Supporting Information

D-A-π-A type sensitizers with 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole donor building-block for dye-sensitized solar cells

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1. DSC performance

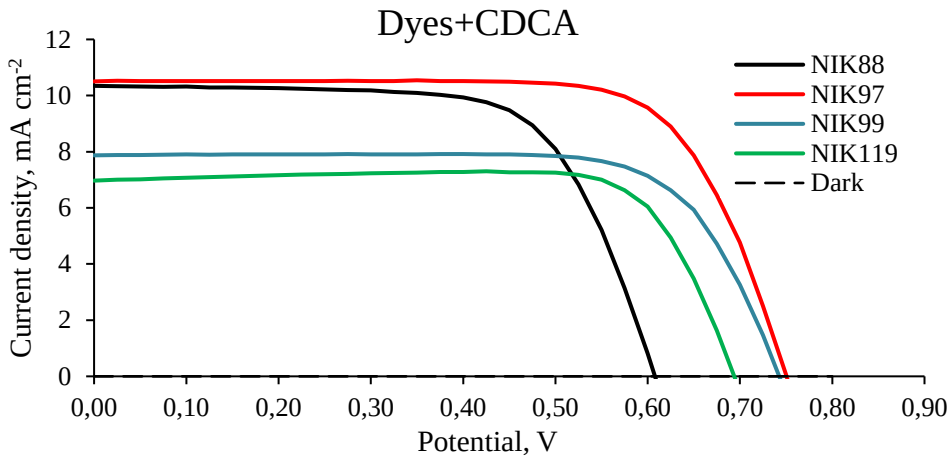


Fig. S1. The *J-V* curves for DSSCs based on the dyes **NIK** series with CDCA addition as co-adsorbent

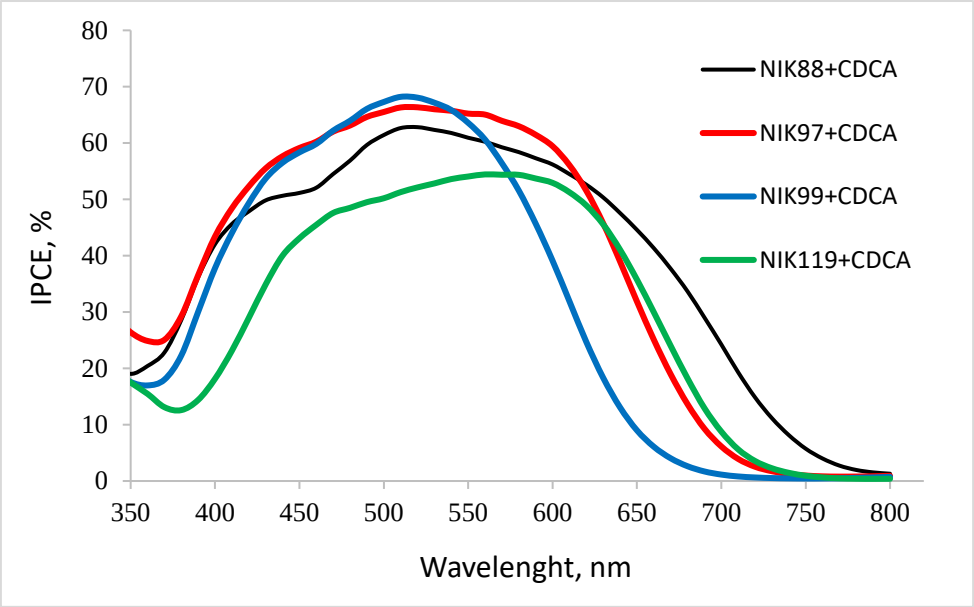


Fig. S2. The IPCE spectra for DSSCs based on the dyes **NIK** series with CDCA addition as co-adsorbent

Table S1. The *J-V* characteristics of DSSCs based on **NIK99** and **NIK119** dyes with the varied thickness of the transparent TiO_2 layer and increased standing time.

Dye	TiO_2 layer (μm)[a]	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	η (%)	Dye loading × 10^{-7} [mol·cm^{-2}]
NIK99	9	0.697	7.52	0.70	3.65	2.56
	13.5	0.717	8.87	0.73	4.63	3.80
NIK99[b]	9	0.709	8.07	0.72	4.09	3.60
NIK119	9	0.703	6.42	0.72	3.26	3.10
	13.5	0.691	6.43	0.75	3.34	4.11

[a] The thickness of the transparent TiO_2 layer. The thickness of the scattering TiO_2 layer was fixed to 4.5 μm
[b] The standing time of the photoanode in the dye solution was doubled

2. Spectral data of intermediates and NIK dyes

2.1. 6-Bromo-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **(3).** White solid (750 mg, 56%).^{1}H NMR (300 MHz, δ, ppm): 7.22-7.10 (m, 5H), 7.08 (d, *J* = 1.95 Hz, 1H), 6.68 (d, *J* = 1.95 Hz, 1H), 4.25 (d, *J* = 8.25 Hz, 1H), 3.29 (d, *J* = 8.40 Hz, 1H), 2.45 (m, 1H), 2.35 (s, 4H), 1.67-1.12 (m, 6H). ^{13}C NMR (75 MHz, δ, ppm): 148.7, 140.6, 135.7, 132.0, 129.9, 127.7, 120.4, 108.9, 108.7, 71.7, 50.2, 43.5, 41.1, 32.4, 28.5, 25.2, 20.8. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{20}H_{19}BrN$) 353.0771, found 353.0774. IR, ν, cm^{-1}: 3905, 3855, 2958, 1593, 1514, 1475, 1371, 1254, 798. R_f = 0,51 (petroleum ether). Mp 127-128°C.

2.2. 6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **(1)**. White solid (500 mg, 95%). ^{1}H NMR (300 MHz, δ, ppm): 7.56 (s, 1H), 7.52 (d, *J* = 8.40 Hz, 1H), 7.24 (d, *J* = 9.90 Hz, 2H), 7.18 (d, *J* = 8.73 Hz, 2H), 6.80 (d, *J* = 8.01 Hz, 1H), 4.28 (d, *J* = 8.40 Hz, 1H), 3.30 (d, *J* = 8.40 Hz, 1H), 2.43 (s, 2H) , 2.36 (s, 3H), 1.63-1.52 (m, 3H), 1.45-1.39 (m, 1H), 1.38 (s, 12H), 1.26-1.09 (m, 2H). ^{13}C NMR (75 MHz, δ, ppm): 152.4, 140.3, 135.3, 132.6, 132.3, 131.3, 129.9, 121.2, 106.5, 83.2, 71.5, 50.1, 43.6, 40.8, 32.3, 28.6, 25.3, 25.0, 24.9, 20.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{26}H_{32}BNO_2$) 400.2551, found 4002557. IR, ν, cm^{-1}: 3905, 3855, 3589, 3504, 3448, 3424, 2974, 2949, 2923, 2908, 2866, 1604, 1517, 1353, 1147, 857. R_f = 0,63 (petroleum ether/ethyl acetate – 10:1). Mp 120-121°C.

2.3. 4-Bromo-7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)-benzo[*c*][1,2,5]thiadiazole (**4a).** Red solid (191 mg, 53%). ^{1}H NMR (300 MHz, δ, ppm): 7.87 (d, *J* = 7.65 Hz, 1H), 7.71 (s, 1H), 7.66 (d, *J* = 8.52 Hz, 1H), 7.52 (d, *J* = 7.65 Hz, 1H), 7.29 (d, *J* = 8.13 Hz, 2H), 7.19 (d, *J* = 8.13 Hz, 2H), 6.95 (d, *J* = 8.31, 1H), 4.36 (d, *J* = 8.16 Hz, 1H), 3.42 (d, *J* = 8.16 Hz, 1H), 2.49 (s, 1H), 2.45 (s, 1H), 2.37 (s, 3H), 1.73-1.31 (m, 6H). ^{13}C NMR (75 MHz, δ, ppm): 150.2, 140.2, 134.4, 134.00, 132.5, 132.2, 129.9, 129.0, 126.3, 126.2, 125.7, 120.8, 110.9, 108.4, 107.2, 71.7, 50.2, 43.7, 40.9, 32.4, 28.6, 25.2, 20.7. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{26}H_{22}BrN_3S$) 487.0712, found 487.0711. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 312/4.52, 478/4.04. IR, ν, cm^{-1}: 3569, 2954, 2944, 2924, 2867, 1605, 1513, 1477, 804. R_f = 0,66 (petroleum ether/ethyl acetate – 10:1). Mp 93-94°C.

2.4. 6-(8-Bromo-2,3-diphenylquinoxalin-5-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole (**4b**). Red solid (199 mg, 43 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.09 (d, *J* = 7.92 Hz, 1H), 7.78 (d, *J* = 7.74 Hz, 2H), 7.74-7.63 (m, 4H), 7.51 (d, *J* = 8.22 Hz, 1H), 7.45-7.27 (m, 8H), 7.22 (d, *J* = 8.01 Hz, 2H), 7.01 (d, *J* = 5.67 Hz, 1H), 4.38 (d, *J* = 4.02 Hz, 1H), 3.42 (d, *J* = 7.08 Hz, 1H), 2.55 (s, 2H), 2.40 (s, 3H), 1.79 – 1.57 (m, 3H), 1.54-1.44 (m, 1H), 1.37-1.20 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 152.5, 151.9, 149.5, 140.5, 140.5, 139.4, 138.8, 138.7, 133.1, 131.8, 131.7, 130.3, 129.9, 129.3, 129.0, 128.4, 128.1, 127.9, 127.2, 121.31, 120.52, 107.0, 71.6, 50.4, 43.7, 41.0, 32.5, 28.7, 25.4, 20.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{40}H_{32}BrN_3$) 633.1779 found 633.1774. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 326/4.21, 464/3.50. IR, ν, cm^{-1}: 3569, 3423, 2953, 2921, 2869, 2361, 2343, 1772, 1603, 1513, 1329, 1023, 696. R_f = 0.63 (petroleum ether/ethyl acetate). Mp 104-105°C.

2.5. 6-(8-Bromo-2,3-bis(4-((2-ethylhexyl)oxy)phenyl)quinoxalin-5-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole (**4c**). Red solid (303 mg, 46 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.02 (d, *J* = 7.92 Hz, 1H), 7.74 (d, *J* = 8.76 Hz, 2H), 7.64 (d, *J* = 8.76 Hz, 4H), 7.49 (d, *J* = 7.95 Hz, 1H), 7.33-7.26 (m, 2H), 7.25-7.16 (m, 2H), 7.08-6.95 (m, 1H), 6.93 (d, *J* = 8.79 Hz,

2H), 6.84 (d, *J* = 8.79 Hz, 2H), 4.37 (s, 1H), 3.92 (d, *J* = 5.76 Hz, 2H), 3.88 (d, *J* = 5.76 Hz, 2H), 3.42 (s, 1H), 2.54 (s, 2H), 2.38 (s, 3H), 1.81-1.70 (m, 3H), 1.62-1.30 (m, 21H), 1.00-0.91 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 160.5, 160.2, 151.9, 151.9, 151.4, 132.5, 131.5, 131.1, 131.1, 130.1, 129.8, 128.6, 128.5, 127.9, 121.0, 120.3, 120.2, 114.4, 114.2, 107.0, 97.42, 70.62, 50.4, 39.3, 32.5, 30.5, 29.1, 29.1, 28.7, 25.3, 23.9, 23.9, 23.1, 20.8, 14.1, 11.1. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{56}H_{64}BrN_3O_2$) 890.4254 found 890.4255. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 304/4.55, 389/4.07. IR, ν, cm^{-1}: 3449, 2957, 2926, 2870, 1606, 1513, 1459, 1380, 1252, 1174, 833, 806. R_f = 0.58 (petroleum ether/ ethylacetate – 10:1). Mp 72-73 ºC.

2.6. 4,7-Bis(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5] thiadiazole (**5a**). Dark red solid (35 mg, 14%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.78 (s, 2H), 7.73 (d, *J* = 8.40 Hz, 4H), 7.31 (d, *J* = 8.20 Hz, 4H), 7.20 (d, *J* =7.80 Hz, 4H), 7.02 (s, 2H), 4.67-4.06 (m, 2H), 3.64-3.19 (m, 2H), 2.50 (m, 4 H), 2.38 (s, 6 H), 1.78-1.42 (m, 10 H), 1.23-1.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 155.1, 150.1, 141.2, 134.6, 132.8, 132.3, 130.5, 129.4, 128.1, 127.4, 126.4, 120.9, 108.1, 72.2, 51.0, 44.4, 41.5, 33.2, 29.3, 26.0, 21.7. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{46}H_{42}N_4S$) 682.3130 found 682.3125. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 322/4.61, 501/4.30. IR, ν, cm^{-1}: 3570, 3431, 2950, 2920, 2869, 1603, 1513, 1474, 1381, 1326, 1254, 805. R_f = 0.56 (petroleum ether/ethyl acetate – 10:1). Mp 57-58ºC.

2.7. 6,6'-(2,3-Diphenylquinoxaline-5,8-diyl)bis(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole) (**5b**). Dark red solid (32 mg, 11%). ^{1}H NMR (300 MHz, DMSO-d^6, δ, ppm): 7.87 (s, 2H), 7.73 (d, *J* = 0.9 Hz, 2H), 7.63 (d, *J* = 6.96 Hz, 4H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.40-7.32 (m, 6H), 7.28 (d, *J* = 8.46 Hz, 4H), 7.19 (d, *J* = 8.40, 4H), 6.94 (d, *J* = 8.34 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 2H), 3.40 (d, *J* = 8.7 Hz, 2H), 2.48 (s, 2H), 2.38 (s, 2H), 2.30 (s, 6H), 1.64-1.41 (m, 8H), 1.34-1.23 (m, 2H), 1.20 -1.11 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d^6, δ, ppm): 150.1, 148.1, 140.1, 138.8, 137.7, 137.6, 137.5, 132.7, 130.7, 129.8, 129.7, 129.6, 128.9, 128.8, 128.05, 127.92, 127.7, 119.5, 106.4, 70.3, 49.5, 43.2, 40.3, 31.9, 28.0, 24.6, 20.4. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{60}H_{52}N_4$) 828.4192 found 828.4188. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 332/4.79, 468/4.11. IR, ν, cm^{-1}: 2952, 2869, 2363, 2345, 1604, 1512, 1460, 1373, 1253, 1024, 804, 694. R_f = 0.47 (petroleum ether). Mp 49-50ºC.

2.8. 6,6'-(2,3-Bis(4-((2-ethylhexyl)oxy)phenyl)quinoxaline-5,8-diyl)bis(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole) (**5c**). Orange solid (48 mg, 12 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.83 (s, 2H), 7.79-7.68 (m, 6H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.20 Hz, 4H), 7.23 (d, *J* = 8.20 Hz, 4H), 7.07 (d, *J* = 8.30 Hz, 2H), 6.88 (d, *J* = 8.60 Hz, 4H), 4.39 (d, *J* = 8.00 Hz, 2H), 3.91 (d, *J* = 5.6 Hz, 4H), 3.46 (d, *J* = 8.00 Hz, 2H), 2.59 (m, 4H), 2.40 (s, 6H), 1.81-1.32 (m, 32H), 1.02-0.94 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 159.9, 149.7, 148.7, 140.9, 138.3, 138.0, 132.9, 131.8, 131.4, 131.2, 130.0, 129.7, 128.5, 128.4, 127.9, 120.04, 114.11, 107.06, 71.43, 70.54, 50.46, 43.59, 40.98, 39.33, 32.48, 30.52, 29.70, 29.08, 28.65, 25.32, 23.84, 23.05, 20.81, 14.09, 11.11. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{76}H_{84}N_4O_2$) 1085.6667 found 1085.6667. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 344/4.77, 463/4.15. IR, ν, cm^{-1}: 3579, 3552, 3434, 2956, 2924, 2869, 1605, 1513, 1464, 1251, 1174, 805. R_f = 0.45 (petroleum ether/ethyl acetate – 10:1). Mp 53-54ºC.

2.9. *Tert*-butyl-2-cyano-3-(5-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**7a**). Purple solid (119 mg, 45%). ^{1}H NMR (300 MHz, δ, ppm): 8.27 (s, 1H), 8.25 (d, *J* = 3.87 Hz, 1H), 8.04 (d, *J* = 7.59 Hz, 1H), 7.88

(d, *J* = 3.69 Hz, 1H), 7.81 (s, 1H), 7.77 (d, *J* = 8.40 Hz, 1H), 7.69 (d, *J* =7.53 Hz, 1H), 7.27 (d, *J* = 4.53 Hz, 2H), 7.19 (d, *J* = 8.04 Hz, 2H), 6.96 (d, *J* = 8.31 Hz, 1H), 4.36 (d, *J* = 7.86 Hz, 1H), 3.42 (d, *J* = 8.13 Hz, 1H), 2.48 (s, 2H), 2.37 (s, 3H), 1.62 (s, 9H), 1.49-1.14 (m, 6H). ^{13}C NMR (75 MHz, δ, ppm): 161.8, 153.9, 152.8, 150.5, 149.2, 145.4, 140.1, 137.8, 135.7, 135.4, 134.0, 132.3, 129.9, 129.3, 127.9, 126.4, 125.8, 125.5, 122.8, 120.9, 116.3, 107.2, 100.1, 83.40, 71.72, 50.2, 43.7, 40.8, 32.4, 28.6, 28.1, 27.8, 25.2, 20.8. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{38}H_{34}N_4O_2S_2$) 642.2118 found 642.2111. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 315/4.56, 412/4.43, 545/4.54. IR, ν, cm^{-1}: 3433, 2954, 2924, 2870, 1711, 1584, 1513, 1478, 1255, 1152, 1093, 805. R_f = 0,45 (petroleum ether/ethyl acetate – 10:1). Mp 108-109ºC.

