

Supplementary Materials

Synthesis, Characterization, Fluorescence Properties, and DFT Modeling of Difluoroboron Biindolediketones

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S1. Synthesis of starting materials

S1.1. 5-Chloro-N-methyl-1H-indole (2b)

Under inert atmosphere 5-chloro-1H-indole (3 g, 20 mmol, 1 equiv.) is dissolved in dry THF (80 mL) and sodium hydride (1.2 g, 60% suspension in mineral oil, 1.5 equiv.) is slowly added at 0 °C. After being stirred at 0 °C for 1.5 h methyl iodide (1.62 mL, 26 mmol, 1.3 equiv.) is added. The mixture is then warmed to rt and stirred overnight. After cooling again to 0 °C, the reaction is quenched with water (40 mL) and extracted with diethyl ether (3x50 mL); the combined organic layers are dried over Na₂SO₄, filtered and the solvent removed under reduced pressure. The resulting crude product is purified via column chromatography (n-Hexane/EtOAc 9:1, R_f = 0.56) to give 5-chloro-N-methyl-1H-indole (2.84 g, 85% yield). ¹H-NMR (CDCl₃) δ = 7.58 (d, *J* = 1.6 Hz, 1H, ArH), 7.26 - 7.15 (m, 2H, ArH), 7.06 (d, *J* = 3.2 Hz, 1H, ArH), 6.42 (d, *J* = 3.2 Hz, 1H, ArH), 3.27 (s, 3H, NCH₃).

S1.2. 5-Methoxy-N-methyl-1H-indole (2c)

Under inert atmosphere, 5-Methoxy-1H-indole (2 g, 13.6 mmol, 1 eq.) is dissolved in dry THF (60 mL) and sodium hydride (0.81 g, 60% suspension in mineral oil, 1.5 eq.) is slowly added 0 °C. After being stirred at 0 °C for 1.5 min, methyl iodide (1.1 mL, 17.7 mmol, 1.3 eq.) is added. The mixture is warmed to rt and stirred overnight. After cooling again to 0 °C, the reaction is quenched with water (40 mL) and extracted with diethyl ether (3x50 mL); the combined organic layers are dried over Na₂SO₄, filtered and the solvent removed under reduced pressure. The resulting crude product is purified via column chromatography (n-Hexane/EtOAc 9:1) to give 5-methoxy-N-methyl-1H-indole (2.09 g, 94% yield). ¹H-NMR (CDCl₃) δ = 7.30 (d, 1H, *J* = 8.5 Hz, ArH), 7.13 (s, 1H, ArH), 7.05 (s, 1 H, ArH), 6.92 (d, 1H, *J* = 8.8 Hz, ArH), 6.43 (d, 1H, *J* = 1.0 Hz, ArH), 3.90 (s, 3H, NCH₃), 3.80 (s, 3H, OCH₃).

S1.3. 1,3-Bis(1-methyl-1H-indol-3-yl)propane-1,3-dione HBIP (3a)

Under inert atmosphere, a solution of malonyl dichloride (1 mL, 10 mmol) in dichloromethane (10 mL) is added dropwise to a stirred solution of 1-methyl-1H-indole (2.55 mL, 20 mmol) in dichloromethane (15 mL) at 0 °C. The reaction is stirred for 2h at rt. The mixture is then added to 5% aqueous sodium carbonate, vigorously stirred for 2 min and extracted with dichloromethane, dried over sodium sulfate and evaporated. The residue is purified via column chromatography (DCM/EtOAc 95:5) to obtain HBIP as a yellow powder (1.42 g, 42% yield). ¹H-NMR (d₆-DMSO) δ = 17.4 (keto-enol, br s, 1H, enol OH) 8.44 (diketo, s, 2H), 8.40 (keto-enol, s, 2H), 8.23 (keto-enol, d, ³*J* = 7.6 Hz, 2H), 8.16 (diketo, d, ³*J* = 7.6 Hz, 2H), 7.56 (diketo/keto-enol, m, 4H), 7.29 (diketo/keto-enol, m, 4H), 7.23 (diketo/keto-enol, m, 4H), 6.77 (keto-enol, s, 1H, enol CH), 4.39 (diketo, s, 2H, diketo CH₂), 3.91 (keto-enol, s, 6H, N-CH₃) 3.89 (diketo, s, 6H, N-CH₃). IR (ATR) $\tilde{\nu}$ (cm⁻¹) = 3105 (w), 1618 (vs), 1575 (w), 1524 (vs), 1487 (vw), 1461 (s), 1421 (vw), 1391 (vw), 1365 (vs), 1334 (w), 1218 (s), 1126 (m), 1089 (s), 1081 (s), 1056 (w), 919 (s), 855 (w), 762 (w), 746 (s), 683 (w).

S1.4 1,3-Bis(5-chloro-1-methyl-1H-indol-3-yl)propane-1,3-dione HBCIIP (3b)

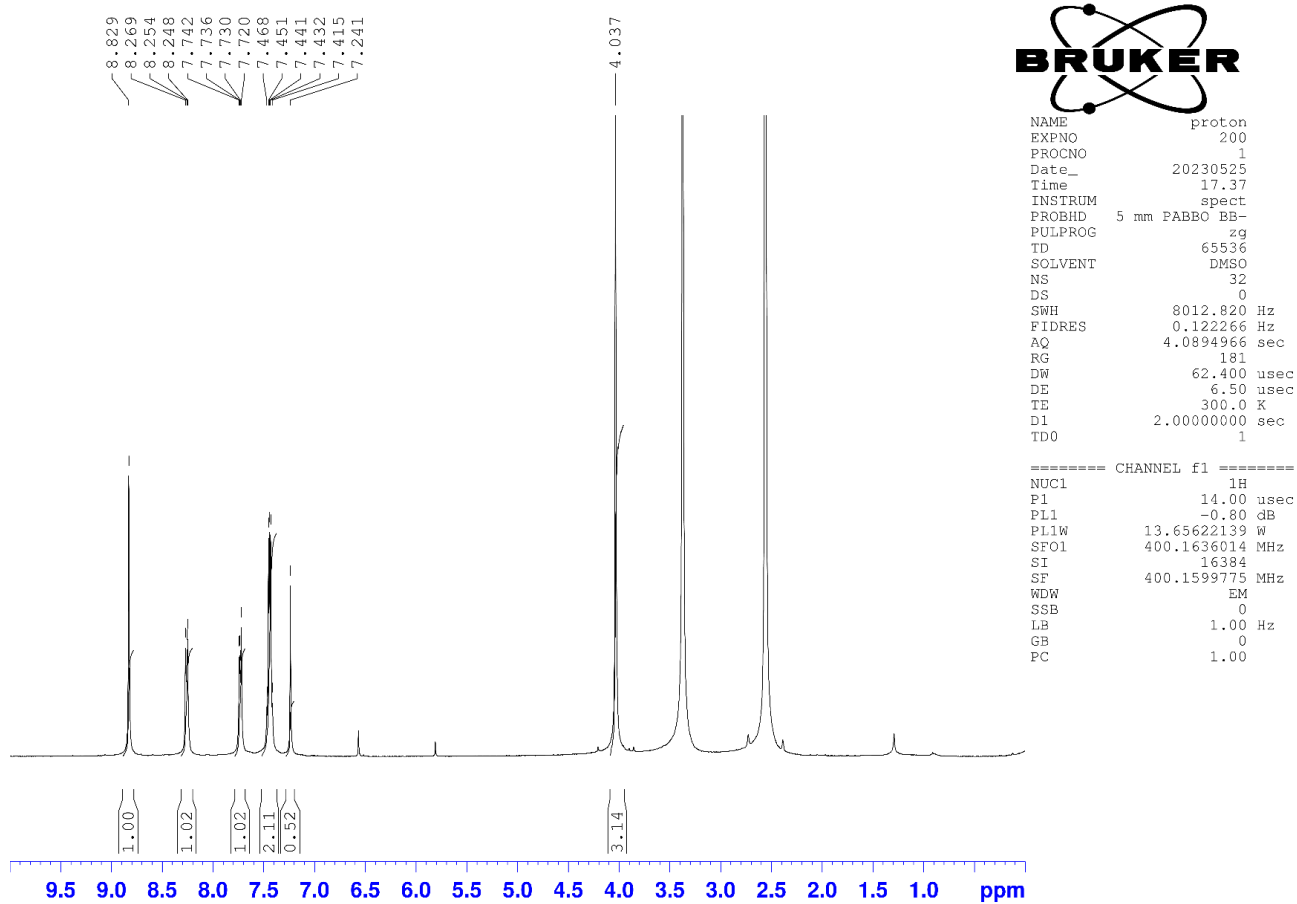
Under inert atmosphere a solution of malonyl dichloride (973 μ L, 10 mmol, 1 eq.) in dichloromethane (10 mL) is added dropwise to a stirred solution of 5-chloro-1-methyl-1H-indole (3.31 g, 20 mmol, 2 eq.) in dichloromethane (20 mL) at 0 °C. The reaction is stirred for 2h at rt and then added to a 5% aqueous sodium carbonate solution, vigorously stirred for 2 min and extracted with dichloromethane, dried over Na₂SO₄ and evaporated. The residue is purified via column chromatography (DCM/n-Hexane 9:1) to obtain HBCIIP as a yellow powder (0.911 g, 23% yield). ¹H-NMR (d₆-DMSO) δ = 8.5 (diketo, s, 2H, H2), 8.47 (keto-enol, s, 2H, H2) 8.19 (keto-enol, d, 2H, ⁴*J* = 1.8 Hz, H4), 8.14 (diketo, d, 2H, ⁴*J* = 1.5 Hz, H4), 7.63 (keto-enol, d, 2H, ³*J* = 8.4 Hz) 7.61 (diketo, d, 2H, ³*J* = 8.7 Hz, H7), 7.32 (diketo/keto-enol dd, ³*J* = 8.8 Hz, ⁴*J* = 1.6 Hz, H6, 4H), 6.77 (keto-enol, s, 1H, enol CH), 4.4 (diketo s, 2H, diketo CH₂), 3.91 (keto-enol, s, 6H, NCH₃), 3.90 (diketo, s, 6H, NCH₃). IR (ATR) $\tilde{\nu}$ (cm⁻¹) = 3105 (vw); 2928 (vw); 2894 (vw); 1645 (m); 1631 (s); 1614 (m); 1572 (w); 1528 (vs); 1471 (sh, m); 1461 (s), 1452 (s), 1421 (w), 1405 (vw), 1385 (w), 1363 (vs), 1341 (sh, w), 1311 (vw), 1289 (vw), 1271 (w), 1235 (m), 1234 (m), 1217 (s), 1176 (w), 1159 (w), 1137 (s), 1089 (vs), 1058 (m), 1044 (m), 972 (w), 955 (w), 916 (vw), 888 (w), 883 (w), 856 (vw), 844 (w), 837, (w), 820 (m), 802 (s), 776 (m), 752 (w), 747 (w), 730 (s).

S1.5 1,3-Bis(5-methoxy-1-methyl-1H-indol-3-yl)propane-1,3-dione HBMIP (3c)

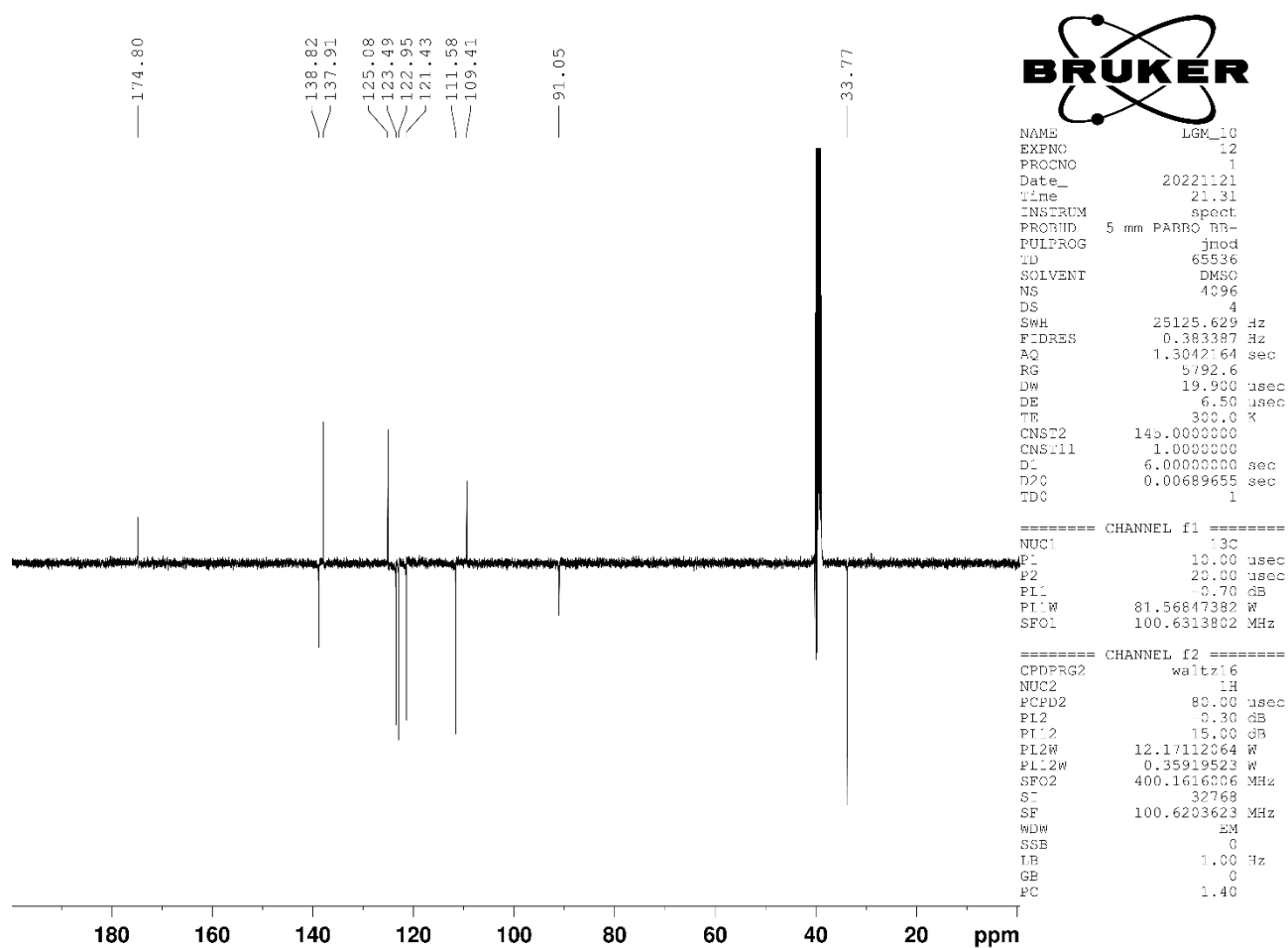
Under inert atmosphere a solution of malonyl dichloride (700 μ L, 7.17 mmol, 1 eq.) in dichloromethane (8 mL) is added dropwise to a stirred solution of 5-methoxy-1-methyl-1H-indole (2.31 g, 14.3 mmol, 2 eq.) in dichloromethane (15 mL) at 0°C. The reaction is then stirred for 2h at rt and then added to a 5% aqueous sodium carbonate solution, vigorously stirred for 2 min and extracted with dichloromethane, dried over Na₂SO₄ and evaporated. The residue is purified via column chromatography (toluene/EtOAc 7:3) to obtain HBMIP (1.26 g, 45% yield) as a yellow solid. ¹H-NMR (d₆-DMSO) δ = 8.36 (diketo, s, 2H, H2) 7.67 (diketo d, ⁴J = 2.1 Hz, 2H, H4), 7.45 (diketo, d, ³J = 9 Hz, 2H, H7), 6.91 (diketo, dd, ³J = 9 Hz, ⁴J = 2.3 Hz, 2H, H6), 4.34 (diketo, s, 2H, diketo CH₂), 3.85 (diketo, s, 6H), 3.77 (diketo, s, 6H). IR (ATR) (cm⁻¹) = 2941 (w), 1713 (w), 1619 (vs), 1521 (s), 1477 (s), 1453 (vs), 1361 (vs), 1264 (s), 1222 (s), 1210 (s), 1181 (m), 1139 (m), 1131 (s), 1083 (s), 1021 (s), 912 (m), 873 (s), 853 (s), 835 (s), 799 (vs), 778 (m), 683 (m), 654 (vs), 640 (s).

