Photomediated core modification of organic photoredox catalysts in radical addition: mechanism and applications

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Materials and Methods

1. General Information

1.1 Sample preparations

Unless otherwise indicated, all the regents and solvents were purchased from commercial suppliers and used without any further purification.

Core modification of OPCs: Flash column chromatography was performed using basic aluminum oxide (100-200 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 nm or 365 nm).

Polymerizations: Methyl methacrylate (MMA) and butyl acrylate (BA) were purchased from Sigma-Aldrich and passed through a plug of basic alumina before use in order to remove the radical inhibitor. All polymerizations were carried out under an argon atmosphere.

Light Source: Sunlight simulation lamps were bought from Osram (ULTRA-VITALUX UV-A, 300 W). Reactions were placed next to the sunlight simulation lamp under vigorous stirring while cooling with flowing air (Fig. S1A). Fig. S1B shows the qualitative emission spectrum of the lamps used in this work.

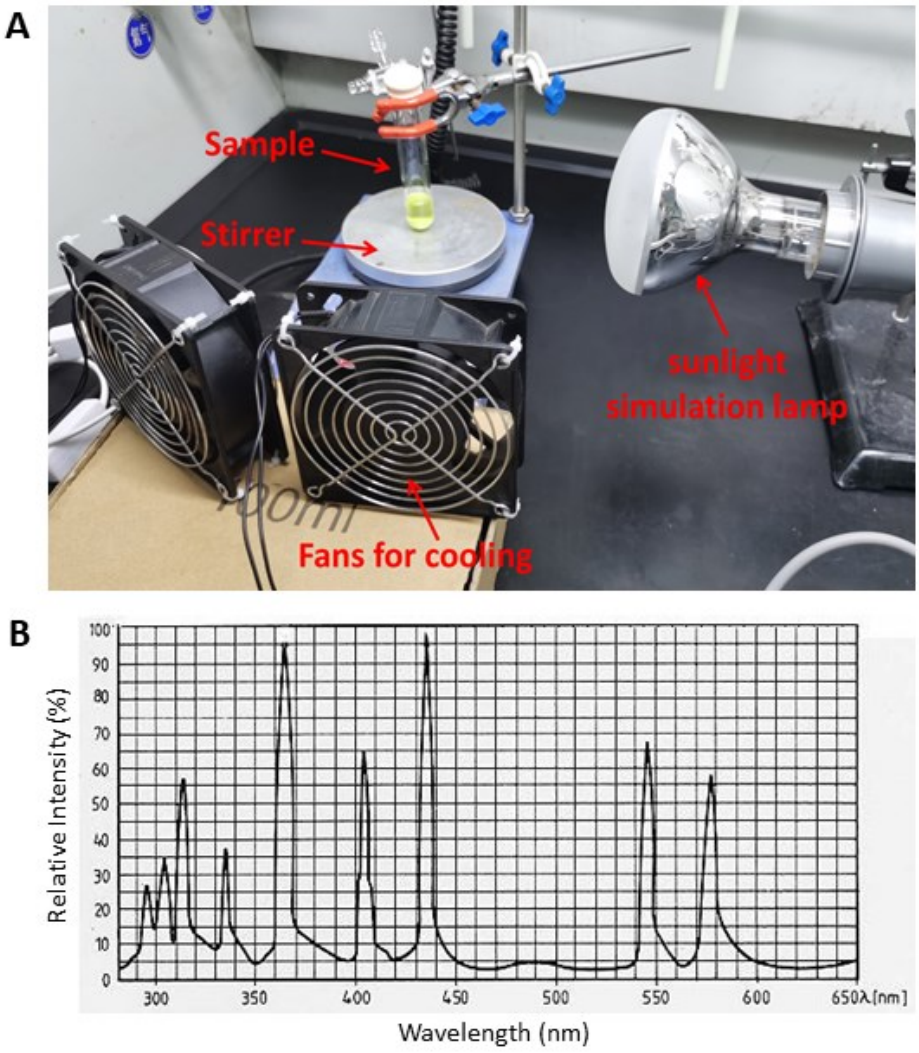


Fig. S1 (A) Reaction set-up of the photoredox-mediated reaction. (B) Emission spectrum of the lamps used in this work.

1.2 Sample measurements

Characterization of noncore-modified OPCs and core-modified OPCs: The noncore-modified OPCs and core-modified OPCs synthesized were characterized by ^{1}H NMR, ^{13}C NMR, and ESI-MS spectroscopy. ^{1}H NMR and ^{13}C NMR were recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. ^{1}H NMR spectra chemical shifts (δ) were reported in parts per million (ppm) referenced to hydrogen resonances in the NMR solvent (C_6D_6). ^{13}C NMR spectra chemical shifts (δ) were reported in parts per million (ppm) referenced to carbon resonances in the NMR solvent (C_6D_6). ESI-MS spectra were recorded on Agilent Q-TOF 6520.

Photophysical and electrochemical properties of OPCs measurements: Ultraviolet-visible spectroscopy was performed on a UV-2400PC spectrophotometer using DMAc as the solvent. Fluorescence spectroscopy was performed on an F-4700 Fluorescence Spectrophotometer using

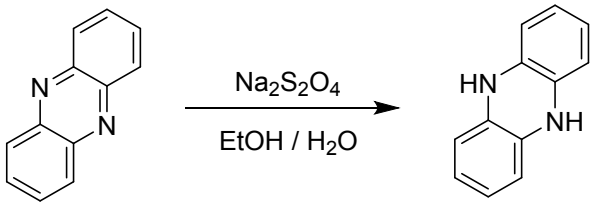
DMAc as the solvent. Cyclic voltammetry was carried out on a CHI660E CH Instruments electrochemical analyzer. Cyclic voltammograms of OPCs were performed in a 3-compartment electrochemical cell with Ag/AgCl (submerged in 3 M KCl solution) as the reference electrode and $TBAPF_6$ in DMAc (0.10 M) as the electrolyte solution under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum wire. *E* (V vs SCE) = *E* (V vs Ag/AgCl) - 0.019 V.

Characterization of synthesized polymers: Size exclusion chromatography (SEC) was performed on Wyatt system equipped with a SSI 1500 pump, a Waters Styragel HR 2.5 μm, 300 mm ×7.8 mm column, a Wyatt Optilab rEX differential refractive index (DRI) detector and a Wyatt DAWN HELEOS-II multi-angle light scattering (MALS) detector (laser at λ = 658 nm) (Wyatt Technology Corporation, U.S.A.). THF was used as the eluent at 35 ^{o}C with a flow rate of 0.7 mL/min^{-1} and a dn/dc value of 0.083. The polymer composition was determined using a ^{1}H NMR spectrometer (magnet system 400'54 ascend purchased from Bruker Biospin AG) with $CDCl_3$ as the solvent. Matrix assisted laser desorption ionization time of fight mass spectra (MALDI TOF MS) were recorded at 25 kV on the Bruker mass spectrometer (ultraextreme).

2. Core modification of OPCs

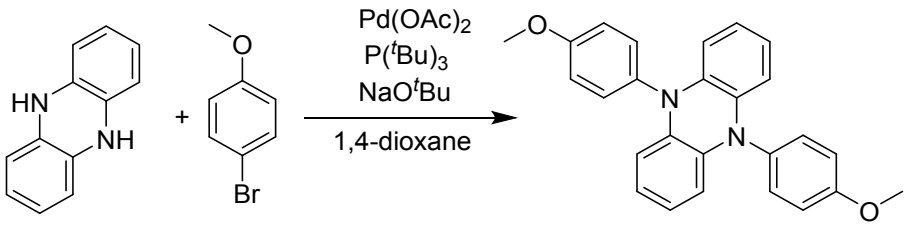
2.1 Synthesis of the noncore modified OPCs

5,10-dihydrophenazine



Synthesis of 5,10-dihydrophenazine[1]: An oven dried 500 mL round bottom flask equipped with a stir bar was charged with phenazine (1.00 g, 5.55 mmol, 1.00 eq.), $Na_2S_2O_4$ (11.65 g, 55.50 mmol, 10.0 eq.), EtOH (25.00 mL) and H_2O (100.00 mL). The mixture was sparged with N_2 for 60 minutes and then refluxed under N_2 for 12 h. After cooling to room temperature, the product was isolated as precipitate via cannula filtration, washed with distilled H_2O (3 x 100.00 mL), and then dried under vacuum to yield a pale green powder (0.86 g, 4.72 mmol, 85 %). The product was stored under nitrogen until further use.

5,10-di(4-methoxyphenyl)-5,10-dihydrophenazine (**1a**)



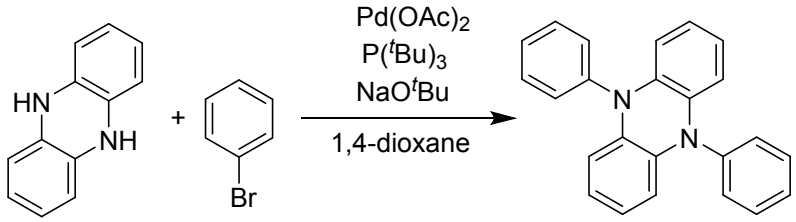
Synthesis of 5,10-di(4-methoxyphenyl)-5,10-dihydrophenazine[2]: An oven-dried vacuum tube equipped with a stir bar was charged with 5,10-dihydrophenazine (1.00 g, 5.50 mmol, 1.00 eq), NaO^tBu (1.58 g, 16.50 mmol, 3.00 eq), $Pd(OAc)_2$ (49 mg, 0.22 mmol, 0.04 eq), Tri-tert-butylphosphine $P(tBu)_3$ (33 mg, 0.165 mmol, 0.03 eq), 4-bromoanisole (2.06 g, 11.00 mmol, 2.00 eq) and 16.00 mL 1,4-dioxane. The vial was sealed under N_2 and and heated at 100 °C for 12 h. After cooling to room temperature, the mixture was concentrated under reduced pressure and purified by flash column chromatography on basic aluminum oxide (Eluent: CH_2Cl_2/hexane). The product was obtained as a light yellow solid (1.06 g, 2.69 mmol, 49%).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.11 – 7.07 (m, 4H), 6.77 – 6.73 (m, 4H), 6.37 – 6.33 (m, 4H), 5.93 – 5.89 (m, 4H), 3.25 (s, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 159.12, 137.31, 132.25, 127.95-127.46 (could not be resolved from NMR solvent peak), 121.03, 116.40, 112.66, 54.59.

HRMS (ESI-TOF): calc'd for M+ $C_{26}H_{22}N_2O_2$, 394.1681; found 394.1677.

5,10-diphenyl-5,10-dihydrophenazine (**1b**)



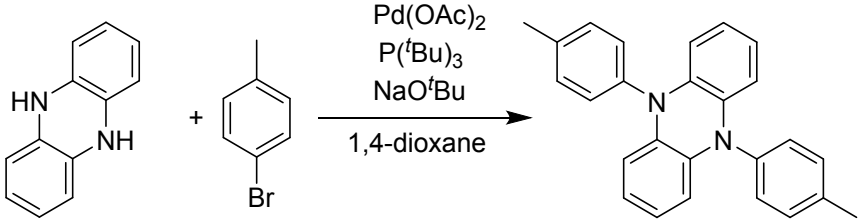
Synthesis of 5,10-diphenyl-5,10-dihydrophenazine[2]: An oven-dried vacuum tube equipped with a stir bar was charged with 5,10-dihydrophenazine (1.00 g, 5.50 mmol, 1.00 eq), NaO^tBu (1.58 g, 16.50 mmol, 3.00 eq)， $Pd(OAc)_2$ (49 mg, 0.22 mmol, 0.04 eq), $P(tBu)_3$ (33 mg, 0.17 mmol, 0.03 eq), bromobenzene (1.71 g, 11.00 mmol, 2.00 eq) and 16.00 mL 1,4-dioxane. The vial was sealed under N_2 and and heated at 100 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure, then the reaction mixture was dissolved in 200 mL CH_2Cl_2 and extracted with 200 mL H_2O for three times. The organic layer was evaporated dryness, and then this crude was purified by washing with CH_2Cl_2 (3 x 5.00 mL) and MeOH (3 x 2.00 mL) to afford the desired product as a light yellow solid (1.13 g, 3.38 mmol, 61%).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.19 (could not be resolved from NMR solvent peak) (m, 8H), 7.10 – 7.05 (m, 2H), 6.33 – 6.28 (m, 4H), 5.87 – 5.83 (m, 4H).

^{13}C NMR (C_6D_6, 101 MHz): δ 140.46, 136.81, 131.28, 131.09, 127.75, 121.09, 112.76.

HRMS (ESI-TOF): calc'd for M+ $C_{24}H_{18}N_2$, 334.1470; found 334.1460.

5,10-di(4-methylphenyl)-5,10-dihydrophenazine (**1c**)



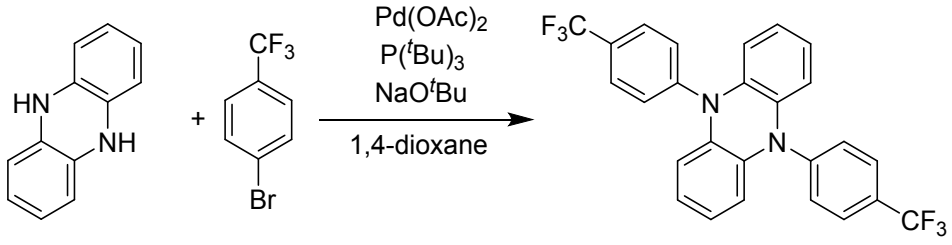
Synthesis of 5,10-di(4-methylphenyl)-5,10-dihydrophenazine[2]: An oven-dried vacuum tube equipped with a stir bar was charged with 5,10-dihydrophenazine (1.00 g, 5.50 mmol, 1.00 eq), NaO^{t}Bu (1.58 g, 16.50 mmol, 3.00 eq)，$Pd(OAc)_2$ (49 mg, 0.22 mmol, 0.04 eq), $P(tBu)_3$ (33 mg, 0.17 mmol, 0.03 eq), 4-bromotoluene (1.88 g, 11.00 mmol, 2.00 eq) and 16.00 mL 1,4-dioxane. The vial was sealed under N_2 and and heated at 100 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure, then the reaction mixture was dissolved in 200 mL CH_2Cl_2 and extracted with 200 mL H_2O for three times. The organic layer was evaporated dryness, and then this crude was purified by washing with CH_2Cl_2 (3 x 5.00 mL) and MeOH (3 x 2.0 mL) to afford the desired product as a light yellow solid (1.43g, 3.95 mmol, 72%).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.15 (d, J = 8.1 Hz, 4H), 7.03 (d, J = 8.0 Hz, 4H), 6.37 (dq, J = 7.4, 3.9 Hz, 4H), 5.95 (dd, J = 5.8, 3.5 Hz, 4H), 2.13 (s, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 137.74, 137.46, 137.07, 131.82, 131.00, 121.00, 112.71, 20.73.

HRMS (ESI-TOF): calc'd for M+ $C_{26}H_{22}N_2$, 362.1783; found 362.1780.

5,10-bis(4-(trifluoromethyl)phenyl)-5,10-dihydrophenazine (**1d**)



Synthesis of 5,10-bis(4-(trifluoromethyl)phenyl)-5,10-dihydrophenazine[2]: An oven-dried vacuum tube equipped with a stir bar was charged with 5,10-dihydrophenazine (1.00 g, 5.50 mmol, 1.00 eq), NaO^{t}Bu (1.58 g, 16.50 mmol, 3.00 eq)，$Pd(OAc)_2$ (49 mg, 0.22 mmol, 0.04 eq), $P(tBu)_3$ (33 mg, 0.17 mmol, 0.03 eq), 4-bromobenzotrifluoride (2.48 g, 11.00 mmol, 2.00 eq) and 16.00 mL 1,4-dioxane. The vial was sealed under N_2 and and heated at 100 °C for 12 h. After cooling to

room temperature, the solvent was removed under reduced pressure, then the reaction mixture was dissolved in 200 mL CH_2Cl_2 and extracted with 200 mL H_2O for three times. The organic layer was evaporated dryness, and then this crude was purified by washing with CH_2Cl_2 (3 x 5.00 mL) and MeOH (3 x 2.0 mL) to afford the desired product as a light yellow solid (1.53g, 3.25 mmol, 59%).

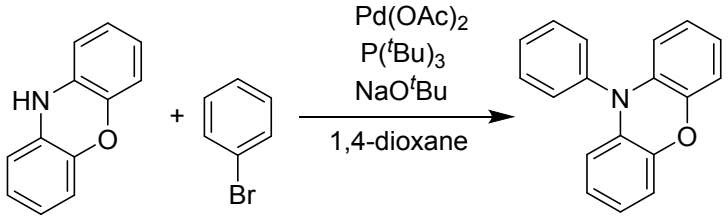
^{1}H NMR (C_6D_6, 400 MHz): δ 7.30 (d, *J* = 8.3 Hz, 4H), 6.94 (d, *J* = 8.1 Hz, 4H), 6.34 – 6.30 (m, 4H), 5.67 – 5.63 (m, 4H).

^{13}C NMR (C_6D_6, 101 MHz): δ 135.98, 131.39, 128.28, 128.24, 128.20, 127.59, 121.71, 113.32.

^{19}F NMR (C_6D_6, 376 MHz): δ -62.17.

HRMS (ESI-TOF): calc'd for M+ $C_{26}H_{16}F_6N_2$, 470.1218; found 470.1207.

N-phenyl phenoxazine (**4a**)

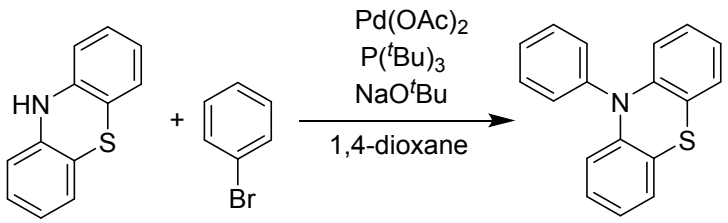


Synthesis of N-phenyl phenoxazine[2]: An oven-dried vacuum tube equipped with a stir bar was charged with phenoxazine (1.00 g, 5.46 mmol, 1.00 eq), NaO^{t}Bu (787.1 mg, 8.19 mmol, 1.50 eq), $Pd(OAc)_2$ (49.4 mg, 0.22 mmol, 0.04 eq), $P(tBu)_3$ (32.4 mg, 0.16 mmol, 0.03 eq), Bromobenzene (857.3 mg, 5.46 mmol, 1.00 eq) and 16.00 mL 1,4-dioxane. The vial was sealed under N_2 and and heated at 100 °C for 12 h. After cooling to room temperature, the mixture was concentrated under reduced pressure and purified by flash column chromatography on basic aluminum oxide (Eluent: Hexane/ethyl acetate). The product was obtained as a white solid (1.08 g, 4.17 mmol, 76%).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.09 (t, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.91 – 6.89 (m, 2H), 6.76 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.48 (td, *J* = 7.6, 1.5 Hz, 2H), 6.41 (td, *J* = 7.7, 1.5 Hz, 2H), 5.90 (dd, *J* = 7.9, 1.5 Hz, 2H).

^{13}C NMR (C_6D_6, 101 MHz): δ 144.25, 139.18, 134.60, 130.76, 130.73, 128.00, 123.30, 121.42, 115.55, 113.42.

N-phenyl phenothiazine (**5a**)



Synthesis of N-phenyl phenothiazine[2]: An oven-dried vacuum tube equipped with a stir bar was charged with phenothiazine (1.00 g, 5.02 mmol, 1.00 eq), NaO^{t}Bu (723.6 mg, 7.53 mmol, 1.50 eq), $Pd(OAc)_2$ (44.9 mg, 0.20 mmol, 0.04 eq), $P(tBu)_3$ (30.3 mg, 0.15 mmol, 0.03 eq), Bromobenzene (788.2 mg, 5.02 mmol, 1.00 eq) and 16.00 mL 1,4-dioxane. The vial was sealed under N_2 and and heated at 100 °C for 12 h. After cooling to room temperature, the mixture was concentrated under reduced pressure and purified by flash column chromatography on basic aluminum oxide (Eluent: Hexane/ethyl acetate). The product was obtained as a white solid (1.14 g, 4.15 mmol, 83%).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.10 – 7.06 (m, 2H), 7.02 – 6.93 (m, 5H), 6.62 – 6.55 (m, 4H), 6.18 – 6.16 (m, 2H).

^{13}C NMR (C_6D_6, 101 MHz): δ 144.50, 141.10, 130.87, 130.46, 127.58 (could not be resolved from NMR solvent peak), 126.79, 126.71, 122.50, 120.46, 116.11.

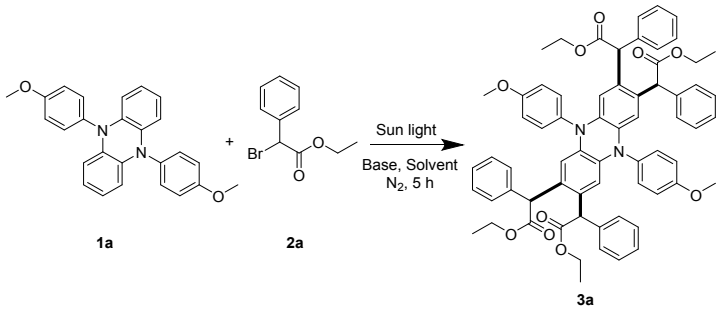
HRMS (ESI-TOF): calc'd for M+ $C_{18}H_{13}NS$, 275.0769; found 275.0758.

2.2 General Procedure for core modified OPCs

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with noncore-modified OPC, bromides and 1,4-Dioxane. The reaction mixture was degassed with three freeze-pump-thaw cycles and the vial was then backfilled with argon. Then, the reaction was vigorously stirred in front of sunlight simulation lamp at room temperature. After the reaction was complete, the solvent was evaporated to dryness and the crude reaction mixture was directly purified by flash column chromatography on basic aluminum oxide. Eluent: Hexane/ethyl acetate (contains 0.5% triethylamine). The crude product was obtained as an umber deep solid and then purified by washing with MeOH to afford the desired product.

2.3 Optimization Results

Table S1. Optimization Results[a]



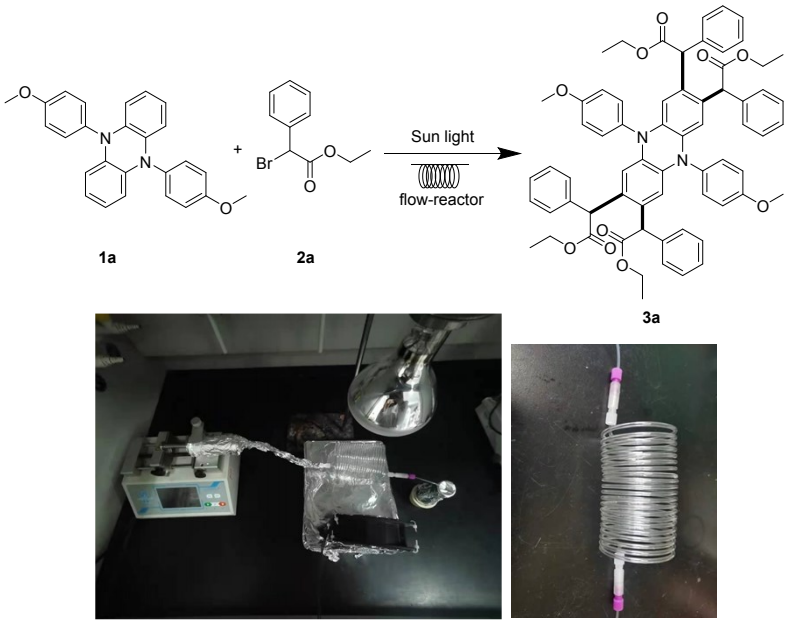
Entry	Solvent	Base	Yield (%)[b]
1	DMAc	None	82
2	1,4-Dioxane	None	87
3	DCE	None	0
4	THF	None	26
5	PhMe	None	44
6	MeCN	None	38
7	1,4-Dioxane	K_3PO_4	80
8	1,4-Dioxane	Cs_2CO_3	83
9	1,4-Dioxane	$NaHCO_3$	79
10	1,4-Dioxane	NaO^tBu	61
11	1,4-Dioxane	Na_2CO_3	70
12	1,4-Dioxane	K_2CO_3	76
13[c]	1,4-Dioxane	None	0

[a] Reaction condition: **1a** (0.25 mmol, 1.00 equiv.), **2a** (10.00 equiv.), and base (4.00 equiv.) in solvent (10 mL) at room temperature under N_2 and a 300 W simulative sunshine bulb for 5 h.

[b] Isolated yields.

[c] Reaction was carried out in the dark.

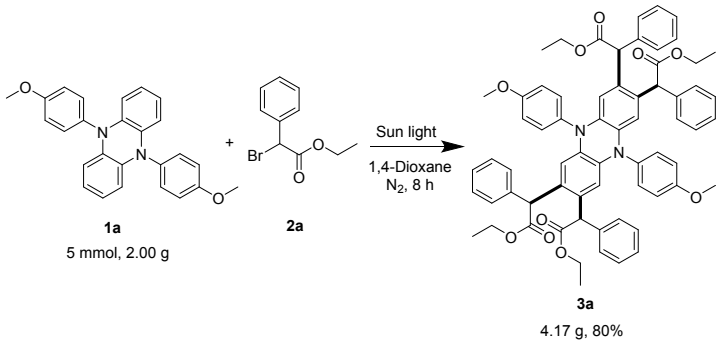
Flow experiments:



Continuous flow reactor details

First, continuous flow reactor was assembled and installed as shown in the figure above, internal volume of the glass tube was 5 mL (6.4 m, 1.0 mm inner diameter, 3.0 mm outer diameter). Second, in a 50 mL beaker **1a** (0.5 g, 1.27 mmol, 1.0 eq), ethyl α-bromophenylacetate (3.1 g, 12.7 mmol, 10.0 eq) were dissolved in 25 mL 1,4-Dioxane. Then, the reaction mixture was pumped into the flow cell via a syringe. The flow rate was 0.167 mL/min and residence time 30 minute. The outflow of the reaction mixture was collected. The solvent was evaporated to dryness and the crude reaction mixture was directly purified by flash column chromatography on basic aluminum oxide. Eluent: Hexane/ethyl acetate (contains 0.5% triethylamine). The crude product was obtained as an umber deep solid and then purified by washing with MeOH (2 x 0.5 mL) to afford the desired product as a dark yellow solid (1.1 g, 1.06 mmol, 83%).

2.4 Gram-Scale Synthesis of 3a



A 250 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (2.0 g, 5.0 mmol, 1.0 eq), ethyl α-bromophenylacetate (12.1 g, 50 mmol, 10.0 eq) and 1,4-Dioxane 100.0 mL. The reaction mixture was degassed with three freeze-pump-thaw cycles and the vial was then backfilled with argon. After that, the reaction was vigorously stirred in front of sunlight simulation lamp at

room temperature for 8 h. The solvent was evaporated to dryness and the crude reaction mixture was directly purified by flash column chromatography on basic aluminum oxide. Eluent: Hexane/ethyl acetate (contains 0.5% triethylamine). The crude product was obtained as an umber deep solid and then purified by washing with MeOH (3 x 1.00 mL) to afford the desired product as a dark yellow solid (4.17 g, 4.0 mmol, 80%).

2.5 Structure of 3a by X-Ray Crystallographic (CCDC 2043491)

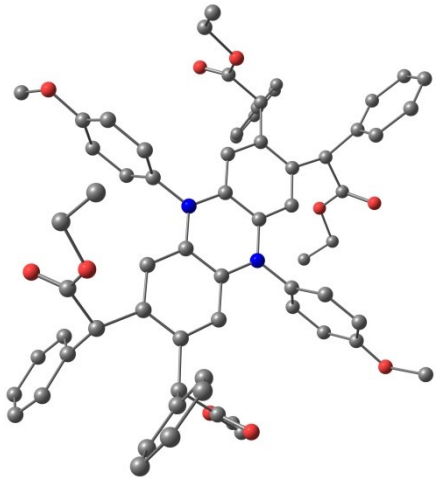
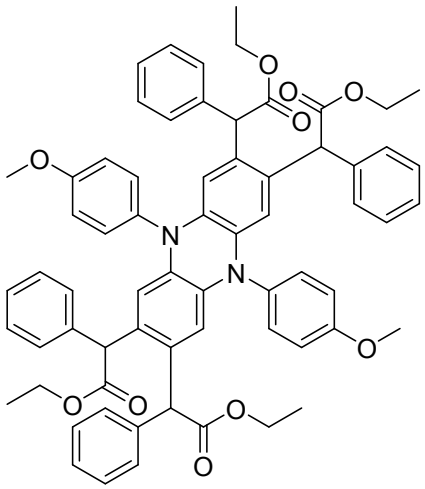


Fig. S2 Structure of **3a** by X-Ray Crystallographic. H atoms are omitted for clarity. Color code, C: black, O: red, N: dark blue (CCDC 2043491).

2.6 Characterization of core modified OPCs



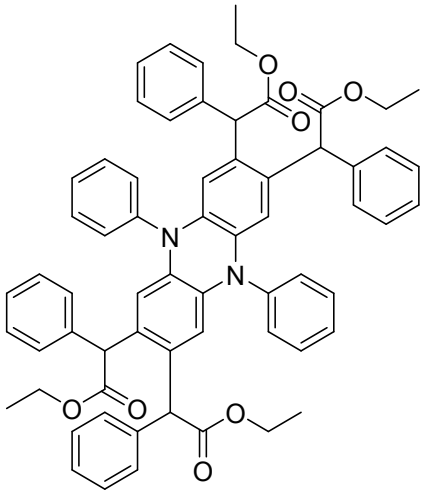
Tetraethyl 2,2',2",2"'-(5,10-bis(4-methoxyphenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(2-phenylacetate) (**3a**)

Dark yellow solid. Yield: 227 mg, 87%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.27 – 7.24 (m, 5H), 7.12 – 6.91 (m, 19H), 6.66 – 6.59 (m, 4H), 6.11 – 6.07 (m, 4H), 5.26 – 5.21 (m, 4H), 3.90 – 3.62 (m, 8H), 3.19 – 3.16 (m, 6H), 0.83 – 0.67 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 171.68, 158.98, 138.95, 136.40, 131.82 – 131.56 (m), 129.74 – 129.61 (m), 128.85, 128.18 – 128.13 (m), 127.59 (could not be resolved from NMR solvent peak), 126.69 – 126.66 (m), 116.13, 113.82, 60.58 – 60.45 (m), 54.51, 52.64, 13.71 – 13.61 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{66}H_{62}N_2O_{10}$, 1042.4404; found 1042.4438



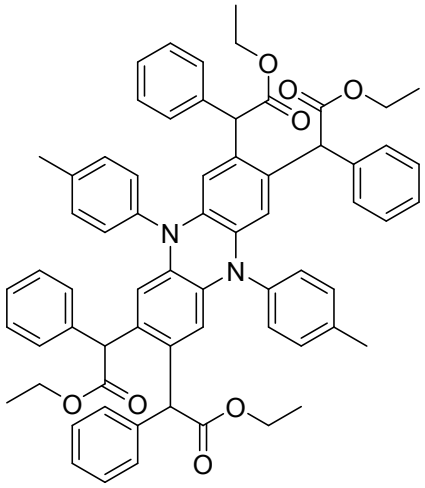
Tetraethyl 2,2',2",2"'-(5,10-diphenyl-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(2-phenylacetate) (**3b**)

Yellow solid. Yield: 146 mg, 65%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.24 – 7.21 (m, 5H), 7.09 – 6.94 (m, 25H), 6.05 – 6.01 (m, 4H), 5.24 – 5.19 (m, 4H), 3.90 – 3.59 (m, 8H), 0.83 – 0.67 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 171.57, 139.54 – 139.51 (m), 138.91 – 138.87 (m), 135.93 – 135.85 (m), 130.81, 130.57 – 130.54 (m), 129.88 – 129.75 (m), 128.77, 128.17 – 128.13 (m), 127.94 – 127.46 (could not be resolved from NMR solvent peak), 126.69 – 126.66 (m), 113.89 – 113.84 (m), 60.53 – 60.39 (m), 52.62 – 52.55 (m), 13.71 – 13.61 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{64}H_{58}N_2O_8$, 982.4193; found 982.4191.



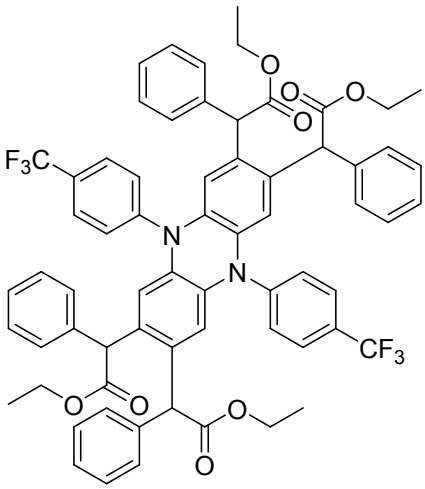
Tetraethyl 2,2',2",2"'-(5,10-di-p-tolyl-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(2-phenylacetate) (**3c**)

Yellow solid. Yield: 203 mg, 72%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.24 – 7.22 (m, 5H), 7.10 – 7.03 (m, 8H), 6.97 – 6.85 (m, 15H), 6.07 – 6.04 (m, 4H), 5.23 – 5.19 (m, 4H), 3.86 – 3.62 (m, 8H), 1.99 – 1.95 (m, 6H), 0.83 – 0.67 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 171.64, 138.94 – 138.90 (m), 137.34, 136.86 – 136.83 (m), 136.16 – 136.09 (m), 131.51, 130.23, 129.68 – 129.57 (m), 128.81, 128.12 – 128.07 (m), 126.62 – 126.59 (m), 113.83, 60.53 – 60.38 (m), 52.65 – 52.60 (m), 20.63, 13.65 – 13.54 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{66}H_{62}N_2O_8$, 1010.4506; found 1010.4484.



Tetraethyl 2,2',2",2"'-(5,10-bis(4-(trifluoromethyl)phenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(2-phenylacetate) **(3d)**

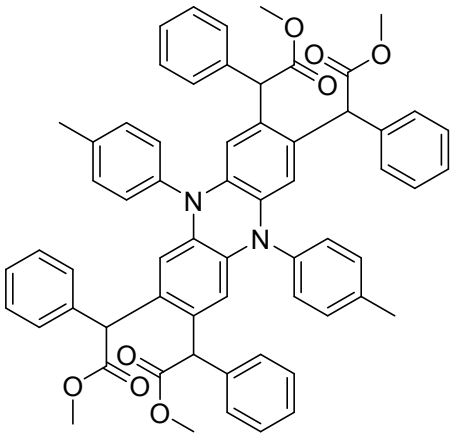
Yellow solid. Yield: 158 mg, 66%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.22 – 7.16 (m, 10H), 7.07 – 6.95 (m, 14H), 6.88 – 6.82 (m, 4H), 5.92 – 5.80 (m, 4H), 5.23 (d, *J* = 15.1 Hz, 4H), 3.89 – 3.66 (m, 8H), 0.82 – 0.68 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 171.48 – 171.32 (m), 143.05 – 142.99 (m), 138.58 – 138.55 (m), 138.41 – 138.38 (m), 134.92 – 134.87 (m), 130.84 – 130.76 (m), 128.58, 128.27, 126.97 – 126.93 (m), 125.57, 122.86, 114.87 – 114.80 (m), 114.68 – 114.62 (m), 60.73 – 60.63 (m), 52.66 – 52.59 (m), 13.63 – 13.55 (m).

^{19}F NMR (C_6D_6, 376 MHz): δ -62.33.

HRMS (ESI-TOF): calc'd for M+ $C_{66}H_{56}F_6N_2O_8$, 1118.3941; found 1118.3919.



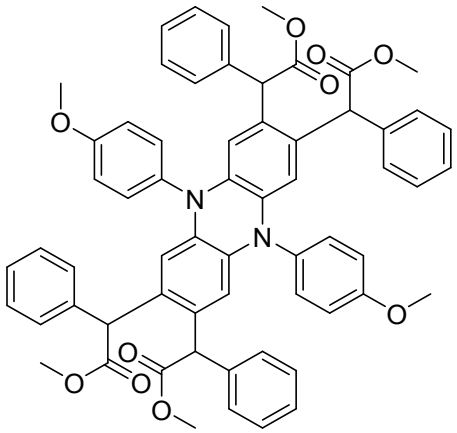
Tetramethyl 2,2',2",2"'-(5,10-di-p-tolyl-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(2-phenylacetate) (**3e**)

Yellow solid. Yield: 204 mg, 76%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.20 – 7.18 (m, 4H), 7.08 – 7.02 (m, 8H), 6.97 – 6.93 (m, 12H), 6.88 – 6.82 (m, 4H), 6.06 – 6.02 (m, 4H), 5.18 (d, *J* = 19.3 Hz, 4H), 3.18 – 3.04 (m, 12H), 1.96 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 171.00 (d, *J* = 6.3 Hz), 137.64 – 137.53 (m), 136.29, 135.68 – 135.66 (m), 135.13 – 135.10 (m), 130.43, 129.09, 128.47 – 128.38 (m), 127.72, 127.11, 127.04, 125.61 (d, *J* = 5.6 Hz), 51.54, 50.12 (d, *J* = 17.0 Hz), 19.57.

HRMS (ESI-TOF): calc'd for M+ $C_{62}H_{54}N_2O_8$, 954.3880; found 954.3903



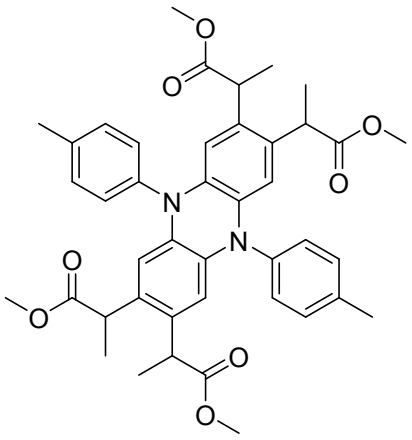
Tetramethyl 2,2',2",2"'-(5,10-bis(4-methoxyphenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(2-phenylacetate) (**3f**)

Yellow solid. Yield: 175 mg, 71%.

^{1}H NMR (C_6D_6, 400 MHz): δ. 7.20 – 7.18 (m, 4H), 7.09 – 6.95 (m, 20H), 6.62 – 6.61 (m, 4H), 6.06 – 6.02 (m, 4H), 5.20 – 5.16 (m, 4H), 3.18 – 3.15 (m, 12H), 3.05 (s, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 172.12 – 172.07 (m), 158.98, 138.73 – 138.64 (m), 136.42, 131.51, 129.56, 128.81, 128.22, 128.16, 126.75 – 126.70 (m), 116.10, 113.93, 54.54, 52.64, 51.32 – 51.16.

HRMS (ESI-TOF): calc'd for M+ $C_{62}H_{54}N_2O_{10}$, 986.3778; found 986.3776.



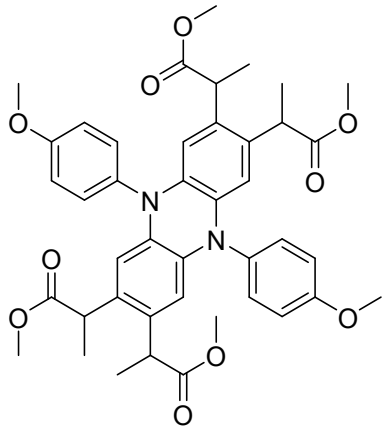
Tetramethyl 2,2',2",2"'-(5,10-di-p-tolyl-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrapropionate (**3g**)

Red solid. Yield: 120 mg, 61%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.12 – 7.10 (could not be resolved from NMR solvent peak) (m, 4H), 7.03 – 7.01 (m, 4H), 5.98 (d, J = 8.6 Hz, 4H), 3.62 (dq, J = 37.5, 6.9 Hz, 4H), 3.25 – 3.18 (m, 12H), 1.98 – 1.94 (m, 6H), 1.22 (dd, J = 18.1, 6.9 Hz, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 173.39 (d, *J* = 5.5 Hz), 137.05, 136.42 – 136.35 (m), 135.43 – 135.35 (m), 130.89, 130.23 (d, *J* = 4.6 Hz), 129.65 (t, *J* = 3.9 Hz), 110.80 (d, *J* = 55.9 Hz), 50.12, 39.58 (d, *J* = 54.4 Hz), 19.87, 17.39 (d, *J* = 19.6 Hz).

HRMS (ESI-TOF): calc'd for M+ $C_{42}H_{46}N_2O_8$, 706.3254; found 706.3292.



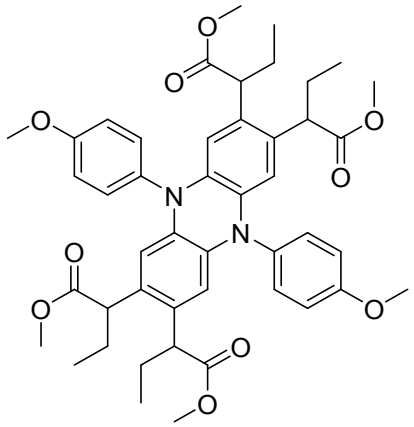
Tetramethyl 2,2',2",2'"-(5,10-bis(4-methoxyphenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrapropionate (**3h**)

Red solid. Yield: 111 mg, 60%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.14 – 7.12 (could not be resolved from NMR solvent peak) (m, 4H), 6.81 (d, *J* = 8.7 Hz, 4H), 6.00 (d, *J* = 8.6 Hz, 4H), 3.71 – 3.57 (m, 4H), 3.24 – 3.21 (m, 12H), 3.17 – 3.16 (m, 6H), 1.27 – 1.21 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 173.41 (d, J = 5.3 Hz), 158.41, 135.60 (d, J = 5.2 Hz), 131.35 (d, J = 3.1 Hz), 130.99 (d, J = 3.2 Hz), 130.27 – 130.23 (m), 115.45, 110.77 (d, J = 55.1 Hz), 53.65, 50.16, 39.61 (d, J = 54.3 Hz), 17.41 (d, J = 19.6 Hz).

HRMS (ESI-TOF): calc'd for M+ $C_{42}H_{46}N_2O_{10}$, 738.3152; found 738.3190.



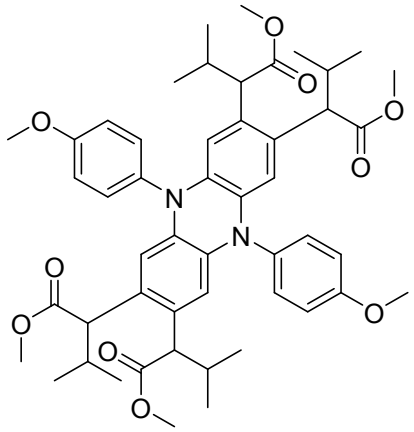
Tetramethyl 2,2',2",2"'-(5,10-bis(4-methoxyphenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrabutyrate (**3i**)

Yellow solid. Yield: 109 mg, 55%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.19 – 7.17 (could not be resolved from NMR solvent peak) (m, 4H), 6.84 (d, *J* = 8.7 Hz, 4H), 6.14 (d, *J* = 10.4 Hz, 4H), 3.66 (dt, *J* = 44.0, 7.5 Hz, 4H), 3.29 – 3.23 (m, 12H), 3.16 (s, 6H), 2.00 – 1.89 (m, 4H), 1.69 – 1.57 (m, 4H), 0.80 (dt, *J* = 28.5, 7.2 Hz, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 172.94 – 172.87 (m), 158.41, 135.66 – 135.56 (m), 131.39, 130.99, 129.16 – 129.12 (m), 115.45, 111.23 – 110.59 (m), 53.60, 50.03 (d, *J* = 5.3 Hz), 46.88 (d, *J* = 51.5 Hz), 25.55 (d, *J* = 8.9 Hz), 11.19 – 11.12 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{46}H_{54}N_2O_{10}$, 794.3778; found 794.3671.



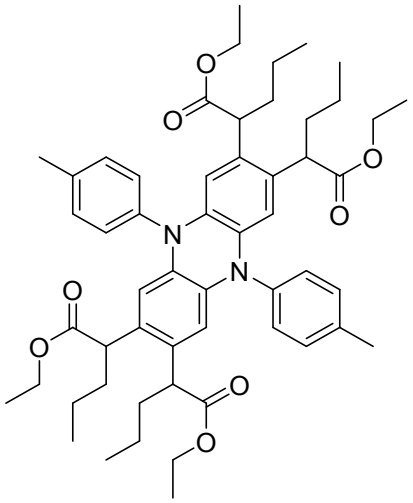
Tetramethyl 2,2',2",2"'-(5,10-bis(4-methoxyphenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrakis(3-methylbutanoate) (**3j**)

Yellow solid. Yield: 108 mg, 51%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.27 – 7.24 (m, 4H), 6.88 (dd, *J* = 8.9, 2.6 Hz, 4H), 6.33 (d, *J* = 12.2 Hz, 4H), 3.61 (dd, *J* = 34.8, 10.7 Hz, 4H), 3.30 – 3.24 (m, 12H), 3.12 (s, 6H), 2.24 – 2.13 (m, 4H), 0.92 – 0.76 (m, 24H).

^{13}C NMR (C_6D_6, 101 MHz): δ 173.63 – 173.53 (m), 159.23, 136.39 – 136.31 (m), 131.80, 129.75, 129.61, 116.29, 111.77 (d, *J* = 74.2 Hz), 54.34, 53.50 – 53.16 (m), 50.73 – 50.58 (m), 31.45 – 31.19 (m), 21.29 – 19.56 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{50}H_{62}N_2O_{10}$, 850.4404; found 850.4440.



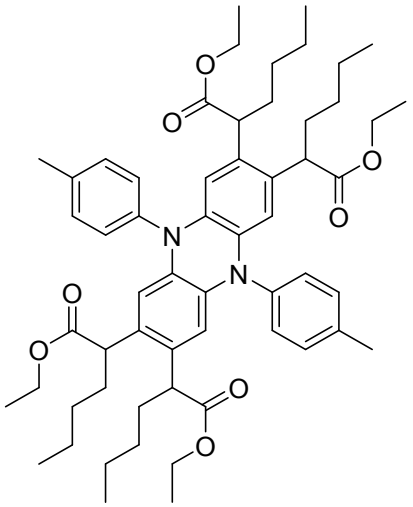
Tetraethyl 2,2',2",2'"-(5,10-di-p-tolyl-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrapentanoate (**3k**)

Yellow solid. Yield: 140 mg, 57%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.19 – 7.17 (m, 4H), 7.08 – 7.06 (m, 4H), 6.18 – 6.15 (m, 4H), 3.93 – 3.84 (m, 8H), 3.82 – 3.76 (m, 4H),1.97 (s, 6H), 1.67 – 1.22 (m, 16H), 0.93 – 0.74 (m, 24H).

^{13}C NMR (C_6D_6, 101 MHz): δ 173.33 (d, *J* = 5.3 Hz), 137.34, 136.17, 136.04, 131.73, 130.54, 130.14, 111.34, 59.96 – 59.91 (m), 45.88 (d, *J* = 60.5 Hz), 35.54 (d, *J* = 6.9 Hz), 20.94, 20.82 – 20.71 (m), 13.83, 13.76 – 13.73(m).

HRMS (ESI-TOF): calc'd for M+ $C_{54}H_{70}N_2O_8$, 874.5132; found 874.5137.



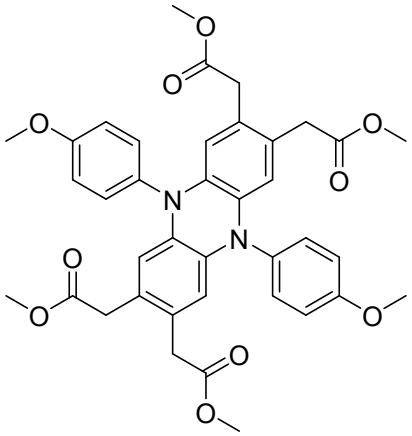
Tetraethyl 2,2',2",2'"-(5,10-di-p-tolyl-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetrahexanoate (**3l**)

Yellow solid. Yield: 125 mg, 48%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.19 (s, 4H), 7.08 (d, *J* = 8.1 Hz, 4H), 6.20 – 6.15 (m, 4H), 3.87 (q, *J* = 7.0 Hz, 12H), 1.99 (s, 6H), 1.71 – 1.67 (m, 4H), 1.33 – 1.20 (m, 20H), 0.84 (dt, *J* = 25.8, 7.1 Hz, 24H).

^{13}C NMR (C_6D_6, 101 MHz): δ 172.52, 137.03, 136.55, 135.30, 130.89, 129.72, 129.41, 110.55, 59.10, 45.02, 32.30, 28.99, 21.78, 19.88, 12.97, 12.94.

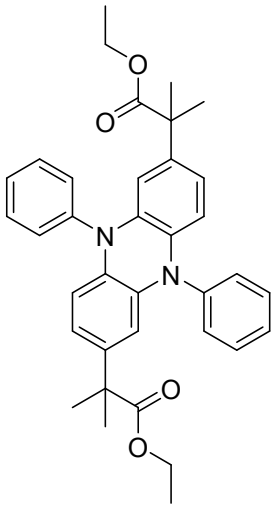
HRMS (ESI-TOF): calc'd for M+ $C_{58}H_{78}N_2O_8$, 930.5758; found 930.5755.



tetramethyl 2,2',2",2"'-(5,10-bis(4-methoxyphenyl)-5,10-dihydrophenazine-2,3,7,8-tetrayl)tetraacetate (**3m**)

Only trace amount of the corresponding tetrasubstituted product **3m** was detected by TLC and MS-ESI.

HRMS (ESI-TOF): calc'd for M+ $C_{38}H_{38}N_2O_{10}$, 682.2526; found 682.2576.



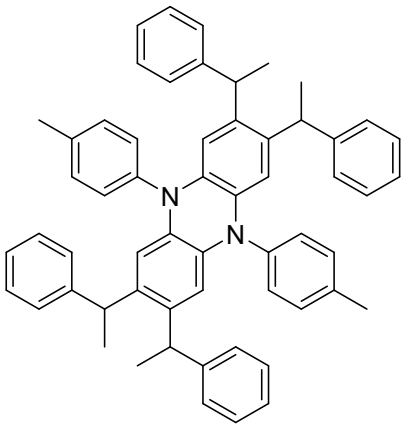
Diethyl 2,2'-(5,10-diphenyl-5,10-dihydrophenazine-2,7-diyl)bis(2-methylpropanoate) (**3n**)

Yellow solid. Yield: 98 mg, 76%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.16 (could not be resolved from NMR solvent peak) (m, 8H), 7.05 – 7.02 (m, 2H), 6.32 (d, *J* = 8.0 Hz, 2H), 5.96 (s, 2H), 5.74 (d, *J* = 8.2 Hz, 2H), 3.82 (q, *J* = 7.1 Hz, 4H), 1.34 (s, 12H), 0.82 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 175.67, 140.35, 137.88, 136.57, 135.36, 131.13, 130.99, 127.58 (could not be resolved from NMR solvent peak), 117.83, 112.57, 110.64, 60.07, 45.45, 26.10, 13.79.

HRMS (ESI-TOF): calc'd for M+ $C_{36}H_{38}N_2O_4$, 562.2832; found 562.2845.



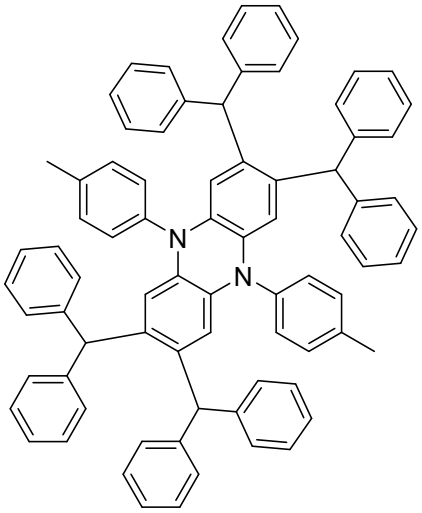
2,3,7,8-tetrakis(1-phenylethyl)-5,10-di-p-tolyl-5,10-dihydrophenazine (**3o**)

Yellow solid. Yield: 120 mg, 55%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.13 – 6.92 (m, 28H), 6.09 – 5.89 (m, 4H), 4.18 – 4.00 (m, 4H), 2.05 – 1.93 (m, 6H), 1.31 – 1.09 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 146.58 – 146.47 (m), 146.08 – 146.01 (m), 137.20, 134.52 – 134.47 (m), 130.60 – 130.54 (m), 129.78 – 129.66 (m), 127.34, 126.75, 124.75, 124.61, 111.62 – 111.47 (m), 38.58 – 38.31 (m), 21.23 – 21.01 (m), 19.86.

HRMS (ESI-TOF): calc'd for M+ $C_{58}H_{54}N_2$, 778.4287; found 778.4258.



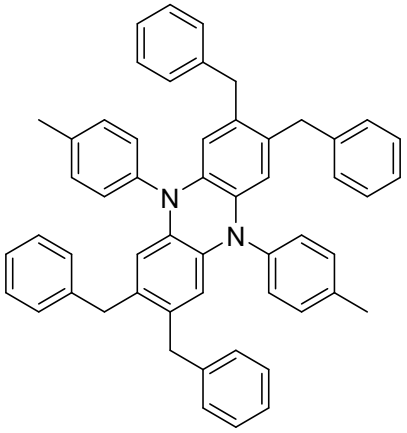
2,3,7,8-tetrabenzhydryl-5,10-di-p-tolyl-5,10-dihydrophenazine (**3p**)

Yellow solid. Yield: 129 mg, 45%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.00 – 6.92 (m, 40H), 6.77 (d, *J* = 8.2 Hz, 4H), 6.65 (d, *J* = 8.1 Hz, 4H), 5.62 (s, 4H), 5.45 (s, 4H), 2.01 (s, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 143.29, 136.25, 135.48, 134.40, 133.57, 130.21, 128.86, 128.55, 126.75 (could not be resolved from NMR solvent peak), 124.99, 114.55, 51.26, 19.76.