2.10. *Tert*-butyl 2-cyano-3-(5-(2,3-diphenyl-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)acrylate (**7b**). Purple solid (100 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.30 (s, 1H), 8.24 (d, *J* = 7.74 Hz, 1H), 7.96-7.80 (m, 5H), 7.73 (d, *J* = 8.79 Hz, 1H), 7.70 (d, *J* = 6.75 Hz, 2H), 7.57 (d, *J* = 8.04 Hz, 1H), 7.47 (m, 3H), 7.37-7.28 (m, 5H), 7.21 (d, *J* = 7.23 Hz, 2H), 7.01 (s, 1H), 4.37 (s, 1H), 3.40 (s, 1H), 2.55 (s, 1H), 2.53 (s, 1H), 2.39 (s, 3H), 1.79-1.70 (m, 1H), 1.64 (s, 9H), 1.53-1.41 (m, 1H), 1.32-1.24 (m, 3H), 0.96-0.86 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm):162.3, 152.0, 151.6, 149.8, 148.9, 146.0, 141.4, 140.5, 139.0, 138.4, 138.1, 137.4, 136.5, 133.3, 131.9, 130.6, 130.3, 129.9, 129.2, 129.1, 128.7, 128.59, 128.38, 128.18, 127.29, 126.75, 120.7, 116.6, 107.1, 99.3, 83.3, 71.7, 50.4, 43.7, 41.0, 32.5, 29.8, 28.7, 28.2, 25.4, 20.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{52}H_{44}N_4O_2S$) 788.3185 found 788.3187. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 332/4.36, 416/4.16, 528/4.24. IR, ν, cm^{-1}: 3433, 2953, 2925, 2869, 1714, 1584, 1513, 1250, 1154, 1100, 696. R_f = 0.21 (petroleum ether/ ethylacetate – 10:1). Mp 102-103ºC.

2.11. *Tert*-butyl-3-(5-(2,3-bis(4-((2-ethylhexyl)oxy)phenyl)-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)-2-cyanoacrylate (**7c**). Purple solid (125 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.30 (s, 1H), 8.20 (d, *J* = 7.44 Hz, 1H), 8.05-7.62 (m, 8H), 7.56 (d, *J* = 7.77 Hz, 1H), 7.38-7.16 (m, 4H), 7.01 (d, *J* = 8.52 Hz, 3H), 6.84 (d, *J* = 8.46 Hz, 2H), 4.40 (s, 1H), 3.95 (d, *J* = 5.52 Hz, 2H), 3.87 (d, *J* = 5.52 Hz, 2H), 3.43 (s, 1H), 2.55 (m, 2H), 2.39 (m, 3H), 1.84-1.66 (m, 5H), 1.64 (s, 9H), 1.57-1.31 (m, 19H), 1.26-1.20 (m, 1H), 1.05-0.90 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 162.4, 160.5, 160.3, 151.6, 151.1, 149.3, 146.0, 141.2, 140.6, 138.3, 138.0, 137.2, 136.4, 132.0, 131.6, 131.47, 130.86, 130.5, 129.9, 128.3, 128.1, 127.6, 126.6, 120.6, 116.7, 114.8, 114.3, 107.1, 99.1, 83.3, 70.7, 39.5, 39.5, 32.6, 30.7, 30.6, 29.8, 29.2, 29.2, 28.7, 28.2, 25.4, 24.0, 24.0, 23.2, 23.1, 20.9, 14.2, 14.2, 11.3, 11.2. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{68}H_{76}N_4O_4S$) 1045.5660, found 1045.5660. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 325/4.59, 406/4.39, 518/4.42. IR, ν, cm^{-1}: 3423, 2957, 2928, 2870, 1713, 1605, 1583, 1512, 1434, 1249, 1173, 1153, 835, 804. R_f = 0.26 (petroleum ether/ ethylacetate – 10:1). Mp 91-92 ºC.

2.12. *Tert*-butyl-2-cyano-3-(4,4-diethylhexyl-6-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)acrylate (**7d**). Purple tar (153 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.23 (s, 1H), 8.19-8.04 (m, 1H), 8.01-7.90 (m, 1H), 7.88-7.60 (m, 4H), 7.28-6.25 (m, 5H), 4.58-4.25 (m,1H), 3.66-3.36 (m,1H), 2.62-2.22 (m, 5H), 2.12-1.95 (m, 4H), 1.60 (s, 9H), 1.51-1.16 (m, 5H), 1.10-0.63 (m, 31H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 163.1, 162.5, 158.5, 154.1, 152.7, 150.0, 149.0, 146.2, 146.1, 145.1, 140.2, 136.6, 136.3, 133.9, 133.7, 132.0, 129.8, 129.0, 126.7, 125.9, 125.7, 125.6, 124.7, 122.5, 122.3, 120.6, 117.2, 107.3, 96.1, 82.9, 71.6, 54.2, 50.2, 43.6, 43.2, 43.1,

40.8, 35.3, 35.3, 34.3, 34.1, 32.4, 29.7, 28.5, 28.5, 28.5, 28.1, 27.8, 27.5, 27.3, 25.2, 22.7, 20.8, 14.0, 10.7, 10.6. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{59}H_{68}N_4O_2S_3$) 961.4548, found 961.4552. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 316/4.26, 555/4.59. IR, ν, cm^{-1}: 3439, 2982, 2949, 2880, 2384, 1703, 1637, 1477, 1395, 1251, 1148. R_f = 0.46 (petroleum ether/ethylacetate 10:1).

2.13. 2-Cyano-3-(5-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl) benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**NIK88**). Dark purple solid (105 mg, 96 %). ^{1}H NMR (300 MHz, DMSO-d6, δ, ppm): 8.36 (s, 1H), 8.26 (d, *J* = 7.71 Hz, 1H), 8.22 (d, *J* = 4.62 Hz, 1H), 7.96 (d, *J* = 3.93 Hz, 1H), 7.91-7.76 (m, 3H), 7.31-7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 6.94-6.87 (m, 1H), 4.44 (d, *J* = 7.47 Hz, 1H), 2.39 (s, 1H), 2.33 (s, 1H), 2.29 (s, 3H), 1.58-1.39 (m, 4 H), 1.25-1.07 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d^6, δ, ppm): 163.8, 152.9, 152.0, 149.2, 145.9, 143.6, 139.4, 137.6, 136.8, 133.6, 133.5, 131.2, 129.7, 129.1, 127.6, 127.2, 125.9, 125.6, 125.5, 122.3, 119.9, 117.7, 106.6, 70.5, 49.2, 43.2, 40.2, 31.8, 27.8, 24.5, 20.4. MS-MALDI (m/z): $[M]^+$ calcd for ($C_{34}H_{26}N_4O_2S_2$) 586.1497, found 586.7792. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 316/4.18, 403/4.0, 559/4.12. IR, ν, cm^{-1}: 3435, 1686, 1604, 1513, 1383, 1210, 1144, 803, 599. R_f = 0,74 (dichloromethane/methanol – 1:1). Mp 212-213ºC.

2.14. 2-Cyano-3-(5-(2,3-diphenyl-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methano-carbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (**NIK97**). Dark purple solid (130 mg, 96 %). ^{1}H NMR (300 MHz, DMSO-d^6, δ, ppm): 8.55 - 8.43 (m, 1H), 8.40 (s, 1H), 8.11 (d, *J* = 3.90 Hz, 1H), 7.94 (d, *J* = 4.08 Hz, 1H), 7.89 (d, *J* = 8.07 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.72 (s, 1H), 7.60 (d, *J* = 6.36 Hz, 2H), 7.49 (d, *J* = 7.38 Hz, 1H), 7.45-7.31 (m, 6H), 7.26 (d, *J* = 8.37 Hz, 2H), 7.18 (d, *J* = 8.22 Hz, 2H), 6.90 (d, *J* = 8.28 Hz, 1H), 4.41 (d, *J* =8.07 Hz, 1H), 3.09 (d, *J* = 7.35 Hz, 1H), 2.44 (s, 1H), 2.35 (s, 1H), 2.29 (s, 3H), 1.61-1.39 (m, 4H), 1.28-1.12 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d^6, δ, ppm): 163.9, 151.2, 151.1, 148.7, 146.0, 144.8, 139.9, 139.8, 138.6, 138.6, 137.8, 137.5, 137.5, 136.2, 132.8, 130.9, 130.3, 130.0, 129.8, 129.1, 129.0, 128.5, 128.3, 128.0, 127.9, 126.9, 126.8, 119.7, 117.6, 106.3, 70.4, 49.3, 45.5, 43.2, 31.9, 28.0, 24.6, 20.4. MS-MALDI (m/z): $[M]^+$ calcd for ($C_{48}H_{36}N_4O_2S$) 733.2558, found 733.3521. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 333/4.55, 356/4.43, 500/4.35. IR, ν, cm^{-1}: 3433, 2985, 2927, 2870, 2217, 1733, 1579, 1512, 1374, 1272, 1255, 802, 696. R_f = 0.71 (dichloromethane/methanol 50:1). Mp 203-204ºC.

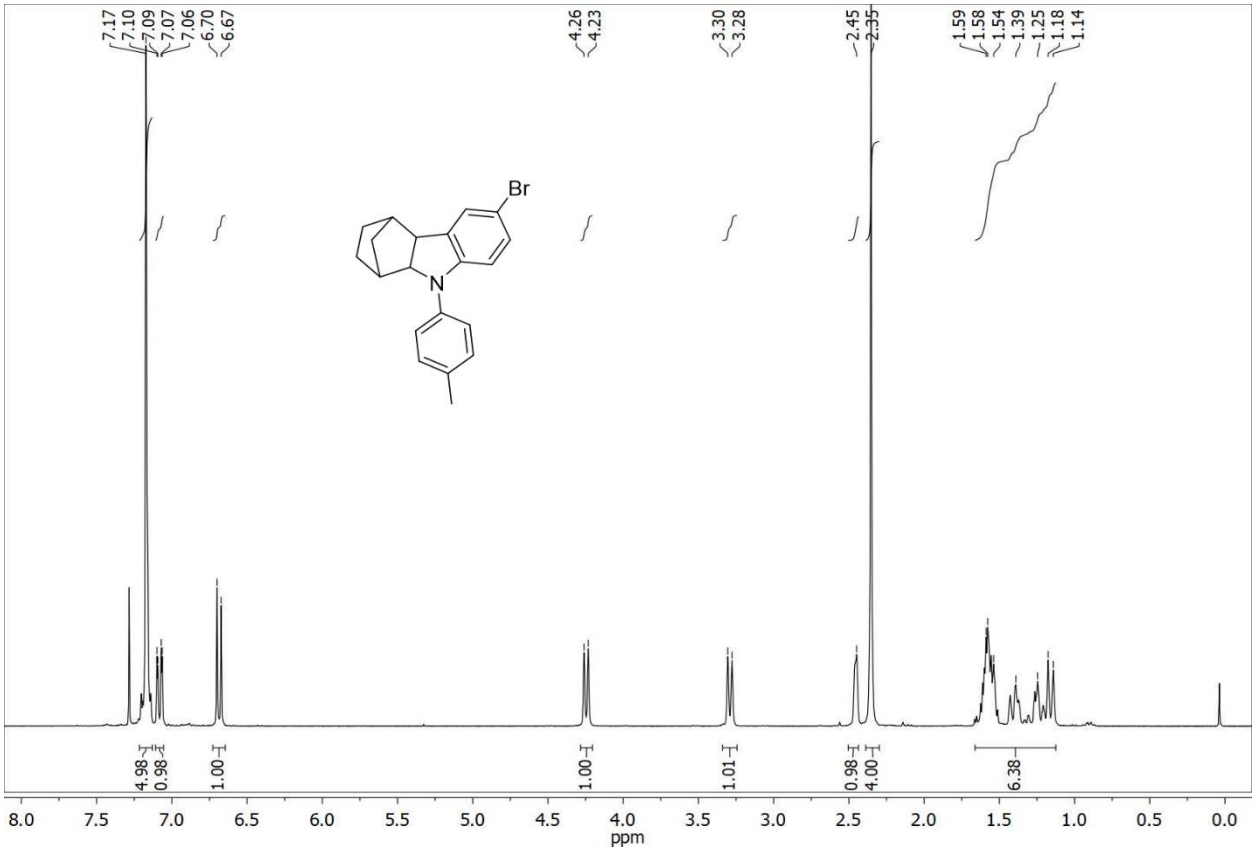
2.15. 3-(5-(2,3-Bis(4-((2-ethylhexyl)oxy)phenyl)-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (**NIK99**). Dark purple solid (176 mg, 96 %). ^{1}H NMR (300 MHz, DMSO-d^6, δ, ppm): 8.45 (d, *J* = 8.13 Hz, 1H), 8.35 (s, 1H), 8.09 (d, *J* = 4.32 Hz, 1H), 7.87 (d, *J* = 8.04 Hz, 1H), 7.85-7.77 (m, 3 H), 7.70 (s, 1H), 7.55 (d, *J* = 8.64 Hz, 2H), 7.49 (d, *J* = 7.17 Hz, 1H), 7.27 (d, *J* = 8.52 Hz, 2H), 7.18 (d, *J* = 8.28 Hz, 2H), 7.00-6.86 (m, 5 H), 4.42 (d, *J* = 8.19 Hz, 1H), 3.88 (d, *J* = 6.03 Hz, 2H) , 3.85 (d, *J* = 5.94 Hz, 2H), 3.14 (d, *J* = 5.34 Hz, 1H), 2.73 (s, 1H), 2.35 (s, 1H), 2.27 (s, 3H), 1.43-1.32 (m, 6H), 1.26-1.16 (m, 18H), 1.14-1.04 (m, 6H), 0.93-0.88 (m, 2H), 0.85-0.81 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d^6, δ, ppm): 163.8, 160.0, 159.8, 150.8, 150.7, 148.8, 145.0, 140.1, 139.7, 139.4, 137.5, 136.3, 133.0, 132.0, 131.7, 131.4, 131.3, 131.1, 130.4, 130.2, 130.0, 128.9, 128.2, 128.0, 127.3, 126.9, 126.8, 120.0, 114.7, 114.4, 106.6, 70.3, 52.3, 49.6, 45.6, 43.5, 38.8, 32.1, 30.2, 30.1, 29.2, 28.7, 28.7, 28.2, 24.9, 23.6, 23.5, 22.7, 22.3, 20.7, 14.2, 14.1, 11.2, 11.1. MS-MALDI (m/z): $[M]^+$ calcd for ($C_{64}H_{68}N_4O_4S$) 989.4961, found 989.8404. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 317/4.42, 386/4.28, 492/4.22.IR, ν, cm^{-1}: 3426, 2956, 2928, 2870, 2212, 1605, 1512, 1374, 1251,1174, 834, 804. R_f = 0.74 (dichloromethane/methanol 5:1). Mp 146-147ºC.

2.16. 2-Cyano-3-(4,4-diethylhexyl-6-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)acrylic acid (**NIK119**). Dark purple solid (136 mg, 81%). ^{1}H NMR (300 MHz, DMSO-d^{6}, δ, ppm): 8.32-8.26 (m, 1H), 8.18-8.08 (m, 2H), 7.91-7.77 (m, 4H), 7.29 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.93 (d, J =8.2 Hz, 1H), 4.45 (d, J = 8.6 Hz, 1H), 3.41 (d, J = 9.8 Hz, 1H), 2.40-2.26 (m, 5H), 2.06-1.95 (m, 4H), 1.58-1.26 (m, 8H),1.19-1.07 (m, 3H), 1.03-0.88 (m, 13H), 0.71-0.54 (m, 12H). ^{13}C NMR (75 MHz, DMSO-d^{6}, δ, ppm): 163.7, 161.4, 161.3, 157.8, 157.7, 153.2, 152.0, 149.1, 142.5, 139.7, 137.5, 137.4, 137.3, 133.6, 132.1, 131.2, 129.9, 128.9, 126.3, 126.3, 126.1, 125.6, 124.2, 122.3, 122.1, 122.0, 119.9, 119.0, 106.8, 70.5, 53.5, 49.3, 45.3, 43.3, 42.4, 42.2, 40.3, 34.8, 33.7, 31.9, 29.0, 28.0, 27.1, 27.1, 24.6, 22.2, 20.5, 13.9, 13.8, 10.7, 10.6. MS-MALDI (m/z): $[M]^{+}$ calcd for ($C_{55}H_{60}N_4O_2S_3$) 905.3909, found 905.5736. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 319/4.34, 558/4.62. IR, ν, cm^{-1}: 3437, 2955, 2922, 2863, 2364, 2335, 2210, 1708, 1605, 1571, 1513, 1477, 1374, 1258, 1158, 809. R_f = 0.47 (petroleum ether/DCM – 5:1). Mp 197-198 ^{o}C.

