Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 371–373

New D–A–D luminophores of the 1,2,5-thiadiazolo[3,4-*d*]pyridazine series

Vladislav M. Korshunov, Timofey N. Chmovzh, German R. Chkhetiani, Ilya V. Taydakov and Oleg A. Rakitin

Table of contents

General information

Chemicals were used as purchased. 4,7-Dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1**,[S1] 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole **3a**,[S2] 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3b**,[S3] 2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **3c**[S4] were prepared as reported. All synthetic operations were performed under a dry argon atmosphere. Solvents were purified by distillation over the appropriate drying agents. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AM-300 NMR spectrometer (at frequencies of 300.1 and 75.5 MHz, respectively) in $CDCl_3$ solutions, with TMS as the standard. *J* values are given in Hz. Multiplicities are assigned as s (singlet), d (doublet), t (triplet), m (multiplet). High resolution mass spectra were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). IR spectra were measured with a Bruker 'Alpha-T' instrument in KBr pellets.

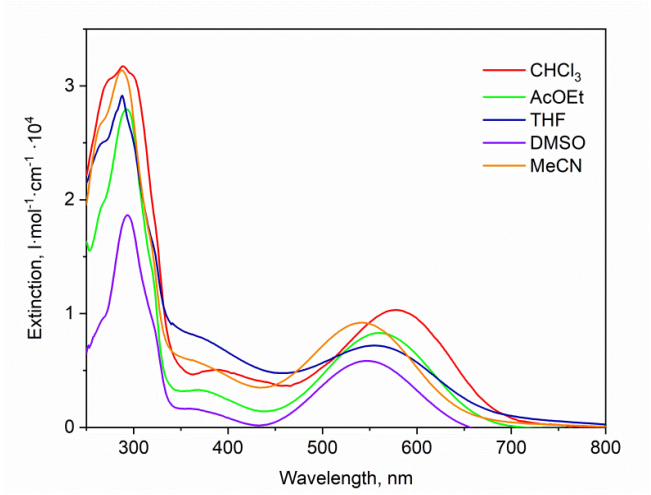
Optical absorption spectra were obtained at ambient temperature using a JASCO V-770 spectrophotometer in the range 180-2500 nm. The experiments were carried out for the compounds in the solutions poured into 1 cm pathlength quartz optical cells. The samples were dissolved in different solvents such as cyclohexane (C_6H_{12}), chloroform ($CHCl_3$), ethyl acetate (AcOEt), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), (HPLC-grade super gradient, Panreac, Spain) with concentrations of about 5×10^{-5} mol dm^{-3}.

Photoluminescence excitation, emission spectra as well as luminescence decays were recorded at room temperature with a Horiba-Jobin-Yvon Fluorolog FL3-22 spectrofluorimeter equipped with a 450 W Xenon lamp and R-928 photomultiplier. This experimental setup is sensitive in the 300-850 emission range. The absolute luminescence quantum yield (Φ) measurements were carried out with a use of the same setup equipped with a G8 Spectralon® - covered sphere (GMP SA, Switzerland) and a Hamamatsu R928 photomultiplier. A diffusing screen was mounted inside the sphere to avoid direct irradiation of the detector. The measurements were carried out at ambient temperature.

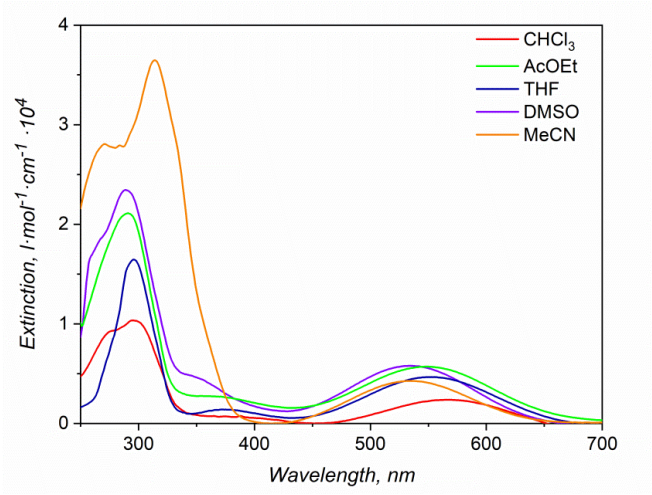
References

S1. T. N. Chmovzh, E. A. Knyazeva, K. A. Lyssenko, V. V. Popov, O. A. Rakitin, *Molecules*, 2018, **23**, 2576.
S2. G. S. Welmaker, J. E. Sabalski, *Tetrahedron Lett.*, 2004, **25**, 4851.
S3. K. Saito, Y. Shibata, M. Yamanaka, T. Akiyama, *J. Am. Chem. Soc.*, 2013, **135**, 11740.
S4. M. Calletani, A. Del Rio, *Russ. Chem. Bull.*, 1998, **47**, 928.

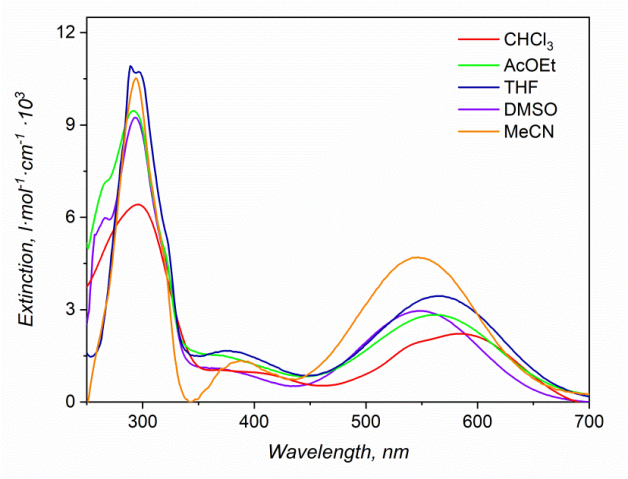
Photophysical properties



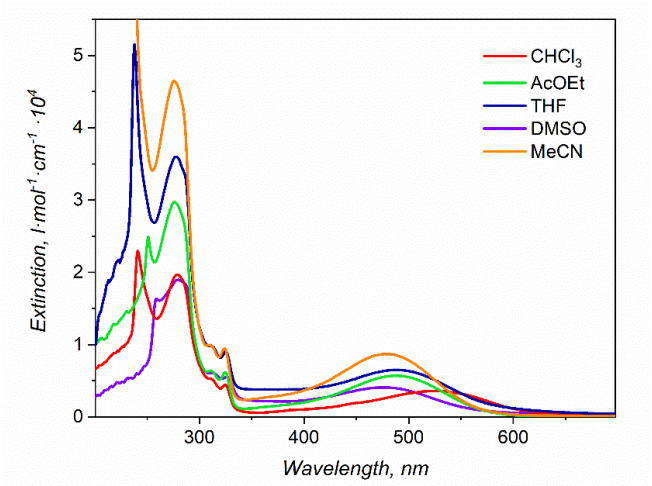
2a



2b



2c



4

Figure S1: UV-Vis spectra recorded for dyes **2a, 2b, 2c** and **4**.