S2. NMR spectroscopy data on 4a

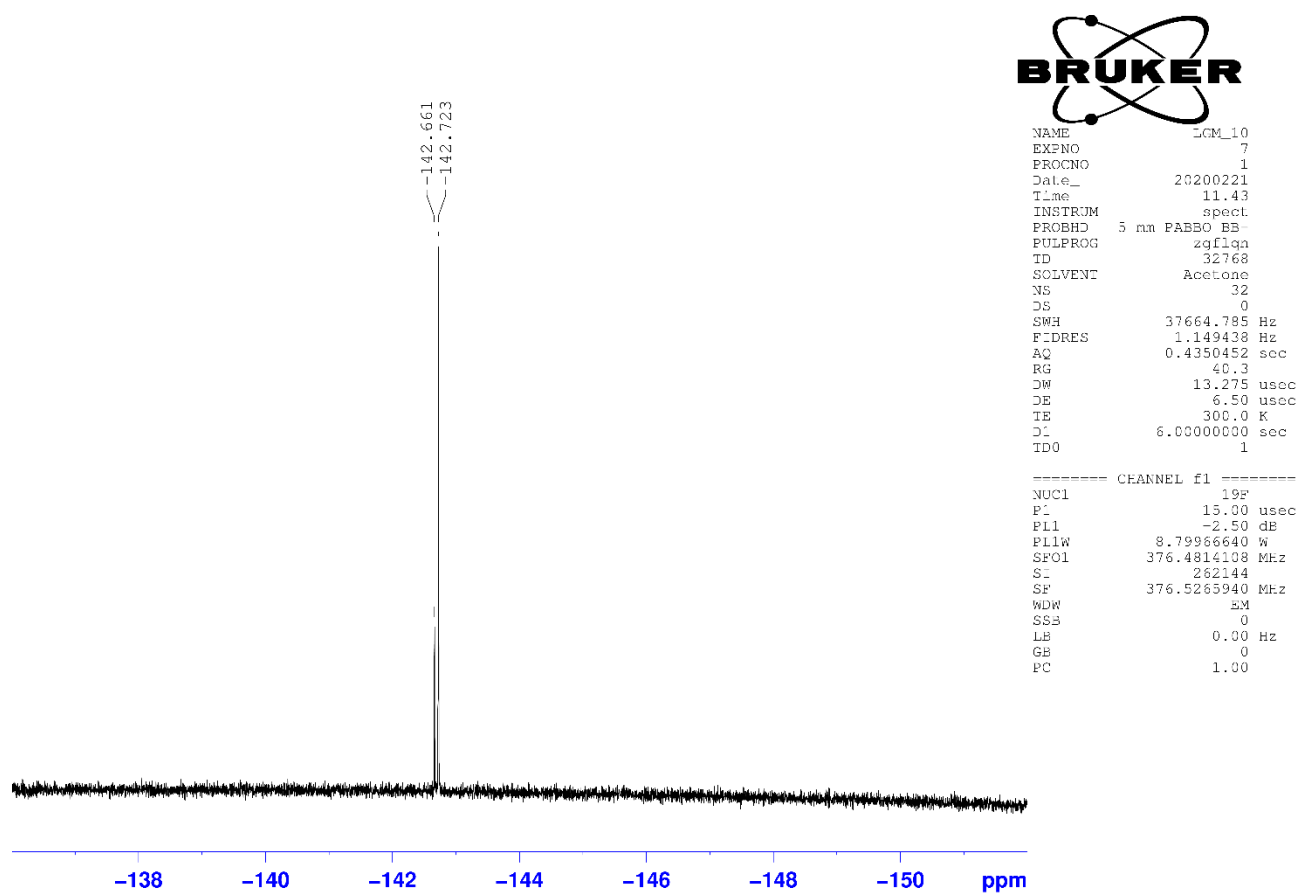
S2.1. ¹H-NMR spectrum of BF₂BIP (4a)



S2.2. ^{13}C -NMR spectrum of BF2BIP (4a)



S2.3. ^{19}F -NMR spectrum of BF2BIP (4a)



S2.4. ^{11}B -NMR spectrum of BF₂BIP (4a)

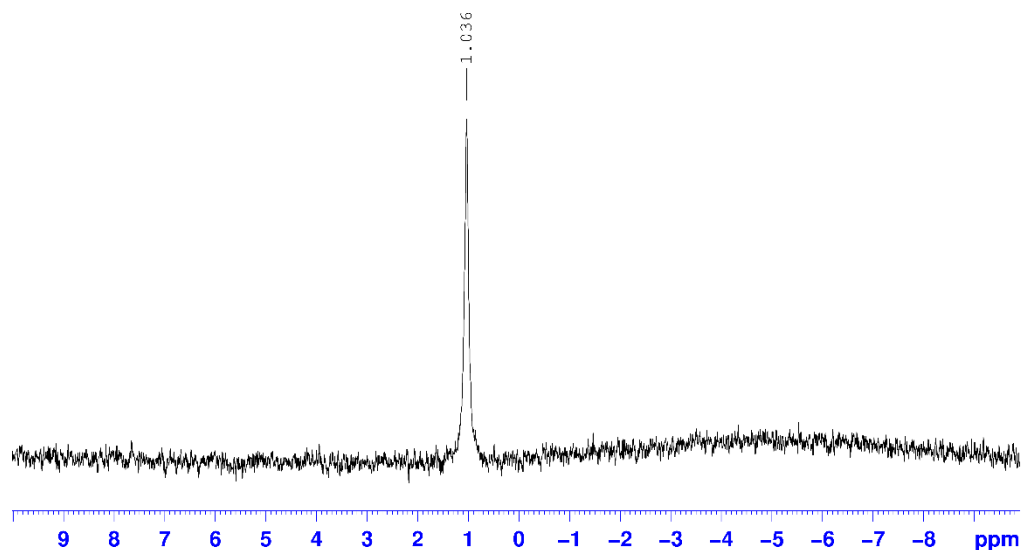


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PULPROG       zg
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SOLVENT       Acetone
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DS            2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
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RG            29193
DW            78.000 usec
DE            6.50 usec
TE            300.0 K
D1            5.0000000 sec
TD0           1

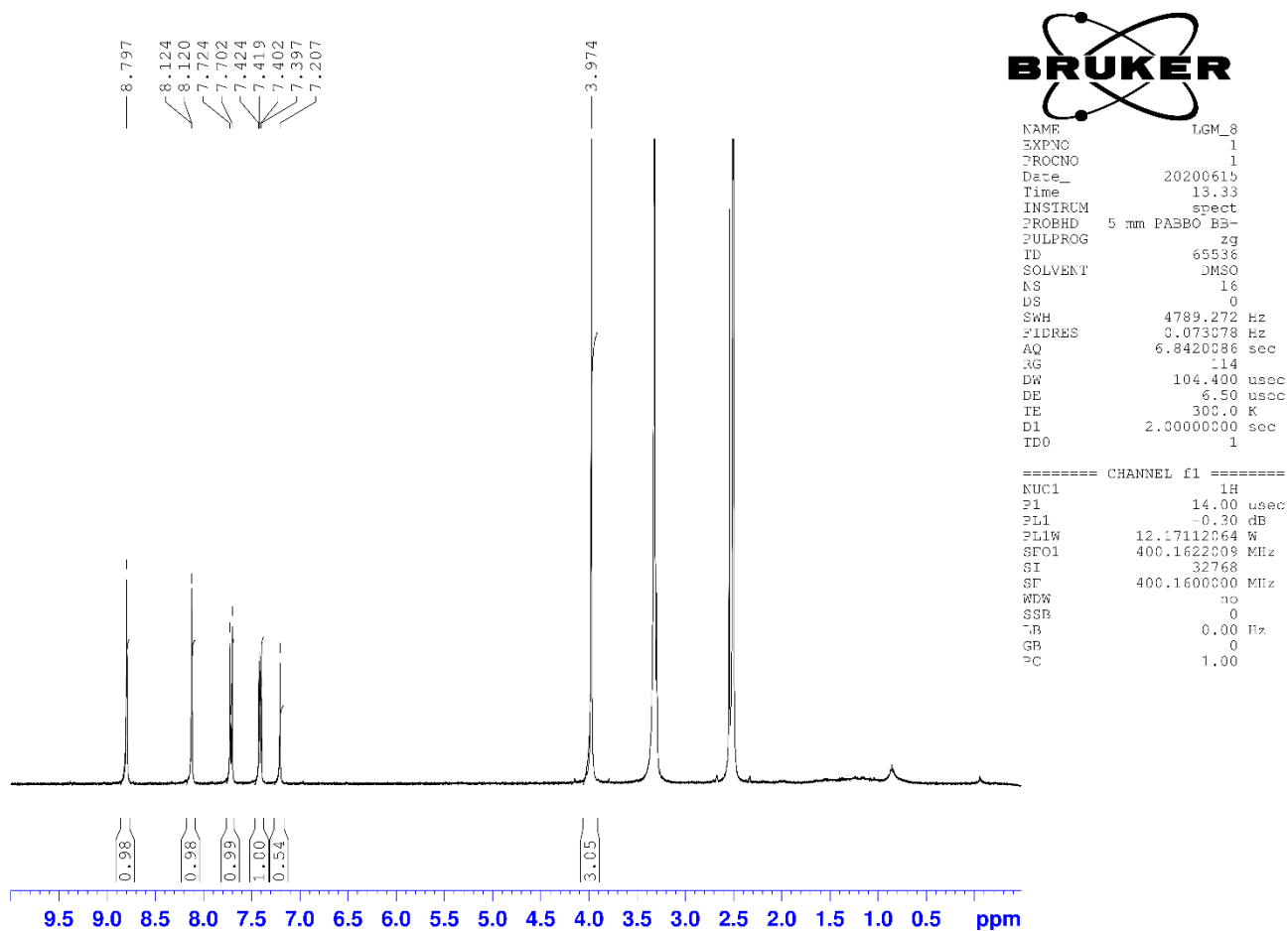
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ST            32768
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WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.00

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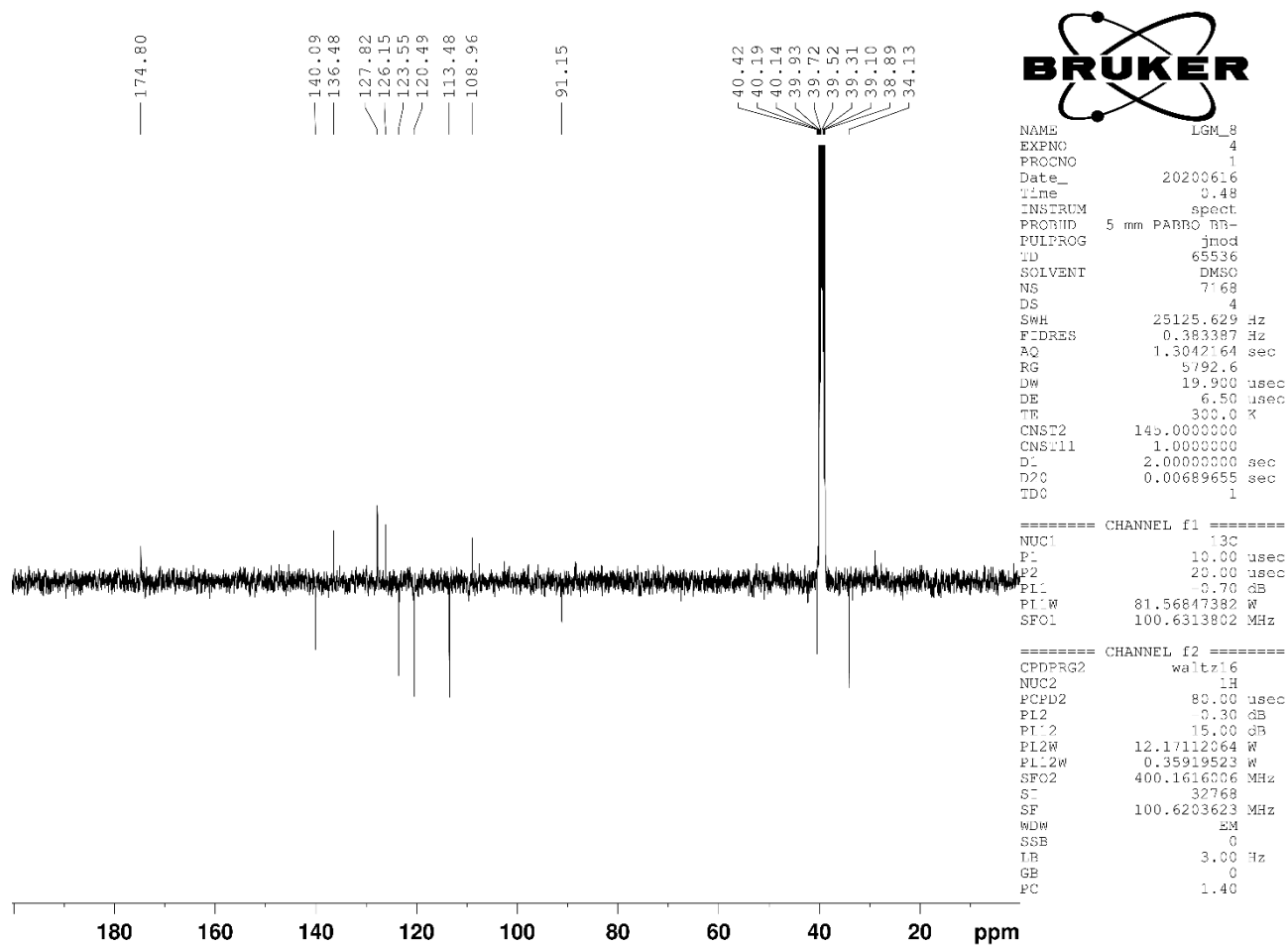


S3. NMR spectroscopy data on 4b

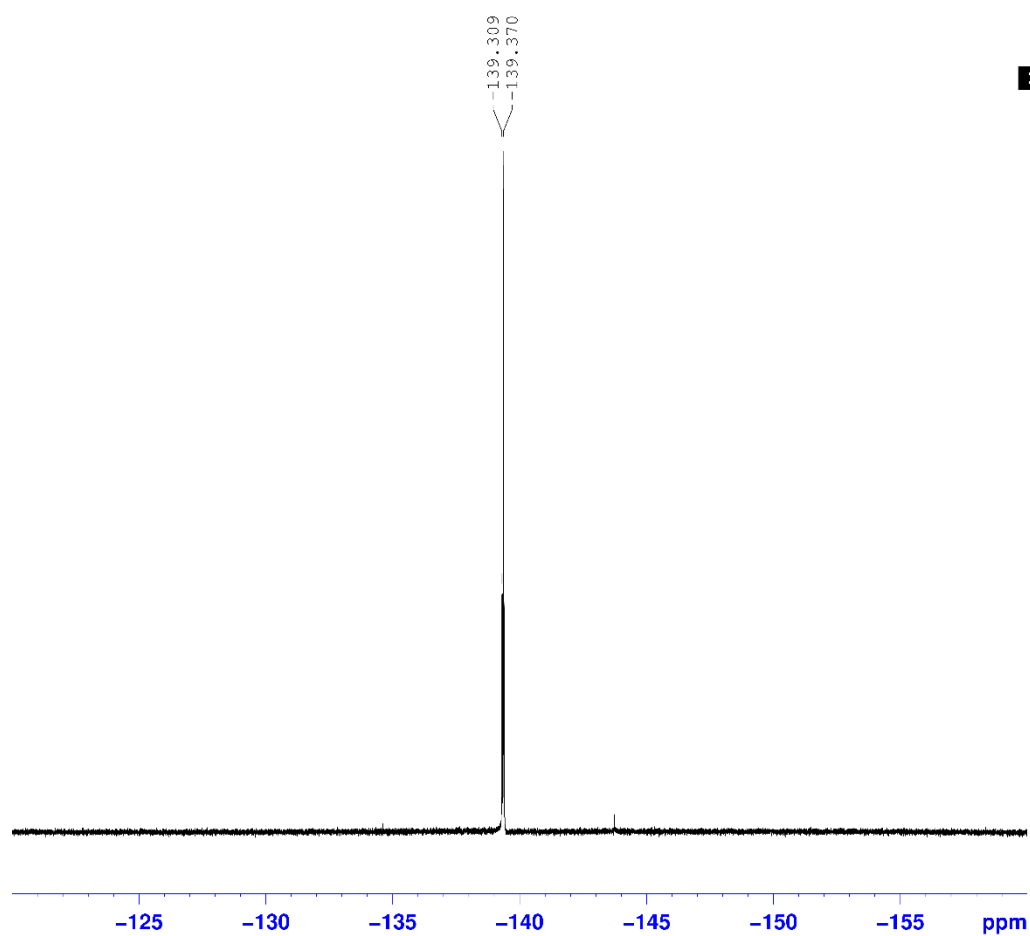
S3.1. ^1H -NMR spectrum of BF₂CIBIP (4b)



S3.2. ^{13}C -NMR spectrum of BF₂CIBIP (4b)



