Supporting Information

Dicyanovinyl Heterotetracenes: Synthesis, Solid State Structures and Photophysical Properties

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1. Materials Synthesis.

Tetrahydrofuran was distilled before use. Other Chemicals and solvents were purchased from commercial suppliers and used without further purification.

Synthesis of 8-dicyanovinyl-6H-indolo[1,2-*b*]naphthalene (**NCN**): Compound NCN was obtained as dark-red solid in a similar procedure with BTCN. ^{1}H NMR (400 MHz, D-DMSO, δ): 7.67–7.71 (t, 1H), 7.74–7.77 (t, 2H), 7.87–7.89 (d, 1H), 8.11–8.13 (d, 1H), 8.28–8.30 (d, 1H), 8.41–8.43 (d, 2H), 8.59–8.61 (d, 1H), 8.71 (s, 1H), 12.84 (s, 1H); ^{13}CNMR (100 MHz, D-DMSO, δ): 77.83, 114.70, 114.95, 115.48, 117.22, 120.12, 120.96, 121.00, 121.50, 122.28, 122.80, 126.55, 127.13, 127.52, 128.41, 129.17, 133.39, 138.48, 139.05, 162.49; Elemental analysis calcd (%) for $C_{20}H_{11}N_3$: C, 81.89; H, 3.79; N, 14.33. Found: C, 81.50; H, 4.13; N, 14.45.

Synthesis of 8-formyl-6H-indolo[1,2-*b*]naphthalene (**2b**): Compound 2b was synthesized in a similar procedure with 2a with compound 3b (1.2 g, 4.3 mmol) and PPh_3 (2.8 g, 10.75 mmol). Pure compound 2b was obtained as brown yellow solid (0.8 g, 76%) with column chromatography on silica gel with petroleum ether: ethyl acetate (5:1) as the eluent. EI-MS: *m*/*z*: 245 (M^+). ^{1}H NMR (400 MHz, D-DMSO, δ): 7.57–7.60 (m, 1H), 7.64–7.66 (d, 2H), 7.74–7.76 (d, 1H), 8.02–8.04 (d, 1H), 8.15 (s, 1H), 8.20–8.23 (d, 1H), 8.29–8.31 (d, 1H), 8.53–8.55 (d, 1H), 10.12 (s, 1H), 12.58 (s, 1H); ^{13}CNMR (100 MHz, D-DMSO, δ): 114.47, 117.16, 120.01, 120.10, 120.47, 120.51, 121.60, 122.64, 126.20, 126.58, 128.34, 129.02, 133.08, 133.17, 138.31, 138.56, 193.13. Elemental analysis calcd (%) for $C_{16}H_{10}NO$: C, 82.74; H, 4.34; N, 6.03. Found: C, 82.56; H, 4.47; N, 5.93.

Synthesis of 4-naphthalen-3-nitrobenzaldehyde (**3b**): Compound 3b was obtained in a similar procedure with 3a as yellow solid (1.2 g, 70%). EI-MS: *m*/*z*: 277 (M^+). ^{1}H NMR (400 MHz, CDCl3): δ = 7.39–7.41 (d, 1H), 7.73–7.75 (d, 1H), 7.85–7.92 (m, 4H), 8.13–8.15 (d, 1H), 8.38 (s, 1H), 10.11 (s, 1H); ^{13}C NMR (400 MHz, CDCl3) δ = 125.05, 125.27, 126.89, 127.14, 127.25, 127.83, 128.32, 128.74, 132.31, 133.13, 133.28, 133.60, 135.89, 141.72, 149.77. Elemental analysis calcd (%) for $C_{17}H_{11}NO_3$: C, 73.64; H, 4.00; N, 5.05. Found: C, 73.31; H, 4.37; N, 4.71.

2. Instruments and measurement

^{1}H-NMR (400 MHz) and ^{13}C-NMR (75 and 100 MHz) spectra were obtained on spectrometers using tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) and EI MS were both recorded on a GCT-MS spectrometer. Elemental analyses were performed on an elemental analyzer. Electronic absorption spectra were measured on an UV−vis spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled instruments at R.T. X-ray diffraction measurements were carried out in the reflection mode at R.T. using a X-ray diffraction system.

3. Z-matrices and Cartesian coordinates and computed total energies of compound BTCN and NCN.

The density functional theory (DFT) calculations were performed using Gaussian 03 at the B3LYP/6-31G(d) level. The Z-matrices and Cartesian coordinates and computed total energies of the two compounds are listed.

BTCN. $C_{18}H_9N_3S$ Total Energy = −1253.7513652 a.u. (Hartree).

Z-matrix

C						
C	1	1.40511551				
C	2	1.39277762	1	120.94357004		
C	3	1.39549164	2	118.69814835	1	-0.00080908
C	4	1.42275243	3	120.92738338	2	-0.00076280
C	1	1.38856438	2	120.64152711	3	0.00136888
S	4	1.77535940	3	125.76371613	2	179.99832602
C	7	1.75384455	4	89.97268775	3	179.99870462
C	8	1.39028996	7	112.28003456	4	0.00396388
C	8	1.42131972	7	139.39770967	4	-179.99525731
C	10	1.43684986	8	105.49079809	7	179.99948799
N	9	1.37773169	8	109.23494834	7	179.99898692
C	10	1.40700251	8	135.90394110	7	0.00943088
C	13	1.38094706	10	118.96557626	8	179.99493549
C	14	1.42768827	13	122.35271360	10	-0.00117194
C	11	1.38538756	10	122.55886786	8	179.99968943
C	15	1.44447965	14	116.45987521	13	179.99571064
C	17	1.37254719	15	131.81516683	14	-179.99704042
C	18	1.43292309	17	119.25491796	15	179.99732767

N	19	1.16409171	18	179.69288868	17	0.54596132
C	18	1.42996316	17	125.10273756	15	0.00119289
N	21	1.16467012	18	179.77417183	17	177.13347473
H	1	1.08595733	6	119.69088071	5	179.99628728
H	2	1.08613832	1	119.67170376	6	-179.99484728
H	3	1.08603145	2	120.60965730	1	-179.99886016
H	6	1.08696983	1	120.29676035	2	179.99691031
H	12	1.00851292	9	126.41618280	8	179.98549158
H	13	1.08579987	10	120.55604443	8	-0.00535781
H	14	1.08649464	13	119.29428477	10	180.00000000
H	16	1.08287495	11	120.36240503	10	-179.99805289
H	17	1.08770159	15	114.30307437	14	0.00121084

