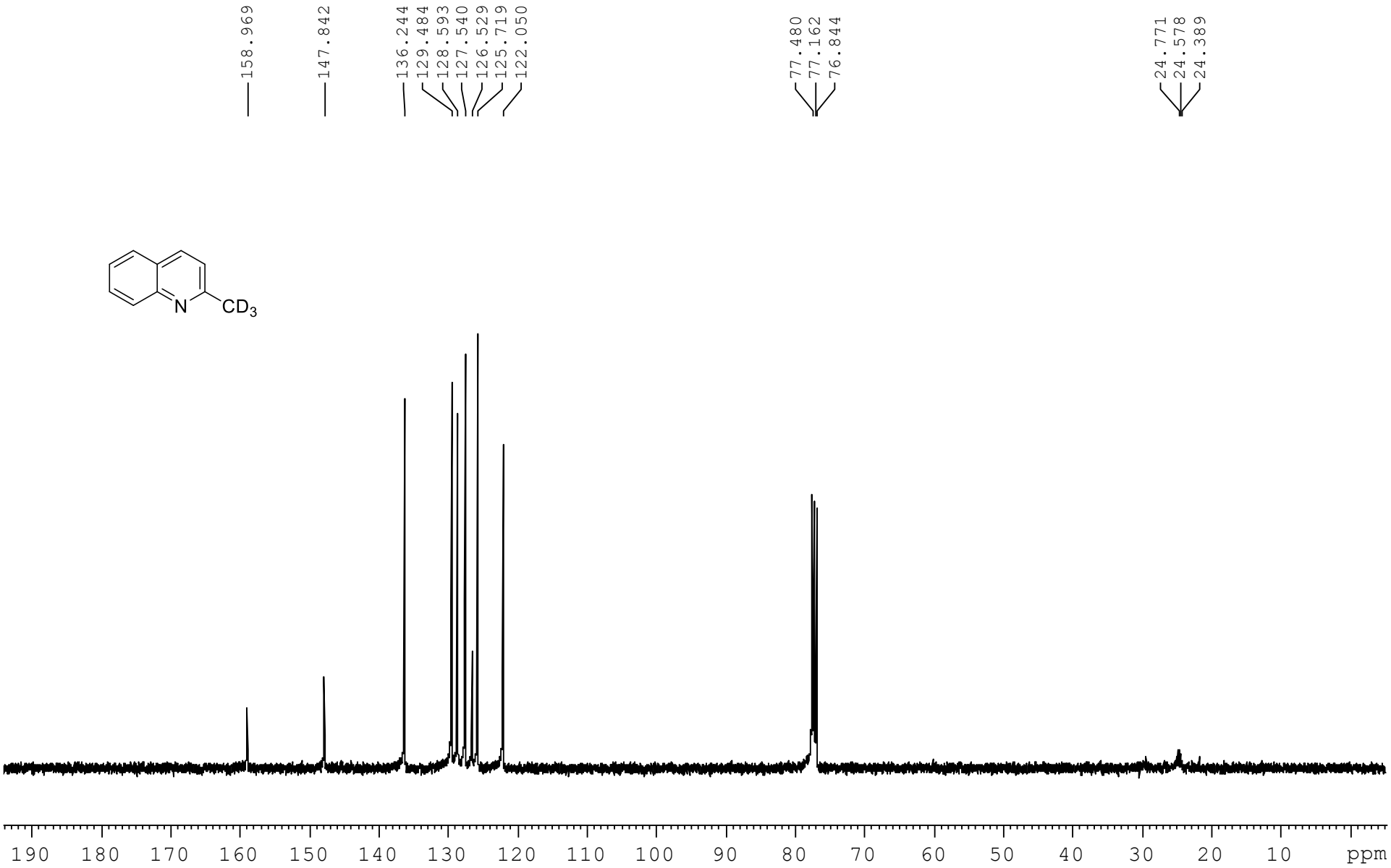

Figure S54. ^{13}C NMR spectra of **1q**-*d3* ($CDCl_3$, 100 M)

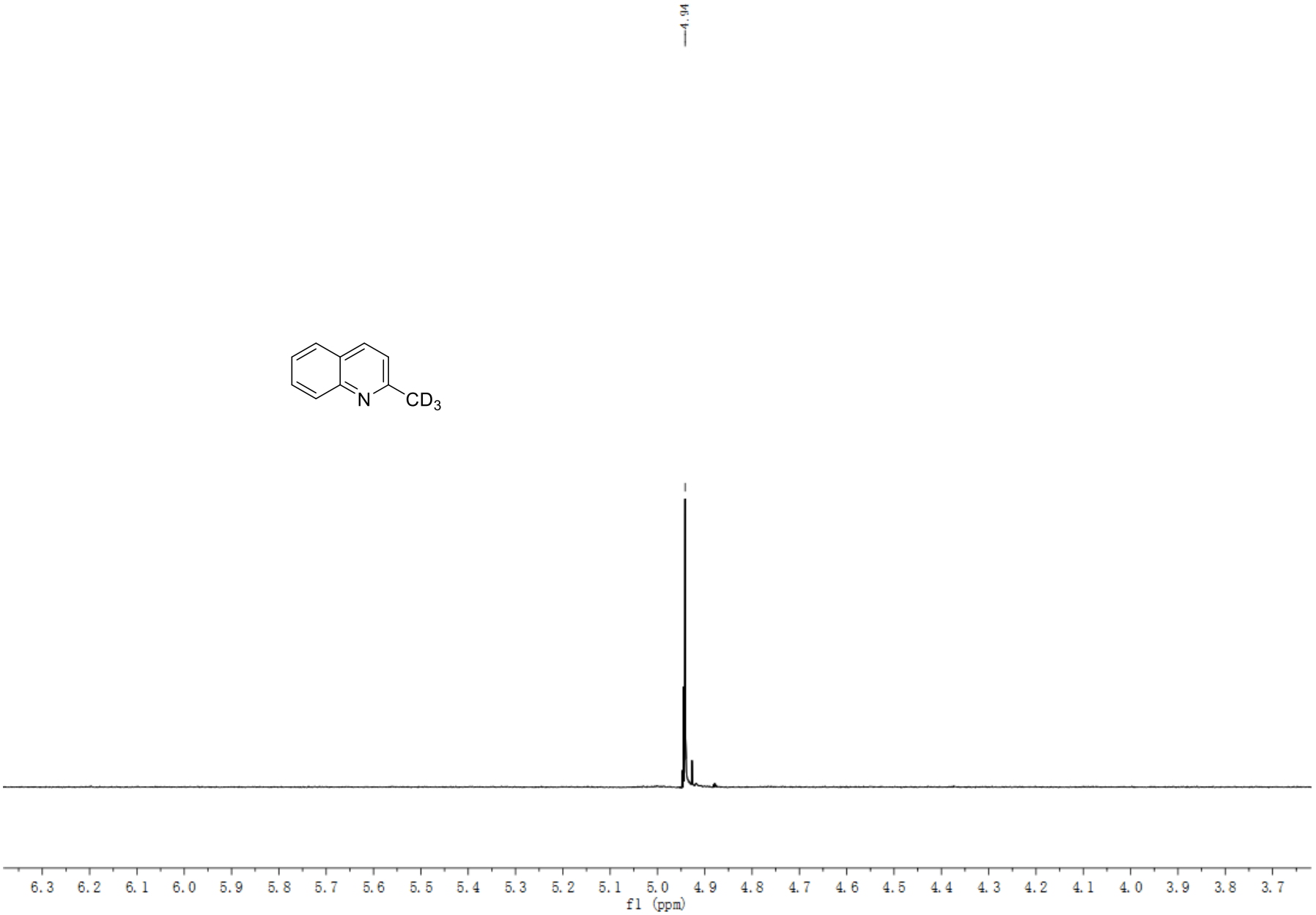

Figure S55. ^{2}H NMR spectra of **1q**-*d*$_3$ (MeCN, 92 M)

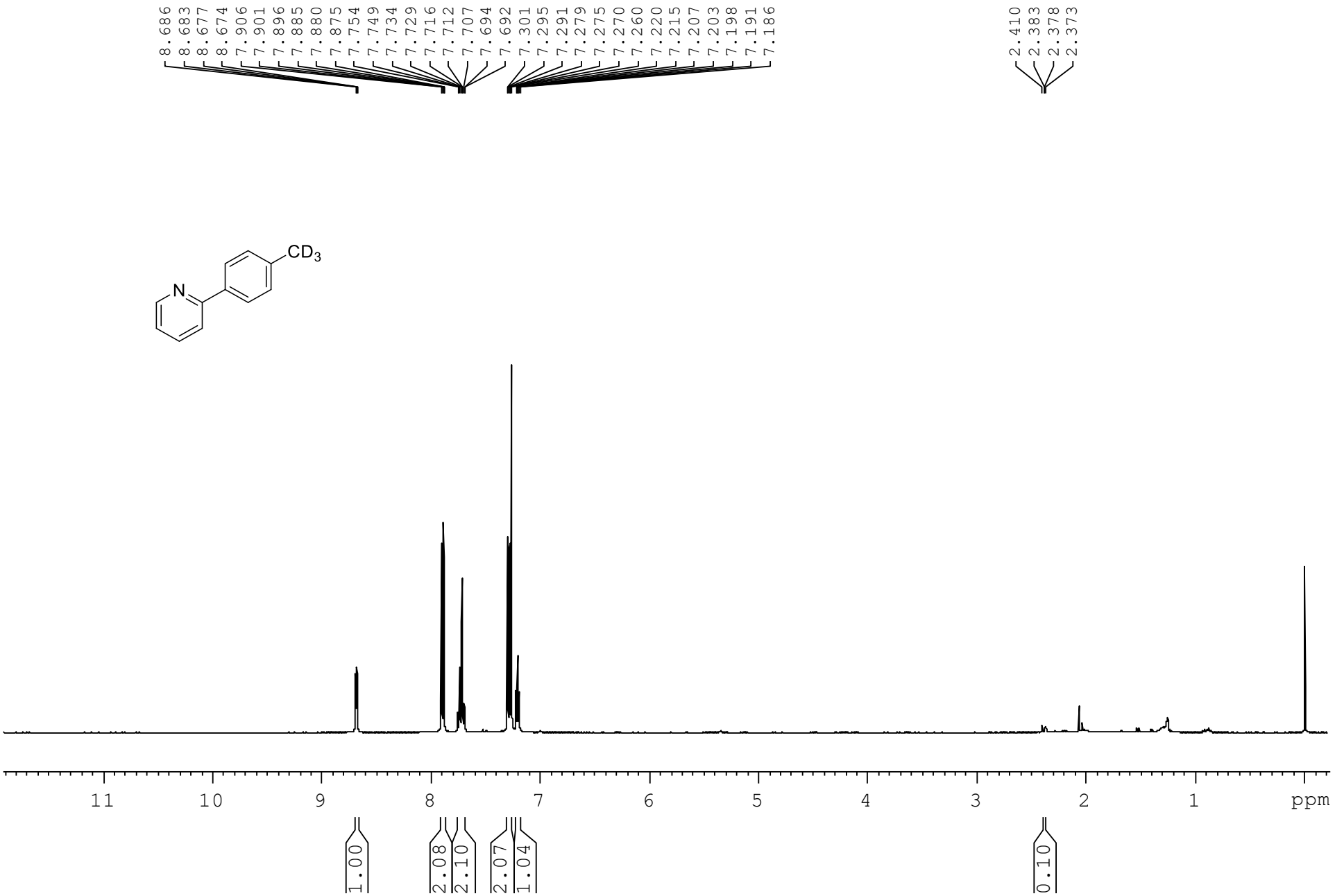

Figure S56. ^{1}H NMR spectra of **1r**-*d*$_3$ ($CDCl_3$, 400 M)

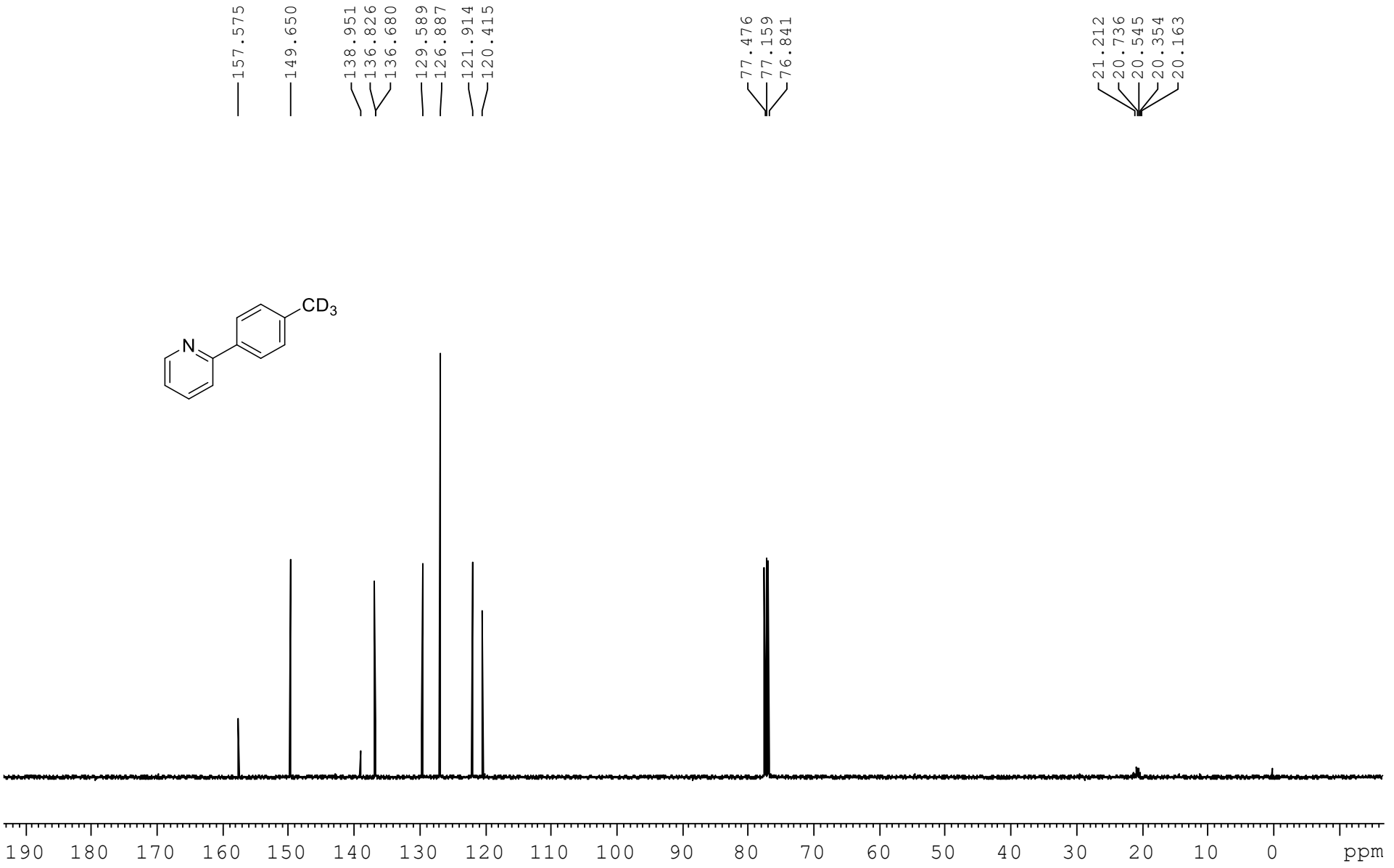

Figure S57. ^{13}C NMR spectra of **1r**-*d3* ($CDCl_3$, 100 M)