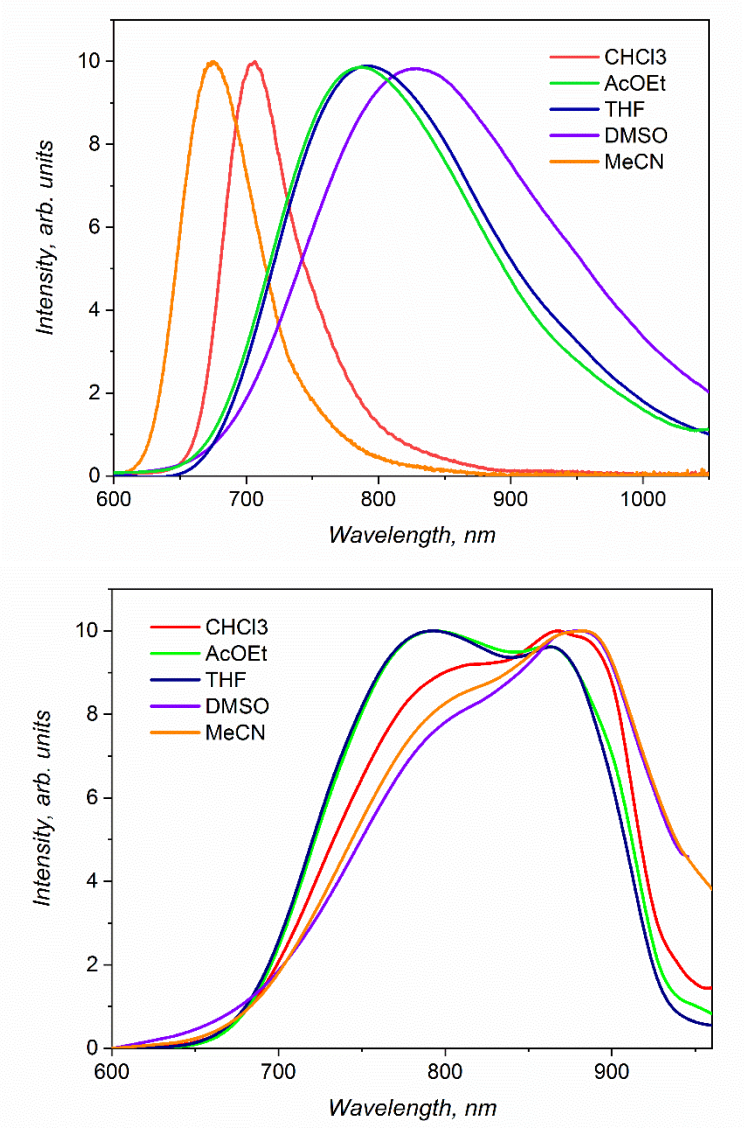


Figure S2: Luminescence spectra recorded for dyes **2a** and **2c**.

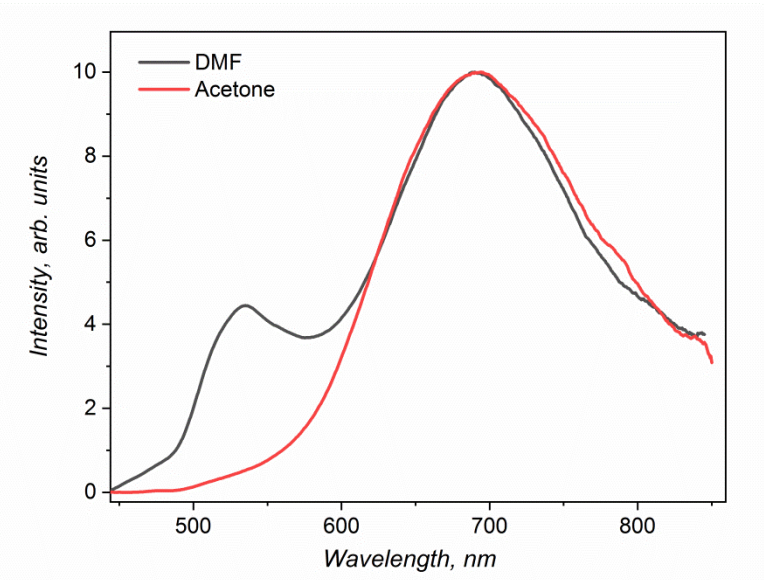
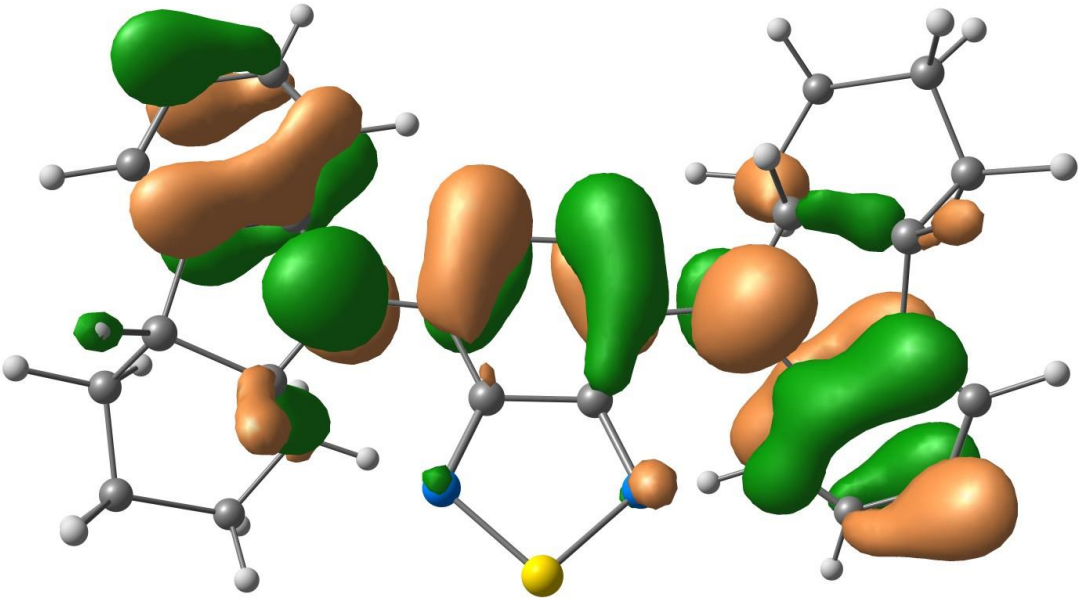


Figure S3: Luminescence spectra recorded for dye **4** dissolved in DMF and acetone.

