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α-Amino acid-assisted autoxidation of naphthalene proton sponge affording 1,4-naphthoquinone nitrogen derivatives

Marina P. Vlasenko, Alexander F. Pozharskii, Oleg P. Demidov, Valery A. Ozeryanskii and Gennady S. Borodkin

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General Remarks

Spectroscopic Measurements and General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 (250 MHz for ^{1}H, 62.9 MHz for ^{13}C), Bruker Avance-400 (400 МГц MHz for ^{1}H, 100.6 MHz for ^{13}C) and Bruker Avance-600 (600 МГц MHz for ^{1}H, 150.9 MHz for ^{13}C) spectrometers with the solvent residual peaks as the internal standard (δ/ppm, ^{n}J/Hz). Mass spectra were obtained from SHIMADZU Nexera LCMS-9030 (ESI), Bruker micrOTOF (ESI) and Bruker Customer 50 (ESI). Thin layer and column chromatography were carried out on Al_2O_3 (Brockmann activity II) and on silica gel (70–230 mesh, Aldrich). The progress of reactions and the purity of products were monitored by TLC on Al_2O_3; development with iodine vapor. The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods. Amines **1b–d** were prepared as described previously [V. A. Ozeryanskii, A. F. Pozharskii, *Russ. Chem. Bull*. **1997**, *46*, 1437].

1,8-Bis(dimethylamino)naphthalene (**1a**) (Alfa Aesar, 98+%), Pd/C 5% (Acros Organics), methyl 2-bromopropionate (97%), ethyl 2-bromopropionate (97%), methyl bromoacetate (97%), methyl α-bromophenylacetate (97%) and ethyl bromoacetate (97%) were purchased from Acros Organics.

X-Ray Diffraction (XRD) Analysis

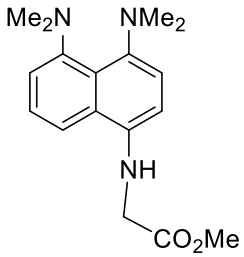
Crystals suitable for X-ray studies were grown up by slow evaporation from solutions of compounds in appropriate solvents: *n*-hexane (for **4c**, **5**, **18**), ethyl acetate (for **16** and **22**), MeCN (for **16**·HBF_4), acetone (for **20**), and EtOH (for **21**). XRD measurements were conducted with Agilent Technologies 'SuperNova' and Rigaku 'XtaLAB SuperNova' diffractometers. The structures were solved using Olex2 [Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009**, *42*, 339–341] with the SHELXS [Sheldrick, G. M. A short history of SHELX. *Acta Cryst. A* **2008**, *64*, 112–122] and SHELXT programs [Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015**, *71*, 3–8]. Structural refinements were carried out with the SHELXL refinement package [Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8] using least squares minimization in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in the riding model with the $U_{iso}(H)$ parameters equal to $n \cdot U_{eq}(C_i)$ (n = 1.2 for CH and CH_2 groups and n = 1.5 for CH_3 groups), where $U(C_i)$ are, respectively, the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The H(N) hydrogen atoms were found in the difference Fourier synthesis and refined in isotropic approximation. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers indicated in the Tables at the end of this SI.

Experimental Procedures

Synthesis of DMAN-based amino acid esters

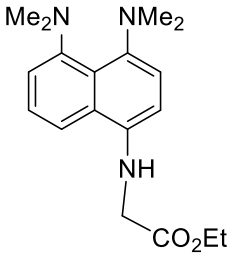
An appropriate bromo ester (1 mmol) was added to a solution of amine **1b** or **1c** (1 mmol) in dry MeCN (25 mL). The mixture was refluxed with $CaCl_2$-tube protection for 72 h until the starting amine was consumed (TLC control, $Al_2O_3/CHCl_3$). The solvent was evaporated, the crude product was washed with diethyl ether. 10% Aqueous KOH (5 mL) was added to the solution of hydrobromide in a minimum volume of MeCN. The mixture was shaken and extracted with *n*-hexane (3×20 mL). The extract was dried with anhydrous Na_2SO_4, and the crude product obtained after solvent evaporation was purified by column chromatography.

Methyl *N*-[4,5-bis(dimethylamino)naphthalen-1-yl]glycinate (4a)



Isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.40), light-beige crystals with mp 76–77 °C (from hexanes), 193 mg (64%). ^{1}H NMR ($CDCl_3$): δ = 2.70 (s, 6H, 4-NMe_2), 2.80 (s, 6H, 5-NMe_2), 3.80 (s, 3H, OMe), 4.01 (s, 2H, CH_2), 4.59 (br. s, 1H, NH), 6.44 (d, *J*=8.3 Hz, 1H, 3-H), 6.86 (d, *J*=8.3 Hz, 1H, 6-H), 6.97 (d, *J*=7.4 Hz, 1H, 2-H), 7.33 (t, *J*=8.3 Hz, 1H, 7-H), 7.51 (dd, *J*=8.3 Hz, *J*=0.8 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 42.0 (5-NMe_2), 44.5 (4-NMe_2), 51.4 (CH_2), 58.8 (OMe), 112.2, 112.5, 116.5, 116.8, 121.7, 125.2, 133.1, 142.9, 147.1, 150.7, 171.3 (C=O). HRMS: MH^+ = 302.1868, calc.: 302.1863.

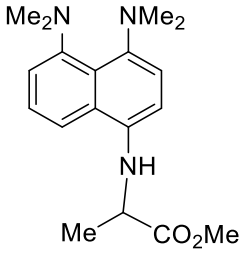
Ethyl *N*-[4,5-bis(dimethylamino)naphthalen-1-yl]glycinate (4b)



Isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.41), light-yellow crystals with mp 92–93 °C (from hexanes), 190 mg (60%). ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, *J*=7.1 Hz, 3H, CH_3), 2.71 (s, 6H, 4-NMe_2), 2.81 (s, 6H, 5-NMe_2), 4.00 (s, 2H, CH_2), 4.28 (q, *J*=7.2 Hz, *J*=7.0 Hz, *J*=7.1 Hz, 2H, CH_2), 4.60 (br. s, 1H, NH), 6.45 (d, *J*=8.2 Hz, 1H, 3-H), 6.87 (d, *J*=8.04 Hz, 1H, 6-H), 6.98 (d, *J*=7.4 Hz, 1H, 2-H), 7.33 (t, *J*=8.2 Hz, 1H, 7-H), 7.50 (d, *J*=8.4 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 44.6 (5-NMe_2), 44.7 (4-NMe_2), 46.9 (CH_2), 61.2

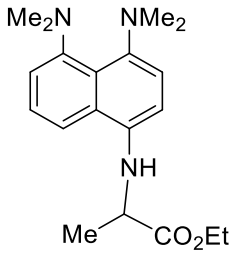
(OMe), 106.9, 113.3, 113.7, 121.5, 125.2, 128.2, 137.7, 143.9, 147.2, 151.0, 171.6 (C=O). MS, *m*/*z* (*I*/%): 316 [M^+] (14), 315 (60), 183 (19), 182 (11), 168 (11), 154 (14), 58 (100), 45 (10), 44 (37), 42 (26), 32 (14), 29 (64), 28 (27), 27 (16). HRMS: MH^+ = 316.2022, calc.: 316.2020.

Methyl *N*-[4,5-bis(dimethylamino)naphthalen-1-yl]alaninate (4c)



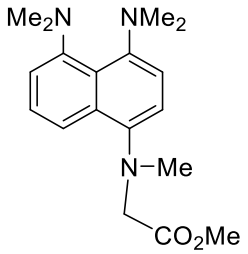
Isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.41). Light-beige crystals with mp 106–107 °C (from hexanes), 243 mg (77%). ^{1}H NMR ($CDCl_3$): δ = 1.56 (d, *J*=6.8, 3H, Me), 2.69 (s, 6H, 4-NMe_2), 2.79 (s, 6H, 5-NMe_2), 3.73 (s, 3H, Me), 4.00 (q, *J*=6.6 Hz, 1H, CH), 4.42 (br. s, 1H, NH), 6.49 (d, *J*=8.2 Hz, 1H, 3-H), 6.83 (d, *J*=8.2 Hz, 1H, 6-H), 6.95 (d, *J*=7.6 Hz, 1H, 2-H), 7.31 (t, *J*=8.2 Hz, 1H, 7-H), 7.50 (d, *J*=8.4 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 19.3 (CH_3), 44.6 (1,8-NMe_2), 52.2 (CH), 53.0 (OMe), 107.0, 113.0, 113.1, 113.6, 121.6, 124.9, 128.7, 136.9, 143.6, 151.0, 175.7 (C=O). HRMS: MH^+ = 316.2024, calc.: 316.2020.

Ethyl *N*-[4,5-bis(dimethylamino)naphthalen-1-yl]alaninate (4d)



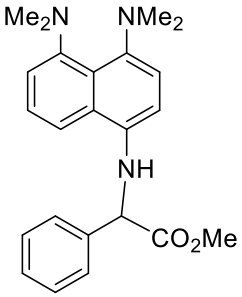
Isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.42). Light-beige crystals with mp 68–69 °C (from hexanes), 230 mg (70%). ^{1}H NMR ($CDCl_3$): δ = 1.27 (t, *J*=7.2 Hz, 3H, CH_3), 1.58 (d, *J*=7.0 Hz, 3H, CH_3), 2.71 (s, 6H, 4-NMe_2), 2.81 (s, 6H, 5-NMe_2), 4.18–4.26 (m, 3H, CH and CH_2), 4.49 (br. s, 1H, NH), 6.53 (d, *J*=8.2 Hz, 1H, 3-H), 6.85 (d, *J*=8.2 Hz, 1H, 6-H), 6.97 (dd, *J*=7.6 Hz, *J*=0.8 Hz, 1H, 2-H), 7.34 (t, *J*=8.4 Hz, 1H, 7-H), 7.54 (dd, *J*=8.3 Hz, *J*=1.0 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 19.3 (CH_3), 44.4 (4,5-NMe_2), 53.1 (CH), 61.1 (OCH_2), 107.1, 113.0, 113.1, 113.7, 121.6, 124.9, 128.7, 137.0, 143.7, 151.1, 175.3 (C=O). HRMS: MH^+ = 330.2184, calc.: 331.2209.

Methyl *N*-[4,5-bis(dimethylamino)naphthalen-1-yl]-*N*-methylglycinate (4e)



Isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.45). Light-yellow oil, 182 mg (58%). ^{1}H NMR ($CDCl_3$): δ = 2.73 (s, 6H, 4-NMe_2), 2.79 (s, 6H, 5-NMe_2), 3.95 (s, 3H, CH_3), 3.71 (s, 3H, OMe), 3.80 (s, 2H, CH_2), 6.85 (m, 2H, 3-H, 6-H), 7.06 (d, *J*=8.1 Hz, 1H, 2-H), 7.29 (d, *J*=8.2 Hz, 1H, 7-H), 7.81 (dd, *J*=7.9 Hz, *J*=0.96 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 29.8 (NMe), 42.1 (4-NMe_2), 44.5 (5-NMe_2), 51.6 (CH_2), 59.0 (OMe), 112.3, 112.5, 116.4, 116.7, 121.6, 125.3, 133.1, 142.9, 147.1, 150.9, 171.8 (C=O). HRMS: MH^+ = 316.2031, calc.: 316.2020.

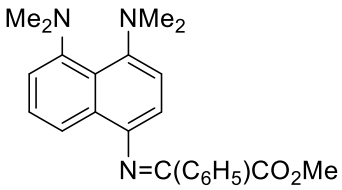
Methyl 2-{[4,5-bis(dimethylamino)naphthalen-1-yl]amino}-2-phenylacetate (4f)



Isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction R_f=0.37, light-beige crystals with mp 131–132 °C (from hexanes), 170 mg (45%). ^{1}H NMR ($CDCl_3$): δ=2.68 (s, 6H, 4-NMe_2), 2.81 (s, 6H, 5-NMe_2), 3.77 (s, 3H, OCH_3), 5.19 (d, *J*=4.9 Hz, 1H, CH), 5.28 (br. s, 1H, NH), 6.35 (d, *J*=8.1 Hz, 1H, 2-H,), 6.76 (d, *J*=8.1 Hz, 1H, 3-H), 6.99 (d, *J*=7.3 Hz, 1H, 6-H), 7.32 (m, 4H, 7-H, Ph), 7.61 (m, 3H, 8-H, Ph). ^{13}C NMR ($CDCl_3$): δ = 44.6 (4 and 5-NMe_2), 51.8 (CH), 61.7 (OMe), 106.8, 111.3, 113.2, 113.5, 121.6, 125.0, 127.4, 128.3, 128.9, 142.9, 136.4, 138.1, 143.3, 151.1, 172.9 (C=O). $C_{23}H_{27}N_3O_2$ (377.49): calcd. C 73.18, H 7.21, N 11.13; found C 73.16, H 7.24, N 11.17.

Figure S1. Air oxidation of ester **4f** to azomethine **5** (view at the bottom of the glass vessel with more colored inclusions of **5**).

Methyl 2-{[4,5-bis(dimethylamino)naphthalen-1-yl]imino}-2-phenylacetate (5)



The hexane remaining after precipitation of the ether was evaporated. Imine was isolated by thin layer chromatography (Al_2O_3, $CHCl_3$, see Figure S2 below) collecting the yellow fraction with R_f=0.46, orange crystals with mp 128–129 °C (from hexanes), 18 mg (5%). ^{1}H NMR ($CDCl_3$): δ = 2.79 (s, 6H, 4-NMe_2), 2.81 (s, 6H, 5-NMe_2), 3.42 (br s, 1H, NH), 3.63 (s, 3H, OMe), 6.78–6.85 (m, 2H, 3-H, 6-H), 6.86 (d, *J*=8.3 Hz, 1H, 7-H), 6.99 (dd, *J*=7.5 Hz, *J*=1.1 Hz, 1H, 8-H), 7.33 (t, *J*=8.1 Hz, 1H, 7-H), 6.49–6.52 (m, 2H, Ph), 7.69 (dd, *J*=8.3 Hz, *J*=1.1 Hz, 1H, 2-H), 7.96–8.00 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ = 44.4 (NMe_2), 51.9 (OMe), 111.9, 113.1, 113.4, 117.3, 120.6, 125.6, 127.9, 128.2, 128.7, 128.9, 131.3, 132.2, 134.6, 140.1, 149.2, 150.7, 157.1 (C=N), 166.5 (C=O). HRMS: MH^+ = 376.2019, calc.: 376.2020.

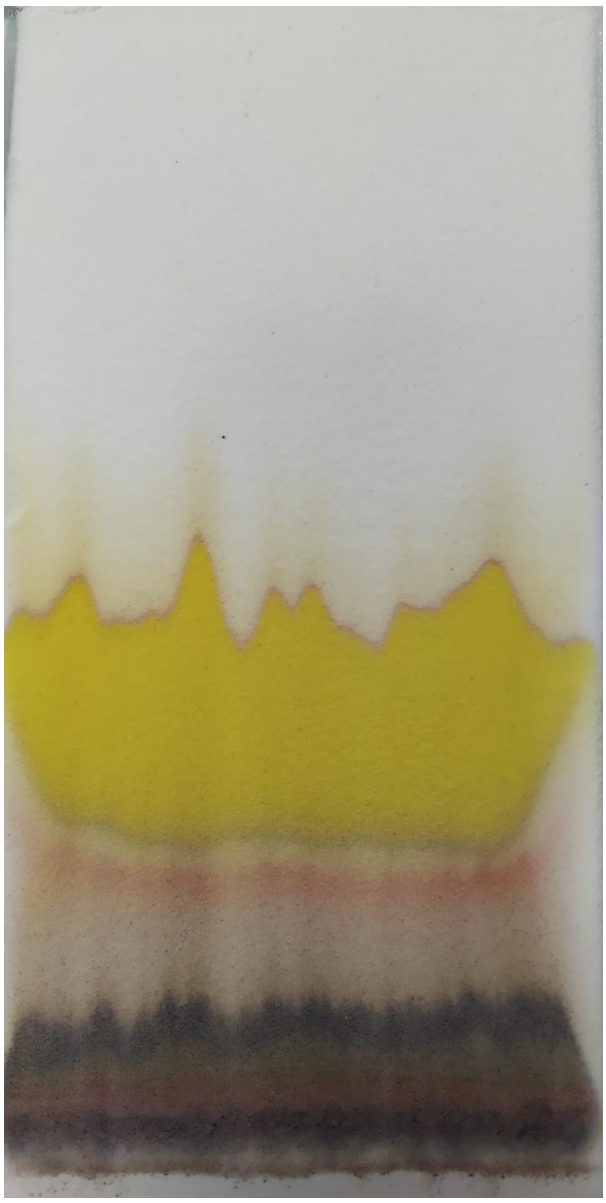
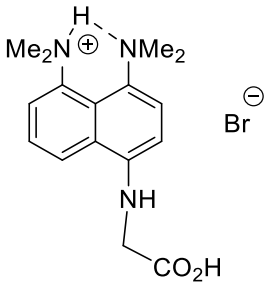


Figure S2. Purification of imine **5** (yellow) by thin layer chromatography.

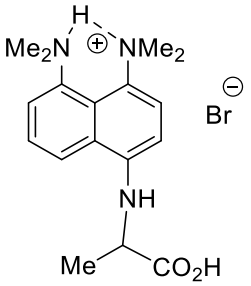
*When the ester **4f** is stirred in methanol in air, it is completely oxidized to imine **5** in 90 hours.

Synthesis of Hydrobromides 6 by Hydrolysis in 45% aq. HBr. A solution of compound **4a**–**e** (0.5 mmol) in 45% aqueous HBr (5 mL) was refluxed for 0.5 h. The crude products obtained after evaporation of volatiles to dryness were washed with diethyl ether to afford **6a**–**c** as light lilac-grey hygroscopic powder.

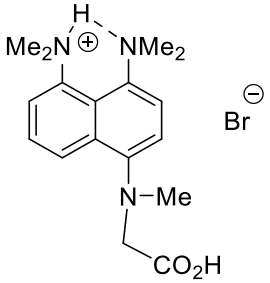
***N*-[4,5-Bis(dimethylamino)naphthalen-1-yl]glycine hydrobromide (6a)** mp 197–199 °C (decomp.); M^+=288.1702, calc.: 288.1707.



***N*-[4,5-Bis(dimethylamino)naphthalen-1-yl]alanine hydrobromide (6b)** M^+= 302.1864, calc.: 302.1863.



***N*-[4,5-Bis(dimethylamino)naphthalen-1-yl]-*N*-methylglycine hydrobromide (6c)** M^+= 302.1866, calc.: 302.1863.



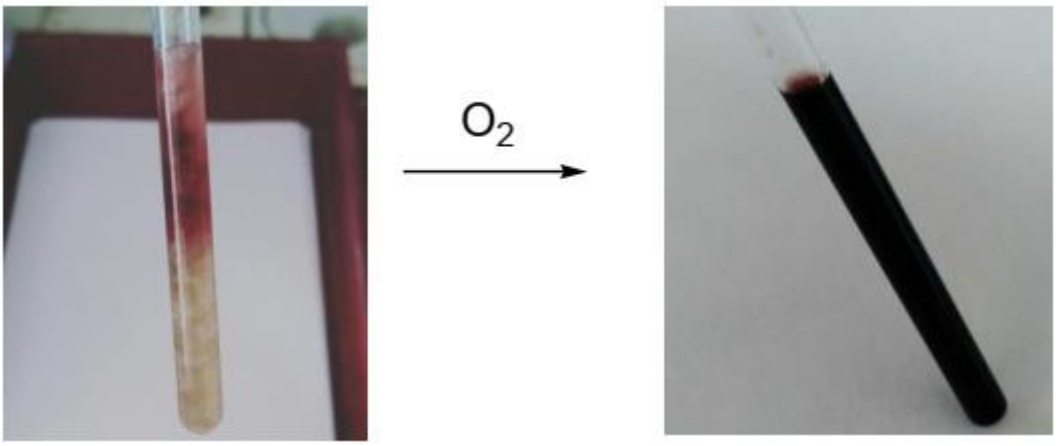
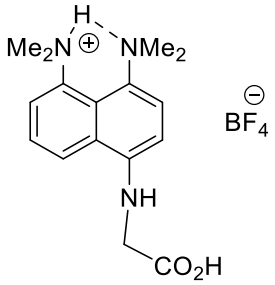


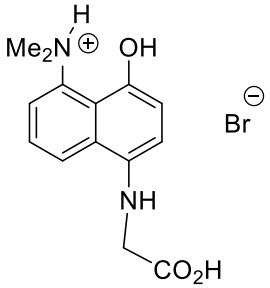
Figure S3. Aerial oxidation of a solution of **6a** in an NMR ampoule (DMSO-d_6, after 1h and 3 h).

***N*-[4,5-Bis(dimethylamino)naphthalen-1-yl]glycine hydrogen tetrafluoroborate (6'a)**



A solution of **4a** (35 mg, 0.116 mmol) in 48% aqueous HBF_4 (0.06 ml, d=1.4 g mL^{-1}, 4 eq., 0.46 mmol) and H_2O (0.3 mL) was kept in a polypropylene tube at 100 °C for 2 h. The crude product obtained after evaporation to dryness was washed with diethyl ether to afford **6'a** as light-grey powder (the yield of a substance is quantitative, 43 mg), mp 186–188 °C (decomp.). ^{1}H NMR (CD_3CN): δ = 3.11 (d, J=1.00 Hz, 6H, 4-NMe_2), 3.12 (s, 6H, J=1.0 Hz, 5-NMe_2), 4.33 (s, 2H, CH_2), 5.76–5.92 (br s, 6H, NH, COOH, H_3O^+), 7.40 (d, J=8.3 Hz, 1H, 2-H), 7.84–7.91 (m, 2H, 3-H, 7-H), 8.03 (dd, J=7.7 Hz, J=0.8 Hz, 1H, 6-H), 8.10 (dd, J=8.5 Hz, J=1.0 Hz, 1H, 8-H), 18.77 (br s, 1H, NH). ^{13}C NMR (CD_3CN): δ = 45.7 and 45.8 (4- and 5-NMe_2), 47.8 (CH_2), 117.7, 120.4, 121.7, 121.9, 122.6, 125.6, 127.5, 129.1, 137.4, 139.5, 145.5, 168.8 (C=O).

***N*-(5-Dimethylamino-4-hydroxynaphthalen-1-yl)glycine hydrobromide (10a)**



Formed from **6a** on standing in a NMR ampoule at room temperature for ca. 2 h. ^{1}H NMR (DMSO-d_6): δ = 3.32 (s, 6H, 5-NMe_2), 3.69 (ABq, 2H, J=5.6 Hz, CH_2), 4.32 (br s, 13H, CO_2H and H_3O^+), 6.88 (d, J=8.4 Hz, 1H, 2-H), 7.94 (d, J=8.3 Hz, 2H, 3-H), 7.57 (t, J=8.1 Hz, 1H, 7-H), 8.02 (d, J=7.2 Hz, 1H, 6-H), 8.20 (d, J=7.8 Hz, 1H, 8-H), 8.42 (br s, 1H, NH), 11.85 (br s, 1H, OH).

Autoxidation of Hydrobromides 6 in Basic Medium. Aqueous ammonia (25%, 10 mL) was added to 0.5 mmol of hydrobromides **6a**–**c**. The resulting mixture was kept in air for 2 h with agitation from time-to-time. The products were extracted with chloroform (3×15 mL), the extract was concentrated to a minimal volume and subjected to first column and then thin layer chromatography (Al_2O_3, $CHCl_3$, see Figure S4 for details).

