

Guanidinium Iodide Salts as Single Component Catalysts in CO₂ to Epoxide Fixation

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Experimental section

General Procedures. For the synthesis of monoguanidines and bis(guanidines) salts all manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques were prepared according to published procedures.¹⁻² The synthesis of guanidinium salts was performed through an acid-base reaction with HI (57% in aqueous solution) at room temperature with varied times depending of monoguanidines or bis(guanidines) utilized. Reagents and reagent-grade solvents were obtained from E. Merck. The solvents commercial were dried using an Innovative Technology Pure Solv Model PS-MD-5.

The following instruments were used for the physical characterization of the compounds. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance-500 spectrometer. Chemical shifts and the coupling constants are reported in parts per million (SiMe₄ as standard) and Hertz, respectively. Most of the NMR assignments were supported by additional 2D experiments and the numbers of scans used for ¹³C{¹H} NMR ranged from 0.5 to 2 K depending on the sample concentration. Mass spectra were acquired using a Micro Tof (Bruker) or a Clarus SQ 8T GC/MS (PerkinElmer). Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid analyzer. For X-ray crystal structure analysis, datasets were collected by Dr. Constantin G. Daniliuc with a refined using the Bruker SHELXTL Software Package, using the space group I41/a, with Z = 8 for the formula unit, C₂₀H₃₈I₂N₆ (**1e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for catalyst screening at 1 bar pressure:

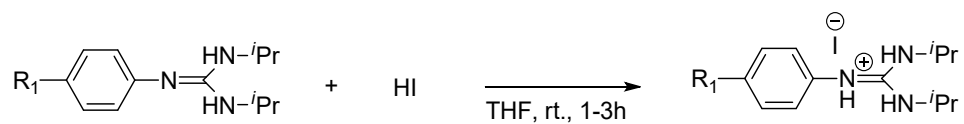
Styrene oxide **2a** (1.66 mmol) and monoguanidines iodide salts **1a–d** (33.2 μmol) or bis(guanidines) **1e–j** (16.6 μmol) were placed in an individual glass reaction tubes with a magnetic stirrer bar in a multi-point reactor Carousel 12 Place Reaction Station under constant pressure of 1 bar of CO₂. The reaction mixture was stirred at 70 °C for 18 h, then the conversion of styrene oxide **2a** into styrene carbonate **3a** was determined by analysis of a sample by ¹H NMR spectroscopy.

General procedure for the synthesis of cyclic carbonates at 1 bar pressure:

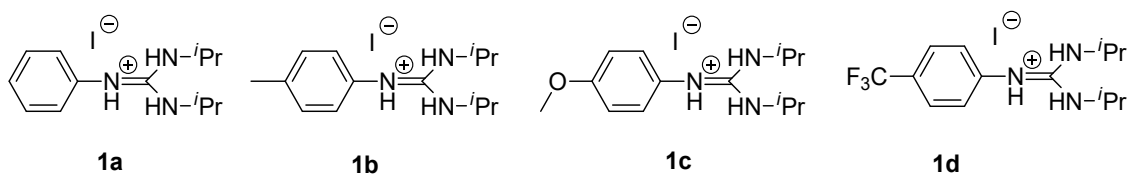
An epoxide **2a–j** (1.66 mmol) and guanidine **1e** (16.6 μmol) were placed an individual glass reaction tubes with a magnetic stirrer bar in a multi-point reactor under constant pressure of 1 bar of CO₂. The reaction mixture was stirred at 70 °C for 18 h. The conversion of epoxide to cyclic carbonate was then determined by analysis of a sample by ¹H NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH₂Cl₂ to remove the catalyst. The eluent was evaporated in vacuo to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane:EtOAc (9:1), then hexane:EtOAc (6:1) then hexane:EtOAc (3:1), then EtOAc to give the pure cyclic carbonate.

General procedure for the synthesis of cyclic carbonates at 10 bar pressure:

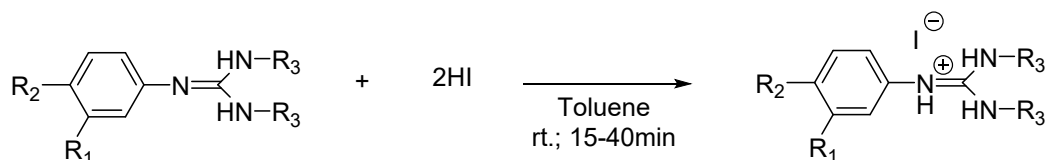
The synthesis and purification of cyclic carbonates **5a,b** were carried out in a manner identical than cyclic carbonates **3a–j** using guanidine **1e** (33.2 μmol). However, in this case the reaction mixture was placed in a stainless-steel reactor with a magnetic stirrer bar at 85 °C and 10 bar of CO₂ pressure for 24 h.



$\text{R}_1 = \text{H}$ (**1a**)
 $\text{R}_1 = \text{Me}$ (**1b**)
 $\text{R}_1 = \text{OMe}$ (**1c**)
 $\text{R}_1 = \text{CF}_3$ (**1d**)



Scheme S1. Synthesis of guanidinium iodide salts **1a–d**

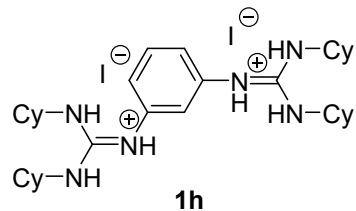
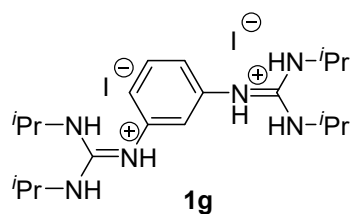
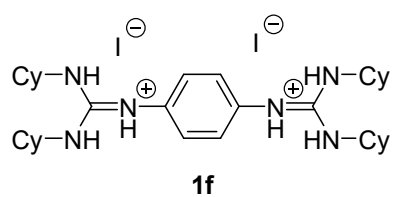
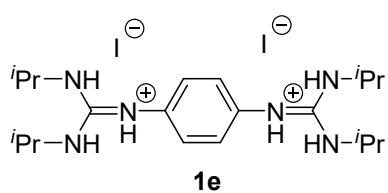


R₁ = H; R₂ = CN₃^{*i*}Pr; R₃ = ^{*i*}Pr; n = 2 (**1e**)

R₁ = H; R₂ = CN₃Cy; R₃ = Cy; n = 2 (**1f**)

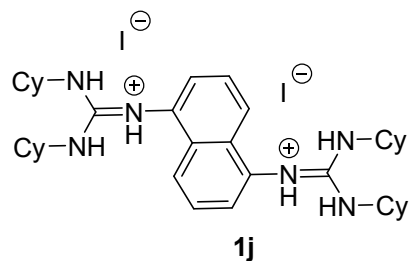
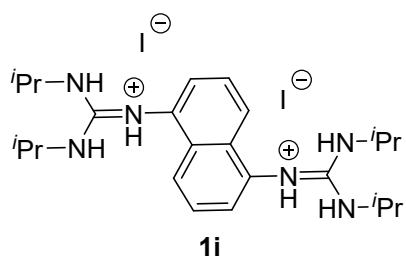
R₂ = H; R₁ = CN₃^{*i*}Pr; R₃ = ^{*i*}Pr; n = 2 (**1g**)

R₂ = H; R₁ = CN₃Cy; R₃ = Cy; n = 2 (**1h**)



R = ^{*i*}Pr (**1i**)

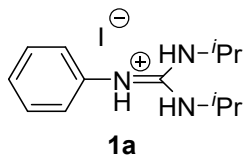
R = Cy (**1j**)



Scheme S2. Synthesis of bis(guanidinium) iodide salts **1e–j**

NMR data for guanidinium iodide salts 1a–j

Synthesis of N-(bis(isopropylamino)methylene)benzenaminium iodide (**1a**)



A solution of 1,3-diisopropyl-2-phenylguanidine (**G1**) (100 mg, 0.46 mmol) was prepared in THF (5 mL), and was added dropwise to HI (0.46 mmol, 102.46 μ L) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 2 hours at room temperature. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. Finally, the oil was washed with previously heated hexane (20 mL) precipitating a yellowish solid. The solid was obtained with a yield of 89% (141 mg). ^1H NMR (500 MHz, CDCl_3). δ = 7.26 (s, 2H, CH-Ar), 7.00 (t, J = 7.4 Hz, 1H, CH-Ar), 6.92 (d, J = 7.4 Hz, 2H, CH-Ar), 4.86 (m, 2H, N-H), 3.80 (Hept, 2H, CH- i Pr), 1.16 ppm (d, J = 6.4 Hz, 12H, CH_3 - i Pr). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3). δ = 151.72 (C=N), 145.84 (C-Ar), 129.36 (CH-Ar), 123.34 (CH-Ar), 122.92 (CH-Ar), 44.07 (CH- i Pr), 22.96 ppm (CH_3 - i Pr).

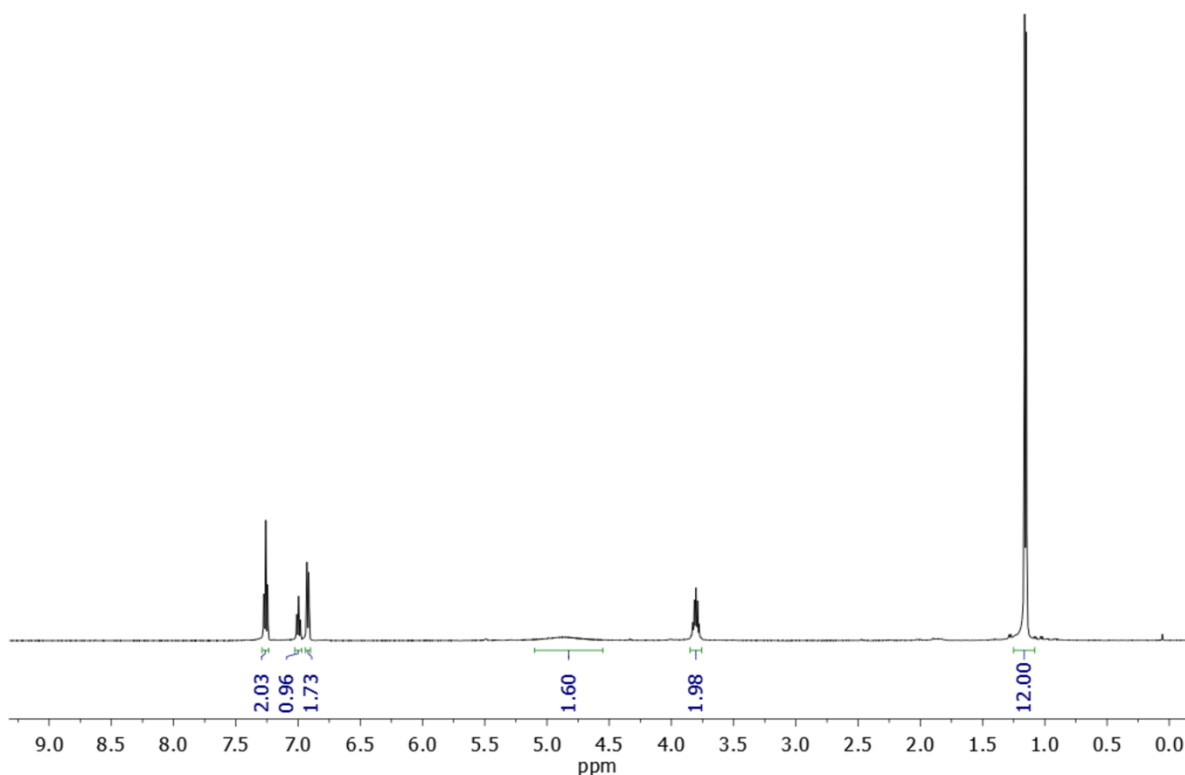


Figure S1. ^1H -NMR of N-(bis(isopropylamino)methylene)benzenaminium iodide (**1a**) in CDCl_3 .

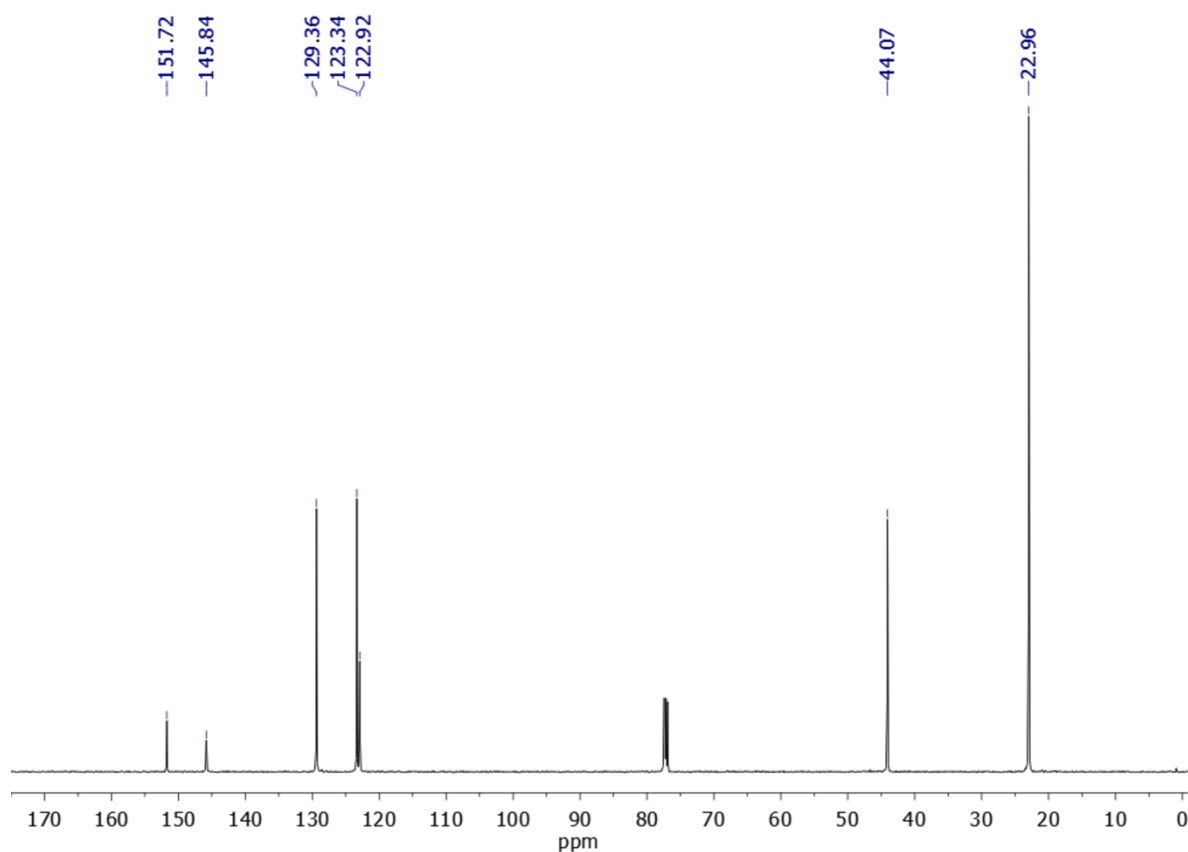
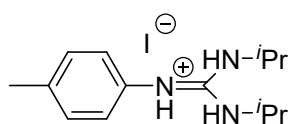


Figure S2. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N-(bis(isopropylamino)methylene)benzenaminium iodide (**1a**) in CDCl_3

Synthesis of N-(bis(isopropylamino)methylene)-4-methylbenzenaminium iodide (**1b**)



1b

A solution of 1,3-diisopropyl-2-(p-tolyl)guanidine (**G2**) (100 mg, 0.43 mmol) was prepared in THF (5 mL), and was added dropwise to HI (0.43 mmol, 96.30 μL) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 1.5 hours at room temperature. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. Finally, the oil was washed with previously heated hexane (20 mL) precipitating a yellowish solid. The solid was obtained with a yield of 85% (132 mg). ^1H NMR (500 MHz, CDCl_3) δ = 7.07 (d, J = 8.1 Hz, 2H, CH-Ar), 6.92 (d, J = 8.2 Hz, 2H, CH-Ar), 6.03 (s, 1H, N-H), 3.92 (Hept, 2H, CH- i Pr), 2.27 (s, 3H, CH_3 -Ar), 1.15 ppm (d, J = 6.4 Hz, 12H, CH_3 - i Pr). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 152.85 (C=N), 138.01 (C-Ar), 134.58 (C-Ar), 130.19 (CH-Ar), 123.62 (CH-Ar), 45.10 (CH- i Pr), 22.79 (CH_3 - i Pr), 20.87 ppm (CH_3 -Ar).

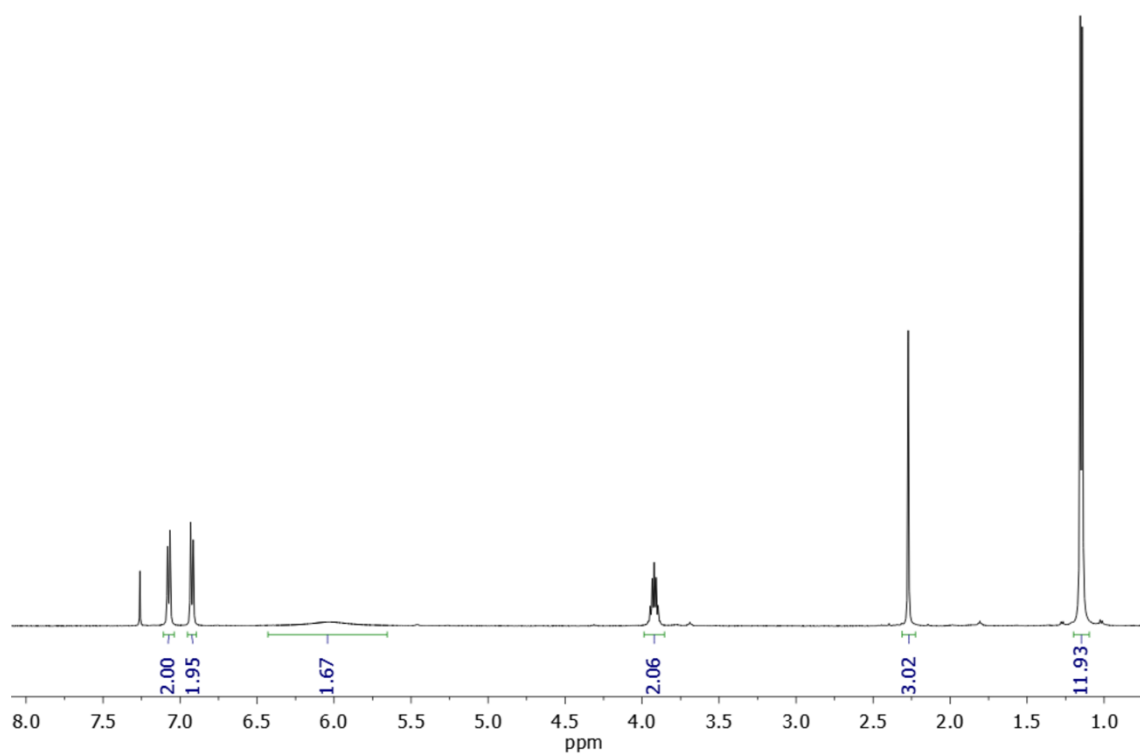


Figure S3. ^1H -NMR of N-(bis(isopropylamino)methylene)-4-methylbenzenaminium iodide (**1b**) in CDCl_3 .

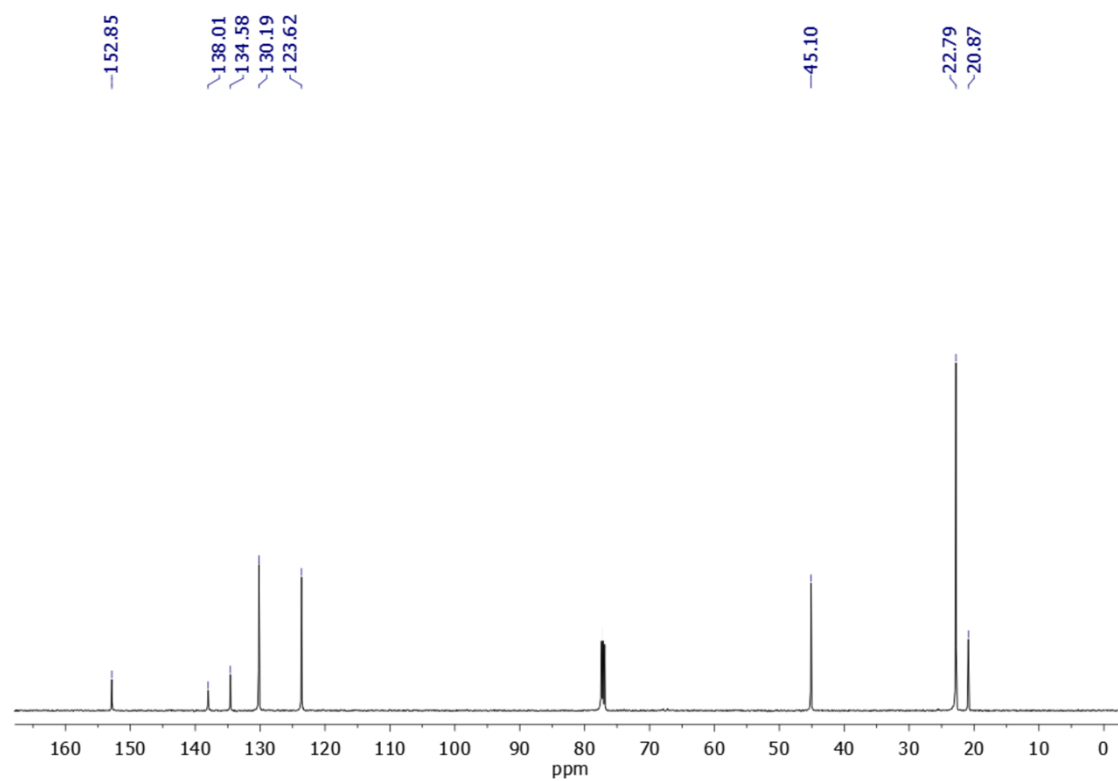
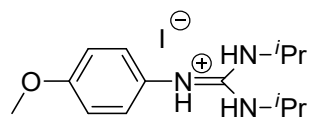


Figure S4. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N-(bis(isopropylamino)methylene)-4-methylbenzenaminium iodide (**1b**) in CDCl_3 .

