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SUPPORTING INFORMATION

Low-generation fluorescent polyurethane dendrimers *via* late-stage modification using azide-alkyne click chemistry

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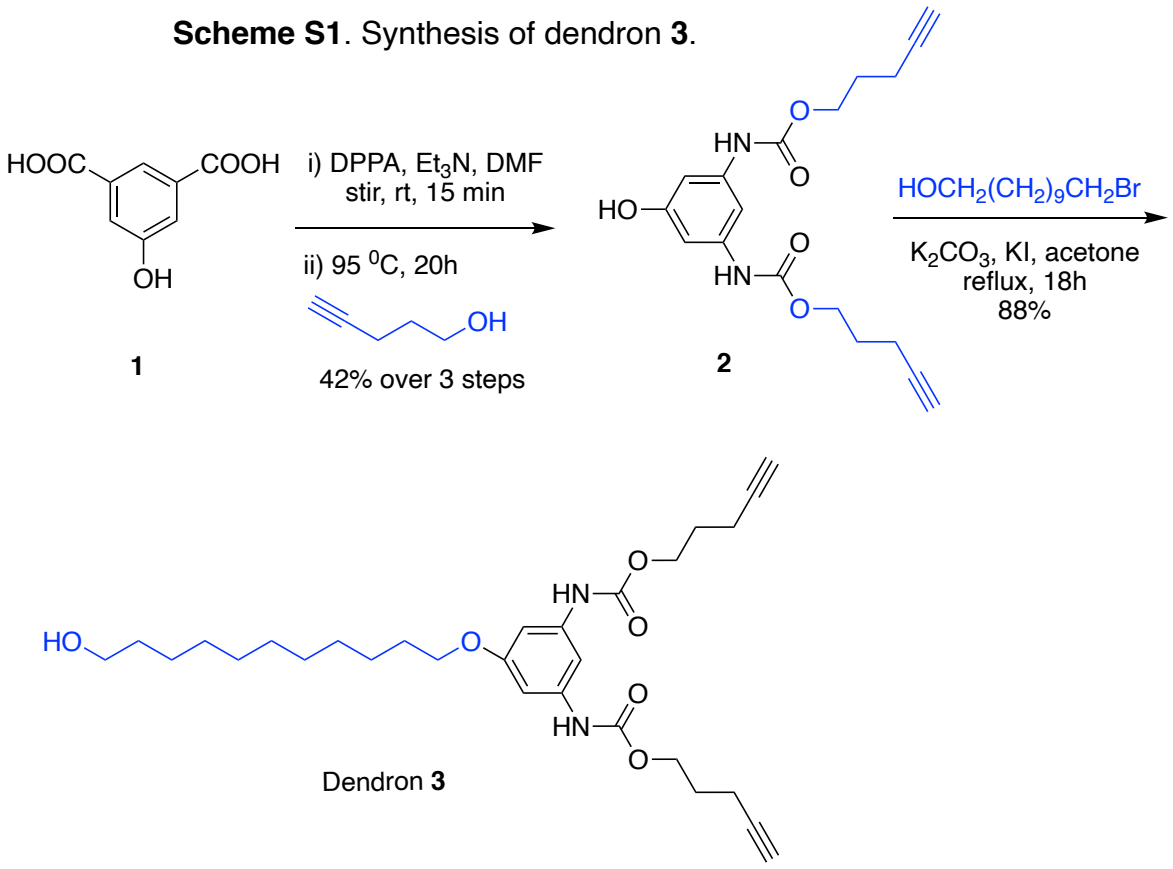
1. Notes on equations for the experimental section

a. Synthesis of dendron **3** using one-pot multicomponent Curtius reaction

Scheme S1. Synthesis of dendron **3**.

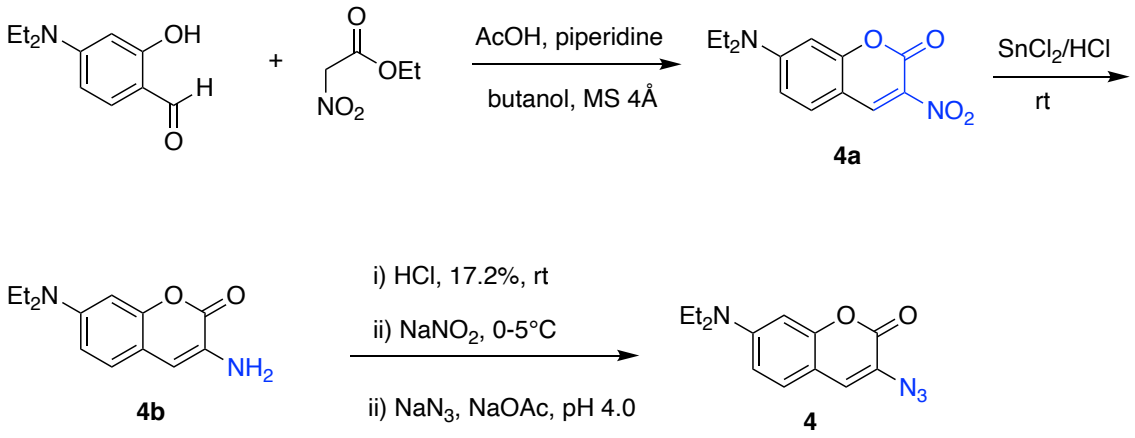


Notes:

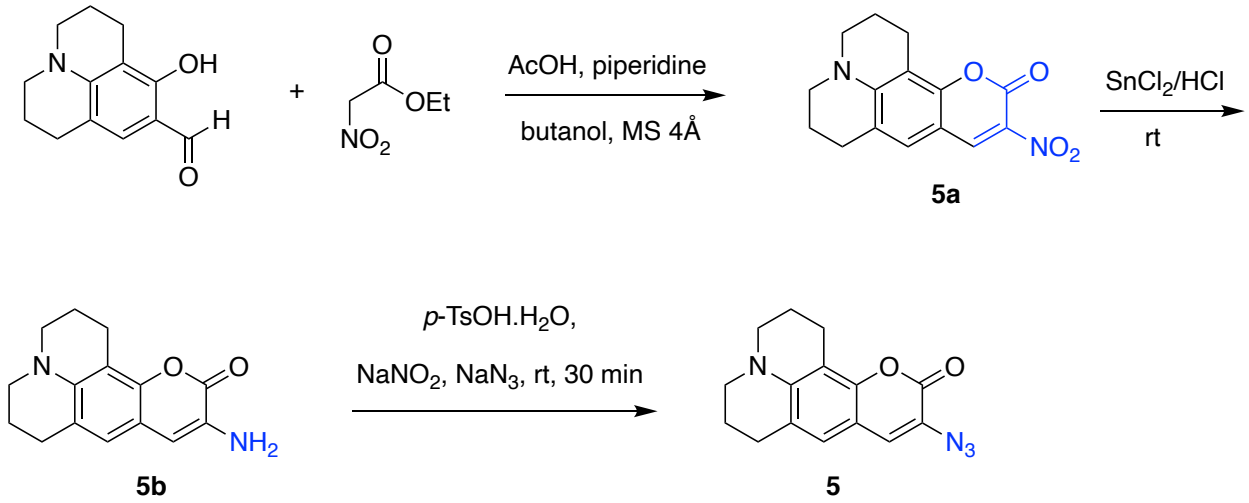
- For a large-scale reaction, it is advised to carry out the addition of DPPA under ice bath because of exothermic nature of the reaction.
- On heating, Curtius rearrangement (CON_3 to NCO) proceeds *violently* releasing N_2 gas *rapidly*. At this point, the reaction vessel should not be sealed completely to prevent possible *explosion*.
- This reaction can be monitored using IR tracking the azide peak at ~ 2100 cm^{-1}.
- Details of this particular reaction including the formation of side products has been discussed previously.[a]

b. Synthesis of azidocoumarins

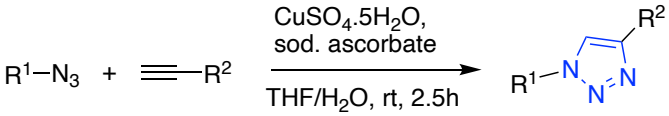
Scheme S2. Synthesis of 3-Azido-7-diethylaminoazidocoumarin **4.**

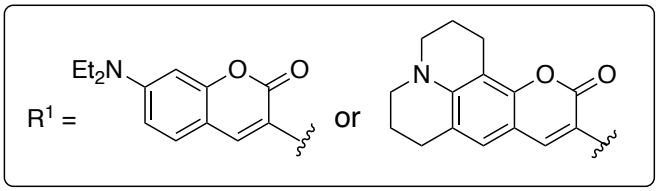


Scheme S3. Synthesis of 9-Azido-2,3,5,6-tetrahydro-1H, 4H-11-oxa-3a-aza-benzo[de]anthracene-10-one **5**

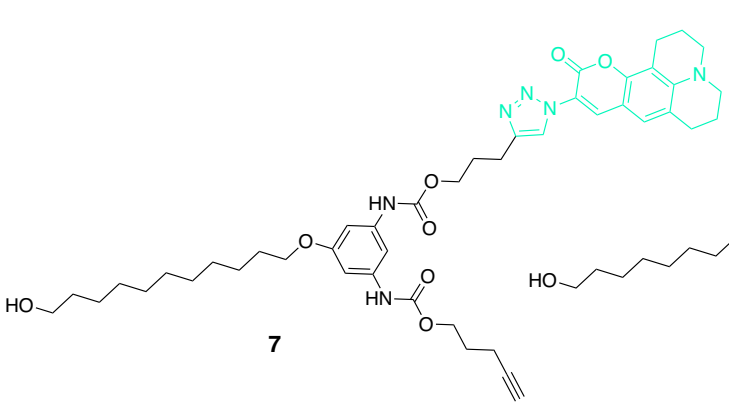


c. Copper catalyzed azide-alkyne click reaction to synthesize fluorescent dendrons





Blue/mint-green fluorescing dendrons **7, 8, and 9**



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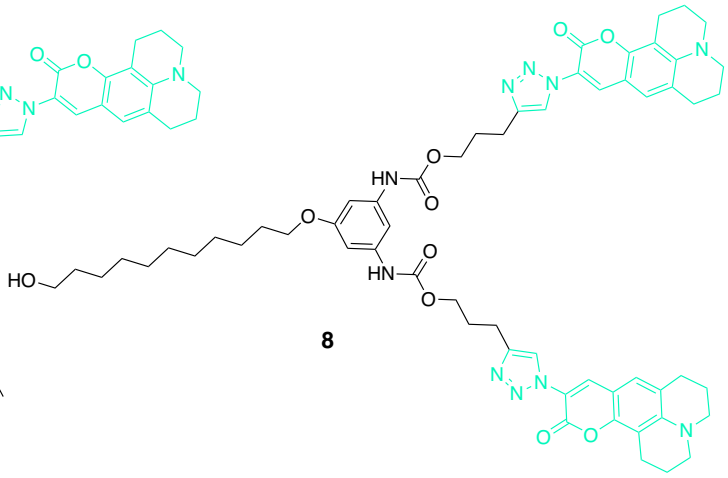

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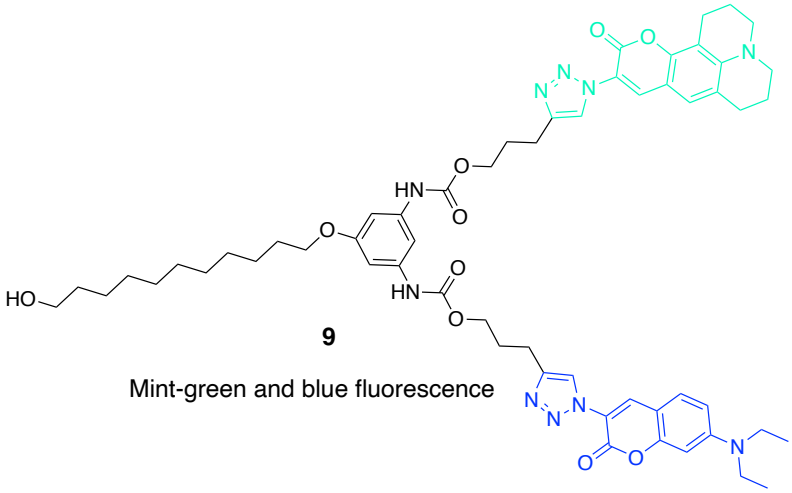

9

Mint-green and blue fluorescence

Notes:

- This particular copper catalyzed azide-alkyne cycloaddition (CuAAC) was found to be very slow under aforementioned conditions. With azidocoumarin **5**, a mixture of products containing one-clicked and two-clicked, were obtained even with longer reaction time (up to 7 days).
- Performing the reaction at 50 °C also yielded the mixture of products though it increased the yield of two-clicked product sightly.
- One-clicked product **7** was subjected to another CuAAC using a different coumarin to afford a dendron having both mint green and blue fluorescence.

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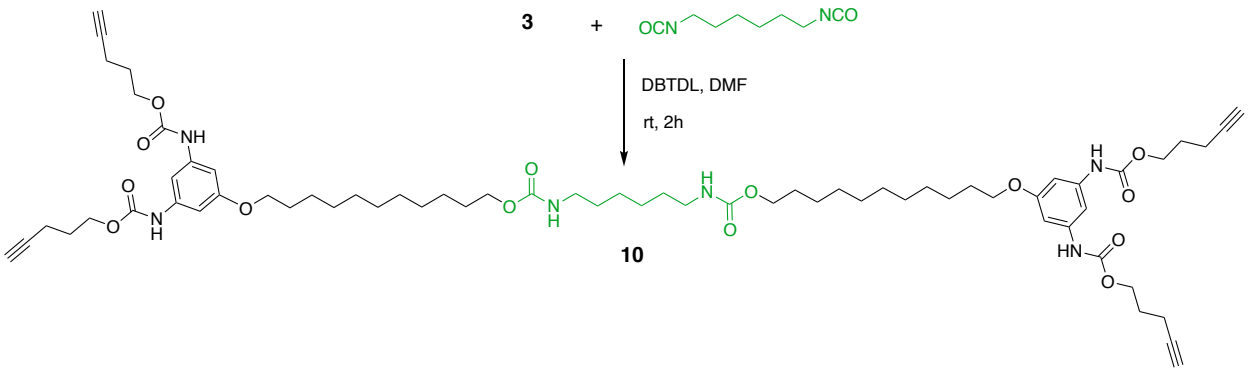
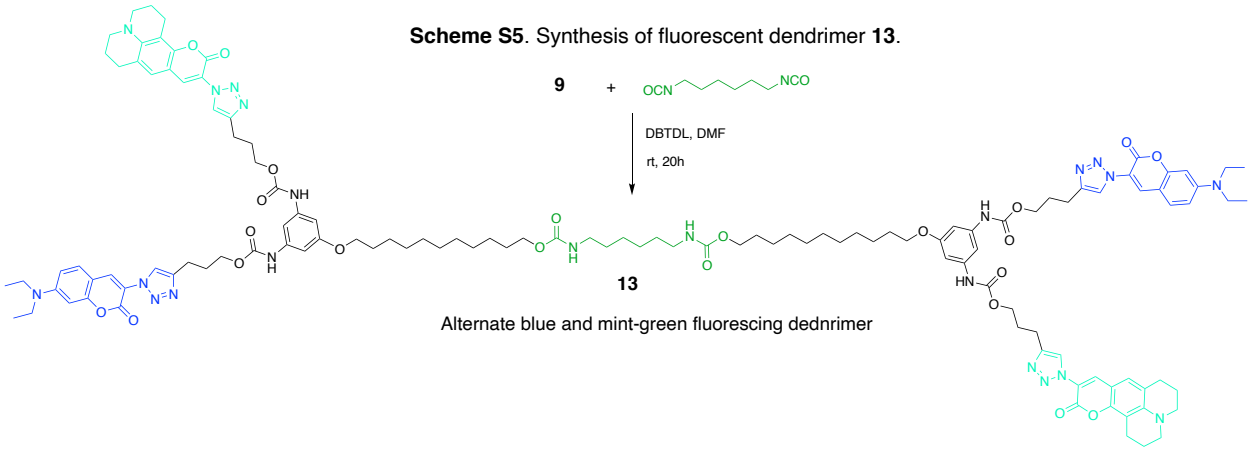
d. Attachment of dendrons to the core

Scheme S4. Synthesis of non-fluorescent dendrimer **10**.

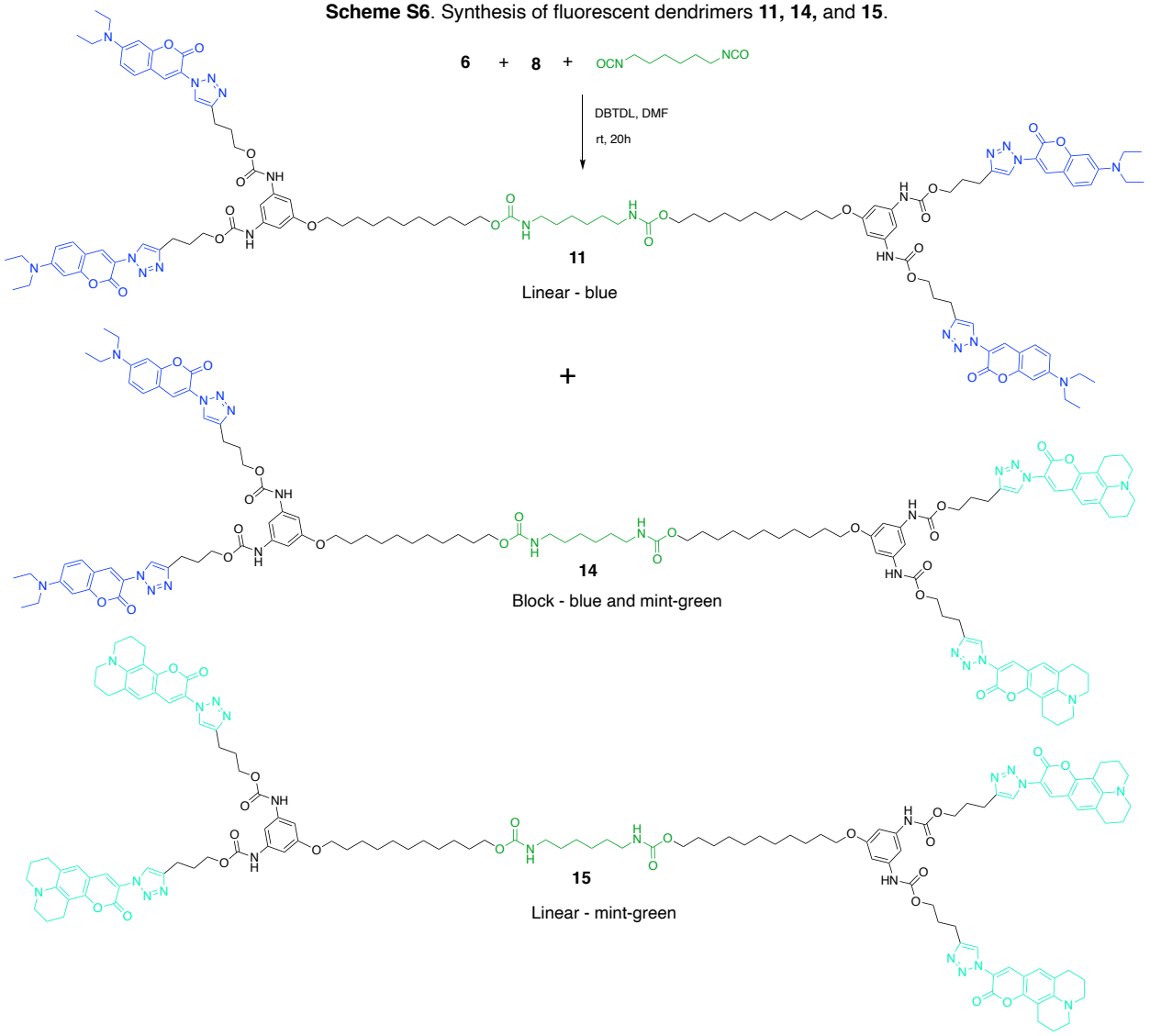


Scheme S5. Synthesis of fluorescent dendrimer **13**.



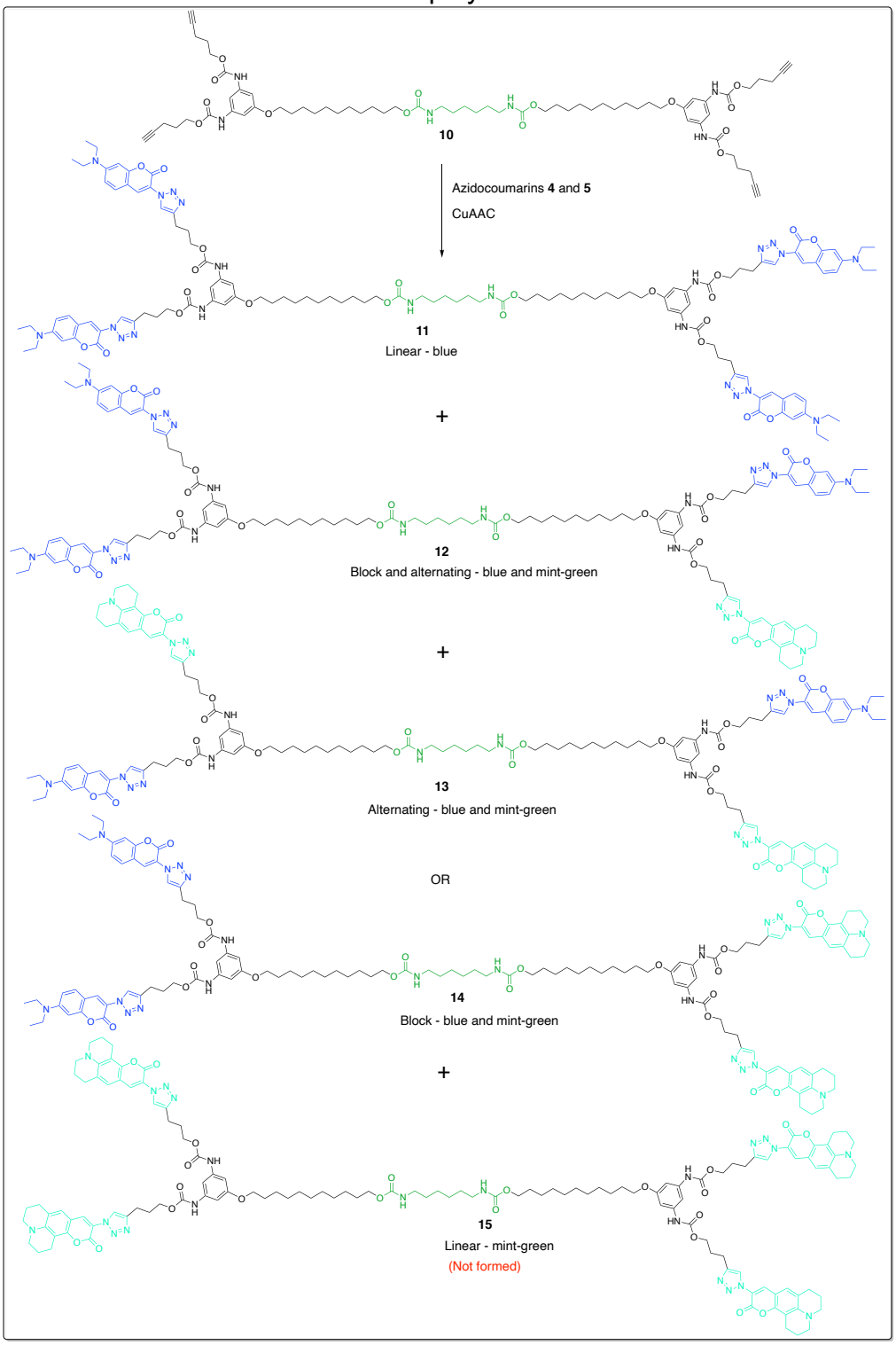
Alternate blue and mint-green fluorescing dednrimer

Scheme S6. Synthesis of fluorescent dendrimers **11, 14,** and **15**.



e. Surface modification of dendrimer **10** via CuAAC using two different coumarins

Scheme S7. Possible fluorescent polyurethane dendrimers *via* CuAAC.



