Ketone Incorporation Extends the Emission Properties of the Xanthene Scaffold Beyond 1000 nm

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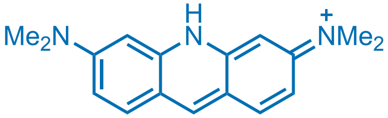
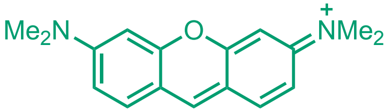
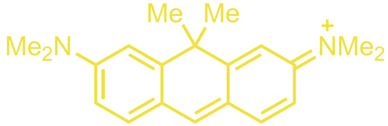
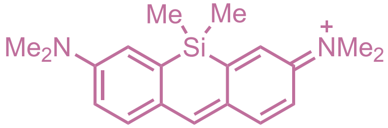
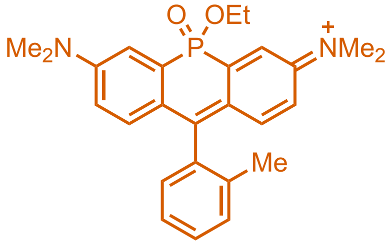
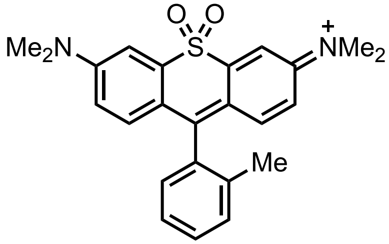
Table of Contents

Section S1: Supplementary Figures and Tables

R Group	Structure	Year	Solvent	$\lambda_{,abs}$ (nm)	ε ($M^{-1}cm^{-1}$)	$\lambda_{,em}$ (nm)	Φ_F	Lit. ref
R1		2015	Aq. buffer	493	50,000	528	0.21	(1)
R2		2011	HEPES, 7.4	547	-	562	0.4	(2)
R3		2011	EtOH	605	-	627	0.71	(3)
R4		2014	PBS	634	48,600	648	0.42	(4) (SI) (2)
R5		2016	PBS 10mM pH 7.4 1% DMSO	700	71,000	722	0.11	(5)
R6		2016	PBS pH 7.4 (0.25% CH_3CN)	703	39,000	734	0.067	(6)

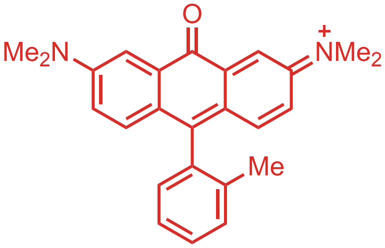
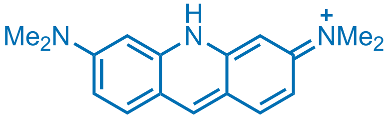
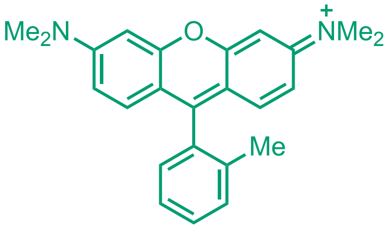
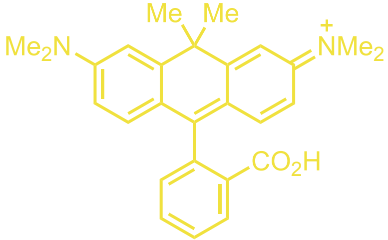
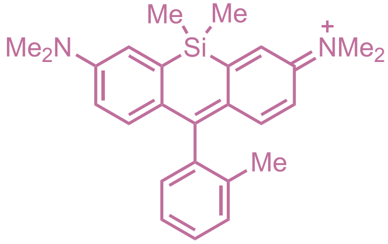
R7		2021	CH_2Cl_2	855	28,400	911	0.013	This work

Table S1: Structures, photophysical properties and literature references of previously reported compounds in Figure 1A.

R Group	Structure	Year	Solvent	$\lambda_{,abs}$ (nm)	ε ($M^{-1}cm^{-1}$)	$\lambda_{,em}$ (nm)	Φ_F	Lit ref
R1		2015	Aq. buffer	493	50,000	528	0.21	(1)
R2		2011	PBS pH 7.4	549	72,000	570	0.31	(6)
R3		2011	Aq. buffer	606	121,000	626	0.52	(1)
R4		2014	20mM PBS pH 7.4	647	110,000	661	0.31	(6)

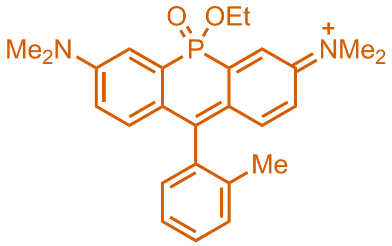
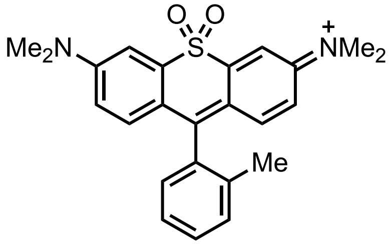
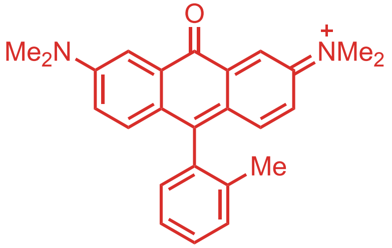
R5		2016	PBS 10mM pH 7.4 1% DMSO	700	71,000	722	0.11	(5)
R6		2016	PBS pH 7.4 (0.25% CH_3CN)	703	62,000	734	0.06	(6)
R7		2021	PBS pH 7.4	862	16,500	1,058	0.00013	This work

Table S2: Structures, photophysical properties and literature references of dyes used in absorbance oscillator strengths (S0 → S1*) and (S1* → S0) vs. extinction coefficient (Figure 1E/ F).

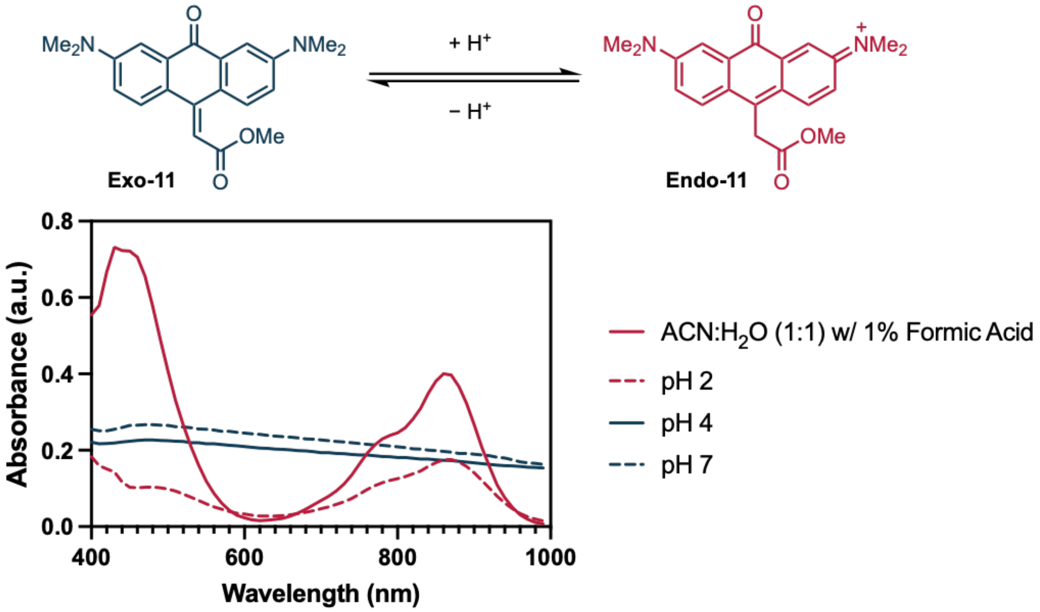


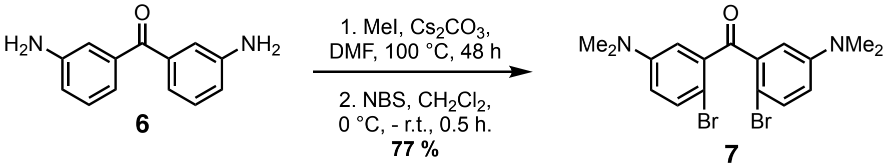
Figure S1: Exo- to endo-switching of dye **11** (200 μM) in acidic media.

Section S2: General Experimental and Materials

Unless stated otherwise, reactions were conducted in oven- dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (passed through activated alumina columns). All commercially obtained reagents were used as received. Flash column chromatography was performed using reversed phase (100 Å, 20-40-micron particle size, RediSep® Rf Gold® Reversed-phase C18 or C18Aq) and silica on a CombiFlash® Rf 200i (Teledyne Isco, Inc.) High-resolution LC/MS analyses were conducted on a ThermoFisher LTQ-Orbitrap-XL hybrid mass spectrometer system with an Ion MAX API electrospray ion source in negative ion mode. Analytical LC/MS was performed using a Shimadzu LCMS-2020 Single Quadrupole utilizing a Kinetex C18 column (100 Å, 2.6 µm, 2.1 x 50 mm) obtained from Phenomenex, Inc (Torrance, CA). Runs employed a gradient of 0-90% MeCN/0.1% aqueous formic acid over 4.5 min at a flow rate of 0.2 mL/min. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker spectrometers (at 400 or 500 MHz or at 100 or 125 MHz) and are reported relative to deuterated solvent signals. Data for ^{1} H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Absorbance curves were obtained on a PerkinElmer UV/Vis Photodiode Array Spectrophotometer Lambda 465 (Scan No. 30. Integration No. 1). Molar absorption coefficients (ε) were determined in PBS (50 mM, pH 7.4), CH_2Cl_2, CH_2Cl_2 supplemented with 5 % Trifluoroacetic Acid or Acetate Buffer (0.05M) at pH 3.6 using Beer's law, from plots of absorbance vs. concentration. Measurements were performed in 10 mm path length quartz cuvettes (Hellma 111-QS) that were maintained at room temperature. Fluorescence traces were recorded on aPTI QuantaMaster steady state spectrofluorometer operated by FelixGX 4.2.2 software, with 15 nm excitation and 20nm emission slit widths with a 1 nm step size and 1 s integration rate. Microplates were read on Synergy Mx microplate reader. pH values were determined using a Fisherbrand™ accumet™ AB150 pH Benchtop Meter. All statistical analyses were carried out by Graphpad Prism version 9.0 (Graphpad Software). See section S7 and S8 for computational chemistry methods and results.

Section S3 Synthetic Procedures

bis(2-bromo-5-(dimethylamino)phenyl)methanone (7)



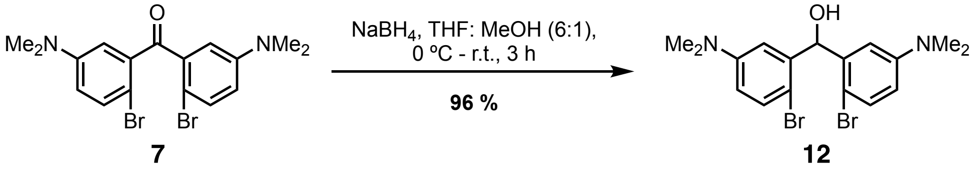
To a solution of bis(2-bromo-5-(dimethylamino)phenyl)methanone (5.0 g, 0.012 mmol, 1.0 eq.) in DMF (19 mL, 0.12 M) at 0 °C under a N_2 atmosphere Cs_2CO_3 (46 g, 0.14 mol, 6.0 eq.) was added. The reaction mixture was sonicated and set to stir at room temperature before addition of iodomethane (7.3 mL, 0.12 mol, 5 eq.) *via* syringe. The suspension was then heated to 100 °C for 48 hours. The reaction was quenched with an excess of $NaHCO_3$ (sat.) and transferred to a separatory funnel with additional H_2O used to dissolve any salts present. The crude mixture was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo* with water heating bath set at 60 °C. Bis(3-(dimethylamino)phenyl)methanone **1** was isolated at a brown oil (5.98 g) was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (t, *J* = 7.9 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.93 (dd, *J* = 8.3, 2.8, Hz, 2H), 2.99 (12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.3, 150.5, 138.9, 128.7, 118.9, 116.3, 113.6, 40.7 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{20}N_2O$ 268.1576; Found 268.1571.

To the resultant crude material **1** (5.98 g, 0.0222 mol, 1.0 eq.) CH_2Cl_2 (225 mL, 0.1 M) was added. The reaction mixture was sonicated to ensure dissolution and set to stir at room temperature under a N_2 atmosphere for 10 minutes before cooling to 0 °C in an ice bath. *N*-bromosuccinimide (7.94 g, 0.0446 mol, 2.0 eq.) was then added portion wise and the reaction was followed by TLC (4:1, Hexanes: EtOAc, R_f: 0.45) with typical reaction times of 30 minutes. Once the reaction was judged to have gone to completion it was quenched with $NaHCO_3$ (sat.), extracted with EtOAc × 2. The organic phase washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The residue was purified by normal-phase column chromatography (120 g C18 column, 0 → 10% hexanes /EtOAc) to afford bis(2-bromo-5 (dimethylamino)phenyl)methanone **7** (7.68 g, 77 %) as a bright yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 3.2 Hz, 2H), 6.68 (dd, *J* = 8.9, 3.2 Hz, 2H), 2.92 (s, 12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.9, 149.5, 139.8, 134.3, 116.4, 115.1, 107.1, 40.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{18}Br_2N_2O$ 425.9765; Found 425.9766.

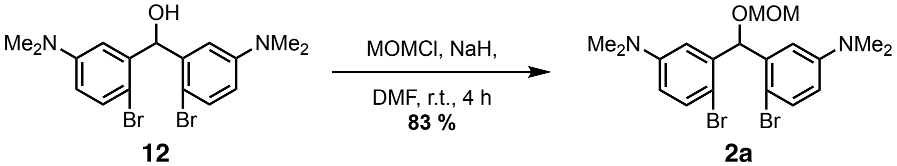
bis(2-bromo-5-(dimethylamino)phenyl)methanol (12)



To bis(2-bromo-5-(dimethylamino)phenyl)methanone **7** (2.55 g, 5.89 mmol, 1.0 eq.) in a 500 mL round bottom flask under a N_2 atmosphere (N_2 balloon) THF (100 mL) was added and set to stir at room temperature. Once fully dissolved the solution was cooled to 0 °C in an ice bath and MeOH (17 mL, 0.05 M) was added. After 15 minutes $NaBH_4$ (2.3 g, 0.059 mol, 10 eq.) was added portion wise. The reaction mixture was kept at 0 °C for 1 hour and allowed to gradually warm to room temperature. The reaction was followed by TLC (4:1, Hexanes: EtOAc, R_f: 0.23) and once judged to have gone to completion the reaction mixture was cooled in an ice bath and quenched carefully using NH_4Cl (sat.). Additional H_2O was used to dissolve any salts present and the reaction mixture was extracted with EtOAc × 2. The organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. Bis(2-bromo-5-(dimethylamino)phenyl)methanol **12** (2.45g, 96 %) was isolated as a light yellow solid and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 3.2 Hz, 2H), 6.53 (dd, *J* = 8.8, 3.2 Hz, 2H), 6.28 (s, 1H), 2.87 (s, 12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 141.20, 133.0, 113.5, 113.0, 110.1, 74.7, 40.7 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{20}Br_2N_2O$ 427.9922; Found 427.9920.

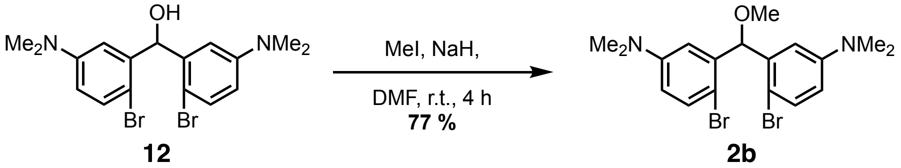
3,3'-((methoxymethoxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2a)



To a stirred solution of bis(2-bromo-5-(dimethylamino)phenyl)methanol **12** (500 mg, 1.17 mmol, 1.0 eq.) in DMF (4.0 mL, 0.29 M) under an Ar atmosphere at 0 °C, sodium hydride (84 mg, 3.5 mol, 3.0 eq.) was added and the reaction was stirred at room temperature for 30 minutes. To the crude reaction mixture at 0 °C chloromethyl methyl ether (130 µL, 1.8 mmol, 1.5 eq.) was added *via* syringe and the reaction set to stir at room temperature for 3.5 hours. Once the reaction was judged to have gone to completion (TLC, 4:1, Hexanes: EtOAc, R_f: 0.4) the reaction mixture was cooled in an ice bath and quenched using NH_4Cl (sat.). The reaction mixture was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The residue was purified by normal-phase column chromatography (12 g C18 gold column, 0 → 10% hexanes /EtOAc) to afford 3,3'-(methoxymethylene)bis(4-bromo-*N*,*N*-dimethylaniline) **2a** (460 mg, 83 %) as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 3.1 Hz, 2H), 6.53 (dd, *J* = 8.8, 3.2 Hz, 2H), 6.26 (s, 1H), 4.80 (s, 2H), 3.46 (s, 3H), 2.88 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.7, 133.2, 113.7, 113.6, 110.8, 95.8, 78.5, 56.8, 40.7 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{24}Br_2N_2O_2$ 472.0184; Found 472.0187.

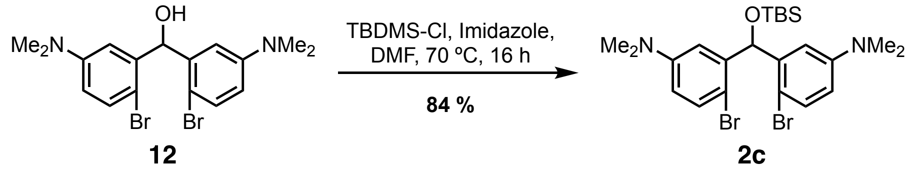
3,3'-(methoxymethylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2b)



To a stirred solution of bis(2-bromo-5-(dimethylamino)phenyl)methanol **12b** (500 mg, 1.17 mmol, 1.0 eq.) in DMF (4.0 mL, 0.29 M) under an Ar atmosphere at 0 °C, sodium hydride (84 mg, 3.5 mol, 3.0 eq.) was added and the reaction was stirred at room temperature for 30 minutes. To the crude reaction mixture at 0 °C iodomethane (110 µL, 1.8 mmol, 1.5 eq.) was added *via* syringe and the reaction set to stir at room temperature for 3.5 hours. Once the reaction was judged to have gone to completion (TLC, 4:1, Hexanes: EtOAc, R_f: 0.5) the reaction mixture was cooled in an ice bath and quenched using NH_4Cl (sat.). The reaction mixture was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The residue was purified by normal-phase column chromatography (12 g C18 gold column, 0 → 10% hexanes /EtOAc) to afford 3,3'-(methoxymethylene)bis(4-bromo-*N*,*N*-dimethylaniline) **2b** (400 mg, 77 %) as light brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 3.1 Hz, 2H), 6.53 (dd, *J* = 8.8, 3.1 Hz, 2H), 5.79 (s, 1H), 3.52 (s, 3H), 2.87 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0, 139.35, 133.1, 113.6, 113.3, 111.3, 83.5, 58.3, 40.7 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{22}Br_2N_2O_2$ 442.0078; Found 442.0080.

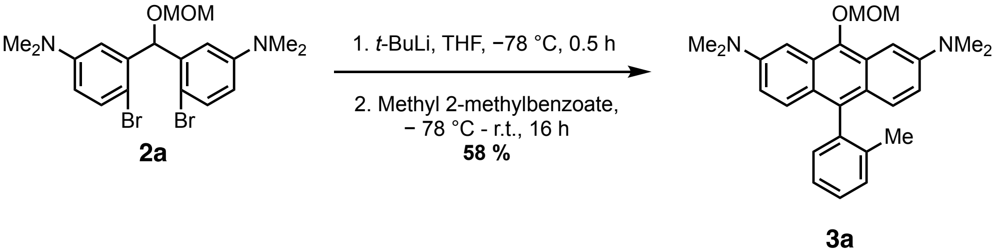
3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2c)



To bis(2-bromo-5-(dimethylamino)phenyl)methanol **12** (2.5 g, 0.0058 mol, 1.0 eq.), imidazole (1.19 g, 0.0175 mol, 3.0 eq.) and *tert*-butyldimethylsilyl chloride (1.76 g, 0.00117 mol, 2.0 eq.) in an Ar flushed round-bottom flash DMF (25 mL, 0.23 M) was added. The reaction was set to stir at room temperature before heating to 70 °C overnight. The cooled reaction mixture was suspended in 2:1 EtOAc/ $NaHCO_3$ (sat.) and extracted with EtOAc. The aqueous phase was re-extracted with additional EtOAc and combined organic phase were washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The residue was purified by normal-phase column chromatography (40 g silica gold column, 0 → 10% hexanes /EtOAc) and dried under hi-vaccum to afford 3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) **2c** (2.7 g, 84 %) as an off-white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.30 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 3.2$ Hz, 2H), 6.59 (dd, $J = 8.9, 3.2$ Hz, 2H), 6.15 (s, 1H), 2.83 (s, 12H), 0.87 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 149.5, 141.6, 132.6, 113.6, 112.9, 108.3, 74.5, 39.9, 25.7, 17.8, − 4.40 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{34}Br_2N_2O_2Si$ 542.0787; Found 542.0790.

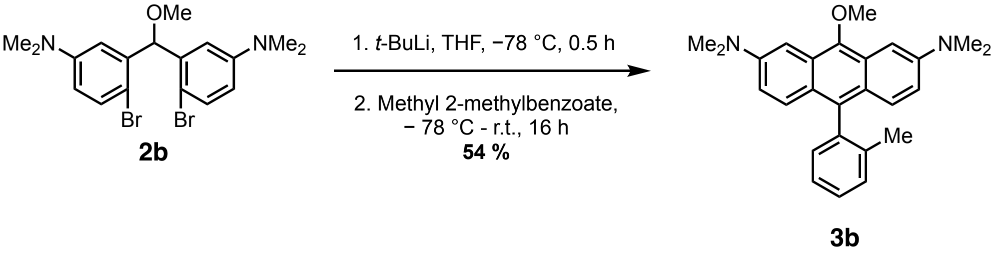
9-(methoxymethoxy)-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine (3a)



To 9-(methoxymethoxy)-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine **2a** (200 mg, 0.423 mmol, 1.0 eq.) in a flame-dried crimped 25 mL microwave vial under an Ar atmosphere, THF (10 mL, 0.042 M) was added. The solution was stirred at room temperature before cooling to − 78 ºC in a dry ice/ acetone bath. The solution was then treated with *tert*-Butyllithium solution (1.1 mL, 1.9 mmol, 4.4 eq.) and allowed stir at − 78 ºC for 0.5 h. A separately prepared solution of methyl 2-methylbenzoate (130 µL, 0.93 mmol, 2.2 eq.) in THF (5.0 mL, 0.17 M) under an Ar atmosphere was then added dropwise to the − 78 ºC reaction mixture. The reaction mixture was allowed stir for 1 hour at − 78 ºC before removal from the cold bath, covering with aluminum foil and allowing to gradually equilibrate to room temperature overnight for a total reaction time of 16 hours. The reaction mixture was then quenched at − 78 ºC with an excess of NH_4Cl (sat.) and transferred to a separatory funnel with additional H_2O used to dissolve any salts present. The crude mixture was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was purified by normal-phase column chromatography (12 g silica gold column, 0 → 10% hexanes /EtOAc) to afford 9-(methoxymethoxy)-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine **3a** (101 mg, 58 %) as a bright yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.47 – 7.41 (m, 2H), 7.40 – 7.34 (m, 1H), 7.19 – 7.06 (m, 7H), 5.31 (s, 2H), 3.74 (s, 3H), 3.03 (s, 12H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.5, 143.3, 138.0, 137.0, 131.6, 130.9, 129.9, 127.7, 127.0, 126.3, 125.9, 122.44, 116.7, 99.2, 97.7, 57.2, 40.2, 19.3 ppm. HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{27}H_{30}N_2O_2$ 414.2307; Found 414.2302.

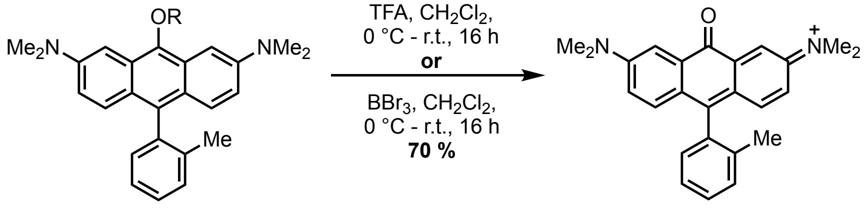
9-methoxy-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine (3b)



To 3,3'-(methoxymethylene)bis(4-bromo-*N,N*-dimethylaniline) **2b** (200 mg, 0.45 mmol, 1.0 eq.) in a flame-dried crimped 25mL microwave vial under an Ar atmosphere, THF (10 mL, 0.045 M) was added. The solution was stirred at room temperature before cooling to − 78 ºC in a dry ice/ acetone bath. The solution was then treated with *tert*-Butyllithium solution (1.2 mL, 2.0 mmol, 4.4 eq.) and allowed stir at − 78 ºC for 0.5 h. A separately prepared solution of methyl 2-methylbenzoate (140 µL, 1.0 mmol, 2.2 eq.) in THF (5 mL, 0.2 M) under an Ar atmosphere was then added dropwise to the − 78 ºC reaction mixture. The reaction mixture was allowed stir for 1 hour at − 78 ºC before removal from the cold bath, covering with aluminum foil and allowing to gradually equilibrate to room temperature overnight for a total reaction time of 16 hours. The reaction mixture was then quenched at − 78 ºC with an excess of NH_4Cl(sat.), and transferred to a separatory funnel with additional H_2O used to dissolve any salts present. The crude mixture was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was purified by normal-phase column chromatography (12 g silica gold column, 0 → 10% hexanes /EtOAc) to afford 9-methoxy-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine (85 mg, 54 %) **3b** as a bright yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.22 (m, 3H), 7.04 (dd, J = 9.5, 2.6 Hz, 2H), 4.17 (s, 3H), 3.11 (s, 12H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: δ 147.8, 146.8, 138.9, 138.2, 132.4, 131.6, 129.9, 128.2, 127.6, 126.2, 125.7, 123.7, 116.6, 98.3, 60.8, 41.0, 19.9 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{28}N_2O_2$ 384.2202; Found 384.2196.

N-(7-(dimethylamino)-9-oxo-10-(*o*-tolyl)anthracen-2(9H)-ylidene)-*N*-methylmethanaminium (KR-1)



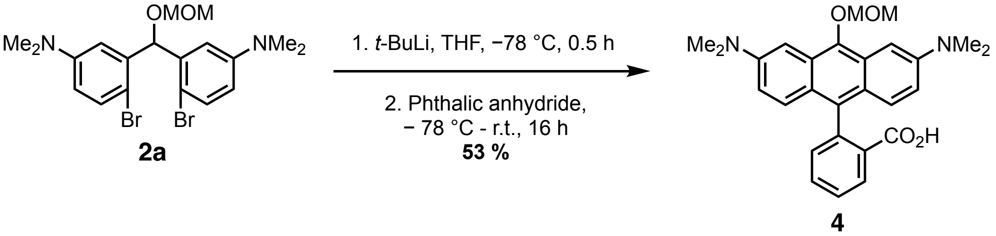
3a; R = MOM
3b; R = Me

KR-1

A solution of **3a** (10 mg, 0.024 mmol, 1.0 eq.) in CH_2Cl_2 (2.4 mL, 0.01 M) or **3b** (10 mg, 0.026 mmol, 1.0 eq.) in CH_2Cl_2 (2.6 mL, 0.01 M) in an oven-dried crimp vial under an Ar atmosphere were cooled to 0 ºC in an ice bath. The solution was then treated with either trifluoroacetic acid (260 µL) or BBr_3 (0.52 mL, 0.52 mmol, 20 eq.). The resulting suspension was sonicated and set to stir at room temperature in the absence of light overnight. The reaction mixture was reduced to dryness under a stream on N_2 before resuspending in CH_2Cl_2 (3 mL) with this process repeated a further two times. The concentrated product was suspended in CH_2Cl_2 before adding $NaHCO_3$ (sat.). The crude mixture was extracted with CH_2Cl_2 × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The dark brown residue was then purified by normal phase chromatography (4 g silica column, 0 → 15% MeOH/ CH_2Cl_2) to afford **KR-1** (6.2 mg, 70 %) as a brown black solid. Yield from **3b** = 5.9 mg, 62 %.

^1H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 2.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.03 – 6.88 (m, 4H), 3.52 (s, 12H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.4, 164.8, 156.7, 138.5, 136.0, 135.0, 133.7, 130.9, 130.0, 129.0, 126.2, 124.0, 116.9, 116.6, 42.2, 19.9 ppm. HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{25}H_{25}N_2O^+$ 369.1961; Found 369.1963.