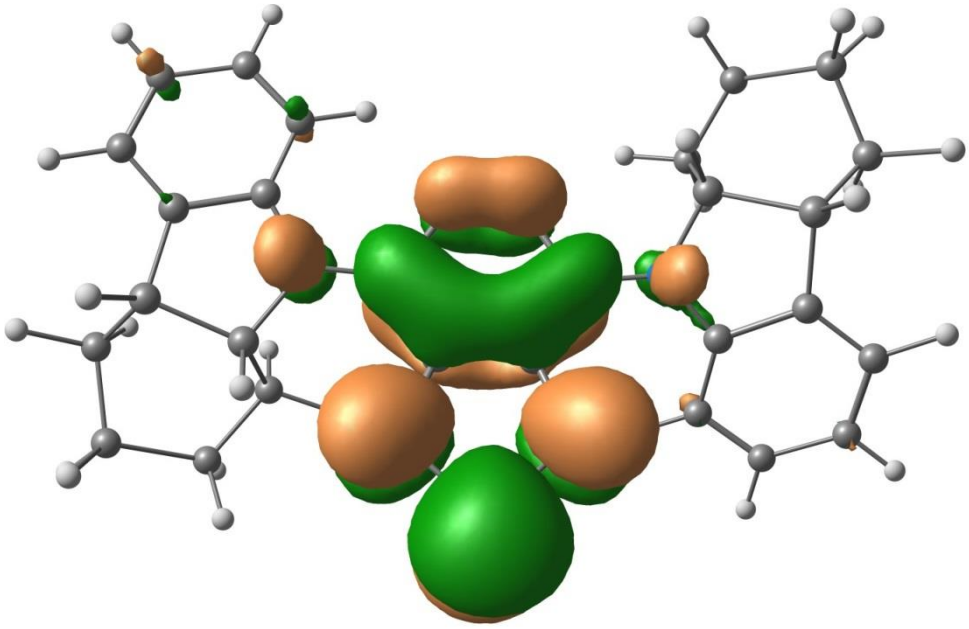
Table S1 Photophysical parameters obtained for dyes **2** and **4**: absorption maximum wavelength λ_{abs}, maximum molar extinction coefficient ε, wavelength of emission maximum λ_{em}, full width half maximum FWHM for the emission spectrum, Stokes shift Δν, oscillator strength.

Solvent	λ_{abs}(LE) nm	λ_{abs}(ICT) nm	$\varepsilon_{max}\times10^3$ mol×l^{-1}×cm^{-1}	λ_{em} nm	FWHM nm	Δν cm^{-1}	f
2a							
$CHCl_3$	289	580.5	31.7	706	125	3062	0.21
AcOEt	292	563	28	787	141	5056	0.12
THF	290	555	29	792	127	5391	0.11
DMSO	293	550	18.7	828	145	6104	0.15
MeCN	290	542	31	675	90	3635	0.25
2b							
$CHCl_3$	296	568	10.2	802	102	5137	0.11
AcOEt	292	550	21.5	794	105	5587	0.31
THF	297	554	23	794	95	5456	0.31
DMSO	293	535	24.4	815	142	6421	0.24
MeCN	314	535	37	820	85	6496	0.19
2c							
$CHCl_3$	297	587	64.4	868	100	5515	0.44
AcOEt	295	564	94.3	792	98	5104	0.39
THF	294	567	109	790	106	4978	0.55
DMSO	295	550	92	880	125	6818	0.45
MeCN	295	547	105	884	87	6916	0.30
4							
$CHCl_3$	277	526	19.6	695	110	4623	0.19
AcOEt	277	488	29.6	675	124	5676	0.22
THF	277	489	36.9	679	120	5722	0.30
DMSO	279	476	20.1	706	140	6844	0.09
MeCN	275	479	46.5	616	85	4643	0.24

DFT calculation



HOMO



LUMO

Figure S4 Frontier molecular orbitals for dye **2b**.

Optimized ground state geometries coordinates for the investigated dyes

Compound **4**

S	5.106879000	10.206216000	17.074152000
N	1.148203000	8.476970000	15.239115000
N	1.811525000	7.043208000	16.927851000
N	2.354455000	11.452742000	13.645326000
N	1.281867000	9.561048000	14.431942000
N	4.380394000	10.910710000	15.791767000
N	4.134317000	8.909922000	17.280616000
C	2.052987000	8.156537000	16.125772000
C	3.207073000	8.993392000	16.329518000
C	2.322913000	10.348422000	14.494277000
C	2.734595000	6.038175000	17.258025000
C	3.346930000	10.130844000	15.483165000
C	2.107900000	5.113962000	18.116824000
C	0.585015000	6.741850000	17.544867000
C	4.042916000	5.845771000	16.810373000
H	4.522082000	6.537585000	16.119302000
C	1.269152000	12.310260000	13.394071000
C	3.084352000	13.062352000	12.196010000
C	-0.624736000	7.437522000	17.511177000
H	-0.747278000	8.328424000	16.898309000
C	-0.329175000	5.075916000	19.058966000
H	-0.215248000	4.167873000	19.653683000
C	2.812908000	3.997258000	18.574741000
H	2.333786000	3.278090000	19.241234000
C	4.726626000	4.727648000	17.276412000
H	5.751880000	4.558086000	16.943242000
C	0.742427000	5.569028000	18.309086000
C	3.456000000	11.898297000	12.896985000
C	4.125375000	3.813652000	18.155990000
H	4.690799000	2.947247000	18.502162000
C	4.719151000	11.324995000	12.739031000
H	5.003117000	10.407321000	13.251705000
C	-0.030601000	12.275939000	13.902189000
H	-0.360633000	11.469964000	14.554662000
C	0.807715000	14.344067000	12.147414000
H	1.130180000	15.139110000	11.472841000
C	1.695302000	13.331465000	12.522477000
C	-1.536948000	5.763409000	19.034542000
H	-2.385466000	5.392525000	19.611412000
C	5.272447000	13.144185000	11.212060000
H	6.002757000	13.622305000	10.557682000
C	5.618637000	11.967441000	11.894562000
H	6.613377000	11.539855000	11.758395000
C	-1.676835000	6.931430000	18.268338000
H	-2.634943000	7.453917000	18.256248000
C	4.003605000	13.693451000	11.353100000
H	3.722591000	14.596241000	10.808146000
C	-0.896274000	13.295854000	13.519199000
H	-1.919455000	13.290194000	13.898866000
C	-0.487685000	14.320363000	12.650686000
H	-1.195331000	15.100921000	12.367320000