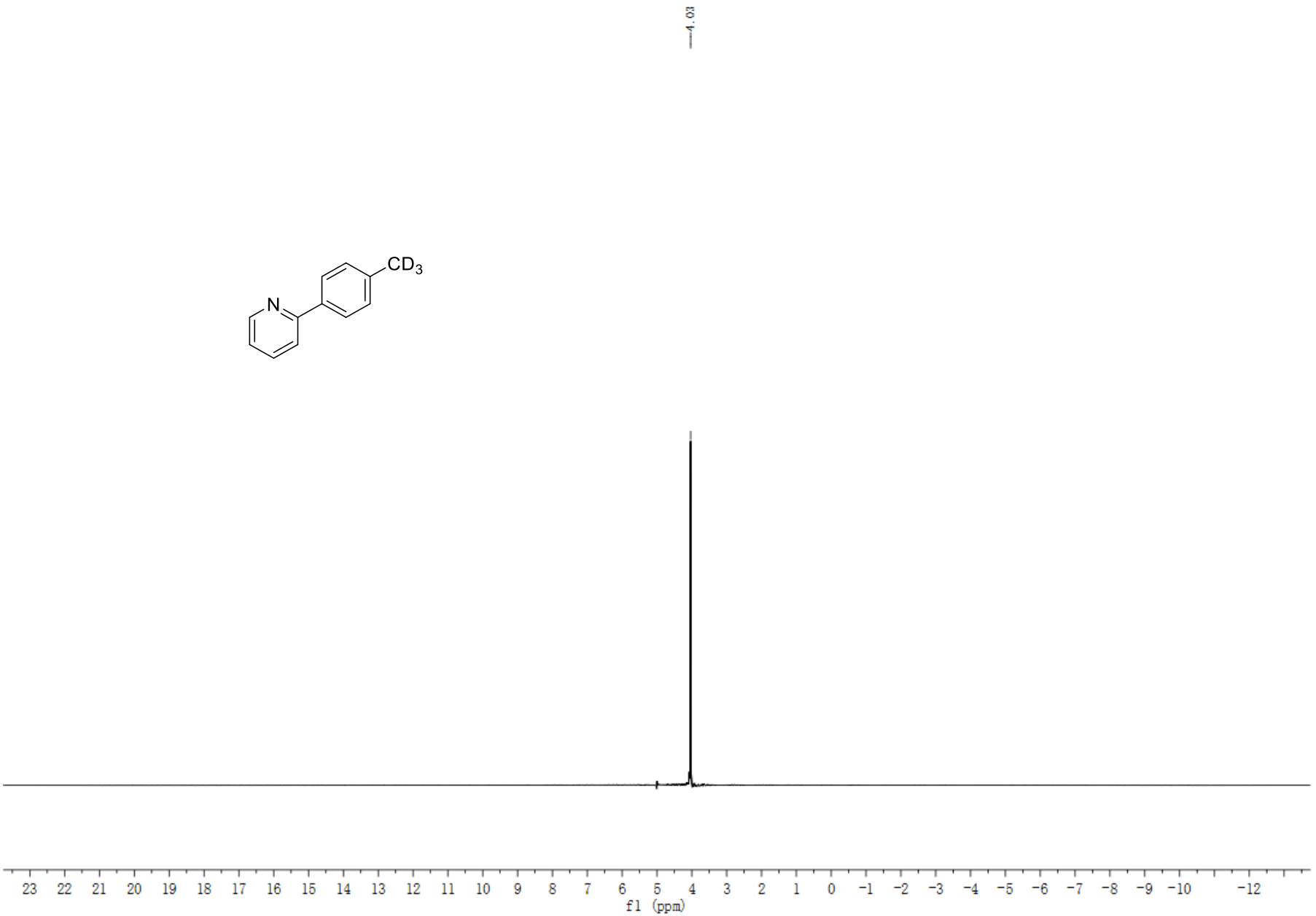

Figure S58. ^{2}H NMR spectra of **1r**-*d*$_3$ (MeCN, 92 M)

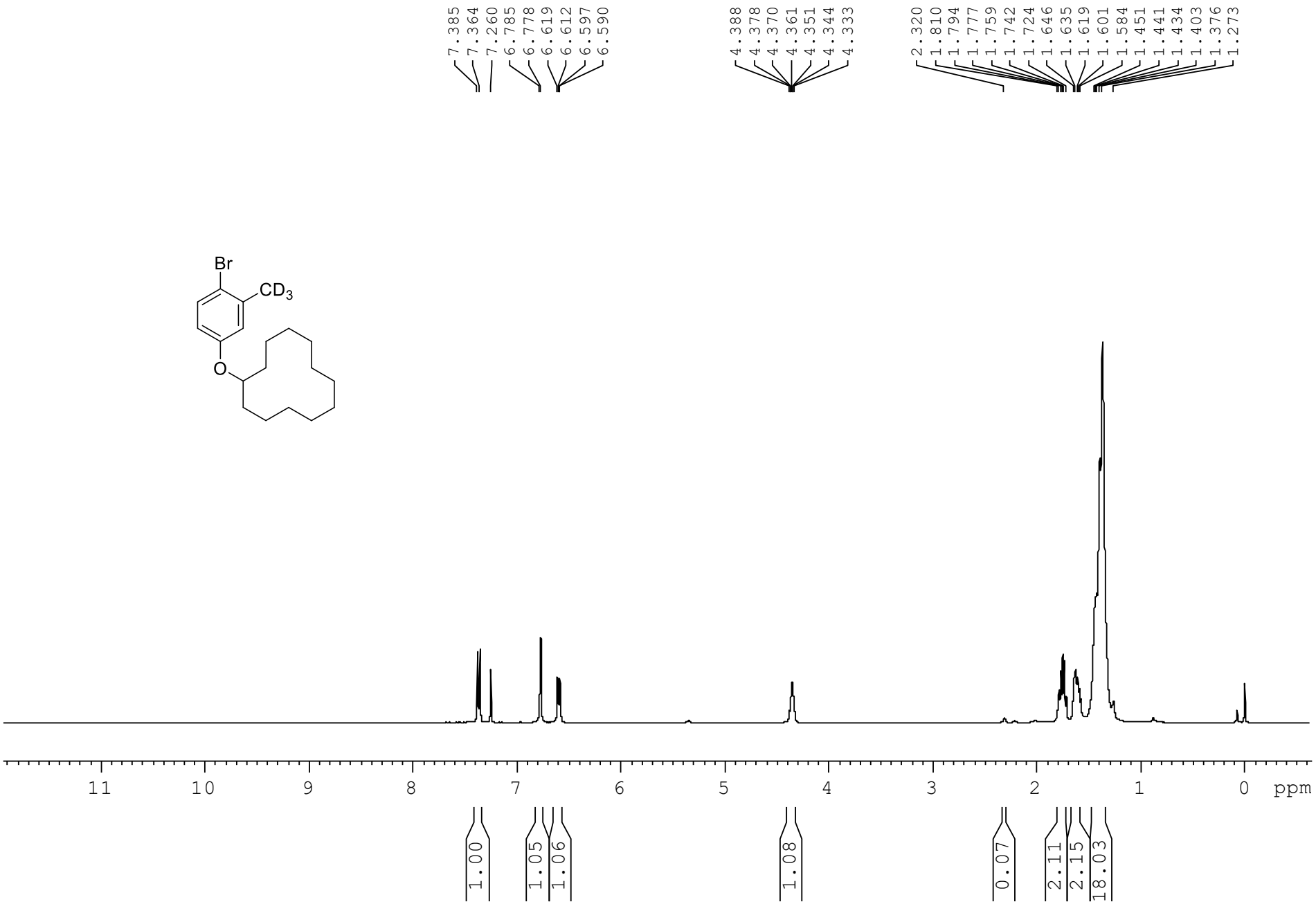

Figure S59. ^{1}H NMR spectra of **1s-*d*$_3$** ($CDCl_3$, 400 M)

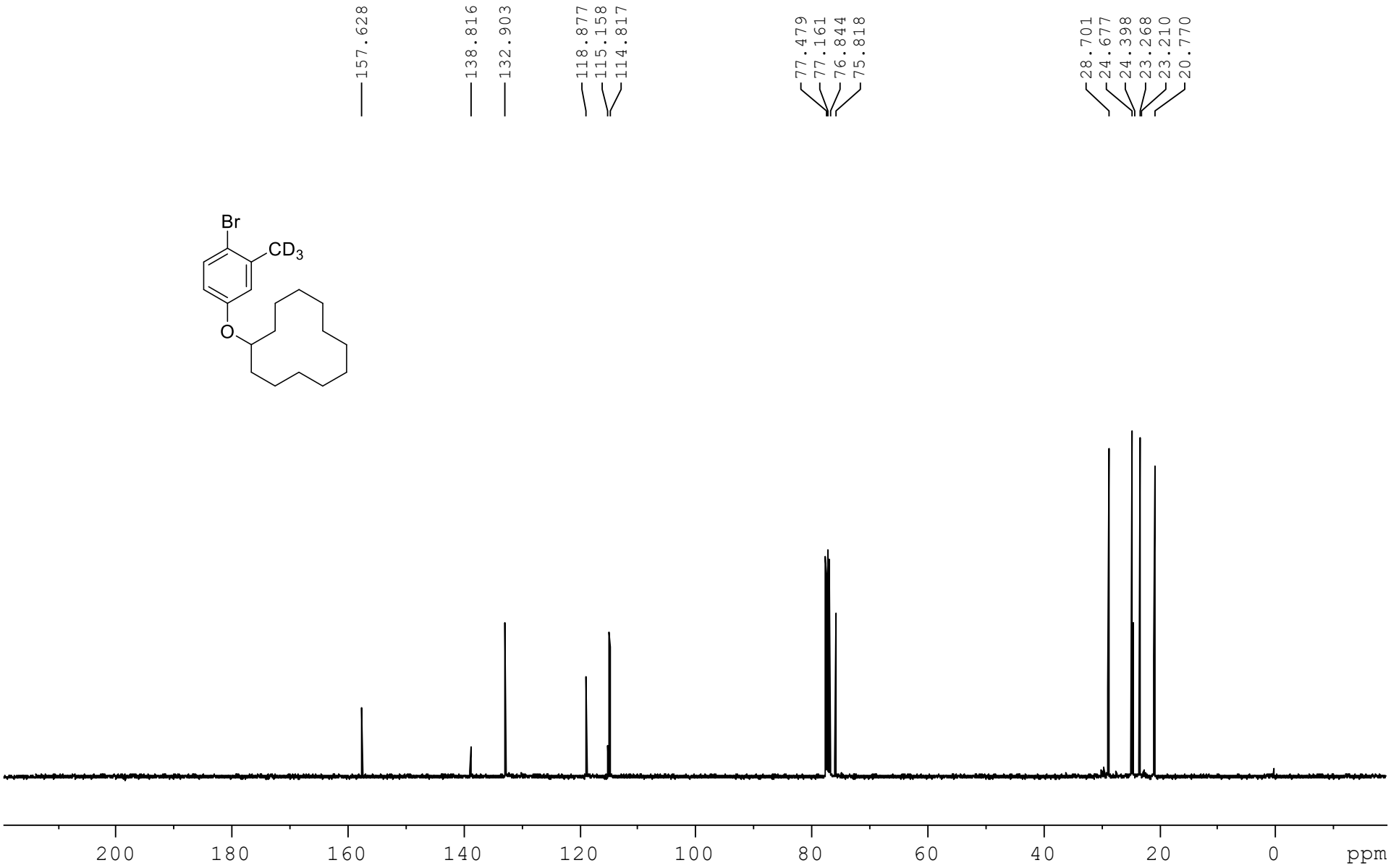

Figure S60. ^{13}C NMR spectra of **1s**-d_3 ($CDCl_3$, 100 M)