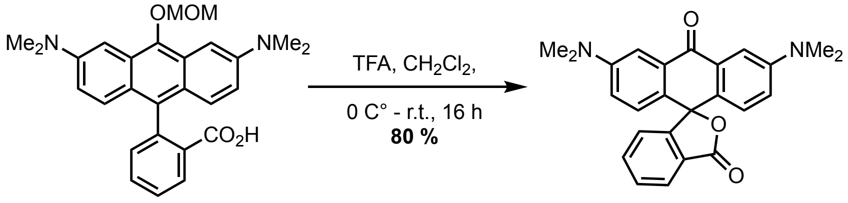
2-(3,6-bis(dimethylamino)-10-(methoxymethoxy)anthracen-9-yl)benzoic acid (4)



To 9-(methoxymethoxy)-N^2,N^2,N^7,N^7-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine **2c** (300 mg, 0.64 mmol, 1.0 eq.) in a flame-dried crimped 25 mL microwave vial under an Ar atmosphere, THF (15 mL, 0.042 M) was added. The solution was stirred at room temperature before cooling to − 78 ºC in a dry ice/ acetone bath. The solution was then treated with *tert*-Butyllithium solution (1.64 mL, 2.79 mmol, 4.4 eq.) and allowed stir at − 78 ºC for 0.5 h. A separately prepared solution of phthalic anhydride (207 mg, 1.40 mmol, 2.2 eq.) in THF (5 mL, 0.28 M) under an Ar atmosphere was then added dropwise to the − 78 ºC reaction mixture. The reaction mixture was allowed stir for 1 hour at – 78 ºC before removal from the cold bath, covering with aluminum foil and allowing to gradually equilibrate to room temperature overnight for a total reaction time of 16 hours. The reaction mixture was then quenched at − 78 ºC with an excess of NH_4Cl(sat.) and transferred to a separatory funnel with additional H_2O used to dissolve any salts present. The crude mixture was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was purified by normal-phase column chromatography (24 g silica gold column, 0 → 10% CH_2Cl_2 /MeOH) to afford 2-(3,6-bis(dimethylamino)-10-(methoxymethoxy)anthracen-9-yl)benzoic acid **4** (282 mg, 53 %) as a bright yellow solid.

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.05 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.70 (td, *J* = 7.5, 1.6 Hz, 1H), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.27 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.18 – 7.00 (m, 6H), 5.31 (s, 2H), 3.75 (s, 3H), 3.02 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 168.0, 147.4, 143.3, 138.9, 133.7, 132.6, 132.4, 131.3, 129.8, 127.8, 127.4, 126.2, 122.8, 116.4, 99.2, 97.6, 57.3, 40.3 ppm. HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{27}H_{28}N_2O_4$ 444.2049; Found 444.2044.

3,6-bis(dimethylamino)-3'*H*,10*H*-spiro[anthracene-9,1'-isobenzofuran]-3',10-dione (KR-2)



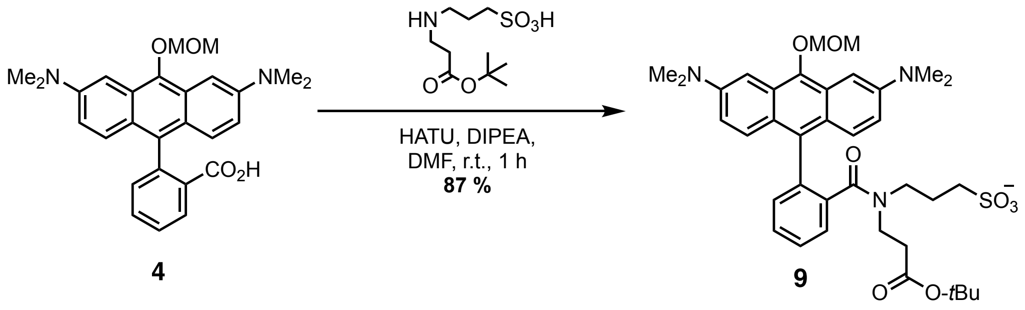
4

KR-2

A solution of **4** (50 mg, 0.11 mmol, 1.0 eq.) in CH_2Cl_2 (11 mL, 0.01 M) under an Ar atmosphere was cooled to 0 ºC in an ice bath. The solution was then treated with trifluoroacetic acid (1.2 mL). The resulting suspension was sonicated and set to stir at room temperature in the absence of light overnight. The reaction mixture was reduced to dryness under a stream on N_2 before resuspending in CH_2Cl_2 (10 mL) with this process repeated a further two times. The crude material was then suspended in CH_2Cl_2 before adding $NaHCO_3$ (sat.). The crude mixture was extracted with CH_2Cl_2 × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The dark brown residue was then purified by normal phase chromatography (12 g silica column, 0 → 5% MeOH/ CH_2Cl_2) to afford **KR-2** (36 mg, 80 %) as a yellow-orange solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.03 – 7.95 (m, 1H), 7.60 (d, *J* = 2.9 Hz, 2H), 7.55 – 7.44 (m, 2H), 6.96 – 6.87 (m, 3H), 6.83 (dd, *J* = 8.8, 2.9 Hz, 2H), 3.02 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ; 184.1, 171.2, 154.7, 150.7, 135.1, 131.9, 129.2, 128.0, 126.7, 125.6, 125.2, 122.8, 117.8, 109.4, 84.5, 40.4 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{22}N_2O_3$ 398.1630; Found 398.1633 ppm.

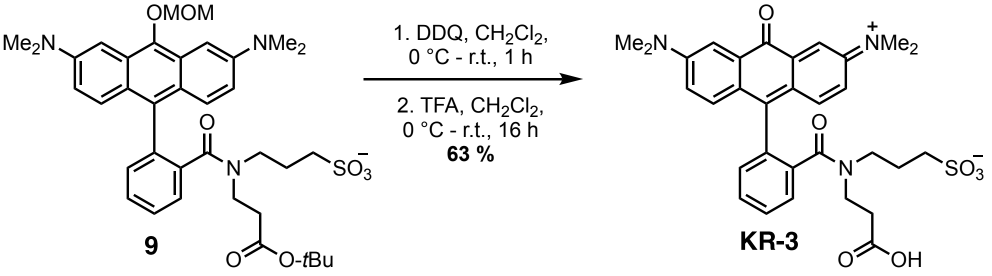
3-(2-(3,6-bis(dimethylamino)-10-(methoxymethoxy)anthracen-9-yl)-*N*-(3-(*tert*-butoxy)-3-oxopropyl)benzamido)propane-1-sulfonate (9)



A solution of **4** (50 mg, 0.11 mmol, 1.0 eq.), HATU (130 mg, 0.34 mmol, 3.0 eq.) and *N*,*N*-diisopropylethylamine (59 µL, 0.33 mmol, 3.0 eq.) in DMF (3 mL) under an Ar atmosphere was set to stir at room temperature. To the solution was then added 3-((3-(*tert*-butoxy)-3-oxopropyl)amino)propane-1-sulfonic acid (45 mg, 0.17 mmol, 1.5 eq.) and the reaction mixture was sonicated for 5 minutes before stirring at room temperature for 1 hour. The reaction mixture was then added to a separatory funnel containing of 4:1, EtOAc: Hexanes and NH_4Cl (sat.). Once extracted the separatory funnel was allowed to rest for 15-20 minutes to aid separation. This process was repeated until minimal crude material was detected in the organic layer by TLC. The organic layers were then combined and washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The residue was purified by normal-phase column chromatography (12 g silica gold column, 0 → 10% CH_2Cl_2 /MeOH) to afford 3-(2-(3,6-bis(dimethylamino)-10-(methoxymethoxy)anthracen-9-yl)-*N*-(3-(*tert*-butoxy)-3-oxopropyl)benzamido)propane-1-sulfonate **9** (68 mg, 87 %) as a bright yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.68 – 7.56 (m, 2H), 7.55 – 7.41 (m, 1H), 7.41 – 7.35 (m, 1H), 7.33 – 7.19 (m, 2H), 7.16 – 6.99 (m, 4H), 5.28 (s, 2H), 3.74 (s, 3H), 3.03 (s, 12H), 2.92 (t, *J* = 7.6 Hz, 1H), 2.16 (br. s, 2H), 1.53 (br. s, 2H), 1.32 (d, *J* = 42.6 Hz, 9H), 0.97 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.1, 168.8, 147.4, 143.5, 138.2, 135.7, 132.2, 132.0, 129.7, 128.6, 127.8, 126.5, 126.1, 116.0, 99.2, 97.3, 79.7, 57.3, 48.4, 44.4, 40.3, 34.0, 30.8, 27.6, 24.3 ppm.HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{37}H_{47}N_3O_8S$ 693.3084; Found 693.3081.

3-(*N*-(2-carboxyethyl)-2-(6-(dimethylamino)-3-(dimethyliminio)-10-oxo-3,10-dihydroanthracen-9-yl)benzamido)propane-1-sulfonate (KR-3)

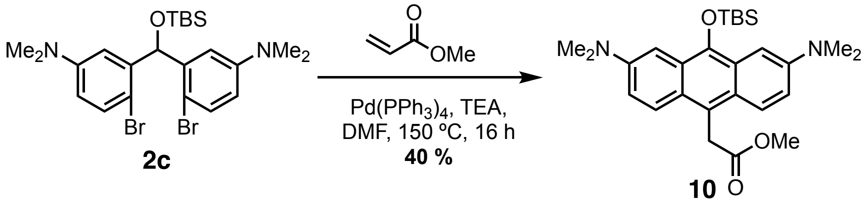


To solution of **9** (66 mg, 0.096 mmol, 1.0 eq.) in CH_2Cl_2 (9.5 mL, 0.01 M) under an Ar atmosphere was added DDQ (24 mg, 0.1057 mmol, 1.1 eq.). The reaction mixture was stirred at room temperature for 1 hour before addition of $NaHCO_3$ (sat.). The crude mixture was extracted with CH_2Cl_2 × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The residue was then purified by normal phase chromatography (12 g silica column, 0 → 10% CH_2Cl_2 /MeOH) to afford 3-(*N*-(3-(*tert*-butoxy)-3-oxopropyl)-2-(6-(dimethylamino)-3-(dimethyliminio)-10-oxo-3,10-dihydroanthracen-9-yl)benzamido)propane-1-sulfonate **12** (40.8 mg, 91 %) as a dark brown solid.

To a solution of **12** (110 mg, 0.17 mmol, 1.0 eq.) in CH_2Cl_2 (15.3 mL, 0.01 M) under an Ar atmosphere was cooled to 0 ºC in an ice bath. The solution was then treated with trifluoroacetic acid (1.7 mL). The resulting solution was sonicated and set to stir at room temperature in the absence of light for 16 hours. The reaction mixture was reduced to dryness under a stream on N_2 before resuspending in CH_2Cl_2 (15 mL) with this process repeated a further two times before drying under high vacuum to afford **KR-3** (138 mg) as a crude TFA salt. The residue could be further purified by reverse-phase chromatography (C18 20 ×150mm, dimensions: 21 mm x 250 mm 10 µm, 0 → 50 % H_2O /CH_3CN) to afford **KR-3** (68 mg, 63 %) as a brown-black solid.

^{1}H NMR (400 MHz, MeOD/ TFA-*d*) δ 7.81 (dd, *J* = 9.5, 2.8 Hz, 1H), 7.76 – 7.53 (m, 3H), 7.46 (ddd, *J* = 14.8, 6.0, 2.8 Hz, 1H), 7.08 (dd, *J* = 19.4, 9.4 Hz, 2H), 6.89 (dd, *J* = 20.8, 9.3 Hz, 2H), 3.53 – 3.47 (m, 1H), 3.41 (s, 12H), 2.65 (t, *J* = 7.2 Hz, 1H), 2.54 (t, *J* = 7.4 Hz, 1H), 2.45 – 2.31 (m, 1H), 2.14 (t, *J* = 6.5 Hz, 1H), 2.06 – 1.84 (m, 1H), 1.70 – 1.46 (m, 1H) ppm. HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{31}H_{33}N_3O_7S^+$ 592.2112; Found 592.2256.

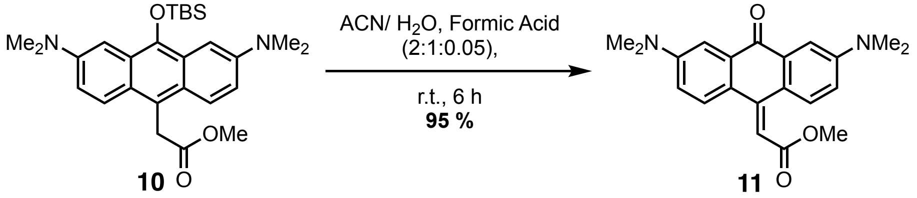
Methyl 2-(10-((tert-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate (10)



To 3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) (50 mg, 0.092 mol, 1.0 eq.), $Pd(PPh_3)_4$ (5.3 mg, 0.0046 mol, 0.05 eq.) and triethylamine (65 µL, 0.46 mmol, 5.0 eq.) in a flame dried, Ar flushed 1 dram vial was added DMF (190 µL, 0.5 M). The reaction was set to stir at room temperature for 5 minutes before the addition of methyl acrylate (12.5 µL, 0.0138 mmol, 1.5 eq.). The vial was flushed with Ar, sealed carefully with parafilm and black electrical tape and heated to 150 °C overnight in the absence of light. Once at room temperature the crude reaction mixture was diluted with EtOAc and passed through a celite plug eluting with additional EtOAc. The eluant was transferred to a separatory funnel and washed with $NaHCO_3$ (sat.). The aqueous phase was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was purified by normal-phase column chromatography (4 g silica, 0 → 10% hexanes /EtOAc) to afford methyl 2-(10-((tert-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate (35 mg, 40 %) **10** as a bright yellow solid.

^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 8.01 (d, J = 9.6 Hz, 2H), 7.26 (dd, J = 9.6, 2.7 Hz, 2H), 6.98 (d, J = 2.6 Hz, 2H), 4.48 (s, 2H), 3.58 (s, 3H), 3.03 (s, 12H), 1.13 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.9, 146.5, 141.1, 125.7, 124.8, 123.4, 119.5, 117.1, 99.2, 51.7, 40.4, 32.9, 25.9, 18.4, − 2.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{38}N_2O_3Si$ 466.2652; Found 466.2645.

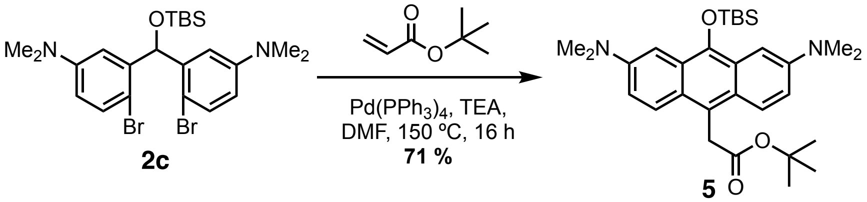
Methyl 2-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10*H*)-ylidene)acetate (11)



To **10** (10 mg, 0.021 mmol, 1.0 eq.) in a solution in 2:1 ACN/ H_2O (3 mL) formic acid (150 μL) was added. The reaction was set to stir at room temperature overnight. The solution was dried under vacuum to give methyl 2-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10*H*)-ylidene)acetate **11** (7.1 mg, 95%) as a yellow-orange solid.

^{1}H NMR (400 MHz, CD_3CN) δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 2.9 Hz, 2H), 7.01 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.93 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.46 (s, 1H), 3.73 (s, 3H), 3.05 (d, *J* = 8.0 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.8, 168.4, 151.2, 150.9, 143.5, 133.1, 132.1, 131.0, 127.5, 125.1, 122.6, 116.7, 114.7, 112.1, 109.0, 108.7, 51.7, 40.4, 40.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}N_2O_3$ 350.1630; Found 350.1637.

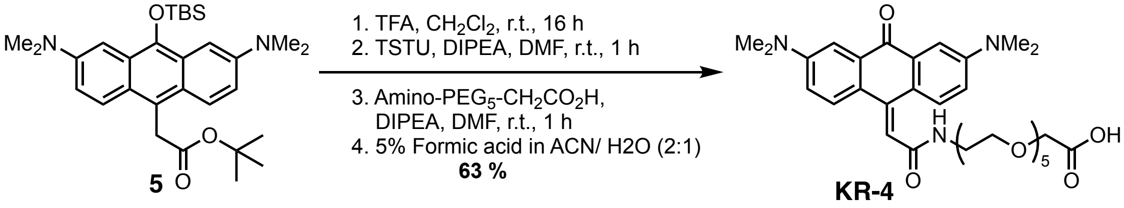
***Tert*-butyl 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate (5)**



To 3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) **2c** (200 mg, 0.37 mol, 1.0 eq.), Pd(PPh$_3$)$_4$ (21 mg, 0.018 mol, 0.05 eq.) and triethylamine (260 µL, 1.8 mmol, 5.0 eq.) in a flame dried, Ar flushed 1 dram vial was added DMF (740 µL, 0.5 M). The reaction was set to stir at room temperature for 5 minutes before the addition of *tert*-butyl acrylate (82 µL, 0.55 mmol, 1.5 eq.). The vial was flushed with Ar, sealed carefully with parafilm and black electrical tape and heated to 150 °C overnight in the absence of light. Once at room temperature the crude reaction mixture was diluted with EtOAc and passed through a celite plug eluting with additional EtOAc. The eluant was transferred to a separatory funnel and washed with NaHCO$_3$ (sat.). The aqueous phase was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na$_2$SO$_4$, filtered and evaporated to dryness *in vacuo*. The yellow residue was purified by normal-phase column chromatography (12 g silica, 0 → 5% hexanes /EtOAc) to afford *tert*-butyl 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate **5** (130 mg, 71 %) as a bright yellow solid.

^{1}H NMR (500 MHz, CD$_3$CN) δ: 8.03 (d, J = 9.7 Hz, 2H), 7.26 (d, J = 2.6 Hz, 1H), 7.24 (d, J = 2.6 Hz, 1H), 7.10 (d, J = 2.6 Hz, 2H), 4.34 (s, 2H), 3.06 (s, 12H), 1.38 (s, 9H), 1.16 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (126 MHz, CD$_3$CN) δ: 172.1, 148.0, 142.7, 126.7, 126.3, 124.8, 121.0, 118.0, 100.9, 81.3, 41.2, 35.4, 28.2, 26.5, 19.4, − 2.2 ppm. HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{30}$H$_{44}$N$_2$O$_3$Si 508.3121; Found 508.3111.

1-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10H)-ylidene)-2-oxo-6,9,12,15,18-pentaoxa-3-azaicosan-20-oic acid (KR-4)



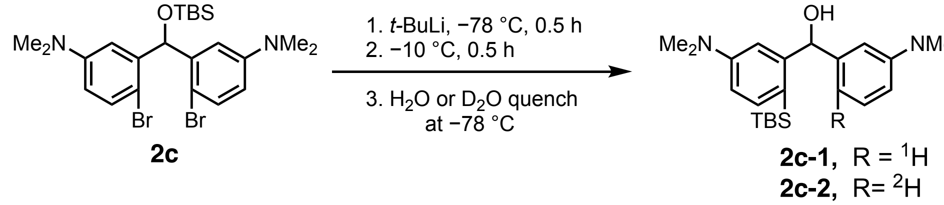
To *tert*-butyl 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate **5** (50 mg, 0.098 mmol, 1.0 eq.) in an Ar flushed round bottom flask CH_2Cl_2 (9mL, 0.01M) was added and the solution was cooled to 0 °C in an ice-bath. To this TFA (1 mL) was added dropwise and the reaction mixture was stirred overnight wrapped in aluminum foil to exclude light. The reaction was reduced to dryness under a stream of N_2 before being redissolved in CH_2Cl_2 (9mL) with this process being repeated for a total of 3 times. The residue was then suspended in EtOAc, transferred to a separatory funnel and washed with $NaHCO_3$ (sat.). The aqueous phase was extracted with EtOAc × 2 with the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was used without purification.

To 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetic acid (45 mg, 0.010 mmol, 1.0 eq.) and TSTU (60 mg, 0.20 mmol, 2.0 eq.) in an Ar flushed 1 dram vial was added DMF (0.5 mL). The reaction mixture was sonicated and set to stir at room temperature for 5 min before adding DIPEA (35 µL, 0.20 mmol, 2.0 eq.). After 1 hour the reaction mixture was added to a partition of EtOAc and 1M HCl in a separatory funnel, the organic layer was recovered and washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was used without purification.

To 2,5-dioxopyrrolidin-1-yl 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate (54 mg, 0.098 mmol, 1 eq.) and Amino-PEG$_5$-CH_2CO_2H (CAS: 141282-35-1) (35 mg, 0.17 mmol, 1.2 eq.) in an Ar flushed 1 dram vial was added DMF (1 mL, 0.1M). The reaction mixture was sonicated and set to stir at room temperature for 5 min before adding DIPEA (34 µL, 0.20 mmol, 2.0 eq.). After 1 hour the reaction mixture was dissolved in CH_2Cl_2, transferred to a separatory funnel and washed with $NaHCO_3$ (sat.). The aqueous phase was extracted with CH_2Cl_2 × 2 and the organic phase then washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The yellow residue was then dissolved in a 5% formic acid solution in 2:1 ACN/ H_2O and stirred for 6 hours at room temperature. Upon drying *in vacuo* the residue was purified by normal-phase column chromatography (12 g silica gold column, 0 → 30 % CH_2Cl_2 /MeOH) to afford 1-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10*H*)-ylidene)-2-oxo-6,9,12,15,18-pentaoxa-3-azaicosan-20-oic acid **KR-4** (38 mg, 63 % over 4 steps) as a bright yellow solid.

^{1}H NMR (400 MHz, CD_3CN/ D_2O; 9:1) δ: 7.80 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.36 (d, *J* = 3.0 Hz, 2H), 7.04 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.95 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.60 (s, 1H), 3.83 (s, 2H), 3.61 – 3.43 (m, 19H), 3.39 (t, *J* = 5.4 Hz, 2H), 3.00 (d, *J* = 2.9 Hz, 12H); ^{13}C NMR (100 MHz, CD_3CN/ D_2O; 9:1) δ: 186.4, 175.8, 170.7, 151.7, 151.7, 135.8, 133.3, 132.3, 130.5, 127.9, 126.0, 124.3, 119.5, 118.6, 117.0, 108.8, 108.7, 70.7, 70.5, 70.5, 70.4, 70.4, 70.3, 40.5, 40.4, 40.0 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{32}H_{43}N_3O_9$ 613.2999; Found 613.2988.

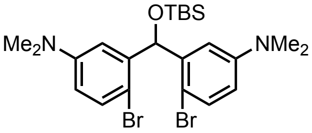
Section S4: Retro-Brook Rearrangement Experiment and NMR Analysis



Scheme S1: Synthetic scheme of H_2O/ D_2O quench experiment with predicted products **2c-1** and **2c-2**.

To 3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N,N*-dimethylaniline) **2c** (20 mg, 0.03687 mmol, 1.0 eq.) in a flame-dried crimped microwave vial under an Ar atmosphere, THF (1 mL) was added. The solution was stirred at room temperature before cooling to − 78 ºC in a dry ice/ acetone bath. The solution was then treated with *tert*-Butyllithium solution (95 µL, 0.01622 mmol, 4.4 eq.) and allowed stir at − 78 ºC for 0.5 h. The reaction mixture was stirred for an additional 0.5 h at − 10 ºC to ensure halogen-metal exchange. The reaction mixture was then quenched at − 10 ºC with an H_2O (3 mL) or D_2O (3 mL) and extracted with EtOAc × 2. The organic phase was washed with brine × 2, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. The resulting colorless oils **2c-1** and **2c-2** were used without further purification and submitted for ^1H NMR analysis in CD_3CN. Additionally, to an NMR sample of H_2O quench experiment **2c-1**, a few drops of MeOD were added and it was also analyzed ^1H NMR.

A - Starting Material

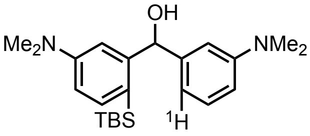


2c

3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N,N*-dimethylaniline) **2c**

^1H NMR (400 MHz, CD_3CN) δ: 7.30 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 3.2 Hz, 2H), 6.57 (dd, J = 8.8, 3.2 Hz, 2H), 6.24 (s, 1H), 2.86 (s, 12H), 0.91 (s, 9H), 0.07 (s, 6H) ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{34}Br_2N_2O_2Si$ 542.0787; Found 542.0790.

B - H_2O quench

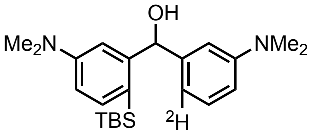


2c-1

(2-(*tert*-butyldimethylsilyl)-5-(dimethylamino)phenyl)(3-(dimethylamino)phenyl-6-*H*)methanol **2c-1**

^{1}H NMR (400 MHz, CD_3CN) δ: 7.37 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.77 (s, 1H), 6.69 – 6.64 (m, 2H), 6.61 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 5.86 (d, *J* = 5.1 Hz, 1H), 3.42 (d, *J* = 5.2 Hz, 1H), 2.85 (d, *J* = 13.8 Hz, 12H), 0.91 (s, 9H), 0.31 (d, *J* = 36.9 Hz, 6H). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{35}{}^{1}HN_2OSi$ 384.2597; Found 384.2272 ppm.

C - D_2O quench

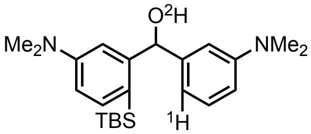


2c-2

(2-(*tert*-butyldimethylsilyl)-5-(dimethylamino)phenyl)(3-(dimethylamino)phenyl-6-*d*)methanol **2c-2**

^{1}H NMR (400 MHz, CD_3CN) δ 7.37 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 6.69 – 6.64 (m, 2H), 6.61 (dd, *J* = 8.3, 2.7 Hz, 1H), 5.86 (d, *J* = 5.2 Hz, 1H), 3.41 (d, *J* = 5.2 Hz, 1H), 2.85 (d, *J* = 13.5 Hz, 12H), 0.91 (s, 8H), 0.31 (d, *J* = 37.0 Hz, 6H) ppm. $C_{23}H_{35}DN_2OSi$ 385.2660; Found 385.2284.

D - ^{2}H exchange experiment in MeOD



2c-3

(2-(*tert*-butyldimethylsilyl)-5-(dimethylamino)phenyl)(3-(dimethylamino)phenyl-6-*H*)methanol-*d* **2c-3**

^{1}H NMR (400 MHz, CD_3CN) δ: 7.45 – 7.29 (m, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.77 (s, 1H), 6.68 – 6.64 (m, 2H), 6.61 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.56 (d, *J* = 7.3 Hz, 1H), 5.85 (s, 1H), 2.84 (d, *J* = 12.4 Hz, 12H), 0.90 (s, 9H), 0.30 (d, *J* = 38.6 Hz, 6H) ppm.

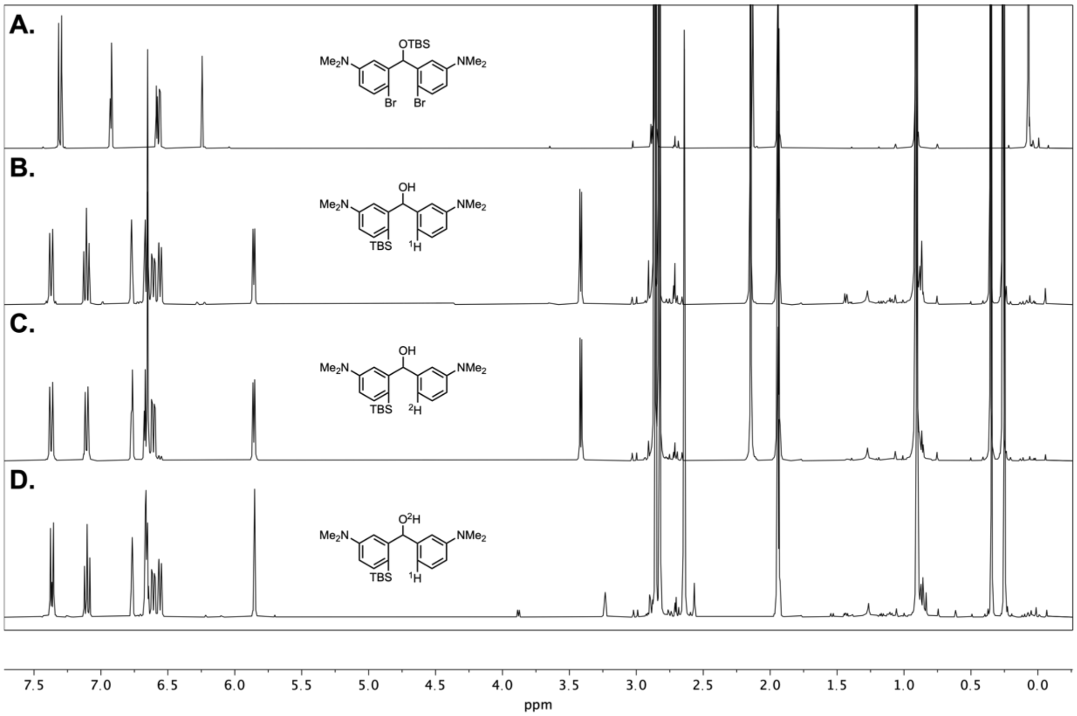


Figure S2: Stacked ^{1}H NMR spectra of compounds **2c**, **2c-1**, **2c-2** and **2c-3** in ACN-d$_3$.

