

Table S1. Geometric parameters of compound 1 (4-CDC) [$\text{\AA}$, $^\circ$].

Cl1—C4	1.7445 (18)	C1—C7	1.487 (2)
N1—C10	1.497 (2)	C2—C3	1.384 (2)
N1—C11	1.5037 (19)	C3—C4	1.389 (2)
N1—C8	1.512 (2)	C4—C5	1.392 (2)
O1—C7	1.221 (2)	C5—C6	1.394 (2)
C1—C6	1.402 (2)	C7—C8	1.5363 (19)
C1—C2	1.4096 (19)	C8—C9	1.532 (2)
C10—N1—C11	109.21 (12)	C5—C4—Cl1	119.00 (13)
C10—N1—C8	116.45 (13)	O1—C7—C1	121.05 (13)
C11—N1—C8	110.83 (12)	O1—C7—C8	120.18 (15)
C6—C1—C2	119.00 (14)	C4—C5—C6	118.69 (15)
C6—C1—C7	123.18 (12)	C5—C6—C1	120.63 (12)
C2—C1—C7	117.82 (14)	C1—C7—C8	118.73 (14)
C3—C2—C1	120.77 (15)	N1—C8—C9	112.98 (13)
C2—C3—C4	118.94 (13)	N1—C8—C7	109.60 (12)
C3—C4—C5	121.95 (15)	C9—C8—C7	110.41 (12)
C3—C4—Cl1	119.05 (11)		

Table S2. Geometric parameters of compound 2 (MDPT) [$\text{\AA}$, $^\circ$].

N1—C8	1.495 (2)	C1—C7	1.483 (3)
N1—C10	1.527 (3)	C2—C3	1.363 (3)
O1—C7	1.225 (3)	C3—C4	1.397 (3)
O2—C3	1.379 (3)	C4—C5	1.369 (3)
O2—C14	1.432 (3)	C5—C6	1.399 (3)
O3—C4	1.373 (2)	C7—C8	1.531 (3)
O3—C14	1.443 (3)	C10—C11	1.521 (3)
C1—C6	1.402 (3)	C10—C12	1.527 (3)
C1—C2	1.414 (3)	C10—C13	1.532 (3)
C8—N1—C10	117.85 (15)	C11—C10—N1	110.09 (17)
C3—C2—C1	116.80 (19)	C11—C10—C12	110.77 (18)
C2—C3—O2	127.9 (2)	N1—C10—C12	105.50 (16)
C2—C3—C4	122.3 (2)	C11—C10—C13	111.67 (18)
O2—C3—C4	109.82 (18)	N1—C10—C13	108.56 (16)
C5—C4—O3	128.5 (2)	C12—C10—C13	110.04 (19)
C5—C4—C3	122.00 (19)	O2—C14—O3	107.81 (17)
O3—C4—C3	109.50 (19)	C4—C5—C6	116.8 (2)
O1—C7—C1	122.00 (19)	C5—C6—C1	121.5 (2)
O1—C7—C8	118.75 (18)	N1—C8—C9	109.30 (16)
C1—C7—C8	119.05 (18)	C7—C8—C9	107.22 (17)
N1—C8—C7	110.15 (16)		

Table S3. Geometric parameters of compound 3 (4F-PHP) [Å, °].

F11—C41	1.379 (9)	F12—C42	1.371 (8)
N11—C81	1.491 (9)	N12—C82	1.490 (9)
N11—C161	1.516 (9)	N12—C162	1.529 (9)
N11—C131	1.534 (9)	N12—C132	1.554 (9)
O11—C71	1.208 (9)	O12—C72	1.212 (9)
C11—C21	1.398 (10)	C12—C62	1.390 (10)
C11—C61	1.415 (11)	C12—C22	1.400 (10)
C11—C71	1.510 (11)	C12—C72	1.506 (10)
C21—C31	1.386 (11)	C22—C32	1.379 (11)
C31—C41	1.362 (12)	C32—C42	1.387 (11)
C41—C51	1.384 (12)	C42—C52	1.380 (11)
C51—C61	1.376 (11)	C52—C62	1.395 (10)
C71—C81	1.537 (10)	C72—C82	1.529 (10)
C81—C91	1.552 (11)	C82—C92	1.524 (10)
C91—C101	1.519 (12)	C92—C102	1.524 (10)
C101—C111	1.529 (11)	C102—C112	1.538 (11)
C111—C121	1.550 (11)	C112—C122	1.550 (12)
C131—C141	1.505 (11)	C132—C142	1.504 (11)
C141—C151	1.518 (12)	C142—C152	1.521 (11)
C151—C161	1.500 (11)	C152—C162	1.531 (11)
C81—N11—C161	112.7 (6)	C82—N12—C162	112.8 (6)
C81—N11—C131	113.1 (6)	C82—N12—C132	113.4 (6)
C161—N11—C131	105.8 (6)	C162—N12—C132	105.8 (5)
C21—C11—C61	118.6 (7)	C62—C12—C22	120.8 (7)
C21—C11—C71	118.7 (7)	C62—C12—C72	122.3 (7)
C61—C11—C71	122.6 (7)	C22—C12—C72	116.9 (7)
C31—C21—C11	121.3 (8)	C32—C22—C12	120.5 (7)
C41—C31—C21	117.6 (7)	C22—C32—C42	117.3 (7)
C31—C41—F11	117.4 (8)	F12—C42—C52	117.2 (7)
C31—C41—C51	124.0 (7)	F12—C42—C32	118.8 (7)
F11—C41—C51	118.6 (8)	C52—C42—C32	124.0 (7)
C61—C51—C41	118.1 (8)	C42—C52—C62	118.0 (7)
C51—C61—C11	120.3 (8)	C12—C62—C52	119.4 (7)
O11—C71—C11	120.9 (7)	O12—C72—C12	122.2 (7)
O11—C71—C81	119.9 (7)	O12—C72—C82	120.3 (7)
C11—C71—C81	119.1 (7)	C12—C72—C82	117.4 (7)
N11—C81—C71	108.5 (6)	N12—C82—C92	113.1 (6)
N11—C81—C91	113.5 (6)	N12—C82—C72	108.3 (6)
C71—C81—C91	108.9 (6)	C92—C82—C72	110.0 (6)
C101—C91—C81	114.2 (6)	C82—C92—C102	116.9 (6)
C91—C101—C111	114.8 (7)	C92—C102—C112	109.1 (7)
C101—C111—C121	113.4 (7)	C102—C112—C122	112.0 (8)
C141—C131—N11	106.1 (6)	C142—C132—N12	104.7 (6)
C131—C141—C151	105.6 (7)	C132—C142—C152	104.7 (7)
C161—C151—C141	103.3 (7)	C142—C152—C162	101.0 (6)
C151—C161—N11	104.3 (6)	N12—C162—C152	104.5 (6)

Table S4. Geometric parameters of compound 4 (3-MEC) [Å, °].

N1—C8	1.493 (2)	C3—C4	1.392 (3)
N1—C10	1.493 (2)	C3—C12	1.511 (2)
O1—C7	1.217 (2)	C4—C5	1.398 (2)
C1—C6	1.400 (3)	C5—C6	1.385 (2)
C1—C2	1.404 (2)	C7—C8	1.531 (2)
C1—C7	1.491 (2)	C8—C9	1.529 (3)
C2—C3	1.393 (2)	C10—C11	1.514 (3)
C8—N1—C10	115.12 (14)	C4—C3—C12	121.10 (15)
C6—C1—C2	119.76 (15)	C2—C3—C12	120.58 (16)
C6—C1—C7	122.11 (14)	C9—C8—C7	109.24 (14)
C2—C1—C7	118.12 (16)	N1—C10—C11	109.67 (15)
C3—C2—C1	121.00 (17)	O1—C7—C1	122.70 (15)
C4—C3—C2	118.31 (15)	O1—C7—C8	119.74 (15)
C3—C4—C5	121.26 (16)	C1—C7—C8	117.48 (15)
C6—C5—C4	120.18 (17)	N1—C8—C9	108.84 (14)
C5—C6—C1	119.47 (15)	N1—C8—C7	110.11 (14)

