Electronic Supplementary Information (ESI) for:

Squaraine rotaxane shuttle as a ratiometric deep-red optical chloride sensor

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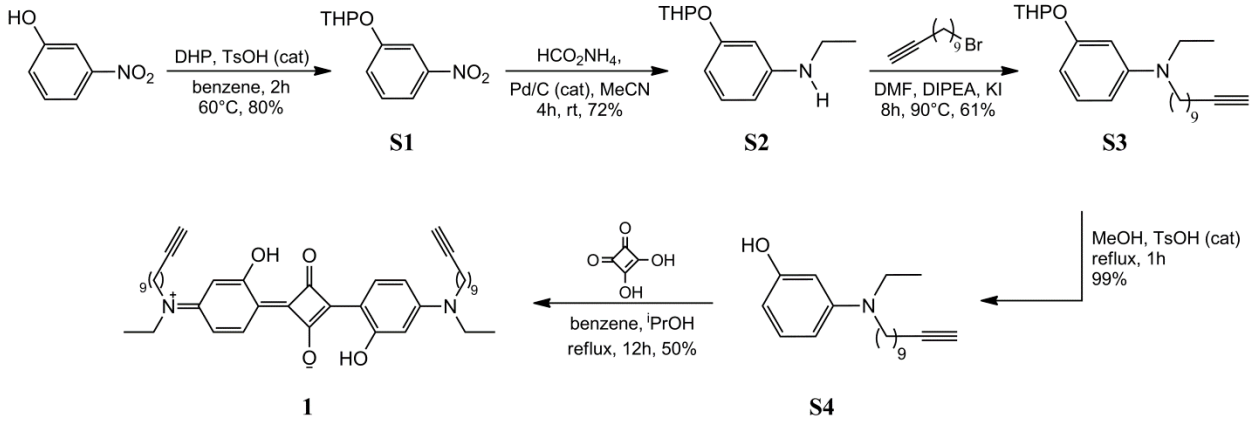
Contents

A. Synthesis



Scheme S1: Synthesis of SqOH **1**.

Synthesis of 2-(3-nitrophenoxy)tetrahydro-2*H*-pyran (S1)
Commercially available 3-nitrophenol was reacted with 3,4-dihydro-2*H*-pyran (DHP) following a previously published literature procedure.[S1]

Synthesis of *N*-ethyl-3-((tetrahydro-2*H*-pyran-2-yl)oxy)aniline (S2)[S2]
Compound **S1** (5.65 g, 25.3 mmol) was dissolved in MeCN (100 mL) and 10 wt% Pd/C catalyst (1.0 g, 0.94 mmol). Ammonium formate (24.1 g, 382 mmol) was slowly added to the reaction over 1 hour. The reaction was allowed to stir for an additional 3 hours, at which time all starting material had been consumed and minimal dialkylated product had formed. Pd/C catalyst was removed by filtrating the mixture over celite and the filtrate was concentrated under reduced pressure. The remaining residue was diluted with H_2O (50 mL) and extracted with chloroform (2x50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The remaining residue was purified with silica gel column chromatography with 15% EtOAc in hexanes as the eluent to yield **S2** (72% yield, 4.01 g, 18.1 mmol) as a clear viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.2 Hz, 1H), 6.45 (ddd, *J* = 8.1 Hz, *J* = 2.3 Hz, *J* = 0.9 Hz, 1H), 6.36 (t, *J* = 2.3 Hz, 1H), 6.28 (ddd, *J* = 8.1 Hz, *J* = 2.3 Hz, *J* = 0.8 Hz, 1H), 5.42 (t, *J* = 3.4 Hz, 1H), 3.93-4.00 (m, 1H), 3.62 (dtd, *J* = 11 Hz, *J* = 4.2 Hz, *J* = 1.2 Hz, 1H), 3.16 (q, *J* = 7.2 Hz, 2H), 1.99-2.08 (m, 1H), 1.84-1.89 (m, 2H), 1.56-1.75 (m, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 149.9, 129.9, 106.7, 105.2, 101.1, 96.3, 62.1, 38.5, 30.6, 25.4, 19.0, 14.9. HRMS (ESI-TOF) calculated for $C_{13}H_{20}NO_2$[M+H$^+$] 222.1489; found 222.1467.

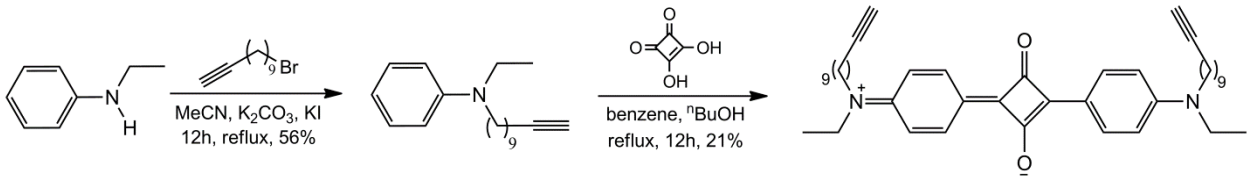
Synthesis of *N*-ethyl-3-((tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-(undec-10-yn-1-yl)aniline (S3)
Compound **S2** (403 mg, 1.82 mmol) was added to a solution containing anhydrous DMF (30 mL), 11-bromoundec-1-yne (494 mg, 2.13 mmol), *N*,*N*-diisopropyethylamine (0.8 mL), and potassium iodide (100 mg, 0.6 mmol) under argon. The reaction was heated to 90°C for 8 hours and its progress monitored via TLC. The reaction was allowed to cool to rt, and the DMF was evaporated under reduced pressure to yield a brown solid that was purified via column chromatography with 10% to 20% EtOAc in hexanes as eluent. Additional impurities were removed under high vacuum overnight to yield pure **S3** (61% yield, 415 mg, 1.12 mmol) as a clear viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.2 Hz, 1H), 6.36-6.39 (m, 2H), 6.32 (d, *J* = 9.1 Hz, 1H), 5.40 (t, *J* = 3.2 Hz, 1H), 3.97 (ddd, *J* = 12 Hz, *J* = 9.1 Hz, *J* = 3.5 Hz, 1H), 3.61 (dt *J* = 12 Hz, *J* = 3.5 Hz, 1H); 3.34 (q, *J* = 7.1 Hz, 2H), 3.23 (t, *J* = 7.9 Hz, 2H), 2.19 (td, *J* = 7.1 Hz, *J* = 2.6 Hz, 2H), 1.99-2.06 (m, 1H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.83-1.89 (m, 2H), 1.64-1.72 (m, 2H), 1.57-1.63 (m,3H), 1.54 (quin, *J* = 7.6 Hz, 2H), 1.40 (quin, *J* = 6.5 Hz, 2H), 1.27-1.37 (m, 8H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 149.5, 129.9, 105.9, 103.2, 100.7, 96.7, 85.0, 68.3, 62.4, 50.7, 45.2, 30.8, 29.7, 29.2, 28.9, 28.7, 27.8, 27.4, 25.5, 19.3, 18.6, 12.6; HRMS (ESI-TOF) calculated for $C_{24}H_{38}NO_2$ [M+H] 372.2897; found 372.2841.

Synthesis of 3-(ethyl(undec-10-yn-1-yl)amino)phenol (S4)

Compound **S3** (45 mg, 0.12 mmol) was dissolved in methanol (40 mL) containing toluenesulfonic acid (10 mg, 5.8 µmol) and heated to reflux for 1 h. The reaction was cooled and the product condensed under reduced pressure. The crude oil was redissolved in ethyl acetate (50 mL), which was then washed consecutively with aqueous sodium bicarbonate (10% w/v, 25 mL) and brine (25 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to yield **S4** (99% yield, 34 mg, 0.12 mmol) as a brown, viscous oil that was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (t, *J* = 8.1Hz, 1H), 6.26 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1H), 6.16 (t, *J* = 2.4 Hz, 1H), 6.11 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 3.33 (q, *J* = 6.9 Hz, 2H), 3.22 (t, *J* = 7.5 Hz, 2H), 2.20 (td, *J* = 6.9 Hz, *J* = 2.7 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.58 (quin, *J* = 7.2 Hz, 2H), 1.54 (quin, *J* = 6.9 Hz, 2H), 1.36-1.45 (m, 2H), 1.26-1.36 (m, 8H), 1.15 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 149.8, 130.3, 104.9, 102.4, 98.8, 85.0, 68.3, 50.7, 45.2, 29.7, 29.6, 29.2, 28.9, 28.7, 27.7, 27.4, 18.6, 12.5; HRMS (ESI-TOF) calculated for $C_{19}H_{30}NO$ [M+H] 288.2322; found 288.2312.

Synthesis of SqOH 1

Compound **S4** (120 mg, 0.418 mmol) and squaric acid (23.9 mg, 0.210 mmol) were dissolved in anhydrous benzene (30 mL) and isopropanol and brought to reflux. A Dean-Stark condenser was used for the azeotropic removal of water as the reaction progressed over 12 hours. The solvent was evaporated under reduced pressure and the crude solid was purified with column chromatrography with silica gel and 5% EtOAc in chloroform as eluent to yield **1** (49% yield, 67.2 mg, 0.103 mmol) as a blue solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.38 (s, 2H), 8.03 (cis rotamer, d, *J* = 9.2 Hz, 2H), 7.88 (trans rotamer, d, *J* = 9.2 Hz, 2H), 6.32 (dd, *J* = 2.4 Hz, *J* = 9.2 Hz, 2H), 6.12 (trans rotamer, d, *J* = 2.4 Hz, 2H), 6.11 (cis rotamer, d, *J* = 2.6 Hz, 2H), 3.47 (q, *J* = 7.2 Hz, 4H), 3.36 (t, *J* = 8.0 Hz, 4H), 2.19 (td, *J* = 2.6 Hz, *J* = 7.2 Hz, 4H), 1.95 (t, *J* = 2.6 Hz, 2H), 1.64 (quin, *J* = 8.2 Hz, 4H), 1.53 (quin, *J* = 7.2 Hz, 4H), 1.37-1.43 (m, 4H), 1.28-1.36 (m, 16H), 1.24 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.2, 172.4, 164.6, 156.4, 132.7, 107.7, 98.6, 84.9, 68.3, 51.2, 46.1, 29.6, 29.5, 29.2, 28.9, 28.6, 28.1, 27.2, 18.6, 13.0; HRMS (ESI-TOF) calculated for $C_{42}H_{57}N_2O_4$ [M+H] 653.4313; found 653.4319.



S5 **2**

Scheme S2: Synthesis of Sq **2**.

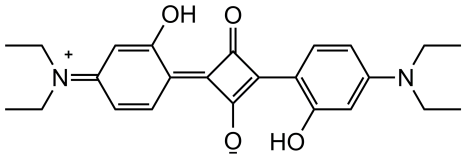
Synthesis of *N*-ethyl-*N*-(undec-10-yn-1-yl)aniline (S5)

A mixture of 11-bromo-1-undecyne (558 mg, 2.41 mmol), *N*-ethyl aniline (606 µL, 4.83 mmol), potassium carbonate (668 mg, 4.83 mmol), and potassium iodide (10 mg, 0.06 mmol) in acetonitrile (10 mL) was refluxed for 24 hours. Evaporation under reduced pressure yielded a brown viscous oil. The oil was diluted in ethyl acetate and the resulting solution was washed with brine (10 mL). The organic layer was isolated and the aqueous layer was extracted with ethyl acetate (3x30 mL). The organic fractions were combined and dried over $MgSO_4$. Filtration followed by evaporation under reduced pressure provided crude material that was further purified by column chromatography with silica gel and 1% EtOAc in hexanes as eluent to yield **S5** (56% yield, 368 mg, 1.36 mmol) as a clear, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.25 (m, 2H), 6.67-6.70 (m, 2H), 6.62-6.67 (m, 1H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.25 (m, 2H), 2.21 (td, *J* = 7.1 Hz, *J* = 2.6 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.60 (quin, *J* = 7.4 Hz, 2H), 1.55 (quin, *J* = 7.6 Hz, 2H), 1.38-1.45 (m, 2H), 1.30-1.37 (m, 8H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 129.4, 115.4, 111.9, 84.9, 68.3, 50.6, 45.1, 29.7, 29.2, 28.9, 28.7, 27.7, 27.4, 18.6, 12.5; HRMS (ESI-TOF) calculated for $C_{19}H_{30}N$ [M+] 272.2373; found 272.2394.

Synthesis of Sq 2

Compound **S5** (385 mg, 1.41 mmol) and squaric acid (85.0 mg, 0.745 mmol) were dissolved in anhydrous benzene (30 mL) and isopropanol and brought to reflux. A Dean-Stark condenser was used for the

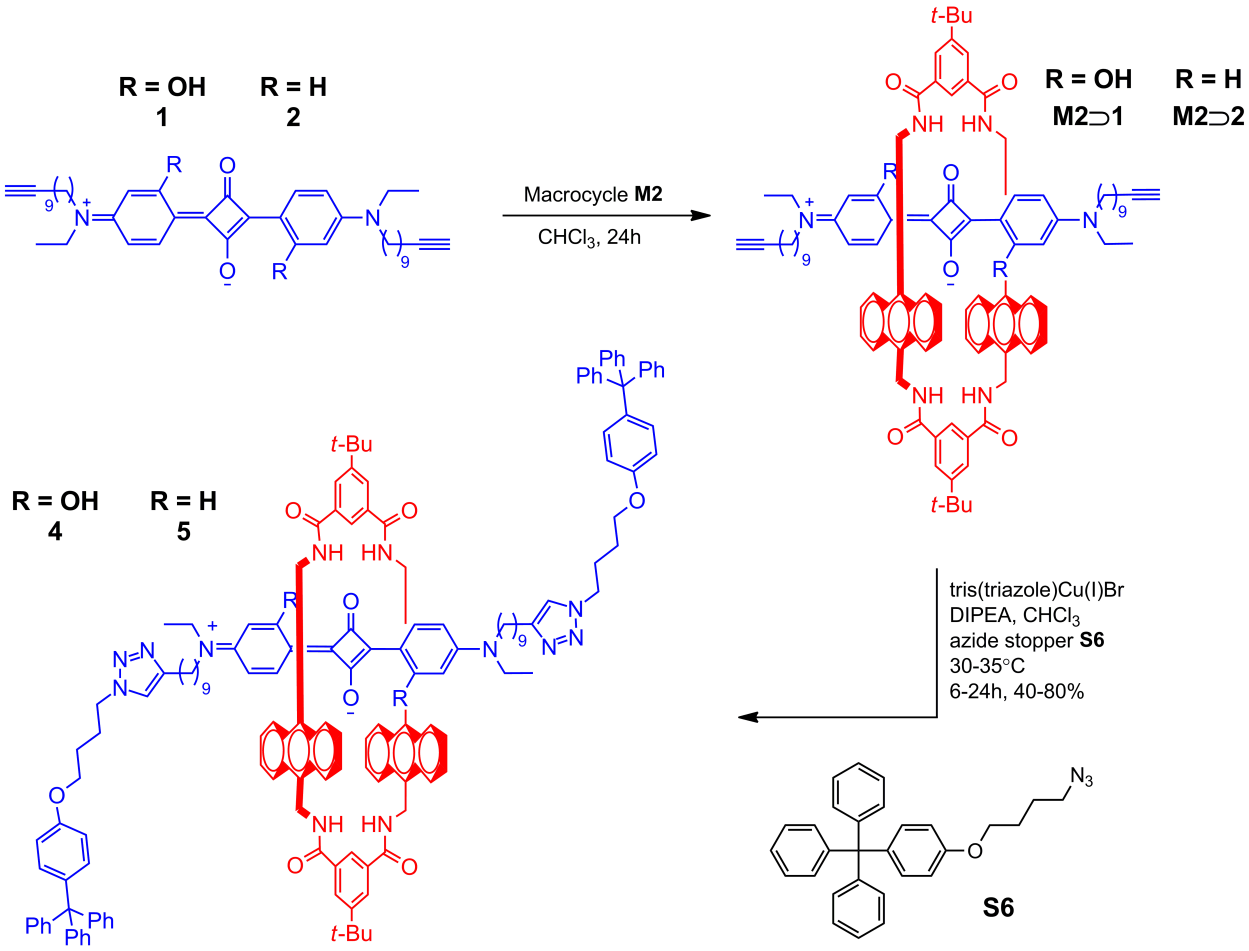
azeotropic removal of water as the reaction progressed over 12 hours. The solvent was evaporated under reduced pressure and the crude solid was purified by column chromatography with silica gel and 5% EtOAc in chloroform as eluent to yield **2** (21% yield, 93.0 mg, 0.150 mmol) as a blue solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.4 Hz, 4H), 6.75 (d, *J* = 9.4 Hz, 4H), 3.55 (dd, *J* = 14.2 Hz, *J* = 7.0 Hz, 4H), 3.44 (t, *J* = 7.9 Hz, 4H), 2.22 (td, *J* = 14.2 Hz, *J* = 7.0 Hz, *J* = 2.6 Hz, 4H), 1.98 (t, *J* = 2.7 Hz, 2H), 1.65-1.26 (m, 28H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.4, 183.7, 153.4, 133.3, 119.7, 112.4, 84.9, 68.4, 51.1, 46.0, 29.7, 29.6, 29.2, 28.9, 28.7, 27.9, 27.2, 18.6, 12.8; HRMS (ESI-TOF) calculated for $C_{42}H_{57}N_2O_2$ [M+H] 621.4422; found 621.4415.



3

Synthesis of SqOH 3

The synthesis of this SqOH derivative has been reported elsewhere and was characterized with ^{1}H NMR, MS, and UV/Vis spectroscopy.[S3]



Scheme S3: Synthesis of squaraine rotaxane derivatives **4** and **5**.

Synthesis of pseudorotaxane M2⊃1

Squaraine **1** (22.3 mg, 35.9 μmol) was combined with macrocycle **M2** (43.2 mg, 51.1 μmol) in chloroform (10 mL) and associated at 30°C for 24 h. Pseudorotaxane was isolated with column chromatography with silica gel and 10% EtOAc in chloroform as eluent to yield **M2⊃1** (31% yield, 16.5 mg, 11.3 μmol) as a

green solid. The complex does slowly dissociate to equilibrium, and therefore, should be used immediately for characterization/synthesis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 2H), 9.13 (t, *J* = 1.6 Hz, 2H), 8.51 (d, *J* = 1.4 Hz, 4H), 8.01 (d, *J* = 9.0 Hz, 4H), 7.95 (d, *J* = 5.4 Hz, 4H), 7.59 (d, *J* = 9.0 Hz, 4H), 7.04 (ddd, *J* = 8.8 Hz, *J* = 6.6 Hz, *J* = 0.8 Hz, 4H), 6.66 (d , *J* = 9.2 Hz, 2H), 6.55 (ddd, *J* = 8.6 Hz, *J* = 6.4 Hz, *J* = 0.8 Hz, 4H), 5.57 (d, *J* = 8.6 Hz, 2H), 5.49 (d, *J* = 2.2 Hz, 2H), 5.38 (dd, *J* = 15 Hz, *J* = 6.0 Hz, 4H), 5.05 (dd, *J* = 14 Hz, *J* = 1.0 Hz, 4H), 3.45 (q, *J* = 7.4 Hz, 4H), 3.36 (t, *J* = 8.0 Hz, 4H), 2.20 (td, *J* = 7.1 Hz, *J* = 2.6 Hz, 4H), 1.95 (t, *J* = 2.6 Hz, 2H), 1.67-1.74 (m, 4H), 1.58-1.64 (m, 4H), 1.55 (s, 18H), 1.20-1.50 (m, 30H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.7, 167.1, 163.6, 163.2, 155.9, 153.3, 133.5, 132.3, 130.8, 130.7, 129.1, 128.6, 126.8, 125.8, 123.8, 123.4, 122.2, 106.8, 106.3, 105.2, 99.1, 84.9, 68.4, 51.3, 46.1, 38.7, 35.7, 31.7, 29.9, 29.8, 29.7, 29.2, 28.9, 28.6, 27.3, 18.6; HRMS (ESI-TOF) calculated for $C_{98}H_{109}N_6O_8$ [M+H] 1497.8301; found 1497.8313.