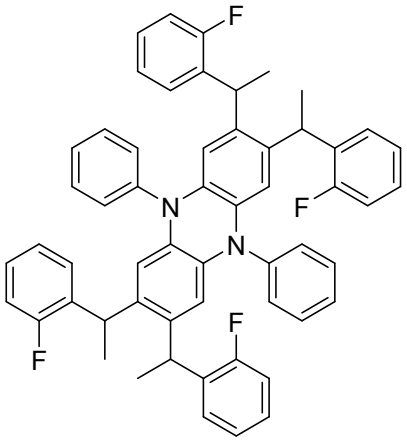
HRMS (ESI-TOF): calc'd for M+ $C_{78}H_{62}N_2$, 1026.4913; found 1026.4898.



2,3,7,8-tetrabenzyl-5,10-di-p-tolyl-5,10-dihydrophenazine (**3q**)

Only trace amount of the corresponding tetrasubstituted product **3q** was detected by TLC and MS-ESI.

HRMS (ESI-TOF): calc'd for M+ $C_{54}H_{46}N_2$, 722.3661; found 722.3662.



2,3,7,8-tetrakis(1-(2-fluorophenyl)ethyl)-5,10-diphenyl-5,10-dihydrophenazine (**3r**)

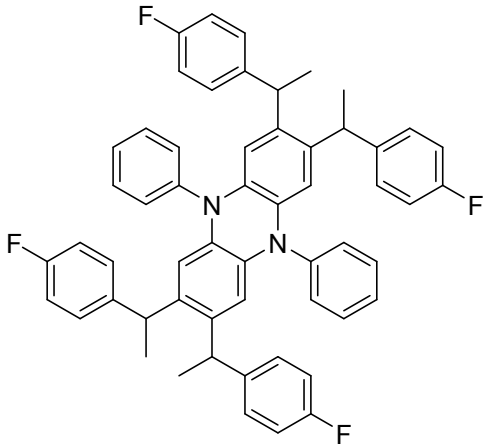
Yellow solid. Yield: 151 mg, 80%.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.11 – 7.07 (m, 8H), 7.02 – 6.98 (m, 4H), 6.91 – 6.87 (m 2H), 6.81 – 6.68 (m, 12H), 5.95 – 5.89 (m, 4H), 4.64 (dt, *J* = 41.0, 5.7 Hz, 4H), 1.21 (ddd, *J* = 44.3, 11.9, 6.8 Hz, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 161.90 – 159.31 (m), 140.60 – 140.54 (m), 135.14 – 135.04 (m), 134.50 – 134.42 (m), 133.98 – 133.21 (m), 130.72 – 130.62 (m), 128.56 – 128.52 (m), 128.22 – 128.18 (m), 127.05 – 126.97 (m), 123.71 – 123.68 (m), 123.36 – 123.33 (m), 115.11 – 114.67 (m), 112.25 – 112.19 (m), 32.59 – 32.28 (m), 21.06 – 20.26 (m).

^{19}F NMR (C_6D_6, 376 MHz): δ -117.19 – -117.66 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{56}H_{46}F_4N_2$, 822.3597; found 822.3597.



2,3,7,8-tetrakis(1-(4-fluorophenyl)ethyl)-5,10-diphenyl-5,10-dihydrophenazine (**3s**)

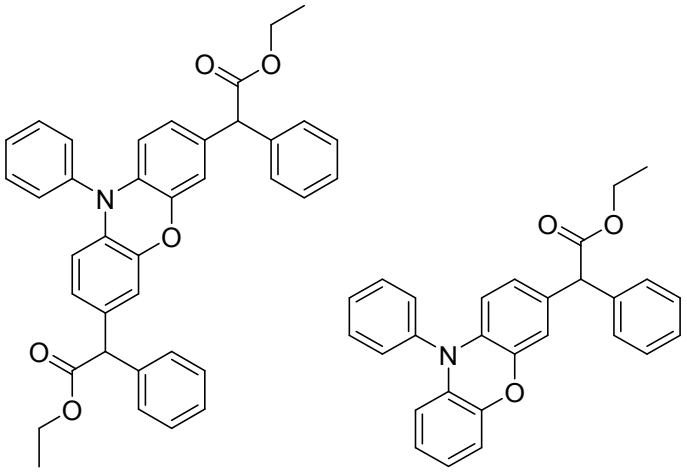
Yellow solid. Yield: 110 mg, 58%.

^{1}H NMR (C_6D_6, 400 MHz): δ 6.87 – 6.85 (m, 4H), 6.77 – 6.74 (m, 4H), 6.60 – 6.41 (m, 18H), 5.61 – 5.49 (m, 4H), 3.73 – 3.68 (m, 4H), 0.93 – 0.76 (m, 12H).

^{13}C NMR (C_6D_6, 101 MHz): δ 162.47 – 160.05 (m), 142.52 – 142.18 (m), 140.43 – 140.39 (m), 135.37, 135.08, 130.76, 130.66 – 130.60 (m), 128.84, 128.75 – 128.66 (m), 114.93 – 114.52 (m), 112.31 – 112.13 (m), 38.48 – 38.28, 21.91 – 21.81.

^{19}F NMR (C_6D_6, 376 MHz): δ -117.40 – -117.59 (m).

HRMS (ESI-TOF): calc'd for M+ $C_{56}H_{46}F_4N_2$, 822.3597; found 822.3562.



Diethyl 2,2'-(10-phenyl-10H-phenoxazine-3,7-diyl)bis(2-phenylacetate) (**6a**) and Ethyl 2-phenyl-2-(10-phenyl-10H-phenoxazin-3-yl)acetate (**6b**)

Disubstituted product **6a** (white solid, 93 mg, 41%) and monosubstituted product **6b** (white solid, 76 mg, 46%).

Characterization of **6a**:

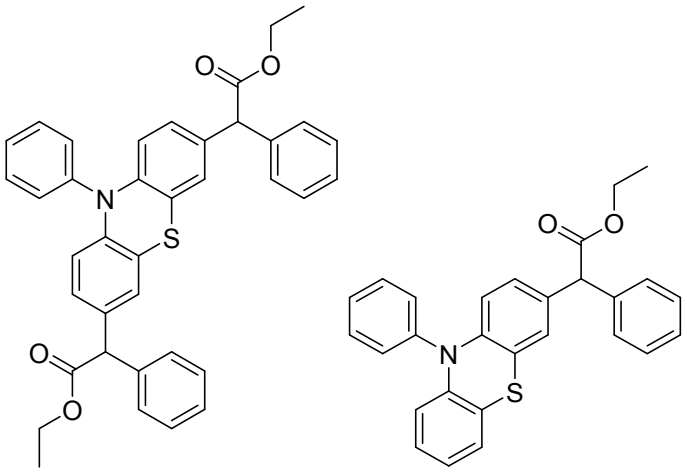
^{1}H NMR (C_6D_6, 400 MHz): δ 7.37 (d, *J* = 7.3 Hz, 4H), 7.13 – 7.00 (m, 9H), 6.97 (d, *J* = 1.9 Hz, 2H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.54 (d, *J* = 10.1 Hz, 2H), 5.78 (d, *J* = 8.3 Hz, 2H), 4.81 (s, 2H), 3.94 – 3.89 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 171.78, 144.07, 139.24, 138.96, 133.47, 132.57, 130.69, 130.54, 128.59, 128.46, 128.03, 127.03, 123.46, 116.02, 113.16, 60.60, 56.19, 13.75.

Characterization of **6b**:

^{1}H NMR (C_6D_6, 400 MHz): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.09 (q, *J* = 7.5 Hz, 4H), 7.02 (t, *J* = 6.8 Hz, 3H), 6.87 (d, *J* = 7.3 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 6.47 (t, *J* = 7.6 Hz, 1H), 6.40 (t, *J* = 7.7 Hz, 1H), 5.89 (d, *J* = 6.7 Hz, 1H), 5.79 (d, *J* = 8.3 Hz, 1H), 4.81 (s, 1H), 3.91 (q, *J* = 6.2, 5.4 Hz, 2H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (C_6D_6, 101 MHz): δ 170.95, 143.35, 143.28, 138.40, 138.22, 133.56, 132.83, 131.71, 129.89, 129.80, 127.74, 127.62, 127.17, 126.18, 122.62, 122.47, 120.59, 115.14, 114.74, 112.50, 112.41, 59.76, 55.36, 12.90.



Diethyl 2,2'-(10-phenyl-10H-phenothiazine-3,7-diyl)bis(2-phenylacetate) (**7a**) and ethyl 2-phenyl-2-(10-phenyl-10H-phenothiazin-3-yl)acetate (**7b**)

Disubstituted product **7a** (white solid, 80 mg, 37%) and monosubstituted product **7b** (white solid, 0.16 mmol, 44%).

Characterization of **7a**:

^{1}H NMR (C_6D_6, 400 MHz): δ 7.34 (d, *J* = 7.2 Hz, 4H), 7.14 (d, *J* = 2.1 Hz, 2H), 7.09 (q, *J* = 7.4 Hz, 6H), 7.03 – 7.01 (m, 3H), 6.92 (d, *J* = 7.0 Hz, 2H), 6.82 (dd, *J* = 8.6, 2.1 Hz, 2H), 6.05 (d, *J* = 8.5 Hz, 2H), 4.81 (s, 2H), 3.92 (q, *J* = 7.1 Hz, 4H), 0.87 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (C_6D_6, 101 MHz): δ 170.88, 142.75, 140.04, 138.36, 132.77, 130.09, 129.58, 127.68, 127.65, 127.00, 126.75, 126.33, 126.19, 119.50, 115.11, 59.80, 55.23, 12.91.

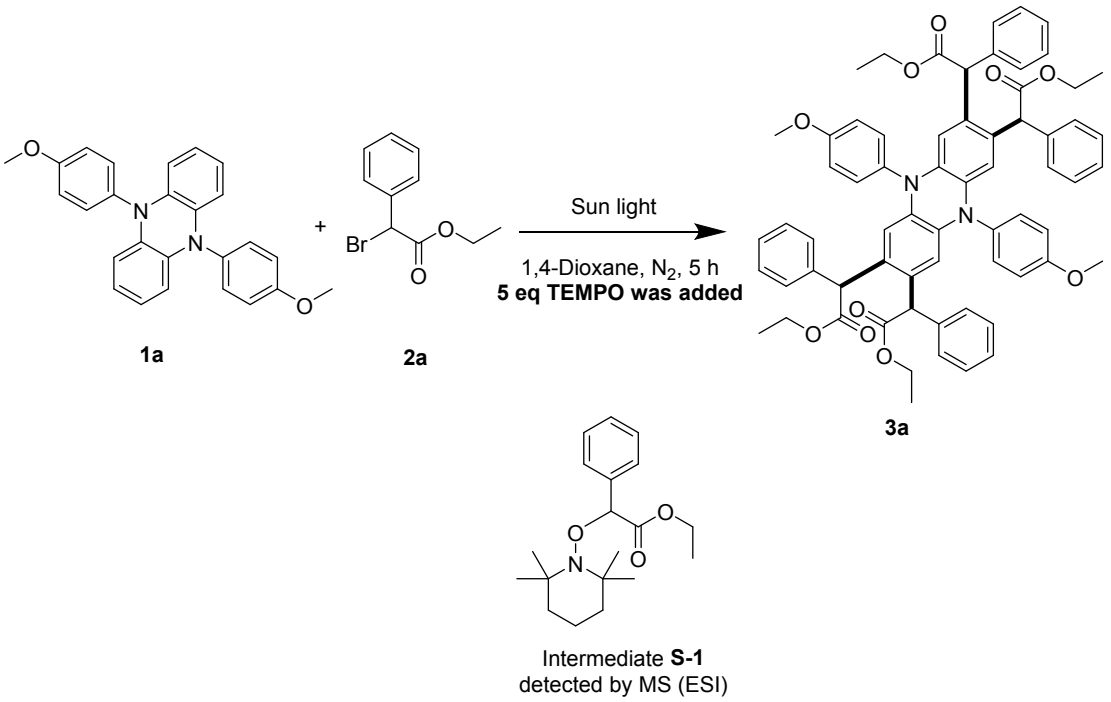
Characterization of **7b**:

^{1}H NMR (C_6D_6, 400 MHz): δ 7.34 (d, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 4H), 7.04 – 6.95 (m, 4H), 6.90 (dd, *J* = 6.7, 2.4 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.60 – 6.56 (m, 2H), 6.15 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.07 (d, *J* = 8.5 Hz, 1H), 4.82 (s, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (C_6D_6, 101 MHz): δ 170.89, 143.58, 142.77, 140.15, 138.34, 132.76, 130.06, 129.61, 127.68, 127.66, 126.97, 126.33, 126.19, 126.12, 125.97, 125.87, 121.65, 119.75, 119.33, 115.26, 115.11, 59.81, 55.22, 12.91.

HRMS (ESI-TOF): calc'd for M+ $C_{28}H_{23}NO_2S$, 437.1449; found 437.1472.

2.7 Mechanistic Studies



Radical-trapping experiment: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 5,10-di(4-methoxyphenyl)-5,10-dihydrophenazine (100.00 mg, 0.25 mmol, 1.00 eq), ethyl α-bromophenylacetate (437.54uL/607.75 mg, 2.50 mmol, 10.00 eq), Tempo (195.30 mg, 1.25 mmol, 5.00 eq) and 1,4-Dioxane 10 mL. The reaction mixture was degassed with three freeze-pump-thaw cycles and the vial was then backfilled with argon. After that, the reaction was vigorously stirred in front of simulative sunshine bulb at room temperature (Fig. S1) for 5 h. No desired product **3a** was detected by TLC or MS-ESI. And, the corresponding radical-trapping intermediate **S-1** was detected by MS-ESI. (Calcd for $C_{19}H_{30}NO_3$ $[M+H]^+$: 320.2220; found: 320.2224. Fig. S3).

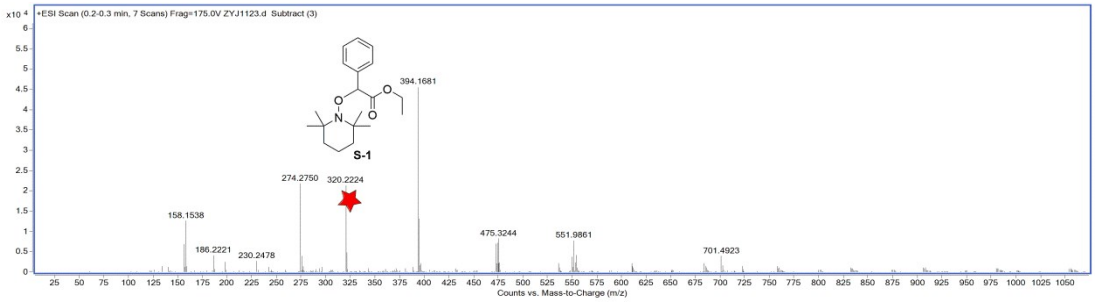
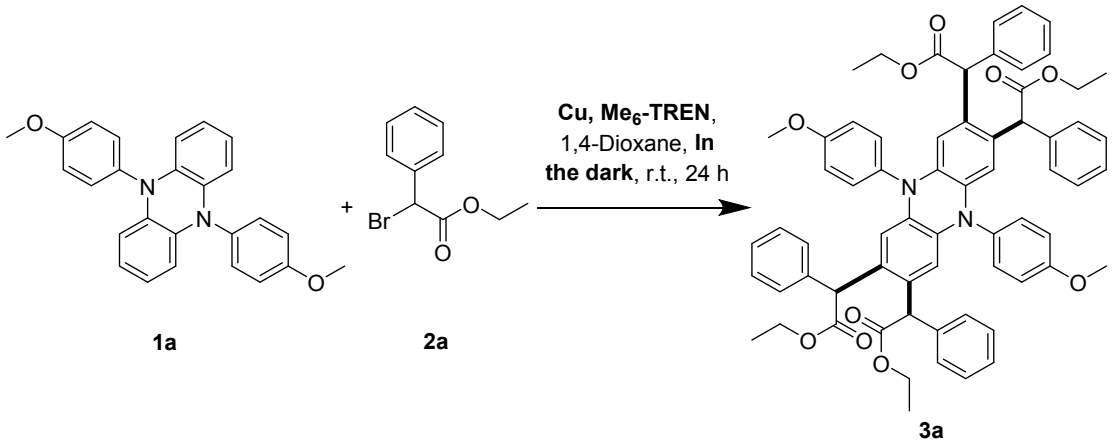


Fig. S3 HR-MS (ESI) analysis of **S-1**.



Control experiments: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 5,10-di(4-methoxyphenyl)-5,10-dihydrophenazine (100.00 mg, 0.25 mmol, 1.00 eq), ethyl α-bromophenylacetate (437.54uL/607.75 mg, 2.50 mmol, 10.00 eq), Cu (1.6 mg, 0.025mmol, 0.1 eq), Me_6-TREN (5.76 mg, 0.025mmol, 0.1 eq) and 1,4-Dioxane 10 mL. The reaction mixture was degassed with three freeze-pump-thaw cycles and the vial was then backfilled with argon. After that, the reaction was vigorously stirred in the dark at room temperature for 24 h. No desired product **3a** was detected by TLC or MS-ESI.

3. Applications of core-modified OPCs in O-ATRP

3.1 General Polymerization Procedure[3]

A 20 mL Schlenk tube equipped with a magnetic stir bar was charged with organic photoredox catalyst (0.1 mol % relative to monomer) and transferred into a nitrogen-atmosphere glovebox. DMAc (1.0 mL), methyl methacrylate (1.0 mL, 9.35 mmol), and ethyl α-bromophenylacetate (16.4 μL, 9.35μmol) were then added sequentially via pipette. Then the vial was sealed and stirred in front of sunlight simulation lamp at room temperature for a while (Fig. S1). For conversion data, a 0.1 mL aliquot of the reaction media was removed via syringe and injected into a vial containing 0.7 mL $CDCl_3$. This aliquot was then analyzed by ^1H NMR for conversion. Then, the reaction mixture was poured into 100 mL of methanol. The mixture was allowed to stir for 1 h, and the polymer was isolated by filtration and dried under vacuum to a constant weight, and then re-dissolved in THF for GPC analysis.

3.2 Noncore-modified OPCs in O-ATRP

MMA (1.00 mL, 9.35 mmol, 1000 eq.), EBP (16.4 μL, 93.5 μmol, 10 eq.), and noncore-modified OPCs (4.4 mg, 9.35 μmol, 1 eq.) were dissolved in 1.00 mL DMA and reacted according to the above general polymerization procedure for 30 min. Then the reaction was poured into 50 mL methanol. The corresponded core-modified OPCs were detected by HR-MS with noncore-modified OPCs entirely consumed. The results were shown in Table S2 and Fig. S4.

Table S2. HR-MS (ESI) analysis of core modification of OPCs in O-ATRP

Entry	Noncore-modified OPCs	Core-modified OPCs detected in reaction at 30 min	HR-MS (ESI) analysis
1	**1a**	**3a**	calc'd for M+ $C_{66}H_{62}N_2O_{10}$, 1042.4404; found 1042.4382
2	**1b**	**3b**	calc'd for M+ $C_{64}H_{58}N_2O_8$, 982.4193; found 982.4186
3	**1c**	**3c**	calc'd for M+ $C_{66}H_{62}N_2O_8$, 1010.4506; found 1010.4458
4	**3n**	**S-2**	calc'd for M+ $C_{56}H_{58}N_2O_8$, 886.4193; found 886.4188

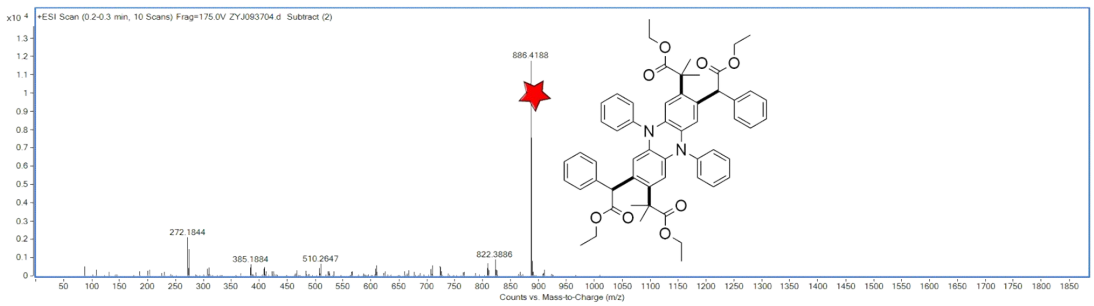


Fig. S4 HR-MS (ESI) analysis of **S-2**.

3.3 Analysis of PMMA by ^{1}H NMR

MMA (0.5 mL, 4.67 mmol, 500 eq.), EBP (16.4 μL, 93.5 μmol, 10 eq.), and **3a** (9.7 mg, 9.35 μmol, 1 eq.) were dissolved in 1.50 mL DMAc and reacted according to the above general polymerization procedure for 6 hours. At this time, the reaction was removed from the glovebox, poured into 100 mL methanol and stirred for 1 hour. The polymer was isolated by filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated twice. Then the product was dried under reduced pressure to reveal a white powder (M_w = 7.92 kDa, $Đ$ =1.06) (^{1}H NMR spectrum was given in Fig. S5).

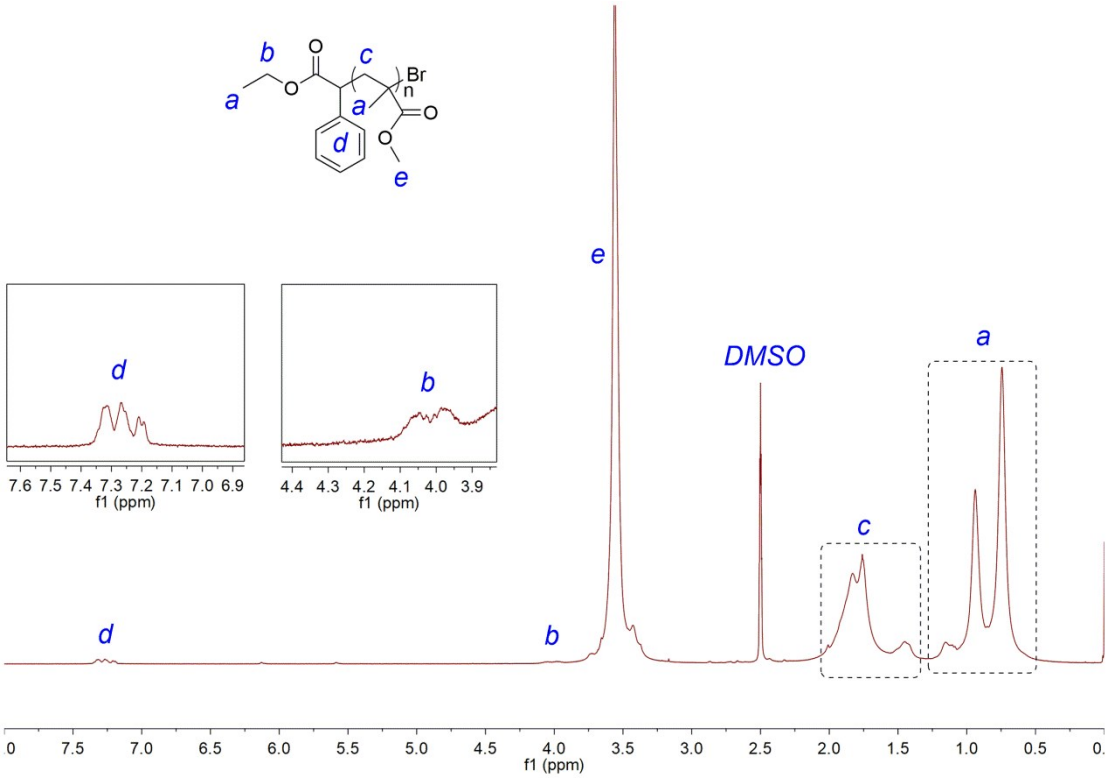


Fig. S5 ^{1}H NMR spectrum of PMMA (DMSO-d_6).

3.4 Analysis of PMMA by MALDI-TOF

MMA (1.00 mL, 9.35 mmol, 400 eq.), EBP (41 μL, 233.8 μmol, 10 eq.), and **3a** (24.3 mg, 23.4 μmol, 1 eq.) were dissolved in 1.00 mL DMAc and reacted according to the above general polymerization procedure for 8 hours. At this time, the reaction was removed from the glovebox, poured into 100 mL methanol and stirred for 1 hour. The mixture was allowed to stir for 1 h, and the polymer was isolated by filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated a total of three times to afford a white powder (M_w = 3.30 kDa, $Đ$ = 1.19) (MALDI-TOF mass spectrum of a PMMA sample was given in Fig. S6).

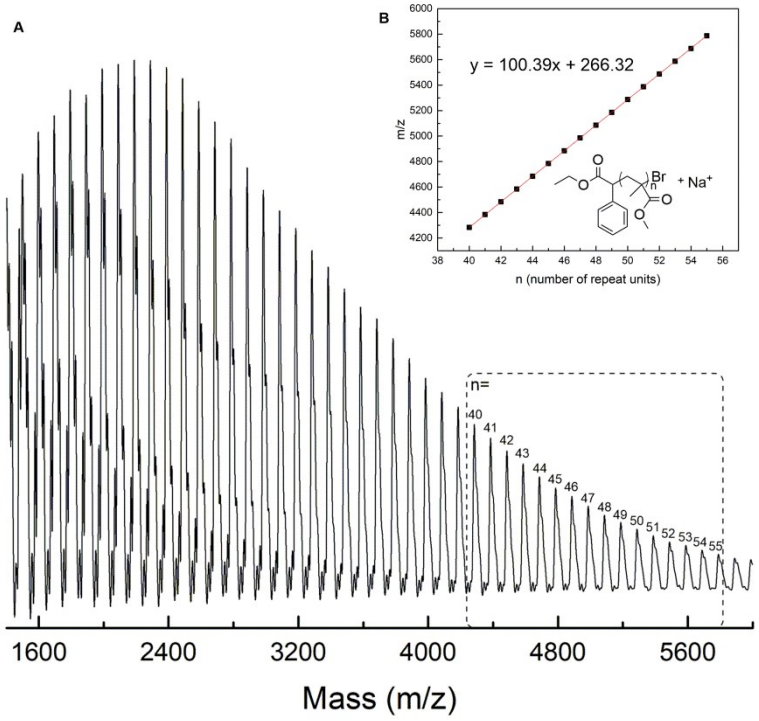
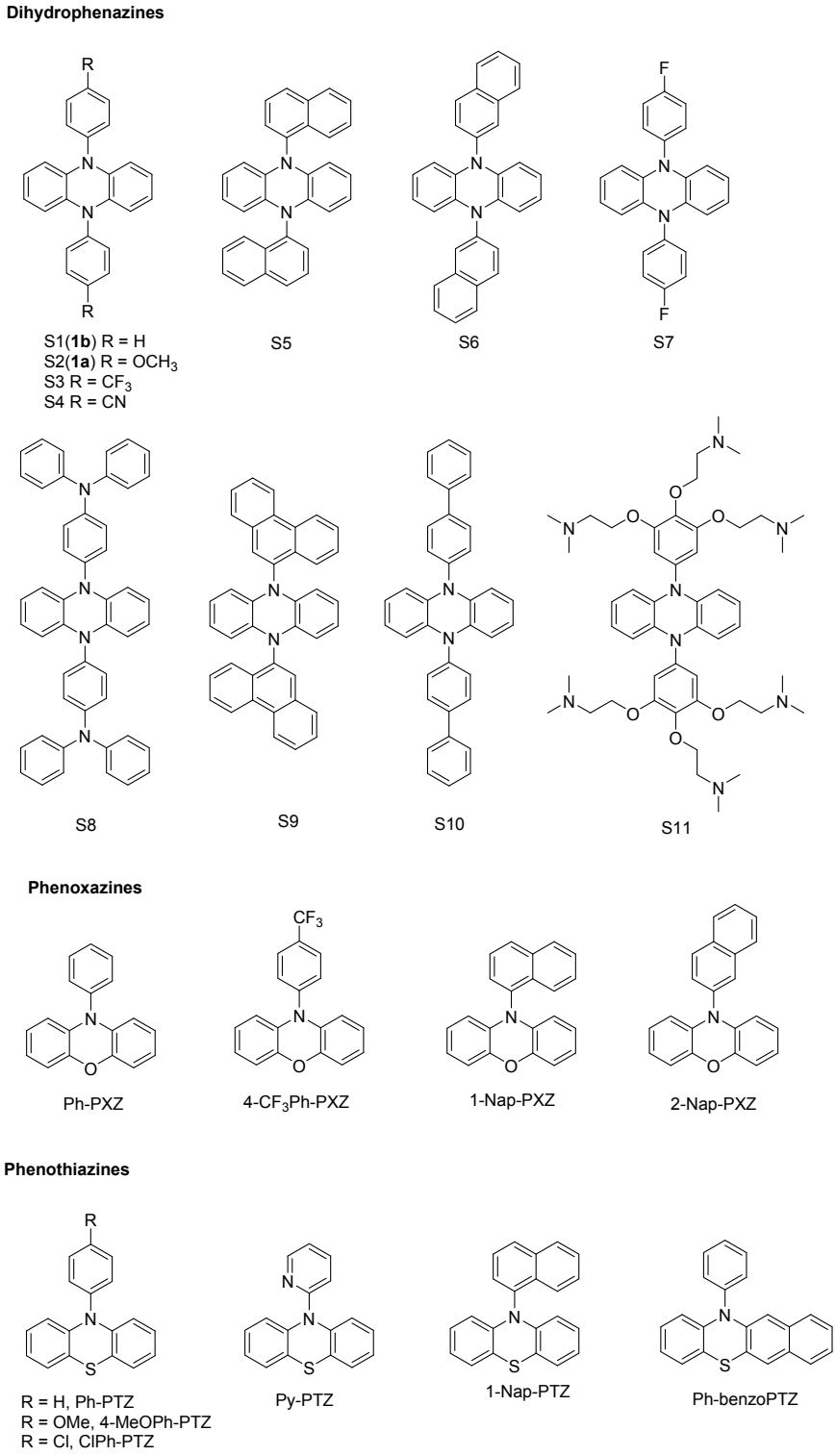


Fig. S6 MALDI-TOF mass spectrum of a PMMA sample. B. Plot of m/z vs number of MMA repeat units revealing a slope equal to the mass of MMA and a yintercept equal to the mass of the EBP chain-end group plus Na.

Supplementary Tables

Table S3. Structure and detailed discussion of previously reported noncore-modified OPCs in O-ATRP.



Enty	Catalyst	Initiator system	Reference
1	S1(**1b**), S2(**1a**), S3, S4, S5, S6	EBP, MBiB	G. M. Miyake et. al. Science **2016**, 1082
2	S5	DBMM	G. M. Miyake et. al. J. Am. Chem. Soc. **2017**, 348
3	S3, S6	DBMM	G. M. Miyake et. al. Macromolecules **2017**, 2668
4	S1, S2, S3, S5, S6, S7, S8, S9, S10	DBMM, M2BP, EBP	G. M. Miyake et. al. JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY **2017**, 3017
5	S3	Endo-BIB	J. R. Alaniz et. al. J. Am. Chem. Soc. **2018**, 5009
6	S1(**1b**), S3	M2BP	A. J. Orr-Ewing et. al. J. Am. Chem. Soc. **2018**, 1285
7	S3, S6	DBMM	G. M. Miyake et. al. J. Am. Chem. Soc. **2019**, 13268
8	S11	EBP	M. F. Cunningham et. al. Macromolecules **2019**, 6725
9	S5	$BaTiO_3$ nanoparticles	X. C. Pang et. al. Scientific Reports **2019**, 1869
10	Ph-PXZ, 4-CF_3Ph-PXZ, 1-Nap-PXZ, 2-Nap-PXZ	DBMM	G. M. Miyake et. al. J. Am. Chem. Soc. **2016**, 11399
11	4-CF3Ph-PXZ	DBMM, PEG-Br	K. Son et. al. European Polymer Journal **2019**, 347
12	Ph-PTZ	EBP	C. J. Hawker et. al. J. Am. Chem. Soc. **2014**, 16096
13	Ph-PTZ, 4-MeOPh-PTZ, Cl-Ph-PTZ, Py-PTZ, 1-Nap-PTZ, Ph-benzoPTZ	EBP, EBiB, EClPA	K. Matyjaszewski et. al. J. Am. Chem. Soc. **2016**, 2411
14	Ph-PTZ	EBP	C. H. Tang et. al. Macromolecules **2016**, 7709
15	Ph-PTZ	P(VDF-*co*-CTFE)	K. Guo et. al. Macromol. Rapid Commun. **2017**, 1700399
16	Ph-PTZ	HAp-Br	Y. Wei et. al. Applied Surface Science, **2017**, 499
17	Ph-PTZ	ATRP Initiator-functionalized wafer	C. J. Hawker et. al. Angew. Chem. Int. Ed. **2018**, 1
18	Ph-PTZ	MIP Macroinitiator	T. Junkers et. al. Macromolecules **2019**, 2304

Table S4. Experimentally measured Photophysical and Electrochemical Properties of OPCs.

OPC	λ_{max} [a] (nm)	ε_{max} [a] (M^{-1} cm^{-1})	$\lambda_{em,max}$ [b] (nm)	$E_{S1,exp}$ [b] (eV)	$E_{1/2}$ ($^2PC^{\bullet+}/^1PC$) [c] (V vs SCE)	E^{0}* ($^2PC^{\bullet+}/^1PC$*)[d] (V vs SCE)
1b	369	6100	466	2.66	0.35	-2.31
1c	371	5500	466	2.66	0.33	-2.33
1d	367	4500	626	1.98	0.44	-1.54
3b	380	10200	487	2.55	0.38	-2.17
3c	381	9800	489	2.54	0.36	-2.18
3d	377	9300	588	2.11	0.48	-1.63
3e	381	9400	489	2.54	0.36	-2.18
3g	376	6800	476	2.61	0.37	-2.24
3k	379	7200	478	2.59	0.35	-2.24
3l	378	6800	478	2.59	0.37	-2.22
3n	372	7700	476	2.61	0.35	-2.26
3o	382	6900	479	2.59	0.25	-2.34
3p	383	7800	494	2.51	0.25	-2.26
3r	380	7300	478	2.59	0.28	-2.31
3s	381	7800	478	2.59	0.28	-2.31
6b	329	10500	397	3.12	0.83	-2.29
7b	323	4600	450	2.76	0.83	-1.93

[a] λ_{max}, maximum absorption wavelength; ε_{max}, molar absorptivity at λ_{max}; [b] $\lambda_{em,max}$, maximum emission wavelength; $E_{S1,exp}$, lowest singlet excited state energy determined from $\lambda_{em,max}$. [c] Measurements were performed in a three-compartment electrochemical cell with Ag/AgCl (submerged in 3 M KCl solution) as the reference electrode and NBu_4PF_6 in DMAc (0.10 M) as the electrolyte solution. [d] Singlet excited state reduction potentials were calculated as E^{0}* ($^2PC^{\bullet+}/^1PC$*) = $E_{1/2}$ ($^2PC^{\bullet+}/^1PC$) - $E_{S1,exp}$.

Table S5. Computed photophysical properties of OPCs **1a-1c**, **3a**, **3h**, **3i**, **3j**.

OPC	Triplet energy (eV)	E^0 ($^2PC^{\bullet+}$ /^1PC) (V vs SCE)	E^0 ($^2PC^{\bullet+}$ / $^3PC^*$) (V vs SCE)
1a	2.39	0.02	-2.37
1b	2.41	0.07	-2.34
1c	2.40	0.04	-2.36
3a	2.41	0.12	-2.29
3h	2.52	0.05	-2.47
3i	2.44	-0.04	-2.48
3j	2.67	0.06	-2.62

Table S6. Results for the O-ATRP of MMA catalyzed by core-modified OPCs using sunlight [a]

OPC	Time (h)	Conv [b] (%)	M_w [c] (kDa)	M_n [c] (kDa)	$Đ$ [d] (M_w/M_n)	$M_{n,theo}$ [e] (kDa)	I^* [f] (%)
3e	6	77.9	17.7	15.7	1.13	17.2	110
3j	6	96.7	15.8	13.7	1.15	12.8	93
3k	6	84.3	13.3	11.4	1.16	12.2	107
3n	6	97.2	15.3	13.5	1.14	15.9	118
3o	6	94.6	17.0	14.6	1.16	10.4	71
3p	6	81.6	15.0	13.1	1.15	10.9	83
3r	6	90.4	16.2	13.7	1.18	13.1	96
3s	6	86.2	16.4	14.7	1.11	14.8	101
5a [g]	10	78.5	17.0	14.4	1.18	13.1	91
7a [g]	10	71.4	18.7	15.6	1.20	12.7	81

[a] All polymerizations were conducted using the initiator ethyl α-bromophenylacetate (EBP) in a ratio of 1000:10:1 of [MMA]:[EBP]:[PC] with DMAc as a solvent. [b] Calculated by ^{1}H NMR results. [c] Detected by SEC. [d] All calculated by M_w/M_n. [e] $M_{n,theo}$ calculated by [MMA]/[EBP] × MW of monomer × yield + MW of initiator. [f] $I^* = M_{n,theo}/M_{n,exp}$. [g] The polymerizations were conducted under a 40 W 365 nm LED.

Table S7. The OPCs and the corresponding initiator efficiencies in O-ATRP.

Noncore-modified PCs and *I**(%)	The corresponding core-modified compounds and *I**(%)						
1a, 84	**3a**, 86	**3f**, 100	**3h**, 88	**3i**, 86	**3j**, 93		
1b, 87	**3b**, 113	**3n**, 118	**3r**, 96	**3s**, 101			
1c, 65	**3c**, 138	**3e**, 110	**3g**, 93	**3k**, 107	**3l**, 86	**3o**, 71	**3p**, 83
1d, 81	**3d**, 84						
4a, 96	**6a**, 98						
5a, 91	**7a**, 81						

Supplementary Figures

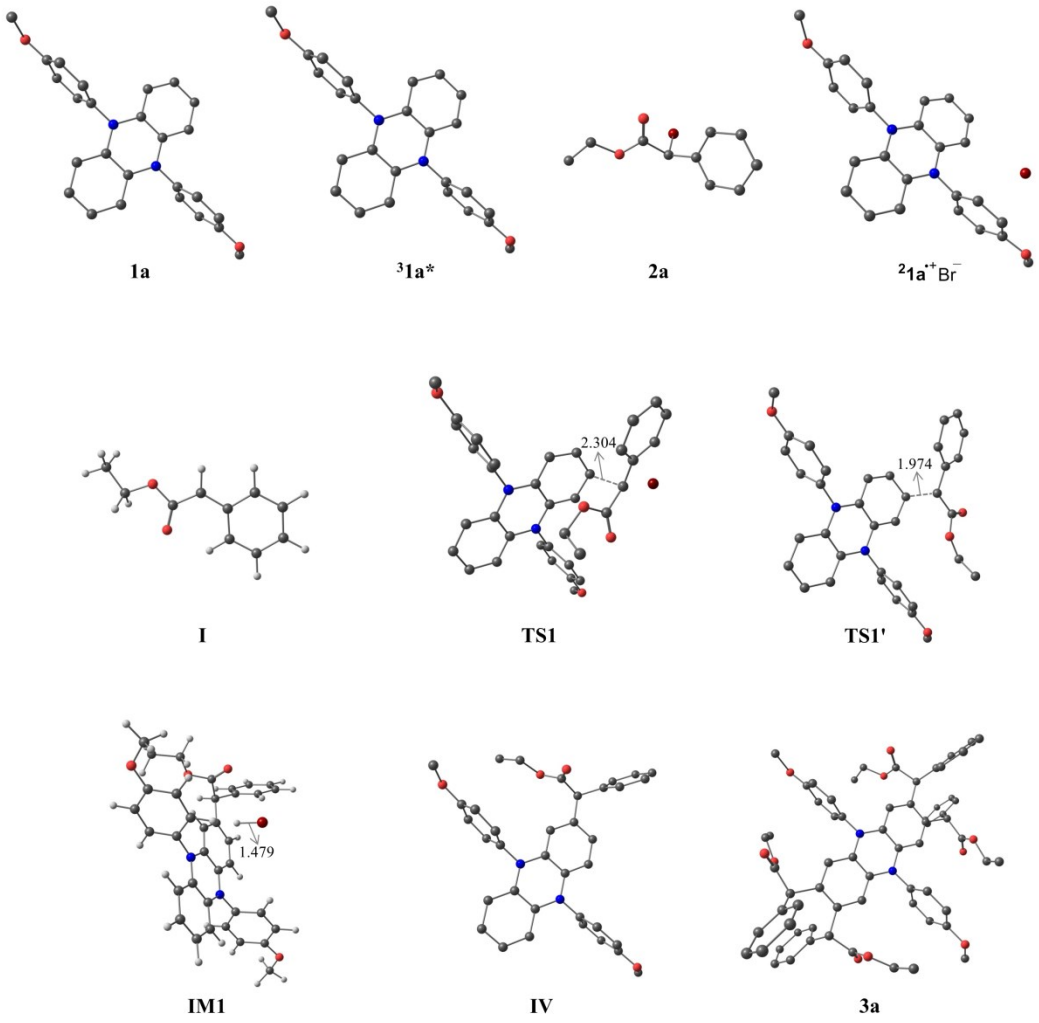


Fig. S7 Optimized geometries of the structure in Fig. 4. Key bond distances are given in Å. Some hydrogen atoms are omitted for clarity (color code, C: black, O: red, H: white, N: blue, Br: dark red).

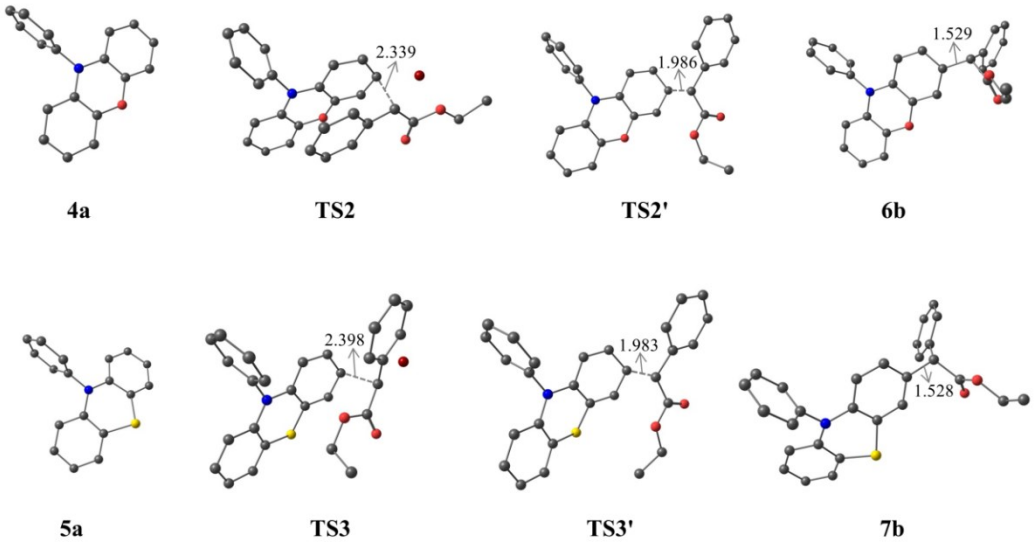


Fig. S8 Optimized geometries of the structure in Fig. 5. Key bond distances are given in Å. Some hydrogen atoms are omitted for clarity (color code, C: black, O: red, H: white, N: blue, S: yellow, Br: dark red).

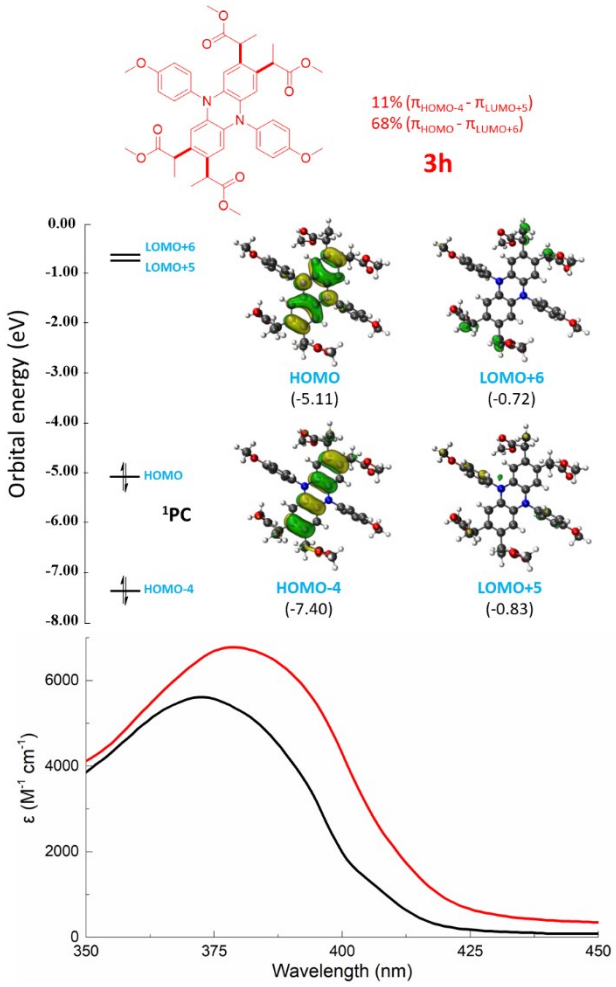


Fig. S9 TD-DFT calculations of orbitals and UV-Vis spectra of **3h**. (Top) TD-DFT calculations and computationally predicted percentage contribution of orbitals involved in photoexcitation of **3h** at its corresponding $\lambda_{max, abs}$. (Bottom) UV-Vis spectra of **3h** acquired in DMAc.

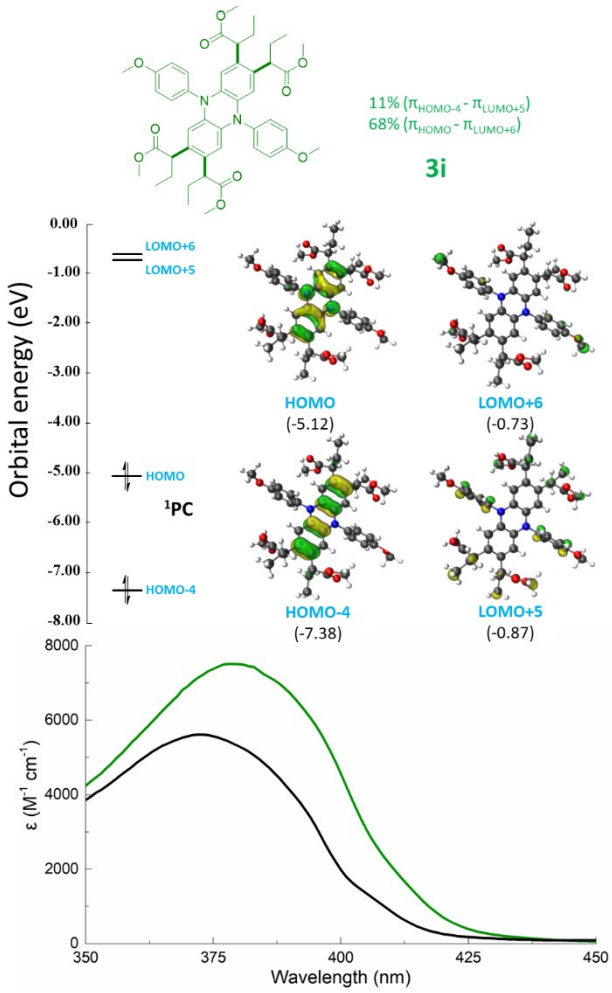


Fig. S10 TD-DFT calculations of orbitals and UV-Vis spectra of **3i**. (Top) TD-DFT calculations and computationally predicted percentage contribution of orbitals involved in photoexcitation of **3i** at its corresponding $\lambda_{max,\ abs}$. (Bottom) UV-Vis spectra of **3i** acquired in DMAc.

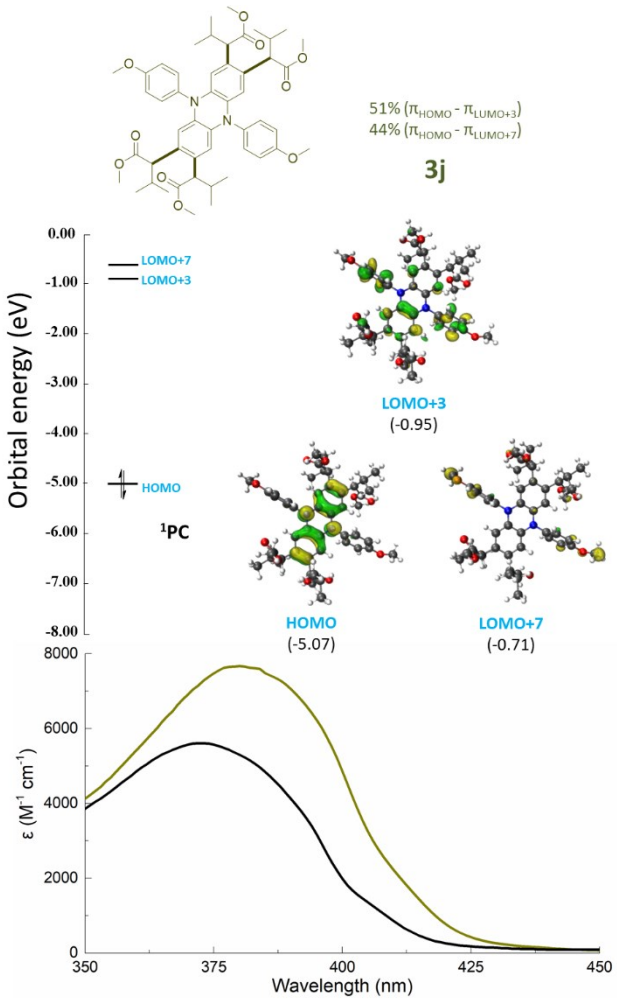


Fig. S11 TD-DFT calculations of orbitals and UV-Vis spectra of **3j**. (Top) TD-DFT calculations and computationally predicted percentage contribution of orbitals involved in photoexcitation of **3j** at its corresponding $\lambda_{max, abs}$. (Bottom) UV-Vis spectra of **3j** acquired in DMAc.

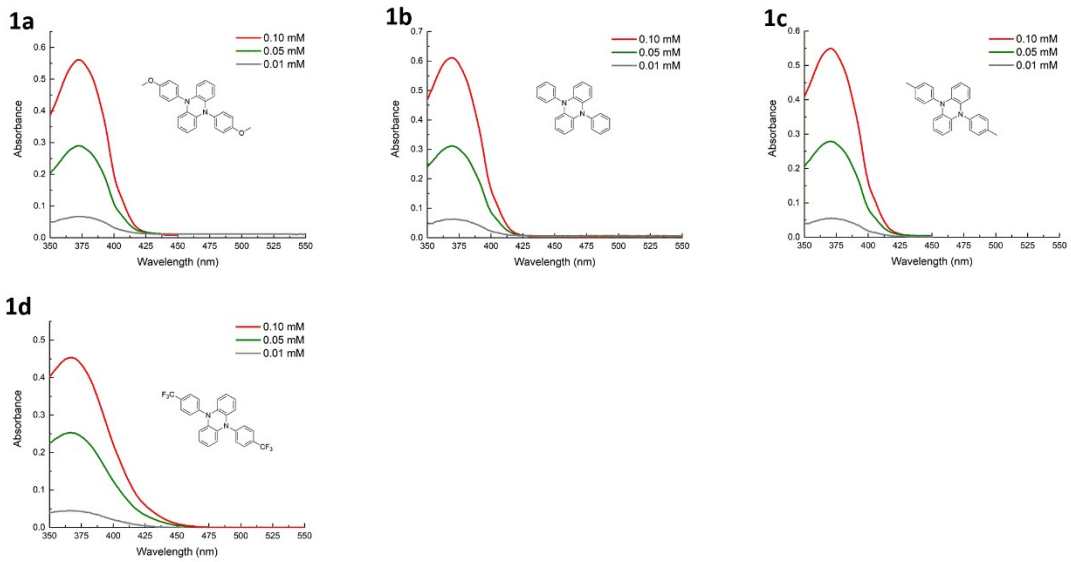


Fig. S12 UV-Vis spectra of OPCs **1a**, **1b**, **1c, 1d** at various concentrations in DMAc.