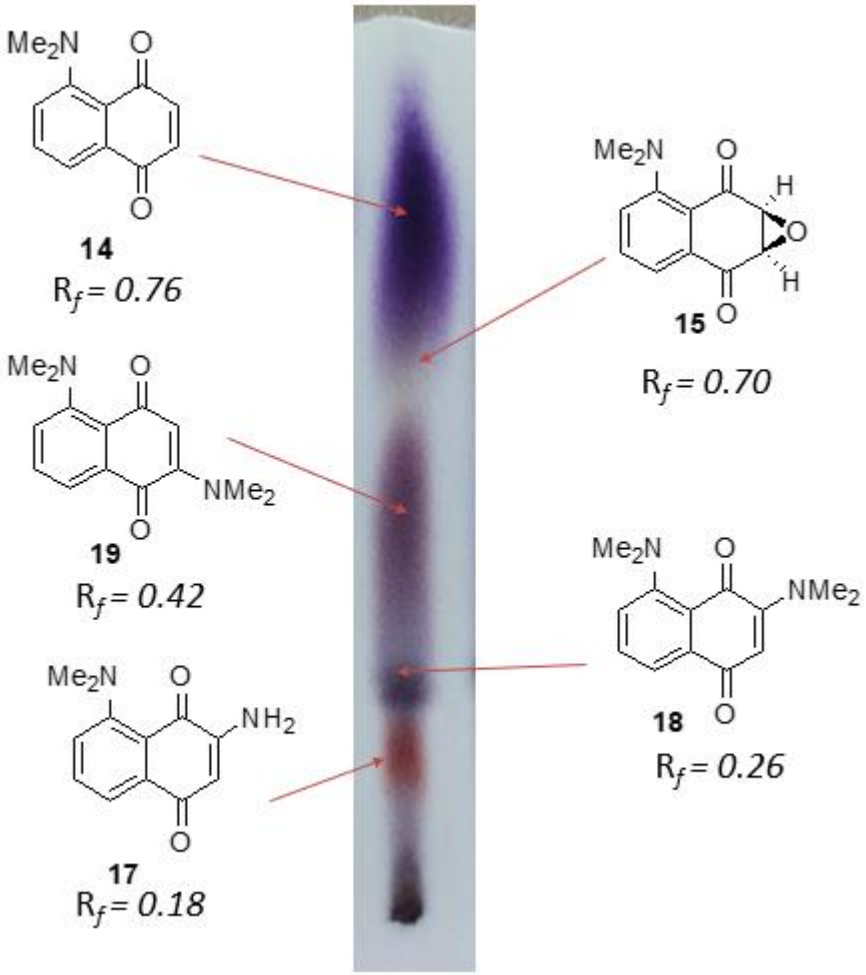
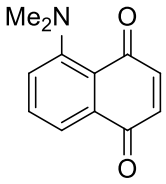


Figure S4. The original (without developing) TLC (Al_2O_3, $CHCl_3$) of hydrolysis/oxidation products.

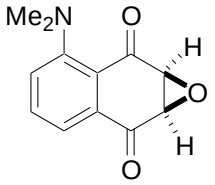
5-(Dimethylamino)naphthalene-1,4-dione (**14**)



Major fraction with R_f=0.76, dark-violet crystals with mp 112–113 °C (from $CDCl_3$), 41–58 mg (41–58%). ^{1}H NMR ($CDCl_3$): δ = 2.95 (s, 6H, NMe_2), 6.79 (d, *J*=10.22 Hz, 1H, 3-H), 6.84 (d, *J*=10.22 Hz, 1H, 2-H), 7.29 (d, *J*=8.39 Hz, 1H, 6-H), 7.49 (t, *J*=8.20 Hz, 1H, 6-H), 7.56 (d, *J*=7.33 Hz, 1H, 8-H). NMR (CD_3CN): δ = 2.93 (s, 6H, NMe_2), 6.80 (d, *J*=10.2 Hz, 1H, 3-H), 6.87 (d, *J*=10.2 Hz, 1H, 2-H), 7.45 (dd, *J*=6.9 Hz, *J*=1.3 Hz, 1H, 6-H), 7.50 (dd, *J*=7.2 Hz, *J*=1.5 Hz, 1H, 8-H), 7.57 (dd, *J*=7.2, *J*=8.3, 1H, 7-H). ^{13}C NMR ($CDCl_3$): δ = 44.1 (5-NMe_2), 118.0, 122.7, 133.2, 135.0, 135.5, 141.2, 152.4, 183.1 (C=O), 186.1 (C=O). IR (nujol), ν/cm^{-1}: 1651 (C=O). HRMS: MH^+ = 202.0854, calc.: 202.0863.

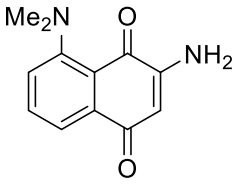
Tetrafluoroborate 14·HBF$_4$: decomposed at 172–174 °C (from MeCN). ^{1}H NMR (CD_3CN): δ = 3.35 (s, 6H, NMe_2), 7.16 (s, 2H, 2-H, 3-H), 8.11 (m, 1H, 7-H), 8.21 (dd, *J*=8.3 Hz, *J*=1.4 Hz, 1H, 8-H), 8.3 (dd, *J*=7.58 Hz, *J*=1.3 Hz, 1H, 6-H), 11.44 (s, 1H, NH).

3-Dimethylamino-1a,7a-dihydronaphtho[2,3-*b*]oxirene-2,7-dione (**15**)



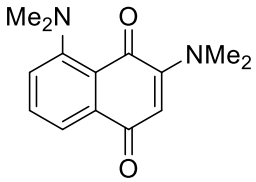
Major fraction with R_f=0.70, yellow crystals with mp 115–116 °C (from hexanes), 2–5 mg (2–5%). ^{1}H NMR ($CDCl_3$): δ = 2.90 (s, 6H, $NMe)_2$, 3.94 and 3.99 (both d, *J*=4.24 Hz, 1H, 1aH,7aH), 7.20 (dd, *J*=8.52 Hz, *J*=1.05 Hz, 1H, 4-H), 7.39 (dd, *J*=7.39 Hz, *J*=1.09 Hz, 1H, 6-H), 7.46 (t, *J*=7.39 Hz, 1H, 6-H). ^{13}C NMR ($CDCl_3$): δ = 43.6 (NMe_2), 54.9, 122.7, 56.7, 116.7, 117.8, 121.7, 133.2, 133.6, 151.8, 191.1 (C=O), 191.6 (C=O). IR (nujol), ν/cm^{-1}: 1687 (C=O). HRMS: MH^+ = 218.0809, calc.: 218.0812.

2-Amino-8-(dimethylamino)naphthalene-1,4-dione (**17**)



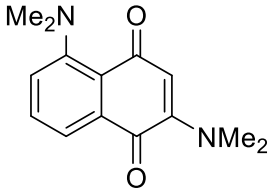
Major fraction with R_f=0.18, red crystals with mp 139–140 °C (from $CDCl_3$), 2–7 mg (2–7%). ^{1}H NMR NMR ($CDCl_3$): δ = 2.93 (s, 6H, 8-NMe_2), 3.13 (s, 6H, 2-NMe_2), 5.69 (s,1H, 3-H). 7.11 (dd, *J*=9.11 Hz, *J*=0.99 Hz, 1H, 7-H), 7.43 (t, *J*=7.29 Hz, 1H, 6-H), 7.55 (dd, *J*=7.34 Hz, *J*=0.94 Hz, 1H, 5-H). ^{13}C NMR ($CDCl_3$): δ = 44.1 (8-NMe_2), 102.8, 116.8, 117.9, 121.1, 134.2, 136.7, 150.4, 153.2, 178.0 (C=O), 184.2 (C=O). IR (nujol), ν/cm^{-1}: 1668 (C=O). HRMS: MH^+ = 217.0972, calc.: 217.0972.

2,8-Bis(dimethylamino)naphthalene-1,4-dione (**18**)



Major fraction with R_f=0.26, dark-orange crystals with mp 164–165 °C (from EtOH), 1–3 mg (1–3%). ^{1}H NMR ($CDCl_3$): δ = 2.93 (s, 6H, 8-NMe_2), 3.13 (s, 6H, 2-NMe_2), 5.69 (s, 1H, 3-H). 7.11 (dd, *J*=8.52 Hz, *J*=0.99 Hz, 1H, 7-H), 7.43 (t, *J*=7.35 Hz, 1H, 6-H), 7.55 (dd, *J*=7.29 Hz, *J*=0.99 Hz, 1H, 5-H). ^{13}C NMR ($CDCl_3$): δ = 41.7 (8-NMe_2), 44.0 (2-NMe_2), 104.5, 116.3, 119.4, 119.7, 133.2, 135.8, 151.4, 156.3, 182.9 (C=O), 183.3 (C=O). IR (nujol), ν/cm^{-1}: 1693 (C=O). HRMS: MNa^+ = 267.1104, calc.: 267.1104.

2,5-Bis(dimethylamino)naphthalene-1,4-dione (**19**)



Major fraction with R_f=0.42, dark-maroon crystals with mp 89–90 °C (from hexanes), 7–14 mg (6–12%). ^{1}H NMR ($CDCl_3$): δ = 2.13 (s, 6H, 5-NMe_2), 3.09 (s, 6H, 2-NMe_2), 5.71 (s, 1H, 3-H). 7.22 (dd, *J*=8.42 Hz, *J*=0.98 Hz, 1H, 6-H), 7.27 (dd, *J*=7.39 Hz, *J*=1.09 Hz, 1H, 3-H), 7.49 (dd, *J*=7.39 Hz, *J*=1.09 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$): δ = 41.8 (5-NMe_2), 44.3 (2-NMe_2), 110.1, 118.4, 119.4, 122.8, 133.2, 131.7, 135.8, 151.1, 151.7, 183.1 (C=O), 184.2 (C=O). IR (nujol), ν/cm^{-1}: 1651 (C=O). HRMS: MH^+ = 245.1285, calc.: 245.1290.

Reaction of 5-(dimethylamino)naphthalene-1,4-dione (14) with hydrogen peroxide

Quinone **14** (35 mg) was stirred with aqueous H_2O_2 (3%, 3 mL) for 2 h at 30 °C. The resulting mixture was evaporated to dryness. The crude product was purified by column chromatography (Al_2O_3, $CHCl_3$) to give epoxide **15** in yield of 35 mg (93%).

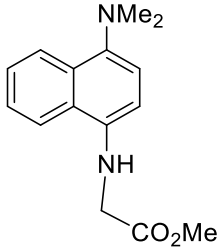
Reaction of 5-(dimethylamino)naphthalene-1,4-dione (14) with dimethylamine

Quinone **14** (35 mg) was stirred with Me_2NH solution (33% aq., 3 mL) at room temperature for 1 h in contact with air. The resulting mixture was evaporated to dryness. The crude product was purified by column chromatography (Al_2O_3, $CHCl_3$) to give diaminoquinones **18** (7.6 mg, 18%) and **19** (9 mg, 21%).

Reaction of 5-(dimethylamino)naphthalene-1,4-dione (14) with NH_4OH

Quinone **14** (40 mg) was stirred with conc. aq. ammonia (5 mL) at room temperature for 1 h in contact with air. The resulting mixture was evaporated to dryness. The crude product was purified by column chromatography (Al_2O_3, $CHCl_3$) to give quinone **17** (1.3 mg, 3%).

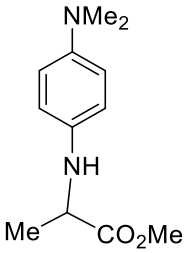
Methyl *N*-(4-dimethylaminonaphthalen-1-yl)glycinate



was isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.40). Light-beige crystals with mp 69–70 °C (from hexanes), 191 mg (74%). ^{1}H NMR ($CDCl_3$): δ = 2.88 (s, 6H, NMe_2), 3.84 (s, 3H, OMe), 4.06 (s, 2H, CH_2), 4.88 (br. s, 1H, NH), 6.44 (d, *J*=8.4 Hz, 1H, 3-H), 7.08 (d, *J*=7.7 Hz, 1H, 7-H), 7.47–7.59 (m, 2H, 2-H, 5-H), 7.93 (dd, *J*=7.0 Hz, *J*=1.5 Hz, 1H, 6-H), 8.37 (d, *J*=7.3 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ = 45.7 (NMe_2), 46.2 (NCH_2), 52.3 (OMe),

104.7, 114.9, 120.6, 124.6, 124.9, 125.2, 125.7, 129.8, 138.6, 142.5, 171.8 (C=O). HRMS: MH^+ = 259.1443, calc.: 259.1441.

Methyl *N*-(4-dimethylaminophenyl)alaninate



was isolated by column chromatography (Al_2O_3, $CHCl_3$) collecting the major fraction (R_f=0.45). Wight crystals with mp 51–52 °C (from hexanes), 138 mg (62%). ^1H NMR ($CDCl_3$): δ = 1.43 (d, *J*=7.0 Hz, 3H, CH_3), 2.80 (s, 6H, NMe_2), 3.69 (s, 3H, CH_3), 3.75 (br. s, 1H, NH), 4.03 (q, *J*=6.8 Hz, 1H, CH), 6.59 (d, *J*=8.7 Hz, 2H, 3-H, 5-H),), 6.69 (d, *J*=8.9 Hz, 2H, 2-H, 6-H). ^{13}C NMR ($CDCl_3$): δ = 19.2 (CH_3), 42.0 (NMe_2), 52.2, 53.0, 115.4, 115.5, 138.7, 144.8, 175.6 (C=O). HRMS: MH^+ = 223.1444, calc.: 223.1441.

Attempted Hydrolysis/Autoxidation of 4f. A solution of ester **4f** (100 mg) in 45% aqueous HBr (2 mL) was refluxed for 0.5 h. The crude product obtained after evaporation of the acid was washed with diethyl ether to afford dark-grey powder, which was treated with aqueous ammonia (25%, 5 mL), and the resulting mixture was kept in air for 2 h. The products were extracted with chloroform (3×10 mL). The chloroform was evaporated and an attempt was made to separate the reaction products by TLC (Al_2O_3, $CHCl_3$, see Figure). However, none of the products was obtained in pure form and could be identified. According to chromatography (Al_2O_3, $CHCl_3$) the reaction mixture does not contain 5-(dimethylamino)naphthalene-1,4-dione (**14**).

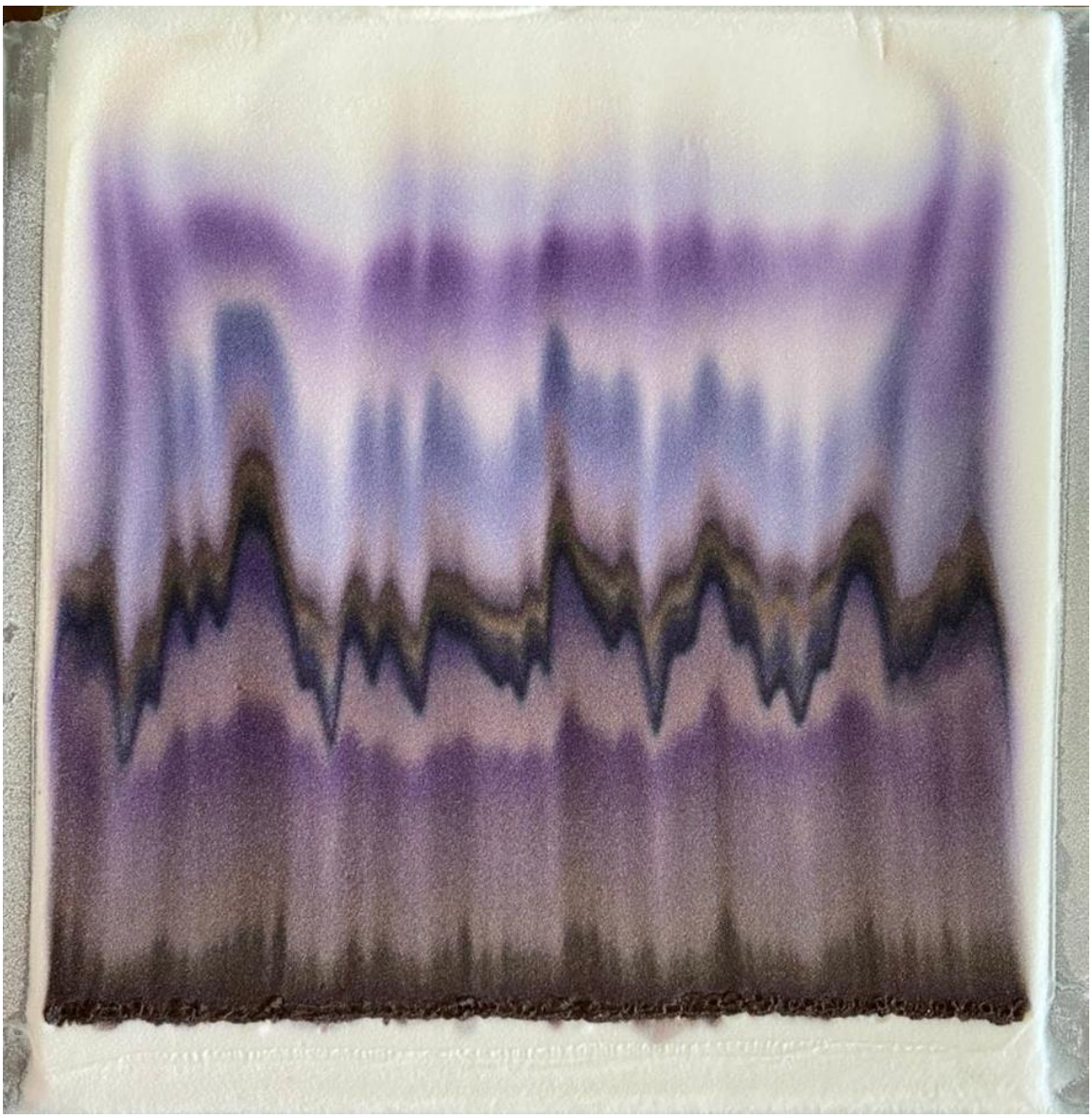


Figure S5. Thin layer chromatogram of hydrolysis/oxidation products derived from **4f**.

Hydrolysis/oxidation of methyl *N*-(4-dimethylaminonaphthalen-1-yl)glycinate under the same conditions (see above) gives a complex mixture that does not contain unsubstituted naphthoquinone-1,4 (Figure S6).

Hydrolysis/oxidation of methyl *N*-(4-dimethylaminophenyl)alaninate under the same conditions (see above) gives *N*,*N*-dimethyl-*p*-phenylenediamine as the sole product.

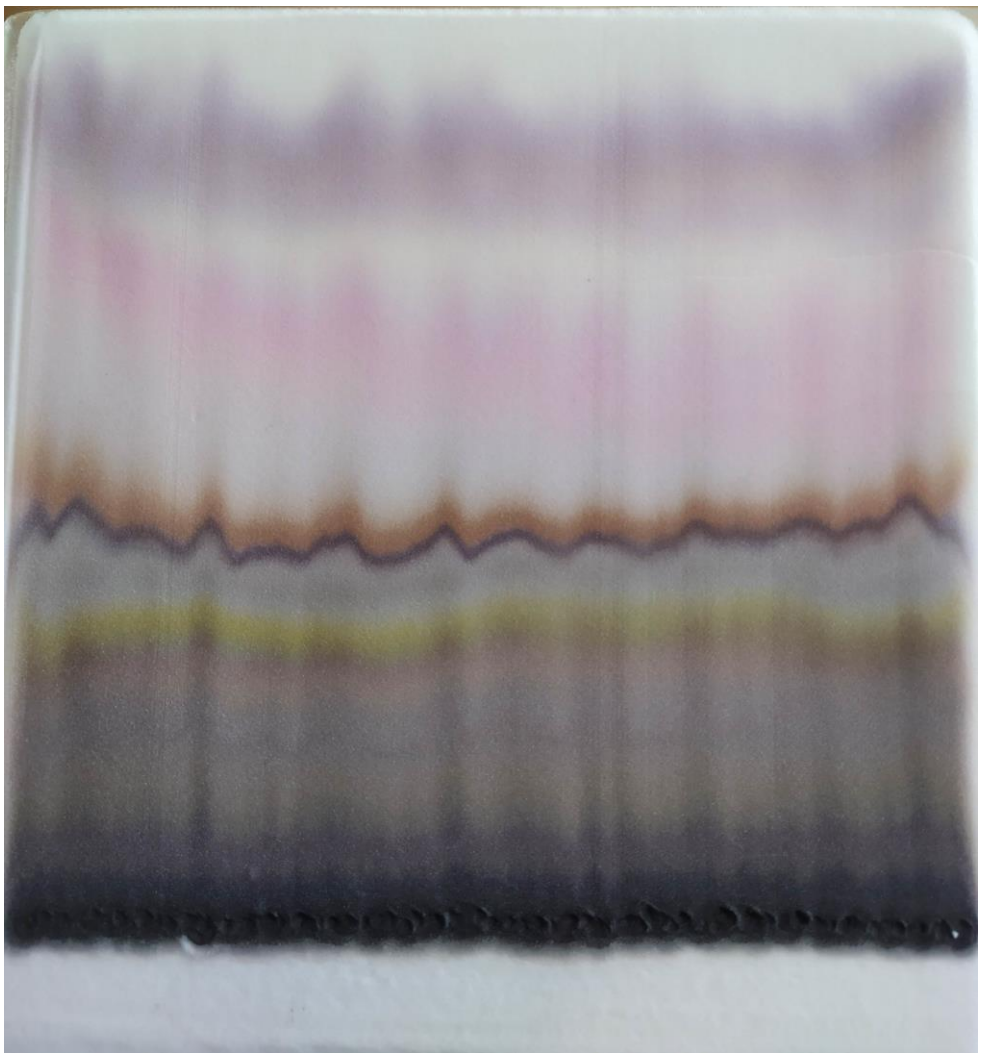
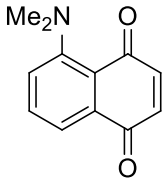
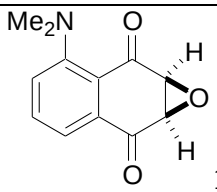
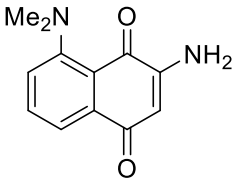
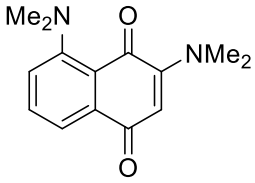
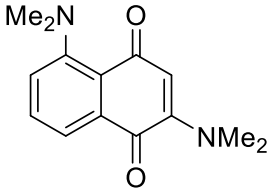


Figure S6. Thin layer chromatogram of hydrolysis/oxidation products derived from methyl *N*-(4-dimethylaminonaphthalen-1-yl)glycinate.

Table S1. UV/Vis Spectroscopic characterization of new naphthoquinones.

Compound	λ_{max}/nm (lgε) ($CHCl_3$)	End absorption up to, nm
 **14**	304 (4.00) 416 (3.05) 544 (3.63)	670
 **15**	324 (3.59) 446 (3.64)	540
 **17**	252 (4.35) 285 (4.17) 411 (3.58) 518 (3.75)	620
 **18**	267 (4.27) 447 (3.79)	620
 **19**	287 (4.23) 526 (3.65)	640

14 **19** **17** **18** **15**

[concentrated (*above*) and diluted (*below*) $CHCl_3$ solutions of the corresponding compounds]

^{1}H and ^{13}C NMR spectra of new compounds

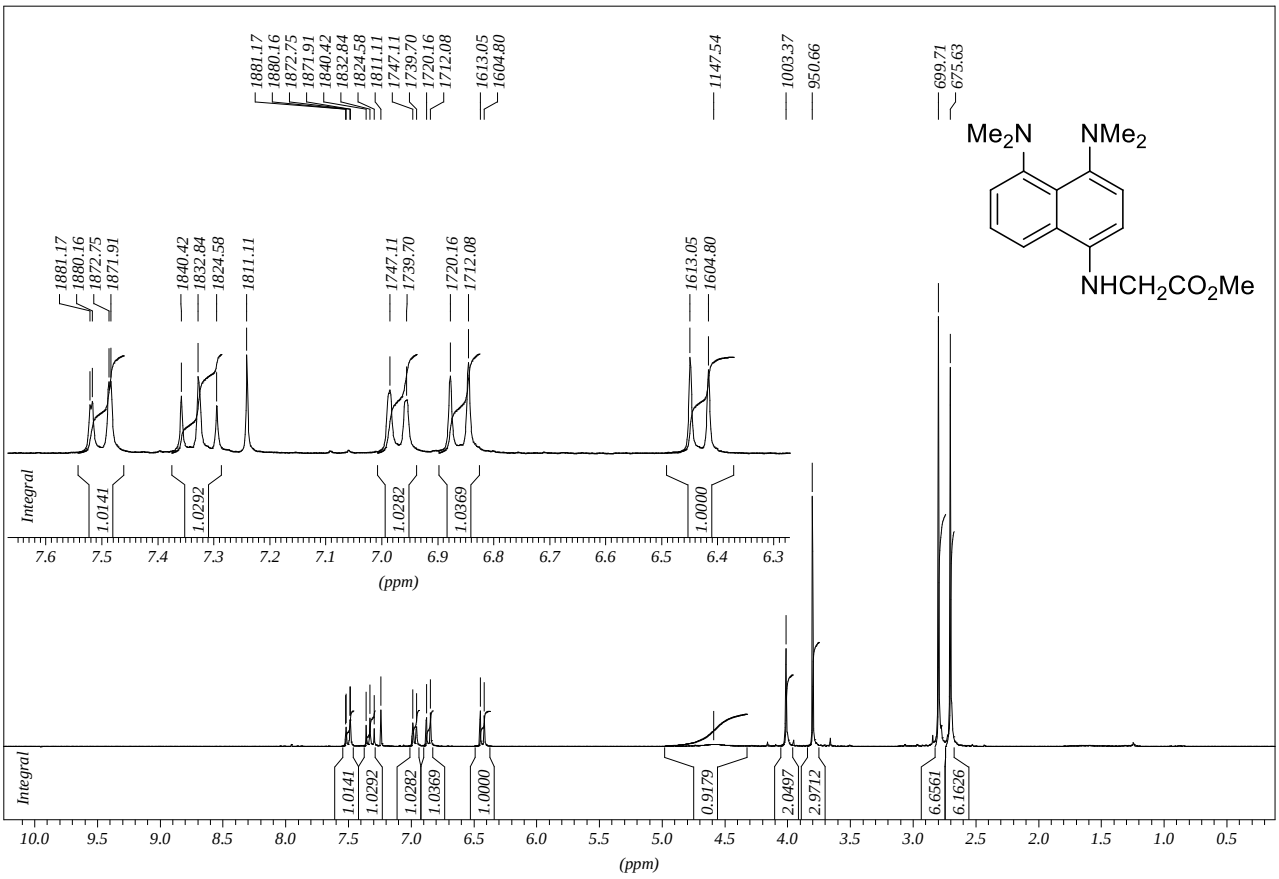


Figure S7. ^{1}H NMR spectrum of **4a** ($CDCl_3$, 250 MHz).

