Supporting Information

Hydroxy-telechelic poly(ethylene-*co*-isobutylene) as a soft segment for thermoplastic polyurethanes

Yanzhao Wang [†] and Marc Hillmyer [†*]

[†] Department of Chemistry, University of Minnesota

Minneapolis, Minnesota 55455-0431

Authors for correspondence: hillmyer@umn.edu

Table of Contents

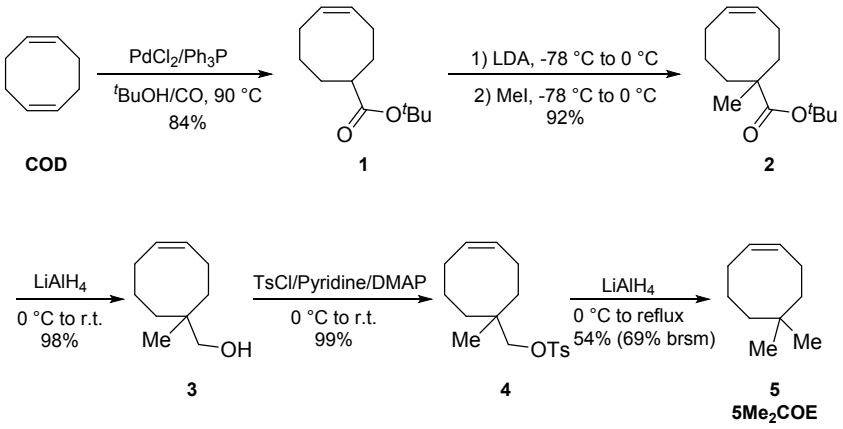
General

Materials. Ethyl acetate (ACS grade), hexanes (ACS grade) and diethyl ether (anhydrous) were purchased from Fisher Scientific and used without further purification. Anhydrous tetrahydrofuran and dichloromethane were obtained from solvent purification system directly. All commercially available reactants/reagents were purchased from Aldrich and used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silicycle silica gel (230-400 mesh).

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA-500 spectrometer, Bruker AV500 spectrometer and a Bruker HD500 spectrometer using residue solvent peaks as internal standards; CDCl3 was used as the solvent. High-resolution mass spectral data (HRMS) was collected on an Agilent Technologies 7200 Accuate-Mass Q-TOF GC/MS using EI conditions. $M_{n,NMR}$ was determined by ^{1}H NMR end group analysis. $M_{n,SEC}$ was determined on a Hewlett-Packard 1100 series liquid chromatograph fitted with a Hewlett-Packard 1047A refractive index detector and three PLgel columns (Polymer Laboratories columns with 500, 103, and 104 Å pore sizes), which were calibrated with polystyrene standards, with chloroform as the eluent at a flow rate of 1 mL/min at 35 °C. $M_{n,LS\text{-}SEC}$ was determined on a system includes a Wyatt OPTILAB RI detector, a Wyatt multiangle light scattering detector (MALS), and three Phenogel columns (Phenomenex of 103, 104, and 105 Å pore sizes). The columns were at ambient temperature, and the RI detector was set at 40 °C; THF was used as the eluent at a flow rate of 1 mL/min. Differential Scanning Calorimetry (DSC) measurements were performed using a TA Instruments Q1000 with N_2 as the purge gas at the rate of 10 °C/min.

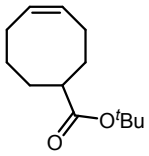
Thermal transition temperatures were determined from the second heating after annealing above the glass transition or melting temperatures for at least 1 min to erase thermal history.

Synthesis of the new monomer 5



Scheme 1. Synthesis of the new monomer **5**: (*Z*)-5,5-dimethylcyclooct-1-ene

tert-Butyl (*Z*)-cyclooct-4-ene-1-carboxylate **1**

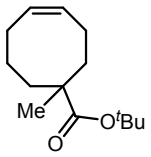


This known compound was prepared via a slightly different procedure from Wagener and coworkers and the spectral data were in accordance with literature data. [1] In a 1 L high pressure reactor (Series 4520 Bench Top Reactors, 1L, Parr Instrument Company) were placed palladium (II) chloride (2 g, 11.3 mmol), triphenylphosphine (12 g, 45.7 mmol), t*ert*-butyl alcohol (69 mL, 718 mmol), 1,5-cyclooctadiene (**COD**, 140 mL, 1141 mmol) and toluene (69 mL). The reactor was sealed and then pressurized to 600 psig with carbon monoxide and then vented down to 25 - 30 psig. This procedure was repeated two more times and then the reactor was pressurized to 400 psig and heated to 90 °C with fast stirring. After the system had equilibrated at this temperature, the reactor was charged with additional carbon monoxide to a pressure of 660 psig. After 24

hours, the pressure dropped significantly and the reactor was then repressurized to 660 psig and stirred for another 24 hours. Then the reactor was cooled to room temperature, vented and disassembled. The yellow solution was filtered with Celite and washed with toluene, and the volatiles were removed *in vacuo*. The crude product was purified by fractional vacuum distillation yielding a clear colorless oil (126 g, 84% yield, b.p. = 67 - 70 °C at 200 - 250 mTorr).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 - 5.57 (m, 2H), 2.42 - 2.28 (m, 2H), 2.20 - 2.02 (m, 3H), 1.97 (dt, J_1 = 14.7 Hz, J_2 = 4.0 Hz, 1H), 1.86 - 1.79 (m, 1H), 1.74 - 1.67 (m, 1H), 1.62 - 1.49 (m, 2H), 1.42 (s, 10H).

tert-Butyl (*Z*)-1-methylcyclooct-4-ene-1-carboxylate **2**



This known compound was prepared via a slightly different procedure from Coates and coworkers. [2] A freshly prepared LDA solution (476 mmol diisopropylamine, 400 ml 2.5 M *n*-butyllithium in hexanes and 800 mL anhydrous tetrahydrofuran) was cooled to -78 °C. A solution of compound **1** (66.7 g, 317 mmol) in 150 mL dry tetrahydrofuran was slowly added to the LDA solution over 30 minutes *via* cannula. The reaction was stirred at -78 °C for 15 minutes and then slowly warmed up to 0 °C over 30 minutes by removing the acetone-dry ice bath. Methyl iodide (41.6 mL, 667 mmol) was added dropwise and the mixture was stirred for 60 minutes at 0 °C. 125 mL of 4 M hydrochloric acid was slowly added at 0 °C, followed by extraction with diethyl ether (3x500 mL). The extracts were combined, washed with saturated sodium bicarbonate (150 mL), saturated sodium chloride (150 mL) and then dried with

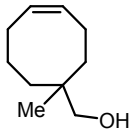
magnesium sulfate. The solvents were removed *in vacuo* and a yellow oil was yielded. The crude product was further purified by fractional vacuum distillation affording a clear, slightly yellow oil (65 g, 92% yield, b.p. = 65 - 68 °C at 250 mTorr).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 - 5.63 (m, 1H), 5.52 - 5.40 (m, 1H), 2.37 - 2.20 (m, 3H), 2.20 - 2.00 (m, 2H), 1.81 - 1.65 (m, 2H), 1.65-1.34 (m, 13H), 1.14 (s, 3H).

^{1}H NMR (500 MHz, C_6D_6) δ 5.72 – 5.65 (m, 1H), 5.53 – 5.45 (m, 1H), 2.45 – 2.35 (m, 2H), 2.35 – 2.27 (m, 1H), 2.10 – 1.97 (m, 2H), 1.88 – 1.82 (m, 1H), 1.82 – 1.74 (m, 1H), 1.68 – 1.61 (m, 1H), 1.52 (m, 1H), 1.42 – 1.37(m,1 H), 1.35 (s, 9H), 1.13 (s, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 177.12, 132.84, 127.44, 79.73, 47.13, 36.86, 33.64, 28.63, 28.58, 26.69, 25.97, 25.52.

(*Z*)-(1-Methylcyclooct-4-en-1-yl)methanol **3**

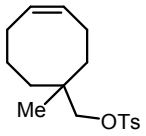


Lithium aluminum hydride (20.9 g, 550 mmol) was placed in a flame-dried two-neck flask under nitrogen and cooled to 0°C. Dry tetrahydrofuran (800 mL) was transferred to the flask *via* cannula and then a solution of compound **2** (61.8 g, 275 mmol) in 100 mL dry tetrahydrofuran was slowly added with an addition funnel. This reaction was stirred at 0 °C for 1 hour and then slowly warmed up to room temperature. After 6 hours, the solution was cooled back to 0 °C and diluted with 1 L diethyl ether; 21 mL water was added extremely slowly to quench the reaction and then followed by 21 mL 15% sodium hydroxide aqueous solution and 63 mL water. The grey mixture was warmed up to room temperature and stirred for 15 minute forming a white slurry. Magnesium sulfate was added and the mixture was filtered through Celite and rinsed with

diethyl ether to afford clear solution, which was concentrated *in vacuo* to yield the alcohol **3** as a slightly yellow oil (41.6 g, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 - 5.63 (m, 1H), 5.50 - 5.40 (m, 1H), 3.32 (s, 2H), 2.35 – 2.10 (m, 4H), 1.67 – 1.30 (m, 7H), 0.94 (s, 3H).

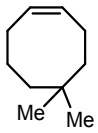
(*Z*)-(1-Methylcyclooct-4-en-1-yl)methyl 4-methylbenzenesulfonate **4**



An oven-dried round-bottom flask was charged with alcohol **3** (20.8 g, 135 mmol), 4-dimethylaminopyridine (1 g, 8.2 mmol) and dry pyridine (100 mL) and then cooled to 0 °C. A solution of 4-toluenesulfonyl chloride (38.6 g, 202 mmol) in dry dichloromethane was added dropwise to the reaction *via* an addition funnel. The ice bath was then removed and the reaction was stirred for 12 h. Saturated sodium bicarbonate aqueous solution (200 mL) was added slowly at 0 °C and the mixture was stirred for 1 hour to quench the excess 4-toluenesulfonyl chloride, followed by extraction with diethyl ether (3x250 mL). The extracts were combined, washed with 4 M hydrochloric acid (250 mL), saturated sodium chloride (150 mL) and then dried with magnesium sulfate. The crude product was afforded in quantitative yield after the removal of solvents *in vacuo* and used directly for the next step.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 5.70 - 5.55 (m, 1H), 5.55 - 5.35 (m, 1H), 3.39 (s, 2H), 2.45 (s, 3H), 2.27 – 1.95 (4H, m), 1.66 – 1.39 (m, 5H), 1.39 – 1.25 (m, 1H), 0.91 (s, 3H).

(*Z*)-5,5-Dimethylcyclooct-1-ene **5** (Me_2COE)



Lithium aluminum hydride (20.5 g, 540 mmol) was placed in a flame-dried two-neck flask under nitrogen and cooled to 0 °C. Dry tetrahydrofuran (400 mL) was transferred to the flask *via* cannula and then a solution of compound **2** (27.7 g, 90 mmol) in 100 mL dry tetrahydrofuran was slowly added with an addition funnel. This reaction was stirred at 0 °C for 30 minutes and heated to gently reflux. After 12 hours, the solution was cooled back to 0 °C and diluted with 500 mL diethyl ether; 20.5 mL water was added extremely slowly to quench the reaction and then followed by 20.5 mL 15% sodium hydroxide aqueous solution and 61.5 mL water. The grey mixture was warmed up to room temperature and stirred for 15 minute forming a white slurry. Magnesium sulfate was added and the mixture was filtered through Celite and rinsed with diethyl ether to afford clear solution, which was concentrated *in vacuo* to give a slightly yellow residue. The residue was filter through silica gel plug with pentane and the final monomer Me_2COE **5** was achieved in 54% yield (6.7 g, 48.6 mmol) after the removal of solvent *in vacuo*. Alcohol **3** (3 g, 19.5 mmol) was also recovered in 22% yield after flash chromatography.

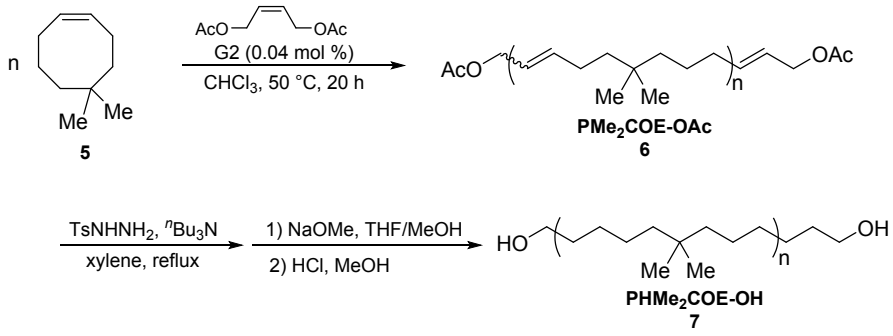
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 - 5.63 (m, 1H), 5.48 - 5.39 (m, 1H), 2.22 (q, J = 7.5 Hz, 2H), 2.18 – 2.13 (m, 2H), 1.61 – 1.49 (m, 4H), 1.40 – 1.31 (m, 2H), 0.92 (6H, s).

^{13}C NMR (125 MHz, $CDCl_3$) δ 132.43, 125.81, 39.96, 35.17, 34.10, 29.99, 26.11, 24.60, 24.49.

HRMS(EI): m/z calcd for C_8H_{10} [M^+]: 138.1409, found: 138.1400.

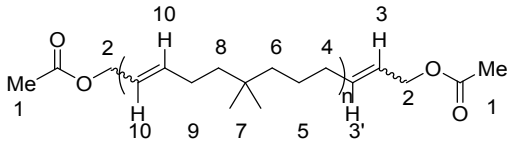
IR (neat): 3005, 2951, 2925, 2866, 1483, 1446, 1363, 736, 726, 654.

Synthesis of telechelic LLDPEs PH(Me_2COE)-OH 7 and PH(COE-*s*-Me_2COE)-OH 9

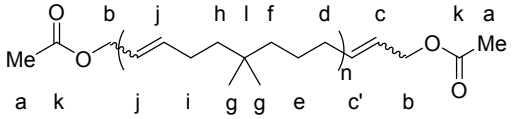


Step 1: ROMP

A 20 ml vial with a Teflon coated magnetic stir-bar was capped with a rubber septa. The vial was flame-dried under high vacuum then back-filled with argon; this evacuation fill cycle was repeated two more times. Anhydrous chloroform (3.3 mL), Me_2COE **5** (1.38 g, 10 mmol) and 1,4-diacetoxy-*cis*-2-butene (45.3 µL, 0.286 mmol) were added to the flask via syringe and the system was purged with argon for 5 minutes and then immersed in an oil bath at 50 °C. G2 catalyst (3.4 mg) was added via syringe as a solution in 0.3 mL of anhydrous-degassed chloroform. After 20 hours the reaction was cooled to room temperature, quenched with 0.1 ml of ethyl vinyl ether, stirred for an additional 15 minutes and then cooled to 0 °C. The polymer was precipitated by adding methanol to the solution and the methanol was decanted to leave viscous beige liquid polymer after stirring for 1 hour. The polymer was dissolved in 10 mL of dichloromethane and then 5 mg of butylated hydroxytoluene (BHT) was added. The solvent was removed *in vacuo* and the polymer was dried under high vacuum at 30 °C. The dried polymer PMe_2COE-OAc was obtained as a viscous clear yellowish liquid with a yield of 90% (1.24 g) and was then characterized by ^{1}H NMR, ^{13}C NMR, SEC, TGA and DSC.



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 - 5.73 ($H_{3'}$, m, 0.05H), 5.61 – 5.52 (H_3, m, 0.06H), 5.47 – 5.20 (H_{10}, m, 2H), 4.62 ($H_{2\text{-}cis}$, d, J = 6.9 Hz, 0.01H), 4.51 ($H_{2\text{-}trans}$, t, J = 6.1 Hz, 0.11H), 2.06 (H_1, s, 0.18H), 2.05 – 1.78 ($H_{4,9}$, m, 4H), 1.36 – 1.08 ($H_{5,6,8}$, m, 6H), 1.00 – 0.70 (H_7, two singles, 6H).



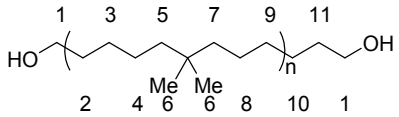
^{13}C NMR (125 MHz, $CDCl_3$) δ 170.81 (C_k), 137.39/136.67 ($C_{c'}$), 131.06 – 129.44 (C_j), 123.76/123.23 (C_c), 65.35/65.30 (C_b), 41.98 – 41.51, 33.54, 33.50, 32.74/32.62 (C_l), 28.08, 27.97, 27.35/27.23 (C_g), 24.23, 24.18, 24.14, 21.03 (C_a).

IR (neat): 2954, 2928, 1745, 1469, 1384, 1364, 1228, 965, 718.

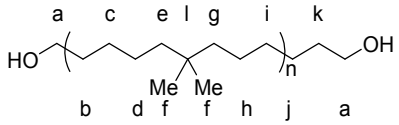
Step 2: hydrogenation and deprotection

A mixture of PMe_2COE-OAc (1.10 g, 8 mmol of olefin), *p*-toluenesulfonhydrazide (5.0 g, 25 mmol), tributylamine (5.2 g, 28 mmol), small amount of BHT (ca. 5 mg), and xylene (50 mL) was refluxed for 6 hours, and then allowed to cool to room temperature. The solvent of reaction mixture was removed *in vacuo* and cold methanol was poured into mixture to precipitate the polymer. The polymer was isolated by decantation and purified by repeating the precipitation using chloroform/methanol system. The polymer was dried under high vacuum at 30 °C overnight to afford hydrogenated poly(5Me_2COE) as a viscous liquid. 12% of the OAc end groups were converted to OH groups under the above reaction conditions. The above polymer was then dissolved in 15 mL tetrahydrofuran and cooled to 0 °C. A 500 mg sodium methoxide in methanol (25 wt.%) was added to the THF solution and this reaction was stirred for 6 hours at 0

°C. The reaction mixture was acidified by slightly acidic methanol and stirred for 1 hour at room temperature. The mixture was decanted, and the polymer was washed with methanol. After the final wash the polymer $PHMe_2COE$-OH was dried under high vacuum at 30 °C to give a viscous clear liquid with an 80% overall yield of two steps (0.88 g) and was then characterized by ^1H NMR, ^{13}C NMR, SEC, TGA and DSC. Note: Being very-low-molecular-weight telechelics, the above polymers were easy to lose during experimental operations.

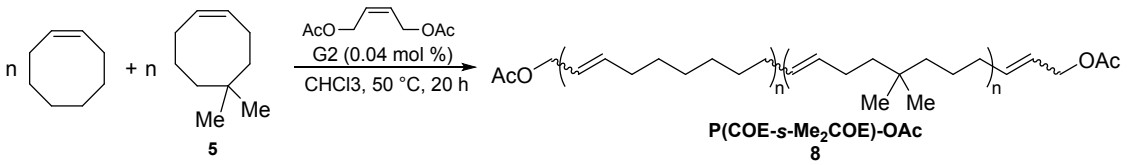


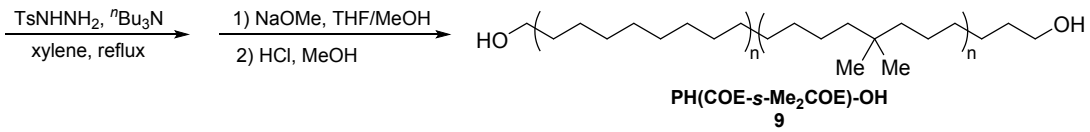
^1H NMR (500 MHz, $CDCl_3$) δ 3.65 (H_1, t, J = 6.6 Hz, 0.09H), 1.62 – 1.58 (H_{11}, m, 0.09H), 1.40 – 1.00 ($H_{2\text{-}5,\ 7\text{-}10}$, m, 14H), 0.90 – 0.70 ($H_6$, s, 6H).



^{13}C NMR (125 MHz, $CDCl_3$) δ 63.12 (C_a), 42.06, 42.02, 32.90 (C_k), 32.60 (C_l), 30.76, 30.75, 30.71, 29.83, 29.81, 27.31 (C_f), 24.06, 24.03.

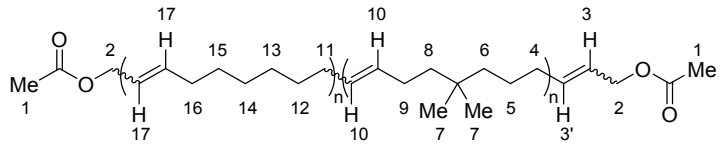
IR (neat): 2924, 2852, 1468, 1384, 1363,722.



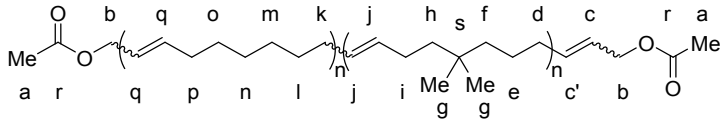


Step 1: ROMP

Following the above ROMP procedure, 1,4-diacetoxy-*cis*-2-butene (47.5 μL, 0.3 mmol), *cis*-cyclooctene (0.66 g, 6 mmol), Me_2COE **5** (0.83 g, 6 mmol), G2 (4.1 mg, 4.8 μmol) and anhydrous $CHCl_3$ (4 mL) were mixed at 50 °C. Upon isolation, the copolymers P(COE-*s*-Me_2COE)-OAc was obtained as a viscous, clear, light yellowish liquid (1.42 g, 95%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 - 5.73 ($H_{3'}$, m, 0.08H), 5.60 – 5.50 (H_3, m, 0.08H), 5.48 – 5.20 (H_{10}, H_{17}, m, 4H), 4.62 ($H_{2\text{-}cis}$, d, J = 6.9 Hz, 0.02H), 4.55 – 4.47 ($H_{2\text{-}trans}$, m, 0.14 H), 2.06 (H_1, s, 0.24H), 2.05 – 1.82 ($H_{4,9,11,16}$, m, 8H), 1.43 – 1.25 ($H_{5,6,8,12\text{-}15}$, m, 10H), 1.25 – 1.11 ($H_{5,6,8}$, m, 4H), 0.95 – 0.70 (H_7, two singles, 6H).

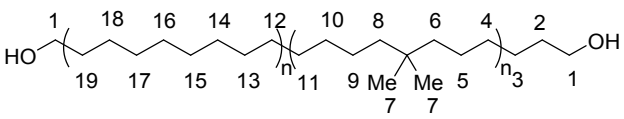


^{13}C NMR (125 MHz, $CDCl_3$) δ 170.86 (C_r), 137.44/136.72 ($C_{c'}$), 131.11 – 129.42 ($C_{j,q}$), 123.65/123.17 (C_c), 65.38/65.34 (C_b), 41.87, 41.48, 33.54, 33.50, 32.72, 32.61, 29.74, 29.63, 29.18, 29.05, 27.34./27.21 (C_g), 24.23, 24.17, 24.14, 21.05 (C_a).

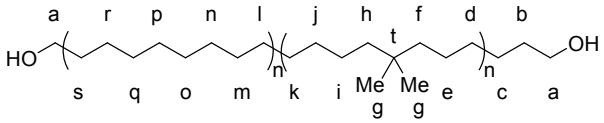
IR (neat): 2924, 2851, 1745, 1464, 1437, 1364, 1228, 964, 723.

Step 2: hydrogenation and deprotection

Following the above hydrogenation and deprotection procedure, the desired product PH(COE-*s*-Me_2COE)-OH was obtained as many small white solid particles (1.15 g, 91%) from 1.24 g precursor P(COE-*s*-Me_2COE)-OAc.



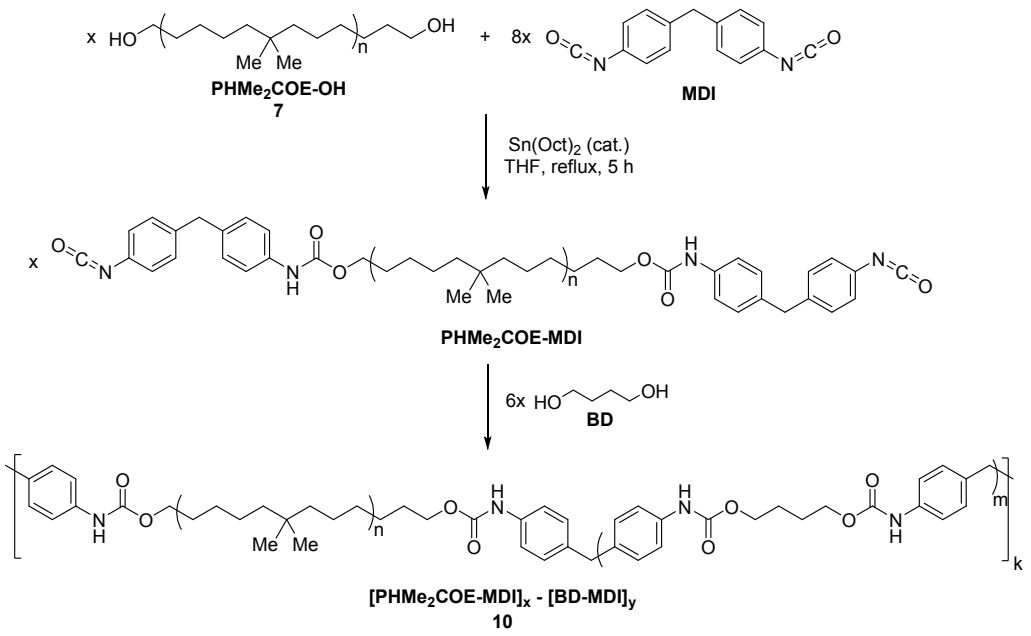
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.64 (H_1, t, J = 6.6 Hz, 0.16H), 1.61 - 1.53 (H_2, m, 0.16H), 1.40 – 1.05 (H_3 – H_6, H_8 – H_{19}, m, 30H), 0.81 (H_7, s, 6H).



^{13}C NMR (125 MHz, $CDCl_3$) δ 63.12 (C_a), 42.01, 32.83 (C_b), 32.58 (C_t), 30.75, 30.71, 29.83, 29.77, 29.73, 27.32 (C_g), 24.04.

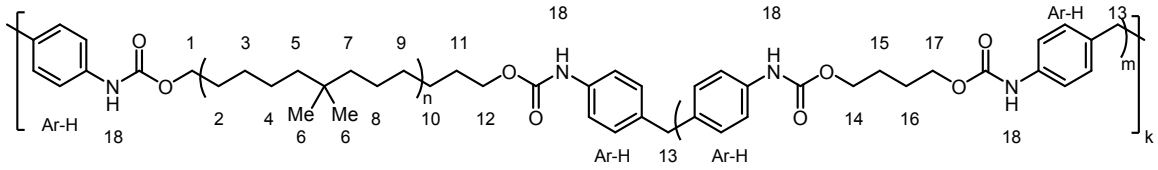
IR (neat): 2919, 2849, 1467, 1364, 720.

