Supporting Information

Plasmon Hybridization Model in Molecules: Molecular Jackhammers

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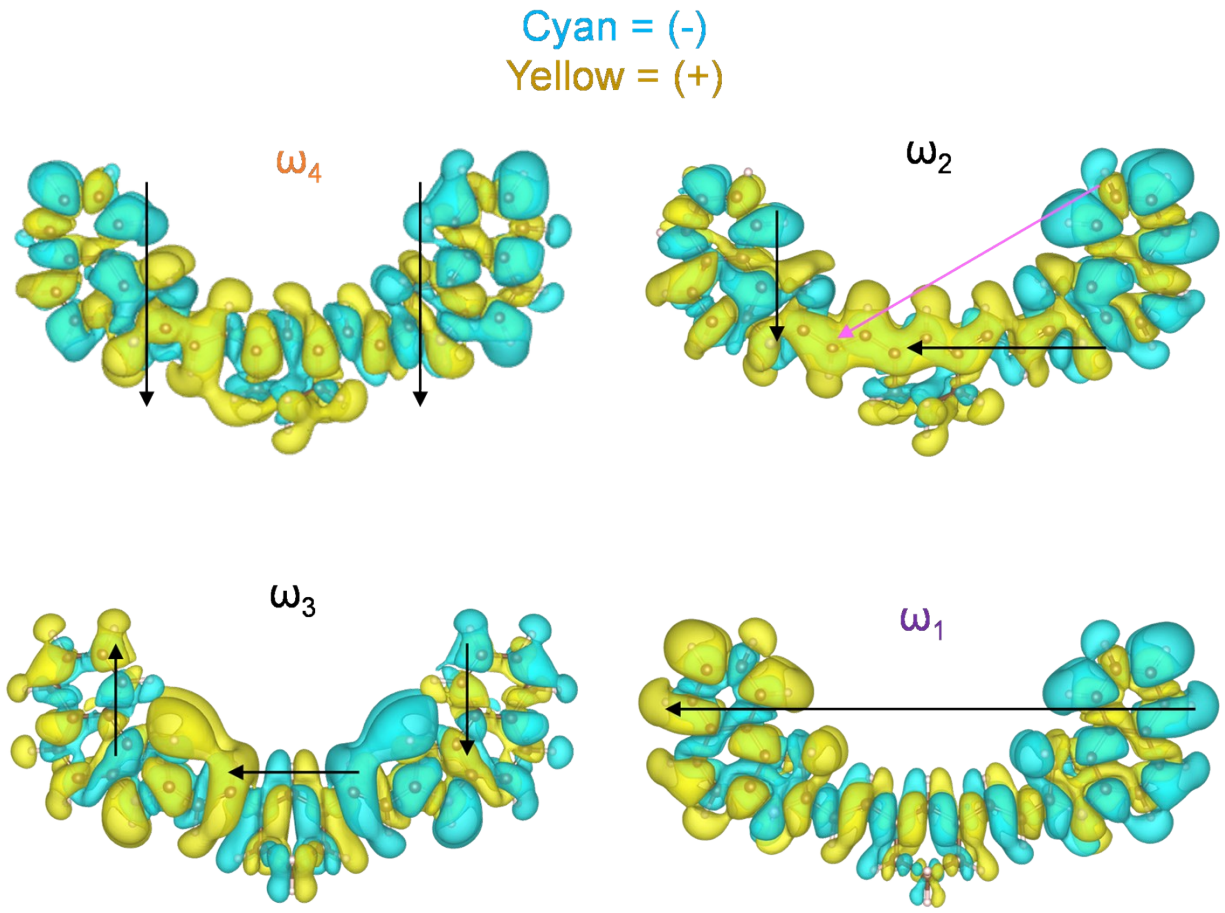


Figure S1. Calculated induced charged density in the optically excited cyanine (MJH). The calculated electron density distribution in the cyanine molecule by TDDFT calculations is presented. The electron density figures are presented in larger sizes than in Figure 1c in order to make it easier to visualize the transversal and longitudinal modes. The black arrows are added to help visualize the electron density dipolar oscillations. The pink arrow is to indicate the oscillation in both directions (transversal and longitudinal). The w_2 mode is a combination of transversal and longitudinal oscillation. Adapted with permission from Springer Nature, copyright 2023.[1]

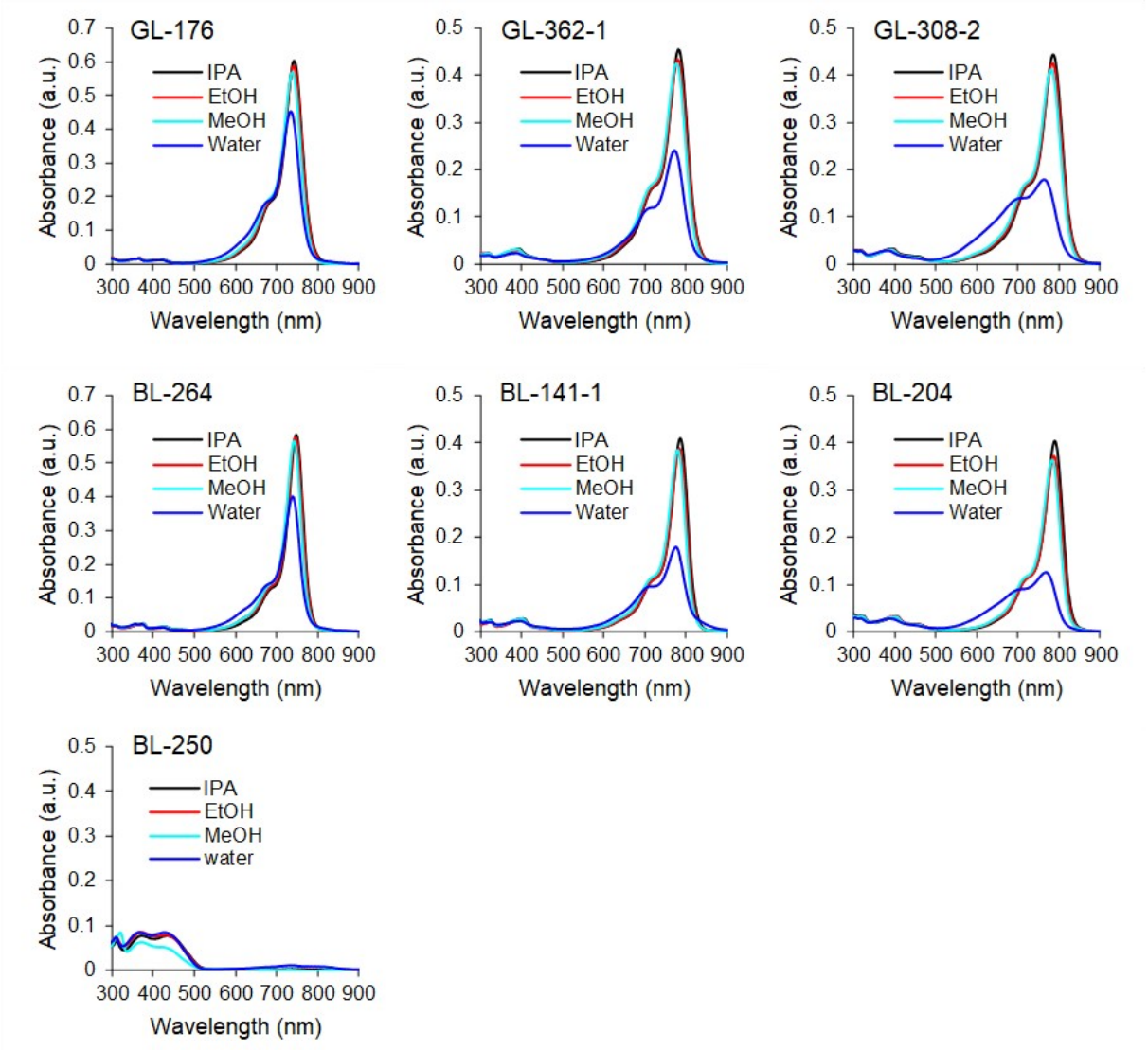


Figure S2. Plasmon resonance shift and extinction change as a function of the dielectric constant on the solvent. Absorption spectra of cyanine molecules in various solvents. IPA = isopropanol (dielectric constant, κ = 19.43), EtOH = ethanol (κ = 24.35), MeOH = methanol (κ =

32.6), water (κ = 78.3). The absorption spectrum of molecule BL-250 in different solvents shows the lack of canonical molecular plasmon resonance modes. BL-250 is a control molecule that does not behave as a molecular plasmon and therefore lacks the property of plasmon resonance shift (λ_{max} shift) as a function of the dielectric constant.

Table S1. Tunability of the molecular plasmon resonance and EPI in molecular jackhammers. The λ_{max} values are converted to eV units.

	IPA		EtOH		MeOH		Water		
Entry	λ_{max}/eV	abs	λ_{max}/eV	abs	λ_{max}/eV	Abs	λ_{max}/eV	abs	EPI
GL-176	1.669	0.603	1.671	0.588	1.678	0.570	1.687	0.452	2.6
BL-264	1.655	0.584	1.657	0.576	1.666	0.565	1.673	0.400	3.2
GL-362-1	1.585	0.455	1.589	0.432	1.596	0.425	1.604	0.240	3.7
BL-141-1	1.575	0.409	1.579	0.398	1.587	0.386	1.598	0.179	4.0
BL-308-2	1.581	0.444	1.581	0.428	1.589	0.412	1.627	0.179	4.6
BL-204	1.571	0.404	1.575	0.373	1.583	0.362	1.616	0.125	4.7
BL-250	2.870	0.077	2.904	0.079	2.995	0.051	2.910	0.083	-0.2

Control molecule BL-250 does not support a whole-molecule vibration and lacks plasmonicity.

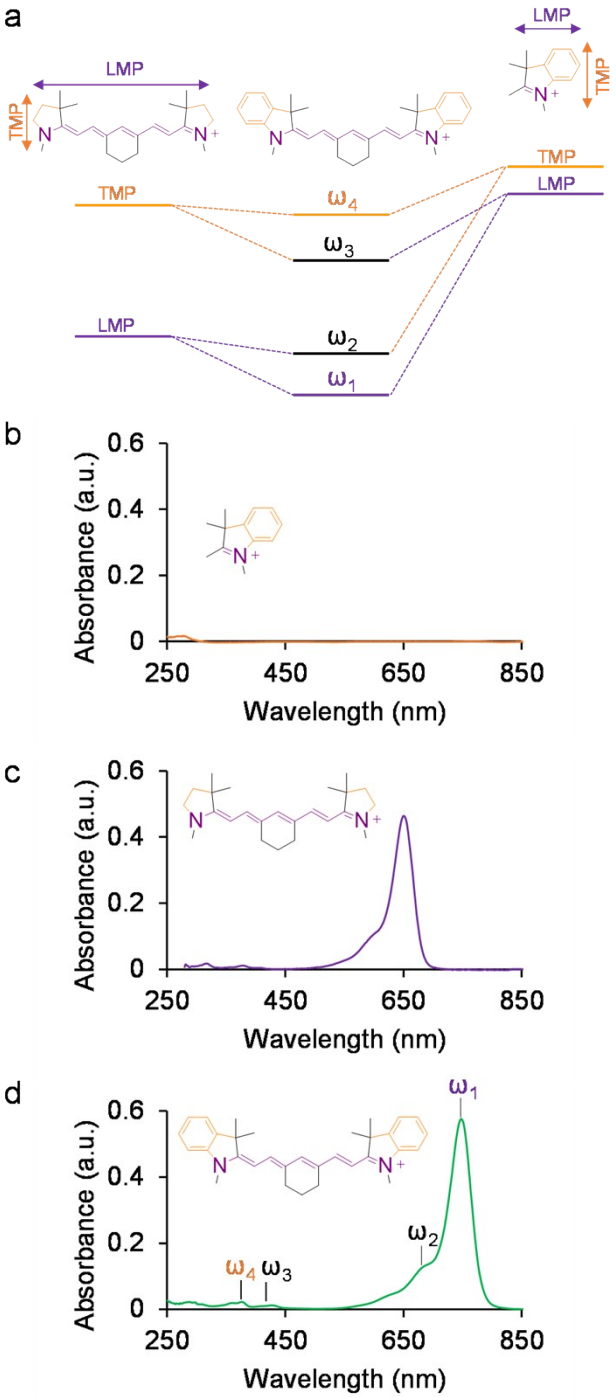


Figure S3. **Construction of molecular plasmon hybridization model in BL-264 (Cy7 cyanine).** This model is an analogy to the molecular orbital theory and the plasmon hybridization theory in metallic nanoparticles. **a**) Hybridization of molecular fragments gives rise to hybridized molecular

plasmon. **b**) Spectrum of benzoindole fragment. **c**) Spectrum of polymethine bridge. **d**) Spectrum of hybridized molecular plasmon.

