Structural features of indoline donors in D-A-π-A type organic sensitizers for dye-sensitized solar cells

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Table of content

1. Statistics of photovoltaic performance of DSSCs fabricated with **MAX** dyes with 4 μm transparent TiO_2 layer and CDCA additions

Table S1.

Dye	J_{SC}/mA·cm^{-2}	V_{OC}/mV	*FF*	PCE (%)
MAX114	10.43	0.54	0.71	4.02
	8.81	0.53	0.70	3.25
	11.98	0.53	0.73	4.63
	11.51	0.57	0.75	4.94
Average	10.68±1.41	0.54±0.02	0.72±0.02	4.21±0.75
MAX140	12.57	0.52	0.64	4.16
	8.04	0.54	0.76	3.29
	11.81	0.55	0.70	4.58
	13.87	0.56	0.66	5.15
Average	11.57±2.50	0.54±0.02	0.69±0.06	4.25±0.74
MAX155	6.47	0.51	0.75	2.47
	9.24	0.46	0.71	3.02
	8.94	0.55	0.76	3.72
	10.99	0.54	0.74	4.38
Average	8.91±1.86	0.52±0.04	0.74±0.02	3.40±0.83
MAX157	12.02	0.58	0.75	5.20
	11.37	0.54	0.67	4.09
	9.70	0.54	0.73	3.83
	11.03	0.58	0.74	4.71
Average	11.03±0.98	0.56±0.02	0.72±0.04	4.46±0.62
MAX157+SQ2	10.83	0.57	0.76	4.71
	12.38	0.62	0.76	5.80
	12.42	0.60	0.74	5.52
Average	11.70±1.21	0.60±0.03	0.75±0.01	5.34±0.57

2. IPCE of one batch of the **MAX** series (a) and the corresponding *J-V* curves at the point of the measurement (b). The *J-V* of the fresh devices (c) follows the trend that is explained in the main text

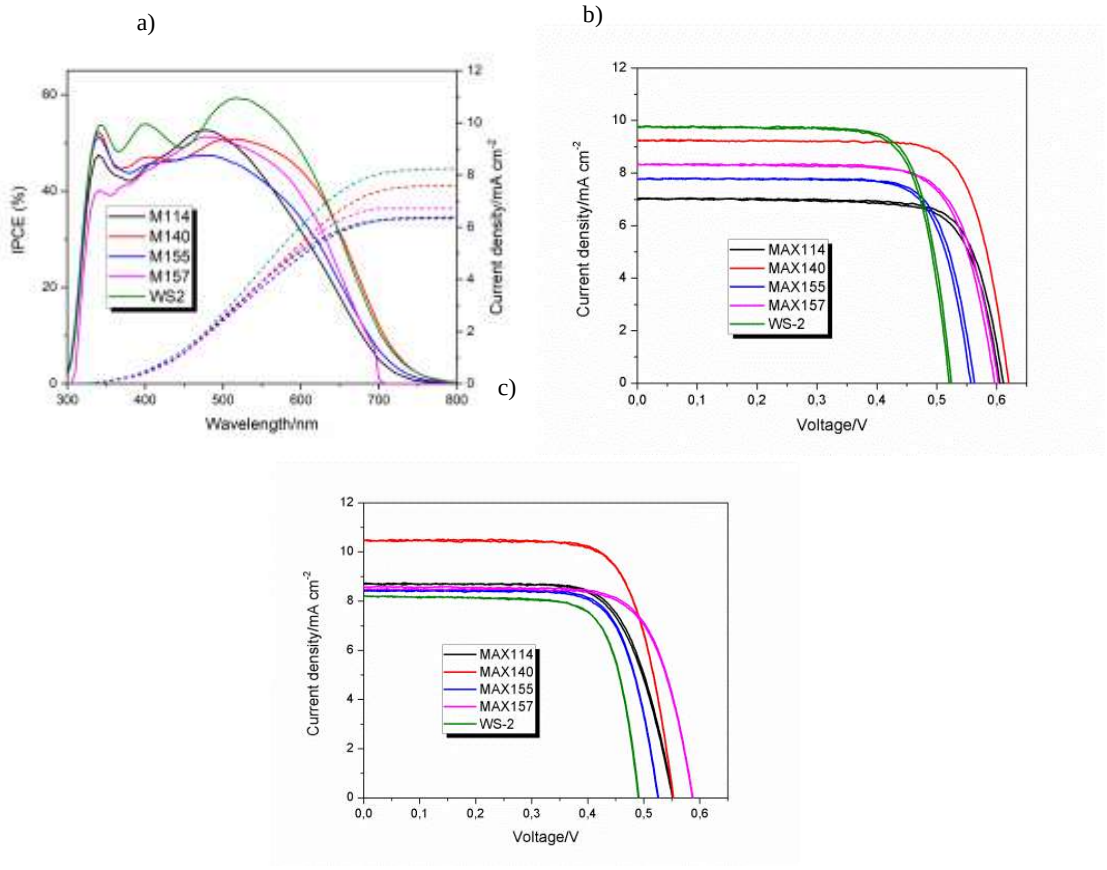


Figure S1

3. Electron lifetime plotted against the chemical capacitance (a), recombination resistance plotted against the V_{OC} (b) and the chemical capacitance plotted against the V_{OC} (c). The values were extracted by fitting the complex plane plot (d) using the equivalent circuit (e). R_s = series resistance, R_c and C_c = resistance and capacitance at the contacts, R_{rec} = recombination resistance at the TiO_2/dye/electrolyte, C_μ = chemical capacitance at the TiO_2/dye/electrolyte. The electron lifetime was derived by $R_{rec} \times C_\mu$.

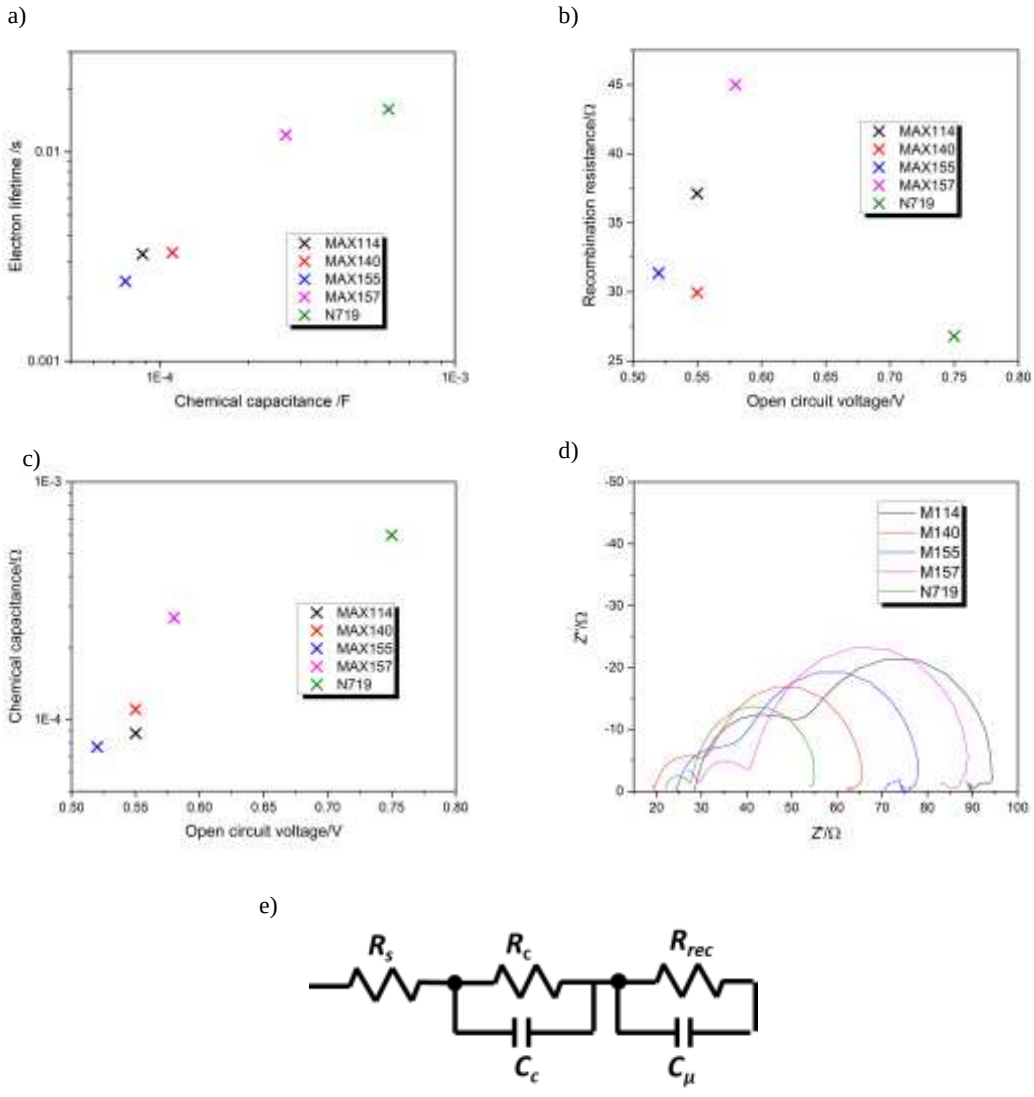


Figure S2.

4. Photovoltaic performance and *J-V* curves of DSSCs based on **MAX140** dye with the thickness of the transparent TiO_2 layer varied from 4 μm to 12 μm. The thickness of the scattering layer was fixed to 4 μm

Table S2.

Dye and TiO_2 layers thickness	J_{SC}/mA·cm^{-2}	V_{OC}/mV	*FF*	PCE (%)
MAX140 (4 μm + 4 μm)	12.75	0.56	0.70	4.98
MAX140 (8 μm + 4 μm)	11.96	0.54	0.74	4.71
MAX140 (12 μm + 4 μm)	11.58	0.52	0.69	4.15
N719 (12 μm + 4 μm)	11.67	0.61	0.74	5.28

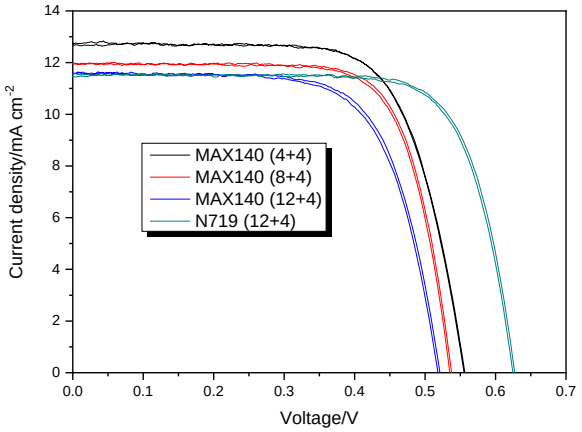


Figure S3.

5. Influence of CDCA addition as co-adsorbent on photovoltaic performance and *J-V* curves of DSSCs based on **MAX140** dye

Table S3.

Dye and addition of CDCA	J_{SC}/mA·cm^{-2}	V_{OC}/mV	*FF*	PCE (%)
MAX140 with CDCA	11.17	0.53	0.72	4.24
MAX140 without CDCA	7.17	0.51	0.73	2.68

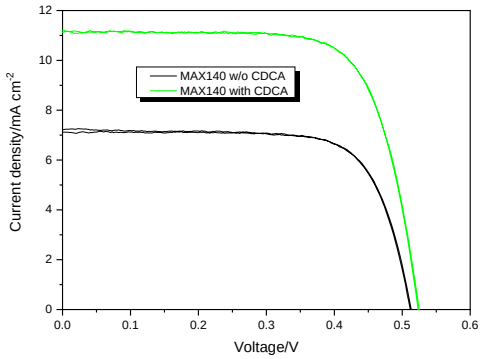


Figure S4.

6. Variation of photovoltaic performance and *J-V* curves with aging time for DSSCs based on **MAX140** dye

Table S4.

Weeks	J_{SC}/mA·cm^{-2}	V_{OC}/mV	*FF*	PCE (%)
Fresh	12.75	0.56	0.70	4.98
1	12.45	0.53	0.75	4.92
4	11.22	0.49	0.74	4.09
5	10.73	0.48	0.74	3.81
9	12.30	0.46	0.75	4.22

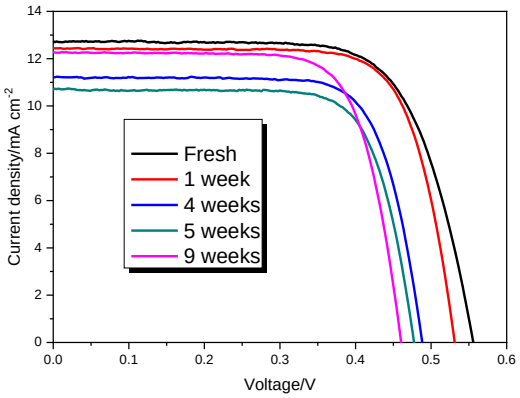


Figure S5.

7. Spectral data of intermediates and **MAX** dyes

6.1. 4-(2-Ethylhexyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**2a**). Clear oil (3.64g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.50 (d, 1H, *J* = 7.2), 7.31 (d, 1H, *J* = 7.6), 7.14 (m, 2H), 3.94 (m, 2H), 3.52 (d, 1H, *J* = 4.5), 2.92 (m, 2H), 2.61 (m, 2H), 1.96 (m, 1H) 1.5-1.3 (m, 7H), 0.96 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 146.5, 141.2, 124.4, 119.7, 118.7, 118.5, 117.5, 109.8, 49.0, 40.2, 30.8, 28.8, 28.5, 25.6, 24.7, 24.1, 23.1, 14.1, 10.8. HRMS-ESI (m/z): [M]+ calcd for ($C_{19}H_{27}N$) 270.2216, found 270.2213. IR, ν, cm-1: 2957, 2859, 1740, 1704, 1459, 1379, 1230, 1068, 1028, 947, 736. R_f = 0.63 (petroleum ether/ethyl acetate 10:1).

6.2. 9-(2-Ethylhexyl)-2,3,4,9-tetrahydro-1*H*-carbazole (**2b**). Clear oil (3.67 g, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.49 (d, *J* = 7.6, 1H), 7.27 (d, *J* = 6.9, 1H), 7.15 (t, *J* = 7.3, 1H), 7.08 (t, *J* = 7.3, 1H), 3.96-3.84 (m, 2H), 2.83-2.69 (m, 4H), 2.04-1.83 (m, 5H), 1.41-1.27 (m, 8 H), 0.94-0.88 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 136.7, 135.8, 127.4, 120.4, 118.5, 117.7, 109.2, 109.2, 47.3, 40.3, 31.0, 28.9, 24.3, 23.6, 23.4, 23.2, 22.8, 21.2, 14.1, 11.0. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{20}H_{29}N$) 284.2372, found 284.2373. IR, ν, cm^{-1}: 3051, 3028, 2957, 2930, 2873, 2856, 1614, 1467, 1375, 1180, 736. R_f = 0.72 (petroleum ether/ethyl acetate 10:1).

6.3. 4-Benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**3c**). Clear oil (3.55g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.45-7.29 (m, 5H), 7.13 (d, *J* =7.2, 1H), 7.07 (d, *J* = 7.7, 1H), 6.69 (t, *J* = 7.3, 1H), 6.33 (d, *J* = 7.8, 1H), 4.54-4.36 (m, 2H), 4.34-4.26 (m, 1H), 3.85 (t, *J* = 7.7, 1H), 2.14-2.01 (m, 1H), 1.97-1.85 (m, 2H), 1.79-1.63 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 152.4, 139.3, 133.6, 128.6, 127.6, 127.3, 126.9, 124.3, 116.7, 105.4, 70.0, 51.2, 45.9, 35.2, 33.3, 24.7. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{18}H_{19}N$) 250.1590, found 250.1590. IR, ν, cm^{-1}: 2950, 2863, 1604, 1491, 1355, 1255, 1156, 1025, 740, 697. R_f = 0.65 (petroleum ether/ethyl acetate 20:1).

6.4. 4-(2-Ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**3a**). Colorless oil (3.03 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.06 (m, 2H), 6.61 (t, 1H, *J* = 7.3), 6.35 (d, 1H, *J* = 7.8), 4.19 (m, 1H), 3.79 (m, 1H), 3.08 (d, 2H, *J* = 7.4), 2.06 (m, 1H) 1,9-1,3 (m, 14H), 0,99 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 152.9, 133.3, 127.4, 123.9, 115.8, 105.0, 70.1, 51.9, 45.8, 38.2, 34.9, 33.2, 31.1, 29.0, 24.6, 24.4, 23.2, 14.2, 10.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{19}H_{29}N$) 272.2373, found 272.2384. IR, ν, cm^{-1}: 2929, 2859, 1605, 1489, 1461, 1381, 1240, 1158, 737, 617. R_f = 0.65 (petroleum ether/ethyl acetate 20:1).

6.5. 9-(2-Ethylheptyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**3b**). Pale yellow oil (3.7 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.07 (t, *J* = 6.3, 1H), 7.04 (d, *J* = 5.4, 1H), 6.66 (t, *J* = 7.3, 1H), 6.46 (d, *J* = 7.7, 1H), 3.53-3.43 (m, 1H), 3.08 (q, *J* = 6.7, 1H), 2.97 -2.80 (m, 2H), 1.78-1.32 (m, 17H), 0.99-0.91 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 152.9, 133.7, 127.2, 122.5, 117.0, 107.0, 64.9, 51.2, 40.8, 39.2, 31.6, 29.3, 27.5, 25.4, 24.9, 24.4, 23.3, 21.8, 14.2, 10.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{20}H_{31}N$) 286.2529, found 286.2529. IR, ν, cm^{-1}: 3048, 3023, 2957, 2929, 2855, 1607, 1479, 1459, 1380, 1118, 742. R_f = 0.57 (petroleum ether/ethyl acetate 20:1).

6.6. 7-Bromo-4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**4a**). Clear oil (3.8 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.05 (m, 2H), 6.13 (d, *J* = 8.1, 1H), 4.16 (m, 1H), 3.71 (m, 1H), 2.97 (d, *J* = 7.3, 2H), 2.00 (m, 1H), 1,9-1,6 (m, 5H), 1,6-1,5 (m, 1H), 1,3 (m, 8H), 0,93 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 151.8, 135.6, 129.8, 126.8, 106.7, 105.9, 69.6, 51.0, 45.5, 37.9, 34.9, 32.8, 31.0, 28.9, 24.4, 24.1, 23.1, 14.1, 10.8. HRMS-ESI (m/z): [M]+ calcd for ($C_{19}H_{28}NBr$) 350.1478, found 350.1470. IR, ν, cm-1: 2929, 2859, 1598,

1489, 1381, 1239, 1106, 793, 617. R_f = 0.67 (petroleum ether/ethyl acetate 20:1).

6.7. 6-Bromo-9-(2-ethylheptyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**4b**). Clear oil (2.54 g, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.14 (d, *J* = 8.2, 1H), 7.10 (s, 1H), 6.31 (d, *J* = 8.3, 1H), 3.49 (q, *J* = 6.2, 1H), 3.08 (q, *J* = 6.7, 1H), 2.95-2.79 (m, 2H), 1.79-1.62 (m, 4H), 1.49-1.30 (m, 13H), 1.00-0.91 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 151.7, 136.0, 135.9, 129.7, 125.6, 108.2, 65.1, 50.8, 40.6, 38.9, 31.2, 29.0, 27.2, 25.3, 24.8, 24.4, 23.3, 21.7, 14.2, 11.22. $[M]^+$ calcd for ($C_{20}H_{30}BrN$) 364.1634, found 364.1634. IR, ν, cm^{-1}: 3056, 3030, 2929, 2856, 1742, 1599, 1475, 1369, 1248, 1104, 800. R_f = 0.74 (petroleum ether/ethyl acetate 10:1).

6.8. 7-Bromo-4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**4c**). Clear oil (2.44 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.43-7.26 (m, 5H), 7.15 (s, 1H), 7.09 (d, *J* = 8.5, 1H), 6.13 (d, *J* = 8.3, 1H), 4.52-4.22 (m, 3H), 3.78 (t, *J* = 8.8 Hz, 1H), 2.11-1.94 (m, 1H), 1.93-1.78 (m, 2H), 1.77-1.56 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 151.3, 138.6, 135.9, 130.0, 128.6, 127.2, 127.1, 107.8, 106.5, 69.9, 50.7, 45.7, 35.1, 33.1, 24.6. HRMS-ESI (m/z): [M]+ calcd for ($C_{18}H_{18}NBr$) 328.0696, found 328.0705. IR, ν, cm-1: 2951, 2864, 1597, 1487, 1353, 1253, 1154, 797, 731, 697. R_f = 0.66 (petroleum ether/ethyl acetate 20:1).

6.9. 7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**5a**). Pale yellow oil (740 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.54 (d, *J* = 7.9, 1H), 7.45 (s, 1H), 6.27 (d, *J* = 7.9, 1H), 4.19 (m, 1H), 3.74 (m, 1H), 3.08 (m, 2H), 2.00 (m, 1H), 1.87-1.60 (m, 5H), 1.35 (m, 21H), 0.92 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 155.2, 135.6, 132.4, 130.2, 103.9, 82.9, 69.3, 50.1, 45.3, 37.9, 35.0, 32.9, 31.0, 28.9, 24.9, 24.8, 24.4, 24.1, 23.2, 14.1, 10.8. HRMS-ESI (m/z): [M]+ calcd for ($C_{25}H_{40}O_2NB$) 398.3229, found 398.3218. IR, ν, cm-1: 2929, 2860, 1606, 1439, 1381, 1146, 1109, 965, 862, 807, 676. R_f = 0.47 (petroleum ether/ethyl acetate 10:1).