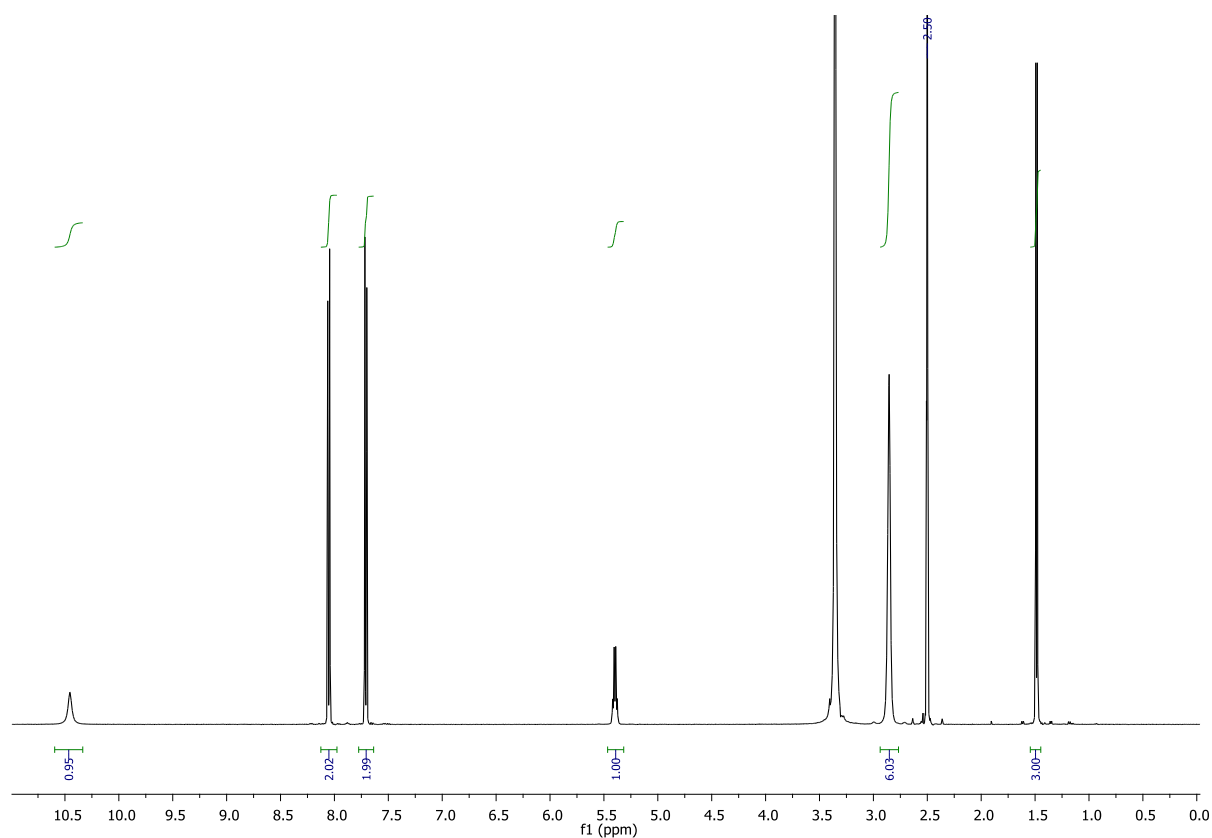


Figure S1. ¹H NMR spectrum of 4-CDC (1); 500MHz, DMSO-d₆, RT.

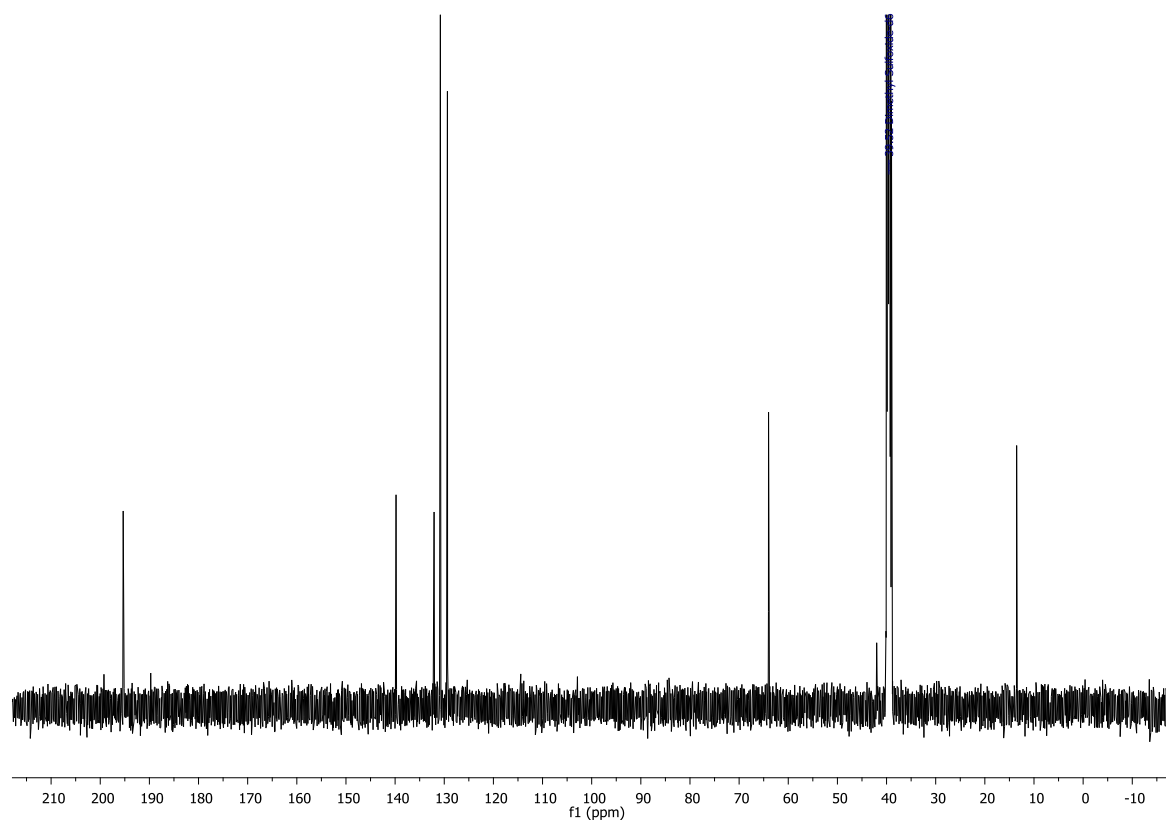


Figure S2. ^{13}C NMR spectrum of 4-CDC (**1**); 126 MHz, DMSO-d_6 , RT.

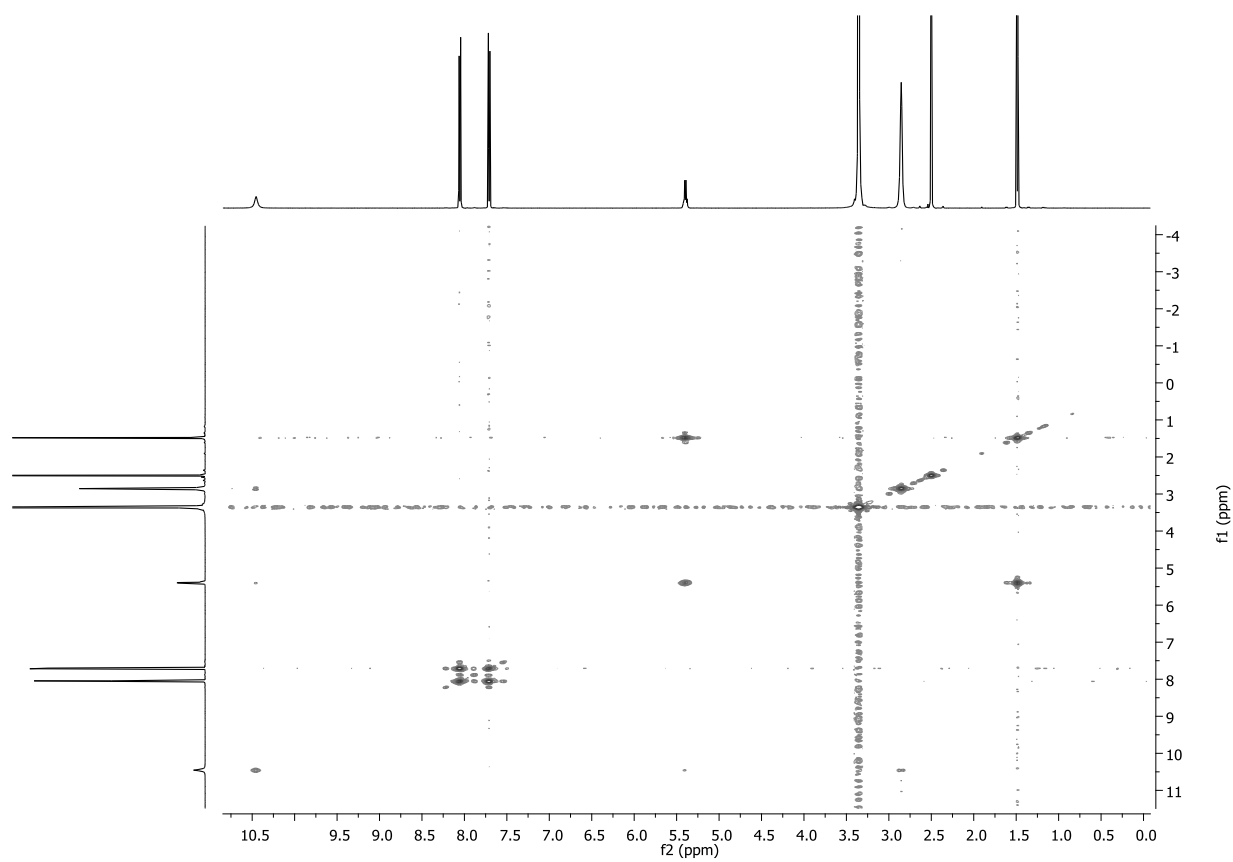


Figure S3. COSY spectrum of 4-CDC (**1**); 500MHz, DMSO-d_6 , RT.