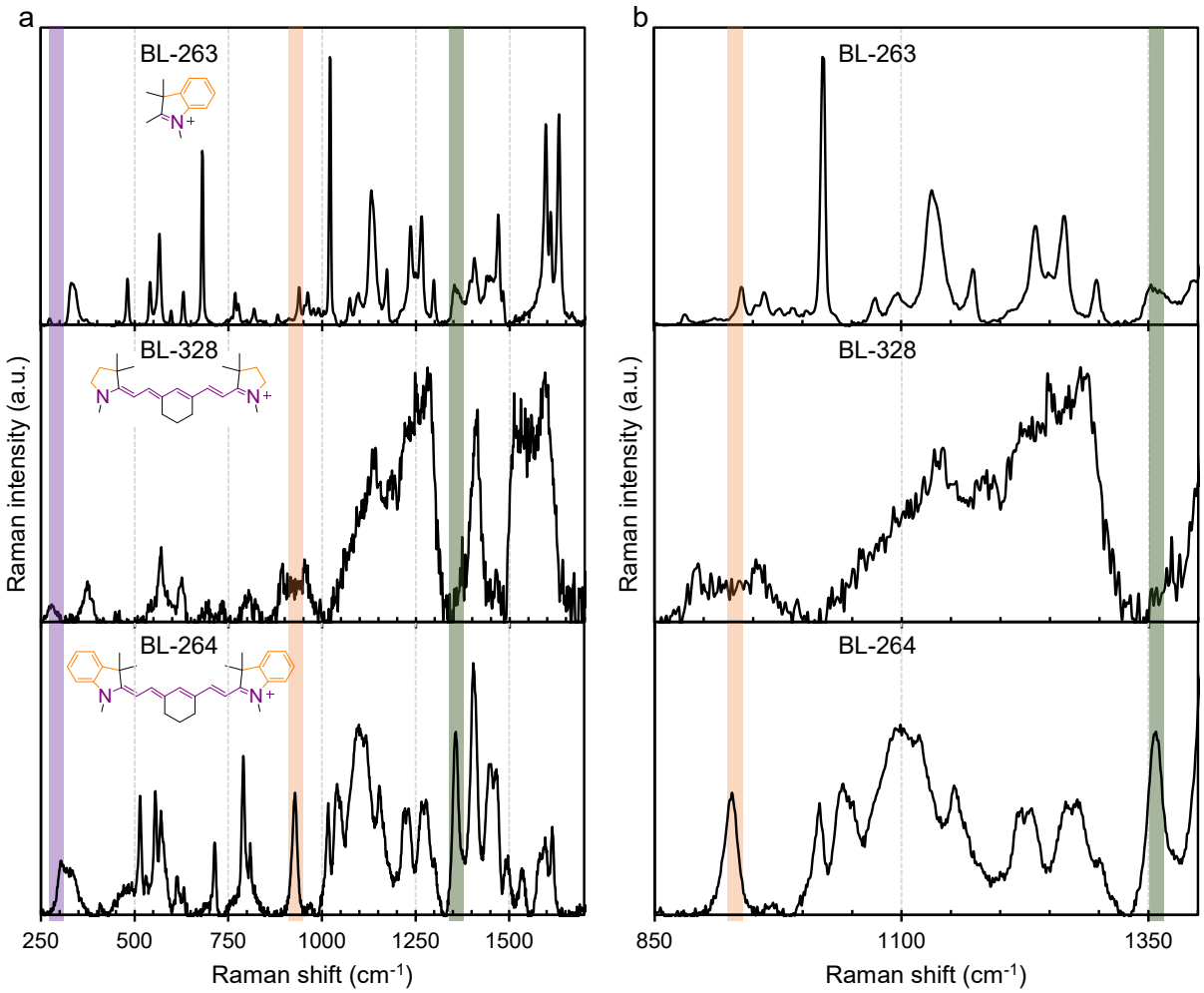


Figure S4. Major vibrational-plasmon modes in MJH (cyanines) resolved by Raman spectroscopy. The spectrum in column (**a**) is for the extended Raman shift range (250 – 1700 cm^{-1}) and the spectrum in (**b**) is for a narrow Raman shift range (850 – 1400 cm^{-1}) for better observation of the peaks. The LMP vibration is highlighted by the purple band at ~302 cm^{-1} for BL-264 and at ~280 cm^{-1} for BL-328, the TMP vibration is highlighted by the orange band at ~928 cm^{-1} for BL-264 and at ~938 cm^{-1} for BL-263, and the concerted whole-molecule vibration is

highlighted by the green band ~1357 cm^{-1}. The Raman spectrum of BL-264 (Cy7) shows the LMP and TMP and whole-molecule vibration. The spectrum of the heptamethine bridge (BL-328) shows the LMP mode and lacks the TMP and the whole-molecule vibration mode as expected. The Raman spectrum of the indole (BL-263) shows the TMP but lacks LMP. The spectrum of BL-263 shows a broad and low-intensity peak at ~ 1350 cm^{-1}. However, the whole-molecule vibration peak is usually a distinctive narrow and high-intensity peak as is observed in BL-264 and many other spectra in Figure 6 and Figure 7.

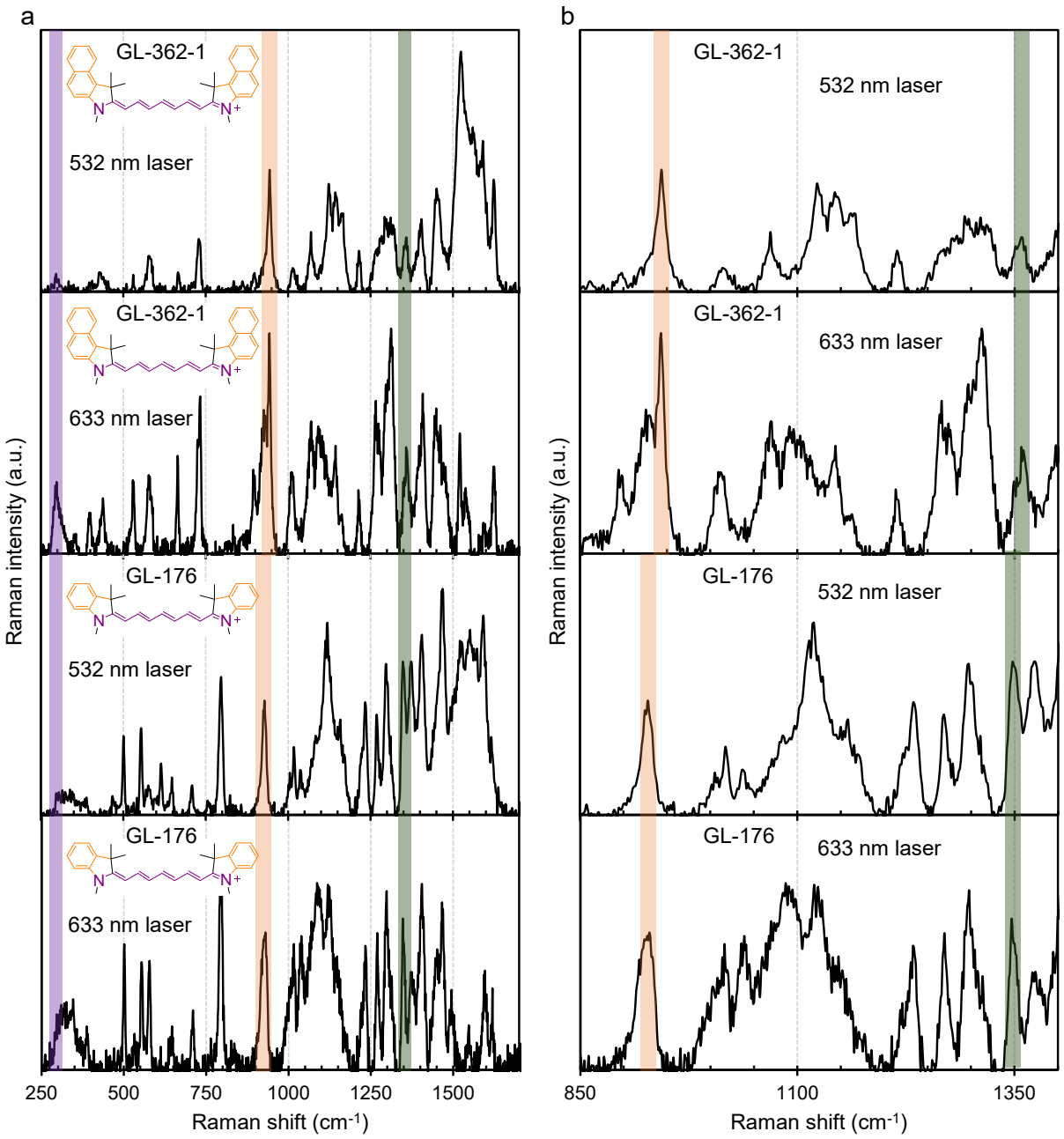


Figure S5. Comparison of Raman spectra in MJH (cyanines) obtained with 532 nm laser excitation versus 633 nm laser excitation. The spectrum in column (**a**) is for the extended Raman shift range (250 – 1700 cm^{-1}) and the spectrum in (**b**) is for a narrow Raman shift range (850 – 1400 cm^{-1}) for better observation of the peaks. The LMP vibration is highlighted by the purple band at ~300 cm^{-1}, the TMP vibration is highlighted by the orange band at ~944 cm^{-1} for BL-362-1

and at ~928 cm^{-1} for BL-176, and the concerted whole-molecule vibration is highlighted by the green band at ~1357 cm^{-1} for BL-362-1 and at ~1348 cm^{-1} for BL-176. The LMP vibration band in the Raman spectrum is enhanced by the excitation with the 633 nm laser since this wavelength is closer to the LMP peak than in the case of the 532 nm laser (See Figure S1 to observe the absorbance of BL-362-1 and BL-176).

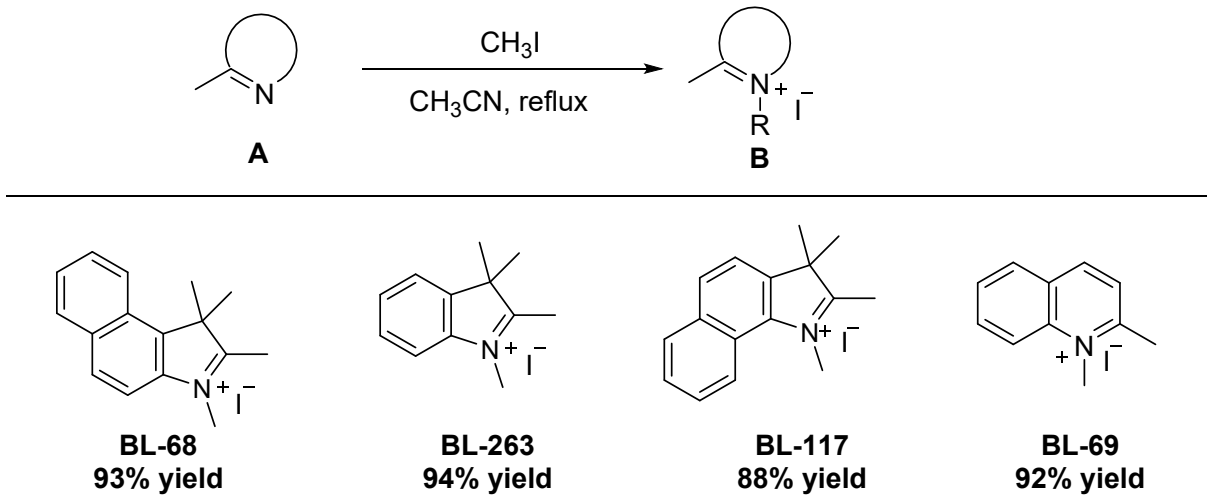
Table S2. Summary of major vibrational modes associated with molecular plasmon oscillations resolved by Raman spectroscopy.