6.10. 9-(2-Ethylheptyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**5b**). Pale yellow oil (0.88 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.63 (d, *J* = 7.8, 1H), 7.50 (s, 1H), 6.46 (d, *J* = 7.9, 1H), 3.56 (q, *J* = 6.3, 1H), 3.13 (q, *J* = 6.5, 1H), 3.07-2.85 (m, 2H), 1.90-1.67 (m, 4H), 1.57-1.33 (m, 25H), 0.99-0.92 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 155.3, 135.5, 132.4, 128.7, 106.0, 83.1, 64.7, 49.5, 40.3, 38.9, 31.4, 29.2, 26.9, 25.4, 25.0, 24.8, 24.8, 24.3, 23.2, 22.9, 21.8, 14.2, 10.9. [M]+ calcd for ($C_{26}H_{42}BNO_2$) 412.3381, found 412.3386. IR, ν, cm-1: 3045, 2958, 2930, 2856, 2727, 2360, 1742, 1609, 1439, 1384, 1143, 1106, 856. R_f = 0.50 (petroleum ether/ethyl acetate 10:1).

6.11. 7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**5c**). Pale yellow oil (0.88 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.63-7.55 (m, 2H), 7.40-7.27 (m, 5H), 6.32 (d, *J* = 7.8, 1H), 4.62-4.34 (m, 2H), 4.32-4.27 (m, 1H), 3.86-3.77 (m, 1H), 2.10-1.82 (m, 3H), 1.74-1.57 (m, 3H), 1.39 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 154.8, 138.6, 135.8, 132.7, 130.5, 128.5, 127.1, 127.0, 104.3, 83.1, 69.2, 49.8, 45.5, 35.3, 33.0, 25.0, 24.8, 24.5. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{24}H_{30}O_2NB$) 376.2447, found 376.2448. IR, ν, cm^{-1}: 2952, 2865, 1606, 1439, 1348, 1145, 1112, 909, 861, 732, 676. R_f = 0.47 (petroleum ether/ethyl acetate 10:1).

6.12. 4-Bromo-7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazole (**6a**). Orange gum (480 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.84 (d, *J* = 7.7, 1H), 7.68 (d, *J* = 8.2, 1H), 7.60 (s, 1H), 7.47 (d, *J* = 7.7, 1H), 6.40 (d, *J* = 8.3, 1H), 4.28 (m, 1H), 3.85 (m, 1H), 3.10 (m, 2H), 2.07 (m, 1H), 1.93-1.53 (m, 6H), 1.36 (m, 8H), 0.95 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 154.0, 153.4, 153.3, 134.9, 133.9, 132.5, 129.3, 125.7, 124.8, 123.9, 110.1, 104.5, 69.5, 50.7, 45.5, 38.0, 35.1, 32.9, 31.1, 28.9, 24.5, 24.1, 23.2, 14.1, 10.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{25}H_{30}N_3SBr$) 486.1397, found

486.1394. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 302/4.38, 492/3.89. IR, ν, cm^{-1}: 2929, 2859, 1609, 1501, 1351, 1253, 1146, 800, 753. R_f = 0.47 (ethyl acetate/petroleum ether 1:20).

6.13. 4-Bromo-7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazole (**6b**). Orange gum (456 mg, 52 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.87 (d, *J* = 7.7, 1H), 7.72 (d, *J* = 8.2, 1H), 7.61 (s, 1H), 7.50 (d, *J* = 7.6, 1H), 6.58 (d, *J* = 8.2, 1H), 3.61 (q, *J* = 6.1, 1H), 3.22 (q, *J* = 6.6, 1H), 3.09-2.87 (m, 2H), 1.88-1.68 (m, 4H), 1.63-1.33 (m, 13H), 1.01-0.90 (m, 6H). ^{13}C NMR (75 MHz, solvent, δ, ppm): 154.1, 153.4, 135.1, 134.1, 132.6, 129.0, 126.3, 125.2, 125.2, 123.5, 110.6, 106.7, 65.2, 50.5, 40.6, 39.1, 31.2, 29.0, 27.3, 25.6, 24.9, 24.4, 23.3, 21.7, 14.2, 11.3. $[M]^+$ calcd for ($C_{26}H_{32}BrN_3S$) 500.1556, found 500.1554. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 299/4.01, 475/3.31. IR, ν, cm^{-1}: 3547, 3412, 3078, 3047, 2953, 2927, 2854, 1612, 1476, 1310, 1184, 936, 875, 826, 587. R_f = 0.46 (ethyl acetate/petroleum ether 1:10).

6.14. 4-(4-Benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-7-bromobenzo[*c*][1,2,5]thiadiazole (**6c**). Orange gum (602 mg, 74 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.84 (d, *J* =7.6, 1H), 7.67 (s, 1H), 7.65 (d, *J* = 9.7, 1H), 7.48 (d, J = 7.7, 1H), 7.44-7.19 (m, 5H), 6.40 (d, *J* = 8.1, 1H), 4.57-4.33 (m, 3H), 3.90 (t, *J* = 8.3, 1H), 2.14-2.00 (m, 1H), 1.98-1.87 (m, 2H), 1.78-1.60 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 154.0, 153.4, 152.8, 138.6, 134.8, 134.1, 132.5, 129.4, 128.6, 127.2, 127.1, 126.0, 125.1, 124.9, 110.5, 105.0, 69.8, 50.3, 45.7, 35.4, 33.1, 24.6. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{24}H_{20}N_3SBr$) 464.0614, found 464.0606. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 300/4.44, 477/3.95. IR, ν, cm^{-1}: 2947, 2862, 1609, 1500, 1478, 1330, 1255, 883, 807, 728, 697. R_f = 0.53 (ethyl acetate/petroleum ether 1:10).

6.15. *tert*-Butyl 2-cyano-3-(5-(7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**8a**). Dark red gum (470 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.25 (s, 1H), 8.19 (d, *J* = 4.1, 1H), 7.97 (d, *J* = 7.6, 1H), 7.85 (d, *J* = 4.2, 1H), 7.79 (d, *J* = 8.3, 1H), 7.70 (s, 1H), 7.62 (d, *J* = 7.7, 1H), 6.41 (d, *J* = 8.4, 1H), 4.30 (m, 1H), 3.86 (m, 1H), 3.11 (m, 2H), 2.08 (m, 1H), 1,90-1.56 (m, 15H), 1.36 (m, 8H), 0.95 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 161.9, 153.9, 153.5, 152.8, 149.4, 145.4, 137.8, 135.9, 135.5, 133.9, 129.7, 128.0, 127.7, 125.0, 124.9, 122.1, 116.3, 104.5, 99.8, 83.3, 69.8, 50.5, 45.5, 38.1, 35.2, 32.7, 31.1, 28.9, 28.1, 24.4, 24.1, 23.2, 14.2, 10.9. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{37}H_{42}N_4O_2S_2$) 639.2822, found 639.2810. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 311/4.17, 414/4.17, 565/4.22. IR, ν, cm^{-1}: 2929, 2858, 2214, 1712, 1583, 1437, 1247, 1152, 1091, 840, 801. R_f = 0.47 (petroleum ether/ethyl acetate 5:1).

6.16. *tert*-Butyl 2-cyano-3-(5-(7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**8b**). Dark red gum (423 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.28 (s, 1H), 8.25 (d, *J* = 4.2, 1H), 8.05 (d, *J* = 7.6, 1H), 7.89 (d, *J* = 4.2, 1H), 7.84 (d, *J* = 8.2, 1H), 7.73 – 7.66 (m, 2H), 6.60 (d, *J* = 8.3, 1H), 3.64 (q, *J* = 6.0, 1H), 3.24 (q, *J* = 6.6, 1H), 3.09 – 2.90 (m, 2H), 1.98-1.67 (m, 7H), 1.57-1.26 (m, 19H), 1.01-0.92 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 161.9, 154.1, 153.6, 152.9, 149.4, 145.6, 137.9, 136.2, 135.7, 134.1, 129.4, 128.1, 125.6, 125.4, 123.6, 122.6, 116.4, 106.7, 100.0, 83.5, 64.8, 50.3, 40.6, 38.8, 31.2, 29.2, 28.1, 27.2, 25.5, 24.8, 24.3, 23.3, 22.9, 21.7, 14.2, 10.9. $[M]^+$ calcd for ($C_{38}H_{44}N_4O_2S_2$) 653.2937, found 653.2933. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 308/4.38, 409/4.33, 542/4.44. IR, ν, cm^{-1}: 3436, 2955, 2929, 2871, 2855, 2215, 1713, 1584, 1476, 1438, 1245, 1152, 1098, 802. R_f = 0.53 (petroleum ether/ethyl acetate 5:1).

6.17. *tert*-Butyl 3-(5-(7-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylate (**8c**). Dark red solid (323 mg, 63%). M.p. 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.27 (s, 1H), 8.24 (d, *J* = 4.1, 1H),

8.02 (d, *J* = 7.6, 1H), 7.88 (d, *J* = 4.1 Hz, 1H), 7.77-7.73 (m, 2H), 7.66 (d, *J* =7.7 Hz, 1H), 7.40-7.25 (m, 5H), 6.40 (d, *J* = 8.8, 1H), 4.58-4.33 (m, 3H), 3.91 (t, *J* = 8.0, 1H), 2.12-2.01 (m, 1H), 1.99-1.87 (m, 2H), 1.76-1.57 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm):161.8, 153.9, 153.0, 152.7, 149.3, 145.4, 138.5, 137.8, 135.6, 134.1, 129.7, 128.6, 128.0, 127.8, 127.2, 127.1, 125.3, 116.3, 105.0, 99.9, 83.4, 69.7, 50.1, 45.6, 35.4, 33.0, 28.1, 24.5. HRMS-ESI (m/z): $[M]^+$ calcd for ($C_{36}H_{32}N_4O_2S_2$) 617.2039, found 617.2027. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 305/4.35, 408/4.32, 540/4.44. IR, ν, cm^{-1}: 2947, 2861, 2360, 1609, 1507, 1478, 1330, 1256, 1164, 846, 804, 755, 697. R_f = 0.45 (petroleum ether/ethyl acetate 5:1).

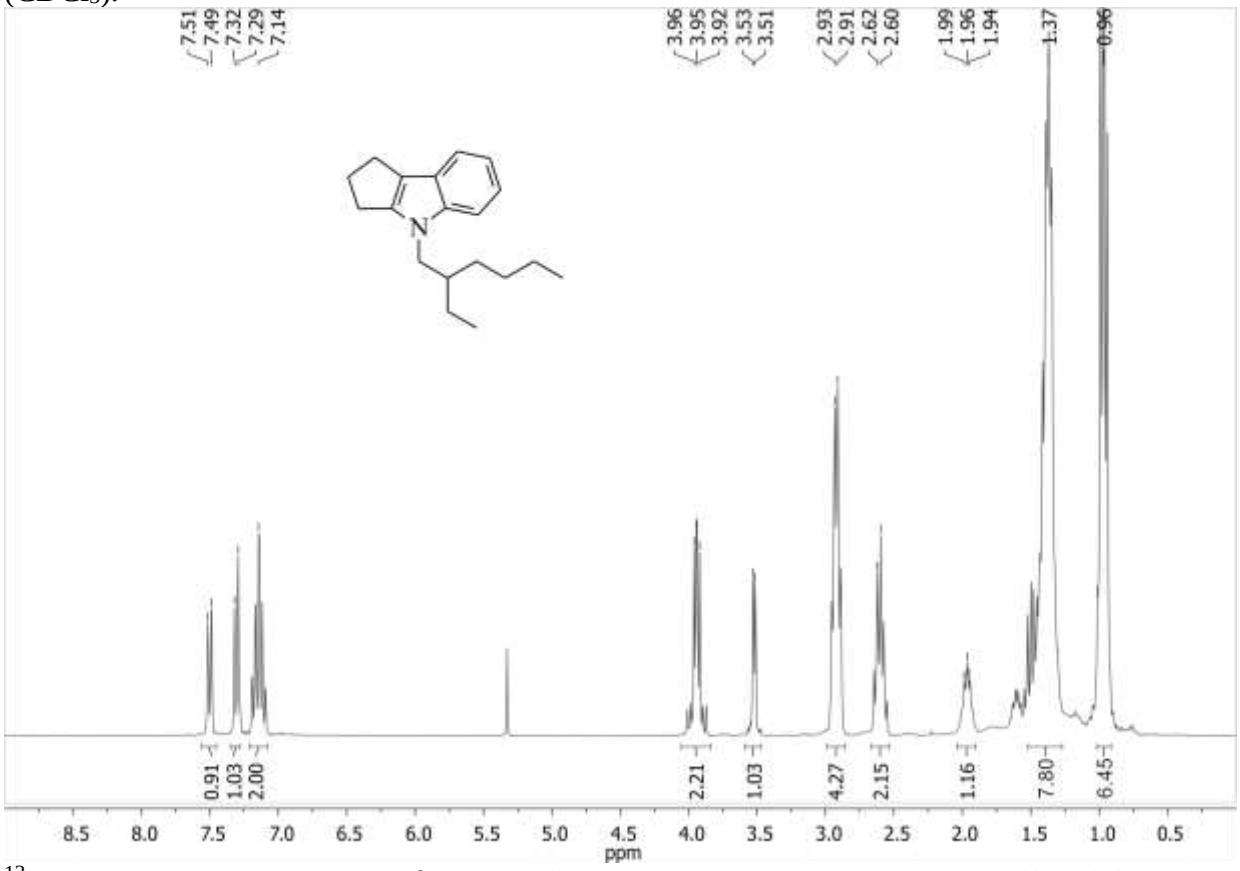
6.18. 2-Cyano-3-(5-(7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**MAX140**). Dark red solid with mp>300 °C (22 mg, 85%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.17 (m, 3H), 7.79 (m, 4H), 6.43 (d, 1H, *J* = 8.3), 4.28 (m, 1H), 3.82 (m, 1H), 3.11 (m, 2H), 2.03 (m, 1H), 1.88-1.62 (m, 6H), 1.31 (m, 8H), 0.90 (m, 6H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 164.6, 153.5, 153.4, 152.6, 145.0, 141.8, 137.7, 136.1, 134.5, 133.7, 129.9, 127.9, 127.5, 125.6, 125.1, 122.4, 119.3, 108.2, 104.7, 69.3, 50.0, 45.3, 37.8, 35.3, 32.8, 30.8, 28.7, 24.5, 24.3, 23.0, 14.4, 11.2. MS-MALDI (m/z): $[M]^+$ calcd for 582.2123, found 582.5653. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 310/4.01, 415/3.96, 567/4.11. IR, ν, cm^{-1}: 2928, 2858, 2212, 1685, 1439, 1380, 1207, 1139, 843, 803, 725. R_f = 0.48 (ethyl acetate/methanol 2:1).

6.19. 2-Cyano-3-(5-(7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**MAX157**). Dark red solid with mp>300 °C (25 mg, 93%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.34 (s, 1H), 8.32 – 8.20 (m, 2H), 7.96 (d, *J* = 4.2, 1H), 7.84 (d, *J* = 8.2, 2H), 7.77 (s, 1H), 6.60 (d, *J* = 8.3, 1H), 3.64-3.58 (m, 1H), 3.29-3.25 (m, 1H), 3.22–3.10 (m, 2H), 1.89-1.64 (m, 4H), 1.52-1.27 (m, 13H), 0.98-0.86 (m, 6H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 163.8, 153.0, 152.8, 152.0, 145.9, 143.3, 137.3, 137.8, 134.3, 133.3, 129.1, 127.6, 127.1, 125.5, 124.8, 123.2, 122.0, 117.9, 106.2, 64.0, 49.0, 38.0, 30.5, 28.5, 26.8, 26.1, 24.9, 24.1, 23.7, 22.5, 22.3, 21.0, 13.9, 10.5. MS-MALDI (m/z): $[M]^+$ calcd for ($C_{34}H_{36}N_4O_2S_2$) 596.8060, found 596.8130. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 298/4.15, 407/4.10, 534/4.21. IR, ν, cm^{-1}: 3492, 3470, 3436, 2928, 2860, 2219, 1687, 1573, 1417, 1248, 1208, 1094, 805. R_f = 0.44 (ethyl acetate/methanol 2:1).

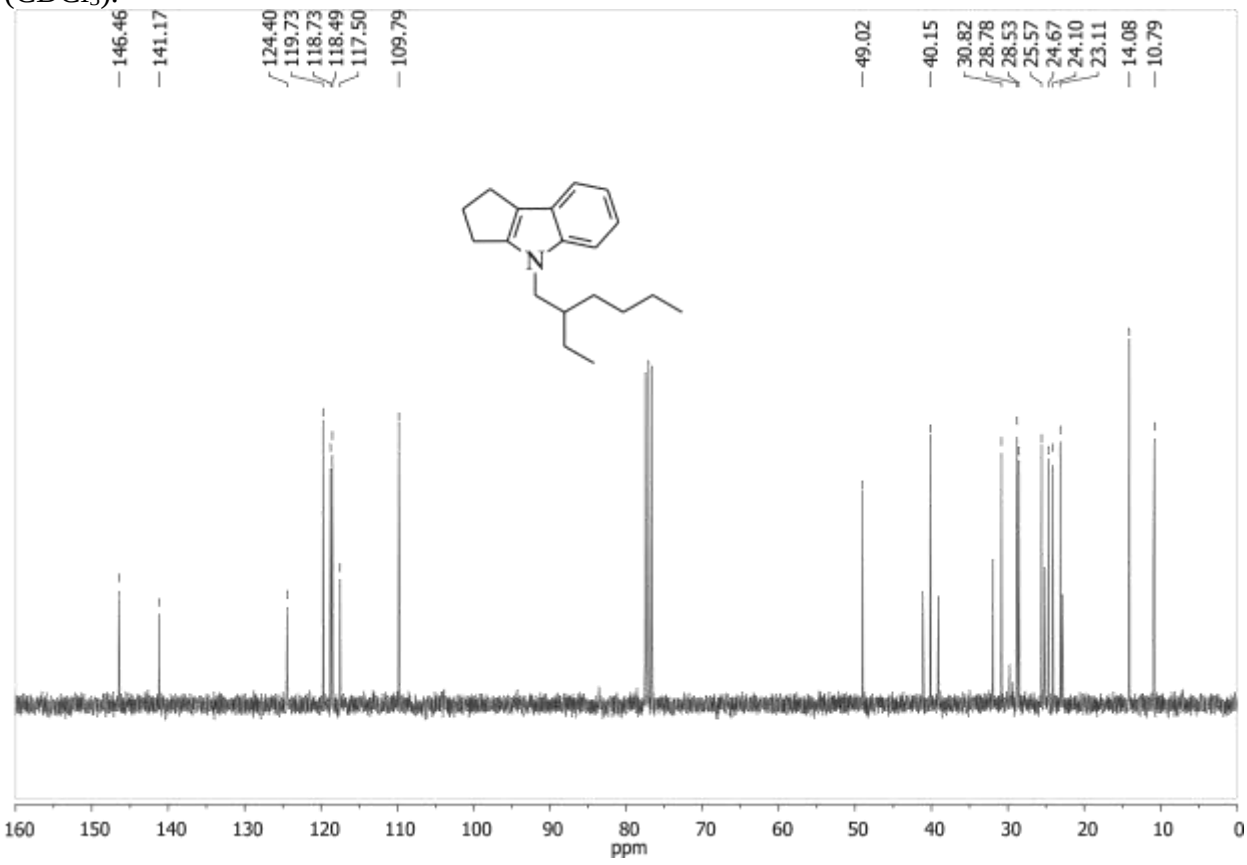
6.20. 3-(5-(7-(4-Benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MAX155**). Dark red solid with mp>300 °C (22 mg, 85%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.22-8.08 (m, 3H), 7.85-7.65 (m, 4H), 7.40-7.22 (m, 5H), 6.44 (d, *J* = 8.0, 1H), 4.65-4.25 (m, 3H), 3.81 (t, *J* = 8.4, 1H), 2.07-1.92 (m, 1H), 1.89-1.73 (m, 2H), 1.70-1.42 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 164.6, 153.4, 152.8, 152.4, 144.7, 141.7, 139.0, 137.8, 135.8, 134.2, 133.9, 129.8, 128.9, 127.7, 127.5, 127.4, 125.7, 125.3, 124.8, 122.5, 119.5, 108.7, 105.1, 69.2, 49.4, 45.3, 35.6, 32.9, 24.5. MS-MALDI (m/z): $[M]^+$ calcd for ($C_{32}H_{24}N_4O_2S_2$) 560.1341, found 560.6937. UV-Vis (CH_2Cl_2, λ_{max}, nm/logε): 306/4.25, 398/4.15, 536/4.28. IR, ν, cm^{-1}: 2933, 2860, 2212, 1609, 1486, 1365, 1260, 1143, 861, 804, 689. R_f = 0.48 (ethyl acetate/methanol 2:1).