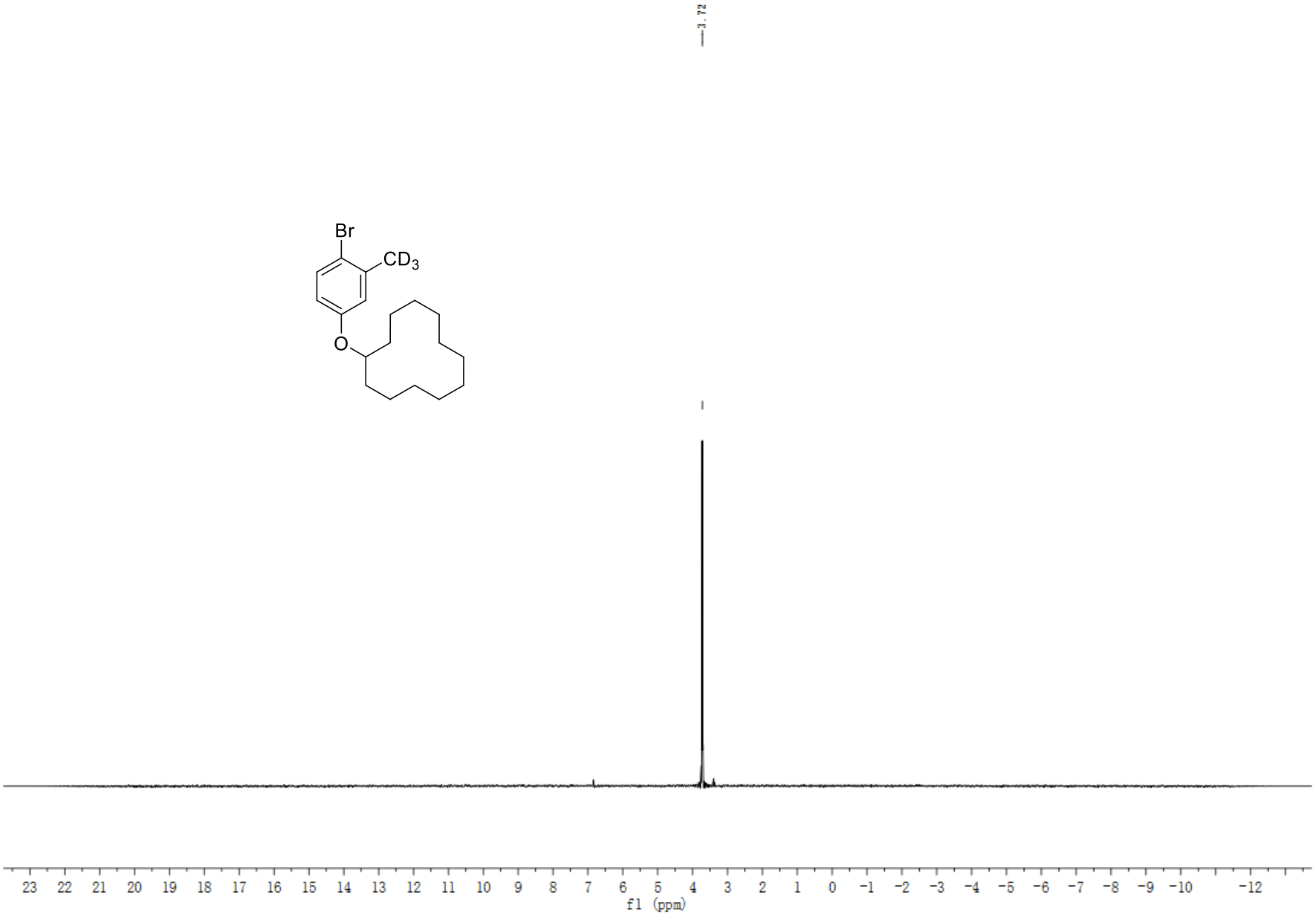

Figure S61. ^{2}H NMR spectra of **1s**-*d*$_3$ (DCM, 92 M)

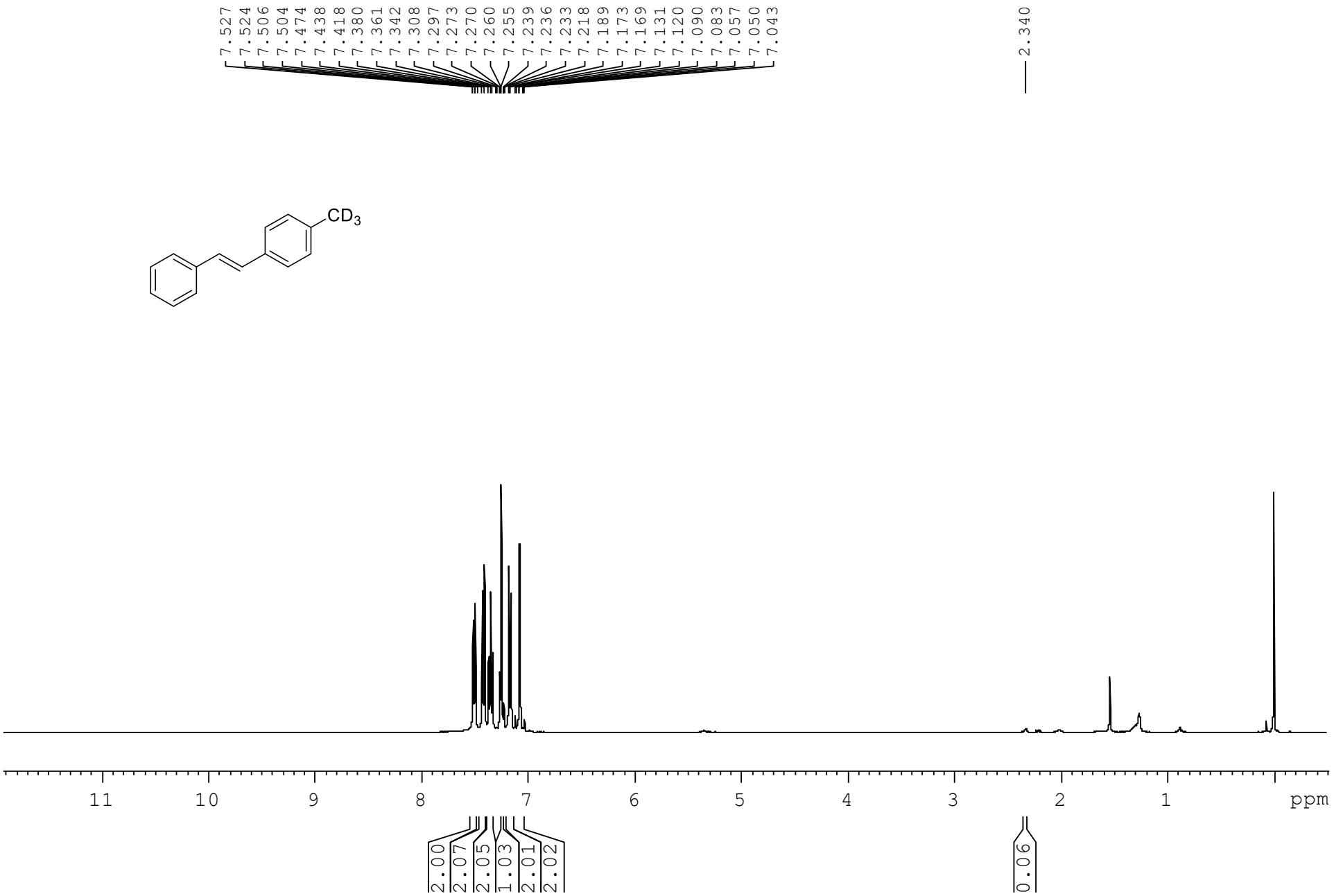

Figure S62. ^{1}H NMR spectra of **1t-*d*$_3$** ($CDCl_3$, 400 M)

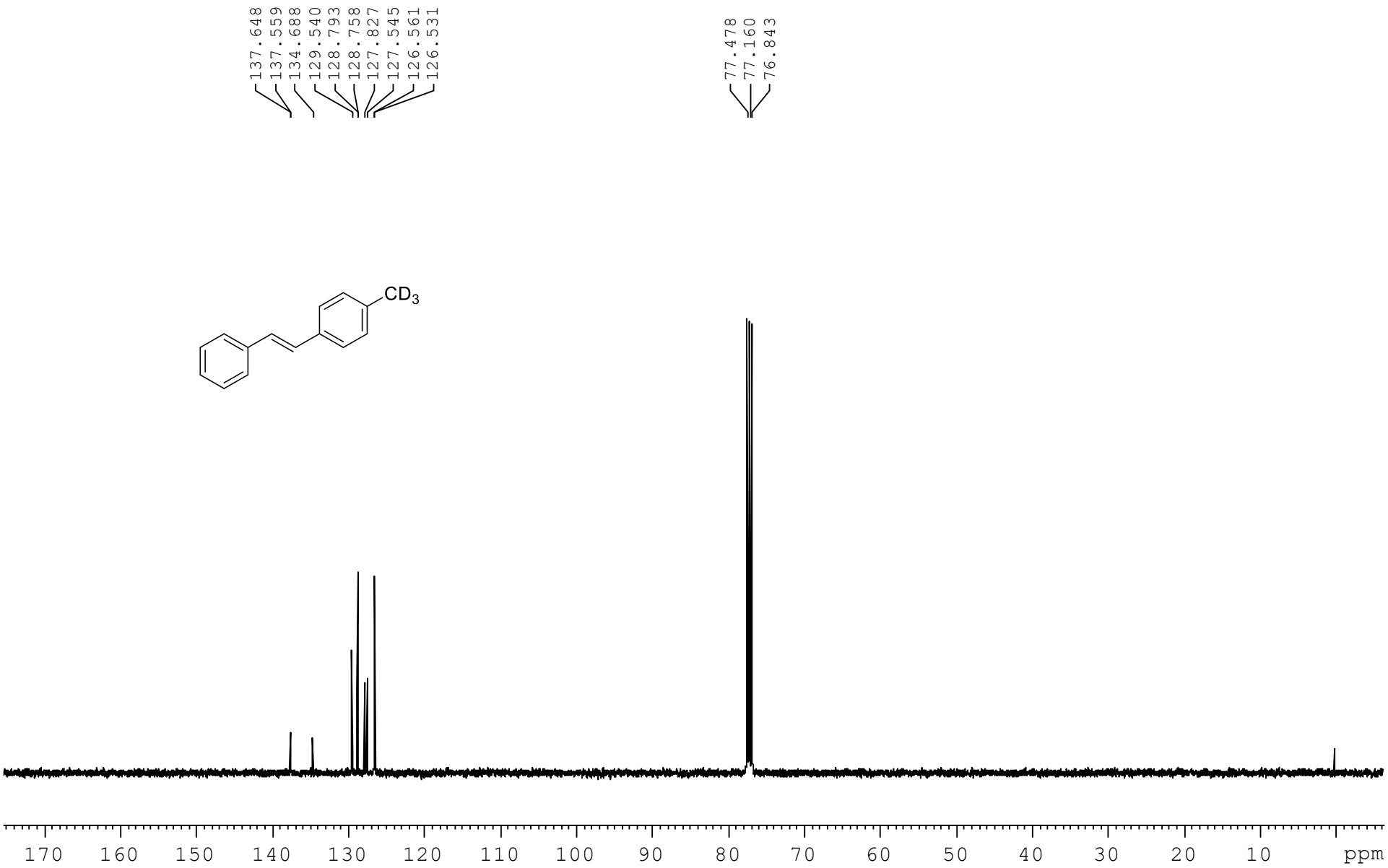

Figure S63. ^{13}C NMR spectra of **1t-*d*3** ($CDCl_3$, 100 M)

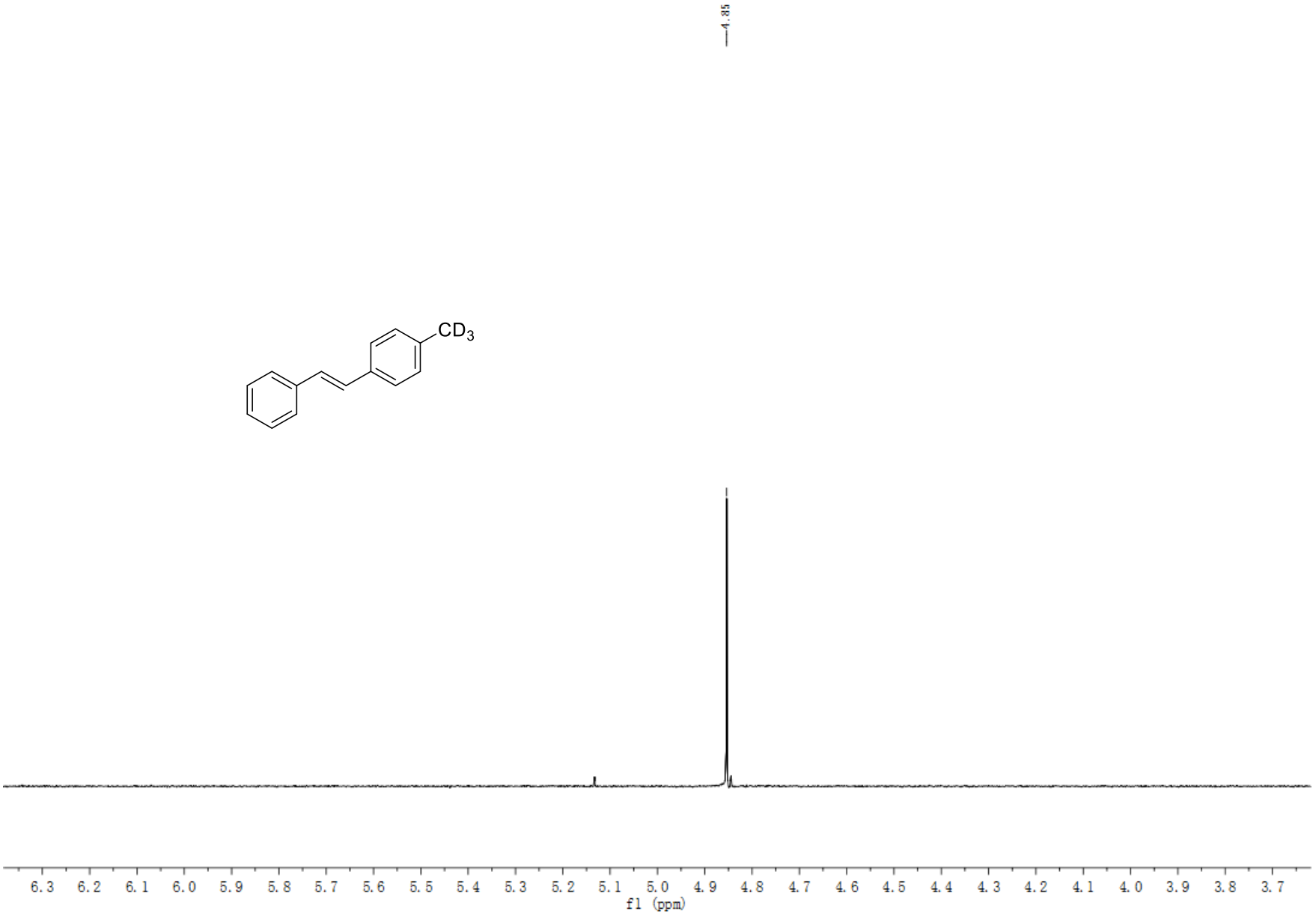

Figure S64. ^{2}H NMR spectra of **1t-*d*$_3$** (DCM, 92 M)