Synthesis of the polyurethane 10 based on hydroxytelechelic PHMe$_2$COE-OH 7

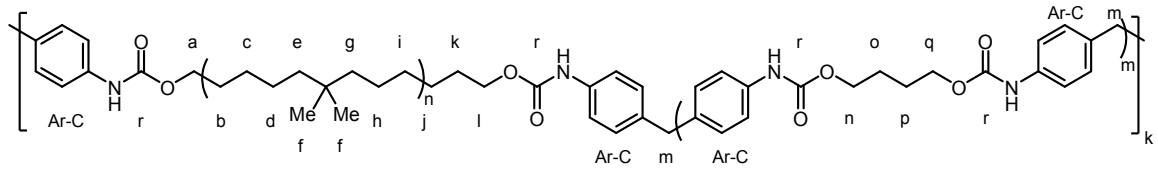


A 20 mL vial with a Teflon coated magnetic stir-bar was capped with a rubber septa. The vial was flame-dried under high vacuum then back-filled with argon; this evacuation fill cycle was repeated two more times. Methylene diphenyl diisocyanate (MDI, 200 mg, 0.8 mmol) was added to the vial and heated at 72°C to melt. PHMe$_2$COE-OH ($M_{n,NMR}$ = 5.8 k) was dissolved in anhydrous THF (116 mg/mL), a solution of which (5 mL, 0.1 mmol) was added to the reaction

vial and followed by the THF solution of $Sn(Oct)_2$ (0.1 mL, 0.002 mmol, 8.1 mg/mL).The reaction mixture was stirred at 72 °C for 4 h and then 0.5 mL solution of butandiol (BD, 54 mg, 0.6 mmol) in THF (108 mg/mL) was added to the vial. The reaction continued for 12 h at 72 °C and then terminated by adding methanol, which precipitated the desired product as off-white solids. The solids were collected by filtration and dried in vacuum oven at 45 °C for 24 h.



^{1}H NMR (500 MHz, $CDCl_3$/TFA-d_1 = 4:1) δ 7.25 - 7.00 (Ar-H, m, 1.62H), 4.26 ($H_{1,12,14,17}$, bs, 0.64H), 1.90 – 1.65 ($H_{15,16}$, two broad singles, 0.64H), 1.45 – 1.00 ($H_{2\text{-}5,7\text{-}11}$, m, 14H), 0.83 ($H_6$, s, 6H).



^{13}C NMR (125 MHz, $CDCl_3$/TFA-d_1) δ 156.3 – 155.8(C_r), 138.2 – 120.5 (Ar-C), 67.4 - 65.5 ($C_{a,l,n,q}$), 42.09, 40.7 – 40.4 (C_m), 32.63, 30.82, 30.77, 29.90, 27.33, 25.22 ($C_{o,p}$), 24.12, 24.09.

IR (neat): 3325, 2925, 2852, 1702, 1529, 1468, 1310, 1228, 1078.

Preparation of PU 10 film

A 20 ml vial with a Teflon coated magnetic stir-bar was charged with 378 mg PU **10** and 1 mL mixing solvent of $CHCl_3$ and TFA (90:10 in volume) and the mixture was stirred until all the solid was dissolved (around 30 min) and a very viscous solution was formed. The stir-bar was then removed and the solvent evaporated overnight at room temperature to form a film with

a loose cap on the vial. The film was further dried under high vacuum at 30 °C for 2 day to give a tough, free-standing, elastic PU film.

References

[1] Lehman, S. E.; Wagener, K. B.; Baugh, L. S.; Rucker, S. P.; Schulz, D. N.; Varma-Nair, M.; Berluche, E. *Macromolecules* **2007**, *40*, 2643.

[2] Robertson, N. J.; Kostalik, H. A.; Clark, T. J.; Mutolo, P. F.; Abruña, H. D.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132*, 3400.

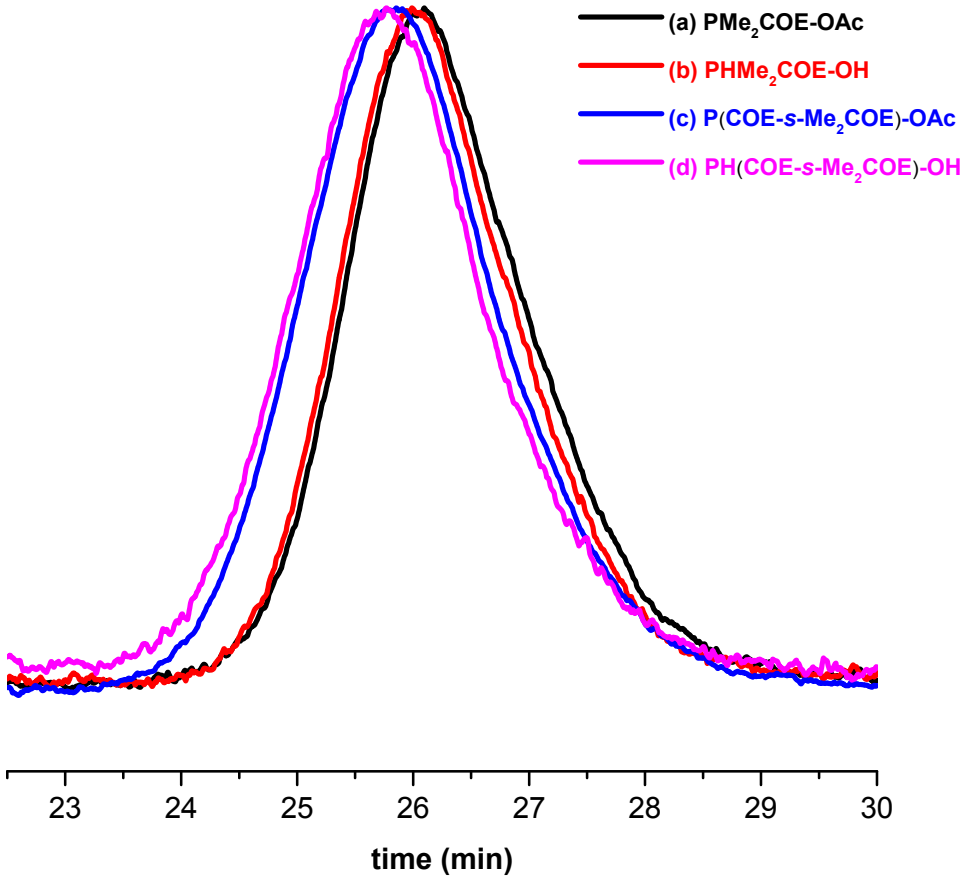


Figure S1 RI-SEC curves of polymers **6** – **9** in THF

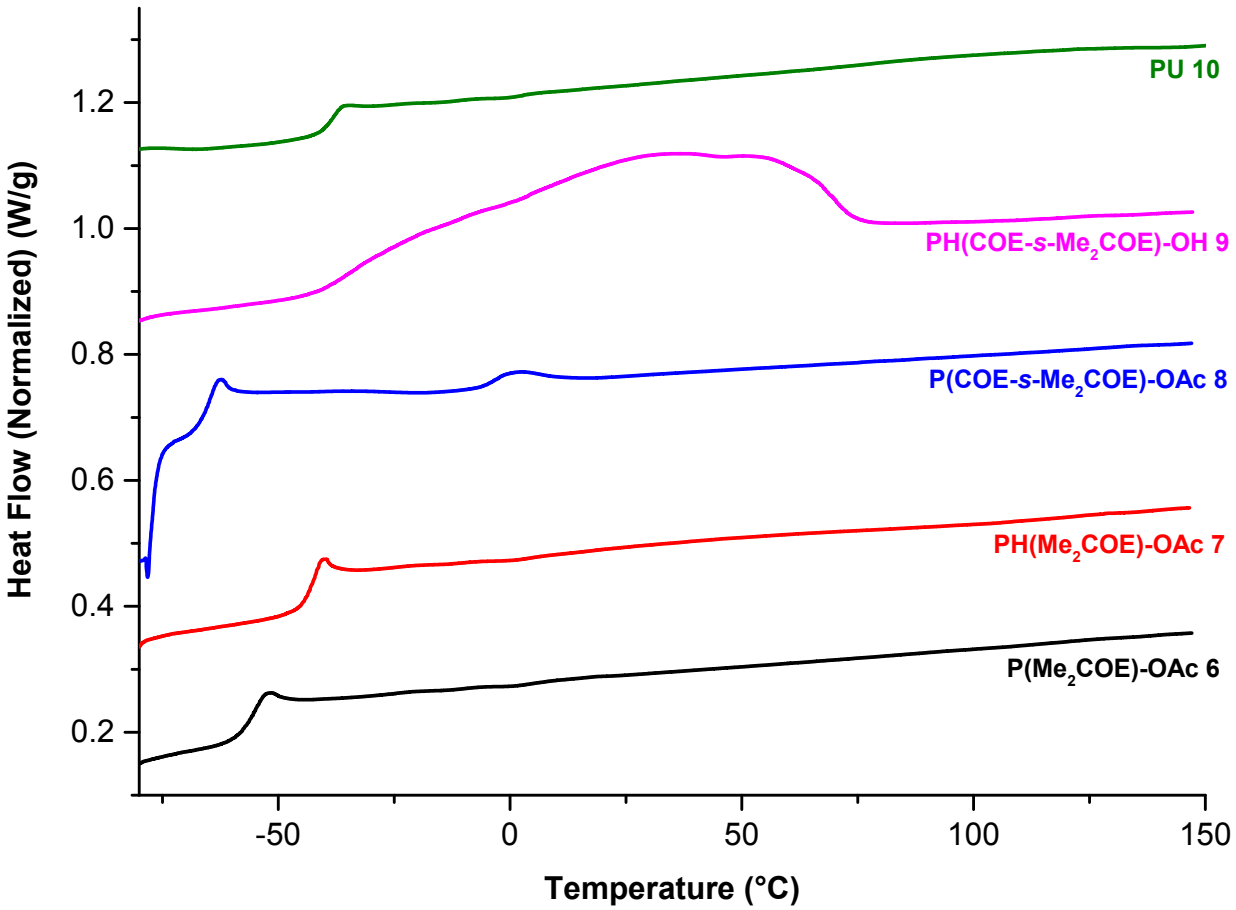


Figure S2 DSC thermograms of polymers **6** -**10** at the heating rate of 10 °C/min.

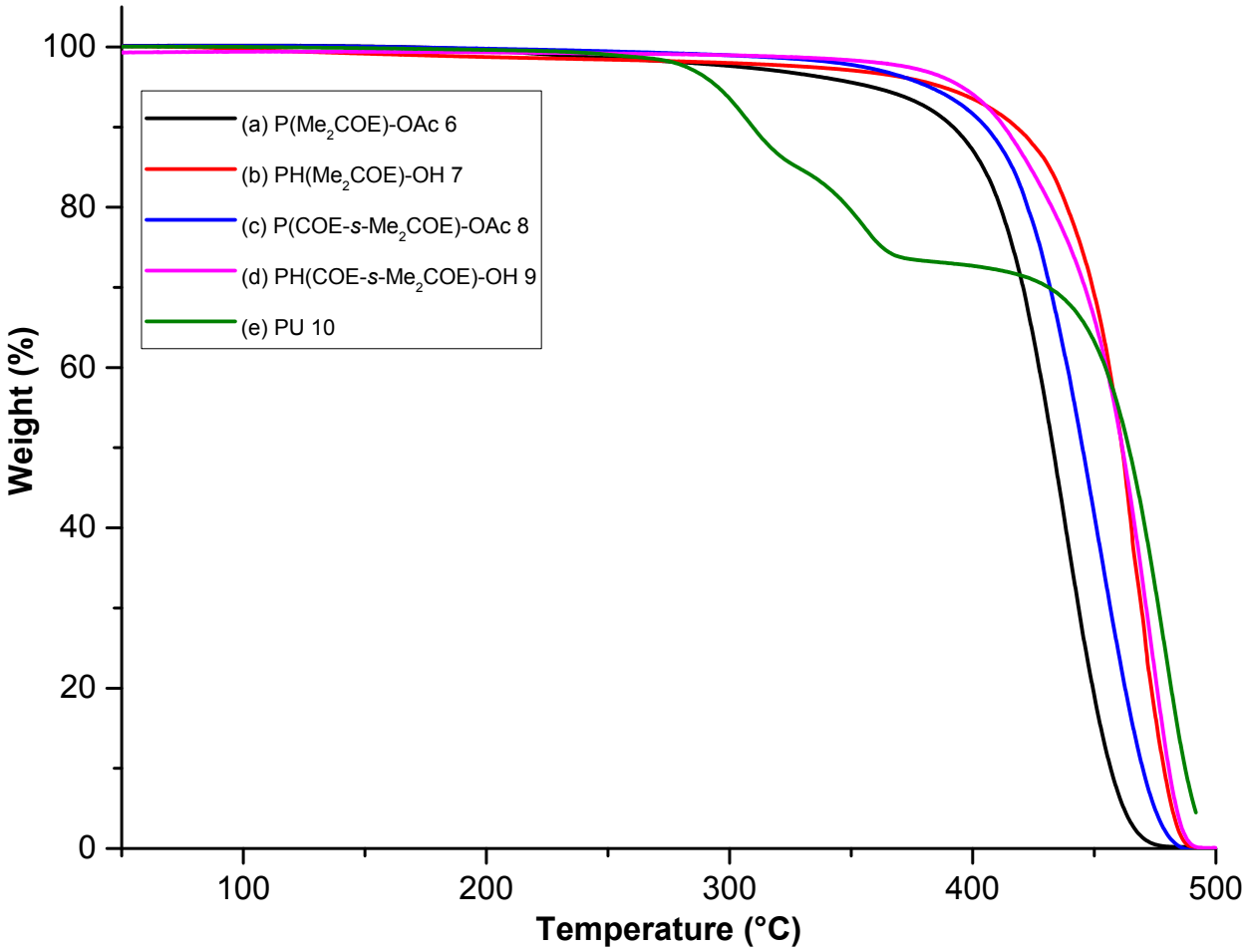


Figure S3 TGA thermograms of polymers (a) P(Me_2COE)-OAc **6**, (b) PH(Me_2COE)-OH **7**, (c) P(COE-*s*-Me_2COE)-OAc **8**, (d) PH(COE-*s*-Me_2COE)-OH **9** and (e) PU **10** at the heating rate of 20 °C/min.

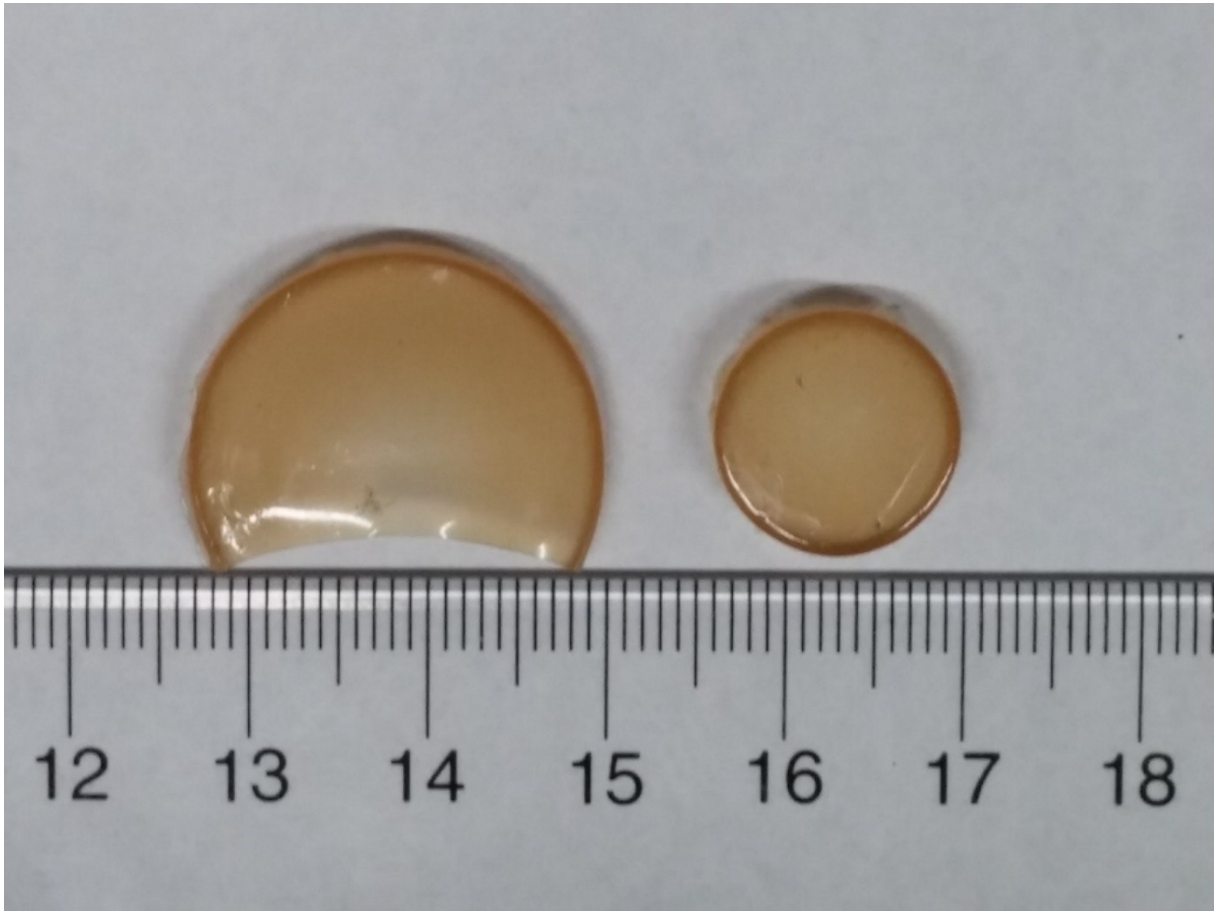
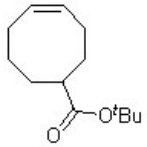
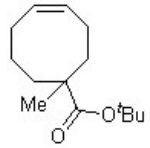


Figure S4 Film of PU **10** from solvent casting

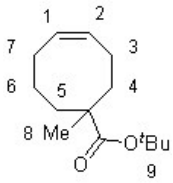
Parameter	Value
1 Title	wyz1-99-pro3.1.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	5.0000
5 Spectrometer Frequency	500.33
6 Nucleus	1H

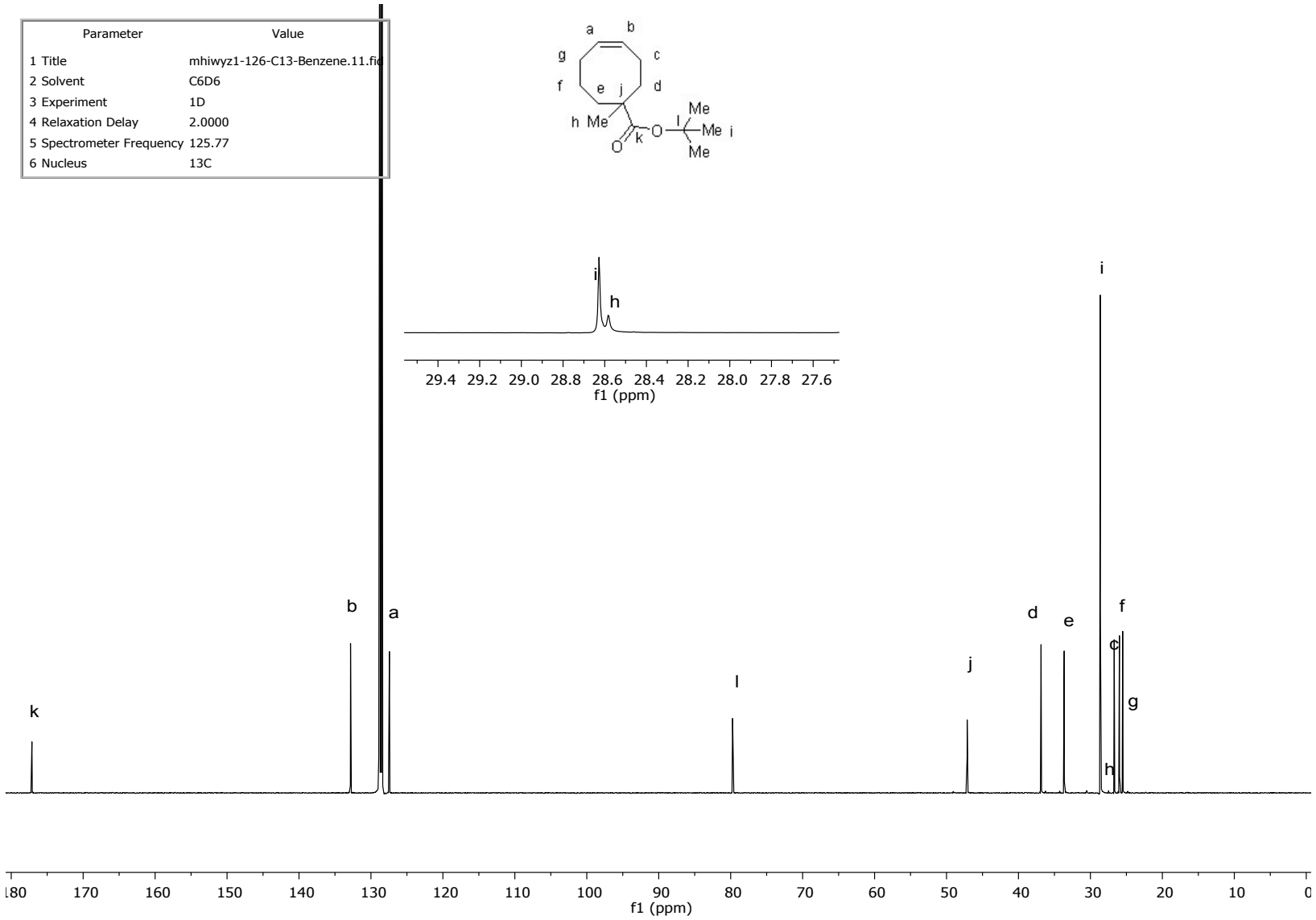


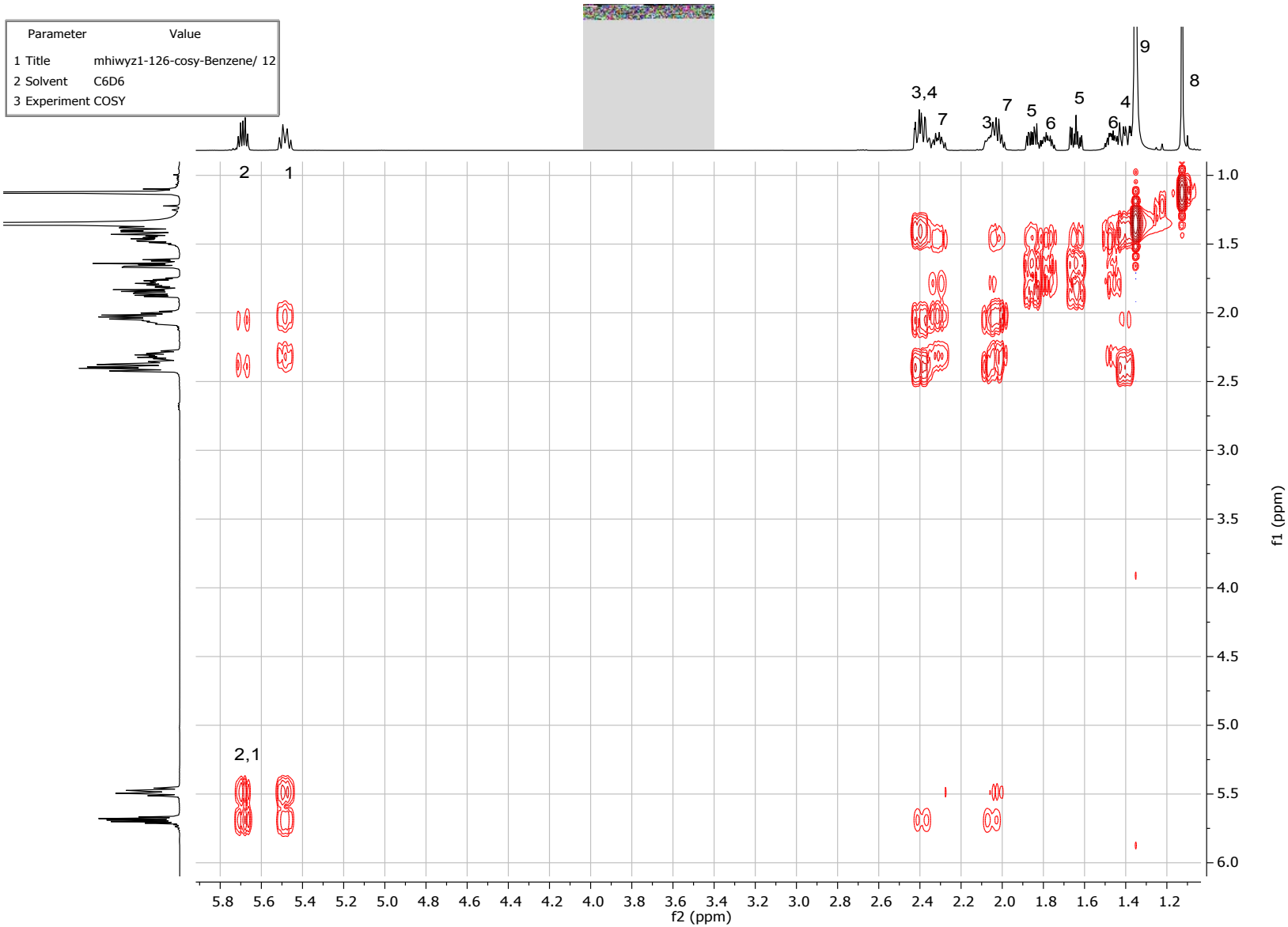
Parameter	Value
1 Title	wyz1-104-pro2
2 Solvent	CDCl3
3 Temperature	29.0
4 Experiment	1D
5 Relaxation Delay	5.0000
6 Nucleus	1H