S3.3. ^{19}F -NMR spectrum of BF₂CIBIP (4b)



```

NAME          LGM_8
EXPNO         3
PROCNO        1
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Time          14.14
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PULPROG       zgpg30
TD            32768
SOLVENT       DMSO
NS            32
DS            0
SWH           30120.492 Hz
FIDRES        0.919204 Hz
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RG            40.3
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TE            300.0 K
D1            6.0000000 sec
TD0           1

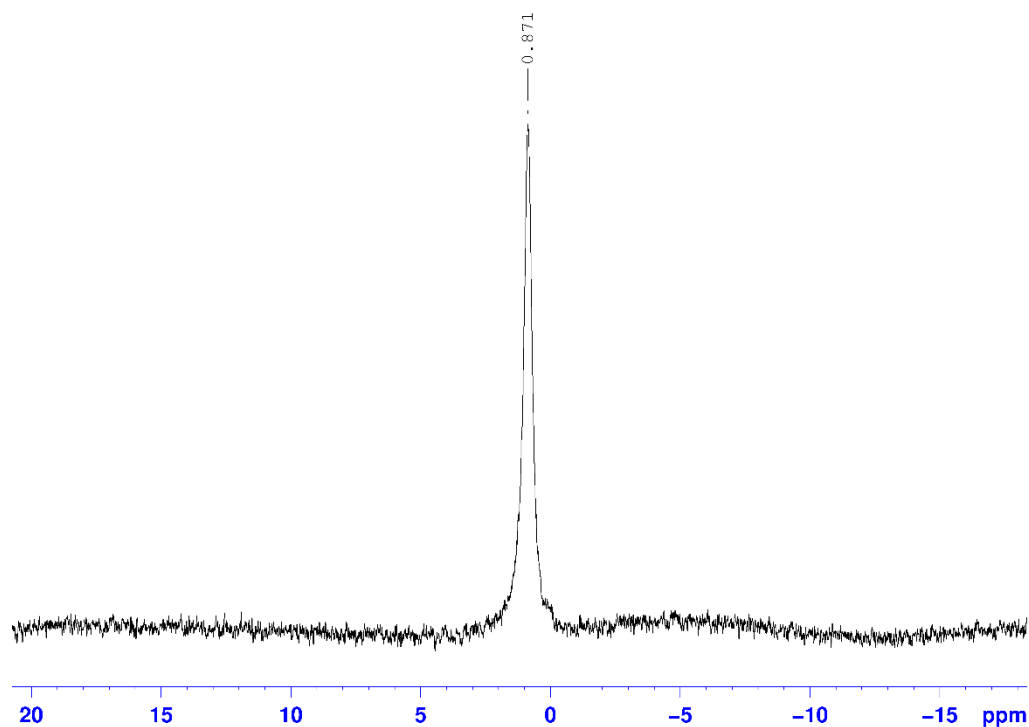
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SI            262144
SF            376.5265940 MHz
WDW           EM
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LB            0.00 Hz
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PC            1.00
    
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S3.4. ^{11}B -NMR spectrum of BF₂ClBIP (4b)



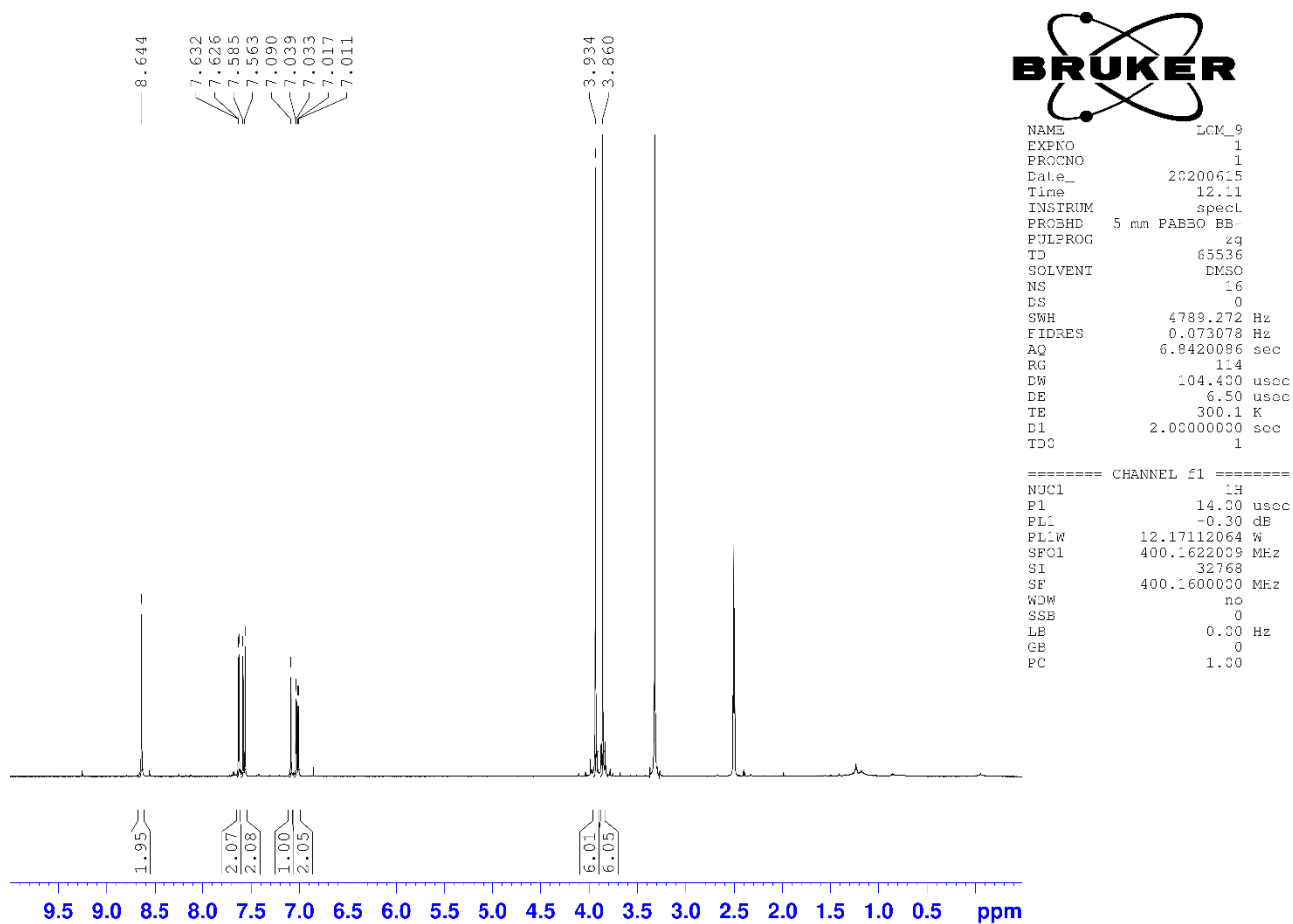
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PULPROG       zg
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SOLVENT       DMSO
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FIDRES        0.097813 Hz
AQ            5.1118579 sec
RG            29193
PW            78.000 usec
DE            6.50 usec
TE            300.1 K
D1            5.00000000 sec
TD0           1
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NUC1          11B
P1            10.20 usec
PL1           -0.70 dB
PL1W          81.56847382 W
SFO1          128.3871016 MHz
SI            65536
SF            128.3872300 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.00
  
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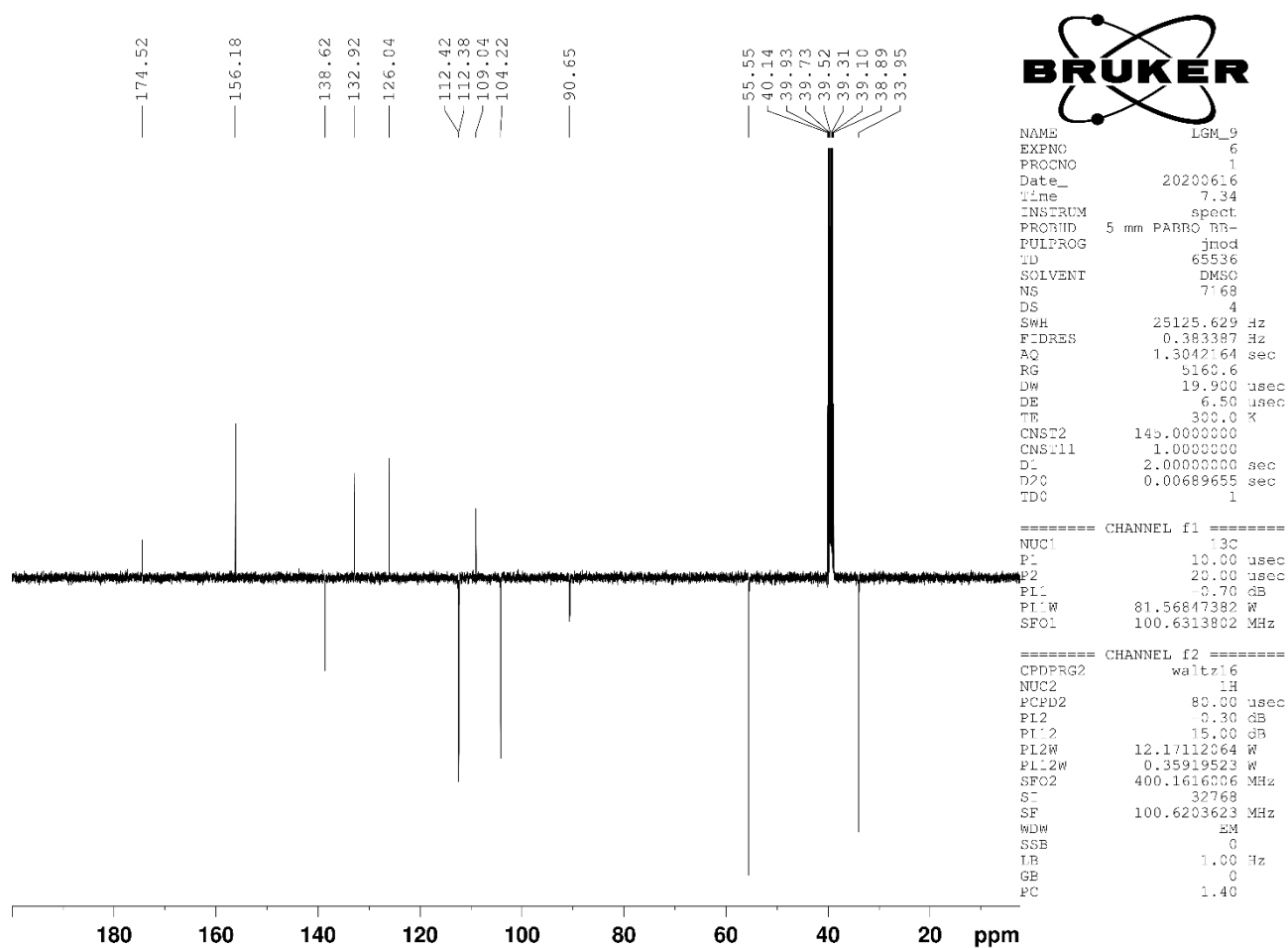


S4. NMR spectroscopy data on 4c

S4.1. ¹H-NMR spectrum of BF₂BMIP (4c)



S4.2. ¹³C-NMR spectrum of BF2BMIP (4c)

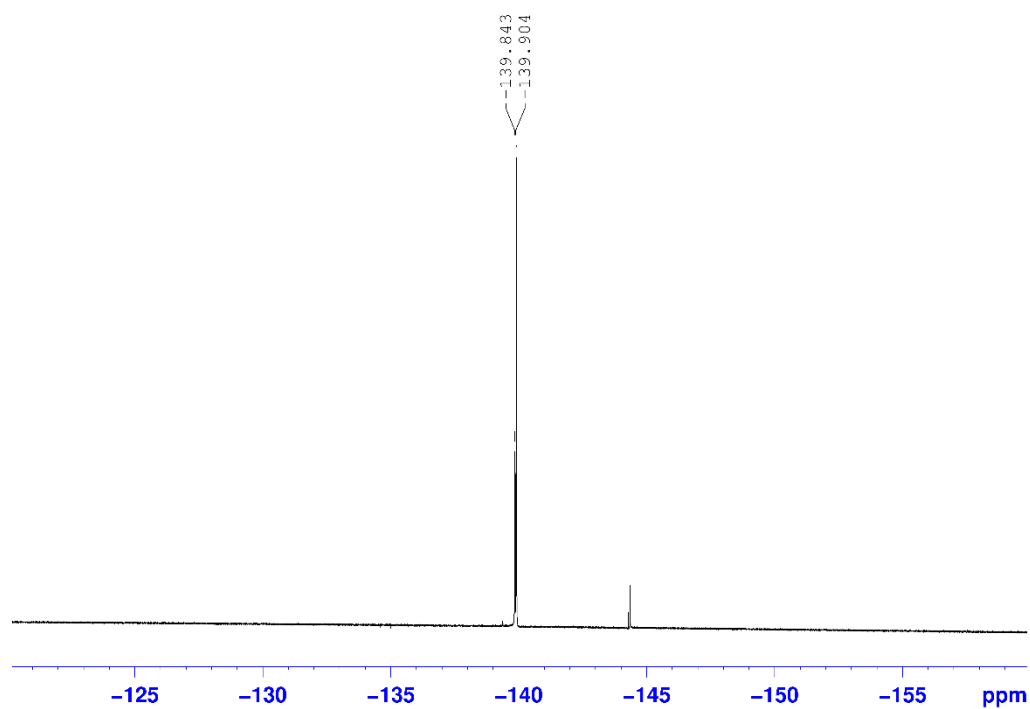


S4.3. ^{19}F -NMR spectrum of BF₂BMIP (4c)



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PROCNO        1
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PULPROG       zgpg30
TD            32768
SOLVENT       DMSO
NS            32
DS            0
SWH           30120.482 Hz
FIDRES        0.919204 Hz
AQ            0.5439988 sec
RG            40.3
DW            16.600 usec
DE            6.50 usec
TE            300.0 K
D1            6.00000000 sec
TD0           1

----- CHANNEL f1 -----
NUC1          19F
P1            15.00 usec
PL1           -2.50 dB
PL1W          8.79966640 W
SFO1          376.4757629 MHz
SI            262144
SF            376.5265940 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
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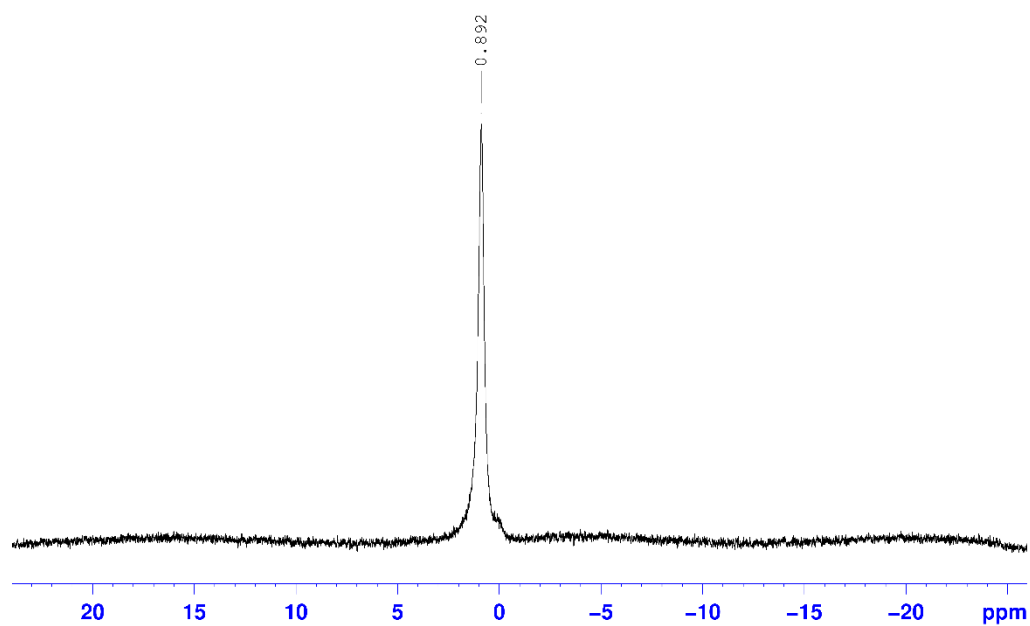
S4.4. ^{11}B -NMR spectrum of BF₂BMIP (4c)



```

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PROCNO        2
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PULPROG       zg
TD            65536
SOLVENT       DMSO
NS            128
DS            2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ            5.1118579 sec
RG            29193
DW            78.000 usec
DE            6.50 usec
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D1            5.00000000 sec
TDC           1