7. ^{1}H and ^{13}C NMR of intermediates and **MAX** dyes

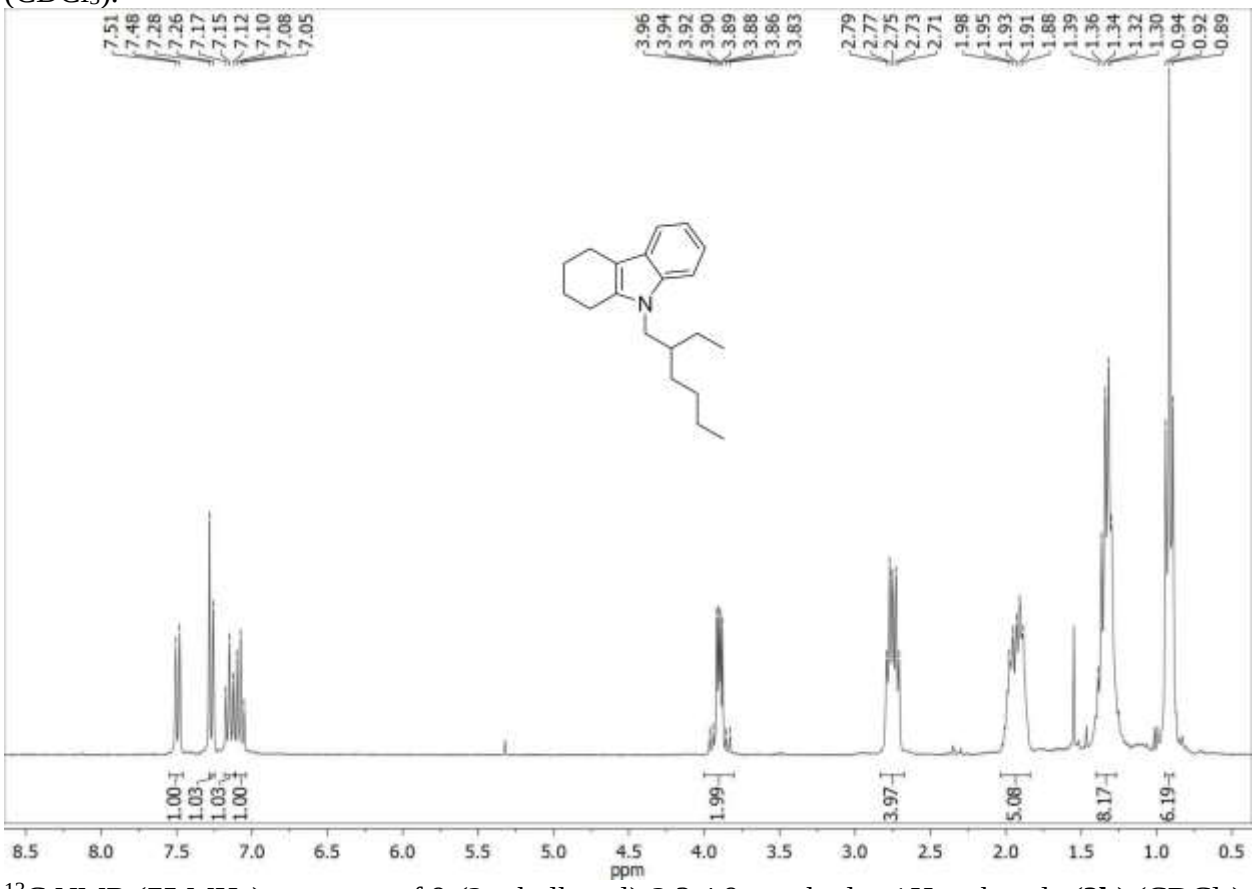
^{1}H NMR (300 MHz) spectrum of 4-(2-ethylhexyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**2a**) ($CDCl_3$).



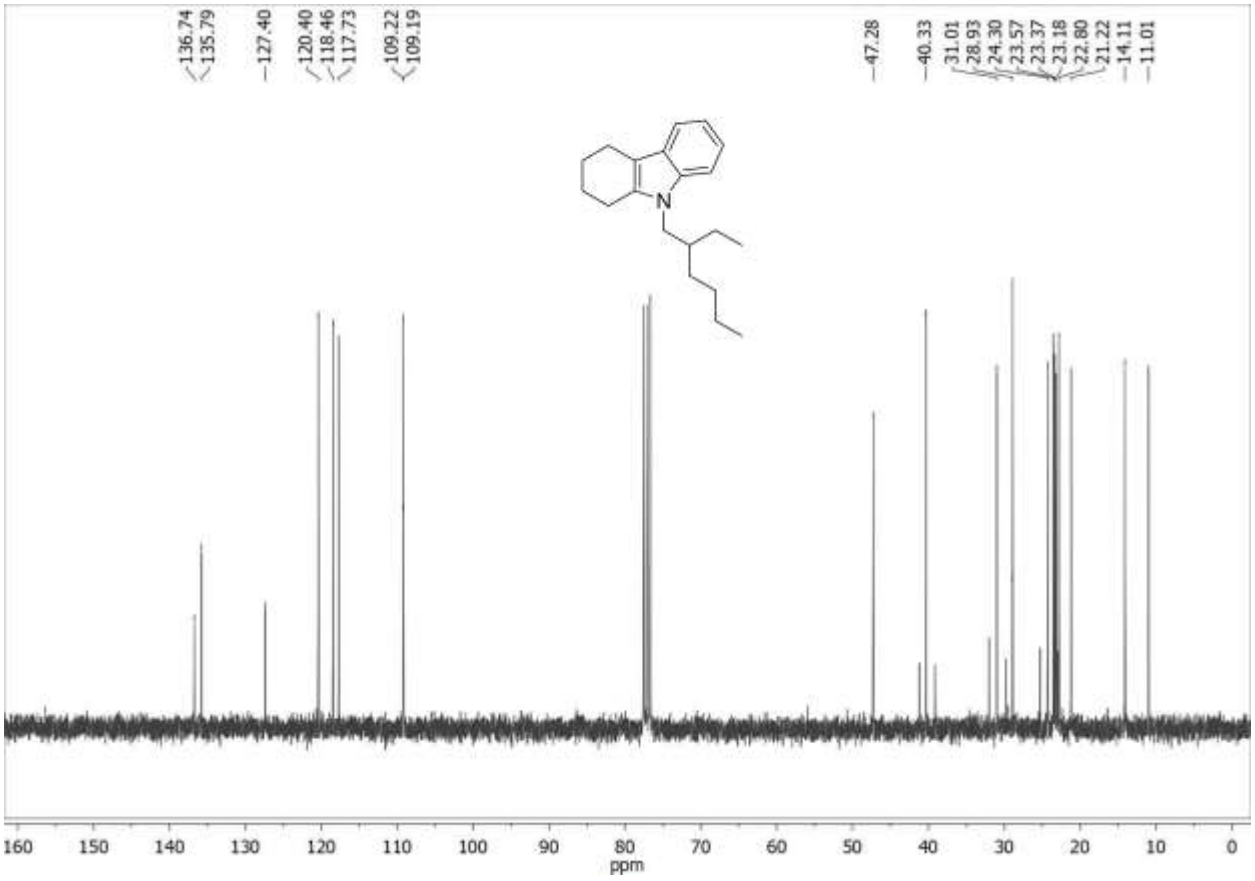
^{13}C NMR (75 MHz) spectrum of 4-(2-ethylhexyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**2a** ($CDCl_3$).



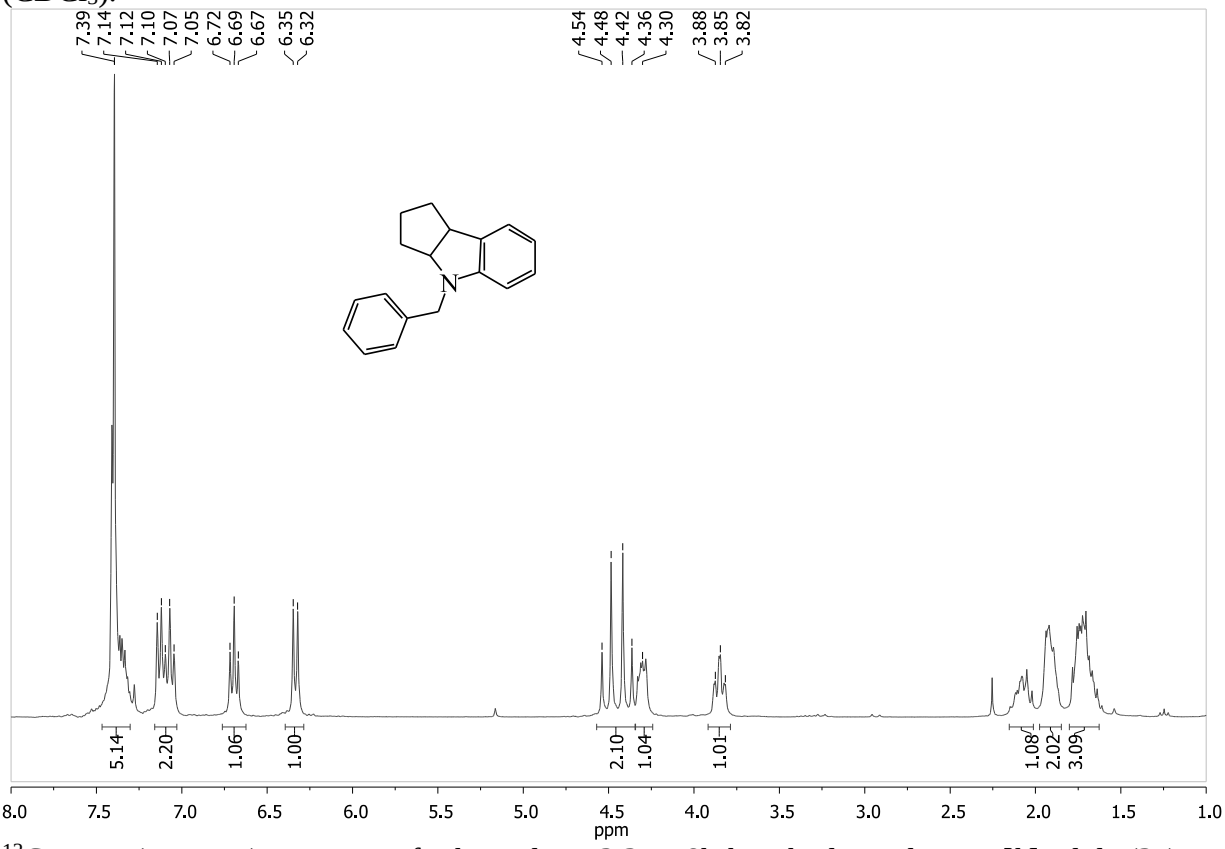
^{1}H NMR (300 MHz) spectrum of 9-(2-ethylhexyl)-2,3,4,9-tetrahydro-1*H*-carbazole (**2b**) ($CDCl_3$).



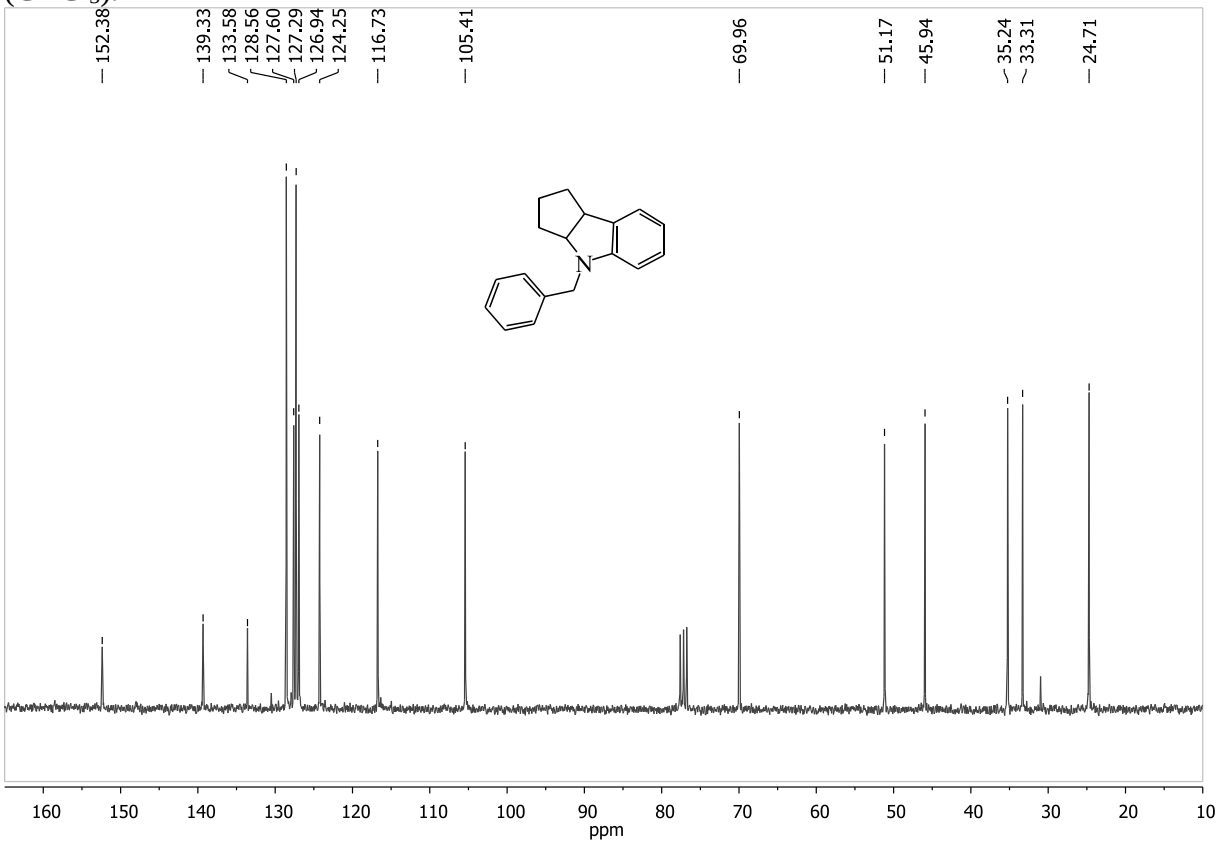
^{13}C NMR (75 MHz) spectrum of 9-(2-ethylhexyl)-2,3,4,9-tetrahydro-1*H*-carbazole (**2b**) ($CDCl_3$).



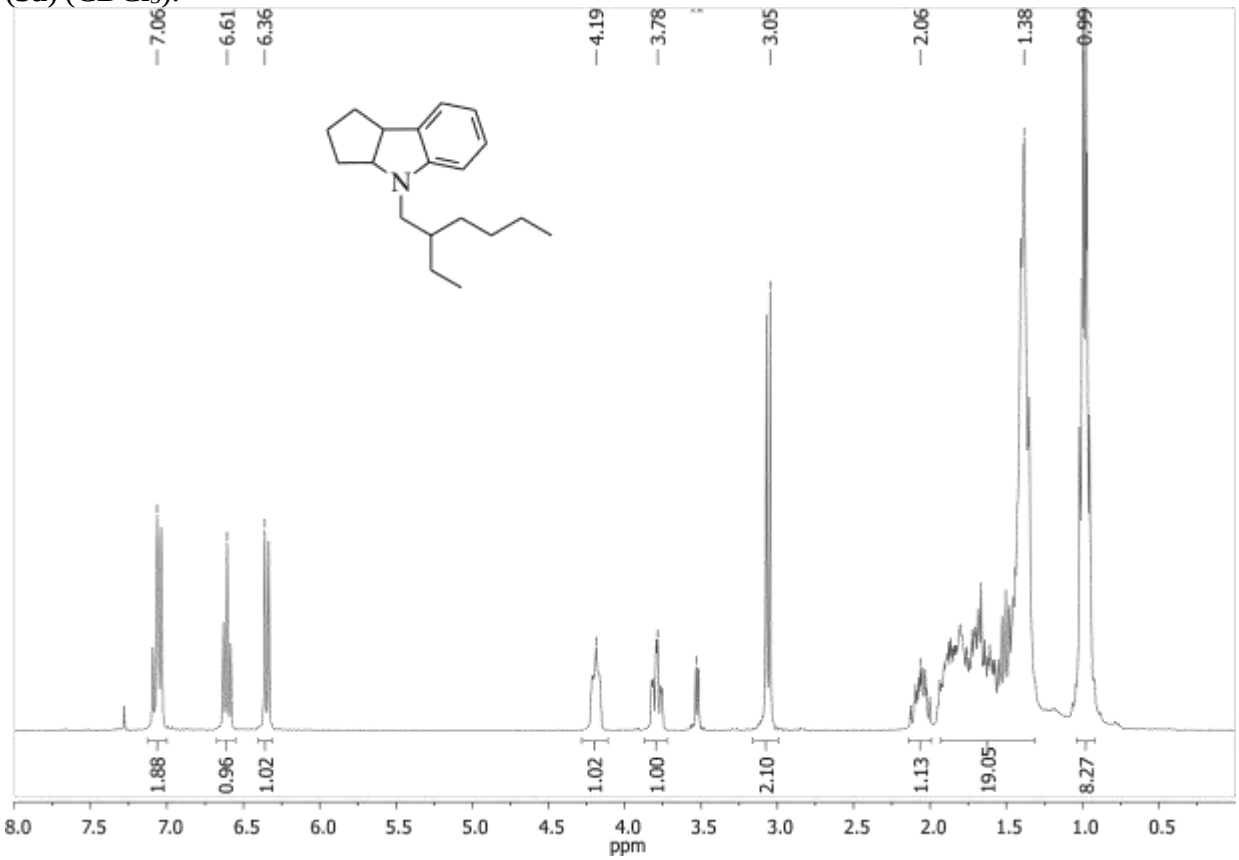
^{1}H NMR (300 MHz) spectrum of 4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**3c**). ($CDCl_3$).



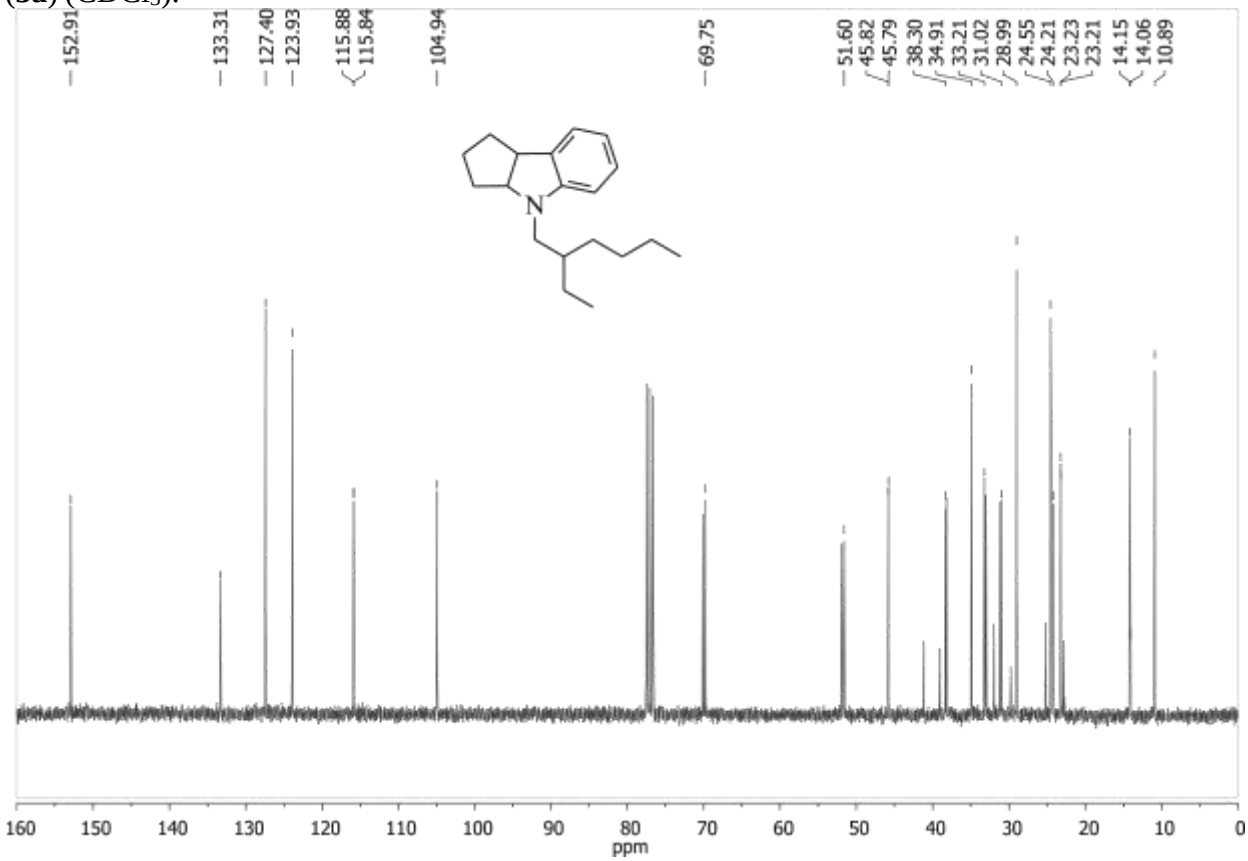
^{13}C NMR (75 MHz) spectrum of 4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**3c**). ($CDCl_3$).



