Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Photoactive benzothiadiazole-*N*-heterocycle derivatives. Synthesis, photophysics and water sensing in organic solvents

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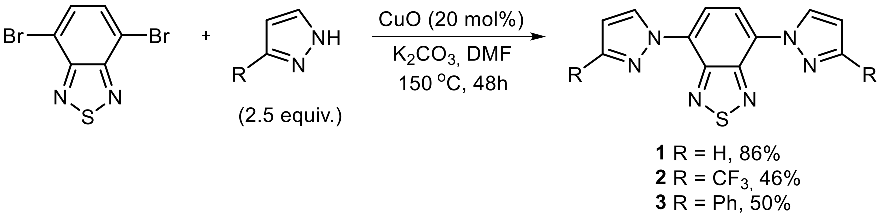
TABLE OF CONTENTS

1. General Information

NMR spectra were recorded in $CDCl_3$ solution on a Varian VNMRJ 400 MHz spectrometer at room temperature. Chemical shifts (δ) are given in parts per million from the peak of tetramethylsilane (δ = 0.00 ppm) as an internal standard in ^{1}H NMR or from the solvent peak of $CDCl_3$ (δ = 77.00 ppm) in ^{13}C NMR. ESI-QTOF-MS measurements were performed in the positive ion mode (m/z 50-2000 range). IR spectra were obtained on an FTIR-ATR instrument. Spectroscopic grade solvents were used in the photophysical study. The UV-Vis absorption spectra in solution were acquired on a Shimadzu UV-2450 spectrophotometer, and the steady-state fluorescence spectra were measured on a Shimadzu spectrofluorometer model RF-5301PC. Flash chromatography was performed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using supported silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under UV light 254 nm or stained with iodine vapor. CuO, CuI, pyrazoles, indole, and phenothiazine were purchased from commercial suppliers and used as received. $Pd(PPh_3)_4$[1] and 4,7-dibromobenzo[c]-1,2,5-thiadiazole[2] were prepared according to procedures described in the literature.

2. General Procedure for the synthesis of compounds 1-3



A Schlenk tube was charged with 4,7-dibromobenzo[c]-1,2,5-thiadiazole (0.2 mmol), indole (0.5 mmol), CuO (0.04 mmol), K_2CO_3 (0.8 mmol), and DMF (2 mL), evacuated and backfilled with argon. The reaction mixture was stirred at 150 °C for 48h. The cooled reaction mixture was extracted with dichloromethane and water. The organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane and ethyl acetate, to provide the desired product.

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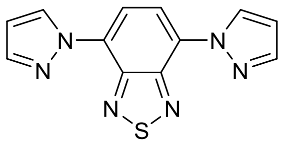
[1]. Barbiéri, R. S. *Quim. Nova* **1991**, *14*, 212.

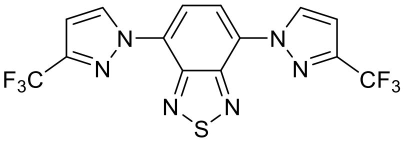
[2] Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629.

Compound 1: 4,7-di(1H-pyrazol-1-yl)benzo[c][1,2,5]thiadiazole



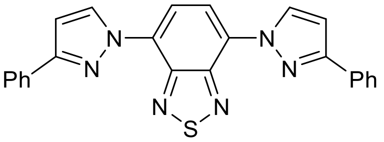
Yellow solid. **Yield**: 46 mg, 86%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 2.5 Hz, 2H), 8.34 (s, 2H), 7.84 (d, *J* = 1.5 Hz, 2H), 6.60 (dd, *J* = 2.5, 1.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 141.6, 131.3, 129.3, 119.4, 107.9. **IR** (vmax, cm^{-1}): 2958, 2853, 1726, 1496, 749. **HRMS** (ESI+): The exact mass calculated for $[M+H]^+$ ($C_{12}H_9N_6S$) requires m/z 269.0609, found: m/z 269.0604.

Compound 2: 4,7-bis(3-(trifluoromethyl)-1H-pyrazol-1-yl)benzo[c][1,2,5]thiadiazole



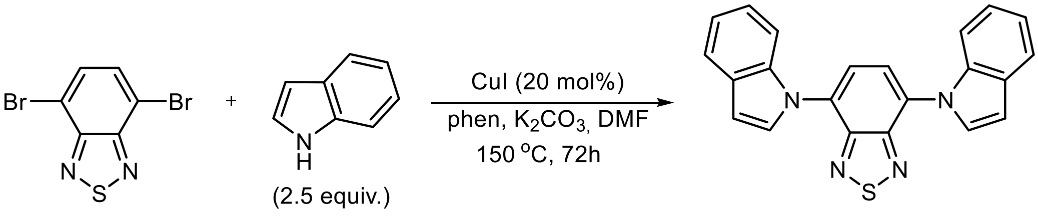
Green solid. **Yield**: 37 mg, 46%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (dd, *J* = 2.5, 0.9 Hz, 2H), 7.19 (s, 2H), 6.78 (d, *J* = 2.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 144.6 (q, *J* = 38.7 Hz), 133.0, 129.2, 121.1 (q, *J* = 267.0 Hz), 120.3, 106.3 (q, *J* = 2.0 Hz). **IR** (vmax, cm^{-1}): 2926, 2850, 1544, 1397, 1270, 1121, 760. **HRMS** (ESI+): The exact mass calculated for $[M+H]^+$ ($C_{14}H_7F_6N_6S$) requires m/z 405.0357, found: m/z 405.0352.

Compound 3: 4,7-bis(3-phenyl-1H-pyrazol-1-yl)benzo[c][1,2,5]thiadiazole



Orange solid. **Yield**: 42 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 2.6 Hz, 2H), 8.51 (s, 2H), 8.02-7.98 (m, 4H), 7.51-7.45 (m, 4H), 7.41-7.36 (m, 2H), 6.91 (d, *J* = 2.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 147.6, 132.8, 132.7, 129.0, 128.8, 128.5, 126.1, 119.2, 105.6. **IR** (vmax, cm^{-1}): 2926, 2853, 1731, 1455, 738. **HRMS** (ESI+): The exact mass calculated for $[M+H]^+$ ($C_{24}H_{17}N_2S$) requires m/z 421.1235, found: m/z 421.1230.

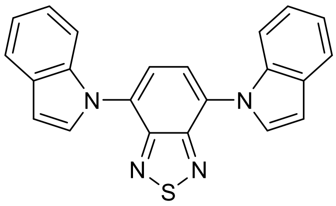
3. Procedure for the synthesis of compound 4



4 85%

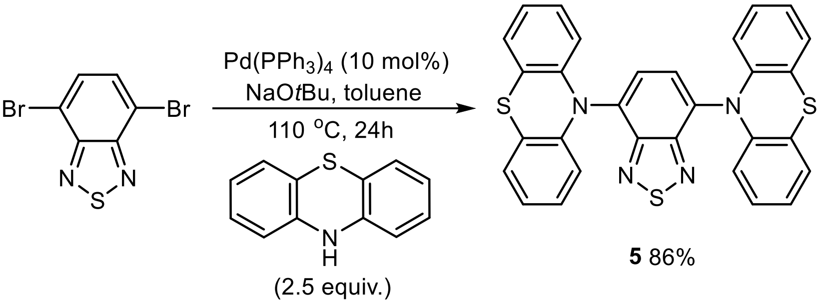
A Schlenk tube was charged with 4,7-dibromobenzo[c]-1,2,5-thiadiazole (0.2 mmol), indole (0.5 mmol), CuI (0.04 mmol), 1,10-phenanthroline (0.04 mmol), K_2CO_3 (0.8 mmol), and DMF (2 mL), evacuated and backfilled with argon. The reaction mixture was stirred at 150 °C for 72h. The cooled reaction mixture was extracted with dichloromethane and water. The organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane and ethyl acetate, to provide the desired product.

Compound 4: 4,7-di(1H-indol-1-yl)benzo[c][1,2,5]thiadiazole



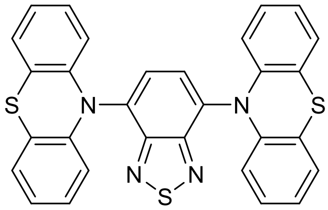
Orange solid. **Yield**: 62 mg, 85%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.73 (d, *J* = 3.3 Hz, 2H), 7.68 (dd, *J* = 7.1, 1.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.23-7.15 (m, 4H), 6.78 (d, *J* = 3.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.6, 136.3, 129.8, 129.5, 129.1, 123.2, 122.7, 121.4, 121.2, 110.7, 104.8. **IR** (vmax, cm^{-1}): 2905, 2857, 1503, 1435, 748. **HRMS** (ESI+): The exact mass calculated for $[M+H]^+$ ($C_{22}H_{15}N_4S$) requires m/z 367.1017, found: m/z 367.1012.

4. Procedure for the synthesis of compound 5



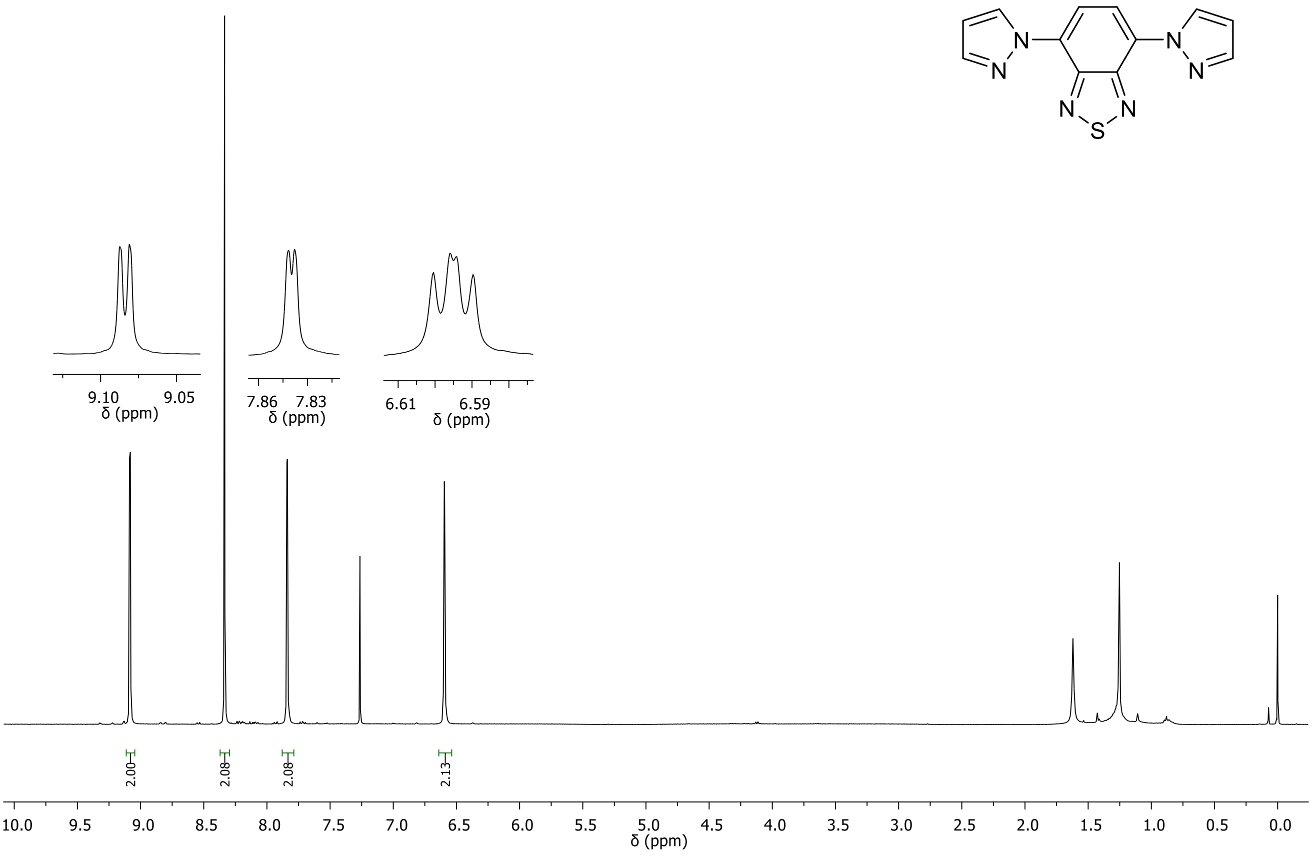
A Schlenk tube was charged with 4,7-dibromobenzo[c]-1,2,5-thiadiazole (0.2 mmol), phenothiazine (0.5 mmol), $Pd(PPh_3)_4$ (0.02 mmol), NaO*t*Bu (0.44 mmol), and toluene (1.5 mL), evacuated and backfilled with argon. The reaction mixture was stirred at 110 °C for 24h. The cooled reaction mixture was extracted with dichloromethane and water. The organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane and ethyl acetate, to provide the desired product.

Compound 5: 4,7-di(10H-phenothiazin-10-yl)benzo[c][1,2,5]thiadiazole

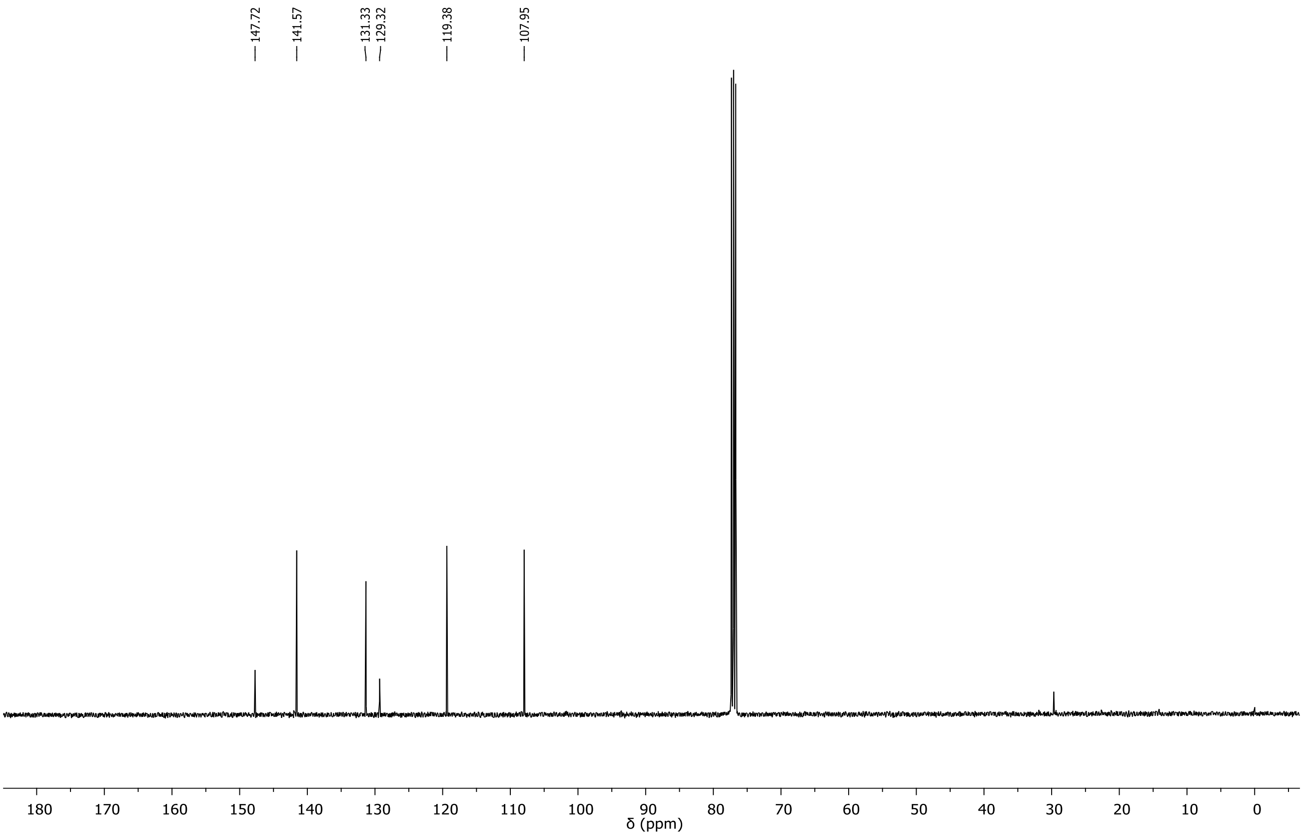


Brown solid. **Yield**: 91 mg, 86%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.18-7.13 (m, 4H), 6.95-6.87 (m, 8H), 6.27-6.21 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 143.4, 134.2, 132.7, 127.2, 127.0, 123.4, 121.8, 116.3. **IR** (vmax, cm^{-1}): 2910, 2851, 1726, 1461, 1041, 723. **HRMS** (ESI+): The exact mass calculated for $[M+H]^+$ ($C_{30}H_{19}N_4S_3$) requires m/z 531.0772, found: m/z 531.0766.