	Raman shift (cm^{-1})			[d]Oscillation frequency × 10^{12} (s^{-1})		
Entry	[a]LMP	[b]TMP	[c]Vibronic mode	LMP	TMP	Vibronic mode
BL-141-1	298	940	1345	8.9	28.2	40.3
GL-362-1	298	944	1357	8.9	28.3	40.7
BL-264	302	928	1357	9.0	27.8	40.7
GL-176	305	928	1348	9.1	27.8	40.4
BL-250	No peak	946	No peak	__	28.4	__
BL-328	280	No Peak	No Peak	8.4	__	__
BL-329	295	No Peak	No Peak	8.8	__	__

Raman shift values of the plasmon-vibration coupling. [a]Vibration associated with the LMP. [b]Vibration associated with the TMP. [c]Concerted whole-molecule vibration longitudinally and axially associated to the quadrupolar molecular plasmon.[1,2] [d]Oscillations frequencies are in the

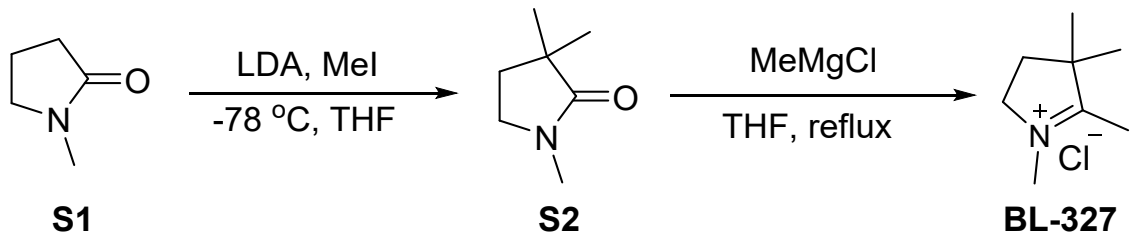
THz range (10^{12} s^{-1}). One single oscillation of the whole-molecule vibronic mode takes ~25 fs. The oscillation rates were calculated by converting the Raman vibrational frequencies in cm^{-1} units to frequencies in Hertz (s^{-1}).

Scheme S1: Synthesis of *N*-heterocyclic salt **B**



General procedure: To a screwed-capped vial charged with compound **A** (1 equiv) and CH_3I (1.5 equiv) was heated to reflux in CH_3CN until compound **A** was consumed. Subsequently, the mixture was permitted to cool to room temperature, then diethyl ether was added to precipitate the product. That product was collected by filtration and washed with diethyl ether to obtained *N*-heterocyclic salt **B**.

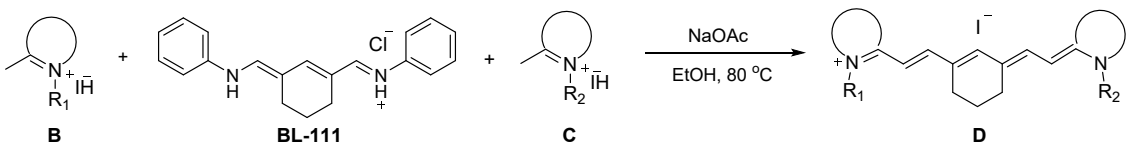
Scheme S2: Synthesis of *N*-heterocyclic salt **BL-327**



To a solution of **S1** (2.00 g, 20.2 mmol, 1 equiv) in THF (30 mL), LDA (12.1 mL, 24.2 mmol, 1.2 equiv, 2 M in THF) was added dropwise via syringe. After 15 min, MeI (1.5 mL, 24.2 mmol, 1.2 equiv) was added neat in a dropwise fashion. The solution was warmed to –20 °C, stirred for 15 min, and re-cooled to –78 °C. The second solution of LDA (12.1 mL, 24.2 mmol, 1.2 equiv, 2 M in THF) was added dropwise via syringe. After stirring for 15 min at –78 °C, neat MeI (1.5 mL, 24.2 mmol, 1.2 equiv) was added dropwise to the lactam solution. The solution was warmed to 25 °C and allowed to stir overnight. The reaction was quenched with water. The organic layer was separated, and the aqueous layer was extracted with DCM (2 × 500 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography gave compound **S2 (**1.54 g, 60% yield**)** as colorless oil.

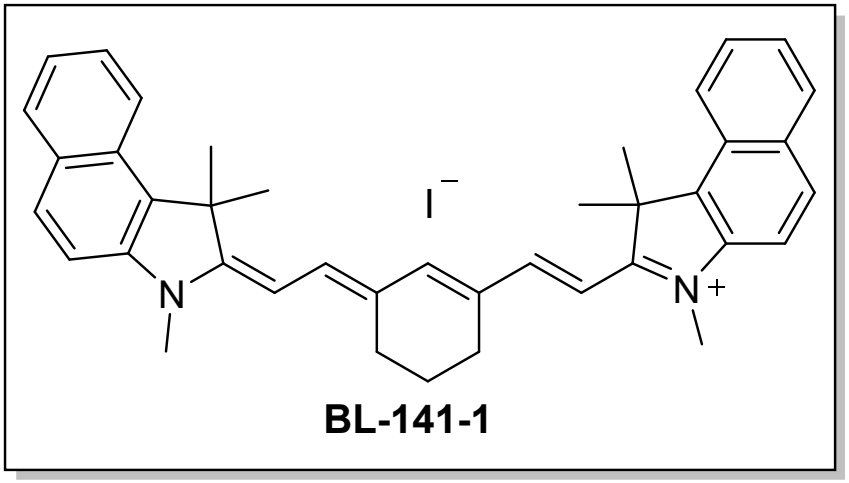
To a Schlenk tube, compound **S2** (250 mg, 1.97 mmol, 1 equiv) was dissolved in anhydrous THF (10 mL) under a N_2 atmosphere. Then, methyl magnesium chloride (0.98 mL, 2.96 mmol, 1.5 equiv, 3.0 M in THF) was added dropwise to the reaction mixture. The reaction was heated to reflux in an oil bath overnight. The reaction was allowed to cool to room temperature and quenched by addition of MeOH. The solvent was removed under vacuum and crude product was purified by column chromatography to provide **BL-327** (133 mg, 43% yield).

Scheme S3: Synthesis of cyanine dye **D**

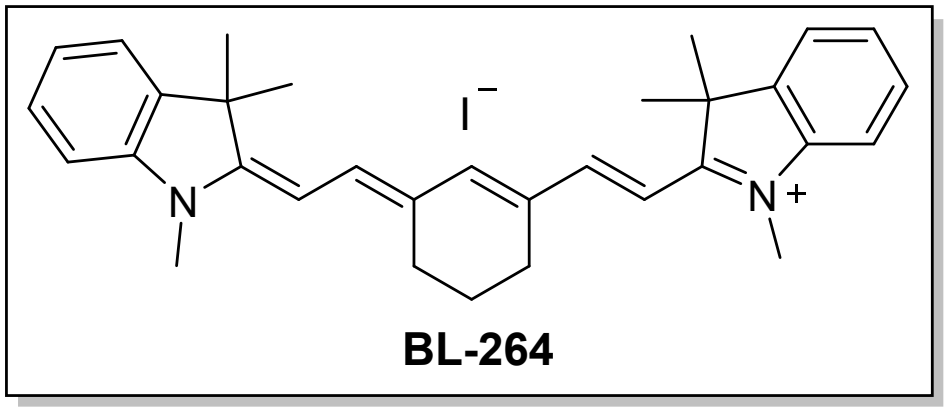


General procedure: A screw-capped vial charged with *N*-heterocyclic salt **B** (1 equiv), **BL-111** (1 equiv), another identical or different salt **C** (1 equiv) and NaOAc (3 equiv) were dissolved in

absolute ethanol. The mixture was heated at 80 °C overnight under a N_2 atmosphere. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography with DCM/MeOH as eluent to afford dye **D**.

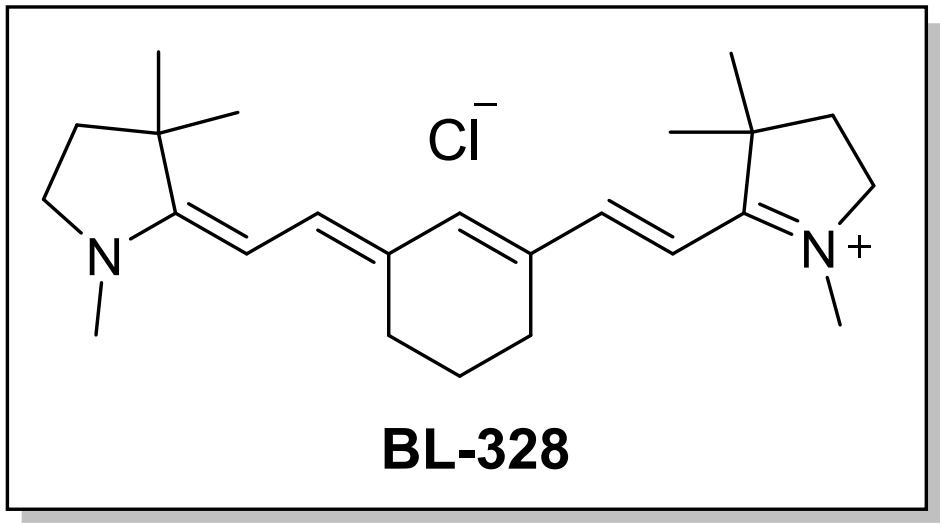


Synthesis of BL-141-1: Prepared according to the general procedure from **BL-68** (176 mg, 0.50 mmol, 1 equiv) and **BL-111** (81 mg, 0.25 mmol, 1 equiv). Dark-green solid. Yield: 88% (149 mg). ^{1}H-NMR (600 MHz, CD_3OD) δ 8.24–8.21 (m, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 14.2 Hz, 2H), 7.64–7.60 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.53 (s, 1H), 7.48–7.44 (m, 2H), 6.19 (d, *J* = 14.1 Hz, 2H), 3.72 (s, 6H), 2.61 (t, *J* = 6.1 Hz, 4H), 2.03–1.95 (m, 14H). ^{13}C-NMR (151 MHz, CD_3OD) δ 174.72, 148.86, 141.83, 134.45, 133.79, 133.77, 133.69, 133.30, 133.10, 133.04, 133.00, 132.30, 131.59, 131.09, 130.02, 129.94, 129.46, 128.65, 125.80, 123.31, 111.80, 100.44, 51.99, 31.82, 27.51, 25.02, 22.77. HRMS (ESI) calculated for [M, $C_{40}H_{41}N_2$]$^+$: 549.3264, found: 549.3275.