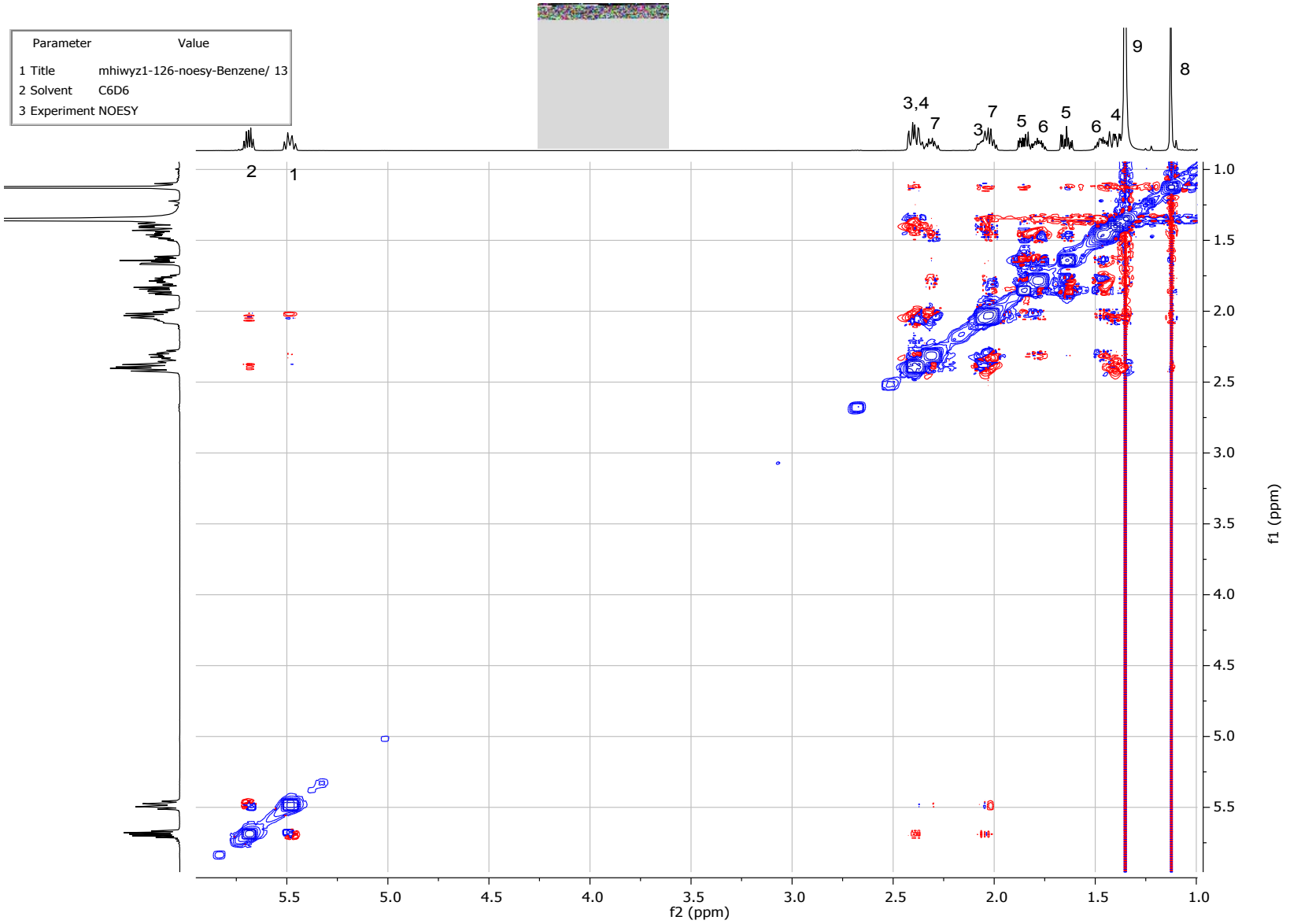


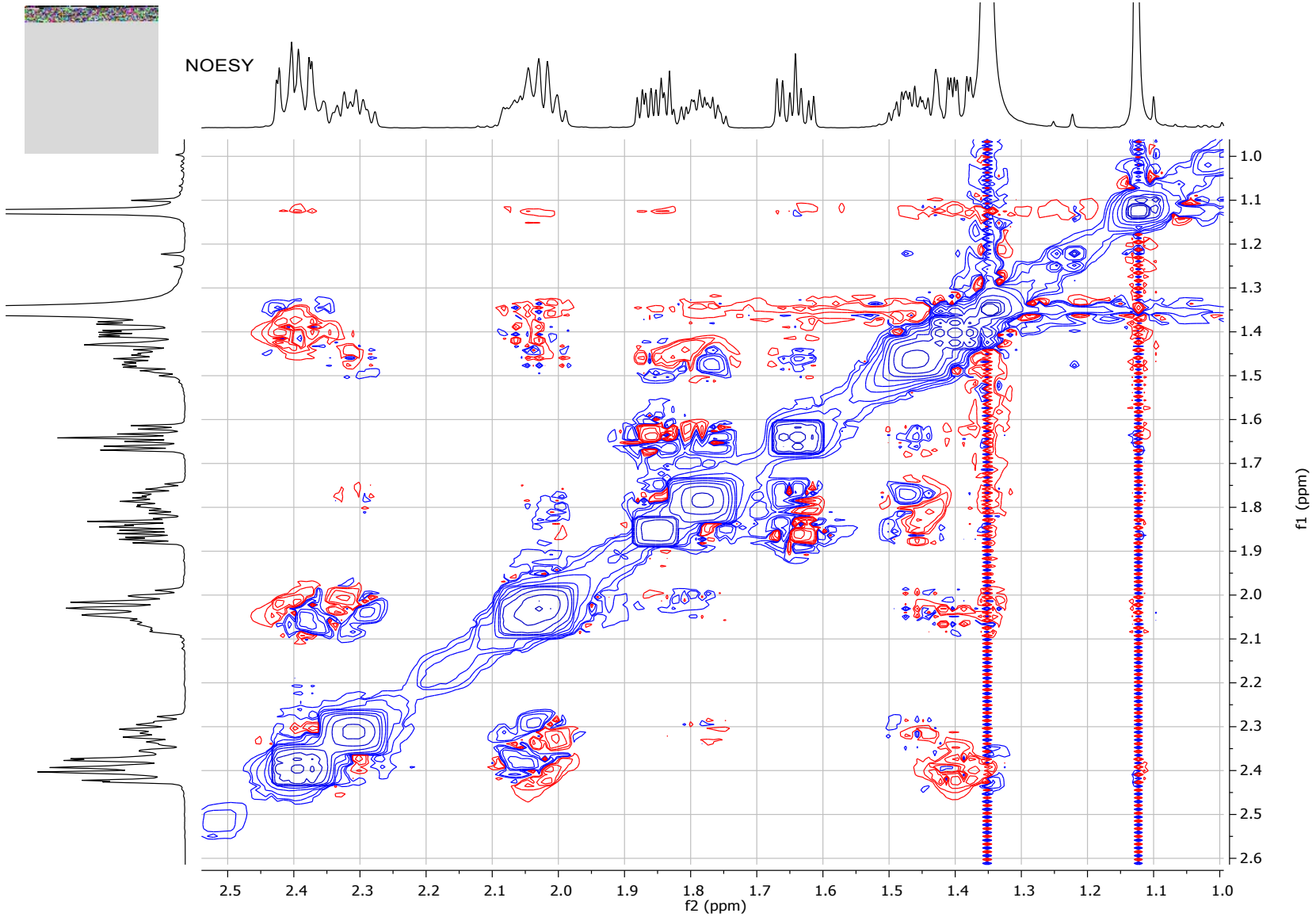
Parameter	Value
1 Title	mhiwyz1-126-H1-Benzene.10.fid
2 Solvent	C6D6
3 Experiment	1D
4 Relaxation Delay	10.0000
5 Spectrometer Frequency	500.13
6 Nucleus	1H

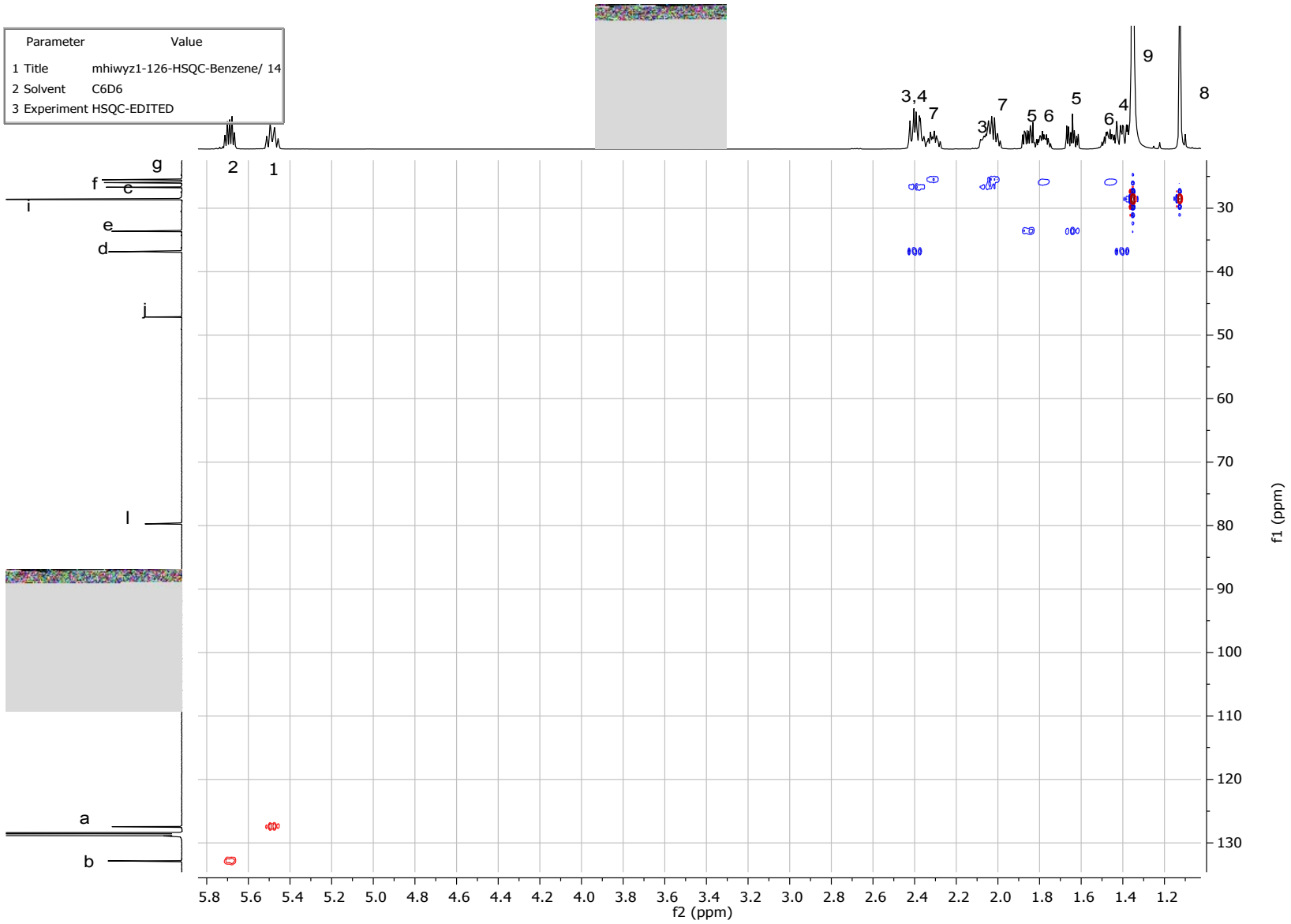



Parameter Value
1 Title mhiwyz1-126-C13-Benzene.11.fi
2 Solvent C6D6
3 Experiment 1D
4 Relaxation Delay 2.0000
5 Spectrometer Frequency 125.77
6 Nucleus 13C
a b c d e f g h i j k l Me
i h
29.4 29.2 29.0 28.8 28.6 28.4 28.2 28.0 27.8 27.6
f1 (ppm)
k b a l j d e i c f g h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

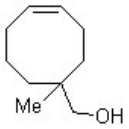

Parameter Value
1 Title mhiwyz1-126-cosy-Benzene/ 12
2 Solvent C6D6
3 Experiment COSY
3,4
7
3
7
5
6
5
6
4
9
8
2
1
2,1
f2 (ppm)
f1 (ppm)

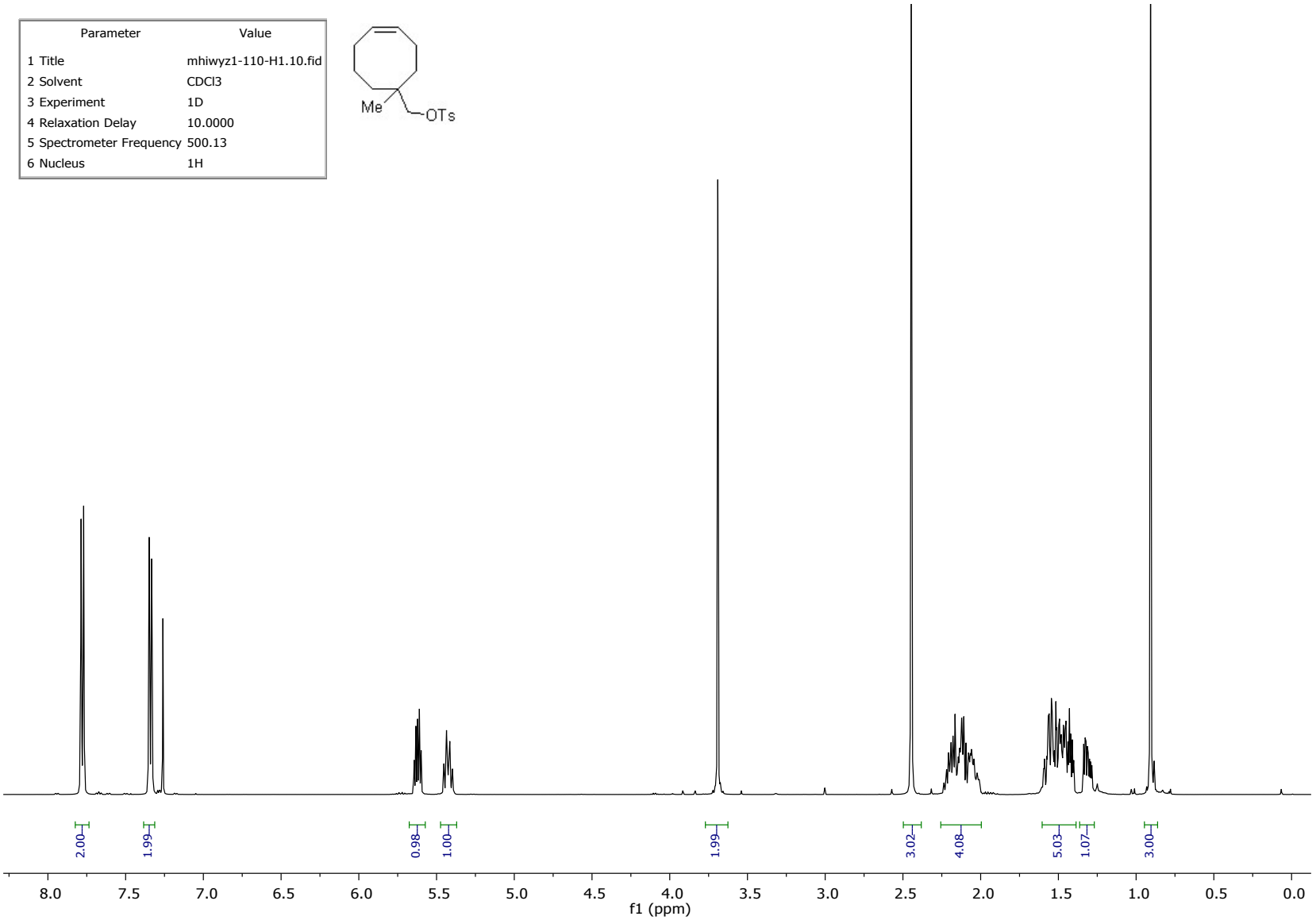

Parameter Value
1 Title mhiwyz1-126-noesy-Benzene/ 13
2 Solvent C6D6
3 Experiment NOESY
2
1
3,4
7
3
7
5
6
5
6
4
9
8
f2 (ppm)
f1 (ppm)


NOESY
f2 (ppm)
f1 (ppm)

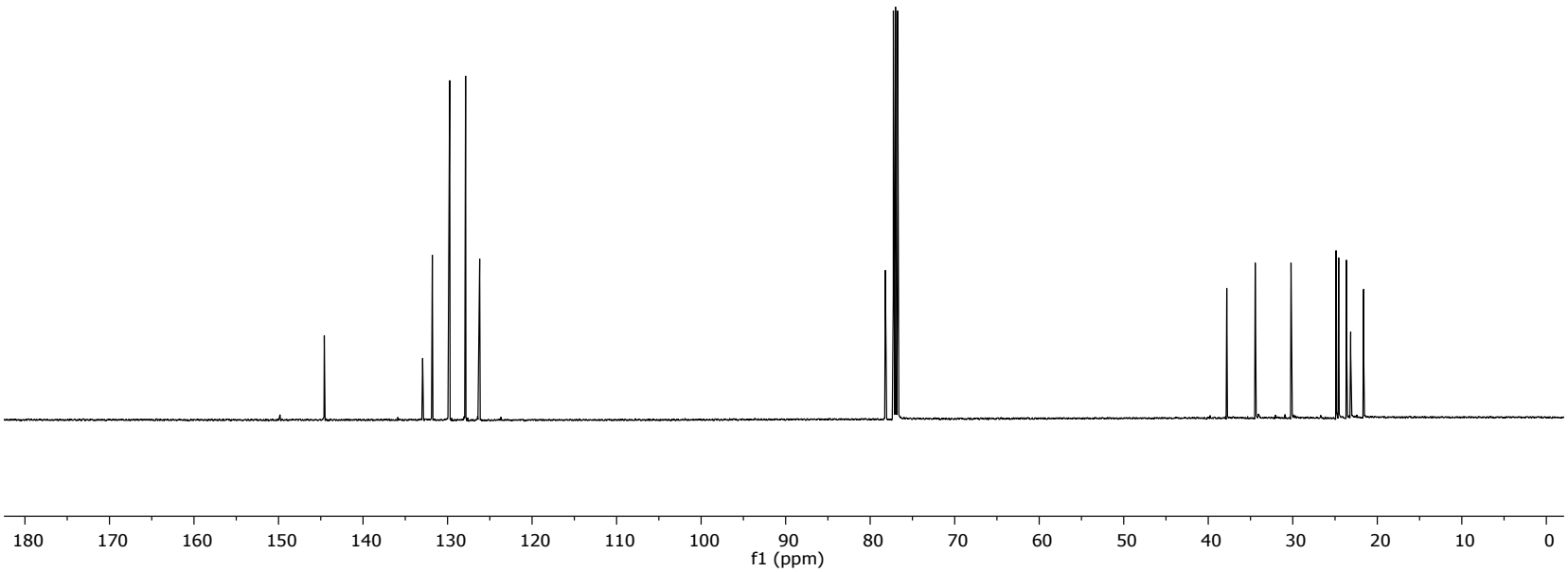

Parameter Value
1 Title mhiwyz1-126-HSQC-Benzene/ 14
2 Solvent C6D6
3 Experiment HSQC-EDITED
3,4
7
3
7
5
6
5
6
4
9
8
2
1
g
f
c
i
e
d
j
l
a
b
f2 (ppm)
f1 (ppm)

Parameter	Value
1 Title	wyz1-116-pro3
2 Solvent	CDCl3
3 Temperature	29.0
4 Experiment	1D
5 Relaxation Delay	5.0000
6 Nucleus	1H

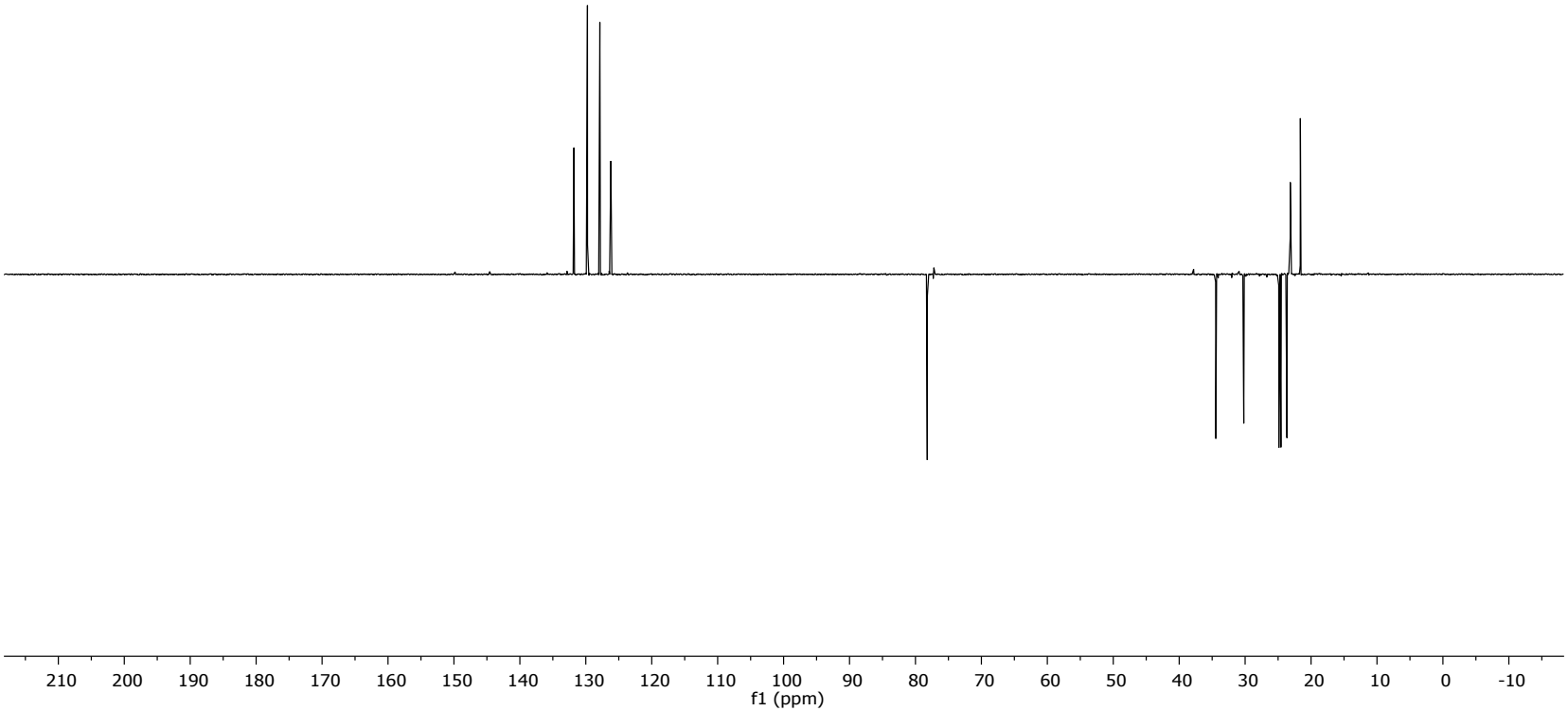


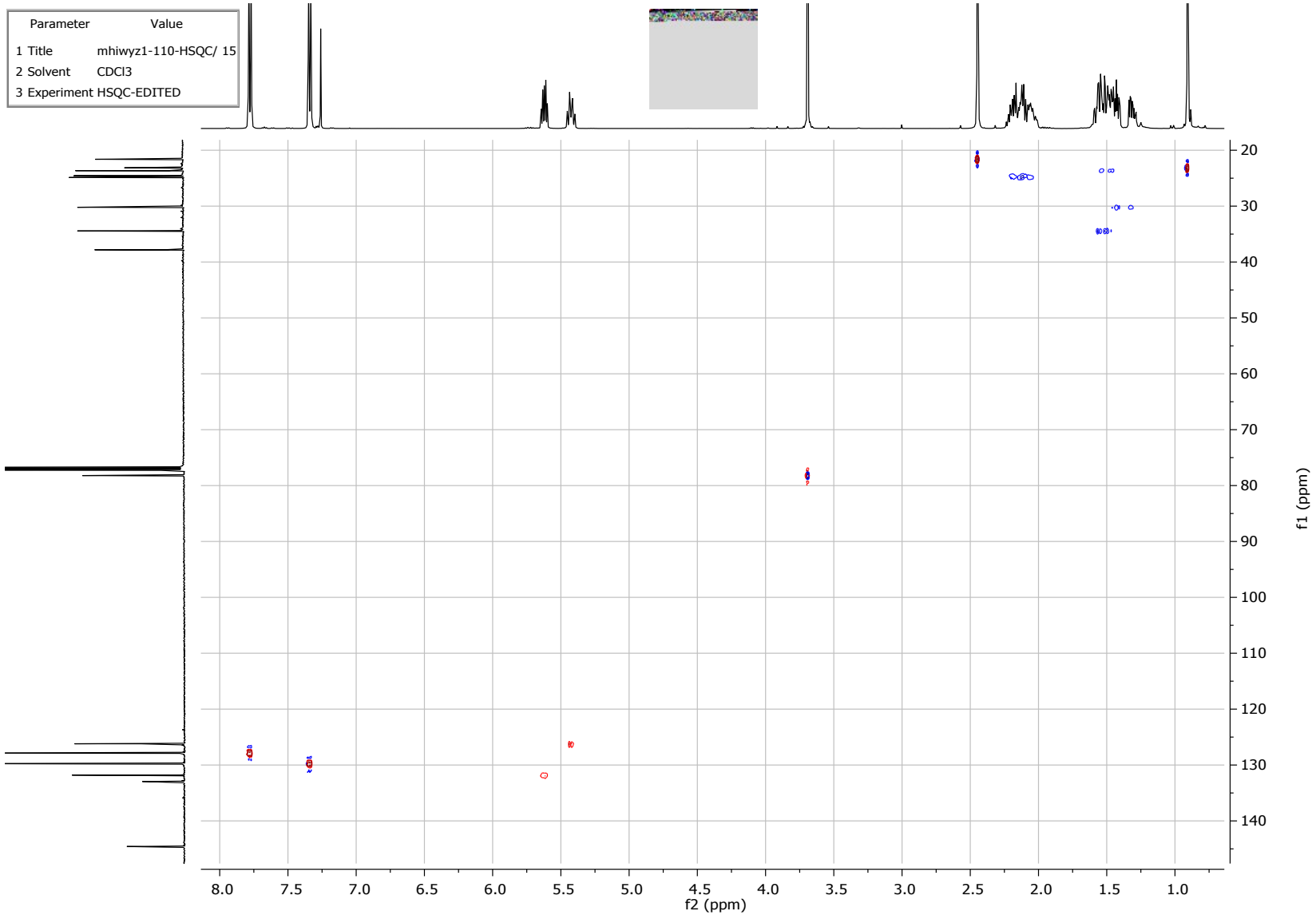

Parameter Value
1 Title mhiwyz1-110-H1.10.fid
2 Solvent CDCl3
3 Experiment 1D
4 Relaxation Delay 10.0000
5 Spectrometer Frequency 500.13
6 Nucleus 1H
Me
OTs
2.00
1.99
0.98
1.00
1.99
3.02
4.08
5.03
1.07
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Parameter	Value
1 Title	mhiwyz1-110-C13.11.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

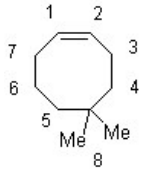


Parameter	Value
1 Title	mhiwyz1-110-DEPT135.12.fid
2 Solvent	CDCl3
3 Experiment	DEPT-135
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