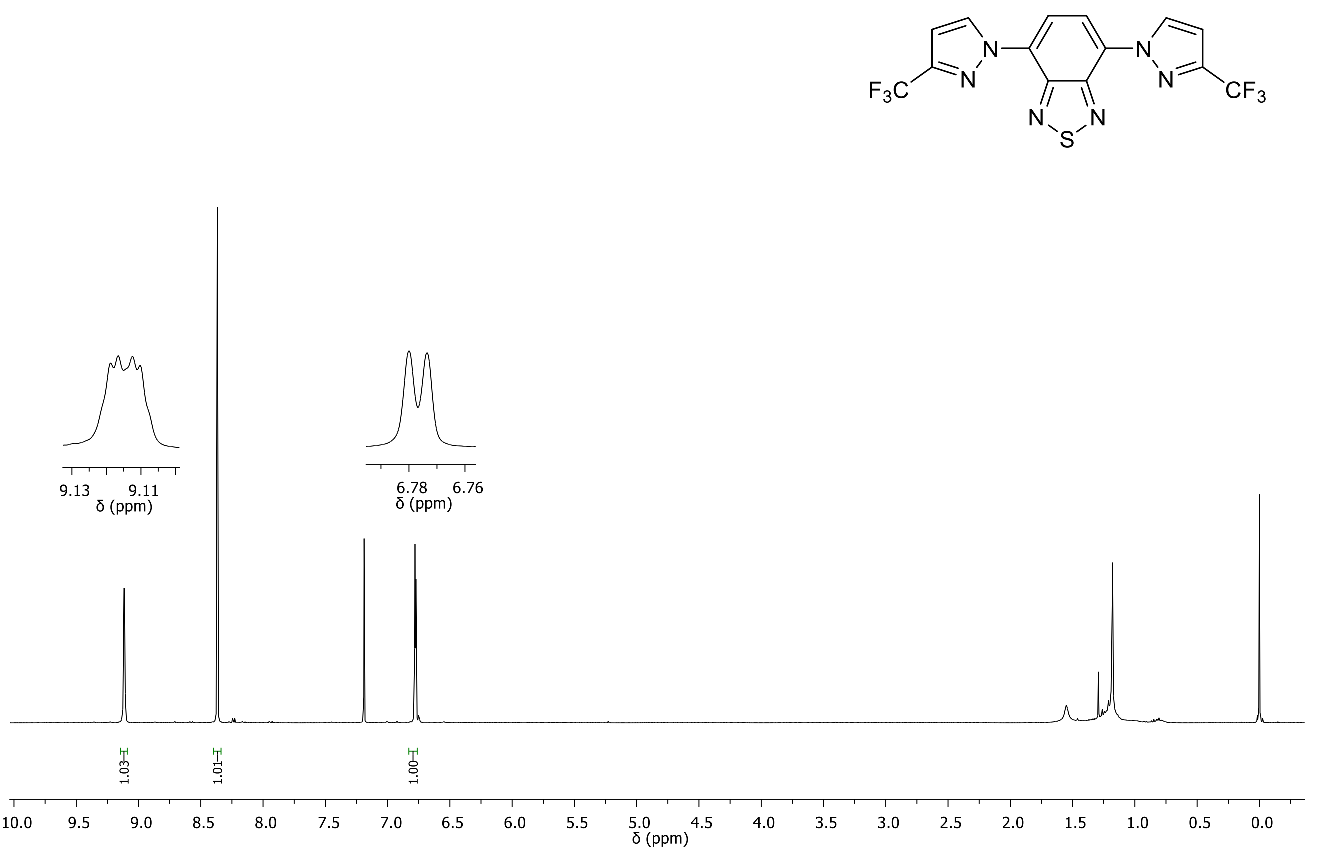
NMR Characterization



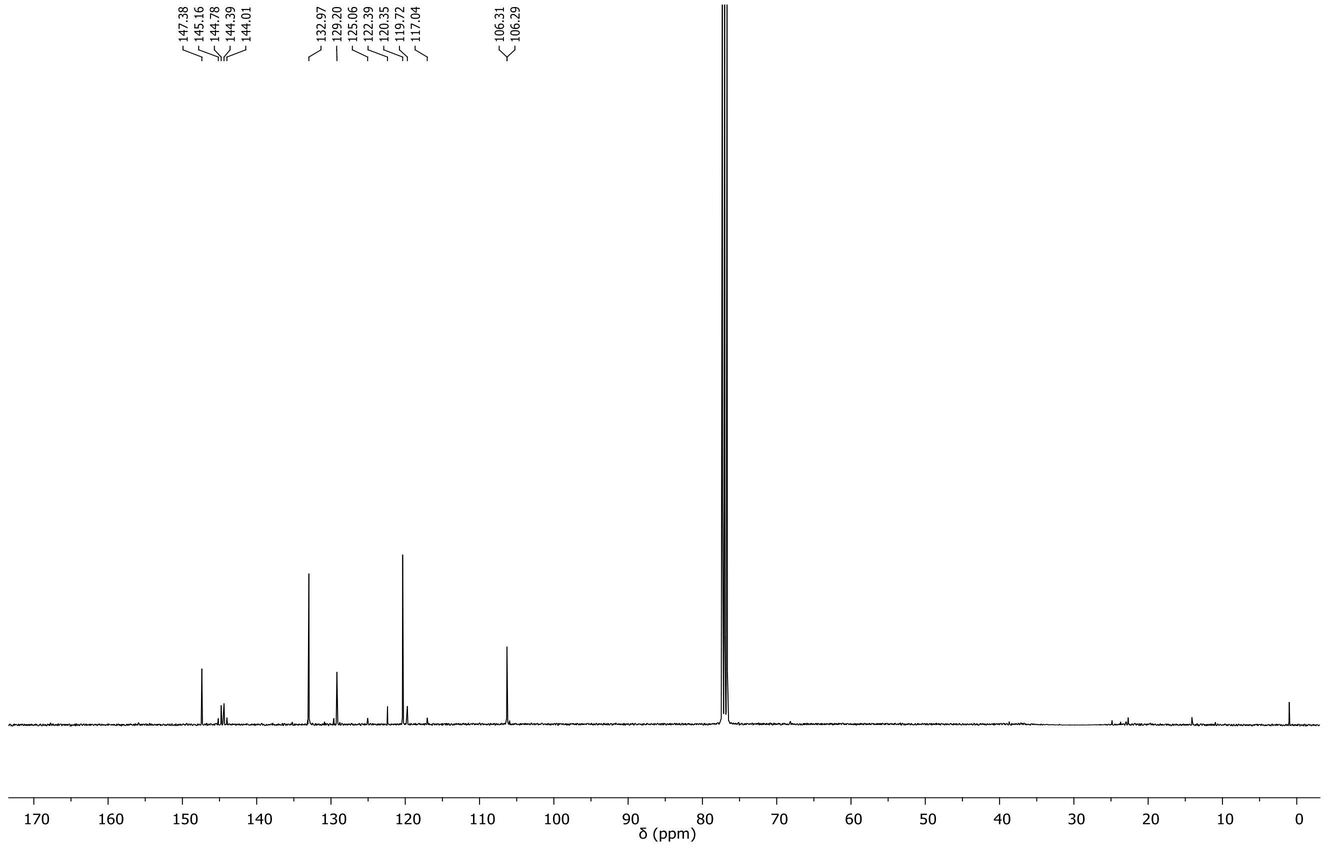
^{1}H NMR spectrum for compound **1** in CDCl$_3$, 400 MHz



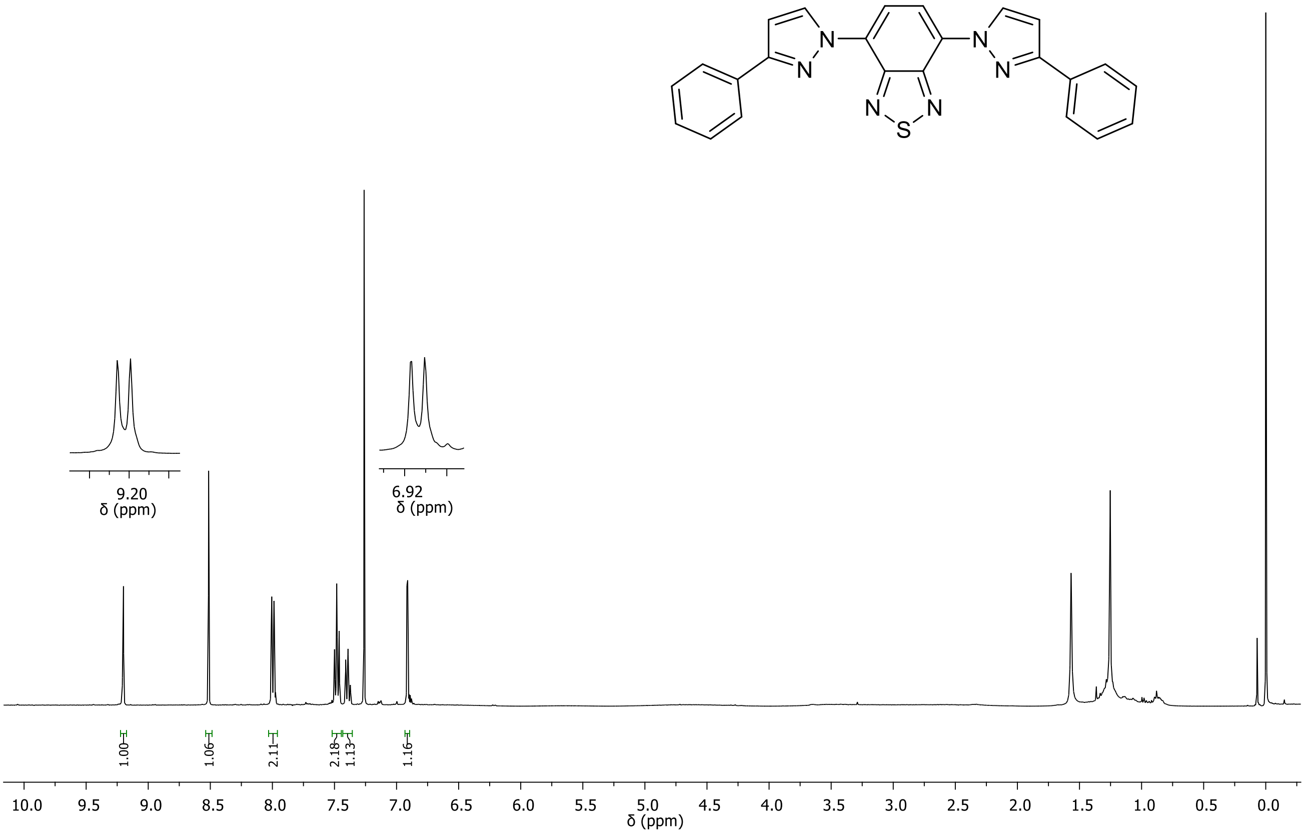
^{13}C NMR spectrum for compound **1** in CDCl$_3$, 100 MHz



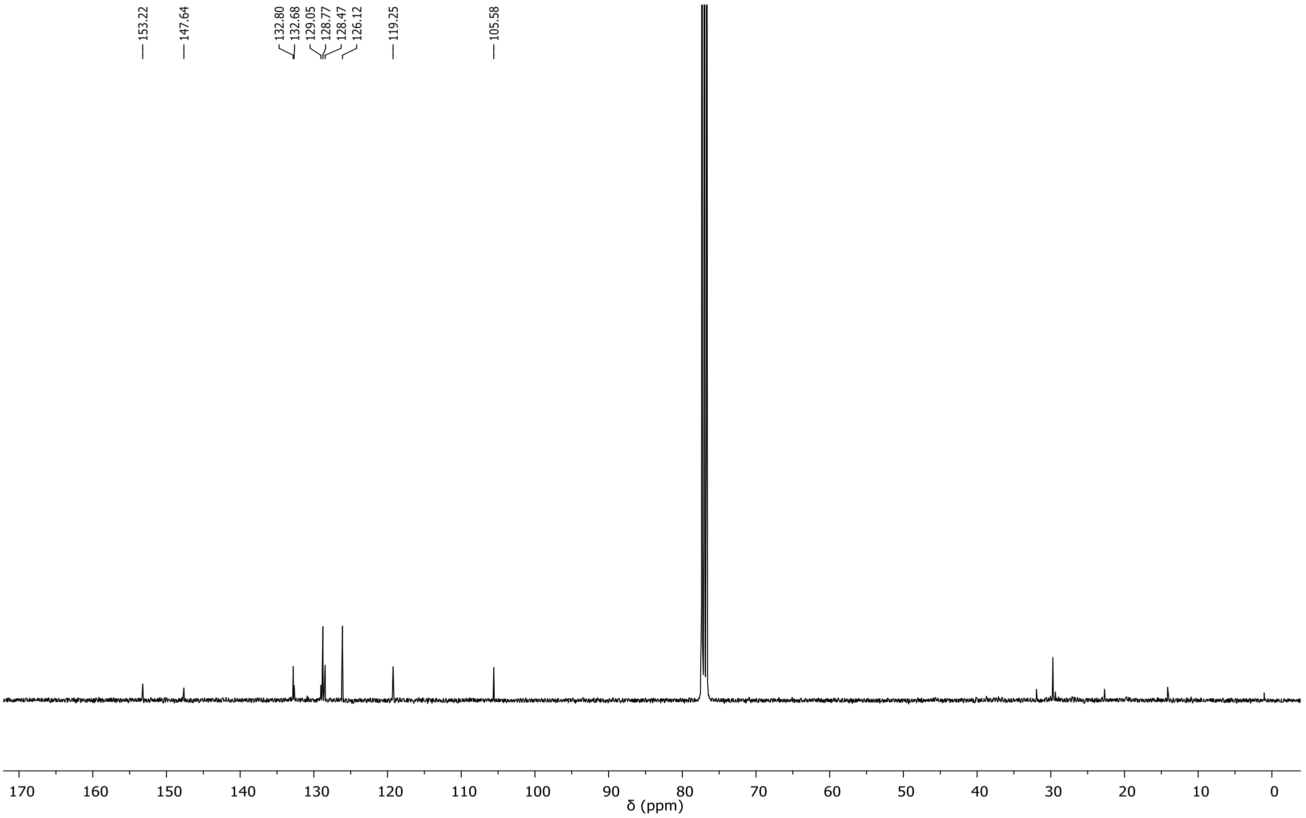
^{1}H NMR spectrum for compound **2** in $CDCl_3$, 400 MHz