Notes:

- Surprisingly, this reaction exclusively formed dendrimer **12** (80% of the products) showing very slow clicking of azidocoumarin **5** with alkyne.
- Other products isolated involved dendrimer **11**, **13**, and **14**. However, **13** and **14** were not distinguished from each other.
- Dendrimer with mint green florescence only was not formed in the reaction, which again supports extremely slow reactivity of azidocoumarin 5.

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f. UV images of fluorescent compounds during isolation

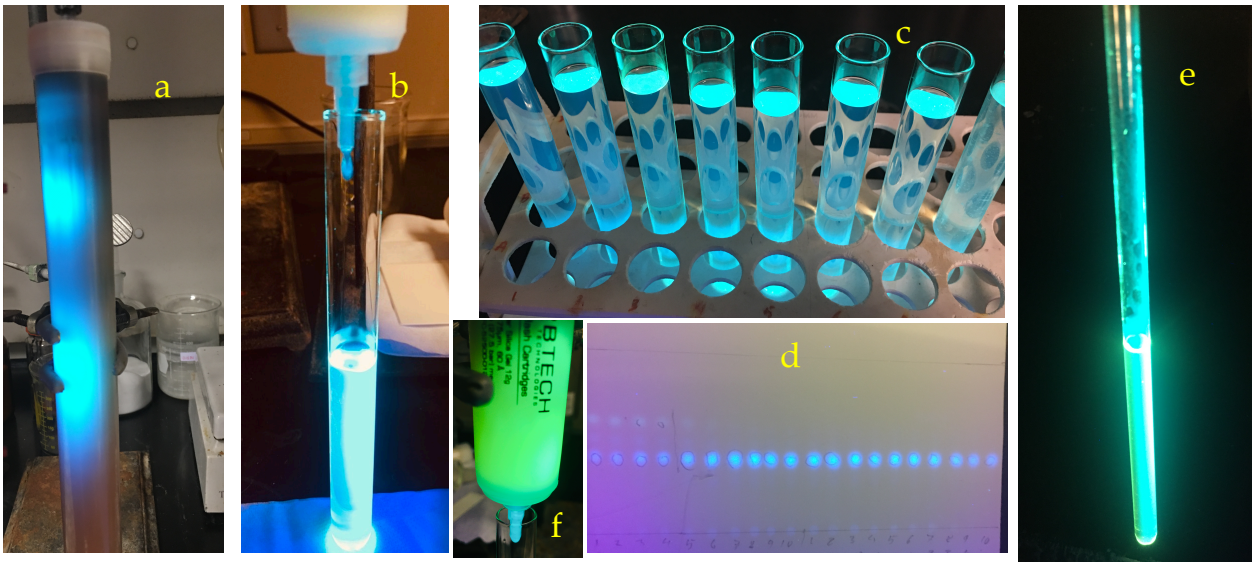


Figure S1. UV Images of fluorescent compounds at different of synthesis; a) blue fluorescing compound showing two distinct bands in column, b) flash chromatography of blue fluorescing compound, c) collected fractions, d) TLC spots showing the separation, e) blue fluorescing compound dissolved in CDCl3 in an NMR tube, and f) flash chromatographic column showing mint green fluorescing compound.

2. NMR spectra of synthesized compounds

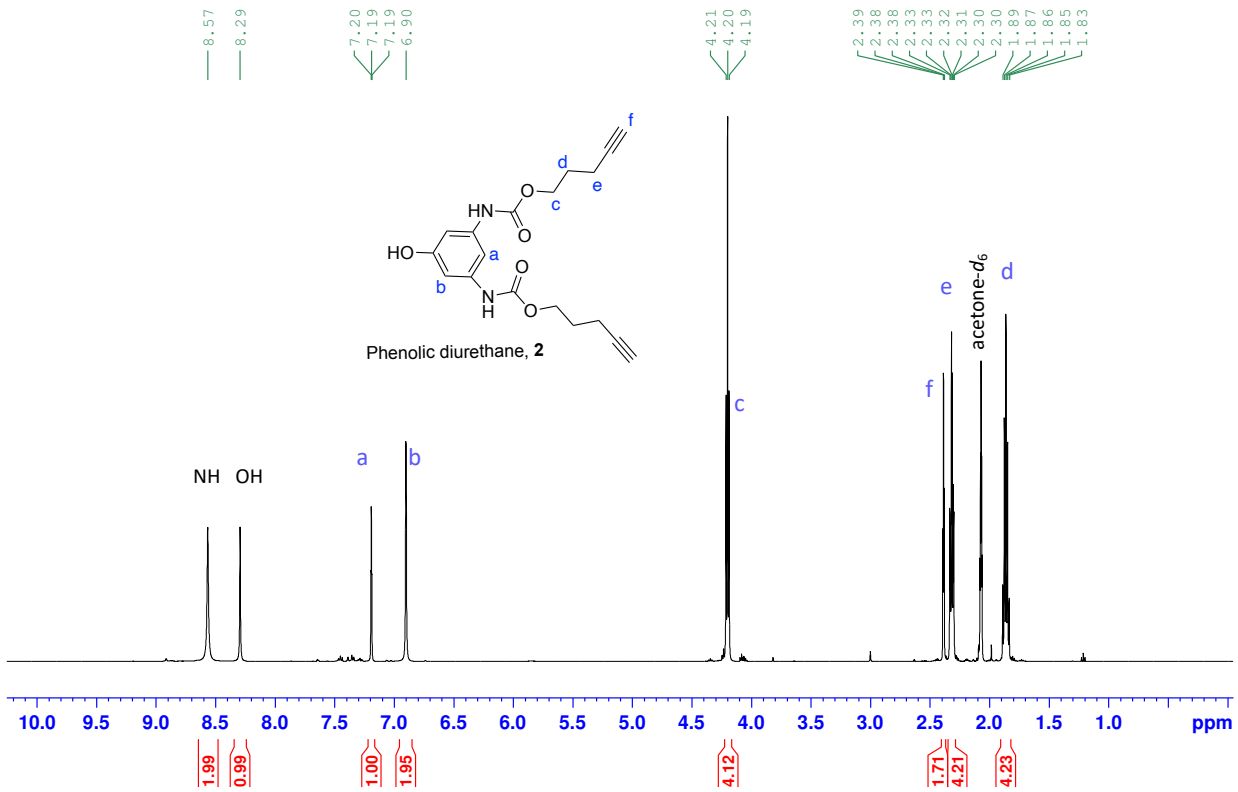


Figure S2. ^{1}H NMR spectrum (500 MHz, CD_3COCD_3, 298 K) of phenolic diurethane **2**.

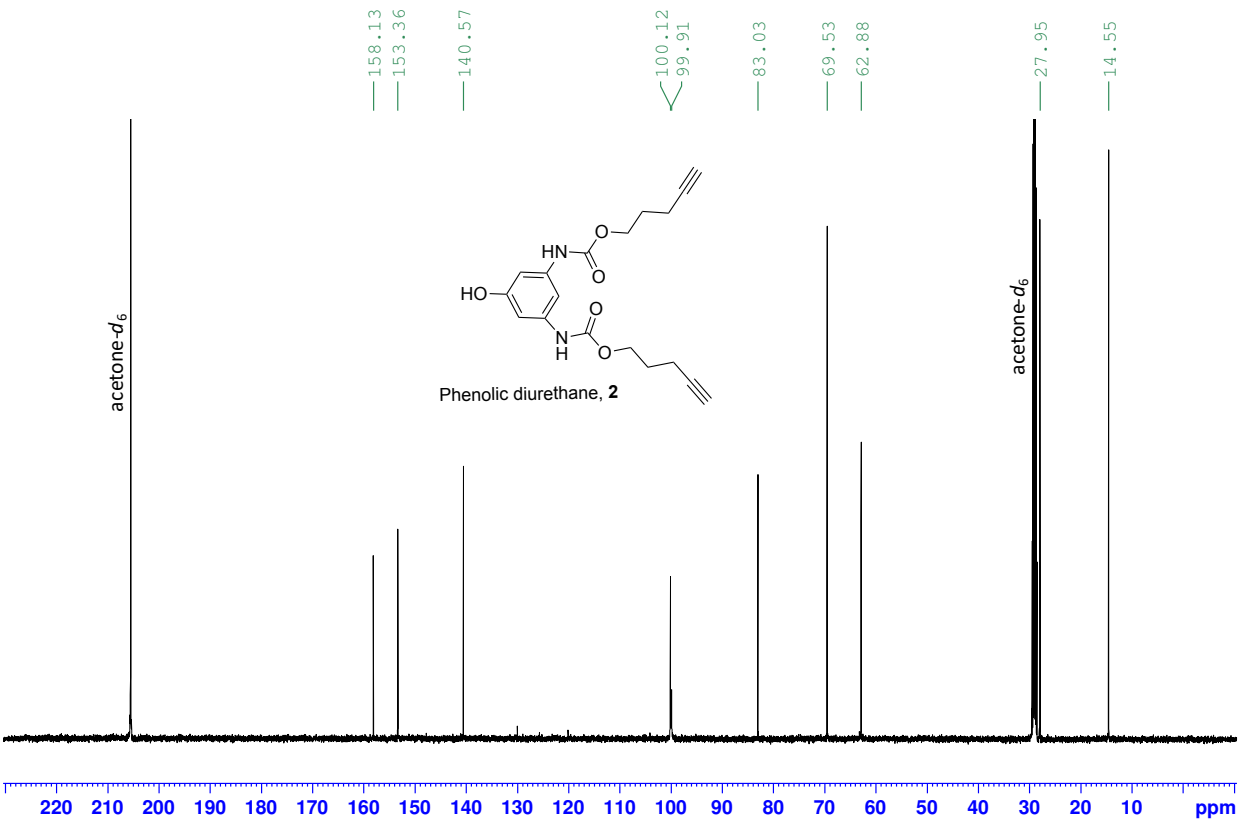


Figure S3. ^{13}C NMR spectrum (500 MHz, CD_3COCD_3, 298 K) of phenolic diurethane **2**.

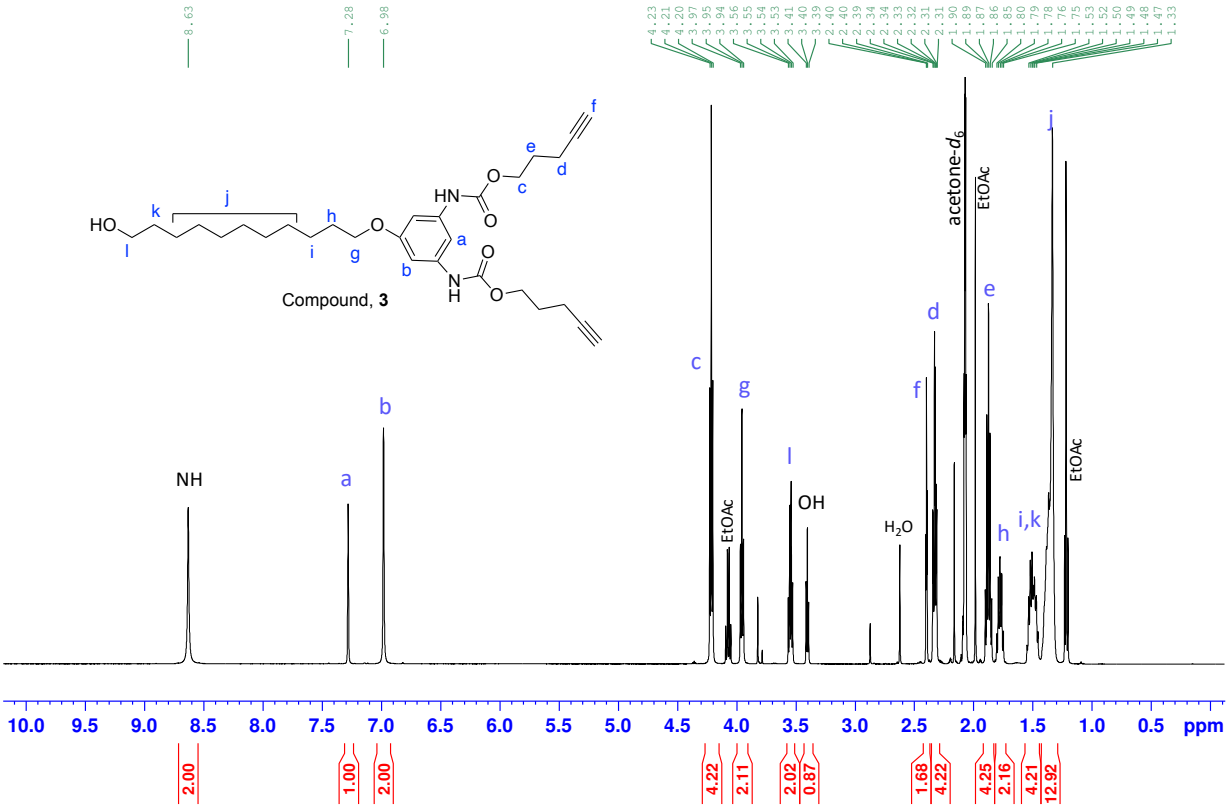


Figure S4. ^{1}H NMR spectrum (500 MHz, CD_3COCD_3, 298 K) of compound **3**.

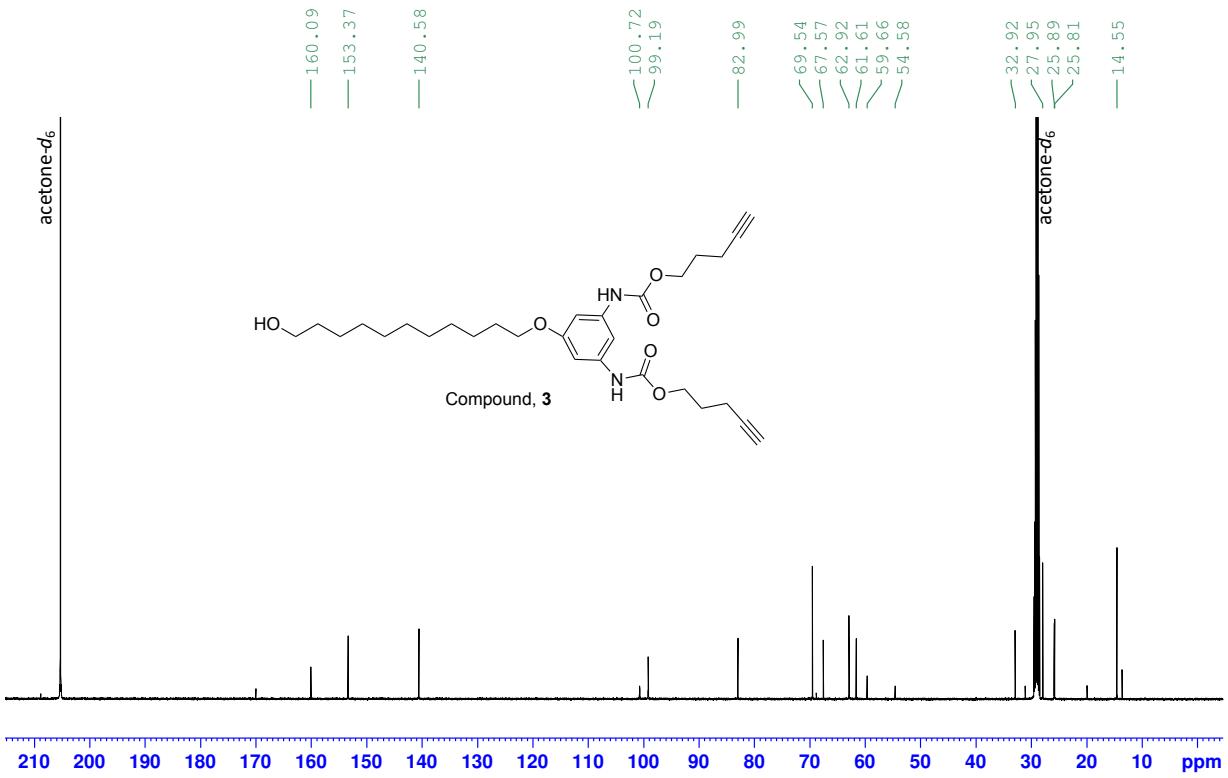


Figure S5. ^{13}C NMR spectrum (126 MHz, CD_3COCD_3, 298 K) of compound **3**.

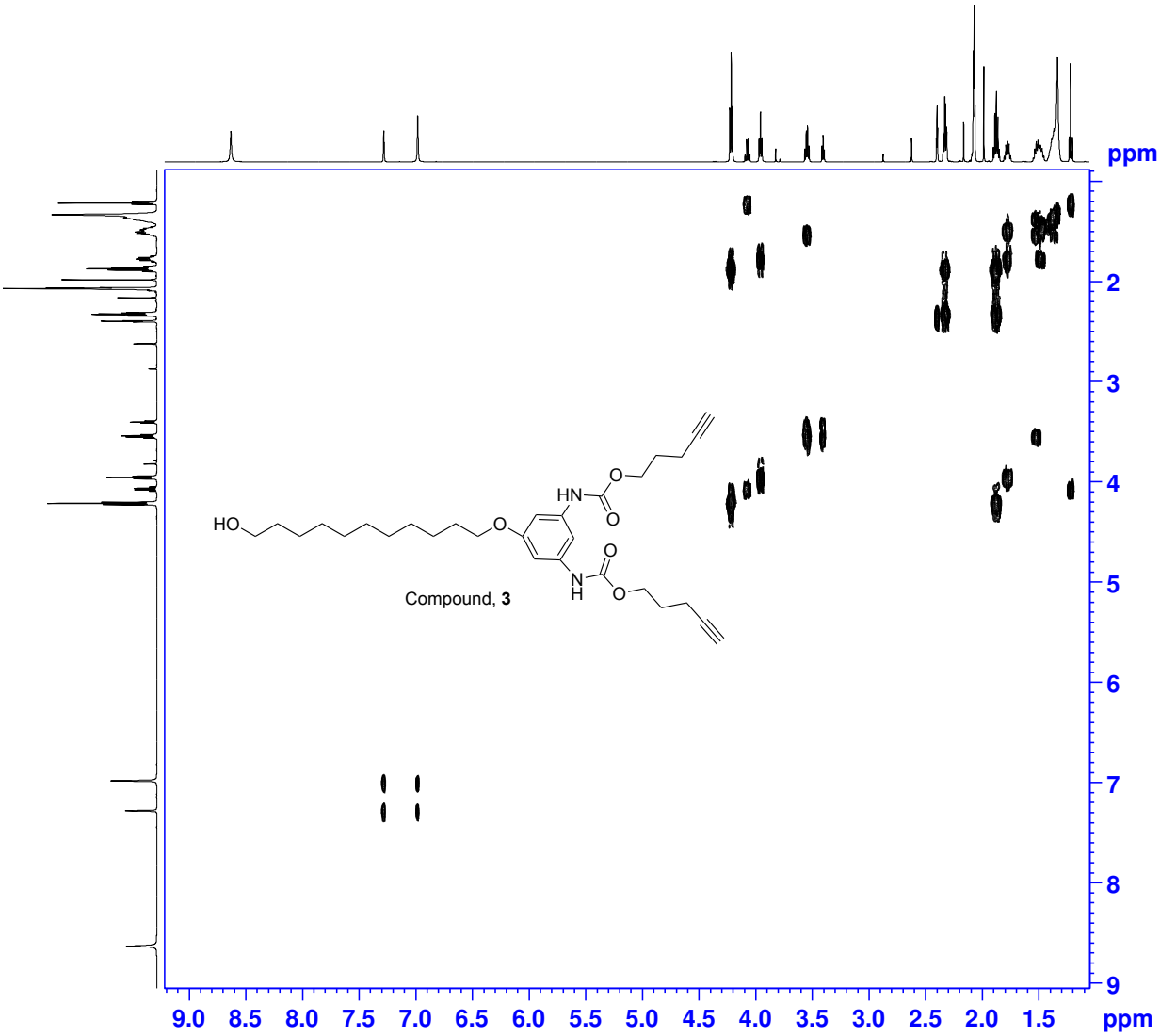


Figure S6. COSY (^{1}H-^{1}H) spectrum (500 MHz, CD_3COCD_3, 298 K) of compound **3**.