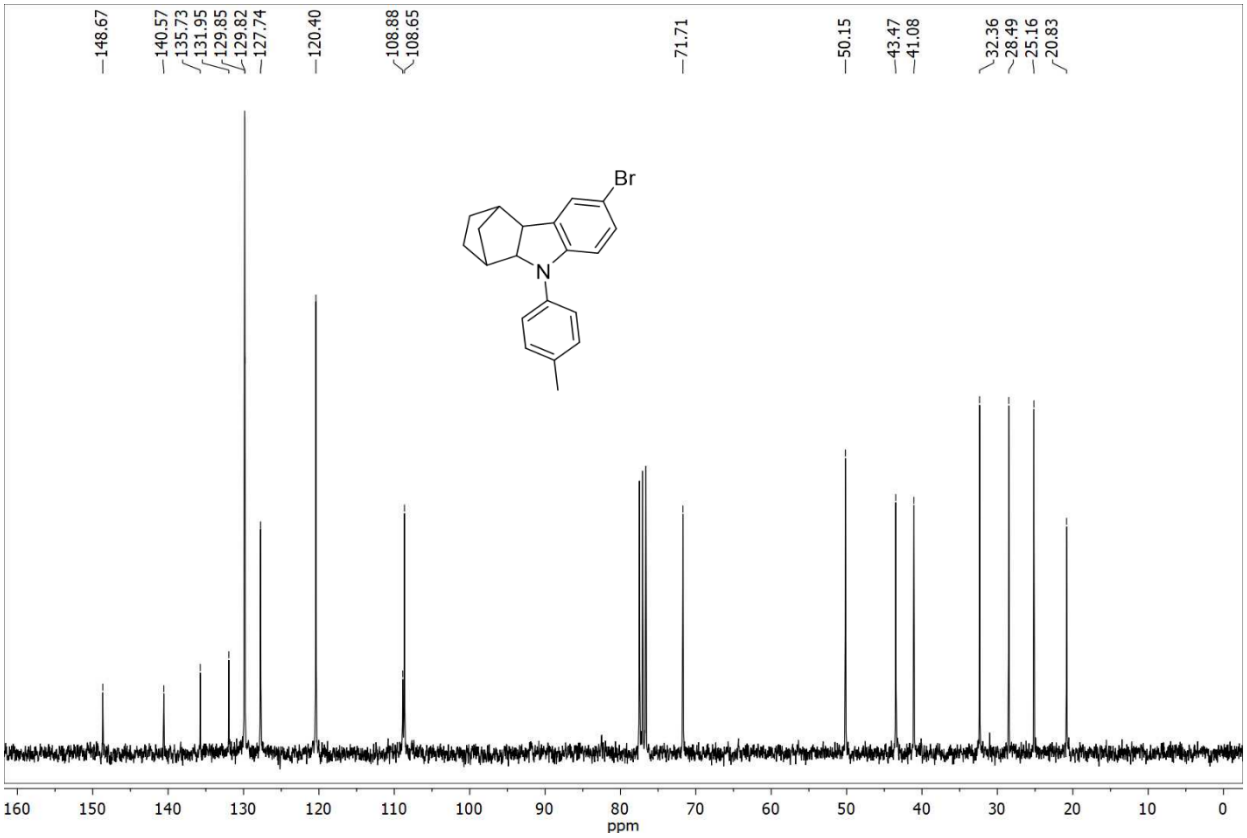
3. ^{1}H and ^{13}C NMR of intermediates and NIK dyes

6-Bromo-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3**)

^{1}H NMR (300 MHz)

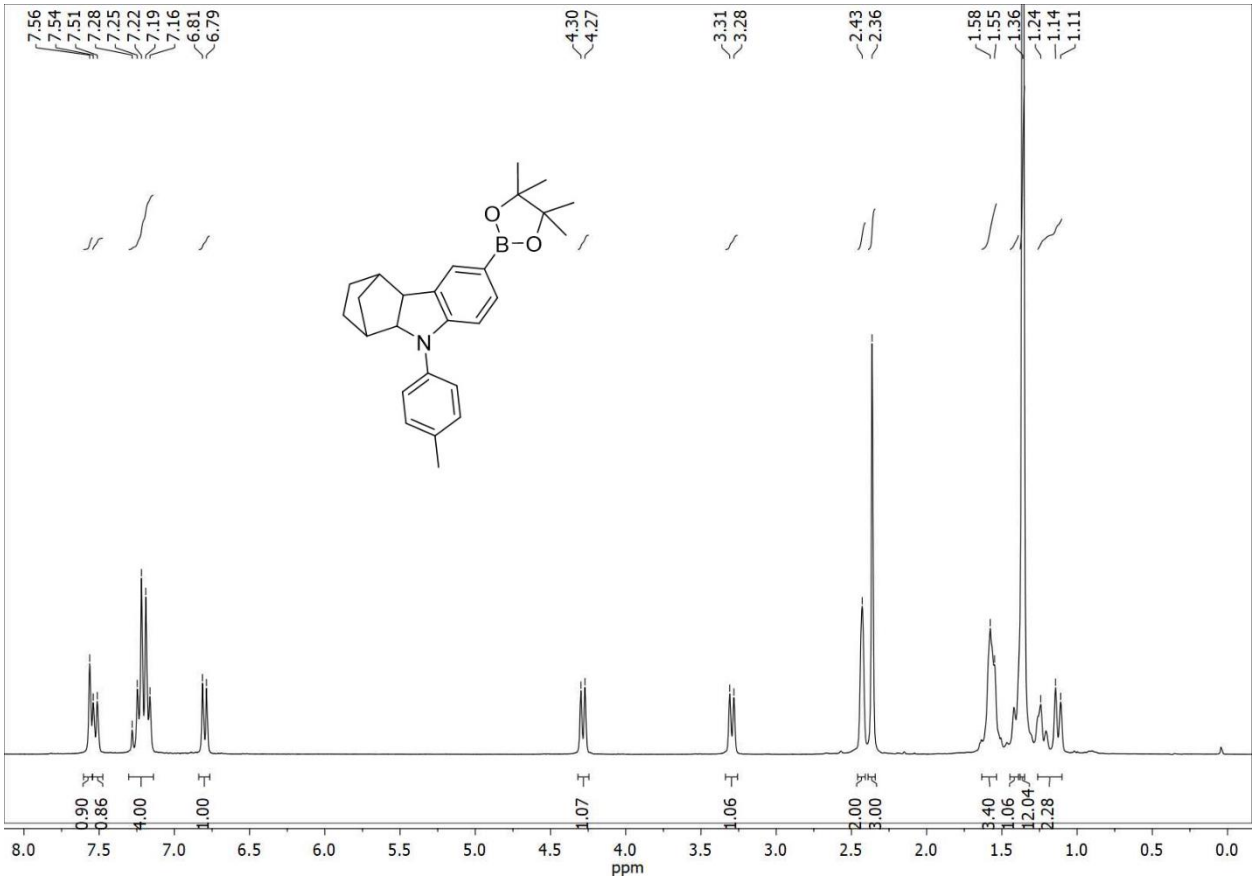


^{13}C NMR (75 MHz)

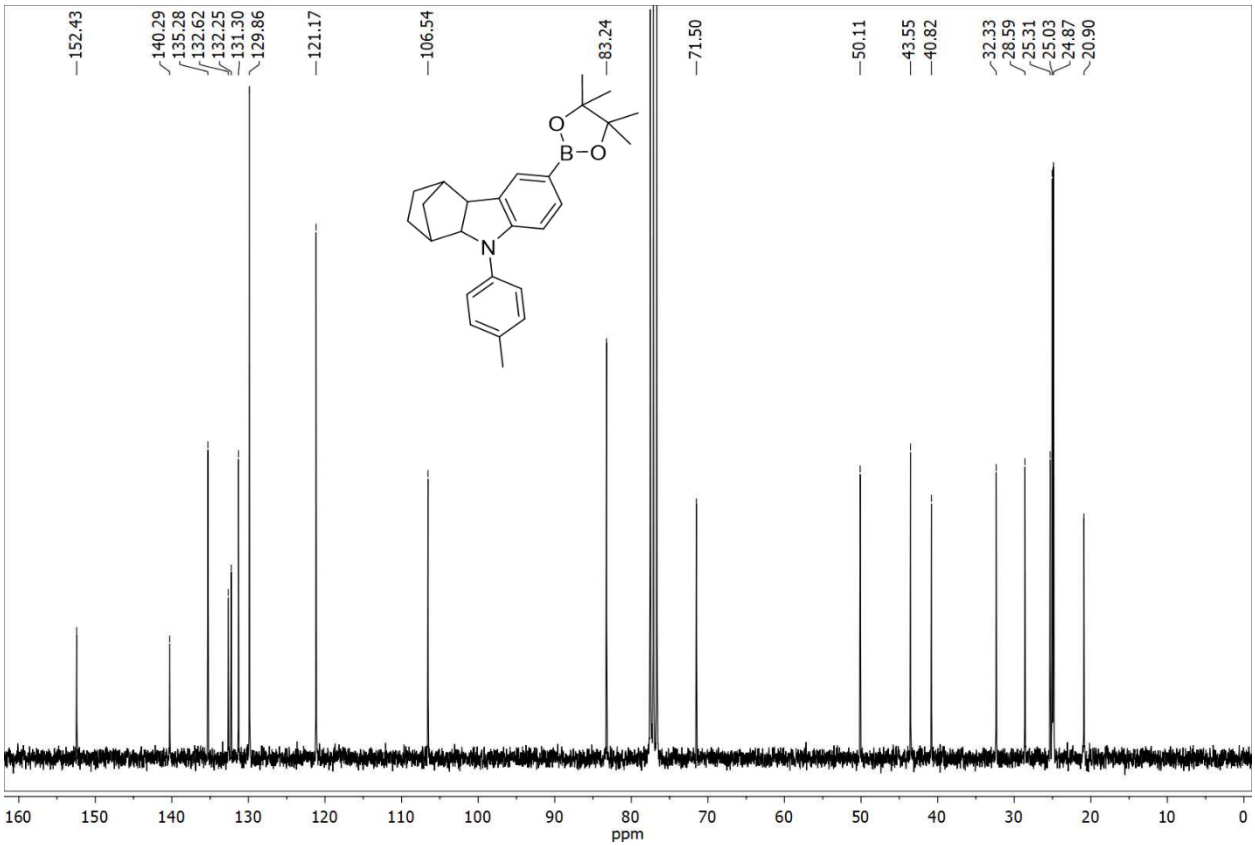


6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**1**)

^{1}H NMR (300 MHz)

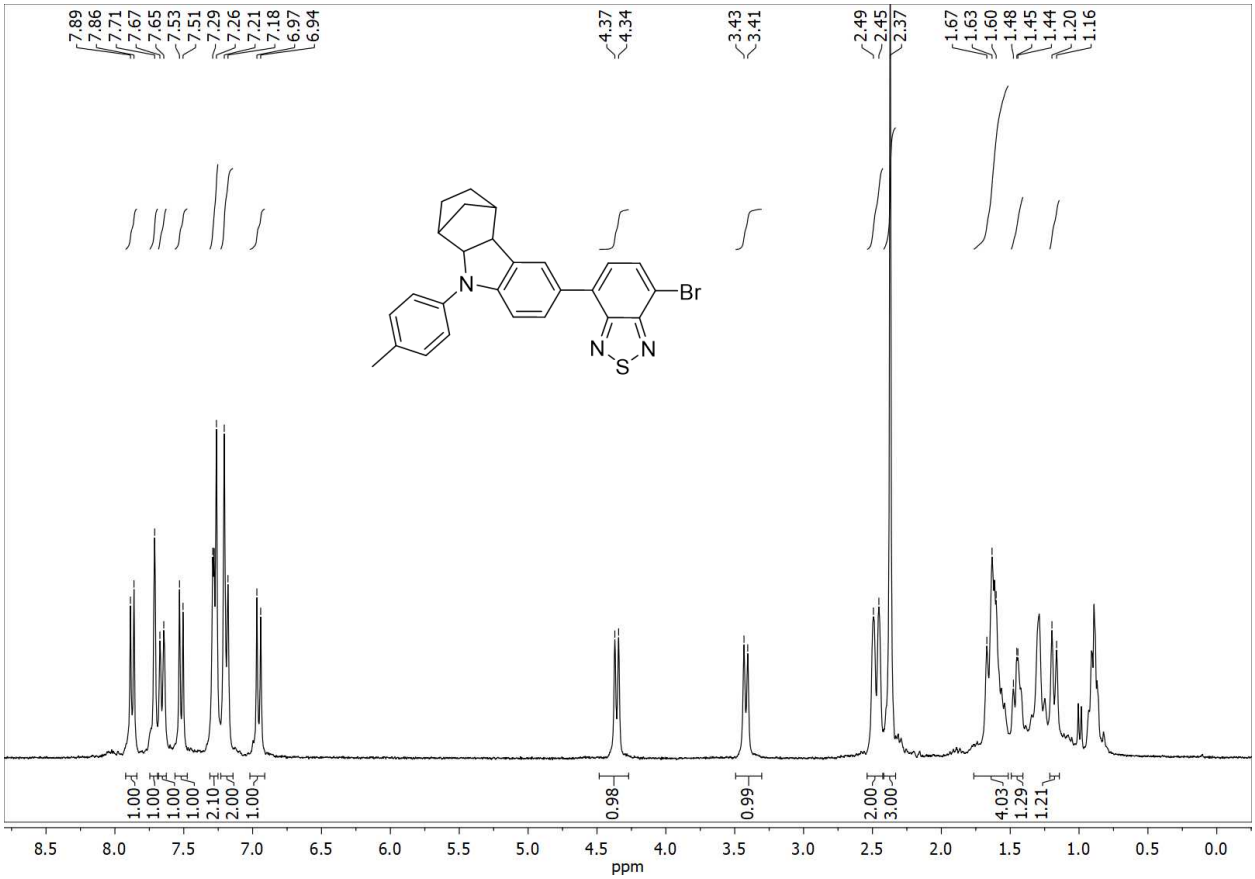


^{13}C NMR (75 MHz)

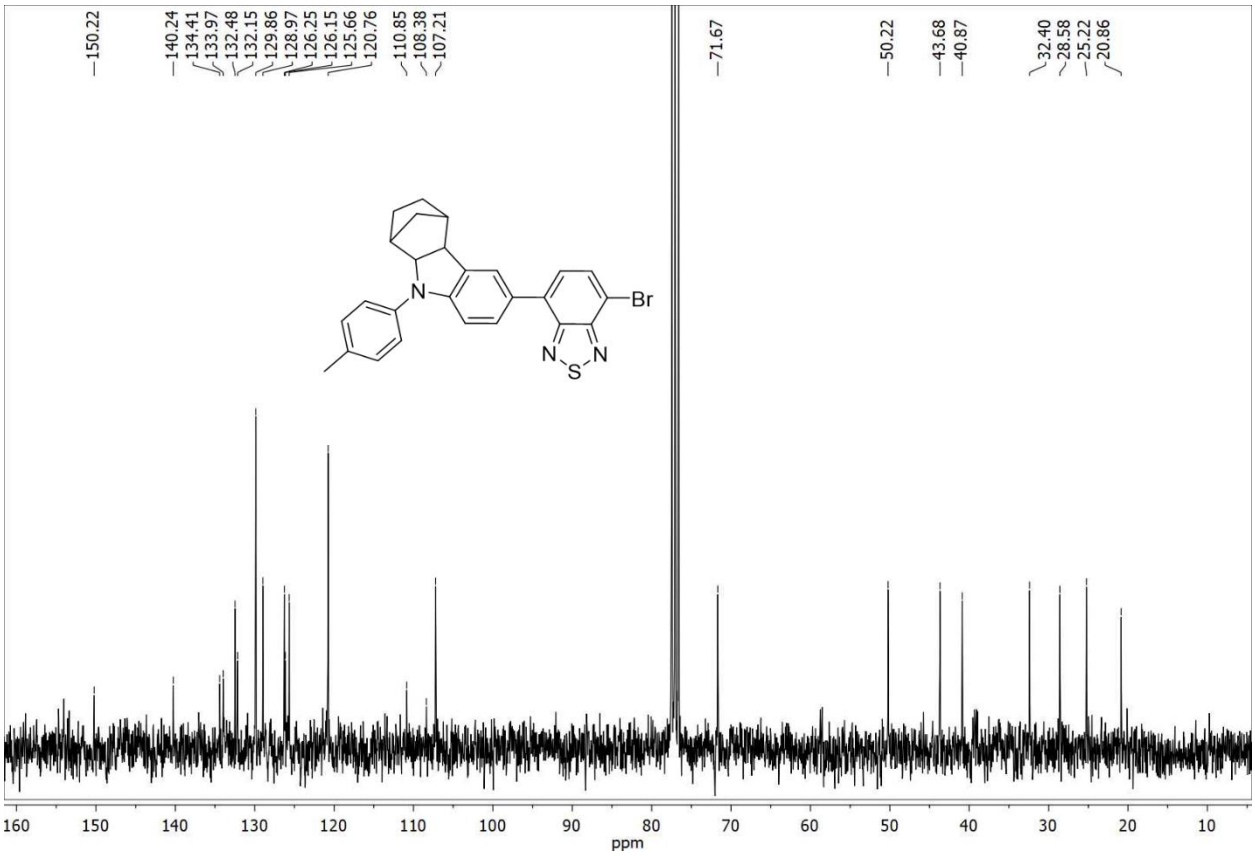


4-Bromo-7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5] thiadiazole (**4a**)

^{1}H NMR (300 MHz)

