Supplementary Data

Irreversible paper-based profluorescent nitroxide probe for selective detection of ascorbic acid

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Contents

Experimental sections

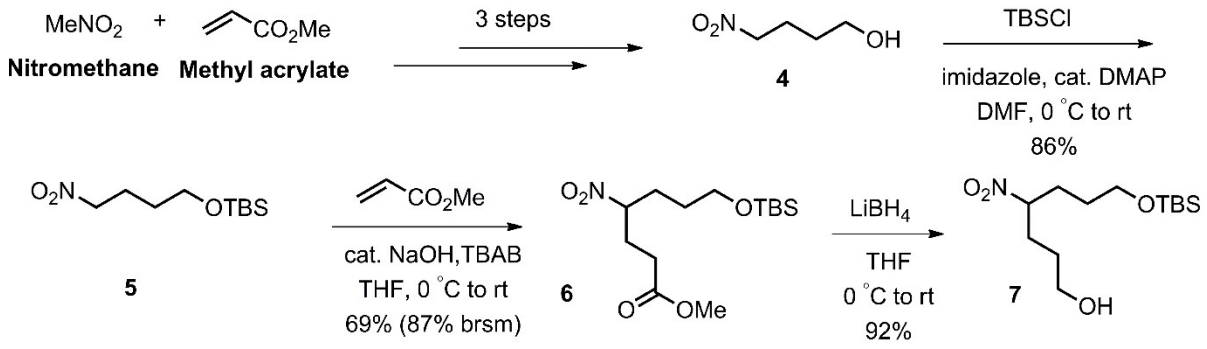
Chemicals and instruments

Chemical reagents were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Analytical grade solvents used for synthesis and analysis were used as received from suppliers. Solvents for extraction and column chromatography were distilled at their boiling point ranges prior to use. Analytical grade solvents for reactions were used as received from suppliers or distilled prior to use using standard procedures. Thin-layer chromatography (TLC) was performed on SiliaPlateTM R10011B-323 (Silicycle) or silica gel 60 GF254 (Merck) and were visualized by fluorescence quenching under UV light and *p*-anisaldehyde stain. Column chromatography was performed on SiliaFlash® G60 Silica (60-200 μm, Silicycle). ^{1}H NMR (300 and 500 MHz) and ^{13}C NMR (75 and 125 MHz) spectroscopic data were recorded on a 300 and 500 MHz Bruker FT-NMR Ultra Shield spectrometer using residual solvent as an internal standard. Chemical shifts are expressed in parts per million (ppm) downfield from TMS (δ 0.00) and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quatet; qn, quintet; m, multiplet. Infrared spectra (IR) were measured on a Perkin Elmer Spectrum GX FT-IR system and recorded on wavenumber (cm^{-1}). High-resolution ESI mass spectra were obtained on a liquid chromatograph-mass spectrometer (2690, LCT, Waters, Micromass). The ESR spectra were performed using an ESR Bruker system, ELEXSYS E-500 model at X-band microwave frequencies (approximately 9.85 GHz), with the following parameters: a central field of 3517 G, a scanning field of 3552 G, 1024 data points, a modulation amplitude of 10 mT, a receiver gain of 60 dB, a time constant of 10.24 ms, a conversion time of 20.48 ms, and a microwave power of 2 mW.

Synthetic routes of probes ProN6 and ProN7

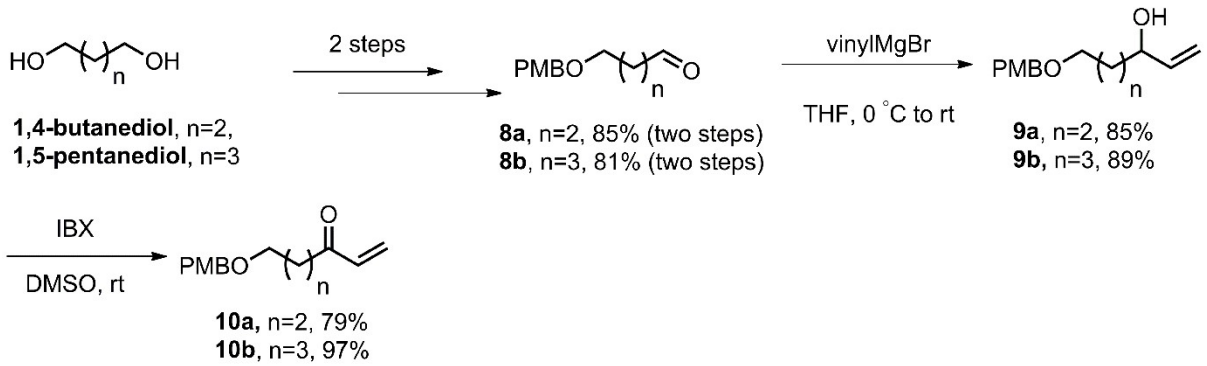
Synthesis of profluorescent nitroxide probes **ProN6** and **ProN7** were performed as shown in **Scheme 1S-4S**. Firstly, nitro compound **7** was ultimately obtained from nitromethane and methyl acrylate following the Yoo's procedure [1] as illustrated in **Scheme 1S**. We started from known δ-hydroxyl nitro compound **4**, which was protected with TBS group [2] to yield silyl ether **5** in 86%. In the presence of catalytic sodium hydroxide (NaOH) and tetrabutylammonium bromide (TBAB), the nitro compound **5** underwent Michael addition on methyl acrylate to generate γ-nitro ester **6** [3] in 69% yield (87% brsm), and a small amount of

undesired double addition adduct was also formed. Reduction of methyl ester **6** gave nitro compound **7** in 92% yield using $LiBH_4$ as a reducing agent.



Scheme 1S. Synthesis of nitro compound **7**

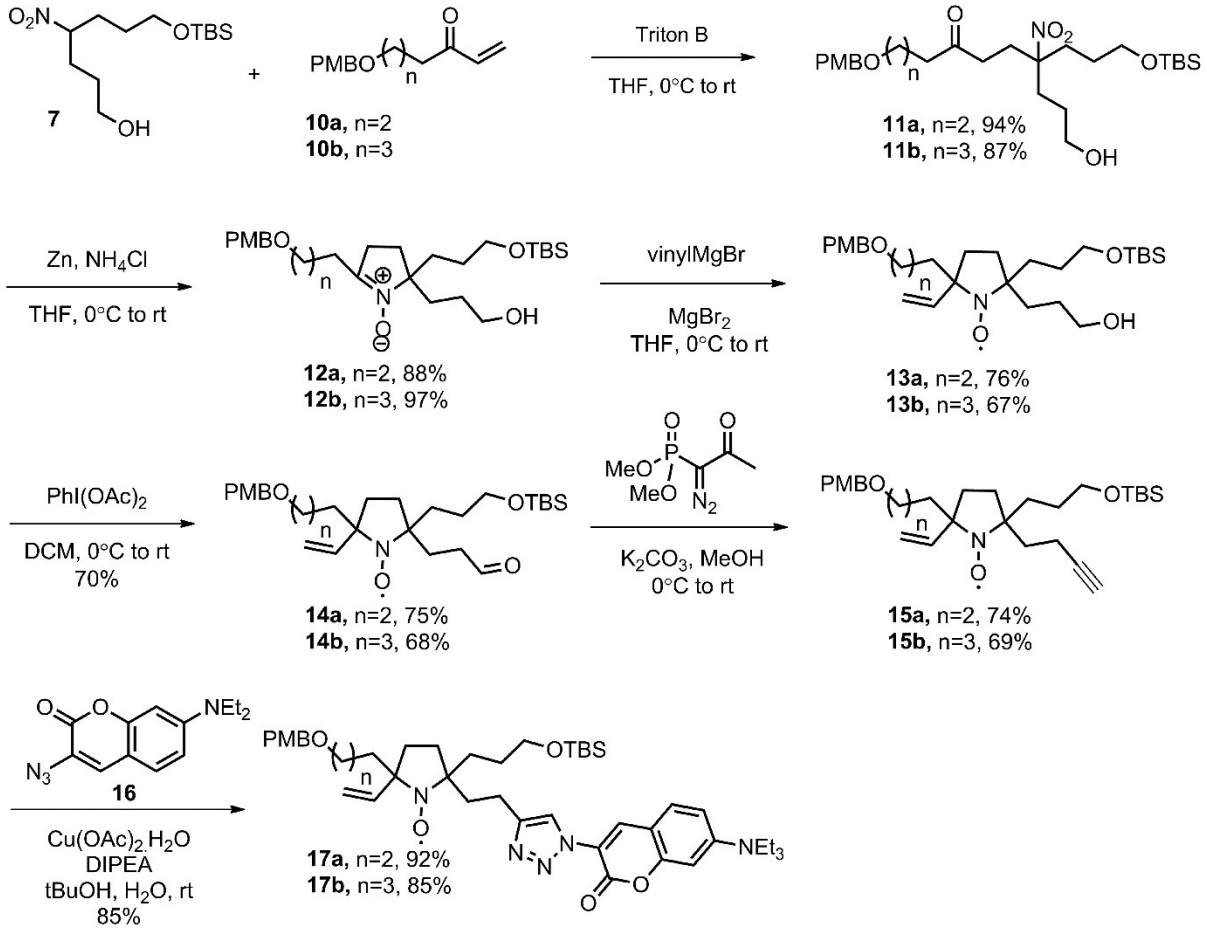
As shown in **Scheme 2S**, vinyl ketone **10a** and **10b** was prepared from 1,4-butanediol and 1,5-pentanediol as starting materials carrying out in 2 steps using Kumar and O'Hagan's protocols [4, 5] to get known aldehydes **8a** and **8b**, respectively. Vinylation of aldehyde **8a** generated allyl acohol **9a** in 85% yield by treatment with vinylMgBr [6]. Allylic alcohol **9a** was then oxidized with IBX to accomplish the corresponding ketone **10a** in 79% yield. Synthetic sequences of vinyl ketone **10b** were the same as those of vinyl ketone **10b** by using aldehyde **8b** as a precursor.



Scheme 2S. Synthetic route of vinyl ketones **10a** and **10b**

With intermediates in hands, the union of nitro compound **7** and vinyl ketone **10a** via Michael addition afforded γ-nitro ketone **11a** in 94% yield utilizing triton B as a base as illustrated in **Scheme 3S**. Upon treatment with Zn powder in the presence of a stoichiometric amount of ammonium chloride, **11a** underwent reductive cyclization [7] to form nitrone **12a** in 88% yield. Exposure of **12a** to vinylmagnesium bromide promoted vinylation utilizing a substoichiometric amount of magnesium bromide ($MgBr_2$) to give the key nitroxide **13a** in

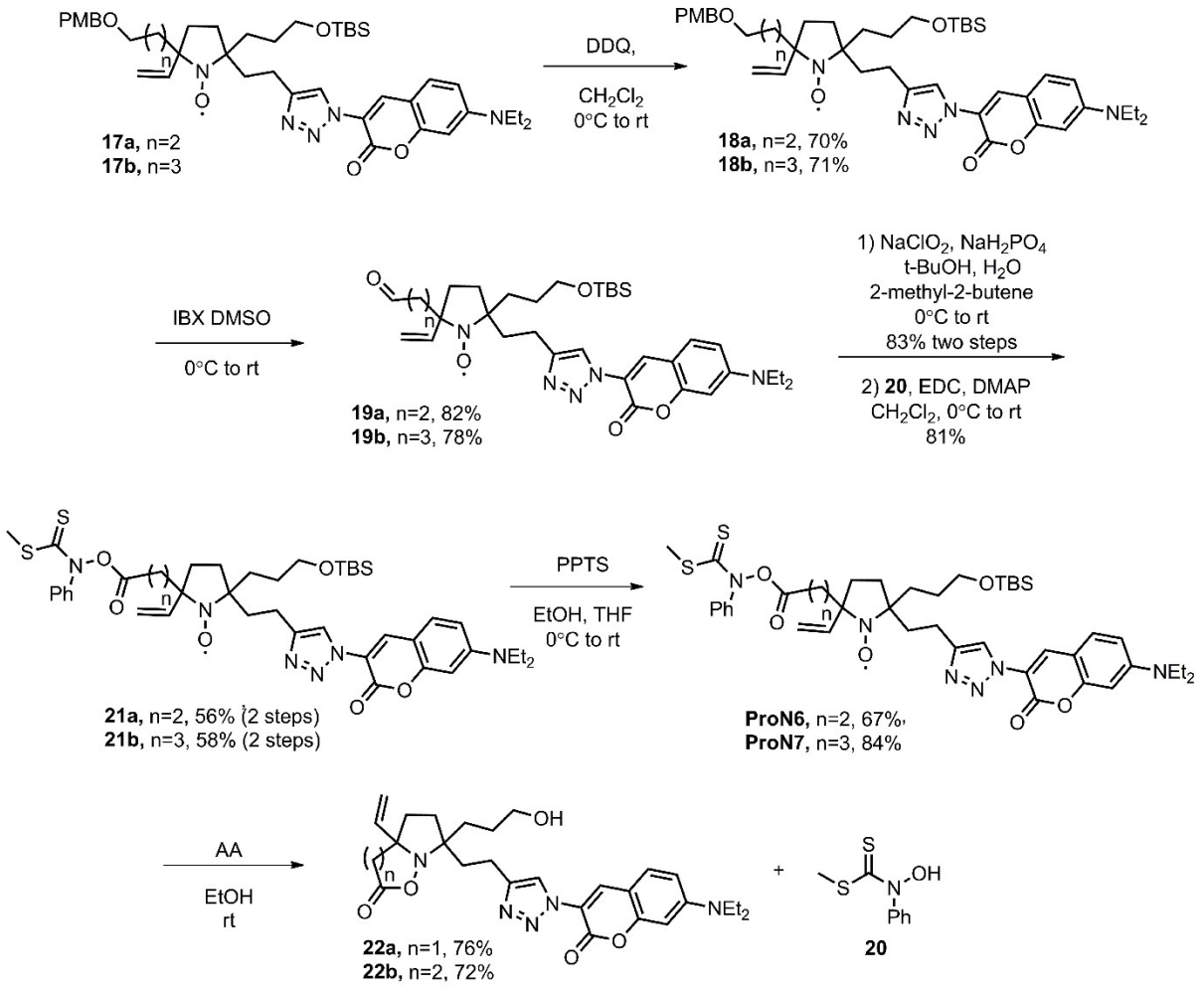
76% yield after immediate oxidation by air. Oxidation of primary alcohol **13a** delivered aldehyde **14a** in 75% yield using iodobenzenediacetate ($PhI(OAc)_2$). The resulting aldehyde **14a** was then subjected to Bestmann-Ohira homologation to produce terminal alkyne **15a** in 74% yield. Installation of coumarin fluorophore **16** on nitroxide **15a** via click coupling using cupric acetate hydrate ($Cu(OAc)_2.H_2O$) as a catalyst generated triazole **17a** in 92% yield. Synthetic sequences of triazole **17b** were the same as those of **17a** by using **10b** as a precursor.



Scheme 3S. Preparation of triazoles **17a** and **17b**

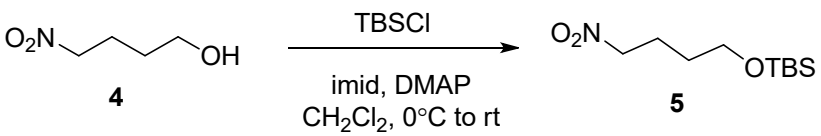
As shown in **Scheme 4S**, PMB group of **17a** were cleaved to obtain primary alcohol **18a** in 70% yield. Alcohol **18a** was then oxidized by IBX to afford aldehyde **19a** in 82% yield. Pinnick oxidation of **19a**, followed by ester coupling of generated carboxylic acid and thiohydroxamic acid **20** provided thiohydroxamate ester **21a** in 56% yield over two steps using EDC and DMAP as coupling agents. Desilylation of **21a** was completed to gratifyingly achieve the desired probe **ProN6** in 67% yield. The synthetic pathway of probe **ProN7** was the same sequence as that of **ProN6** except one more carbon atom (n) on the vinyl ketone. Additionally, **ProN6** and **ProN7** were treated with stoichiometric amount of AA to generate cyclized *O*-

acylalkoxylamines **22a** and **22b**, respectively, for identification of products and proof that **ProN6** and **ProN7** can act as sensors for AA. Notably, conversion of all synthesized paramagnetic nitrioxides to diamagnetic ethoxylamines by trapping with ethyl radical, generated by triethylborane (Et_3B) under opened air, allowed indirect determination of nitroxide structures using ^{1}H and ^{13}C NMR. Information of IR spectroscopy and mass spectrometry could be obtained directly from nitroxides.

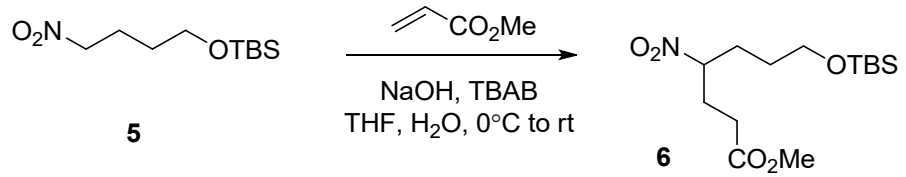


Scheme 4S. Complete synthesis of profluorescent nitroxide probes **ProN6** and **ProN7**

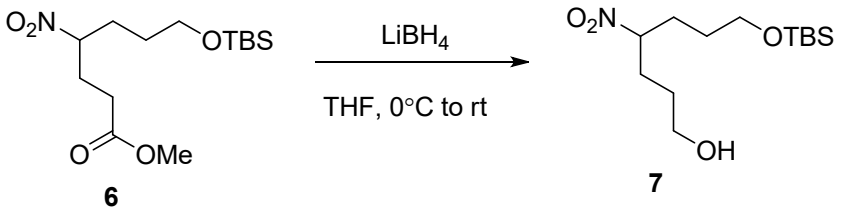
Synthetic methods and characterization



***tert*-Butyl(4-nitrobutoxy)diphenylsilane (5).** To a solution of 4-nitrobutane-1-ol (**4**, 6.64 g, 55.7 mmol) in CH_2Cl_2 were added imidazole (7.96 g, 116.9 mmol) and DMAP (338 mg, 3.02 mmol) respectively. The resulting mixture was cooled to 0 °C, and TBSCl (16.7 g, 111 mmol) was added. The reaction mixture was stirred for 16 hours. CH_2Cl_2 was removed under reduced pressure. The crude residue was purified by column chromatography with 20% CH_2Cl_2 in hexane to give 11.57 g (89% yield) of **5** as a colorless viscous oil: R_f = 0.67 (20% CH_2Cl_2 in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.43 (t, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 2.12 (qn, *J* = 7.2 Hz, 2H), 1.61 (qn, *J* = 7.2 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 75.7 (CH_2), 62.1 (CH_2), 29.4 (CH_2), 26.0 (3 x CH_3), 24.6 (CH_2), 18.4 (C), -5.3 (2 x CH_3) ppm; IR (thin film): 2955, 2858, 1557, 1256, 1102, 838 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{23}NO_3S_i$ $(M+Na)^+$ 256.1345, found 256.1348.



Methyl 7-((*tert*-butyldimethylsilyl)oxy)-4-nitroheptanoate (6). To a solution of *tert*-butyldimethyl(4-nitrobutoxy)silane (**5**, 7.50 g, 32.1 mmol) in THF:H_2O (24:8 mL) were added TBAB (1.06 g, 32.1 mmol), NaOH (128 mg, 3.21 mmol) and methyl acrylate (2.87 mL, 32.1 mmol), respectively at 0 °C. The reaction mixture was stirred overnight. THF was removed under reduced pressure. Crude product was extracted with CH_2Cl_2 (3 x 20 mL). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography with 2% EtOAc in hexane to give 7.02 g (69% yield, 87% brsm) of **6** as a colorless viscous oil: R_f = 0.33 (2% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63-4.55 (m, 1H), 3.68 (s, 3H), 3.66-3.56 (m 2H), 2.41-2.34 (m, 2H), 2.30-2.19 (m, 1H), 2.18-2.09 (m, 1H), 2.08-1.96 (m, 1H), 1.93-1.81 (m, 1H), 1.57-1.48 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 172.5 (C), 87.7 (CH), 62.0 (CH_2), 52.0 (CH_3), 30.6 (CH_2), 30.1 (CH_2), 28.8 (2 x CH_2), 26.0 (3 x CH_3), 18.4 (C), -5.3 (2 x CH_3) ppm; IR (thin film): 2955, 2858, 1736, 1555, 1258, 1104, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{29}NO_5S_i$ $(M+Na)^+$ 342.1713, found 342.1715.



6 **7**

7-((tert-butyldimethylsilyl)oxy)-4-nitroheptan-1-ol (7). To a solution of methyl 7-((*tert*-butyldimethylsilyl)oxy)-4-nitroheptanoate (**6**, 7.04 g, 22.1 mmol) in THF (110 mL) was added $LiBH_4$ (4M in THF, 11 mL, 22 mmol) at 0 °C. The reaction mixture was stirred for 3 hours. Water (3 mL) was added to reaction mixture at 0 °C. White precipitate was filtered under reduced pressure. THF in the filtrate was removed under reduced pressure. The crude product was extracted with CH_2Cl_2 (3 x 15 mL). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography with 30% EtOAc in hexane to give 5.90 g (92% yield) of **7** as a colorless viscous oil: R_f = 0.43 (30% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.61-4.52 (m, 1H), 3.73-3.65 (m, 2H), 3.64-3.55 (m, 2H), 2.17-1.97 (m, 2H), 1.95-1.81 (m, 2H), 1.65-1.48 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 88.7 (CH), 62.0 (CH_2), 61.6 (CH_2), 30.6 (CH_2), 30.4 (CH_2), 28.8 (2 x CH_2), 26.0 (3 x CH_3), 18.3 (C), -5.3 (2 x CH_3) ppm; ppm IR (thin film): 3420, 2953, 2857, 1542, 1098, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{29}NO_4S_i$ $(M+Na)^+$ 314.1764, found 314.1761. check calculated mass

General procedure for vinylation on aldehyde: To a solution of an aldehyde derivative (1.0 equiv) in anhydrous THF (0.2 M) was slowly added vinyl magnesiumbromide (1.1 equiv) at 0 °C. The reaction mixture was stirred for an hour. Then, excess vinyl magnesiumbromide was quenched with sat. NH_4Cl at 0 °C to until the bubble disappeared and white precipitate was observed. The white solid was filtered under reduced pressure. THF in the filtrate was removed under reduced pressure. Distilled water was added to the crude product, which was extracted with EtOAc (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding allyl alcohol derivative.

General procedure for Michael addition: To a solution of 7-((tert-butyldimethylsilyl)oxy)-4-nitroheptan-1-ol (**7**, 1.0 equiv) in THF (0.2 M) was added triton B (40% in methanol, 10 mol%) at 0 °C. The resulting mixture was stirred for a few minutes. Then a solution of a vinyl ketone derivative (1.4 equiv) in THF (0.2 M) was added to the above solution. The reaction

mixture was stirred for 5 hours. After the reaction mixture was quenched by sat. NH_4Cl at 0 °C, THF was removed under reduced pressure. Distilled water was added to the crude product, which was then extracted with CH_2Cl_2 (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding γ-nitro ketone derivative.

General procedure for reductive cyclization: To a solution of a γ-nitro ketone derivative (1.0 equiv) in THF:H_2O (0.1 M, 3:1 by volume) was added NH_4Cl (1.1 equiv). The resulting mixture was cooled to 0 °C, and Zn powder (4.0 equiv) was slowly added. The reaction mixture was stirred overnight. ZnO and excess Zn powder was filtered through celite pad. After THF in the filtrate was removed under reduced pressure, the crude product was extracted with EtOAc (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding nitrone derivative.

General procedure for vinylation on nitrone: To a solution of a nitrone derivative (1.0 equiv) in anhydrous THF (0.2 M) was added $MgBr_2$ (50 mol%). After the resulting mixture was cooled to 0 °C, a solution of vinyl magnesiumbromide (1M in THF, 6.0 equiv) was added to above solution. The reaction mixture was stirred overnight. After the starting material was completely consumed, sat. NH_4Cl was slowly added to the above solution at 0 °C to quench excess vinyl magnesium bromide until the bubble disappeared, and the white precipitate was observed. The white solid was filtered under reduced pressure. THF in the filtrate was removed under reduced pressure. Distilled water was added to the crude product, which was extracted with EtOAc (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding nitroxide derivative.

General procedure for *N*-oxoammonium oxidation: To a solution of a primary alcohol derivative (1.0 equiv) in anhydrous CH_2Cl_2 (0.1 M) was added $PhI(OAc)_2$ (1.0 equiv) at 0 °C. The resulting mixture was stirred for 4 hours. CH_2Cl_2 was removed under reduced pressure. The crude product was purified by column chromatography to the corresponding aldehyde derivative.

General procedure for Bestmann-Ohira homologation: To a solution of Bestmann-Ohira reagent (1.5 equiv) in methanol (0.25 M) was added K_2CO_3 (2.0 equiv) at 0 °C. The resulting

mixture was stirred for 30 minutes before a solution of aldehyde derivatives (1.0 equiv) in methanol (0.25 M) was slowly added. The reaction mixture was stirred for 6 hours. Methanol was removed under reduced pressure. Water was added to the crude residue, which was extracted with CH_2Cl_2 (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding alkyne derivative.

General procedure for click coupling: To a solution of an alkyne derivative (1.0 equiv) in ^{t}BuOH (0.3 M) were added 3-azido-7-(diethylamino)-2*H*-chromen-2-one (**16**, 1.0 equiv), DIPEA (1.0 equiv) and cupric acetate hydrate (10 mol%) in distilled water, respectively. The reaction mixture was stirred for 6 hours. Extra distilled water was added to crude mixture, which was extracted with CH_2Cl_2 (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding triazole derivative.

General procedure for PMB deprotection: To a solution of a PMB derivative (1.0 equiv) in CH_2Cl_2 (0.1 M) was added DDQ (1.5 equiv) at 0 °C. Distilled water was added to the above solution. The reaction mixture was stirred for 2 hrs. Extra distilled water was added to crude mixture, which was then extracted with CH_2Cl_2 (x3). Combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding primary alcohol derivative.

General procedure for IBX oxidation: To a solution of a primary alcohol derivative (1.0 equiv) in DMSO (0.3 M) was added IBX (1.5 equiv). The mixture was stirred for 4 hrs. After distilled water was added to the above solution, white precipitate was observed. The solid was filtered under reduced pressure. EtOAc was added to the filtrate, which was then washed with distilled water (x6). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography to give the corresponding aldehyde derivative.

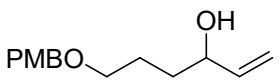
General procedure for Pinnick oxidation and ester coupling: To a solution of an aldehyde derivative (1.0 equiv) in ^{t}BuOH (0.2 M) was added NaH_2PO_4 (2.0 equiv). A solution of NaO_2Cl (2.0 equiv) in distilled water (0.2 M) and 2-methyl-2-butene (1.1 equiv) were added to the above solution, respectively. The reaction mixture was stirred for 1.5 hrs. Extra distilled water was added to crude mixture, and pH of reaction mixture was adjusted to 6 by adding 1M H_2SO_4. The crude product was then extracted with EtOAc (x3). Combined organic layer was

dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the corresponding carboxylic acid derivative without further purification. To a solution of the carboxylic acid derivative (1.0 equiv) in CH_2Cl_2 (0.2 M) were added DMAP (10 mol%) and EDC (1.5 equiv) at 0 °C, respectively. The reactuion mixture was stirred for 30 min, and a solution of thiohydroxamic acid (1.2 equiv) in in CH_2Cl_2 (0.2 M) was added to the above solution. The reaction mixture was stirred for 3 hrs. CH_2Cl_2 was removed under reduced pressure to obtain the crude product, which was purified by column chromatography to give the corresponding thiohydroxamate ester derivative.

General procedure for TBS deprotection: To a solution of a thiohydroxamate ester derivative (1.0 equiv) in THF:EtOH (0.1 M, 2:1 by volume) was added PPTS (2.5 equiv) at 0 °C. The reaction mixture was allowed to stir at room temperature overnight. Solvents were removed under reduced pressure to give the crude product, which was then purified by column chromatography to give the corresponding profluorescent nitroxide probe.

General procedure for reductive lactonization: To a solution of a profluorescent nitroxide probe derivative (1.0 equiv) in ethanol (0.1 M) was added AA (1.5 equiv) at room temperature. The reaction mixture was allowed to stir at room temperature for 1-2 hrs. Ethanol was removed under reduced pressure to give the crude product which was then purified by column chromatography to give the corresponding cyclic *N*-acylamine derivative.

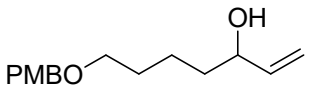
General procedure for nitroxide radical trapping: To a solution of nitroxide derivative (1.0 equiv) in toluene (0.1 M) was added triethylborane (1M in THF, 1.5 equiv) at 0 °C. The reaction mixture was allowed to stir at room temperature under open air for 1-2.5 hrs. Toluene was removed in *vacuo*. The crude residue was purified by column chromatography to give the corresponding ethoxylamine derivative.



9a

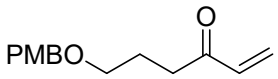
Allyl alcohol 9a: Allyl alcohol **9a** was prepared from aldehyde **8a** (7.05 g, 33.9 mmol) using a general procedure for vinylation on aldehyde. The crude residue was purified by column chromatography with 10% EtOAc in hexane to give 6.84 g of **9a** (85% yield) as a colorless viscous oil: R_f = 0.20 (10% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 5.89-5.77 (m, 1H), 5.19 (td, J = 1.0, 17.2 Hz, 1H), 5.06 (td,

J = 1.0, 10.5 Hz, 1H), 4.43 (s, 2H), 4.11-4.05 (m, 1H), 3.77 (s, 3H), 3.46 (t, *J* = 5.9 Hz, 2H), 1.74-1.50 (m, 4H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 159.2 (C), 141.2 (CH), 130.3 (C), 129.4 (2 x CH), 114.4 (CH_2), 113.8 (2 x CH), 72.7 (CH), 72.7 (CH_2), 70.1 (CH_2), 55.3 (CH_3), 34.3 (CH_2), 25.8 (CH_2) ppm; IR (thin film): 3420, 2953, 2847, 1630, 1102, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{20}O_3$ $(M+Na)^+$ 259.1310, found 259.1313.



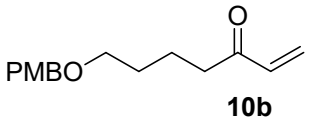
9b

Allyl alcohol 9b: Allyl alcohol **9b** was prepared from aldehyde **8b** (6.21 g, 27.9 mmol) using a general procedure for vinylation on aldehyde. The crude residue was purified by column chromatography with 10% EtOAc in hexane to give 6.21 g of **9b** (89% yield) as colorless viscous oil: R_f = 0.20 (10% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 2H), 5.91-5.80 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.42 (s, 2H), 4.12-4.06 (m, 1H), 3.79 (s, 3H), 3.44 (t, *J* = 6.5 Hz, 2H), 1.67-1.35 (m, 6H); ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 159.2 (C), 141.3 (CH), 130.7 (C), 129.3 (2 x CH), 114.6 (CH_2), 113.8 (2 x CH), 73.1 (CH), 72.6 (CH_2), 70.0 (CH_2), 55.3 (CH_3), 36.8 (CH_2), 29.6 (CH_2), 22.1 (CH_2) ppm; IR (thin film): 3421, 2954, 2847, 1632, 1102, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{22}O_3$ $(M+Na)^+$ 273.1467, found 273.1462.



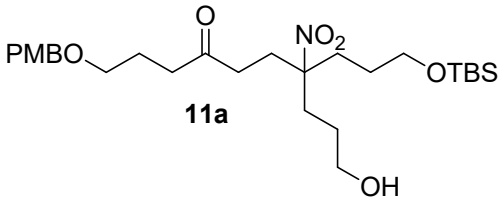
10a

Vinyl Ketone 10a: Vinyl Ketone **10a** was prepared from Allyl alcohol **9a** (6.84 g, 28.9 mmol) using a general procedure for IBX oxidation. The crude residue was purified by column chromatography with 5% EtOAc in hexane to give 5.35 g of **10a** (79% yield) as a colorless viscous oil: R_f = 0.27 (5% EtOAc in hexane); IR (thin film): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.1 Hz, 2H), 6.89 (d, *J* = 9.1 Hz 2H), 6.36 (dd, 10.2, 17.6 Hz 1H), 5.83 (dd, 1.4, 10.2 Hz, 1H), 6.23 (dd, *J* = 1.4, 17.6 Hz, 1H), 4.43 (s, 2H), 3.82 (s, 3H), 3.49 (t, *J* = 7.1 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 1.94 (qn, *J* = 7.1 Hz, 2H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 200.6 (C), 159.3 (C), 136.8 (CH), 130.7 (C), 129.4 (2 x CH), 128.0 (CH_2) 113.9 (2 x CH), 72.7 (CH_2), 69.1 (CH_2), 55.4 (CH_3), 36.3 (CH_2), 24.1 (CH_2) ppm; 2987, 2846, 1690, 1539, 1248, 1096, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{18}O_3$ $(M+Na)^+$ 257.1154, found 257.1150.



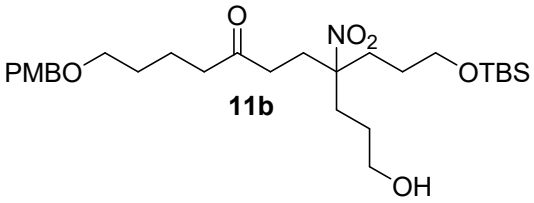
10b

Vinyl Ketone 10b: Vinyl Ketone **10b** was prepared from allyl alcohol **9b** (5.38 g, 21.4 mmol) using a general procedure for IBX oxidation. The crude residue was purified by column chromatography with 5% EtOAc in hexane to give 5.15 g of **10b** (97 % yield) as colorless viscous oil: R_f = 0.27 (5% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4, 2H), 6.33 (dd, J = 10.3, 17.6 Hz, 1H), 6.18 (dd, J = 1.1, 17.6 Hz, 1H), 5.79 (dd, J = 1.1, 10.3 Hz, 1H), 4.41 (s, 2H), 3.78 (s, 3H), 3.44 (t, J = 7.3 Hz, 2H), 2.60 (t, J = 7.3 Hz, 2H), 1.75-1.16 (m, 4H), ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 200.6 (C), 159.1 (C), 136.5 (CH), 130.6 (C), 129.2 (2 x CH), 127.9 (CH_2), 113.7 (2 x CH), 72.5 (CH_2), 69.6 (CH_2), 55.1 (CH_3), 39.1 (CH_2), 29.1 (CH_2), 20.7 (CH_2), ppm; IR (thin film): 2987, 2845, 1692, 1539, 1242, 1094, 832 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}O_3$ $(M+Na)^+$ 271.1310, found 271.1313.



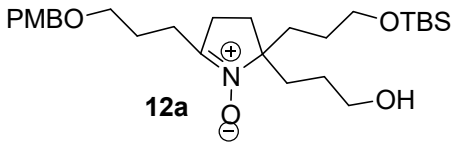
11a

γ-Nitro ketone 11a: γ-Nitro ketone **11a** was prepared from nitro compound **7** (1.26 g, 3.19 mmol) using a general procedure for Michael addition. The crude residue was purified by column chromatography with 20% EtOAc in hexane to give 1.57 g of **11a** (94% yield) as a colorless viscous oil: R_f = 0.30 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 4.36 (s, 2H), 3.77 (s, 3H), 3.58-3.53 (m, 4H), 3.42 (t, J = 6.0 Hz, 2H), 2.47 (t, J = 7.1 Hz, 2H), 2.37-2.32 (m, 2H) 2.20 (brs, 1H), 2.15-2.10 (m, 2H), 1.98-1.89 (m, 4H), 1.84 (qn, J = 6.9 Hz, 2H), 1.42-1.31 (m, 4H), 0.86 (s, 9H), 0.02 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 208.8 (C), 159.2 (C), 130.4 (C), 129.4 (2 x CH), 113.8 (2 x CH), 93.6 (C), 72.5 (CH_2), 69.0 (CH_2), 62.3 (CH_2), 62.0 (CH_2), 55.3 (CH_3), 39.8 (CH_2), 36.7 (CH_2), 32.0 (CH_2), 31.8 (CH_2), 29.5 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 25.9 (3 x CH_3), 24.0 (CH_2), 18.3 (C), -5.3 (2 x CH_3) ppm; IR (thin film): 3442, 2953, 2857, 1716, 1539, 1248, 1096, 835 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{47}NO_7Si$ $(M+Na)^+$ 525.3122, found 525.3123.