Cartesian coordinate

C	5.17490800	2.09802100	0.00015800
C	5.95425200	0.92884500	0.00012300
C	5.35750000	-0.32961300	0.00001900
C	3.96436200	-0.41062800	-0.00003300
C	3.16351600	0.76532700	0.00003500
C	3.78830400	2.02426200	0.00011800
S	3.01214700	-1.90902300	-0.00020700
C	1.53235900	-0.96764200	-0.00012400
C	1.77814800	0.40074900	-0.00006200
C	0.12535700	-1.16887600	-0.00008700
C	-0.45057900	0.14749600	-0.00000600
N	0.57805900	1.07745500	-0.00002200
C	-0.73631600	-2.28116000	0.00005900
C	-2.10101100	-2.06992000	0.00015100
C	-2.67152900	-0.76117900	0.00012800
C	-1.81917900	0.36251400	0.00004300
C	-4.11415100	-0.68794500	0.00013600
C	-4.97622900	0.38009400	0.00006700
C	-6.38885900	0.13979200	0.00003900
N	-7.53540200	-0.06157500	0.00007600
C	-4.58236100	1.75474400	-0.00006000
N	-4.26597500	2.87561700	-0.00039300
H	5.66193400	3.06864400	0.00016100
H	7.03772500	1.00488900	0.00024000
H	5.96512100	-1.22975800	0.00001100
H	3.19087200	2.93232500	0.00019600
H	0.45518000	2.07845400	0.00023100
H	-0.33520700	-3.29015600	0.00009400
H	-2.77131600	-2.92500000	0.00026300
H	-2.21488900	1.37049800	0.00007200
H	-4.61149200	-1.65528500	0.00018000

NCN. $C_{20}H_{11}N_3$. Total Energy = –932.9995574 a.u. (Hartree).

Z-matrix

C						
C	1	1.41215750				
C	2	1.38000484	1	120.27533011		
C	3	1.41679059	2	121.25118127	1	0.00046792
C	4	1.43427308	3	118.15228611	2	0.00000000
C	1	1.37962980	2	120.14476646	3	-0.00027363
C	4	1.43271676	3	121.43869484	2	179.99746426
C	7	1.37080360	4	121.68015499	3	-180.00000000
C	8	1.41933395	7	119.27542781	4	0.00049893
C	9	1.40842334	8	119.80856299	7	0.00213587
C	9	1.43780297	8	133.29354359	7	179.99839760
C	11	1.42684994	9	106.75377105	8	-179.99507732
N	10	1.38169040	9	108.86917619	8	-179.99826003
C	11	1.40369498	9	134.55001306	8	0.00243191
C	14	1.38336600	11	119.01541889	9	-179.99391069
C	15	1.42578454	14	122.12828390	11	0.00209539
C	12	1.38656937	11	122.82359120	9	179.99175232
C	16	1.44598598	15	116.31970153	14	179.98699840
C	18	1.37152882	16	131.82742685	15	-179.96980607
C	19	1.43334806	18	119.23194878	16	179.98568250
N	20	1.16400216	19	179.67560711	18	0.56331831
C	19	1.43022847	18	125.18510253	16	-0.01602966
N	22	1.16453029	19	179.59474869	18	-163.67627485
H	1	1.08621194	6	119.97310876	5	-179.99626641
H	2	1.08638543	1	119.69166538	6	179.99607666
H	3	1.08727238	2	120.19858820	1	-179.99765871
H	6	1.08748210	1	119.45076376	2	179.99966421
H	7	1.08658526	4	118.10263700	3	-0.00051429
H	8	1.08635984	7	120.61479684	4	179.99930054
H	13	1.00823792	10	125.74292436	9	-179.96368043
H	14	1.08613029	11	120.69680672	9	0.00593095
H	15	1.08649143	14	119.42073773	11	-179.99569658
H	17	1.08281758	12	120.54911960	11	-179.99794758
H	18	1.08767249	16	114.26386780	15	0.02874990

Cartesian coordinate

C	4.88521300	2.31802200	-0.00017500
C	5.89931700	1.33528000	-0.00037800
C	5.56955800	-0.00474700	-0.00039400
C	4.21779400	-0.42904600	-0.00021900
C	3.19342000	0.57484500	-0.00002000
C	3.55741400	1.94341800	0.00000300
C	3.87088800	-1.81913000	-0.00028900

C	2.56474200	-2.23516500	-0.00012100
C	1.52766700	-1.26615300	0.00011800
C	1.85043600	0.10478700	0.00013400
C	0.09278000	-1.35767700	0.00030300
C	-0.40466000	-0.02034600	0.00038900
N	0.68019900	0.83937100	0.00042400
C	-0.82628300	-2.41865900	0.00036200
C	-2.17999400	-2.13375900	0.00043000
C	-2.67332700	-0.79604300	0.00039800
C	-1.75877900	0.27787600	0.00040200
C	-4.11118900	-0.64298000	0.00018300
C	-4.91252500	0.47010200	-0.00044200
C	-6.33660500	0.30736700	-0.00081300
N	-7.49231400	0.16866700	-0.00104700
C	-4.44538200	1.82189000	-0.00073400
N	-4.07250300	2.92510700	0.00134000
H	5.15200100	3.37096100	-0.00009400
H	6.94252300	1.63852000	-0.00058200
H	6.35136700	-0.76035000	-0.00051200
H	2.78569100	2.70961700	0.00016400
H	4.67691700	-2.54781700	-0.00049000
H	2.32134300	-3.29390700	-0.00018900
H	0.61644300	1.84559100	-0.00002000
H	-0.48339600	-3.44924500	0.00035200
H	-2.89716100	-2.94993000	0.00054700
H	-2.09570500	1.30694100	0.00043500
H	-4.66060900	-1.58168600	0.00056600

4. Single-crystal X-ray analysis of compound BTCN and NCN.

The measurements about BTCN and NCN were made on a diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 113(2) K. Their structures were solved and defined by direct methods and SHELXS-97. Hydrogen atoms were located at the calculated positions. Absorption correction was applied using semi-empirical from equivalents.