Compound **2c**

S	5.196762000	9.720185000	16.573985000

N	0.874705000	8.487904000	15.186774000
N	1.014688000	9.599276000	14.424531000
N	4.349181000	10.611208000	15.494275000
N	4.115104000	8.524271000	16.853099000
C	1.804397000	8.072421000	16.015061000
C	3.047026000	8.805634000	16.113897000
C	2.098076000	10.341124000	14.439635000
C	3.194538000	9.979080000	15.311102000
N	1.580477000	6.871793000	16.655972000
C	0.788833000	5.828380000	15.987022000
C	1.877660000	6.503379000	17.978082000
C	0.776789000	4.634732000	16.988686000
C	1.438998000	5.231227000	14.716589000
H	-0.216130000	6.210175000	15.764095000
C	1.448026000	5.187808000	18.214401000
C	2.433738000	7.262528000	19.007638000
C	1.470982000	3.508151000	16.184232000
H	-0.252064000	4.323448000	17.221985000
C	2.941695000	5.000086000	14.956736000
C	0.897650000	3.790414000	14.782548000
H	1.209169000	5.797892000	13.806002000
C	1.623385000	4.604117000	19.459917000
C	2.604037000	6.661088000	20.257613000
H	2.734489000	8.296536000	18.856566000
C	2.962704000	3.832752000	15.985751000
H	1.281545000	2.507520000	16.594213000
H	3.426127000	4.709583000	14.012955000
H	3.456197000	5.896750000	15.327716000
H	-0.200894000	3.732406000	14.742212000
H	1.318130000	3.141544000	13.999678000
C	2.217139000	5.341834000	20.489707000
H	1.286646000	3.579697000	19.633748000
H	3.043445000	7.247050000	21.067238000
H	3.455029000	4.109366000	16.929004000
H	3.490835000	2.955556000	15.583950000
H	2.360136000	4.893703000	21.474089000
N	2.063925000	11.507394000	13.704801000
C	0.784223000	12.209705000	13.523066000
C	3.079618000	12.115987000	12.949156000
C	1.141707000	13.481788000	12.697591000
C	0.163183000	12.779550000	14.820164000
H	0.069637000	11.553499000	13.009127000
C	2.593578000	13.293350000	12.358486000
C	4.376149000	11.674664000	12.684819000
C	0.725024000	14.632250000	13.646894000
H	0.538140000	13.541128000	11.779958000
C	1.258382000	13.427377000	15.686305000
C	-0.551216000	14.023488000	14.258128000
H	-0.464195000	12.055015000	15.353496000
C	3.414067000	14.065292000	11.550077000
C	5.191378000	12.462623000	11.867824000

Compound **2a**

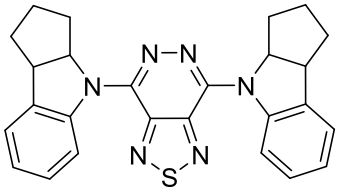
S	4.916727000	10.526145000	17.626206000
N	1.631755000	8.377052000	15.045709000
N	1.804883000	9.470579000	14.261077000
N	4.403356000	11.143517000	16.199740000

N	4.050580000	9.137748000	17.644698000
C	2.363945000	8.138167000	16.105361000
C	3.344863000	9.118119000	16.520699000
C	2.719092000	10.386125000	14.493706000
C	3.535628000	10.272970000	15.694276000
N	2.053477000	7.022570000	16.851071000
C	2.892794000	6.218178000	17.634917000
C	0.695167000	6.456152000	16.823966000
C	2.112921000	5.332654000	18.390835000
C	4.285111000	6.156514000	17.674113000
C	0.646785000	5.521278000	18.068857000
C	0.385932000	5.546330000	15.606823000
H	-0.014800000	7.290961000	16.877241000
C	2.716608000	4.418583000	19.240992000
C	4.880850000	5.231896000	18.535781000
H	4.901825000	6.805042000	17.054863000
C	-0.045066000	4.239877000	17.580915000
H	0.118837000	5.980822000	18.918170000
C	0.436299000	4.106135000	16.134161000
H	-0.627291000	5.779672000	15.243943000
H	1.076753000	5.739822000	14.777479000
C	4.112873000	4.374069000	19.322972000
H	2.106102000	3.731021000	19.830841000
H	5.970331000	5.177995000	18.580541000
H	-1.138634000	4.378131000	17.606754000
H	0.193408000	3.368045000	18.207649000
H	1.471989000	3.728406000	16.121591000
H	-0.175942000	3.412775000	15.539910000
H	4.599567000	3.658674000	19.987617000
N	2.840424000	11.443288000	13.626823000
C	1.983843000	11.737596000	12.544194000
C	3.987001000	12.382019000	13.653187000
C	2.433028000	12.895650000	11.894993000
C	0.834022000	11.077793000	12.099114000
C	3.686325000	13.425169000	12.539442000
C	5.319893000	11.714986000	13.251439000
H	4.050500000	12.836673000	14.645479000
C	1.746776000	13.409542000	10.805691000
C	0.150604000	11.611523000	11.001551000
H	0.494176000	10.174011000	12.592876000
C	4.918517000	13.408590000	11.611930000
H	3.509477000	14.427577000	12.954808000
C	5.457761000	11.983980000	11.750347000
H	6.138328000	12.207398000	13.800664000
H	5.349224000	10.647779000	13.511277000
C	0.591944000	12.763041000	10.353470000
H	2.108539000	14.313115000	10.309612000
H	-0.748472000	11.102680000	10.648092000
H	5.667772000	14.130010000	11.976477000
H	4.663308000	13.686815000	10.579238000
H	4.824703000	11.284438000	11.179213000
H	6.489081000	11.872637000	11.386943000
H	0.041906000	13.157983000	9.497789000

General procedure for the preparation of compounds 2a-c and 4

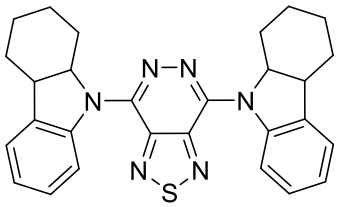
Amine **3a-c** (0.34 mmol) and Et_3N (34 mg, 0.34 mmol) were added with stirring to a solution of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** (50 mg, 0.17 mmol) in dry MeCN (15 ml). The mixture was stirred at reflux for 10–30 h. Then the mixture was poured into water (25 ml) and extracted with EtOAc (3×35 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

4,7-Bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)[1,2,5]thiadiazolo[3,4-*d*]pyridazine 2a