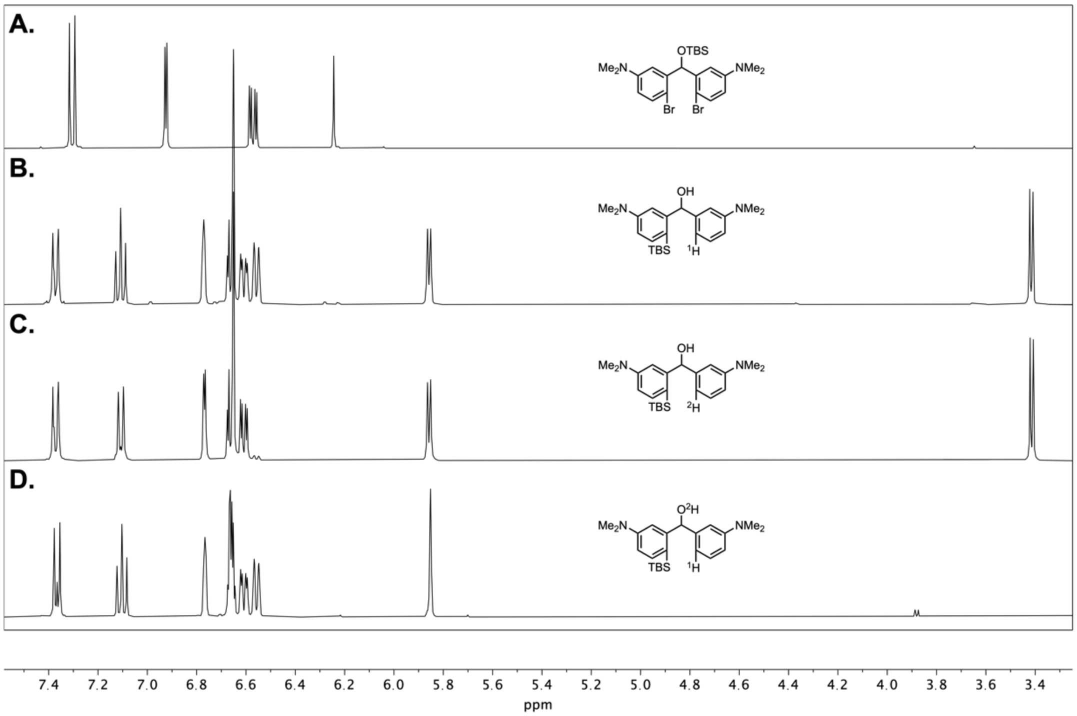


Figure S3: Stacked ^{1}H NMR spectra of compounds **2c**, **2c-1**, **2c-2** and **2c-3** in ACN-d$_3$ (zoom 7.5 - 3.3 ppm).

Section S5: Photophysical Measurements

Determination of molar absorption coefficients and fluorescence quantum yields.

All spectroscopic measurements were carried out in duplicate at room temperature using 10 mm × 10 mm quartz cuvettes (Hellma GmbH) and high-purity spectroscopic grade solvents. High purity water ($\sigma < 55\ \mu S$) was obtained using a MilliPore filter system. Dichloromethane (CH_2Cl_2; anhydrous, ≥99.8 %), Dimethylsulfoxide (DMSO; for molecular biology) and Trifluoroacetic acid (TFA; HPLC grade) were purchased from Millipore Sigma. Phosphate buffered saline (PBS 1x; gibco) was purchased from Fisher Scientific. Acetate buffer (pH 3.6) was prepared by adding 0.099 g of Sodium Acetate (Millipore Sigma - 791741-500g) and 1.429 g of Acetic Acid (VWR - BDH3094-2.5LG) to 400 mL H_2O and adjusting the solution to pH 3.6 using HCl or NaOH before adding H_2O to a final volume of 500 mL in a volumetric flask,

The reference dyes IR140 was purchased from Lambda Physik and used to determine the fluorescence quantum yield of **KR-1** (see main body text).

Molar absorption coefficients (ε) at the respective absorbance maximum were determined using a PerkinElmer UV/Vis Photodiode Array Spectrophotometer Lambda 465 (Scan No. 30, Integration No. 1) in CH_2Cl_2, PBS (pH 7.4), CH_2Cl_2 supplemented with 5 % TFA or acetate buffer at pH 3.6 using Beer's law, from plots of absorbance vs. concentration. Measurements were performed in 10 mm path length quartz cuvettes (Hellma 111-QS), maintained at 25 °C, with absorbance at the highest concentration ≤ 0.20.

Fluorescence traces were recorded on a PTI QuantaMaster steady state spectrofluorometer operated by FelixGX 4.2.2 software, with 827 nm excitation, 15 nm excitation and 20 nm emission slit widths with a 1 nm step size, 1 s integration rate and a collection range of 855 nm - 1300 nm (organic solvent) or 855 nm - 1500 nm (aqueous solvent).

Previously measured KR-1 quantum yield value of 1.3 % in CH_2Cl_2 was used as the internal standard (ST below) for all subsequent measurements which were determined using a relative method and calculated according to the following equation:

$$\phi_x = \phi_{ST}\left(\frac{(Grad_x}{(Grad_{ST}}\right)\left(\frac{(n_x^2}{(n_{ST}^2}\right)$$

where Φ is the fluorescence quantum yield, subscript x and ST denote the test and standard respectively, Grad is the gradient from the plot of the integrated intensity vs. absorbance at excitation wavelength (827 nm) and n is the refractive index of the solvent used.

All fluorescent measurements were manually background subtracted using fluorescent traces of the appropriate blank taken under identical conditions to that of the corresponding samples (827 nm excitation, 15 nm excitation and 20 nm emission slit widths with a 1 nm step size and 1 s integration rate).

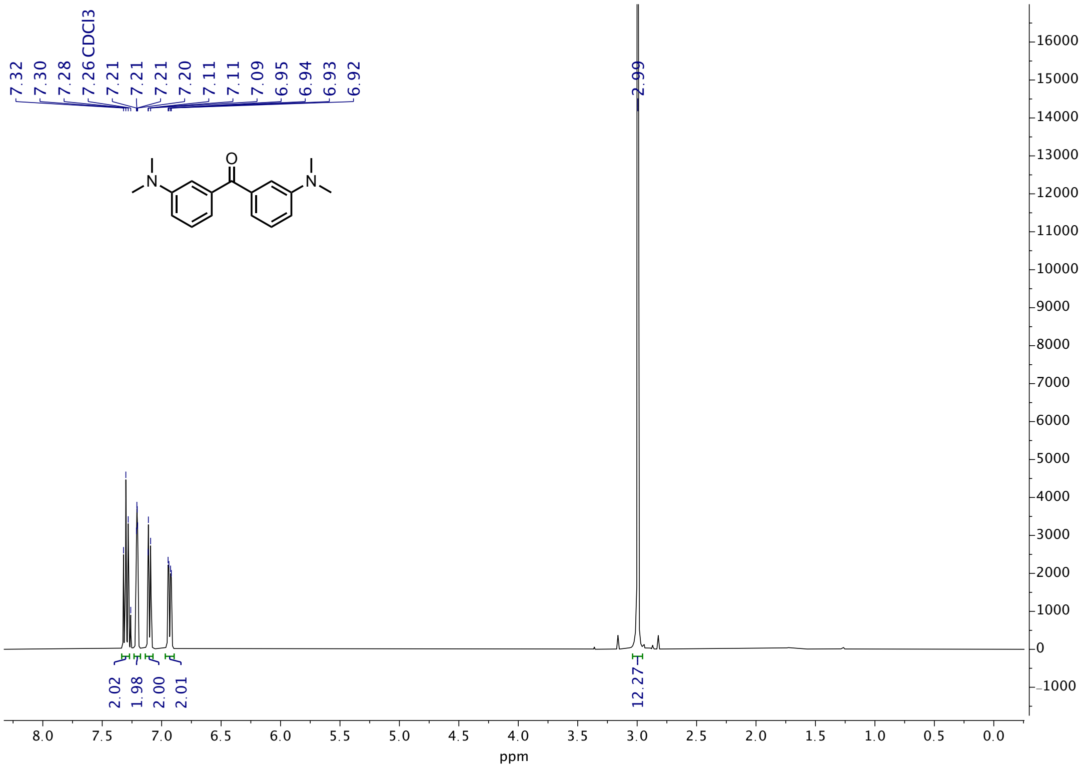
Figure 2, Panel D: A 2mM stock of **KR-2** was prepared in DMSO. 10 µM - 50 µM samples (5 mL) were prepared in CH_2Cl_2 supplemented with 5 % TFA and separately a 50 µM sample of **KR-2** was prepared in CH_2Cl_2 with all samples containing a final DMSO concentration of 2.5 %. All samples were vortexed and sonicated before allowing to equilibrate at ambient temperature in the absence of light before absorbance/ fluorescence measurements.

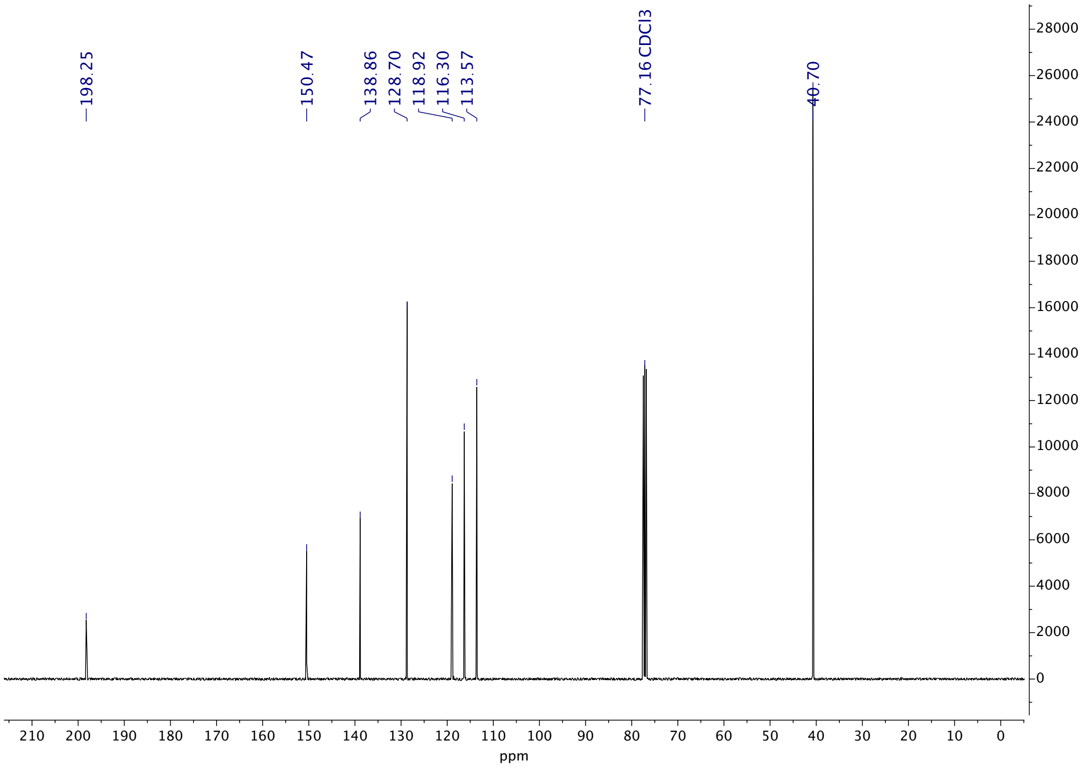
Figure 2, Panel E: A 10 mM stock of **KR-4** in DMSO was diluted to 250 µM in PBS pH 7.4 (10 mL). This solution was adjusted from pH 7.4 to pH 3.5 using 0.1 M, 0.5 M and 1M NaOH/ HCl in decrements of pH 0.5. Once the desired pH was obtained a 200 µL sample was removed and absorbance curve was generated using a Synergy Mx microplate reader (300 nm - 999nm, step size 5 nm).

Figure 2, Panel F: pK_a was determined by plotting the λ_{max} Abs (870 nm) vs. each pH value. Sigmoidal plot fit resulted in apparent pKa = 4.4.

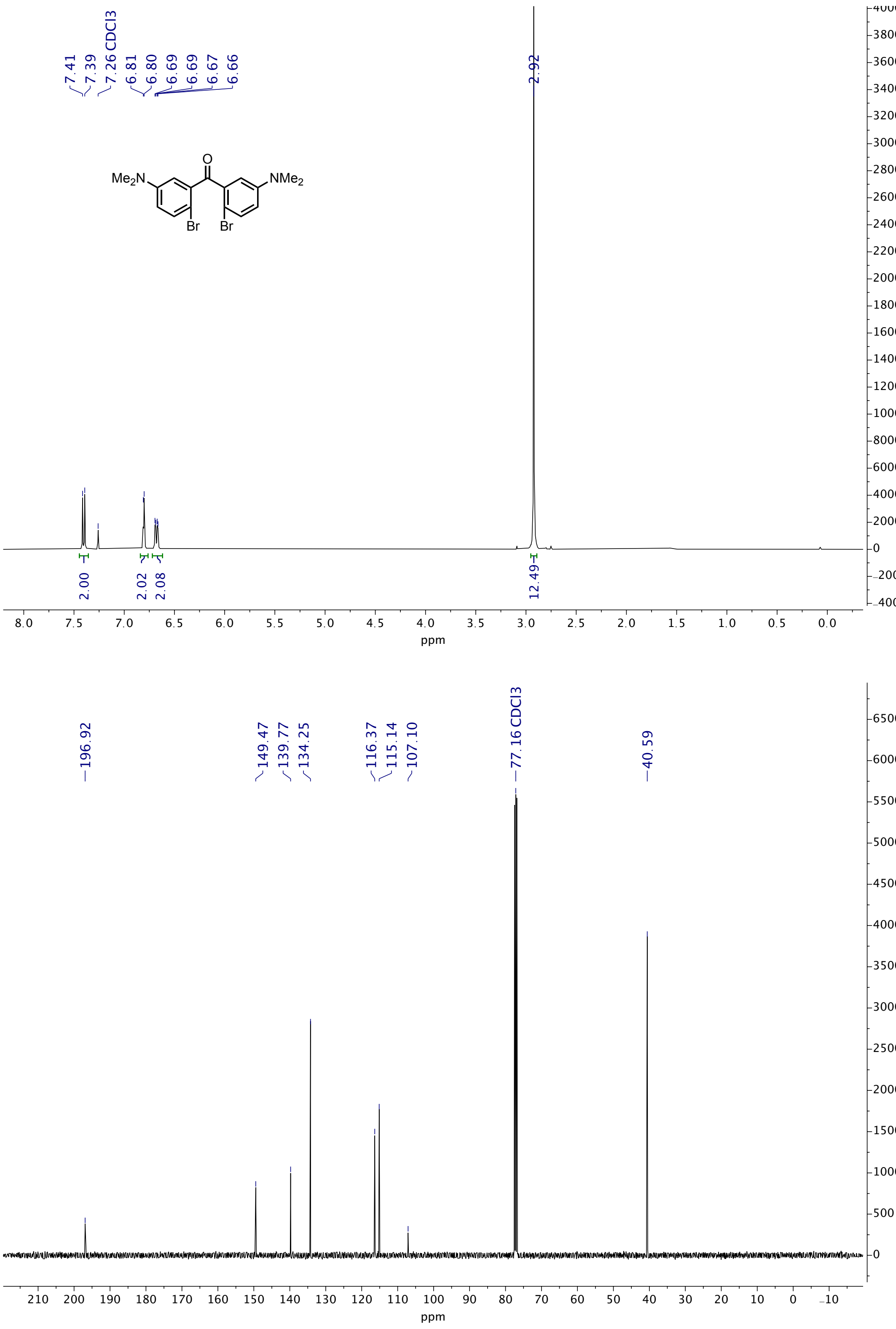
Section S6: ^{1} H, ^{13}C and Associated 2D NMR Spectra

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **bis(3-(dimethylamino)phenyl)methanone (1)**

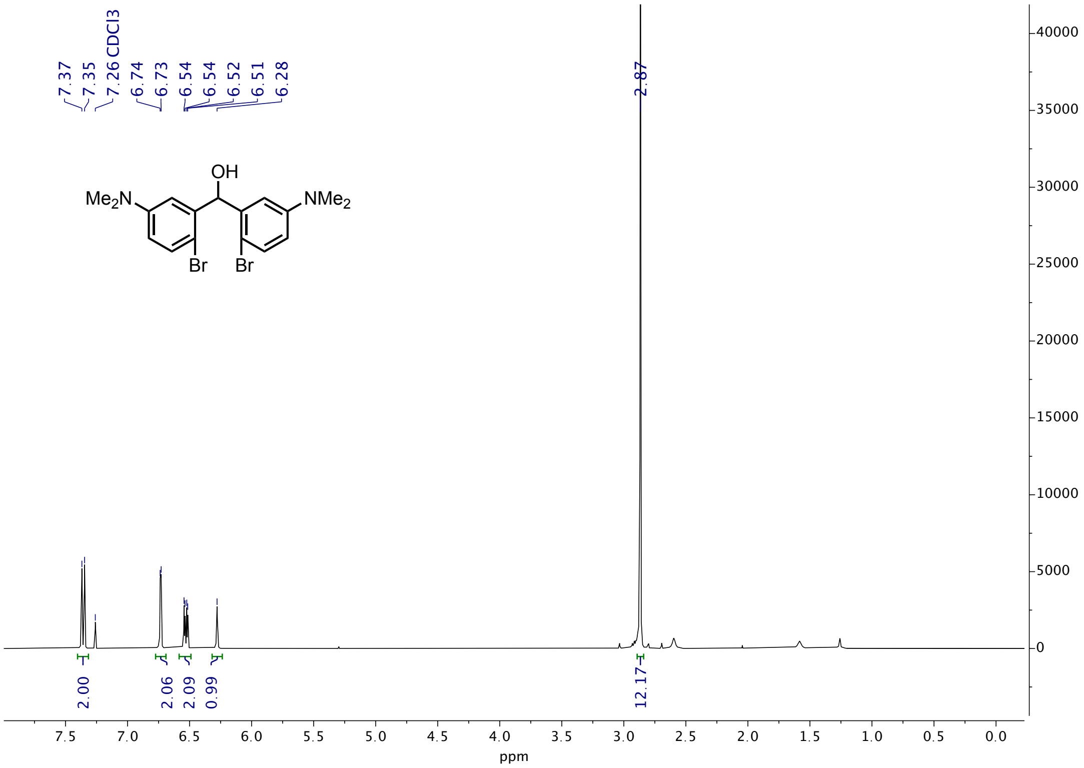


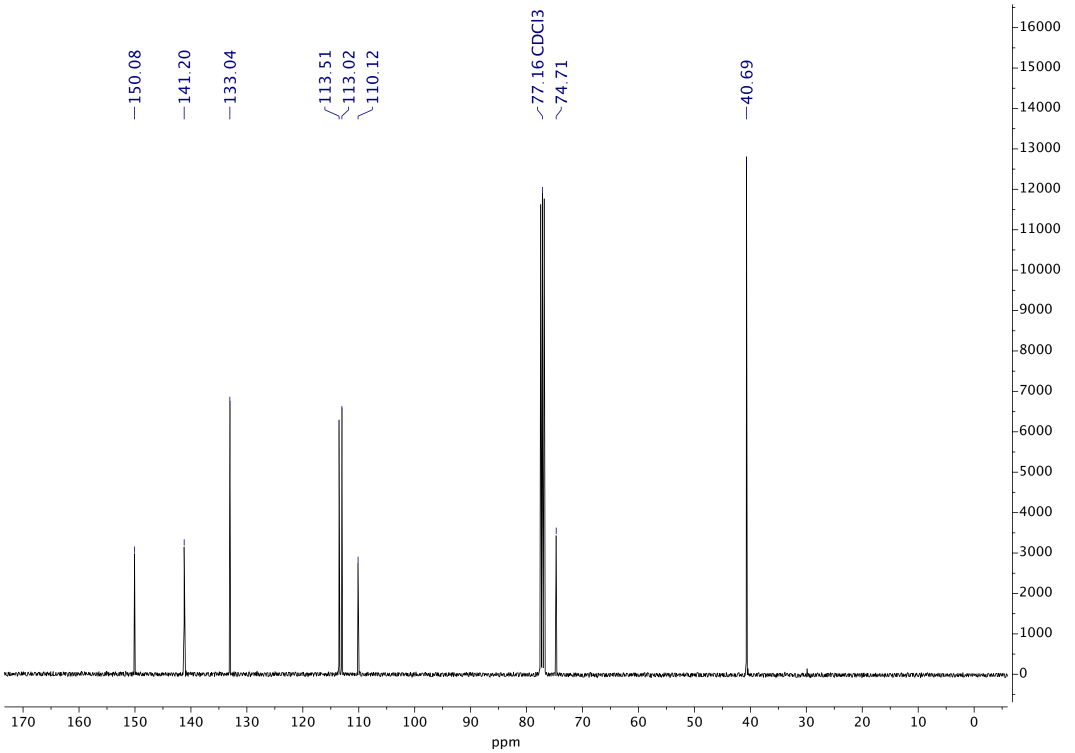


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **bis(2-bromo-5-(dimethylamino)phenyl)methanone (7)**

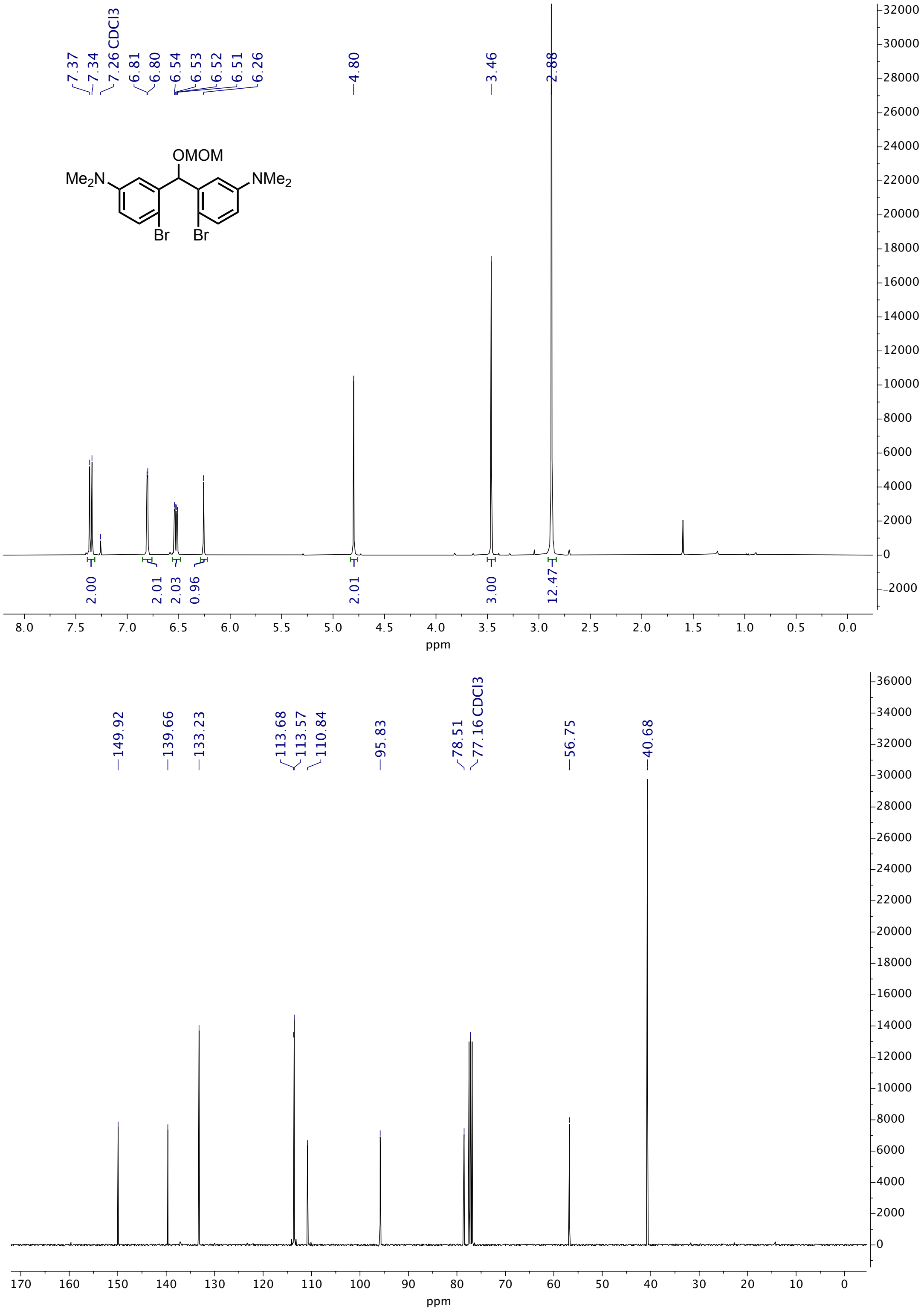


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **bis(2-bromo-5-(dimethylamino)phenyl)methanol (12)**

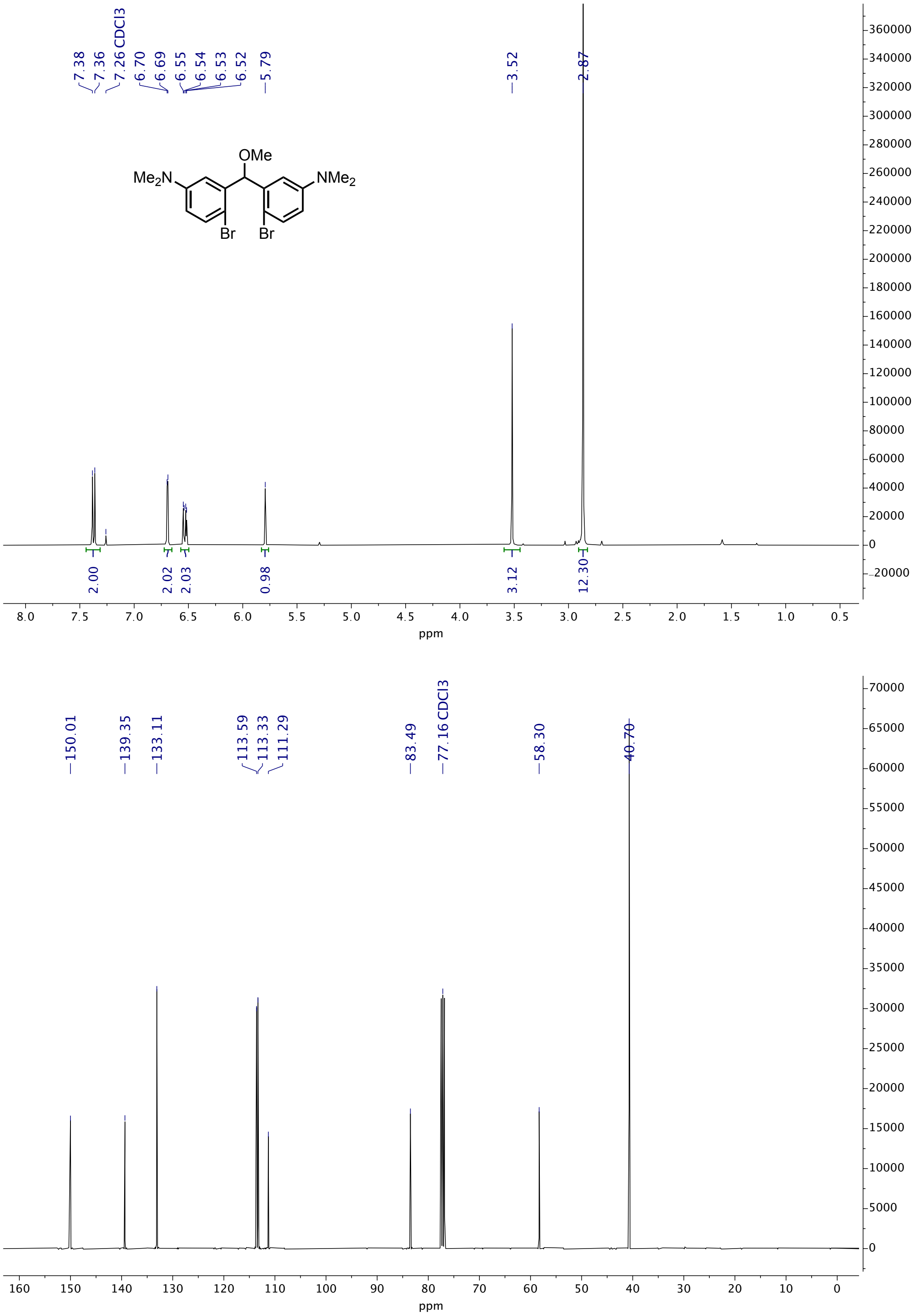




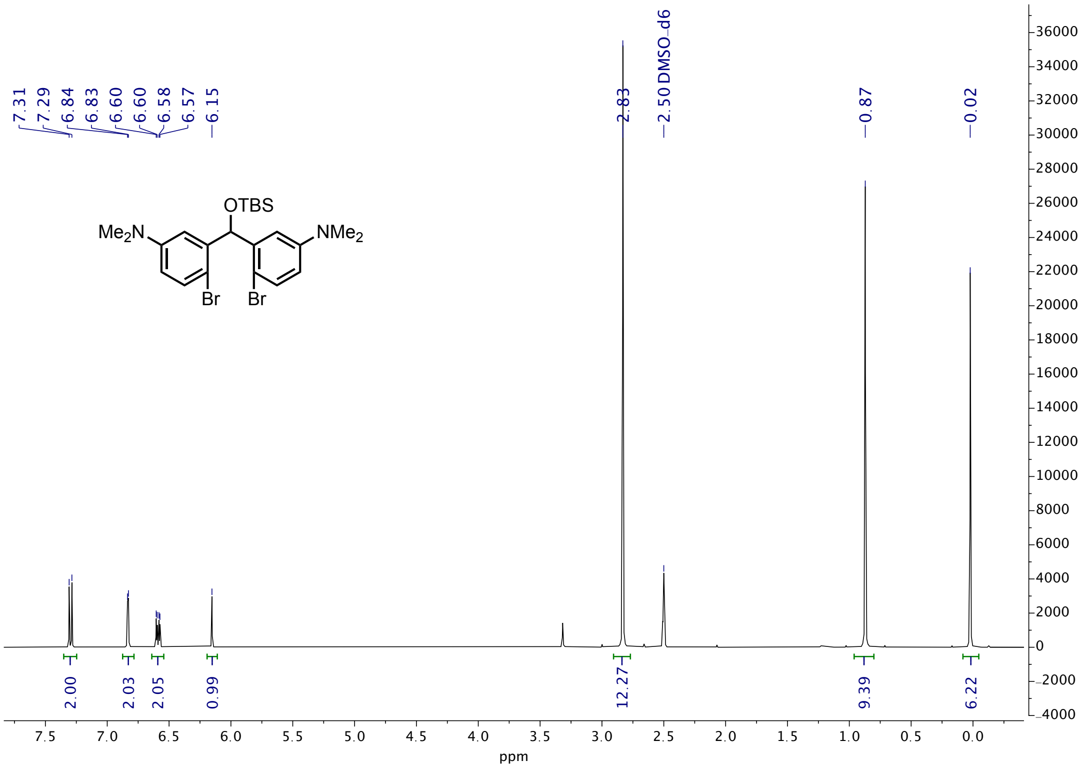
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3,3'-((methoxymethoxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2a)**