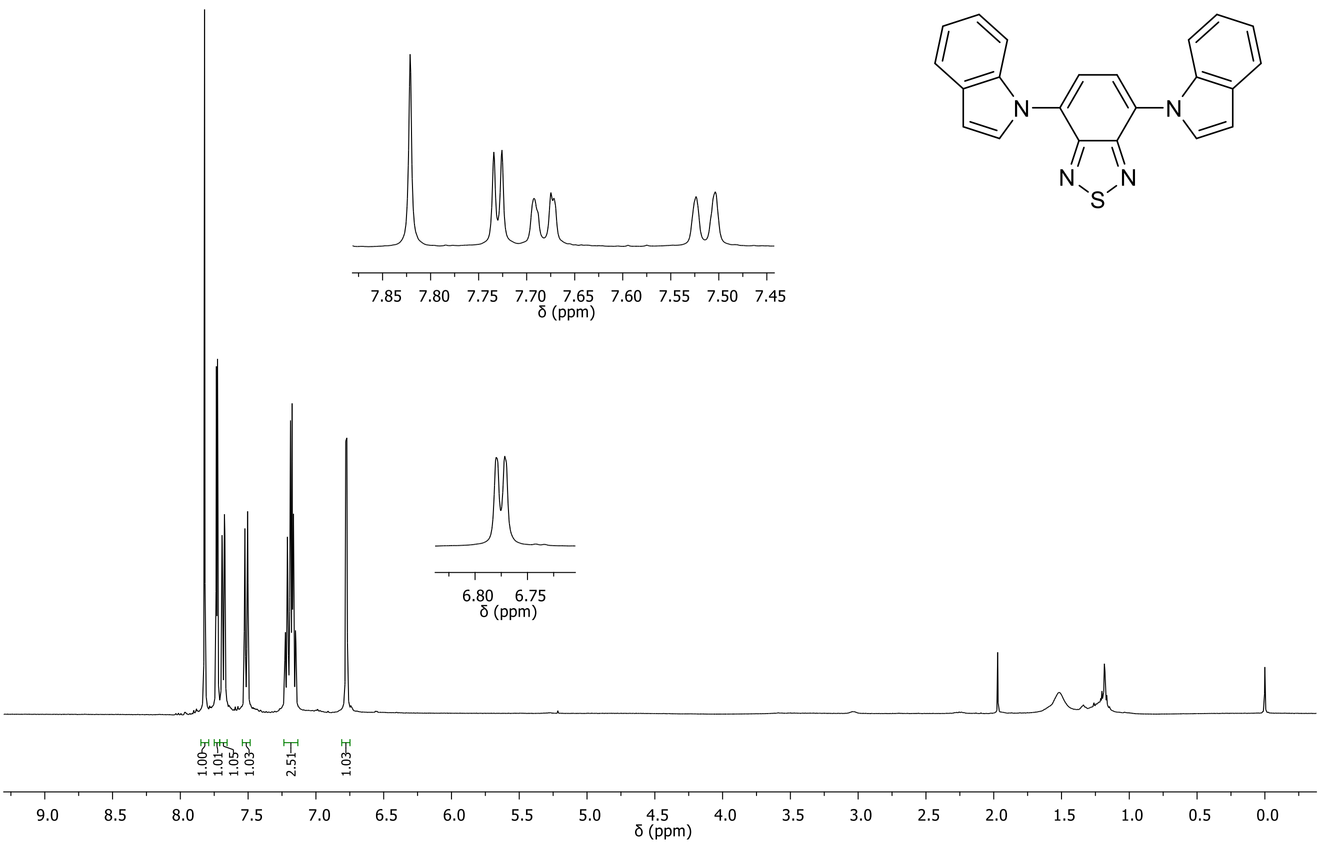
^{13}C NMR spectrum for compound **2** in $CDCl_3$, 100 MHz



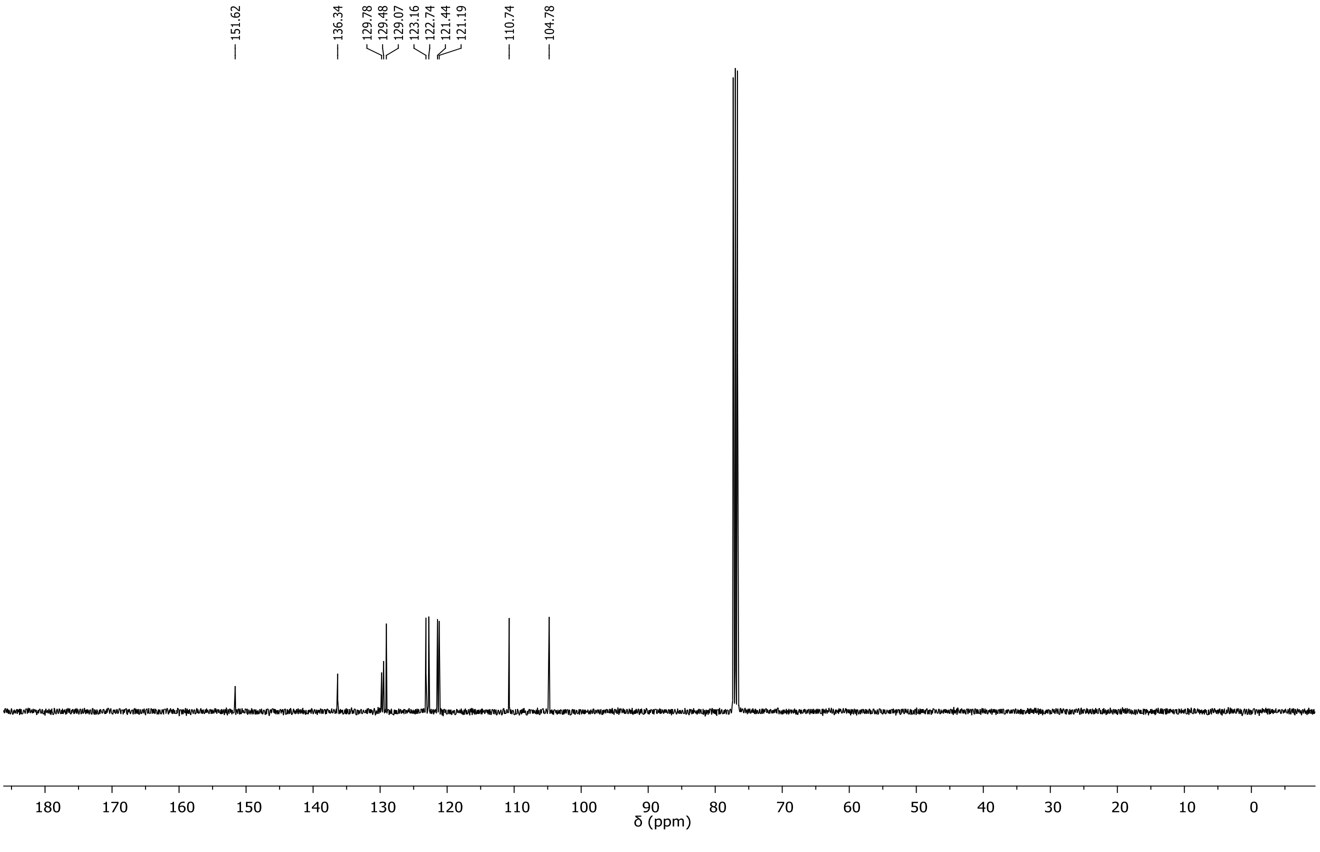
^{1}H NMR spectrum for compound **3** in $CDCl_3$, 400 MHz



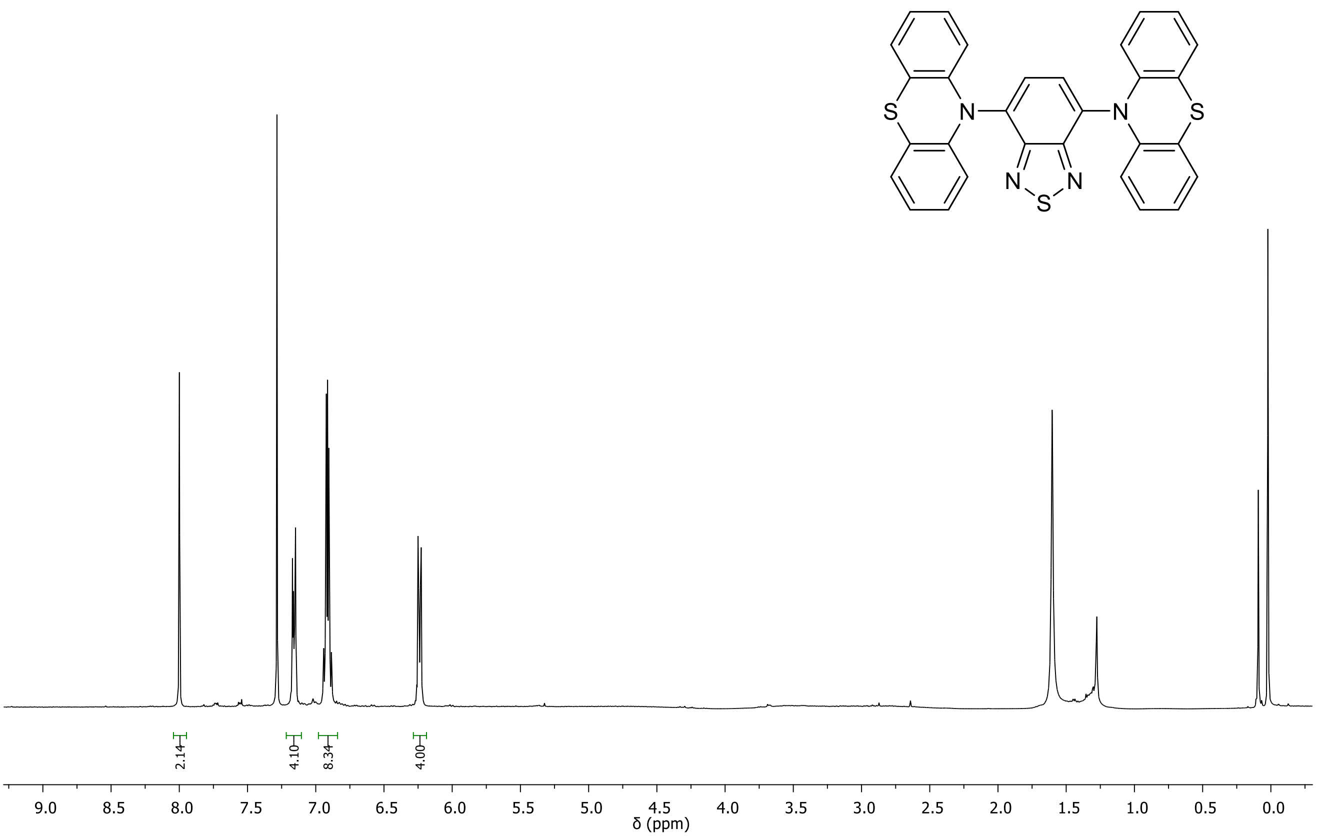
^{13}C NMR spectrum for compound **3** in $CDCl_3$, 100 MHz



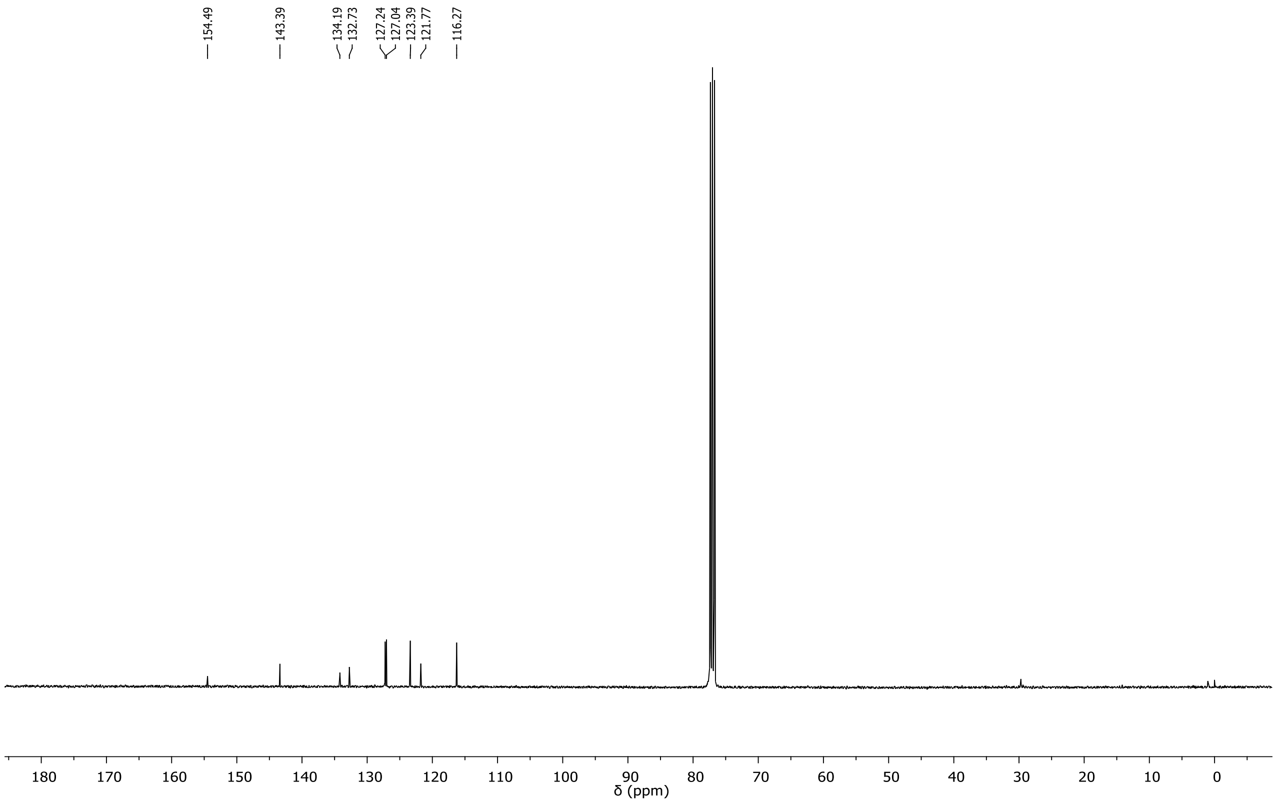
^{1}H NMR spectrum for compound **4** in $CDCl_3$, 400 MHz