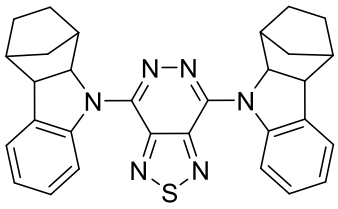
Violet solid, 67 mg (88%), R_f = 0.58 (CH_2Cl_2). Mp = 209-211 ^oC. Eluent was CH_2Cl_2/hexane, 1:1 (v/v). IR *n*max (KBr, cm^{-1}): 2951, 2934, 2861, 1477, 1433, 1344, 1263, 1227, 1176, 1142, 1025, 898, 845, 749, 669, 515. ^1H NMR (300 MHz, $CDCl_3$): 8.44 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.00 (t, *J* = 7.3 Hz, 2H), 6.01 – 5.93 (m, 2H), 4.04 (t, *J* = 7.7 Hz, 2H), 2.20 – 2.02 (m, 6H), 1.85 – 1.76 (m, 2H), 1.71 – 1.64 (m, 2H), 1.60–1.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 147.4, 146.4, 145.0, 135.3, 127.4, 124.0, 122.1, 115.7, 67.5, 45.8, 36.4, 34.6, 24.0. HRMS (ESI-TOF), m/z: calcd for $C_{26}H_{25}N_6S$ $[M + H]^+$, 453.1856, found, 453.1863.

4,7-Bis(2,3,4,4a-tetrahydro-1*H*-carbazol-9(9a*H*)-yl)[1,2,5]thiadiazolo[3,4-*d*]pyridazine 2b



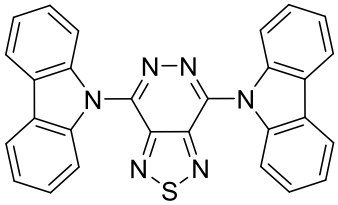
Violet solid, 73 mg (90%), R_f = 0.6 (CH_2Cl_2). Mp = 239-241 ^oC. Eluent was CH_2Cl_2/hexane, 1:1 (v/v). IR *n*max (KBr, cm^{-1}): 2927, 2853, 1526, 1475, 1435, 1270, 1164, 1132, 877, 752, 574. ^1H-NMR (300 MHz, $CDCl_3$): 8.27 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.29 (m, 4H), 7.05 (t, *J* = 7.3 Hz, 2H), 5.50 – 5.59 (m, 2H), 3.63 – 3.67 (m, 2H), 2.37 (d, *J* = 13.2 Hz, 2H), 2.08 – 2.14 (m, 2H), 1.91 – 2.00 (m, 2H), 1.61 – 1.64 (m, 4H), 1.36 – 1.54 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.0, 146.1, 144.2, 134.3, 127.0, 122.3, 122.0, 117.2, 63.4, 40.3, 27.7, 24.9, 22.6, 21.3. HRMS (ESI-TOF), m/z: calcd for $C_{28}H_{29}N_6S$ $[M + H]^+$, 481.2169, found, 481.2150.

4,7-Bis(1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanocarbazol-9-yl)[1,2,5]thiadiazolo-[3,4-*d*]pyridazine 2c



Violet solid, 78 mg (92%), R_f = 0.62 (CH_2Cl_2). Mp = 228-230 ºC. Eluent is CH_2Cl_2/hexane, 1:1 (v/v). IR_{max} (KBr, cm^{-1}): 2956, 2925, 2868, 1478, 1432, 1346, 1296, 1253, 1174, 1143, 1205, 896, 751, 566. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.47 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.19 (m, 4H), 6.96 (t, *J* = 7.3 Hz, 2H), 5.48 (d, *J* = 8.1 Hz, 2H), 3.50 (d, *J* = 8.1 Hz, 2H), 2.29 – 2.46 (m, 4H), 1.72 – 1.63 (m,. 2H), 1.59 – 1.51 (m, 8H), 1.11 (d, *J* = 10.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 147.0, 146.4, 146.3, 134.1, 127.6, 124.2, 121.9, 115.5, 69.2, 50.6, 43.6, 43.4, 32.0, 28.2, 25.3. HRMS (ESI-TOF), m/z: calcd for $C_{30}H_{28}N_6S$ $[M]^+$, 504.2091, found, 504.2086.