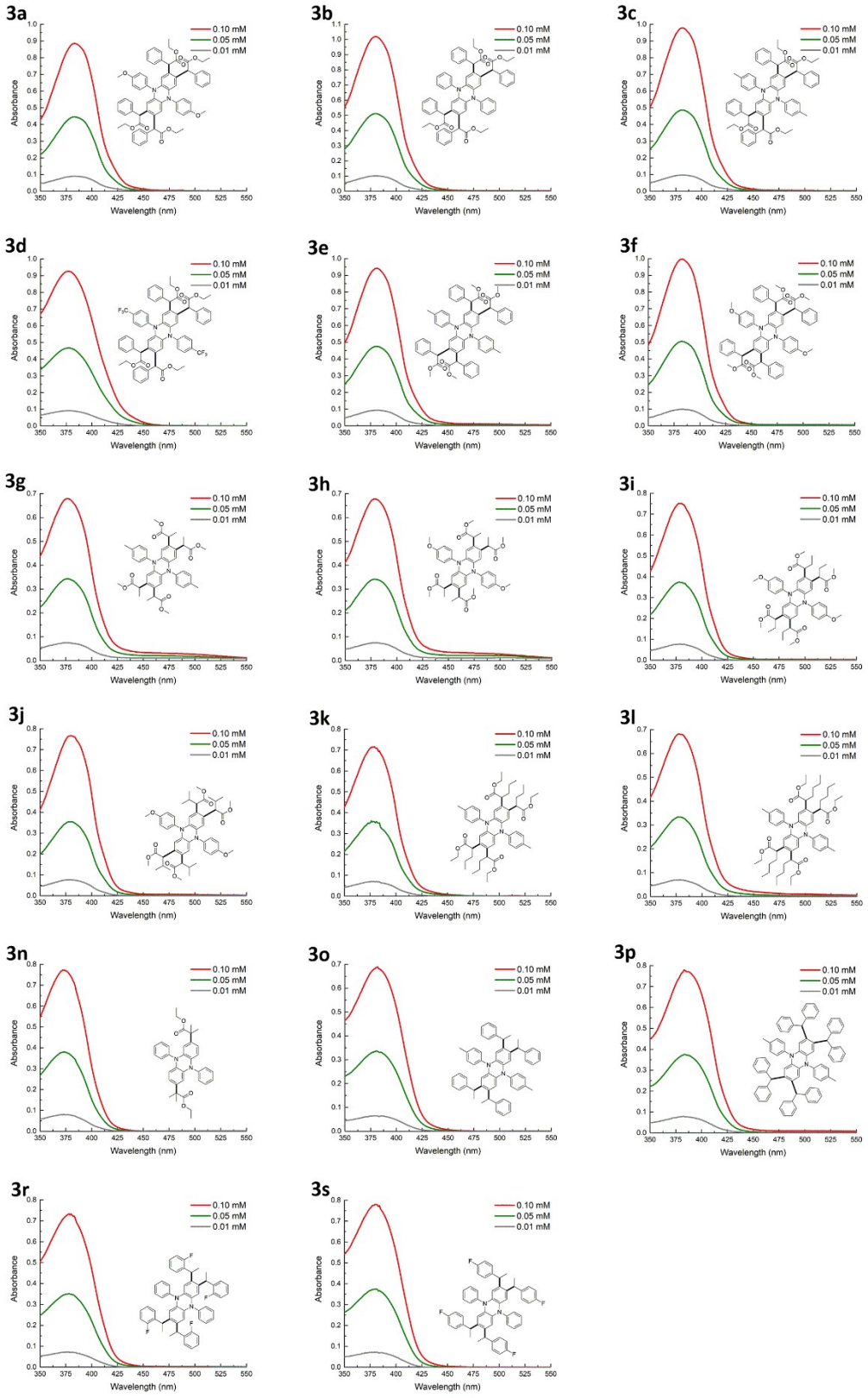


Fig. S13 UV-Vis spectra of OPCs **3a** – **3s** at various concentrations in DMAc.

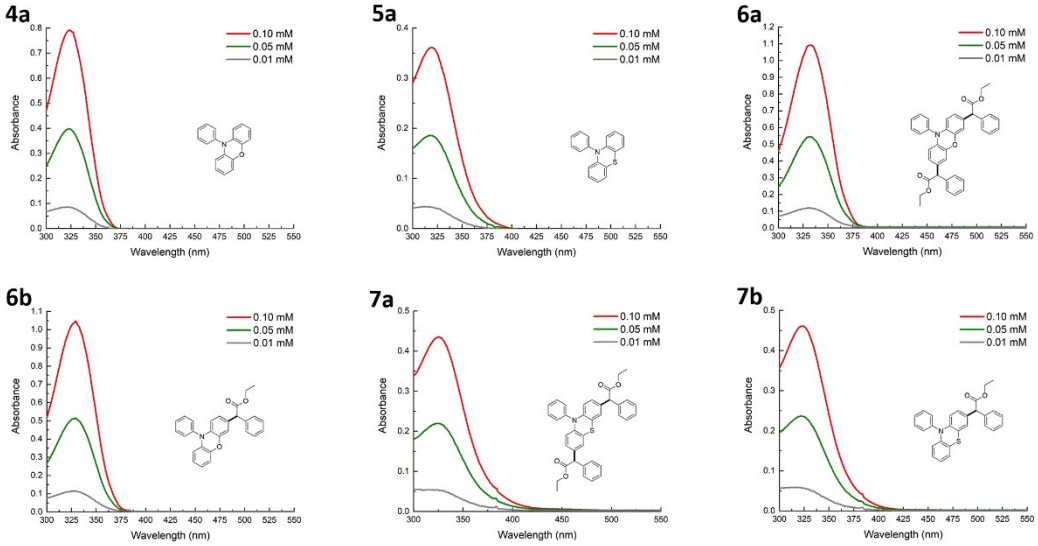


Fig. S14 UV-Vis spectra of OPCs **4a**, **5a**, **6a**, **6b**, **7a**, **7b** at various concentrations in DMAc.

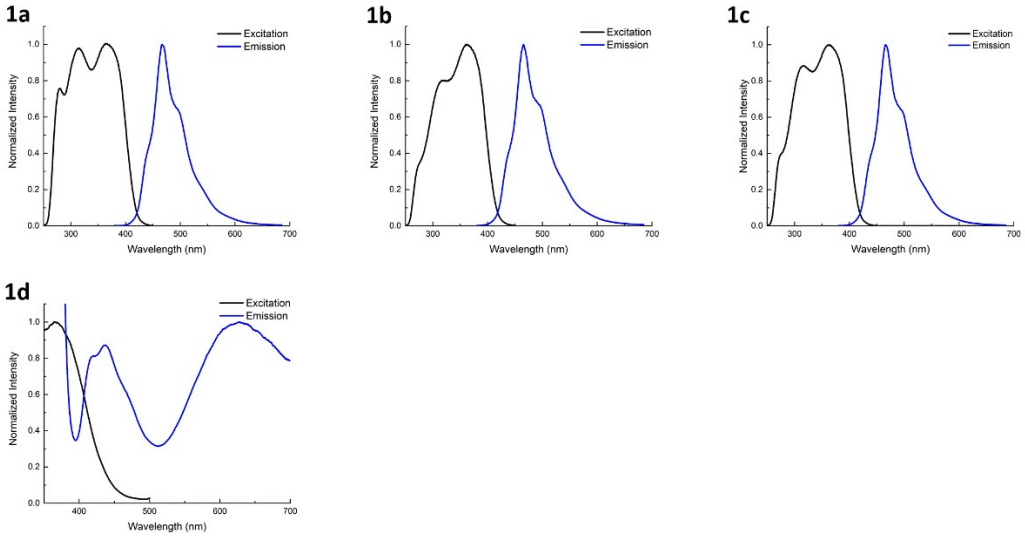


Fig. S15 Fluorescence spectra of OPCs **1a**, **1b**, **1c**, **1d**. Black line is excitation spectra and blue line is emission spectrum.

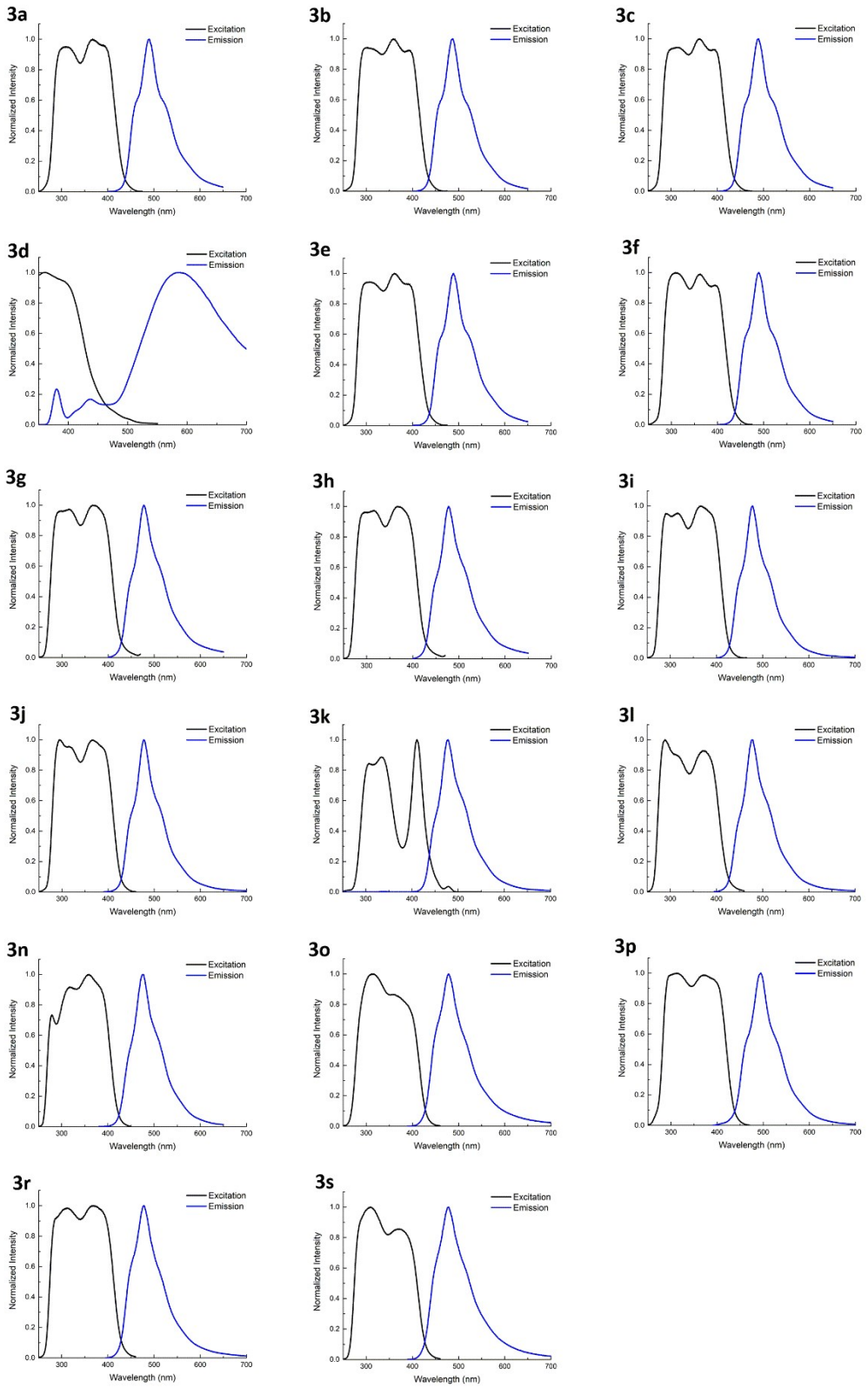


Fig. S16 Fluorescence spectra of OPCs **3a** – **3s**. Black line is excitation spectra and blue line is emission spectrum.

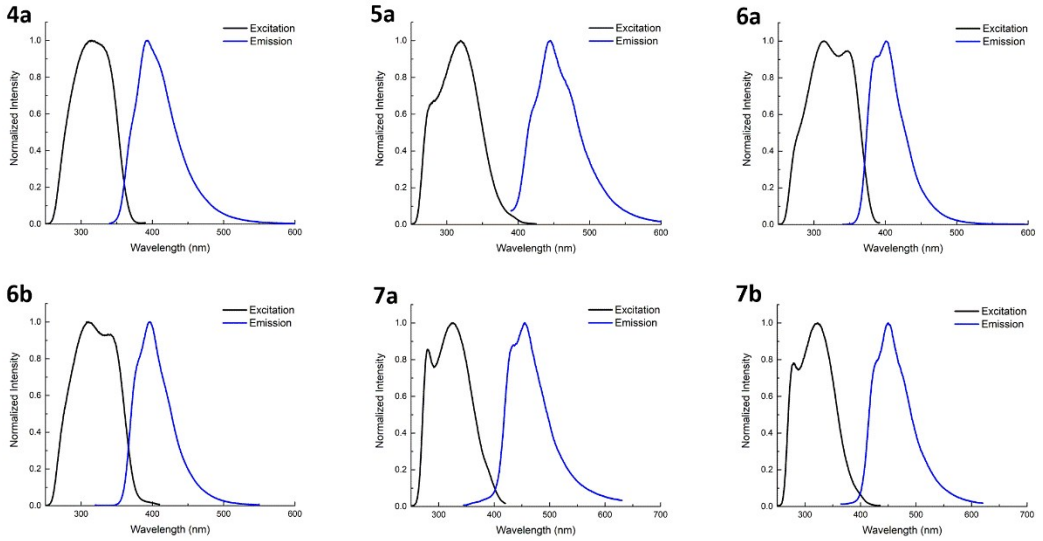


Fig. S17 Fluorescence spectra of OPCs **4a**, **5a**, **6a**, **6b**, **7a**, **7b**. Black line is excitation spectra and blue line is emission spectrum.

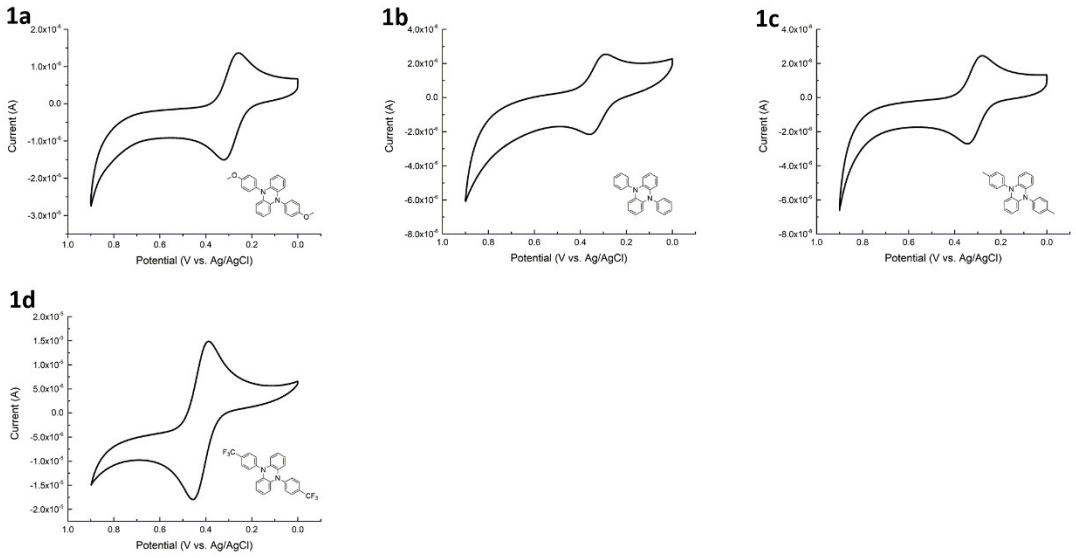


Fig. S18 Cyclic voltammogram of OPCs **1a**, **1b**, **1c**, **1d**.

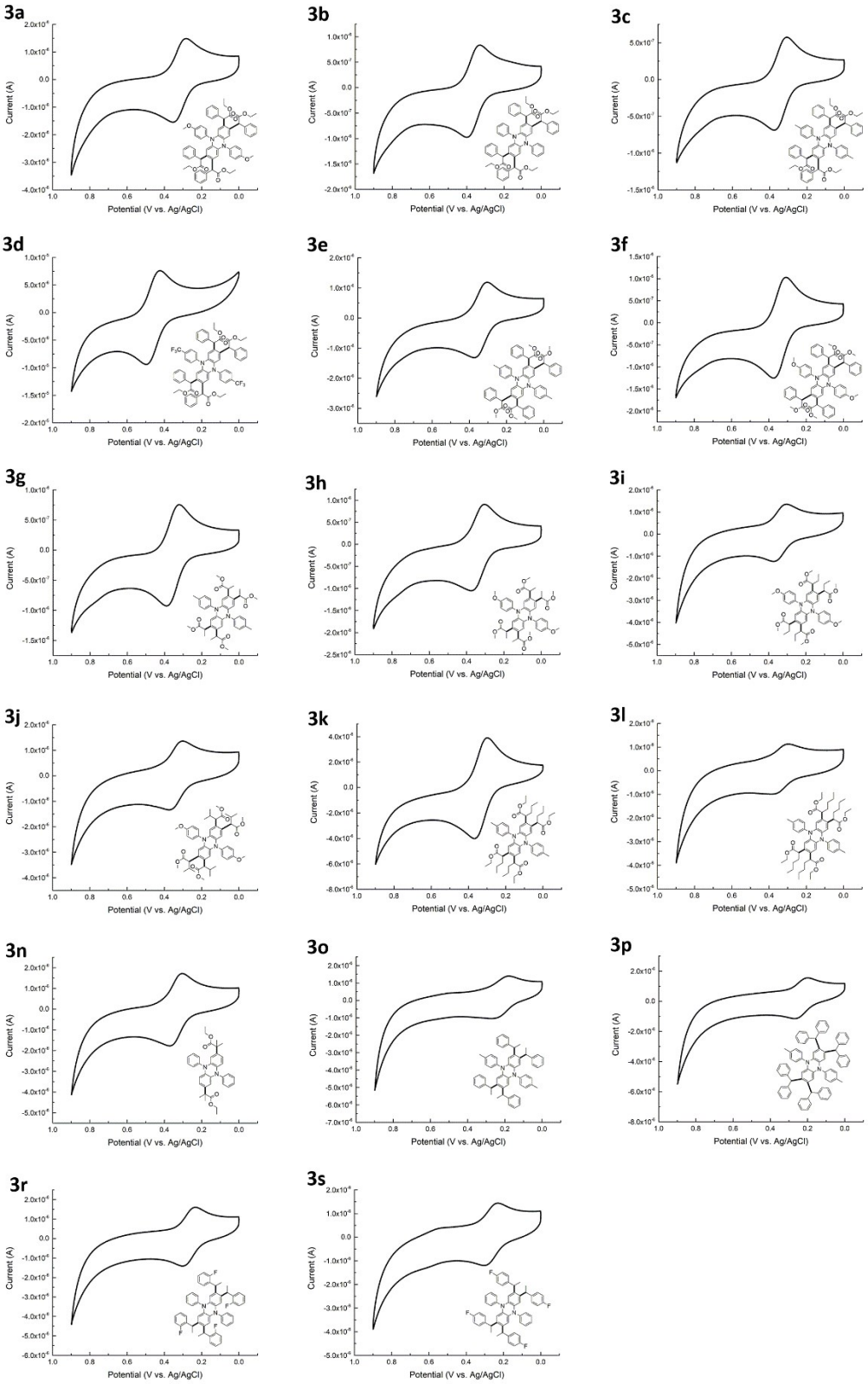


Fig. S19 Cyclic voltammogram of OPCs **3a** – **3s**.

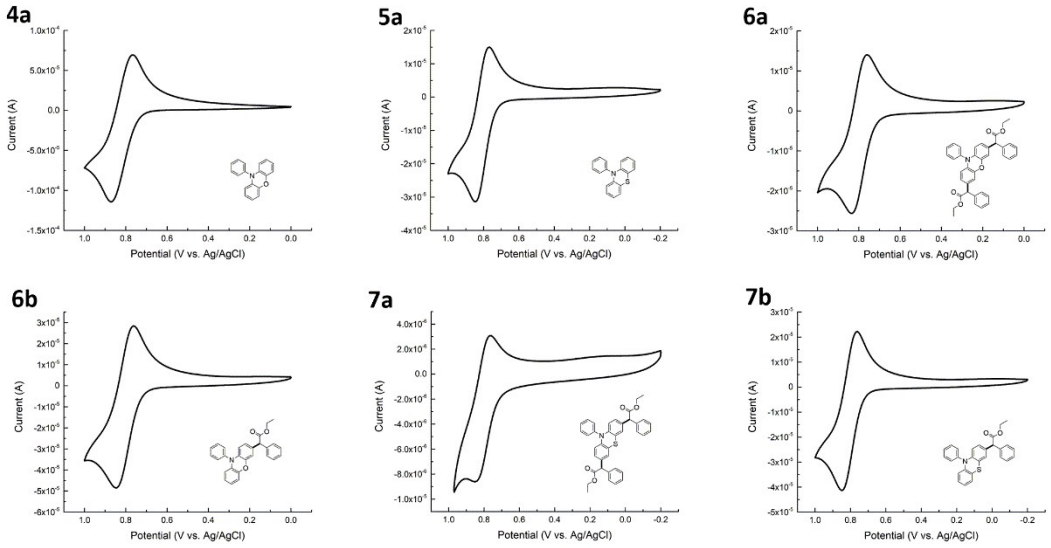


Fig. S20 Cyclic voltammogram of OPCs **4a**, **5a**, **6a**, **6b**, **7a**, **7b**.

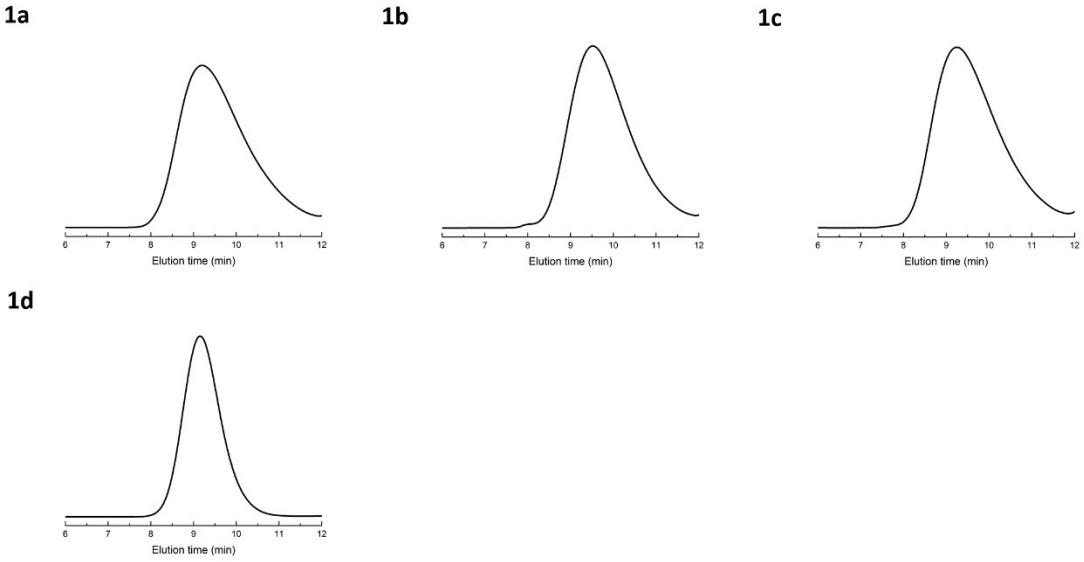


Fig. S21 GPC traces of polymerizations mediated by OPCs **1a**, **1b**, **1c**, **1d**.

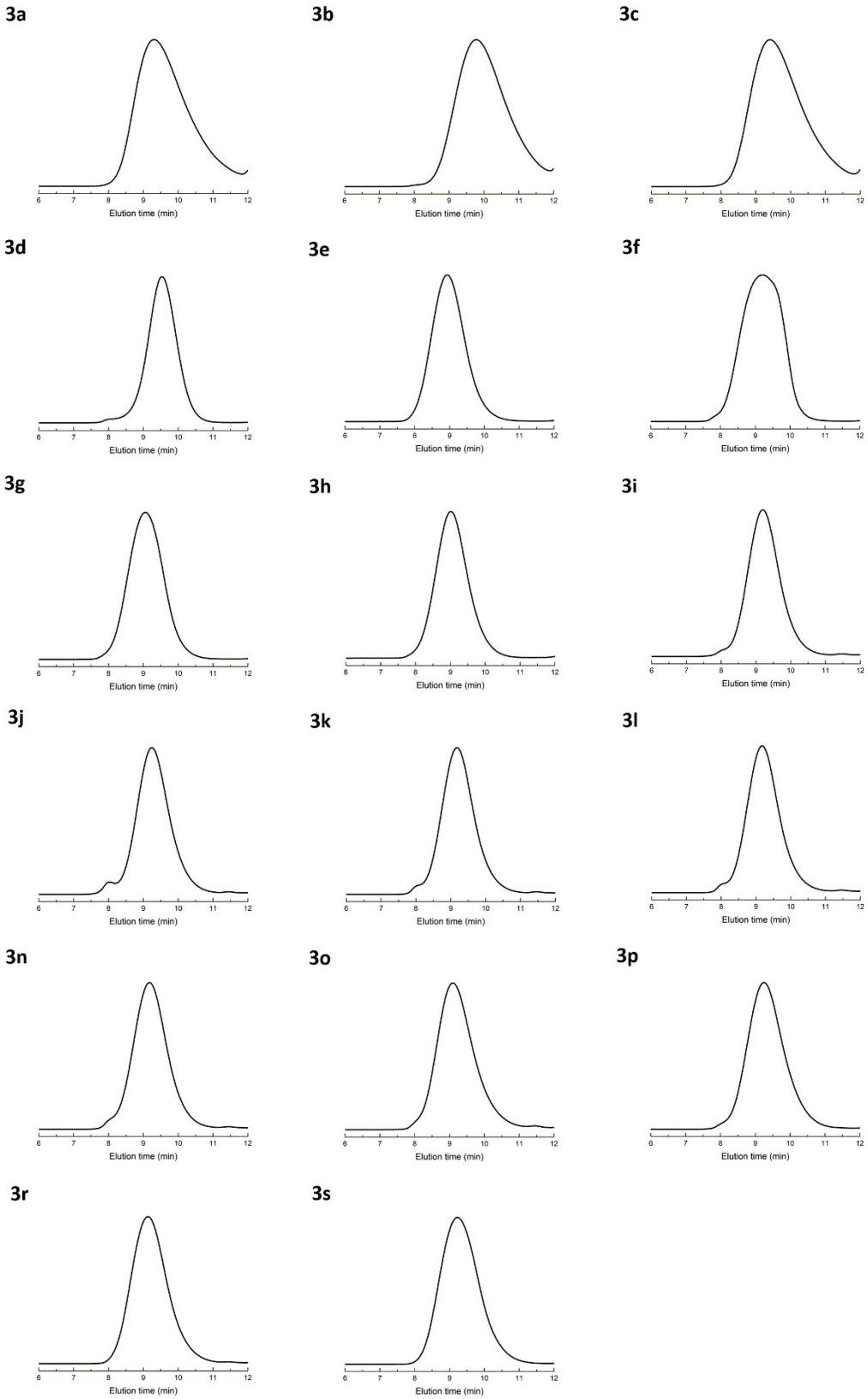


Fig. S22 GPC traces of polymerizations mediated by OPCs **3a** – **3s**.

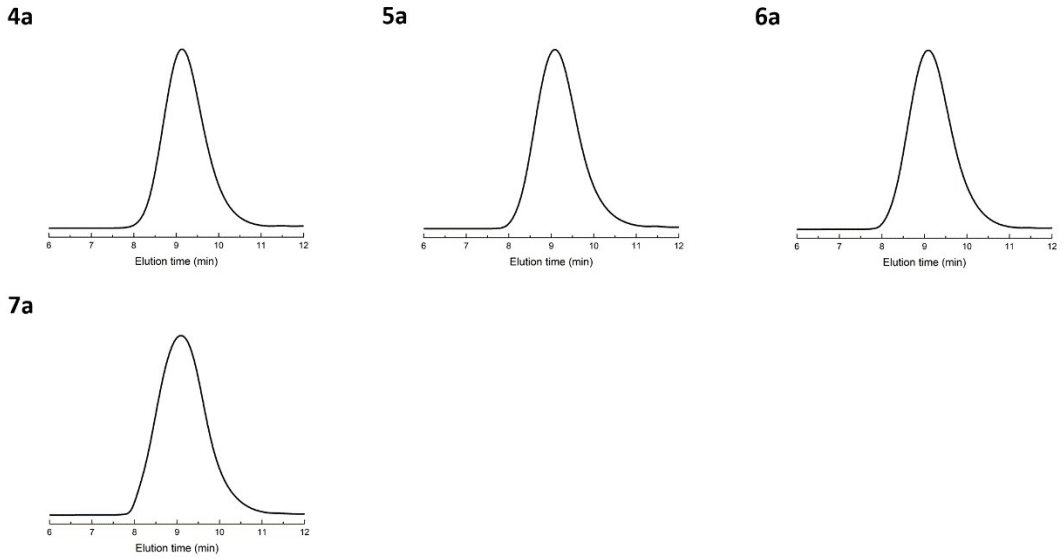
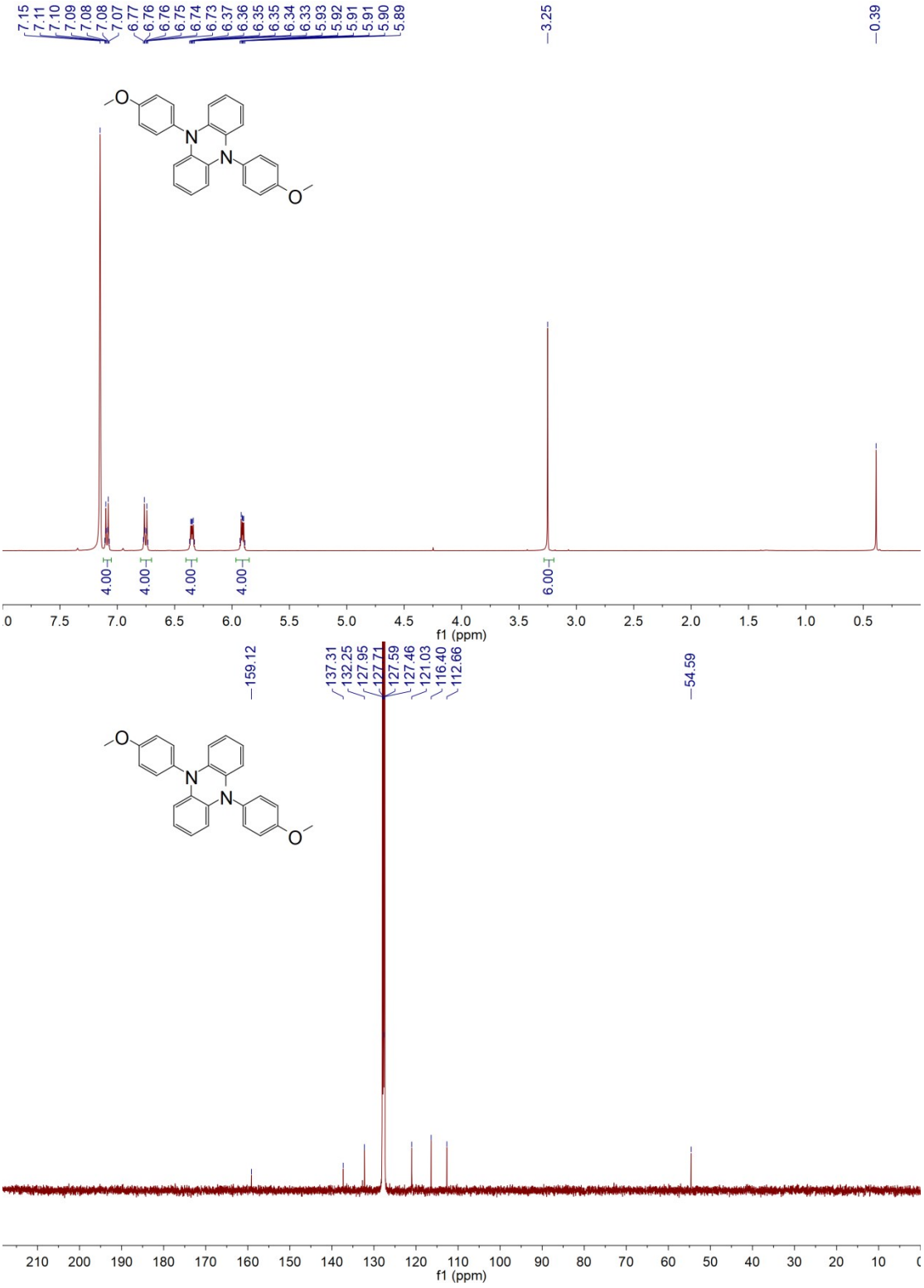


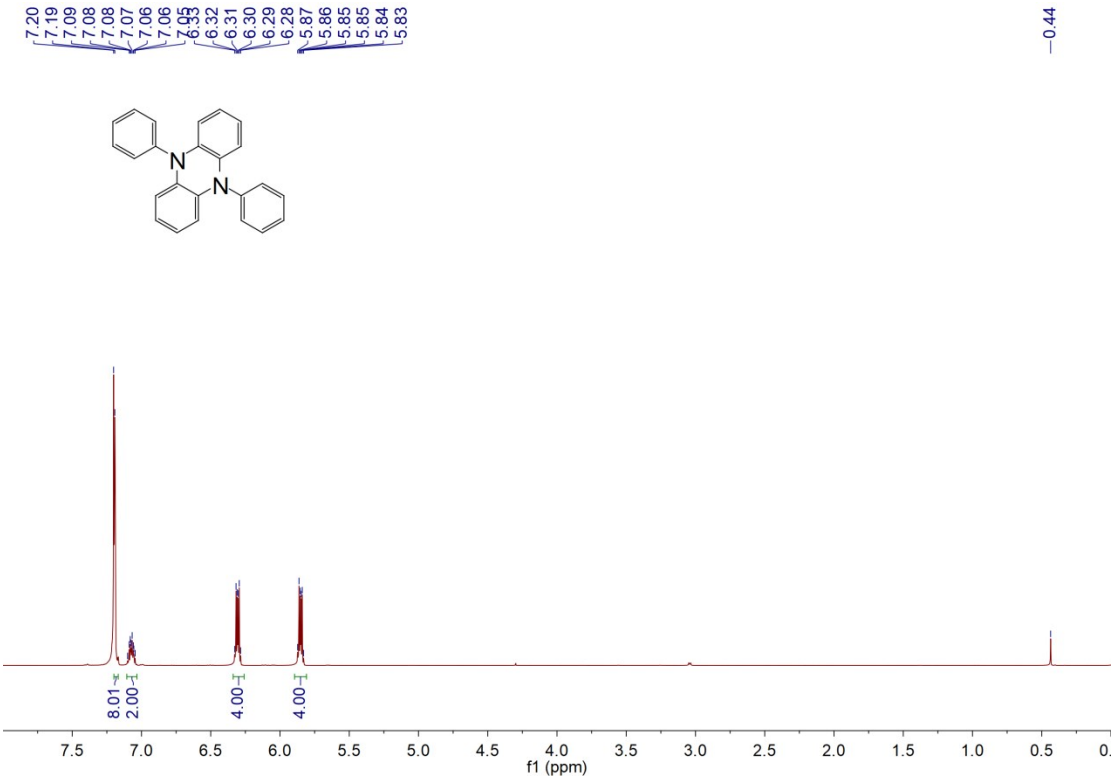
Fig. S23 GPC traces of polymerizations mediated by OPCs **4a**, **5a**, **6a**, **7a**.

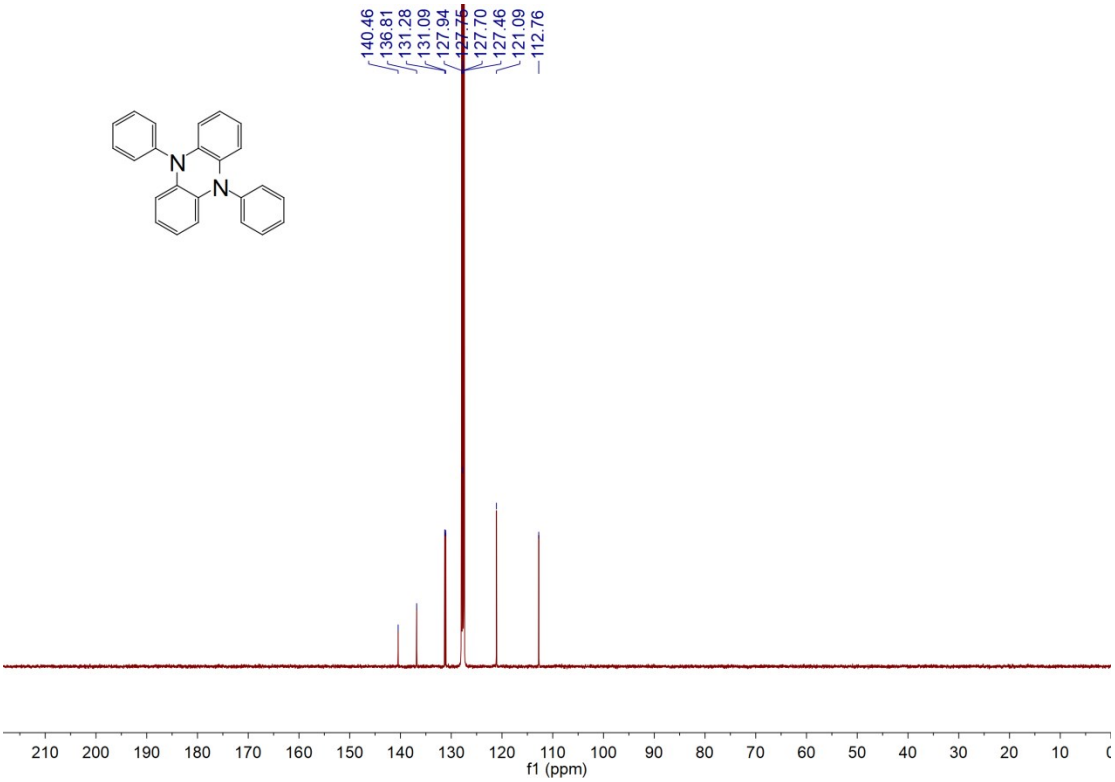
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

5,10-di(4-methoxyphenyl)-5,10-dihydrophenazine (**1a**)

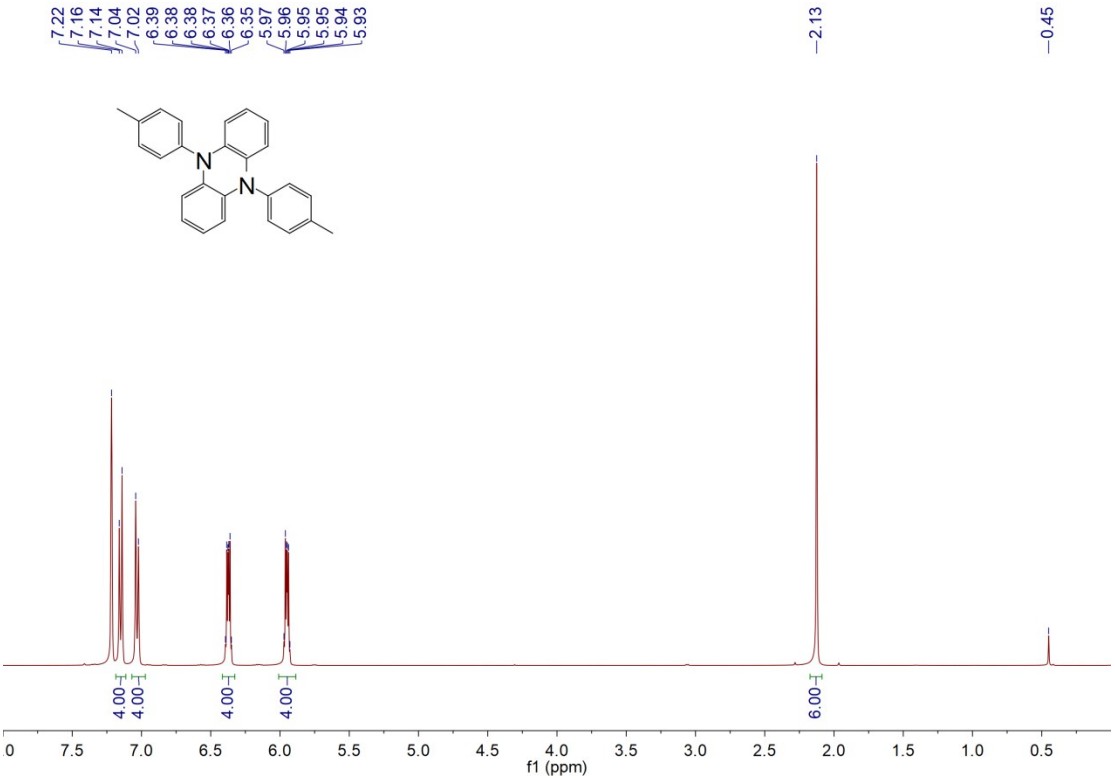


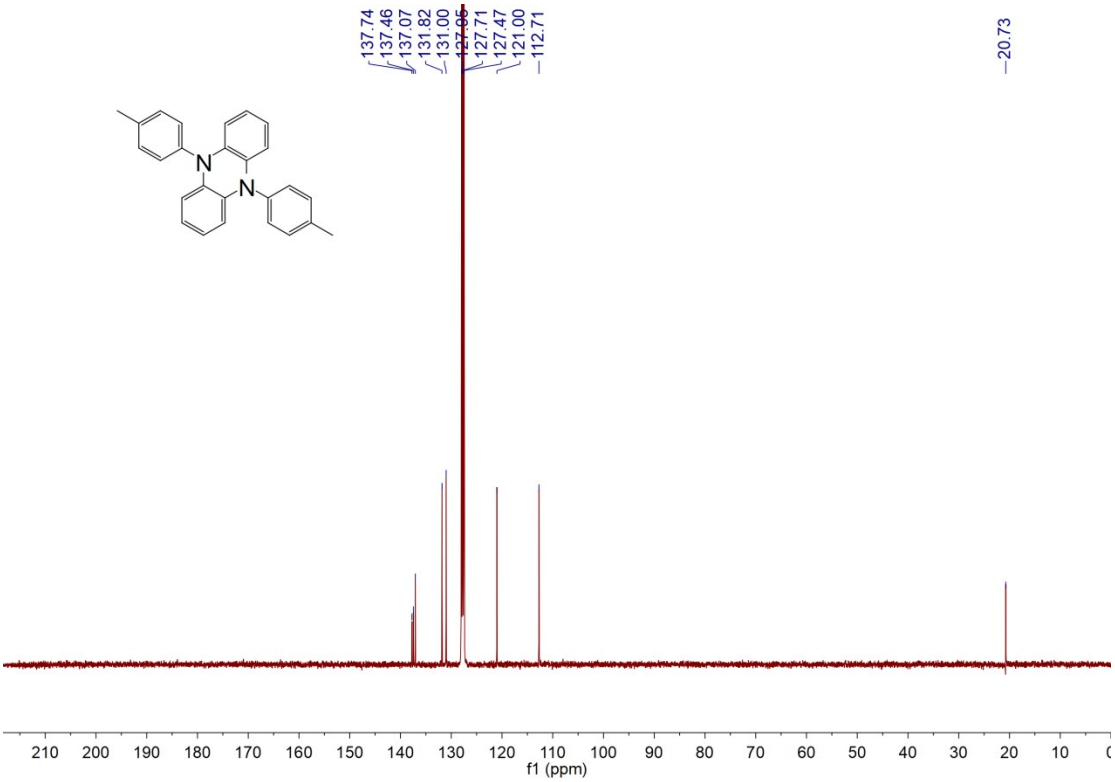
5,10-diphenyl-5,10-dihydrophenazine (**1b**)



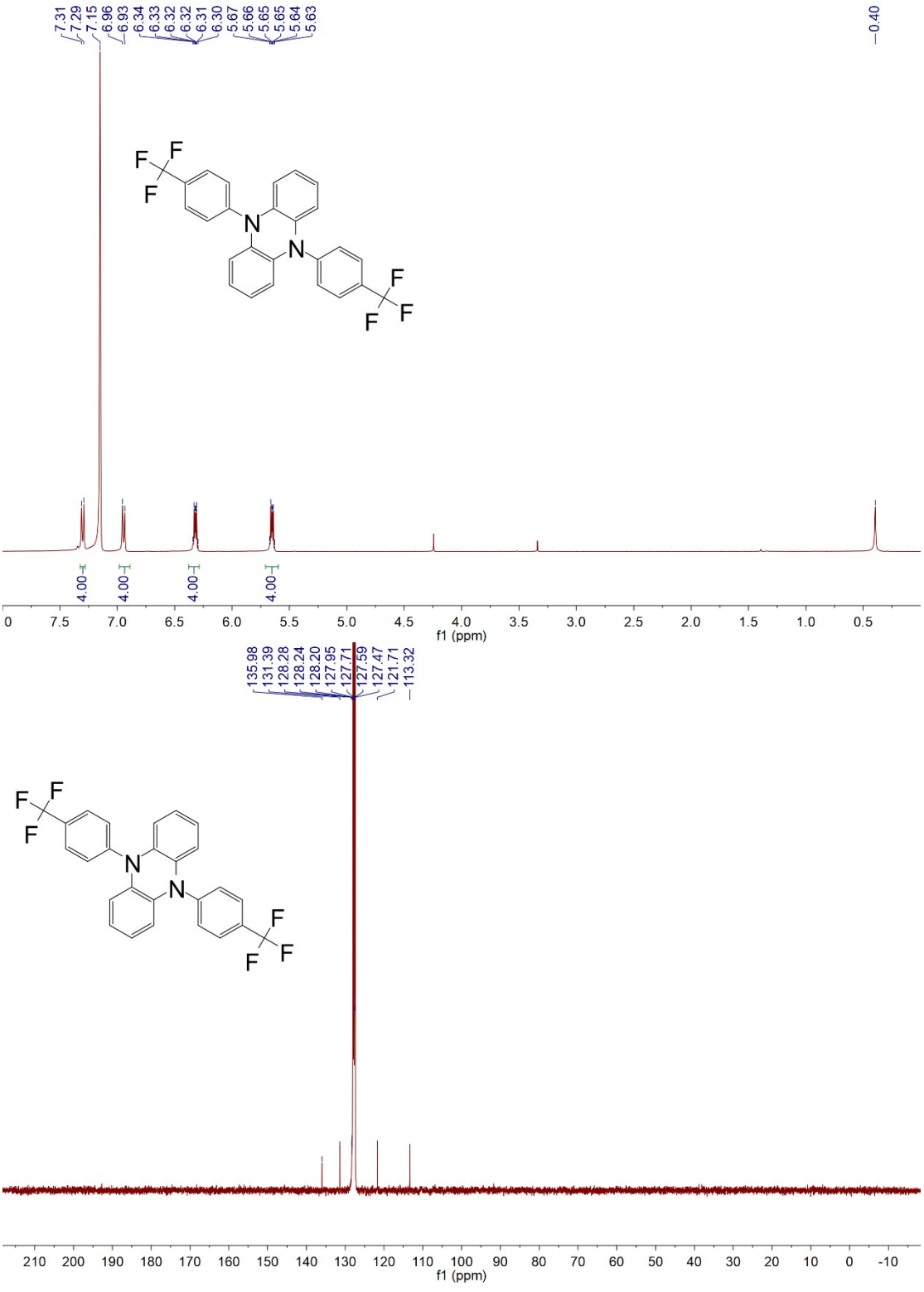


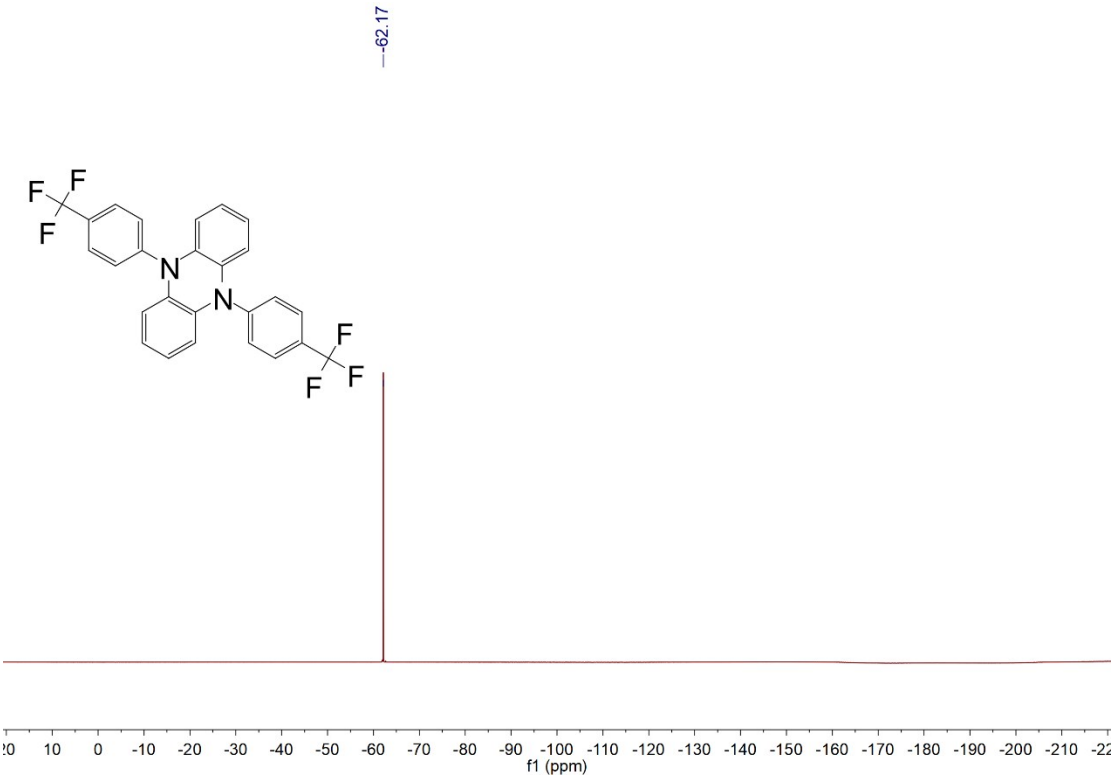
5,10-di(4-methylphenyl)-5,10-dihydrophenazine (**1c**)





5,10-bis(4-(trifluoromethyl)phenyl)-5,10-dihydrophenazine (**1d**)

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F
F
F
N
N
F
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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-160
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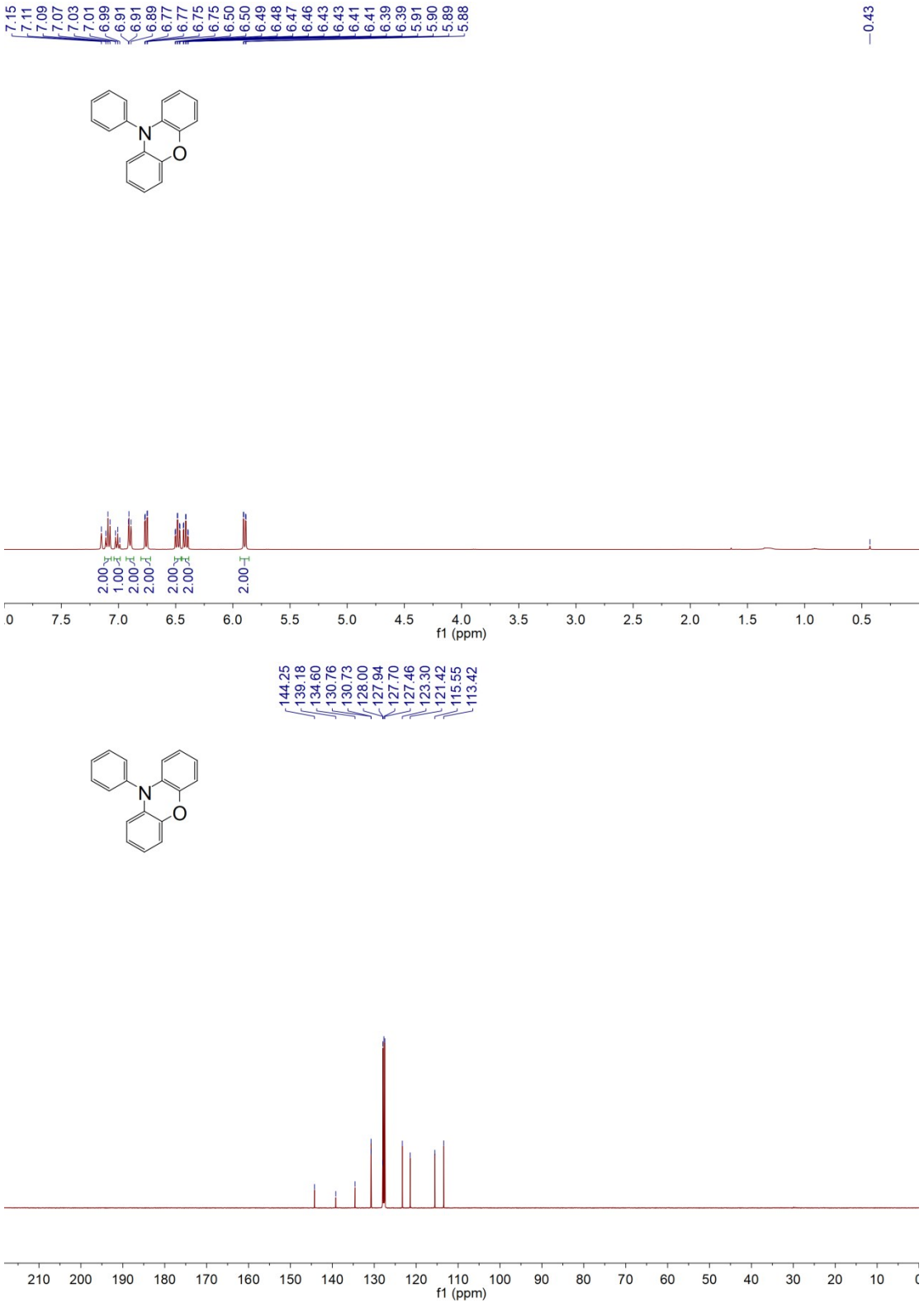
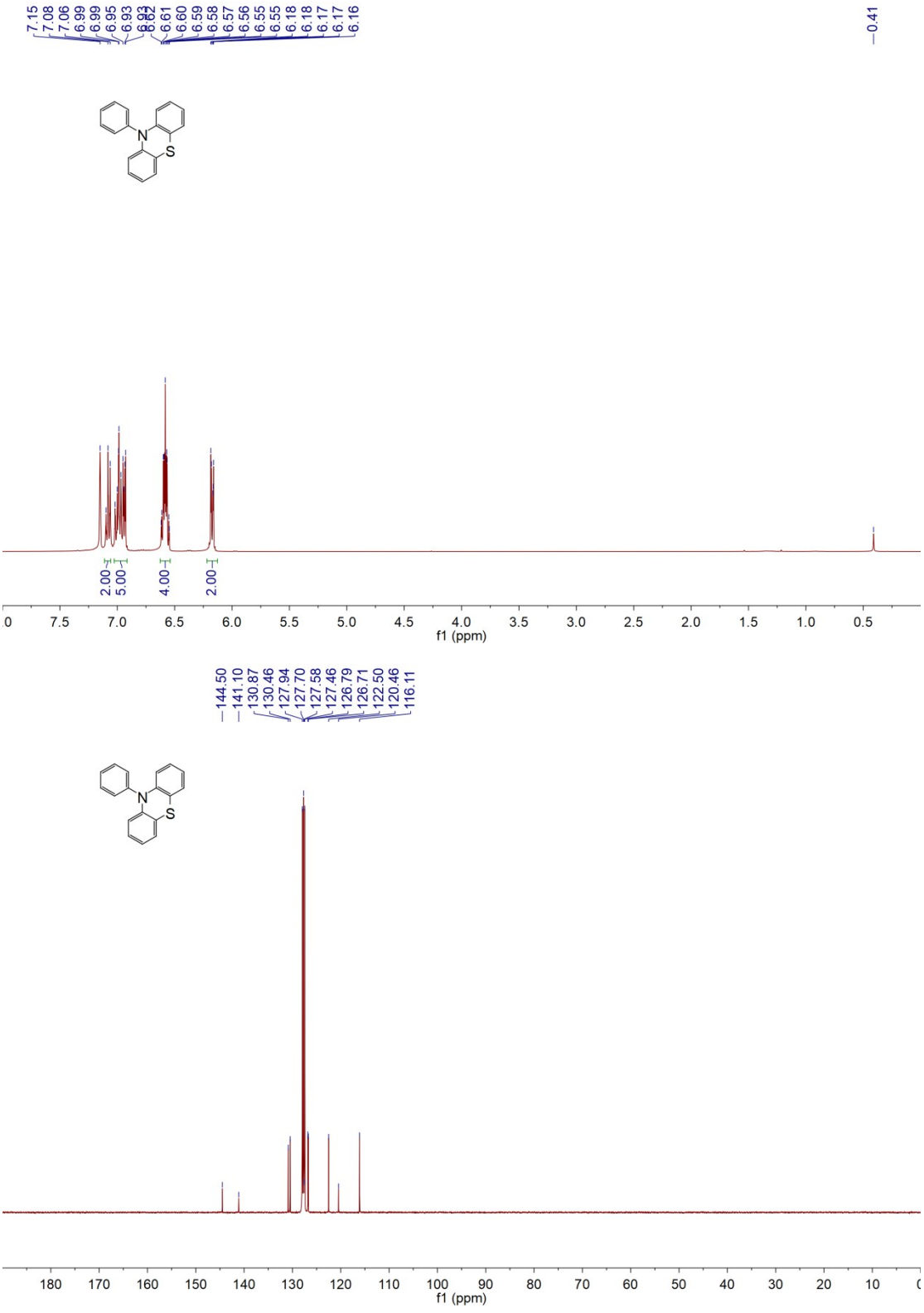
-180
-190
-200
-210
f1 (ppm)