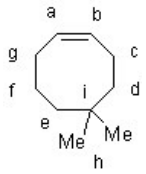


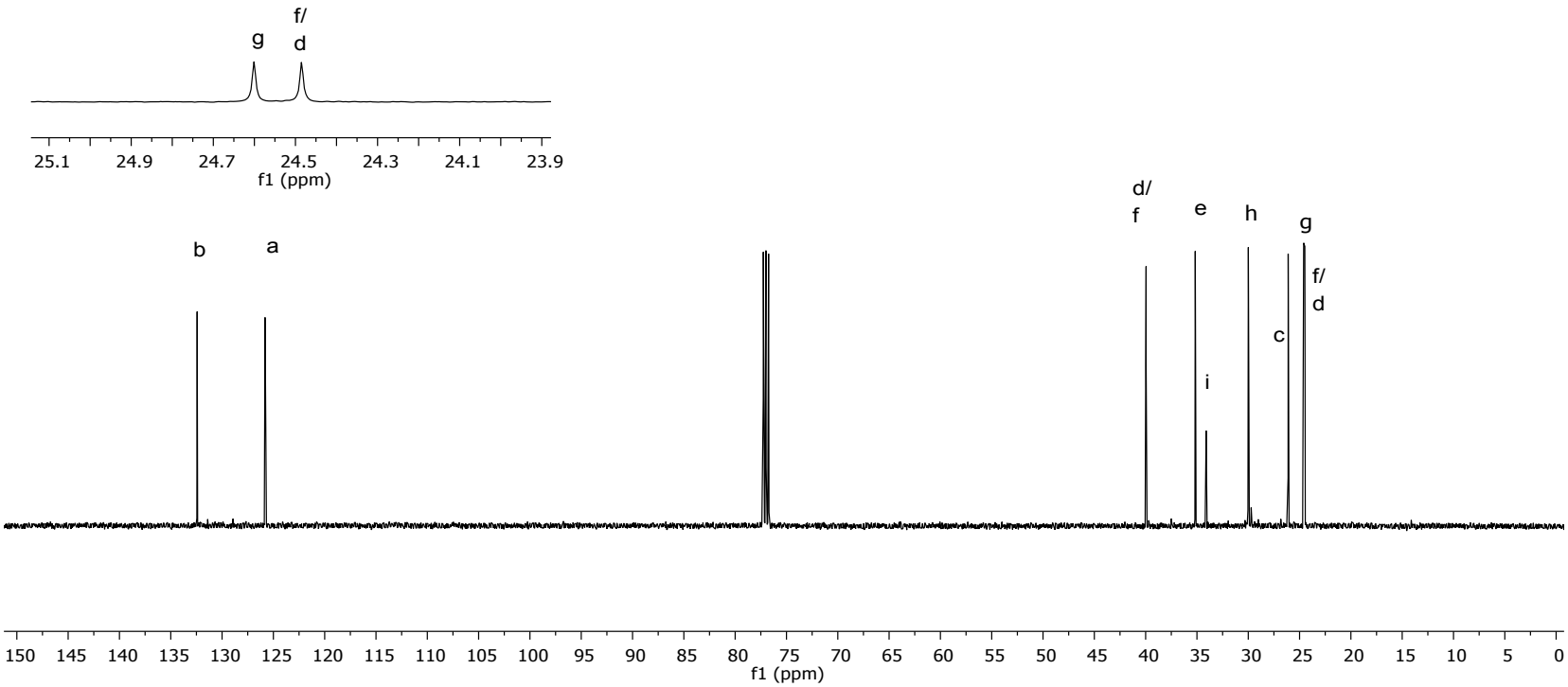

Parameter Value
1 Title mhiwyz1-110-HSQC/ 15
2 Solvent CDCl3
3 Experiment HSQC-EDITED
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

Parameter	Value
1 Title	wyz1-118-pro-H1.1.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	5.0000
5 Spectrometer Frequency	500.33
6 Nucleus	1H

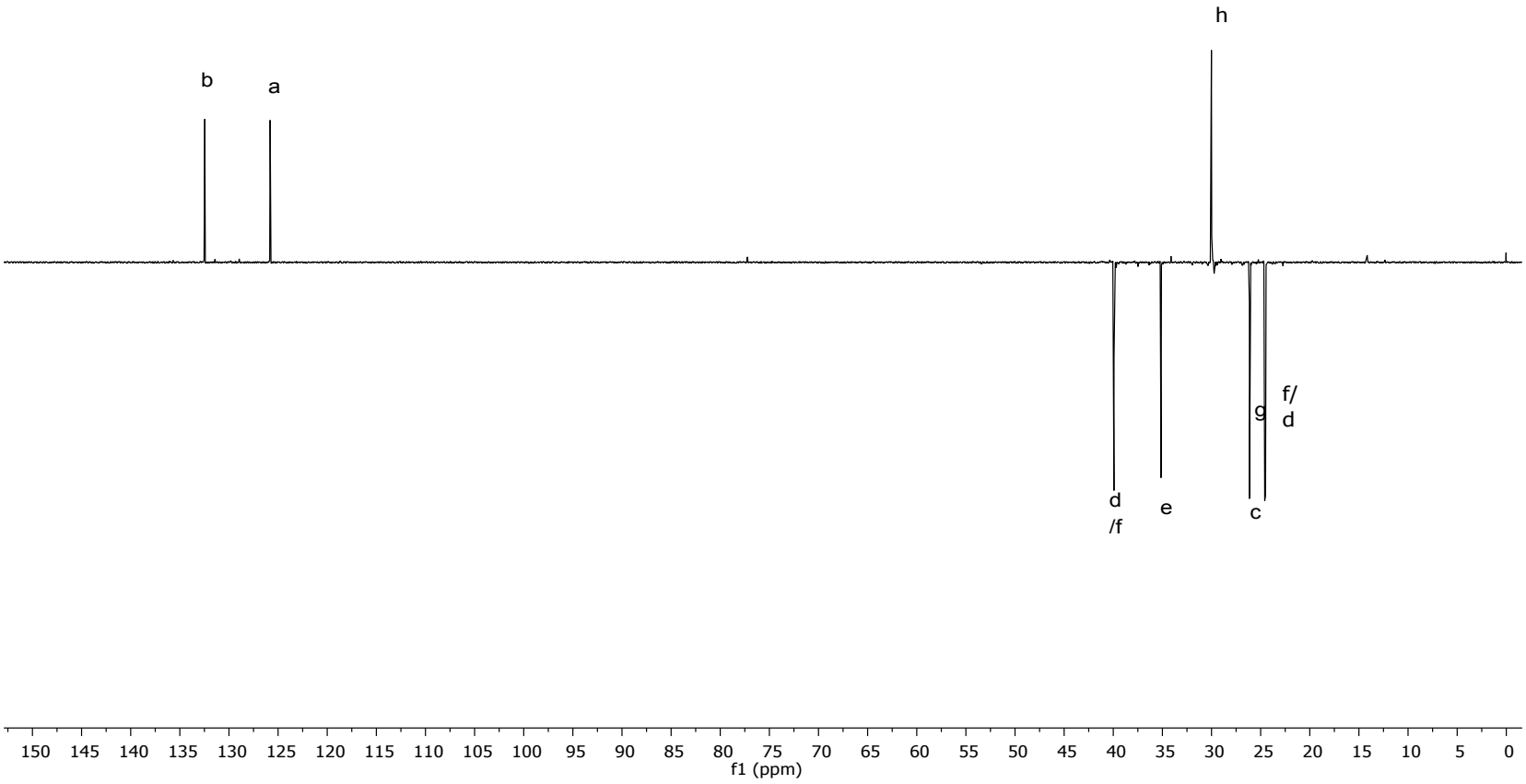


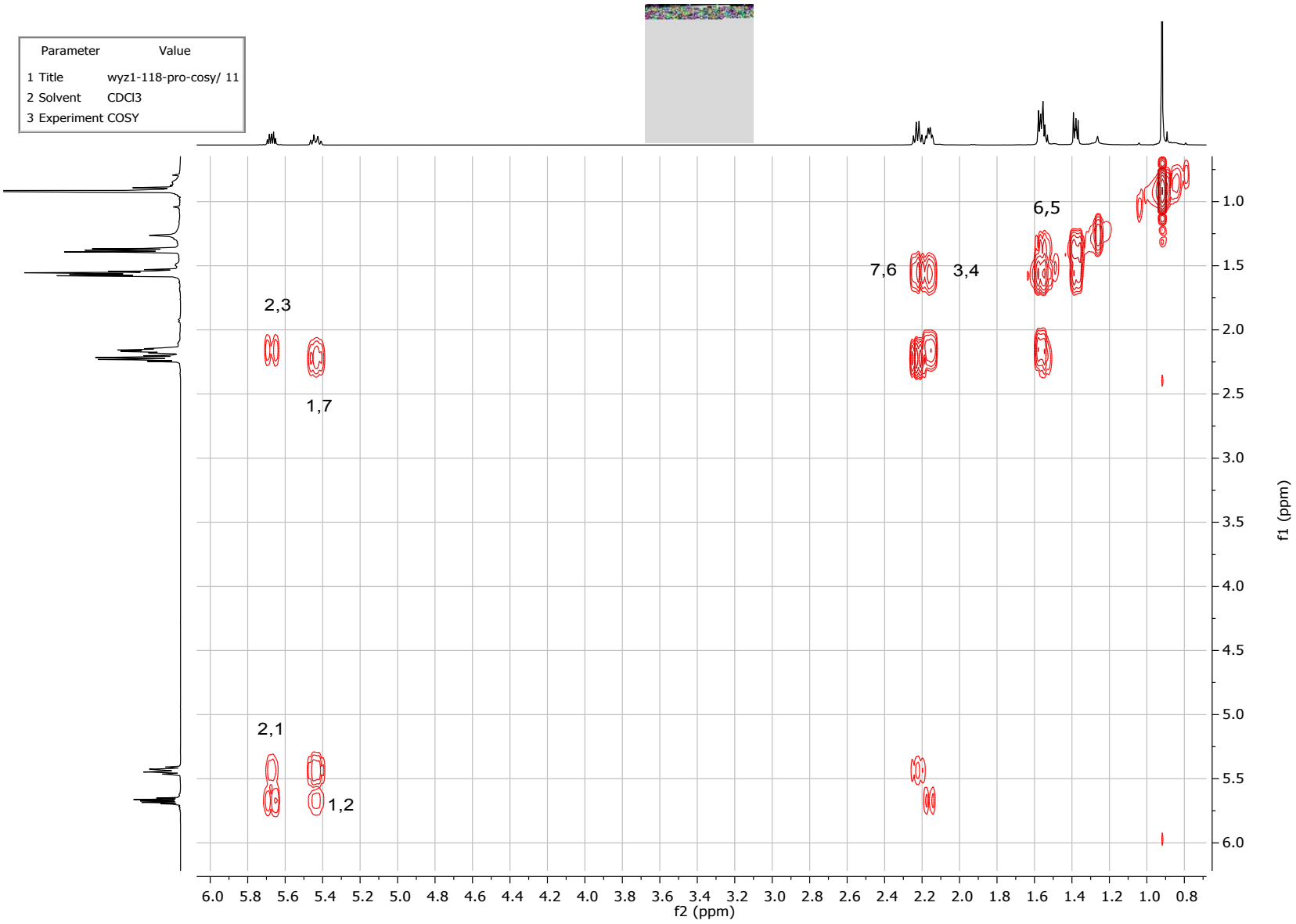
Parameter	Value
1 Title	wyz1-118-pro-C13.1.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.82
6 Nucleus	13C

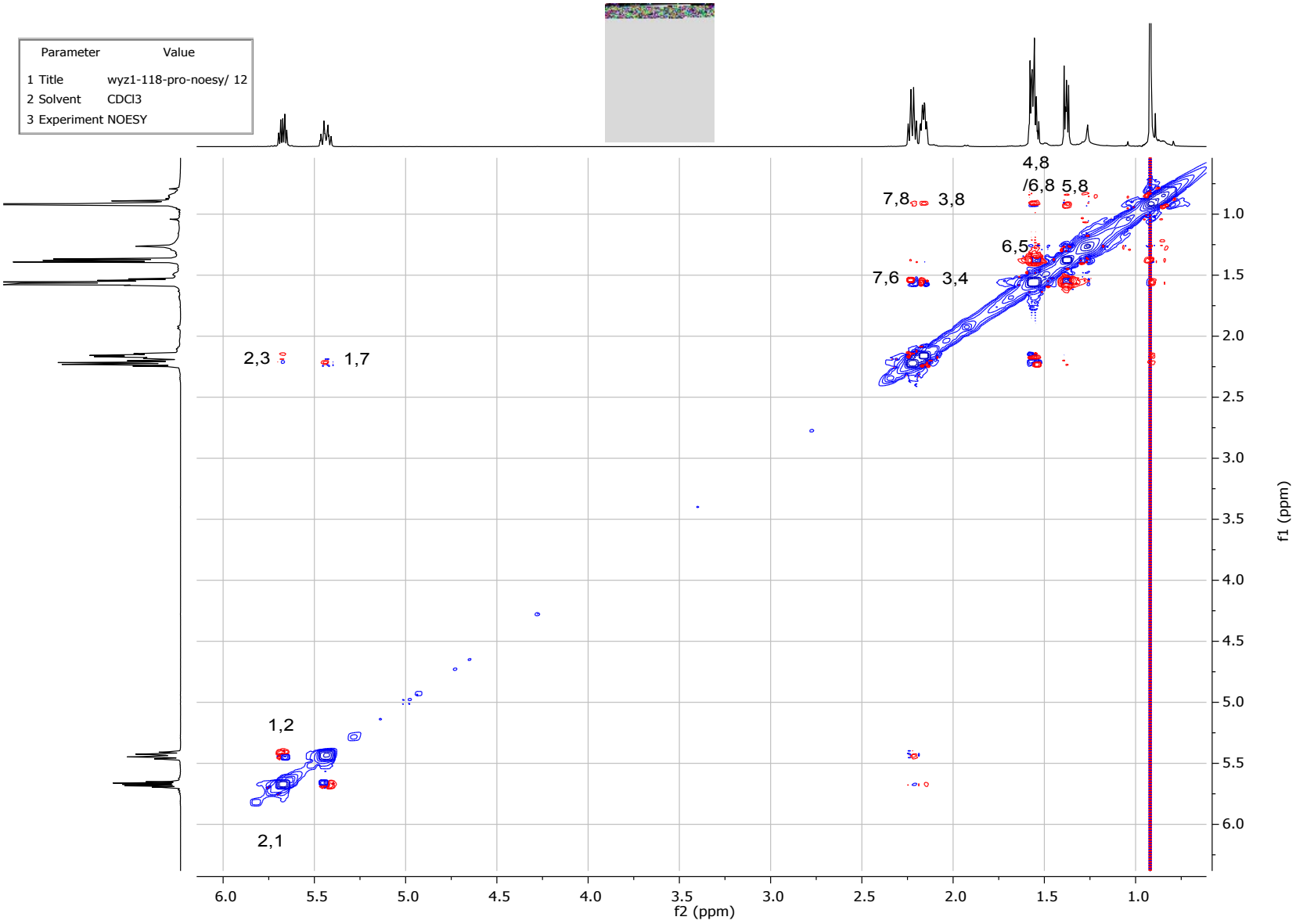


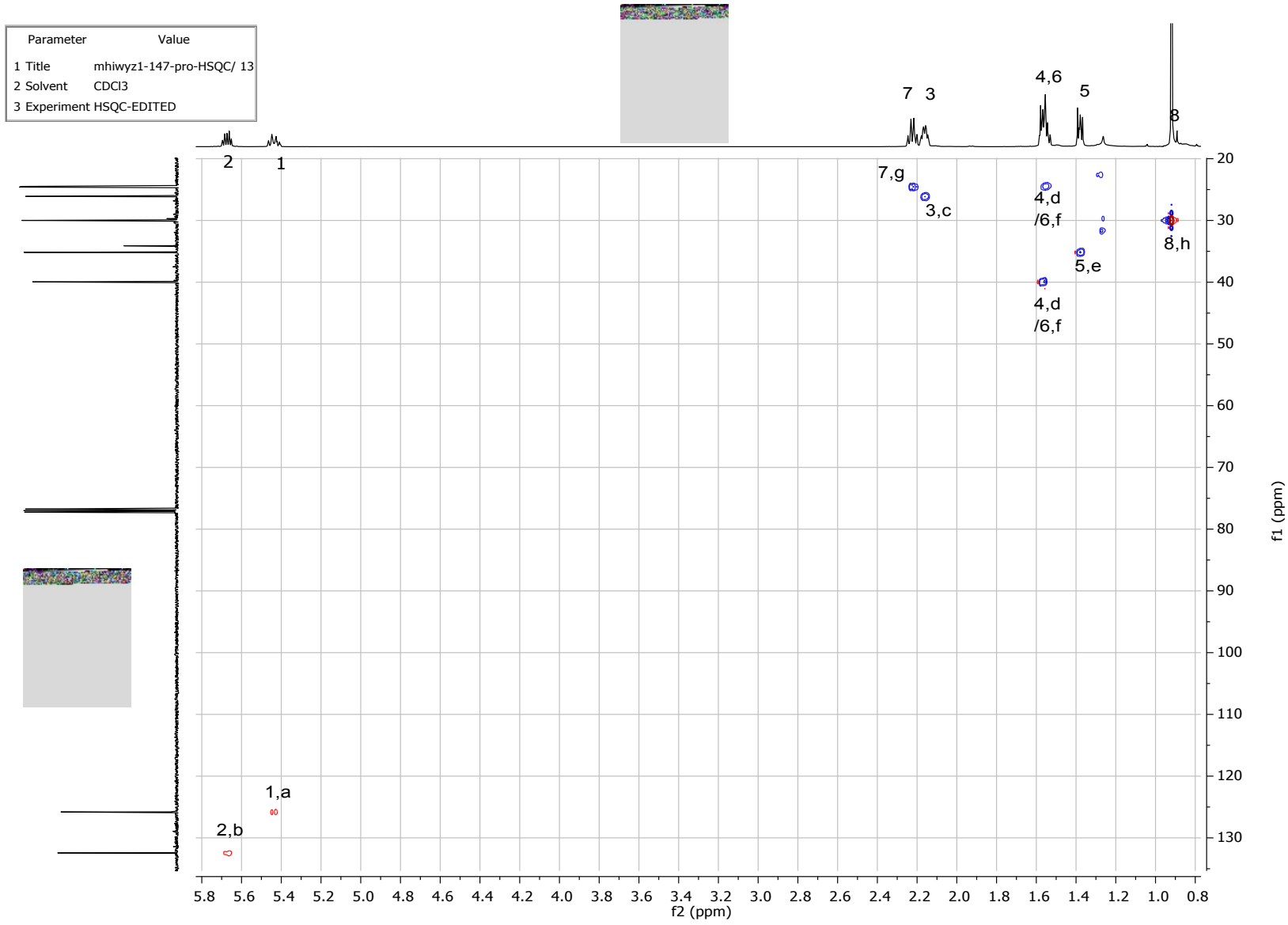


Parameter	Value
1 Title	mhiwyz-147-dept135.12.fid
2 Solvent	CDCl3
3 Experiment	DEPT-135
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

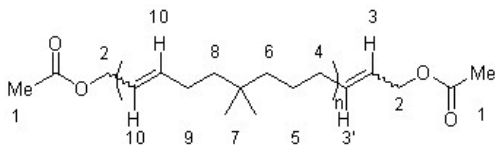


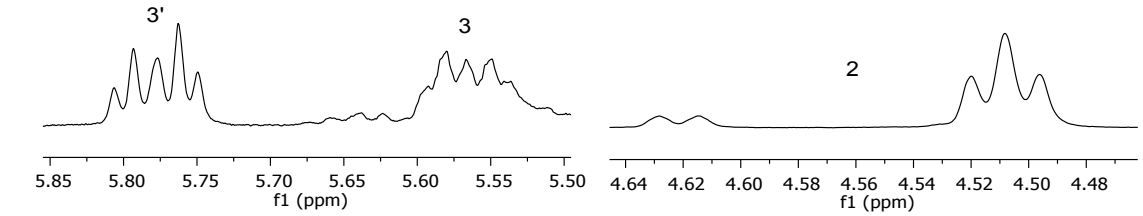

Parameter Value
1 Title wyz1-118-pro-cosy/ 11
2 Solvent CDCl3
3 Experiment COSY
2,3
1,7
7,6
3,4
6,5
2,1
1,2
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wyz1-118-pro-noesy/ 12
2 Solvent CDCl3
3 Experiment NOESY
4,8
/6,8 5,8
7,8 3,8
6,5
7,6 3,4
2,3
1,7
1,2
2,1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)

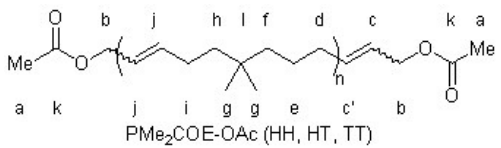

Parameter Value
1 Title mhiwyz1-147-pro-HSQC/ 13
2 Solvent CDCl3
3 Experiment HSQC-EDITED
2
1
7 3
4,6
5
8
7,g
3,c
4,d
/6,f
5,e
8,h
1,a
2,b
f2 (ppm)
f1 (ppm)

Parameter	Value
1 Title	wyz1-134-pro-H1/ 1
2 Solvent	CDCl3
3 Experiment	1D
4 Spectrometer Frequency	500.33
5 Nucleus	1H

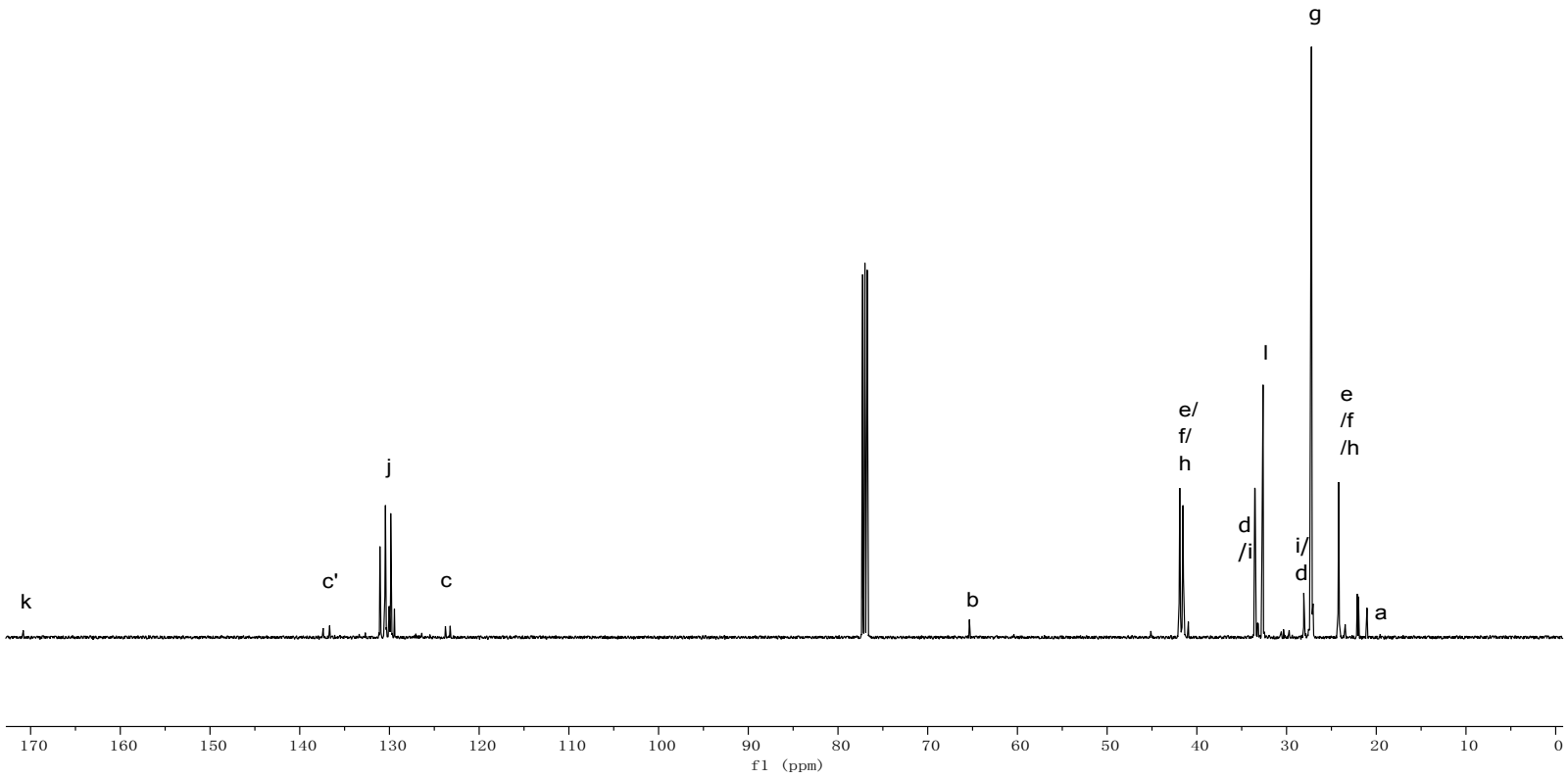




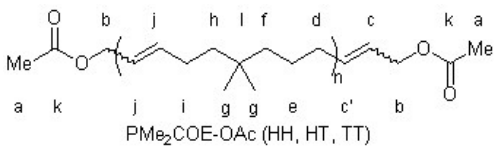
Parameter	Value
1 Title	wyz1-134-pro-C13.1.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.82
6 Nucleus	13C



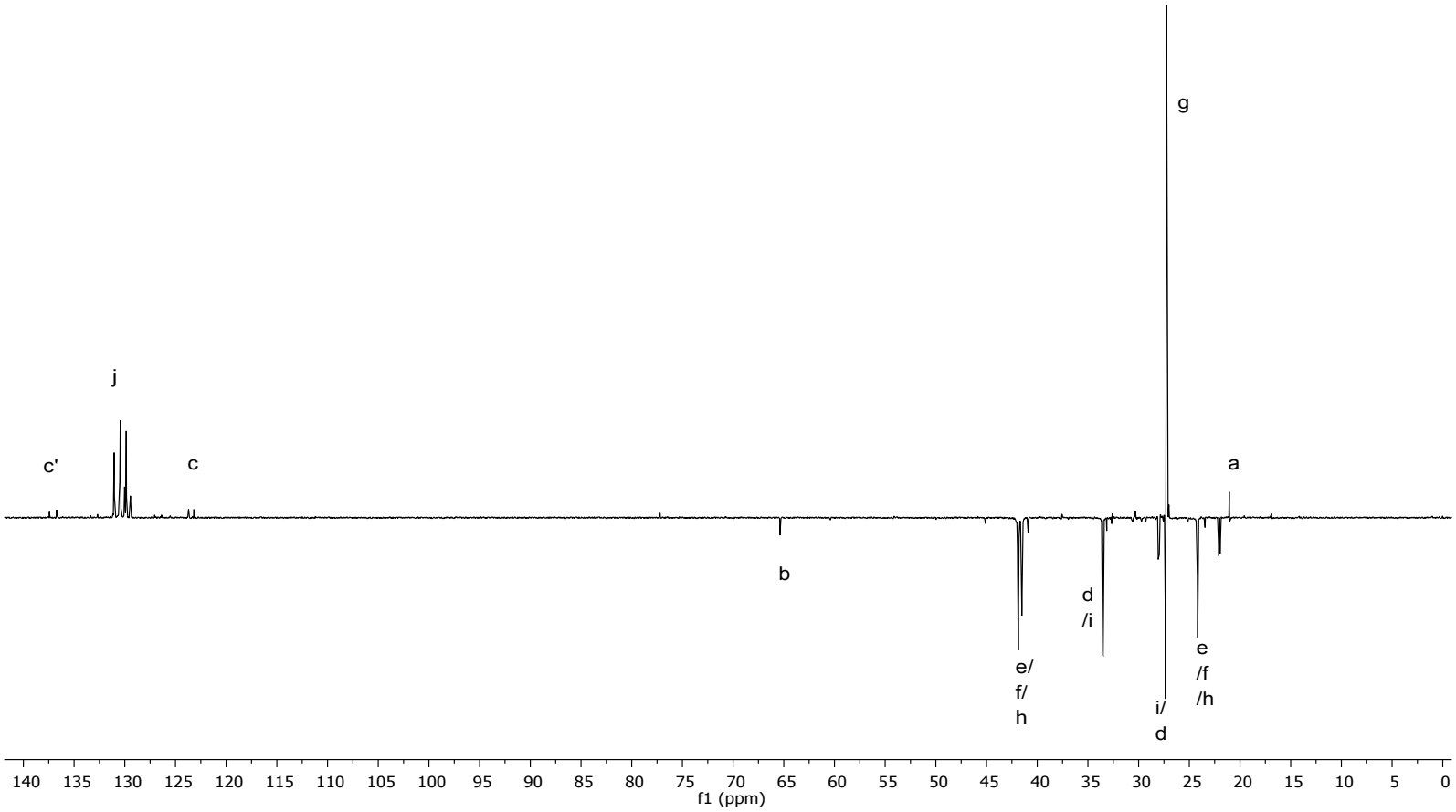
PMe_2COE-OAc (HH, HT, TT)