4,7-Di(9*H*-carbazol-9-yl)[1,2,5]thiadiazolo[3,4-*d*]pyridazine 4

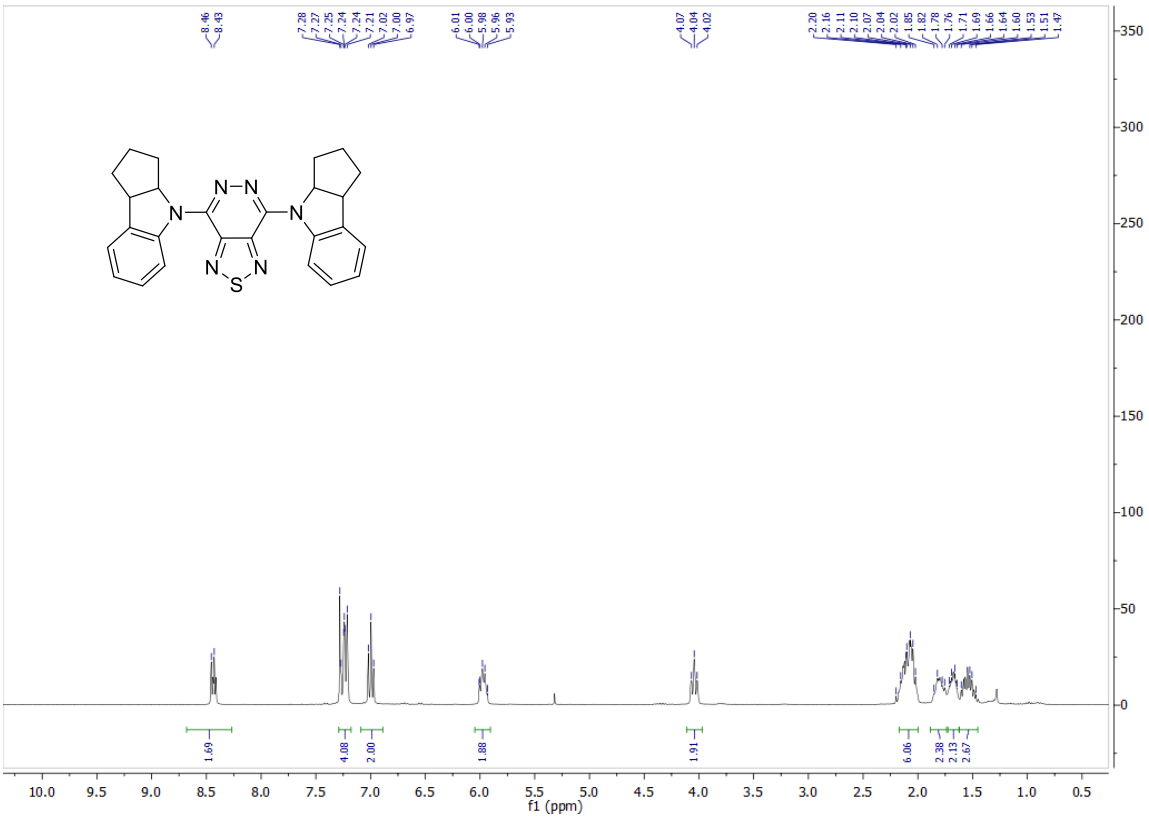


2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (74 mg, 0.32 mmol) was added to a solution of amine **3b** (60 mg, 0.13 mmol) in toluene (12 ml). The mixture was refluxed for 7 h, diluted with EtOAc (30 ml), washed with aq. $NaHSO_3$, Na_2CO_3, water, and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/hexane, 2:1, v/v) to afford 46 mg (75%) of product **4** as a dark red solid, R_f = 0.4 (CH_2Cl_2). Mp > 260 ºC. IR ν_{max} (KBr, cm^{-1}): 3044, 2921, 2851, 1599, 1490, 1479, 1446, 1332, 1264, 1223, 1151, 865, 739, 717, 511. 1H-NMR (300 MHz, $CDCl_3$): 8.20 (d, J = 7.2 Hz, 4H), 7.86 (d, J = 7.8 Hz, 4H), 7.43 – 7.54 (m, 8H). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.5, 148.4, 140.0, 126.8, 125.8, 122.9, 120.7, 113.1. HRMS (ESI-TOF), m/z: calcd for $C_{28}H_{17}N_6S$ $[M + H]^+$, 469.1230, found, 469.1247.

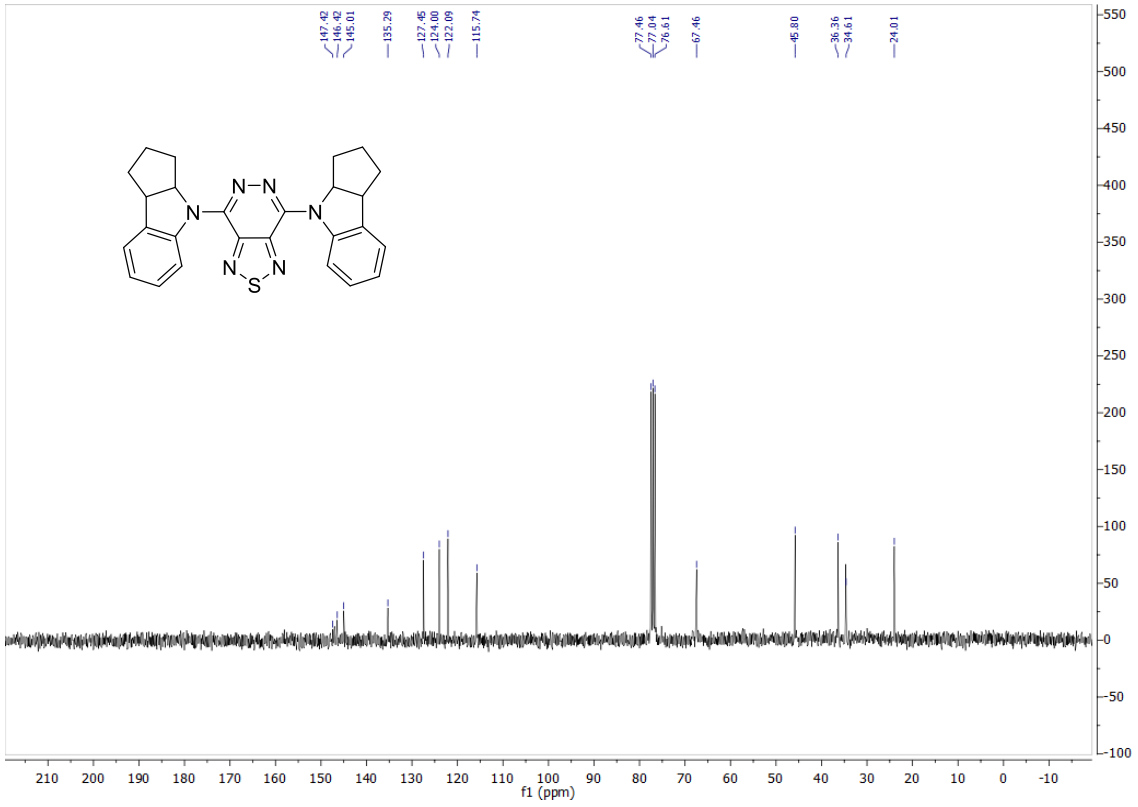
^{1}H and ^{13}C NMR spectra

4,7-Bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)[1,2,5]thiadiazolo[3,4-*d*]pyridazine 2a

^{1}H NMR (300 MHz)

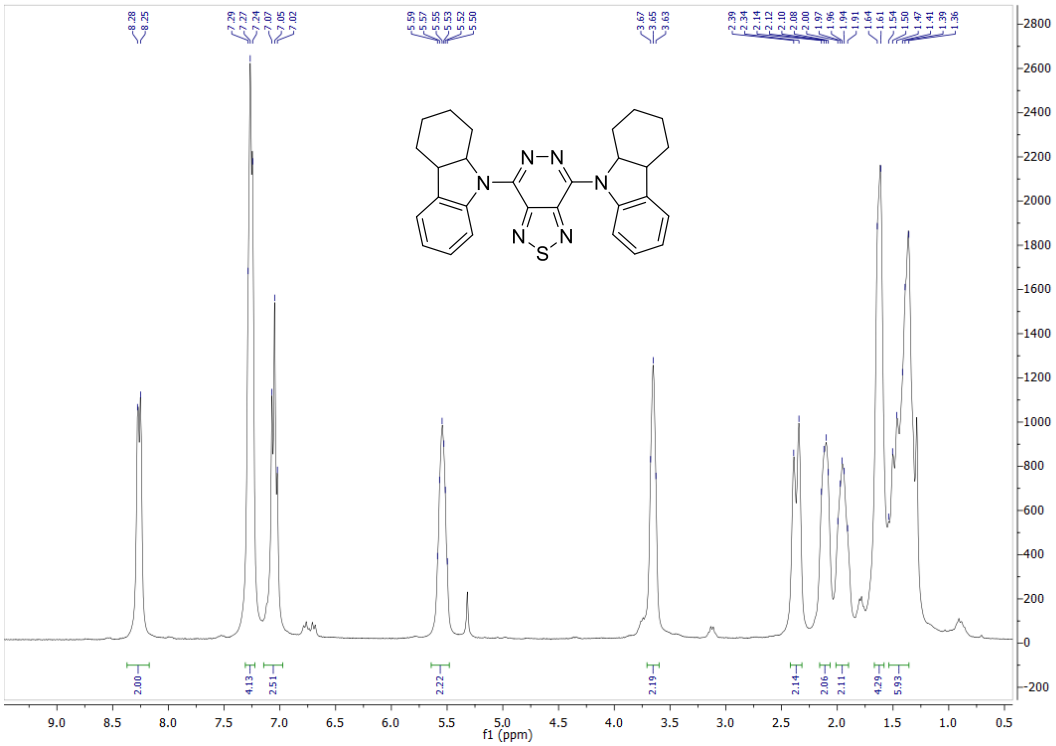


^{13}C NMR(75 MHz)

