ELECTRONIC SUPPLEMENTARY INFORMATION

Bis-arylsulfenyl- and bis-arylselanyl-benzo-2,1,3-thiadiazoles: synthesis and photophysical characterization

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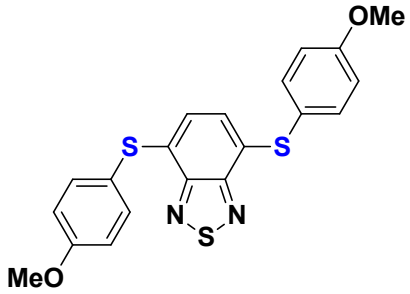
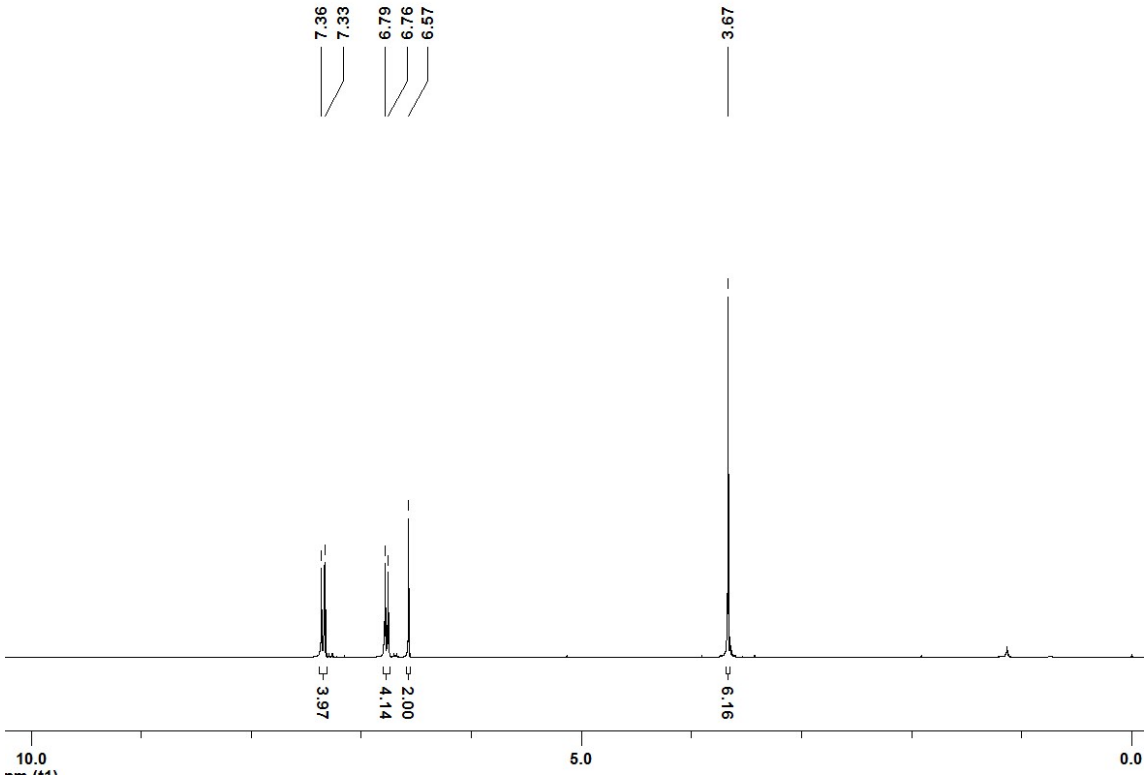
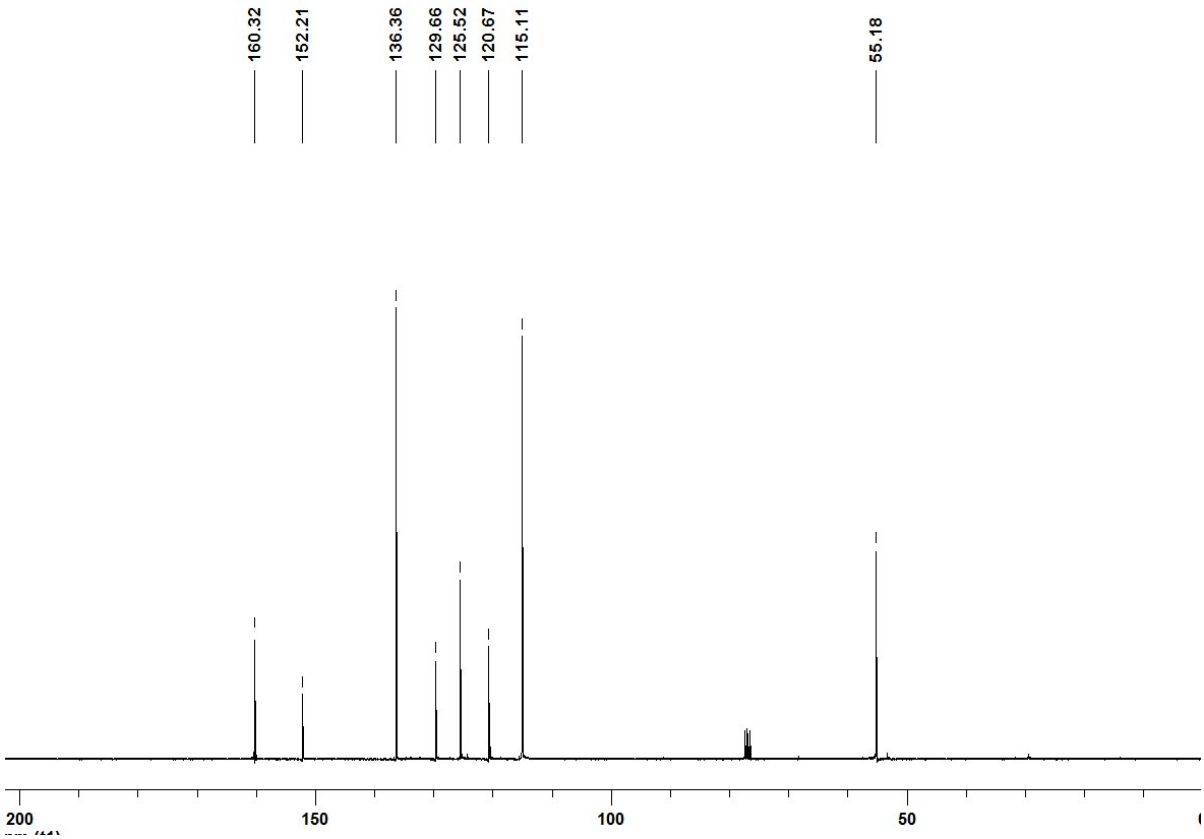
Summary

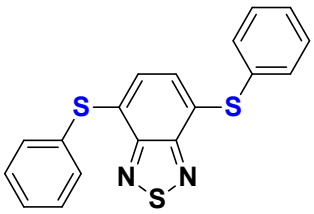
1. Spectroscopic characterization



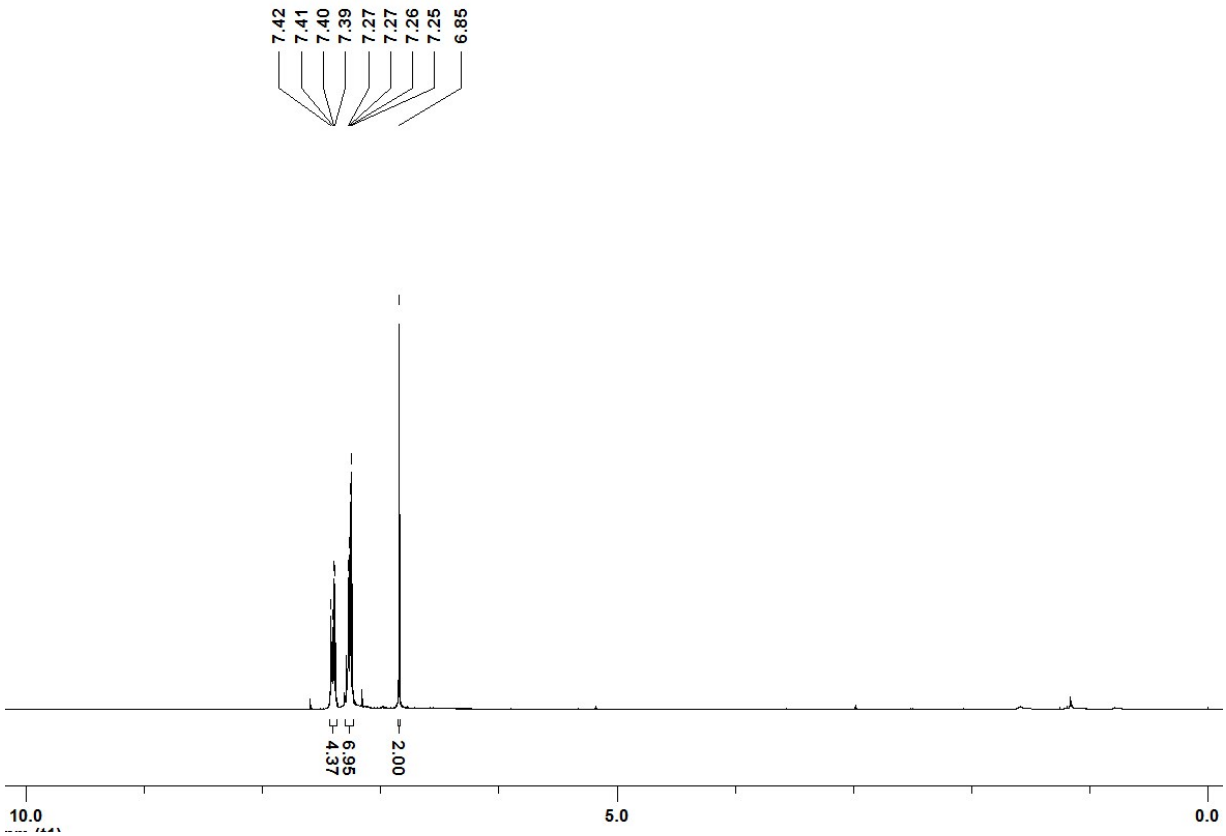
4,7-bis((4-methoxyphenyl)thio)benzo[*c*][1,2,5]thiadiazole: Yield: 0.179 g (87%); orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (d, J = 8.8 Hz, 4H); 6.77 (d, J = 8.8 Hz, 4H); 6.57 (s, 2H); 3.67 (s, 6H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 160.32, 152.21, 136.36, 129.66, 125.52, 120.67, 115.11, 55.18. MS (relative intensity) m/z: 412 (59), 273 (100), 207 (23), 139 (28), 96 (16), 77 (11). HRMS calcd. for $C_{20}H_{17}N_2O_2S_3$ $[M + H]^+$ 413.0446. Found: 413.0422.