===== CHANNEL f1 =====
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P1            10.20 usec
PL1           -0.70 dB
PL1W          81.56847382 W
SFO1          128.3871016 MHz
SI            65536
SF            128.3872300 MHz
WDW           EM
SSB           0
LB            1.00 Hz
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PC            1.00
  
```



S5. IR spectra

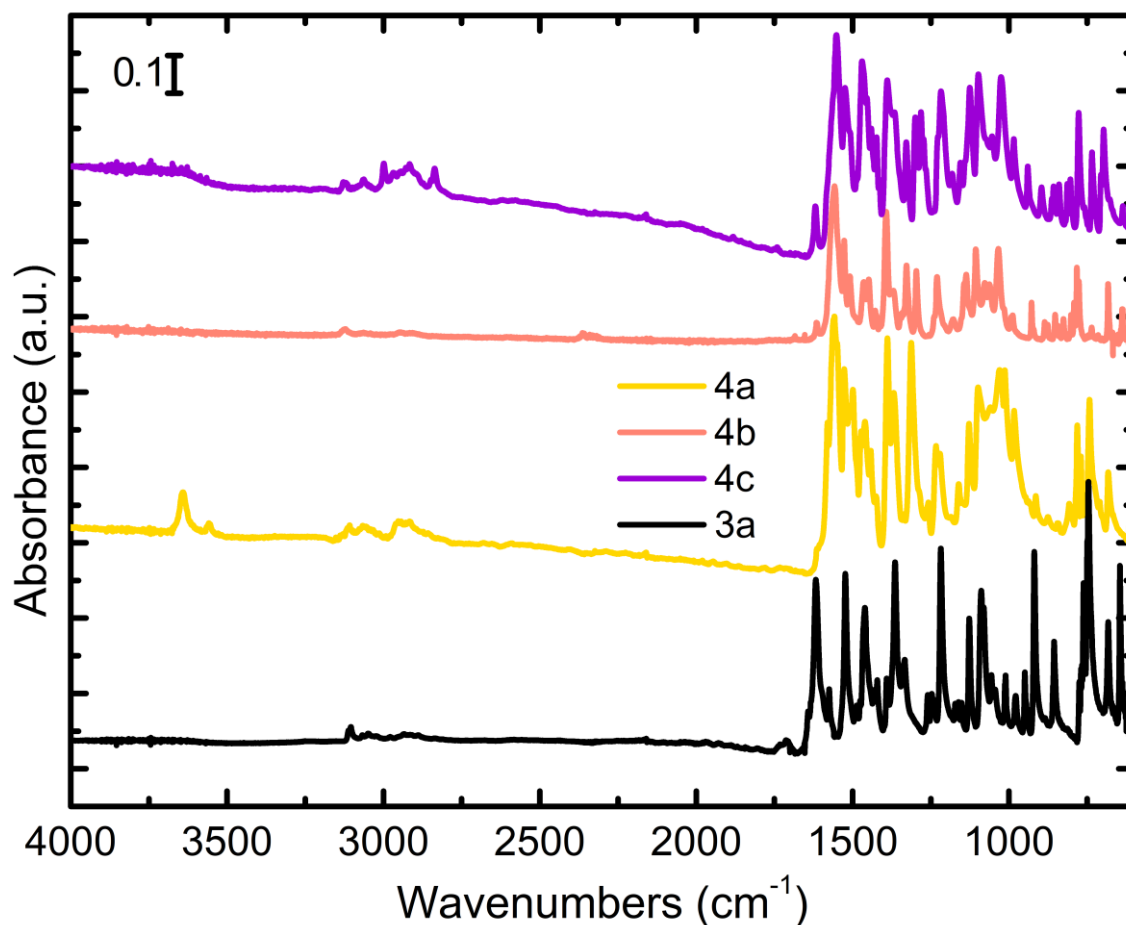


Figure S1. ATR-IR spectra recorded on loose powders in the air of **3a** before (black curve) and after difluoroboronation (**4a**, yellow curve), **4b** (pink), **4c** (violet). The peaks at ~ 3600 cm^{-1} in **4a** are associated to impurities (based on NMR spectra, boronic acids formed from the decomposition of BF_3).

Table S1. Carbonyl stretching frequency ($\tilde{\nu}_{\text{C=O}}$) as measured by ATR-IR in the air of the as-synthesized bdks (**3**) and BF_2 bdks (**4**). The corresponding experimental shift of this frequency are also reported ($\Delta\tilde{\nu}_{\text{C=O}}$). All the values are in cm^{-1} .

Entry	$\tilde{\nu}_{\text{C=O}}$ bdk 3	$\tilde{\nu}_{\text{C=O}}$ BF_2 bdk 4	$\Delta\tilde{\nu}_{\text{C=O}}$
a	1618	1560	-58
b	1630	1557	-73
c	1617	1555	-62

The computed DFT spectra for the three conformers of **3a** are reported in Figure S2. The calculations confirm the redshift of the carbonyl stretching mode after difluoroboronation (**4a**, yellow curve), although the computed $\Delta\tilde{\nu}_{\text{C=O}}$ are on average larger than the experimental values: -126 (trans-diketo, black curve), -163 (cis-diketo, pink), -42 cm^{-1} (keto-enol, violet) as computed at the B3LYP level. The difference between the computed and the experimental values is likely associated to the conditions used in the calculations (gas phase) and in the experiment (bulk phase).

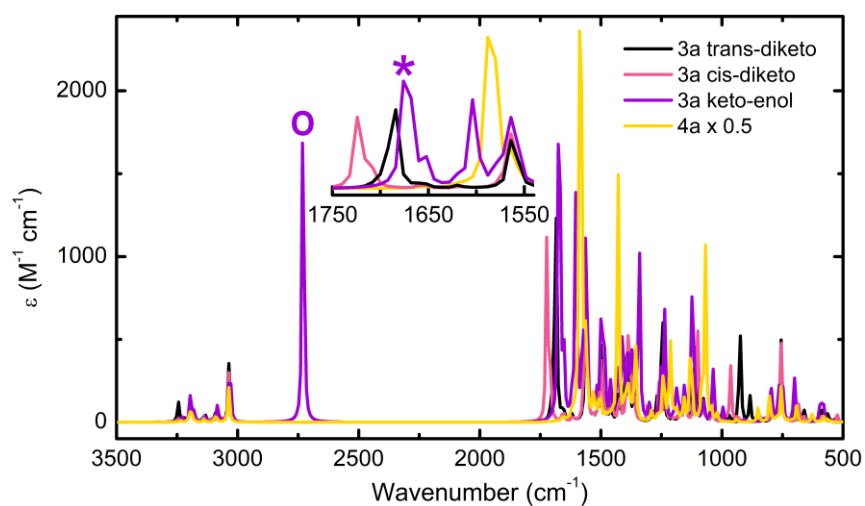


Figure S2. Theoretical IR spectra computed at the B3LYP/def2-TZVPD in the gas phase for the three possible conformers of **3a**: trans-diketo (black curve), cis-diketo (pink), keto-enol (violet). “O” and “*” mark the O-H stretching and bending modes in keto-enol, respectively. The spectrum of the corresponding BF₂bdk **4a** is also shown for comparison (yellow curve). Inset: enlarged view of the carbonyl stretching region.

S6. Supplementary experimental UV-Vis absorption spectroscopy data

The UV-Vis absorption spectra of **3a**, **3b**, and **3c** in different solvents are shown in Figure S3.

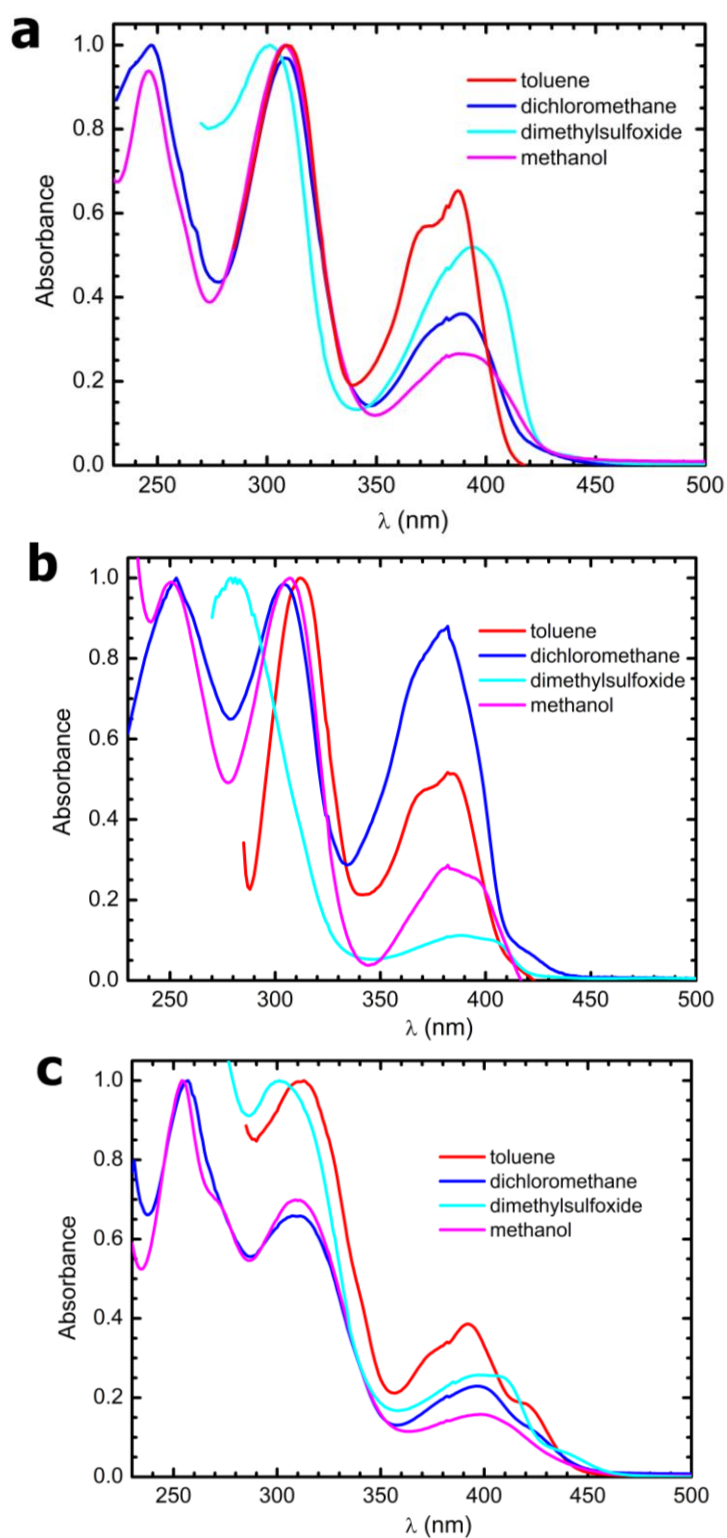


Figure S3. UV-Vis absorption spectra of HBIP (**3a**, top), BCIIP (**3b**, middle) and BMIP (**3c**, below) in representative solvents.

S7. Supplementary theoretical UV-Vis absorption spectra and data

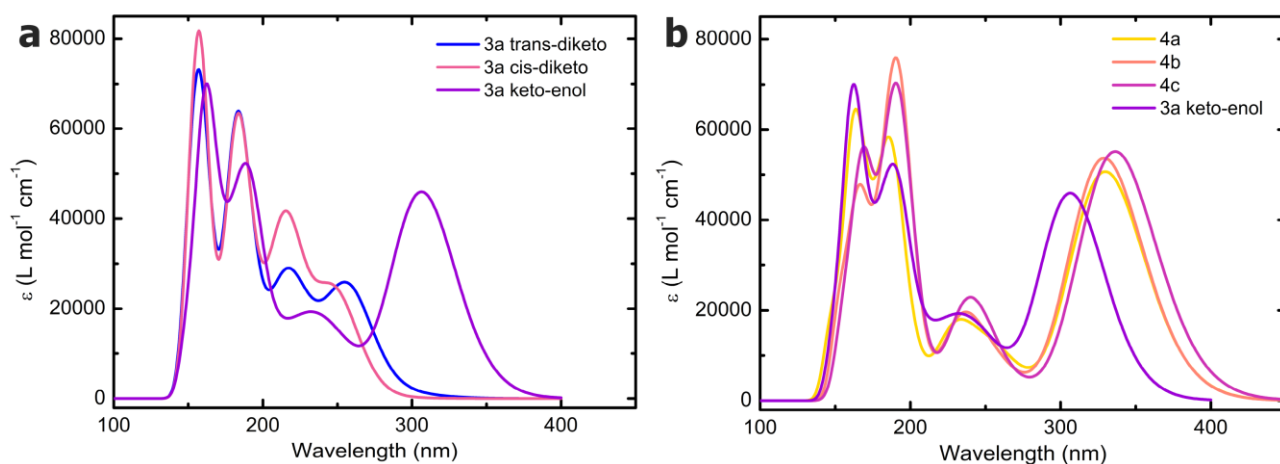


Figure S4. Electronic absorption spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA- ω B97X-D/def2-TZVPD including the first 100 excitations.

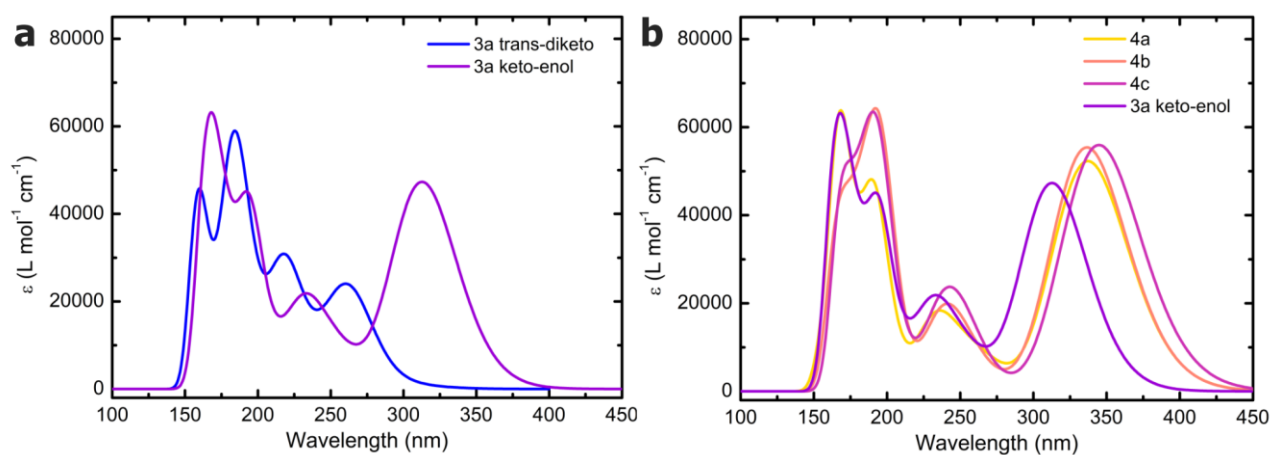


Figure S5. Electronic absorption spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA-M06-2X/def2-TZVPD including the first 100 excitations.

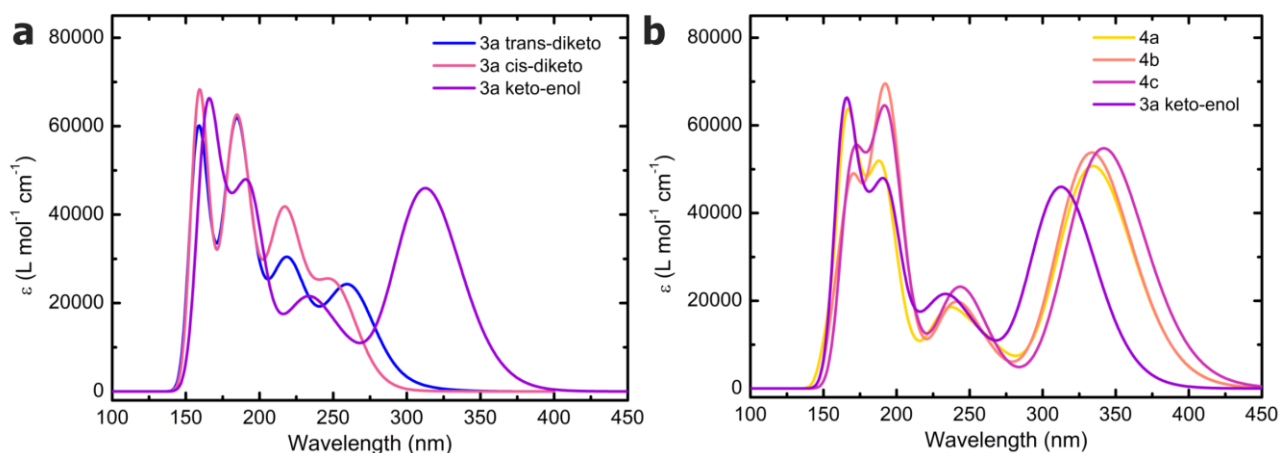


Figure S6. Electronic absorption spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA-CAM-B3LYP-D3/def2-TZVPD including the first 100 excitations.

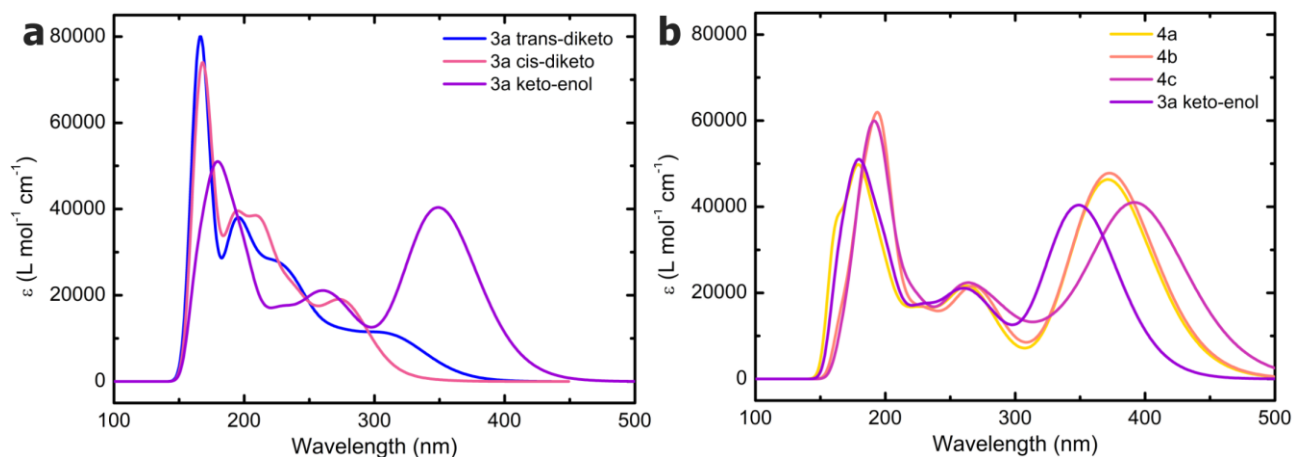


Figure S7. Electronic absorption spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA-B3LYP-D3/def2-TZVPD including the first 100 excitations.

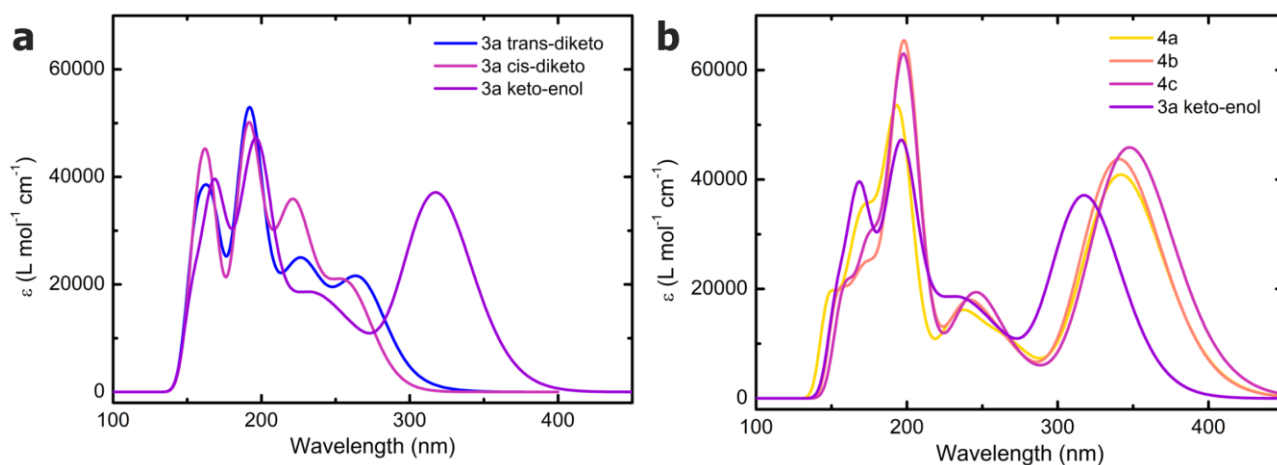


Figure S8. Electronic absorption spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TD- ω B97X-D/def2-TZVPD including the first 100 excitations.

S7.1. TD-B3LYP-D3: Excitation energies and oscillator strengths of the first excited states

3a keto-enol

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.4247 eV 362.02 nm f=0.7873 <S**2>=0.000
87 -> 88 0.70215
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1071.41850459
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9809 eV 311.45 nm f=0.0001 <S**2>=0.000
82 -> 88 0.67923

Excited State 3: Singlet-A 4.0132 eV 308.94 nm f=0.0006 <S**2>=0.000
84 -> 88 0.10257
85 -> 88 -0.10853
86 -> 88 -0.41945
87 -> 89 0.53520

3a cis-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.8096 eV 325.45 nm f=0.0075 <S**2>=0.000
82 -> 88 0.16969
84 -> 88 -0.16259
87 -> 88 0.65105
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1071.39857189
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8330 eV 323.46 nm f=0.0020 <S**2>=0.000
82 -> 88 -0.40108
82 -> 90 0.13407
84 -> 88 0.46566
84 -> 90 -0.12042
87 -> 88 0.25657

Excited State 3: Singlet-A 3.9552 eV 313.47 nm f=0.0010 <S**2>=0.000
82 -> 89 0.18655
84 -> 89 0.61163
84 -> 91 0.18304
86 -> 89 -0.16251

Excited State 4: Singlet-A 4.2665 eV 290.60 nm f=0.1496 <S**2>=0.000
82 -> 88 -0.19292
86 -> 88 0.48338
87 -> 89 0.44092

3a trans-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.7419 eV 331.34 nm f=0.0831 <S**2>=0.000
82 -> 89 0.14560
83 -> 88 0.57985
87 -> 88 -0.34553
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1071.41128221
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9447 eV 314.30 nm f=0.0212 <S**2>=0.000
82 -> 88 -0.12465
86 -> 88 0.66244
87 -> 89 0.14646

Excited State 3: Singlet-A 3.9450 eV 314.28 nm f=0.1423 <S**2>=0.000
83 -> 88 0.31898
86 -> 89 0.10968
87 -> 88 0.59930

4a

98 HOMO, 99 LUMO

Excited State 1: Singlet-A 3.2070 ev 386.60 nm f=0.8815 <S**2>=0.000
98 -> 99 0.70450
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1295.66360691
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8302 ev 323.70 nm f=0.0283 <S**2>=0.000
97 -> 99 0.67666
98 ->100 0.16215

Excited State 3: Singlet-A 3.9196 ev 316.32 nm f=0.0002 <S**2>=0.000
95 -> 99 0.65628
97 -> 99 0.12835
98 ->100 -0.21155

4b

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.2105 ev 386.18 nm f=0.9422 <S**2>=0.000
114 -> 115 0.70129
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2214.92008102
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.6795 ev 336.96 nm f=0.0009 <S**2>=0.000
111 -> 115 -0.19951
113 -> 115 0.66962

Excited State 3: Singlet-A 3.7437 ev 331.18 nm f=0.0035 <S**2>=0.000
112 -> 115 0.69260

4c

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.0596 ev 405.23 nm f=0.8498 <S**2>=0.000
114 -> 115 0.70059
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1524.81651337
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3875 ev 366.00 nm f=0.0006 <S**2>=0.000
113 -> 115 0.69728

Excited State 3: Singlet-A 3.6135 ev 343.12 nm f=0.1013 <S**2>=0.000
112 -> 115 0.69440

S7.2. TDA-B3LYP-D3: Excitation energies and oscillator strengths of the first excited states

3a keto-enol

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.5491 ev 349.34 nm f=0.9917 <S**2>=0.000
87 -> 88 0.68865
This state for optimization and/or second-order correction.
Total Energy, E(CIS/TDA) = -1071.41393316
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9946 ev 310.38 nm f=0.0001 <S**2>=0.000
82 -> 88 0.68211

Excited State 3: Singlet-A 4.0481 eV 306.27 nm f=0.0013 <S**2>=0.000
 84 -> 88 0.11597
 85 -> 88 -0.13822
 86 -> 88 -0.38677
 87 -> 89 0.55022

3a cis-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.8161 eV 324.90 nm f=0.0084 <S**2>=0.000
 82 -> 88 0.10938
 87 -> 88 0.67921
 This state for optimization and/or second-order correction.
 Total Energy, E(CIS/TDA) = -1071.39833283
 Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8505 eV 321.99 nm f=0.0028 <S**2>=0.000
 82 -> 88 -0.41869
 82 -> 90 0.13853
 84 -> 88 0.48938
 84 -> 90 -0.12342
 87 -> 88 0.15888

Excited State 3: Singlet-A 3.9753 eV 311.89 nm f=0.0011 <S**2>=0.000
 82 -> 89 0.18370
 84 -> 89 0.61252
 84 -> 91 0.18039
 86 -> 89 -0.16374

Excited State 4: Singlet-A 4.3454 eV 285.32 nm f=0.0011 <S**2>=0.000
 85 -> 88 0.65914
 86 -> 88 -0.13378
 87 -> 89 -0.13424

Excited State 5: Singlet-A 4.3697 eV 283.74 nm f=0.1722 <S**2>=0.000
 82 -> 88 -0.30926
 84 -> 88 -0.17148
 85 -> 88 0.23400
 86 -> 88 0.41641
 87 -> 89 0.30592

3a trans-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.7661 eV 329.21 nm f=0.0850 <S**2>=0.000
 82 -> 89 0.15024
 83 -> 88 0.59178
 87 -> 88 -0.31966
 This state for optimization and/or second-order correction.
 Total Energy, E(CIS/TDA) = -1071.41039462
 Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9927 eV 310.52 nm f=0.1414 <S**2>=0.000
 83 -> 88 0.29240
 86 -> 89 0.19591
 87 -> 88 0.59091

Excited State 3: Singlet-A 3.9932 eV 310.49 nm f=0.0186 <S**2>=0.000
 82 -> 88 -0.16690
 83 -> 89 -0.12654
 86 -> 88 0.61689
 87 -> 89 0.23781

4a

98 HOMO, 99 LUMO

Excited State 1: Singlet-A 3.3366 eV 371.59 nm f=1.1408 <S**2>=0.000
 98 -> 99 0.69334
 This state for optimization and/or second-order correction.
 Total Energy, E(CIS/TDA) = -1295.65884438

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9015 ev 317.79 nm f=0.0190 <S**2>=0.000
 95 -> 99 -0.23319
 97 -> 99 0.58747
 98 -> 100 0.29024

Excited State 3: Singlet-A 3.9639 ev 312.78 nm f=0.0017 <S**2>=0.000
 95 -> 99 0.62057
 97 -> 99 0.29500
 98 -> 100 -0.11722

4b

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.3228 ev 373.13 nm f=1.1695 <S**2>=0.000
 112 -> 115 -0.14749
 114 -> 115 0.68405

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -2214.91595357

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.7238 ev 332.95 nm f=0.0026 <S**2>=0.000
 111 -> 115 -0.25441
 113 -> 115 0.64664

Excited State 3: Singlet-A 3.8001 ev 326.27 nm f=0.0386 <S**2>=0.000
 112 -> 115 0.67468
 114 -> 115 0.13424

4c

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.1431 ev 394.47 nm f=0.9753 <S**2>=0.000