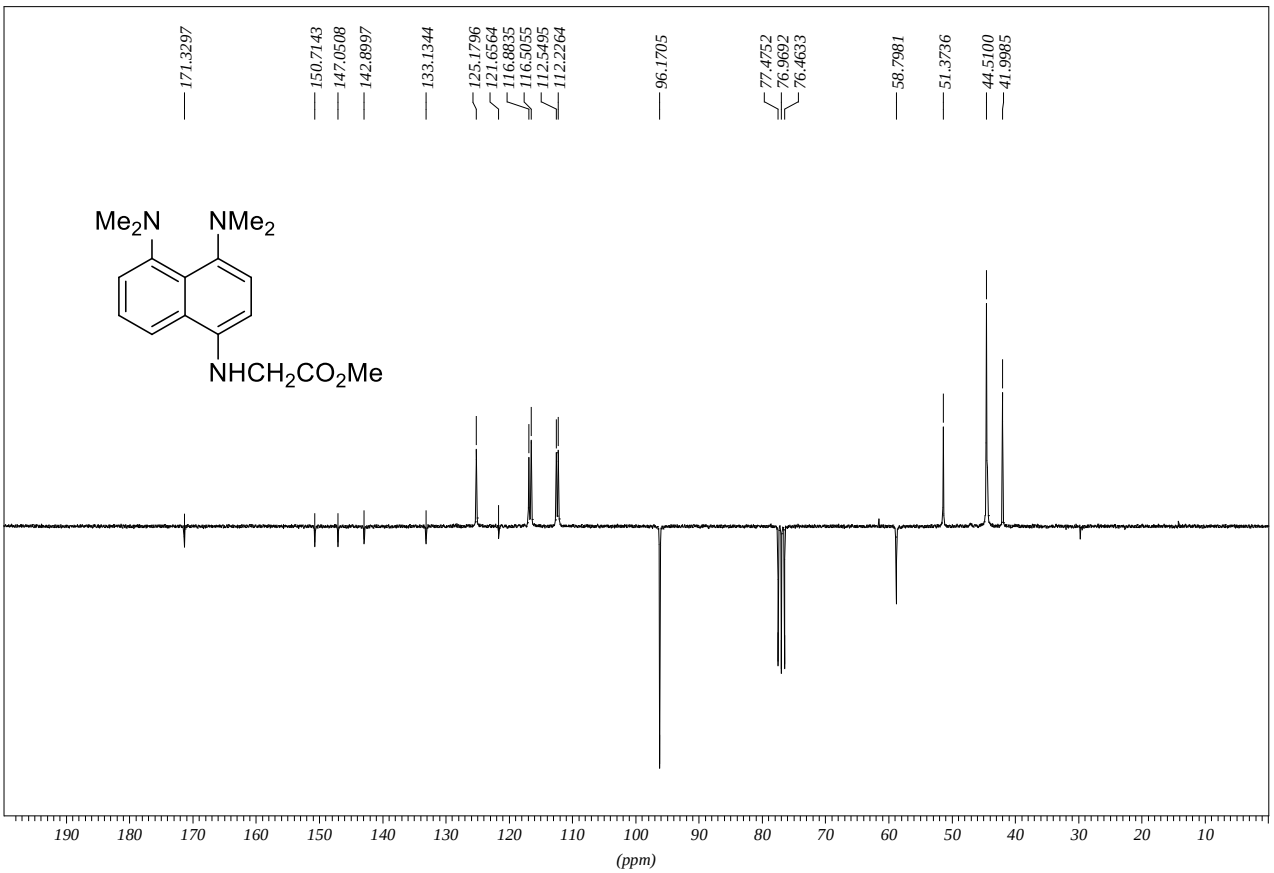


Figure S8. ^{13}C{^{1}H} APT-NMR spectrum of **4a** ($CDCl_3$, 62.9 MHz).

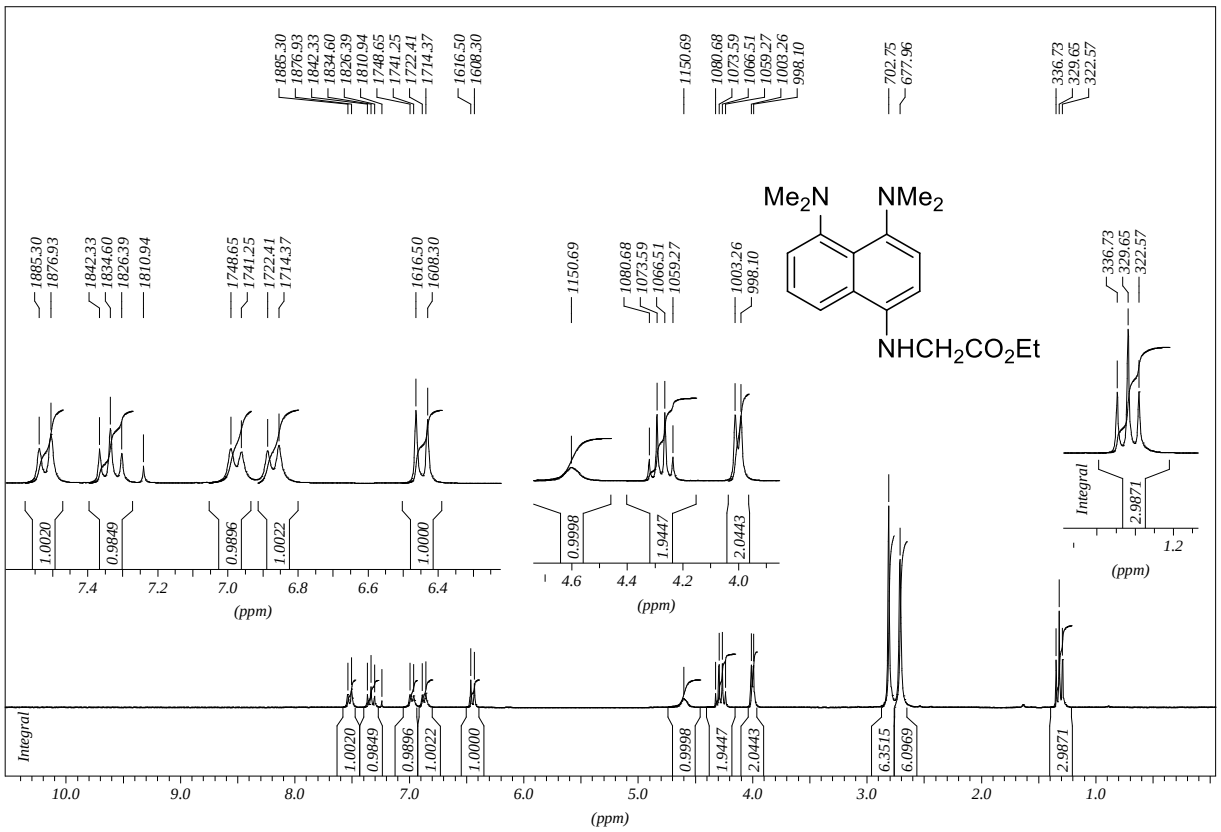


Figure S9. ^{1}H NMR spectrum of **4b** ($CDCl_3$, 250 MHz).

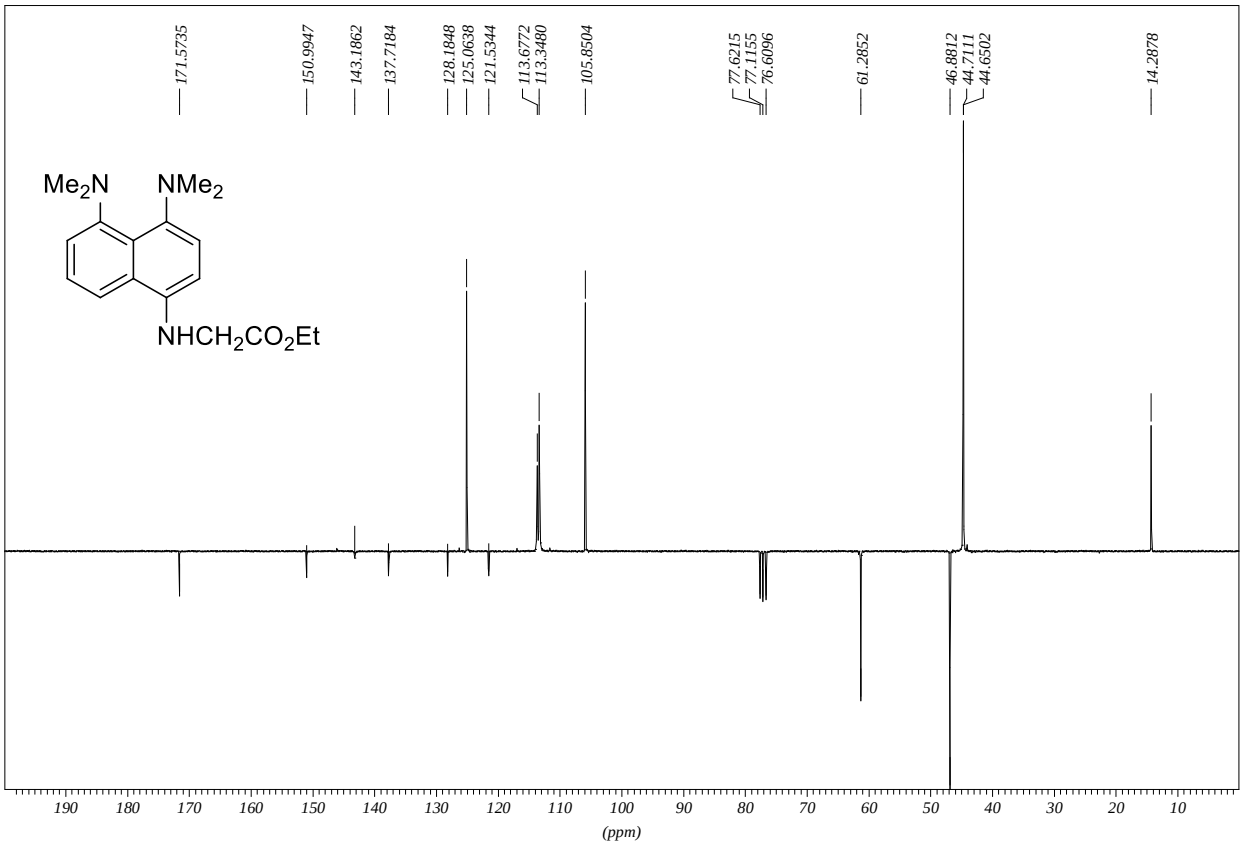


Figure S10. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4b** ($CDCl_3$, 62.9 MHz).

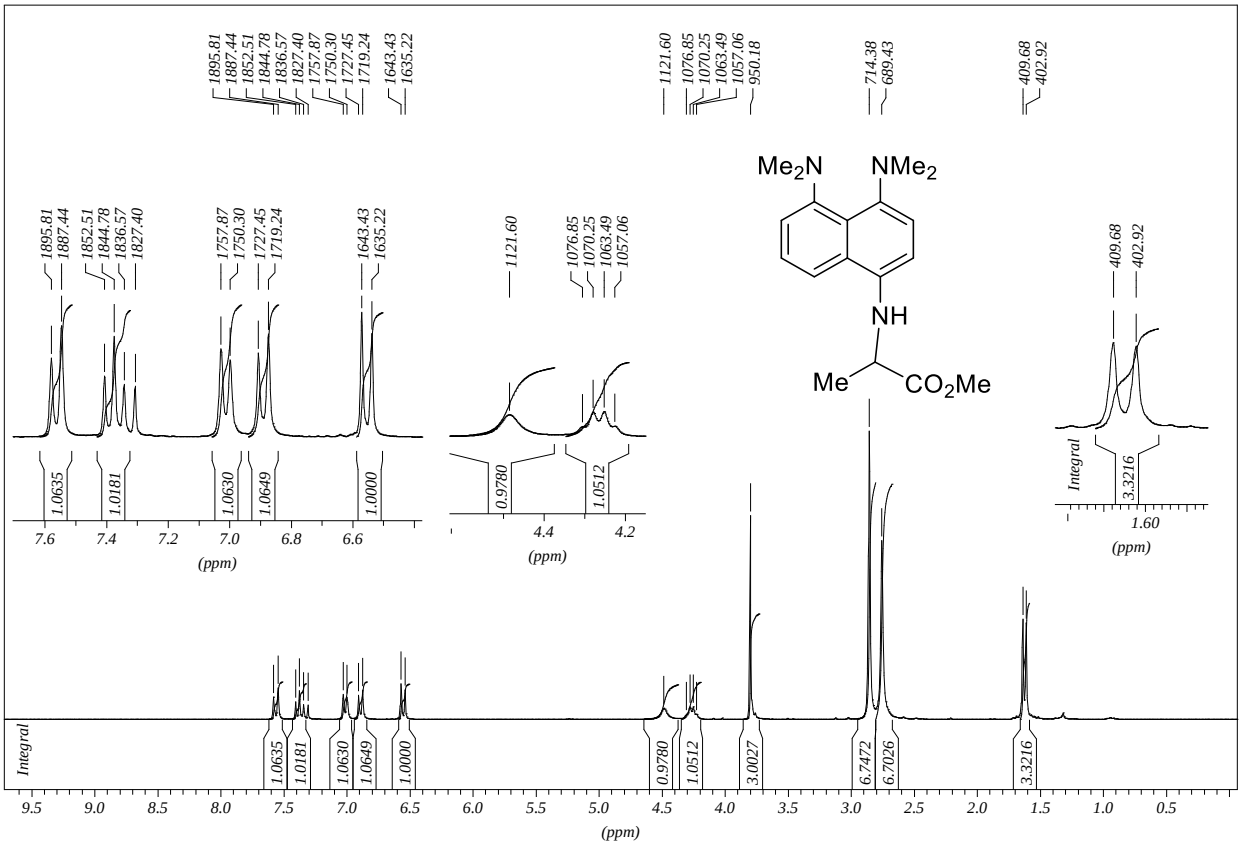


Figure S11. ^{1}H NMR spectrum of **4c** ($CDCl_3$, 250 MHz).

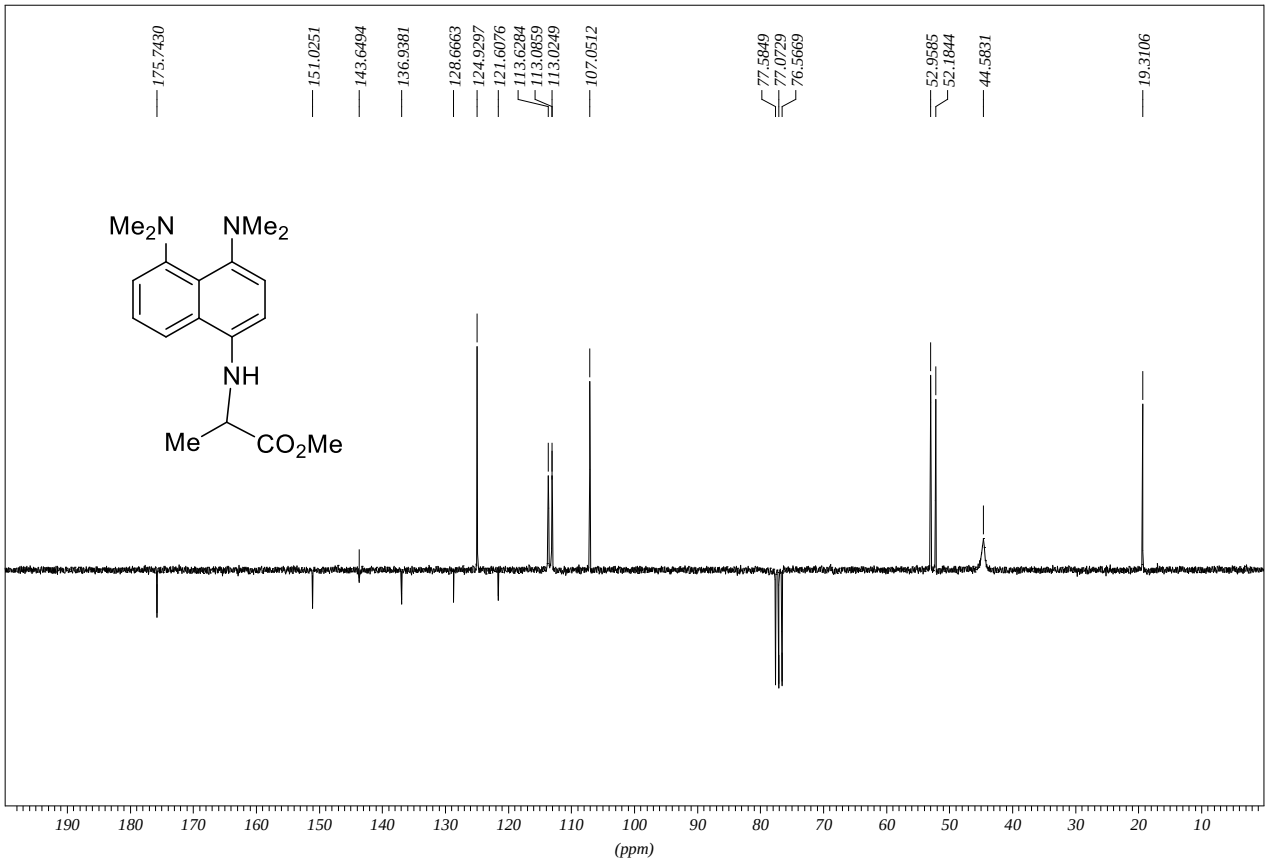


Figure S12. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4c** ($CDCl_3$, 62.9 MHz).

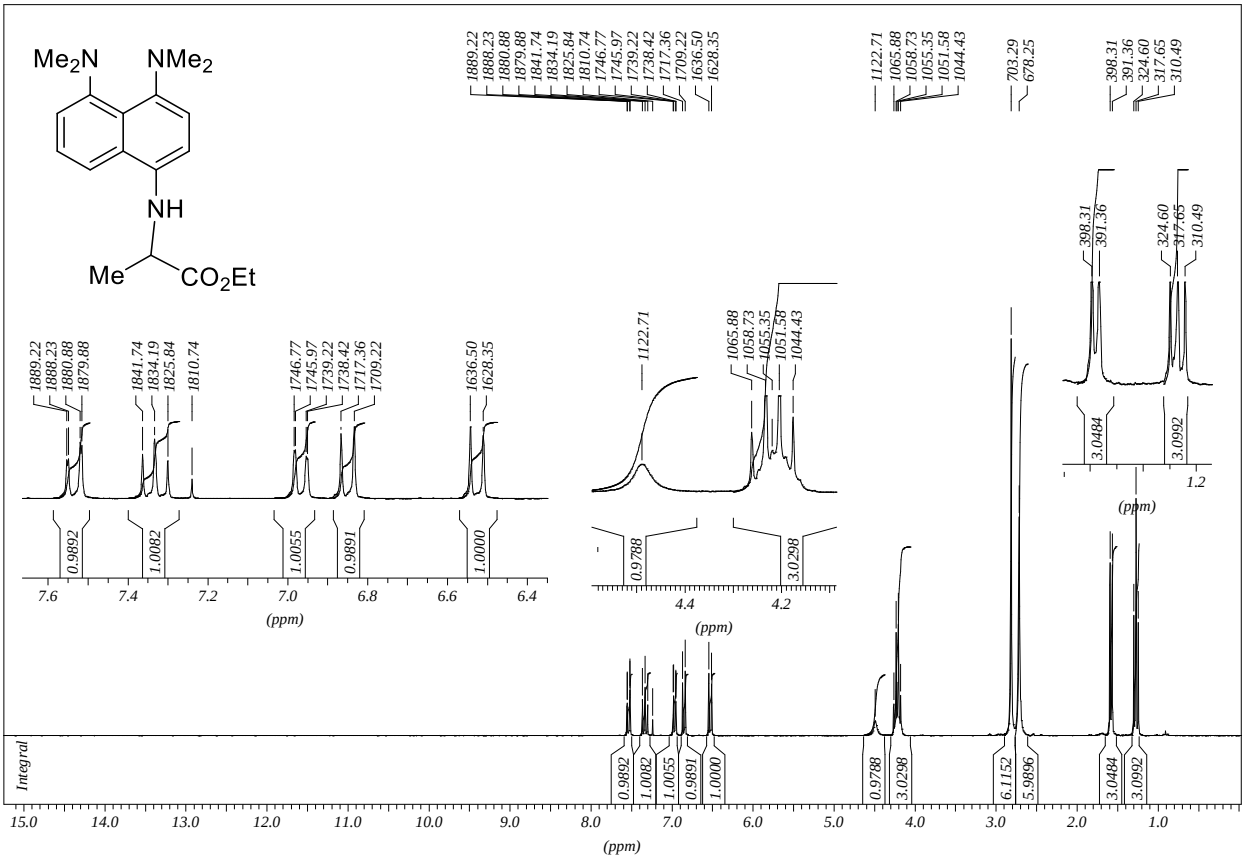


Figure S13. ^{1}H NMR spectrum of **4d** ($CDCl_3$, 250 MHz).

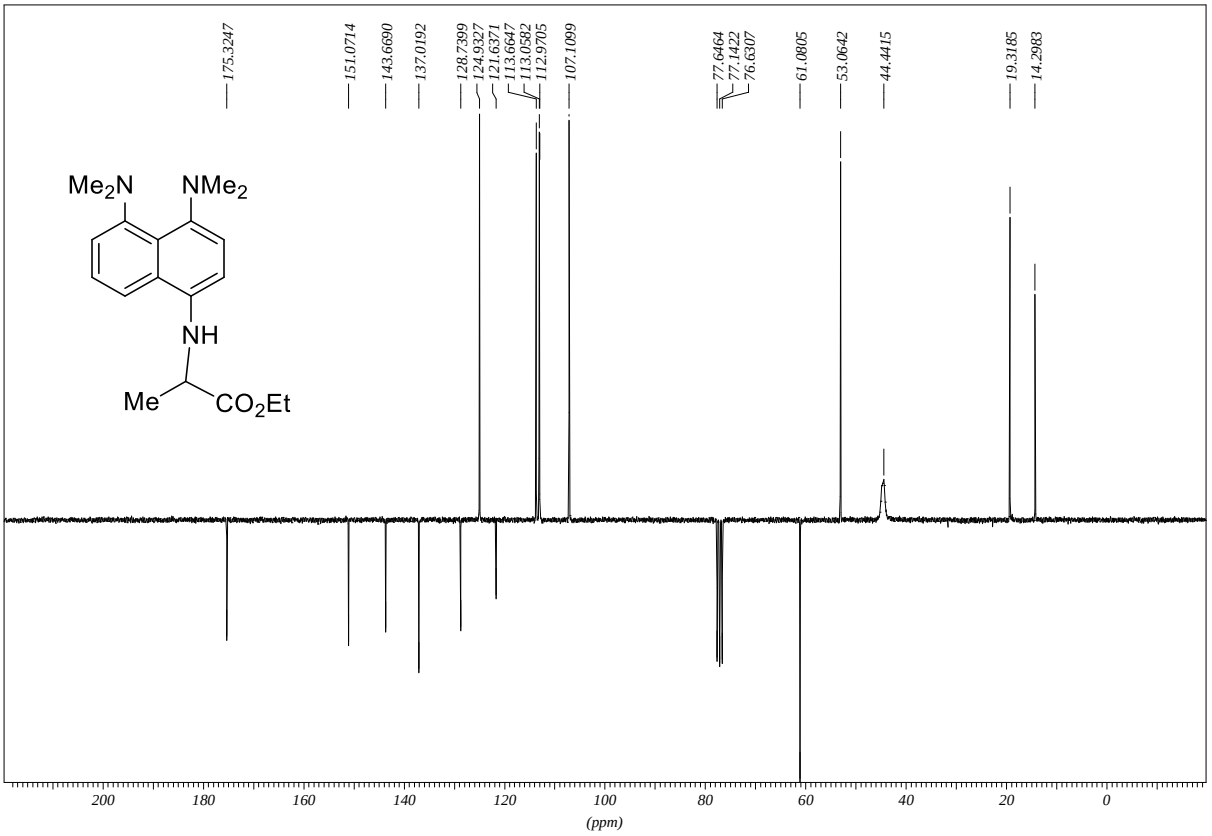


Figure S14. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4d** ($CDCl_3$, 62.9 MHz).