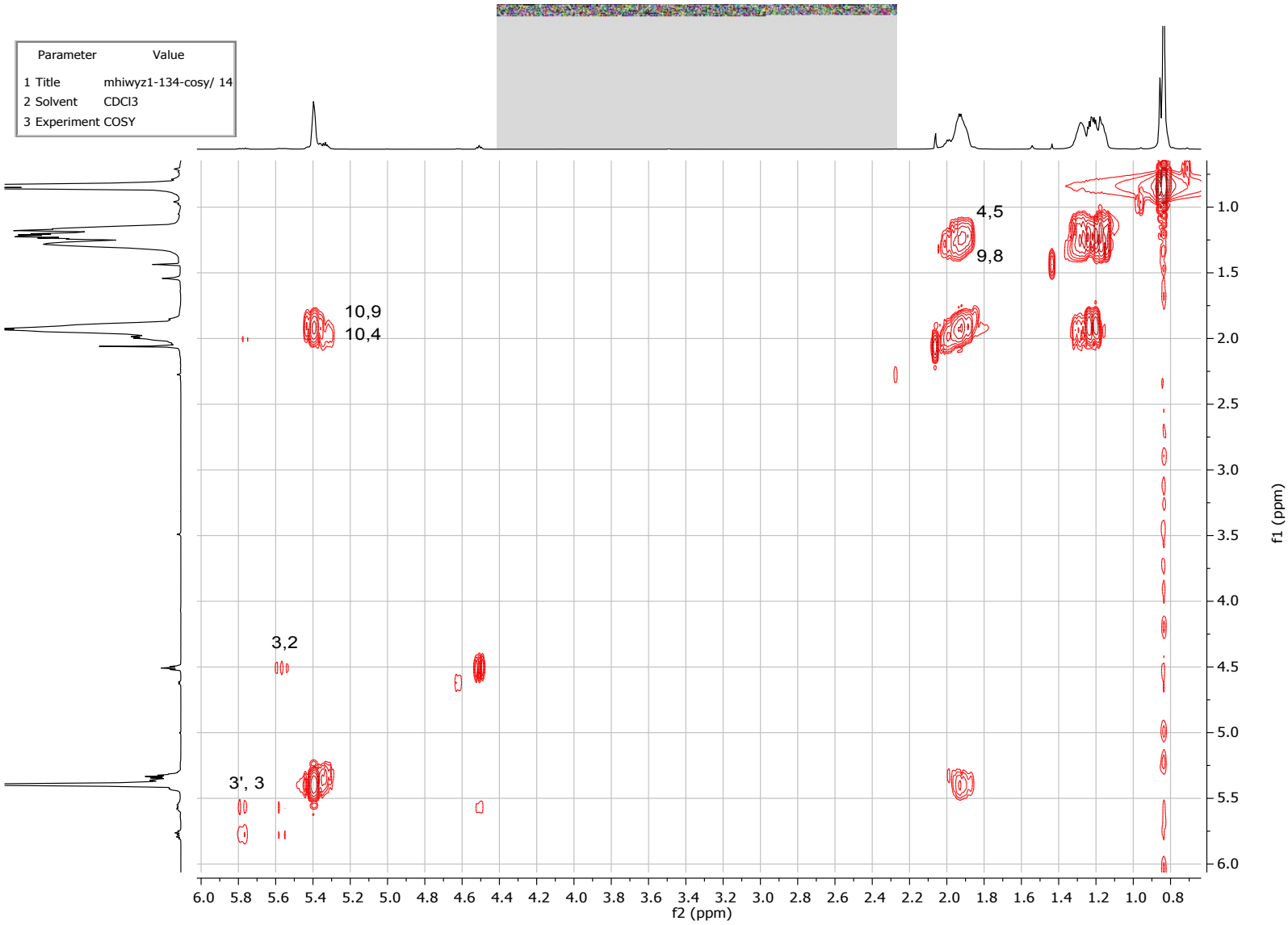


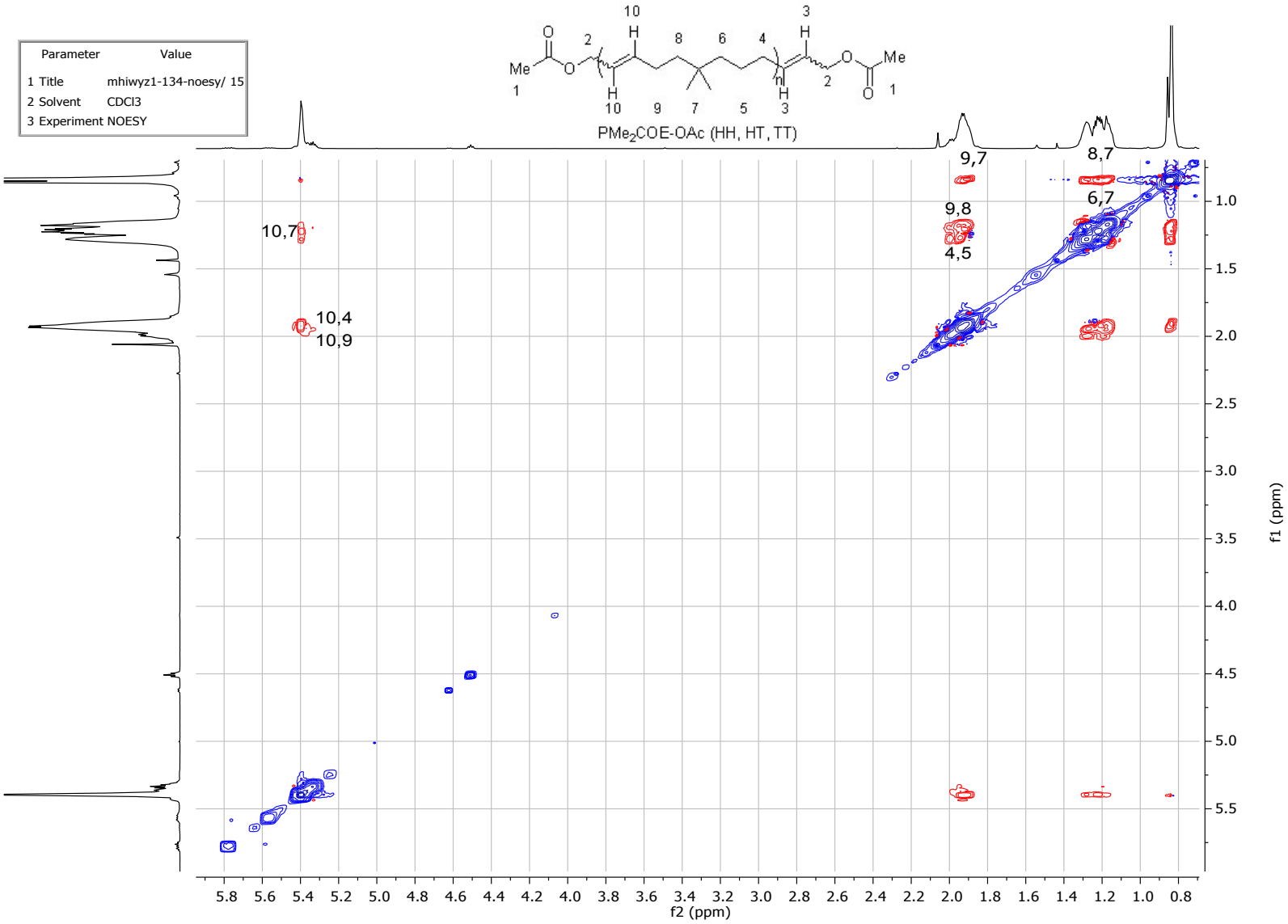
Parameter	Value
1 Title	mhiwyz1-134-dept135.12.fid
2 Solvent	CDCl3
3 Experiment	DEPT-135
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

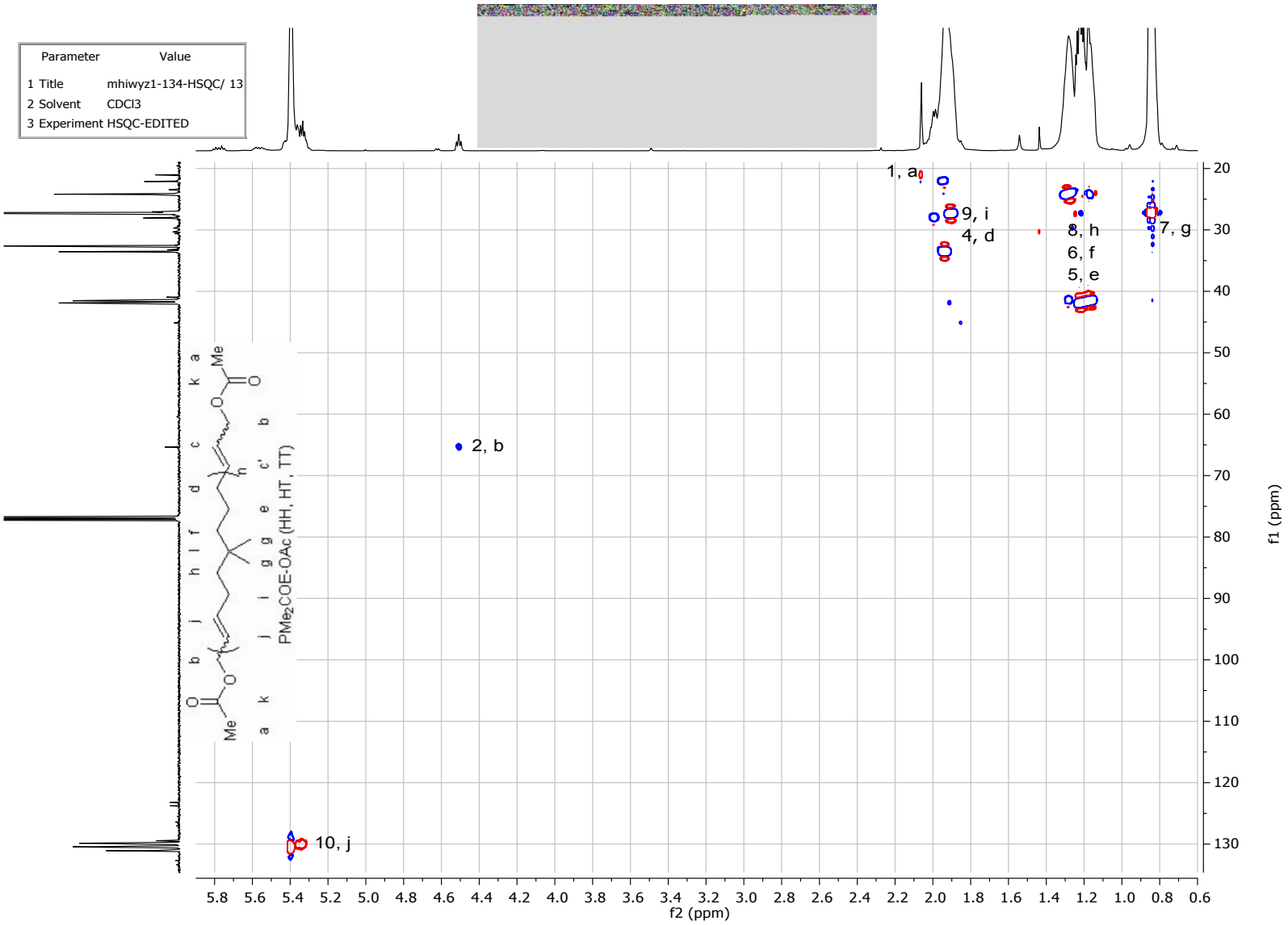


$PMe_2COE\text{-}OAc$ (HH, HT, TT)

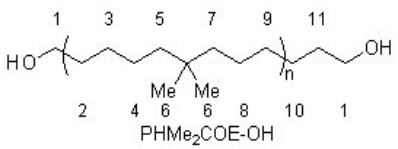


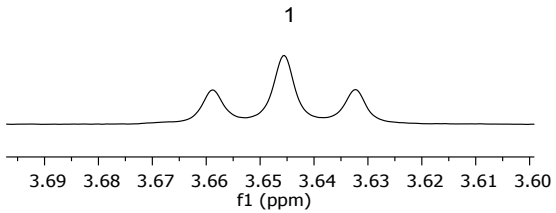

Parameter Value
1 Title mhiwyz1-134-cosy/ 14
2 Solvent CDCl3
3 Experiment COSY
4,5
9,8
10,9
10,4
3,2
3', 3
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title mhiwyz1-134-noesy/ 15
2 Solvent CDCl3
3 Experiment NOESY
PMe2COE-OAc (HH, HT, TT)
10,7
10,4
10,9
9,7
9,8
4,5
8,7
6,7
f2 (ppm)
f1 (ppm)

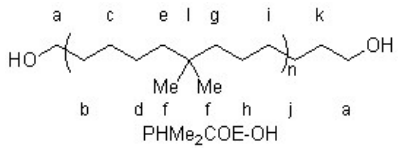

Parameter Value
1 Title mhiwyz1-134-HSQC/ 13
2 Solvent CDCl3
3 Experiment HSQC-EDITED
1, a
9, i
4, d
8, h
6, f
5, e
7, g
2, b
10, j
PMe2COE-OAc (HH, HT, TT)
f2 (ppm)
f1 (ppm)

Parameter	Value
1 Title	wyz1-141-pro.1.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	10.0000
5 Spectrometer Frequency	500.33
6 Nucleus	1H

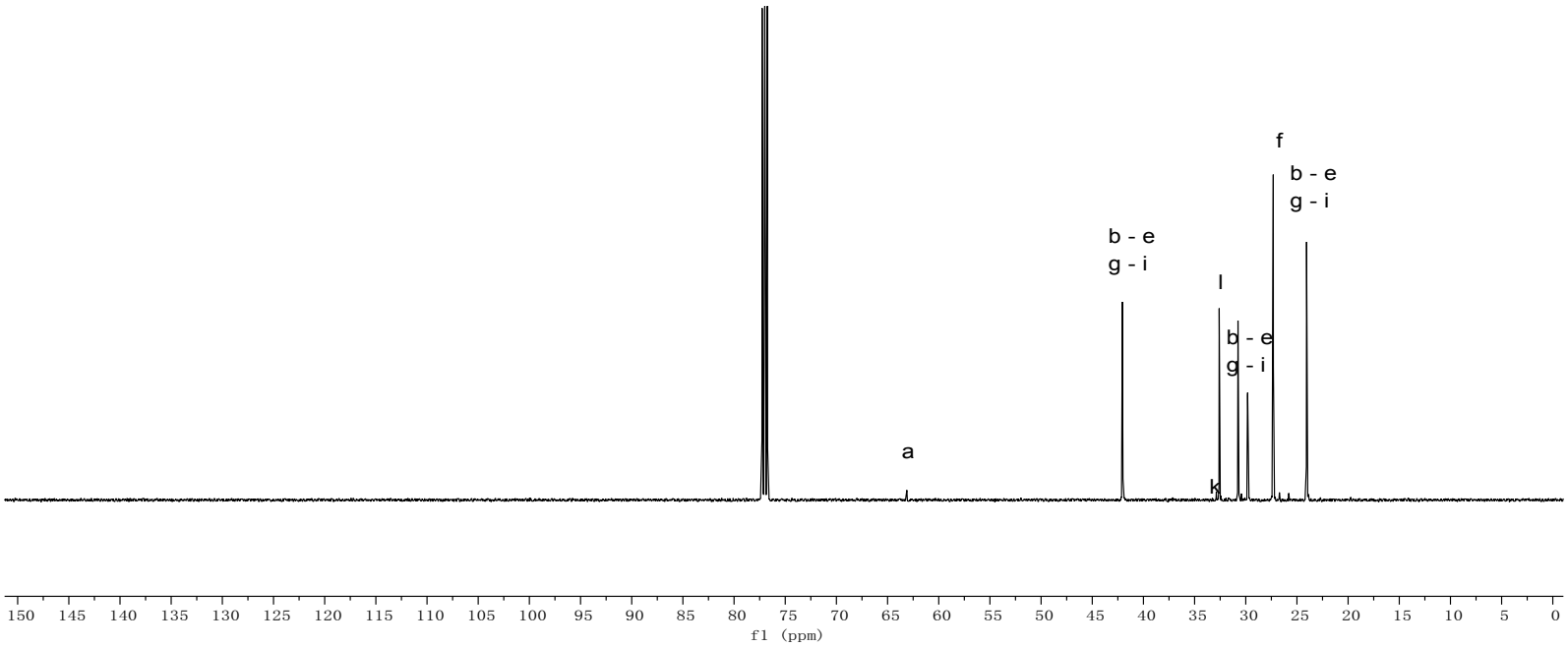




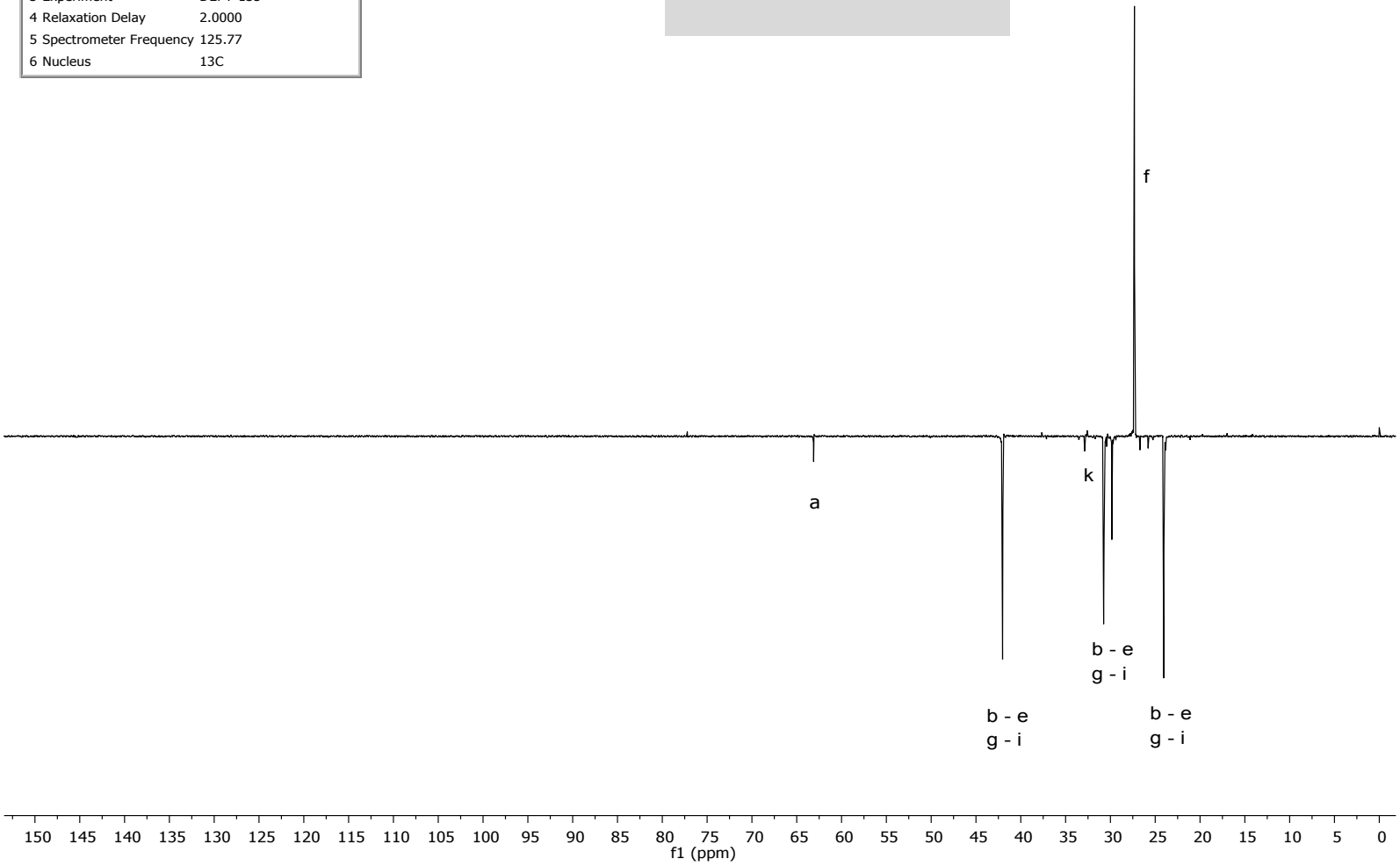
Parameter	Value
1 Title	wyz1-141-pro-C13.1.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.82
6 Nucleus	13C

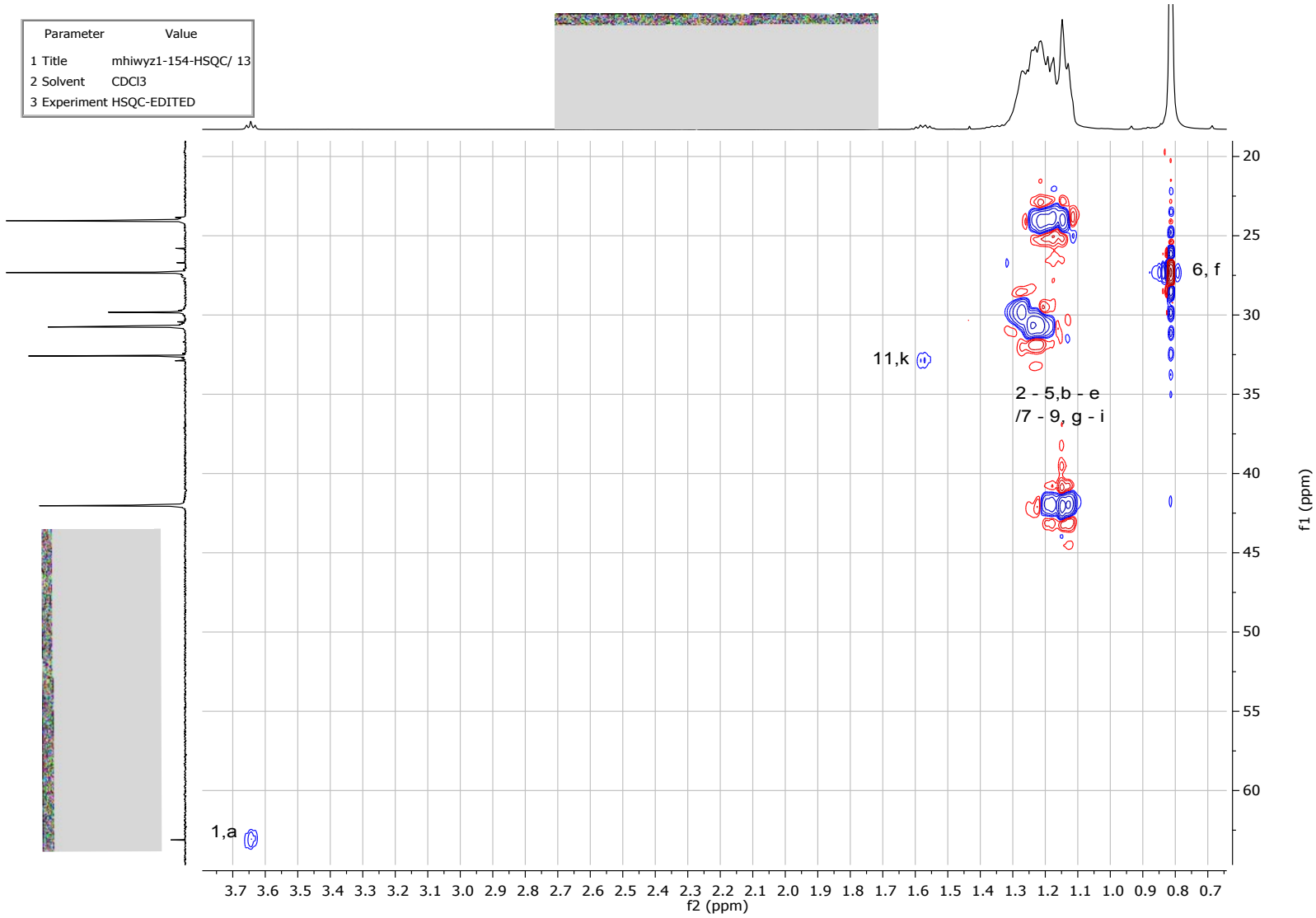


$PHMe_2COE\text{-}OH$

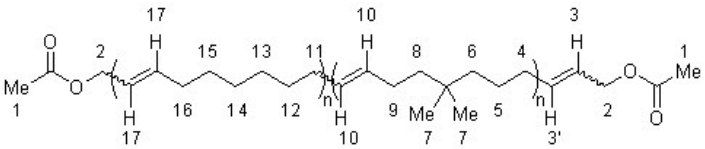


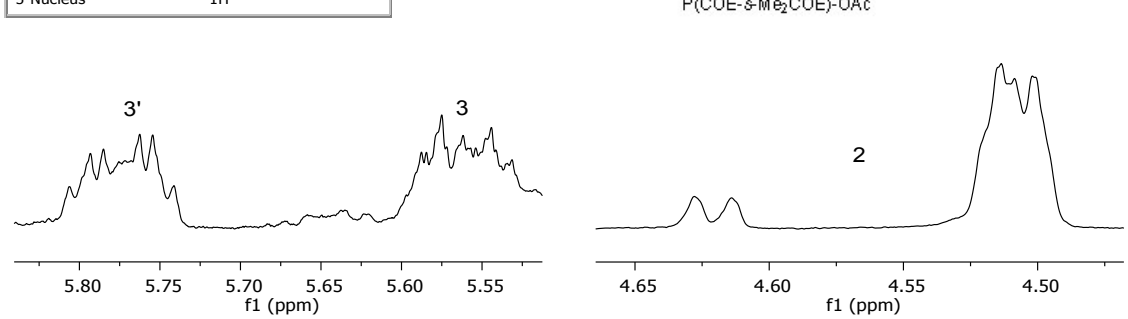
Parameter	Value
1 Title	mhiwyz1-154-DEPT.12.fid
2 Solvent	CDCl3
3 Experiment	DEPT-135
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C