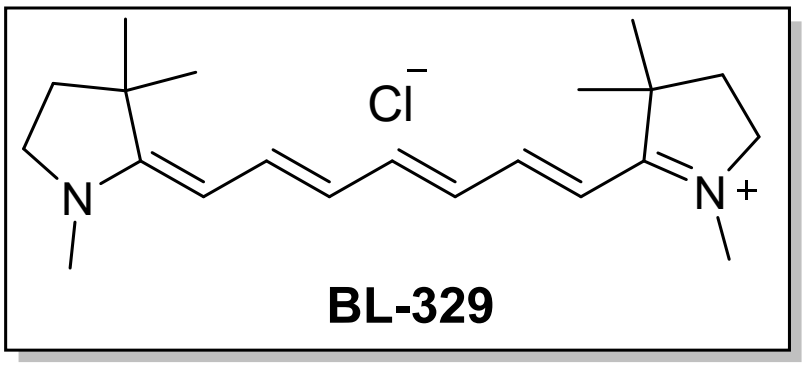
BL-264

Synthesis of BL-264: Prepared according to the general procedure from **BL-263** (60 mg, 0.2 mmol, 2 equiv) and **BL-111** (33 mg, 0.1 mmol, 1 equiv). Dark-green solid. Yield: 70% (40 mg). ^{1}H-NMR (600 MHz, CD_3OD) δ 7.76 (d, *J* = 14.0 Hz, 2H), 7.49–7.44 (m, 3H), 7.39 (td, *J* = 7.7, 1.2 Hz, 2H), 7.27–7.21 (m, 4H), 6.15 (d, *J* = 14.0 Hz, 2H), 3.60 (s, 6H), 2.57 (t, *J* = 6.2 Hz, 4H), 1.98–1.92 (m, 2H), 1.71 (s, 12H). ^{13}C-NMR (151 MHz, CD_3OD) δ 173.41, 149.81, 144.46, 142.27, 133.79, 129.68, 125.85, 123.24, 111.46, 100.77, 50.15, 31.40, 27.91, 24.96, 22.73. HRMS (ESI) calculated for [M, $C_{32}H_{37}N_2$]$^{+}$: 449.2951, found: 449.2946.



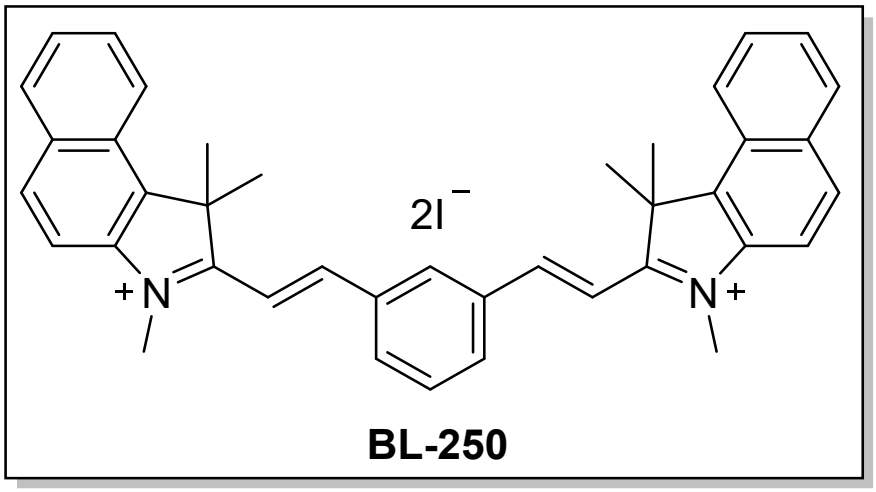
BL-328

Synthesis of BL-328: Prepared according to the general procedure from **BL-327** (50 mg, 0.3 mmol, 2 equiv) and **BL-111** (50 mg, 0.15 mmol, 1 equiv). Yield: 50% (30 mg). ^{1}H-NMR (600 MHz, CD_3OD) δ 7.49 (d, *J* = 14.2 Hz, 2H), 7.08 (s, 1H), 5.52 (d, *J* = 14.1 Hz, 2H), 3.70 (t, *J* = 7.2 Hz, 4H), 3.15 (s, 6H), 2.40 (t, *J* = 6.2 Hz, 4H), 2.00–1.94 (m, 4H), 1.88–1.82 (m, 2H), 1.47 (s, 12H). ^{13}C-NMR (151 MHz, CD_3OD) δ 174.96, 155.01, 149.29, 129.21, 96.97, 55.24, 48.03, 39.05, 35.82, 27.61, 24.91, 22.79. HRMS (ESI) calculated for [M, $C_{24}H_{37}N_2$]$^+$: 353.2951, found: 353.2957.



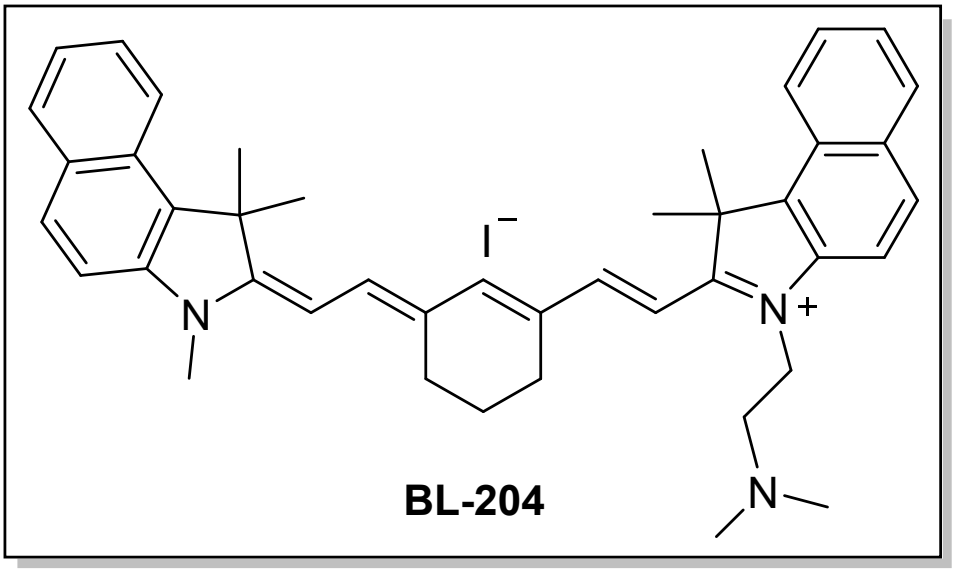
BL-329

Synthesis of BL-329: Prepared according to the general procedure from **BL-327** (50 mg, 0.3 mmol, 2 equiv) and glutacondianil hydrochloride (44 mg, 0.15 mmol, 1 equiv). Yield: 55% (30 mg). ^{1}H-NMR (600 MHz, CD_3OD) δ 7.68 (t, *J* = 13.1 Hz, 2H), 7.27 (t, *J* = 12.7 Hz, 1H), 6.19 (t, *J* = 12.6 Hz, 2H), 5.64 (d, *J* = 13.8 Hz, 2H), 3.69 (t, *J* = 7.2 Hz, 4H), 3.14 (s, 6H), 2.00–1.92 (m, 4H), 1.46 (s, 12H). ^{13}C-NMR (151 MHz, CD_3OD) δ 175.33, 152.49, 131.51, 122.46, 100.84, 55.32, 48.13, 38.90, 35.82, 27.56. HRMS (ESI) calculated for [M, $C_{21}H_{33}N_2$]$^+$: 313.2638, found: 313.2645.

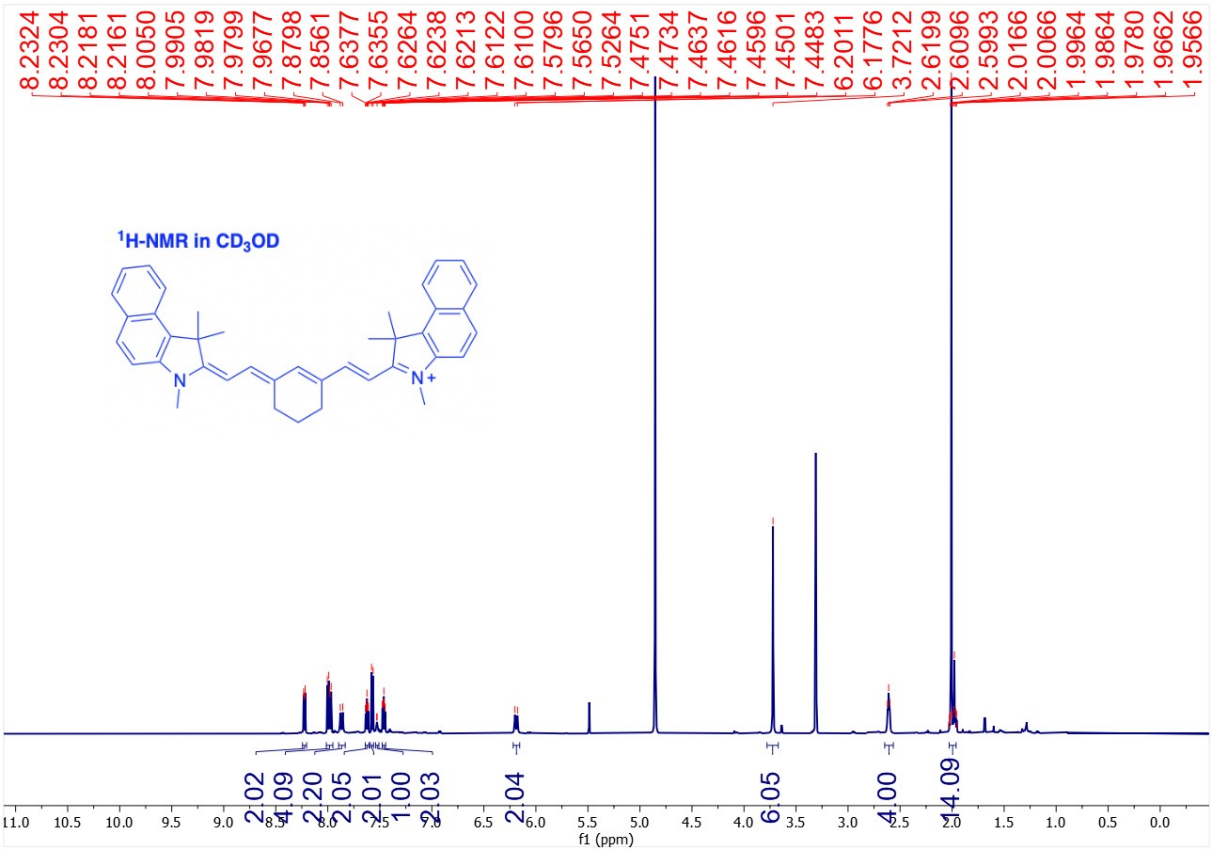


BL-250

Synthesis of BL-250: To a screw-capped vial charged with *m*-phthalaldehyde (70 mg, 0.52 mmol, 1 equiv), **BL-68** (365 mg, 1.04 mmol, 2 equiv) and NaOAc (128 mg, 1.56 mmol, 3 equiv) were dissolved in absolute ethanol. The mixture was heated at 80 °C overnight under N_2 atmosphere. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography with DCM/MeOH as eluent to afford **BL-250** with 50% yield (208 mg) as yellow solid. ^{1}H-NMR (600 MHz, DMSO-d6) δ 8.92 (s, 1H), 8.56 (d, *J* = 16.5 Hz, 2H), 8.51–8.46 (m, 4H), 8.35 (d, *J* = 8.9 Hz, 2H), 8.27–8.24 (m, 2H), 8.18 (d, *J* = 8.9 Hz, 2H), 7.92 (d, *J* = 16.6 Hz, 2H), 7.88–7.83 (m, 3H), 7.79–7.75 (m, 2H), 4.39 (s, 6H), 2.08 (s, 12H). ^{13}C-NMR (151 MHz, DMSO-d6) δ 182.43, 150.19, 139.48, 138.52, 135.45, 133.39, 132.08, 131.00, 130.12, 130.08, 128.55, 127.46, 126.60, 123.35, 114.20, 113.53, 54.06, 35.61, 24.95. HRMS (ESI) calculated for [M, $C_{40}H_{38}N_2$]$^{+}$: 546.3024, found: 546.3015.