11b

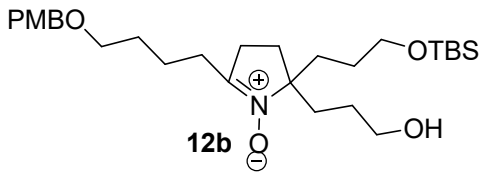
γ-Nitro ketone 11b: γ-Nitro ketone **11b** was prepared from nitro compound **7** (528 mg, 1.81 mmol) using a general procedure for Michael addition. The crude residue was purified by column chromatography with 20% EtOAc in hexane to give 850.1 mg of **11b** (87% yield) as a colorless viscous oil: R_f = 0.23 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.43 (s, 2H), 3.82 (s, 3H), 3.67 (t, *J* = 4.9 Hz, 2H), 3.61 (t, *J* = 5.9 Hz, 2H), 3.45 (t, *J* = 5.9 Hz, 2H), 2.43 (t, J = 6.8 Hz, 2H), 2.40-2.34 (m, 2H), 2.23-2.17 (m, 2H), 2.11-1.91 (m, 4H), 1.72 (brs, 1H), 1.71-1.55 (m, 4H), 1.51-1.37 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 208.8 (C), 159.3 (C), 130.7 (C), 129.4 (2 x CH), 113.9 (2 x CH), 93.7 (C), 72.7 (CH_2), 69.7 (CH_2), 62.4 (CH_2), 62.2 (CH_2), 55.4 (CH_3), 42.7 (CH_2), 36.8 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 29.7 (CH_2), 29.2 (CH_2), 27.1 (CH_2), 26.9 (CH_2), 26.0 (3 x CH_3), 20.7 (CH_2), 18.4 (C), -5.3 (2 x CH_3) ppm; IR (thin film): 3447, 2952, 2855, 1716, 1538, 1248, 1097, 835 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{28}H_{49}NO_7Si$ $(M+Na)^+$ 562.3176, found 562.3170.



12a

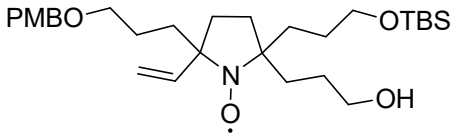
Nitrone 12a: Nitrone **12a** was prepared from γ-nitro ketone **11a** (1.52 g, 2.89 mmol) using a general procedure for reductive cyclization. The crude residue was purified by column chromatography with 20% EtOAc in hexane, followed by 10% methanol in EtOAc to give 1.26 g of **12a** (88% yield) as a colorless viscous oil: R_f = 0.33 (20% EtOAc in methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.63-3.53 (m, 4H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.58-2.53 (m, 4H), 2.10-2.01 (m, 1H), 2.00-1.94 (m, 4H), 1.89-1.80 (m, 2H), 1.77-1.68 (m, 1H), 1.66-1.62 (m, 1H), 1.60-1.46 (m, 1H), 1.43-1.27 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 159.1 (C), 148.3 (C), 130.2 (C), 129.2 (2 x CH), 113.7 (2 x CH), 79.0 (C), 72.6 (CH_2), 69.3 (CH_2), 62.8 (CH_2), 61.8 (CH_2), 55.1 (CH_3), 34.3 (CH_2), 33.8 (CH_2), 28.6 (CH_2), 26.7 (CH_2), 26.3 (CH_2), 25.9 (3 x CH_3), 25.1 (2 x CH_2), 23.9 (CH_2), 18.2 (C), -5.4 (2 xCH_3) ppm; IR (thin

film): 3360, 2928, 2857, 1611, 1249, 1096, 843 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{27}H_{47}NO_5Si$ $(M+Na)^+$ 515.2230, found 515.2215.



12b

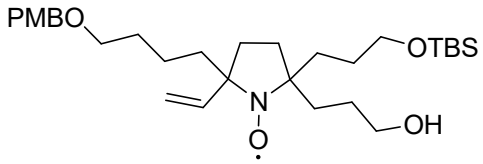
Nitrone 12b: Nitrone **12b** was prepared from γ-Nitro ketone **11b** (2.10 g, 3.89 mmol) using a general procedure for reductive cyclization. The crude residue was purified by column chromatography with 20% EtOAc in hexane, followed by 10% EtOAc in methanol to give 1.91 g (97% yield) of **12b** as a colorless viscous oil: R_f = 0.37 (10% EtOAc in methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (dd, *J* = 8.6 Hz, , 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.66-3.51 (m, 4H), 3.46 (t, *J* = 5.9 Hz, 2H), 2.56 (d, *J* = 7.5 Hz, 2H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.09-1.96 (m, 5H), 1.87-1.76 (m, 2H), 1.68-1.58 (m, 4H), 1.53-1.42 (m, 1H), 1.40-1.30 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 159.1 (C), 148.8 (C), 130.5 (C), 129.3 (2 x CH), 113.8 (2 x CH), 79.2 (C), 72.6 (CH_2), 69.3 (CH_2), 62.9 (CH_2), 62.0 (CH_2), 55.3 (CH_3), 34.5 (CH_2), 33.8 (CH_2), 29.7 (CH_2), 28.5 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 26.4 (3 x CH_3), 26.0 (CH_2), 25.2 (CH_2), 21.8 (CH_2), 18.3 (C), -5.3 (2 x CH_3) ppm; IR (thin film): 3360, 2929, 2856, 1611, 1247, 1096, 843 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{49}NO_5Si$ $(M+Na)^+$ 543.2417, found 543.2420.



13a

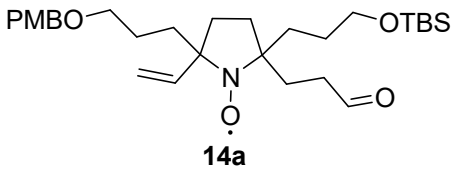
Nitroxide 13a: Nitroxide **13a** was prepared from nitrone **12a** (2.83 g, 5.57 mmol) using a general procedure for vinylation on nitrone. The crude residue was purified by column chromatography with 30% EtOAc in hexane to give 1.26 g of **13a** (76% yield) as a yellow-orange viscous oil: R_f = 0.33 (30% EtOAc in hexane) ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivatives as diastereomers: δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, , 2H), 6.24 (m, 1H), 5.07 (d, *J* = 11.0 Hz, 1H), 4.99 (d, *J* = 17.9 Hz, 1H), 4.41 (s, 2H), 3.78 (s, 3H), 3.77-3.74 (m, 2H), 3.65-3.59 (m, 2H), 3.56-3.53 (m, 2H), 3.41-3.38 (m, 2H), 1.86-1.81 (m, 2H), 1.66-1.60 (m, 4H), 1.58-1.52 (m, 4H), 1.51-1.47 (m, 4H), 1.44-1.40 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivatives as diastereomers: δ 159.2 (C), 140.5 (CH), 130.9 (C), 129.3 (2 x CH),

113.9 (2 x CH), 112.6 (CH_2), 72.6 (CH_2), 71.1 (CH_2), 70.8 (CH_2), 70.6 (C), 67.5 (C), 64.1 (CH_2), 63.9 (CH_2), 55.3 (CH_3), 36.0 (2 x CH_2), 33.3 (CH_2), 30.6 (CH_2), 28.6 (2 x CH_2), 27.9 (CH_2), 26.1 (3 x CH_3), 25.3 (CH_2), 18.4 (C), 14.3 (CH_3), -5.3 (2 x CH_3) ppm; IR (thin film): 3393, 2953, 2857, 1249, 1096, 834 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{50}NO_5Si$ $(M+Na)^+$ 543.3356, found 543.3351.



13b

Nitroxide 13b: Nitroxide **13b** was prepared from nitrone **12b** (319 mg, 0.628 mmol) using a general procedure for vinylation on nitrone. The crude residue was purified by column chromatography with 30% EtOAc in hexane to give 222 mg of **13a** (67% yield) as a yellow-orange viscous oil: R_f = 0.40 (30% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) of ethoxylamine derivatives as diastereomers: δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.18 (dd, *J* = 11.4, 17.8 Hz, 1H), 5.06 (d, *J* = 11.4 Hz, 1H), 4.98 (d, *J* = 17.8 Hz, 1H) 4.40 (s, 2H), 3.80-3.73 (m, 2H), 3.77 (s, 3H), 3.61-3.52 (m, 4H), 3.40 (t, *J* = 6.5 Hz, 2H), 1.83-1.81 (m, 2H), 1.62-1.54 (m, 6H), 1.48-1.56 (m, 8H), 1.30-1.18 (m, 2H), 1.10 (t, *J* = 6.9 Hz, 3H), 0.87 (s, 9H), 0.02 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) of ethoxylamine derivatives as diastereomers: δ 159.2 (C), 140.3 (CH), 130.8 (C), 129.3 (2 x CH), 113.8 (2 x CH), 112.6 (CH_2), 72.5 (CH_2), 71.1 (CH_2), 70.9 (C), 70.1 (CH_2), 67.4 (C), 64.1 (CH_2), 63.8 (CH_2), 55.3 (CH_3), 39.4 (CH_2), 36.1 (CH_2), 33.3 (CH_2), 30.5 (CH_2), 30.4 (CH_2), 28.6 (CH_2), 28.4 (CH_2) 27.8 (CH_2), 26.1 (3 x CH_3), 21.4 (CH_2), 18.4 (C), 14.3 (CH_3), -5.2 (2 x CH_3) ppm; IR (thin film): 3420, 2951, 2857, 1247, 1095, 834 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{52}NO_5Si$ $(M+Na)^+$ 557.3512, found 557.3514.

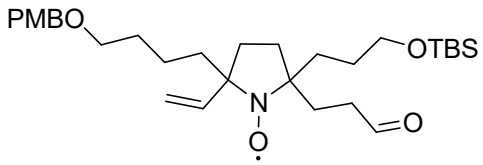


14a

Aldehyde 14a: Aldehyde **14a** was prepared from alcohol **13a** (1.50 g, 2.88 mmol) using a general procedure for *N*-oxoammonium oxidation. The crude residue was purified by column chromatography with 10% EtOAc in hexane to give 1.13 g (75% yield) of **14a** as a yellow-orange viscous oil: R_f = 0.40 (30% EtOAc in hexane); Major diastereomer (968 mg): ^{1}H NMR

(500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 9.79 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.22-6.16 (m, 1H) 5.05 (d, *J* = 11.1 Hz, 1H), 4.96 (d, *J* = 18.0 Hz, 1H), 4.39 (s, 2H), 3.75 (s, 3H), 3.70 (qn, *J* = 7.3 Hz, 2H), 3.58-3.48 (m, 2H), 3.38 (t, *J* = 6.4 Hz, 2H), 2.75-2.72 (m, 1H), 2.44-2.34 (m, 1H), 1.84-1.80 (m, 1H), 1.75-1.72 (m, 2H), 1.70-1.65 (m, 2H), 1.55-1.44 (m, 6H), 1.40-1.35 (m, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.02 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) δ 203.1 (CH), 159.1 (C), 140.0 (CH), 130.7 (C), 129.2 (2 x CH), 113.7 (2 x CH), 112.6 (CH_2), 72.5 (CH_2), 71.3 (CH_2), 70.5 (CH_2), 70.4 (C), 66.5 (C), 63.8 (CH_2), 55.2 (CH_3), 39.8 (CH_2), 36.1 (CH_2), 33.2 (CH_2), 31.2 (CH_2), 30.4 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 25.9 (3 x CH_3), 25.1 (CH_2), 18.3 (C), 14.2 (CH_3), -5.3 (2 x CH_3) ppm; IR (thin film): 2952, 1724, 1513, 1248, 1099, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{48}NO_5Si$ $(M+Na)^+$ 541.3199, found 541.3195.

Minor diastereomer (162 mg): ^1H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 9.71 (s, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, , 2H), 6.34-6.15 (m, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 5.01 (d, *J* = 18.1 Hz, 1H), 4.41 (s, 2H), 3.79 (s, 3H), 3.75-3.71 (m, 2H), 3.62-3.60 (m, 2H), 3.42-3.38 (m, 2H), 2.49-2.44 (m, 1H), 2.38-2.31 (m, 1H), 2.12-1.98 (m, 1H), 1.88-1.69 (m, 4H), 1.62-1.41 (m, 6H), 1.10 (t, *J* = 7.1 Hz, 3H) 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) δ 203.1 (CH), 159.2 (C), 140.8 (CH), 131.9 (C), 129.3 (2 x CH), 113.9 (2 x CH), 112.7 (CH_2), 72.6 (CH_2), 71.4 (CH_2), 70.8 (CH_2), 70.4 (C), 67.7 (C), 63.8 (CH_2), 55.3 (CH_3), 40.3 (CH_2), 36.6 (CH_2), 35.5 (CH_2), 31.1 (CH_2), 29.6 (CH_2), 28.3 (CH_2), 27.9 (CH_2), 26.1 (3 x CH_3), 25.2 (CH_2), 18.4 (C), 14.4 (CH_3), -5.3 (2 x CH_3) ppm; IR (thin film): 2952, 1724, 1513, 1248, 1099, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{47}NO_5Si$ $(M+Na)^+$ 541.3199, found 541.3195.

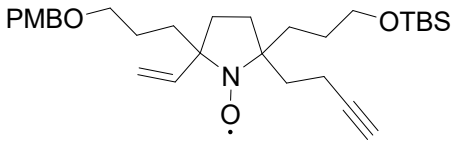


14b

Aldehyde 14b: Aldehyde **14b** was prepared from alcohol **13b** (2.20 g, 4.11 mmol) using a general procedure for *N*-oxoammonium oxidation. The crude residue was purified by column chromatography with 10% EtOAc in hexane to give 1.46 g (68% yield) of **14b** as a yellow-orange viscous oil: R_f = 0.43 (10% EtOAc in hexane); Major diastereomer (1.22 g): ^1H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 9.77 (s, 1H), 7.21 (brs, 2H), 6.82 (brs, 2H), 6.20-6.15 (m, 1H), 5.04-5.03 (m, 1H), 4.95 (d, *J* = 15.0 Hz, 1H), 4.37 (s, 2H), 3.73 (s, 3H),

3.71-3.67 (m, 2H), 3.54-3.51 (m, 2H), 3.41-3.37 (m, 2H), 2.77-2.67 (m, 1H), 2.41-2.34 (m, 1H), 1.86-1.81 (m, 1H), 1.78-1.63 (m, 4H), 1.58-1.44 (m, 7H), 1.41-1.33 (m, 2H), 1.29-1.24 (m, 2H), 1.08-1.07 (m, 3H), 0.88 (s, 9H), 0.02 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) δ 202.7 (CH), 159.0 (C), 140.3 (CH), 130.7 (C), 129.0 (2 x CH), 113.6 (2 x CH), 112.3 (CH_2), 72.3 (CH_2), 71.1 (CH_2), 70.6 (CH_2), 69.9 (C), 66.5 (C), 63.6 (CH_2), 55.0 (CH_3), 39.7 (CH_2), 39.4 (CH_2), 33.2 (CH_2), 31.0 (CH_2), 30.4 (CH_2), 30.2 (CH_2), 28.4 (CH_2), 28.3 (CH_2), 25.9 (3 x CH_3), 21.2 (CH_2), 18.2 (C), 14.1 (CH_3), -5.4 (2 x CH_3) ppm; IR (thin film): 2952, 2857, 1724, 1513, 1248, 1099, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{52}NO_5Si$ $(M+Na)^+$ 555.3356, found 555.3360.

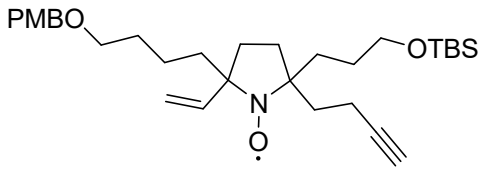
Minor diastereomer (243 mg): R_f = 0.44 (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.29-6.19 (m, 1H), 5.11-5.09 (m, 1H), 5.02 (d, *J* = 16.7 Hz, 1H), 4.43 (s, 2H), 3.81 (s, 3H), 3.78-3.72 (m, 2H), 3.62-3.60 (m, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.54-2.48 (m, 1H), 2.41-2.32 (m, 1H), 2.11-2.00 (m, 1H), 1.90-1.85 (m, 1H), 1.79-1.68 (m, 4H), 1.62-1.53 (m, 6H), 1.47-1.40 (m, 2H), 1.31-1.26 (m, 2H), 1.11 (t, *J* = 6.5 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 203.1 (CH), 159.3 (C), 140.7 (CH), 131.0 (C), 129.2 (2 x CH), 113.9 (2 x CH), 112.8 (CH_2), 72.6 (CH_2), 71.5 (CH_2), 70.7 (C), 70.2 (CH_2) 69.9 (C), 63.8 (CH_2), 55.4 (CH_3), 40.3 (2 x CH_2), 35.6 (CH_2), 35.0 (CH_2), 31.3 (CH_2), 30.5 (CH_2), 29.6 (CH_2) 27.9 (2 x CH_2), 26.1 (3 x CH_3), 21.5 (CH_2), 18.5 (C), 14.4 (CH_3), -5.1 (2 x CH_3) ppm.



15a

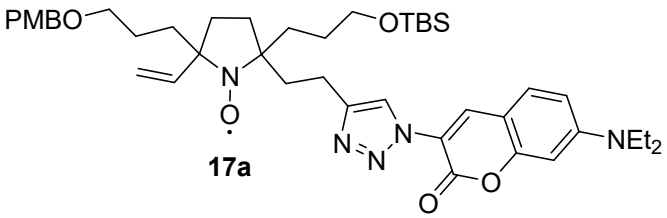
Alkyne 15a: Alkyne **15a** was prepared from aldehyde **14a** (major diastereomer, 2.91 g, 5.61 mmol) using a general procedure for Bestmann-Ohira homologation. The crude residue was purified by column chromatography with 10% EtOAc in hexane to give 2.14 g (74% yield) of **15a** as a yellow-orange viscous oil: R_f = 0.37 (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.26-6.40 (m, 1H), 5.01 (d, *J* = 11.1 Hz, 1H), 4.98 (d, *J* = 17.9 Hz, 1H), 4.42 (s, 2H), 3.78 (s, 3H), 3.75-3.72 (m, 2H), 3.60-3.50 (m, 2H), 3.40 (t, *J* = 6.1 Hz, 2H), 2.62-2.54 (m, 1H), 2.15-2.09 (m, 1H), 1.92 (s, 1H), 1.84-1.77 (m, 2H) 1.66-1.61 (m, 4H), 1.57-1.55 (m, 4H), 1.49-1.45 (m, 2H), 1.38-1.32 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR,

DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 159.2 (C), 140.4 (CH), 130.8 (C), 129.2 (2 x CH), 113.8 (2 x CH), 112.5 (CH_2), 85.8 (C), 72.5 (CH_2), 71.2 (CH_2), 70.7 (CH_2), 70.2 (C), 67.7 (CH), 66.8 (C), 63.9 (CH_2), 55.2 (CH_3), 38.4 (CH_2), 36.5 (CH_2), 33.0 (2 x CH_2), 30.3 (CH_2), 28.4 (CH_2), 26.0 (3 x CH_3), 25.1 (CH_2), 18.3 (C), 14.3 (CH_3), 13.6 (CH_2), -5.2 (2 x CH_3) ppm; IR (thin film): 3310, 2951, 2857, 1513, 1248, 1099, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{48}NO_4Si$ $(M+Na)^+$ 537.3250, found 537.3246.



15b

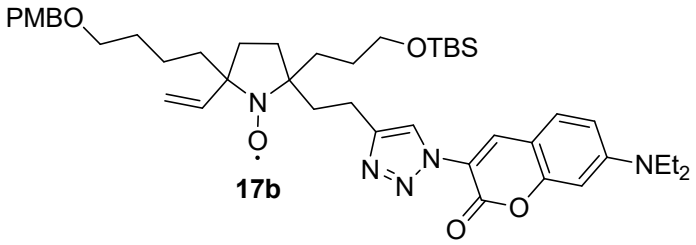
Alkyne 15b: Alkyne **15b** was prepared from aldehyde **14b** (major diastereomer, 1.60 g, 3.0 mmol) using a general procedure for Bestmann-Ohira homologation. The crude residue was purified by column chromatography with 10% EtOAc in hexane to give 1.10 g (66% yield) of **15b** as a yellow-orange viscous oil: R_f = 0.40 (10% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.30-6.21 (m, 1H), 5.10-4.99 (m, 2H), 4.41 (s, 2H), 3.78 (s, 3H), 3.75-3.70 (m, 2H), 3.62-3.60 (m, 2H), 3.42 (t, *J* = 6.6 Hz, 2H), 2.27-2.21 (m, 1H), 2.15-2.00 (m, 2H), 1.91 (s, 1H), 1.87-1.78 (m, 2H) 1.73-1.68 (m, 1H), 1.61-1.58 (m, 4H), 1.52-1.42 (m, 6H), 1.32-1.25 (m, 2H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 159.2 (C), 140.8 (CH), 130.9 (C), 129.2 (2 x CH), 113.8 (2 x CH), 112.4 (CH_2), 85.7 (C), 72.5 (CH_2), 71.3 (CH_2), 70.4 (C), 70.2 (CH_2), 67.7 (CH), 66.8 (C), 63.8 (CH_2), 55.3 (CH_3), 40.2 (CH_2), 36.6 (CH_2), 35.3 (CH_2), 30.8 (CH_2), 30.5 (CH_2), 28.3 (CH_2), 28.2 (CH_2), 27.7 (CH_2), 26.1 (3 x CH_3), 21.3 (CH_2), 18.3 (C), 14.3 (CH_3), -5.2 (2 x CH_3) ppm; IR (thin film): 3310, 2952, 2856, 1513, 1248, 1098, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{31}H_{50}NO_4Si$ $(M+Na)^+$ 551.3407, found 551.3404.



17a

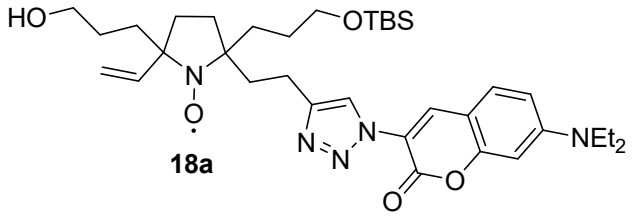
Triazole 17a: Triazole **17a** was prepared from alkyne **15a** (2.04 g, 3.96 mmol) using a general procedure for click coupling. The crude residue was purified by column chromatography with

20% EtOAc in hexane, followed by 40% EtOAc in hexane to give 2.82 g (92% yield) of **17a** as a brown-yellow viscous oil: R_f = 0.37 (40% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.17 (s, 1H), 8.14 (s, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 9.0 Hz, 1H), 6.33 (s, 1H), 6.22-6.14 (m, 1H), 4.97 (d, *J* = 11.1 Hz, 1H), 4.91 (d, *J* = 17.9 Hz, 1H), 4.29 (s, 2H), 3.75-3.74 (m, 2H), 3.62 (s, 3H), 3.50-3.41 (m, 2H), 3.33-3.30 (m, 2H), 3.25 (q, *J* = 7.0 Hz, 4H), 3.16-3.08 (m, 1H), 2.63-2.57 (m, 1H), 1.87-1.83 (m, 1H), 1.77-1.71 (m, 2H), 1.67-1.63 (m, 2H), 1.56-1.54 (m, 2H), 1.51-1.43 (m, 6H), 1.38-1.31 (m, 1H), 1.06 (t, *J* = 7.0 Hz, 6H), 1.03 (t, *J* = 7.0 Hz, 3H), 0.77 (s, 9H), -0.07 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 158.8 (C), 156.5 (C), 155.3 (C), 151.1 (C), 148.5 (C), 140.6 (CH), 133.7 (CH), 130.6 (C), 129.5 (CH), 128.8 (2 x CH), 121.0 (CH), 116.9 (C), 113.4 (2 x CH), 112.0 (CH_2), 109.7 (CH), 106.8 (C), 96.6 (CH), 72.1 (CH_2), 70.9 (CH_2), 70.4 (CH_2), 70.0 (C), 66.9 (C), 63.6 (CH_2), 54.9 (CH_3), 44.6 (2 x CH_2), 38.6 (CH_2), 36.3 (CH_2), 32.9 (CH_2), 30.3 (CH_2), 28.2 (2 x CH_2), 25.7 (3 x CH_3), 24.9 (CH_2), 20.5 (CH_2), 18.0 (C), 14.0 (CH_3), 12.2 (2 x CH_3), -5.5 (2 x CH_3) ppm; IR (thin film): 2953, 2856, 1723, 1622, 1607, 1524, 1454, 1248, 1096, 835 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{43}H_{62}N_5O_6Si$ $(M+Na)^+$ 795.4367, found 795.4349.



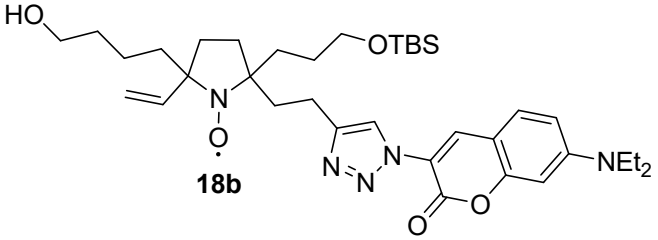
Triazole 17b: Triazole **17b** was prepared from alkyne **15b** (589 mg, 1.11 mmol) using a general procedure for click coupling. The crude residue was purified by column chromatography with 40% EtOAc in hexane to give 772 mg (85% yield) of **17a** as a brown-yellow viscous oil: R_f = 0.37 (40% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: 8.34 (s, 1H), 8.28 (s, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.67 (dd, *J* = 2.4, 8.9 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 6.28-6.20 (m, 1H), 5.12-5.11 (m, 1H), 5.05 (d, *J* = 15.0 Hz, 1H), 4.43 (s, 2H), 3.79 (s, 3H), 3.63-3.59 (m, 1H), 3.57-3.54 (m, 1H), 3.49-3.43 (m, 6H), 3.28-3.08 (m, 1H), 2.83-2.65 (m, 1H), 2.03-1.90 (m, 1H), 1.75-1.71 (m, 2H), 1.64-1.52 (m, 12H), 1.48-1.41 (m, 1H), 1.37-1.27 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H), 1.18-1.15 (m, 3H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 158.8 (C), 156.7 (C), 155.4 (C), 151.1 (C), 148.6 (C), 140.3 (CH), 134.0 (CH), 130.5 (C), 129.7 (CH), 128.9 (2 x CH), 121.1 (CH),

116.9 (C), 113.4 (2 x CH), 112.1 (CH_2), 109.7 (CH), 106.8 (C), 96.6 (CH), 72.2 (CH_2), 71.0 (CH_2), 70.2 (C), 69.8 (CH_2), 66.7 (C), 63.7 (CH_2), 54.9 (CH_3), 44.7 (2 x CH_2), 39.8 (CH_2), 38.8 (CH_2), 32.9 (CH_2), 30.4 (CH_2), 30.1 (CH_2), 28.3 (2 x CH_2), 25.8 (3 x CH_3), 21.1 (CH_2), 20.5 (CH_2), 18.1 (C), 14.1 (CH_3), 12.2 (CH_3), -5.5 (2 x CH_3) ppm; IR (thin film): 2952, 2857, 1723, 1623, 1607, 1514, 1430, 1248, 1098, 835 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{44}H_{64}N_5O_6Si$ $(M+Na)^+$ 829.4524, found 829.4519.



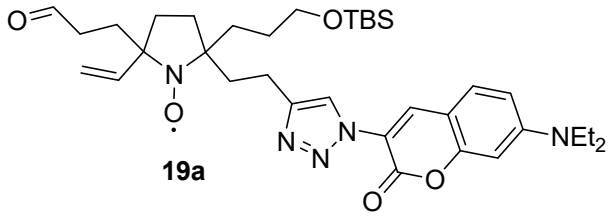
18a

Alcohol 18a: Alcohol **18a** was prepared from triazole **17a** (2.37 g, 3.23 mmol) using a general procedure for PMB deprotection. The crude residue was purified by column chromatography with 20% EtOAc in hexane, followed by 40% EtOAc in hexane to give 1.47 g (70% yield) of **18a** as a yellow viscous oil: R_f = 0.17 (20% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.24 (s, 1H), 8.19 (s, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 6.56 (dd, *J* = 1.8, 8.9 Hz, 1H), 6.43 (d, *J* = 1.8 Hz, 1H), 6.23-6.17 (m, 1H), 5.01 (d, *J* = 11.1 Hz, 1H), 4.95 (d, *J* = 17.9 Hz, 1H), 3.76-3.74 (m, 2H), 3.57 (t, *J* = 6.4 Hz, 2H), 3.51-3.43 (m, 2H), 3.34 (q, *J* = 7.0 Hz, 4H), 3.17-3.07 (m, 1 H), 2.73-2.62 (m, 2H), 1.89-1.82 (m, 2H), 1.76-1.58 (m, 4H), 1.54-1.46 (m, 6H), 1.38-1.32 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 6H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.80 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative δ 156.9 (C), 155.6 (C), 151.4 (C), 148.7 (C), 140.7 (CH), 134.3 (CH), 129.8 (CH), 121.3 (CH), 117.1 (C), 112.3 (CH_2), 110.0 (CH), 107.1 (C), 96.9 (CH), 71.1 (CH_2), 70.3 (C), 67.3 (C), 63.8 (CH_2), 63.2 (CH_2), 44.9 (2 x CH_2), 38.7 (CH_2), 36.0 (CH_2), 33.0 (CH_2), 30.6 (CH_2), 28.6 (CH_2), 28.4 (CH_2), 28.1 (CH_2), 25.9 (3 x CH_3), 20.7 (CH_2), 18.2 (C), 14.2 (CH_3), 12.3 (2 x CH_3), -5.3 (2 x CH_3) ppm; IR (thin film): 3406, 2953, 1724, 1622, 1607, 1430, 1355, 1132, 1041, 833 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{35}H_{54}N_5O_5Si$ $(M+Na)^+$ 675.3792, found 675.3788.



18b

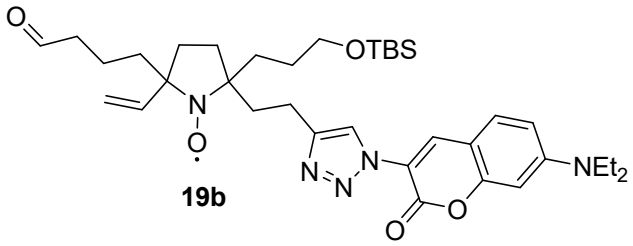
Alcohol 18b: Alcohol **18b** was prepared from triazole **17b** (368 mg, 0.468 mmol) using a general procedure for PMB deprotection. The crude residue was purified by column chromatography with 20% EtOAc in hexane, followed by 40% EtOAc in hexane to give 221 mg (71% yield) of **18b** as a yellow viscous oil: R_f = 0.20 (20% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.34 (s, 1H), 8.28 (s, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 6.66 (d, *J* = 8.9 Hz, 1H), 6.55 (s, 1H), 6.28-6.22 (m, 1H), 5.12 (d, *J* = 8.9 Hz, 1H), 5.03 (d, *J* = 17.5 Hz, 1H), 3.93-3.80 (m, 2H), 3.65 (t, *J* = 6.2 Hz, 2H), 3.60 (m, 1H), 3.45 (q, *J* = 7.0 Hz, 4H), 3.22-3.13 (m, 1H), 2.78-2.71 (m, 1H), 2.00-1.84 (m, 2H), 1.84-1.67 (m, 8H), 1.60-1.54 (m, 6H), 1.47-1.41 (m, 1H), 1.38-1.32 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 6H), 1.15-1.13 (m, 3H), 0.88 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 156.6 (C), 155.3 (C), 151.1 (C), 148.5 (C), 140.2 (CH), 134.0 (CH), 129.6 (CH), 121.1 (CH), 116.6 (C), 112.0 (CH_2), 109.7 (CH), 106.7 (C), 96.5 (CH), 70.9 (CH_2), 70.2 (C), 66.7 (C), 63.6 (CH_2), 62.1 (CH_2), 44.6 (2 x CH_2), 39.7 (CH_2), 38.6 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 30.3 (CH_2), 28.1 (CH_2), 25.7 (3 x CH_3), 20.7 (2 x CH_2), 20.4 (CH_2) 18.0 (C), 14.0 (CH_3), 12.1 (2 x CH_3), -5.5 (2 x CH_3) ppm; IR (thin film): 3360, 2932, 1723, 1607, 1430, 1354, 1132, 1042, 834 cm^{-1}; $C_{36}H_{56}N_5O_5Si$ $(M+Na)^+$ 689.3948, found 689.3944.



19a

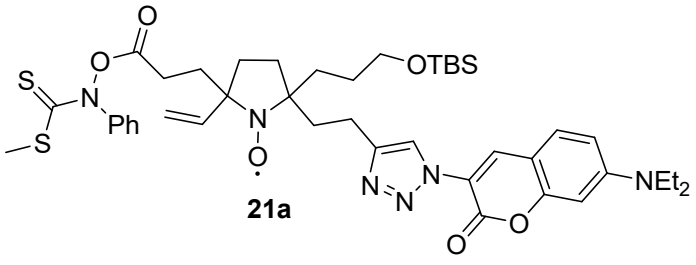
Aldehyde 19a: Aldehyde **19a** was prepared from Alcohol **18a** (120 mg, 0.18 mmol) using a general procedure for IBX oxidation. The crude residue was purified by column chromatography with 30% EtOAc in hexane to give 96 mg (82% yield) of **19a** as a yellow viscous oil: R_f = 0.30 (30% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of ethoxylamine derivative: δ 9.77 (s, 1H), 8.34 (s, 1H), 8.26 (s, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 6.67 (dd, *J* = 2.4, 8.9 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.26 (dd, *J* = 11.4, 17.1 Hz, 1H), 5.13 (d, *J* = 11.4 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 3.87-3.79 (m, 2H), 3.59-3.50 (m, 2H), 3.44 (q, *J* = 7.1 Hz, 4 H), 3.22-3.08 (m, 1H), 2.76-2.66 (m, 1H), 2.54-2.41 (m, 2H), 2.03-1.92 (m, 2H), 1.87-1.81 (m, 2H), 1.76-1.70 (m, 2H), 1.63-1.61 (m, 2H), 1.57-1.47 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 6H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.02 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) of ethoxylamine derivative: δ 202.4 (CH), 156.8 (C), 155.5 (C), 151.2 (C), 148.4 (C), 139.9 (CH), 134.2 (CH), 129.7 (CH), 121.2 (CH), 116.9 (C), 113.0 (CH_2), 109.8 (CH), 106.9 (C), 96.7

(CH), 71.1 (CH_2), 69.6 (C), 67.1 (C), 63.7 (CH_2), 44.8 (2 x CH_2), 39.8 (CH_2), 38.6 (CH_2), 32.9 (CH_2), 31.4 (CH_2), 30.3 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 25.8 (3 x CH_3), 20.6 (CH_2), 18.1 (C), 14.1 (CH_3), 12.3 (2 x CH_3), -5.4 (2 x CH_3) ppm; IR (thin film): 2954, 2858, 1724, 1623, 1607, 1429, 1354, 1132, 1039, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{35}H_{52}N_5O_6Si$ $(M+Na)^+$ 673.3635, found 673.3629.