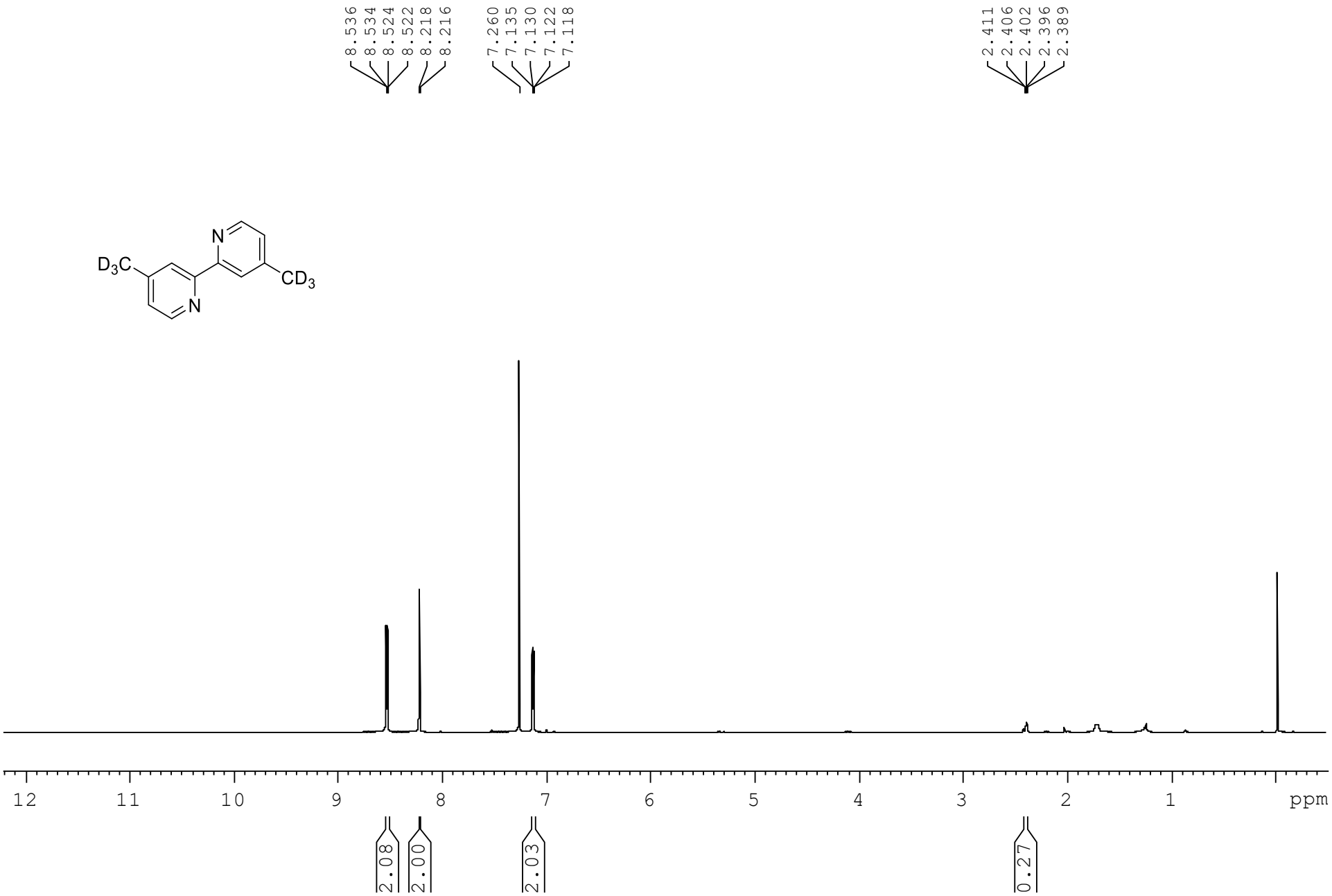

Figure S65. ^{1}H NMR spectra of **1u**-*d6* ($CDCl_3$, 400 M)

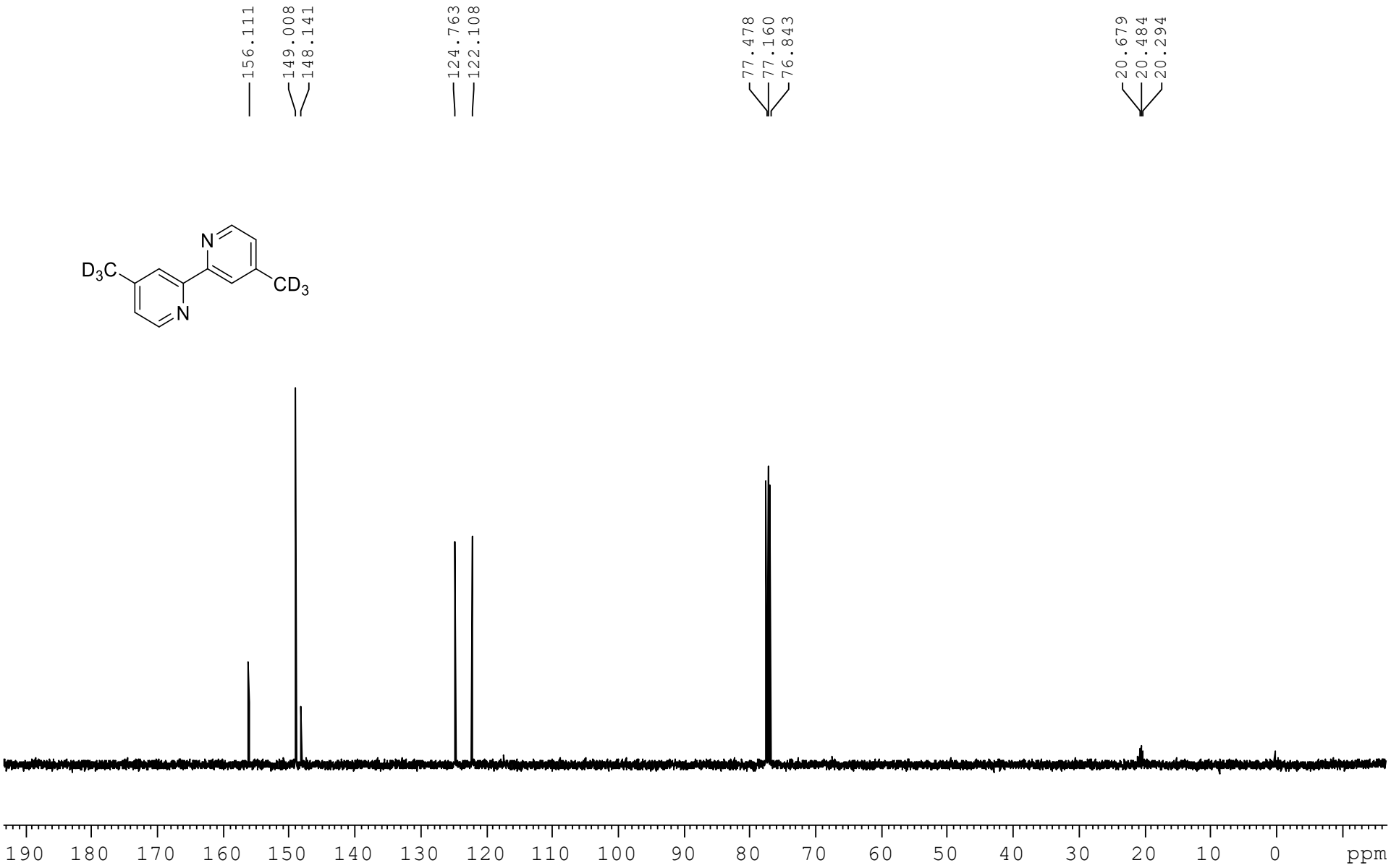

Figure S66. ^{13}C NMR spectra of **1u**-*d6* ($CDCl_3$, 100 M)

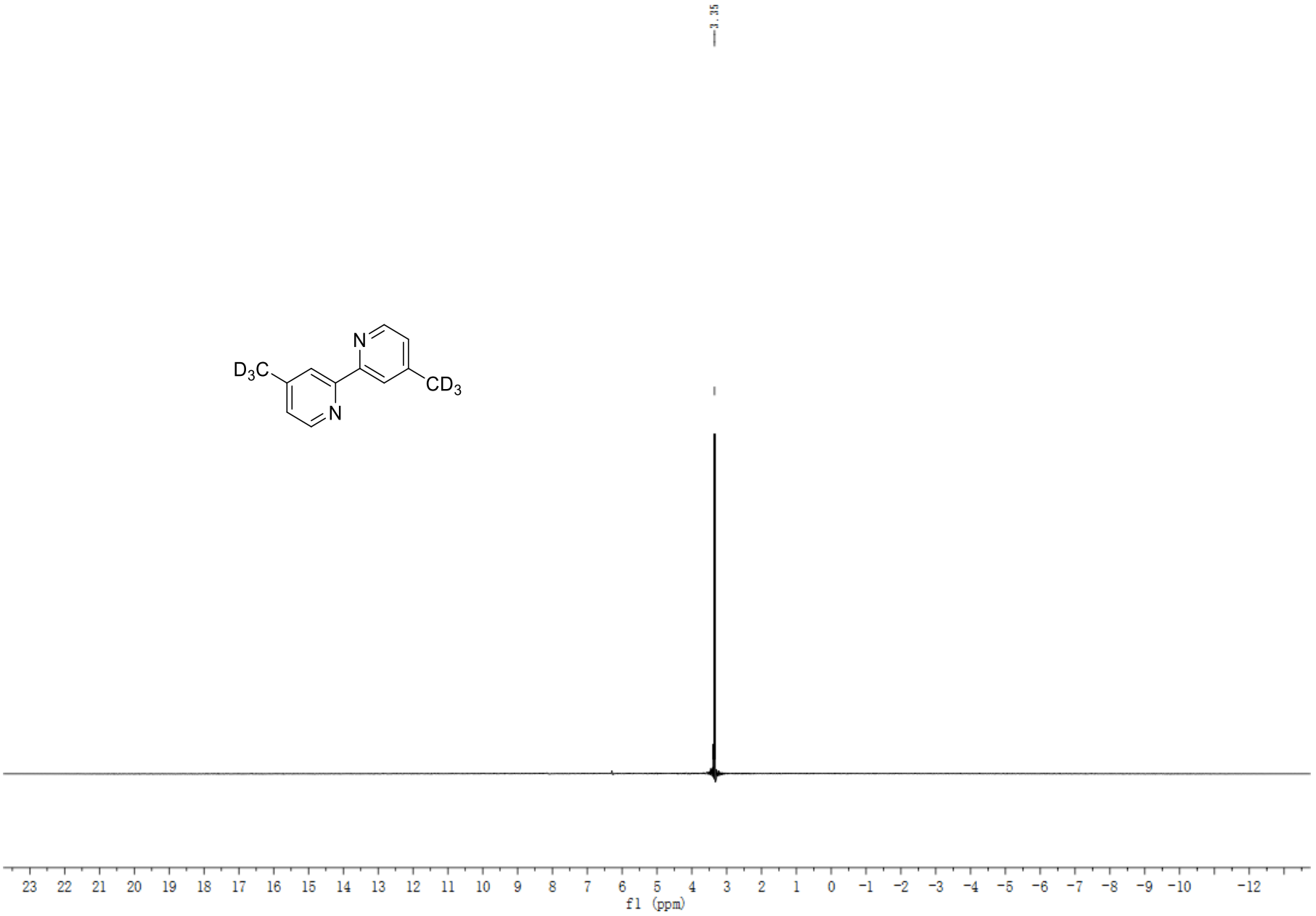

Figure S67. ^{2}H NMR spectra of **1u**-*d*$_6$ (DCM, 92 M)