 112 -> 115 -0.15674
 114 -> 115 0.68445

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1524.81344658

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.4386 ev 360.56 nm f=0.0014 <S**2>=0.000
 111 -> 115 -0.11489
 113 -> 115 0.68862

Excited State 3: Singlet-A 3.7037 ev 334.76 nm f=0.2405 <S**2>=0.000
 112 -> 115 0.67211
 114 -> 115 0.14773

Excited State 4: Singlet-A 3.9019 ev 317.75 nm f=0.0002 <S**2>=0.000
 111 -> 115 0.45519
 114 -> 116 0.52300

Excited State 5: Singlet-A 4.2324 ev 292.94 nm f=0.1124 <S**2>=0.000
 109 -> 115 -0.12204
 111 -> 115 0.49539
 114 -> 116 -0.44998

S7.3. TDA- ω B97X-D: Excitation energies and oscillator strengths of the first excited states

3a keto-enol

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 4.0442 ev 306.58 nm f=1.1314 <S**2>=0.000
 83 -> 88 0.11660
 87 -> 88 0.66536

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.93226768

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3596 eV 284.39 nm f=0.0009 <S**2>=0.000
82 -> 88 0.64539
82 -> 89 0.11441
82 -> 91 0.15711
83 -> 88 0.10033

Excited State 3: Singlet-A 4.8527 eV 255.50 nm f=0.1610 <S**2>=0.000
84 -> 88 -0.15318
84 -> 96 0.11778
86 -> 88 -0.33196
86 -> 91 0.15728
87 -> 89 0.51507
87 -> 91 0.11107

3a cis-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 4.1641 eV 297.75 nm f=0.0021 <S**2>=0.000
82 -> 88 0.46321
82 -> 89 -0.10256
82 -> 91 -0.25114
83 -> 88 -0.35194
83 -> 89 0.11171
83 -> 91 0.18796

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.92552459

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2544 eV 291.42 nm f=0.0007 <S**2>=0.000
82 -> 89 0.23394
82 -> 93 0.12336
83 -> 88 0.12474
83 -> 89 0.53174
83 -> 93 0.28043

Excited State 3: Singlet-A 4.9015 eV 252.95 nm f=0.1682 <S**2>=0.000
86 -> 88 0.35050
87 -> 88 0.24831
87 -> 89 0.49118

Excited State 4: Singlet-A 4.9949 eV 248.22 nm f=0.3387 <S**2>=0.000
84 -> 88 0.10186
84 -> 91 -0.10223
84 -> 95 0.11479
86 -> 88 0.53685
87 -> 88 -0.15358
87 -> 89 -0.30638

Excited State 5: Singlet-A 5.0172 eV 247.12 nm f=0.0180 <S**2>=0.000
84 -> 88 0.14681
85 -> 88 0.14524
85 -> 89 0.46564
85 -> 93 -0.15392
87 -> 88 0.10567
87 -> 93 -0.29011
87 -> 98 0.20787

3a trans-diketo

87 HOMO, 88 LUMO

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 4.1293 eV 300.26 nm f=0.0207 <S**2>=0.000
82 -> 89 0.22324
82 -> 93 -0.17836
83 -> 88 0.59029
83 -> 90 -0.16359
87 -> 88 0.11313

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.93622230

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3627 eV 284.19 nm f=0.0027 <S**2>=0.000
82 -> 88 0.47919

82 -> 90 -0.14227
 83 -> 89 0.37114
 83 -> 93 -0.26375

Excited State 3: Singlet-A 4.7932 ev 258.67 nm f=0.4866 <S**2>=0.000
 86 -> 89 0.23471
 87 -> 88 0.60854

4a

98 HOMO, 99 LUMO

Excited State 1: Singlet-A 3.7600 ev 329.75 nm f=1.2508 <S**2>=0.000
 94 -> 99 -0.13207
 98 -> 99 0.66959

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1295.11002172

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.7716 ev 259.84 nm f=0.1825 <S**2>=0.000
 95 -> 102 0.10139
 97 -> 99 0.57703
 98 -> 100 -0.31810

Excited State 3: Singlet-A 4.8580 ev 255.22 nm f=0.0001 <S**2>=0.000
 95 -> 99 0.47783
 96 -> 100 0.24504
 97 -> 99 -0.12465
 97 -> 102 -0.20931
 98 -> 100 -0.28672
 98 -> 106 -0.14907

4b

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.7686 ev 328.99 nm f=1.3250 <S**2>=0.000
 110 -> 115 -0.12484
 114 -> 115 0.66924

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -2214.33140936

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.7138 ev 263.02 nm f=0.0280 <S**2>=0.000
 112 -> 116 -0.12851
 112 -> 121 -0.11189
 113 -> 115 0.49343
 113 -> 117 -0.13983
 114 -> 116 -0.39032

Excited State 3: Singlet-A 4.7638 ev 260.26 nm f=0.0431 <S**2>=0.000
 111 -> 116 0.11366
 111 -> 121 0.14911
 112 -> 115 0.47669
 112 -> 117 -0.14570
 113 -> 116 -0.31530
 114 -> 117 -0.24636
 114 -> 122 0.11315

4c

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.6857 ev 336.40 nm f=1.3609 <S**2>=0.000
 110 -> 115 -0.11926
 112 -> 115 -0.11490
 113 -> 116 -0.10371
 114 -> 115 0.65979

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1524.17658990

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.4779 ev 276.88 nm f=0.0227 <S**2>=0.000
 113 -> 115 0.55153

113 -> 118	-0.12259				
114 -> 116	-0.36084				
Excited State 3:	Singlet-A	4.5964 eV	269.74 nm	f=0.0219	<S**2>=0.000
111 -> 127	0.12685				
112 -> 115	0.48297				
113 -> 116	-0.34185				
114 -> 118	-0.27987				

S7.4. TDA-M06-2X: Excitation energies and oscillator strengths of the first excited states

3a keto-enol

87 HOMO, 88 LUMO

Excited State 1:	Singlet-A	3.9629 eV	312.86 nm	f=1.1661	<S**2>=0.000
87 -> 88	0.67537				

This state for optimization and/or second-order correction.
Total Energy, E(CIS/TDA) = -1070.86805747
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:	Singlet-A	4.3550 eV	284.70 nm	f=0.0001	<S**2>=0.000
82 -> 88	0.63773				
82 -> 90	-0.12554				
82 -> 92	0.16984				
82 -> 102	-0.11073				

Excited State 3:	Singlet-A	4.7764 eV	259.57 nm	f=0.1360	<S**2>=0.000
84 -> 88	0.17203				
86 -> 88	0.27093				
86 -> 92	-0.12580				
87 -> 90	0.56117				
87 -> 92	-0.12231				

Excited State 4:	Singlet-A	4.8098 eV	257.78 nm	f=0.0031	<S**2>=0.000
86 -> 91	-0.10399				
87 -> 89	0.64902				
87 -> 93	0.17301				

3a cis-diketo

87 HOMO, 88 LUMO

Excited State 1:	Singlet-A	4.0458 eV	306.45 nm	f=0.0169	<S**2>=0.000
82 -> 89	-0.22005				
82 -> 93	-0.11152				
82 -> 95	0.16970				
83 -> 88	0.55502				
83 -> 92	-0.18225				
87 -> 88	0.10803				

This state for optimization and/or second-order correction.
Total Energy, E(CIS/TDA) = -1070.86858006
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:	Singlet-A	4.2341 eV	292.82 nm	f=0.0026	<S**2>=0.000
82 -> 88	0.44624				
82 -> 92	-0.15527				
83 -> 89	-0.33538				
83 -> 93	-0.15883				
83 -> 95	0.23885				

Excited State 3:	Singlet-A	4.7160 eV	262.90 nm	f=0.4831	<S**2>=0.000
86 -> 89	0.15947				
87 -> 88	0.64319				

Excited State 4:	Singlet-A	4.7554 eV	260.73 nm	f=0.0523	<S**2>=0.000
86 -> 88	0.63397				
87 -> 89	0.19995				

Excited State 5:	Singlet-A	5.0235 eV	246.81 nm	f=0.0455	<S**2>=0.000
84 -> 89	-0.31351				
85 -> 88	0.45831				
85 -> 92	0.11502				

86 -> 89	0.15245
86 -> 95	0.13755
86 -> 101	0.10200
87 -> 92	0.24128
87 -> 102	-0.12257

3a trans-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 4.0458 eV 306.45 nm f=0.0169 <S**2>=0.000
 82 -> 89 -0.22008
 82 -> 93 0.11158
 82 -> 95 -0.16965
 83 -> 88 0.55501
 83 -> 92 -0.18222
 87 -> 88 0.10816

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.86857954

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2341 eV 292.82 nm f=0.0026 <S**2>=0.000
 82 -> 88 0.44625
 82 -> 92 -0.15526
 83 -> 89 -0.33542
 83 -> 93 0.15893
 83 -> 95 -0.23877

Excited State 3: Singlet-A 4.7160 eV 262.90 nm f=0.4829 <S**2>=0.000
 86 -> 89 0.15943
 87 -> 88 0.64318

4a

98 HOMO, 99 LUMO

Excited State 1: Singlet-A 3.6760 eV 337.28 nm f=1.2909 <S**2>=0.000
 94 -> 99 -0.10776
 98 -> 99 0.67919

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1295.05039901

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.6698 eV 265.50 nm f=0.1373 <S**2>=0.000
 97 -> 99 0.63999
 98 -> 101 -0.19149

Excited State 3: Singlet-A 4.7548 eV 260.76 nm f=0.0014 <S**2>=0.000
 95 -> 99 0.49836
 96 -> 101 0.15667
 97 -> 99 -0.13493
 97 -> 103 -0.16909
 98 -> 100 0.12466
 98 -> 101 -0.35686

4b

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.6835 eV 336.60 nm f=1.3679 <S**2>=0.000
 110 -> 115 -0.10316
 114 -> 115 0.67952

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -2214.25683363

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.5870 eV 270.29 nm f=0.0163 <S**2>=0.000
 111 -> 115 -0.10000
 113 -> 115 0.58309
 114 -> 116 -0.32225

Excited State 3: Singlet-A 4.6655 eV 265.75 nm f=0.0148 <S**2>=0.000
 111 -> 123 0.10704
 112 -> 115 0.58978
 113 -> 116 -0.23552

114 -> 118 -0.21862

4c

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.5958 eV 344.81 nm f=1.3811 <S**2>=0.000
114 -> 115 0.67700

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1524.09980894

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3489 eV 285.09 nm f=0.0134 <S**2>=0.000
113 -> 115 0.63020
114 -> 116 0.10965
114 -> 117 -0.24573

Excited State 3: Singlet-A 4.5163 eV 274.53 nm f=0.0004 <S**2>=0.000
112 -> 115 0.59954
113 -> 117 -0.22164
114 -> 119 -0.21858

S7.5. TDA-CAM-B3LYP-D3: Excitation energies and oscillator strengths of the first excited states

3a keto-enol

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.9641 eV 312.77 nm f=1.1325 <S**2>=0.000
83 -> 88 0.10074
87 -> 88 0.67289

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.79296311

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.4009 eV 281.72 nm f=0.0001 <S**2>=0.000
82 -> 88 0.65290
82 -> 89 0.12235
82 -> 92 0.16258

Excited State 3: Singlet-A 4.7644 eV 260.23 nm f=0.1473 <S**2>=0.000
84 -> 88 -0.15899
84 -> 96 0.10652
86 -> 88 -0.28953
86 -> 92 0.13893
87 -> 89 0.55348
87 -> 92 0.10465

3a cis-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 4.1779 eV 296.76 nm f=0.0017 <S**2>=0.000
82 -> 88 0.46503
82 -> 91 0.25389
83 -> 88 0.34916
83 -> 89 -0.11163
83 -> 91 0.18547

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.77942857

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2617 eV 290.92 nm f=0.0006 <S**2>=0.000
82 -> 89 -0.22593
82 -> 94 0.12422
83 -> 88 0.11363
83 -> 89 0.52285
83 -> 90 -0.12195
83 -> 94 -0.28656

Excited State 3: Singlet-A 4.8528 eV 255.49 nm f=0.1571 <S**2>=0.000
86 -> 88 0.30873
87 -> 88 0.34030

87 -> 89 0.46278

Excited State 4: Singlet-A 4.9498 eV 250.48 nm f=0.3211 <S**2>=0.000