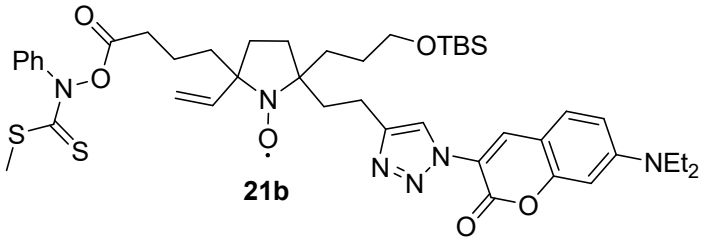
19b

Aldehyde 19b: Aldehyde **19b** was prepared from alcohol **18b** (375 mg, 0.562 mmol) using a general procedure for IBX oxidation. The crude residue was purified by column chromatography with 20% EtOAc in hexane to give 293 mg (78% yield) of **19a** as a yellow viscous oil: R_f = 0.33 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) of ethoxylamine derivative: δ 9.76 (s, 1H), 8.35 (s, 1H), 8.27 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 6.66 (dd, *J* = 8.8 Hz, 1H), 6.55 (s, 1H), 6.29-6.20 (m, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 5.05 (d, *J* = 18.0 Hz, 1H), 3.91-3.78 (m, 2H) 3.60-3.52 (m, 2H), 3.45 (q, *J* = 7.0 Hz, 4H), 3.22-3.11 (m, 1H), 2.76-2.69 (m, 1H), 2.45-2.41 (m, 2H), 2.04-1.86 (m, 2H), 1.81-1.70 (m, 4H), 1.68-1.59 (m, 6H), 1.55-1.52 (m, 4H), 1.24 (t, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) of ethoxylamine derivative: δ 202.2 (CH), 156.6 (C), 155.4 (C), 151.2 (C), 148.4 (C), 140.2 (CH), 134.0 (CH), 129.6 (CH), 121.1 (CH), 116.8 (C), 112.4 (CH_2), 109.8 (CH), 106.8 (C), 96.6 (CH), 71.0 (CH_2), 70.1 (C), 67.0 (C), 63.6 (CH_2), 44.7 (2 x CH_2), 44.1 (CH_2), 39.2 (CH_2), 38.5 (CH_2), 33.0 (CH_2), 30.4 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 25.7 (3 x CH_3), 20.5 (CH_2), 18.0 (C), 17.3 (CH_2), 14.1 (CH_3), 12.2 (2 x CH_3), -5.5 (2 x CH_3) ppm; IR (thin film): 2954, 2858, 1731, 1614, 1429, 1354, 1132, 1099, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{36}H_{54}N_5O_6Si$ $(M+Na)^+$ 687.3792, found 687.3785.



21a

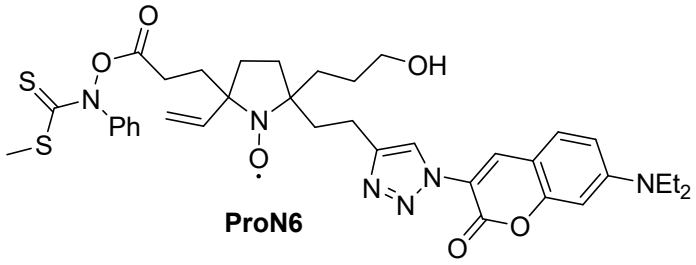
Thiohydroxamate ester 21a: Thiohydroxamate ester **21a** was prepared from aldehyde **19a** (970 mg, 1.49 mmol) using a general procedure for Pinnick oxidation and ester coupling. The crude residue was purified by column chromatography with 20% EtOAc in hexane to give 708 mg (56% yield, two steps) of **21a** as a brown yellow viscous oil: R_f = 0.53 (30% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.26 (s, 1H), 8.22 (s, 1H), 7.51 (d, *J* = 6.5 Hz, 2H), 7.41-7.35 (m, 3H), 7.31 (d, *J* = 8.9 Hz, 1H), 6.59 (dd, *J* = 2.0, 8.9 Hz, 1H), 6.46 (s, 1H), 6.27-6.18 (m, 1H), 5.05 (d, *J* = 10.6 Hz 1H), 4.99 (d, *J* = 16.9 Hz, 1H), 3.83-3.72 (m, 2H), 3.56-3.50 (m, 2H), 3.36 (q, *J* = 7.1 Hz, 4H), 3.16-3.06 (m, 1H), 2.70-2.61 (m, 1H), 2.56-2.42 (m, 2H), 2.53 (s, 3H), 2.01-1.91 (m, 2H), 1.77-1.73 (m, 2H), 1.69-1.66 (m, 2H), 1.54-1.33 (m, 6H), 1.16 (t, *J* = 7.1 Hz, 6H), 1.08 (t, *J* = 7.0 Hz, 3H), 0.83 (s, 9H), -0.02 (s, 6H), ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) of ethoxylamine derivative: δ 197.4 (C), 170.3 (C), 156.8 (C), 155.5 (C), 151.3 (C), 148.4 (C) 141.2 (C), 139.7 (CH), 134.2 (CH), 129.8 (CH), 129.7 (CH), 129.2 (2 x CH), 128.1 (2 x CH), 121.3 (CH), 117.0 (C), 113.3 (CH_2), 109.9 (CH), 106.9 (C), 96.8 (CH), 71.1 (CH_2), 69.5 (C), 67.2 (C), 63.6 (CH_2), 44.8 (2 x CH_2), 38.6 (CH_2), 33.7 (CH_2), 32.9 (CH_2), 30.4 (CH_2), 28.6 (2 x CH_2), 27.3 (CH_2), 25.8 (3 x CH_3), 20.7 (CH_2) 19.1 (CH_3), 18.1 (C), 14.1 (CH_3), 12.3 (2 x CH_3), -5.4 (2 x CH_3) ppm; IR (thin film): 2955, 2858, 1726, 1623, 1606, 1430, 1355, 1253, 1098, 836 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{43}H_{59}N_6O_6S_2Si$ $(M+Na)^+$ 870.3604, found 870.3612.



21b

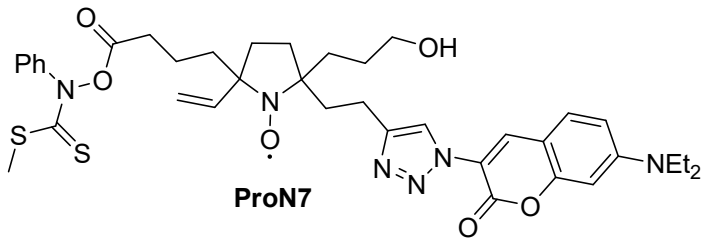
Thiohydroxamate ester 21b: Thiohydroxamate ester **21b** was prepared from aldehyde **19b** (293 mg, 0.441 mmol) using a general procedure for Pinnick oxidation and ester coupling. The crude residue was purified by column chromatography with 20% EtOAc in hexane to give 220 mg (58% yield, two steps) of **21a** as a brown yellow viscous oil: R_f = 0.57 (30% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.26 (s, 1H), 8.22 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.39-7.34 (m, 3H), 7.31 (d, *J* = 8.9 Hz, 1H), 6.58 (d, *J* = 8.9 Hz, 1H), 6.45 (s, 1H), 6.32-6.13 (m, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 4.96 (d, *J* = 18.0 Hz, 1H), 3.78-3.67 (m, 2H), 3.54-3.50 (m, 2H), 3.40-3.32 (m, 4H), 3.17-3.05 (m, 1H), 2.68-2.60 (m, 1H), 2.51 (s, 3H), 2.45-2.41 (m, 4H), 1.96-1.79 (m, 4H), 1.74-1.55 (m, 8H), 1.15 (t, *J* = 6.9 Hz, 6H), 1.06 (t, *J* = 6.9 Hz, 3H), 0.83 (s, 9H), -0.02 (s, 6H), ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) of

ethoxylamine derivative: δ 197.3 (C), 169.7 (C), 156.8 (C), 155.5 (C), 151.2 (C), 148.5 (C) 141.2 (C), 140.1 (CH), 134.2 (CH), 129.7 (2 x CH), 129.1 (2 x CH), 127.9 (2 x CH), 121.2 (CH), 117.0 (C), 112.6 (CH_2), 109.9 (CH), 106.9 (C), 96.8 (CH), 71.1 (CH_2), 70.0 (C), 67.0 (C), 63.7 (CH_2), 44.8 (2 x CH_2), 39.1 (CH_2), 38.6 (CH_2), 33.0 (CH_2), 31.8 (CH_2), 30.4 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 25.8 (3 x CH_3), 20.6 (CH_2), 19.9 (CH_2), 19.0 (CH_3) 18.1 (C), 14.1 (CH_3), 12.3 (2 x CH_3), -5.4 (2 x CH_3) ppm; IR (thin film) 2928, 2854, 1723, 1623, 1606, 1429, 1354, 1255, 1039, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{44}H_{61}N_6O_6S_2Si$ $(M+Na)^+$ 884.3761, found 884.3753.

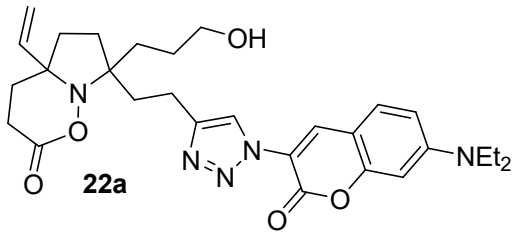


ProN6

ProN6: ProN6 was prepared from thiohydroxamate ester **21a** (250 mg, 0.28 mmol) using a general procedure for TBS deprotection. The crude residue was purified by column chromatography with 20% EtOAc in hexane, followed by 100% EtOAc to give 138 mg (67% yield) of profluorescent nitroxide **Ib** as a yellow viscous oil: R_f = 0.50 (50% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.32 (s, 1H), 8.25 (s, 1H), 7.53 (dd, *J* = 1.9, 8.3 Hz, 2H), 7.46-7.41 (m, 3H), 7.37 (d, *J* = 8.9 Hz, 1H), 6.65 (dd, *J* = 1.9, 8.9 Hz, 1H), 6.52 (d, *J* = 1.9 Hz, 1H), 6.29-6.19 (m, 1H), 5.09 (d, *J* = 11.9 Hz, 1H), 5.03 (d, *J* = 19.0 Hz, 1H), 3.85-3.75 (m, 2H), 3.59-3.57 (m, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 3.16-3.06 (m, 1H), 2.73-2.62 (m, 1H), 2.57 (s, 3H), 2.54-2.44 (m, 2H), 2.03-1.91 (m, 4H), 1.86-1.69 (m, 4H), 1.62-1.36 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 6H), 1.12 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) ethoxylamine derivative: δ 197.2 (C), 170.0 (C), 156.6 (C), 153.3 (C), 151.1 (C), 148.0 (C), 141.0 (C), 139.4 (CH), 134.1 (CH), 129.5 (2 x CH), 129.0 (2 x CH), 127.8 (2 x CH), 121.1 (CH), 116.6 (C), 113.2 (CH_2), 109.7 (CH), 106.7 (C), 96.5 (CH), 71.0 (CH_2), 69.3 (C), 67.0 (C), 63.0 (CH_2), 44.6 (2 x CH_2), 38.3 (CH_2), 33.4 (CH_2), 32.7 (CH_2), 30.3 (CH_2), 27.9 (2 x CH_2), 27.0 (CH_2), 20.4 (CH_3), 18.8 (CH_2), 13.9 (CH_3), 12.1 (2 x CH_3) ppm; IR (thin film): 3444, 2930, 2858, 1723, 1622, 1606, 1430, 1253, 1132, 835 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{45}N_6O_6S_2$ $(M+Na)^+$ 770.2896, found 770.2894.

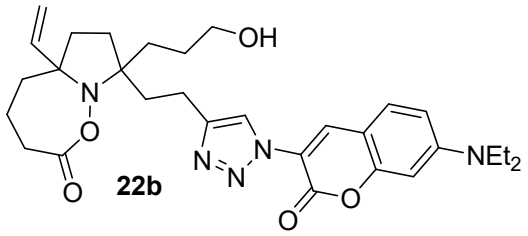


ProN7: ProN7 was prepared from thiohydroximate ester **21b** (263 mg, 0.31 mmol) using a general procedure for TBS deprotection. The crude residue was purified by column chromatography with 20% EtOAc in hexane, followed by 100% EtOAc to give 196 mg (84% yield) of profluorescent nitroxide **Ic** as a yellow viscous oil: R_f = 0.50 (50% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) of ethoxylamine derivative: δ 8.34 (s, 1H), 8.26 (s, 1H), 7.54 (dd, *J* = 1.8, 8.2 Hz, 2H), 7.47-7.40 (m, 3H), 7.39-7.37 (m, 1H), 6.66 (dd, *J* = 2.1, 8.9 Hz, 1H), 6.64 (d, *J* = 2.1 Hz, 1H), 6.25-6.15 (m, 1H), 5.11 (d, *J* = 11.1 Hz, 1H), 5.02 (d, *J* = 17.9 Hz, 1H), 3.83-3.69 (m, 2H), 3.61-3.57 (m, 2H), 3.44 (q, *J* = 7.1 Hz, 2H), 3.19-3.06 (m, 1H), 2.27-2.64 (m, 1H), 2.58 (s, 3H), 2.50-2.45 (m, 2H), 1.95-1.89 (m, 2H), 1.85-1.83 (m, 4H), 1.69-1.61 (m, 6H), 1.57-1.47 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H), 1.11 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) of ethoxylamine derivative: δ 197.5 (C), 169.7 (C), 156.9 (C), 155.6 (C), 151.3 (C), 148.5 (C), 141.3 (C), 140.1 (CH), 134.3 (CH), 129.8 (2 x CH), 129.2 (2 x CH), 128.0 (2 x CH), 121.3 (CH), 117.0 (C), 112.9 (CH_2), 109.9 (CH), 107.0 (C), 96.8 (CH), 71.2 (CH_2), 70.1 (C), 67.1 (C), 63.4 (CH_2), 44.8 (2 x CH_2), 39.1 (CH_2), 38.7 (CH_2), 33.0 (CH_2), 31.9 (CH_2), 30.5 (CH_2), 28.6 (CH_2), 28.2 (CH_2), 20.6 (CH_2), 19.9 (CH_2), 19.1 (CH_3) 14.2 (CH_3), 12.3 (2 x CH_3) ppm; IR (thin film): 3420, 2954, 2858, 1716, 1625, 1606, 1436, 1262, 1098, 819 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $C_{38}H_{47}N_6O_6S_2$ $(M+Na)^+$ 770.2896, found 770.2892.



Cyclic *O*-acylalkoxylamine 22a: Cyclic *O*-acylalkoxylamine **22a** was prepared from profluorescent nitroxide probe **ProN6** (16.2 mg, 0.022 mmol) using a general procedure for reductive lactonization. The crude residue was purified by column chromatography with 50% EtOAc in hexane to give 8.9 mg (76% yield) of cyclic *O*-acylalkoxylamine **22a** as a bright blue-green viscous oil: R_f = 0.47 (50% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.30 (s, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 6.68 (d, J = 7.2 Hz, 1H), 6.55 (s, 1H), 6.05 (dd, *J* =

10.5, 17.3 Hz, 1H), 5.34 (d, *J* = 17.3 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 3.65 (brs, 2H), 3.45 (q, *J* = 6.9 Hz, 4H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.58-2.54 (m, 2H), 2.25-2.21 (m, 4H), 1.95-1.90 (m, 2H), 1.85-1.81 (m, 2H), 1.79-1.72 (m, 2H), 1.68-1.60 (m, 2H), 1.12 (t, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$) δ 174.4 (C), 157.1 (C), 155.9 (C), 151.6 (C), 147.9 (C), 141.0 (CH), 134.8 (CH), 130.0 (CH), 121.9 (CH), 117.3 (C), 115.2 (CH_2), 110.1 (CH), 107.3 (C), 97.2 (CH), 70.2 (C), 68.2 (C), 63.2 (CH_2), 45.1 (2 x CH_2), 36.1 (CH_2), 34.0 (CH_2), 33.9 (CH_2), 32.8 (CH_2), 32.6 (CH_2), 27.7 (CH_2), 27.0 (CH_2), 21.2 (CH_2), 12.5 (2 x CH_3), ppm; IR (thin film): 3393, 2936, 1727, 1604, 1431, 1354, 1240, 1132, 1011, 920 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{37}N_5O_5$ $(M+Na)^+$ 558.2696, found 558.2693.



Cyclic *O*-acylalkoxylamine 22b: Cyclic *O*-acylalkoxylamine **22b** was prepared from profluorescent nitroxide probe **ProN7** (23.9 mg, 0.031 mmol) using a general procedure for reductive lactonization. The crude residue was purified by column chromatography with 50% EtOAc in hexane to give 12.3 mg (72% yield) of cyclic *O*-acylalkoxylamine **22b** as a bright blue-green viscous oil: R_f = 0.47 (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.29 (s, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.59 (s, 1H), 6.40 (dd, *J* = 11.3, 17.6 Hz, 1H), 5.19 (d, *J* = 11.3 Hz, 1H), 5.15 (d, *J* = 17.6 Hz, 1H), 3.67-3.64 (m, 2H), 3.46 (q, *J* = 7.1 Hz, 4H), 3.19-3.15 (m, 1H), 2.90-2.78 (m, 2H), 2.51-2.47 (m, 1H), 2.21-2.14 (m, 1H), 2.09-2.08 (m, 1H), 2.04-1.97 (m, 4H), 1.81-1.77 (m, 2H), 1.74-1.71 (m, 2H), 1.65-1.63 (m, 2H), 1.60-1.54 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$) δ 178.1 (C), 157.1 (C), 155.9 (C), 151.4 (C), 148.0 (C), 139.8 (CH), 134.7 (CH), 130.1 (CH), 121.8 (CH), 117.5 (C), 114.7 (CH_2), 110.5 (CH), 107.7 (C), 97.7 (CH), 69.8 (C), 69.5 (C), 63.4 (CH_2), 45.4 (2 x CH_2), 42.0 (CH_2), 37.3 (CH_2), 36.2 (CH_2), 34.5 (CH_2), 30.6 (CH_2), 29.9 (CH_2), 28.6 (CH_2), 20.7 (CH_2), 19.8 (CH_2), 12.5 (2 x CH_3) ppm. IR (thin film): 3395, 2933, 1727, 1604, 1430, 1353, 1240, 1132, 1011, 920 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{39}N_5O_5$ $(M+Na)^+$ 572.2849, found 572.2851.