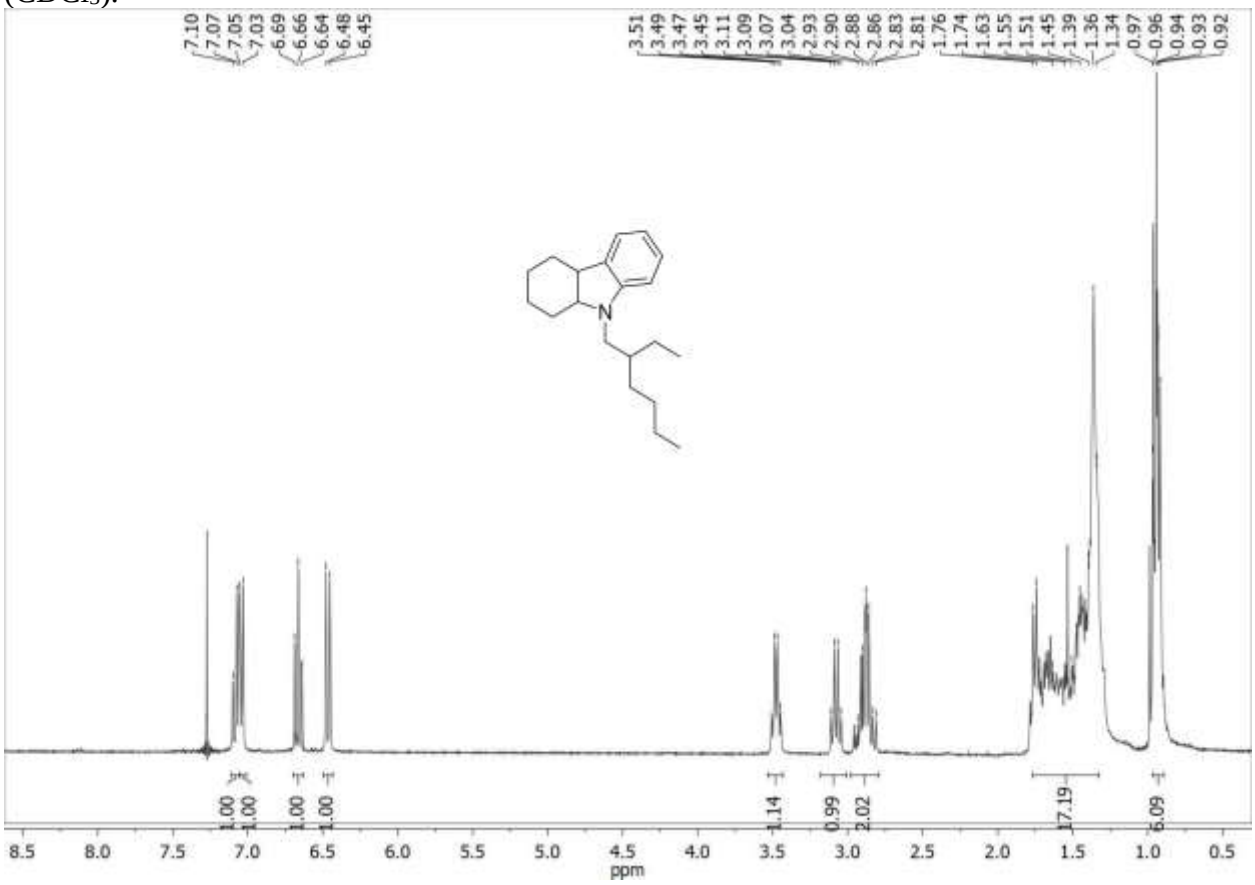
^{1}H NMR (300 MHz) spectrum of 4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**3a**) ($CDCl_3$).



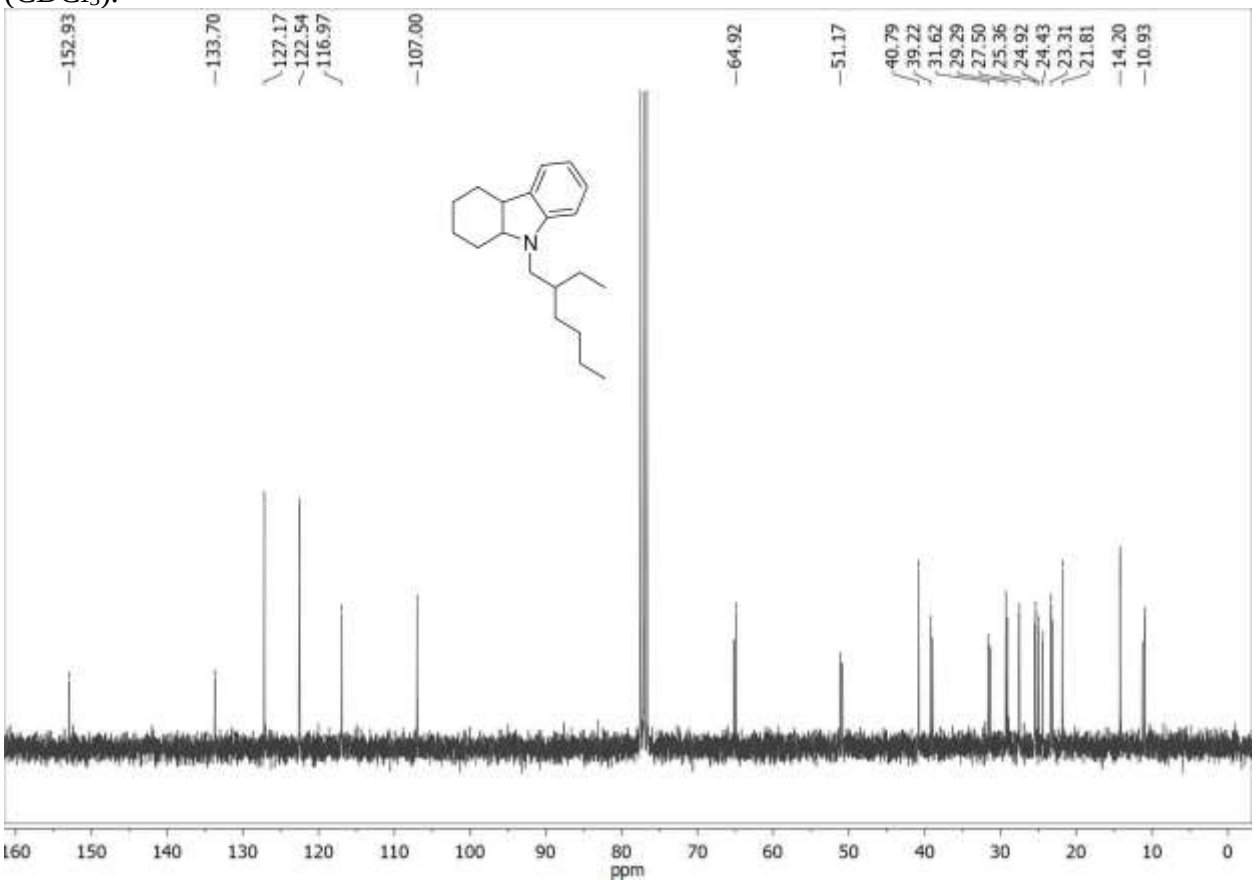
^{13}C NMR (75 MHz) spectrum of 4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**3a**) ($CDCl_3$).



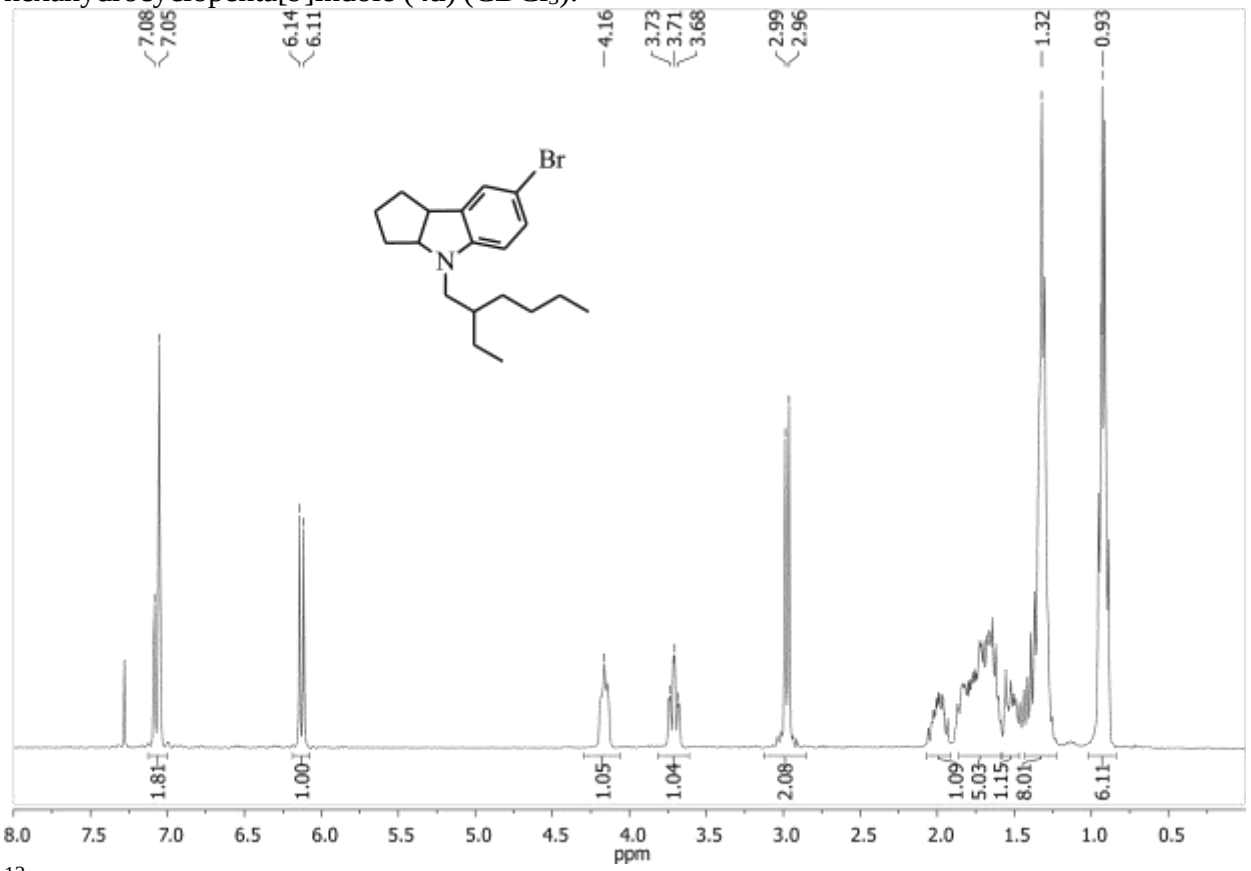
^{1}H NMR (300 MHz) spectrum of 9-(2-ethylheptyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**3b**) ($CDCl_3$).



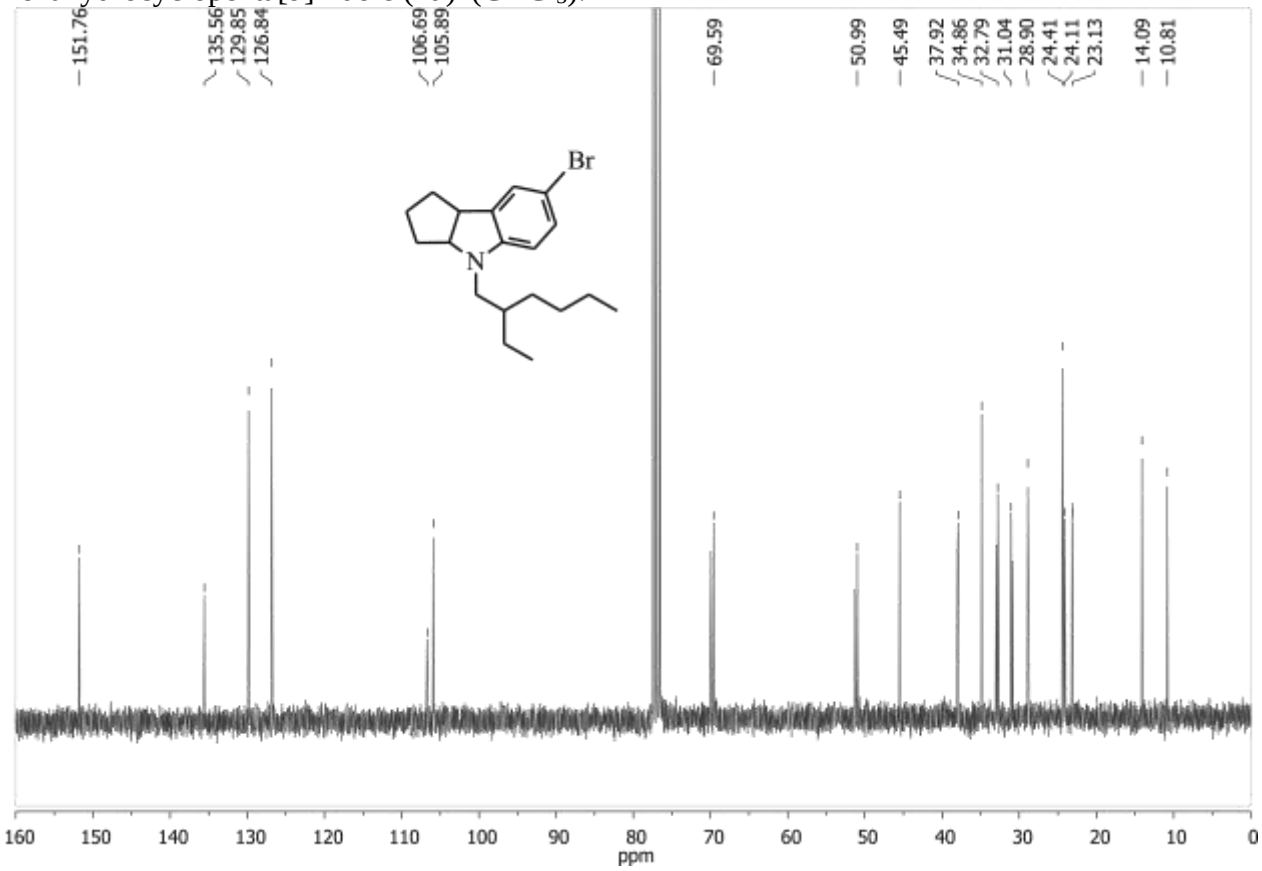
^{13}C NMR (75 MHz) spectrum of 9-(2-ethylheptyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**3b**) ($CDCl_3$).



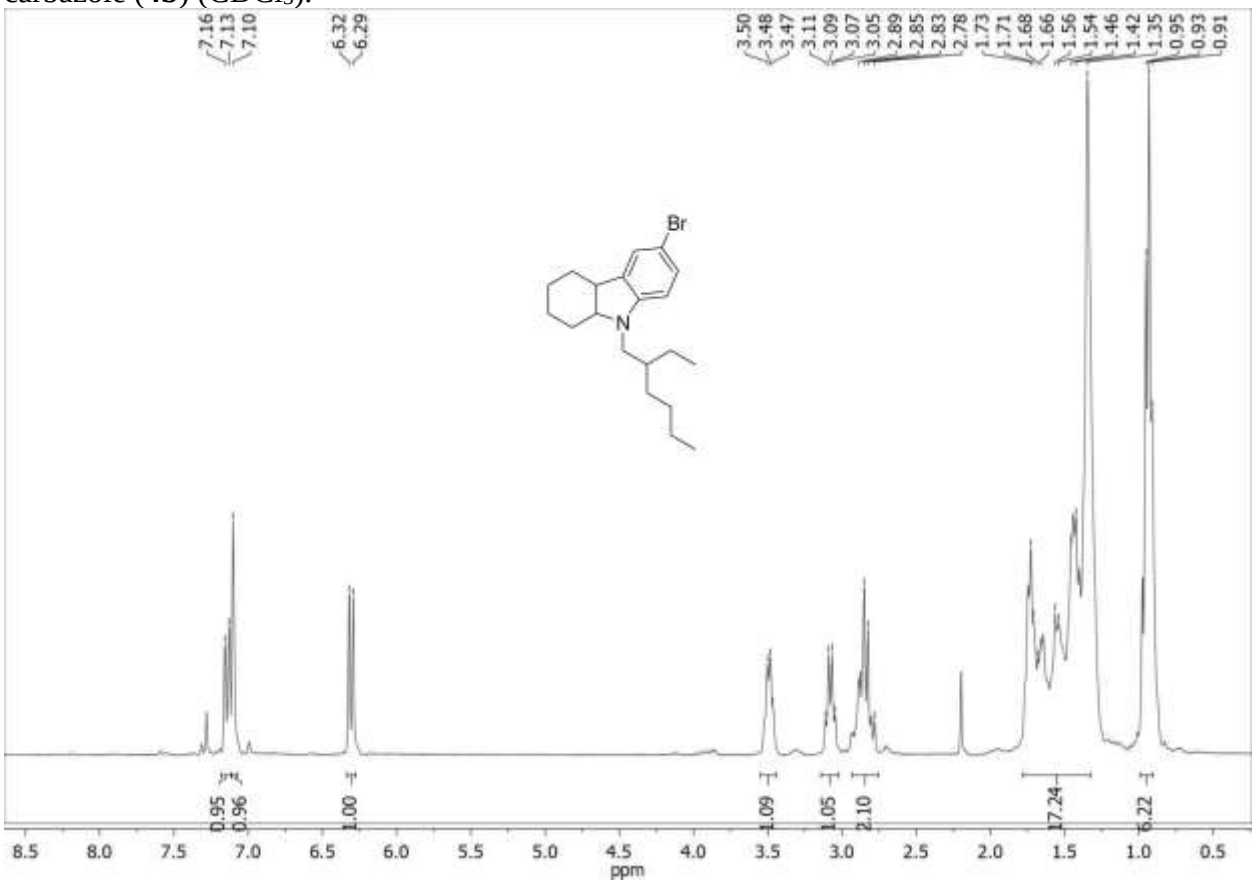
^{1}H NMR (300 MHz) spectrum of 7-bromo-4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**4a**) ($CDCl_3$).



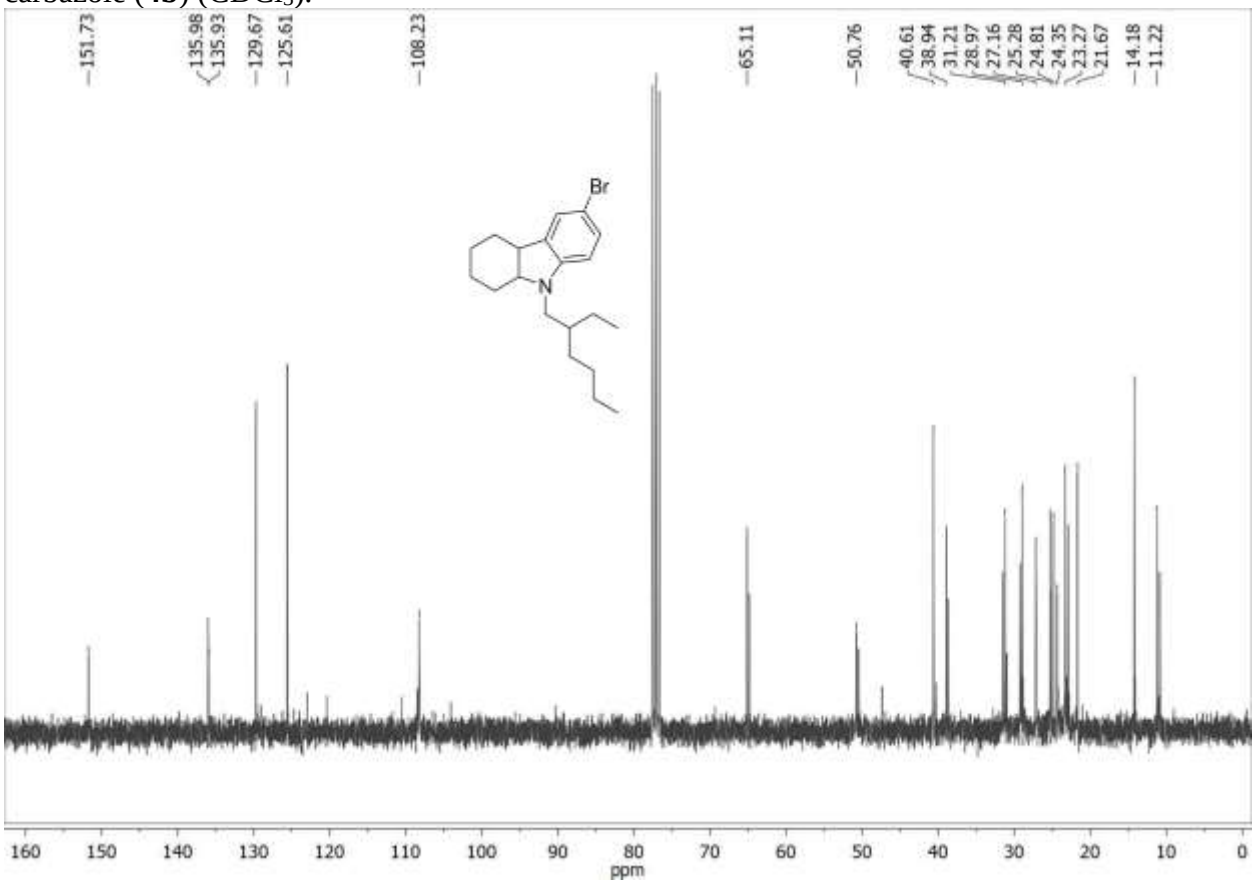
^{13}C NMR (75 MHz) spectrum of 7-bromo-4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**4a**) ($CDCl_3$).