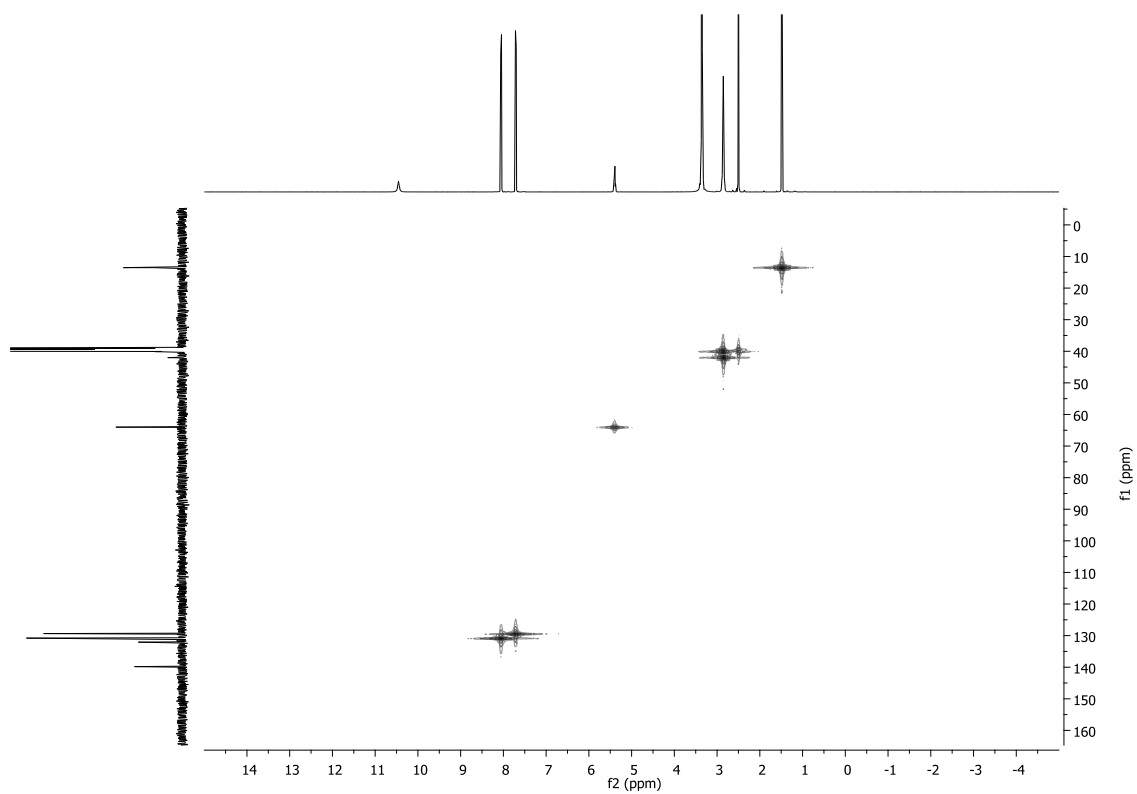


Figure S4. ^1H - ^{13}C HMQC spectrum of 4-CDC (**1**); 500MHz, DMSO- d_6 , RT.

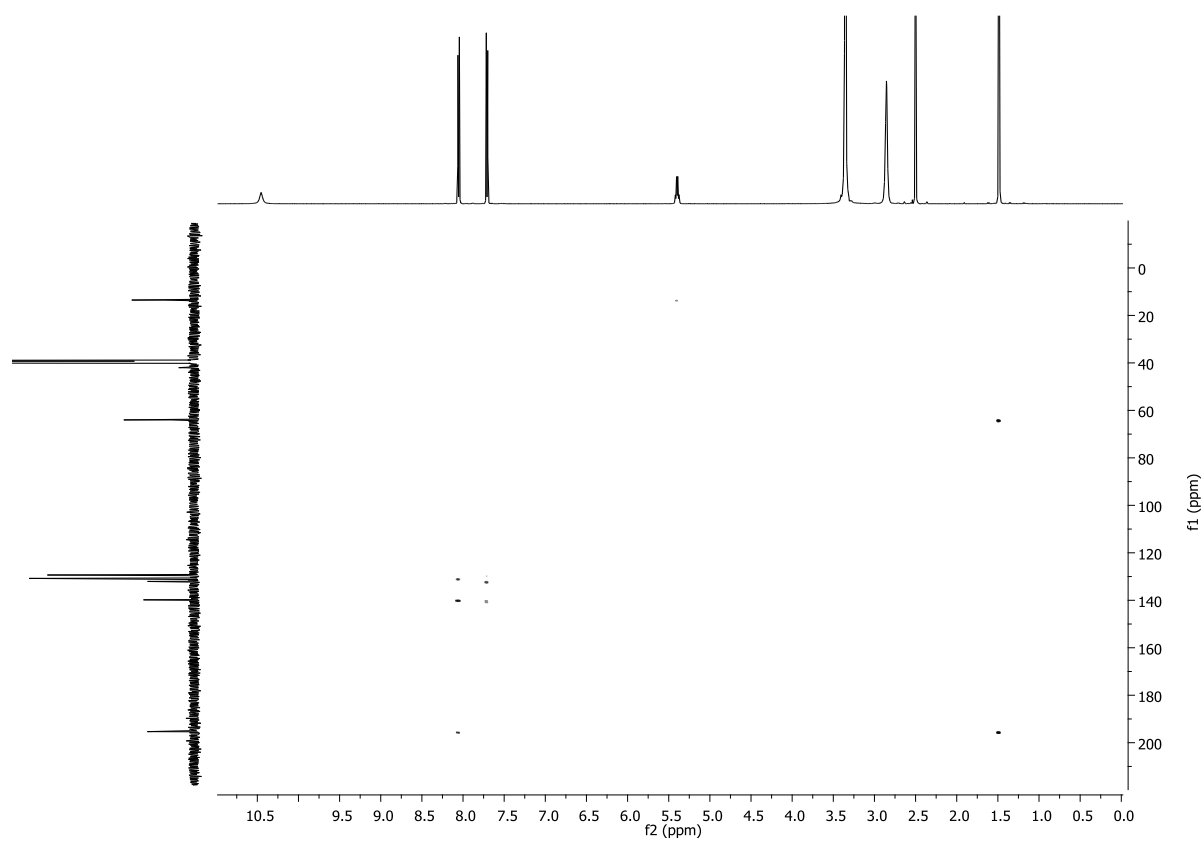


Figure S5. ^1H - ^{13}C HMBC spectrum of 4-CDC (**1**); 500MHz, DMSO- d_6 , RT.

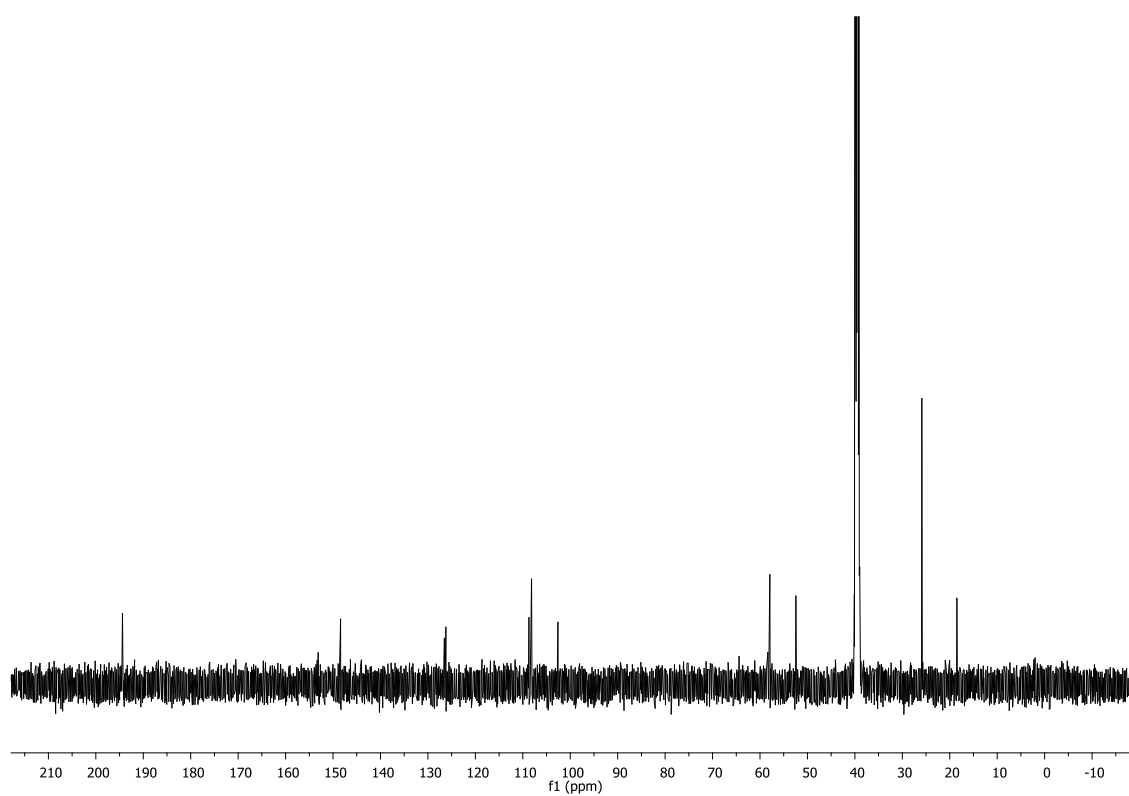


Figure S6. ^{13}C NMR spectrum of MDPT (2); 126 MHz, DMSO-d_6 , RT.