^{13}C NMR spectrum for compound **4** in $CDCl_3$, 100 MHz



^{1}H NMR spectrum for compound **5** in CDCl$_3$, 400 MHz



^{13}C NMR spectrum for compound **5** in CDCl$_3$, 100 MHz

Photophysical Characterization

Absorption, emission and excitation spectra

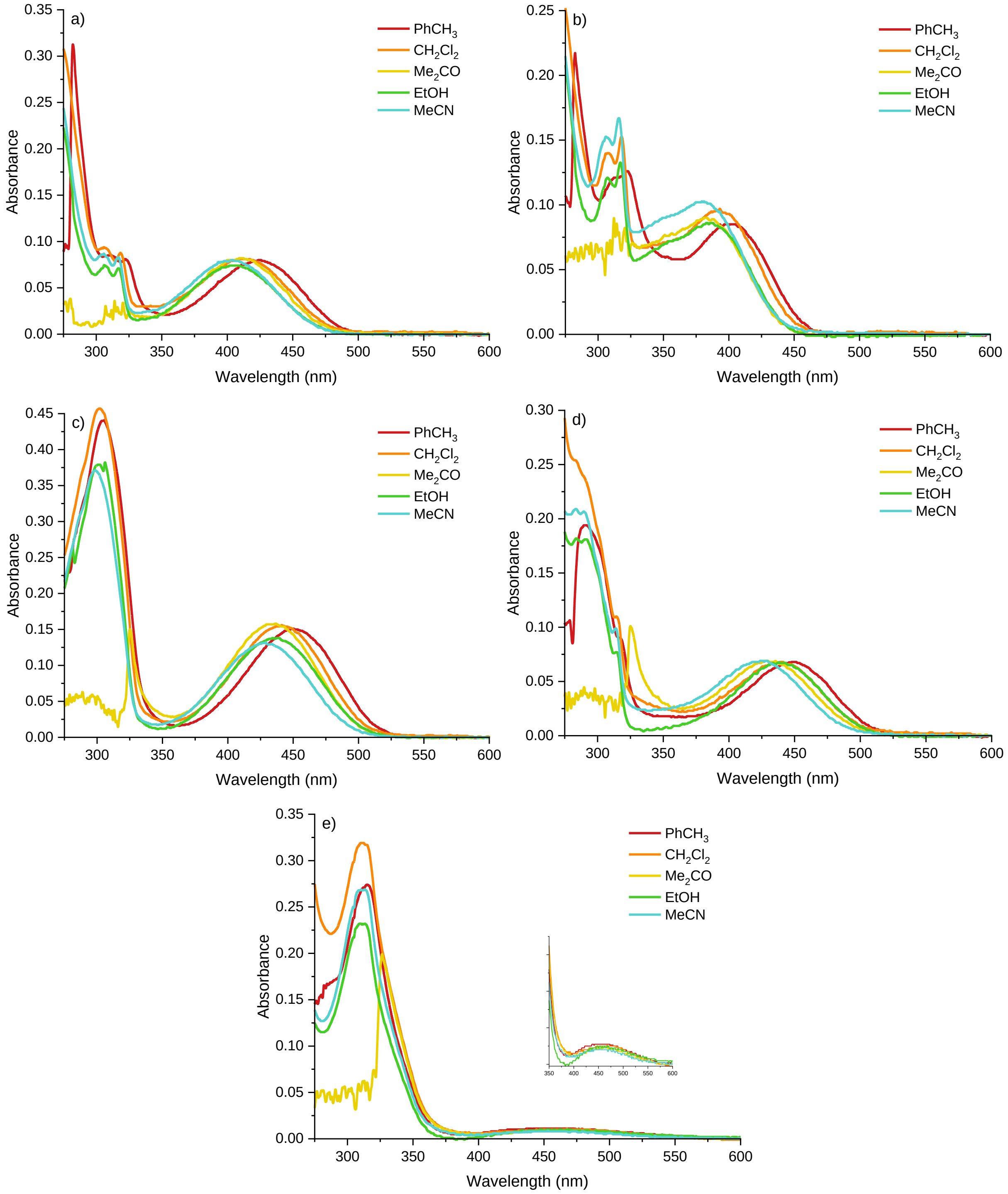


Figure S1. UV-Vis absorption spectra in solution of compounds a) **1**, b) **2**, c) **3**, d) **4**, and e) **5** in different organic solvents (ca 10^{-5} M).

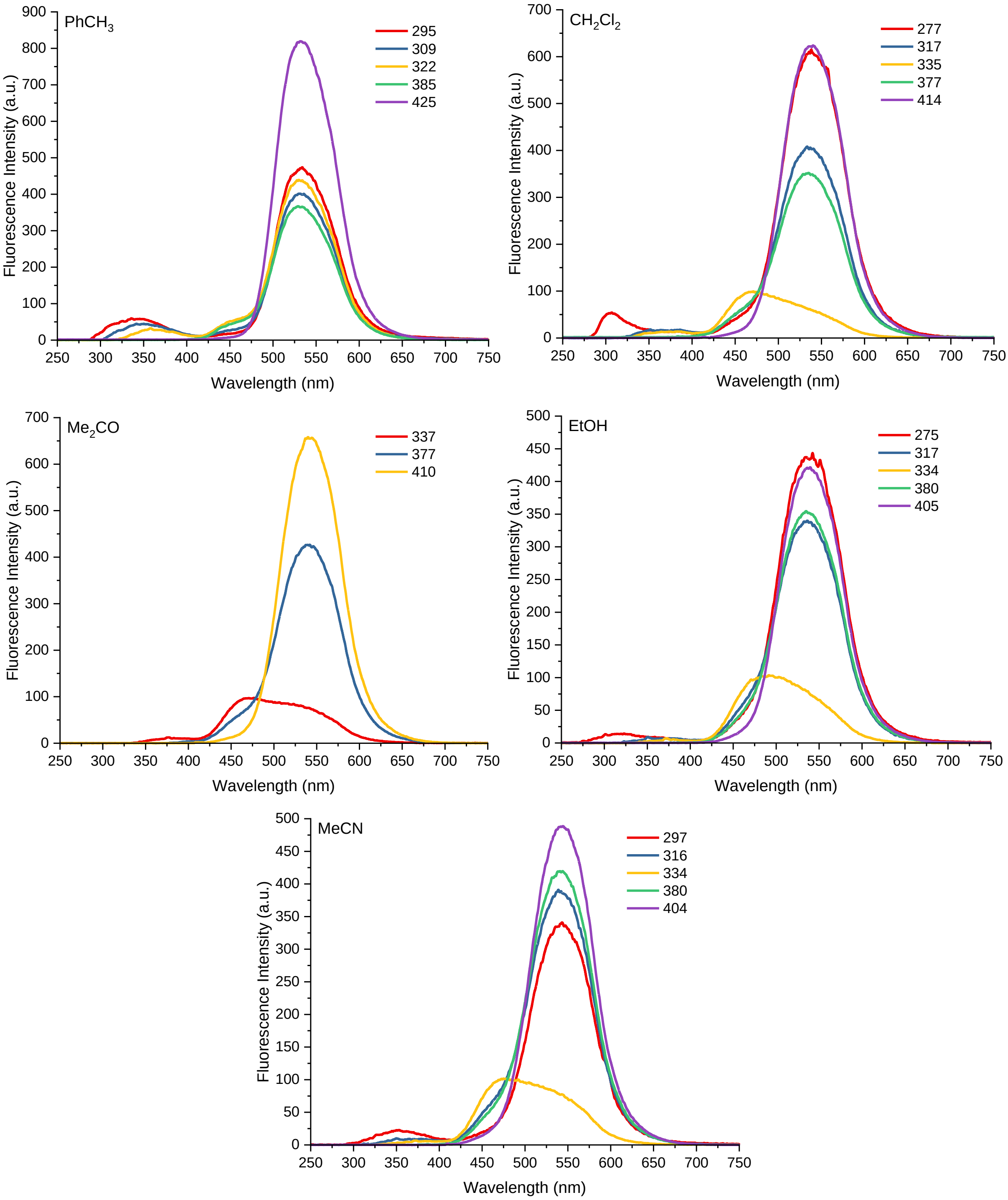


Figure S2. Steady-state fluorescence emission spectra of compound **1** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different excitation wavelengths (nm).

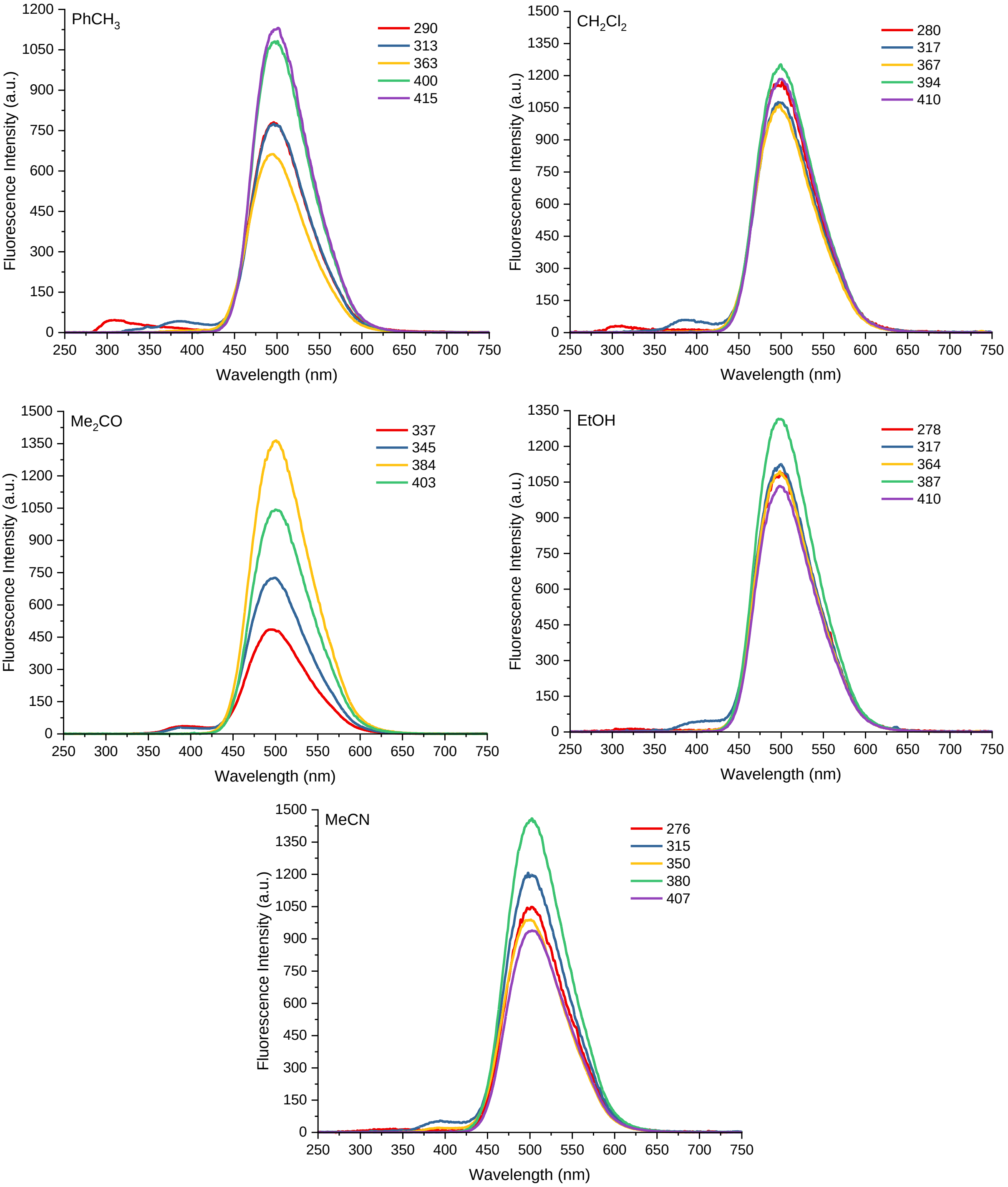


Figure S3. Steady-state fluorescence emission spectra of compound **2** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different excitation wavelengths (nm).

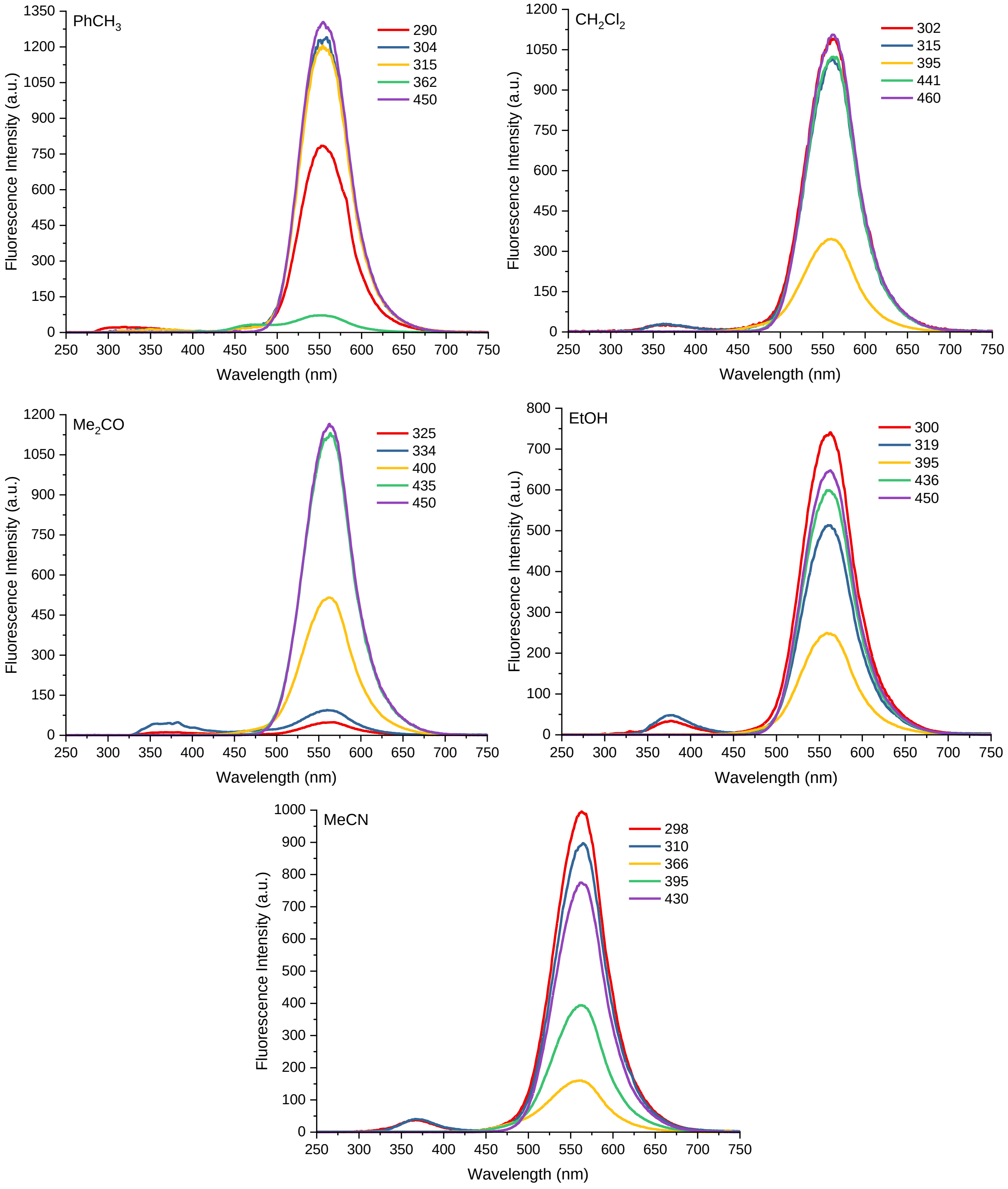


Figure S4. Steady-state fluorescence emission spectra of compound **3** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different excitation wavelengths (nm).