Figures and tables

^{1}H and ^{13}C NMR spectra

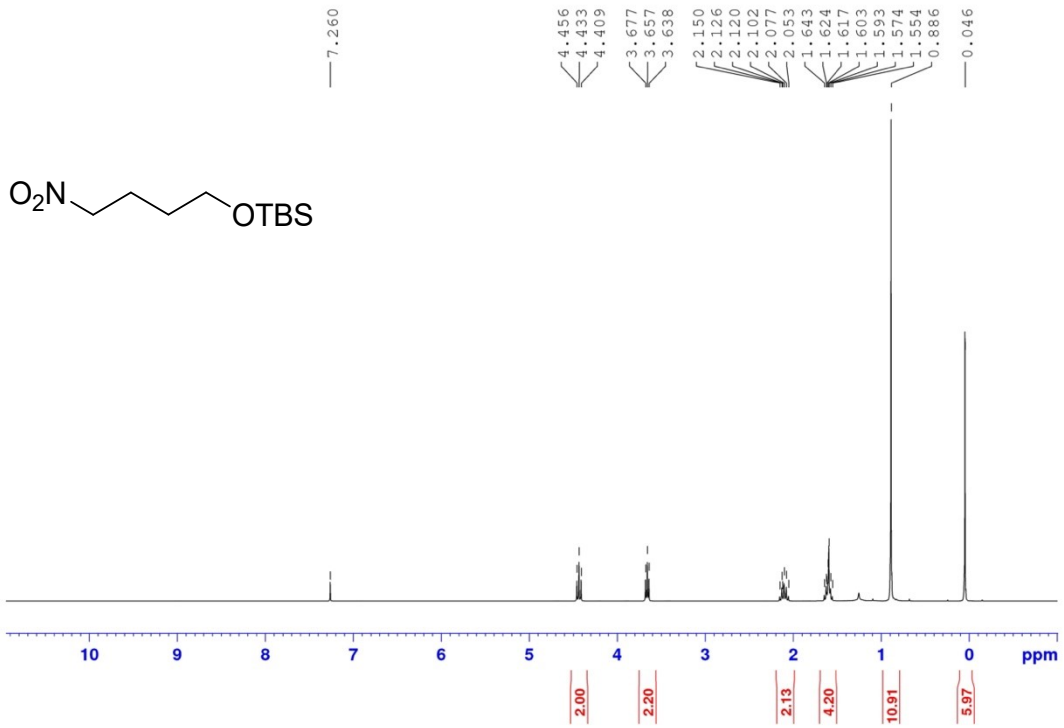


Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **5**

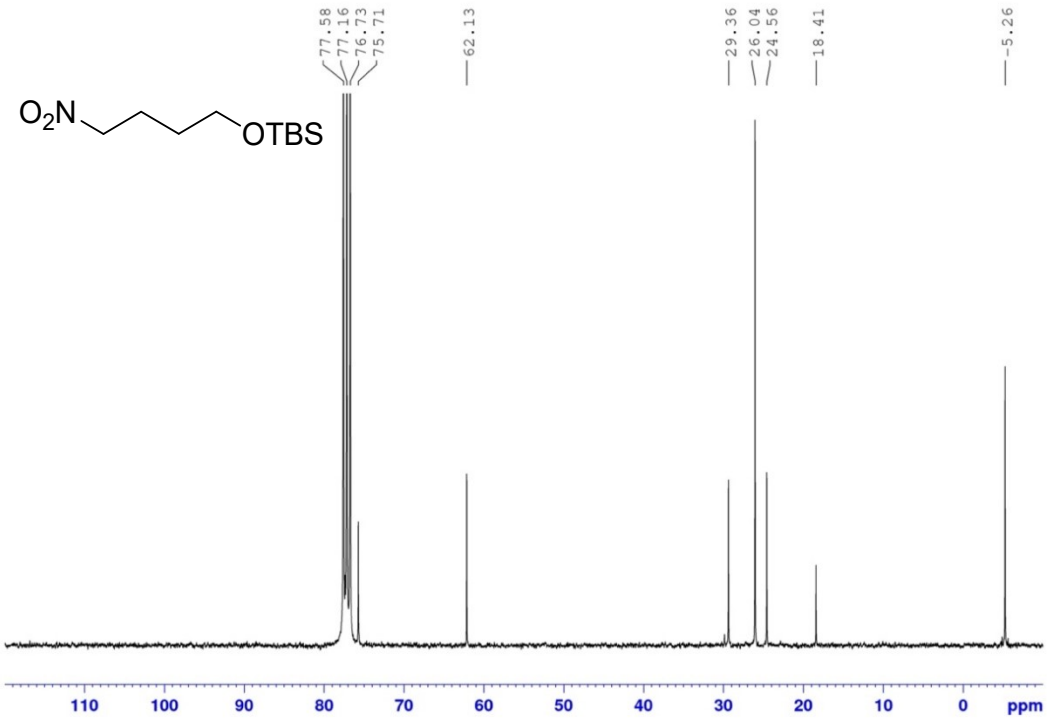


Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **5**

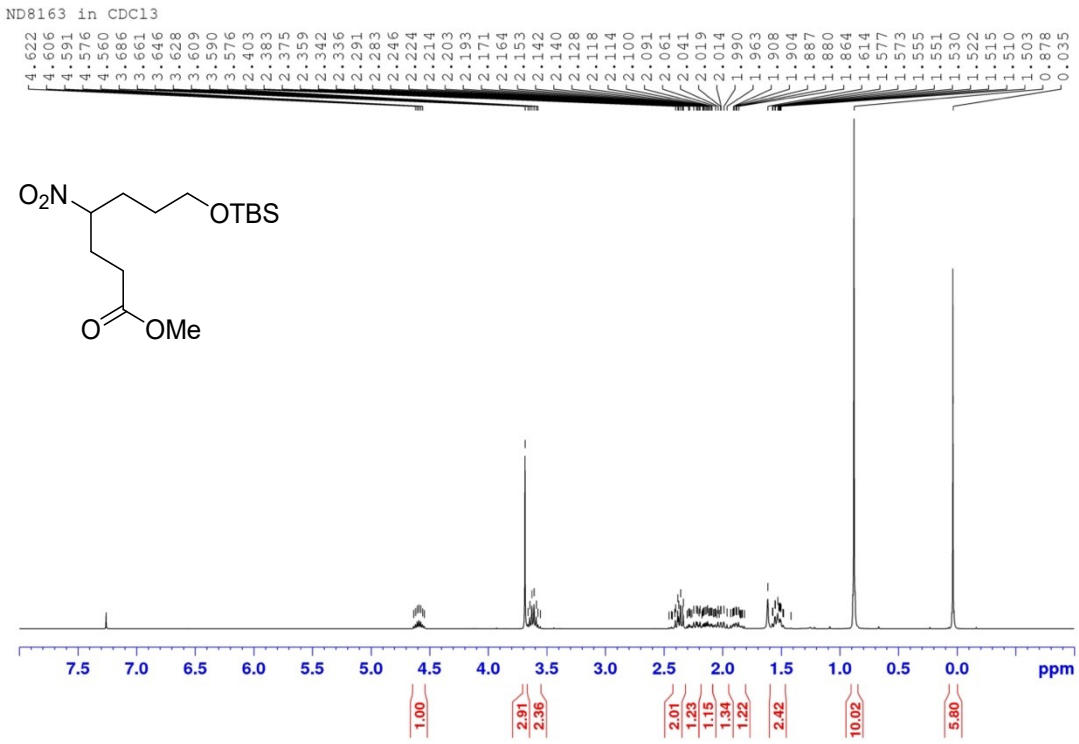


Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6**

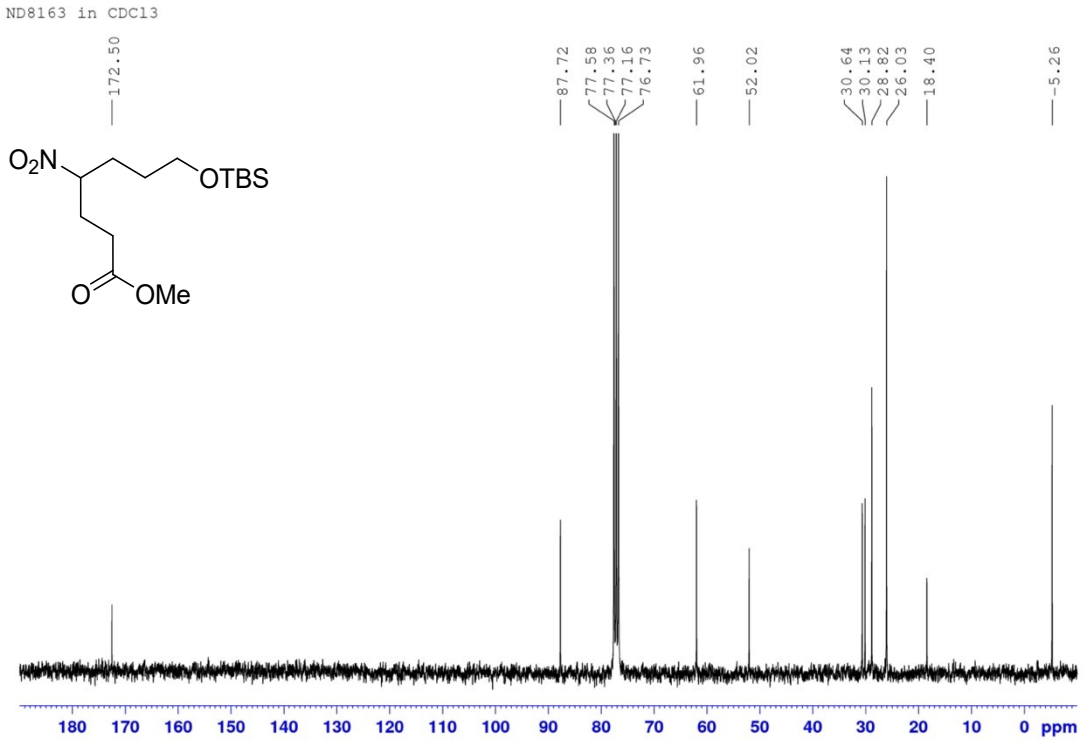


Figure S4. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6**

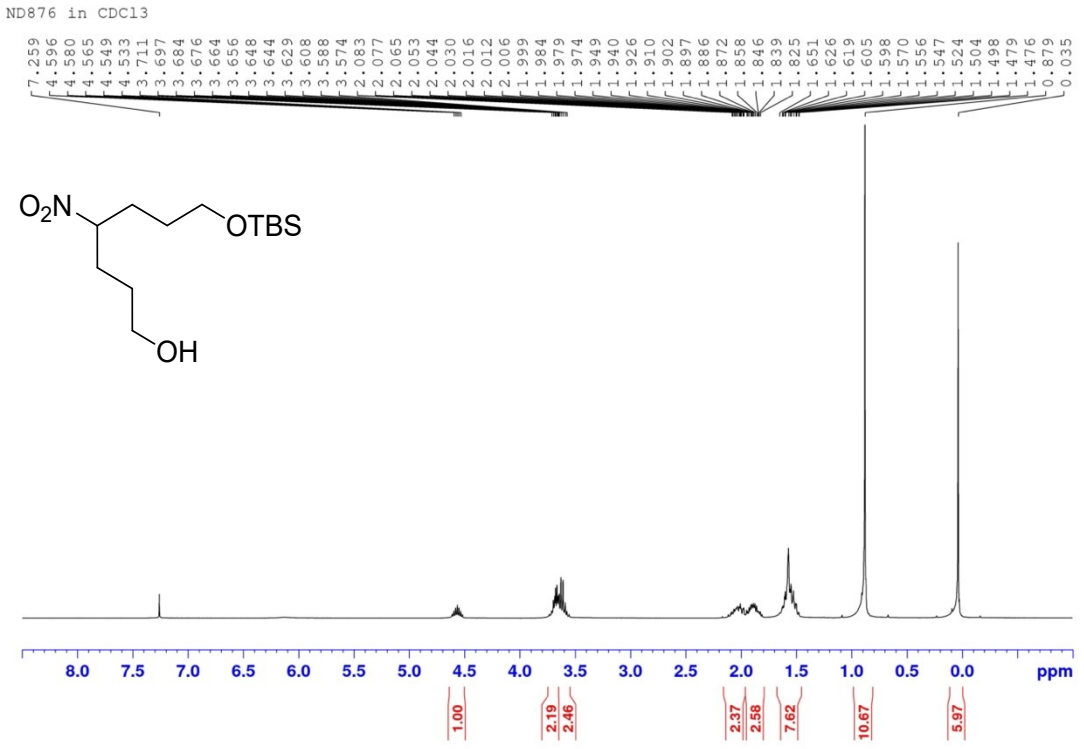


Figure S5. ^{13}C NMR (300 MHz, $CDCl_3$) spectrum of compound **7**

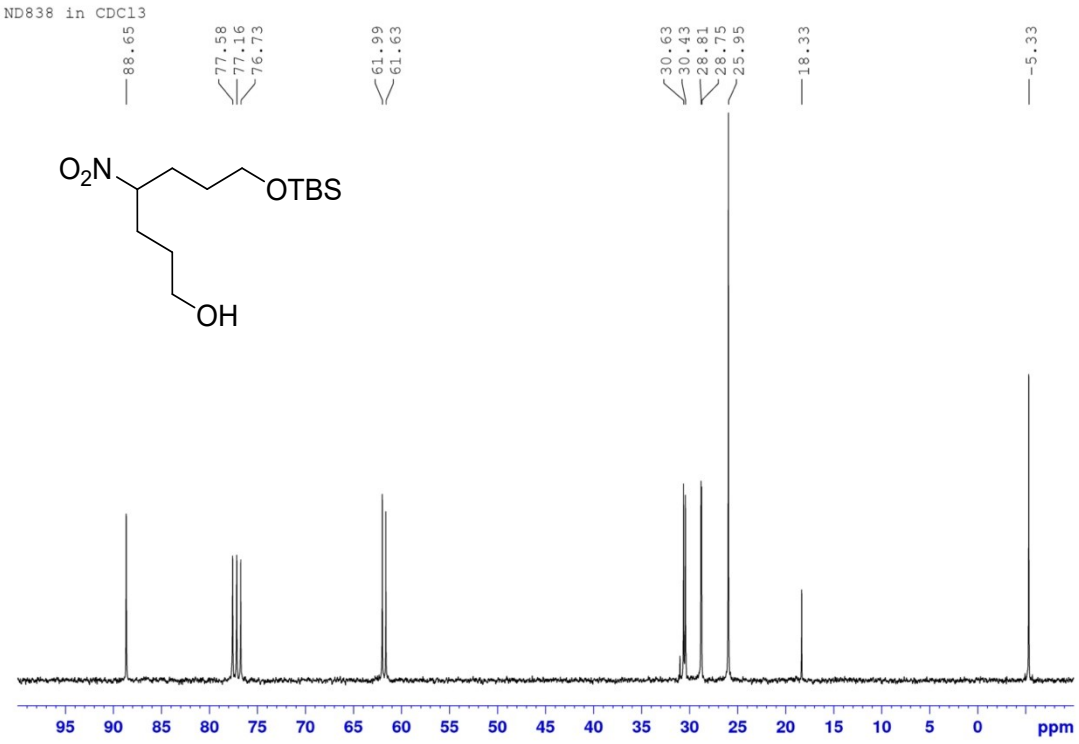


Figure S6. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **7**

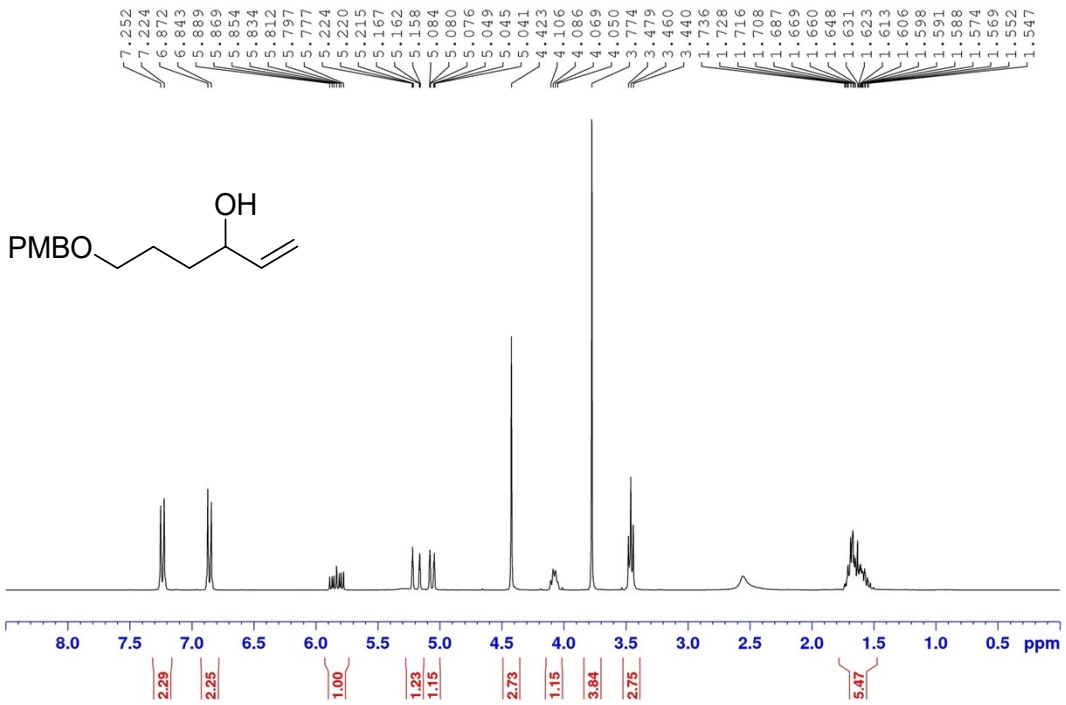


Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **9a**

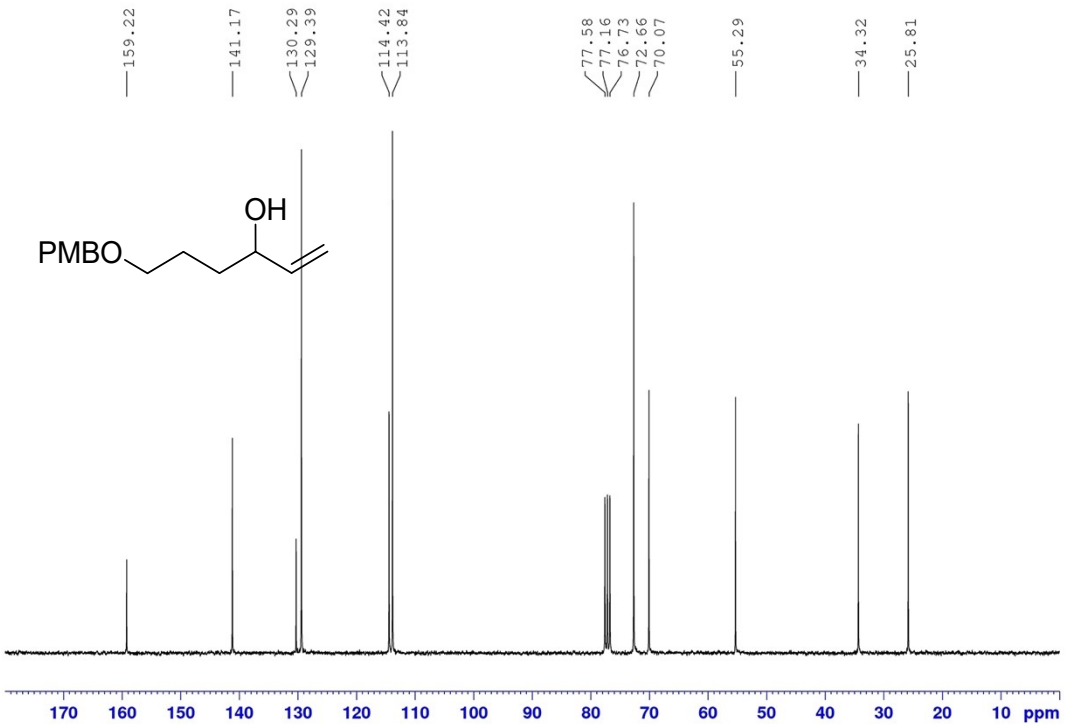


Figure S8. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **9a**

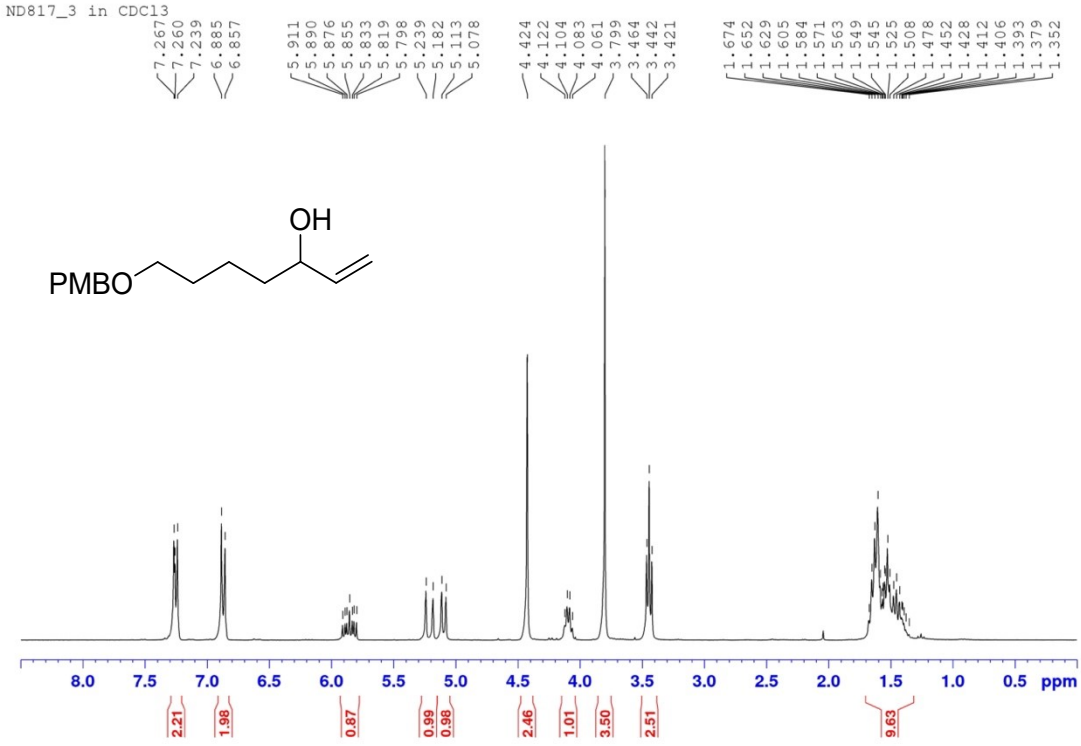


Figure S9. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **9b**

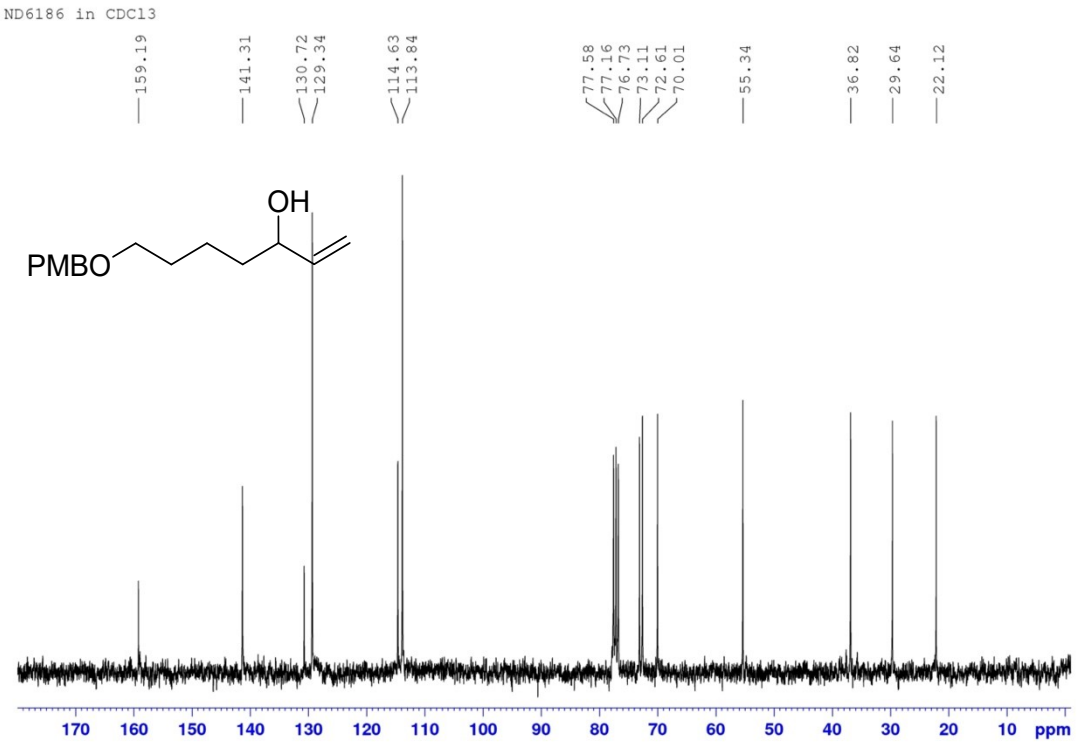


Figure S10. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **9b**

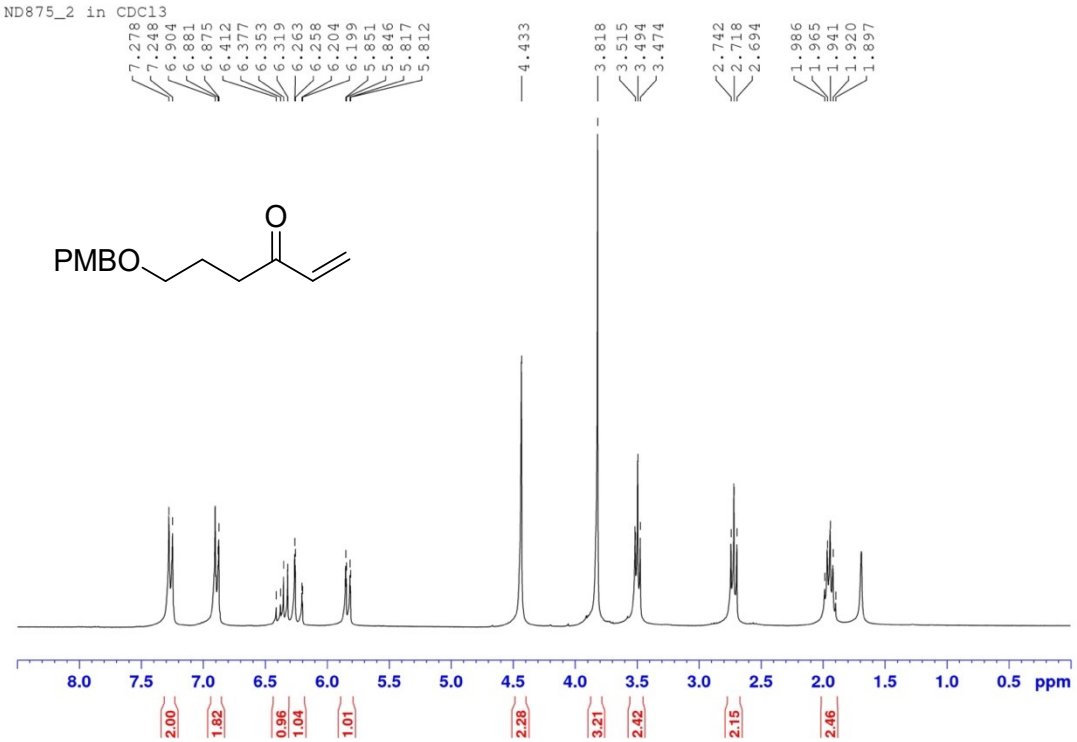


Figure S11. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **10a**

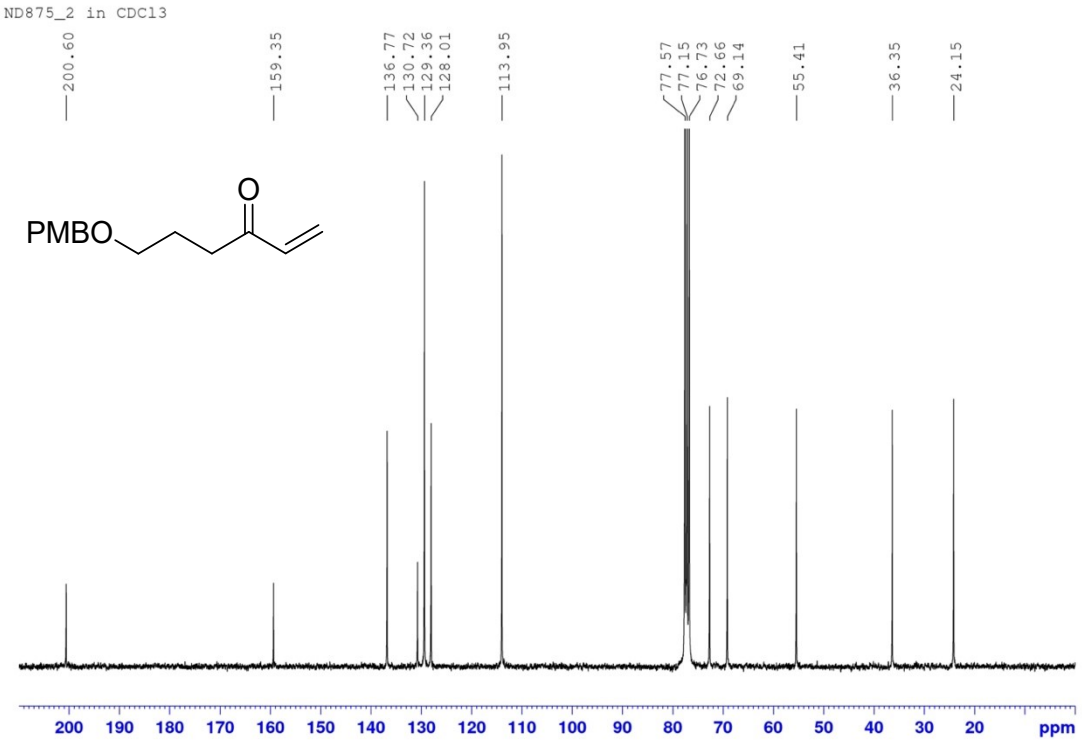


Figure S12. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **10a**

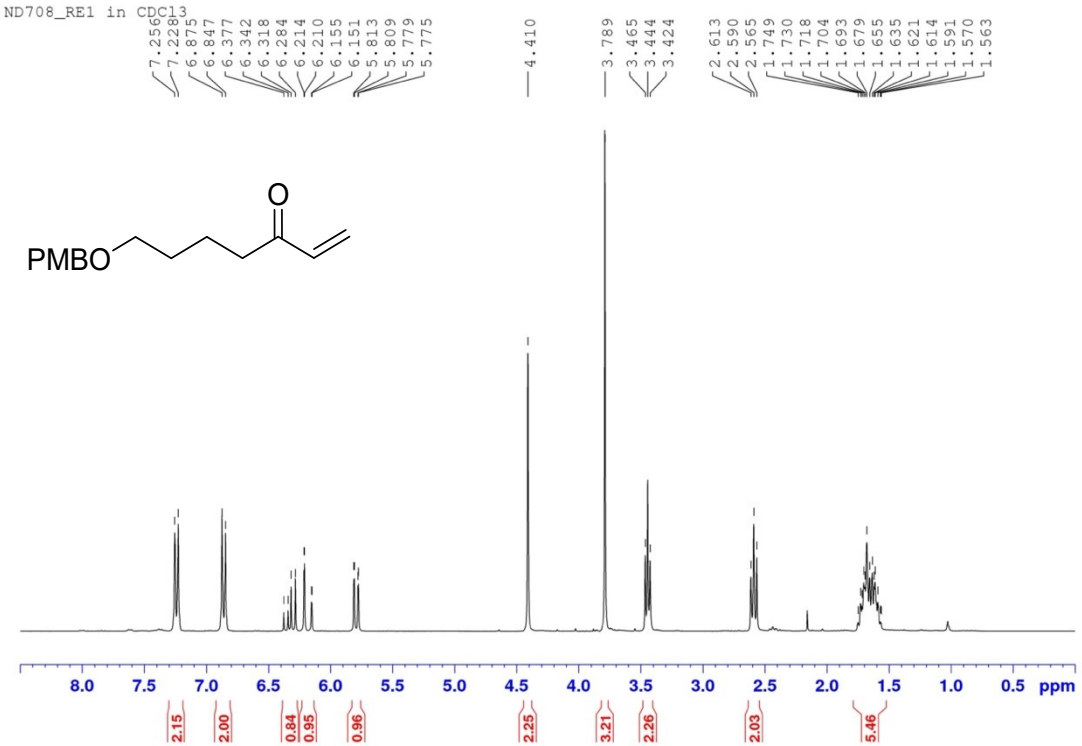


Figure S13. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **10b**

Figure S14. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **10b**

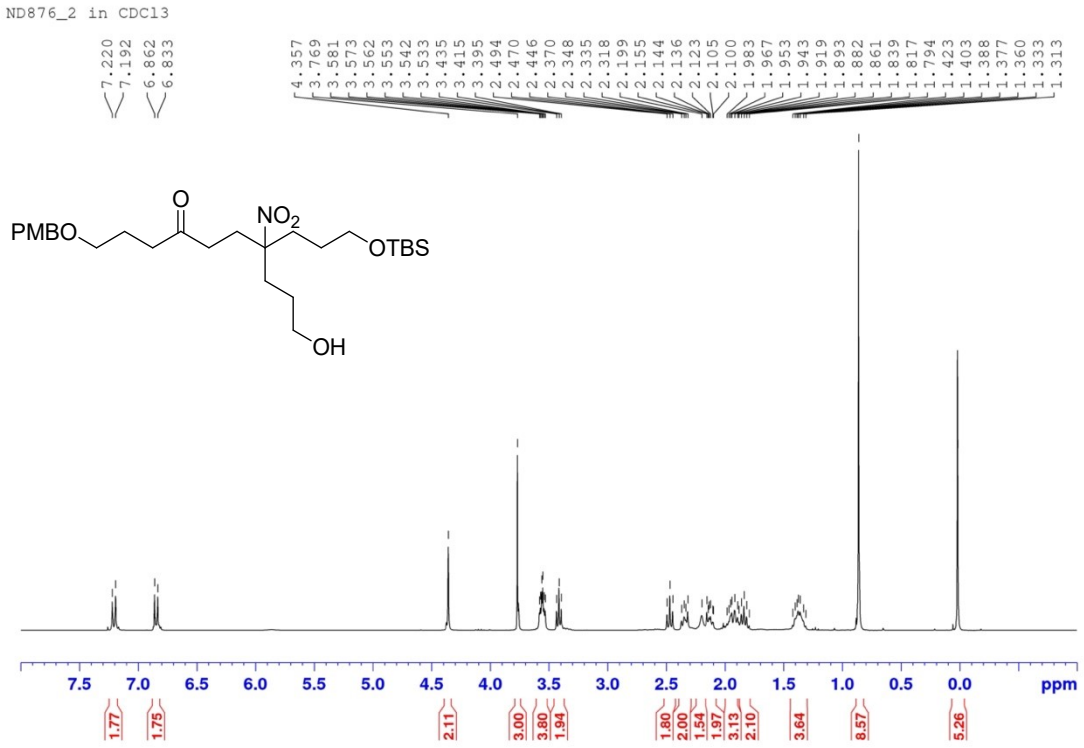


Figure S15. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **11a**

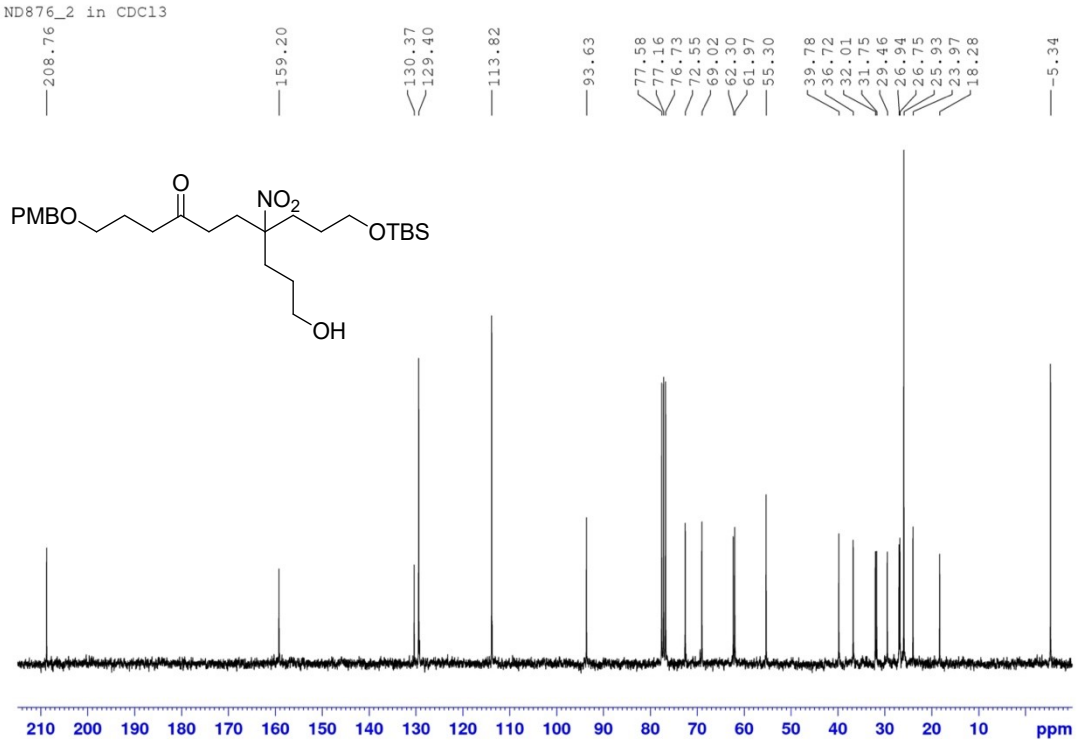


Figure S16. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **11a**

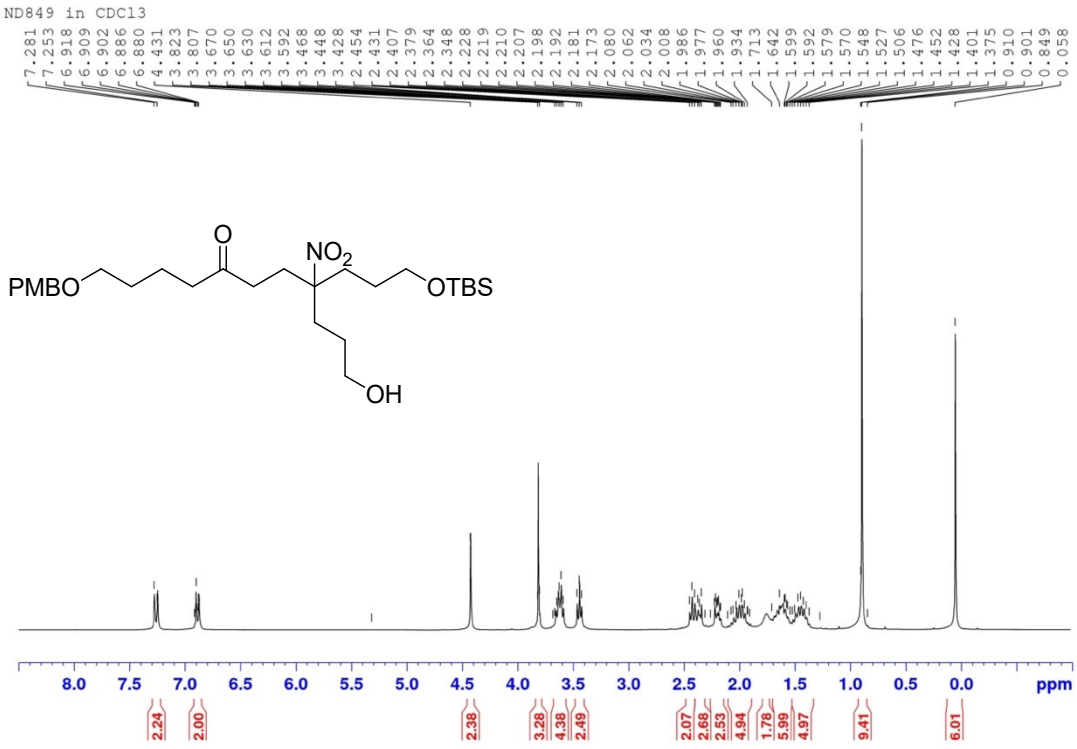