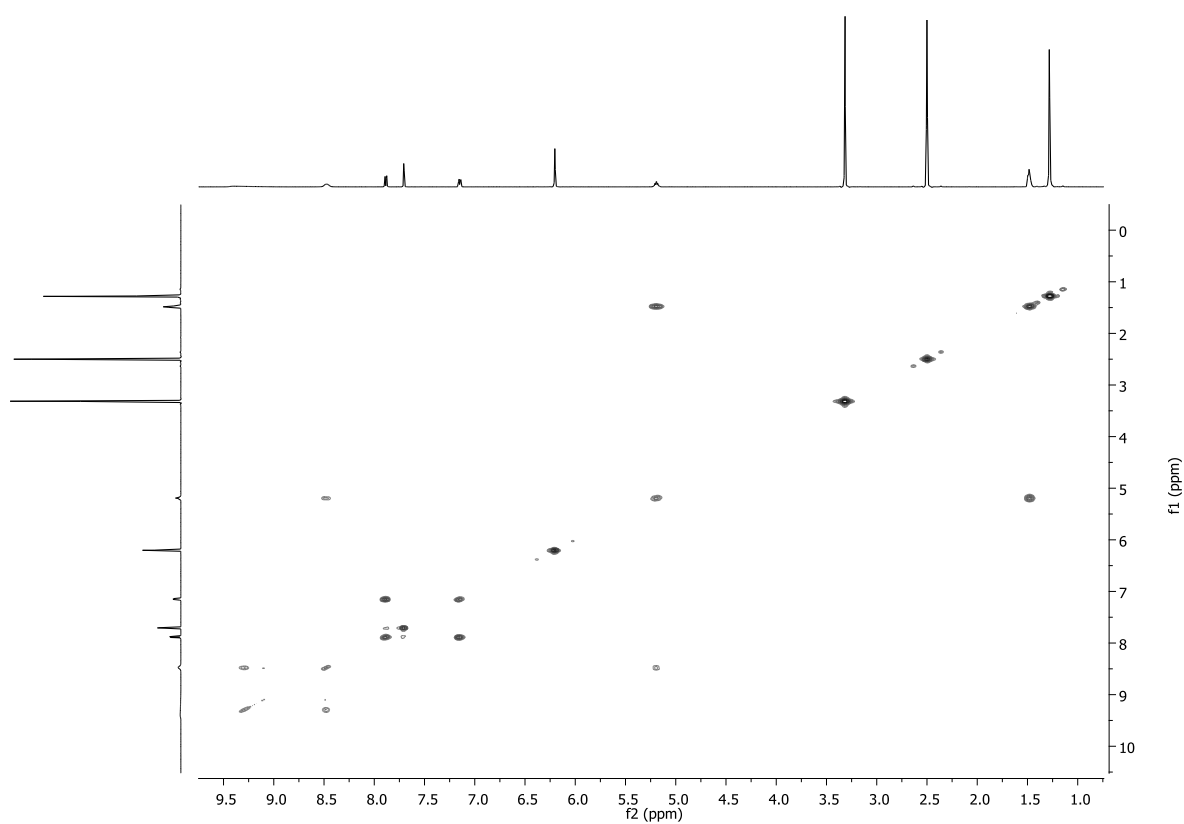


Figure S7. COSY spectrum of MDPT (2); 500MHz, DMSO-d_6 , RT.

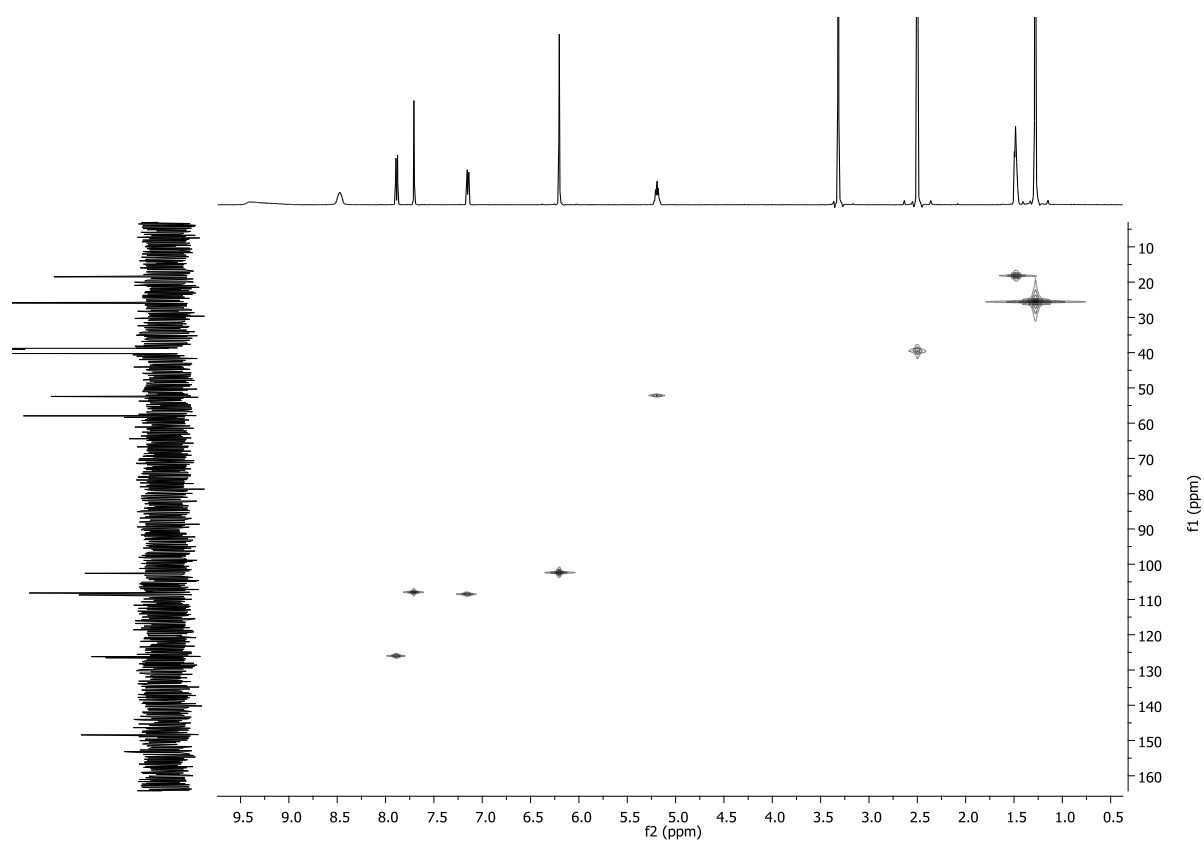


Figure S8. ^1H - ^{13}C HMQC spectrum of MDPT (2); 500MHz, DMSO- d_6 , RT.

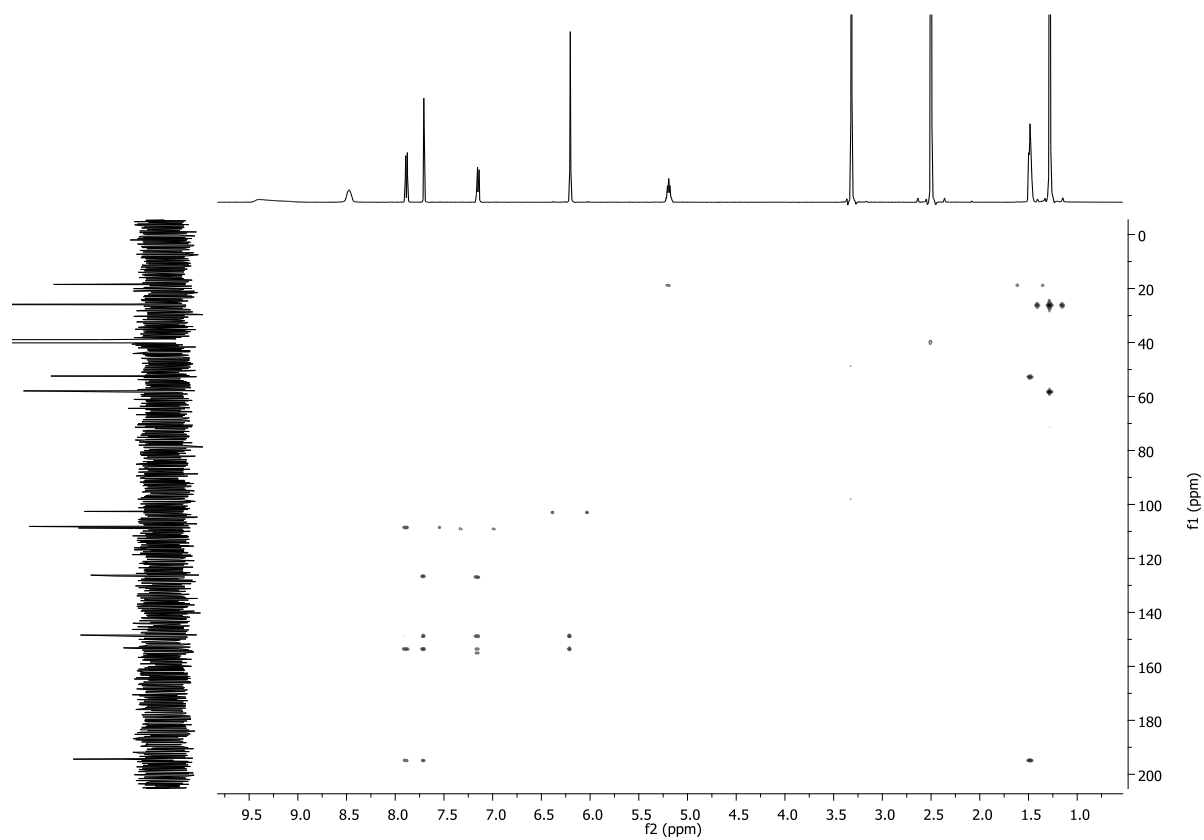


Figure S9. ^1H - ^{13}C HMBC spectrum of MDPT (2); 500MHz, DMSO- d_6 , RT.