Synthesis of pseudorotaxane M2⊃2

Squaraine **2** (14 mg, 23 μmol) was combined with macrocycle **M2** (23 mg, 23 μmol) in chloroform (10 mL) and associated at 30°C for 24 h. Pseudorotaxane was isolated with column chromatrography with silica gel and 10% EtOAc in chloroform as eluent to yield **M2⊃2** (44% yield, 14.9 mg, 10.2 μmol) as a green solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.39 (t, *J* = 1.5 Hz, 2H), 8.53 (d, *J* = 1.5 Hz, 4H), 8.26 (t, *J* = 4.4 Hz, 4H), 7.73 (dd, *J* = 6.8 Hz, *J* = 3.2 Hz, 8H), 6.98 (d, *J* = 9.1 Hz, 4H), 6.67 (dd, *J* = 6.7 Hz, *J* = 2.9 Hz, 8H), 6.07 (d, *J* = 9.4 Hz, 4H), 5.20 (d, *J* = 4.1 Hz, 8H), 3.50 (q, *J* = 7.0 Hz, 4H), 3.39 (t, *J* = 7.9 Hz, 4H), 2.20 (td, *J* = 7.1 Hz, *J* = 2.6 Hz, 4H), 1.95 (t, *J* = 2.6 Hz, 2H), 1.71 (quin, *J* = 7.1 Hz, 4H), 1.55 (s, 18H), 1.34-1.46 (m, 24H), 1.32 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.3, 178.9, 167.4, 153.1, 153.0, 133.6, 133.2, 130.6, 129.1, 128.7, 125.9, 124.2, 123.0, 117.1, 111.5, 84.9, 68.4, 51.2, 45.6, 38.2, 35.6, 31.7, 29.8, 29.7, 29.2, 28.9, 28.6, 28.3, 27.3, 18.6, 13.1; HRMS (ESI-TOF) calculated for $C_{98}H_{109}N_6O_6$ [M+] 1465.8403; found 1465.8411.

Synthesis of squaraine rotaxane 4

Pseudorotaxane **M2⊃1** (15.8 mg, 10.8 μmol) was combined with **S6** (18.9 mg, 43.6 μmol) in chloroform (5 mL). *N*,*N*-Diisopropyethylamine (2 drops) and organic soluble tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine copper(I)bromide[S4] (4.5 mg, 7.0 μmol) were added and the reaction was stirred at 30°C for 6 h. The reaction was washed with an aqueous saturated EDTA solution and the organic layer isolated. Concentration under reduced pressure provided crude product that was further purified by column chromatography with silica gel and 20% to 30% EtOAc in chloroform as eluent to give **4** (65% yield, 10.6 mg, 4.48 μmol) as a green solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.81 (s, 2H), 9.13 (br s, 2H), 8.51 (br s, 4H), 8.01 (d, *J* = 9.1 Hz, 4H), 7.95 (d, *J* = 5.9 Hz, 4H), 7.58 (d, *J* = 9.1 Hz, 4H), 7.16-7.26 (m, 32H), 7.10 (d, *J* = 9.1 Hz, 4H), 7.04 (m, 4H), 6.74 (d, *J* = 8.8 Hz, 4H), 6.65 (d, *J* = 9.1 Hz, 2H), 6.55 (m, 4H), 5.57 (d, *J* = 8.5 Hz, 2H), 5.49 (s, 2H), 5.38 (dd, *J* = 15 Hz, *J* = 6.2 Hz, 4H), 5.05 (d, *J* = 15 Hz, 4H), 4.40 (t, *J* = 7.3 Hz, 4H), 3.95 (t, *J* = 5.8 Hz, 4H), 3.45 (q, *J* = 8.0 Hz, 4H), 3.36 (t, *J* = 9.4 Hz, 4H), 2.72 (t, *J* = 8.2 Hz, 4H), 2.09 (quin, *J* = 7.9 Hz, 4H), 1.78 (quin, *J* = 7.1 Hz, 4H), 1.64-1.73 (m, 8H), 1.54 (s, 18H), 1.36-1.45 (m, 20H), 1.30 (t, *J* = 7.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.7, 167.1, 163.7, 163.2, 156.8, 155.9, 153.3, 147.2, 139.4, 133.5, 132.4, 132.3, 131.3, 130.8, 130.7, 129.1, 128.7, 127.6, 126.9, 126.1, 125.8, 123.8, 123.4, 122.3, 113.3, 106.8, 106.3, 99.1, 66.9, 64.5, 51.2, 50.9, 50.2, 46.1, 38.7, 35.6, 31.7, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.5, 27.3, 26.5, 26.1, 25.8, 22.9; HRMS (ESI-TOF) calculated for $C_{156}H_{162}N_{12}O_{10}Na$ [M+Na] 2386.2429; found 2387.2434.

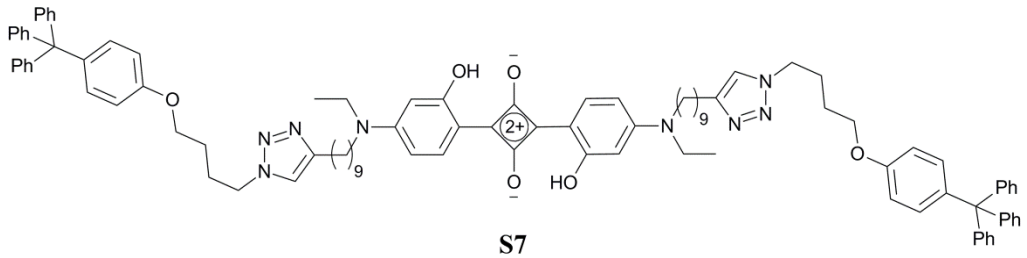
Synthesis of squaraine rotaxane 5

Pseudorotaxane **M2⊃2** (19.0 mg, 13.0 μmol) was combined with **S6** (21.1 mg, 48.7 μmol) in chloroform (5 mL). *N*,*N*-diisopropylethylamine (2 drops) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine copper(I)bromide (2.3 mg, 3.4 μmol) were added and the reaction was stirred at 35°C for 16 h. The reaction was washed with an aqueous EDTA solution (saturated) and the organic layer isolated. Concentration under reduced pressure provided crude product that was further purified by column chromatography with silica gel and 20% to 30% EtOAc in chloroform as eluent to give **5** (70% yield, 21.2 mg, 9.08 μmol) as a green solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (t, *J* = 1.4 Hz, 2H), 8.54 (d, *J* = 1.2 Hz, 4H), 8.31 (t, *J* = 4.4 Hz, 4H), 7.75 (dd, *J* = 7.0 Hz, *J* = 3.4 Hz, 8H), 7.32 (s, 2H), 7.16-7.26 (m, 30H), 7.10 (d, *J* = 9.0 Hz, 4H), 6.99 (d, *J* = 9.0 Hz, 4H), 6.73 (d, *J* = 9.0 Hz, 4H), 6.68 (dd, *J* = 6.8 Hz, *J* = 3.0 Hz, 8H), 6.07 (d, *J* = 9.0 Hz, 4H), 5.23 (d, *J* = 3.0 Hz, 8H), 4.40 (t, *J* = 7.2 Hz, 4H), 3.94 (t, *J* = 6.0 Hz, 4H), 3.50 (q, *J* = 6.6 Hz, 4H), 3.39 (t, *J* = 7.4 Hz, 4H), 2.74 (s, 4H), 2.09 (quin, *J* = 7.6 Hz, 4H), 1.78 (quin, *J* =

6.0 Hz, 4H), 1.70 (m, 8H), 1.55 (s, 18H), 1.37-1.45 (m, 20H), 1.32 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.9, 167.4, 156.8, 153.1, 147.2, 139.4, 133.6, 133.2, 132.4, 131.3, 130.7, 129.2, 128.8, 127.6, 126.1, 126.0, 124.2, 123.0, 117.1, 113.3, 66.9, 64.5, 51.2, 50.2, 38.3, 35.6, 31.7, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 28.3, 27.5, 27.3, 26.5, 25.7, 13.1; HRMS (ESI-TOF) calculated for $C_{156}H_{162}N_{12}O_8$ $[M+2Na]^{2+}$ 1188.6212; found 1188.6199.

Synthesis of trityl azide stopper (S6)

4-Tritylphenol (6.24 g, 18.5 mmol) was combined with 1,4-dibromobutane (7.90 g, 36.6 mmol) and K_2CO_3 (4.03 g, 29.2 mmol) in DMF (50 mL). The reaction was heated to 50°C and stirred overnight. The reaction was cooled to room temperature and filtered. The precipitate was washed with EtOAc (300 mL) and the filtrate was collected. Water (300 mL) was added to the filtrate and the product was extracted with EtOAc (3 x 100 mL). The organic layers were combined, washed with brine (2 x 100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting white solid was used immediately without further purification. This solid was dissolved in DMSO (100 mL) containing NaN_3 (5.0 g, 77 mmol). The reaction mixture was stirred at 60°C for 12 h, at which time TLC indicated complete consumption of the bromide precursor. The reaction cooled to rt, then quenched with water (200 mL) and filtered. The filtrate was extracted with EtOAc (3 x 100 mL) and the organic layers were combined, washed with brine (2 x 100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting crude solid was purified by column chromatography with silica gel and chloroform as eluent to give **S6** (60% yield, 4.77 g, 11.0 mmol) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.30 (m, 15H), 7.15 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 4.00 (t, *J* = 5.9 Hz, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 1.87-1.92 (m, 2H), 1.79-1.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 147.2, 139.2, 132.4, 131.3, 127.6, 126.0, 113.4, 67.2, 64.5, 51.4, 26.7, 26.0; HRMS (ESI-TOF) calculated for $C_{29}H_{27}N_3ONa$ [M+Na] 456.2046; found 456.2026.



S7

Synthesis of trityl capped SqOH (S7)

Squaraine **1** (20.2 mg, 32.5 μmol) was combined with **S6** (35 mg, 81 μmol) in chloroform (5 mL). *N*,*N*-diisopropyl-ethylamine (2 drops) and organic soluble tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine copper(I) bromide (6.0 mg, 8.9 μmol) were added and the reaction was stirred at 32°C for 12 h. The reaction was washed with an aqueous saturated EDTA solution (5 mL) and the organic layer isolated. Concentration under reduced pressure provided crude product that was further purified by column chromatography with silica gel and 20% to 30% EtOAc in chloroform as eluent to give **S7** (66% yield, 32.1 mg, 21.6 μmol) as a blue solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.09 (trans rotamer, s, 2H), 11.38 (cis rotamer, s, 2H), 8.03 (cis rotamer, d, *J* = 10.2 Hz, 2H), 7.88 (trans rotamer, d, *J* = 9.0 Hz, 2H), 7.34 (s, 2H), 7.17-7.27 (m, 30H), 7.10 (d, *J* = 9.6 Hz, 4H), 6.74 (d, *J* = 9.0 Hz, 4H), 6.32 (d, *J* = 9.6 Hz, 2H), 6.12 (s, 2H), 4.41 (t, *J* = 7.2 Hz, 4H), 3.95 (t, *J* = 5.4 Hz, 4H), 3.46 (q, *J* = 6.6 Hz, 4H), 3.35 (t, *J* = 7.2 Hz, 4H), 2.10 (quin, *J* = 7.8 Hz, 4H), 1.79 (quin, *J* = 6.6 Hz, 4H), 1.67 (quin, *J* = 7.8 Hz, 4H), 1.60-1.66 (m, 4H), 1.26-1.38 (m, 18H), 1.23 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.0, 172.0, 164.4, 156.6, 147.0, 139.1, 132.4, 132.2, 131.1, 127.4, 125.8, 113.1, 109.8, 107.5, 98.4, 66.8, 64.3, 51.0, 45.9, 29.7, 29.4, 29.3, 29.2, 29.1, 27.8, 27.3, 26.9, 26.2, 25.6, 12.8. HRMS (ESI-TOF) calculated for $C_{100}H_{111}N_8O_6$ [M+H] 1519.8621; found 1519.8638.

B. Photophysical Properties

Optical spectra were acquired using a Perkin Elmer Lambda 25 UV-Vis spectrometer and a Horiba Scientific Fluoromax-4 spectrofluorometer. Spectrophotometric grade solvents were purchased from commercial sources and used without further purification. All measurements were made at 25°C unless stated otherwise. Bis[4-(dimethylamino)phenyl]squaraine (Φ_f = 0.70 in chloroform) was used as a standard for quantum yield measurements.[S5]

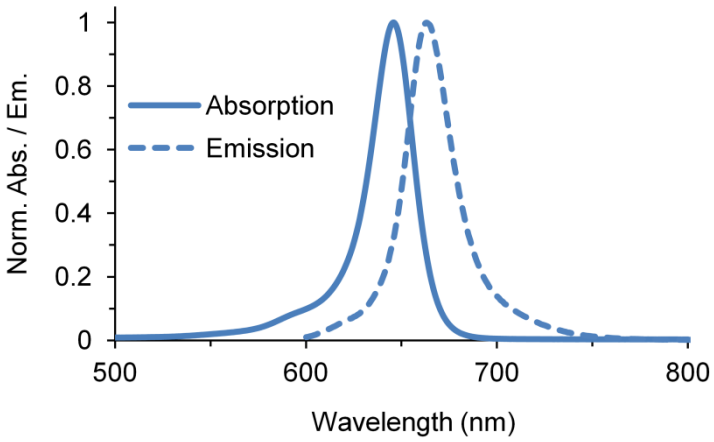


Figure S1: Absorption and emission spectra of squaraine dye **1** in chloroform (3.0 μM, ex: 600 nm).

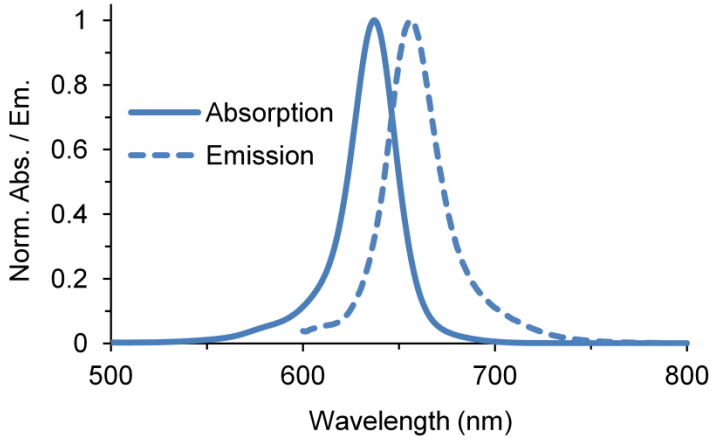


Figure S2: Absorption and emission spectra of squaraine dye **2** in chloroform (3.0 μM, ex: 600 nm).

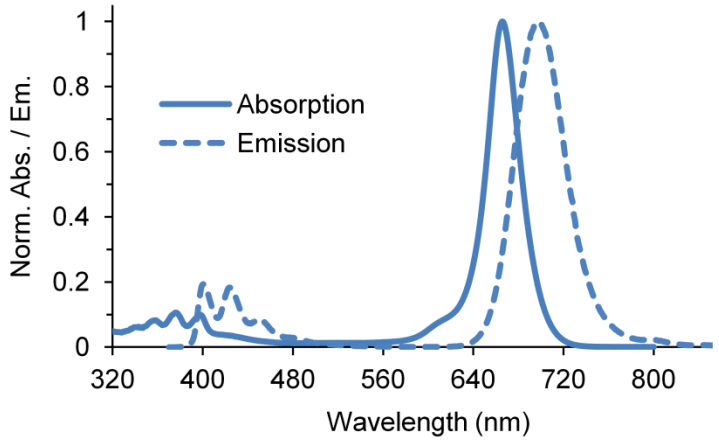


Figure S3: Absorption and emission spectra of rotaxane **4** in chloroform (3.0 μM, ex: 365 nm).

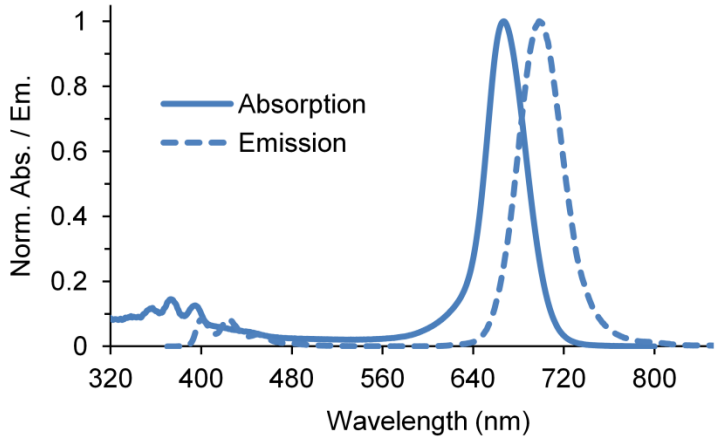


Figure S4: Absorption and emission spectra of rotaxane **5** in chloroform (3.0 μM, ex: 365 nm).

Table S1: Photophysical data of squaraine dyes and squaraine rotaxanes in chloroform (3.0 μM).

Compound	λ_{abs} (nm)	log ε	λ_{em} (nm)	Φ_f	Brightness[S6]
1	637	5.55	656	0.61	2.2×10^5
2	645	5.66	663	0.58	2.7×10^5
4	666	5.24	697	0.36	6.3×10^4
5	667	5.17	698	0.31	4.6×10^4

Table S2: Photophysical data of squaraine dyes and squaraine rotaxanes in acetone (3.0 μM).

Compound	λ_{abs} (nm)	log ε	λ_{em} (nm)
1	639	5.54	660
2	645	5.59	663
4[S7]	662	N/A	699
5	669	5.08	699

C. Squaraine Chemical Stability

Decomposition profiles of SqOH dye **1** and Sq dye **2** in Figure S5 were acquired by monitoring absorption spectra of samples (3.0 μM) in an acetone solution containing water (3.0 % v/v). The decay profiles obey pseudo first order kinetics.

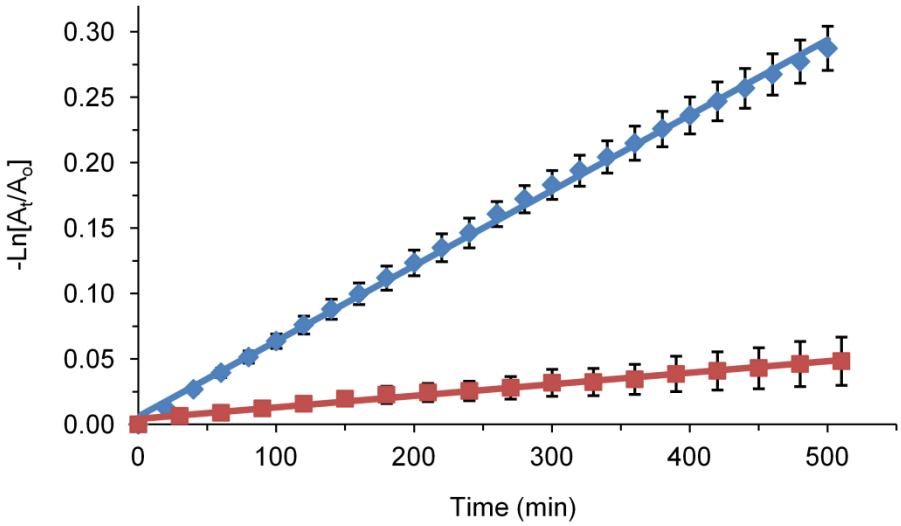


Figure S5: Decomposition kinetics of **1** (red) and **2** (blue) in a water/acetone solution (3.0 % v/v).

Table S3: Decomposition kinetic data of **1** and **2** in a water/acetone solution (3.0 % v/v).

Compound	k_{decomp} (min^{-1})	$t_{1/2}$ (h)
1	$8.8x10^{-5}$	130
2	$5.8x10^{-4}$	20

D. Pseudorotaxane Studies

Table S4: Photophysical data for pseudorotaxanes in chloroform (3.0 μM).

