Supporting Information

Tailored strength neighboring group interactions switch polymerization to dimerization catalysis

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1. Experimental procedures and spectroscopic data

1.1 General considerations

Unless noted otherwise, all manipulations of air and moisture sensitive materials were carried out under inert gas atmosphere using standard glovebox and Schlenk techniques.

1.1.1 Solvents and reagents

Solvents were dried and degassed using standard laboratory techniques. THF was distilled from sodium benzophenone ketyl, benzene from sodium, dichloromethane was distilled from CaH_2 and pentane and toluene were dried and degassed by passing through columns, equipped with alumina and BASF R3-11 catalyst. [(tmeda)$NiMe_2$] and 3-(9-anthryl)salicylaldehyde were prepared according to literature procedures[1]. Ethylene (grade 3.5) and hydrogen (grade 5.0) was supplied by Air Liquide and used as received. 2,6-Difluoronitrobenzene and 3,5-bis(trifluoromethyl)benzyl bromide were supplied by Apollo Scientific. $Pd(OAc)_2$ was obtained from MCAT. All other commercially available reagents and starting materials were supplied by Sigma Aldrich, Acros, ABCR or Activate Scientific. $CDCl_3$ was supplied by Sigma Aldrich, all other deuterated solvents by Eurisotop.

1.1.2 Analytical methods and techniques

NMR spectra were recorded on a Bruker Avance III HD 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{19}F: 376.1 MHz), a Bruker Avance III 400 or a Bruker Avance III 600 spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz). ^{1}H chemical shifts were referenced to the solvents residual proton signals ($CDCl_3$: 7.26 ppm, $C_2D_2Cl_4$: 5.91 ppm, C_6D_6: 7.16 ppm). ^{13}C chemical shifts were referenced to the carbon signal of the deuterated solvent ($CDCl_3$: 77.16 ppm, $C_2D_2Cl_4$: 74.30 ppm, C_6D_6: 128.06 ppm). ^{19}F chemical shifts were referenced to external $BF_3{\cdot}OEt_2$. NMR spectra of polyethylenes were recorded with addition of 5 mg mL^{-1} of $Cr(acac)_3$ as paramagnetic relaxation agent.
DSC measurements were carried out on a Netzsch DSC 204 F1 with a bicyclic temperature program from 20 to 160 °C with heating and cooling rates of 10 K min^{-1} for samples with molecular weights over 500 g mol^{-1} and a temperature program from - 160 to 20 °C for samples with molecular weights of under 500 g mol^{-1} in closed 40 µL alumina pans under a nitrogen atmosphere.
Gel permeation chromatographic analyses (GPC) were conducted on a Polymer Laboratories PL-GPC220 instrument equipped with Olexis columns with differential refractive index, viscosity and light scattering detectors (15° and 90°) in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1}. For the polymers data were determined against linear PE standard calibration and triple detection employing the PL GPC-220 software algorithm. As the instrument records light scattering at only two angles, data analysis involves iteration for the calculation of molecular weights and form factors for each measured interval. The instrument was calibrated with narrow polystyrene and polyethylene standards.
Elemental analyses were obtained on a Vario MICRO CUBE by the Analytical Service at the Department of Chemistry at the University of Konstanz. Data for non-fluorinated compounds are given as average of two runs, data of fluorinated compounds were measured once.
X-ray diffraction analysis were performed at 100 K on a STOE IPDS-II diffractometer, equipped with a graphite-monochromated radiation source (λ = 0.71073 Å) and an image plate detection system. Crystals were placed on a fine glass fiber with grease or oil. The selection, integration and averaging procedure of the measured reflex intensities, the determination of the unit cell dimensions and a least-squares fit of the 2Θ values as well as data reduction, LP-correction and space group determination were performed using the X-Area software package delivered with the diffractometer.[2] Using Olex2[3], the structure was solved

with the ShelXT.[4] Structure solution program using Intrinsic Phasing and refined with the olex2.refine[5] refinement package using Gauss-Newton minimization. Graphical representation were created by the ORTEP-3 V2.02. for Windows XP software package.[6]
Gas chromatographic (GC) analyses were carried out on a Perkin Elmer Clarus 500 GC system equipped with an Elite-5 capillary column (30 m × 0.25 mm × 0.25 µm, phase description: 5 % diphenyl - 95 % dimethyl polysiloxane) using a flame-ionization detector (FID). Helium was used as the carrier gas with a gas flow of 1.5 mL min^{-1}. An injection volume of 1.0 µL was used. The oven program started with 50 °C and the column was then heated at a rate of 25 °C min^{-1} to 230 °C, to 330 °C with a rate of 10 °C min^{-1} and kept isothermal at this temperature for 10 min (injector temperature 350 °C; detector temperature 350 °C).
Cyclic voltammetry (CV) measurements were performed in a custom-built one-compartment cell in a glovebox. A spiral-shaped Pt wire and an Ag wire as the counter and reference electrodes are sealed into glass capillaries that are introduced via Quickfit screws at opposite sides of the cell. A Pt electrode is introduced as the working electrode through the top port. It is polished with first 1 µm and then 0.25 µm diamond paste (Buehler-Wirtz) just before measurements. The experiments were performed with approximately 5 mL of dichloromethane. $^{n}Bu_4NPF_6$ was used as supporting electrolyte. Referencing was done with addition of $[(Me_5Cp)_2Fe]$ as an internal standard after all data have been acquired. The scans were repeated with internal standard. Final referencing was performed against ferrocene/ferrocenium ($Cp_2Fe^{0/+}$) with $E_{1/2}(Cp_2Fe^{0/+})$ = -550 mV vs. $Cp_2Fe^{0/+}$. Electrochemical data were acquired with a computer-controlled BASi potentiostat.

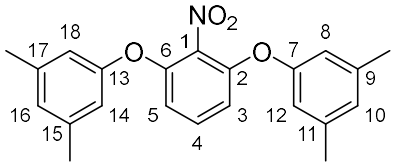
1.2 Synthesis of the oxygen bridged complexes

1.2.1 Synthesis of 2-nitro-1,3-diphenoxy benzenes

General procedure for the preparation of 2-nitro-1,3-bis(3,5-di-R1-phenoxy)-benzenes 1-R[1]:

NaH (26.4 mmol, 2.1 equiv.) was suspended in 25 mL of dry DMSO. The respective phenol (26.23 mmol, 2.1 equiv.) was added carefully and the reaction mixture was heated to 65 °C for 1 h. 2,6-difluoronitrobenzene (12.5 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was heated to 130 °C for 2 h. After cooling to room temperature, 50 mL of water and 50 mL of Et_2O were added. The aqueous layer was extracted with Et_2O (3 x 80 mL). The combined organic layers were washed with 1 M $NaOH_{aq}$ (3 x 60 mL) and water (6 x 50 mL) and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure to give the desired product.

<u>2-Nitro-1,3-bis(3,5-dimethylphenoxy)benzene (**1-CH$_3$**):</u>



Following the general procedure, 4.0 g (11.0 mmol, 88 %) of 5,5'-((2-nitro-1,3-phenylene)bis(oxy))bis(1,3-dimethyl-benzene) **1-CH$_3$** was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.18 (t, $^3J_{HH}$ = 8.5 Hz, 1H, 4-H), 6.84 (s, 2H, 16- and 10-H), 6.74 (s, 4H, 8-H, 12-H, 14-H and 18-H), 6.59 (d, $^3J_{HH}$ = 8.5 Hz, 2H, 3- and 5-H), 2.31 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.4 (C7 and C13), 150.8 (C2 and C6), 140.1 (C9, C11, C15 and C17), 134.8 (C1), 130.8 (C4), 126.8 (C10 and C16), 117.7 (C8, C12, C14 and C18), 111.9 (C3 and C5), 21.4 (CH_3).

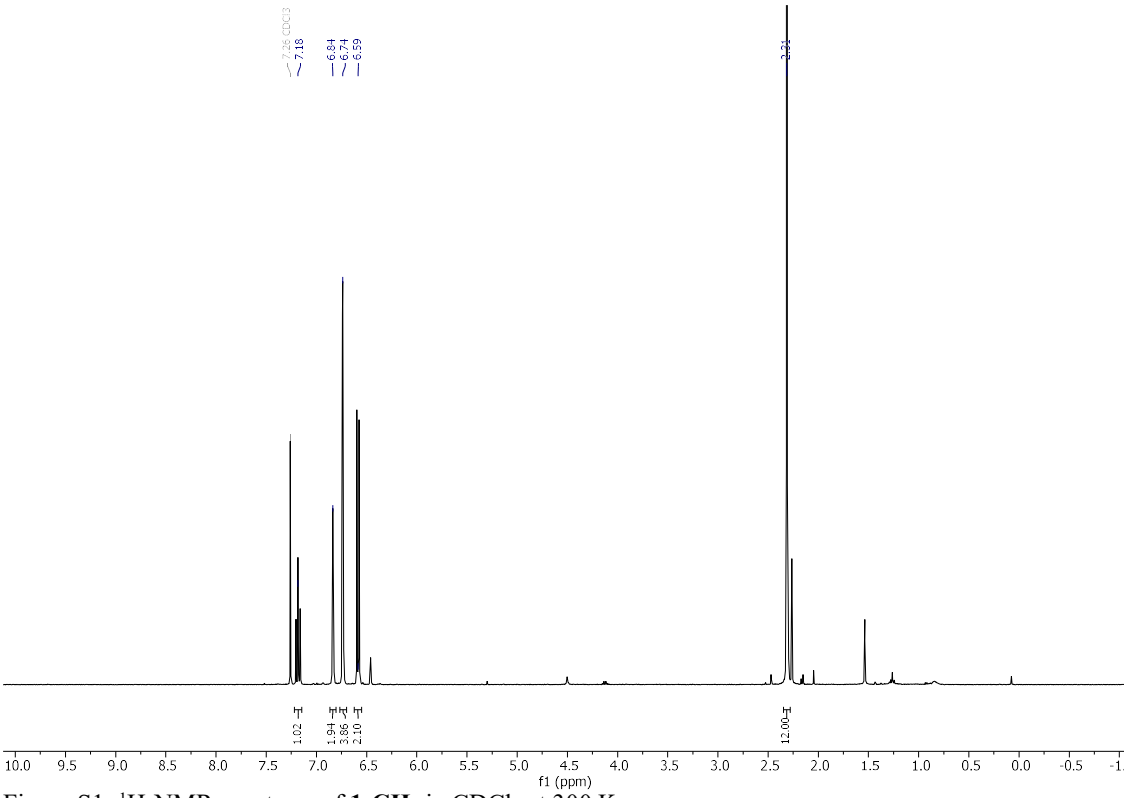


Figure S1: ^{1}H-NMR spectrum of **1-CH$_3$** in $CDCl_3$ at 300 K.

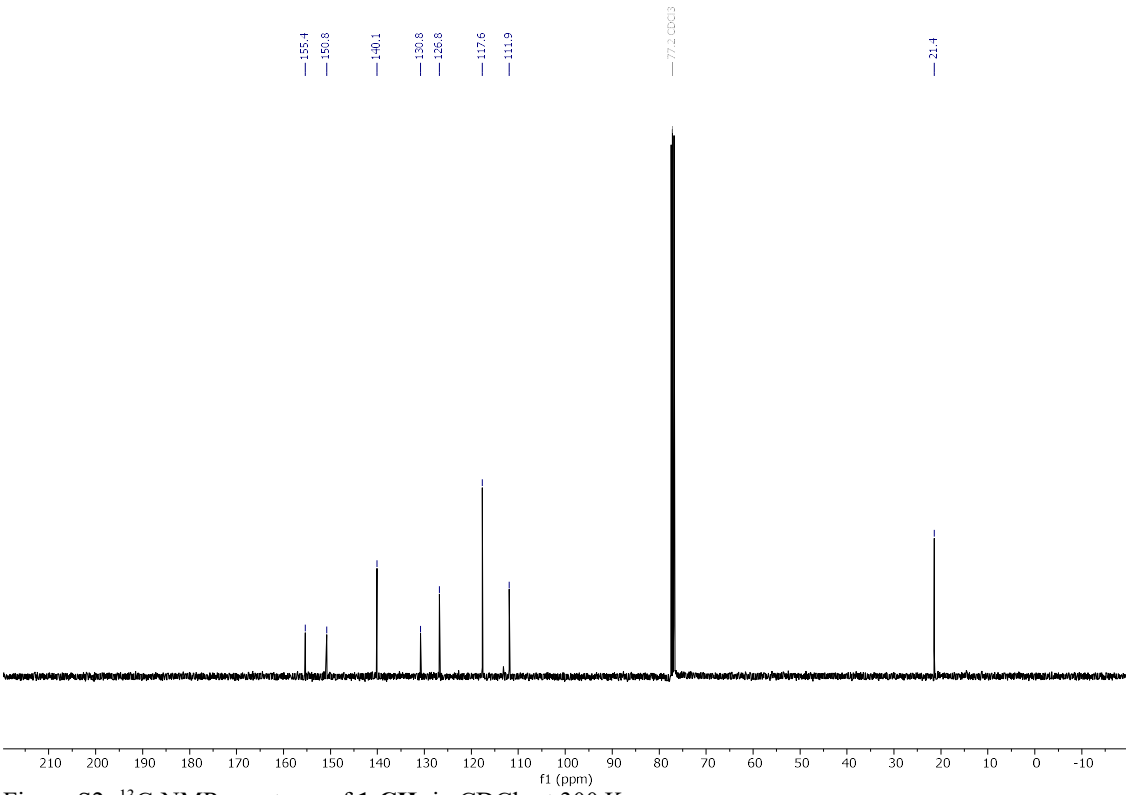
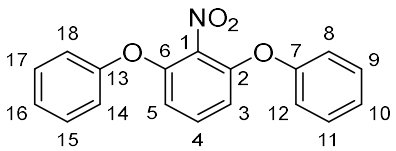


Figure S2: ^{13}C-NMR spectrum of **1-CH$_3$** in $CDCl_3$ at 300 K.

<u>(2-Nitro-1,3-diphenoxy)-benzene (**1-H**):</u>



Following the general procedure, 3.3 g (10.7 mmol, 86 %) of (2-nitro-1,3-diphenoxy)-benzene **1-H** was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.44 – 7.36 (m, 4H, 9-, 11-, 15- and 17-H), 7.24 – 7.20 (m, 2H, 10- and 16-H), 7.24 – 7.18 (m, 1H, 4-H), 7.16 – 7.08 (m, 4H, 8-, 12-, 14- and 18-H), 6.61 (d, $^3J_{HH}$ = 8.5 Hz, 2H, 3- and 5-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.5 (C7 and C13), 150.6 (C2 and C6), 135.6 (C1), 130.9 (C10 and C16), 130.2 (C9, C11, C15 and C17), 125.2 (C4), 120.0 (C8, C12, C14 and C18), 112.2 (C3 and C5).

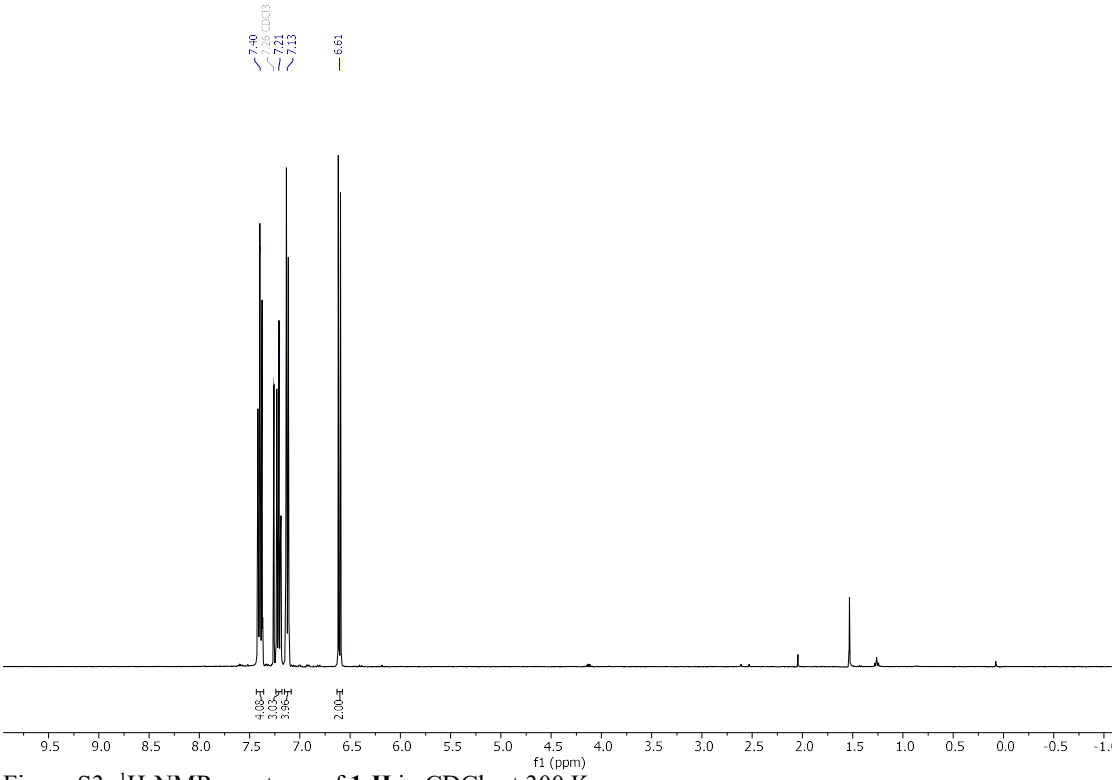


Figure S3: ^{1}H-NMR spectrum of **1-H** in $CDCl_3$ at 300 K.

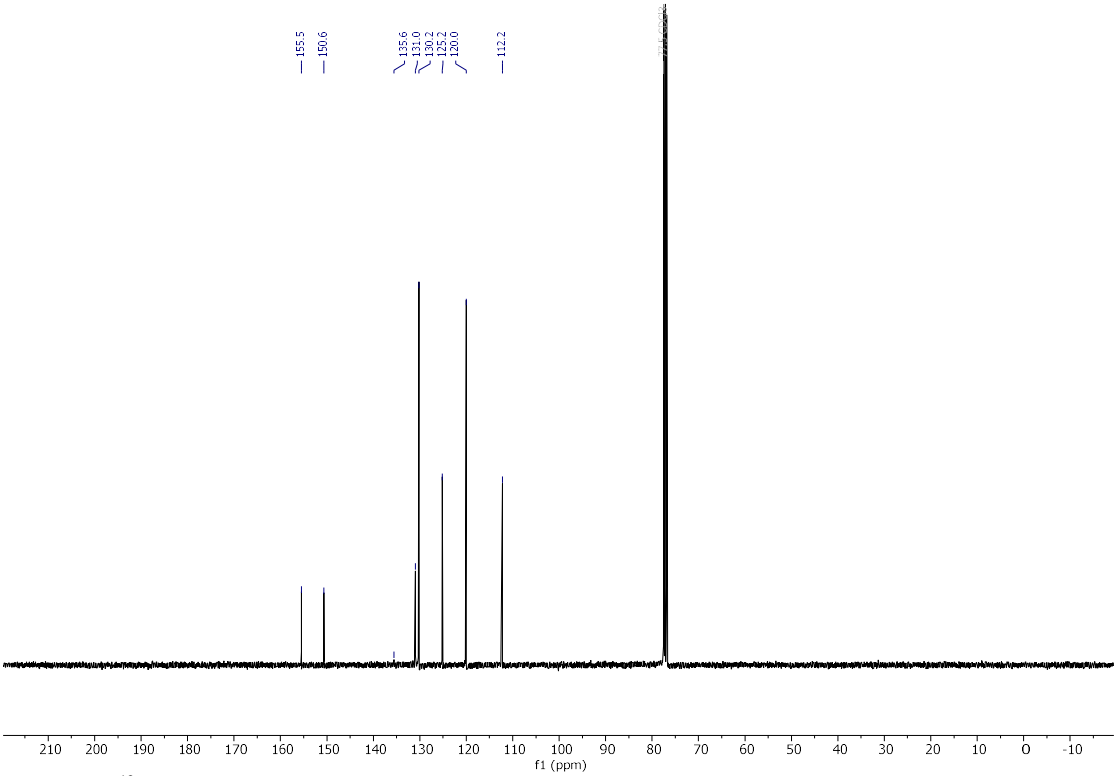
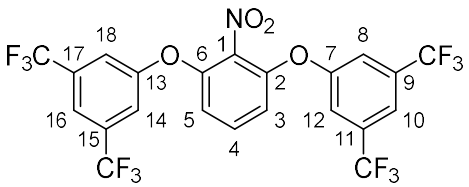


Figure S4: ^{13}C-NMR spectrum of **1-H** in $CDCl_3$ at 300 K.

2-Nitro-1,3-bis(3,5-bis(trifluormethyl)phenoxy)-benzene (**1-CF$_3$**):



Following the general procedure, 6.21 g (10.7 mmol, 86 %) of 2-nitro-1,3-bis(3,5-di-trifluormethyl-phenoxy)-benzene **1-CF$_3$** was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 – 7.72 (m, 2H, 10- and 16-H), 7.56 (d, 4H, 8-, 12-, 14- and 18-H), 7.50 (t, $^3J_{HH}$ = 8.5 Hz, 1H, 4-H), 6.88 (d, $^3J_{HH}$ = 8.5 Hz, 2H, 3- and 5-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.5 (C7 and C13), 148.9 (C2 and C6), 136.7 (C1) 134.0 (q, $^2J_{FC}$ = 34.2 Hz, C9, C11, C15 and C17), 132.5 (C4), 124.1 (q, $^1J_{FC}$ = 272.5 Hz, CF_3), 119.4 (C8, C12, C14 and C18), 118.8 (m, C10 and C16), 115.4 (C3 and C5).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.0 (s, CF_3).

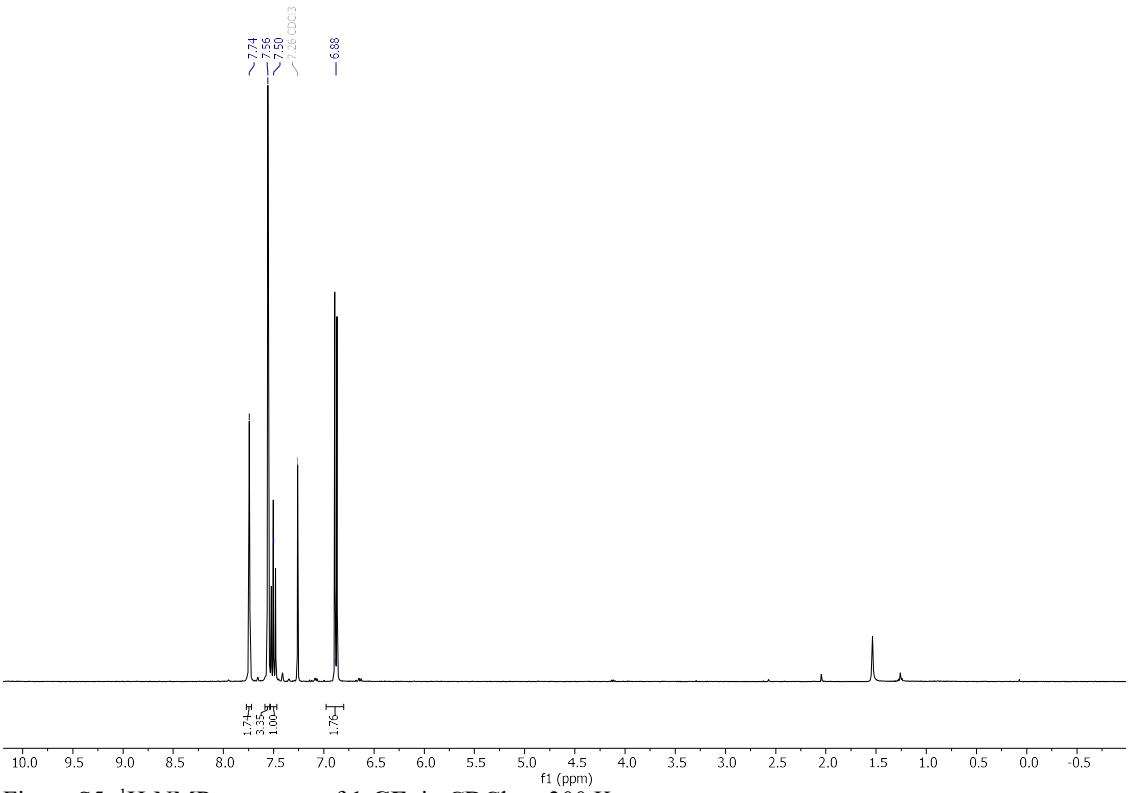


Figure S5: ^{1}H-NMR spectrum of **1-CF$_3$** in $CDCl_3$ at 300 K.

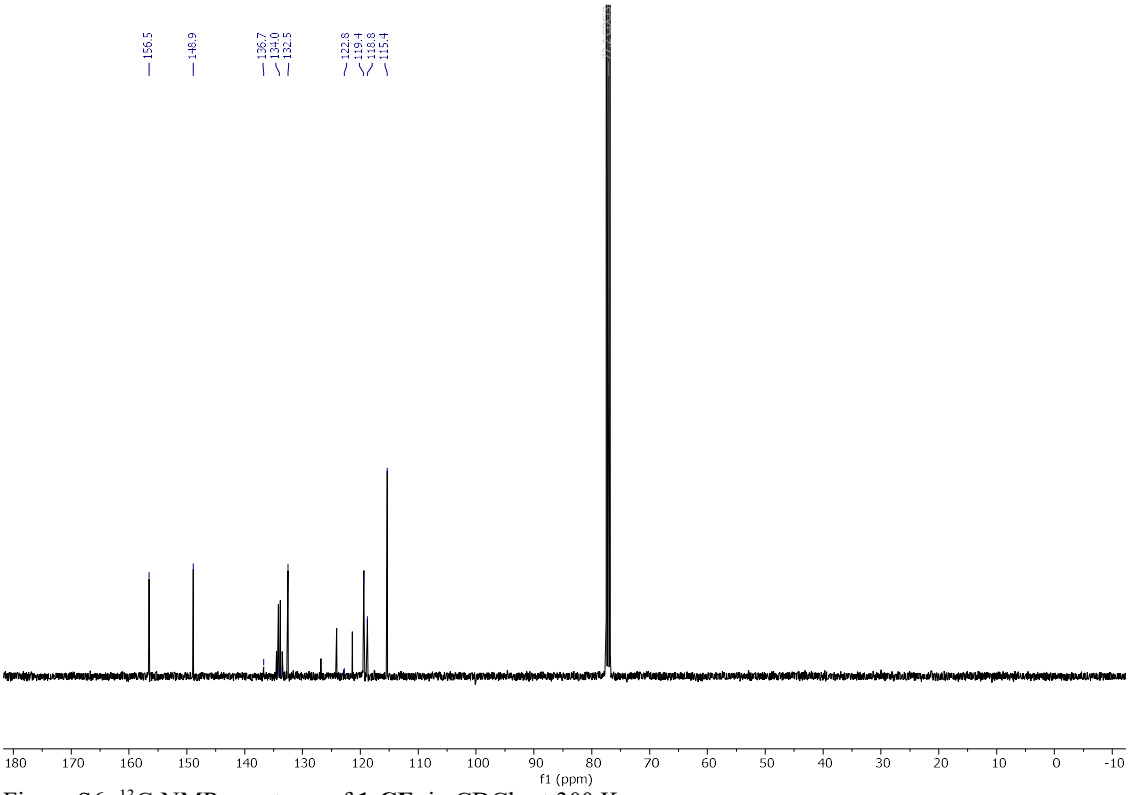


Figure S6: ^{13}C-NMR spectrum of **1-CF$_3$** in $CDCl_3$ at 300 K.

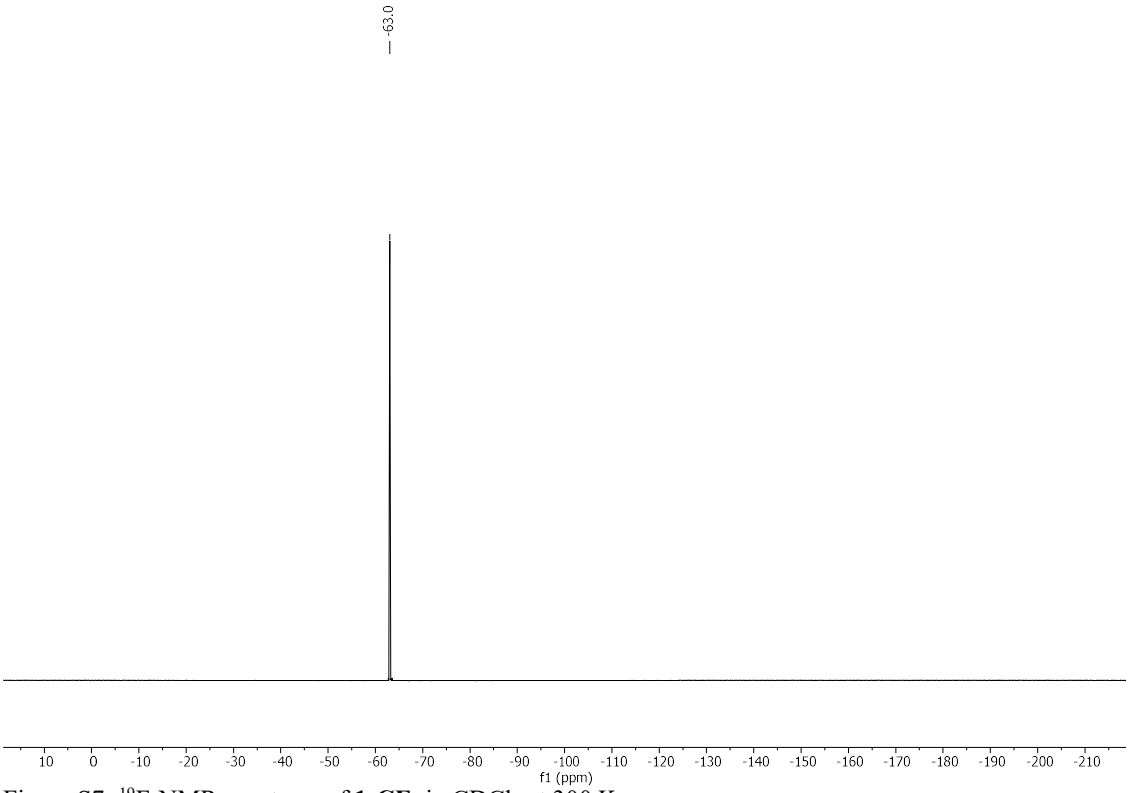


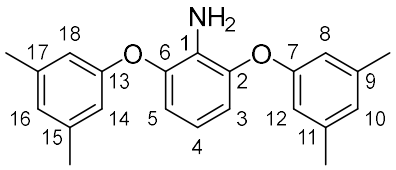
Figure S7: ^{19}F-NMR spectrum of **1-CF$_3$** in $CDCl_3$ at 300 K.

1.2.2 Synthesis of 2,6-diphenoxy anilines

General procedure for the preparation of 2,6-bis(3,5-di-R^1-phenoxyanilines):

The corresponding nitrobenzenes **1-R^1** (2.0 g) were dissolved in 9.0 mL of a 1:6 mixture of MeOH and THF in a 10 mL glass inlay. 40 mg of palladium catalyst (10 wt.% on charcoal) was added. The glass inlay was placed in a high pressure steel reactor and pressurized with 5 bar hydrogen. The reaction mixture was stirred at room temperature for 3-4 days. After venting, the reaction mixture was filtered over celite and the solvent removed under reduced pressure.

2,6-Bis(3,5-dimethylphenoxy)aniline (**2-CH$_3$**):



Following the general procedure, 1.65 g of 2,6-bis(3,5-dimethylphenoxy)aniline **2-CH$_3$** was obtained as a brown solid after 3 days with 5 bar of hydrogen pressure. ^{1}H-NMR analysis showed 78 % conversion.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.72 (d, $^3J_{HH}$ = 5.5 Hz, 2H, 3- and 5-H), 6.70 (s 2H, 10- and 15-H), 6.65 (s, 4H, 8-, 12-, 14- and 18-H), 6.64 (t, $^3J_{HH}$ = 5.5 Hz, 1H, 4-H), 3.90 (s, 2H, NH_2), 2.30 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.4 (C2 and C6), 144.5 (C7 and C13), 139.7 (C9, C11, C15 and C17), 131.6 (C1), 124.8 (C3 and C5), 117.6 (C4), 115.5 (C10 and C16), 115.2 (C8, C12, C14 and C18), 21.5 (CH_3).

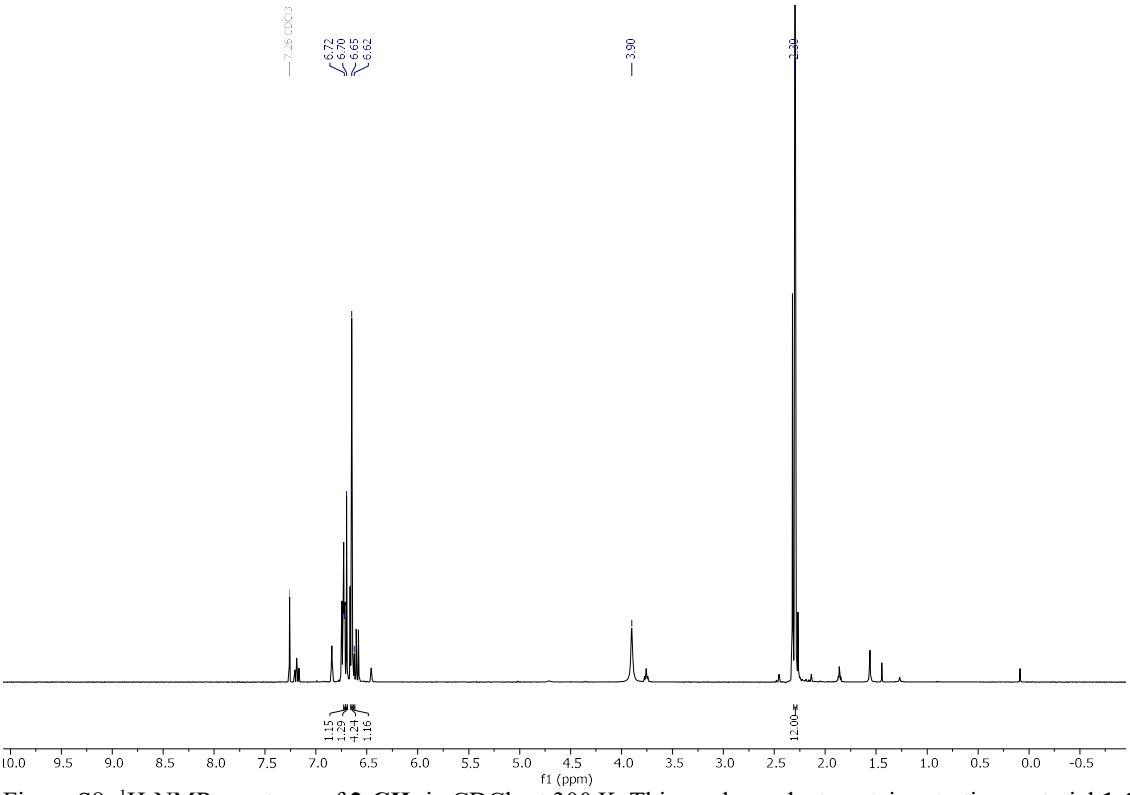


Figure S8: ^{1}H-NMR spectrum of **2-CH$_3$** in $CDCl_3$ at 300 K. This crude product contains starting material **1-CH$_3$**, which is removed in the following step by washing with methanol.

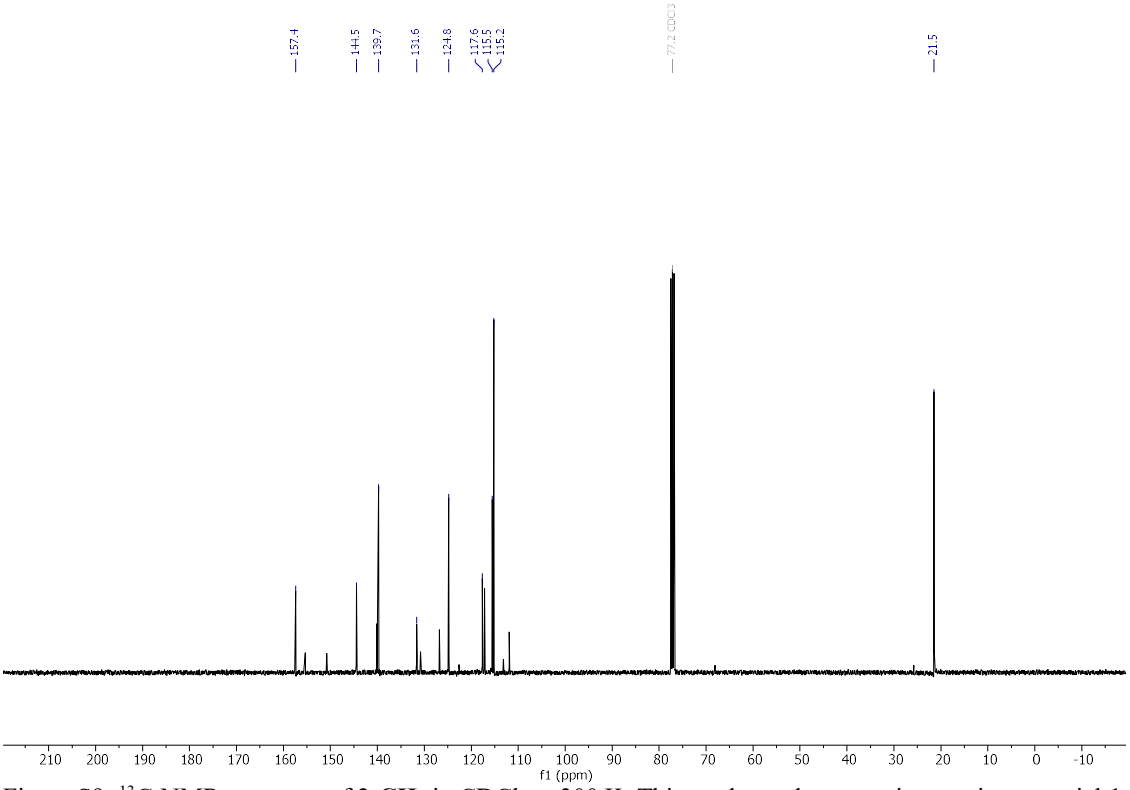
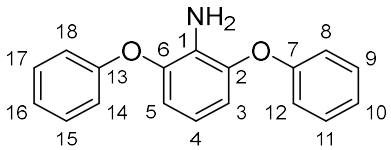


Figure S9: ^{13}C-NMR spectrum of **2-CH$_3$** in $CDCl_3$ at 300 K. This crude product contains starting material **1-CH$_3$**, which is removed in the following step by washing with methanol.

2,6-Diphenoxyaniline (**2-H**):



Following the general procedure, 1.8 g (6.5 mmol, quantitative) of 2,6-diphenoxyaniline **2-H** was obtained as a brown oil after 4 days of 5 bar of hydrogen pressure.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37 – 7.30 (m, 4H, 9-, 11-, 15- and 17-H), 7.09 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, 10- and 16-H), 7.06 – 7.00 (m, 4H, 8-, 12-, 14-, and 18-H), 6.75 – 6.54 (m, 3H, 3-, 4- and 5-H), 3.90 (s, 2H, NH_2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.4 (C7 and C13), 144.4 (C2 and C6), 131.6 (C1), 129.9 (C9, C11, C15 and C17), 123.1 (C10 and C16), 117.6 (C8, C12, C14 and C18), 117.3 (C4), 115.5 (C3 and C5).

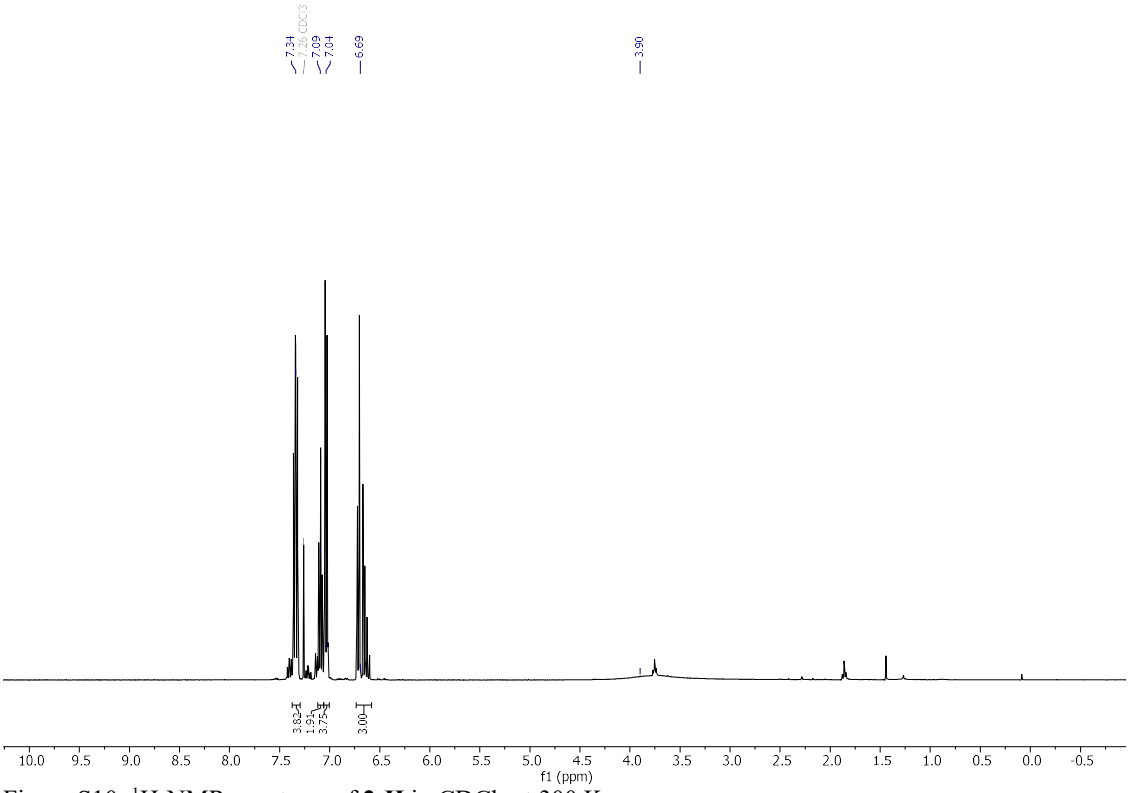


Figure S10: ^{1}H-NMR spectrum of **2-H** in $CDCl_3$ at 300 K.

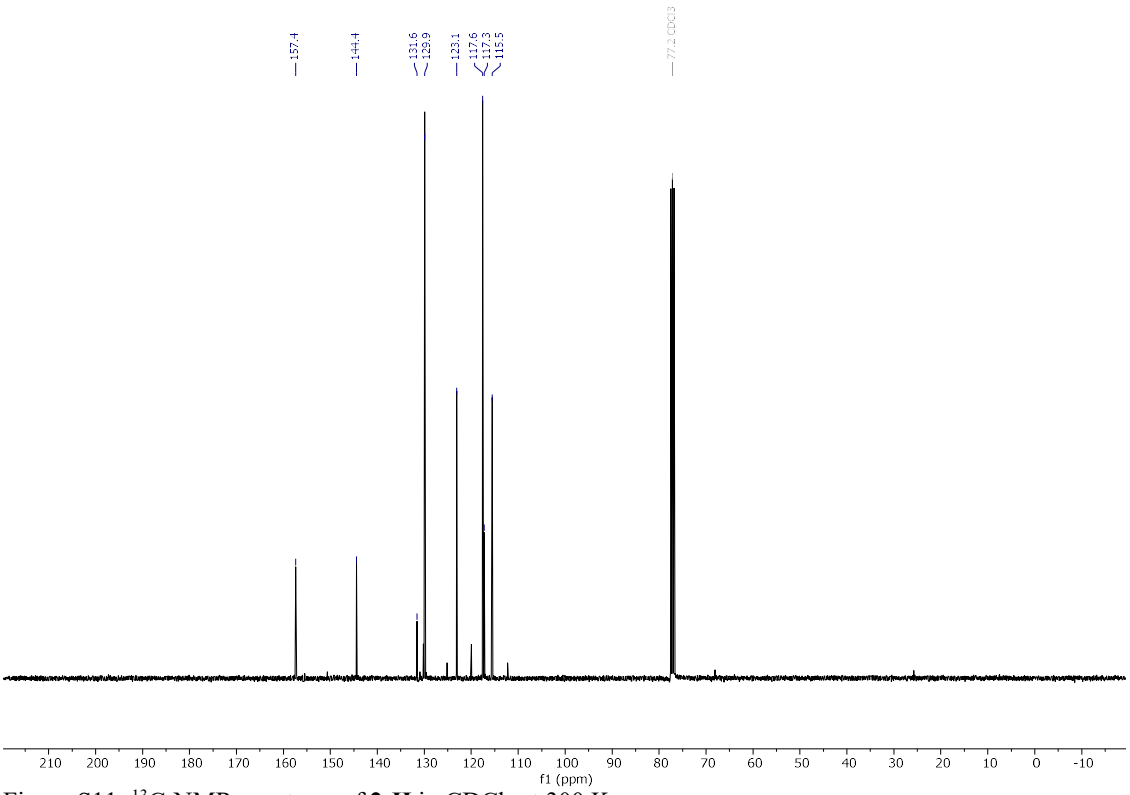
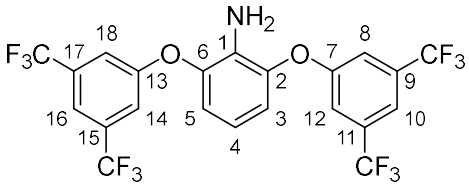


Figure S11: ^{13}C-NMR spectrum of **2-H** in $CDCl_3$ at 300 K.

<u>2,6-Bis(3,5-bis(trifluormethyl)phenoxy)aniline (**2-CF$_3$**):</u>



Following the general procedure, 1.68 g (3.06 mmol, 89 %) of 2,6-bis(3,5-bis(trifluormethyl)phenoxy)aniline **2-CF$_3$** was obtained as a light orange solid after 4 days at 5 bar of hydrogen pressure.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.61 (s, 2H, 10- and 16-H), 7.43 (s, 4H, 8-, 12-, 14- and 18-H), 6.89 – 6.74 (m, 3H, 3-, 4- and 5-H), 3.92 (s, 2H, NH_2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 158.1 (C7 and C13), 142.8 (C2 and C6), 133.6 (q, $^2J_{FC}$ = 33.8 Hz, C9, C11 , C15 and C17), 132.2 (C1), 123.0 (q, $^1J_{FC}$ = 272.8 Hz, CF_3), 118.2 (C4), 117.5 (C3 and C5), 117.3 (m, C8, C12, C14 and C18), 116.8 (m, C10 and C16).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.1 (s, CF_3).

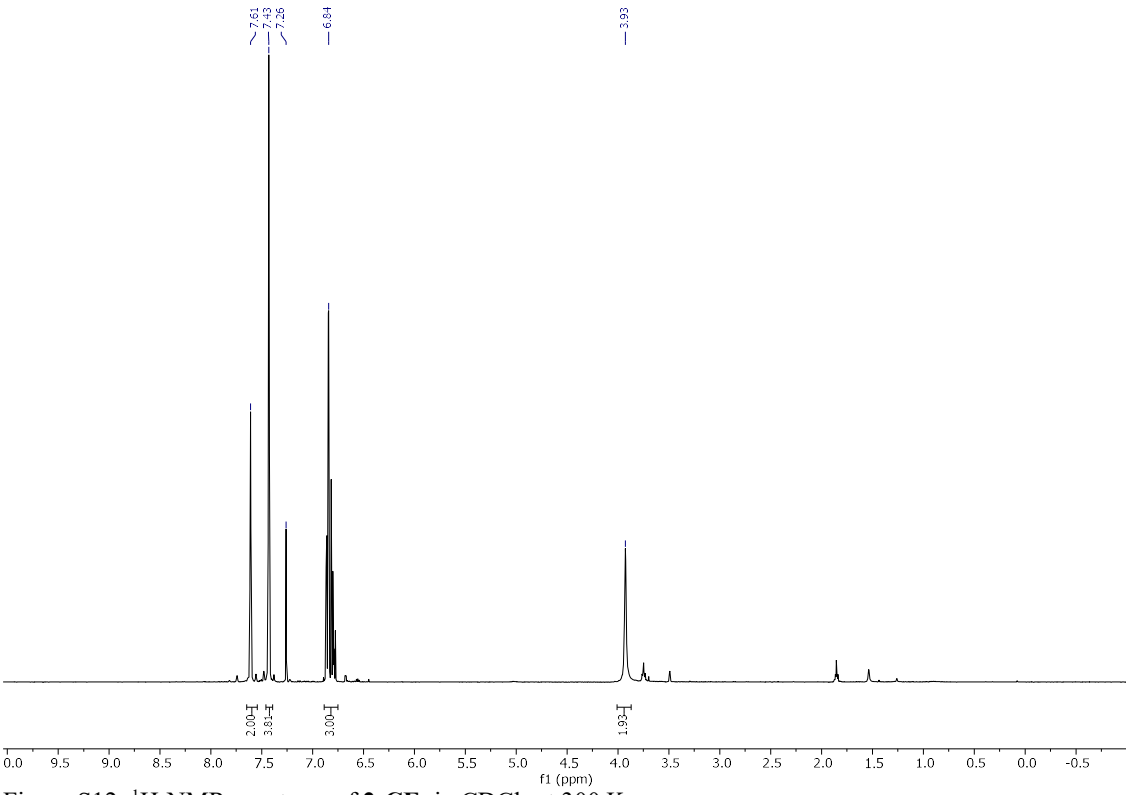


Figure S12: ^{1}H-NMR spectrum of **2-CF$_3$** in $CDCl_3$ at 300 K.

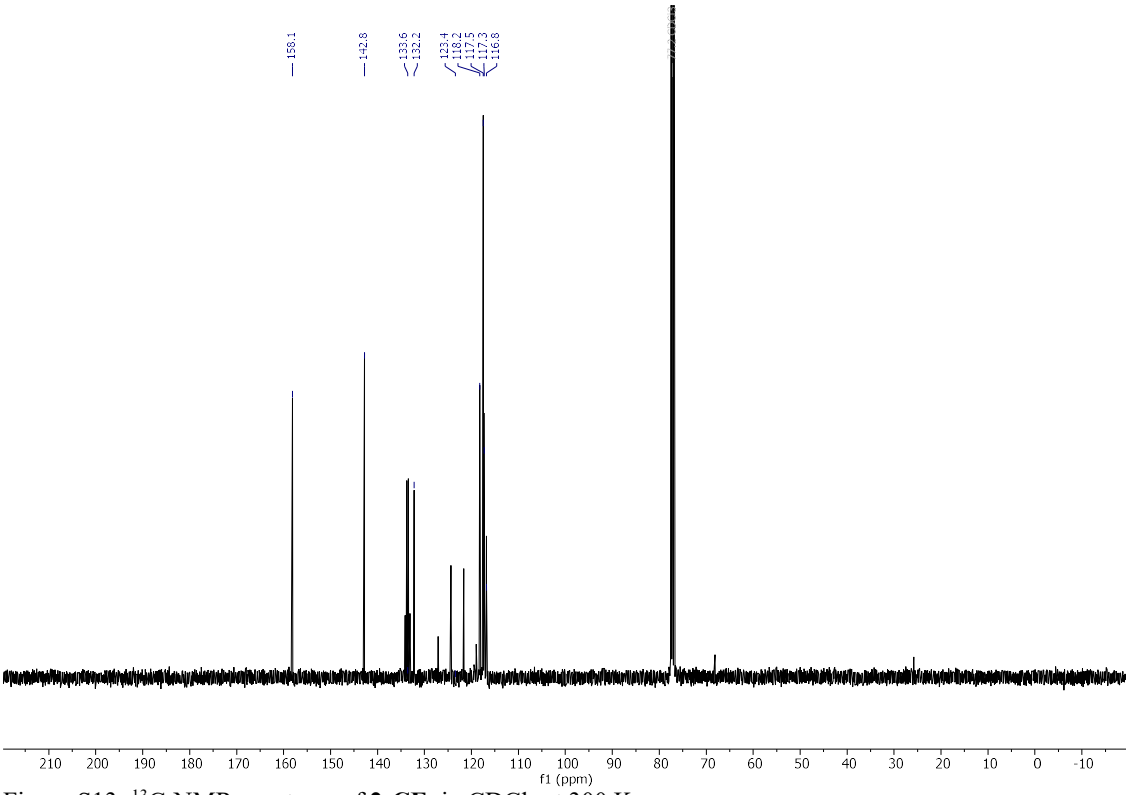


Figure S13: ^{13}C-NMR spectrum of **2-CF$_3$** in $CDCl_3$ at 300 K.

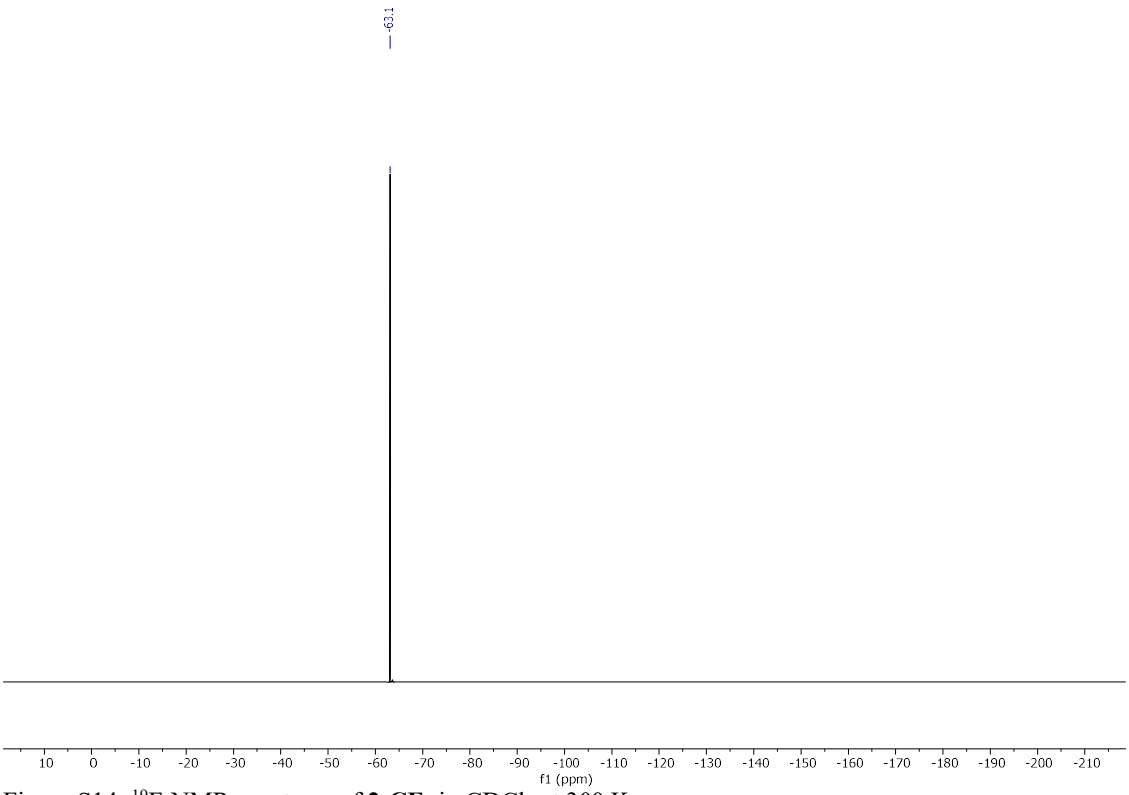
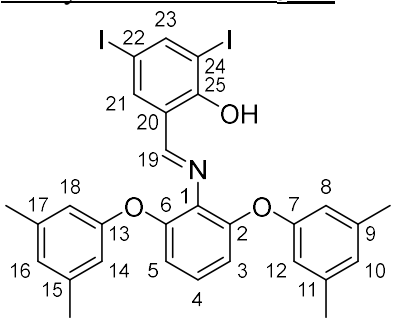


Figure S14: ^{19}F-NMR spectrum of **2-CF$_3$** in $CDCl_3$ at 300 K.

1.2.3 Synthesis of salicylaldimines

<u>Salicylaldimine **3-CH$_3$-I2**:</u>



The crude 2,6-bis(3,5-dimethylphenoxy)aniline **2-CH$_3$** (0.90 mmol, 1.0 equiv., as a mixture of the aniline **2-CH$_3$** and nitrobenzene **1-CH$_3$** in 78 % purity) was dissolved in 30 mL of MeOH. 3,5-Diiodosalicylaldehyde (450 mg, 1.2 mmol, 1.3 equiv.) was dissolved in 10 mL of MeOH and added. *p*-Toluenesulfonic acid (PTSA) monohydrate (5.0 mg) was added. After stirring for 30 min at room temperature, an orange precipitate was filtered off. The filtrate was stirred over night at room temperature and filtered off again. The crude product was washed with MeOH (1 x 8 mL) and pentane (1 x 8 mL) to give **3-CH$_3$-I2** as an orange solid (623 mg, 0.90 mmol, quantitative) after drying under reduced pressure.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.71 (s, 1H, OH···N), 8.83 (s, 1H, 19-H), 8.02 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 23-H), 7.51 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 21-H), 7.05 (t, $^3J_{HH}$ = 8.3 Hz, 1H, 4-H), 6.78 (s, 2H, 10- and 16-H), 6.67 (s, 4H, 8-, 12-, 14- and 18-H), 6.67 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3- and 5-H), 2.30 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.3 (C19), 161.0 (C25), 156.4 (C7 and C13), 151.7 (C2 and C6), 149.0 (C23), 140.7 (C21), 139.9 (C9, C11, C15, and C17), 128.6 (C1), 127.4 (C4), 125.9 (C10 and C16), 121.3 (C20), 117.1 (C8, C12, C14, and C18), 113.6 (C3 and C5), 87.8 (C22), 79.3 (C24), 21.5 (CH_3).