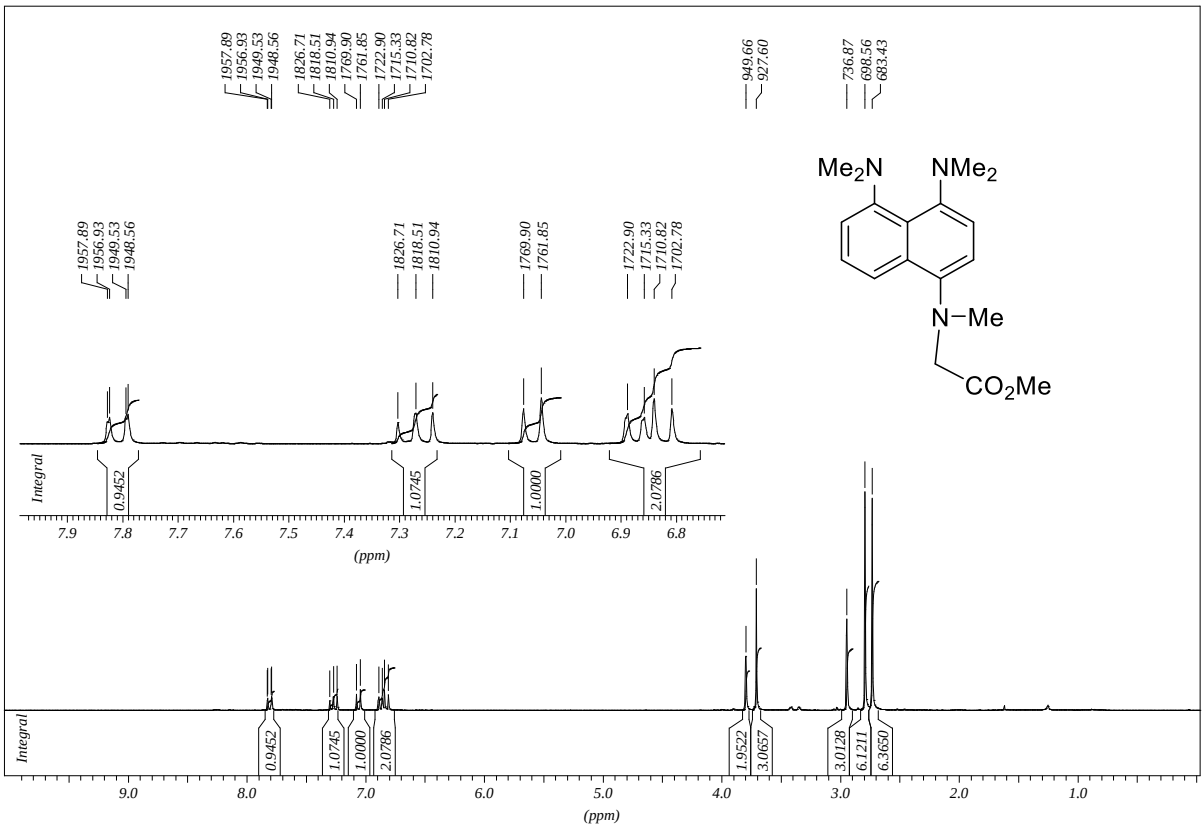


Figure S15. ^{1}H NMR spectrum of **4d** ($CDCl_3$, 250 MHz).

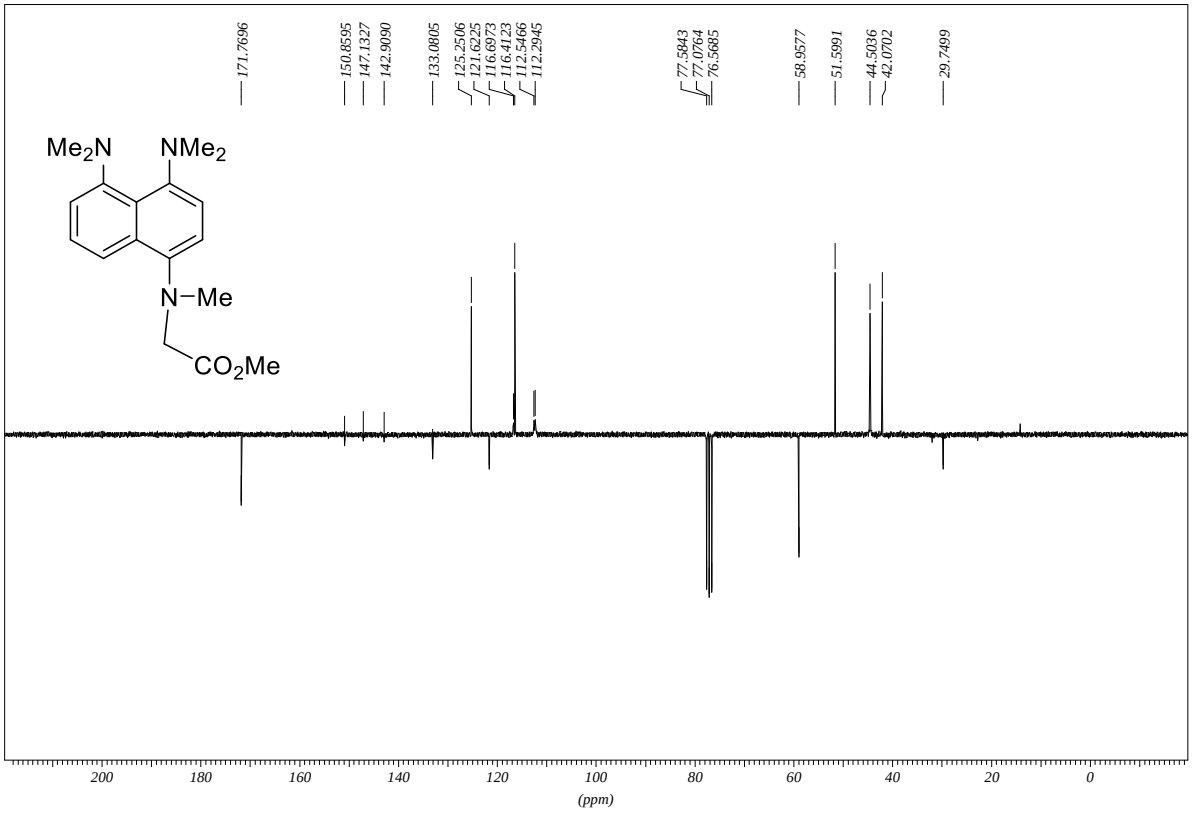


Figure S16. ^{13}C{^{1}H} APT-NMR spectrum of **4d** ($CDCl_3$, 62.9 MHz).

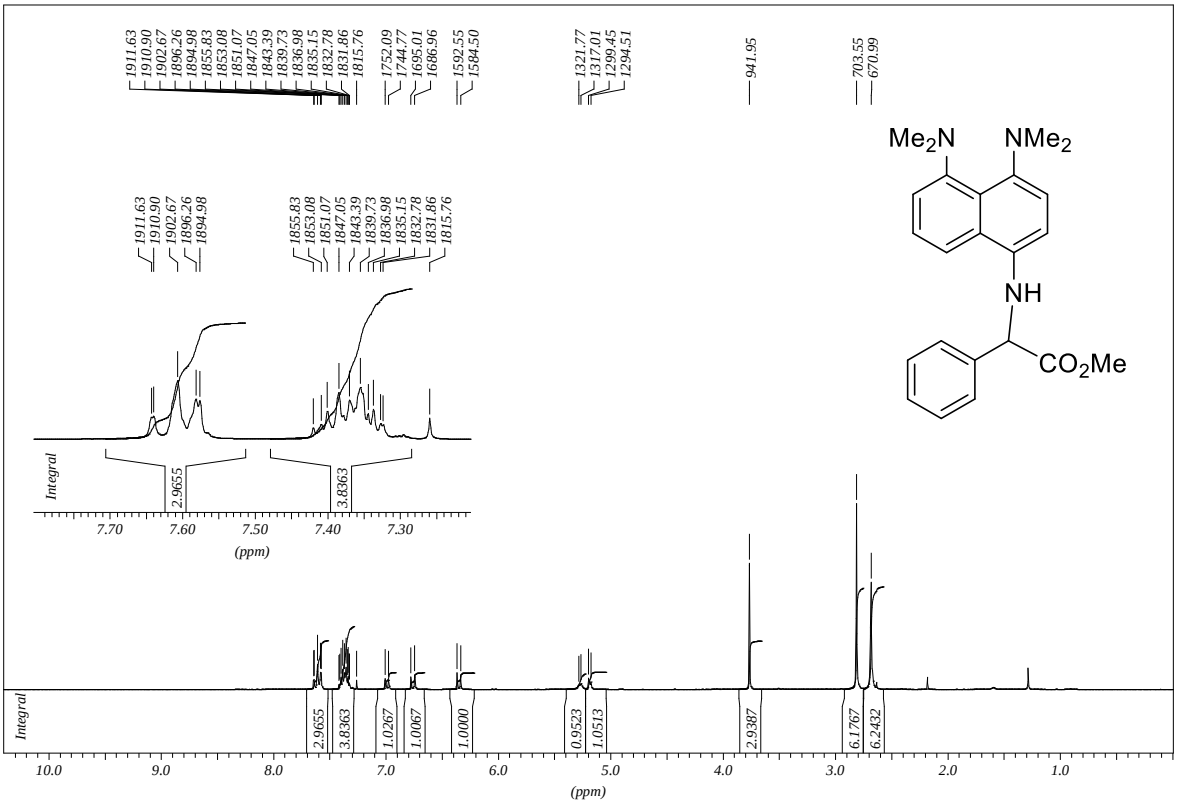


Figure S17. ^{1}H NMR spectrum of **4f** ($CDCl_3$, 250 MHz).

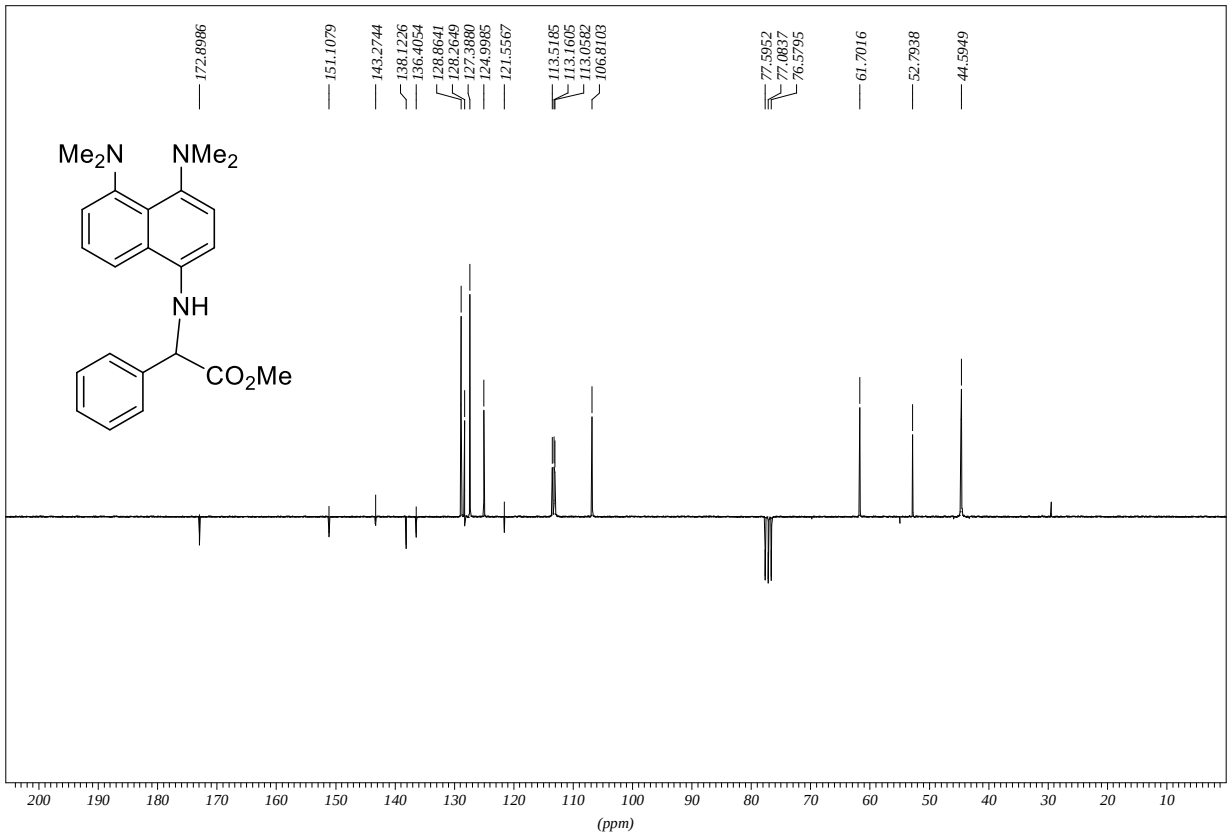


Figure S18. ^{13}C{^{1}H} APT-NMR spectrum of **4f** ($CDCl_3$, 62.9 MHz).

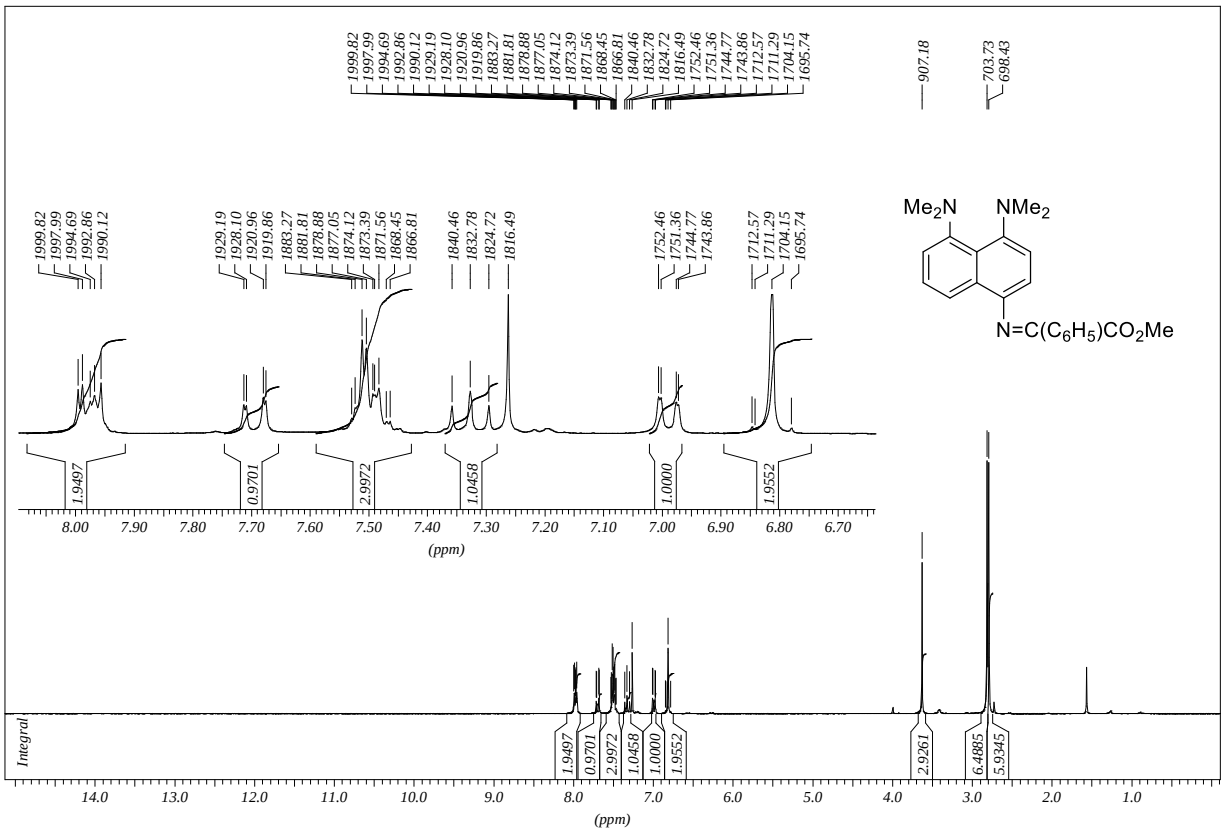


Figure S19. ^{1}H NMR spectrum of **5** ($CDCl_3$, 250 MHz).

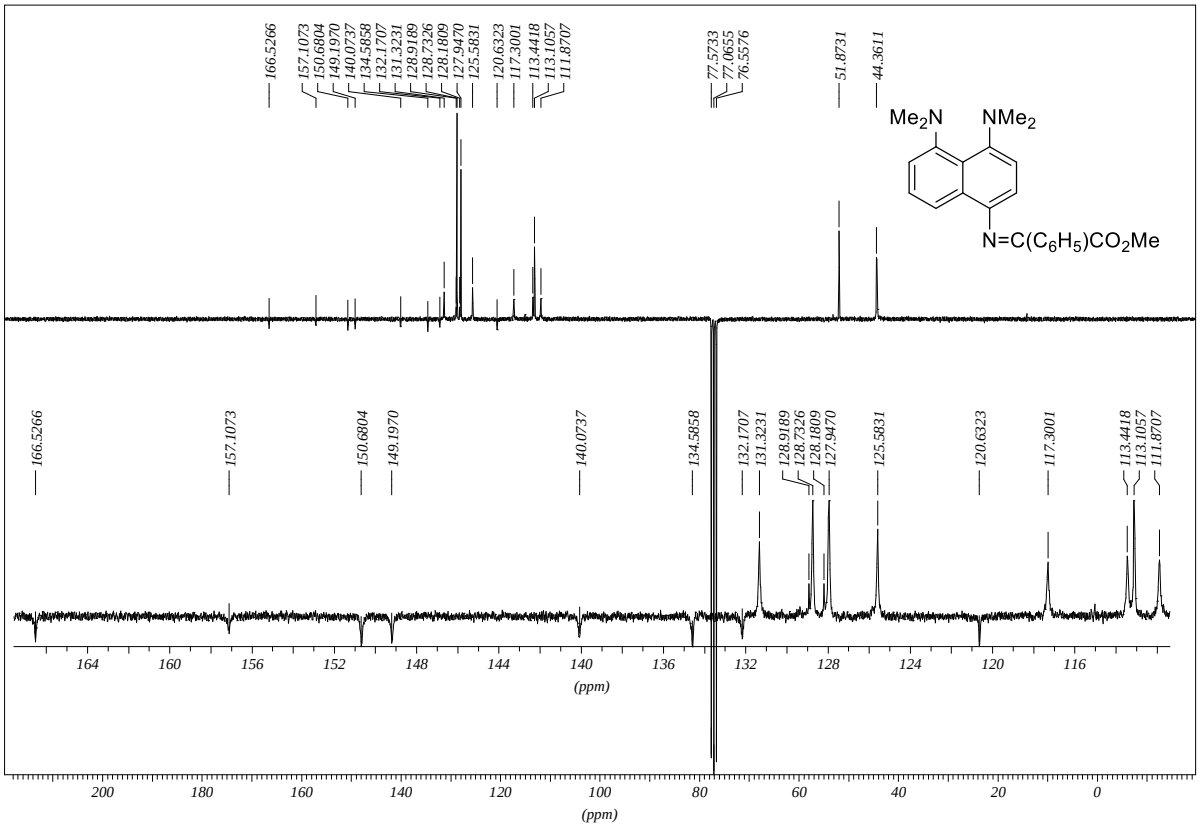


Figure S20. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4** ($CDCl_3$, 62.9 MHz).

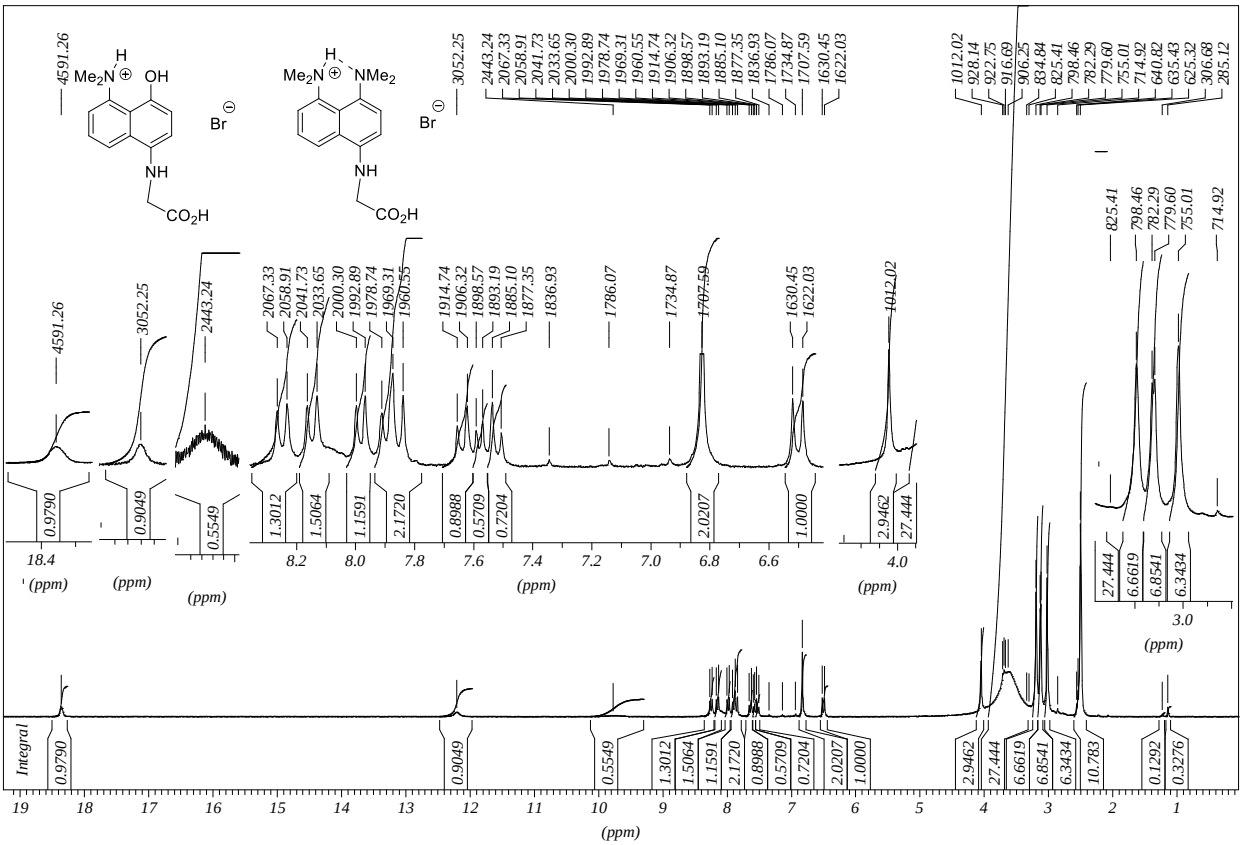


Figure S21. ^{1}H NMR spectrum of **10a** and **6a** as a ~1:1 mixture (DMSO-d_6, 250 MHz).