Compound	λ_{abs} (nm)	log ε	λ_{em} (nm)
M2⊃1	665	5.32	700
M2⊃2	666	5.10	700

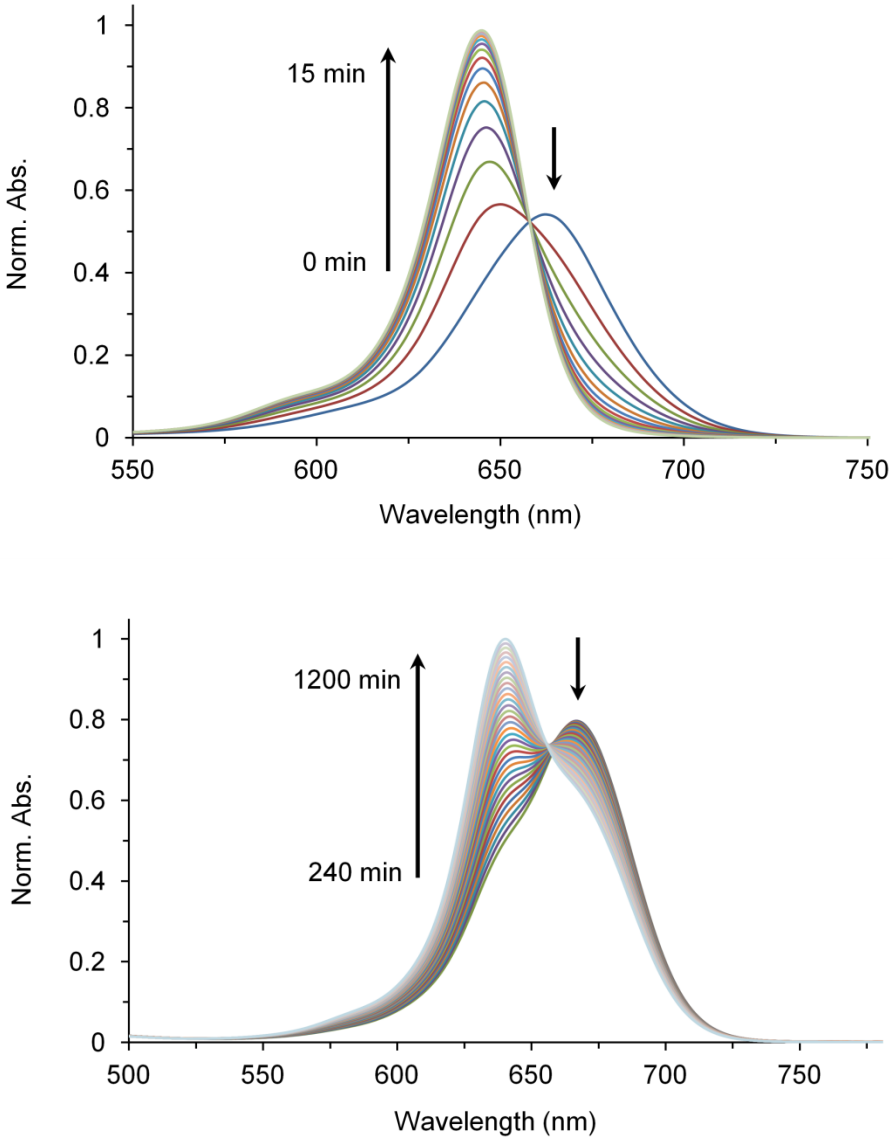


Figure S6: Time-dependent absorption spectra in acetone showing that dethreading of: (*top*) **M2⊃1** (5 μM) is complete after 15 min; (*bottom*) **M2⊃2** (5 μM) is complete after more than 1200 min. In other words, dethreading of **M2⊃1** is more than fifty times faster than **M2⊃2**.

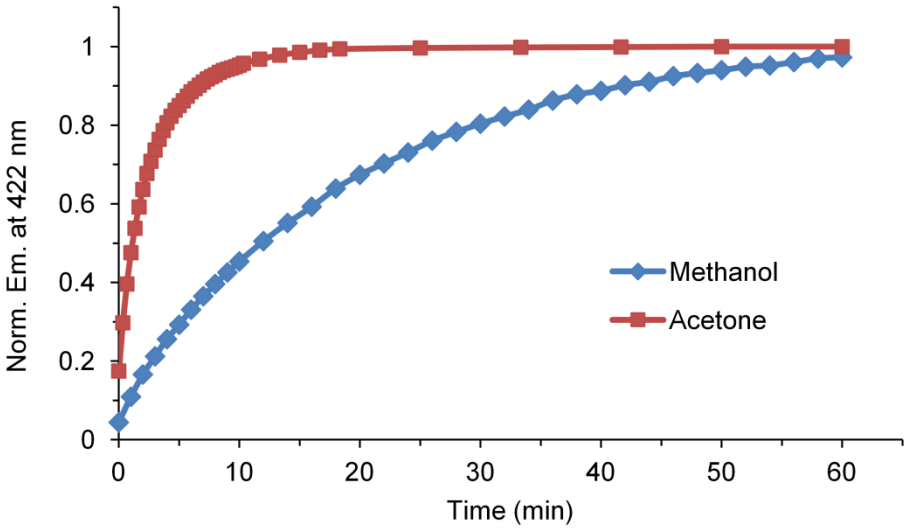


Figure S7: Dethreading of **M2⊃1** (5 μM) is much faster in acetone than in methanol, as determined by the growth of anthracene fluorescence band (ex: 365 nm) due to release of free macrocycle **M2**.

E. Pseudorotaxane Association

The association between Dye (**3**) and Macrocycle (**M2**) at equilibrium is:

$$\mathbf{3} + \mathbf{M2} \underset{}{\overset{K_a}{\rightleftharpoons}} \mathbf{M2 \supset 3}$$

Therefore:

$$K_a = \frac{[R]}{[D] \cdot [M]}$$

The initial concentrations of Dye ($[D]_o$) and Macrocycle ($[M]_o$) were as follows:

$$[D]_o = 5.0\ \mu M$$

$$[M]_o = 50 \cdot [D]_o = 250\ \mu M$$

At equilibrium, the concentration of free dye ([D]) is given by:

$$[D] = [D]_o - [R]$$

and the concentration of pseudorotaxane ([R]):

$$[R] = [M]_o - [M]$$

$$\therefore [R] = 50 \cdot [D]_o - [M]$$

Substitution into the equilibrium expression above yields the following relationship:

$$K_a = \frac{[R]}{([D]_o - [R]) \cdot (50 \cdot [D]_o - [R])} = \frac{[R]}{50 \cdot [D]_o^2 - 51 \cdot [R] \cdot [D]_o + [R]^2}$$

Because the absorbance profiles for the free dye (A_{max} = 642 nm) and the pseudorotaxane (A_{max} = 660 nm) overlap, the contribution of both species to the absorbance at each wavelength can be calculated using Beer's law:

$$A_\lambda = (\varepsilon_{\lambda 1} \cdot b \cdot c_1) + (\varepsilon_{\lambda 2} \cdot b \cdot c_2)$$

$$\therefore A_\lambda = (\varepsilon_{\lambda R} \cdot b \cdot c_R) + (\varepsilon_{\lambda D} \cdot b \cdot c_D)$$

The cell length (b) is 1 cm, and the molar absorptivities of the chromophores at the respective wavelengths are:

$$\varepsilon_{D642} = 3.73\text{x}10^5\ \text{M}^{-1}\text{cm}^{-1} \qquad \varepsilon_{D660} = 8.48\text{x}10^4\ \text{M}^{-1}\text{cm}^{-1}$$

$$\varepsilon_{R642} = 9.84\text{x}10^4\ \text{M}^{-1}\text{cm}^{-1} \qquad \varepsilon_{R660} = 2.48\text{x}10^5\ \text{M}^{-1}\text{cm}^{-1}$$

Since b = 1 cm, the absorption at a specific wavelength, λ, is:

$$A_\lambda = \varepsilon_{\lambda R} \cdot [R] + \varepsilon_{\lambda D} \cdot ([D]_o - [R])$$

$$\therefore [R] = \frac{A_\lambda - \varepsilon_{\lambda D} \cdot [D]_o}{\varepsilon_{\lambda R} - \varepsilon_{\lambda D}}$$

The absorption measured at 642 nm provides the association constant of **3** plus **M2** to form pseudorotaxane **M2⊃3** at 298 K in chloroform as K_a = 1.5 (± 0.2) x10^4 M^{-1}. Binding constants for non-hydroxylated Sq dyes were previously reported as K_a = 1.8 (± 0.4) x10^5 M^{-1},[S8] demonstrating an order of magnitude decrease in association constant with the dihydroxyl SqOH dye **3**.

F. Rotaxane Studies

Figures S8 and S9 show that addition of TBA^+Cl^- to rotaxane **5** produced no significant spectral changes.

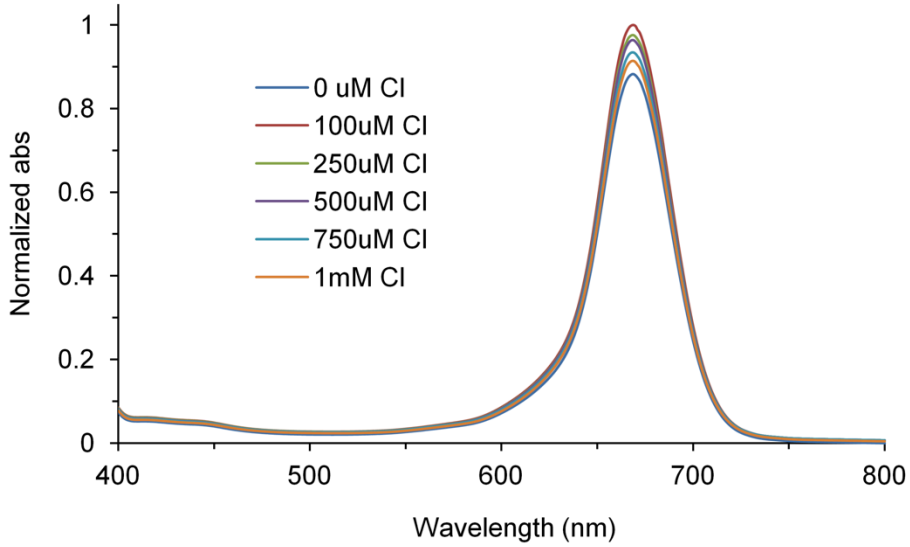


Figure S8: Absorption profiles for titration of TBA^+Cl^- into a solution of rotaxane **5** (3.0 μM) in acetone at 25°C.

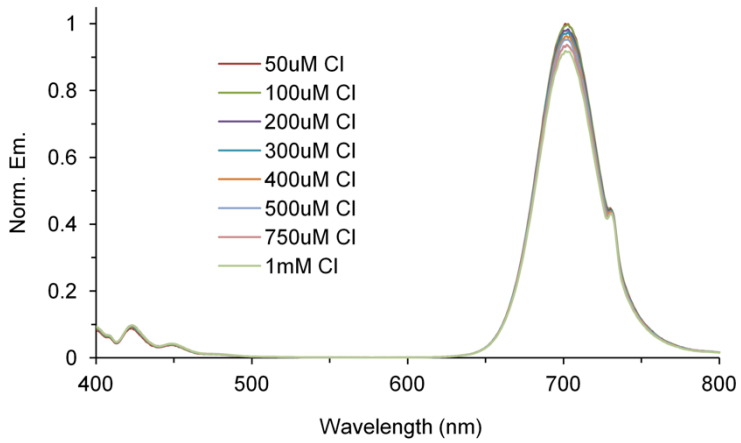


Figure S9: Emission profiles for titration of TBA^+Cl^- into a solution of rotaxane **5** (3.0 μM) in acetone at 25°C with excitation at 365 nm.

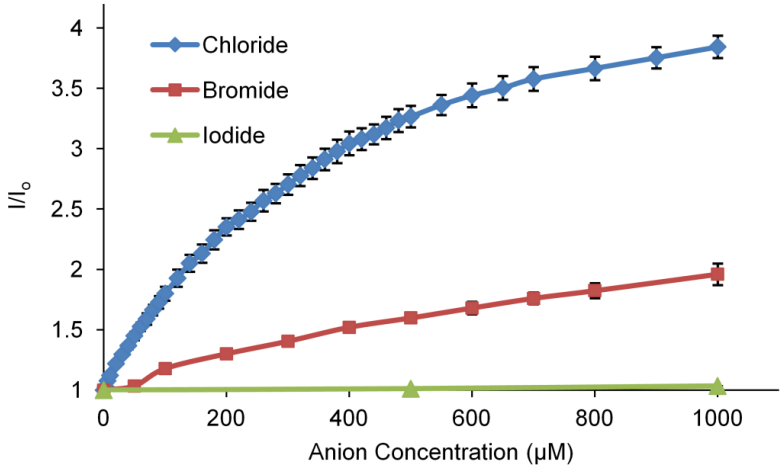


Figure S10: Titration of TBA^+ halides into a solution of rotaxane **4** (3.0 μM) in acetone at 25°C. Excitation at 365 nm and the I/I_o is change in fluorescence emission intensity of emerging maxima band at 660 nm.

Table S5: Halide binding constants from the titration of TBA^+ halides into a solution of rotaxane **4** (3.0 μM) in acetone at 25°C.

Halide Salt	K_a (M^{-1})	I/I_o[a]
TBA^+Cl^-	$1.9(\pm0.2)\times10^3$	3.8
TBA^+Br^-	$2.8(\pm1.1)\times10^2$	1.9
TBA^+I^-	--	1.0

[a]The ratio I/I_o is change in fluorescence intensity at 660 nm after addition of 1 mM halide salt.

Additional titration studies added TBA^+F^- or TBA^+OAc^- to rotaxane **4** in acetone. The result was deprotonation of a phenolic OH on the encapsulated SqOH dye by these basic anions, as judged by large, reversible blue shifts of the squaraine absorbance and fluorescence maxima along with greatly decreased fluorescence quantum yield. These spectral changes closely match those reported by other workers who have studied deprotonation of homologous SqOH dyes.[S9]

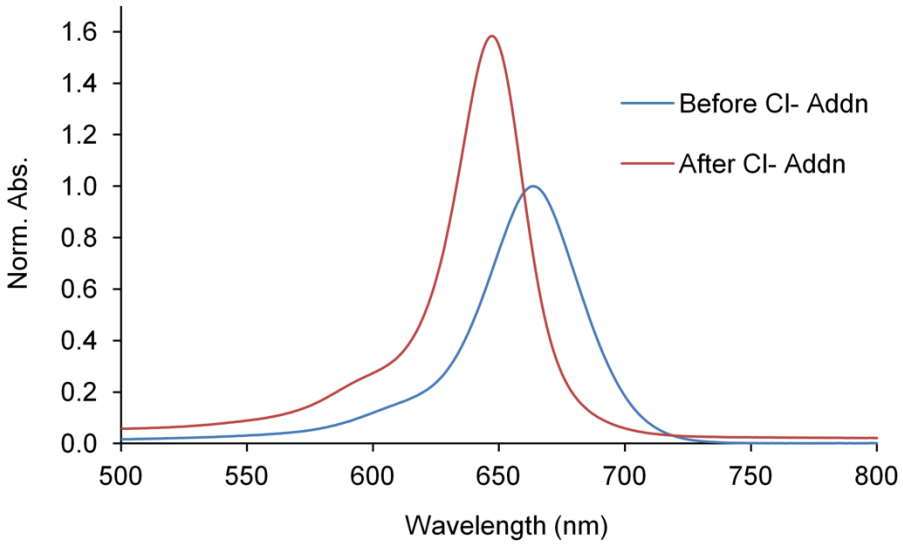


Figure S11: Absorption spectra of **4** (1.5 μM, 25°C) in acetone before and after TBA^+Cl^- addition (1000 molar equivalents).

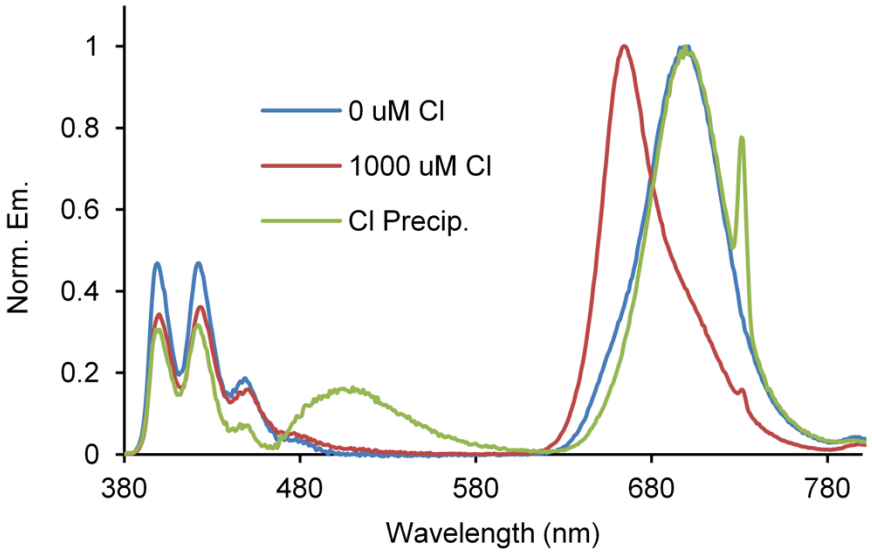


Figure S12: Fluorescence spectra demonstrating that chloride binding to **4** is reversed upon addition of a chloride precipitating agent ($AgPF_6$). The spectra in acetone were acquired in the following order: (a) sample of **4** with no added chloride (blue), (b) addition of TBA^+Cl^- (red), (c) addition of excess $AgPF_6$ (green).

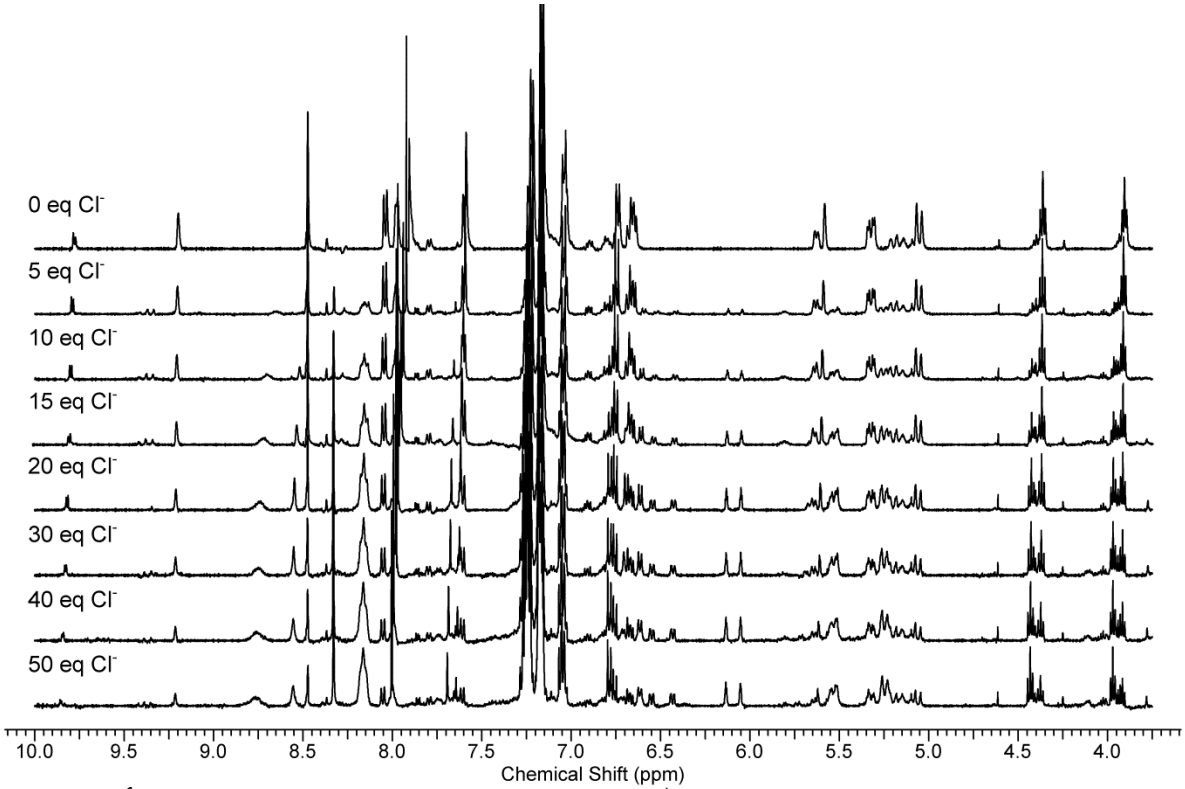


Figure S13: ^{1}H NMR spectra showing titration of $TBA^{+}Cl^{-}$ into a solution of **4** at 25°C in a 1:4 $CDCl_3$:acetone-d_6 solvent mixture.