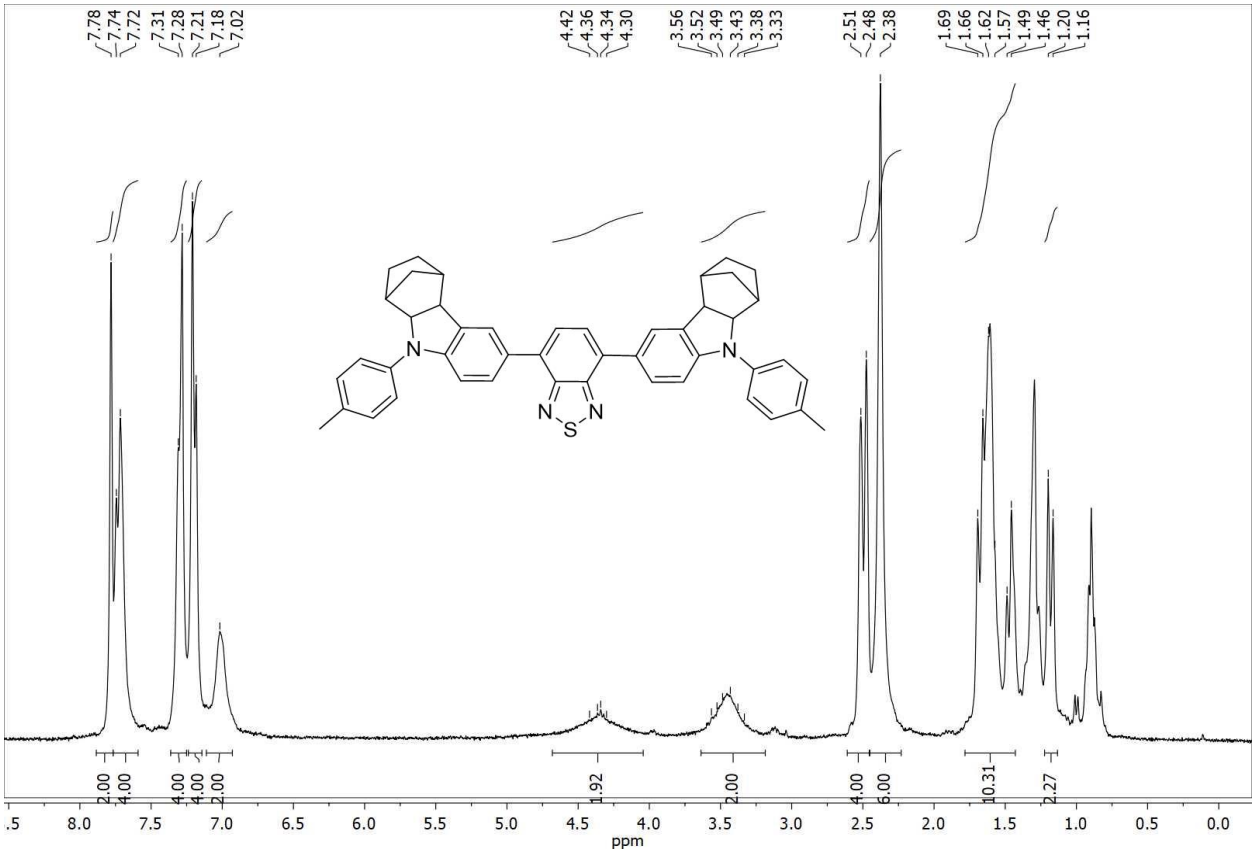


^{13}C NMR (75 MHz)

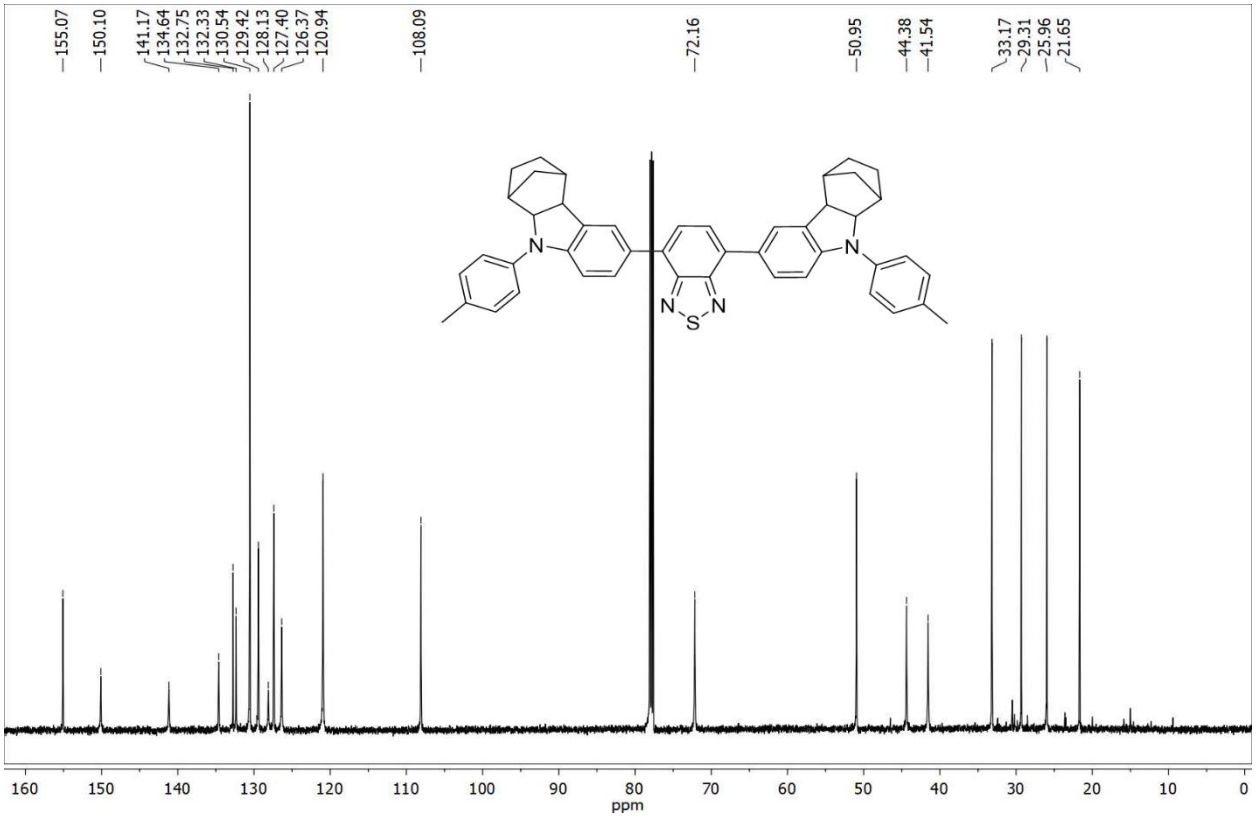


4,7-Bis(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5] thiadiazole (**5a**)

^{1}H NMR (300 MHz)

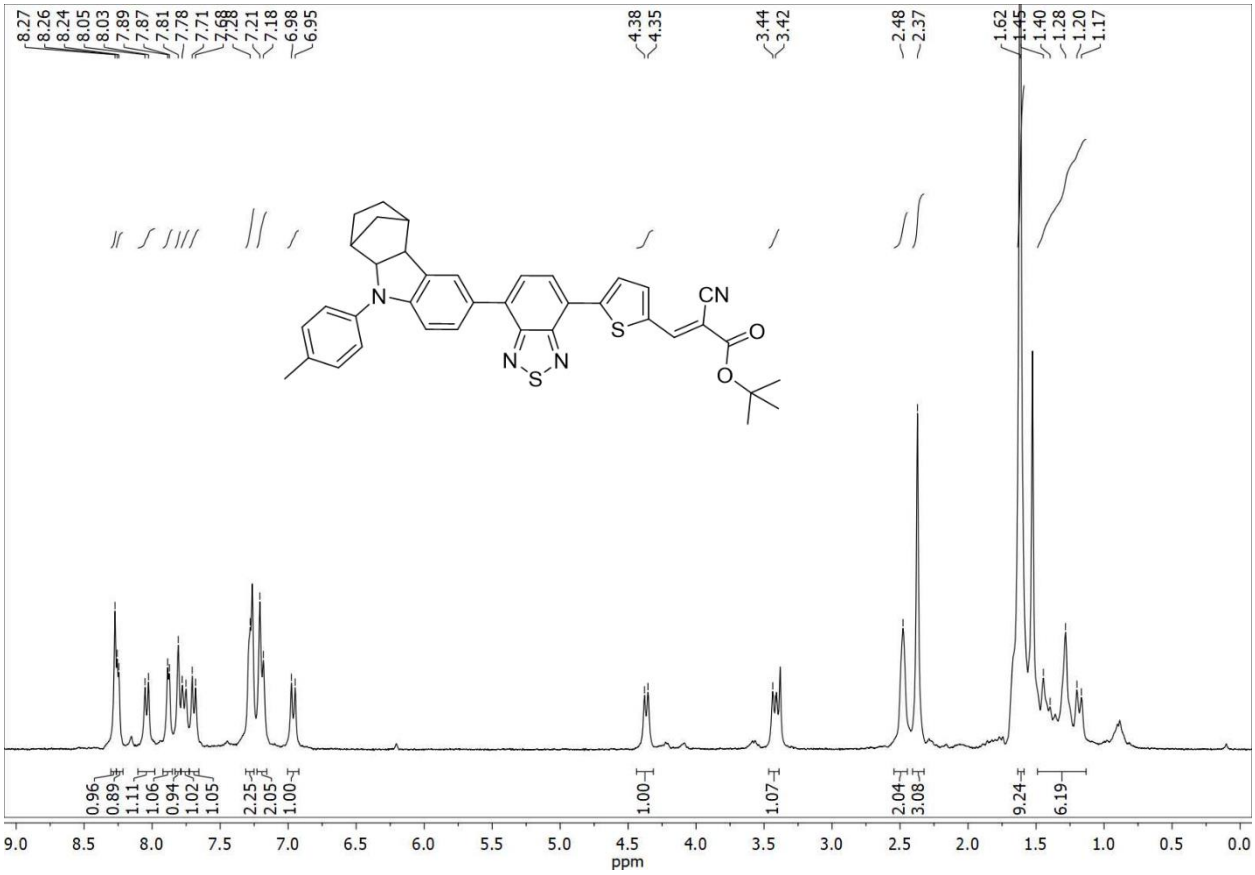


^{13}C NMR (75 MHz)

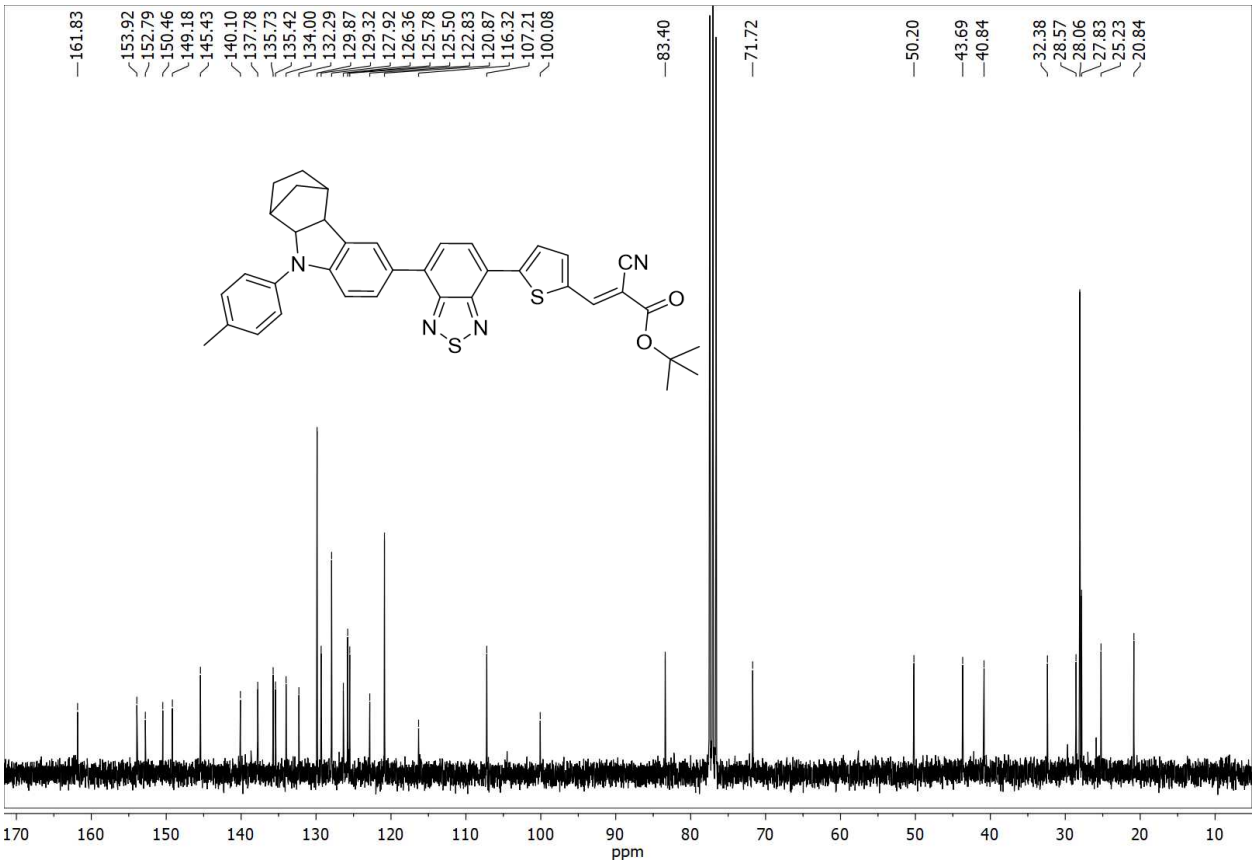


Tert-butyl-2-cyano-3-(5-(7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**7a**)

^{1}H NMR (300 MHz)

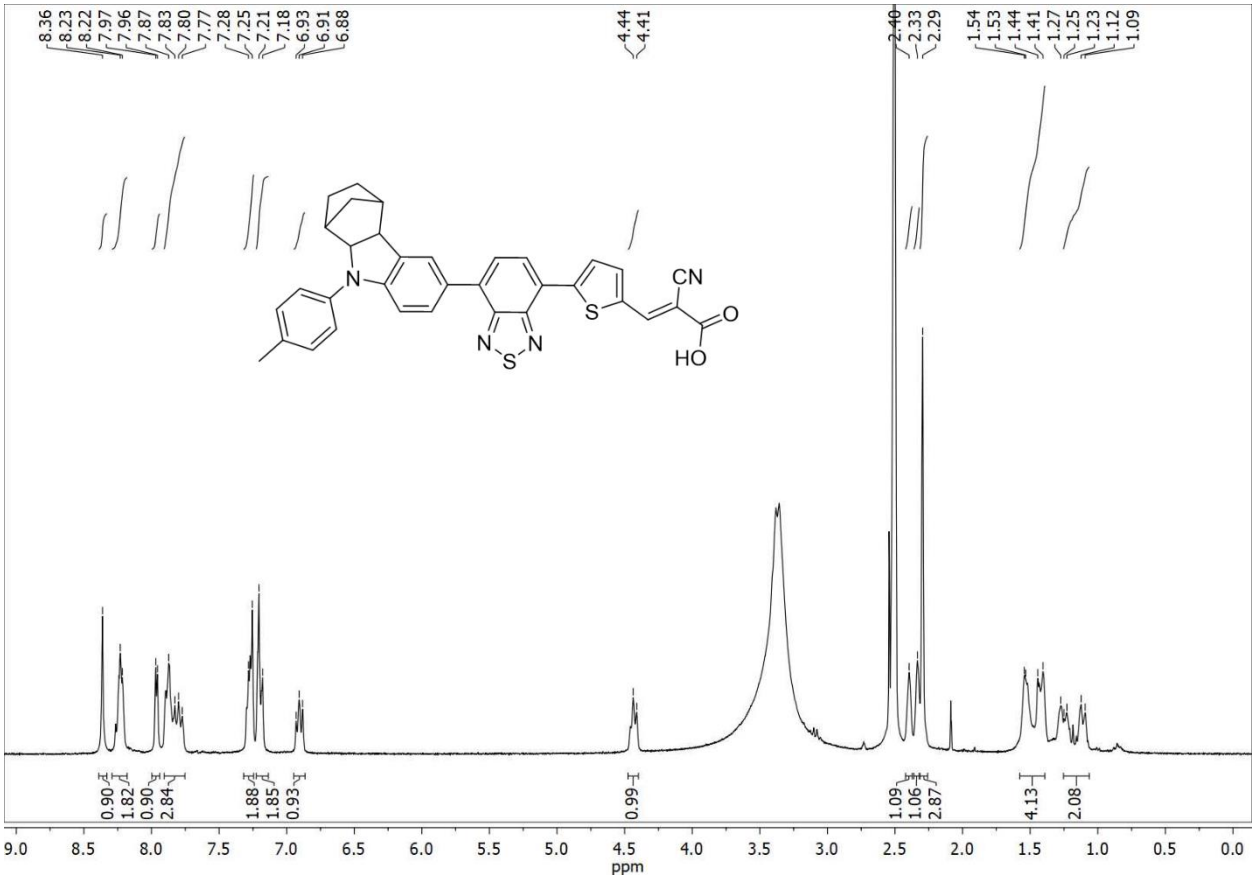


^{13}C NMR (75 MHz)