Anal. Calcd. for $C_{29}H_{25}I_2NO_3$ (688.99 g mol^{-1}): C, 50.53; H, 3.66; N, 2.03. Found: C, 50.73; H, 3.79; N, 2.30.

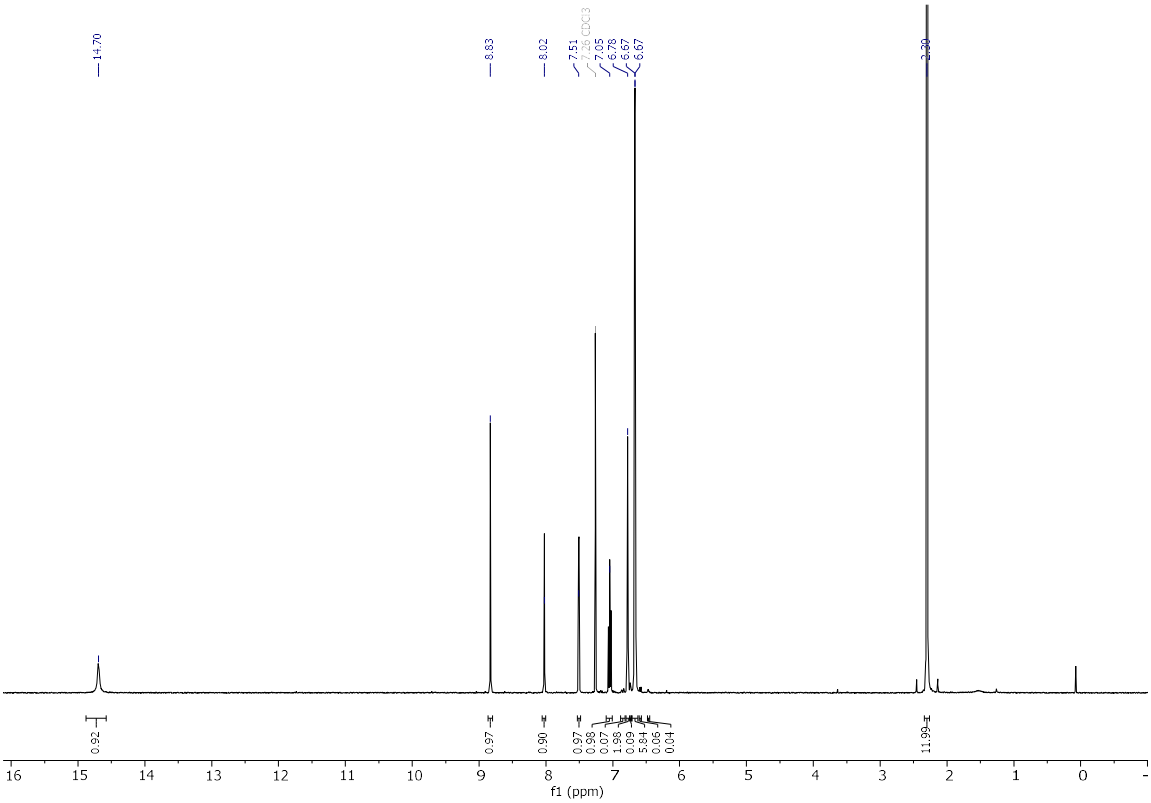


Figure S15: ^{1}H-NMR spectrum of **3-CH$_3$–I2** in $CDCl_3$ at 300 K.

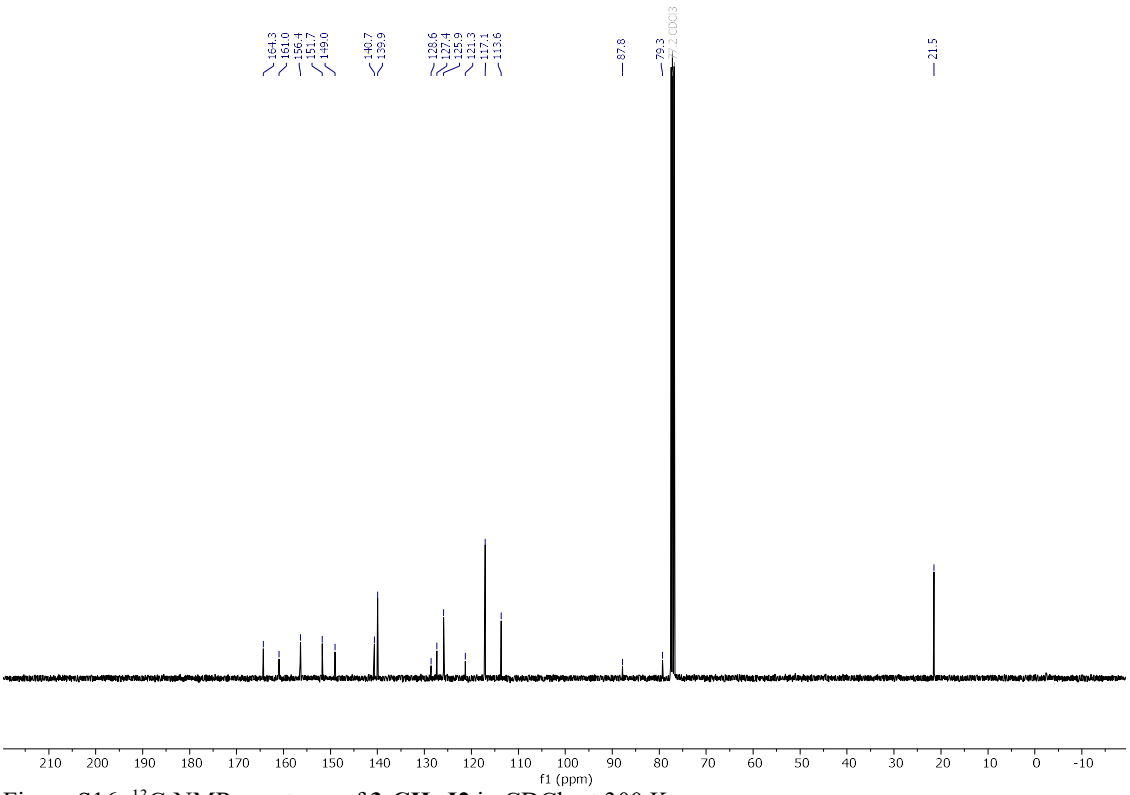
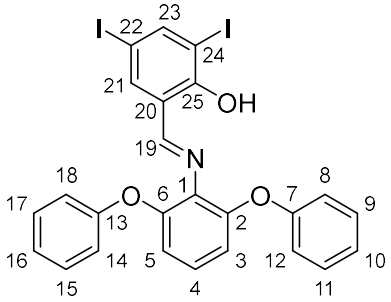


Figure S16: ^{13}C-NMR spectrum of **3-CH$_3$-I2** in $CDCl_3$ at 300 K.

Salicylaldimine **3-H-I2**:



2,6-Diphenoxyaniline **2-H** (400 mg, 1.44 mmol, 1.0 equiv.) and 3,5-diiodosalicylaldehyde (594 mg, 1.58 mmol, 1.1 equiv.) were dissolved in 100 mL of MeOH. PTSA monohydrate (5.0 mg) was added. The reaction mixture was stirred at room temperature overnight. The orange precipitate was filtered off and the filtrate stirred at room temperature overnight. The precipitate was filtered off again. The crude product was washed with MeOH and dried under vacuum to give **3-H-I2** as orange solid (735 mg, 1.1 mmol, 81 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.54 (s, 1H, OH···N), 8.82 (s, 1H, 19-H), 8.03 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 23-H), 7.51 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 21-H), 7.36 (t*v*t, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 2.3 Hz, 4H, 9-, 11-, 15- and 17-H), 7.19 – 7.10 (m, 2H, 10- and 16-H), 7.07 (t, $^3J_{HH}$ = 8.3 Hz, 1H, 4-H), 7.05 (d*v*t, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.1 Hz, 4H, 8-, 12-, 14- and 18-H), 6.70 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3- and 5-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.7 (C19), 160.8 (C25), 156.5 (C7 and C13), 151.4 (C2 and C6), 149.2 (C23), 140.7 (C21), 130.1 (C9, C11, C15, and C17), 129.3 (C1) 127.5 (C4), 124.2 (C10 and C16), 121.2 (C20), 119.2 (C8, C12, C14, and C18), 114.1 (C3 and C5), 87.7 (C22), 79.5 (C24).

Anal. Calcd. for $C_{25}H_{17}I_2NO_3$ (633.22 g mol^{-1}): C, 47.42; H, 2.71; N, 2.21. Found: C, 47.36; H, 2.93; N, 2.56.

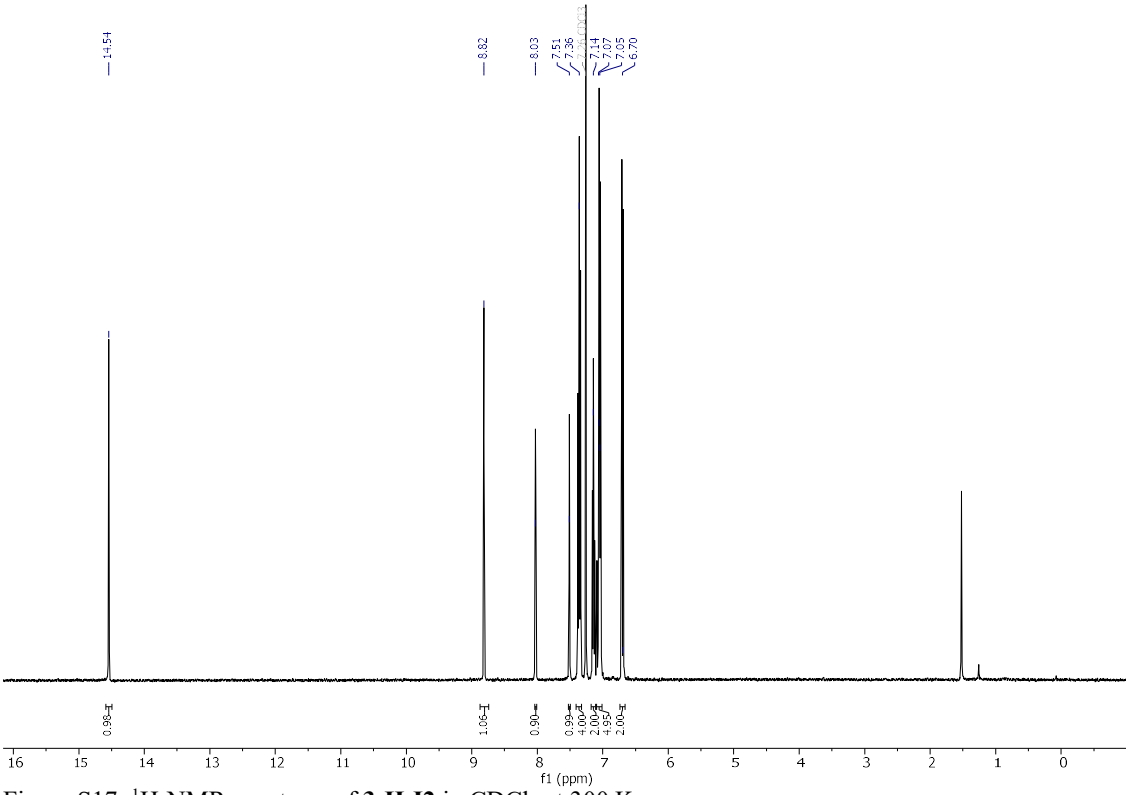


Figure S17: ^{1}H-NMR spectrum of **3-H-I2** in $CDCl_3$ at 300 K.

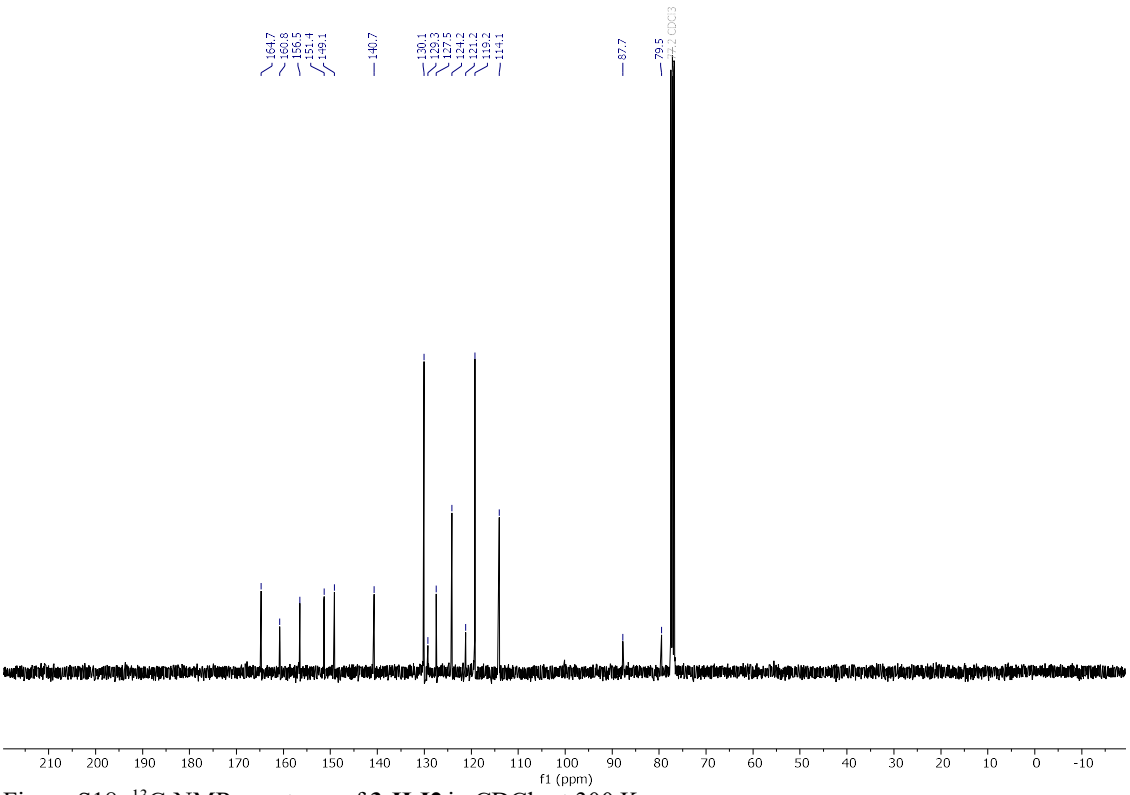
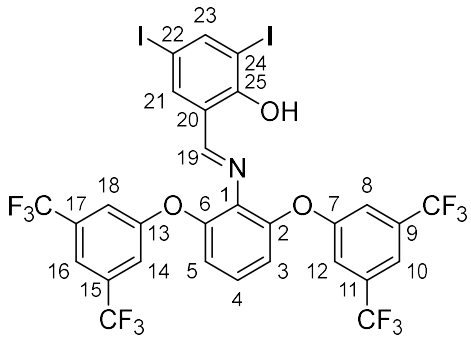


Figure S18: ^{13}C-NMR spectrum of **3-H-I2** in $CDCl_3$ at 300 K.

Salicylaldimine **3-CF$_3$-I2**:



2,6-bis(3,5-bis(trifluoromethyl)phenoxy)aniline **2-CF$_3$** (600 mg, 1.09 mmol, 1.0 equiv.) and 3,5-diiodosalicylaldehyde (429 mg, 1.15 mmol, 1.05 equiv.) were dissolved in 15 mL of dry MeOH. PTSA monohydrate (5.0 mg) was added. The reaction mixture was stirred at room temperature overnight. The product **3-CF$_3$-I2** was obtained after filtering the precipitate off as light orange solid after removal of the solvent (525 mg, 0.58 mmol, 58 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.59 (s, 1H, OH···N), 8.62 (s, 1H, 19-H), 8.07 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 23-H), 7.65 (s, 2H, 10- and 16-H), 7.54 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 21-H), 7.46 – 7.42 (m, 4H, 8-, 12-, 14 and 18-H), 7.29 (t, $^3J_{HH}$ = 8.3 Hz, 1H, 4-H), 6.92 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3- and 5-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7 (C19), 160.2 (C25), 157.4 (C7 and C13), 150.2 (C23), 149.2 (C2 and C6), 140.9 (C21), 133.7 (q, $^2J_{FC}$ = 34.0 Hz, C9, C11, C15, C17), 131.4 (C1), 128.2 (C4), 122.9 (d, $^1J_{FC}$ = 272.8 Hz, CF_3), 120.5 (C20), 118.9 – 117.9 (m, C8, C12, C14 and C18) 118.0 – 117.5 (m, C10 and C16), 116.7 (C3 and C5), 87.4 (C22), 80.2 (C24).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.0 (s, CF_3).

Anal. Calcd. for $C_{29}H_{13}F_{12}I_2NO_3$ (904.88 g mol^{-1}): C, 38.48; H, 1.45; N, 1.55. Found: C, 38.35; H, 1.91; N, 1.82.

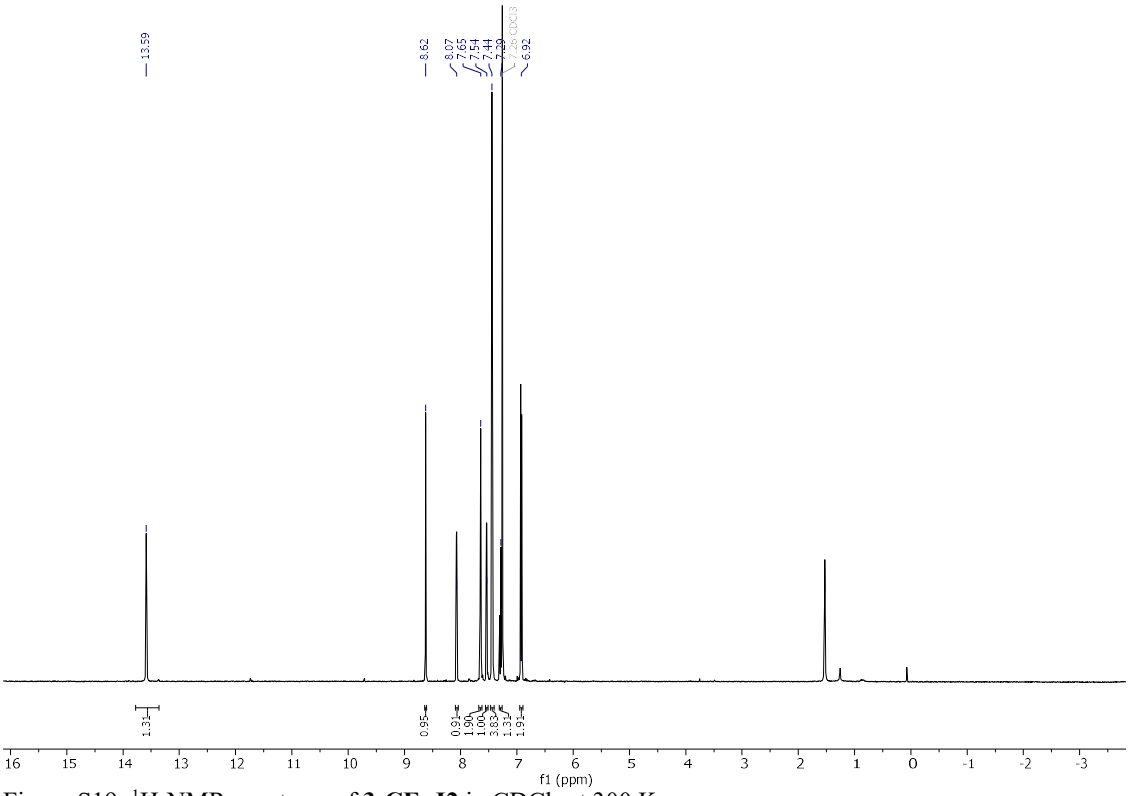


Figure S19: ^{1}H-NMR spectrum of **3-CF$_3$-I2** in $CDCl_3$ at 300 K.

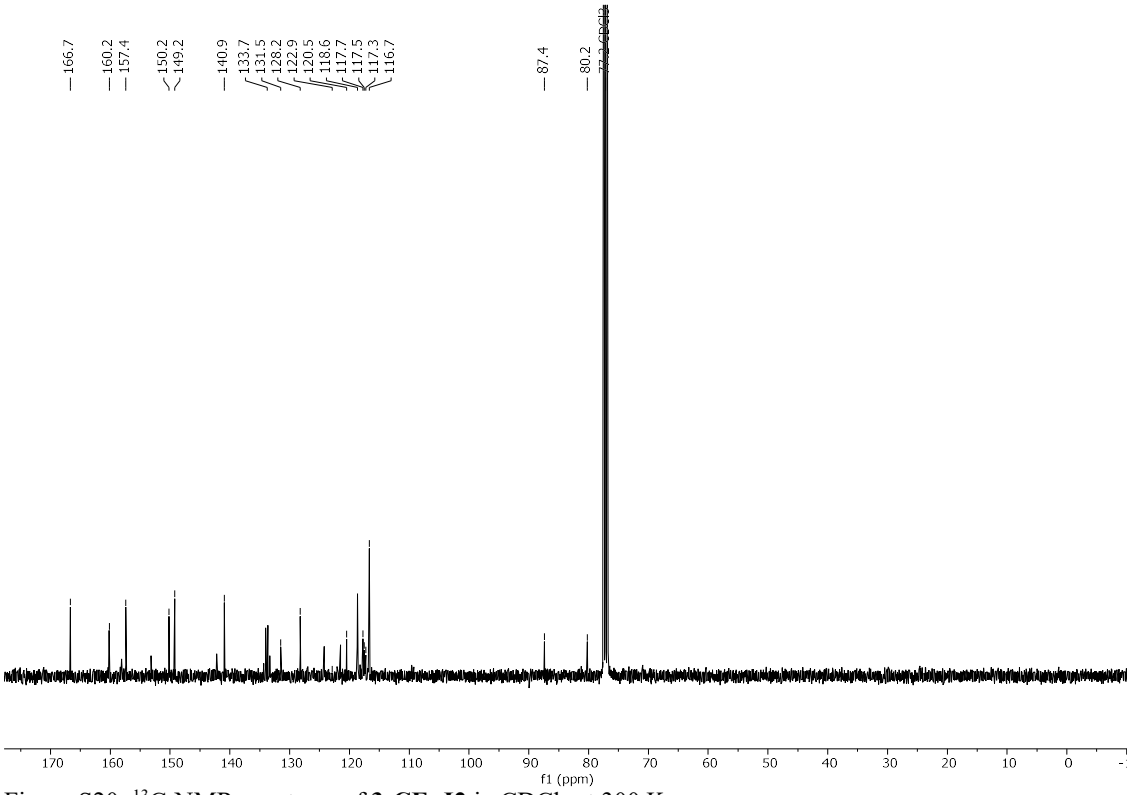


Figure S20: ^{13}C-NMR spectrum of **3-CF$_3$-I2** in $CDCl_3$ at 300 K.

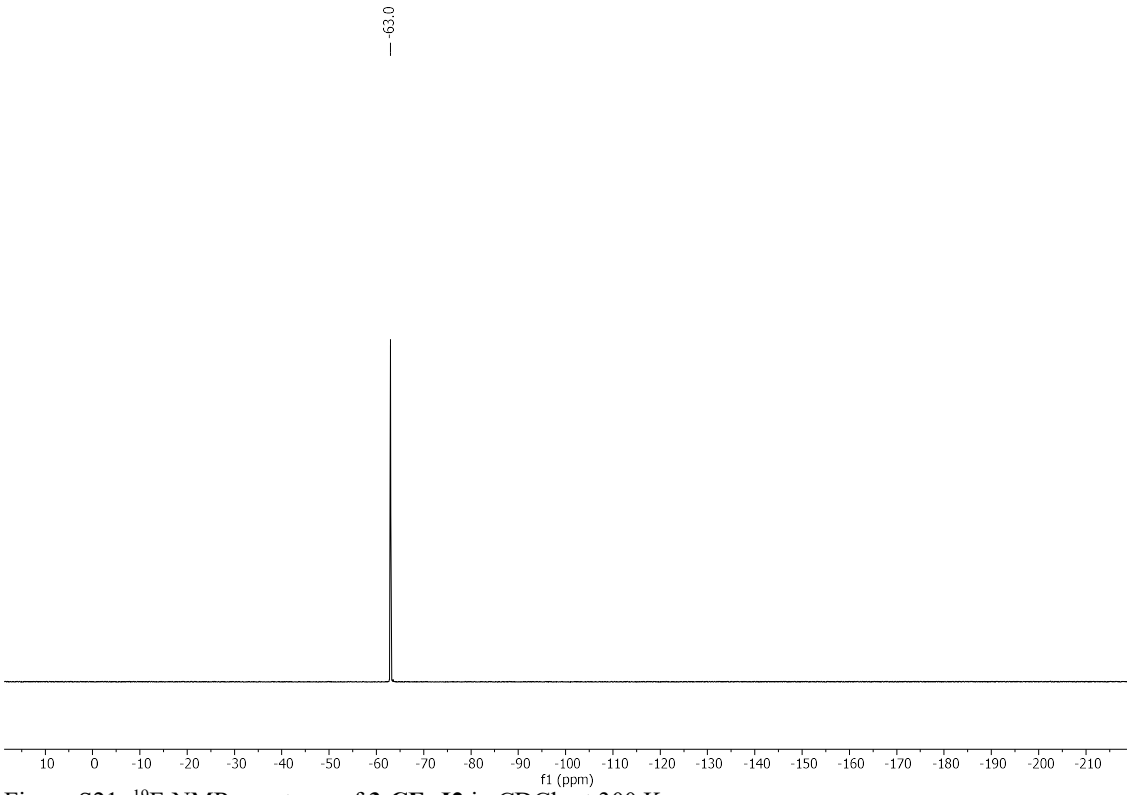
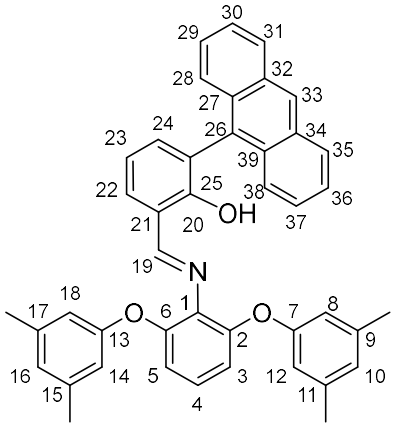


Figure S21: ^{19}F-NMR spectrum of **3-CF$_3$-I2** in $CDCl_3$ at 300 K.

Synthesis of Anthryl-Salicylaldimines

Salicylaldimine **3-CH$_3$-ant**:



The crude 2,6-bis(3,5-dimethylphenoxy)aniline **2-CH$_3$** (0.45 g, 0.90 mmol, 1.21 equiv., as a mixture of the aniline **2-CH$_3$** and nitrobenzene **1-CH$_3$** in 78 % purity) and 2-hydroxy-3-(9-anthryl)benzaldehyde · $^1/_2$ DCM (253 mg, 0.74 mmol, 1.0 equiv.) were dissolved in 120 mL of dry toluene in a 250 mL round flask, equipped with a soxhlet extractor containing 4 Å molecular sieves. PTSA monohydrate (5.0 mg) was added. The reaction mixture was heated to 140 °C for 3 days. The crude product filtered, was washed with MeOH (4 x 15 mL) and dried under vacuum. **3-CH$_3$-ant** was obtained as a light yellow solid (354 mg, 0.57 mmol, 76 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.30 (s, 1H, OH···N), 9.06 (s, 1H, 19-H), 8.50 (s, 1H, 33-H), 8.04 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, 28- and 38-H), 7.66 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.6 Hz, 2H, 31- and 35-H), 7.52 – 7.40 (m, 3H, 24-, 29- and 37-H), 7.40 – 7.29 (m, 3H, 22-, 30- and 36-H), 7.08 (t, $^3J_{HH}$ = 7.6, 1H, 23-H), 7.01 (*v*t, $^3J_{HH}$ = 8.4 Hz, 4-H), 6.73 – 6.64 (m, 4H, 3-, 5-, 10- and 16-H), 6.62 (s, 4H, 8-, 12-, 14-, and 18-H), 2.23 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.9 (C19), 159.9 (C25), 156.9 (C7 and C13), 150.9 (C2 and C6), 139.7 (C9, C11, C15 and C17), 136.5 (C22), 132.9 (C32 and C34), 132.7 (C24), 131.7 (C21), 131.4 (C1), 130.6 (C27, and C39), 129.2 (C33) 128.6 (C28 and C38), 126.9 (C26, C31 and C35), 126.2 (C4), 125.4 (C10 and C16), 125.4 (C30 and C36), 125.1 (C29 and C37), 119.9 (C20), 118.6 (C23), 116.7 (C8, C12, C14 and C18), 114.3 (C3 and C5), 21.4 (CH_3).

Anal. Calcd. for $C_{43}H_{35}NO_3$ (613.76 g mol^{-1}): C, 84.15; H, 5.75; N, 2.28. Found: C, 84.13; H, 5.77; N, 2.49.

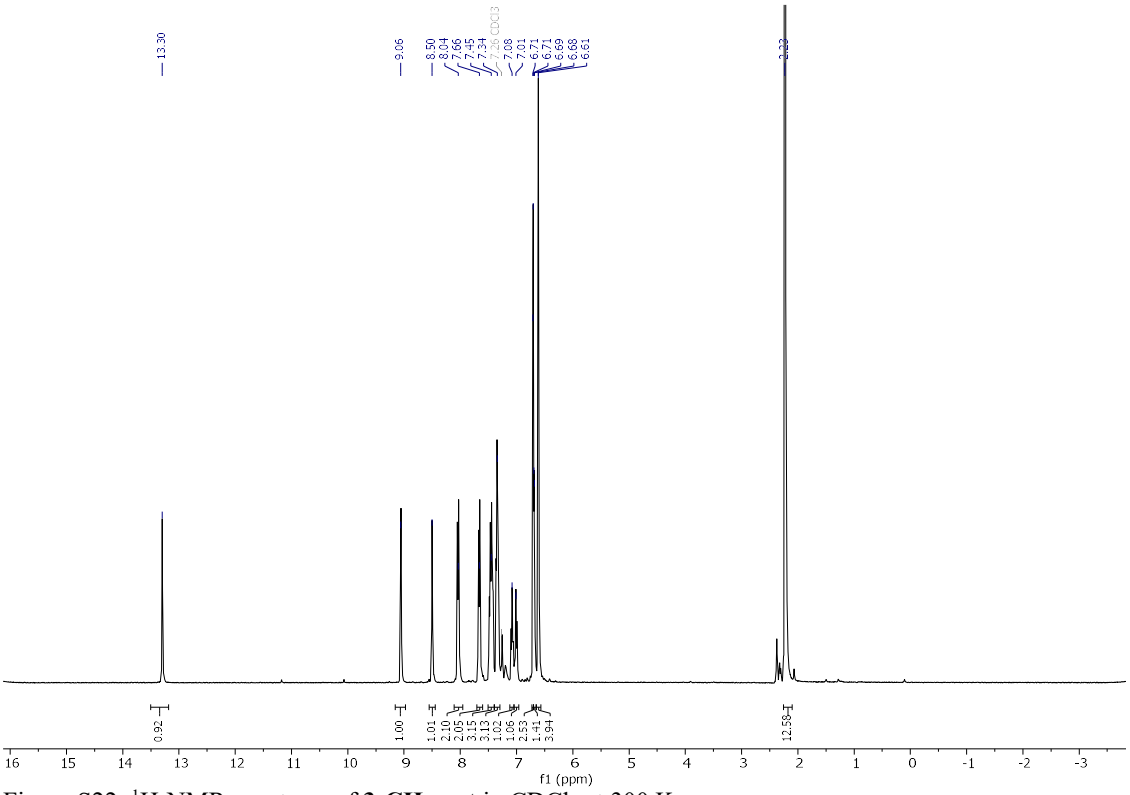


Figure S22: ^{1}H-NMR spectrum of **3-CH$_3$-ant** in $CDCl_3$ at 300 K.

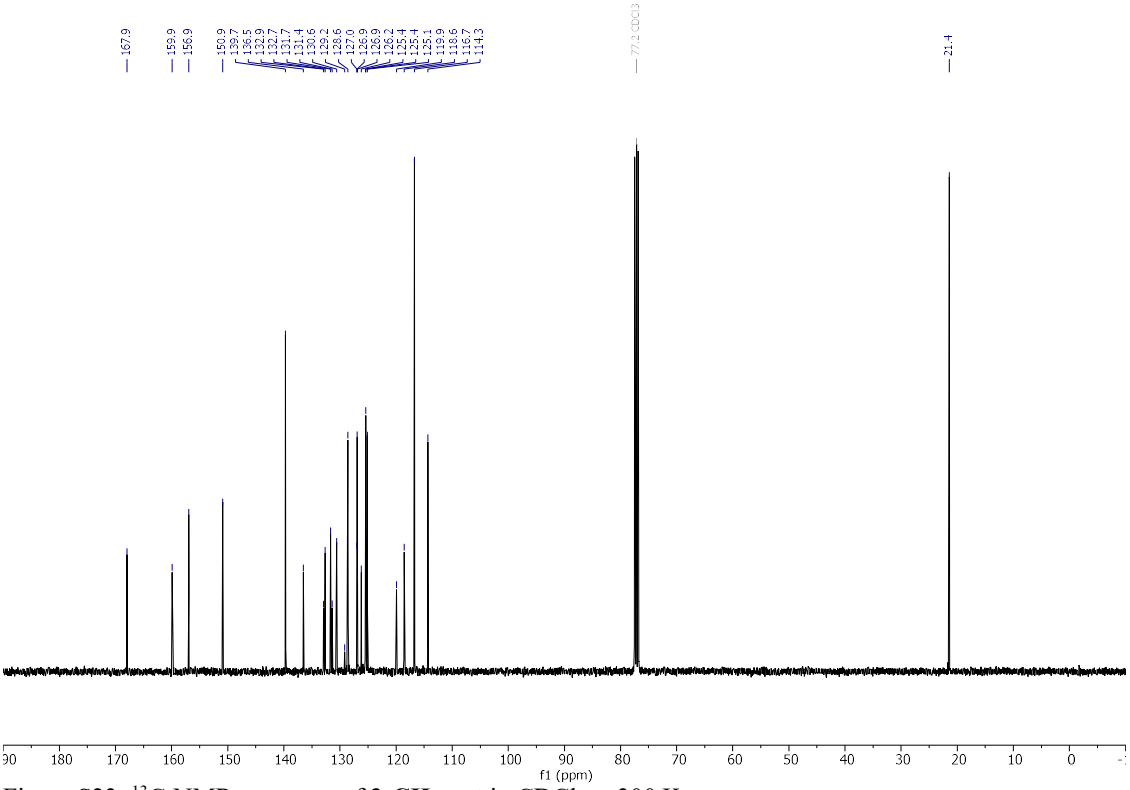
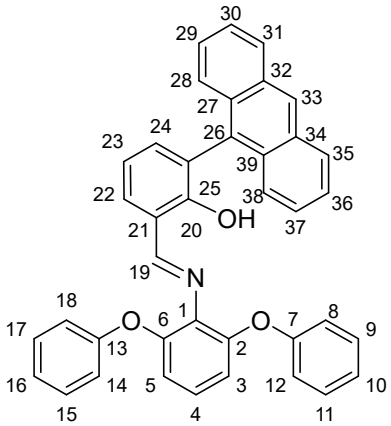


Figure S23: ^{13}C-NMR spectrum of **3-CH$_3$-ant** in $CDCl_3$ at 300 K.

Salicylaldimine **3-H-ant**:



2,6-Diphenoxyaniline **2-H** (400 mg, 1.44 mmol, 1.14 equiv.) and 2-hydroxy-3-(9-anthryl)benzaldehyde · $^{1}/_{2}$ DCM (430 mg, 1.26 mmol, 1.0 equiv.) were dissolved in 70 mL of MeOH. PTSA monohydrate (5.0 mg) was added. The reaction mixture was stirred at room temperature overnight. The precipitate was filtered off. The filtrate was stirred at room temperature overnight to give an additional crop. The product **3-H-ant** was obtained after washing with MeOH and drying as a light yellow solid (465 mg, 0.83 mmol, 66 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.21 (s, 1H, OH···N), 9.02 (s, 19-H), 8.55 (s, 1H, 33-H), 8.09 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, 28- and 38-H), 7.67 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 31- and 35-H), 7.54 – 7.45 (m, 3H, 22-, 29- and 37-H), 7.44 – 7.25 (m, 9H, 9-, 10-, 11-, 15-, 16-, 17-, 23-, 30- and 36-H), 7.17 – 7.05 (m, 2H, 4- and 24-H), 7.05 – 6.94 (m, 4H, 8-, 12-, 14- and 18-H), 6.79 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, 3- and 5-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.2 (C19), 159.8 (C25), 157.1 (C7 and C13), 150.5 (C2 and C6), 136.6 (C9, C11, C15 and C17), 132.8 (C24), 132.7 (C22), 132.0 (C21), 131.7 (C1), 130.5 (C26), 129.9 (C29 and C37), 128.6 (C28 and C38), 127.0 (C30 and C35), 126.9 (C4), 126.3 (C20), 125.5 (C32 and C34), 125.1 (C27 and C39), 123.6 (C10 and C16), 119.7 (C31, C33 and C35), 118.8 (C8, C12, C14 and C18), 118.7 (C23), 115.0 (C3 and C5).

Anal. Calcd. for $C_{39}H_{27}NO_3$ (557.65 g mol^{-1}): C, 84.00; H, 4.88; N, 2.51. Found: C, 84.11; H, 4.97; N, 2.80

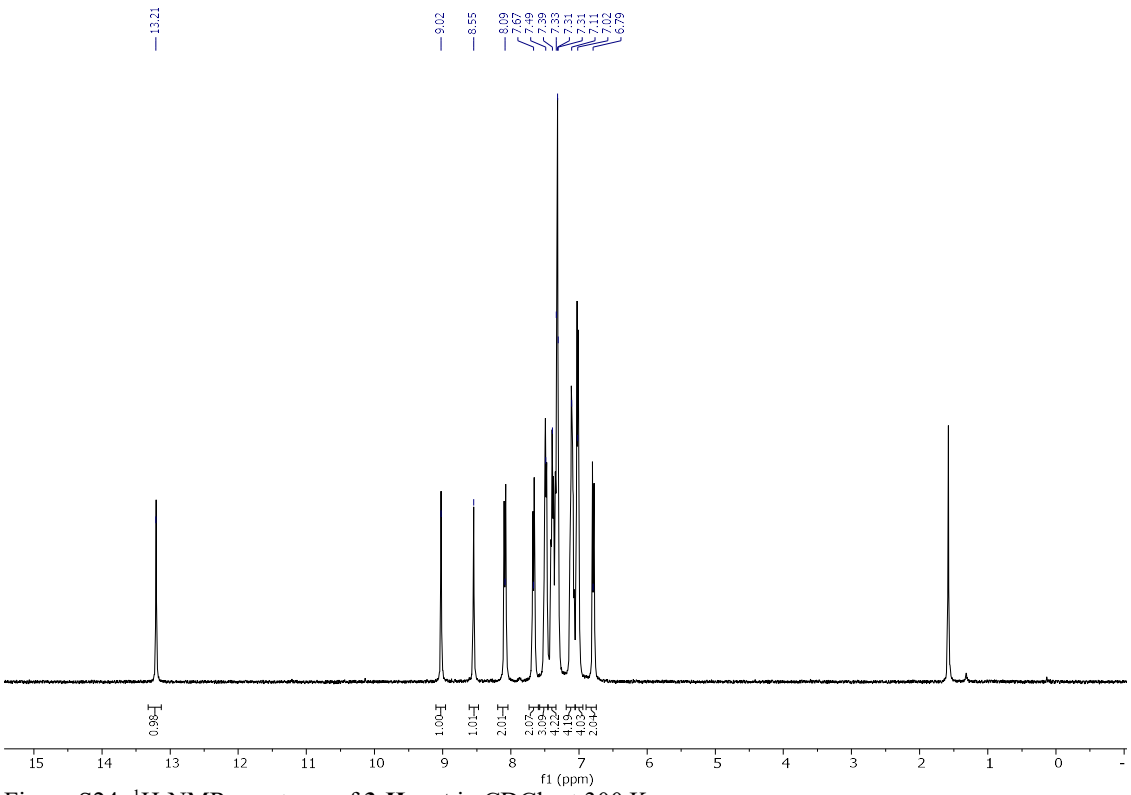


Figure S24: ^{1}H-NMR spectrum of **3-H-ant** in $CDCl_3$ at 300 K.

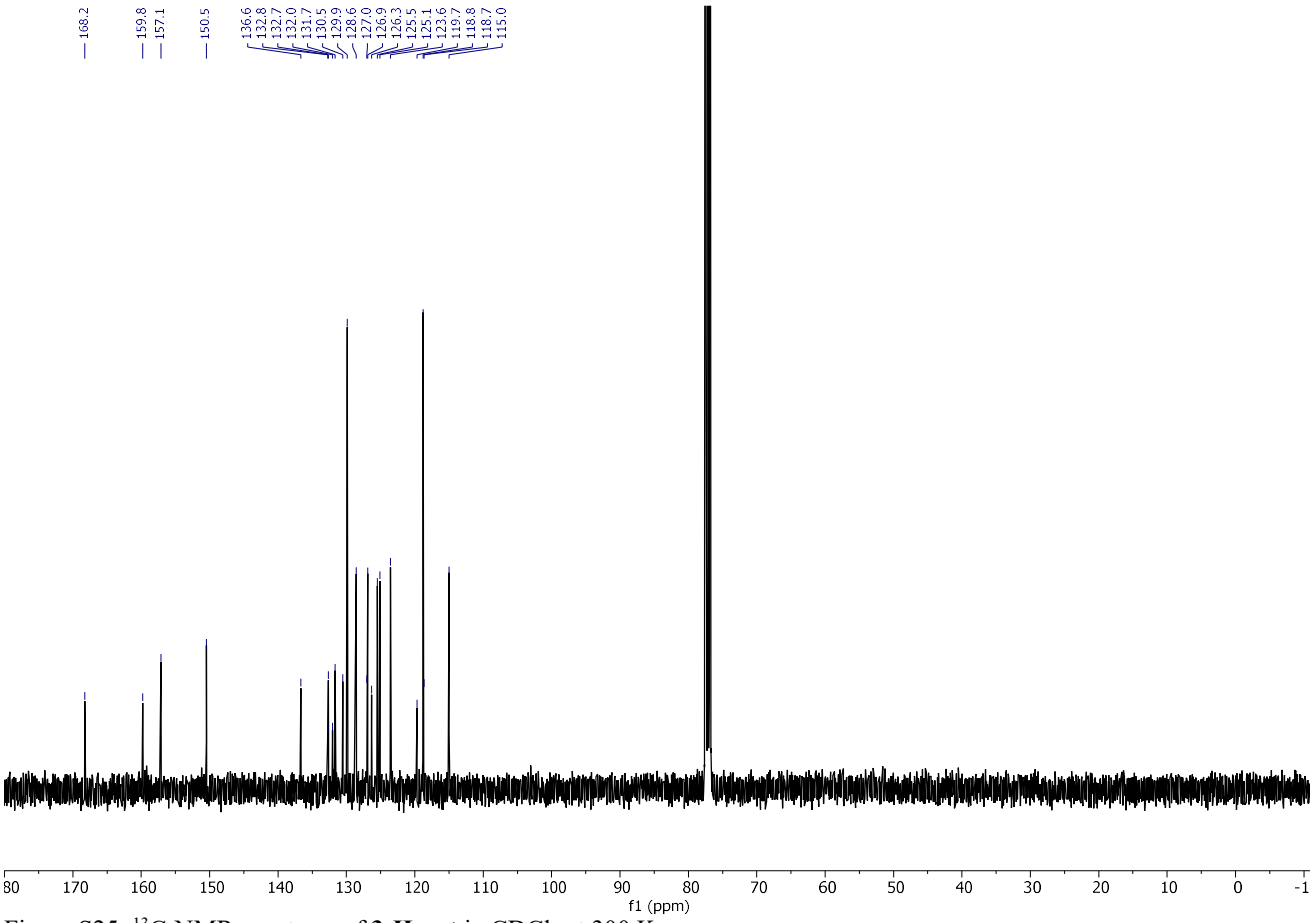
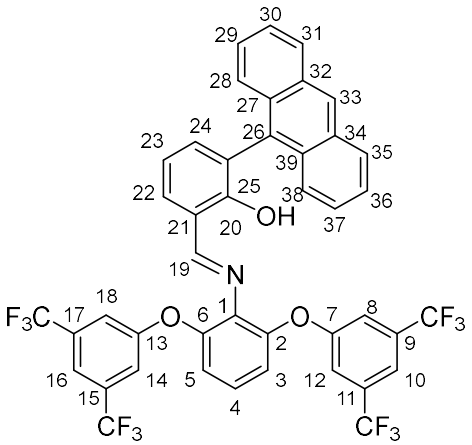


Figure S25: ^{13}C-NMR spectrum of **3-H-ant** in $CDCl_3$ at 300 K.

Salicylaldimine **3-CF$_3$-ant**:



2,6-bis(3,5-bis(trifluormethyl)phenoxy)aniline **2-CF$_3$** (548 mg, 1.0 mmol, 1.14 equiv.) and 2-hydroxy-3-(9-anthryl)benzaldehyde · $^1/_2$ DCM (298 mg, 0.86 mmol, 1.0 equiv.) were dissolved in 40 mL of dry MeOH. PTSA monohydrate (5.0 mg) was added. The reaction mixture was stirred at room temperature overnight. The precipitate was filtered off and washed with MeOH. The product was obtained after drying as a light yellow solid (458 mg, 0.55 mmol, 63 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.57 (s, 1H, OH···N), 8.95 (s, 1H, 19-H), 8.58 (s, 1H, 33-H), 8.11 (m, 2H, 28- and 38-H), 7.65 (s, 2H, 10- and 16-H), 7.62 – 7.58 (m, 2H, 31-H and 35-H), 7.57 – 7.42 (m, 8H, 8-, 12-, 14- 18-, 22-, 24- 29- and 37-H), 7.42 – 7.36 (m, 2H, 30- and 36-H), 7.32 (t, $^3J_{HH}$ = 8.3 Hz, 1H, 4-H), 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 23-H), 7.00 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3- and 5-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.5 (C19), 159.7 (C25), 157.7 (C7 and C13), 148.7 (C2 and C6), 137.7 (C24), 133.6 (q, $^2J_{CF}$ = 33.8 Hz, C9, C11, C15 and C17), 133.3 (C1), 132.9 (C21), 132.0 (C26), 131.6 (C27 and C39), 130.5 (C32 and C34), 128.7 (C28 and C38), 127.4 (C33), 127.3 (C20), 127.3 (C4), 126.4 (C31 and C35), 125.6 (C30 and C36), 125.2 (C29 and C37), 122.9 (q, $^1J_{CF}$ = 273.0 Hz, CF_3), 119.3 (C23), 119.0 (C22), 118.5 – 118.2 (m, C8, C12, C14 and C18), 117.5 – 117.2 (m, C10 and C16), 117.0 (C3 and C5).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.1 (s, CF_3).

Anal. Calcd. for $C_{43}H_{23}F_{12}NO_3$ (829.15 g mol^{-1}): C, 62.25; H, 2.79; N, 1.69. Found: C, 62.16; H, 3.24; N, 1.93.

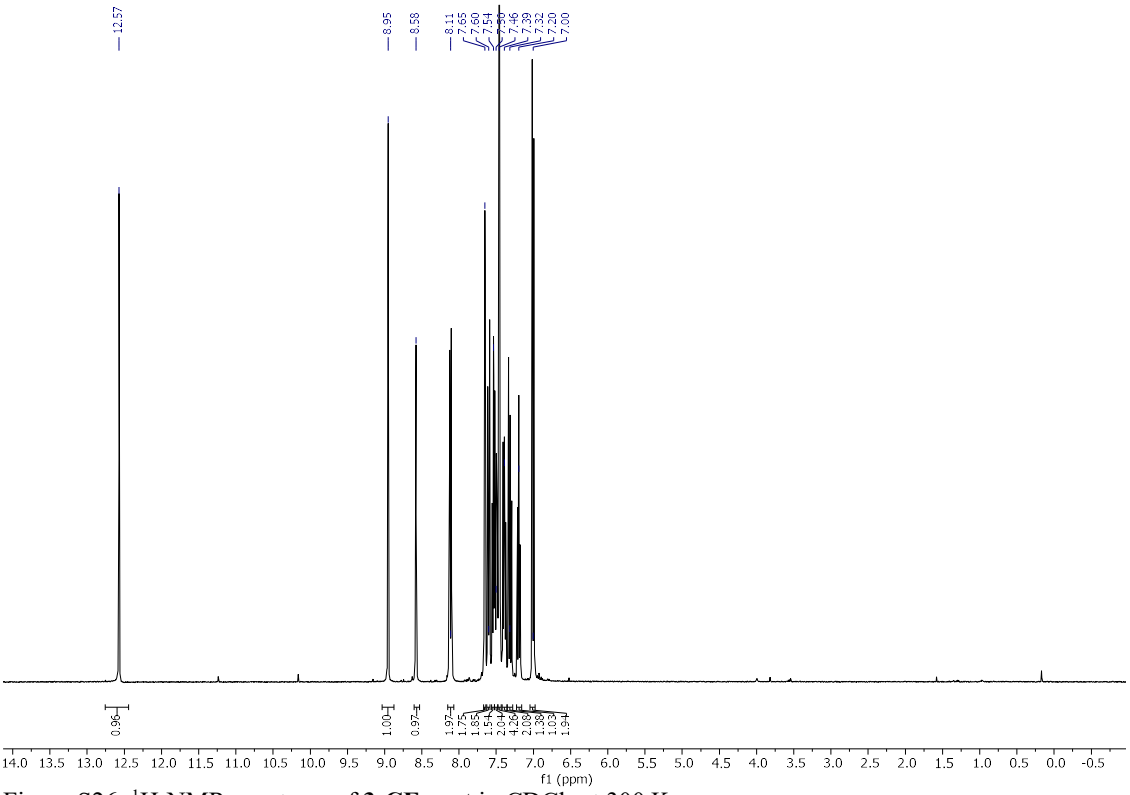


Figure S26: ^{1}H-NMR spectrum of **3-CF$_3$-ant** in $CDCl_3$ at 300 K.

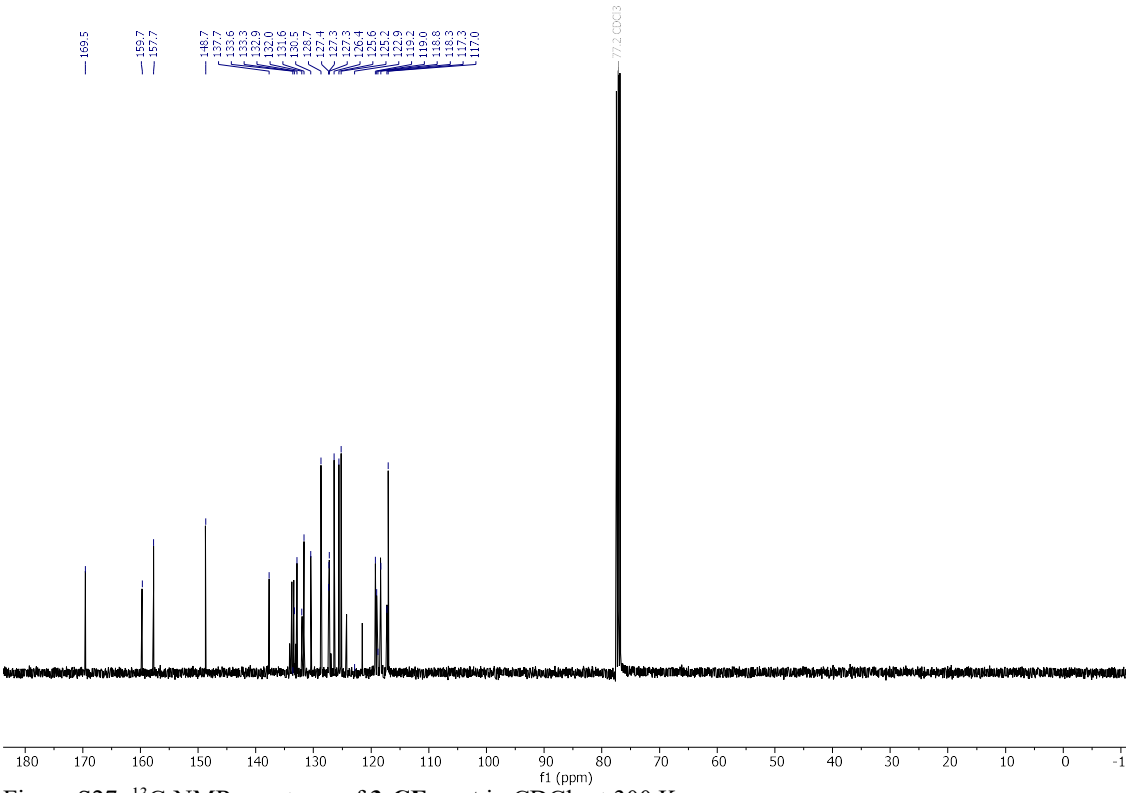


Figure S27: ^{13}C-NMR spectrum of **3-CF$_3$-ant** in $CDCl_3$ at 300 K.

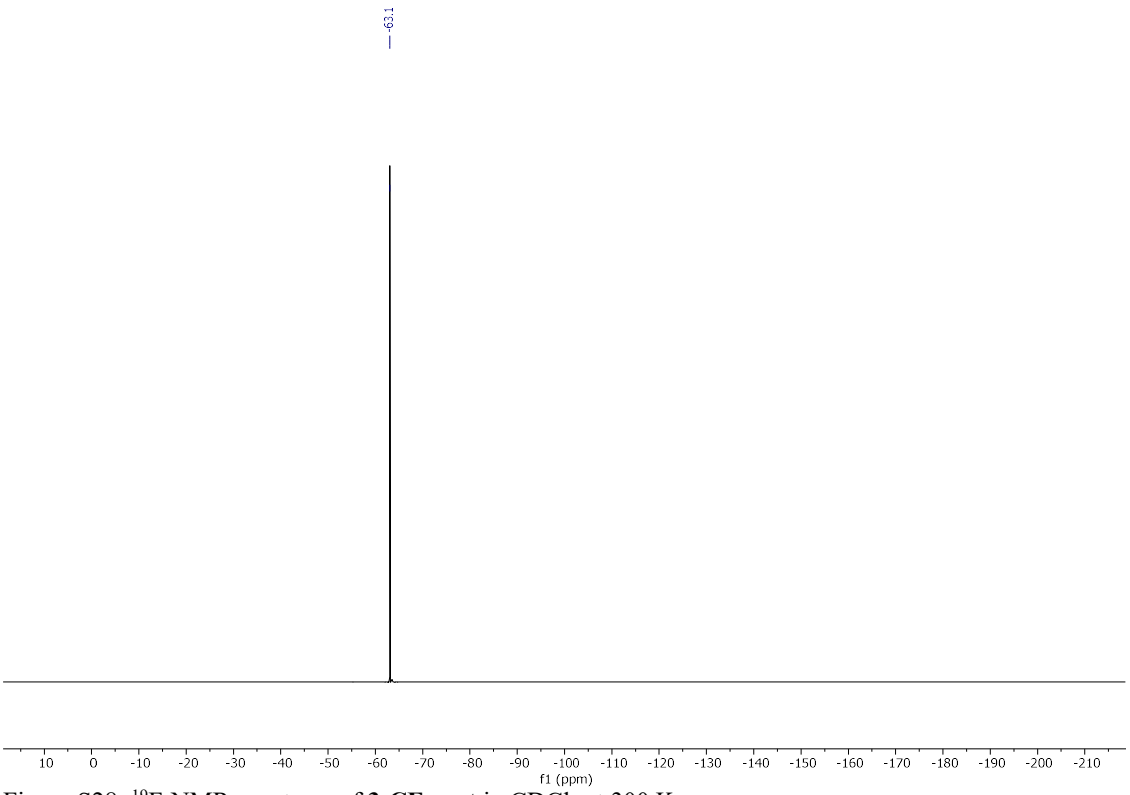


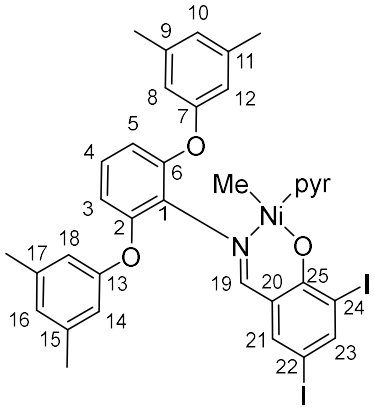
Figure S28: ^{19}F-NMR spectrum of **3-CF$_3$-ant** in $CDCl_3$ at 300 K.

1.2.4 Synthesis of oxygen bridged complexes

General procedure for the preparation of the oxygen bridged catalyst precursors:

A solution of pyridine (160 mg, 2.0 mmol, 20 equiv.) in benzene (5 mL) was added to a mixture of [(tmeda)NiMe$_2$] (22.4 mg, 110 µmol, 1.1 equiv.) and the respective salicylaldimine **4** (100 µmol, 1.0 equiv.) in a 8 mL vial. The reaction mixture was stirred immediately at room temperature for 20 - 150 min. The resulting red solution was centrifuged. The supernatant was separated from the black precipitate. The precipitate was washed with 3 mL of benzene. The combined solutions were frozen in liquid nitrogen and the volatiles were removed under vacuum whilst warming up to room temperature. Optionally, unreacted ligand was removed by washing with pentane. The complexes were obtained as red solids in 85 % - 95 % yield.