Crystal data for **BTCN**: $C_{18}H_9N_3S$ (299.34), dark red plate, crystal size 0.36 × 0.32 × 0.10 mm^3; *triclinic*, space group P–1; a = 7.4403(15), b = 9.4488(19), c = 10.329(2) Å; α = 74.08(3), β = 75.46(3), γ = 82.38(3); V = 674.3(2) $Å^3$; Z = 2, ρ_{calcd} = 1.474 g cm^{-3}; μ = 0.238 mm^{-1}; T = 173(2) K; 8276 data (3096, R_{int} = 0.0287, 2.67 ≤ θ ≤ 27.47); GOF = 1.076; 199 parameters; R_1 = 0.0469, wR_2 = 0.1043 for all reflections.

Crystal data for **NCN**: $C_{20}H_{11}N_3$ (293.32), red plate, crystal size 0.35 × 0.18 × 0.05 mm^3; *triclinic*, space group P -1; a = 7.4759(15), b = 9.3116(19), c = 10.642(2) Å; α = 76.16(3), β = 74.69(3), γ = 81.38(3); V = 690.8(2) $Å^3$, Z = 2, ρ_{calcd} = 1.410 g cm^{-3}; μ = 0.086 mm^{-1}; T = 173(2) K; 7061 data (2424, R_{int} = 0.0296, 2.70 ≤ θ ≤ 25.00); GOF = 1.121; 208 parameters; R_1 = 0.0526, wR_2 = 0.1050 for all reflections.

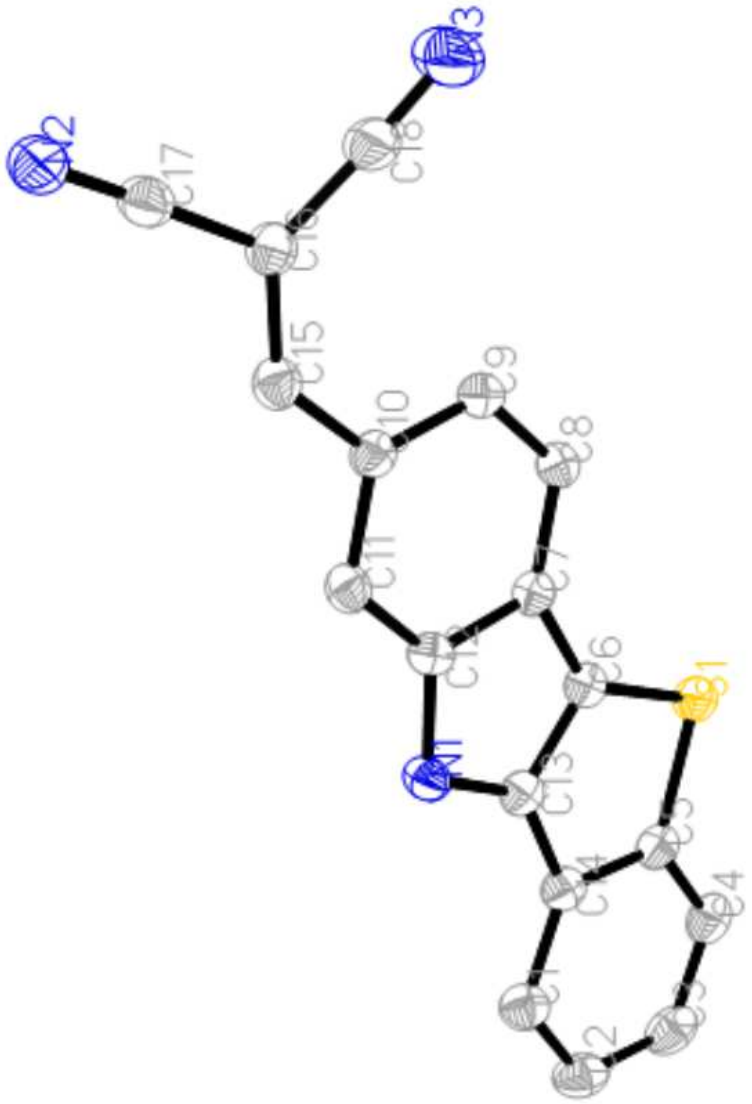


Figure S1. ORTEP drawing of BTCN (50% probability for thermal ellipsoids).