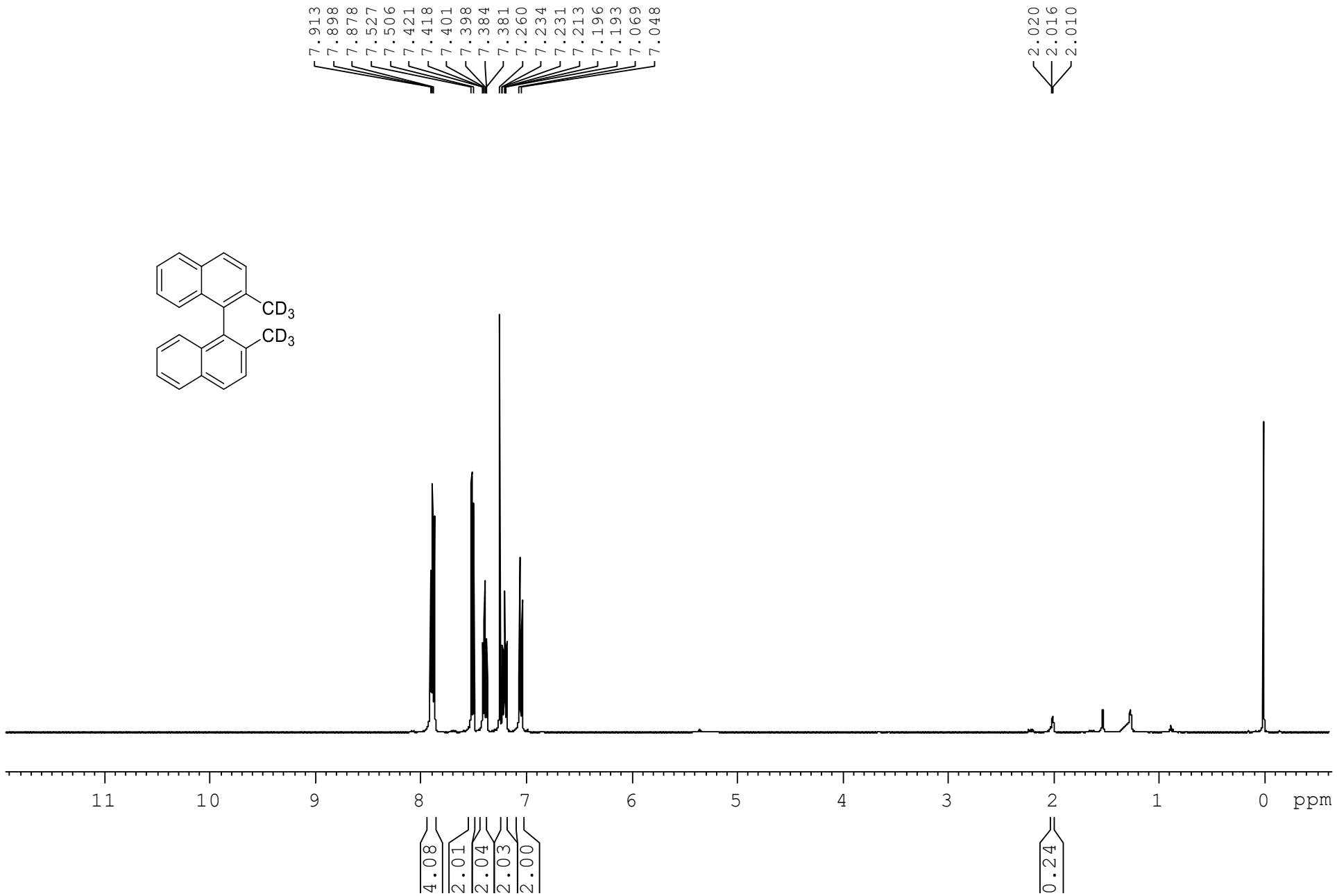

Figure S68. ^{1}H NMR spectra of **1v**-*d6* ($CDCl_3$, 400 M)

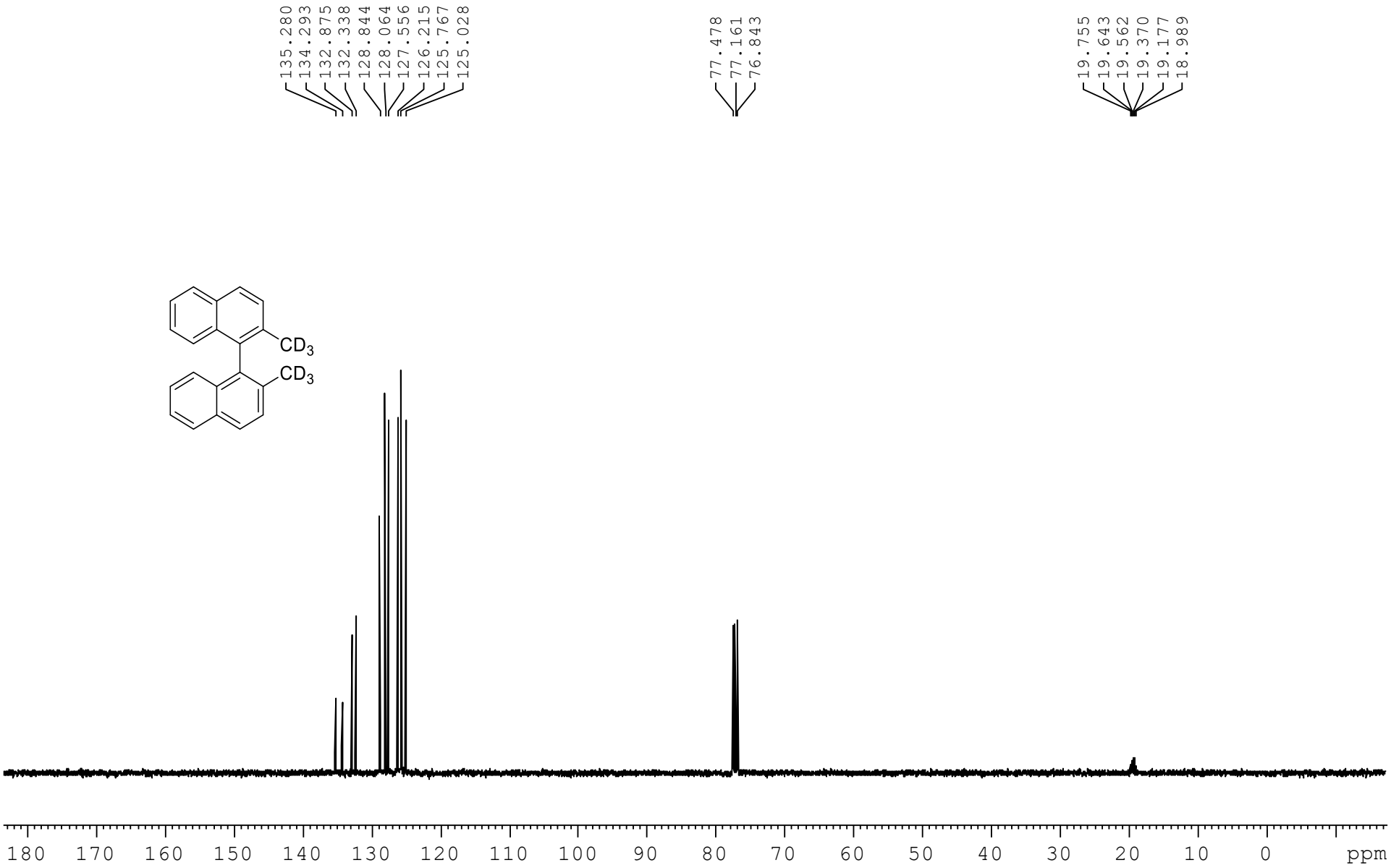

Figure S69. ^{13}C NMR spectra of **1v**-*d6* ($CDCl_3$, 100 M)

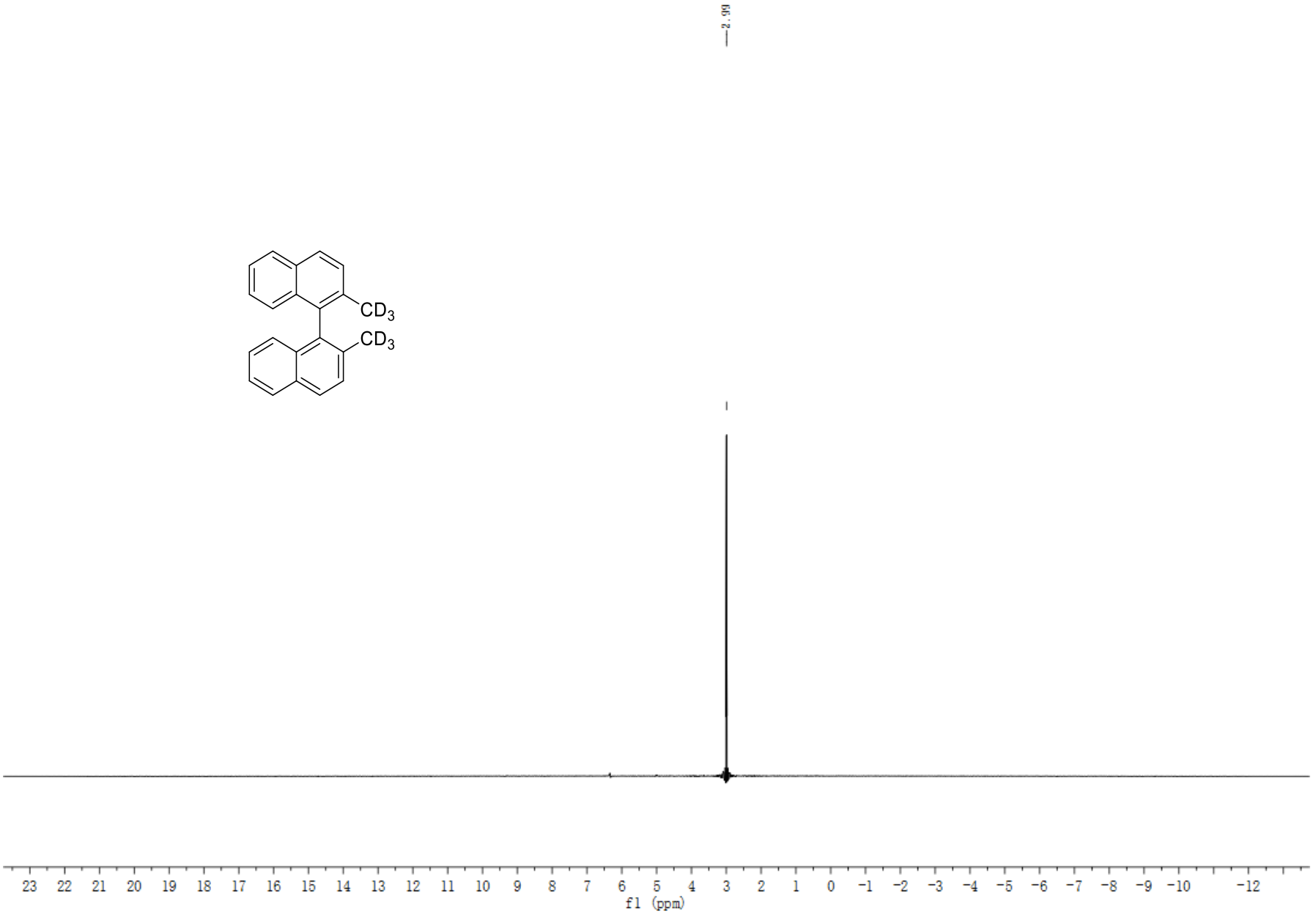

Figure S70. ^{2}H NMR spectra of **1v**-*d*$_6$ (DCM, 92 M)

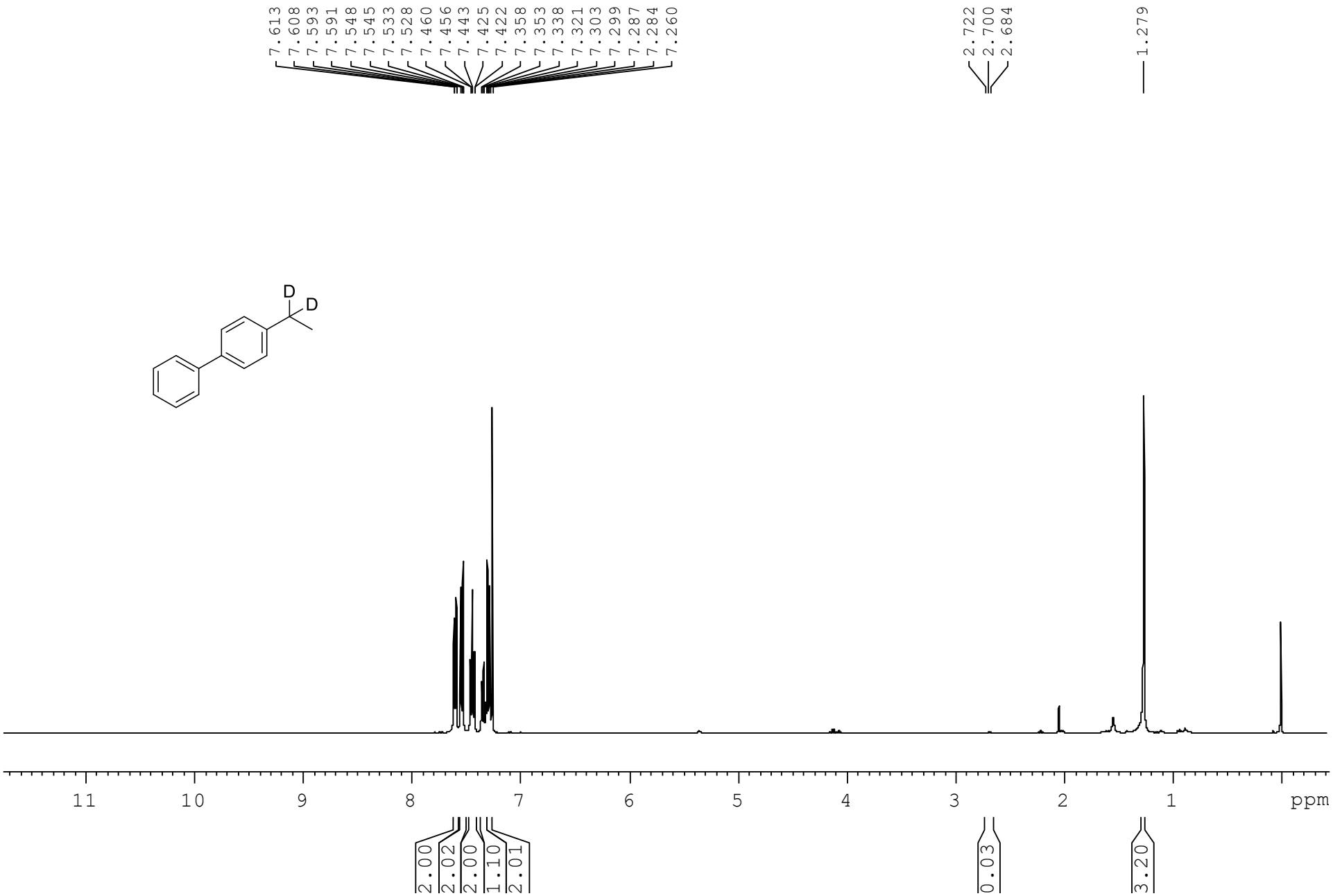

Figure S71. ^{1}H NMR spectra of **1w**-*d*$_2$ ($CDCl_3$, 400 M)