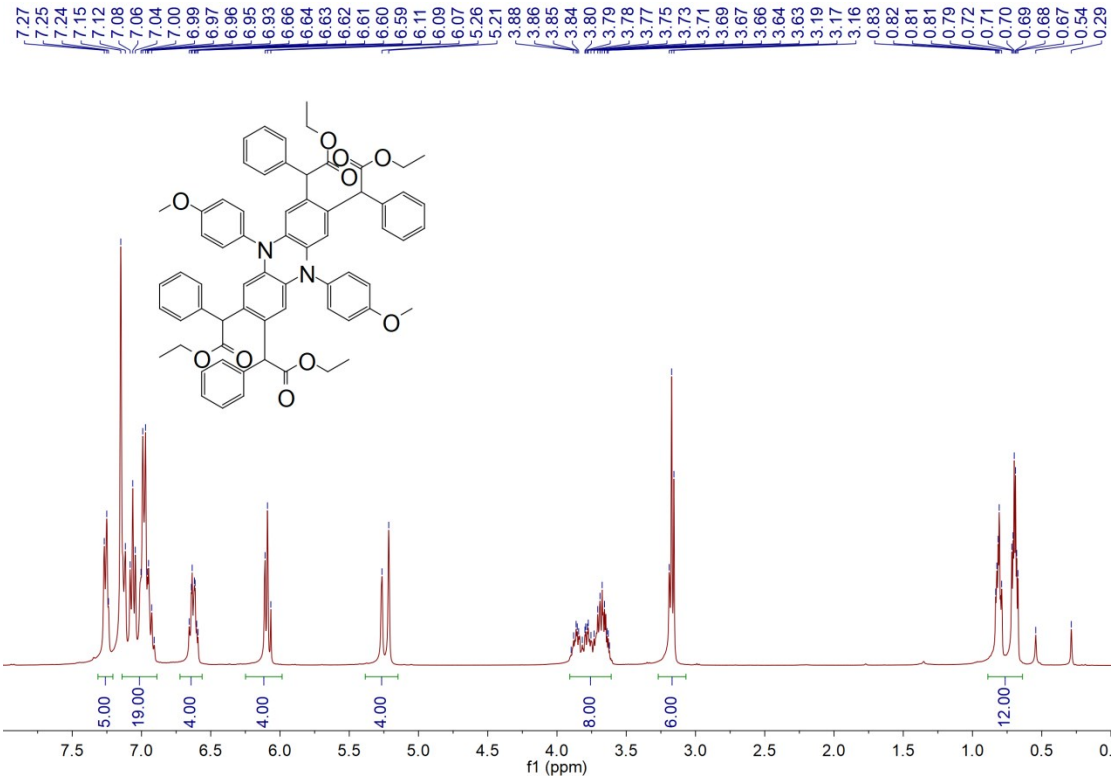
N-phenyl phenoxazine (**4a**)



N-phenyl phenothiazine (**5a**)



Product **3a**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6.61
6.60
6.59
6.11
6.09
6.07
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5.21
3.88
3.86
3.85
3.84
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3.69
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3.63
3.19
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0.83
0.82
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0.71
0.70
0.69
0.68
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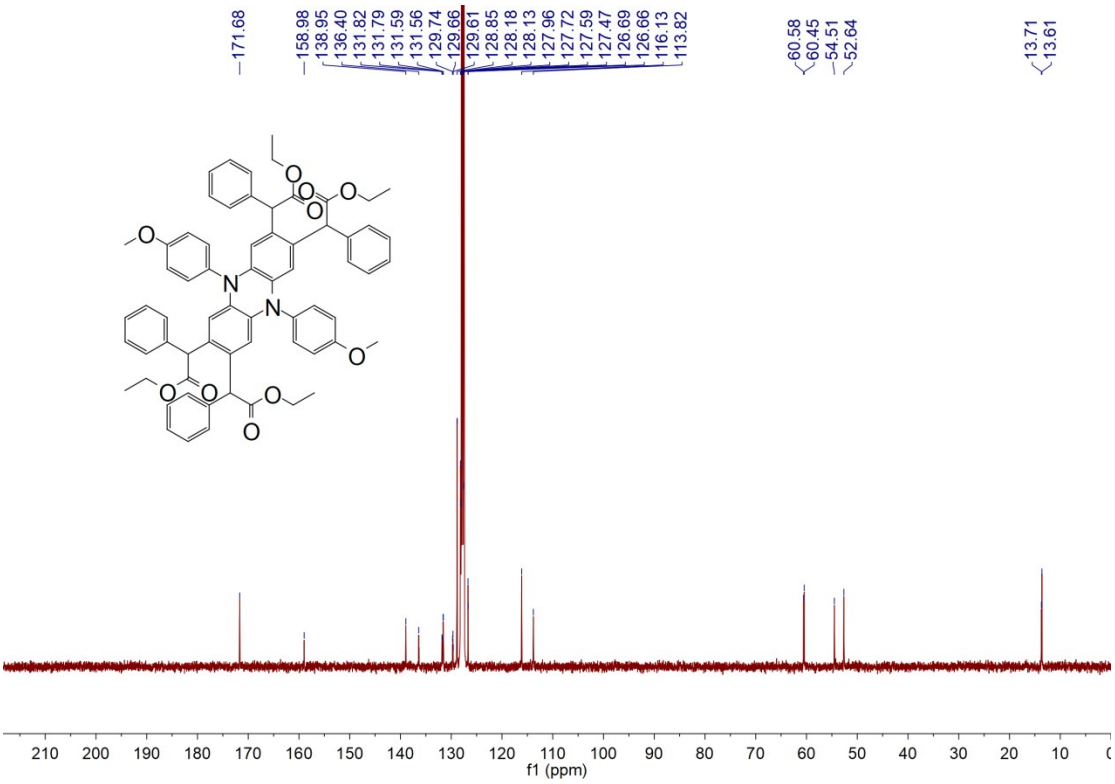
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127.59
127.47
126.69
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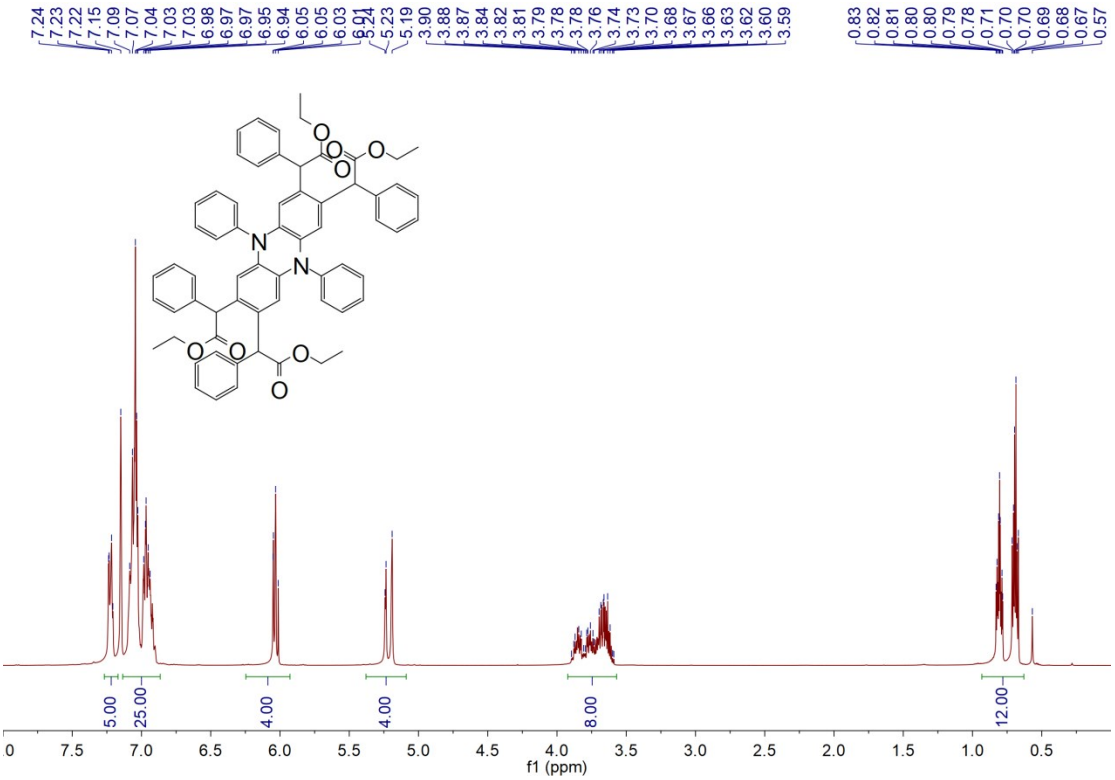
52.64
13.71
13.61
f1 (ppm)

Product **3b**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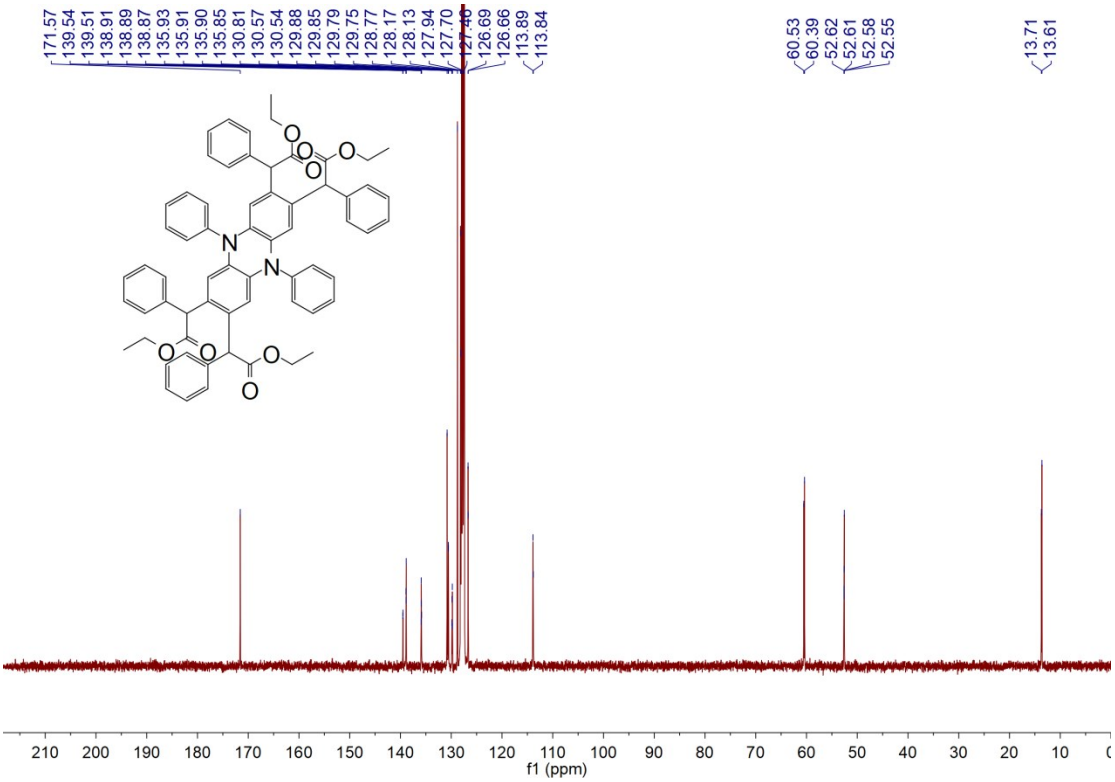
0.83 0.82 0.81 0.80 0.80 0.79 0.78 0.71 0.70 0.70 0.69 0.68 0.67 0.57
5.00 25.00 4.00 4.00 8.00 12.00
f1 (ppm)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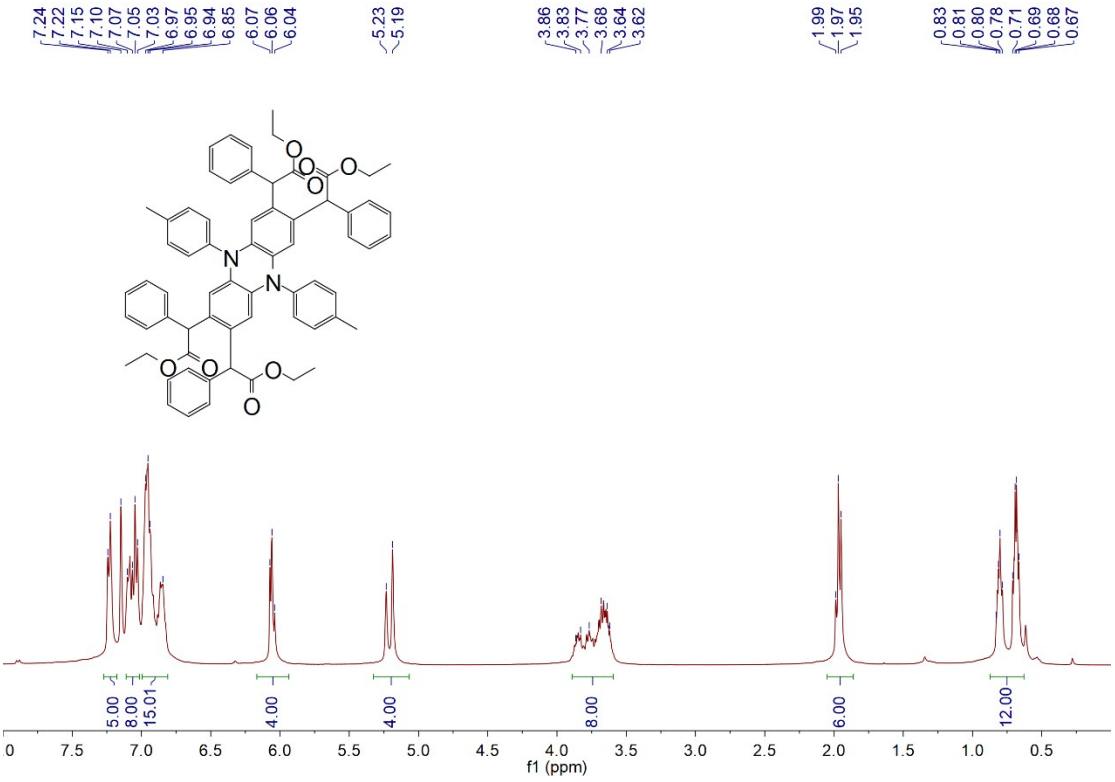
60.53 60.39 52.62 52.61 52.58 52.55
13.71 13.61
f1 (ppm)

Product **3c**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6.94
6.85
6.07
6.06
6.04
5.23
5.19
3.86
3.83
3.77
3.68
3.64
3.62
1.99
1.97
1.95
0.83
0.81
0.80
0.78
0.71
0.69
0.68
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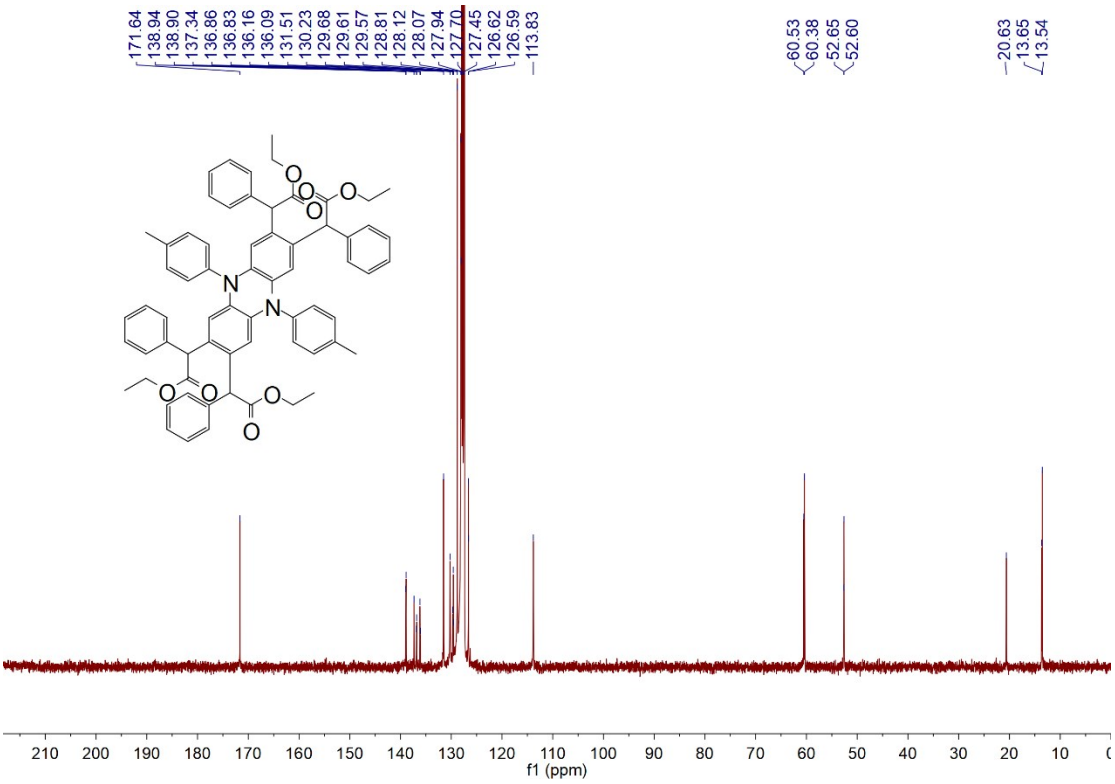
5.00
8.00
15.01
4.00
4.00
8.00
6.00
12.00
f1 (ppm)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136.16
136.09
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130.23
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129.57
128.81
128.12
128.07
127.94
127.70
127.45
126.62
126.59
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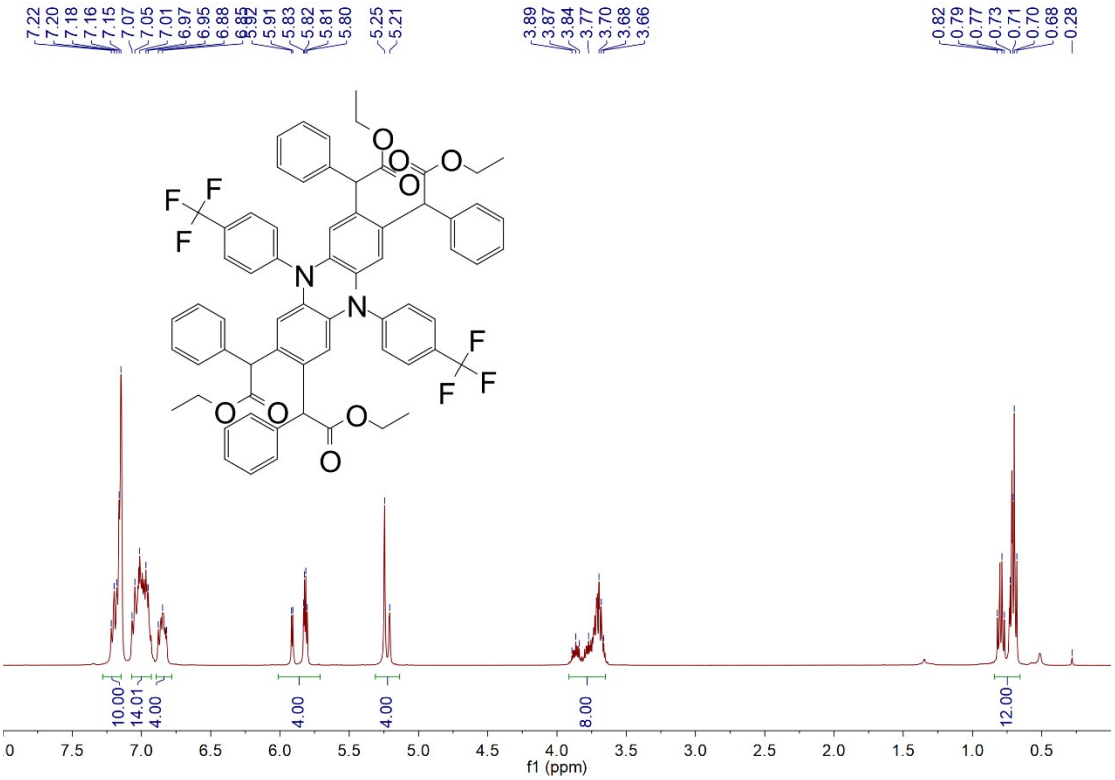
52.65
52.60
20.63
13.65
13.54
f1 (ppm)

Product **3d**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7.01
6.97
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6.88
5.91
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5.81
5.80
5.25
5.21
3.89
3.87
3.84
3.77
3.70
3.68
3.66
0.82
0.79
0.77
0.73
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14.01
4.00
4.00
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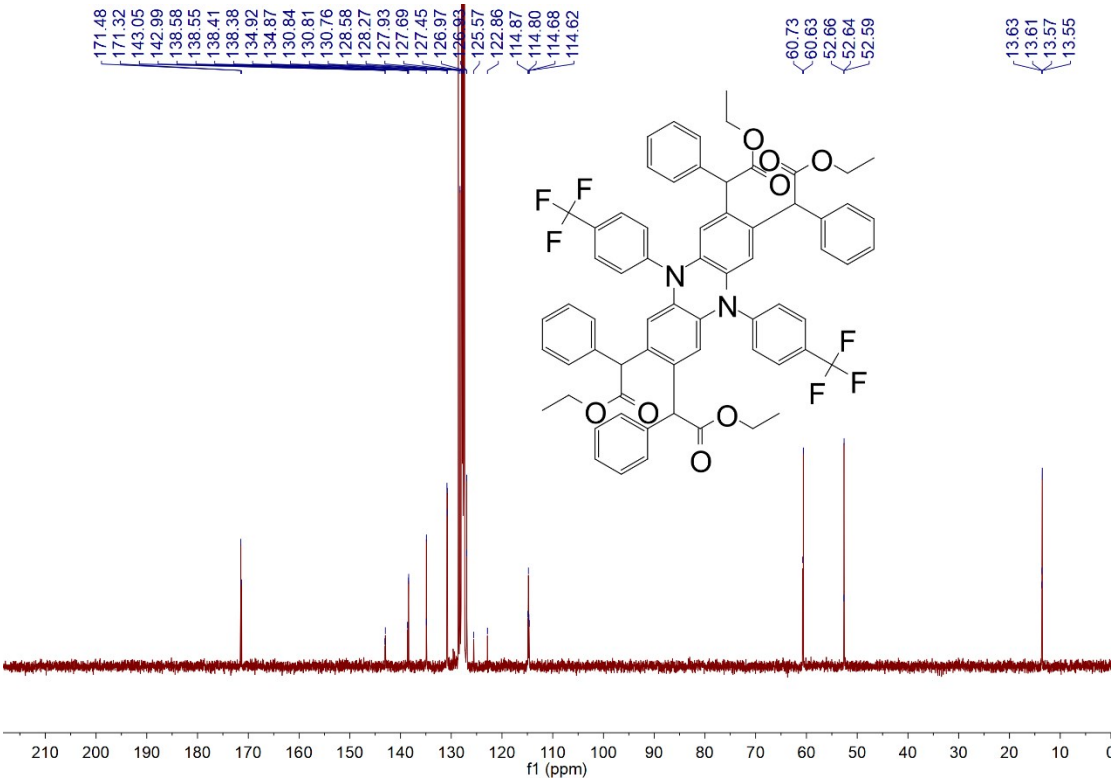
12.00
f1 (ppm)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127.69
127.45
126.97
125.57
122.86
114.87
114.80
114.68
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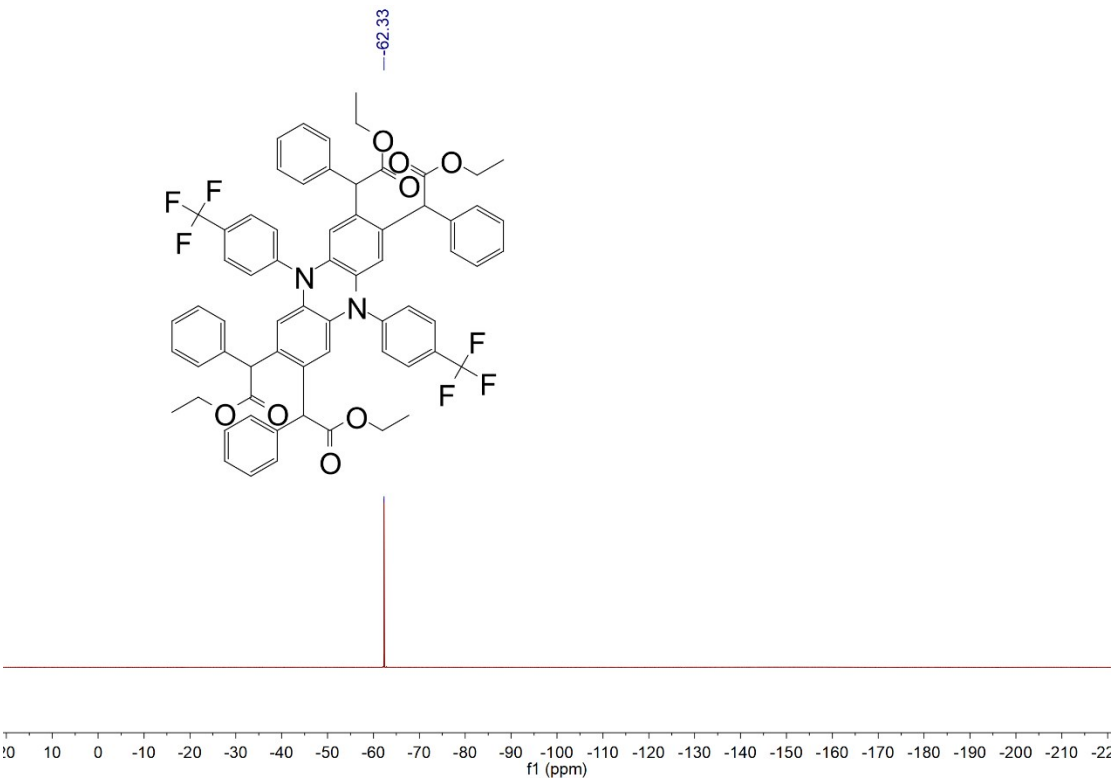
60.63
52.66
52.64
52.59
13.63
13.61
13.57
13.55
f1 (ppm)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F
N
N
F
F
F
O
O
O
O
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O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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-150
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-190
-200
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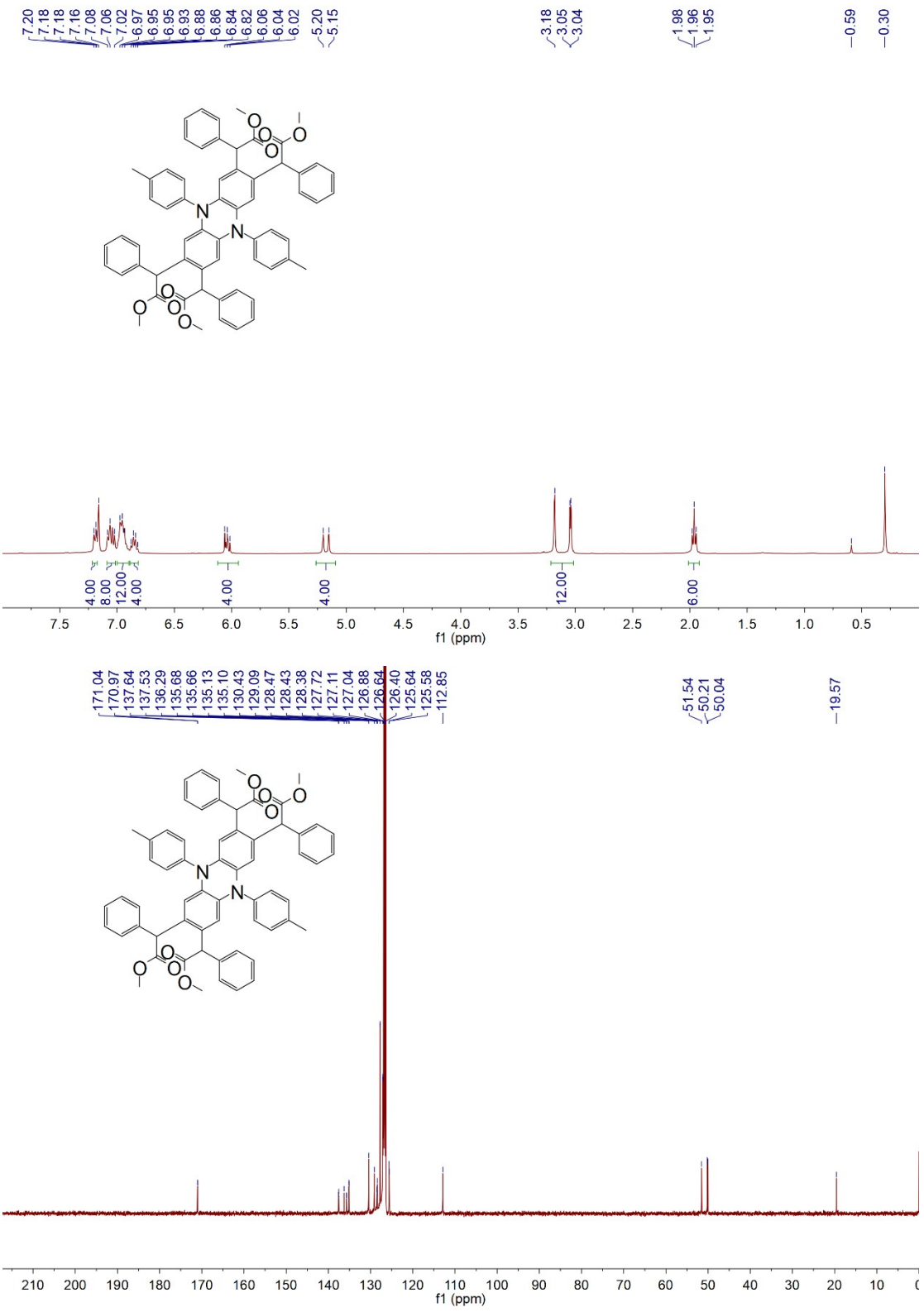
f1 (ppm)

Product **3e**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6.86
6.84
6.82
6.06
6.04
6.02
5.20
5.15
3.18
3.05
3.04
1.98
1.96
1.95
0.59
0.30
4.00
8.00
12.00
4.00
4.00
4.00
12.00
6.00
f1 (ppm)
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135.13
135.10
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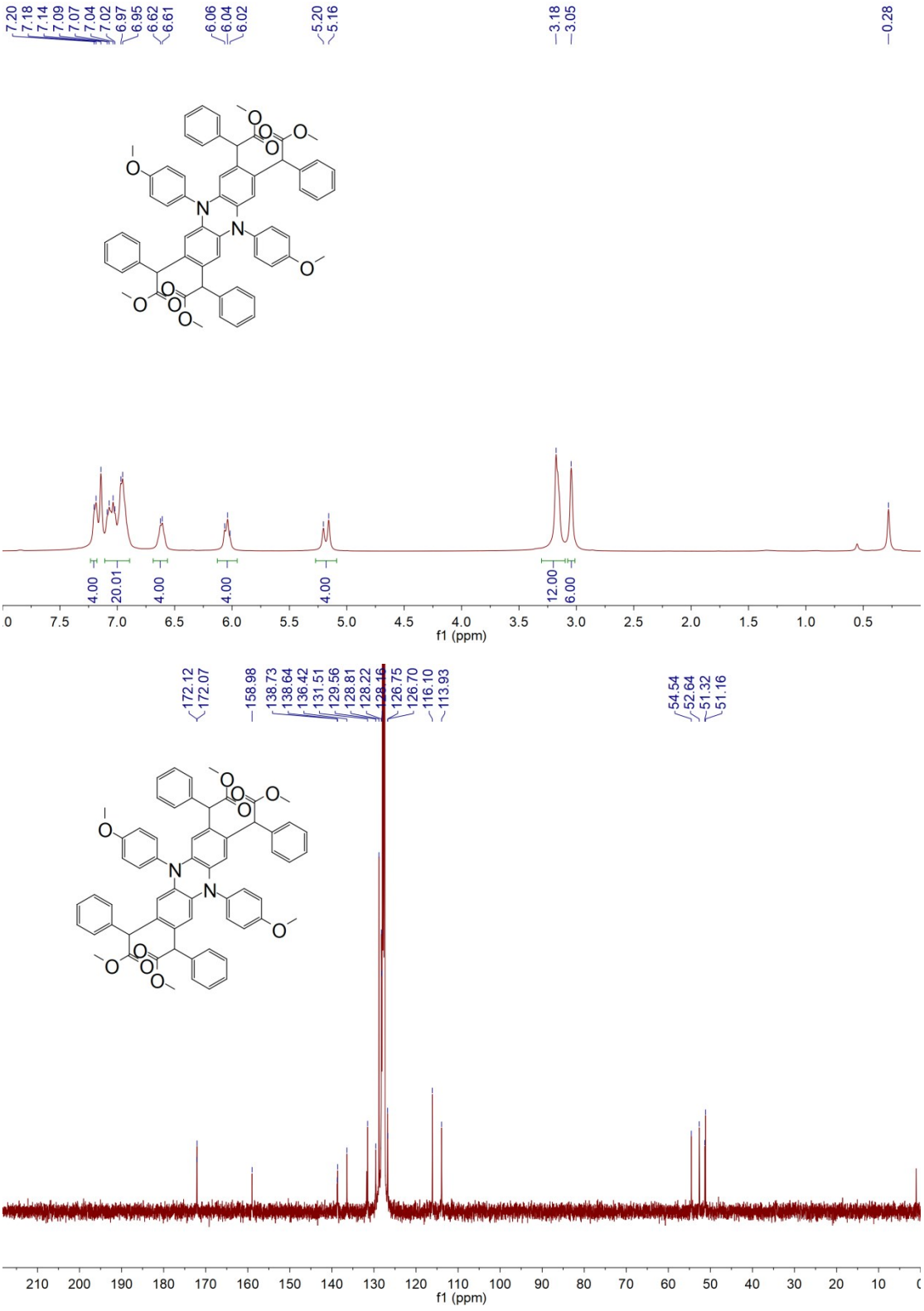
Product **3f**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6.04
6.02
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5.16
3.18
3.05
0.28
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20.01
4.00
4.00
4.00
12.00
6.00
f1 (ppm)
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172.07
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131.51
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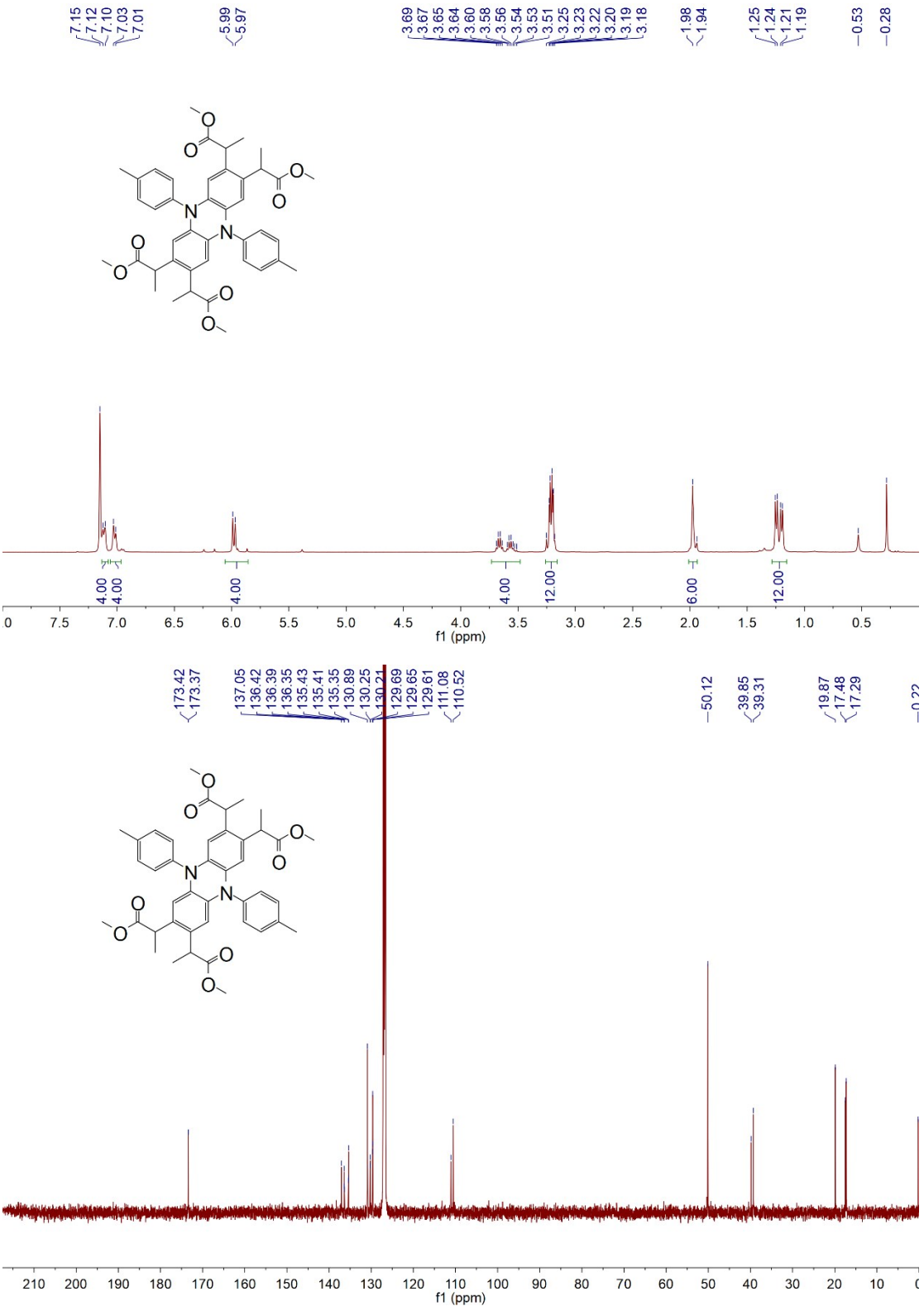
f1 (ppm)

Product **3g**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3.56
3.54
3.53
3.51
3.25
3.23
3.22
3.20
3.19
3.18
1.98
1.94
1.25
1.24
1.21
1.19
0.53
0.28
4.00
4.00
4.00
4.00
12.00
6.00
12.00
f1 (ppm)
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173.37
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136.39
136.35
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129.65
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50.12
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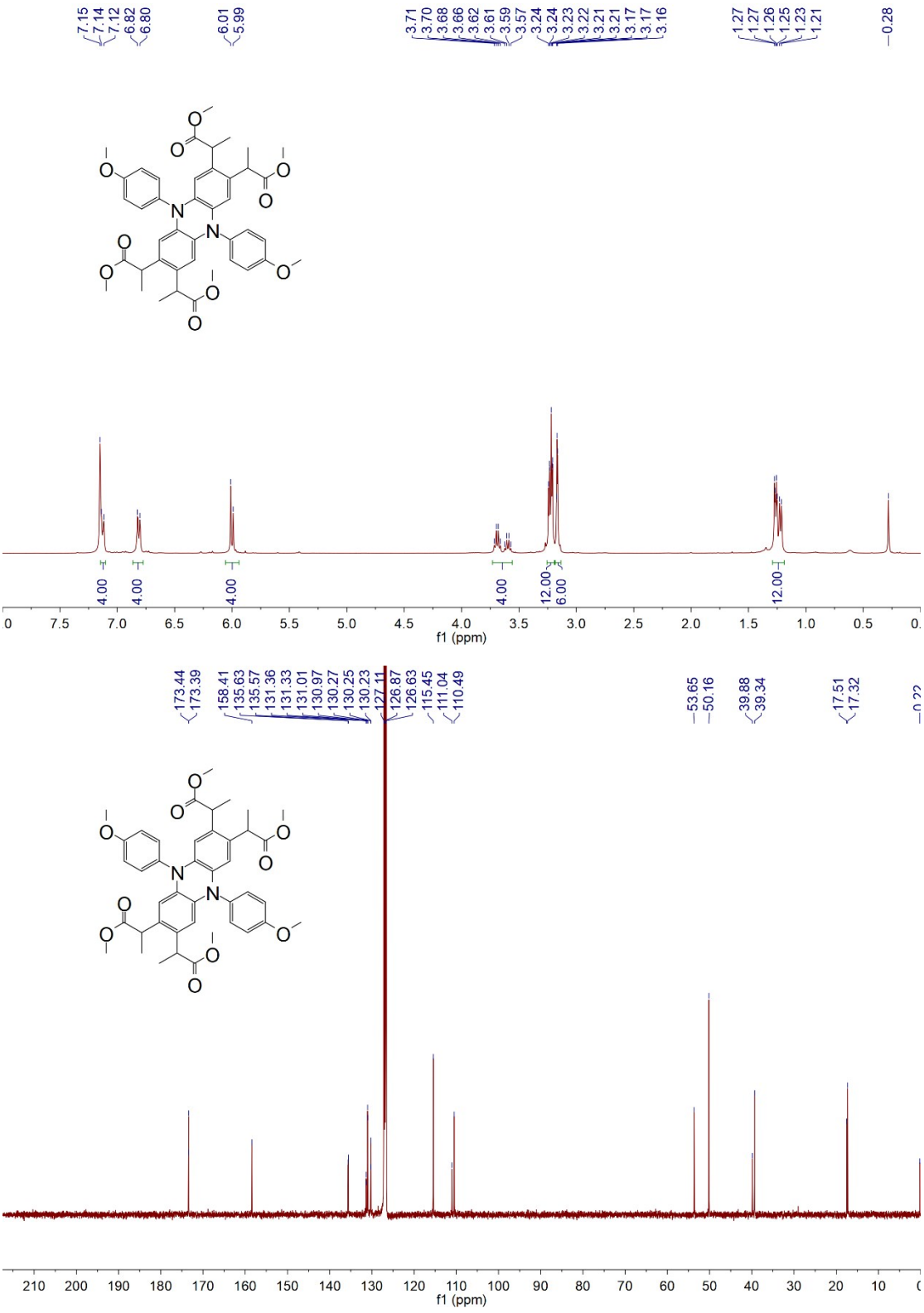
19.87
17.48
17.29
f1 (ppm)

Product **3h**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3.22
3.21
3.21
3.17
3.17
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1.27
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1.23
1.21
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4.00
4.00
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12.00
f1 (ppm)
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173.39
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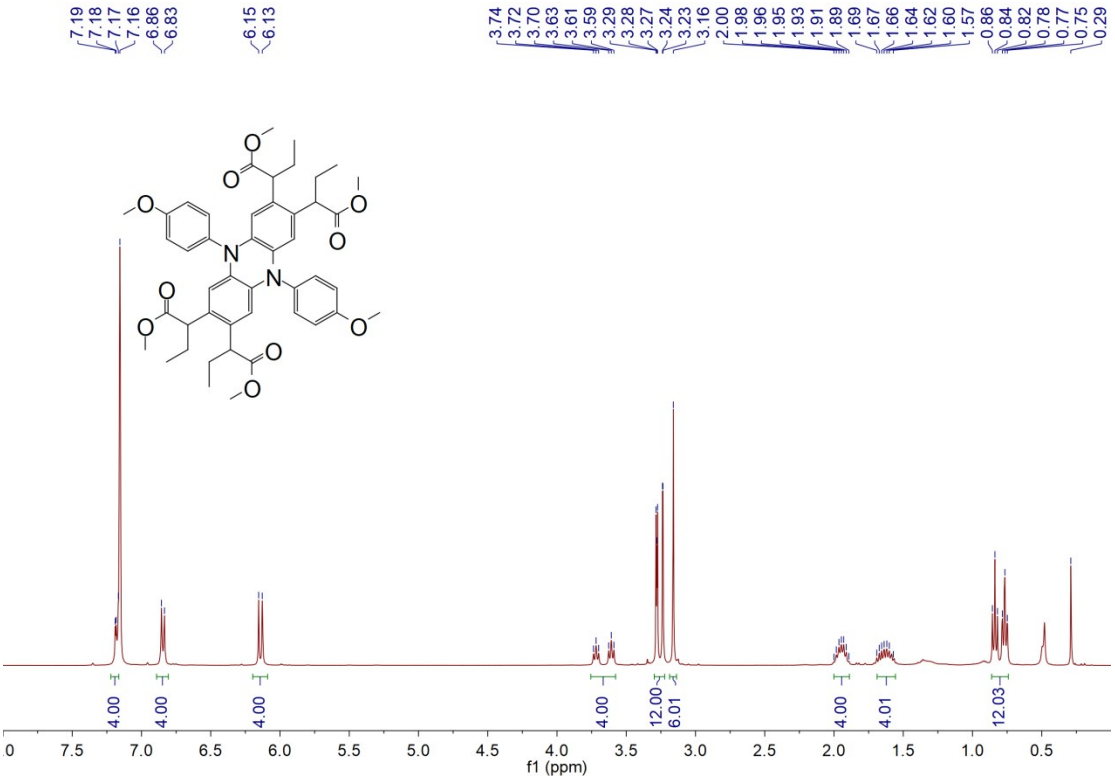
f1 (ppm)

Product **3i**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3.28
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1.67
1.66
1.64
1.62
1.60
1.57
0.86
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0.82
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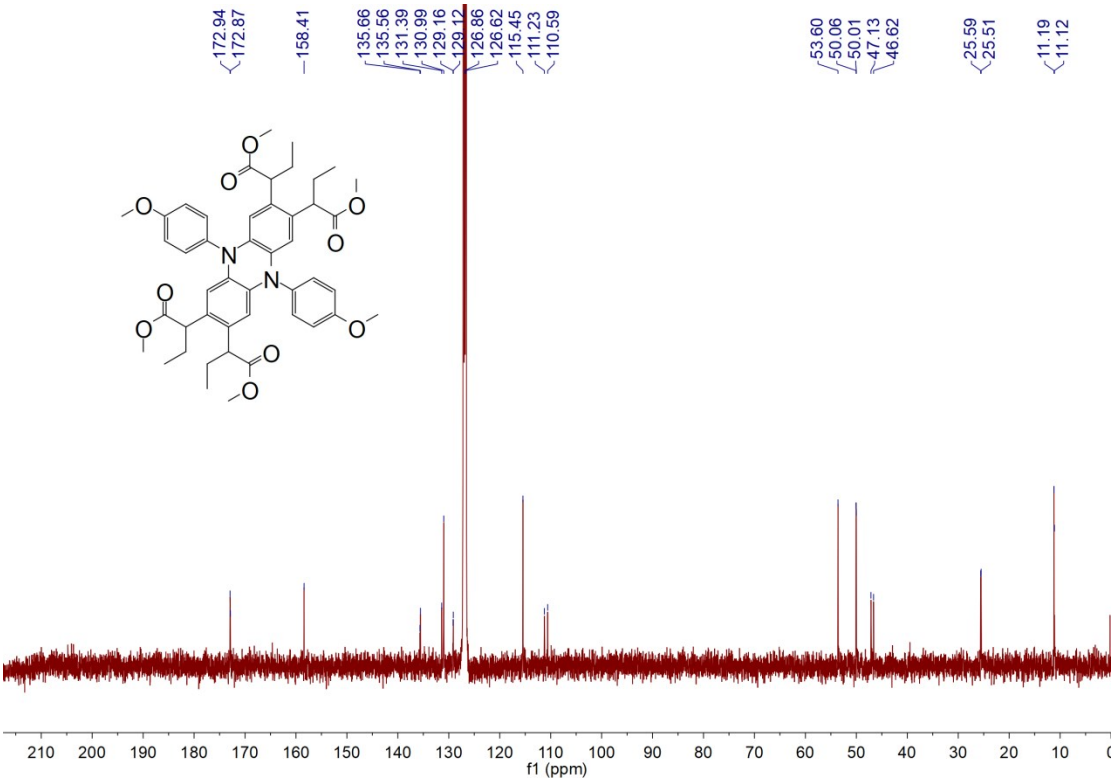
12.03
f1 (ppm)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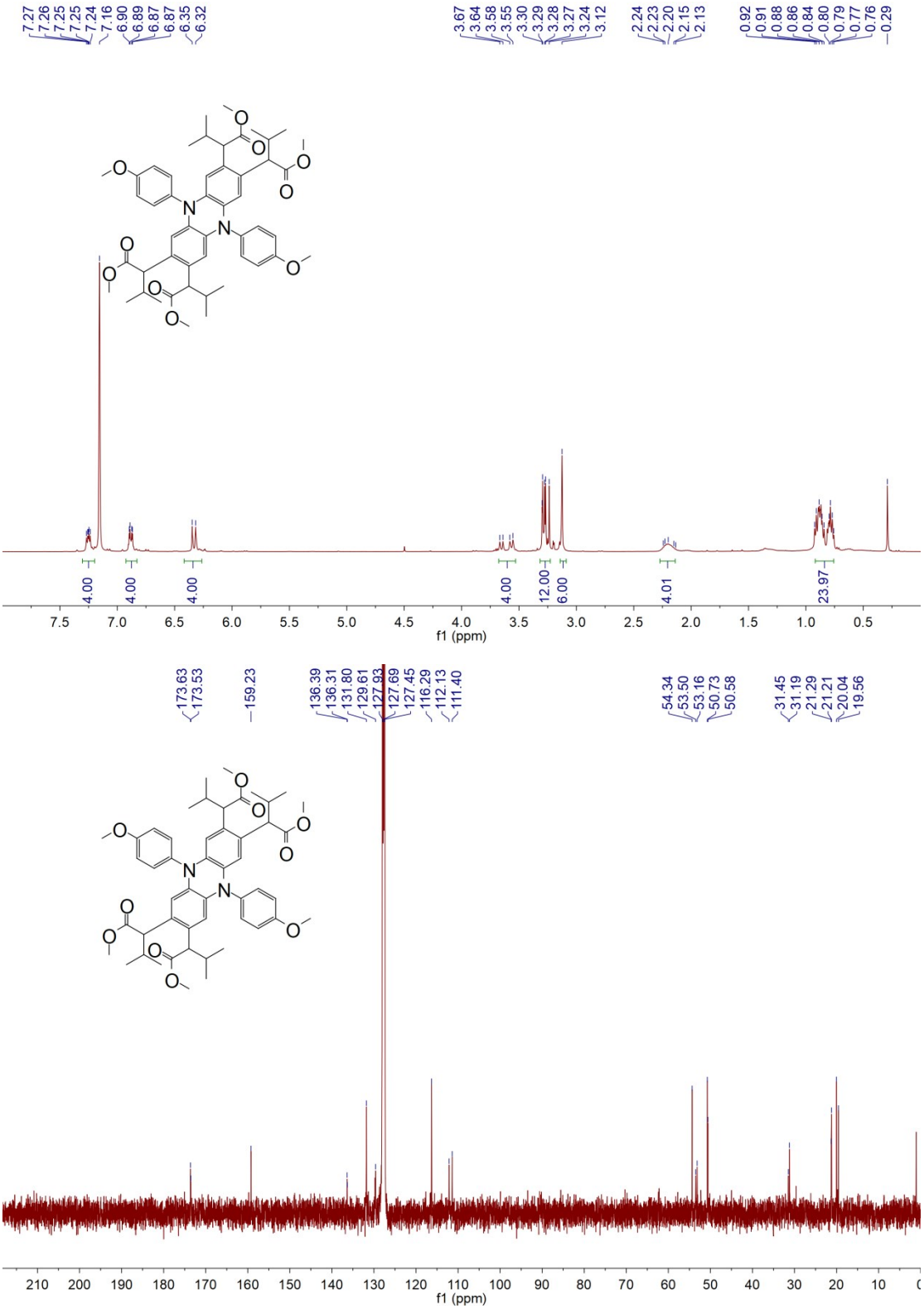
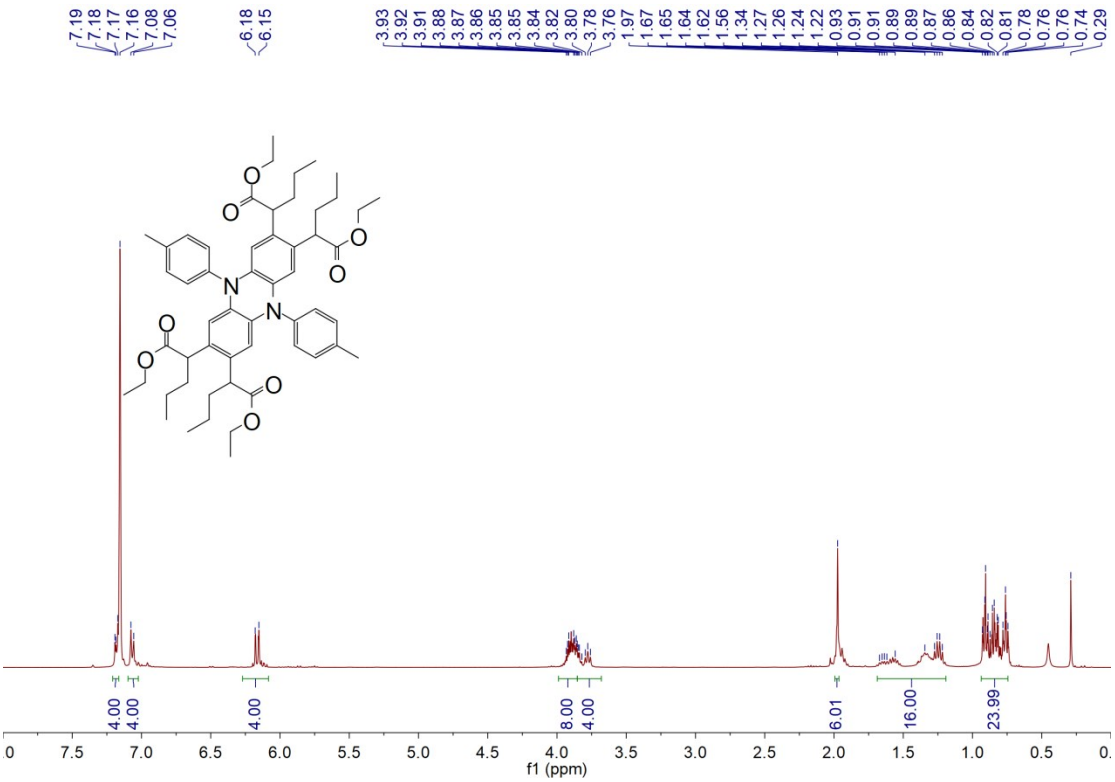
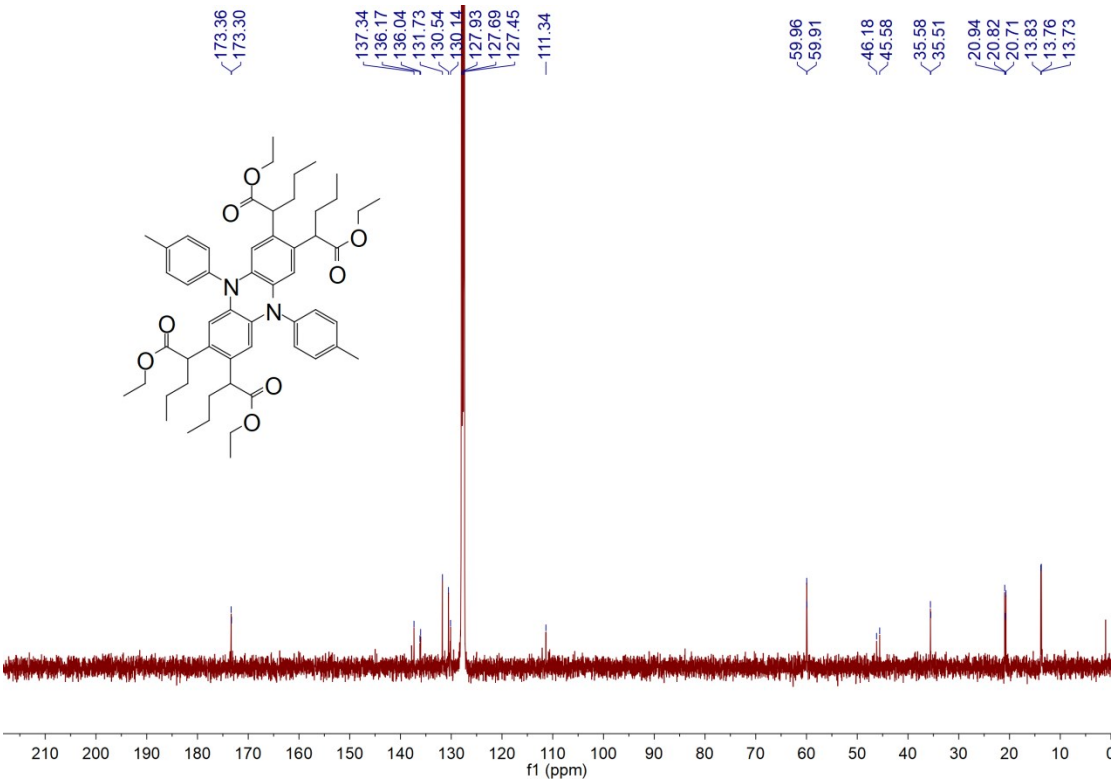
129.12
126.86
126.62
115.45
111.23
110.59
53.60
50.06
50.01
47.13
46.62
25.59
25.51
11.19
11.12
f1 (ppm)