Complex **4-CH$_3$-I2**:



Following the general procedure for the synthesis of the oxygen-bridged catalyst precursors, complex **4-CH$_3$-I2** was obtained after stirring for 20 min and further work-up as a red solid (79.8 mg, 95 µmol, 95 %).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.52 (m, 2H, *o*-H pyridine), 8.04 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 23-H), 7.44 (s, 1H, 19-H), 7.03 (s, 4H, 8-, 12-, 14-, and 18-H), 7.01 – 6.95 (m, 1H, 4-H) 6.94 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 21-H), 6.79 – 6.72 (m, 3H, 10-, 16-H and *p*-H pyridine), 6.66 – 6.50 (m, 4H, 3-, 5-, 10- and 16-H), 6.25 (t, $^3J_{HH}$ = 6.9 Hz, 2H, *m*-H pyridine), 2.06 (s, 12H, CH_3), -0.29 (s, 3H, Ni-CH_3).

^{13}C-NMR analysis not possible due to the instability of the product in solution over several hours. A decomposition towards [$NiI_2(pyr)_2$] (see crystallographic data) is likely. Nevertheless, this comparable slow decomposition should effect the pressure reactor experiments to a minor extent.

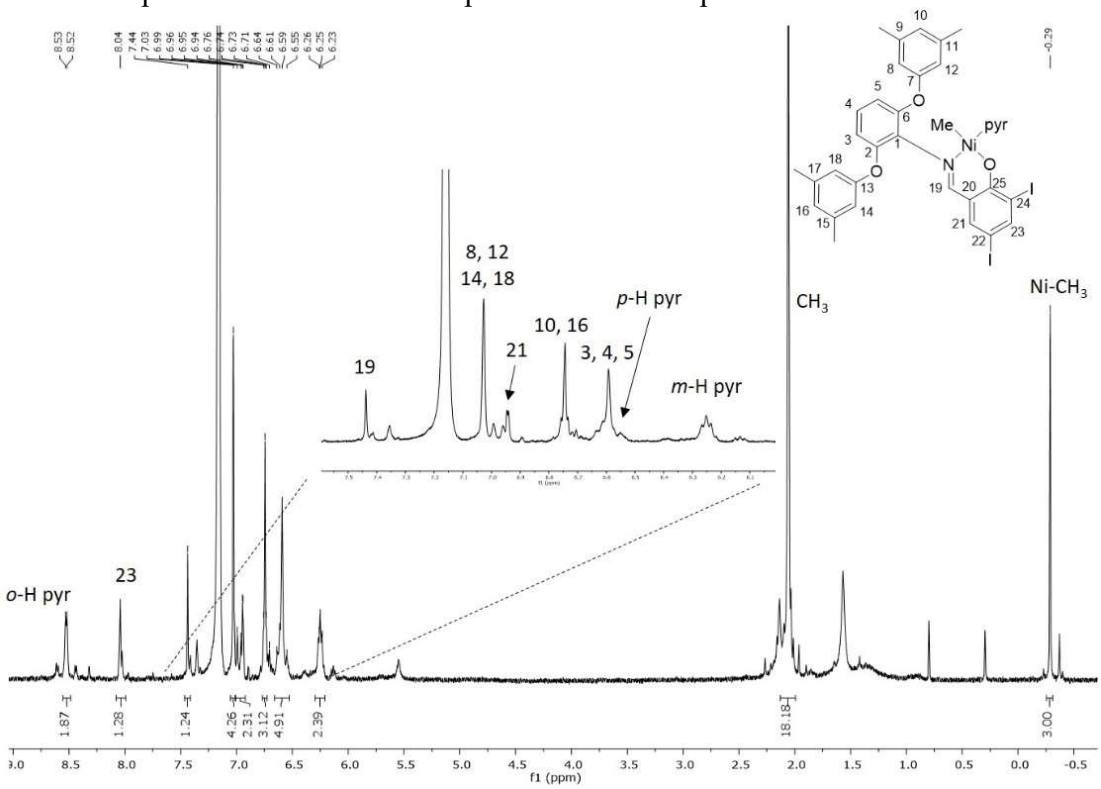
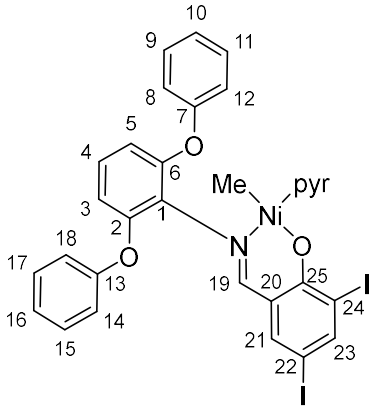


Figure S29: ^{1}H-NMR spectrum of **4-CH$_3$-I2** in C_6D_6 at 300 K.

Complex **4-H-I2**:



Following the general procedure for the synthesis of the oxygen-bridged precursors, complex **4-H-I2** was obtained from **3-H-I2** (78.4 mg, 100 µmol) after stirring for 20 min and further work-up as a red solid (65.0 mg, 92 µmol, 92 %).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.45 (d, $^3J_{HH}$ = 5.5, 2H, *o*-H pyridine), 8.03 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 23-H), 7.33 (s, 1H, 19-H), 7.25 – 7.19 (m, 4H, 8-, 12-, 14- and 18-H), 7.10 – 7.01 (m, 4H, 9-, 11-, 15- and 17-Hz), 6.91 (d, $^4J_{HH}$ =2.3 Hz, 1H, 21-H), 6.90 – 6.84 (m, 2H, 10- and 16-H), 6.71 – 6.54 (m, 4H, 3-, 4-, 5- and *p*-H pyridine), 6.24 (t, $^3J_{HH}$ = 6.7 Hz, 2H, *m*-H-pyridine), -0.40 (s, 3H, Ni-CH_3).

^{13}C-NMR analysis not possible due to the instability of the product in solution over several hours. A decomposition towards [$NiI_2(pyr)_2$] (see crystallographic data) is likely. Nevertheless, this comparable slow decomposition should effect the pressure reactor experiments to a minor extent.

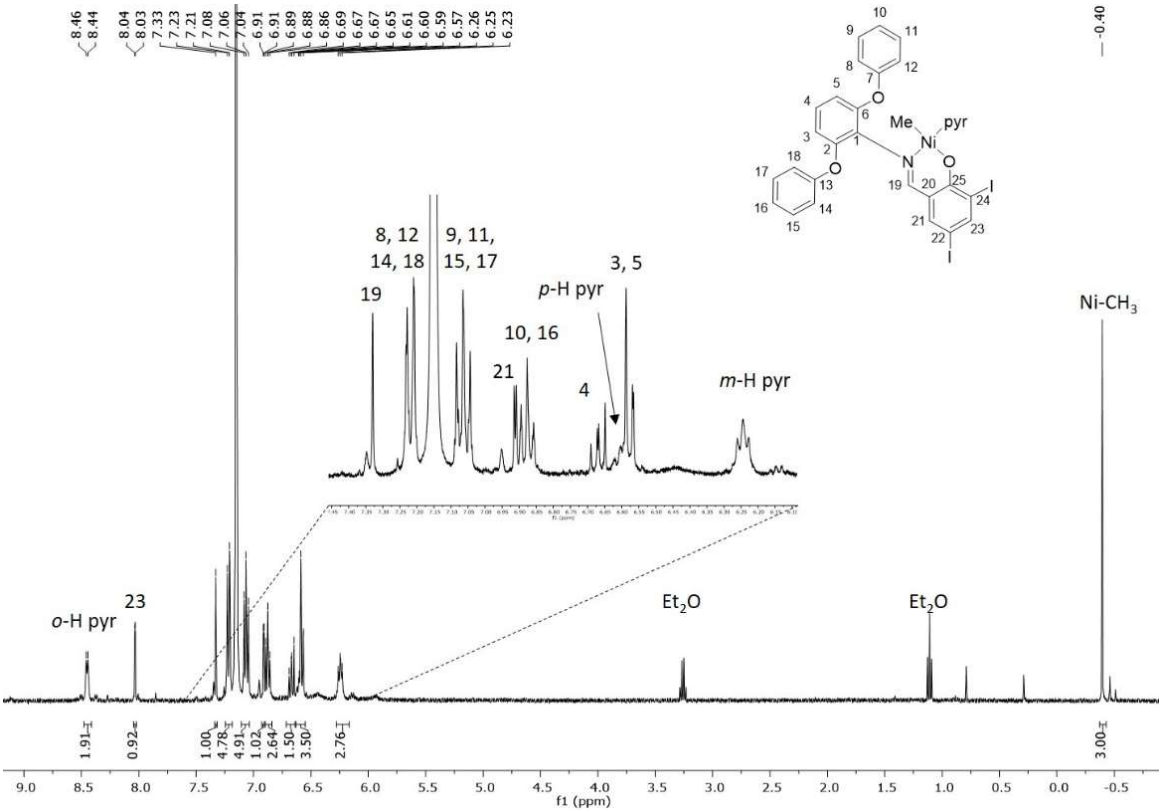
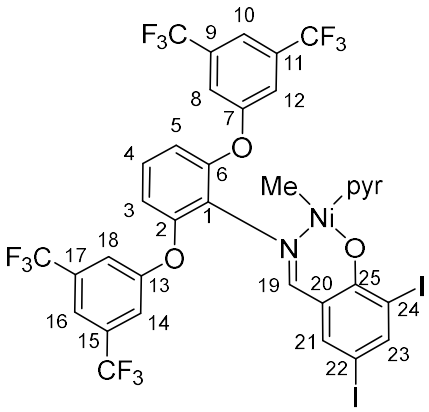


Figure S30: ^{1}H-NMR spectrum of **4-H-I2** in C_6D_6 at 300 K.

Complex **4-CF$_3$-I2**:



Following the general procedure for the synthesis of the oxygen bridged catalyst precursors, complex **4-CF$_3$-I2** was obtained after stirring for 30 min and washing with pentane as a red solid in quantitative yield.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.43 – 8.32 (m, 2H, *o*-H pyridine), 7.99 (d, $^4J_{HH}$ = 2.2 Hz, 1H, 23-H), 7.57 (d, $^4J_{HH}$ = 1.4 Hz, 4H, 8-, 12-, 14- and 18-H), 7.51 (s, 2H, 10- and 18-H), 7.19 (s, 1H, 19-H), 7.04 (d, $^4J_{HH}$ = 2.2 Hz, 1H, 21-H), 6.64 – 6.47 (m, 2H, 4-H and *p*-H pyridine), 6.35 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3- and 5-H), 6.32 – 6.19 (m, 2H, *m*-H pyridine), -0.61 (s, 3H, Ni-CH_3).

^{13}C-NMR analysis not possible due to the instability of the product in solution over several hours. A decomposition towards [$NiI_2(pyr)_2$] (see crystallographic data) is likely. Nevertheless, this comparable slow decomposition should effect the pressure reactor experiments to a minor extent.
Anal. Calcd. for $C_{35}H_{20}F_{12}N_2NiO_3$ (1057.04 g mol^{-1}): C, 39.77; H, 1.91; N, 2.65. Found: C, 40.08; H, 2.46; N, 3.12.

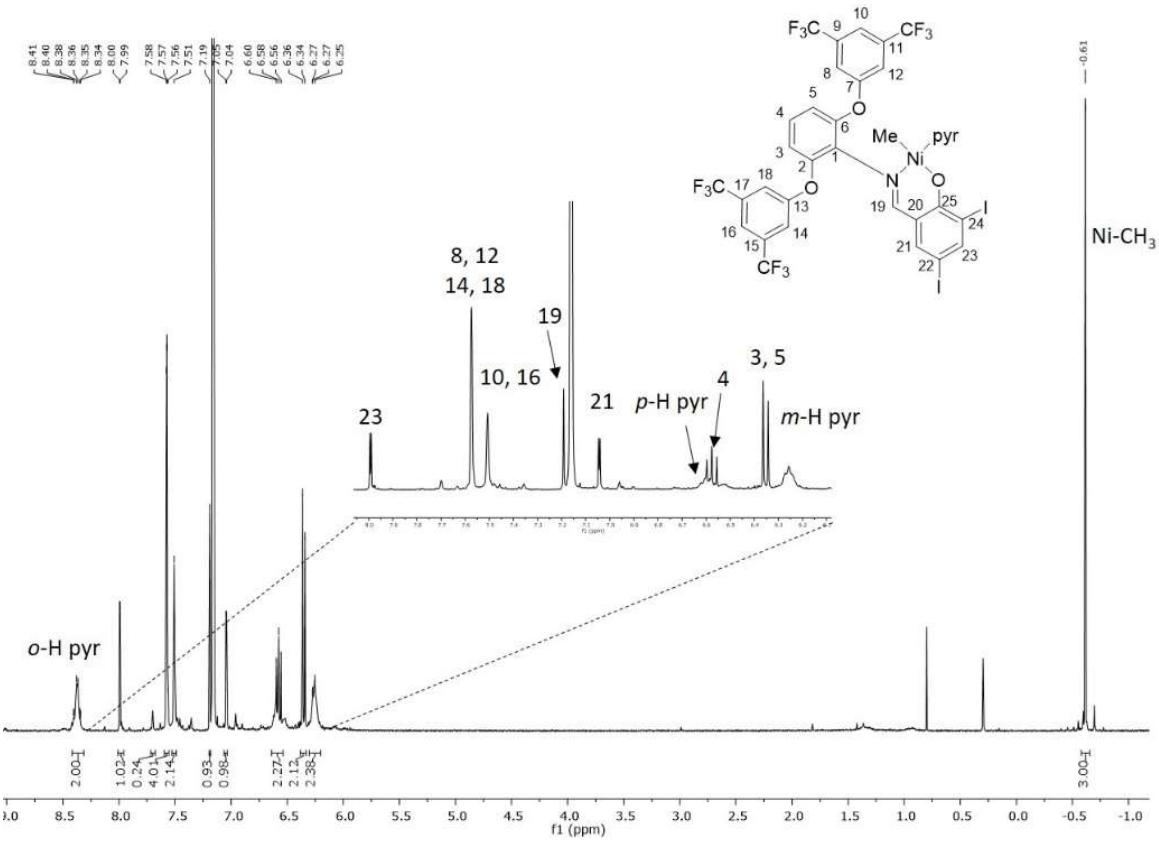
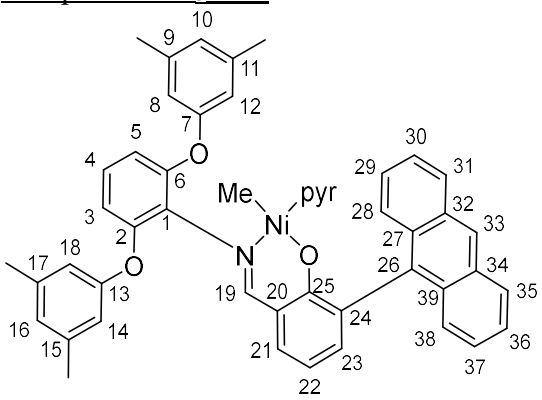


Figure S31: ^{1}H-NMR spectrum of **4-CF$_3$-I2** in C_6D_6 at 300 K.

Complex **4-CH$_3$-ant**:



Following the general procedure for the synthesis of the oxygen bridged catalyst precursors, complex **4-CH$_3$-ant** was obtained after stirring for 35 min and further work-up as a red solid (72.0 mg, 94 µmol, 94 %).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.12 (s, 1H, 19-H), 8.12 (s, 1H, 33-H), 7.98 (d, $^3J_{HH}$ = 8.7 Hz, 2H, 28- and 38-H), 7.78 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 31- and 35-H), 7.75 – 7.70 (m, 2H, *o*-H pyridine), 7.29 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, 23-H), 7.22 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, 21-H), 7.00 – 6.93 (m, 6H, 8-, 12-, 14-, 18-, 29- and 37-H), 6.81 – 6.68 (m, 3H, 3-, 4- and 5-H), 6.64 – 6.55 (m, 3H, 10-, 16- and 22-H), 6.29 – 6.16 (m, 1H, *p*-H pyridine) 5.62 – 5.48 (m, 2H, *o*-H pyridine), 2.06 (s, 12H, CH$_3$), -0.42 (s, 3H, Ni-CH$_3$).
The signals for 30- and 36-H are overlapped by the solvent residue signal.

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 168.8 (C19), 166.5 (C25), 157.3 (C7 and C13), 152.4 (C2 and C6), 151.6 (*o*-H pyridine), 139.7 (C9, C11, C15 and C17), 137.4 (C23), 137.1 (C24), 136.9 (C26), 134.7 (*p*-C pyridine) 134.4 (C21), 132.0 (C33) 131.3 (either C27 and C39 or C32 and C34), 131.1 (either C27 and C39 or C32 and C34), 128.7 (C31 and C35), 128.6 (C1) 125.9 (C4), 125.8 (C10 and C16), 125.5 (C29 and C37 or C30 and C36), 125.1 (C29 and C37 or C30 and C36), 125.0 (C28 and C38), 121.9 (*m*-C pyridine), 121.1 (C20), 118.2 (C8, C12, C14 and C18), 113.4 (C22), 112.6 (C3 and C5), 21.3 (CH_3), -8.9 (Ni-CH_3).

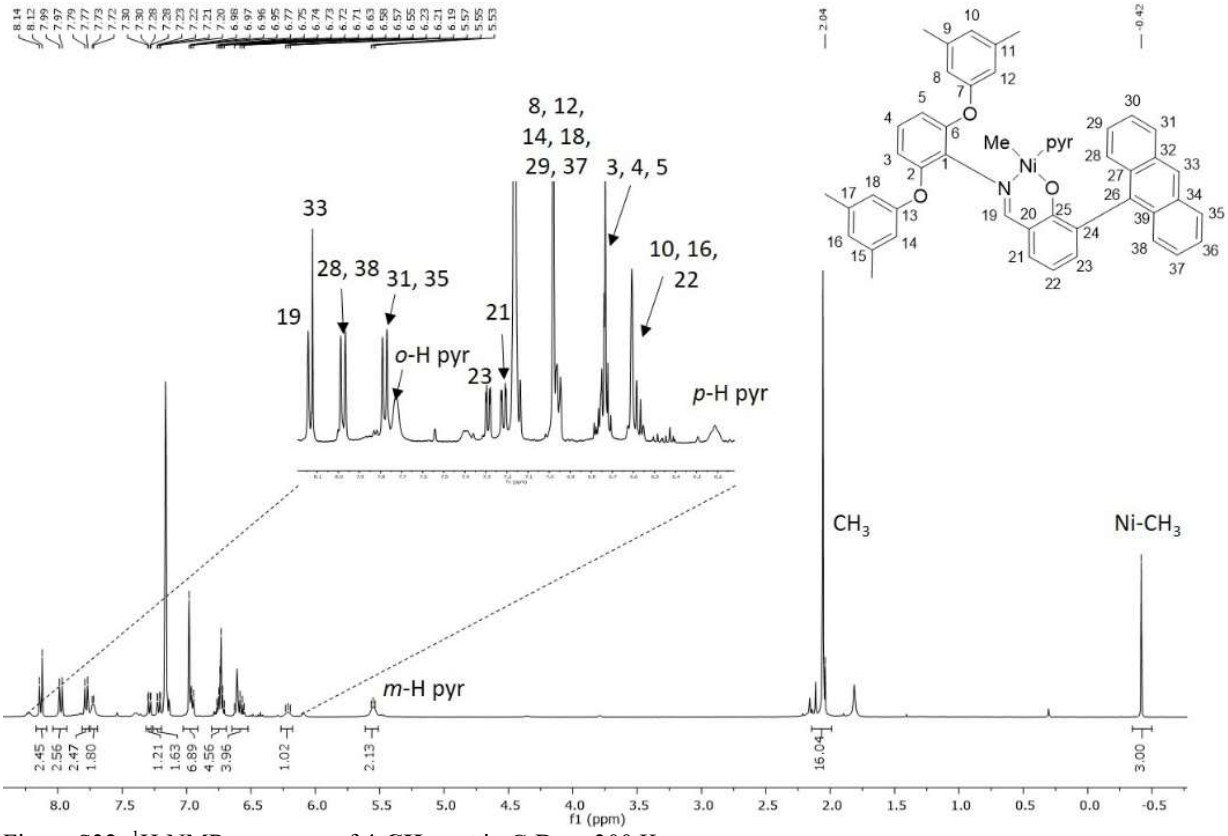


Figure S32: ^{1}H-NMR spectrum of **4-CH$_3$-ant** in C_6D_6 at 300 K.

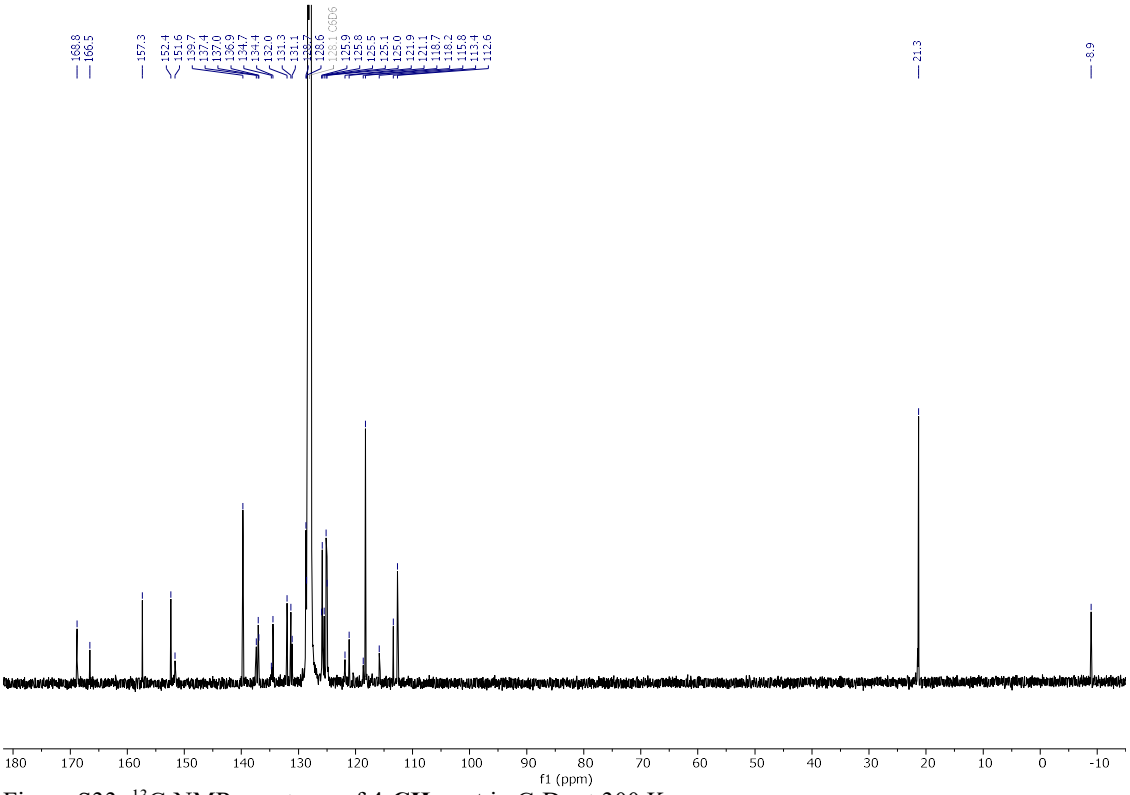
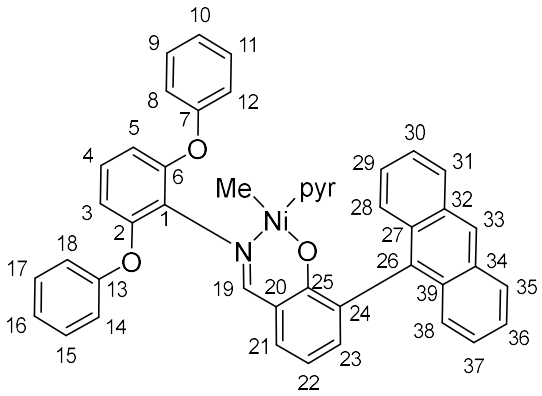


Figure S33: ^{13}C-NMR spectrum of **4-CH$_3$-ant** in C_6D_6 at 300 K.

Complex **4-H-ant**:



Following the general procedure for the synthesis of the oxygen bridged catalyst precursors, complex **4-H-ant** was obtained from **3-H-ant** (61.3 mg, 100 µmol) after stirring for 150 min and further work-up as a red solid (65.2 mg, 92 µmol, 92 %) with impurities (tmeda and unreacted ligand).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.13 (s, 1H, 33-H), 7.99 – 7.92 (m, 3H, 19-, 28- and 38-H), 7.77 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 31- and 35-H), 7.66 (d, $^3J_{HH}$ = 5.4 Hz, 2H, *o*-H pyridine), 7.26 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ 1.9, 1H, 23-H), 7.23 – 7.19 (m, 4H, 8-, 12-, 14- and 18-H), 7.18 – 7.13 (m, 2H, 30- and 36-H), 7.10 – 7.05 (m, 5H, 9-, 12-, 15-,17- and 21-H), 6.98 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, 29- and 37-H), 6.90 – 6.85 (m, 2H, 10- and 16-H), 6.70 – 6.58 (m, 3H, 3-, 4-, and 5-H), 6.55 (dd, $^3J_{HH}$ =8.0 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, 22-H), 6.24 – 6.17 (m, 1H, *p*-H pyridine), 5.54 (s, 2H, *m*-H pyridine), -0.53 (s, 3H, Ni-CH$_3$).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 168.7 (C19), 166.5 (C25), 157.6 (C7 and C13), 152.0 (*o*-C pyridine), 151.27 (C 10 and C16) 137.3 (C2 and C6), 137.1 (C23), 134.7 (C1) 134.4 (C21), 133.3 (*p*-C pyridine), 131.3 (C24 or C26), 131.1 (C24 or C26), 130.1 (C9, C11, C15 and C17), 128.6 (C28 and C38), 126.0 (C4), 125.5 (C33), 125.1 (either C27 and C39 or C32 and C34), 124.9 (either C27 and C39 or C32 and C34), 123.8 (*m*-C pyridine), 121.0 (C20), 120.2 (C8, C12, C14 and C18), 117.8 (C30 and 36), 115.9 (C29 and 37)113.4 (C22), 113.3 (C3 and C5), -9.11 (Ni-CH_3).
The signals for C31 and C35 are overlapped by the solvent signal.

Anal. Calcd. for $C_{45}H_{34}N_2NiO_3$ (708.19 g mol^{-1}): C, 76.18; H, 4.83; N, 3.95. Found: C, 73.90; H, 5.19; N, 4.73.
The discrepancy of the expected and measured values for the elemental analysis are due to impurities in the product (unreacted salicylaldimine **3-H-ant** and remaining tmeda). These impurities should not alter the catalytic properties drastically, as **3-H-ant** is not active itself and pyridine is a by far stronger ligand compared to pyridine.

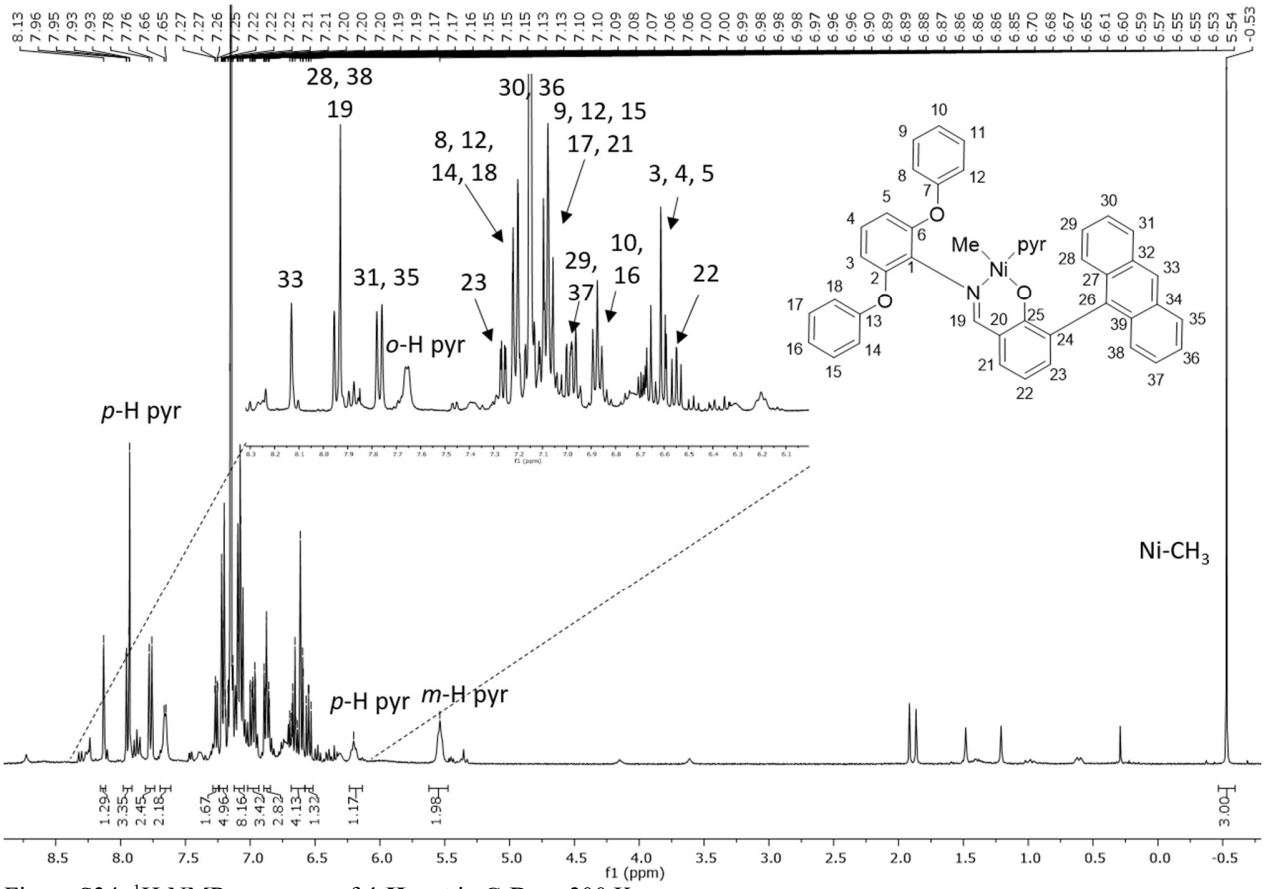


Figure S34: ^{1}H-NMR spectrum of **4-H-ant** in C_6D_6 at 300 K.

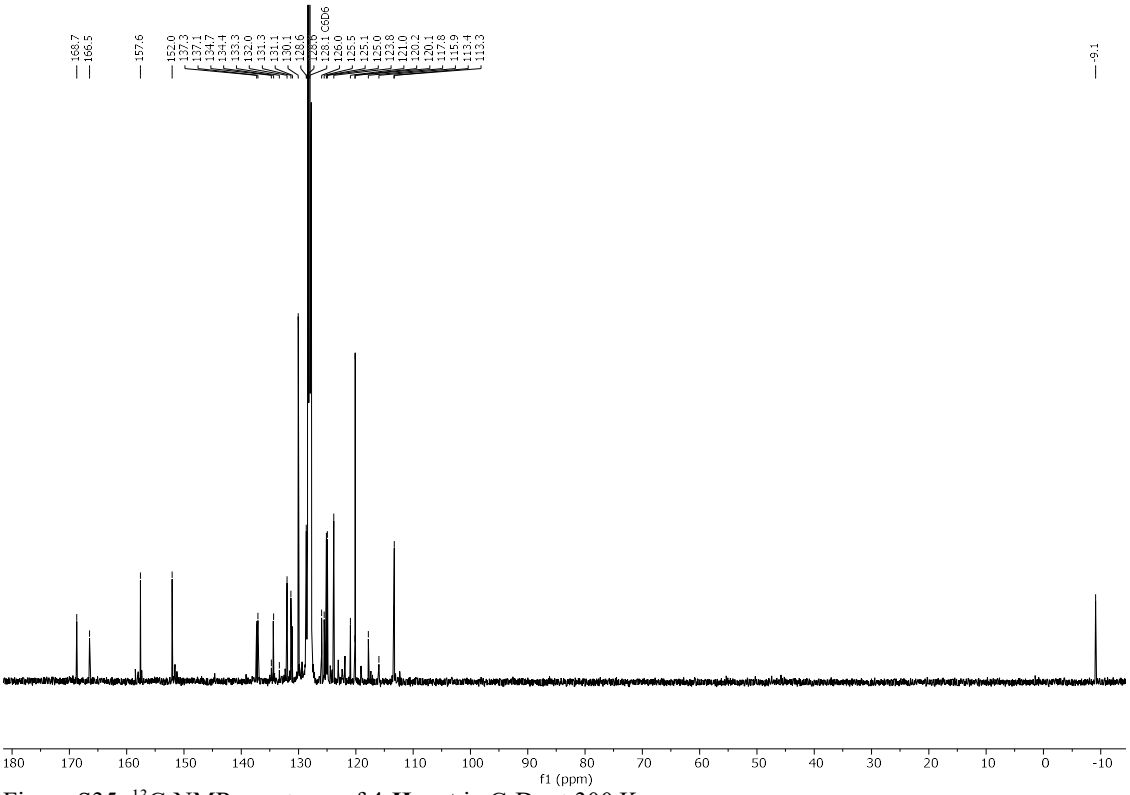
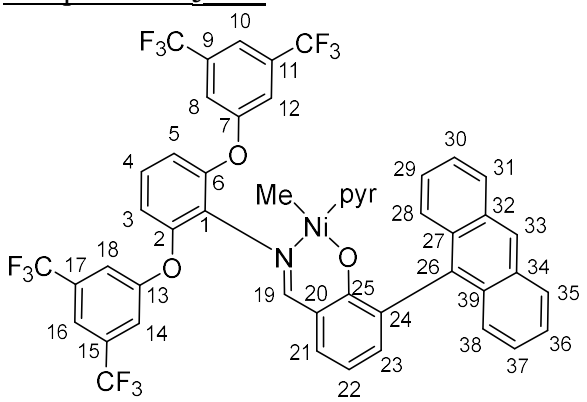


Figure S35: ^{13}C-NMR spectrum of **4-H-ant** in C_6D_6 at 300 K.

Complex **4-CF$_3$-ant**:



Following the general procedure for the synthesis of the oxygen bridged catalyst precursors, complex **4-CF$_3$-ant** was obtained after stirring for 120 min and further work-up as a red solid (96.1 mg, 91 µmol, 91 %).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.09 (s, 1H, 33-H), 7.93 – 7.88 (m, 3H, 19-, 28- and 38-H), 7.83 (d, $^3J_{HH}$ = 8.5 Hz, 2H, 31- and 35-H), 7.67 – 7.54 (m, 2H, *o*-H pyridine and 8-, 10-, 12-, 14-, 16- and 18-H), 7.36 – 7.13 (m, 7H, 21, 23-, 30- and 36-H), 7.09 – 6.96 (m, 2H, 29- and 37-H), 6.75 – 6.62 (m, 2H, 4- and 22-H), 6.43 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3- and 5-H), 6.40 – 6.12 (m, 1H, *p*-H pyridine) 5.65 (s, 2H, *m*-H pyridine), -0.62 (s, 3H, Ni-CH_3).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 168.6 (C19), 166.8 (C25), 158.2 (C7 and C13), 150.2 (C2 and C6), 138.5 (C1), 138.0 (C23), 136.3 (C26), 134.1 (C21), 133.9 (q, $^2J_{CF}$ = 33.7, C9, C11, C15 and C17), 131.9 (C32 and C34), 131.9 (C24), 131.1 (C27 and C39), 128.6 (C28 and C38), 127.0 (C4), 125,7 (C33), 125.0 and 124.8 (either C29 and C37 or C30 and C36), 124.8 (either C29 and C37 or C30 and

C36), 122.1 (q, $^1J_{CF}$ = 273.0, CF_3), 120.2 (C20), 119.3 – 119.1 (m, C8, C12, C14 and C18), 117.3 (m, C10 and C16), 115.4 (C3 and C5), 114.3 (C22), -9.4 (Ni-CH_3).
The signals for C31, C35 are overlapped by the solvent signal.

^{19}F-NMR (376 MHz, C_6D_6, 300 K): δ (ppm) = -62.8 (s, CF_3).

Anal. Calcd. for $C_{49}H_{30}F_{12}N_2NiO_3$ (980.14 g mol^{-1}): C, 59.97; H, 3.08; N, 2.85. Found: C, 60.82; H, 4.62; N, 3.62.

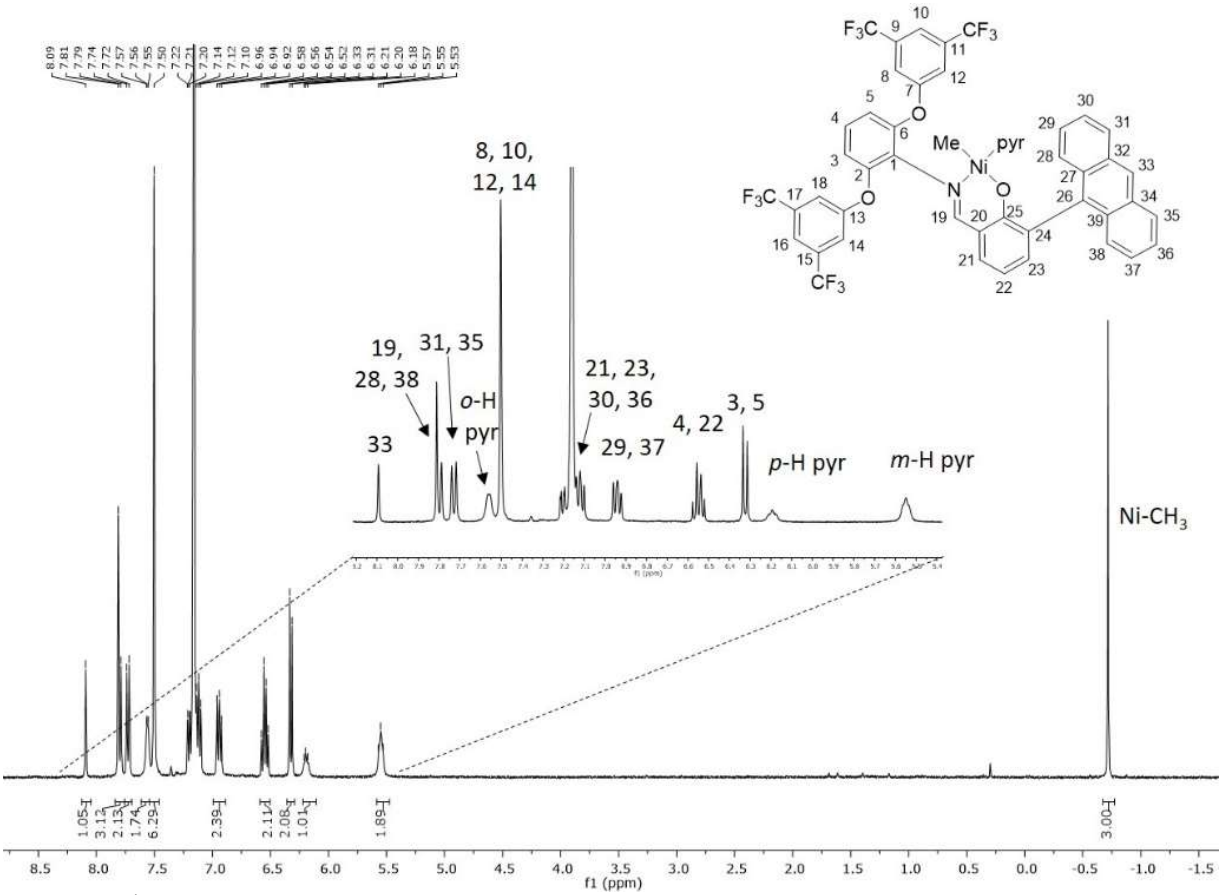


Figure S36: ^{1}H-NMR spectrum of **4-CF$_3$-ant** in C_6D_6 at 300 K.

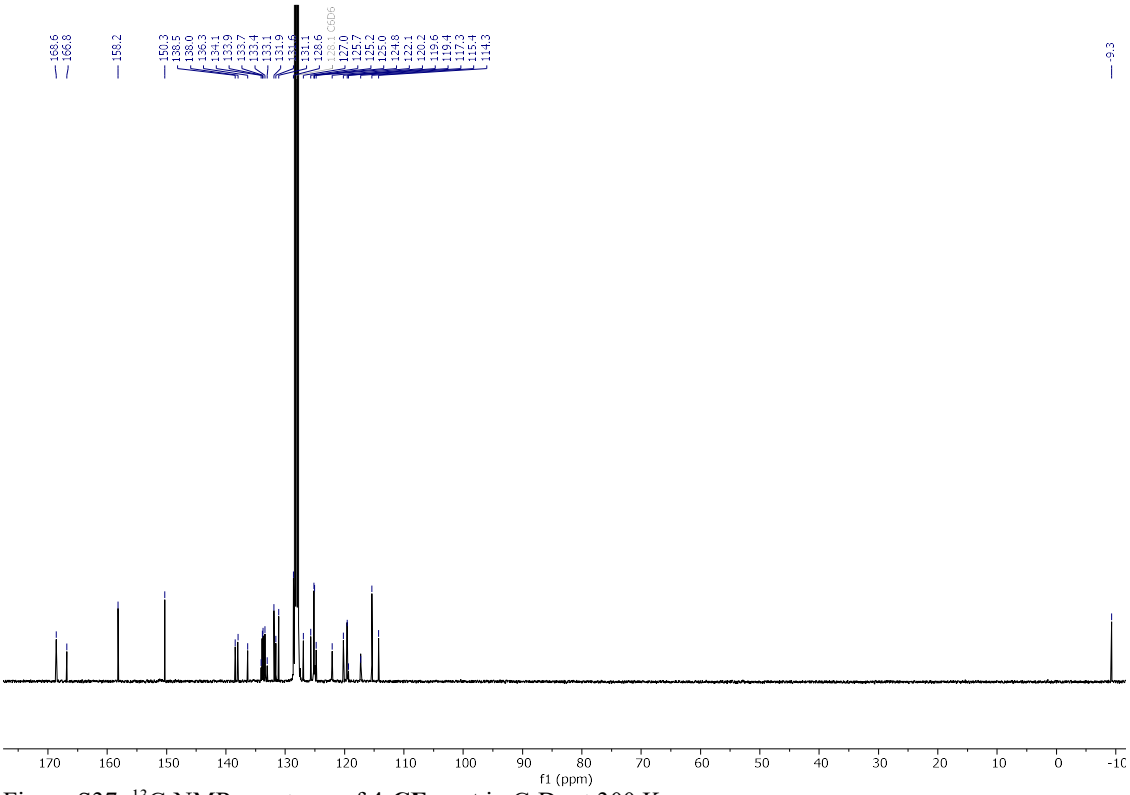


Figure S37: ^{13}C-NMR spectrum of **4-CF$_3$-ant** in C_6D_6 at 300 K.

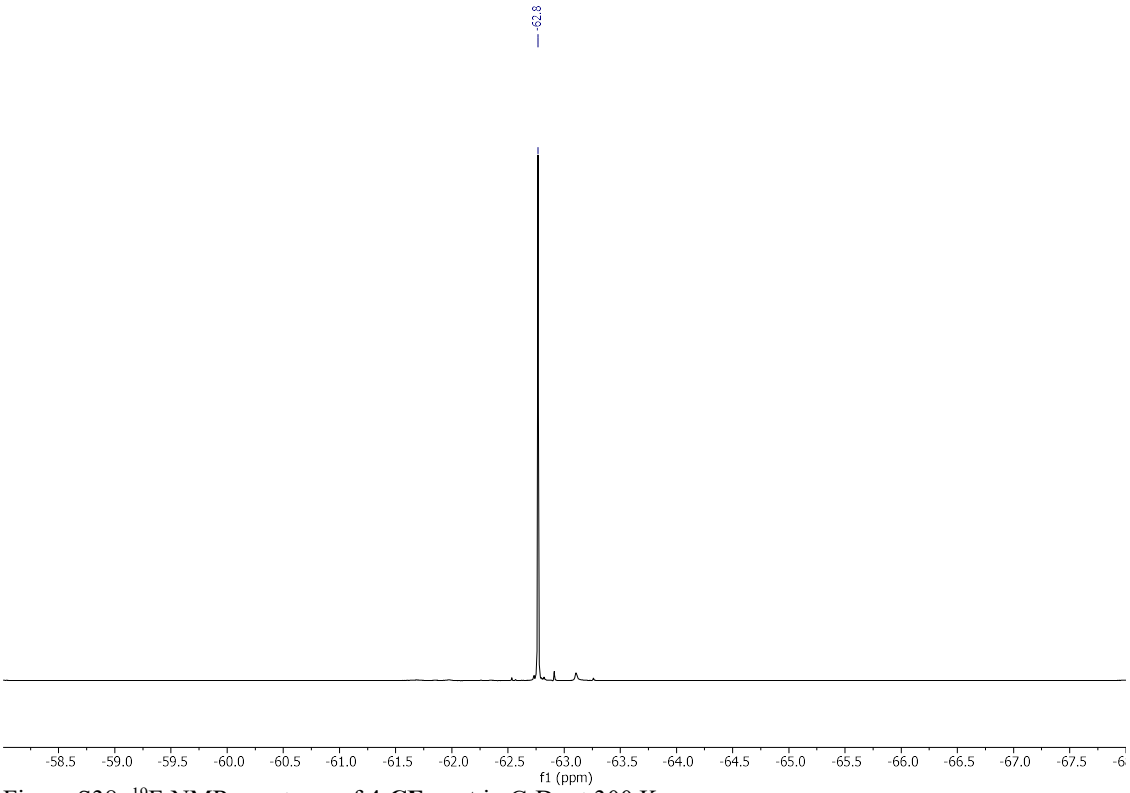


Figure S38: ^{19}F-NMR spectrum of **4-CF$_3$-ant** in C_6D_6 at 300 K.

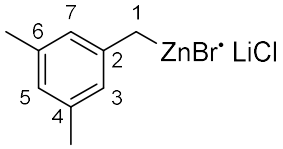
1.3 Synthesis of methylene bridged complexes

1.3.1 Synthesis of zincorganyles

General procedure for the preparation of the zincorganyles

Anhydrous LiCl (426 mg, 10 mmol, 1.0 equiv.) was placed in a Schlenk tube and dried to remove remaining traces of water. Zinc powder (919 mg, 14.0 mmol, 1.4 equiv.) was added and the mixture heated under vacuum. THF (10 mL) was added and the zinc was activated with 1,2-dibromethane (93 mg, 0.5 mmol, 5 mol%) and TMS-Cl (10.9 mg, 0.1 mmol, 1 mol%). The 3,5-substituted benzylbromide (10 mmol, 1.0 equiv.) was added at room temperature The reaction mixture was heated to 50 °C over night. The zincorganyl was separated from the zinc powder using a syringe filter and used as a solution in THF for the following reaction. The conversion was checked *via* ^{1}H-NMR analysis.

<u>3,5-Dimethyl-benzylzincbromide (**5-CH$_3$**):</u>



Following the general procedure for the preparation of the zincorganyles, 3,5-dimethyl-benzylzincbromide **5-CH$_3$** was obtained as a solution in THF with 91 % conversion.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 6.99 (s, 2H, 3- and 7-H), 6.48 (s, 1H, 5-H), 2.23 (s, 2H, 1-H), 2.20 (s, 6H, CH_3).

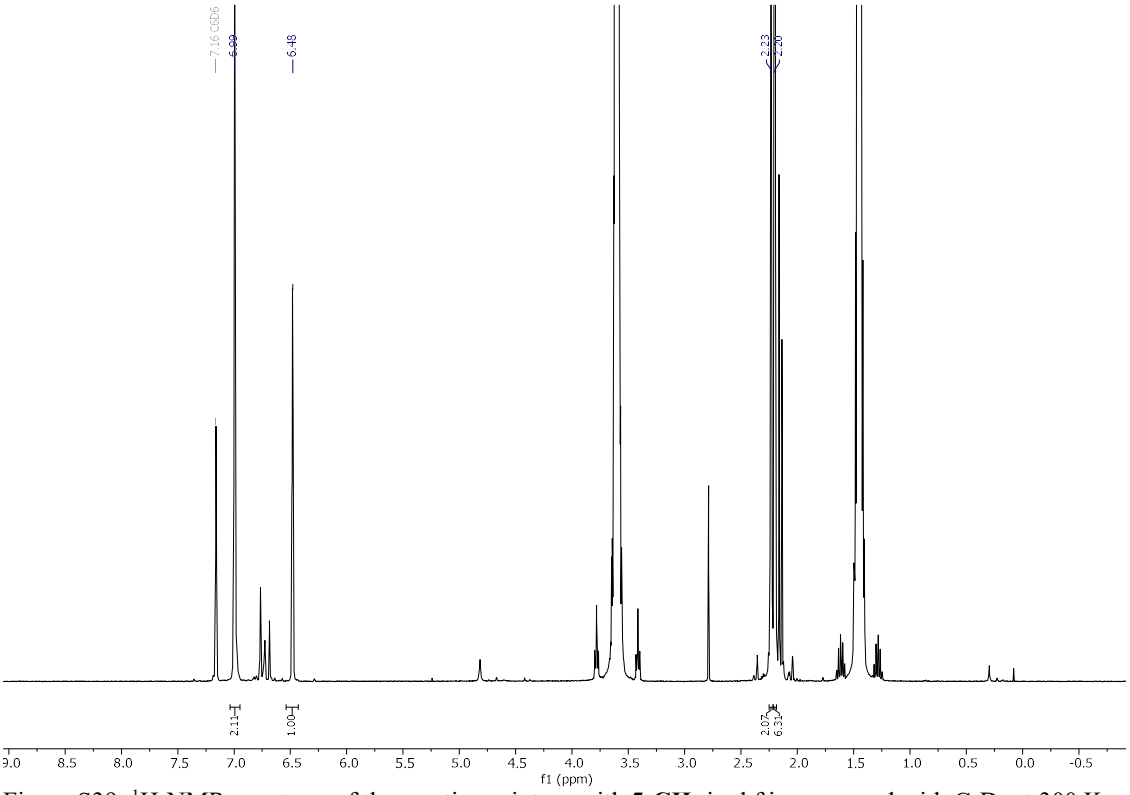
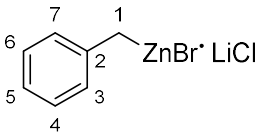


Figure S39: ^{1}H-NMR spectrum of the reaction mixture with **5-CH$_3$** in thf in measured with C_6D_6 at 300 K.

Benzylzincbromide (**5-H**):



Following the general procedure for the preparation of the zincorganyles, benzyl zincbromide **5-H** was obtained as a solution in THF with 97 % conversion.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 7.44 – 7.24 (m, 2H, 3- and 7-H or 4- and 6-H), 7.16 – 6.94 (m, 2H, 3- and 7-H or 4- and 6-H), 6.93 – 6.78 (m, 1H, 5-H), 2.33 – 2.17 (m, 2H, 1-H).

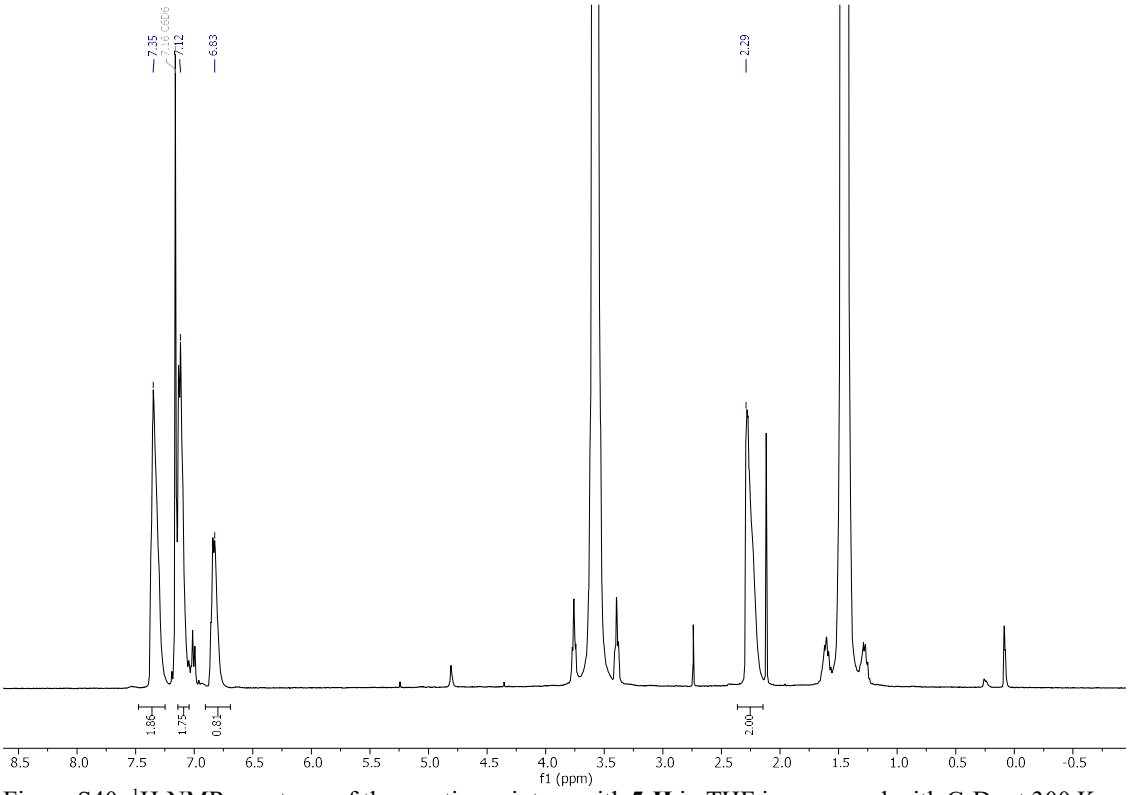
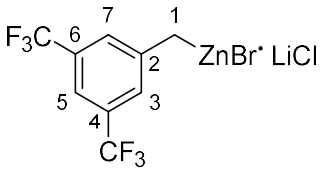


Figure S40: ^{1}H-NMR spectrum of the reaction mixture with **5-H** in THF in measured with C_6D_6 at 300 K.

3,5-Bis(trifluoromethyl)-benzylzincbromide (**5-CF$_3$**):



Following the general procedure for the preparation of the zincorganyles, 3,5-di-CF_3-benzylzincbromide **5-CF$_3$** was obtained as a solution in THF with 90 % conversion.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 7.68 (s, 2H, 3- and 7-H), 7.38 (s, 1H, 5-H), 2.25 (s, 2H, 1-H).

^{19}F-NMR (376 MHz, C_6D_6, 300 K): δ (ppm) = -62.6 (s, CF_3).

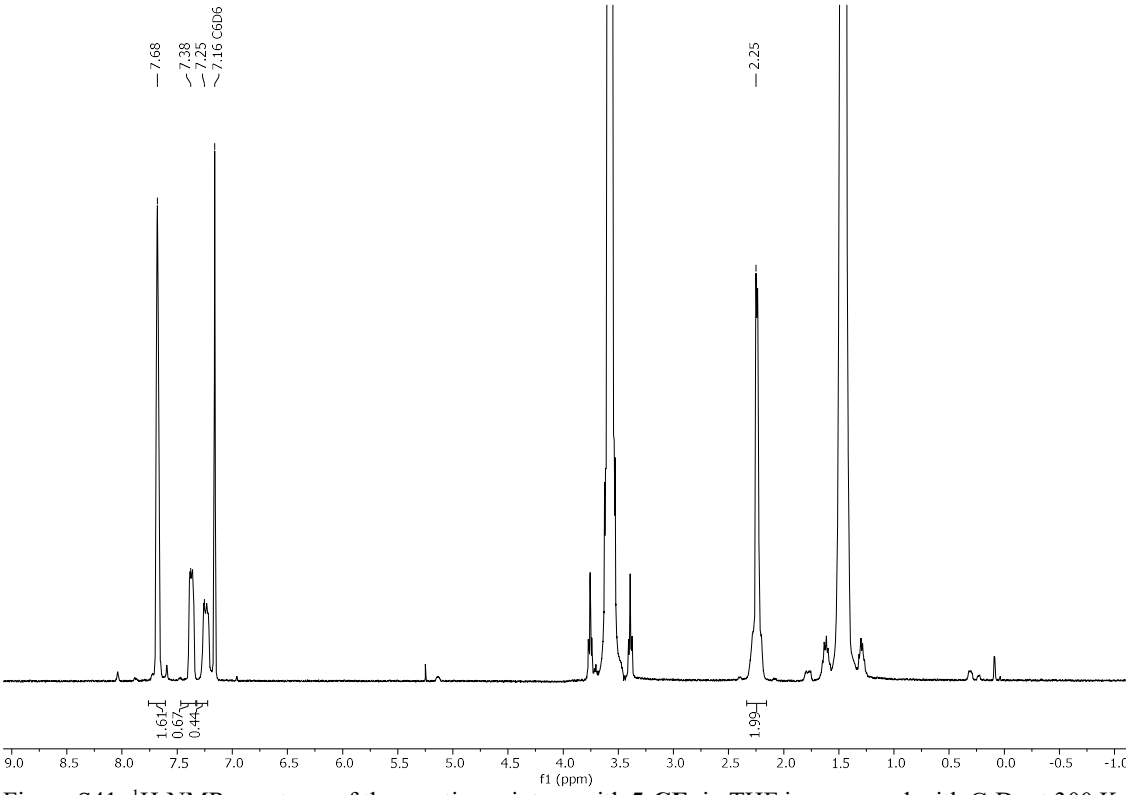


Figure S41: ^{1}H-NMR spectrum of the reaction mixture with **5-CF$_3$** in THF in measured with C_6D_6 at 300 K.