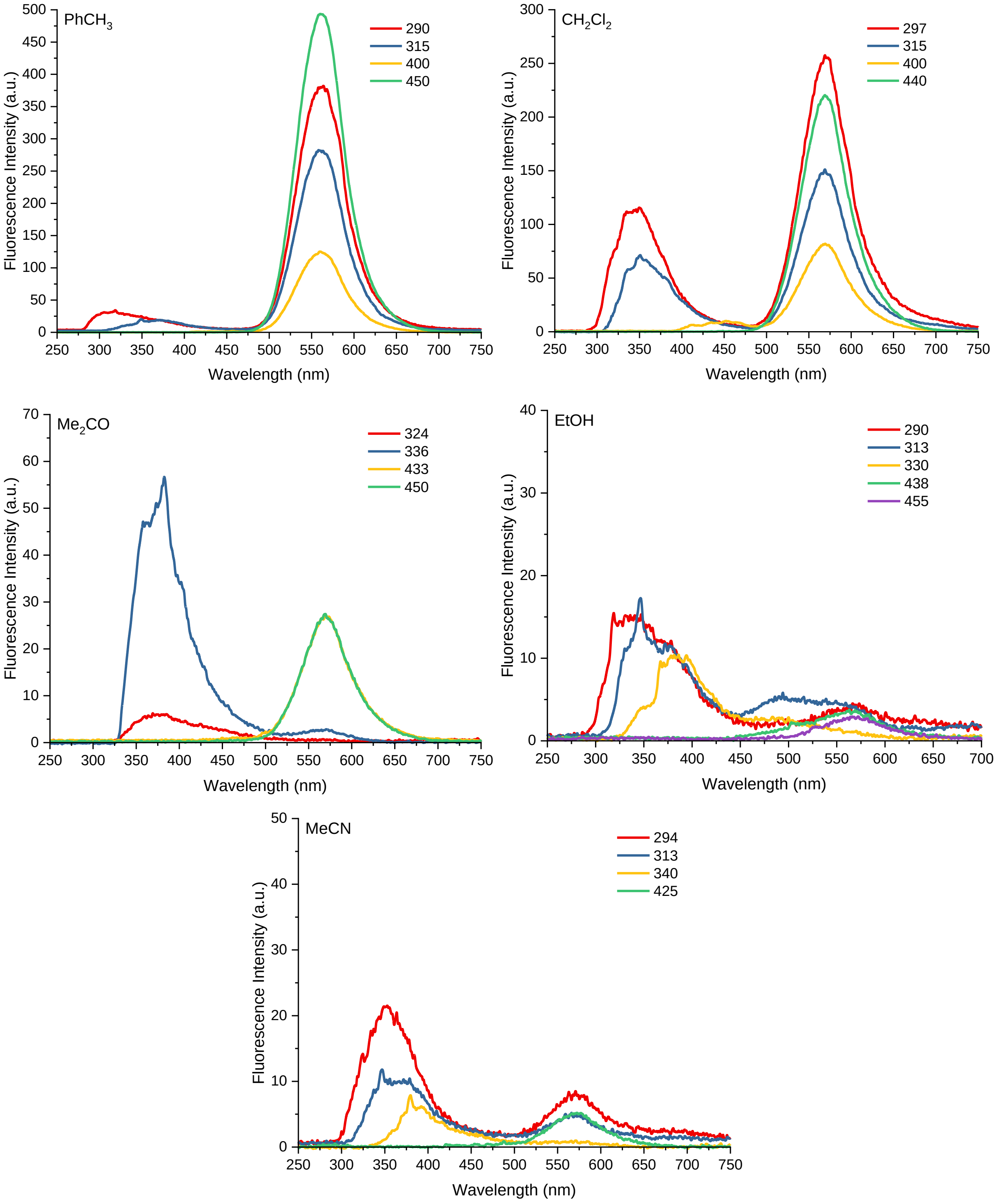


Figure S5. Steady-state fluorescence emission spectra of compound **4** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different excitation wavelengths (nm).

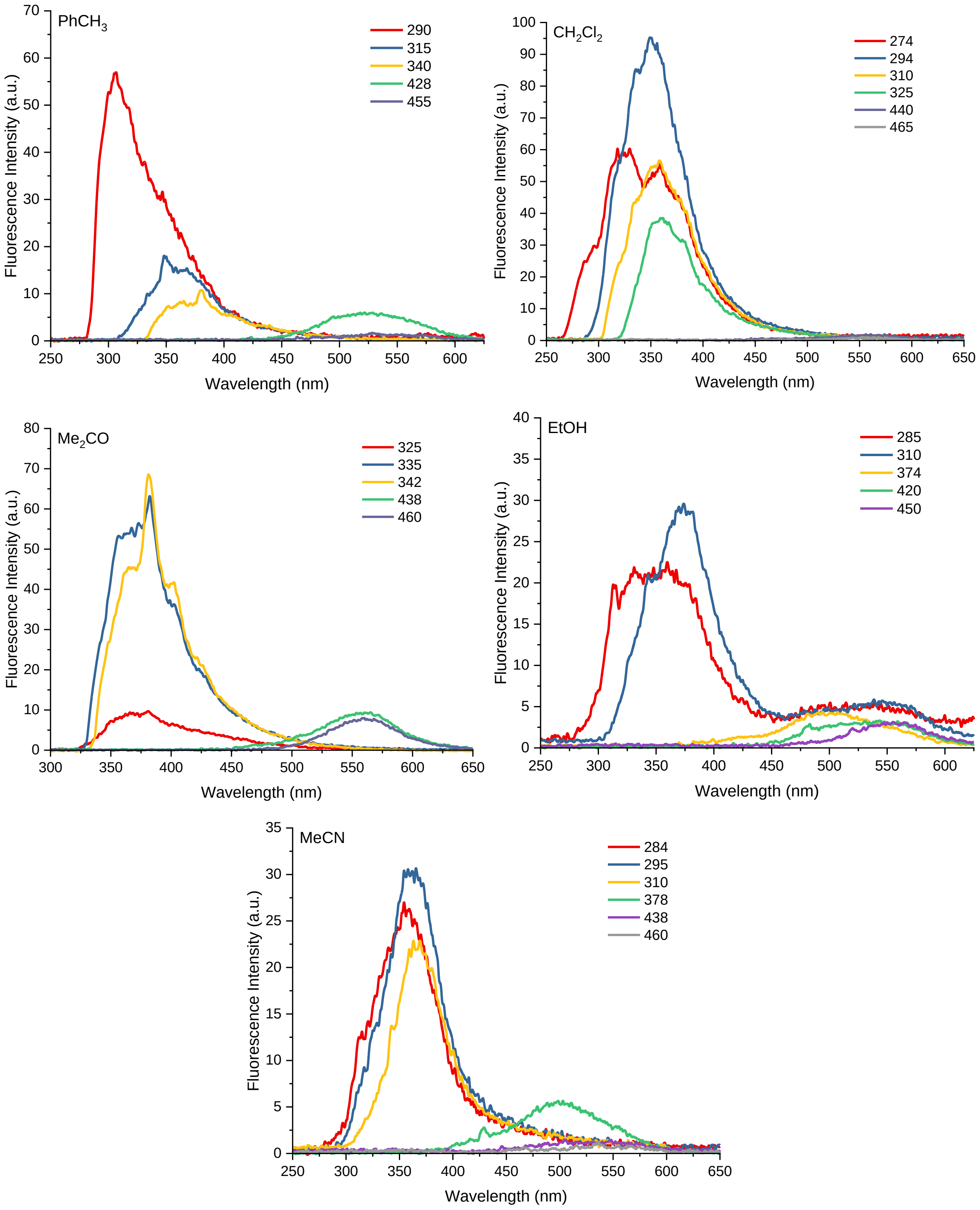


Figure S6. Steady-state fluorescence emission spectra of compound **5** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different excitation wavelengths (nm).

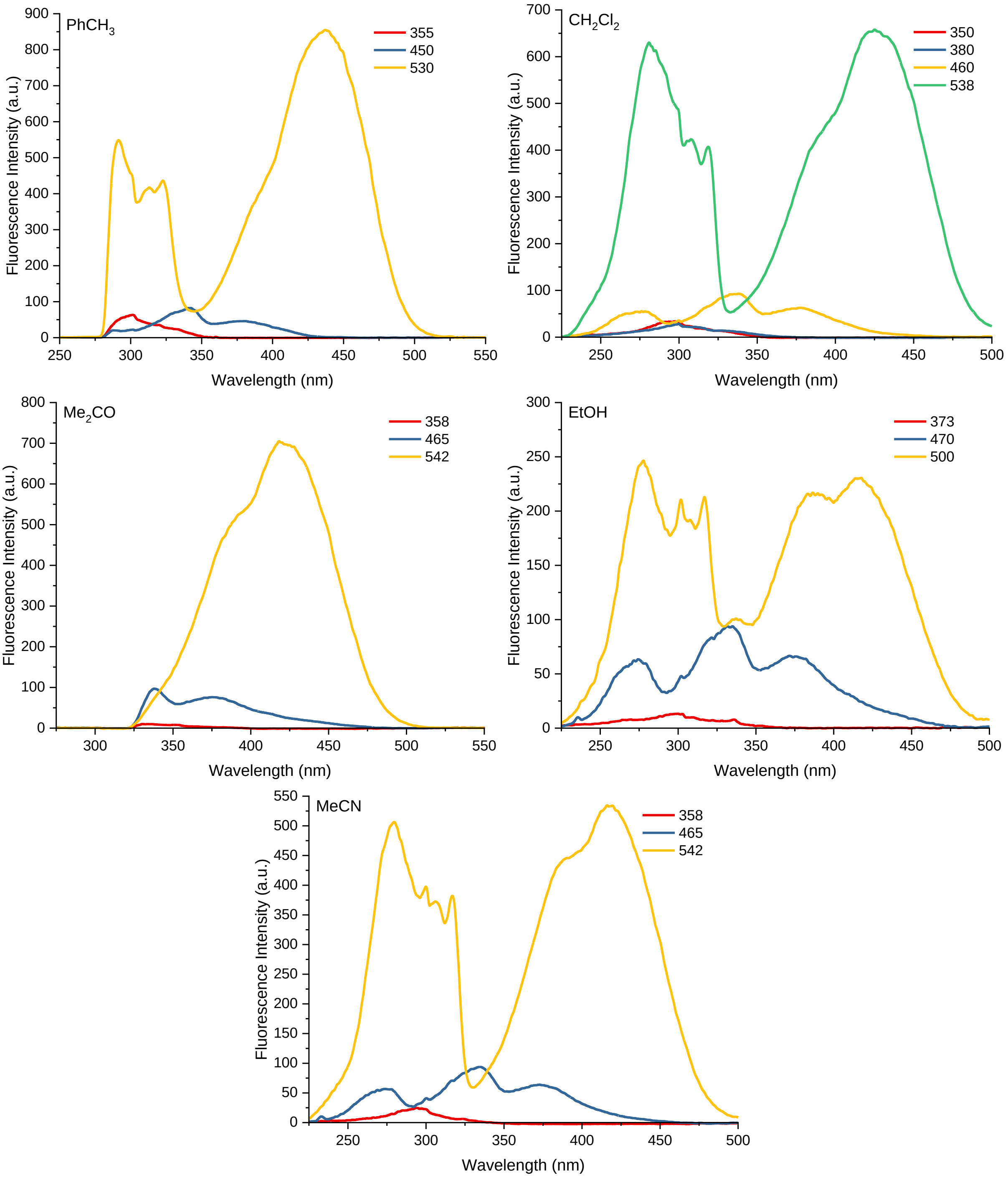


Figure S7. Excitation spectra of compound **1** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different observation wavelengths (nm).

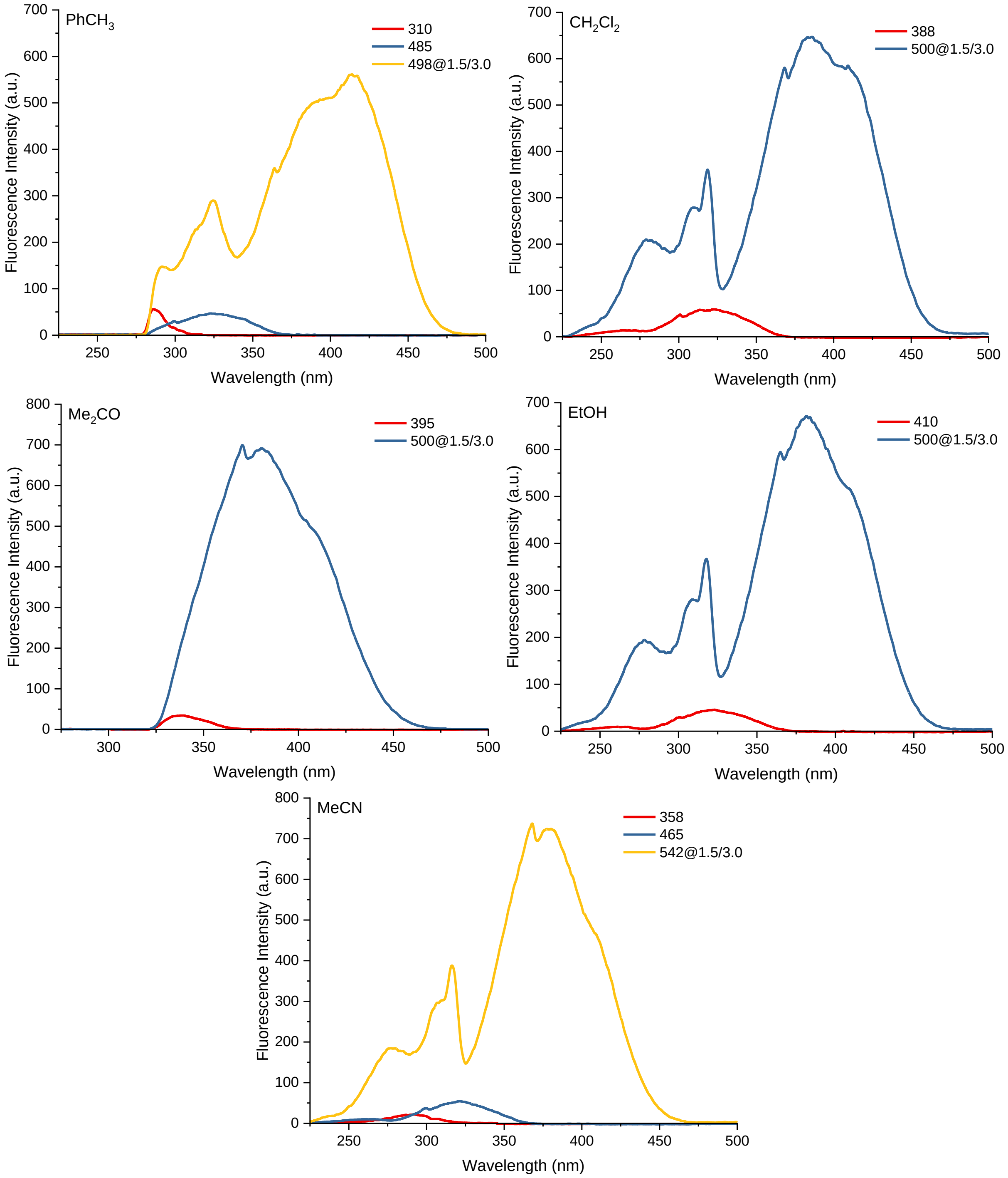


Figure S8. Excitation spectra of compound **2** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different observation wavelengths (nm).