4,7-bis(phenylthio)benzo[*c*][1,2,5]thiadiazole: Yield: 0.151 g (86%); yellow solid; mp 125-126°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42-7.39 (m, 4H); 7.27-7.25 (m, 6H); 6.84 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 152.89, 133.47, 131.41, 129.56, 128.91, 128.60, 127.64. MS (relative intensity) m/z: 352 (60), 243 (93), 207 (48), 109 (40), 77 (100), 51 (88). HRMS calcd. for $C_{18}H_{13}N_2S_3$ $[M + H]^+$ 353.0235. Found: 353.0238.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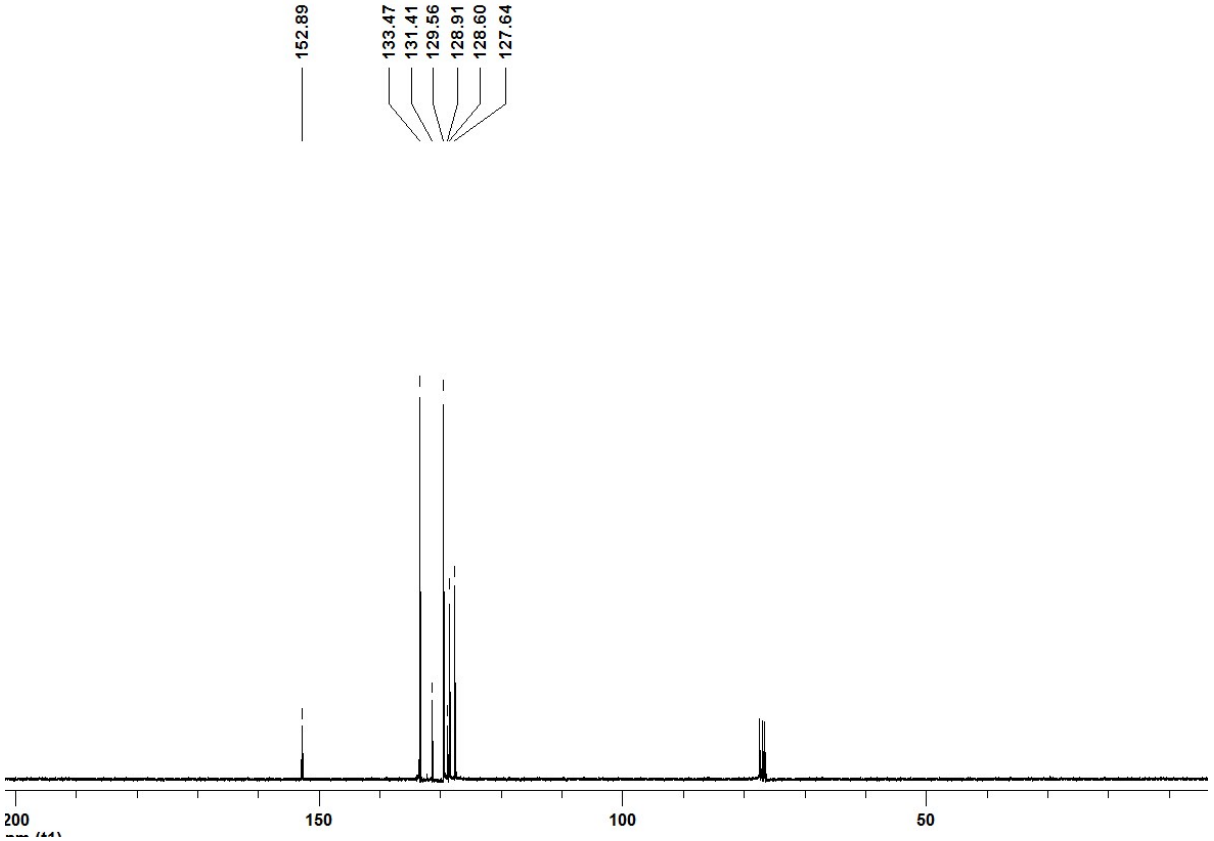
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200
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100
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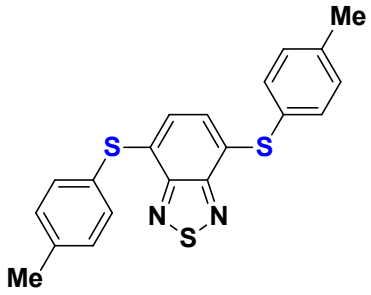
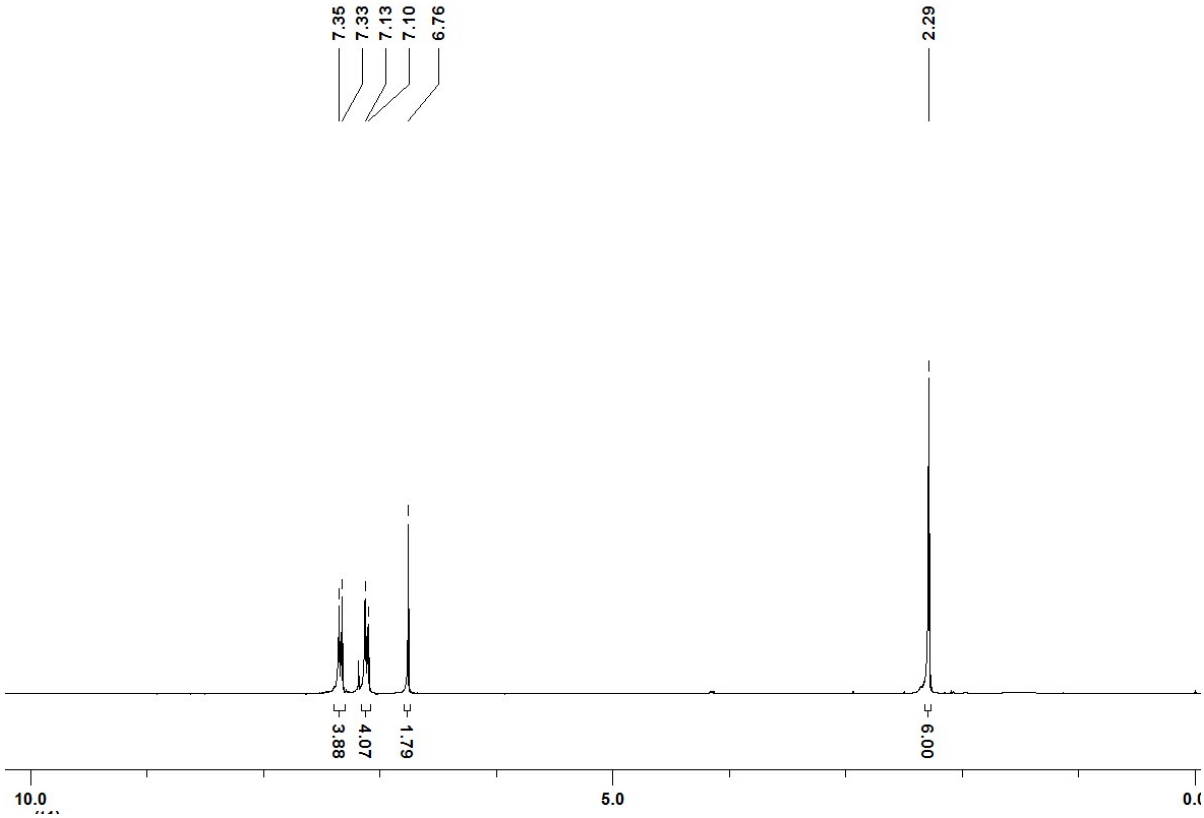
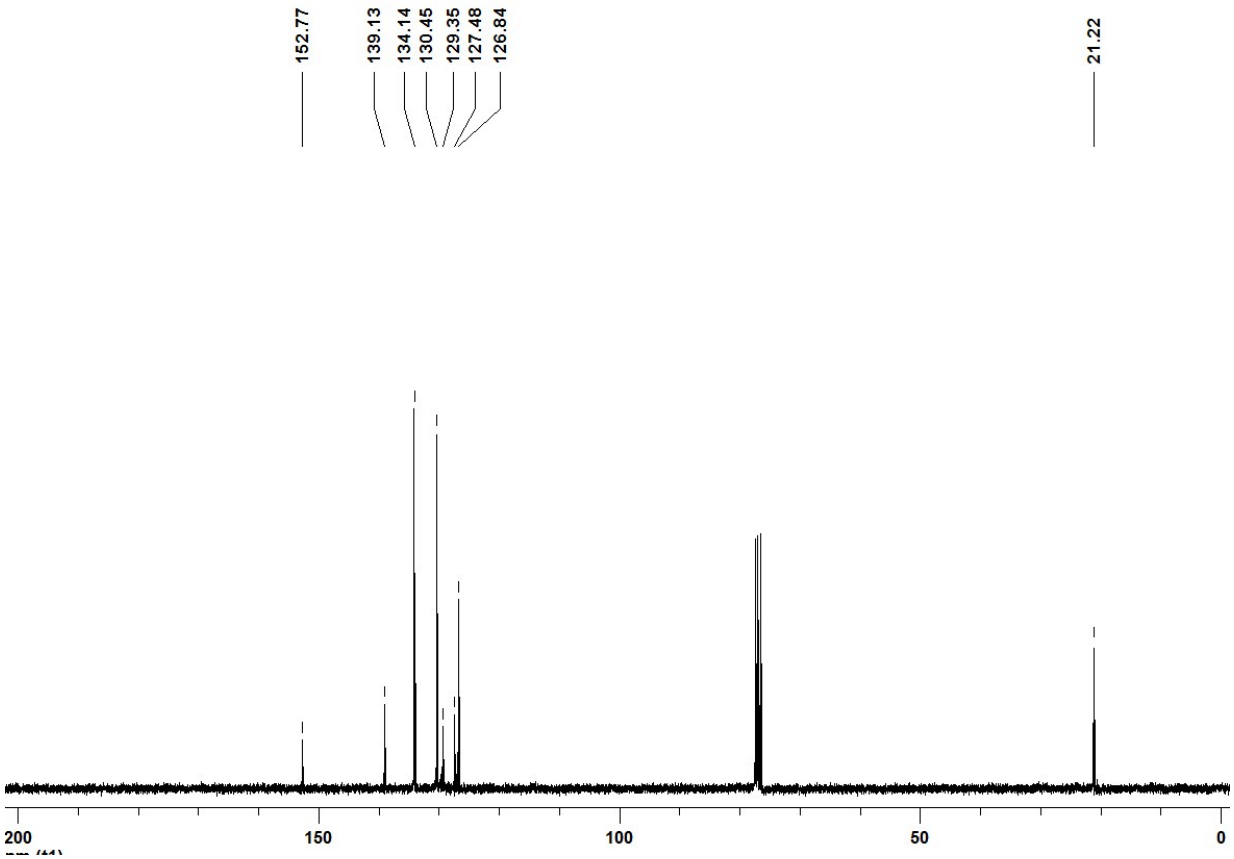
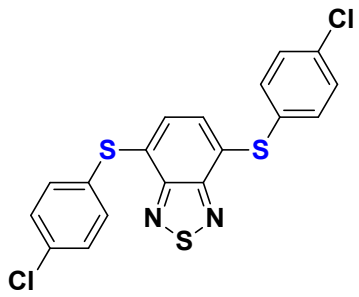


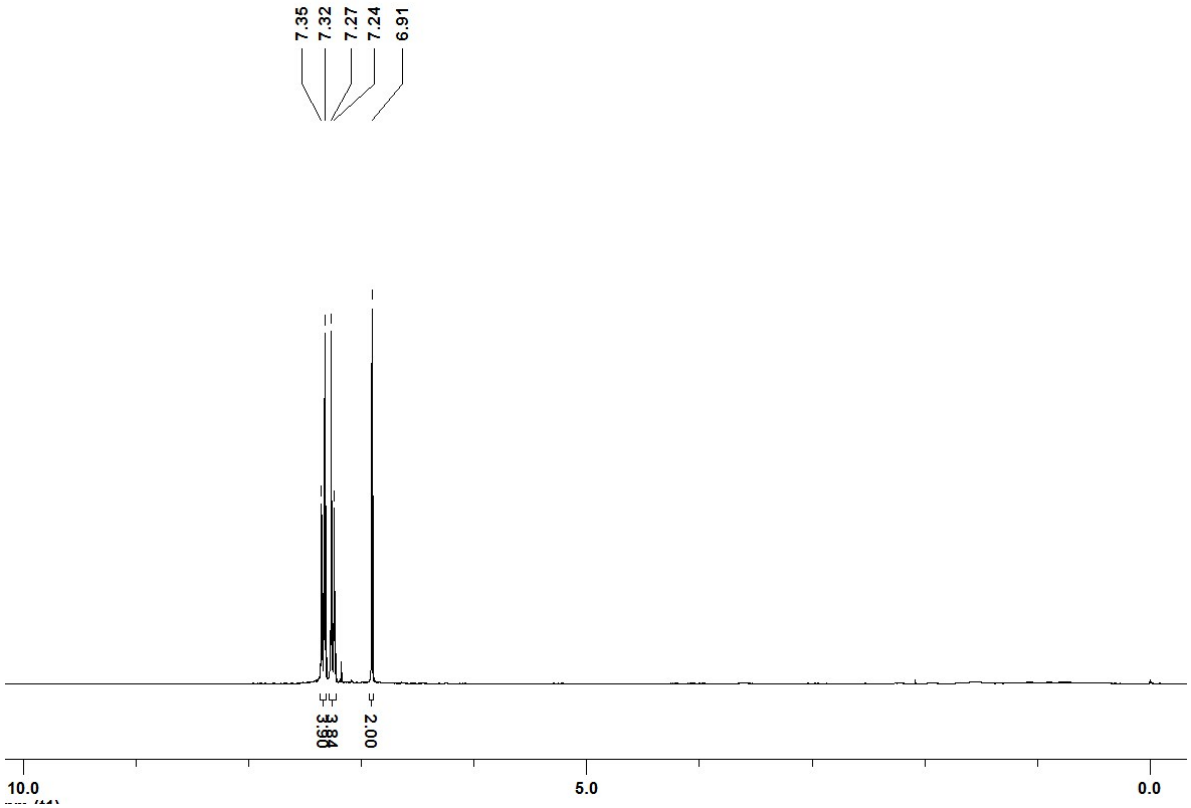
4,7-bis(p-tolylthio)benzo[*c*][1,2,5]thiadiazole: Yield: 0.158 g (83%); orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (d, J = 8.1 Hz, 4H); 7.12 (d, J = 8.1 Hz, 4H); 6.76 (s, 2H); 2.29 (s, 6H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 152.77, 139.13, 134.14, 130.45, 129.35, 127.48, 126.84, 21.22. MS (relative intensity) m/z: 380 (14), 281 (25), 257 (25), 207 (100), 73 (20), 40 (41). HRMS calcd. for $C_{20}H_{17}N_2S_3$ $[M + H]^+$ 381.0548. Found: 381.0548.