Figure S17. H NMR (300 MHz, $CDCl_3$) spectrum of compound **11b**

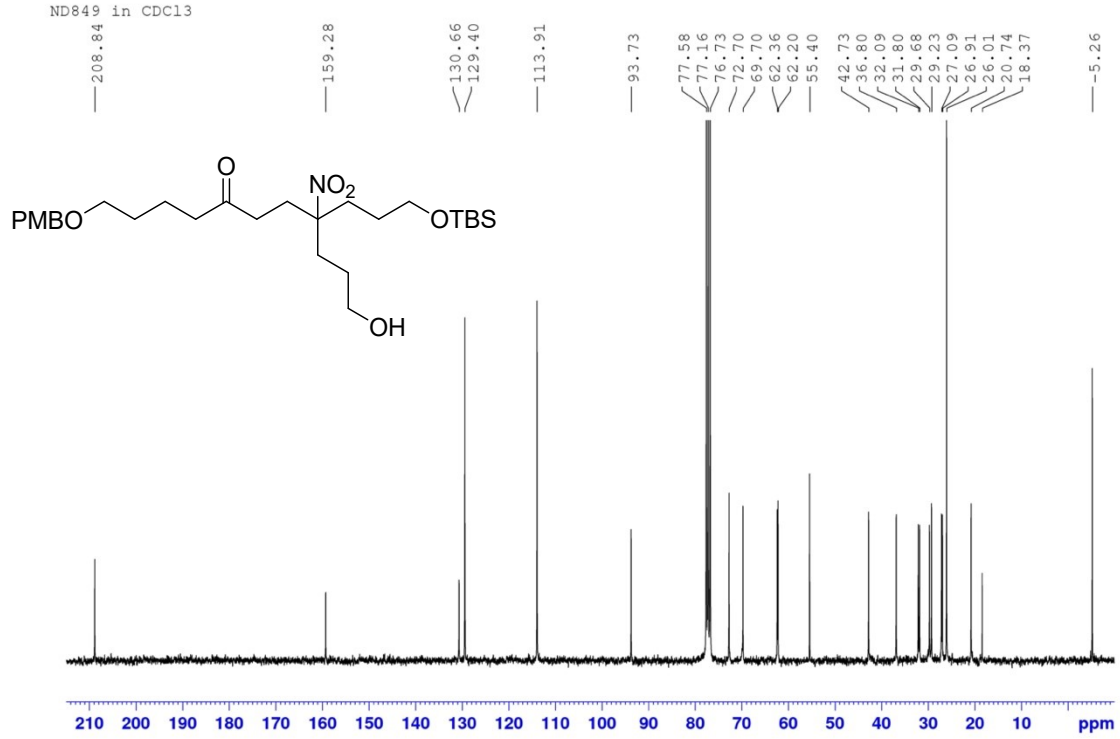


Figure S18. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **11b**

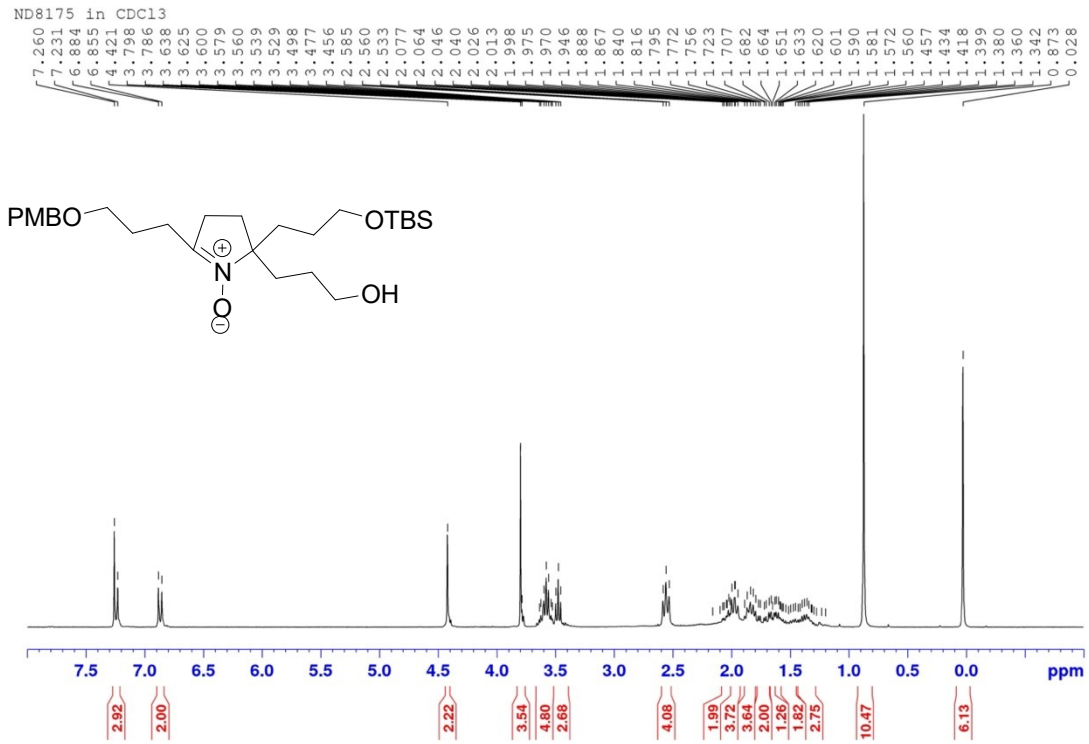


Figure S19. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **12a**

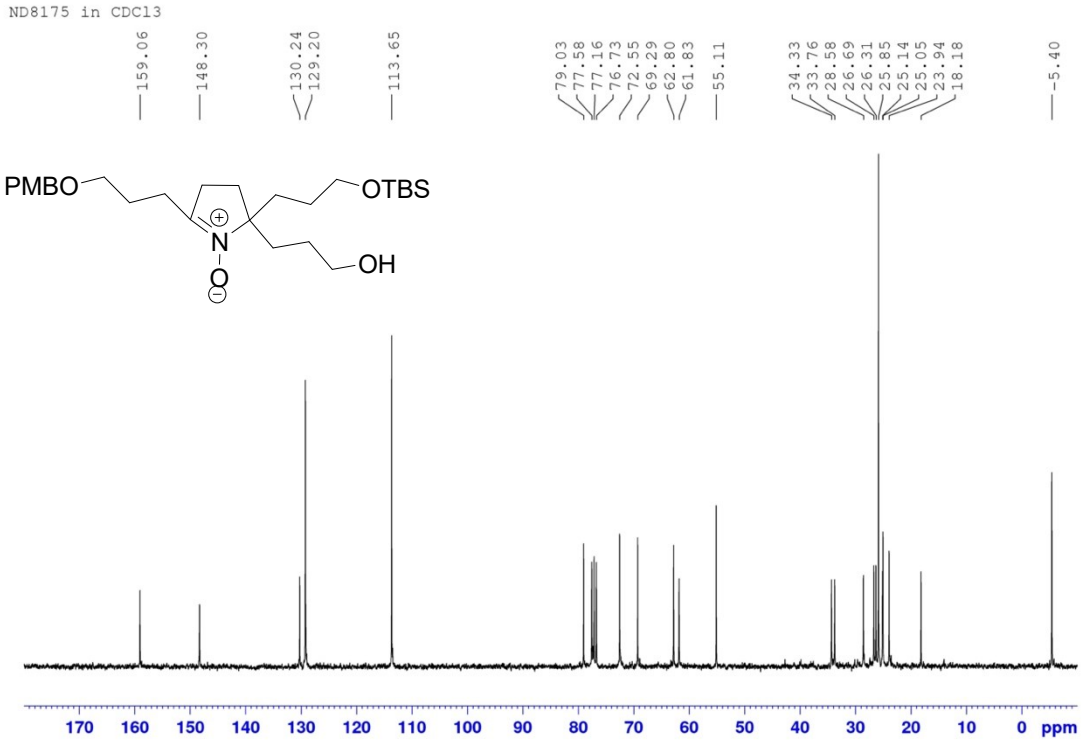


Figure S20. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **12a**

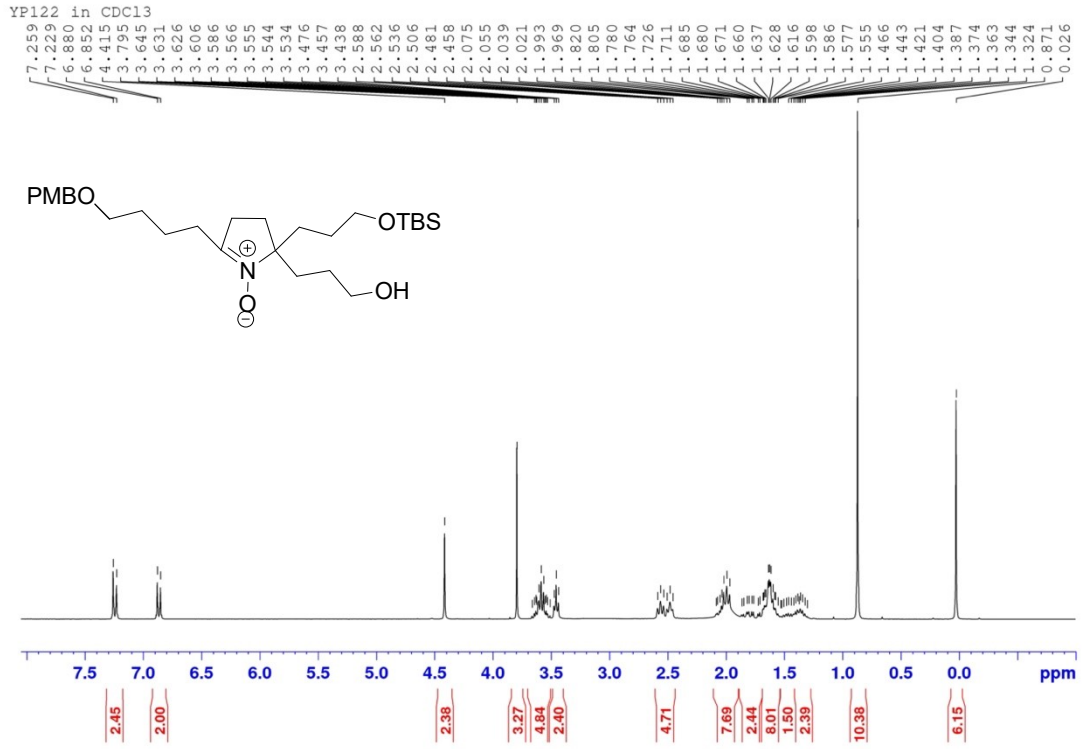


Figure S21. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **12b**

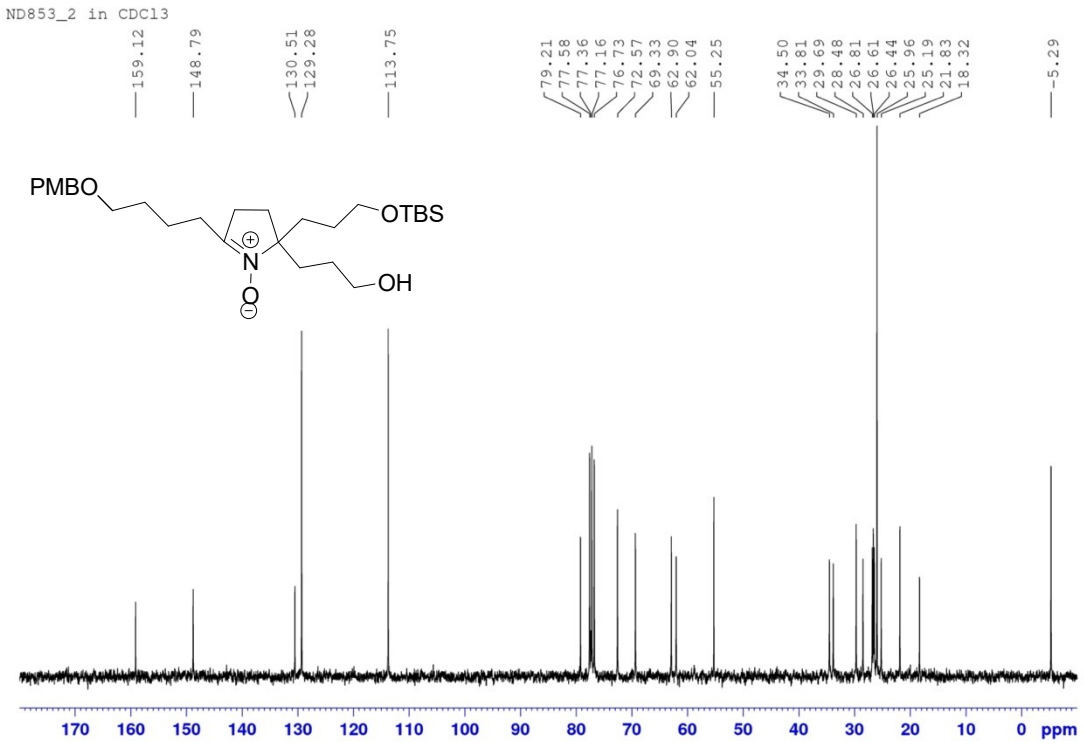


Figure S22. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **12b**

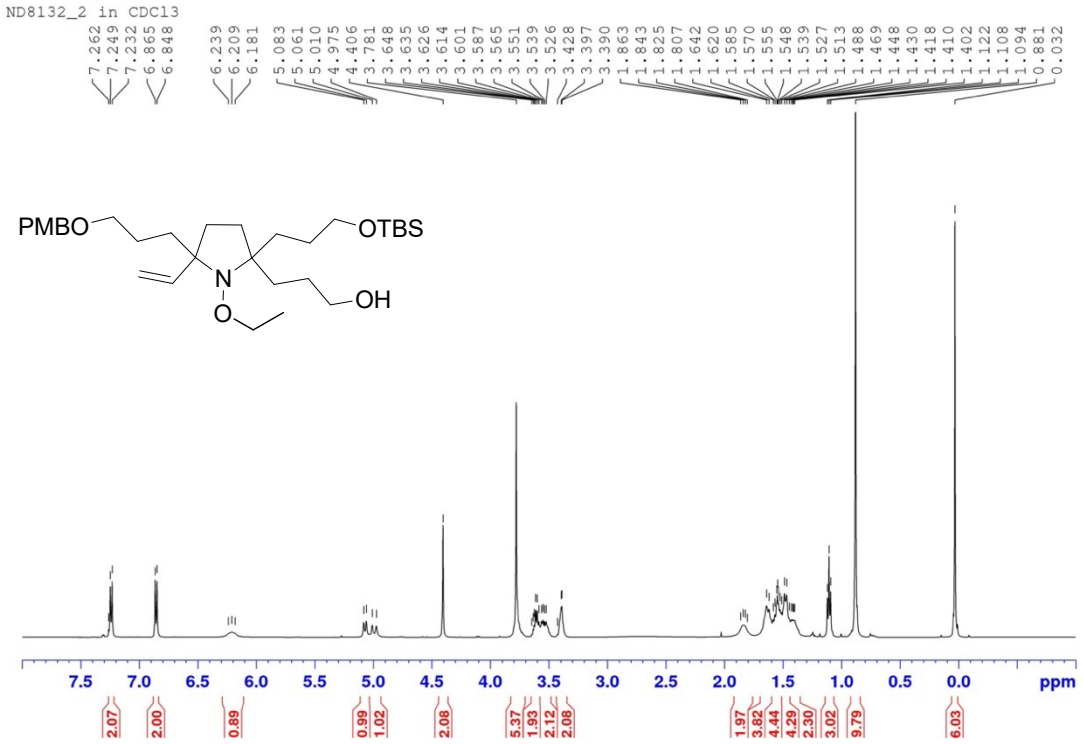


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **13a**

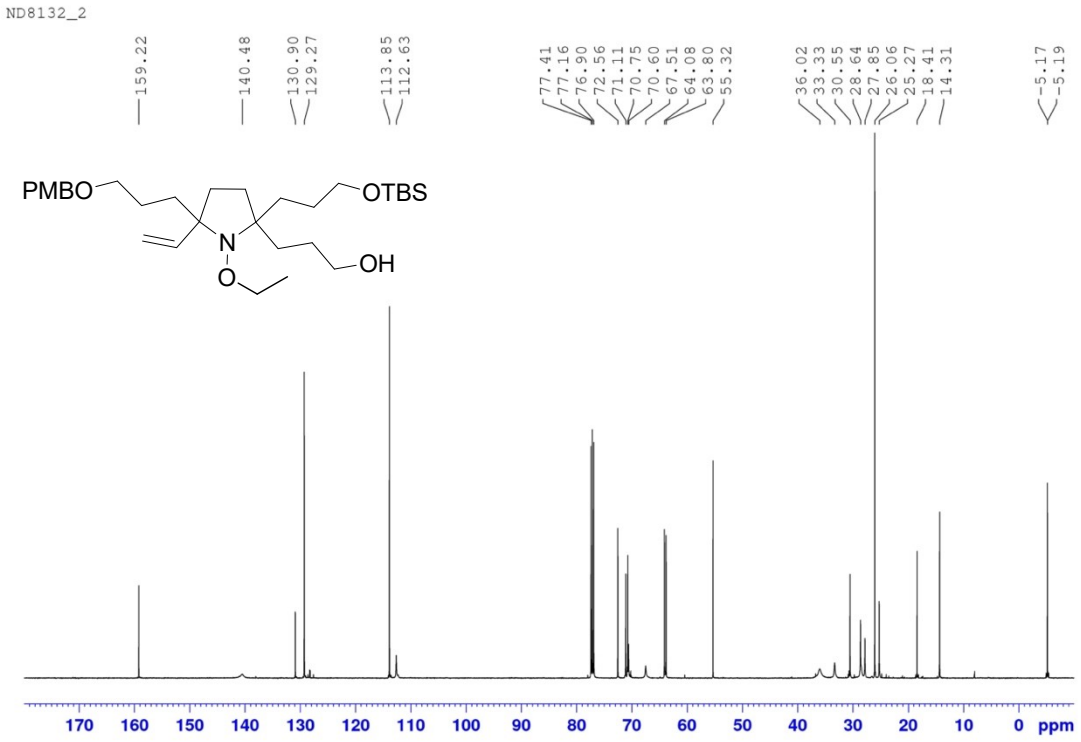


Figure S24. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **13a**

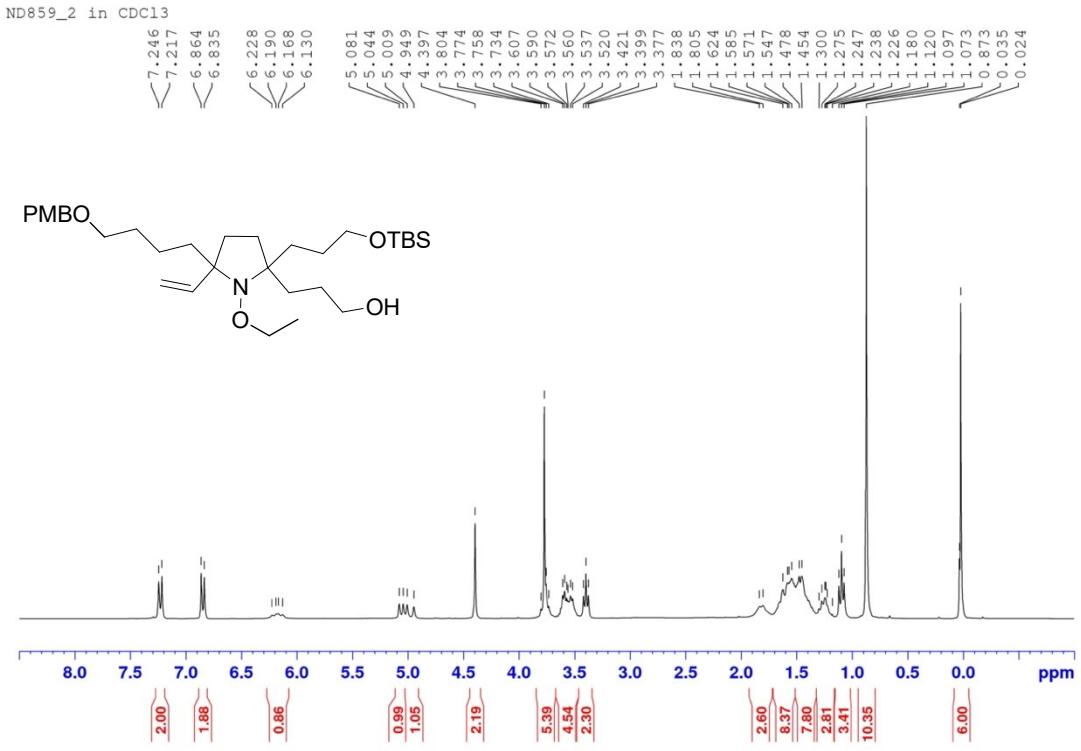


Figure S25. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **13b**

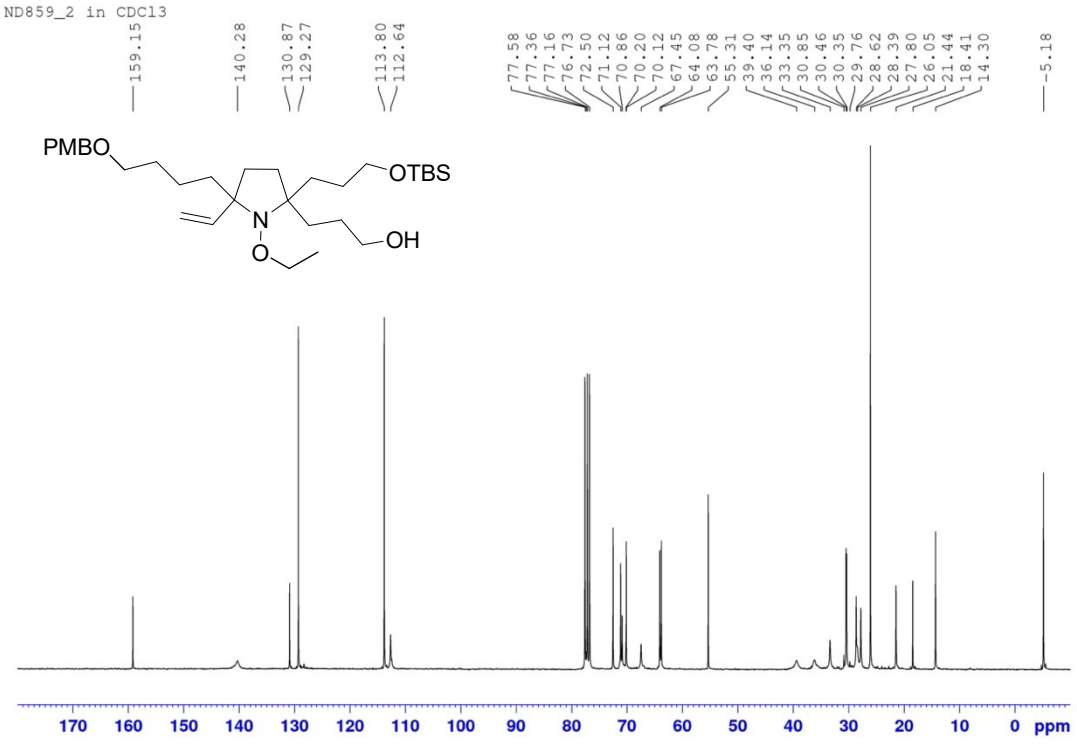


Figure S26. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **13b**

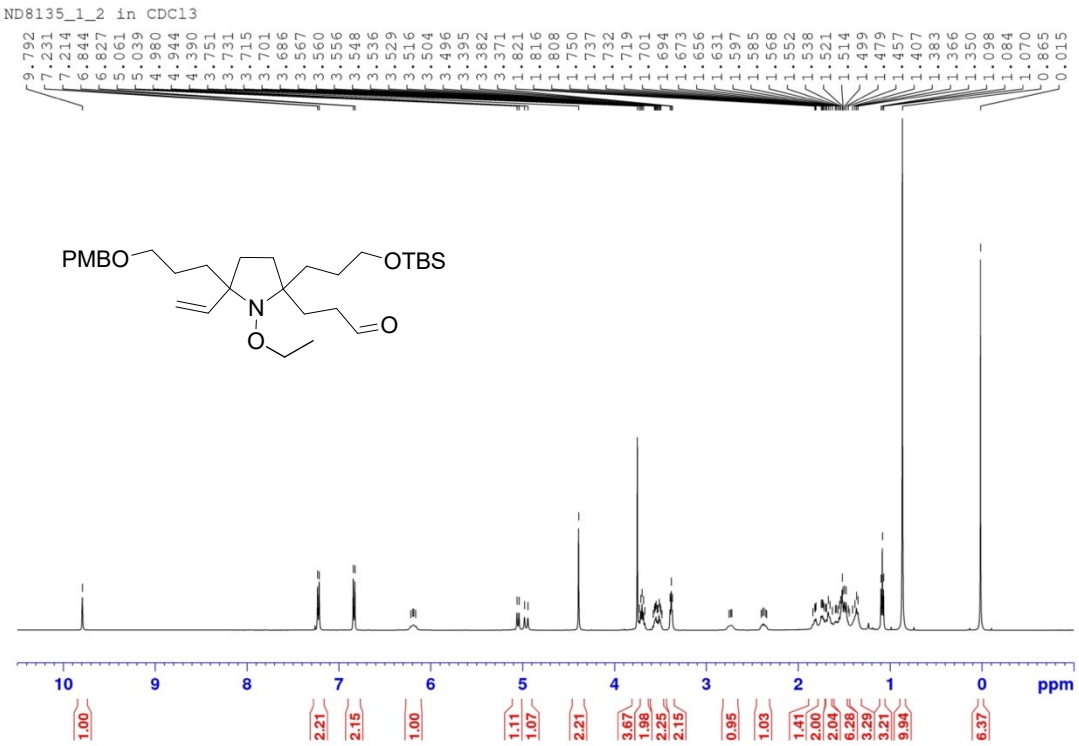


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14a (major)**

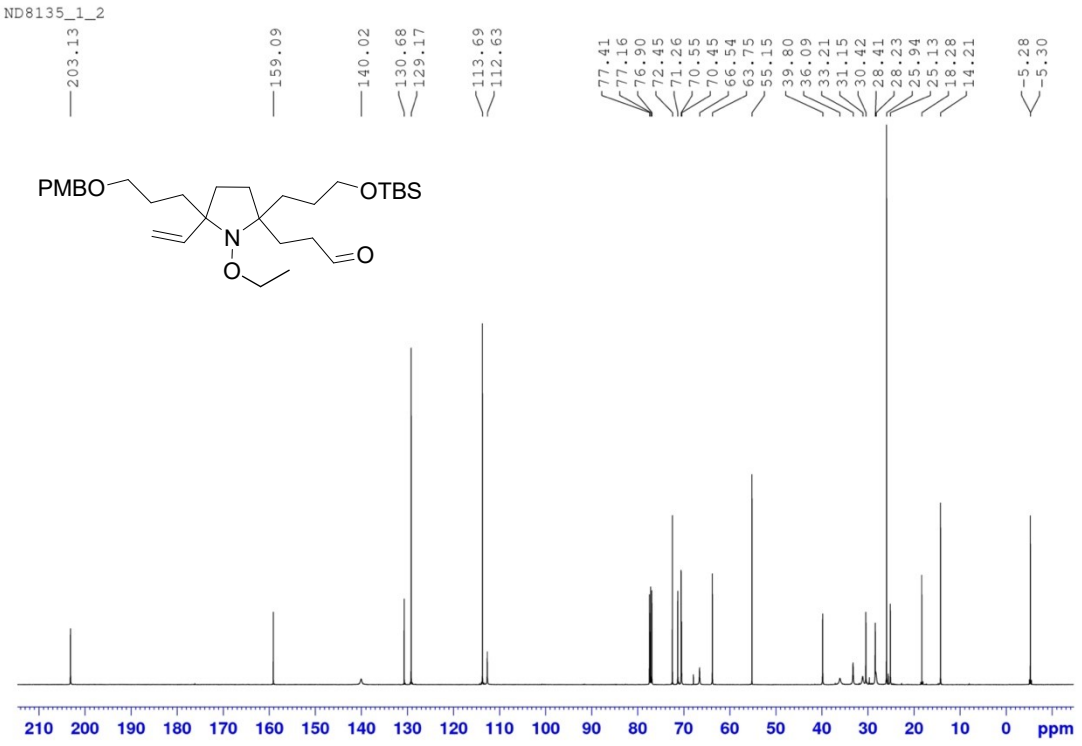


Figure S28. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14a (major)**

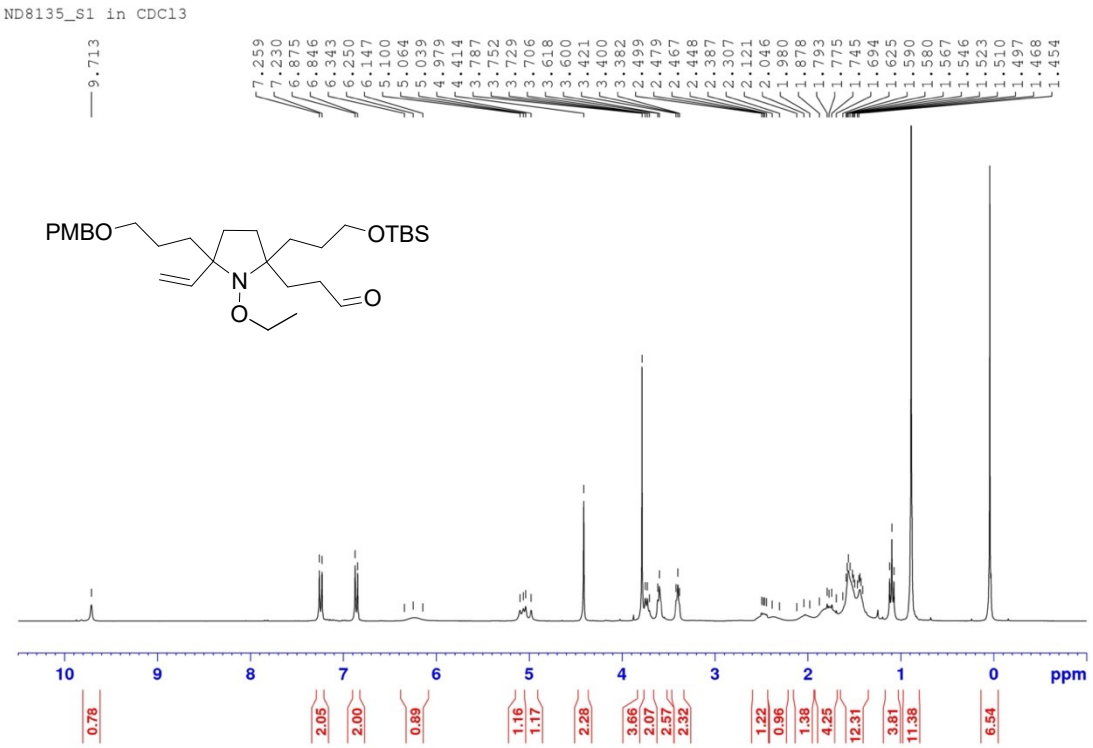


Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14a (minor)**

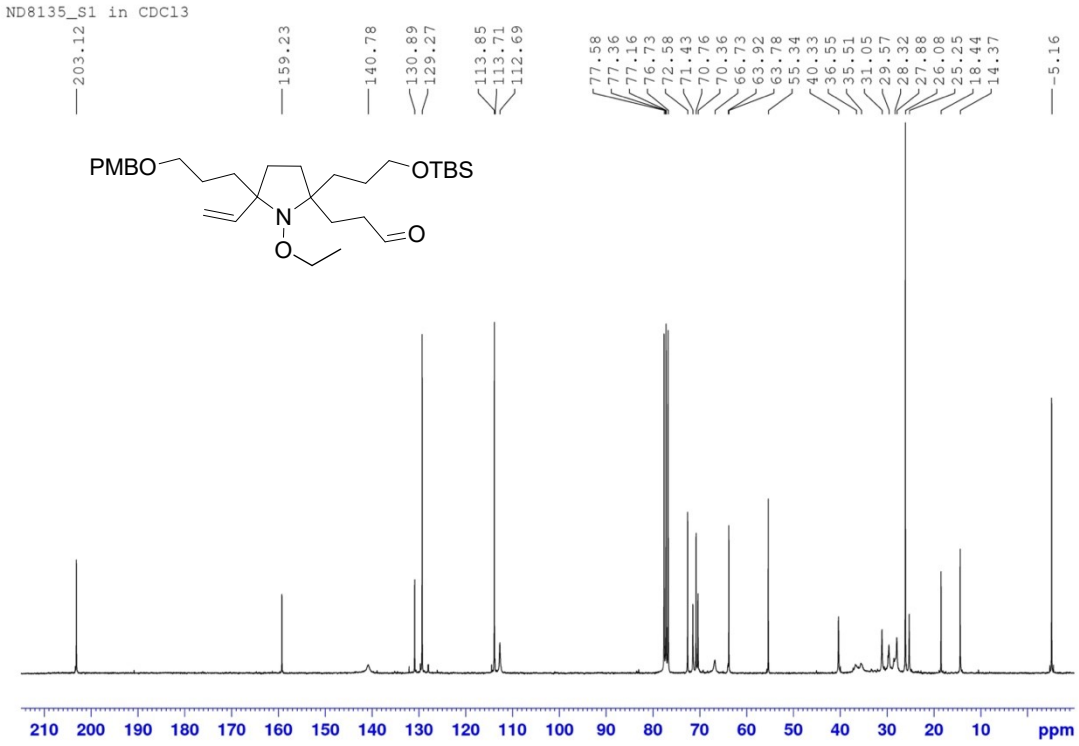


Figure S30. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14a (minor)**

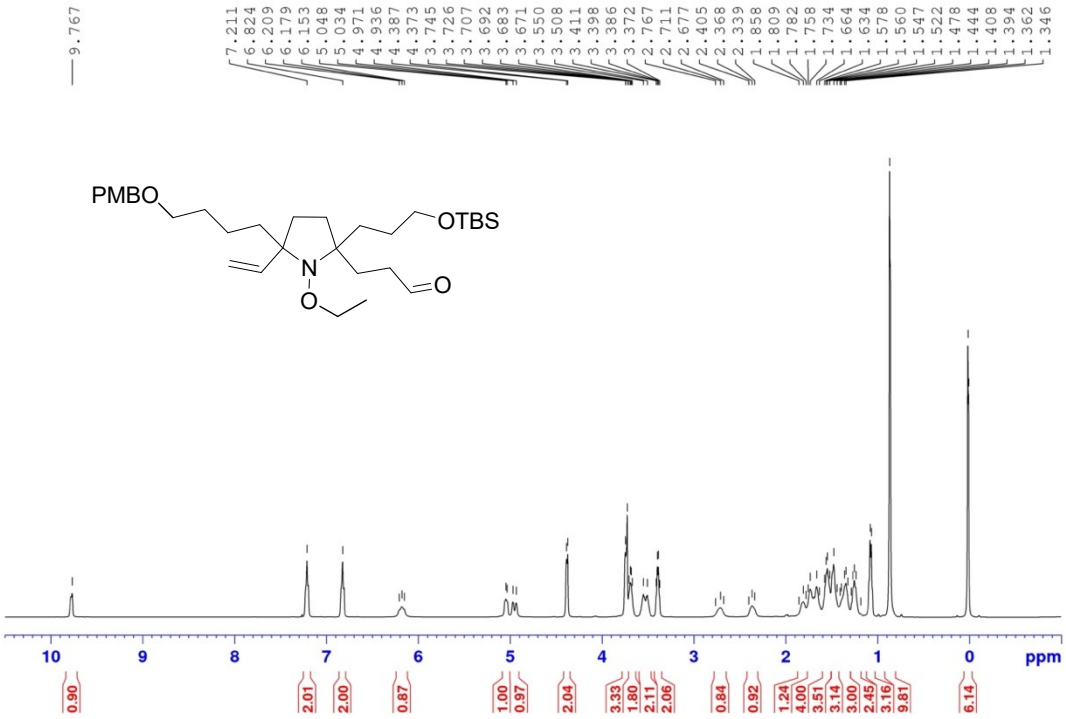


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14b (major)**

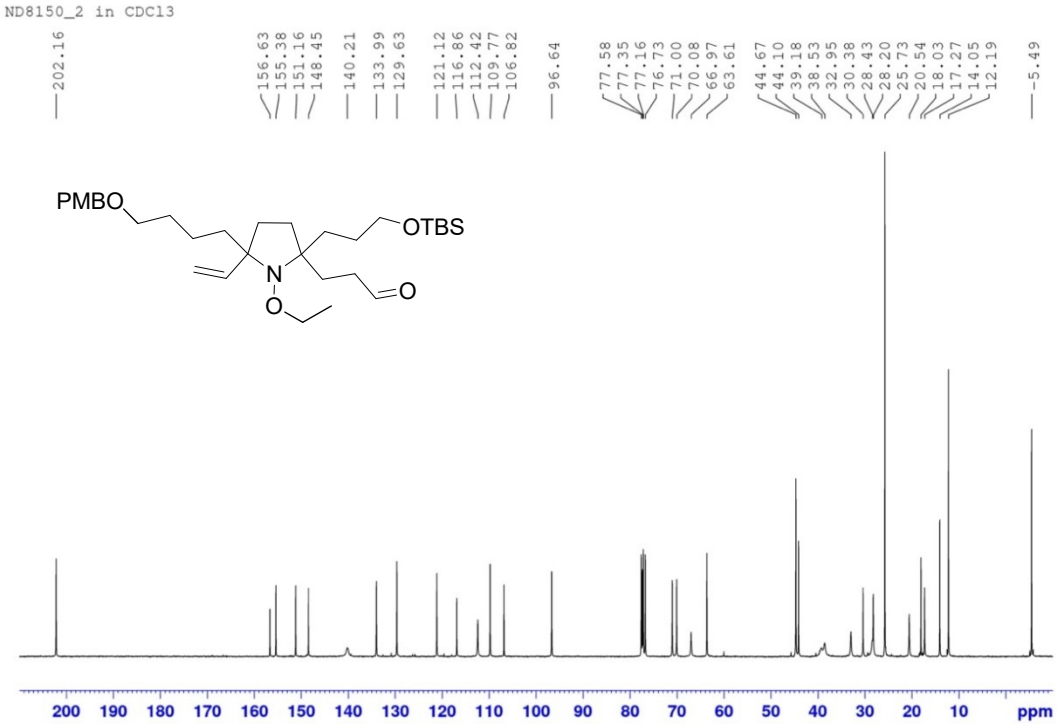


Figure S32. ^{1}H NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14b (major)**