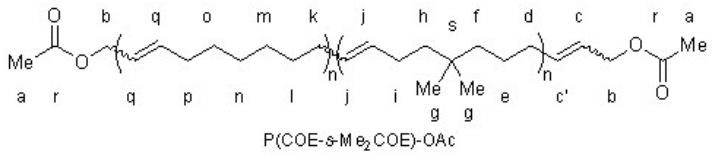

Parameter Value
1 Title mhiwyz1-154-HSQC/ 13
2 Solvent CDCl3
3 Experiment HSQC-EDITED
11,k
2 - 5,b - e
/7 - 9, g - i
6, f
1,a
f2 (ppm)
f1 (ppm)

Parameter	Value
1 Title	wyz2-12-pro-H1-again/ 1
2 Solvent	CDCl3
3 Experiment	1D
4 Spectrometer Frequency	500.33
5 Nucleus	1H

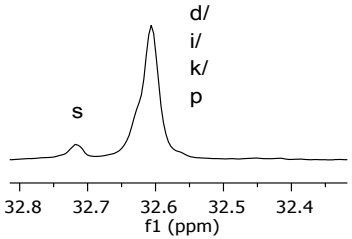


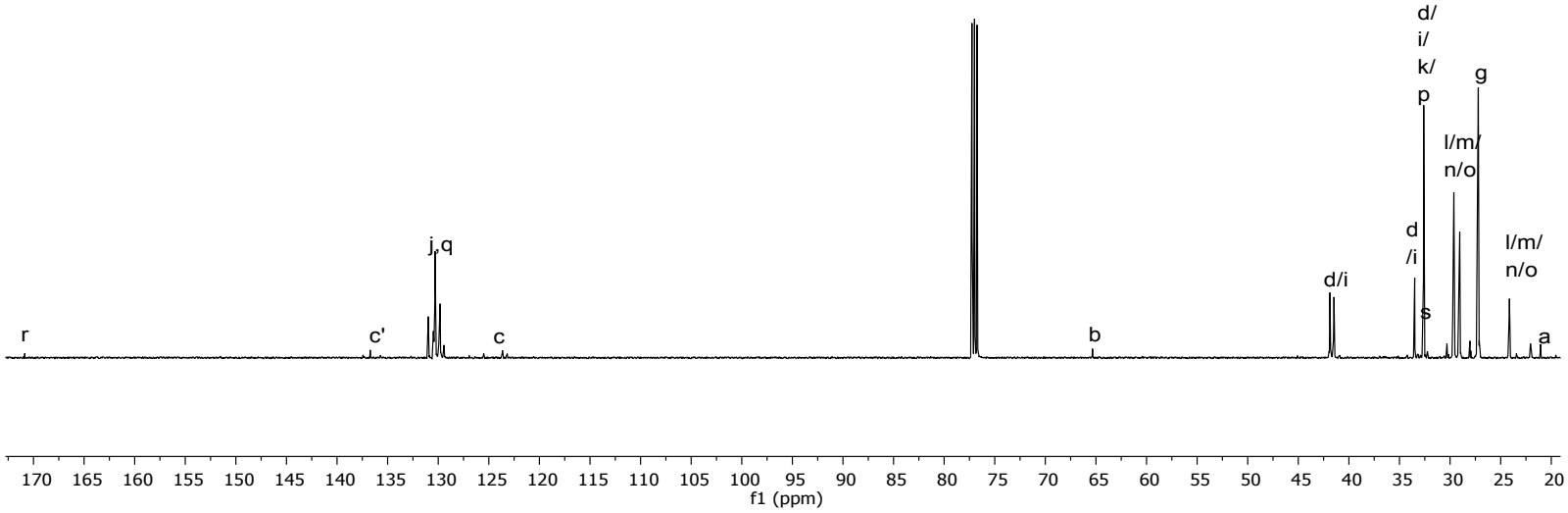


Parameter	Value
1 Title	mhiwyz2-12-pro-c13.11.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

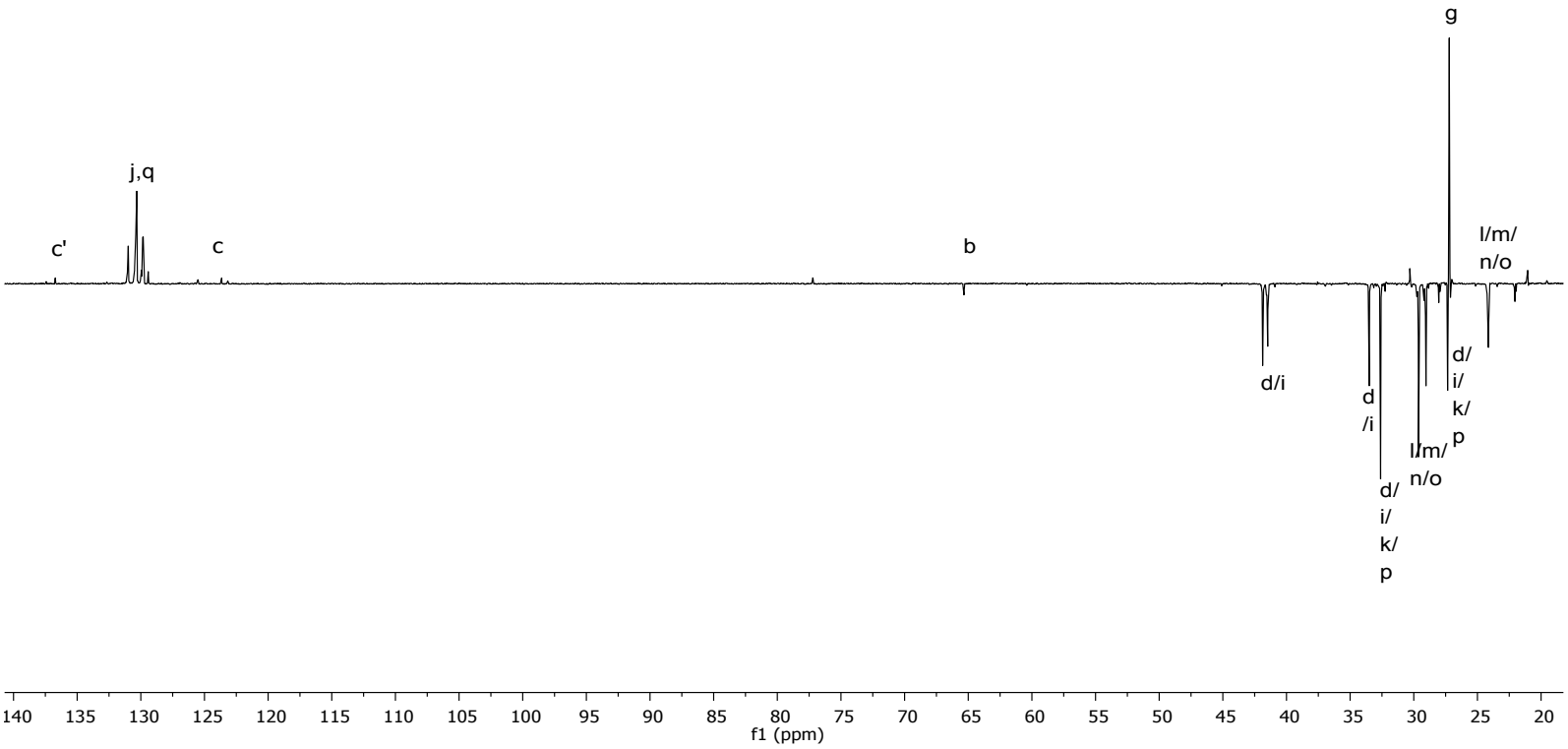


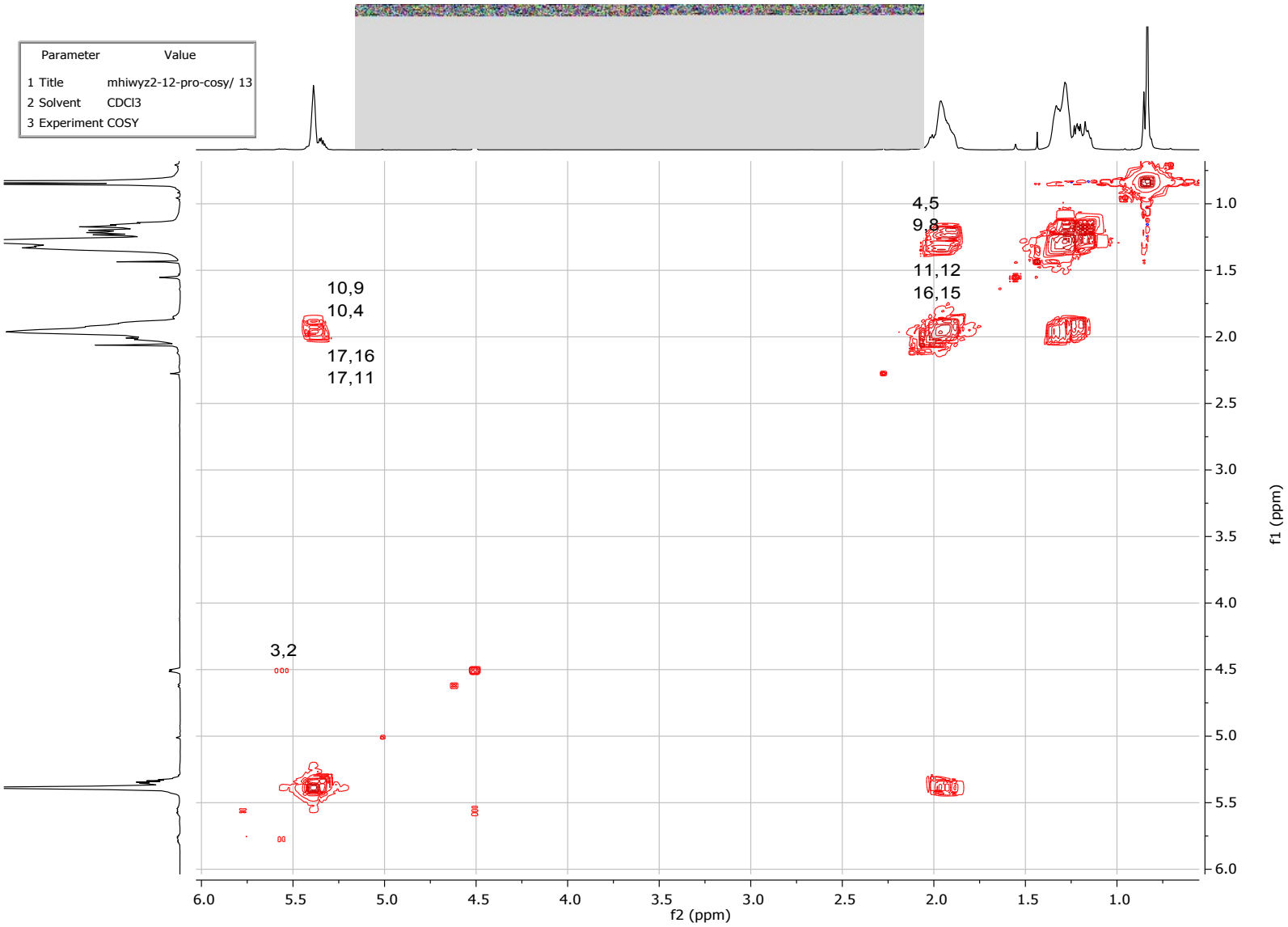
P(COE-*s*-Me$_2$COE)-OAc

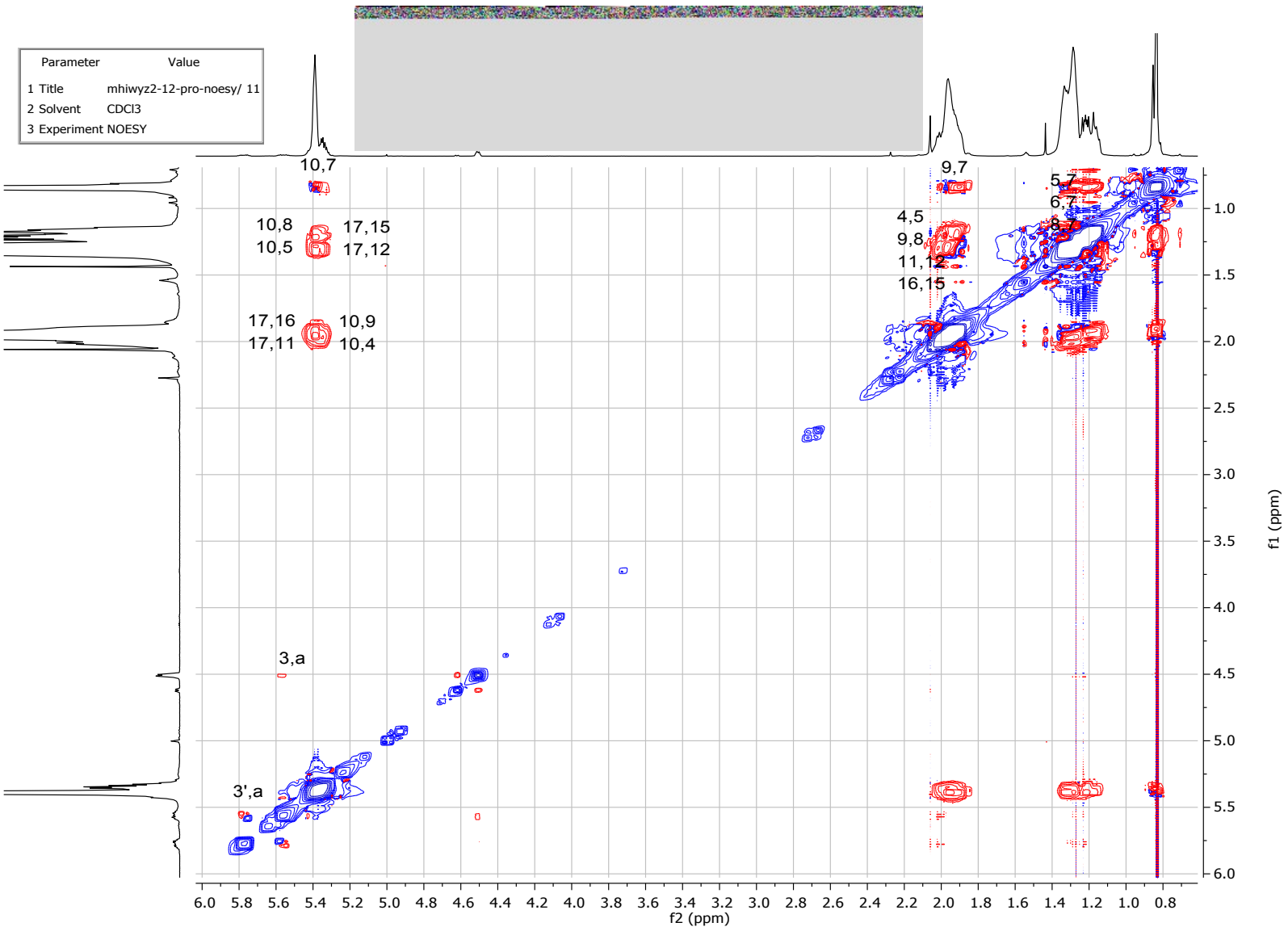


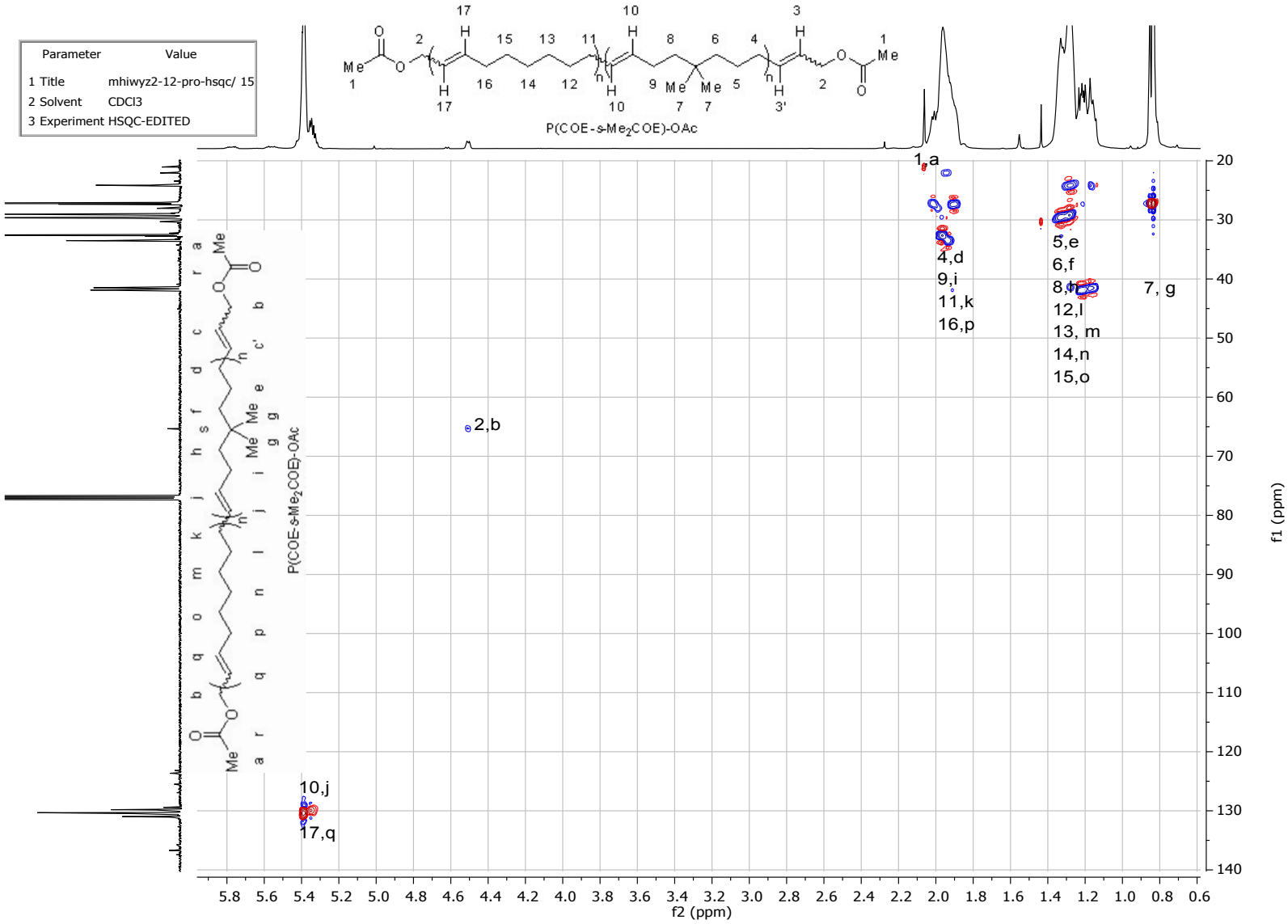


Parameter	Value
1 Title	mhiwyz2-12-pro-dept135.12.fid
2 Solvent	CDCl3
3 Experiment	DEPT-135
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

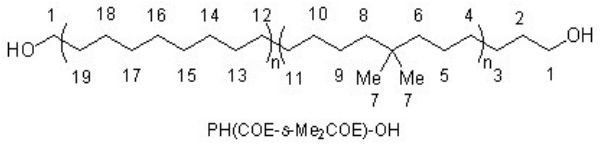



Parameter Value
1 Title mhiwyz2-12-pro-cosy/ 13
2 Solvent CDCl3
3 Experiment COSY
4,5
9,8
11,12
16,15
10,9
10,4
17,16
17,11
3,2
f2 (ppm)
f1 (ppm)

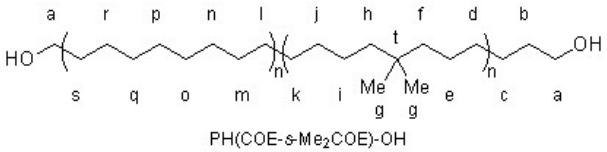

Parameter Value
1 Title mhiwyz2-12-pro-noesy/ 11
2 Solvent CDCl3
3 Experiment NOESY
10,7
10,8
10,5
17,15
17,12
17,16
17,11
10,9
10,4
3,a
3',a
9,7
5,7
6,7
4,5
9,8
11,12
16,15
f2 (ppm)
f1 (ppm)

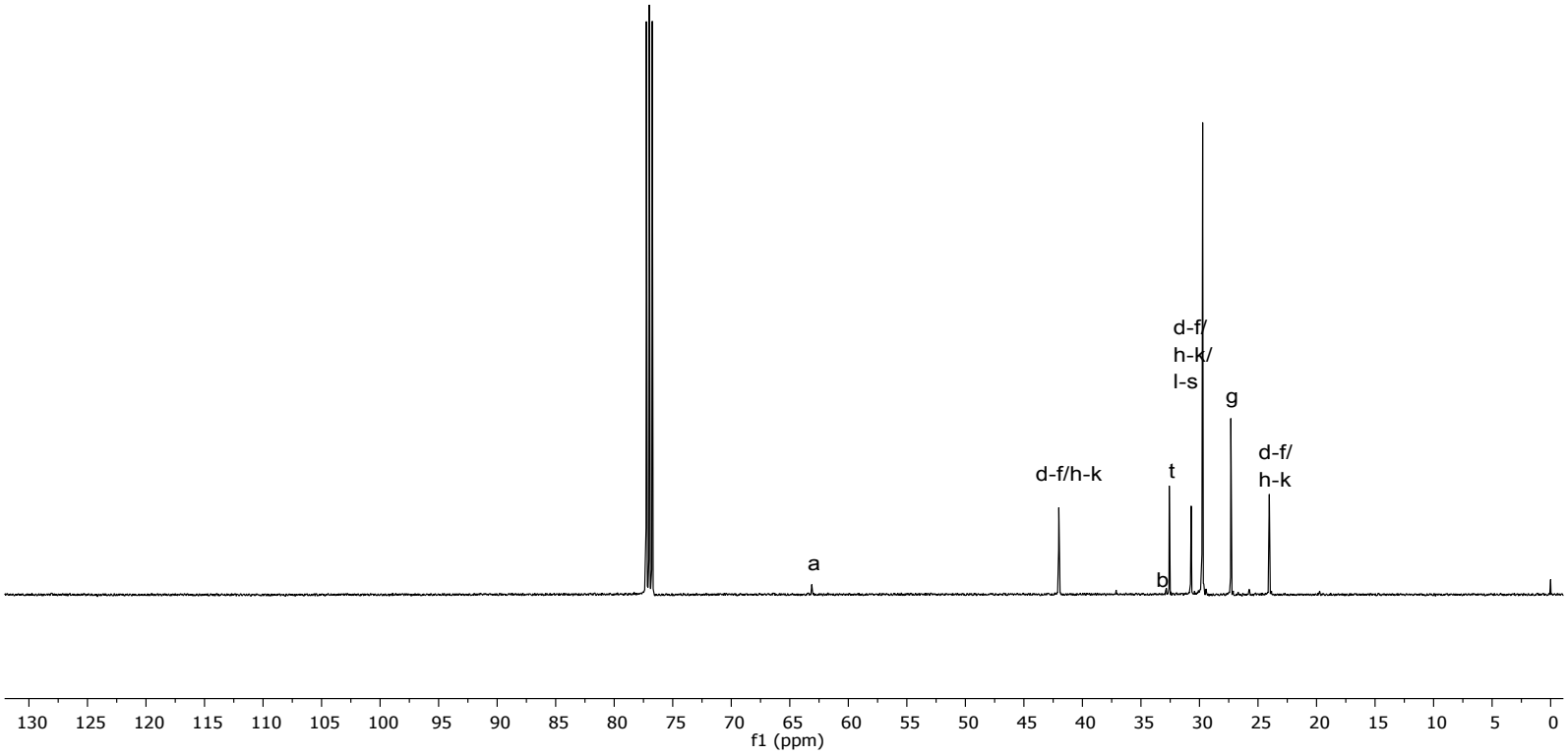

Parameter Value
1 Title mhiwyz2-12-pro-hsqc/ 15
2 Solvent CDCl3
3 Experiment HSQC-EDITED
P(COE-s-Me2COE)-OAc
1,a
4,d
9,i
11,k
16,p
5,e
6,f
8,h
12,l
13, m
14,n
15,o
7, g
2,b
10,j
17,q
f2 (ppm)
f1 (ppm)

Parameter	Value
1 Title	wyz2-14-pro-H1-again
2 Solvent	CDCl3
3 Temperature	29.0
4 Experiment	1D
5 Relaxation Delay	10.0000
6 Nucleus	1H