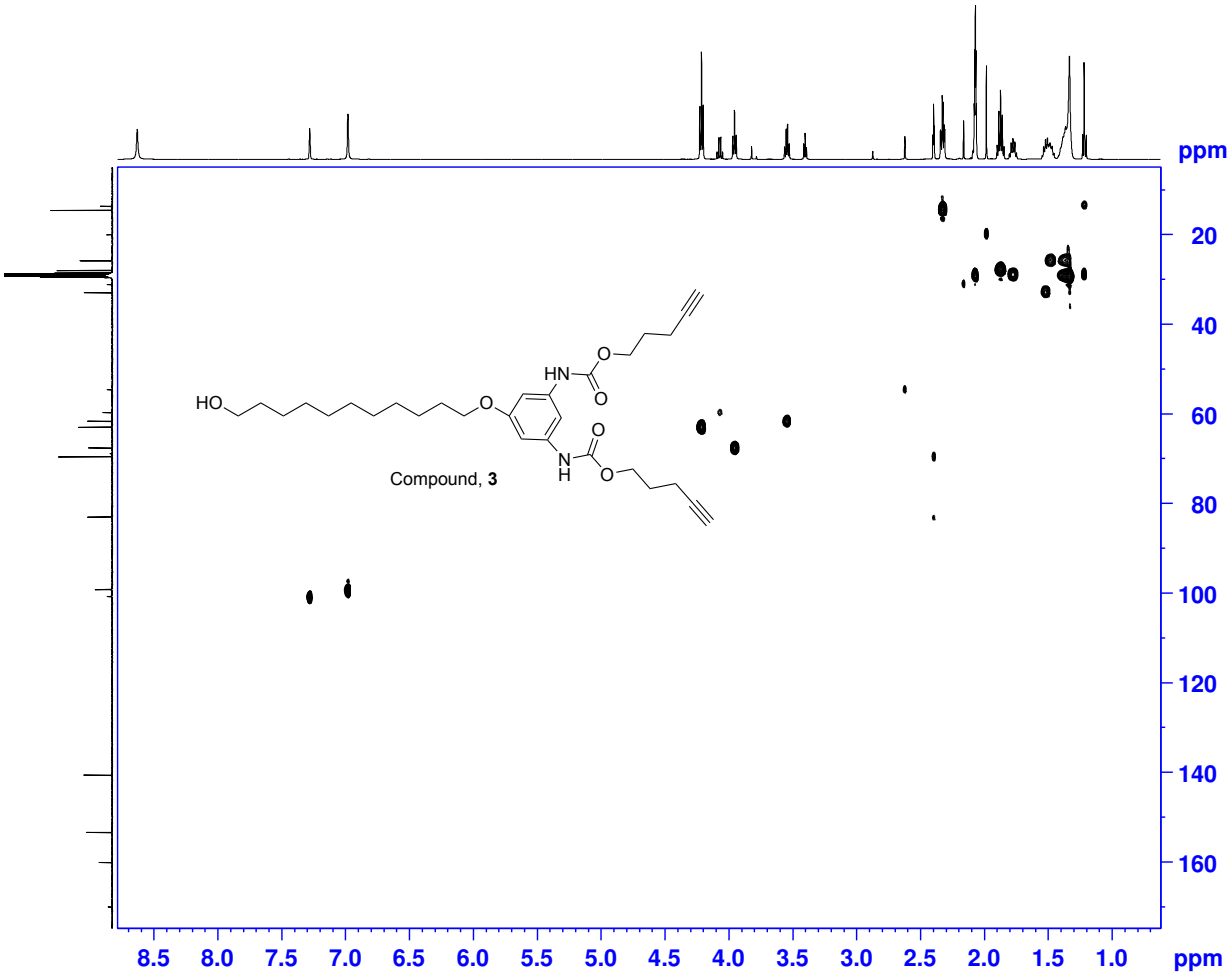


Figure S7. HSQC (^{1}H-^{13}C) spectrum (500 MHz, CD_3COCD_3, 298 K) of compound **3**.

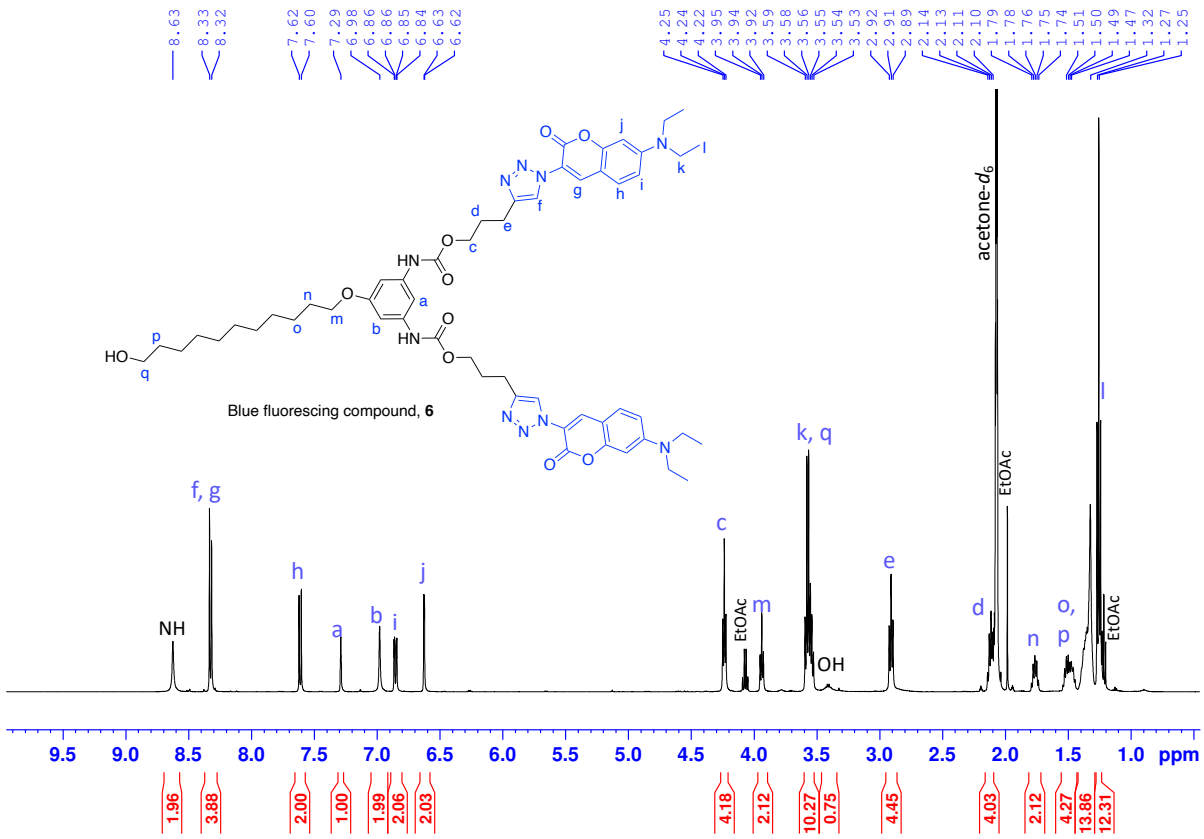


Figure S8. ^{1}H NMR spectrum (500 MHz, CD_3COCD_3, 298 K) of blue fluorescing compound **6**.

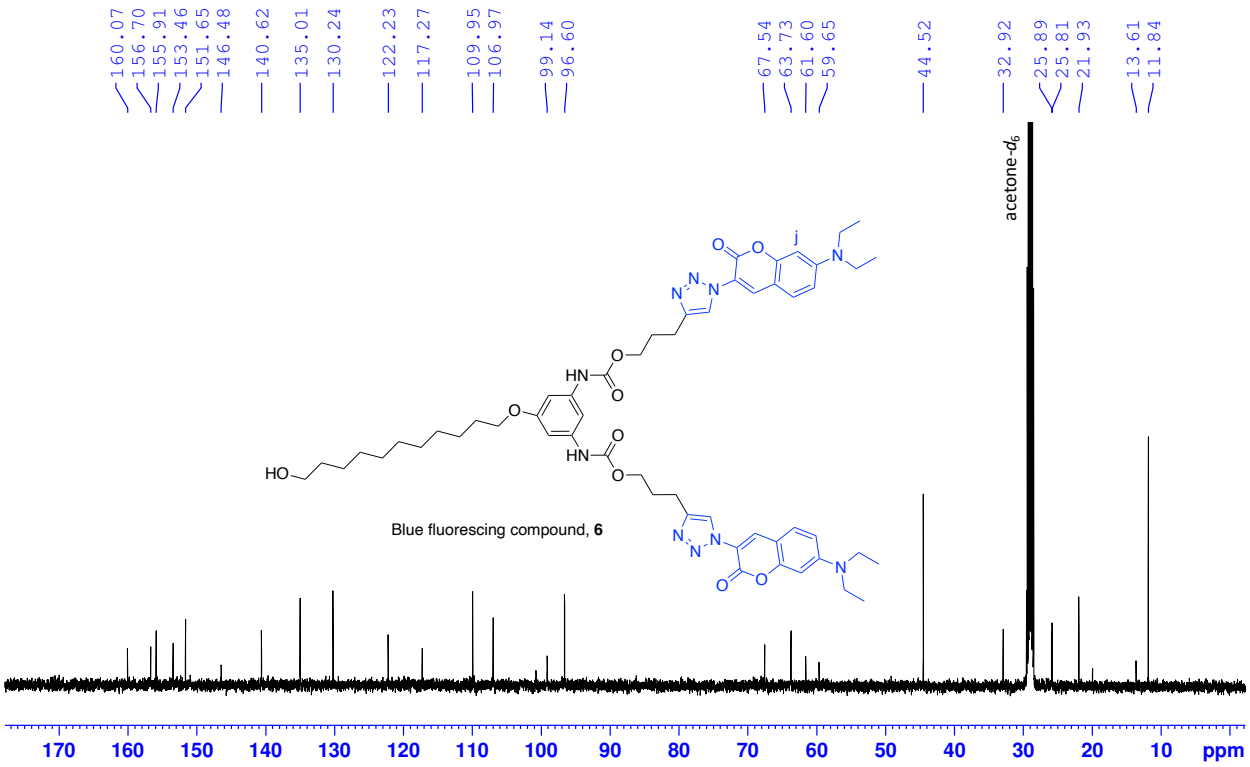


Figure S9. ^{13}C NMR spectrum (126 MHz, CD_3COCD_3, 298 K) of blue fluorescing compound **6**.

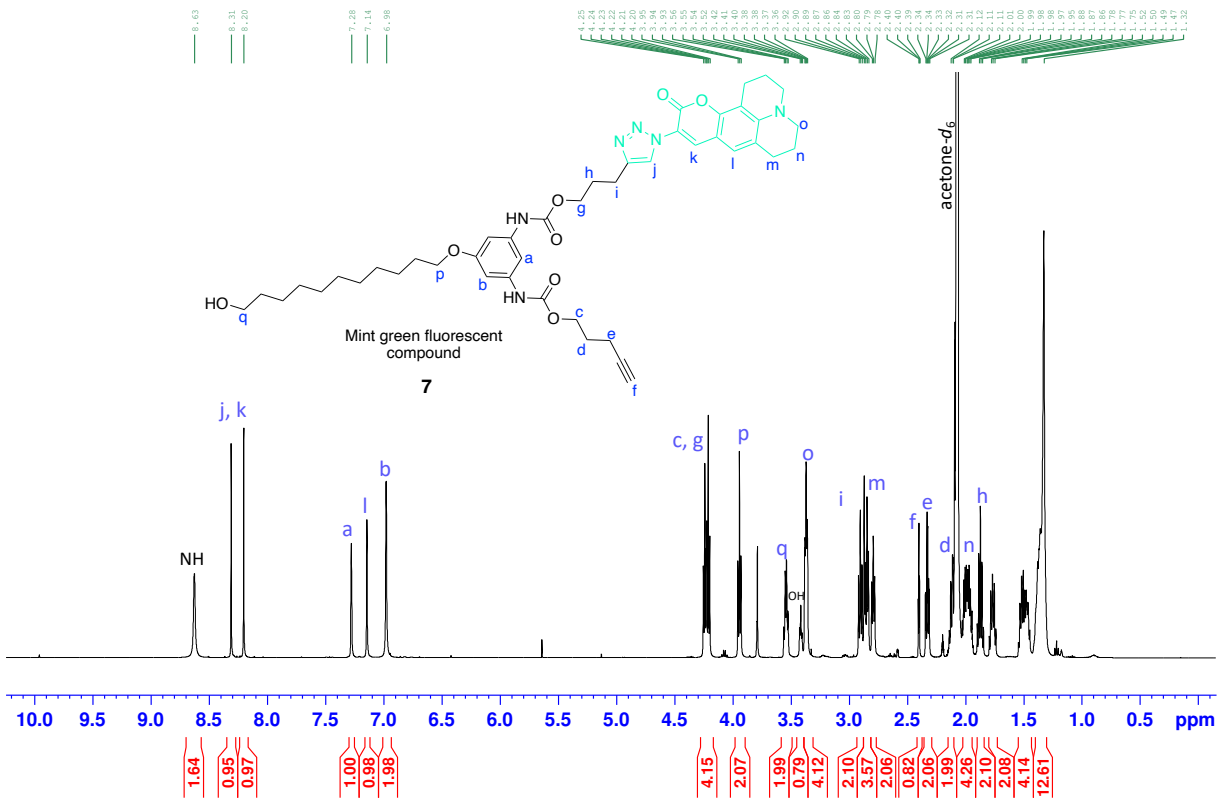


Figure S10. ^{1}H spectrum (500 MHz, CD_3COCD_3, 298 K) of one-clicked mint green fluorescing compound **7**.

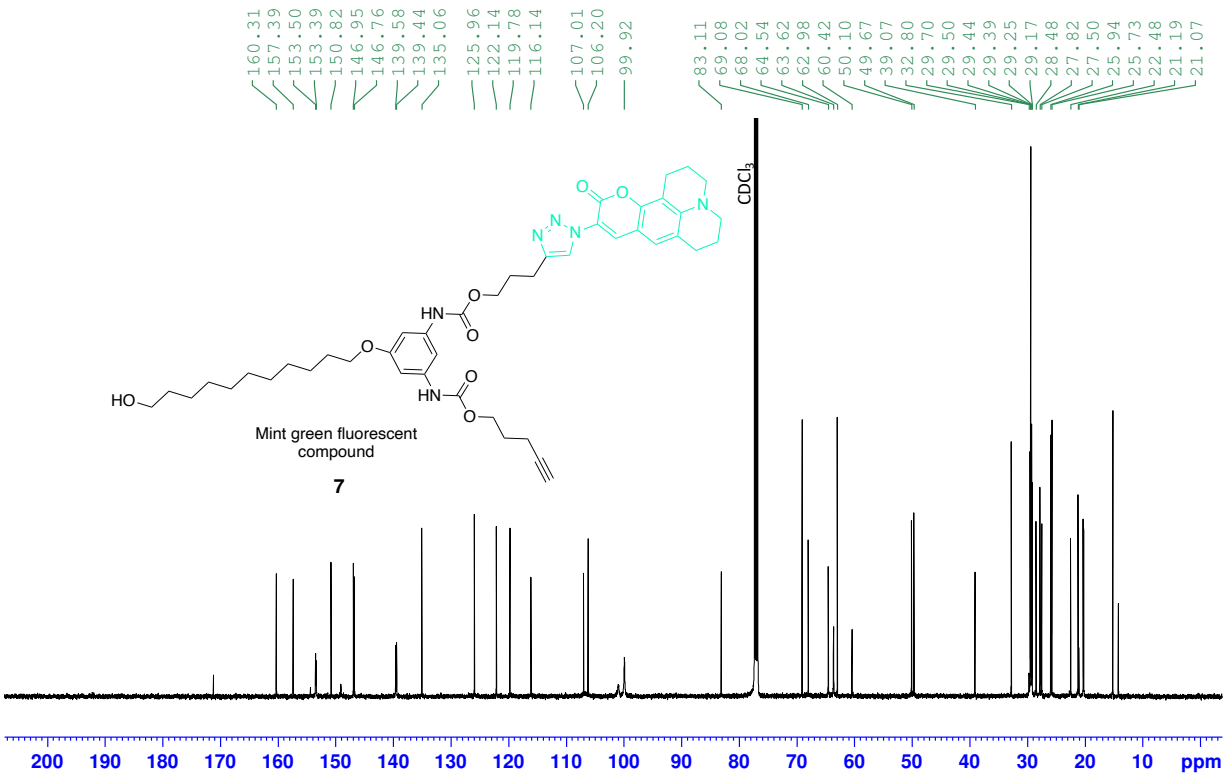


Figure S11. ^{13}C spectrum (500 MHz, CD_3COCD_3, 298 K) of one-clicked mint green fluorescing compound **7**.

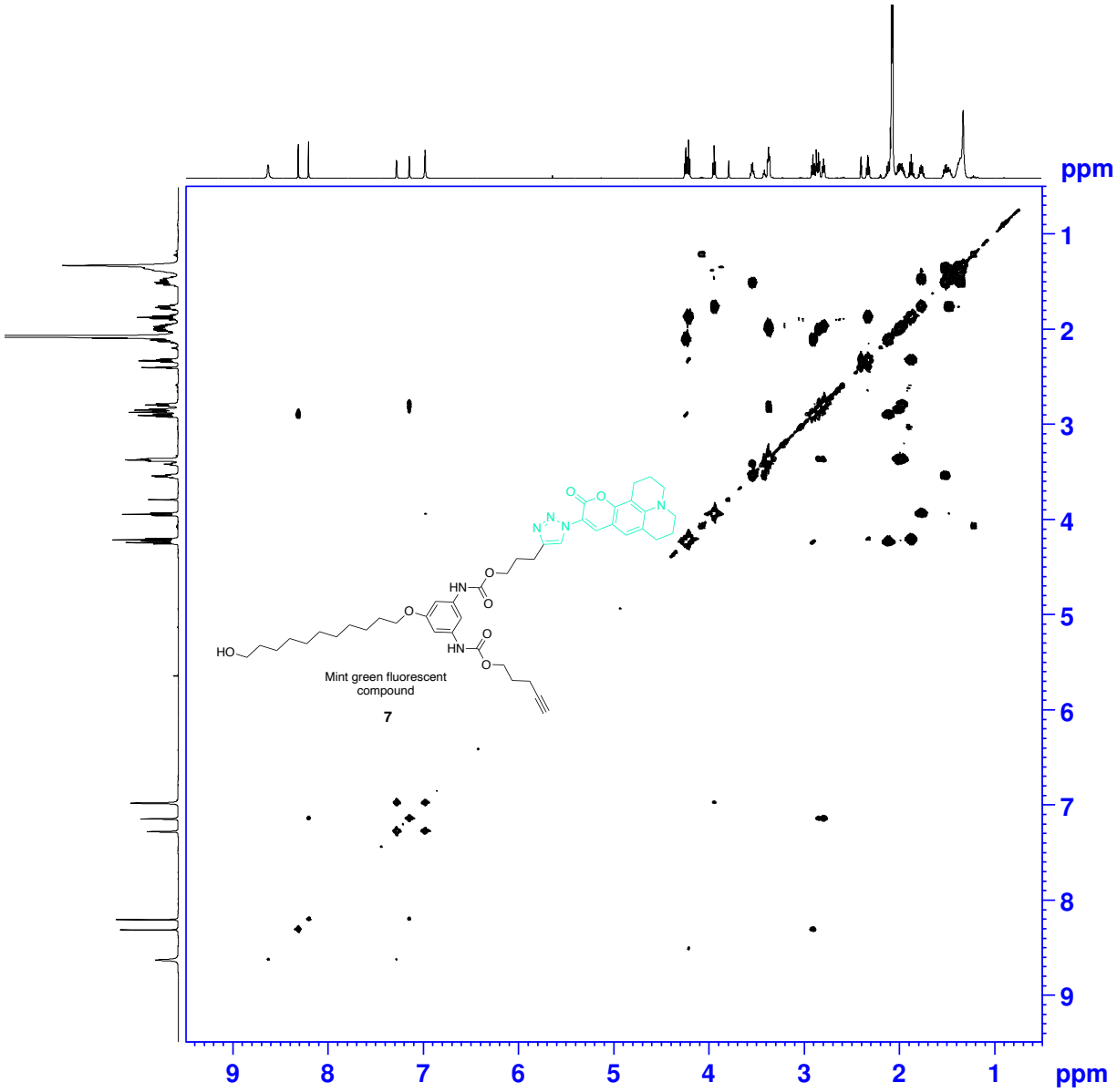


Figure S12. COSY (^{1}H-^{1}H) spectrum (500 MHz, CD_3COCD_3, 298 K) of one-clicked mint green fluorescing compound **7**.

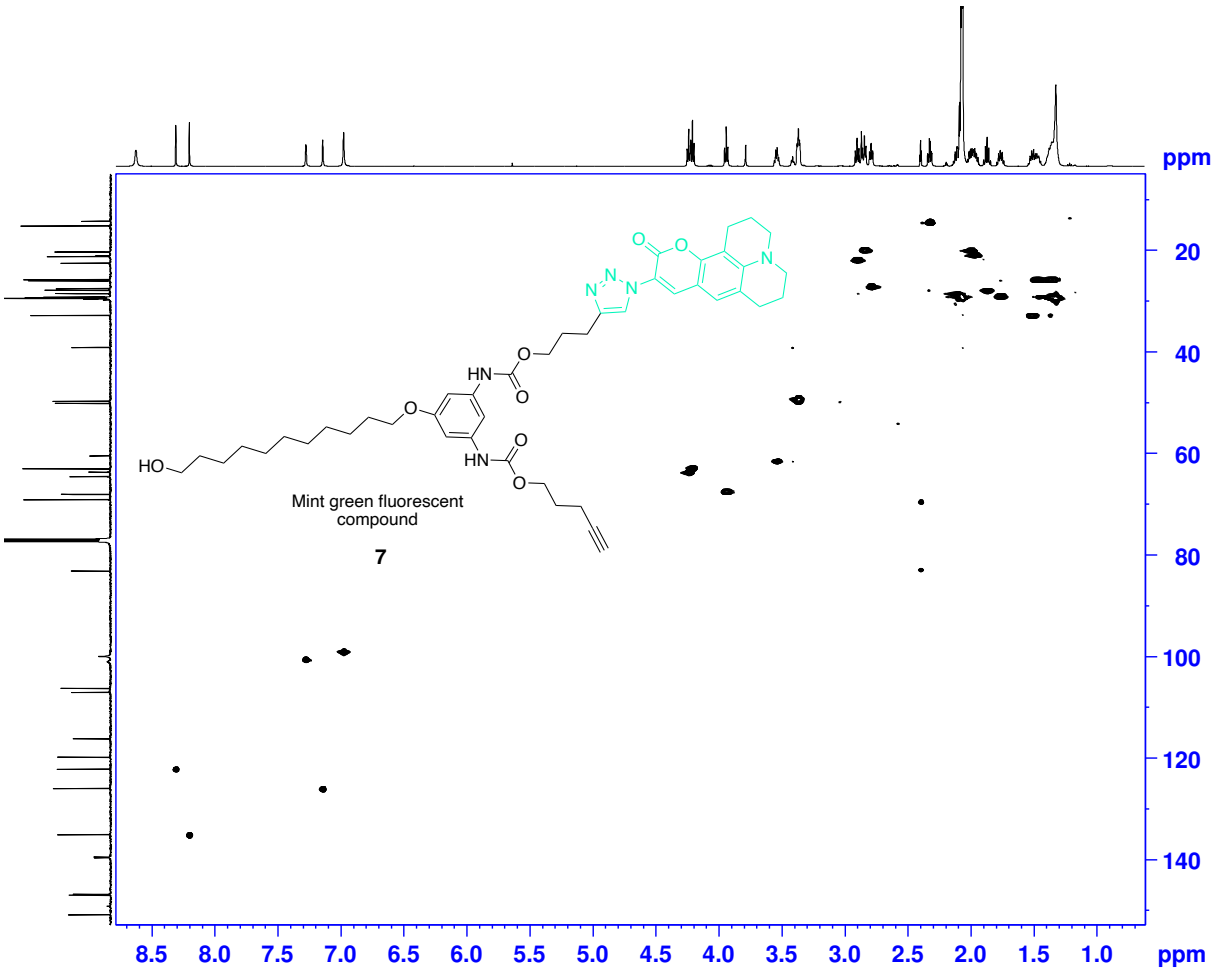


Figure S13. HSQC (^{1}H-^{13}C) spectrum (500 MHz, CD_3COCD_3, 298 K) of one-clicked mint green fluorescing compound **7**.