Synthesis of N-(1-(isopropylamino)-3-methylbutylidene)-4-methoxybenzenaminium iodide (**1c**)



1c

A solution of 1,3-diisopropyl-2-(4-methoxyphenyl)guanidine (**G3**) (100 mg, 0.40 mmol) was prepared in THF (5 mL), and was added dropwise to HI (0.40 mmol, 90.11 μ L) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 1.5 hours at room temperature. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. Finally, the oil was washed with previously heated hexane (20 mL) precipitating a yellowish solid. The solid was obtained with a yield of 92% (139 mg). ^1H NMR (500 MHz, CDCl_3) δ = 6.89 (d, J = 8.8 Hz, 2H, CH-Ar), 6.82 (d, J = 8.8 Hz, 2H, CH-Ar), 5.25 (m, 2H, N-H), 3.85 (Hept, 2H, CH- i Pr), 3.76 (s, 3H, $\text{CH}_3\text{O-Ar}$), 1.15 ppm (d, J = 6.4 Hz, 12H, CH_3-i Pr). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 156.39 (C-Ar), 152.41 (C=N), 136.51 (C-Ar), 125.13 (CH-Ar), 114.92 (CH-Ar), 55.57 ($\text{CH}_3-\text{CH}_3\text{O}$), 44.51 (CH- i Pr), 23.10 ppm (CH_3-i Pr).

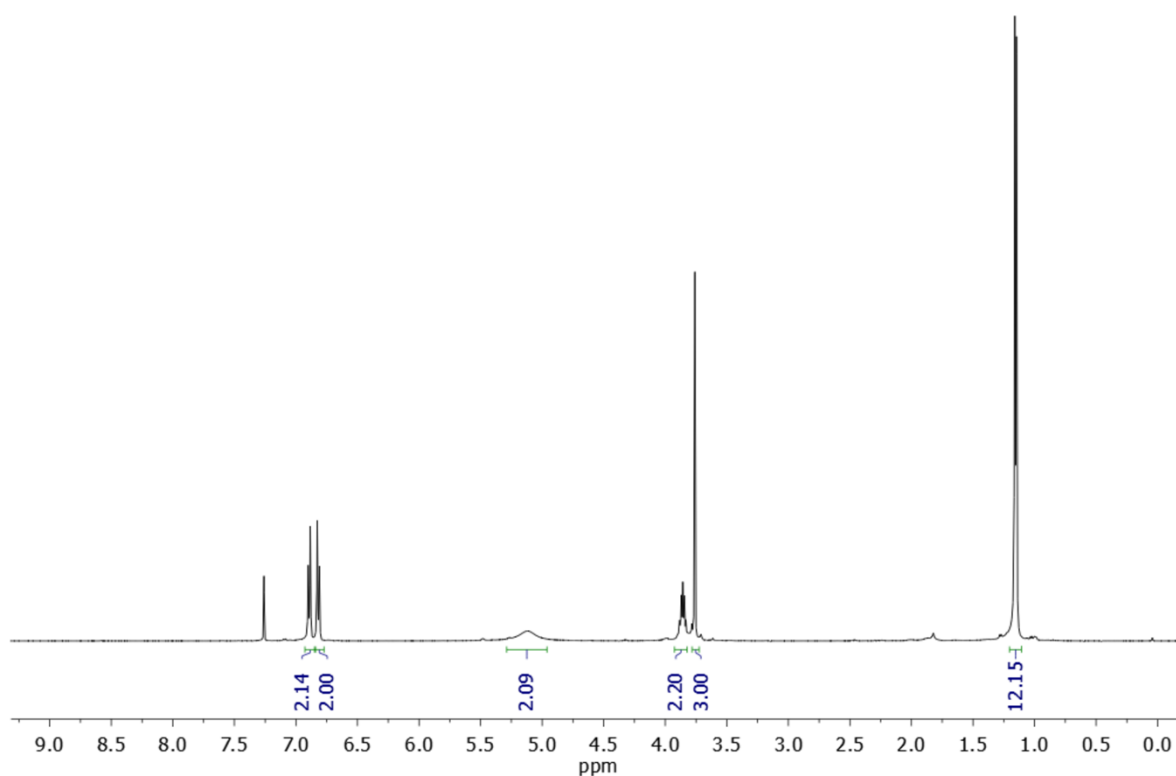


Figure S5. ^1H -NMR of N-(1-(isopropylamino)-3-methylbutylidene)-4-methoxybenzenaminium iodide (**1c**) in CDCl_3

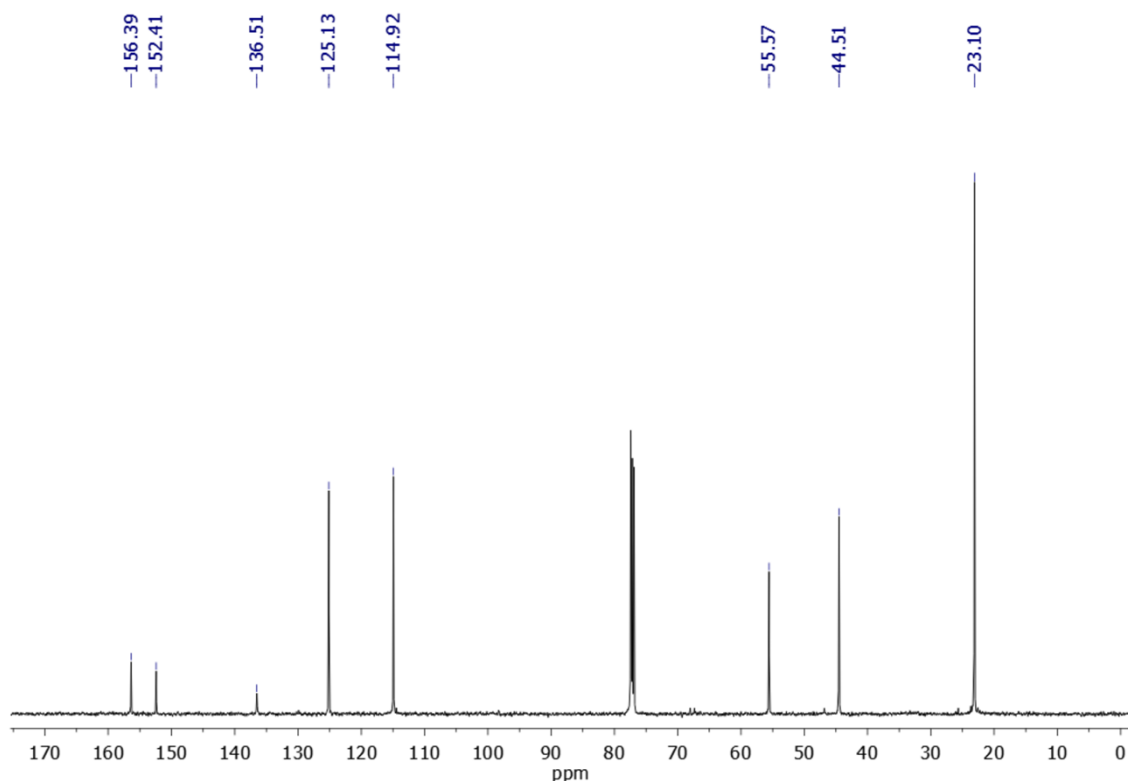
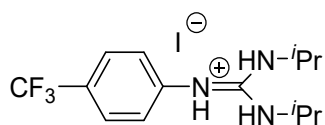


Figure S6. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N-(1-(isopropylamino)-3-methylbutylidene)-4-methoxybenzenaminium iodide (**1c**) in CDCl_3 .

Synthesis of N-(bis(isopropylamino)methylene)-4-(trifluoromethyl)benzenaminium iodide (1d**)**



1d

A solution of 1,3-diisopropyl-2-(4-(trifluoromethyl)phenyl)guanidine (**G4**) (100 mg, 0.34 mmol) was prepared in THF (5 mL), and was added dropwise to HI (0.34 mmol, 78.26 μL) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 1.5 hours at room temperature. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. Finally, the oil was washed with previously heated hexane (20 mL) precipitating a yellowish solid. The solid was obtained with a yield of 97% (140 mg). ^1H NMR (500 MHz, CDCl_3) δ = 9.15 (s, 1H, N-H), 7.63 (d, J = 8.5 Hz, 2H, CH-Ar), 7.45 (d, J = 8.4 Hz, 2H, CH-Ar), 7.05 (s, 2H, N-H), 4.08 (m, 2H, CH-*i*Pr), 1.29 ppm (d, J = 6.4 Hz, 12H, CH_3 -*i*Pr). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 153.98 (C-Ar), 139.66 (C=N), 127.21 (CH-Ar), 124.87 (C-Ar), 122.51 (CH-Ar), 47.25 (CH-*i*Pr), 22.82 ppm (CH_3 -*i*Pr). ^{19}F NMR (471 MHz, CDCl_3) δ = -62.45 ppm.

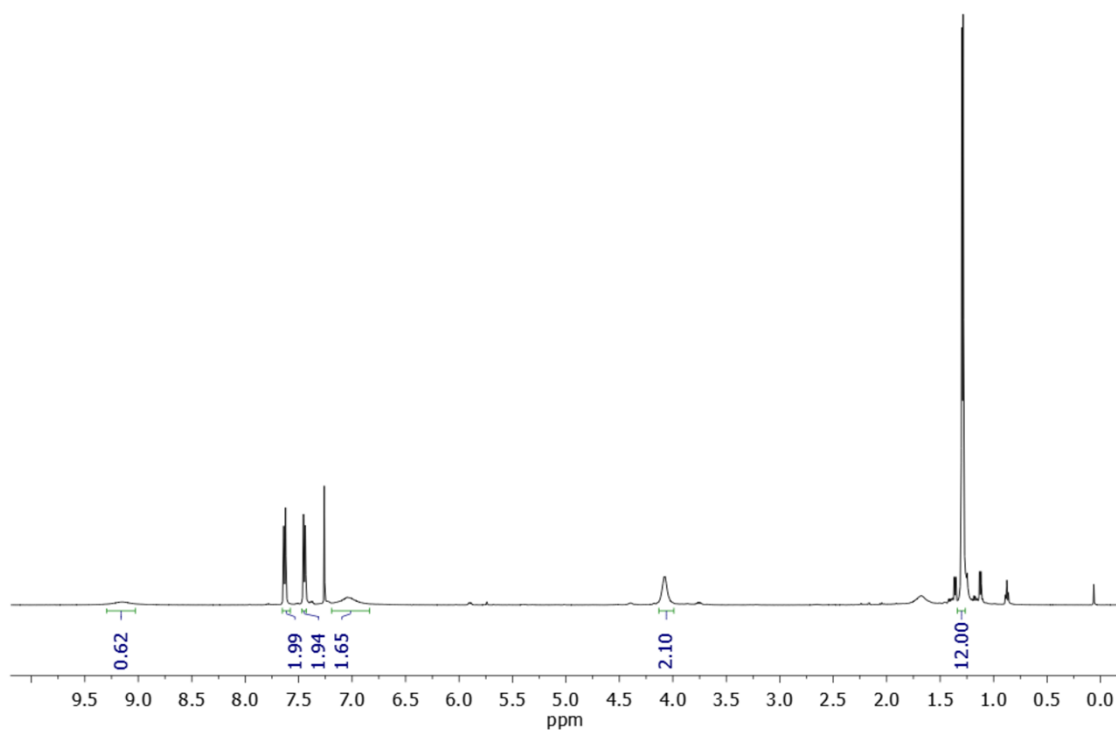


Figure S7. ^1H NMR of N-(bis(isopropylamino)methylene)-4-(trifluoromethyl)benzenaminium iodide (**1d**) in CDCl_3 .

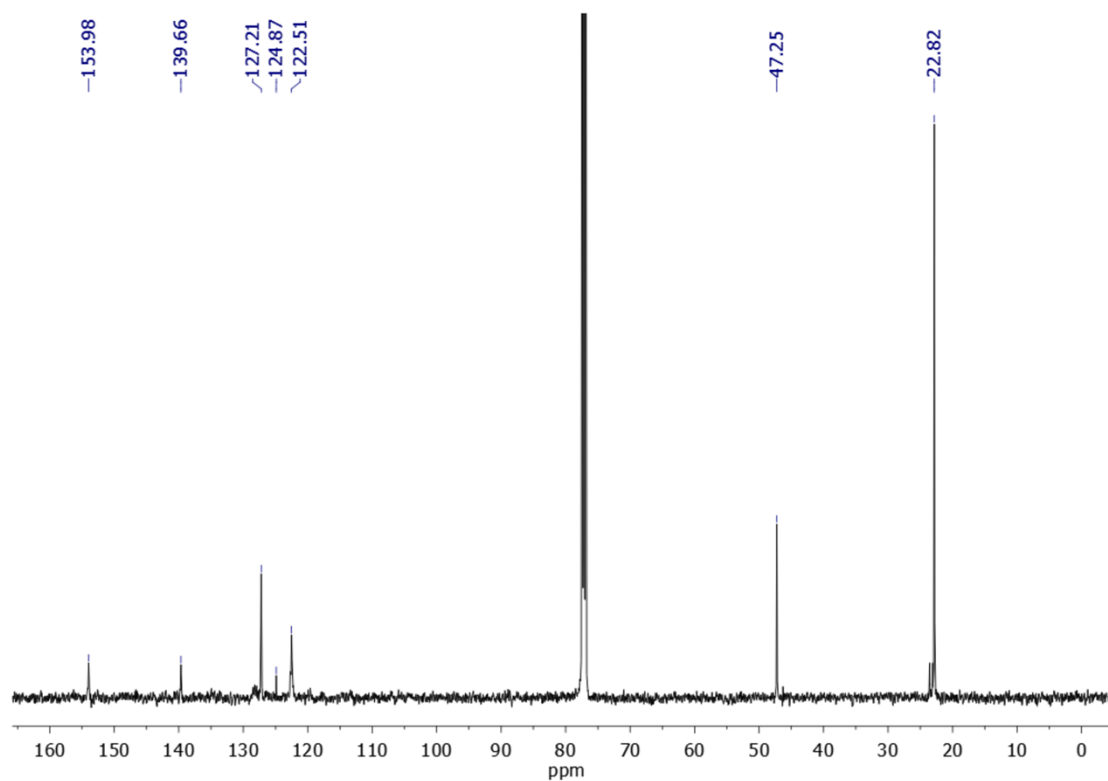


Figure S8. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N-(bis(isopropylamino)methylene)-4-(trifluoromethyl)benzenaminium iodide (**1d**) in CDCl_3 .

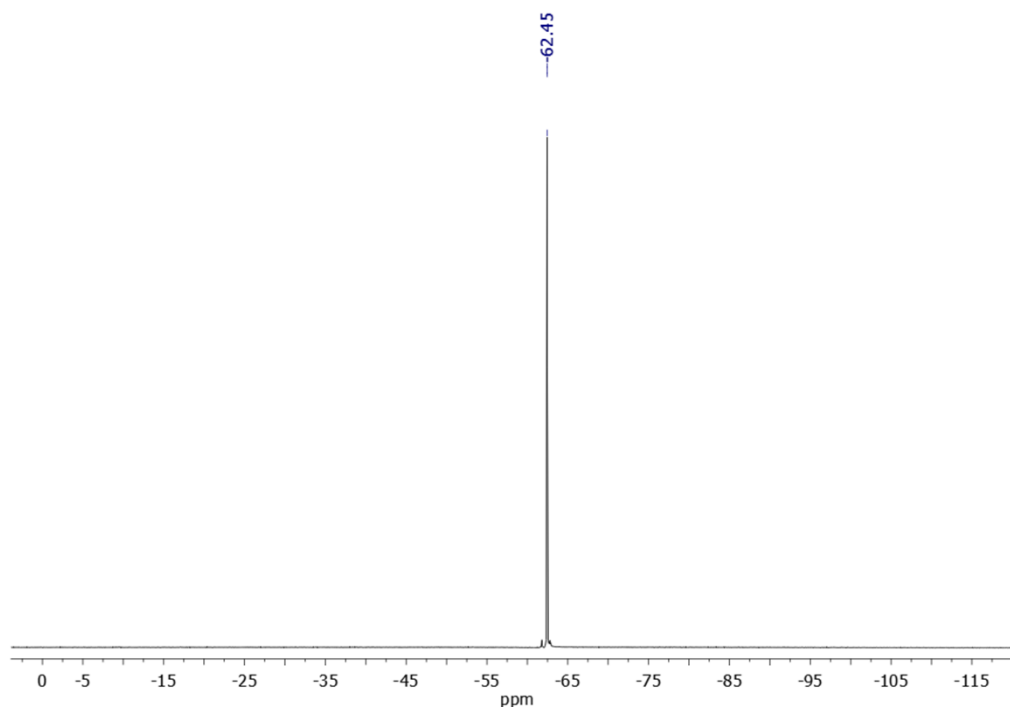
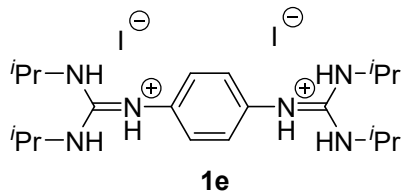


Figure S9. ^{19}F NMR of N-(bis(isopropylamino)methylene)-4-(trifluoromethyl)benzenaminium iodide (**1d**) in CDCl_3 .

Synthesis of N^1, N^4 -bis(bis(isopropylamino)methylene)benzene-1,4-diaminium Diiodide (1e**).**



A solution of 2', 2'-(1,4-phenylene)-bis (1,3-diisopropylguanidine) (**L1**) (100 mg, 0.28 mmol) was prepared in THF (5 mL), and was added dropwise to HI solution (0.1M in THF, 0.55mmol, 5.55mL). The reaction mixture was then stirred vigorously for 15 min at room temperature obtaining a yellowish precipitate. The solid was collected by filtration, washed with THF and pentane, until a white solid was obtained with a yield of 96% (165 mg). ^1H NMR (400 MHz, CD_3CN) δ = 7.97 (s, 1H, N-H), 7.28 (s, 2H, Ar-H), 6.15 (s, 2H, N-H), 3.92 (m, 2H, CH- i Pr), 1.28 ppm (d, 12H, CH_3 - i Pr). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) δ = 153.32 (C=N), 135.40 (Ar-C), 127.71 (Ar-CH), 46.29 (CH- i Pr), 22.64 ppm (CH_3 - i Pr). $\text{C}_{20}\text{H}_{38}\text{N}_6\text{I}_2$ (616.34) calc.: C: 38.97, H: 6.21, N: 13.64, (%). Found: C, 38.87; H, 6.17; N, 12.94.