4,7-bis((4-chlorophenyl)thio)benzo[*c*][1,2,5]thiadiazole: Yield: 0.168 g (80%); orange solid; mp 110-112°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (d, J = 8.5 Hz, 4H); 7.25 (d, J = 8.5 Hz, 4H); 6.91 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 152.89, 134.94, 134.58, 130.07, 129.81, 128.75, 127.97. MS (relative intensity) m/z: 420 (15), 277 (100), 242 (39), 207 (17), 108 (32), 75 (26). HRMS calcd. for $C_{18}H_{11}Cl_2N_2S_3$ $[M + H]^+$ 420.9455. Found: 420.9451.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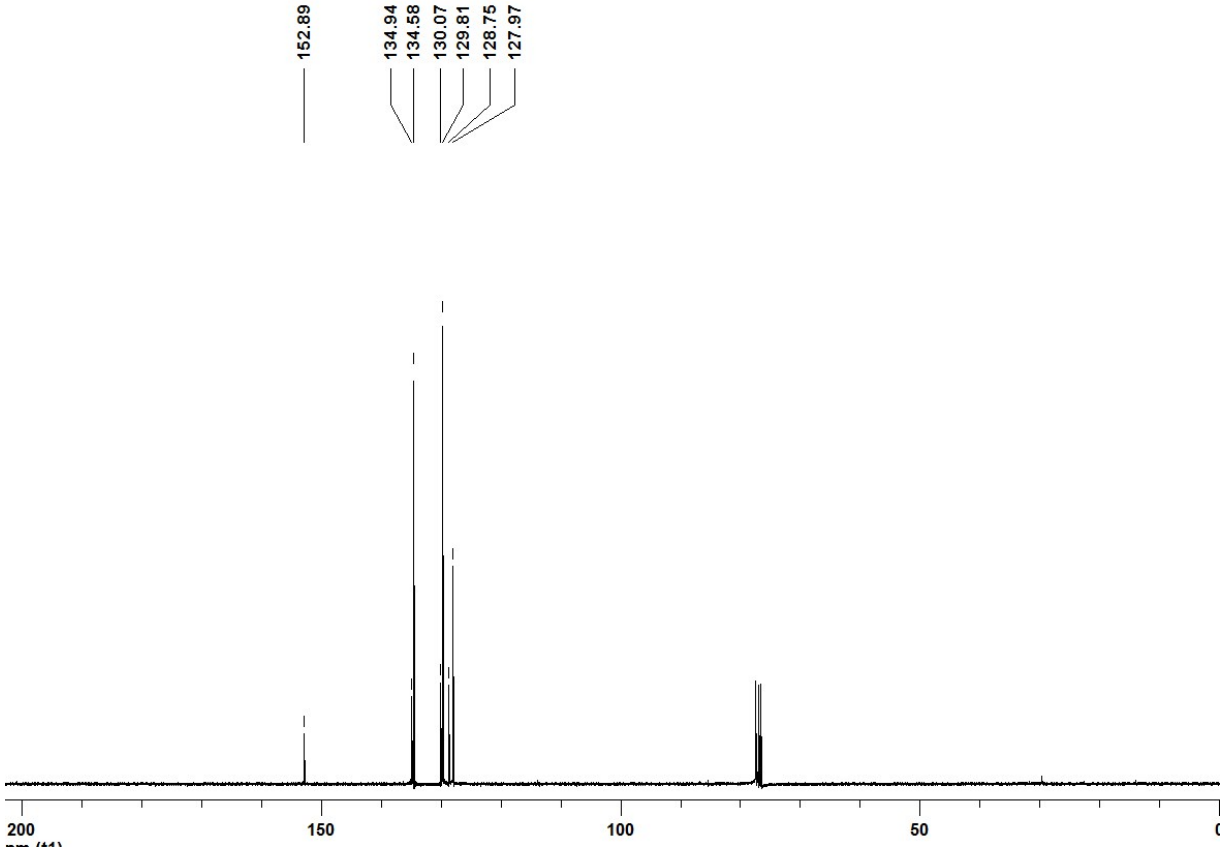
152.89
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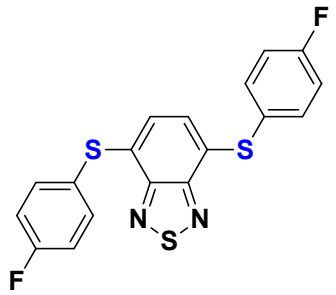
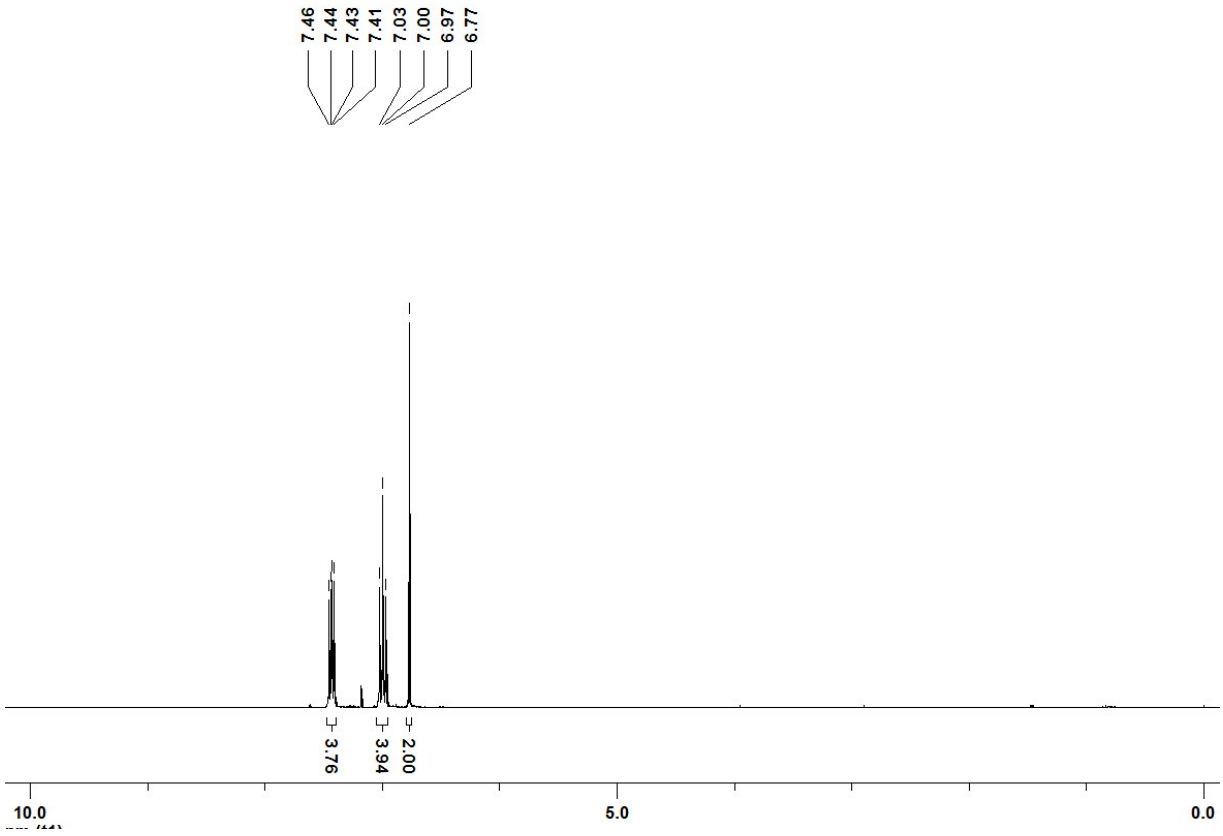
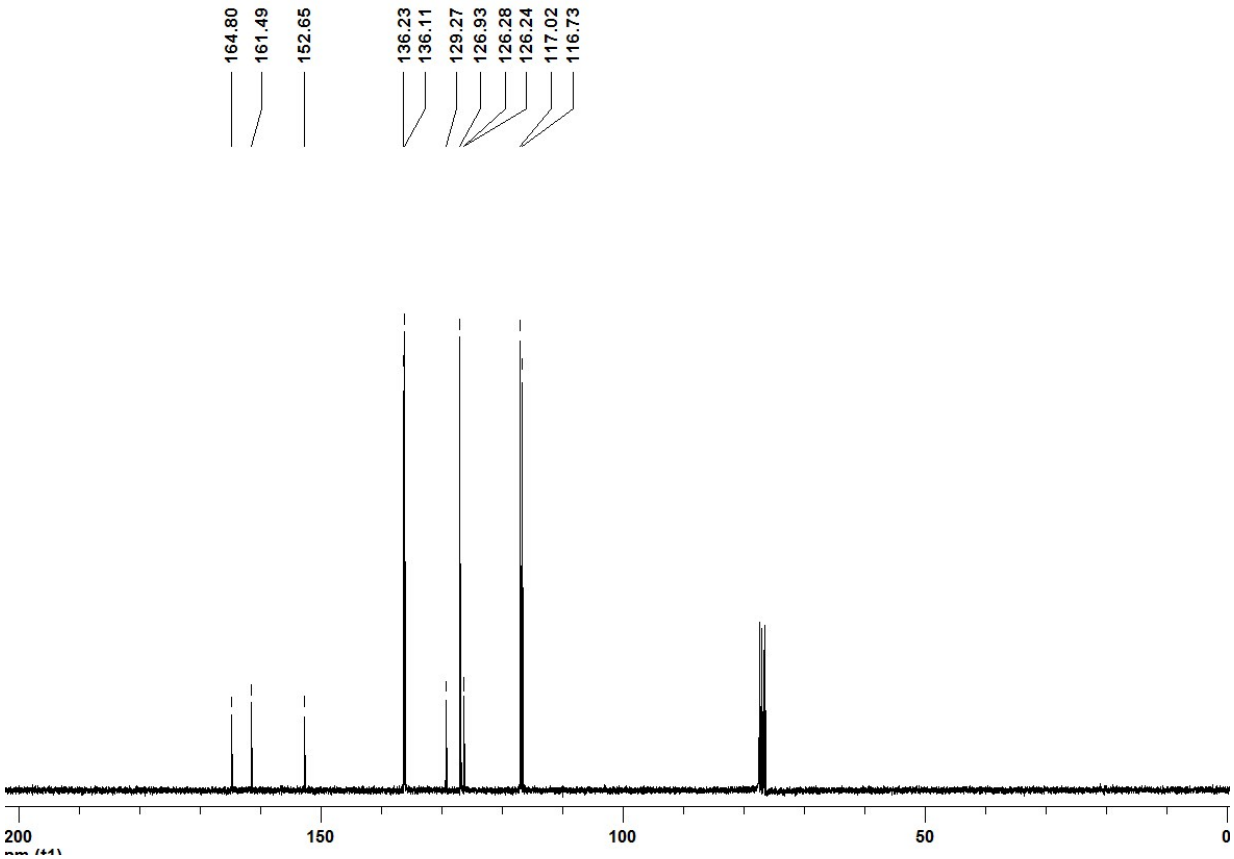
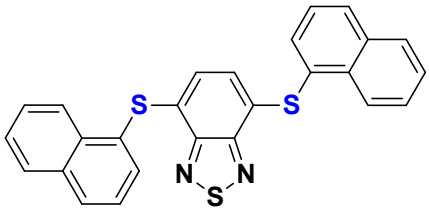
134.58
130.07
129.81
128.75
127.97
200
150
100
50



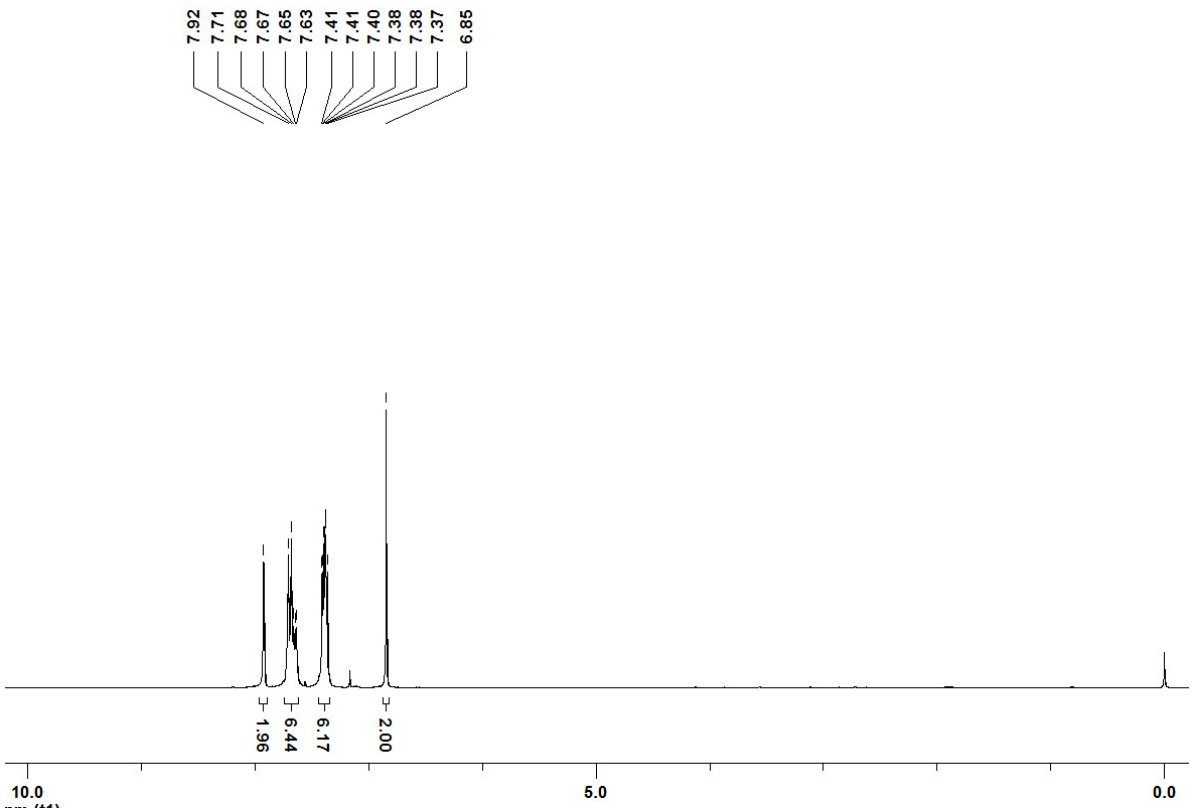
4,7-bis((4-fluorophenyl)thio)benzo[*c*][1,2,5]thiadiazole: Yield: 0.173 g (89%); yellow solid; mp 132-134°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (dd, J = 8.8 and 5.2 Hz, 4H); 7.00 (t, J = 8.8 Hz, 4H); 6.77 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 163.14 (d, J = 249.7 Hz), 152.65, 136.17 (d, J = 8.4 Hz), 129.27, 126.93, 126.26 (d, J = 3.7 Hz), 116.87 (d, J = 22.0 Hz). MS (relative intensity) m/z: 388 (23), 281 (27), 261 (36), 207 (100), 73 (23). HRMS calcd. for $C_{18}H_{11}F_2N_2S_3$ $[M + H]^+$ 389.0046. Found: 389.0043.