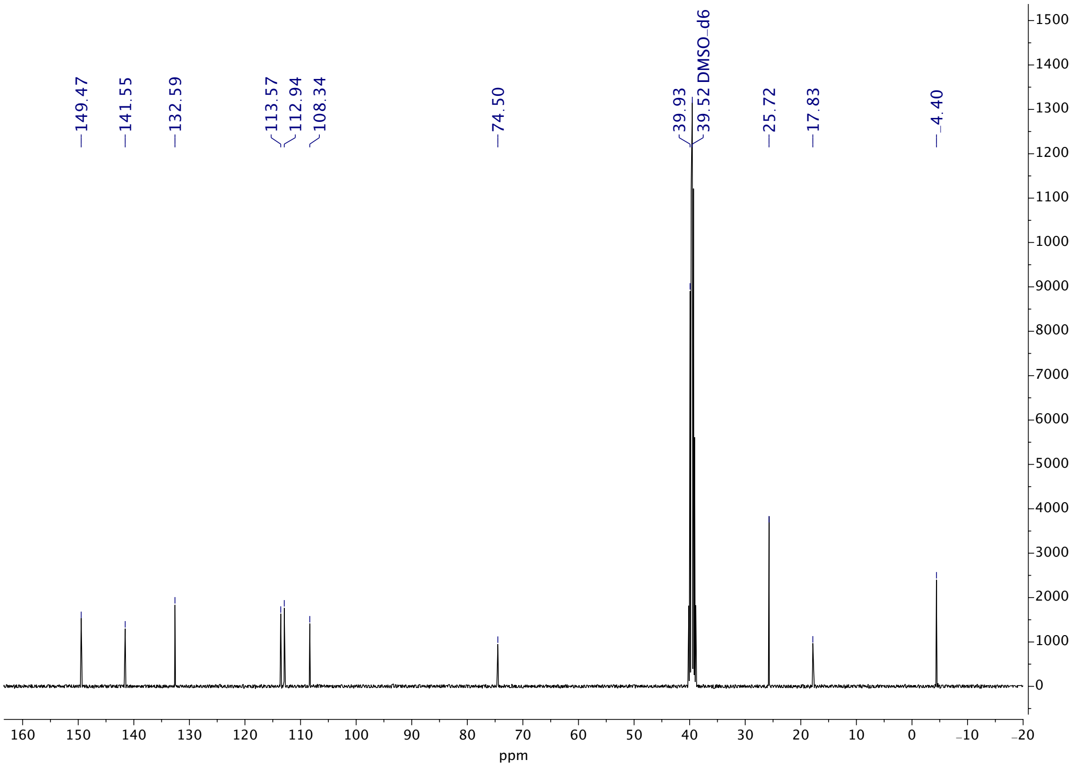


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of
3,3'-(methoxymethylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2b)

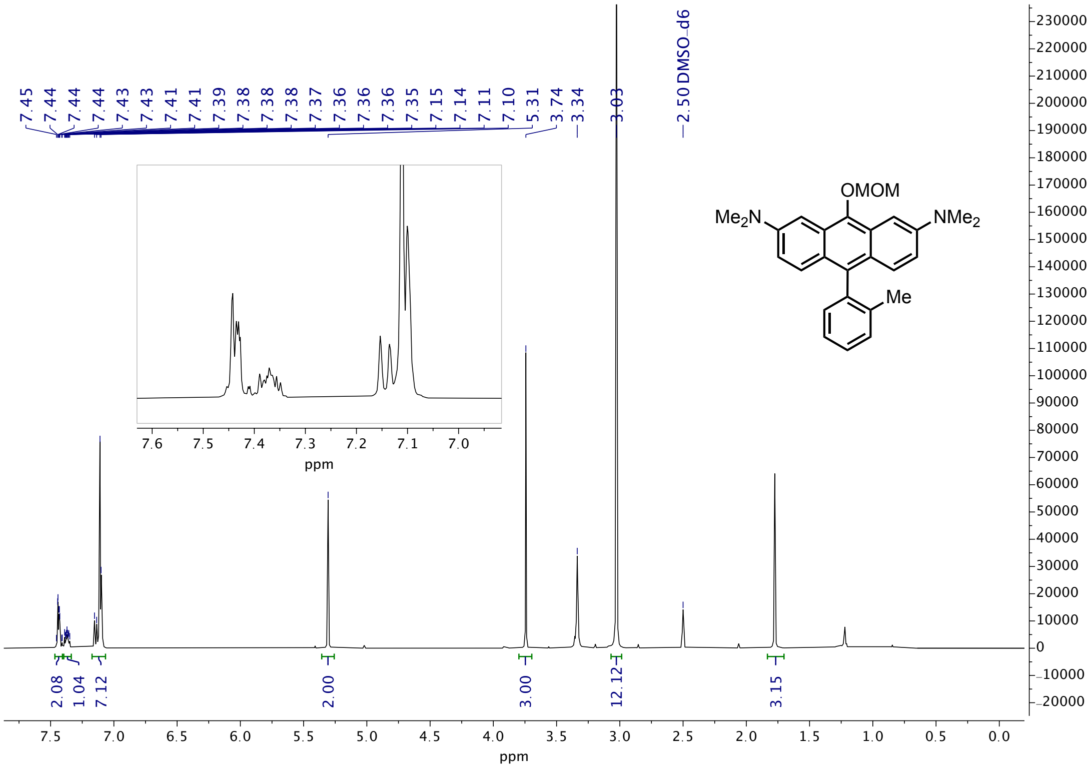


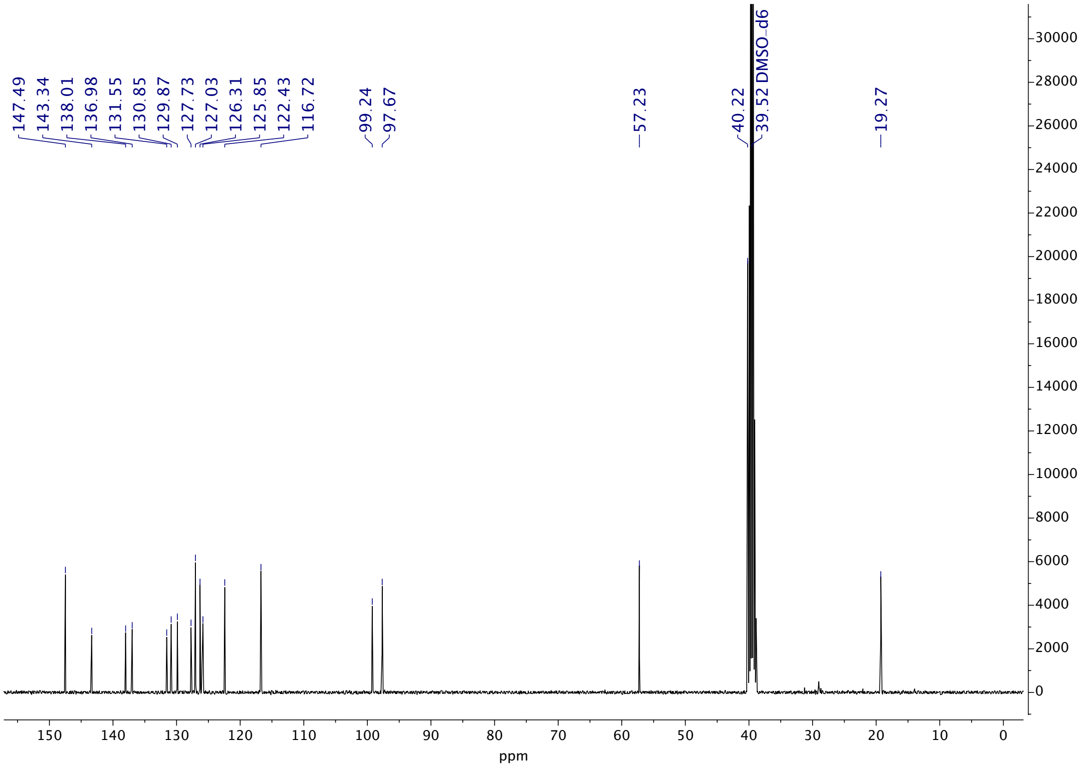
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2c)**



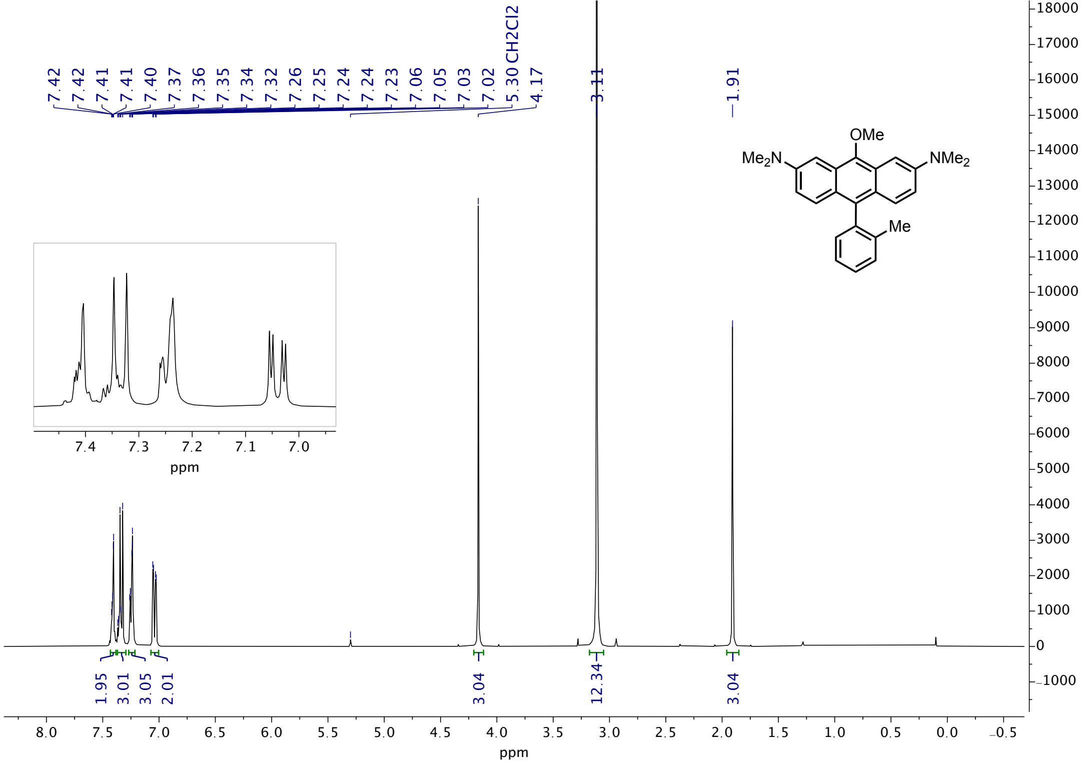


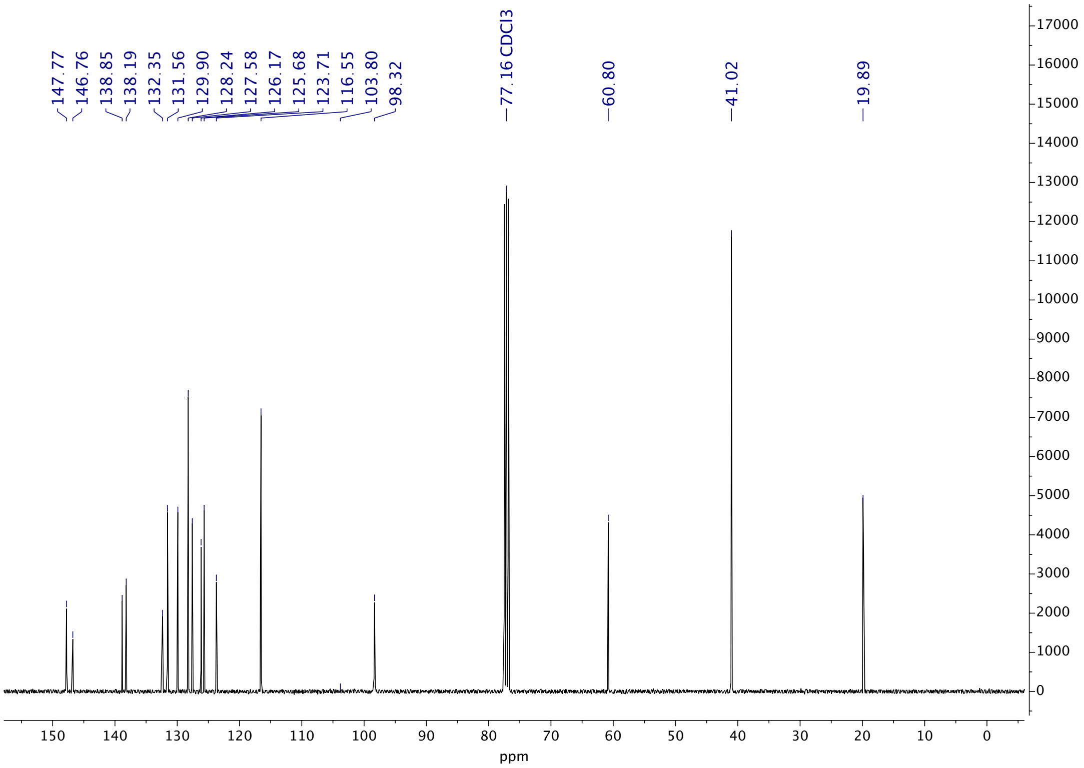
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **9-(methoxymethoxy)-N2,N2,N7,N7-tetramethyl-10-(o-tolyl)anthracene-2,7-diamine (3a)**



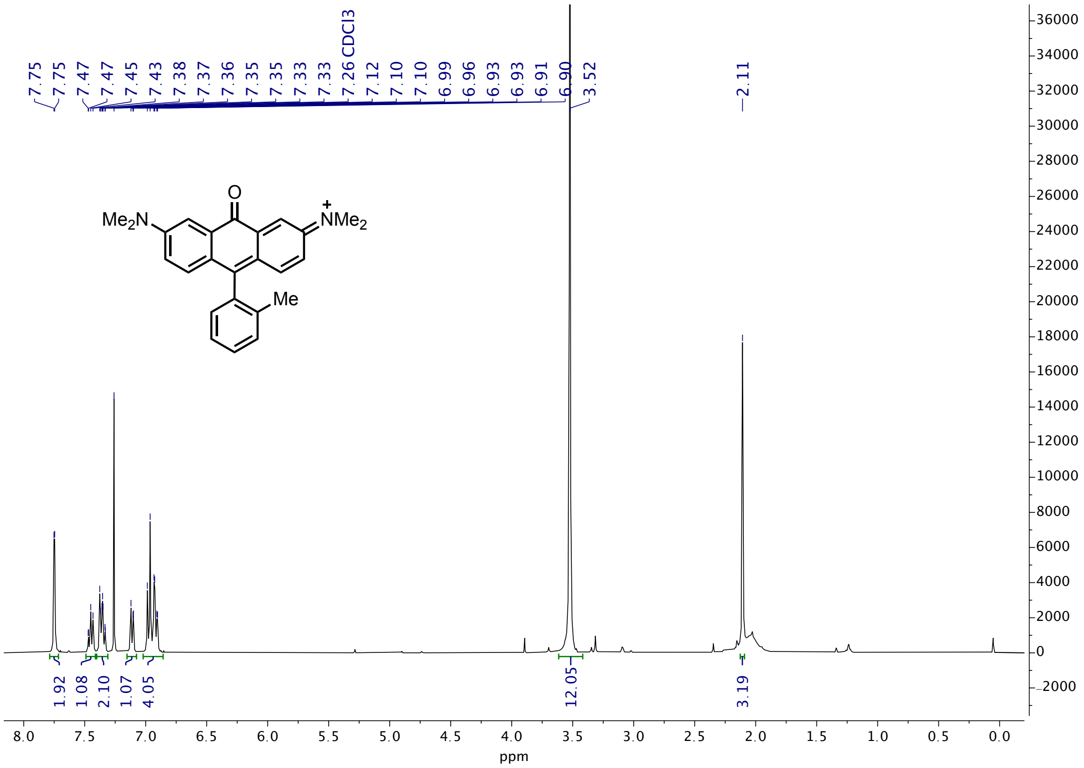


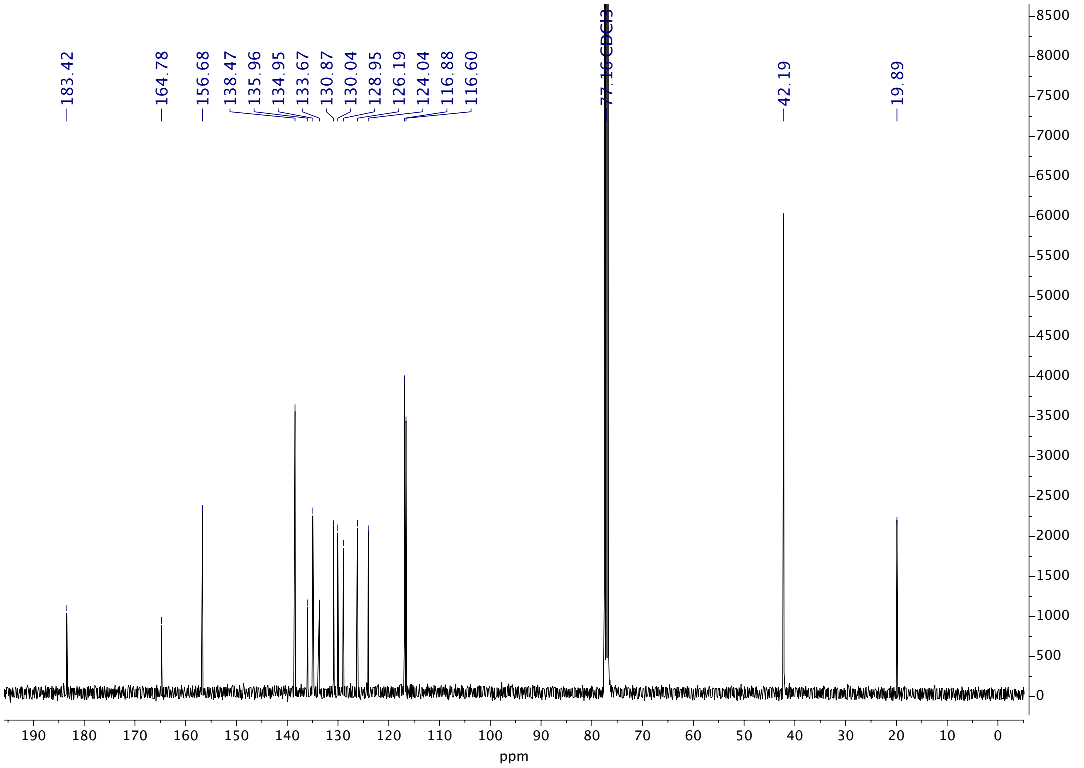
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **9-methoxy-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetramethyl-10-(*o*-tolyl)anthracene-2,7-diamine (3b)**



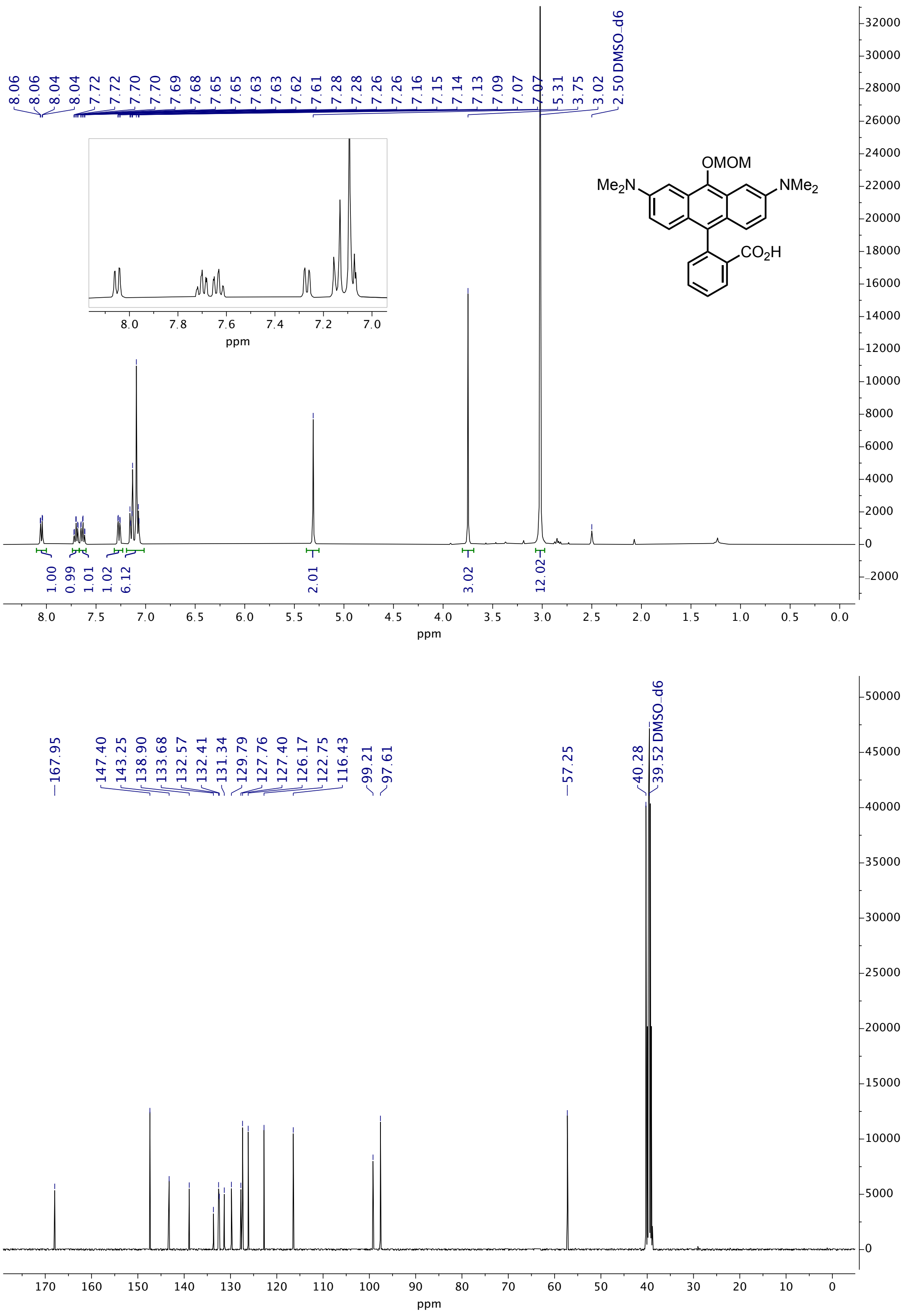


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of ***N*-(7-(dimethylamino)-9-oxo-10-(*o*-tolyl)anthracen-2(9*H*)-ylidene)-*N*-methylmethanaminium (KR-1)**

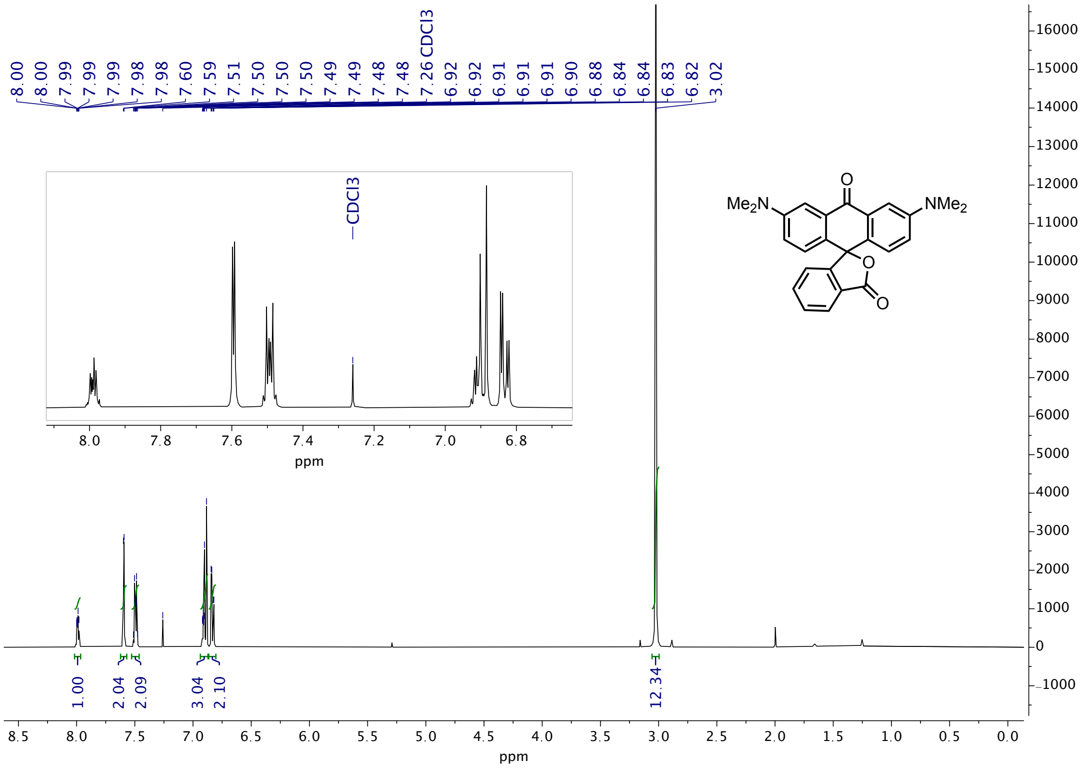


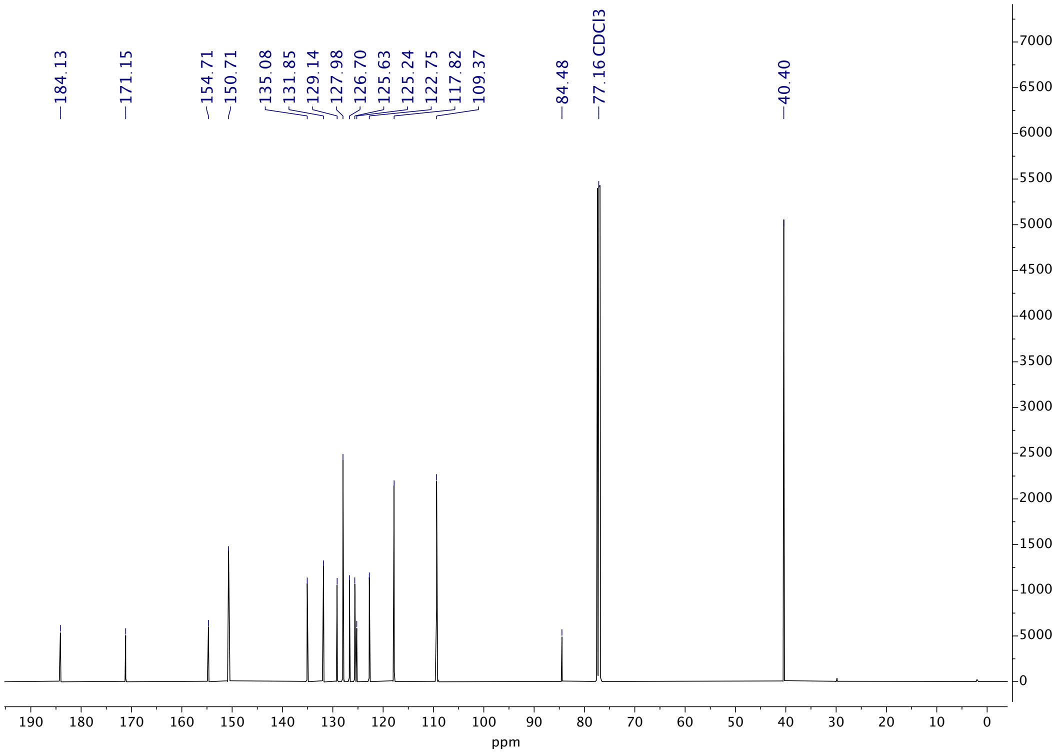


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2-(3,6-bis(dimethylamino)-10-(methoxymethoxy)anthracen-9-yl)benzoic acid (4)**