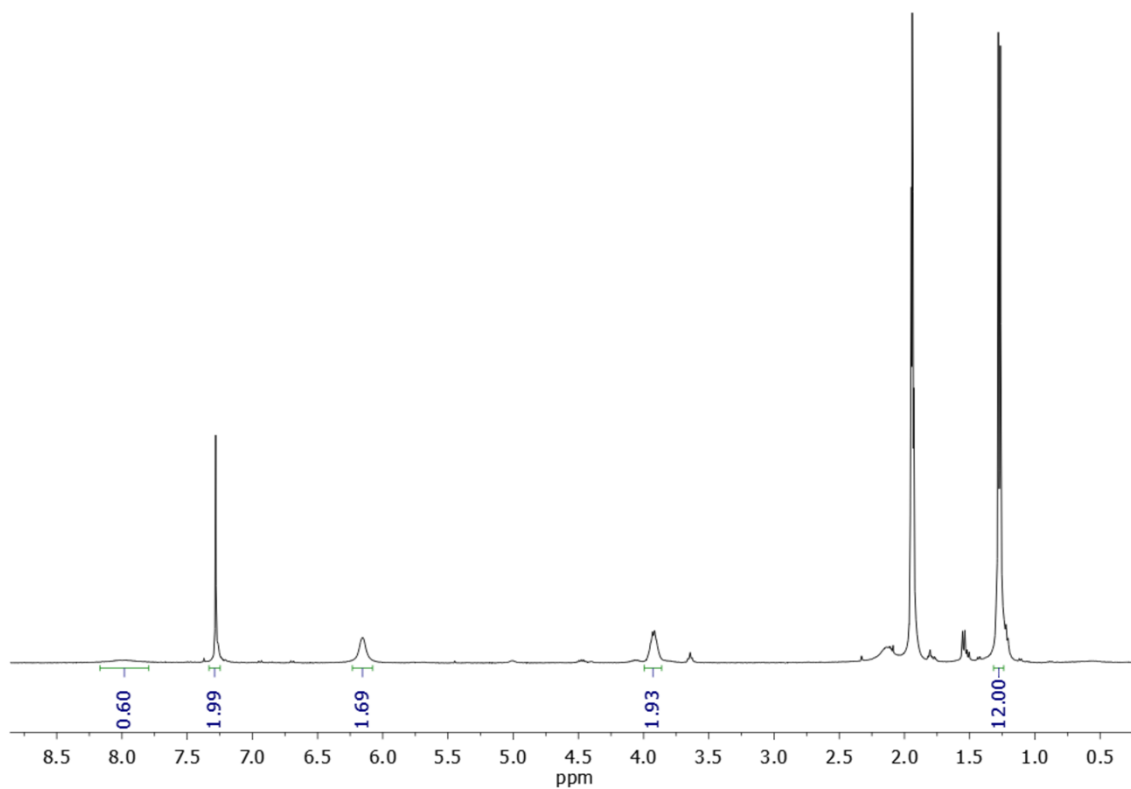


Figure S10. ^1H -NMR of N^1,N^4 -bis(bis(isopropylamino)methylene)benzene-1,4-diaminium diiodide (**1e**) in CD_3CN

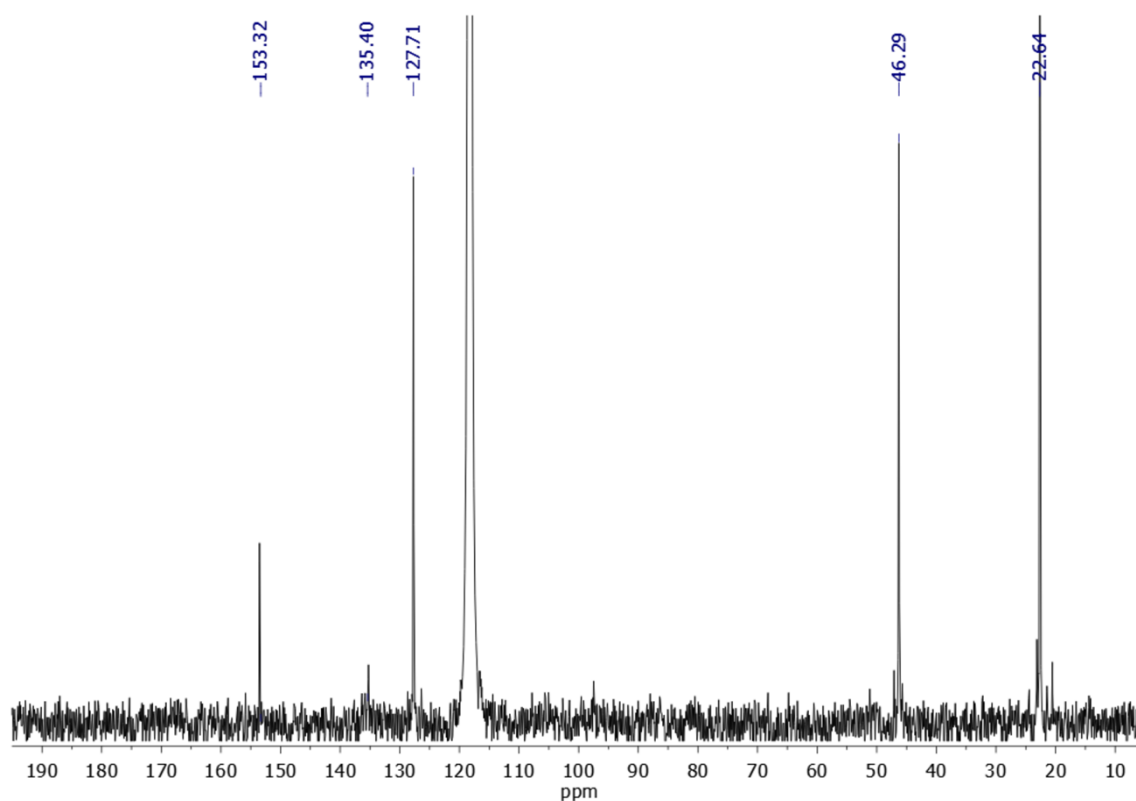


Figure S11. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N^1,N^4 -bis(bis(isopropylamino)methylene)benzene-1,4-diaminium diiodide (**1e**) in CD_3CN .

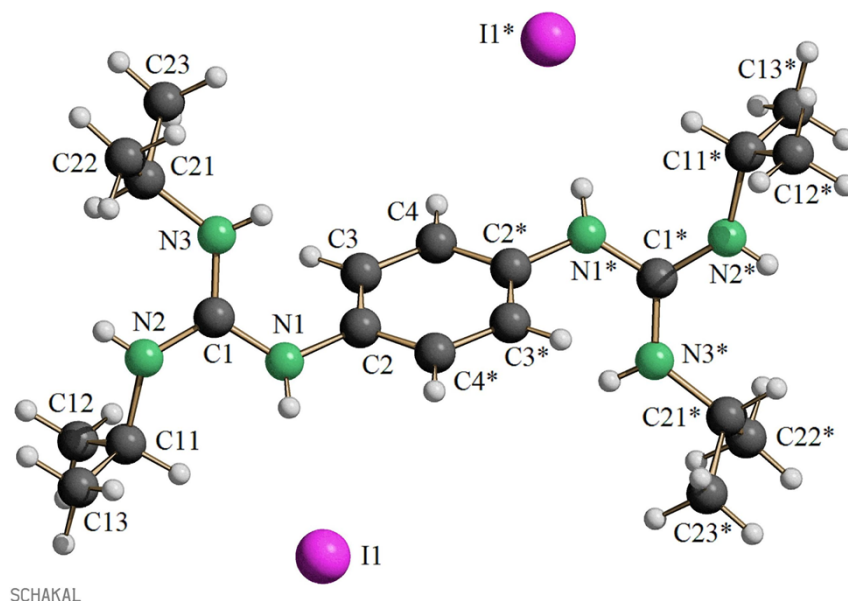


Figure S12. X ray crystal structure of N^1,N^4 -bis(bis(isopropylamino)methylene)benzene-1,4-diaminium diiodide (**1e**). Thermal ellipsoids are shown with 50 % probability.

X-ray crystal structure report of N^1,N^4 -bis(bis(isopropylamino)methylene)benzene-1,4-diaminium diiodide (1e**):** A colorless needle-like specimen of $C_{20}H_{38}I_2N_6$, approximate dimensions 0.052 mm x 0.112 mm x 0.424 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

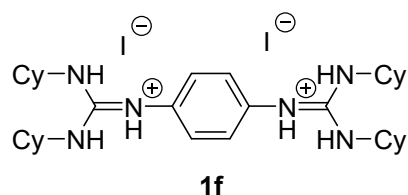
A total of 1731 frames were collected. The total exposure time was 8.58 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a tetragonal unit cell yielded a total of 36089 reflections to a maximum q angle of 70.07° (0.82 \AA resolution), of which 2425 were independent (average redundancy 14.882, completeness = 99.8%, $R_{int} = 5.29\%$, $R_{sig} = 2.07\%$) and 2256 (93.03%) were greater than $2s(F_2)$. The final cell constants of $a = 28.4678(8) \text{ \AA}$, $b = 28.4678(8) \text{ \AA}$, $c = 6.3147(2) \text{ \AA}$, volume = $5117.5(3) \text{ \AA}^3$, are based upon the refinement of the XYZ centroids of 9787 reflections above 20 s(I) with $8.785^\circ < 2q < 139.9^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.567. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0450 and 0.4320.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $I41/a$, with $Z = 8$ for the formula unit, $C_{20}H_{38}I_2N_6$. The final anisotropic full-matrix least-squares refinement on F_2 with 143 variables converged at $R_1 = 1.97\%$, for the observed data and $wR_2 = 5.18\%$ for all data. The goodness-of-fit was 1.082. The largest peak in the final difference electron density synthesis was 0.540 e-/\AA^3 and the largest hole was -0.551 e-/\AA^3 with an RMS deviation of 0.085 e-/\AA^3 . On the basis of the final model, the calculated density was 1.600 g/cm^3 and $F(000)$, 2448 e-.

Table S1. Crystallographic data for salt **1e**

Empirical formula	C ₂₀ H ₃₈ I ₂ N ₆
Formula weight	295.42
Temperature (K)	616.36 g/mol
Wavelength (Å)	100(2) K
Crystal system	1.54178 Å
Space group	0.052 x 0.112 x 0.424 mm
a(Å)	colorless needle
b(Å)	tetragonal
c(Å)	I 41/a
α(°)	a = 28.4678(8) Å α = 90°
β(°)	b = 28.4678(8) Å β = 90°
γ(°)	c = 6.3147(2) Å γ = 90°
Volume (Å ³)	5117.5(3) Å ³
Z	8
Density (calculated) (g/cm ³)	1.600
Absorption coefficient (mm ⁻¹)	19.425
F(000)	2448
Index ranges	-34 ≤ h ≤ 34 -34 ≤ k ≤ 34 -7 ≤ l ≤ 7
Reflections collected	36089
Independent reflections	2425 [R(int) = 0.0529]
Data/restraints/parameters	2425 / 0 / 143
Goodness-of-fit on F ²	1.082
Final R indices [I > 2σ(I)]	R1 = 0.0218 wR ² = 0.0518
R indices (all data)	R1 = 0.0197 wR ² = 0.0489
Largest diff. peak / hole, e.Å ⁻³	0.540 and -0.551

Synthesis of N¹, N⁴-bis(bis(cyclohexylamino)methylene)benzene-1,4-diaminium diiodide (**1f**)



A solution of 2',2'-(1,4-phenylene)-bis(1,3-dicyclohexylguanidine) (**L2**) (100 mg, 0.19 mmol) was prepared in benzene (5 mL), and was added dropwise to HI (0.38 mmol, 86.29 μL) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 40 min at room temperature obtaining a yellowish precipitate. The solid was collected by filtration and washed with acetone until a yellowish solid was obtained. The solid was obtained with a yield of 95 % (140 mg). ¹H NMR (500 MHz, CD₃CN) δ = 8.12 (s, 1H, N-H), 7.31 (d, 2H, Ar-H), 6.32 (s, 2H, N-H), 3.64 (m, 2H, CH-Cy), 1.76 (d, J = 13.2 Hz, 5H, CH₂-Cy), 1.62 (d, J = 12.9 Hz, 3H, CH₂-Cy), 1.52–1.27 (m, 10H), 1.22–1.10 ppm (m, 2H, CH₂-Cy). ¹³C {¹H} NMR (126 MHz, CD₃CN) δ = 153.44 (C=N), 134.81 (Ar-C), 127.73 (Ar-CH), 53.08 (CH-Cy), 33.18

(CH₂-Cy), 25.69 (CH₂-Cy), 25.54 ppm (CH₂-Cy). C₃₂H₅₄N₆I₂ (776.61). Calc: C:49.49, H:7.01, N:10.82(%). Found: C: 49,58, H:6,91, N: 10,07(%).

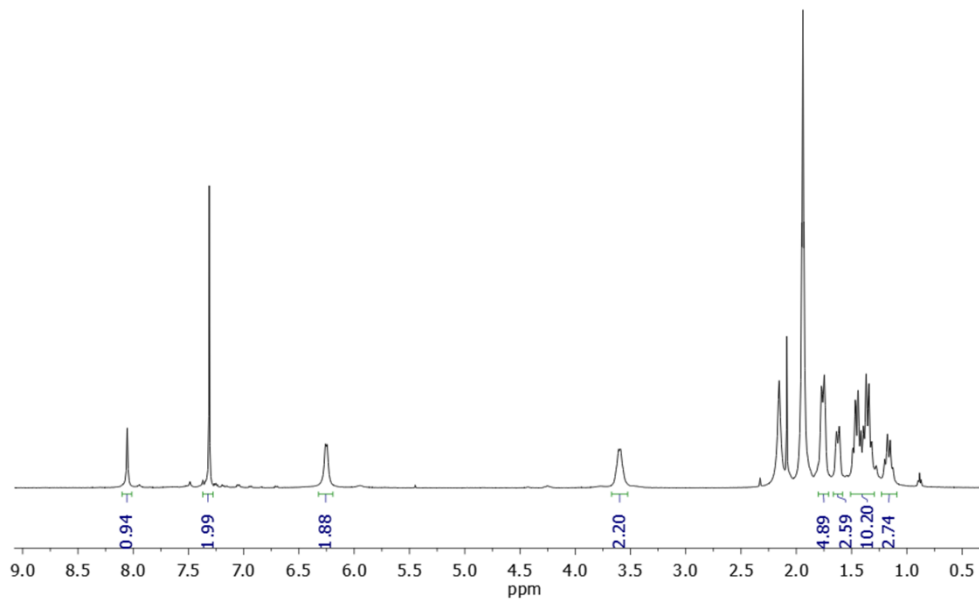


Figure S13. ¹H-NMR of N¹,N⁴-bis(bis(cyclohexylamino)methylene)benzene-1,4-diaminium diiodide (**1f**) in CD₃CN.

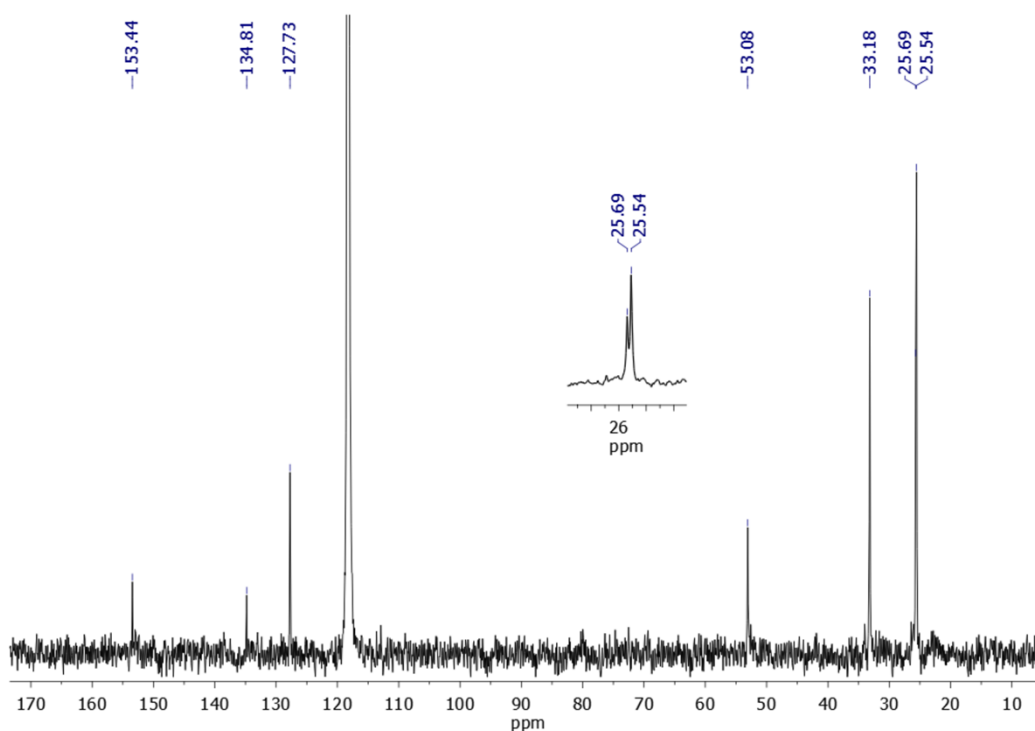
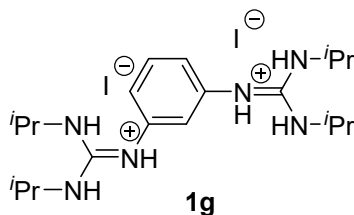


Figure S14. ¹³C-¹H-NMR of N¹,N⁴-bis(bis(cyclohexylamino)methylene)benzene-1,4-diaminium diiodide (**1f**) in CD₃CN.

Synthesis of N¹, N³-bis(bis(isopropylamino)methylene)benzene-1,3-diaminium Diiodide (**1g**).



A solution of 2,2'-(1,3-phenylene) bis (1,3-diisopropylguanidine) (**L5**) (100 mg, 0.28 mmol) was prepared in dichloromethane (5 mL), and was added dropwise to HI (0.56 mmol, 125.84 μ L) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 40 min at room temperature obtaining a yellowish precipitate. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. The oil was washed with previously heated pentane precipitating a yellowish solid. The solid was collected by filtration, washed with acetone and pentane, and dried overnight. The solid is obtained with a yield of 93% (202 mg). ¹H NMR (500 MHz, CD₃CN) δ = 8.34 (s, 2H, NH), 7.48 (t, J = 8.0 Hz, 1H, Ar-CH), 7.24 (s, 1H, Ar-CH), 7.21 (dd, J = 8.0, 2.0 Hz, 2H, Ar-CH), 6.48 (s, 4H, NH), 4.07 (d, J = 6.0 Hz, 4H, CH-^{*i*}Pr), 1.29 ppm (d, J = 6.4 Hz, 24H, CH₃-^{*i*}Pr). ¹³C{¹H} NMR (126 MHz, CD₃CN) δ = 153.65 (C=N), 137.80 (Ar-C), 132.14 (Ar-C), 124.53 (Ar-CH), 123.02 (Ar-CH), 46.69 (CH-^{*i*}Pr), 22.74 (CH₃-^{*i*}Pr). C₂₀H₃₈N₆I₂ (616.34) Calc: C: 38.97, H: 6.21, N: 13.64 (%). Found: C: 38.63, H: 5.90, N: 12.86(%).

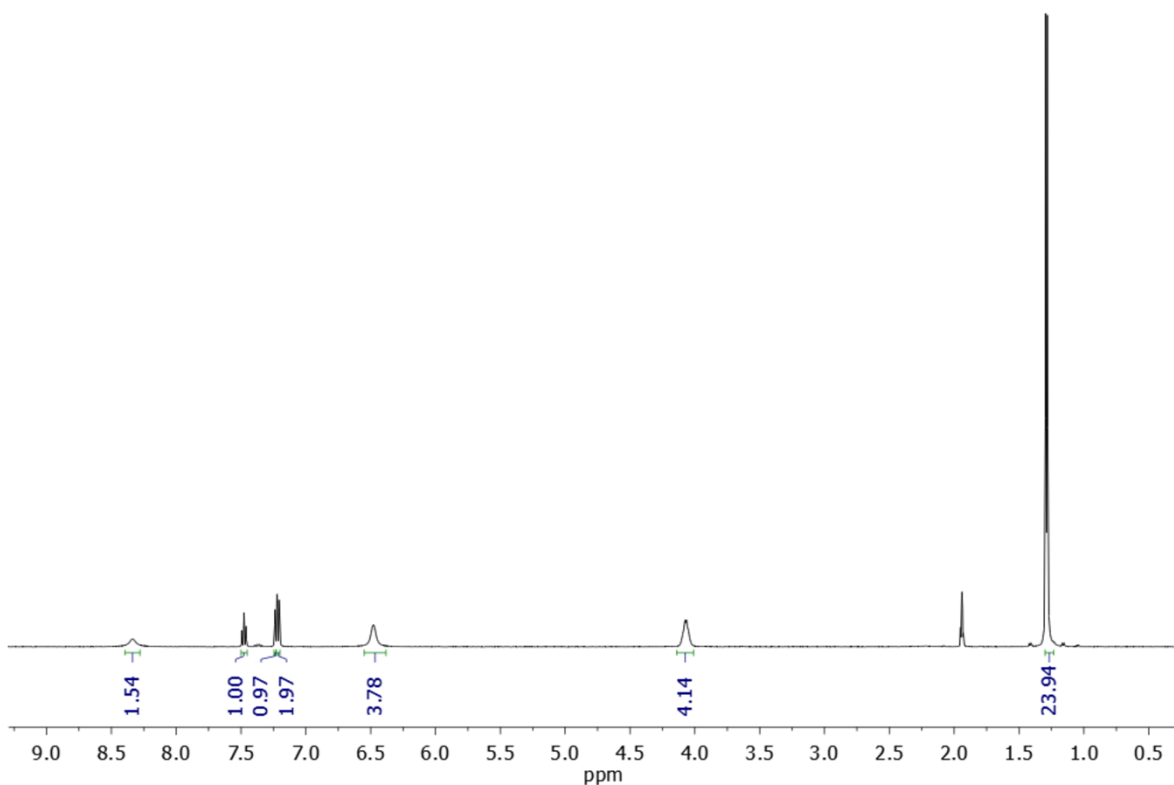


Figure S15. ¹H-NMR of N¹, N³-bis(bis(isopropylamino)methylene)benzene-1,3-diaminium diiodide (**1g**) in CD₃CN

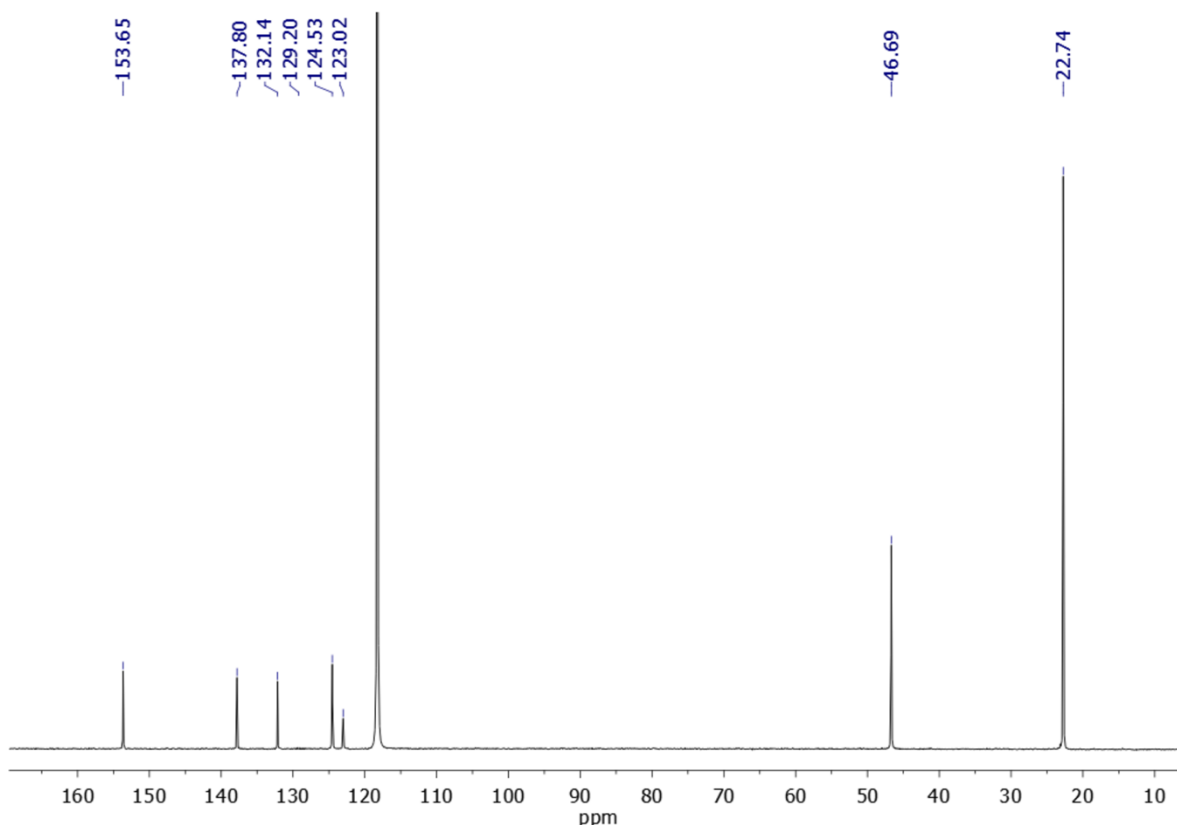
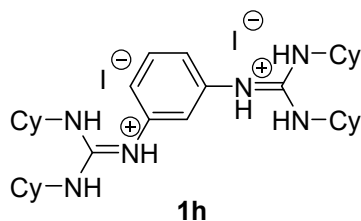