4,7-bis(naphthalen-1-ylthio)benzo[*c*][1,2,5]thiadiazole: Yield: 0.203 g (90%); yellow solid; mp 104-106°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92 (m, 2H); 7.71-7.63 (m, 6H); 7.41-7.37 (m, 6H); 6.85 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 152.92, 133.70, 132.91, 132.81, 129.93, 129.26, 128.88, 128.59, 127.82, 127.65, 127.54, 126.83, 126.65. MS (relative intensity) m/z: 452 (2), 368 (11), 111 (25), 83 (23), 55 (100), 43 (93). HRMS calcd. for $C_{26}H_{17}N_2S_3$ $[M + H]^+$ 453.0548. Found: 453.0547.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6.44
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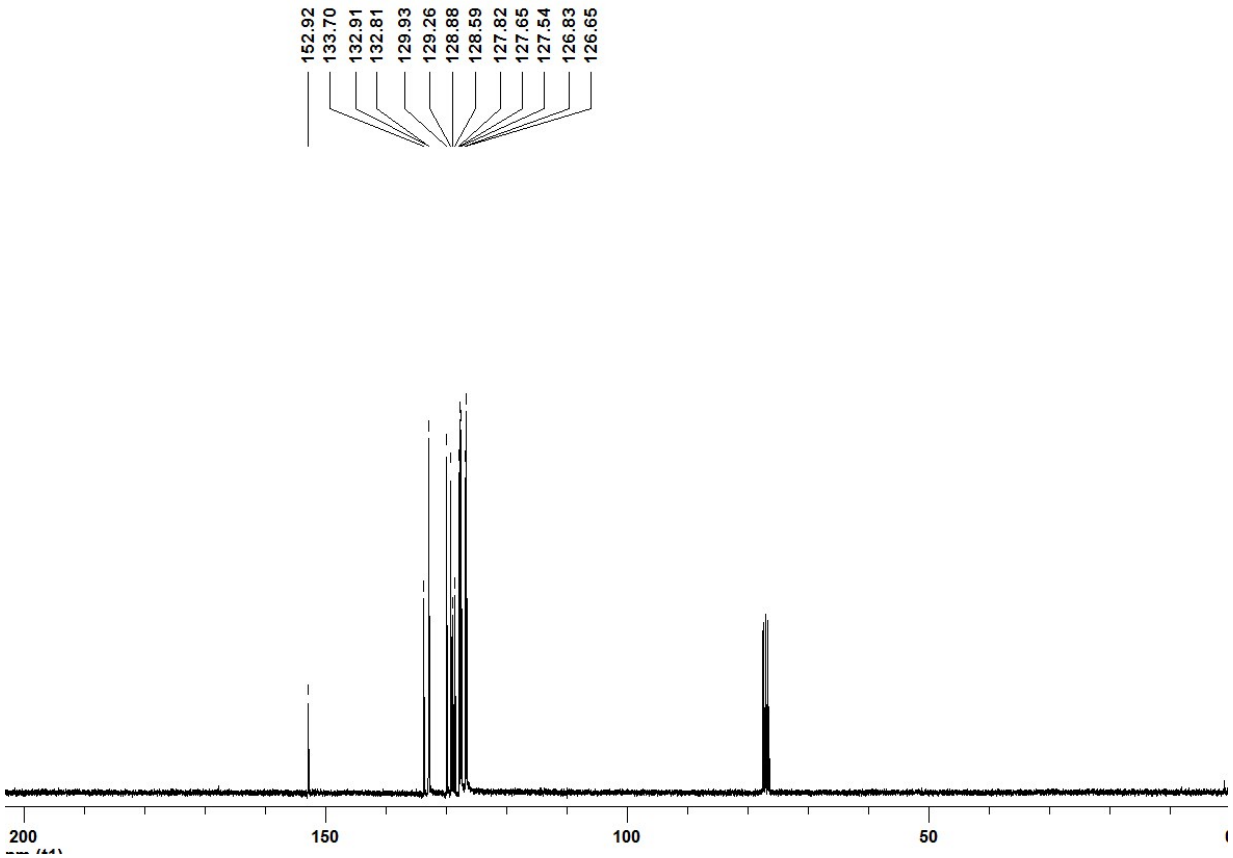
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100
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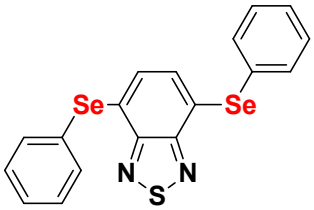
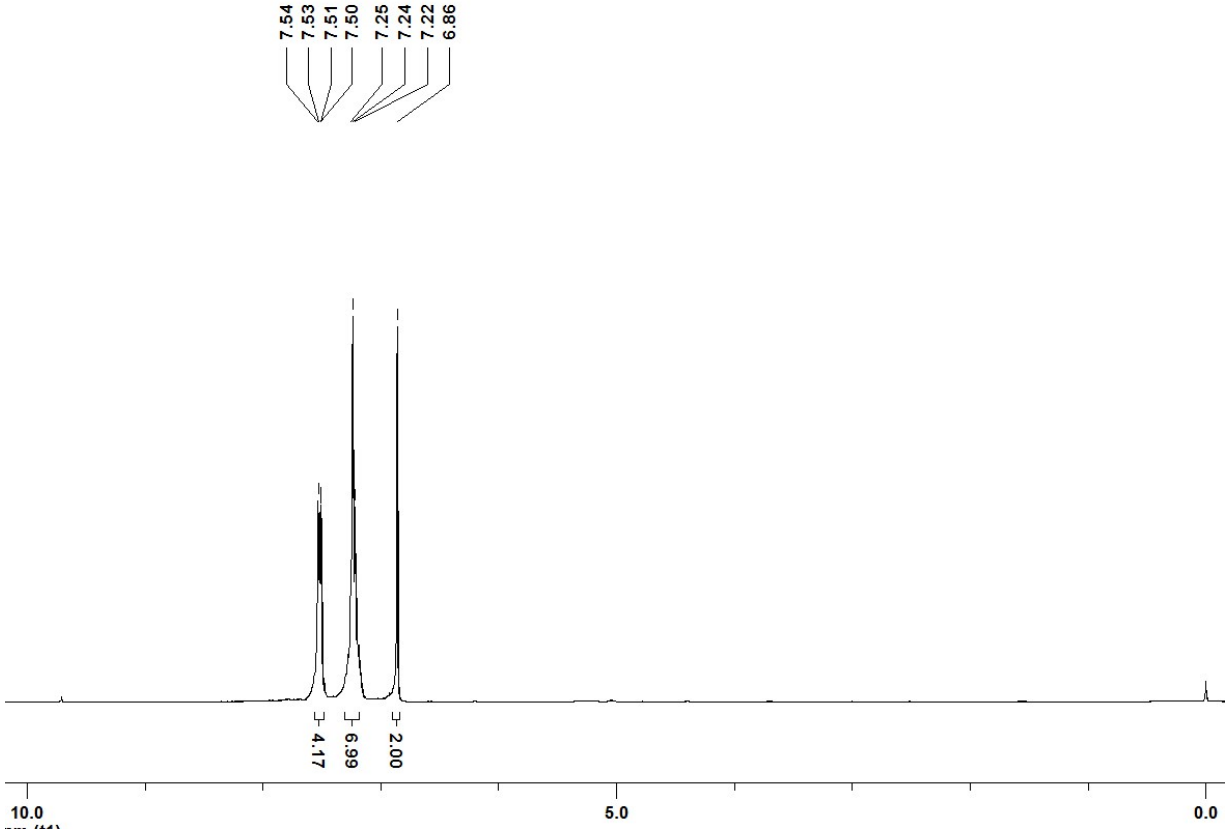
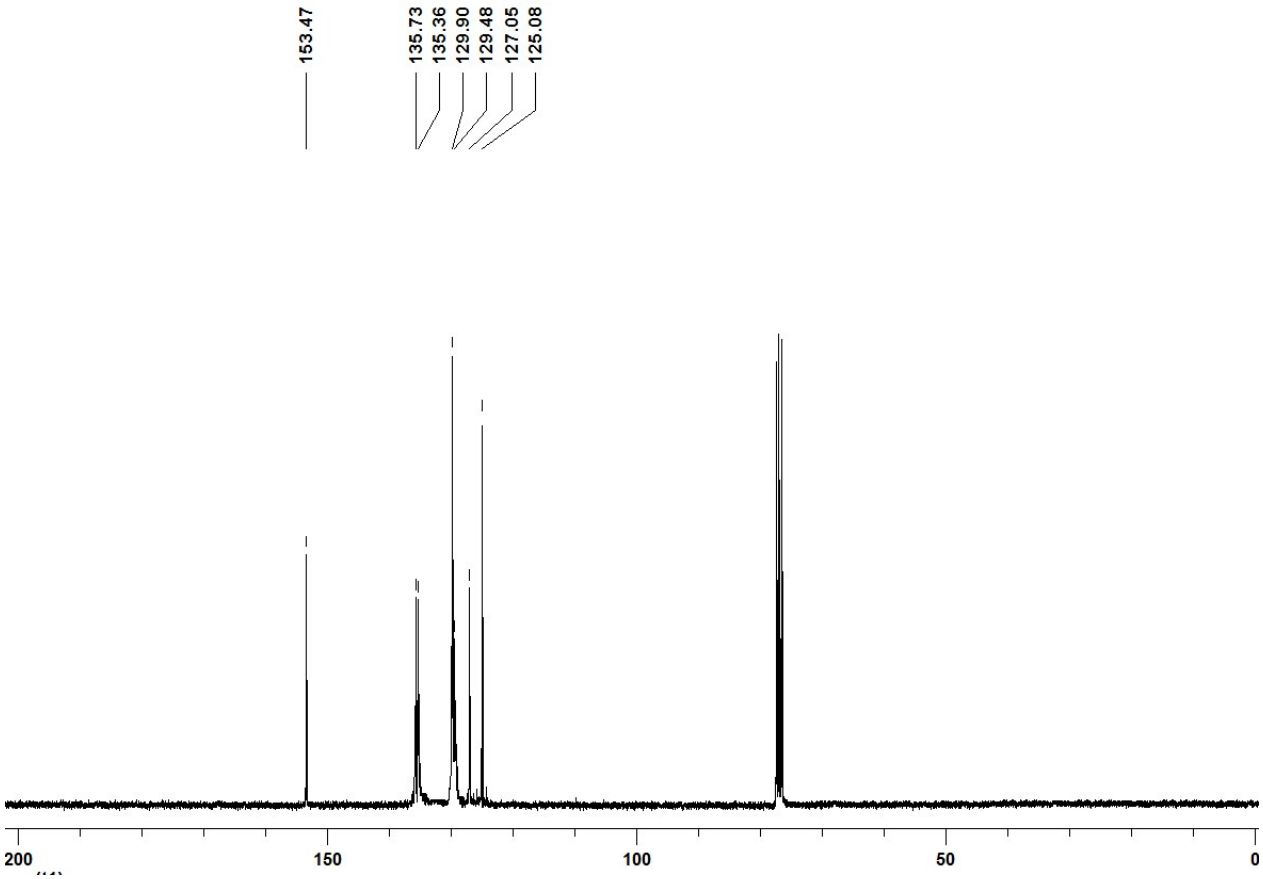
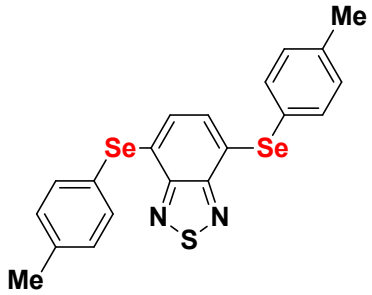


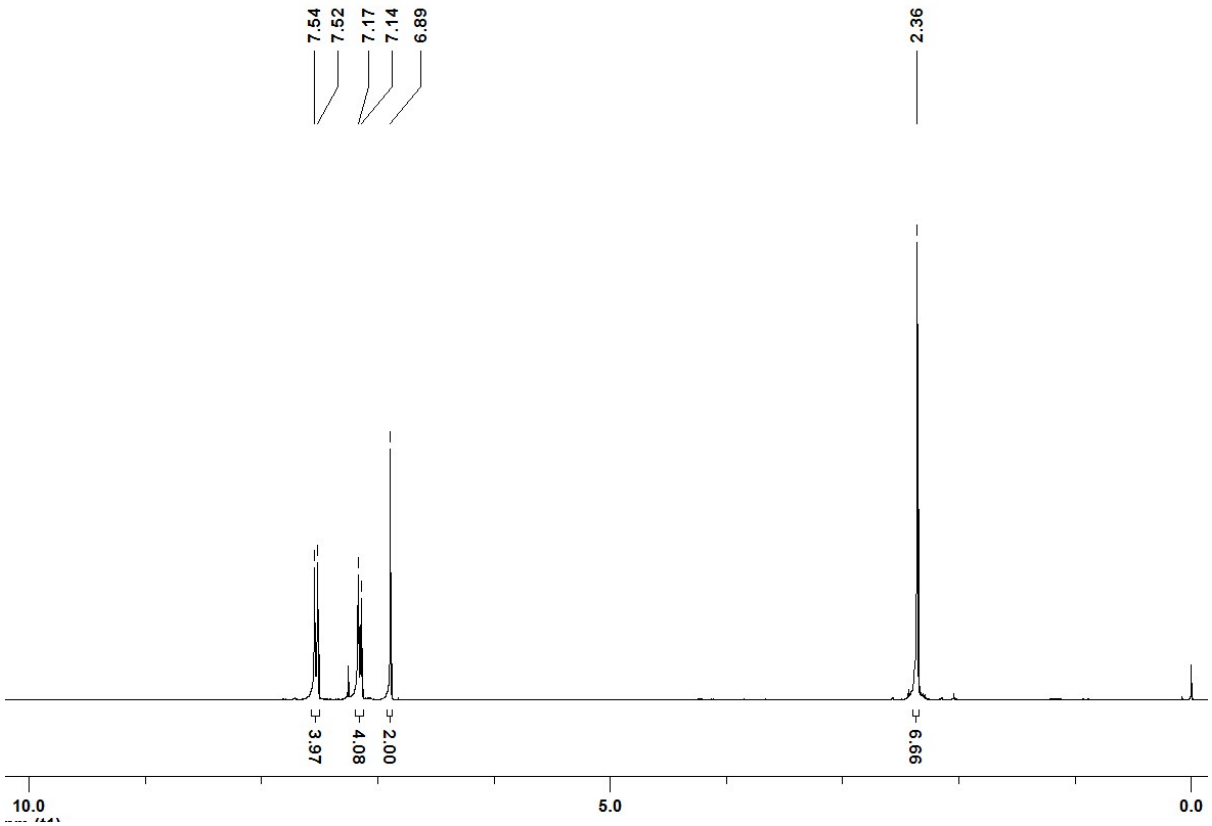
4,7-bis(phenylselanyl)benzo[*c*][1,2,5]thiadiazole: Yield: 0.175 g (78%); dark yellow solid; mp 129-131°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54-7.50 (m, 4H); 7.25-7.22 (m, 6H); 6.86 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 153.47, 135.73, 135.36, 129.90, 129.48, 127.05, 125.08. MS (relative intensity) m/z: 448 (9), 291 (25), 207 (14), 77 (79), 51 (51), 40 (100). HRMS calcd. for $C_{18}H_{13}N_2SSe_2$ $[M + H]^+$ 448.9126. Found: 448.9107.