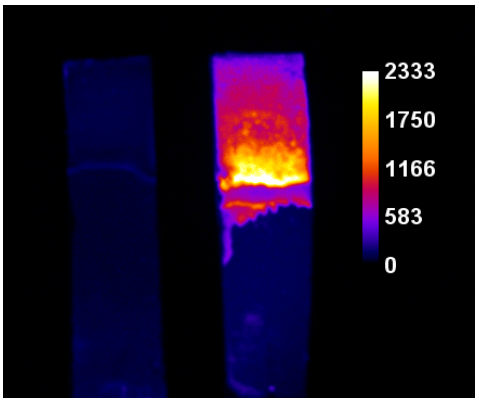
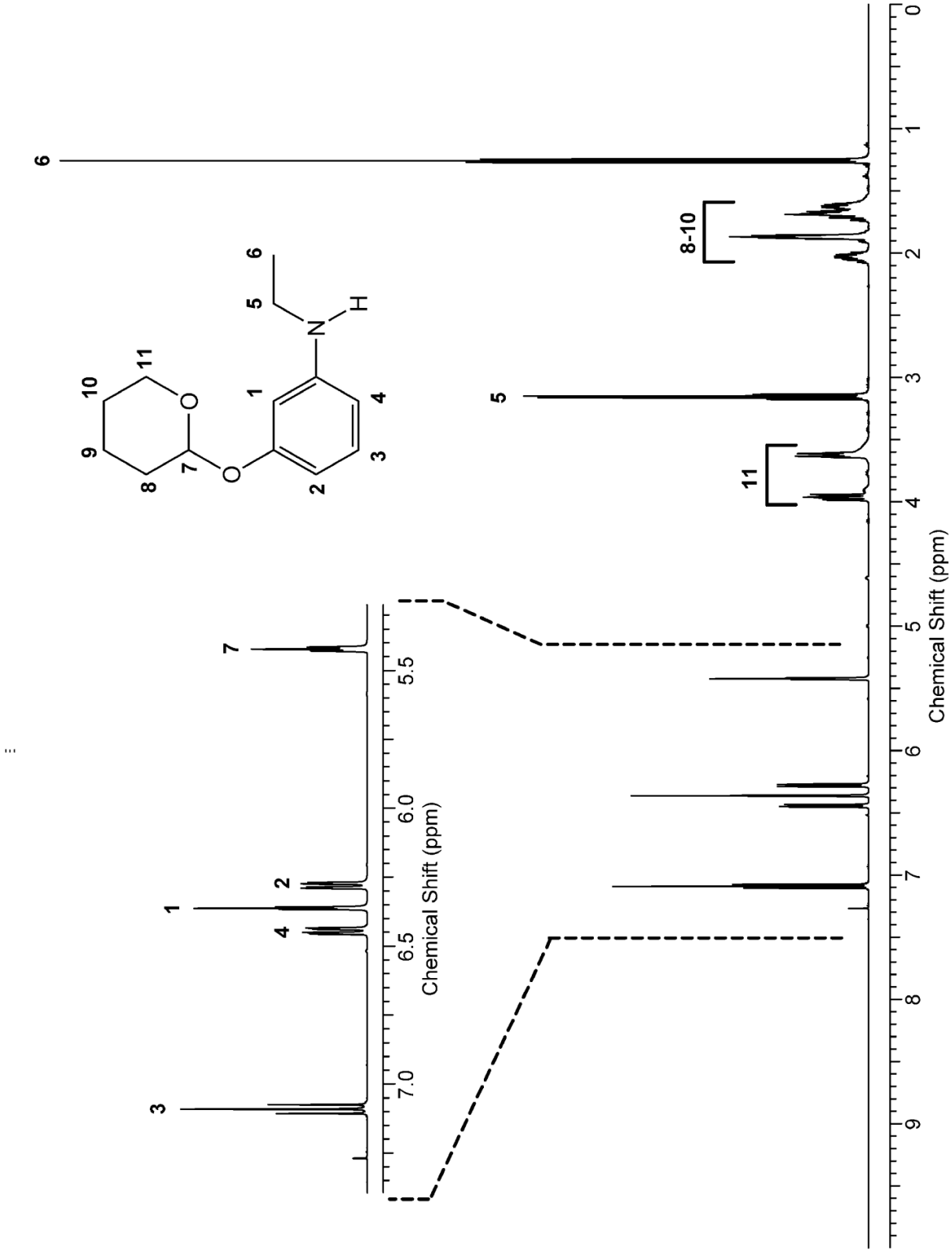
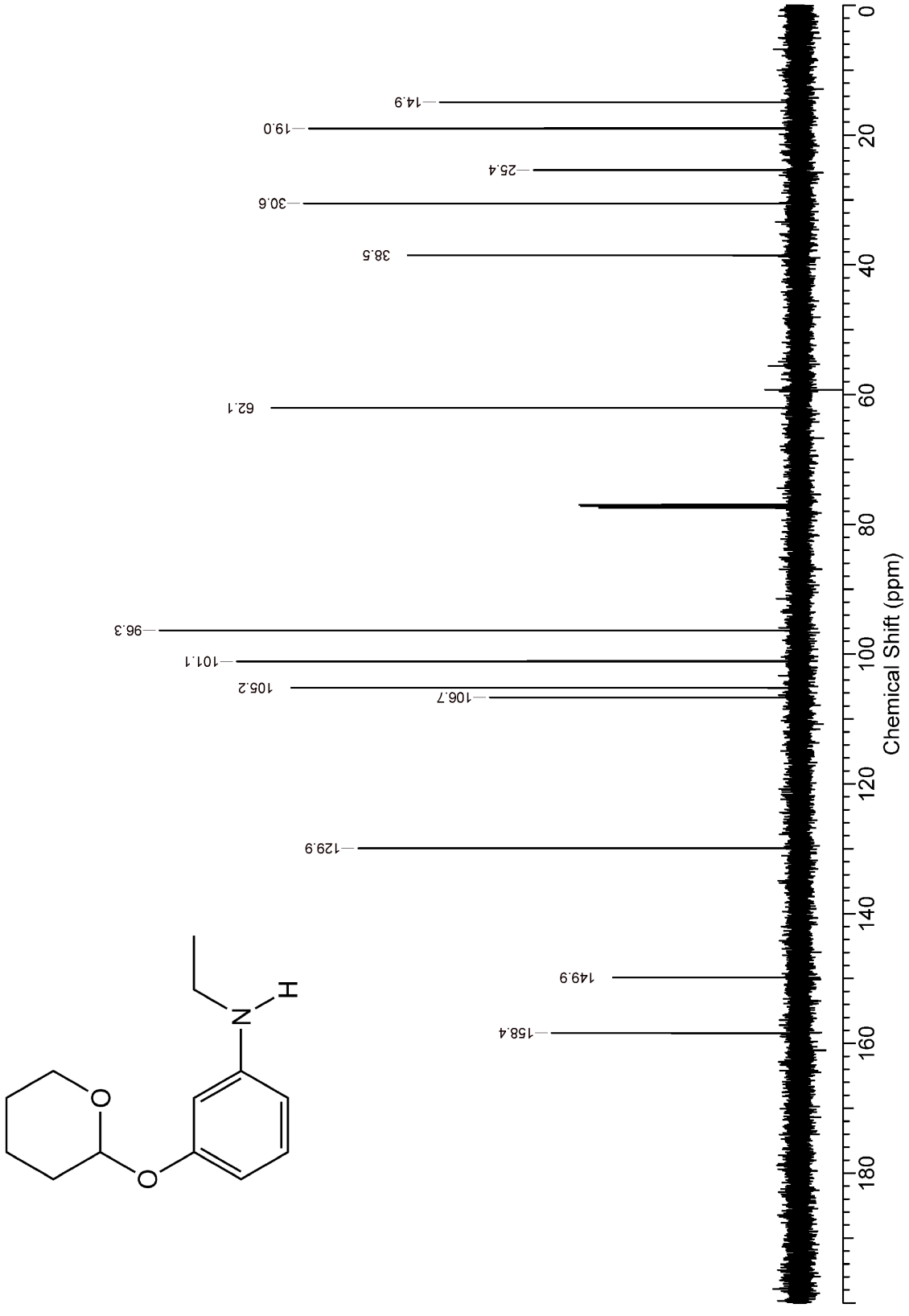


Figure S14: False-colored fluorescence intensity images of two dipsticks composed of C18-coated, reverse-phase silica gel plate with adsorbed **4**: (*left*) a pristine dipstick, (*right*) a dipstick after brief immersion in an aqueous solution containing $TBA^{+}Cl^{-}$ (1 M) followed by mild heating until dry. The images show that exposure to the $TBA^{+}Cl^{-}$ solution induces a 10-fold fluorescent intensity enhancement. Image acquisition filters; ex: 500-550 nm, em: 575-650 nm.

G. ^{1}H and ^{13}C NMR Spectra



^{1}H NMR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60
80
100
120
140
160
180
Chemical Shift (ppm)
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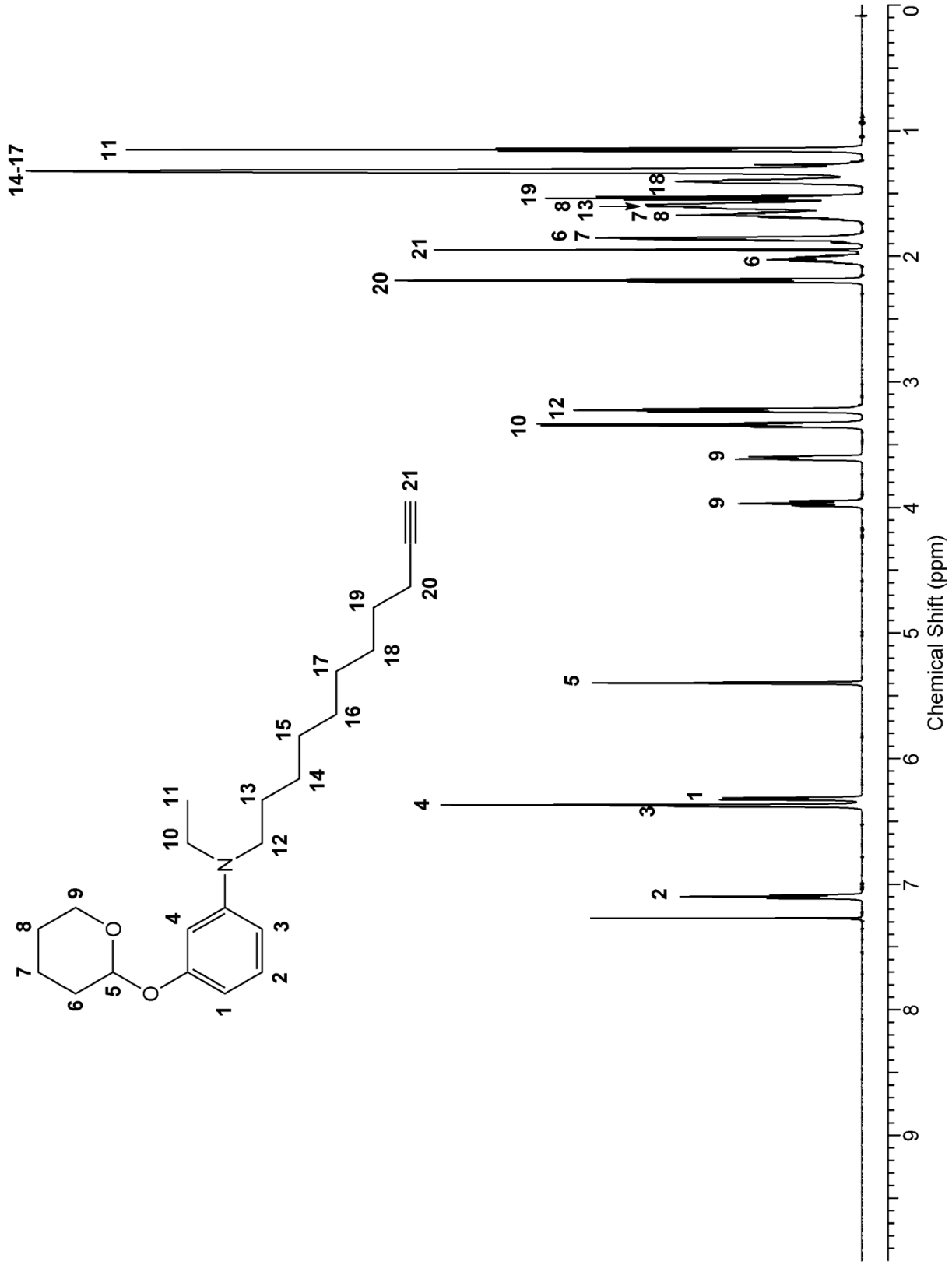
N
O
O

^{13}C NMR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4
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3
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Chemical Shift (ppm)
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2
3
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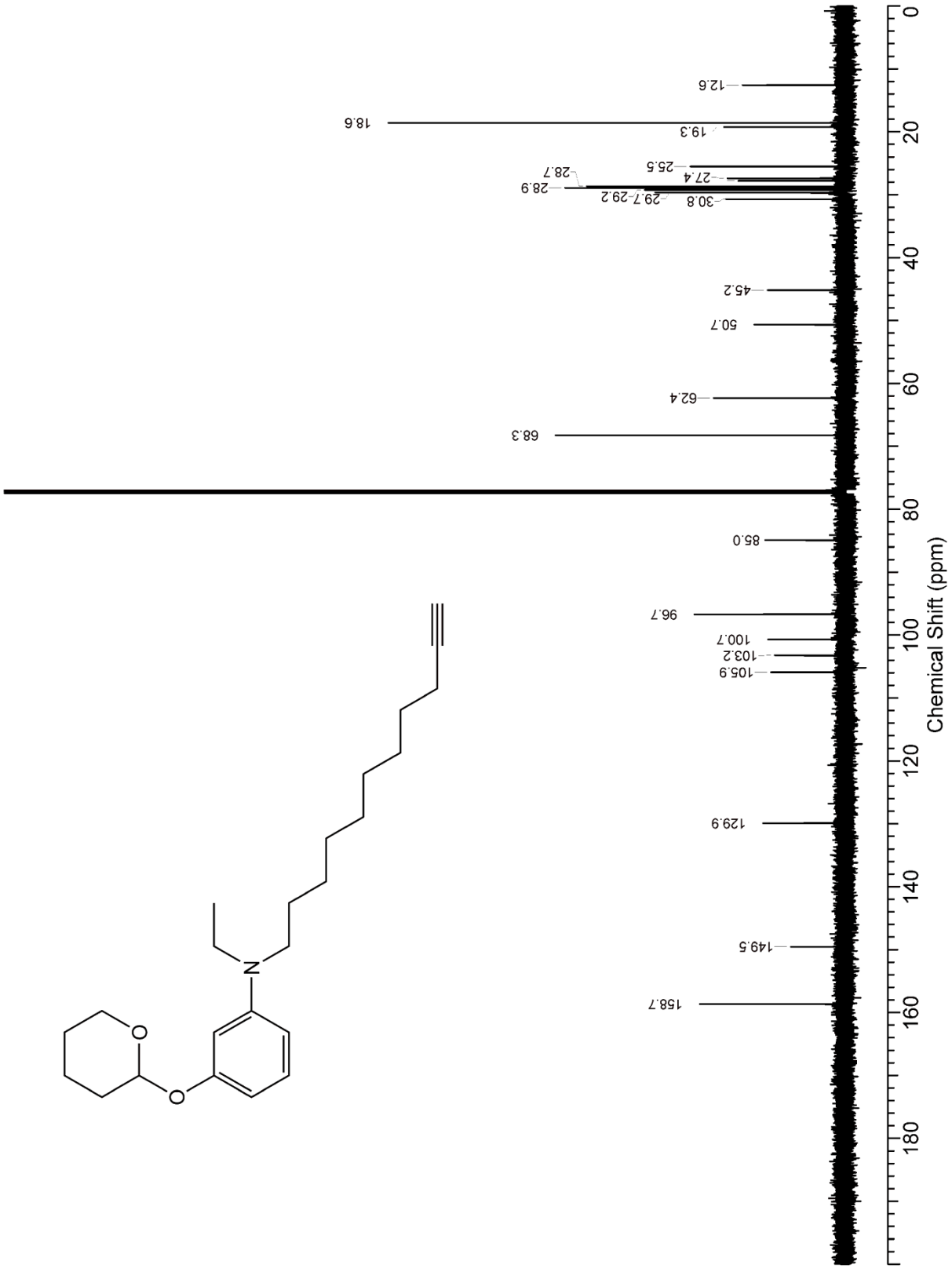
5
6
7
8
9
N
O
O

^{1}H NMR



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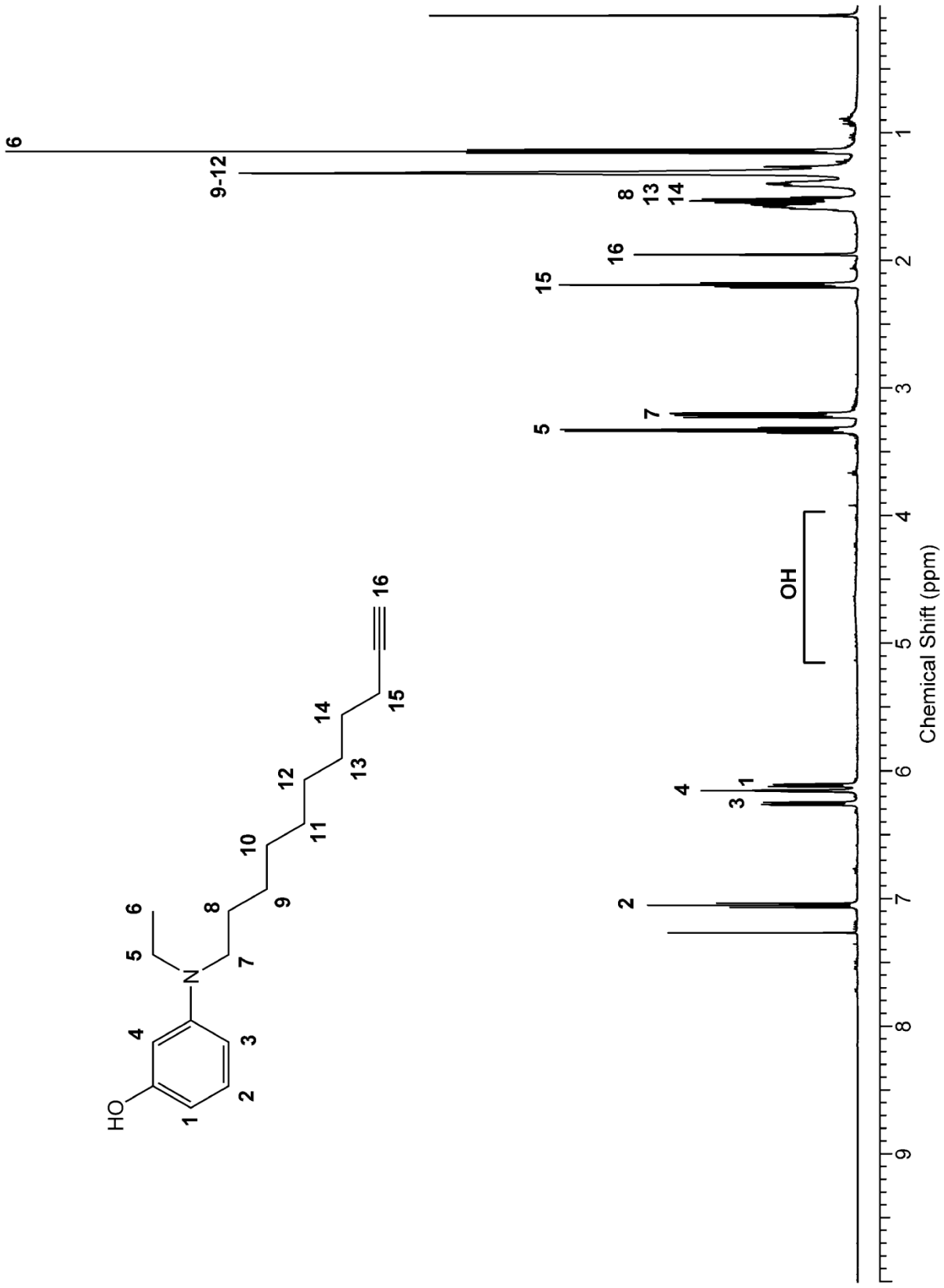