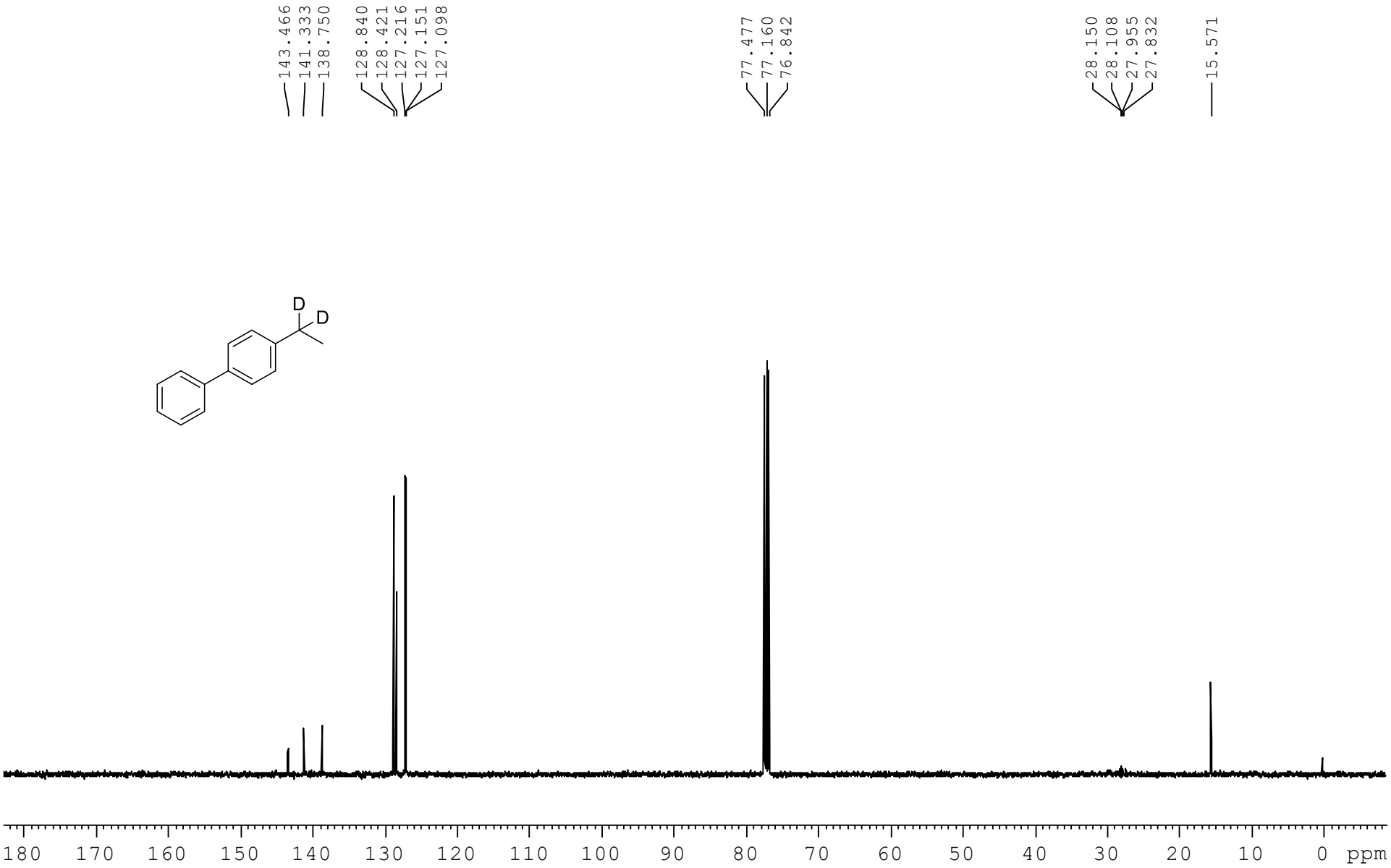

Figure S72. ^{13}C NMR spectra of **1w-*d2*** ($CDCl_3$, 100 M)

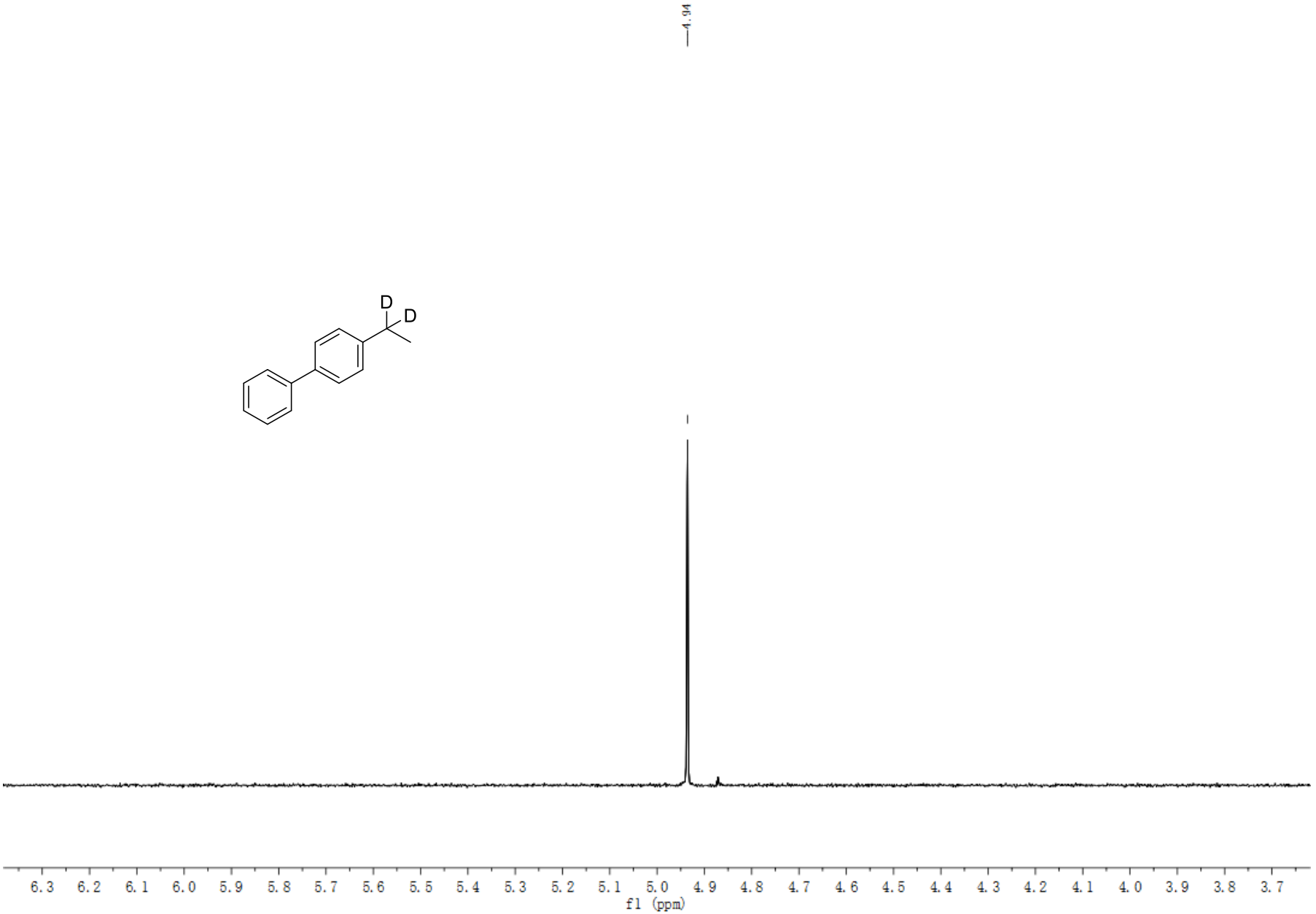

Figure S73. ^{2}H NMR spectra of **1w**-d_2 (MeCN, 92 M)

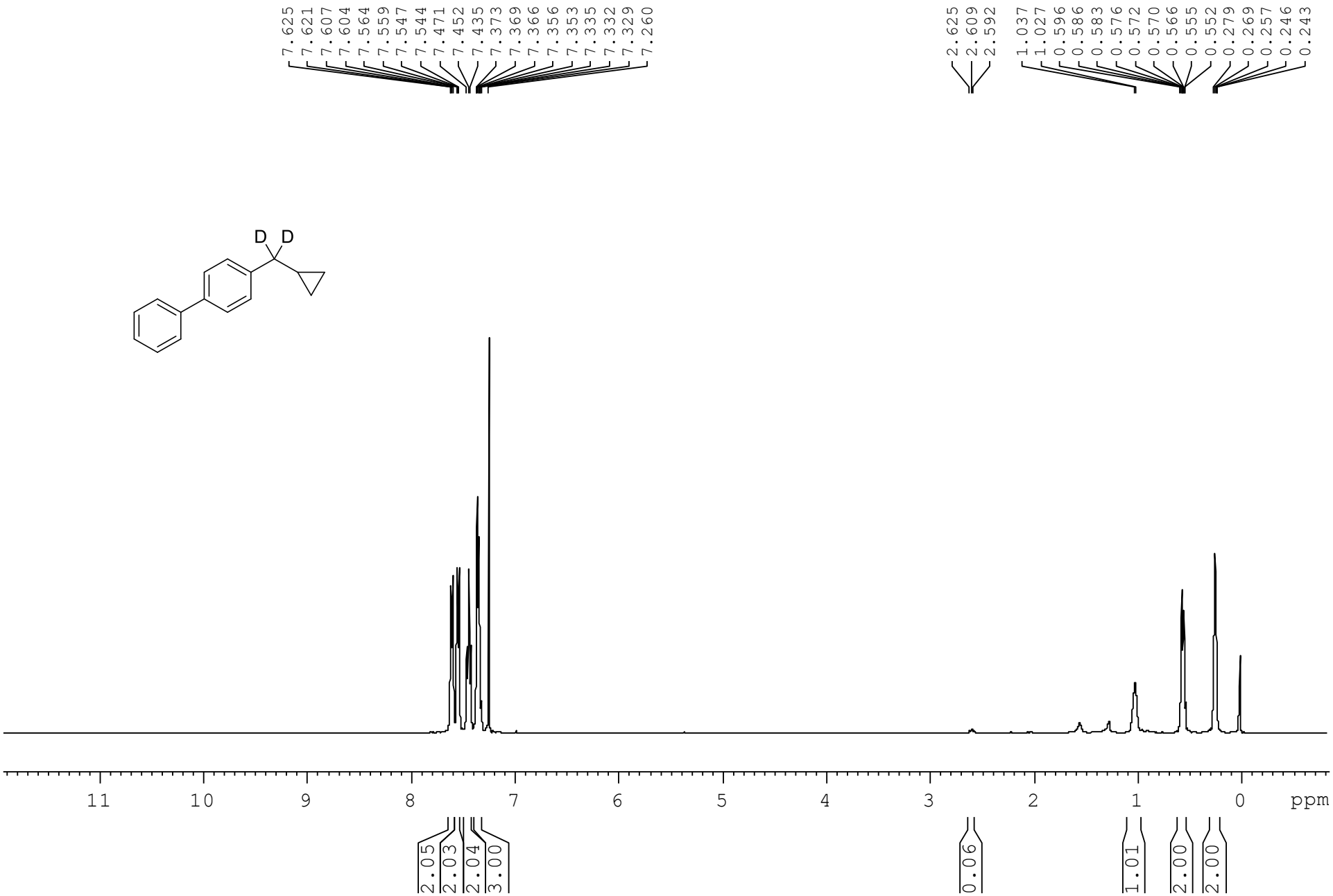

Figure S74. ^{1}H NMR spectra of **1x-*d*$_2$** ($CDCl_3$, 400 M)

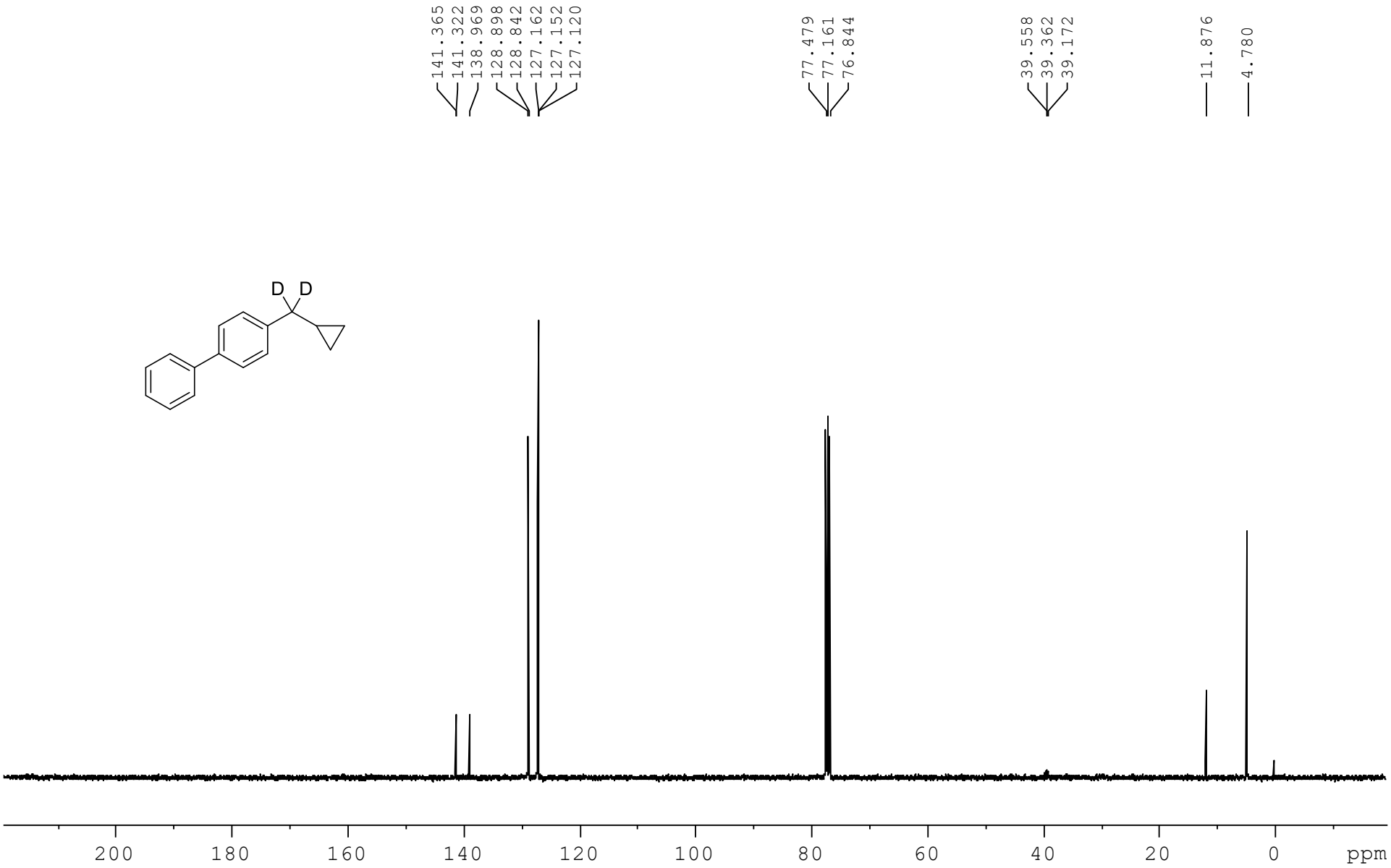

Figure S75. ^{13}C NMR spectra of **1x**-d_2 ($CDCl_3$, 100 M)