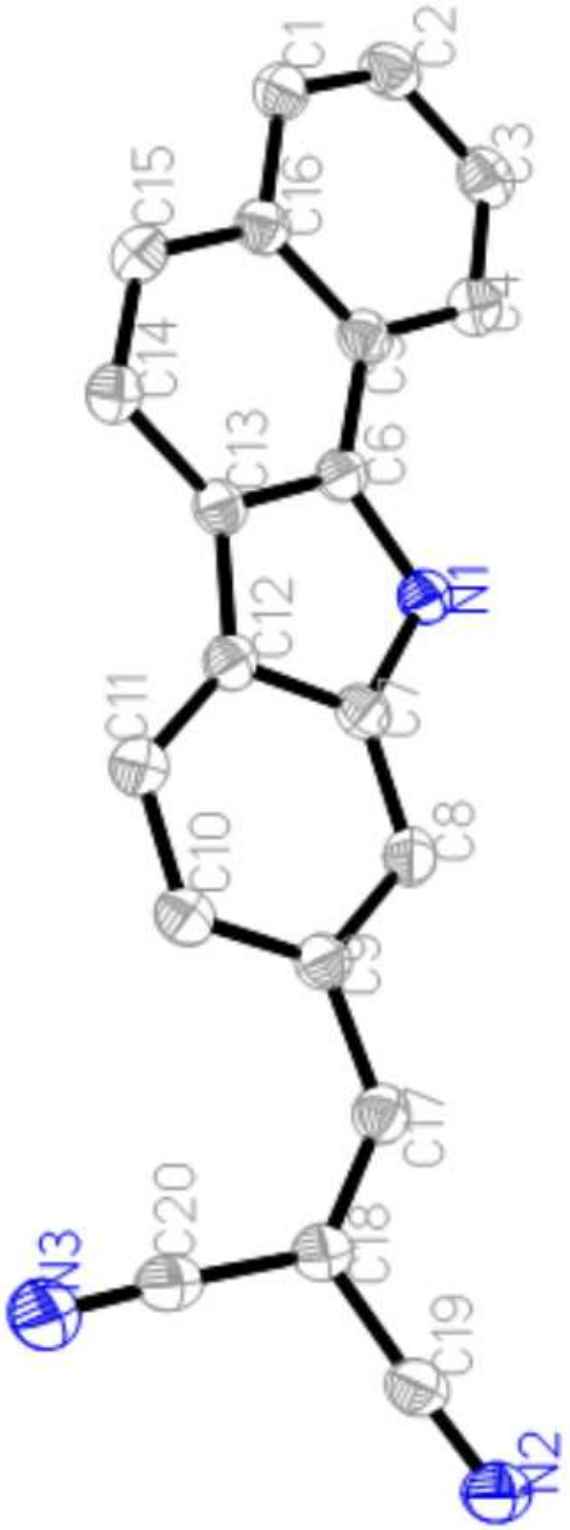


Figure S2. ORTEP drawing of BTCN (50% probability for thermal ellipsoids).

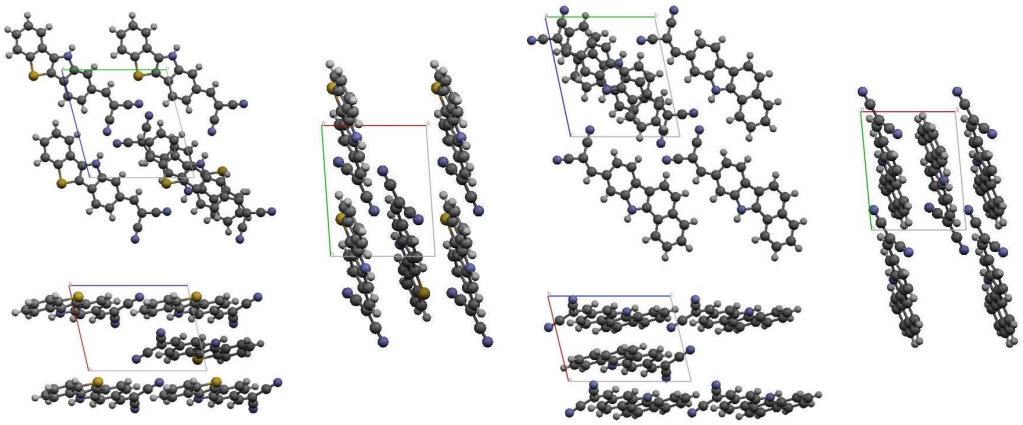


Figure S3. Stacking structures of BTCN (left) and NCN (right), view down a, b, c axis, respectively.

5. Photophysical properties of BTCN and NCN.

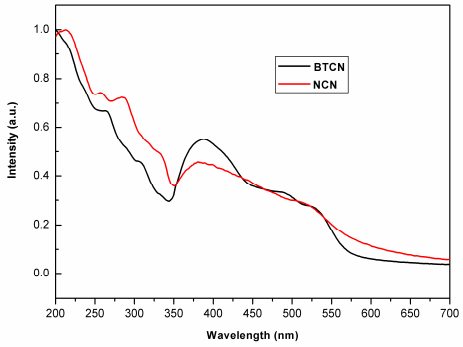


Figure S4. UV−vis spectra of BTCN and NCN in the thin films.

Figure S5. UV−vis of BTCN (left) and NCN (right) in different solvents.

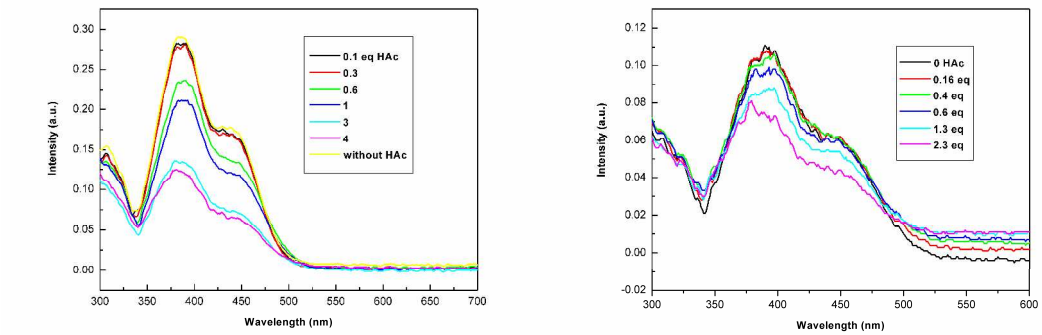


Figure S6. Absorption changes of BTCN (left) and NCN (right) in CH_2Cl_2 upon addition of HAc. For NCN, 10^{-2} M methanol was added to increase the polarity of the solution.