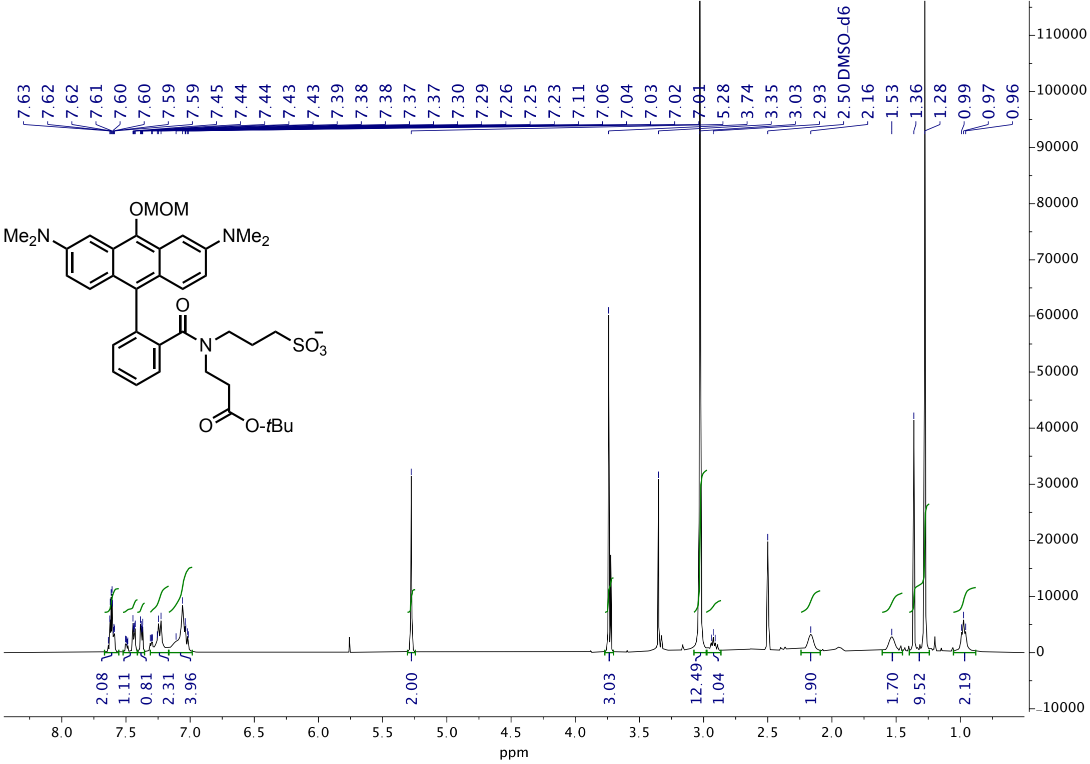


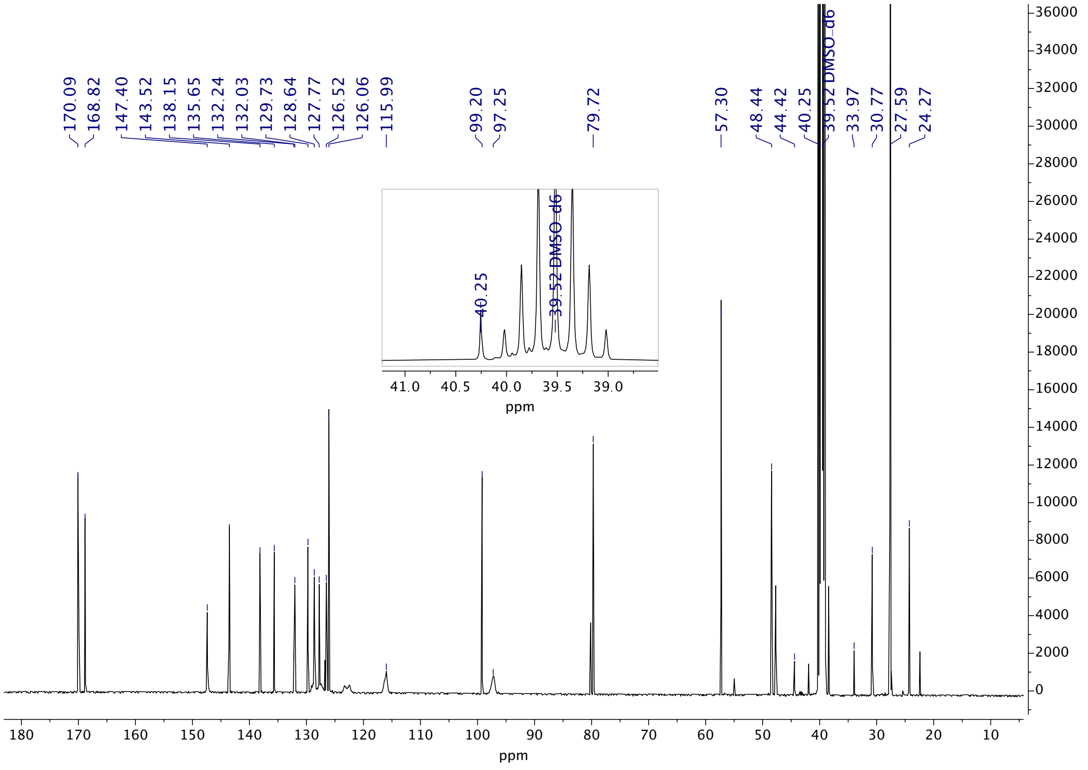
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **3,6-bis(dimethylamino)-3'*H*,10*H*-spiro[anthracene-9,1'-isobenzofuran]-3',10-dione (KR-2)**



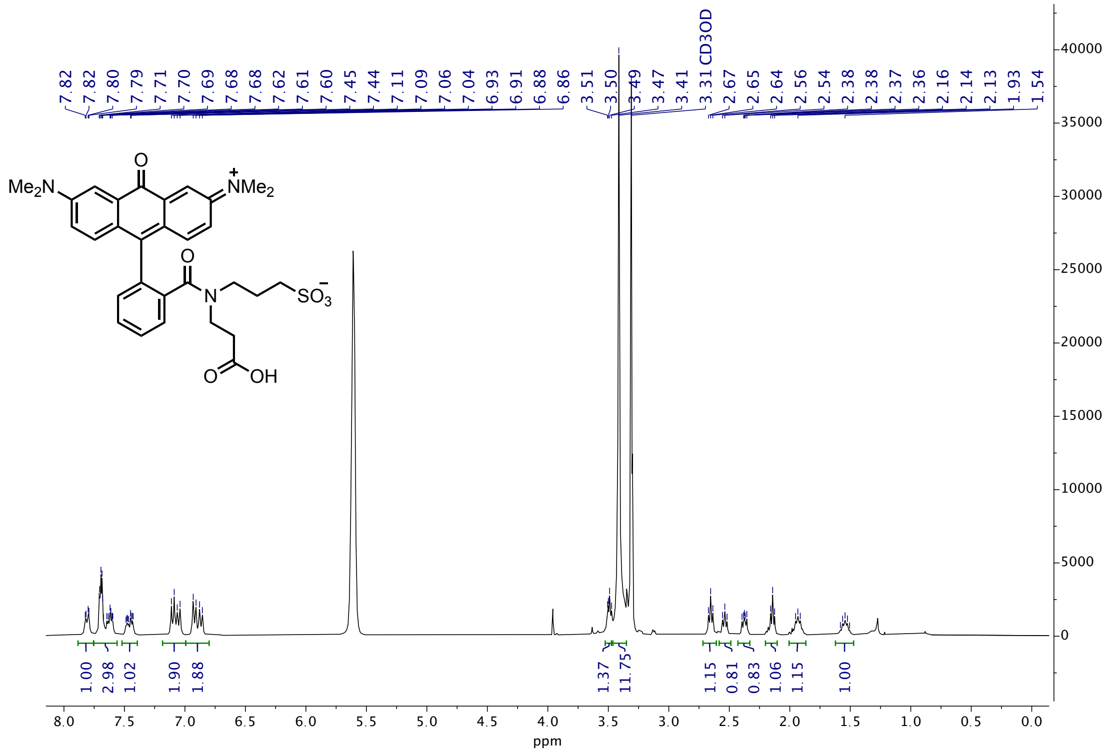


^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **3-(2-(3,6-bis(dimethylamino)-10-(methoxymethoxy)anthracen-9-yl)-*N*-(3-(*tert*-butoxy)-3-oxopropyl)benzamido)propane-1-sulfonate (9)**

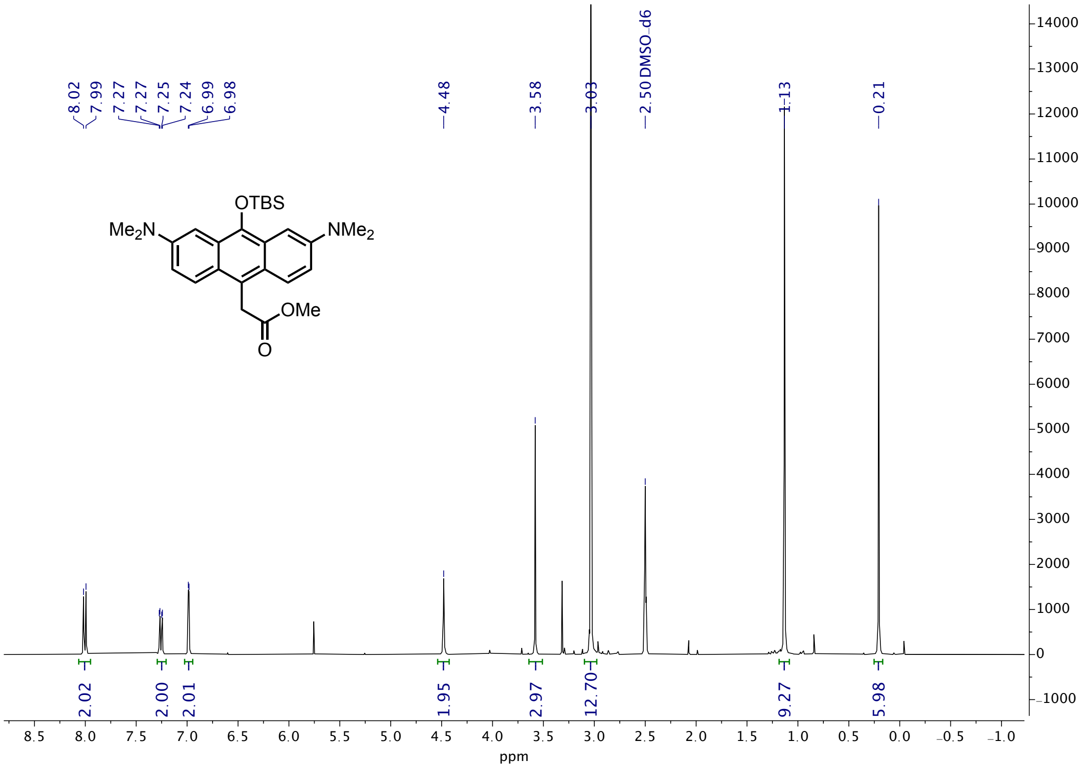


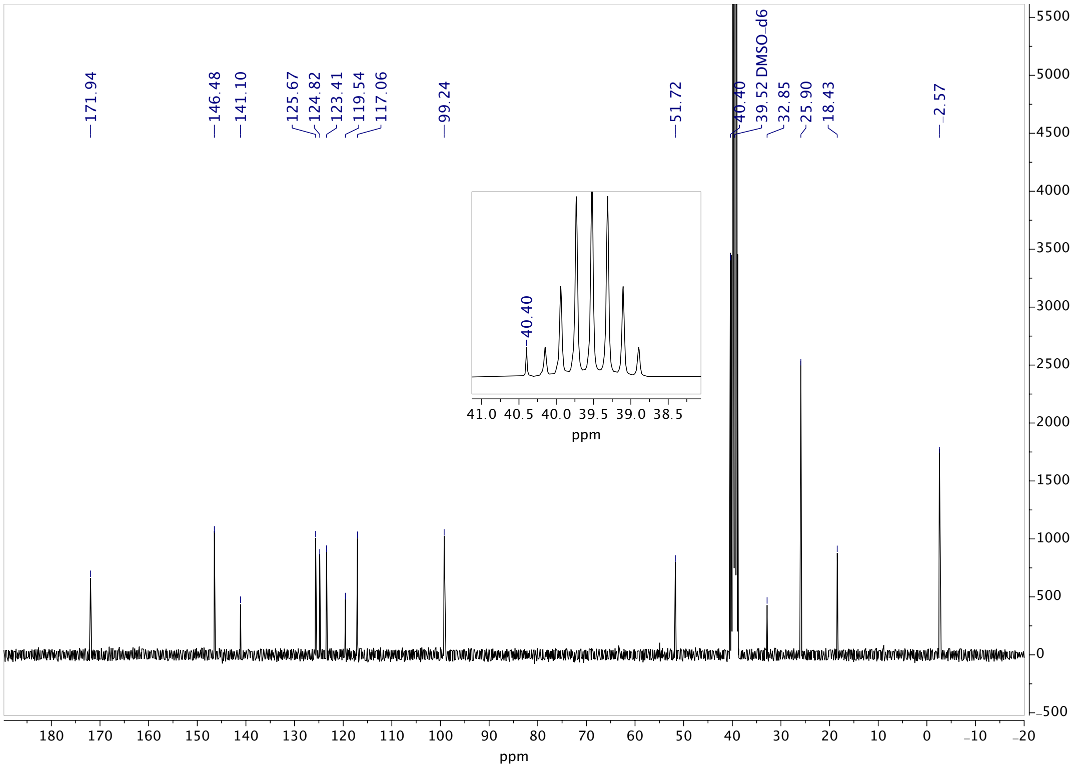


^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3-(*N*-(2-carboxyethyl)-2-(6-(dimethylamino)-3-(dimethyliminio)-10-oxo-3,10-dihydroanthracen-9-yl)benzamido)propane-1-sulfonate (KR-3)**

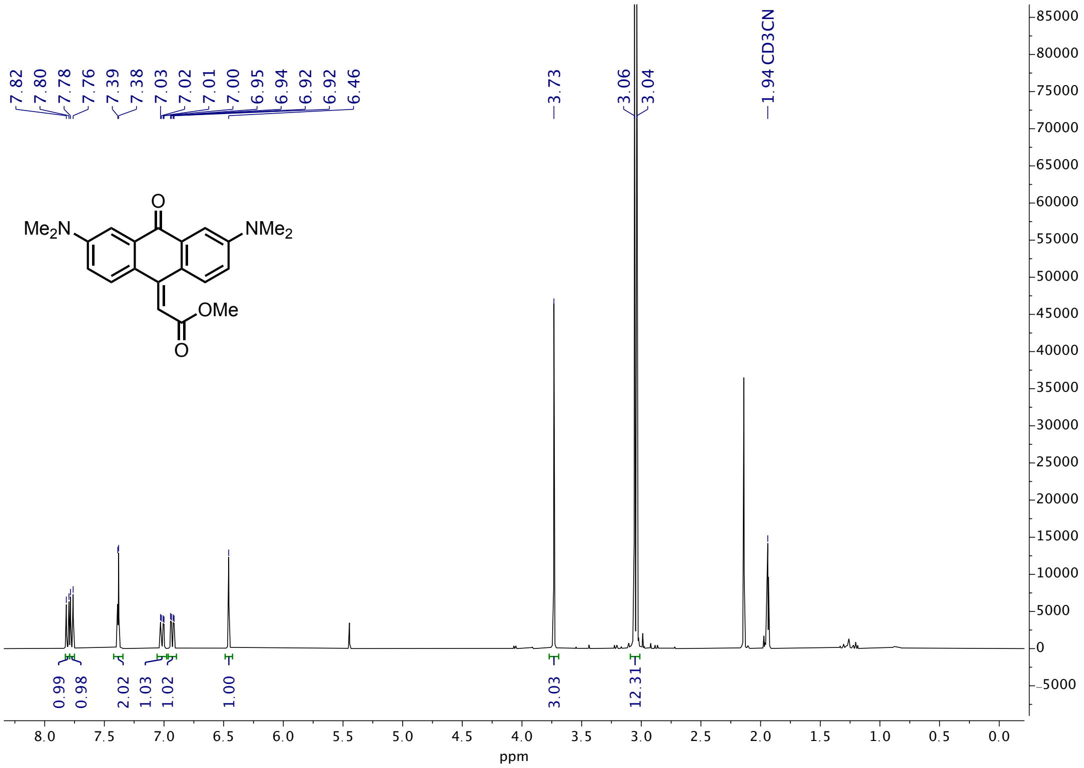


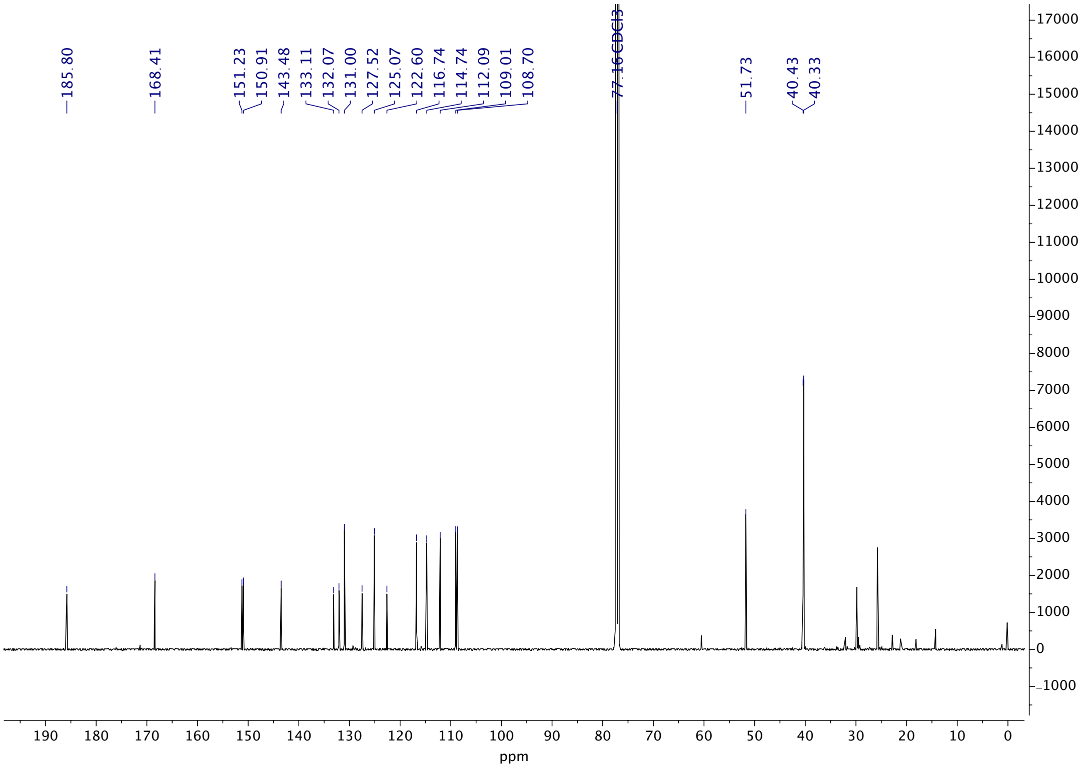
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **methyl 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate (10)**



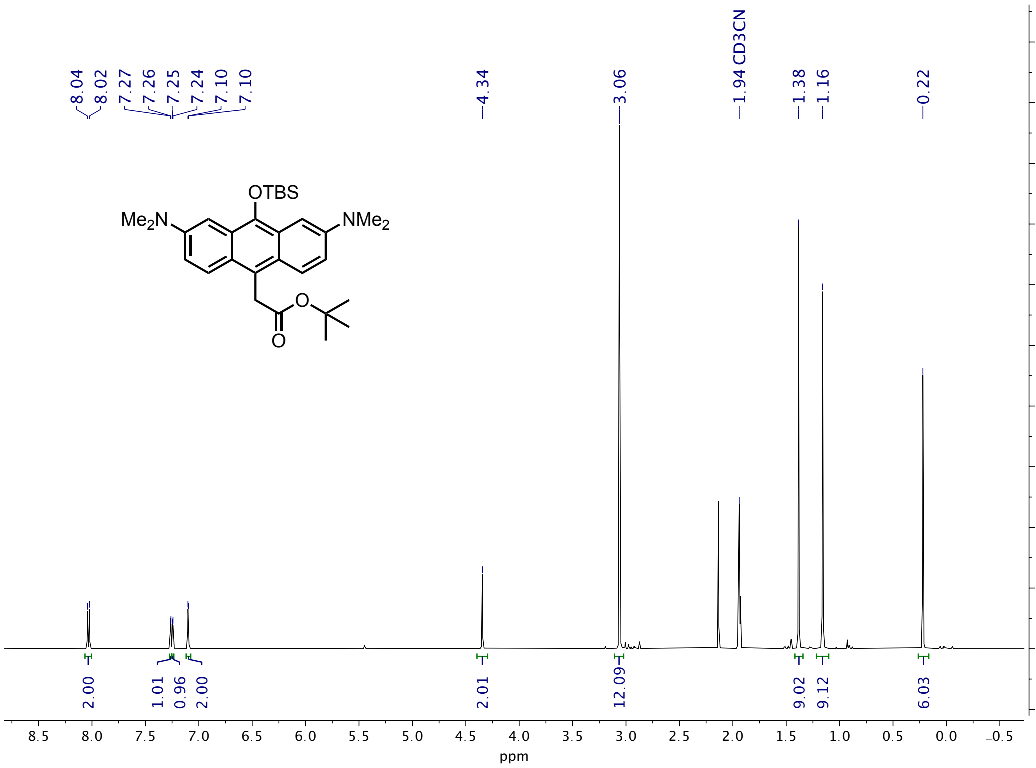


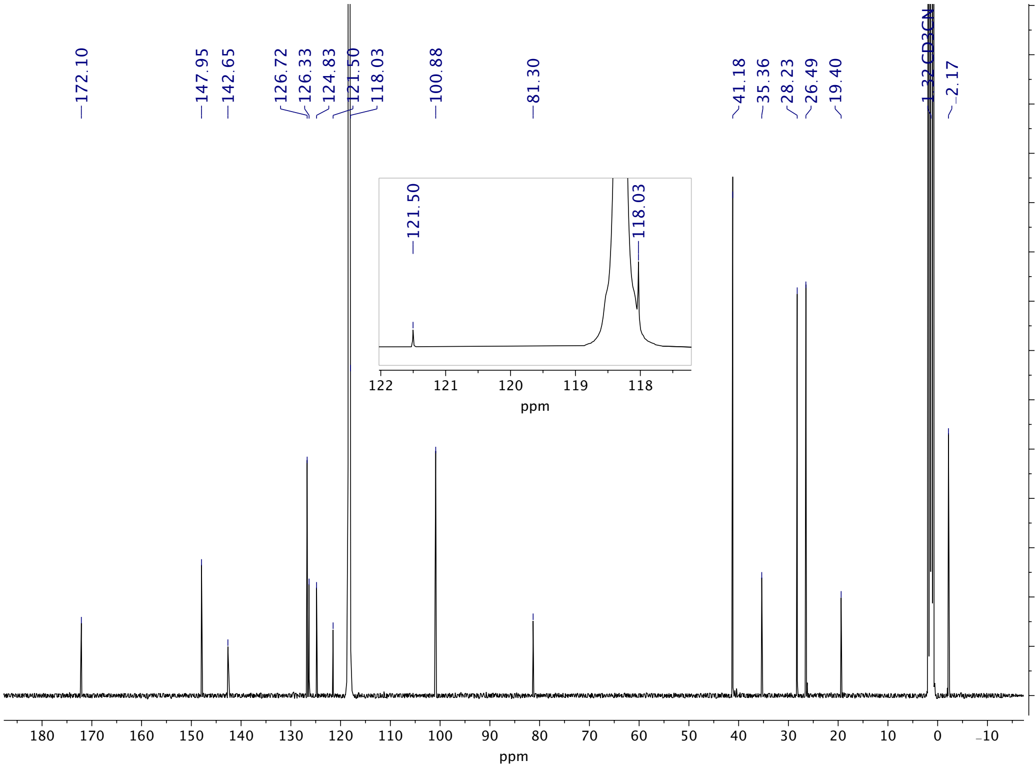
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **methyl 2-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10*H*)-ylidene)acetate (11)**



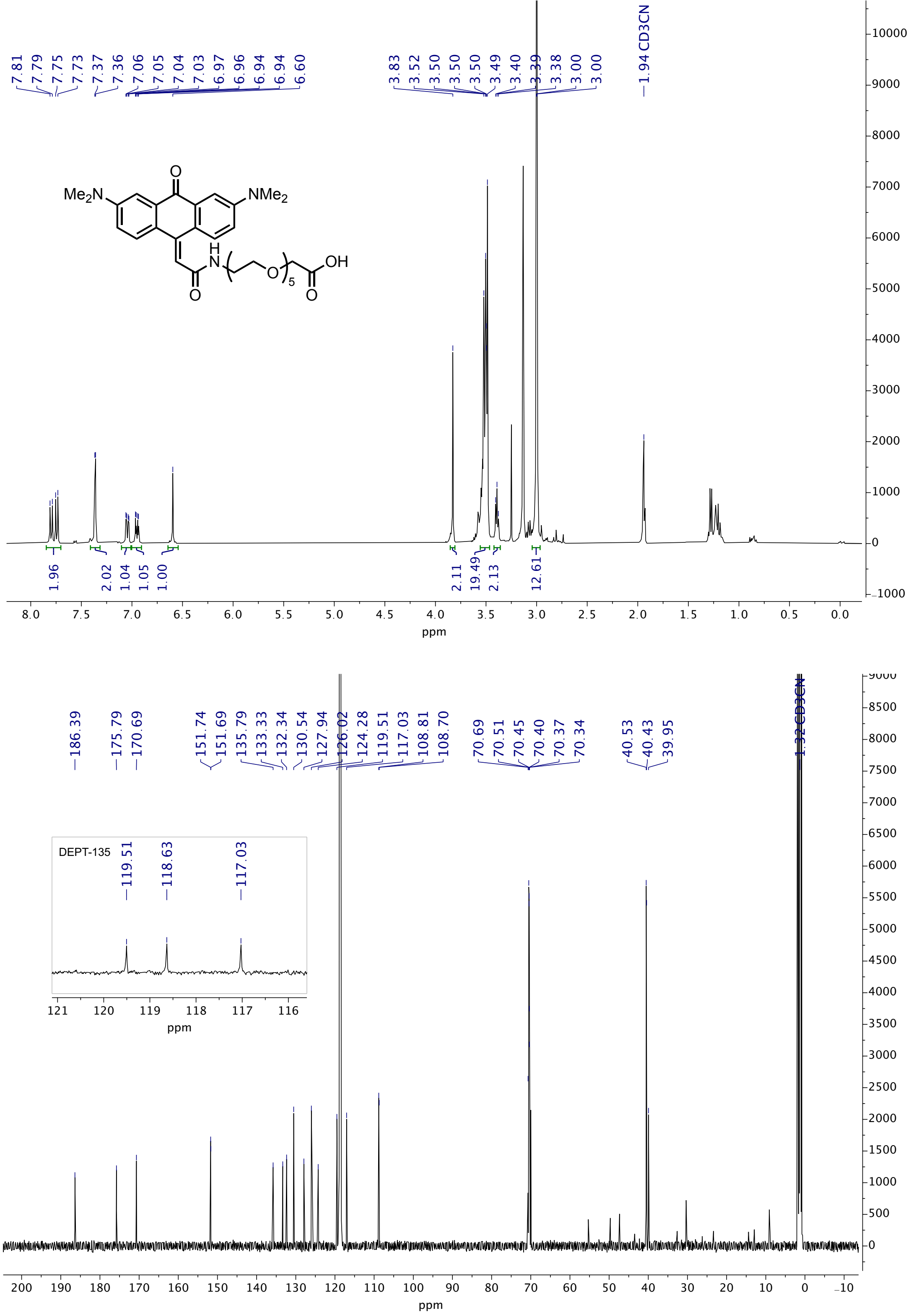


^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of ***tert*-butyl 2-(10-((*tert*-butyldimethylsilyl)oxy)-3,6-bis(dimethylamino)anthracen-9-yl)acetate (5)**