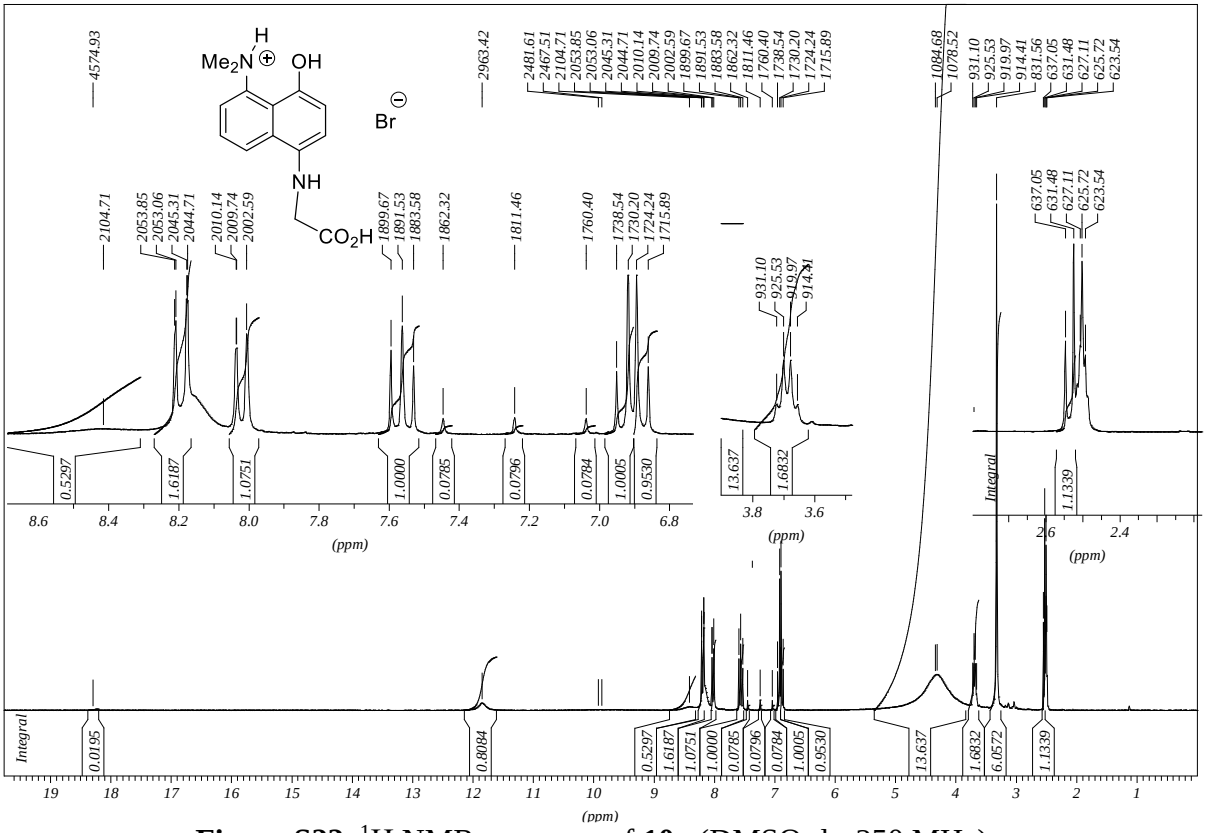


Figure S22. ^{1}H NMR spectrum of **10a** (DMSO-d_6, 250 MHz).

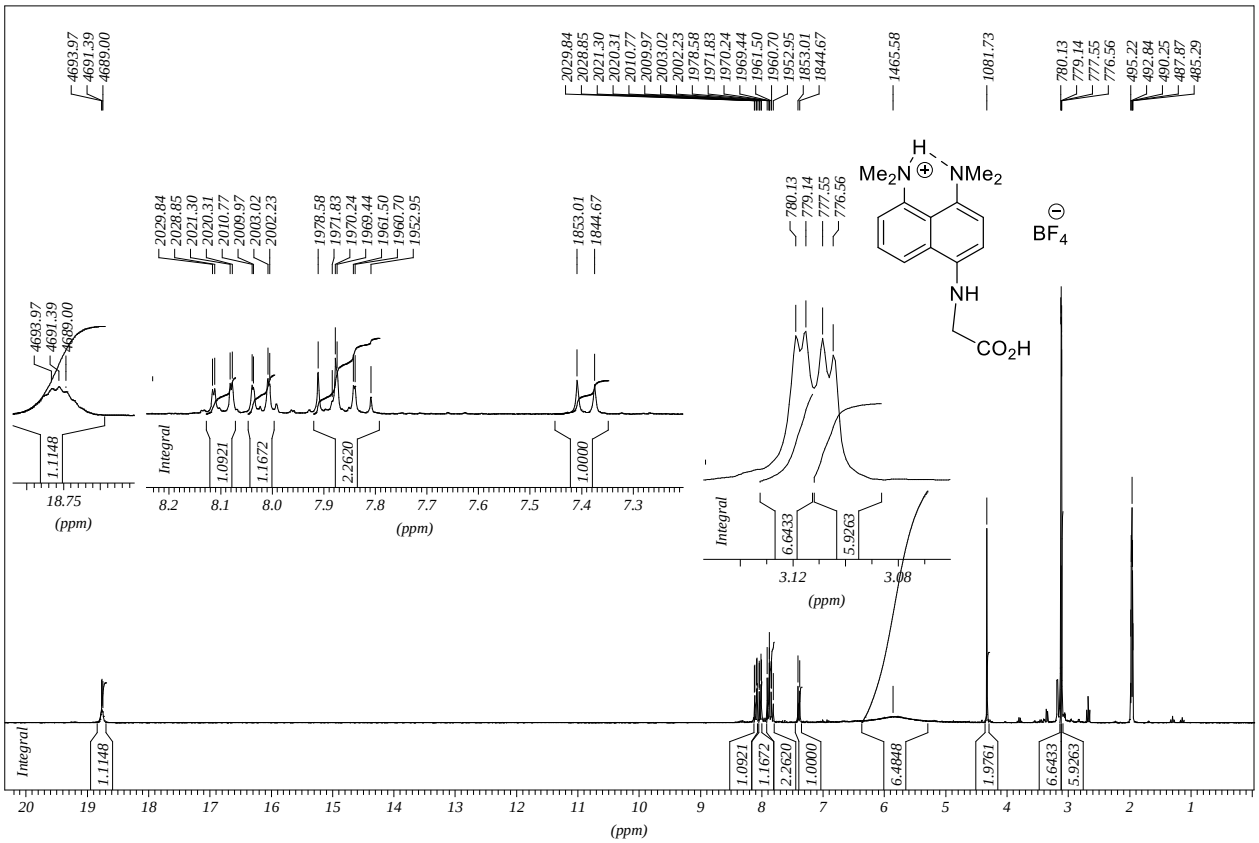


Figure S23. ^{1}H NMR spectrum of **6'a** (CD_3CN, 250 MHz).

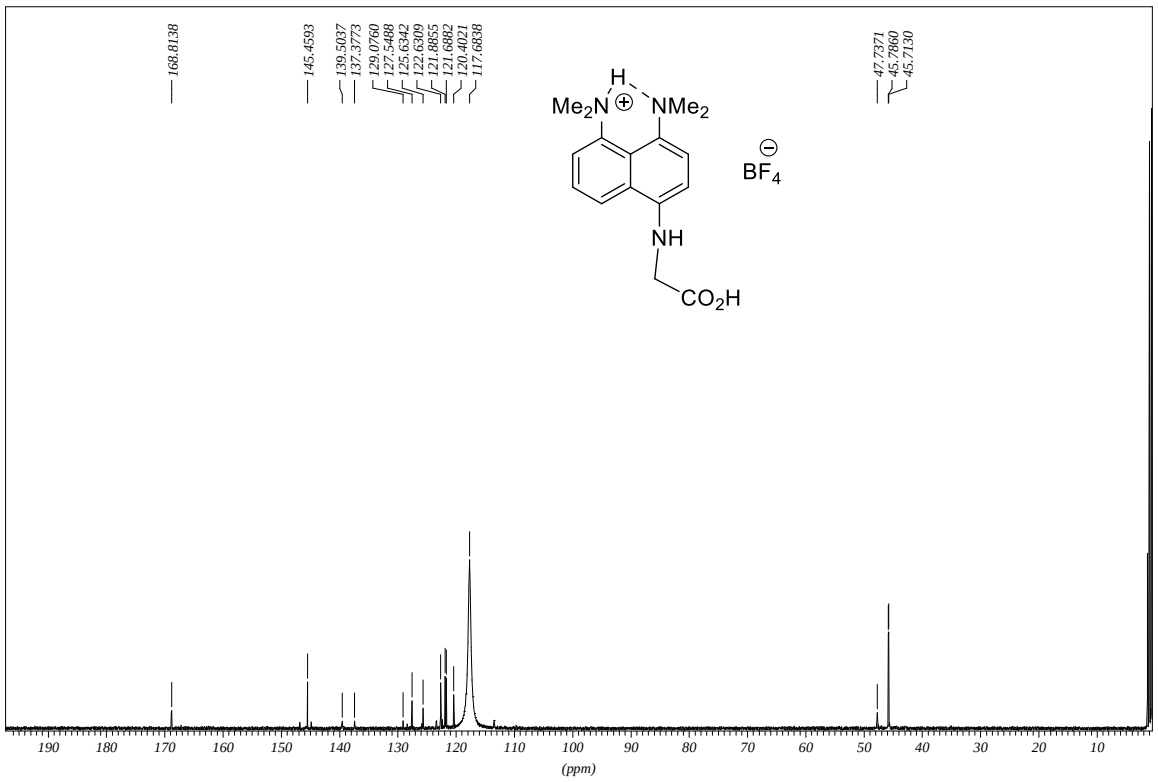


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **6'a** (CD_3CN, 62.9 MHz).

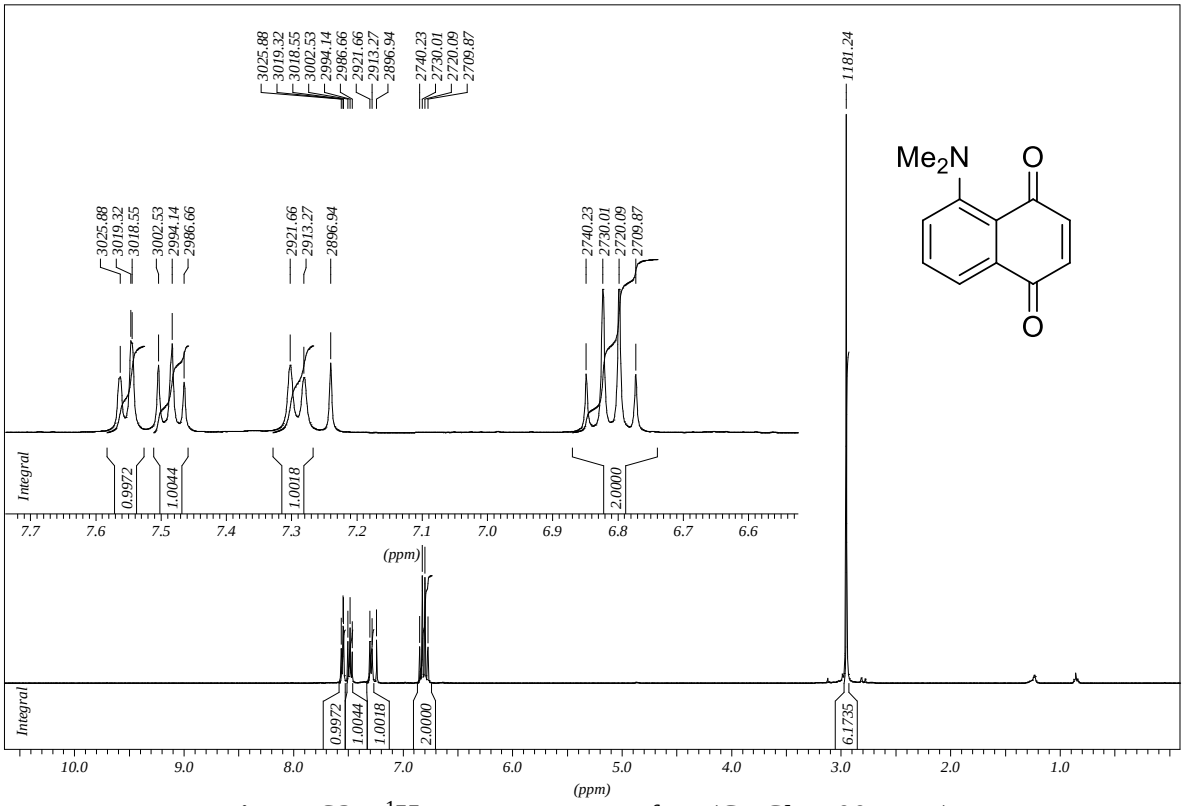


Figure S25. ^{1}H NMR spectrum of **14** ($CDCl_3$, 400 MHz).

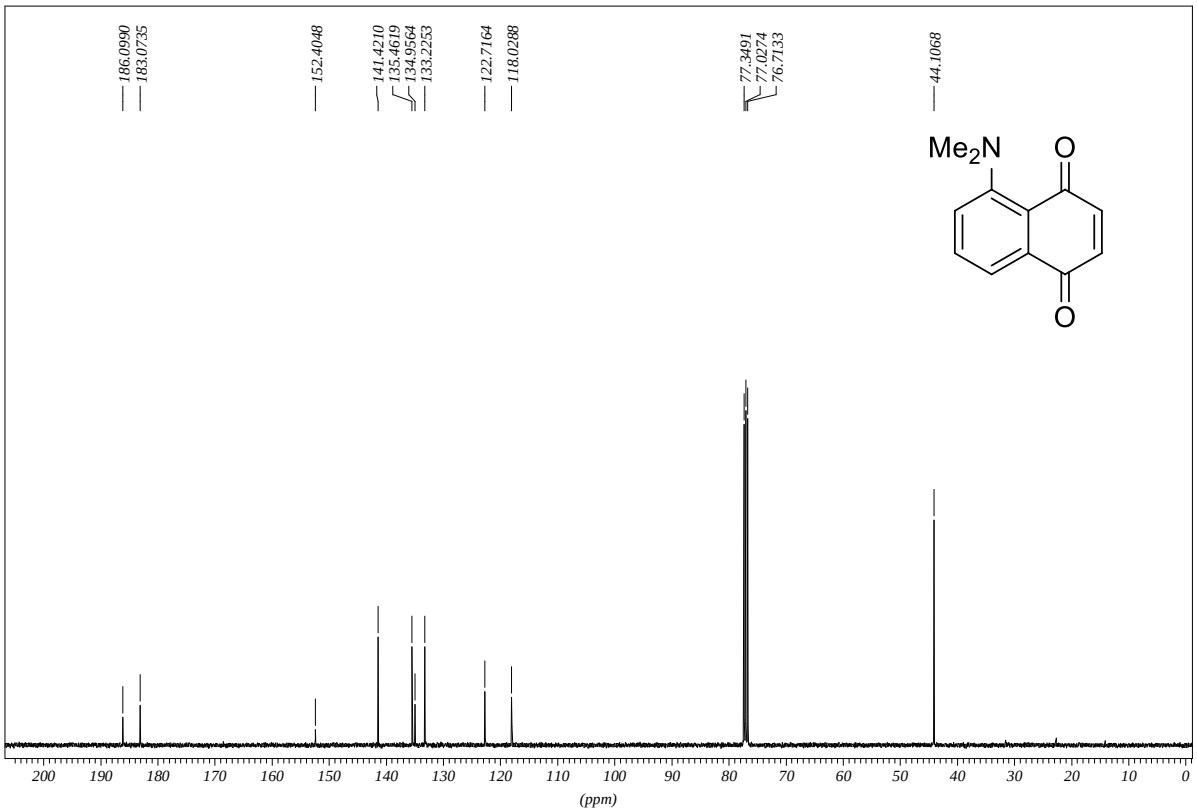


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **14** ($CDCl_3$, 100.6 MHz).

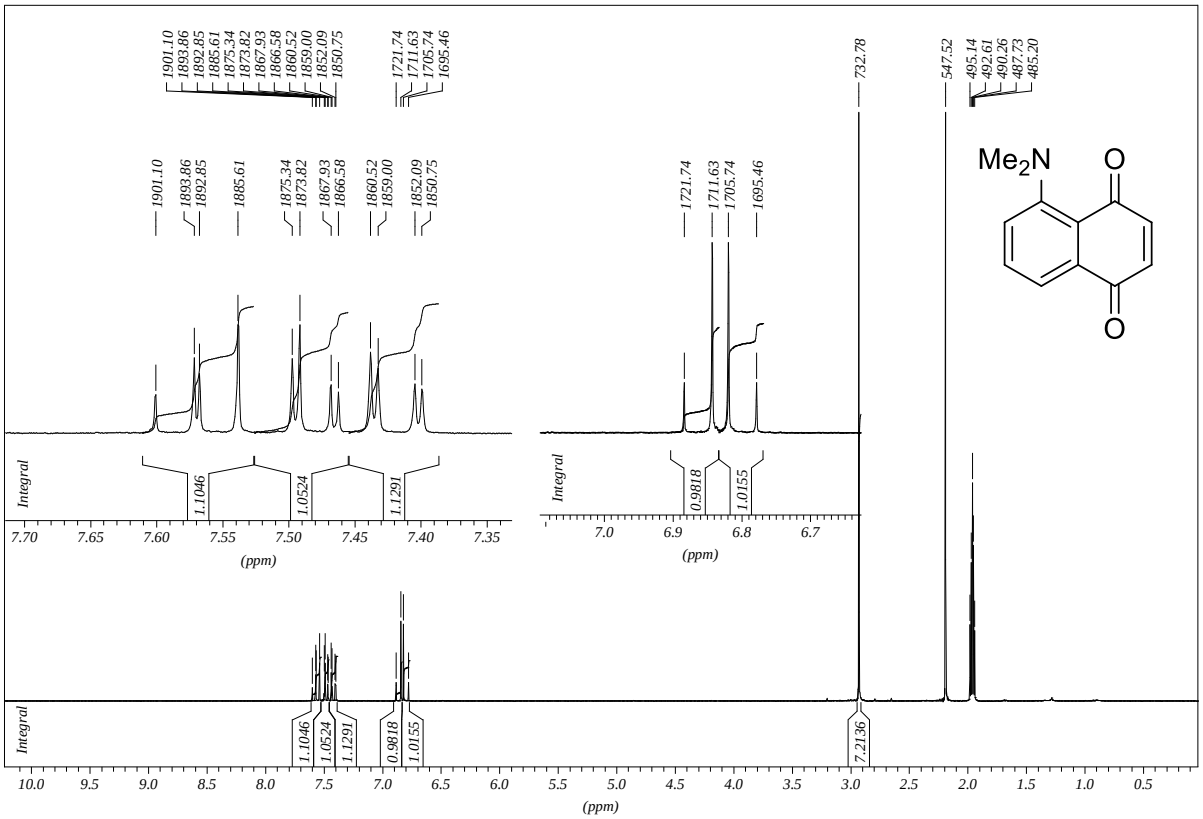


Figure S27. ^{1}H NMR spectrum of **14** (CD_3CN, 250 MHz).

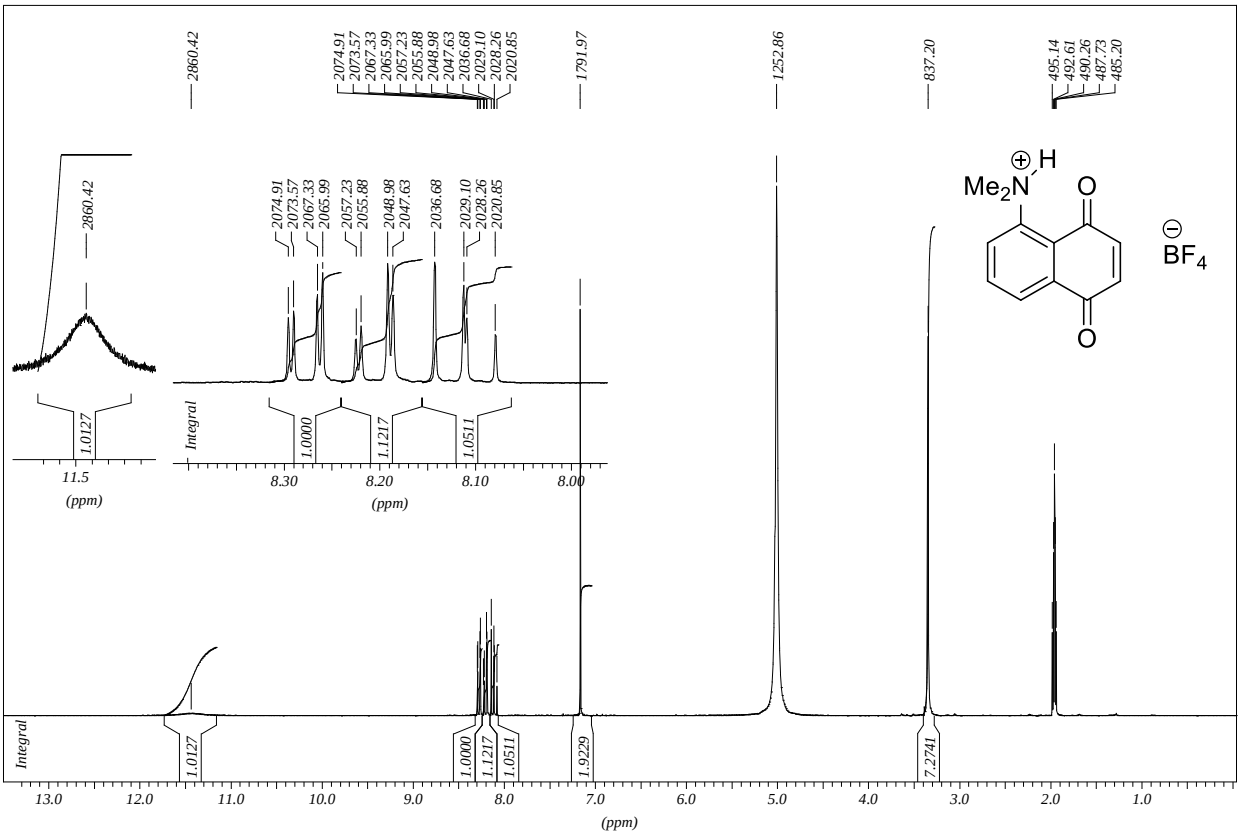


Figure S28. ^{1}H NMR spectrum of **14·HBF$_4$** (CD_3CN, 250 MHz).

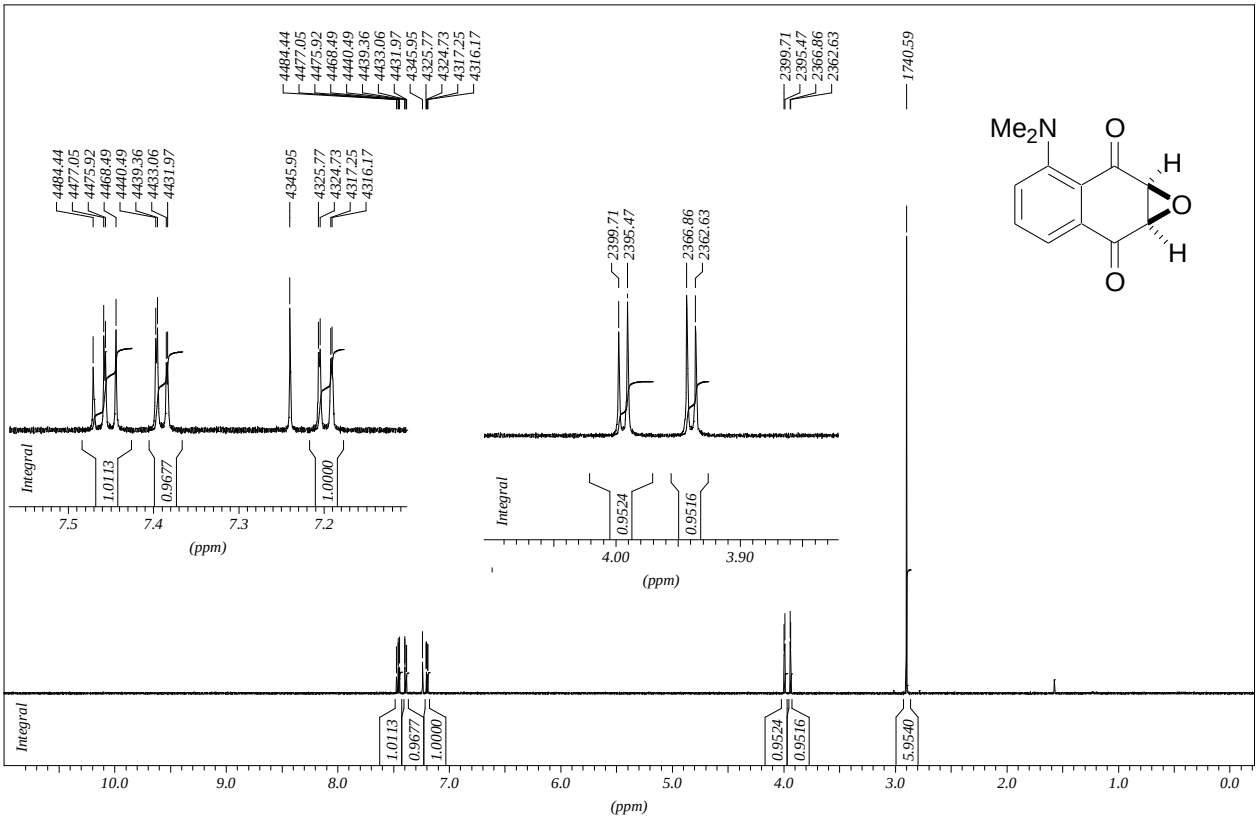


Figure S29. ^{1}H NMR spectrum of **15** ($CDCl_3$, 600 MHz).