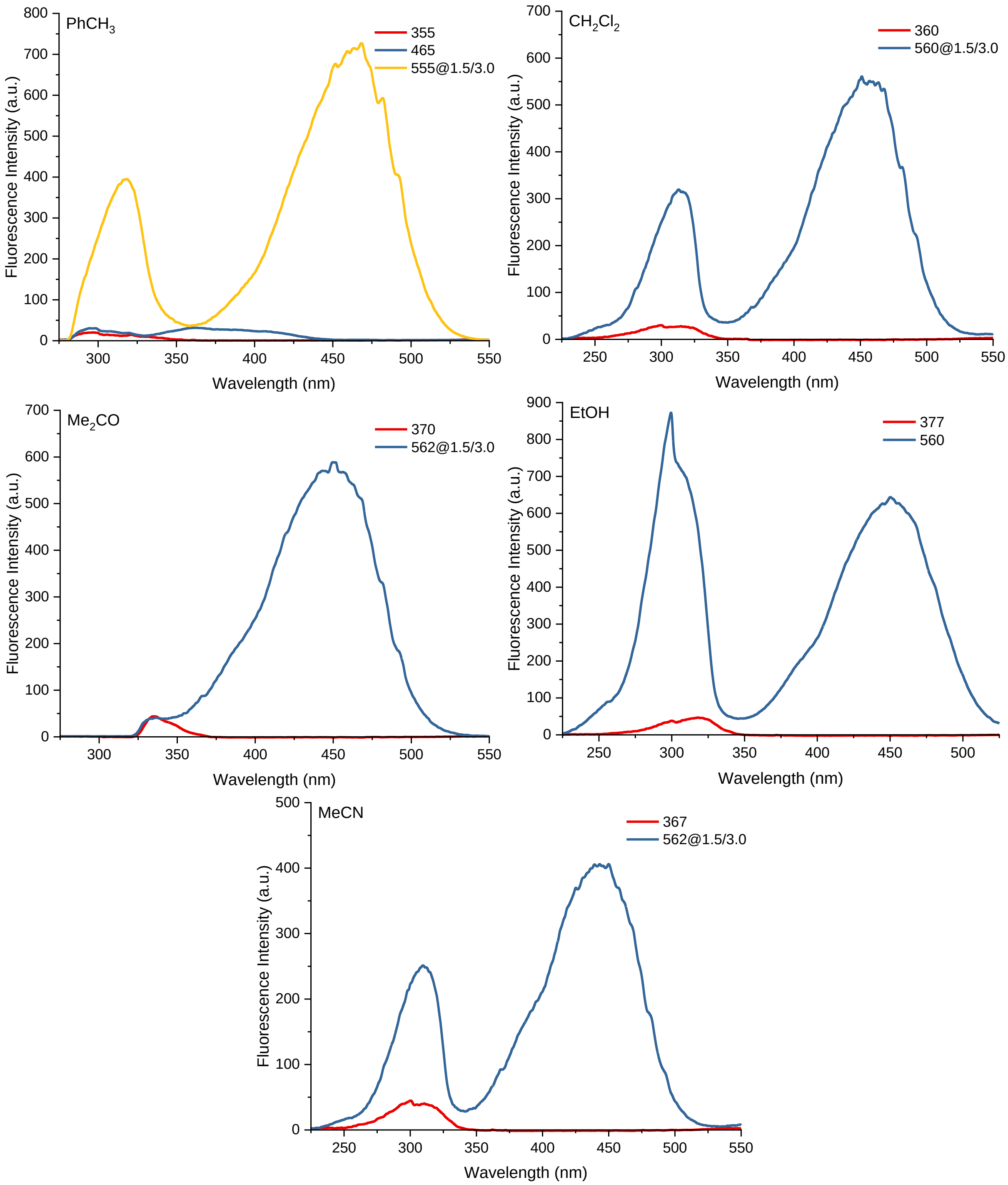


Figure S9. Excitation spectra of compound **3** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different observation wavelengths (nm).

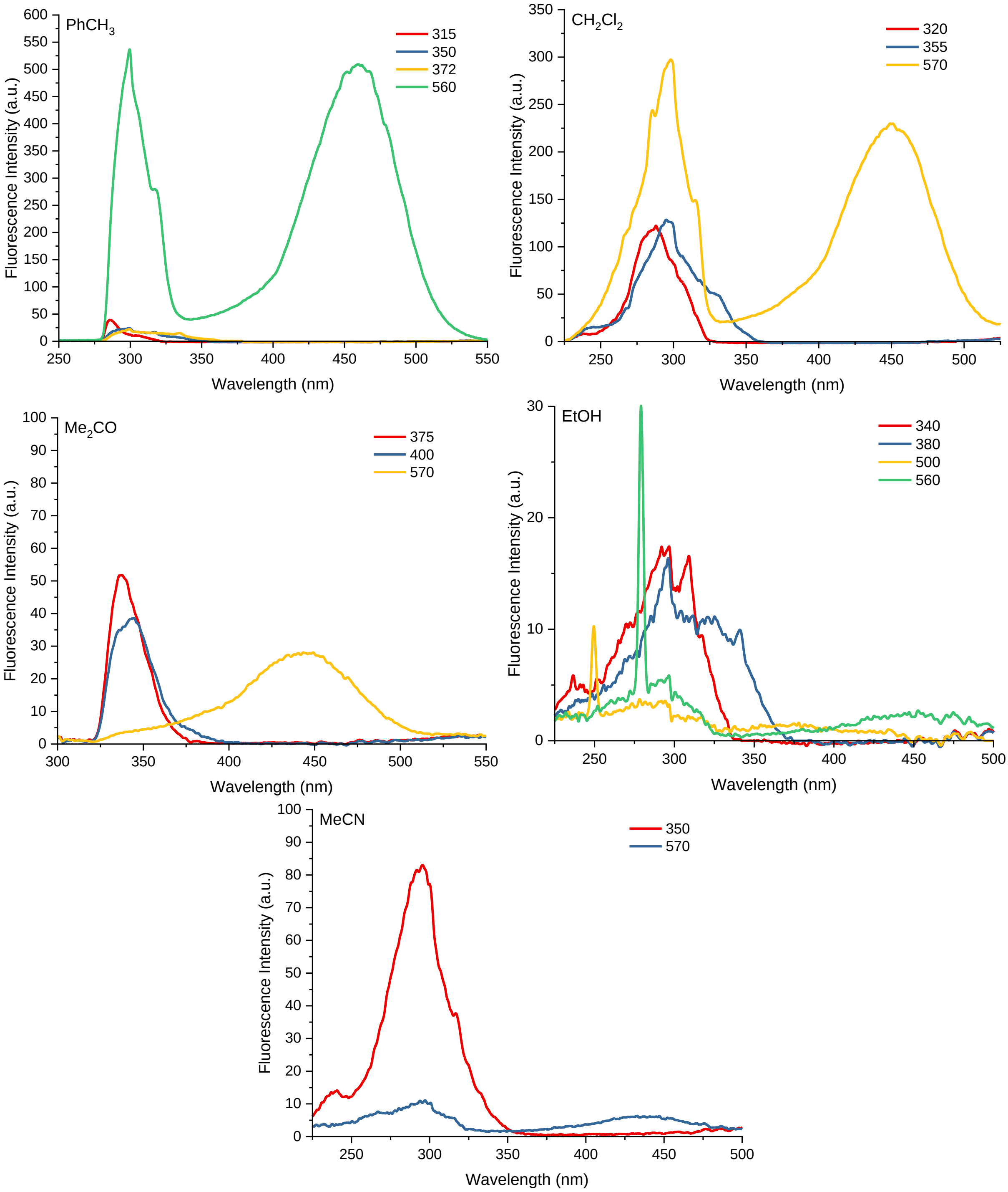


Figure S10. Excitation spectra of compound **4** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different observation wavelengths (nm).

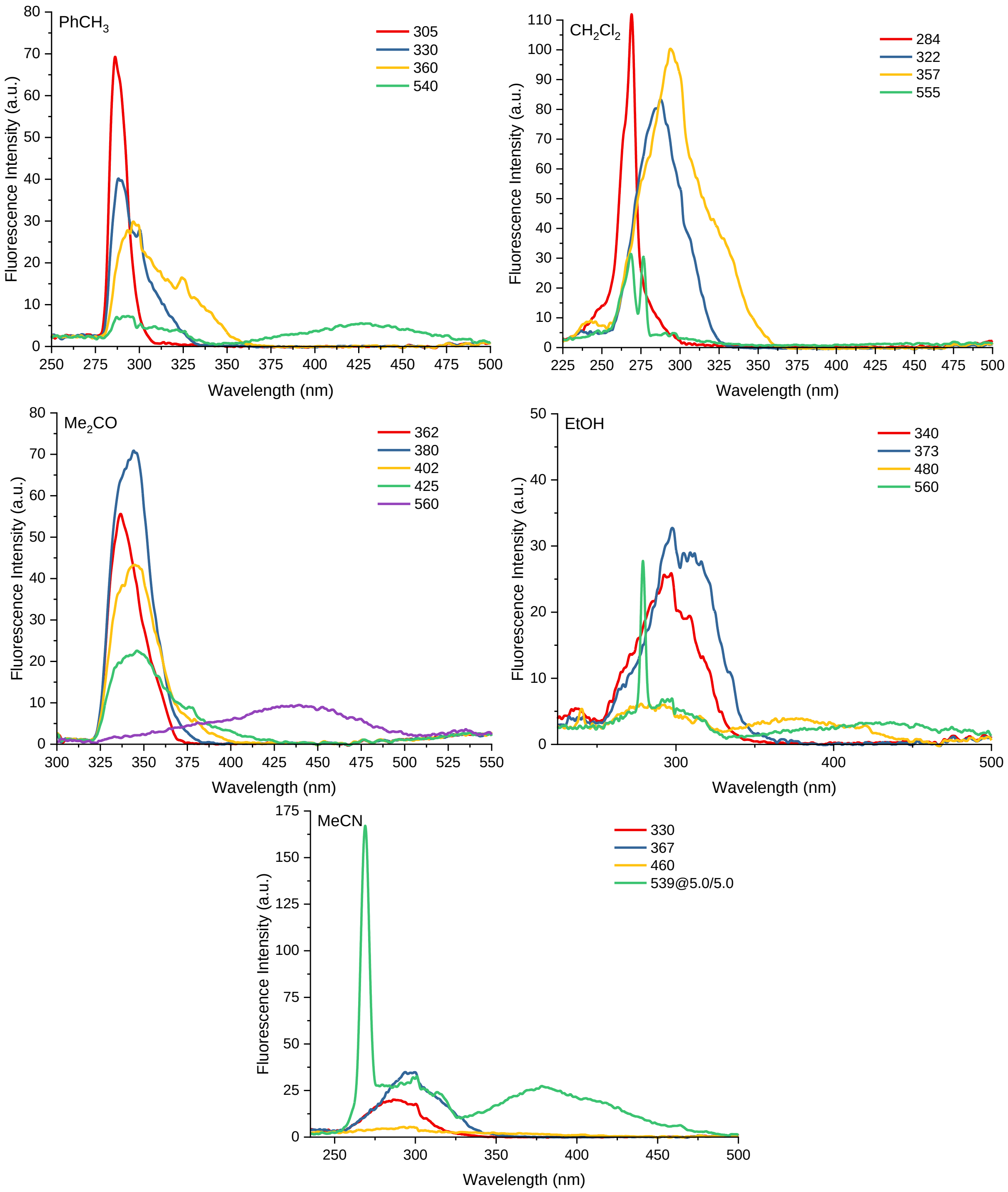


Figure S11. Excitation spectra of compound **5** in different organic solvents (ca 10^{-5} M, excitation/emission slits: 3.0/3.0 nm) at different observation wavelengths (nm).