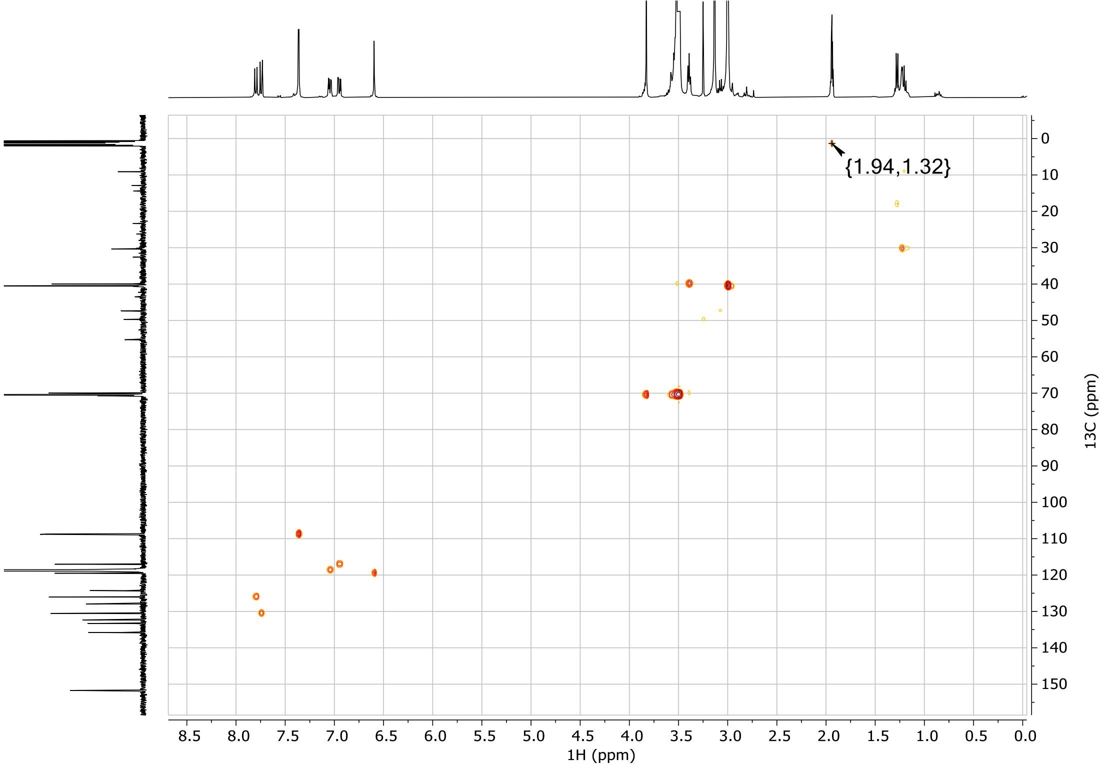




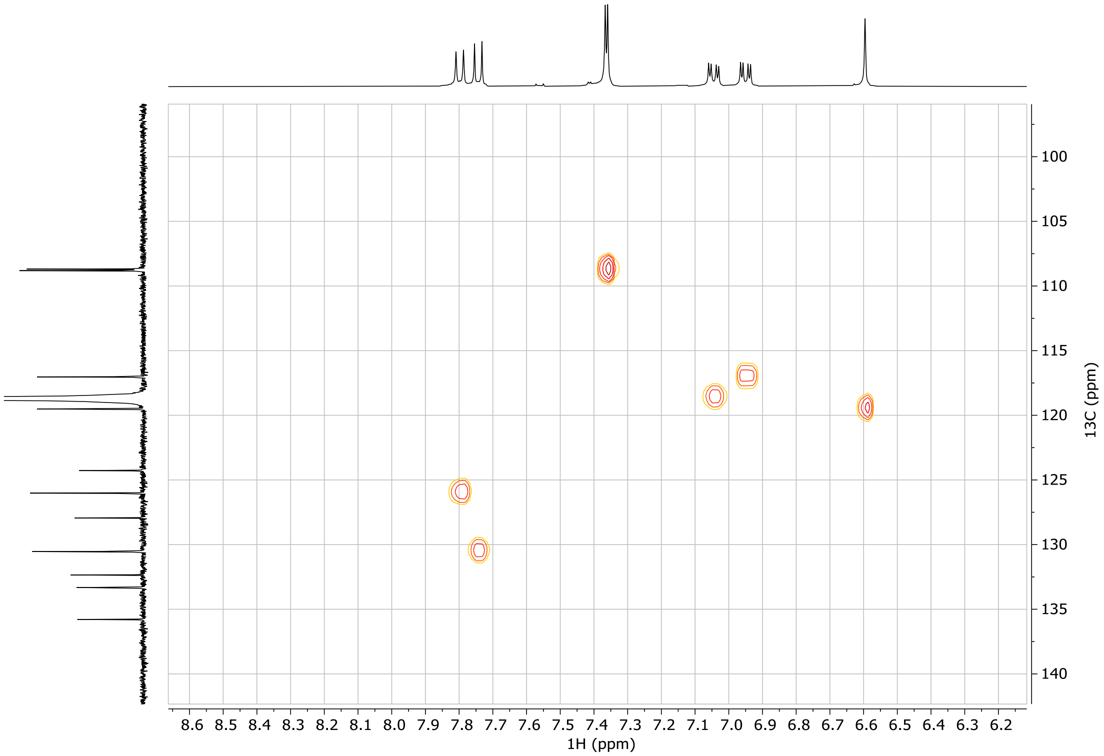
^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **1-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10*H*)-ylidene)-2-oxo-6,9,12,15,18-pentaoxa-3-azaicosan-20-oic acid (KR-4)**



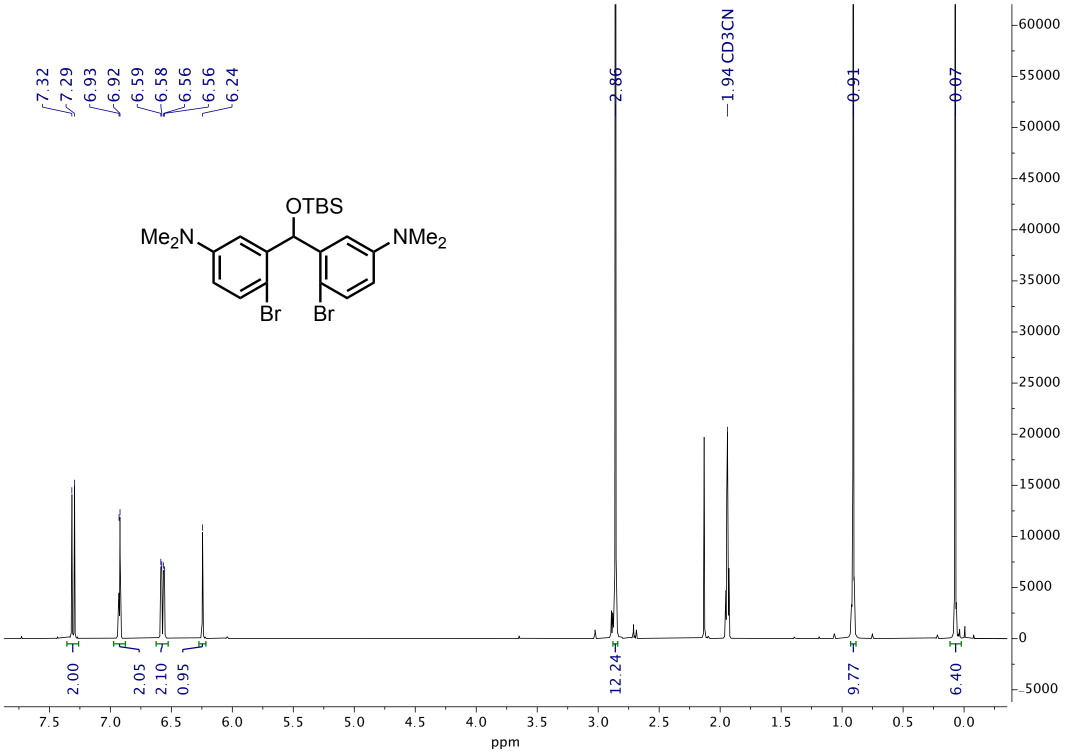
HSQC spectra of **1-(3,6-bis(dimethylamino)-10-oxoanthracen-9(10*H*)-ylidene)-2-oxo-6,9,12,15,18-pentaoxa-3-azaicosan-20-oic acid (KR-4)**



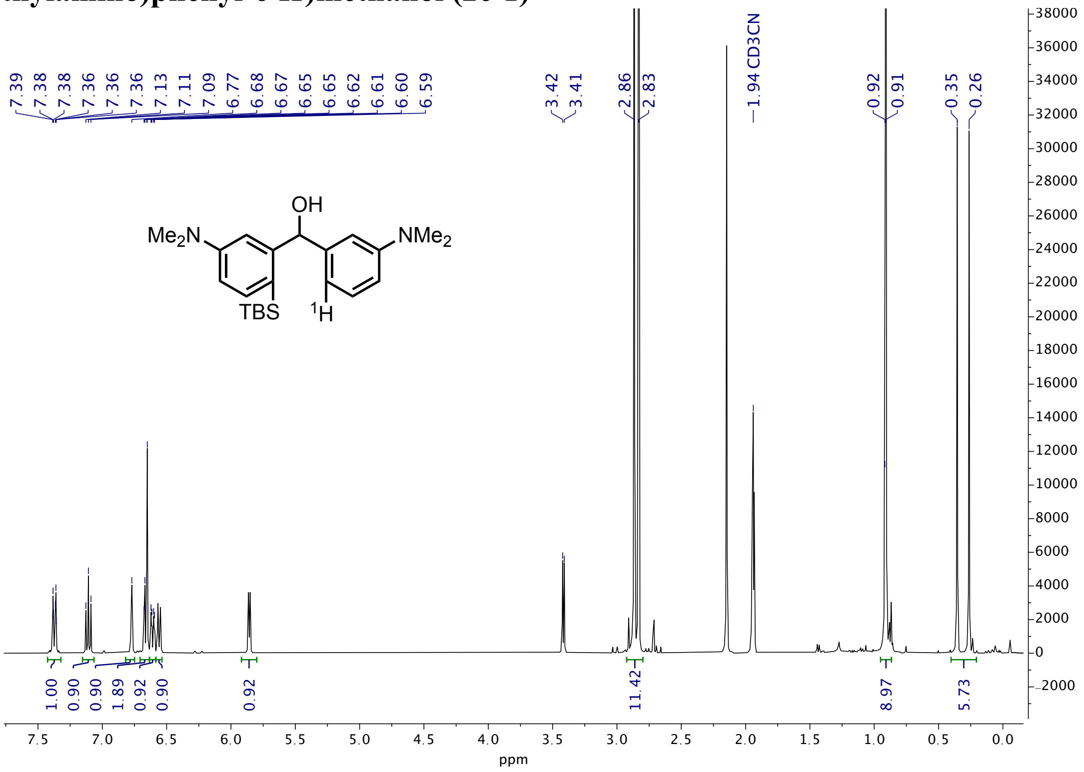
HSQC - Zoomed area of interest for **KR-4**



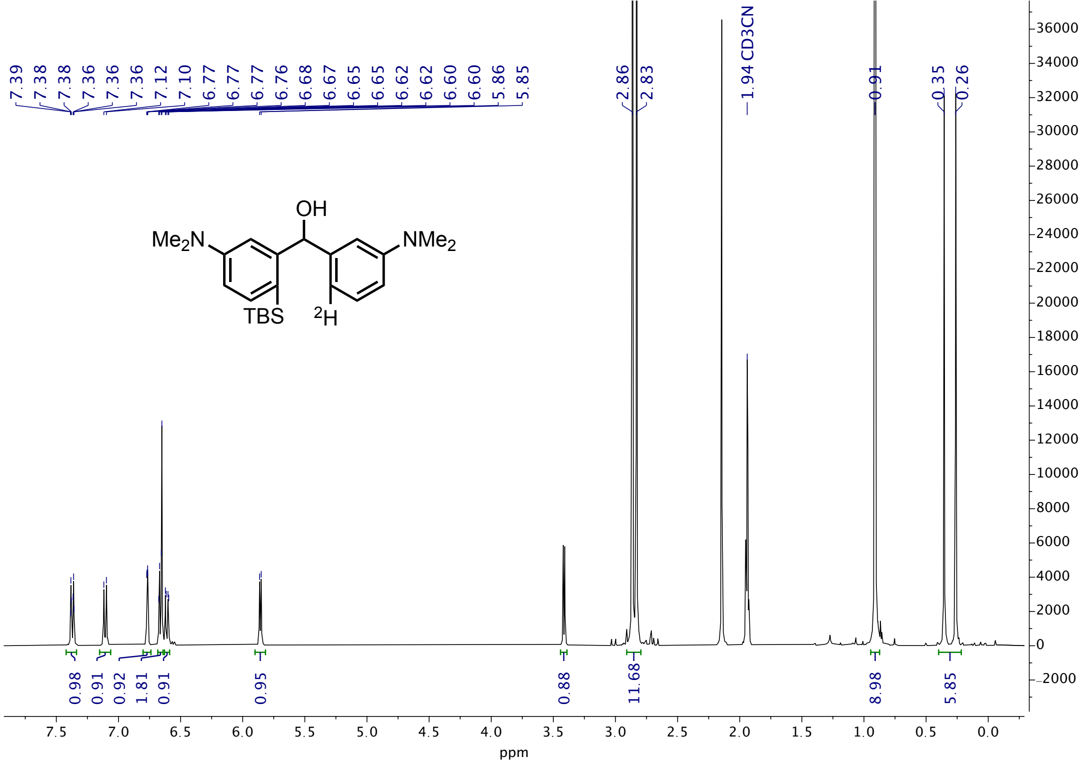
^{1}H (400 MHz) NMR spectra of **3,3'-(((*tert*-butyldimethylsilyl)oxy)methylene)bis(4-bromo-*N*,*N*-dimethylaniline) (2c)**



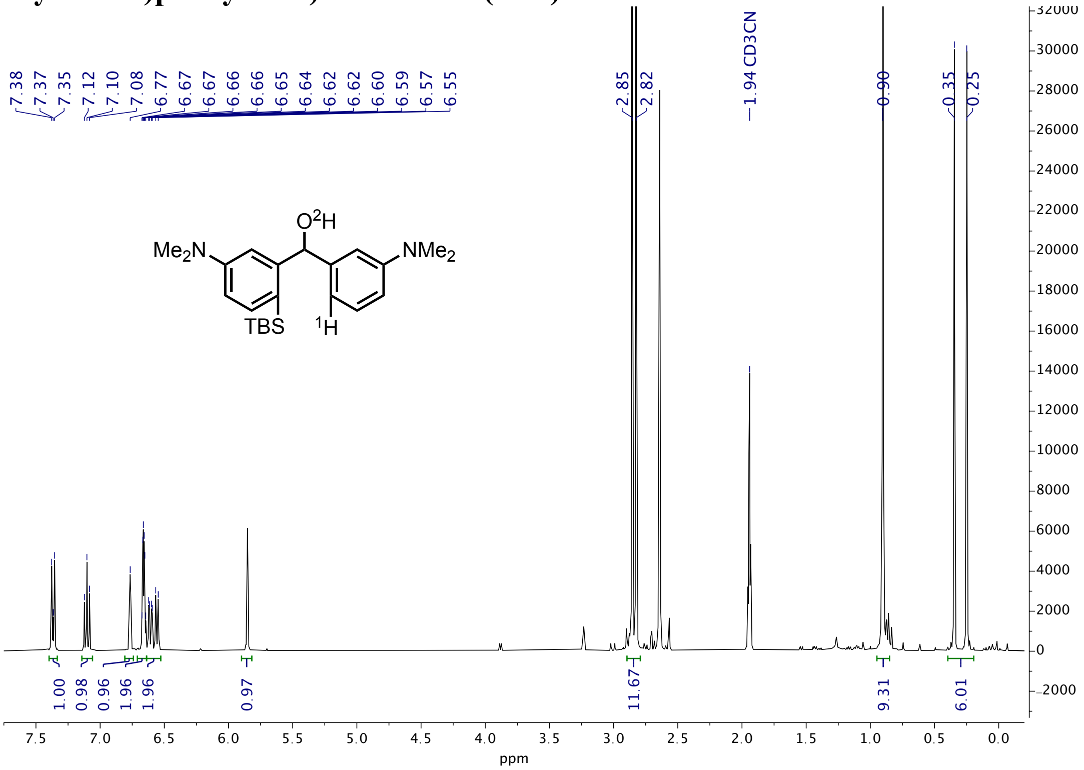
^{1}H (400 MHz) NMR spectra of **(2-(*tert*-butyldimethylsilyl)-5-(dimethylamino)phenyl)(3-(dimethylamino)phenyl-6-*H*)methanol (2c-1)**



^{1}H (400 MHz) NMR spectra of **(2-(*tert*-butyldimethylsilyl)-5-(dimethylamino)phenyl)(3-(dimethylamino)phenyl-6-*d*)methanol (2c-2)**



^{1}H (400 MHz) NMR spectra of **(2-(*tert*-butyldimethylsilyl)-5-(dimethylamino)phenyl)(3-(dimethylamino)phenyl-6-*H*)methanol-*d* (2c-3)**



Section S7: Computational Chemistry

Quantum chemistry calculations were performed using a local version of the GAMESS package(7, 8) where cc-pVTZ basis sets (spherical harmonics) were used throughout(9, 10). Molecular orbitals were illustrated with MacMolPlt(11).

Density functional theory (DFT)(12) utilizing the B3LYP functional(13-15) was used to optimize ground state (S0) geometries. The time-dependent density functional theory (TDDFT) method(16-18) was used to compute vertical excitation, or absorbance, energies (S0 → S1*) at ground state (S0) optimized geometries, as well as deexcitation, or emission, energies (S1 → S0*) at singlet excited state optimized geometries (S1)(19) Ground state (S0) DFT and excited state (S1) TDDFT computations used the Euler-MacLaurin radial(20) and Lebedev angular(21) grids with respective dimensions (96, 302) and (48, 110).

The occupation restricted multiple active space (ORMAS)(22, 23) method with second-order perturbation theory correction (ORMAS-PT2)(24) was also used to compute vertical excitation (absorbance) energies and deexcitation (emission) energies. ORMAS-PT2 calculations were performed at B3LYP ground state (S0; vertical excitation energy) and TDDFT-B3LYP excited state (S1; deexcitation energy) optimized geometries. ORMAS active spaces consisted of all valence π electrons and orbitals partitioned into three groups as follows:

1. All valence π bonding/lone-pair orbitals not including HOMO-like orbital (numbering N) with allowed total minimum & maximum occupation of (2N-2) & 2N, i.e., single & double excitations are allowed from this first group of N orbitals.
2. HOMO-like orbital and LUMO-like orbital with total minimum & maximum occupation of 0 and 4, i.e., single & double electron excitations are allowed into and out of this second group of two orbitals.
3. All remaining valence π antibonding orbitals with total minimum & maximum occupation of 0 and 2, i.e., single & double electron excitations are allowed into this third group.

For example, for R = NH and O the $DET/$ORMAS GAMESS input specifications are:

```
$det   ncore=62 nels=18 nact=16 nstate=3 wstate(1)=1,1 $end
$ormas nspace=3 mstart(1)=63,71,73 mine(1)=14,0,0 maxe(1)=16,4,2 $end
```

The numbers of orbitals in each group and associated occupancy minima/maxima are given in **Table S3** below:

R-group	No. orbitals in group 1 (min/max e^-)	No. of orbitals in group 2 (min/max e^-)	No. orbitals in group 3 (min/max e^-)
NH,O	8 (14/16)	2 (0/4)	6 (0/2)
CMe_2, $SiMe_2$, SO_2, POOEt	7 (12/14)	2 (0/4)	6 (0/2)
C=O	8 (14/16)	2 (0/4)	7 (0/2)

The ORMAS ground state (S0) and singlet excited state (S1) wavefunctions were simultaneously optimized (for orbitals and configuration interaction coefficients) by minimizing the average of the two energies. Final improved ORMAS-PT2 energies for each state (S0 and S1) were then computed by modeling all single and double valence electron excitations out of the individual S0 and S1 ORMAS wavefunctions using second-order perturbation theory (1s orbitals were kept core).

The polarizable continuum model (PCM)(25-27) approach was used to model water solvent effects for the DFT(28), TDDFT(29), ORMAS(26), and ORMAS-PT2 methods. All calculations used a high density of tesserae (NTSALL = 960 in $TESCAV).

Mulliken electron population analysis(30) was used to analyze the B3LYP-PCM highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Specifically, for each orbital we determined 1) $C{-}C_{10'}$ bond orders (see Figure 1A and Table SZ), and 2) the total electron populations on the R-groups that were then multiplied by the sign of the $C{-}C_{10'}$ bond order, i.e., the R-group electron populations were penalized to be negative if they introduced a node between ring-bound R-group atom and neighboring carbon atoms.

Table S4: Computed absorbance and emission energies (in eV with oscillator strengths in parentheses) vs. experimentally measured. Calculations included water solvent effects via the Polarizable Continuum Model (PCM). Mean unsigned errors (MUEs) for each method shown at bottom. See Methods for full details.

R-Group	Computed absorbance		Experimental absorbance	Computed emission		Experimental emission
	TDDFT-B3LYP	ORPT2		TDDFT-B3LYP	ORPT2	
N(H)	2.791 (0.90)	2.588	2.515[x]	2.517 (1.22)	2.465	2.348
O	2.666 (1.06)	2.386	2.267[x]	2.366 (1.32)	2.288	2.206
C(Me)$_2$	2.498 (1.14)	2.060	2.050[x]	2.204 (1.39)	1.996	1.978
Si(Me)$_2$	2.401 (1.14)	1.972	1.956[x]	2.100 (1.39)	1.903	1.914
S(O)$_2$	2.247 (0.95)	1.846	1.771[x]	1.924 (1.14)	1.746	1.717
P(OOEt)	2.223 (0.92)	1.824	1.764[x]	1.863 (1.03)	1.684	1.689
C(O)	1.727 (0.41)	1.547	1.450[a]	1.405 (0.48)	1.373	1.361
MUE	0.397	0.065		0.167	0.039	

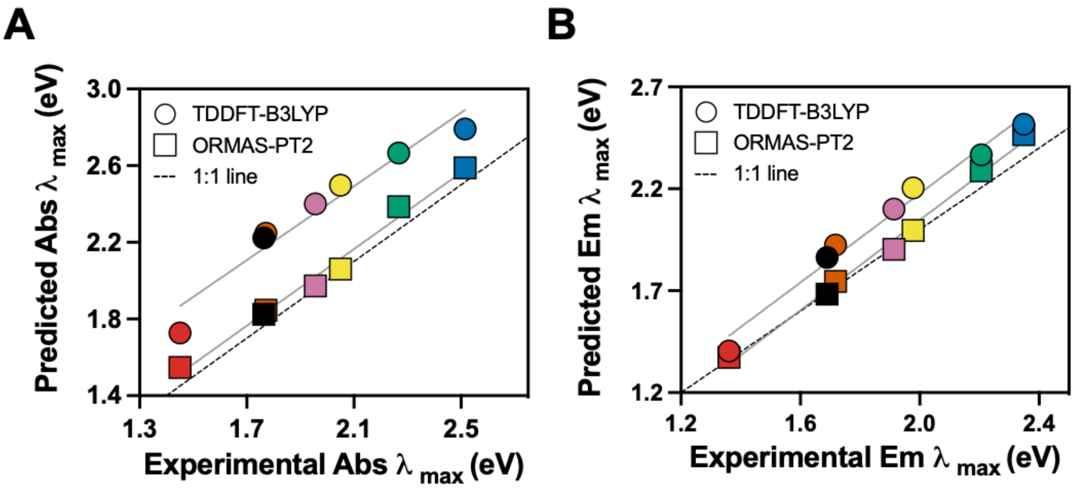


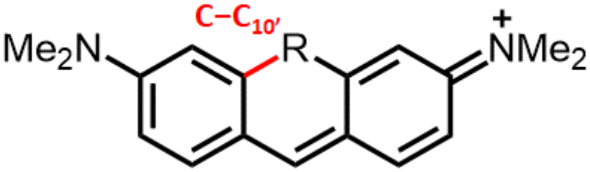
Figure S4. Experimental vs. predicted absorbance (A) and emission (B) energies (eV) using TDDFT-B3LYP-PCM(H_2O) and ORMAS-PT2-PCM(H_2O) methods. Mean unsigned errors (MUEs) in absorbance/emission predictions are 0.397/0.167 and 0.065/0.039 for TDDFT-B3LYP and ORMAS-PT2, respectively.

Table S5: Experimental and computed (TDDFT-B3LYP-PCM) absorbance energies (eV), C−C10’ bond orders, and signed R-group electron populations in the LUMOs. Properties determined at ground state optimized geometries. Calculations included water solvent effects via the Polarizable Continuum Model (PCM). See Methods for full details. Correlation coefficients (R^2) between experimental (left) and computed (right) absorbances vs. LUMO C−C10’ bond orders and signed R-group electron populations are shown at bottom.

R-group	Experimental absorbance	Computed absorbance	LUMO C−C10’ bond orders	LUMO R-group e^- population
N(H)	2.515	2.791	−0.049	−0.065[a]
O	2.267	2.666	−0.039	−0.042[a]
C(Me)$_2$	2.050	2.498	−0.001	−0.026[a]
Si(Me)$_2$	1.956	2.401	0.002	0.035
S(O)$_2$	1.771	2.247	0.024	0.045
P(OOEt)	1.764	2.223	0.021	0.047
C(O)	1.450	1.727	0.054	0.181
R^2			0.94 / 0.87	0.88 / 0.97

[a] These Mulliken populations are penalized to be negative since each R-group introduces a node to the LUMO that passes between the ring-bound R-group atom (not in parentheses) and neighboring carbon atoms, i.e., in these systems there is a negative C−$C_{10'}$ bond order in the LUMO. For the other molecules the C−$C_{10'}$ bond order is positive. See **Table S6** for further details.

Table S6: Examinations of HOMOs and LUMOs in the C10’ substituted series via Mulliken electronic population analysis. For each orbital, the C−C10’ bond order is provided along with the total electron population on the R group. Analyses were performed at ground state optimized geometries.