84 -> 91 0.11146
84 -> 97 -0.10318
86 -> 88 0.56810
87 -> 88 -0.20175
87 -> 89 -0.22410

Excited State 5: Singlet-A 4.9925 eV 248.34 nm f=0.0225 <S**2>=0.000

84 -> 88 0.10528
85 -> 88 0.12322
85 -> 89 0.43328
85 -> 90 -0.10180
85 -> 94 0.14229
87 -> 88 0.19197
87 -> 89 -0.20233
87 -> 94 0.26624
87 -> 99 -0.12783
87 -> 100 0.11226
87 -> 101 -0.11527

3a trans-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 4.1349 eV 299.85 nm f=0.0212 <S**2>=0.000

82 -> 89 -0.22255
82 -> 93 0.17606
83 -> 88 0.58699
83 -> 92 -0.16496
87 -> 88 0.11999

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1070.79082359

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3668 eV 283.93 nm f=0.0033 <S**2>=0.000

82 -> 88 0.47661
82 -> 92 -0.14440
83 -> 89 -0.36777
83 -> 93 0.25877

Excited State 3: Singlet-A 4.7218 eV 262.58 nm f=0.4670 <S**2>=0.000

86 -> 89 0.18284
87 -> 88 0.63279

Excited State 4: Singlet-A 4.7505 eV 260.99 nm f=0.0496 <S**2>=0.000

84 -> 92 0.10658
86 -> 88 0.61653
87 -> 89 0.22490

Excited State 5: Singlet-A 4.9806 eV 248.93 nm f=0.0510 <S**2>=0.000

84 -> 89 0.32872
85 -> 88 0.45321
85 -> 92 0.11557
86 -> 89 -0.13535
86 -> 93 -0.16968
86 -> 97 0.11895
87 -> 92 -0.23559
87 -> 98 -0.12718

4a

98 HOMO, 99 LUMO

Excited State 1: Singlet-A 3.7065 eV 334.51 nm f=1.2530 <S**2>=0.000

94 -> 99 0.11252
98 -> 99 0.67648

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1294.98467519

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.6928 eV 264.20 nm f=0.1657 <S**2>=0.000

97 -> 99 0.60405
98 -> 100 -0.28870

Excited State 3: Singlet-A 4.7604 eV 260.45 nm f=0.0001 <S**2>=0.000
 95 -> 99 0.50282
 96 -> 100 0.19871
 97 -> 99 0.15992
 97 -> 103 0.18332
 98 -> 100 0.31898
 98 -> 107 0.12002

4b

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.7156 eV 333.68 nm f=1.3283 <S**2>=0.000
 110 -> 115 0.10701
 114 -> 115 0.67646
 This state for optimization and/or second-order correction.
 Total Energy, E(CIS/TDA) = -2214.24613977
 Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.6102 eV 268.93 nm f=0.0163 <S**2>=0.000
 111 -> 115 -0.13431
 112 -> 116 -0.10384
 113 -> 115 0.53778
 114 -> 116 0.35674

Excited State 3: Singlet-A 4.6716 eV 265.40 nm f=0.0274 <S**2>=0.000
 111 -> 121 0.12260
 112 -> 115 0.55712
 113 -> 116 -0.26800
 114 -> 118 0.22231

Excited State 4: Singlet-A 4.7522 eV 260.90 nm f=0.0776 <S**2>=0.000
 111 -> 115 0.52307
 112 -> 116 0.23946
 113 -> 115 0.22574
 113 -> 118 0.21945
 114 -> 121 0.16116

Excited State 5: Singlet-A 5.0066 eV 247.64 nm f=0.1107 <S**2>=0.000
 111 -> 118 -0.10566
 112 -> 116 0.12742
 113 -> 115 -0.35434
 114 -> 116 0.54050

4c

114 HOMO, 115 LUMO

Excited State 1: Singlet-A 3.6268 eV 341.85 nm f=1.3519 <S**2>=0.000
 110 -> 115 0.10187
 114 -> 115 0.67085
 This state for optimization and/or second-order correction.
 Total Energy, E(CIS/TDA) = -1524.04043612
 Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3615 eV 284.27 nm f=0.0132 <S**2>=0.000
 113 -> 115 0.60504
 114 -> 116 0.30459

Excited State 3: Singlet-A 4.5069 eV 275.10 nm f=0.0046 <S**2>=0.000
 111 -> 129 0.10380
 112 -> 115 0.56684
 113 -> 116 -0.28012
 114 -> 119 -0.22848

Excited State 4: Singlet-A 4.6826 eV 264.78 nm f=0.0067 <S**2>=0.000
 111 -> 115 0.40546
 112 -> 116 0.20431
 113 -> 115 0.24377
 113 -> 119 -0.30455
 114 -> 116 -0.27631
 114 -> 129 0.12609

Excited State 5: Singlet-A 4.8875 eV 253.68 nm f=0.2098 <S**2>=0.000

111 -> 115	0.30616
112 -> 116	0.25966
113 -> 115	-0.21638
114 -> 116	0.48503

S7.3. TD-@B97X-D: Excitation energies and oscillator strengths of the first excited states

3a keto-enol

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 3.9016 eV 317.78 nm f=0.9123 <S**2>=0.000
 83 -> 88 0.13946
 86 -> 89 -0.10641
 87 -> 88 0.66706

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1070.93750704

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3362 eV 285.93 nm f=0.0006 <S**2>=0.000
 82 -> 88 0.64507
 82 -> 89 0.11498
 82 -> 91 0.15750
 83 -> 88 0.10138

Excited State 3: Singlet-A 4.6779 eV 265.04 nm f=0.1734 <S**2>=0.000
 86 -> 88 -0.41743
 86 -> 91 0.14807
 87 -> 89 0.50054

Excited State 4: Singlet-A 4.8843 eV 253.84 nm f=0.0122 <S**2>=0.000
 84 -> 88 -0.29301
 84 -> 89 0.24499
 84 -> 91 0.14525
 85 -> 88 0.15980
 86 -> 88 0.17677
 86 -> 89 0.26976
 86 -> 96 -0.11071
 87 -> 91 0.33302
 87 -> 96 -0.12250

Excited State 5: Singlet-A 4.9032 eV 252.87 nm f=0.0087 <S**2>=0.000
 84 -> 88 0.13896
 84 -> 89 -0.10884
 85 -> 88 0.32141
 85 -> 89 0.31754
 85 -> 91 -0.18387
 86 -> 88 -0.23053
 86 -> 91 -0.23172
 86 -> 97 -0.16957
 87 -> 89 -0.12062
 87 -> 96 0.12134
 87 -> 97 0.13343

3a cis-diketo

87 HOMO, 88 LUMO

Excited State 1: Singlet-A 4.1346 eV 299.87 nm f=0.0020 <S**2>=0.000
 82 -> 88 0.46341
 82 -> 89 -0.10278
 82 -> 91 -0.25212
 83 -> 88 -0.35098
 83 -> 89 0.11241
 83 -> 91 0.18863

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1070.92660669

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2242 eV 293.51 nm f=0.0006 <S**2>=0.000
 82 -> 89 0.23480
 82 -> 93 0.12407
 83 -> 88 0.12462
 83 -> 89 0.53109

83 -> 93	0.28142					
Excited State 3:	Singlet-A	4.7166 ev	262.87 nm	f=0.1403	<S**2>=0.000	
86 -> 88	0.35015					
87 -> 88	0.22517					
87 -> 89	0.52687					
Excited State 4:	Singlet-A	4.8000 ev	258.30 nm	f=0.2824	<S**2>=0.000	
86 -> 88	0.56583					
87 -> 88	-0.10361					
87 -> 89	-0.33578					
Excited State 5:	Singlet-A	4.9327 ev	251.35 nm	f=0.0341	<S**2>=0.000	
84 -> 88	0.19235					
85 -> 88	0.15281					
85 -> 89	0.47810					
85 -> 93	-0.16407					
86 -> 91	0.10137					
87 -> 93	-0.27254					
87 -> 98	0.18316					

3a trans-diketo

87 HOMO, 88 LUMO

Excitation energies and oscillator strengths:

Excited State 1:	Singlet-A	4.1012 ev	302.31 nm	f=0.0189	<S**2>=0.000
82 -> 89	0.22287				
82 -> 93	-0.17807				
83 -> 88	0.59010				
83 -> 90	-0.16479				
87 -> 88	0.11583				

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1070.93725221

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:	Singlet-A	4.3316 ev	286.23 nm	f=0.0027	<S**2>=0.000
82 -> 88	0.47829				
82 -> 90	-0.14284				
83 -> 89	0.37109				
83 -> 93	-0.26471				

Excited State 3:	Singlet-A	4.6346 ev	267.52 nm	f=0.4189	<S**2>=0.000
86 -> 89	0.29562				
87 -> 88	0.59945				

Excited State 4:	Singlet-A	4.6373 ev	267.36 nm	f=0.0414	<S**2>=0.000
86 -> 88	0.58281				
87 -> 89	0.32970				

Excited State 5:	Singlet-A	4.9272 ev	251.63 nm	f=0.0439	<S**2>=0.000
84 -> 89	0.36085				
85 -> 88	0.41951				
85 -> 90	0.16037				
86 -> 89	0.10856				
86 -> 93	0.18138				
86 -> 97	-0.12495				
87 -> 90	0.23506				
87 -> 98	-0.11822				

4a

98 HOMO, 99 LUMO

Excitation energies and oscillator strengths:

Excited State 1:	Singlet-A	3.6254 ev	341.98 nm	f=1.0097	<S**2>=0.000
94 -> 99	-0.15585				
98 -> 99	0.67085				

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1295.11496532

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:	Singlet-A	4.5762 ev	270.94 nm	f=0.1701	<S**2>=0.000
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97 -> 99	0.56293					
98 -> 100	-0.36801					
Excited State 3:	Singlet-A	4.7832 ev	259.21 nm	f=0.0003	<S**2>=0.000	
95 -> 99	0.47658					
95 -> 102	-0.11702					
96 -> 100	0.27009					
97 -> 99	-0.14143					
97 -> 102	-0.21204					
98 -> 100	-0.25790					
98 -> 106	-0.14636					
Excited State 4:	Singlet-A	4.8025 ev	258.17 nm	f=0.0648	<S**2>=0.000	
95 -> 100	0.28352					
96 -> 99	0.50349					
96 -> 102	-0.14362					
97 -> 100	0.17187					
97 -> 106	0.13438					
98 -> 102	0.23073					
98 -> 108	0.10280					
Excited State 5:	Singlet-A	5.0807 ev	244.03 nm	f=0.1051	<S**2>=0.000	
94 -> 99	0.45014					
95 -> 100	0.18933					
96 -> 102	-0.18454					
97 -> 100	-0.29876					
98 -> 102	-0.27431					
98 -> 108	0.11797					

4b

114 HOMO, 115 LUMO

Excitation energies and oscillator strengths:

Excited State 1:	Singlet-A	3.6388 ev	340.73 nm	f=1.0796	<S**2>=0.000
110 -> 115	-0.14825				
114 -> 115	0.66936				

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -2214.33618114

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:	Singlet-A	4.5644 ev	271.63 nm	f=0.0748	<S**2>=0.000
111 -> 115	0.13026				
111 -> 117	-0.10265				
112 -> 121	-0.10000				
113 -> 115	0.49870				
114 -> 116	-0.41782				

Excited State 3:	Singlet-A	4.6708 ev	265.45 nm	f=0.0575	<S**2>=0.000
111 -> 116	0.11549				
111 -> 121	0.13595				
112 -> 115	0.47184				
112 -> 117	-0.16465				
113 -> 116	-0.33965				
114 -> 117	-0.24691				

Excited State 4:	Singlet-A	4.7037 ev	263.59 nm	f=0.0509	<S**2>=0.000
111 -> 115	0.49841				
112 -> 116	0.31817				
113 -> 117	0.26383				
114 -> 121	-0.17568				

Excited State 5:	Singlet-A	5.0308 ev	246.45 nm	f=0.0829	<S**2>=0.000
110 -> 115	0.36462				
111 -> 116	-0.32967				
112 -> 115	0.18564				
112 -> 117	0.31604				
113 -> 121	-0.18041				
114 -> 117	-0.16958				
114 -> 122	-0.15799				

4c

114 HOMO, 115 LUMO

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.5655 eV 347.73 nm f=1.1315 <S**2>=0.000
 110 -> 115 -0.13902
 112 -> 115 -0.14567
 113 -> 116 -0.10200
 114 -> 115 0.65508

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1524.18100447

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3391 eV 285.74 nm f=0.0336 <S**2>=0.000
 113 -> 115 0.52757
 113 -> 118 -0.15175
 114 -> 116 -0.39917

Excited State 3: Singlet-A 4.4691 eV 277.42 nm f=0.0391 <S**2>=0.000
 111 -> 127 0.10889
 112 -> 115 0.45614
 112 -> 118 -0.12401
 113 -> 116 -0.37477
 114 -> 118 -0.29415

Excited State 4: Singlet-A 4.6275 eV 267.93 nm f=0.0395 <S**2>=0.000
 111 -> 115 0.43794
 112 -> 116 0.30124
 113 -> 115 0.17670
 113 -> 118 0.32155
 114 -> 124 0.13538
 114 -> 127 -0.13597

Excited State 5: Singlet-A 4.8964 eV 253.21 nm f=0.1641 <S**2>=0.000