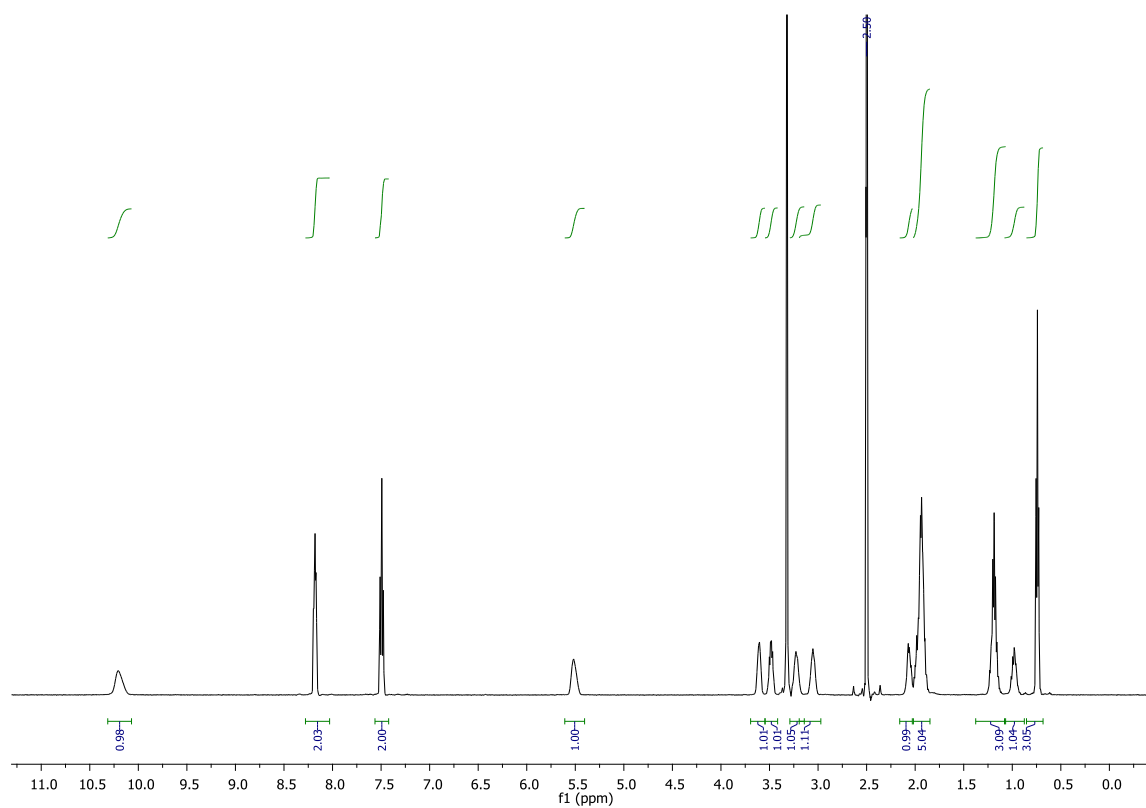


Figure S10. ¹H NMR spectrum of 4F-PHP (3); 500MHz, DMSO-d₆, RT.

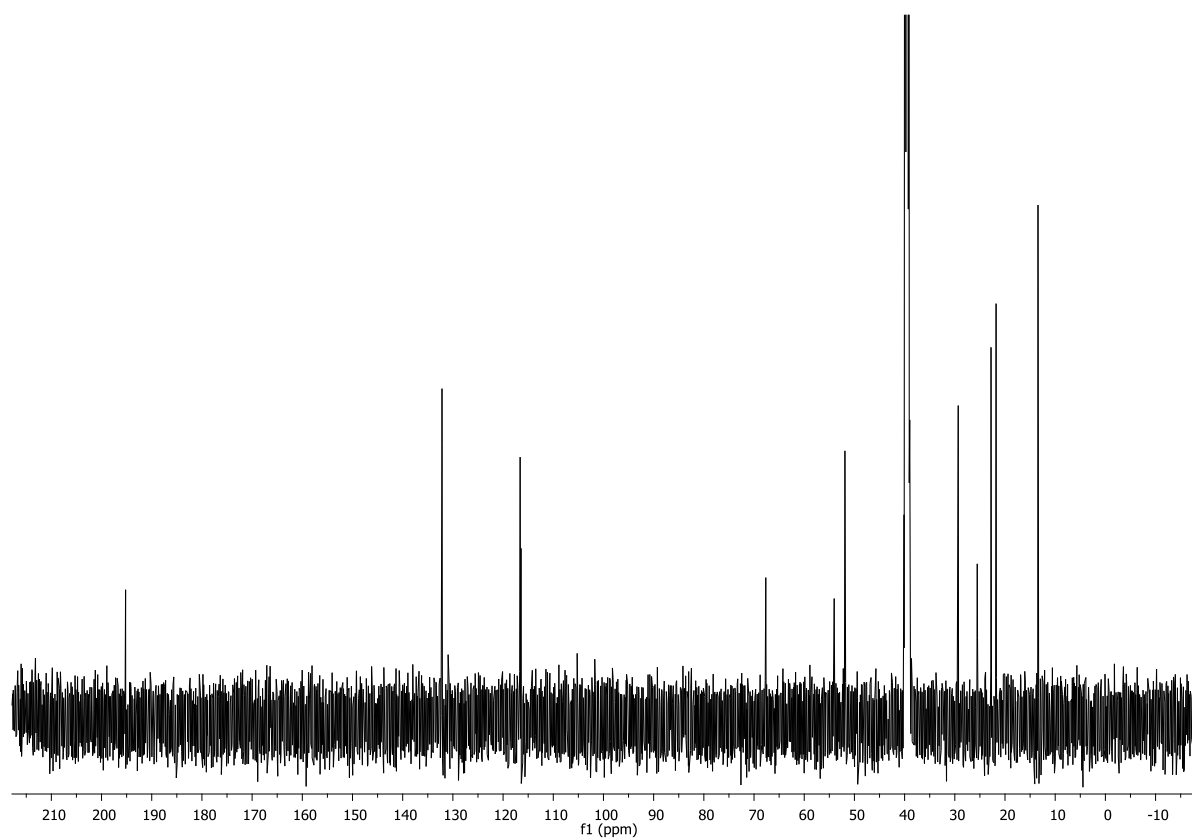


Figure S11. ¹³C NMR spectrum of 4F-PHP (3); 126 MHz, DMSO-d₆, RT.

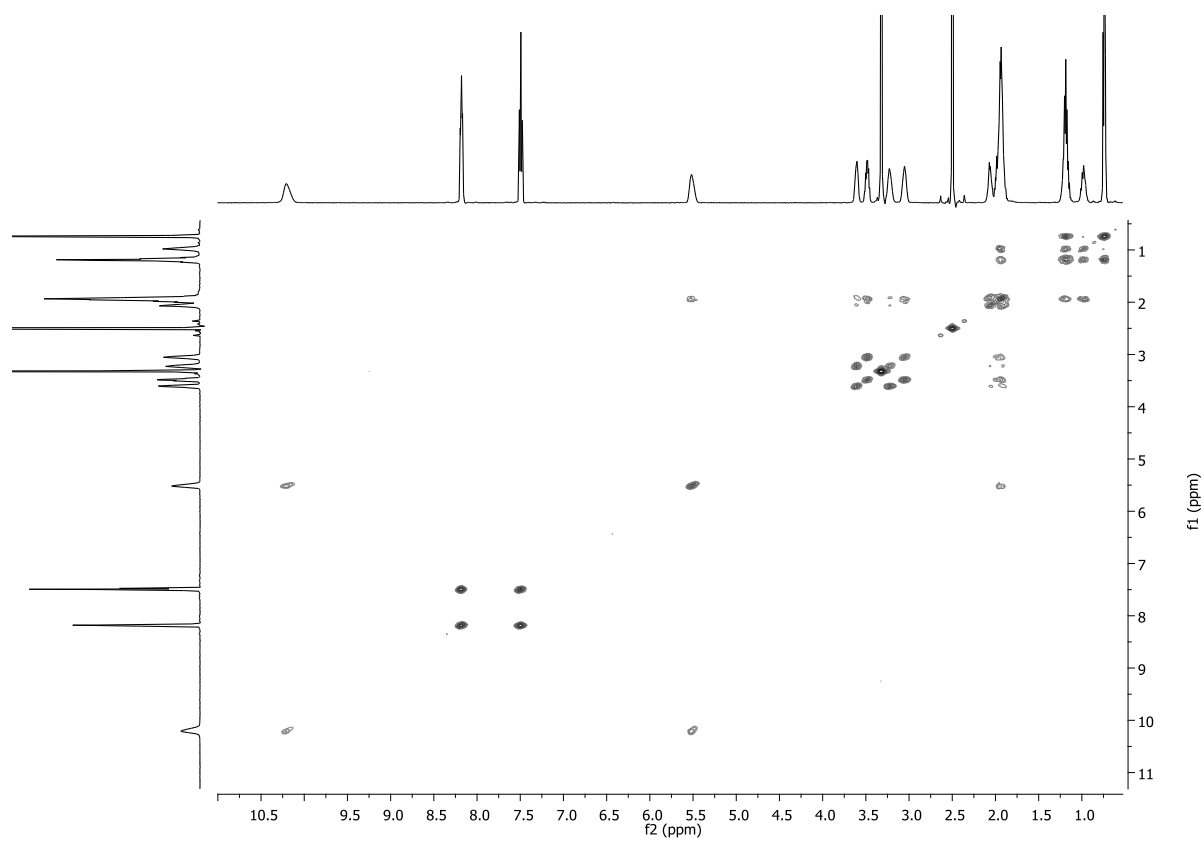


Figure S12. COSY spectrum of 4F-PHP (**3**); 500MHz, DMSO- d_6 , RT.