Synthesis of BL-204: Prepared according to the general procedure **b** from **BL-68** (70 mg, 0.2 mmol, 1 equiv), **BL-111** (65 mg, 0.2 mmol, 1 equiv) and **BL-157** (107 mg, 0.2 mmol, 1 equiv). Dark-green solid. Yield: 18% (26 mg). ^{1}H-NMR (600 MHz, CD_3OD) δ 8.24–8.18 (m, 2H), 8.01–7.92 (m, 5H), 7.83 (d, *J* = 13.9 Hz, 1H), 7.65–7.57 (m, 4H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.48–7.41 (m, 2H), 6.24 (d, *J* = 14.2 Hz, 1H), 6.18 (d, *J* = 13.9 Hz, 1H), 4.28 (t, *J* = 7.4 Hz, 2H), 3.75 (s, 3H), 2.77–2.72 (m, 2H), 2.60 (t, *J* = 6.2 Hz, 4H), 2.41 (s, 6H), 2.03–1.93 (m, 14H). ^{13}C-NMR (151 MHz, CD_3OD) δ 175.75, 173.16, 156.23, 149.99, 147.70, 141.67, 141.20, 134.93, 134.06, 133.63, 133.47, 133.13, 131.66, 131.59, 131.11, 131.07, 129.57, 129.36, 128.73, 128.60, 126.04, 125.64, 123.39, 123.27, 111.98, 111.64, 101.27, 99.81, 56.61, 52.29, 51.81, 46.01, 43.08, 32.13, 27.68, 27.48, 25.02, 22.77. HRMS (ESI) calculated for [M, $C_{43}H_{48}N_3$]$^{+}$: 606.3843, found: 606.3847.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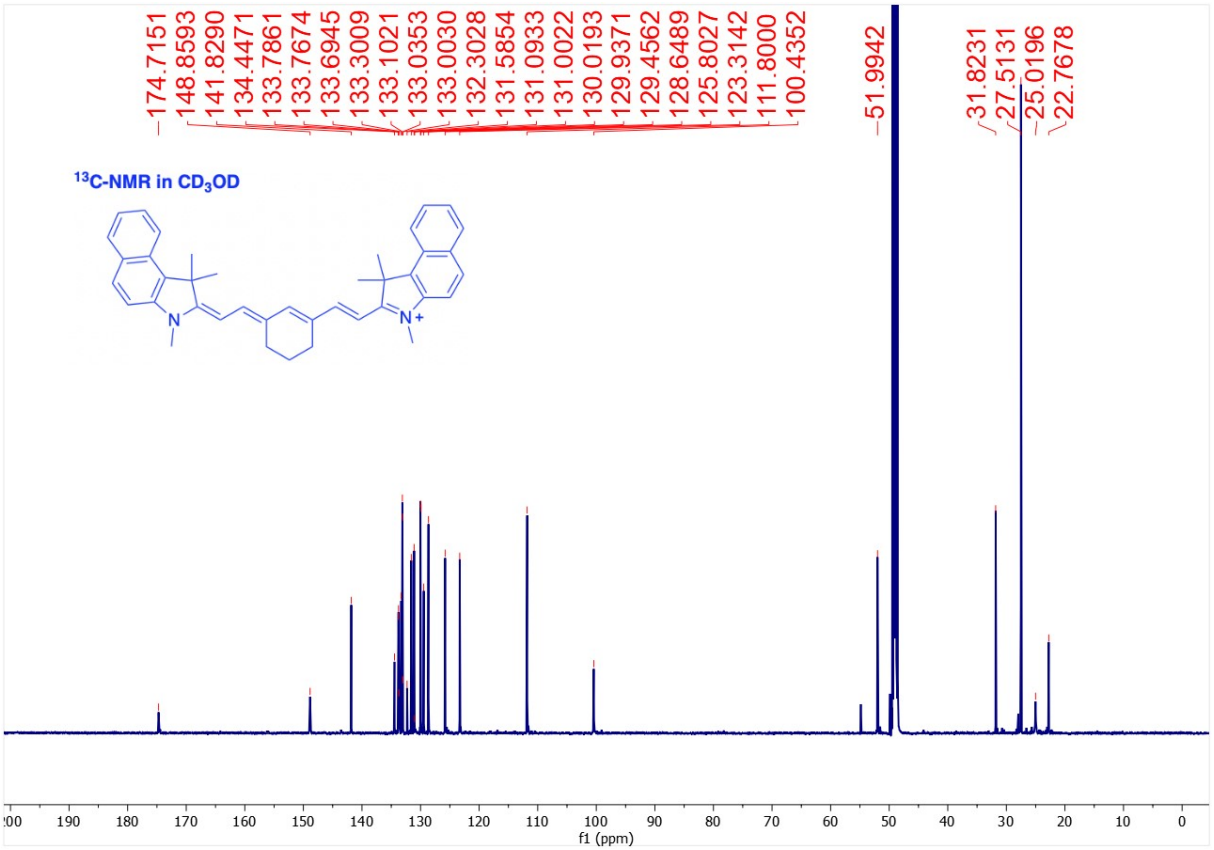
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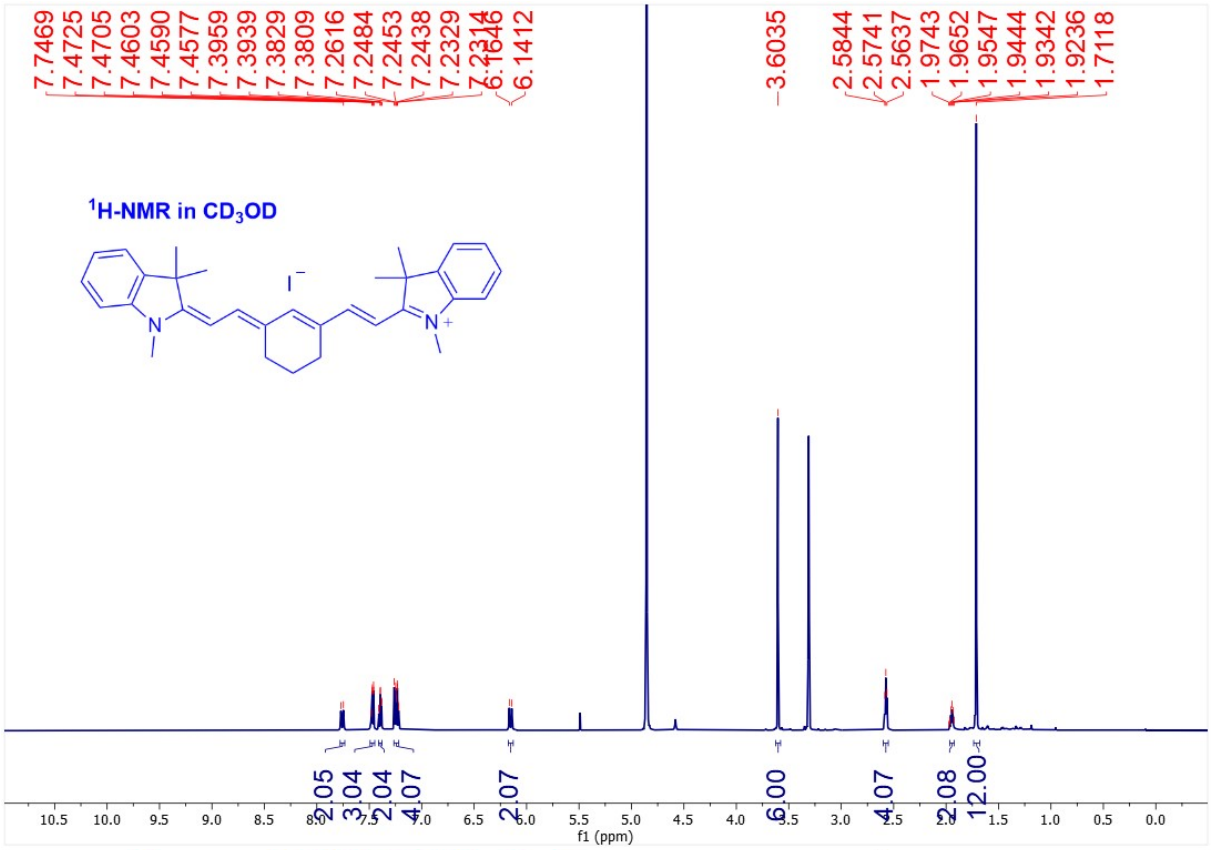
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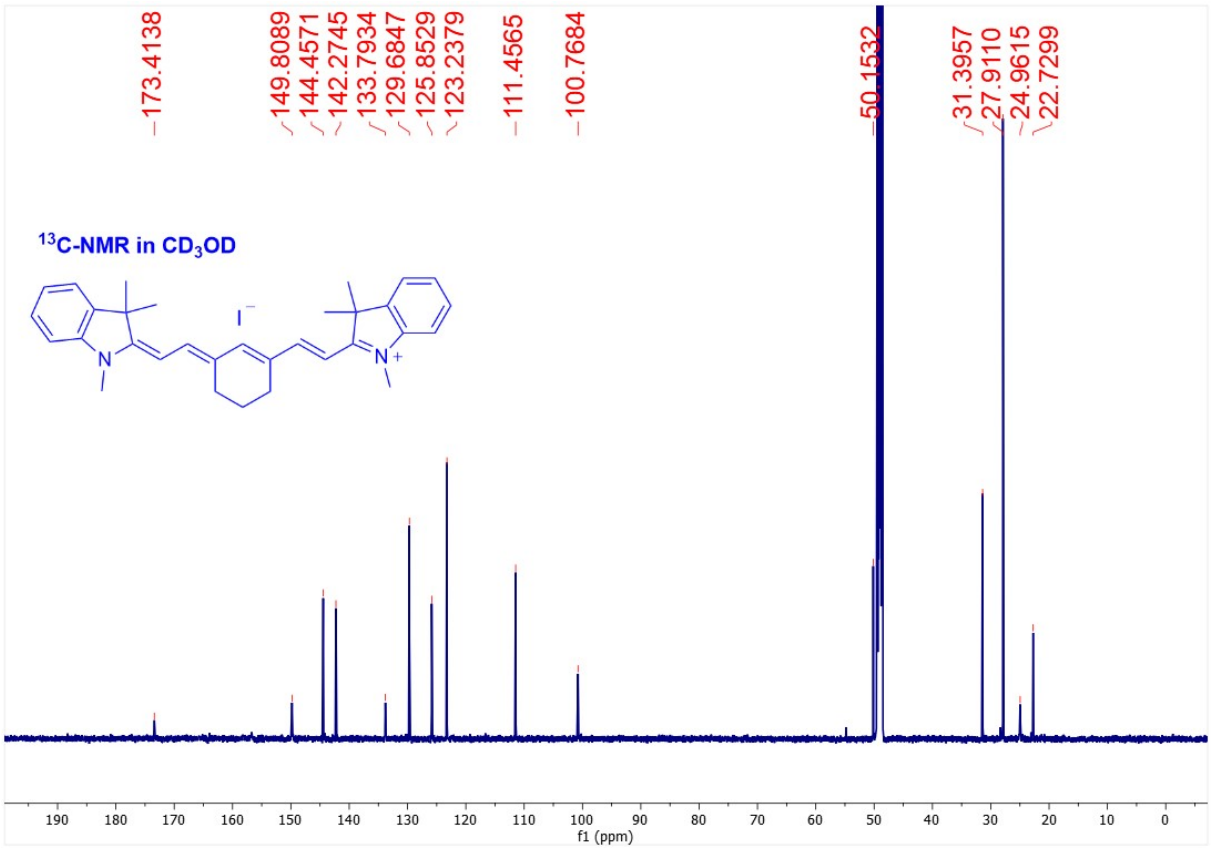
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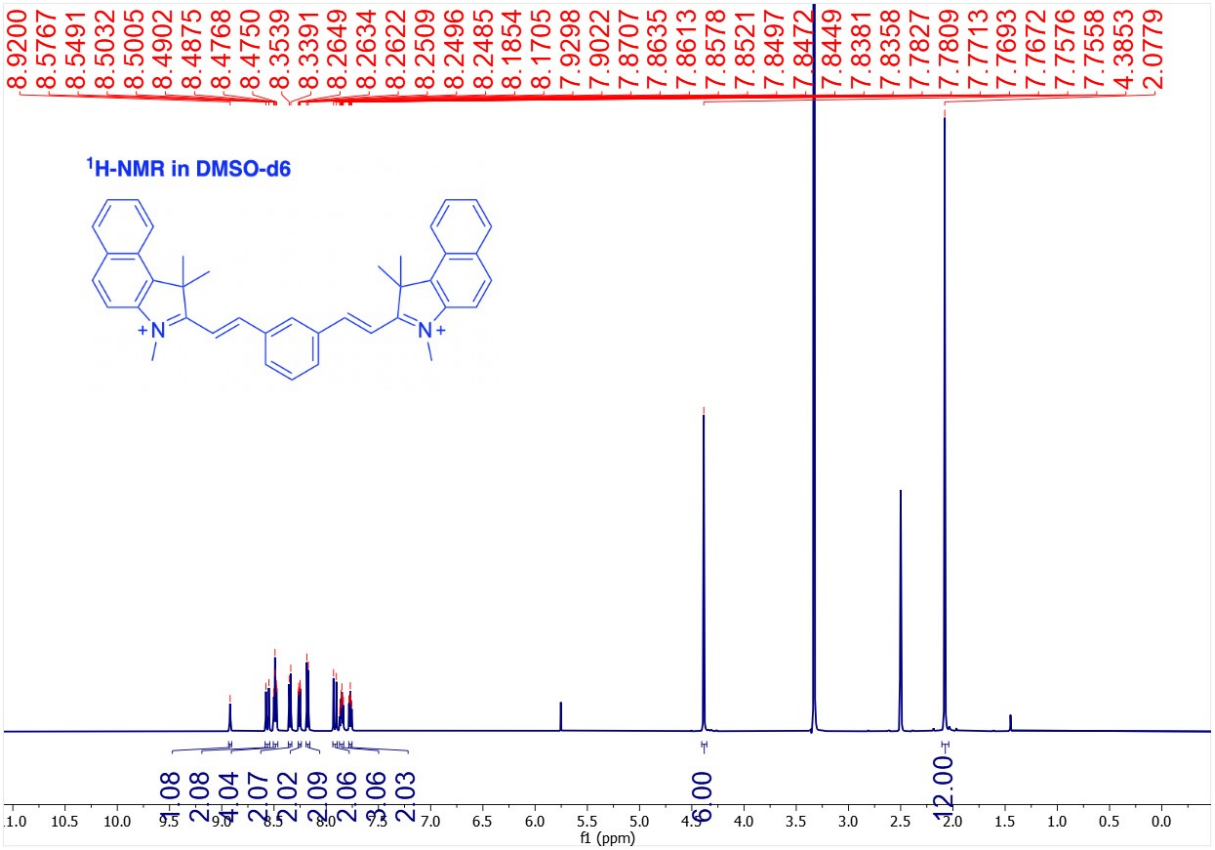
f1 (ppm)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8.2649