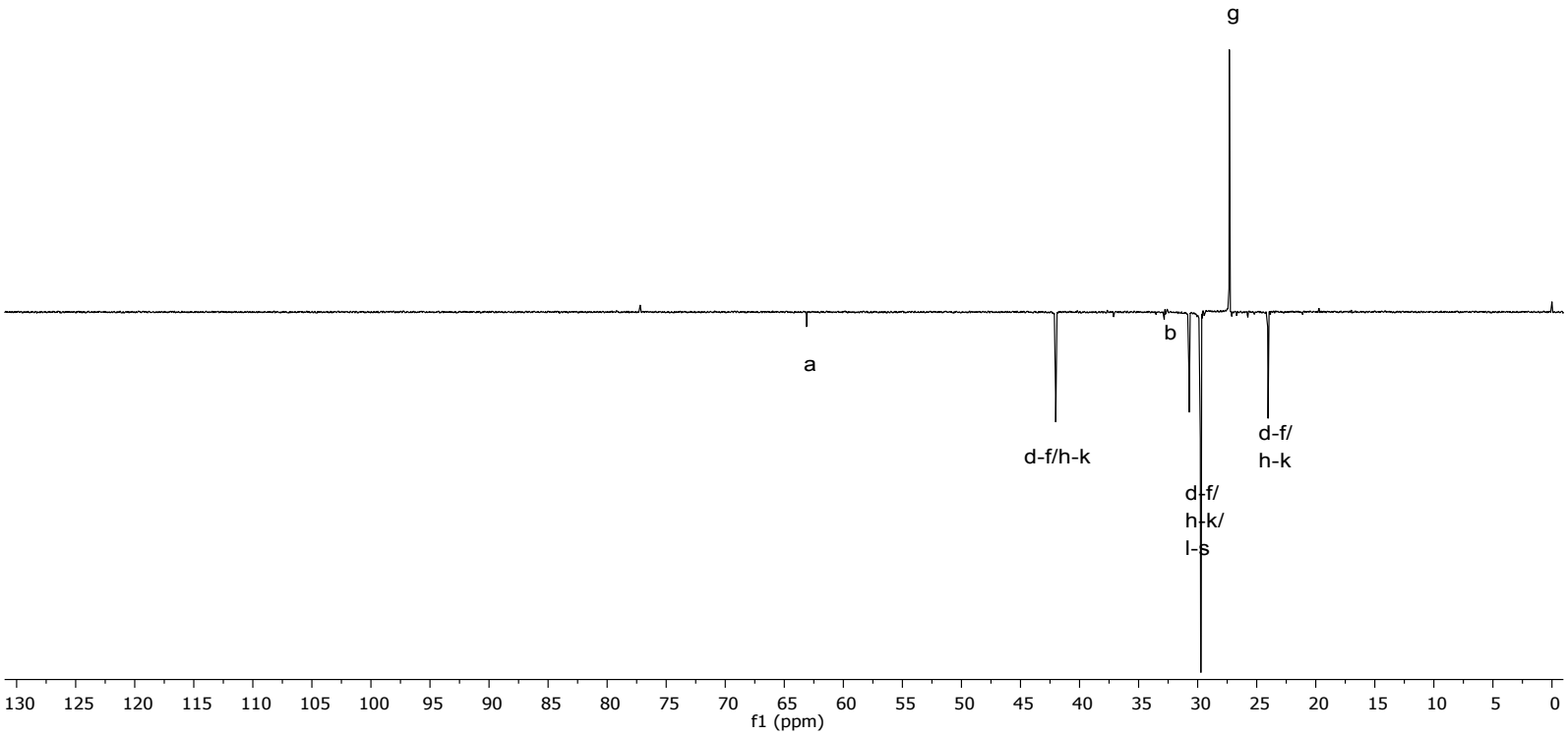


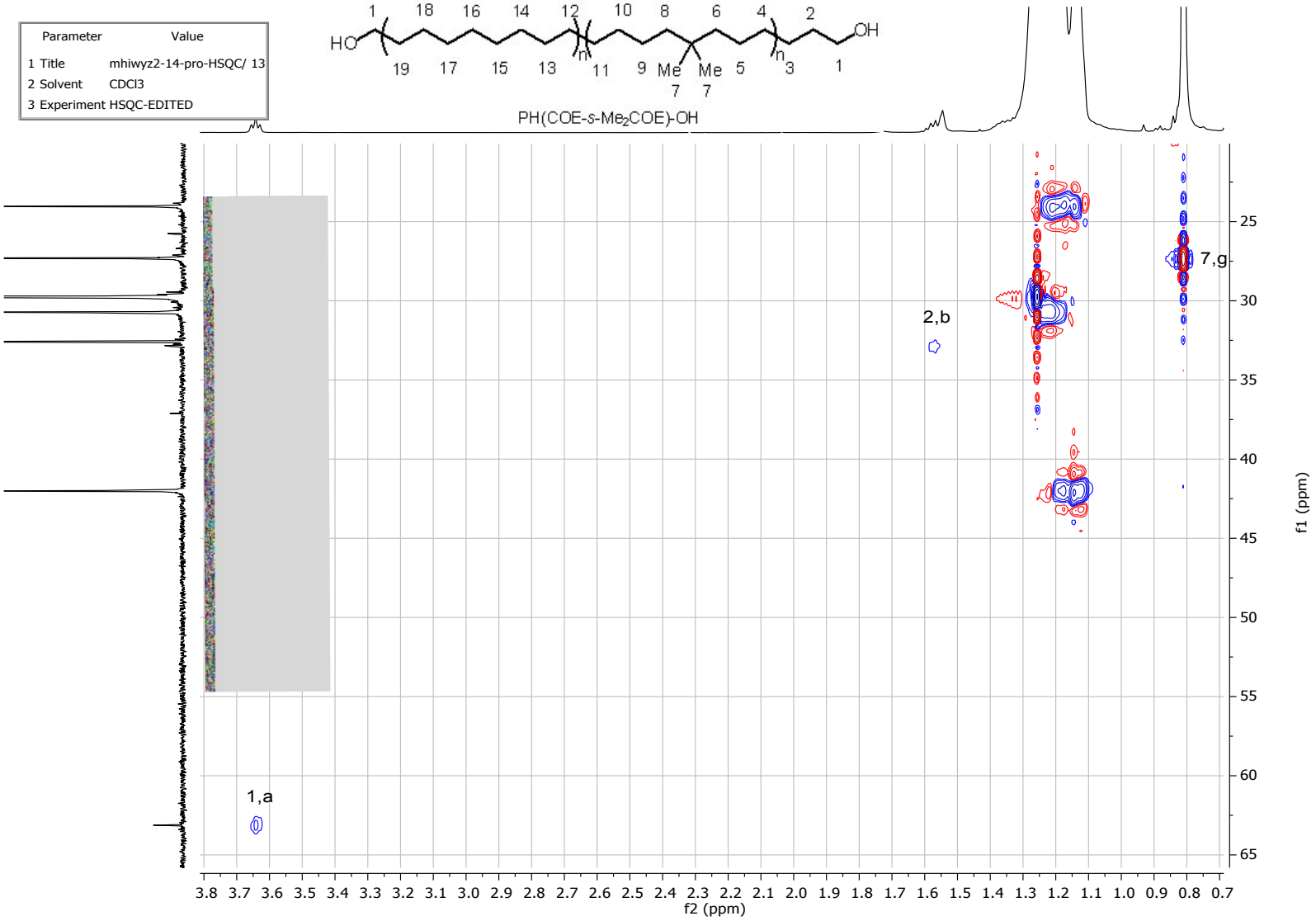
Parameter	Value
1 Title	mhiwyz2-14-pro-C13.11.fid
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

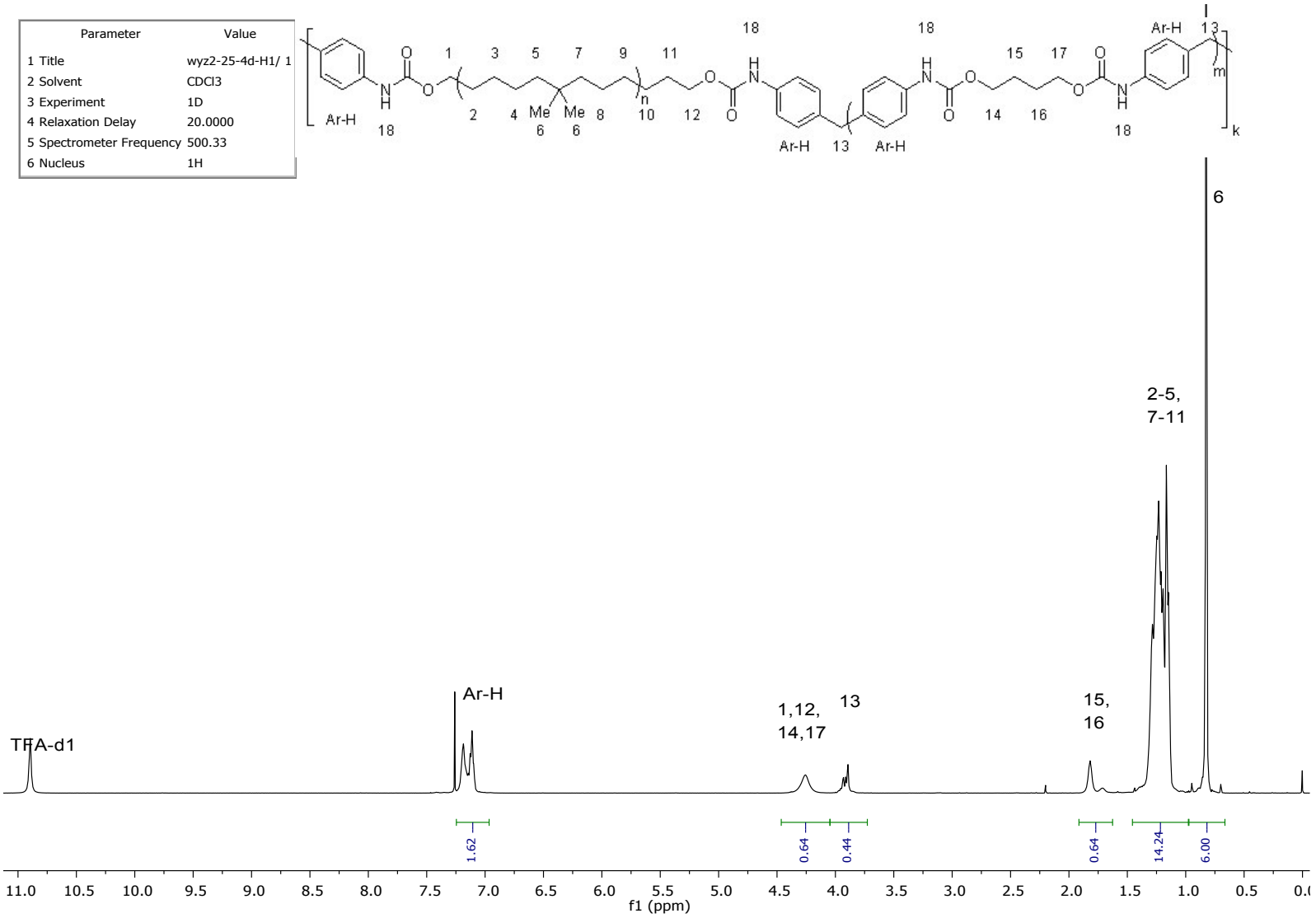




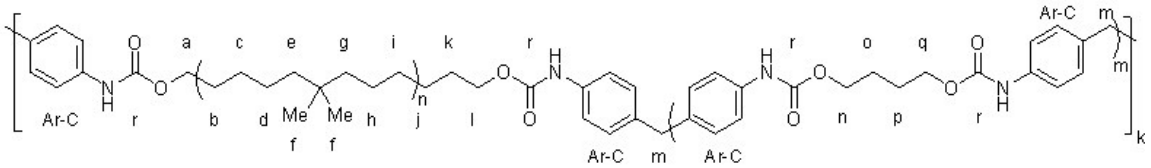
Parameter	Value
1 Title	mhiwyz2-14-pro-DEPT135.12.fid
2 Solvent	CDCl3
3 Experiment	DEPT-135
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

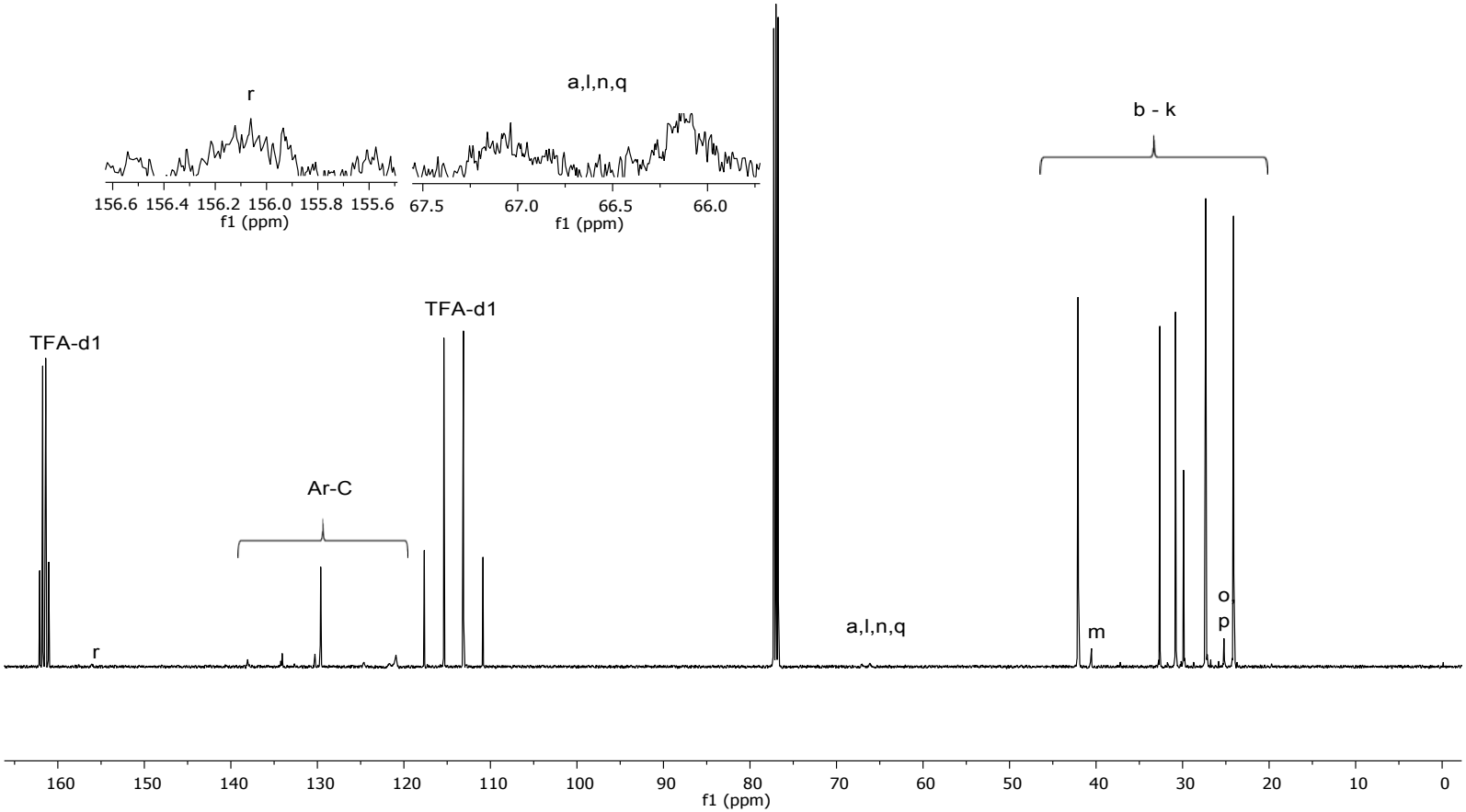


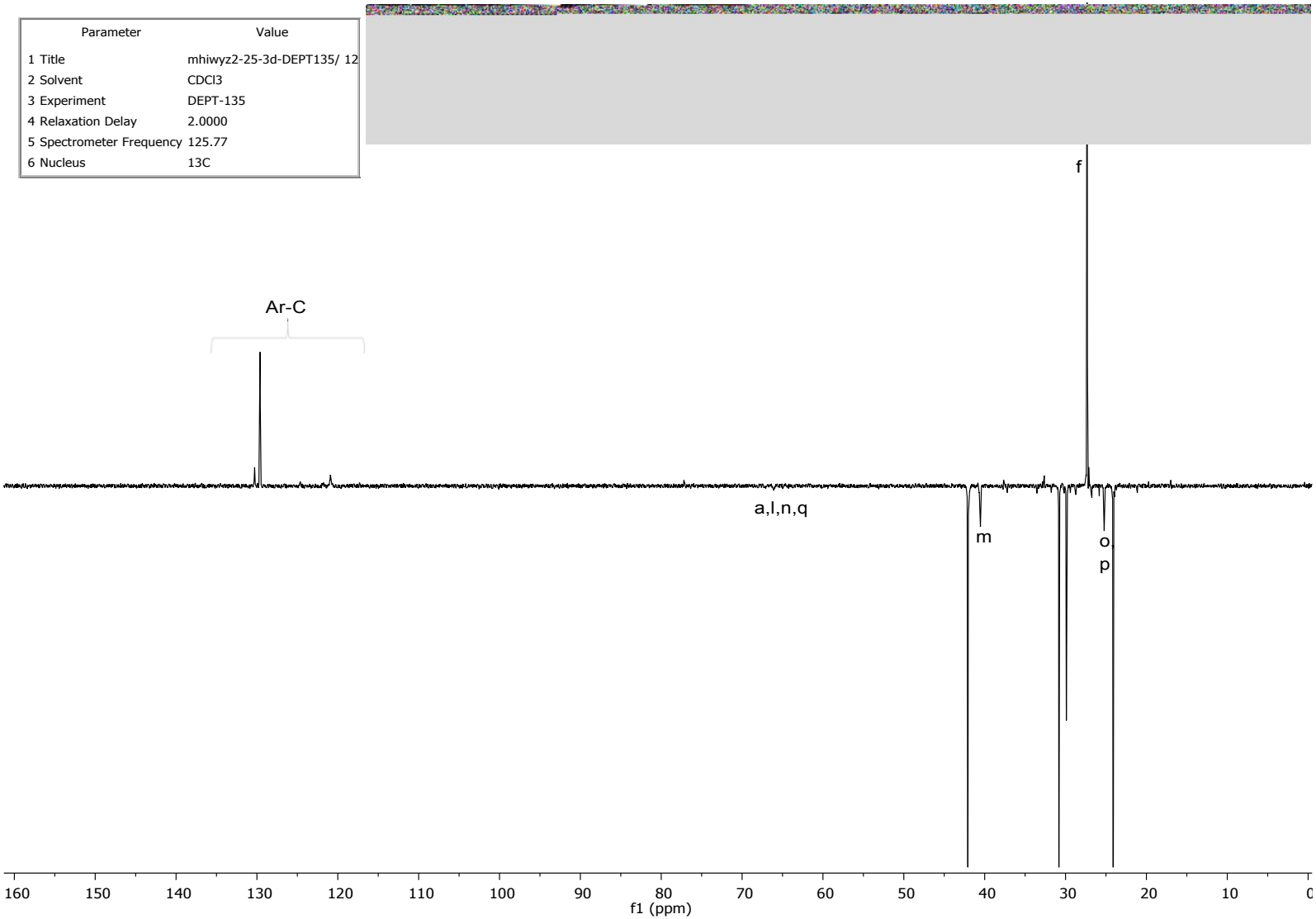

Parameter Value
1 Title mhiwyz2-14-pro-HSQC/ 13
2 Solvent CDCl3
3 Experiment HSQC-EDITED
PH(COE-s-Me2COE)-OH
2,b
7,g
1,a
f2 (ppm)
f1 (ppm)

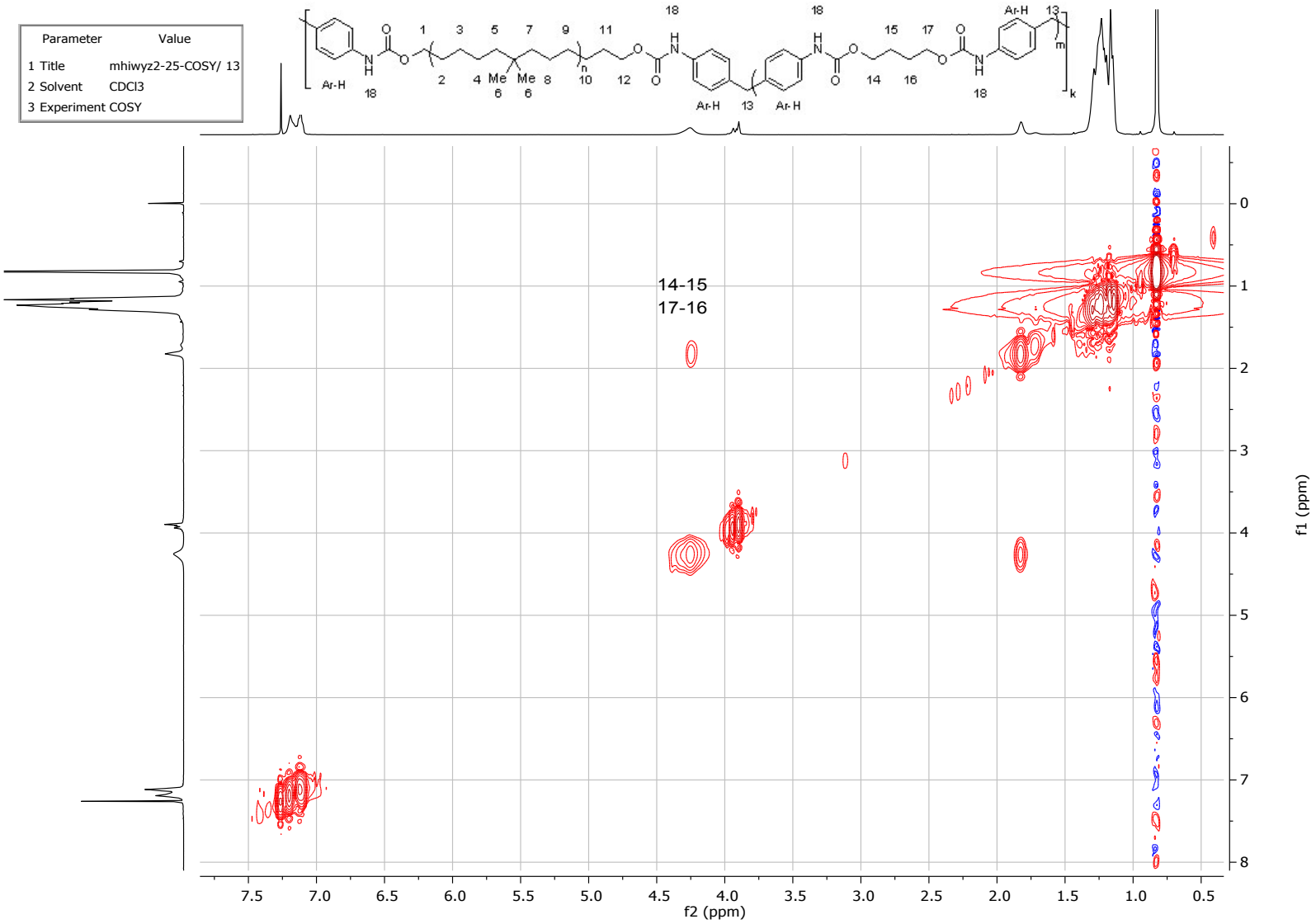

Parameter Value
1 Title wyz2-25-4d-H1/ 1
2 Solvent CDCl3
3 Experiment 1D
4 Relaxation Delay 20.0000
5 Spectrometer Frequency 500.33
6 Nucleus 1H
Ar-H
Me
Me
Ar-H
Ar-H
Ar-H
TFA-d1
Ar-H
1,12,
14,17
13
15,
16
2-5,
7-11
6
1.62
0.64
0.44
0.64
14.24
6.00
f1 (ppm)

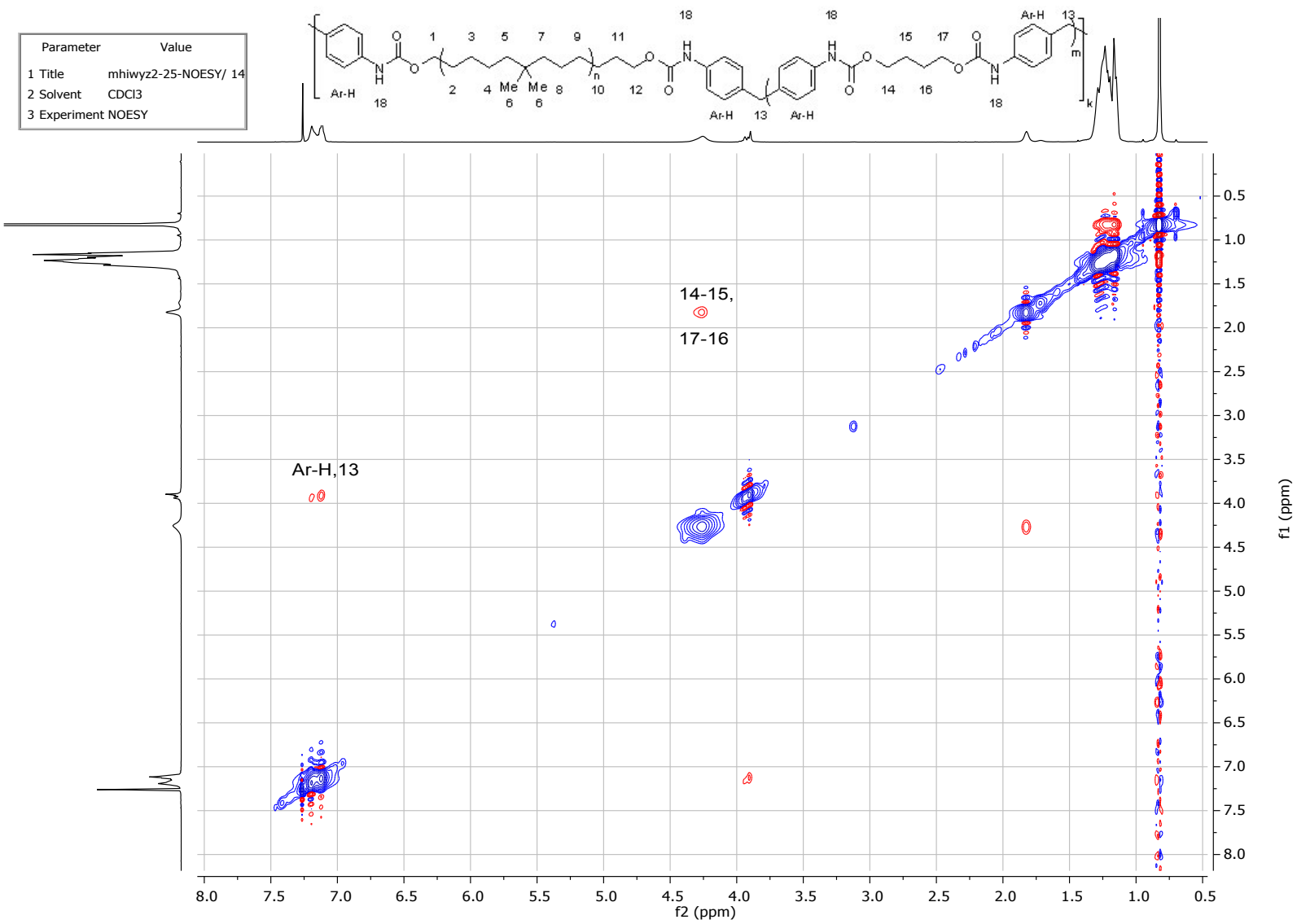
Parameter	Value
1 Title	mhiwyz2-25-3d-C13/ 11
2 Solvent	CDCl3
3 Experiment	1D
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	125.77
6 Nucleus	13C