 111 -> 115 -0.22738
 111 -> 118 0.10715
 112 -> 116 -0.20511
 112 -> 124 0.11024
 113 -> 115 0.38124
 113 -> 118 0.17603
 114 -> 116 0.43332

S8. Supplementary electronic-state transition spectroscopy data

Table S2. Fluorescence decay times, τ_i , and relative amplitudes, f_i , of compounds **3a**, **3b**, and **3c**, as retrieved from fitting the experimental decay patterns measured upon excitation at 280 nm to a biexponential decay model function. The reported values are averaged over three parallels. The pertaining errors are the corresponding standard deviations.

Compound	Solvent	τ_1 (ps)	f_1	τ_2 (ps)	f_2
3a	ethyl acetate	-	0	2072 \pm 11	1
	dichloromethane	222 \pm 1	0.93 \pm 0.01	2248 \pm 4	0.07 \pm 0.01
	acetonitrile	209 \pm 1	0.97 \pm 0.01	2368 \pm 24	0.03 \pm 0.01
	dimethylformamide	249 \pm 1	0.58 \pm 0.01	2163 \pm 1	0.42 \pm 0.01
	dimethyl sulfoxide	258 \pm 1	0.94 \pm 0.01	2188 \pm 24	0.06 \pm 0.01
	butanol	431 \pm 1	0.98 \pm 0.01	2653 \pm 1	0.02 \pm 0.01
	ethanol	360 \pm 1	\cong 1	\cong 3660	<0.01
	methanol	388 \pm 2	0.97 \pm 0.01	2434 \pm 21	0.03 \pm 0.01
3b	ethyl acetate	202 \pm 2	0.95 \pm 0.01	1940 \pm 8	0.05 \pm 0.01
	dichloromethane	262 \pm 3	0.97 \pm 0.01	2057 \pm 13	0.03 \pm 0.01
	acetonitrile	205 \pm 2	0.96 \pm 0.01	2207 \pm 29	0.04 \pm 0.01
	dimethylformamide	257 \pm 2	0.91 \pm 0.01	2933 \pm 1	0.09 \pm 0.01
	dimethyl sulfoxide	271 \pm 1	0.96 \pm 0.01	2471 \pm 5	0.04 \pm 0.01
	butanol	451 \pm 4	0.75 \pm 0.01	4011 \pm 20	0.25 \pm 0.01
	ethanol	281 \pm 2	0.99 \pm 0.01	2612 \pm 71	0.01 \pm 0.01
	methanol	275 \pm 1	0.89 \pm 0.01	2460 \pm 14	0.11 \pm 0.01
3c	ethyl acetate	309 \pm 2	0.89 \pm 0.03	1669 \pm 22	0.11 \pm 0.03
	dichloromethane	735 \pm 52	0.30 \pm 0.01	1602 \pm 17	0.70 \pm 0.01
	acetonitrile	501 \pm 15	0.30 \pm 0.01	1863 \pm 9	0.70 \pm 0.01
	dimethylformamide	362 \pm 5	0.76 \pm 0.01	2325 \pm 7	0.24 \pm 0.01
	dimethyl sulfoxide	406 \pm 3	0.71 \pm 0.01	2232 \pm 4	0.29 \pm 0.01
	butanol	730 \pm 6	0.37 \pm 0.01	2501 \pm 6	0.63 \pm 0.01
	ethanol	644 \pm 23	0.45 \pm 0.01	1590 \pm 12	0.55 \pm 0.01
	methanol	545 \pm 1	0.98 \pm 0.01	2657 \pm 24	0.02 \pm 0.01

Table S3. Fluorescence decay times, τ_i , and relative amplitudes, f_i , of compounds **3a**, **3b**, and **3c**, as retrieved from fitting the experimental decay patterns measured upon excitation at 420 nm to a biexponential decay model function. The reported values are averaged over three parallels. The pertaining errors are the corresponding standard deviations.

Compound	Solvent	τ_1 (ps)	f_1	τ_2 (ps)	f_2	τ_3 (ps)	f_3
3a	toluene	-	0	361 ± 3	0.87 ± 0.01	2058 ± 5	0.13 ± 0.01
	ethyl acetate	30 ± 2	0.13 ± 0.01	-	0	2059 ± 3	0.87 ± 0.01
	dichloromethane	11 ± 4	0.28 ± 0.04	282 ± 2	0.63 ± 0.03	2467 ± 1	0.09 ± 0.01
	acetone	19 ± 1	0.37 ± 0.02	277 ± 1	0.21 ± 0.01	2154 ± 8	0.42 ± 0.03
	acetonitrile	16 ± 1	0.30 ± 0.03	243 ± 2	0.63 ± 0.03	2454 ± 18	0.07 ± 0.01
	dimethylformamide	-	0	273 ± 8	0.32 ± 0.01	2098 ± 1	0.68 ± 0.01
	dimethyl sulfoxide	-	0	291 ± 4	0.92 ± 0.01	2244 ± 9	0.08 ± 0.01
	butanol	-	0	405 ± 6	≅ 1	≅ 3700	<0.001
	ethanol	-	0	353 ± 10	≅ 1	≅ 2800	<0.01
	methanol	-	0	371 ± 6	0.96 ± 0.01	2224 ± 1	0.04 ± 0.01
3b	toluene	-	0	412 ± 4	0.94 ± 0.01	1269 ± 24	0.06 ± 0.01
	ethyl acetate	29 ± 2	0.35 ± 0.01	213 ± 1	0.64 ± 0.01	2226 ± 7	0.01 ± 0.01
	dichloromethane	-	0	320 ± 1	0.92 ± 0.01	2336 ± 6	0.08 ± 0.01
	acetone	53 ± 3	0.46 ± 0.01	202 ± 3	0.53 ± 0.01	2010 ± 46	0.01 ± 0.01
	acetonitrile	51 ± 1	0.61 ± 0.01	236 ± 1	0.33 ± 0.01	2069 ± 2	0.06 ± 0.01
	dimethylformamide	75 ± 9	0.19 ± 0.03	207 ± 4	0.77 ± 0.03	1345 ± 61	0.04 ± 0.01
	dimethyl sulfoxide	-	0	247 ± 1	0.97 ± 0.01	2333 ± 6	0.03 ± 0.01
	butanol	-	0	328 ± 2	0.97 ± 0.01	3198 ± 15	0.03 ± 0.01
	ethanol	-	0	252 ± 2	0.98 ± 0.01	1720 ± 41	0.02 ± 0.01
	methanol	-	0	279 ± 2	0.90 ± 0.01	2031 ± 6	0.10 ± 0.01
3c	toluene	-	0	416 ± 1	0.98 ± 0.01	2360 ± 15	0.02 ± 0.01
	ethyl acetate	32 ± 1	0.39 ± 0.02	229 ± 1	0.59 ± 0.02	2259 ± 17	0.02 ± 0.01
	dichloromethane	22 ± 1	0.28 ± 0.01	371 ± 1	0.71 ± 0.01	≅ 3700	<0.01
	acetone	38 ± 1	0.51 ± 0.01	196 ± 1	0.47 ± 0.01	1553 ± 37	0.02 ± 0.01
	acetonitrile	38 ± 1	0.49 ± 0.01	225 ± 1	0.38 ± 0.01	2017 ± 2	0.12 ± 0.01
	dimethylformamide	-	0	320 ± 1	0.77 ± 0.01	2197 ± 2	0.23 ± 0.01
	dimethyl sulfoxide	-	0	349 ± 1	0.98 ± 0.01	3117 ± 8	0.02 ± 0.01
	butanol	-	0	397 ± 1	0.91 ± 0.01	1270 ± 5	0.09 ± 0.01
	ethanol	-	0	546 ± 2	0.92 ± 0.01	1716 ± 10	0.08 ± 0.01
	methanol	-	0	579 ± 1	0.93 ± 0.01	1943 ± 15	0.07 ± 0.01

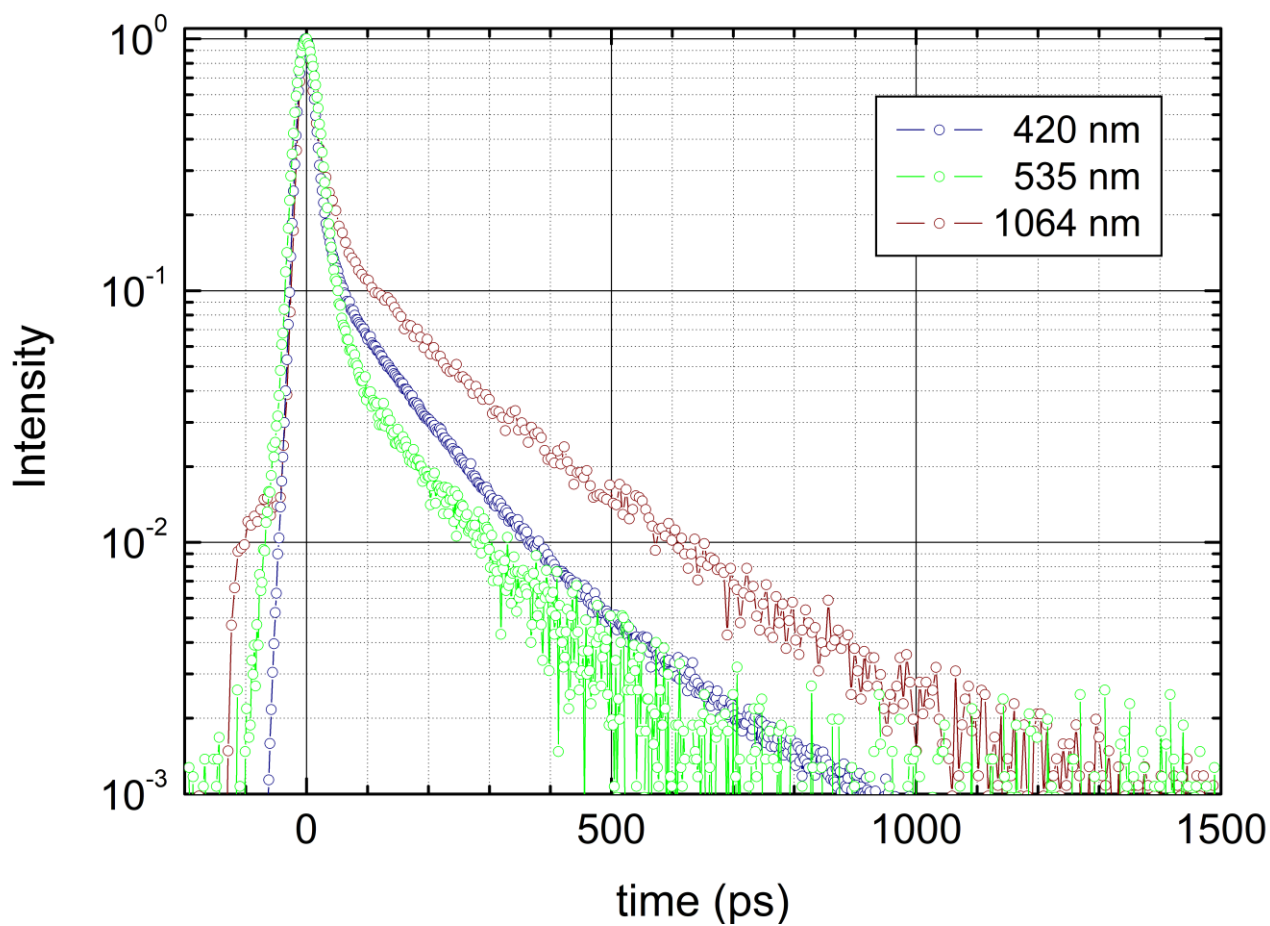


Figure S9. The TCSPC apparatus instrumental response to <10 ps laser pulses at 420 nm (violet, laser pulse duration 2.8 ps), 532 nm (green, laser pulse duration 6.4 ps), and 1064 nm (dark red, laser pulse duration 9 ps). The full-width at half maximum of the temporal point-spread functions is in any case <30 ps.

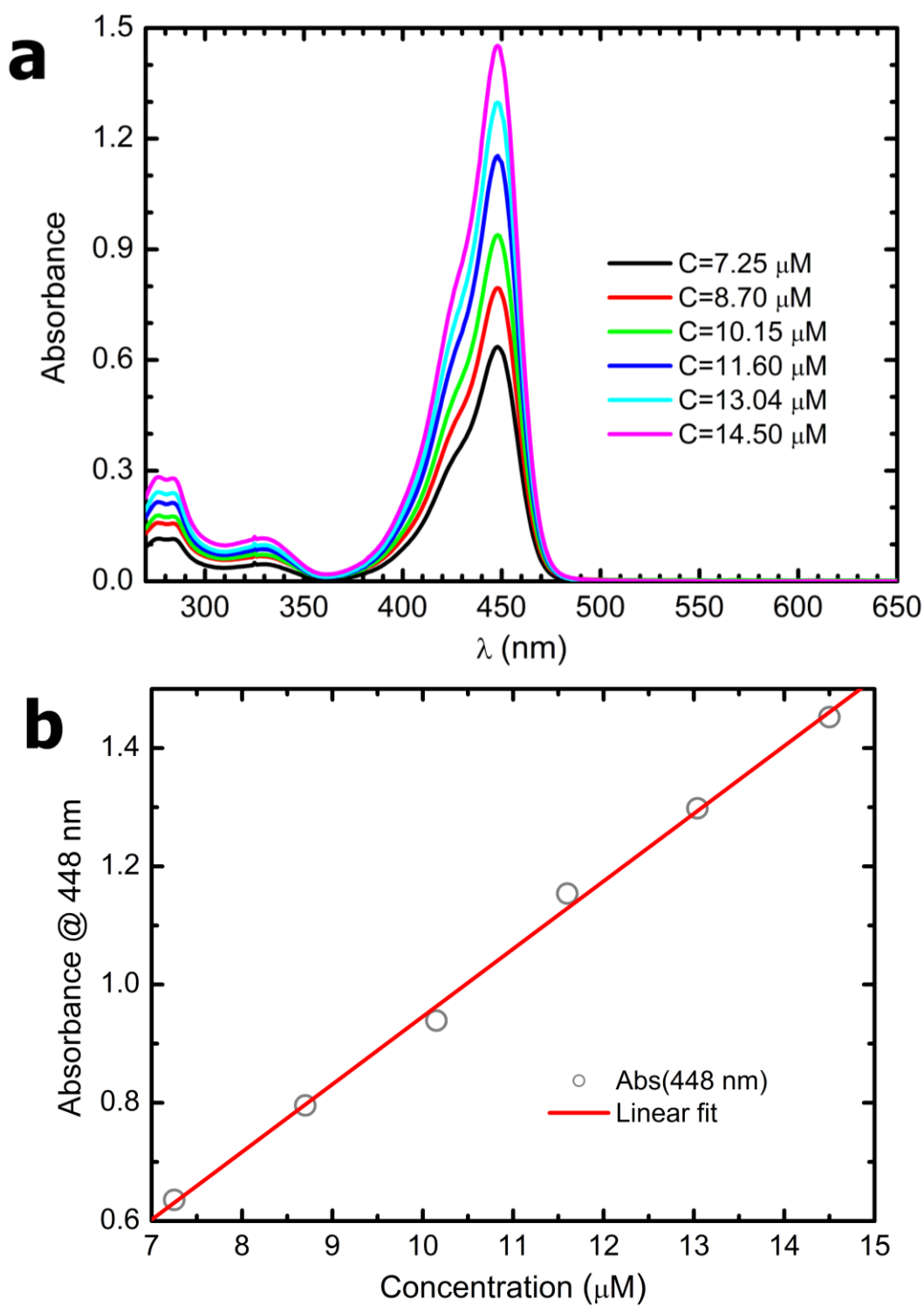


Figure S10. Exemplary dataset for determination of molar extinction coefficient values (namely 4a in dimethyl sulfoxide). a) Absorption spectra recorded for six solutions obtained by dilution of the stock at known concentration (determined by weight, see Materials and Methods); b) peak absorbance versus nominal concentration (dots) and linear regression of the data (red line). The slope is the molar extinction coefficient (in the case at hand $0.1144 \mu\text{M}^{-1}\text{cm}^{-1}$).

S9. Supplementary theoretical emission data

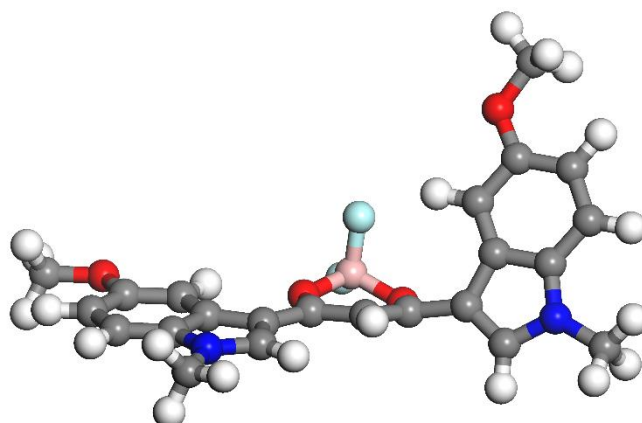


Figure S11. Global minimum geometry for the first excited state of **4c** as obtained at the TD- and TDA-B3LYP-D3/def2-TZVPD. Color code: red (oxygen), pink (boron), blue (nitrogen), light blue (fluoride), grey (carbon), white (hydrogen).

Table S4. Excited state properties of **3a** keto-enol, **3a** trans-diketo, **4a**, **4b**, and **4c** as computed at DFT/TDA-DFT with ω B97X-D/def2-TZVPD. Vertical (ΔE_{vert}), adiabatic (ΔE_{adia}), and ZPVE-corrected adiabatic ($\Delta E_{\text{adiaZPVE}}$) excitation energies for the $S_0 \rightarrow S_1$ transition in the gas phase. The HOMO to LUMO energy difference in S_0 ($\Delta E_{\text{HOMO-LUMO}}$) and the vertical de-excitation energy for $S_1 \rightarrow S_0$ transition ($\Delta E'_{\text{vert}}$) is also showed for comparison. The energies are defined in Figure 8. All the energies are reported in eV. The absorption wavelength ($\lambda_{\text{abs}\omega\text{B97}}$, nm) corresponding to the $S_0 \rightarrow S_1$ transition is also showed with its oscillator strength ($f_{\text{abs}\omega\text{B97}}$, a.u.), the dipole moment associated with the transition ($\mu_{S_0 \rightarrow S_1}$ a.u.), and the radiative decay rates of the S_1 state ($k_{\text{rad}\omega\text{B97}}$, s^{-1}), defined as in Equation 4. $k_{\text{rad}\omega\text{B97}}$ is computed considering the intensity and the maximum of the corresponding band in the computed spectrum. The emission wavelength ($\lambda_{\text{flu}\omega\text{B97}}$) corresponding to $S_1 \rightarrow S_0$ computed on S_1 geometry and its oscillator strength ($f_{\text{flu}\omega\text{B97}}$) is also reported.

	3a keto-enol	3a trans-diketo ¹	4a	4b	4c
$\Delta E_{\text{HOMO-LUMO}}$	7.51	8.13	7.15	7.19	7.04
ΔE_{vert}	4.04	4.13	3.76	3.77	3.69
ΔE_{adia}	3.86	3.95	3.65	3.65	3.57
$\Delta E_{\text{adiaZPVE}}$	3.73	3.84	3.54	3.54	3.46
$\Delta E'_{\text{vert}}$	-3.69	-3.68	-3.54	-3.54	-3.46
$\mu_{S_0 \rightarrow S_1}$	11.4	(0.2, 0.0, 4.1)	13.6	14.4	15.1
$\lambda_{\text{abs}\omega\text{B97}}$	306.6	255.1 (300.26, 284.19, 258.67)	329.8	329.0	336.4
$f_{\text{abs}\omega\text{B97}}$	1.13	(0.02, 0.00, 0.49)	1.25	1.33	1.36
$k_{\text{rad}\omega\text{B97}}$	9.17×10^9	2.01×10^9	1.04×10^{10}	1.17×10^{10}	1.21×10^{10}
$\lambda_{\text{flu}\omega\text{B97}}$	335.8	263.6 (336.74, 298.3, 266.1)	350.6	350.4	357.8
$f_{\text{flu}\omega\text{B97}}$	1.10	(0.014, 0.01, 0.49)	1.26	1.33	1.37

¹ The lowest energy band in the absorption, emission, and excitation spectra of **3a** trans-diketo is the result of the convolution of more than one signal. The wavelength value is the maximum of the band resulting from the convolution of these signals, while in parentheses are reported the three lowest energy transitions contributing to this band. For **3a** trans-diketo, k_{radB3} is computed for the third transition, i.e. the one having the higher oscillator strength.

Table S5. Excited state properties of **3a** keto-enol, **3a** trans-diketo, **4a**, **4b**, and **4c** as computed at DFT/TD-DFT with ω B97X-D/def2-TZVPD. Vertical (ΔE_{vert}), adiabatic (ΔE_{adia}), and ZPVE-corrected adiabatic ($\Delta E_{\text{adiaZPVE}}$) excitation energies for the $S_0 \rightarrow S_1$ transition in the gas phase. The HOMO to LUMO energy difference in S_0 ($\Delta E_{\text{HOMO-LUMO}}$) and the vertical de-excitation energy for $S_1 \rightarrow S_0$ transition ($\Delta E'_{\text{vert}}$) is also showed for comparison. The energies are defined in Figure 8. All the energies are reported in eV. The absorption wavelength ($\lambda_{\text{abs}\omega\text{B97}}$, nm) corresponding to the $S_0 \rightarrow S_1$ transition is also showed with its oscillator strength ($f_{\text{abs}\omega\text{B97}}$, a.u.), the dipole moment associated with the transition ($\mu_{S_0 \rightarrow S_1}$ a.u.), and the radiative decay rates of the S_1 state ($k_{\text{rad}\omega\text{B97}}$, s^{-1}), defined as in Equation 4. $k_{\text{rad}\omega\text{B97}}$ is computed considering the intensity and the maximum of the corresponding band in the computed spectrum. The emission wavelength ($\lambda_{\text{flu}\omega\text{B97}}$) corresponding to $S_1 \rightarrow S_0$ computed on S_1 geometry and its oscillator strength ($f_{\text{flu}\omega\text{B97}}$) is also reported.