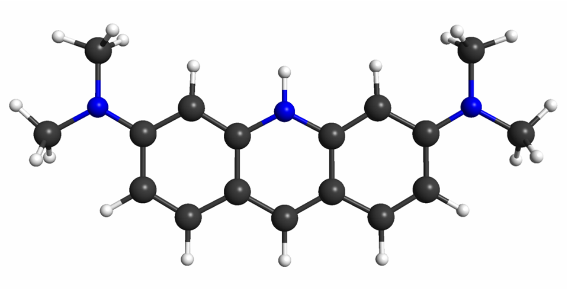


R-group	HOMO		LUMO	
	C−C10’ bond order	R e^- population	C−C10’ bond order	R e^- population
N(H)	0.000	0.000	−0.049	0.065
O	0.000	0.000	−0.039	0.042
$C(Me)_2$	0.000	0.001	−0.001	0.026
$Si(Me)_2$	0.000	0.001	0.022	0.035
$S(O)_2$	0.000	0.001	0.024	0.045
P(OOEt)	0.000	0.000	0.021	0.047
C(O)	0.000	0.000	0.054	0.181

Section S8: Raw Computational Chemistry Data

I. Energies (S0 & S1* in hartree), oscillator strengths (S0 → S1*), HOMO and LUMO energies (hartree), excitation/de-excitation amplitudes, and S0 optimized structures (Å)

a. R1 (NH)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -823.753609
E(S1) = -823.651047*
Oscillator strength = 0.8956
E(HOMO) = -0.2084; E(LUMO) = -0.0954

```
             EXCITATION  DE-EXCITATION
 OCC    VIR  AMPLITUDE      AMPLITUDE
  I      A    X(I->A)        Y(A->I)
 ---    ---  --------       --------
 68      72  -0.042187     -0.006089
 71      72  -0.987340      0.086689
 69      73   0.058654      0.025205
 70      73  -0.149761     -0.038580
 69      74  -0.043578     -0.007822
```

```
 ATOM   CHARGE       X              Y              Z
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C          6.0  -1.2226311806   0.6677218834  -0.0449552379
C          6.0  -2.2602567210  -0.3138660898  -0.0065562156
C          6.0  -1.9160583604  -1.6623065593  -0.0310673043
C          6.0  -0.5895440976  -2.0777994523  -0.0884399778
C          6.0   0.4451749848  -1.0932229219  -0.1241529030
N          7.0   0.0708497181   0.2236533337  -0.1041878502
C          6.0  -2.8431158499   2.4716235052   0.0534042466
C          6.0  -3.8879748719   1.4842292919   0.0885132213
C          6.0  -3.5984866918   0.1557159806   0.0588000280
C          6.0  -1.5108919399   2.0262393918  -0.0196271326
H          1.0  -4.9183632801   1.7962451348   0.1372421984
H          1.0  -4.3991506569  -0.5717731078   0.0852000967
H          1.0  -0.6939709348   2.7299110812  -0.0487530416
N          7.0  -3.1461413002   3.7896397426   0.0907972073
C          6.0  -2.0865431514   4.7892171070   0.0221113938
```
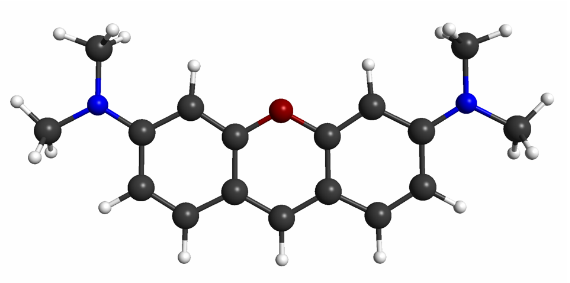

C	6.0	-4.5320767499	4.2425551450	0.1815757554
H	1.0	-2.5302397588	5.7784039093	0.0572403549
H	1.0	-1.5172808350	4.7010862109	-0.9063260075
H	1.0	-4.5411875231	5.3247165599	0.2568657121
H	1.0	-5.1077180282	3.9572341900	-0.7016281706
H	1.0	-1.3944086994	4.6934882674	0.8621437480
H	1.0	-5.0246961059	3.8372617767	1.0665588697
H	1.0	-2.7011442403	-2.4083928427	-0.0025864590
C	6.0	-0.1938077300	-3.4413052146	-0.1097146466
C	6.0	1.7849360127	-1.4548510171	-0.1774965618
C	6.0	1.1158649676	-3.8025630614	-0.1631911177
C	6.0	2.1568978413	-2.8114980010	-0.2017775402
N	7.0	3.4550608180	-3.1876737532	-0.2585483562
C	6.0	3.8320064862	-4.5982206395	-0.3147623786
C	6.0	4.5110148565	-2.1821756937	-0.2592907958
H	1.0	2.5310759978	-0.6767154968	-0.2038791914
H	1.0	-0.9627426483	-4.2020470302	-0.0792650060
H	1.0	1.3718119483	-4.8494197921	-0.1722586369
H	1.0	4.9072856813	-4.6651270539	-0.4403333001
H	1.0	3.3604990868	-5.1010197246	-1.1602336895
H	1.0	5.4742746497	-2.6804928738	-0.2710962992
H	1.0	4.4608252562	-1.5548855485	0.6336144981
H	1.0	4.4469772502	-1.5368629744	-1.1390060544
H	1.0	3.5612070847	-5.1262034023	0.6023532392
H	1.0	0.8037349552	0.9194231997	-0.1284159547

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) = -822.284283 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.940 / 0.072
E(S1) = -822.189168 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.183 / 0.830*

b. R2 (O)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -843.601869
E(S1) = -843.503894*
Oscillator strength = 1.0637
E(HOMO) = -0.2123; E(LUMO) = -0.1072

```
            EXCITATION  DE-EXCITATION
   OCC    VIR  AMPLITUDE     AMPLITUDE
    I      A    X(I->A)       Y(A->I)
   ---    ---  --------      --------
   68      72    0.037796      0.004803
   71      72    0.996944     -0.111461
   69      73    0.065997      0.028503
   70      73   -0.086145     -0.029931
   71      74   -0.033024     -0.004508
   69      75   -0.032036     -0.005688

  ATOM   CHARGE       X              Y              Z
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C          6.0  -1.2543120786   0.6019886662  -0.0407150587
C          6.0  -2.2996166459  -0.3604024924  -0.0015587917
C          6.0  -1.9677077307  -1.7111897978  -0.0295958563
C          6.0  -0.6376981422  -2.1138261050  -0.0894503835
C          6.0   0.3785562827  -1.1207484173  -0.1221968550
O          8.0   0.0443767480   0.1986608014  -0.1018446185
C          6.0  -2.8205310698   2.4350584267   0.0579192632
C          6.0  -3.8857721896   1.4735837228   0.0982021627
C          6.0  -3.6266960571   0.1375419941   0.0677812265
C          6.0  -1.4908650575   1.9547420499  -0.0168869061
H          1.0  -4.9084645653   1.8088340750   0.1508437686
H          1.0  -4.4429735724  -0.5720258797   0.0968743584
H          1.0  -0.6478566172   2.6251325968  -0.0500200502
N          7.0  -3.0839076551   3.7560248397   0.0905678010
C          6.0  -1.9981005865   4.7295093908   0.0126120473
C          6.0  -4.4587586880   4.2475838233   0.1727649378
H          1.0  -2.4171677927   5.7288521952   0.0522197851
H          1.0  -1.4419808079   4.6256204490  -0.9213360050
H          1.0  -4.4397453274   5.3302136449   0.2332311007
H          1.0  -5.0367431958   3.9632448922  -0.7086717364
H          1.0  -1.3033764978   4.6147461893   0.8469909511
H          1.0  -4.9618072205   3.8652494350   1.0617491144
H          1.0  -2.7520870330  -2.4575543639  -0.0021650819
C          6.0  -0.2135802718  -3.4676000873  -0.1158475113
C          6.0   1.7156490169  -1.4309408313  -0.1747839187
C          6.0   1.1052402344  -3.7996510618  -0.1700243631
C          6.0   2.1219061857  -2.7866803957  -0.2031614103
N          7.0   3.4256526459  -3.1229939878  -0.2586497345
C          6.0   3.8400555974  -4.5241565133  -0.3153094490
C          6.0   4.4584007538  -2.0904537320  -0.2519936081
H          1.0   2.4309264791  -0.6255045667  -0.1977520688
H          1.0  -0.9661360652  -4.2444825592  -0.0886430178
H          1.0   1.3841599022  -4.8403382007  -0.1832668828
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 H          1.0   4.9168761730  -4.5639553655  -0.4372824952
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 H          1.0   4.3790110355  -1.4441278809  -1.1288107189
 H          1.0   3.5778518533  -5.0564326569   0.6012735192
```
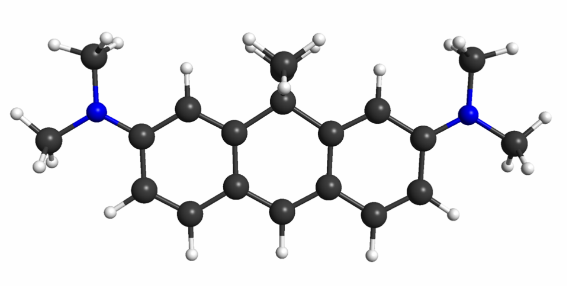

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) =   -842.115491 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.945 / 0.068
E(S1) = -842.027793 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.023 / 0.988*

c. R3 (CMe_2)



TDDFT-B3LYP-PCM(H_2O)

E(S0) =   -886.268540
E(S1) = -886.176729*
Oscillator strength = 1.1385
E(HOMO) = -0.2070; E(LUMO) = -0.1104

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    79     80    1.002508      -0.134081
    76     81    0.035302       0.019047
    79     81   -0.055473      -0.008565
    77     82   -0.049856      -0.024708
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 C          6.0  -1.8065520253  -1.5592849299   0.0743685659
 C          6.0  -0.4889366835  -1.9986045685  -0.0432123114
 C          6.0   0.5738408138  -1.0611756156  -0.1981089499
 C          6.0   0.2985324569   0.4456010379  -0.2491399530
 C          6.0  -2.9441095056   2.5048835651   0.0062272515
 C          6.0  -3.9204822941   1.4750465993   0.1532425941
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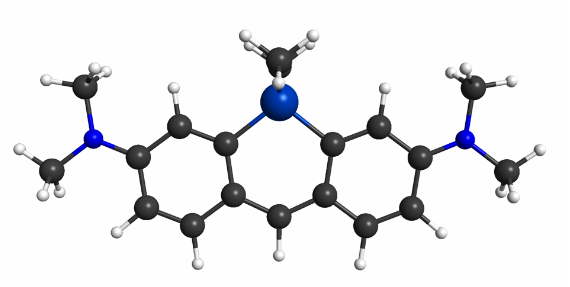
C	6.0	-3.5347478180	0.1677837592	0.1729581040
C	6.0	-1.5809721817	2.1165183842	-0.1240414266
H	1.0	-4.9649639667	1.7232828512	0.2486453804
H	1.0	-4.2806156373	-0.6086378280	0.2858980411
H	1.0	-0.8380708498	2.8879977900	-0.2390160583
N	7.0	-3.3012650497	3.8050474800	-0.0066116748
C	6.0	-2.2983755020	4.8572021671	-0.1600998549
C	6.0	-4.7003279119	4.1969727197	0.1552771003
H	1.0	-2.7972501444	5.8199267933	-0.1604053389
H	1.0	-1.7563690540	4.7523338559	-1.1014070042
H	1.0	-4.7620424975	5.2795083674	0.1552957885
H	1.0	-5.3166612772	3.8172193935	-0.6617388975
H	1.0	-1.5808611235	4.8419145920	0.6624911984
H	1.0	-5.1045515368	3.8294280194	1.0997009607
H	1.0	-2.5866248116	-2.3030178772	0.1918493860
C	6.0	-0.1822117957	-3.3841679000	-0.0107611515
C	6.0	1.8607417769	-1.5299840908	-0.3078132007
C	6.0	1.0962927656	-3.8419627749	-0.1243908035
C	6.0	2.1732108114	-2.9190502726	-0.2769205760
N	7.0	3.4458087578	-3.3488793265	-0.3888976909
C	6.0	3.7549995951	-4.7779258412	-0.3999163708
C	6.0	4.5511912325	-2.4000774187	-0.5028813856
H	1.0	2.6676679776	-0.8264377074	-0.4280826639
H	1.0	-0.9944325796	-4.0898847598	0.1091028065
H	1.0	1.2868284340	-4.9023675181	-0.0919474259
H	1.0	4.8188342306	-4.9036872780	-0.5676033325
H	1.0	3.2196878188	-5.2897779924	-1.2008902452
H	1.0	5.4858208656	-2.9495706429	-0.5142293983
H	1.0	4.5683669329	-1.7142059267	0.3452118427
H	1.0	4.4834198147	-1.8180352059	-1.4243461836
H	1.0	3.4976074562	-5.2496505498	0.5506803341
C	6.0	0.8005712542	0.9887804141	-1.6140591336
C	6.0	1.0841368063	1.1280133926	0.9025574706
H	1.0	0.2655339819	0.5185862705	-2.4393259322
H	1.0	0.6492439852	2.0649946936	-1.6770730984
H	1.0	1.8637113378	0.7903199009	-1.7379491462
H	1.0	2.1503943749	0.9295622702	0.8103852679
H	1.0	0.7491704223	0.7595668082	1.8722250189
H	1.0	0.9410384973	2.2069033606	0.8788168302

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) = -884.672184 : ORMAS-PCM natural orbitals 79 / 80 occupations = 1.945 / 0.068
E(S1) = -884.596467 : ORMAS-PCM natural orbitals 79 / 80 occupations = 1.020 / 0.991*

d. R4 (SiMe$_2$)



TDDFT-B3LYP-PCM(H$_2$O)

E(S0) =   -1137.678861
E(S1) = -1137.590633*
Oscillator strength = 1.1388
E(HOMO) = -0.2078; E(LUMO) = -0.1151

```
             EXCITATION  DE-EXCITATION
  OCC    VIR  AMPLITUDE      AMPLITUDE
   I      A    X(I->A)        Y(A->I)
  ---    ---  --------       --------
   80     84   0.044641       0.005492
   83     84   1.001235      -0.138984
   80     85  -0.048737      -0.025170
   83     85  -0.065898      -0.011229
   81     86   0.039006       0.019489
```

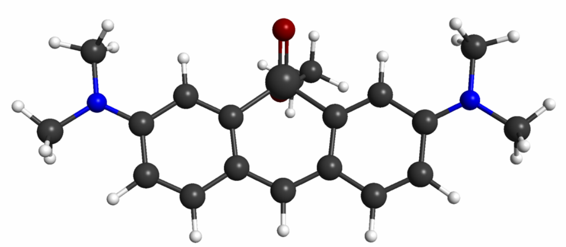
```
 ATOM   CHARGE       X              Y              Z
------------------------------------------------------------
C          6.0  -1.2082030246   1.0527659644  -0.0210967970
C          6.0  -2.0911782649  -0.0747052931   0.0143045388
C          6.0  -1.6527920117  -1.4082039944  -0.0137065050
C          6.0  -0.3481095455  -1.9234454159  -0.0815575095
C          6.0   0.8266262931  -1.1057832558  -0.1338037208
SI        14.0   0.6609955540   0.7763323390  -0.1042139194
C          6.0  -3.1454826175   2.5662371675   0.0753362072
C          6.0  -4.0082144181   1.4336418227   0.1115844827
C          6.0  -3.4892053961   0.1709954872   0.0812847196
C          6.0  -1.7378715518   2.3198347786   0.0099458316
H          1.0  -5.0769061918   1.5642935958   0.1644139350
H          1.0  -4.1637580664  -0.6757631339   0.1099575203
H          1.0  -1.0742276996   3.1713484042  -0.0179997515
N          7.0  -3.6353604214   3.8197096016   0.1017703524
C          6.0  -2.7439677435   4.9784192066   0.0802869147
C          6.0  -5.0778081849   4.0523730688   0.1614121241
H          1.0  -3.3417252657   5.8815858925   0.1314359157
H          1.0  -2.1546574495   5.0063934062  -0.8378024100
```

H	1.0	-5.2651221277	5.1203263198	0.1429754081
H	1.0	-5.5834290936	3.5995590162	-0.6927785740
H	1.0	-2.0642693744	4.9680103262	0.9337641304
H	1.0	-5.5048687480	3.6420391755	1.0783294160
H	1.0	-2.4416374169	-2.1527847009	0.0204980554
C	6.0	-0.1828785154	-3.3343037813	-0.1023522498
C	6.0	2.0597809297	-1.7068108866	-0.2049023466
C	6.0	1.0471334936	-3.9243850373	-0.1712409909
C	6.0	2.2255957076	-3.1261996430	-0.2268619379
N	7.0	3.4481487259	-3.6859201445	-0.2967405603
C	6.0	3.6024435267	-5.1395997951	-0.2887739128
C	6.0	4.6523498047	-2.8597270685	-0.3728449103
H	1.0	2.9443433705	-1.0887474378	-0.2419259284
H	1.0	-1.0656310960	-3.9603928435	-0.0635583856
H	1.0	1.1163831417	-5.0000407192	-0.1866928931
H	1.0	4.6596150674	-5.3800138423	-0.3052732169
H	1.0	3.1311486935	-5.5918226312	-1.1634552845
H	1.0	5.5150213070	-3.5075479785	-0.4821322330
H	1.0	4.7819018380	-2.2623885673	0.5318212420
H	1.0	4.6161321668	-2.1903676480	-1.2333443046
H	1.0	3.1641764903	-5.5757401757	0.6101183130
C	6.0	1.3638600178	1.5209718678	-1.6778276615
C	6.0	1.4928244901	1.4865273858	1.4217405085
H	1.0	1.1999814780	2.6001735404	-1.7027622833
H	1.0	2.4393652285	1.3451003253	-1.7445491854
H	1.0	2.5659530666	1.2862969546	1.4071556782
H	1.0	1.3556748605	2.5689695092	1.4666654492
H	1.0	1.0768842211	1.0531229216	2.3322862694
H	1.0	0.8923819315	1.0851867863	-2.5597952704

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) = -1135.721772 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.945 / 0.072
E(S1) = -1135.649301 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.020 / 0.993*

e. R5 (POOEt)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -1339.411043

E(S1) = -1339.328473*
Oscillator strength = 0.9473
E(HOMO) = -0.2159; E(LUMO) = -0.1287

```
               EXCITATION  DE-EXCITATION
   OCC     VIR  AMPLITUDE      AMPLITUDE
    I       A    X(I->A)        Y(A->I)
   ---     ---  --------       --------
   89      92  -0.080762      -0.011031
   91      92   0.999309      -0.148276
   89      93   0.051754       0.026437
   91      93  -0.078222      -0.013468
```

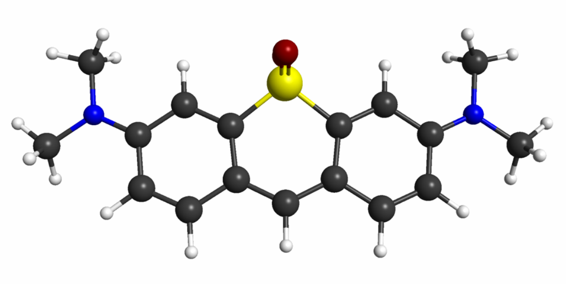
```
  ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 C          6.0  -1.0187910832   1.0011175626   0.1968931977
 C          6.0  -1.9414543636  -0.0795820571   0.3489633220
 C          6.0  -1.5446340044  -1.4230262834   0.3684354462
 C          6.0  -0.2508791853  -1.9344499763   0.1916797199
 C          6.0   0.9010504585  -1.1057109501   0.0422867827
 P         15.0   0.7600578120   0.6762366226   0.2916746947
 C          6.0  -2.8529272474   2.6070074799   0.0672066504
 C          6.0  -3.7682047315   1.5346889071   0.2728261056
 C          6.0  -3.3211359376   0.2502584906   0.3998100471
 C          6.0  -1.4563668749   2.2880702698   0.0472836124
 H          1.0  -4.8280322080   1.7276022898   0.3084713433
 H          1.0  -4.0394528762  -0.5497064424   0.5252690898
 H          1.0  -0.7333100914   3.0757535518  -0.0952521925
 N          7.0  -3.2752069732   3.8687920683  -0.1059254563
 C          6.0  -2.3275318433   4.9532418331  -0.3682239064
 C          6.0  -4.7030287115   4.1880203552  -0.0698003999
 H          1.0  -2.8835293193   5.8690473609  -0.5328735231
 H          1.0  -1.7343722516   4.7456067119  -1.2593004054
 H          1.0  -4.8256929720   5.2582677205  -0.1890249728
 H          1.0  -5.2373308647   3.6837513917  -0.8769604669
 H          1.0  -1.6561921930   5.1049816159   0.4782976172
 H          1.0  -5.1443466724   3.8931920387   0.8828152571
 H          1.0  -2.3368690158  -2.1548974297   0.4787078477
 C          6.0  -0.0506657214  -3.3363036830   0.1011087440
 C          6.0   2.1327760939  -1.6388631018  -0.2163403159
 C          6.0   1.1771609703  -3.8832295520  -0.1457195979
 C          6.0   2.3207784937  -3.0534958944  -0.3300709771
 N          7.0   3.5319235840  -3.5679464489  -0.5948647625
 C          6.0   3.7178437246  -5.0138342052  -0.7181896255
 C          6.0   4.7058497720  -2.7040788481  -0.7329505216
 H          1.0   2.9765832931  -0.9778425846  -0.3363801321
```

H	1.0	-0.9053484466	-3.9888472230	0.2241630872
H	1.0	1.2720890009	-4.9553092233	-0.2026060070
H	1.0	4.7343901025	-5.2086313133	-1.0405916227
H	1.0	3.0358543197	-5.4308714598	-1.4590089409
H	1.0	5.5759322718	-3.3251757759	-0.9124534916
H	1.0	4.8776008554	-2.1267765473	0.1765313749
H	1.0	4.5925641689	-2.0169264181	-1.5726585194
H	1.0	3.5520561055	-5.5151101760	0.2374062477
O	8.0	1.5794396157	1.5410963810	-0.5856839307
O	8.0	1.1228597274	0.7462706044	1.8444796534
C	6.0	1.1984065019	2.0081745657	2.5748150631
C	6.0	1.8368795710	1.7356160420	3.9166054140
H	1.0	1.7866168732	2.7132236715	1.9885446282
H	1.0	0.1861793038	2.3975983769	2.6892198186
H	1.0	2.8464068255	1.3439021035	3.7932138539
H	1.0	1.2480209489	1.0191486176	4.4893013053
H	1.0	1.8937134640	2.6658655008	4.4833297140

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) = -1337.259355 : ORMAS-PCM natural orbitals 91 / 92 occupations = 1.942 / 0.079
E(S1) = -1337.191502 : ORMAS-PCM natural orbitals 91 / 92 occupations = 1.024 / 0.992*

f. R6 (SO_2)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -1316.949052
E(S1) = -1316.867343*
Oscillator strength = 0.9217
E(HOMO) = -0.2217; E(LUMO) = -0.1356

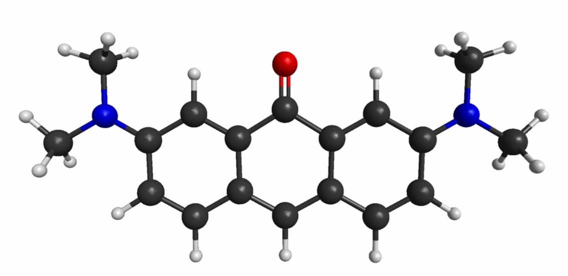
```
         EXCITATION  DE-EXCITATION
 OCC    VIR  AMPLITUDE     AMPLITUDE
  I      A    X(I->A)       Y(A->I)
 ---    ---  --------      --------
 78     84   0.040368     -0.004842
 81     84   0.086272      0.012996
 83     84  -0.999111      0.150971
 81     85  -0.054551     -0.028631
```

```
   83      85    0.078604       0.013445
   79      93   -0.032413      -0.019220

  ATOM   CHARGE       X             Y             Z
---------------------------------------------------------
C          6.0  -1.1715837556   0.9561906046   0.1479396286
C          6.0  -2.0868354438  -0.1256352919   0.2617883714
C          6.0  -1.6826254294  -1.4628743511   0.3048939614
C          6.0  -0.3722527928  -1.9357579812   0.1853070106
C          6.0   0.7558830334  -1.0795077950   0.0615338272
S         16.0   0.5800212648   0.6742290049   0.3285971512
C          6.0  -2.9632747052   2.5822249286   0.0049712537
C          6.0  -3.8936056558   1.5103196129   0.1461946208
C          6.0  -3.4646956734   0.2202259859   0.2660191565
C          6.0  -1.5698871329   2.2528242515   0.0167077799
H          1.0  -4.9518484741   1.7137803561   0.1564335150
H          1.0  -4.1922405912  -0.5753884475   0.3579323031
H          1.0  -0.8289471759   3.0302772233  -0.0779348205
N          7.0  -3.3655568312   3.8524416720  -0.1330702623
C          6.0  -2.3956365997   4.9453636590  -0.2331472189
C          6.0  -4.7906185783   4.1832756037  -0.1834924902
H          1.0  -2.9321410396   5.8867640531  -0.2522961606
H          1.0  -1.8052306421   4.8642320242  -1.1473050607
H          1.0  -4.8947808531   5.2418419732  -0.3913501125
H          1.0  -5.2906060498   3.6252884242  -0.9754137855
H          1.0  -1.7254316858   4.9493353483   0.6262996925
H          1.0  -5.2791446552   3.9641897594   0.7676115682
H          1.0  -2.4640944383  -2.2080216867   0.3916401210
C          6.0  -0.1078898835  -3.3290492529   0.1097464005
C          6.0   2.0184813348  -1.5437032076  -0.1582086236
C          6.0   1.1464309432  -3.8247318088  -0.1000908994
C          6.0   2.2623592840  -2.9510552894  -0.2615566373
N          7.0   3.4959382464  -3.4161575766  -0.4995881861
C          6.0   3.7415041727  -4.8544710806  -0.6190491164
C          6.0   4.6387245829  -2.5069101781  -0.6114006276
H          1.0   2.8339463585  -0.8451310428  -0.2567142319
H          1.0  -0.9392046386  -4.0141628141   0.2113478339
H          1.0   1.2858516936  -4.8921734667  -0.1475859393
H          1.0   4.7666508551  -5.0073938010  -0.9361767136
H          1.0   3.0805773073  -5.2985879961  -1.3626216033
H          1.0   5.5349802404  -3.0941404854  -0.7743712560
H          1.0   4.7682931458  -1.9274982506   0.3034592559
H          1.0   4.5153993086  -1.8232167743  -1.4523415376
H          1.0   3.5911293185  -5.3585510798   0.3373446565
O          8.0   0.9148975928   0.9402383782   1.7121753226
O          8.0   1.3001207225   1.3995081749  -0.6926710178
```

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) =   -1314.939256 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.941 / 0.082
E(S1) = -1314.872218 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.021 / 0.997*

g. R7 (CO)



TDDFT-B3LYP-PCM(H_2O)

E(S0) =   -881.696896
E(S1) = -881.633414*
Oscillator strength = 0.4134
E(HOMO) = -0.2145; E(LUMO) = -0.1409

```
            EXCITATION  DE-EXCITATION
   OCC    VIR  AMPLITUDE      AMPLITUDE
    I      A    X(I->A)        Y(A->I)
   ---    ---  --------      --------
   69      75   -0.061780      -0.000915
   71      75   -0.100900      -0.020839
   74      75    0.991644      -0.145842
   71      76    0.053784       0.034598
   74      76   -0.139133      -0.028770
```

```
  ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 C          6.0  -1.2034425071   0.7691982394  -0.0449898645
 C          6.0  -2.2053617971  -0.2437510631  -0.0081977412
 C          6.0  -1.8447886866  -1.5945321176  -0.0286292581
 C          6.0  -0.5174591035  -2.0275096269  -0.0833140722
 C          6.0   0.5464688429  -1.0802773752  -0.1233196937
 C          6.0   0.2402299540   0.3843377050  -0.1088102282
 C          6.0  -2.9078844556   2.5103030043   0.0495966452
 C          6.0  -3.9058611984   1.4930654817   0.0770387468
 C          6.0  -3.5568122123   0.1702007706   0.0497504223
 C          6.0  -1.5424017398   2.0950304407  -0.0200080341
 H          1.0  -4.9493530441   1.7595754845   0.1179770638
```

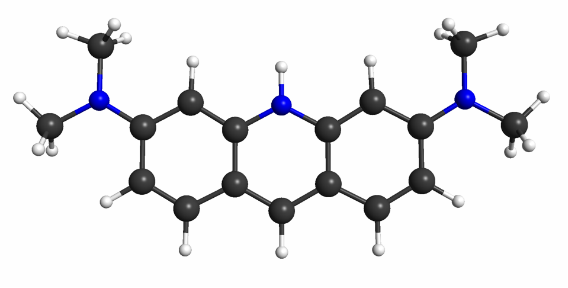
H	1.0	-4.3322845391	-0.5844359892	0.0720884996
H	1.0	-0.7485276554	2.8236531784	-0.0482766655
N	7.0	-3.2282632483	3.8149854620	0.0902347498
C	6.0	-2.1946889100	4.8497905108	0.0316122047
C	6.0	-4.6259786846	4.2329631518	0.1854749735
H	1.0	-2.6730558161	5.8219501618	0.0663557091
H	1.0	-1.6214366684	4.7810459892	-0.8938959631
H	1.0	-4.6639532583	5.3121408369	0.2806956627
H	1.0	-5.1859975104	3.9424833377	-0.7055927929
H	1.0	-1.5107291744	4.7716580335	0.8779849091
H	1.0	-5.1036707277	3.7914636651	1.0606727089
H	1.0	-2.6304308232	-2.3403286275	0.0006052367
C	6.0	-0.1766386152	-3.4011946346	-0.0999410104
C	6.0	1.8510075985	-1.4899090557	-0.1767804179
C	6.0	1.1241363445	-3.8205039629	-0.1544174782
C	6.0	2.1922720311	-2.8781300090	-0.1968948318
N	7.0	3.4757827598	-3.2708627268	-0.2559706272
C	6.0	3.8175682012	-4.6913148057	-0.3206917558
C	6.0	4.5651932272	-2.2937580483	-0.2663143500
H	1.0	2.6196352214	-0.7348876802	-0.2091887771
H	1.0	-0.9706424758	-4.1359233887	-0.0666366604
H	1.0	1.3350951580	-4.8775081640	-0.1605544964
H	1.0	4.8894249776	-4.7873640332	-0.4500487483
H	1.0	3.3232701028	-5.1718903867	-1.1657171644
H	1.0	5.5096660324	-2.8247509101	-0.2354114803
H	1.0	4.5116202125	-1.6389562274	0.6036698310
H	1.0	4.5398473588	-1.6838451303	-1.1710615061
H	1.0	3.5296237724	-5.2089765296	0.5964929630
O	8.0	1.1254564564	1.2226474892	-0.1462959683

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) = -880.145356 : ORMAS-PCM natural orbitals 74 / 75 occupations = 1.944 / 0.086
E(S1) = -880.088493 : ORMAS-PCM natural orbitals 74 / 75 occupations = 1.019 / 1.003*

II. Energies (S0* & S1 in hartree), oscillator strengths (S1 → S0*), HOMO and LUMO energies (hartree), excitation/de-excitation amplitudes, and S1 optimized structures (Å)

a. R1 (NH)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -823.751804*
E(S1) = -823.659290
Oscillator strength = 1.2158
E(HOMO) = -0.2093; E(LUMO) = -0.1003

```
            EXCITATION  DE-EXCITATION
 OCC    VIR  AMPLITUDE      AMPLITUDE
  I      A    X(I->A)        Y(A->I)
 ---    ---  --------       --------
 71      72   0.995506      -0.059008
 69      73   0.031813       0.019036
 70      73  -0.072873      -0.025075
 69      74   0.041775       0.008802
```