Product **3j**

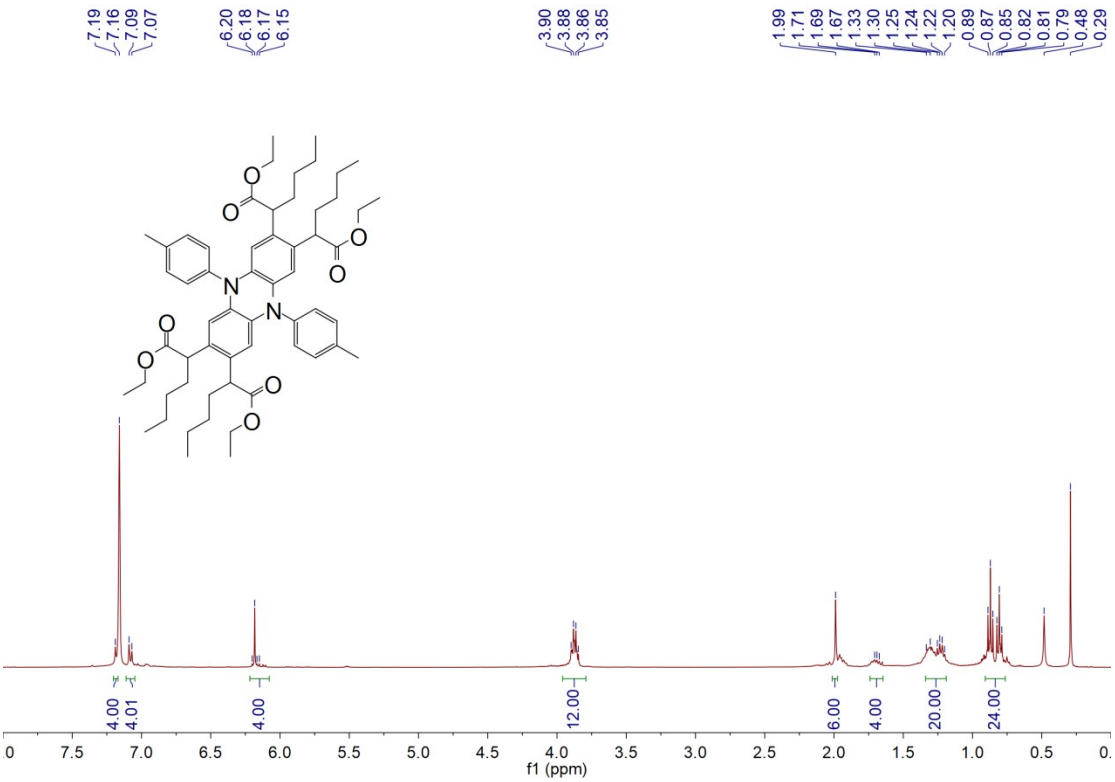

7.27
7.26
7.25
7.25
7.24
7.16
6.90
6.89
6.87
6.87
6.35
6.32
3.67
3.64
3.58
3.55
3.30
3.29
3.28
3.27
3.24
3.12
2.24
2.23
2.20
2.15
2.13
0.92
0.91
0.88
0.86
0.84
0.80
0.79
0.77
0.76
0.29
4.00
4.00
4.00
4.00
12.00
6.00
4.01
23.97
f1 (ppm)
173.63
173.53
159.23
136.39
136.31
131.80
129.61
127.93
127.69
127.45
116.29
112.13
111.40
54.34
53.50
53.16
50.73
50.58
31.45
31.19
21.29
21.21
20.04
19.56
f1 (ppm)

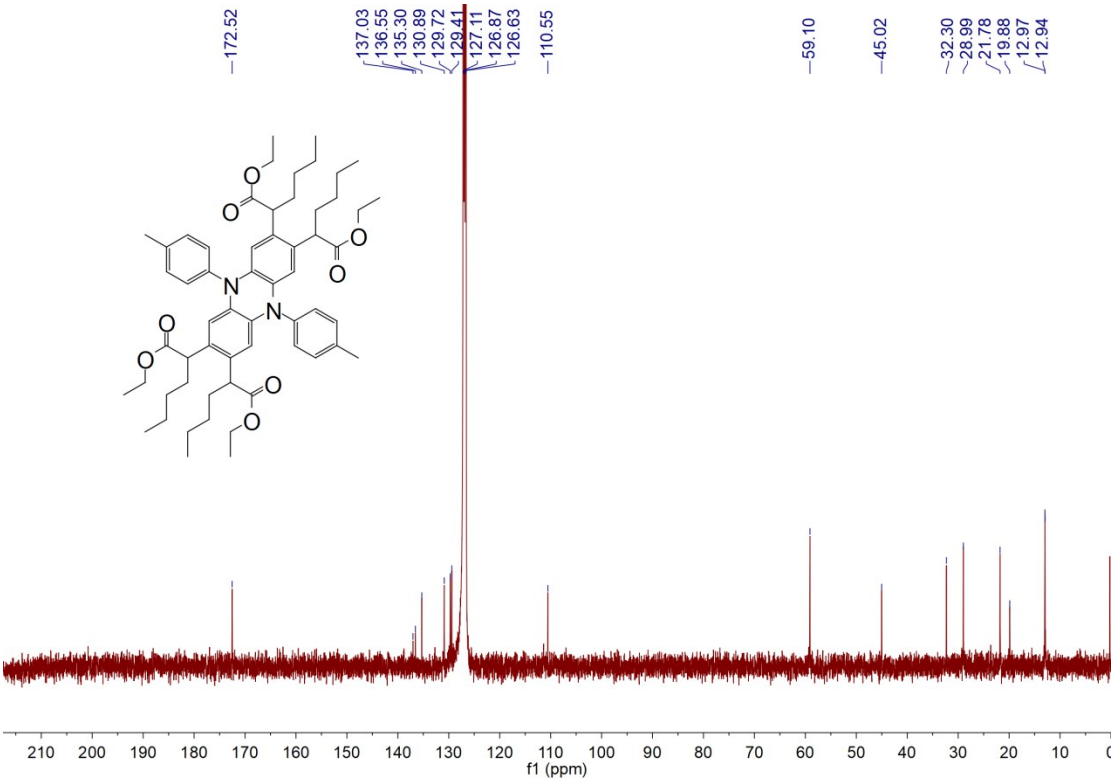
Product **3k**


7.19
7.18
7.17
7.16
7.08
7.06
6.18
6.15
3.93
3.92
3.91
3.88
3.87
3.86
3.85
3.85
3.84
3.82
3.80
3.78
3.76
1.97
1.67
1.65
1.64
1.62
1.56
1.34
1.27
1.26
1.24
1.22
0.93
0.91
0.91
0.89
0.89
0.87
0.86
0.84
0.82
0.81
0.78
0.76
0.76
0.74
0.29
4.00
4.00
4.00
8.00
4.00
6.01
16.00
23.99
f1 (ppm)

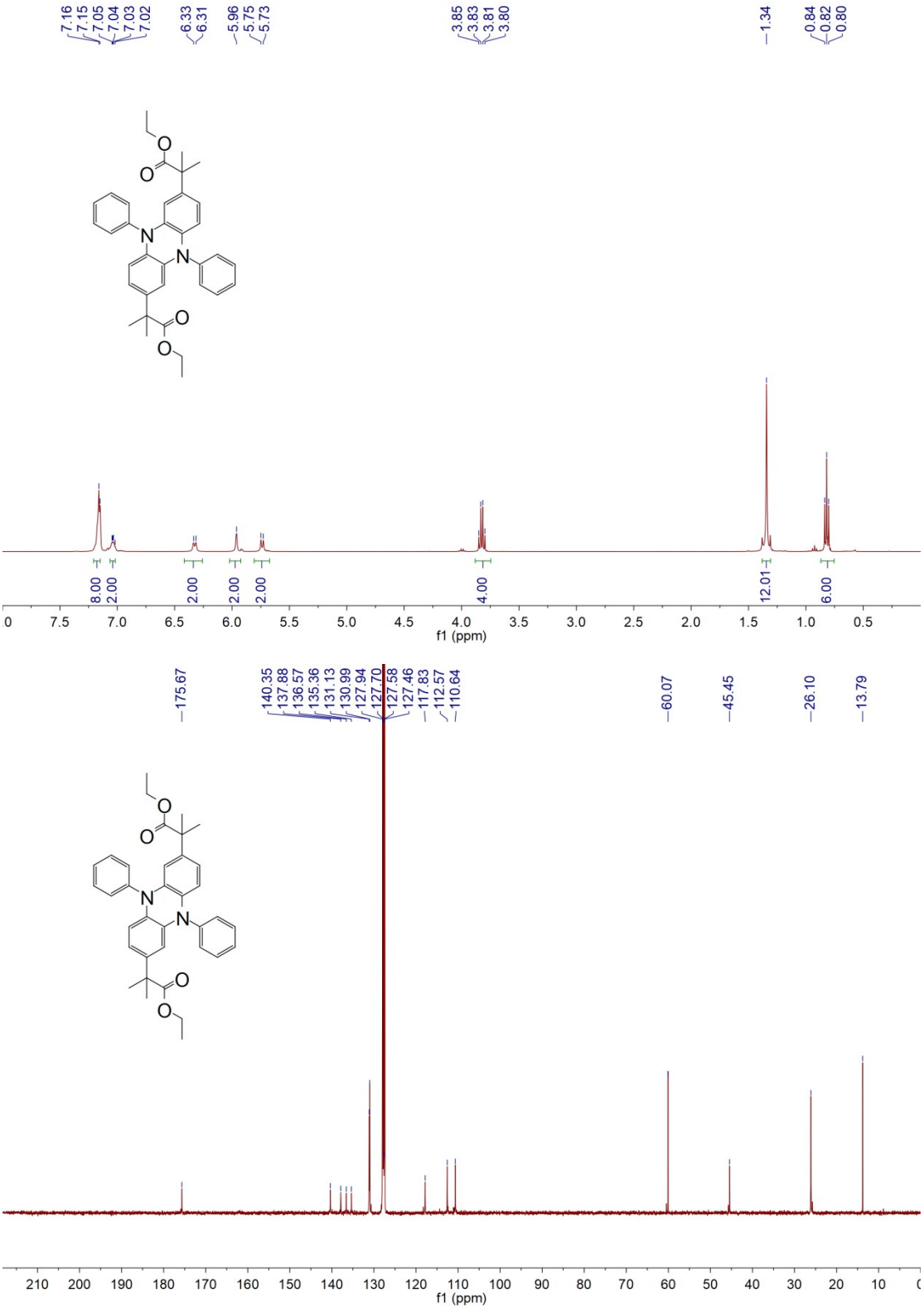

173.36
173.30
137.34
136.17
136.04
131.73
130.54
130.14
127.93
127.69
127.45
111.34
59.96
59.91
46.18
45.58
35.58
35.51
20.94
20.82
20.71
13.83
13.76
13.73
f1 (ppm)

Product **3l**

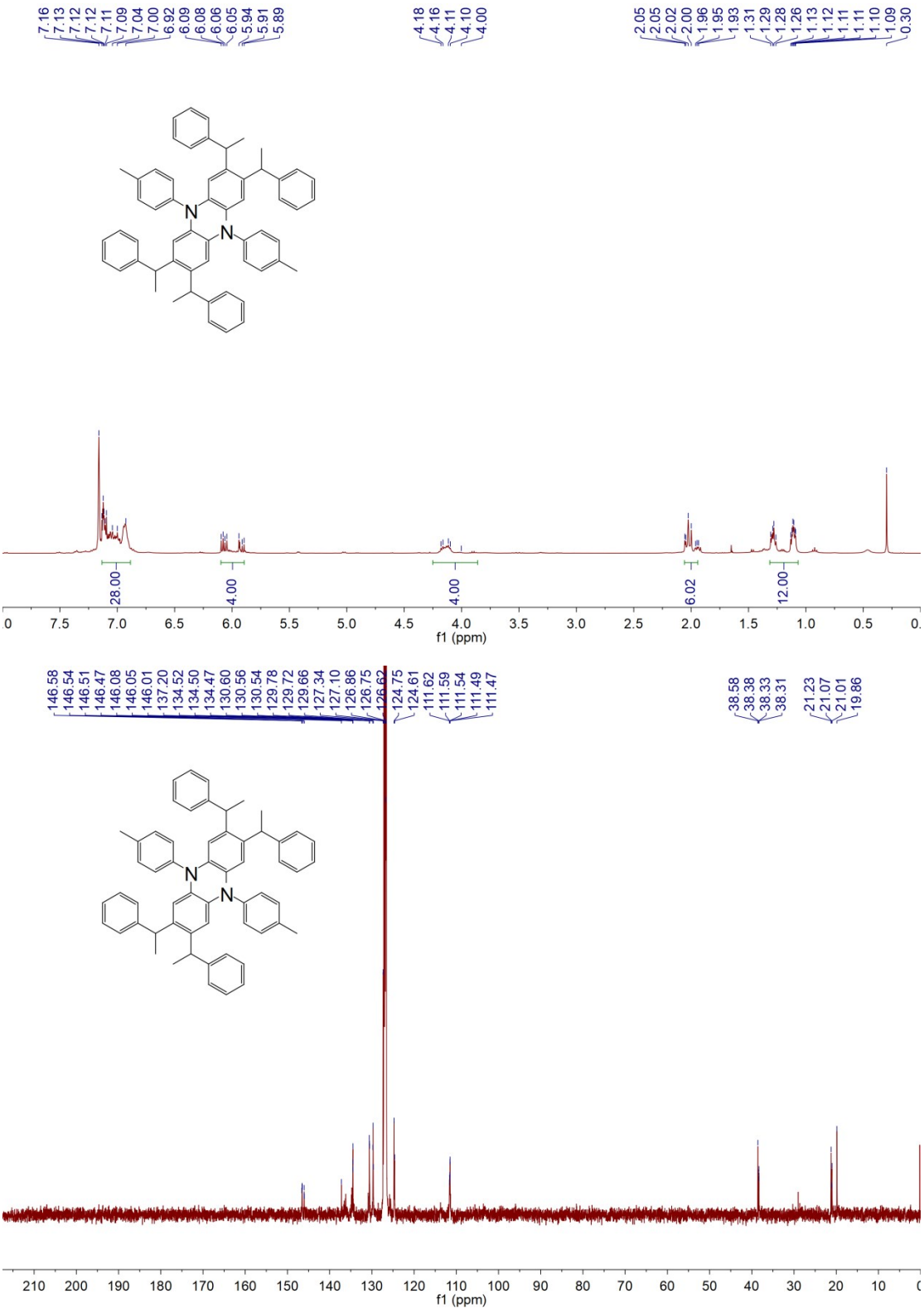

7.19
7.16
7.09
7.07
6.20
6.18
6.17
6.15
3.90
3.88
3.86
3.85
1.99
1.71
1.69
1.67
1.33
1.30
1.25
1.24
1.22
1.20
0.89
0.87
0.85
0.82
0.81
0.79
0.48
0.29
4.00
4.01
4.00
12.00
6.00
4.00
20.00
24.00
f1 (ppm)


172.52
137.03
136.55
135.30
130.89
129.72
129.41
127.11
126.87
126.63
110.55
59.10
45.02
32.30
28.99
21.78
19.88
12.97
12.94
f1 (ppm)

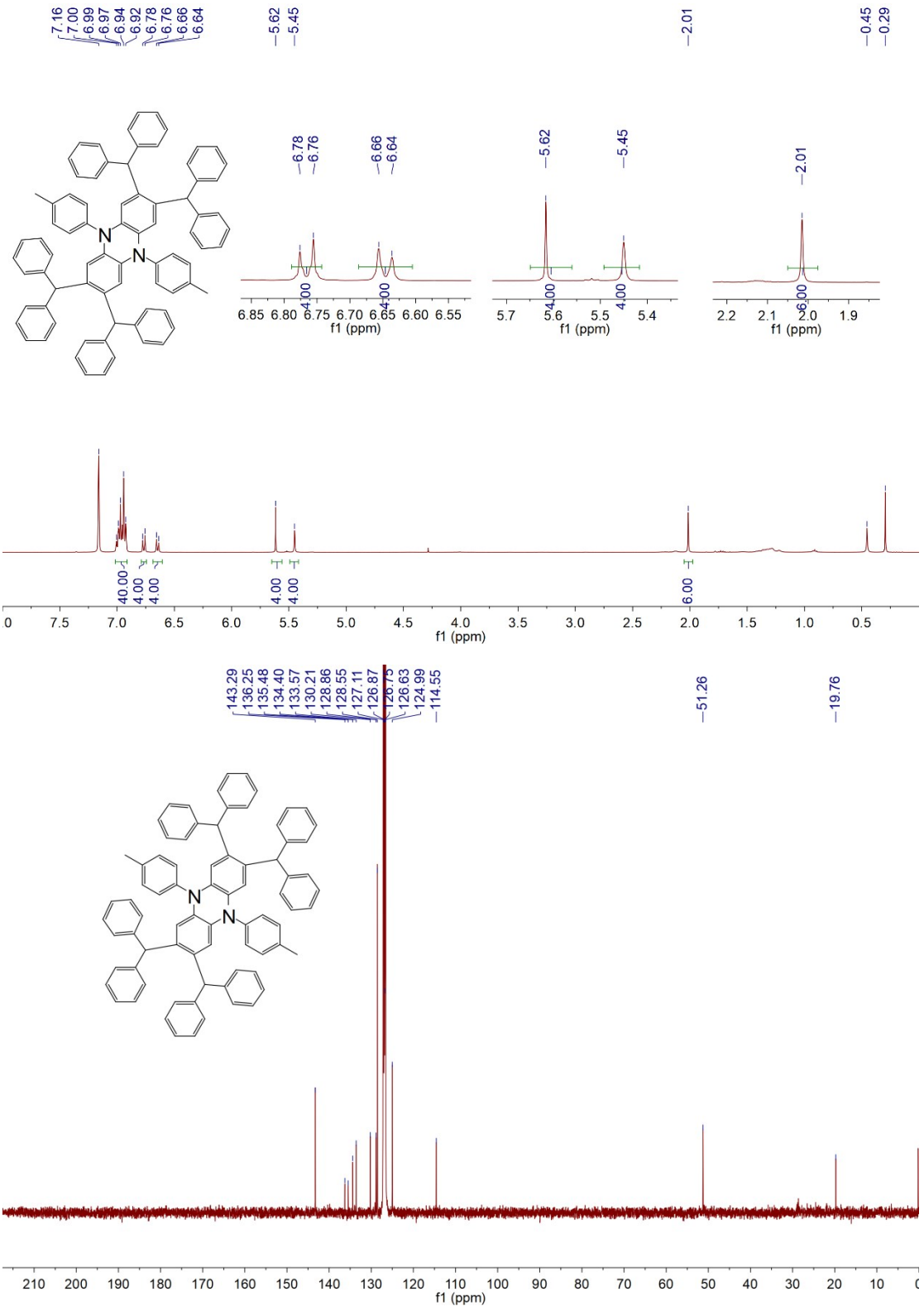
Product **3n**


7.16
7.15
7.05
7.04
7.03
7.02
6.33
6.31
5.96
5.75
5.73
3.85
3.83
3.81
3.80
1.34
0.84
0.82
0.80
8.00
2.00
2.00
2.00
2.00
4.00
12.01
6.00
f1 (ppm)
175.67
140.35
137.88
136.57
135.36
131.13
130.99
127.94
127.70
127.58
127.46
117.83
112.57
110.64
60.07
45.45
26.10
13.79
f1 (ppm)

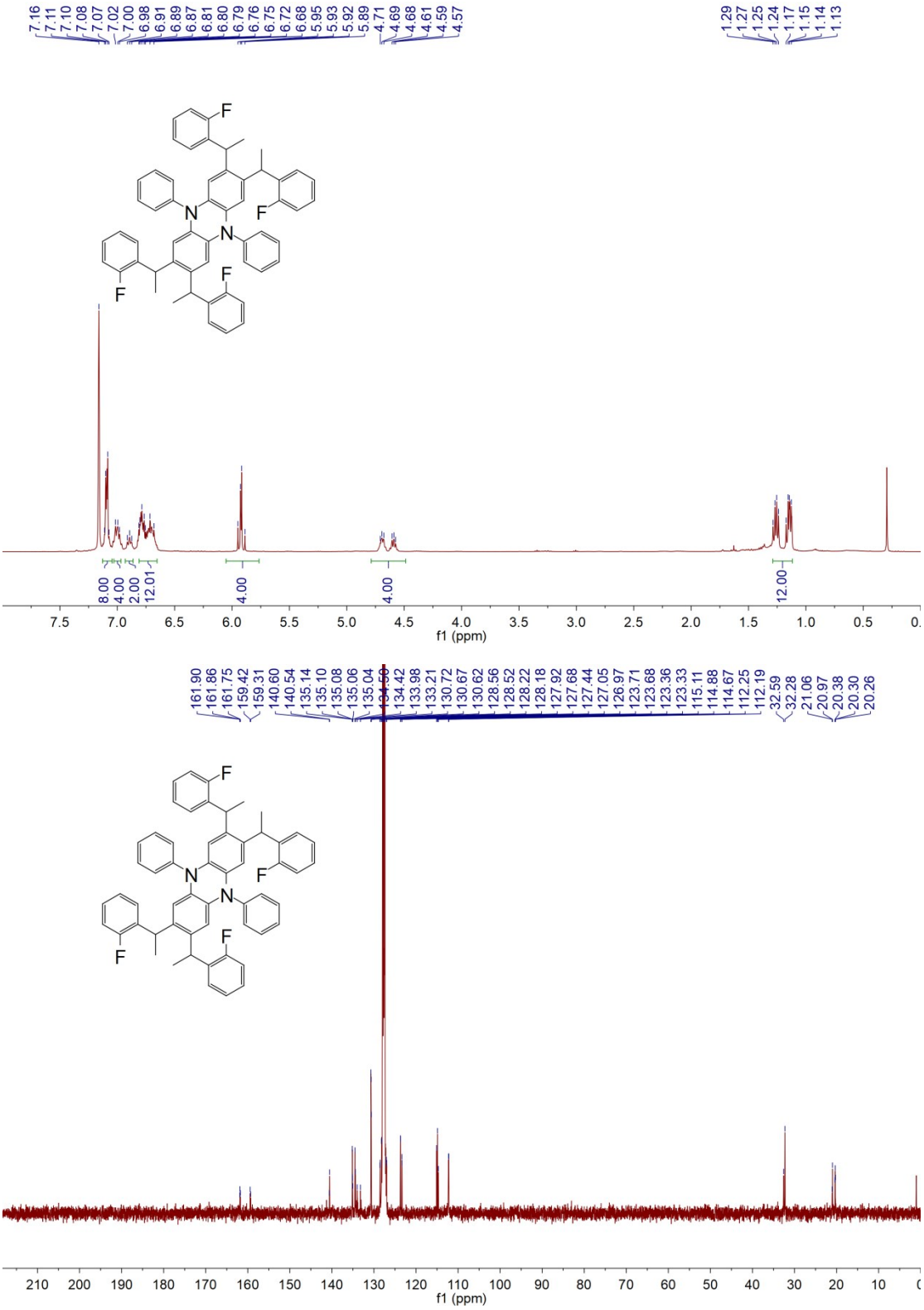
Product **3o**

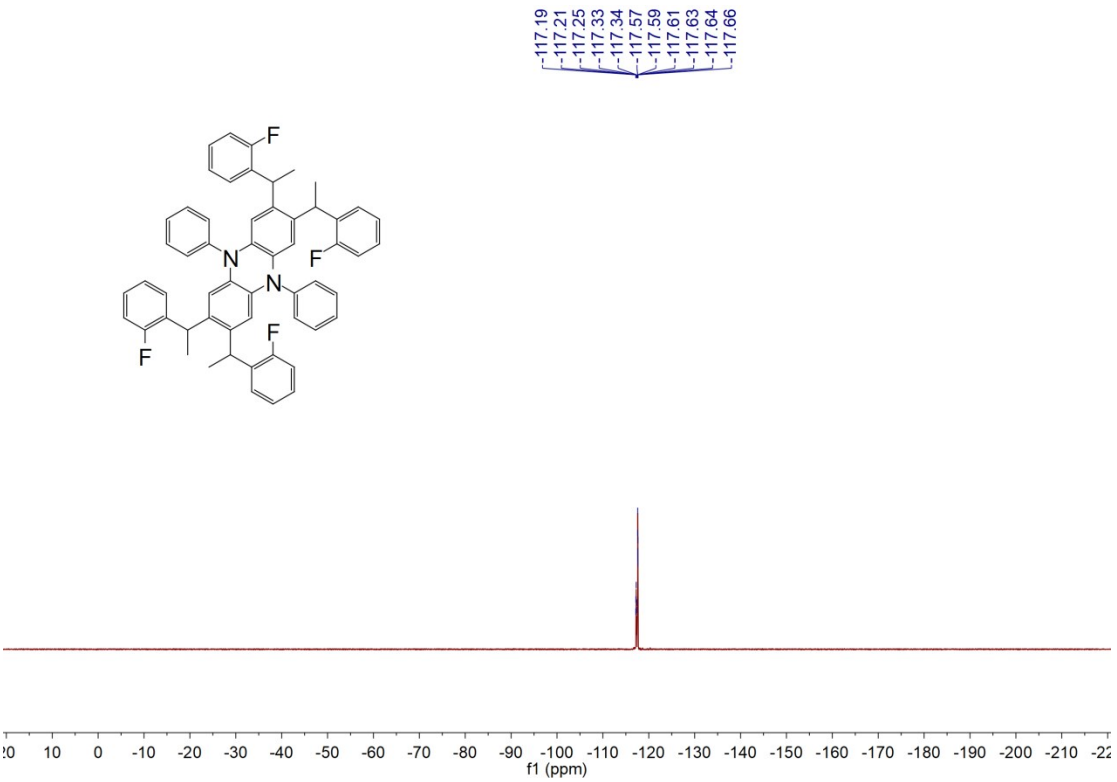

7.16
7.13
7.12
7.12
7.11
7.09
7.04
7.00
6.92
6.09
6.08
6.06
6.05
5.94
5.91
5.89
4.18
4.16
4.11
4.10
4.00
2.05
2.05
2.02
2.00
1.96
1.95
1.93
1.31
1.29
1.28
1.26
1.13
1.12
1.11
1.11
1.10
1.09
0.30
N
N
28.00
4.00
4.00
6.02
12.00
f1 (ppm)
146.58
146.54
146.51
146.47
146.08
146.05
146.01
137.20
134.52
134.50
134.47
130.60
130.56
130.54
129.78
129.72
129.66
127.34
127.10
126.86
126.75
126.62
124.75
124.61
111.62
111.59
111.54
111.49
111.47
38.58
38.38
38.33
38.31
21.23
21.07
21.01
19.86
N
N
f1 (ppm)

Product **3p**

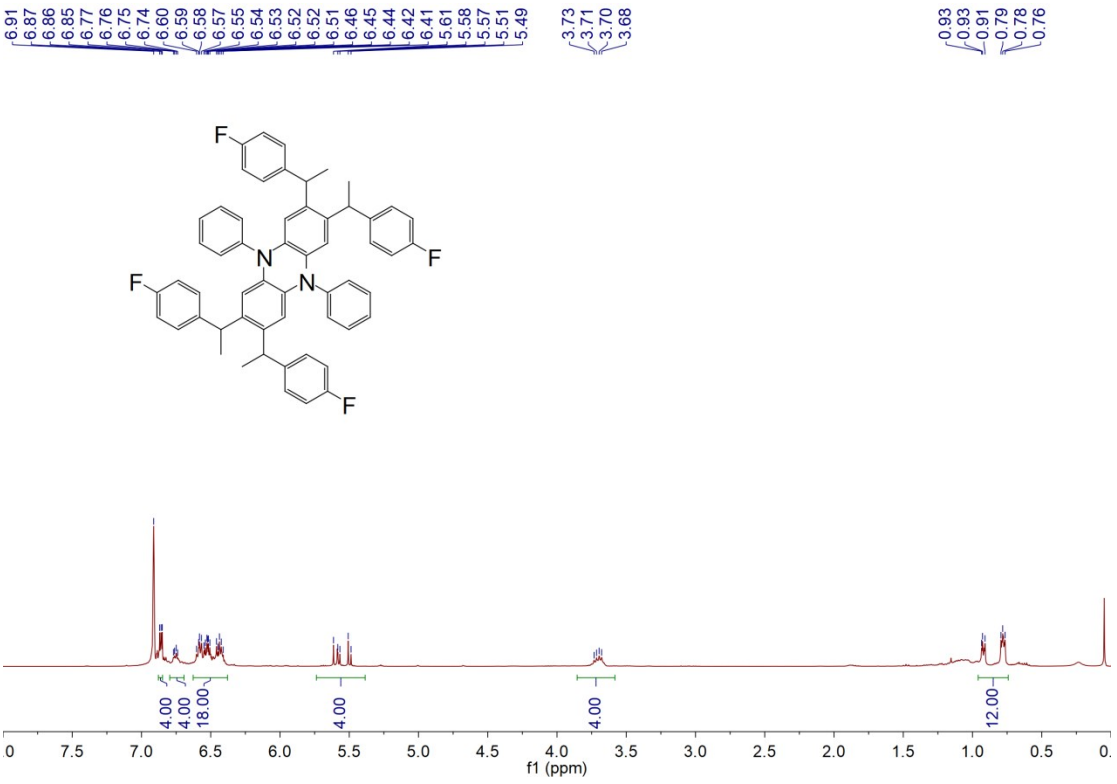

7.16
7.00
6.99
6.97
6.94
6.92
6.78
6.76
6.66
6.64
5.62
5.45
2.01
0.45
0.29
f1 (ppm)
40.00
4.00
4.00
4.00
4.00
6.00
143.29
136.25
135.48
134.40
133.57
130.21
128.86
128.55
127.11
126.87
126.75
126.63
124.99
114.55
51.26
19.76

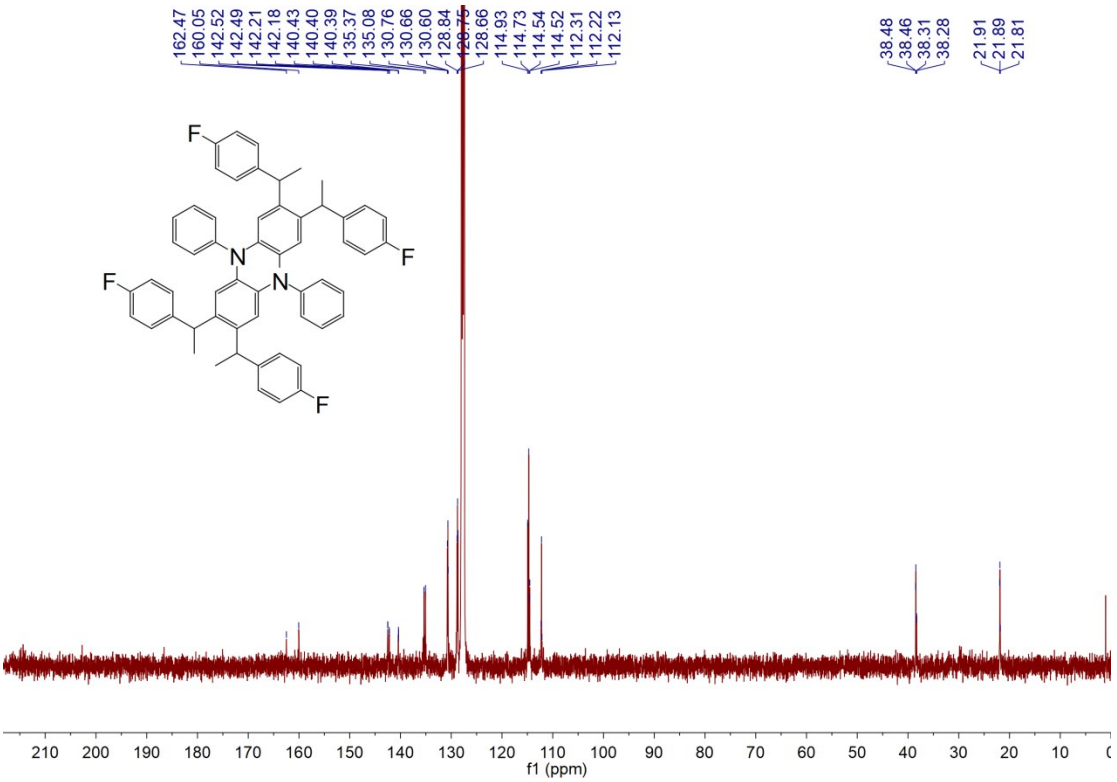
Product **3r**

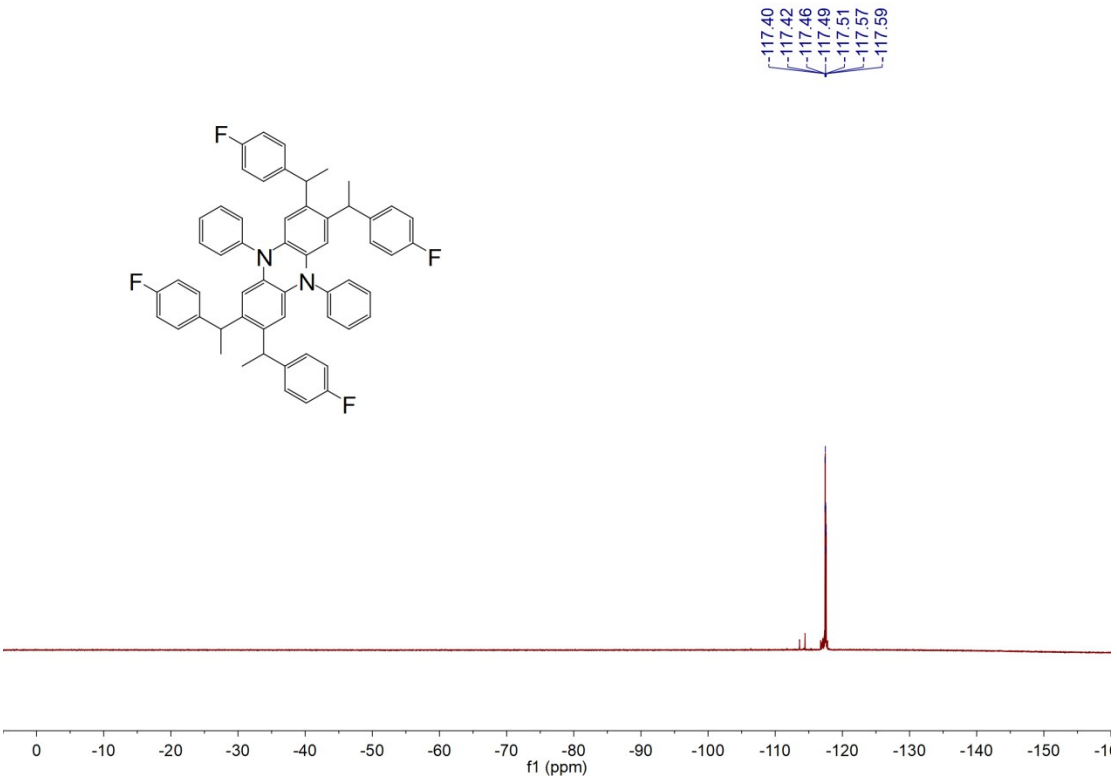

7.16
7.11
7.10
7.08
7.07
7.02
7.00
6.98
6.91
6.89
6.87
6.81
6.80
6.79
6.76
6.75
6.72
6.68
5.95
5.93
5.92
5.89
4.71
4.69
4.68
4.61
4.59
4.57
1.29
1.27
1.25
1.24
1.17
1.15
1.14
1.13
F
N
N
F
F
F
8.00
4.00
2.00
12.01
4.00
4.00
12.00
f1 (ppm)
161.90
161.86
161.75
159.42
159.31
140.60
140.54
135.14
135.10
135.08
135.06
135.04
134.60
134.42
133.98
133.21
130.72
130.67
130.62
128.56
128.52
128.22
128.18
127.92
127.68
127.44
127.05
126.97
123.71
123.68
123.36
123.33
115.11
114.88
114.67
112.25
112.19
32.59
32.28
21.06
20.97
20.38
20.30
20.26
f1 (ppm)


-117.19
-117.21
-117.25
-117.33
-117.34
-117.57
-117.59
-117.61
-117.63
-117.64
-117.66
F
N
N
F
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

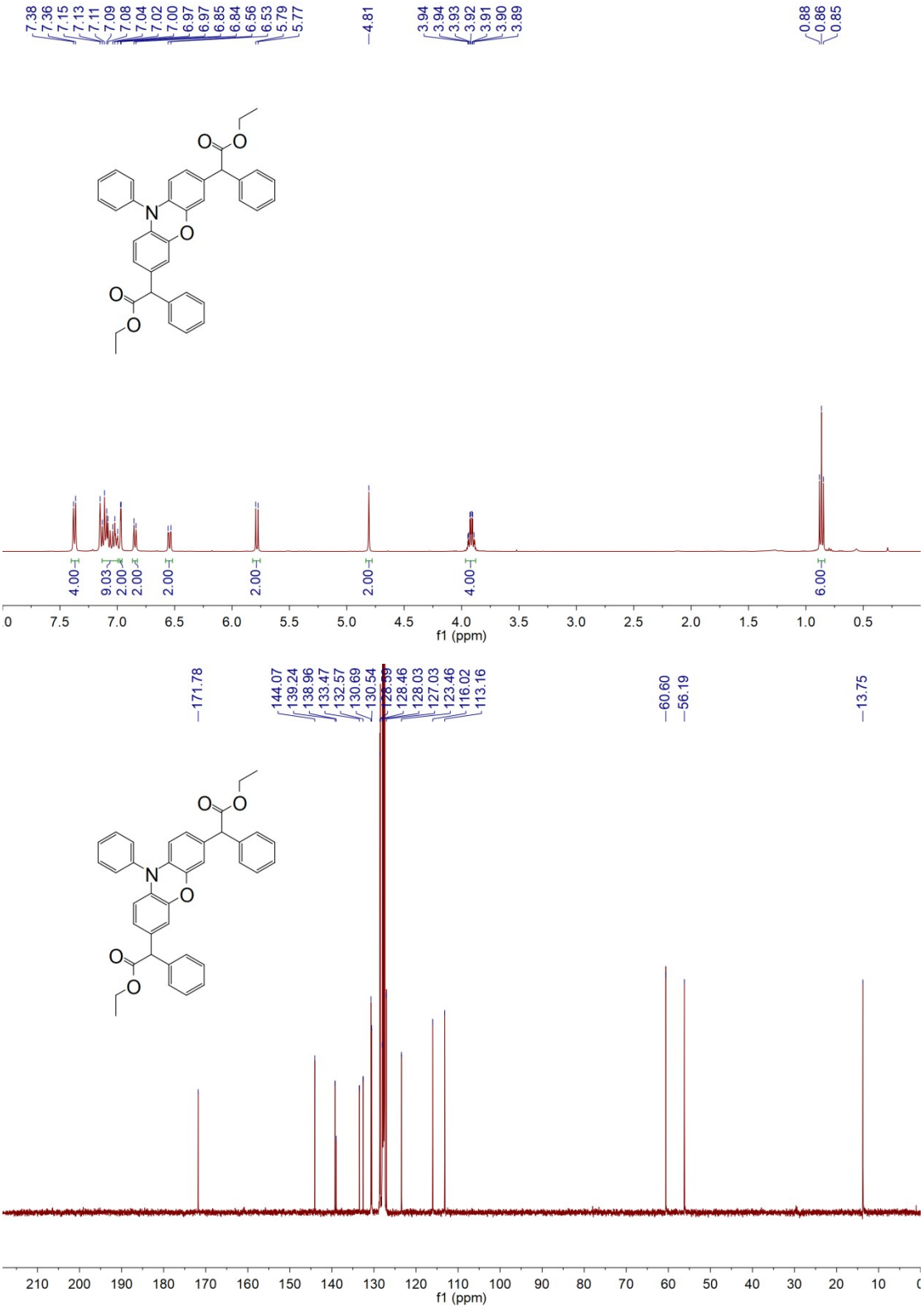
Product **3s**


6.91
6.87
6.86
6.85
6.77
6.76
6.75
6.74
6.60
6.59
6.58
6.57
6.55
6.54
6.53
6.52
6.52
6.51
6.46
6.45
6.44
6.42
6.41
5.61
5.58
5.57
5.51
5.49
3.73
3.71
3.70
3.68
0.93
0.93
0.91
0.79
0.78
0.76
F
N
N
F
F
F
4.00
4.00
18.00
4.00
4.00
12.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

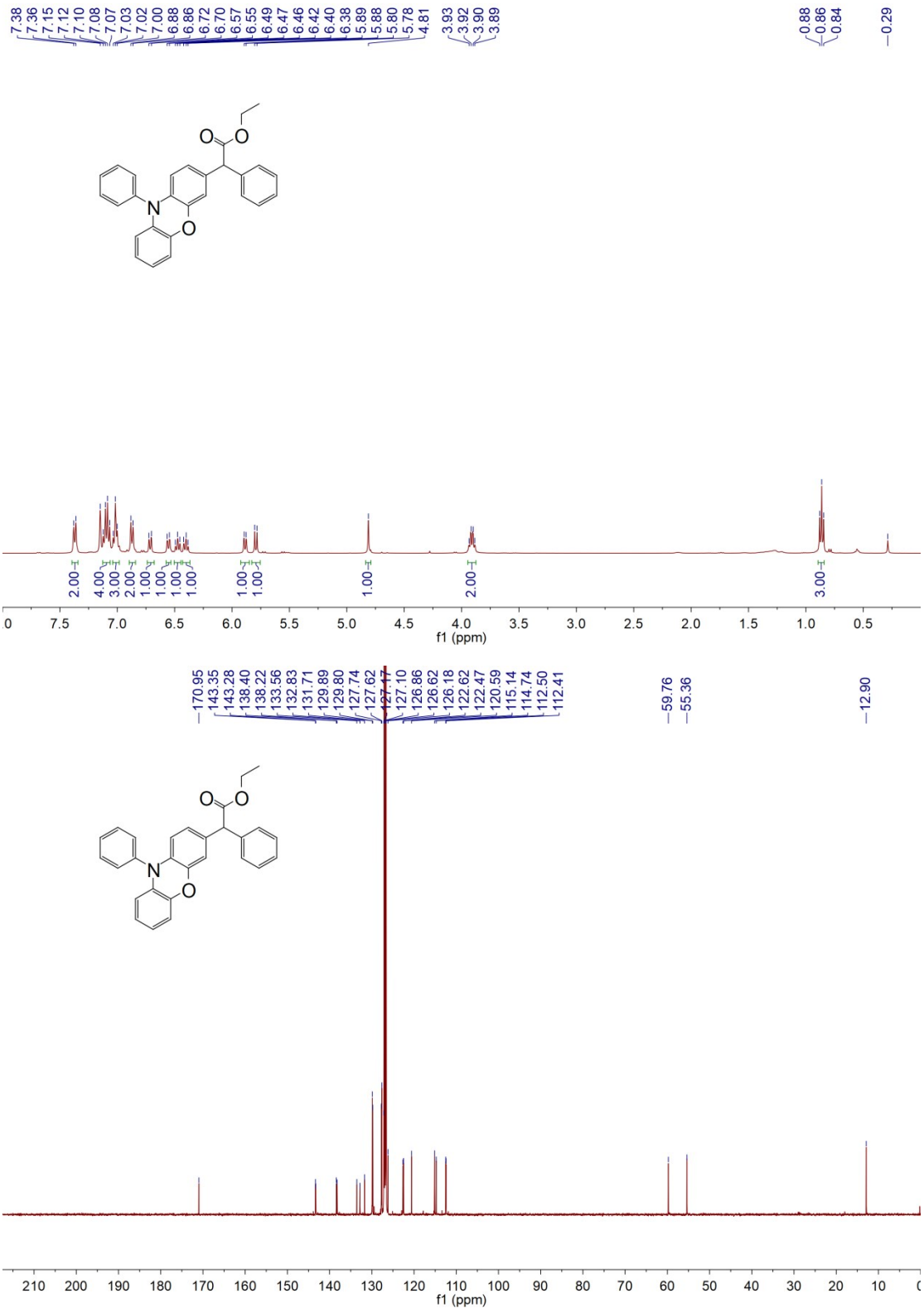

162.47
160.05
142.52
142.49
142.21
142.18
140.43
140.40
140.39
135.37
135.08
130.76
130.66
130.60
128.84
128.75
128.66
114.93
114.73
114.54
114.52
112.31
112.22
112.13
38.48
38.46
38.31
38.28
21.91
21.89
21.81
F
F
F
F
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-117.40
-117.42
-117.46
-117.49
-117.51
-117.57
-117.59
F
F
F
F
N
N
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

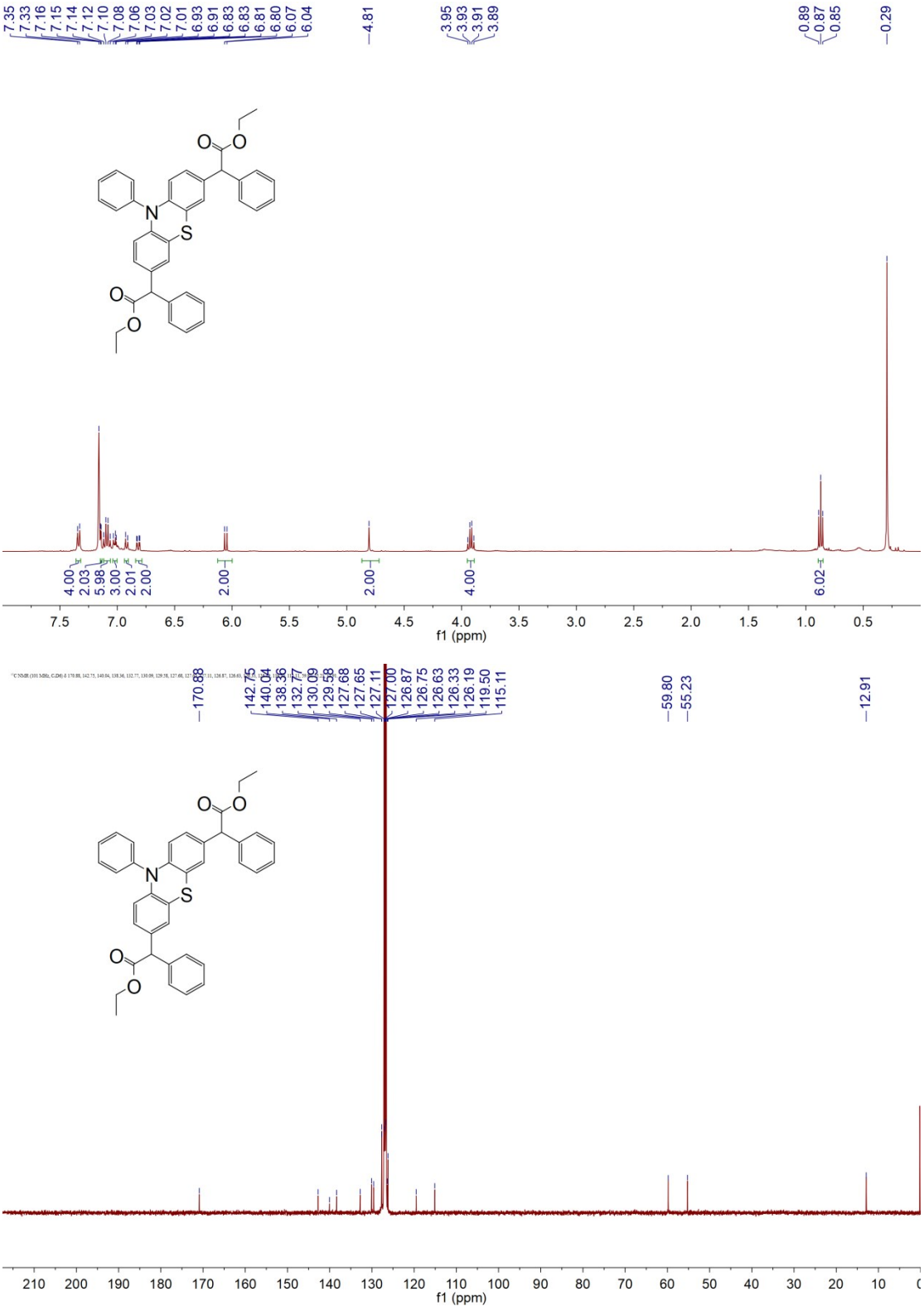
Product **6a**


7.38
7.36
7.15
7.13
7.11
7.09
7.08
7.04
7.02
7.00
6.97
6.97
6.85
6.84
6.56
6.53
5.79
5.77
4.81
3.94
3.94
3.93
3.92
3.91
3.90
3.89
0.88
0.86
0.85
O
O
N
O
O
O
4.00
9.03
2.00
2.00
2.00
2.00
2.00
4.00
6.00
f1 (ppm)
171.78
144.07
139.24
138.96
133.47
132.57
130.69
130.54
128.46
128.03
127.03
123.46
116.02
113.16
60.60
56.19
13.75
f1 (ppm)

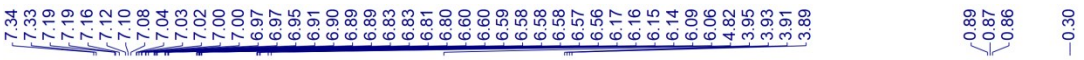
Product **6b**

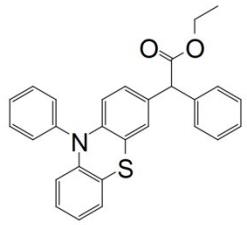

7.38
7.36
7.15
7.12
7.10
7.08
7.07
7.03
7.02
7.00
6.88
6.86
6.72
6.70
6.57
6.55
6.49
6.47
6.46
6.42
6.40
6.38
5.89
5.88
5.80
5.78
4.81
3.93
3.92
3.90
3.89
0.88
0.86
0.84
0.29
O
O
N
O
2.00
4.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)
170.95
143.35
143.28
138.40
138.22
133.56
132.83
131.71
129.89
129.80
127.74
127.62
127.47
127.10
126.86
126.62
126.18
122.62
122.47
120.59
115.14
114.74
112.50
112.41
59.76
55.36
12.90
f1 (ppm)

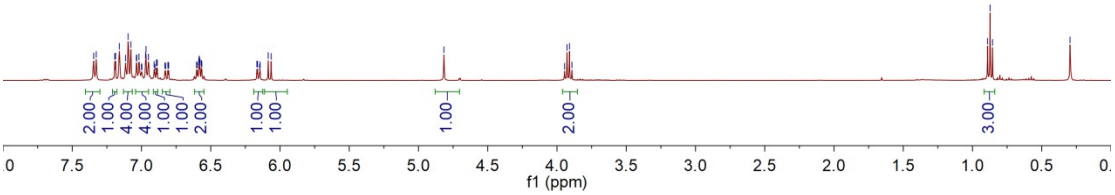
Product **7a**


7.35
7.33
7.16
7.15
7.14
7.12
7.10
7.08
7.06
7.03
7.02
7.01
6.93
6.91
6.83
6.81
6.80
6.07
6.04
4.81
3.95
3.93
3.91
3.89
0.89
0.87
0.85
0.29
O
O
N
S
O
O
4.00
2.03
5.98
3.00
2.01
2.00
2.00
2.00
4.00
6.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
170.88
142.75
140.04
138.36
132.77
130.09
129.58
127.68
127.65
127.11
127.00
126.87
126.75
126.63
126.33
126.19
119.50
115.11
59.80
55.23
12.91
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

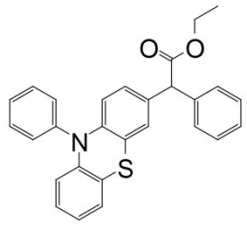
Product **7b**

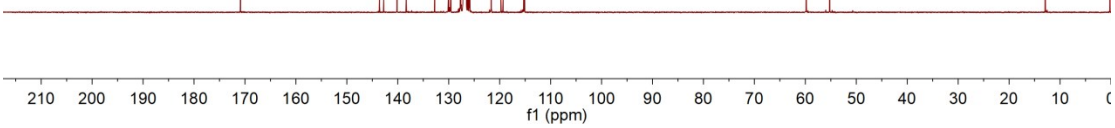

7.34
7.33
7.19
7.19
7.16
7.12
7.10
7.08
7.04
7.03
7.02
7.00
7.00
6.97
6.97
6.95
6.91
6.90
6.89
6.89
6.83
6.83
6.81
6.80
6.60
6.60
6.59
6.58
6.58
6.58
6.57
6.56
6.17
6.16
6.15
6.14
6.09
6.06
4.82
3.95
3.93
3.91
3.89
0.89
0.87
0.86
0.30


O
O
N
S


2.00
1.00
4.00
4.00
1.00
1.00
2.00
1.00
1.00
1.00
2.00
3.00
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


170.89
143.58
142.77
140.15
138.34
132.76
130.06
129.61
127.68
127.66
127.10
126.97
126.86
126.62
126.33
126.19
126.12
125.97
125.87
121.65
119.75
119.33
115.26
115.11
59.81
55.22
12.91


O
O
N
S


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Computational Details

Mechanistic Study: For the mechanistic study, the geometries were optimized without symmetry constraint within the DFT (density functional theory) framework using the BP86 functional[4, 5] in combination with the Grimme Dispersion corrections with the Becke-Johnson damping function D3(BJ)[6, 7] and the Ahlrichs def2-SVP basis function[8], which included solvation effect of experimentally used dimethylacetamide with the CPCM solvent model[9, 10]. Frequency consequences were examined at the same level to confirm the stationary points as transition states (only one imaginary frequency) or minima (no imaginary frequencies). The energetic results were further improved by the single point calculations by using the larger basis set def2-TZVPP[11], which denoted as BP86+D3(BJ)/def2-TZVPP(CPCM, SOL=DMAC)//BP86+D3(BJ)/def2-SVP(CPCM, SOL=DMAC) level of theory. These calculations were performed using Gaussian 16 A03 software[12].