8.2634
8.2622
8.2509
8.2496
8.2485
8.1854
8.1705
7.9298
7.9022
7.8707
7.8635
7.8613
7.8578
7.8521
7.8497
7.8472
7.8449
7.8381
7.8358
7.7827
7.7809
7.7713
7.7693
7.7672
7.7576
7.7558
4.3853
2.0779
1H-NMR in DMSO-d6
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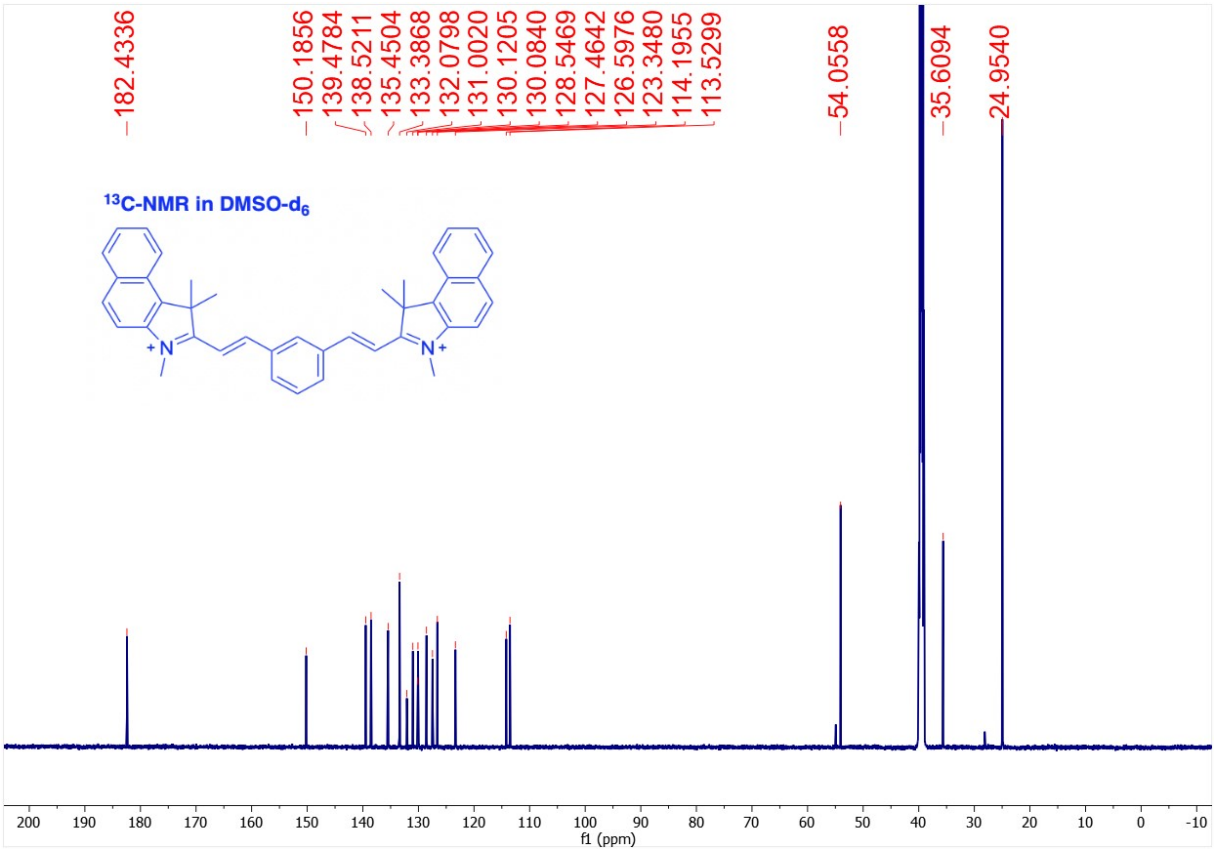
3.06
2.03
6.00
12.00
f1 (ppm)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139.4784
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135.4504
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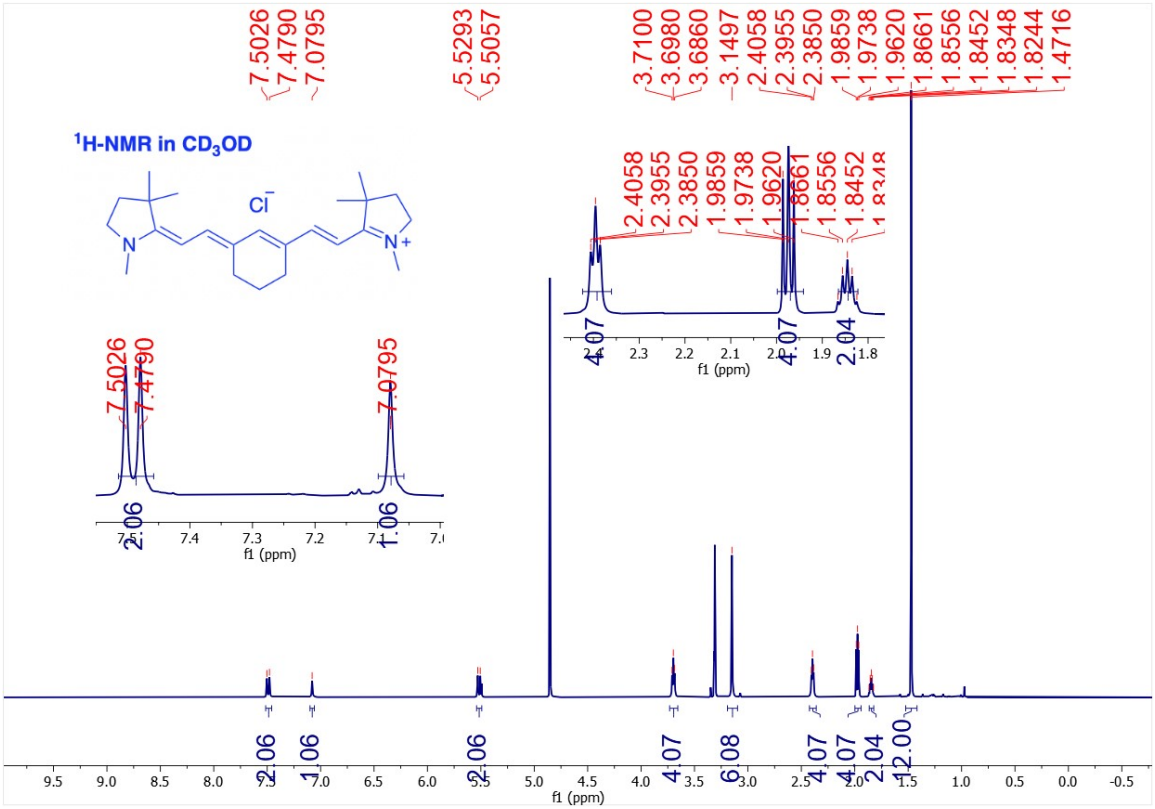
128.5469
127.4642
126.5976
123.3480
114.1955
113.5299
54.0558
35.6094
24.9540
13C-NMR in DMSO-d6
f1 (ppm)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5.5057
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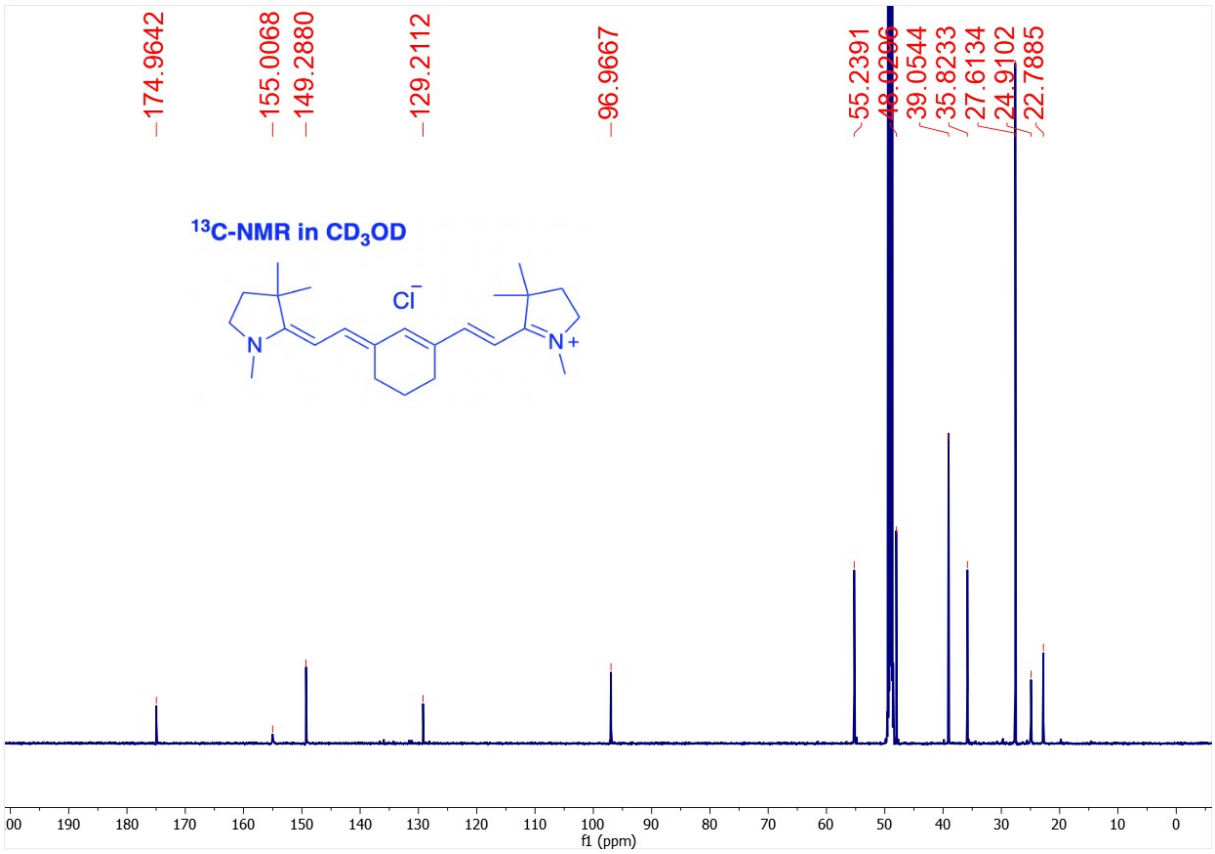
2.3850
1.9859
1.9738
1.9620
1.8661
1.8556
1.8452
1.8348
1.8244
1.4716
1H-NMR in CD3OD
Cl−
N
N+
2.06
1.06
2.06
4.07
6.08
4.07
4.07
2.04
12.00
f1 (ppm)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129.2112
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55.2391
48.0296
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35.8233
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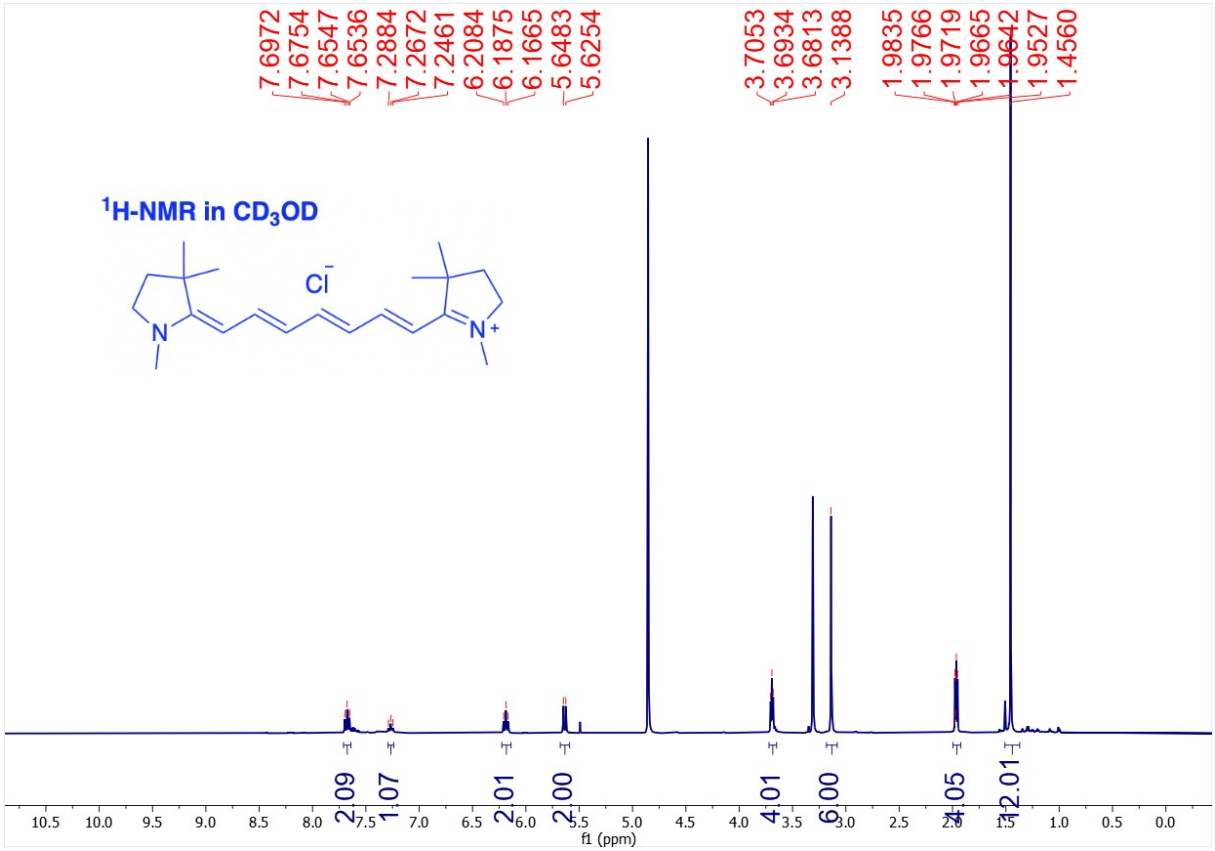
24.9102
22.7885
13C-NMR in CD3OD
Cl−
N
N+
f1 (ppm)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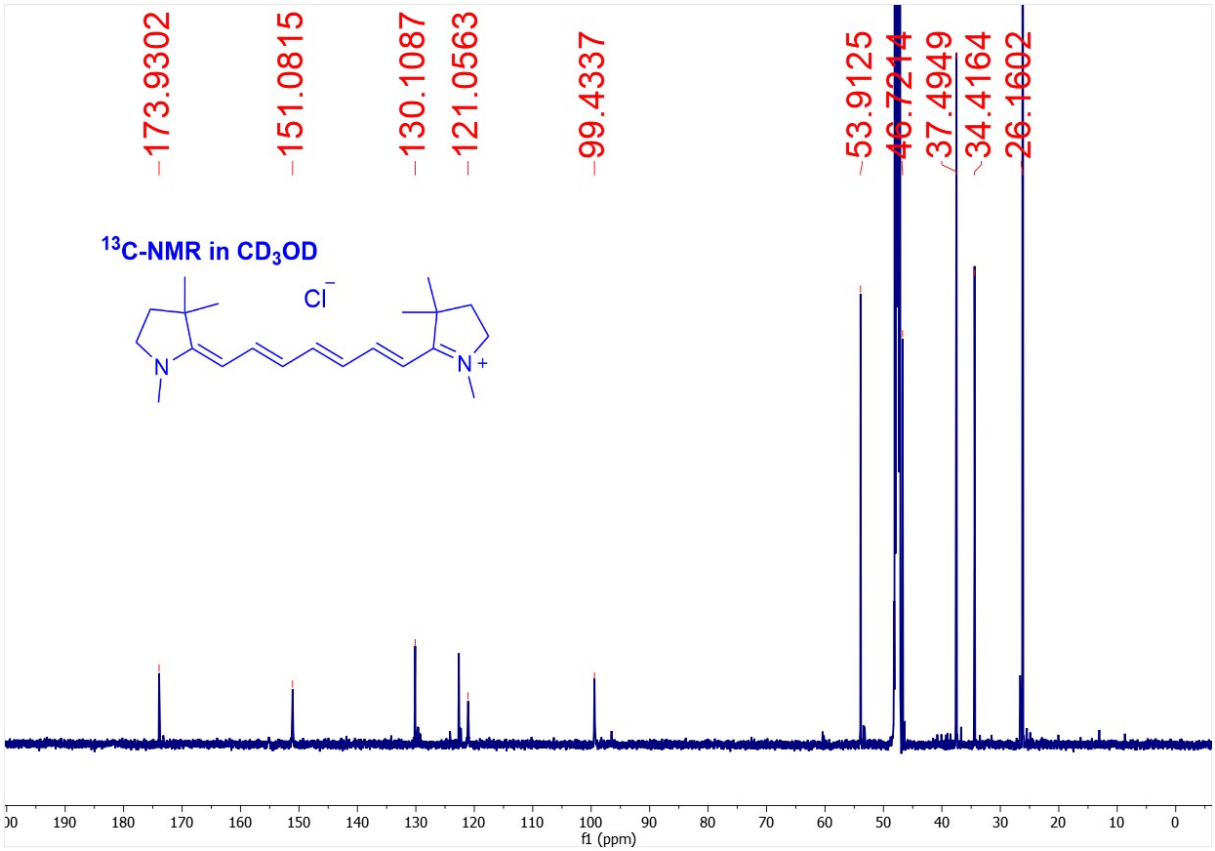