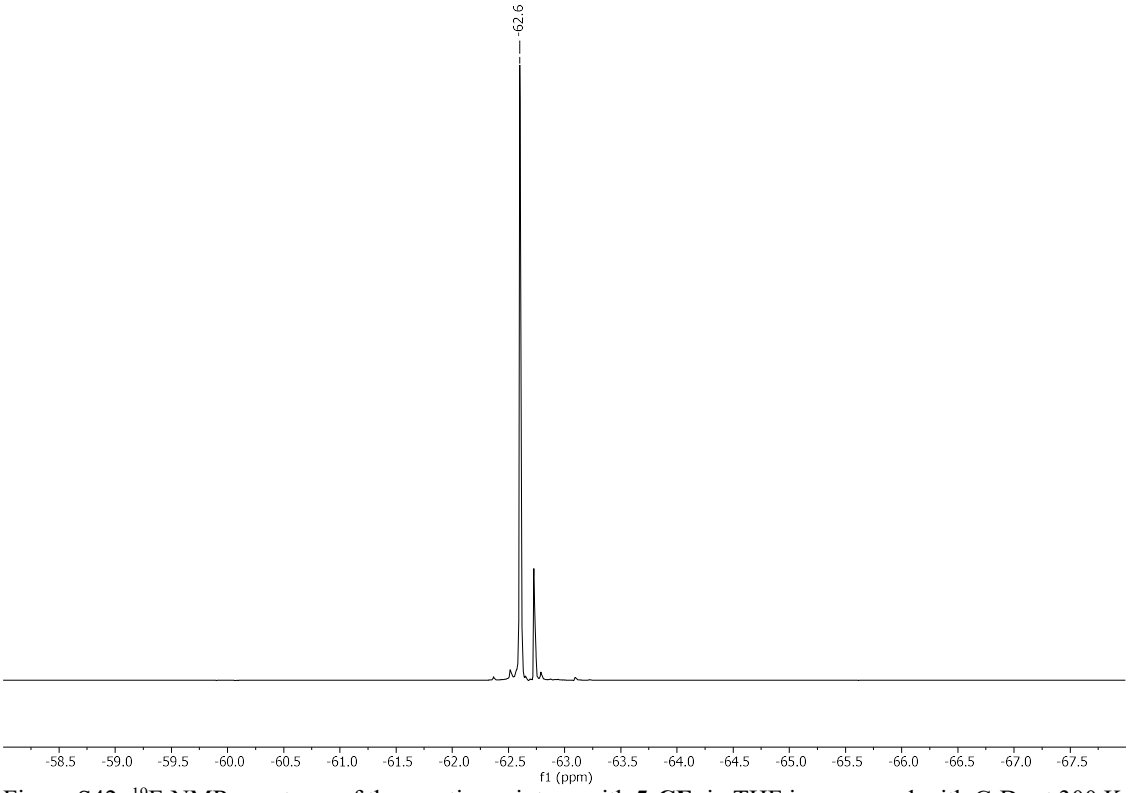


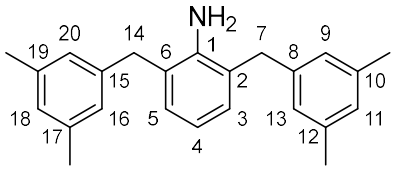
Figure S42: ^{19}F-NMR spectrum of the reaction mixture with **5-CF$_3$** in THF in measured with C_6D_6 at 300 K.

1.3.2 Synthesis of 2,6-dibenzylanilines

General procedure for the preparation of the dibenzyl anilines

2,6-Dibromoaniline (3.8 mmol, 1.0 equiv.), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 76 µmol, 2 mol%) and $Pd(OAc)_2$ (38 µmol, 1 mol%) were placed in a Schlenk tube and degassed. THF (5 mL) was added and the solution stirred until it turned red. The zincorganyl (9.2 mmol, 2.4 equiv.) was added dropwise as a solution in THF. The reaction mixture was stirred at r.t for 2 h. The reaction was quenched with a saturated aq. NH_4Cl solution and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with aq. thiourea solution and dried over Na_2SO_4. The dibenzyl anilines were obtained as white solids after removing the solvents and flash column chromatography.

2,6-Bis(3,5-dimethylbenzylaniline) **6-CH$_3$**:



Following the general procedure for the preparation of the dibenzyl anilines, 2,6-bis(3,5-dimethylbenzyl aniline **6-CH$_3$** (709 mg, 2.16 mmol, 63 %) was obtained after column chromatography (EtOAc : PE = 1 : 10).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.02 (d, $^3J_{HH}$ = 7.5 Hz, 2H, 3- and 5-H), 6.84 (s, 2H, 11- and 18-H), 6.79 (s, 4H, 9-, 13-, 16- and 20-H), 6.77 (t, $^3J_{HH}$ = 7.5 Hz, 1H, 4-H), 3.84 (s, 4H, 7- and 14-H), 3.46 (s, br, 2H, NH_2) 2.26 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.3 (C1), 139.5 (C2 and C6), 138.3 (C10, C12, C17 and C19), 129.6 (C3 and C5), 128.2 (C11 and C18), 126.4 (C8 and C15), 125.5 (C9, C13, C16 and C20), 118.2 (C4), 38.3 (C7 and C14), 21.4 (CH_3).

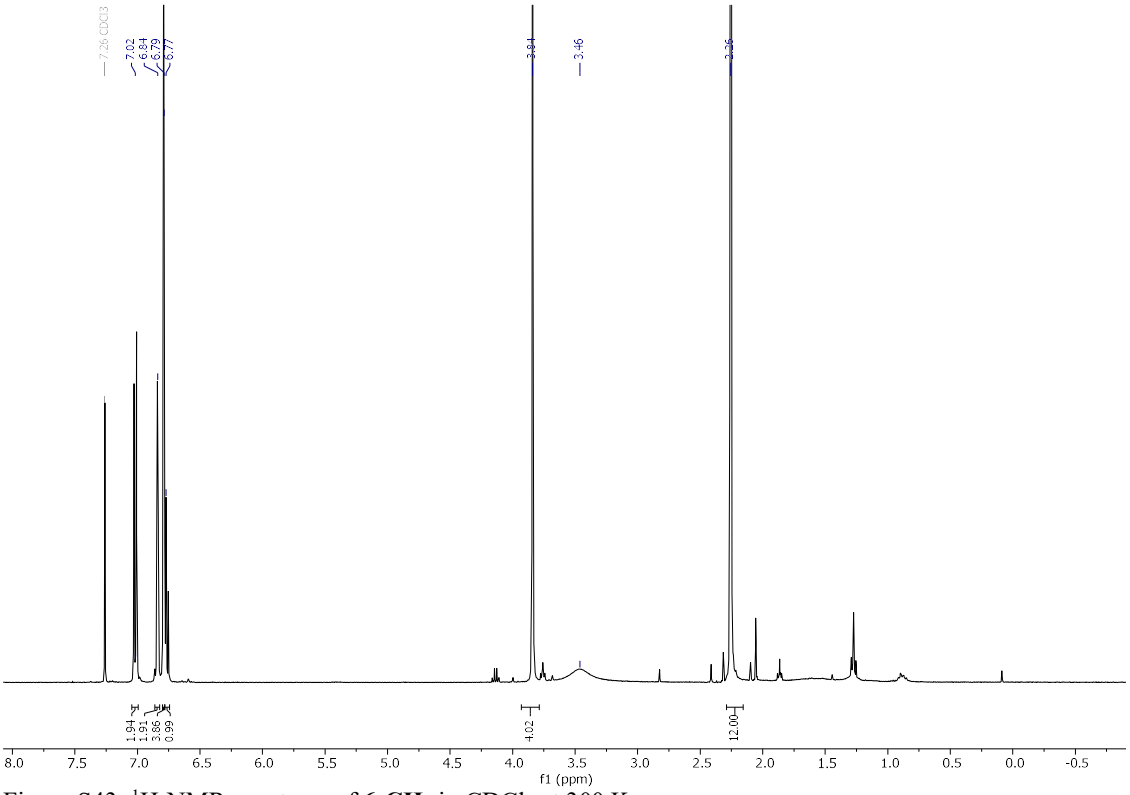


Figure S43: ^{1}H-NMR spectrum of **6-CH$_3$** in $CDCl_3$ at 300 K.

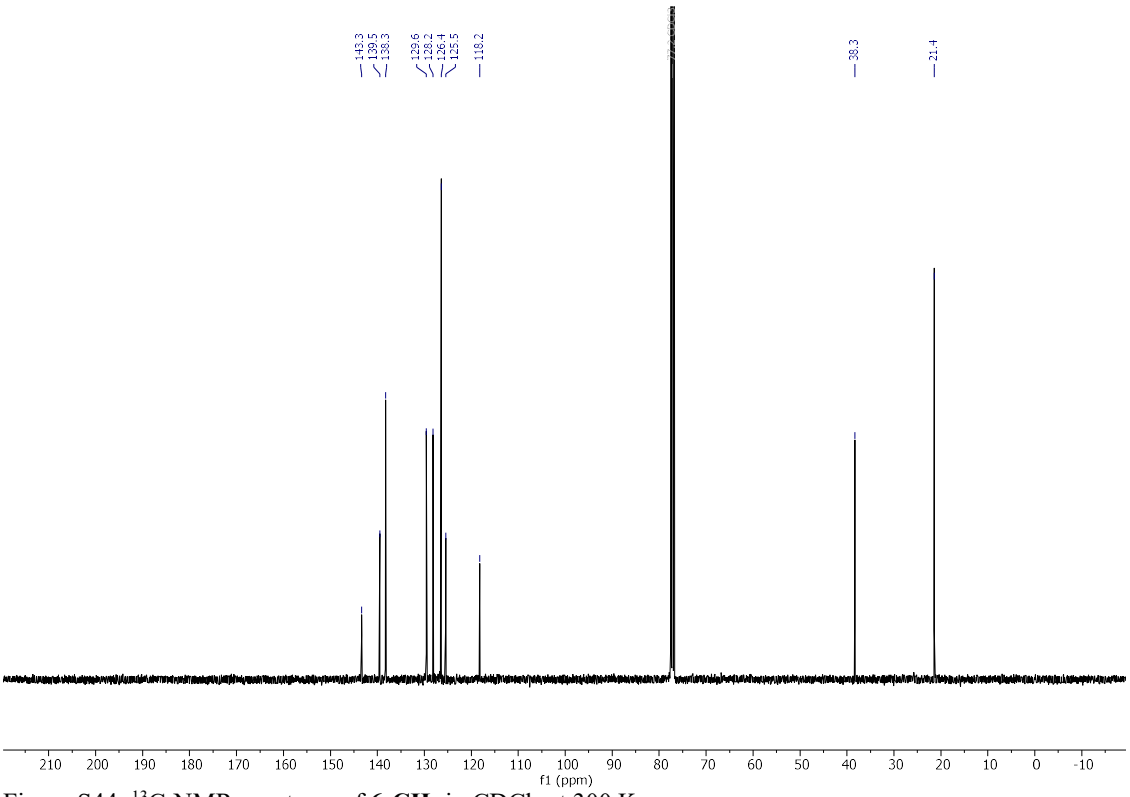
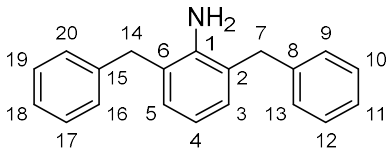


Figure S44: ^{13}C-NMR spectrum of **6-CH$_3$** in $CDCl_3$ at 300 K.

2,6-Dibenzyl aniline (**6-H**):



Following the general procedure for the preparation of the dibenzyl anilines, 2,6-dibenzyl aniline **6-H** (425 mg, 1.65 mmol, 65 %) was obtained after column chromatography (EtOAc : PE = 2 : 10).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 – 7.12 (m, 10 H, 9-, 10-, 11-, 12-, 13- 16-, 17-, 18-19-, and 20-H), 7.01 (d, $^3J_{HH}$ = 7.5 Hz, 2H, 3- and 5-H), 6.76 (t, $^3J_{HH}$ = 7.5 Hz, 1H, 4-H), 3.91 (s, 4H, 7- and 14-H), 3.45 (s, 2H, NH_2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.1 (C1), 139.5 (C2 and C6), 129.6 (C3 and C5), 128.8 (C9, C13, C16 and C20) 128.1 (C10, C12, C17 and C19), 126.5 (C8 and C15), 125.3 (C11 and C18) 118.3 (C4), 38.4 (C7 and C14).

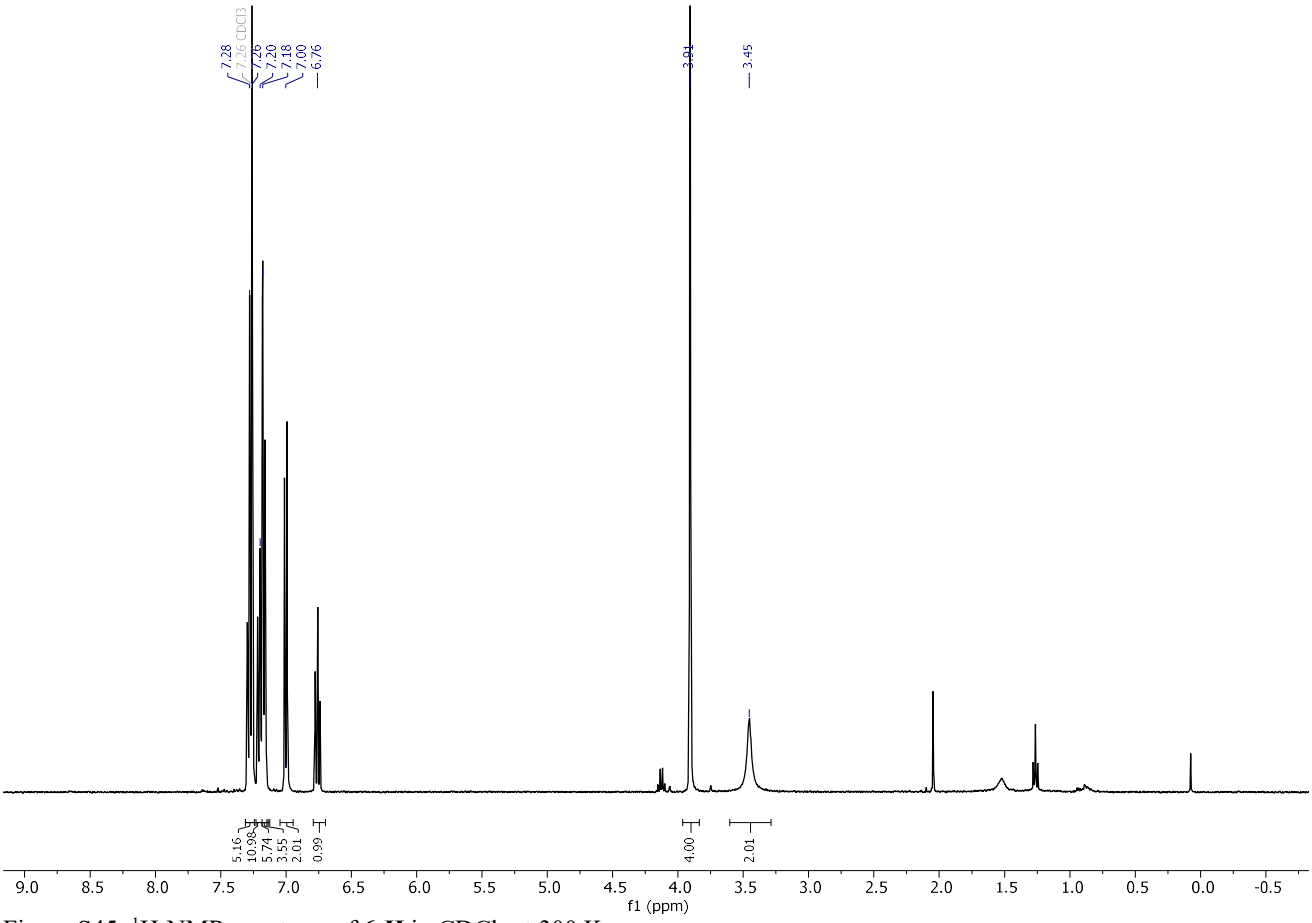


Figure S45: ^{1}H-NMR spectrum of **6-H** in $CDCl_3$ at 300 K.

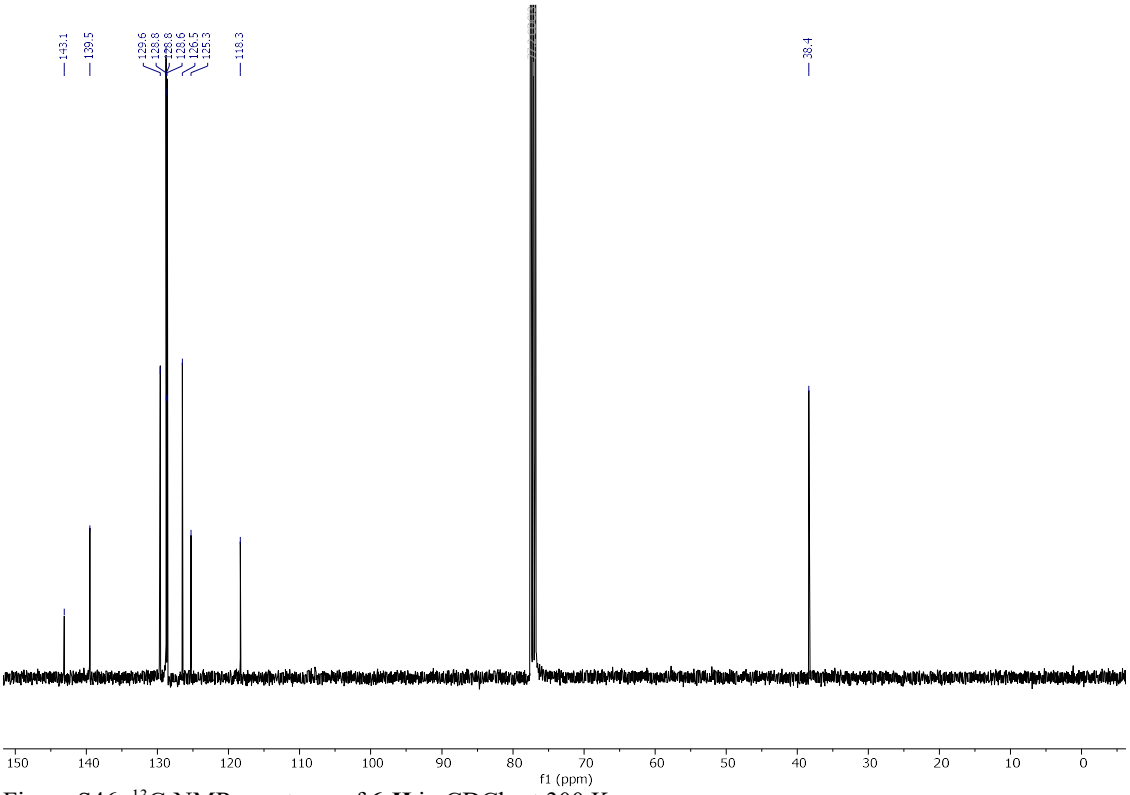
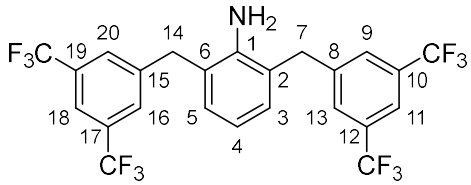


Figure S46: ^{13}C-NMR spectrum of **6-H** in $CDCl_3$ at 300 K.

2,6-Bis(3,5-bis(trifluoromethyl)benzyl)aniline (**6-CF$_3$**):



Following the general procedure for the preparation of the dibenzyl anilines, 2,6-bis(3,5-bis(trifluoromethyl)benzyl)aniline **6-CF$_3$** (852 mg, 1.56 mmol, 41 %) was obtained after column chromatography (EtOAc : PE = 1 : 12.5).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 7.74 (s, 2H, 11- and 18-H), 7.61 (s, 4H, 9-, 13-, 16- and 20-H), 7.01 (d, $^3J_{HH}$ = 7.5 Hz, 2H, 3- and 5-H), 6.84 (t, $^3J_{HH}$ = 7.5 Hz, 1H, 4-H), 4.03 (s, 4H, 7- and 14-H), 3.40 (s, 2H, NH_2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5 (C1), 142.0 (C2 and C6), 132.2 (q, $^2J_{CF}$ = 33.2 Hz, C10, C12, C17 and C19), 130.4 (C3 and C5), 128.7 (C9, C13, C16 and C20), 123.4 (q, $^1J_{CF}$ = 272.8 Hz), 123.4 (C8 and C15), 121.2 – 120.6 (m, C11 and C18), 119.3 (C4), 37.8 (C7 and C14).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.0 (s, CF_3).

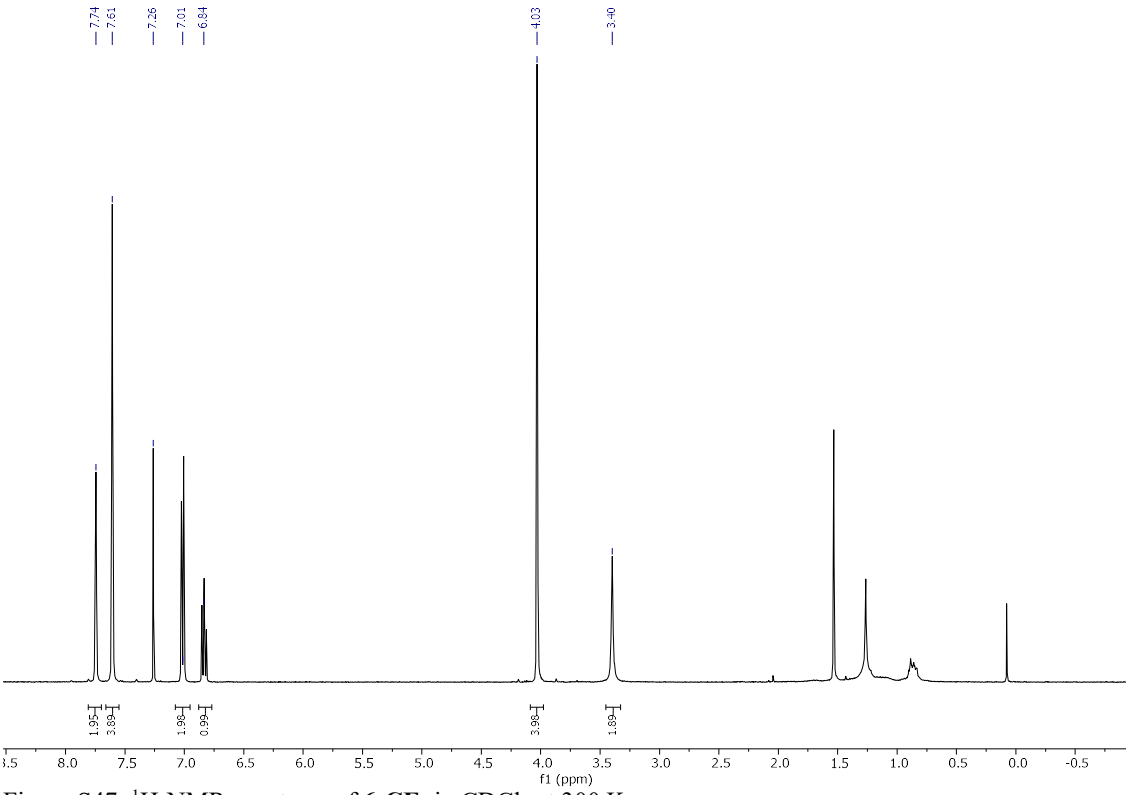


Figure S47: ^{1}H-NMR spectrum of **6-CF$_3$** in $CDCl_3$ at 300 K.

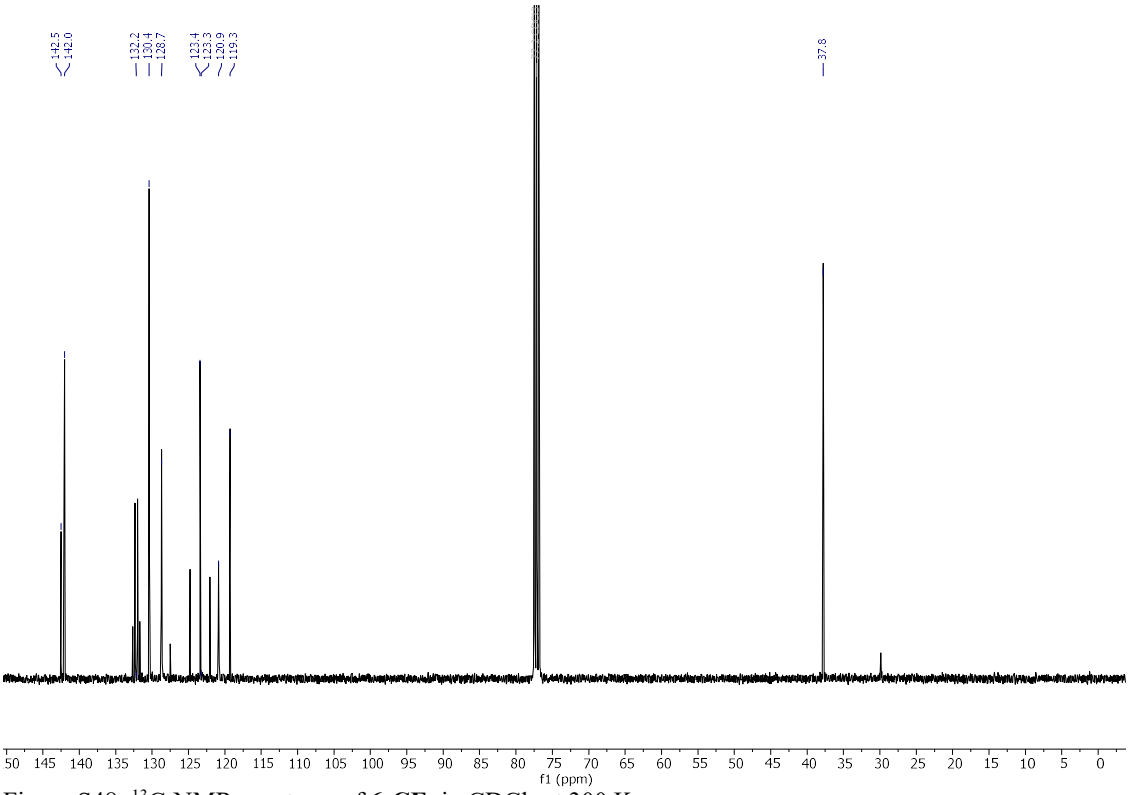


Figure S48: ^{13}C-NMR spectrum of **6-CF$_3$** in $CDCl_3$ at 300 K.

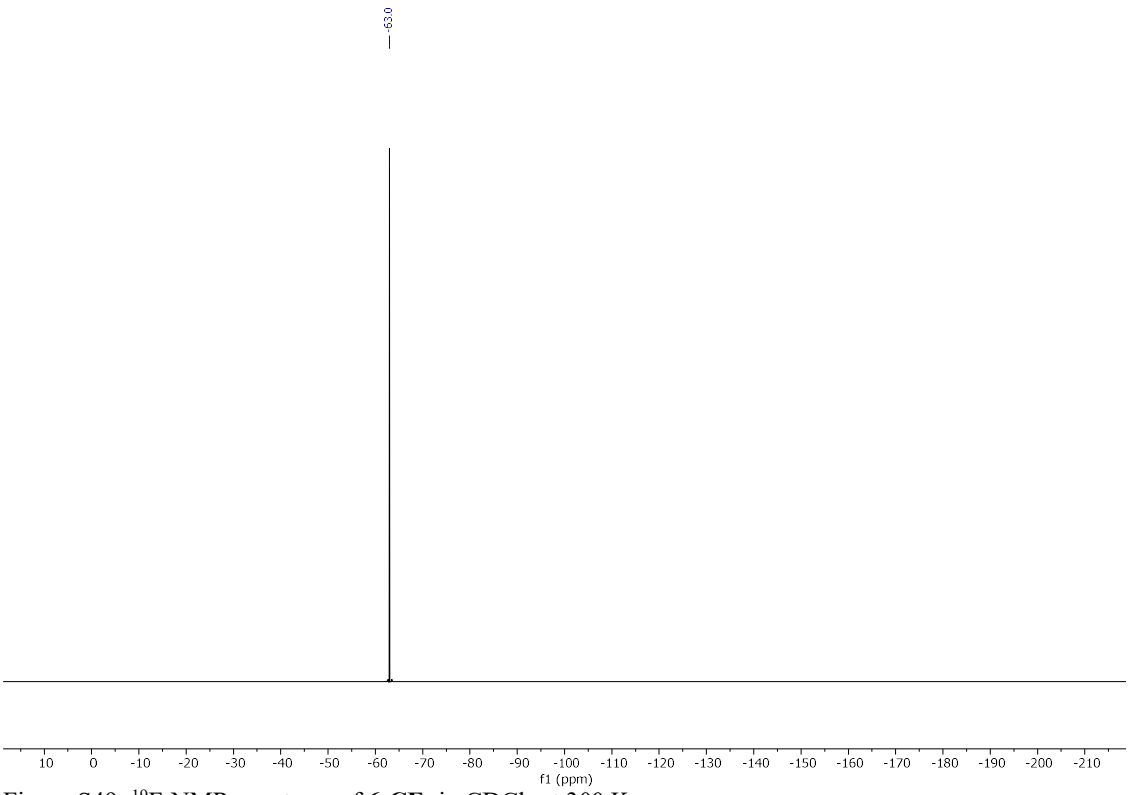


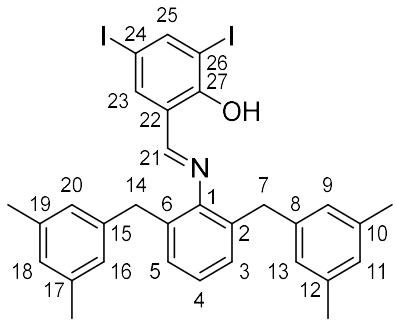
Figure S49: ^{19}F-NMR spectrum of **6-CF$_3$** in $CDCl_3$ at 300 K.

1.3.3 Synthesis of salicylaldimines

General procedure for the preparation of salicylaldimines

2,6-Dibenzyl aniline and the salicylaldehyde (3,5-diiodosalicylaldehyde or 2-hydroxy-3-(9-anthryl)benzaldehyde*1/2 DCM) were dissolved in 5 – 20 mL of toluene. PTSA monohydrate (5.0 mg) was added. The reaction mixture was stirred at 50 °C overnight. The solvent was removed. The product was obtained as yellow solid after washing with methanol or purification with column chromatography.

Salicylaldimine **7-CH$_3$-I2**:



Following the general procedure, salicylaldimines **7-CH$_3$-I2** (311 mg, 0.45 mmol, 75 %) was obtained from 3,5-diiodosalicylaldehyde (238 mg, 0.64 mmol, 1.05 equiv.) and 2,6-bis(3,5-dimethylbenzyl aniline **7-CH$_3$** (200 mg, 0.61 mmol, 1.0 equiv.) after washing with MeOH (3 x 10 mL).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.88 (s, 1H, OH···N), 8.10 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, 25-H), 7.25 – 7.14 (m, 3H, 3-, 4- and 5-H), 7.06 (s, 1H, 21-H), 6.91 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, 23-H), 6.76 (s, 2H, 11- and 18-H), 6.59 (s, 4H, 9-, 13-, 16- and 20-H), 3.72 (s, 4H, 7- and 14-H), 2.14 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8 (C21), 160.1 (C27), 149.1 (C25), 147.6 (C1), 140.7 (C2, C6 and C23,), 138.1 (C10, C12, C17 and C19), 132.1 (C8 and C15), 129.4 (C3 and C5), 127.9 (C11 and C18), 126.9 (C9, C13, C16 and C20), 125.6 (C4), 120.1 (C22), 87.1 (C24), 79.7 (C26), 38.6 (C7 and C14), 21.3 (CH_3).

Anal. Calcd. for $C_{31}H_{29}I_2F_{12}NO$ (685.39 g mol^{-1}): C, 54.33; H, 4.27; N, 2.04. Found: C, 54.16; H, 4.38; N, 2.19.

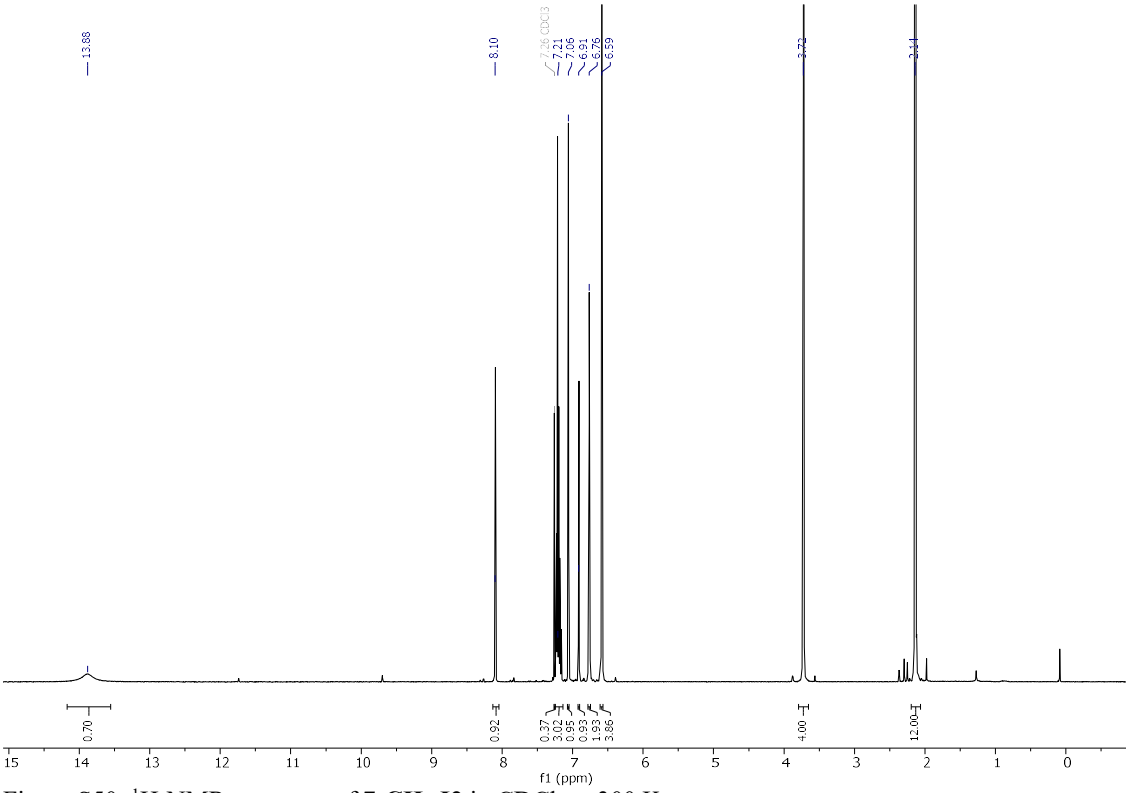


Figure S50: ^{1}H-NMR spectrum of **7-CH$_3$–I2** in $CDCl_3$ at 300 K.

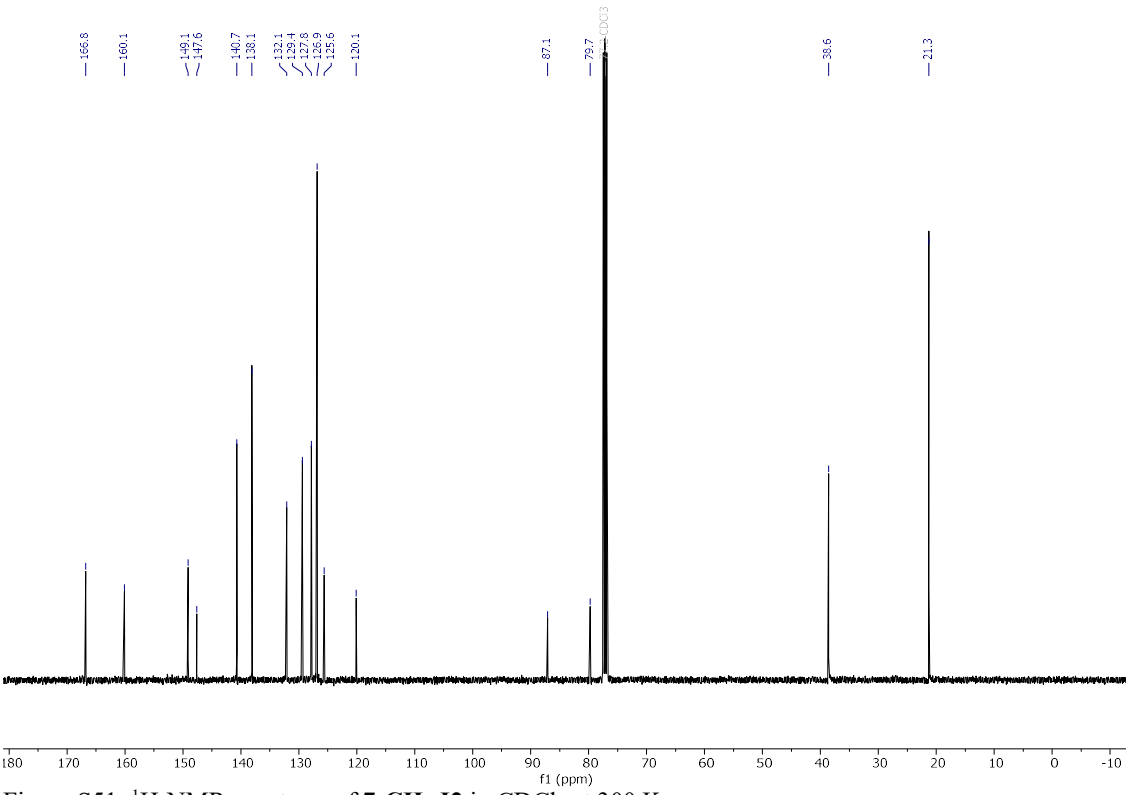
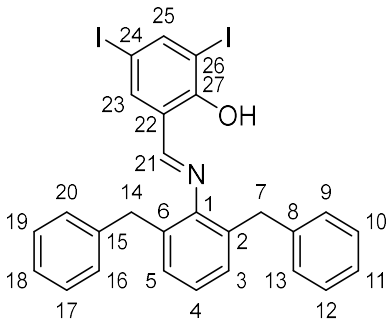


Figure S51: ^{1}H-NMR spectrum of **7-CH$_3$-I2** in $CDCl_3$ at 300 K.

Salicylaldimine **7-H-I2**:



Following the general procedure, salicylaldimine **7-H-I2** (223 mg, 0.35 mmol, 65 %) was obtained from 3,5-diiodosalicylaldehyde (215 mg, 0.58 mmol, 1.05 equiv.) and 2,6-dibenzyl aniline **6-H** (150 mg, 0.55 mmol, 1.0 equiv.) after column chromatography (EtOAc : PE = 1 : 10).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.81 (s, br, 1H, OH···N), 8.08 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, 25-H), 7.26 (21-H), 7.22 – 7.10 (m, 10H, 9-, 10-, 11-, 12-, 13-, 16-, 17-, 18-, 19- and 20-H), 7.03 – 6.97 (m, 4H, 3-, 4- and 5-H), 6.96 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, 23-H), 3.83 (s, 4H-, 7- and 14-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.3 (C21), 160.1 (C27), 149.3 (C25), 147.5 (C1), 140.7 (C2 and C6), 131.8 (C8 and C15), 129.5 and 128.9 and 126.3 (C9, C10, C11, C12 C23, C13, C16, C17, C18, C19 and C20), 128.6 (C3 and C5), 125.8 (C4), 120.0 (C22), 87.1 (C24), 79.8 (C26), 38.4 (C7 and C14).

Anal. Calcd. for $C_{27}H_{21}I_2NO$ (629.28 g mol^{-1}): C, 51.53; H, 3.36; N, 2.23. Found: C, 51.88; H, 3.58; N, 2.31.

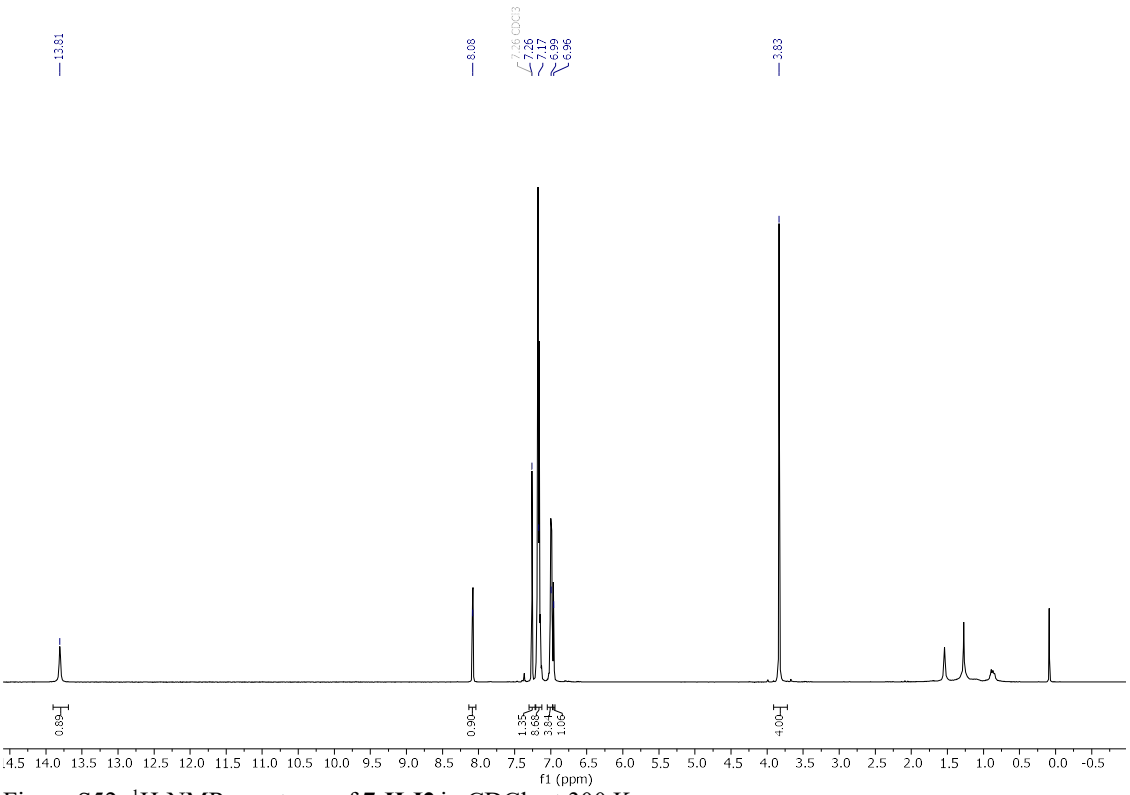


Figure S52: ^{1}H-NMR spectrum of **7-H-I2** in $CDCl_3$ at 300 K.

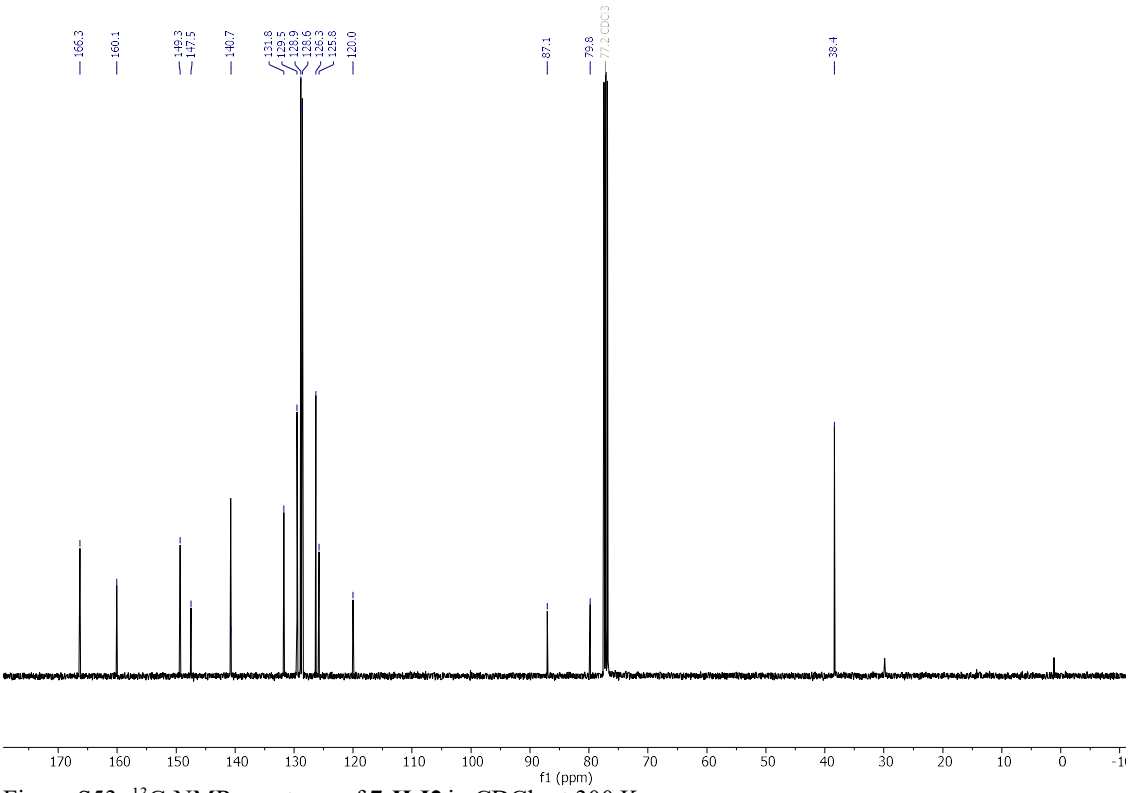
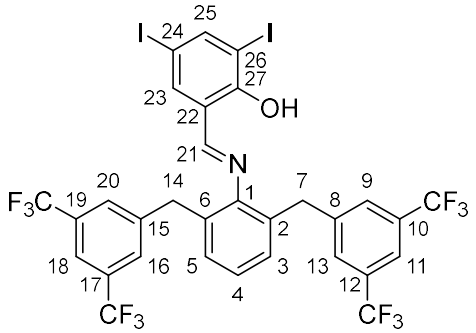


Figure S53: ^{13}C-NMR spectrum of **7-H-I2** in $CDCl_3$ at 300 K.

Salicylaldimine **7-CF$_3$-I2**:



Following the general procedure, salicylaldimine **7-CF$_3$-I2** (214 mg, 0.24 mmol, 53 %) was obtained from 3,5-diiodosalicylaldehyde (180 mg, 0.48 mmol, 1.05 equiv.) and 2,6-bis(3,5-bis(trifluoromethyl)benzyl)aniline **6-CF$_3$** (250 mg, 0.45 mmol, 1.0 equiv.) after washing with MeOH.

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.17 (s, 1H, OH···N), 8.16 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 25-H), 7.70 (s, 2H, 11- and 18-H), 7.52 (s, 1H, 21-H), 7.48 (s, 4H, 9-, 13-, 16 and 20-H), 7.35 – 7.19 (m, 3H, 3-, 4- and 5-H), 7.14 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 23-H), 3.99 (s, 4H, 7- and 14-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.5 (C21), 159.8 (C27), 150.5 (C25), 147.6 (C1), 142.6 (C2 and C6), 140.5 (C23), 132.1 (q, $^2J_{CF}$ = 33.3 Hz, C10, C12, C17 and C19), 130.2 (C3 and C5 or C8 and C15), 130.1 (C3 and C5 or C8 and C15), 128.9 (C9, C13, C16 and C20), 126.8 (C4), 123.3 (q, $^1J_{CF}$ = 272.8 Hz, CF_3), 121.1 – 120.5 (m, C11 and C18), 119.2 (C22), 87.3 (C24), 80.5 (C26), 38.1 (C7 and C14).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = -63.0 (s, CF_3).

Anal. Calcd. for $C_{31}H_{17}F_{12}I_2NO$ (901.27 g mol^{-1}): C, 41.31; H, 1.90; N, 1.55. Found: C, 41.45; H, 2.33; N, 1.80.

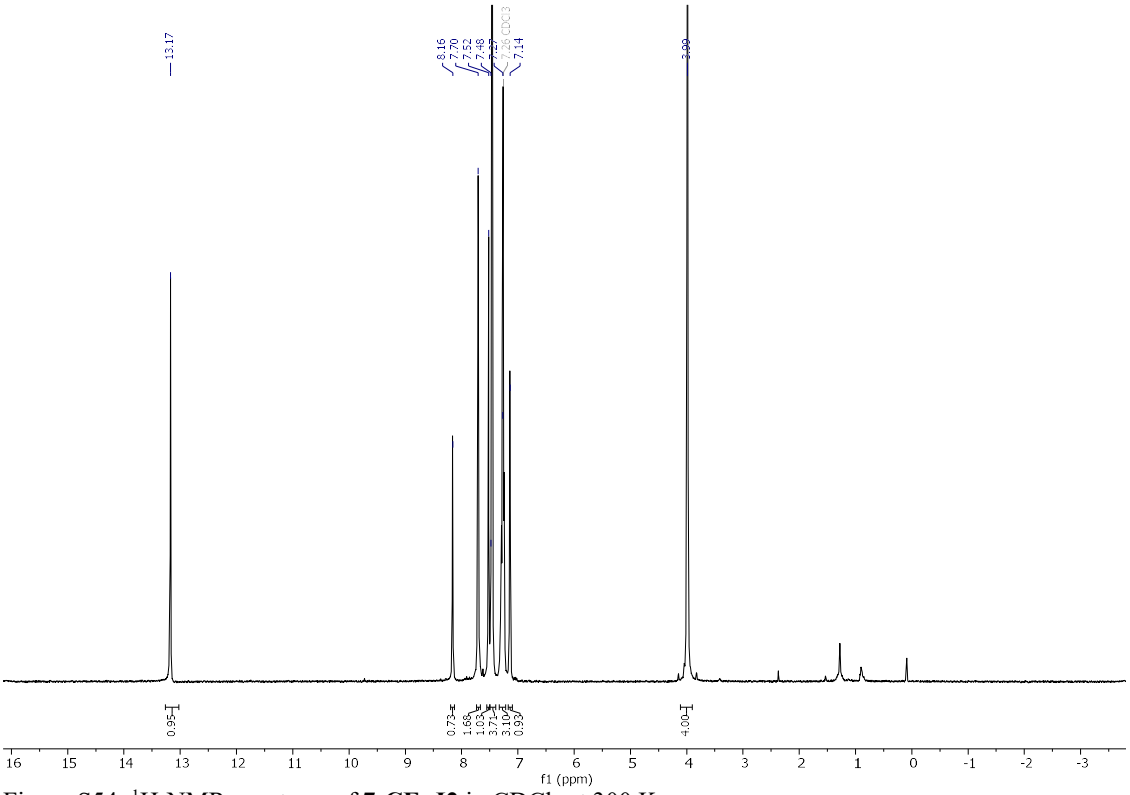


Figure S54: ^{1}H-NMR spectrum of **7-CF$_3$-I2** in $CDCl_3$ at 300 K.

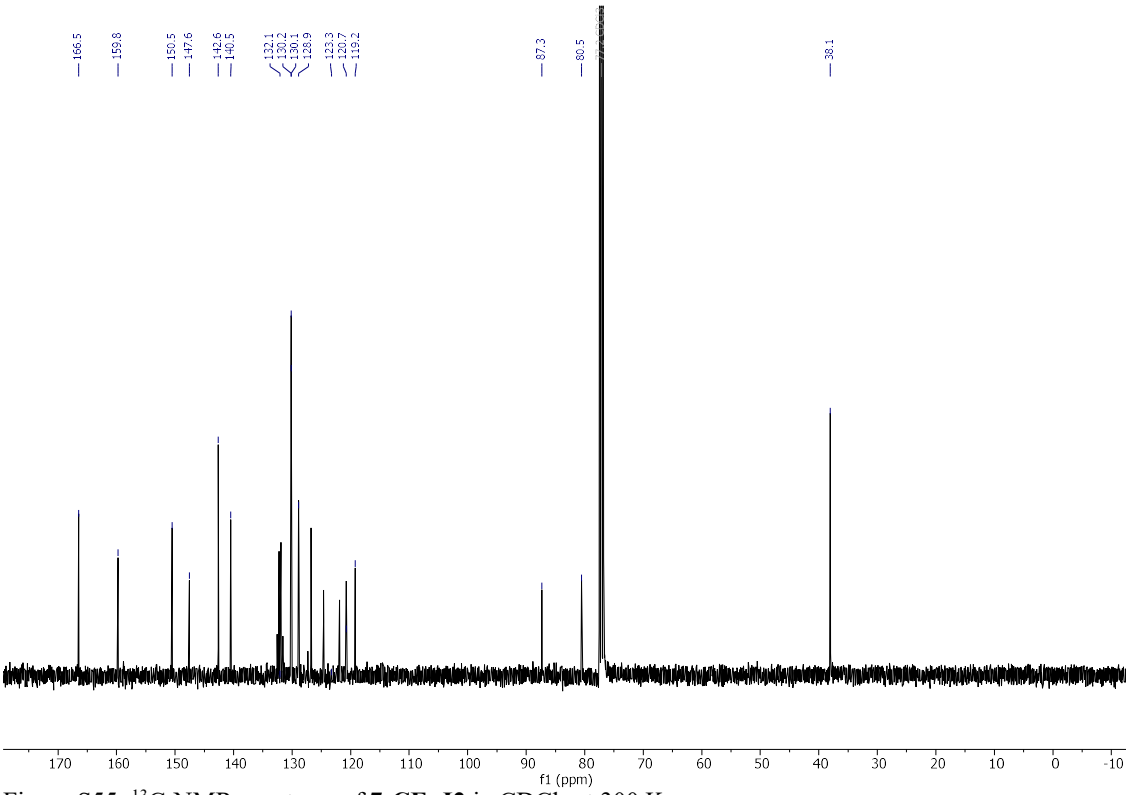


Figure S55: ^{13}C-NMR spectrum of **7-CF$_3$-I2** in $CDCl_3$ at 300 K.

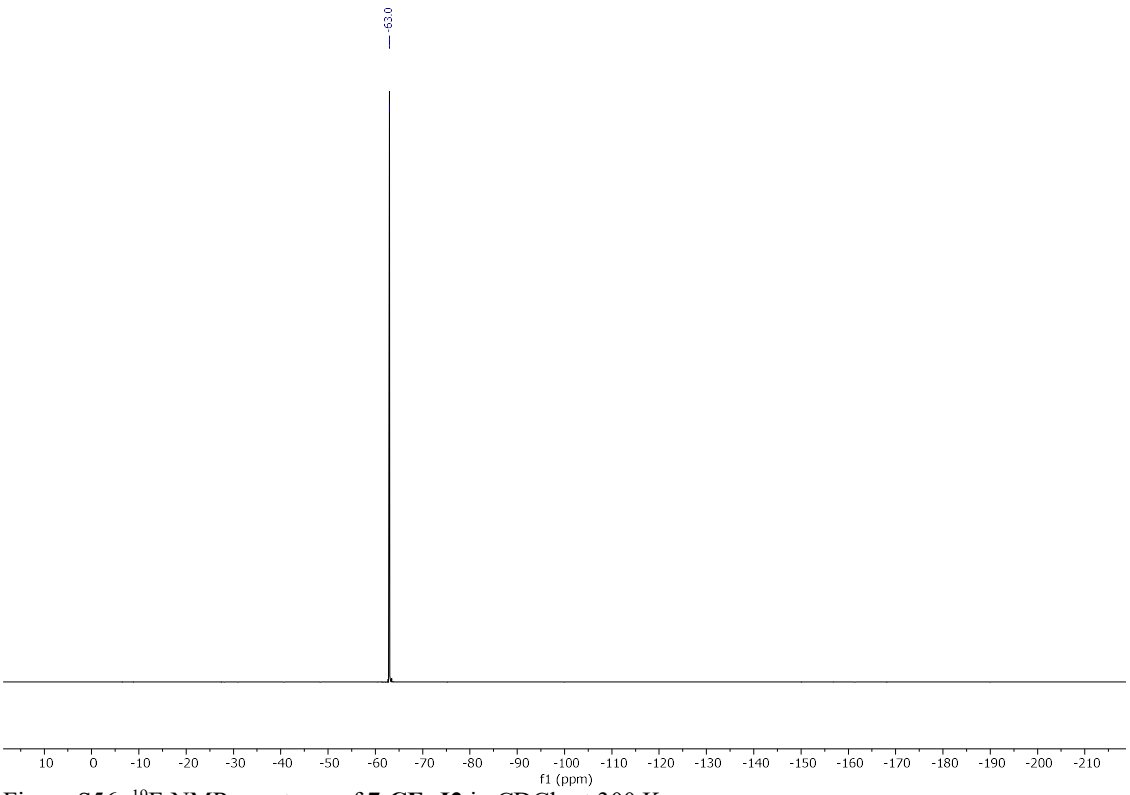
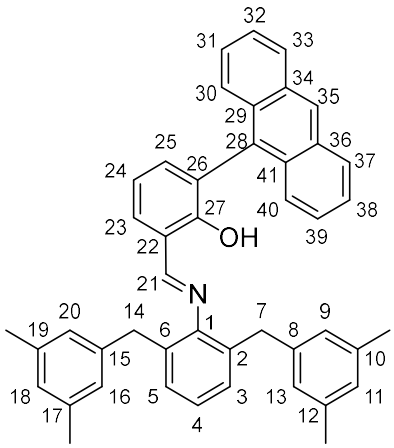


Figure S56: ^{19}F-NMR spectrum of **7-CF$_3$-I2** in $CDCl_3$ at 300 K.