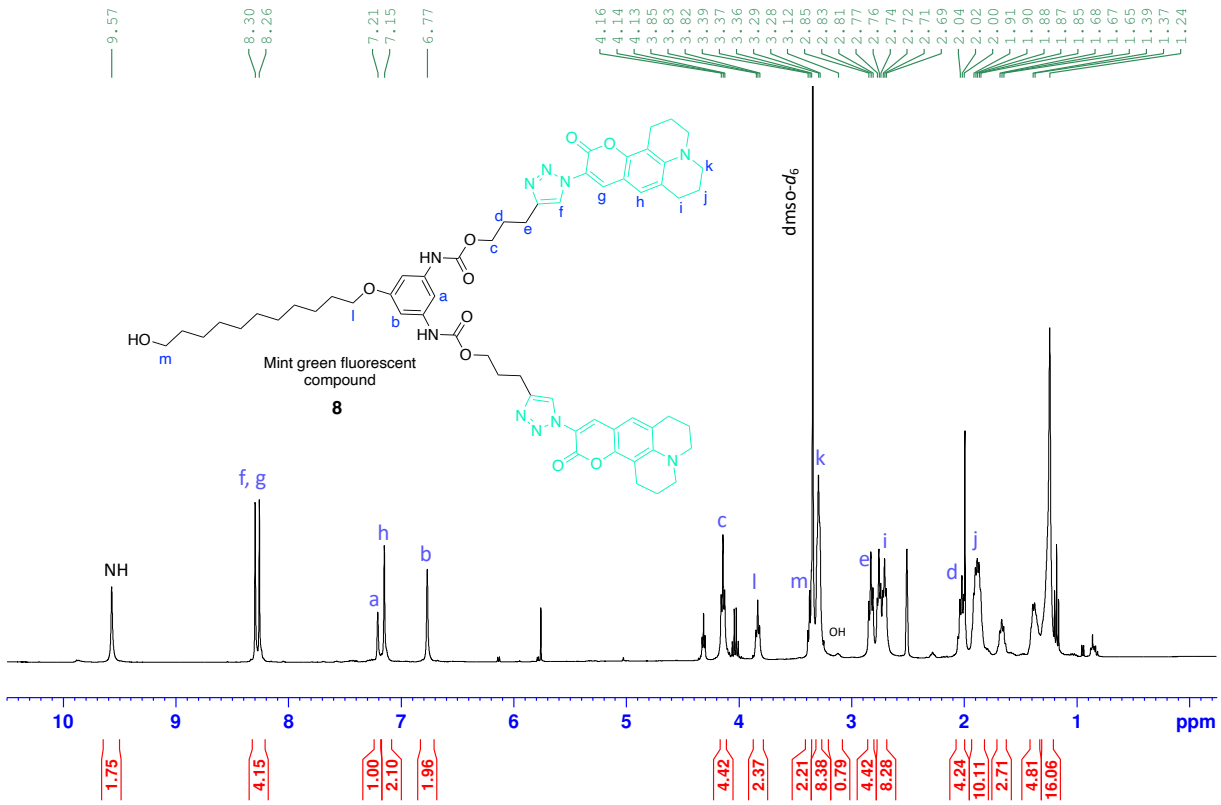


Figure S14. ^{1}H NMR spectrum (400 MHz, CD_3SOCD_3, 298 K) of mint green fluorescing compound **8**.

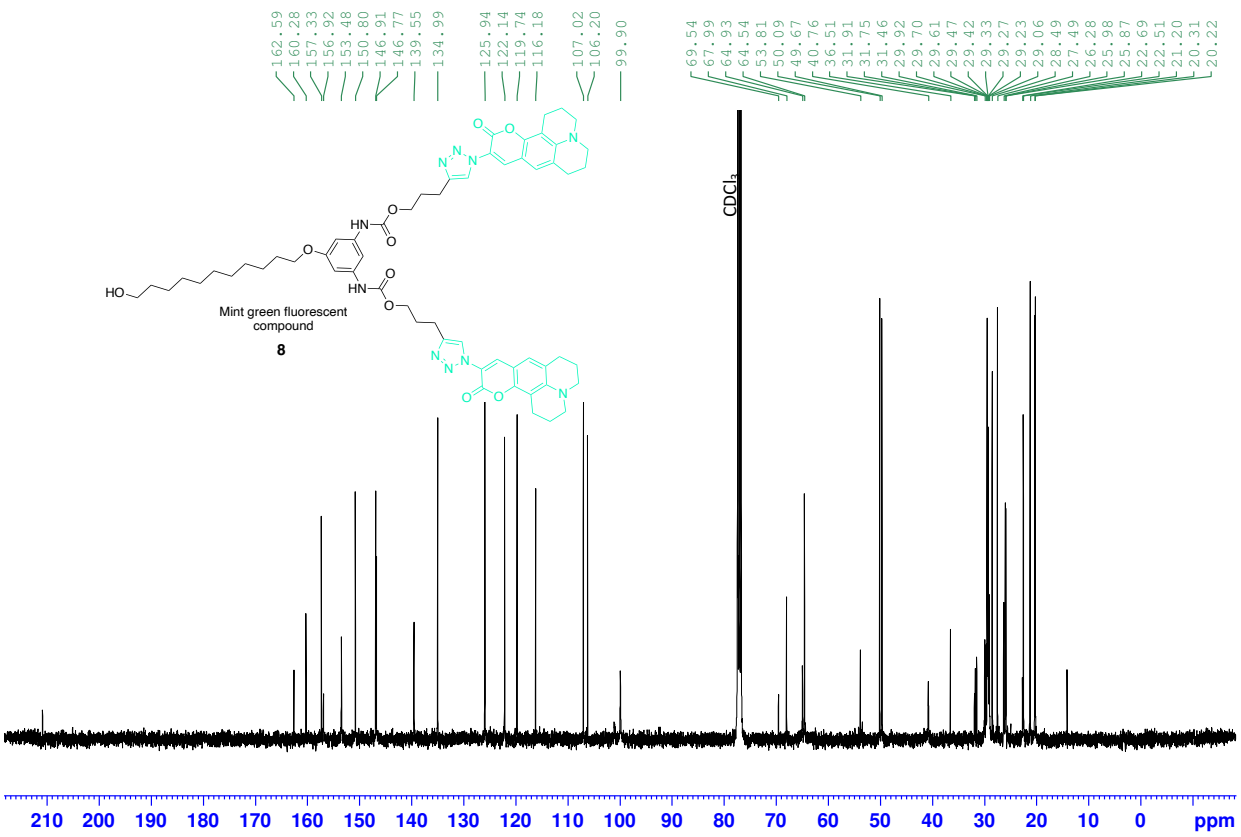


Figure S15. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of minet green fluorescing compound **8**.

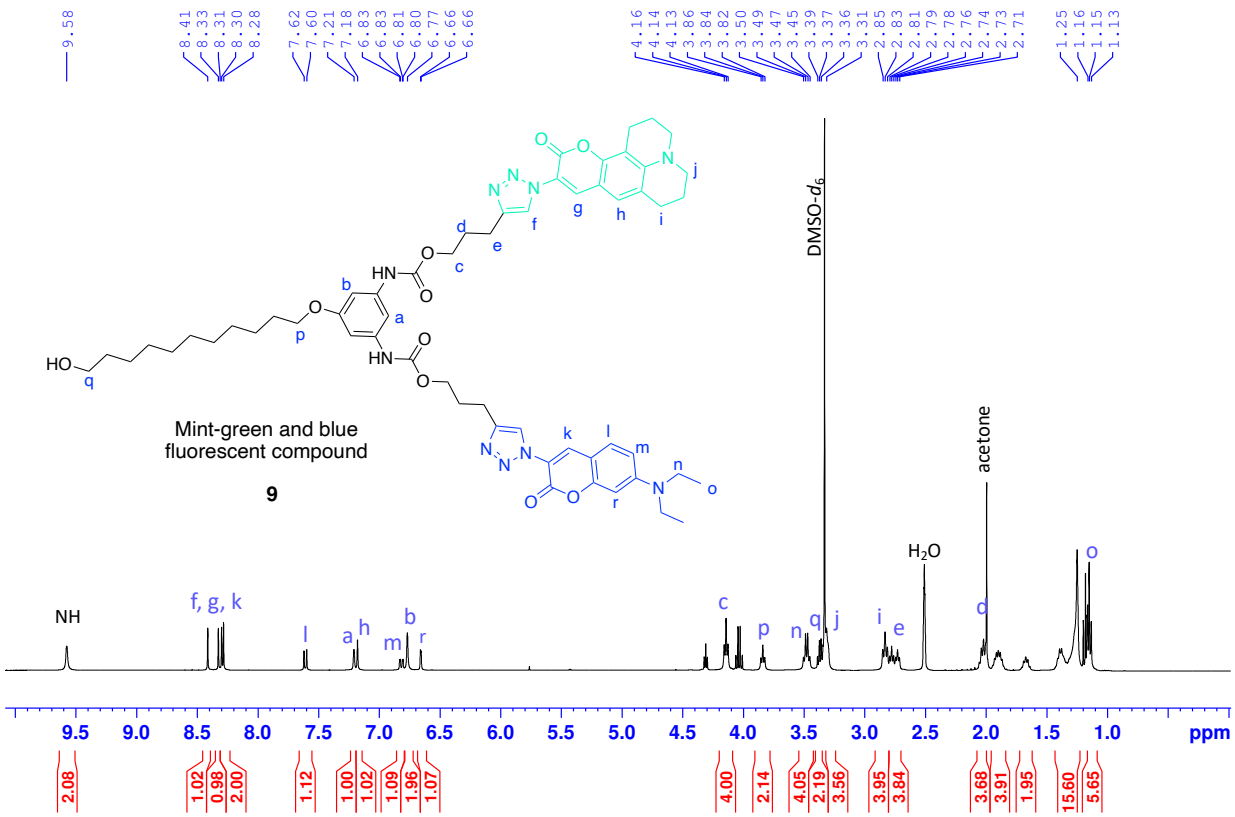


Figure S16. ^{1}H NMR spectrum (400 MHz, CD_3SOCD_3, 298 K) of blue and mint green fluorescing compound **9**.

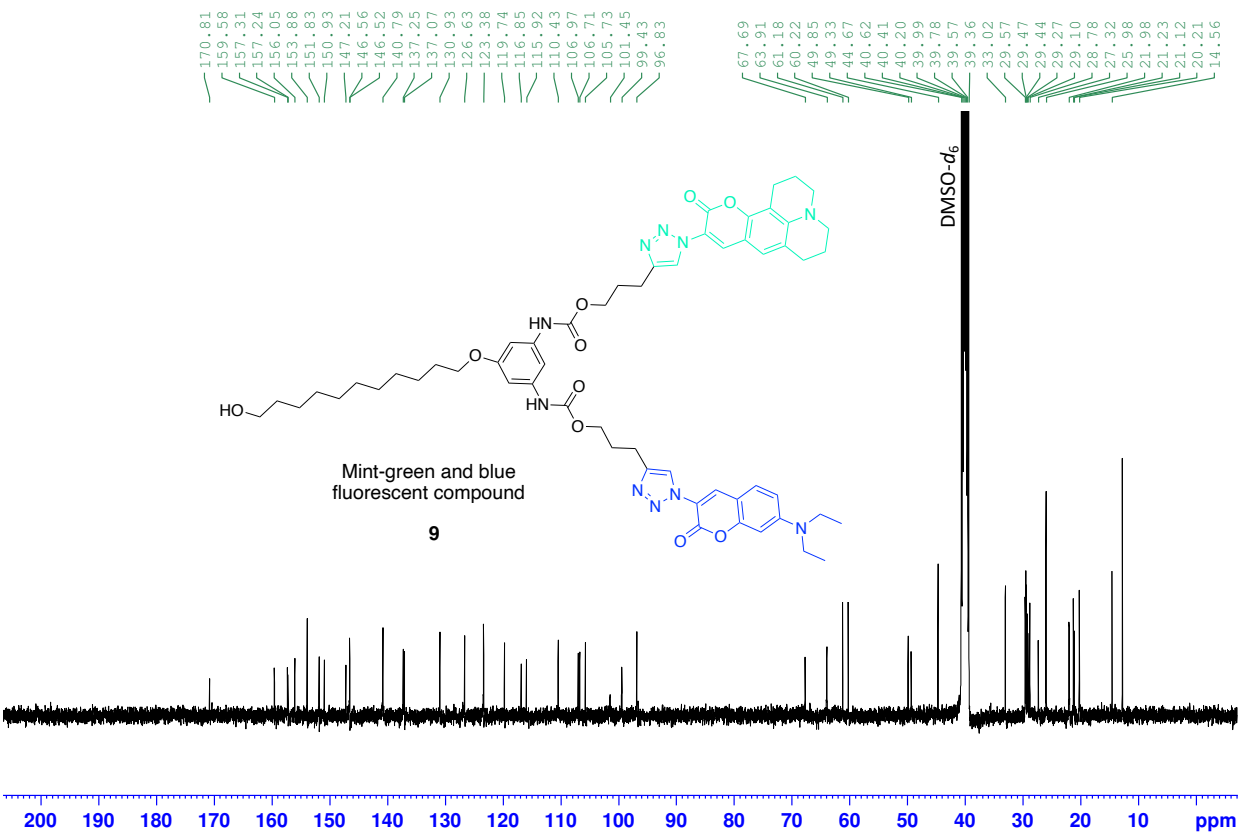


Figure S17. ^{13}C NMR spectrum (101 MHz, CD_3SOCD_3, 298 K) of blue and mint green fluorescing compound **9**.

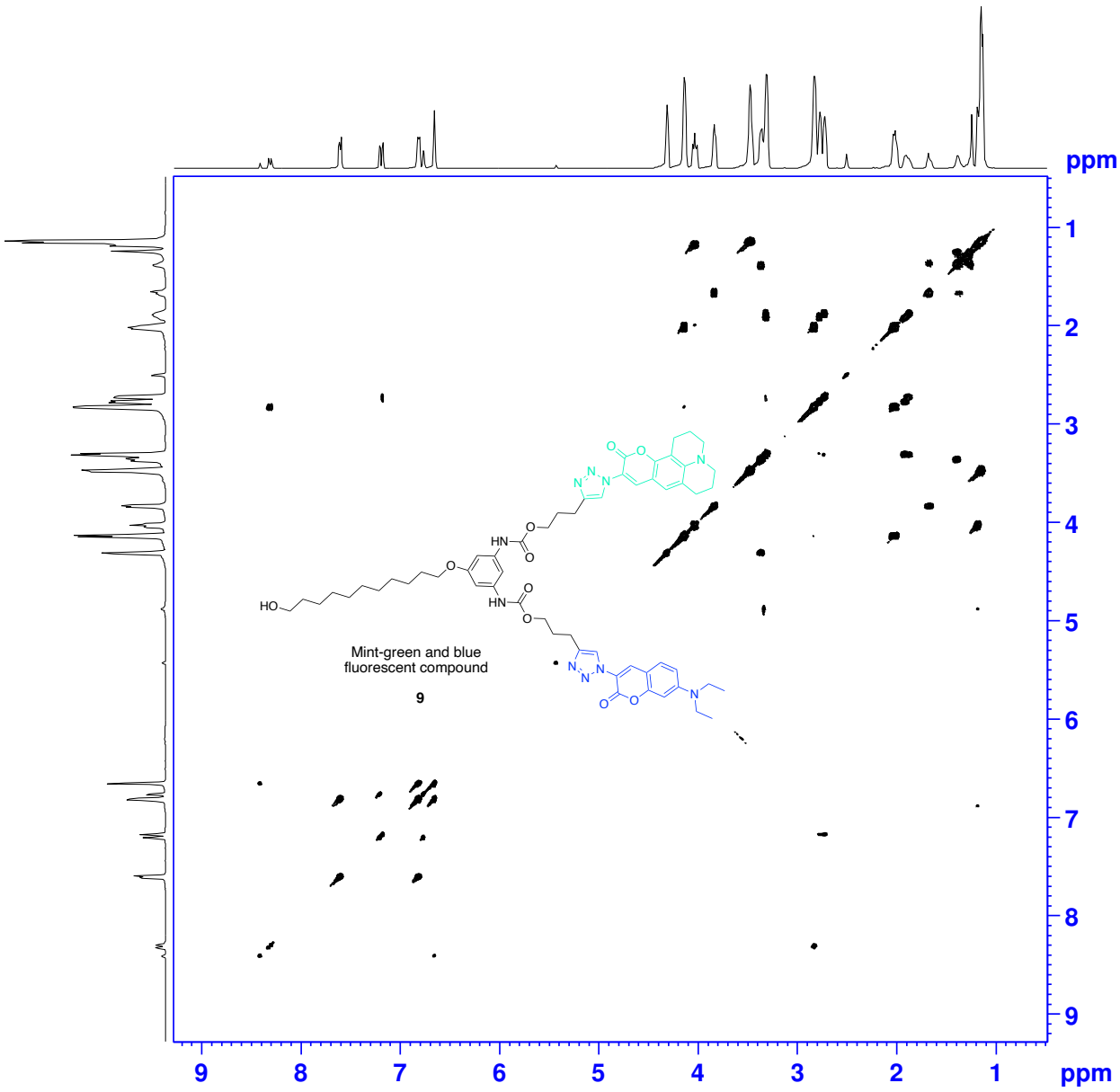


Figure S18. COSY (^{1}H-^{1}H) spectrum (400 MHz, CD_3SOCD_3, 298 K) of blue and mint green fluorescing compound **9**.

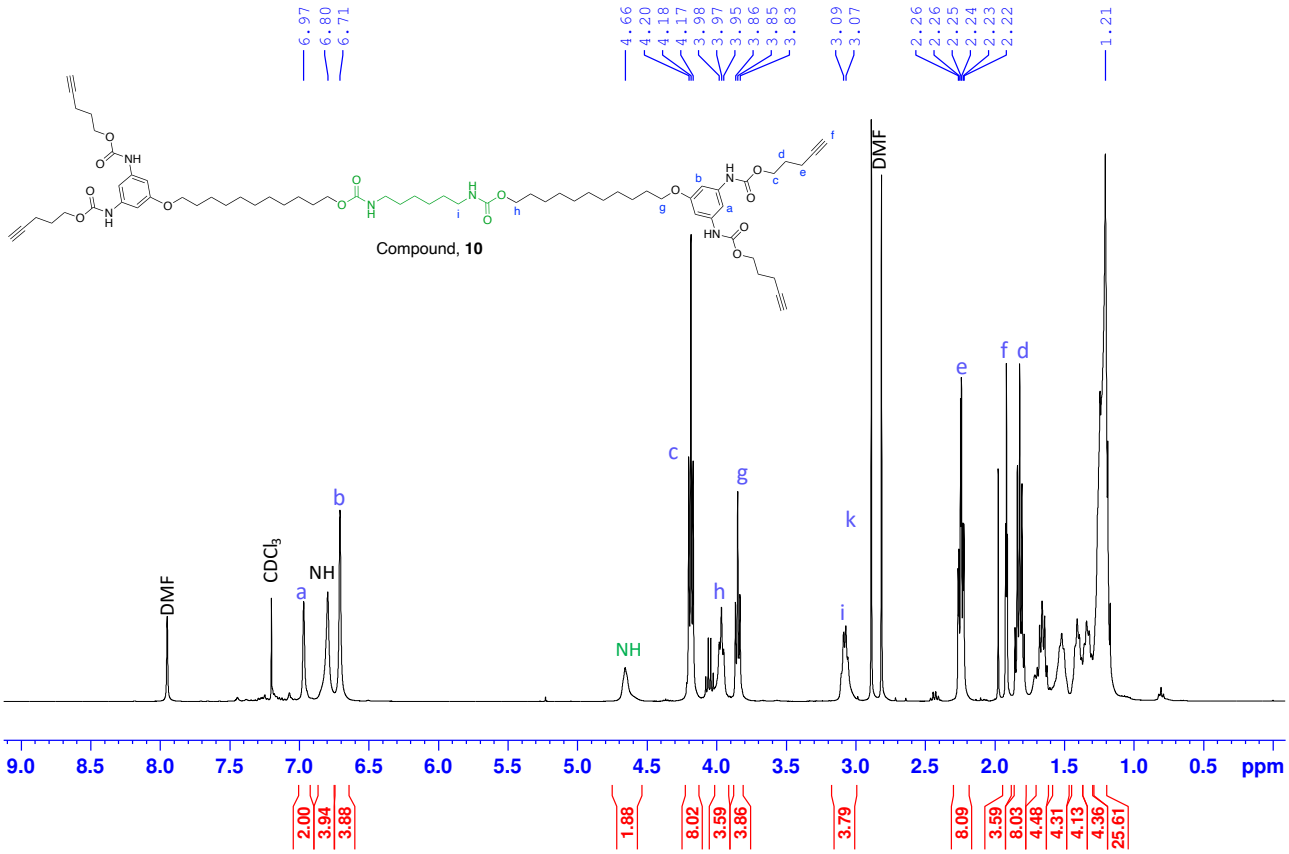


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **10**.

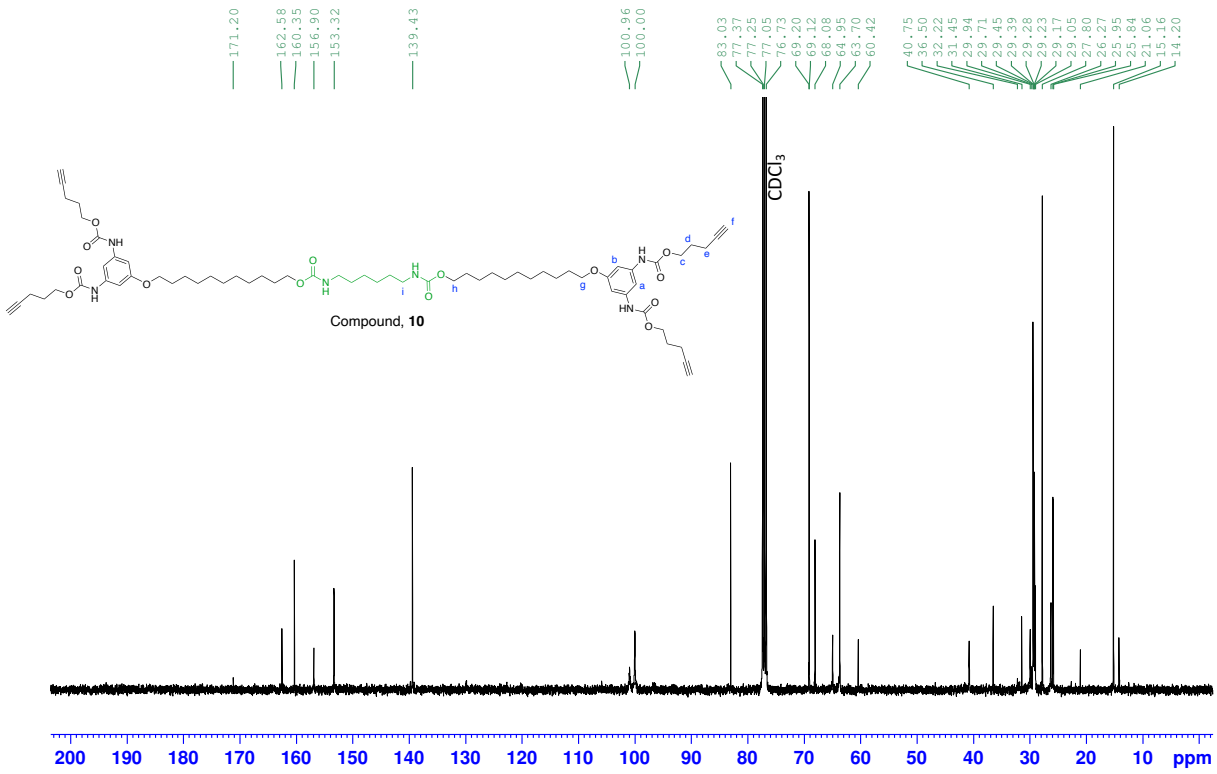


Figure S20. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of compound **10**.