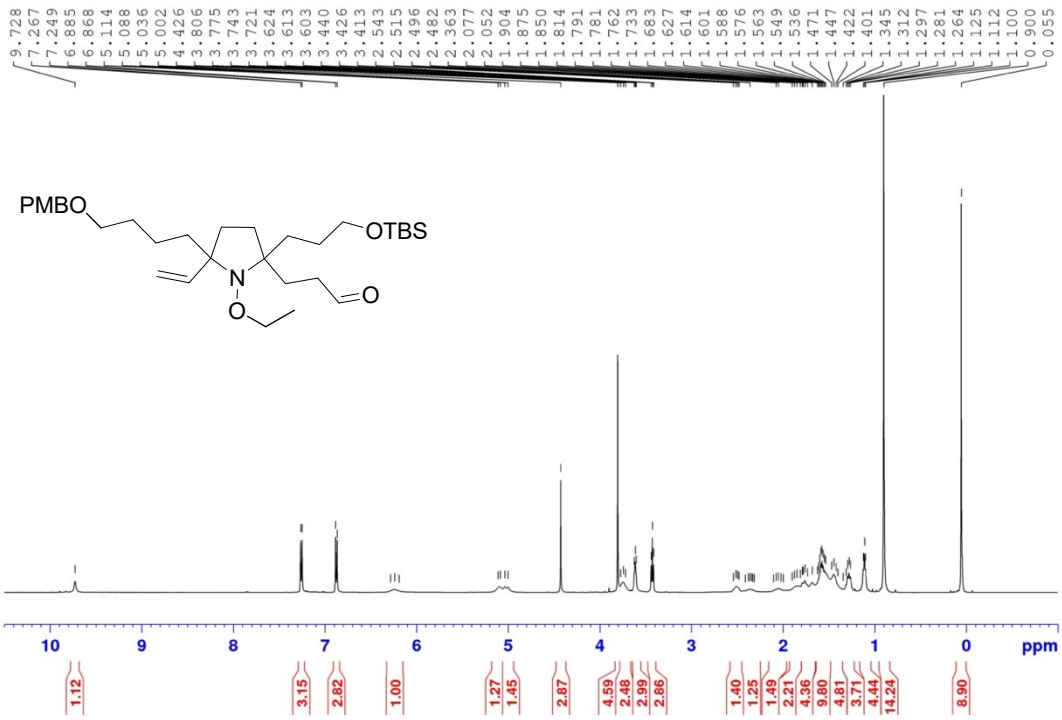


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14b (minor)**

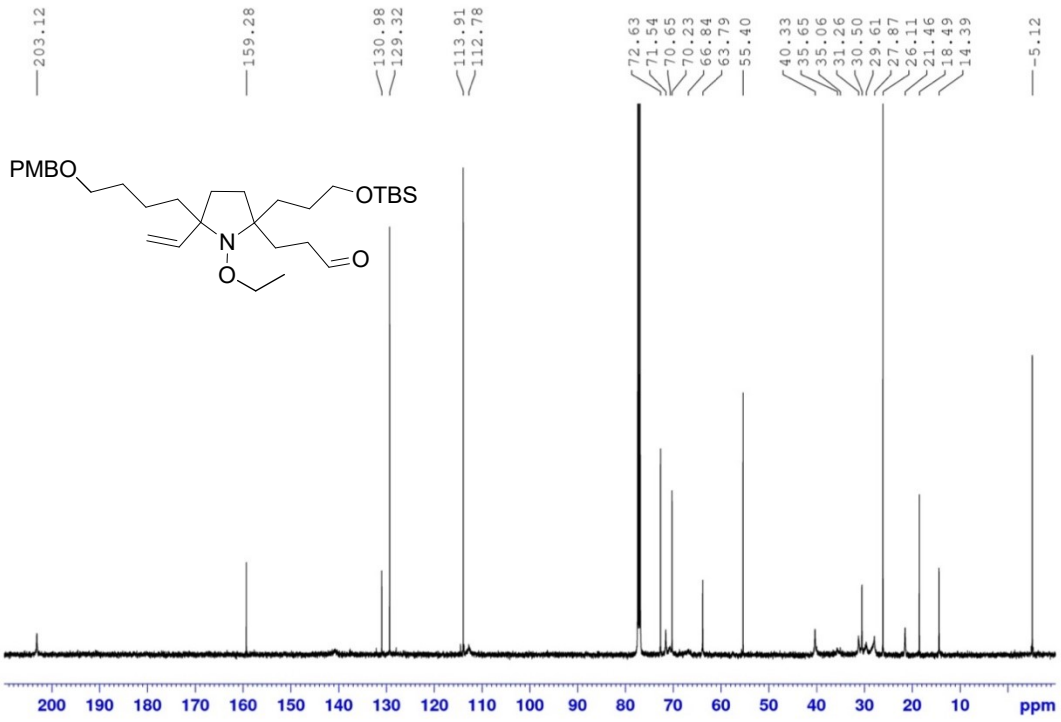


Figure S34. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **14b (minor)**

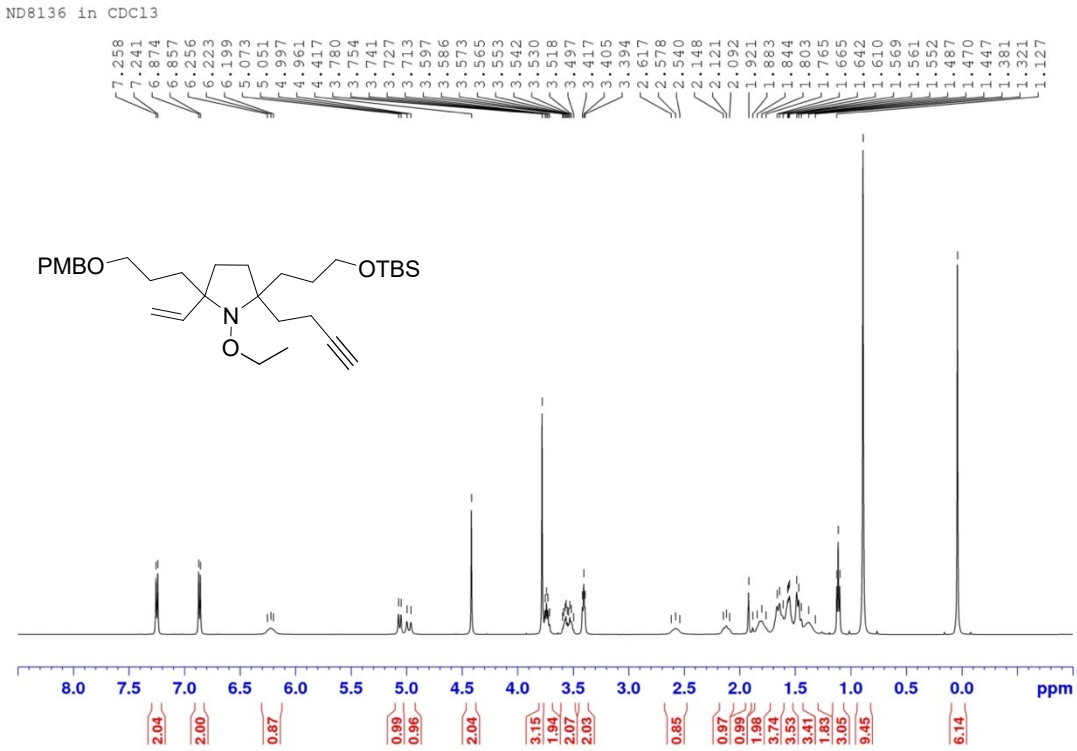


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **15a**

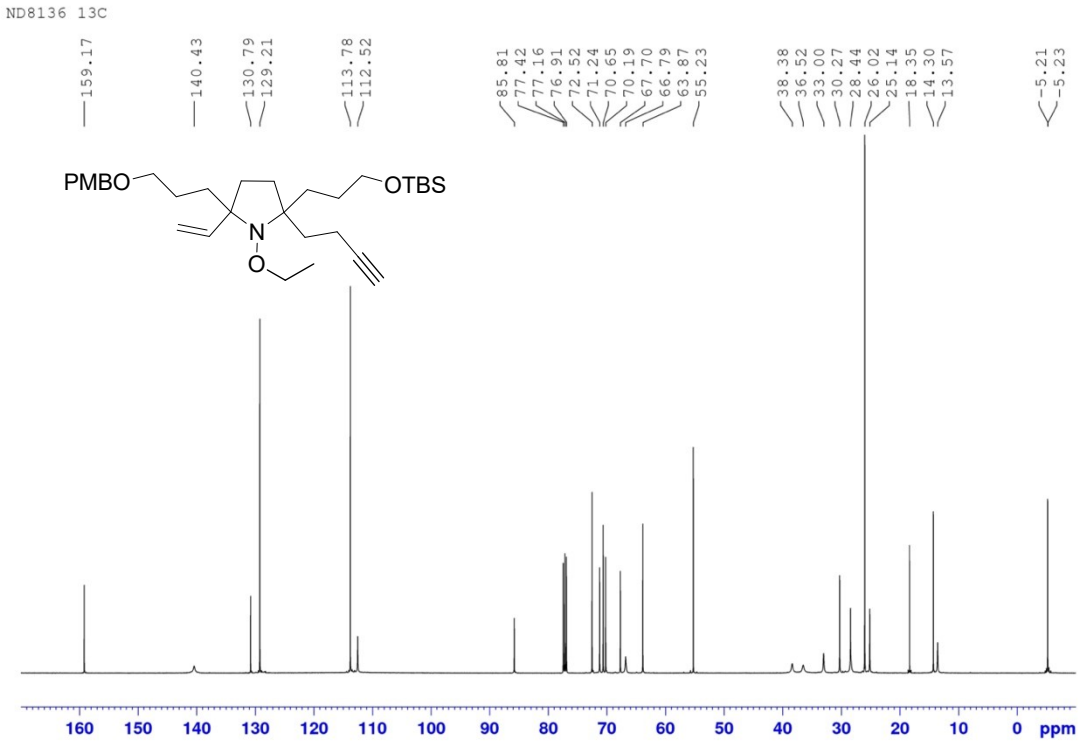


Figure S36. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **15a**

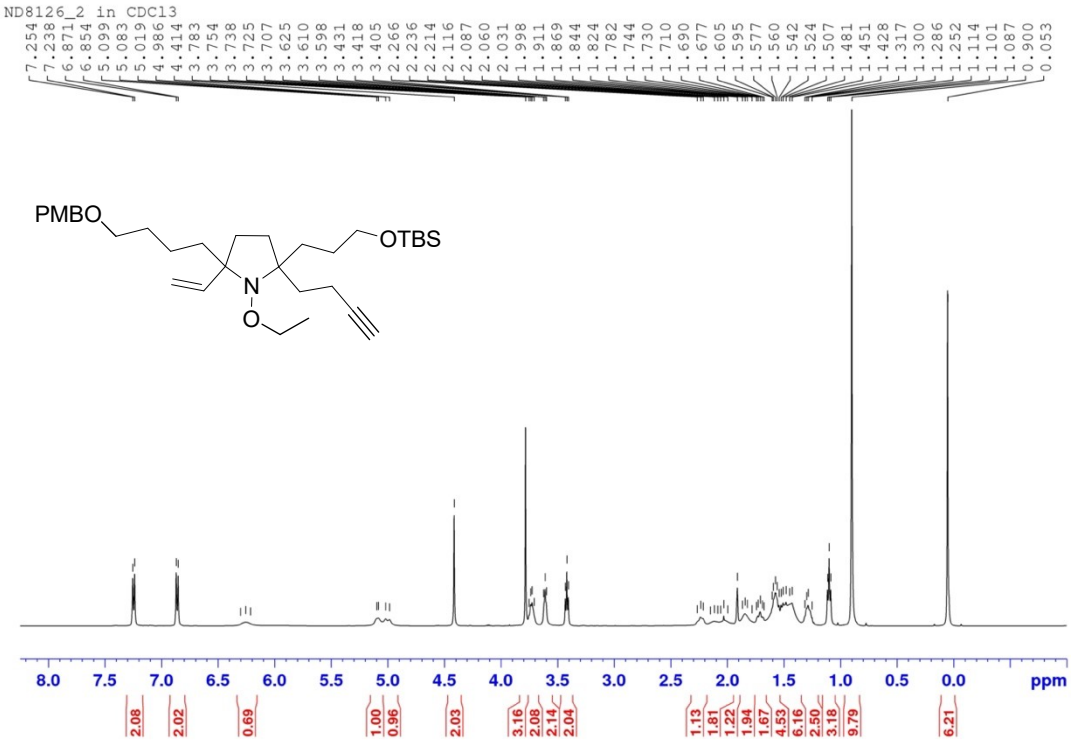


Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **15b**

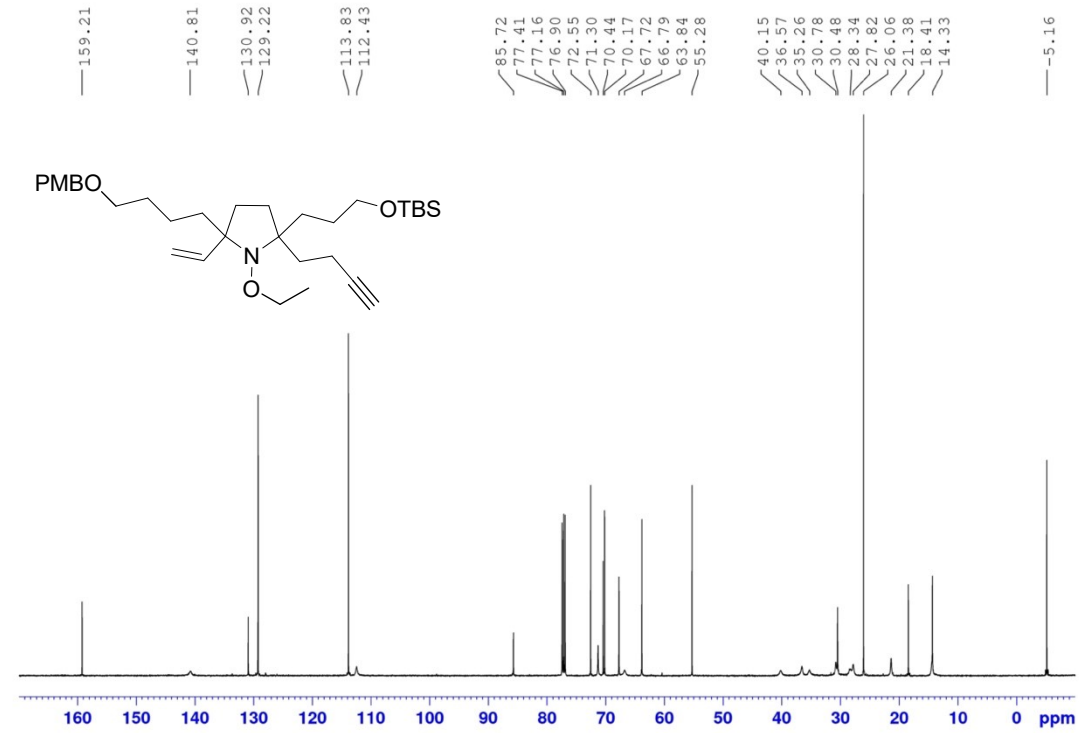


Figure S38. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **15b**

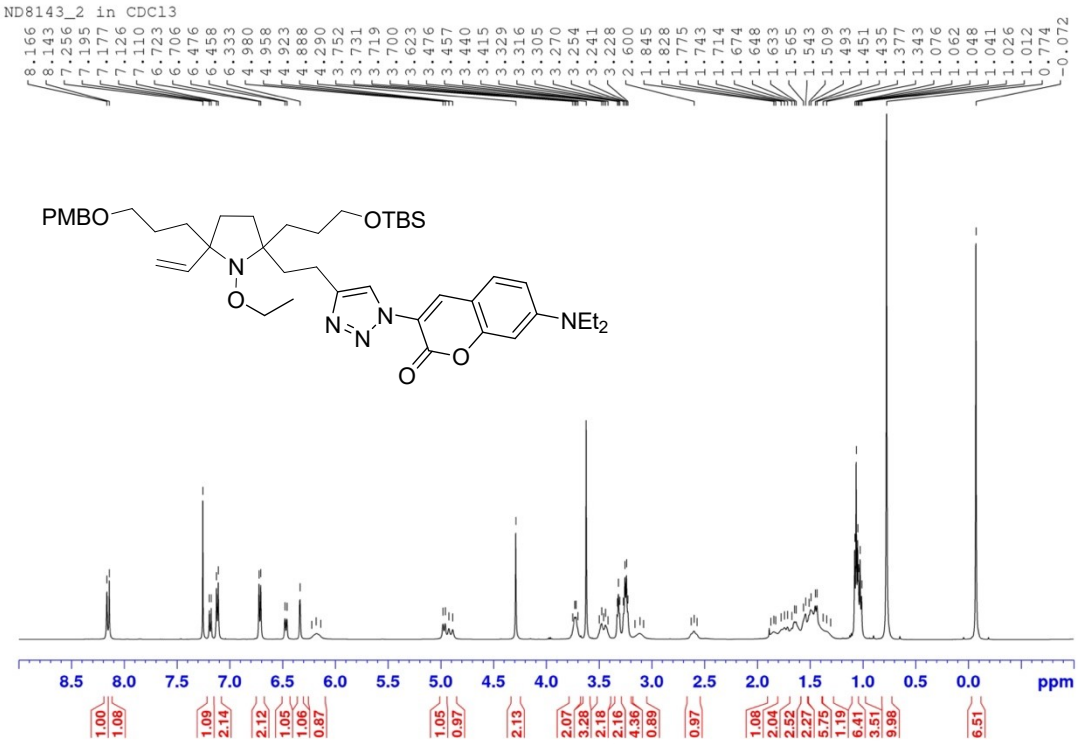


Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **17a**

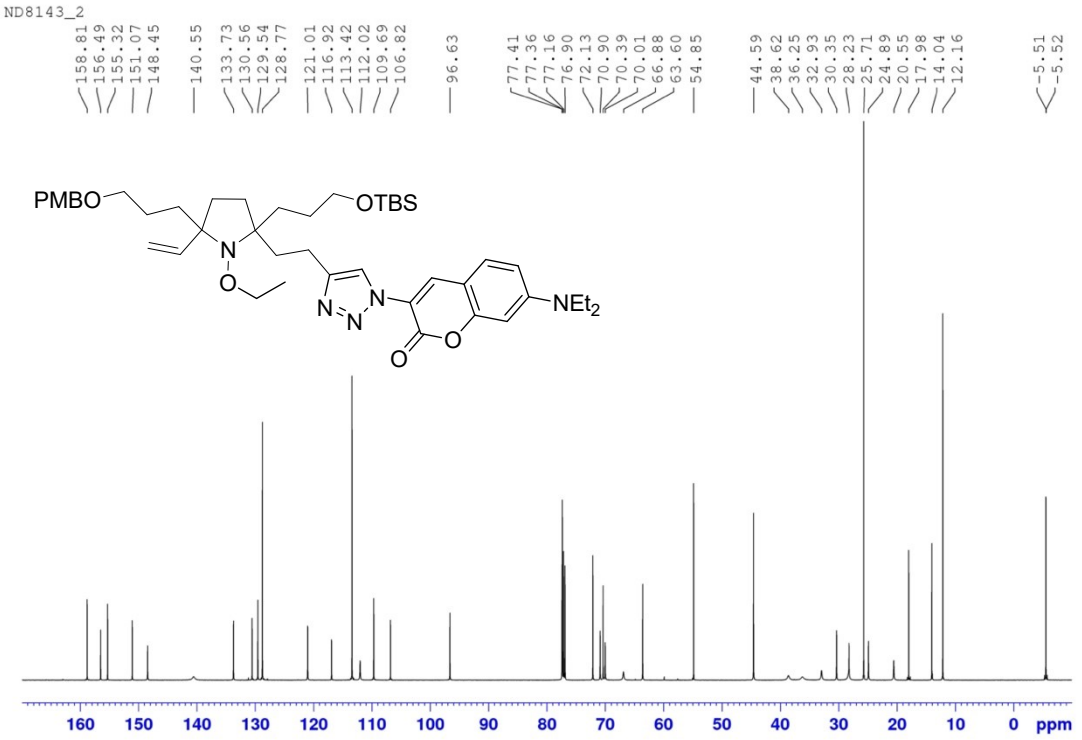


Figure S40. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **17a**

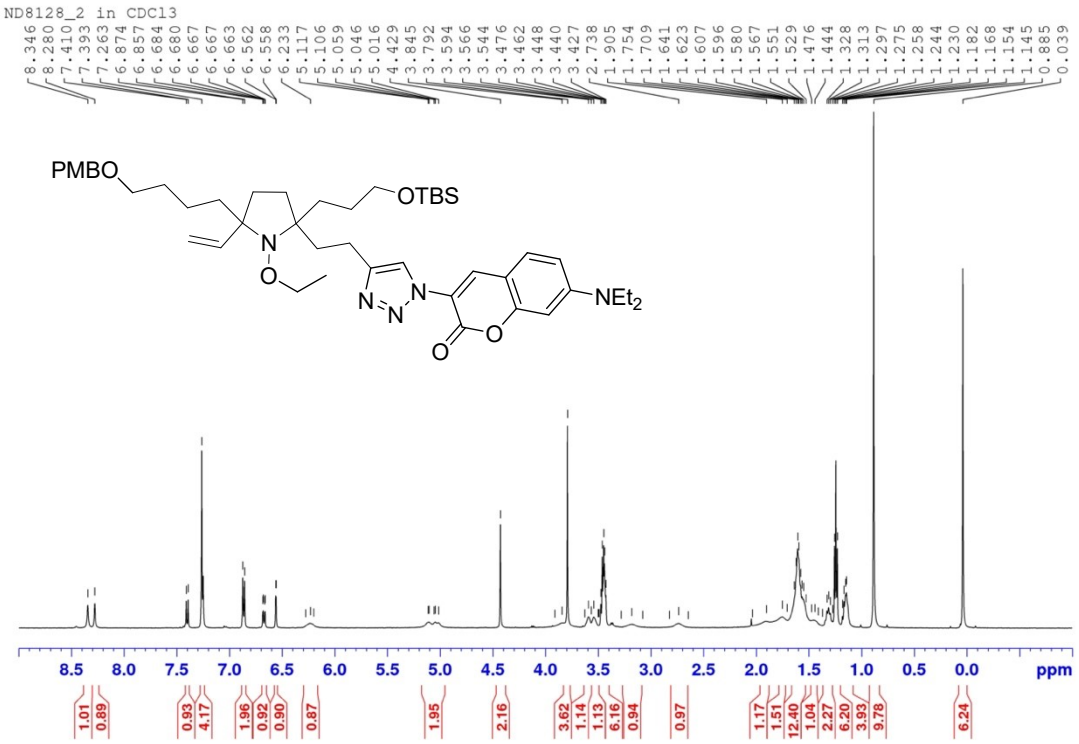


Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **17b**

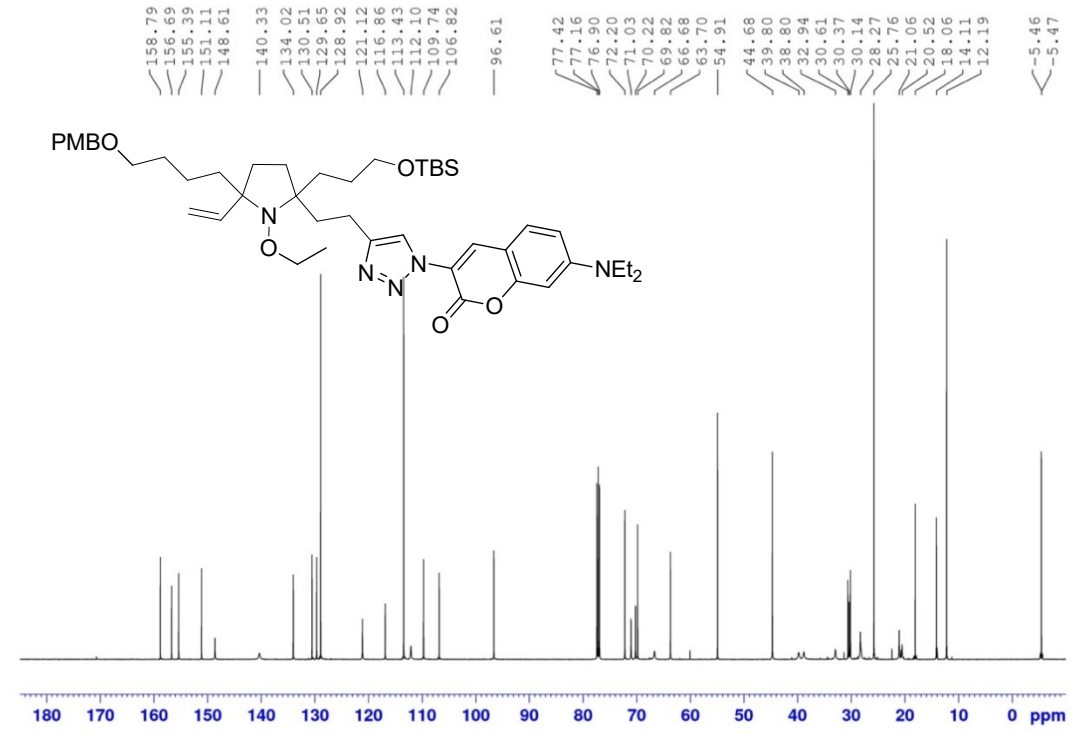


Figure S42. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **17b**

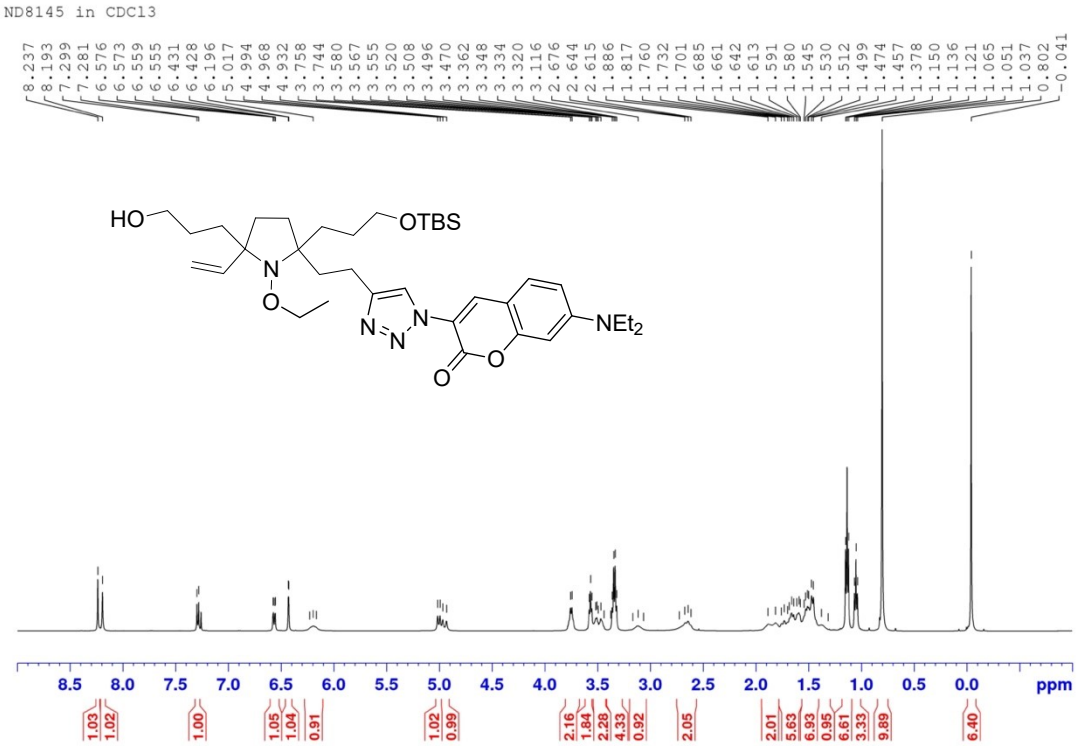


Figure S43. ^{1}H NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **18a**

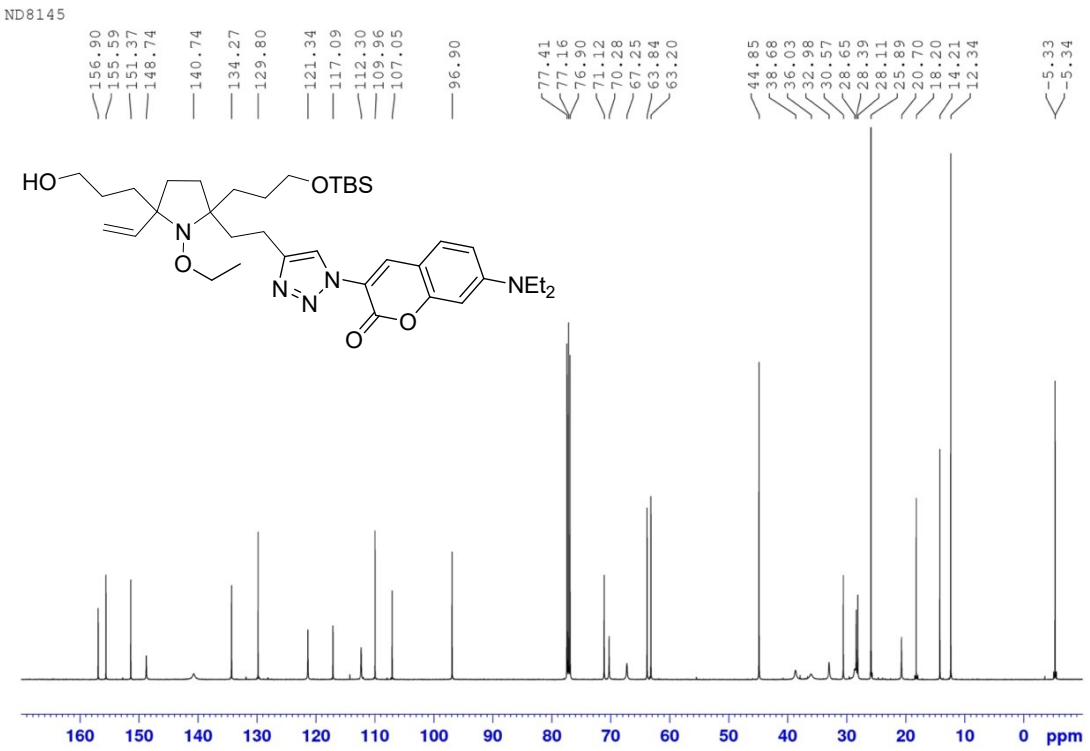


Figure S44. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **18a**

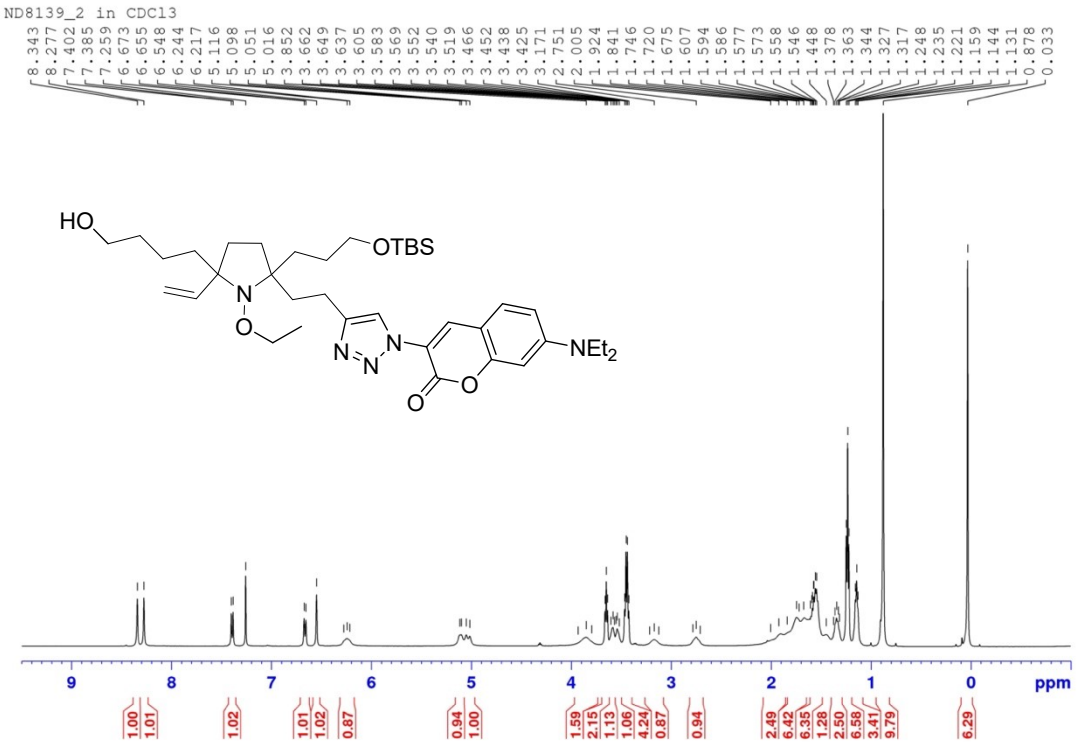


Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **18b**

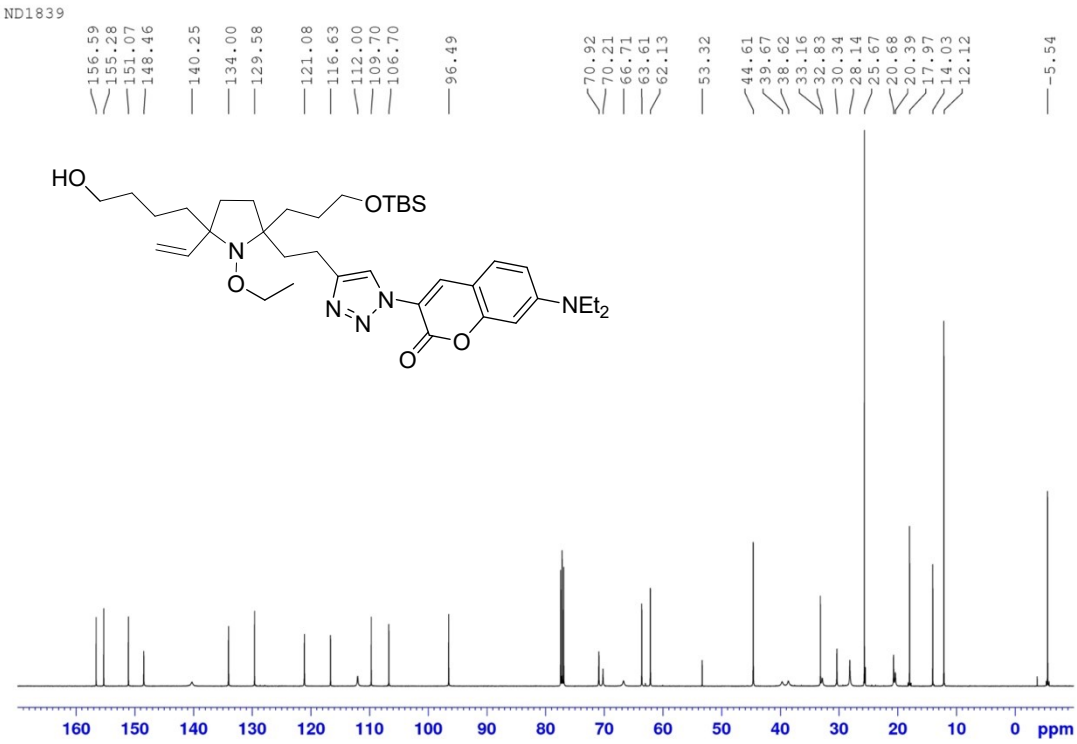


Figure S46. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **18b**

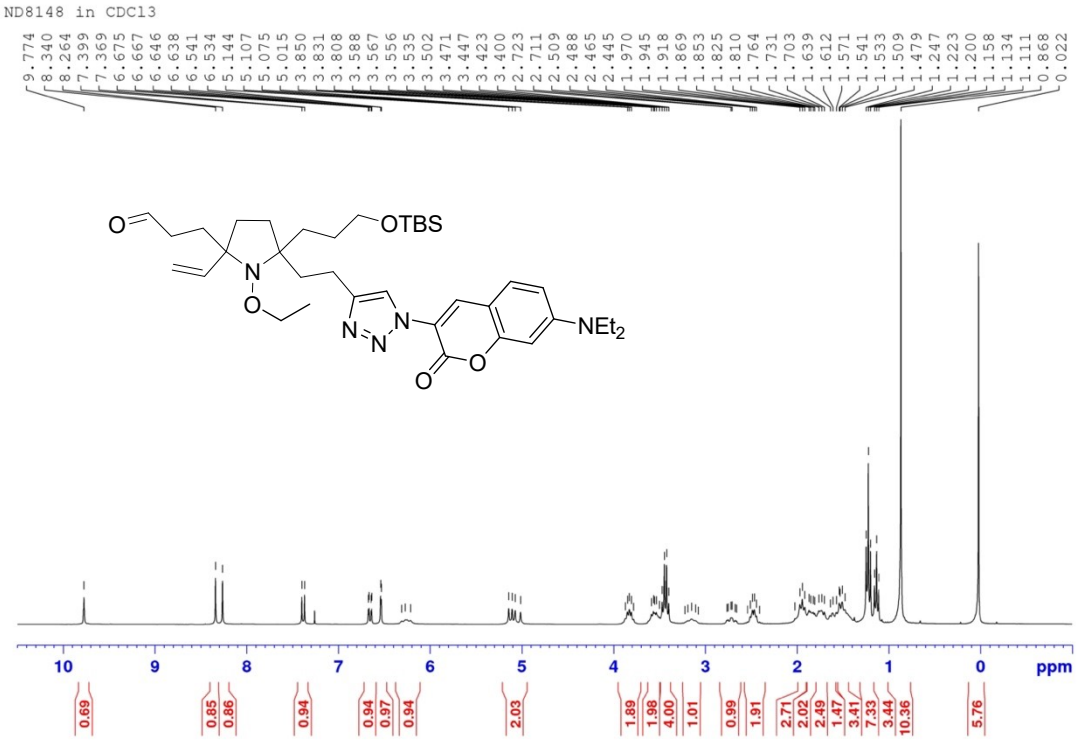


Figure S47. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **19a**

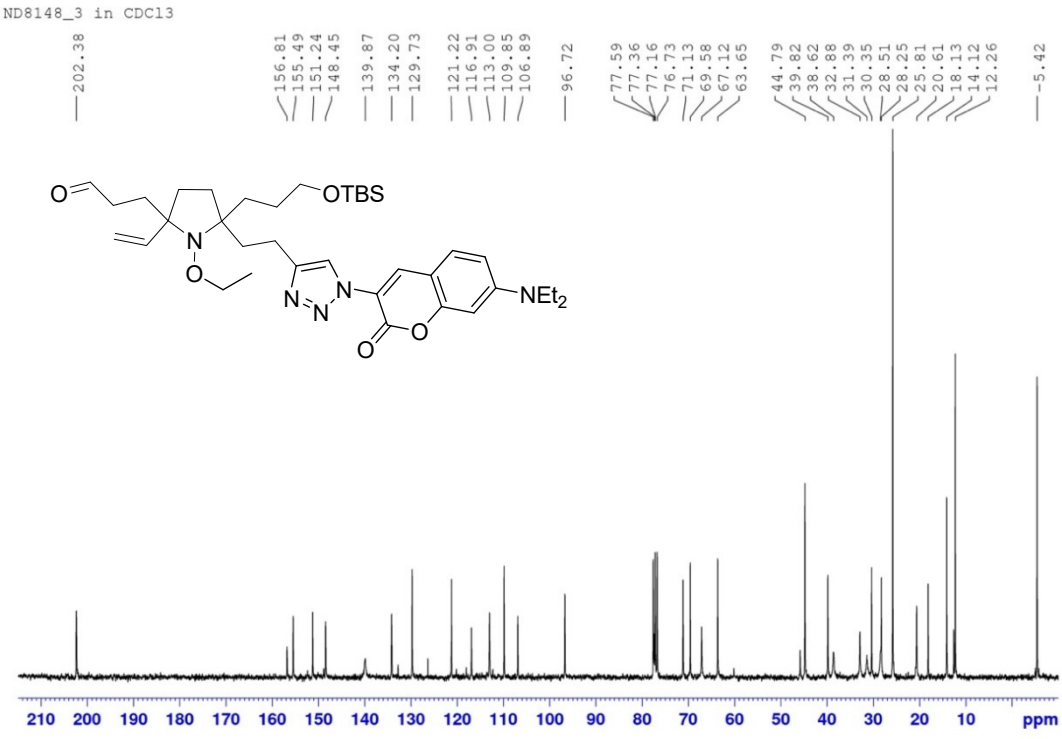


Figure S48. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **19a**

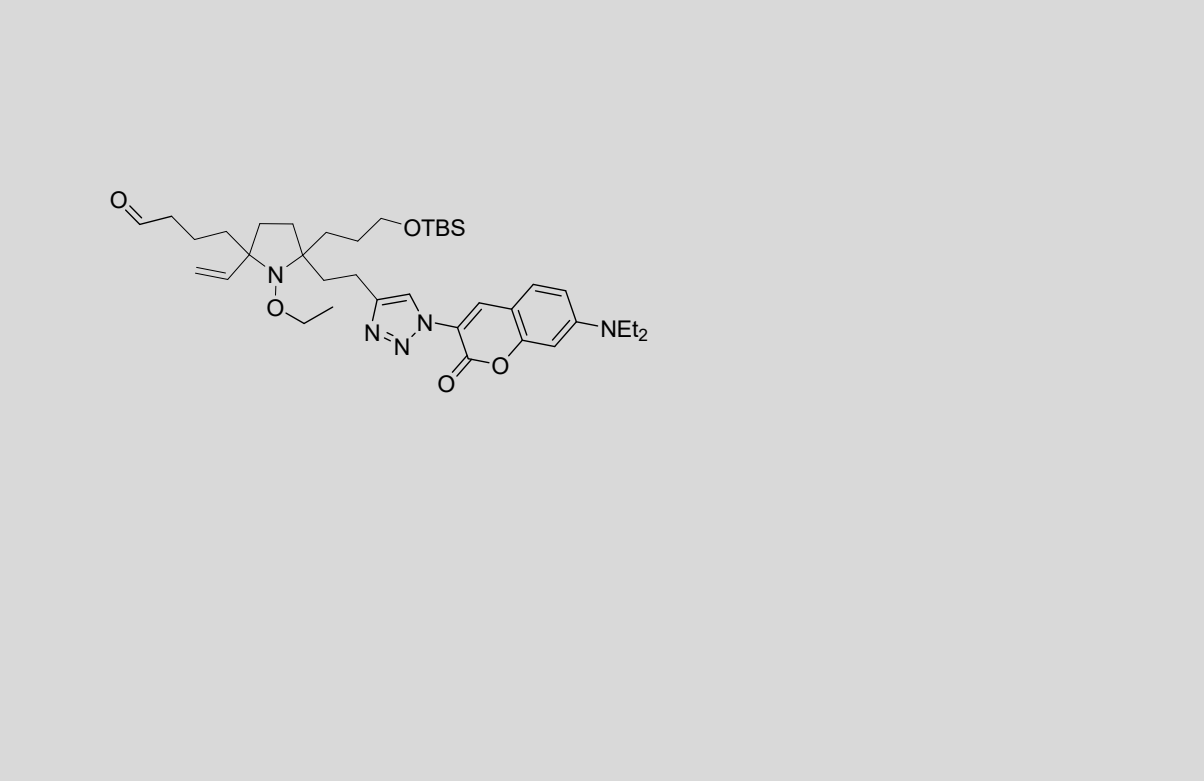


Figure S49. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **19b**

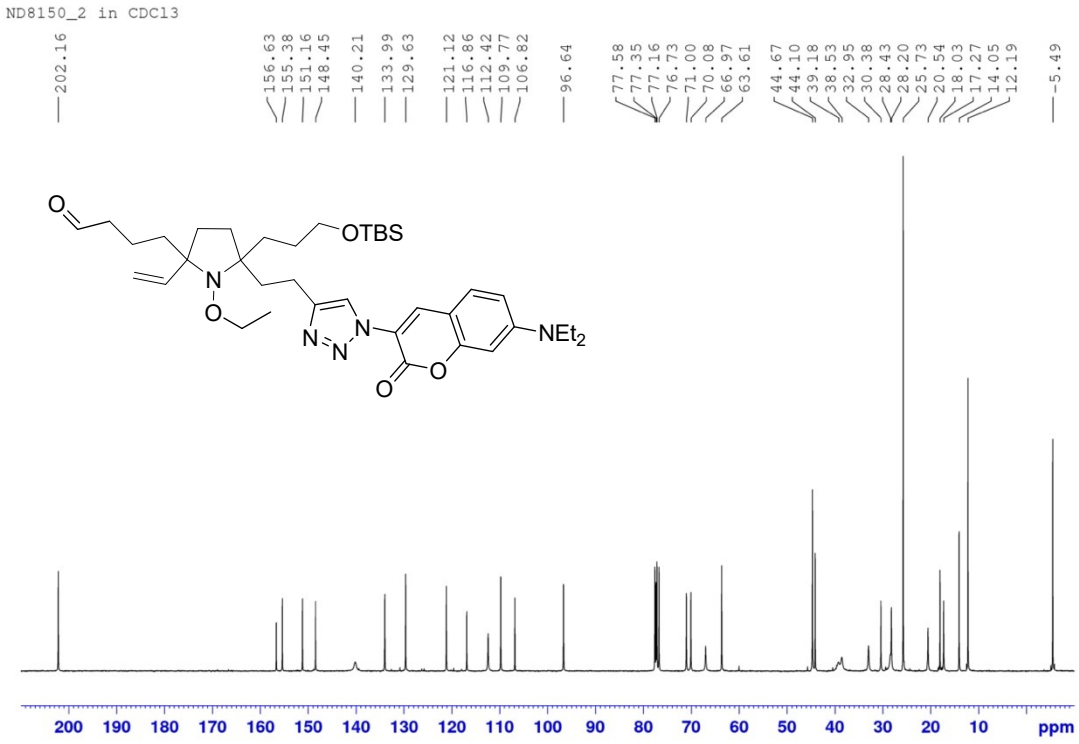


Figure S50. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **19b**

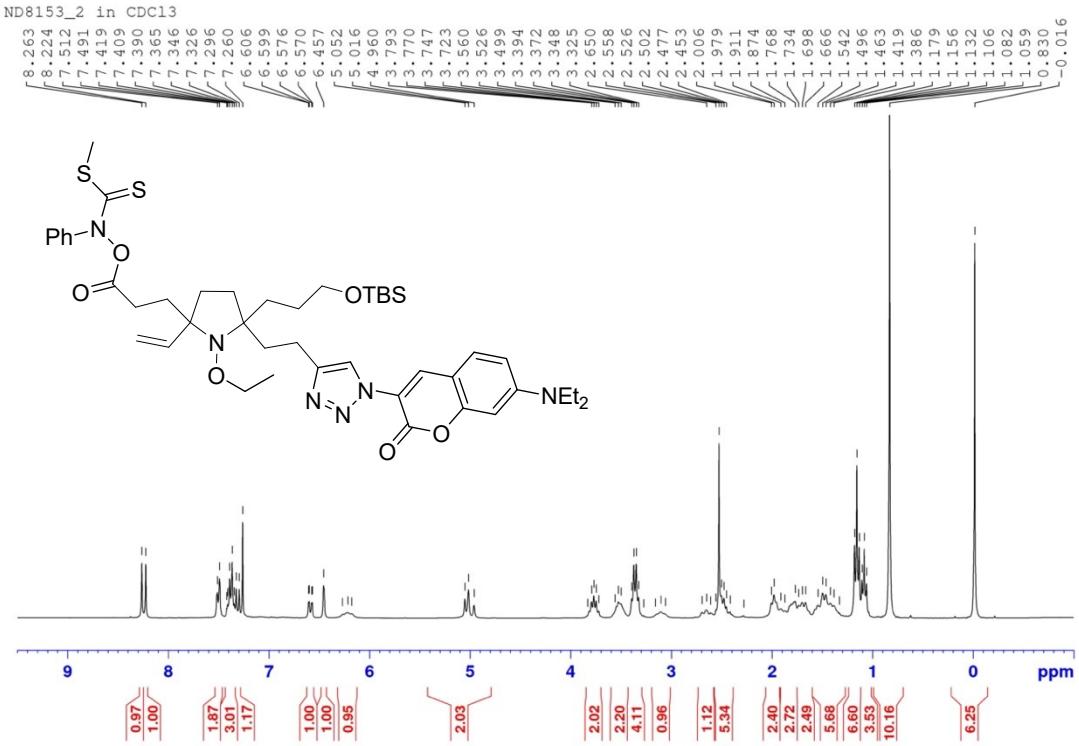


Figure S51. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **21a**

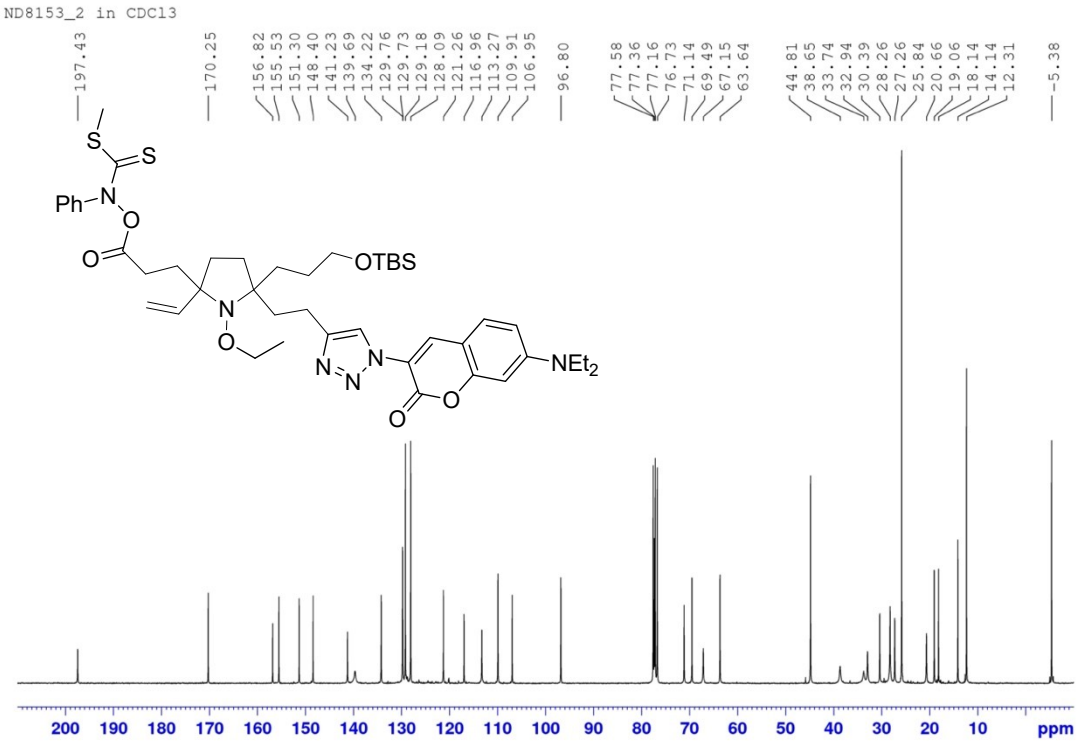