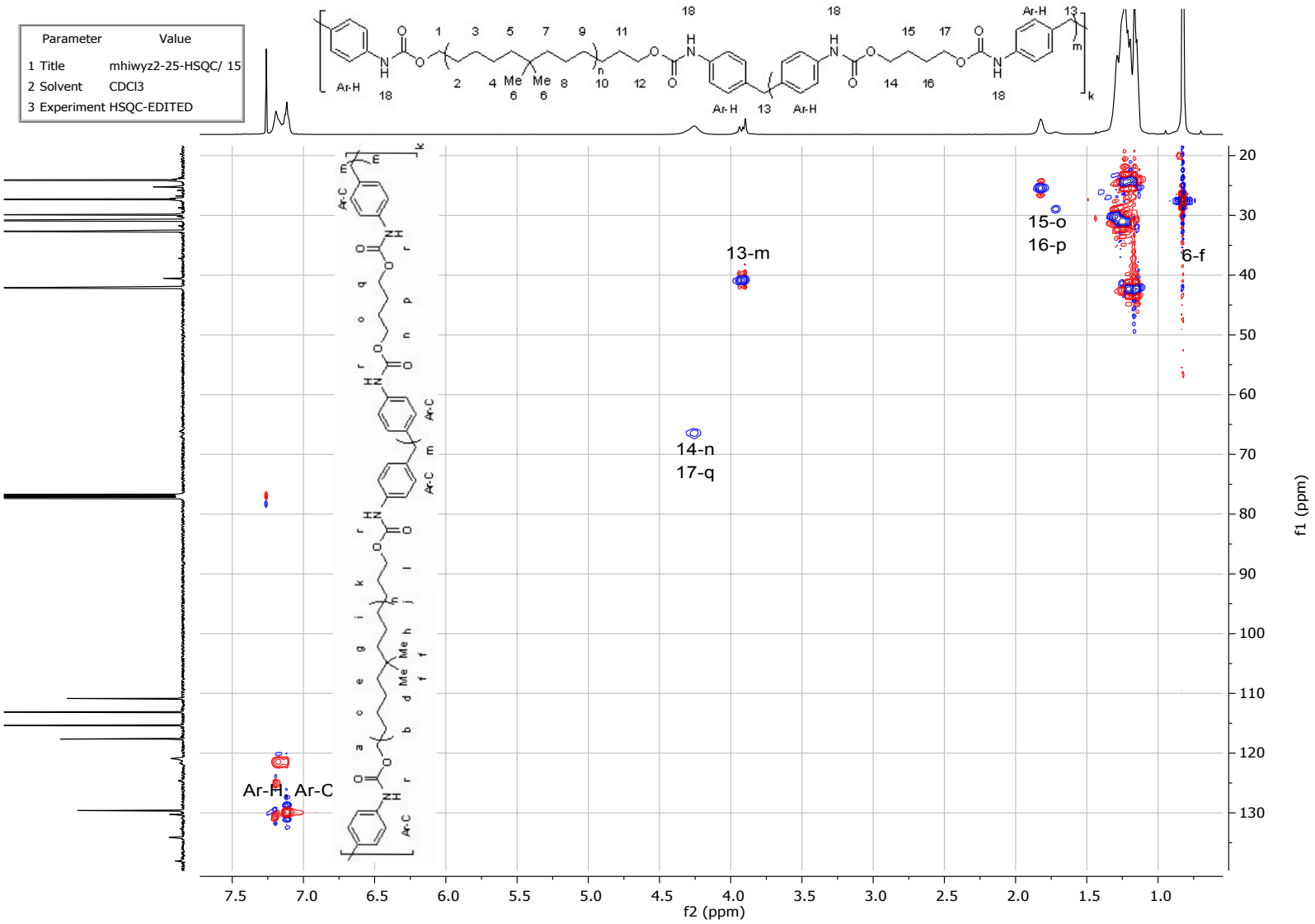


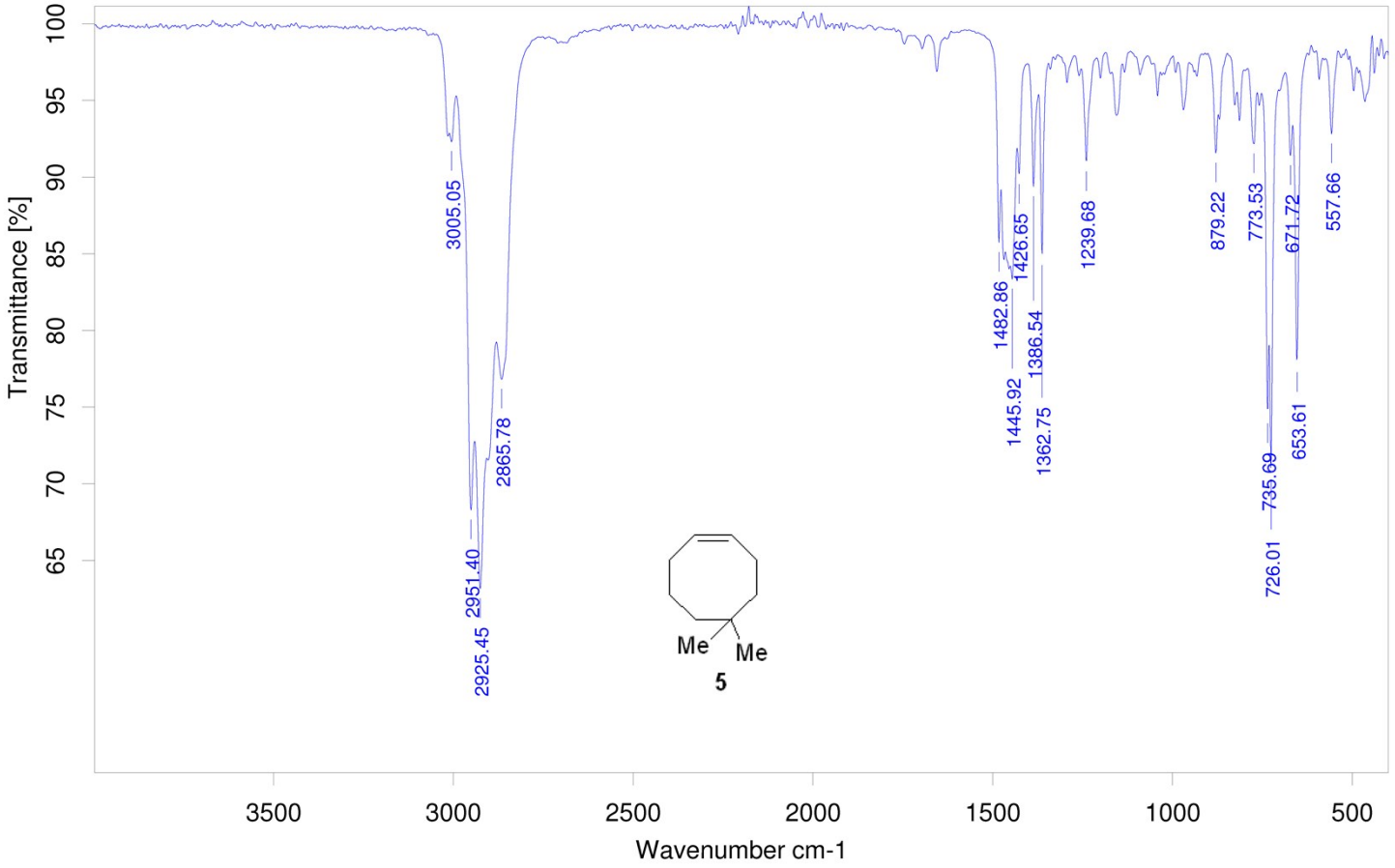



Parameter Value
1 Title mhiwyz2-25-3d-DEPT135/ 12
2 Solvent CDCl3
3 Experiment DEPT-135
4 Relaxation Delay 2.0000
5 Spectrometer Frequency 125.77
6 Nucleus 13C
f
Ar-C
a,l,n,q
m
o
p
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

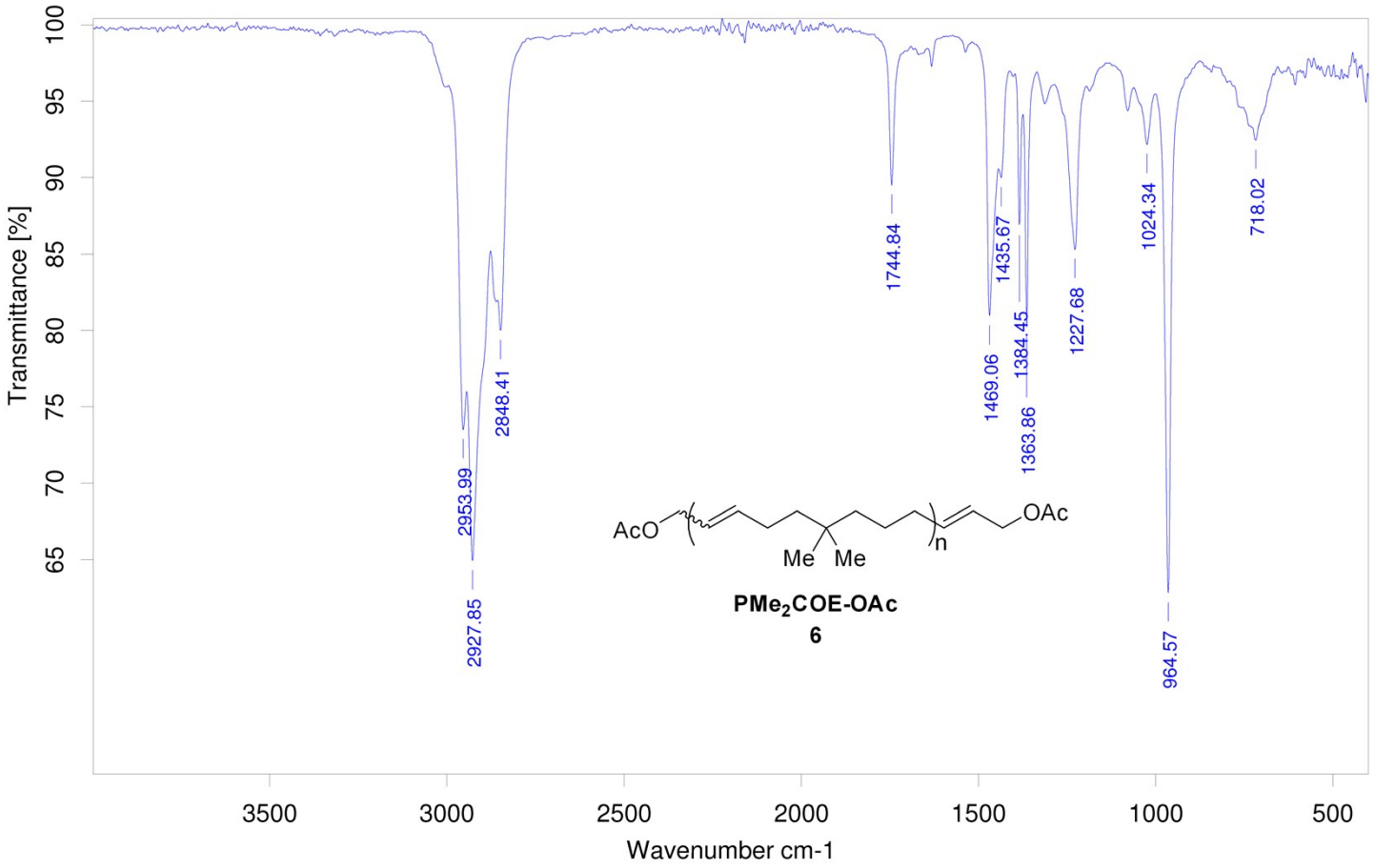

Parameter Value
1 Title mhiwyz2-25-COSY/ 13
2 Solvent CDCl3
3 Experiment COSY
14-15
17-16
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title mhiwyz2-25-NOESY/ 14
2 Solvent CDCl3
3 Experiment NOESY
Ar-H
Me
Me
14-15,
17-16
Ar-H,13
f2 (ppm)
f1 (ppm)

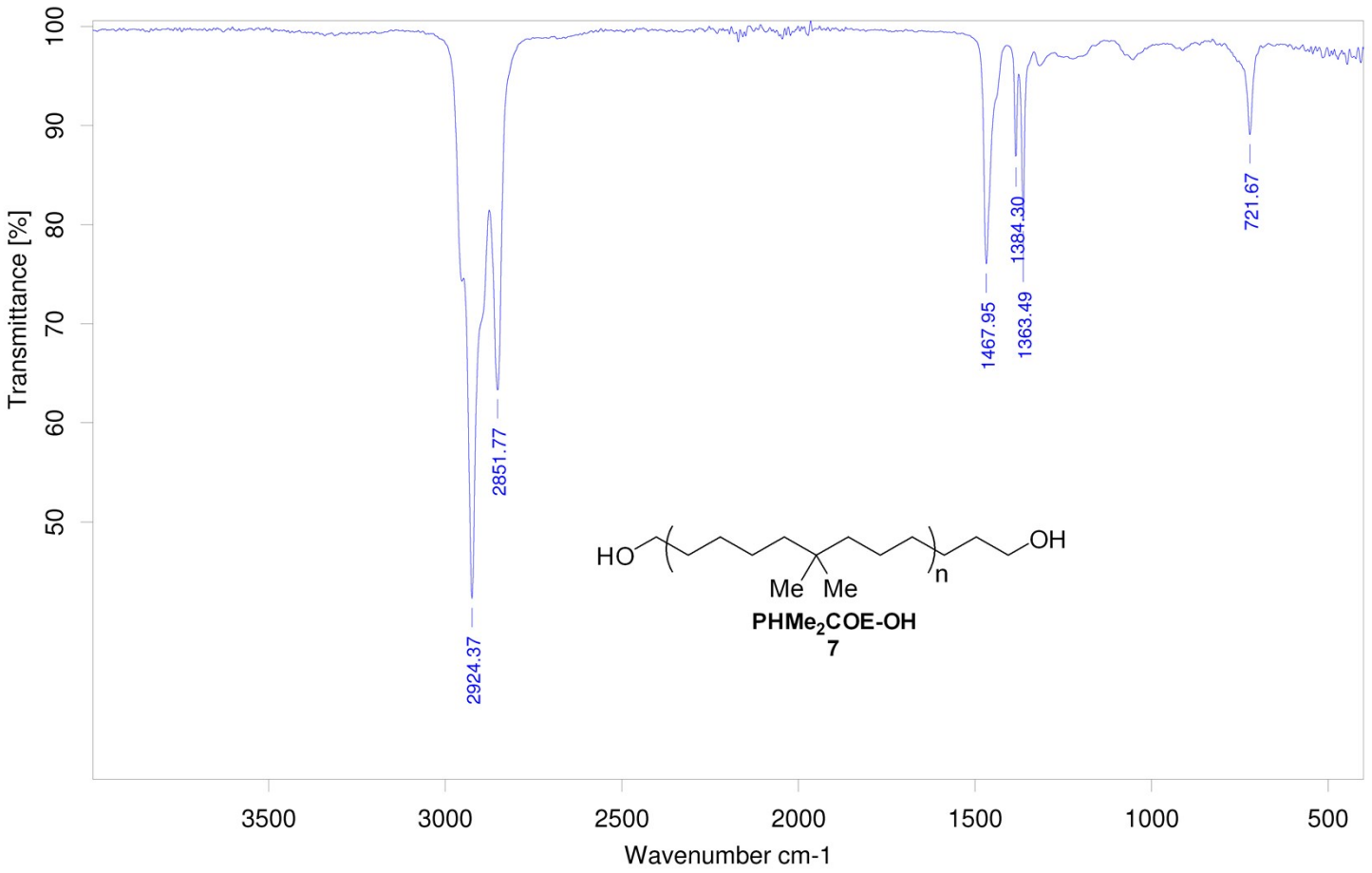

Parameter Value
1 Title mhiwyz2-25-HSQC/ 15
2 Solvent CDCl3
3 Experiment HSQC-EDITED
Ar-H
Ar-C
13-m
14-n
17-q
15-o
16-p
6-f
f2 (ppm)
f1 (ppm)



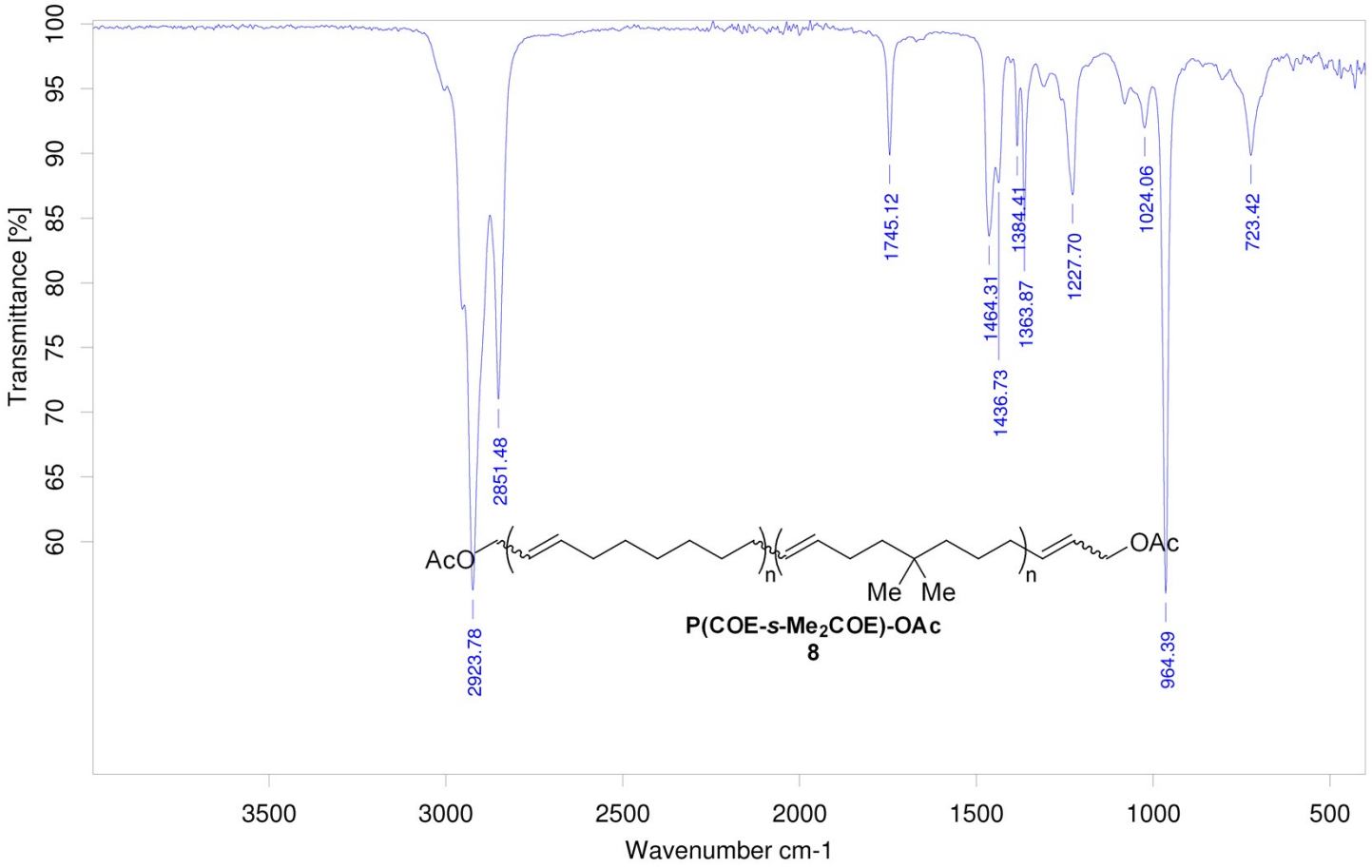
C:\IR DATA\wyz\wyz1-147.0	wyz1-147	Bruker ALPHA-P FT-IR with diamond ATR	3/25/2015



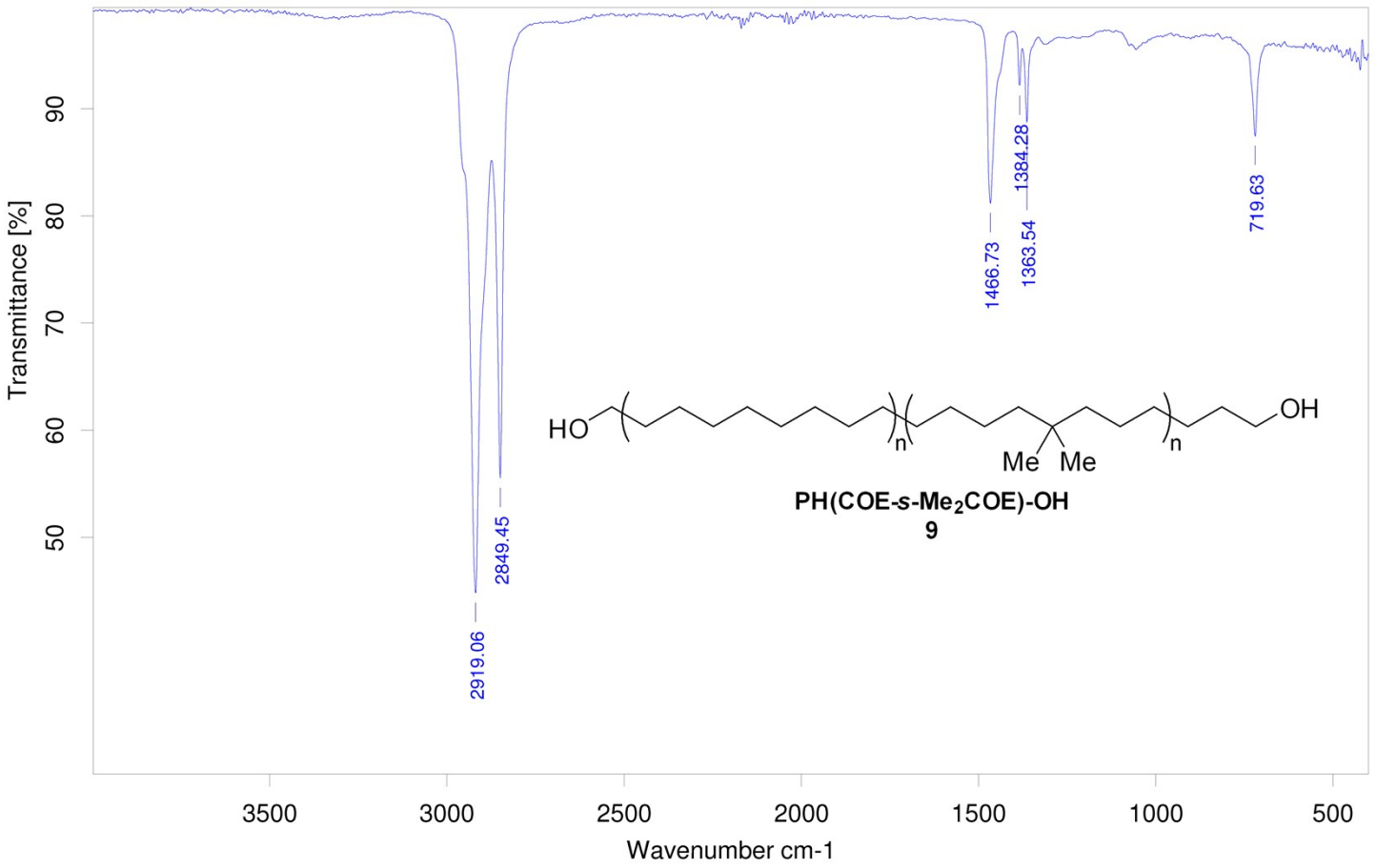
C:\IR DATA\wyz\wyz1-134-PMe2COE.0	wyz1-134-PMe2COE	Bruker ALPHA-P FT-IR with diamond ATR	3/24/2015



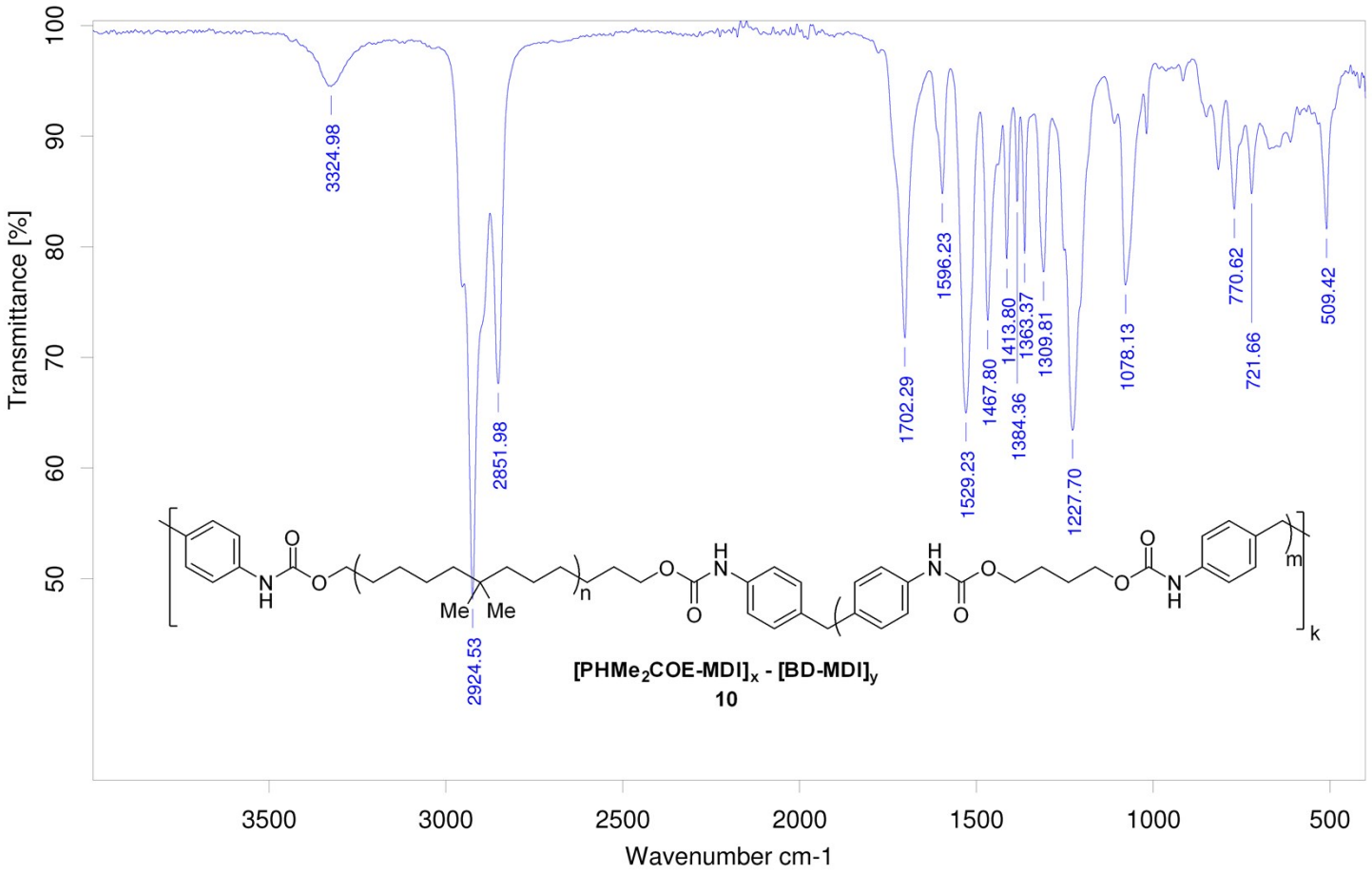
C:\IR DATA\wyz\wyz1-141-PHMe2COE.0	wyz1-141-PHMe2COE	Bruker ALPHA-P FT-IR with diamond ATR	3/24/2015



C:\IR DATA\wyz\wyz2-12-P(COE-Me2COE).0	wyz2-12-P(COE-Me2COE)	Bruker ALPHA-P FT-IR with diamond ATR	3/24/2015



C:\IR DATA\wyz\wyz2-14-PH(COE-Me2COE).0	wyz2-14-PH(COE-Me2COE)	Bruker ALPHA-P FT-IR with diamond ATR	3/24/2015



C:\IR DATA\wyz\wyz2-25-PU.8	wyz2-25-PU	Bruker ALPHA-P FT-IR with diamond ATR	4/7/2015