6. Cyclic voltammograms.

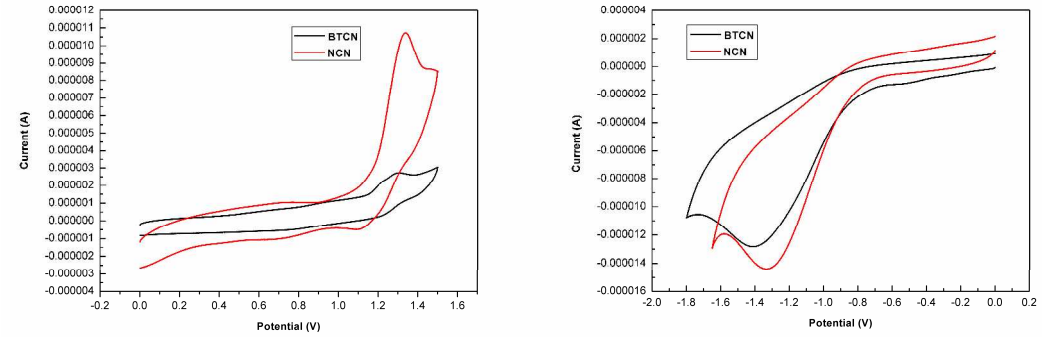
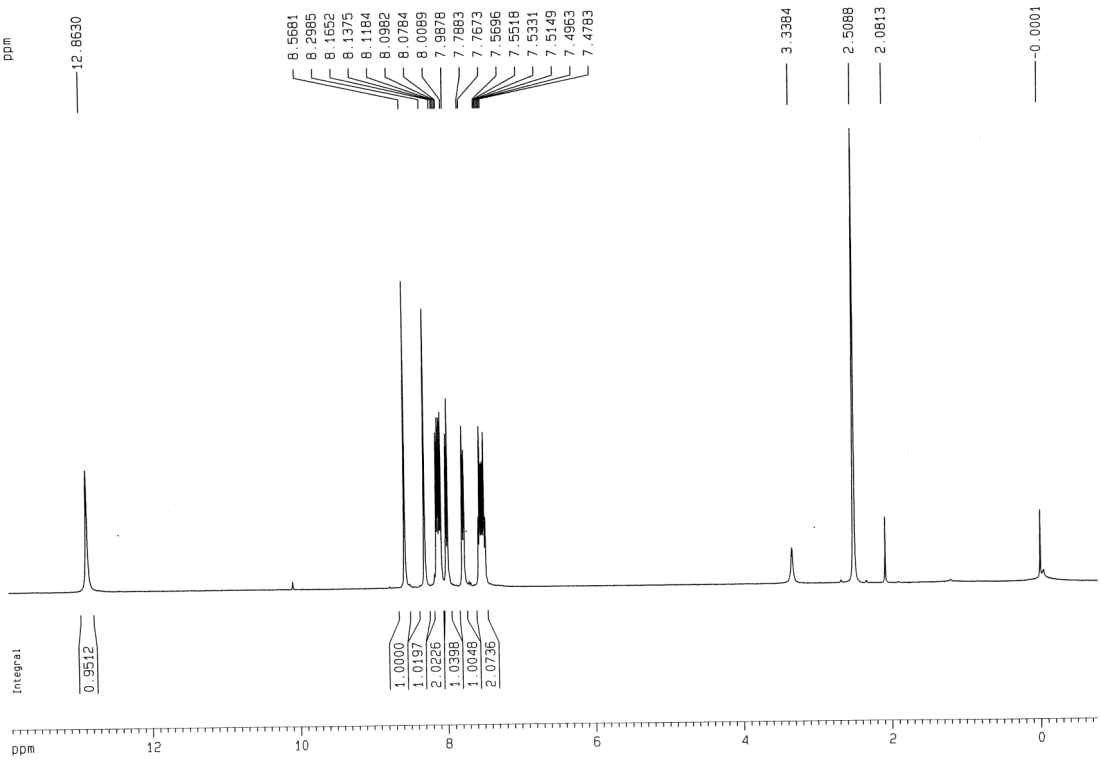
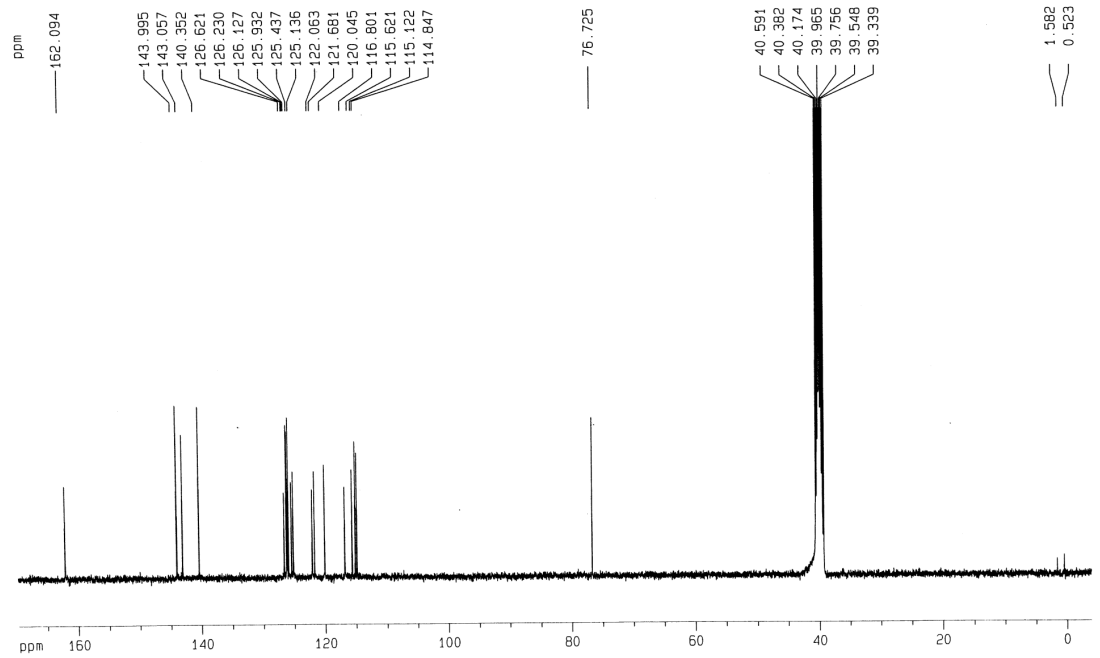


Figure S7. Cyclic voltammograms of BTCN (black) and NCN (red) measured in CH_2Cl_2 solution, containing 0.1 M n-Bu_4NPF_6 at 20 °C.