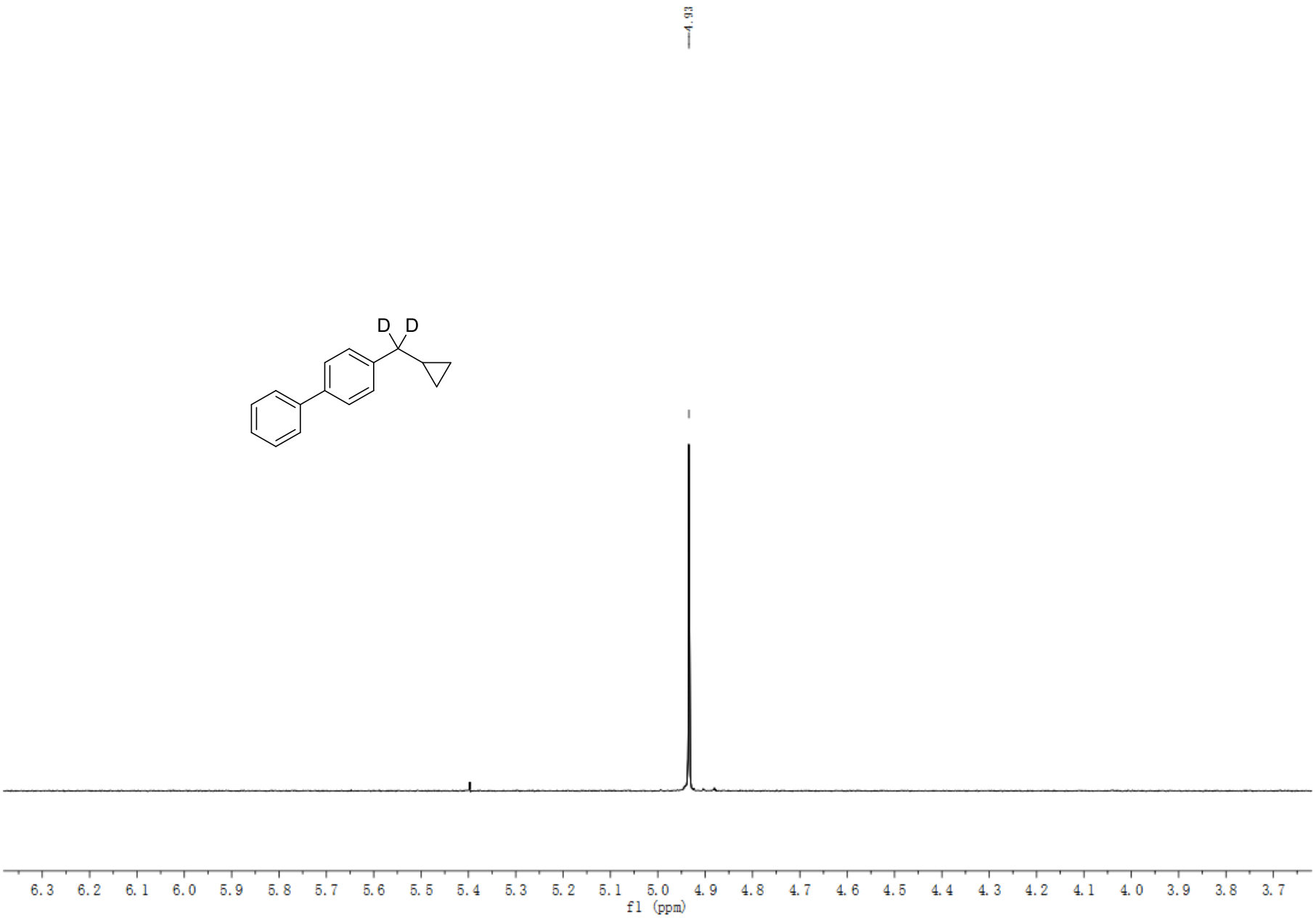

Figure S76. ^{2}H NMR spectra of **1x**-*d*$_2$ (MeCN, 92 M)

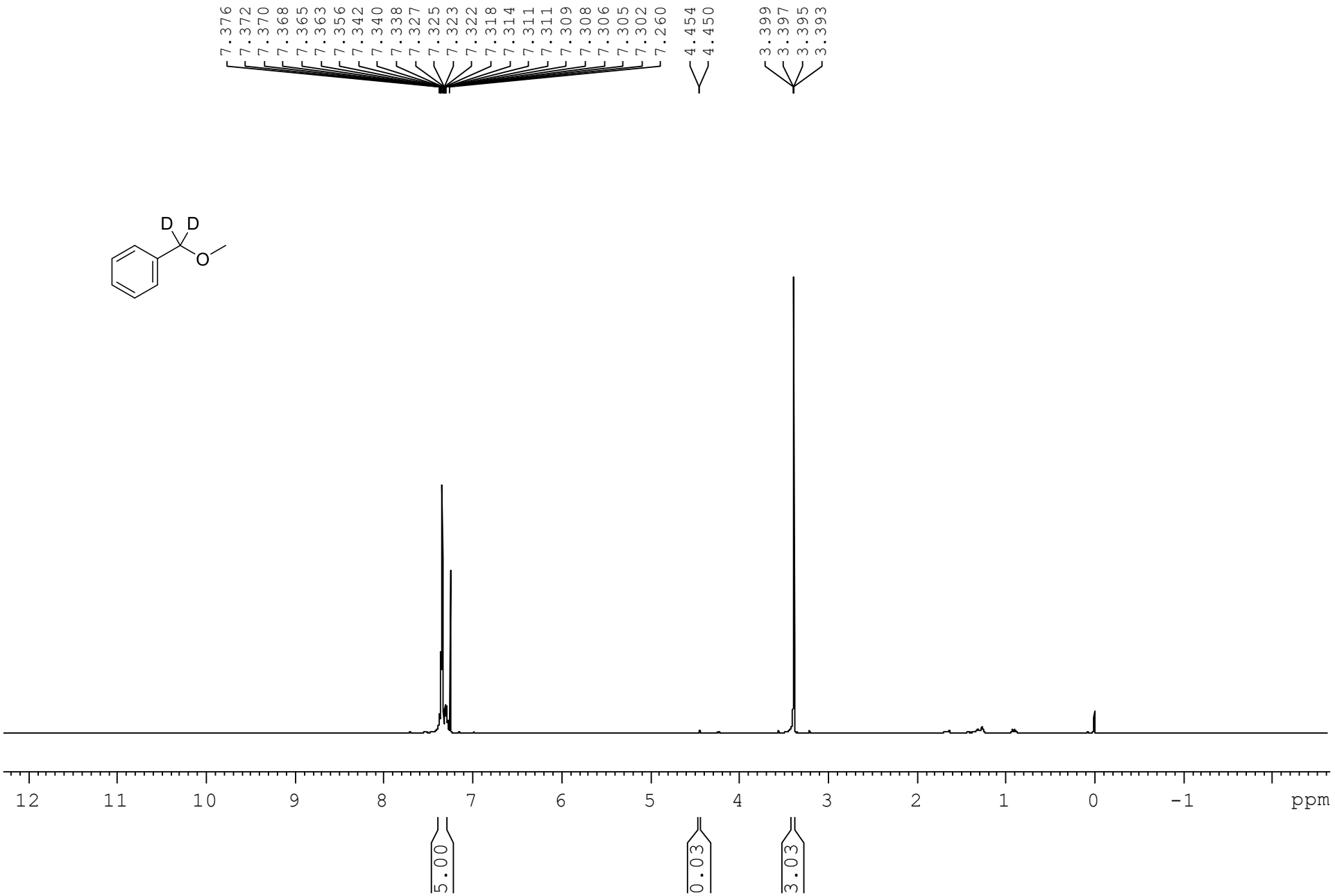

Figure S77. ^{1}H NMR spectra of **1y**-d_2 ($CDCl_3$, 400 M)

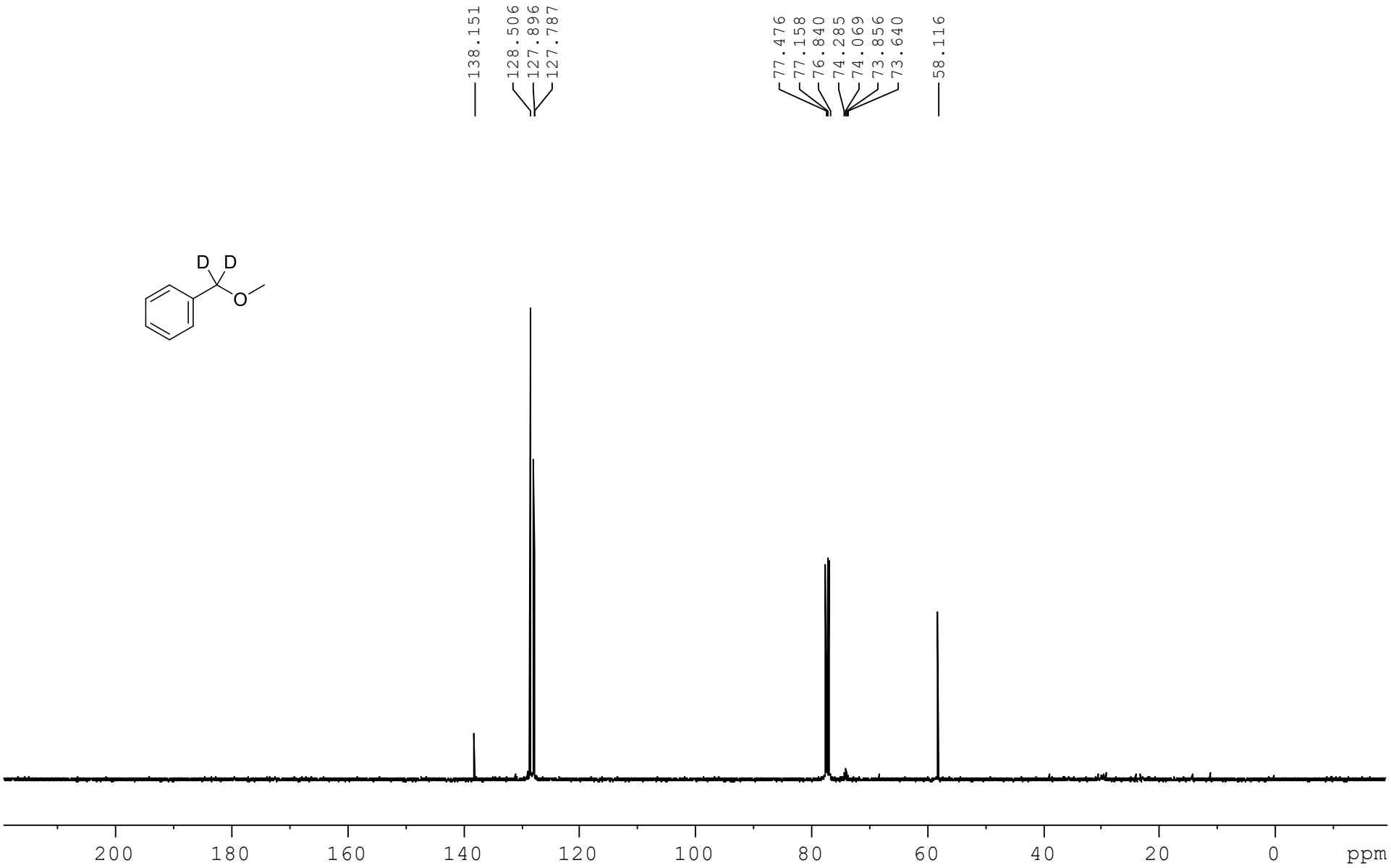

Figure S78. ^{13}C NMR spectra of **1y**-d_2 ($CDCl_3$, 100 M)