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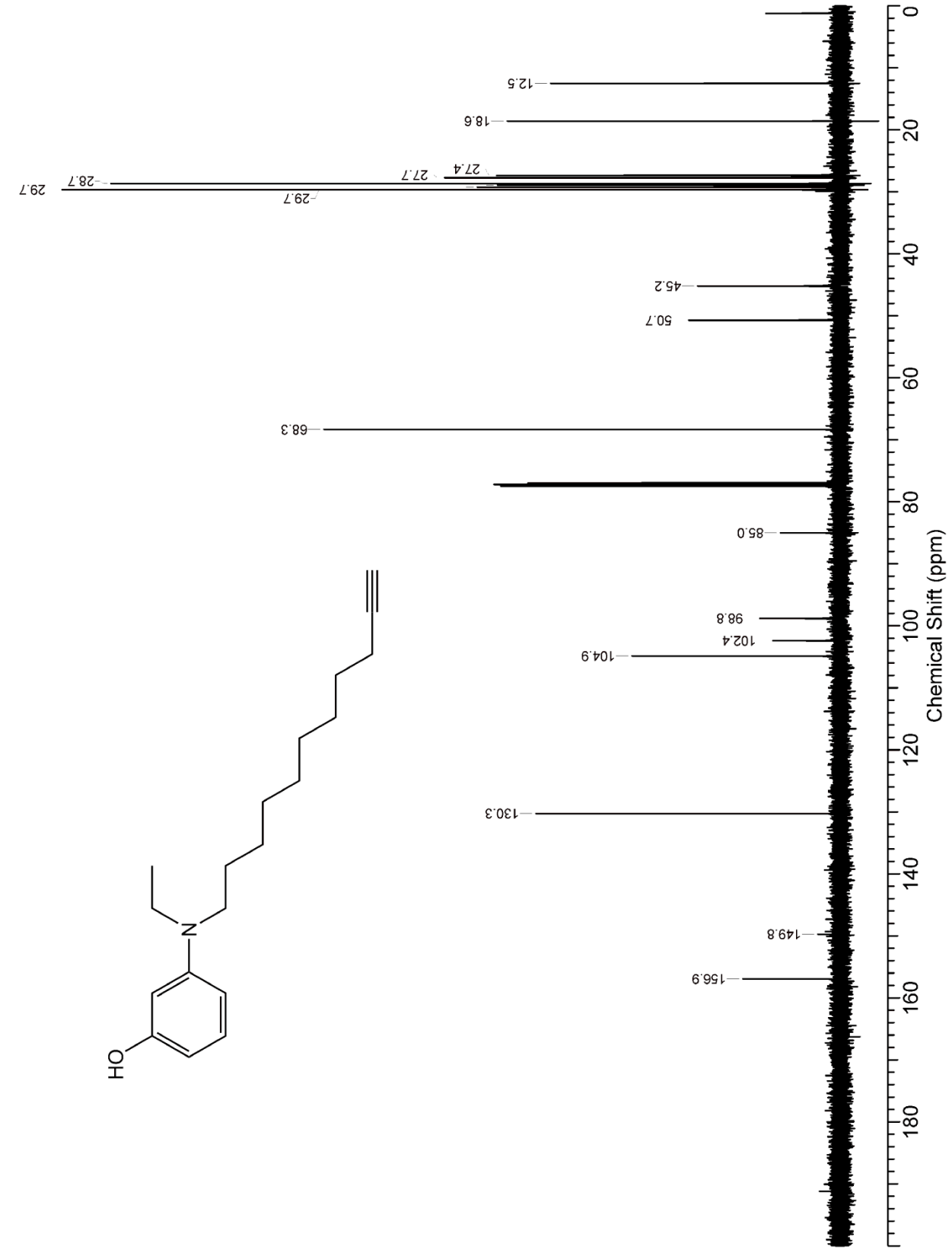
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104.9
130.3
149.8
156.9
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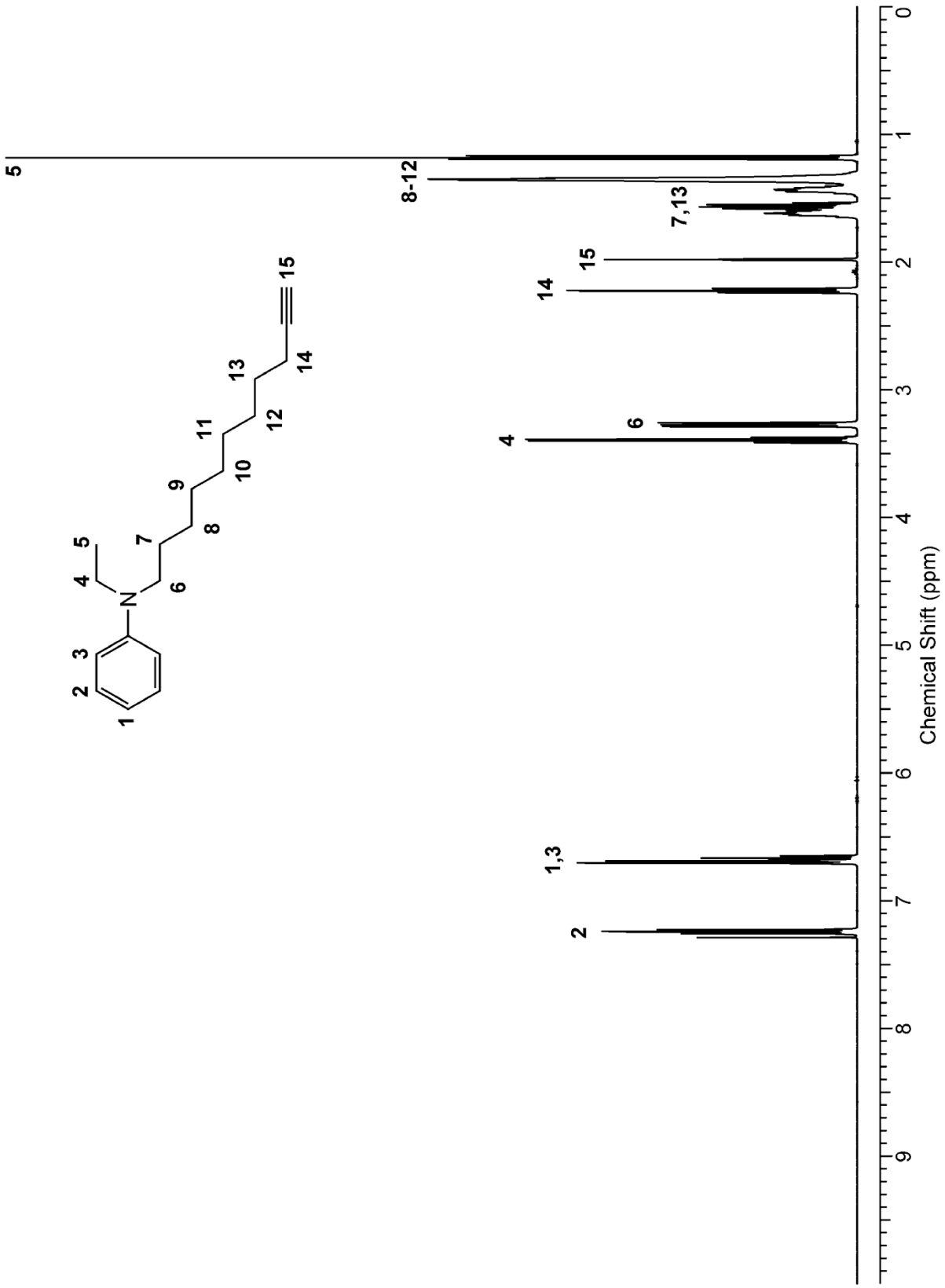
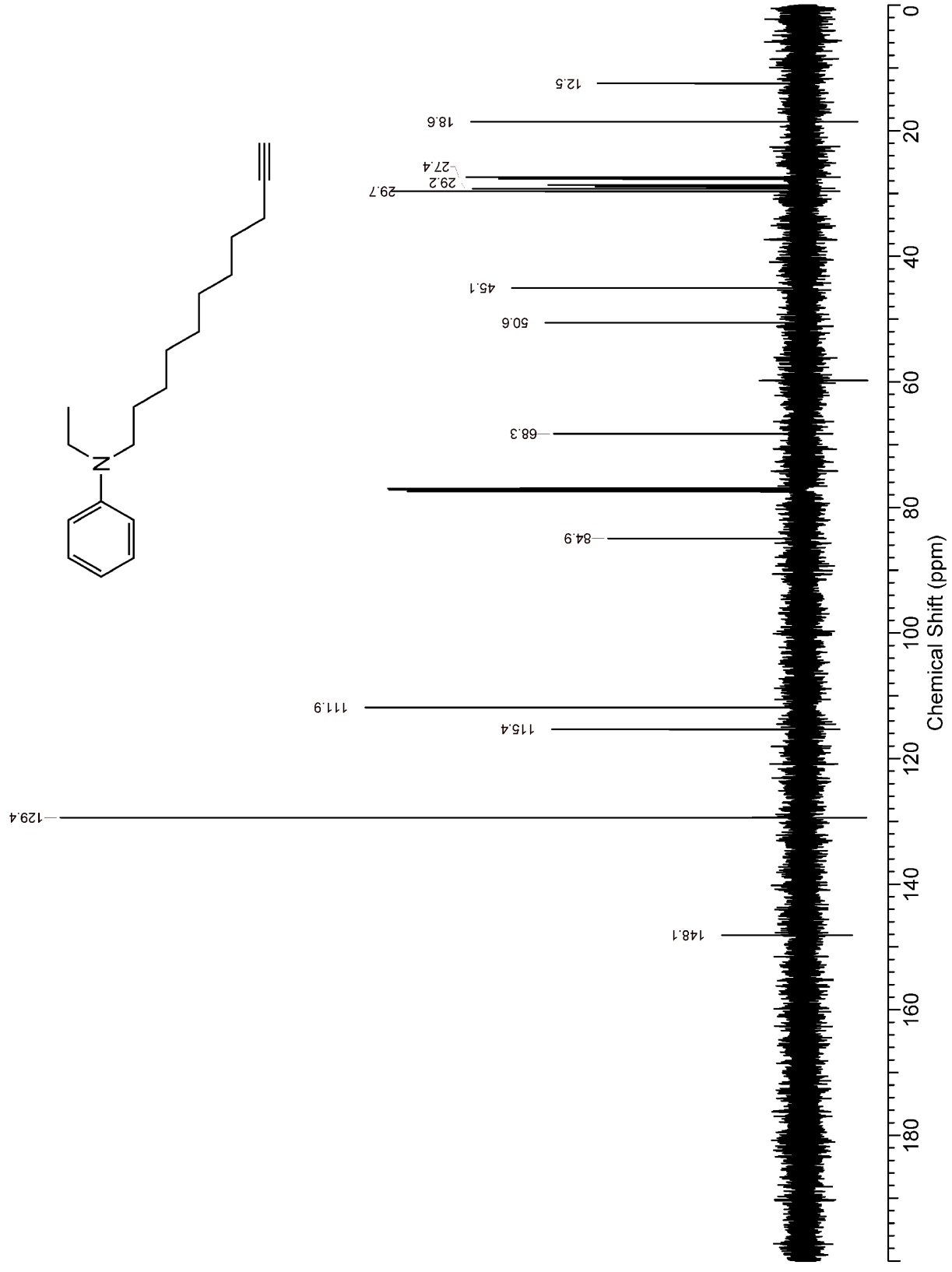
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)
N
HO

^{13}C NMR



^{1}H NMR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29.7
45.1
50.6
68.3
84.9
111.9
115.4
129.4
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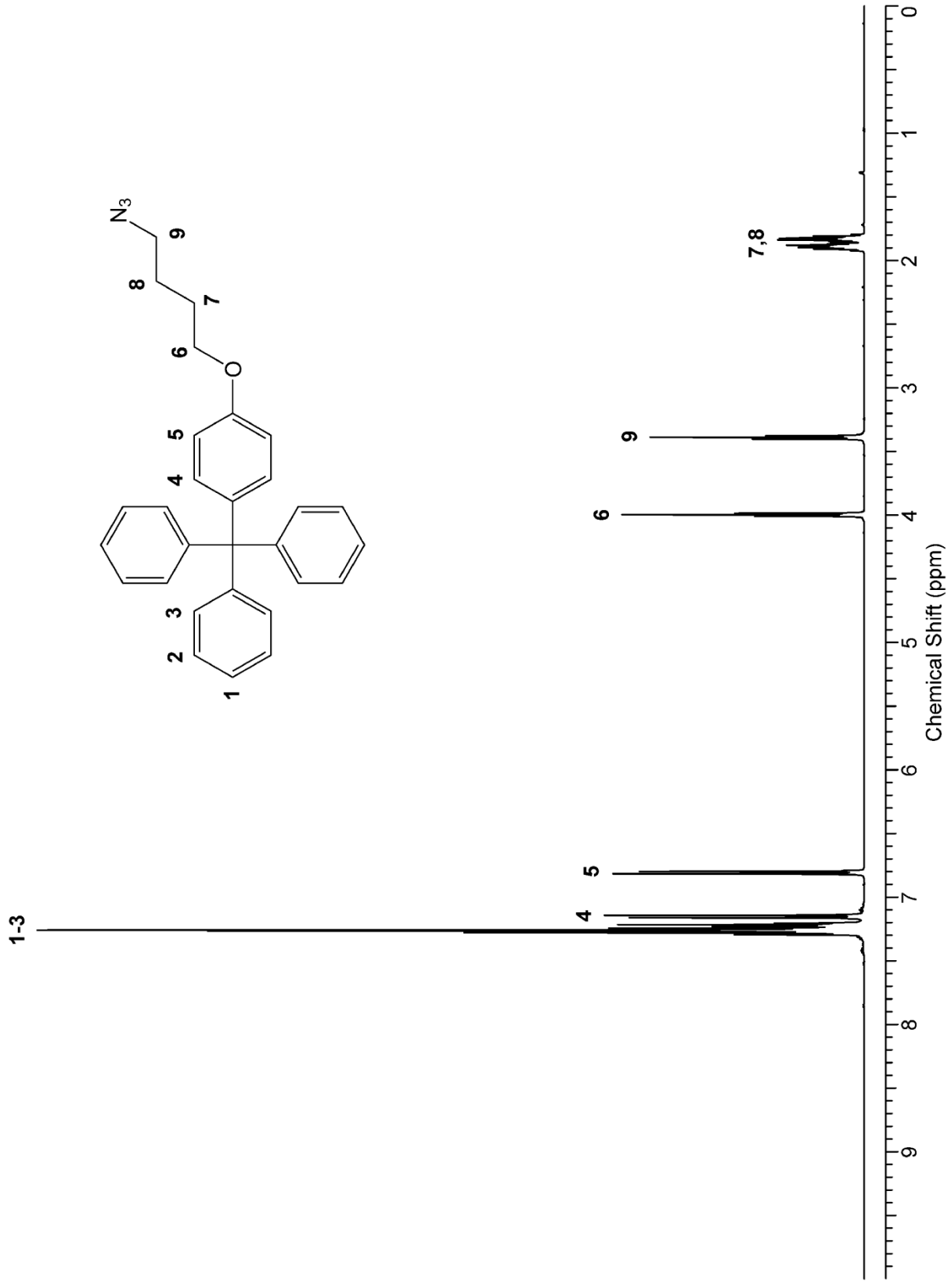
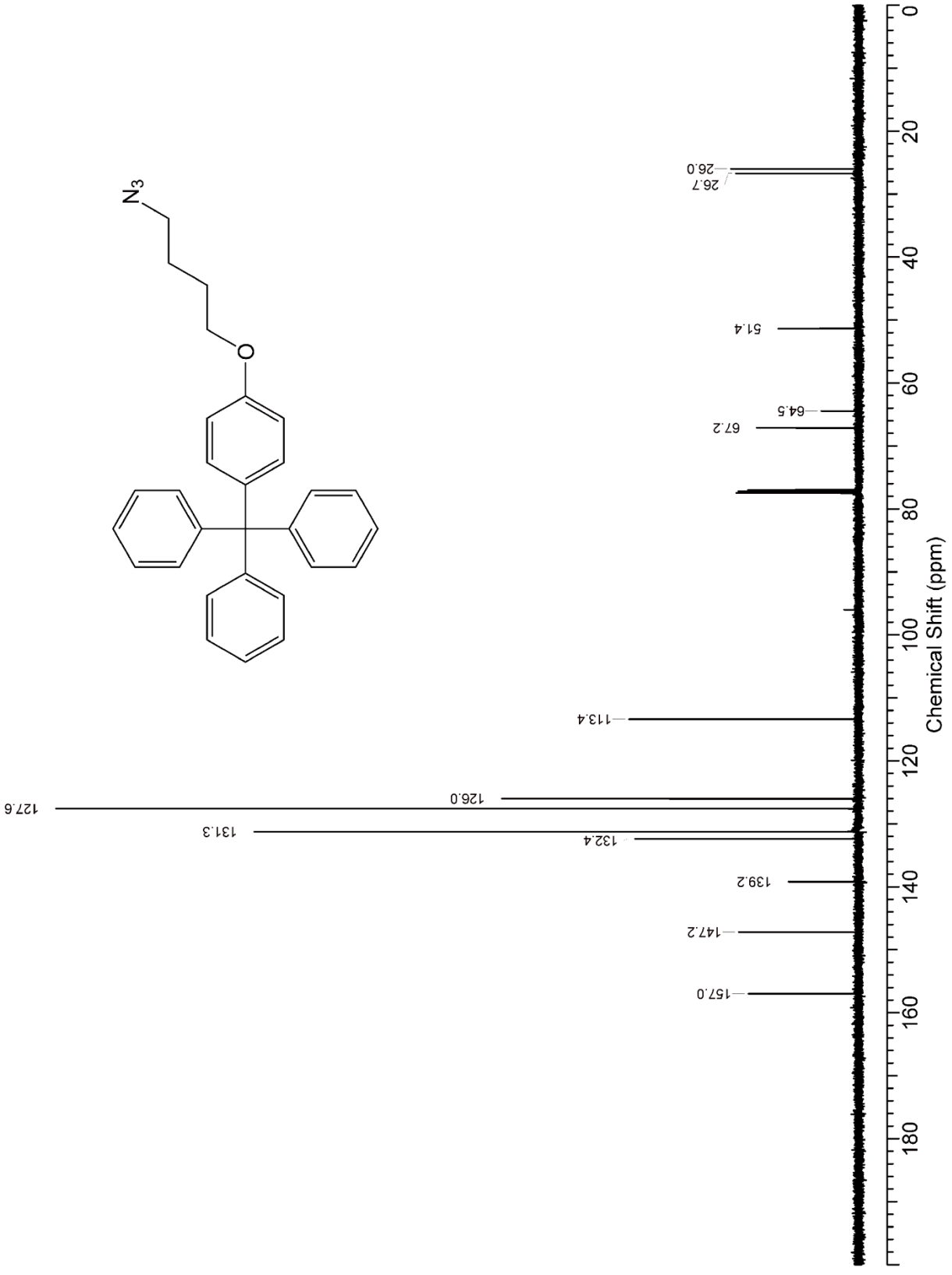
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)
N