Figure S16. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N^1, N^3 -bis(bis(isopropylamino)methylene)benzene-1,3-diaminium Diiodide (**1g**) in CD_3CN

Synthesis of N^1, N^3 -bis(bis(cyclohexylamino)methylene)benzene-1,3-diaminium Diiodide (1h**).**



A solution of 2,2'-(1,3-phenylene) bis(1,3-dicyclohexylguanidine) (L6) (100mg, 0.19mmol) was prepared in dichloromethane (5 mL), and was added dropwise to HI (0.38 mmol, 86.30 μL) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 40 min at room temperature obtaining a yellowish precipitate. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. The oil was washed with previously heated pentane precipitating a yellowish solid. The solid was collected by filtration, washed with acetone and pentane, and dried overnight. The solid was obtained with a yield of 91% (136 mg). ^1H NMR (500 MHz, CD_3CN) δ = 8.10 (s, 2H, NH), 7.49 (t, J = 8.1 Hz, 1H, Ar-H), 7.20 (dd, J = 8.0, 1.9 Hz, 2H, Ar-H), 7.15 (s, 1H, Ar-H), 6.27 (s, 1H, NH), 3.62 (m, J = 23.7 Hz, 4H, CH-Cy), 1.84–1.70 (m, 11H, CH_2 -Cy), 1.63 (d, J = 12.9 Hz, 6H, CH_2 -Cy), 1.50–1.28 (m, 21H, CH_2 -Cy), 1.16 ppm (dd, J = 25.1, 12.6 Hz, 6H, CH_2 -Cy). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_3CN) δ = 153.41 (C=N), 137.64 (Ar-C), 132.29 (Ar-CH), 124.87 (Ar-CH), 123.21 (Ar-CH), 53.18, 33.20 (CH-Cy), 25.68 (CH₂-Cy), 25.55 ppm (CH₂-Cy). $\text{C}_{32}\text{H}_{54}\text{N}_6\text{I}_2$ (776.61) Calc: C: 49.49, H: 7.07, N: 10.82(%). Found: C: 47.50, H: 6.57, N: 9.57.

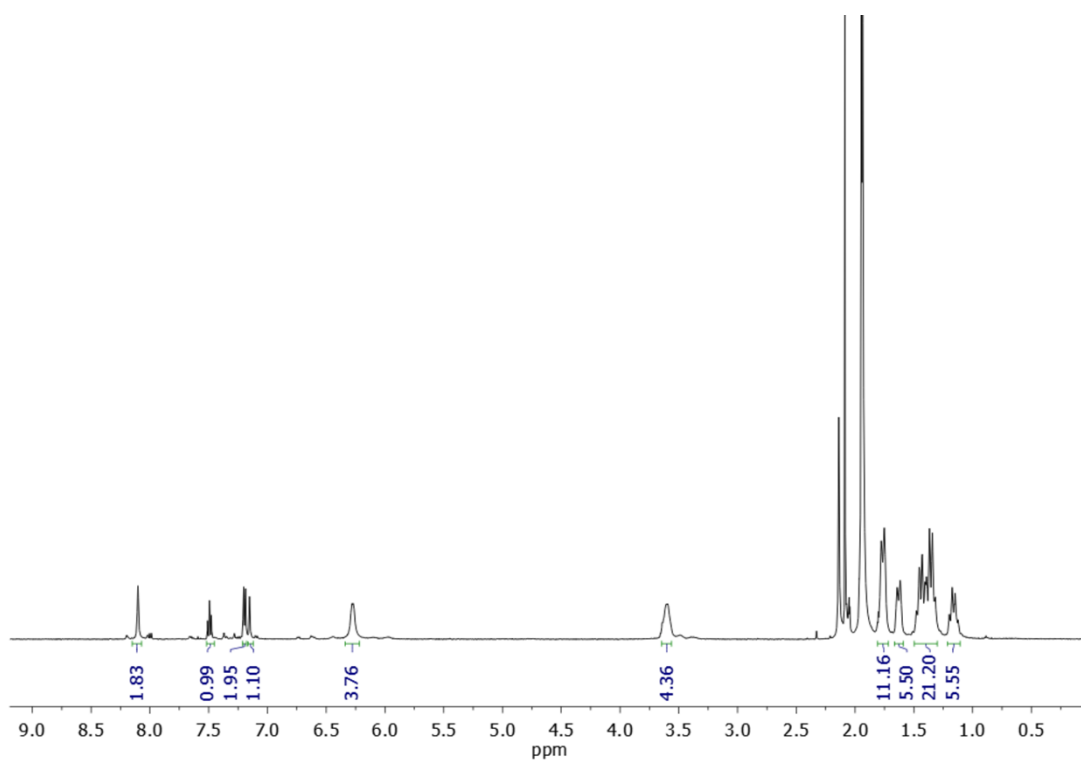


Figure S17. ^1H -NMR of N^1 , N^3 -bis(bis(cyclohexylamino)methylene)benzene-1,3-diaminium diiodide (**1g**) in CD_3CN .

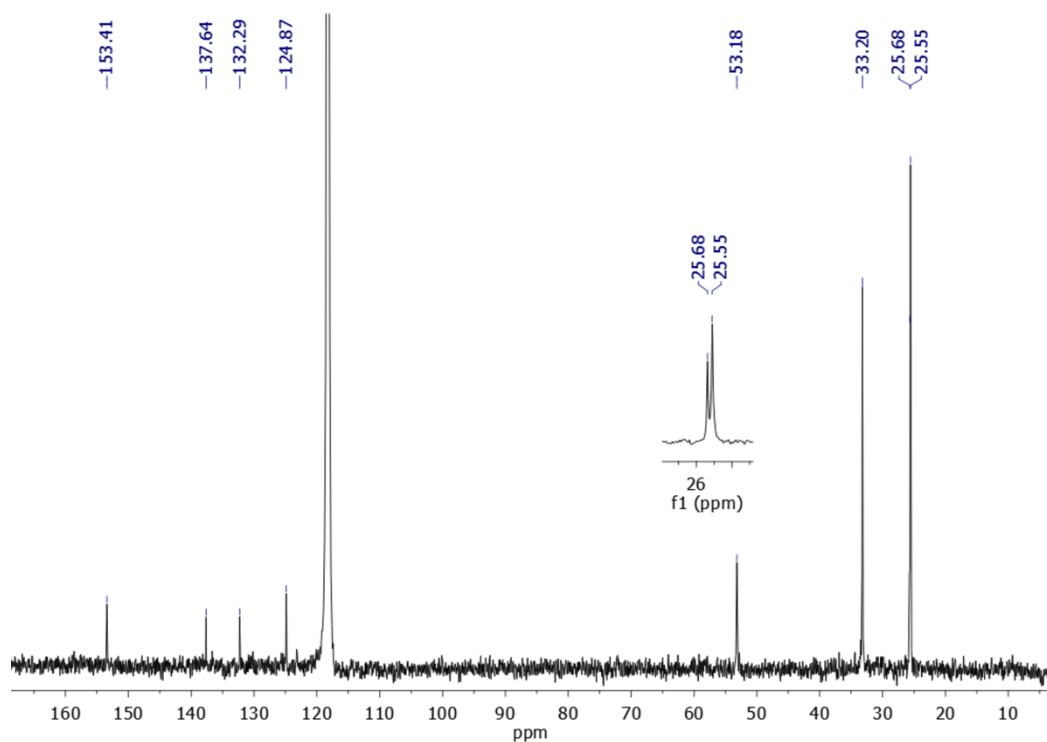
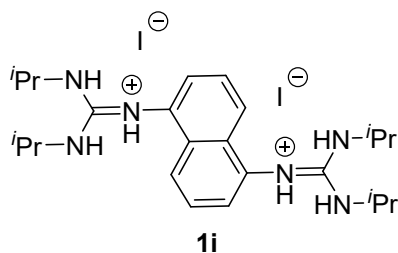


Figure S18. ^{13}C - $\{^1\text{H}\}$ -NMR of N^1 , N^3 -bis(bis(cyclohexylamino)methylene)benzene-1,3-diaminium diiodide (**1g**) in CD_3CN .

Synthesis of N¹, N⁵-bis(bis(isopropylamino)methylene) naphthalene-1,5-diaminium Diiodide (**1i**)



A solution of 2',2'-(naphthalene-1,5-diyl)bis(1,3-diisopropylguanidine) (**L3**) (100 mg, 0.24 mmol) was prepared in dichloromethane (5 mL), and was added dropwise to HI (0.48 mmol, 109.46 μ L) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 25 min at room temperature obtaining a yellowish precipitate. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. The solid was collected by filtration, washed with dichloromethane and acetone, and dried overnight. The solid was obtained with a yield of 93% (151 mg). ¹H NMR (500 MHz, CD₃CN) δ = 8.33 (s, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.69 (t, J = 8.4, 7.4 Hz, 1H), 7.60 (d, J = 7.2, 0.7 Hz, 1H), 6.11 (s, 2H), 4.02 (hept, J = 6.3 Hz, 2H), 1.21 ppm (d, J = 27.9, 3.5 Hz, 12H). ¹³C{¹H} NMR (126 MHz, CD₃CN) δ = 154.43 (C=N), 132.39 (Ar-C), 132.01 (Ar-C), 128.13 (Ar-CH), 127.65 (Ar-CH), 124.42 (Ar-CH), 46.39 (CH-^{*i*}Pr), 22.65 ppm (CH₃-^{*i*}Pr). C₂₄H₄₀N₆I₂ (666.43) Calc: C:43.25, H:6.05, N:12.61(%). Found: C: 42.96, H: 5.95, N: 12.20(%).

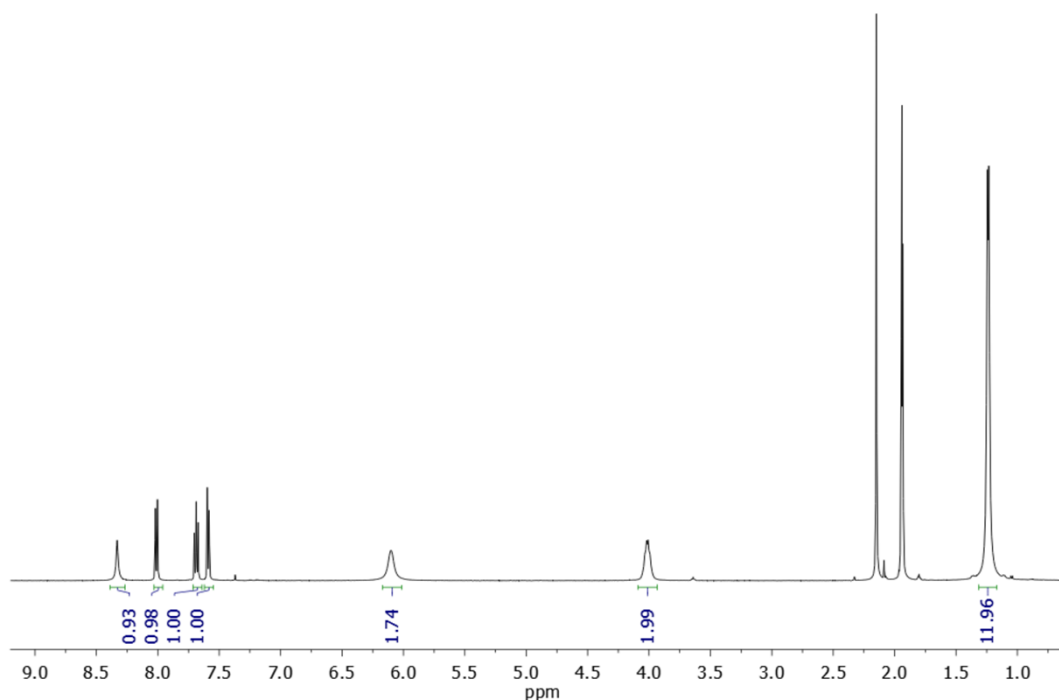


Figure S19. ¹H-NMR of N¹, N⁵-bis(bis(isopropylamino)methylene) naphthalene-1,5-diaminium diiodide (**1i**) in CD₃CN.

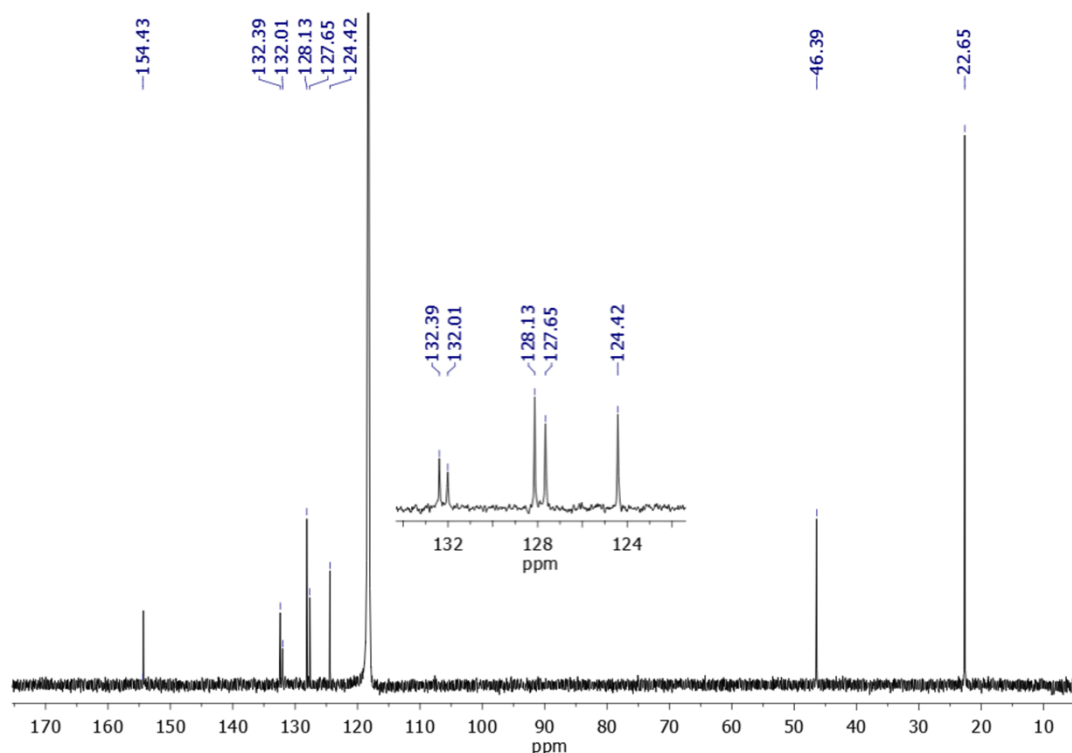
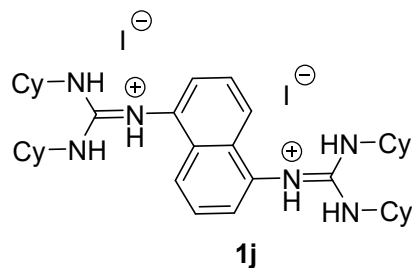


Figure S20. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N^1 , N^5 -bis(bis(isopropylamino)methylene)naphthalene-1,5-diaminium Diiodide (**1i**) in CD_3CN .

Synthesis of N^1 , N^5 -bis(bis(cyclohexylamino)methylene)naphthalene-1,5-diaminium diiodide (**1j**).



A solution of 2',2'-(naphthalene-1,5-diyl)bis(1,3-dicyclohexylguanidine) (**L4**) (100 mg, 0.18 mmol) was prepared in dichloromethane (5 mL), and was added dropwise to HI (0.36 mmol, 78.72 \square L) 57% in aqueous solution. The reaction mixture was then stirred vigorously for 40 min at room temperature obtaining a yellowish precipitate. After that, the solvent was removed under reduced pressure obtaining a yellow oil as reaction crude. The solid obtained was washed with acetone and pentane until a yellowish white solid finally appeared. The solid was obtained with a yield of 82% (119 mg). ^1H NMR (500 MHz, CD_3CN) δ = 8.28 (s, 1H, NH), 7.98 (d, J = 8.4 Hz, 1H, Ar-H), 7.68 (t, J = 7.9 Hz, 1H, Ar-H), 7.58 (d, J = 7.3 Hz, 1H, Ar-H), 6.04 (s, 2H, NH), 3.61 (s, 2H, CH-Cy), 1.72 (m, 6H, CH_2 -Cy), 1.60 (d, J = 12.7 Hz, 3H CH_2 -Cy), 1.32 (m, 8H CH_2 -Cy), 1.12 ppm (m, 3H CH_2 -Cy). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_3CN) δ = 154.11 (C=N), 137.57 (Ar-C), 132.30 (Ar-C), 128.15 (Ar-CH), 127.71 (Ar-CH), 124.41 (Ar-CH), 52.97 (CH-Cy), 33.23 (CH_2 -Cy), 25.66 (CH_2 -Cy), 25.51 ppm (CH_2 -Cy). $\text{C}_{36}\text{H}_{56}\text{N}_6\text{I}_2$ (826.71) Calc: C: 52.30, H: 6.83, N: 10.16(%). Found: C: 51.95, H: 6.47, N: 10.07(%).

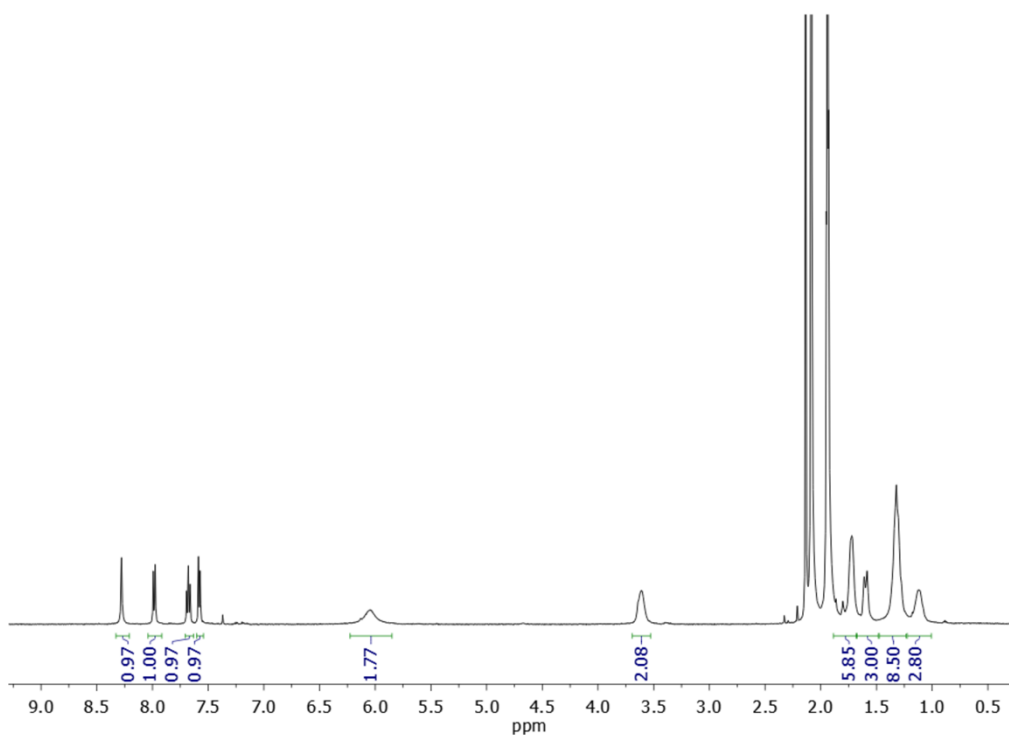


Figure S21. ^1H -NMR of N^1, N^5 -bis(bis(cyclohexylamino)methylene)naphthalene-1,5-diaminium diiodide (**1j**) in CD_3CN .