Salicylaldimine **7-CH$_3$-ant**:



Following the general procedure, salicylaldimine **7-CH$_3$-ant** (252 mg, 0.41 mmol, 53 %) was obtained from 2-hydroxy-3-(9-anthryl)benzaldehyde · $^1/_2$ DCM (258 mg, 0.76 mmol, 1.0 equiv.) and 2,6-bis(3,5-dimethylbenzylaniline **7-CH$_3$** (300 mg, 0.90 mmol, 1.2 equiv.) after column chromatography (toluene).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.03 (s, 1H, OH···N), 8.50 (s, 1H, 35-H), 8.03 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 30- and 40-H), 7.76 (d, $^3J_{HH}$ = 8.6 Hz, 2H, 33- and 37-H), 7.61 (s, 1H, 21-H), 7.49 – 7.29 (m, 5H, 25- 30-, 31-, 38- and 39-H), 7.18 – 6.93 (m, 5H, 3-, 4-, 5-, 23- and 24-H), 6.72 (s, 2H, 11- and 18-H), 6.66 (s, 4H, 9-, 13-, 16- and 20-H), 3.73 (s, 4H, 7- and 14-H), 2.10 (s, 12H, CH_3).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.7 (C21), 159.5 (C27), 148.6 (C1), 140.9 (C2 and C6), 137.8 (C10, C12, C17 and C19), 136.5 (C25), 132.6 (C23), 132.3 (C4), 132.1 (C8 and C15), 131.7 and 130.6 (C29, C22, C26 and C41), 129.0 (C28), 128.7 (C30 and C40), 128.4 (C34 and C36), 127.7 (C11 and C18), 127.2 (C35), 127.0 (C9, C13, C16 and C20), 126.9 (C9, C13, C16 and C20), 126.7 (C33

and C37), 125.6 and 125.2 (C31, C38 and C39), 125.0 (C3 and C5), 118.9 and 118.8 (C24), 38.4 (C7 and C14), 21.3 (CH_3).

Anal. Calcd. for $C_{45}H_{39}NO$ (609.30 g mol^{-1}): C, 88.63; H, 6.45; N, 2.30. Found: C, 88.53; H, 6.38; N, 2.32.

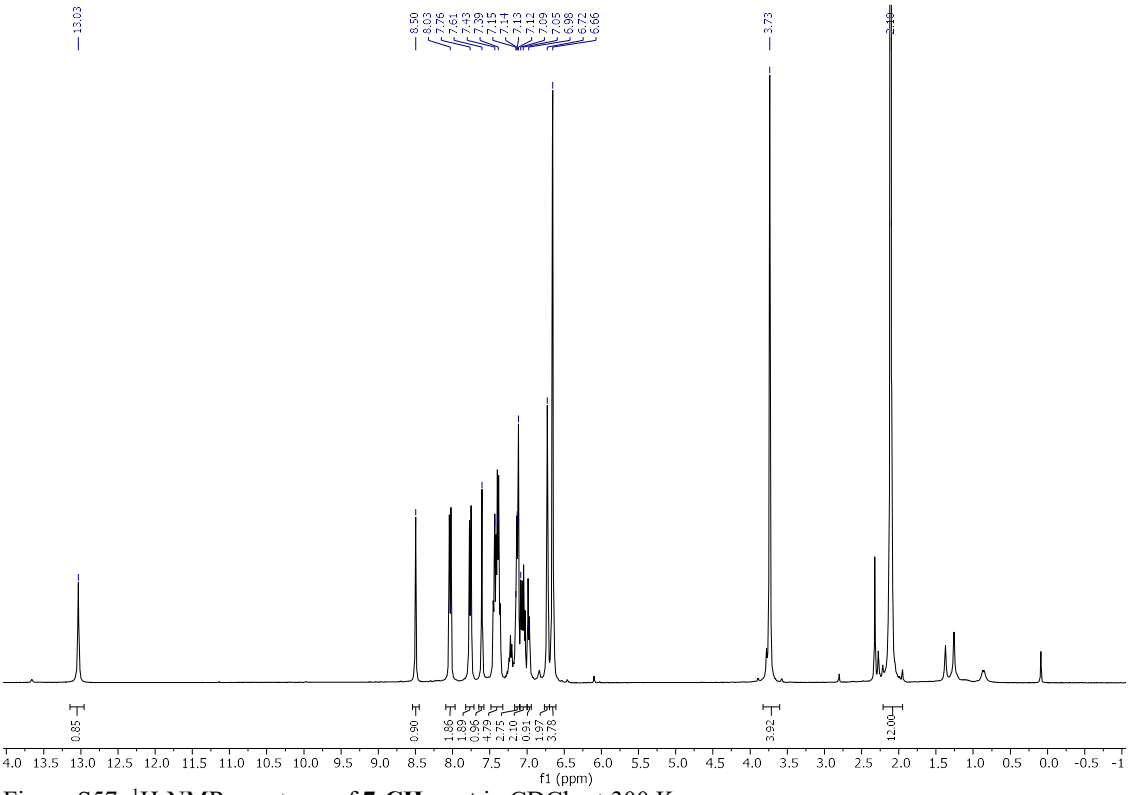


Figure S57: ^{1}H-NMR spectrum of **7-CH_3-ant** in $CDCl_3$ at 300 K.

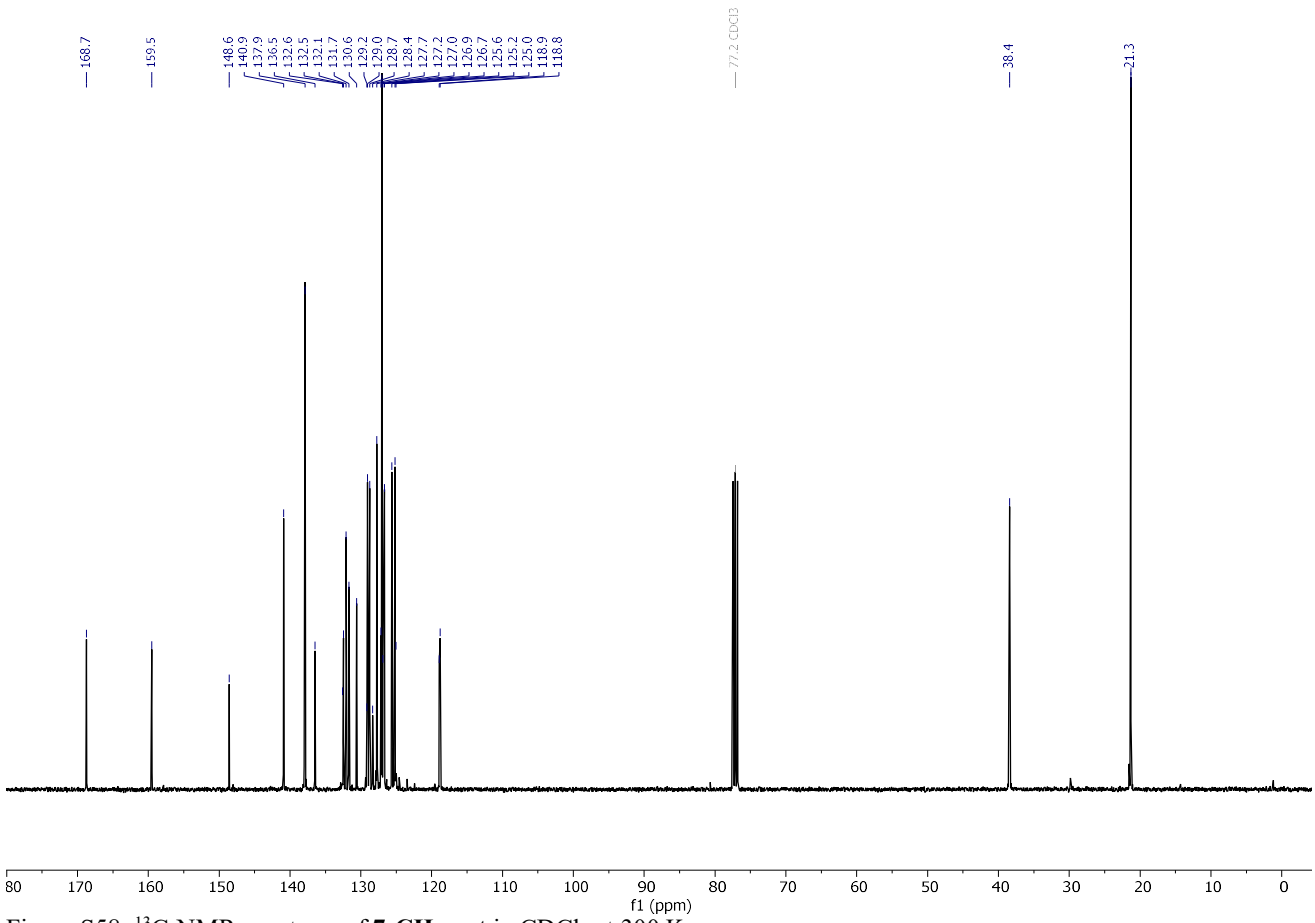
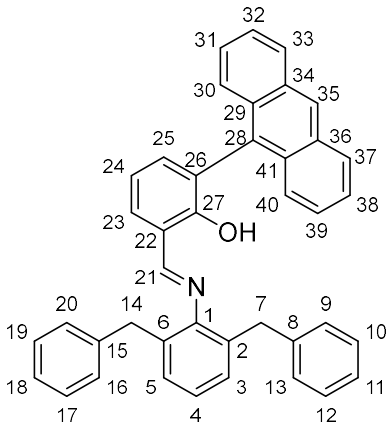


Figure S58: ^{13}C-NMR spectrum of **7-CH$_3$-ant** in $CDCl_3$ at 300 K.

<u>Salicylaldimine **7-H-ant**:</u>



Following the general procedure, salicylaldimine **7-H-ant** (160 mg, 0.29 mmol, 63 %) was obtained from 2-hydroxy-3-(9-anthryl)benzaldehyde · $^1/_2$ DCM (150 mg, 0.46 mmol, 1.0 equiv.) and 2,6-dibenzyl aniline **6-H** (150 mg, 0.55 mmol, 1.2 equiv.) after column chromatography (toluene).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.93 (s, 1H, OH···N), 8.52 (s, 1H, 35-H), 8.05 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 30- and 40-H), 7.76 – 7.68 (m, 3H, 21-, 33- and 37-H), 7.49 – 7.35 (m, 5H, 25-, 31-, 32-, 38- and 39-H), 7.19 – 7.01 (m, 14H, 3-, 4-, 5-, 9-, 10-, 11-, 12-, 13-, 16, 17-, 18-, 19- and 23-H), 7.01 – 6.95 (m, 1H, 24-H), 3.85 (s, 4H, 7- and 14-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.2 (C21), 159.4 (C27), 148.5 (C1), 141.0 (C2 and C6), 136.6 (C25), 132.5 (C23), 132.4 (C8 and C15), 131.8 and 131.7 (C34 and C36 or C29 and C41), 130.6 (C3 and C5), 129.3 (C26), 129.0 (C9, C13, C16 and C20), 128.8 (C30 and C40), 128.5 (C10, C12, C17 and C19), 127.2 (C35), 126.9 (C28), 126.6 (C33 and C37), 126.1 (C11 and C18), 125.61 (C4), 125.2 and 125.2 (C31 and C39 or C32 and C38), 118.8 and 118.8 (C24 or C22), 38.4 (C7 and C14).

Anal. Calcd. for $C_{41}H_{31}NO$ (553.24 g mol^{-1}): C, 88.94; H, 5.64; N, 2.53. Found: C, 88.04; H, 5.43; N, 2.76.

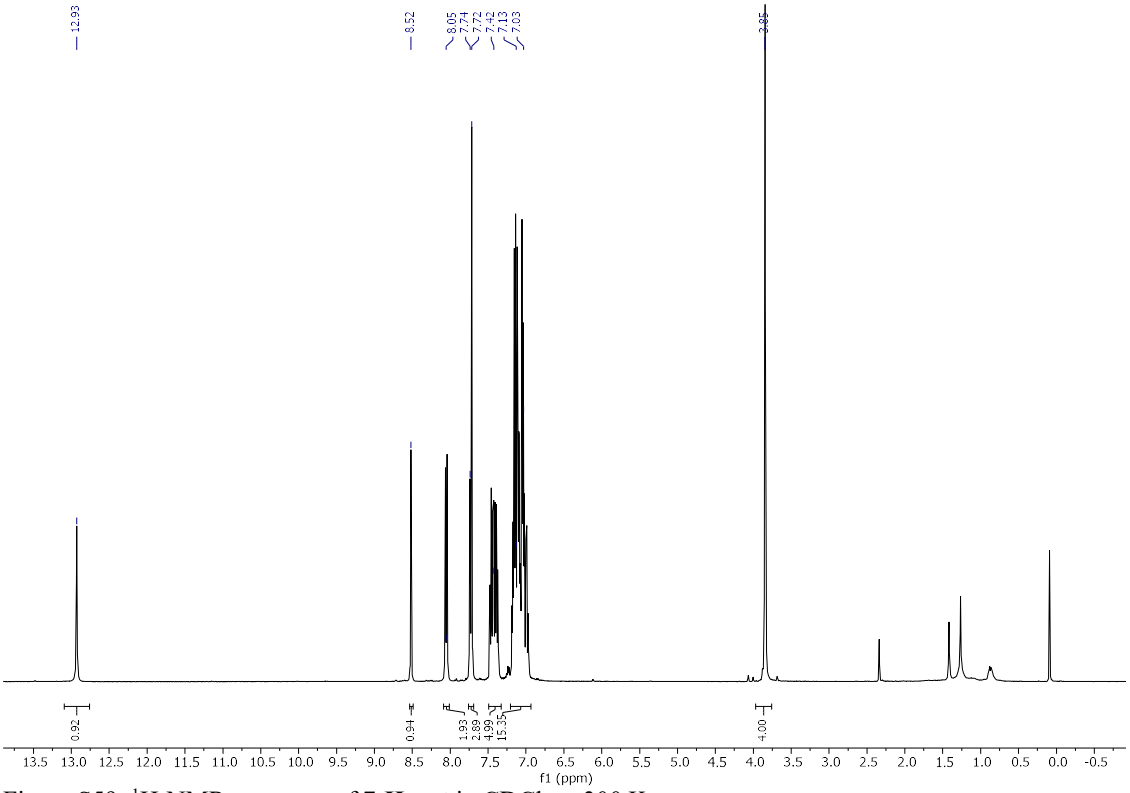


Figure S59: ^{1}H-NMR spectrum of **7-H-ant** in $CDCl_3$ at 300 K.

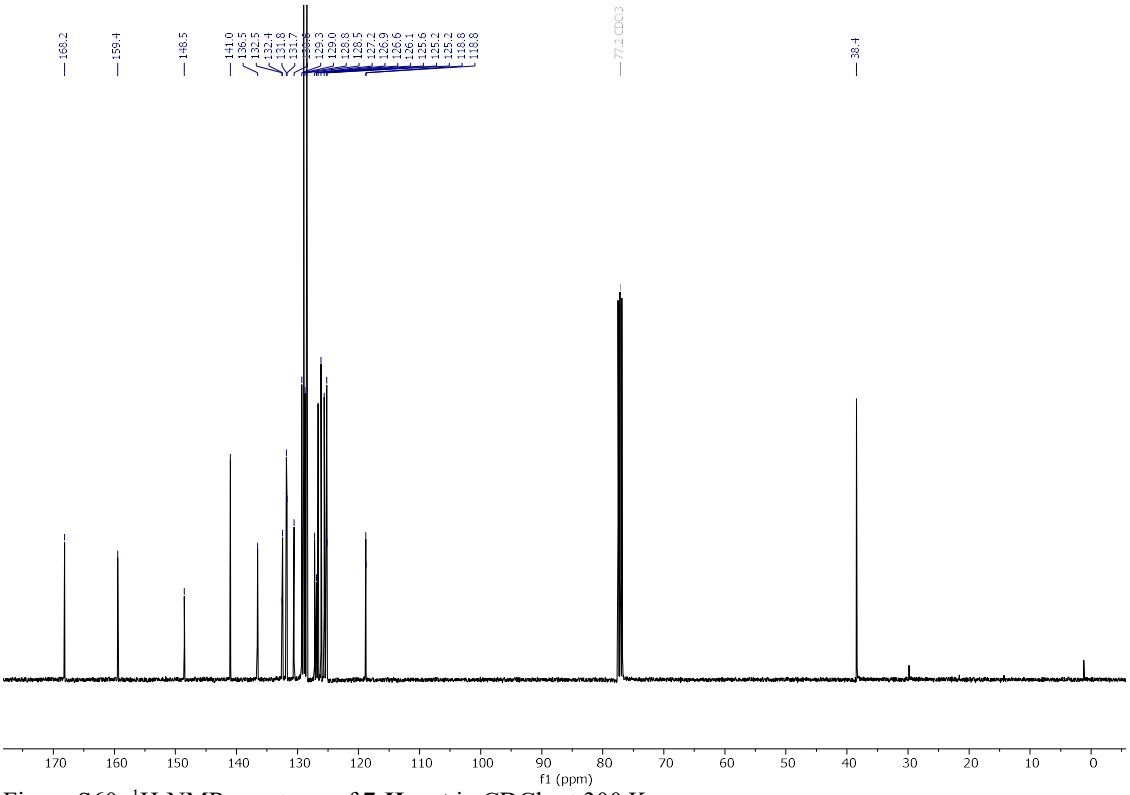
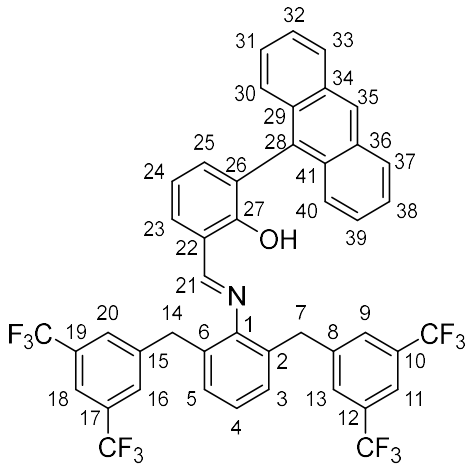


Figure S60: ^{1}H-NMR spectrum of **7-H-ant** in $CDCl_3$ at 300 K.

Salicylaldimine **7-CF$_3$-ant**:



Following the general procedure, salicylaldimine **7-CF$_3$-ant** (290 mg, 0.35 mmol, 57 %) was obtained from 2-hydroxy-3-(9-anthryl)benzaldehyde · $^{1}/_{2}$ DCM (318 mg, 0.94 mmol, 1.0 equiv.) and 2,6-bis(3,5-bis(trifluoromethyl)benzyl)aniline **6-CF$_3$** (340 mg, 0.62 mmol, 1.0 equiv.) after column chromatography (toluene).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.50 (s, 1H, OH···N), 8.51 (s, 1H, 35-H), 8.04 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, 30- and 40-H), 7.69 (s, 2H, 11- and 18-H), 7.67 – 7.63 (m, 3H, 21-, 33-, and 37-H), 7.49 (d, $^{4}J_{HH}$ = 1.6 Hz, 4H, 9-, 13-, 16- and 20-H), 7.48 – 7.42 (m, 3H, 25-, 31-, and 39-H), 7.38 (ddd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.4 Hz, 2H, 32- and 38-H), 7.23 – 7.12 (m, 3H, 3-, 4-, and 5-H), 7.07 (vt, $^{3}J_{HH}$ = 7.6 Hz, 1H, 24-H), 6.95 (dd, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, 23-H), 3.97 (s, 4H, 7- and 14-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.8 (C21), 159.3 (C27), 148.5 (C1), 143.3 (C2 and C6), 137.7 (C25), 132.4 (C23), 131.9 (C34 and C36), 131.9 (q, $^2J_{CF}$ = 33.2 Hz, C10, C12, C17 and C19), 131.7 (C8 and C15), 130.6 (C29 and C41), 130.2 (C26), 123.0 (C3 and C5), 129.2 (C28), 129.0 (m, C9, C13, C16 and C20), 128.7 (C30 and C40), 127.4 (C35), 126.4 (C33 and C37), 126.2 (C4), 125.7 (C32 and C38), 125.3 (C31 and C39), 123.4 (q, $^1J_{CF}$ = 272.8 Hz, CF_3), 120.8 – 120.3 (m, C11 and C18), 119.6 (C24), 118.0 (C22), 38.0 (C7 and C14).

^{19}F-NMR (376 MHz, $CDCl_3$, 300 K): δ (ppm) = 62.9 (CF_3).

Anal. Calcd. for $C_{45}H_{27}F_{12}NO$ (825.70 g mol^{-1}): C, 65.43; H, 3.30; N, 1.70. Found: C, 66.06; H, 4.14; N, 2.03.

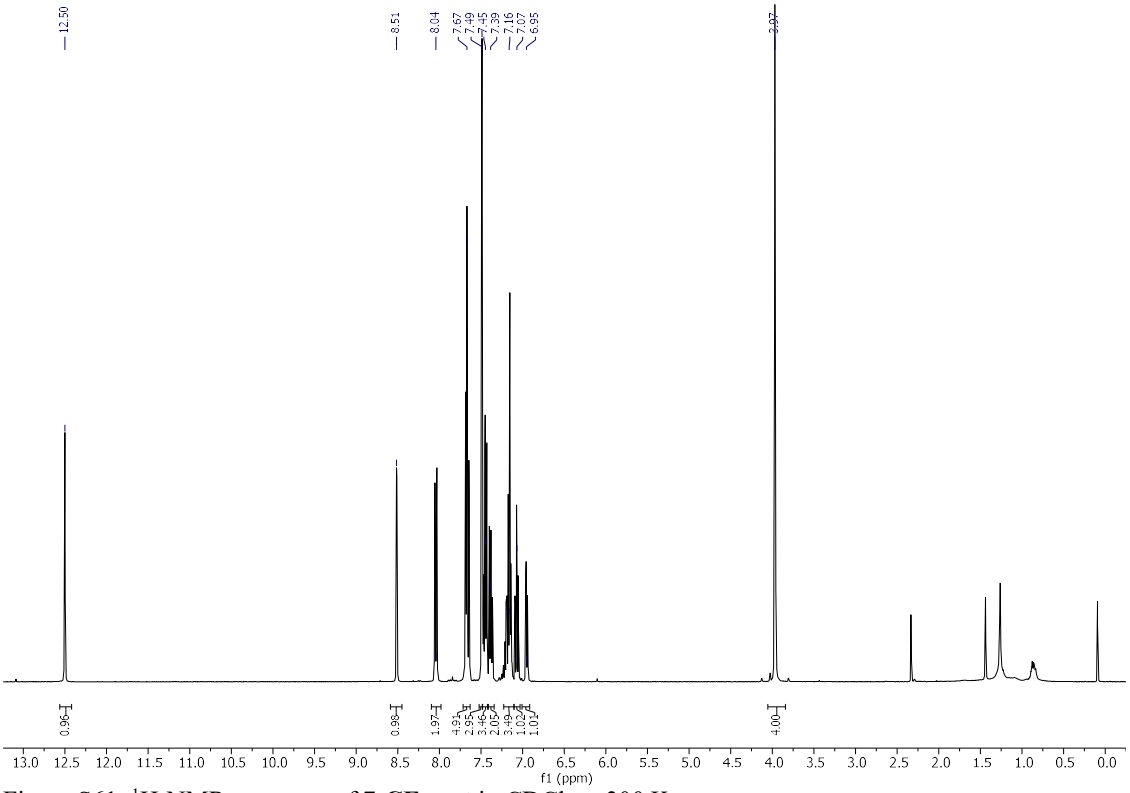


Figure S61: ^{1}H-NMR spectrum of **7-CF$_3$-ant** in $CDCl_3$ at 300 K.

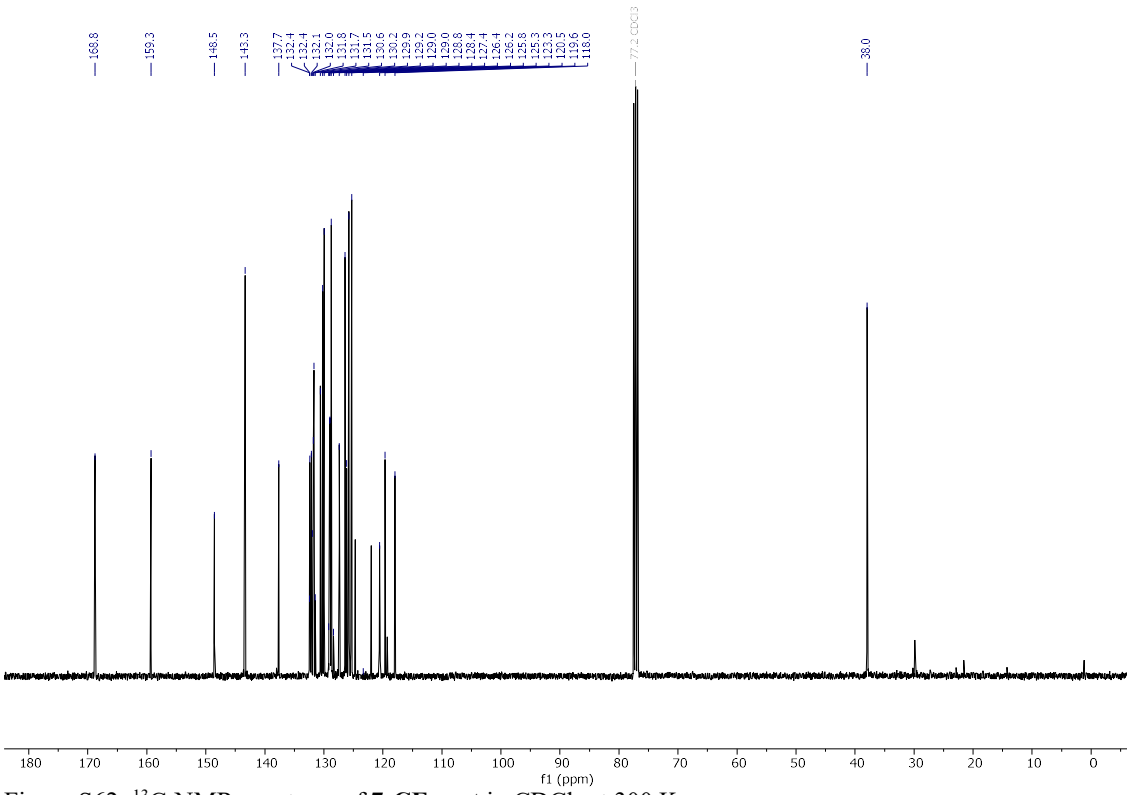


Figure S62: ^{13}C-NMR spectrum of **7-CF$_3$-ant** in CDCl$_3$ at 300 K.

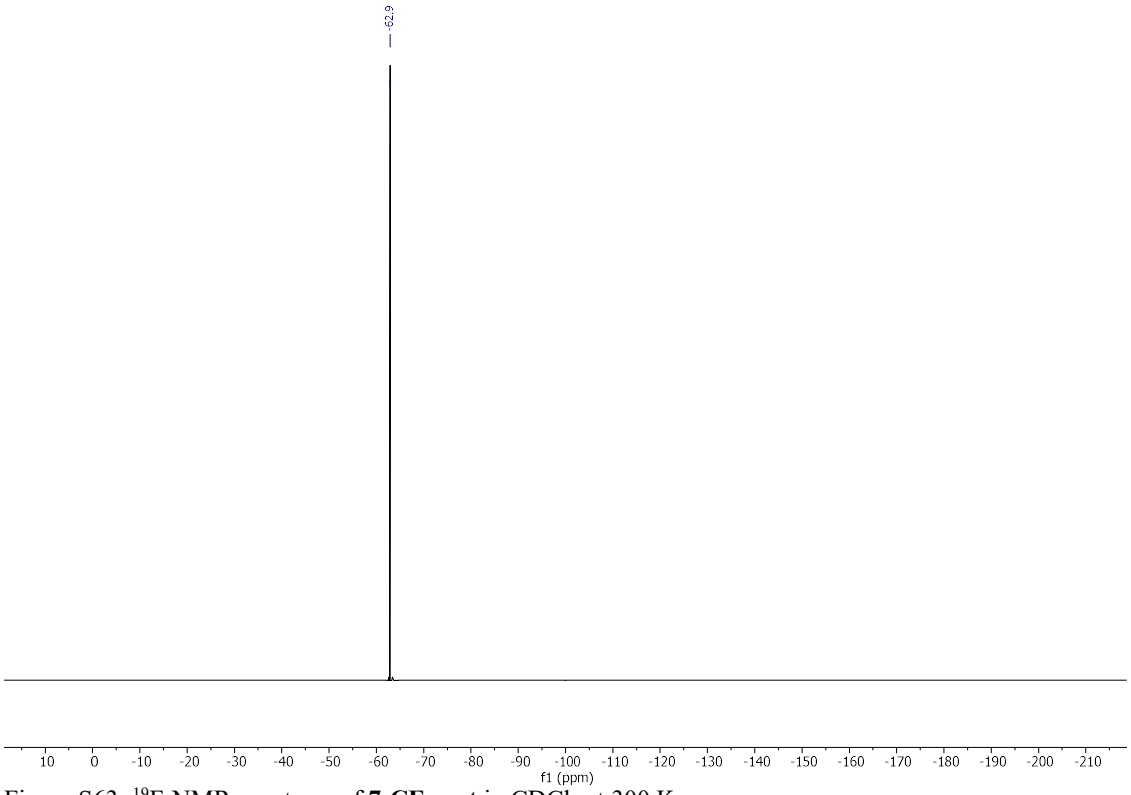
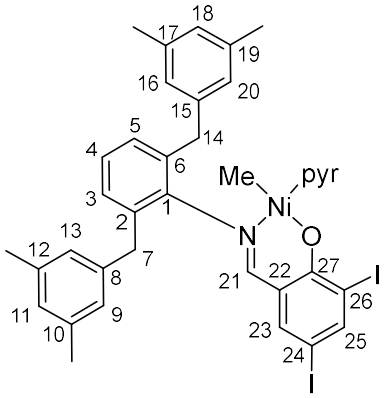


Figure S63: ^{19}F-NMR spectrum of **7-CF$_3$-ant** in CDCl$_3$ at 300 K.

1.3.4 Synthesis of methylene bridged complexes

General procedure for the synthesis of the methylene bridged complexes
A solution of pyridine (160 mg, 2.0 mmol, 20 equiv.) in benzene (5 mL) was added to [(tmeda)$NiMe_2$] (22.4 mg, 110 µmol, 1.1 equiv.) and the respective salicylaldimine (100 µmol, 1.0 equiv.) in a 8 mL vial. The reaction mixture was stirred immediately at room temperature for 30 min. The resulting red solution was centrifuged. The supernatant was separated from the black precipitate. The solution was frozen in liquid nitrogen and the volatiles were removed under vacuum whilst warming up to room temperature. The solid was washed with pentane to remove residual aldimine. The complexes were obtained as orange to red solids in 85 % - 95 % yield.

Complex **8-CH_3-I2**:



Following the general procedure for the preparation of the methylene bridged complexes, complex **8-CH_3-I2** (78 mg, 94 µmol, 94 %) was obtained.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.70 (d, $^3J_{HH}$ = 5.5 Hz, 2H, *o*-H pyridine), 8.13 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 25-H), 7.11 (d, $^3J_{HH}$ = 7.5 Hz, 2H, 3- and 5-H), 7.02 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, 4-H), 6.91 (s, 4H, 9-, 13-, 16- and 20-H), 6.73 – 6.66 (m, 3H, 11- and 18-H and *p*-H pyridine), 6.48 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 23-H), 6.42 (s, 1H, 21-H), 6.40 – 6.31 (m, 2H, *m*-H pyridine), 4.69 (d, $^2J_{HH}$ = 14.7 Hz, 2H, 7- and 14-H), 4.21 (d, $^2J_{HH}$ = 14.7 Hz, 2H, 7- and 14-H), 2.01 (s, 12H, CH_3), -0.61 (s, 3H, Ni-CH_3).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 168.1 (C21), 163.8 (C27), 152.4 (*o*-C pyridine), 151.4 (C1), 148.9 (C25), 142.7 (C23), 140.3 (C2 and C6), 138.1 (C10, C12, C19 and C17), 136.2 (*p*-C pyridine), 134.5 (C8 and C15), 129.2 (C3 and C5), 126.2 (C4), 123.2 (*m*-C pyridine), 121.1 (C22), 96.8 (C24), 72.0 (C26), 39.5 (C7 and C14), 21.2 (CH_3), -7.2 (Ni-CH_3).
The signals for C9, C11, C13, C16, C18 and C20 are overlapped by the solvent signal.

Anal. Calcd. for $C_{37}H_{36}I_2N_2NiO$ (836.03 g mol^{-1}): C, 53.08; H, 4.33; N, 3.35. Found: C, 53.39; H, 4.57; N, 4.05.

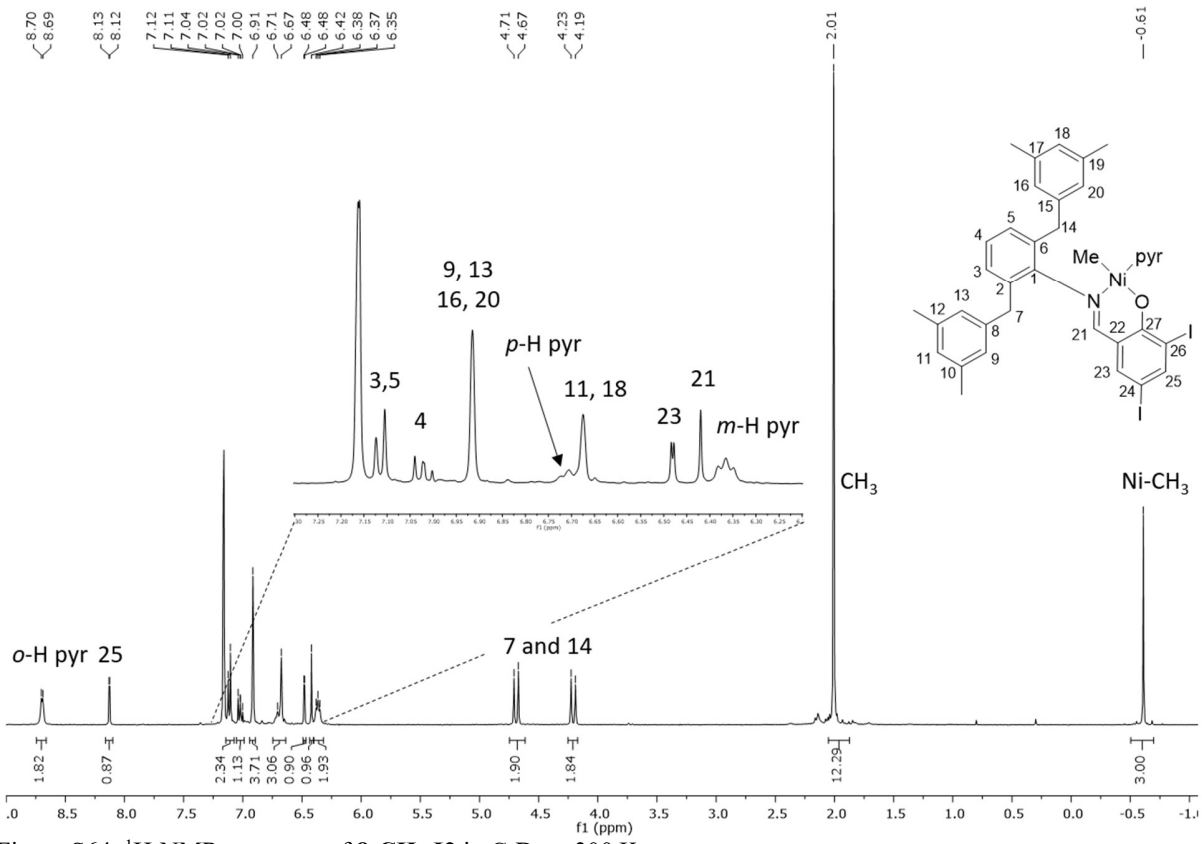


Figure S64: ^{1}H-NMR spectrum of **8-CH$_3$-I2** in C_6D_6 at 300 K.

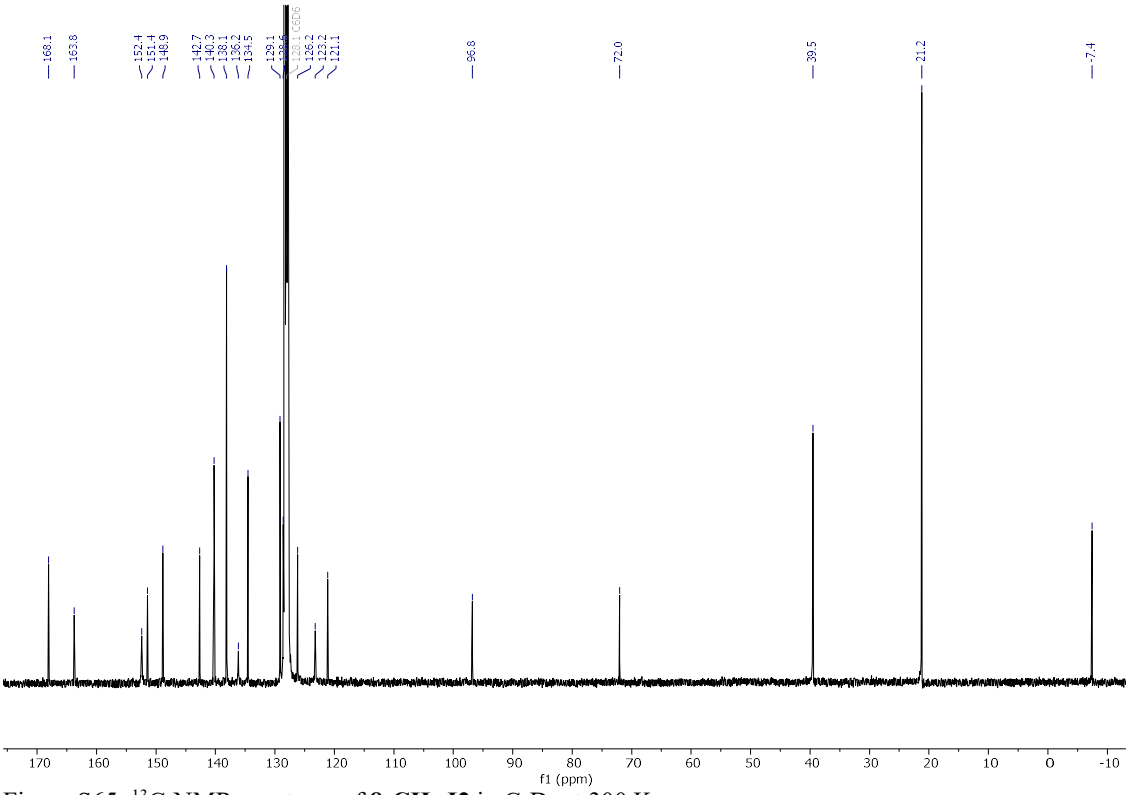
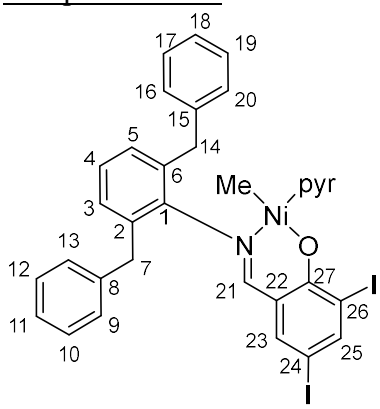


Figure S65: ^{13}C-NMR spectrum of **8-CH$_3$-I2** in C_6D_6 at 300 K.

Complex **8-H-I2**:



Following the general procedure for the preparation of the methylene bridged complexes, complex **8-H-I2** (78 mg, quantitative) was obtained.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.64 (d, $^3J_{HH}$ = 5.6 Hz, 2H, *o*-H pyridine), 8.11 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 25-H), 7.22 – 7.17 (m, 4H, 9-, 13-, 16- and 20-H), 7.05 – 6.99 (m, 6H, 10-, 11-, 12-, 17-, 18- and 19-H), 6.99 – 6.90 (m, 3H, 3-, 4- and 5-H), 6.75 – 6.67 (m, 1H, *p*-H pyridine), 6.49 (d, $^4J_{HH}$ = 2.3 Hz, 1H, 23-H), 6.42 (s, 1H, 21-H), 6.36 (vt, $^3J_{HH}$ = 6.9 Hz, 2H, *m*-H pyridine), 4.46 (d, $^2J_{HH}$ = 15.3 Hz, 2H, 7- and 14-H), 4.32 (d, $^2J_{HH}$ = 15.3 Hz, 2H, 7- and 14-H), -0.68 (s, 3H, Ni-CH$_3$).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 167.2 (C21), 163.8 (C27), 152.4 (*o*-C pyridine), 151.3 (C1), 149.1 (C25), 142.6 (C23), 140.4 (C2 and C6), 136.2 (*p*-C pyridine), 134.1 (C8 and C15), 129.8 (C9, C13, C16 and C20), 129.0 (C10, C12, C17 and C19), 128.8 (C3 and C5), 126.4 (C11 and C18), 126.1 (C4), 123.2 (*m*-C pyridine), 121.0 (C22), 96.8 (C24), 72.0 (C26), 39.2 (C7 and C14), -7.4 (Ni-CH$_3$).

Anal. Calcd. for $C_{33}H_{28}I_2N_2NiO$ (779.96 g mol^{-1}): C, 50.74; H, 3.61; N, 3.59. Found: C, 51.01; H, 3.88; N, 3.90.

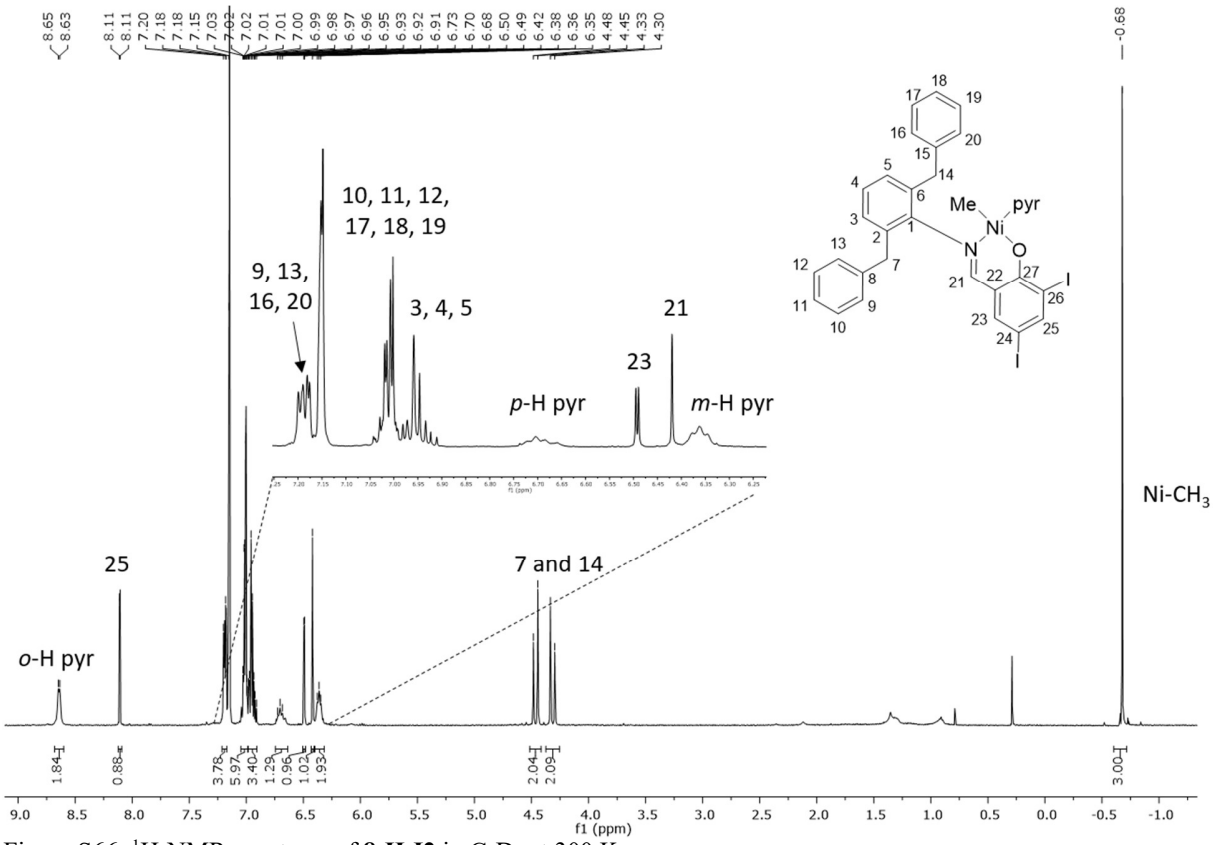


Figure S66: ^{1}H-NMR spectrum of **8-H-I2** in C_6D_6 at 300 K.

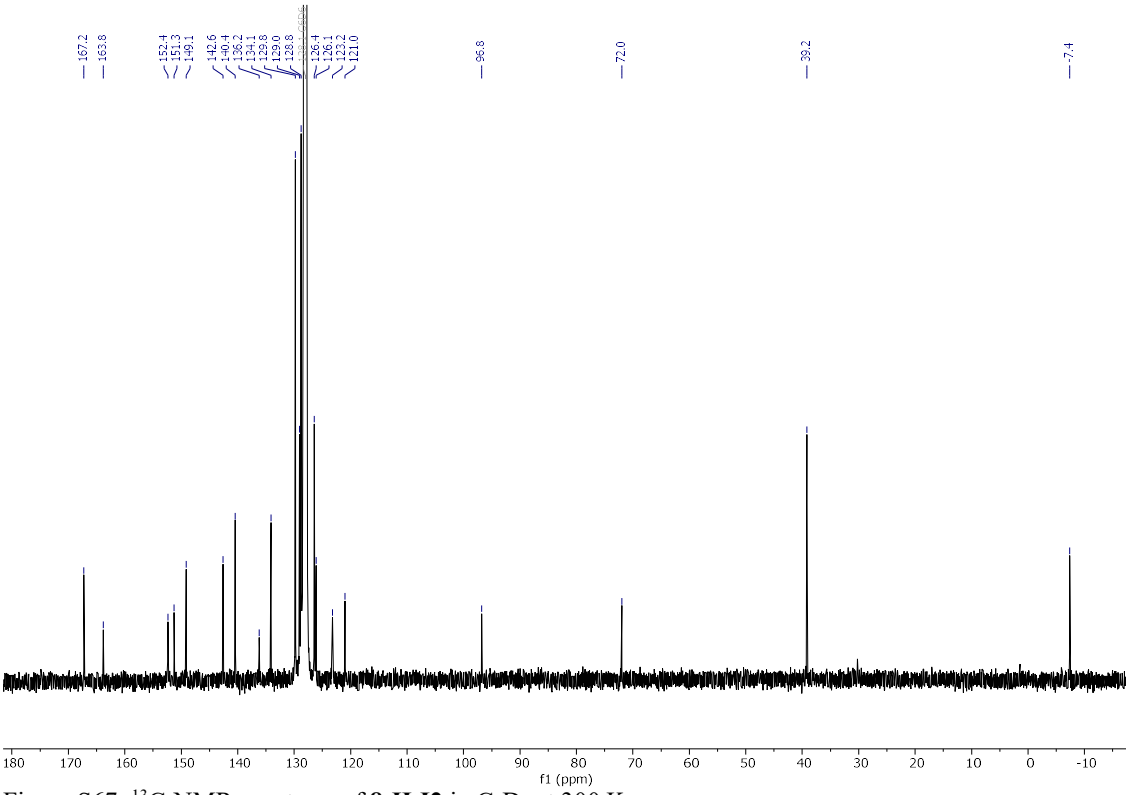
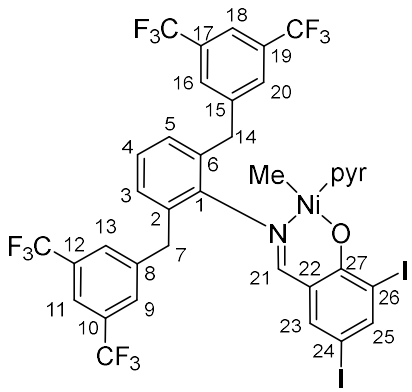


Figure S67: ^{13}C-NMR spectrum of **8-H-I2** in C_6D_6 at 300 K.

Complex **8-CF$_3$-I2**:



Following the general procedure for the preparation of the methylene bridged complexes, complex **8-CF$_3$-I2** (102 mg, 97 µmol, 97 %) was obtained.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.57 (s, 2H, *o*-H pyridine), 8.12 (d, $^4J_{HH}$ = 2.2 Hz, 1H, 25-H), 7.66 (s, 2H, 11- and 18-H), 7.57 (s, 4H, 9-, 13-, 16- and 20-H), 6.87 – 6.72 (m, 1H, 4-H), 6.75 – 6.60 (m, 4H, 3-, 5-, 23-H and *p*-H pyridine), 6.44 – 6.32 (m, 21- and *m*-H pyridine), 4.19 (d, $^2J_{HH}$ = 15.5 Hz, 2H, 7- and 14-H), 3.92 (d, $^2J_{HH}$ = 15.5 Hz, 2H, 7- and 14-H), -0.91 (s, 3H, Ni-CH$_3$).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 166.6 (C21), 164.0 (C27), 152.1 (*o*-C pyridine), 151.3 (C1), 150.2 (C25), 143.0 (C2 and C6), 141.7 (C23), 136.7 (*p*-C pyridine), 132.1 (q, $^2J_{CF}$ = 33.2 Hz, C10, C12, C17 and C19), 130.0 – 129.6 (m, C9, C13, C16 and C20), 129.3 (C3 and C5), 128.6 (C8 and C15), 126.8 (C4), 123.8 (q, $^1J_{CF}$ = 273.0 Hz, CF$_3$), 123.4 (*m*-C pyridine), 120.6 (q, $^3J_{CF}$ = 7.8 Hz, C11 and C18), 119.9 (C22), 97.2 (C24), 73.0 (C26), 38.1 (C7 and C14), -7.4 (Ni-CH$_3$).

^{19}F-NMR (376 MHz, C_6D_6, 300 K): δ (ppm) = -62.6 (s, CF_3).

Anal. Calcd. for $C_{37}H_{24}F_{12}N_2NiO$ (1051.91 g mol^{-1}): C, 42.20; H, 2.30; N, 2.66. Found: C, 42.29; H, 2.70; N, 3.18.

The experimental value for the nitrogen content is slightly higher than expected. This and the broadened signal for pyridine in the ^{1}H-NMR spectrum could indicate a slight excess of pyridine in the product.

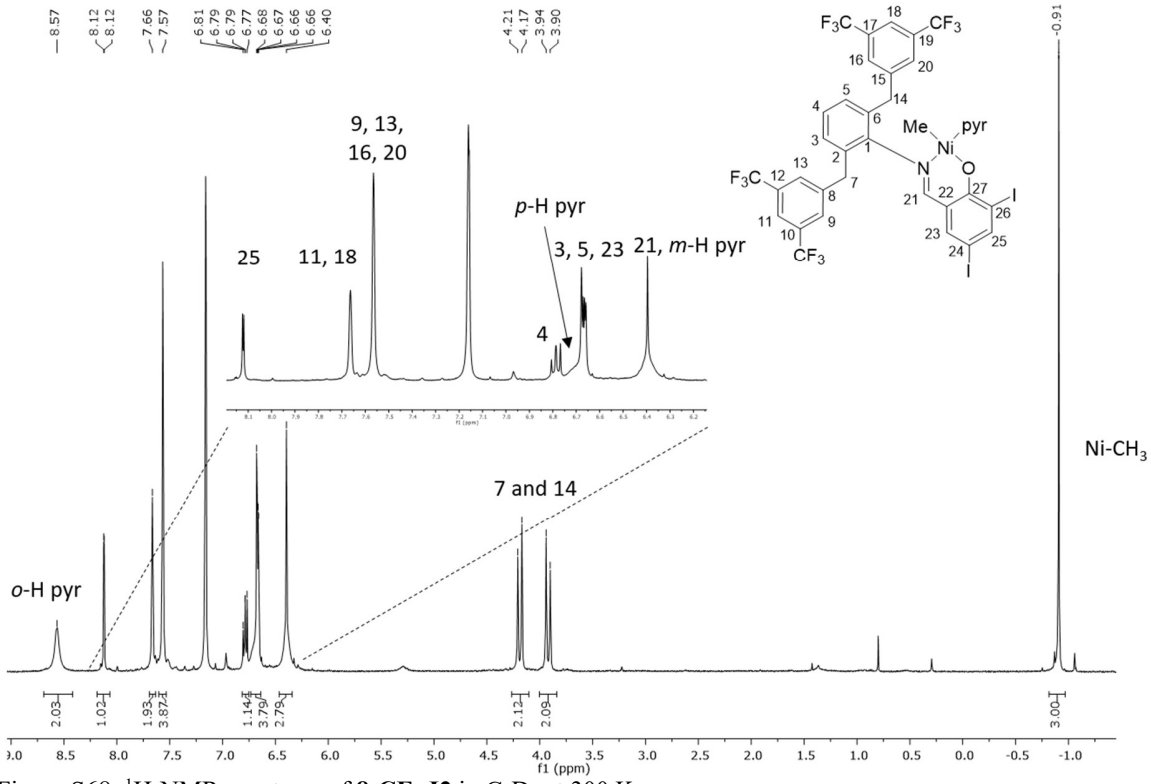


Figure S68: ^{1}H-NMR spectrum of **8-CF$_3$-I2** in C_6D_6 at 300 K.

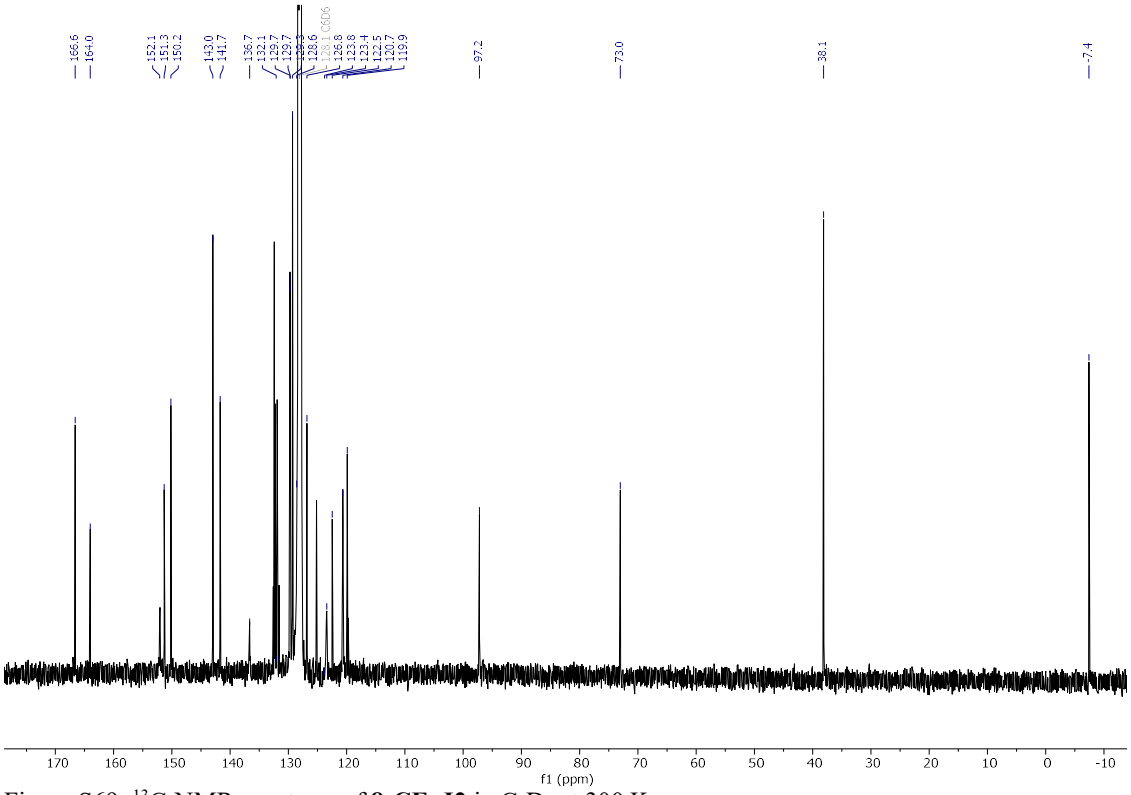


Figure S69: ^{13}C-NMR spectrum of **8-CF$_3$-I2** in C_6D_6 at 300 K.