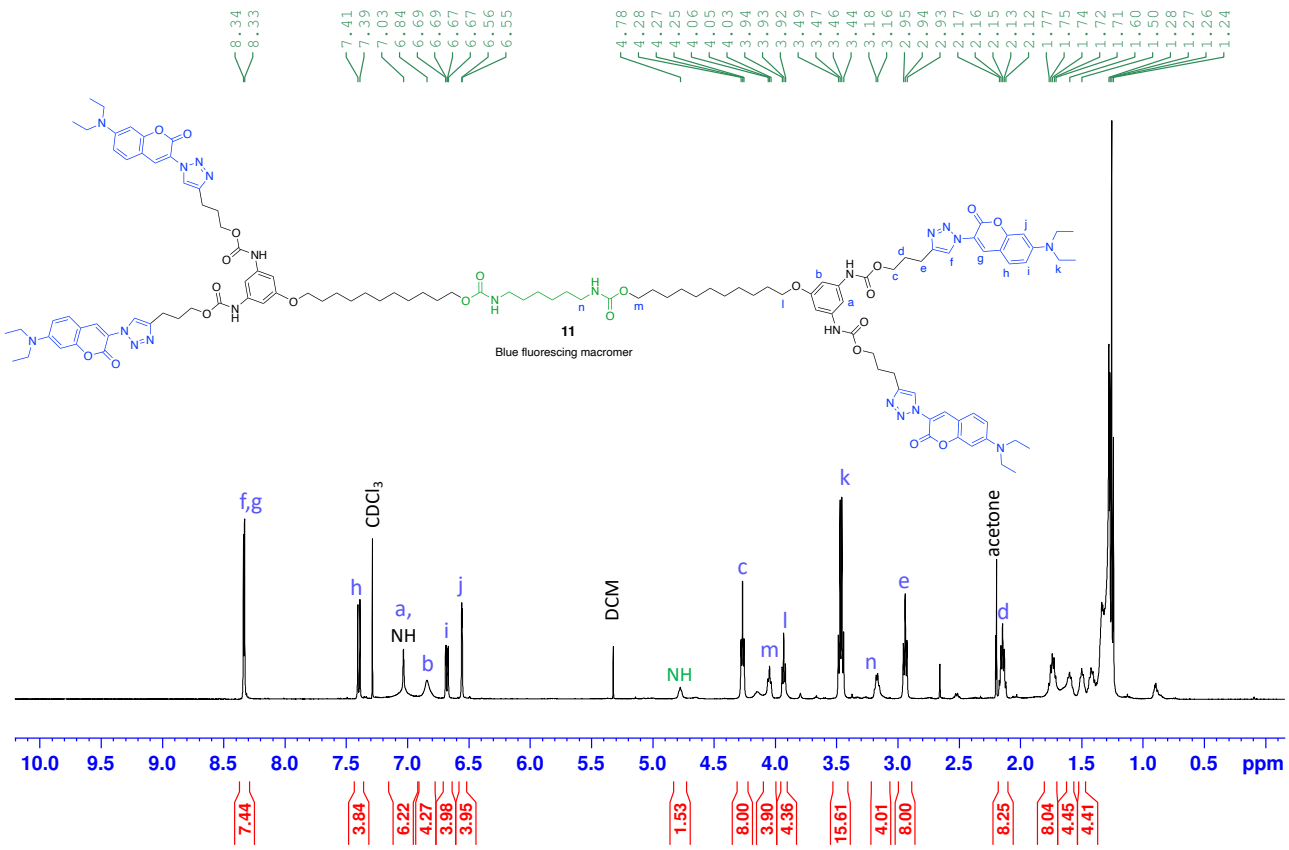


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of blue fluorescing dendrimer **11**.

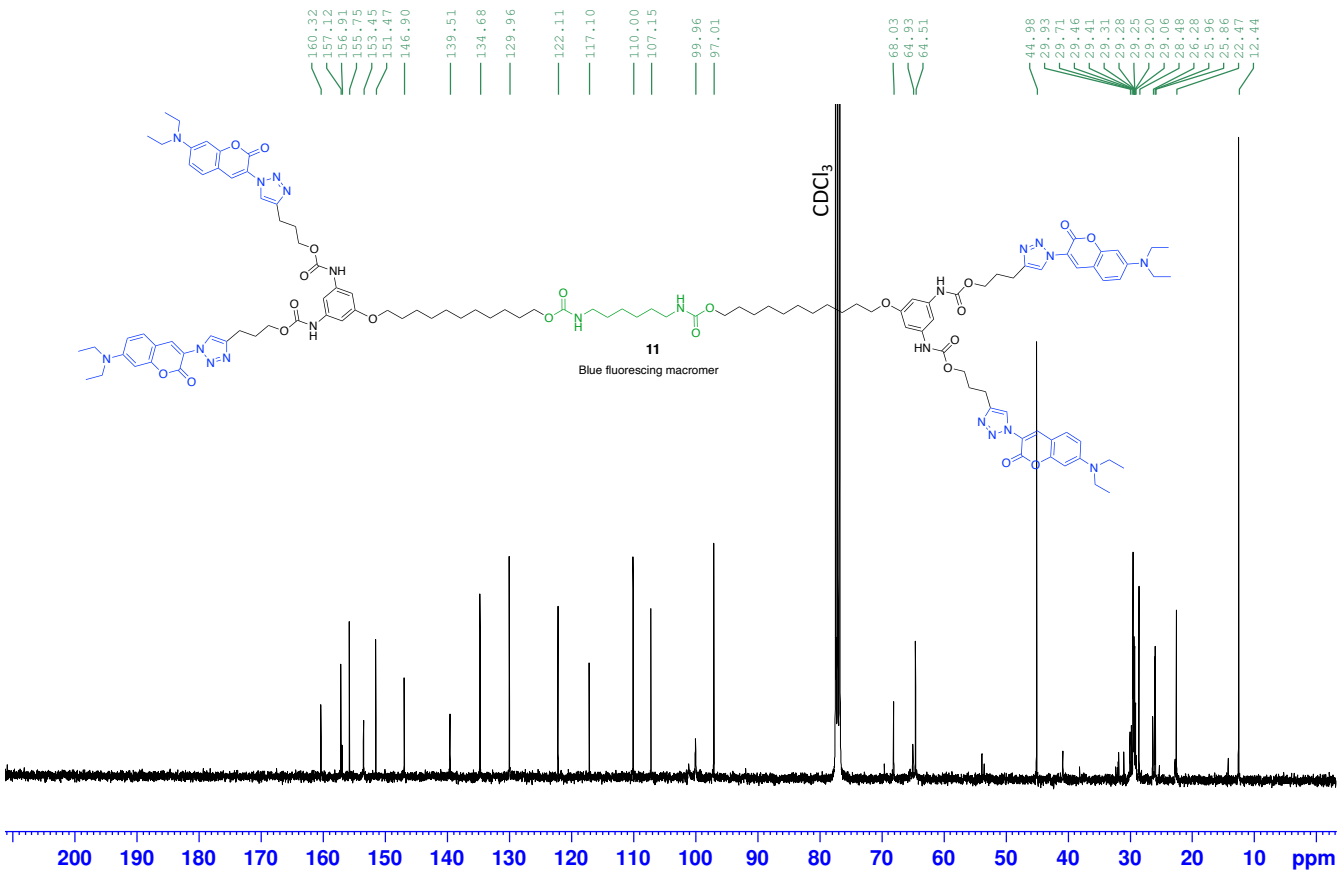


Figure S22. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of blue fluorescing dendrimer. **11**.

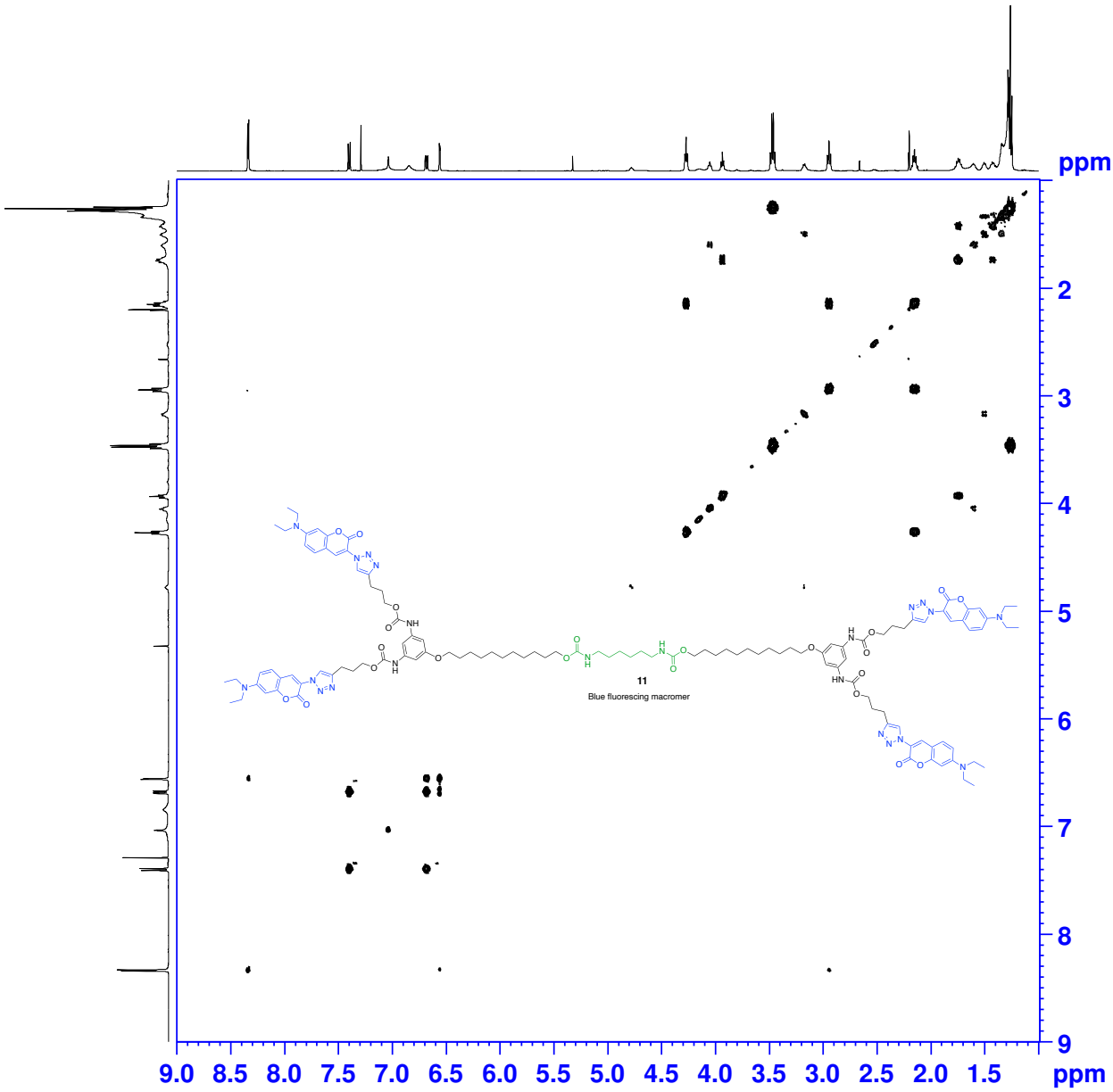


Figure S23. COSY (^{1}H-^{1}H) spectrum (400 MHz, $CDCl_3$, 298 K) of blue fluorescing dendrimer **11**.

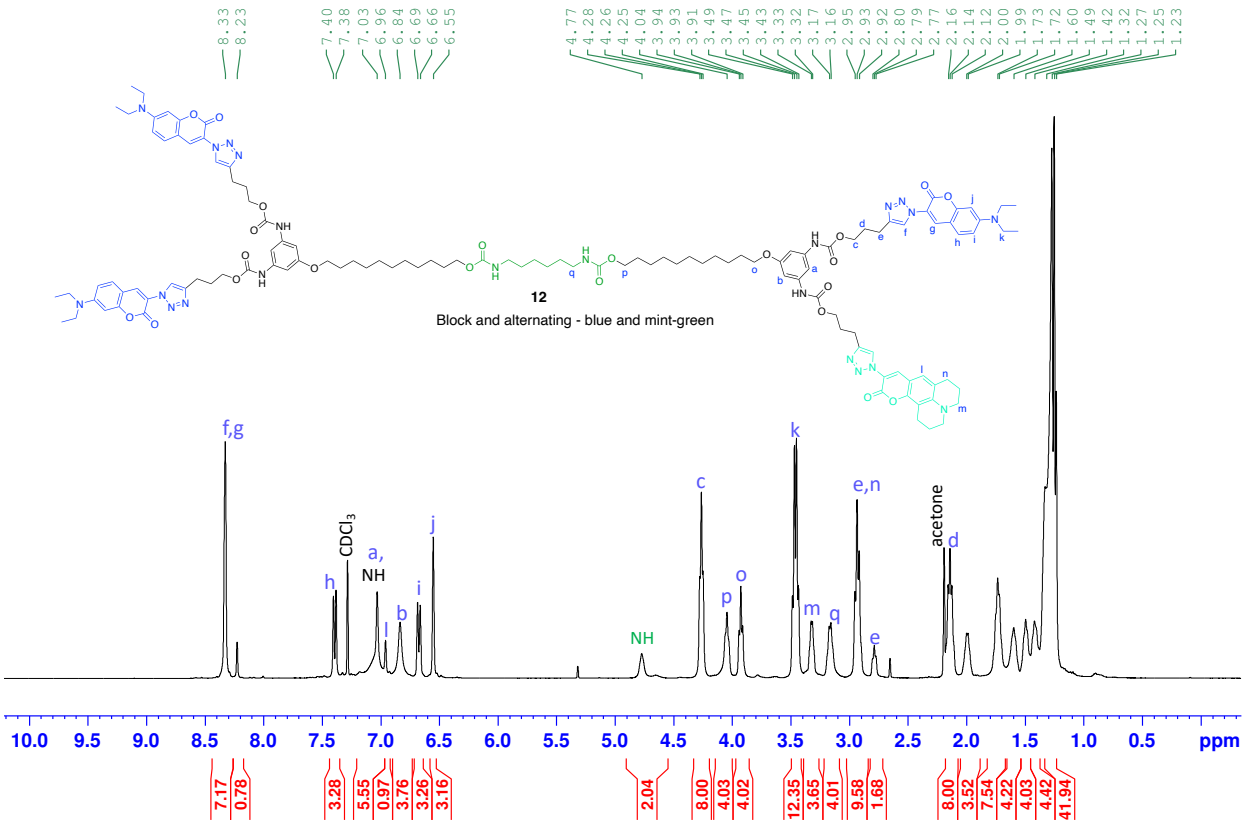


Figure S24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of blue and mint green fluoescing dendrimer **12**.

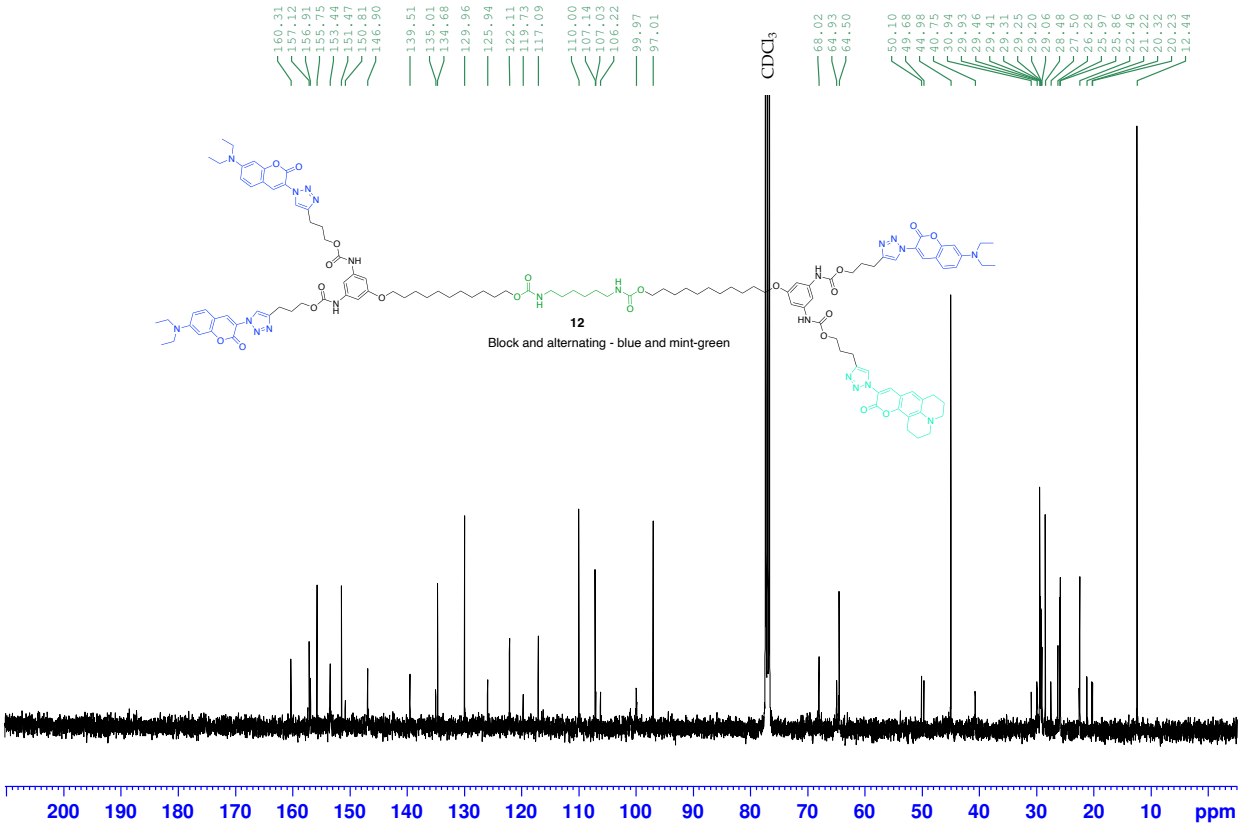


Figure S25. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of blue and mint green fluoescing dendrimer **12**.

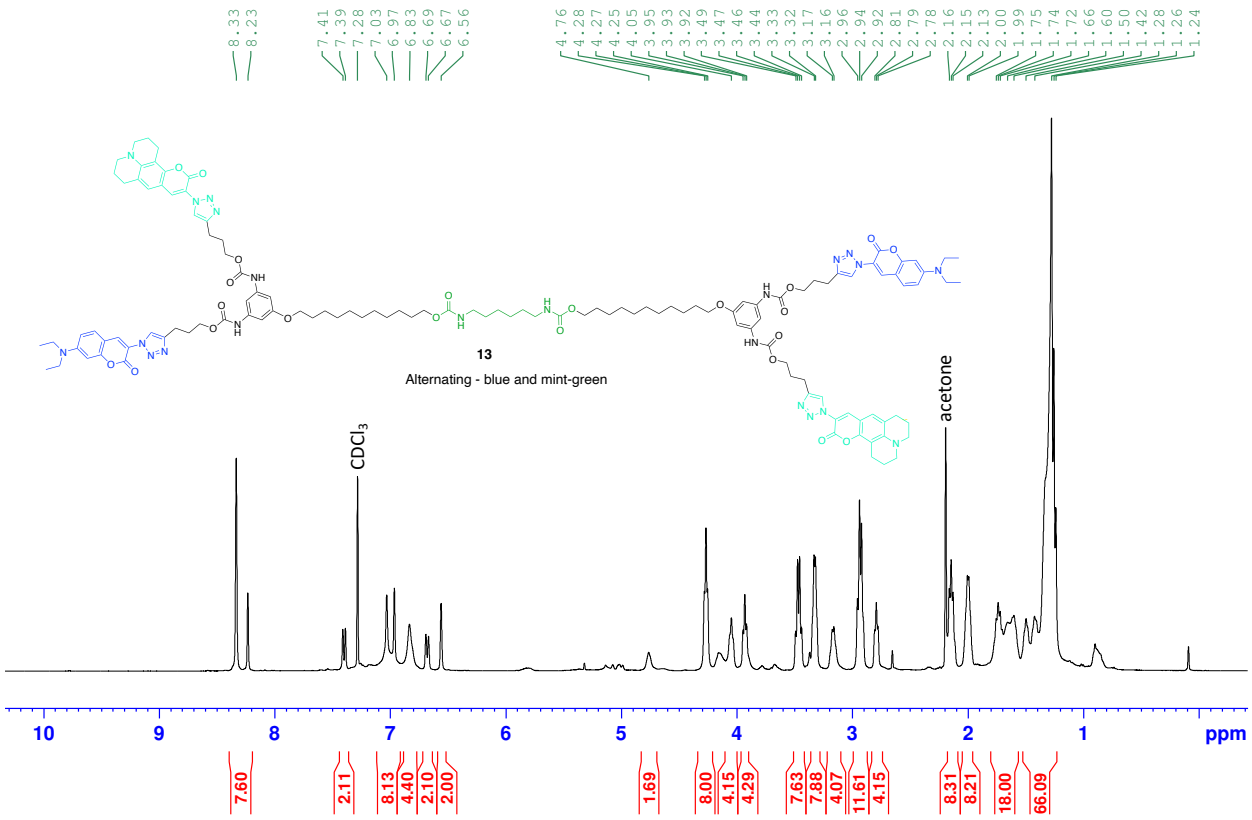


Figure S26. ^{1}H spectrum (400 MHz, $CDCl_3$, 298 K) of alternating blue and mint green fluorescing dendrimer **13**.