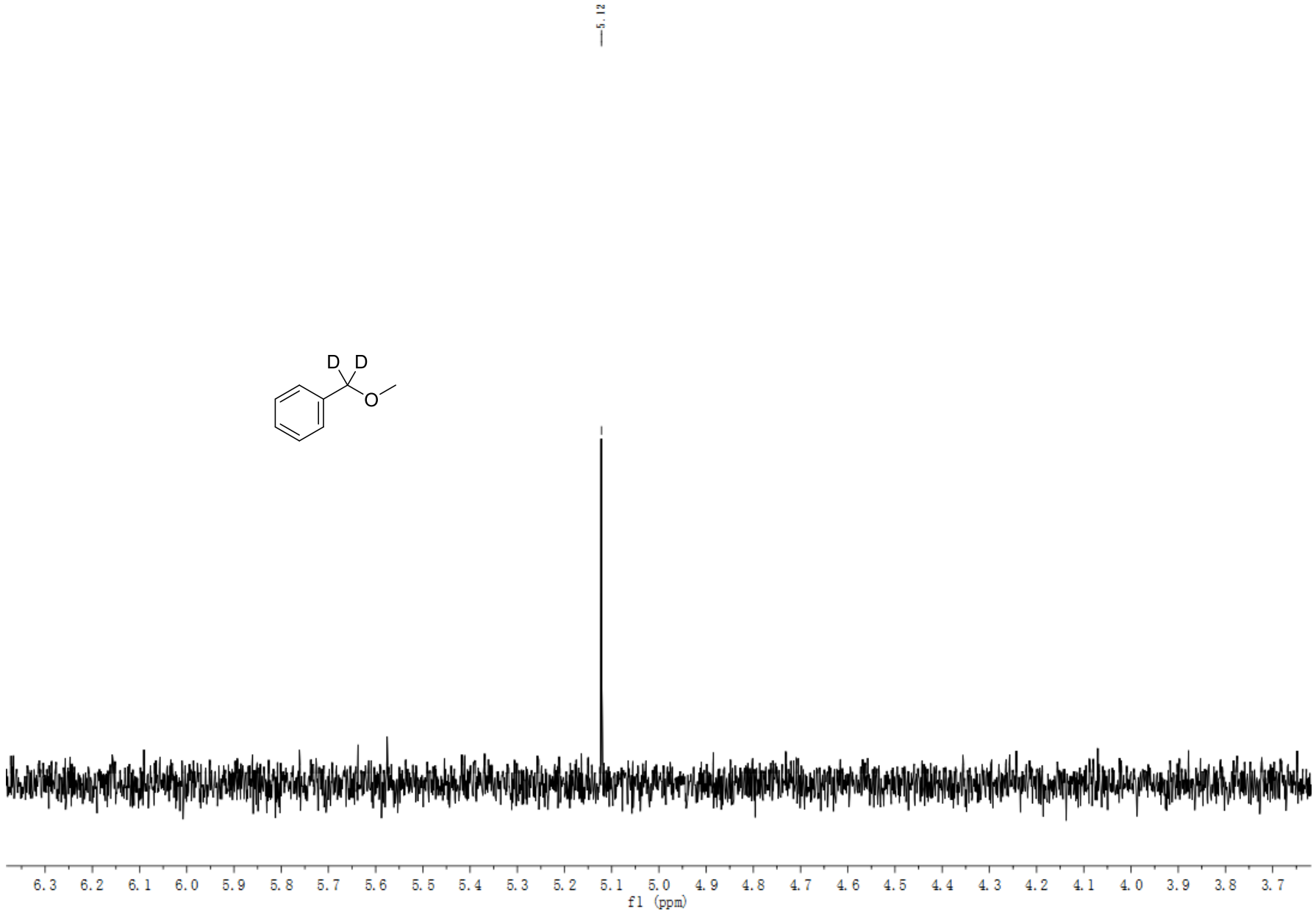

Figure S79. ^{2}H NMR spectra of **1y**-d_2 (DCM, 92M)

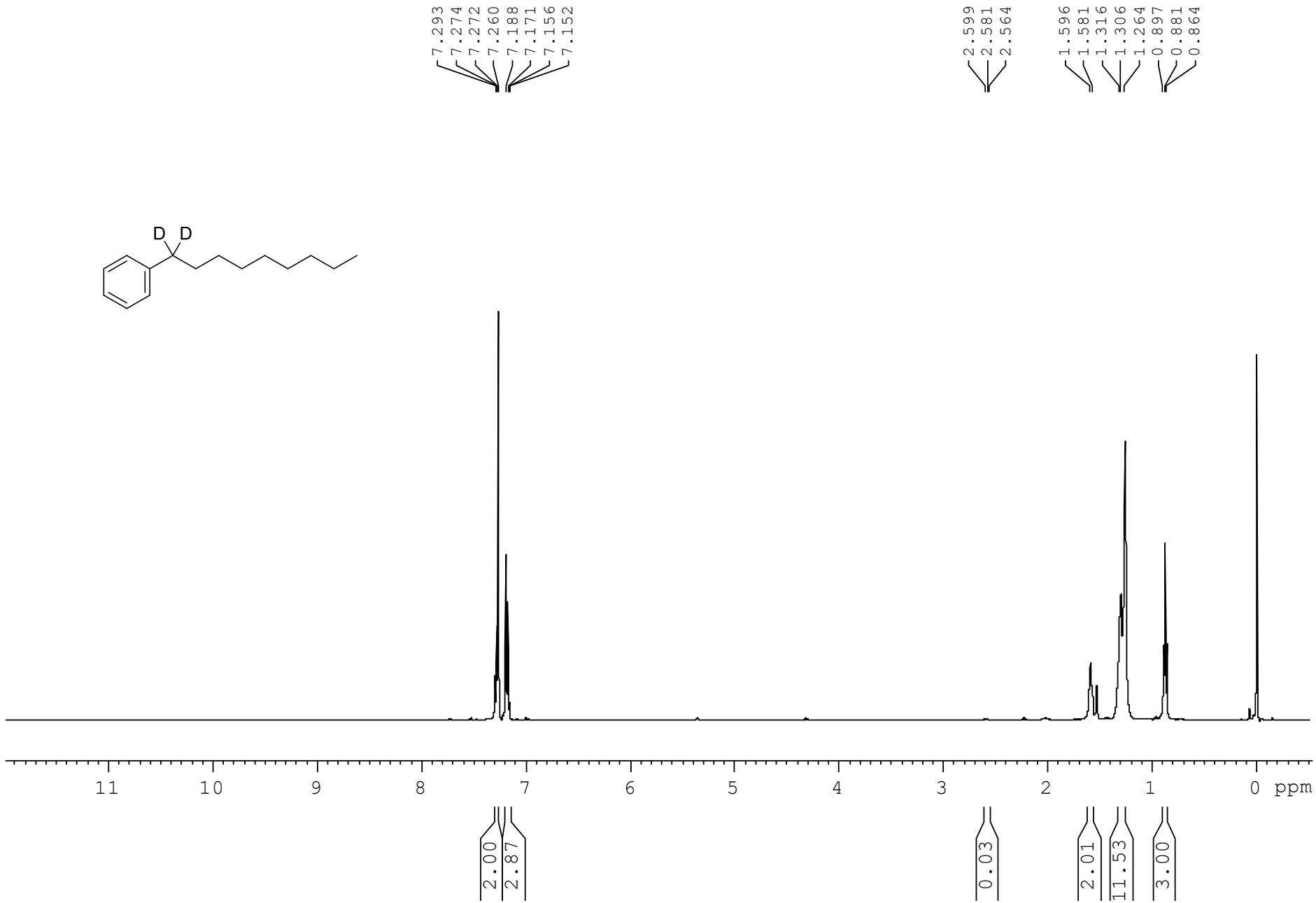

Figure S80. ^{1}H NMR spectra of **1z-*d*$_2$** ($CDCl_3$, 400 M)

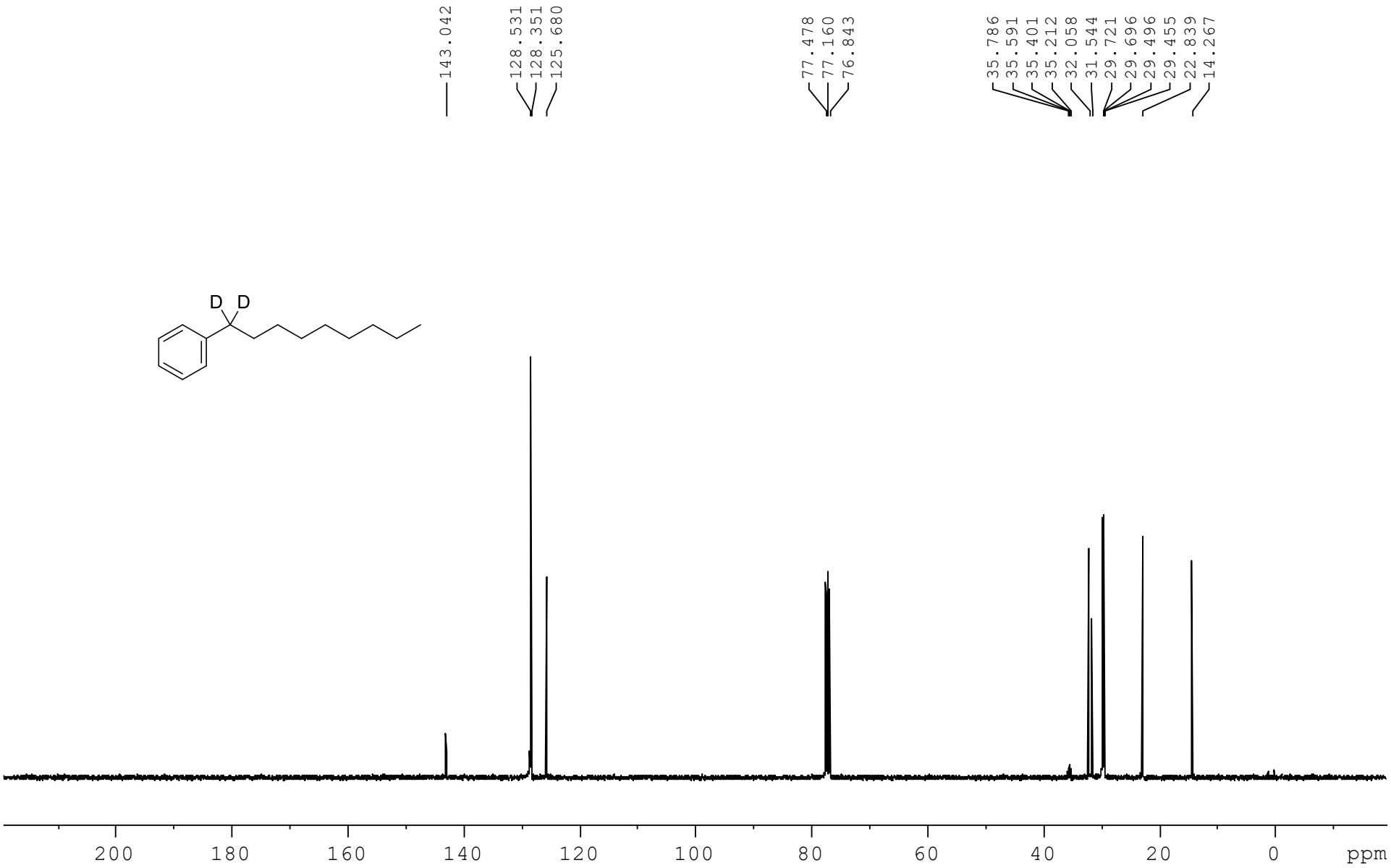

Figure S81. ^{13}C NMR spectra of **1z**-d_2 ($CDCl_3$, 100 M)

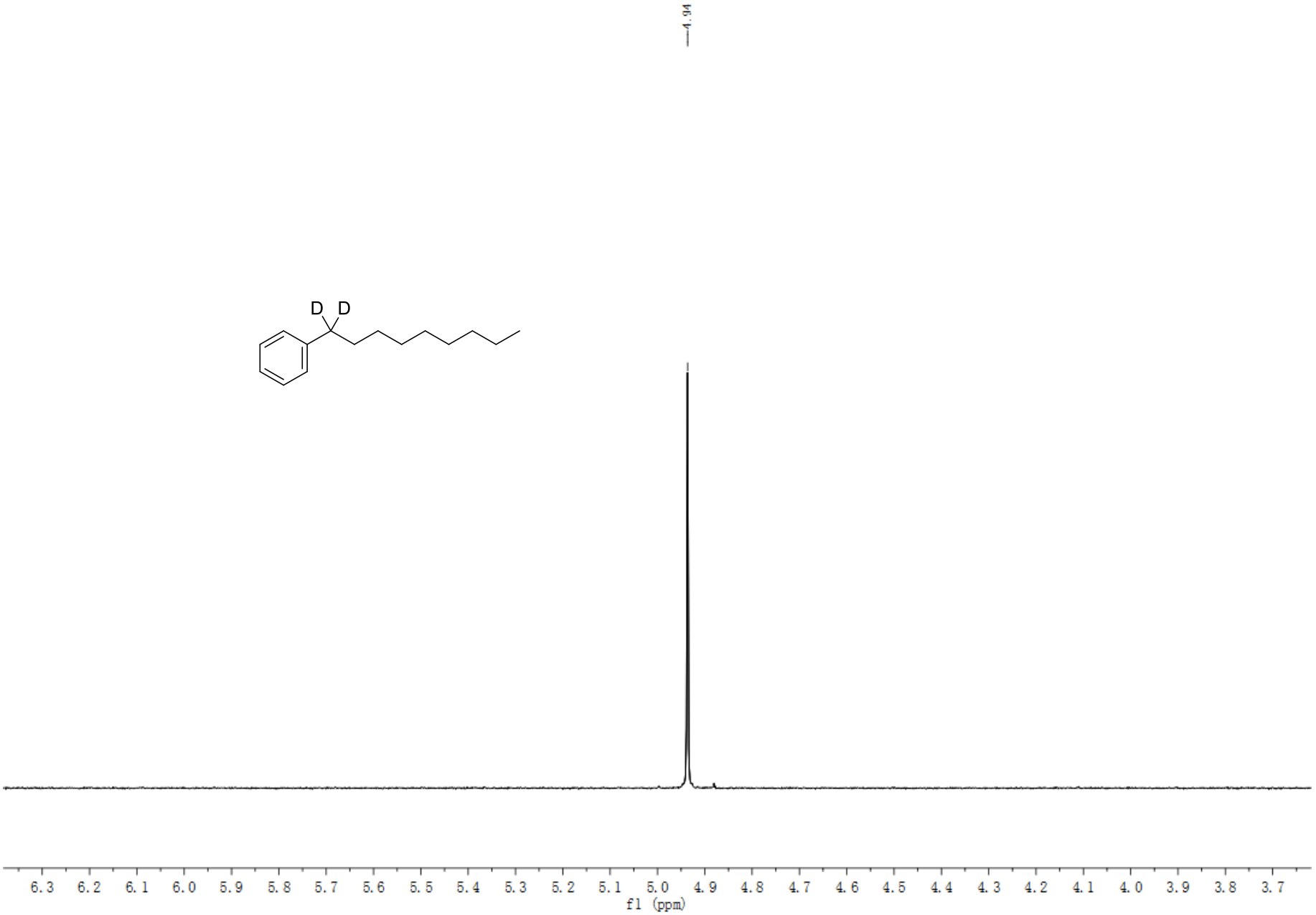

Figure S82. ^{2}H NMR spectra of **1z**-d_2 (MeCN, 92 M)