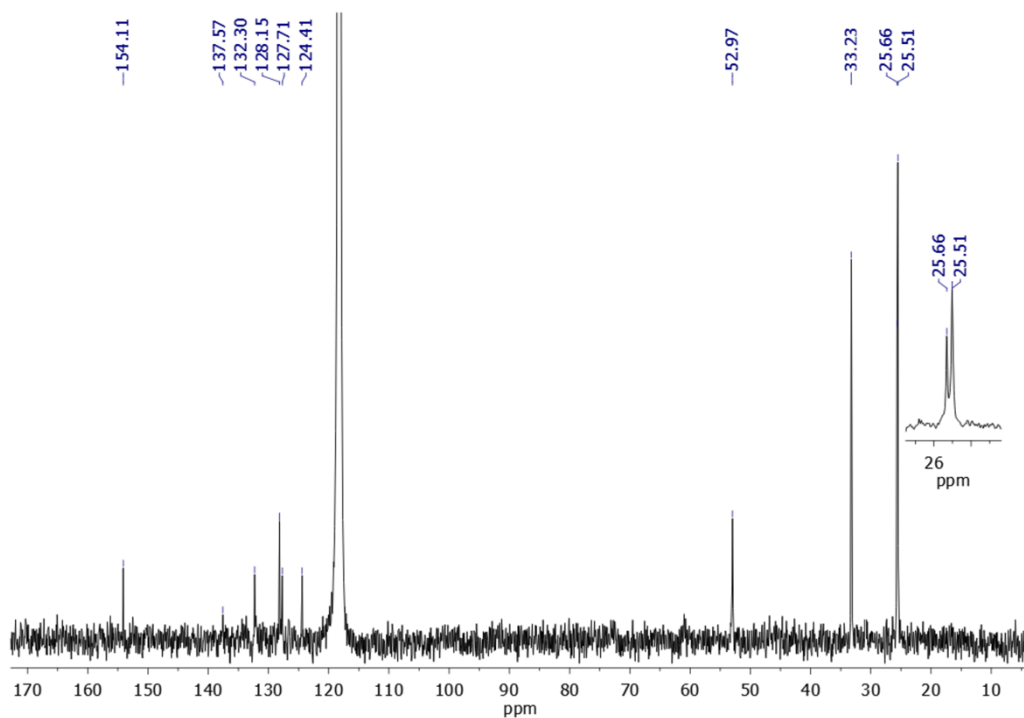


Figure S22. $^{13}\text{C}\{-^1\text{H}\}$ -NMR of N^1, N^5 -bis(bis(cyclohexylamino)methylene)naphthalene-1,5-diaminium diiodide (**1j**) in CD_3CN .

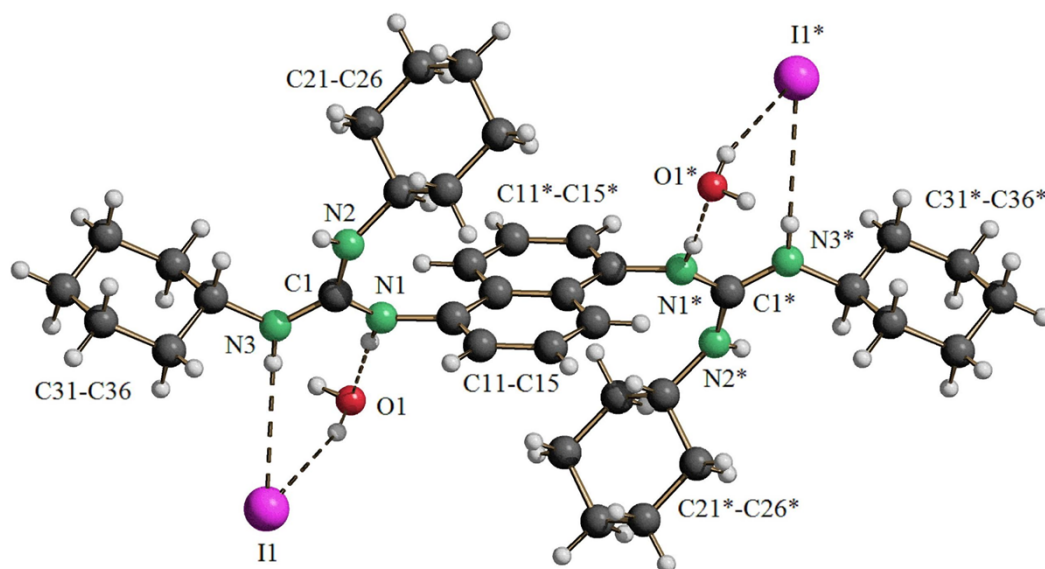


Figure S23. X-ray crystal structure of salt 1j. Thermal ellipsoids are shown with 50 % probability.

X-ray crystal structure report of Salt 1j A colorless prism-like specimen of $C_{36}H_{60}I_2N_6O_2$, approximate dimensions 0.080 mm x 0.180 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1595 frames were collected. The total exposure time was 19.50 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 25772 reflections to a maximum θ angle of 66.63° (0.84 \AA resolution), of which 3425 were independent (average redundancy 7.525, completeness = 100.0%, $R_{\text{int}} = 4.36\%$, $R_{\text{sig}} = 2.34\%$) and 3279 (95.74%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.8424(2) \text{ \AA}$, $b = 14.7304(3) \text{ \AA}$, $c = 12.1460(2) \text{ \AA}$, $\beta = 113.8630(10)^\circ$, volume = $1937.66(6) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9938 reflections above $20 \sigma(I)$ with $8.164^\circ < 2\theta < 133.2^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.603. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.1620 and 0.4220.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P 1 21/c 1$, with $Z = 2$ for the formula unit, $C_{36}H_{60}I_2N_6O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 228 variables converged at $R1 = 2.24\%$, for the observed data and $wR2 = 5.47\%$ for all data. The goodness-of-fit was 1.073. The largest peak in the final difference electron density synthesis was $0.544 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.608 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.071 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.479 g/cm^3 and $F(000)$, 880 e^- .

Table S2. Crystallographic data for salt **1j**.

Empirical formula	C ₃₆ H ₆₀ I ₂ N ₆ O ₂
Formula weight	862.70 g/mol
Temperature (K)	100(2) K
Wavelength (Å)	1.54178 Å
Crystal system	0.080 x 0.180 x 0.220 mm
Space group	colorless prism
a(Å)	monoclinic
b(Å)	P 1 21/c 1
c(Å)	a = 11.8424(2) Å b = 14.7304(3) Å c = 12.1460(2) Å
α(°)	1937.66(6) Å ³
β(°)	2
γ(°)	1.479 g/cm ³
Volume (Å ³)	13.039 mm ⁻¹
Z	880
Density (calculated) (g/cm ³)	C ₃₆ H ₆₀ I ₂ N ₆ O ₂
Absorption coefficient (mm ⁻¹)	862.70 g/mol
F(000)	100(2) K
Index ranges	-14 ≤ h ≤ 14 -17 ≤ k ≤ 17 -14 ≤ l ≤ 14
Reflections collected	25772
Independent reflections	3425 [R(int) = 0.0436]
Data/restraints/parameters	3425 / 0 / 228
Goodness-of-fit on F ²	1.073
Final R indices [I > 2σ(I)]	R1 = 0.0224 wR ² = 0.0542
R indices (all data)	R1 = 0.0235 wR ² = 0.0547
Largest diff. peak / hole, e.Å ⁻³	0.544 and -0.608

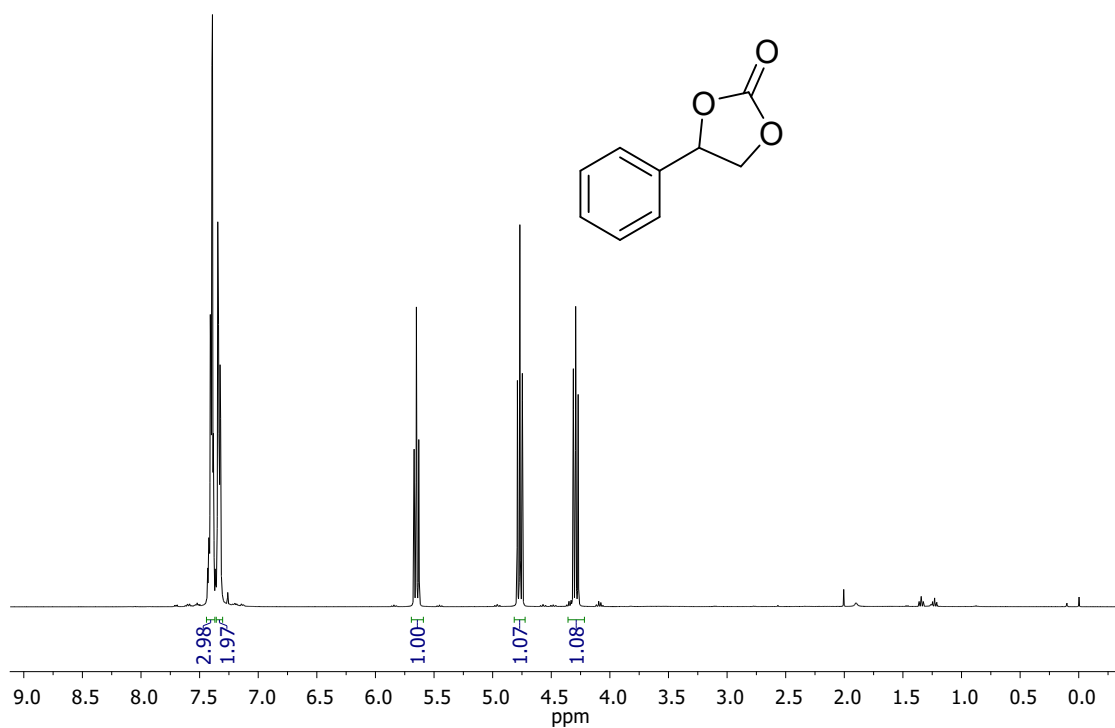


Figure S24. ^1H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one, **3a** in CDCl_3 .

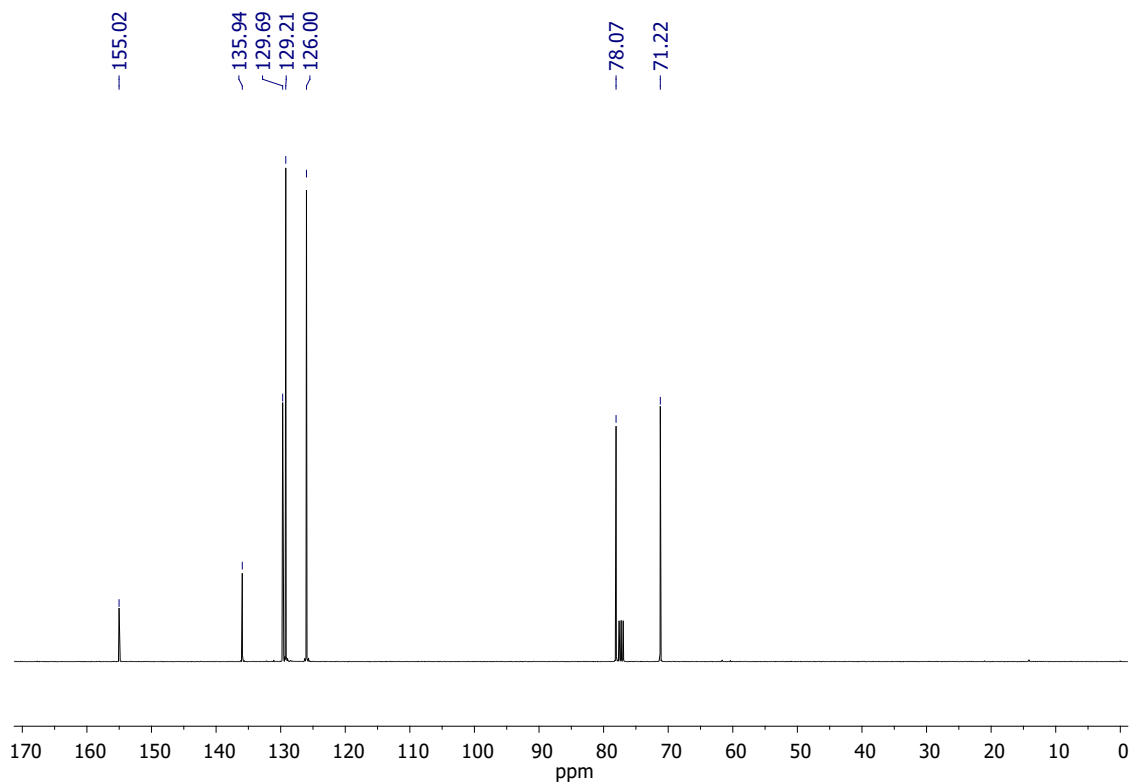


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-phenyl-1,3-dioxolan-2-one, **3a** in CDCl_3 .

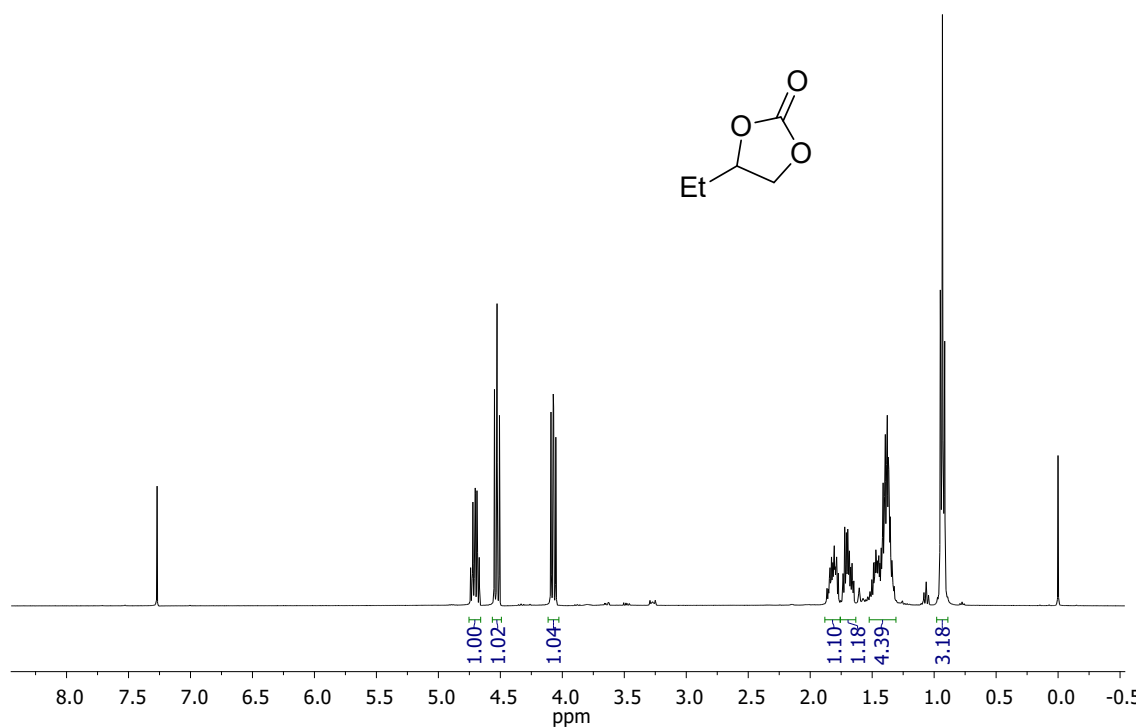


Figure S26. ^1H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one, **3b** in CDCl_3 .

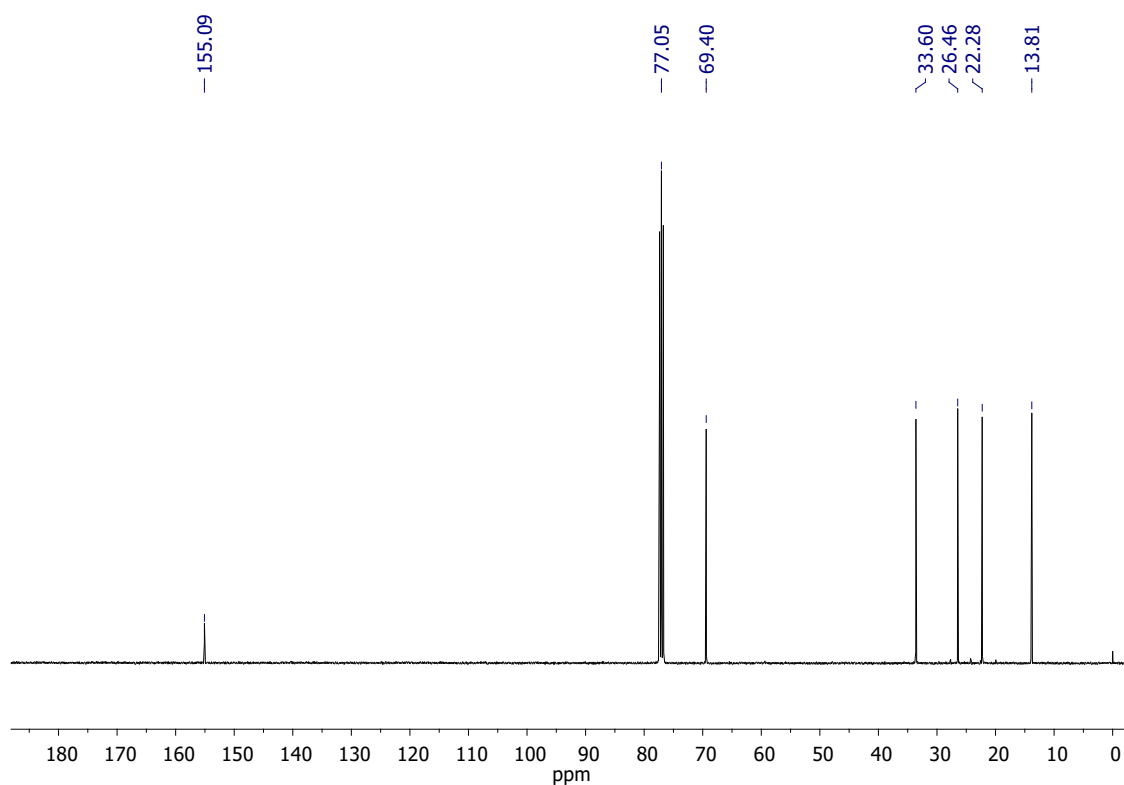


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-ethyl-1,3-dioxolan-2-one, **3b** in CDCl_3 .

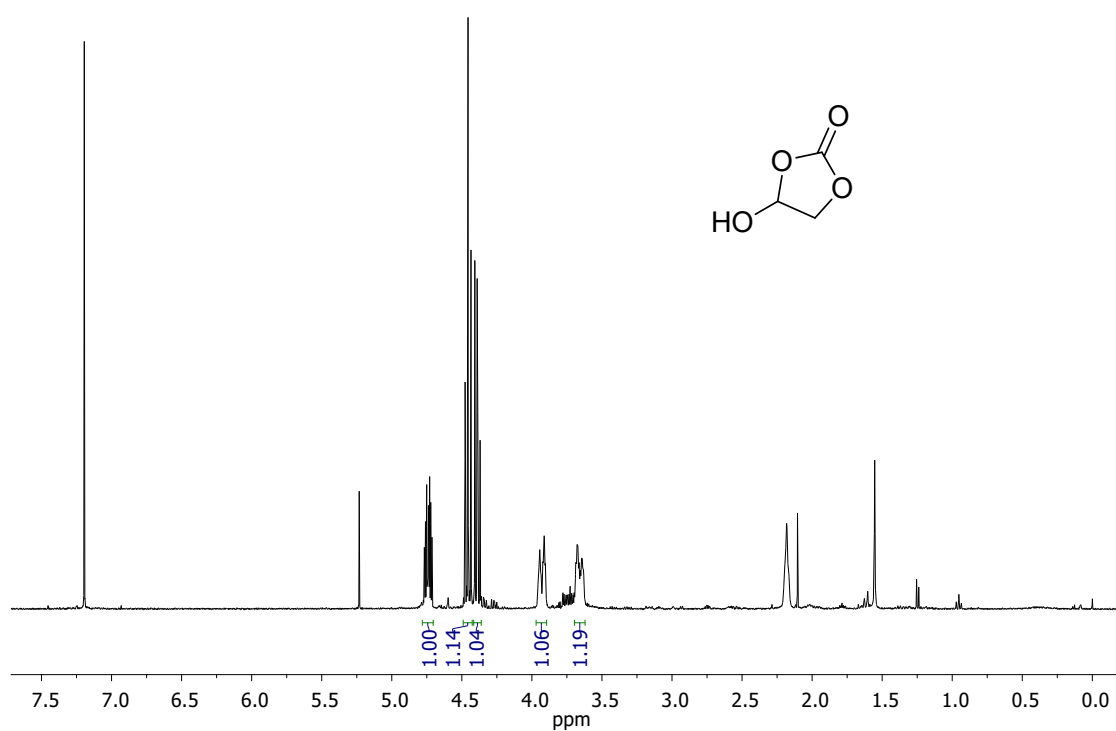


Figure S28. ^1H NMR spectrum of 4-hydroxy-1,3-dioxolan-2-one, **3c** in CDCl_3 .

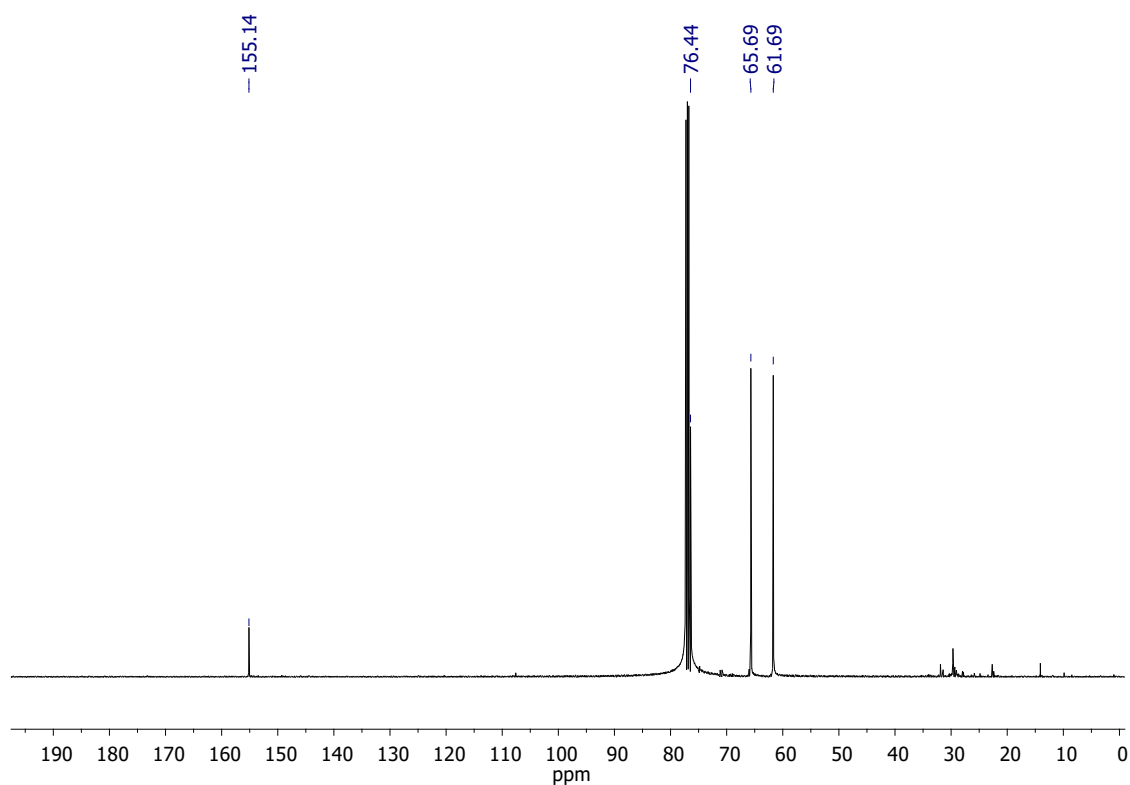


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-hydroxy-1,3-dioxolan-2-one, **3c** in CDCl_3 .