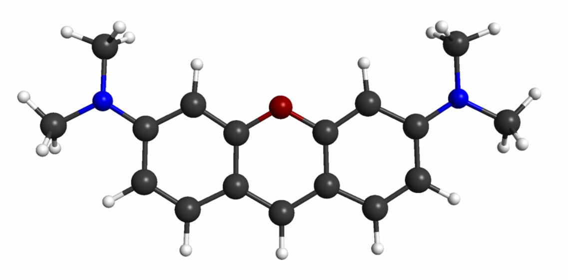
```
  ATOM   CHARGE       X              Y              Z
--------------------------------------------------------
C         6.0  -1.2434941764   0.6555102058  -0.0470436165
C         6.0  -2.2849583635  -0.3221392607  -0.0094916940
C         6.0  -1.9488236656  -1.6931271856  -0.0361514567
C         6.0  -0.5992220001  -2.1014072238  -0.0912159301
C         6.0   0.4319643031  -1.1127785979  -0.1266506782
N         7.0   0.0612407653   0.2151048405  -0.1089456657
C         6.0  -2.8626633144   2.4704940255   0.0541532164
C         6.0  -3.9072635687   1.5017494106   0.0891659377
C         6.0  -3.6155763237   0.1602782365   0.0566597082
C         6.0  -1.5270806977   2.0112463067  -0.0188639316
H         1.0  -4.9376733835   1.8141158068   0.1378537912
H         1.0  -4.4220314293  -0.5607226128   0.0827094972
H         1.0  -0.7070481430   2.7119583358  -0.0454343876
N         7.0  -3.1408826402   3.8056123098   0.0919623724
C         6.0  -2.0736144639   4.7911982048   0.0077771919
C         6.0  -4.5152879088   4.2730323055   0.1977735191
H         1.0  -2.5065743503   5.7849462620   0.0346481781
```

H	1.0	-1.5094798942	4.6831146773	-0.9222461730
H	1.0	-4.5167547630	5.3542806678	0.2797862059
H	1.0	-5.0993311742	3.9902136367	-0.6826077957
H	1.0	-1.3770287898	4.6939891017	0.8448927601
H	1.0	-5.0028866764	3.8564039613	1.0815632200
H	1.0	-2.7319711434	-2.4375366216	-0.0093471997
C	6.0	-0.1903185536	-3.4580038252	-0.1111116148
C	6.0	1.7694077354	-1.4696894384	-0.1782058544
C	6.0	1.1322751929	-3.8219990191	-0.1637057352
C	6.0	2.1548963291	-2.8302110626	-0.2013157805
N	7.0	3.4715577710	-3.1831039576	-0.2585109589
C	6.0	3.8625937964	-4.5839294501	-0.3185188371
C	6.0	4.5147770921	-2.1689187618	-0.2499128484
H	1.0	2.5130533547	-0.6887163586	-0.2052291369
H	1.0	-0.9532009590	-4.2247835495	-0.0813648343
H	1.0	1.3889439993	-4.8688166817	-0.1719644143
H	1.0	4.9384235399	-4.6445704411	-0.4386137931
H	1.0	3.3895534222	-5.0863384229	-1.1648074022
H	1.0	5.4827955990	-2.6571643221	-0.2617732805
H	1.0	4.4519521422	-1.5453116641	0.6454987212
H	1.0	4.4439331705	-1.5185374636	-1.1263042165
H	1.0	3.5841974448	-5.1151032511	0.5962441918
H	1.0	0.7926669646	0.9096043368	-0.1324805349

ORMAS-PT2-PCM(H_2O) at TDDFT-B3LYP-PCM(H_2O) optimized geometry

E(S0) = -822.282254 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.938 / 0.074*
E(S1) = -822.191649 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.197 / 0.817

b. R2 (O)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -843.600340*
E(S1) = -843.513375
Oscillator strength = 1.3147
E(HOMO) = -0.2133; E(LUMO) = -0.1115

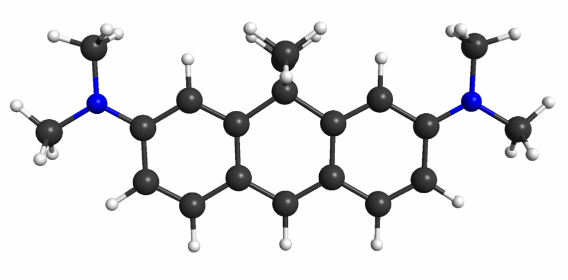
```
          EXCITATION  DE-EXCITATION
  OCC    VIR  AMPLITUDE     AMPLITUDE
   I      A    X(I->A)       Y(A->I)
  ---    ---  --------      --------
  71      72  -0.998267      0.072716
  69      73   0.035667      0.020514
  70      73   0.036749      0.017419
  69      75   0.030021      0.006552

 ATOM   CHARGE      X            Y            Z
------------------------------------------------------------
C         6.0  -1.2755569776   0.5844106185  -0.0428430322
C         6.0  -2.3232886781  -0.3732412156  -0.0043803752
C         6.0  -2.0059623276  -1.7471524338  -0.0344944940
C         6.0  -0.6517921717  -2.1360525889  -0.0921887659
C         6.0   0.3599687787  -1.1403048662  -0.1245159556
O         8.0   0.0356781724   0.1910678717  -0.1067265126
C         6.0  -2.8329741871   2.4342599670   0.0582204072
C         6.0  -3.8994189434   1.4875761093   0.0988488350
C         6.0  -3.6434030322   0.1412727236   0.0663831647
C         6.0  -1.5059614275   1.9394599721  -0.0163423069
H         1.0  -4.9216919852   1.8251348164   0.1517610877
H         1.0  -4.4668601101  -0.5597919165   0.0956283762
H         1.0  -0.6568503901   2.6029402032  -0.0476213187
N         7.0  -3.0772241971   3.7711631859   0.0901765200
C         6.0  -1.9841754063   4.7286824523  -0.0009688478
C         6.0  -4.4406013999   4.2750682210   0.1878619840
H         1.0  -2.3908090385   5.7333640807   0.0231281964
H         1.0  -1.4271702163   4.6004182393  -0.9325254445
H         1.0  -4.4140910291   5.3568015348   0.2557149037
H         1.0  -5.0287097102   3.9953079211  -0.6905143736
H         1.0  -1.2884281229   4.6155194183   0.8345351648
H         1.0  -4.9399533576   3.8825983089   1.0760888352
H         1.0  -2.7880831193  -2.4916019249  -0.0089440824
C         6.0  -0.2107822065  -3.4837409977  -0.1178779634
C         6.0   1.6998736888  -1.4444715605  -0.1756209977
C         6.0   1.1185432816  -3.8132652163  -0.1711174221
C         6.0   2.1206711783  -2.7982423682  -0.2032262072
N         7.0   3.4413870101  -3.1166454530  -0.2586938435
C         6.0   3.8677254140  -4.5082110147  -0.3163503377
C         6.0   4.4596872714  -2.0760137148  -0.2453134002
H         1.0   2.4087224760  -0.6327535355  -0.1985448871
H         1.0  -0.9553993827  -4.2681846719  -0.0918658488
H         1.0   1.3998544405  -4.8536336462  -0.1844849361
H         1.0   4.9455710624  -4.5424251391  -0.4279331605
H         1.0   3.4133144793  -5.0207821618  -1.1665011213
```

H	1.0	5.4391812314	-2.5403571844	-0.2644347969
H	1.0	4.3834788719	-1.4618659345	0.6555264922
H	1.0	4.3684516733	-1.4214636080	-1.1163772174
H	1.0	3.5951157371	-5.0448669118	0.5966625321

ORMAS-PT2-PCM(H_2O) at TDDFT-B3LYP-PCM(H_2O) optimized geometry

E(S0) = -842.114045 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.945 / 0.069*
E(S1) = -842.029965 : ORMAS-PCM natural orbitals 71 / 72 occupations = 1.023 / 0.988

c. R3 (CMe$_2$)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -886.267502*
E(S1) = -886.186503
Oscillator strength = 1.3897
E(HOMO) = -0.2075; E(LUMO) = -0.1132

```
            EXCITATION  DE-EXCITATION
 OCC     VIR  AMPLITUDE      AMPLITUDE
  I      A    X(I->A)        Y(A->I)
 ---    ---   --------       --------
  79     80    0.999975      -0.086413
```

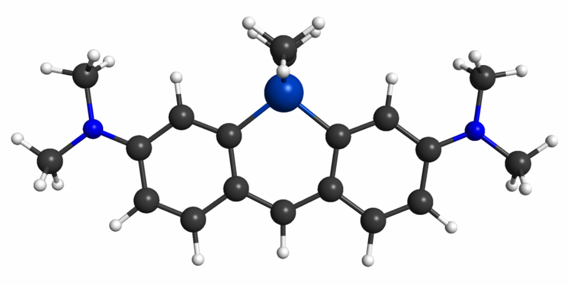
ATOM	CHARGE	X	Y	Z
C	6.0	-1.1968613423	0.7819047415	-0.1091392652
C	6.0	-2.1925478885	-0.2295478929	0.0423808544
C	6.0	-1.8449829415	-1.5952281862	0.0687908457
C	6.0	-0.5059503406	-2.0162359651	-0.0482293453
C	6.0	0.5535810235	-1.0722760695	-0.2020719300
C	6.0	0.2885975717	0.4367611209	-0.2615194248
C	6.0	-2.9430358280	2.5066536808	0.0100146921
C	6.0	-3.9274306817	1.4842818351	0.1535305592
C	6.0	-3.5521725327	0.1713878550	0.1682358073
C	6.0	-1.5877056856	2.1061341086	-0.1233321802
H	1.0	-4.9704905296	1.7393112618	0.2513585369
H	1.0	-4.3064711279	-0.5968151203	0.2793921531
H	1.0	-0.8371560453	2.8705823539	-0.2380452970

N	7.0	-3.2938329355	3.8192100418	0.0037873075
C	6.0	-2.2857209571	4.8604519825	-0.1462817150
C	6.0	-4.6861118761	4.2193677039	0.1653402665
H	1.0	-2.7737948294	5.8284674850	-0.1391285182
H	1.0	-1.7442194466	4.7522364009	-1.0890619866
H	1.0	-4.7424450475	5.3020169094	0.1686994802
H	1.0	-5.3047808175	3.8421167943	-0.6529311087
H	1.0	-1.5633095682	4.8293706864	0.6733784633
H	1.0	-5.0944866831	3.8469166439	1.1074952016
H	1.0	-2.6233966771	-2.3368055147	0.1845881525
C	6.0	-0.1799736627	-3.4017522415	-0.0134430907
C	6.0	1.8494700346	-1.5364028315	-0.3082025782
C	6.0	1.1050483465	-3.8494046912	-0.1223401175
C	6.0	2.1748030366	-2.9183955768	-0.2734988718
N	7.0	3.4603390350	-3.3430640497	-0.3807805711
C	6.0	3.7783736415	-4.7655679820	-0.4014595430
C	6.0	4.5560407850	-2.3880992142	-0.4758298945
H	1.0	2.6495052790	-0.8247714921	-0.4296802488
H	1.0	-0.9843038942	-4.1162818978	0.1055542644
H	1.0	1.3030470353	-4.9087814639	-0.0857706057
H	1.0	4.8415775103	-4.8848223996	-0.5768239387
H	1.0	3.2363799093	-5.2774137572	-1.1993172981
H	1.0	5.4964409626	-2.9274906947	-0.4743129234
H	1.0	4.5495652289	-1.7003372319	0.3723303782
H	1.0	4.4940218793	-1.8020988837	-1.3971045594
H	1.0	3.5272073681	-5.2446394948	0.5490311118
C	6.0	0.7866335375	0.9762498802	-1.6308403155
C	6.0	1.0857648594	1.1305025134	0.8769516866
H	1.0	0.2473291229	0.5040612228	-2.4523330658
H	1.0	0.6382561462	2.0530369396	-1.6984986693
H	1.0	1.8495551767	0.7781294760	-1.7608117239
H	1.0	2.1522451715	0.9345209636	0.7784976499
H	1.0	0.7596594182	0.7703317109	1.8528394045
H	1.0	0.9454895189	2.2098846795	0.8468208198

ORMAS-PT2-PCM(H_2O) at TDDFT-B3LYP-PCM(H_2O) optimized geometry

E(S0) = -884.671127 : ORMAS-PCM natural orbitals 79 / 80 occupations = 1.945 / 0.069*
E(S1) = -884.597771 : ORMAS-PCM natural orbitals 79 / 80 occupations = 1.020 / 0.991

d. R4 (SiMe$_2$)



TDDFT-B3LYP-PCM(H$_2$O)

E(S0) = -1137.677685*
E(S1) = -1137.600506
Oscillator strength = 1.3907
E(HOMO) = -0.2084; E(LUMO) = -0.1180

```
              EXCITATION  DE-EXCITATION
    OCC     VIR  AMPLITUDE      AMPLITUDE
     I       A    X(I->A)        Y(A->I)
    ---     ---   --------       --------
    78      84   -0.034581       0.005232
    83      84    0.999707      -0.090040
```

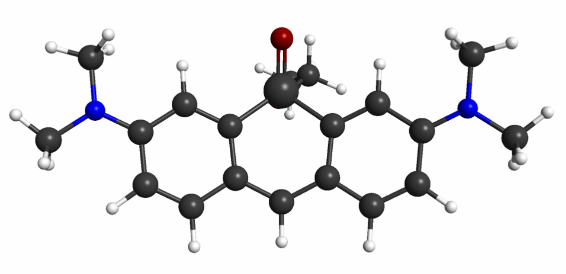
```
  ATOM   CHARGE       X              Y              Z
 ----------------------------------------------------------
 C          6.0  -1.2147714315   1.0275961553   0.0069642133
 C          6.0  -2.1102480726  -0.0962401736   0.0626204198
 C          6.0  -1.6913247871  -1.4482053224   0.0546472410
 C          6.0  -0.3675570788  -1.9434693186  -0.0305589655
 C          6.0   0.8034334456  -1.1123787090  -0.1033821997
 SI        14.0   0.6467477598   0.7601549945  -0.0491282835
 C          6.0  -3.1388426899   2.5657320163   0.0567151636
 C          6.0  -4.0141005705   1.4382793175   0.1197553704
 C          6.0  -3.5103774762   0.1700592234   0.1225627309
 C          6.0  -1.7414964495   2.3067335817   0.0045472919
 H          1.0  -5.0820871465   1.5806824158   0.1651279218
 H          1.0  -4.1947400414  -0.6676194802   0.1686944133
 H          1.0  -1.0679072251   3.1502467830  -0.0380503092
 N          7.0  -3.6310705944   3.8286349879   0.0497976656
 C          6.0  -2.7356381932   4.9766932509  -0.0062922732
 C          6.0  -5.0682473383   4.0707891071   0.1175399938
 H          1.0  -3.3255271564   5.8861312974  -0.0179568072
 H          1.0  -2.1191755805   4.9502248372  -0.9078855770
 H          1.0  -5.2494651258   5.1393662841   0.0868648882
 H          1.0  -5.5850170568   3.6073497006  -0.7256892599
 H          1.0  -2.0737760251   5.0012544084   0.8630847815
```

H	1.0	-5.4908094532	3.6730004812	1.0432478300
H	1.0	-2.4770109385	-2.1913964263	0.1056391448
C	6.0	-0.1823943148	-3.3572634838	-0.0555337069
C	6.0	2.0467532609	-1.7097880187	-0.2070297134
C	6.0	1.0521131376	-3.9314286970	-0.1552070457
C	6.0	2.2246898405	-3.1191420187	-0.2386422101
N	7.0	3.4547538122	-3.6796032831	-0.3432386605
C	6.0	3.6195118246	-5.1288053395	-0.3404259729
C	6.0	4.6451375612	-2.8470393601	-0.4600307500
H	1.0	2.9237039563	-1.0817324312	-0.2611939134
H	1.0	-1.0559073033	-3.9942611190	0.0012767885
H	1.0	1.1326772456	-5.0066038371	-0.1760443540
H	1.0	4.6778463180	-5.3623512176	-0.3695505066
H	1.0	3.1391922751	-5.5834871648	-1.2106392683
H	1.0	5.5122702002	-3.4855970548	-0.5853997247
H	1.0	4.7893138214	-2.2356390190	0.4348882683
H	1.0	4.5753026941	-2.1820785195	-1.3237712105
H	1.0	3.1917990612	-5.5703435802	0.5617749129
C	6.0	1.3998102355	1.5502879595	-1.5824691920
C	6.0	1.4704531729	1.4624522059	1.4914171181
H	1.0	1.2398497502	2.6306467912	-1.5806259881
H	1.0	2.4776388473	1.3783438027	-1.6206954458
H	1.0	2.5446623921	1.2660970869	1.4823012146
H	1.0	1.3319542805	2.5446347036	1.5448853572
H	1.0	1.0512236991	1.0217811835	2.3970954711
H	1.0	0.9580706372	1.1428218684	-2.4929125928

ORMAS-PT2-PCM(H_2O) at TDDFT-B3LYP-PCM(H_2O) optimized geometry

E(S0) = -1135.720747 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.944 / 0.073*
E(S1) = -1135.650797 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.020 / 0.993

e. R5 (POOEt)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -1339.409126*
E(S1) = -1339.338413
Oscillator strength = 1.1349
E(HOMO) = -0.2161; E(LUMO) = -0.1327

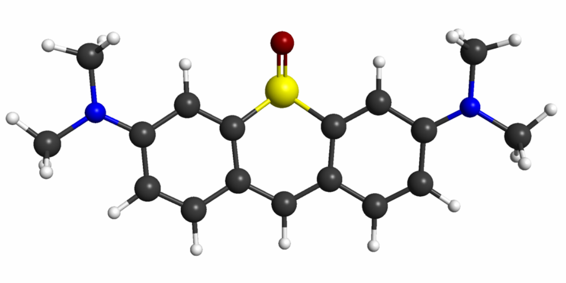
```
          EXCITATION  DE-EXCITATION
 OCC     VIR  AMPLITUDE     AMPLITUDE
  I       A    X(I->A)       Y(A->I)
 ---     ---  --------      --------
  89      92  -0.051166     -0.006417
  91      92   0.999508     -0.102031
  91      93  -0.036225     -0.005631

 ATOM   CHARGE       X              Y              Z
------------------------------------------------------------
C         6.0  -1.0005154787   0.9876924978   0.2657291401
C         6.0  -1.9374171612  -0.0884804299   0.4419522455
C         6.0  -1.5570610279  -1.4445888201   0.5153546202
C         6.0  -0.2518440397  -1.9353687919   0.2995080562
C         6.0   0.8949037286  -1.0886550546   0.1250413241
P        15.0   0.7582160937   0.6699144454   0.4243489462
C         6.0  -2.8221663232   2.5955628811   0.0197523553
C         6.0  -3.7510312512   1.5346685195   0.2701056897
C         6.0  -3.3180870863   0.2557589029   0.4681452873
C         6.0  -1.4379793881   2.2758005585   0.0400875774
H         1.0  -4.8100234856   1.7370555317   0.2834269330
H         1.0  -4.0441640370  -0.5313389065   0.6233919414
H         1.0  -0.7052668035   3.0520214295  -0.1157967908
N         7.0  -3.2525117977   3.8535716687  -0.2167547189
C         6.0  -2.3022318560   4.9161110177  -0.5259552093
C         6.0  -4.6747530000   4.1837537872  -0.1826840020
H         1.0  -2.8494387552   5.8213536562  -0.7623324840
H         1.0  -1.6848669559   4.6456271938  -1.3846114488
H         1.0  -4.7892870354   5.2501860939  -0.3380417253
H         1.0  -5.2192005931   3.6562544457  -0.9695232823
H         1.0  -1.6462640427   5.1167040968   0.3251863743
H         1.0  -5.1147671634   3.9234640336   0.7814521979
H         1.0  -2.3431811117  -2.1739713539   0.6570022452
C         6.0  -0.0378191118  -3.3378182046   0.1869252956
C         6.0   2.1235009420  -1.6152284287  -0.2117429607
C         6.0   1.1815985576  -3.8630241163  -0.1289420610
C         6.0   2.3115821654  -3.0145272806  -0.3634515962
N         7.0   3.5140489274  -3.5329606823  -0.6955836901
C         6.0   3.7079799611  -4.9760681758  -0.8083356907
C         6.0   4.6647138851  -2.6618566625  -0.9081217972
H         1.0   2.9558790158  -0.9426411591  -0.3472494943
H         1.0  -0.8782173253  -4.0022019552   0.3382080142
H         1.0   1.2852254111  -4.9331714832  -0.2090384259
H         1.0   4.7184415653  -5.1662649982  -1.1513343241
H         1.0   3.0109187532  -5.4091415613  -1.5271045693
```

```
H         1.0   5.5206641162  -3.2678245482  -1.1814126113
H         1.0   4.9065665452  -2.1041698340  -0.0000201001
H         1.0   4.4705534859  -1.9481380029  -1.7116179069
H         1.0   3.5678710997  -5.4685019756   0.1569685638
O         8.0   1.6213265589   1.5624795285  -0.3871783692
O         8.0   1.0830128272   0.7187515041   1.9954290858
C         6.0   1.1963942253   1.9802273796   2.7158418215
C         6.0   1.7972687906   1.6980344917   4.0737955084
H         1.0   1.8226950928   2.6568479373   2.1353508608
H         1.0   0.1993077060   2.4138745234   2.8081325251
H         1.0   2.7921768941   1.2638667008   3.9745121309
H         1.0   1.1695686605   1.0115940463   4.6423336123
H         1.0   1.8814100916   2.6306820938   4.6333107764
```

ORMAS-PT2-PCM(H_2O) at TDDFT-B3LYP-PCM(H_2O) optimized geometry

E(S0) = -1337.257894 : ORMAS-PCM natural orbitals 91 / 92 occupations = 1.941 / 0.081*
E(S1) = -1337.193723 : ORMAS-PCM natural orbitals 91 / 92 occupations = 1.023 / 0.995

f. R6 (SO_2)



TDDFT-B3LYP-PCM(H_2O)

E(S0) = -1316.946196*
E(S1) = -1316.877747
Oscillator strength = 1.0264
E(HOMO) = -0.2216; E(LUMO) = -0.1404

```
            EXCITATION  DE-EXCITATION
   OCC    VIR  AMPLITUDE      AMPLITUDE
    I      A    X(I->A)        Y(A->I)
   ---    ---   --------      --------
   79     84    0.046159     -0.001455
   81     84    0.061224      0.008771
   83     84    0.999317     -0.106741
   81     85   -0.031286     -0.021279
   83     85   -0.037629     -0.005749
```

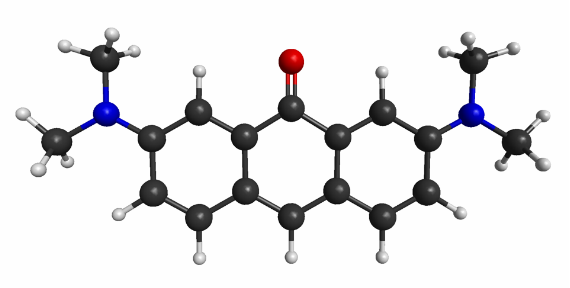
```
  ATOM   CHARGE       X             Y             Z
 ------------------------------------------------------------
```

C	6.0	-1.1568498409	0.9115469366	0.4079459283
C	6.0	-2.1033103295	-0.1616204350	0.4900852224
C	6.0	-1.7243881673	-1.5143487408	0.5621022522
C	6.0	-0.3996575764	-1.9608514473	0.3913166976
C	6.0	0.7238475108	-1.0751797233	0.3151333521
S	16.0	0.5227806774	0.5964284073	0.8337325779
C	6.0	-2.8999680271	2.5421149763	-0.0109245949
C	6.0	-3.8633177432	1.4928334439	0.1544780773
C	6.0	-3.4732965803	0.2066125719	0.3909854728
C	6.0	-1.5280394413	2.2077012680	0.1443488216
H	1.0	-4.9154122978	1.7117373383	0.0692759266
H	1.0	-4.2219605639	-0.5696163424	0.4744913586
H	1.0	-0.7663089236	2.9681787879	0.0837709541
N	7.0	-3.2872012012	3.8034935587	-0.2866255299
C	6.0	-2.2959600565	4.8515142486	-0.5091109960
C	6.0	-4.7020938525	4.1589405721	-0.3666611971
H	1.0	-2.8033474208	5.7571598515	-0.8202955659
H	1.0	-1.5943885224	4.5564333101	-1.2907985177
H	1.0	-4.7833437149	5.2266666192	-0.5332969421
H	1.0	-5.1908168925	3.6390080237	-1.1936819925
H	1.0	-1.7344354510	5.0607657324	0.4051318757
H	1.0	-5.2205561967	3.9106716922	0.5607041540
H	1.0	-2.5049772180	-2.2586100542	0.6333079236
C	6.0	-0.1221355467	-3.3392195994	0.1817577255
C	6.0	1.9842312212	-1.5035923155	-0.0264355643
C	6.0	1.1255907113	-3.7866076477	-0.1431580912
C	6.0	2.2265485707	-2.8792242926	-0.2847036382
N	7.0	3.4511106597	-3.3231722407	-0.6333071168
C	6.0	3.6999267034	-4.7452928737	-0.8610133252
C	6.0	4.5679969734	-2.3940131780	-0.7670023014
H	1.0	2.7863736714	-0.7850835164	-0.0779570192
H	1.0	-0.9385143097	-4.0451516519	0.2534665339
H	1.0	1.2744351705	-4.8413010364	-0.3085161551
H	1.0	4.7418565857	-4.8791083970	-1.1269123459
H	1.0	3.0801851984	-5.1224210034	-1.6765373238
H	1.0	5.4410211885	-2.9377294226	-1.1082018988
H	1.0	4.8000936302	-1.9230041953	0.1914846877
H	1.0	4.3388048126	-1.6111601176	-1.4927479625
H	1.0	3.4903052145	-5.3281763109	0.0378439468
O	8.0	0.6319401299	0.6331732089	2.2814577316
O	8.0	1.4062879245	1.4679353741	0.0866239876

ORMAS-PT2-PCM(H_2O) at TDDFT-B3LYP-PCM(H_2O) optimized geometry

E(S0) = -1314.937967 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.938 / 0.086*
E(S1) = -1314.876096 : ORMAS-PCM natural orbitals 83 / 84 occupations = 1.029 / 0.992

g. R7 (CO)



TDDFT-B3LYP-PCM(H_2O)

E(S0) =   -881.693547
E(S1) = -881.641925*
Oscillator strength = 0.4808
E(HOMO) = -0.2137; E(LUMO) = -0.1461

```
              EXCITATION  DE-EXCITATION
   OCC     VIR  AMPLITUDE      AMPLITUDE
    I       A    X(I->A)        Y(A->I)
   ---     ---  --------       --------
   69      75  -0.057007      -0.001654
   71      75   0.068986       0.014047
   74      75   0.998298      -0.112927
   71      76  -0.031047      -0.026474
   74      76  -0.071029      -0.015802
```

```
  ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 C          6.0  -1.1741695982   0.7639262670  -0.0474247369
 C          6.0  -2.1981986903  -0.2511697300  -0.0089774924
 C          6.0  -1.8589870663  -1.6081777584  -0.0281540467
 C          6.0  -0.5242123799  -2.0193735948  -0.0834717457
 C          6.0   0.5428377495  -1.0497694651  -0.1249938904
 C          6.0   0.2398903392   0.3846032459  -0.1107223583
 C          6.0  -2.8812765802   2.5041179819   0.0499233022
 C          6.0  -3.8963327945   1.4822486903   0.0782845280
 C          6.0  -3.5567551698   0.1653341627   0.0497011499
 C          6.0  -1.5265380379   2.0981691811  -0.0203959539
 H          1.0  -4.9375803402   1.7576035718   0.1192201207
 H          1.0  -4.3313967513  -0.5893872824   0.0712995844
 H          1.0  -0.7315430490   2.8246028326  -0.0476469458
 N          7.0  -3.2244820113   3.8041225151   0.0901573563
 C          6.0  -2.1987540054   4.8429415944   0.0283845531
 C          6.0  -4.6234716097   4.2225807909   0.1876968876
```

H	1.0	-2.6781236070	5.8142934488	0.0576645156
H	1.0	-1.6219850549	4.7631092384	-0.8948131290
H	1.0	-4.6571265565	5.2999189482	0.3007018971
H	1.0	-5.1785009431	3.9495896637	-0.7118385682
H	1.0	-1.5141823634	4.7628845037	0.8751241266
H	1.0	-5.1049274473	3.7686625512	1.0535265600
H	1.0	-2.6432121871	-2.3528792721	0.0015134948
C	6.0	-0.1811407504	-3.4003363610	-0.0993637953
C	6.0	1.8550522564	-1.4735483694	-0.1804987030
C	6.0	1.1141453346	-3.8098361883	-0.1548631885
C	6.0	2.1875940916	-2.8505538510	-0.1999985330
N	7.0	3.4650604450	-3.2661337134	-0.2572910319
C	6.0	3.8068629654	-4.6881479506	-0.3230967586
C	6.0	4.5589215820	-2.2980063532	-0.2593516070
H	1.0	2.6215481863	-0.7173903862	-0.2154502280
H	1.0	-0.9751919465	-4.1340883534	-0.0637301494
H	1.0	1.3340577987	-4.8650479876	-0.1589559806
H	1.0	4.8760078997	-4.7802573874	-0.4737221022
H	1.0	3.2978217880	-5.1729527396	-1.1558675039
H	1.0	5.5016803013	-2.8308902463	-0.2236246364
H	1.0	4.4941907314	-1.6408575136	0.6088310245
H	1.0	4.5340903531	-1.6857423199	-1.1635777437
H	1.0	3.5402004196	-5.2003192384	0.6035112653
O	8.0	1.1447620984	1.2420393241	-0.1484187969

ORMAS-PT2-PCM(H_2O) at B3LYP-PCM(H_2O) optimized geometry

E(S0) = -880.142357 : ORMAS-PCM natural orbitals 74 / 75 occupations = 1.940 / 0.094
E(S1) = -880.091888 : ORMAS-PCM natural orbitals 74 / 75 occupations = 1.019 / 1.006*

Section S9: References

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