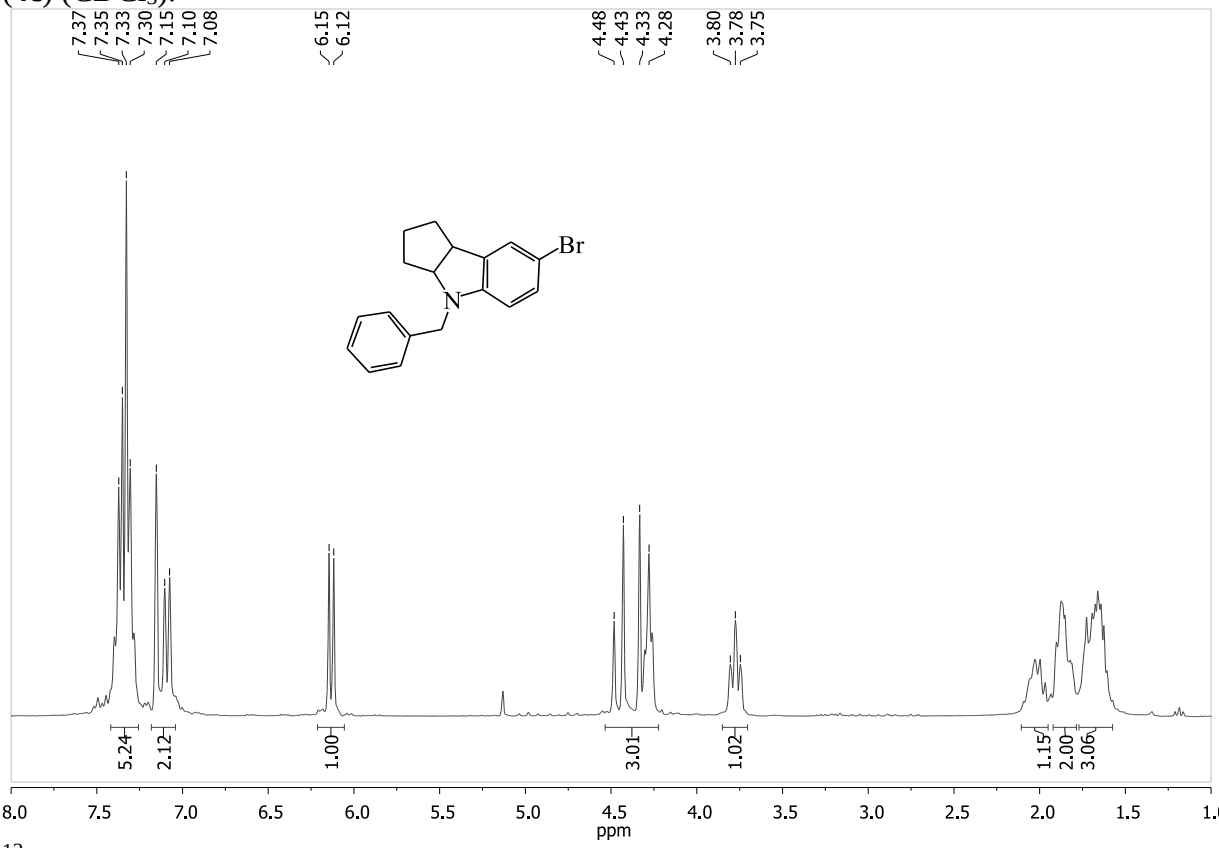
^{1}H NMR (300 MHz) spectrum of 6-bromo-9-(2-ethylheptyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**4b**) ($CDCl_3$).



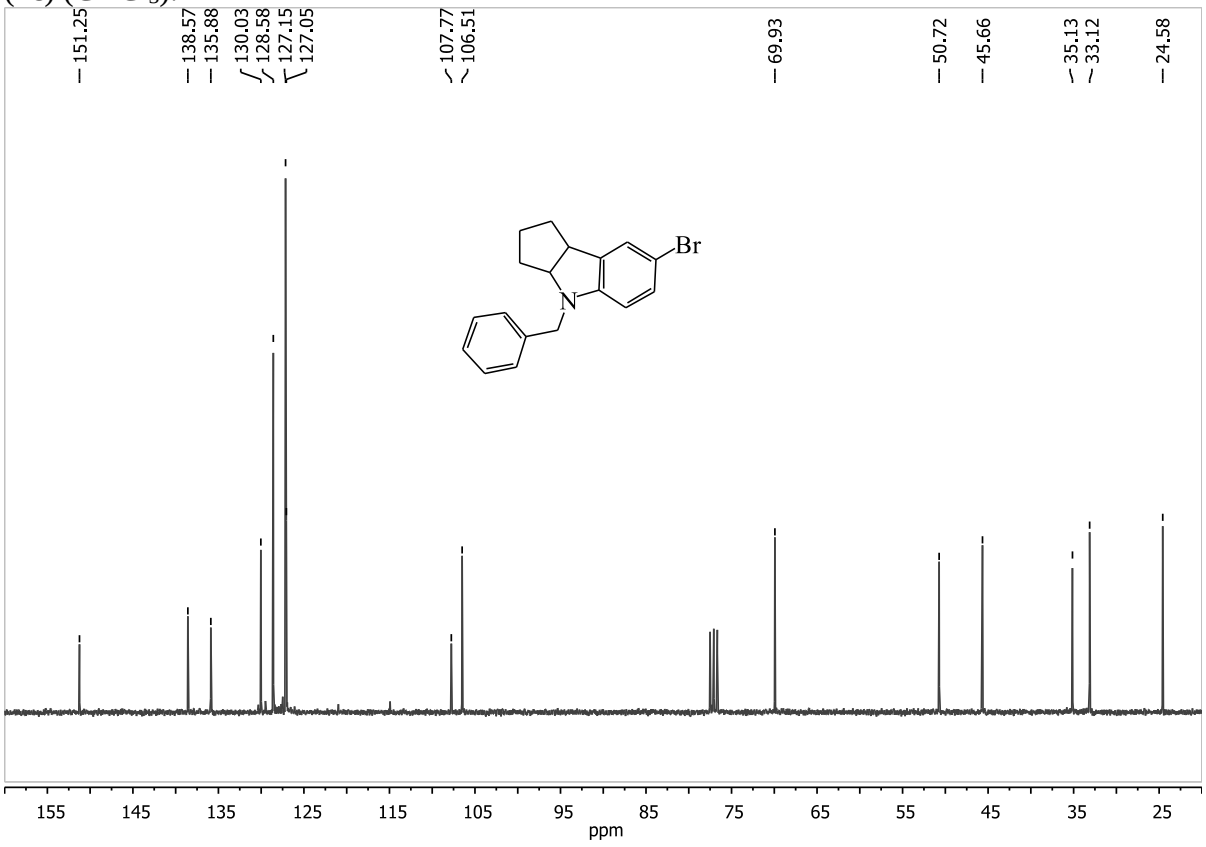
^{13}C NMR (75 MHz) spectrum of 6-bromo-9-(2-ethylheptyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**4b**) ($CDCl_3$).



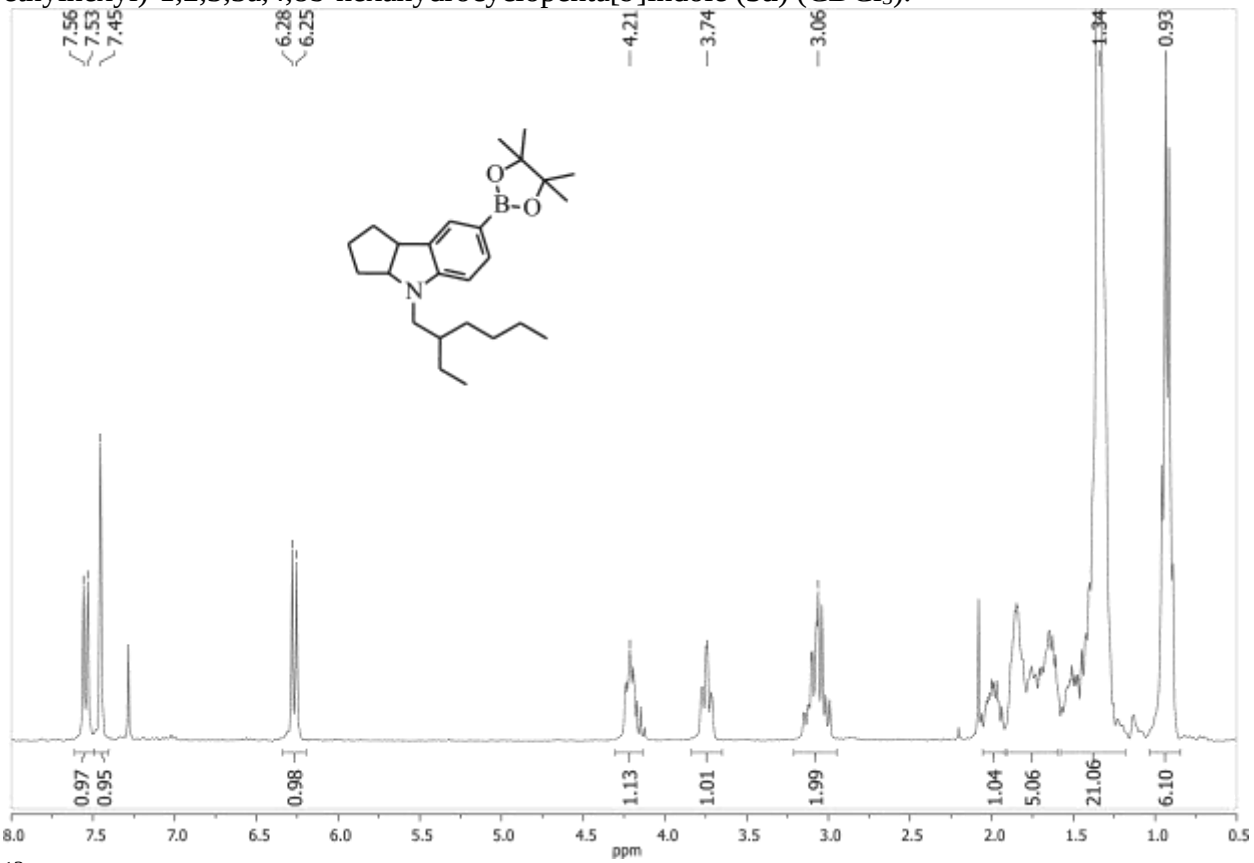
^{1}H NMR (300 MHz) spectrum of 7-bromo-4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**4c**) ($CDCl_3$).



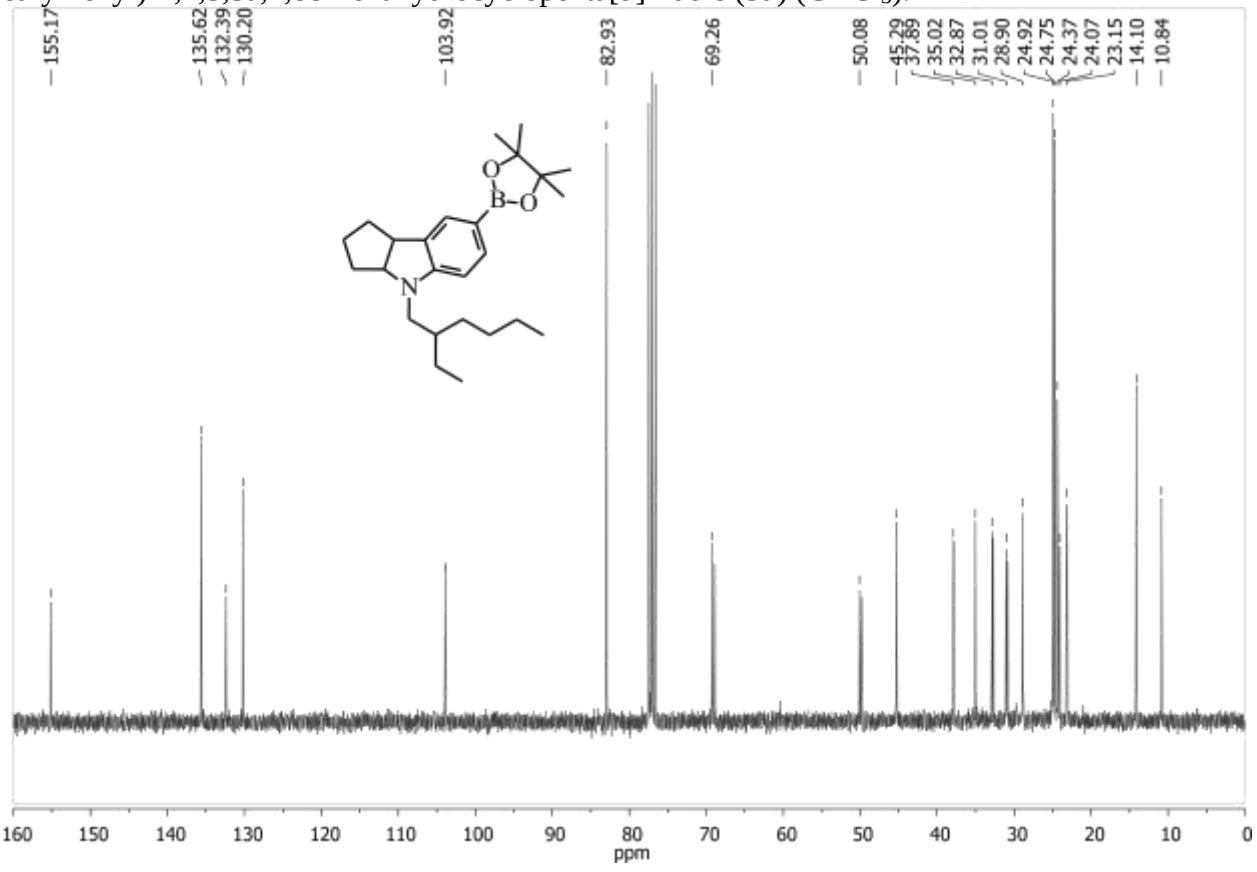
^{13}C NMR (75 MHz) spectrum of 7-bromo-4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**4c**) ($CDCl_3$).



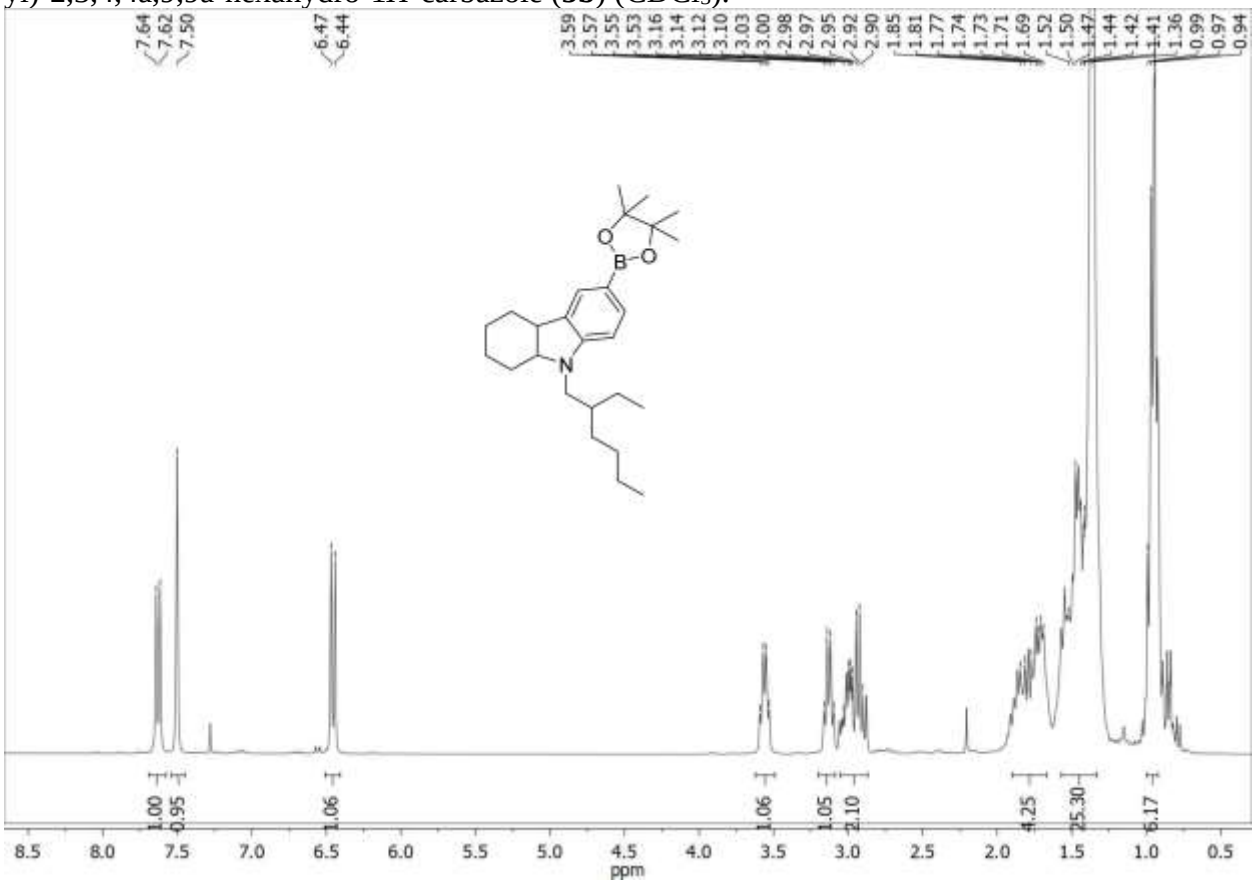
^{1}H NMR (300 MHz) spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**5a**) ($CDCl_3$).



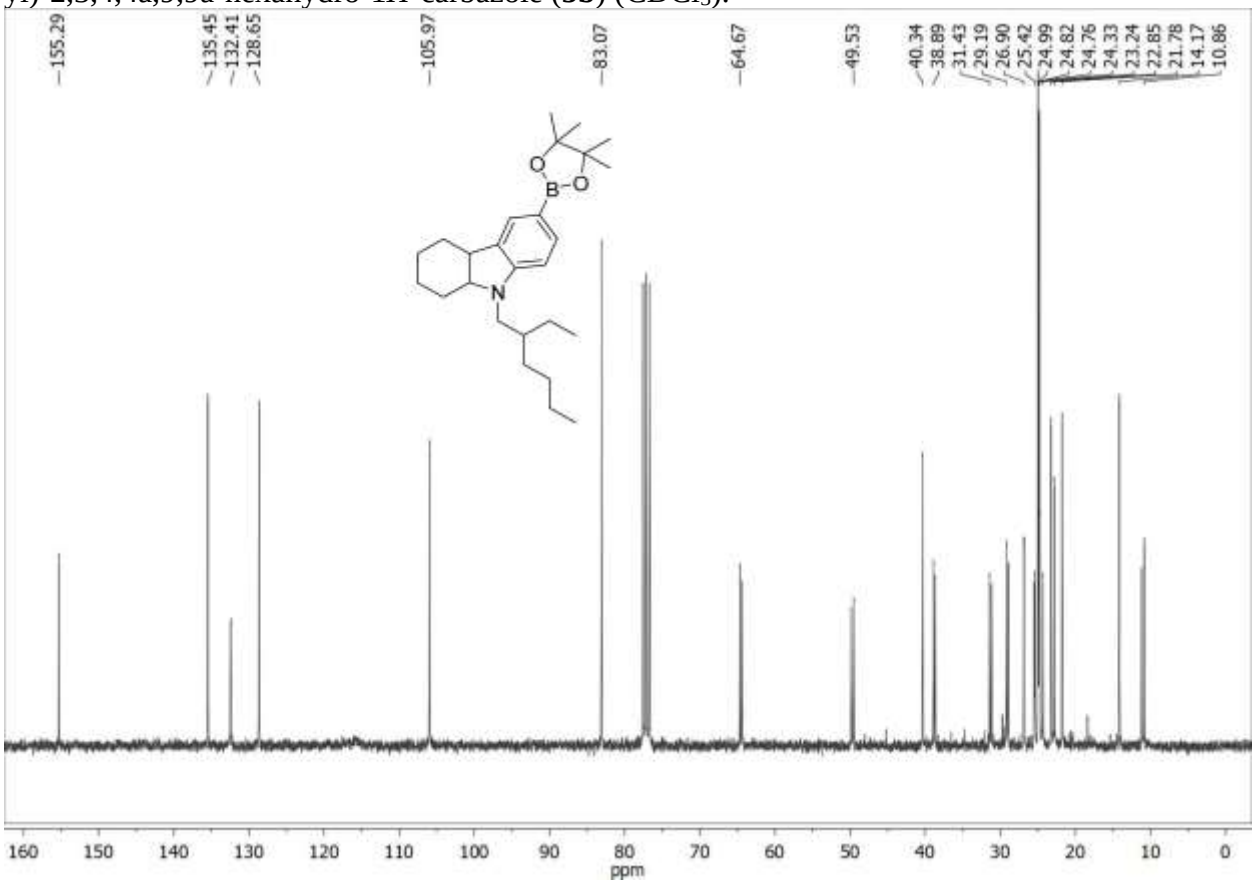
^{13}C NMR (75 MHz) spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**5a**) ($CDCl_3$).



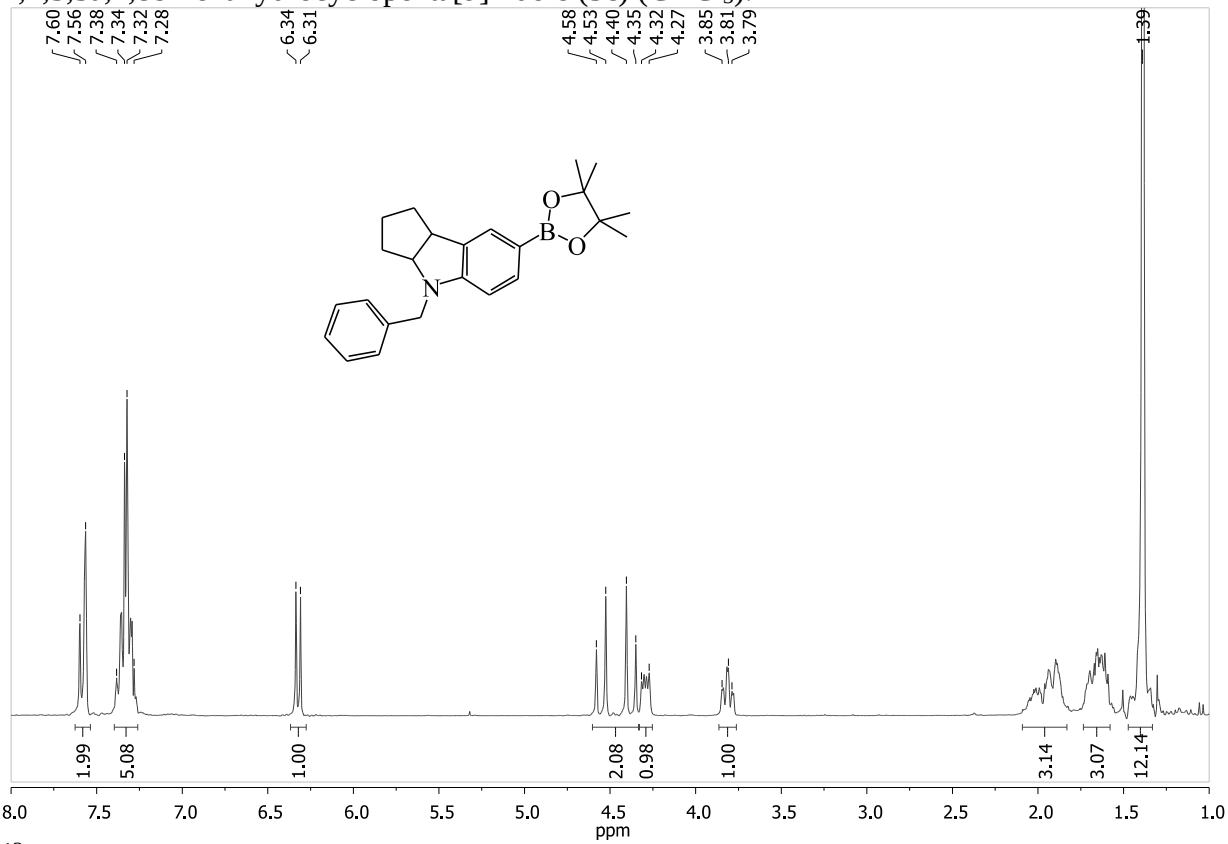
^{1}H NMR (300 MHz) spectrum of 9-(2-ethylheptyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**5b**) ($CDCl_3$).