^{13}C NMR



^{1}H NMR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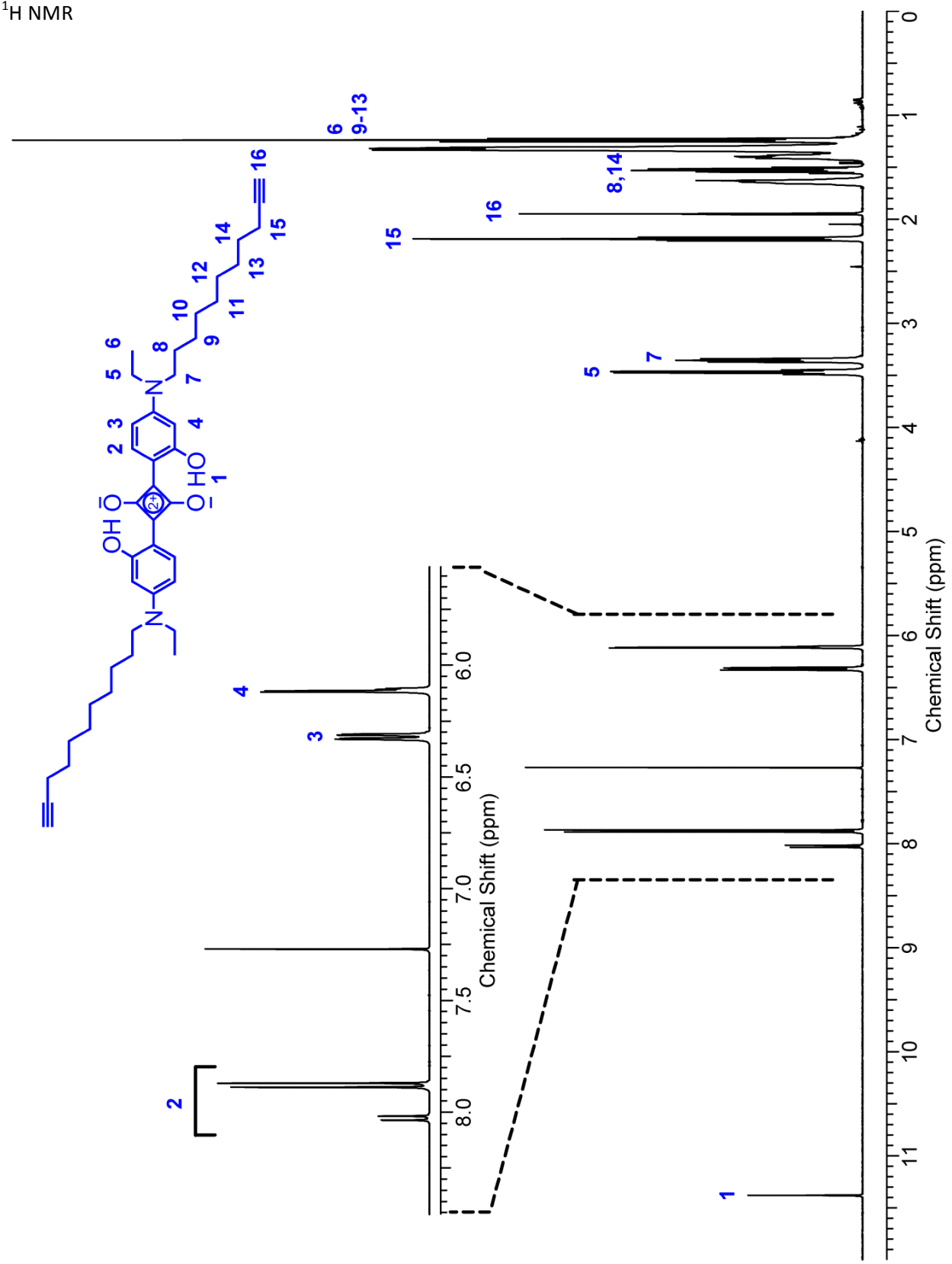
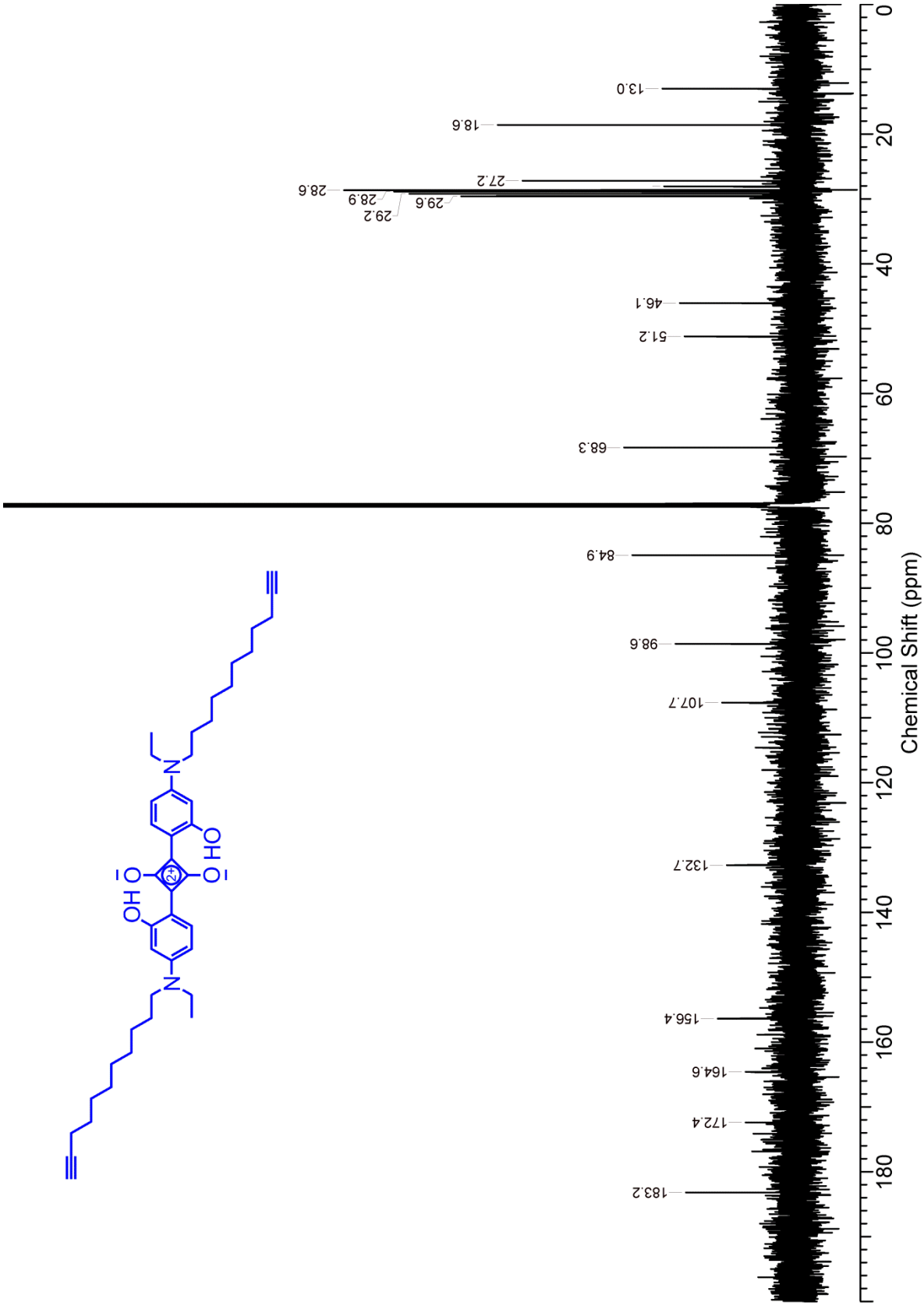
67.2
113.4
126.0
127.6
131.3
132.4
139.2
147.2
157.0
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)

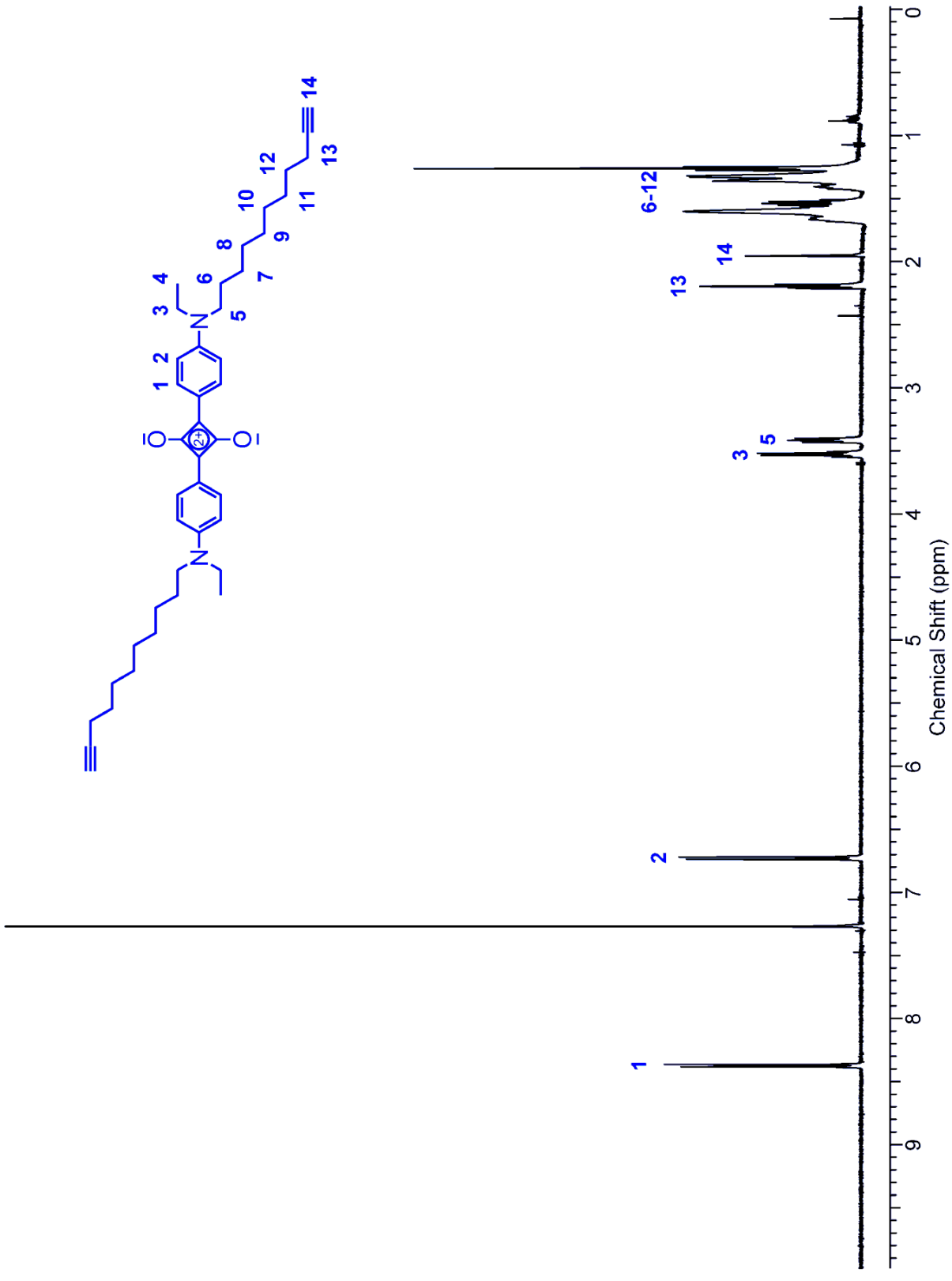
^{13}C NMR

^{1}H NMR

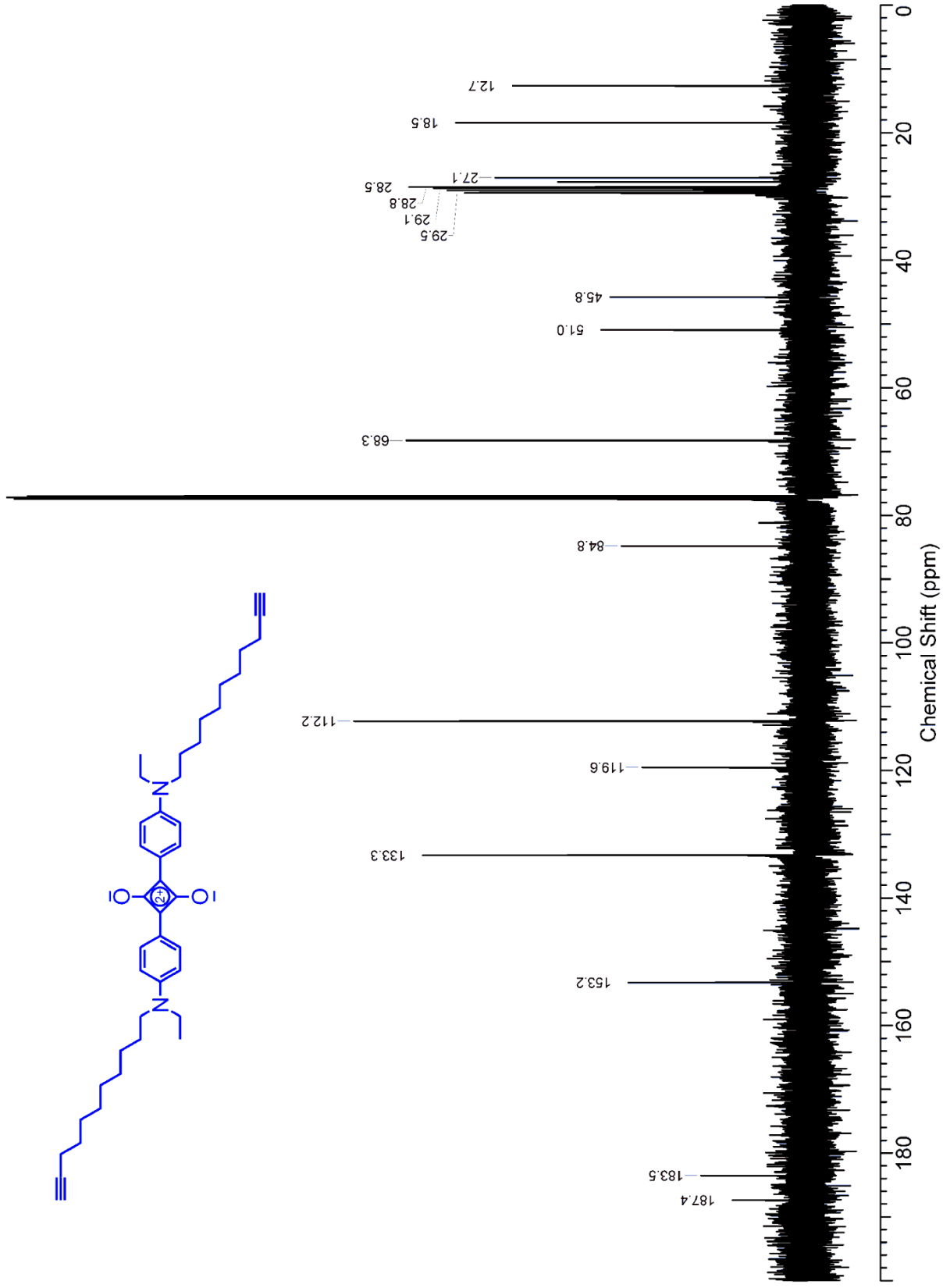



13.0
18.6
27.2
28.6
28.9
29.2
29.6
46.1
51.2
68.3
84.9
98.6
107.7
132.7
156.4
164.6
172.4
183.2
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)
HO
HO
O
O
N
N

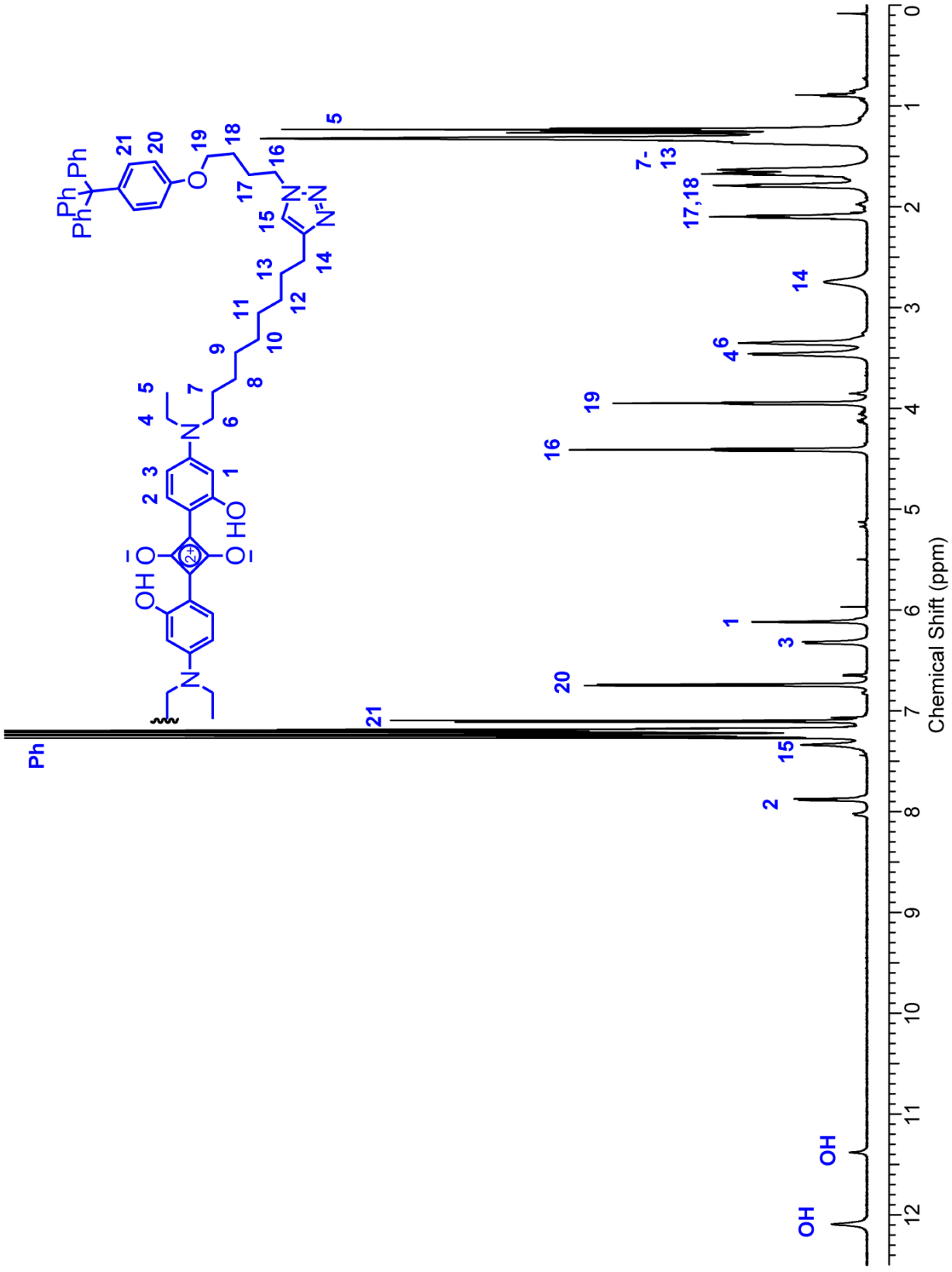
^{13}C NMR

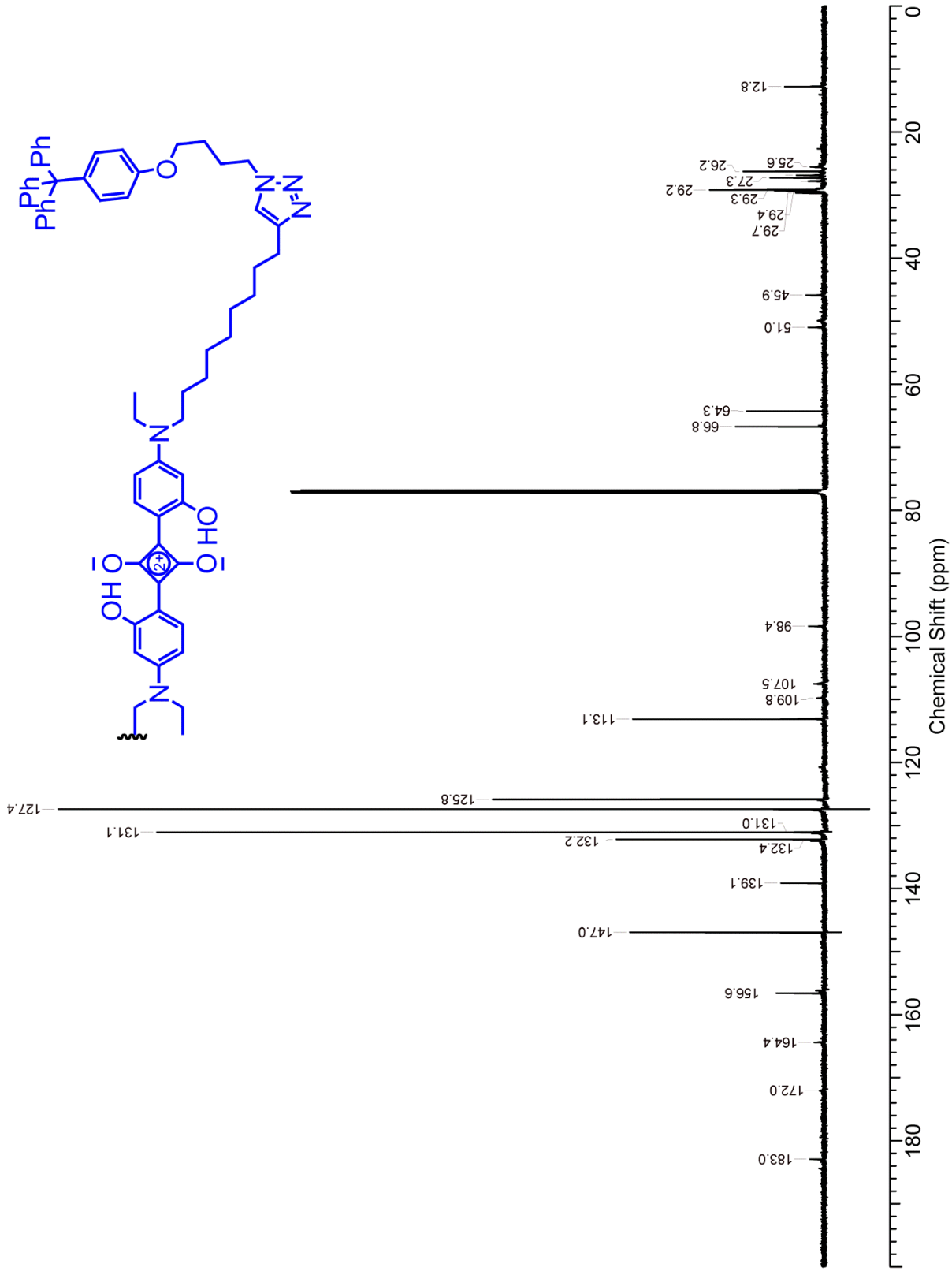


^{1}H NMR

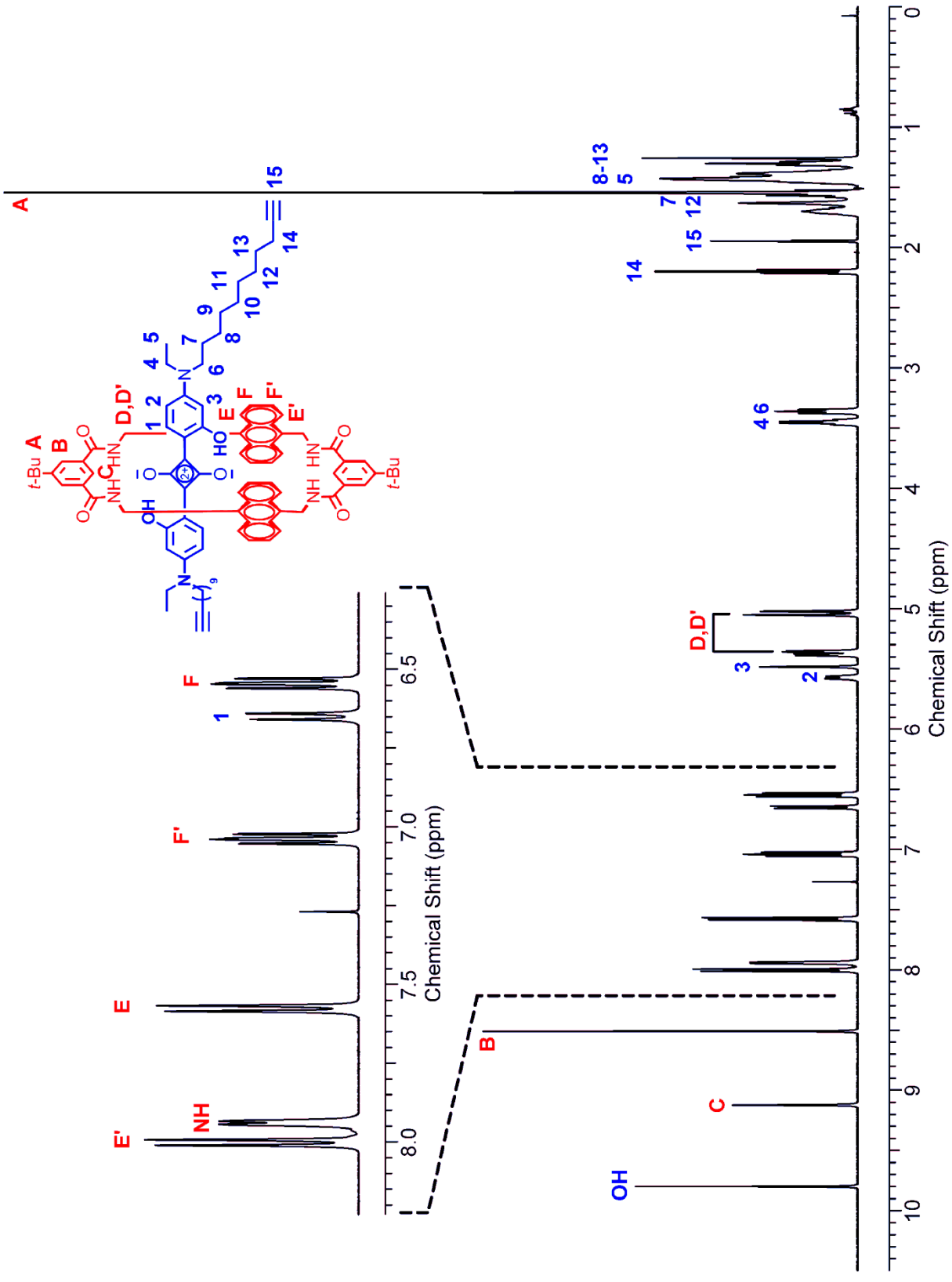

12.7
18.5
27.1
28.5
28.8
29.1
29.5
45.8
51.0
68.3
84.8
112.2
119.6
133.3
153.2
183.5
187.4
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)