7.6547
7.6536
7.2884
7.2672
7.2461
6.2084
6.1875
6.1665
5.6483
5.6254
3.7053
3.6934
3.6813
3.1388
1.9835
1.9766
1.9719
1.9665
1.9642
1.9527
1.4560
1H-NMR in CD3OD
Cl−
N
N+
2.09
1.07
2.01
2.00
4.01
6.00
4.05
12.01
f1 (ppm)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130.1087
121.0563
99.4337
53.9125
46.7214
37.4949
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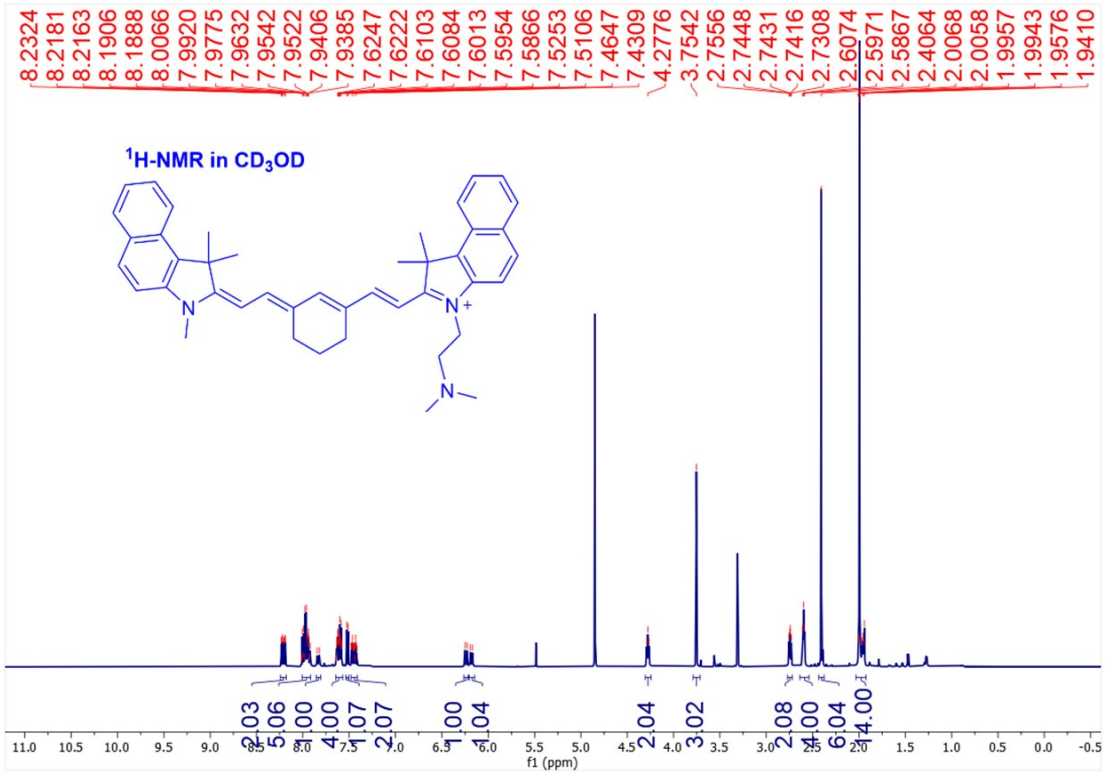
26.1602
13C-NMR in CD3OD
Cl−
N
N+
f1 (ppm)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7.9542
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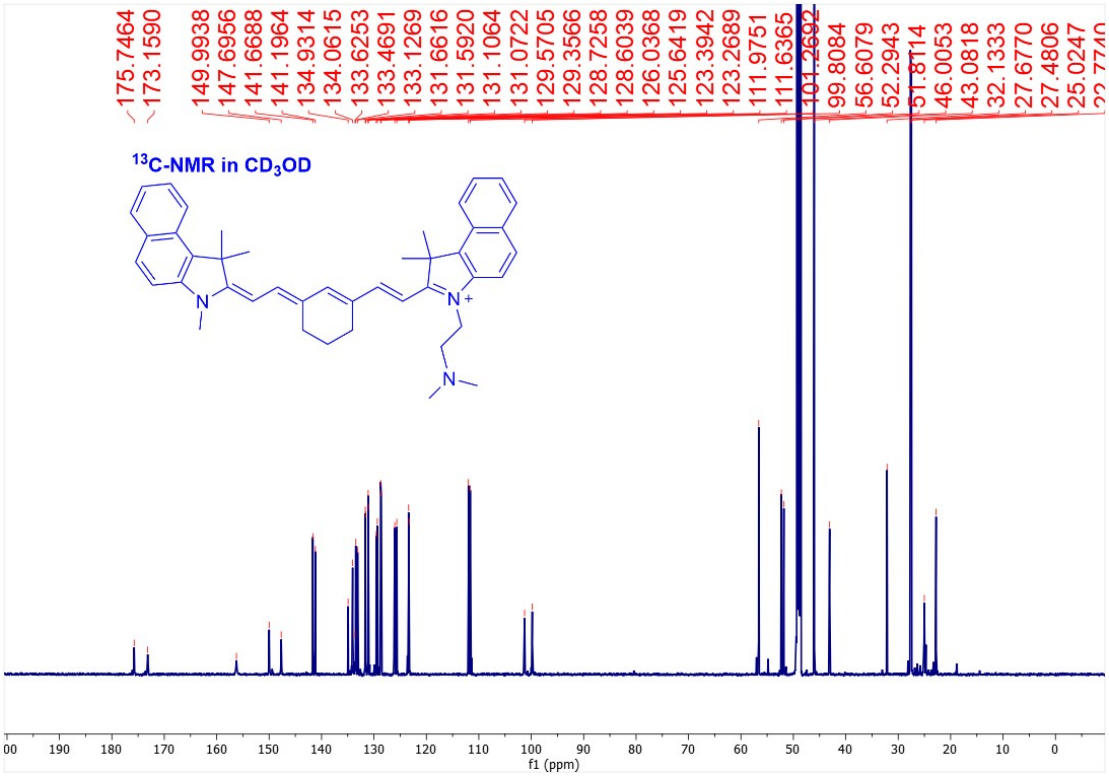
7.9406
7.9385
7.6247
7.6222
7.6103
7.6084
7.6013
7.5954
7.5866
7.5253
7.5106
7.4647
7.4309
4.2776
3.7542
2.7556
2.7448
2.7431
2.7416
2.7308
2.6074
2.5971
2.5867
2.4064
2.0068
2.0058
1.9957
1.9943
1.9576
1.9410
^{1}H-NMR in CD$_3$OD
2.03
5.06
1.00
4.00
1.07
2.07
1.00
1.04
2.04
3.02
2.08
4.00
6.04
14.00
f1 (ppm)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149.9938
147.6956
141.6688
141.1964
134.9314
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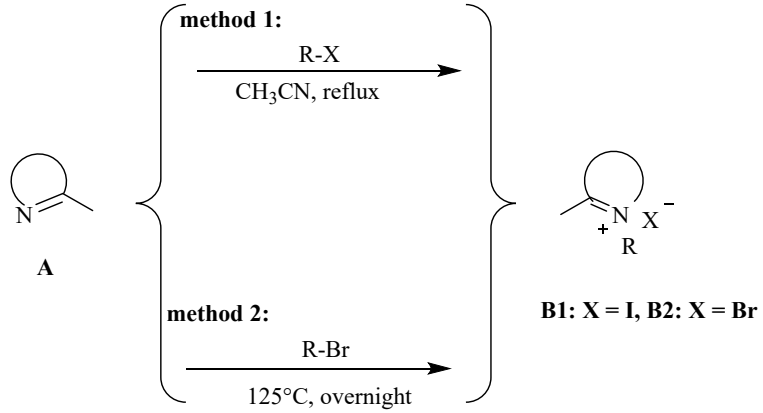
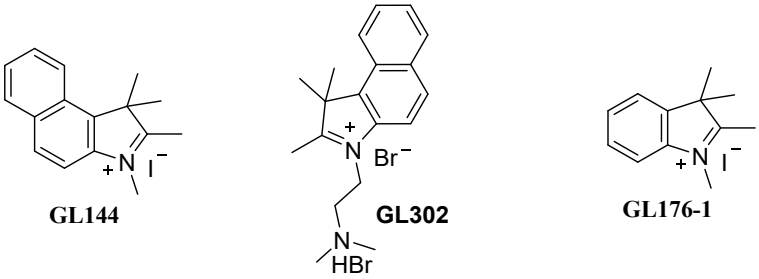
131.6616
131.5920
131.1064
131.0722
129.5705
129.3566
128.7258
128.6039
126.0368
125.6419
123.3942
123.2689
111.9751
111.6365
101.2692
99.8084
56.6079
52.2943
51.8714
46.0053
43.0818
32.1333
27.6770
27.4806
25.0247
^{13}C-NMR in CD$_3$OD
f1 (ppm)