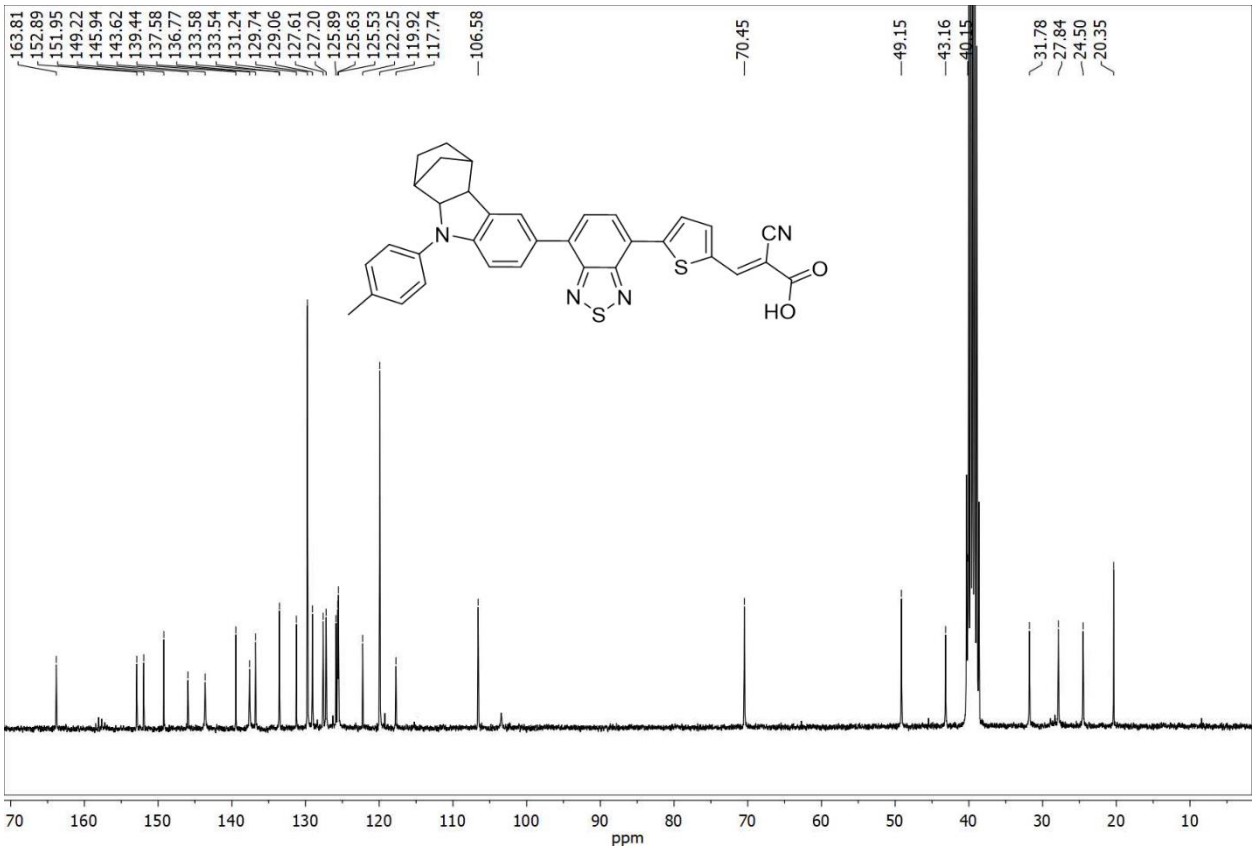


2-Cyano-3-(5-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid **(NIK88)**

^{1}H NMR (300 MHz)

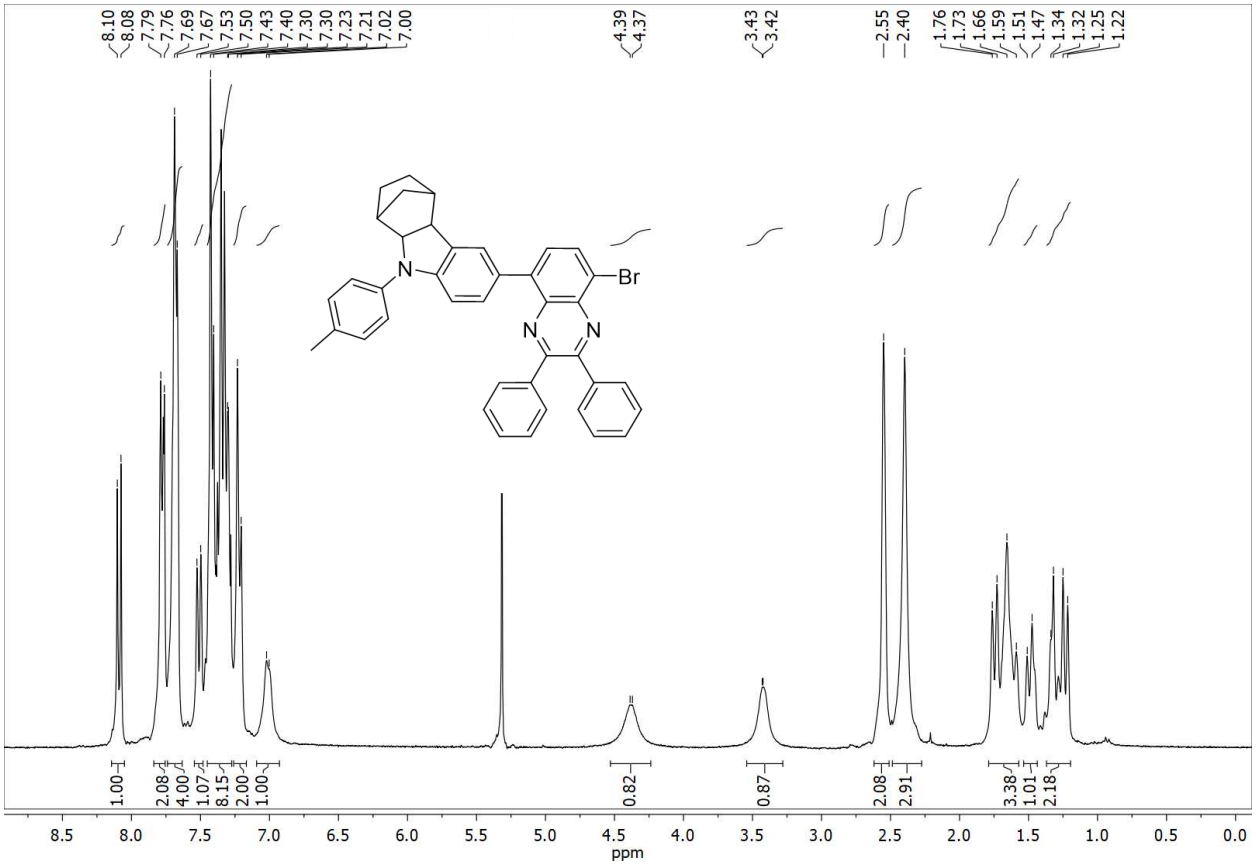


^{13}C NMR (75 MHz)

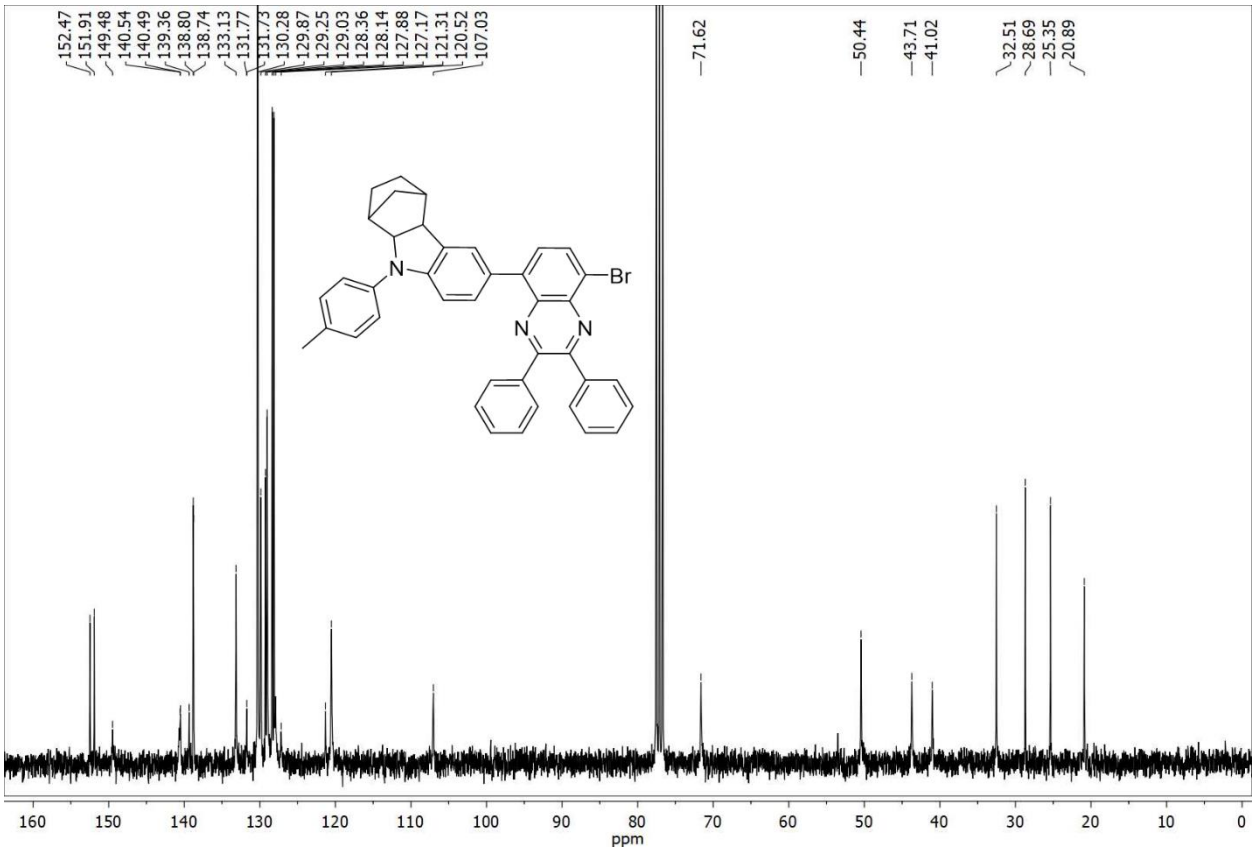


6-(8-Bromo-2,3-diphenylquinoxalin-5-yl)-9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methano-carbazole (**4b**)

^{1}H NMR (300 MHz)

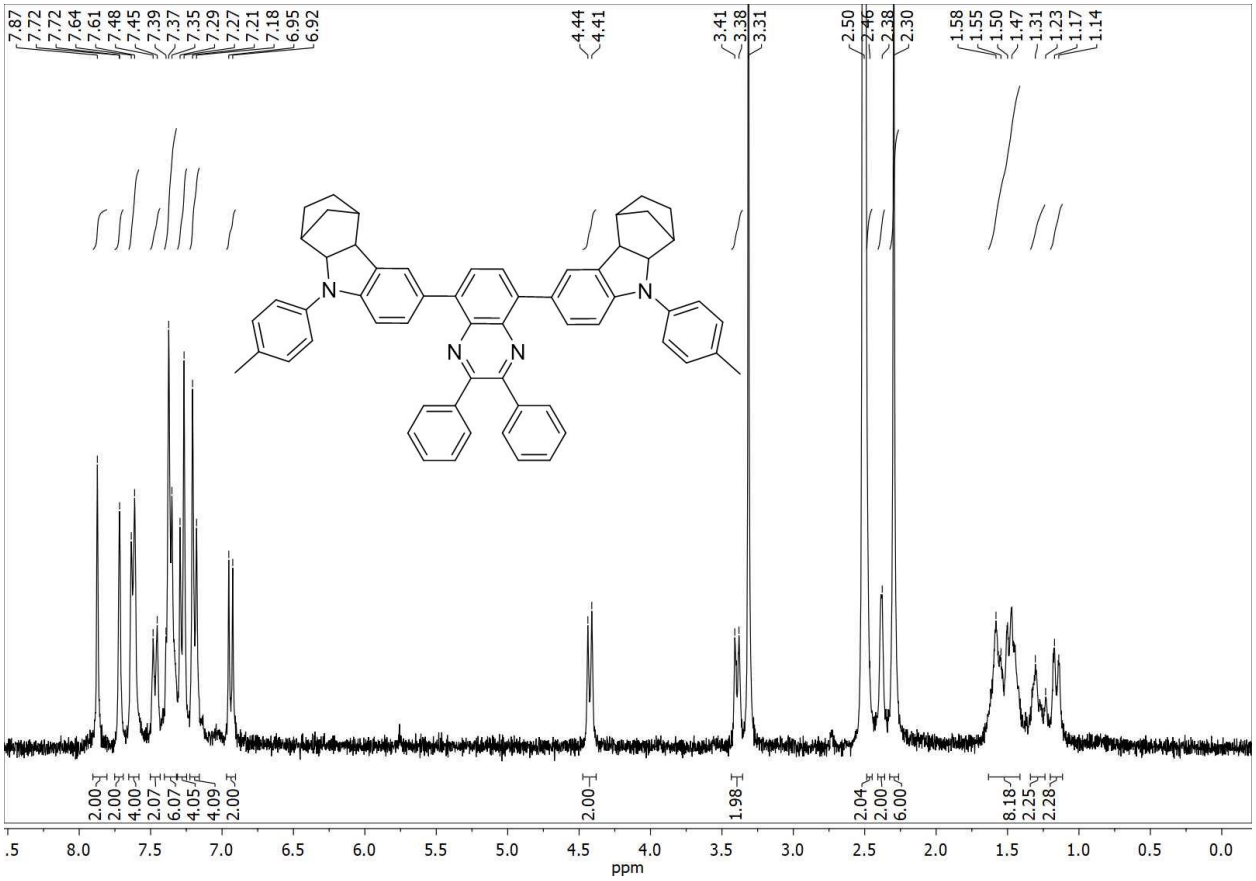


^{13}C NMR (75 MHz)

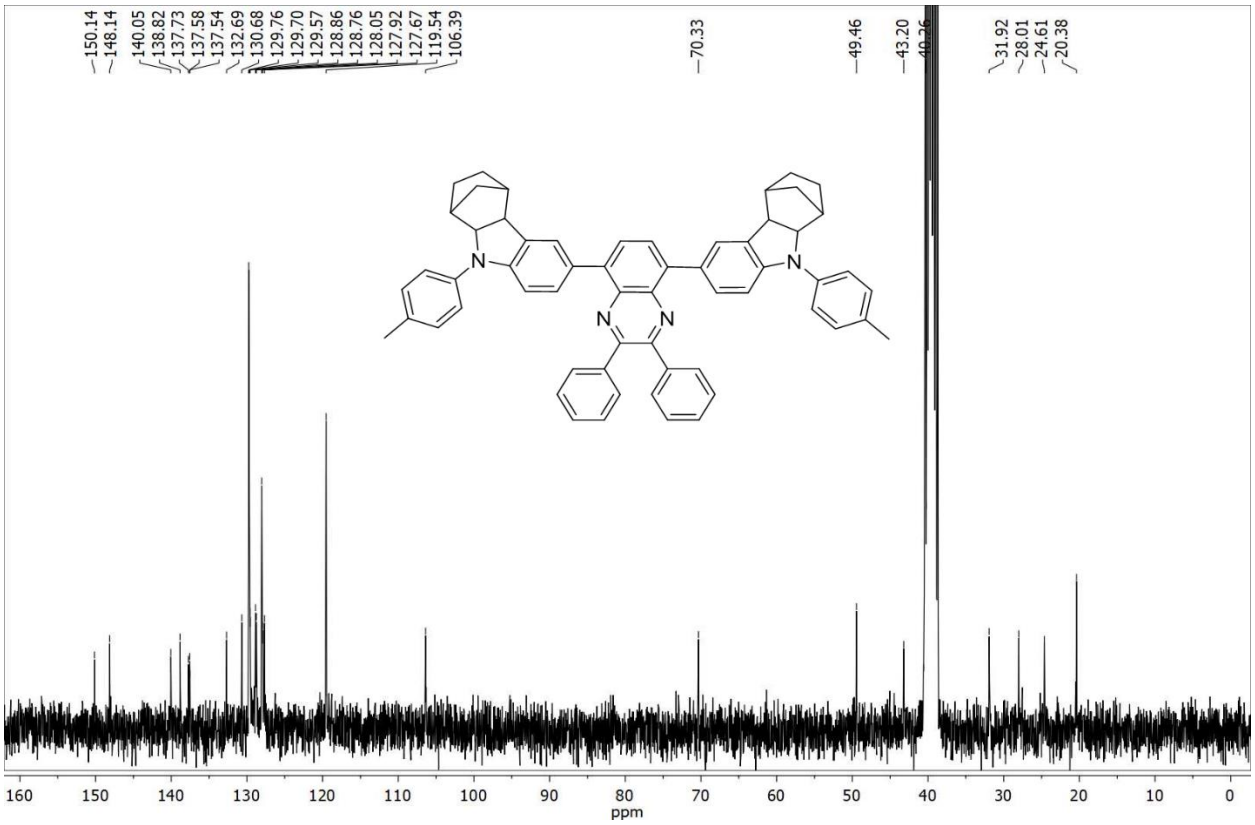


6,6'-(2,3-diphenylquinoxaline-5,8-diyl)bis(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole) (**5b**)