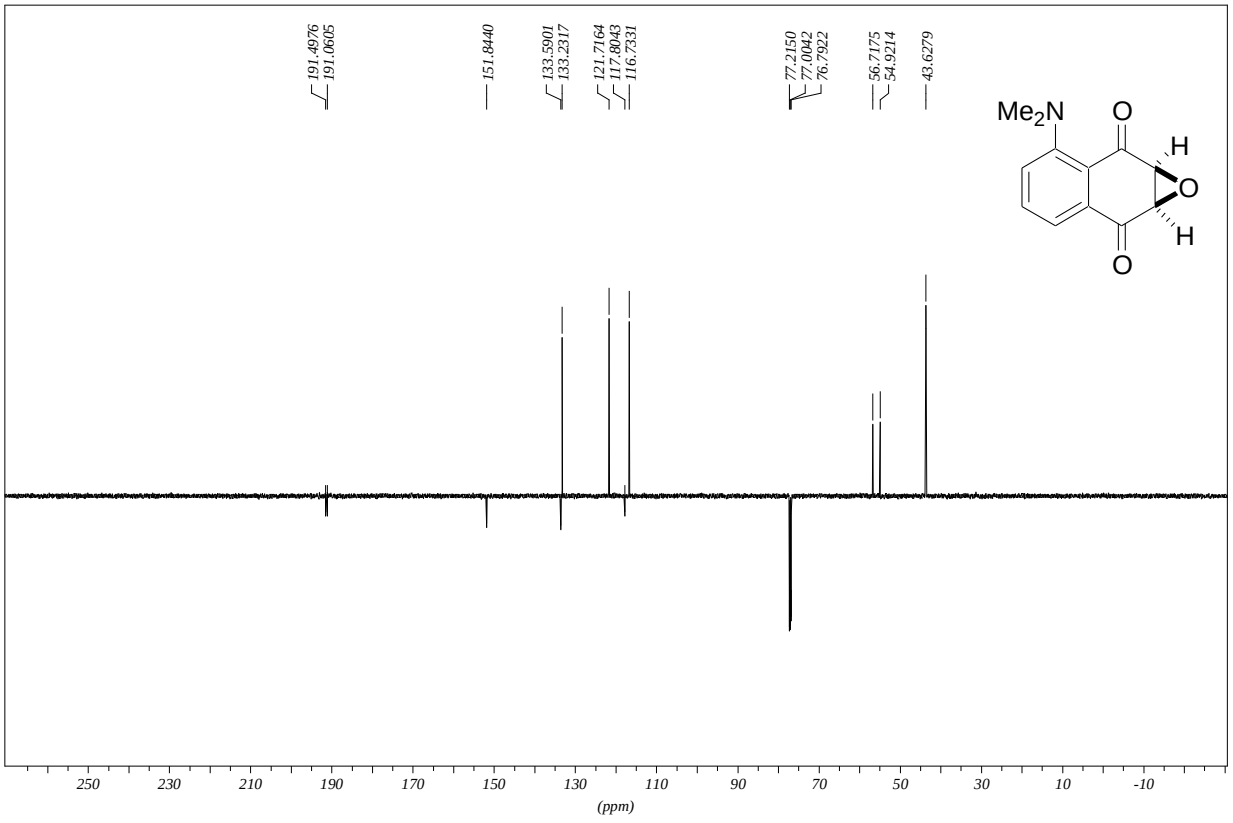


Figure S30. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **15** ($CDCl_3$, 150.9 MHz).

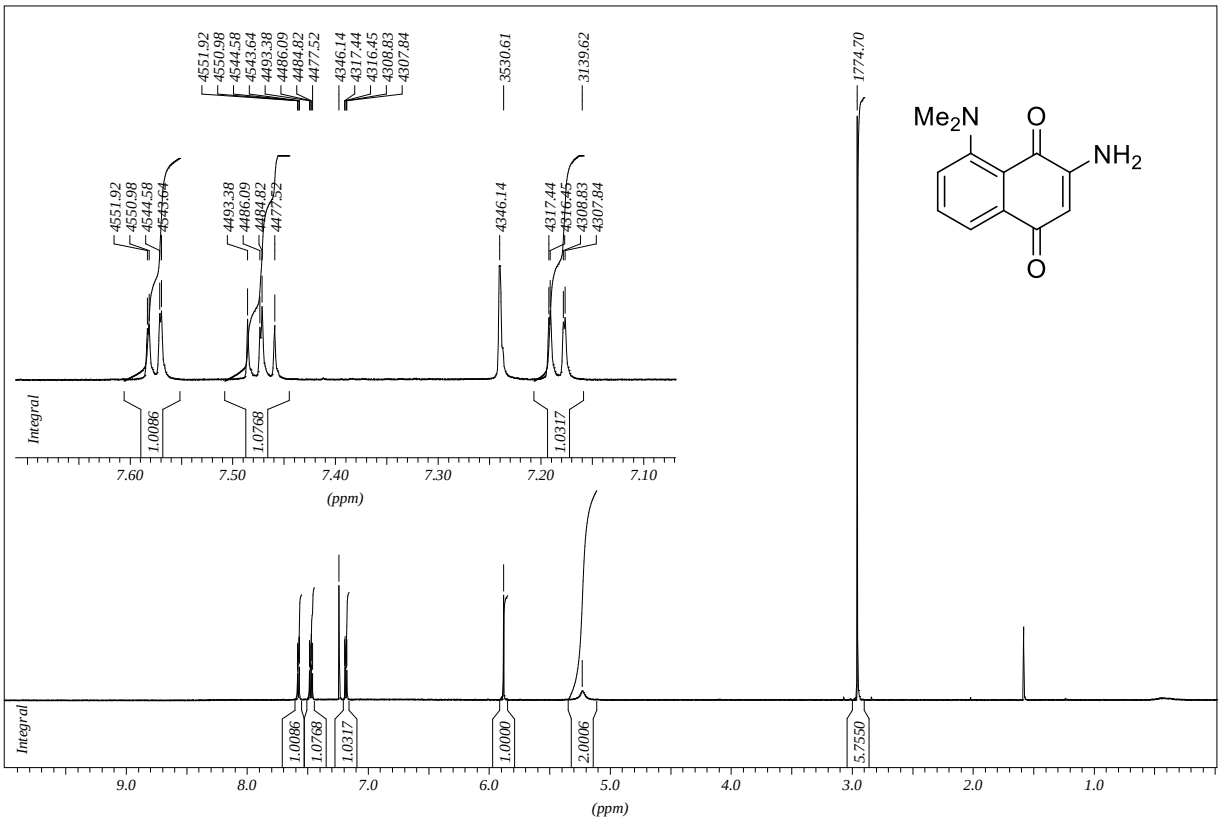


Figure S31. ^{1}H NMR spectrum of **17** ($CDCl_3$, 600 MHz).

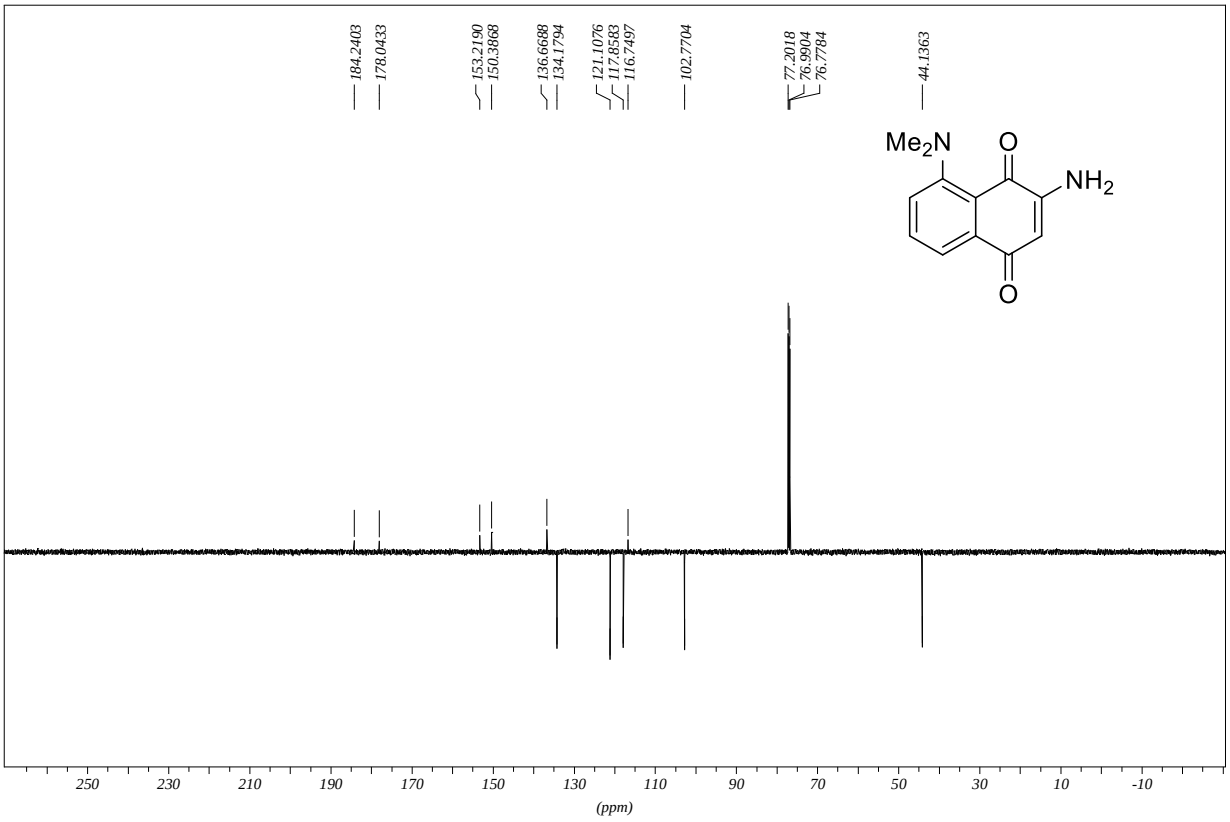


Figure S32. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **17** ($CDCl_3$, 150.9 MHz).

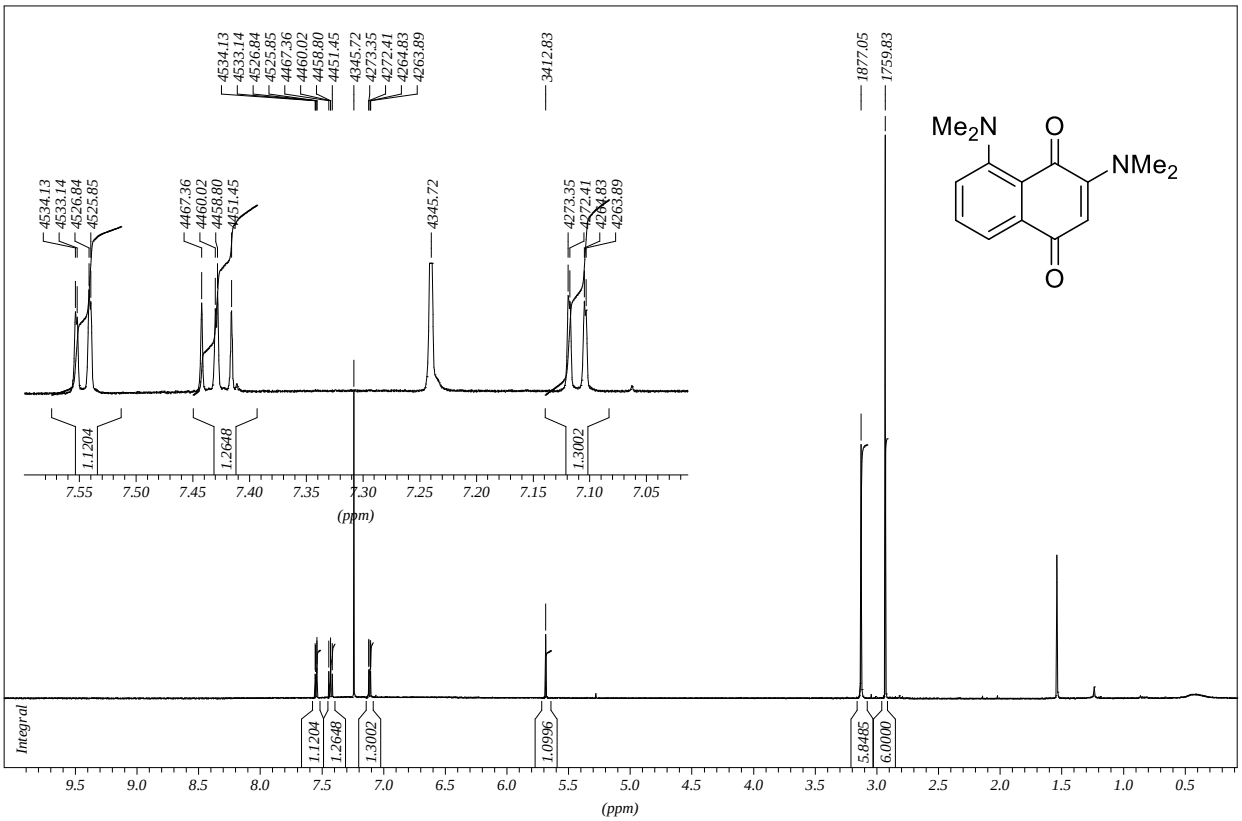


Figure S33. ^{1}H NMR spectrum of **18** ($CDCl_3$, 600 MHz).

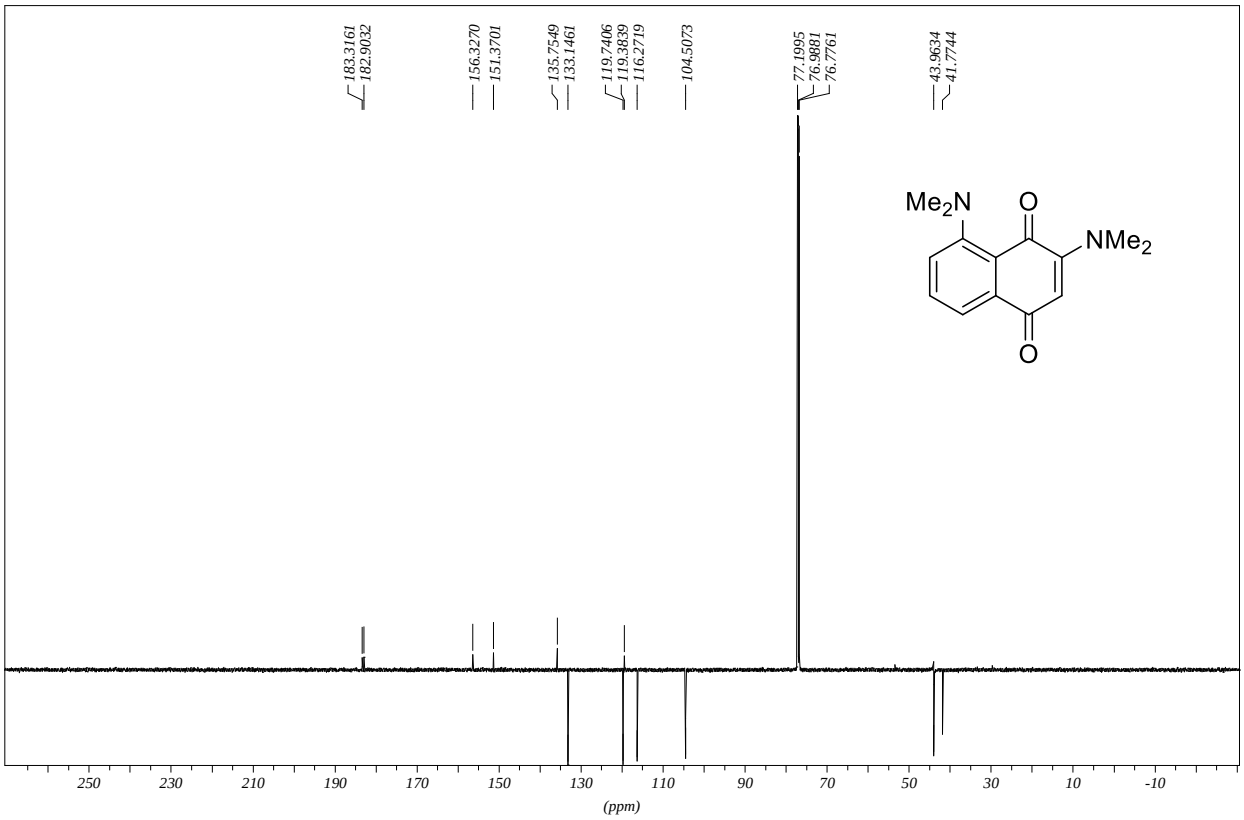


Figure S34. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **18** ($CDCl_3$, 150.9 MHz).

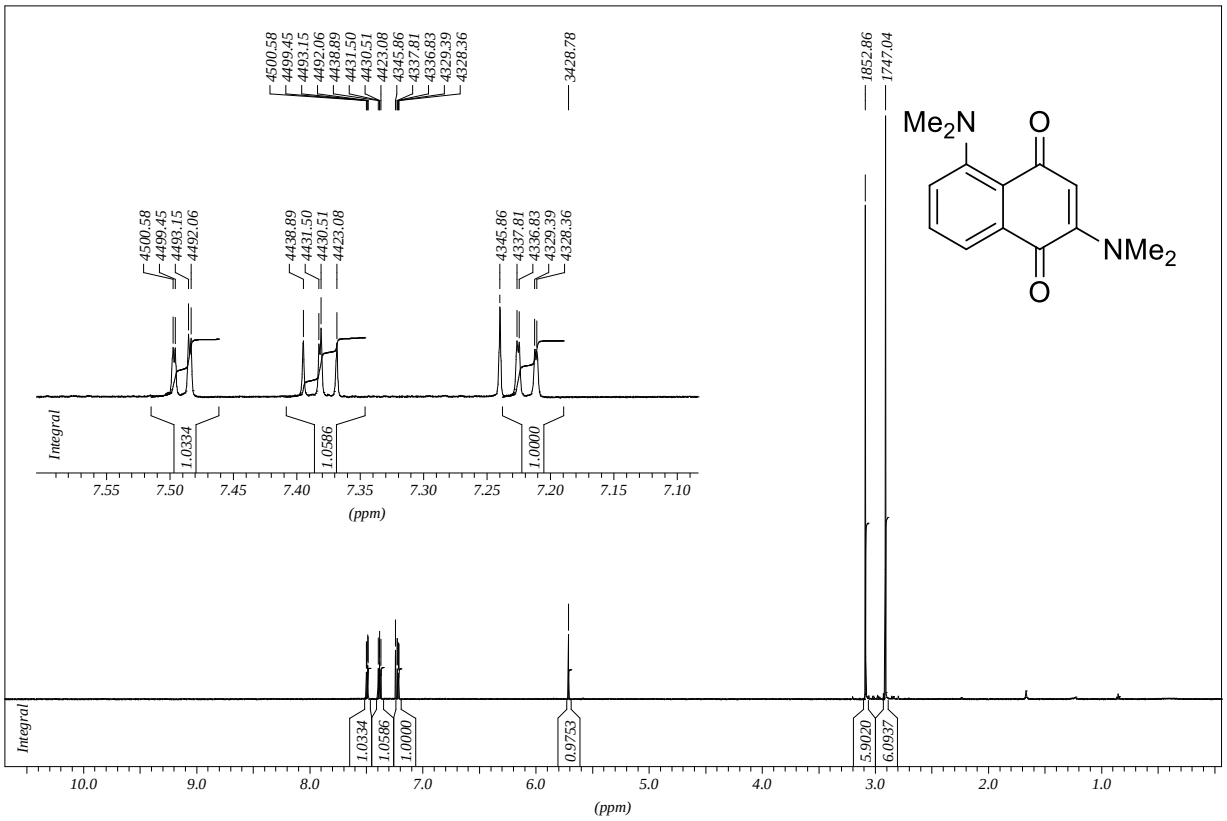


Figure S35. ^{1}H NMR spectrum of **19** ($CDCl_3$, 600 MHz).

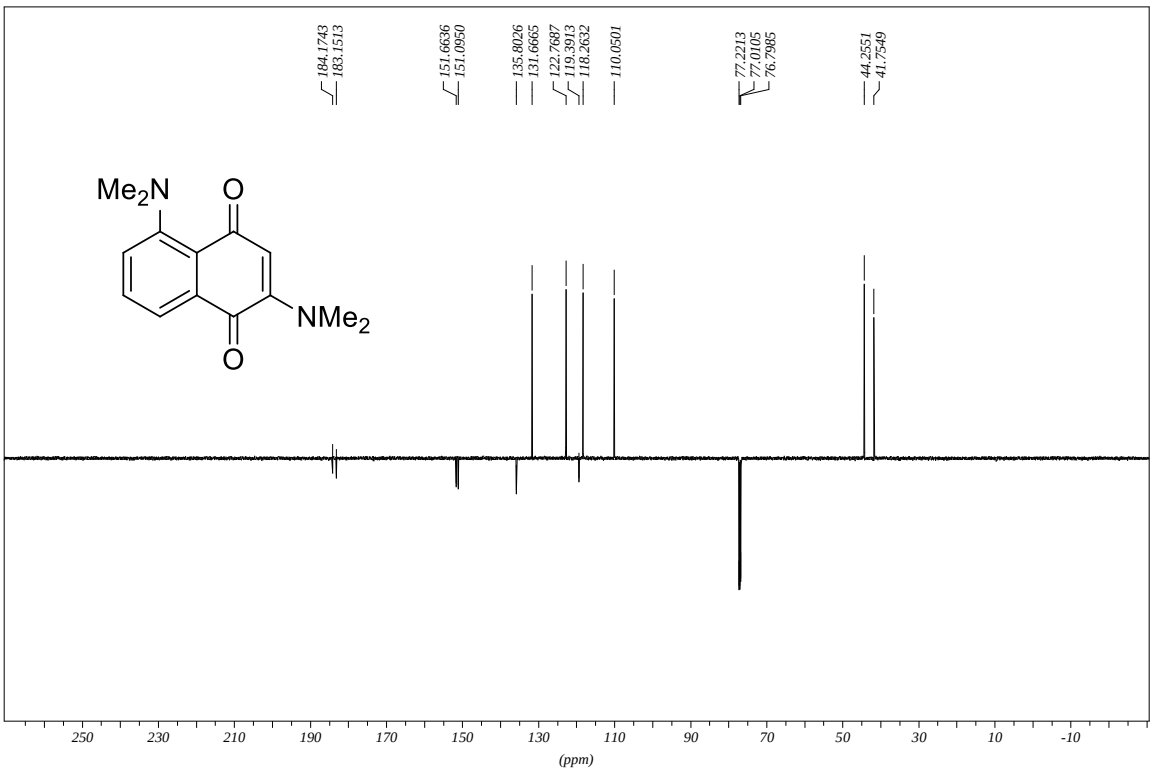


Figure S36. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **19** ($CDCl_3$, 150.9 MHz).

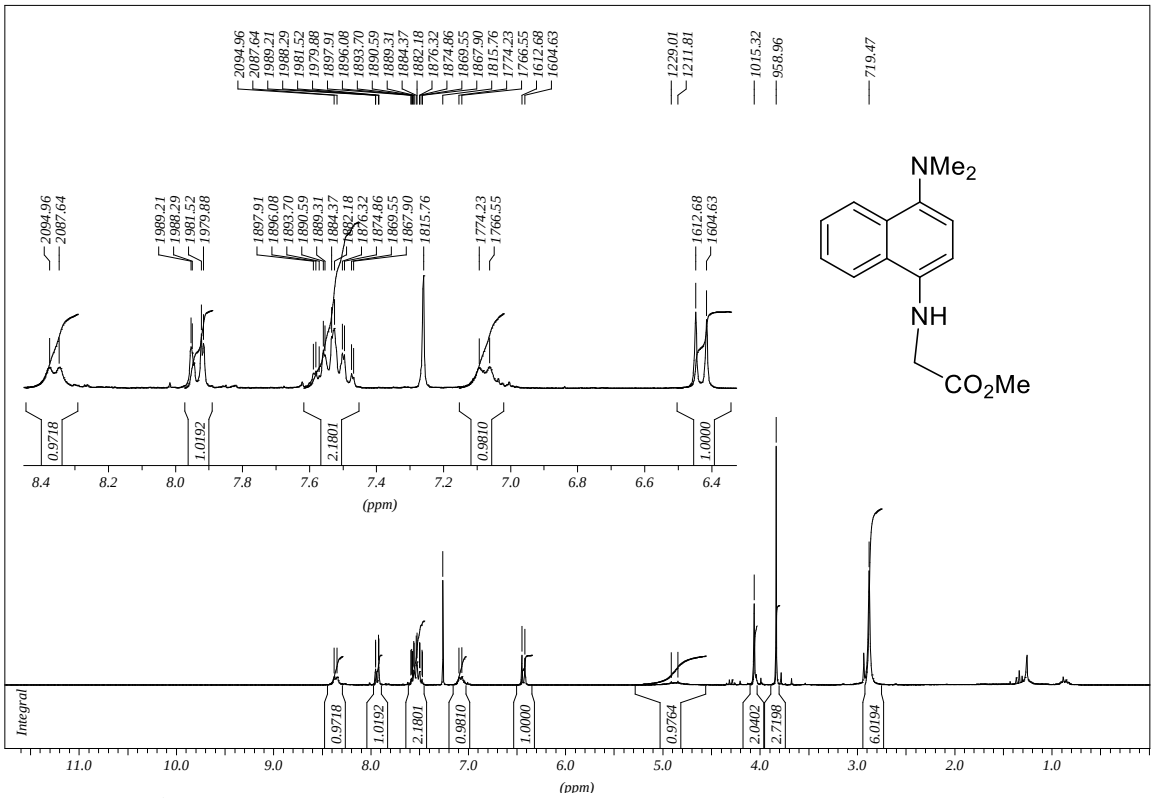


Figure S37. ^{1}H NMR spectrum of **methyl *N*-(4-dimethylaminonaphthalen-1-yl)glycinate** ($CDCl_3$, 250 MHz).