Figure S52. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **21a**

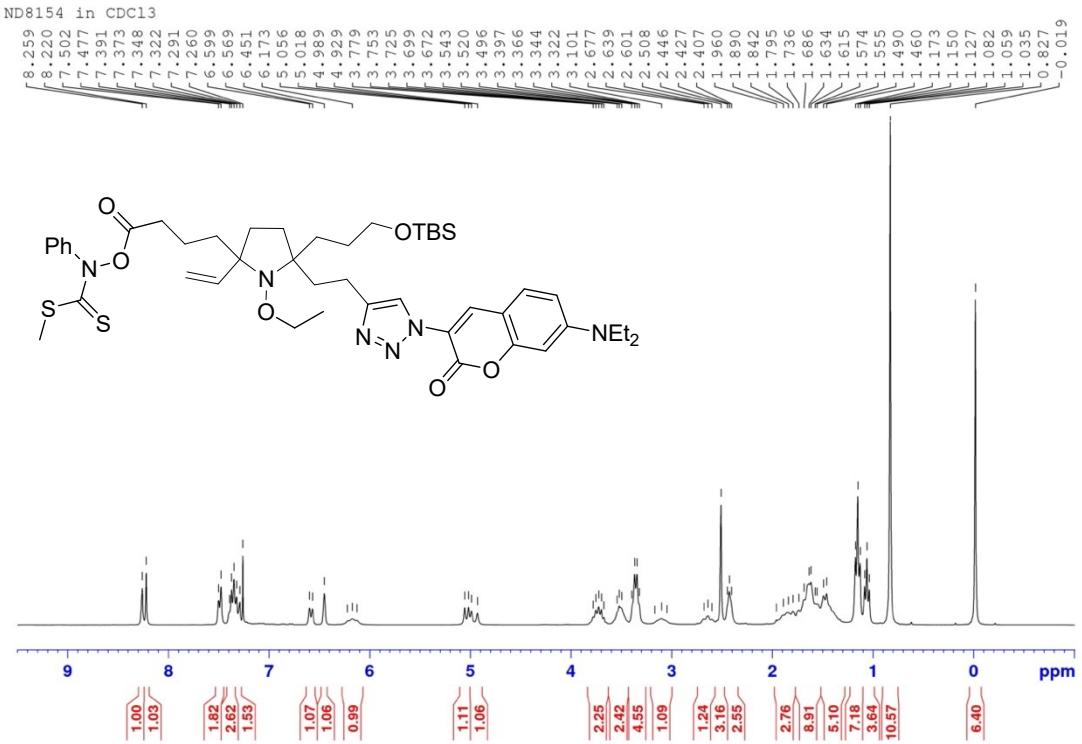


Figure S53. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **21b**

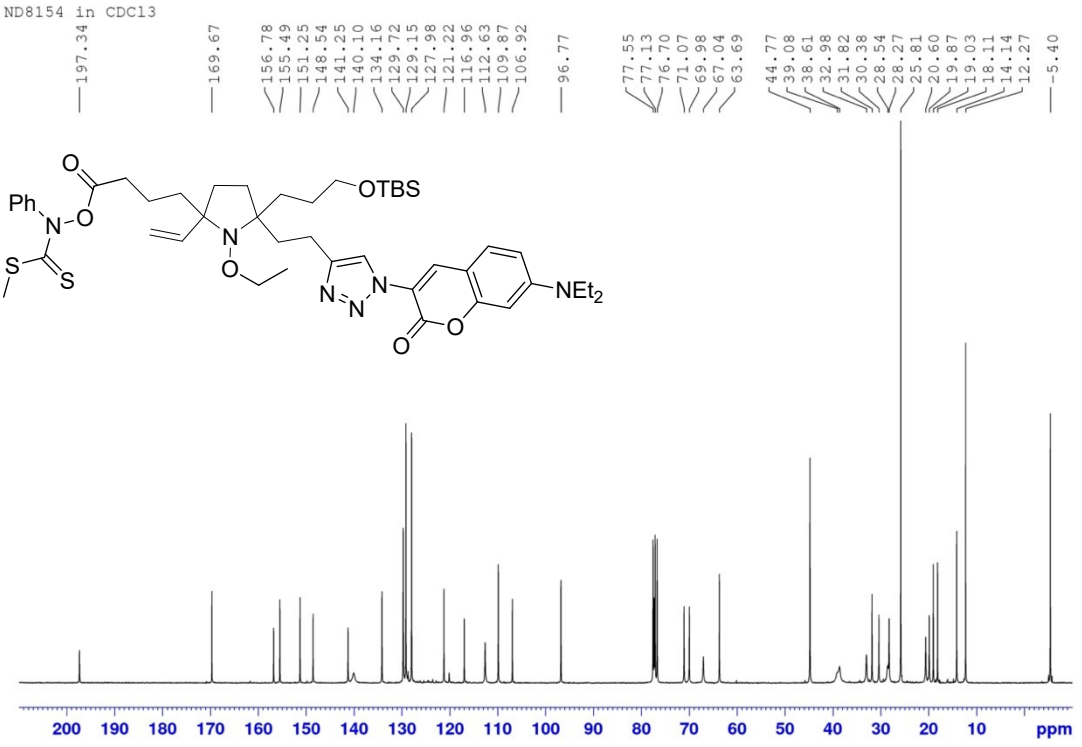


Figure S54. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **21b**

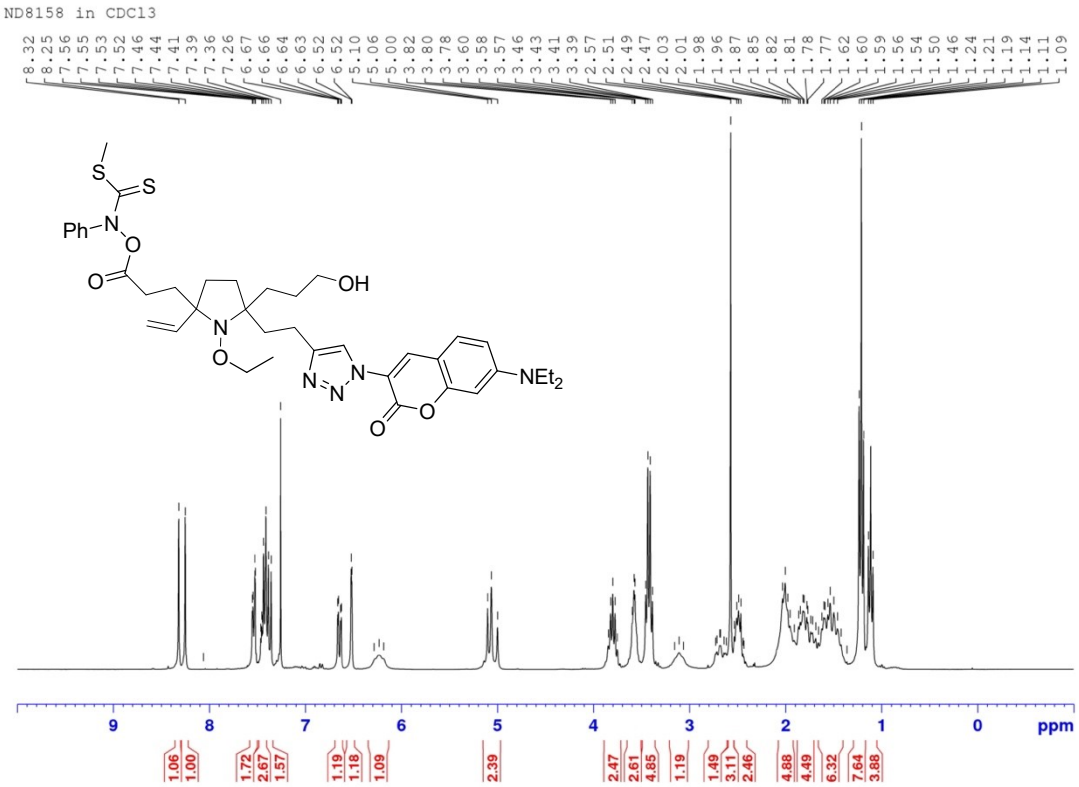


Figure S55. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of **ProN6**

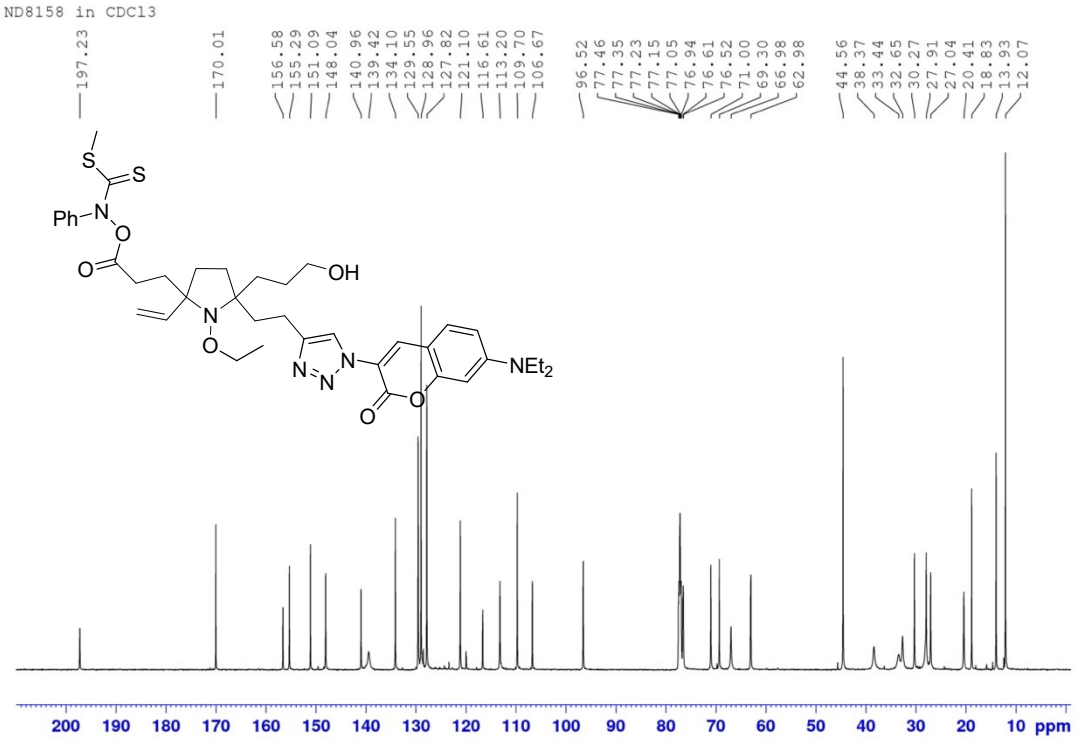


Figure S56. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of **ProN6**

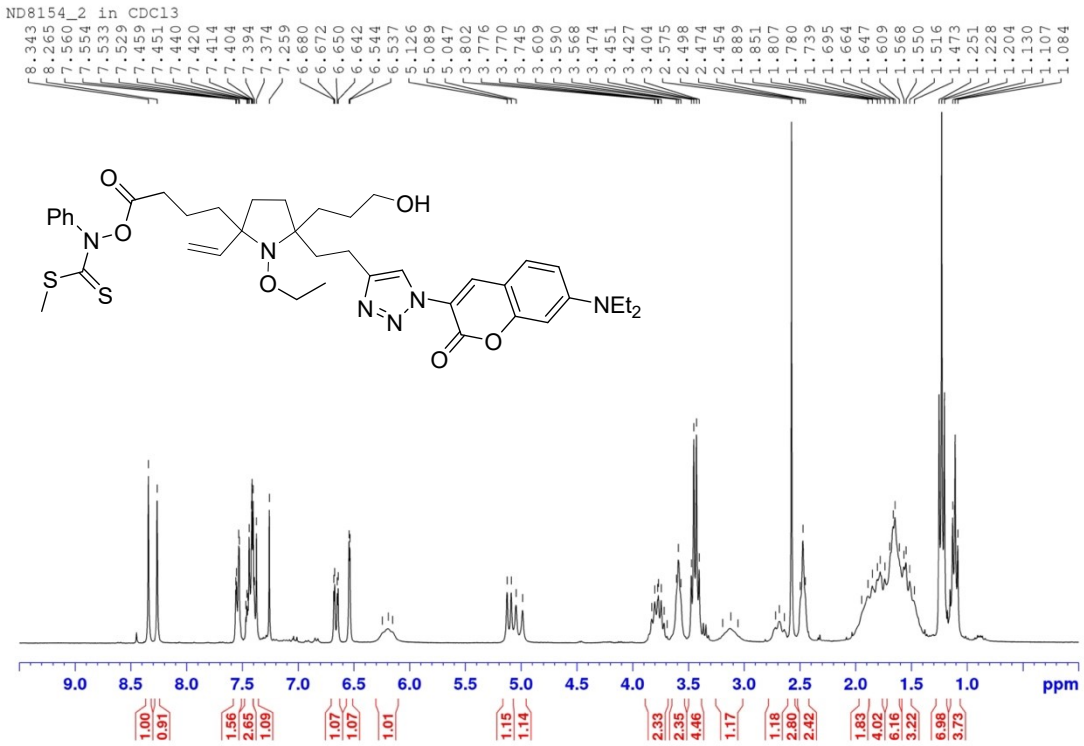


Figure S57. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of compound **ProN7**

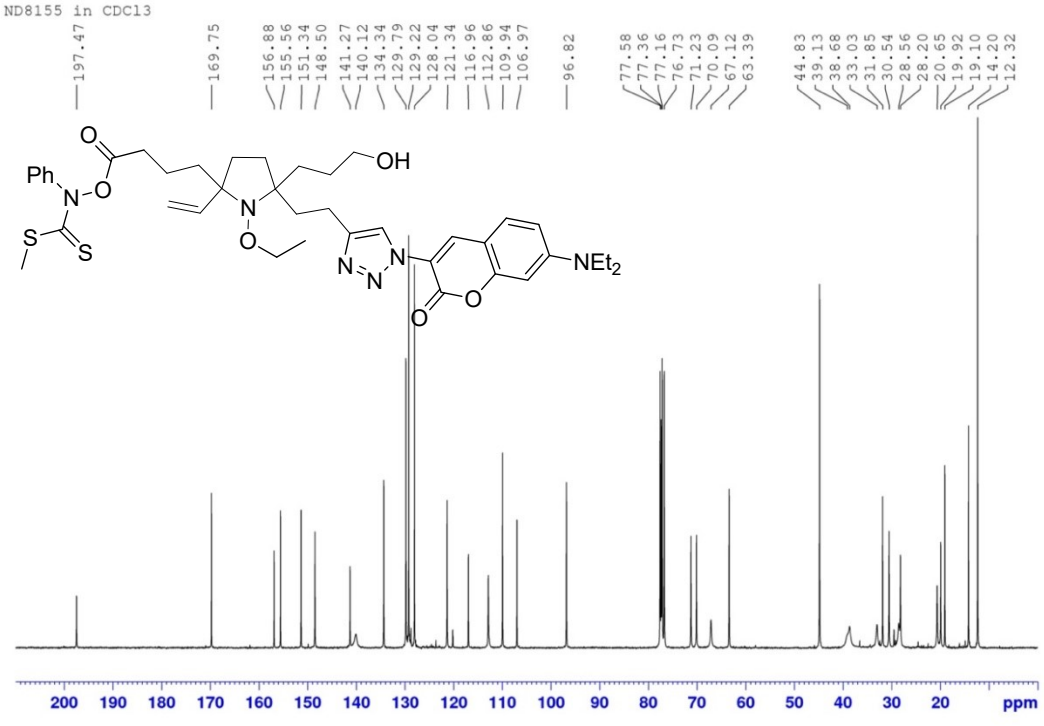


Figure S58. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ethoxylamine derivative of **ProN7**

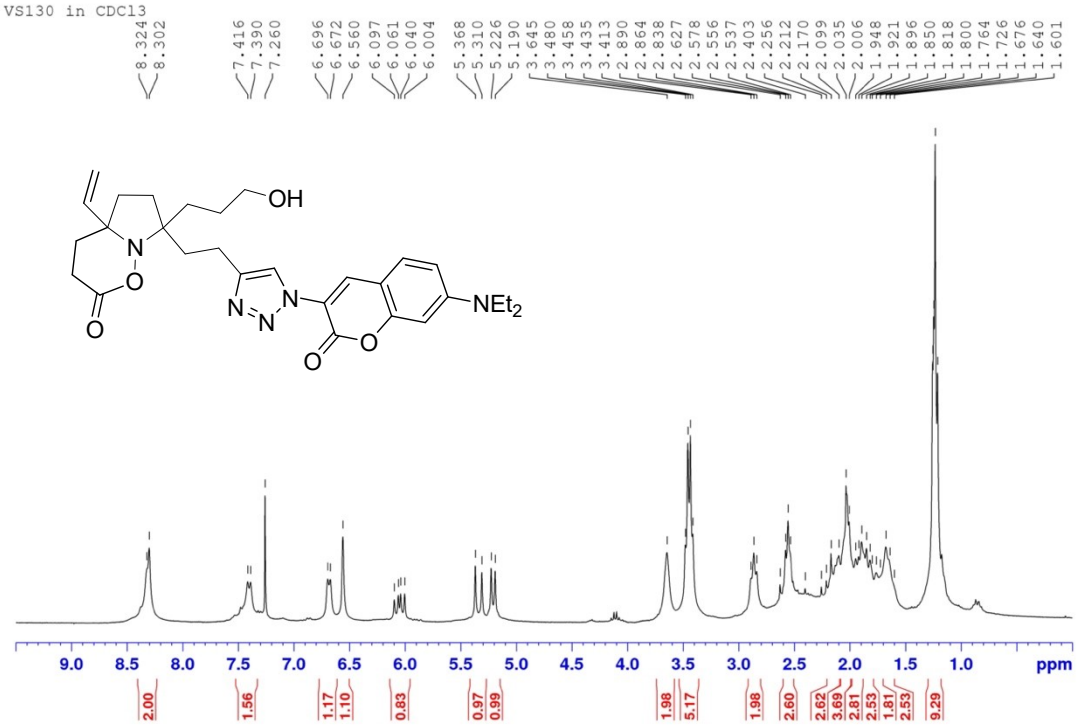


Figure S59. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **cyclic *N*-acylamine 22a**

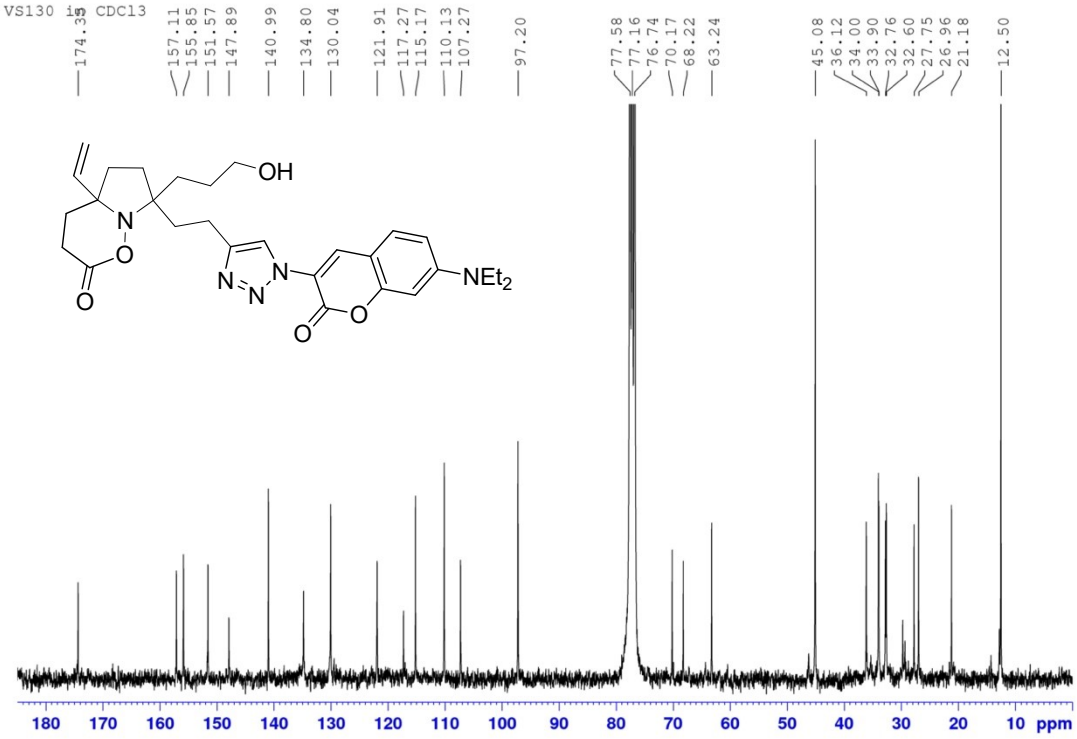


Figure S60. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **cyclic *N*-acylamine 22a**

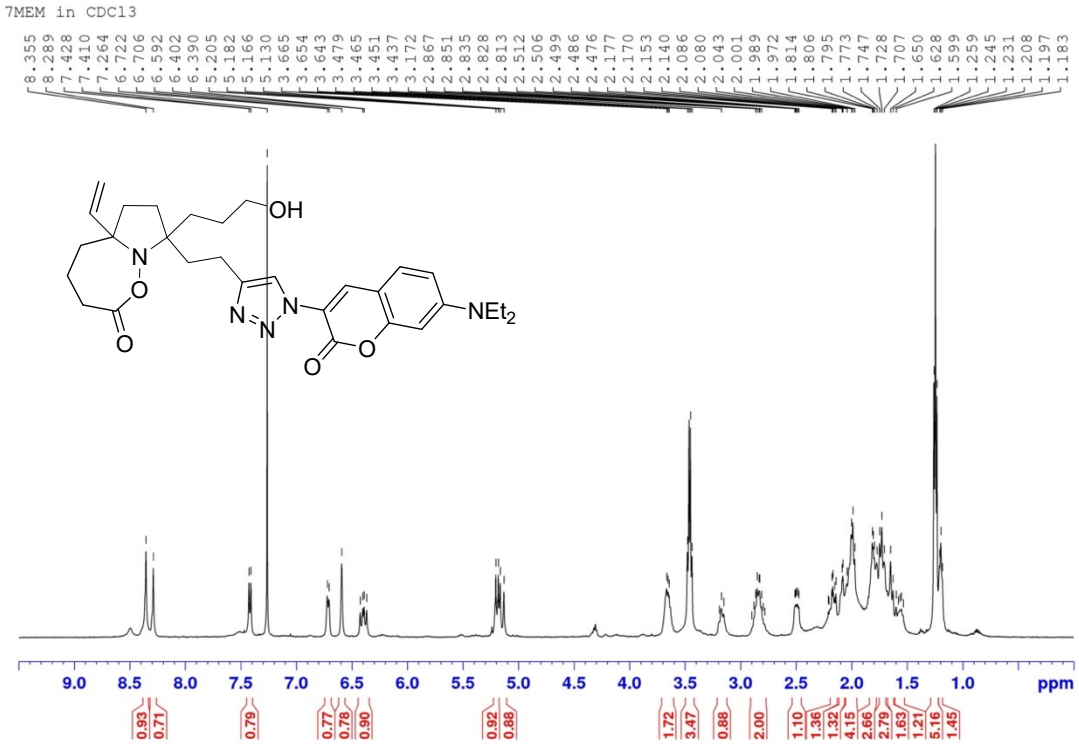


Figure S61. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **cyclic *N*-acylamine 22b**

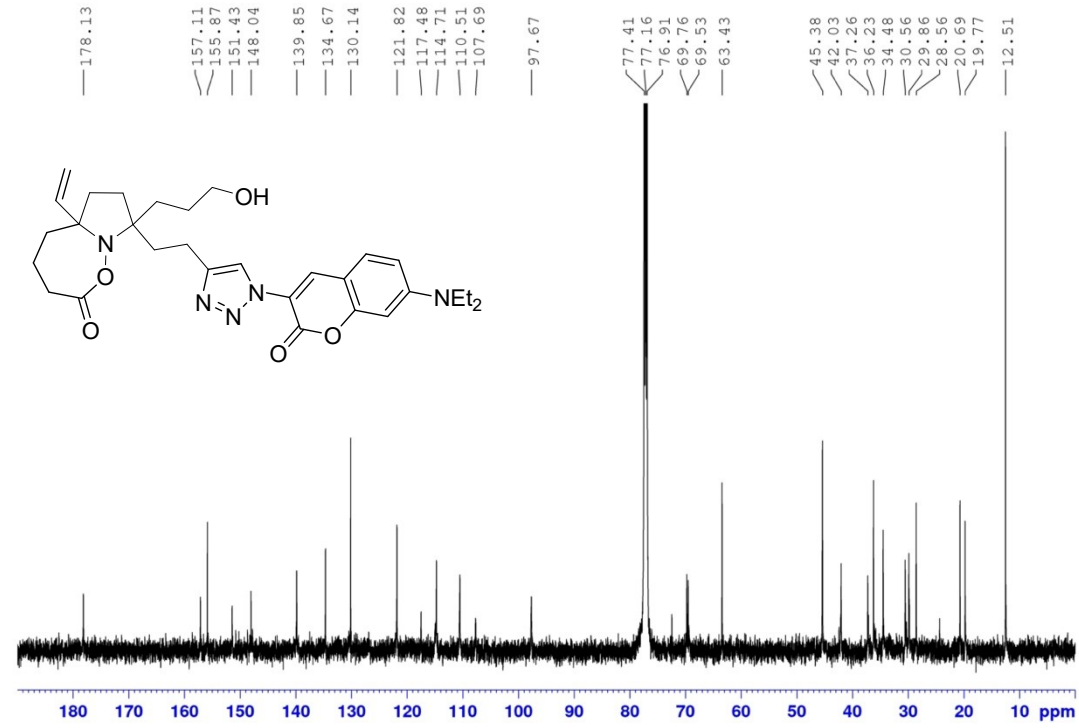


Figure S62. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **cyclic *N*-acylamine 22b**

Figure S63. Photographs of paper-based sensors after AA analysis of samples A, B and C

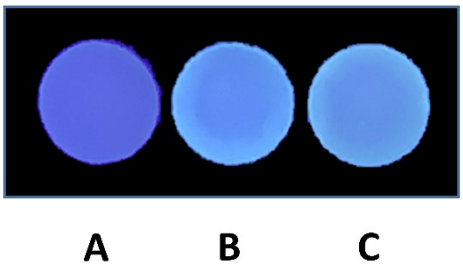


Table S1. Data obtained from ImageJ for green intensities and AA amounts in samples A, B and C

		#1	#2	#3	#4	Average	SD
Green intensity	Water (I_0)	61.8	69.2	62.5	61.2	63.7	3.2
	Sample A (I)	107.8	105.9	105.5	107.7	106.7	1.1
	Sample B (I)	154.6	156.7	159.0	154.1	156.1	1.9
	Sample C (I)	158.6	160.2	157.8	158.9	158.9	0.8
AA content	Sample A (mg)	310	280	273	308	293	16
	Sample B (mg)	1042	1075	1076	1076	1067	15
	Sample C (mg)	1105	1093	1120	1109	1107	10

UV-vis absorption spectra of ProN6 in the absence and presence of AA

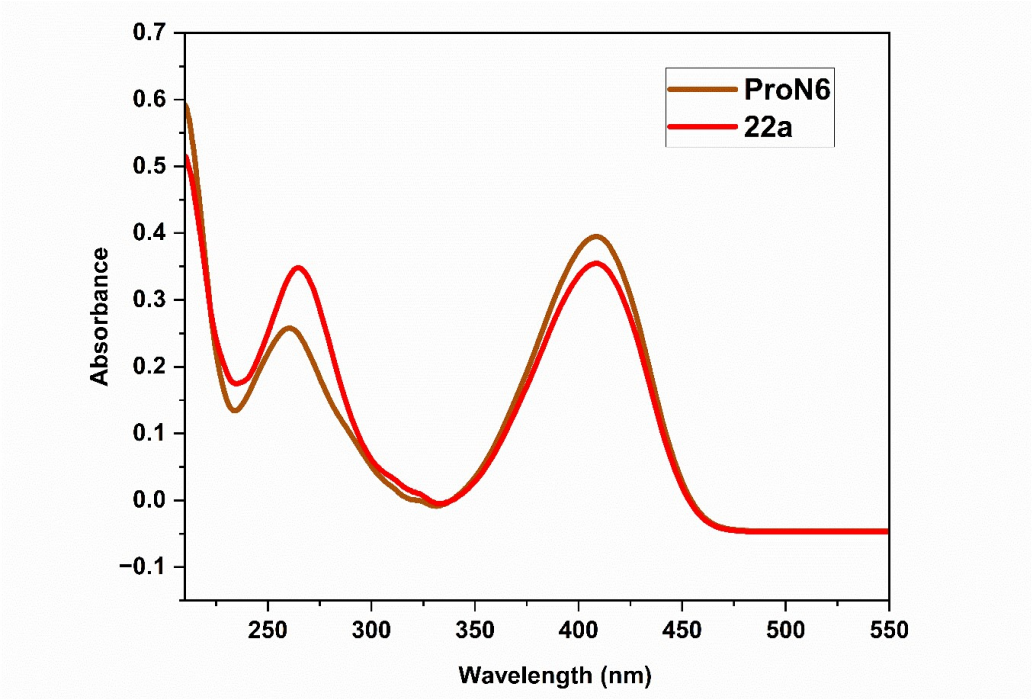


Figure S64. UV-vis absorption spectra of **ProN6** (20 μM in ethanol) in the absence and presence of AA (**22a**)