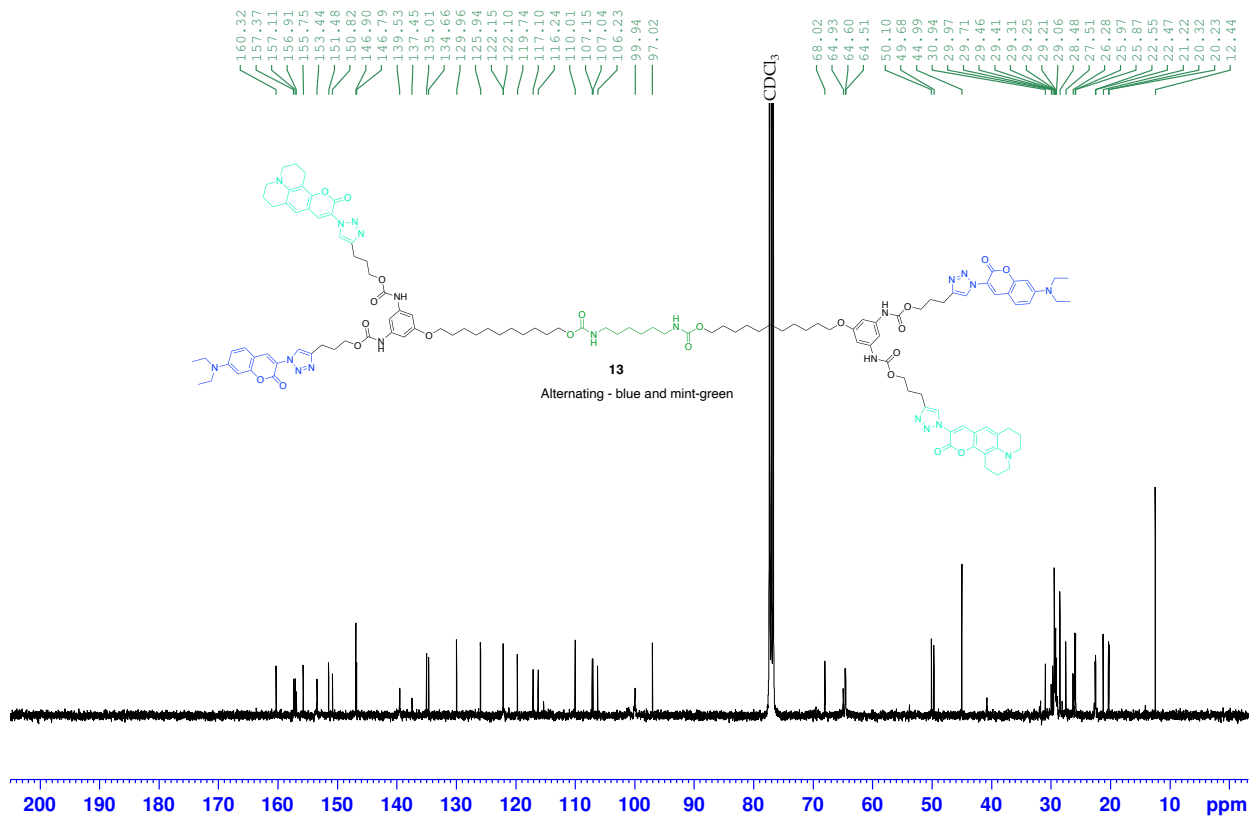


Figure S27. ^{13}C spectrum (101 MHz, $CDCl_3$, 298 K) of alternating blue and mint green fluorescing dendrimer **13**.

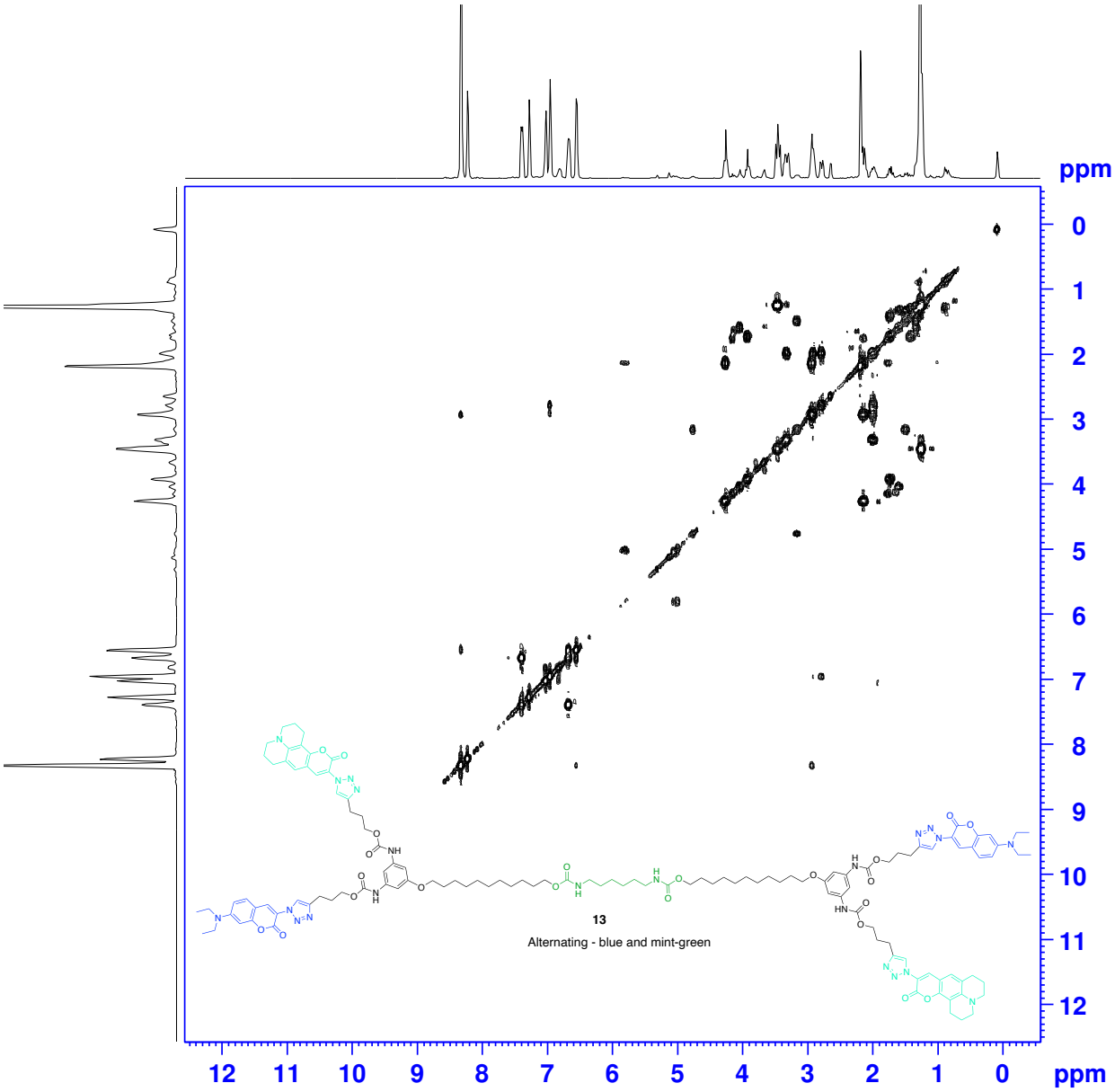


Figure S28. COSY (^{1}H-^{1}H) spectrum (400 MHz, $CDCl_3$, 298 K) of alternating blue and mint green fluorescing dendrimer **13**.

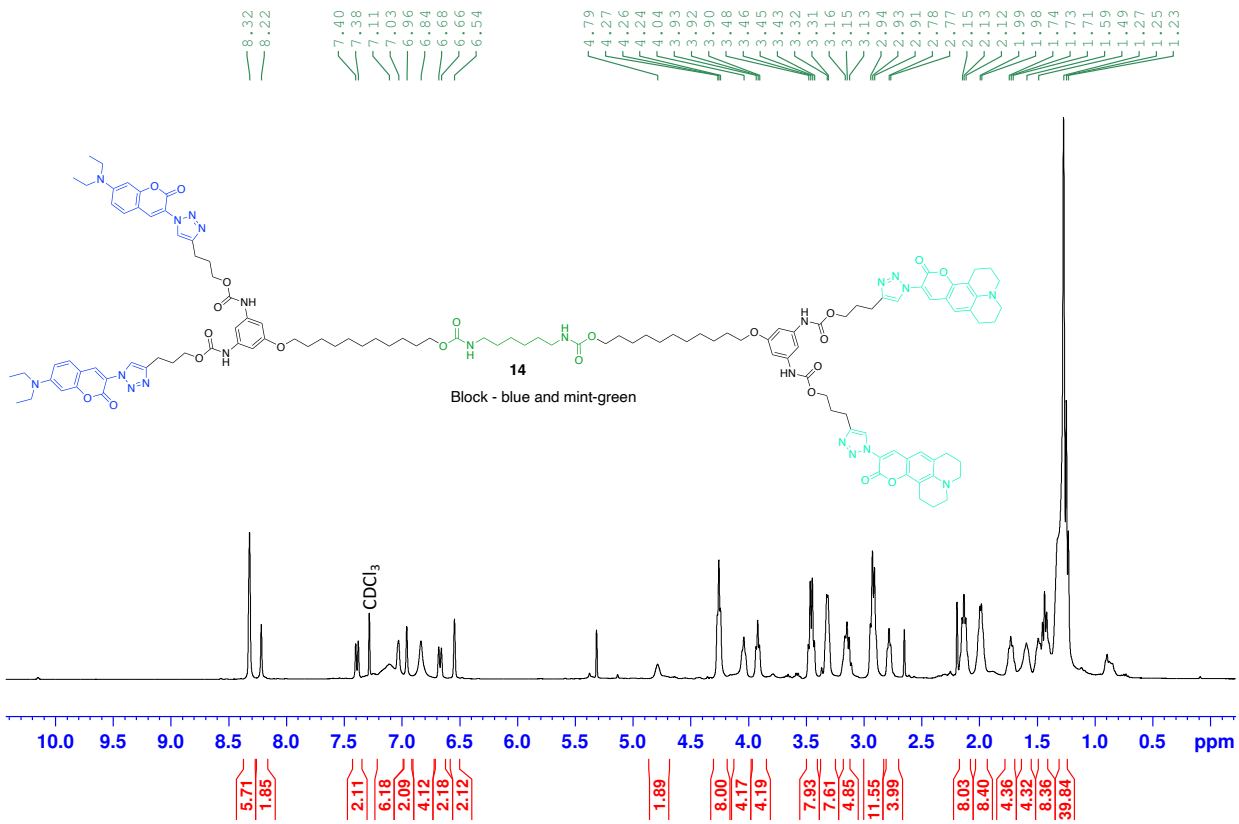


Figure S29. ^{1}H spectrum (400 MHz, $CDCl_3$, 298 K) of block blue and mint green fluorescing dendrimer **14**.

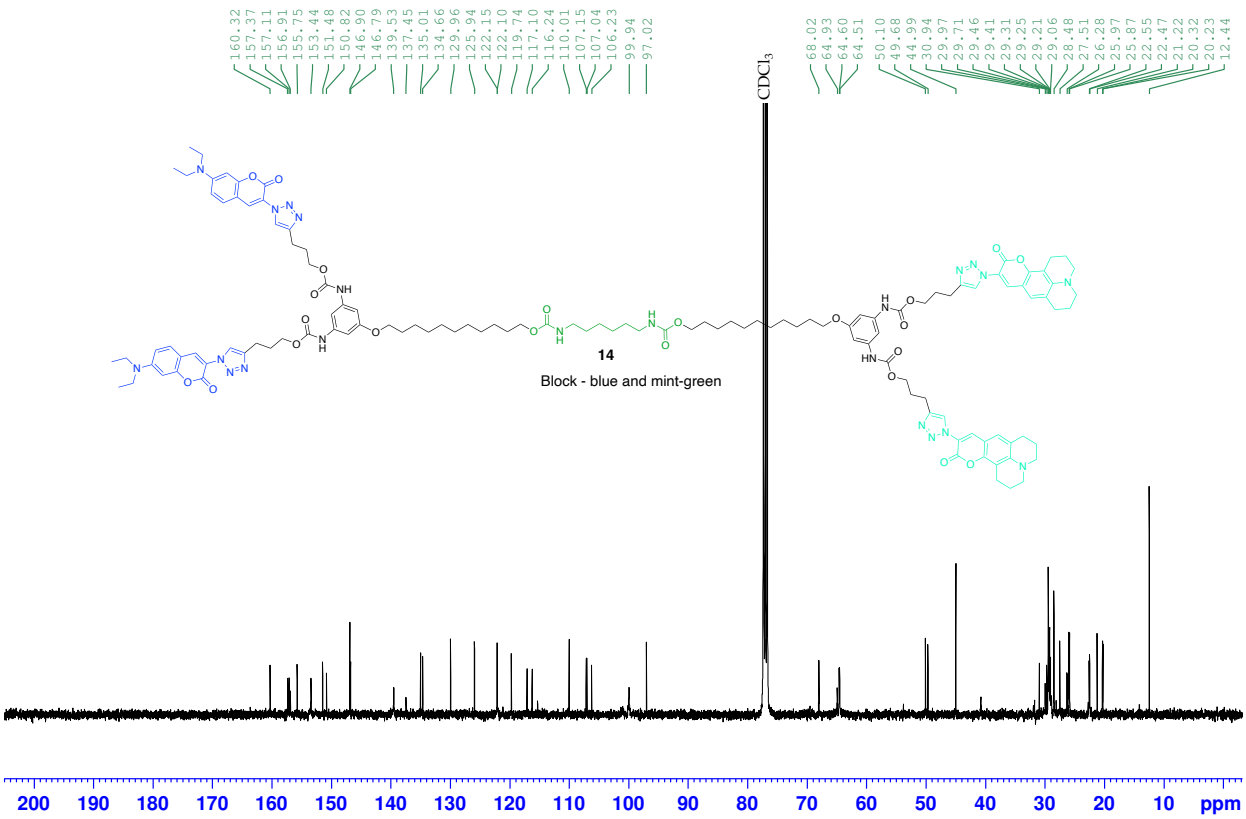


Figure S30. ^{13}C spectrum (101 MHz, $CDCl_3$, 298 K) of block blue and mint green fluorescing dendrimer **14**.

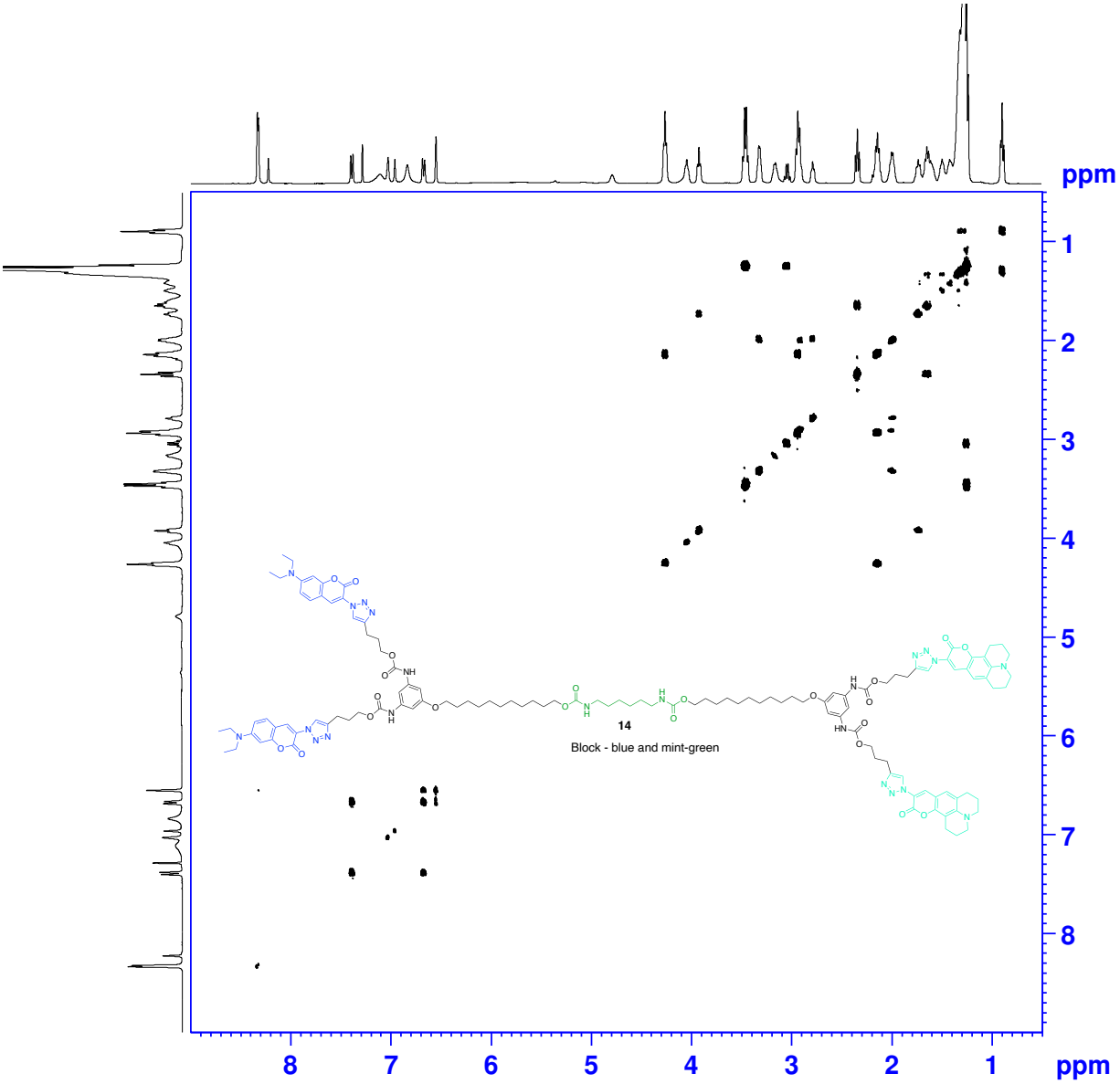


Figure S31. COSY (^{1}H-^{1}H) spectrum (400 MHz, $CDCl_3$, 298 K) of block blue and mint green fluorescing dendrimer **14**.

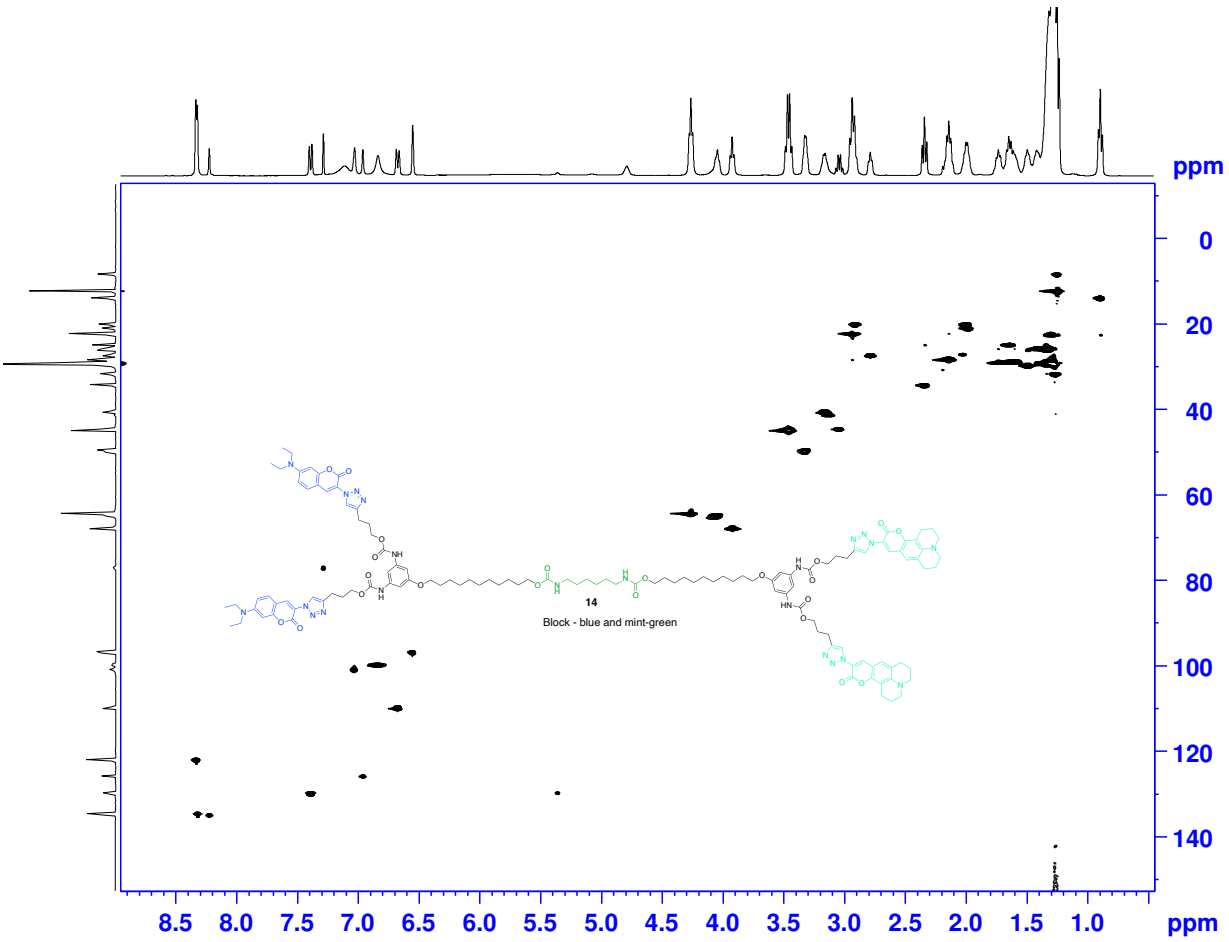


Figure S32. HSQC (^{1}H-^{13}C) spectrum (400 MHz, $CDCl_3$, 298 K) of blue and mint green (block) fluorescing dendrimer **14**.

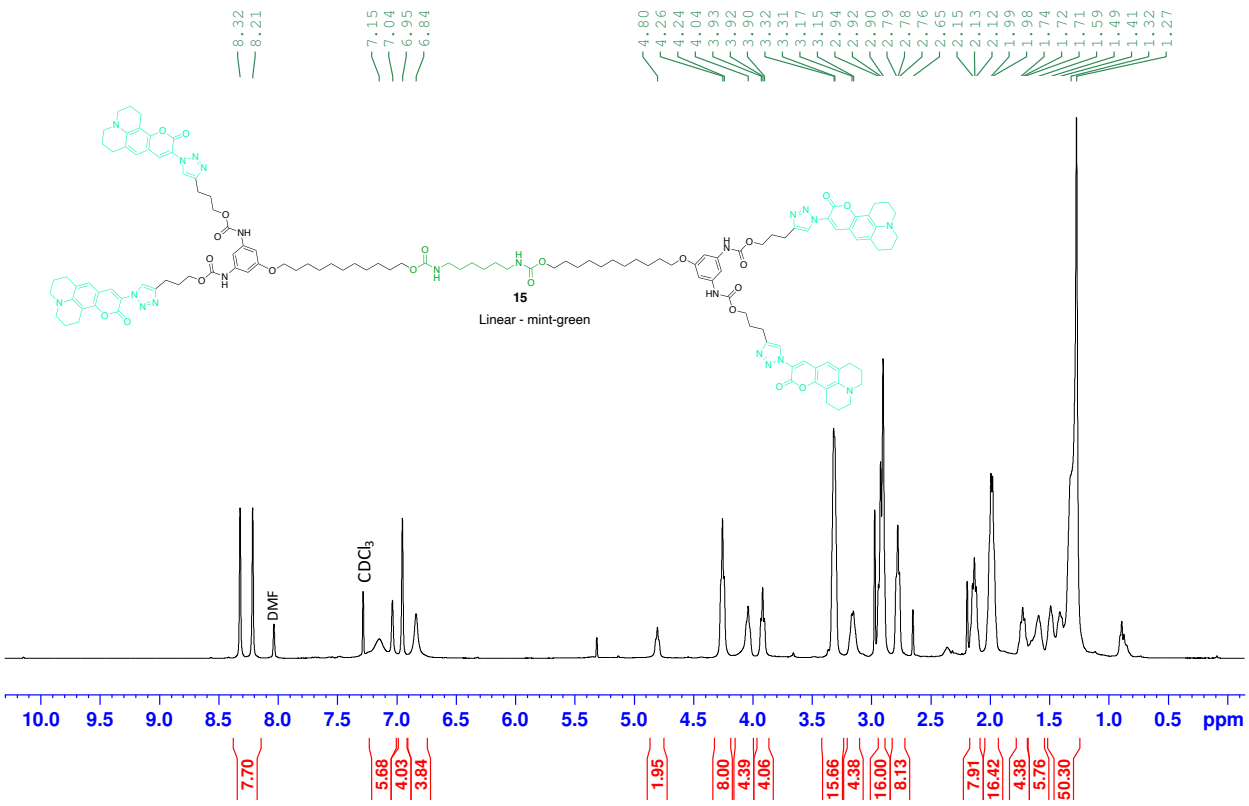


Figure S33. ^{1}H spectrum (400 MHz, $CDCl_3$, 298 K) of mint green fluorescing dendrimer **15**.