Photophysical Properties: Standard reduction potentials (E^0) were calculated following previously reported procedures[13-16]. A value of -100.5 kcal/mol was assumed for the reduction free energy of the standard hydrogen electrode (SHE) as described in Ref. 13. Thus, E^0 = (-100.5 - ΔG_{red})/23.06 (V vs. SHE); for E^0 ($PC^{\bullet+}/{}^3PC^*$), ΔG_{red} = G($^3PC^*$) - G($PC^{\bullet+}$) while for E^0 ($PC^{\bullet+}$/PC), ΔG_{red} = G(PC) - G($PC^{\bullet+}$). The Gibbs free energies of $^3PC^*$, $PC^{\bullet+}$, and PC were calculated at the unrestricted M06[16]/6-31G**[17] level of theory, the energetic results were further improved by the single point calculations by using the larger basis set 6-311+G** in CPCM-H2O solvent, which denoted as uM06/6-311+G**(CPCM, SOL= H2O)//uM06/6-31G** level of theory. To reference to the Saturated Calomel Electrode (SCE), E^0 (vs. SHE) is converted to E^0 (vs. SCE) using E^0 (vs. SCE) = E^0 (vs. SHE) - 0.24 V. Triplet energies (in eV) of PCs were obtained by [G($^3PC^*$) - G(PC), in kcal/mol]/23.06.

All coordinates are reported as XYZ Cartesian coordinates.

Coordinates and energies (in hatree) of the calculated structures at the BP86+D3(BJ)/def2-TZVPP(CPCM, SOL=DMAC)//BP86+D3(BJ)/def2-SVP(CPCM, SOL=DMAC) level of theory.

1a

Free Energy = -1264.179733

Energy = -1264.529264

N	1.402613000	-0.000011000	-0.059230000
C	0.713518000	1.229119000	-0.030637000
C	1.398390000	2.458343000	-0.060789000
H	2.496124000	2.451648000	-0.108120000
C	0.698725000	3.683704000	-0.030599000
O	7.002549000	-0.000070000	-0.425289000

C	-0.698667000	3.683716000	0.030486000
C	-1.398352000	2.458367000	0.060713000
H	-2.496086000	2.451691000	0.108034000
C	2.834089000	-0.000023000	-0.126563000
C	3.485038000	-0.000105000	-1.378068000
H	2.882308000	-0.000157000	-2.298826000
C	4.880991000	-0.000117000	-1.446238000
H	5.404717000	-0.000179000	-2.413954000
C	5.653102000	-0.000044000	-0.258865000
C	5.003122000	0.000040000	0.996824000
H	5.577632000	0.000095000	1.932935000
C	3.599149000	0.000049000	1.051524000
H	3.086507000	0.000111000	2.025437000
C	7.829717000	0.000097000	0.736462000
H	8.873837000	0.000139000	0.373552000
H	7.659482000	0.905648000	1.359151000
H	7.659613000	-0.905362000	1.359320000
C	0.713500000	-1.229131000	-0.030608000
N	-1.402613000	0.000011000	0.059230000
C	-0.713518000	-1.229119000	0.030637000
C	-1.398390000	-2.458343000	0.060789000
H	-2.496124000	-2.451648000	0.108120000
C	-0.698725000	-3.683704000	0.030598000
O	-7.002549000	0.000070000	0.425289000
C	0.698667000	-3.683716000	-0.030487000
C	1.398352000	-2.458367000	-0.060713000
H	2.496086000	-2.451691000	-0.108035000

C	-2.834089000	0.000023000	0.126564000
C	-3.485038000	0.000105000	1.378068000
H	-2.882309000	0.000157000	2.298826000
C	-4.880991000	0.000117000	1.446239000
H	-5.404717000	0.000179000	2.413954000
C	-5.653102000	0.000044000	0.258865000
C	-5.003122000	-0.000040000	-0.996824000
H	-5.577631000	-0.000095000	-1.932935000
C	-3.599149000	-0.000049000	-1.051523000
H	-3.086507000	-0.000111000	-2.025436000
C	-7.829717000	-0.000097000	-0.736462000
H	-8.873837000	-0.000139000	-0.373552000
H	-7.659482000	-0.905648000	-1.359151000
H	-7.659613000	0.905362000	-1.359320000
C	-0.713500000	1.229131000	0.030608000
H	-1.262316000	-4.628970000	0.055339000
H	1.262243000	-4.628991000	-0.055198000
H	-1.262243000	4.628991000	0.055197000
H	1.262316000	4.628970000	-0.055340000

^{3}1a*

Free Energy = -1264.108758

Energy = -1264.451265

N	1.390469000	-0.000004000	-0.070091000
C	0.717444000	1.216778000	-0.035322000
C	1.425843000	2.451963000	-0.062249000

H	2.521962000	2.441508000	-0.105534000
C	0.707768000	3.658015000	-0.030050000
O	6.991550000	-0.000023000	-0.424202000
C	-0.707756000	3.658019000	0.029885000
C	-1.425835000	2.451971000	0.062138000
H	-2.521954000	2.441521000	0.105415000
C	2.833953000	-0.000008000	-0.135619000
C	3.470519000	-0.000069000	-1.389591000
H	2.865400000	-0.000112000	-2.308281000
C	4.875322000	-0.000072000	-1.454178000
H	5.402116000	-0.000118000	-2.419609000
C	5.639611000	-0.000014000	-0.259693000
C	4.993748000	0.000048000	0.996075000
H	5.568137000	0.000092000	1.931842000
C	3.580413000	0.000050000	1.053398000
H	3.062434000	0.000097000	2.023714000
C	7.815967000	0.000055000	0.738265000
H	8.861241000	0.000051000	0.378129000
H	7.644466000	0.905179000	1.361662000
H	7.644496000	-0.905007000	1.361762000
C	0.717440000	-1.216782000	-0.035273000
N	-1.390469000	0.000004000	0.070091000
C	-0.717444000	-1.216778000	0.035322000
C	-1.425843000	-2.451963000	0.062249000
H	-2.521962000	-2.441508000	0.105534000
C	-0.707768000	-3.658015000	0.030050000
O	-6.991550000	0.000023000	0.424202000

C	0.707756000	-3.658019000	-0.029885000
C	1.425835000	-2.451971000	-0.062138000
H	2.521954000	-2.441521000	-0.105415000
C	-2.833953000	0.000008000	0.135619000
C	-3.470519000	0.000069000	1.389591000
H	-2.865400000	0.000112000	2.308281000
C	-4.875322000	0.000072000	1.454178000
H	-5.402116000	0.000118000	2.419609000
C	-5.639611000	0.000014000	0.259693000
C	-4.993748000	-0.000048000	-0.996075000
H	-5.568137000	-0.000092000	-1.931842000
C	-3.580413000	-0.000050000	-1.053398000
H	-3.062434000	-0.000097000	-2.023714000
C	-7.815967000	-0.000055000	-0.738265000
H	-8.861241000	-0.000051000	-0.378129000
H	-7.644466000	-0.905179000	-1.361662000
H	-7.644496000	0.905007000	-1.361762000
C	-0.717440000	1.216782000	0.035273000
H	-1.254922000	-4.612873000	0.051979000
H	1.254907000	-4.612880000	-0.051767000
H	-1.254907000	4.612880000	0.051767000
H	1.254922000	4.612873000	-0.051979000

2a

Free Energy = -3112.693203

Energy = -3112.833354

O	-2.251035000	-0.753803000	-0.351219000
O	-1.002681000	-0.919305000	1.538904000
C	-0.072584000	0.128302000	-0.471537000
H	-0.362047000	0.079283000	-1.535052000
C	-1.134916000	-0.574741000	0.376472000
C	-3.379275000	-1.368264000	0.335978000
H	-3.057378000	-2.359465000	0.718245000
H	-3.635061000	-0.739096000	1.214380000
C	-4.522509000	-1.473122000	-0.653317000
H	-5.399596000	-1.936134000	-0.158374000
H	-4.822234000	-0.472250000	-1.024189000
H	-4.242458000	-2.103059000	-1.521596000
C	1.338331000	-0.328520000	-0.258859000
C	2.101688000	-0.719203000	-1.380297000
H	1.652585000	-0.672432000	-2.385254000
C	3.423518000	-1.168482000	-1.220508000
H	4.008189000	-1.472468000	-2.102548000
C	3.995273000	-1.225590000	0.062071000
H	5.032114000	-1.574076000	0.189441000
C	3.240632000	-0.830921000	1.184030000
H	3.687653000	-0.870532000	2.189641000
C	1.921118000	-0.382794000	1.028093000
H	1.329894000	-0.072525000	1.900805000
Br	-0.275131000	2.092503000	-0.028564000

^{2}1a$^{\bullet+}$ Br^{-}

Free Energy = -3838.642461

Energy = -3838.989351

N	2.157825000	0.214618000	-0.074913000
C	1.730831000	1.540513000	-0.072358000
C	2.654679000	2.610786000	-0.123232000
H	3.728744000	2.387228000	-0.156897000
C	2.200961000	3.931140000	-0.132525000
O	7.641536000	-0.898182000	-0.375724000
C	0.816245000	4.211633000	-0.095797000
C	-0.112412000	3.170945000	-0.042583000
H	-1.190029000	3.378778000	-0.016613000
C	3.572181000	-0.071956000	-0.127692000
C	4.210149000	-0.209069000	-1.376015000
H	3.628899000	-0.097056000	-2.303115000
C	5.577801000	-0.486461000	-1.423505000
H	6.100200000	-0.598509000	-2.384900000
C	6.321908000	-0.629883000	-0.225836000
C	5.672077000	-0.490492000	1.023221000
H	6.224411000	-0.596679000	1.966183000
C	4.297258000	-0.211556000	1.064938000
H	3.784151000	-0.101523000	2.031779000
C	8.444402000	-1.054970000	0.795156000
H	9.469585000	-1.264069000	0.439624000
H	8.451414000	-0.128855000	1.409863000
H	8.091969000	-1.905362000	1.418246000
C	1.248453000	-0.841280000	-0.031117000
N	-0.581574000	0.772205000	0.036889000

C	-0.156613000	-0.556151000	0.032585000
C	-1.084285000	-1.622207000	0.096147000
H	-2.172614000	-1.438032000	0.148891000
C	-0.629072000	-2.941247000	0.080535000
O	-6.111276000	1.500738000	0.468374000
C	0.753084000	-3.226602000	0.008241000
C	1.684553000	-2.186957000	-0.043731000
H	2.760251000	-2.399267000	-0.094694000
C	-1.997031000	1.045408000	0.110899000
C	-2.588035000	1.315644000	1.359958000
H	-1.962199000	1.364809000	2.263326000
C	-3.970706000	1.492617000	1.441700000
H	-4.461834000	1.682642000	2.407342000
C	-4.774172000	1.380158000	0.281353000
C	-4.165923000	1.146648000	-0.973260000
H	-4.767204000	1.066966000	-1.887944000
C	-2.777583000	0.979914000	-1.052484000
H	-2.298261000	0.771202000	-2.020335000
C	-6.975130000	1.182709000	-0.624498000
H	-8.006741000	1.264891000	-0.236263000
H	-6.790603000	0.145006000	-0.978048000
H	-6.848164000	1.893256000	-1.470048000
C	0.325704000	1.825584000	-0.022226000
H	-1.374549000	-3.749846000	0.125042000
H	1.105623000	-4.268682000	-0.003344000
H	0.462481000	5.252972000	-0.111080000
H	2.930662000	4.753187000	-0.172677000

Br	-4.623371000	-2.484870000	-0.011904000

I

Free Energy = -538.2190206

Energy = -538.3611156

O	2.437232000	-0.443183000	-0.000082000
O	1.213506000	1.479379000	-0.000191000
C	0.131323000	-0.686838000	0.000037000
H	0.399263000	-1.754693000	0.000117000
C	1.257116000	0.246147000	-0.000029000
C	3.640350000	0.358373000	-0.000170000
H	3.631081000	1.020480000	-0.893059000
H	3.630612000	1.021401000	0.892021000
C	4.830467000	-0.582939000	0.000603000
H	5.771791000	0.002657000	0.000507000
H	4.825774000	-1.230742000	0.900649000
H	4.826196000	-1.231707000	-0.898750000
C	-1.252194000	-0.343463000	-0.000007000
C	-2.221402000	-1.401869000	0.000068000
H	-1.866863000	-2.444880000	0.000156000
C	-3.589234000	-1.125501000	0.000029000
H	-4.316052000	-1.952624000	0.000087000
C	-4.042302000	0.211763000	-0.000085000
H	-5.121726000	0.428812000	-0.000116000
C	-3.106743000	1.269391000	-0.000159000
H	-3.461375000	2.312098000	-0.000247000

C	-1.735152000	1.007855000	-0.000121000
H	-0.997993000	1.822122000	-0.000177000

TS1

Free Energy = -4376.851638

Energy = -4377.366008

N	-1.821597000	-1.595020000	-0.490342000
C	-1.354722000	-2.836980000	-0.006521000
C	-2.252557000	-3.860627000	0.355534000
H	-3.331728000	-3.687394000	0.252243000
C	-1.770132000	-5.082426000	0.843548000
O	-7.324934000	-0.941056000	-1.337651000
C	-0.383891000	-5.284979000	0.974893000
C	0.519901000	-4.274944000	0.617992000
H	1.601483000	-4.430796000	0.723653000
C	-3.244258000	-1.415369000	-0.679554000
C	-3.832046000	-1.796925000	-1.901105000
H	-3.206976000	-2.225563000	-2.698280000
C	-5.204810000	-1.624993000	-2.089376000
H	-5.687612000	-1.913117000	-3.034670000
C	-6.005168000	-1.069659000	-1.059969000
C	-5.405950000	-0.689120000	0.163796000
H	-6.001029000	-0.255063000	0.977869000
C	-4.025933000	-0.866229000	0.347011000
H	-3.556964000	-0.567036000	1.295559000
C	-8.181614000	-0.383390000	-0.339930000

H	-9.196763000	-0.373706000	-0.776332000
H	-8.185519000	-1.001842000	0.583678000
H	-7.882796000	0.656114000	-0.083406000
C	-0.966359000	-0.566448000	-0.785632000
N	0.928547000	-2.011342000	-0.234373000
C	0.462436000	-0.759015000	-0.644598000
C	1.323084000	0.300335000	-0.932646000
H	2.407948000	0.162541000	-0.844358000
C	0.810313000	1.587731000	-1.238368000
O	6.459967000	-2.827283000	0.175749000
C	-0.593702000	1.744262000	-1.443126000
C	-1.465385000	0.693989000	-1.225313000
H	-2.546980000	0.823896000	-1.351792000
C	2.350778000	-2.228592000	-0.147949000
C	3.067057000	-1.770458000	0.975884000
H	2.547396000	-1.210878000	1.767580000
C	4.444989000	-1.985781000	1.050938000
H	5.027126000	-1.633339000	1.915282000
C	5.123694000	-2.663066000	0.007607000
C	4.399668000	-3.113987000	-1.120591000
H	4.901189000	-3.636637000	-1.945831000
C	3.015655000	-2.888507000	-1.192607000
H	2.445131000	-3.233802000	-2.067812000
C	7.198706000	-3.494146000	-0.847548000
H	8.249804000	-3.513483000	-0.506589000
H	7.137681000	-2.949211000	-1.814731000
H	6.841999000	-4.537053000	-0.993384000

C	0.051013000	-3.040090000	0.120888000
H	1.526343000	2.364653000	-1.570582000
H	-0.990955000	2.725466000	-1.740219000
H	0.002794000	-6.239562000	1.362108000
H	-2.480096000	-5.874294000	1.123315000
Br	3.702344000	3.738111000	-1.175708000
O	-0.492583000	1.034069000	1.775376000
O	1.762147000	1.048562000	2.082615000
C	0.794257000	2.756830000	0.746598000
H	1.831530000	3.035370000	0.475586000
C	0.749486000	1.560109000	1.609644000
C	-0.592261000	-0.161765000	2.596387000
H	0.261322000	-0.827209000	2.358276000
H	-1.526629000	-0.648213000	2.258452000
C	-0.641626000	0.174894000	4.077769000
H	-0.787755000	-0.755093000	4.664022000
H	0.305335000	0.646157000	4.406191000
H	-1.482741000	0.861613000	4.300853000
C	-0.172027000	3.833345000	0.688667000
C	-1.497390000	3.762138000	1.208919000
H	-1.829858000	2.840668000	1.704255000
C	-2.364557000	4.851950000	1.079098000
H	-3.385146000	4.786450000	1.487660000
C	-1.944062000	6.029932000	0.426951000
H	-2.635425000	6.881157000	0.326670000
C	-0.637292000	6.114468000	-0.093923000
H	-0.305573000	7.033069000	-0.602832000

C	0.241341000	5.033711000	0.035881000
H	1.266175000	5.075252000	-0.373835000

TS1'

Free Energy = -1802.372798

Energy = -1802.888289

N	2.007347000	-1.439141000	0.279540000
C	1.467785000	-2.711143000	0.016557000
C	2.291888000	-3.805173000	-0.320095000
H	3.377693000	-3.651770000	-0.384651000
C	1.738887000	-5.072402000	-0.571622000
O	7.565497000	-0.724051000	0.030129000
C	0.349775000	-5.255837000	-0.484458000
C	-0.484362000	-4.172662000	-0.155392000
H	-1.571829000	-4.313250000	-0.089115000
C	3.430571000	-1.251453000	0.193139000
C	4.249105000	-1.525710000	1.307391000
H	3.791401000	-1.884791000	2.241306000
C	5.631312000	-1.340151000	1.220882000
H	6.288113000	-1.547741000	2.078735000
C	6.215698000	-0.874631000	0.017273000
C	5.392101000	-0.599205000	-1.098815000
H	5.819010000	-0.237323000	-2.043670000
C	4.004117000	-0.791235000	-1.002089000
H	3.356021000	-0.579665000	-1.865807000
C	8.208797000	-0.257186000	-1.154805000

H	9.288252000	-0.209323000	-0.922166000
H	8.048970000	-0.953290000	-2.007098000
H	7.851137000	0.756099000	-1.440850000
C	1.200979000	-0.365792000	0.652742000
N	-0.771197000	-1.795198000	0.389486000
C	-0.233225000	-0.532535000	0.712574000
C	-1.033720000	0.534679000	1.092104000
H	-2.118402000	0.384394000	1.160993000
C	-0.493649000	1.874000000	1.274113000
O	-6.310368000	-2.296385000	-0.352465000
C	0.955078000	1.960507000	1.372176000
C	1.759294000	0.888553000	1.017244000
H	2.853049000	0.992098000	1.035506000
C	-2.192097000	-1.933148000	0.239908000
C	-2.759334000	-1.895389000	-1.051377000
H	-2.104625000	-1.755221000	-1.924399000
C	-4.137762000	-2.040132000	-1.218282000
H	-4.596521000	-2.018904000	-2.217555000
C	-4.980337000	-2.196187000	-0.090725000
C	-4.414373000	-2.230901000	1.204013000
H	-5.043832000	-2.356156000	2.095104000
C	-3.021989000	-2.109428000	1.357987000
H	-2.575188000	-2.145449000	2.362877000
C	-7.209032000	-2.437942000	0.746356000
H	-8.223696000	-2.491492000	0.311340000
H	-7.151603000	-1.566404000	1.434564000
H	-7.008109000	-3.368539000	1.320861000

C	0.052371000	-2.891070000	0.089489000
H	-1.062145000	2.531764000	1.958111000
H	1.418713000	2.913031000	1.666399000
H	-0.097523000	-6.243869000	-0.672093000
H	2.401319000	-5.911286000	-0.833223000
O	-2.947289000	1.826183000	-0.942018000
O	-3.160577000	3.589973000	0.497974000
C	-0.982508000	2.926652000	-0.322368000
H	-0.593997000	2.248862000	-1.100551000
C	-2.453164000	2.877479000	-0.217806000
C	-4.342019000	1.477545000	-0.769886000
H	-4.366077000	0.541900000	-0.171339000
H	-4.838942000	2.280578000	-0.190391000
C	-4.979473000	1.269946000	-2.132266000
H	-5.018426000	2.217544000	-2.707387000
H	-4.412791000	0.523032000	-2.723782000
H	-6.014671000	0.891557000	-2.008051000
C	-0.260011000	4.209676000	-0.235697000
C	-0.710193000	5.307232000	0.544074000
H	-1.682355000	5.227642000	1.050212000
C	0.065107000	6.472463000	0.654636000
H	-0.305930000	7.314563000	1.261198000
C	1.309255000	6.572737000	0.003087000
H	1.914578000	7.488231000	0.095549000
C	1.771846000	5.488767000	-0.767393000
H	2.743602000	5.552419000	-1.282927000
C	0.999141000	4.323898000	-0.882264000

H	1.368462000	3.476441000	-1.482269000

IM1

Free Energy = -4376.880394

Energy = -4377.391448

N	2.514418000	-1.106485000	-0.437990000
C	2.243670000	-2.472410000	-0.207917000
C	3.277166000	-3.395831000	0.034551000
H	4.316087000	-3.038362000	0.043806000
C	2.994095000	-4.758260000	0.264639000
O	7.752467000	0.803867000	0.177268000
C	1.668299000	-5.205983000	0.256829000
C	0.622346000	-4.290192000	0.018338000
H	-0.422562000	-4.630622000	0.014378000
C	3.859004000	-0.624141000	-0.311504000
C	4.333321000	-0.191636000	0.945107000
H	3.660980000	-0.227845000	1.815748000
C	5.640811000	0.282041000	1.077057000
H	6.028430000	0.624047000	2.048387000
C	6.498917000	0.330264000	-0.049337000
C	6.023826000	-0.101219000	-1.309111000
H	6.667990000	-0.072828000	-2.198173000
C	4.705959000	-0.574052000	-1.429789000
H	4.328297000	-0.910948000	-2.406979000
C	8.660369000	0.875142000	-0.920591000
H	9.604890000	1.281749000	-0.515190000

H	8.852661000	-0.129299000	-1.357410000
H	8.283918000	1.552133000	-1.718471000
C	1.475234000	-0.182762000	-0.631134000
N	-0.146719000	-2.006277000	-0.458309000
C	0.125627000	-0.645756000	-0.641281000
C	-0.919195000	0.290228000	-0.776907000
H	-1.946411000	-0.091880000	-0.809006000
C	-0.672933000	1.681193000	-0.931165000
O	-5.566762000	-3.436011000	-0.275993000
C	0.655625000	2.118235000	-0.939362000
C	1.712650000	1.193472000	-0.794117000
H	2.750036000	1.554882000	-0.784947000
C	-1.517283000	-2.424816000	-0.378382000
C	-2.194362000	-2.867124000	-1.532965000
H	-1.651062000	-2.928144000	-2.487761000
C	-3.547273000	-3.211865000	-1.464189000
H	-4.093265000	-3.556416000	-2.354881000
C	-4.248431000	-3.109066000	-0.238304000
C	-3.567394000	-2.674258000	0.922191000
H	-4.086162000	-2.587669000	1.886214000
C	-2.205832000	-2.339763000	0.843464000
H	-1.673882000	-1.981592000	1.737908000
C	-6.325594000	-3.334201000	0.928561000
H	-7.355929000	-3.639903000	0.671050000
H	-6.339098000	-2.291363000	1.313761000
H	-5.929451000	-4.009467000	1.717873000
C	0.892585000	-2.930826000	-0.215984000

H	-0.642902000	0.558404000	1.185274000
H	0.888352000	3.187739000	-1.040821000
H	1.430161000	-6.265460000	0.436059000
H	3.823109000	-5.458128000	0.450219000
Br	-0.322915000	0.659831000	2.625541000
O	-3.823164000	1.334068000	-1.188405000
O	-3.314751000	2.192935000	0.847470000
C	-1.851702000	2.654612000	-1.073593000
H	-2.128476000	2.704663000	-2.148552000
C	-3.070521000	2.069794000	-0.340996000
C	-4.917782000	0.578500000	-0.592631000
H	-4.488689000	-0.105417000	0.170599000
H	-5.592411000	1.286744000	-0.068794000
C	-5.614035000	-0.177809000	-1.705430000
H	-6.423626000	-0.803891000	-1.281474000
H	-6.057267000	0.516126000	-2.447880000
H	-4.903408000	-0.851089000	-2.224943000
C	-1.539149000	4.057539000	-0.584117000
C	-1.686619000	5.159723000	-1.448382000
H	-2.022948000	4.993174000	-2.484775000
C	-1.405153000	6.464239000	-1.002399000
H	-1.521298000	7.315388000	-1.691696000
C	-0.975327000	6.677587000	0.318375000
H	-0.752883000	7.697282000	0.670369000
C	-0.826063000	5.580434000	1.188361000
H	-0.486371000	5.740649000	2.223942000
C	-1.103710000	4.279242000	0.741153000

H	-0.977855000	3.422086000	1.419374000

IV

Free Energy = -1801.829968

Energy = -1802.338402

N	-0.179206000	-1.922540000	-0.127828000
C	0.863285000	-2.858729000	0.017898000
C	0.603653000	-4.237706000	0.118067000
H	-0.439267000	-4.582844000	0.083456000
C	1.655503000	-5.167585000	0.259758000
O	-5.588861000	-3.408356000	-0.151286000
C	2.979154000	-4.716505000	0.302978000
C	3.253194000	-3.335410000	0.208592000
H	4.290654000	-2.975280000	0.246576000
C	-1.546188000	-2.353456000	-0.105411000
C	-2.197540000	-2.726787000	-1.299230000
H	-1.634644000	-2.723350000	-2.244705000
C	-3.548492000	-3.086045000	-1.281235000
H	-4.072990000	-3.377788000	-2.203307000
C	-4.275352000	-3.068642000	-0.066198000
C	-3.622709000	-2.701330000	1.133027000
H	-4.161803000	-2.682425000	2.089664000
C	-2.263089000	-2.350120000	1.102869000
H	-1.751543000	-2.051891000	2.030473000
C	-6.370740000	-3.396068000	1.042199000
H	-7.392392000	-3.695440000	0.745357000

H	-5.980890000	-4.118110000	1.792402000
H	-6.404758000	-2.381781000	1.496585000
C	0.086532000	-0.543390000	-0.218238000
N	2.476912000	-1.013296000	-0.017728000
C	1.433060000	-0.078204000	-0.148925000
O	-3.891706000	1.449812000	-0.693433000
C	1.669290000	1.306644000	-0.211814000
H	2.704078000	1.671704000	-0.154121000
O	-3.326455000	2.251645000	1.351178000
C	0.608440000	2.230124000	-0.335341000
O	7.762919000	0.829618000	0.368441000
C	-0.715100000	1.778342000	-0.416677000
C	-0.954022000	0.384802000	-0.369299000
H	-1.978101000	0.001500000	-0.454866000
C	-1.902048000	2.740089000	-0.594221000
H	-2.178039000	2.748946000	-1.670194000
C	-3.110553000	2.156521000	0.153949000
C	-4.979596000	0.688156000	-0.095453000
H	-5.634403000	1.386135000	0.466202000
H	-4.541364000	-0.025835000	0.634382000
C	-5.710035000	-0.024118000	-1.215813000
H	-6.524845000	-0.645988000	-0.795716000
H	-5.021764000	-0.695065000	-1.767512000
H	-6.153216000	0.699093000	-1.929881000
C	-1.609989000	4.166323000	-0.163876000
C	-1.682654000	5.214906000	-1.102176000
H	-1.954583000	4.987485000	-2.145907000

C	-1.408991000	6.541265000	-0.721328000
H	-1.467669000	7.348431000	-1.468437000
C	-1.061351000	6.832943000	0.608731000
H	-0.846002000	7.870139000	0.910382000
C	-0.986381000	5.791245000	1.552913000
H	-0.712390000	6.012588000	2.596687000
C	-1.255650000	4.467708000	1.169769000
H	-1.195596000	3.653894000	1.906493000
C	3.829745000	-0.546101000	0.055101000
C	4.408852000	-0.243564000	1.305431000
H	3.812106000	-0.372210000	2.221095000
C	5.727104000	0.214557000	1.378571000
H	6.194594000	0.454952000	2.345232000
C	6.491498000	0.379536000	0.197609000
C	5.912787000	0.078057000	-1.056729000
H	6.483106000	0.197454000	-1.987753000
C	4.586765000	-0.382479000	-1.116663000
H	4.129709000	-0.619429000	-2.089390000
C	8.578383000	1.014376000	-0.787021000
H	9.555893000	1.378394000	-0.421167000
H	8.142890000	1.769128000	-1.477968000
H	8.727042000	0.060443000	-1.338992000
C	2.214228000	-2.396387000	0.068874000
H	3.813131000	-5.426668000	0.411938000
H	0.833167000	3.305942000	-0.366434000
H	1.422818000	-6.240837000	0.335011000

3a

Free Energy = -3414.796045

Energy = -3415.777184

N	-0.034079000	-1.385080000	0.282875000
C	1.185794000	-0.692470000	0.157576000
O	4.351846000	3.549751000	0.533088000
C	2.416208000	-1.339826000	0.335509000
H	2.385263000	-2.398719000	0.618785000
O	4.618410000	3.495397000	-1.718451000
C	3.656645000	-0.684664000	0.176603000
O	4.618008000	-3.495433000	1.718499000
C	4.960768000	-1.455455000	0.401130000
H	5.556017000	-1.398616000	-0.535043000
O	4.351490000	-3.550475000	-0.533024000
O	0.170118000	-6.974272000	-0.137084000
C	4.651982000	-2.939354000	0.632662000
C	3.800212000	-4.893362000	-0.427739000
H	4.571381000	-5.562992000	0.007084000
H	2.946455000	-4.864924000	0.283462000
C	3.364202000	-5.329932000	-1.811470000
H	2.879821000	-6.324868000	-1.747934000
H	2.624609000	-4.618087000	-2.228758000
H	4.225664000	-5.400032000	-2.505956000
C	5.800900000	-0.900381000	1.541320000
C	5.193749000	-0.407526000	2.713882000
H	4.095430000	-0.405800000	2.792373000

C	5.978595000	0.094379000	3.765052000
H	5.492550000	0.482497000	4.674090000
C	7.381791000	0.105916000	3.656605000
H	7.996827000	0.506485000	4.477703000
C	7.994656000	-0.394730000	2.494052000
H	9.092072000	-0.389059000	2.400767000
C	7.206480000	-0.897127000	1.444145000
H	7.685100000	-1.282664000	0.529929000
C	3.656702000	0.684271000	-0.177335000
C	2.416319000	1.339505000	-0.336353000
H	2.385459000	2.398419000	-0.619578000
C	4.960888000	1.454965000	-0.401724000
H	5.556164000	1.397778000	0.534410000
C	4.652316000	2.938966000	-0.632781000
C	3.800831000	4.892783000	0.428236000
H	4.571986000	5.562311000	-0.006766000
H	2.946801000	4.864653000	-0.282650000
C	3.365448000	5.329185000	1.812214000
H	2.881259000	6.324239000	1.749086000
H	2.625859000	4.617418000	2.229643000
H	4.227197000	5.398939000	2.506378000
C	5.800947000	0.900077000	-1.542066000
C	7.206539000	0.896971000	-1.445004000
H	7.685196000	1.282467000	-0.530790000
C	7.994678000	0.394787000	-2.495036000
H	9.092104000	0.389237000	-2.401854000
C	7.381770000	-0.105804000	-3.657591000

H	7.996792000	-0.506199000	-4.478784000
C	5.978567000	-0.094442000	-3.765907000
H	5.492472000	-0.482527000	-4.674933000
C	5.193752000	0.407252000	-2.714608000
H	4.095426000	0.405396000	-2.792993000
C	-0.027161000	-2.818835000	0.226436000
C	-0.146299000	-3.459498000	-1.026062000
H	-0.273078000	-2.849436000	-1.933100000
C	-0.095243000	-4.851369000	-1.113476000
H	-0.181223000	-5.365556000	-2.081687000
C	0.092189000	-5.631175000	0.053836000
C	0.196966000	-4.993513000	1.311051000
H	0.334262000	-5.575174000	2.232265000
C	0.129235000	-3.590753000	1.387898000
H	0.215721000	-3.088100000	2.362855000
C	0.386759000	-7.808994000	0.999874000
H	0.428240000	-8.845619000	0.618951000
H	1.346726000	-7.565462000	1.505132000
H	-0.443859000	-7.721682000	1.733679000
C	-1.252089000	-0.694736000	0.150860000
N	-0.033960000	1.384992000	-0.283754000
C	-1.252034000	0.694736000	-0.151535000
O	-4.452410000	-3.389766000	-0.924869000
C	-2.480891000	1.349856000	-0.312400000
H	-2.453031000	2.413958000	-0.582245000
O	-4.704598000	-3.680717000	1.311419000
C	-3.718287000	0.689341000	-0.153095000

O	-4.704244000	3.680853000	-1.312356000
C	-5.028313000	1.460611000	-0.318252000
H	-5.647033000	1.267910000	0.583912000
O	-4.451873000	3.390550000	0.923973000
O	0.170694000	6.973908000	0.139888000
C	-4.737751000	2.964890000	-0.324484000
C	-3.936064000	4.744763000	1.043619000
H	-4.718005000	5.456351000	0.705041000
H	-3.067838000	4.850436000	0.357951000
C	-3.541114000	4.962497000	2.490294000
H	-3.126789000	5.983183000	2.613350000
H	-2.763597000	4.235185000	2.798928000
H	-4.413903000	4.856638000	3.165898000
C	-5.825576000	1.043573000	-1.544350000
C	-5.177582000	0.717930000	-2.752723000
H	-4.077953000	0.750463000	-2.800468000
C	-5.923898000	0.339262000	-3.880923000
H	-5.406249000	0.083218000	-4.818850000
C	-7.328416000	0.281944000	-3.813149000
H	-7.912843000	-0.022370000	-4.695614000
C	-7.982148000	0.611753000	-2.612345000
H	-9.080890000	0.567516000	-2.550277000
C	-7.232943000	0.992793000	-1.485656000
H	-7.743596000	1.246519000	-0.542780000
C	-3.718337000	-0.689024000	0.152676000
C	-2.481018000	-1.349714000	0.311823000
H	-2.453292000	-2.413819000	0.581681000

C	-5.028417000	-1.460133000	0.317990000
H	-5.647324000	-1.267109000	-0.583975000
C	-4.738126000	-2.964446000	0.323758000
C	-3.937050000	-4.744106000	-1.045023000
H	-4.719465000	-5.455579000	-0.707296000
H	-3.069242000	-4.850537000	-0.358950000
C	-3.541431000	-4.961124000	-2.491625000
H	-3.127768000	-5.982016000	-2.615187000
H	-2.763284000	-4.234103000	-2.799355000
H	-4.413785000	-4.854217000	-3.167633000
C	-5.825343000	-1.043254000	1.544373000
C	-7.232727000	-0.992601000	1.486089000
H	-7.743655000	-1.246300000	0.543354000
C	-7.981645000	-0.611737000	2.613033000
H	-9.080407000	-0.567613000	2.551269000
C	-7.327596000	-0.281969000	3.813673000
H	-7.911786000	0.022212000	4.696343000
C	-5.923055000	-0.339147000	3.881030000
H	-5.405136000	-0.083131000	4.818816000
C	-5.177026000	-0.717643000	2.752580000
H	-4.077382000	-0.750079000	2.800016000
C	-0.026897000	2.818722000	-0.226315000
C	-0.145510000	3.458554000	1.026663000
H	-0.272018000	2.847902000	1.933341000
C	-0.094278000	4.850358000	1.114969000
H	-0.179825000	5.363929000	2.083547000
C	0.092678000	5.630929000	-0.051907000

C	0.196940000	4.994109000	-1.309585000
H	0.333874000	5.576374000	-2.230468000
C	0.129138000	3.591393000	-1.387317000
H	0.215216000	3.089370000	-2.362634000
C	0.386800000	7.809386000	-0.996621000
H	0.428476000	8.845755000	-0.615026000
H	-0.444169000	7.722563000	-1.730087000
H	1.346524000	7.566186000	-1.502499000
C	1.185857000	0.692241000	-0.158451000

4a

Free Energy = -823.8766361

Energy = -824.0865421

C	-1.970257000	-1.190368000	0.000073000
C	-2.709901000	-2.376593000	0.000810000
H	-3.807927000	-2.303410000	0.001626000
C	-2.052246000	-3.624167000	0.000543000
C	-0.650747000	-3.663494000	-0.000456000
C	0.095780000	-2.468736000	-0.001198000
H	1.194434000	-2.501211000	-0.001975000
C	-1.970257000	1.190368000	0.000076000
N	0.155566000	0.000000000	-0.001783000
C	-0.550096000	1.215759000	-0.000945000
C	0.095780000	2.468736000	-0.001186000
H	1.194434000	2.501211000	-0.001960000
C	-0.650747000	3.663494000	-0.000441000

C	-2.052246000	3.624167000	0.000555000
C	-2.709901000	2.376593000	0.000816000
H	-3.807927000	2.303410000	0.001631000
C	1.589663000	-0.000000000	-0.000649000
C	2.287478000	-0.000024000	1.221783000
H	1.720082000	-0.000043000	2.164657000
C	3.692481000	-0.000025000	1.220154000
H	4.240545000	-0.000044000	2.175018000
C	4.395751000	0.000000000	0.001671000
C	3.694483000	0.000025000	-1.217950000
H	4.244165000	0.000044000	-2.171883000
C	2.289467000	0.000024000	-1.221913000
H	1.723652000	0.000043000	-2.165732000
C	-0.550096000	-1.215759000	-0.000949000
H	-0.120079000	4.627870000	-0.000651000
H	-2.642127000	4.552974000	0.001143000
H	-0.120079000	-4.627870000	-0.000672000
H	-2.642127000	-4.552974000	0.001129000
H	5.496764000	0.000000000	0.002575000
O	-2.676139000	0.000000000	0.000351000

TS2

Free Energy = -3936.543601

Energy = -3936.920408

C	1.907749000	2.428642000	-0.114271000
C	2.260919000	3.735127000	0.241668000

H	1.471817000	4.499702000	0.281721000
C	3.602017000	4.034570000	0.531230000
C	4.582045000	3.028039000	0.453340000
C	4.227599000	1.718836000	0.095055000
H	4.991492000	0.932731000	0.030486000
C	0.176933000	0.895876000	-0.621086000
N	2.466846000	0.094933000	-0.527364000
C	1.138747000	-0.182394000	-0.701180000
C	0.672417000	-1.501283000	-0.984383000
H	1.403538000	-2.313901000	-1.080564000
C	-0.685046000	-1.737743000	-1.126017000
C	-1.631305000	-0.682017000	-0.947876000
C	-1.169730000	0.654186000	-0.815034000
H	-1.893831000	1.480376000	-0.799569000
C	3.464481000	-0.896870000	-0.870476000
C	3.734905000	-1.121409000	-2.232513000
H	3.187751000	-0.551780000	-2.998253000
C	4.701958000	-2.074023000	-2.589913000
H	4.915980000	-2.257883000	-3.653597000
C	5.395078000	-2.785001000	-1.593471000
C	5.122572000	-2.543469000	-0.235519000
H	5.664257000	-3.096307000	0.546617000
C	4.152886000	-1.596551000	0.133156000
H	3.927418000	-1.394953000	1.187397000
C	2.883265000	1.404842000	-0.181349000
H	-2.701754000	-0.812246000	-1.197009000
H	5.634718000	3.260403000	0.671016000

H	3.880262000	5.060739000	0.813340000
Br	-4.702542000	0.690987000	-2.073528000
O	-4.184429000	-1.073532000	1.255098000
O	-3.038282000	0.828017000	1.754981000
C	-1.872288000	-1.252273000	1.307427000
H	-2.122311000	-2.309625000	1.133649000
C	-3.056723000	-0.365241000	1.467015000
C	-5.435619000	-0.334489000	1.343947000
H	-5.552846000	0.023965000	2.389062000
H	-5.356033000	0.538348000	0.662548000
C	-6.550484000	-1.267097000	0.917492000
H	-6.582990000	-2.181538000	1.544368000
H	-7.525075000	-0.746789000	1.012735000
H	-6.417608000	-1.557232000	-0.144256000
C	-0.580803000	-0.972801000	1.860190000
C	-0.142929000	0.347978000	2.193839000
H	-0.852315000	1.177211000	2.078229000
C	1.149297000	0.565320000	2.687361000
H	1.471039000	1.586317000	2.941685000
C	2.034145000	-0.515470000	2.856502000
H	3.044892000	-0.336829000	3.255301000
C	1.625638000	-1.825205000	2.525269000
H	2.316137000	-2.671123000	2.660028000
C	0.348009000	-2.049054000	2.011490000
H	0.032415000	-3.067649000	1.738832000
H	-1.040689000	-2.760026000	-1.321778000
O	0.589857000	2.184697000	-0.420181000

H	6.153202000	-3.530612000	-1.877487000

TS2'

Free Energy = -1362.065939

Energy = -1362.439763

N	2.488586000	-0.249355000	-0.227352000
C	3.224582000	0.940937000	-0.091993000
C	4.549771000	0.963000000	0.392046000
H	5.028879000	0.017047000	0.680507000
C	5.248667000	2.177337000	0.501468000
C	4.633956000	3.386036000	0.133442000
C	3.309375000	3.377596000	-0.342722000
H	2.794432000	4.304945000	-0.634908000
C	3.094071000	-1.508240000	0.113952000
C	3.888145000	-2.177952000	-0.834268000
H	4.035771000	-1.730667000	-1.828578000
C	4.478753000	-3.406689000	-0.494817000
H	5.101479000	-3.935262000	-1.232777000
C	4.271144000	-3.960314000	0.781645000
C	3.473455000	-3.285198000	1.723507000
H	3.311250000	-3.717691000	2.722707000
C	2.883163000	-2.054030000	1.393040000
H	2.258113000	-1.509618000	2.116570000
C	1.169967000	-0.208838000	-0.671855000
C	0.573479000	1.059426000	-0.986348000
C	-0.735368000	1.151094000	-1.407258000

H	-1.132536000	2.142626000	-1.667878000
C	-1.603147000	-0.016471000	-1.397842000
C	-0.926902000	-1.300160000	-1.291574000
C	0.395234000	-1.382310000	-0.880700000
H	0.869046000	-2.362562000	-0.729465000
C	2.610898000	2.169837000	-0.453822000
H	-2.476532000	0.026531000	-2.073200000
H	-1.501710000	-2.223035000	-1.456175000
H	5.177287000	4.339149000	0.216637000
H	6.282217000	2.171129000	0.879242000
O	-2.432732000	2.308227000	0.863820000
O	-4.196540000	1.839039000	-0.504926000
C	-2.711763000	0.074588000	0.247551000
H	-1.905256000	-0.015537000	0.994036000
C	-3.237636000	1.452937000	0.164996000
C	-2.732865000	3.721263000	0.756306000
H	-1.760660000	4.226200000	0.921212000
H	-3.082084000	3.934629000	-0.274779000
C	-3.769479000	4.152552000	1.784859000
H	-4.743656000	3.661389000	1.590267000
H	-3.439986000	3.896120000	2.812356000
H	-3.919109000	5.250665000	1.733359000
C	-3.622595000	-1.084088000	0.205305000
C	-4.830442000	-1.093553000	-0.540847000
H	-5.135160000	-0.174120000	-1.060198000
C	-5.624751000	-2.249166000	-0.599840000
H	-6.561726000	-2.233997000	-1.179656000

C	-5.233465000	-3.424239000	0.069958000
H	-5.859221000	-4.329060000	0.018128000
C	-4.032892000	-3.432017000	0.805364000
H	-3.714757000	-4.344773000	1.334006000
C	-3.237779000	-2.278346000	0.869953000
H	-2.298175000	-2.289374000	1.445672000
O	1.314857000	2.224606000	-0.918485000
H	4.733845000	-4.924174000	1.044062000

6b

Free Energy = -1361.526921

Energy = -1361.892215

N	2.700921000	-0.057197000	0.062196000
C	3.253316000	0.974569000	-0.716957000
C	4.642021000	1.121005000	-0.908386000
H	5.323723000	0.402550000	-0.431733000
C	5.152673000	2.170353000	-1.697396000
C	4.284401000	3.087577000	-2.306272000
C	2.892867000	2.950992000	-2.122631000
H	2.178670000	3.649645000	-2.583871000
C	1.307415000	-0.146694000	0.208943000
C	0.479559000	0.809759000	-0.434441000
C	-0.910867000	0.758218000	-0.314497000
H	-1.503277000	1.528557000	-0.829462000
C	-1.532077000	-0.251946000	0.455412000
O	-3.950854000	1.691276000	-0.413720000

C	-3.052837000	-0.372412000	0.554659000
H	-3.285231000	-0.842718000	1.529566000
O	-3.882420000	1.439839000	1.839894000
C	-3.687906000	1.021031000	0.573863000
C	-4.407526000	2.787473000	2.002641000
H	-5.387771000	2.847724000	1.484781000
H	-3.719778000	3.495496000	1.494041000
C	-4.523019000	3.063169000	3.488908000
H	-4.920102000	4.085768000	3.648434000
H	-3.533785000	2.994392000	3.984993000
H	-5.212588000	2.344274000	3.975852000
C	-3.649703000	-1.240255000	-0.548602000
C	-3.358130000	-1.005668000	-1.908806000
H	-2.673251000	-0.191212000	-2.186535000
C	-3.929849000	-1.809796000	-2.908298000
H	-3.692991000	-1.615667000	-3.966421000
C	-4.797820000	-2.862575000	-2.562516000
H	-5.241565000	-3.494946000	-3.347491000
C	-5.090867000	-3.104736000	-1.209270000
H	-5.765764000	-3.928269000	-0.927270000
C	-4.520652000	-2.295674000	-0.210197000
H	-4.752211000	-2.486348000	0.850418000
C	-0.716689000	-1.197933000	1.099652000
C	0.683400000	-1.148671000	0.978607000
H	1.306844000	-1.895433000	1.489972000
C	2.385274000	1.910031000	-1.340116000
H	6.241582000	2.261127000	-1.830079000

H	4.676059000	3.909647000	-2.923838000
H	-1.175911000	-1.994433000	1.705440000
C	3.555022000	-1.015017000	0.702639000
C	4.045648000	-0.758622000	1.996738000
C	3.895206000	-2.205132000	0.032565000
C	4.881563000	-1.699210000	2.621729000
H	3.766541000	0.178254000	2.502011000
C	4.730640000	-3.142718000	0.662608000
H	3.500204000	-2.384769000	-0.978684000
C	5.223748000	-2.890320000	1.955808000
H	5.266936000	-1.501202000	3.633849000
H	4.998011000	-4.074574000	0.140825000
H	5.878532000	-3.626286000	2.447573000
O	1.009750000	1.831136000	-1.200684000

5a

Free Energy = -1146.882291

Energy = -1147.08992

C	1.821333000	1.361582000	0.128250000
C	2.472706000	2.587842000	-0.090932000
H	3.565371000	2.639276000	0.037816000
C	1.739526000	3.736975000	-0.436218000
C	0.346642000	3.639319000	-0.576903000
C	-0.306104000	2.407723000	-0.398020000
H	-1.395291000	2.349318000	-0.524444000
C	1.821333000	-1.361582000	0.128250000

N	-0.239837000	0.000000000	0.129774000
C	0.415968000	-1.242508000	-0.047080000
C	-0.306104000	-2.407723000	-0.398021000
H	-1.395291000	-2.349318000	-0.524445000
C	0.346642000	-3.639319000	-0.576904000
C	1.739525000	-3.736975000	-0.436219000
C	2.472706000	-2.587842000	-0.090932000
H	3.565371000	-2.639276000	0.037816000
C	-1.680618000	0.000000000	0.145634000
C	-2.346397000	-0.000001000	1.383612000
H	-1.752479000	-0.000001000	2.309853000
C	-3.751615000	-0.000001000	1.419374000
H	-4.273578000	-0.000001000	2.388749000
C	-4.486984000	-0.000000000	0.220737000
C	-3.817111000	0.000001000	-1.016939000
H	-4.391041000	0.000001000	-1.956447000
C	-2.413233000	0.000001000	-1.057653000
H	-1.876319000	0.000001000	-2.018401000
C	0.415968000	1.242508000	-0.047080000
H	-0.250180000	-4.526708000	-0.838464000
H	2.256823000	-4.696591000	-0.585777000
H	-0.250180000	4.526708000	-0.838463000
H	2.256823000	4.696591000	-0.585777000
H	-5.587583000	-0.000000000	0.250078000
S	2.768832000	-0.000000000	0.776358000