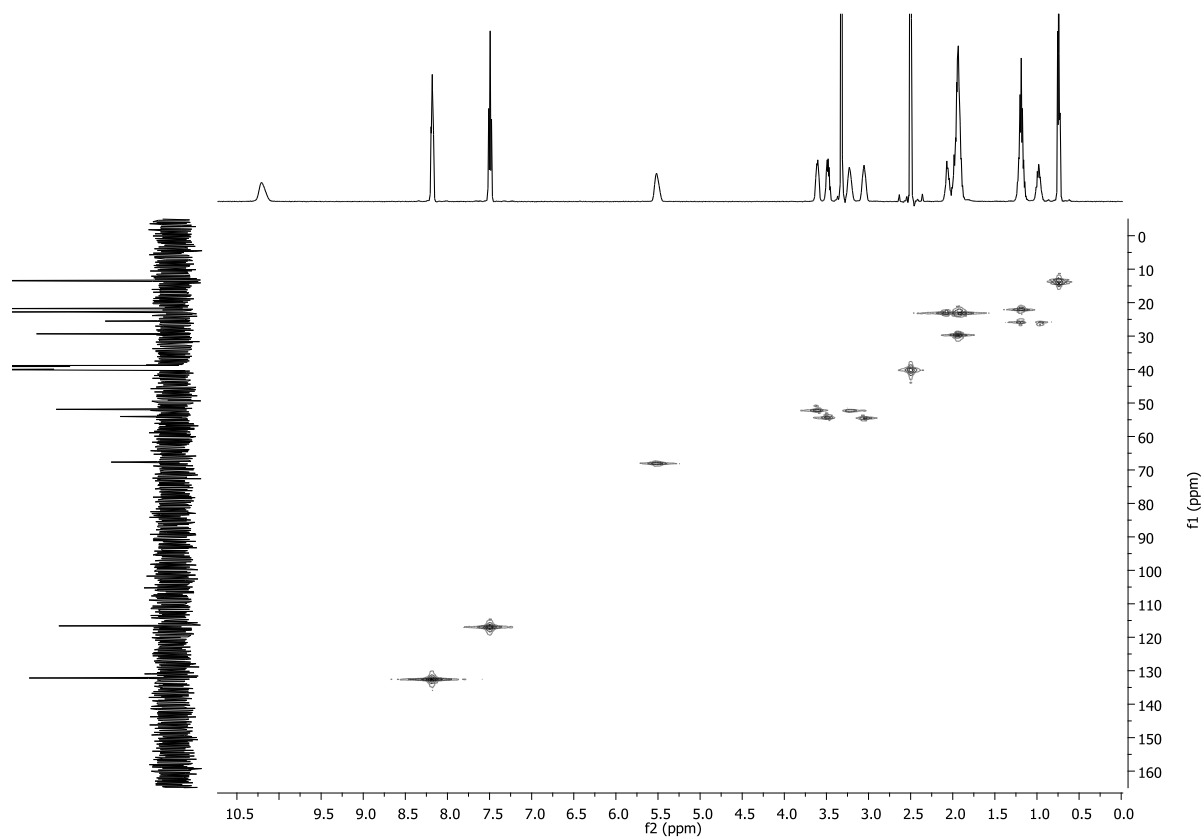


Figure S13. ^1H - ^{13}C HMQC spectrum of 4F-PHP (**3**); 500MHz, DMSO- d_6 , RT.

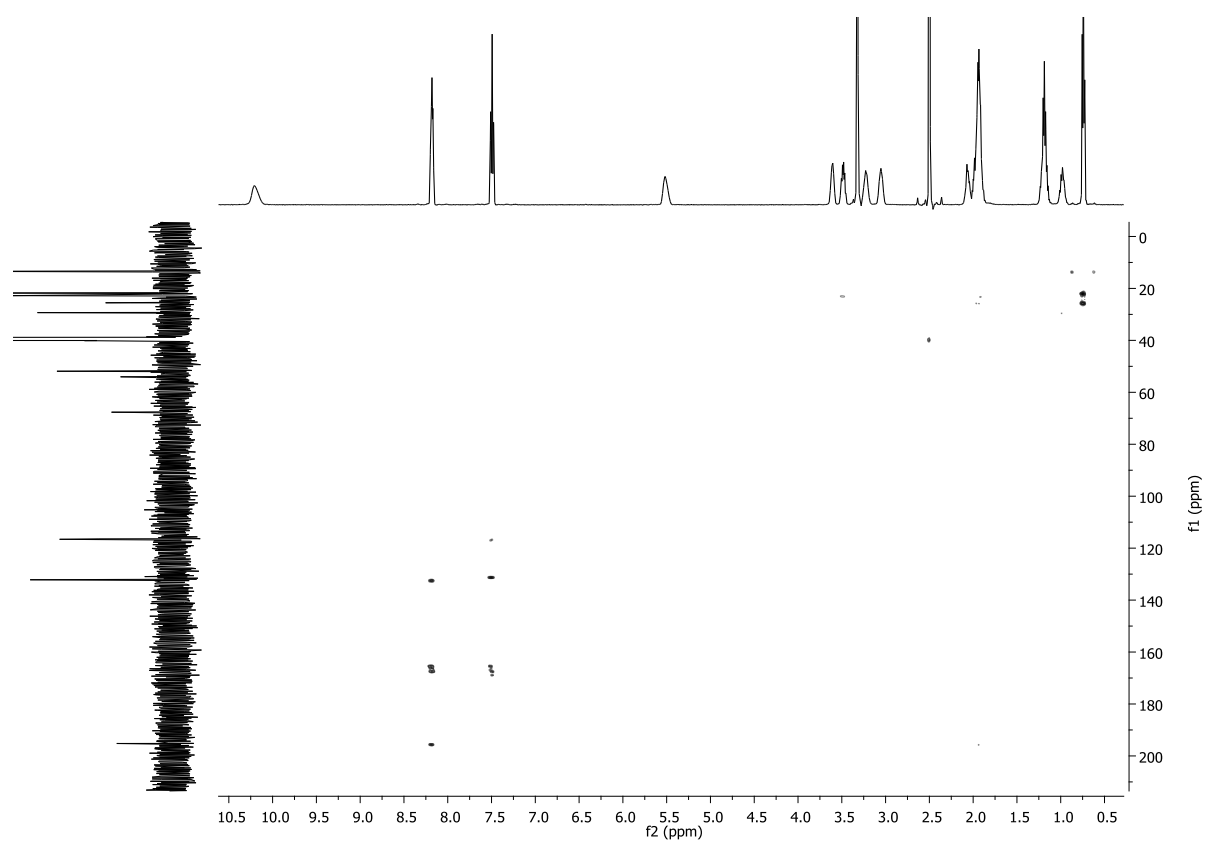


Figure S14. ^1H - ^{13}C HMBC spectrum of 4F-PHP (**3**); 500MHz, DMSO- d_6 , RT.

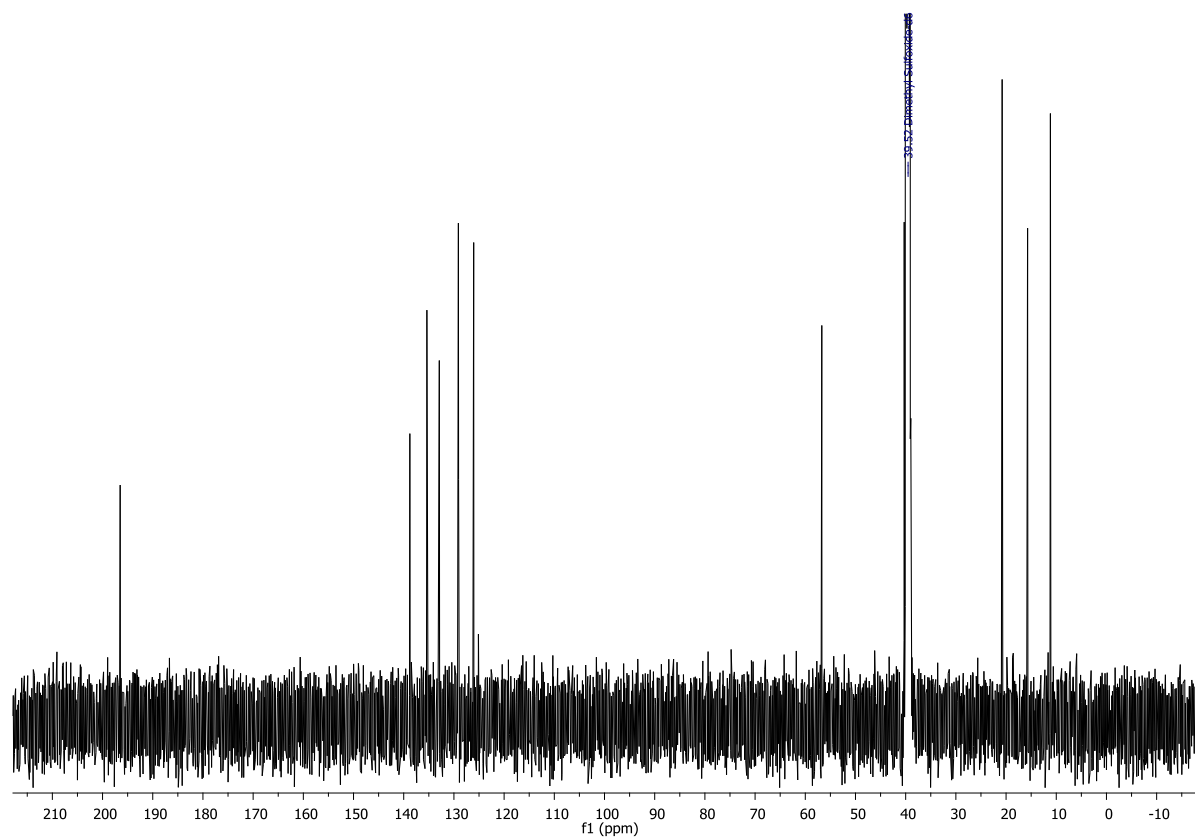


Figure S15. ^{13}C NMR spectrum of 3-MEC (**4**); 126 MHz, DMSO- d_6 , RT.