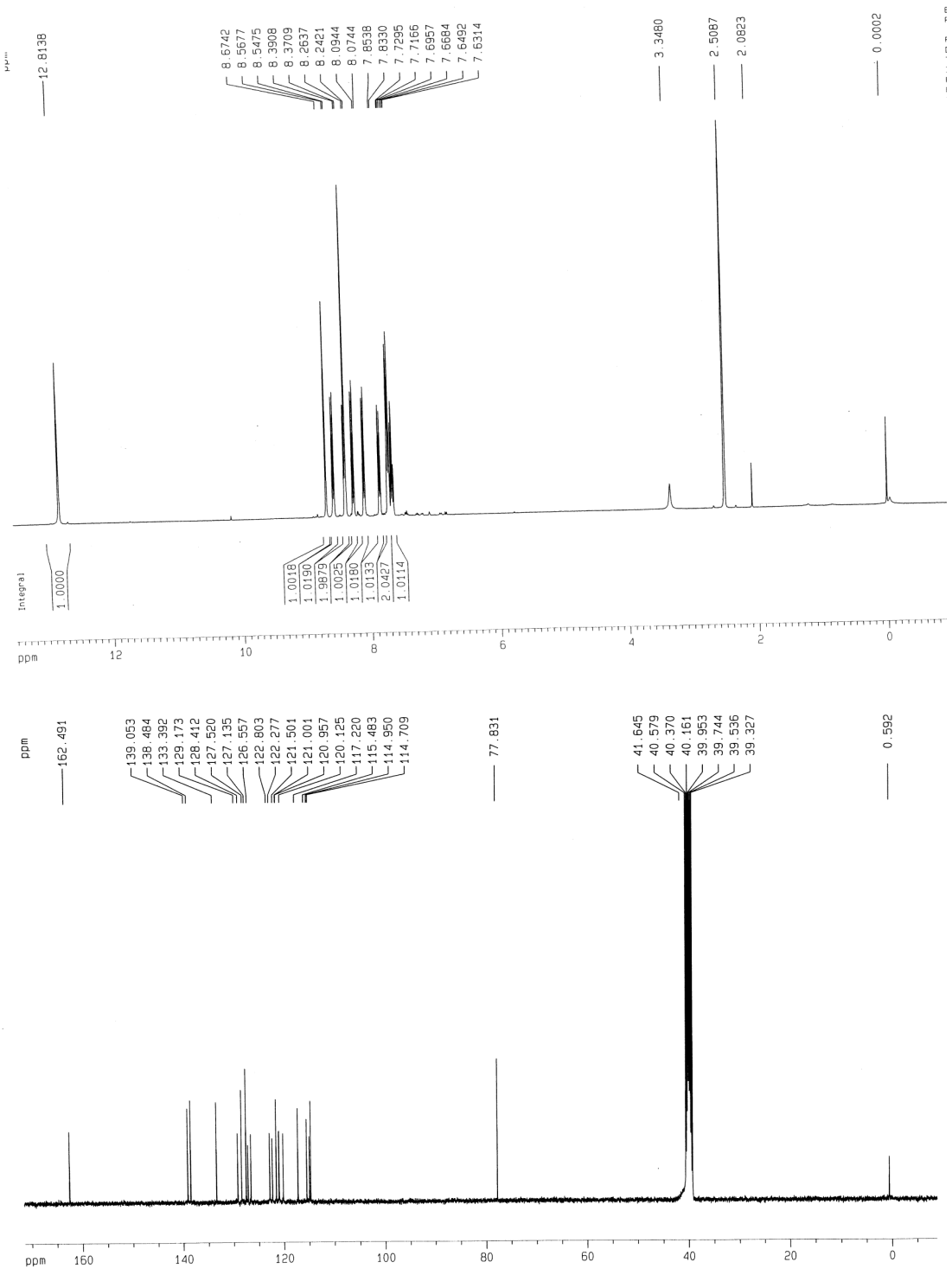
7. ^{1}H NMR and ^{13}C NMR spectra of the new compounds.

^{1}H NMR and ^{13}C NMR of BTCN.