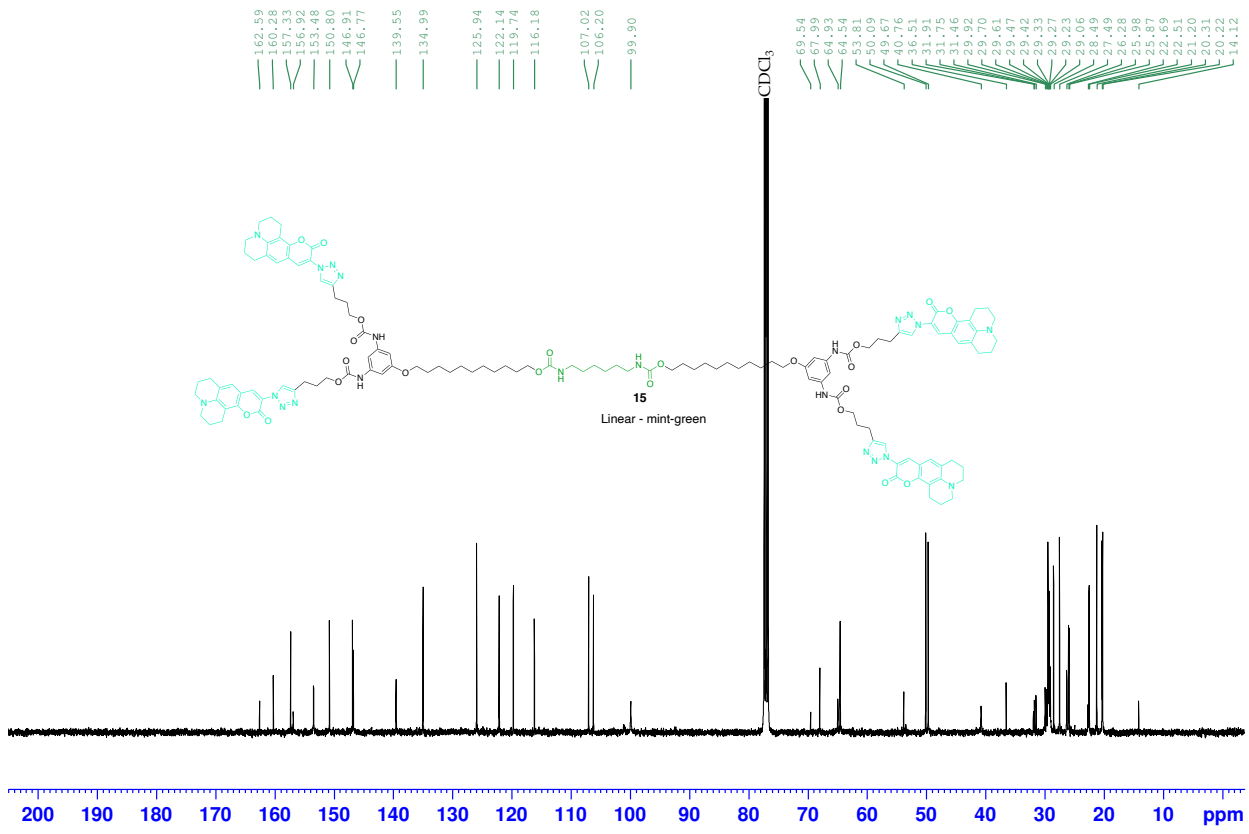


Figure S34. ^{13}C spectrum (101 MHz, $CDCl_3$, 298 K) of mint green fluorescing dendrimer **15**.

3. Mass spectra of synthesized compounds

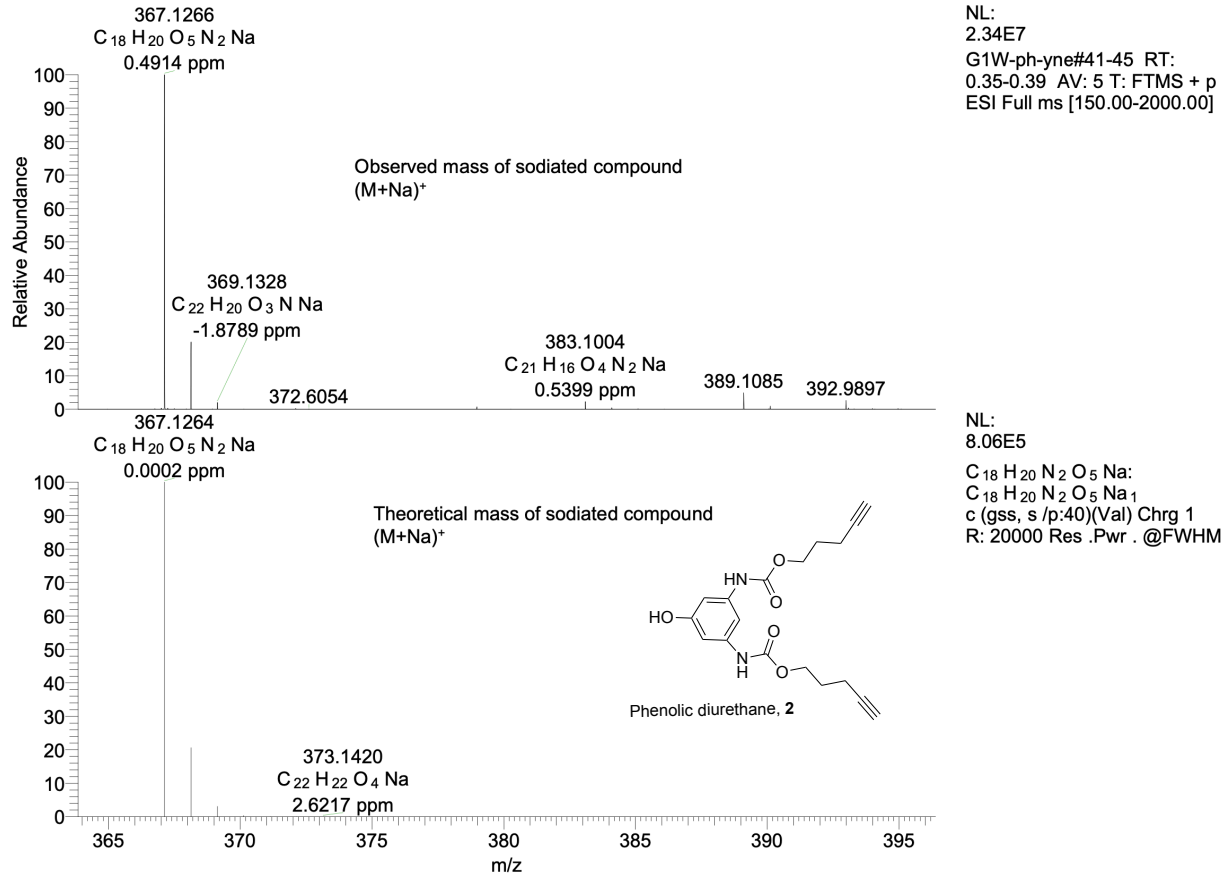


Figure S35. HRMS (ESI-LTQ-Orbitrap) spectrum of phenolic diurethane 2.

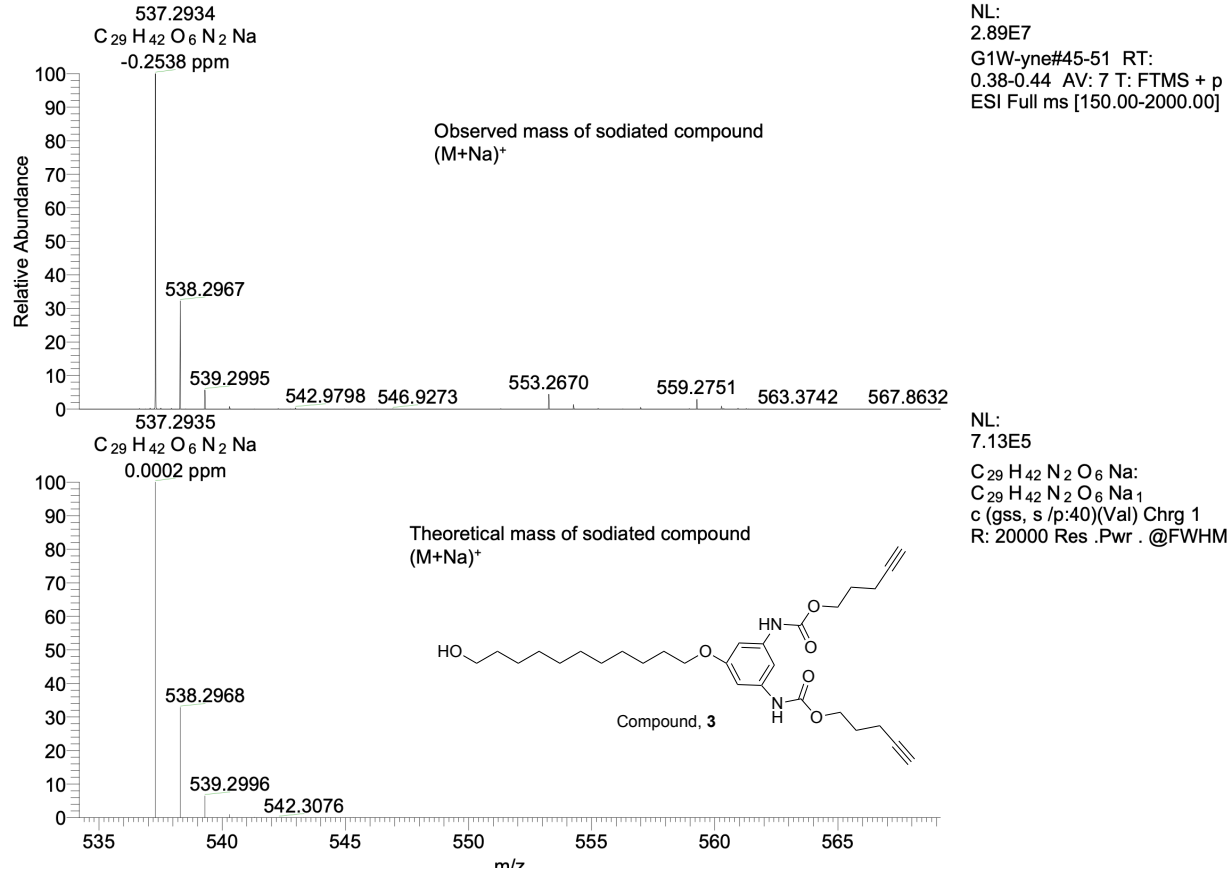


Figure S36. HRMS (ESI-LTQ-Orbitrap) spectrum of compound **3**.

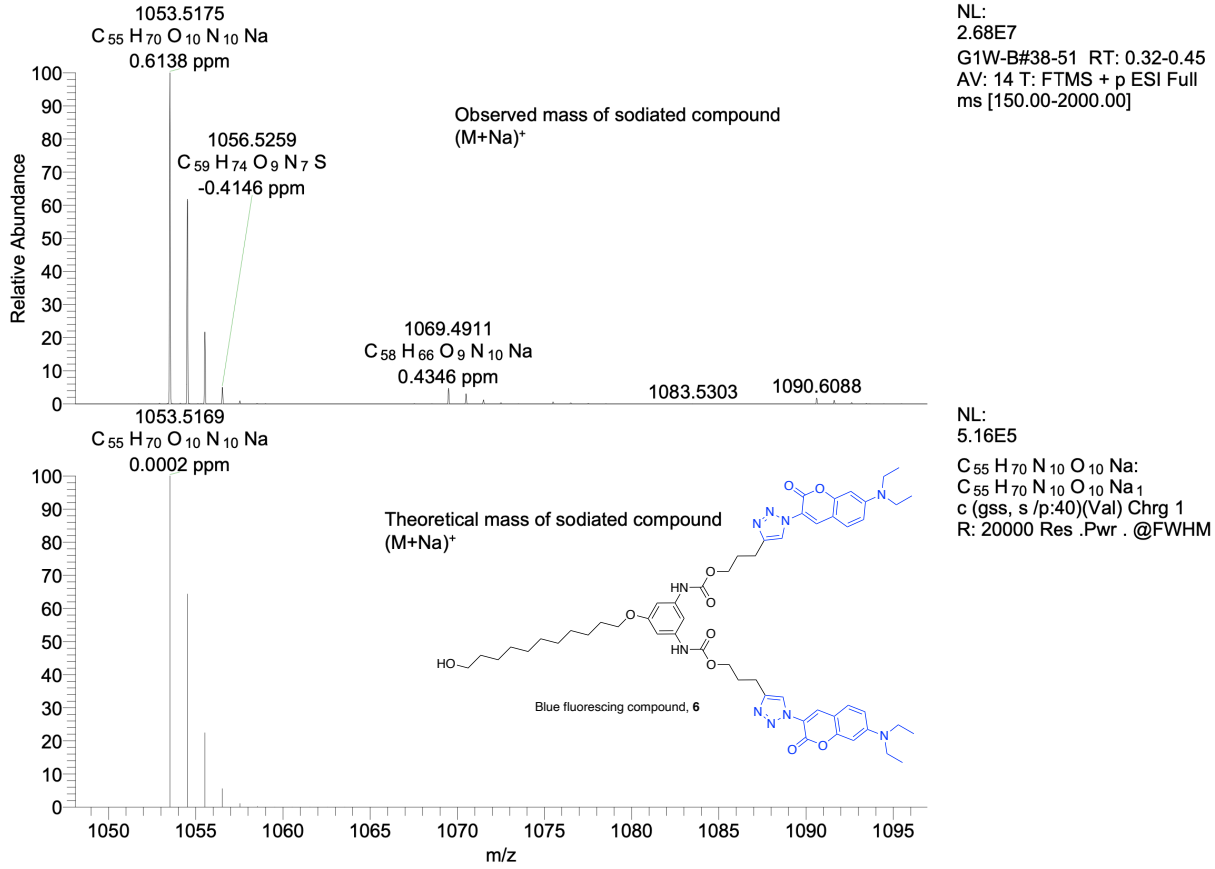


Figure S37. HRMS (ESI-LTQ-Orbitrap) blue fluorescing compound **6**.

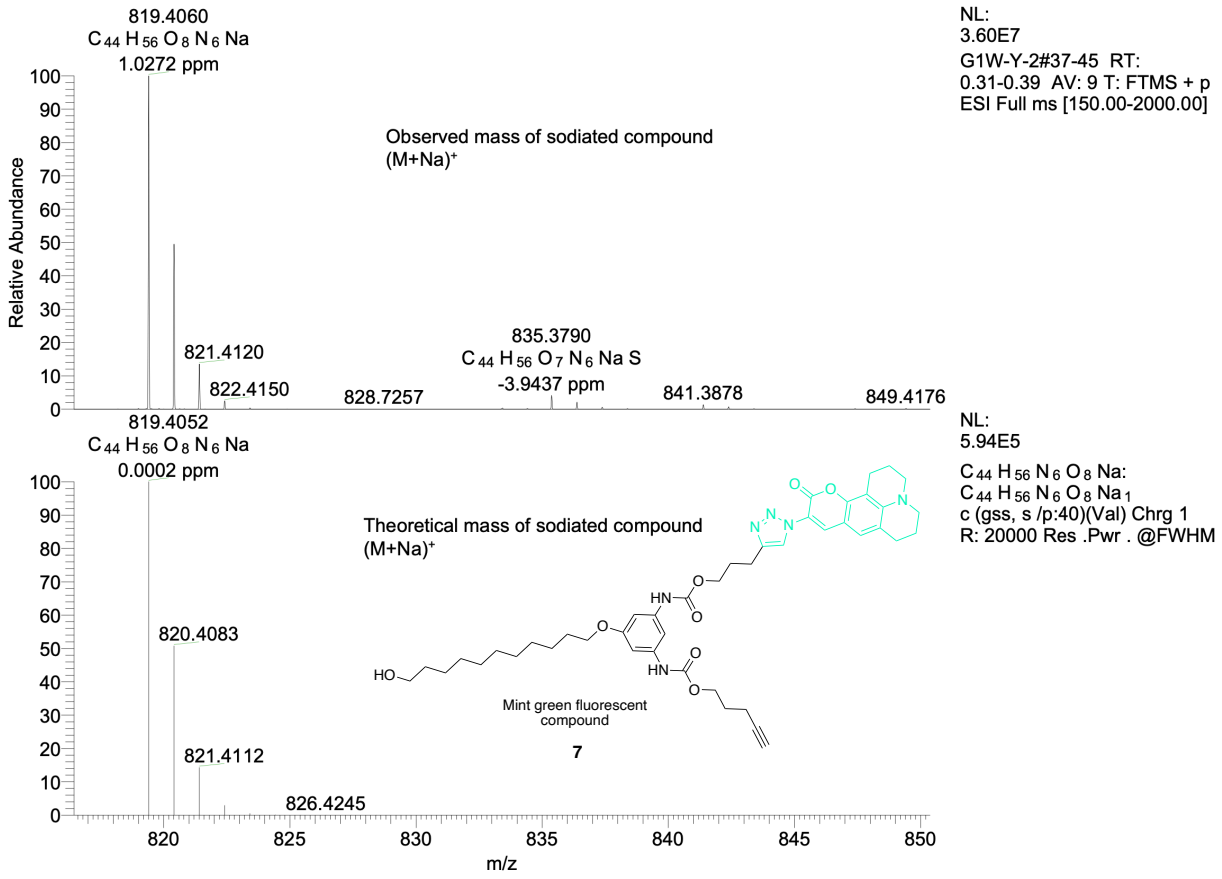


Figure S38. HRMS (ESI-LTQ-Orbitrap) spectrum of one-clicked mint green fluorescing compound **7**.

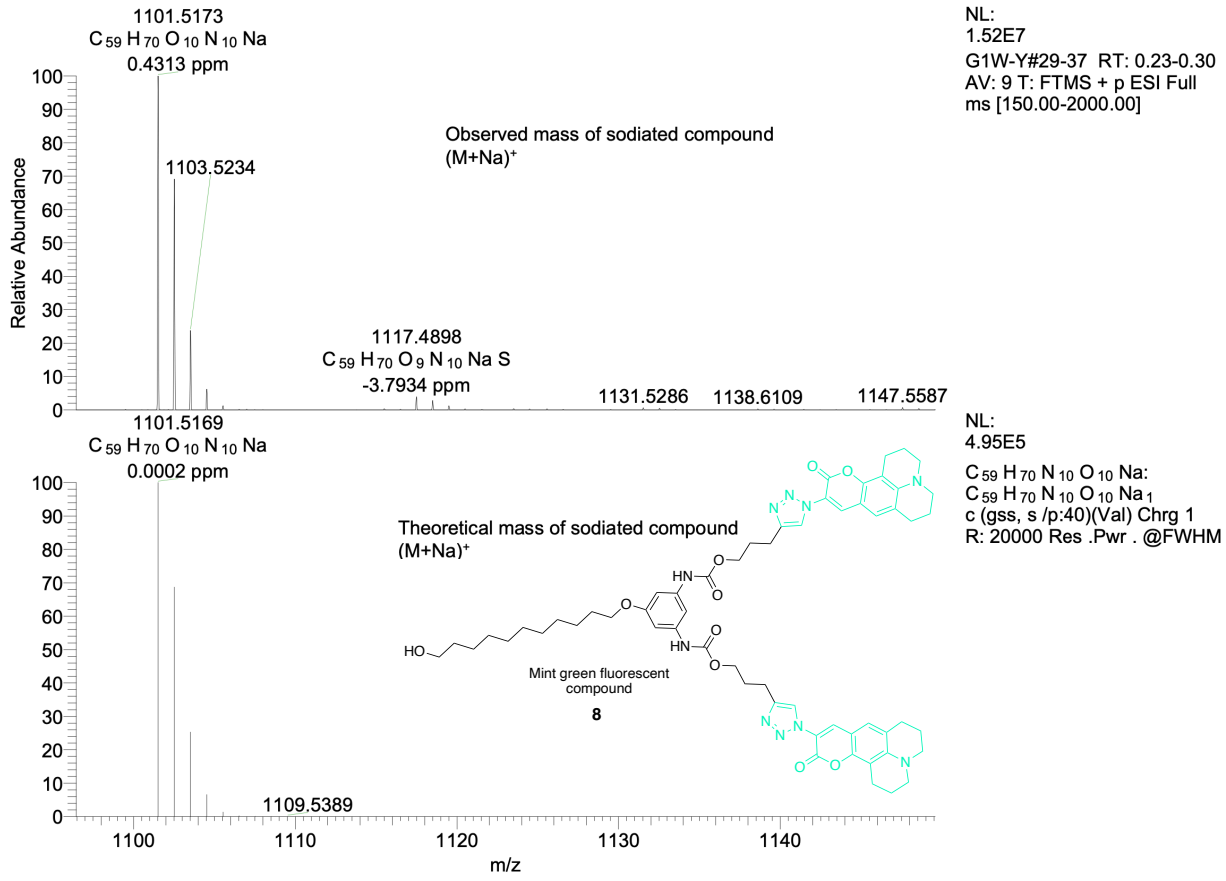


Figure S39. HRMS (ESI-LTQ-Orbitrap) spectrum of both-clicked mint green fluorescing compound **8**.