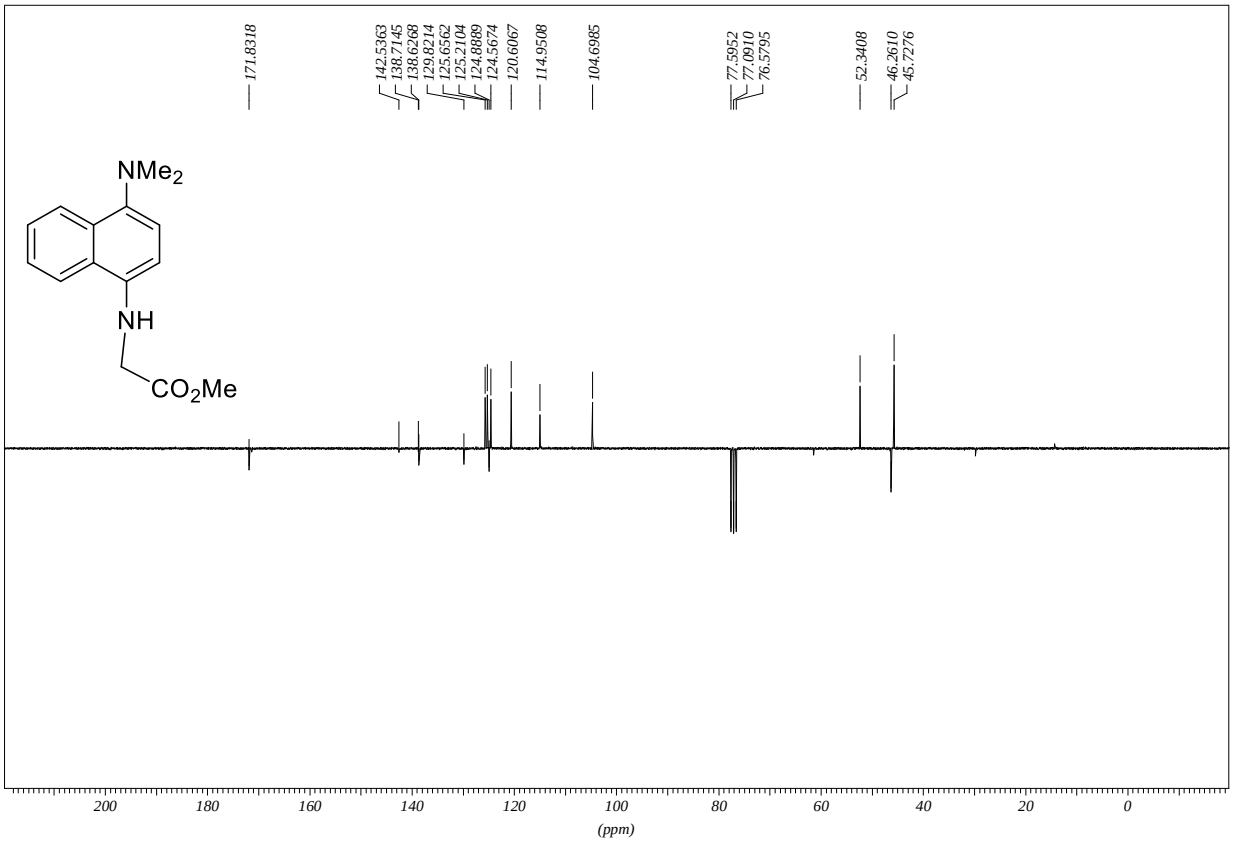


Figure S38. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **methyl *N*-(4-dimethylaminonaphthalen-1-yl)glycinate** ($CDCl_3$, 62.9 MHz).

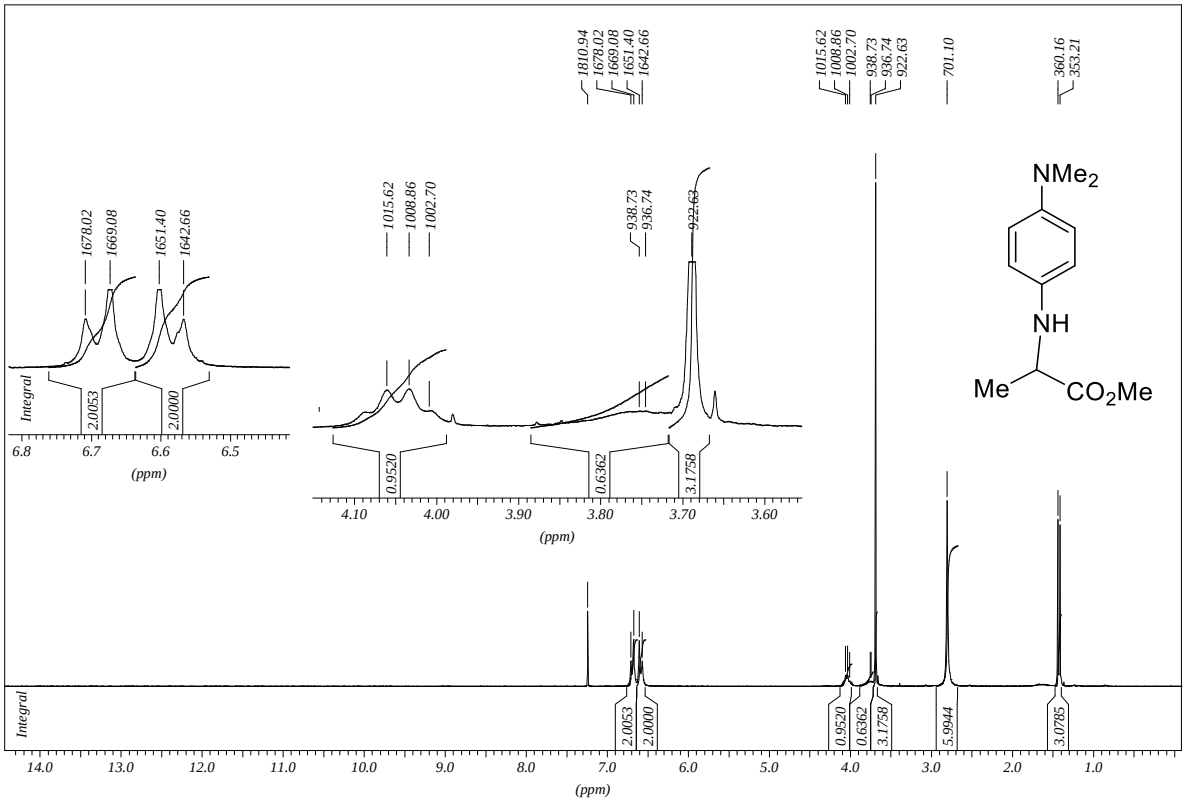


Figure S39. ^{1}H NMR spectrum of **methyl *N*-(4-dimethylaminophenyl)glycinate** ($CDCl_3$, 250 MHz).

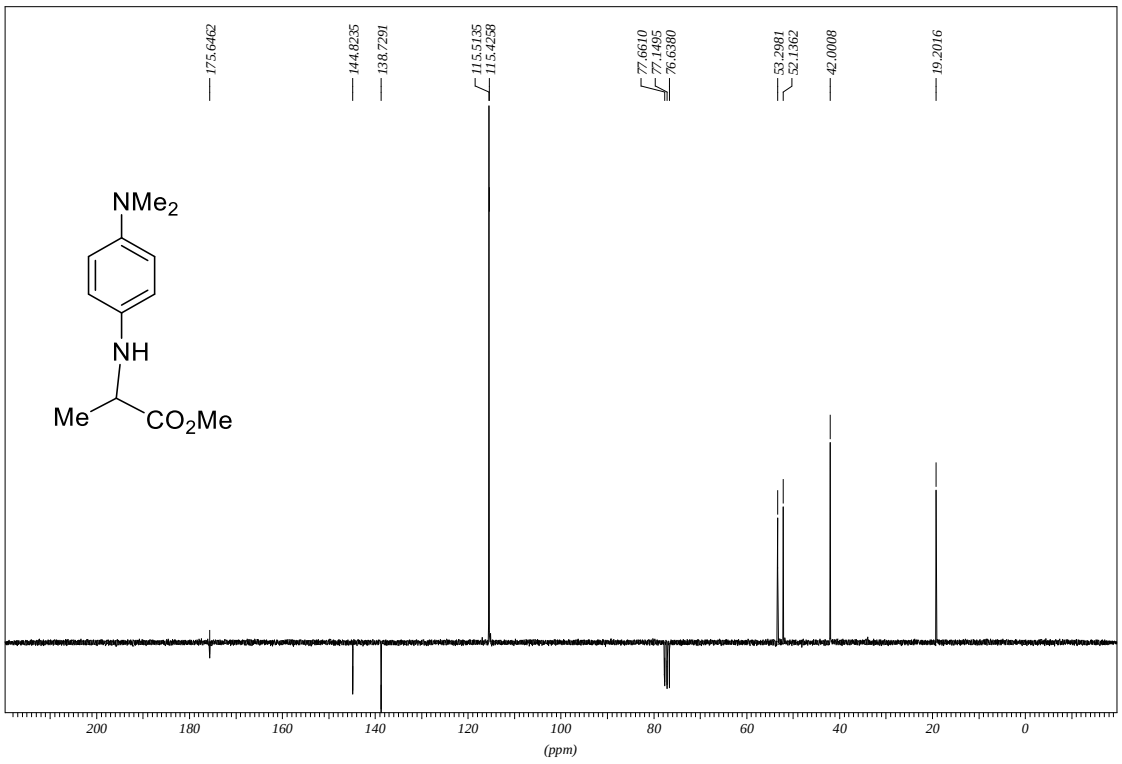


Figure S40. ^{13}C{^{1}H} APT-NMR spectrum of **methyl *N*-(4-dimethylaminophenyl)glycinate** ($CDCl_3$, 62.9 MHz).

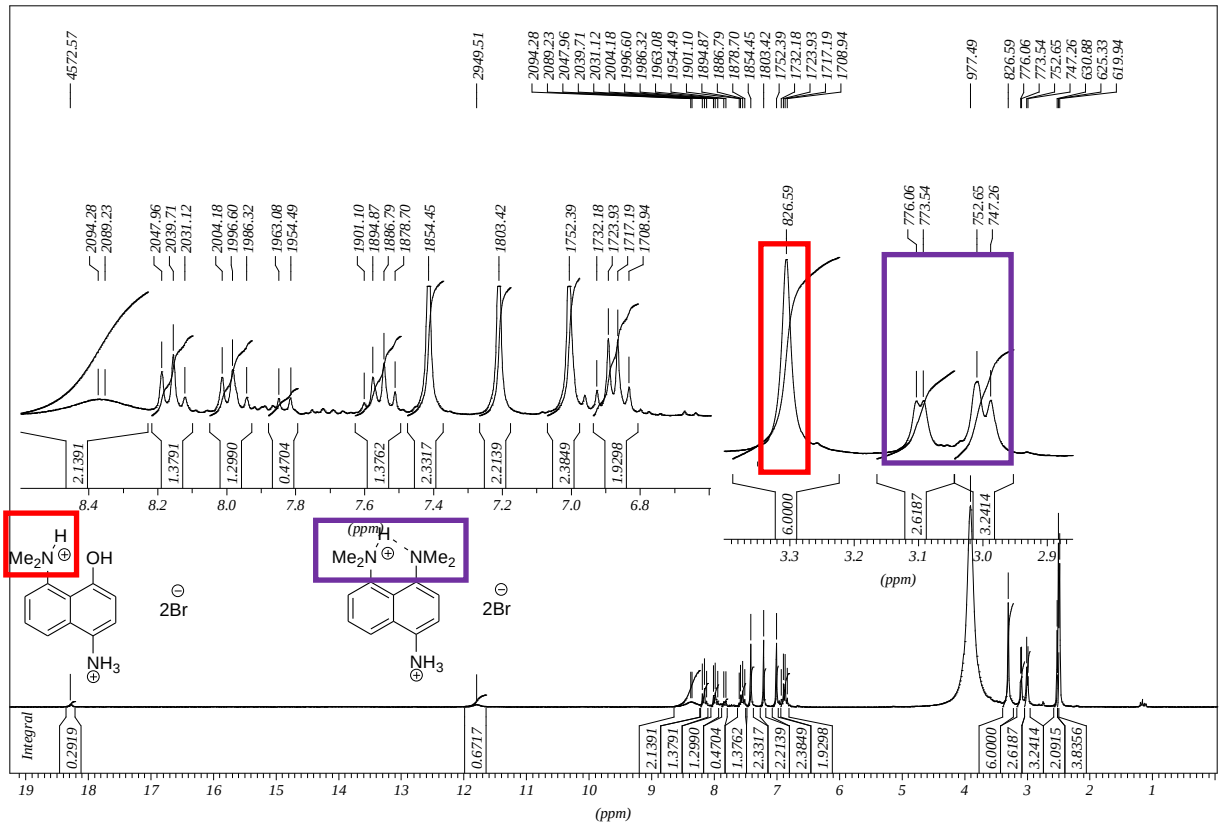
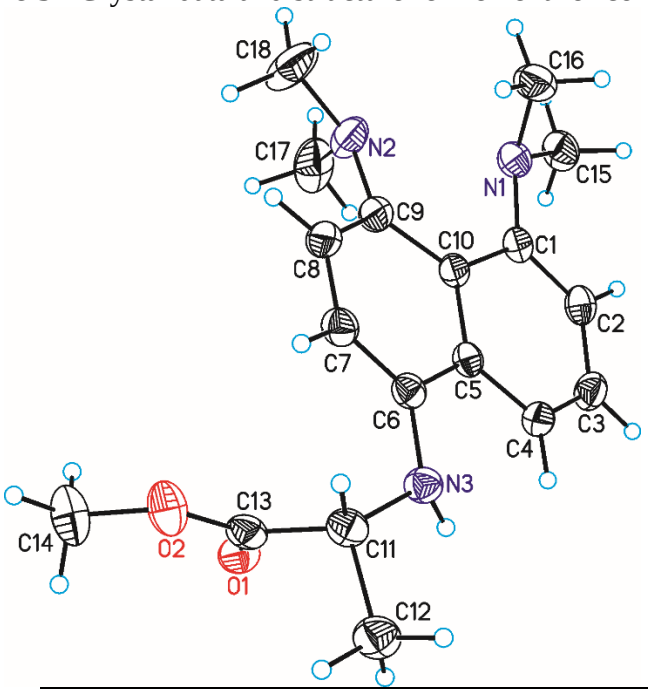


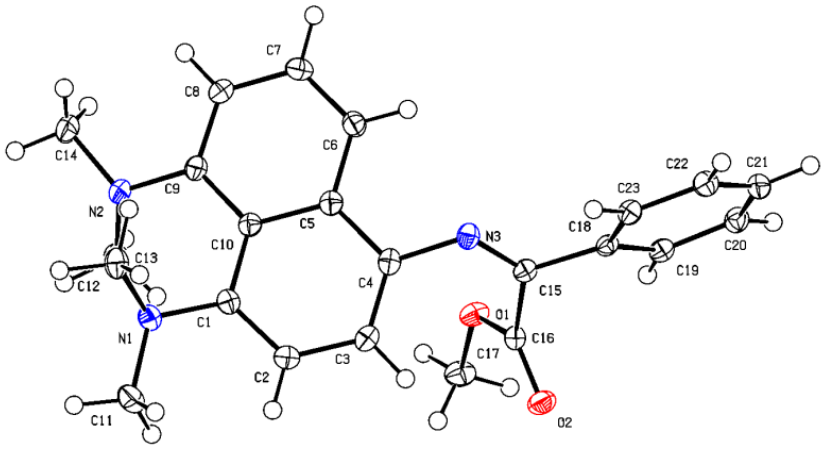
Figure S41. ^{1}H NMR spectrum of **1b** after heating it with 45% aq. HBr for 8 h (DMSO-d_6, 250 MHz).

Table S2 Crystal data and structure refinement for compound **4c**



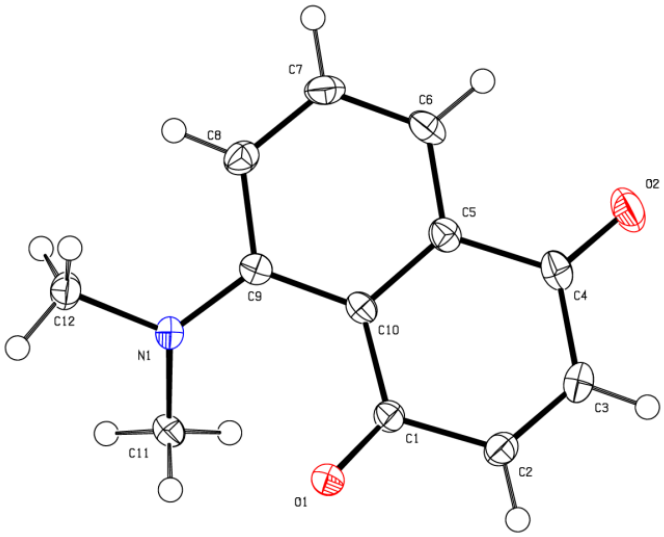
Parameter	
Empirical formula	$C_{18}H_{25}N_3O_2$
Formula weight	315.41
T (K)	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.7279(13)
b (Å)	14.2068(12)
c (Å)	8.5852(8)
β (°)	105.997(2)
V (Å^3)	1726.8(3)
Z, D_c (Mg m^{-3})	4, 1.213
μ (mm^{-1})	0.080
Reflections collected/unique	11082/3450
R(int)	0.0241
R_1, wR_2 (all data)	0.0582, 0.1194
R factor (%)	4.90
CCDC reference number	2184194

Table S3 Crystal data and structure refinement for compound **5**



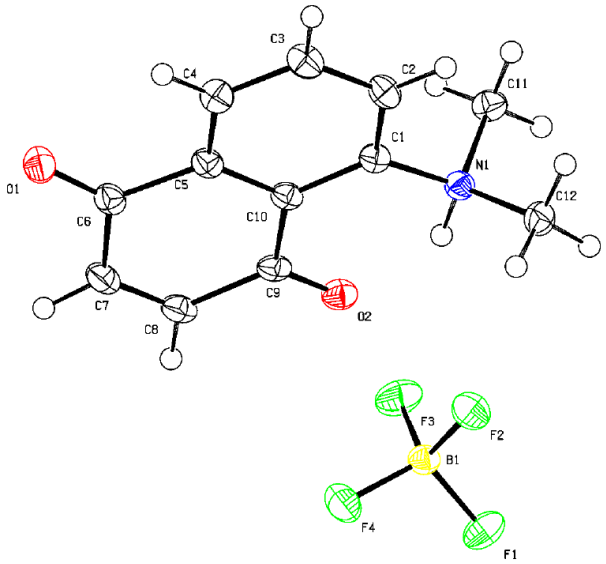
Parameter	
Empirical formula	$C_{23}H_{25}N_3O_2$
Formula weight	375.46
T (K)	100(2)
Crystal system	triclinic
Space group	*P-1*
a (Å)	8.7560(2)
b (Å)	9.7996(2)
c (Å)	12.4948(3)
α (°)	82.162(2)
β (°)	69.925(2)
γ (°)	83.117(2)
V (Å^3)	994.50(4)
Z, D_c (Mg m^{-3})	2, 1.254
μ (mm^{-1})	0.646
Reflections collected/unique	20131/4155
R(int)	0.0179
R_1, wR_2 (all data)	0.0352, 0.0886
R factor (%)	3.52
CCDC reference number	2184192

Table S4 Crystal data and structure refinement for compound **14**



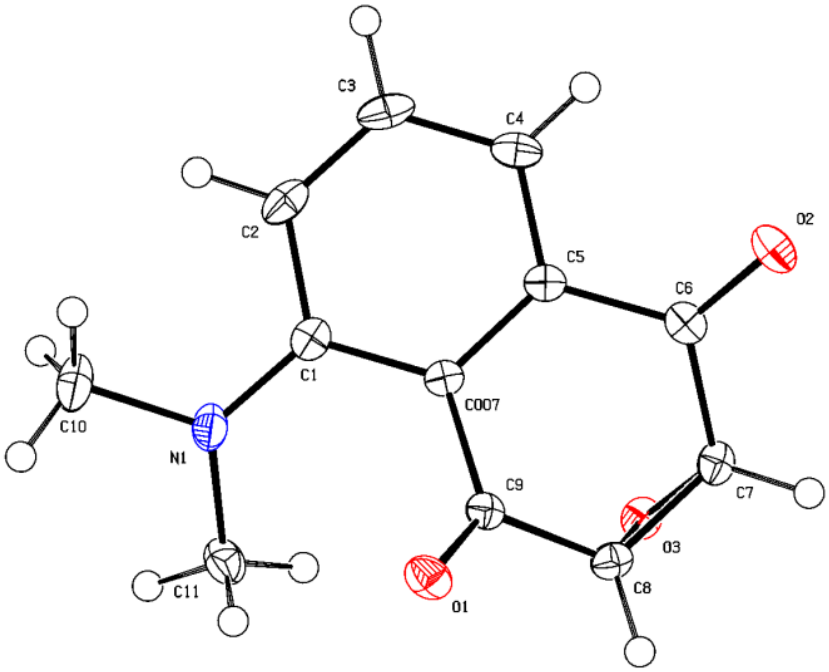
Parameter	
Empirical formula	$C_{12}H_{11}NO_2$
Formula weight	201.22
T (K)	100(2)
Crystal system	monoclinic
Space group	*Pn*
a (Å)	3.82850(10)
b (Å)	9.6276(2)
c (Å)	12.8281(2)
β (º)	92.367(2)
V (Å^3)	472.431(17)
Z, D_c (Mg m^{-3})	2, 1.415
μ (mm^{-1})	0.790
Reflections collected/unique	12156/1766
R(int)	0.0355
R_1, wR_2 (all data)	0.0267, 0.0711
R factor (%)	2.63
CCDC reference number	2184197

Table S5 Crystal data and structure refinement for compound **14·HBF$_4$**



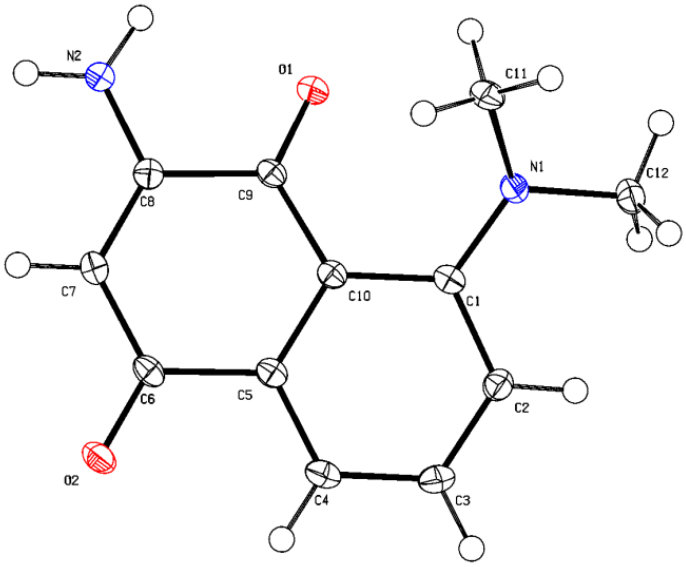
Parameter	
Empirical formula	$C_{12}H_{12}BF_4NO_2$
Formula weight	289.04
T (K)	99.9(5)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.4103(2)
b (Å)	7.91110(10)
c (Å)	13.6375(2)
β (º)	90.274(2)
V (Å^3)	1231.02(3)
Z, D_c (Mg m^{-3})	4, 1.560
μ (mm^{-1})	1.268
Reflections collected/unique	7667/2256
R(int)	0.0246
R_1, wR_2 (all data)	0.0325, 0.0756
R factor (%)	2.86
CCDC reference number	2184190