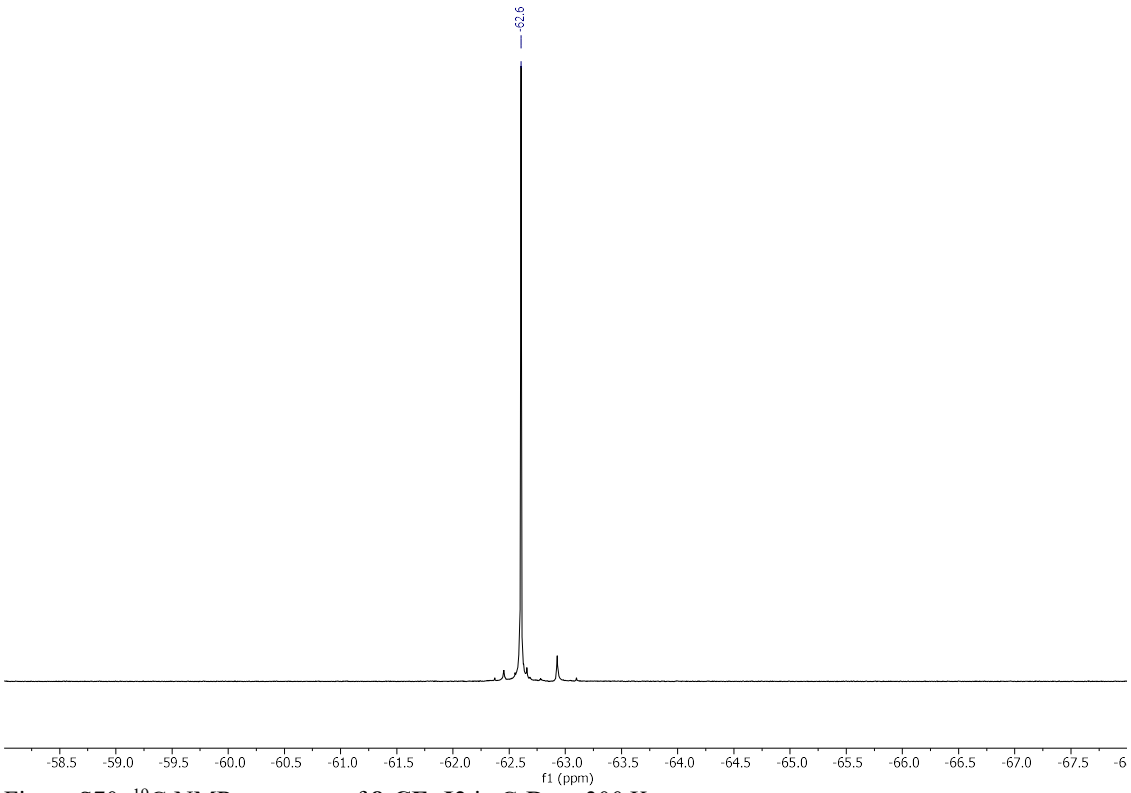
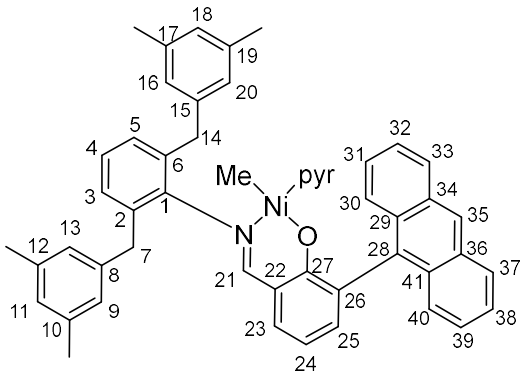


Figure S70: ^{19}C-NMR spectrum of **8-CF$_3$-I2** in C_6D_6 at 300 K.

Complex **8-CH_3-ant**:



Following the general procedure for the preparation of the methylene bridged complexes, complex **8-CH_3-ant** (70 mg, 92 µmol, 92 %) was obtained.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.28 – 8.11 (m, 3H, 30-, 35- and 40-H), 7.83 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 33- and 37-H), 7.73 (d, $^3J_{HH}$ = 5.5 Hz, 2H, *o*-H pyridine), 7.33 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, 25-H), 7.22 – 7.17 (m, 2H, 32- and 38-H), 7.16 – 7.06 (m, 4H, 3-, 5-, 31- and 39-H), 7.08 (s, 1H, 21-H) 7.05 – 6.98 (m, 5H, 4-, 9-, 13-, 16- and 20-H), 6.76 – 6.70 (m, 3H, 11-, 18- and 23-H), 6.55 (vt, $^3J_{HH}$ = 7.2 Hz, 1H, 24-H), 6.29 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-H pyridine), 5.64 (vt, $^3J_{HH}$ = 6.8 Hz, 2H, *m*-H pyridine), 4.73 (d, $^2J_{HH}$ = 14.8 Hz, 2H, 7- and 14-H), 4.34 (d, $^2J_{HH}$ = 14.8 Hz, 2H, 7- and 14-H), 2.09 (s, 12H, CH_3), -0.81 (s, 3H, Ni-CH_3).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 168.5 (C21), 166.0 (C27), 152.0 (C1), 151.5 (*o*-C pyridine), 140.5 (C2 and C6), 137.9 (C10, C12, C17 and C19), 137.4 (C28), 136.8 (C25), 135.0 (*p*-C pyridine), 134.9 (C8 and C15), 134.3 (C23), 132.1 (C32 and C38), 131.3 (C31 and C39), 130.6 (C26), 128.9 (C9, C13, C16 and C20), 127.4 (C22), 125.9 (C4), 125.6 (C35), 125.3 (C29 and C41), 125.1 (C34 and C36), 122.1 (*m*-C pyridine), 120.8 (C3 and C5), 113.3 (C24), 39.4 (C7 and C14), 21.4 (CH_3), -7.9 (Ni-CH_3).
The signals for C11, C18, C30, C33, C37 and C40 are overlapped by the solvent signal.

Anal. Calcd. for $C_{50}H_{45}N_2O$ (761.29 g mol^{-1}): C, 78.75; H, 5.95; N, 5.51. Found: C, 77.86; H, 6.19; N, 4.99.

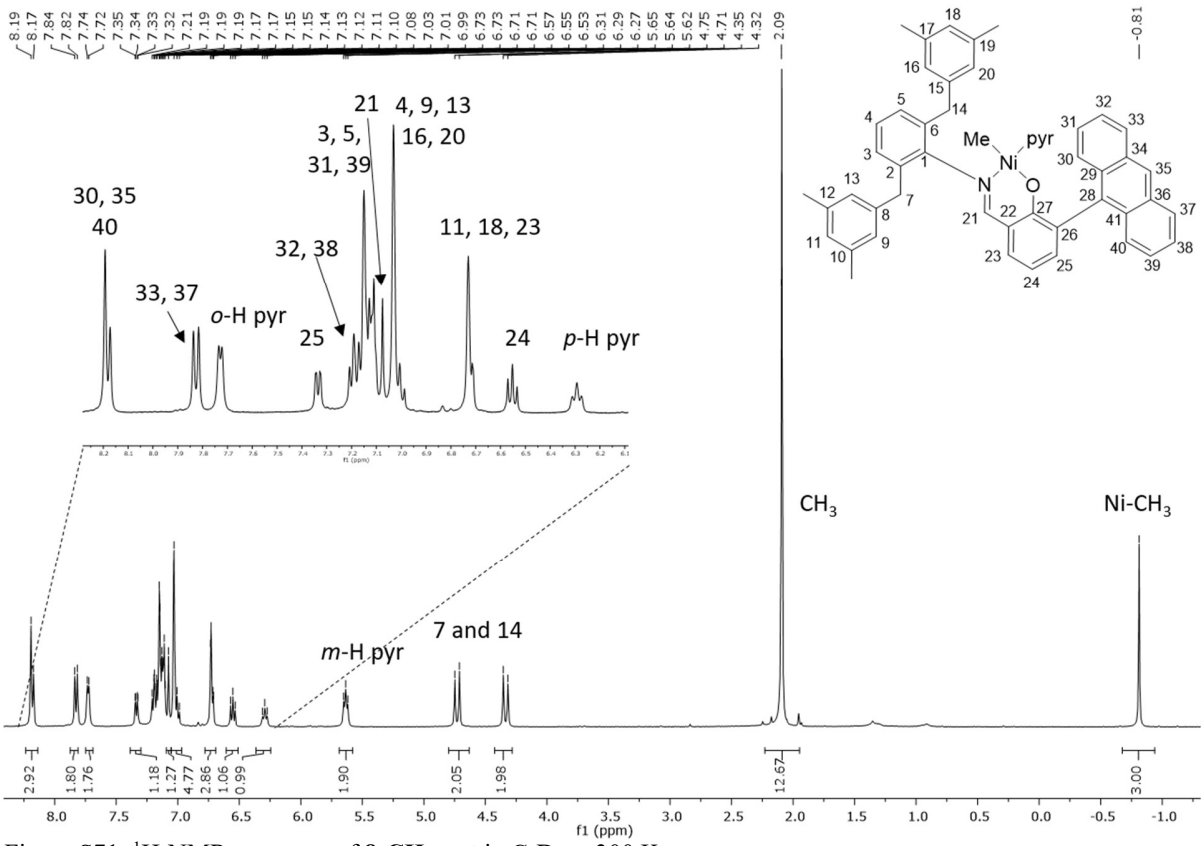


Figure S71: ^{1}H-NMR spectrum of **8-CH$_3$-ant** in C_6D_6 at 300 K.

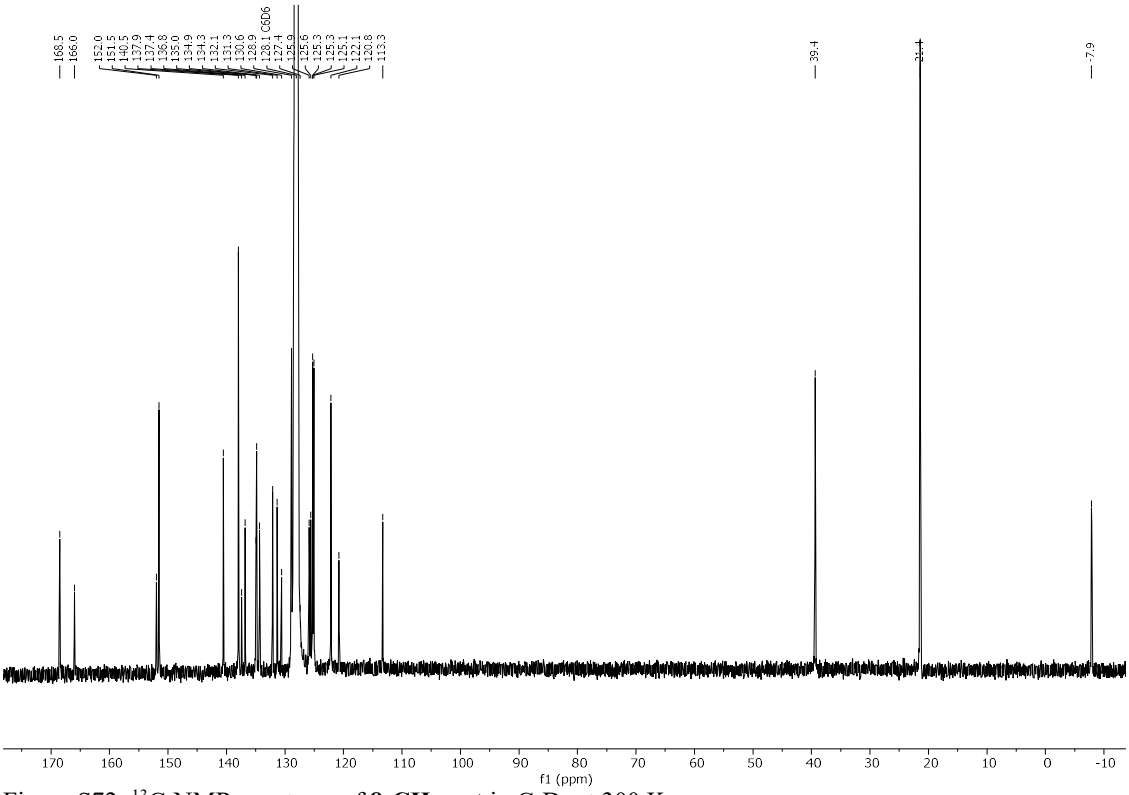


Figure S72: ^{13}C-NMR spectrum of **8-CH$_3$-ant** in C_6D_6 at 300 K.

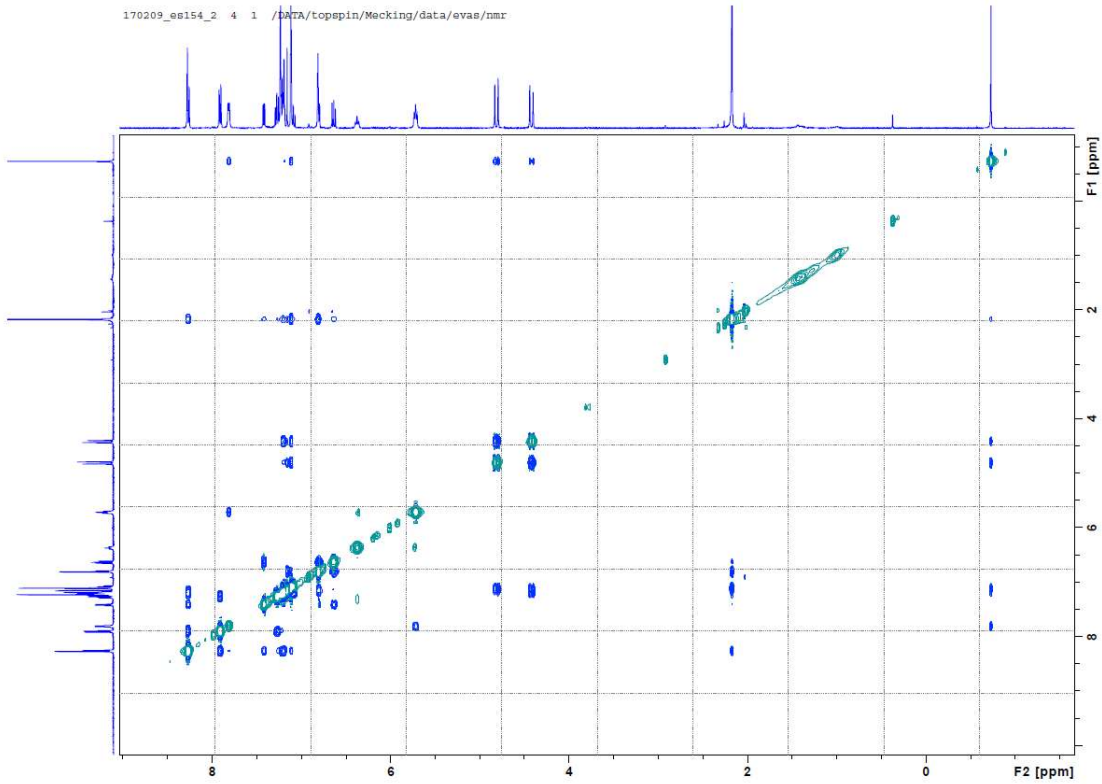
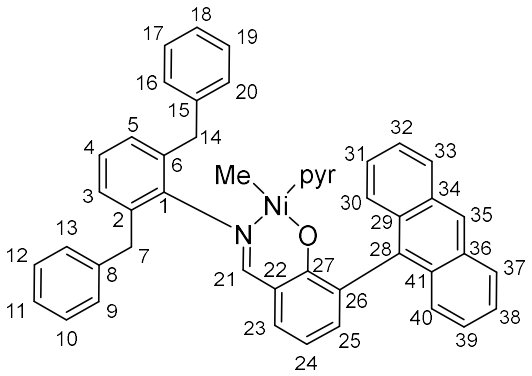


Figure S73: NOESY spectrum of **8-CH$_3$-ant** in C_6D_6 at 300 K. The methylene groups are located in spatial proximity to the Ni-Me group.

Complex **8-H-ant**:



Following the general procedure for the preparation of the methylene bridged complexes, complex **8-H-ant** (71 mg, quantitative) was obtained.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.18 (s, 1H, 35-H), 8.16 – 8.10 (m, 2H, 30- and 40-H), 7.82 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 33- and 37-H), 7.74 – 7.67 (m, 2H, *o*-H pyridine), 7.36 – 7.28 (m, 5H,9-, 13-, 16-, 20- and 25-H), 7.22 – 7.07 (m, 10 H, 10-, 12-, 17-, 19-, 31-, 32-, 38- and 39-H), 7.08 – 6.98 (m, 5H, 3-, 5-, 11-, 18- and 21-H), 6.95 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, 4-H), 6.69 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 1.9 Hz, 1H, 23-H), 6.55 (dd, $^3J_{HH}$ =7.9 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, 24-H), 6.29 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-H pyridine), 5.63 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *m*-H pyridine), 4.72 (d, $^2J_{HH}$ = 15.2 Hz, 2H, 7- and 14-H), 4.39 (d, $^2J_{HH}$ = 15.2 Hz, 2H, 7- and 14-H), -0.85 (s, 3H, Ni-CH_3).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 167.8 (C21), 165.9 (C27), 152.0 (C1), 151.5 (*o*-C pyridine), 140.8 (C2 and C6), 137.4 (C28), 136.9 (C25), 135.0 (*p*-C pyridine), 134.5 (C23), 134.3 (C9, C13, C16 and C20), 132.1 and 131.3 (C29, C34, C36 and C41), 130.7 (C26), 103.0 (C8 and C15), 128.9 (C30 and C40), 128.7 (C11 and C18), 128.3 (C10, C12, C17 and C19), 126.3 (C3 and C5), 125.8 (C4), 125.6 (C35), 125.3 and 125.0 (C31, C32, C38 and C39), 122.1 (*m*-C pyridine), 120.7 (C22), 113.3 (C24), 39.2 (C7 and C14), -8.1 (Ni-CH_3).
The signals for C33 and C37 are overlapped by the solvent signal.

Anal. Calcd. for $C_{47}H_{38}NiN_2O$ (705.53 g mol^{-1}): C, 80.01; H, 5.43; N, 3.97. Found: C, 79.17; H, 5.46; N, 4.15.

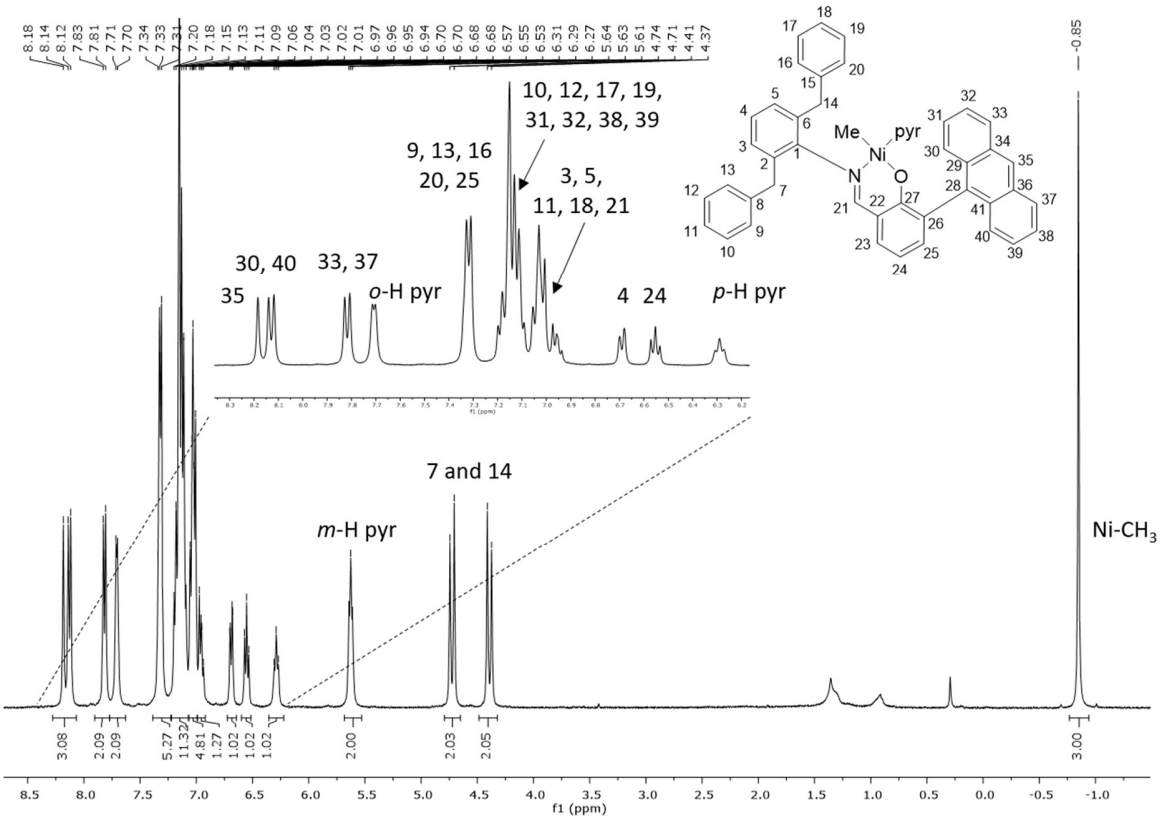


Figure S74: ^{1}H-NMR spectrum of **8-H-ant** in C_6D_6 at 300 K.

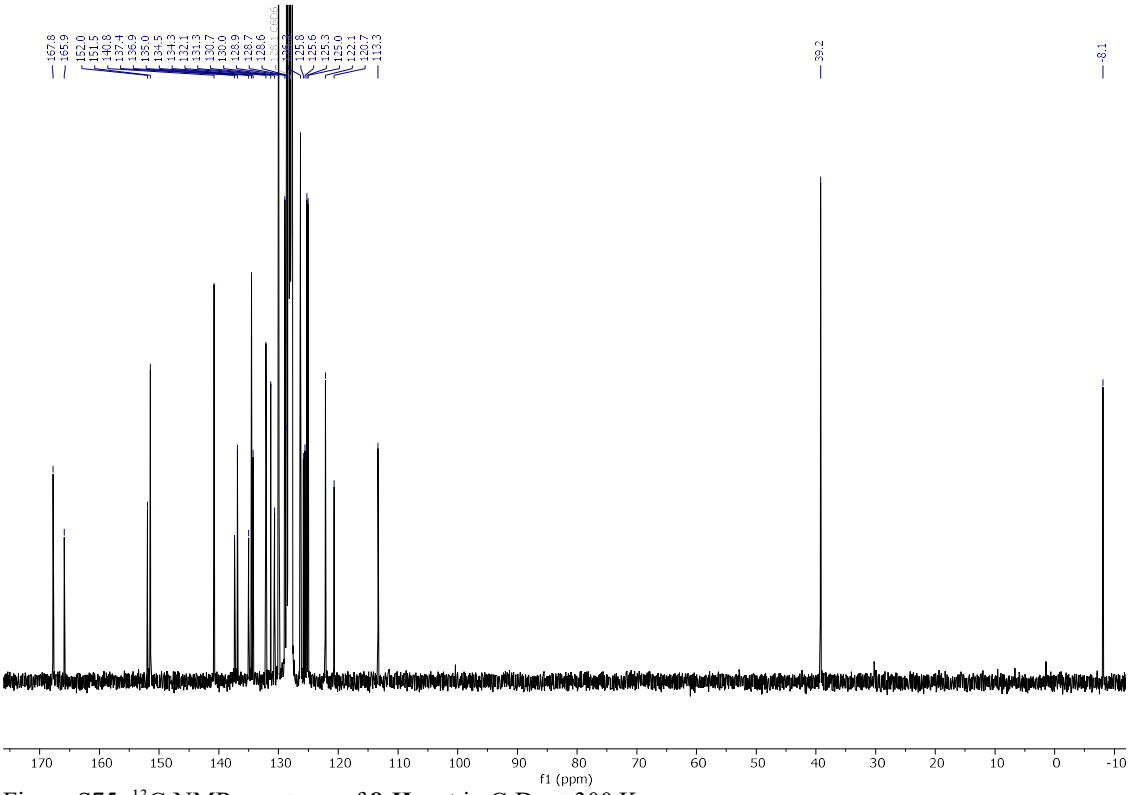
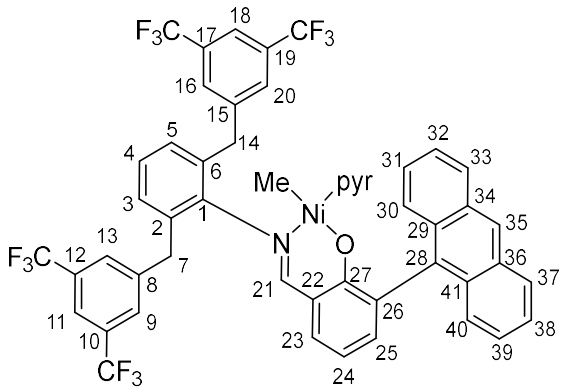


Figure S75: ^{13}C-NMR spectrum of **8-H-ant** in C_6D_6 at 300 K.

Complex **8-CF$_3$-ant**:



Following the general procedure for the preparation of the methylene bridged complexes, complex **8-CF$_3$-ant** (90 mg, 92 µmol, 92 %) was obtained.

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 8.17 (s, 1H, 35-H), 8.07 (m, 2H, 30- and 40-H), 7.82 – 7.77 (m, 2H, 33- and 37-H), 7.71 – 7.63 (m, 4H, 11-, 18-H, *o*-H pyridine), 7.57 (s, 4H, 9-, 13-, 16 – and 20-H), 7.30 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, 25-H), 7.22 – 7.13 (m, 4H, 31-, 32-, 38- and 39-H), 6.98 (s, 1H, 21-H), 6.82 – 6.71 (m, 2H, 4- and 23-H), 6.64 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 3- and 5-H), 6.55 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, 24-H), 6.36 – 6.24 (m, 1H, *p*-H pyridine), 5.74 – 5.59 (m, 2H, *m*-H pyridine), 4.27 (d, $^2J_{HH}$ = 15.8 Hz, 2H, 7- and 14-H), 4.09 (d, $^3J_{HH}$ = 15.8 Hz, 2H, 7- and 14-H), -1.02 (s, 3H, Ni-CH$_3$).

^{13}C-NMR (101 MHz, C_6D_6, 300 K): δ (ppm) = 167.2 (C21), 166.3 (C27), 151.8 (C1), 151.2 (*o*-C pyridine), 143.2 (C2 and C6), 137.9 (C25), 136.6 (C28), 135.5 (*p*-C pyridine), 133.3 (C23), 132.9 (C8 and C15), 132.0 (C26), 132.0 (q, $^2J_{CF}$ = 33.1 Hz, C10, C12, C17 and C19), 131.3 (C34 and C36 or C29 and C41), 131.2 (C34 and C36 or C29 and C41), 123.0 – 129.6 (m, C9, C13, C16 and C20), 129.1 (C3 and

C5), 126.5 (C4), 125.8 (C35), 125.3 (either C31 and C39 or C32 and C38), 125.2 (either C31 and C39 or C32 and C38), 121.1 (q, $^1J_{CF}$ = 296.1 Hz, CF_3), 120.7 – 120.3 (m, C11 and C18), 119.6 (C22) 114.4 (C24), 38.0 (C7 and C14), -8.1 (Ni-CH_3).
The signal for C30, C33, C37 and C40 are overlapped by the solvent signal.

^{19}F-NMR (376 MHz, C_6D_6, 300 K): δ (ppm) = -62.6 (s, CF_3).

Anal. Calcd. for $C_{51}H_{34}F_{12}N_2NiO$ (976.18 g mol^{-1}): C, 62.66; H, 3.51; N, 2.87. Found: C, 61.56; H, 4.16; N, 3.15.

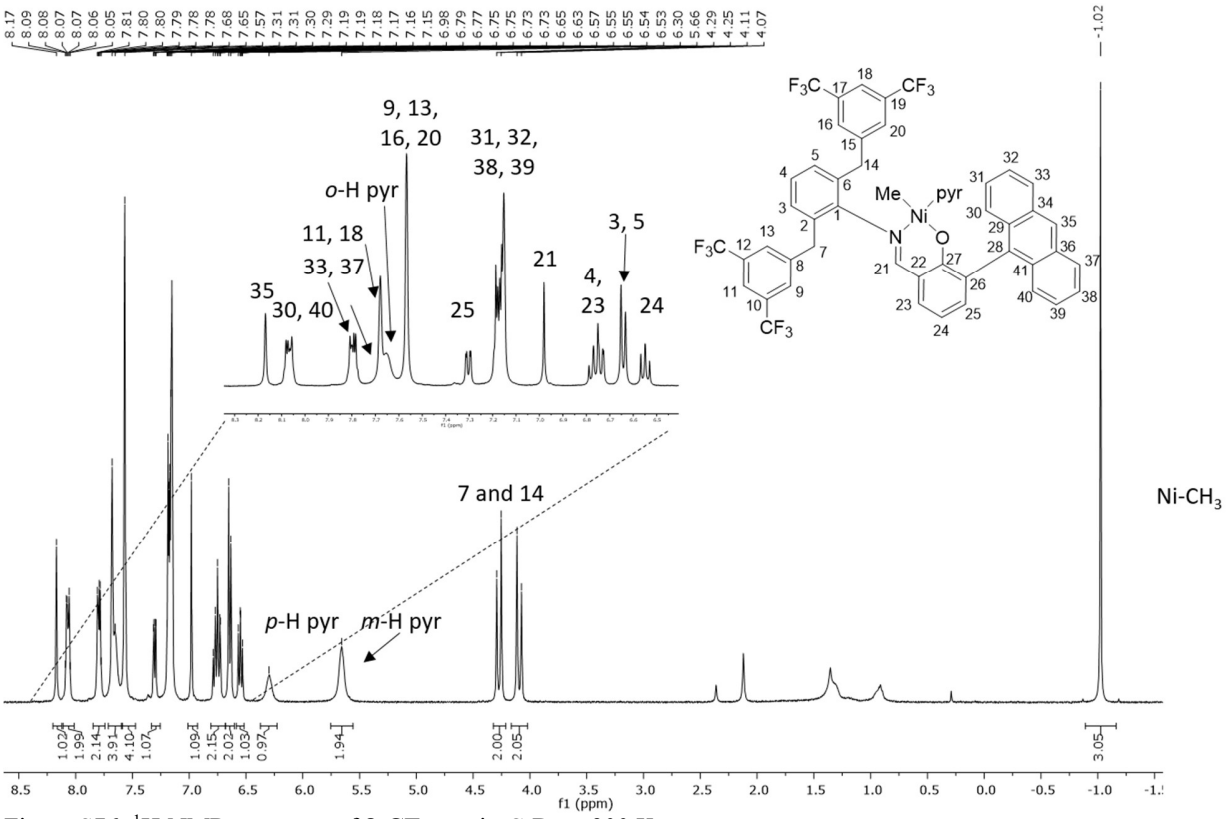


Figure S76: ^{1}H-NMR spectrum of **8-CF$_3$-ant** in C_6D_6 at 300 K.

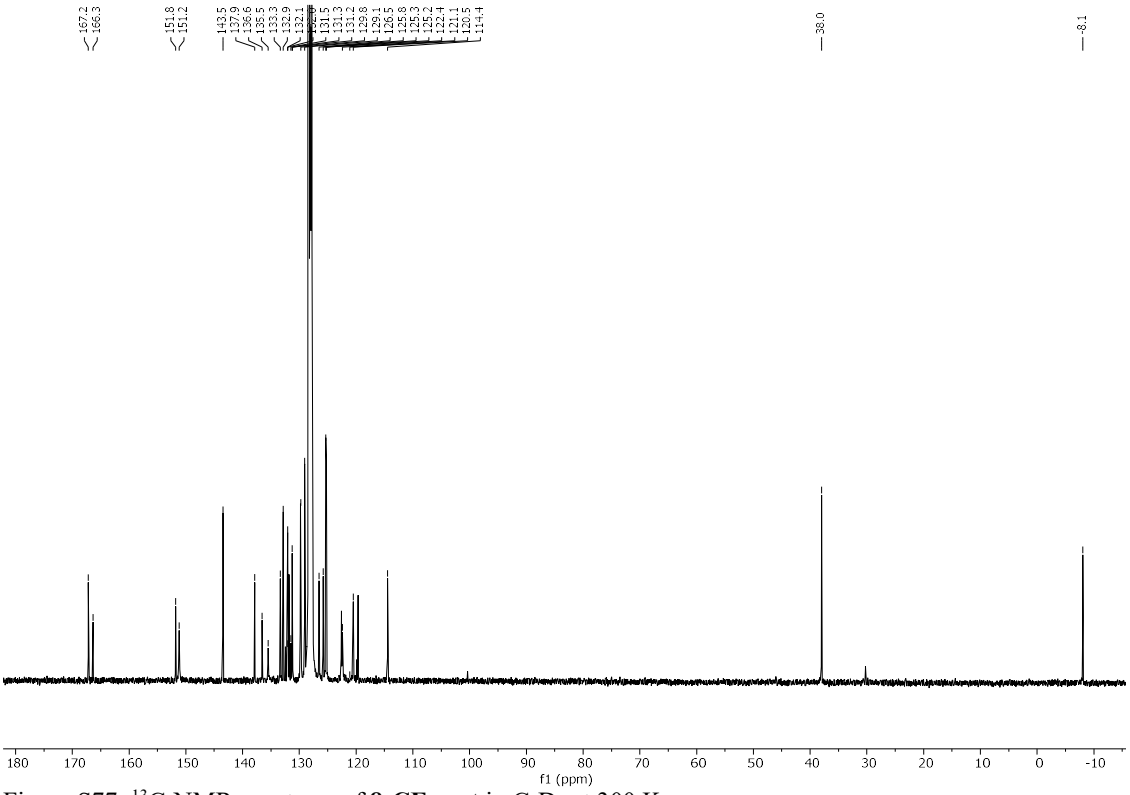


Figure S77: ^{13}C-NMR spectrum of **8-CF$_3$-ant** in C_6D_6 at 300 K.

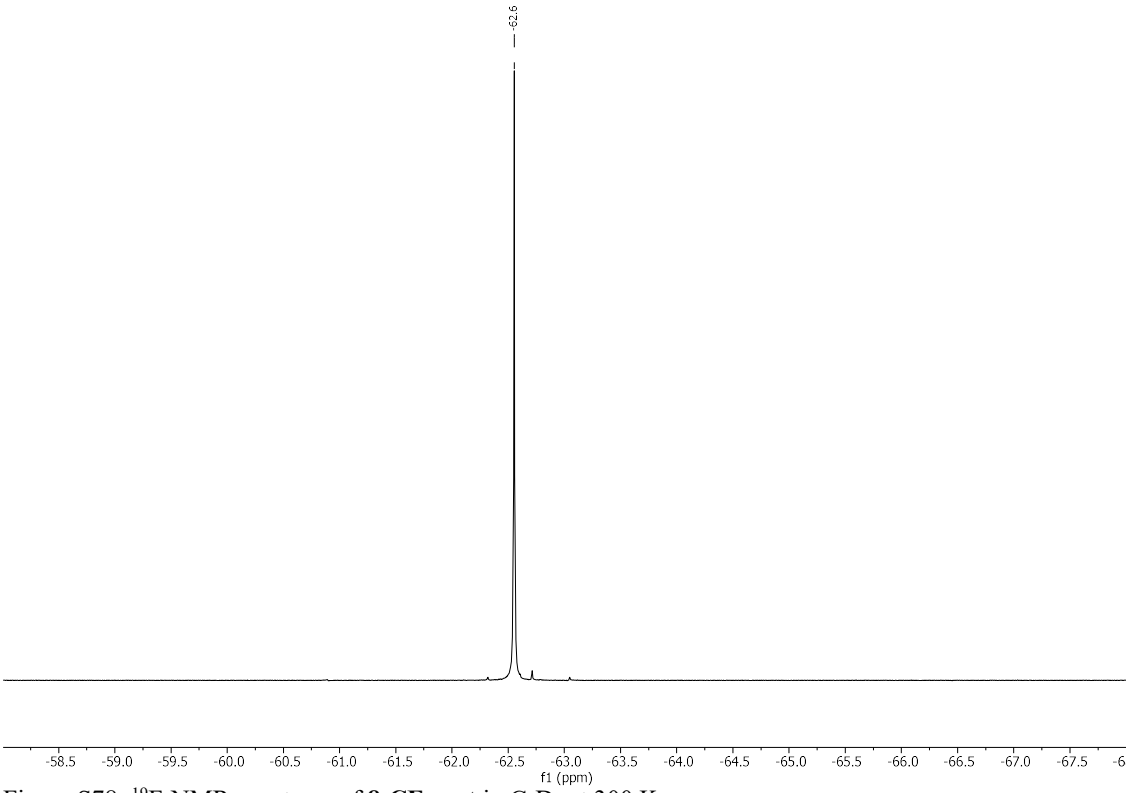


Figure S78: ^{19}F-NMR spectrum of **8-CF$_3$-ant** in C_6D_6 at 300 K.

1.4 Polymerizations

1.4.1 General oligomerization/polymerization procedure

Polymerization experiments were performed in a BÜCHI miniclave pressure reactor with a 200 mL steel vessel, equipped with a heating and cooling jacket and a pitched blade stirrer. The temperature was regulated via a JULABO FB 50 thermostat, controlled via a temperature sensor dipping in the reaction mixture. Prior to polymerization, the reactor was heated to 90 °C under reduced pressure for at least 30 min. The reactor was filled with argon and evacuated three times at an internal temperature > 60 °C. Afterwards, the reactor was cooled down to a temperature 5 °C below the desired reaction temperature. 100 mL of dry and oxygen-free toluene was transferred to the reactor via cannula in an argon counter stream. The catalyst precursor was dissolved in 5 mL of toluene and transferred to the reactor via syringe. The reaction mixture was stirred at 1000 rpm and the reactor was pressurized to the desired pressure, while the temperature rose. During polymerization, the temperature of the thermostat was adjusted to achieve the desired internal temperature (± 1 °C) and the ethylene mass flow was recorded by a Bronkhorst mass flow meter and Bronkhorst flow plot software. At the end of the predetermined polymerization time, ethylene flow was stopped and the reactor was carefully vented.
For the polymerizations with catalyst precursors **4-CH_3-I2**, **4-H-I2**, **4-CH_3-ant** and **4-H-ant**, all volatiles were removed under reduced pressure. For the polymerizations with the catalyst precursors **4-CF_3-I2**, **4-CF_3-ant** and **8**, the reaction mixture was poured into ca. 600 mL of technical grade MeOH and stirred for at least 1 h. The precipitated polymer was filtered off, washed with MeOH and dried under vacuum (50 °C, 20 mbar).

1.4.2 Determination of yields

The activity, stability and productivity of the catalysts was monitored by the ethylene uptake of the reaction mixture. This data also allows for the determination of yields for reactions with catalysts **4**, which forms volatile products.
For calibration and validation, exemplarily mass flow traces of the methylene bridged catalysts (**8**) were plotted and the productivity of the catalysts calculated. These catalysts produce high molecular weight polymers, which are quantitatively precipitated in methanol. The polymer yield should match with the ethylene mass flows.

Table S1: Comparison of the isolated yield and the productivity calculated from the mass flow data for selected catalysts.

#	catalyst	polymerization temperature	Isolated polymer [g]	Ethylene mass flow [g]
1	**8-CH_3-I2**	30	1.9	2.0
2	**8-H-I2**	30	0.9	1.3
3	**8-CF_3-I2**	60	6.8	6.7
4	**8-CH_3-ant**	30	15.6	14.8

This data confirms, that the mass flow is a reliably measure for the amount of ethylene converted. At a low consumption of ~2 g h^{-1} accuracy effects to some extent.

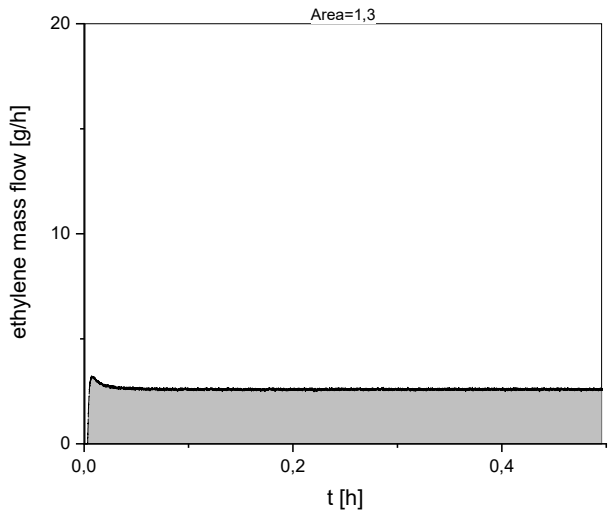


Figure S79: Mass flow plot of the polymerization with **8-H-I2** at T = 30°C (Table S1, entry 2). Example for a mass flow for a catalyst with a low activity.

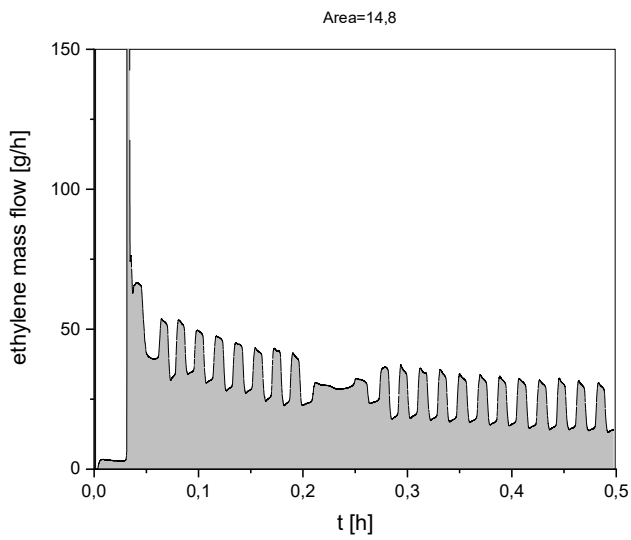


Figure S80: Mass flow plot of the polymerization with **8-CF$_3$-I2** at T = 60°C (Table S1, entry 3).

With the oxygen bridged complexes **4**, butenes are a major product. These are lost upon venting the reactor. The further work-up procedure removes volatiles in vacuo. Comparison of the ethylene consumption as recorded by the mass flow data (Table S2) with the amount on non-volatile products shows that the largest part of the products formed are volatiles (C_4, C_6, C_8).

Table S2: Oligomerization results with oxygen bridged catalyst precursors **4**.

#	precatalyst	T [°C]	non-volatile products [g]	Yield mass flow [g]
1	**4-CH_3-I2**	30	0.65	5.4
2	**4-CH_3-I2**	50	0.61	3.2
3	**4-CH_3-I2**	70	0.17	1.3
4	**4-H-I2**	30	1.43	2.4
5	**4-H-I2**	50	1.69	2.5
6	**4-H-I2**	70	0.73	1.3
7	**4-CF_3-I2**	30	0.33	1.4
8	**4-CF_3-I2**	50	1.82	2.0
9	**4-CF_3-I2**	70	1.06	1.5
10	**4-CH_3-ant**	30	1.10	3.3
11	**4-CH_3-ant**	50	2.43	7.4
12	**4-CH_3-ant**	70	1.50	6.6
13	**4-H-ant**	30	0.71	4.3
14	**4-H-ant**	50	3.60	7.9
15	**4-H-ant**	70	3.20	7.6
16	**4-CF_3-ant**	30	1.21	1.6
17	**4-CF_3-ant**	50	6.72	8.0
18	**4-CF_3-ant**	70	14.4	17.6

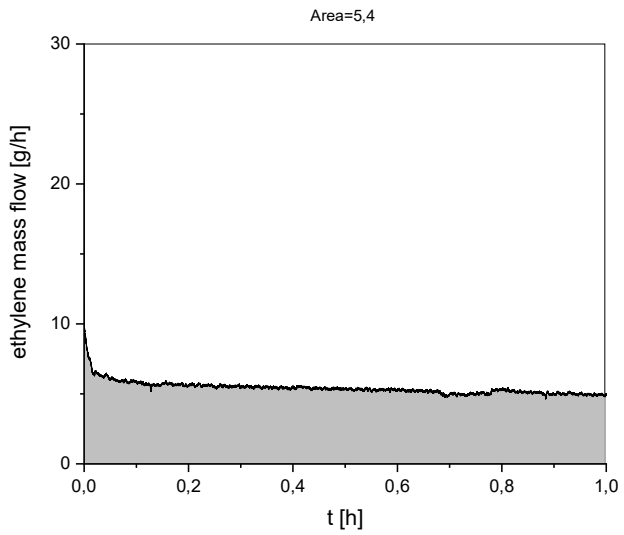


Figure S81: Mass flow plot of the polymerization with **4-CH_3-I2** at T = 30°C.

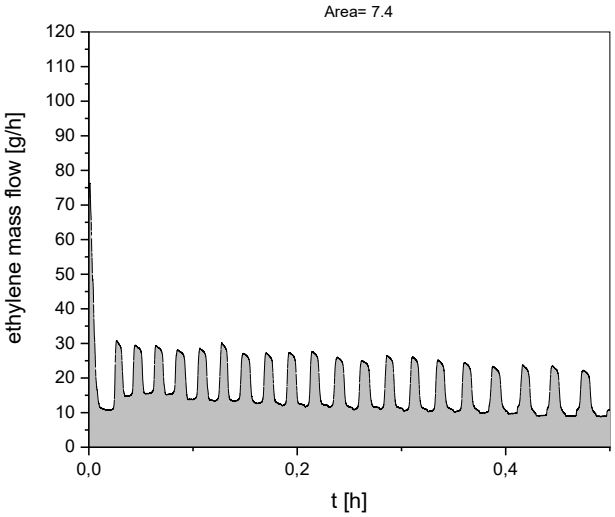


Figure S82: Mass flow plot of the polymerization with **4-CH$_3$-ant** at T = 50°C.

1.4.3. Thermal properties

The oligomers obtained by the catalyst precursors **4-CH$_3$-I2**, **4-H-I2**, **4-CH$_3$-ant** and **4-H-ant** are low viscous liquids with no observable melting point or glass transition point. An exemplary DSC-trace is shown in Figure S83. For the oligomers from catalyst precursors **4-CF$_3$-I2** and **4-CF$_3$-ant** a melting point could be observed (for an exemplary DSC trace see Figure S84).

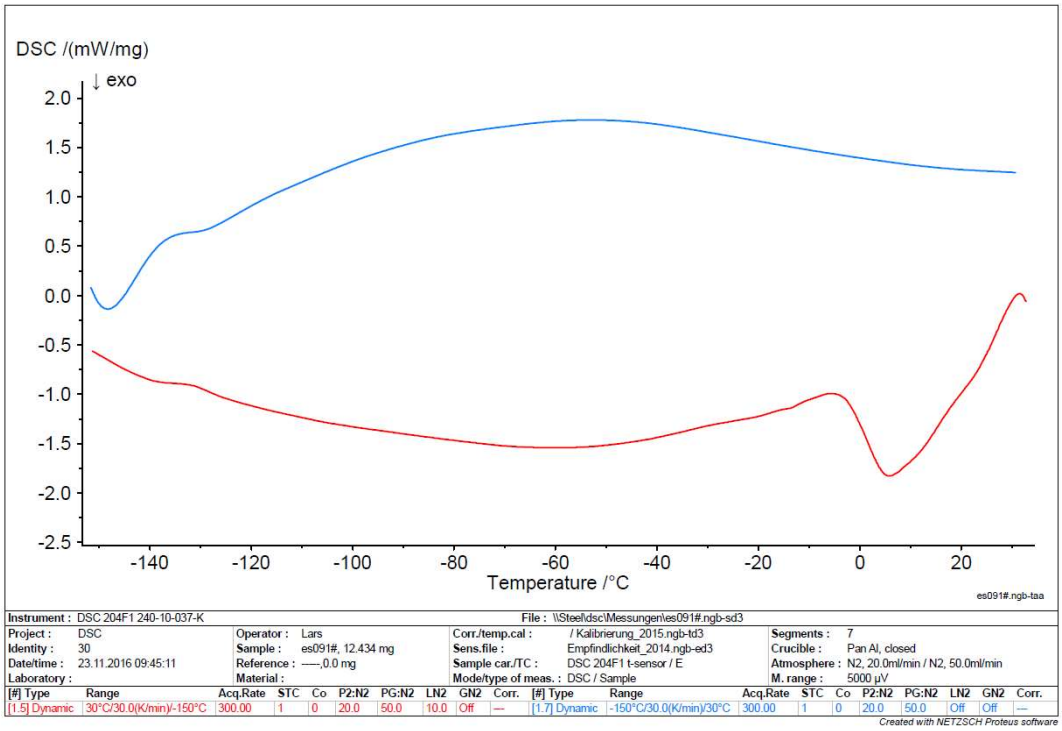


Figure S83: DSC trace of the non-volatile products obtained with complex **4-H-ant**, oligomerization conditions: 40 bar of ethylene, T = 60 °C, t = 30 min, n(cat) = 10 µmol.

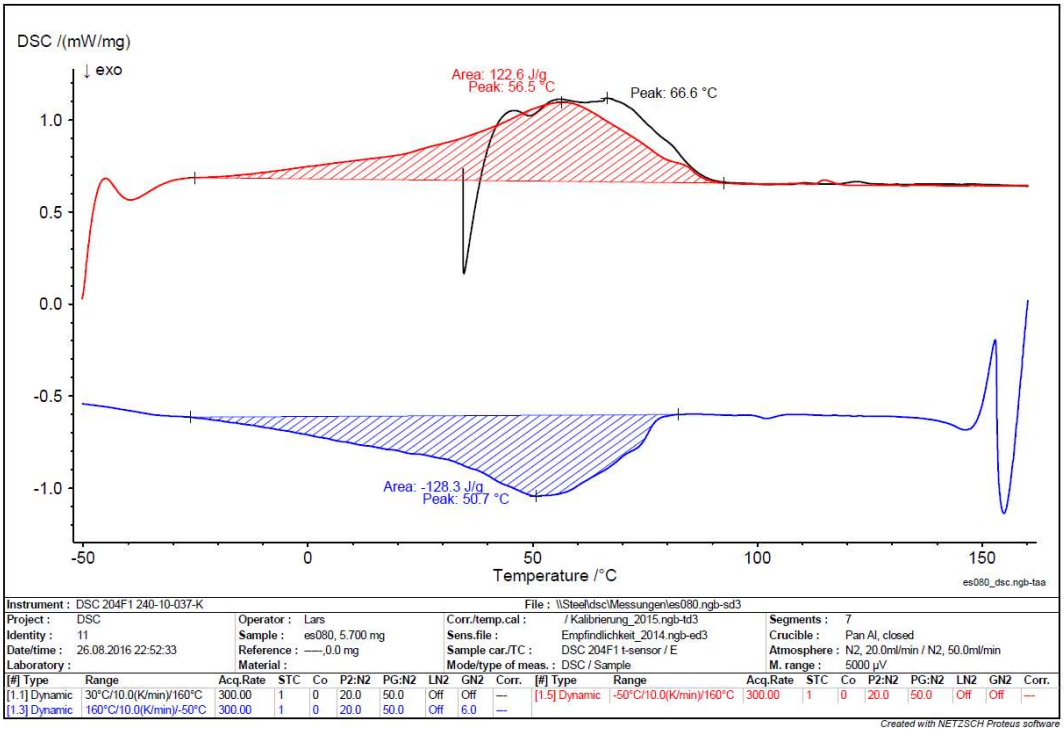


Figure S84: DSC trace of an oligomer obtained with complex **4-CF_3-I2**, oligomerization conditions: 40 bar of ethylene, T = 70 °C, t = 30 min, n(cat) = 10 µmol.

Melting points were obtained by DSC measurements. For exemplarily traces see Figure S85, Figure S86 and Figure S87.

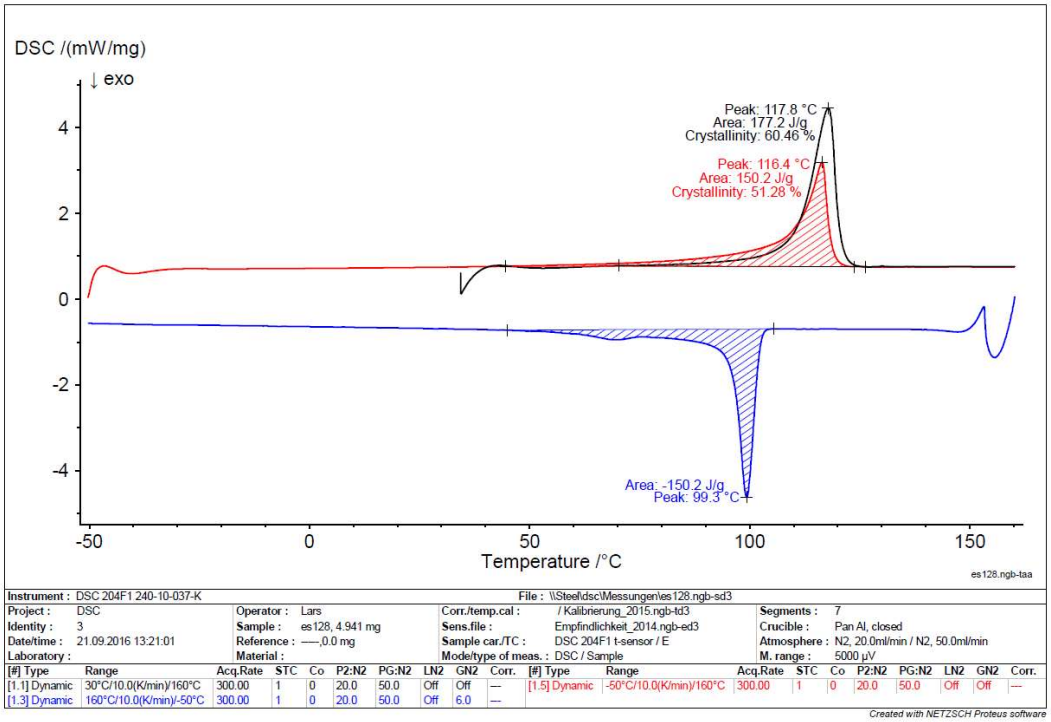


Figure S85: DSC trace of a polymer obtained with complex **8-CH$_3$-I2**, polymerization conditions: 40 bar of ethylene, T = 60 °C, t = 30 min, n(cat) = 10 µmol.

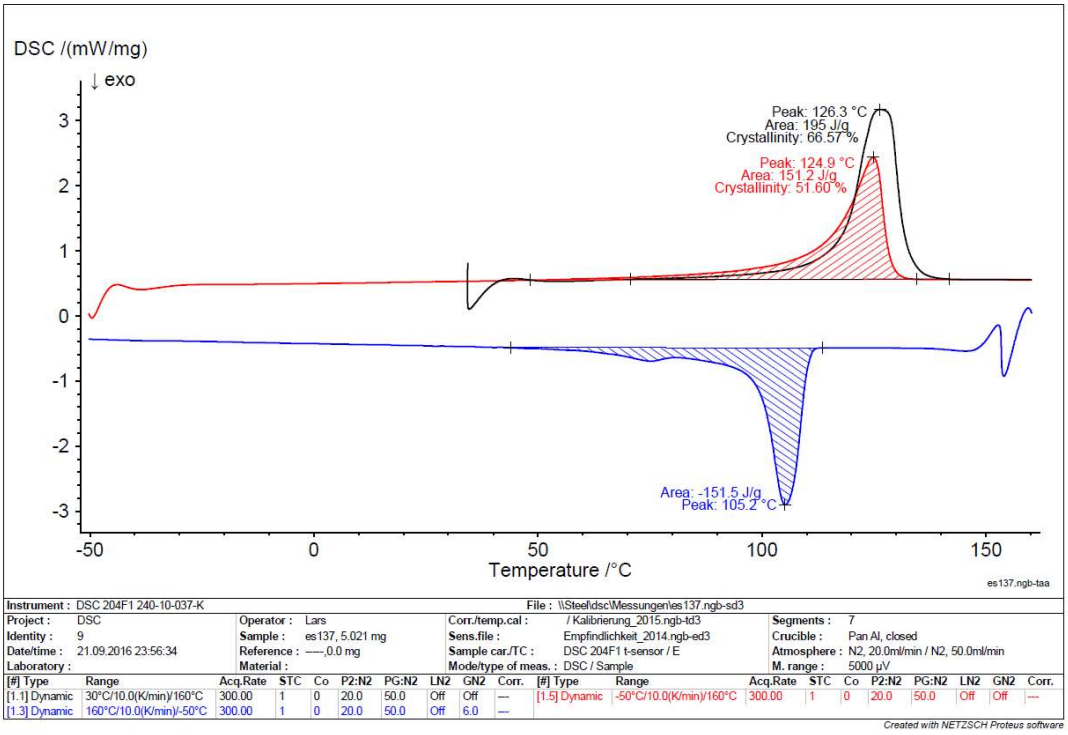


Figure S86: DSC trace of a polymer obtained with complex **8-H-ant**, polymerization conditions: 40 bar of ethylene, T = 60 °C, t = 30 min, n(cat) = 10 µmol.

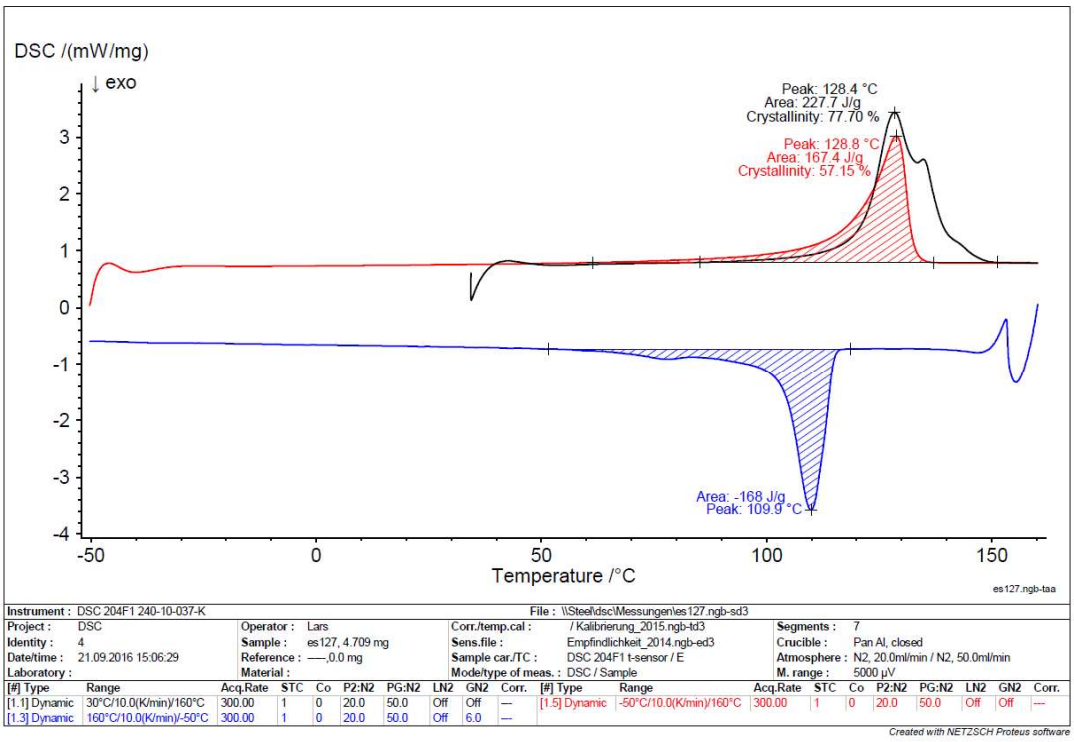


Figure S87: DSC trace of a polymer obtained with **8-CF$_3$-I2**, polymerization conditions: 40 bar of ethylene, T = 60 °C, t = 30 min, n(cat) = 10 µmol.