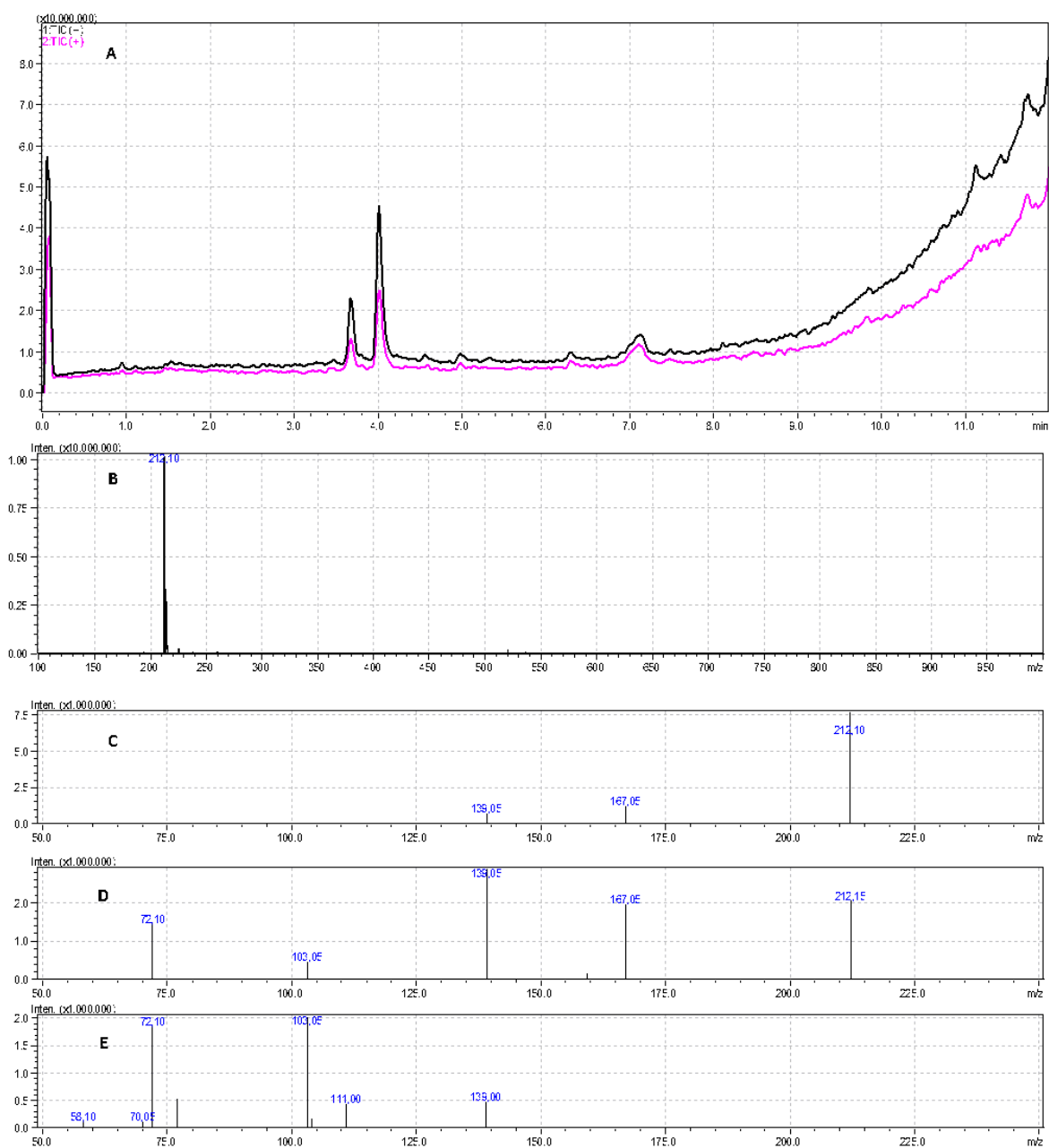


Figure S16. Total ion chromatogram (TIC) of sample with 4-CDC and IS (A); Mass spectrum of precursor ion (B) and Product Ion Scan with collision energy: -10 V, -20V and -35 V respectively (C,D,E).

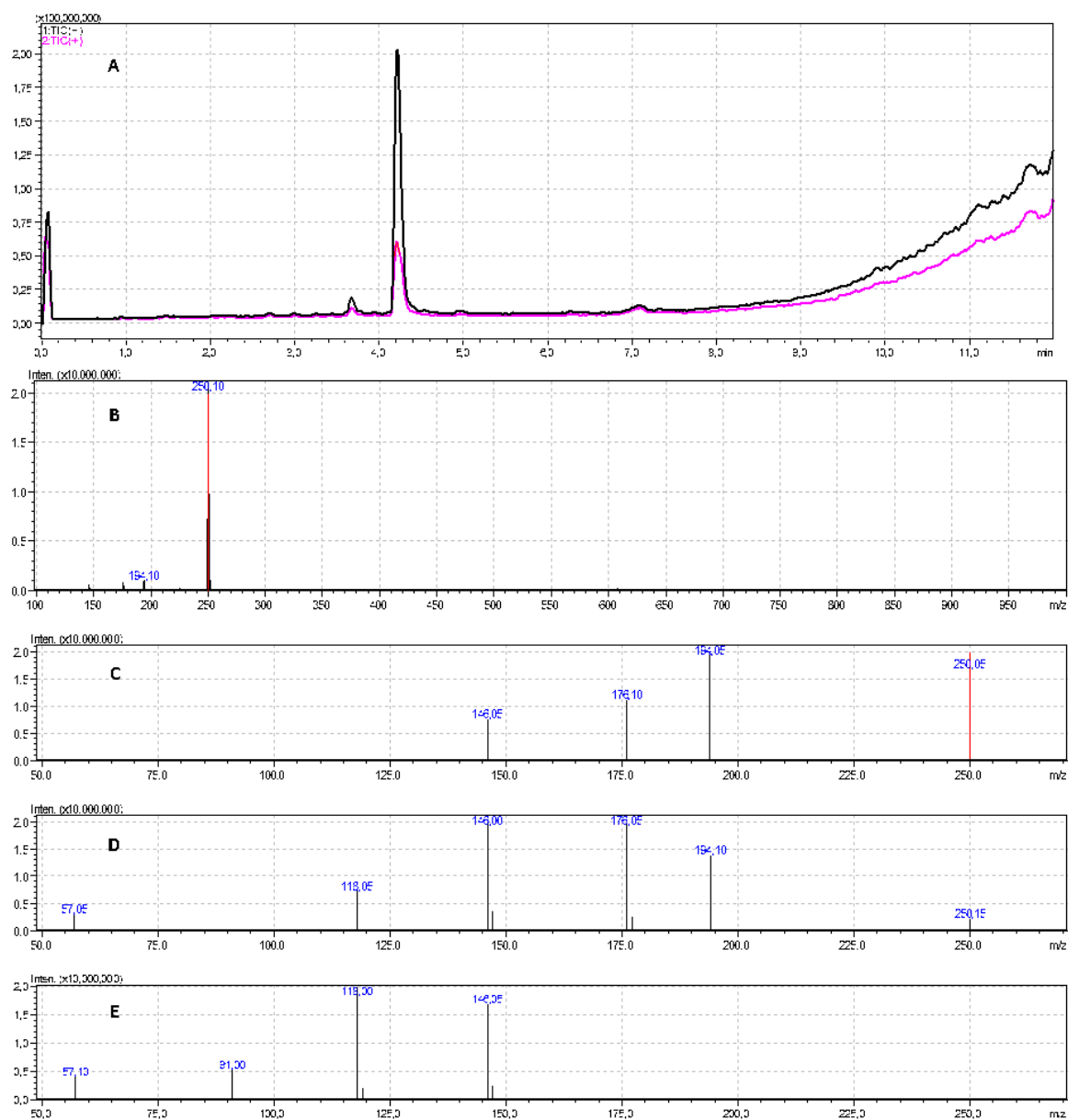


Figure S17. Total ion chromatogram (TIC) of sample with MDPT and IS (A); Mass spectrum of precursor ion (B) and Product Ion Scan with collision energy: -10 V, -20V and -35 V respectively (C,D,E).