UV absorption spectra of AA at different concentrations

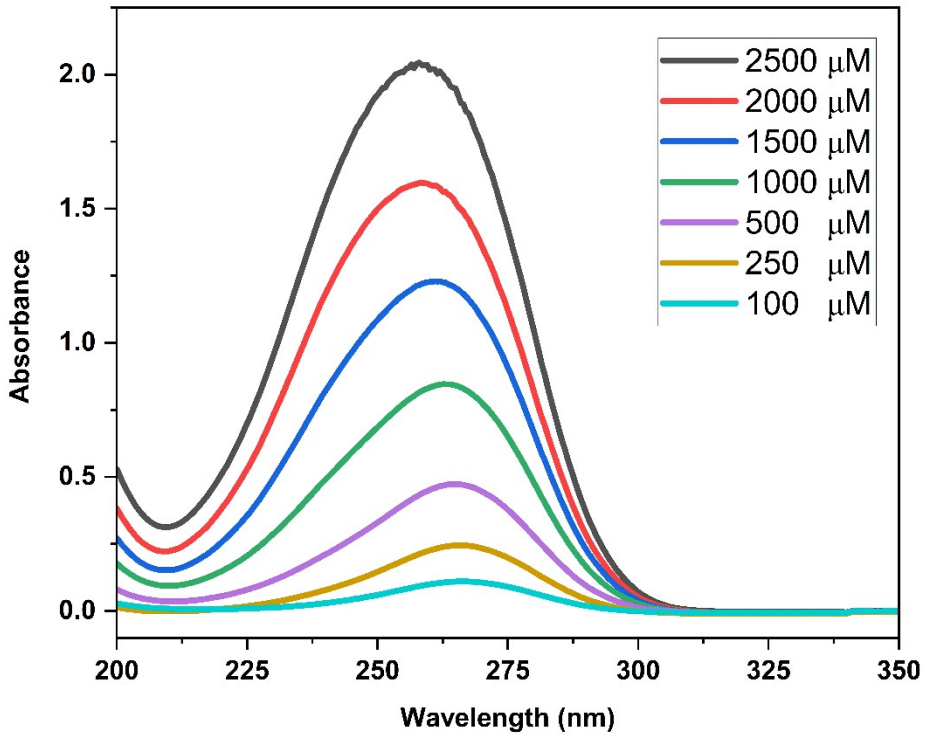


Figure S65. UV absorption spectra of AA at concentrations of 100-2500 µM

UV calibration profile

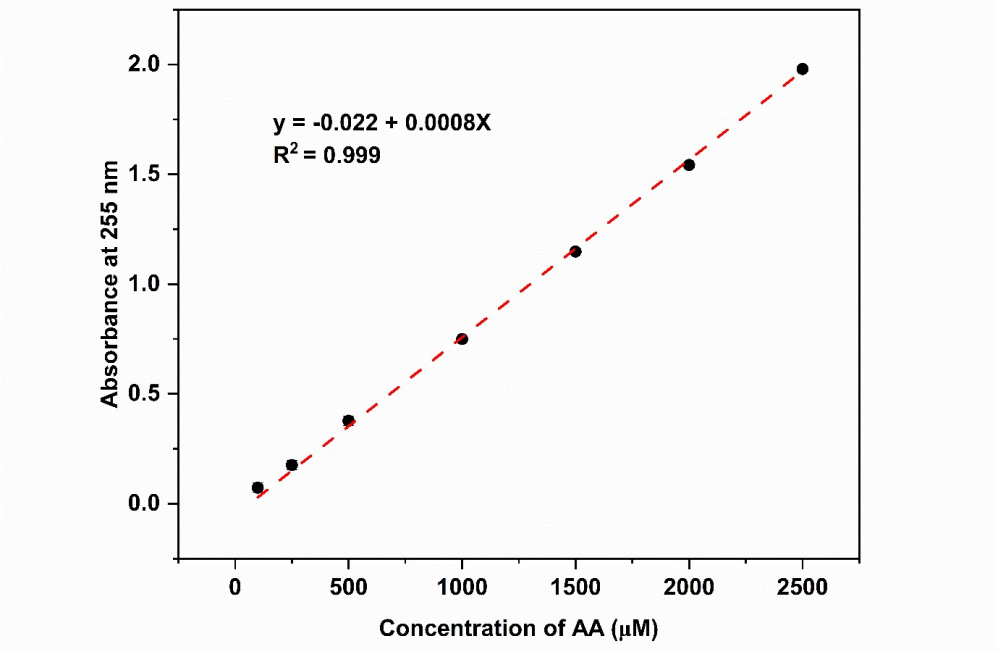
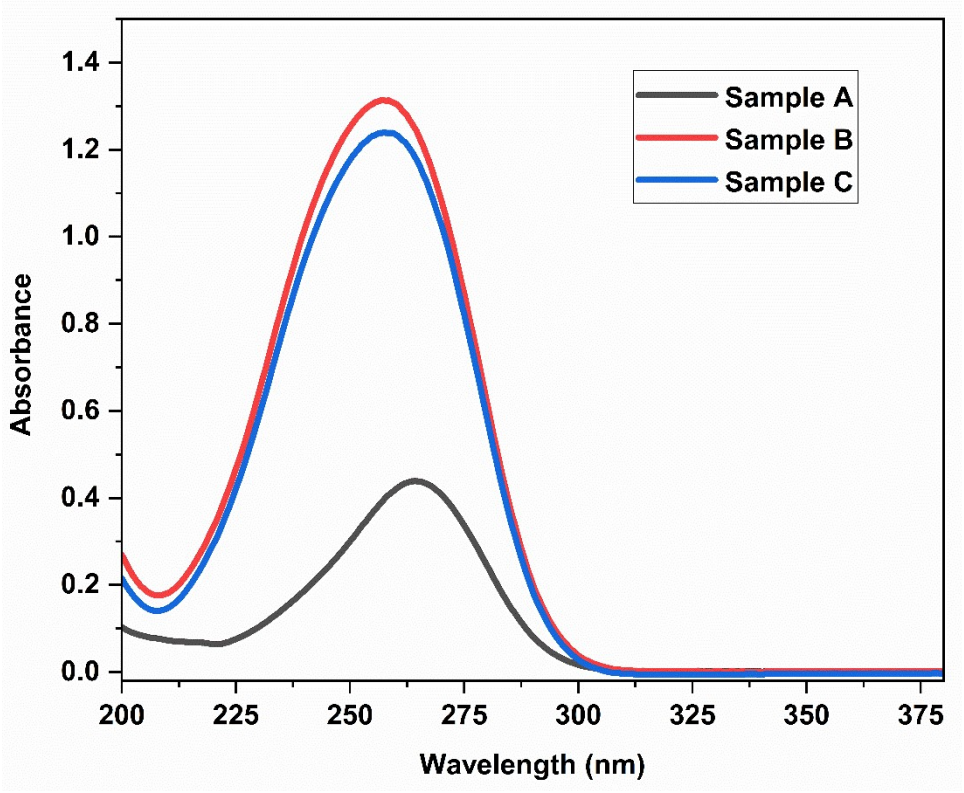


Figure S66. UV calibration curve of AA absorbance at 255 nm

Figure S67. UV absorption spectra of samples A, B and C



Coordinates and calculated energies of the optimized structures

Table S2. Energies (E), Thermal Correction to Gibbs Free Energy (tcG) and Gibbs Free Energies (G) (in Hartree) of the structures calculated at the B3LYP/6-311G** level in ethanol.

Compounds	**E**	**tcG**	**G**
Profluorescent nitroxide **ProN5**	-2975.0304	0.6687	-2974.3617
Profluorescent nitroxide **ProN6**	-3014.3520	0.6934	-3013.6586
Profluorescent nitroxide **ProN7**	-3053.6807	0.7187	-3052.9620
5- membered *O*-acylalkoxylamine, **22c**	-1738.2718	0.5355	-1737.7363
6- membered *O*-acylalkoxylamine, **22a**	-1777.6122	0.5587	-1777.0536
7- membered *O*-acylalkoxylamine, **22b**	-1816.9375	0.5867	-1816.3508
thiohydroxamate ester, **20**	-1236.7412	0.1160	-1236.6252

Cartesian coordinates of the optimized structures

Profluorescent nitroxide **ProN5**

C	-0.25365800	-0.15460900	0.04519600
C	1.04627400	0.42492400	-0.57126200
C	0.82542400	1.94527800	-0.67788100
C	-0.18493500	2.30946600	0.42996600
N	-1.00951700	1.06776000	0.44641900
H	1.88531500	0.20785500	0.08689200
H	0.40299300	2.19954400	-1.65352300
H	1.76160900	2.49623900	-0.57468500
H	1.27064400	-0.02089700	-1.54153200
C	-1.08094200	-0.86328100	-1.09222100
H	-0.52650800	-1.73594700	-1.44057800
H	-1.20672200	-0.15644200	-1.91220500
C	-0.02588900	-1.14974400	1.16973600
C	1.01212200	-1.97391500	1.27862000
H	1.06857300	-2.68851400	2.09241600
H	1.83919200	-1.97758600	0.57614300
C	0.45534200	2.68291100	1.78896700
H	0.89126900	3.67799400	1.67455400
H	-0.36259000	2.79025400	2.50745500
C	1.52530700	1.76637000	2.38880300
H	1.13978700	0.75721200	2.54892300
H	2.38621600	1.68053300	1.71799700
C	2.02785100	2.30505000	3.72090300
H	1.19514000	2.37569800	4.43425600
H	2.44068000	3.31461600	3.58803000
O	3.03404300	1.41067100	4.20986200
H	3.35136900	1.75638600	5.05025900
C	-1.14301400	3.44482200	-0.02143700
H	-1.90076000	3.59853000	0.75304200
H	-1.66831400	3.06439400	-0.90091700
C	-0.52376900	4.81453700	-0.39031300
H	-1.21609600	5.30558900	-1.08220100
H	0.40875100	4.68021400	-0.94444600
C	-0.28215200	5.75392800	0.75322000
C	0.87792200	6.37202300	1.15931300
N	0.51814800	7.11395200	2.24222900
H	1.88851400	6.33604900	0.79615000
N	-1.28235900	6.15072400	1.59487800
N	-0.80685100	6.96203100	2.49442600
C	1.30612000	7.96778900	3.05438400
C	0.79085100	9.12320200	3.56377800
C	2.65966300	7.54057300	3.36247300
C	1.56124300	9.94154800	4.42638600

H	-0.22366900	9.40822900	3.31267700
C	2.87648800	9.53979800	4.72691900
C	1.11427500	11.14352100	5.01538100
C	3.71263500	10.26249400	5.55470300
C	1.92374100	11.88294300	5.84276000
H	0.10482800	11.48268400	4.81224800
C	3.26400200	11.47455500	6.13443100
H	4.70110800	9.86967400	5.73573000
H	1.52504600	12.78678600	6.27721200
O	3.21543800	6.53963200	2.96533800
O	3.37942600	8.38103800	4.19137000
N	4.08035100	12.22911100	6.93013700
C	3.61577700	13.48626800	7.53274300
H	4.50274400	14.09056000	7.72773900
H	3.03073600	14.04053500	6.79552500
C	2.81482700	13.31729500	8.82879200
H	3.41962100	12.84849200	9.60758600
H	2.49276000	14.29673900	9.19295900
H	1.92472000	12.70375400	8.67381200
C	5.44697200	11.79261700	7.24550400
H	6.01015100	12.68518900	7.52072100
H	5.91554100	11.40828500	6.33602300
C	5.54579900	10.75707800	8.37184600
H	6.59118400	10.47142700	8.51713100
H	5.17118800	11.16256200	9.31379500
H	4.97760000	9.85373600	8.14035200
C	-2.42769500	-1.35555400	-0.64040300
O	-2.69116500	-2.37865900	-0.08146100
O	-3.40709400	-0.40445800	-0.96705900
N	-4.71098300	-0.74915300	-0.52701800
C	-5.02125400	-0.26406900	0.78918800
C	-5.04342600	-1.15458500	1.85995000
C	-5.24438000	1.10139800	0.97747400
C	-5.30784700	-0.66999500	3.13866700
H	-4.85242200	-2.20432300	1.68316900
C	-5.49675800	1.57661900	2.26265600
H	-5.22755400	1.77367600	0.12818400
C	-5.53135800	0.69158200	3.34065700
H	-5.33221100	-1.35548700	3.97719900
H	-5.67101500	2.63429400	2.41911400
H	-5.73118000	1.06445900	4.33823800
C	-5.59842200	-1.12176700	-1.48044400
S	-7.21667000	-1.35383700	-1.13512200
S	-4.84955400	-1.33910600	-3.07794700
C	-6.23603000	-1.94916700	-4.08271300
H	-5.80286100	-2.10069700	-5.07232400

H	-6.61221400	-2.89218300	-3.69230100
H	-7.03240700	-1.21031500	-4.13358300
O	-1.75710000	0.90735000	1.64807000
H	-2.67093400	1.06265100	1.37651300
H	-0.82561700	-1.19980200	1.89904800

Profluorescent nitroxide **ProN6**

C	1.87842500	-0.96254500	0.33220100
C	3.18994700	-0.17629200	0.11694600
C	2.75668700	1.29961900	0.08717900
C	1.51788500	1.40611500	1.01729200
N	1.22038500	-0.04056100	1.29276900
H	3.85806000	-0.36336900	0.95845700
H	2.48196400	1.58319400	-0.93120700
H	3.56237100	1.96716700	0.39564400
H	3.70666400	-0.47529700	-0.79567000
C	1.16366400	-1.18306900	-1.04197000
H	1.91572900	-1.59350600	-1.72105600
H	0.86379200	-0.22430800	-1.47001700
C	-0.03359400	-2.14238500	-1.04576400
H	-0.85265100	-1.81183700	-0.40315600
H	0.24998000	-3.12985700	-0.67084800
C	1.80865300	2.09359600	2.37153900
H	1.99578900	3.15529400	2.19172700
H	0.89022200	2.04004500	2.96816600
C	2.96887800	1.51712300	3.18749800
H	2.79508100	0.45711700	3.38768900
H	3.90981000	1.59279300	2.63197300
C	3.14963000	2.24773700	4.50958600
H	2.23517100	2.16371800	5.11310400
H	3.33303400	3.31585100	4.32784700
O	4.26015600	1.65777500	5.19546000
H	4.37863300	2.13208800	6.02452200
C	0.33516800	2.11911200	0.30444400
H	-0.52885500	2.15319300	0.97358500
H	0.04342800	1.51684600	-0.56175300
C	0.58315600	3.55437400	-0.22268900
H	-0.15061800	3.73648600	-1.01462500
H	1.56361000	3.63183500	-0.69813000
C	0.44465000	4.65078600	0.79000400
C	1.34458400	5.62085800	1.16527900
N	0.69617000	6.35034500	2.11336900
H	2.35360100	5.83442700	0.86424200
N	-0.69827100	4.83893800	1.51348800
N	-0.55093400	5.85369300	2.31499600

C	1.14186500	7.48437000	2.83810900
C	0.28553700	8.49777700	3.15363100
C	2.52791800	7.49913700	3.27227200
C	0.72313000	9.60137000	3.92717500
H	-0.74235800	8.44900100	2.81506500
C	2.06830700	9.63229900	4.34117200
C	-0.08564500	10.69046900	4.31653600
C	2.60085600	10.66223300	5.09071000
C	0.41681000	11.72845700	5.06285300
H	-1.12889900	10.70029000	4.02176100
C	1.78937700	11.76040700	5.46703100
H	3.64081600	10.59284100	5.36960100
H	-0.25020900	12.52923400	5.34307000
O	3.36801200	6.65357900	3.05427500
O	2.91462400	8.60657500	4.00354600
N	2.29890500	12.81303200	6.17466500
C	1.45667200	13.95008500	6.57133200
H	2.12302300	14.80165900	6.71511300
H	0.80233200	14.21677800	5.73842600
C	0.63272300	13.72430900	7.84401300
H	1.27930300	13.54359300	8.70506800
H	0.02886300	14.61153300	8.05340900
H	-0.04233500	12.87191800	7.74103700
C	3.70632700	12.83457300	6.59478100
H	3.97681200	13.88024600	6.74690400
H	4.32810400	12.47827600	5.76959300
C	4.00778100	12.03679200	7.86878100
H	5.07796700	12.08529300	8.08761600
H	3.46799800	12.44430700	8.72585300
H	3.73195400	10.98564100	7.76117600
C	-0.59916600	-2.32953100	-2.42759800
O	-0.28058400	-1.79058100	-3.44485700
O	-1.62311800	-3.28264900	-2.36326500
N	-2.27465000	-3.51469600	-3.60014700
C	-3.42151100	-2.67745100	-3.82086000
C	-3.32033000	-1.59666200	-4.69349300
C	-4.60068500	-2.93776500	-3.12347800
C	-4.42699100	-0.77237900	-4.88216200
H	-2.38675400	-1.41319300	-5.20817900
C	-5.69862900	-2.10344400	-3.31316200
H	-4.65333300	-3.78355600	-2.44890000
C	-5.61323500	-1.02447700	-4.19356200
H	-4.36049400	0.06773700	-5.56311400
H	-6.62002200	-2.29791100	-2.77731100
H	-6.47124300	-0.37902800	-4.34101400
C	-1.98127600	-4.67323100	-4.23663900

S	-0.65109200	-5.56927100	-3.46776600
S	-2.80354700	-5.16219600	-5.60691200
C	-0.40629200	-6.96596200	-4.60487900
H	-0.13092500	-6.61401800	-5.59659100
H	0.41945300	-7.52697600	-4.16509500
H	-1.29662500	-7.58862200	-4.65248500
O	-0.13790200	-0.33378300	1.57691700
H	-0.67262100	-0.03442600	0.82547000
C	2.06698800	-2.29429700	1.03291800
H	1.22277900	-2.60163400	1.64451900
C	3.13374200	-3.08341000	0.94176400
H	3.99944300	-2.82270800	0.34144400
H	3.17884300	-4.02821500	1.47231800

Profluorescent nitroxide **ProN7**

C	-0.13299600	-1.68210700	1.47317000
C	1.36772700	-1.39549900	1.25609200
C	1.42178200	0.10138600	0.89630600
C	0.22249900	0.76563800	1.62964600
H	1.91010800	-1.58742700	2.18325800
H	1.31366400	0.22942800	-0.18284600
H	2.37676500	0.55034000	1.17301500
H	1.79987100	-2.02462900	0.47648900
C	-0.81179600	-1.95229700	0.09123600
H	-0.29664600	-2.82714700	-0.32299300
H	-0.59220000	-1.12367600	-0.58829000
C	-2.32096500	-2.22962000	0.07795800
H	-2.87246000	-1.35533000	0.41972100
H	-2.55900100	-3.04084000	0.77132500
C	-2.79062000	-2.62359100	-1.32505900
H	-2.57527000	-1.83193400	-2.05240000
H	-2.26864900	-3.51341900	-1.69114700
O	-4.56805100	-3.42144600	-2.65889100
N	-5.94761000	-3.66203600	-2.87341000
C	-6.64989100	-2.55027800	-3.45300900
C	-7.47303100	-1.76722200	-2.64737100
C	-6.45820400	-2.25036400	-4.80128300
C	-8.12768300	-0.67343800	-3.20847600
H	-7.58914800	-2.01795300	-1.60154600
C	-7.11121500	-1.15068200	-5.35080100
H	-5.81037800	-2.87333900	-5.40580400
C	-7.94748000	-0.36550900	-4.55664300
H	-8.77435200	-0.06083900	-2.59167000
H	-6.97007400	-0.90986600	-6.39771100
H	-8.45684400	0.48798500	-4.98870100

C	-6.35287500	-4.95341500	-2.84999900
S	-7.90709900	-5.40182900	-3.27163600
S	-5.07427400	-6.07169600	-2.32127100
C	-5.94436200	-7.66645400	-2.26258800
H	-6.30546400	-7.94877400	-3.24879600
H	-5.18463200	-8.37326700	-1.92621800
H	-6.76461000	-7.63414200	-1.54895700
C	0.64631300	1.65298900	2.82431700
H	1.16475600	2.53478200	2.44012100
H	-0.26979300	2.02357600	3.30122100
C	1.52703000	0.98541100	3.88429500
H	1.02594400	0.10097100	4.28507900
H	2.47279200	0.64910600	3.44579200
C	1.85483600	1.93212400	5.02915800
H	0.92890200	2.25920000	5.52252400
H	2.36175500	2.82797500	4.64445800
O	2.69822800	1.23697700	5.95528000
H	2.91005900	1.84405100	6.67146900
C	-0.66799500	1.57863300	0.65218300
H	-1.53944600	1.95237900	1.19134300
H	-1.05144000	0.89083100	-0.10441000
C	0.00425900	2.75938100	-0.09121000
H	-0.56421700	2.92901000	-1.01177900
H	1.01714300	2.49802200	-0.40876800
C	0.05124200	4.05673600	0.65981600
C	1.12848500	4.84776300	0.98588900
N	0.59738000	5.89840800	1.66902200
H	2.18435800	4.74761000	0.81462900
N	-1.07250100	4.66188200	1.14668100
N	-0.75066000	5.76428400	1.75922800
C	1.24264500	7.02351500	2.24115500
C	0.64100600	8.24748300	2.25218900
C	2.54010200	6.81118100	2.85928600
C	1.25969900	9.35348600	2.88608100
H	-0.32745400	8.36672400	1.78169500
C	2.51819100	9.15887000	3.48590400
C	0.71259200	10.65173100	2.96735700
C	3.20640100	10.16565000	4.13348600
C	1.37508100	11.67284100	3.60411300
H	-0.25691600	10.84052800	2.52047300
C	2.65796300	11.46944500	4.20499900
H	4.15844600	9.91648000	4.57597900
H	0.90384800	12.64292800	3.64433500
O	3.16468300	5.77376100	2.90418200
O	3.11335000	7.92354200	3.44704700
N	3.33022200	12.49362300	4.81160200

C	2.74608500	13.83811700	4.91683900
H	3.57544400	14.53276300	5.05539400
H	2.28670100	14.10461200	3.96205300
C	1.73767100	14.01061500	6.05853400
H	2.20782200	13.83942500	7.02896500
H	1.34147600	15.02969400	6.04828500
H	0.89768900	13.31967400	5.96083200
C	4.64840600	12.27926400	5.42315400
H	5.15259600	13.24635900	5.43976000
H	5.24352700	11.63975100	4.76664400
C	4.61097600	11.69590900	6.84063700
H	5.63150200	11.54590700	7.20339100
H	4.10183200	12.37117700	7.53121800
H	4.09770600	10.73236300	6.86650100
C	-0.42287700	-2.83534800	2.41291100
H	-1.37645900	-2.76531600	2.93029800
C	0.35497000	-3.89314100	2.62592200
H	1.31282600	-4.01933600	2.13155700
H	0.05684900	-4.67967600	3.31080100
C	-4.26874400	-2.89128800	-1.39494200
O	-5.10328000	-2.70375000	-0.56170700
N	-0.49496000	-0.42882200	2.18309300
O	-1.90672300	-0.23240300	2.29385100
H	-2.05589300	-0.20713100	3.24567300

5- membered *O*-acylalkoxylamine, **22c**

C	-0.15008300	-1.71437600	1.38046600
C	0.64285700	-1.54685400	0.08173700
C	1.35246300	-0.18020200	0.34697200
C	0.34085300	0.71954100	1.14738900
N	-0.69608600	-0.32655600	1.41904400
H	1.35615500	-2.34777400	-0.11593200
H	1.65128500	0.30302700	-0.58680000
H	2.25703500	-0.34698400	0.93634600
H	-0.03744700	-1.48275500	-0.77264400
C	-1.50717800	-2.42711900	1.55693500
H	-1.45528300	-3.45130200	1.92818900
H	-2.11198100	-2.40768600	0.64322400
C	0.71392100	-2.14723000	2.56070400
C	1.83251300	-2.87023800	2.49971400
H	2.32874300	-3.19619300	3.40977100
H	2.30068000	-3.17086600	1.56690700
C	0.91116800	1.48572800	2.36207100
H	1.66232100	2.17201400	1.95387500
H	0.10543500	2.12543400	2.74480900

C	1.54679500	0.74907300	3.54529800
H	0.80324400	0.14471100	4.07319500
H	2.34228300	0.07149400	3.21815600
C	2.14019500	1.74355100	4.53989100
H	1.35129200	2.41365100	4.91635100
H	2.89196400	2.37525000	4.04016400
O	2.72788900	1.00001600	5.60814200
H	3.08622500	1.63850200	6.24425900
C	-0.34705200	1.73604100	0.19036200
H	-1.24727600	2.11993900	0.68153600
H	-0.67690200	1.17315200	-0.68942700
C	0.48696200	2.93877300	-0.31353400
H	0.09385600	3.21595400	-1.29968800
H	1.53140100	2.65129300	-0.47868200
C	0.44297100	4.15723400	0.56385900
C	1.47175800	4.90700100	1.09117300
N	0.85765700	5.89834900	1.79443300
H	2.54333700	4.81697200	1.04176100
N	-0.73606600	4.72478200	0.96299100
N	-0.49410500	5.76962200	1.70846700
C	1.42365300	6.96953000	2.53042900
C	0.78430500	8.17446600	2.62307700
C	2.68027000	6.72401800	3.22010600
C	1.32548500	9.22173700	3.41243800
H	-0.15026900	8.32566700	2.09230000
C	2.54272200	8.99001700	4.08575000
C	0.73972500	10.49617200	3.58282000
C	3.15642600	9.93896600	4.88401700
C	1.32836400	11.46062500	4.36911600
H	-0.20075400	10.71249800	3.08381600
C	2.56904500	11.21995200	5.04414700
H	4.08321100	9.66442100	5.36830200
H	0.82751500	12.41352500	4.47223200
O	3.33571300	5.69693800	3.19906900
O	3.17473800	7.77708600	3.96533700
N	3.16999000	12.19277200	5.79964100
C	2.55223700	13.51401400	5.97798700
H	3.35586400	14.20691300	6.24128800
H	2.16197100	13.85764700	5.01464000
C	1.45534800	13.57080100	7.04859000
H	1.85335700	13.31525200	8.03557300
H	1.04200200	14.58442200	7.10012500
H	0.63590200	12.88061300	6.82358900
C	4.41796700	11.92345700	6.52599800
H	4.89334400	12.88970200	6.71378800
H	5.09988300	11.37396500	5.86834800

C	4.23708400	11.17368000	7.85212300
H	5.21604100	10.98863000	8.30842000
H	3.63799400	11.75846800	8.55708100
H	3.74286100	10.20828400	7.70460500
C	-2.16474900	-1.51811700	2.60876500
O	-3.05247000	-1.75726000	3.38433900
O	-1.54310600	-0.28008500	2.60625700
H	0.30626700	-1.91737600	3.54283700

6- membered *O*-acylalkoxylamine, **22a**

C	1.85599200	-1.21358400	-2.54475000
C	3.30328200	-0.83578900	-2.18755400
C	3.29337200	0.70036100	-2.09573900
C	1.86448600	1.10577800	-1.63528800
N	1.12783600	-0.21243000	-1.72619200
H	3.56454600	-1.27929300	-1.22609200
H	3.50293200	1.13491000	-3.07533000
H	4.06195300	1.06858800	-1.41534600
H	4.01064500	-1.20307000	-2.93273700
C	1.57065100	-1.03065000	-4.05098500
H	2.04839300	-1.83361300	-4.61643300
H	2.00695400	-0.09194300	-4.39862800
C	0.06412600	-1.03581100	-4.31157400
H	-0.32576200	-2.05924000	-4.27244300
H	-0.18237900	-0.65405800	-5.30321800
C	1.79998200	1.56613400	-0.16088300
H	2.33081400	2.51725800	-0.07521300
H	0.75026300	1.77854400	0.07357800
C	2.36033600	0.59319500	0.88017800
H	1.83212000	-0.36175200	0.82661000
H	3.41986000	0.38944600	0.69097900
C	2.23763700	1.14656500	2.29234700
H	1.18093400	1.32706200	2.53354400
H	2.76623100	2.10697000	2.36817600
O	2.80298700	0.18950300	3.19518400
H	2.72686000	0.54584600	4.08607100
C	1.25314000	2.18772500	-2.56299600
H	0.22779800	2.39574400	-2.25260700
H	1.19589400	1.77886700	-3.57488600
C	2.01481500	3.53252900	-2.66459700
H	1.72814600	3.99036500	-3.61699100
H	3.09401000	3.37104800	-2.72269300
C	1.72655900	4.52172700	-1.57508500
C	2.59136400	5.17919300	-0.73135800
N	1.79237000	5.95208400	0.05402000

H	3.65886900	5.14994100	-0.61453800
N	0.45816200	4.92761700	-1.27268300
N	0.49059900	5.78088600	-0.29068500
C	2.14286700	6.84612300	1.09697600
C	1.43446800	7.99271600	1.30641800
C	3.24650500	6.46814000	1.96256200
C	1.74691100	8.84956600	2.39078400
H	0.61602700	8.23964700	0.64103400
C	2.81982100	8.49657800	3.23084200
C	1.06380400	10.04440200	2.70267200
C	3.20778300	9.25785800	4.31551900
C	1.42674400	10.82096800	3.77597200
H	0.22877600	10.34831400	2.08171400
C	2.52466600	10.46062000	4.62019700
H	4.03504400	8.89876300	4.90803100
H	0.86017100	11.71781300	3.97452000
O	3.93864800	5.47782100	1.87006000
O	3.52943700	7.34711300	2.99143200
N	2.90443100	11.25008000	5.66961400
C	2.18350000	12.48748100	5.99875600
H	2.87789400	13.11980200	6.55345900
H	1.95793700	13.02618600	5.07556400
C	0.90633400	12.28462200	6.82193900
H	1.12943300	11.83246500	7.79033800
H	0.42645800	13.25069500	7.00099300
H	0.19147700	11.64205100	6.30345700
C	4.02506000	10.86826000	6.53895700
H	4.39564900	11.78393100	7.00146400
H	4.84213600	10.49133100	5.91866000
C	3.67341000	9.84928700	7.62928700
H	4.57075800	9.60002300	8.20216100
H	2.93104700	10.25210900	8.32124100
H	3.27594600	8.92533300	7.20399600
C	-0.76730700	-0.26083800	-3.31822200
O	-1.90404100	0.08811700	-3.52354700
O	-0.26980000	-0.02573300	-2.06709100
C	1.43166500	-2.59705600	-2.08874400
H	0.37196500	-2.70904500	-1.87318600
C	2.23177500	-3.65052600	-1.95581100
H	3.29715800	-3.60150600	-2.15557500
H	1.84234000	-4.61133900	-1.63823700

7- membered *O*-acylalkoxylamine, **22b**

C	-0.37707700	-3.79614100	0.63215200
C	1.09587600	-4.21002400	0.90457600

C	1.98339700	-3.13341900	0.24324500
C	1.13039700	-1.84711800	0.15804900
H	1.27291800	-4.24932700	1.97797400
H	2.26298600	-3.44490000	-0.76606600
H	2.90603600	-2.97072200	0.80224600
H	1.30802500	-5.20183000	0.50156300
C	-1.03998100	-4.71248700	-0.42990800
H	-1.17184900	-5.71213500	-0.00463900
H	-0.34148200	-4.80037400	-1.26903700
C	-2.38924500	-4.20633400	-0.95580400
H	-3.14081300	-4.22439700	-0.15965700
H	-2.74039700	-4.90662800	-1.71846800
C	-2.36465200	-2.80220400	-1.60765700
H	-1.49936700	-2.72059200	-2.27030600
H	-3.26925600	-2.65607500	-2.19847000
C	1.25159300	-0.91172900	1.38739500
H	2.21349100	-0.40212200	1.29864900
H	0.48940800	-0.13385500	1.27973100
C	1.16833000	-1.50553100	2.79658500
H	0.20470000	-1.98769100	2.97170800
H	1.94044000	-2.26739000	2.94392200
C	1.36487900	-0.43188900	3.85784200
H	0.59036600	0.34076400	3.75654900
H	2.34149500	0.05386100	3.72574100
O	1.28453000	-1.05911200	5.14258000
H	1.40306000	-0.37631100	5.81059200
C	1.43022700	-1.04419600	-1.13651900
H	0.74234400	-0.19571800	-1.19851500
H	1.18467600	-1.70786100	-1.96887400
C	2.87473800	-0.53178300	-1.35130200
H	3.01491500	-0.41200800	-2.43074300
H	3.60254900	-1.28415900	-1.03692500
C	3.21402400	0.77688700	-0.70224200
C	4.22864100	1.09155500	0.17204700
N	4.07060100	2.41916800	0.42738300
H	5.00608500	0.50637200	0.62761200
N	2.49964500	1.91682700	-0.93963500
N	3.00505100	2.90428500	-0.25924700
C	4.84434200	3.27955800	1.24634300
C	5.06174200	4.57819200	0.89080600
C	5.35153000	2.74040200	2.49587700
C	5.78364700	5.45122500	1.74170100
H	4.66568800	4.94454300	-0.04854600
C	6.28791800	4.93624200	2.95089700
C	6.04545400	6.81166600	1.47296100
C	7.00573500	5.69817400	3.85130100

C	6.75569600	7.59392600	2.35060100
H	5.66962800	7.24560200	0.55327700
C	7.27624000	7.06026100	3.57227600
H	7.33982900	5.21886200	4.75840700
H	6.91659300	8.63111800	2.09950500
O	5.21729000	1.60900700	2.90879200
O	6.06950600	3.62271800	3.28168700
N	8.01462000	7.83084700	4.42662400
C	8.26600800	9.25271100	4.15368400
H	9.16152700	9.52777700	4.71225300
H	8.52013200	9.37539800	3.09818900
C	7.11541100	10.19087100	4.53568300
H	6.90953100	10.14572700	5.60696000
H	7.38182200	11.22109500	4.28408500
H	6.19632000	9.93897100	4.00215200
C	8.55496300	7.27638400	5.67462800
H	9.42244800	7.88138400	5.94224200
H	8.93649100	6.27148100	5.47874200
C	7.56710300	7.24975700	6.84672900
H	8.04421600	6.79418300	7.71873600
H	7.25327200	8.25872400	7.12153600
H	6.67380400	6.66878700	6.60774000
C	-1.24141600	-3.76278700	1.88396500
H	-1.92577800	-2.92634500	1.97610300
C	-1.25553500	-4.70808400	2.82050300
H	-0.60074700	-5.57352800	2.78753200
H	-1.93040400	-4.64505700	3.66692000
C	-2.34018000	-1.65238100	-0.62695900
O	-3.22269400	-0.84189000	-0.48844200
N	-0.20373400	-2.47052100	-0.04597000
O	-1.26252700	-1.53977700	0.21114200

Thiohydroxamate ester, **20**

O	-2.85175000	-0.10972300	-0.10549200
N	-3.66146200	1.02496500	-0.29432600
C	-4.34847900	1.46250000	0.88897000
C	-5.39057200	0.69059500	1.40132900
C	-3.91679400	2.61459900	1.54202100
C	-6.01368000	1.08808000	2.58076800
H	-5.70379700	-0.20563100	0.88005300
C	-4.55050000	3.00842200	2.71839200
H	-3.10146700	3.19370000	1.12615700
C	-5.59692600	2.24676600	3.23715900
H	-6.82583400	0.49565600	2.98507800
H	-4.22454300	3.90652300	3.22931800
H	-6.08686500	2.55433600	4.15357500
C	-3.94952400	1.37140000	-1.56713500

S	-5.06847500	2.55798500	-1.94822000
S	-2.99937700	0.44024300	-2.75177000
C	-3.51263100	1.17844000	-4.33250500
H	-2.94133100	0.62862700	-5.08190700
H	-4.57783000	1.03717000	-4.50111500
H	-3.25718400	2.23505200	-4.37241100
H	-1.99966500	0.23432000	0.20600100

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