^{13}C NMR

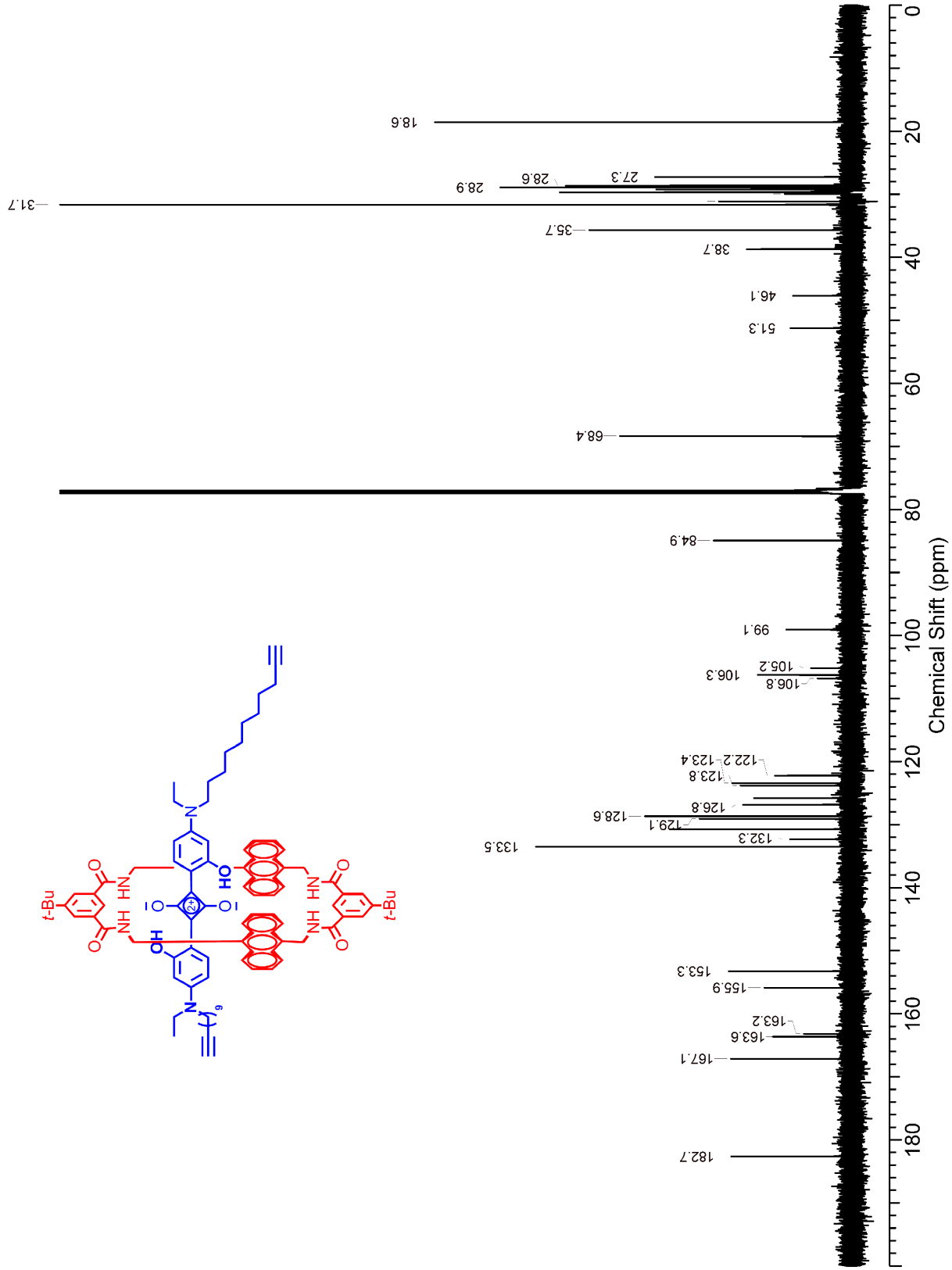

Chemical Shift (ppm)
0
1
2
3
4
5
6
7
8
9
10
11
12
Ph
21
20
19
16
5
7-13
17,18
14
4
6
19
16
1
3
20
15
2
OH
OH


Ph
Ph
Ph
O
N
N
N
N
N
HO
O
O
OH
2+
12.8
25.6
26.2
27.3
29.2
29.3
29.4
29.7
45.9
51.0
64.3
66.8
98.4
107.5
109.8
113.1
125.8
127.4
131.0
131.1
132.2
132.4
139.1
147.0
156.6
164.4
172.0
183.0
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)

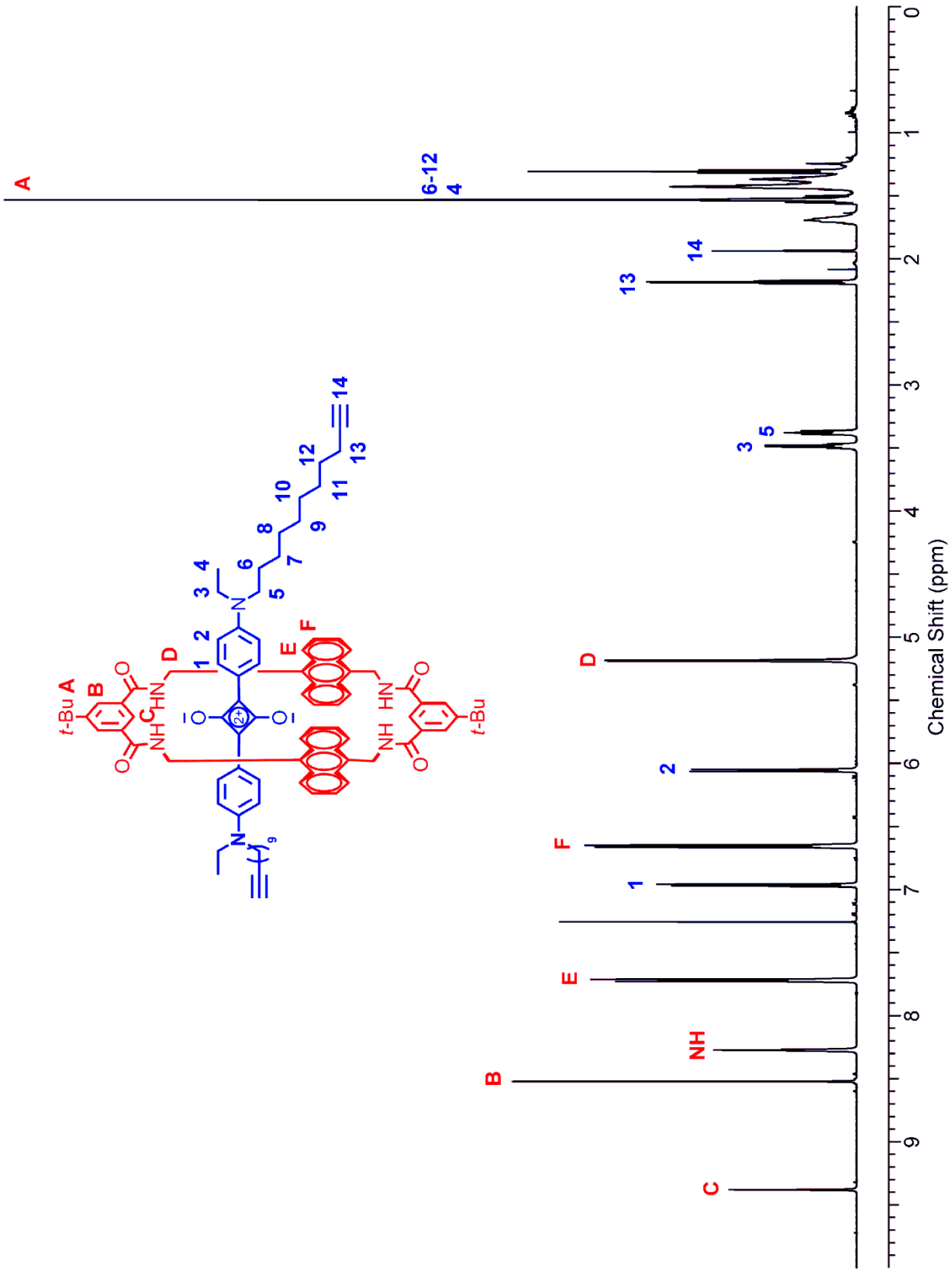
^{13}C NMR


A
8-13
5
7
12
15
14
4 6
D,D'
3
2
B
C
OH
E'
NH
E
F'
F
1
Chemical Shift (ppm)
Chemical Shift (ppm)

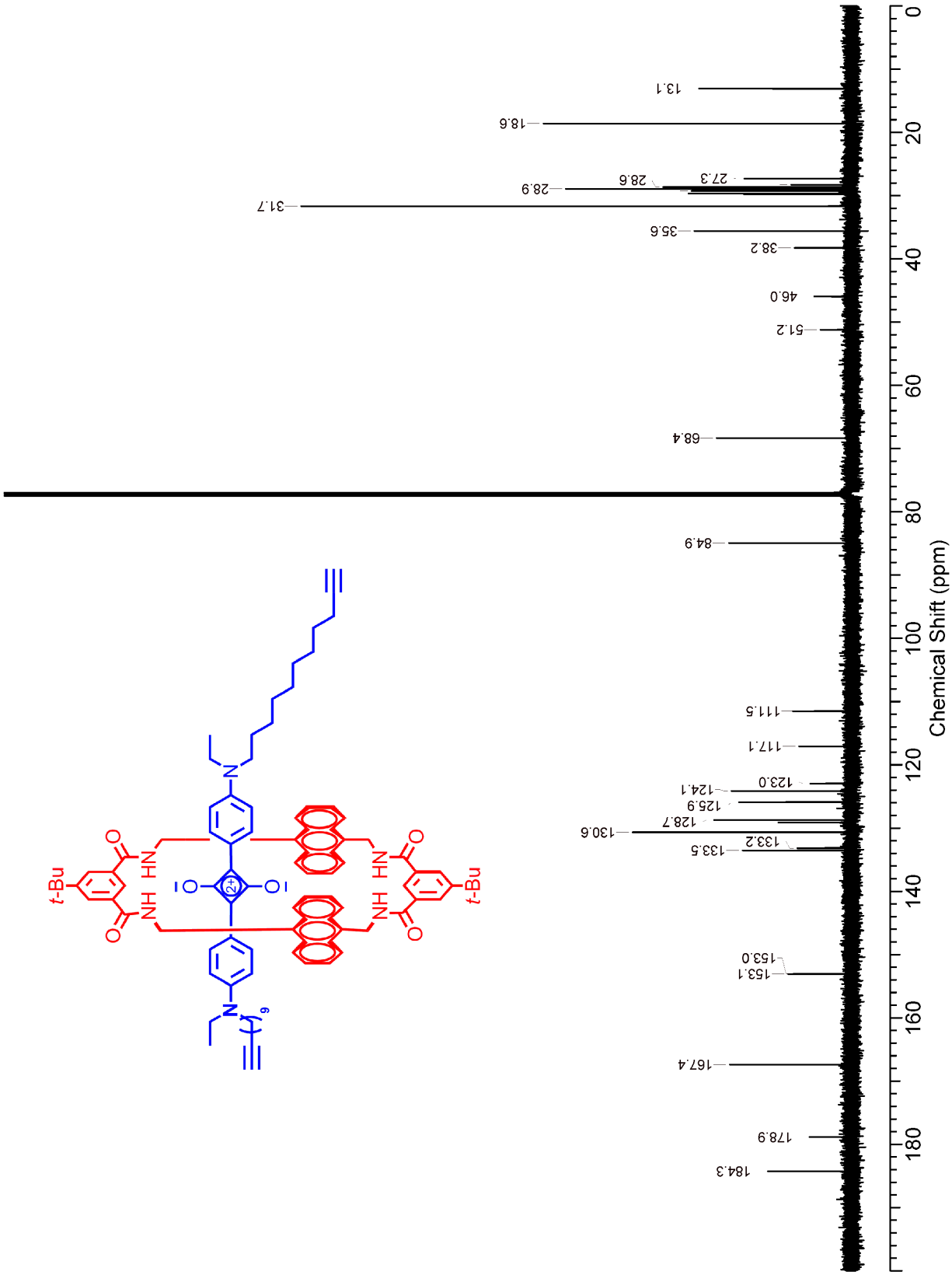
^{1}H NMR


18.6
27.3
28.6
28.9
31.7
35.7
38.7
46.1
51.3
68.4
84.9
99.1
105.2
106.3
106.8
122.2
123.4
123.8
126.8
128.6
129.1
132.3
133.5
153.3
155.9
163.2
163.6
167.1
182.7
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)
t-Bu
t-Bu
HO
HO
NH
HN
NH
HN
O
O
O
O
N
N
N
N
9

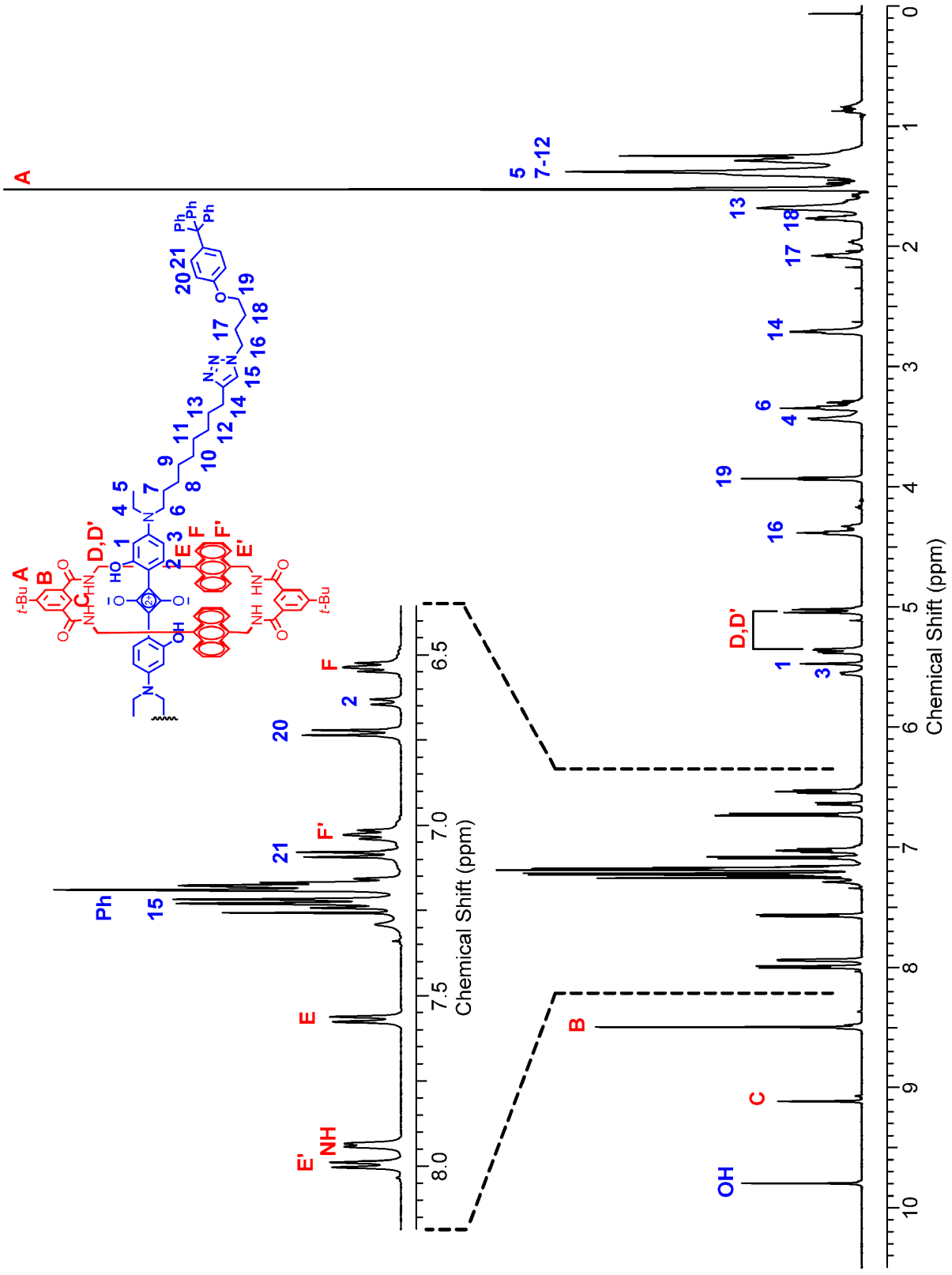
^{13}C NMR



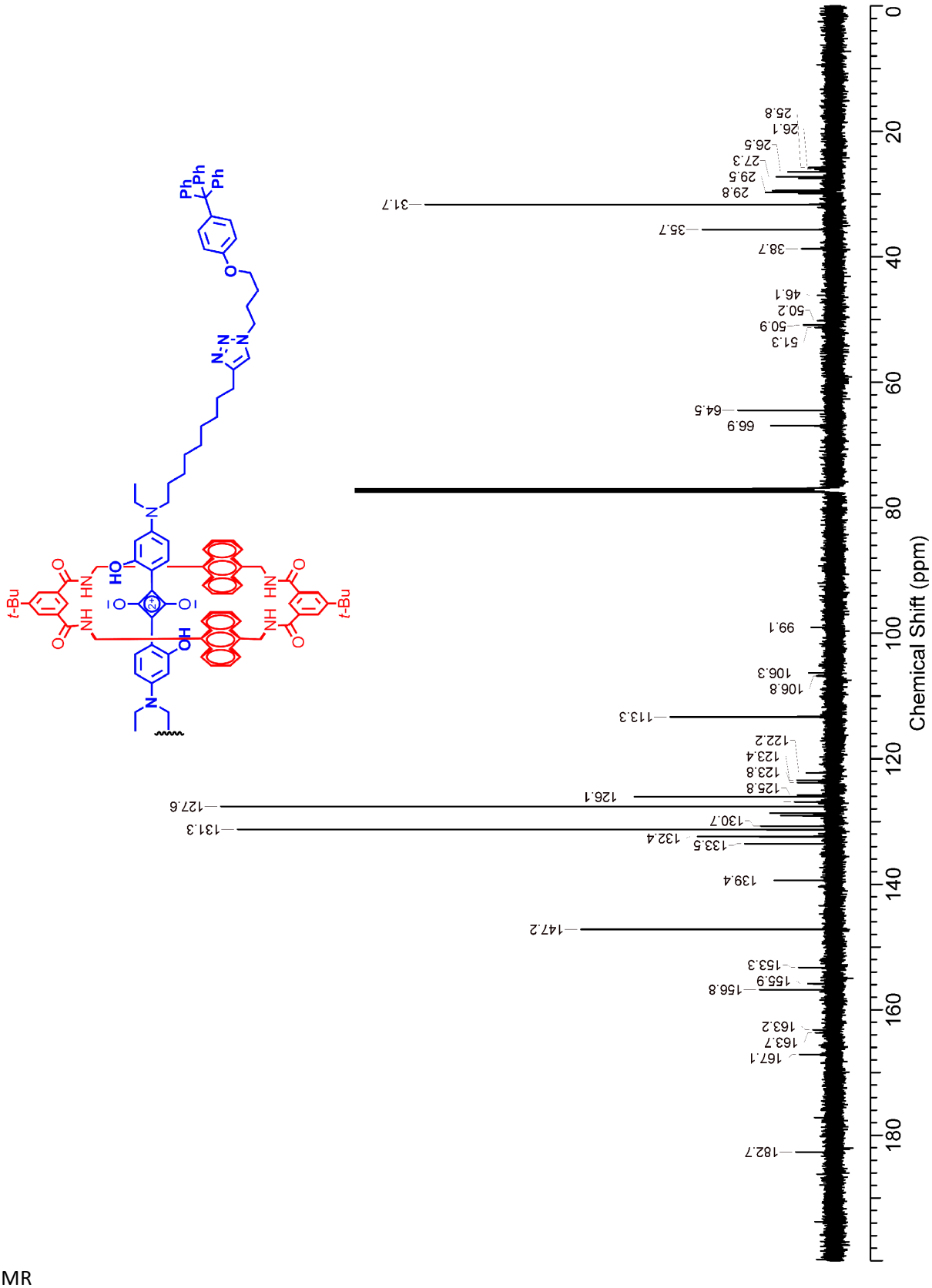
^{1}H NMR


13.1
18.6
27.3
28.6
28.9
31.7
35.6
38.2
46.0
51.2
68.4
84.9
111.5
117.1
123.0
124.1
125.9
128.7
130.6
133.2
133.5
153.0
153.1
167.4
178.9
184.3
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)
t-Bu
t-Bu
NH HN
NH HN
O
O
N
N
2+
9