Study of water influence

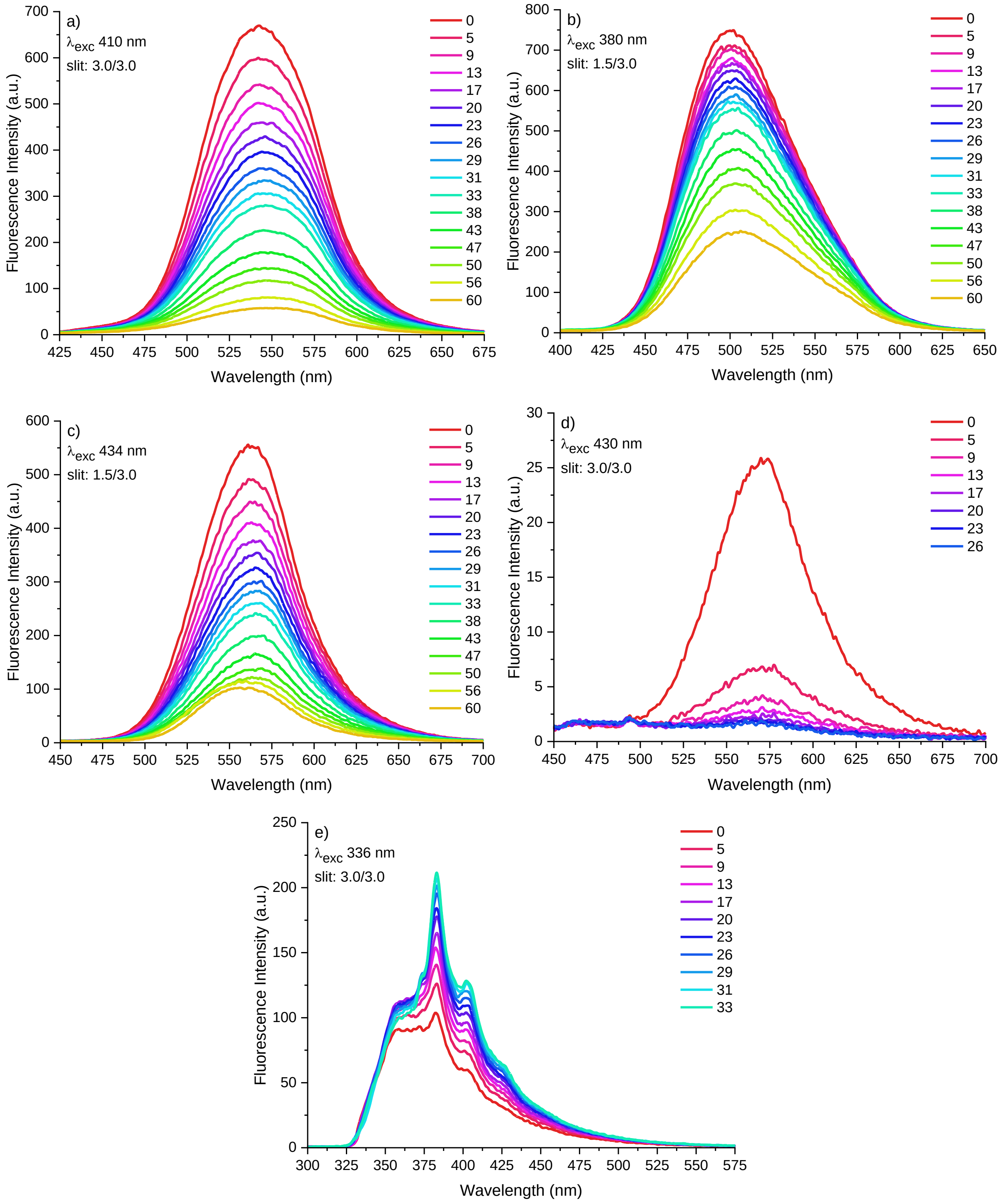
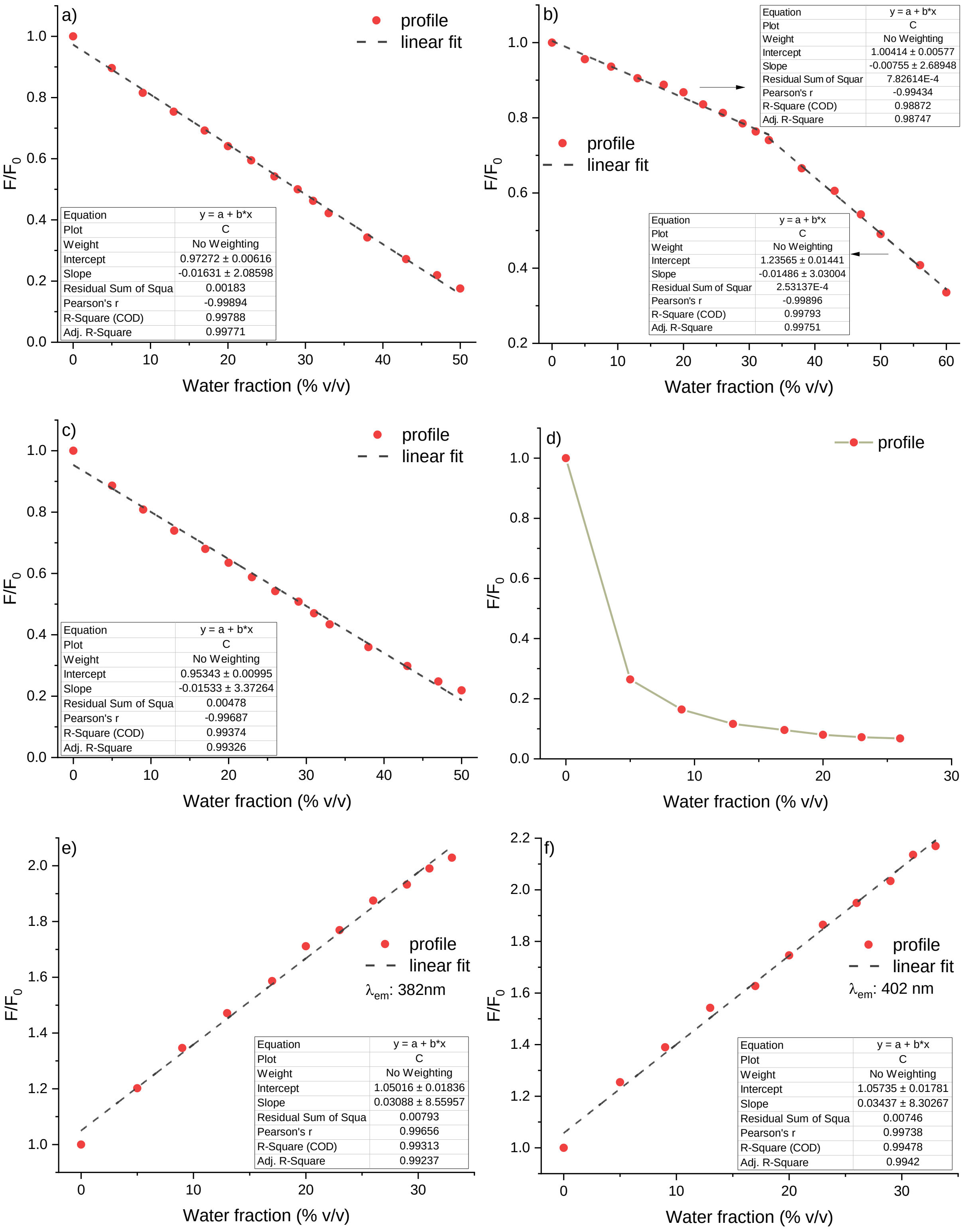


Figure S12. Steady-state fluorescence emission spectra in acetone solution of compounds a) **1**, b) **2**, c) **3**, d) **4**, and e) **5** (ca 10^{-5} M) upon successive addition of water (% v/v).



a)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	0.97272 ± 0.00616
Slope	-0.01631 ± 2.08598
Residual Sum of Squa	0.00183
Pearson's r	-0.99894
R-Square (COD)	0.99788
Adj. R-Square	0.99771

b)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.00414 ± 0.00577
Slope	-0.00755 ± 2.68948
Residual Sum of Squar	7.82614E-4
Pearson's r	-0.99434
R-Square (COD)	0.98872
Adj. R-Square	0.98747

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.23565 ± 0.01441
Slope	-0.01486 ± 3.03004
Residual Sum of Squar	2.53137E-4
Pearson's r	-0.99896
R-Square (COD)	0.99793
Adj. R-Square	0.99751

c)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	0.95343 ± 0.00995
Slope	-0.01533 ± 3.37264
Residual Sum of Squa	0.00478
Pearson's r	-0.99687
R-Square (COD)	0.99374
Adj. R-Square	0.99326

e)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.05016 ± 0.01836
Slope	0.03088 ± 8.55957
Residual Sum of Squa	0.00793
Pearson's r	0.99656
R-Square (COD)	0.99313
Adj. R-Square	0.99237

f)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.05735 ± 0.01781
Slope	0.03437 ± 8.30267
Residual Sum of Squa	0.00746
Pearson's r	0.99738
R-Square (COD)	0.99478
Adj. R-Square	0.9942

Figure S13. Fluorescence emission ratio F/F$_0$ of compounds a) **1**, b) **2**, c) **3**, d) **4**, and e) **5** at λ_{em} 382 nm and f) **5** at λ_{em} 402 nm in acetone (ca 10^{-5} M) upon successive addition of water (% v/v).

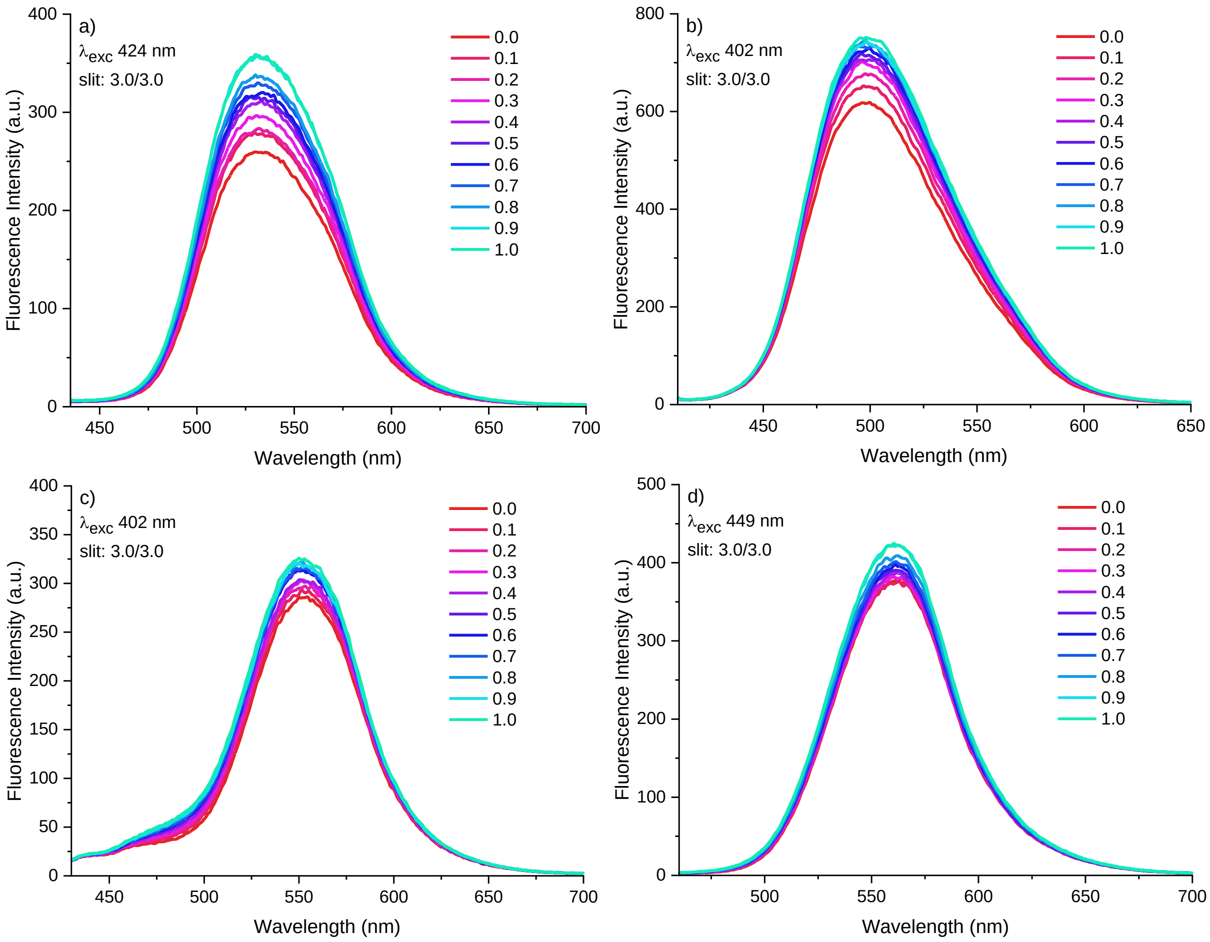


Figure S14. Steady-state fluorescence emission spectra in dry toluene solution of compounds a) **1**, b) **2**, c) **3**, and d) **4** (ca 10^{-5} M) upon successive addition of water (% v/v).

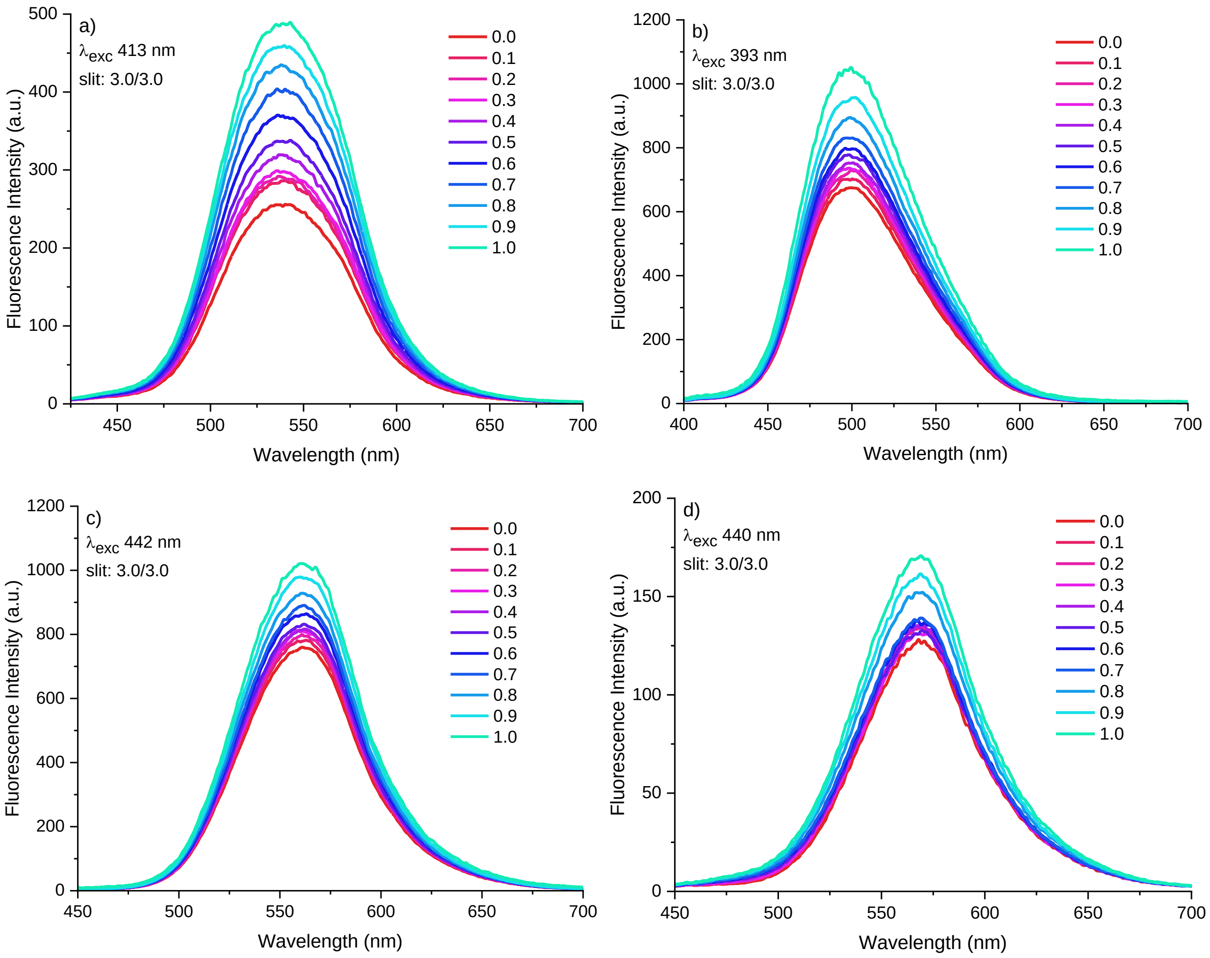
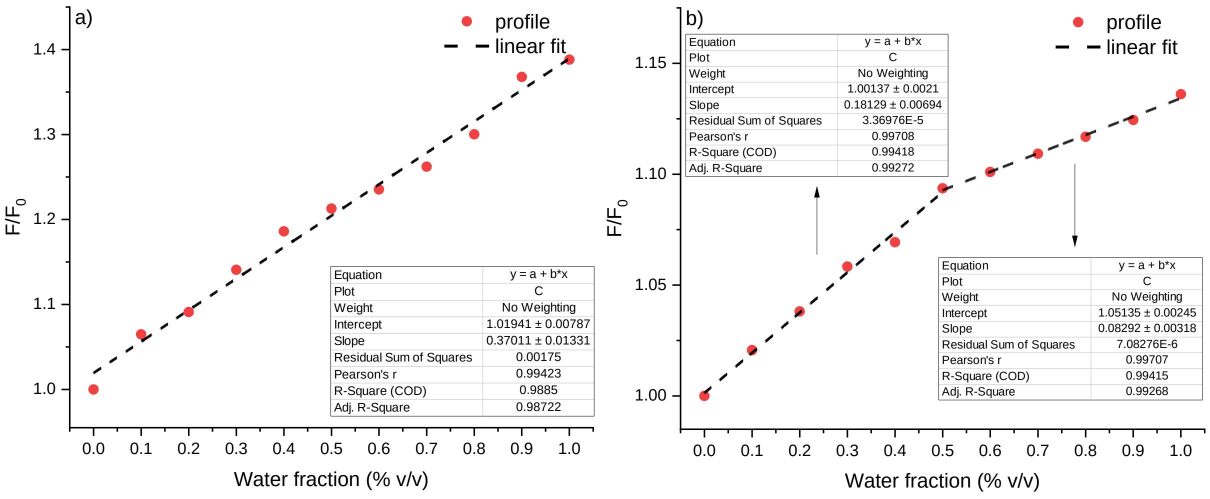


Figure S15. Steady-state fluorescence emission spectra in dry dichloromethane solution of compounds a) **1**, b) **2**, c) **3**, and d) **4** (ca 10^{-5} M) upon successive addition of water (% v/v).