4,7-bis(p-tolylselanyl)benzo[*c*][1,2,5]thiadiazole: Yield: 0.164 g (69%); yellow solid; mp 101-103°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, J = 8.1 Hz, 4H); 7.15 (d, J = 8.1 Hz, 4H); 6.89 (s, 2H); 2.36 (s, 6H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 153.50, 139.12, 136.04, 130.56, 129.43, 125.41, 123.22, 21.24. MS (relative intensity) m/z: 476 (5), 305 (12), 111 (17), 81 (57), 69 (100), 43 (88). HRMS calcd. for $C_{20}H_{17}N_2SSe_2$ $[M + H]^+$ 476.9439. Found: 476.9392.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4.08
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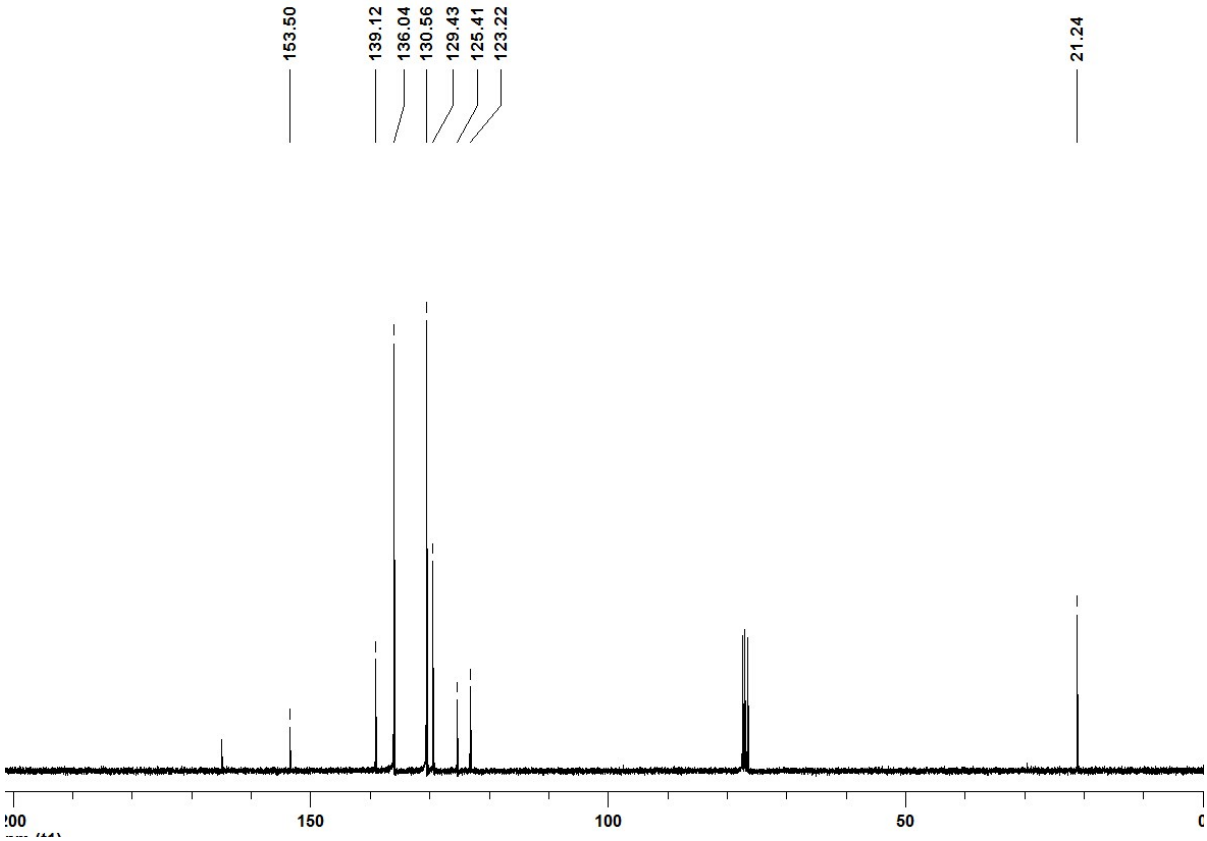
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139.12
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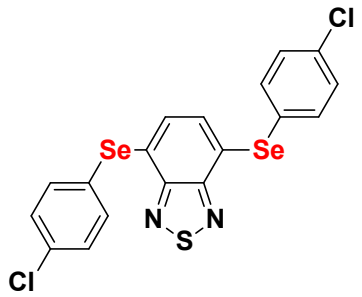
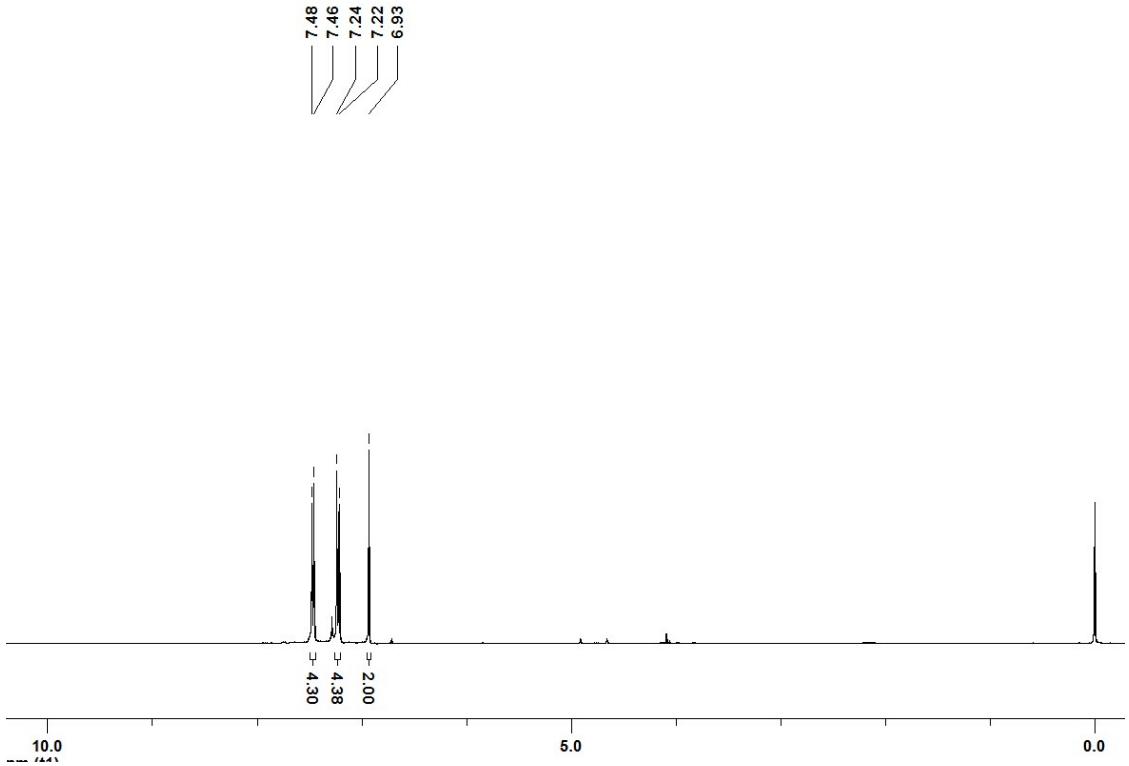
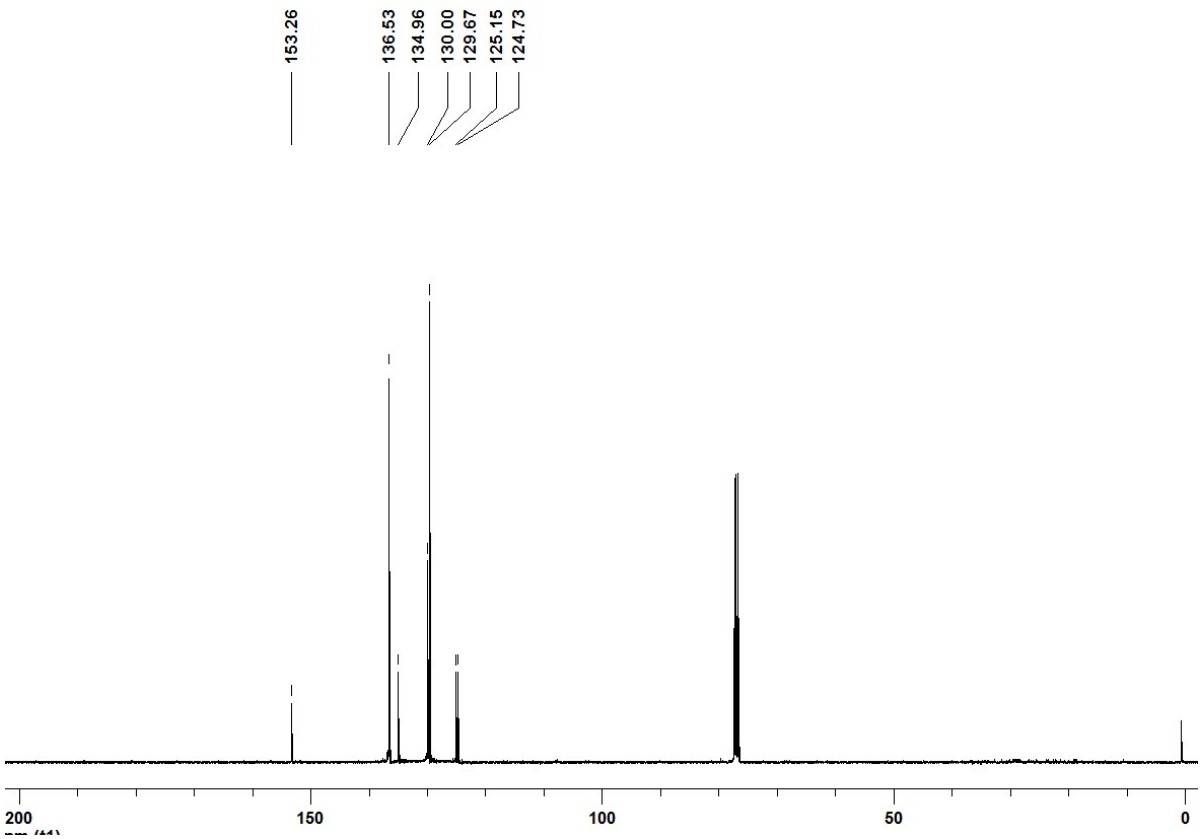
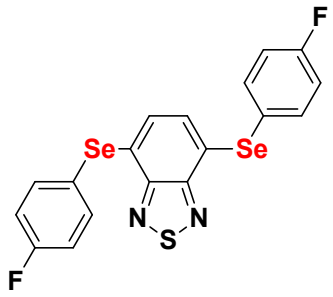
100
50



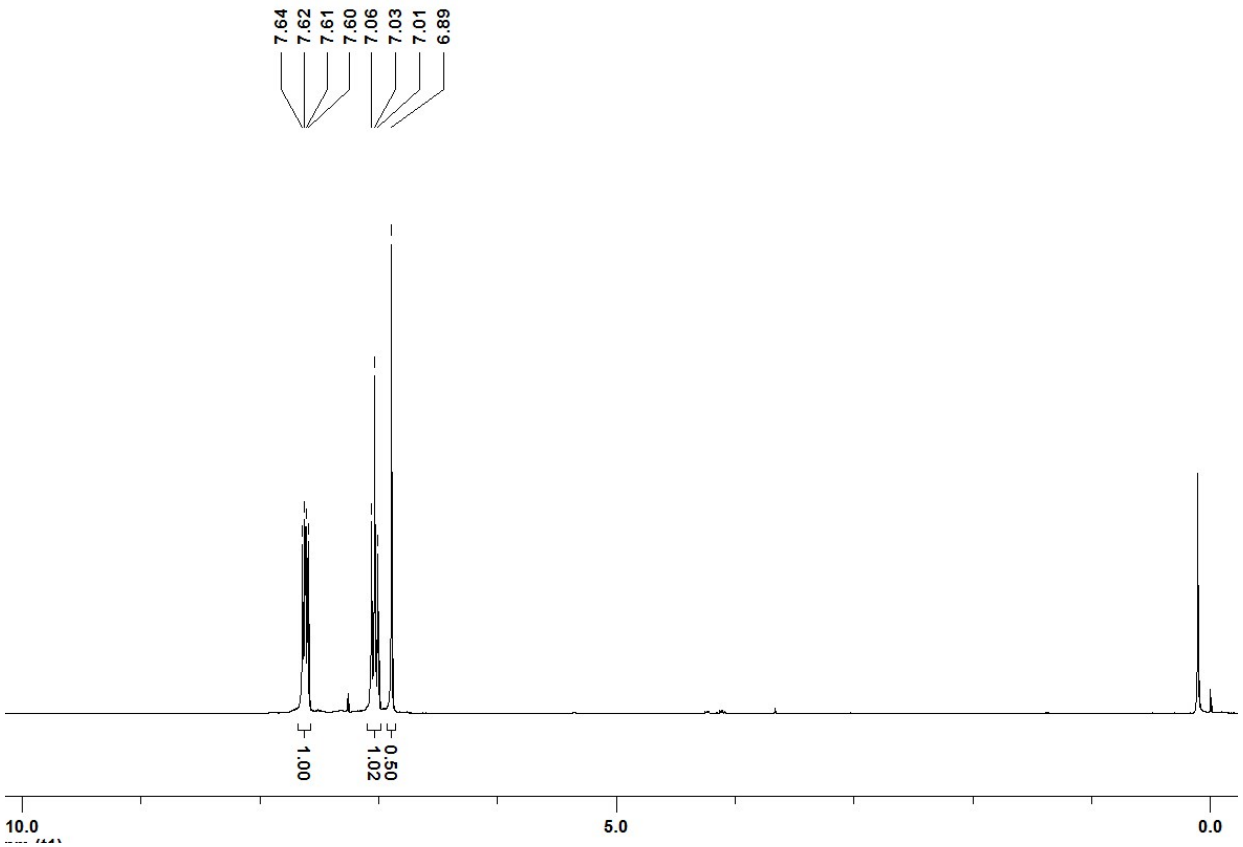
4,7-bis((4-chlorophenyl)selanyl)benzo[*c*][1,2,5]thiadiazole: Yield: 0.188 g (73%); orange solid; mp 87-89°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47 (d, J = 8.4 Hz, 4H); 7.23 (d, J = 8.4 Hz, 4H); 6.93 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 153.26, 136.53, 134.96, 130.00, 129.67, 125.15, 124.73. MS (relative intensity) m/z: 516 (8), 325 (25), 290 (5), 81 (63), 69 (100), 41 (33). HRMS calcd. for $C_{18}H_{11}Cl_2N_2SSe_2$ $[M + H]^+$ 516.8339. Found: 516.8318.