^{1}H NMR (300 MHz)

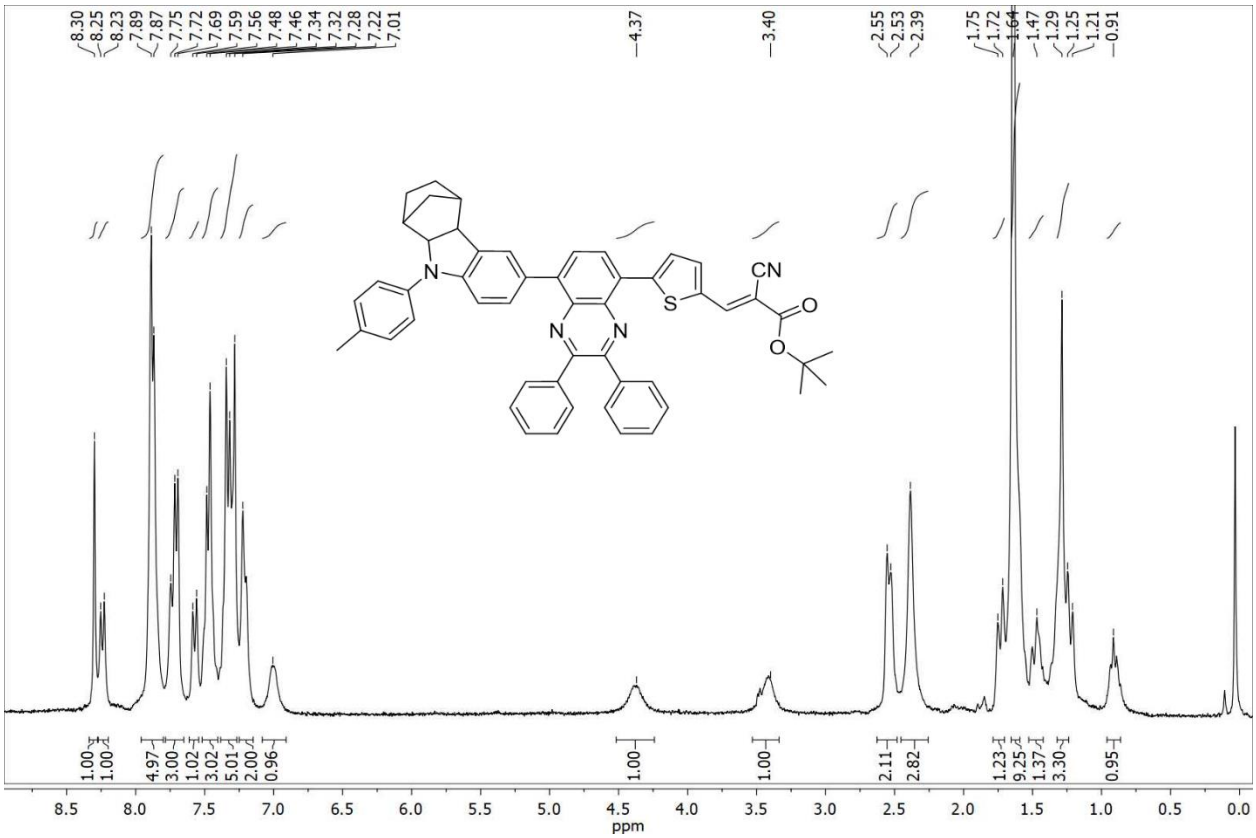


^{13}C NMR (75 MHz)

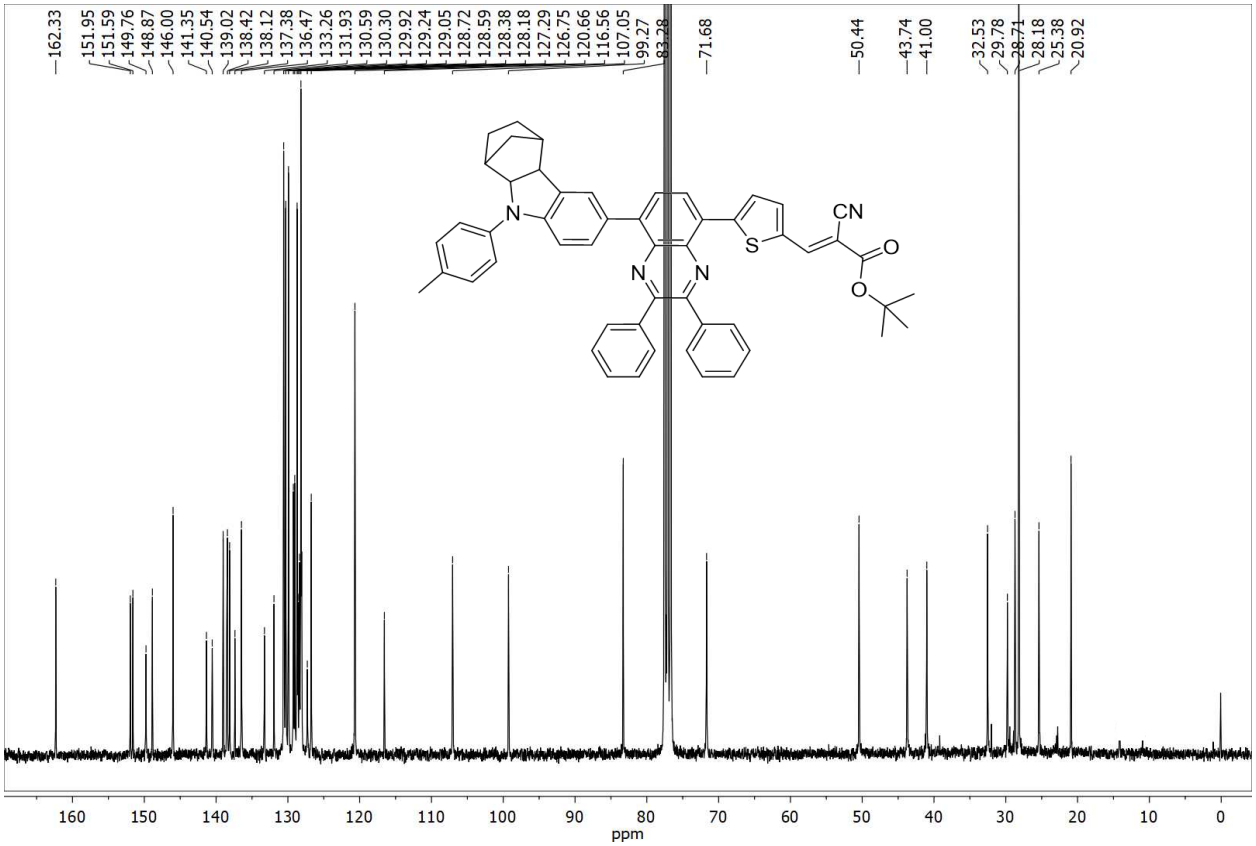


Tert-butyl-2-cyano-3-(5-(2,3-diphenyl-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methano-carbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)acrylate (**7b**)

^{1}H NMR (300 MHz)

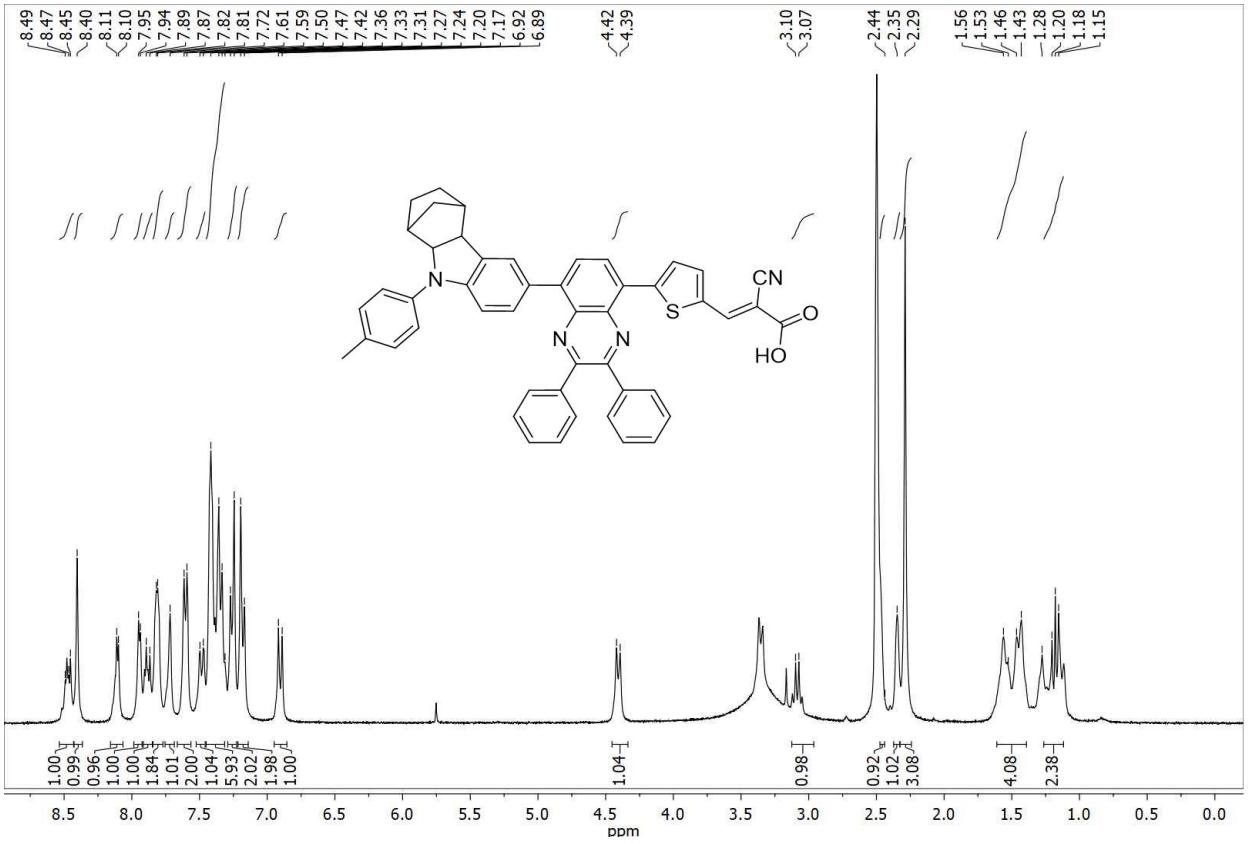


^{13}C NMR (75 MHz)

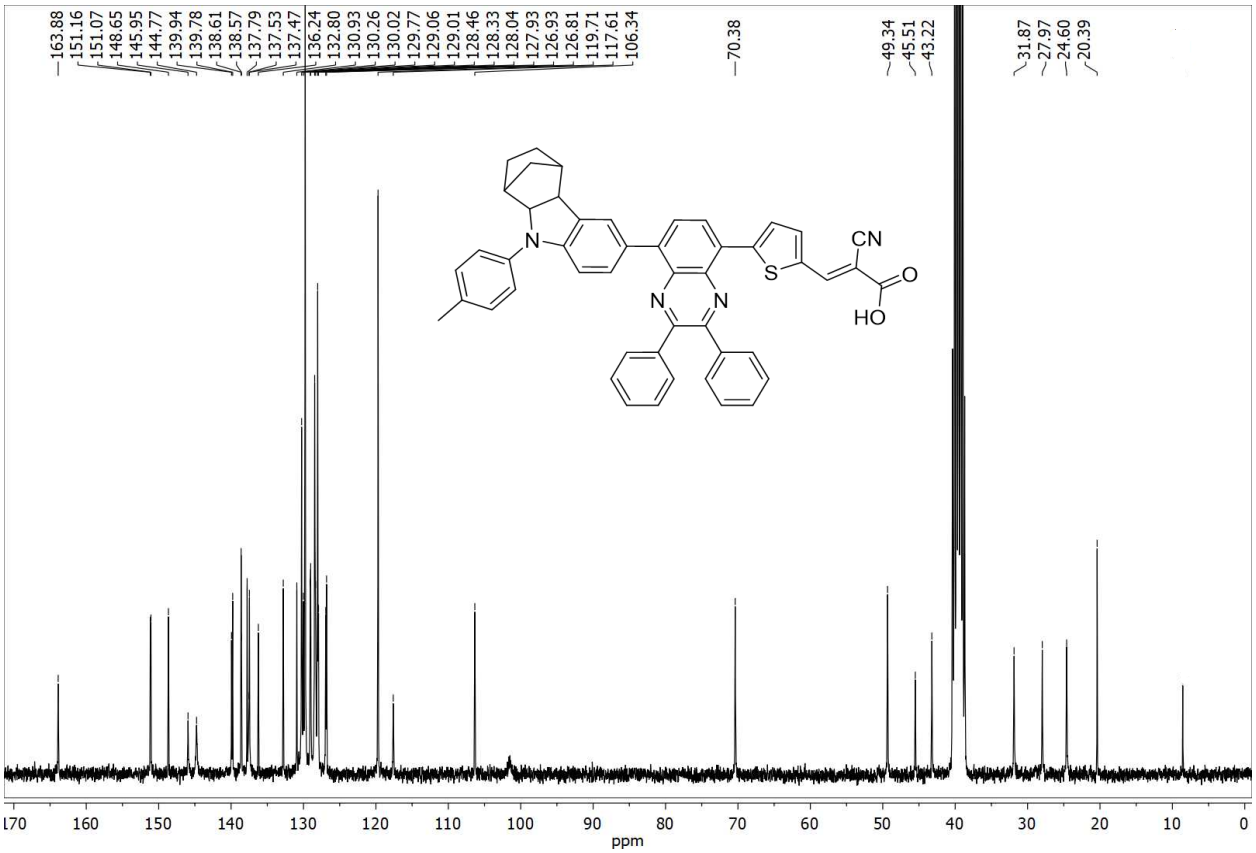


(2-Cyano-3-(5-(2,3-diphenyl-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methano-carbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl) acrylic acid (**NIK 97**)

^{1}H NMR (300 MHz)

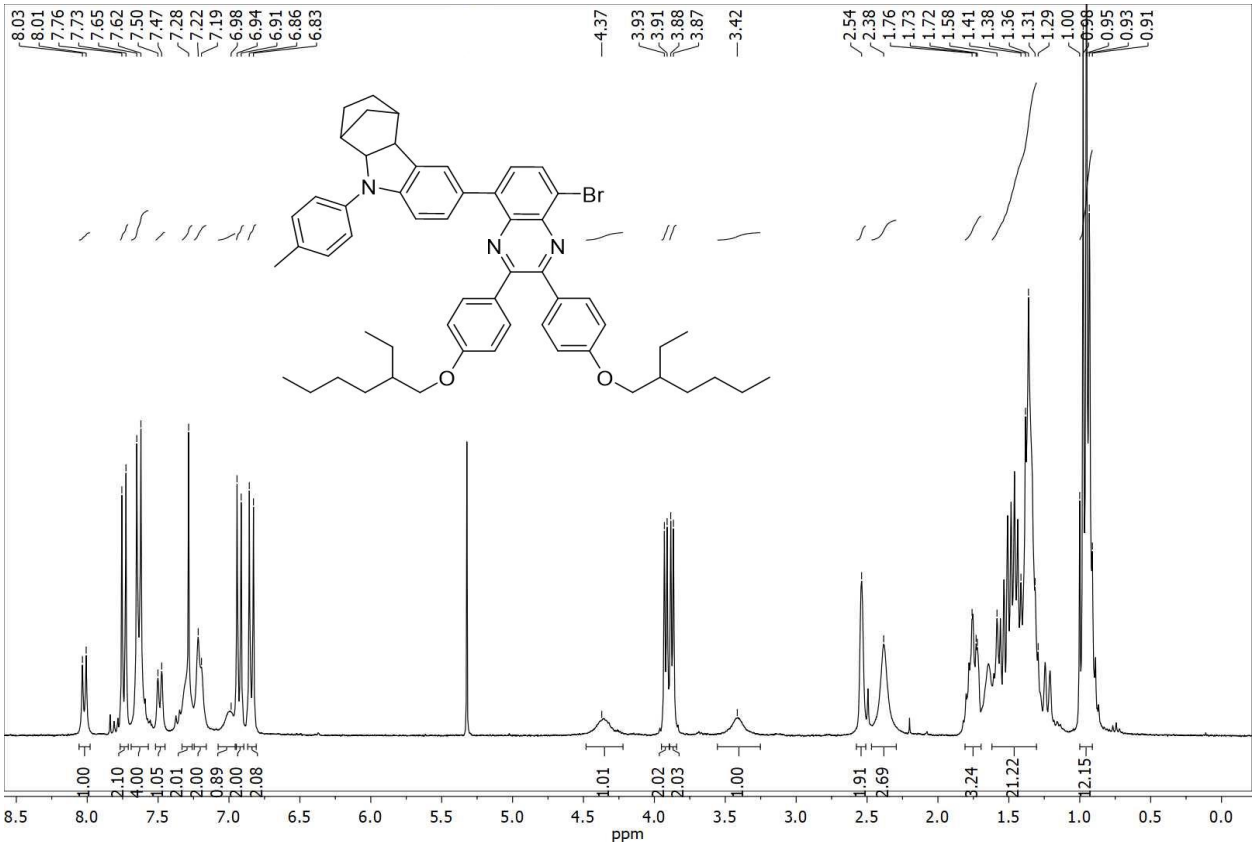


^{13}C NMR (75 MHz)