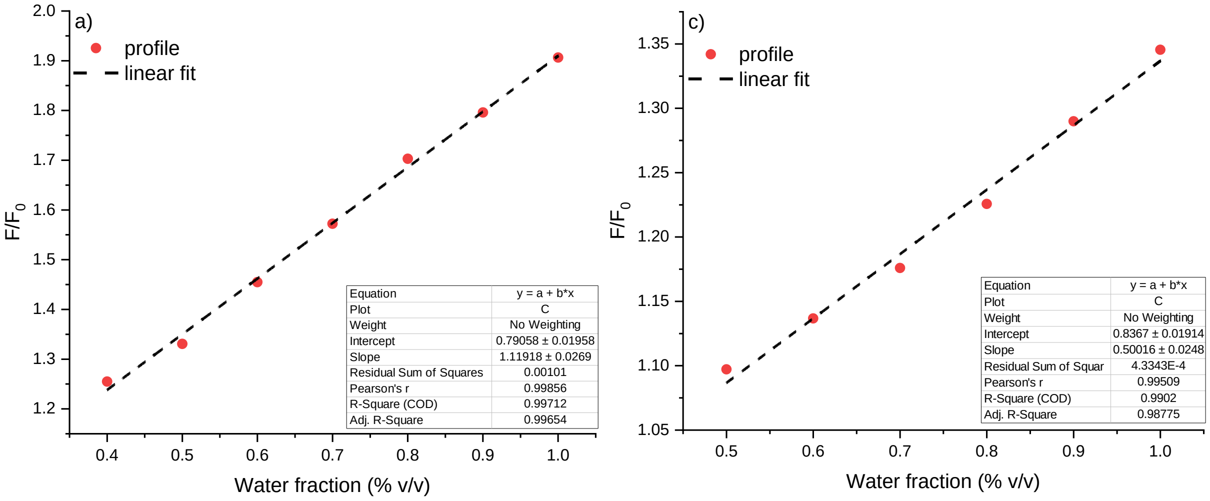
Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.01941 ± 0.00787
Slope	0.37011 ± 0.01331
Residual Sum of Squares	0.00175
Pearson's r	0.99423
R-Square (COD)	0.9885
Adj. R-Square	0.98722

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.00137 ± 0.0021
Slope	0.18129 ± 0.00694
Residual Sum of Squares	3.36976E-5
Pearson's r	0.99708
R-Square (COD)	0.99418
Adj. R-Square	0.99272

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	1.05135 ± 0.00245
Slope	0.08292 ± 0.00318
Residual Sum of Squares	7.08276E-6
Pearson's r	0.99707
R-Square (COD)	0.99415
Adj. R-Square	0.99268

Figure S16. Fluorescence emission ratio F/F_0 of compounds a) **1** and b) **3** in dry toluene (ca 10^{-5} M) upon successive addition of water (% v/v).

.



Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	0.79058 ± 0.01958
Slope	1.11918 ± 0.0269
Residual Sum of Squares	0.00101
Pearson's r	0.99856
R-Square (COD)	0.99712
Adj. R-Square	0.99654

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	0.8367 ± 0.01914
Slope	0.50016 ± 0.0248
Residual Sum of Squar	4.3343E-4
Pearson's r	0.99509
R-Square (COD)	0.9902
Adj. R-Square	0.98775

Figure S17. Fluorescence emission ratio F/F_0 of compounds a) **1** and b) **3** in dry dichloromethane (ca 10^{-5} M) upon successive addition of water (% v/v).

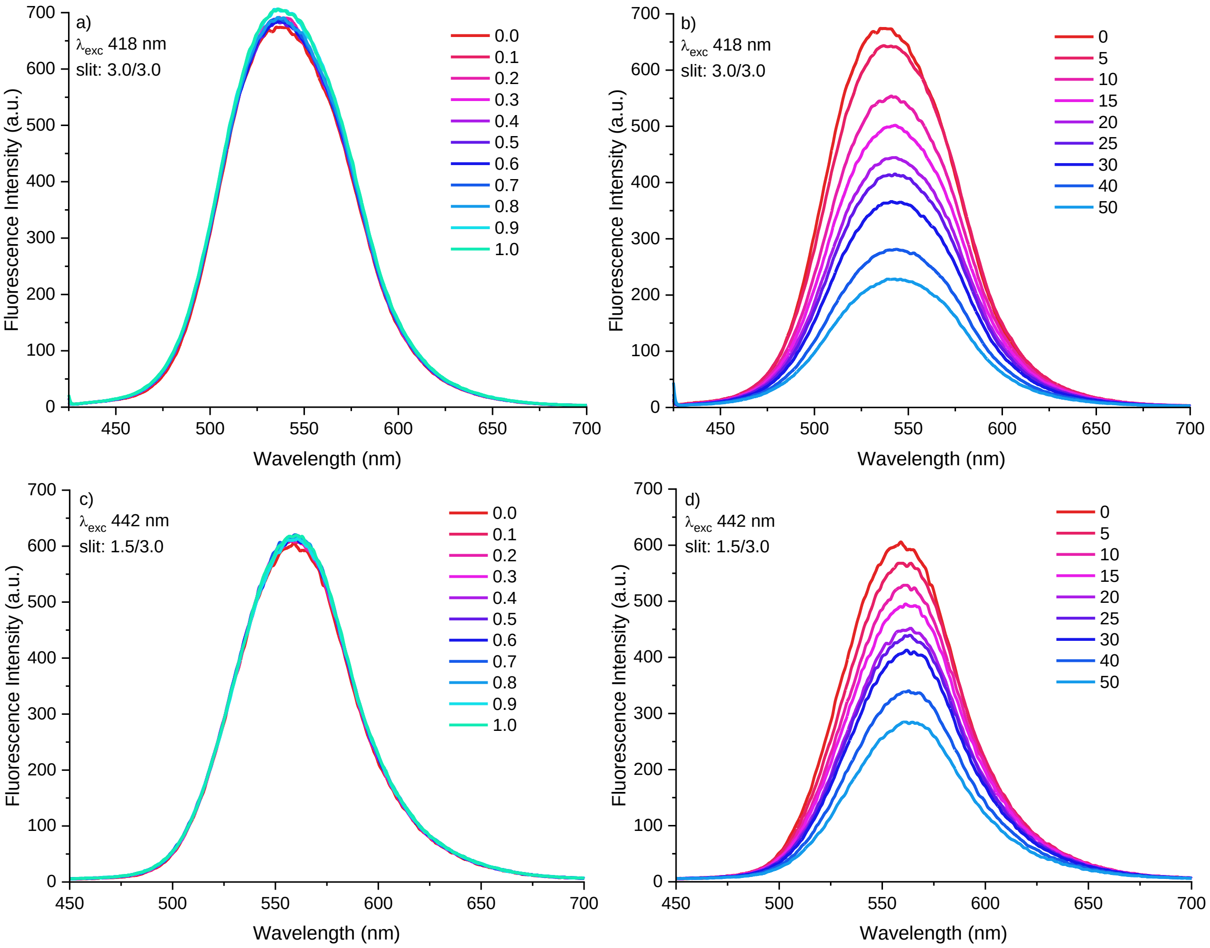
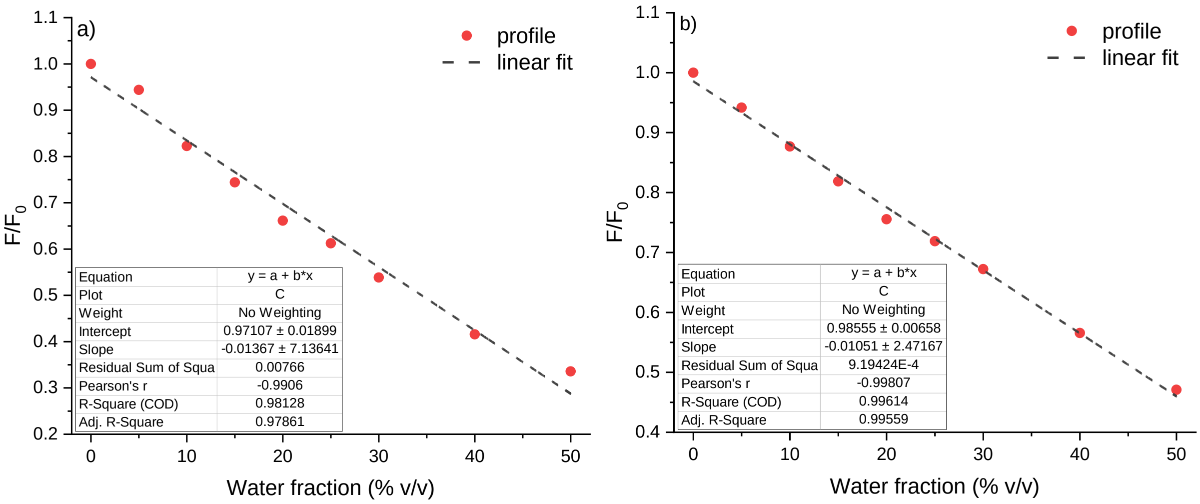


Figure S18. Steady-state fluorescence emission spectra in dry THF solution of compounds a) **1** in the range of 0 – 1%, b) **1** in the range of 0 – 50%, c) **3** in the range of 0 – 1%, and d) **3** in the range of 0 – 50% (ca 10^{-5} M) upon successive addition of water (% v/v).



a)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	0.97107 ± 0.01899
Slope	-0.01367 ± 7.13641
Residual Sum of Squa	0.00766
Pearson's r	-0.9906
R-Square (COD)	0.98128
Adj. R-Square	0.97861

b)

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	0.98555 ± 0.00658
Slope	-0.01051 ± 2.47167
Residual Sum of Squa	9.19424E-4
Pearson's r	-0.99807
R-Square (COD)	0.99614
Adj. R-Square	0.99559

Figure S19. Fluorescence emission ratio F/F_0 of compounds a) **1** and b) **3** in dry THF (ca 10^{-5} M) upon successive addition of water (% v/v).

Theoretical Calculations

Table S1. The photophysics data from theoretical predictions where the conditions at vacuum level or solvent simulated by CPCM, λ_{calc} is the first electronic transition (nm), f is oscillator strength, Assignment of orbitals concerning the first transition, D is the dipole moment expressed in Debye, λ_{exp} is the experimental maximum absorption (nm), ΔE is the difference of energy between theoretical and experimental absorption (eV), L and R is a side of two substitutions on the benzothiadiazole moiety, and the respective angle between the benzothiadiazole plane (degrees), and the level HOMO and LUMO (eV). For compound **5**, the S_1 and T_1 are the energy of the first level singlet and triplet, and ΔE is the difference of energy between the two states.

Dye	Condition	$\lambda_{calc.}$ (nm)	f	Assignment	Dipole (D)	$\lambda_{exp.}$ (nm)	ΔE (eV)	L (º)	R (º)	HOMO (eV)	LUMO (eV)
1	Vacuum	439	0.25	H→L 96%	2.3	-	-	0.4	1.1	-6.20	-2.81
	$PhCH_3$	429	0.33	H→L 97%	3.2	424	-0.03	19.5	20.1	-6.28	-2.74
	CH_2Cl_2	414	0.32	H→L 97%	3.9	413	-0.01	24.5	27.3	-6.34	-2.71
	EtOH	409	0.32	H→L 96%	4.1	405	-0.03	26.4	28.5	-6.36	-2.70
	Me_2CO	410	0.32	H→L 96%	4.0	411	0.01	26.2	28.5	-6.35	-2.70
	MeCN	409	0.32	H→L 96%	4.1	403	-0.04	26.7	29.0	-6.36	-2.70
2	Vacuum	412	0.29	H→L 97%	6.1	-	-	-9.8	12.1	-6.85	-328
	$PhCH_3$	397	0.37	H→L 97%	6.7	402	0.04	-25.0	24.5	-6.79	-3.04
	CH_2Cl_2	383	0.37	H→L 96%	7.3	393	0.08	-29.2	28.7	-6.75	-2.90
	EtOH	379	0.36	H→L 96%	7.4	386	0.06	-30.5	30.1	-6.75	-2.86
	Me_2CO	380	0.36	H→L 96%	7.4	383	0.03	-29.9	29.8	-6.75	-2.87
	MeCN	378	0.36	H→L 96%	7.4	379	0.01	-30.8	30.5	-6.75	-2.85
3	Vacuum	452	0.42	H→L 97%	1.5	-	-	45.1	-1.0	-6.06	-2.75
	$PhCH_3$	450	0.52	H→L 98%	2.0	451	0.00	46.0	-2.0	-6.10	-2.72
	CH_2Cl_2	441	0.52	H→L 98%	2.4	442	0.01	46.7	-2.8	-6.13	-2.71
	EtOH	443	0.52	H→L 98%	2.3	436	-0.05	46.8	-2.8	-6.14	-2.71
	Me_2CO	441	0.52	H→L 98%	2.4	435	-0.04	46.8	-2.8	-6.13	-2.71
	MeCN	441	0.52	H→L 98%	2.4	428	-0.08	46.8	-2.8	-6.14	-2.71
4	Vacuum	503	0.18	H→L 98%	0.1	-	-	-4.4	45.1	-5.86	-2.75
	$PhCH_3$	492	0.21	H→L 99%	0.1	449	-0.24	-45.5	47.6	-5.89	-2.68
	CH_2Cl_2	478	0.20	H→L 99%	0.3	440	-0.22	-46.9	49.3	-5.92	-2.63
	EtOH	474	0.20	H→L 99%	0.4	438	-0.22	-47.3	49.8	-5.92	-2.62
	Me_2CO	476	0.20	H→L 99%	0.3	431	-0.27	-46.7	49.0	-5.91	-2.62
	MeCN	473	0.19	H→L 99%	0.4	424	-0.30	-47.4	49.9	-5.93	-2.62

Dye	Condition	$\lambda_{calc.}$ (nm)[a]	f	S_1	T_1	$\lambda_{exp.}$ (nm)	ΔE_{st} (eV)	L (º)	R (º)	HOMO (eV)	LUMO (eV)
5	Vacuum	410	0.001	1.824	1.814	-	0.01	81.3	80.7	-5.51	-2.92
	$PhCH_3$	394	0.002	1.950	1.940	450	0.01	81.3	80.8	-5.55	-2.83
	CH_2Cl_2	383	0.002	2.055	2.045	450	0.01	81.2	80.7	-5.58	-2.77
	EtOH	381	0.002	2.035	2.025	450	0.01	81.2	80.7	-5.58	-2.76
	Me_2CO	381	0.002	2.054	2.044	448	0.01	81.2	80.7	-5.58	-2.76
	MeCN	380	0.002	2.059	2.049	443	0.01	81.1	80.7	-5.59	-2.76

[a] relation to the state 3 transition.