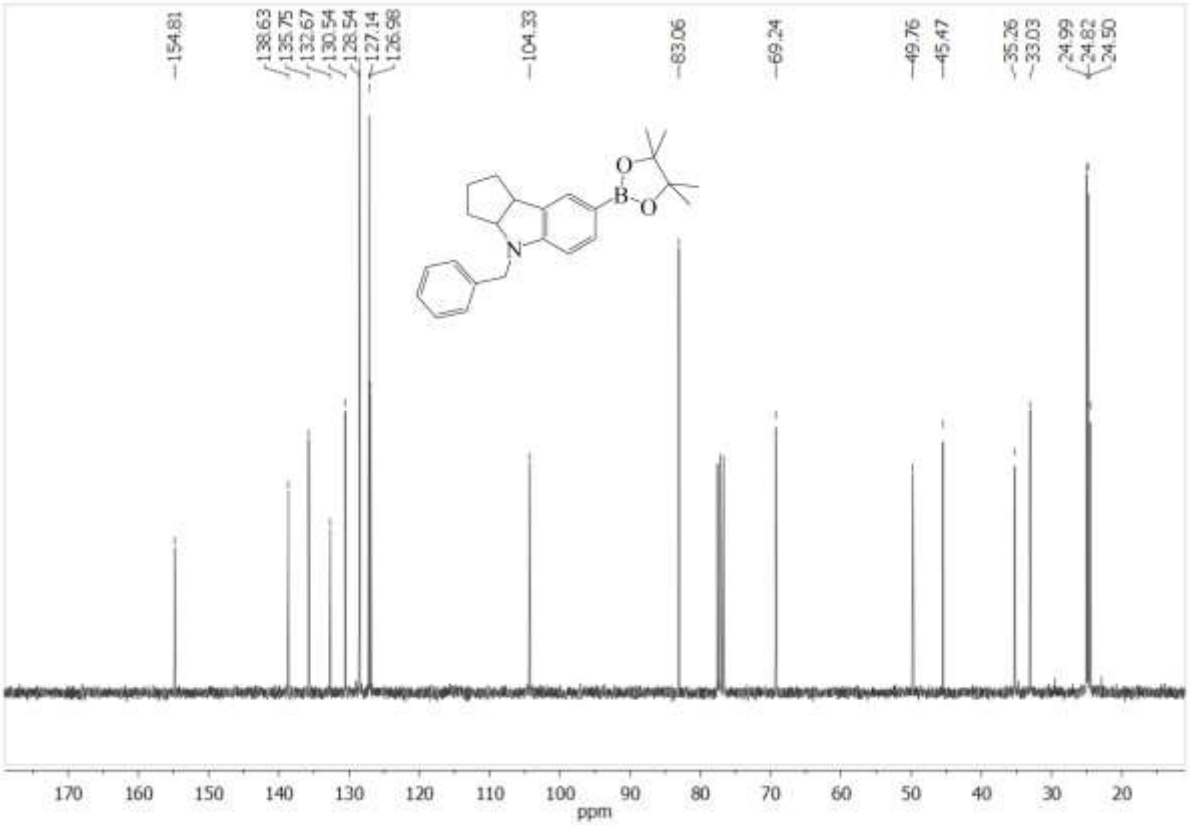
^{13}C NMR (75 MHz) spectrum of 9-(2-ethylheptyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (**5b**) ($CDCl_3$).



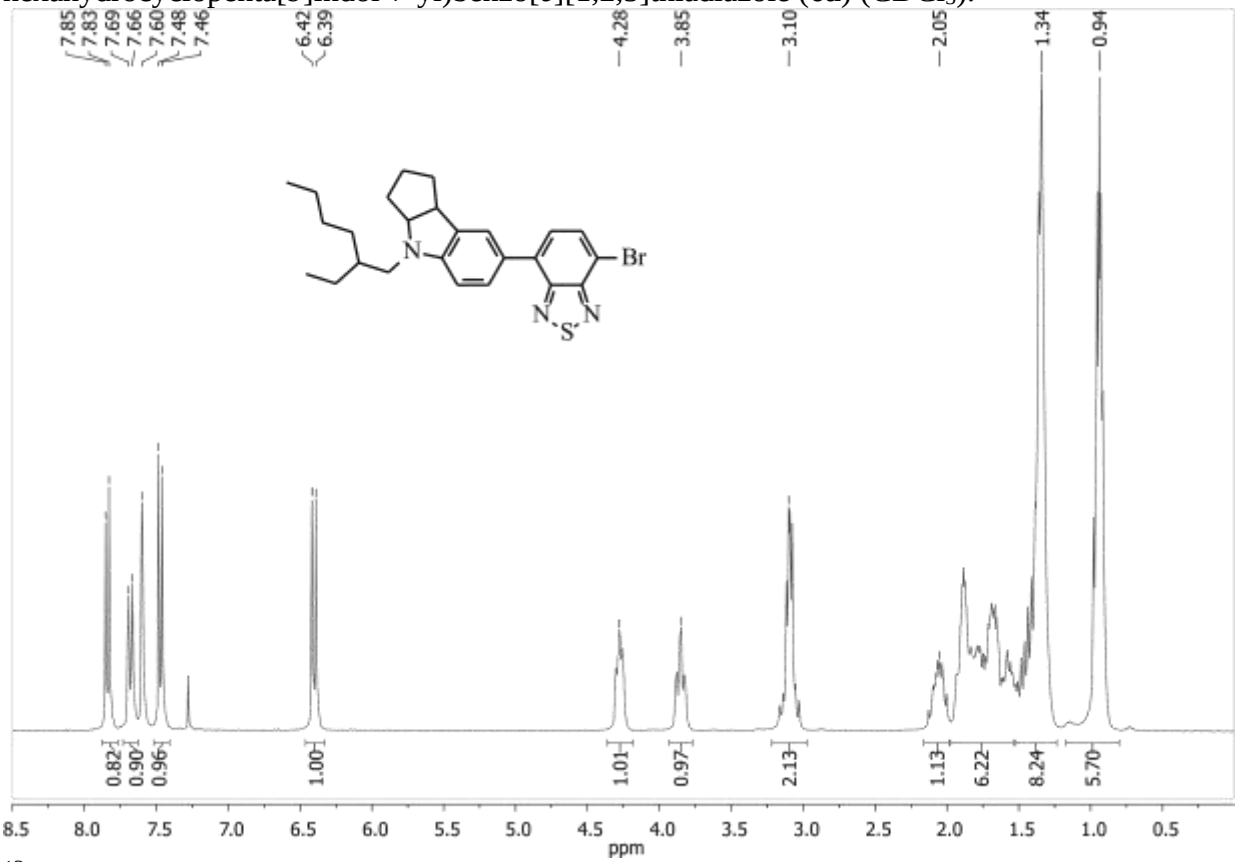
^{1}H NMR (300 MHz) spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**5c**) ($CDCl_3$).



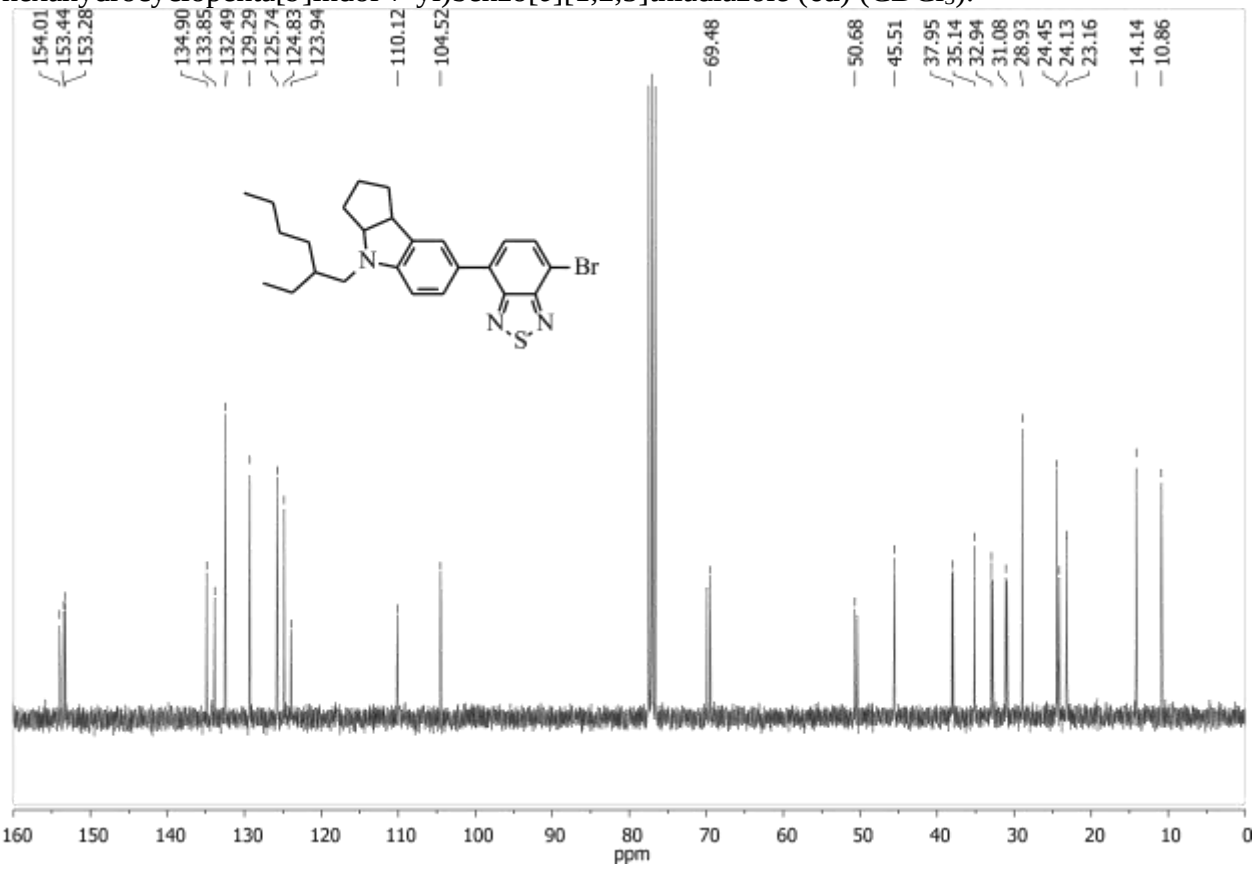
^{13}C NMR (75 MHz) spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (5c) (CDC_{l3}).



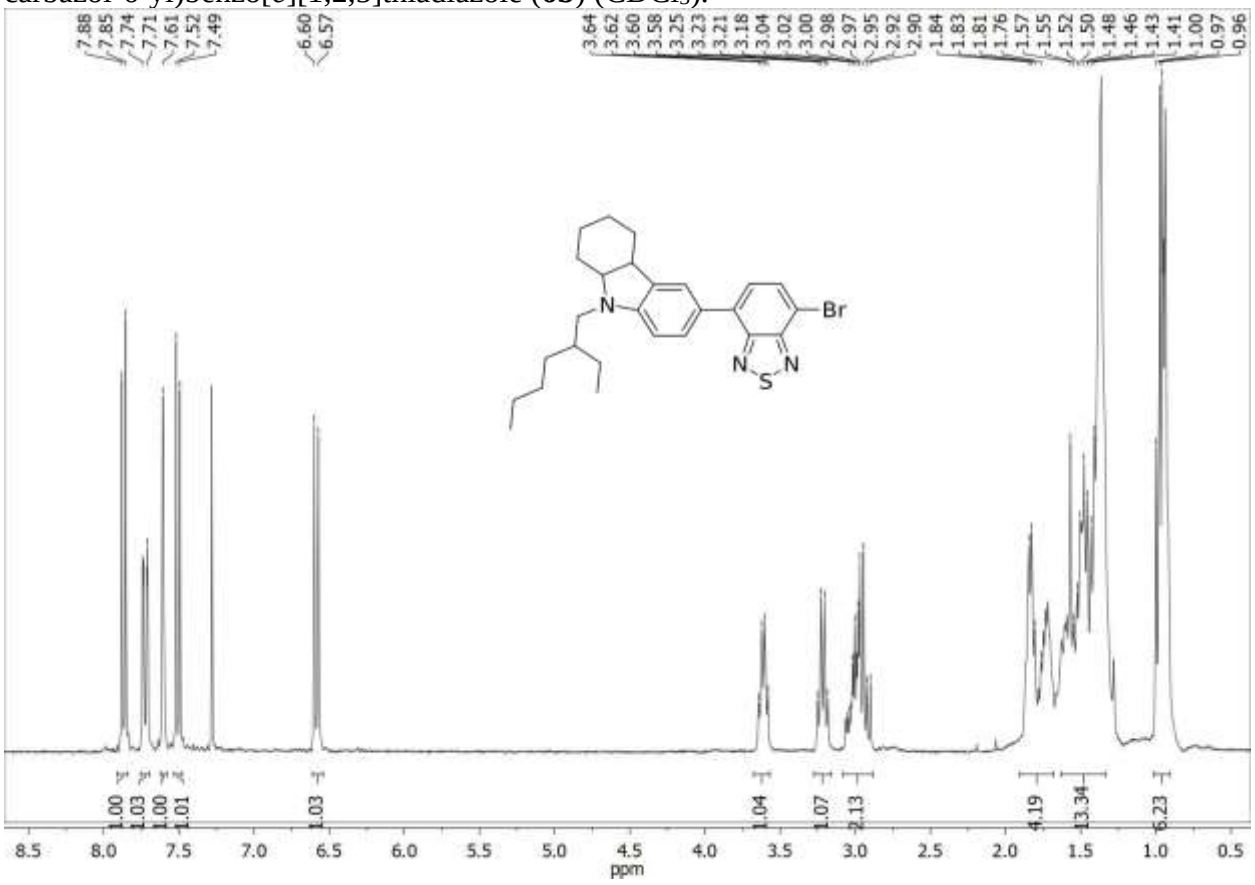
^{1}H NMR (300 MHz) spectrum of 4-bromo-7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazole (**6a**) ($CDCl_3$).



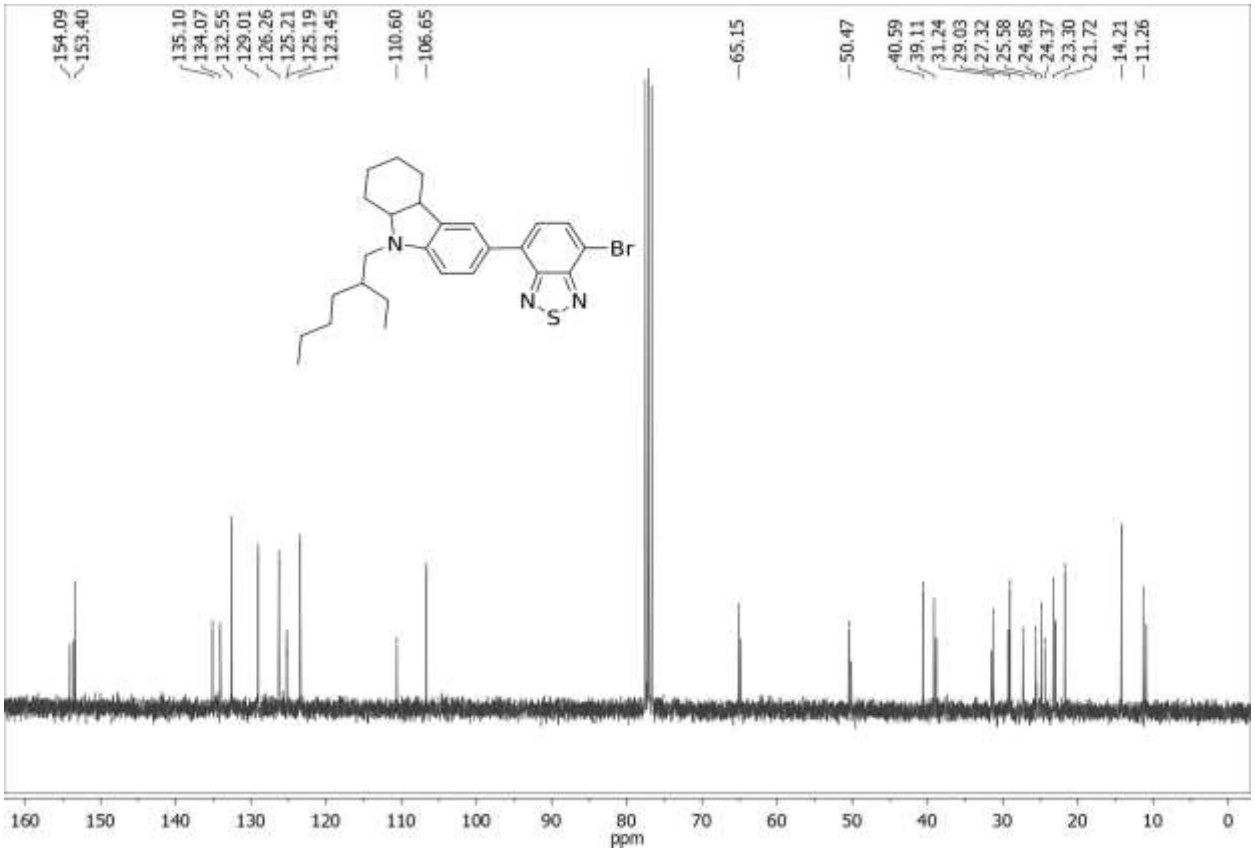
^{13}C NMR (75 MHz) spectrum of 4-bromo-7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazole (**6a**) ($CDCl_3$).



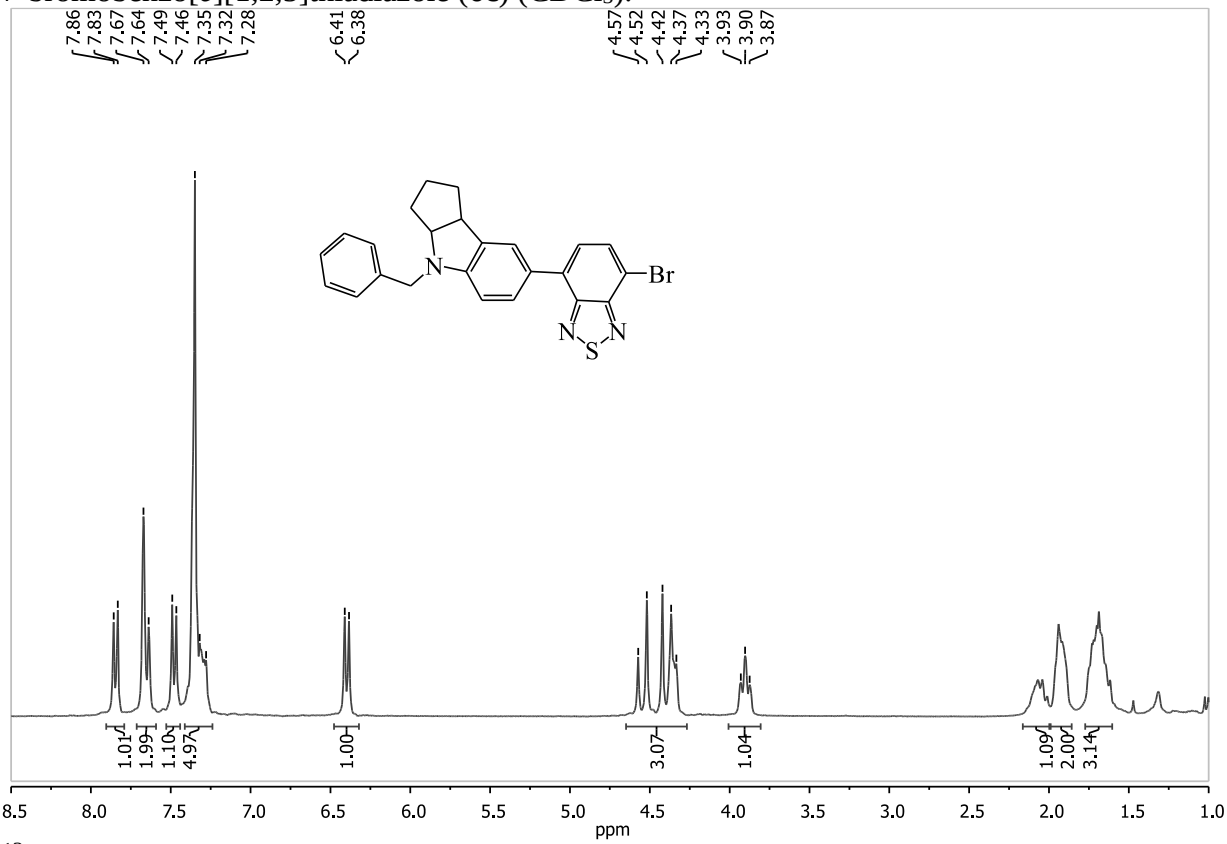
^{1}H NMR (300 MHz) spectrum of 4-bromo-7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazole (**6b**) ($CDCl_3$).