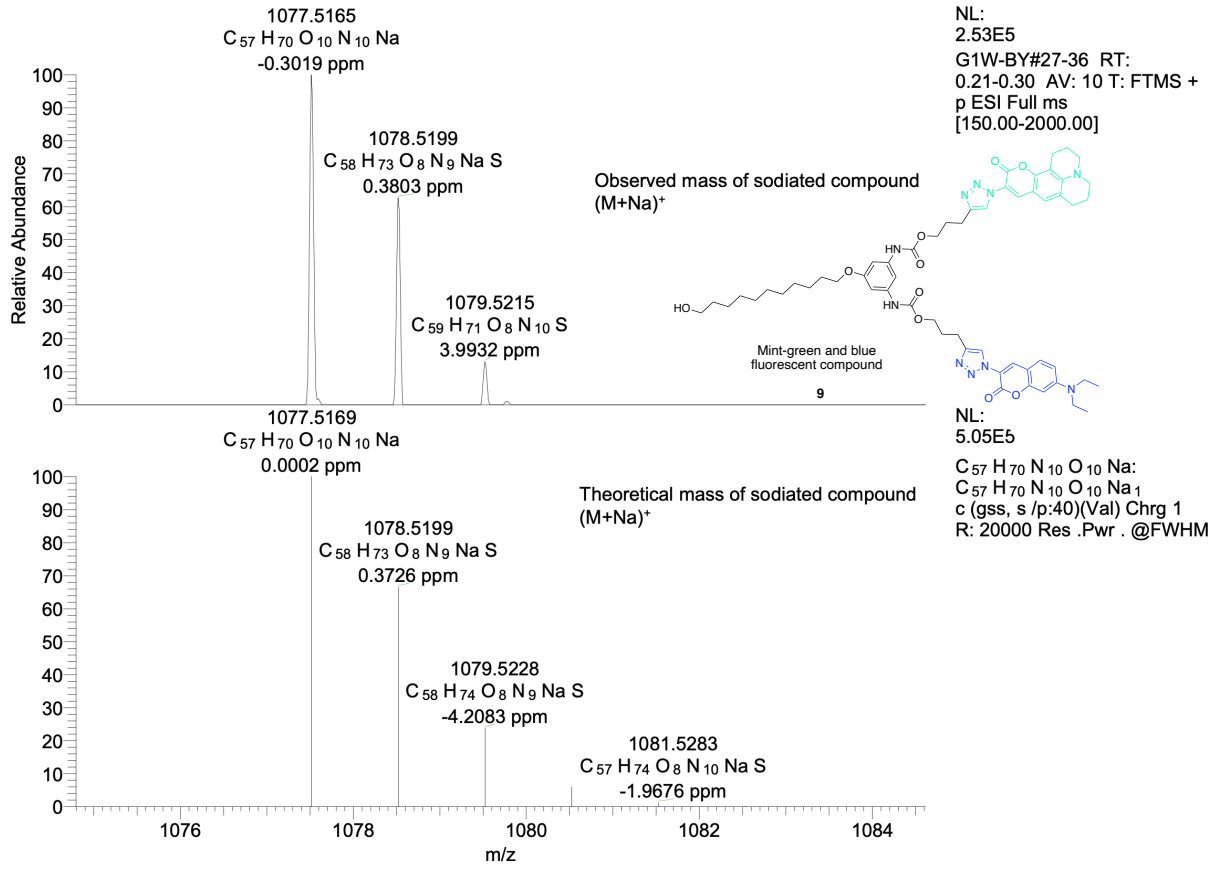


Figure S40. HRMS (ESI-LTQ-Orbitrap) spectrum of mint green and blue fluorescing compound **9**.

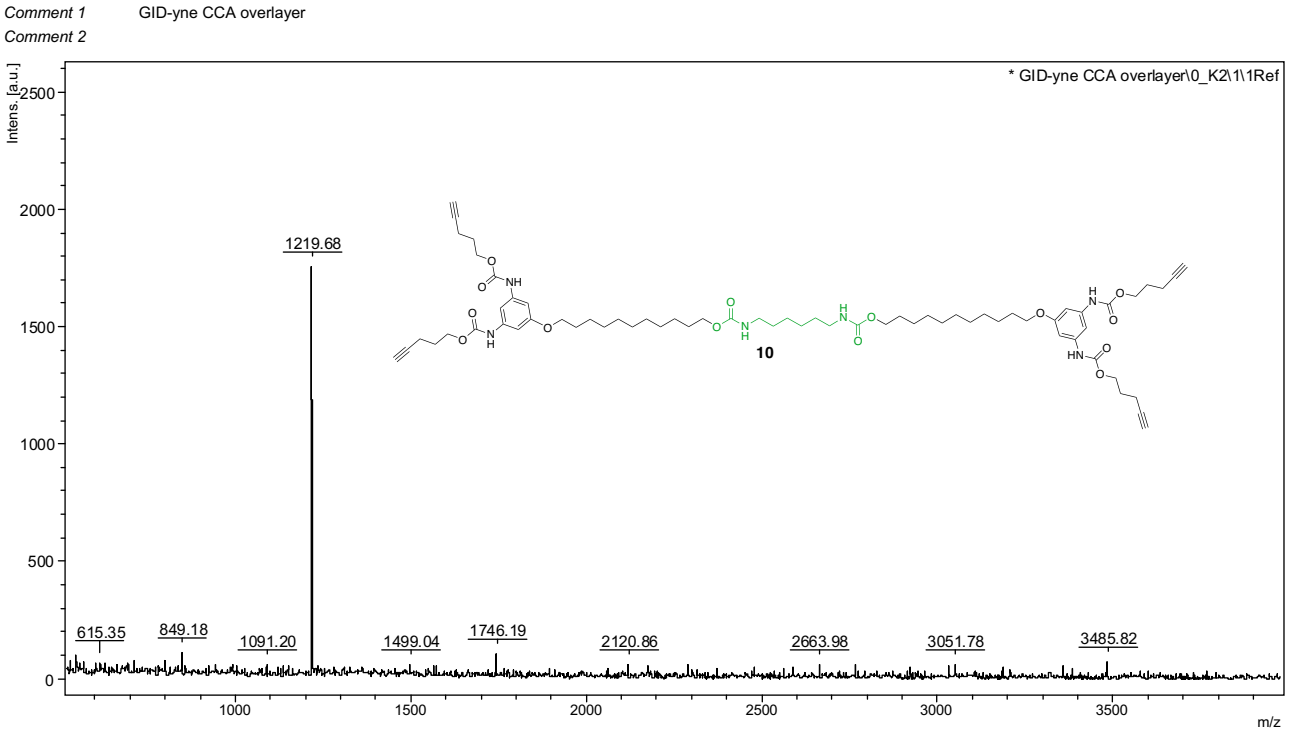


Figure S41. LRMS (MALDI-TOF-MS) of compound **10**.

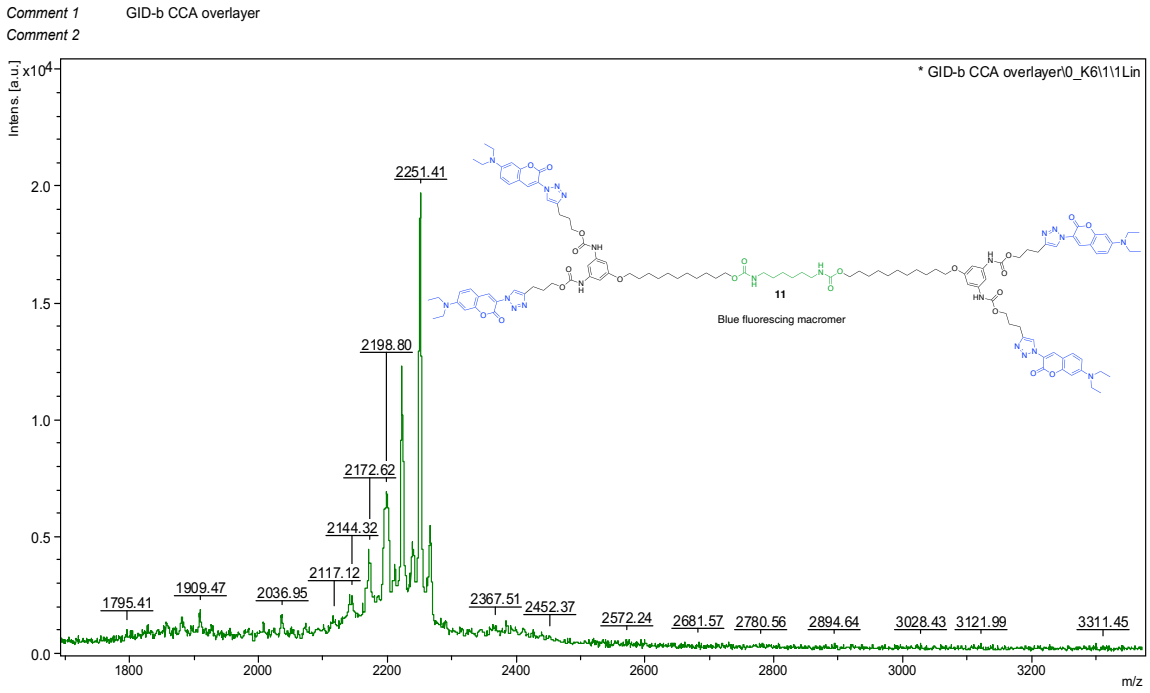


Figure S42. LRMS (MALDI-TOF-MS) of blue fluorescing dendrimer **11**.

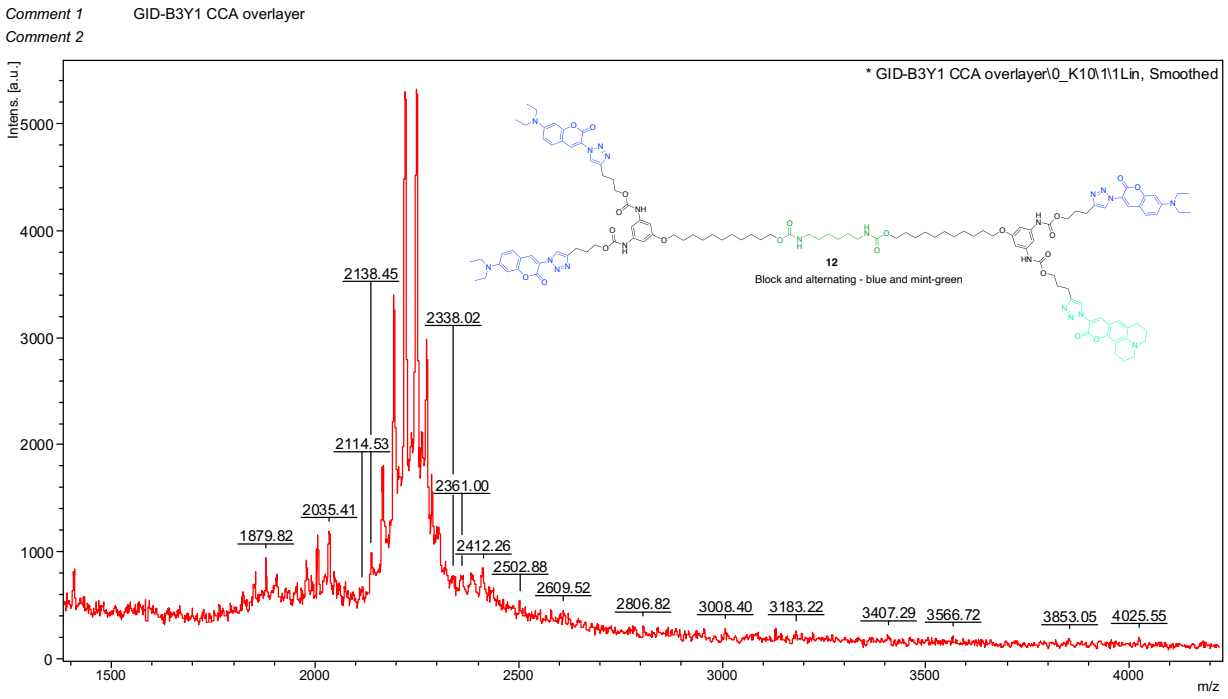


Figure S43. LRMS (MALDI-TOF-MS) of blue and mint green fluorescing dendrimer **12**.

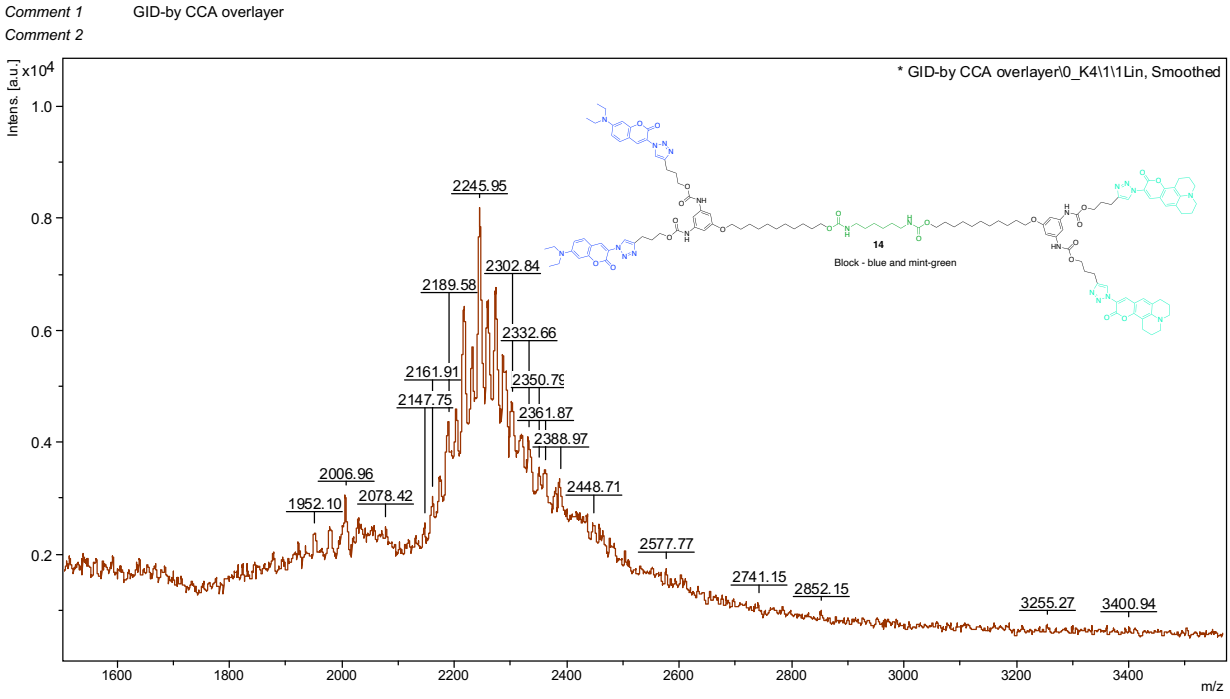


Figure S44. LRMS (MALDI-TOF-MS) of block blue and mint green fluorescing dendrimer **14**.

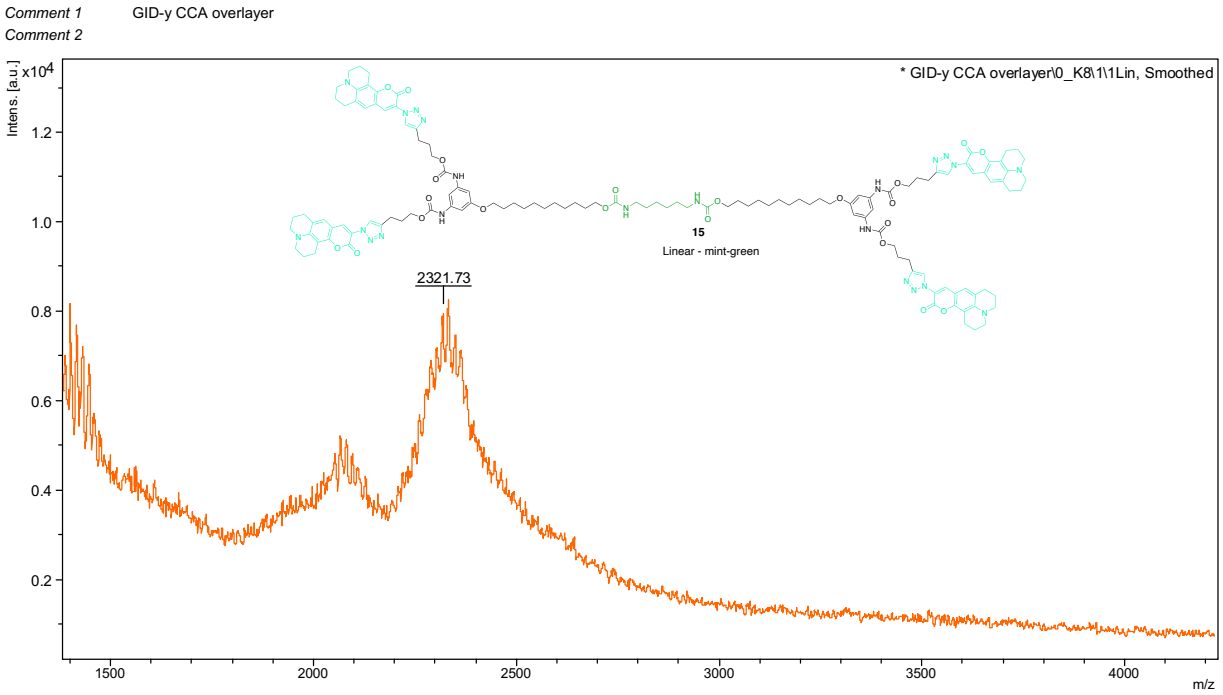
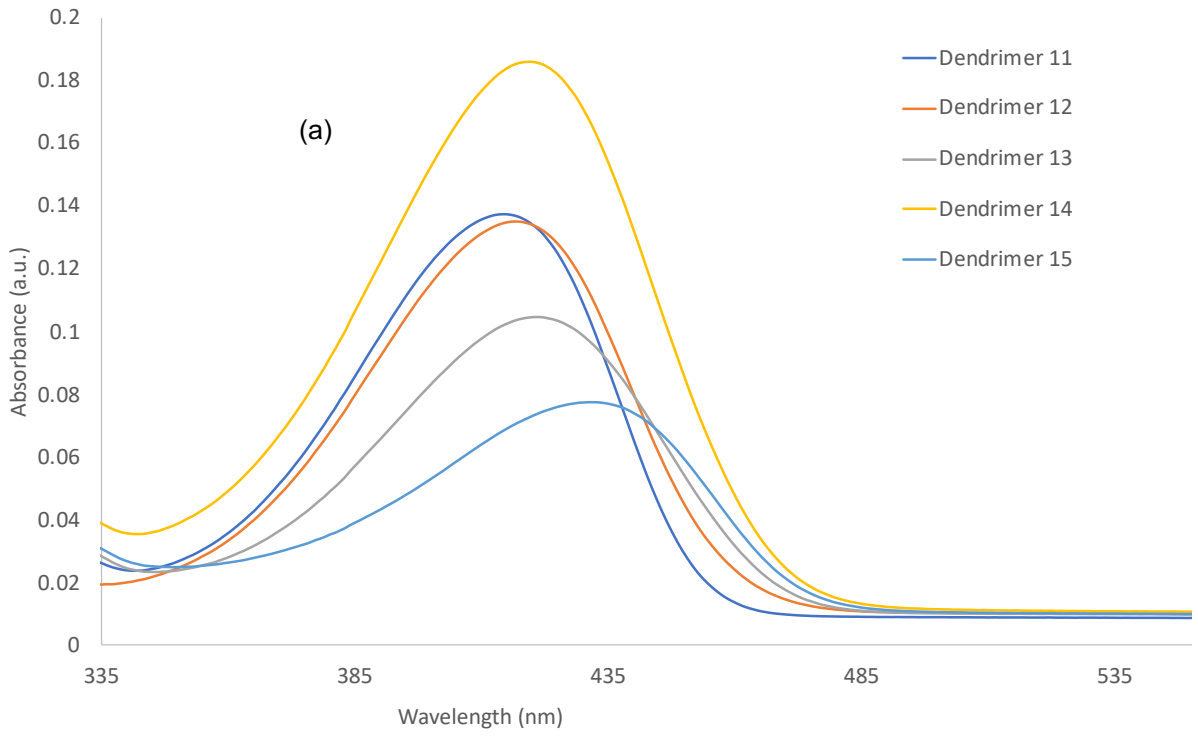


Figure S45. LRMS (MALDI-TOF-MS) of mint green fluorescing dendrimer **11**.

4. UV-Vis and fluorescence spectra of PUDs 11 – 15.



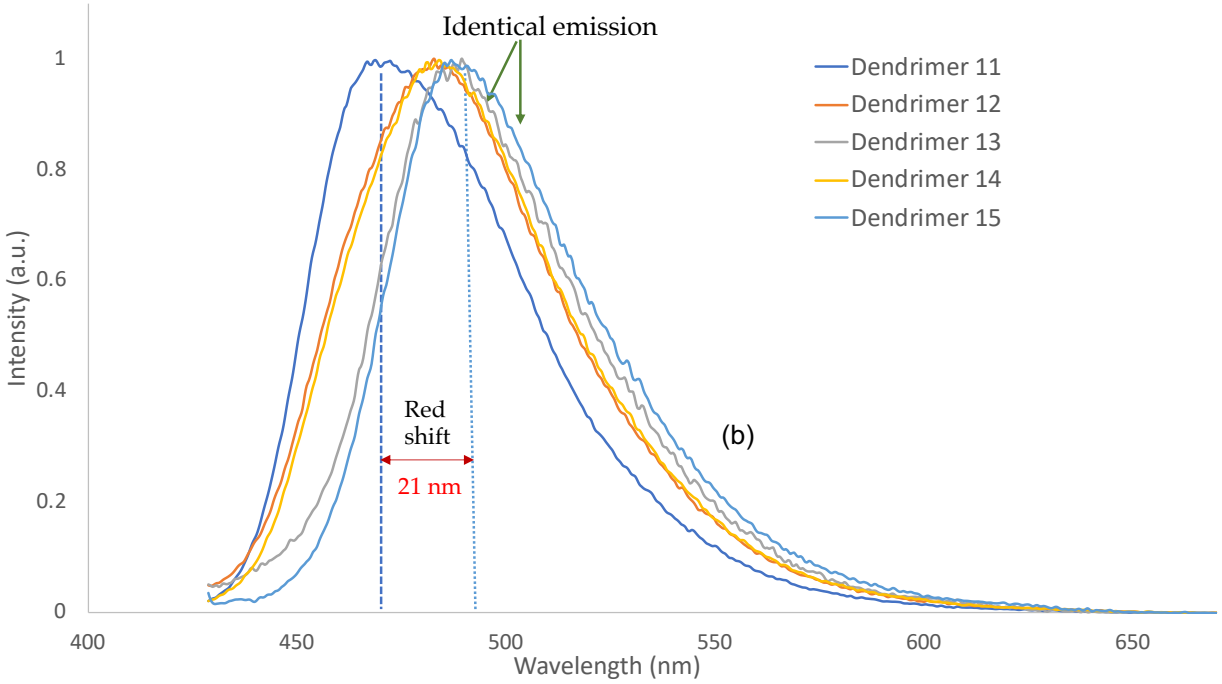


Figure S46. a) UV-vis absorption and (b) fluorescence emission spectra of PUDs **11** – **15**.

5. References

a. Poudel DP, Taylor RT. A Model for Late-Stage Modification of Polyurethane Dendrimers Using Thiol–Ene Click Chemistry. *ACS Omega*, 2021, **6**, 12375-12381.