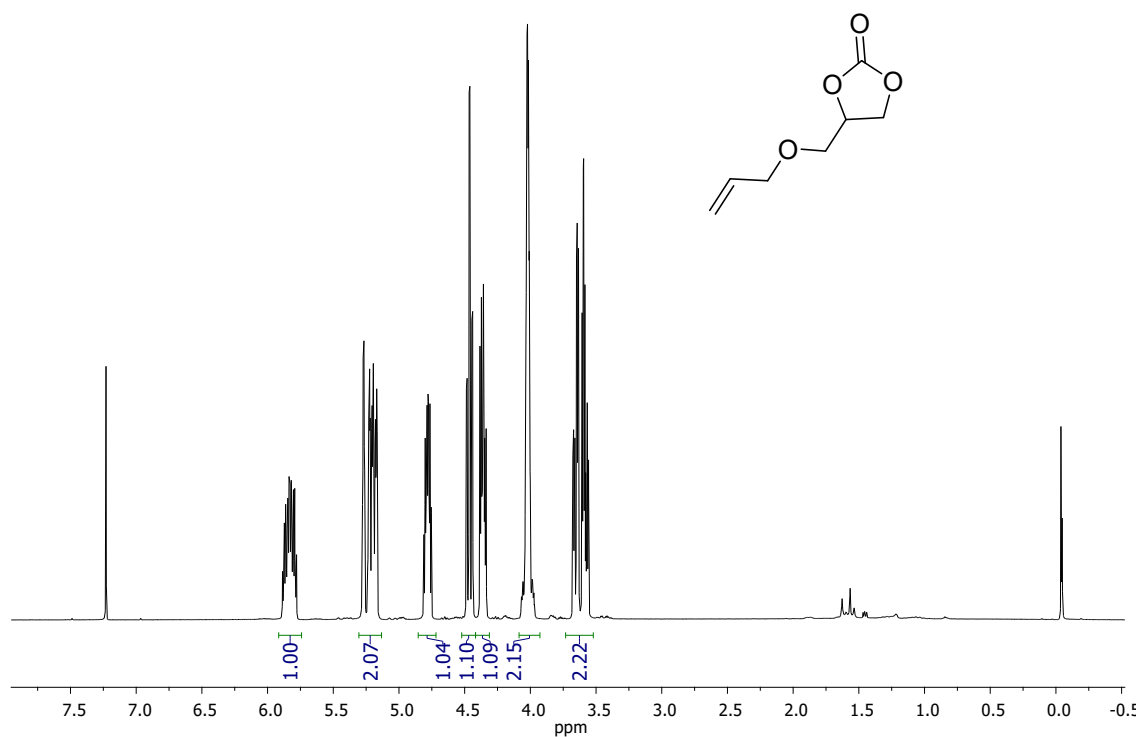


Figure S30. ^1H NMR spectrum of 4-((allyloxy)methyl)-1,3-dioxolan-2-one, **3d** in CDCl_3 .

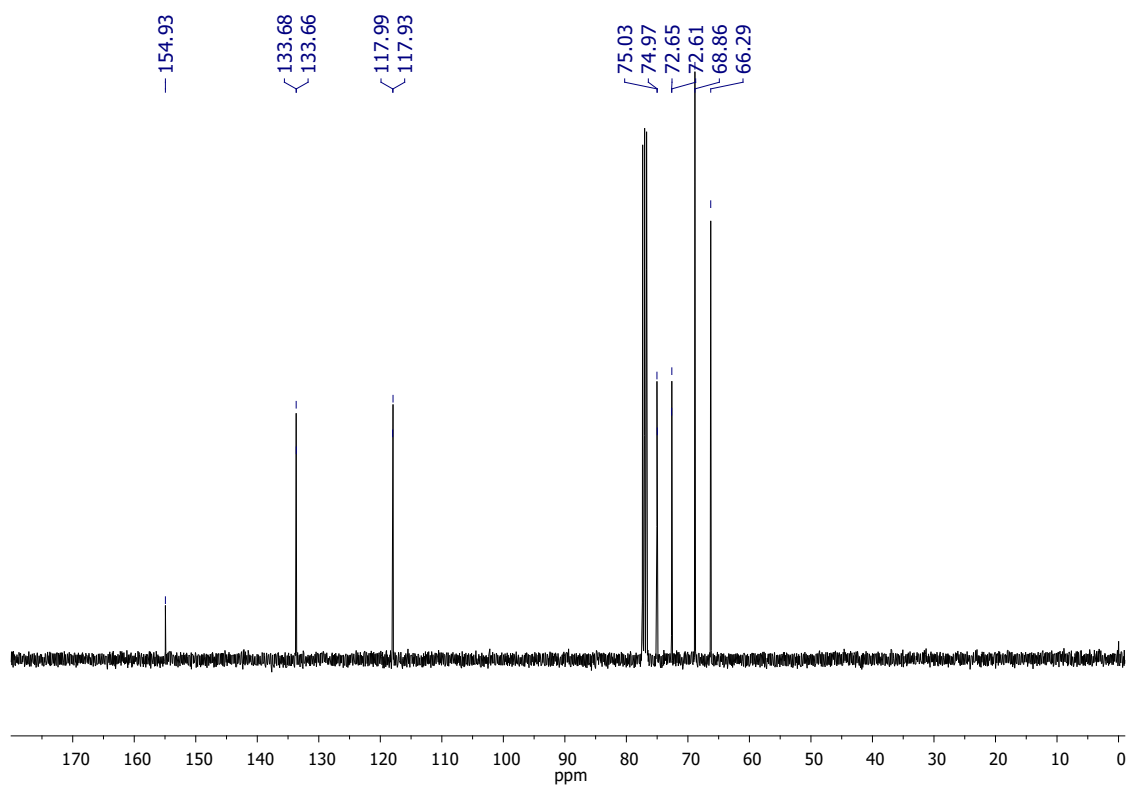


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-((allyloxy)methyl)-1,3-dioxolan-2-one, **3d** in CDCl_3 .

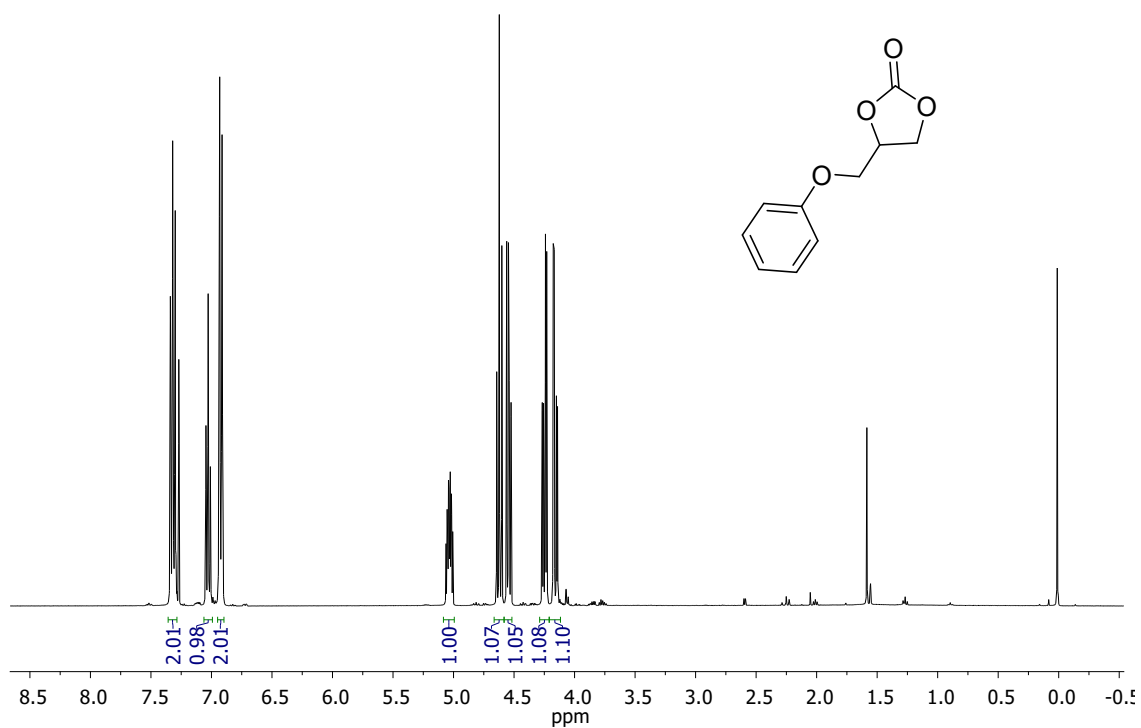


Figure S32. ¹H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one, **3e** in CDCl₃.

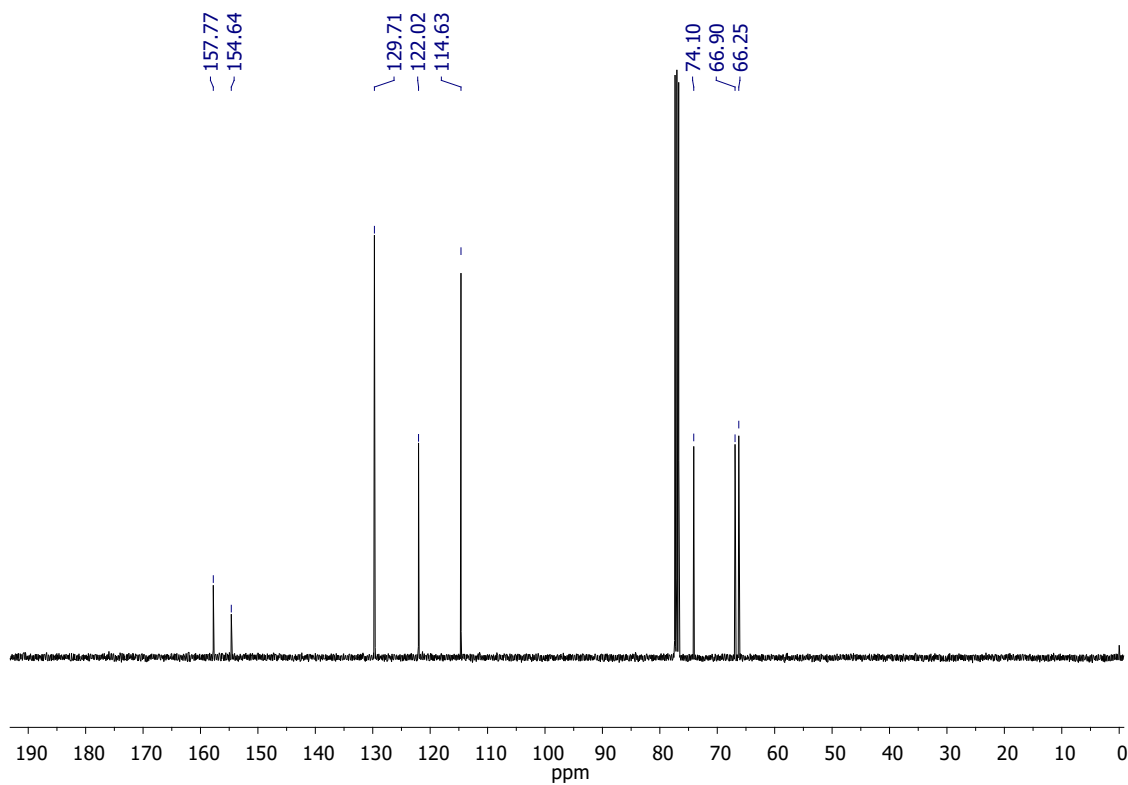


Figure S33. ¹³C{¹H} NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one, **3e** in CDCl₃.

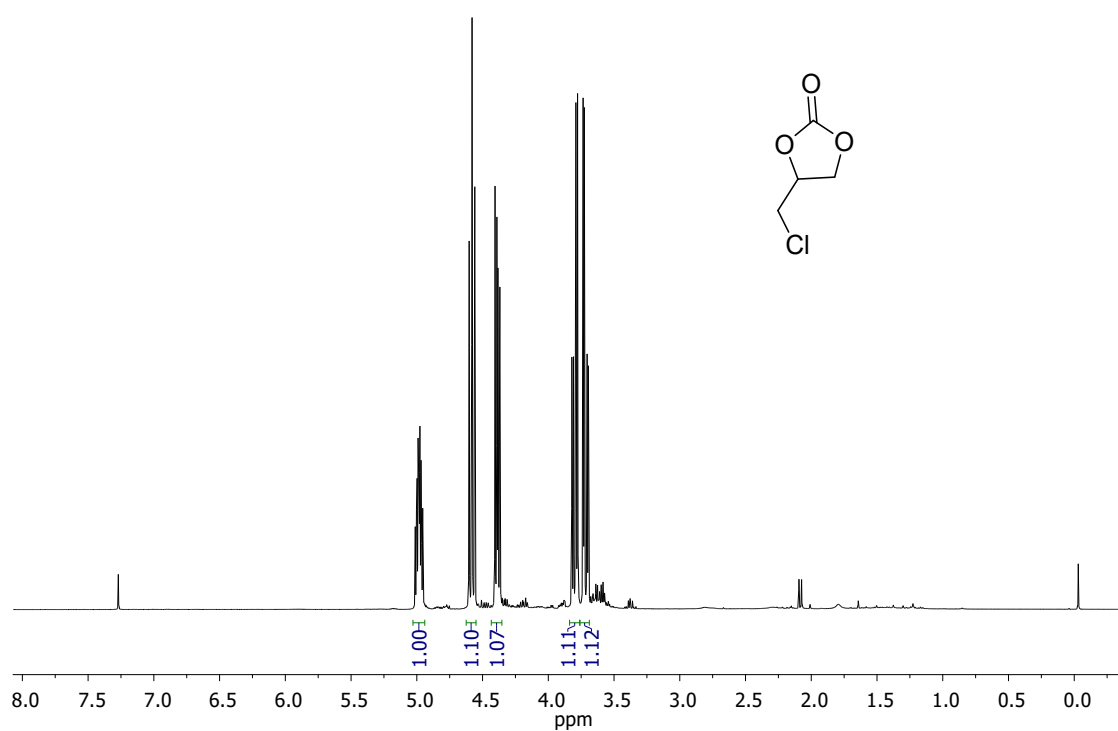


Figure S34. ^1H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one, **3f** in CDCl_3 .

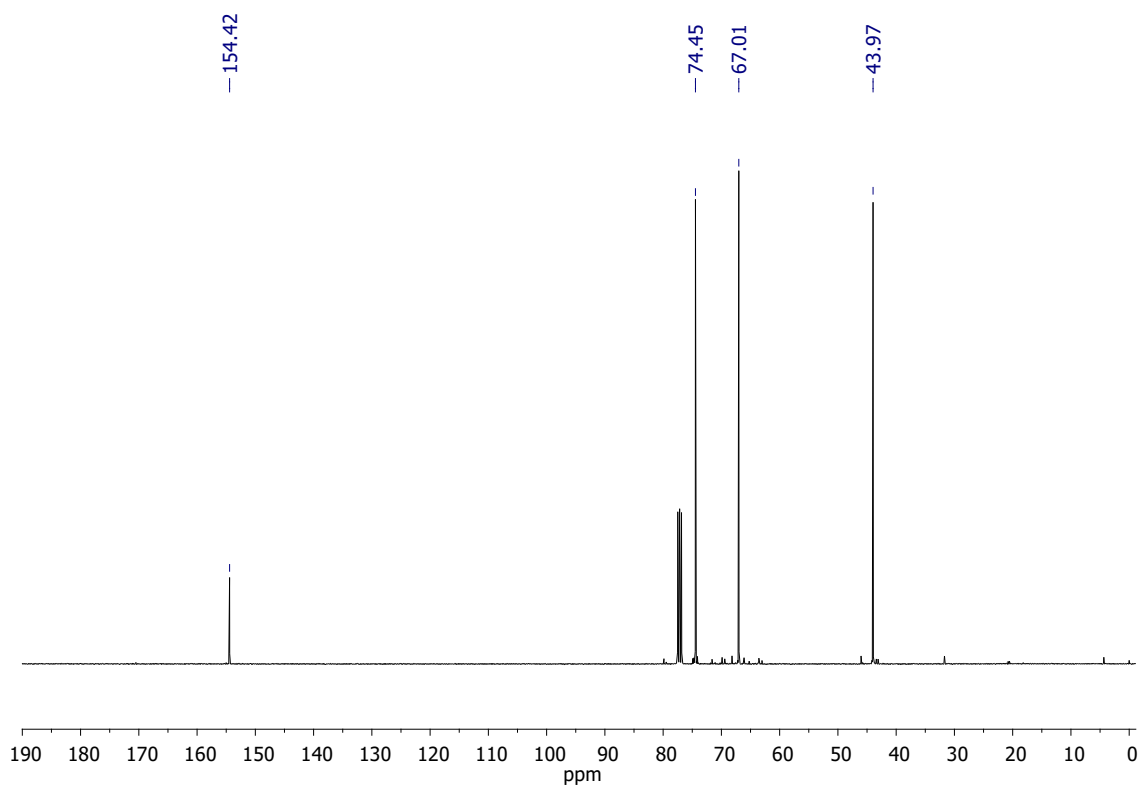


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one, **3f** in CDCl_3 .

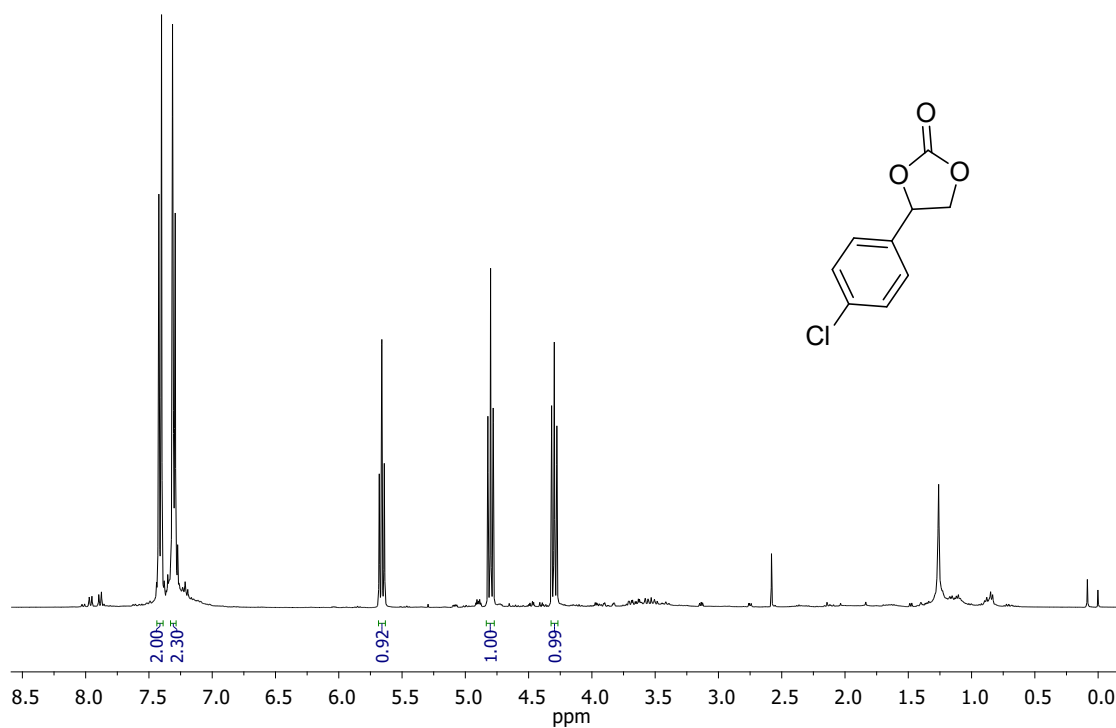


Figure S36. ^1H NMR spectrum of 4-(4-chlorophenyl)-1,3-dioxolan-2-one, **3g** in CDCl_3 .