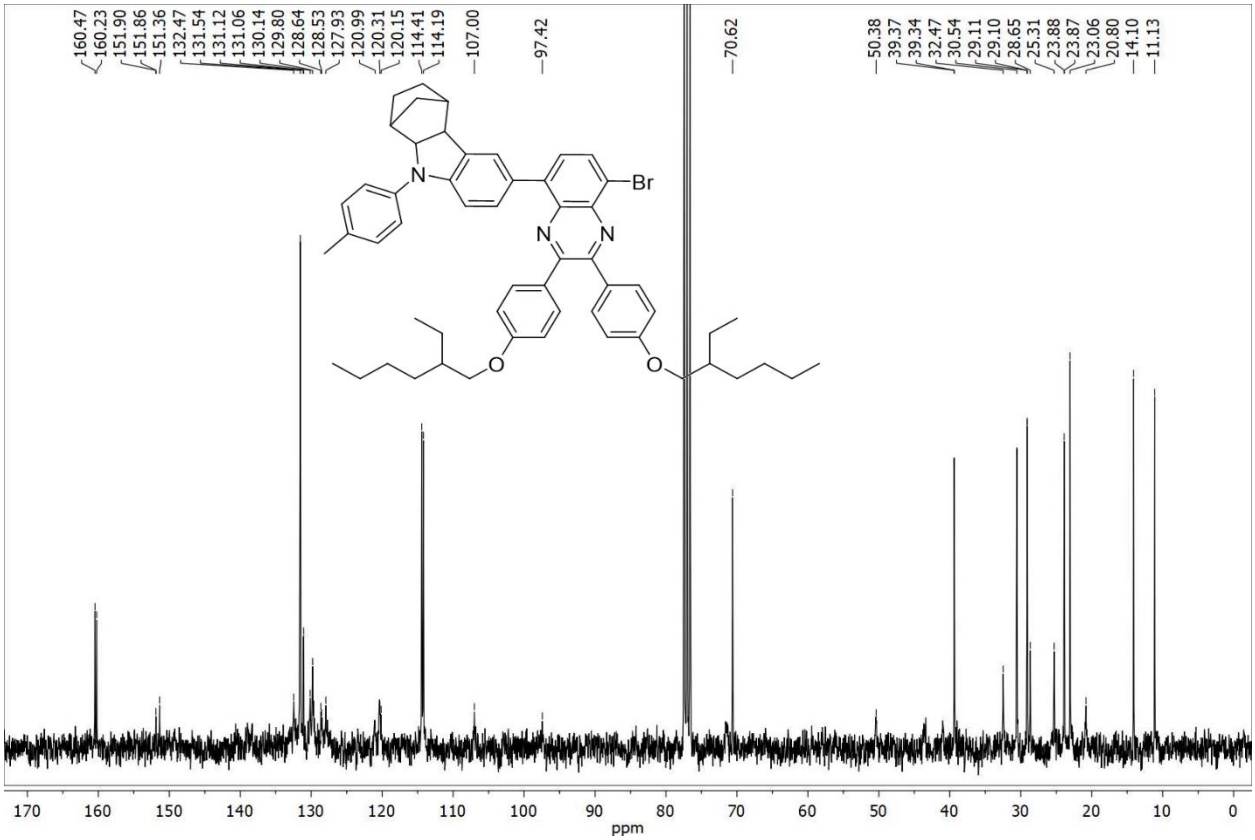


6-(8-Bromo-2,3-bis(4-((2-ethylhexyl)oxy)phenyl)quinoxalin-5-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**4c**)

^{1}H NMR (300 MHz)

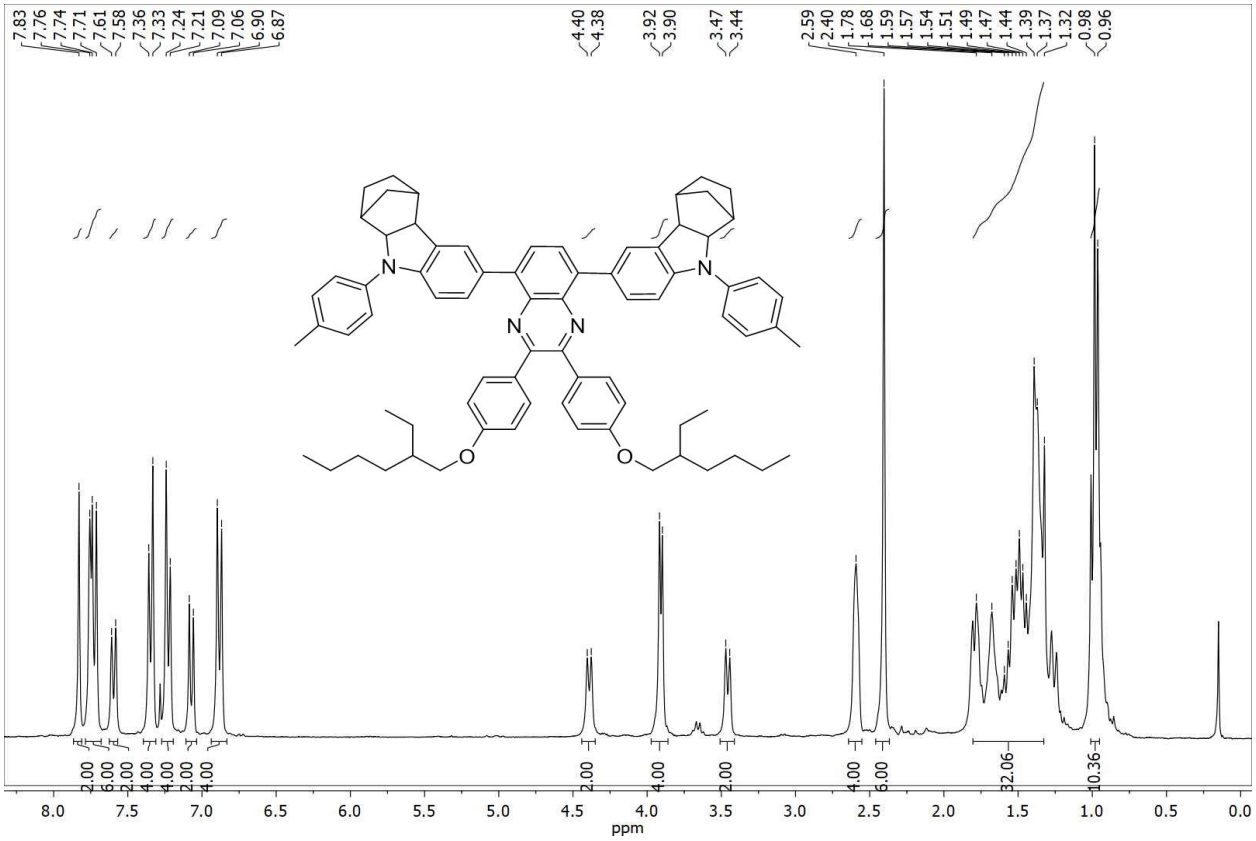


^{13}C NMR (75 MHz)

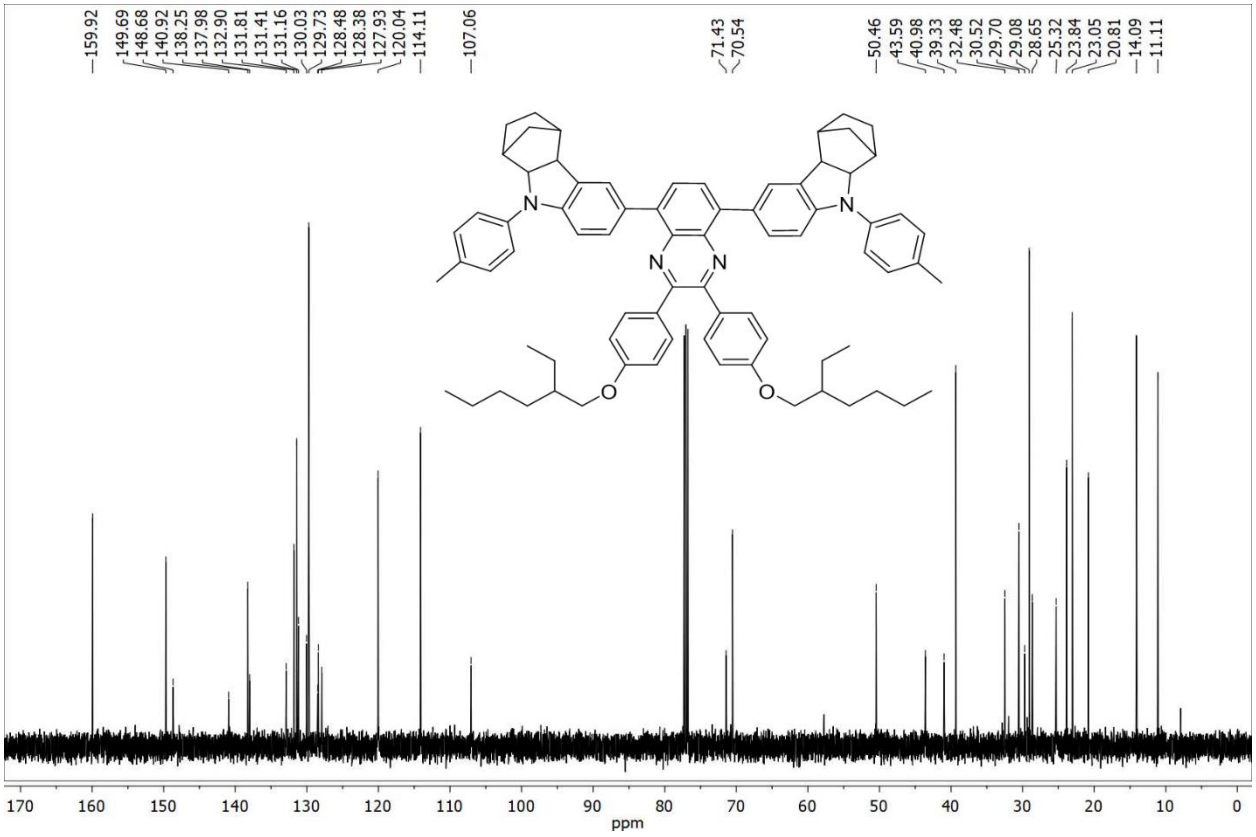


6,6'-(2,3-Bis(4-((2-ethylhexyl)oxy)phenyl)quinoxaline-5,8-diyl)bis(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole) (**5c**)

^{1}H NMR (300 MHz)

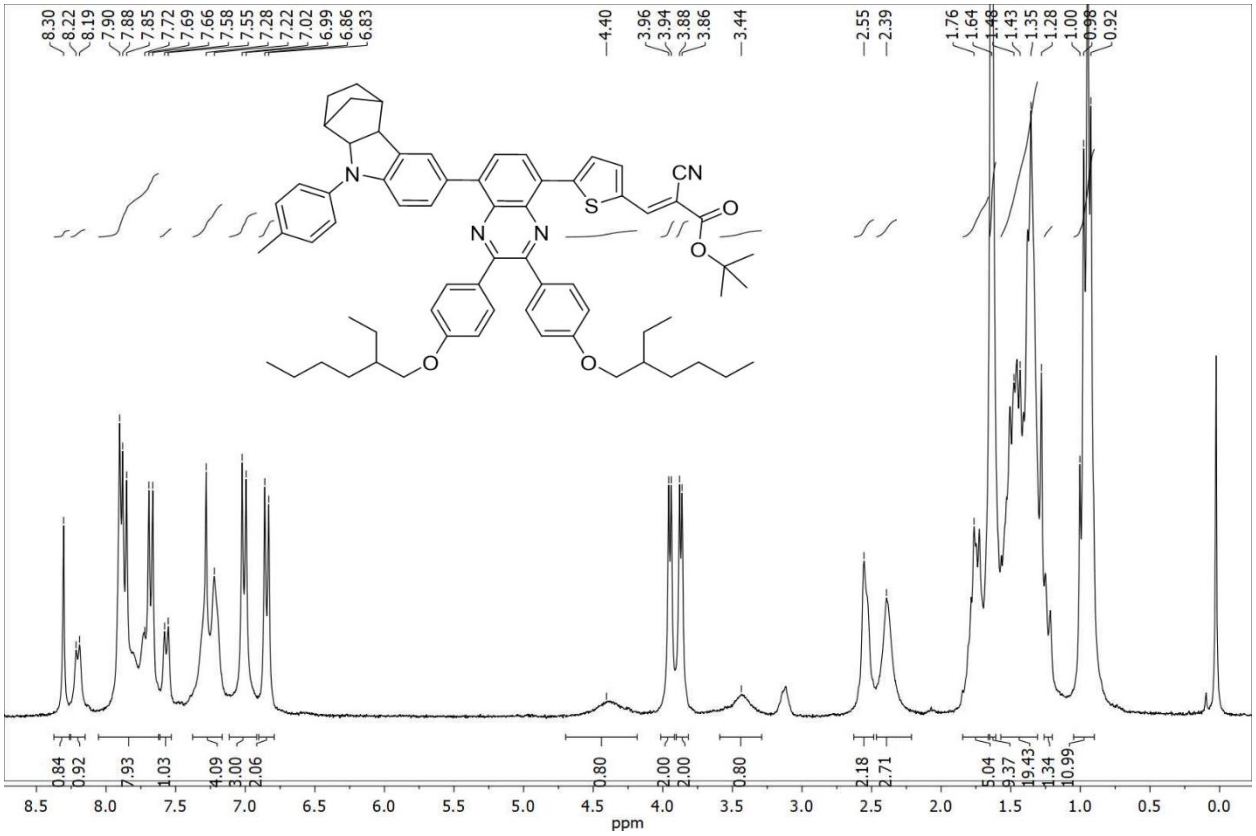


^{13}C NMR (75 MHz)

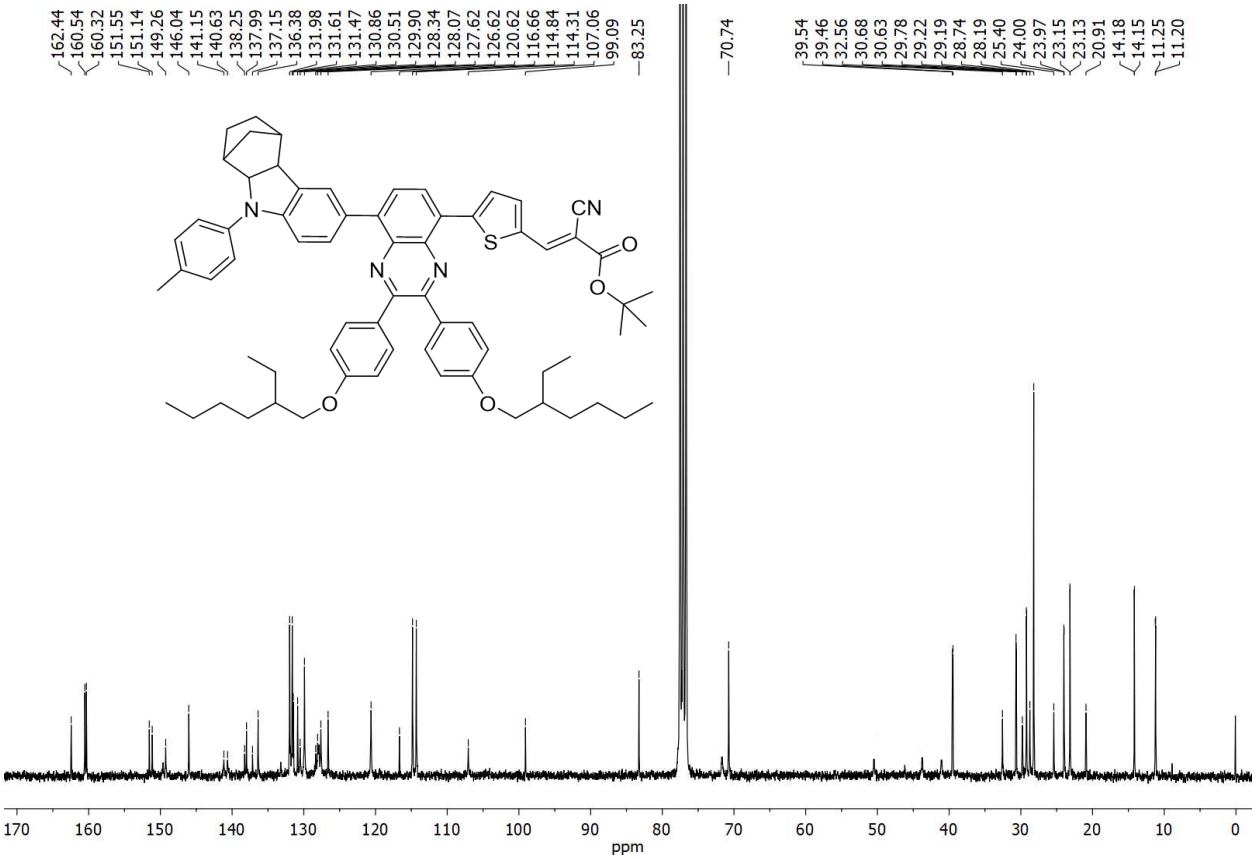


Tert-butyl 3-(5-(2,3-bis(4-((2-ethylhexyl)oxy)phenyl)-8-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)-2-cyanoacrylate (**7c**)