4,7-bis((4-fluorophenyl)selanyl)benzo[*c*][1,2,5]thiadiazole: Yield: 0.189 g (78%); orange solid; mp 151-153°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (dd, J = 8.8 and 5.4 Hz, 4H); 7.03 (t, J = 8.8 Hz, 4H); 6.89 (s, 2H). RMN ^{13}C ($CDCl_3$ 75 MHz): δ 163.39 (d, J = 249.8 Hz), 141.03, 138.06 (d, J = 8.1 Hz), 129.72, 125.48, 121.87 (d, J = 3.6 Hz), 117.03 (d, J = 22.0 Hz). MS (relative intensity) m/z: 484 (39), 324 (40), 309 (100), 229 (30), 83 (35), 69 (24). HRMS calcd. for $C_{18}H_{11}F_2N_2SSe_2$ $[M + H]^+$ 484.8937. Found: 484.8906.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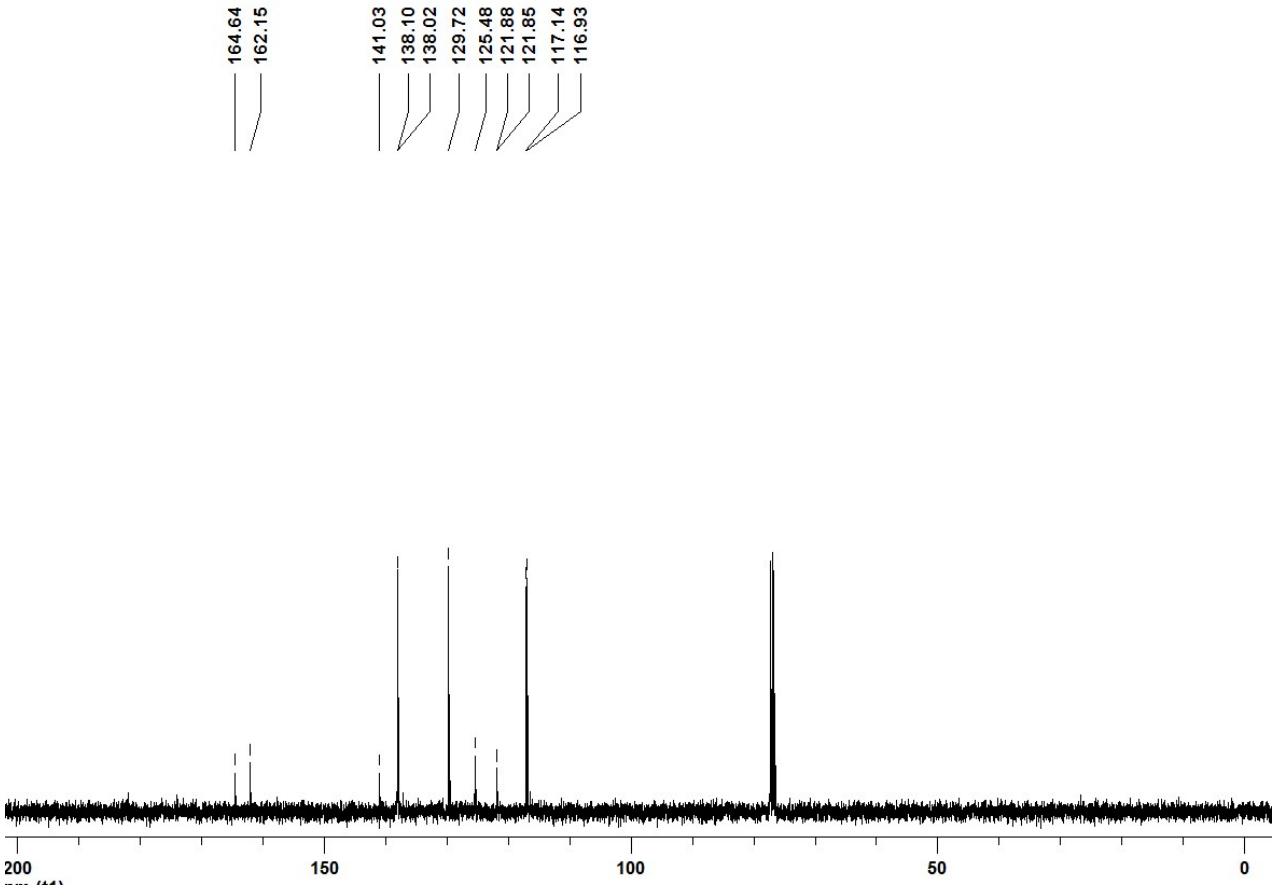
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138.02
129.72
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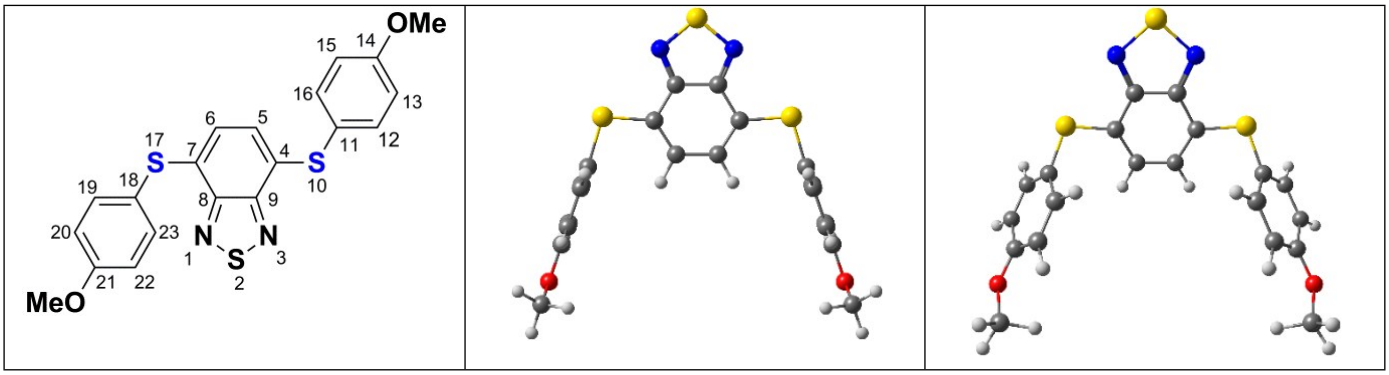
121.88
121.85
117.14
116.93
200
150
100
50
0

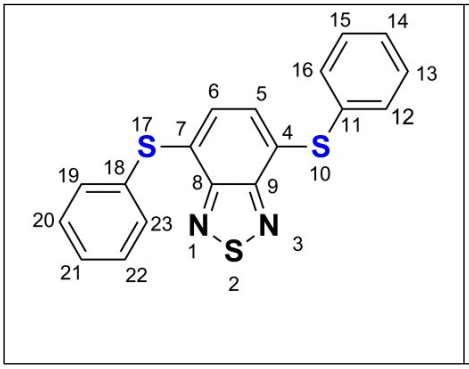
2. Theoretical calculations

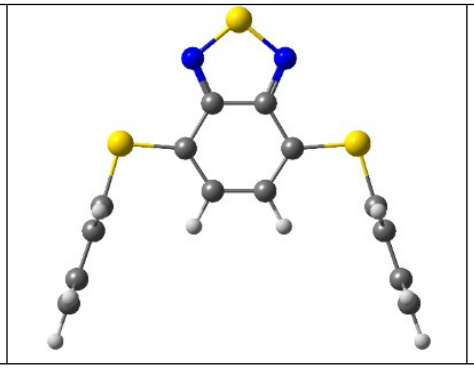
Table ESI1. Theoretical structural data of **3a-f** and **5a-d** in different organic solvents, where the bond lengths (**r**) are presented in Å and angles (**a**) and dihedral angles (**d**) are given in degrees. Geometries calculated with PBE1PBE/jun-cc-pVTZ//PBE1PBE/cc-pVDZ. The representative equilibrium structures are plotted at the same level using hexane as solvent. The ground state structures are given on the left and first excited state structures are given on the right. In hexane, the structural data is also given with CAM-B3LYP/jun-cc-pVTZ//CAM-B3LYP/cc-pVDZ (marked with a *). For all structures: d1 = C_7-S_{17}-C_{18}-C_{19} / r1= C_7-S_{17} / r2 = S_{17}-C_{18} / r3 = N_1-S_2 / a1 = C_7-S_{17}-C_{18} / a2 =N_1-S_2-N_3 , except for **3f**, where d1 = C_7-S_{21}-C_{22}-C_{23} / r1= C_7-S_{21} / r2 = S_{21}-C_{22} / r3 = N_1-S_2 / a1 = C_7-$S_{21}C_{22}$ / a3 =N_1-S_2-N_3

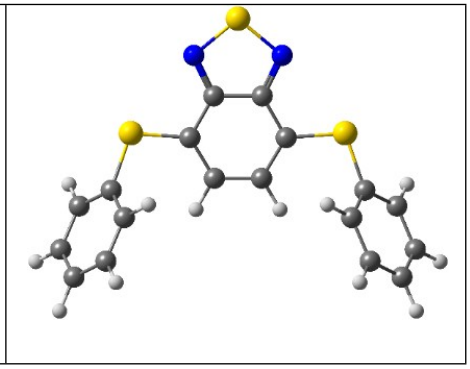


Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
3a	Hexane	92.67	1.778	1.786	1.641	102.31	99.43	68.90	1.737	1.783	1.697	104.37	98.64
	Hexane	92.32	1.772	1.781	1.639	102.16	100.09	49.22	1.745	1.766	1.690	104.63	99.80
	Toluene	92.17	1.772	1.781	1.639	102.21	100.07	49.35	1.745	1.766	1.691	104.68	99.74
	DCM	91.94	1.772	1.781	1.639	102.44	99.97	49.39	1.743	1.766	1.693	104.92	99.52
	Ethanol	91.54	1.773	1.781	1.639	102.51	99.94	49.31	1.743	1.766	1.693	105.00	99.45
	DMF	91.51	1.773	1.781	1.639	102.53	99.93	49.30	1.742	1.766	1.693	105.02	99.43

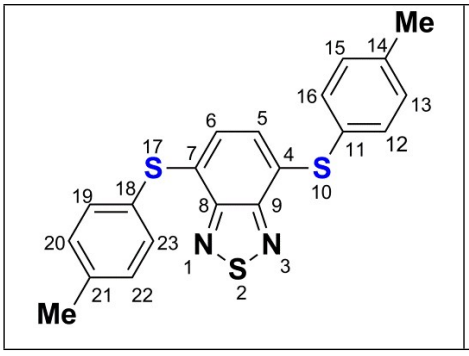
Table ESI1. continuation

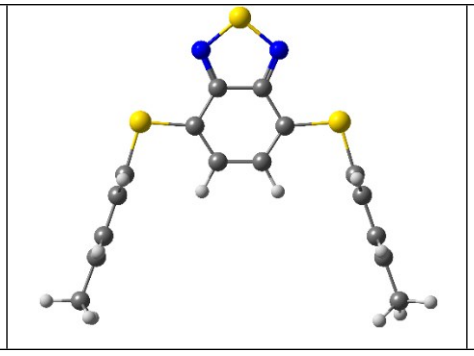


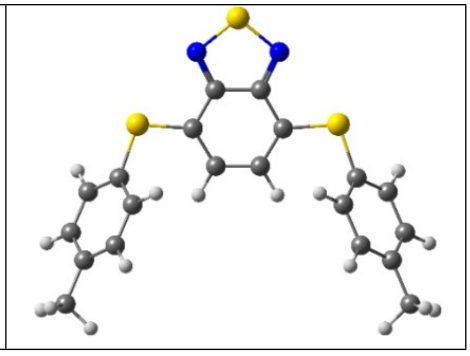




Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
3b	Hexane	91.58	1.777	1.791	1.641	102.09	99.41	69.76	1.737	1.788	1.697	104.15	98.61
	Hexane	91.65	1.771	1.786	1.639	101.95	100.08	56.47	1.739	1.776	1.692	104.54	99.79
	Toluene	91.64	1.771	1.786	1.639	102.01	100.06	56.66	1.738	1.776	1.692	104.58	99.73
	DCM	91.61	1.771	1.786	1.639	102.22	99.96	56.96	1.737	1.777	1.694	104.78	99.51
	Ethanol	91.60	1.771	1.786	1.639	102.29	99.93	56.97	1.736	1.777	1.694	104.86	99.44
	DMF	91.60	1.771	1.786	1.639	102.30	99.92	56.97	1.736	1.777	1.694	104.87	99.43

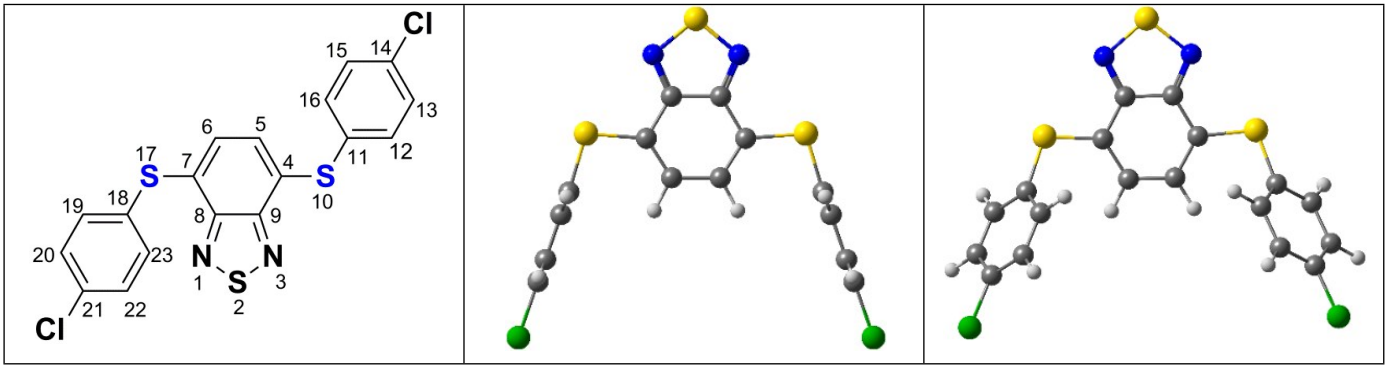




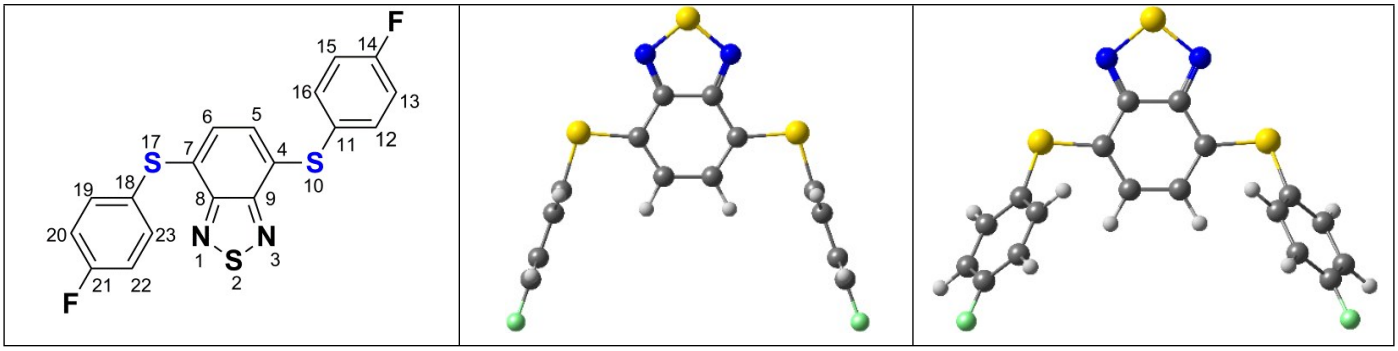


Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
3c	Hexane	91.18	1.778	1.789	1.641	102.21	99.42	69.50	1.737	1.786	1.697	104.24	98.63
	Hexane	91.79	1.771	1.784	1.639	102.09	100.09	54.41	1,740	1.773	1.691	104.61	99.80
	Toluene	91.78	1.771	1.784	1.639	102.15	100.06	54.56	1,740	1.773	1.692	104.66	99.74
	DCM	91.79	1.771	1.784	1.639	102.36	99.96	54.87	1,738	1.773	1.694	104.87	99.52
	Ethanol	92.32	1.772	1.784	1.639	102.42	99.93	54.80	1.738	1.773	1.694	104.95	99.45
	DMF	92.33	1.772	1.784	1.639	102.44	99.93	54.80	1.738	1.773	1.694	104.97	99.43