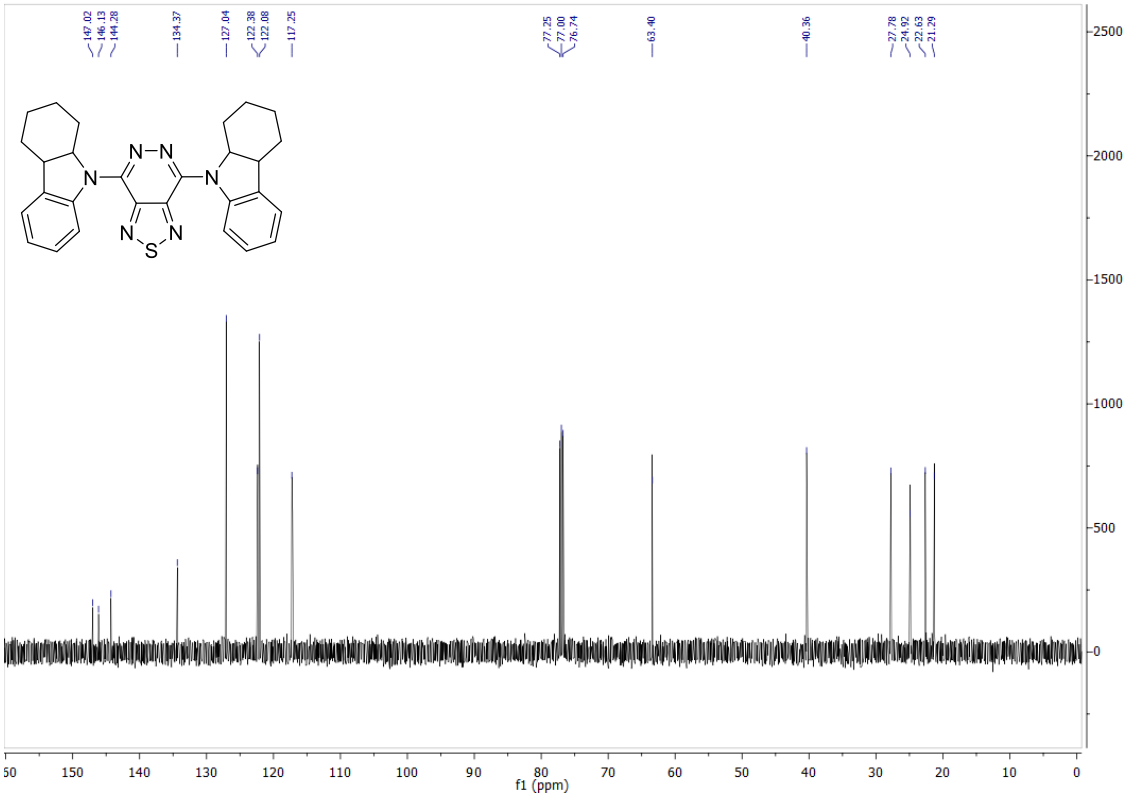


4,7-Bis(2,3,4,4a-tetrahydro-1*H*-carbazol-9(9a*H*)-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine 2b

^{1}H NMR (300 MHz)

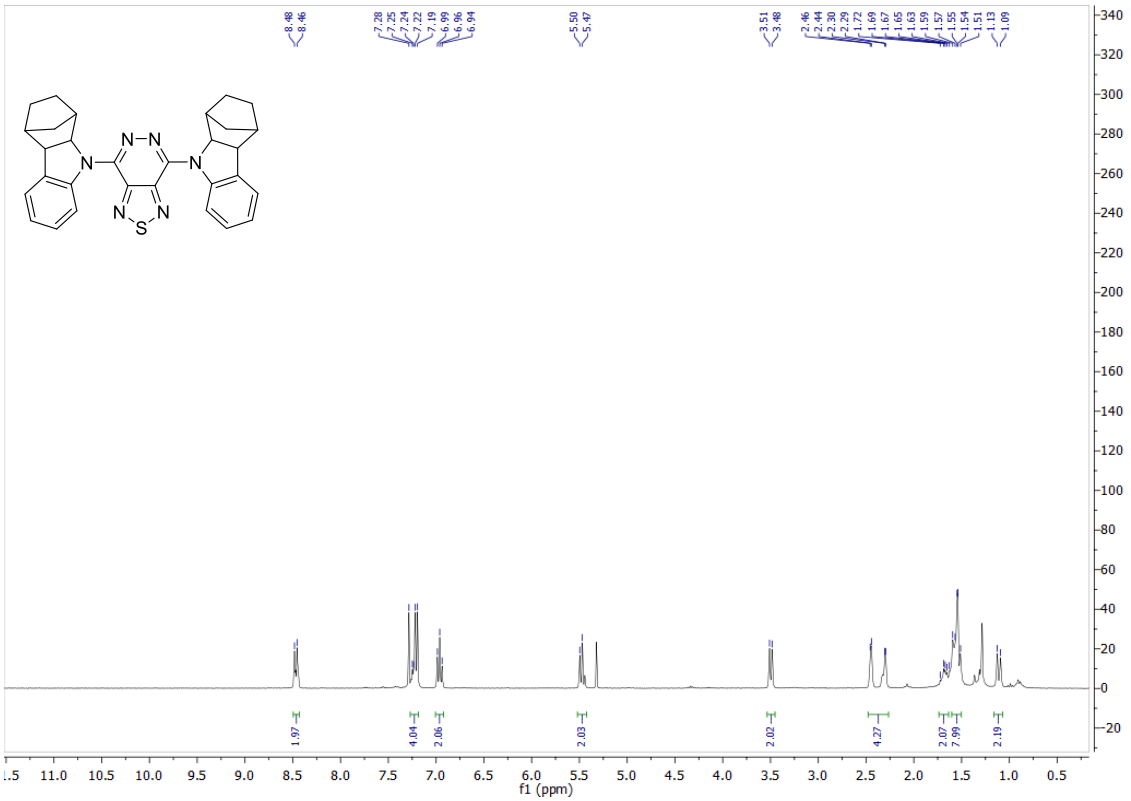


^{13}C NMR(75 MHz)