Synthesis section II:

General information: All glassware was oven-dried overnight prior to use. All reactions were carried out under a N_2 atmosphere unless otherwise noted. **GL176-1** and other chemicals were purchased from commercial suppliers and used without further purification. **GL-176 and GL-362-1** were synthesized following the literature procedures.[3]

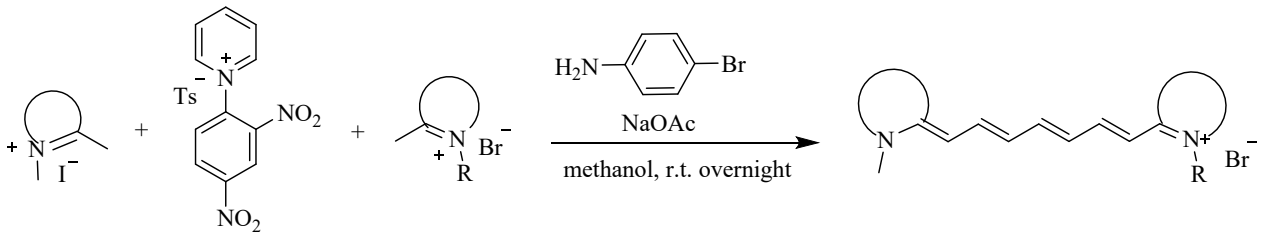




General procedure for the synthesis of heterocyclic salt:

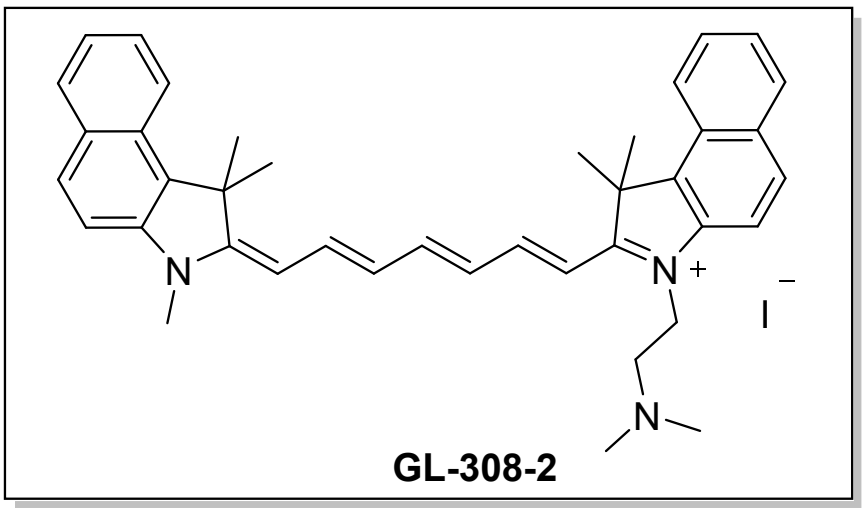
Method 1: Compound A (1 equiv) and R-X (1.2-1.5 equiv) were mixed in CH_3CN in a screwed-capped vial. The mixture was stirred and heated to reflux overnight. The filter cake solid was filtered and washed with ether and dried in vacuum.

Method 2: Compound A (1 equiv) and R-Br (1.0 equiv) were mixed in an 8 mL of screwed-capped vial. The mixture was stirred and heated to 125 °C overnight. The black solid was washed with ethyl acetate, ether and recrystallized from methanol/ether.



B1 **GL175** **B2** **D**

General procedure: The corresponding pyridinium salt **GL175** (1 equiv) and 4-bromoaniline (1 equiv) were dissolved in methanol (4 mL) in an 8 mL of vial, and the mixture was stirred at room temperature for 30 min. Next, a heterocyclic salt **B1** (1 equiv), **B2** (1.3 equiv) and sodium acetate (3 equiv.) were added. The reaction mixture was stirred for additional overnight at room temperature. The crude product was purified by flash column chromatography (silica gel, dichloromethane/methanol).



Synthesis of GL-308-2: Prepared according to the general procedure from **GL175** (206 mg, 0.48 mmol), 4-bromoaniline (103 mg, 0.65 mmol), sodium acetate (246 mg), **GL302** (286 mg, 0.65 mmol) and **GL144** (176 mg, 0.5 mmol) in methanol and the reaction mixture was stirred for 16 h. The crude product was purified by flash column chromatography (silica gel, dichloromethane/methanol, 20:1, 10:1), affording 58 mg of green solid **GL-308-2**. Yield: 19%. ^{1}H NMR (600 MHz, Methanol-d4) δ 8.27 (d, J = 8.17 Hz, 1H), 8.23 (d, J = 8.17 Hz, 1H), 8.11 (t, 1H), 8.06-7.98 (m, 5H), 7.69-7.63 (m, 4H), 7.55 (d, J = 8.80 Hz, 1H), 7.52 (t, 1H), 7.48 (t, 1H), 6.67-6.58 (m, 2H), 6.42 (d, J = 13.82 Hz, 1H), 6.27 (d, J = 13.82 Hz, 1H), 4.29 (t, 2H), 3.79 (s, 3H), 2.77 (t, 2H), 2.43 (s, 6H), 2.02 (d, J = 4.66 Hz, 12H). ^{13}C NMR (150 MHz, Methanol-d4) δ 174.95, 171.89, 171.50, 149.47, 140.24, 139.83, 133.86, 132.70, 132.20, 131.76, 130.37, 130. 24, 129.74, 129.69, 128.20, 127.95, 127.41, 127.24, 125.96, 125.61, 124.85, 124.32, 122.01, 121.84, 110.66, 110.25, 104.22, 102.16, 55.27, 51.09, 50.45, 48.16, 44.52, 41.59, 30.71, 26.27, 25.97. HRMS (ESI) for $C_{40}H_{44}N_3^+$ $[M-I]^+$: 566.3530. Found: 566.3534.

REFERENCES

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2 H. Mustroph and A. Towns, *ChemPhysChem*, 2018, **19**, 1016–1023.

3 L. Štacková, P. Štacko and P. Klán, *J Am Chem Soc*, 2019, **141**, 7155–7162.