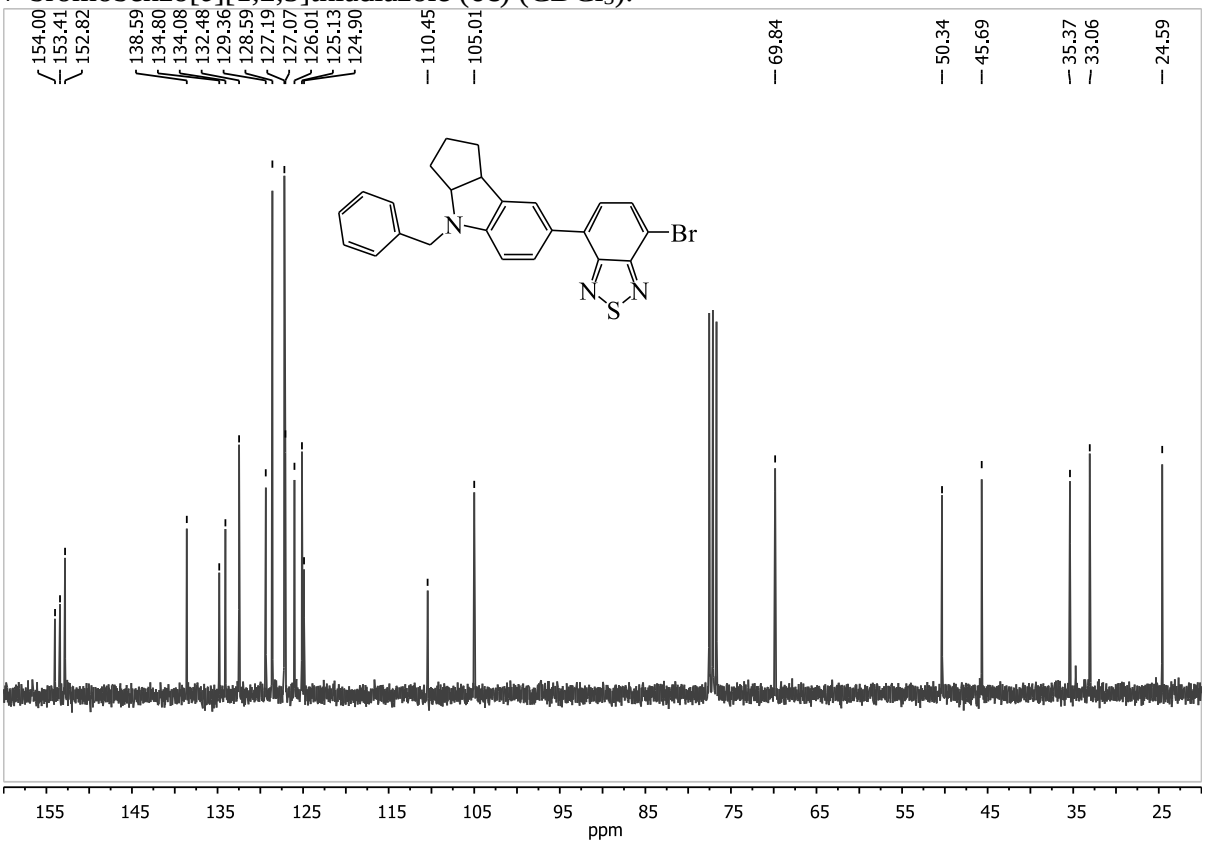
^{13}C NMR (75 MHz) spectrum of 4-bromo-7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazole (**6b**) ($CDCl_3$).



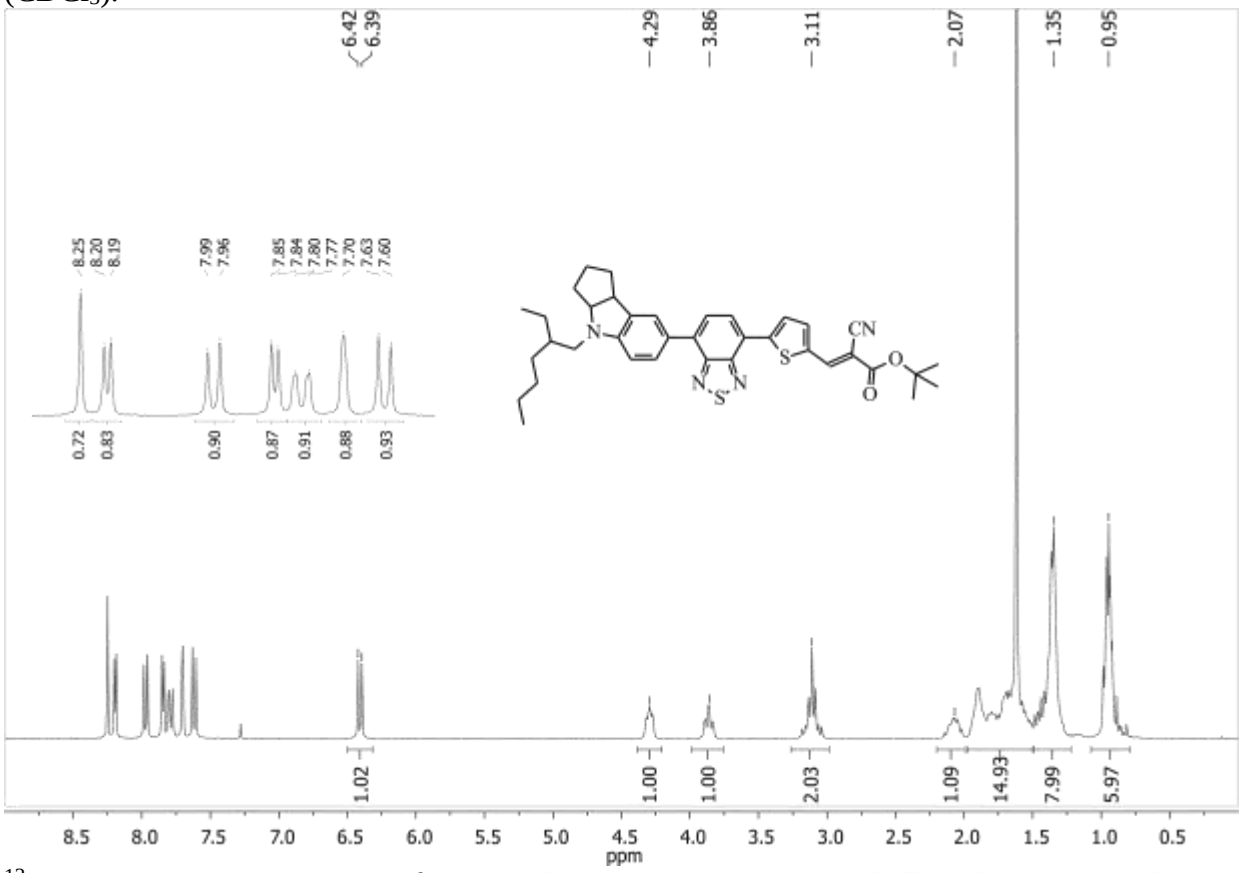
^{1}H NMR (300 MHz) spectrum of 4-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-7-bromobenzo[*c*][1,2,5]thiadiazole (**6c**) ($CDCl_3$).



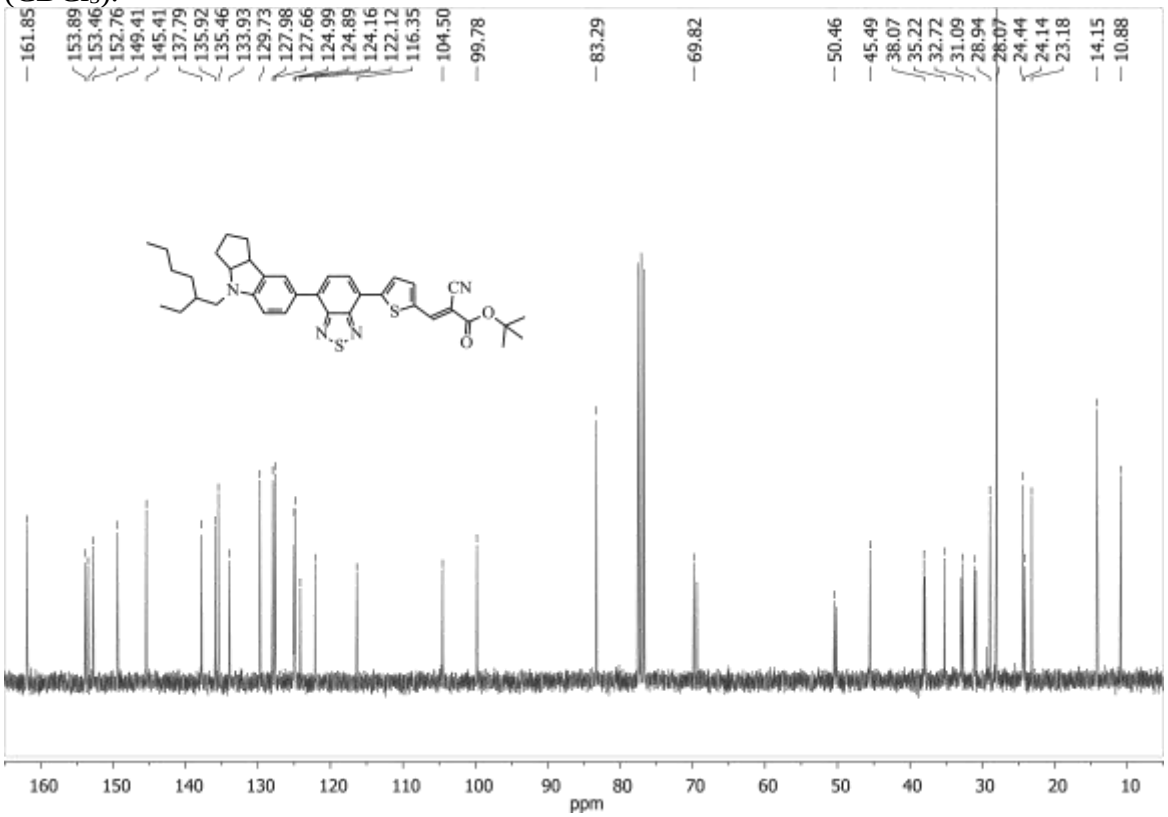
^{13}C NMR (75 MHz) spectrum of 4-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-7-bromobenzo[*c*][1,2,5]thiadiazole (**6c**) ($CDCl_3$).



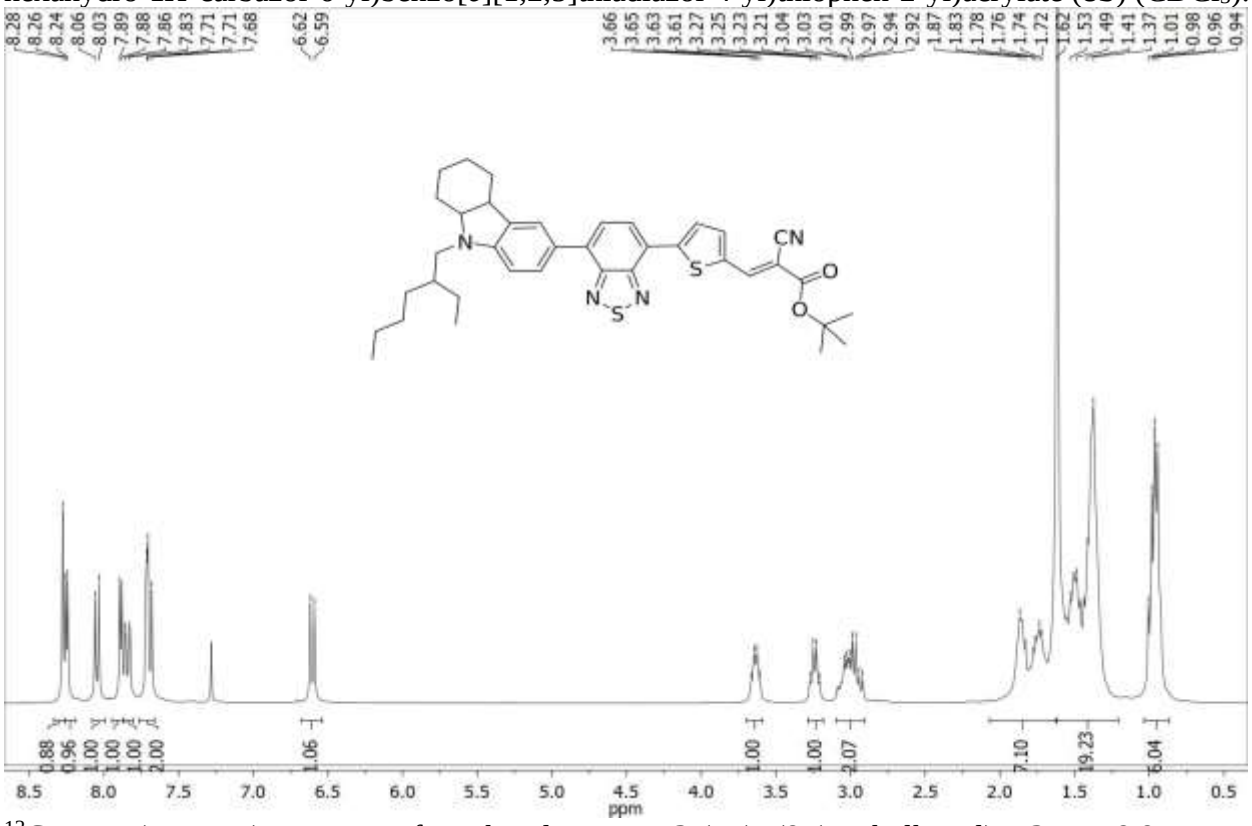
^{1}H NMR (300 MHz) spectrum of *tert*-butyl 2-cyano-3-(5-(7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**8a**) ($CDCl_3$).



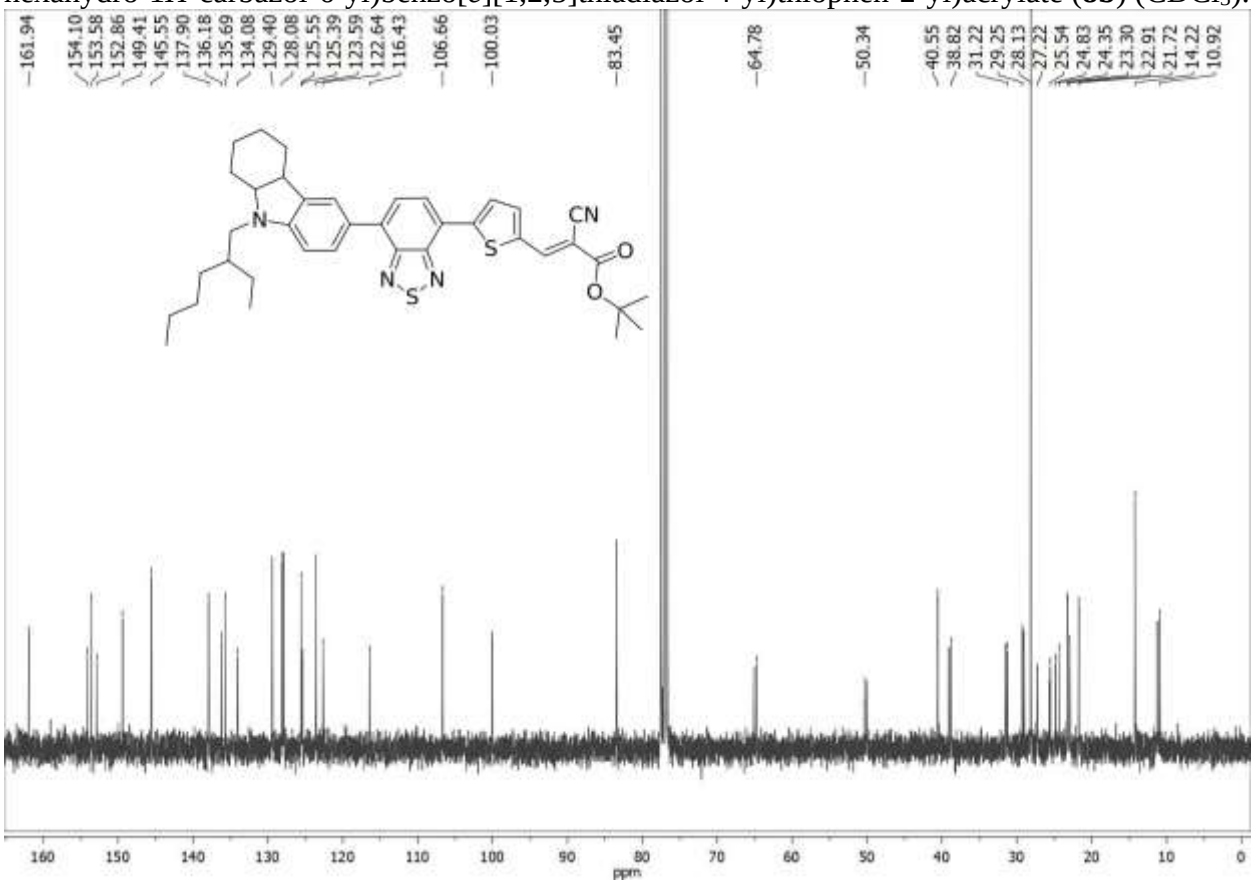
^{13}C NMR (75 MHz) spectrum of *tert*-butyl 2-cyano-3-(5-(7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**8a**) ($CDCl_3$).



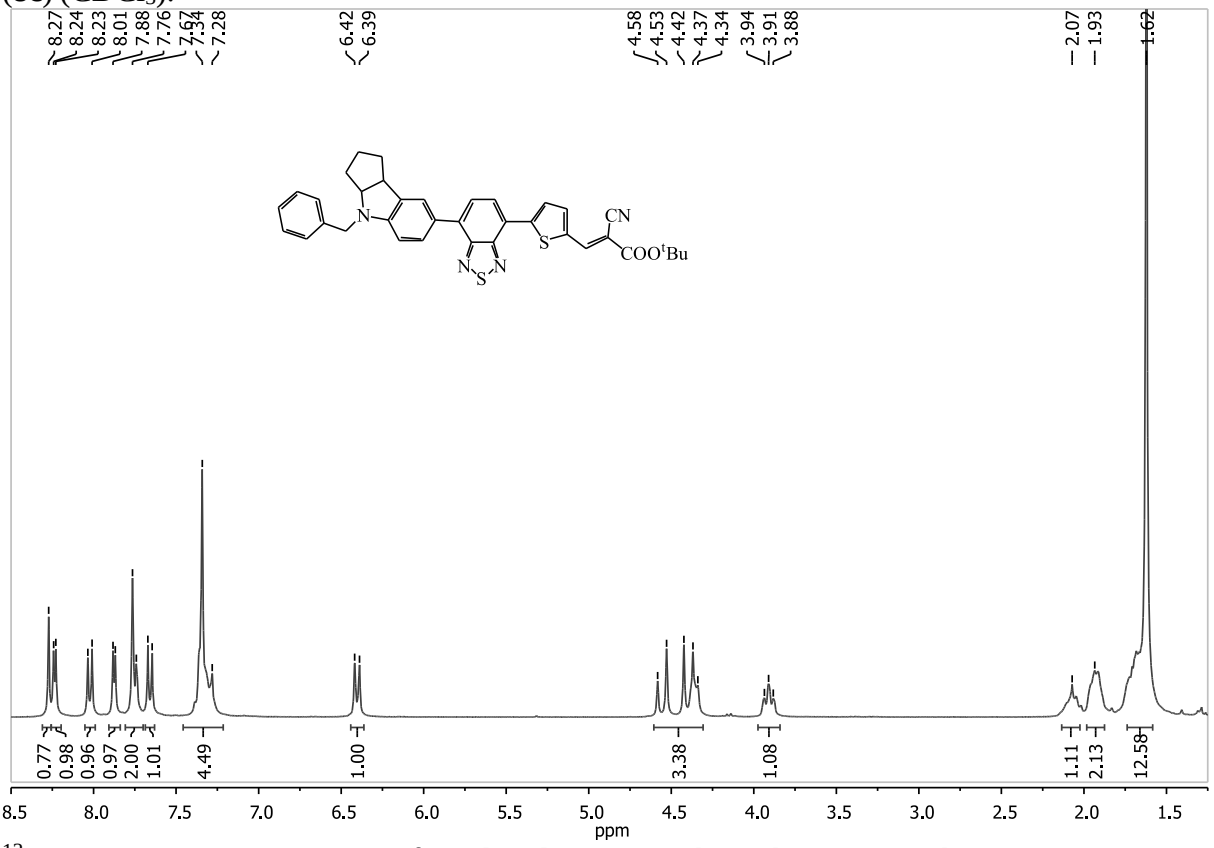
^{1}H NMR (300 MHz) spectrum of *tert*-butyl 2-cyano-3-(5-(7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**8b**) ($CDCl_3$).