TS3

Free Energy = -4259.541887

Energy = -4259.912824

N	-2.381336000	0.123652000	-0.787107000
C	-3.387626000	-0.769781000	-0.337156000
C	-4.632384000	-0.256967000	0.100060000
H	-4.803474000	0.826586000	0.085502000
C	-5.645542000	-1.112208000	0.549992000
C	-5.437974000	-2.502198000	0.582062000
C	-4.207229000	-3.025983000	0.164351000
H	-4.025153000	-4.111414000	0.193669000
C	-2.717414000	1.534977000	-0.804503000
C	-3.317845000	2.090036000	-1.945201000
H	-3.532674000	1.451060000	-2.814293000
C	-3.630049000	3.460188000	-1.950978000
H	-4.099789000	3.907109000	-2.840179000
C	-3.340605000	4.255997000	-0.827939000
C	-2.738492000	3.685434000	0.308558000
H	-2.510467000	4.306915000	1.187563000
C	-2.424499000	2.317338000	0.325608000
H	-1.948891000	1.853998000	1.202243000
C	-1.078947000	-0.219789000	-1.081074000
C	-0.599513000	-1.578382000	-1.006921000
C	0.760721000	-1.849221000	-1.142096000
H	1.118682000	-2.884914000	-1.041615000
C	1.695051000	-0.805061000	-1.359015000
C	1.197844000	0.506278000	-1.592193000

C	-0.146152000	0.799927000	-1.444018000
H	-0.499388000	1.829262000	-1.574671000
C	-3.183584000	-2.174304000	-0.294300000
H	2.759017000	-1.051516000	-1.551125000
H	1.899883000	1.315229000	-1.840747000
H	-6.228437000	-3.180078000	0.936426000
H	-6.602798000	-0.683144000	0.880770000
Br	5.227164000	-1.580632000	-0.992601000
O	0.235118000	-0.324004000	1.645140000
O	1.645587000	-2.083818000	1.960821000
C	2.469099000	-0.174216000	0.821644000
H	3.347267000	-0.787641000	0.533787000
C	1.432267000	-0.953206000	1.536220000
C	-0.823589000	-1.060470000	2.323496000
H	-0.765076000	-2.122023000	2.009621000
H	-1.758716000	-0.619281000	1.929050000
C	-0.729740000	-0.910789000	3.833009000
H	-1.588307000	-1.428179000	4.307482000
H	0.203941000	-1.364765000	4.218665000
H	-0.761516000	0.156872000	4.129449000
C	2.682541000	1.245896000	0.879832000
C	1.725013000	2.188302000	1.365293000
H	0.764677000	1.825564000	1.751831000
C	2.009376000	3.555390000	1.333872000
H	1.265410000	4.275722000	1.707119000
C	3.241341000	4.017553000	0.823497000
H	3.454976000	5.097555000	0.801037000

C	4.199380000	3.099794000	0.344405000
H	5.159818000	3.463729000	-0.051992000
C	3.929140000	1.729752000	0.371270000
H	4.652494000	0.989951000	-0.016658000
S	-1.690427000	-2.952641000	-0.823002000
H	-3.585233000	5.329064000	-0.838458000

TS3'

Free Energy = -1685.072431

Energy = -1685.44394

N	-2.220547000	0.577947000	-0.375323000
C	-3.076017000	-0.465796000	0.047265000
C	-4.188942000	-0.187164000	0.878404000
H	-4.386308000	0.849115000	1.182756000
C	-5.040670000	-1.212038000	1.315785000
C	-4.794956000	-2.546852000	0.951888000
C	-3.692124000	-2.841858000	0.134132000
H	-3.482113000	-3.880449000	-0.166002000
C	-2.635883000	1.930837000	-0.089273000
C	-3.422837000	2.618959000	-1.027750000
H	-3.705694000	2.117187000	-1.965063000
C	-3.834010000	3.934417000	-0.752219000
H	-4.450452000	4.478117000	-1.484459000
C	-3.456494000	4.553549000	0.452843000
C	-2.667091000	3.857650000	1.387151000
H	-2.371514000	4.340896000	2.331009000

C	-2.254911000	2.542154000	1.119442000
H	-1.638837000	1.982218000	1.839014000
C	-0.915791000	0.382705000	-0.841936000
C	-0.433766000	-0.917427000	-1.220098000
C	0.898218000	-1.119910000	-1.531701000
H	1.234442000	-2.121837000	-1.839058000
C	1.875316000	-0.052398000	-1.392787000
C	1.312973000	1.286719000	-1.325513000
C	-0.017495000	1.482929000	-0.993909000
H	-0.396403000	2.503764000	-0.850580000
C	-2.847659000	-1.817341000	-0.331851000
H	2.807658000	-0.174671000	-1.971807000
H	1.976570000	2.156271000	-1.441567000
H	-5.454091000	-3.356437000	1.299364000
H	-5.899195000	-0.957995000	1.955963000
O	1.927682000	-2.366330000	0.988470000
O	3.921046000	-2.360645000	-0.112749000
C	2.755678000	-0.281887000	0.369272000
H	1.905117000	0.007550000	1.008253000
C	2.985964000	-1.743721000	0.397699000
C	1.879317000	-3.810186000	0.903245000
H	2.210942000	-4.120629000	-0.110000000
H	2.606243000	-4.234238000	1.629944000
C	0.455238000	-4.243221000	1.200685000
H	0.137828000	-3.908090000	2.209141000
H	-0.245944000	-3.820873000	0.451254000
H	0.382107000	-5.349088000	1.165002000

C	3.880643000	0.669382000	0.397265000
C	5.145967000	0.388159000	-0.182338000
H	5.315416000	-0.606710000	-0.617755000
C	6.161663000	1.356338000	-0.182991000
H	7.139243000	1.116693000	-0.631466000
C	5.940712000	2.628455000	0.379005000
H	6.740492000	3.385583000	0.373108000
C	4.687141000	2.924451000	0.947448000
H	4.501705000	3.915886000	1.390554000
C	3.670428000	1.958241000	0.954677000
H	2.690787000	2.193242000	1.401327000
H	-3.778808000	5.584442000	0.665758000
S	-1.581804000	-2.248791000	-1.499140000

7b

Free Energy = -1684.533234

Energy = -1684.895823

N	2.651350000	-0.054998000	0.257210000
C	3.312240000	0.963434000	-0.471877000
C	4.636327000	0.784989000	-0.937573000
H	5.162041000	-0.154038000	-0.719408000
C	5.291613000	1.792891000	-1.665194000
C	4.635328000	2.995205000	-1.970154000
C	3.317738000	3.187149000	-1.518223000
H	2.783802000	4.125955000	-1.734205000
C	1.242926000	-0.171931000	0.301798000

C	0.401710000	0.951917000	0.088429000
C	-0.996305000	0.819424000	0.088789000
H	-1.612820000	1.712657000	-0.095819000
C	-1.610552000	-0.420987000	0.356247000
O	-4.069719000	1.652726000	0.182656000
C	-3.127116000	-0.604507000	0.323391000
H	-3.379413000	-1.422056000	1.026068000
O	-4.087589000	0.544384000	2.162346000
C	-3.820971000	0.657138000	0.846521000
C	-4.677147000	1.709309000	2.805971000
H	-5.629474000	1.951838000	2.289472000
H	-3.992922000	2.572051000	2.662812000
C	-4.883874000	1.374552000	4.270000000
H	-5.330846000	2.244642000	4.791519000
H	-3.920902000	1.132315000	4.763363000
H	-5.568485000	0.510522000	4.389034000
C	-3.644947000	-0.984978000	-1.060160000
C	-3.265705000	-0.262886000	-2.210805000
H	-2.561924000	0.577611000	-2.119630000
C	-3.772090000	-0.616639000	-3.472221000
H	-3.466818000	-0.044581000	-4.362666000
C	-4.661344000	-1.699894000	-3.601455000
H	-5.053819000	-1.978957000	-4.591935000
C	-5.041065000	-2.426887000	-2.459745000
H	-5.732790000	-3.279205000	-2.550529000
C	-4.536165000	-2.068464000	-1.197136000
H	-4.835578000	-2.638955000	-0.302843000

C	-0.780121000	-1.527503000	0.611723000
C	0.617051000	-1.411641000	0.572428000
H	1.235082000	-2.298306000	0.765862000
C	2.670238000	2.198831000	-0.756681000
H	6.326037000	1.622304000	-2.001131000
H	5.139833000	3.783579000	-2.548681000
S	1.089886000	2.588958000	-0.033602000
H	-1.228985000	-2.508502000	0.832883000
C	3.430196000	-1.193192000	0.674786000
C	3.944432000	-1.222805000	1.982574000
C	3.672403000	-2.260888000	-0.211607000
C	4.705064000	-2.326040000	2.407082000
H	3.741545000	-0.376907000	2.656323000
C	4.432585000	-3.361145000	0.217348000
H	3.262261000	-2.221229000	-1.232155000
C	4.949111000	-3.394569000	1.526001000
H	5.108190000	-2.350288000	3.431273000
H	4.622716000	-4.196678000	-0.473869000
H	5.544726000	-4.258256000	1.859855000

Coordinates and energies (in hatree) of the calculated structures at the uM06/6-311+G**(CPCM, SOL=H_2O)//uM06/6-31G** level of theory.

1a

Ground state

Free Energy = -1262.988967

Energy = -1263.34924

C	-0.691044000	3.638835000	-0.432337000
C	-1.383858000	2.431619000	-0.331435000
C	-0.705126000	1.222945000	-0.223161000
C	0.705142000	1.222935000	-0.223153000
C	1.383892000	2.431600000	-0.331427000
C	0.691095000	3.638825000	-0.432335000
C	0.705126000	-1.222985000	-0.223121000
C	-0.705142000	-1.222974000	-0.223134000
C	-1.383891000	-2.431639000	-0.331403000
H	-2.470297000	-2.429354000	-0.325594000
C	-0.691093000	-3.638867000	-0.432280000
C	0.691047000	-3.638877000	-0.432262000
C	1.383860000	-2.431660000	-0.331370000
H	-1.247789000	4.569213000	-0.508555000
H	-2.470264000	2.429350000	-0.325606000
H	2.470297000	2.429316000	-0.325594000
H	1.247853000	4.569195000	-0.508553000
H	-1.247850000	-4.569237000	-0.508493000
H	1.247792000	-4.569256000	-0.508458000
H	2.470266000	-2.429390000	-0.325532000
C	-2.811261000	-0.000005000	-0.031843000

C	-3.570743000	0.000061000	-1.205097000
C	-3.456419000	-0.000091000	1.197027000
C	-4.952161000	0.000055000	-1.143123000
H	-3.056501000	0.000128000	-2.164432000
C	-4.847065000	-0.000110000	1.274049000
H	-2.855173000	-0.000154000	2.103526000
C	-5.597901000	-0.000031000	0.098405000
H	-5.564226000	0.000114000	-2.041125000
H	-5.328292000	-0.000199000	2.247204000
C	2.811259000	-0.000038000	-0.031827000
C	3.570737000	-0.000044000	-1.205083000
C	3.456422000	-0.000043000	1.197041000
C	4.952155000	-0.000046000	-1.143114000
H	3.056492000	-0.000038000	-2.164417000
C	4.847069000	-0.000051000	1.274058000
H	2.855179000	-0.000044000	2.103543000
C	5.597900000	-0.000047000	0.098412000
H	5.564217000	-0.000043000	-2.041119000
H	5.328299000	-0.000070000	2.247212000
N	-1.388146000	-0.000008000	-0.086713000
N	1.388144000	-0.000027000	-0.086691000
O	-6.951954000	-0.000068000	0.053043000
C	-7.650518000	0.000273000	1.273896000
H	-7.423584000	0.894355000	1.871910000
H	-8.713032000	0.000512000	1.023678000
H	-7.424057000	-0.893770000	1.872151000
O	6.951952000	-0.000075000	0.053044000

C	7.650522000	0.000290000	1.273895000
H	8.713034000	0.000484000	1.023673000
H	7.423620000	0.894403000	1.871875000
H	7.424032000	-0.893722000	1.872185000

Triplet excited state

Free Energy = -1262.90124

Energy = -1263.25392

C	0.698198000	-3.626038000	-0.148593000
C	1.417061000	-2.435117000	-0.150147000
C	0.708520000	-1.212113000	-0.159071000
C	-0.708526000	-1.212109000	-0.159076000
C	-1.417074000	-2.435110000	-0.150170000
C	-0.698217000	-3.626034000	-0.148607000
C	-0.708520000	1.212117000	-0.159026000
C	0.708526000	1.212113000	-0.159034000
C	1.417075000	2.435114000	-0.150089000
H	2.500815000	2.429337000	-0.150581000
C	0.698217000	3.626038000	-0.148483000
C	-0.698198000	3.626041000	-0.148468000
C	-1.417062000	2.435121000	-0.150063000
H	1.236497000	-4.570511000	-0.144937000
H	2.500801000	-2.429346000	-0.150604000
H	-2.500814000	-2.429333000	-0.150653000
H	-1.236521000	-4.570505000	-0.144964000
H	1.236520000	4.570509000	-0.144811000

H	-1.236496000	4.570515000	-0.144781000
H	-2.500803000	2.429350000	-0.150526000
C	2.811426000	-0.000005000	-0.121307000
C	3.533362000	-0.000054000	-1.310515000
C	3.454335000	0.000042000	1.107259000
C	4.923707000	-0.000056000	-1.265609000
H	3.001578000	-0.000091000	-2.259209000
C	4.853311000	0.000042000	1.160719000
H	2.862965000	0.000082000	2.019946000
C	5.581034000	-0.000008000	-0.029364000
H	5.524355000	-0.000094000	-2.170403000
H	5.350443000	0.000083000	2.125179000
C	-2.811426000	0.000009000	-0.121304000
C	-3.533363000	0.000062000	-1.310511000
C	-3.454334000	-0.000039000	1.107263000
C	-4.923708000	0.000066000	-1.265603000
H	-3.001580000	0.000099000	-2.259205000
C	-4.853310000	-0.000035000	1.160724000
H	-2.862962000	-0.000079000	2.019949000
C	-5.581034000	0.000017000	-0.029357000
H	-5.524358000	0.000105000	-2.170396000
H	-5.350441000	-0.000070000	2.125185000
N	1.374101000	-0.000002000	-0.160109000
N	-1.374101000	0.000006000	-0.160107000
O	6.934890000	-0.000009000	-0.093364000
C	7.651011000	-0.000003000	1.116729000
H	7.432651000	-0.893849000	1.718355000

H	8.709947000	-0.000039000	0.851257000
H	7.432704000	0.893884000	1.718315000
O	-6.934891000	0.000028000	-0.093356000
C	-7.651010000	-0.000059000	1.116738000
H	-8.709946000	-0.000067000	0.851267000
H	-7.432655000	-0.893956000	1.718291000
H	-7.432696000	0.893778000	1.718396000

Cation Radical

Free Energy = -1262.819185

Energy = -1263.181398

C	-0.701082000	-3.618002000	0.190023000
C	-1.398919000	-2.429135000	0.177575000
C	-0.709892000	-1.207044000	0.167230000
C	0.709598000	-1.207223000	0.167207000
C	1.398344000	-2.429471000	0.177461000
C	0.700230000	-3.618176000	0.189949000
C	0.709893000	1.206948000	0.167216000
C	-0.709597000	1.207129000	0.167173000
C	-1.398340000	2.429381000	0.177398000
H	-2.483359000	2.425407000	0.176964000
C	-0.700222000	3.618084000	0.189880000
C	0.701090000	3.617905000	0.189972000
C	1.398923000	2.429036000	0.177549000
H	-1.245273000	-4.557536000	0.200337000
H	-2.483936000	-2.424943000	0.177249000

H	2.483364000	-2.425493000	0.177044000
H	1.244195000	-4.557841000	0.200183000
H	-1.244183000	4.557752000	0.200093000
H	1.245285000	4.557437000	0.200282000
H	2.483941000	2.424844000	0.177234000
C	-2.829964000	0.000245000	0.107965000
C	-3.559802000	0.000234000	1.296778000
C	-3.472933000	0.000180000	-1.121329000
C	-4.940091000	0.000179000	1.245092000
H	-3.038786000	0.000274000	2.251958000
C	-4.861966000	0.000100000	-1.178963000
H	-2.885216000	0.000131000	-2.037130000
C	-5.602227000	0.000115000	0.008187000
H	-5.541882000	0.000177000	2.149242000
H	-5.354772000	-0.000062000	-2.145651000
C	2.829962000	-0.000334000	0.107985000
C	3.559806000	-0.000020000	1.296784000
C	3.472926000	-0.000572000	-1.121321000
C	4.940102000	0.000076000	1.245096000
H	3.038806000	0.000149000	2.251974000
C	4.861951000	-0.000475000	-1.178957000
H	2.885193000	-0.000818000	-2.037111000
C	5.602226000	-0.000118000	0.008196000
H	5.541880000	0.000319000	2.149254000
H	5.354775000	-0.000692000	-2.145635000
N	-1.388706000	0.000127000	0.152588000
N	1.388706000	-0.000222000	0.152606000

O	-6.941321000	-0.000026000	0.070096000
C	-7.675760000	0.000328000	-1.139321000
H	-7.463203000	-0.896226000	-1.735989000
H	-8.728593000	0.000812000	-0.856448000
H	-7.462379000	0.896700000	-1.735968000
O	6.941327000	0.000082000	0.070081000
C	7.675743000	0.000371000	-1.139349000
H	8.728579000	0.000891000	-0.856494000
H	7.463179000	-0.896227000	-1.735953000
H	7.462346000	0.896701000	-1.736059000

1b

Ground state

Free Energy = -1034.056502

Energy = -1034.358639

C	-0.690974000	-3.646094000	0.081743000
C	-1.383329000	-2.436538000	0.013477000
C	-0.705031000	-1.224748000	-0.058947000
C	0.705048000	-1.224740000	-0.059009000
C	1.383364000	-2.436523000	0.013365000
C	0.691027000	-3.646087000	0.081690000
C	0.705035000	1.224745000	-0.059024000
C	-0.705045000	1.224736000	-0.058951000
C	-1.383356000	2.436519000	0.013491000
H	-2.469797000	2.434800000	0.011315000
C	-0.691014000	3.646083000	0.081742000

C	0.690987000	3.646093000	0.081658000
C	1.383337000	2.436538000	0.013326000
H	-1.248021000	-4.577870000	0.133231000
H	-2.469771000	-2.434830000	0.011278000
H	2.469805000	-2.434805000	0.011074000
H	1.248089000	-4.577857000	0.133136000
H	-1.248071000	4.577852000	0.133245000
H	1.248037000	4.577870000	0.133086000
H	2.469778000	2.434833000	0.011017000
C	-2.815457000	-0.000016000	-0.072227000
C	-3.442477000	-0.000007000	1.172331000
C	-3.574193000	-0.000019000	-1.238725000
C	-4.829992000	0.000002000	1.247814000
H	-2.826544000	-0.000006000	2.069665000
C	-4.963169000	-0.000007000	-1.160073000
H	-3.060289000	-0.000024000	-2.197400000
C	-5.590573000	0.000004000	0.081561000
H	-5.319966000	0.000010000	2.218466000
H	-5.556651000	-0.000007000	-2.071069000
C	2.815454000	0.000011000	-0.072278000
C	3.442395000	0.000037000	1.172320000
C	3.574263000	-0.000016000	-1.238728000
C	4.829905000	0.000037000	1.247889000
H	2.826408000	0.000057000	2.069617000
C	4.963235000	-0.000017000	-1.159990000
H	3.060417000	-0.000038000	-2.197433000
C	5.590560000	0.000010000	0.081683000

H	5.319817000	0.000057000	2.218572000
H	5.556774000	-0.000038000	-2.070948000
N	-1.392067000	-0.000011000	-0.152555000
N	1.392067000	0.000005000	-0.152709000
H	6.676221000	0.000010000	0.141676000
H	-6.676238000	0.000013000	0.141483000

Triplet excited state

Free Energy = -1033.96799

Energy = -1034.26247

C	0.697070000	3.627950000	-0.034385000
C	1.418664000	2.436488000	-0.036022000
C	0.707636000	1.213729000	-0.041509000
C	-0.707637000	1.213729000	-0.041500000
C	-1.418665000	2.436488000	-0.036003000
C	-0.697071000	3.627950000	-0.034375000
C	-0.707636000	-1.213731000	-0.041511000
C	0.707636000	-1.213731000	-0.041516000
C	1.418664000	-2.436489000	-0.036036000
H	2.502234000	-2.432114000	-0.036094000
C	0.697071000	-3.627951000	-0.034409000
C	-0.697070000	-3.627952000	-0.034406000
C	-1.418664000	-2.436489000	-0.036028000
H	1.234822000	4.572780000	-0.031681000
H	2.502233000	2.432113000	-0.036086000

H	-2.502234000	2.432113000	-0.036051000
H	-1.234823000	4.572779000	-0.031664000
H	1.234823000	-4.572780000	-0.031710000
H	-1.234821000	-4.572781000	-0.031705000
H	-2.502233000	-2.432115000	-0.036083000
C	2.808703000	0.000000000	-0.001563000
C	3.445713000	0.000003000	1.232657000
C	3.519613000	-0.000001000	-1.194004000
C	4.842786000	0.000004000	1.271373000
H	2.848140000	0.000005000	2.141248000
C	4.916922000	-0.000001000	-1.146478000
H	2.979040000	-0.000004000	-2.137649000
C	5.567918000	0.000002000	0.083773000
H	5.358135000	0.000006000	2.228113000
H	5.489974000	-0.000002000	-2.069761000
C	-2.808703000	-0.000001000	-0.001536000
C	-3.445701000	-0.000019000	1.232690000
C	-3.519625000	0.000018000	-1.193970000
C	-4.842774000	-0.000018000	1.271419000
H	-2.848120000	-0.000034000	2.141276000
C	-4.916933000	0.000020000	-1.146431000
H	-2.979061000	0.000032000	-2.137620000
C	-5.567918000	0.000002000	0.083826000
H	-5.358114000	-0.000031000	2.228165000
H	-5.489994000	0.000035000	-2.069708000
N	1.370501000	-0.000000000	-0.039404000
N	-1.370501000	-0.000001000	-0.039390000

H	-6.655108000	0.000003000	0.117144000
H	6.655109000	0.000002000	0.117080000

Cation Radical

Free Energy = -1033.885125

Energy = -1034.189592

C	-0.700737000	-3.618775000	-0.061816000
C	-1.398976000	-2.430001000	-0.055780000
C	-0.709719000	-1.208152000	-0.051191000
C	0.709665000	-1.208182000	-0.051183000
C	1.398879000	-2.430055000	-0.055765000
C	0.700597000	-3.618804000	-0.061811000
C	0.709719000	1.208159000	-0.051155000
C	-0.709665000	1.208188000	-0.051150000
C	-1.398880000	2.430062000	-0.055712000
H	-2.483948000	2.427981000	-0.054760000
C	-0.700597000	3.618811000	-0.061733000
C	0.700737000	3.618782000	-0.061736000
C	1.398976000	2.430008000	-0.055722000
H	-1.244732000	-4.558406000	-0.066441000
H	-2.484045000	-2.427889000	-0.054831000
H	2.483948000	-2.427974000	-0.054805000
H	1.244558000	-4.558454000	-0.066425000
H	-1.244558000	4.558461000	-0.066334000
H	1.244732000	4.558413000	-0.066345000
H	2.484045000	2.427897000	-0.054778000

C	-2.829440000	0.000046000	0.006787000
C	-3.458083000	-0.000062000	1.246524000
C	-3.551562000	0.000140000	-1.180851000
C	-4.847441000	-0.000076000	1.294301000
H	-2.860322000	-0.000124000	2.155492000
C	-4.940979000	0.000110000	-1.119838000
H	-3.026162000	0.000230000	-2.133469000
C	-5.585353000	0.000003000	0.113925000
H	-5.353806000	-0.000158000	2.255332000
H	-5.520287000	0.000184000	-2.038739000
C	2.829440000	-0.000044000	0.006788000
C	3.458084000	-0.000090000	1.246525000
C	3.551561000	0.000008000	-1.180850000
C	4.847443000	-0.000084000	1.294300000
H	2.860324000	-0.000141000	2.155493000
C	4.940978000	0.000026000	-1.119839000
H	3.026160000	0.000035000	-2.133469000
C	5.585354000	-0.000019000	0.113923000
H	5.353808000	-0.000122000	2.255331000
H	5.520285000	0.000064000	-2.038741000
N	-1.386380000	0.000033000	-0.041850000
N	1.386380000	-0.000027000	-0.041848000
H	6.670963000	0.000007000	0.155852000
H	-6.670963000	-0.000030000	0.155855000

1c

Ground state

Free Energy = -1112.59819

Energy = -1112.94846

C	-0.692695000	-3.645744000	0.065002000
C	-1.384374000	-2.435720000	-0.002478000
C	-0.705692000	-1.224049000	-0.073763000
C	0.704566000	-1.224714000	-0.073638000
C	1.382149000	-2.436986000	-0.001891000
C	0.689307000	-3.646368000	0.065351000
C	0.705688000	1.224040000	-0.073693000
C	-0.704570000	1.224705000	-0.073725000
C	-1.382159000	2.436979000	-0.002064000
H	-2.468600000	2.435127000	-0.004083000
C	-0.689323000	3.646361000	0.065253000
C	0.692679000	3.645734000	0.065064000
C	1.384365000	2.435709000	-0.002330000
H	-1.250219000	-4.577344000	0.115610000
H	-2.470795000	-2.432761000	-0.004969000
H	2.468590000	-2.435132000	-0.003782000
H	1.245982000	-4.578454000	0.116312000
H	-1.246002000	4.578447000	0.116144000
H	1.250199000	4.577334000	0.115736000
H	2.470785000	2.432748000	-0.004689000
C	-2.815943000	0.001226000	-0.086905000
C	-3.448781000	0.001411000	1.154678000
C	-3.578569000	0.007551000	-1.249784000
C	-4.834740000	0.006720000	1.226325000

H	-2.838009000	0.001821000	2.055677000
C	-4.966575000	0.012864000	-1.168855000
H	-3.069673000	0.012722000	-2.211247000
C	-5.614890000	0.009316000	0.066761000
H	-5.326433000	0.010958000	2.198391000
H	-5.560469000	0.021608000	-2.081805000
C	2.815946000	-0.001233000	-0.086815000
C	3.448850000	-0.001378000	1.154732000
C	3.578509000	-0.007586000	-1.249738000
C	4.834815000	-0.006679000	1.226306000
H	2.838125000	-0.001765000	2.055762000
C	4.966519000	-0.012889000	-1.168881000
H	3.069564000	-0.012787000	-2.211174000
C	5.614901000	-0.009302000	0.066701000
H	5.326559000	-0.010887000	2.198346000
H	5.560364000	-0.021656000	-2.081862000
N	-1.392682000	0.000627000	-0.165794000
N	1.392682000	-0.000637000	-0.165621000
C	7.111634000	0.014827000	0.152862000
H	7.485519000	1.038860000	0.279226000
H	7.474068000	-0.566982000	1.007344000
H	7.573592000	-0.389987000	-0.753535000
C	-7.111618000	-0.014797000	0.153015000
H	-7.485493000	-1.038802000	0.279637000
H	-7.474002000	0.567204000	1.007388000
H	-7.573632000	0.389812000	-0.753445000

Triplet excited state

Free Energy = -1112.51007

Energy = -1112.85267

C	0.697945000	3.627090000	-0.056840000
C	1.418391000	2.435721000	-0.050785000
C	0.708053000	1.212898000	-0.042993000
C	-0.707746000	1.213102000	-0.043280000
C	-1.417715000	2.436085000	-0.052128000
C	-0.696925000	3.627282000	-0.057640000
C	-0.708067000	-1.212890000	-0.042910000
C	0.707731000	-1.213082000	-0.043342000
C	1.417720000	-2.436071000	-0.052292000
H	2.501341000	-2.430986000	-0.053274000
C	0.696933000	-3.627263000	-0.057705000
C	-0.697936000	-3.627080000	-0.056711000
C	-1.418393000	-2.435709000	-0.050578000
H	1.236068000	4.571705000	-0.062756000
H	2.502007000	2.430316000	-0.050313000
H	-2.501337000	2.431014000	-0.052931000
H	-1.234796000	4.572035000	-0.064332000
H	1.234805000	-4.572017000	-0.064472000
H	-1.236056000	-4.571699000	-0.062536000
H	-2.502009000	-2.430321000	-0.049930000
C	2.809956000	-0.000388000	-0.001849000
C	3.462374000	-0.003353000	1.223710000
C	3.516054000	0.002001000	-1.197455000

C	4.856158000	-0.003826000	1.250860000
H	2.875692000	-0.005603000	2.139749000
C	4.913905000	0.001576000	-1.155138000
H	2.974719000	0.003913000	-2.140593000
C	5.593770000	-0.000978000	0.060433000
H	5.380402000	-0.006505000	2.205112000
H	5.480785000	0.003189000	-2.084462000
C	-2.809960000	0.000400000	-0.001483000
C	-3.462162000	0.003362000	1.224197000
C	-3.516275000	-0.002032000	-1.196951000
C	-4.855939000	0.003786000	1.251589000
H	-2.875320000	0.005620000	2.140133000
C	-4.914114000	-0.001655000	-1.154394000
H	-2.975106000	-0.003967000	-2.140186000
C	-5.593764000	0.000914000	0.061305000
H	-5.380014000	0.006440000	2.205936000
H	-5.481157000	-0.003321000	-2.083619000
N	1.371782000	-0.000179000	-0.029787000
N	-1.371799000	0.000193000	-0.029664000
C	-7.092326000	-0.001416000	0.109836000
H	-7.471521000	-0.895340000	0.620077000
H	-7.473162000	0.865308000	0.663605000
H	-7.529919000	0.022409000	-0.893049000
C	7.092339000	0.001479000	0.108707000
H	7.471585000	0.896319000	0.617297000
H	7.473303000	-0.864255000	0.663925000
H	7.529766000	-0.024042000	-0.894211000

Cation Radical

Free Energy = -1112.42764

Energy = -1112.780431

C	-0.699337000	-3.618591000	-0.077069000
C	-1.397924000	-2.430066000	-0.070747000
C	-0.709242000	-1.207842000	-0.066451000
C	0.710155000	-1.207312000	-0.066676000
C	1.399740000	-2.429062000	-0.071665000
C	0.701970000	-3.618075000	-0.077636000
C	0.709242000	1.207845000	-0.066453000
C	-0.710155000	1.207315000	-0.066669000
C	-1.399740000	2.429065000	-0.071651000
H	-2.484800000	2.425527000	-0.071024000
C	-0.701970000	3.618077000	-0.077623000
C	0.699337000	3.618594000	-0.077063000
C	1.397924000	2.430068000	-0.070747000
H	-1.242979000	-4.558462000	-0.081492000
H	-2.482964000	-2.427058000	-0.069364000
H	2.484800000	-2.425524000	-0.071047000
H	1.246316000	-4.557534000	-0.082597000
H	-1.246316000	4.557537000	-0.082578000
H	1.242979000	4.558465000	-0.081486000
H	2.482964000	2.427061000	-0.069368000
C	-2.829755000	-0.000890000	-0.008600000
C	-3.464372000	0.005168000	1.227929000

C	-3.557653000	-0.000399000	-1.192312000
C	-4.851866000	0.011279000	1.272669000
H	-2.871691000	0.009564000	2.140418000
C	-4.945220000	0.005545000	-1.128304000
H	-3.037821000	-0.000345000	-2.148184000
C	-5.612810000	0.008612000	0.099724000
H	-5.357647000	0.020320000	2.236111000
H	-5.524094000	0.009997000	-2.049655000
C	2.829756000	0.000891000	-0.008612000
C	3.464375000	-0.005184000	1.227920000
C	3.557650000	0.000417000	-1.192321000
C	4.851865000	-0.011297000	1.272658000
H	2.871694000	-0.009591000	2.140409000
C	4.945221000	-0.005527000	-1.128315000
H	3.037819000	0.000378000	-2.148193000
C	5.612810000	-0.008614000	0.099708000
H	5.357650000	-0.020352000	2.236098000
H	5.524092000	-0.009963000	-2.049668000
N	-1.387278000	-0.000549000	-0.057154000
N	1.387278000	0.000551000	-0.057162000
C	7.108630000	0.012970000	0.159038000
H	7.481568000	1.043336000	0.207766000
H	7.483559000	-0.508510000	1.044984000
H	7.553767000	-0.451443000	-0.725978000
C	-7.108631000	-0.012984000	0.159014000
H	-7.481600000	-1.043388000	0.206699000
H	-7.483568000	0.507637000	1.045457000

H	-7.553731000	0.452308000	-0.725562000

3a

Ground state

Free Energy = -3411.684767

Energy = -3412.705503

N	0.000032000	-1.360392000	0.394073000
C	1.212252000	-0.672364000	0.197871000
O	4.369084000	3.450240000	0.677204000
C	2.430565000	-1.303769000	0.406700000
H	2.404478000	-2.332441000	0.758011000
O	4.520588000	3.543591000	-1.563954000
C	3.659040000	-0.670737000	0.202336000
O	4.520317000	-3.544171000	1.564344000
C	4.952308000	-1.446994000	0.417390000
H	5.566085000	-1.330071000	-0.488925000
O	4.369441000	-3.449879000	-0.676819000
O	-0.000355000	-6.878469000	-0.365089000
C	4.622382000	-2.926679000	0.532423000
C	3.793960000	-4.764397000	-0.666502000
H	4.502896000	-5.464725000	-0.208184000
H	2.895396000	-4.750851000	-0.030577000
C	3.460155000	-5.123209000	-2.088589000
H	2.966666000	-6.100775000	-2.123221000
H	2.778537000	-4.380102000	-2.516524000
H	4.360331000	-5.162974000	-2.710128000

C	5.758387000	-0.986956000	1.611521000
C	5.136320000	-0.665972000	2.817260000
H	4.052110000	-0.733178000	2.889368000
C	5.890178000	-0.263289000	3.912392000
H	5.393456000	-0.014727000	4.847440000
C	7.275952000	-0.178094000	3.816028000
H	7.864265000	0.141706000	4.672936000
C	7.904923000	-0.503231000	2.619461000
H	8.987646000	-0.441342000	2.536319000
C	7.147988000	-0.907894000	1.524804000
H	7.637296000	-1.160131000	0.583682000
C	3.659069000	0.670614000	-0.201358000
C	2.430631000	1.303625000	-0.405997000
H	2.404623000	2.332283000	-0.757337000
C	4.952370000	1.446912000	-0.416069000
H	5.565767000	1.330278000	0.490547000
C	4.622366000	2.926530000	-0.531747000
C	3.793455000	4.764691000	0.666117000
H	4.502535000	5.464923000	0.207877000
H	2.895209000	4.750813000	0.029757000
C	3.458889000	5.124043000	2.087884000
H	2.964793000	6.101335000	2.121763000
H	2.777506000	4.380770000	2.515912000
H	4.358761000	5.164656000	2.709805000
C	5.759008000	0.986691000	-1.609760000
C	7.148607000	0.908141000	-1.522538000
H	7.637512000	1.160882000	-0.581343000

C	7.906053000	0.503351000	-2.616794000
H	8.988768000	0.441861000	-2.533263000
C	7.277599000	0.177572000	-3.813461000
H	7.866310000	-0.142336000	-4.670054000
C	5.891831000	0.262274000	-3.910332000
H	5.395515000	0.013214000	-4.845463000
C	5.137463000	0.665101000	-2.815603000
H	4.053255000	0.731939000	-2.888098000
C	-0.000004000	-2.781683000	0.239960000
C	0.000082000	-3.336428000	-1.043564000
H	0.000227000	-2.671528000	-1.905811000
C	-0.000019000	-4.708331000	-1.211195000
H	0.000044000	-5.163721000	-2.199062000
C	-0.000230000	-5.551915000	-0.092725000
C	-0.000271000	-5.005030000	1.191319000
H	-0.000381000	-5.638651000	2.072409000
C	-0.000159000	-3.618912000	1.345923000
H	-0.000199000	-3.177150000	2.339883000
C	-0.001076000	-7.771792000	0.724533000
H	-0.001426000	-8.777487000	0.300641000
H	0.893271000	-7.646253000	1.350710000
H	-0.895659000	-7.645395000	1.350199000
C	-1.212164000	-0.672322000	0.197865000
N	0.000079000	1.360065000	-0.394229000
C	-1.212147000	0.672204000	-0.197533000
O	-4.369549000	-3.449780000	-0.676793000
C	-2.430478000	1.303711000	-0.405980000

H	-2.404436000	2.332368000	-0.757317000
O	-4.520330000	-3.543986000	1.564381000
C	-3.658937000	0.670744000	-0.201343000
O	-4.520342000	3.543768000	-1.563901000
C	-4.952222000	1.447076000	-0.416063000
H	-5.565628000	1.330445000	0.490550000
O	-4.368903000	3.450365000	0.677254000
O	0.000048000	6.878895000	0.359367000
C	-4.622203000	2.926694000	-0.531710000
C	-3.793231000	4.764793000	0.666206000
H	-4.502323000	5.465071000	0.208052000
H	-2.895020000	4.750932000	0.029792000
C	-3.458587000	5.124050000	2.087982000
H	-2.964432000	6.101310000	2.121907000
H	-2.777220000	4.380718000	2.515934000
H	-4.358429000	5.164666000	2.709944000
C	-5.758851000	0.986870000	-1.609761000
C	-5.137282000	0.665200000	-2.815572000
H	-4.053066000	0.731960000	-2.888028000
C	-5.891634000	0.262392000	-3.910318000
H	-5.395299000	0.013274000	-4.845423000
C	-7.277412000	0.177783000	-3.813497000
H	-7.866112000	-0.142113000	-4.670102000
C	-7.905889000	0.503633000	-2.616863000
H	-8.988612000	0.442213000	-2.533368000
C	-7.148459000	0.908407000	-1.522590000
H	-7.637385000	1.161205000	-0.581421000

C	-3.658952000	-0.670614000	0.202337000
C	-2.430500000	-1.303691000	0.406683000
H	-2.404449000	-2.332376000	0.757966000
C	-4.952251000	-1.446822000	0.417380000
H	-5.566018000	-1.329886000	-0.488940000
C	-4.622389000	-2.926516000	0.532445000
C	-3.794242000	-4.764372000	-0.666471000
H	-4.503298000	-5.464607000	-0.208194000
H	-2.895706000	-4.750971000	-0.030506000
C	-3.460440000	-5.123211000	-2.088550000
H	-2.967291000	-6.100949000	-2.123205000
H	-2.778532000	-4.380316000	-2.516391000
H	-4.360582000	-5.162631000	-2.710159000
C	-5.758337000	-0.986754000	1.611496000
C	-7.147940000	-0.907735000	1.524771000
H	-7.637240000	-1.160024000	0.583659000
C	-7.904888000	-0.503049000	2.619412000
H	-8.987613000	-0.441194000	2.536266000
C	-7.275926000	-0.177842000	3.815965000
H	-7.864246000	0.141979000	4.672860000
C	-5.890149000	-0.262992000	3.912333000
H	-5.393436000	-0.014373000	4.847371000
C	-5.136279000	-0.665701000	2.817220000
H	-4.052067000	-0.732875000	2.889326000
C	0.000101000	2.781499000	-0.241477000
C	0.000335000	3.337558000	1.041479000
H	0.000530000	2.673555000	1.904420000

C	0.000321000	4.709638000	1.207681000
H	0.000490000	5.166035000	2.195085000
C	0.000061000	5.552069000	0.088345000
C	-0.000168000	5.003856000	-1.195135000
H	-0.000357000	5.636552000	-2.076886000
C	-0.000136000	3.617584000	-1.348299000
H	-0.000315000	3.174795000	-2.341799000
C	-0.000482000	7.771130000	-0.731153000
H	-0.000568000	8.777246000	-0.308265000
H	-0.895116000	7.644336000	-1.356664000
H	0.893817000	7.644735000	-1.357222000
C	1.212280000	0.672162000	-0.197535000

Triplet excited state

Free Energy = -3411.59628

Energy = -3412.61326

N	-0.003815000	1.371395000	-0.117614000
C	1.203603000	0.702862000	-0.052035000
O	4.397554000	-3.255105000	-1.209169000
C	2.427471000	1.393158000	-0.164228000
H	2.400903000	2.459608000	-0.358581000
O	4.569496000	-3.748408000	0.977933000
C	3.641702000	0.706413000	-0.071934000
O	4.561441000	3.753193000	-0.974239000
C	4.943503000	1.487218000	-0.187127000
H	5.572043000	1.215757000	0.675291000

O	4.395580000	3.291563000	1.220059000
O	-0.001749000	6.930876000	-0.197295000
C	4.643321000	2.972305000	-0.058123000
C	3.823224000	4.591041000	1.427905000
H	4.567170000	5.357166000	1.177091000
H	2.977611000	4.719696000	0.735707000
C	3.380882000	4.657313000	2.864138000
H	2.918965000	5.627379000	3.074191000
H	2.645647000	3.871319000	3.069111000
H	4.226511000	4.520053000	3.545501000
C	5.712388000	1.209460000	-1.459553000
C	5.055861000	1.101073000	-2.684763000
H	3.972391000	1.204868000	-2.716350000
C	5.775700000	0.866224000	-3.849339000
H	5.252946000	0.783057000	-4.799408000
C	7.161260000	0.738485000	-3.803546000
H	7.722551000	0.550387000	-4.715773000
C	7.824040000	0.852407000	-2.587029000
H	8.906541000	0.756474000	-2.542770000
C	7.101368000	1.088946000	-1.422014000
H	7.617565000	1.178935000	-0.465995000
C	3.643571000	-0.691458000	0.119064000
C	2.431528000	-1.380744000	0.221155000
H	2.409348000	-2.447915000	0.412596000
C	4.947079000	-1.470818000	0.221179000
H	5.572740000	-1.188497000	-0.639559000
C	4.648284000	-2.954251000	0.072969000

C	3.826813000	-4.552077000	-1.435115000
H	4.568138000	-5.321119000	-1.185532000
H	2.975027000	-4.687044000	-0.751781000
C	3.396739000	-4.604008000	-2.875640000
H	2.937101000	-5.572129000	-3.099208000
H	2.662787000	-3.816531000	-3.079255000
H	4.248316000	-4.459735000	-3.548107000
C	5.718741000	-1.205118000	1.494357000
C	7.106914000	-1.076301000	1.453256000
H	7.619927000	-1.151365000	0.494243000
C	7.832718000	-0.851162000	2.618575000
H	8.914521000	-0.748855000	2.571575000
C	7.173987000	-0.756836000	3.838948000
H	7.737725000	-0.577867000	4.751507000
C	5.789270000	-0.892353000	3.888181000
H	5.269661000	-0.824329000	4.841179000
C	5.066276000	-1.115710000	2.723309000
H	3.983491000	-1.225362000	2.757675000
C	-0.005250000	2.808129000	-0.175424000
C	-0.013749000	3.530145000	1.015537000
H	-0.021341000	2.996130000	1.963794000
C	-0.012401000	4.919612000	0.974958000
H	-0.017843000	5.517860000	1.882372000
C	-0.002539000	5.580068000	-0.262946000
C	0.005758000	4.850950000	-1.451742000
H	0.013598000	5.348439000	-2.415522000
C	0.004472000	3.452409000	-1.402221000

H	0.011674000	2.865216000	-2.317279000
C	0.009397000	7.649742000	-1.408864000
H	0.008780000	8.707684000	-1.140571000
H	0.908725000	7.429681000	-2.000570000
H	-0.880694000	7.432457000	-2.015407000
C	-1.209346000	0.699520000	-0.054543000
N	-0.000354000	-1.365108000	0.187724000
C	-1.207650000	-0.695584000	0.123789000
O	-4.416627000	3.290256000	1.183668000
C	-2.431673000	-1.385049000	0.228991000
H	-2.405593000	-2.450406000	0.430434000
O	-4.573993000	3.731341000	-1.015553000
C	-3.645737000	-0.700849000	0.121194000
O	-4.579751000	-3.746122000	1.031350000
C	-4.947471000	-1.482609000	0.229572000
H	-5.568634000	-1.217349000	-0.640044000
O	-4.376627000	-3.291578000	-1.161457000
O	0.007794000	-6.923111000	0.014682000
C	-4.645602000	-2.968268000	0.111422000
C	-3.802636000	-4.592219000	-1.357271000
H	-4.558431000	-5.356240000	-1.137176000
H	-2.981838000	-4.728857000	-0.637396000
C	-3.310016000	-4.651355000	-2.777267000
H	-2.853630000	-5.625791000	-2.979515000
H	-2.555728000	-3.874291000	-2.945366000
H	-4.128257000	-4.495477000	-3.487444000
C	-5.727258000	-1.196798000	1.493499000

C	-5.081061000	-1.082735000	2.723717000
H	-3.998026000	-1.187452000	2.765275000
C	-5.810361000	-0.841305000	3.880985000
H	-5.295554000	-0.754042000	4.835010000
C	-7.195316000	-0.712283000	3.822773000
H	-7.764142000	-0.519113000	4.729252000
C	-7.847866000	-0.831516000	2.601230000
H	-8.929840000	-0.734623000	2.547333000
C	-7.115686000	-1.074831000	1.443561000
H	-7.623846000	-1.169295000	0.483687000
C	-3.647265000	0.695434000	-0.081144000
C	-2.434958000	1.384697000	-0.173510000
H	-2.410774000	2.450248000	-0.373766000
C	-4.950830000	1.471170000	-0.209370000
H	-5.582691000	1.205765000	0.652431000
C	-4.656825000	2.958484000	-0.092772000
C	-3.854227000	4.595408000	1.383133000
H	-4.601551000	5.354109000	1.120091000
H	-3.004868000	4.723185000	0.695533000
C	-3.422081000	4.678325000	2.821573000
H	-2.969249000	5.653921000	3.025650000
H	-2.681951000	3.900270000	3.038854000
H	-4.271215000	4.540657000	3.498475000
C	-5.712181000	1.178267000	-1.482976000
C	-7.100884000	1.053042000	-1.451414000
H	-7.622315000	1.150510000	-0.498990000
C	-7.816616000	0.802300000	-2.617743000

H	-8.898976000	0.702855000	-2.578132000
C	-7.147126000	0.678701000	-3.829647000
H	-7.702984000	0.479493000	-4.742835000
C	-5.761848000	0.811164000	-3.869591000
H	-5.233845000	0.720549000	-4.816065000
C	-5.048957000	1.060268000	-2.703707000
H	-3.965736000	1.167822000	-2.730958000
C	0.000949000	-2.803379000	0.188293000
C	-0.019528000	-3.469248000	-1.035166000
H	-0.037205000	-2.890987000	-1.957102000
C	-0.016951000	-4.858422000	-1.061125000
H	-0.033234000	-5.412487000	-1.996087000
C	0.007154000	-5.576814000	0.143887000
C	0.027969000	-4.904531000	1.365611000
H	0.046964000	-5.447594000	2.304404000
C	0.024226000	-3.504680000	1.382951000
H	0.040698000	-2.961892000	2.324864000
C	0.030860000	-7.697780000	1.191205000
H	0.027246000	-8.742052000	0.873883000
H	-0.853076000	-7.509146000	1.816077000
H	0.936086000	-7.505462000	1.783568000
C	1.205527000	-0.692902000	0.122190000

Cation Radical

Free Energy = -3411.511442

Energy = -3412.530455

N	-0.005069000	-1.373601000	0.203959000
C	1.198740000	-0.694222000	0.129334000
O	4.446027000	3.393698000	1.037215000
C	2.419066000	-1.363078000	0.247758000
H	2.387057000	-2.429488000	0.449899000
O	4.446940000	3.640477000	-1.198554000
C	3.634910000	-0.710094000	0.138568000
O	4.428947000	-3.682871000	1.207793000
C	4.924993000	-1.502738000	0.268000000
H	5.531806000	-1.284458000	-0.624072000
O	4.385831000	-3.395004000	-1.022879000
O	-0.041540000	-6.924224000	-0.049570000
C	4.588986000	-2.987652000	0.235436000
C	3.844952000	-4.721816000	-1.160081000
H	4.565079000	-5.443037000	-0.756923000
H	2.935335000	-4.792437000	-0.543159000
C	3.555562000	-4.940597000	-2.619200000
H	3.128937000	-5.936783000	-2.773044000
H	2.838992000	-4.197410000	-2.985812000
H	4.467488000	-4.860847000	-3.218391000
C	5.725007000	-1.158453000	1.505728000
C	5.098327000	-0.943751000	2.732440000
H	4.013594000	-1.010712000	2.800911000
C	5.850844000	-0.654575000	3.864223000
H	5.352999000	-0.488587000	4.816296000
C	7.237702000	-0.583126000	3.781905000
H	7.825338000	-0.355587000	4.667524000

C	7.870573000	-0.808398000	2.564117000
H	8.954454000	-0.761994000	2.494915000
C	7.116514000	-1.095867000	1.431879000
H	7.609968000	-1.273466000	0.476574000
C	3.641462000	0.694887000	-0.089544000
C	2.431583000	1.360692000	-0.189420000
H	2.409247000	2.427427000	-0.390365000
C	4.940165000	1.472825000	-0.229052000
H	5.545920000	1.260798000	0.664881000
C	4.619783000	2.961423000	-0.216799000
C	3.924861000	4.729998000	1.160206000
H	4.641264000	5.432906000	0.719788000
H	2.998967000	4.797732000	0.567876000
C	3.681949000	4.985592000	2.621826000
H	3.268144000	5.988633000	2.764794000
H	2.972296000	4.257731000	3.029794000
H	4.611554000	4.912839000	3.194133000
C	5.735723000	1.101085000	-1.461465000
C	7.122006000	0.973933000	-1.375831000
H	7.614487000	1.125503000	-0.415519000
C	7.871409000	0.652661000	-2.502278000
H	8.951339000	0.555630000	-2.424155000
C	7.238908000	0.458802000	-3.725569000
H	7.822725000	0.205352000	-4.606675000
C	5.857448000	0.594568000	-3.819381000
H	5.360610000	0.452854000	-4.775898000
C	5.109565000	0.916367000	-2.693530000

H	4.029712000	1.033051000	-2.770377000
C	-0.011344000	-2.815207000	0.186127000
C	-0.003487000	-3.466662000	-1.048188000
H	0.010231000	-2.882254000	-1.966365000
C	-0.014630000	-4.848010000	-1.091356000
H	-0.011606000	-5.387386000	-2.035092000
C	-0.032120000	-5.590828000	0.099827000
C	-0.038769000	-4.929788000	1.332437000
H	-0.052471000	-5.485004000	2.264288000
C	-0.028496000	-3.539299000	1.368874000
H	-0.034887000	-3.015953000	2.322459000
C	-0.058325000	-7.732278000	1.112879000
H	-0.062913000	-8.765712000	0.765460000
H	0.833917000	-7.562602000	1.729204000
H	-0.958986000	-7.549094000	1.712858000
C	-1.203412000	-0.684263000	0.129964000
N	0.006289000	1.391343000	-0.147505000
C	-1.197834000	0.713134000	-0.068427000
O	-4.438819000	-3.348011000	-1.031083000
C	-2.418872000	1.380561000	-0.192694000
H	-2.386622000	2.446270000	-0.397817000
O	-4.443009000	-3.649758000	1.198283000
C	-3.634517000	0.725959000	-0.088910000
O	-4.430003000	3.669176000	-1.223941000
C	-4.926807000	1.515075000	-0.226635000
H	-5.527448000	1.318665000	0.674361000
O	-4.395857000	3.443480000	1.013796000

O	0.028715000	6.947263000	-0.198536000
C	-4.592941000	3.000876000	-0.233366000
C	-3.861198000	4.776203000	1.116144000
H	-4.586796000	5.483292000	0.698009000
H	-2.954463000	4.836455000	0.494013000
C	-3.568260000	5.032403000	2.568476000
H	-3.148570000	6.035079000	2.696807000
H	-2.845470000	4.303346000	2.950890000
H	-4.477599000	4.960888000	3.172609000
C	-5.736576000	1.138371000	-1.448069000
C	-5.122882000	0.938474000	-2.684012000
H	-4.043131000	1.048328000	-2.771733000
C	-5.883012000	0.610151000	-3.799684000
H	-5.395952000	0.456436000	-4.759359000
C	-7.264285000	0.483172000	-3.691691000
H	-7.857724000	0.224482000	-4.564807000
C	-7.884331000	0.692491000	-2.464554000
H	-8.964018000	0.602365000	-2.375522000
C	-7.122632000	1.020246000	-1.348235000
H	-7.605104000	1.183211000	-0.384676000
C	-3.639593000	-0.678508000	0.142558000
C	-2.429420000	-1.342439000	0.249130000
H	-2.407361000	-2.409114000	0.451183000
C	-4.935881000	-1.459353000	0.280312000
H	-5.550559000	-1.229782000	-0.603201000
C	-4.614594000	-2.946954000	0.233181000
C	-3.915050000	-4.679520000	-1.187011000

H	-4.628864000	-5.394713000	-0.762434000
H	-2.987772000	-4.759105000	-0.598380000
C	-3.674240000	-4.899492000	-2.654790000
H	-3.258279000	-5.897832000	-2.822629000
H	-2.967527000	-4.160000000	-3.046922000
H	-4.605251000	-4.815484000	-3.223325000
C	-5.718574000	-1.114875000	1.529104000
C	-7.110331000	-1.040718000	1.471124000
H	-7.615655000	-1.208773000	0.520301000
C	-7.849617000	-0.754590000	2.613360000
H	-8.933790000	-0.699303000	2.556403000
C	-7.201675000	-0.542073000	3.825488000
H	-7.777708000	-0.315764000	4.719007000
C	-5.814598000	-0.624648000	3.891937000
H	-5.305003000	-0.468455000	4.839450000
C	-5.076806000	-0.912392000	2.750066000
H	-3.991944000	-0.988007000	2.806240000
C	0.011859000	2.831566000	-0.199312000
C	-0.004676000	3.551709000	0.996141000
H	-0.022868000	3.020688000	1.946080000
C	0.002232000	4.933734000	0.959583000
H	-0.010012000	5.526130000	1.870893000
C	0.024680000	5.607696000	-0.271805000
C	0.040755000	4.877355000	-1.464731000
H	0.058452000	5.377784000	-2.426949000
C	0.034074000	3.487686000	-1.420975000
H	0.046968000	2.910508000	-2.342960000