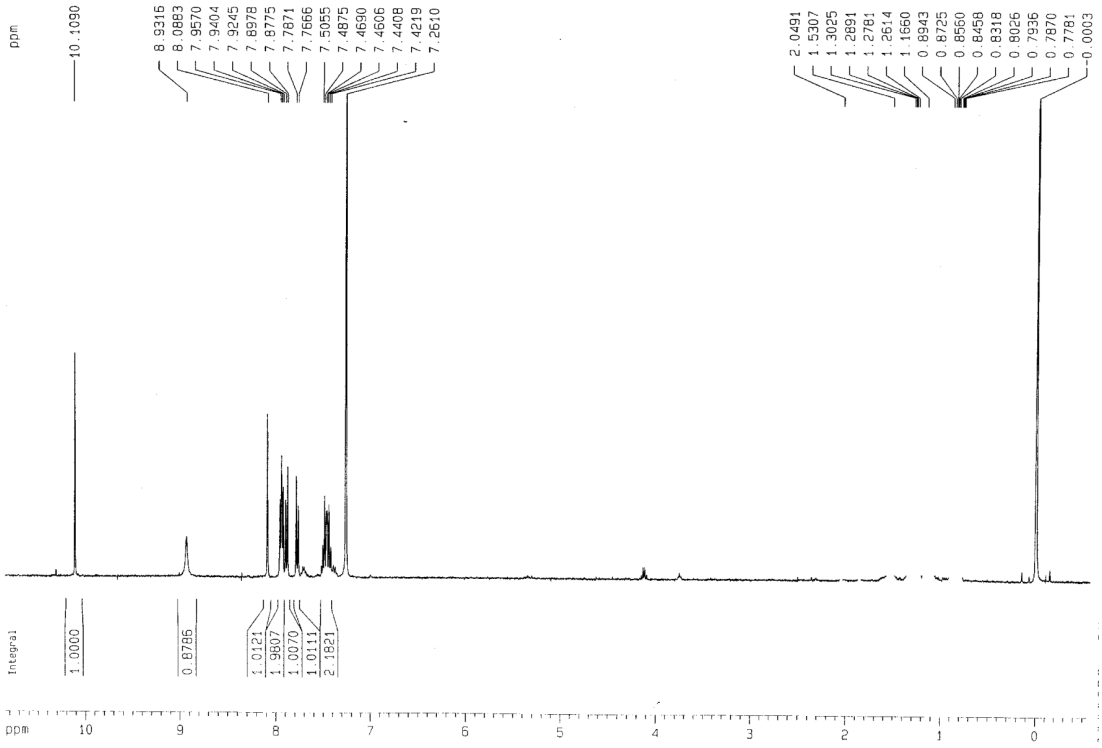


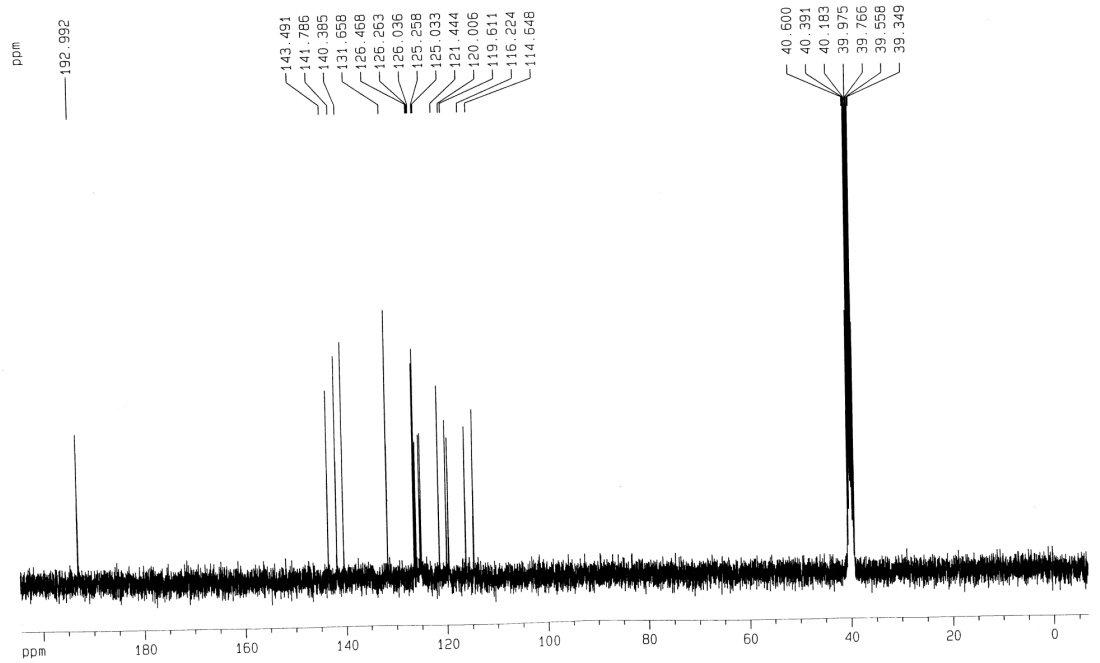


^{1}H NMR and ^{13}C NMR of NCN.