Table ESI1. continuation

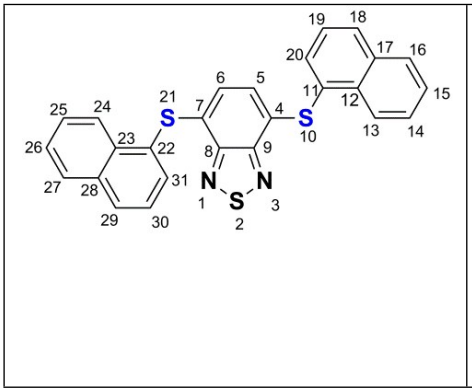


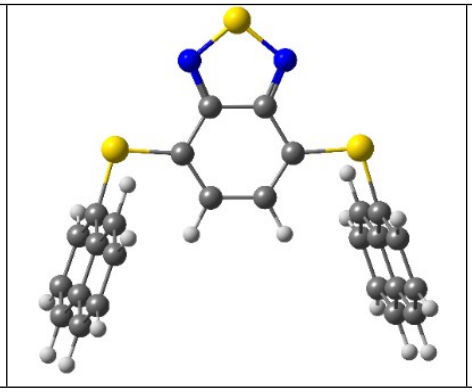
Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
3d	Hexane	91.67	1.778	1.789	1.641	102.07	99.41	66.84	1.737	1.786	1.696	104.21	98.56
	Hexane	91.73	1.771	1.784	1.639	101.93	100.07	52.71	1.740	1.772	1.690	104.53	99.72
	Toluene	91.73	1.771	1.784	1.639	101.98	100.05	53.01	1.740	1.772	1.691	104.56	99.65
	DCM	91.69	1.772	1.784	1.639	102.16	99.96	53.70	1.738	1.773	1.693	104.75	99.46
	Ethanol	91.68	1.772	1.784	1.639	102.22	99.93	53.77	1.737	1.773	1.693	104.82	99.39
	DMF	91.68	1.772	1.784	1.639	102.23	99.92	53.78	1.737	1.773	1.693	104.83	99.38

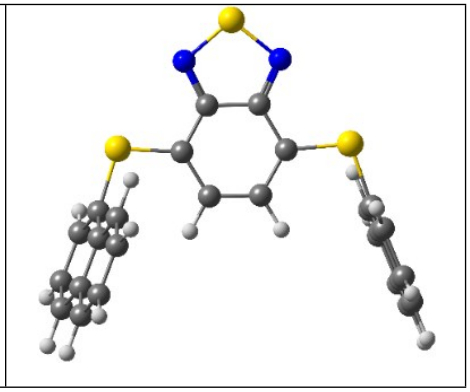


Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
3e	Hexane	91.67	1.778	1.788	1.641	102.18	99.41	92.04	1.737	1.789	1.698	103.86	98.61
	Hexane	91.75	1.771	1.783	1.639	102.05	100.08	56.39	1.740	1.774	1.692	104.42	99.77
	Toluene	91.74	1.771	1.783	1.639	102.10	100.06	56.58	1.739	1.774	1.692	104.47	99.72
	DCM	91.69	1.772	1.783	1.639	102.28	99.96	57.04	1.738	1.774	1.694	104.67	99.50
	Ethanol	91.68	1.772	1.783	1.639	102.28	99.93	57.11	1.737	1.774	1.694	104.73	99.43
	DMF	91.67	1.772	1.783	1.639	102.36	99.92	57.12	1.737	1.774	1.694	104.75	99.42

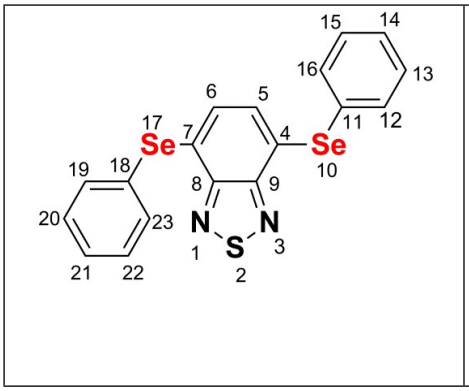
Table ESI1. continuation

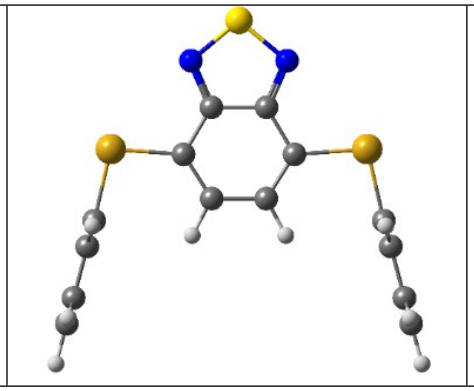


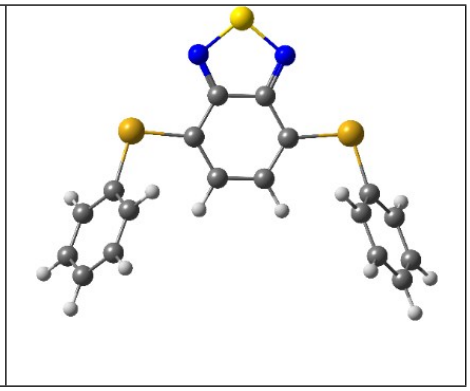




Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
3f	Hexane	82.44	1.778	1.792	1.641	102.38	99.42	83.66	1.737	1.792	1.698	104.05	98.63
	Hexane	81.08	1.772	1.786	1.639	102.24	100.09	77.99	1.736	1.787	1.695	103.74	99.87
	Toluene	81.04	1.772	1.786	1.639	102.28	100.07	78.23	1.736	1.787	1.695	103.77	99.81
	DCM	80.61	1.772	1.786	1.639	102.47	99.97	78.61	1.735	1.787	1.697	103.93	99.59
	Ethanol	80.39	1.772	1.786	1.639	102.53	99.95	78.65	1.734	1.786	1.697	103.99	99.51
	DMF	80.35	1.772	1.786	1.639	102.54	99.94	78.66	1.734	1.786	1.697	104.00	99.50

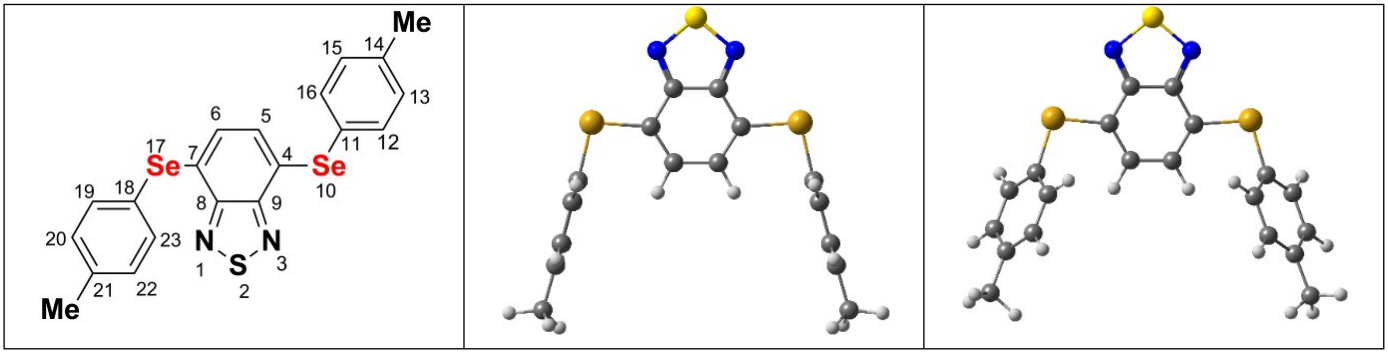




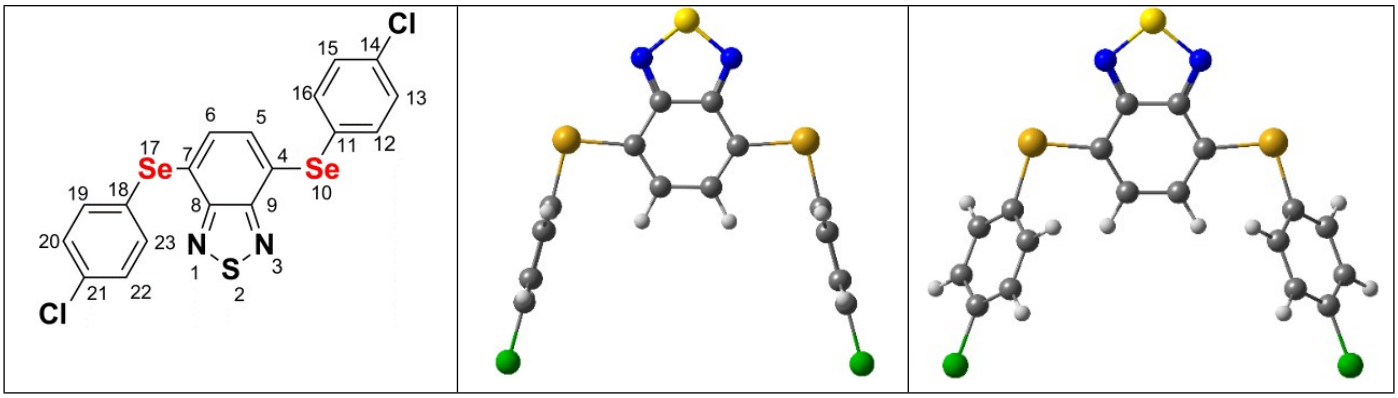


Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
5a	Hexane	91.31	1.915	1.926	1.641	99.23	99.38	84.46	1.871	1.926	1.698	100.89	98.62
	Hexane	91.24	1.908	1.922	1.640	98.91	100.05	61.09	1.875	1.915	1.693	101.48	99.80
	Toluene	91.23	1.908	1.922	1.640	98.95	100.03	61.53	1.874	1.915	1.693	101.50	99.75
	DCM	91.22	1.909	1.921	1.640	99.13	99.94	61.94	1.872	1.915	1.695	101.68	99.52
	Ethanol	91.21	1.909	1.922	1.640	99.20	99.92	61.46	1.872	1.915	1.695	101.76	99.44
	DMF	91.21	1.909	1.922	1.639	99.21	99.91	61.42	1.872	1.915	1.695	101.78	99.43

Table ESI1. continuation

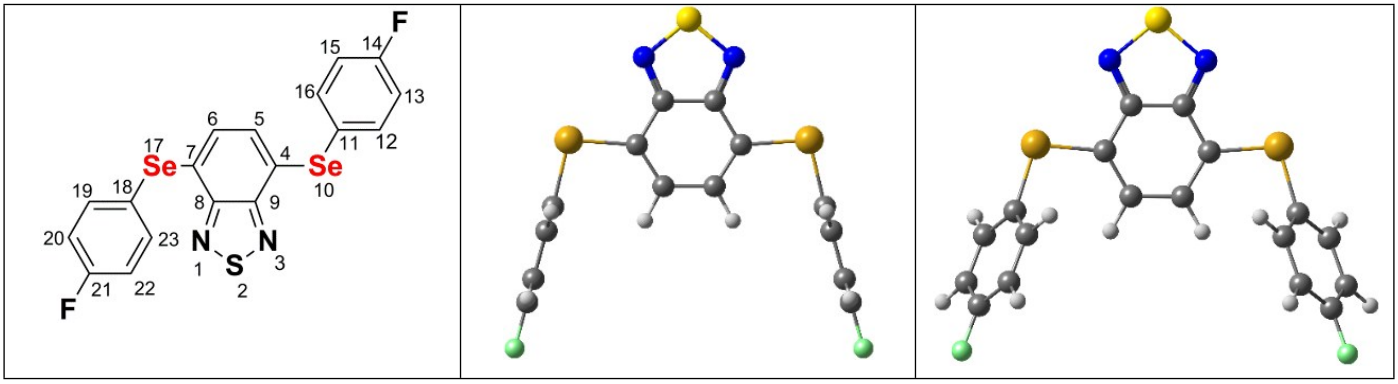


Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
5b	Hexane	91.72	1.915	1.924	99.35	99.35	99.39	82.09	1.871	1.924	1.698	101.04	98.63
	Hexane	91.59	1.909	1.920	1.640	99.04	100.06	58.17	1.876	1.912	1.692	101.63	99.81
	Toluene	91.61	1.909	1.920	1.640	99.09	100.03	58.24	1.875	1.911	1.693	101.69	99.75
	DCM	92.07	1.909	1.920	1.640	99.27	99.95	58.10	1.874	1.911	1.694	101.90	99.52
	Ethanol	92.07	1.910	1.920	1.640	99.33	99.92	58.26	1.873	1.911	1.695	101.97	99.45
	DMF	92.12	1.910	1.920	1.640	99.34	99.91	58.32	1.873	1.911	1.695	101.99	99.44



Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
5c	Hexane	91.40	1.915	1.924	1.641	99.21	99.38	86.96	1.871	1.925	1.698	100.82	98.58
	Hexane	91.33	1.909	1.920	1.640	98.89	100.04	57.25	1.875	1.911	1.692	101.51	99.74
	Toluene	91.32	1.909	1.920	1.640	98.92	100.02	57.30	1.875	1.911	1.692	101.51	99.69
	DCM	91.31	1.909	1.920	1.639	99.08	99.94	57.70	1.873	1.911	1.694	101.71	99.47
	Ethanol	91.30	1.910	1.920	1.639	99.14	99.91	58.07	1.873	1.911	1.694	101.75	99.40
	DMF	91.30	1.910	1.920	1.639	99.15	99.91	58.16	1.872	1.912	1.694	101.76	99.39

Table ESI1. continuation



Dye	Solvent	S_0						S_1					
		d1	**r1**	**r2**	**r3**	**a1**	**a2**	**d1**	**r1**	**r2**	**r3**	**a1**	**a2**
5d	Hexane	91.40	1.915	1.923	1.641	99.33	99.38	91.69	1.871	1.924	1.698	100.96	98.60
	Hexane	91.33	1.909	1.919	1.640	99.00	100.05	61.54	1.875	1.913	1.693	101.35	99.79
	Toluene	91.32	1.909	1.919	1.640	99.04	100.03	61.90	1.875	1.913	1.693	101.38	99.73
	DCM	91.29	1.910	1.919	1.640	99.20	99.94	61.32	1.873	1.912	1.695	101.56	99.51
	Ethanol	91.28	1.910	1.919	1.639	99.26	99.92	61.83	1.872	1.912	1.695	101.64	99.44
	DMF	91.28	1.910	1.919	1.639	99.27	99.91	61.71	1.872	1.912	1.695	101.66	99.42

Table ESI2. Calculated photophysical data of **3a-f** and **5a-d**. The λ_{abs} is the absorption maxima (nm), λ_{em} is the emission maxima, f_e is the oscillator strength and μ is the dipole moment (D) for molecules in their respective S_0 and S_1 electronic states.