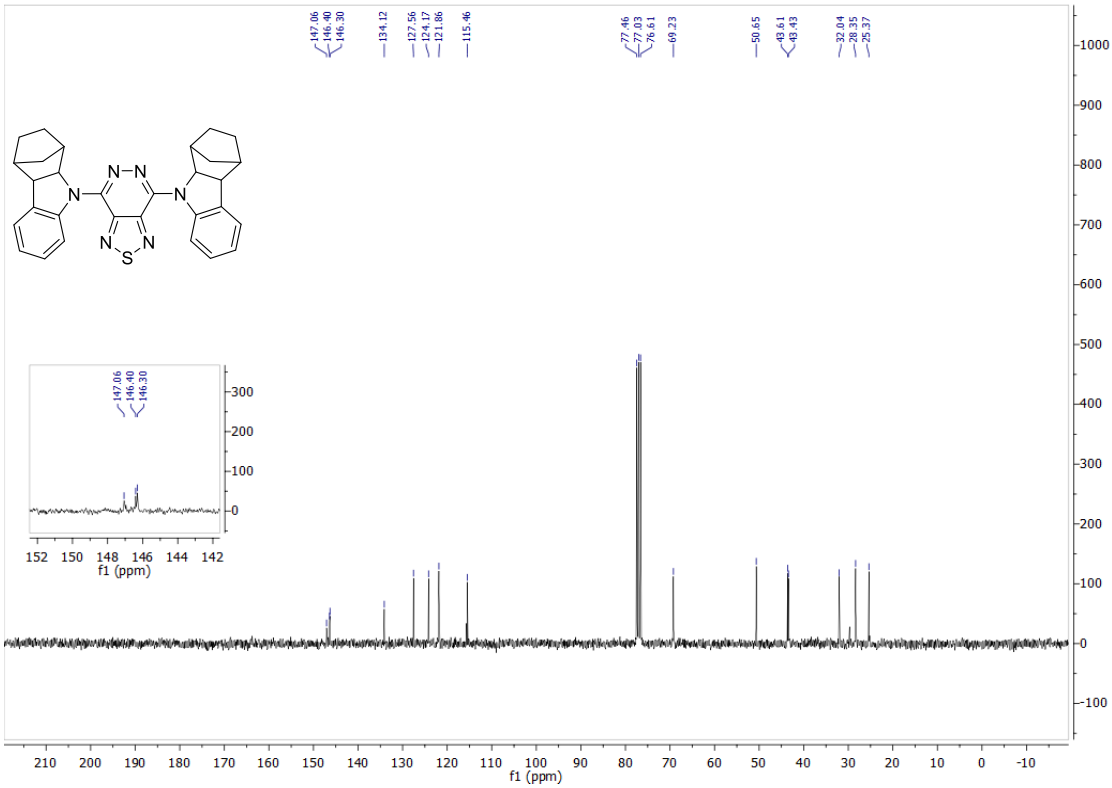


4,7-Bis(1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanocarbazol-9-yl)[1,2,5]thiadiazolo-[3,4-*d*]pyridazine 2c

^{1}H NMR (300 MHz)

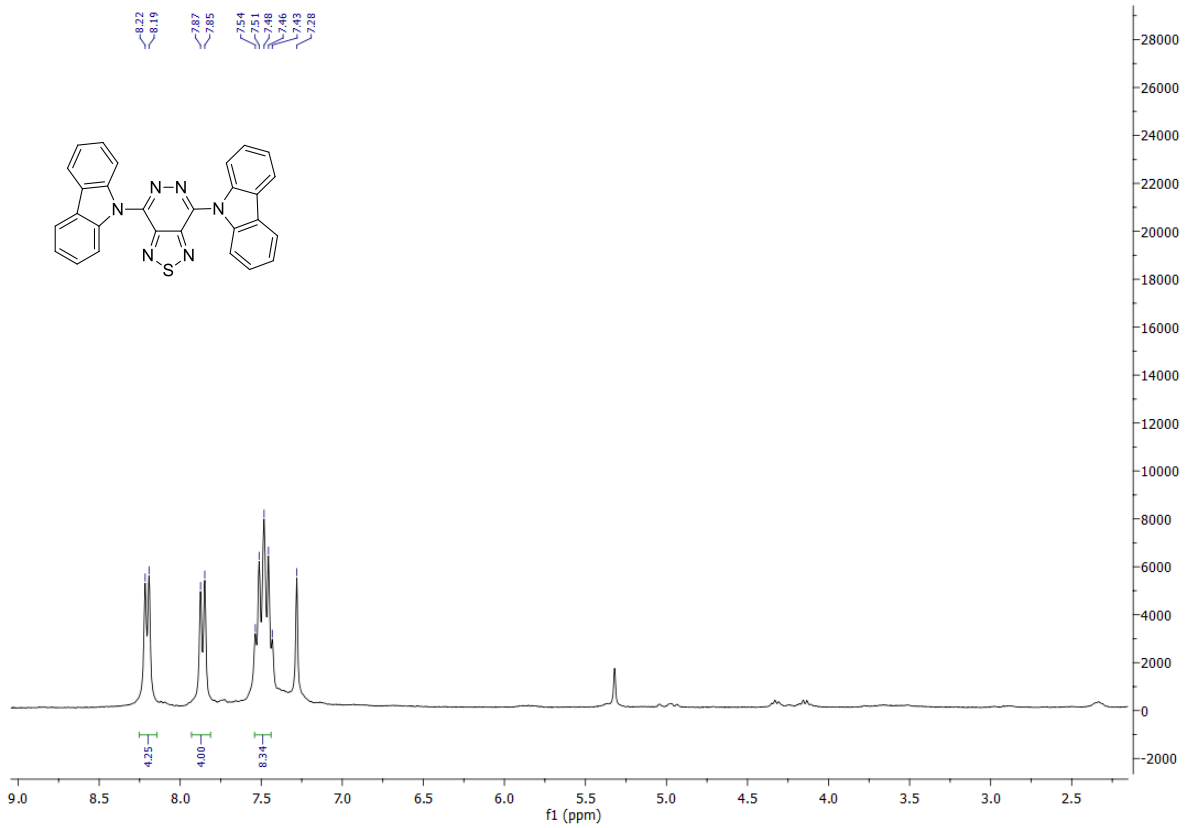


^{13}C NMR(75 MHz)



4,7-Di(9*H*-carbazol-9-yl)[1,2,5]thiadiazolo[3,4-*d*]pyridazine 4

^{1}H NMR (300 MHz)



^{13}C NMR(75 MHz)