Table S6 Crystal data and structure refinement for compound **15**



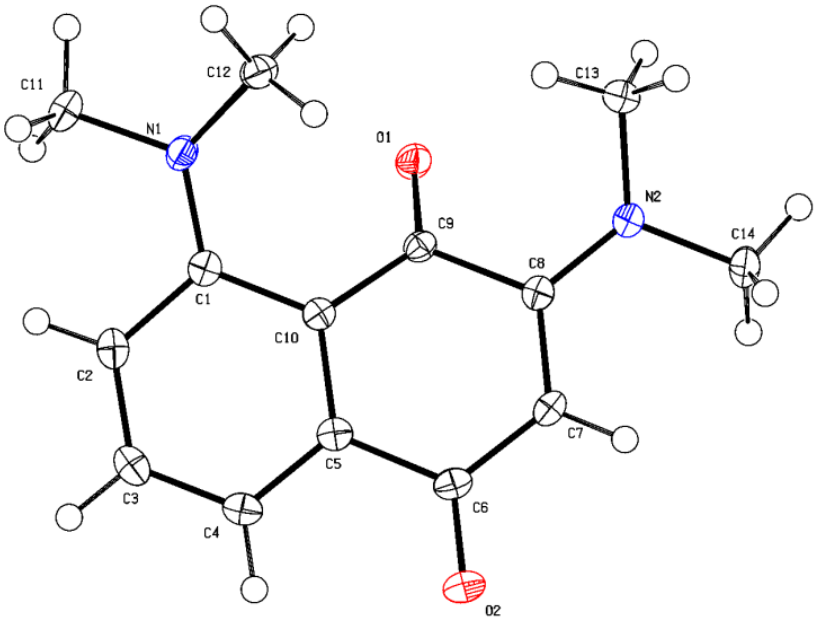
Parameter	
Empirical formula	$C_{12}H_{11}NO_3$
Formula weight	217.22
T (K)	100
Crystal system	orthorhombic
Space group	$Pna2_1$
a (Å)	9.14710(10)
b (Å)	14.4156(2)
c (Å)	7.61640(10)
V (Å^3)	1004.31(2)
Z, D_c (Mg m^{-3})	4, 1.437
μ (mm^{-1})	0.865
Reflections collected/unique	9915/1819
R(int)	0.0267
R_1, wR_2 (all data)	0.0252, 0.0659
R factor (%)	2.47
CCDC reference number	2184196

Table S7 Crystal data and structure refinement for compound **17**



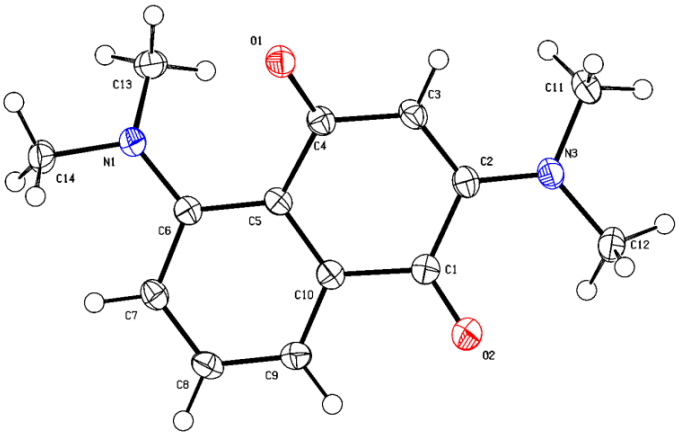
Parameter	
Empirical formula	$C_{12}H_{12}N_2O_2$
Formula weight	216.24
T (K)	100
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.5001(2)
b (Å)	3.88460(10)
c (Å)	17.7321(3)
β (º)	94.2170(10)
V (Å^3)	996.09(3)
Z, D_c (Mg m^{-3})	4, 1.442
μ (mm^{-1})	0.819
Reflections collected/unique	6662/2057
R(int)	0.0235
R_1, wR_2 (all data)	0.0370, 0.0923
R factor (%)	3.26
CCDC reference number	2184191

Table S8 Crystal data and structure refinement for compound **18**



Parameter	
Empirical formula	$C_{14}H_{16}N_2O_2$
Formula weight	244.29
T (K)	100
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.8500(2)
b (Å)	10.92090(10)
c (Å)	10.86420(10)
β (°)	111.487(2)
V (Å^3)	1197.85(3)
Z, D_c (Mg m^{-3})	4, 1.355
μ (mm^{-1})	0.742
Reflections collected/unique	8178/2436
R(int)	0.0142
R_1, wR_2 (all data)	0.0367, 0.0937
R factor (%)	3.55
CCDC reference number	2184195

Table S9 Crystal data and structure refinement for compound **19**



Parameter	
Empirical formula	$C_{14}H_{16}N_2O_2$
Formula weight	244.29
T (K)	100
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	11.01580(10)
b (Å)	13.5847(2)
c (Å)	16.2616(2)
V (Å^3)	2433.49(5)
Z, D_c (Mg m^{-3})	8, 1.334
μ (mm^{-1})	0.731
Reflections collected/unique	13506/2538
R(int)	0.0263
R_1, wR_2 (all data)	0.0378, 0.0946
R factor (%)	3.66
CCDC reference number	2184193

Oxidation Questions

1. Autoxidation: general information

It is known that the process of autoxidation proceeds according to the radical mechanism [Waters, W. A. Mechanism of Oxidation of Organic Compounds, J. Wiley & Sons, London–New York, 1963]. Each oxygen molecule accepts one electron from the substrate, turning into the superoxide radical anion $O_2^{-}\cdot$. The latter can theoretically turn into a peroxide anion HO_2^{-} or a radical $HO_2\cdot$, capturing a hydrogen atom or a proton, respectively, usually from the C–H bonds of an organic compound. Formation of an anion is thermodynamically more favorable and the homolytic rupture should touch the weakest C–H bonds. In our case (Scheme 3), such bonds are most likely the C–H bonds of the methyl groups of the dimethylamine splitting off during the formation of naphthol **10** or the N–H bonds of ammonia and ammonium ions, while the dissociation energy of aromatic C–H bonds is significantly (>10 kcal mol^{-1}) higher. For similar reasons, decarboxylation occurs most readily in the carboxylate radical $RCO_2\cdot$ rather than in the anion RCO_2^{-} [Benson, S. W. *J. Chem. Educ*., **1965**, *37*, 502–518]. To avoid unnecessary details these issues are not reflected in Scheme 3. Due to usually lower selectivity of radical processes and the abundance of various substances in solution, autoxidation often proceeds with the formation of some polymer products of different composition. Apparently, this also occurs in our case, slightly reducing the yield of the main reaction product, naphthoquinone **14**.

It thus follows from the above that the oxidation of each dianion **11a**–**c** to quinone structure **14** formally should require two oxygen molecules.

2. Oxidation of 1,8-diaminonaphthalenes and proton sponges

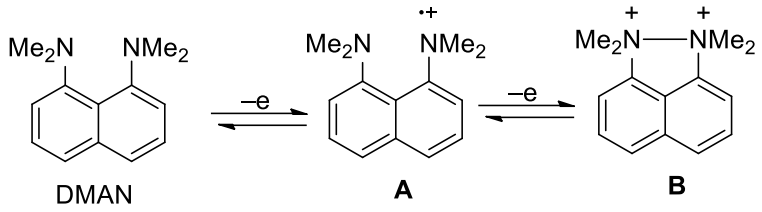
One of the features of DMAN is that, despite its high basicity and equally high C-nucleophilicity (ring electron excessity), its molecule is very resistant to autoxidation. At the same time, its homologues with three, two, and one N-methyl group, like 1,8-diaminonaphthalene itself, darken rather quickly in air. This seems surprising, since the first gas-phase ionization potentials (IP-1) of DMAN and its partially methylated derivatives (precursors) are very close, both on the basis of mass spectroscopy (electron impact) (Pozharskii, A. F.; Suslov, A. N.; Starshikov, N. M.; Popova, L. L.; Klyuev, N. A.; Adanin, V. A. *Zh. Org. Khim.*, **1980**, *16*, 2216; *Chem. Abstr.*, **1981**, *94*, 120385s) and photoionization data (Maier, J. P. *Helv. Chim. Acta*, **1974**, *57*, 994).

1,8-Diaminonaphthalene	IP-1 = 7.47 eV (electron impact)
1-Methylamino-8-aminonaphthalene	IP-1 = 7.40 eV (electron impact)
1-Dimethylamino-8-aminonaphthalene	IP-1 = 7.43 eV (electron impact)
1,8-Bis(methylamino)naphthalene	IP-1 = 7.38 eV (electron impact)
1-Dimethylamino-8-methylaminonaphthalene	IP-1 = 7.40 eV (electron impact)
DMAN	IP-1 = 7.38 eV (electron impact)

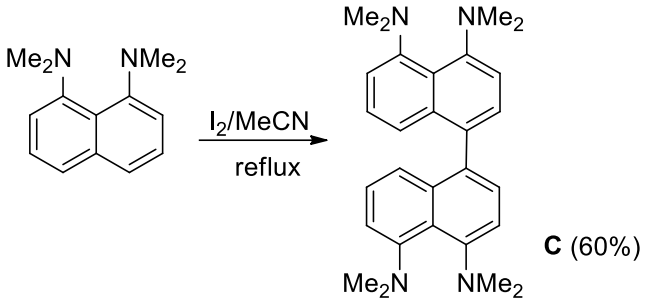
1,8-Diaminonaphthalene	IP-1 = 7.10 eV (photoionization)
DMAN	IP-1 = 7.05 eV (photoionization)

Anodic oxidation of DMAN on a platinum electrode in MeCN proceeds in two single-electron waves with $E_{1/2}^{ox}$ = 0.36 и 1.02 V, respectively (Berberova, N. T.; Okhlobystin, O. Y. *Zh. Org.*

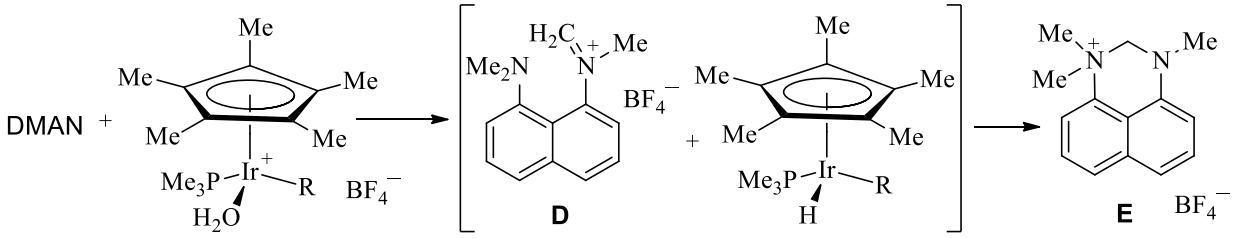
Khim., **1983**, *19*, 1114; *Chem. Abstr.*, **1983**, *99*, 175024g). It is assumed that the products of this oxidation are radical cation **A** and dication **B**. The radical cation was also generated by the action of lead dioxide on DMAN. The ESR spectrum of the cation radical does not have a hyperfine structure. In terms of its electron-donating properties, DMAN ranks between dimethylaniline and tetramethyl-*p*-phenylenediamine.



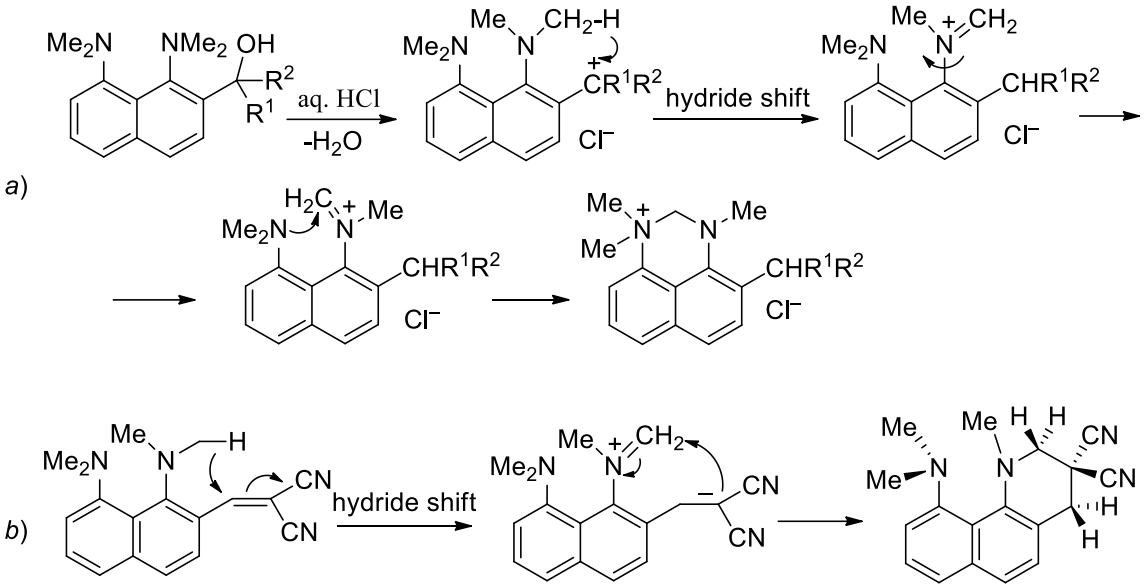
Two main types of chemical oxidation of DMAN and its derivatives have been described. Thus, treatment of DMAN with iodine in acetonitrile (Ozeryanskii, V. A.; Pozharskii, A. F.; Fomchenkov, A. M. *Russ. Chem. Bull.*, **1998**, *47*, 313) gives the 1,1'-binaphthyl derivative **C**. This dimer is also formed as a by-product (~10%) during DMAN nitration.



The second type of oxidation is associated with the elimination of the hydride ion from the NMe_2 group of DMAN upon treatment with transition metal complexes, in particular, iridium (Hughes, R. P.; Kovacik, I.; Lindner, D.; Smith, J. M.; Willemsen, S.; Zhang, D.; Guzei, I. A.; Rheingold, A. L. *Organometallics*, **2001**, *20*, 3190). The resulting methyleneimmonium ion **D** immediately cyclizes to the NMe_2 group unaffected by oxidation, which leads to the formation of 1,1,3-trimethyl-2,3-dihydroperimidinium salt **E**.



An important variation of this reaction is the transfer of a hydride ion to an electron-withdrawing substituent in 2(7) position of the naphthalene system and subsequent cyclization of the same or another type (Schemes *a* and *b*). [Ryabtsova, O. V.; Pozharskii, A. F.; Degtyarev, A. V.; Ozeryanskii, V. A. *Mendeleev Commun.*, **2006**, *14*, 313. Pozharskii, A. F.; Povalyakhina, M. A.; Degtyarev, A. V.; Ryabtsova, O. V.; Ozeryanskii, V. A.; Dyablo, O. V.; Tkachuk, A. V.; Kazheva, O. N.; Chekhlov, A. N.; Dyachenko, O. A. *Org. Biomol. Chem.*, **2011**, *9*, 1887].



As can be seen from the above information, the type of reaction discovered by us in this work is a fundamentally new and the deepest yet known oxidative transformation in the proton sponge series.

HRMS of 3c hydrolysis products

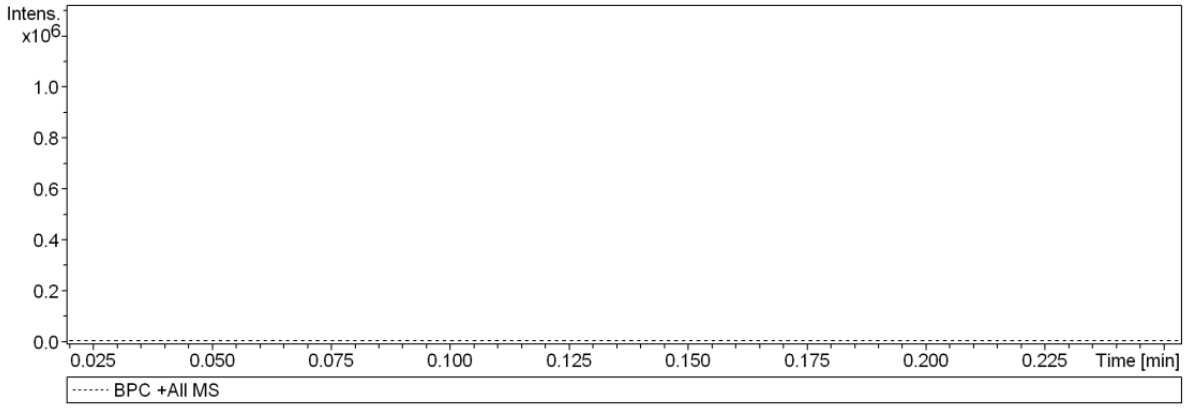
Display Report

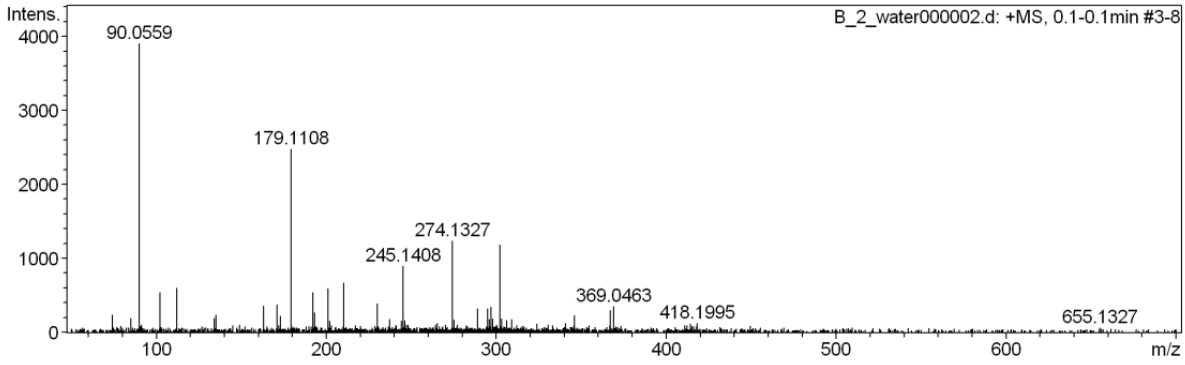
Analysis Info

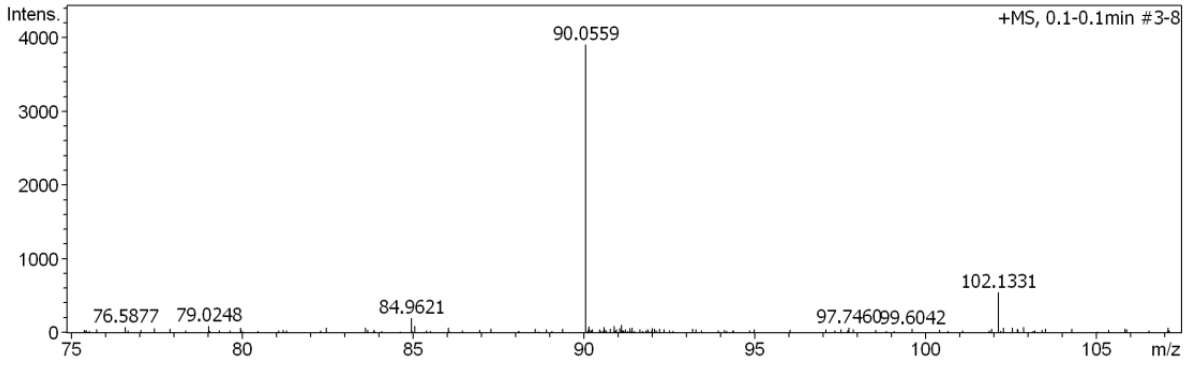
Analysis Name	D:\Data\demidov\B_2_water000002.d	Acquisition Date	9/29/2022 3:13:42 PM
Method	Direct_Infusion_50-500.m	Operator	Demidov
Sample Name	1	Instrument	maXis impact 282001.00109
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	700 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste







Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
90.0559	1	C3H8NO2	90.0550	-10.3	18.3	1	100.00	0.5	even	ok
	1	C3H8NO2	90.0550	-10.3	18.3	1	100.00	0.5	even	ok

+MS, 0.1-0.1min #3-8

HRMS of water fraction

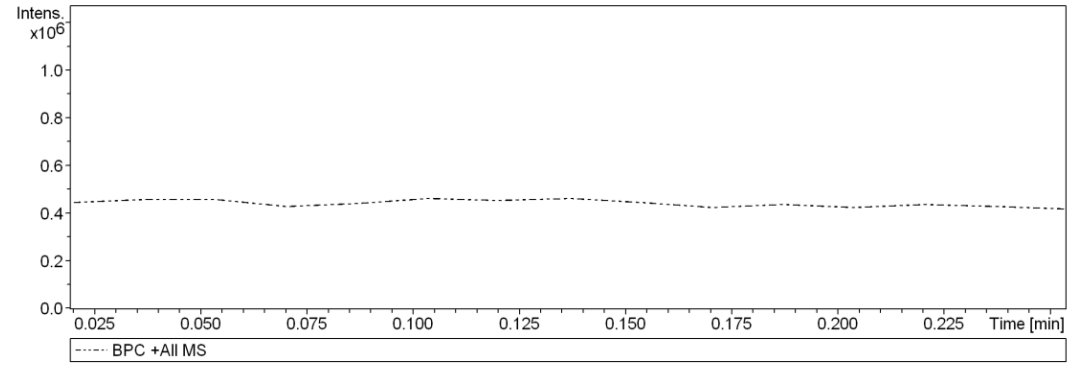
Display Report

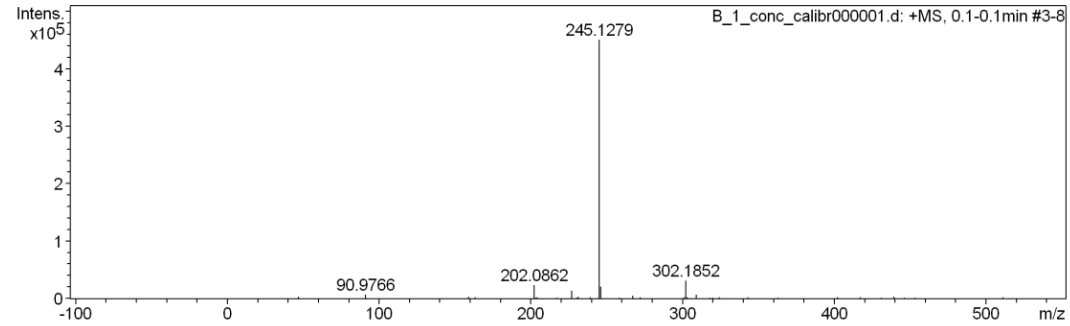
Analysis Info

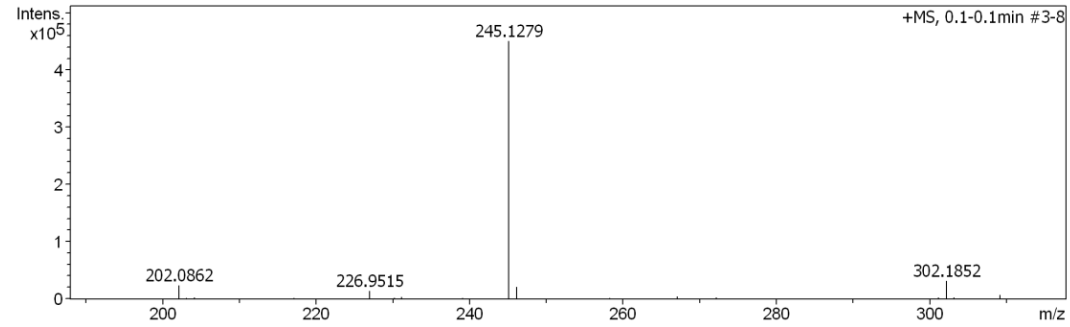
Analysis Name	D:\Data\demidov\B_1_conc_calibr000001.d	Acquisition Date	9/29/2022 12:37:07 PM
Method	Direct_Infusion_50-500.m	Operator	Demidov
Sample Name	1	Instrument	maXis impact 282001.00109
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	700 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste







Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
202.0862	1	C12H12NO2	202.0863	0.2	45.9	1	100.00	7.5	even	ok
	1	C12H12NO2	202.0863	0.2	45.9	1	100.00	7.5	even	ok
	1	C12H12NO2	202.0863	0.2	45.9	1	100.00	7.5	even	ok
245.1279	1	C14H17N2O2	245.1285	2.1	66.4	1	100.00	7.5	even	ok
	1	C14H17N2O2	245.1285	2.1	66.4	1	100.00	7.5	even	ok
302.1852	1	C17H24N3O2	302.1863	3.8	72.7	2	79.35	7.5	even	ok
	2	C13H20N9	302.1836	-5.1	59.5	1	100.00	8.5	even	ok
	1	C15H25N3NaO2	302.1839	-4.2	60.2	1	100.00	4.5	even	ok
	1	C12H29KN3O3	302.1840	-3.6	57.4	1	100.00	-0.5	even	ok
	1	C17H24N3O2	302.1863	3.8	72.7	2	79.35	7.5	even	ok
	2	C13H20N9	302.1836	-5.1	59.5	1	100.00	8.5	even	ok
	1	C17H24N3O2	302.1863	3.8	72.7	2	79.35	7.5	even	ok
	2	C13H20N9	302.1836	-5.1	59.5	1	100.00	8.5	even	ok

+MS, 0.1-0.1min #3-8

HRMS of organic fraction