Dye	Solvent	S_0			S_1		
		λ_{abs}	f_e	μ	λ_{em}	f_e	μ
3a	Hexane*	413.43	0.187	7.7	547.71	0.170	13.0
	Hexane	486.20	0.130	8.0	673.01	0.121	14.2
	Toluene	487.70	0.136	8.3	677.36	0.128	14.7
	DCM	487.58	0.131	9.3	694.23	0.156	16.7
	Ethanol	486.93	0.127	9.6	699.43	0.165	17.3
	DMF	487.59	0.130	9.6	700.54	0.167	17.5
3b	Hexane*	410.96	0.184	5.6	541.05	0.166	11.3
	Hexane	482.58	0.129	5.7	638.03	0.118	11.1
	Toluene	484.10	0.134	5.9	641.65	0.126	11.6
	DCM	484.16	0.129	6.7	655.65	0.155	13.2
	Ethanol	483.59	0.124	7.0	660.23	0.165	13.7
	DMF	484.27	0.128	7.0	661.17	0.167	13.8
3c	Hexane*	413.11	0.186	6.7	545.19	0.168	12.3
	Hexane	485.63	0.130	6.9	649.01	0.121	12.6
	Toluene	487.17	0.136	7.2	653.34	0.129	13.1
	DCM	487.12	0.130	8.1	667.69	0.158	14.8
	Ethanol	486.46	0.126	8.4	672.60	0.167	15.4
	DMF	487.12	0.130	8.4	673.59	0.169	15.5
3d	Hexane*	406.24	0.193	1.8	534.79	0.180	7.3
	Hexane	476.02	0.135	2.1	631.31	0.133	7.8
	Toluene	477.52	0.141	2.2	634.54	0.141	8.1
	DCM	478.09	0.135	2.6	648.03	0.170	9.3
	Ethanol	477.83	0.130	2.7	652.77	0.180	9.7
	DMF	478.55	0.134	2.8	653.77	0.182	9.8
3e	Hexane*	407.27	0.186	2.3	530.07	0.159	7.9
	Hexane	477.65	0.130	2.6	634.28	0.119	8.3
	Toluene	479.23	0.136	2.7	637.88	0.126	8.6
	DCM	479.95	0.130	3.2	652.47	0.155	10.0
	Ethanol	479.69	0.125	3.4	657.44	0.164	10.4
	DMF	480.43	0.129	3.5	658.47	0.166	10.5
3f	Hexane*	411.69	0.190	5.5	552.24	0.220	13.8
	Hexane	482.55	0.135	5.6	622.34	0.102	11.7
	Toluene	483.86	0.141	5.8	625.78	0.109	12.1
	DCM	483.27	0.136	6.6	638.20	0.137	13.8
	Ethanol	482.43	0.132	6.9	641.89	0.147	14.3
	DMF	491.90	0.190	7.0	642.63	0.149	14.4
5a	Hexane*	419.06	0.188	5.3	543.59	0.164	10.7
	Hexane	501.71	0.132	5.5	654.68	0.112	10.8
	Toluene	502.96	0.138	5.7	657.27	0.120	11.3
	DCM	501.66	0.133	6.4	668.33	0.151	12.8
	Ethanol	500.67	0.128	6.7	672.41	0.162	13.3
	DMF	501.33	0.132	6.7	673.24	0.165	13.4
5b	Hexane*	420.96	0.190	6.5	546.93	0.165	12.0
	Hexane	504.54	0.133	6.7	665.06	0.114	12.2
	Toluene	505.79	0.139	6.9	668.13	0.122	12.7
	DCM	504.37	0.134	7.8	679.98	0.153	14.3
	Ethanol	503.28	0.130	8.1	683.68	0.164	14.9
	DMF	503.92	0.133	8.2	684.45	0.166	15.0
5c	Hexane*	414.53	0.196	1.4	536.27	0.171	6.9
	Hexane	495.22	0.137	1.7	648.25	0.122	7.3
	Toluene	496.48	0.143	1.8	650.93	0.130	7.6
	DCM	495.77	0.137	2.1	661.92	0.162	8.7
	Ethanol	495.10	0.133	2.3	665.61	0.172	9.1
	DMF	495.80	0.137	2.3	666.35	0.174	9.2
5d	Hexane*	415.46	0.191	1.9	537.60	0.166	7.3
	Hexane	496.74	0.133	2.2	649.36	0.112	7.8
	Toluene	498.07	0.140	2.3	651.96	0.120	8.1
	DCM	497.47	0.133	2.8	663.73	0.151	9.4
	Ethanol	496.80	0.129	3.0	668.44	0.162	9.8
	DMF	497.52	0.133	3.0	669.74	0.164	9.9

DCM=Dichloromethane; DMF=N,N-dimethylformamide. *Calculated with CAM-B3LYP/jun-cc-pVTZ//CAM-B3LYP/cc-pVDZ. The remaining data were calculated with PBE1PBE/jun-cc-pVTZ//PBE1PBE/cc-pVDZ.

Table ESI3. Computed vertical absorption energies and vertical emission energies in hexane and in dichloromethane for **3b** structure of optimized S_0 and S_1 state at the CAM-B3LYP/jun-cc-pVTZ level.

Structure*		**Energy (eV)**	**Wavelength**	**Force**	**Transition**	**coefficient**
3b Hexane (S_0 geometry)	S0 → S1	3.017	410.96	0.184	91 → 92	0.703
	S0 → S2	4.463	277.78	0.244	89 → 92	0.605
	S0 → S3	4.575	270.98	0.000	91 → 93	0.629
	S0 → S4	4.625	268.06	0.000	91 → 94	0.624
3b Hexane (S_1 geometry)	S0 → S1	2.292	541.05	0.166	91 → 92	0.704
	S0 → S2	4.086	303.41	0.148	90 → 92	0.493
	S0 → S3	4.327	286.55	0.079	91 → 93	0.650
3b DCM (S_0 geometry)	S0 → S1	3.011	411.83	0.184	91 → 92	0.70275
	S0 → S2	4.451	278.55	0.262	87 → 92	0.49671
	S0 → S3	4.669	265.53	0 .000	91 → 93	0.62625
	S0 → S4	4.720	262.66	0.000	91 → 94	0.61892
3b DCM (S_1 geometry)	S0 → S1	2.219	558.72	0.2156	91 → 92	0.704
	S0 → S2	4.030	307.66	0.2715	90 → 92	0.425
	S0 → S3	4.306	287.92	0.0771	90 → 92	0.500

Table ESI4. Computed vertical absorption energies and vertical emission energies in hexane and in dichloromethane for **3b** structure of optimized S_0 and S_1 state at the PBE1PBE /jun-cc-pVTZ level.

Structure*		Energy (eV)	Wavelength	Force	Transition	coefficient
3b Hexane (S_0 geometry)	S0 → S1	2.569	482.58	0.129	91 → 92	0.704
	S0 → S2	3.906	317.44	0.000	91 → 93	0.692
	S0 → S3	3.951	313.84	0.000	91 → 94	0.690
	S0 → S4	4.072	304.45	0.014	90 → 92	0.700
3b Hexane (S1 geometry)	S0 → S1	1.943	638.03	0.118	91 → 92	0.706
	S0 → S2	3.314	374.18	0.026	90 → 92	0.703
	S0 → S3	3.747	330.87	0.141	91 → 93	0.696
3b DCM (S_0 geometry)	S0 → S1	2.561	484.16	0.129	91 → 92	0.705
	S0 → S2	4.014	308.91	0.000	91 → 93	0.691
	S0 → S3	4.061	305.34	0.000	91 → 94	0.690
	S0 → S4	4.067	304.86	0.012	90 → 92	0.689
3b DCM (S_1 geometry)	S0 → S1	1.891	655.65	0.155	91 → 92	0.706
	S0 → S2	3.287	377.17	0.034	90 → 92	0.702
	S0 → S3	3.791	327.10	0.192	91 → 93	0.689

Figure ESI1. Molecular orbitals involved in the four vertical transitions of lower energy at the optimized ground state geometry calculated for 3b with CAM-B3LYP and PCM/hexane as solvent effect.

MO 89: HOMO-2 MO 91: HOMO MO 92: LUMO MO 93: LUMO +1 MO 94: LUMO +2

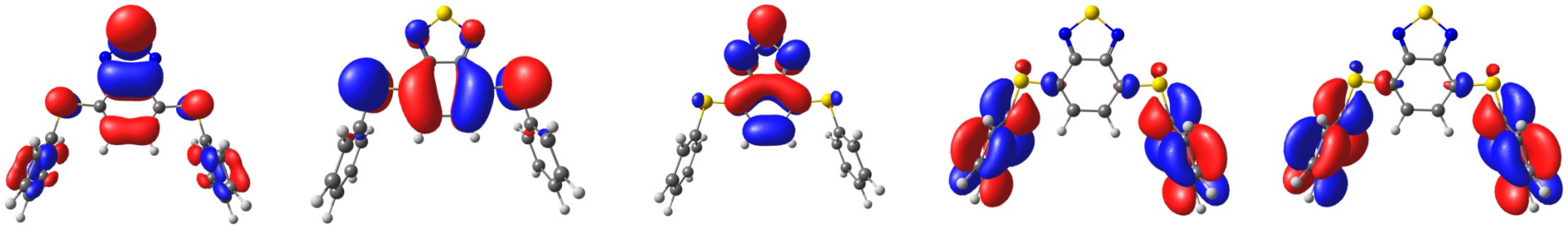


Figure ESI2. Molecular orbitals involved in the four vertical transitions of lower energy at the optimized first excited state geometry calculated for 3b with CAM-B3LYP and PCM/hexane as solvent effect.

MO 90: HOMO-1 MO 91: HOMO MO 92: LUMO MO 93: LUMO +1

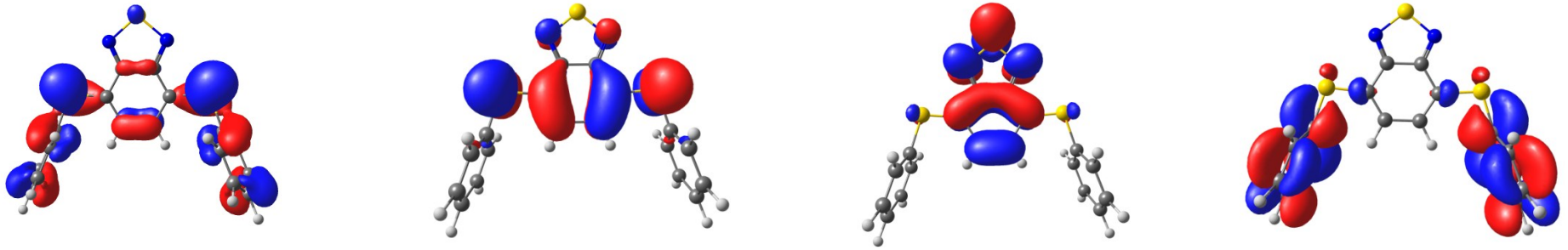


Figure ESI3. Molecular orbitals involved in the four vertical transitions of lower energy at the optimized ground state geometry calculated for 3b with PBE1PBE and PCM/hexane as solvent effect.

MO 90: HOMO-1 MO 91: HOMO MO 92: LUMO MO 93: LUMO +1 MO 94: LUMO +2

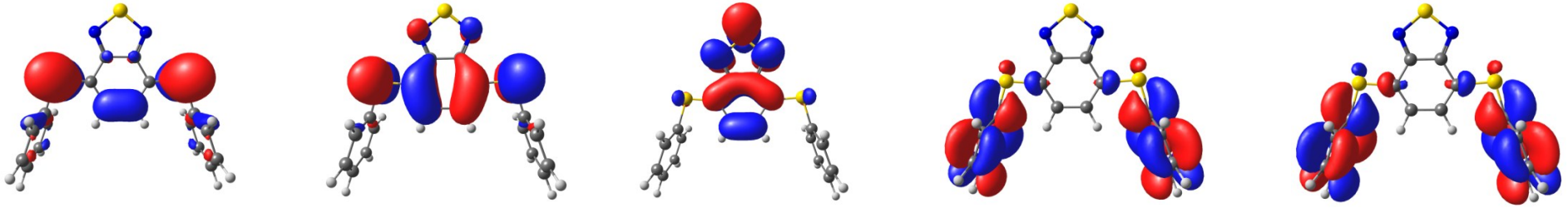


Figure ESI4. Molecular orbitals involved in the four vertical transitions of lower energy at the optimized first excited state geometry calculated for 3b with PBE1PBE and PCM/hexane as solvent effect.

MO 90: HOMO-1 MO 91: HOMO MO 92: LUMO MO 93: LUMO +1