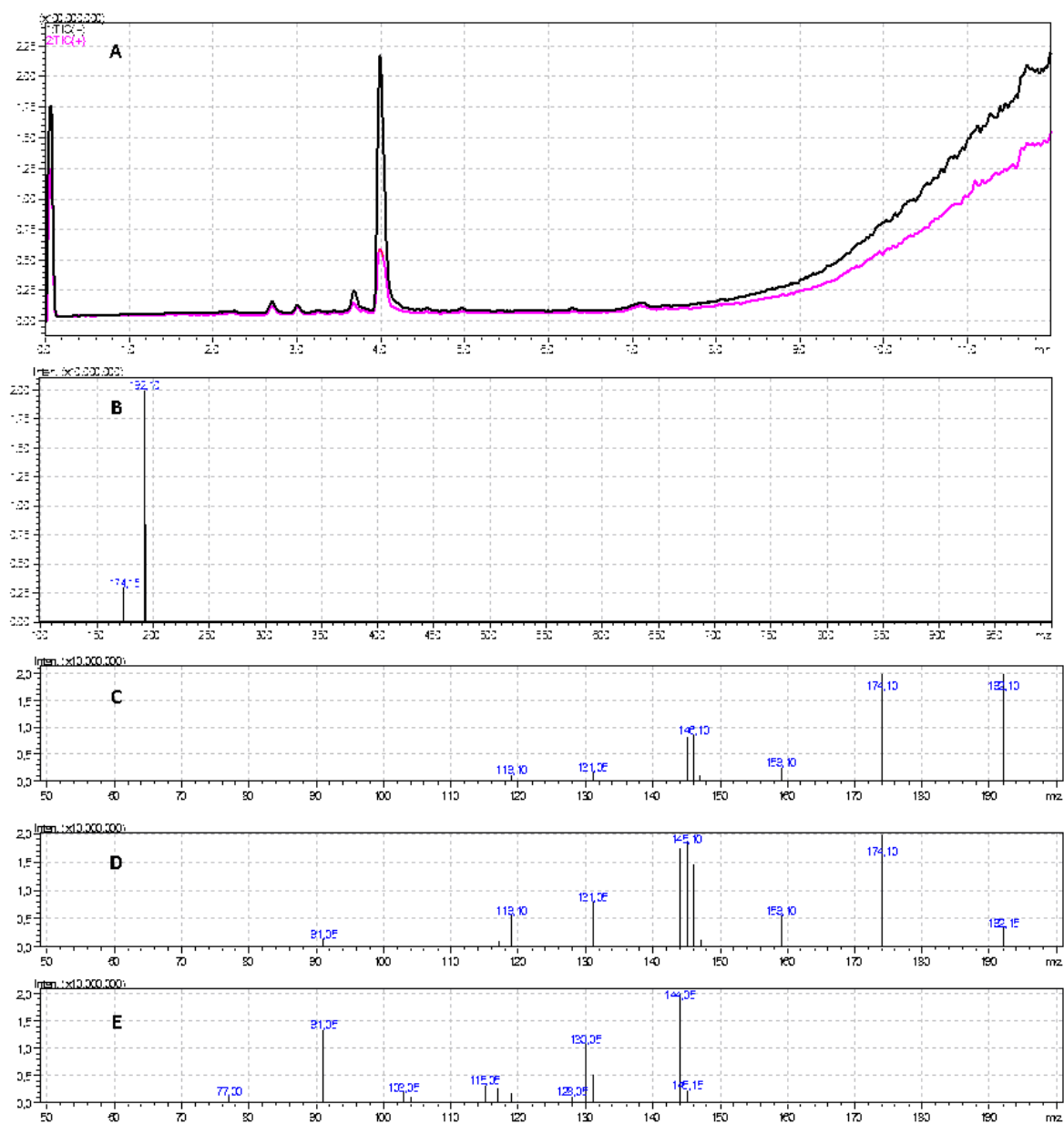


Figure S18. Total ion chromatogram (TIC) of sample with 3-MEC and IS (A); Mass spectrum of precursor ion (B) and Product Ion Scan with collision energy: -10 V, -20V and -35 V respectively (C,D,E).

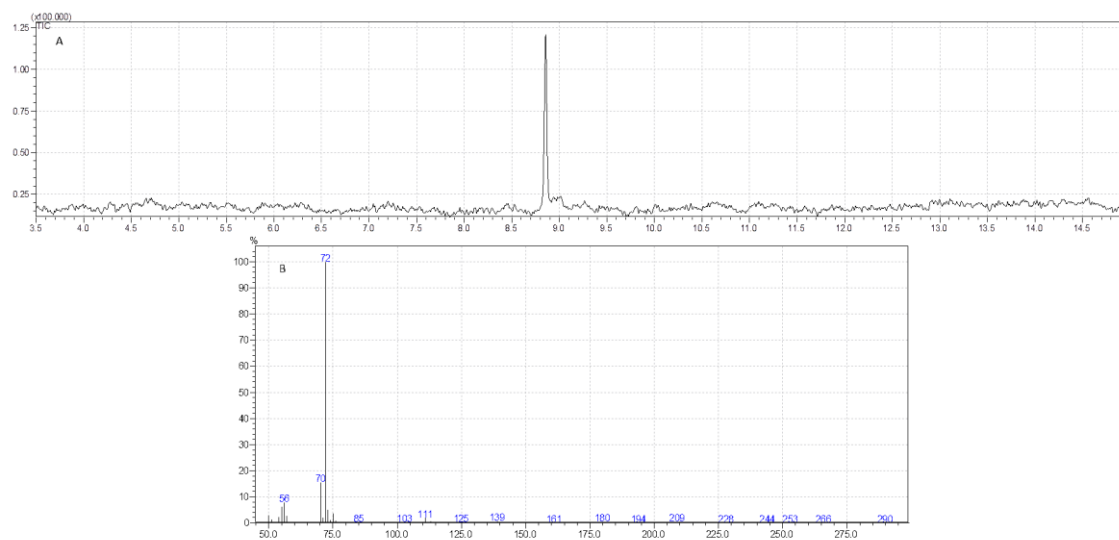


Figure S19. Gas chromatography (A) and mass spectrometry data (B) of 4-CDC (1).

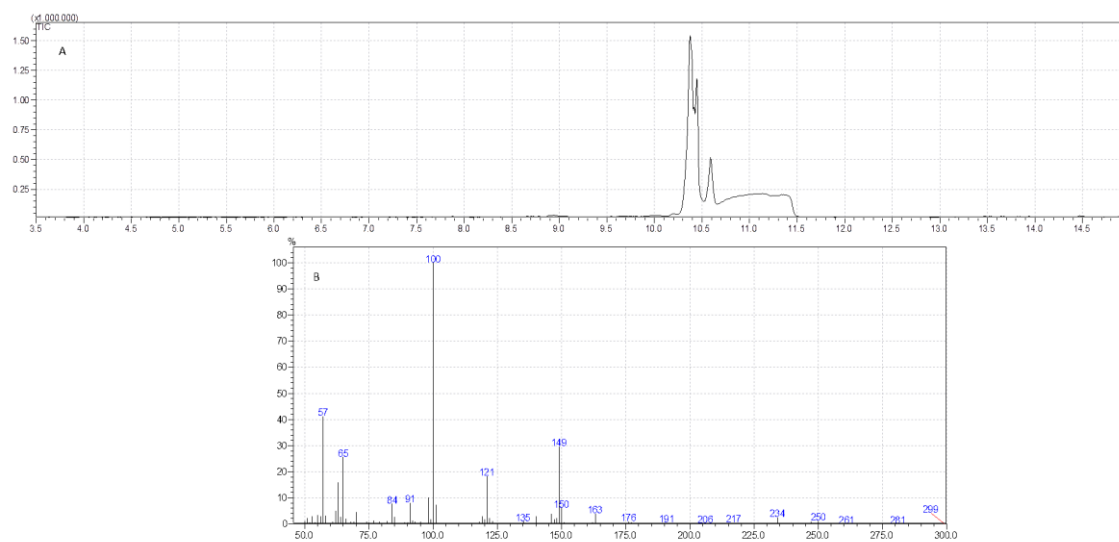


Figure S20. Gas chromatography (A) and mass spectrometry data (B) of MDPT (2).

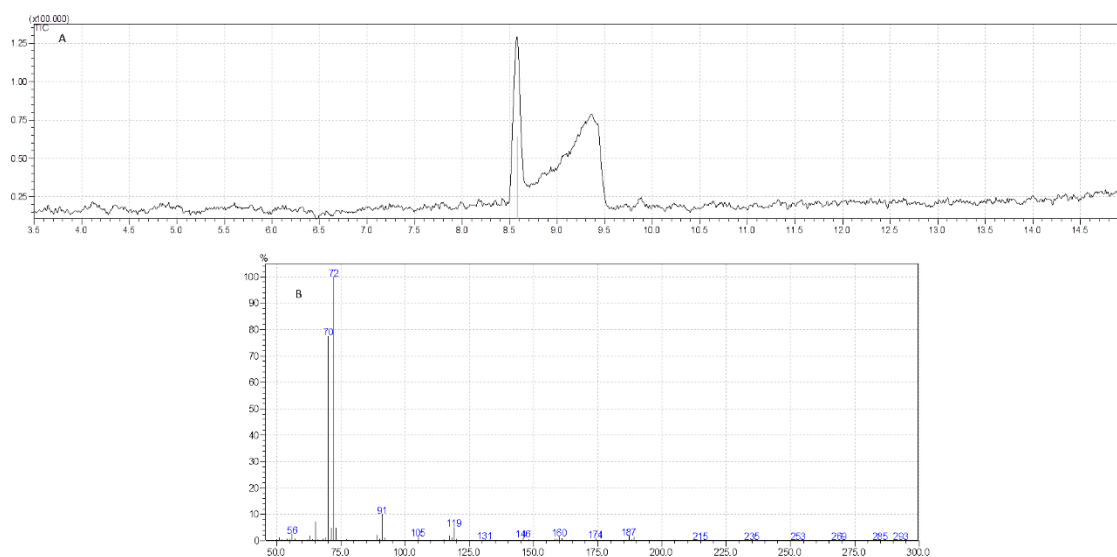


Figure S21. Gas chromatography (A) and mass spectrometry data (B) of 3-MEC(4).