C	0.049830000	7.688417000	-1.404737000
H	0.049050000	8.739794000	-1.116159000
H	-0.838212000	7.481018000	-2.015557000
H	0.954652000	7.474793000	-1.988136000
C	1.204914000	0.703344000	-0.067944000

3h

Ground state

Free Energy = -2488.271661

Energy = -2488.992767

N	-1.383957000	0.096372000	-0.181905000
C	-0.612729000	1.266326000	-0.097446000
O	3.033320000	4.547457000	-1.787471000
C	-1.182340000	2.524598000	-0.222289000
H	-2.254561000	2.598937000	-0.397927000
O	4.214607000	4.348574000	0.116325000
C	-0.425170000	3.700943000	-0.132499000
O	-3.542067000	4.925048000	-0.085114000
C	-1.130970000	5.029702000	-0.326945000
H	-0.534804000	5.821818000	0.144831000
O	-2.241972000	5.089846000	1.743150000
O	-6.931272000	0.471801000	-0.344348000
C	-2.446785000	5.016957000	0.415763000
C	-3.418567000	4.982558000	2.536857000
H	-4.122785000	5.786520000	2.301841000
H	-3.916635000	4.023902000	2.358006000

C	0.947405000	3.604025000	0.069908000
C	1.524273000	2.333363000	0.201624000
H	2.595896000	2.254807000	0.379499000
C	1.838947000	4.823039000	0.217978000
H	1.391753000	5.660033000	-0.335208000
C	3.168401000	4.559195000	-0.449582000
C	4.205751000	4.172636000	-2.502137000
H	5.031568000	4.857419000	-2.286741000
H	4.514904000	3.159028000	-2.224240000
C	-2.803913000	0.195631000	-0.255424000
C	-3.560552000	0.253291000	0.917115000
H	-3.047104000	0.223748000	1.876360000
C	-4.938662000	0.345732000	0.853476000
H	-5.550878000	0.393426000	1.750264000
C	-5.582218000	0.381408000	-0.388758000
C	-4.831943000	0.324270000	-1.563712000
H	-5.311752000	0.350305000	-2.536911000
C	-3.445105000	0.231713000	-1.486001000
H	-2.845199000	0.185162000	-2.392611000
C	-7.628986000	0.511959000	-1.566145000
H	-8.688794000	0.584253000	-1.315230000
H	-7.342933000	1.386478000	-2.167208000
H	-7.462438000	-0.399160000	-2.157756000
C	-0.786533000	-1.170072000	-0.081606000
N	1.372037000	-0.097751000	0.237923000
C	0.602771000	-1.267783000	0.135315000
O	-3.060686000	-4.600021000	1.721389000

C	1.174441000	-2.525958000	0.249705000
H	2.245193000	-2.599210000	0.434958000
O	-4.209958000	-4.368449000	-0.198283000
C	0.421904000	-3.702805000	0.135564000
O	3.546087000	-4.914774000	0.153873000
C	1.129358000	-5.032955000	0.314505000
H	0.553286000	-5.814447000	-0.198775000
O	2.304639000	-4.992366000	-1.720277000
O	6.918648000	-0.507096000	0.342286000
C	2.467554000	-4.986238000	-0.385226000
C	3.502305000	-4.812262000	-2.467952000
H	4.221729000	-5.608236000	-2.253044000
H	3.965754000	-3.850838000	-2.220821000
C	-0.948469000	-3.606680000	-0.080803000
C	-1.528845000	-2.335981000	-0.195393000
H	-2.599025000	-2.257800000	-0.381986000
C	-1.830162000	-4.827359000	-0.267765000
H	-1.387183000	-5.672880000	0.275705000
C	-3.172556000	-4.585007000	0.381384000
C	-4.247415000	-4.246300000	2.423047000
H	-5.065269000	-4.931298000	2.179784000
H	-4.557889000	-3.229129000	2.160023000
C	2.792658000	-0.200414000	0.295826000
C	3.534703000	-0.293711000	-0.884060000
H	3.009756000	-0.286362000	-1.837627000
C	4.912650000	-0.396018000	-0.834515000
H	5.513677000	-0.471373000	-1.737034000

C	5.571069000	-0.404593000	0.400661000
C	4.835531000	-0.310773000	1.582387000
H	5.326738000	-0.315344000	2.550208000
C	3.448330000	-0.210330000	1.518874000
H	2.859689000	-0.136713000	2.430963000
C	7.630961000	-0.522038000	1.556256000
H	8.686942000	-0.610142000	1.294521000
H	7.344805000	-1.378267000	2.183017000
H	7.479439000	0.405428000	2.126091000
C	0.777581000	1.168257000	0.114220000
H	-4.003275000	-4.305953000	3.484289000
H	3.211808000	-4.834899000	-3.518896000
H	3.943648000	4.212669000	-3.560018000
H	-3.092957000	5.053327000	3.575286000
C	-1.329735000	5.338349000	-1.804818000
H	-1.955994000	4.570123000	-2.270067000
H	-1.820303000	6.306178000	-1.952956000
H	-0.359799000	5.346917000	-2.315591000
C	2.019917000	5.199754000	1.682479000
H	1.043121000	5.385478000	2.143860000
H	2.504236000	4.379819000	2.223014000
H	2.644868000	6.091833000	1.796064000
C	-1.981897000	-5.174560000	-1.742937000
H	-2.464863000	-4.347871000	-2.274324000
H	-0.995008000	-5.340527000	-2.190607000
H	-2.595659000	-6.070082000	-1.886628000
C	1.285054000	-5.382313000	1.788425000

H	1.776136000	-6.351665000	1.924175000
H	1.893816000	-4.624428000	2.292362000
H	0.300940000	-5.408824000	2.270579000

Triplet excited state

Free Energy = -2488.17885

Energy = -2488.89590

N	-1.361491000	-0.106410000	0.148702000
C	-0.608105000	-1.264433000	0.088144000
O	3.065704000	-4.465232000	1.779123000
C	-1.206683000	-2.538286000	0.201115000
H	-2.276879000	-2.617632000	0.366551000
O	4.231684000	-4.327717000	-0.139966000
C	-0.411811000	-3.691818000	0.120385000
O	-3.512656000	-4.959494000	0.097114000
C	-1.097265000	-5.031951000	0.301716000
H	-0.501370000	-5.813145000	-0.188333000
O	-2.235323000	-5.010106000	-1.754121000
O	-6.895745000	-0.530025000	0.418296000
C	-2.423819000	-5.009110000	-0.422720000
C	-3.418740000	-4.819880000	-2.521752000
H	-4.147555000	-5.611205000	-2.322401000
H	-3.877941000	-3.855186000	-2.277500000
C	0.971084000	-3.585862000	-0.062821000
C	1.575078000	-2.325904000	-0.178131000
H	2.643967000	-2.239682000	-0.348869000

C	1.856714000	-4.808963000	-0.206290000
H	1.418119000	-5.641933000	0.359476000
C	3.191960000	-4.524563000	0.442005000
C	4.222002000	-3.993787000	2.462410000
H	5.085871000	-4.634884000	2.263463000
H	4.461777000	-2.974523000	2.136571000
C	-2.789953000	-0.215985000	0.253109000
C	-3.550058000	-0.306676000	-0.910447000
H	-3.049472000	-0.294090000	-1.876354000
C	-4.929403000	-0.411353000	-0.819278000
H	-5.557186000	-0.484253000	-1.702872000
C	-5.547649000	-0.425061000	0.437154000
C	-4.781968000	-0.334108000	1.599796000
H	-5.246559000	-0.343055000	2.580179000
C	-3.393360000	-0.229226000	1.499706000
H	-2.776644000	-0.155927000	2.392543000
C	-7.572979000	-0.550273000	1.652165000
H	-8.635861000	-0.639212000	1.420381000
H	-7.267404000	-1.408181000	2.267284000
H	-7.406361000	0.375495000	2.220429000
C	-0.793701000	1.152310000	0.068205000
N	1.353552000	0.100234000	-0.167827000
C	0.601156000	1.258206000	-0.101172000
O	-3.005919000	4.556686000	-1.824499000
C	1.204778000	2.531913000	-0.196480000
H	2.276756000	2.609890000	-0.349591000
O	-4.232568000	4.346141000	0.049699000

C	0.411557000	3.686011000	-0.106993000
O	3.516737000	4.937903000	-0.015511000
C	1.104841000	5.026262000	-0.254605000
H	0.506742000	5.801148000	0.242568000
O	2.211047000	4.957350000	1.816778000
O	6.890308000	0.501923000	-0.420943000
C	2.420290000	4.982442000	0.488562000
C	3.380629000	4.739550000	2.598105000
H	4.121268000	5.525931000	2.424464000
H	3.832236000	3.774065000	2.342674000
C	-0.973750000	3.581125000	0.058453000
C	-1.583317000	2.321126000	0.154087000
H	-2.654475000	2.236598000	0.309681000
C	-1.856791000	4.804578000	0.209798000
H	-1.395073000	5.651289000	-0.315293000
C	-3.172821000	4.555424000	-0.490313000
C	-4.154576000	4.163392000	-2.567225000
H	-4.999761000	4.828076000	-2.364814000
H	-4.445504000	3.140577000	-2.301870000
C	2.782552000	0.207463000	-0.268112000
C	3.542846000	0.247759000	0.898389000
H	3.042039000	0.199426000	1.863137000
C	4.923089000	0.347168000	0.811191000
H	5.551117000	0.382669000	1.696970000
C	5.541646000	0.406108000	-0.443905000
C	4.775667000	0.365585000	-1.609195000
H	5.240371000	0.410195000	-2.588531000

C	3.386241000	0.265310000	-1.513059000
H	2.769236000	0.231421000	-2.408047000
C	7.567854000	0.566631000	-1.653141000
H	8.631221000	0.639842000	-1.418122000
H	7.267550000	1.449953000	-2.233920000
H	7.395615000	-0.335025000	-2.257362000
C	0.785650000	-1.157914000	-0.088446000
H	-3.870892000	4.216460000	-3.618947000
H	3.057037000	4.743719000	3.639584000
H	3.974782000	-4.004727000	3.524567000
H	-3.110498000	-4.839909000	-3.567670000
C	-1.277243000	-5.359763000	1.778725000
H	-1.898830000	-4.597002000	2.258467000
H	-1.765813000	-6.329599000	1.918510000
H	-0.302345000	-5.374236000	2.279765000
C	2.022977000	-5.194581000	-1.671003000
H	1.043347000	-5.391177000	-2.121889000
H	2.495145000	-4.373511000	-2.220022000
H	2.653995000	-6.082232000	-1.783966000
C	-2.066227000	5.147693000	1.679584000
H	-2.560920000	4.314897000	2.189652000
H	-1.098801000	5.322725000	2.164576000
H	-2.693518000	6.037087000	1.799684000
C	1.306591000	5.381270000	-1.722351000
H	1.802854000	6.350514000	-1.837041000
H	1.929828000	4.623833000	-2.208386000
H	0.338327000	5.411341000	-2.235441000

Cation Radical

Free Energy = -2488.100703

Energy = -2488.82015

N	-0.806356000	1.108588000	-0.150665000
C	0.567628000	1.268661000	-0.093241000
O	5.611096000	0.704456000	-1.814404000
C	1.159784000	2.530117000	-0.203372000
H	0.523051000	3.399112000	-0.353218000
O	5.905969000	-0.492557000	0.069749000
C	2.532456000	2.697733000	-0.125629000
O	1.343463000	5.737133000	-0.079806000
C	3.105649000	4.090488000	-0.293074000
H	4.084221000	4.137583000	0.198532000
O	2.499500000	5.091196000	1.741144000
O	-4.051490000	5.604587000	-0.433161000
C	2.218452000	5.081566000	0.432528000
C	1.672941000	5.948728000	2.532256000
H	1.770528000	6.986527000	2.202533000
H	0.622961000	5.651958000	2.446442000
C	3.361651000	1.562533000	0.042376000
C	2.781475000	0.309415000	0.153970000
H	3.414038000	-0.562606000	0.304464000
C	4.865069000	1.690435000	0.179689000
H	5.199111000	2.581090000	-0.365544000
C	5.534251000	0.509144000	-0.492594000

C	6.174355000	-0.380353000	-2.556004000
H	7.194316000	-0.585954000	-2.220349000
H	5.573772000	-1.285766000	-2.423794000
C	-1.650564000	2.271326000	-0.259130000
C	-2.055061000	2.928503000	0.903020000
H	-1.732093000	2.555918000	1.873153000
C	-2.860356000	4.045805000	0.806586000
H	-3.194912000	4.584501000	1.688498000
C	-3.269913000	4.514843000	-0.450241000
C	-2.860353000	3.849862000	-1.610041000
H	-3.167088000	4.197160000	-2.591013000
C	-2.047847000	2.726512000	-1.507264000
H	-1.721958000	2.200022000	-2.401975000
C	-4.501446000	6.131318000	-1.666340000
H	-5.110819000	7.001784000	-1.422003000
H	-3.659669000	6.446278000	-2.296619000
H	-5.115731000	5.402695000	-2.211144000
C	-1.381607000	-0.146789000	-0.051727000
N	0.820992000	-1.122230000	0.178197000
C	-0.552816000	-1.282783000	0.116903000
O	-5.634592000	-0.627946000	1.809168000
C	-1.145117000	-2.545075000	0.217289000
H	-0.508386000	-3.417142000	0.349008000
O	-5.874787000	0.490777000	-0.129297000
C	-2.518897000	-2.710295000	0.149133000
O	-1.323833000	-5.713578000	-0.097157000
C	-3.088901000	-4.106339000	0.305047000

H	-4.099372000	-4.132852000	-0.117189000
O	-2.677734000	-5.093237000	-1.785695000
O	4.115509000	-5.580899000	0.478123000
C	-2.260333000	-5.075550000	-0.514378000
C	-1.932944000	-5.946803000	-2.658676000
H	-1.981303000	-6.982922000	-2.313146000
H	-0.884003000	-5.637817000	-2.692472000
C	-3.349174000	-1.572686000	-0.002768000
C	-2.767590000	-0.320297000	-0.114338000
H	-3.398133000	0.553887000	-0.259466000
C	-4.853720000	-1.703526000	-0.126410000
H	-5.185068000	-2.565624000	0.465275000
C	-5.525348000	-0.489733000	0.483015000
C	-6.208197000	0.490125000	2.490911000
H	-7.215973000	0.691300000	2.117889000
H	-5.595213000	1.384415000	2.341355000
C	1.668743000	-2.281983000	0.291428000
C	2.112584000	-2.915657000	-0.869350000
H	1.809363000	-2.533164000	-1.841963000
C	2.932511000	-4.021695000	-0.768665000
H	3.297149000	-4.542292000	-1.649409000
C	3.316517000	-4.503726000	0.491174000
C	2.866060000	-3.863530000	1.649821000
H	3.152322000	-4.221519000	2.633167000
C	2.040164000	-2.750293000	1.542678000
H	1.684396000	-2.241513000	2.436273000
C	4.543314000	-6.118745000	1.714175000

H	5.173281000	-6.975187000	1.472479000
H	3.691618000	-6.457268000	2.318443000
H	5.131444000	-5.388535000	2.285140000
C	1.396155000	0.133526000	0.082059000
H	-6.238333000	0.217812000	3.545581000
H	-2.393799000	-5.849958000	-3.641260000
H	6.171529000	-0.066754000	-3.599568000
H	2.020533000	5.840256000	3.559288000
C	3.241251000	4.438288000	-1.771986000
H	2.255130000	4.459486000	-2.246545000
H	3.698750000	5.423265000	-1.904056000
H	3.859619000	3.692130000	-2.284194000
C	5.257044000	1.791950000	1.650667000
H	4.739042000	2.632031000	2.127812000
H	4.985118000	0.870781000	2.175711000
H	6.335864000	1.936092000	1.761579000
C	-5.250951000	-1.876865000	-1.590040000
H	-4.981685000	-0.980096000	-2.157007000
H	-4.734476000	-2.737340000	-2.030353000
H	-6.330166000	-2.026467000	-1.689695000
C	-3.125443000	-4.511506000	1.775429000
H	-3.575378000	-5.501186000	1.898722000
H	-2.110886000	-4.550554000	2.184059000
H	-3.708820000	-3.787432000	2.355227000

3i

Ground state

Free Energy = -2645.328136

Energy = -2646.156654

N	-0.000759000	1.376341000	-0.257527000
C	1.218741000	0.689462000	-0.132277000
O	4.879801000	-2.755158000	-1.626346000
C	2.434019000	1.348976000	-0.248475000
H	2.428261000	2.418839000	-0.451923000
O	4.607171000	-3.865916000	0.309381000
C	3.659597000	0.685933000	-0.114462000
O	4.588808000	3.871281000	-0.325972000
C	4.945322000	1.470825000	-0.292823000
H	5.742025000	0.994932000	0.298497000
O	4.756749000	2.793112000	1.639905000
O	-0.002236000	6.928692000	0.102877000
C	4.763117000	2.850134000	0.297003000
C	4.408485000	4.012800000	2.286609000
H	5.104844000	4.812469000	2.017117000
H	3.396952000	4.320099000	1.997543000
C	3.660035000	-0.686212000	0.122036000
C	2.434961000	-1.354839000	0.234679000
H	2.431127000	-2.424810000	0.437261000
C	4.945505000	-1.462458000	0.334571000
H	5.759894000	-0.967525000	-0.215136000
C	4.806102000	-2.833096000	-0.286413000
C	4.614795000	-3.974780000	-2.311440000
H	5.325910000	-4.751933000	-2.015481000

H	3.602351000	-4.326852000	-2.086114000
C	-0.001006000	2.801681000	-0.201500000
C	-0.007237000	3.446026000	1.038201000
H	-0.011944000	2.843019000	1.944495000
C	-0.007684000	4.826988000	1.106699000
H	-0.012499000	5.353026000	2.058031000
C	-0.001527000	5.586716000	-0.069461000
C	0.004710000	4.949286000	-1.309932000
H	0.009453000	5.520157000	-2.232995000
C	0.004746000	3.557687000	-1.365076000
H	0.009537000	3.044829000	-2.324548000
C	0.003674000	7.739163000	-1.048232000
H	0.002103000	8.773247000	-0.698886000
H	0.901497000	7.568669000	-1.658687000
H	-0.888058000	7.568986000	-1.667645000
C	-1.220633000	0.689945000	-0.134638000
N	-0.001272000	-1.386714000	0.211529000
C	-1.220764000	-0.697567000	0.103510000
O	-4.777691000	2.794874000	1.612635000
C	-2.436500000	-1.352883000	0.239841000
H	-2.431714000	-2.421816000	0.448462000
O	-4.596271000	3.866395000	-0.355708000
C	-3.661636000	-0.685915000	0.121071000
O	-4.602423000	-3.865241000	0.362723000
C	-4.947424000	-1.463113000	0.328951000
H	-5.754165000	-0.984795000	-0.246583000
O	-4.806122000	-2.792473000	-1.602747000

O	-0.037816000	-6.940610000	-0.117703000
C	-4.784748000	-2.845232000	-0.259791000
C	-4.477326000	-4.016008000	-2.252373000
H	-5.173736000	-4.810511000	-1.968095000
H	-3.462763000	-4.329012000	-1.980595000
C	-3.661416000	0.684567000	-0.124090000
C	-2.436032000	1.348376000	-0.256636000
H	-2.430588000	2.417348000	-0.464932000
C	-4.947485000	1.465253000	-0.316642000
H	-5.748501000	0.989417000	0.268849000
C	-4.773557000	2.847138000	0.269515000
C	-4.436182000	4.017346000	2.257712000
H	-5.131805000	4.814949000	1.980316000
H	-3.423010000	4.325237000	1.975021000
C	-0.005385000	-2.812096000	0.163751000
C	-0.042081000	-3.463061000	-1.071777000
H	-0.064090000	-2.864950000	-1.980953000
C	-0.052882000	-4.844278000	-1.132615000
H	-0.080749000	-5.375299000	-2.080722000
C	-0.025483000	-5.597654000	0.047081000
C	0.011816000	-4.953737000	1.283746000
H	0.033202000	-5.519804000	2.209549000
C	0.020334000	-3.561988000	1.331274000
H	0.047758000	-3.044124000	2.287739000
C	-0.014102000	-7.744717000	1.037546000
H	-0.029804000	-8.780690000	0.694169000
H	-0.891904000	-7.564944000	1.673945000

H	0.897029000	-7.577200000	1.628838000
C	1.218984000	-0.698901000	0.102505000
H	-4.488311000	3.821187000	3.329199000
H	-4.539983000	-3.818783000	-3.323096000
H	4.712302000	-3.753947000	-3.374907000
H	4.453013000	3.813039000	3.357775000
C	5.367976000	1.527850000	-1.760568000
H	4.629286000	2.132071000	-2.304198000
H	5.300509000	0.508854000	-2.168399000
C	5.311142000	-1.540005000	1.816774000
H	5.222459000	-0.526824000	2.235266000
H	4.555406000	-2.155126000	2.323401000
C	-5.356647000	1.515006000	-1.788479000
H	-4.614847000	2.119109000	-2.327957000
H	-5.282245000	0.494361000	-2.191168000
C	-5.338873000	-1.512108000	1.805637000
H	-4.591987000	-2.117836000	2.336187000
H	-5.257349000	-0.491646000	2.207444000
C	-6.735079000	-2.063828000	2.033548000
H	-6.814101000	-3.095078000	1.672426000
H	-6.997705000	-2.063136000	3.096380000
H	-7.486849000	-1.460713000	1.506795000
C	-6.754289000	2.069789000	-1.999554000
H	-7.500927000	1.468338000	-1.463670000
H	-6.826736000	3.101232000	-1.637618000
H	-7.029779000	2.069580000	-3.059123000
C	6.765828000	2.087593000	-1.956705000

H	7.050876000	2.092193000	-3.013736000
H	6.832065000	3.117856000	-1.590274000
H	7.509351000	1.486236000	-1.416419000
C	6.703288000	-2.095842000	2.059124000
H	6.788735000	-3.120866000	1.682060000
H	7.464079000	-1.484076000	1.555944000
H	6.947404000	-2.113325000	3.126222000

Triplet excited state

Free Energy = -2645.23843

Energy = -2646.06120

N	-0.000272000	-1.362494000	-0.129721000
C	-1.212180000	-0.699395000	-0.075161000
O	-4.799252000	2.571804000	-1.908965000
C	-2.436293000	-1.402360000	-0.131885000
H	-2.430817000	-2.482486000	-0.240740000
O	-4.623297000	3.874705000	-0.084452000
C	-3.646043000	-0.698744000	-0.059523000
O	-4.611138000	-3.878373000	0.084596000
C	-4.937655000	-1.485208000	-0.161335000
H	-5.738229000	-0.941303000	0.361534000
O	-4.767792000	-2.576291000	1.911547000
O	0.052049000	-6.918770000	-0.230567000
C	-4.770863000	-2.789796000	0.584368000
C	-4.426610000	-3.714243000	2.696025000
H	-5.127991000	-4.535693000	2.522197000

H	-3.417274000	-4.058771000	2.443140000
C	-3.647212000	0.697428000	0.049094000
C	-2.438161000	1.404138000	0.111789000
H	-2.435294000	2.483922000	0.224153000
C	-4.939450000	1.480572000	0.166143000
H	-5.744931000	0.934343000	-0.346626000
C	-4.785888000	2.785473000	-0.581836000
C	-4.476064000	3.711861000	-2.697887000
H	-5.182922000	4.527248000	-2.517655000
H	-3.467517000	4.065952000	-2.455531000
C	0.004836000	-2.797981000	-0.188356000
C	0.075919000	-3.526481000	0.996849000
H	0.122460000	-2.997334000	1.946472000
C	0.090370000	-4.912635000	0.946441000
H	0.144918000	-5.517129000	1.847481000
C	0.033131000	-5.567681000	-0.289888000
C	-0.038199000	-4.833271000	-1.473970000
H	-0.082771000	-5.326326000	-2.439286000
C	-0.050753000	-3.437930000	-1.414999000
H	-0.104971000	-2.844692000	-2.324901000
C	-0.002533000	-7.632809000	-1.442275000
H	0.023008000	-8.691775000	-1.178926000
H	-0.929428000	-7.422960000	-1.994187000
H	0.857667000	-7.402913000	-2.086486000
C	1.210668000	-0.696707000	-0.082602000
N	-0.001757000	1.369978000	0.093937000
C	1.210474000	0.705965000	0.046405000

O	4.719004000	-2.612601000	1.873391000
C	2.435218000	1.406609000	0.125160000
H	2.431529000	2.484456000	0.253873000
O	4.597636000	-3.877806000	0.018103000
C	3.644513000	0.699706000	0.060940000
O	4.624287000	3.877213000	-0.029705000
C	4.935899000	1.480236000	0.200561000
H	5.746942000	0.938264000	-0.307793000
O	4.828397000	2.593588000	-1.864839000
O	0.003932000	6.925331000	0.237992000
C	4.793614000	2.793040000	-0.535839000
C	4.526846000	3.743991000	-2.647145000
H	5.238380000	4.551069000	-2.448573000
H	3.518333000	4.105462000	-2.416444000
C	3.644427000	-0.694652000	-0.069146000
C	2.435110000	-1.398421000	-0.155439000
H	2.430543000	-2.475496000	-0.290413000
C	4.935957000	-1.481314000	-0.173288000
H	5.731376000	-0.951350000	0.371615000
C	4.751814000	-2.800153000	0.542611000
C	4.331368000	-3.758488000	2.623773000
H	5.019318000	-4.591882000	2.453344000
H	3.322349000	-4.074370000	2.333027000
C	-0.001950000	2.804892000	0.163056000
C	0.020662000	3.543543000	-1.017471000
H	0.037972000	3.022568000	-1.972490000
C	0.022002000	4.929062000	-0.956167000

H	0.039604000	5.541135000	-1.853501000
C	0.000739000	5.573661000	0.286678000
C	-0.021797000	4.829118000	1.466385000
H	-0.038201000	5.314174000	2.436659000
C	-0.022830000	3.434559000	1.396379000
H	-0.040238000	2.833494000	2.302608000
C	-0.016606000	7.629188000	1.456672000
H	-0.010477000	8.690397000	1.201318000
H	0.867135000	7.402991000	2.069577000
H	-0.922154000	7.405664000	2.037896000
C	-1.213105000	0.704559000	0.044211000
H	4.348547000	-3.457245000	3.671784000
H	4.588631000	3.428807000	-3.689335000
H	-4.525130000	3.387028000	-3.737777000
H	-4.467901000	-3.390739000	3.736668000
C	-5.342145000	-1.705592000	-1.619564000
H	-4.602121000	-2.372855000	-2.080755000
H	-5.261160000	-0.739535000	-2.138943000
C	-5.326715000	1.700382000	1.629195000
H	-5.236327000	0.734753000	2.147830000
H	-4.583150000	2.370118000	2.080999000
C	5.358285000	-1.673250000	-1.630364000
H	4.622092000	-2.328504000	-2.114328000
H	5.287109000	-0.696906000	-2.131402000
C	5.305928000	1.684221000	1.670407000
H	4.557431000	2.349366000	2.120797000
H	5.208911000	0.712855000	2.177030000

C	6.704777000	2.244107000	1.858815000
H	6.800405000	3.229943000	1.390921000
H	6.951775000	2.354548000	2.919660000
H	7.457399000	1.580884000	1.411511000
C	6.759031000	-2.242029000	-1.772634000
H	7.499481000	-1.588409000	-1.292065000
H	6.830333000	-3.232614000	-1.310472000
H	7.043944000	-2.344927000	-2.824696000
C	-6.742957000	-2.272503000	-1.768269000
H	-7.014915000	-2.395298000	-2.821612000
H	-6.823631000	-3.253540000	-1.287607000
H	-7.487127000	-1.607093000	-1.310179000
C	-6.727345000	2.262988000	1.794978000
H	-6.817003000	3.243650000	1.315160000
H	-7.475027000	1.595145000	1.346240000
H	-6.986687000	2.385198000	2.851568000

Cation Radical

Free Energy = -2645.160758

Energy = -2645.98627

N	0.010585000	1.385367000	-0.115468000
C	1.209875000	0.695686000	-0.054843000
O	5.148344000	-2.617195000	-1.885861000
C	2.437030000	1.363869000	-0.107645000
H	2.442448000	2.446275000	-0.211138000
O	4.383913000	-3.859091000	-0.171477000

C	3.639123000	0.681179000	-0.029523000
O	4.448373000	3.820478000	0.105041000
C	4.935174000	1.457728000	-0.119540000
H	5.724770000	0.905690000	0.407642000
O	5.006980000	2.615640000	1.921821000
O	0.122971000	6.933447000	-0.296766000
C	4.781236000	2.775648000	0.612602000
C	4.822700000	3.789095000	2.717330000
H	5.508389000	4.579303000	2.399853000
H	3.796722000	4.157968000	2.622012000
C	3.629401000	-0.732687000	0.065498000
C	2.417463000	-1.400969000	0.124173000
H	2.408516000	-2.484588000	0.217338000
C	4.915438000	-1.522491000	0.178868000
H	5.731943000	-0.955690000	-0.286801000
C	4.791106000	-2.809617000	-0.611137000
C	5.025950000	-3.762872000	-2.732746000
H	5.658808000	-4.576820000	-2.368876000
H	3.989122000	-4.110866000	-2.758928000
C	0.026981000	2.823956000	-0.194329000
C	0.080467000	3.572293000	0.981646000
H	0.099459000	3.064060000	1.943739000
C	0.112201000	4.950662000	0.908926000
H	0.153700000	5.567162000	1.802204000
C	0.089106000	5.592879000	-0.337491000
C	0.033828000	4.835501000	-1.511386000
H	0.015232000	5.313913000	-2.484935000

C	0.004224000	3.447926000	-1.432413000
H	-0.035854000	2.846375000	-2.338187000
C	0.103072000	7.645931000	-1.517960000
H	0.136576000	8.703542000	-1.254868000
H	0.975612000	7.401032000	-2.137568000
H	-0.816254000	7.444322000	-2.083131000
C	-1.199835000	0.715161000	-0.064951000
N	-0.010602000	-1.385429000	0.115443000
C	-1.209896000	-0.695745000	0.054836000
O	-5.148722000	2.617305000	1.885785000
C	-2.437066000	-1.363903000	0.107700000
H	-2.442501000	-2.446304000	0.211231000
O	-4.383596000	3.858982000	0.171542000
C	-3.639152000	-0.681193000	0.029592000
O	-4.448605000	-3.820510000	-0.105224000
C	-4.935201000	-1.457742000	0.119692000
H	-5.724853000	-0.905649000	-0.407345000
O	-5.007023000	-2.615328000	-1.921838000
O	-0.122923000	-6.933512000	0.296736000
C	-4.781351000	-2.775570000	-0.612628000
C	-4.822850000	-3.788675000	-2.717528000
H	-5.508626000	-4.578864000	-2.400188000
H	-3.796914000	-4.157674000	-2.622249000
C	-3.629414000	0.732665000	-0.065499000
C	-2.417468000	1.400921000	-0.124249000
H	-2.408515000	2.484535000	-0.217485000
C	-4.915453000	1.522474000	-0.178834000

H	-5.731947000	0.955680000	0.286851000
C	-4.791105000	2.809605000	0.611146000
C	-5.026314000	3.762989000	2.732659000
H	-5.658996000	4.577017000	2.368659000
H	-3.989442000	4.110841000	2.759009000
C	-0.026989000	-2.824017000	0.194300000
C	-0.080995000	-3.572345000	-0.981659000
H	-0.100430000	-3.064106000	-1.943740000
C	-0.112708000	-4.950713000	-0.908937000
H	-0.154609000	-5.567205000	-1.802202000
C	-0.089056000	-5.592945000	0.337462000
C	-0.033270000	-4.835579000	1.511341000
H	-0.014259000	-5.313999000	2.484877000
C	-0.003700000	-3.448002000	1.432368000
H	0.036777000	-2.846460000	2.338131000
C	-0.102449000	-7.646014000	1.517910000
H	-0.136027000	-8.703622000	1.254818000
H	-0.974721000	-7.401160000	2.137913000
H	0.817122000	-7.444373000	2.082673000
C	1.199820000	-0.715221000	0.064914000
H	-5.349130000	3.442314000	3.722755000
H	-5.031168000	-3.492663000	-3.745328000
H	5.348548000	-3.442125000	-3.722889000
H	5.031072000	3.493263000	3.745171000
C	5.343466000	1.662970000	-1.581658000
H	4.601970000	2.323359000	-2.050813000
H	5.274203000	0.693036000	-2.095832000

C	5.256940000	-1.789327000	1.648545000
H	5.180809000	-0.836917000	2.193825000
H	4.486096000	-2.453352000	2.061974000
C	-5.256995000	1.789288000	-1.648509000
H	-4.486089000	2.453200000	-2.062004000
H	-5.180995000	0.836836000	-2.193738000
C	-5.343332000	-1.663091000	1.581832000
H	-4.601779000	-2.323487000	2.050892000
H	-5.274029000	-0.693176000	2.096041000
C	-6.740612000	-2.239412000	1.722580000
H	-6.811443000	-3.227262000	1.254205000
H	-7.016729000	-2.354024000	2.774797000
H	-7.487341000	-1.586091000	1.253691000
C	-6.637585000	2.394840000	-1.826275000
H	-7.413844000	1.740947000	-1.409295000
H	-6.711026000	3.368473000	-1.329108000
H	-6.868680000	2.548317000	-2.884376000
C	6.740773000	2.239258000	-1.722276000
H	7.017013000	2.353833000	-2.774465000
H	6.811585000	3.227127000	-1.253933000
H	7.487432000	1.585936000	-1.253278000
C	6.637600000	-2.394716000	1.826346000
H	6.711191000	-3.368298000	1.329102000
H	7.413795000	-1.740685000	1.409460000
H	6.868662000	-2.548251000	2.884445000

3j

Ground state

Free Energy = -2802.391984

Energy = -2803.323825

N	-0.007238000	-1.397783000	-0.040901000
C	-1.227757000	-0.704736000	-0.011426000
O	-4.810630000	2.432193000	-2.055511000
C	-2.443745000	-1.371224000	-0.018180000
H	-2.439912000	-2.459122000	-0.040760000
O	-4.661041000	3.888174000	-0.354508000
C	-3.672559000	-0.697398000	-0.011662000
O	-4.660567000	-3.891458000	0.349300000
C	-4.952053000	-1.507525000	-0.097303000
H	-5.755656000	-0.937833000	0.392797000
O	-4.817811000	-2.435758000	2.049848000
O	-0.154366000	-6.958740000	-0.061005000
C	-4.806946000	-2.757401000	0.743016000
C	-4.538823000	-3.515791000	2.933982000
H	-5.276846000	-4.315658000	2.821038000
H	-3.545016000	-3.929327000	2.729745000
C	-3.672982000	0.694837000	0.011273000
C	-2.444569000	1.369354000	0.023146000
H	-2.441410000	2.457255000	0.045438000
C	-4.953330000	1.504191000	0.091234000
H	-5.754458000	0.933881000	-0.402208000
C	-4.805337000	2.754007000	-0.748690000
C	-4.528346000	3.512209000	-2.938634000

H	-5.267079000	4.311849000	-2.828813000
H	-3.535506000	3.926059000	-2.730398000
C	-0.017799000	-2.822818000	-0.078294000
C	0.180349000	-3.558338000	1.092049000
H	0.375163000	-3.027459000	2.021778000
C	0.138158000	-4.939868000	1.062748000
H	0.297465000	-5.535007000	1.957720000
C	-0.119376000	-5.608051000	-0.139019000
C	-0.320251000	-4.879433000	-1.312239000
H	-0.522722000	-5.378238000	-2.254825000
C	-0.259491000	-3.489649000	-1.272480000
H	-0.421961000	-2.906877000	-2.177375000
C	-0.425903000	-7.678642000	-1.238915000
H	-0.416822000	-8.735337000	-0.965384000
H	-1.412304000	-7.423736000	-1.651359000
H	0.339313000	-7.502025000	-2.008079000
C	1.211910000	-0.704349000	-0.027489000
N	-0.008050000	1.397169000	0.057733000
C	1.211503000	0.704461000	0.038679000
O	5.355232000	-2.013209000	2.140315000
C	2.426552000	1.367523000	0.085537000
H	2.425083000	2.453844000	0.137394000
O	4.377224000	-3.660558000	0.967551000
C	3.660335000	0.697003000	0.046897000
O	4.365539000	3.661132000	-0.971255000
C	4.908453000	1.560632000	0.124090000
H	5.798673000	0.940128000	-0.047203000

O	5.348313000	2.017635000	-2.145435000
O	-0.158949000	6.958178000	0.065156000
C	4.843383000	2.551604000	-1.019445000
C	5.231964000	2.830222000	-3.308075000
H	5.808977000	3.753543000	-3.196696000
H	4.186284000	3.095748000	-3.491264000
C	3.660710000	-0.695100000	-0.045157000
C	2.427274000	-1.366642000	-0.078627000
H	2.426456000	-2.453043000	-0.129940000
C	4.909327000	-1.557456000	-0.128174000
H	5.799592000	-0.936061000	0.039714000
C	4.850442000	-2.549042000	1.015146000
C	5.244737000	-2.826675000	3.302921000
H	5.825166000	-3.747655000	3.189892000
H	4.200541000	-3.096405000	3.488376000
C	-0.019365000	2.822295000	0.091899000
C	0.186757000	3.555709000	-1.078506000
H	0.389156000	3.023276000	-2.005737000
C	0.143637000	4.937230000	-1.052262000
H	0.309387000	5.530629000	-1.947216000
C	-0.123456000	5.607663000	0.146185000
C	-0.332459000	4.881261000	1.319310000
H	-0.542276000	5.381806000	2.259368000
C	-0.270123000	3.491424000	1.282888000
H	-0.438718000	2.910440000	2.187793000
C	-0.439885000	7.680208000	1.239545000
H	-0.429595000	8.736364000	0.963978000

H	0.319675000	7.505761000	2.014790000
H	-1.429140000	7.425315000	1.645101000
C	-1.228179000	0.703567000	0.022090000
H	5.636228000	-2.229509000	4.127833000
H	5.623923000	2.234315000	-4.133673000
H	-4.562725000	3.097397000	-3.946615000
H	-4.577480000	-3.101130000	3.941868000
C	-5.398759000	-1.761488000	-1.553212000
H	-5.508355000	-0.752880000	-1.988746000
C	-5.406551000	1.758252000	1.545070000
H	-5.517573000	0.749709000	1.980396000
C	5.074711000	-2.273603000	-1.479694000
H	4.235430000	-2.977442000	-1.585126000
C	5.078912000	2.277783000	1.474457000
H	4.239066000	2.980389000	1.583427000
C	6.378047000	3.073243000	1.496527000
H	6.407759000	3.835043000	0.710418000
H	6.505399000	3.583468000	2.458289000
H	7.240552000	2.404367000	1.363506000
C	6.374987000	-3.067013000	-1.508368000
H	7.237047000	-2.396781000	-1.379325000
H	6.409750000	-3.829071000	-0.722739000
H	6.498451000	-3.576591000	-2.470984000
C	-6.760647000	-2.443524000	-1.593963000
H	-7.134738000	-2.502052000	-2.622621000
H	-6.697160000	-3.465951000	-1.203904000
H	-7.504116000	-1.895938000	-0.999838000

C	-6.768957000	2.439622000	1.579628000
H	-6.704274000	3.461948000	1.189508000
H	-7.509523000	1.891465000	0.982410000
H	-7.147592000	2.498275000	2.606611000
C	-4.381705000	-2.510727000	-2.406369000
H	-4.759428000	-2.609347000	-3.431201000
H	-3.424523000	-1.979193000	-2.453913000
H	-4.198918000	-3.515206000	-2.009599000
C	-4.393617000	2.508247000	2.402474000
H	-3.436622000	1.976855000	2.454874000
H	-4.209190000	3.512516000	2.005876000
H	-4.776132000	2.607491000	3.425469000
C	5.051669000	1.283049000	2.625249000
H	4.109360000	0.725591000	2.667241000
H	5.861121000	0.546360000	2.523254000
H	5.187306000	1.800974000	3.582125000
C	5.040700000	-1.278319000	-2.629840000
H	4.097349000	-0.722296000	-2.667327000
H	5.849472000	-0.540449000	-2.531130000
H	5.172780000	-1.795549000	-3.587594000

Triplet excited state

Free Energy = -2802.29367

Energy = -2803.22136

N	-0.018573000	1.377666000	-0.037782000
C	1.192237000	0.703984000	-0.002882000

O	4.768141000	-2.367570000	-2.115046000
C	2.422515000	1.421610000	0.009723000
H	2.421361000	2.504170000	0.027320000
O	4.639556000	-3.869326000	-0.451933000
C	3.633902000	0.701289000	0.002527000
O	4.639745000	3.869135000	0.451896000
C	4.924662000	1.494405000	-0.052715000
H	5.718749000	0.907816000	0.432552000
O	4.768378000	2.367382000	2.115011000
O	0.241123000	6.928906000	-0.106230000
C	4.775008000	2.723937000	0.816427000
C	4.432940000	3.414360000	3.017150000
H	5.140507000	4.245237000	2.938075000
H	3.426728000	3.791757000	2.800351000
C	3.633874000	-0.701429000	-0.002509000
C	2.422436000	-1.421711000	-0.009659000
H	2.421274000	-2.504270000	-0.027169000
C	4.924597000	-1.494605000	0.052670000
H	5.718689000	-0.908058000	-0.432640000
C	4.774863000	-2.724133000	-0.816466000
C	4.432598000	-3.414528000	-3.017166000
H	5.140122000	-4.245445000	-2.938125000
H	3.426375000	-3.791866000	-2.800317000
C	-0.002713000	2.812262000	-0.095080000
C	-0.308494000	3.555052000	1.042539000
H	-0.609556000	3.040154000	1.952452000
C	-0.227551000	4.936796000	1.002778000

H	-0.460475000	5.547163000	1.870186000
C	0.177136000	5.579303000	-0.174900000
C	0.481153000	4.834225000	-1.313570000
H	0.798740000	5.316334000	-2.232384000
C	0.384595000	3.442823000	-1.270048000
H	0.632676000	2.843194000	-2.142531000
C	0.678212000	7.625810000	-1.247908000
H	0.675344000	8.685069000	-0.984351000
H	1.696440000	7.330079000	-1.536746000
H	0.004443000	7.468065000	-2.102053000
C	-1.225957000	0.702913000	-0.036749000
N	-0.018642000	-1.377674000	0.037970000
C	-1.225987000	-0.702851000	0.036893000
O	-5.361238000	2.064816000	2.103874000
C	-2.451139000	-1.379242000	0.110895000
H	-2.449864000	-2.461913000	0.193181000
O	-4.369823000	3.676159000	0.891825000
C	-3.669739000	-0.697919000	0.061240000
O	-4.369851000	-3.675880000	-0.891844000
C	-4.922804000	-1.552814000	0.153708000
H	-5.811161000	-0.935400000	-0.034345000
O	-5.361426000	-2.064609000	-2.103854000
O	0.240643000	-6.928943000	0.106134000
C	-4.853545000	-2.570967000	-0.967797000
C	-5.248608000	-2.905661000	-3.247872000
H	-5.825850000	-3.825257000	-3.111626000
H	-4.203465000	-3.175780000	-3.426875000

C	-3.669715000	0.698105000	-0.061184000
C	-2.451064000	1.379371000	-0.110796000
H	-2.449711000	2.462042000	-0.193085000
C	-4.922726000	1.553073000	-0.153718000
H	-5.811131000	0.935716000	0.034307000
C	-4.853459000	2.571223000	0.967791000
C	-5.248369000	2.905847000	3.247902000
H	-5.825582000	3.825467000	3.111687000
H	-4.203212000	3.175928000	3.426885000
C	-0.002868000	-2.812270000	0.095193000
C	-0.308802000	-3.554995000	-1.042433000
H	-0.609897000	-3.040036000	-1.952299000
C	-0.227970000	-4.936744000	-1.002740000
H	-0.461032000	-5.547049000	-1.870155000
C	0.176768000	-5.579340000	0.174869000
C	0.480945000	-4.834333000	1.313546000
H	0.798574000	-5.316507000	2.232311000
C	0.384490000	-3.442927000	1.270094000
H	0.632694000	-2.843363000	2.142587000
C	0.677744000	-7.625934000	1.247756000
H	0.674756000	-8.685182000	0.984157000
H	0.004046000	-7.468157000	2.101951000
H	1.696020000	-7.330313000	1.536536000
C	1.192215000	-0.704066000	0.003052000
H	-5.642536000	2.329684000	4.086109000
H	-5.642778000	-2.329499000	-4.086079000
H	4.466427000	-2.978656000	-4.016417000

H	4.466796000	2.978485000	4.016399000
C	5.394421000	1.780209000	-1.496526000
H	5.494236000	0.782076000	-1.957312000
C	5.394415000	-1.780427000	1.496463000
H	5.494402000	-0.782293000	1.957206000
C	-5.096070000	2.239612000	-1.520062000
H	-4.257007000	2.940026000	-1.645772000
C	-5.096258000	-2.239369000	1.520034000
H	-4.257213000	-2.939797000	1.645784000
C	-6.396297000	-3.032548000	1.555007000
H	-6.424018000	-3.812314000	0.786751000
H	-6.526416000	-3.520606000	2.527607000
H	-7.257896000	-2.366364000	1.404409000
C	-6.396097000	3.032803000	-1.555161000
H	-7.257713000	2.366624000	-1.404634000
H	-6.423881000	3.812579000	-0.786919000
H	-6.526122000	3.520845000	-2.527781000
C	6.768229000	2.439724000	-1.498081000
H	7.154332000	2.529550000	-2.520188000
H	6.717360000	3.448222000	-1.071299000
H	7.495958000	1.858157000	-0.916731000
C	6.768126000	-2.440142000	1.497952000
H	6.717084000	-3.448651000	1.071214000
H	7.495895000	-1.858700000	0.916527000
H	7.154286000	-2.529979000	2.520036000
C	4.404097000	2.568148000	-2.345636000
H	4.790215000	2.666866000	-3.367841000

H	3.431413000	2.066635000	-2.395013000
H	4.249369000	3.572513000	-1.936948000
C	4.404021000	-2.568187000	2.345660000
H	3.431432000	-2.066496000	2.395113000
H	4.249084000	-3.572529000	1.936994000
H	4.790204000	-2.666966000	3.367834000
C	-5.071364000	-1.219616000	2.648723000
H	-4.129534000	-0.660410000	2.682108000
H	-5.881912000	-0.486698000	2.531013000
H	-5.206967000	-1.717382000	3.615960000
C	-5.071104000	1.219843000	-2.648737000
H	-4.129294000	0.660599000	-2.682032000
H	-5.881690000	0.486955000	-2.531090000
H	-5.206603000	1.717599000	-3.615994000

Cation Radical

Free Energy = -2802.220865

Energy = -2803.154149

N	0.016174000	-1.392054000	-0.070541000
C	-1.184579000	-0.701102000	-0.025097000
O	-5.870955000	2.838354000	-1.664825000
C	-2.408884000	-1.374474000	0.010240000
H	-2.416730000	-2.459093000	0.042816000
O	-4.110481000	3.722492000	-0.591401000
C	-3.617739000	-0.698793000	0.010606000
O	-4.120542000	-3.682700000	0.650093000

C	-4.913421000	-1.478992000	-0.016046000
H	-5.709690000	-0.870904000	0.426722000
O	-5.849782000	-2.741080000	1.726240000
O	-0.132093000	-6.943043000	-0.219514000
C	-4.877026000	-2.749974000	0.808475000
C	-5.972480000	-3.940063000	2.495709000
H	-6.193181000	-4.789552000	1.842277000
H	-5.045847000	-4.145877000	3.038228000
C	-3.614673000	0.722622000	-0.035758000
C	-2.402510000	1.392996000	-0.043269000
H	-2.406349000	2.477823000	-0.070548000
C	-4.910462000	1.501419000	0.006402000
H	-5.702437000	0.905913000	-0.461560000
C	-4.877957000	2.802341000	-0.769830000
C	-6.001809000	4.069184000	-2.380604000
H	-6.199041000	4.892444000	-1.687247000
H	-5.086875000	4.290220000	-2.936804000
C	0.000866000	-2.829957000	-0.140613000
C	0.341478000	-3.584850000	0.982056000
H	0.653437000	-3.085280000	1.896537000
C	0.293742000	-4.962773000	0.916440000
H	0.559293000	-5.579928000	1.769406000
C	-0.108204000	-5.600398000	-0.264751000
C	-0.447354000	-4.839558000	-1.387709000
H	-0.756478000	-5.313420000	-2.313605000
C	-0.384620000	-3.453231000	-1.319648000
H	-0.649656000	-2.849938000	-2.185894000

C	-0.538024000	-7.647253000	-1.374568000
H	-0.491192000	-8.706579000	-1.119751000
H	-1.566962000	-7.390454000	-1.659401000
H	0.133748000	-7.451382000	-2.220964000
C	1.222190000	-0.709393000	-0.056052000
N	0.024908000	1.396580000	0.022878000
C	1.226651000	0.705107000	0.016435000
O	5.938723000	-2.485556000	1.836828000
C	2.451001000	1.373292000	0.074840000
H	2.458468000	2.457479000	0.119979000
O	4.067755000	-3.495871000	1.110012000
C	3.662185000	0.697970000	0.028925000
O	4.118954000	3.507618000	-1.046008000
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H	5.801888000	0.888667000	-0.132476000
O	5.969903000	2.481192000	-1.799869000
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C	4.925594000	2.608664000	-0.974848000
C	6.109556000	3.523123000	-2.769380000
H	6.232554000	4.490045000	-2.272057000
H	5.227842000	3.569634000	-3.414283000
C	3.657365000	-0.719114000	-0.043211000
C	2.442303000	-1.385878000	-0.102997000
H	2.444347000	-2.470165000	-0.143870000
C	4.918717000	-1.553070000	-0.069308000
H	5.795363000	-0.928646000	0.133117000
C	4.891860000	-2.615200000	1.015031000

C	6.059849000	-3.504860000	2.832649000
H	6.165038000	-4.486089000	2.359893000
H	5.177736000	-3.518834000	3.478513000
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C	0.388961000	3.579230000	-1.037032000
H	0.701259000	3.070377000	-1.946277000
C	0.365643000	4.957956000	-0.977356000
H	0.650818000	5.566758000	-1.829990000
C	-0.035854000	5.607507000	0.197501000
C	-0.399468000	4.857443000	1.319947000
H	-0.708954000	5.340610000	2.240877000
C	-0.361055000	3.469972000	1.258087000
H	-0.644504000	2.875311000	2.124522000
C	-0.438762000	7.666198000	1.295431000
H	-0.370046000	8.723487000	1.037117000
H	0.221431000	7.461324000	2.148764000
H	-1.474864000	7.429493000	1.571569000
C	-1.180832000	0.713581000	-0.016222000
H	6.952540000	-3.260105000	3.407355000
H	6.997593000	3.276820000	-3.350620000
H	-6.841937000	3.933519000	-3.060971000
H	-6.794552000	-3.769022000	3.190037000
C	-5.374652000	-1.806615000	-1.469922000
H	-5.522438000	-0.826285000	-1.952870000
C	-5.376627000	1.777056000	1.470402000
H	-5.504465000	0.780658000	1.925664000
C	5.153583000	-2.234489000	-1.440124000

H	4.272060000	-2.861162000	-1.648221000
C	5.164323000	2.164222000	1.469821000
H	4.297582000	2.812202000	1.675161000
C	6.422895000	3.021367000	1.456342000
H	6.347500000	3.860474000	0.754426000
H	6.613155000	3.441452000	2.449663000
H	7.299107000	2.421307000	1.175493000
C	6.386577000	-3.126912000	-1.391883000
H	7.274404000	-2.548347000	-1.102555000
H	6.274112000	-3.954042000	-0.680776000
H	6.582741000	-3.565482000	-2.376039000
C	-6.713851000	-2.532934000	-1.443520000
H	-7.117140000	-2.631482000	-2.456746000
H	-6.603954000	-3.548627000	-1.038790000
H	-7.456033000	-2.005496000	-0.832788000
C	-6.728619000	2.479173000	1.469842000
H	-6.639925000	3.507091000	1.091754000
H	-7.464569000	1.954776000	0.849080000
H	-7.127575000	2.543270000	2.487568000
C	-4.352776000	-2.582388000	-2.289000000
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H	-3.416184000	2.010256000	2.406701000
H	-4.156843000	3.531330000	1.870325000
H	-4.765697000	2.702240000	3.316290000

C	5.255780000	1.091571000	2.545317000
H	4.341977000	0.488613000	2.610312000
H	6.094532000	0.408576000	2.348808000
H	5.425075000	1.545956000	3.527535000
C	5.294031000	-1.183945000	-2.531821000
H	4.408480000	-0.541584000	-2.608925000
H	6.161708000	-0.536946000	-2.340039000
H	5.447746000	-1.659050000	-3.506714000

References

1. Z. Zheng, Q. Dong, L. Gou, J.-H. Su and J. Huang, *J. Mater. Chem. C*, 2014, **2**, 9858-9865.
2. T. Okamoto, E. Terada, M. Kozaki, M. Uchida, S. Kikukawa and K. Okada, *Org. Lett.*, 2003, **5**, 373-376.
3. G. M. Miyake and J. C. Theriot, *Macromolecules*, 2014, **47**, 8255-8261.
4. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.
5. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
6. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
7. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
8. A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571-2577.
9. J. Tomasi and M. Persico, *Chem. Rev.*, 1994, **94**, 2027-2094.
10. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669-681.
11. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
12. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox Gaussian 16, Revision A.03. Gaussian, Inc.: Wallingford CT, 2016.
13. J. A. Tossell, *Comput. Theor. Chem.*, 2011, **977**, 123-127.
14. P. Winget, C. J. Cramer and D. G. Truhlar, *Theor. Chem. Acc.*, 2004, **112**, 217-227.
15. H. He, P. Zapol and L. A. Curtiss, *J. Phys. Chem. C*, 2010, **114**, 21474-21481.
16. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
17. G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193-2218.