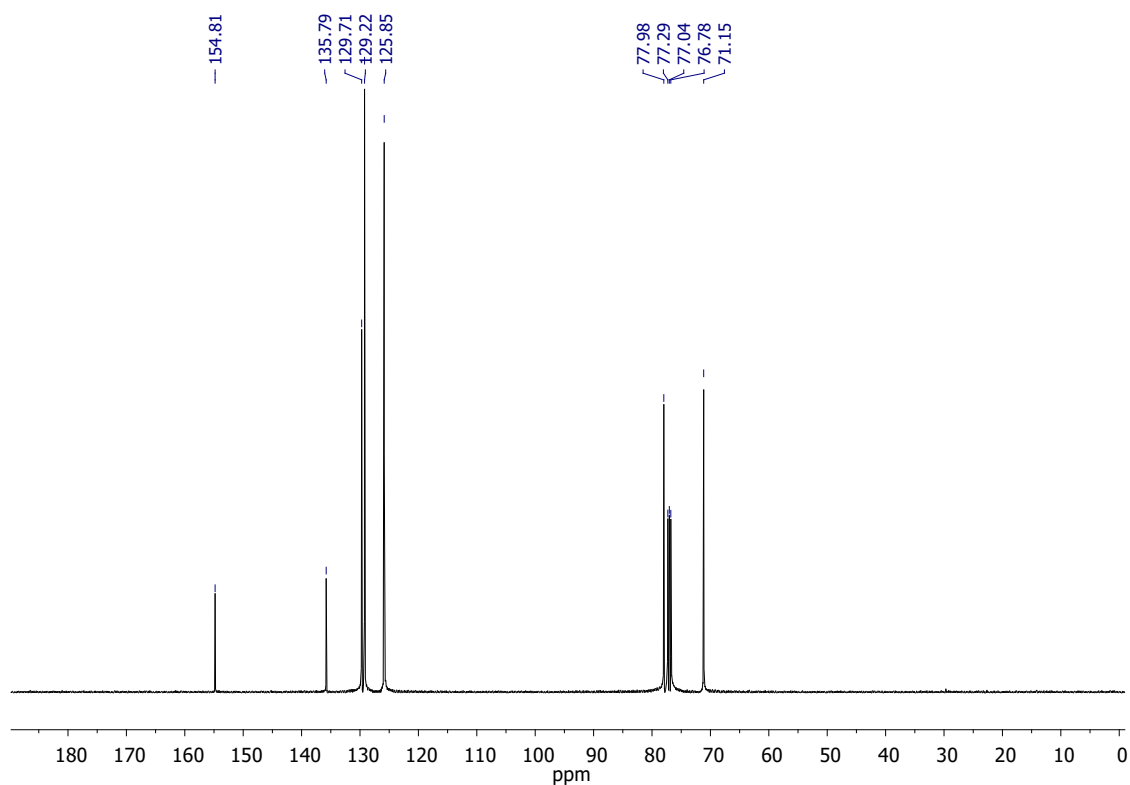


Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-(4-chlorophenyl)-1,3-dioxolan-2-one, **3g** in CDCl_3 .

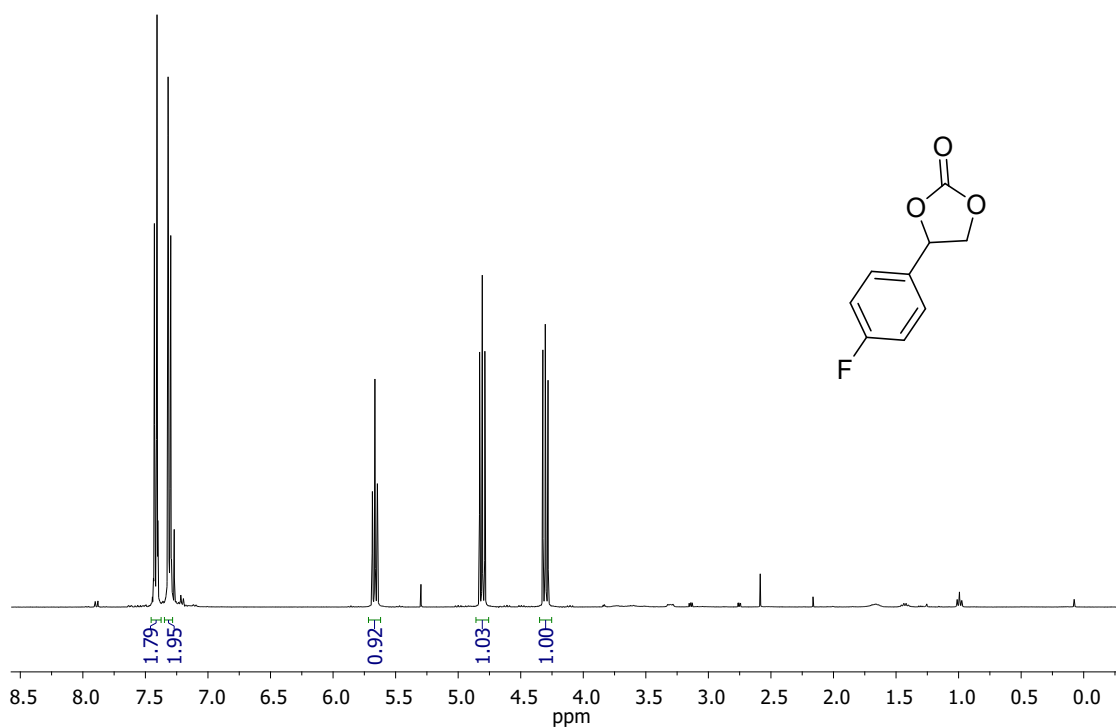


Figure S38. ¹H NMR spectrum of 4-(4-fluorophenyl)-1,3-dioxolan-2-one, **3h** in CDCl₃.

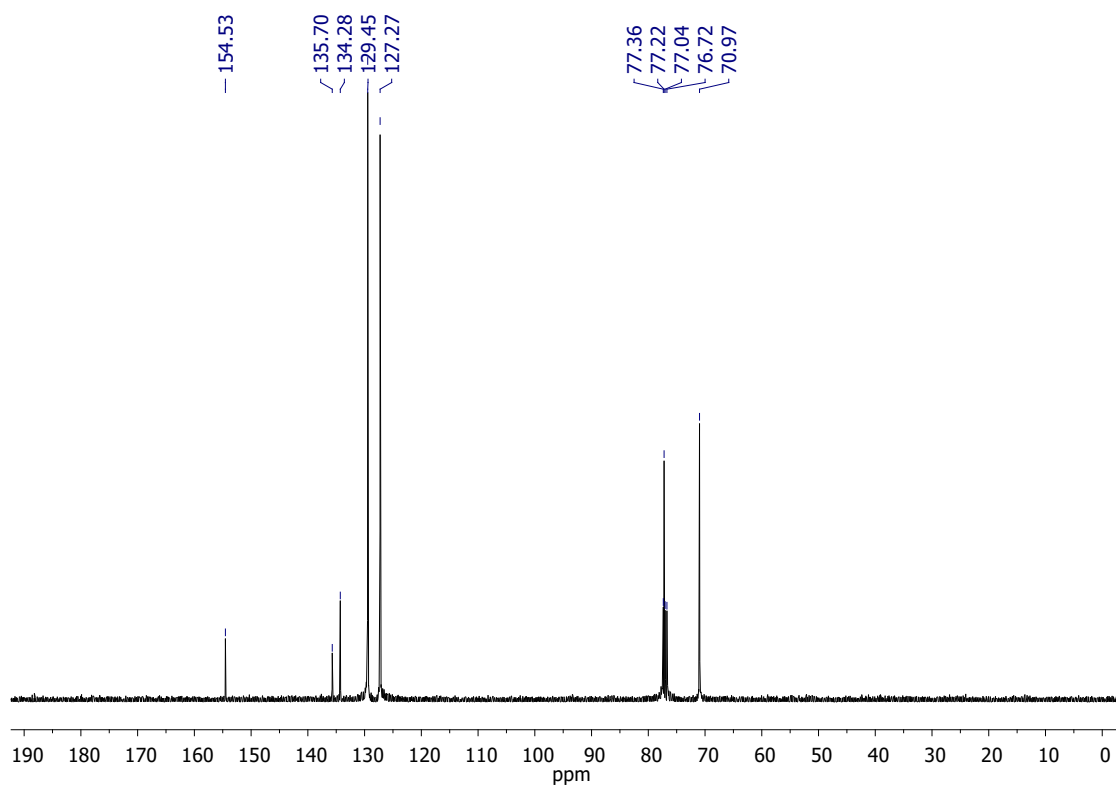


Figure S39. ¹³C{¹H} NMR spectrum of 4-(4-fluorophenyl)-1,3-dioxolan-2-one, **3h** in CDCl₃.

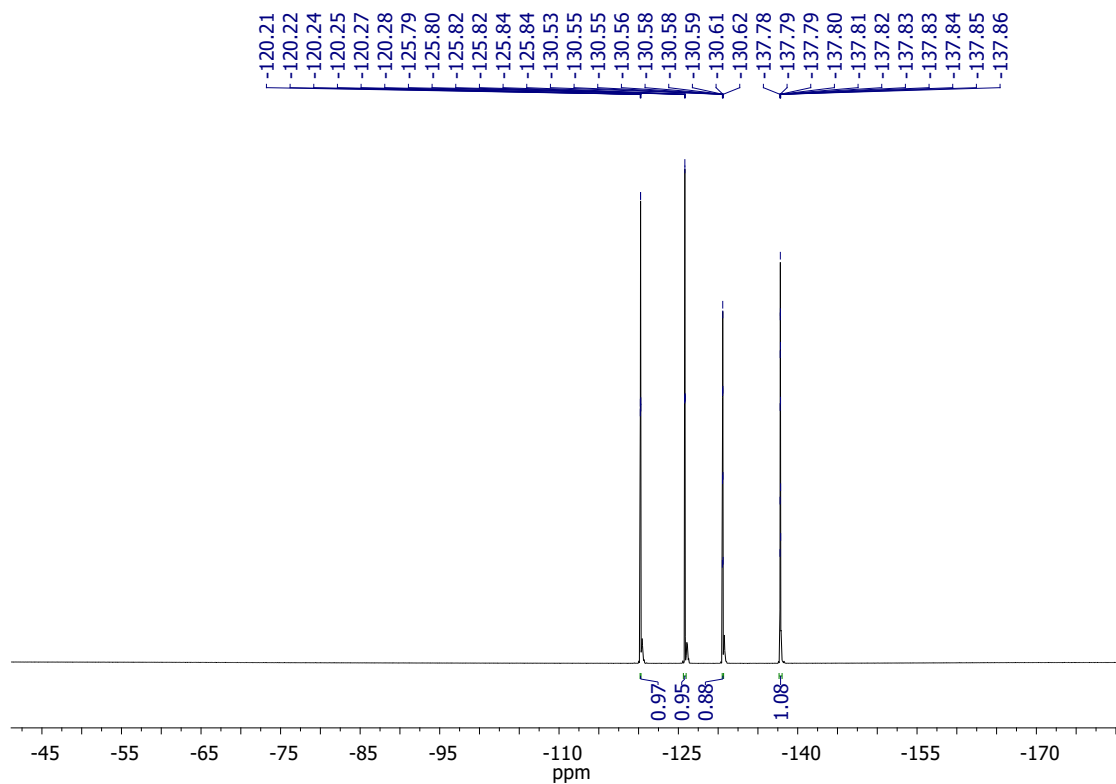


Figure S42. ^{19}F NMR spectrum of 4-(((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)methyl)-1,3-dioxolan-2-one, **3i** in CDCl_3 .

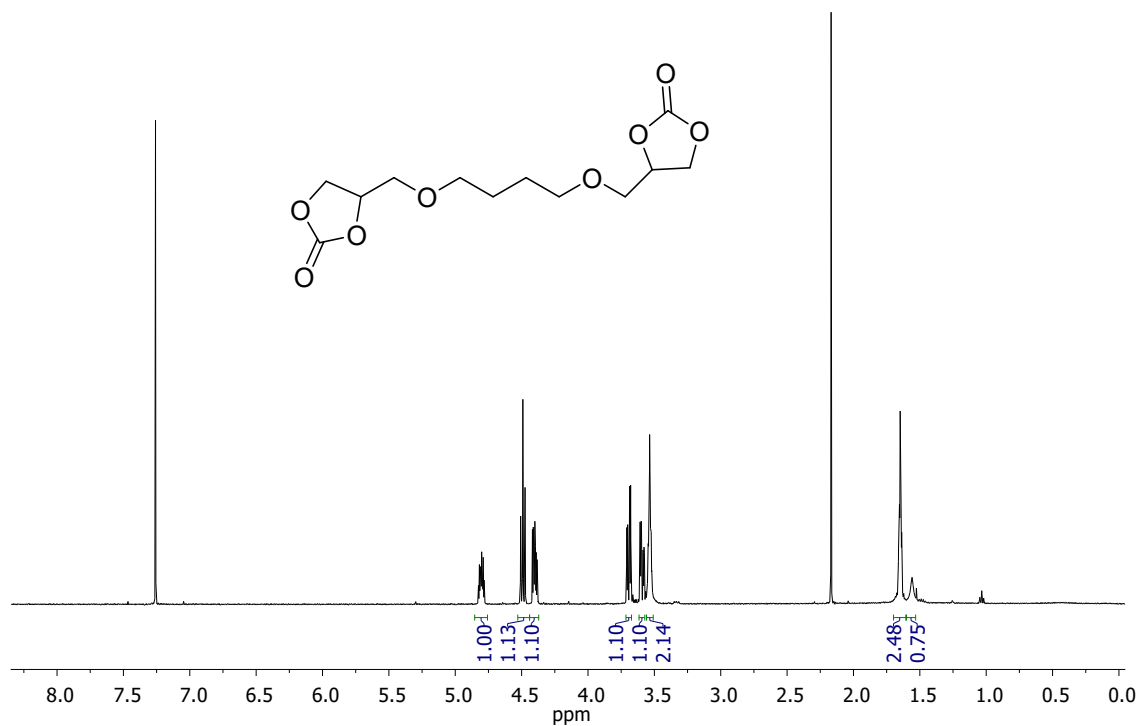


Figure S43. ^1H NMR spectrum of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one), **3j** in CDCl_3 .

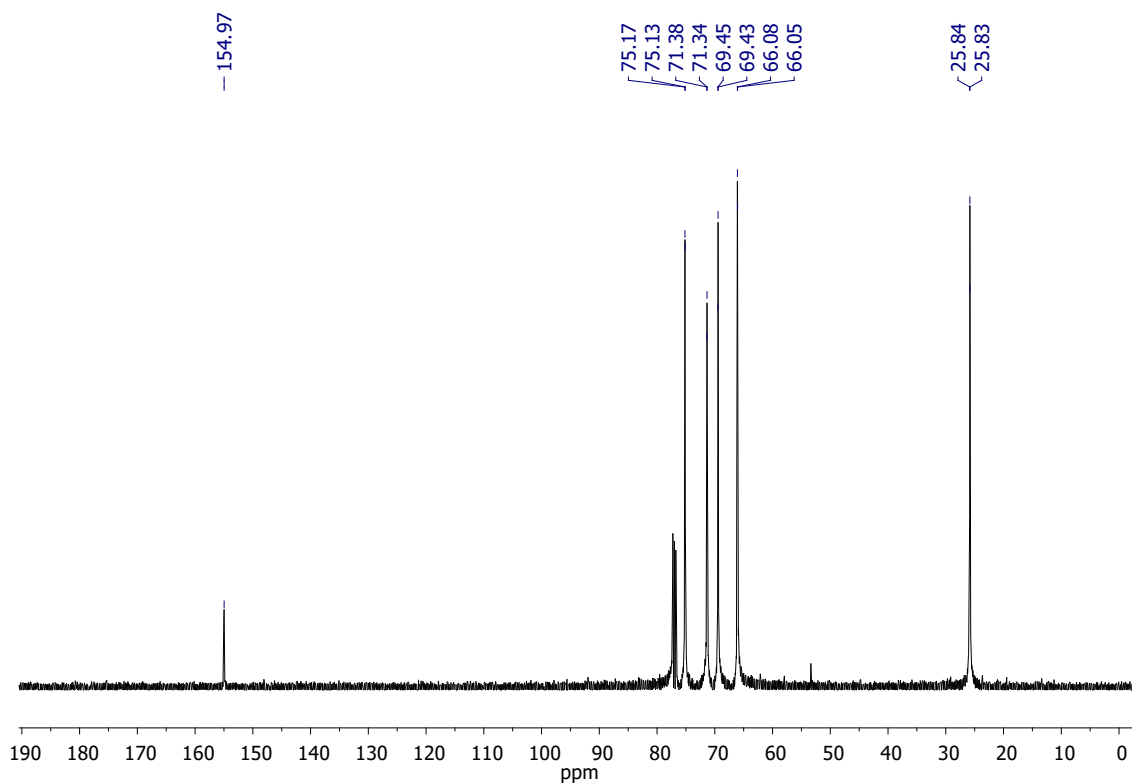


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one), **3j** in CDCl_3 .

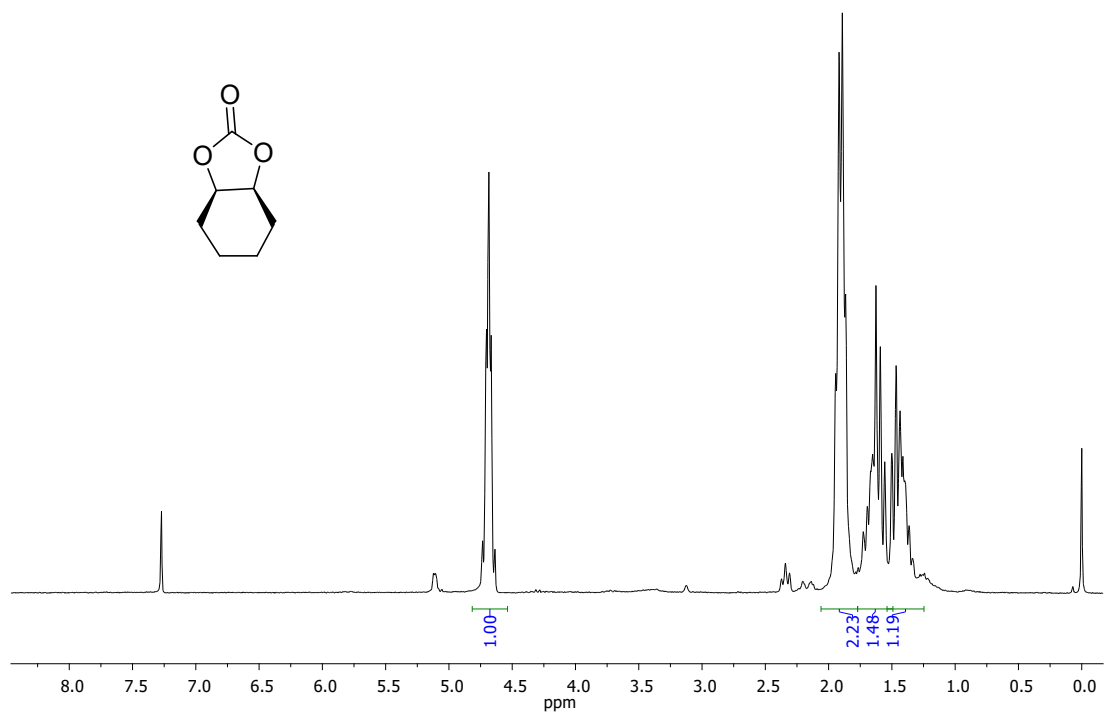


Figure S45. ^1H NMR spectrum of *cis*-1,2-cyclohexene carbonate, **5a** in CDCl_3 .

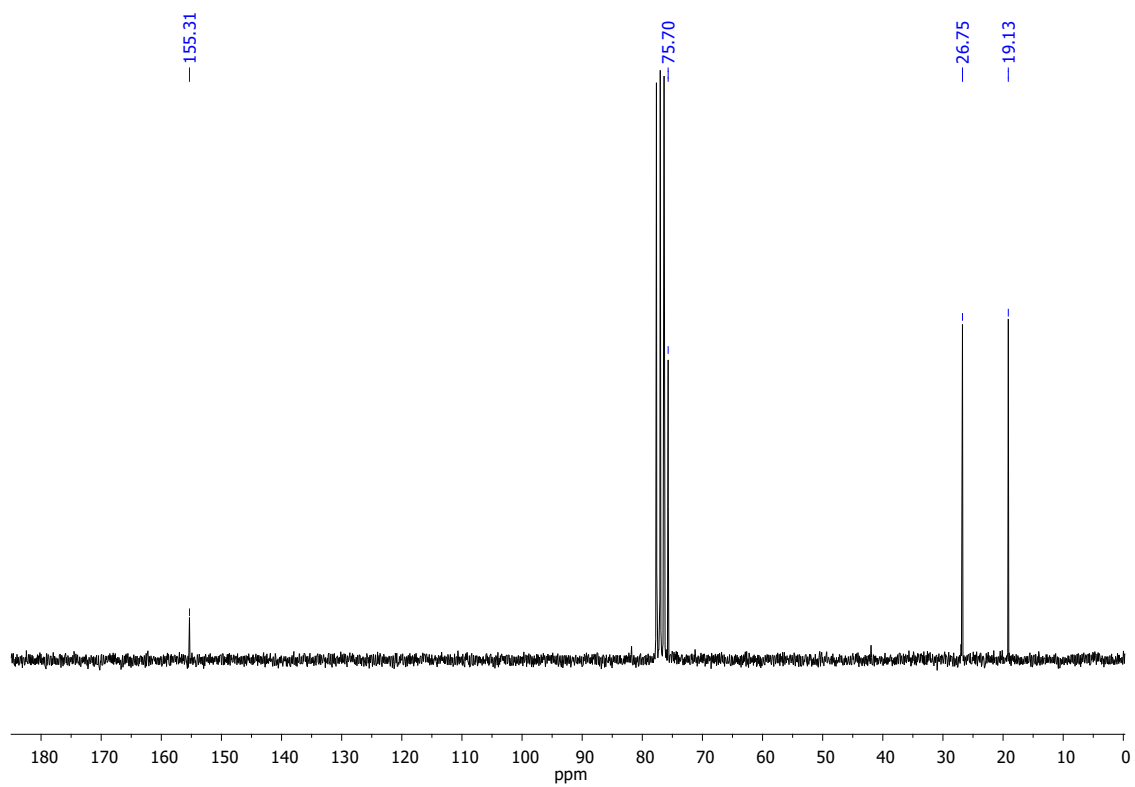


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *cis*-1,2-cyclohexene carbonate, **5a** in CDCl_3 .