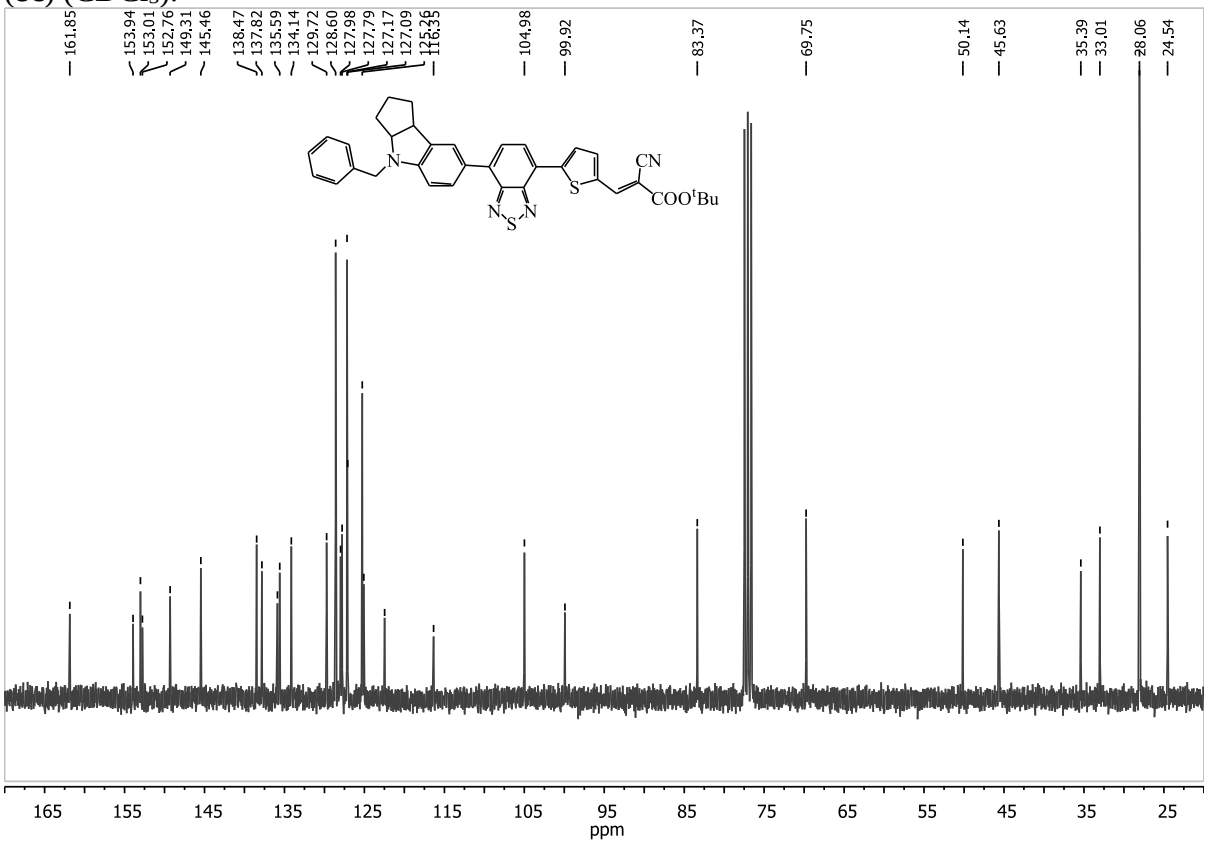
^{13}C NMR (75 MHz) spectrum of *tert*-butyl 2-cyano-3-(5-(7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate (**8b**) ($CDCl_3$).



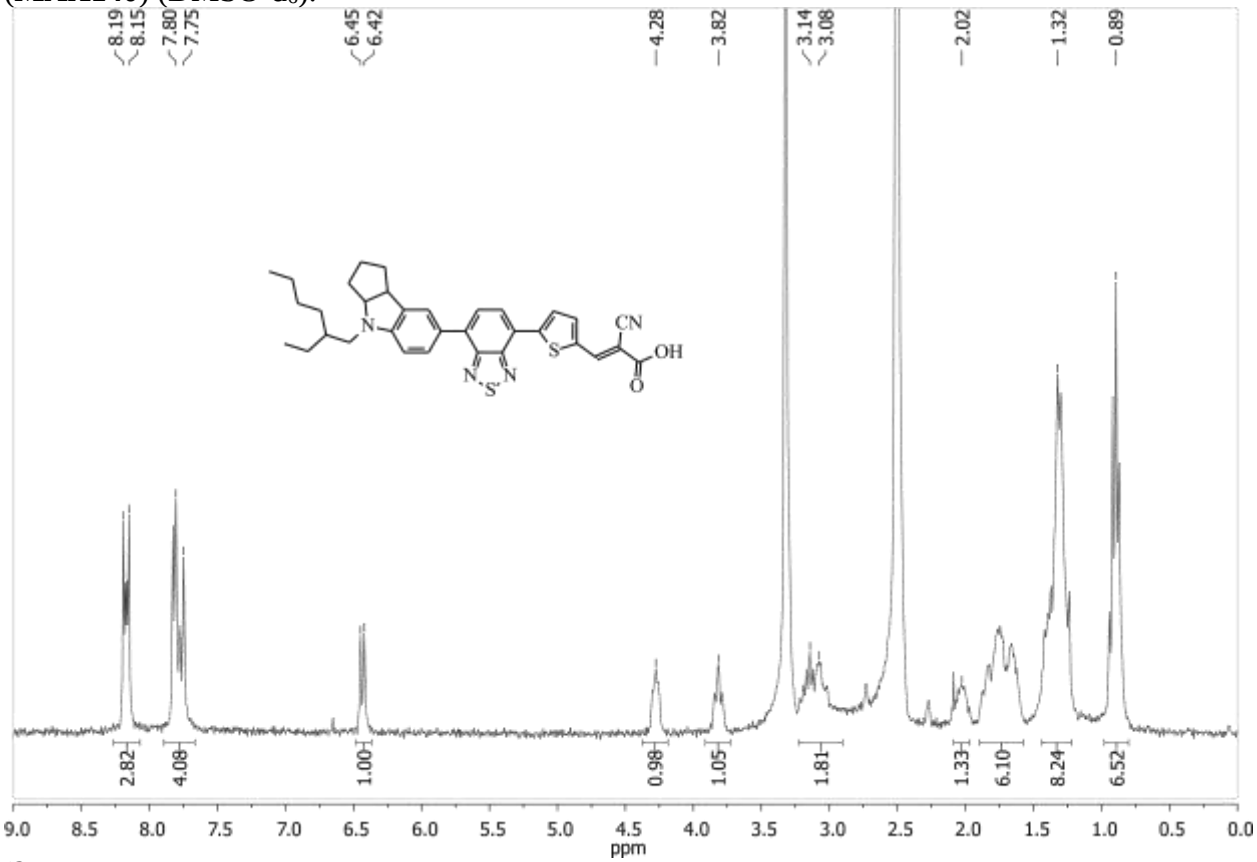
^{1}H NMR (300 MHz) spectrum of *tert*-butyl 3-(5-(7-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylate (**8c**) ($CDCl_3$).



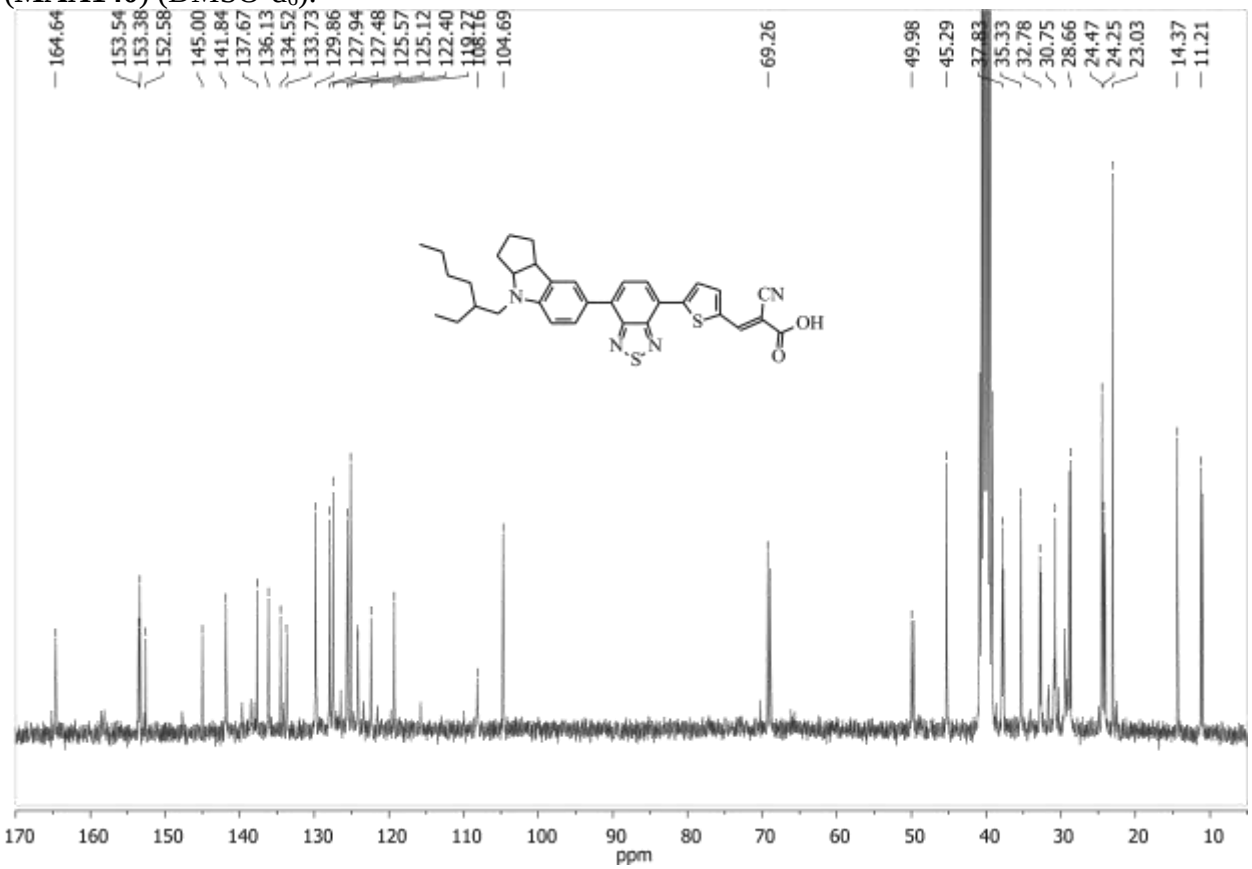
^{13}C NMR (75 MHz) spectrum of *tert*-butyl 3-(5-(7-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylate (**8c**) ($CDCl_3$).



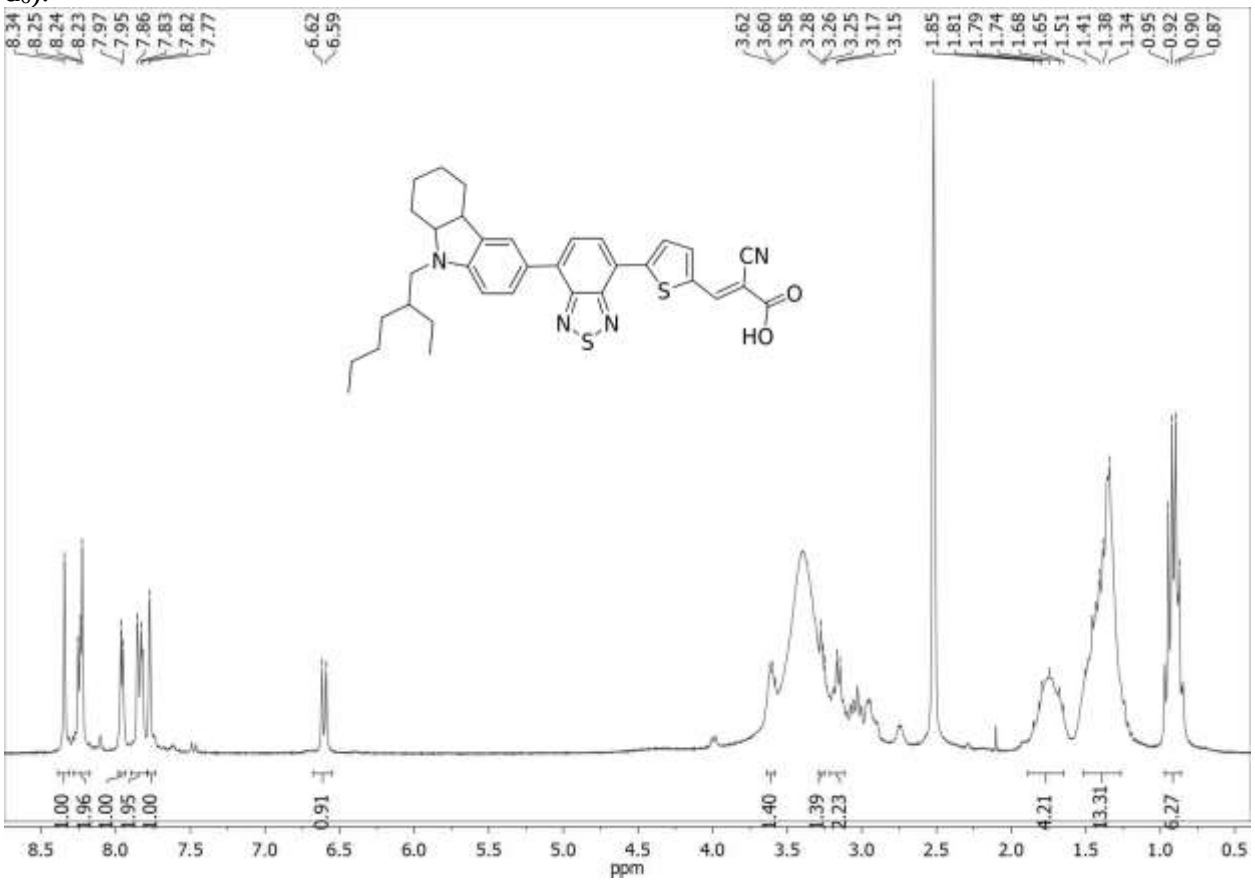
^{1}H NMR (300 MHz) spectrum of 2-cyano-3-(5-(7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**MAX140**) (DMSO-d_6).



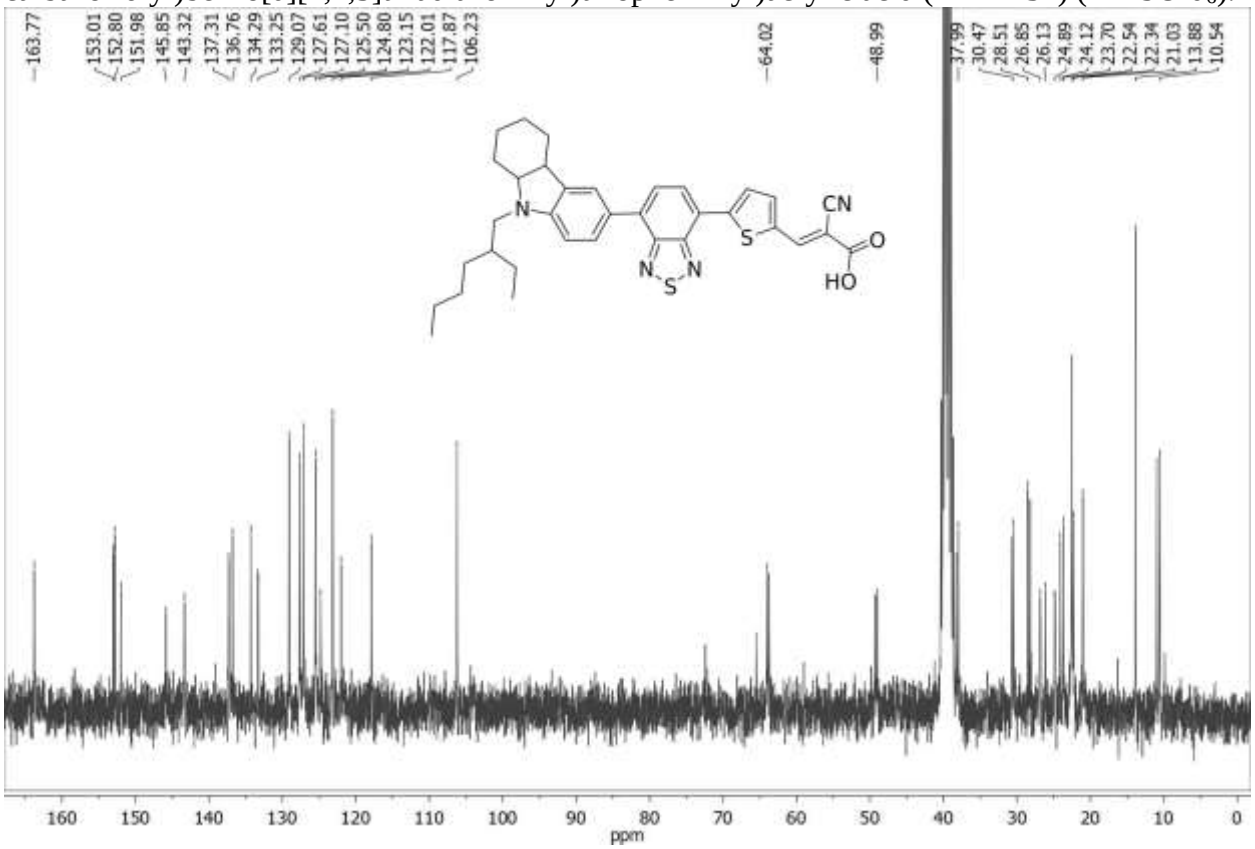
^{13}C NMR (75 MHz) spectrum of 2-cyano-3-(5-(7-(4-(2-ethylhexyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**MAX140**) (DMSO-d_6).



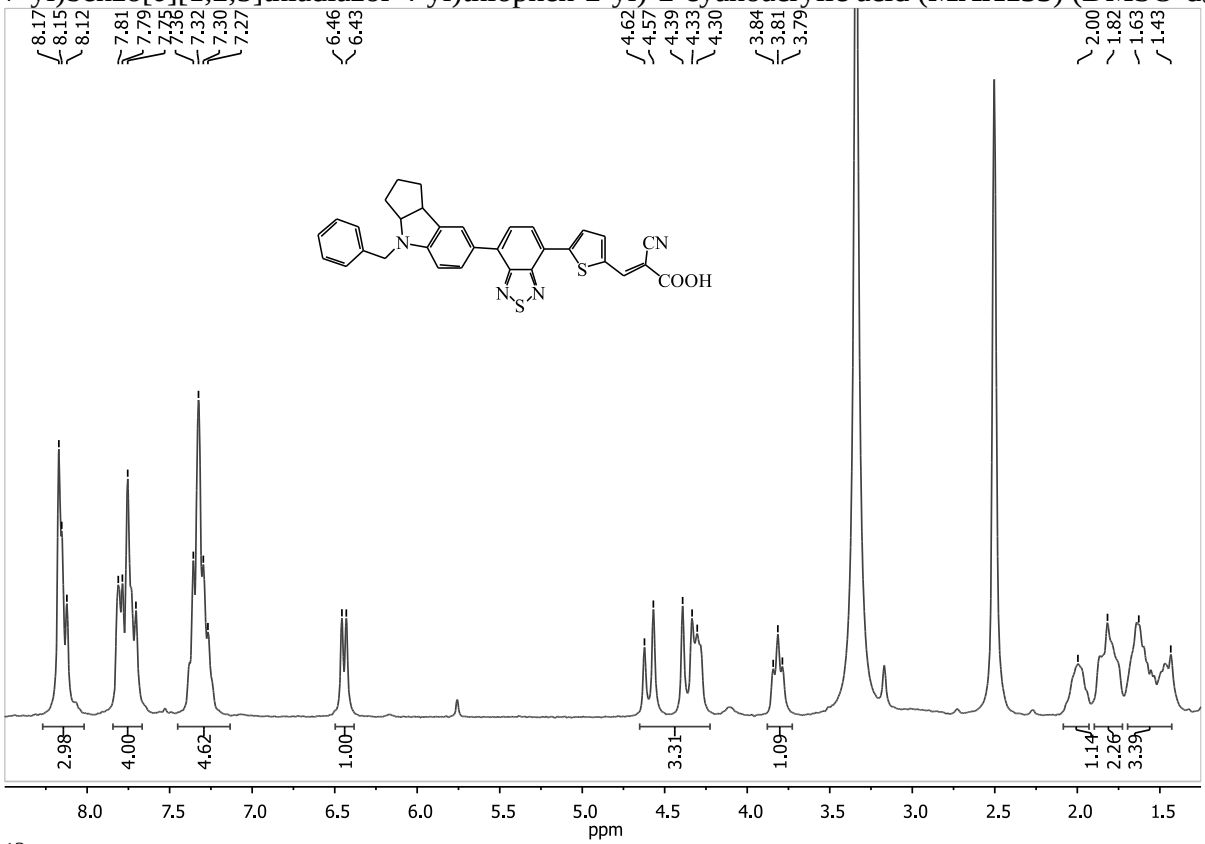
^{1}H NMR (300 MHz) spectrum of 2-cyano-3-(5-(7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**MAX157**) (DMSO-d_6).



^{13}C NMR (75 MHz) spectrum of 2-cyano-3-(5-(7-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (**MAX157**) (DMSO-d_6).



^{1}H NMR (300 MHz) spectrum of 3-(5-(7-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MAX155**) (DMSO-d_6).



^{13}C NMR (75 MHz) spectrum of 3-(5-(7-(4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MAX155**) (DMSO-d_6)