1.4.4 Molecular weight and microstructure determination

*Non-volatile products obtained by precatalysts **4***

The molecular weight was determined by NMR spectroscopy. For the oligomers obtained by the catalyst precursors **4-CH$_3$-I2**, **4-H-I2**, **4-CH$_3$-ant** and **4-H-ant** at least 50.0 mg oligomer was dissolved and ^{1}H spectra measured in $CDCl_3$ at room temperature. For the oligomers from catalyst precursors **4-CF$_3$-I2** and **4-CF$_3$-ant** the NMR analysis was obtained in $C_2D_2Cl_4$ at 388 K. $Cr(acac)_3$ (5 mg mL^{-1}) was added as paramagnetic relaxation agent.

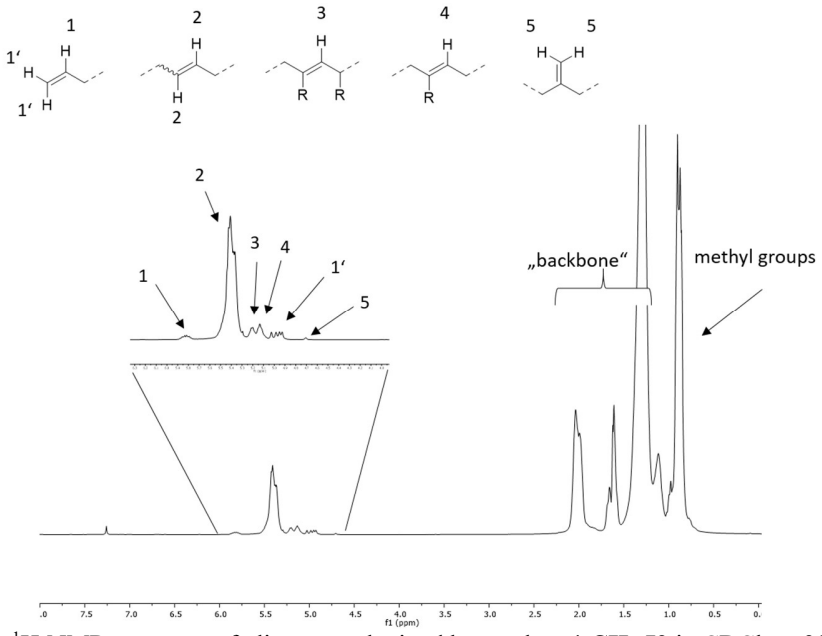


Figure S88: Exemplary ^{1}H-NMR spectrum of oligomers obtained by catalyst **4-CH$_3$-I2** in $CDCl_3$ at 300K.

The molecular weight was obtained according to:[7]

$$M_n = \frac{\left(\frac{I_{tot}}{4}\right)}{\left(\frac{I_2 + 2I_3 + 2I_4 + I_{1'} + I_5}{2}\right)} \cdot 28\ \frac{g}{mol}$$

I_{tot} is the integral of all signals.

Branching microstructures were determined by quantitative ^{13}C NMR spectra and analyzed[8] compared to previously reported highly branched oligomers.[7] The very low molecular weight and consequently large number of unsaturated groups from chain transfer gives rise to additional resonances and complicates assignments. Notably, methyl, ethyl and propyl branches can be identified and sec-butyl motifs (end-groups, that is a methyl branching in γ-position to a saturated chain end and possible a smaller amount of sec-Butyl branches).

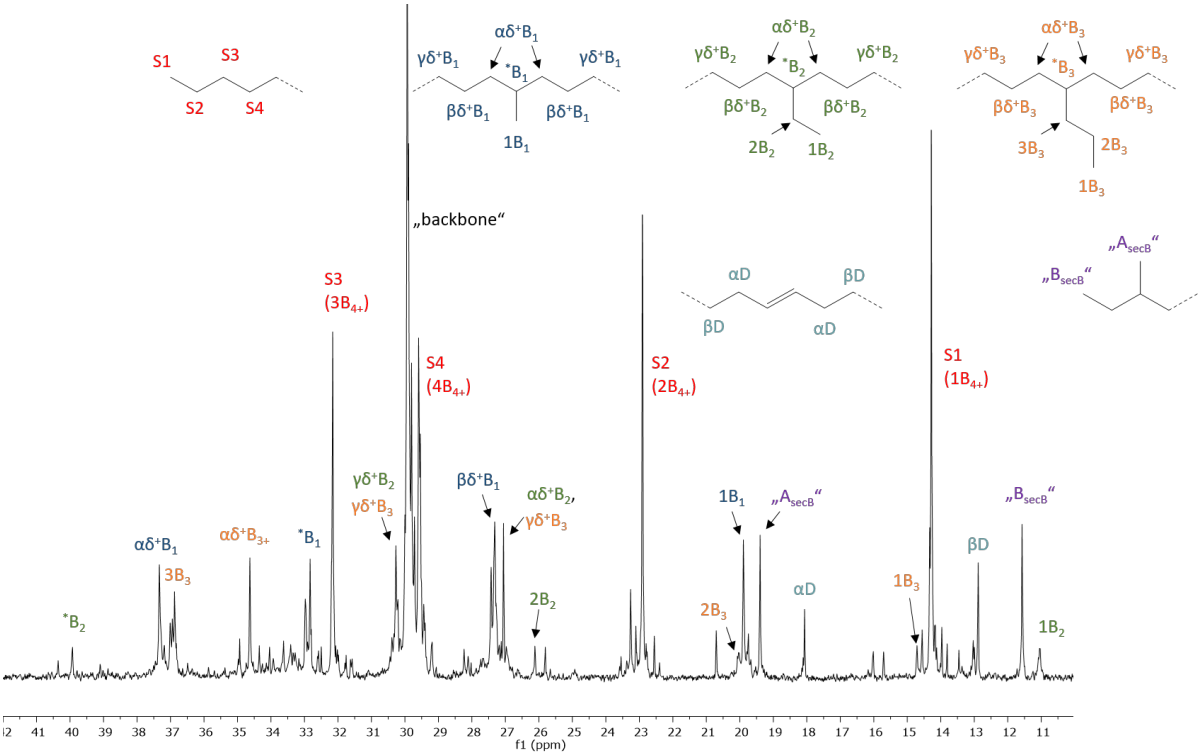


Figure S89: Exemplary ^{13}C-NMR spectrum of oligomers obtained by the catalyst **4-CH$_3$-I2** in CDCl$_3$ at 300K.

Degrees of branching were estimated according to

$$\frac{branches}{1000\ C} = \frac{I_{^1B_1} + I_{^1B_2} + I_{^1B_3} + I_{B_{secB}}}{I_{tot}}$$

Table S3: Microstructure analysis for the polymers obtained with oxygen bridged catalyst precursors **4**.

entry	precatalyst	t [min]	T [°C]	M_n [g mol^{-1}][a,b]	B[b,c]	methyl [%][b,d]	ethyl [%][b,d]	propyl [%][b,d]	sec-Butyl groups [%][b,d, e]
1	**4-CH_3-I2**	60	30	293	61	53	10	9	31
2	**4-CH_3-I2**	30	50	331	72	53	13	8	26
3	**4-CH_3-I2**	30	70	282	81	55	17	5	24
4	**4-H-I2**	60	30	281	56	67	6	5	22
5	**4-H-I2**	30	50	303	61	54	13	6	26
6	**4-H-I2**	30	70	267	70	50	14	5	31
7	**4-CF_3-I2**	30	30	1022	21	91	4	2	3
8	**4-CF_3-I2**	30	50	810	27	85	7	2	6
9	**4-CF_3-I2**	30	70	896	35	87	7	1	4
10	**4-CH_3-ant**	30	30	386	51	59	10	8	23
11	**4-CH_3-ant**	30	50	275	55	55	12	8	26
12	**4-CH_3-ant**	30	70	290	69	43	17	7	33
13	**4-H-ant**	30	30	338	42	59	8	13	20
14	**4-H-ant**	30	50	321	51	52	10	12	26
15	**4-H-ant**	30	70	321	50	42	17	9	32
16	**4-CF_3-ant**	30	30	1380	16	94	3	2	1
17	**4-CF_3-ant**	30	50	895	17	90	4	3	4
18	**4-CF_3-ant**	30	70	791	23	84	8	3	5

Oligomerization conditions: 100 mL of toluene, 40 bar of ethylene, n(cat) = 10 µmol, 1000 rpm. [a]Determined by ^{1}H-NMR spectroscopy comparing the unsaturated end groups with the backbone. [b]Volatiles not included [c]Branches per 1000 C atoms, determined by ^{13}C-NMR spectroscopy (inverse gated decoupled). [d]Determined by ^{13}C-NMR spectroscopy (inverse gated decoupled) [e]Relative to all branches.

*Polymers obtained by precatalysts **8***

Molecular weights were determined by GPC. Exemplary traces are given in Figure S90, Figure S91, Figure S92 and Figure S93.

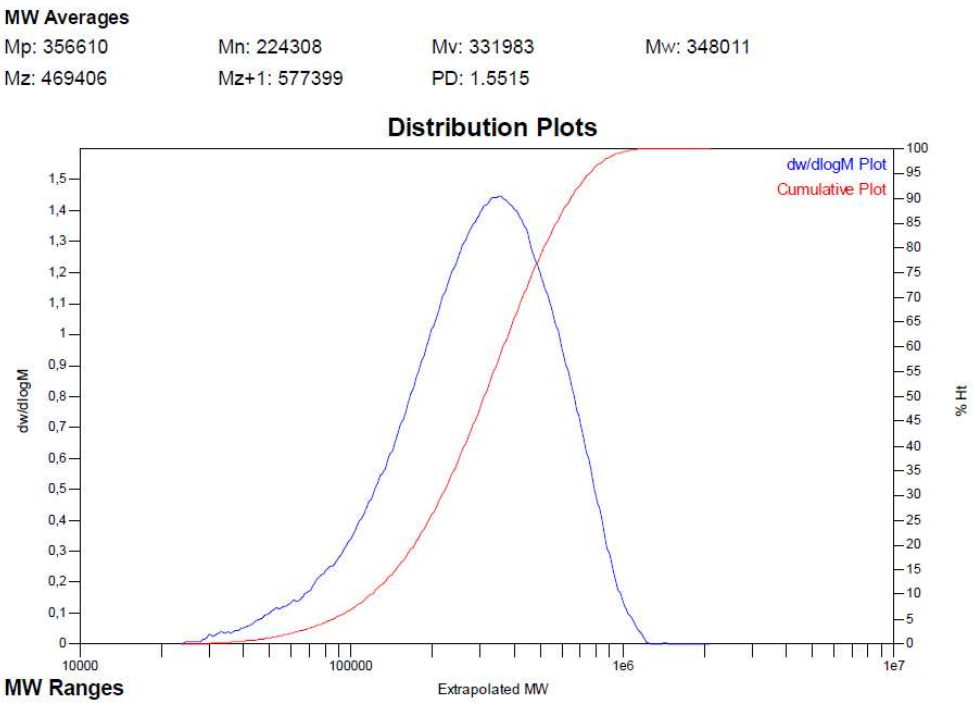


Figure S90: GPC trace of polymer obtained with **8-CH$_3$-I2**. Polymerization conditions: T = 30 °C, n = 10 µmol, p = 40 bar, t = 30 min.

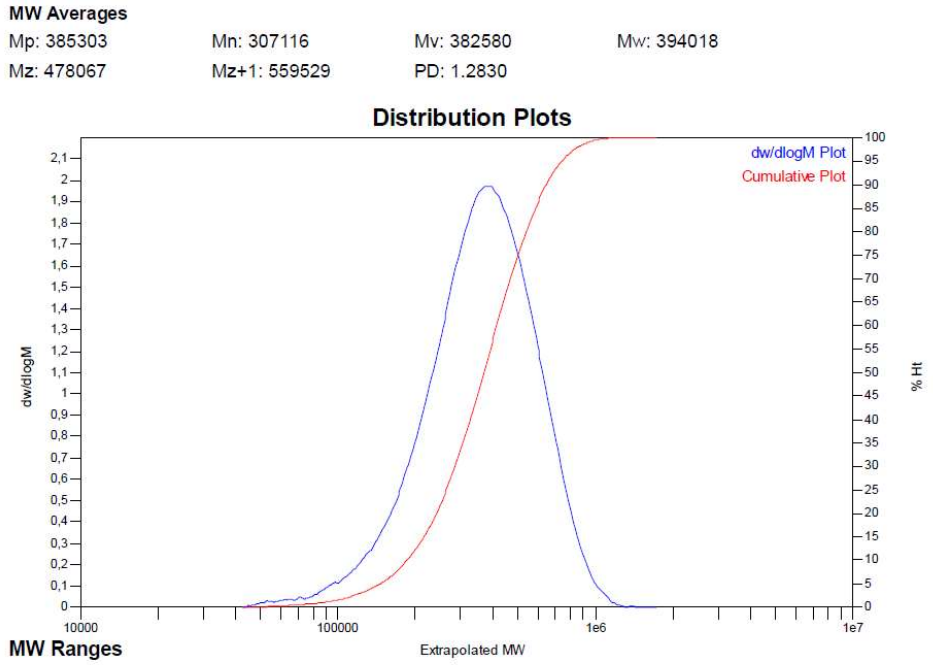


Figure S91: GPC trace of polymer obtained with **8-CF$_3$-ant**. Polymerization conditions: T = 30 °C, n = 10 µmol, p = 40 bar, t = 30 min.

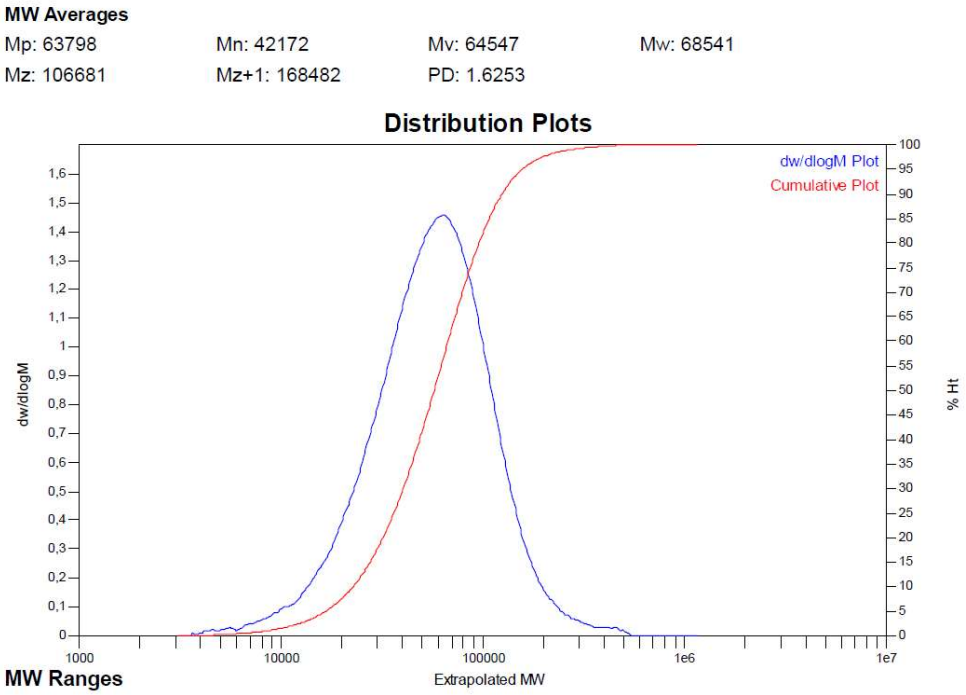


Figure S92: GPC trace of polymer obtained with **8-H-I2**. Polymerization conditions: T = 60 °C, n = 10 µmol, p = 40 bar, t = 30 min.

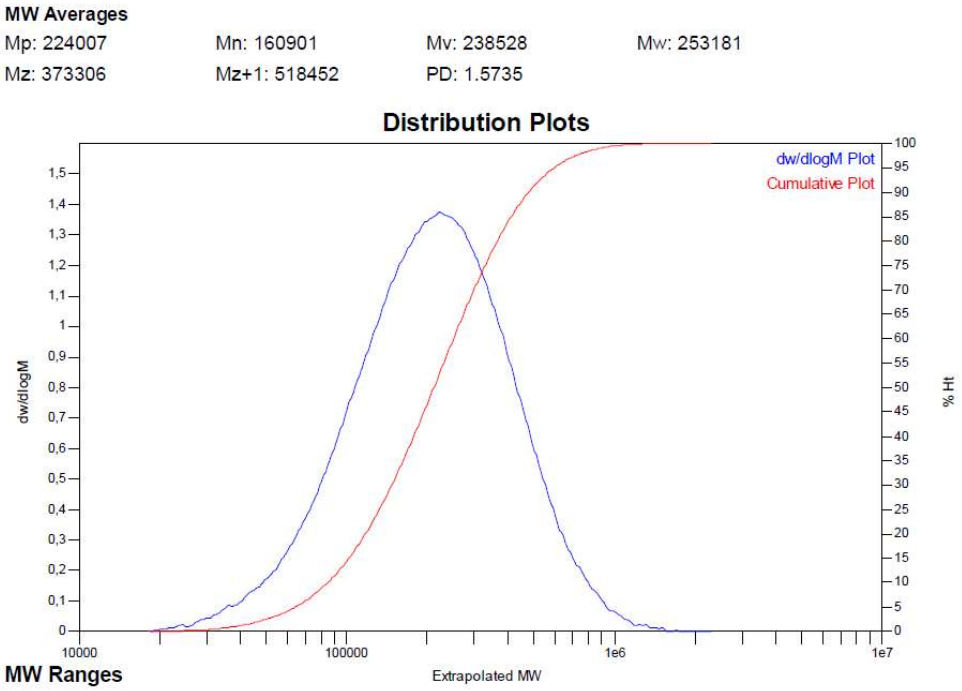


Figure S93: GPC trace of polymer obtained with **8-CF$_3$-ant**. Polymerization conditions: T = 60 °C, n = 10 µmol, p = 40 bar, t = 30 min.

Microstructures were determined by ^{13}C-NMR analysis was obtained in $C_2D_2Cl_4$ at 388 K. NMR spectra were recorded with addition of 5 mg mL^{-1} of Cr(acac)$_3$ as paramagnetic relaxation agent. At least 10 000 scans were performed.

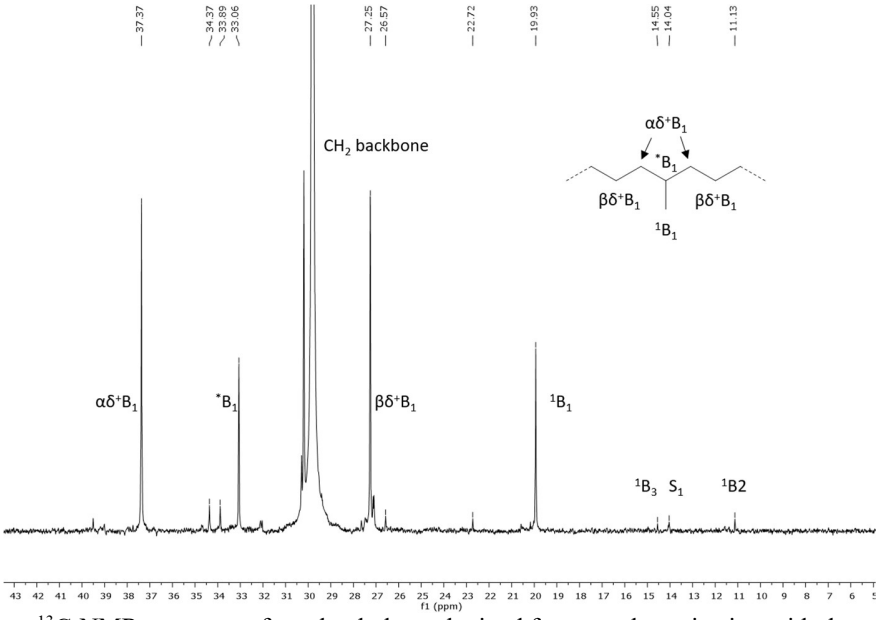


Figure S94: Exemplary ^{13}C-NMR spectrum of a polyethylene obtained from a polymerization with the catalyst precursors **8**.

The branching was calculated according to

$$\frac{branches}{1000\ C} = \frac{I_{1_{B_1}} + I_{1_{B_2}} + I_{1_{B_3}}}{I_{tot}}$$

I_{tot} is the integral of all signals.

Table S4: Microstructures of selected polymers obtained with CH_2-bridged precatalysts **8**.

entry	precatalyst	n (cat) [μmol]	T [°C]	M_n [kg mol^{-1}][a]	B[b]	methyl [%][c]	ethyl [%][c]	propyl [%][c]	C_{4+} [%][c]
1	**8-CH_3-I2**	10	60	57	11	98	2	/[d]	/[d]
2	**8-CH_3-I2**	10	30	224	4	100	/[d]	/[d]	/[d]
3	**8-H-I2**	10	60	42	15	95	3	2	/[d]
4	**8-H-I2**	10	30	127	4	100	/[d]	/[d]	/[d]
5	**8-CF_3-I2**	5	60	45	7	100	/[d]	/[d]	/[d]
6	**8-CF_3-I2**	10	60	32	6	100	/[d]	/[d]	/[d]
7	**8-CF_3-I2**	10	30	192	2	100	/[d]	/[d]	/[d]

[a]*D*etermined by GPC *versus* linear polyethylene standards at 160 °C. [b]Branches per 1000 C atoms, determined by ^{13}C-NMR spectroscopy. [c]Determined by ^{13}C-NMR spectroscopy. [d]Below the detection limit.

2. Cyclic voltammetry

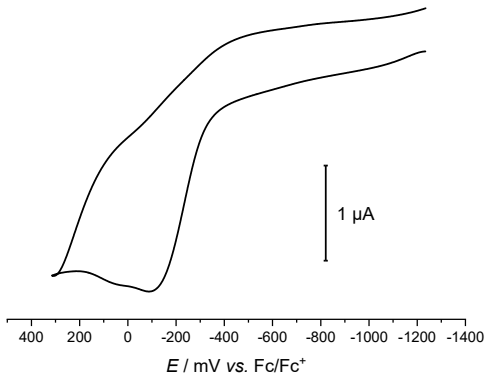


Figure S95: Cyclic voltamogramm of complex **4-CH$_3$-I2**.

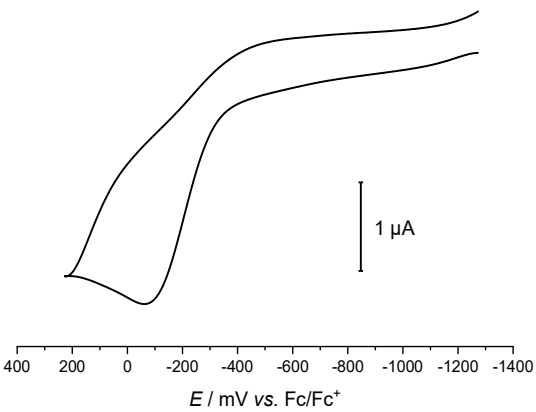


Figure S96: Cyclic voltamogramm of complex **4-H-I2**.

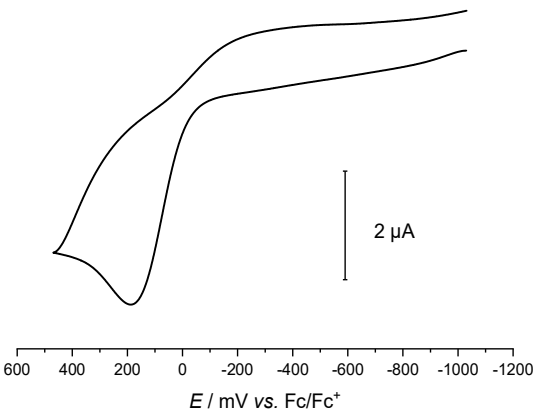


Figure S97: Cyclic voltamogramm of complex **4-CF$_3$-I2**.

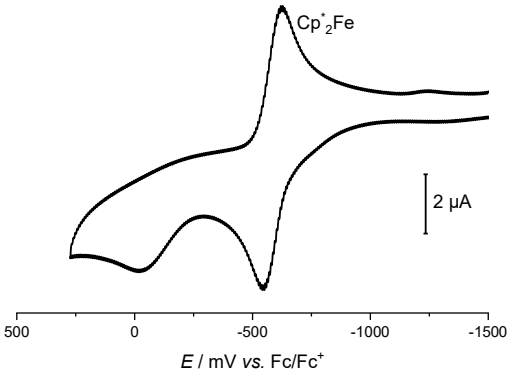


Figure S98: Cyclic voltamogramm of complex **4-CH$_3$-ant**. Due to the low stability of the complex in DCM, this CV was measured in THF. [Cp$_2^*$Fe] was added before adding the complex **4-CH$_3$-ant**.

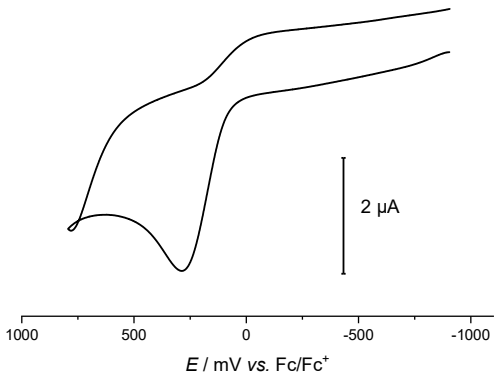


Figure S99 Cyclic voltamogramm of complex **4-CF$_3$-ant**.

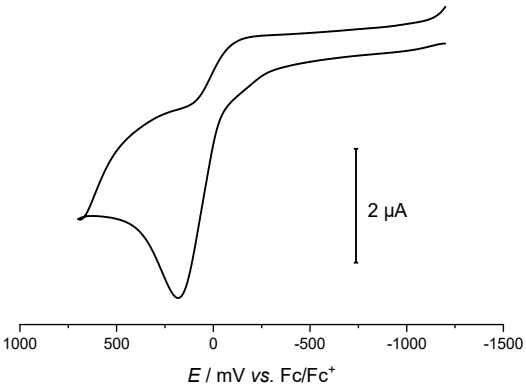


Figure S100: Cyclic voltamogramm of complex **8-CH$_3$-I2**.

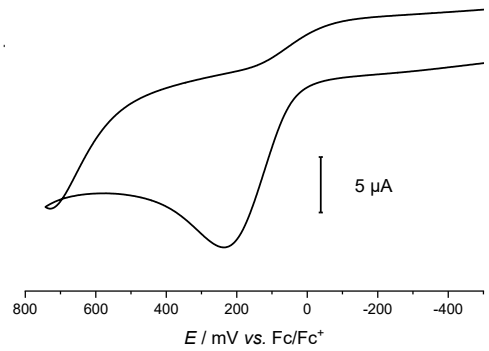


Figure S101: Cyclic voltamogramm of complex **8-H-I2**.

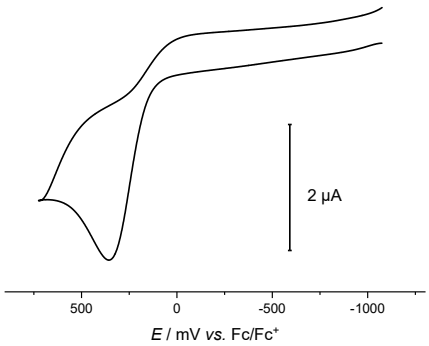


Figure S102: Cyclic voltamogramm of complex **8-CF$_3$-I2**.

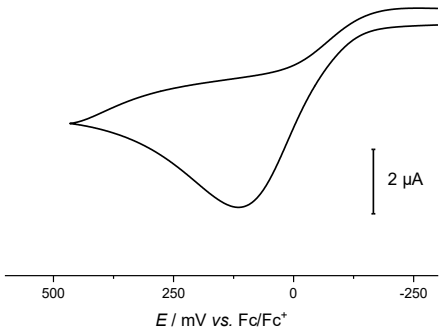


Figure S103 Cyclic voltamogramm of complex **8-CH$_3$-ant**.

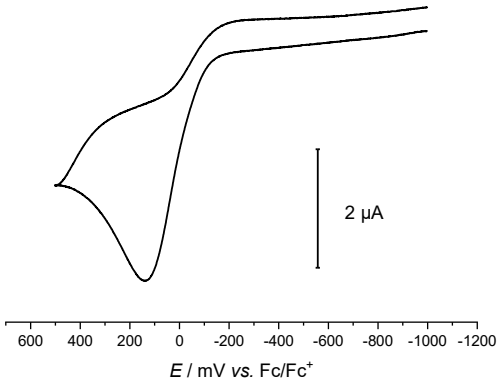


Figure S104: Cyclic voltamogramm of complex **8-H-ant**.

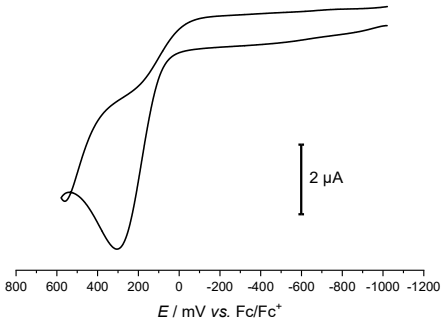


Figure S105: Cyclic voltamogramm of complex **8-CF$_3$-ant**.

3. Crystallographic data

3.1 Complex $[NiI_2(pyr)_2]$

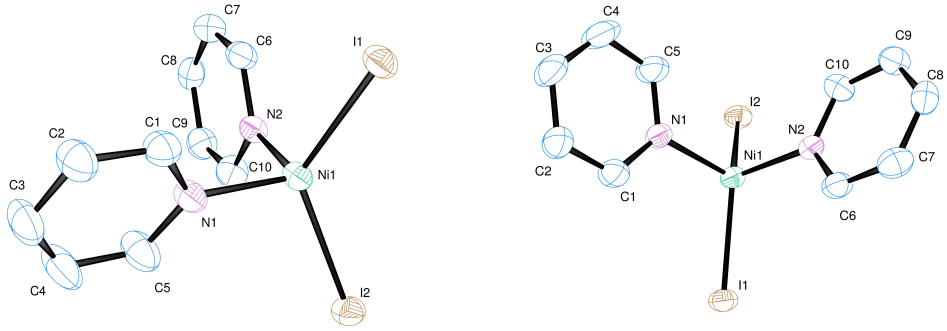


Table S5: Crystal data and structure refinement for complex $[(pyr)_2NiI_2]$.

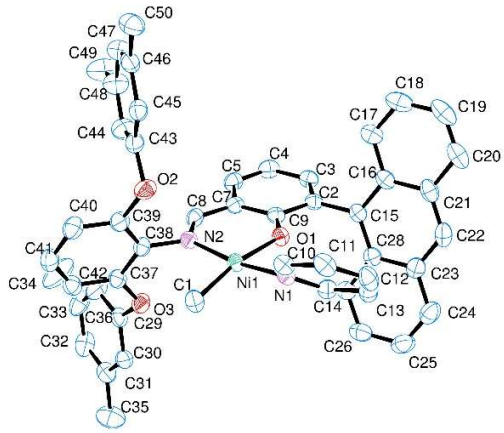
Identification code	CCDC 1885917
Empirical formula	$C_{10}H_{10}N_2NiI_2$
Formula weight	470.71
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.1754(9)
b/Å	17.7040(13)
c/Å	8.5606(8)
α/°	90
β/°	100.520(7)
γ/°	90
Volume/Å^3	1367.2(2)
Z	4
ρ_{calc}g/cm^3	2.2866
μ/mm^{-1}	5.906
F(000)	870.4
Crystal size/mm^3	0.35 × 0.15 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.52 to 53.64
Index ranges	$-11 \leq h \leq 11$, $-22 \leq k \leq 22$, $-10 \leq l \leq 10$
Reflections collected	12164
Independent reflections	2922 [R_{int} = 0.1661, R_{sigma} = 0.0926]
Data/restraints/parameters	2922/0/136
Goodness-of-fit on F^2	0.779
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.1081
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.1142
Largest diff. peak/hole / e Å^{-3}	1.40/-1.97

Experimental

Single crystals of $C_{10}H_{10}N_2NiI_2$ $[NiI_2(pyr)_2]$ were obtained by layering a saturated benzene solution with pentane. A suitable crystal was selected and placed on a STOE IPDS 2T diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[3], the structure was solved with the ShelXT.[4] Structure

solution program using Intrinsic Phasing and refined with the olex2.refine[5] refinement package using Gauss-Newton minimization. Graphical representation were created by the ORTEP-3 V2.02. for Windows XP software package.[6]

3.2 Complex **4-CH$_3$-ant**



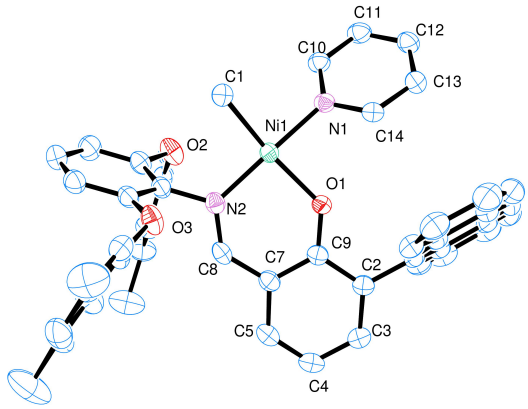


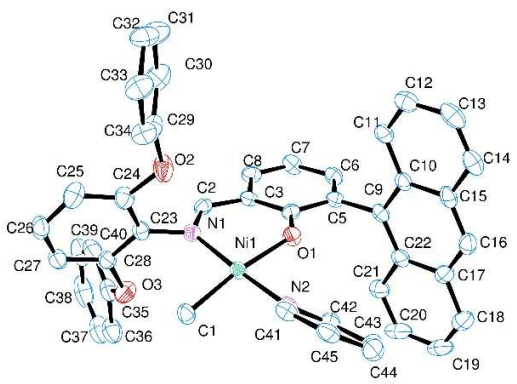
Table S6: Crystal data and structure refinement for complex **4-CH$_3$-ant**

Identification code	CCDC 1885914
Empirical formula	$C_{49}H_{42}N_2NiO_3$
Formula weight	765.58
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.7542(7)
b/Å	11.3286(5)
c/Å	22.9072(9)
α/°	90
β/°	108.497(3)
γ/°	90
Volume/Å^3	3877.1(3)
Z	4
ρ_{calc}g/cm^3	1.3115
μ/mm^{-1}	0.546
F(000)	1610.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.74 to 53.68
Index ranges	$-19 \leq h \leq 19$, $-14 \leq k \leq 14$, $-28 \leq l \leq 29$
Reflections collected	55504
Independent reflections	8267 [R_{int} = 0.0703, R_{sigma} = 0.0444]
Data/restraints/parameters	8267/0/501
Goodness-of-fit on F^2	0.815
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1088
Final R indexes [all data]	R_1 = 0.0657, wR_2 = 0.1222
Largest diff. peak/hole / e Å^{-3}	0.69/-0.58

Experimental

Single crystals of $C_{49}H_{42}N_2NiO_3$ [**4-CH$_3$-ant**] were obtained by layering a saturated benzene solution with pentane. A suitable crystal was selected and placed on a STOE IPDS 2T diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[3], the structure was solved with the ShelXT.[4] Structure solution program using Intrinsic Phasing and refined with the olex2.refine[5] refinement package using Gauss-Newton minimization. Graphical representation were created by the ORTEP-3 V2.02. for Windows XP software package.[6]

3.3 Complex **4-H-ant**



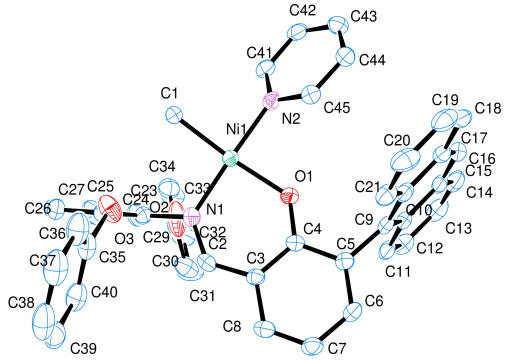


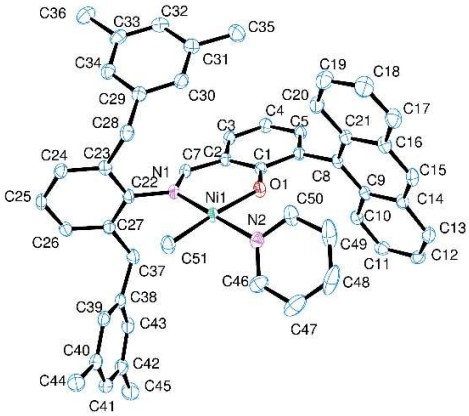
Table S7: Crystal data and structure refinement for complex **4-H-ant**.

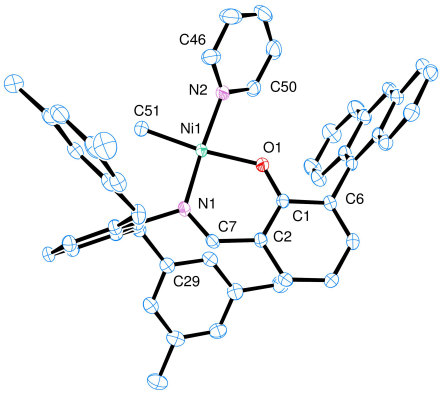
Identification code	CCDC 1885913
Empirical formula	$C_{45}H_{34}N_2NiO_3$
Formula weight	709.48
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2893(10)
b/Å	22.876(3)
c/Å	15.2872(14)
α/°	90
β/°	100.720(8)
γ/°	90
Volume/Å^3	3535.5(6)
Z	4
ρ_{calc}g/cm^3	1.3328
μ/mm^{-1}	0.593
F(000)	1482.0
Crystal size/mm^3	0.5 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.24 to 53.72
Index ranges	$-13 \leq h \leq 12$, $-29 \leq k \leq 28$, $-18 \leq l \leq 19$
Reflections collected	52357
Independent reflections	7540 [R_{int} = 0.3823, R_{sigma} = 0.1892]
Data/restraints/parameters	7540/0/461
Goodness-of-fit on F^2	0.819
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1219
Final R indexes [all data]	R_1 = 0.1319, wR_2 = 0.1683
Largest diff. peak/hole / e Å^{-3}	0.85/-1.04

Experimental

Single crystals of $C_{45}H_{34}N_2NiO_3$ [**4-H-ant**] were obtained by layering a saturated benzene solution with pentane. A suitable crystal was selected and placed on a STOE IPDS 2T diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[3], the structure was solved with the ShelXT.[4] Structure solution program using Intrinsic Phasing and refined with the olex2.refine[5] refinement package using Gauss-Newton minimization. Graphical representation were created by the ORTEP-3 V2.02. for Windows XP software package.[6]

3.4 Complex **8-CH$_3$-ant**





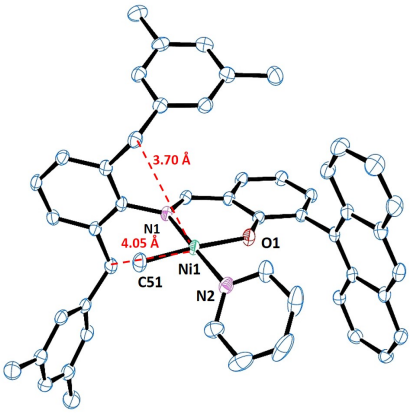


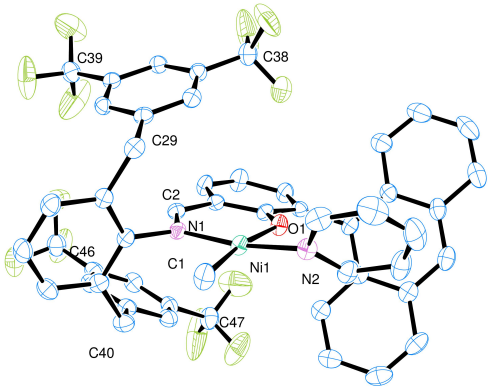
Table S8: Crystal data and structure refinement for complex **8-CH_3-ant**.

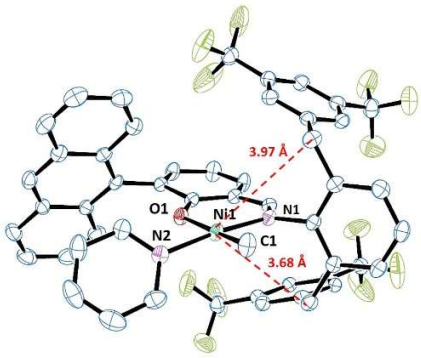
Identification code	CCDC 1885915
Empirical formula	$C_{51}H_{46}N_2NiO$
Formula weight	761.64
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.7735(9)
b/Å	11.6801(5)
c/Å	23.4151(15)
α/°	90
β/°	81.618(5)
γ/°	90
Volume/Å^3	3997.3(4)
Z	4
ρ_{calc}g/cm^3	1.2655
μ/mm^{-1}	0.526
F(000)	1610.0
Crystal size/mm^3	0.4 × 0.1 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.08 to 53.68
Index ranges	$-18 \leq h \leq 18$, $-13 \leq k \leq 14$, $-29 \leq l \leq 29$
Reflections collected	51427
Independent reflections	8489 [R_{int} = 0.1064, R_{sigma} = 0.0545]
Data/restraints/parameters	8489/0/501
Goodness-of-fit on F^2	0.762
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0954
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.1047
Largest diff. peak/hole / e Å^{-3}	0.43/-0.49

Experimental

Single crystals of $C_{51}H_{46}N_2NiO$ [**8-CH_3-ant**] were obtained by layering a saturated benzene solution with pentane. A suitable crystal was selected and placed on a STOE IPDS 2T diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[3], the structure was solved with the ShelXT.[4] Structure solution program using Intrinsic Phasing and refined with the olex2.refine[5] refinement package using Gauss-Newton minimization. Graphical representation were created by the ORTEP-3 V2.02. for Windows XP software package.[6]

3.5 Complex **8-CF$_3$-ant**





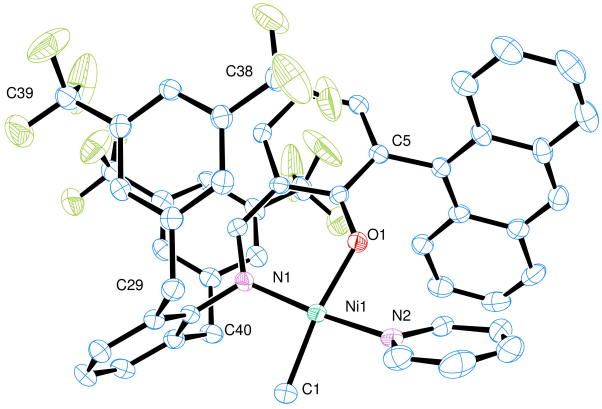


Table S9: Crystal data and structure refinement for complex **8-CF_3-ant**.

Identification code	CCDC 1885916
Empirical formula	$C_{51}H_{34}F_{12}N_2NiO$
Formula weight	977.53
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	11.9265(9)
b/Å	13.2159(10)
c/Å	14.9495(11)
α/°	100.980(6)
β/°	102.267(6)
γ/°	104.288(6)
Volume/$Å^3$	2156.7(3)
Z	2
ρ_{calc}g/cm^3	1.5089
μ/mm^{-1}	0.545
F(000)	804.0
Crystal size/mm^3	0.8 × 0.5 × 0.3
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.3 to 53.64
Index ranges	$-14 \leq h \leq 15$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	31956
Independent reflections	9166 [R_{int} = 0.1069, R_{sigma} = 0.0976]
Data/restraints/parameters	9166/0/605
Goodness-of-fit on F^2	0.862
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1337
Final R indexes [all data]	R_1 = 0.1026, wR_2 = 0.1586
Largest diff. peak/hole / e $Å^{-3}$	0.90/-0.65

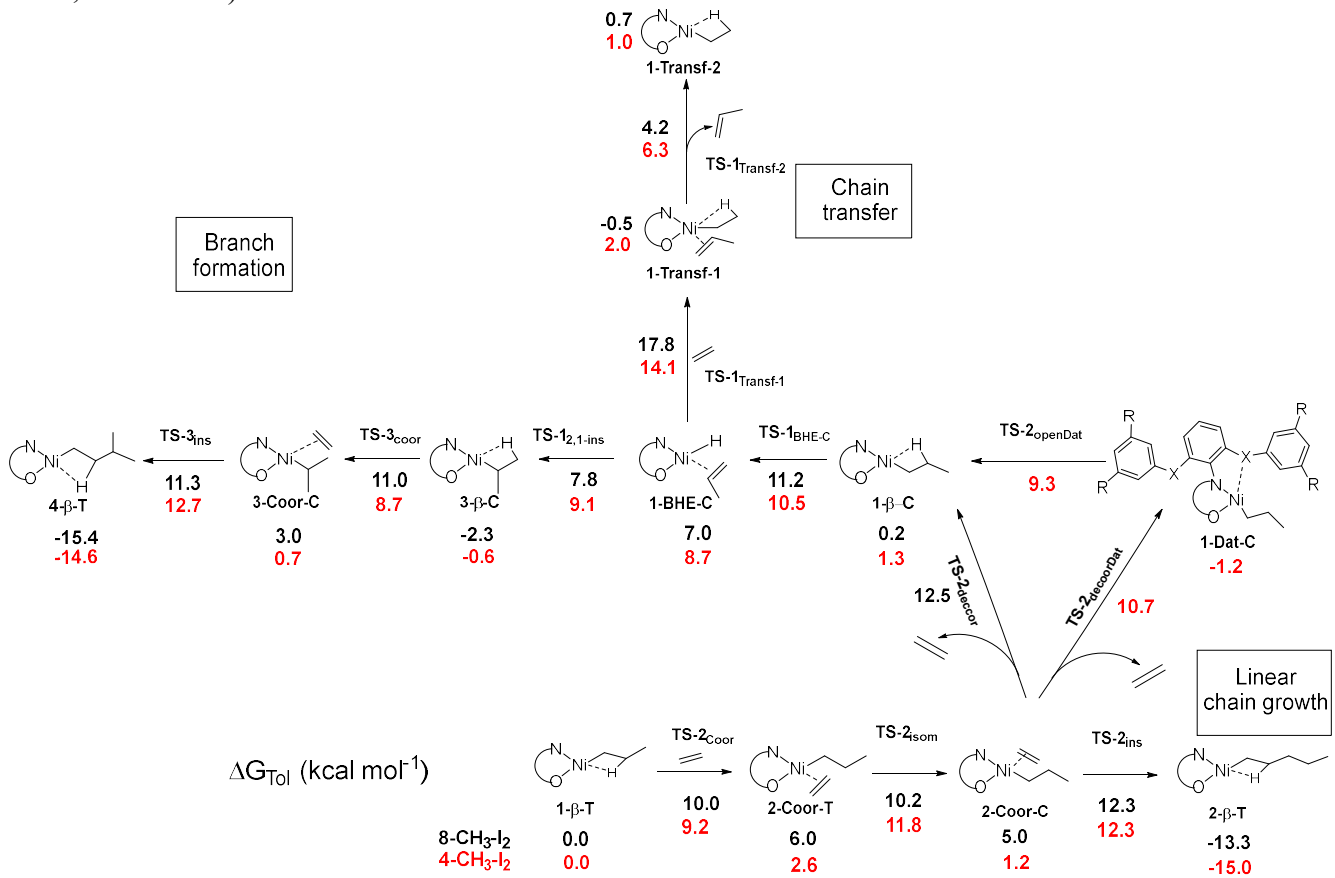
Experimental

Single crystals of $C_{51}H_{34}F_{12}N_2NiO$ [**8-CF_3-ant**] were obtained by layering a saturated benzene solution with pentane. A suitable crystal was selected and placed on a STOE IPDS 2T diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[3], the structure was solved with the ShelXT.[4] Structure solution program using Intrinsic Phasing and refined with the olex2.refine[5] refinement package using Gauss-Newton minimization. Graphical representation were created by the ORTEP-3 V2.02. for Windows XP software package.[6]

4. Computational details

All DFT geometry optimizations were performed at the GGA BP86[9,10,11] level with the Gaussian09 package.[12] The electronic configuration of the systems was described with the 631G basis set for H, C, N, F, and O while for I and Ni the quasi-relativistic LANL2DZ ECP effective core potential was adopted.[13] All geometries were characterized as minimum or transition state, respectively, through frequency calculations. The reported free energies were built through single point energy calculations on the BP86/6-31G level geometries using the M06 functional and the triple-ζ TZVP[14, 15] basis set on main group atoms. Solvent effects were included with the PCM model using toluene as the solvent.[16,17] To this M06/TZVP electronic energy in solvent, thermal corrections were included from the gas-phase frequency calculations at the BP86/6-31G.

We performed calculations of all important intermediates and transition states involved in the linear chain growth, branch formation and chain transfer reaction during the polymerization, starting from the product of the first ethylene insertion into an Ni-Me bond (**1-β-T**, as a reference point, Gibbs free energies in kcal mol^{-1}; Scheme S1).



Scheme S1: Gibbs free energies (ΔG_{Tol} in kcal mol^{-1}) of all important intermediates and transition states for linear chain growth, chain transfer, and branch formation with **8-CH$_3$-I$_2$** (black) and **4-CH$_3$-I$_2$** (red). Energies are relative to the **1-β-T**.

Starting from **1-β-T**, ethylene coordination occurs by opening of the β-agostic interaction and requires overcoming a free energy barrier of 10.0 (**8-CH$_3$-I**) and 9.2 (**4-CH$_3$-I**) kcal mol^{-1}. For both complexes the resulting **2-Coor-T** (at 6.0 and 2.6 kcal mol^{-1} from **1-β-T**, respectively) undergoes isomerization to the slightly less stable **2-Coor-C** intermediate via the tetrahedral four-coordinated transition state **TS-2$_{isom}$**. Once the system reaches **2-Coor-C**, calculation results show that an ethylene decoordination reaction competes with the ethylene insertion. Migratory insertion via **TS-2$_{ins}$** yields the stable β-agostic complex, **2-β-T**. The overall energy barrier from **1-β-T** to **TS-2$_{ins}$** amounts to 12.3 kcal mol^{-1} for both systems **8-**

CH_3-I and **4-CH_3-I**, so the two systems behave similarly in the linear chain growth step. The ethylene insertion transition state assumes a square-planar geometry (Figure S106).

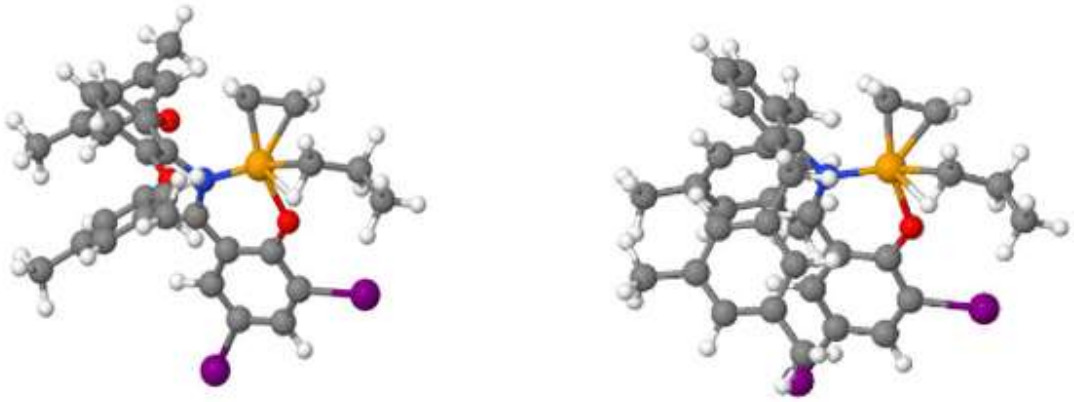
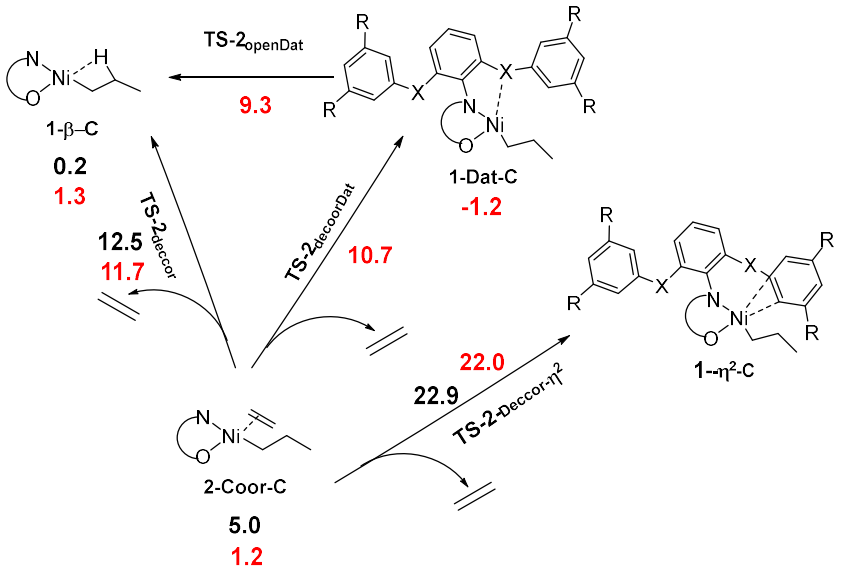


Figure S106. Ethylene insertion transition **TS-2_{ins}** for **4-CH_3-I** (left) and **8-CH_3-I** (right).

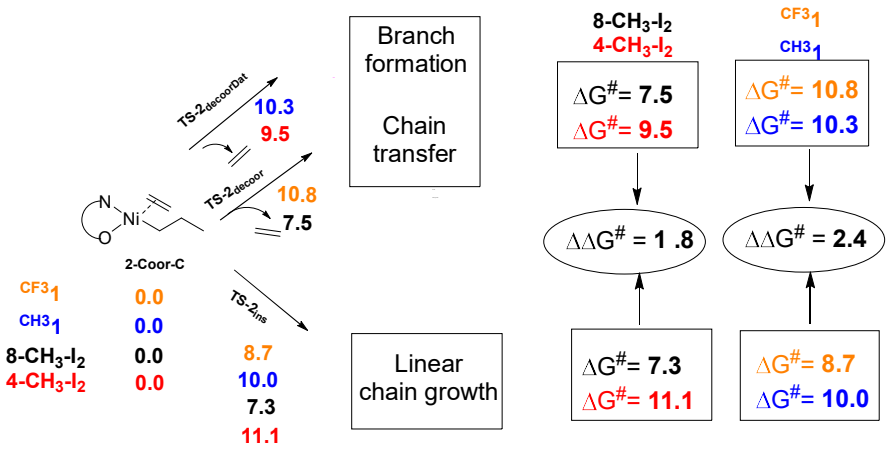
Considering the competitive monomer decoordination, the release of ethylene preferentially occurs direct by **2-TS_{decoor}** in the case of the ethylene bridged system **8-CH_3-I** and preferentially via the two step pathway (**TS-$2_{decoorDat}$** and **TS-$2_{openDat}$**) in the case of the oxygen-bridged system.
In fact, in the case of **8-CH_3-I** the ethylene decoordination is mediated by the hydrogen involved in the β-agostic intermediate and requires overcoming an energetic barrier of 12.5 kcal mol^{-1}, 0.2 kcal mol^{-1} higher than the competitive insertion barrier ($\Delta\Delta G^{\#}$ of -0.2 kcal mol^{-1}).
Both **TS-$2_{decoorDat}$** and **TS-2_{decoor}** are penta-coordinated species with a pyramidal geometry.
In the case of **4-CH_3-I**, first ethylene is displaced by a coordination of the oxygen atom of the bridge to the Ni center (formation of **1-Dat-C**, 1.2 kcal mol^{-1} more stable than **1-β-T**), then this coordination is replaced by the β-agostic interaction of the chain (**1-β-C**). The rate determining step in this case is **TS-$2_{decoorDat}$** with a barrier of 10.7 kcal mol^{-1}, 1.6 kcal mol^{-1} lower than the competitive insertion barrier ($\Delta\Delta G^{\#}$of 1.6 kcal mol^{-1}). All these results account for an easier formation of **1-β-C** from **1-β-T** for the oxygen-bridged system. Since both chain transfer and branch formation pathways start from **1-β-T**, these results agree with the experimentally observed behavior of **4-CH_3-I2** to produce low molecular weight oligomers.

From **1-β-C** the β-hydrogen elimination leads to formation of the intermediate **1-BHE-C**. Considering the branch formation pathway, the coordinated propene in **1-BHE-C** can reinsert in a 2,1-fashion via **TS-$1_{2,1\text{-}ins}$**, leading to the β-agostic resting state **3-β-C**. Coordination of a new ethylene molecule displaces the agostic interaction, leading to intermediate **3-Coor-C**. Finally, monomer insertion into the Ni-isopropyl bond via **TS-3_{ins}** leads to the methyl branched product **4-β-T**. For both **4-CH_3-I** and **8-CH_3-I** this insertion is the rate-determining step along the branch formation pathway with an energetic barrier of 12.9 and 11.3 kcal mol^{-1} for **4-CH_3-I** and **8-CH_3-I**, respectively.
From **1-β-C**, chain transfer occurs via coordination and direct insertion of an incoming ethylene molecule via the penta-coordinate transition state **TS-$1_{Transf\text{-}1}$**, with an overall barrier of 15.3 kcal mol^{-1} for **4-CH_3-I** and of 17.8 kcal mol^{-1} for **8-CH_3-I**. The following release of propene leads to the β-agostic complex **1-Transf-2**, which can start the growth of a new polymer chain.



Scheme S2: Gibbs free energies (ΔG_{Tol} in kcal mol^{-1}) of different ethylene decoordination transition states with **8-CH$_3$-I$_2$** (black) and **4-CH$_3$-I$_2$** (red).