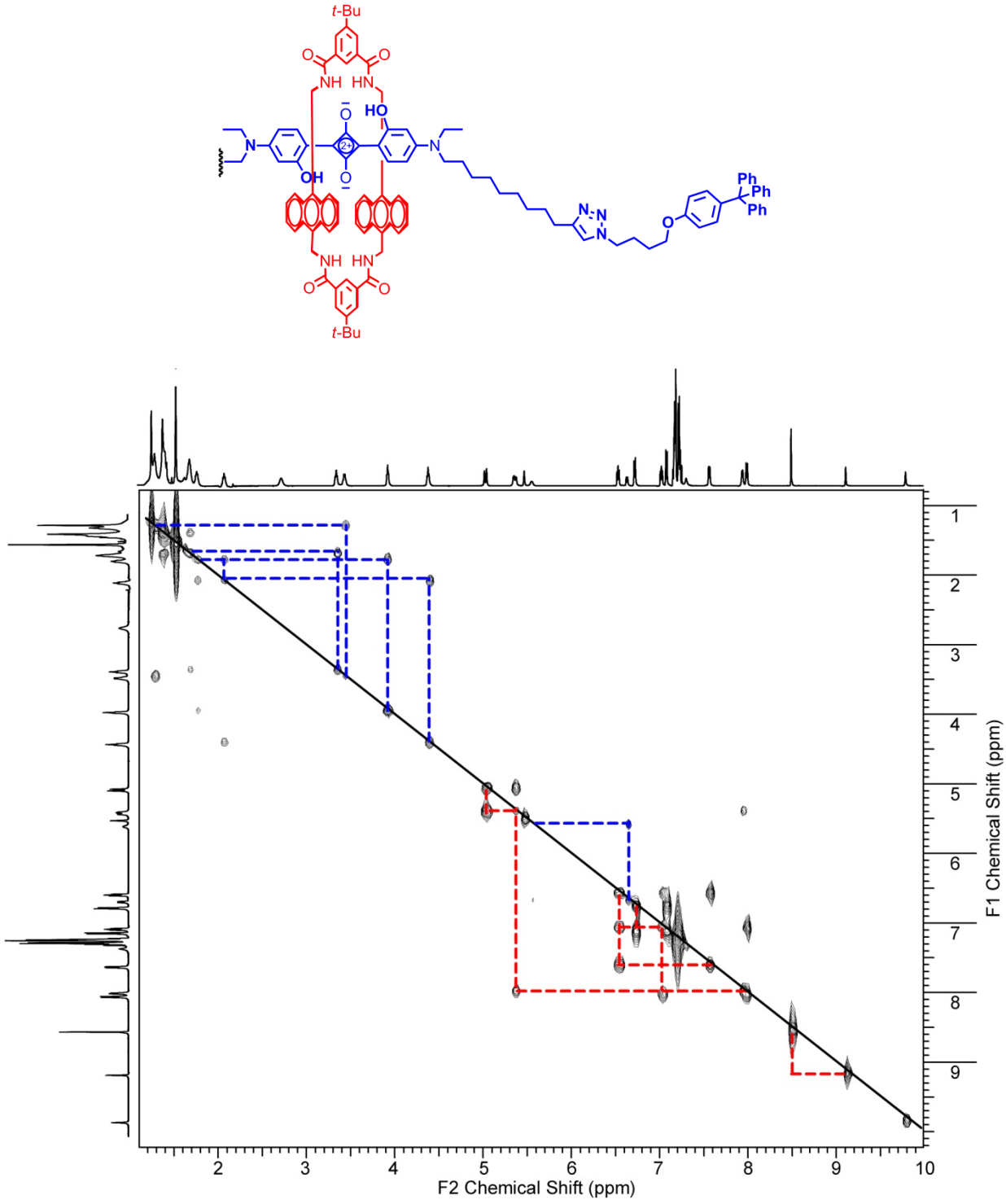
^{13}C NMR


A
5
7-12
13
18
17
14
6
4
19
16
D,D'
1
3
B
C
OH
E'
NH
E
F
2
20
F'
21
Ph
15
Chemical Shift (ppm)
Chemical Shift (ppm)

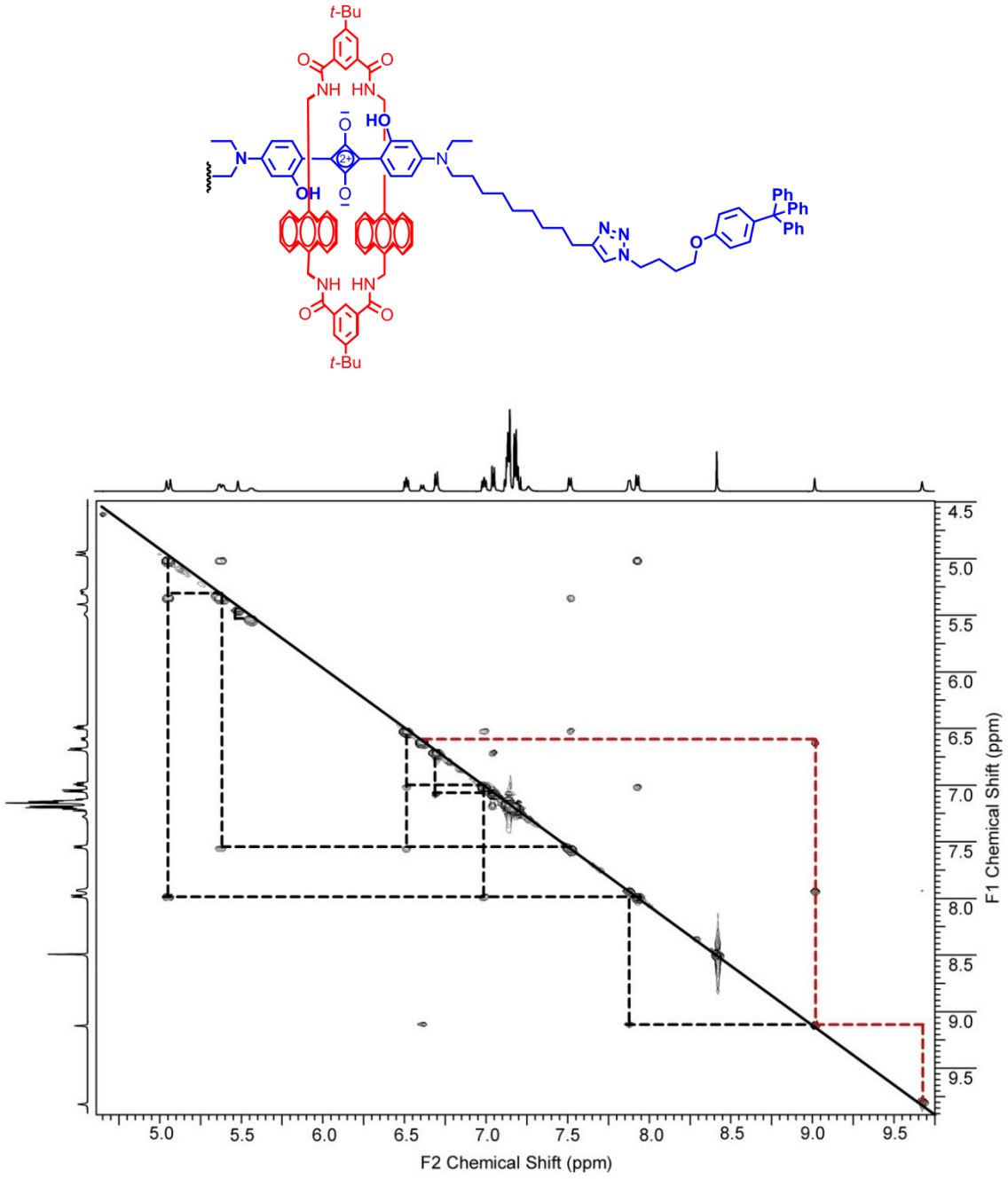
^{1}H NMR


Ph
Ph
Ph
O
N
N
N
HO
OH
NH
HN
O
t-Bu
31.7
35.7
38.7
46.1
50.2
50.9
51.3
64.5
66.9
99.1
106.3
106.8
113.3
122.2
123.4
123.8
125.8
126.1
127.6
130.7
131.3
132.4
133.5
139.4
147.2
153.3
155.9
156.8
163.2
163.7
167.1
182.7
25.8
26.1
26.5
27.3
29.5
29.8
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)

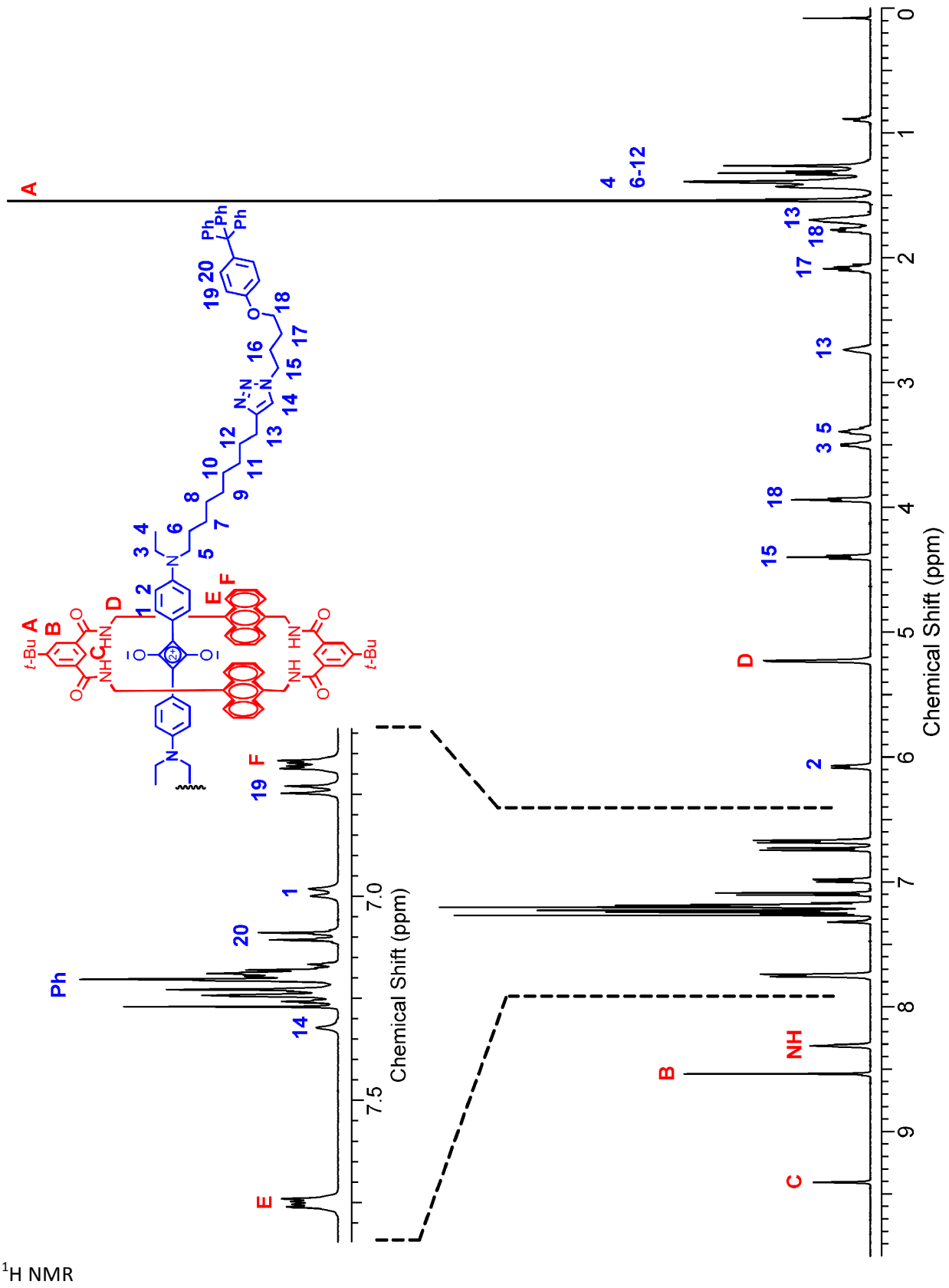
^{13}C NMR



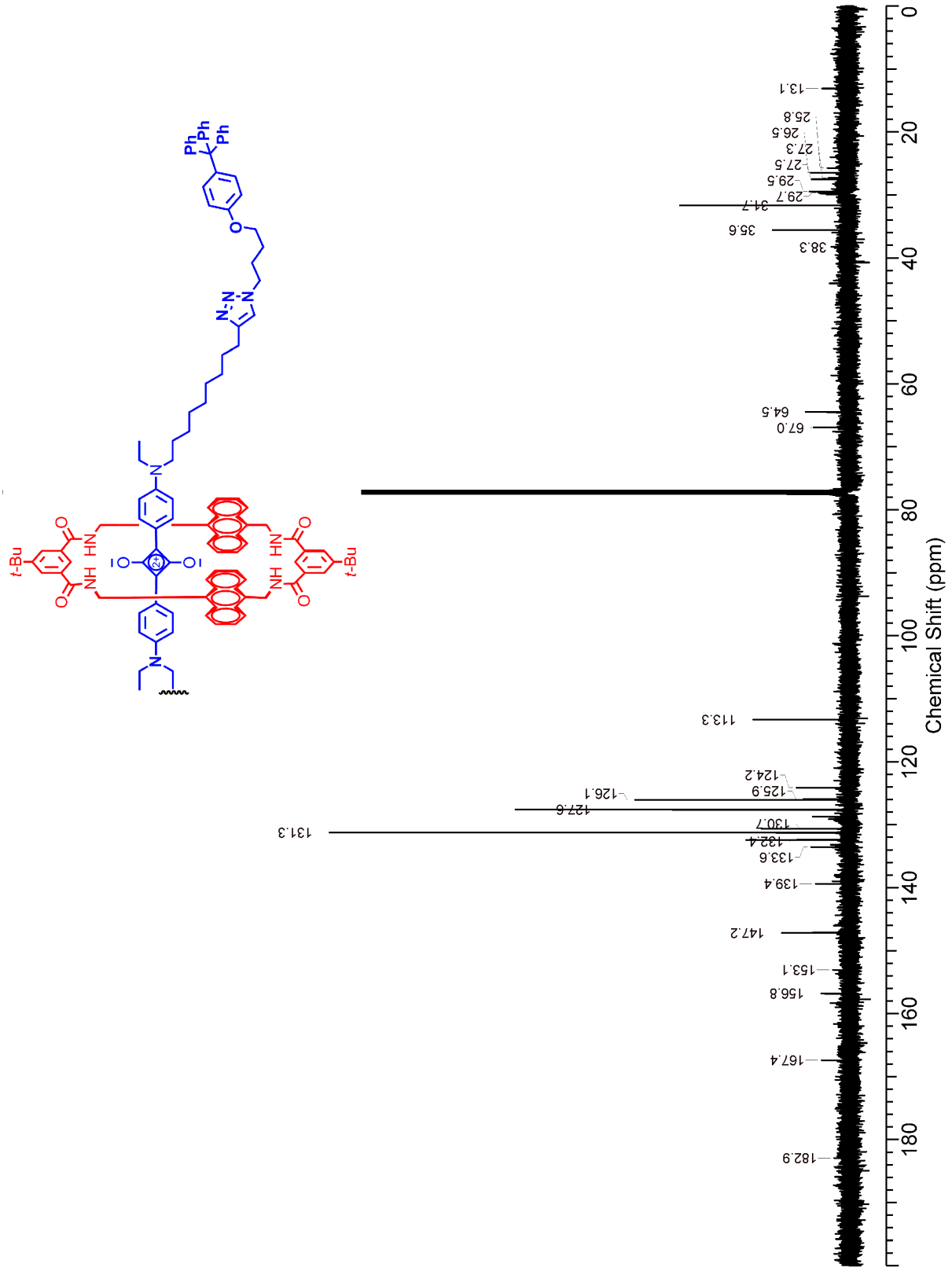
COSY of **4** (structure shown above spectrum) in $CDCl_3$. Red and blue cross-peaks correspond to macrocycle and squaraine proton couplings, respectively. COSY was used to make definitive squaraine assignments in the ^1H NMR spectrum.



ROESY of **4** (structure shown above spectrum) in $CDCl_3$ (mixing time is 400 ms). Red cross-peaks correspond to correlations between the squaraine and macrocycle. ROESY was used to make definitive anthracene assignments in the ^1H NMR spectrum.



^{1}H NMR


Ph
Ph
Ph
O
N
N
N
N
N
t-Bu
NH
HN
O
O
O
O
t-Bu
13.1
25.8
26.5
27.3
27.5
29.5
29.7
31.7
35.6
38.3
64.5
67.0
113.3
124.2
125.9
126.1
127.6
130.7
131.3
132.4
133.6
139.4
147.2
153.1
156.8
167.4
182.9
0
20
40
60
80
100
120
140
160
180
Chemical Shift (ppm)

^{13}C NMR

H. References

[S1] H. Sekizaki, K. Itoh, E. Toyota and K. Tanizawa, *Heterocycles*, 2003, **59**, 237-243.
[S2] R. Nacario, S. Kotakonda, D. M. D. Fouchard, L. M. V. Tillekeratne and R. A. Hudson, *Org. Lett.*, 2005, **7**, 471-474.
[S3] K.-Y. Law, F. C. Bailey and L. J. Bluett, *Can. J. Chem.*, 1986, **64**, 1607-1619.
[S4] E. H. Christen, R. J. Gübeli, B. Kaufmann, L. Merkel, R. Schoenmakers, N. Budisa, M. Fussenegger, W. Weber and B. Wiltschi, *Org. Biomol. Chem.*, 2012, **10**, 6629-6632.
[S5] K.-Y. Law, *J. Phys. Chem.*, 1987, **91**, 5184-5193.
[S6] Brightness is defined as the product of molar absorptivity and quantum yield.
[S7] Initial scans indicate the maximum absorbance at 664 nm, but the structure equilibrates slightly and after 1 hour the maximum absorbance is 662 nm.
[S8] J. J. Gassensmith, E. Arunkumar, L. Barr, J. M. Baumes, B. C. Noll and B. D. Smith, *J. Am. Chem. Soc.*, 2007, **129**, 15054-15060.
[S9] (a) Y. G. Isgor, E. U. Akkaya *Tetrahedron Lett.* 1997, **38**, 7417-7420. (b) K. J. Wallace, M. Gray, Z. Zhong, V. M. Lynch, E. V. Anslyn, *Dalton Trans.* 2005, 2436-2441.