^{1}H NMR (300 MHz)

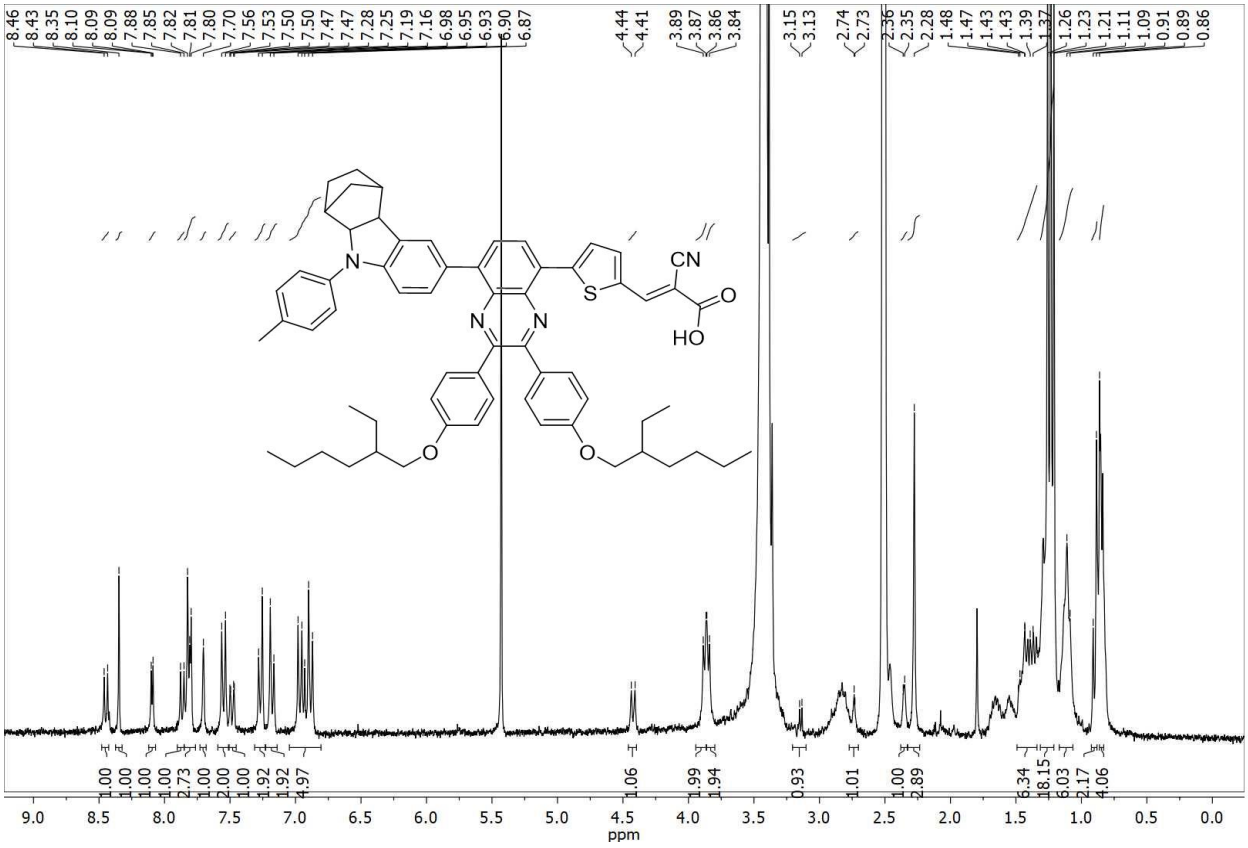


^{13}C NMR (75 MHz)

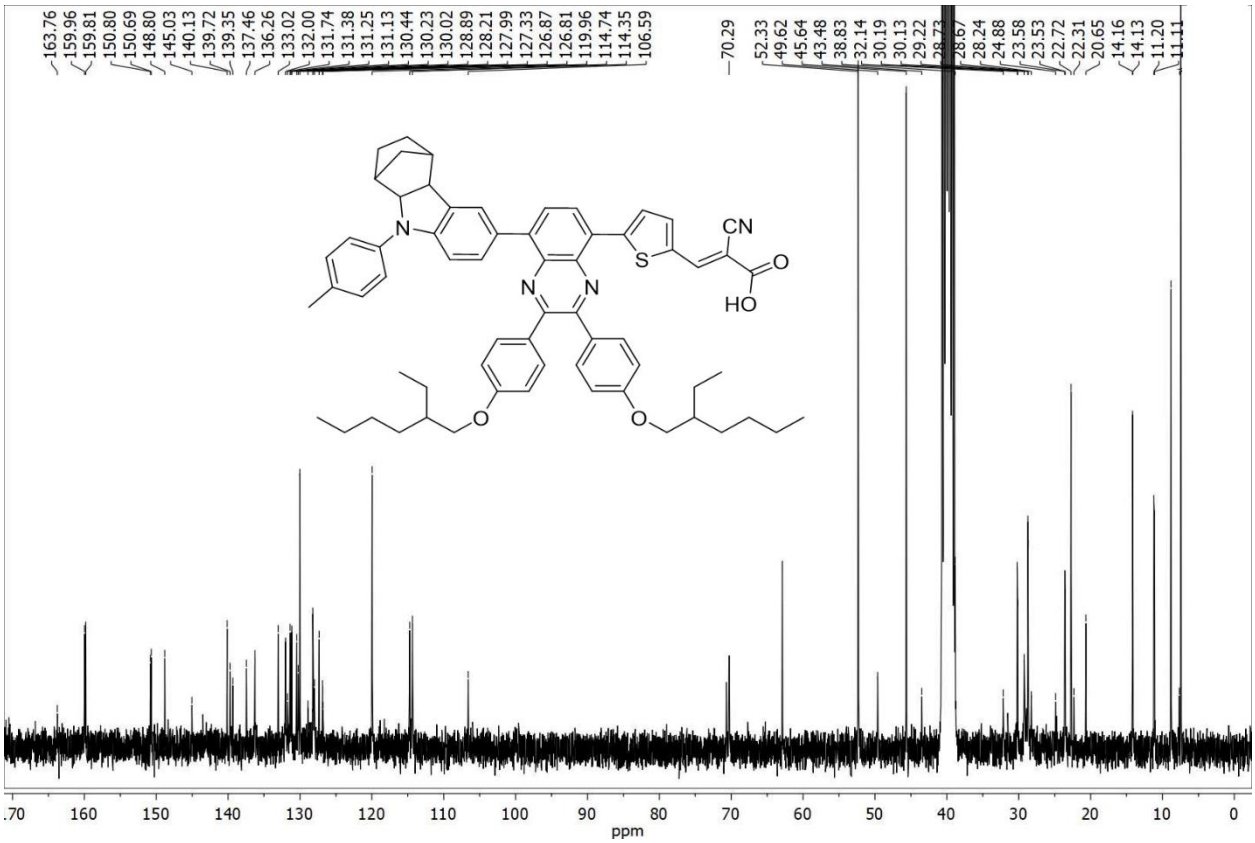


3-(5-(2,3-Bis(4-((2-ethylhexyl)oxy)phenyl)-8-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)quinoxalin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (**NIK99**)

^{1}H NMR (300 MHz)

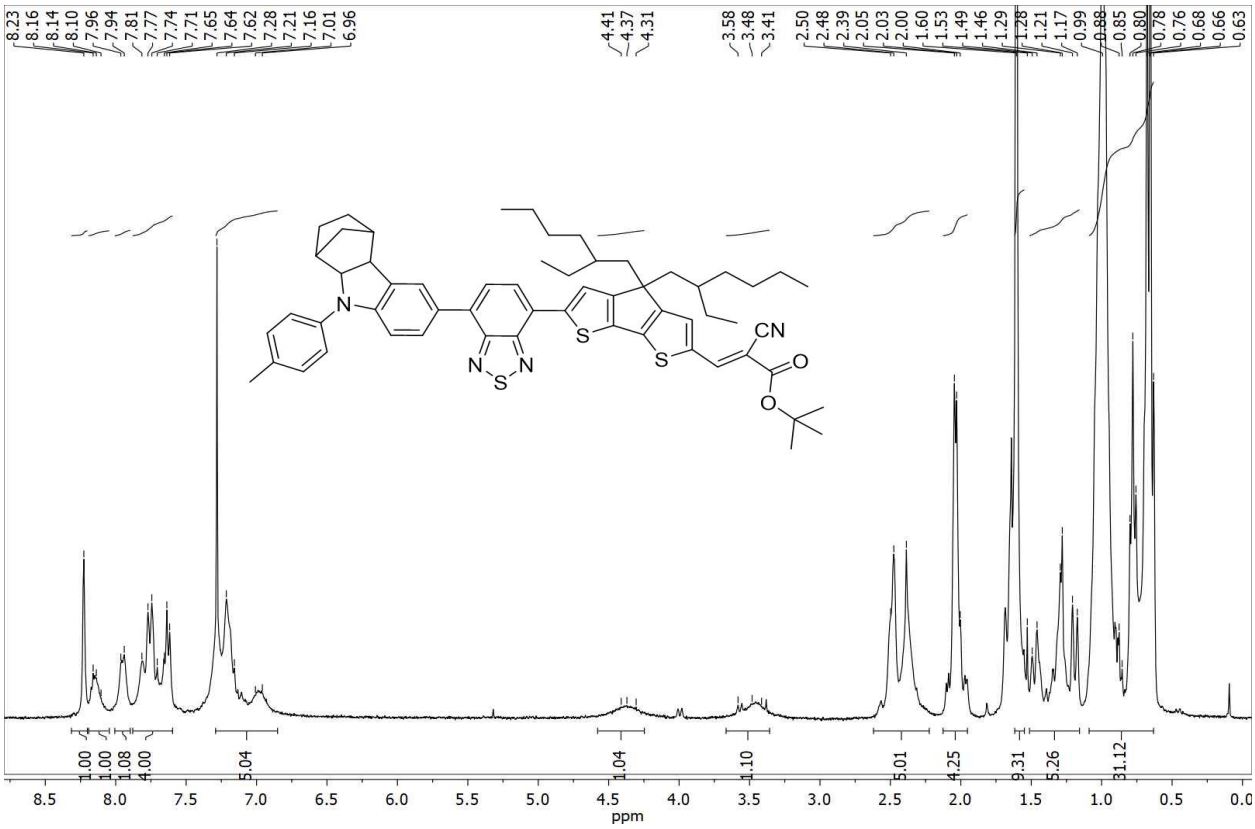


^{13}C NMR (75 MHz)

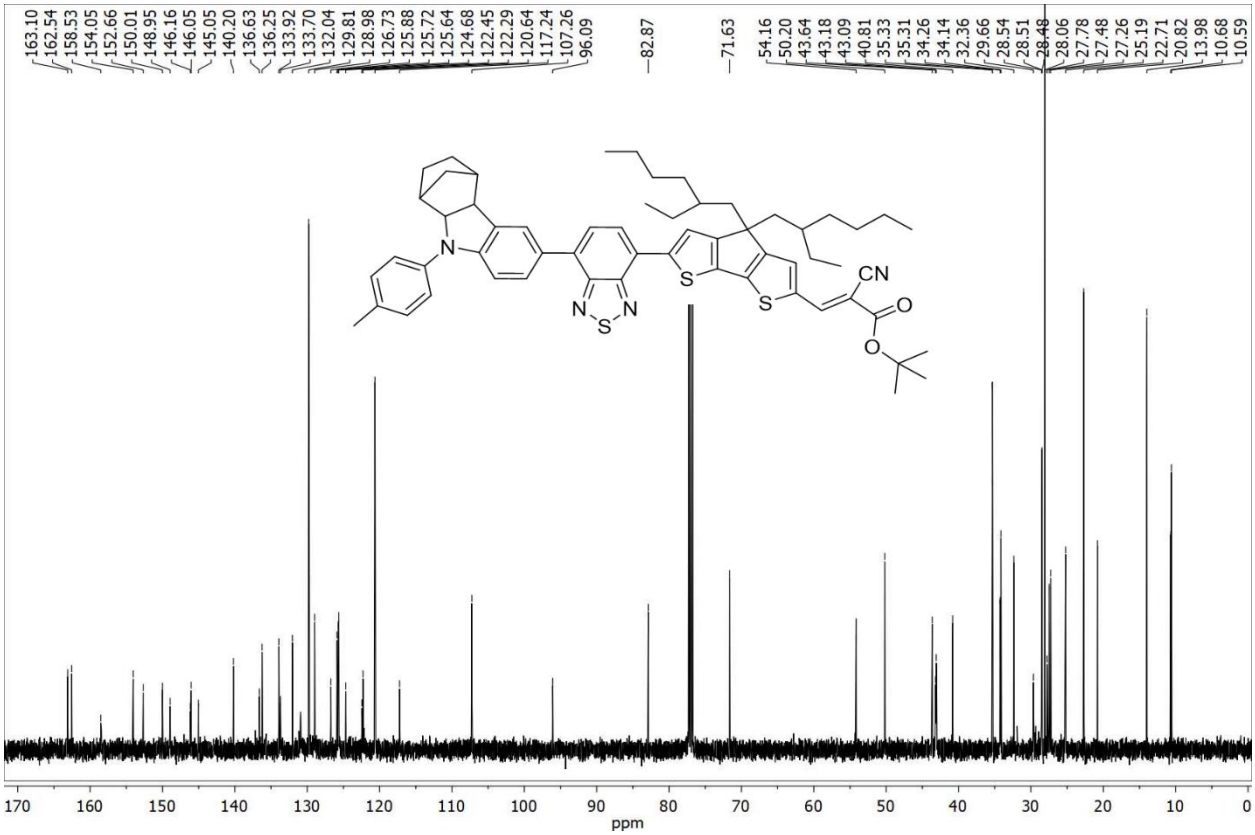


Tert-butyl 3-(4,4-bis(2-ethylhexyl)-6-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methano-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylate (**7d)**

^{1}H NMR (300 MHz)

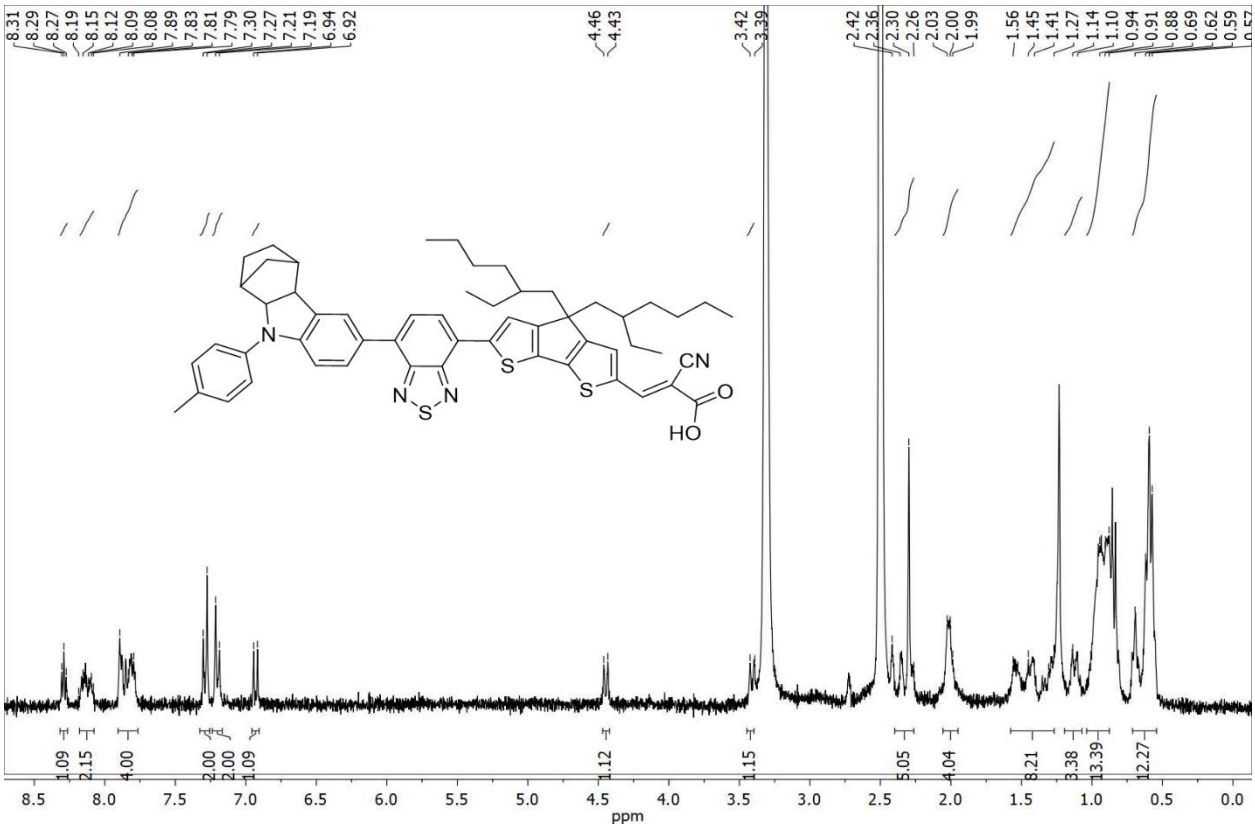


^{13}C NMR (75 MHz)



3-(4,4-Bis(2-ethylhexyl)-6-(7-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylic acid (**NIK119**)

^{1}H NMR (300 MHz)



^{13}C NMR (75 MHz)