	3a keto-enol	3a trans-diketo ¹	4a	4b	4c
$\Delta E_{\text{HOMO-LUMO}}$	7.51	8.13	7.15	7.19	7.04
ΔE_{vert}	3.90	4.10	3.63	3.64	3.57
ΔE_{adia}	3.69	3.92	3.50	3.51	3.44
$\Delta E_{\text{adiaZPVE}}$	3.57	3.81	3.40	3.41	3.33
$\Delta E'_{\text{vert}}$	-3.49	-3.65	-3.38	-3.38	-3.33
$\mu_{S_0 \rightarrow S_1}$	9.5	(0.2, 0.0, 3.7)	11.4	12.1	13.0
$\lambda_{\text{abs}\omega\text{B97}}$	317.8	263.5 (302.31, 286.23, 267.52)	342.0	340.7	347.7
$f_{\text{abs}\omega\text{B97}}$	0.91	(0.02, 0.00, 0.42)	1.01	1.08	1.13
$k_{\text{rad}\omega\text{B97}}$	5.75×10^9	1.44×10^9	6.55×10^9	7.51×10^9	8.08×10^9
$\lambda_{\text{flu}\omega\text{B97}}$	355.2	272.4 (339.36, 300.46, 277.1, 274.44)	367.2	366.4	372.9
$f_{\text{flu}\omega\text{B97}}$	0.84	(0.01, 0.01, 0.15, 0.34)	0.99	1.06	1.12

¹ The lowest energy band in the absorption, emission, and excitation spectra of **3a** trans-diketo is the result of the convolution of more than one signal. The wavelength value is the maximum of the band resulting from the convolution of these signals, while in parentheses are reported the three lowest energy transitions contributing to this band. For **3a** trans-diketo, k_{radB3} is computed for the third transition, i.e. the one having the higher oscillator strength.

Table S6. Excited state properties of **3a** keto-enol, **3a** trans-diketo, **4a**, **4b**, and **4c** as computed at DFT/TDA-DFT with M06-2X/def2-TZVPD. Vertical (ΔE_{vert}), adiabatic (ΔE_{adia}), and ZPVE-corrected adiabatic ($\Delta E_{\text{adiaZPVE}}$) excitation energies for the $S_0 \rightarrow S_1$ transition in the gas phase. The HOMO to LUMO energy difference in S_0 ($\Delta E_{\text{HOMO-LUMO}}$) and the vertical de-excitation energy for $S_1 \rightarrow S_0$ transition ($\Delta E'_{\text{vert}}$) is also showed for comparison. The energies are defined in Figure 8. All the energies are reported in eV. The absorption wavelength (λ_{absM06} , nm) corresponding to the $S_0 \rightarrow S_1$ transition is also showed with its oscillator strength (f_{absM06} , a.u.), the dipole moment associated with the transition ($\mu_{S_0 \rightarrow S_1}$ a.u.), and the radiative decay rates of the S_1 state (k_{radM06} , s^{-1}), defined as in Equation (4). k_{radM06} is computed considering the intensity and the maximum of the corresponding band in the computed spectrum. The emission wavelength (λ_{fluM06}) corresponding to $S_1 \rightarrow S_0$ computed on S_1 geometry, and its oscillator strength (f_{fluM06}) is also reported.

	3a keto-enol	3a trans-diketo ¹	4a	4b	4c
$\Delta E_{\text{HOMO-LUMO}}$	5.95	6.57	5.60	5.64	5.51
ΔE_{vert}	3.96	4.05	3.68	3.57	3.60
ΔE_{adia}	3.80	3.90	3.57	3.68	3.49
$\Delta E_{\text{adiaZPVE}}$	3.66	3.77	3.46	3.46	3.37
$\Delta E'_{\text{vert}}$	-3.64	-3.69	-3.47	-3.58	-3.38
$\mu_{S_0 \rightarrow S_1}$	12.0	(0.2, 0.0, 4.2)	14.3	15.2	15.7
λ_{absM06}	312.9	260.0 (306.45, 292.82, 262.90)	337.3	336.6	344.8
f_{absM06}	1.17	(0.02, 0.00, 0.48)	1.29	1.37	1.38
k_{radM06}	9.54×10^9	1.95×10^9	1.08×10^{10}	1.11×10^{10}	1.21×10^{10}
λ_{fluM06}	340.2	268.4 (336.35, 302.58, 270.81, 268.45)	357.7	357.8	366.5
f_{fluM06}	1.15	(0.011, 0.009, 0.376, 0.1749)	1.31	1.39	1.41

¹ The lowest energy band in the absorption, emission, and excitation spectra of **3a** *trans*-diketo is the result of the convolution of more than one signal. The wavelength value is the maximum of the band resulting from the convolution of these signals, while in parentheses are reported the three lowest energy transitions contributing to this band. For **3a** *trans*-diketo, k_{radB3} is computed for the third transition, i.e. the one having the higher oscillator strength.

Table S7. Excited state properties of **3a** keto-enol, **3a** *trans*-diketo, **4a**, **4b**, and **4c** as computed at DFT/TDA-DFT with CAM-B3LYP-D3/def2-TZVPD. Vertical (ΔE_{vert}), adiabatic (ΔE_{adia}), and ZPVE-corrected adiabatic ($\Delta E_{\text{adiaZPVE}}$) excitation energies for the $S_0 \rightarrow S_1$ transition in the gas phase. The HOMO to LUMO energy difference in S_0 ($\Delta E_{\text{HOMO-LUMO}}$) and the vertical de-excitation energy for $S_1 \rightarrow S_0$ transition ($\Delta E'_{\text{vert}}$) is also showed for comparison. The energies are defined in Figure 8. All the energies are reported in eV. The absorption wavelength (λ_{absCAM} , nm) corresponding to the $S_0 \rightarrow S_1$ transition is also showed with its oscillator strength (f_{absCAM} , a.u.), the dipole moment associated with the transition ($\mu_{S_0 \rightarrow S_1}$ a.u.), and the radiative decay rates of the S_1 state (k_{radCAM} , s⁻¹), defined as in Equation (4). k_{radCAM} is computed considering the intensity and the maximum of the corresponding band in the computed spectrum. The emission wavelength (λ_{fluoCAM}) corresponding to $S_1 \rightarrow S_0$ computed on S_1 geometry, and its oscillator strength (f_{fluoCAM}) is also reported.

	3a keto-enol	3a trans-diketo ¹	4a	4b	4c
$\Delta E_{\text{HOMO-LUMO}}$	6.32	6.94	5.99	6.03	5.89
ΔE_{vert}	3.96	4.13	3.71	3.72	3.63
ΔE_{adia}	3.81	3.96	3.60	3.61	3.52
$\Delta E_{\text{adiaZPVE}}$	3.68	3.82	3.49	3.50	3.41
$\Delta E'_{\text{vert}}$	-3.66	-3.69	-3.50	-3.50	-3.42
$\mu_{S_0 \rightarrow S_1}$	11.7	(0.2, 0.0, 4.0)	13.8	14.6	15.2
λ_{absCAM}	312.8	259.3 (299.85, 283.93, 262.58)	334.5	333.7	341.9
f_{absCAM}	1.13	(0.02, 0.00, 0.47)	1.25	1.33	1.35
k_{radCAM}	9.00×10^9	1.66×10^9	1.03×10^{10}	1.16×10^{10}	1.17×10^{10}
λ_{fluoCAM}	339.2	269.2 (335.65, 297.65, 272.1, 270.22)	354.5	354.3	363.0
f_{fluoCAM}	1.10	(0.01, 0.01, 0.28, 0.25)	1.26	1.34	1.37

¹ The lowest energy band in the absorption, emission, and excitation spectra of **3a** *trans*-diketo is the result of the convolution of more than one signal. The wavelength value is the maximum of the band resulting from the convolution of these signals, while in parentheses are reported the three lowest energy transitions contributing to this band. For **3a** *trans*-diketo, k_{radB3} is computed for the third transition, i.e. the one having the higher oscillator strength.

Table S8. Excited state properties of **3a** keto-enol, **3a** trans-diketo, **4a**, **4b**, and **4c** as computed at DFT/TDA-DFT with B3LYP-D3/def2-TZVPD. Vertical (ΔE_{vert}), adiabatic (ΔE_{adia}), and ZPVE-corrected adiabatic ($\Delta E_{\text{adiaZPVE}}$) excitation energies for the $S_0 \rightarrow S_1$ transition in the gas phase. The HOMO to LUMO energy difference in S_0 ($\Delta E_{\text{HOMO-LUMO}}$) and the vertical de-excitation energy for $S_1 \rightarrow S_0$ transition ($\Delta E'_{\text{vert}}$) is also showed for comparison. The energies are defined in Figure 8. All the energies are reported in eV. The absorption wavelength (λ_{absB97} , nm) corresponding to the $S_0 \rightarrow S_1$ transition is also showed with its oscillator strength (f_{absB97} , a.u.), the dipole moment associated with the transition ($\mu_{S_0 \rightarrow S_1}$ a.u.), and the radiative decay rates of the S_1 state (k_{radB97} , s^{-1}), defined as in Equation 4. k_{radB97} is computed considering the intensity and the maximum of the corresponding band in the computed spectrum. The emission wavelength ($\lambda_{\text{fluoB3TDA}}$) corresponding to $S_1 \rightarrow S_0$ computed on S_1 geometry, and its oscillator strength ($f_{\text{fluoB3TDA}}$) is also reported. The S_1 used in the energy and emission spectra calculations have been the CAM-B3LYP-D3 geometries.

	3a keto-enol	3a trans-diketo ¹	4a	4b	4c ²
$\Delta E_{\text{HOMO-LUMO}}$	3.84	4.41	3.58	3.61	3.49
ΔE_{vert}	3.55	3.77	3.34	3.32	3.14
ΔE_{adia}	3.49	3.59	3.31	3.30	3.10
$\Delta E_{\text{adiaZPVE}}$	3.48	3.57	3.33	3.30	3.13
$\Delta E'_{\text{vert}}$	-3.37	-3.34	-3.24	-3.21	-3.03
$\mu_{S_0 \rightarrow S_1}$	11.4	(0.92, 1.45, 0.19)	14.0	14.4	12.7
$\lambda_{\text{absB3TDA}}$	349.3	308.8 (329.21, 310.52, 310.49)	371.6	373.1	394.5
f_{absB3TDA}	0.99	(0.09, 0.14, 0.02)	1.14	1.17	0.98
k_{radB3TDA}	6.18×10^9	4.82×10^7	7.69×10^9	8.05×10^9	5.30×10^9
$\lambda_{\text{fluoB3TDA}}$	368.1	314 (371.08, 328.8, 320.12)	383.1	385.7	409.8
$f_{\text{fluoB3TDA}}$	0.97	(0.03, 0.11, 0.03)	1.19	1.23	1.03

¹ The lowest energy band in the absorption, emission, and excitation spectra of **3a trans-diketo** is the result of the convolution of more than one signal. The wavelength value is the maximum of the band resulting from the convolution of these signals, while in parentheses are reported the three lowest energy transitions contributing to this band.

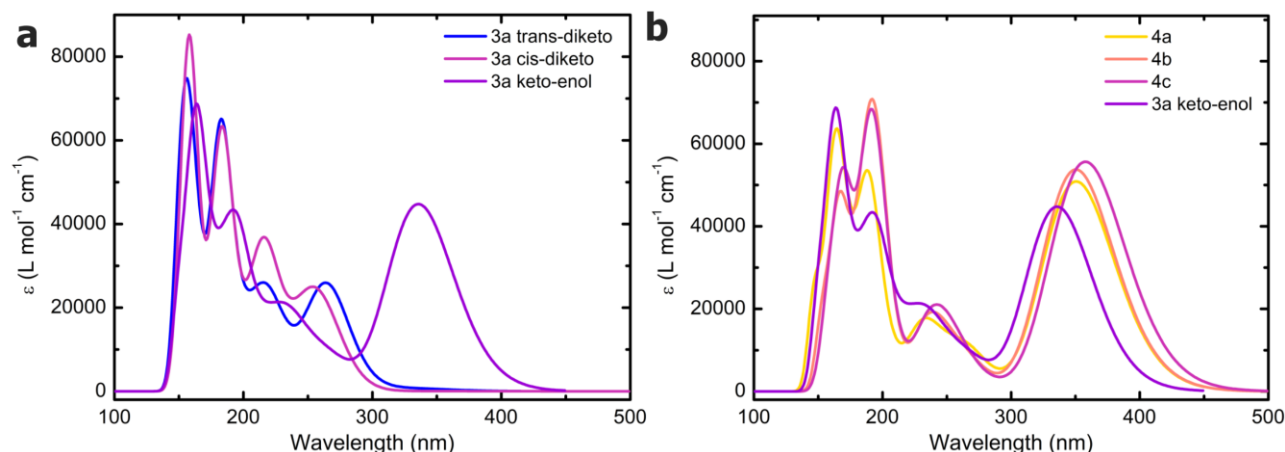


Figure S12. Electronic fluorescence spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA- ω B97X-D/def2-TZVPD for S_1 including the first 100 excitations.

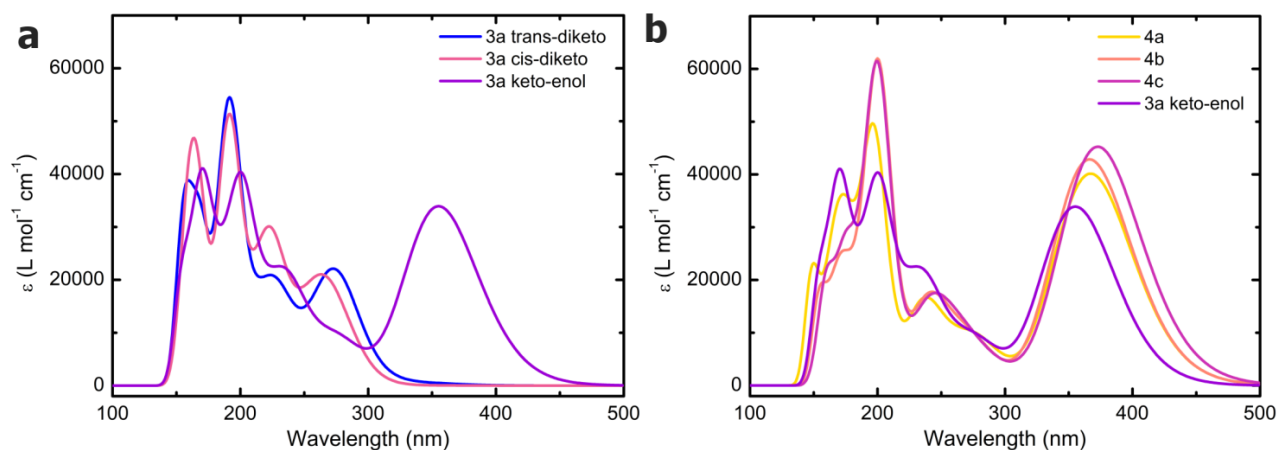


Figure S13. Electronic fluorescence spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TD- ω B97X-D/def2-TZVPD for S_1 including the first 100 excitations.

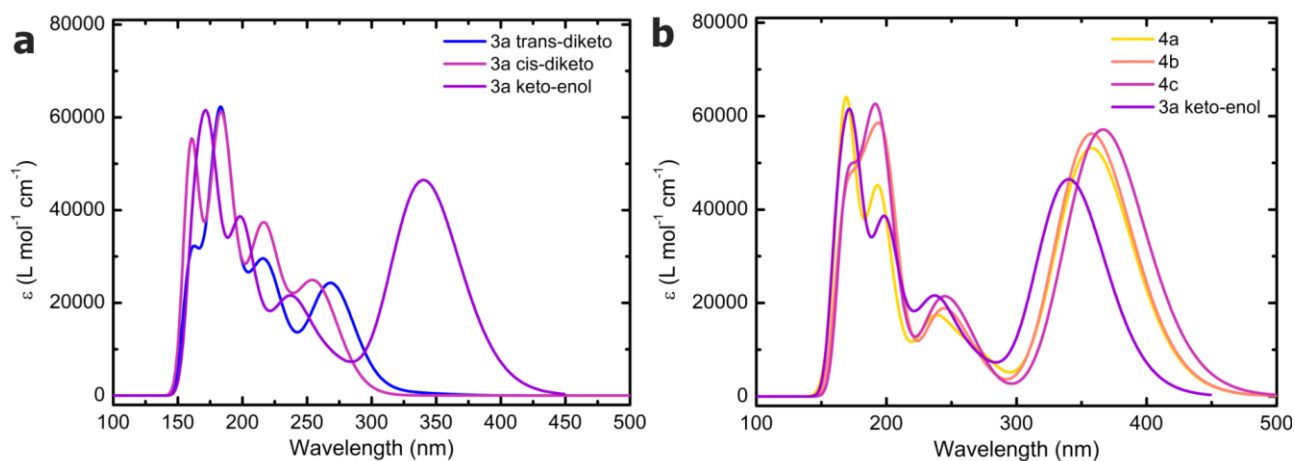


Figure S14. Electronic fluorescence spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA-M06-2X/def2-TZVPD for S_1 including the first 100 excitations.

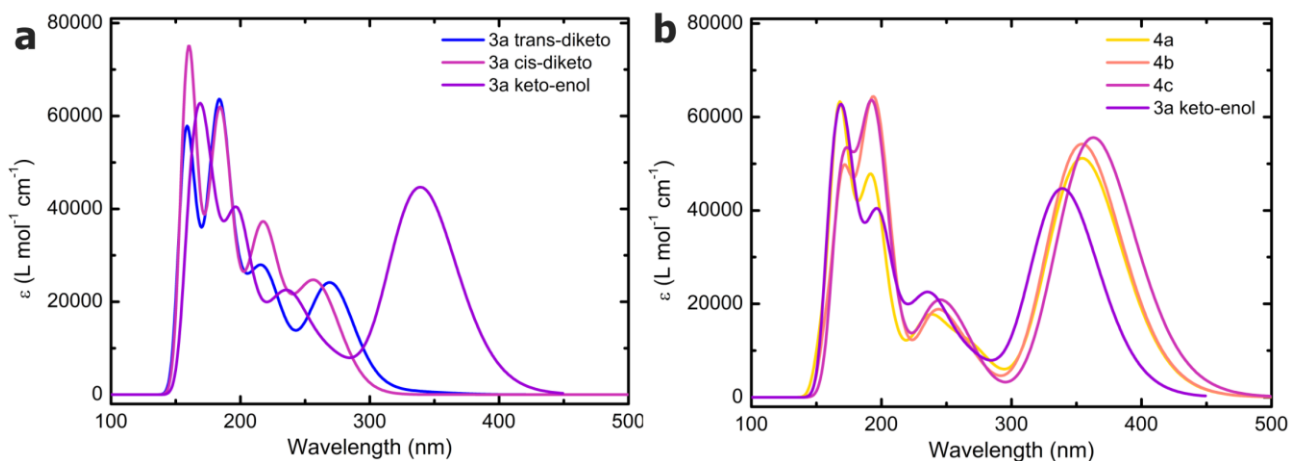


Figure S15. Electronic fluorescence spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA-CAM-B3LYP-D3/def2-TZVPD for S_1 including the first 100 excitations.

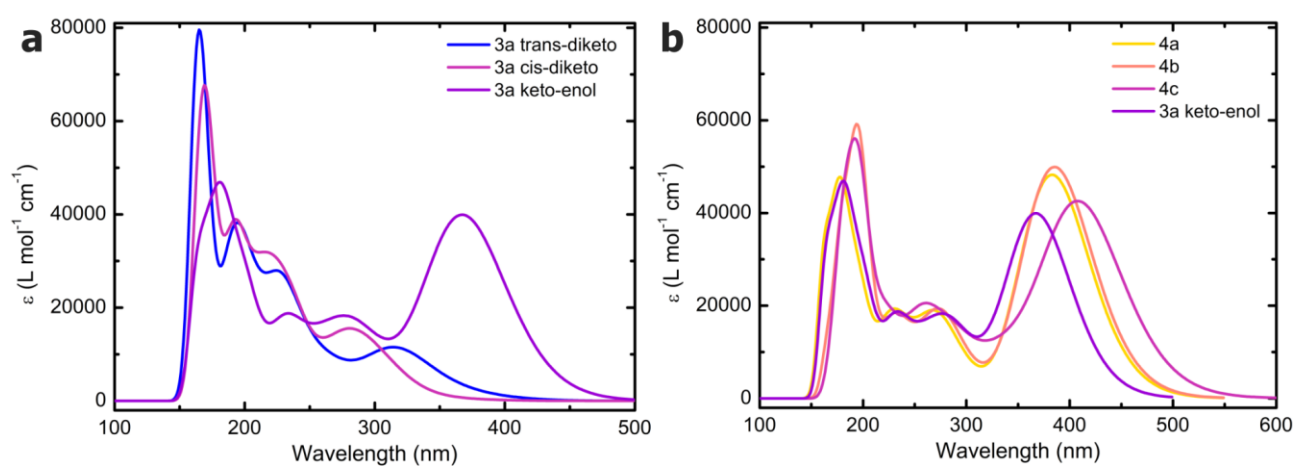


Figure S16. Electronic fluorescence spectra of (a) the three conformers of **3a** and (b) the BF₂bdks compounds as computed at the TDA-B3LYP-D3/def2-TZVPD for S_1 including the first 100 excitations. The spectra are obtained on the TDA-CAM-B3LYP-D3 geometry for S_1 .