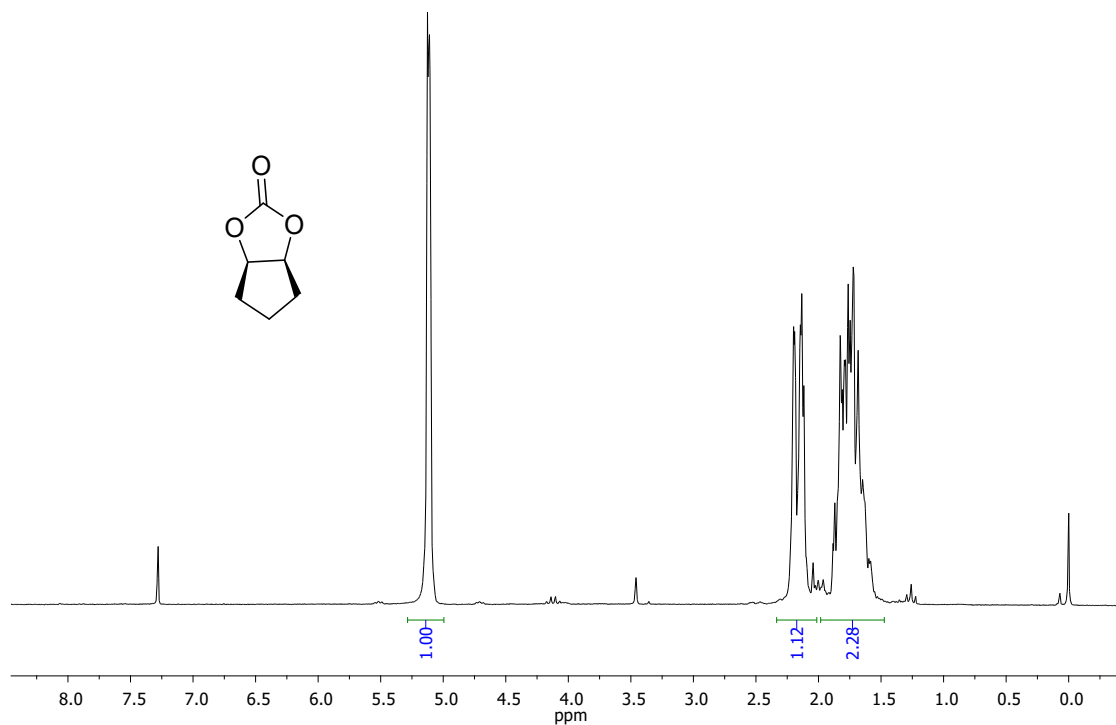


Figure S47. ^1H NMR spectrum of *cis*-1,2-cyclopentane carbonate, **5b** in CDCl_3 .

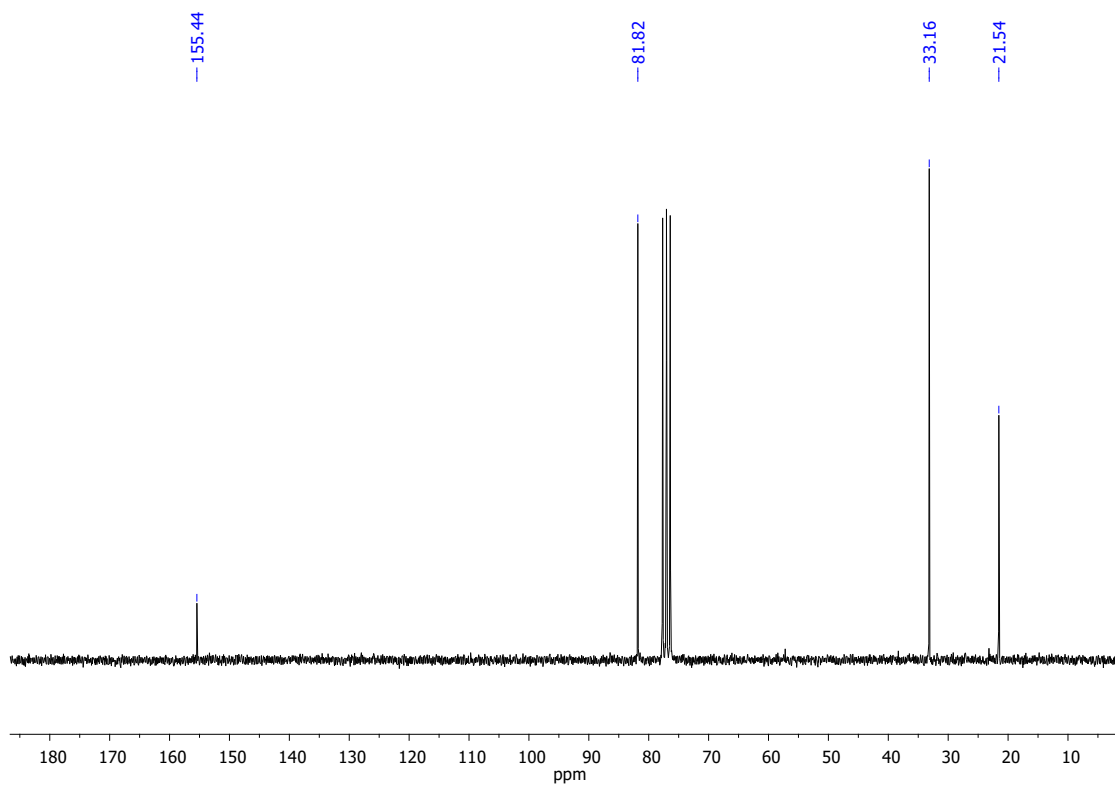


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *cis*-1,2-cyclopentane carbonate, **5b** in CDCl_3 .

X-Ray diffraction: Data sets for compounds **1e** and **1j** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0¹ (Bruker AXS Inc., **2021**); cell refinement: *SAINTE* Version 8.40B (Bruker AXS Inc., **2021**); data reduction: *SAINTE* Version 8.40B (Bruker AXS Inc., **2021**); absorption correction, *SADABS* Version 2016/2 (Bruker AXS Inc., **2021**); structure solution *SHELXT*-Version 2018-3² (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL*- Version 2018-3³ (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8) and graphics, *XP*⁴ (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *wR*² values are given for all reflections.

X-ray crystal structure analysis of 1e (dan9579): A colorless needle-like specimen of C₂₀H₃₈I₂N₆, approximate dimensions 0.052 mm x 0.112 mm x 0.424 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1731 frames were collected. The total exposure time was 8.58 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a tetragonal unit cell yielded a total of 36089 reflections to a maximum θ angle of 70.07° (0.82 Å resolution), of which 2425 were independent (average redundancy 14.882, completeness = 99.8%, *R*_{int} = 5.29%, *R*_{sig} = 2.07%) and 2256 (93.03%) were greater than 2 σ (*F*²). The final cell constants of *a* = 28.4678(8) Å, *b* = 28.4678(8) Å, *c* = 6.3147(2) Å, volume = 5117.5(3) Å³, are based upon the refinement of the XYZ-centroids of 9787 reflections above 20 σ (*I*) with 8.785° < 2 θ < 139.9°. Data were corrected for absorption effects using the multi-scan method (*SADABS*). The ratio of minimum to maximum apparent transmission was 0.567. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0450 and 0.4320. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *I4*₁/*a*, with *Z* = 8 for the formula unit, C₂₀H₃₈I₂N₆. The final anisotropic full-matrix least-squares refinement on *F*² with 143 variables converged at *R*1 = 1.97%, for the observed data and *wR*2 = 5.18% for all data. The goodness-of-fit was 1.082. The largest peak in the final difference electron density synthesis was 0.540 e-/Å³ and the largest hole was -0.551 e-/Å³ with an RMS deviation of 0.085 e-/Å³. On the basis of the final model, the calculated density was 1.600 g/cm³ and *F*(000), 2448 e⁻. Hydrogen atoms at N1, N2 and N3 were refined freely. CCDC Nr.: 2267508.

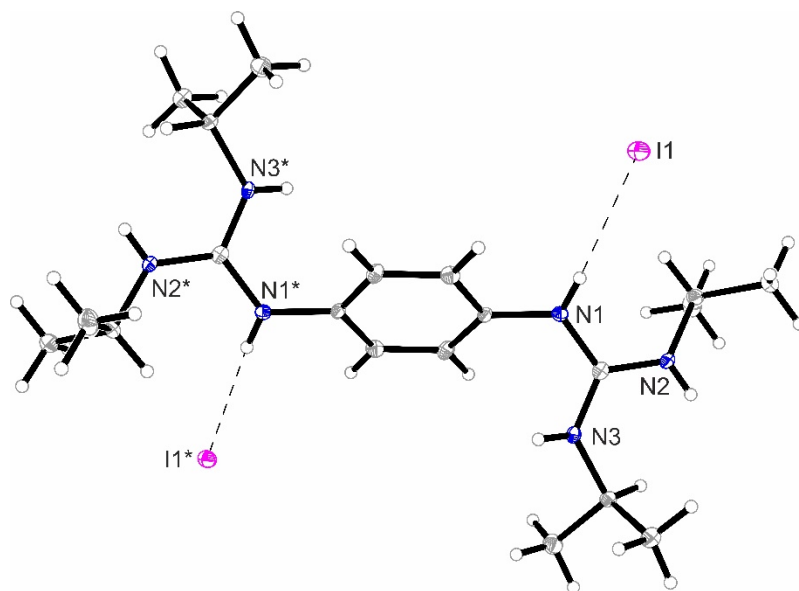
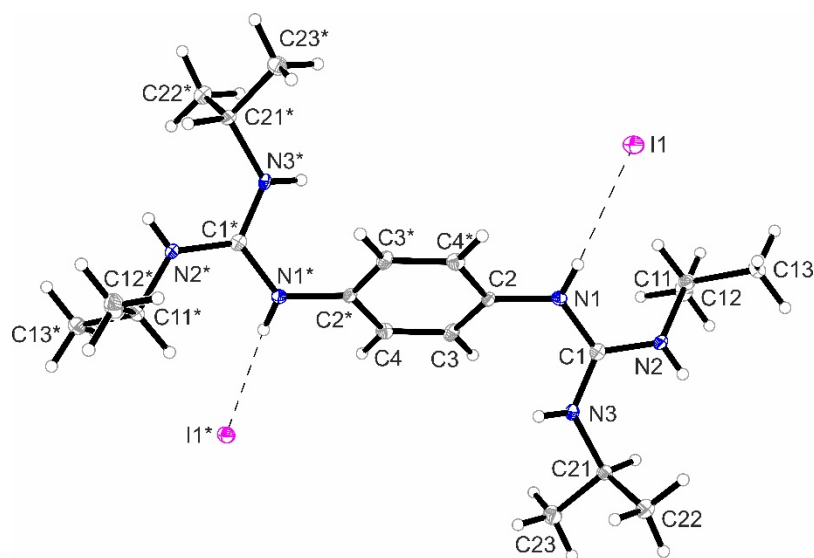


Figure S49. Crystal structure of compound **1e**. Thermal ellipsoids are shown at 50% probability.

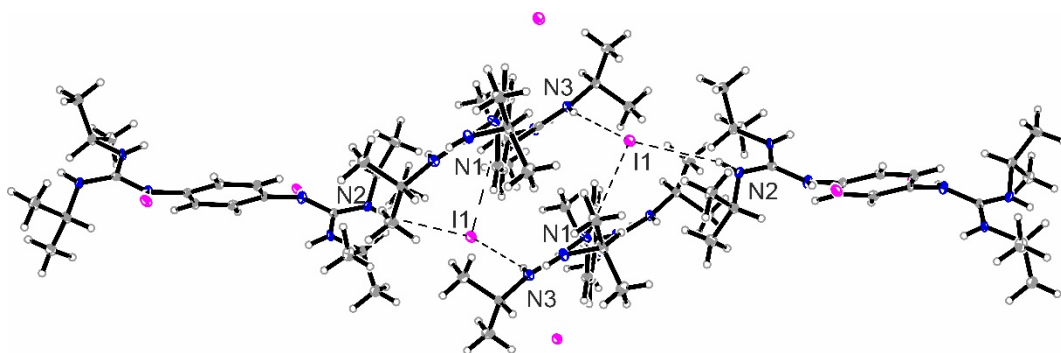


Figure S50. Dimer type formation involving N-H...I hydrogen bond interactions between the NH group and the iodine anion in compound **1e**.

Table S3. Non-covalent intermolecular interactions in compound **1e** (Å and deg)

<i>D-H...A</i>	<i>d(D-H)</i>	<i>d(H...A)</i>	<i>d(D...A)</i>	$\angle(DHA)$
N1-H1...I1	0.83(3)	2.85(3)	3.674(2)	172(3)
N2-H2...I1 ^{#1}	0.80(3)	3.06(3)	3.808(2)	158(2)
N3-H3...I1 ^{#2}	0.80(3)	2.96(3)	3.685(2)	153(2)

Symmetry transformations used to generate equivalent atoms: ^{#1} -y+3/4, x+1/4, z+1/4; ^{#2} -x+1, -y+1, -z+1.

X-ray crystal structure analysis of 1j (stu10488): A colorless prism-like specimen of C₃₆H₆₀I₂N₆O₂, approximate dimensions 0.080 mm x 0.180 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1595 frames were collected. The total exposure time was 19.50 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 25772 reflections to a maximum θ angle of 66.63° (0.84 Å resolution), of which 3425 were independent (average redundancy 7.525, completeness = 100.0%, R_{int} = 4.36%, R_{sig} = 2.34%) and 3279 (95.74%) were greater than 2 σ (F²). The final cell constants of *a* = 11.8424(2) Å, *b* = 14.7304(3) Å, *c* = 12.1460(2) Å, β = 113.863(1)°, volume = 1937.66(6) Å³, are based upon the refinement of the XYZ-centroids of 9938 reflections above 20 σ (I) with 8.164° < 2 θ < 133.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.603. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.1620 and 0.4220. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P2₁/c*, with *Z* = 2 for the formula unit, C₃₆H₆₀I₂N₆O₂. The final anisotropic full-matrix least-squares refinement on F² with 228 variables converged at R1 = 2.24%, for the observed data and wR2 = 5.47% for all data. The goodness-of-fit was 1.073. The largest peak in the final difference electron density synthesis was 0.544 e⁻/Å³ and the largest hole was -0.608 e⁻/Å³ with an RMS deviation of 0.071 e⁻/Å³. On the basis of the final model, the calculated density was 1.479 g/cm³ and F(000), 880 e⁻. Hydrogen atoms at N1, N2, N3 and O1 were refined freely. CCDC Nr.: 2267509.

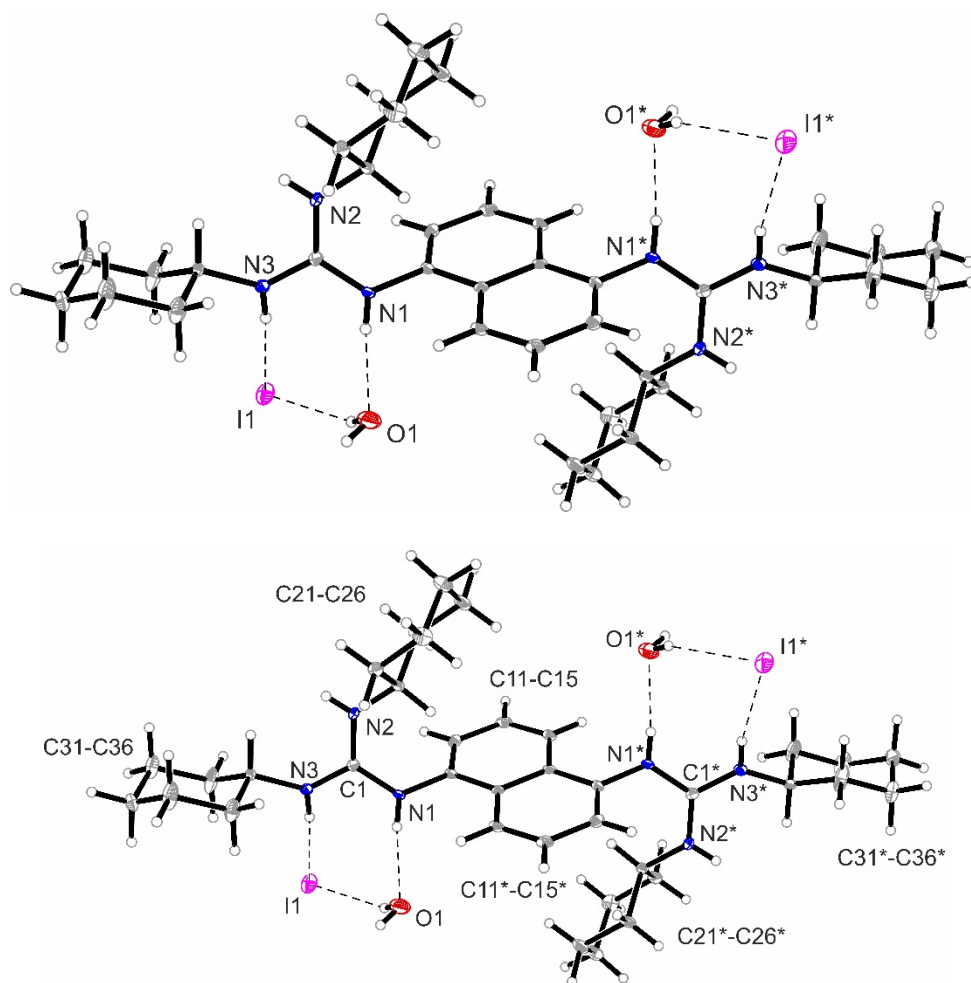


Figure S51. Crystal structure of compound **1j**. Thermal ellipsoids are shown at 50% probability.

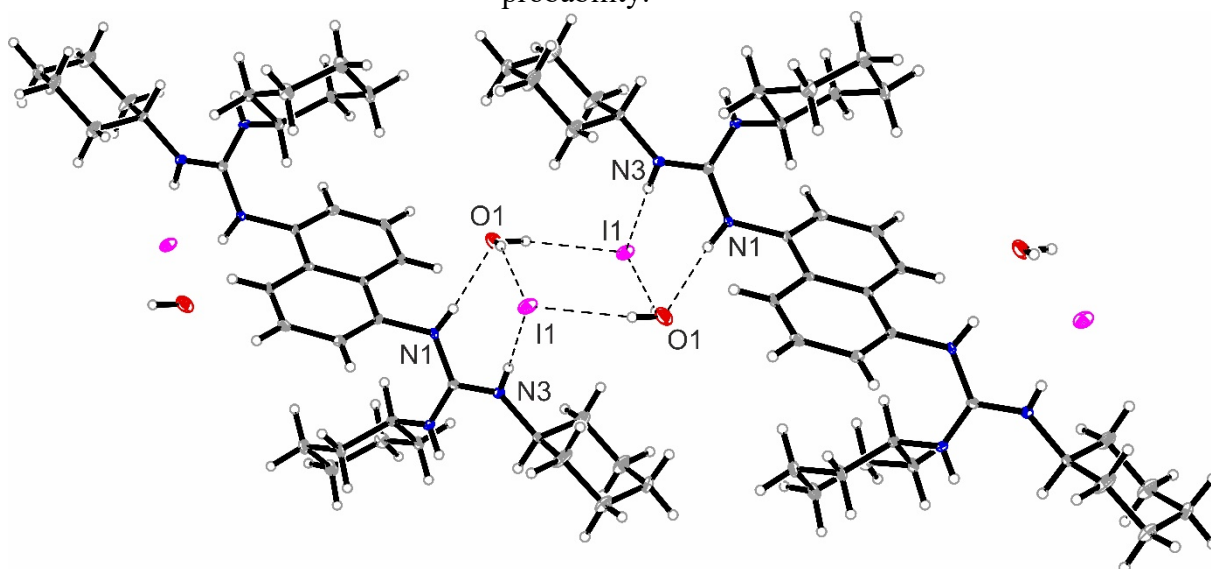


Figure S52. Dimer type formation involving N-H...I, O-H...I and N-H...O hydrogen bond interactions between the NH groups, the iodine anions and the water molecules in compound **1j**.

Table S4. Non-covalent intermolecular interactions in compound **1j** (Å and deg)

$D-H\cdots A$ H)	$d(D-H)$	$d(H\cdots A)$	$d(D\cdots A)$	$\angle(DHA)$
N1-H1 \cdots O1	0.80(3)	2.00(3)	2.790(3)	174(3)
N2-H2 \cdots I1 ^{#1}	0.80(3)	2.96(3)	3.730(2)	163(2)
N3-H3 \cdots I1	0.83(3)	2.92(3)	3.710(2)	160(2)
O1-H1A \cdots I1	0.77(4)	2.81(4)	3.532(2)	158(4)
O1-H2A \cdots I1 ^{#2}	0.86(5)	2.69(5)	3.538(2)	172(4)

Symmetry transformations used to generate equivalent atoms: ^{#1} -x+1, y+1/2, -z+1/2; ^{#2} -x+1, -y+1, -z.

References X-Ray Part: (siehe auch oben)

1. Bruker AXS (2021) *APEX4 Version 2021.4-0*, *SAINT Version 8.40B* and *SADABS Bruker AXS area detector scaling and absorption correction Version 2016/2*, Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M., *SHELXT – Integrated space-group and crystal-structure determination*, *Acta Cryst.*, **2015**, *A71*, 3-8.
3. Sheldrick, G.M., *Crystal structure refinement with SHELXL*, *Acta Cryst.*, **2015**, *C71 (1)*, 3-8.
4. Bruker AXS (1998) *XP – Interactive molecular graphics, Version 5.1*, Bruker AXS Inc., Madison, Wisconsin, USA.