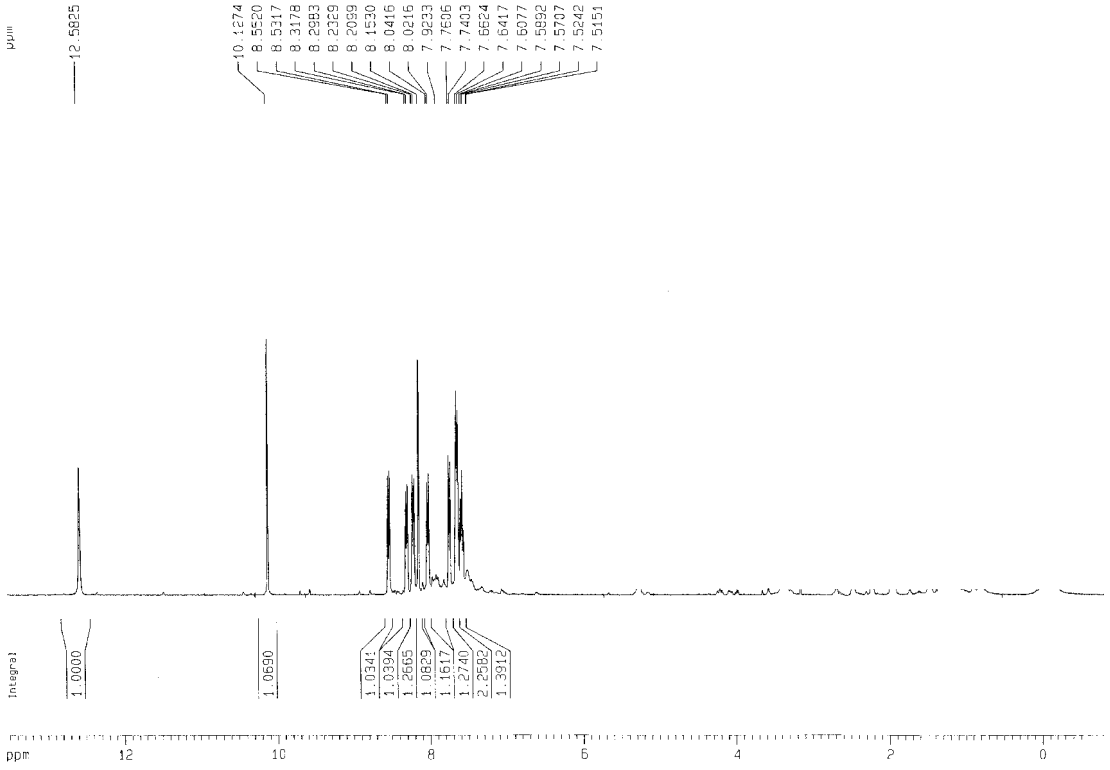


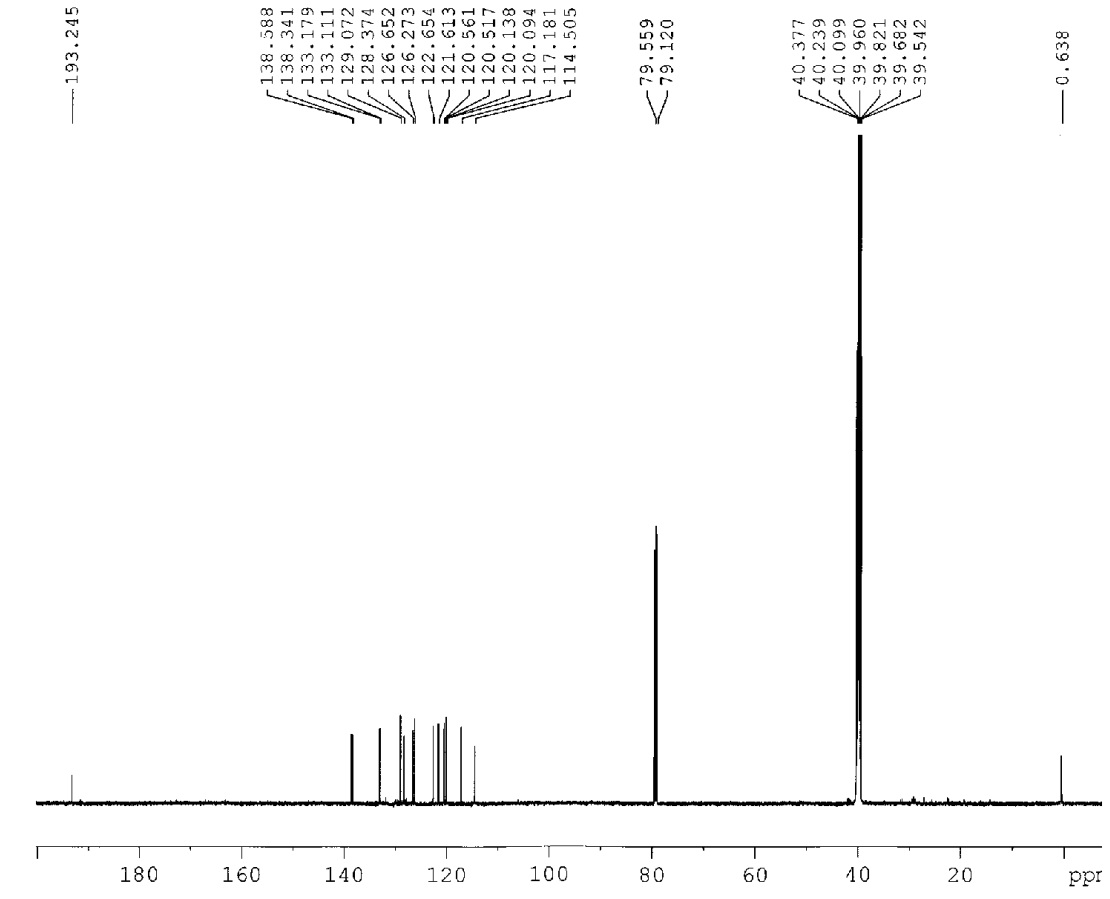
^{1}H NMR and ^{13}C NMR of compound 2a.



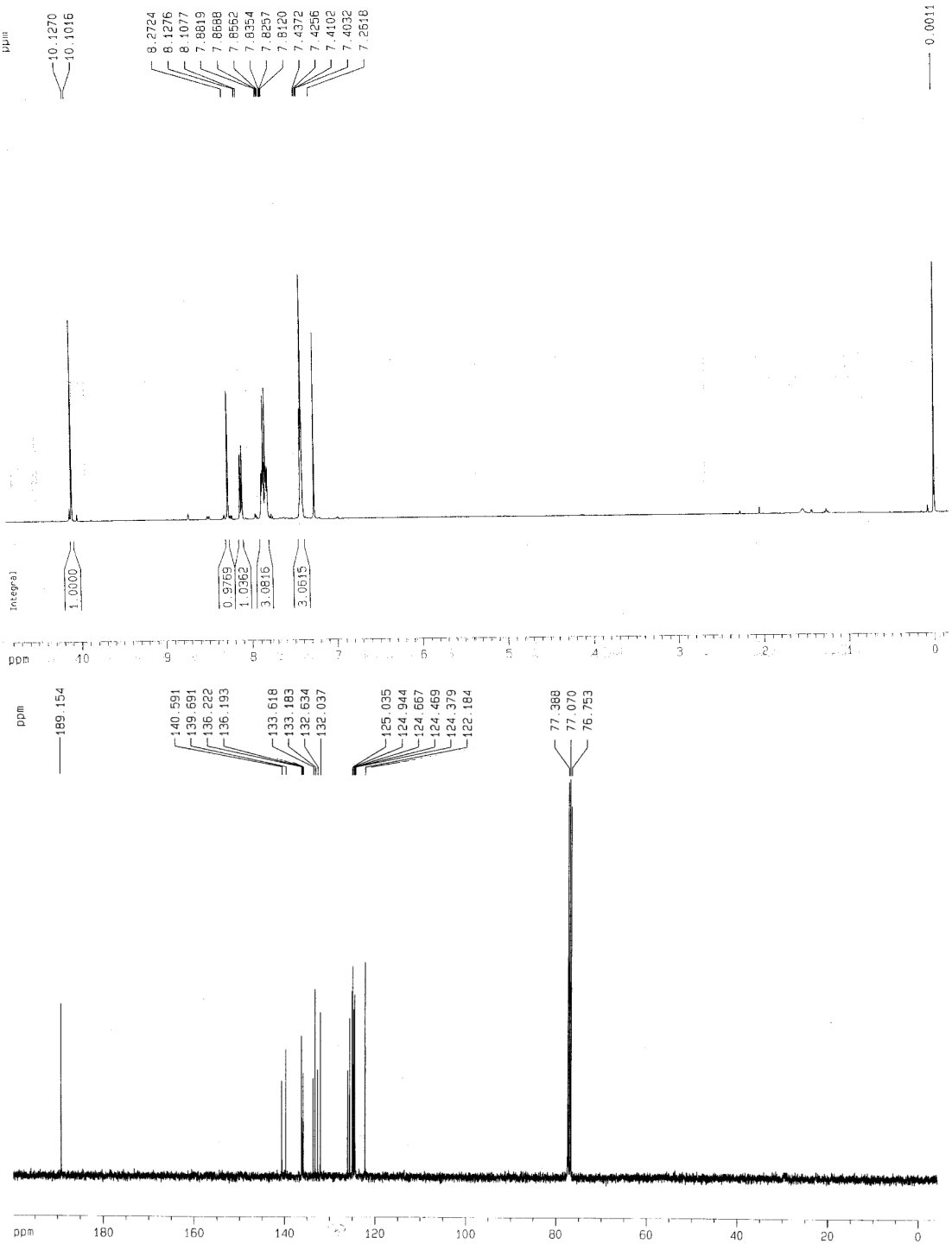


^{1}H NMR and ^{13}C NMRof compound 2b.





^{1}H NMR and ^{13}C NMR of compound 3a.



^{1}H NMR and ^{13}C NMR of compound 3b.