In order to highlight the effect of the ligands' steric demand on the reaction barriers we compare the results obtained in this work with previously reported data for a related N-terphenyl system.[18]



Scheme S3: Comparison between the two competitive pathways of the ethylene decoordination and insertion leading to branch formation /chain transfer reactions and linear chain growth, respectively for ^{CH3}**1** (blue)[18], ^{CF3}**1** (orange)[18], **8-CH$_3$-I2** (black) and **4-CH$_3$-I2** (red). Free energies (ΔG_{Tol} in kcal mol^{-1}).

In detail, both monomer insertion barriers and decoordination barriers are lower with **8-CH$_3$-I and 4-CH$_3$-I** systems due to the flexibility of the salicylaldiminato ligand that can be pushed away from the metal leaving more space for the substrate (Figure S107).

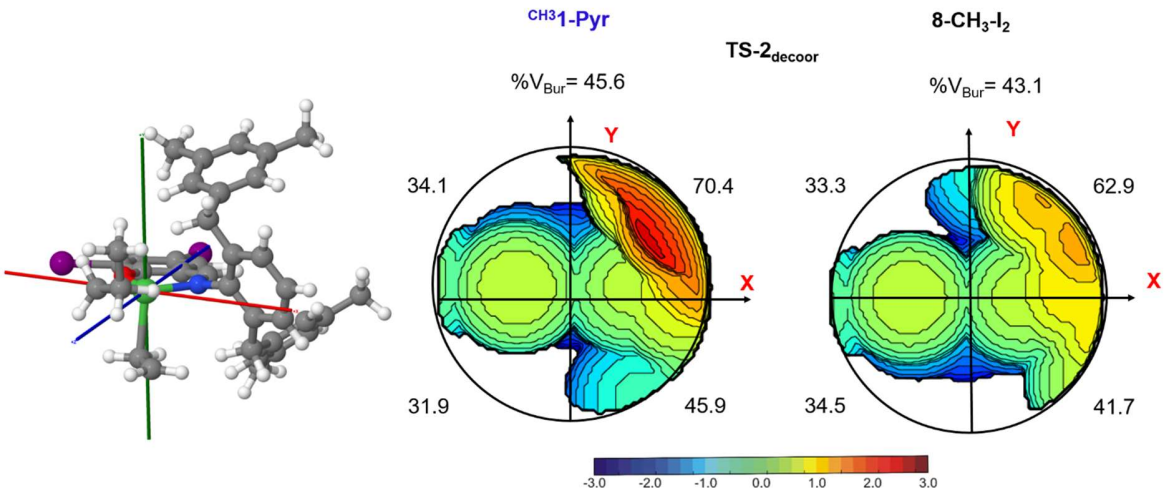


Figure S107: Buried volume analysis and topographic steric maps of the N,O ligand in **TS-2$_{decoor}$** species for **^{CH3}1**[18] and **8-CH$_3$-I2**. The complexes are oriented as shown for **^{CH3}1** on the left. In **^{CH3}1** the high steric hindrance in the NW quadrant pushes the methyl of the chain towards the monomer; in the **8-CH$_3$-I2** the methyl group of the chain is orientated further from the monomer thanks to the lower steric hindrance.

Since decoordination transition states are penta-coordinated species with a pyramidal geometry, they suffer the steric pressure of the ligand to a greater extent. As a consequence, the corresponding barriers decrease more with less hindered systems, i.e. **8-CH$_3$-I** and **4-CH$_3$-I**.

Going further, the molecular mass/branch ratio depends on the competition between monomer insertion and de-coordination starting from **2-Coor-C**. To this extent, the $\Delta\Delta^{\#}G$ is calculated as 1.8 kcal mol^{-1} for **8-CH$_3$-I** and **4-CH$_3$-I** systems and 2.4 kcal mol^{-1} for **^{Me}1**[18], **^{CF3}1**[18] (see Scheme S3). As consequence the results explain the higher degree of branching (and lower molecular mass) for **^{Me}1** and **4-CH$_3$-I** respect to **^{CF3}1** and **8-CH$_3$-I,** as observed experimentally.

Moreover, the system **4-CH$_3$-I** shows the lowest decoordination barrier (10.7 kcal mol^{-1}) and, above all, the highest $\Delta\Delta^{\#}G$ between insertion and decoordination of the monomer ((11.1-9.5) kcal mol^{-1}), in agreement with the high number of branches and lowest molecular mass for the product obtained with **4-CH$_3$-I**.

4.1 Internal energies (A.U.) in gas phase

Table S10: Internal energies (A.U.) in gas phase

	E_Lan2dz_6-31G(d)			E_Lan2dz_6-31G(d)
4-CH_3-I_2	A.U.		**8-CH_3-I_2**	A.U.
ethylene	-78,581395302		**ethylene**	-78,581395302
1-β-T	-1710,756351490		**1-β-T**	-1638,950834150
TS-2$_{Coor}$	-1789,159251000		**TS-2$_{Coor}$**	-1717,528515720
2-Coor-T	-1789,357025860		**2-Coor-T**	-1717,521789000
TS-2$_{isom}$	-1789,349011630		**TS-2$_{isom}$**	-1717,512640000
2-Coor-C	-1788,961524110		**2-Coor-C**	-1717,852148000
TS-2$_{ins}$	-1789,336697550		**TS-2$_{ins}$**	-1717,530931720
TS-2$_{ins-T}$	-1789,329245750		**TS-2$_{ins-T}$**	-1717,521084680
TS-2-$_{Deccor-\eta^2}$	-1789,318148440		**TS-2-$_{Deccor-\eta^2}$**	-1717,512133890
TS-2$_{deccorDat}$	-1789,334222550		**TS-2$_{decoor}$**	-1717,520890100
2-β-T	-1788,265354010		**2-β-T**	-1717,550785350
TS-2$_{decoor}$	-1789,328037240		**1-η2-C**	-1638,942145230
1-Dat-C	-1710,760569010		**1-β-C**	-1638,948032050
TS-2$_{openDAT}$	-1710,744314340		**TS-1$_{BHE-C}$**	-1638,933058870
1-β-C	-1710,750623180		**1-BHE-C**	-1638,965413500
TS-1$_{BHE-C}$	-1710,737955110		**TS-1$_{2,1-ins}$**	-1638,938990440
1-BHE-C	-1710,744809580		**3-β-C**	-1638,950492350
TS-1$_{2,1-ins}$	-1710,741335800		**TS-3$_{coor}$**	-1717,525000860
3-β-C	-1710,755471780		**3-Coor-C**	-1717,524294060
TS-3$_{coor}$	-1789,332663940		**4-β-T**	-1717,575833050
3-Coor-C	-1789,398136730		**TS-3$_{ins}$**	-1717,531197440
TS-3$_{ins}$	-1789,336625220		**TS-1$_{Transf-1}$**	-1717,512919700
4-β-T	-1789,378900250		**1-Transf-1**	-1717,598413200
TS-1$_{Transf-1}$	-1789,318920240		**TS-1$_{Transf-2}$**	-1717,568974120
1-Transf-1	-1789,332748980		**1-Transf-2**	-1599,646443000
TS-1$_{Transf-2}$	-1789,338864680			
1-Transf-2	-1671,439068670			

4.2 Cartesian coordinates.

Internal energies -M06/TZVP- (A.U.) in toluene are reported.

4.2.1 4-CH_3-I2

Table S11: Internal energy and cartesian coordinates for **1-β-T**.

SCF Done: -1709.92132576 A.U.

Ni	-0.393844	0.032574	-2.291499
N	-0.970586	0.031181	-0.542883
C	-2.367139	0.042859	-0.216346
C	-3.078512	-1.169373	-0.053260
C	-4.458782	-1.160609	0.219712
C	-5.125838	0.067831	0.330408
C	-4.447091	1.283869	0.167037
C	-3.066935	1.267548	-0.105844
O	-2.320933	2.403621	-0.354222
C	-2.695064	3.628291	0.203605
C	-3.020623	3.758156	1.563869
C	-3.302528	5.032192	2.091596
C	-3.249883	6.150972	1.235627
C	-2.910679	6.026836	-0.125616
C	-2.638415	4.744870	-0.641238
H	-3.052961	2.870389	2.204868
H	-2.377947	4.600746	-1.695508
H	-3.477297	7.145135	1.641591
C	-3.628056	5.197377	3.563441
C	-2.828342	7.246888	-1.021577
C	1.998934	-0.003375	1.674641
C	1.306473	0.010254	0.427783
C	2.038981	0.017764	-0.825146
C	3.472644	0.010455	-0.711484
C	4.138632	-0.003279	0.507667
C	3.382317	-0.010034	1.705961
I	4.418379	-0.030578	3.595199
H	5.231291	-0.008602	0.540443
I	4.612714	0.021036	-2.529964
H	-0.573970	0.017073	1.481691
C	-0.124383	0.018951	0.475803
C	-2.033637	0.017172	-3.252090
O	-2.342782	-2.322287	-0.251529
C	-2.742776	-3.521706	0.342587
C	-2.709372	-4.664397	-0.464856
H	-2.445803	-4.560191	-1.523087
C	-2.996705	-5.926210	0.095369
H	-3.550655	-6.979870	1.903172
C	-3.323957	-6.000950	1.461201
C	-3.361787	-4.851689	2.279956
C	-3.727433	-4.963597	3.747310
H	-3.066343	-2.694660	2.323318
C	-3.060254	-3.602437	1.710337
C	-2.939831	-7.173518	-0.764441
H	-4.994141	-2.106703	0.335400
H	-6.202178	0.077353	0.534525
H	-4.973140	2.239201	0.242669
H	1.416065	-0.008521	2.601711
O	1.460246	0.030659	-1.983518
C	-1.067622	-0.025972	-4.402505
C	-1.066720	-1.305331	-5.258217
H	-1.111406	0.888322	-5.023835
H	-2.631326	-0.892685	-3.083307
H	-2.615638	0.942641	-3.124629
H	0.031923	0.062525	-3.997946
H	-2.003078	-1.365510	-5.840337
H	-0.218395	-1.324709	-5.964529
H	-1.001591	-2.202087	-4.618103
H	-3.338149	-8.051552	-0.227844
H	-3.523301	-7.050575	-1.695336
H	-1.900501	-7.407446	-1.063966
H	-3.446858	-4.054313	4.306258
H	-4.816650	-5.111394	3.879914
H	-3.224658	-5.824603	4.223438
H	-4.262107	6.083934	3.739391
H	-4.155744	4.314278	3.964974
H	-2.707720	5.329144	4.164847
H	-3.195112	7.028252	-2.040265
H	-3.421197	8.085543	-0.617048
H	-1.783559	7.599474	-1.121349

Table S12: Internal energy and cartesian coordinates for **TS-2$_{Coor}$**.

SCF Done: -1789.40139927509 A.U.

Ni	-0.619786	-0.346757	1.977307
N	-0.942931	0.190722	0.229904
C	-2.255683	0.508808	-0.255927
C	-2.759998	1.826896	-0.183952
C	-3.072247	-0.504192	-0.818942
C	-4.356719	-0.203150	-1.305587
C	-4.834970	1.112247	-1.208198
C	-4.053725	2.130841	-0.647806
H	-4.428006	3.155353	-0.572138
H	-5.838683	1.346099	-1.579797
H	-4.966136	-0.990081	-1.757082
O	-1.939395	2.762797	0.421545
O	-2.483257	-1.751265	-0.903604
C	-1.979267	4.094365	0.000763
C	-3.259853	-2.873844	-1.211021
C	0.027498	0.251929	-0.670543
H	-0.270527	0.571498	-1.682126
C	1.417214	-0.057647	-0.502754
C	2.255740	0.094816	-1.645716
H	1.813742	0.458212	-2.579576
C	3.602960	-0.215382	-1.572128
I	4.861604	0.015255	-3.306415
C	4.175148	-0.691833	-0.367384
H	5.238746	-0.938094	-0.317827
C	3.366305	-0.842427	0.752437
I	4.236221	-1.562660	2.579038
C	1.961128	-0.533480	0.757209
O	1.245352	-0.670717	1.825173
C	-2.404215	-0.492479	2.637445
H	-2.809119	0.476273	2.970556
H	-3.082098	-1.008044	1.939002
C	-1.782375	-1.369879	3.698371
H	-0.632404	-1.321738	3.596039
H	-1.913246	-0.948664	4.714154
C	-2.162213	-2.859225	3.641639
C	0.358853	1.259211	4.320348
H	1.356814	0.809891	4.369210
C	-0.069856	1.899069	3.210404
H	-0.278187	1.153077	5.207140
H	0.588095	2.056093	2.349554
H	-1.056435	2.372118	3.154691
C	-2.003241	4.445543	-1.361518
C	-1.951909	5.800640	-1.730326
C	-1.863571	6.780727	-0.718302
C	-1.827611	6.434605	0.644063
C	-1.893406	5.071428	0.999656
H	-2.058754	3.663753	-2.126515
C	-1.993624	6.205180	-3.191171
H	-1.816582	7.840043	-1.002263
C	-1.713701	7.498327	1.718196
H	-1.868264	4.759961	2.049684
C	-2.860708	-3.642948	-2.309387
C	-3.546839	-4.837714	-2.612962
C	-4.629227	-5.219479	-1.800147
C	-5.033083	-4.450558	-0.687413
C	-4.334725	-3.266050	-0.393956
H	-2.012975	-3.305450	-2.915779
C	-3.120130	-5.684135	-3.796000
H	-5.172450	-6.143849	-2.035747
C	-6.180375	-4.909816	0.191178
H	-4.619253	-2.648387	0.465064
H	-2.965858	6.665028	-3.453343
H	-1.211288	6.949686	-3.425891
H	-1.847043	5.337559	-3.857130
H	-2.512259	7.396298	2.476209
H	-0.748929	7.425106	2.254992
H	-1.781914	8.512636	1.289210
H	-6.583197	-4.081420	0.799072
H	-7.008276	-5.325529	-0.410820
H	-5.857022	-5.705785	0.889436
H	-3.792807	-6.547266	-3.936901
H	-3.119564	-5.098179	-4.733843
H	-2.094244	-6.075318	-3.660571
H	-3.223820	-2.993011	3.916431
H	-2.019402	-3.256586	2.621637
H	-1.549872	-3.463545	4.334036

Table S13: Internal energy and cartesian coordinates for **2-Coor-T**.

SCF Done: -1788.48368271 A.U.

C	-2.019335	-0.629150	-0.755837
C	-1.449879	0.071881	0.374476
C	-2.266313	0.503741	1.460437
C	-3.627611	0.256330	1.447732
C	-4.230721	-0.433931	0.365829
C	-3.441031	-0.861164	-0.693367
C	-0.044759	0.320786	0.472564
N	0.916548	0.038653	-0.392531
C	2.224440	0.390866	0.089475
C	2.697374	1.721928	0.009598
C	3.989697	2.057447	0.454131
C	4.807498	1.052882	0.988899
C	4.366542	-0.275058	1.082555
C	3.074767	-0.601825	0.632469
O	1.836892	2.620319	-0.595865
C	1.926711	3.985708	-0.314953
O	2.563886	-1.885866	0.627380
I	-4.864253	0.912874	3.084593
I	-4.354926	-1.903432	-2.332199
O	-1.316787	-1.030734	-1.757944
Ni	0.584811	-0.770062	-2.165885
C	-0.001022	-1.318792	-4.075212
C	0.445490	-2.427023	-3.350764
C	2.441855	-0.415653	-2.706932
H	4.342253	3.088831	0.371019
H	5.817675	1.307171	1.328254
H	5.011429	-1.055289	1.494992
H	0.271978	0.797797	1.415258
H	-1.797060	1.032036	2.297291
H	-5.306197	-0.629212	0.366025
H	1.444537	-2.849179	-3.503535
H	-0.272961	-3.048727	-2.804596
H	-1.067170	-1.072563	-4.088026
H	0.629618	-0.836564	-4.826028
C	2.998717	-0.567857	-4.123640
H	2.534606	0.638504	-2.387329
H	3.000130	-1.057448	-1.998529
C	4.520484	-0.297392	-4.154541
H	2.817023	-1.581986	-4.530918
H	2.503138	0.143372	-4.813095
H	4.920671	-0.385641	-5.181839
H	4.750517	0.718569	-3.785066
H	5.064155	-1.015664	-3.513749
C	1.819913	4.856896	-1.404966
C	1.799120	6.250320	-1.188021
C	1.900834	6.731875	0.129346
C	2.008030	5.857927	1.232777
C	2.014584	4.471435	1.002221
H	1.743740	4.438716	-2.414685
C	1.658124	7.202073	-2.359583
H	1.891530	7.815577	0.304231
C	2.113337	6.407562	2.642117
H	2.085385	3.769286	1.839921
H	1.858287	8.244701	-2.058727
H	2.354963	6.943666	-3.177697
H	0.636251	7.167094	-2.783251
H	2.070963	5.602479	3.395506
H	3.063524	6.955192	2.790343
H	1.295095	7.118471	2.859720
C	3.100986	-2.855217	1.479920
C	3.452779	-4.082064	0.905915
C	3.911288	-5.132771	1.727403
C	4.014731	-4.911739	3.112689
C	3.655564	-3.678573	3.697757
C	3.192906	-2.643207	2.866695
H	3.363279	-4.208138	-0.178626
C	4.279558	-6.471995	1.119972
H	4.381410	-5.721453	3.756783
C	3.740174	-3.484122	5.199162
H	2.902538	-1.675516	3.290298
H	3.760982	-2.414302	5.469984
H	2.869653	-3.937285	5.711535
H	4.645118	-3.960168	5.617510
H	4.796965	-7.117474	1.850205
H	3.379801	-7.015213	0.773173
H	4.941219	-6.351388	0.242788

Table S14: Internal energy and cartesian coordinates for **TS-2$_{isom}$**.

SCF Done: -1788.46902425677 A.U.

C	-1.961320	-0.447459	-0.533736
C	-1.138056	-0.180461	0.633515
C	-1.714804	-0.114923	1.935553
C	-3.071732	-0.321217	2.113818
C	-3.911491	-0.604566	1.009686
C	-3.363142	-0.657382	-0.265108
C	0.283506	0.015916	0.555210
N	1.034054	-0.018275	-0.525697
C	2.431757	0.207470	-0.325854
C	2.949704	1.522094	-0.221426
C	4.332135	1.745523	-0.093387
C	5.205064	0.648183	-0.062275
C	4.722852	-0.664055	-0.166923
C	3.338940	-0.877904	-0.295974
O	2.017466	2.541039	-0.328147
C	2.275059	3.786392	0.249121
O	2.778979	-2.132691	-0.480611
C	3.343910	-3.251721	0.134164
I	-3.942351	-0.212242	4.080371
I	-4.651789	-1.104249	-1.923954
O	-1.508278	-0.512547	-1.743895
Ni	0.280053	-0.188287	-2.403038
C	1.914069	-0.525916	-3.487323
C	0.750574	-1.010758	-4.142297
C	-0.311514	1.401203	-3.379377
H	0.539268	1.716632	-4.008459
C	-1.627244	1.342628	-4.133683
H	4.710382	2.769063	-0.024049
H	6.282932	0.820461	0.029717
H	5.403339	-1.519866	-0.151316
H	0.783646	0.206152	1.522636
H	-1.060810	0.093986	2.789501
H	-4.980362	-0.777214	1.157639
H	-0.357581	2.021961	-2.463527
H	0.449029	-2.062533	-4.032165
H	0.345088	-0.506182	-5.025941
H	2.538836	-1.206522	-2.895967
H	2.410865	0.390092	-3.831755
C	-2.072075	2.761486	-4.566938
H	-1.530316	0.704751	-5.032226
H	-2.403791	0.884633	-3.499569
H	-3.028812	2.713269	-5.118262
H	-2.220759	3.418349	-3.690477
H	-1.323836	3.240207	-5.225599
C	1.987744	4.913384	-0.530637
C	2.122278	6.202135	0.024474
C	2.560547	6.322402	1.356092
C	2.856462	5.191032	2.145434
C	2.702371	3.911461	1.582838
H	1.650146	4.773229	-1.563451
C	1.786511	7.428590	-0.800977
H	2.671480	7.322900	1.793774
C	3.345352	5.351262	3.571888
H	2.910889	3.013819	2.175162
H	3.138524	4.450596	4.175694
H	4.438610	5.524720	3.604382
H	2.865359	6.212991	4.068629
H	2.125644	8.353917	-0.304580
H	2.257479	7.386090	-1.800046
H	0.695132	7.517228	-0.962266
C	3.795421	-3.228055	1.464145
C	4.280091	-4.410769	2.053924
C	4.299217	-5.595376	1.290718
C	3.833688	-5.626948	-0.038211
C	3.359536	-4.434780	-0.618005
H	3.769289	-2.292886	2.033748
C	4.744850	-4.412267	3.497444
H	4.684615	-6.517524	1.744646
C	3.830441	-6.919343	-0.830572
H	2.999222	-4.412796	-1.652373
H	4.056738	-6.743254	-1.897166
H	4.572157	-7.636026	-0.437074
H	2.840141	-7.412565	-0.785665
H	3.900424	-4.597496	4.189366
H	5.494365	-5.202375	3.678811
H	5.192694	-3.443826	3.782360

Table S15: Internal energy and cartesian coordinates for **2-Coor-C**.

SCF Done: -1788.48604811653 A.U.

Ni	0.239150	-1.720111	-2.168828
N	1.204764	-0.487688	-0.809407
C	2.637733	-0.369588	-0.783046
C	3.352832	0.688127	-1.432570
C	3.371679	-1.381216	-0.105686
C	4.780048	-1.355236	-0.104689
C	5.475932	-0.343375	-0.769998
C	4.763375	0.666732	-1.423159
H	5.301662	1.455710	-1.959108
H	6.570724	-0.337869	-0.775603
H	5.326127	-2.128309	0.443825
O	2.753879	1.825787	-2.145193
O	2.684510	-2.461730	0.603666
C	2.651208	3.200580	-1.737467
C	2.757794	-2.784485	1.999089
C	0.560584	0.337895	-0.005453
H	1.169824	1.006776	0.627125
C	-0.857261	0.449890	0.186707
C	-1.308750	1.382989	1.166991
H	-0.565052	1.972484	1.713633
C	-2.662395	1.529801	1.420087
I	-3.348916	2.931515	2.900479
C	-3.616535	0.758712	0.712759
H	-4.683652	0.878855	0.916403
C	-3.186406	-0.154350	-0.241958
I	-4.645991	-1.314742	-1.297314
C	-1.796196	-0.356585	-0.558639
O	-1.453311	-1.220740	-1.460715
C	1.740025	-1.735413	-3.553239
C	-0.877431	-2.829408	-3.359912
H	1.290751	-1.759660	-4.552518
H	2.402883	-0.885496	-3.350661
C	1.812760	-2.880171	-2.749092
H	2.511550	-2.915670	-1.907701
H	1.432736	-3.849318	-3.087691
C	-1.445788	-4.007506	-2.576985
H	-1.651613	-2.096525	-3.644111
H	-0.315232	-3.154188	-4.254180
C	-2.440437	-4.826936	-3.434925
H	-0.632789	-4.677616	-2.232711
H	-1.966146	-3.634201	-1.677567
H	-2.847943	-5.676638	-2.856677
H	-3.288949	-4.198270	-3.759486
H	-1.953113	-5.233940	-4.340200
C	3.719278	4.055224	-2.036831
C	3.663738	5.410710	-1.677898
C	2.526144	5.901159	-1.020899
C	1.447824	5.050773	-0.724398
C	1.514307	3.693896	-1.083380
H	4.598291	3.663796	-2.552077
C	4.791663	6.306463	-1.992347
H	2.476041	6.955492	-0.741547
C	0.256012	5.587337	-0.044150
H	0.679510	3.031173	-0.864007
H	-0.483560	4.797146	0.104702
H	0.533603	6.001642	0.930420
H	-0.194422	6.381598	-0.647945
H	4.576250	7.320078	-1.642368
H	5.703816	5.949600	-1.503172
H	4.960642	6.333755	-3.073681
C	1.583526	-2.749025	2.758518
C	1.622287	-3.069472	4.124968
C	2.844973	-3.423023	4.717971
C	4.026180	-3.460637	3.957793
C	3.977822	-3.139695	2.592941
H	0.638936	-2.472803	2.286644
C	0.385727	-3.032634	4.926551
H	2.877835	-3.672203	5.780480
C	5.304689	-3.835189	4.589157
H	4.889363	-3.170103	1.995829
H	6.112095	-3.811255	3.851509
H	5.543344	-3.136662	5.397612
H	5.236432	-4.845167	5.005975
H	0.600781	-3.308315	5.962920
H	-0.044018	-2.025893	4.909955
H	-0.348426	-3.734624	4.518335

Table S16: Internal energy and cartesian coordinates for **2-β-T**.

SCF Done: -1788.51192915955 A.U.

Ni	0.418378	-0.422189	1.980859
N	0.859848	-0.026090	0.240850
C	2.228289	-0.004319	-0.178112
C	2.873248	-1.184630	-0.613561
C	4.227229	-1.178632	-0.989606
C	4.948584	0.022625	-0.934658
C	4.340671	1.207980	-0.496800
C	2.985935	1.188836	-0.122930
O	2.337515	2.295985	0.405534
C	2.804147	3.588783	0.139211
C	-2.311616	0.650591	-1.649685
C	-1.459645	0.328797	-0.545367
C	-2.102114	0.066513	0.739446
C	-3.530769	0.148902	0.830671
C	-4.276443	0.468652	-0.286432
C	-3.692642	0.726190	-1.554318
I	-4.656944	1.111257	-2.900367
H	-5.361644	0.530513	-0.205131
I	-4.234973	-0.160131	2.346782
H	0.356501	0.490789	-1.690083
C	-0.041764	0.268391	-0.689672
C	2.113582	-0.757815	2.777757
O	2.118992	-2.348830	-0.554897
C	2.186252	-3.283710	-1.573594
C	1.890999	-4.607799	-1.208081
H	1.677908	-4.841926	-0.161773
C	1.854568	-5.601869	-2.195841
H	2.072534	-6.066342	-4.308597
C	2.114969	-5.290140	-3.540477
C	2.408502	-3.962409	-3.886560
C	2.727178	-3.635249	-5.262755
H	2.649105	-1.916272	-3.202748
C	2.442595	-2.949795	-2.914234
C	1.604744	-6.979314	-1.818040
H	4.705406	-2.108068	-1.312396
H	6.005598	0.031476	-1.219889
H	4.908573	2.140781	-0.433823
H	-1.909556	0.854842	-2.642020
O	-1.437609	-0.238726	1.812457
C	1.219797	-1.024419	3.955609
C	1.179391	-2.470288	4.481815
H	1.365367	-0.289679	4.769547
H	2.633692	-1.632750	2.356015
H	2.752903	0.136814	2.831967
H	0.105273	-0.781604	3.668477
C	2.441037	-2.794602	5.118656
H	0.372593	-2.615093	5.221279
H	1.019440	-3.182217	3.653729
H	1.612150	-7.606874	-2.708003
H	2.380997	-7.313908	-1.131457
H	0.633456	-7.051668	-1.330919
H	2.925862	-2.567724	-5.345435
H	3.608795	-4.193728	-5.573838
H	1.886214	-3.898588	-5.902562
C	2.397105	-4.157310	5.612208
H	3.248781	-2.696531	4.394879
H	2.613829	-2.112802	5.950048
H	3.344646	-4.400882	6.090498
H	1.589362	-4.255381	6.335986
H	2.224313	-4.839110	4.780816
C	2.140753	4.697388	0.678564
C	2.607384	5.990186	0.412241
C	3.737409	6.174380	-0.393436
C	4.400804	5.065775	-0.932789
C	3.934173	3.772977	-0.666466
H	1.261755	4.554113	1.305266
C	1.920297	7.138386	0.970858
H	4.100383	7.179992	-0.600597
C	5.571188	5.256546	-1.767240
H	4.450199	2.910640	-1.086007
H	5.947500	4.287522	-2.091744
H	5.302612	5.851984	-2.638585
H	6.342450	5.773407	-1.198092
H	2.424332	8.051207	0.656806
H	0.890348	7.152431	0.617407
H	1.930186	7.073855	2.057898

Table S17: Internal energy and cartesian coordinates for **TS-2$_{ins}$**.

SCF Done: -1788.46745841 A.U.

Ni	1.224685	-0.794141	-1.426968
N	0.840057	0.579505	-0.167705
C	1.784933	1.628152	0.085104
C	1.561734	2.945867	-0.378187
C	2.983264	1.350793	0.788444
C	3.920635	2.367559	1.040941
C	3.674048	3.663582	0.562700
C	2.508383	3.963187	-0.153662
O	3.105684	0.058214	1.261192
C	-0.283511	0.652507	0.523917
H	-0.380378	1.500158	1.222481
C	-1.394024	-0.251599	0.494138
C	-2.520090	0.087158	1.298933
C	-1.369079	-1.477710	-0.282531
O	-0.368537	-1.837422	-1.017164
C	-2.550152	-2.296356	-0.173308
C	2.012204	-2.587838	-2.185301
C	-3.623632	-0.747139	1.345491
C	-3.649521	-1.953544	0.604866
I	-2.609407	-4.132523	-1.286165
H	-4.522653	-2.610092	0.645428
I	-5.328205	-0.222090	2.553701
H	-2.495007	1.020311	1.872009
C	2.040068	-0.850988	-3.314946
C	2.513430	0.225669	-2.477865
H	3.563854	0.213205	-2.154605
H	2.755130	-1.438746	-3.901994
H	2.073531	1.224898	-2.581395
H	1.099498	-0.699140	-3.867246
C	1.258881	-3.541913	-3.103190
H	3.108000	-2.670806	-2.258043
H	1.738283	-2.778549	-1.125306
O	0.422304	3.132165	-1.144441
C	-0.252634	4.353697	-1.114768
H	4.408535	4.454131	0.751762
H	2.322831	4.968841	-0.540601
H	4.826449	2.141699	1.609675
C	-0.446321	5.078142	0.074057
C	-1.204299	6.263275	0.049072
C	-1.753604	6.696610	-1.175055
C	-1.574340	5.966350	-2.365231
C	-0.807595	4.785333	-2.327024
H	-0.004880	4.722042	1.011168
C	-1.449474	7.045927	1.324688
H	-2.338165	7.625375	-1.199898
C	-2.200400	6.430800	-3.665407
H	-0.634903	4.191577	-3.231395
H	-1.527805	6.259087	-4.524725
H	-3.139793	5.883372	-3.874609
H	-2.446433	7.506308	-3.633231
H	-2.424600	6.779352	1.776332
H	-0.671407	6.845302	2.081652
H	-1.468017	8.133546	1.133053
C	4.362750	-0.438707	1.617734
C	4.466241	-1.061110	2.866742
C	5.679610	-1.673302	3.245434
C	6.765382	-1.631080	2.352549
C	6.667571	-1.003130	1.091858
C	5.448183	-0.408451	0.723891
H	3.593944	-1.072181	3.529516
C	5.797408	-2.369285	4.586994
H	7.713127	-2.103522	2.641736
C	7.859347	-0.966575	0.154903
H	5.335894	0.076398	-0.252006
H	7.560350	-0.692306	-0.871475
H	8.611691	-0.226510	0.489636
H	8.368240	-1.946416	0.111029
H	6.838569	-2.669252	4.795591
H	5.460051	-1.716127	5.412675
H	5.172257	-3.281687	4.622235
C	1.497607	-5.013042	-2.704460
H	0.179672	-3.317893	-3.039234
H	1.569171	-3.391986	-4.156689
H	0.959347	-5.694529	-3.387968
H	2.571353	-5.275889	-2.741665
H	1.132524	-5.206760	-1.680095

Table S18: Internal energy and cartesian coordinates for **TS-2$_{deccor}$**.

SCF Done: -1788.46738038 A.U.

Ni	-0.073290	1.594359	-1.915152
N	-0.930687	0.869810	-0.328440
C	-2.227315	1.318683	0.064094
C	-3.377921	0.502355	-0.105683
C	-2.411820	2.626958	0.567523
C	-3.685948	3.121004	0.885223
C	-4.806031	2.298892	0.694674
C	-4.659790	0.993936	0.200544
H	-5.807009	2.676864	0.928507
H	-3.776928	4.139173	1.275088
O	-3.150037	-0.747569	-0.654299
O	-1.303077	3.459055	0.684572
C	-0.621800	3.493989	1.903210
C	-0.374362	-0.074664	0.403489
H	-0.926224	-0.433845	1.288456
C	0.908564	-0.680830	0.180997
C	1.303944	-1.686588	1.111097
H	0.609613	-1.958876	1.913175
C	2.538071	-2.302791	1.001492
I	3.120897	-3.821206	2.415804
C	3.437466	-1.940830	-0.029946
H	4.414115	-2.424412	-0.111254
C	3.063544	-0.959766	-0.939644
I	4.440759	-0.410920	-2.493880
C	1.791387	-0.285463	-0.901397
O	1.516976	0.605779	-1.806068
C	-0.449878	3.637261	-2.861961
H	-1.215123	3.806332	-3.643282
C	0.004942	4.949484	-2.203158
C	0.635199	2.709501	-3.308832
H	-1.099869	3.083444	-2.054321
H	0.541138	2.248095	-4.302337
H	1.668513	2.990074	-3.057199
C	-1.182245	-0.025756	-3.453640
H	-0.323348	-0.081210	-4.131216
H	-1.227404	-0.780513	-2.661593
C	-2.219468	0.817998	-3.675903
H	-3.105919	0.818513	-3.032363
H	-2.215518	1.529151	-4.510780
C	-4.111002	-1.756516	-0.516923
C	-4.526907	-2.402876	-1.686027
C	-5.422313	-3.489547	-1.601136
C	-5.884303	-3.886901	-0.333283
C	-5.462846	-3.241509	0.849186
C	-4.564564	-2.164544	0.749290
H	-4.145265	-2.055290	-2.652355
C	-5.866841	-4.213101	-2.856766
H	-6.589700	-4.724892	-0.261039
C	-5.950040	-3.719434	2.203178
H	-4.215635	-1.643974	1.647958
H	-6.736713	-4.863228	-2.661198
H	-6.143500	-3.503269	-3.657211
H	-5.056892	-4.852011	-3.257876
H	-5.781820	-2.960985	2.986999
H	-7.029118	-3.956012	2.183042
H	-5.422683	-4.641199	2.515557
C	0.510974	4.324737	1.940266
C	1.255444	4.443043	3.125226
C	0.839347	3.725369	4.266599
C	-0.291516	2.890932	4.235268
C	-1.030580	2.778776	3.038587
H	0.795120	4.876541	1.037921
C	2.498048	5.310595	3.168325
H	1.411161	3.820717	5.198569
C	-0.709775	2.104447	5.462685
H	-1.926907	2.150960	3.002348
H	-1.809273	2.038077	5.548971
H	-0.322655	1.067500	5.426413
H	-0.322183	2.565396	6.387748
H	2.633140	5.773822	4.161805
H	3.407319	4.714226	2.959943
H	2.456498	6.117775	2.416334
H	-5.532313	0.354101	0.041631
H	0.441565	5.620187	-2.964437
H	-0.832380	5.474940	-1.713094
H	0.776446	4.746630	-1.441084

Table S19: Internal energy and cartesian coordinates for **TS-2$_{deccor-\eta2}$**.

SCF Done: -1788.45895351 A.U.

Ni	-2.208190	0.263396	0.033158
C	-1.518576	1.742253	2.810253
C	-2.608839	2.385280	2.352608
C	-3.348001	1.641148	-1.397401
C	-3.202276	0.306561	-1.891737
C	-4.373343	-0.512665	-2.034078
C	-5.591204	-0.022864	-1.571302
C	-5.725511	1.268538	-0.969032
C	-4.606254	2.095287	-0.899960
H	-4.689491	3.127972	-0.541771
C	-7.076683	1.727002	-0.461109
H	-7.386405	1.151681	0.432509
H	-7.863359	1.580934	-1.224638
H	-7.064847	2.794836	-0.183248
H	-6.489400	-0.645058	-1.679195
H	-3.769761	-1.810492	-3.670624
C	-4.251053	-1.875351	-2.676378
H	-5.237138	-2.353267	-2.804209
H	-5.498723	-1.777931	2.726866
C	-4.466891	-2.166145	2.814463
H	-4.292504	-2.431727	3.873853
H	-4.401586	-3.092955	2.216272
C	-3.425935	-1.126122	2.329748
C	-3.672062	-0.745799	0.876834
H	-4.551326	-0.091944	0.743934
H	-3.763197	-1.646561	0.248204
H	-3.482377	-0.238285	2.986201
H	-2.416196	-1.561435	2.437598
O	-1.166496	-1.317073	0.444275
C	0.638357	0.792144	-0.592028
N	-0.553098	1.336199	-0.430050
H	-1.595869	0.808365	3.377376
H	-0.507275	2.124022	2.635027
H	-2.527550	3.326541	1.796716
H	-3.622577	2.009610	2.534124
H	1.480079	1.455336	-0.851684
C	0.971760	-0.597361	-0.472746
C	2.300098	-0.967830	-0.834753
H	2.972147	-0.193932	-1.220645
C	2.727502	-2.276640	-0.695262
I	4.737143	-2.824041	-1.244283
C	1.859539	-3.268312	-0.177173
H	2.199272	-4.301750	-0.068338
I	-0.737019	-4.427165	0.977244
C	0.568589	-2.912721	0.193972
C	0.045927	-1.574413	0.068442
O	1.222250	2.990544	1.124340
C	-0.623908	2.750664	-0.412794
C	0.255995	3.588764	0.321986
C	0.086980	4.985211	0.335853
H	0.777987	5.591926	0.929333
C	-0.950883	5.574406	-0.397726
H	-1.074033	6.662404	-0.390988
H	-2.652083	5.201833	-1.724928
C	-1.841481	4.770683	-1.129805
C	-1.677650	3.380916	-1.119350
C	2.568213	3.312207	0.943748
C	3.076727	3.845902	-0.249534
H	2.402648	4.085437	-1.079000
C	3.414713	3.005071	2.023387
H	2.979449	2.583443	2.935893
C	4.795881	3.231139	1.914644
C	5.304355	3.777715	0.715599
H	6.382175	3.964509	0.626514
C	4.463502	4.087035	-0.366681
C	5.022609	4.679811	-1.645527
H	6.125782	4.691028	-1.634732
H	4.677910	5.721196	-1.792096
H	4.698614	4.105947	-2.533360
C	5.728299	2.876023	3.055673
H	5.178285	2.742189	4.002910
H	6.267735	1.931585	2.849676
H	6.493171	3.658167	3.211187
H	-3.622241	-2.546455	-2.060109
O	-2.472631	2.604129	-1.938973
H	-2.308842	0.072253	-2.483793

Table S20: Internal energy and cartesian coordinates for **1-β-C**.

SCF Done: -1709.91896618 A.U.

Ni	-0.041972	-1.896863	-1.744794
N	0.957553	-1.017787	-0.360124
C	2.279304	-1.454355	-0.045120
C	3.420169	-0.655758	-0.328080
C	2.489478	-2.752395	0.479524
C	3.778767	-3.248593	0.718948
C	4.888619	-2.443409	0.420724
C	4.716970	-1.154029	-0.103079
H	5.580562	-0.530966	-0.351919
H	5.901007	-2.824387	0.592365
H	3.889445	-4.256300	1.130062
O	3.164988	0.567195	-0.918713
O	1.394923	-3.586178	0.683749
C	4.113413	1.592495	-0.858827
C	0.639988	-3.431982	1.849815
C	0.504496	0.049933	0.269928
H	1.153875	0.517224	1.028068
C	-0.778269	0.660762	0.076796
C	-1.074843	1.800626	0.880578
H	-0.315087	2.157457	1.584135
C	-2.297564	2.439006	0.770431
I	-2.735978	4.160584	1.989660
C	-3.277146	1.975731	-0.140321
H	-4.241912	2.482089	-0.224321
C	-2.996453	0.867360	-0.929695
I	-4.485857	0.172994	-2.311558
C	-1.748986	0.154156	-0.872233
O	-1.570239	-0.873636	-1.651921
C	0.664062	-3.561356	-2.981216
H	1.373826	-3.345571	-3.801170
C	0.718830	-5.031808	-2.532123
C	-0.676884	-2.959499	-3.202102
H	1.218390	-2.978268	-2.089563
H	-0.829933	-2.338226	-4.095376
H	-1.557251	-3.552754	-2.913571
C	4.378089	2.273255	-2.051824
C	5.244208	3.386853	-2.044623
C	5.829344	3.779925	-0.827925
C	5.566927	3.095626	0.378914
C	4.693555	1.994664	0.358030
H	3.894908	1.935591	-2.975274
C	5.531803	4.136382	-3.330403
H	6.504111	4.645605	-0.815088
C	6.215418	3.543912	1.674203
H	4.459099	1.453422	1.281263
H	5.776801	3.030311	2.546837
H	7.301870	3.332435	1.674024
H	6.099386	4.632390	1.827240
H	6.196434	4.999271	-3.154312
H	6.019072	3.482930	-4.078341
H	4.600869	4.514897	-3.791845
C	-0.576621	-4.131742	1.882420
C	-1.388667	-4.071418	3.028074
C	-0.953556	-3.308631	4.131511
C	0.264051	-2.604688	4.103676
C	1.070484	-2.673904	2.948810
H	-0.876066	-4.720304	1.008292
C	-2.721900	-4.792182	3.062385
H	-1.579859	-3.261896	5.031502
C	0.702732	-1.767390	5.289558
H	2.033358	-2.153116	2.914625
H	1.799862	-1.785720	5.417728
H	0.406401	-0.707735	5.164088
H	0.243547	-2.125105	6.227512
H	-3.020654	-5.039473	4.096096
H	-3.524591	-4.164423	2.629562
H	-2.692896	-5.730321	2.480324
H	0.424762	-5.683273	-3.373670
H	1.730979	-5.323597	-2.203397
H	0.022964	-5.209451	-1.695623

Table S21: Internal energy and cartesian coordinates for **Ts-2$_{decoorDat}$**.

SCF Done: -1788.46959356 A.U.

Ni	1.692963	-0.690168	-0.654223
N	0.445582	0.799729	-0.315530
O	0.456873	-2.092543	-0.388537
C	-0.809532	-1.944238	-0.143237
C	-1.646807	-3.113041	-0.036605
I	-0.727628	-5.033939	-0.321043
C	-3.009892	-3.060634	0.225590
H	-3.596708	-3.980893	0.286230
C	-3.624352	-1.798640	0.411871
I	-5.739974	-1.710783	0.816187
C	-2.884805	-0.632911	0.331073
H	-3.360006	0.343478	0.473695
C	-1.485888	-0.671705	0.047498
C	-0.823556	0.600651	-0.000385
H	-1.448595	1.464934	0.257303
C	1.024542	2.089037	-0.296693
C	0.364288	3.340400	-0.479388
O	-0.978962	3.301167	-0.815524
C	1.074421	4.552659	-0.427611
H	0.534348	5.489829	-0.588162
C	2.454009	4.548669	-0.190703
H	3.000333	5.496801	-0.150451
C	3.151172	3.340142	-0.038224
H	4.231900	3.325611	0.120270
C	2.435037	2.141562	-0.118002
C	3.043544	-2.074461	-0.755254
O	3.052403	0.887918	-0.043858
C	4.393311	0.827049	0.400404
C	4.647237	0.801534	1.777796
C	5.976623	0.694215	2.228461
C	7.008609	0.606427	1.270030
C	6.751828	0.626895	-0.113877
C	5.414621	0.744096	-0.550109
H	3.811489	0.859152	2.483504
C	6.291257	0.688539	3.711029
H	8.046341	0.513669	1.615411
C	7.877932	0.503877	-1.120675
H	5.163283	0.765823	-1.615600
C	-1.827099	4.358190	-0.466727
C	-2.734018	4.781756	-1.444887
C	-3.683133	5.776967	-1.132477
C	-3.683986	6.327832	0.161995
C	-2.775556	5.898707	1.153315
C	-1.838557	4.901578	0.829892
H	-2.692752	4.329185	-2.441683
C	-4.681996	6.234786	-2.176755
H	-4.412671	7.110896	0.408666
C	-2.827449	6.485043	2.550678
H	-1.119753	4.548808	1.577641
H	-1.904094	6.271538	3.116105
H	-2.965248	7.580974	2.523157
H	-3.674102	6.067278	3.128578
H	-5.199461	7.157104	-1.862102
H	-4.192146	6.432449	-3.147512
H	-5.455152	5.463474	-2.356682
H	6.484044	1.713404	4.083482
H	5.453499	0.277802	4.300651
H	7.190877	0.087236	3.929705
H	7.796956	1.268144	-1.914921
H	8.863841	0.616870	-0.638564
H	7.861223	-0.483918	-1.619189
H	2.684011	-2.819990	-1.486739
H	3.936022	-1.549502	-1.153737
C	3.288559	-2.702285	0.611010
C	4.359940	-3.818967	0.566772
H	3.611208	-1.931268	1.339241
H	2.339514	-3.128050	0.985795
H	4.511191	-4.265910	1.567420
H	4.055750	-4.627217	-0.123287
H	5.333957	-3.427161	0.219170
C	1.347970	-0.614688	-3.023101
C	2.381591	0.255466	-3.174651
H	0.315708	-0.261303	-2.923897
H	3.400720	-0.100397	-3.364989
H	2.237618	1.339939	-3.112935
H	1.476012	-1.691302	-3.176219

Table S22: Internal energy and cartesian coordinates for **1-Dat-C**.

Done: -1709.92587900 A.U.

Ni	1.683042	-0.739140	0.209360
N	0.476695	0.772233	-0.123314
O	0.402449	-2.056086	0.316794
C	-0.878418	-1.893156	0.143744
C	-1.744007	-3.038497	0.242790
I	-0.850346	-4.940277	0.685062
C	-3.120542	-2.973210	0.065856
H	-3.732125	-3.875133	0.150568
C	-3.715073	-1.721454	-0.225660
I	-5.850029	-1.613466	-0.503855
C	-2.945104	-0.578125	-0.331216
H	-3.404559	0.390889	-0.552391
C	-1.529584	-0.632297	-0.149136
C	-0.832195	0.613236	-0.268090
H	-1.453699	1.485664	-0.495368
C	1.119128	2.022193	-0.219591
C	0.550096	3.325965	-0.372211
O	-0.824641	3.419300	-0.507306
C	1.361663	4.470205	-0.454705
H	0.883757	5.444455	-0.589630
C	2.754003	4.359444	-0.371008
H	3.376625	5.257299	-0.439842
C	3.359926	3.105551	-0.205137
H	4.444648	3.006018	-0.132368
C	2.537635	1.978659	-0.132524
C	2.944842	-2.180662	0.533058
H	3.866721	-1.719681	0.938390
H	2.461415	-2.793625	1.313853
C	3.210290	-2.991286	-0.732594
H	3.634265	-2.343315	-1.527127
H	2.251107	-3.386452	-1.116495
C	4.182255	-4.170338	-0.489983
H	5.164046	-3.810334	-0.129449
H	4.351923	-4.749012	-1.417787
H	3.778362	-4.861928	0.271880
O	3.059567	0.684518	0.070909
C	4.463554	0.519952	-0.098075
C	5.278649	0.552868	1.033453
C	6.671190	0.372674	0.877401
C	7.181975	0.174195	-0.418206
C	6.351166	0.141181	-1.559772
C	4.965978	0.318793	-1.388703
H	4.831110	0.706727	2.021182
C	7.582079	0.375361	2.088473
H	8.263451	0.035154	-0.545284
C	6.940673	-0.087679	-2.937046
H	4.280773	0.299325	-2.242574
C	-1.496038	4.577298	-0.090769
C	-2.428697	5.118936	-0.980326
C	-3.215003	6.220741	-0.579751
C	-3.027320	6.750178	0.708857
C	-2.086193	6.204589	1.609979
C	-1.316232	5.102902	1.200720
H	-2.539319	4.674644	-1.975725
C	-4.239010	6.811704	-1.528362
H	-3.633036	7.609096	1.025592
C	-1.924148	6.789283	2.999512
H	-0.586494	4.647266	1.878662
H	-1.140665	6.264190	3.571874
H	-1.651076	7.860239	2.956557
H	-2.865584	6.719893	3.575899
H	-4.725994	7.700718	-1.092836
H	-3.776426	7.113761	-2.486312
H	-5.031537	6.078914	-1.770706
H	8.644886	0.389078	1.793183
H	7.395595	1.252864	2.734056
H	7.418648	-0.524627	2.710848
H	6.163336	-0.066782	-3.719221
H	7.693157	0.683593	-3.185945
H	7.450307	-1.067336	-2.995388

Table S23: Internal energy and cartesian coordinates for **TS-2$_{openDat}$**.

SCF Done: -1709.90803381179 A.U.

Ni	1.797666	-0.700930	-1.155556
N	0.697298	0.757163	-0.534908
C	1.267238	2.054930	-0.529068
C	0.571821	3.274227	-0.778126
C	2.665957	2.148139	-0.306606
C	3.340329	3.373956	-0.241904
C	2.614519	4.555459	-0.450714
C	1.242508	4.508503	-0.736766
H	0.682147	5.424211	-0.945917
H	3.128461	5.522001	-0.422301
H	4.416647	3.389276	-0.048031
O	-0.753173	3.167874	-1.161949
O	3.356729	0.935326	-0.235722
C	-1.666056	4.180047	-0.851570
C	-0.520849	0.555890	-0.059333
H	-1.095149	1.415929	0.312439
C	-1.172510	-0.717770	0.042748
C	-2.501733	-0.703192	0.564190
H	-2.944075	0.261252	0.835802
C	-3.213481	-1.878703	0.719534
I	-5.214757	-1.834279	1.517601
C	-2.641564	-3.125152	0.366802
H	-3.206937	-4.052710	0.488064
C	-1.347090	-3.153229	-0.136172
I	-0.481270	-5.048745	-0.654921
C	-0.543686	-1.974230	-0.324218
O	0.667285	-2.110318	-0.787310
C	3.069136	-1.869858	-1.953866
H	3.804578	-2.129053	-1.171853
H	2.601158	-2.762040	-2.395381
C	3.468576	-0.771983	-2.918333
H	2.949911	0.196648	-2.605994
C	3.090823	-1.026788	-4.387167
H	3.303588	-0.148645	-5.022938
H	3.658865	-1.886085	-4.785958
H	2.015534	-1.262583	-4.474588
H	4.539263	-0.498989	-2.816514
C	-2.600874	4.499760	-1.842470
C	-3.618882	5.436304	-1.566638
C	-3.661374	6.034312	-0.294272
C	-2.720202	5.715700	0.708295
C	-1.716971	4.773136	0.422939
H	-2.531988	4.005801	-2.817881
C	-4.643629	5.782252	-2.628713
H	-4.450085	6.764977	-0.073431
C	-2.790030	6.380283	2.069431
H	-0.979078	4.498493	1.184708
H	-5.345889	6.556171	-2.274969
H	-4.159750	6.159395	-3.548886
H	-5.237618	4.895118	-2.918165
H	-2.125739	5.884489	2.797872
H	-2.488177	7.443754	2.013315
H	-3.817308	6.358112	2.476378
C	4.262323	0.725142	0.820393
C	3.997734	1.184563	2.118661
C	4.910959	0.897457	3.151168
C	6.070180	0.155163	2.848275
C	6.332663	-0.312994	1.546280
C	5.414441	-0.012611	0.521001
H	3.087901	1.758862	2.323010
C	4.630222	1.353595	4.569469
H	6.787261	-0.065208	3.649333
C	7.572078	-1.132702	1.247373
H	5.589194	-0.342454	-0.508693
H	5.562915	1.468146	5.148693
H	4.094493	2.319099	4.588122
H	3.998675	0.619537	5.106136
H	8.012481	-0.862000	0.271127
H	8.345364	-0.992732	2.022248
H	7.334853	-2.213301	1.208258

Table S24: Internal energy and cartesian coordinates for **TS-2**$_{\mathbf{deccor\text{-}\eta 2}}$.

TS-1$_{\mathbf{BHE\text{-}C}}$ SCF Done: -1709.90318464 A.U.

Ni	-1.061951	-0.754499	-1.665135
N	-0.912401	0.351935	-0.128500
C	-1.942357	1.296992	0.203324
C	-3.127531	0.875948	0.850525
C	-1.799078	2.665426	-0.132118
C	-2.821754	3.588088	0.155397
C	-3.978061	3.144876	0.811485
C	-4.139641	1.798677	1.169886
H	-4.769599	3.863362	1.051101
H	-2.702515	4.635417	-0.134611
O	-3.165608	-0.458283	1.214059
O	-0.652138	2.991161	-0.832034
C	0.170210	0.412398	0.626885
H	0.152807	1.133860	1.460699
C	1.369084	-0.357739	0.491046
C	2.394724	-0.147347	1.458118
C	1.544838	-1.308486	-0.586774
O	0.653572	-1.544168	-1.496060
C	2.804295	-2.005426	-0.601512
C	-4.387345	-1.109585	1.384369
C	3.580273	-0.857695	1.382697
C	3.797921	-1.800082	0.347564
I	3.134382	-3.437505	-2.167204
H	4.736316	-2.358129	0.293802
I	5.127757	-0.540482	2.847610
H	2.224561	0.582281	2.257083
C	-1.183880	-1.722311	-3.430220
C	-2.501580	-1.643848	-2.938933
H	-0.571423	-2.614093	-3.260746
H	-3.196016	-0.963914	-3.453349
C	-3.161896	-2.777531	-2.180258
H	-0.841452	-1.032295	-4.211686
H	-2.424633	-0.198900	-1.852163
H	-3.747245	-3.397018	-2.888902
H	-2.415284	-3.425526	-1.691580
H	-3.857125	-2.405948	-1.408639
C	-0.141998	4.289914	-0.788437
C	0.312117	4.822820	-2.000046
C	0.934274	6.088595	-2.019275
C	1.073208	6.792394	-0.810028
C	0.618241	6.259472	0.415718
C	0.008874	4.993230	0.421080
H	0.184212	4.238730	-2.918076
C	1.441866	6.668983	-3.324665
H	1.551961	7.780242	-0.818623
C	0.795683	7.037981	1.704965
H	-0.344430	4.550530	1.358658
C	-5.453863	-0.960970	0.477073
C	-6.628376	-1.713395	0.656453
C	-6.702014	-2.616261	1.738690
C	-5.634764	-2.777112	2.640819
C	-4.468141	-2.006485	2.456590
H	-5.366045	-0.257719	-0.358133
C	-7.799667	-1.552376	-0.293084
H	-7.614287	-3.210654	1.878118
C	-5.724159	-3.762191	3.789606
H	-3.612536	-2.101166	3.134251
H	-8.210702	-2.532044	-0.597273
H	-8.626310	-0.988972	0.181031
H	-7.509359	-1.006205	-1.207105
H	-6.723705	-4.225926	3.845906
H	-4.981558	-4.574928	3.680129
H	-5.522775	-3.271387	4.759795
H	0.405524	6.479921	2.573236
H	1.862095	7.258848	1.897938
H	0.268316	8.009676	1.664819
H	1.837949	7.689286	-3.184794
H	2.252648	6.048863	-3.751315
H	0.640201	6.717740	-4.084867
H	-5.035172	1.460393	1.697715

Table S25: Internal energy and cartesian coordinates for **1-BHE-C**.

SCF Done: -1709.90925624 A.U.

Ni	-1.511845	-0.786634	-1.276380
N	-0.871670	0.608026	-0.154087
C	-1.664064	1.781443	0.066691
C	-2.920632	1.674225	0.710952
C	-1.243024	3.056559	-0.383422
C	-2.063936	4.186890	-0.216701
C	-3.298967	4.051014	0.430884
C	-3.733276	2.803672	0.903486
H	-4.690143	2.697209	1.421998
H	-3.934454	4.932127	0.571345
H	-1.728773	5.154933	-0.599431
O	-3.236825	0.424820	1.211603
O	-0.052586	3.095850	-1.089949
C	-4.566981	0.005212	1.249830
C	0.789562	4.203587	-0.984136
C	0.324256	0.597817	0.411955
H	0.588951	1.475356	1.024097
C	1.316919	-0.430721	0.344534
C	2.539924	-0.200950	1.042025
H	2.673249	0.746340	1.575363
C	3.537295	-1.160048	1.035357
I	5.387246	-0.812543	2.082377
C	3.364859	-2.383760	0.341510
H	4.157511	-3.136174	0.340808
C	2.176625	-2.616731	-0.337934
I	1.919158	-4.471386	-1.388691
C	1.094585	-1.667686	-0.379659
O	0.007258	-1.929990	-1.027010
H	-2.657107	0.076812	-1.603536
C	-2.078605	-1.965644	-2.850914
C	-2.860826	-2.327463	-1.749111
H	-2.469290	-1.281637	-3.612992
H	-1.180849	-2.540180	-3.106794
C	-2.611448	-3.524907	-0.867638
H	-3.851277	-1.864466	-1.645393
H	-3.313653	-4.335510	-1.152726
H	-1.579932	-3.896417	-0.960458
H	-2.811879	-3.287695	0.192660
C	-5.455325	0.230788	0.181929
C	-6.758452	-0.294342	0.241840
C	-7.138548	-1.052026	1.370674
C	-6.250538	-1.287635	2.435932
C	-4.950552	-0.745062	2.368473
H	-5.123322	0.806980	-0.688260
C	-7.741474	-0.046575	-0.886191
H	-8.151834	-1.471571	1.416818
C	-6.672711	-2.109559	3.638085
H	-4.225618	-0.906914	3.173950
H	-8.321680	-0.956475	-1.123471
H	-8.471443	0.741050	-0.616493
H	-7.228754	0.281060	-1.807012
H	-6.605142	-1.522368	4.573094
H	-7.712542	-2.464709	3.538181
H	-6.024044	-2.996037	3.767830
C	1.503373	4.548984	-2.138464
C	2.440982	5.600602	-2.093733
C	2.629128	6.290541	-0.882153
C	1.915508	5.944998	0.284999
C	0.988733	4.889021	0.228410
H	1.321263	3.988991	-3.062314
C	3.231539	5.970632	-3.333229
H	3.350120	7.117414	-0.844133
C	2.157638	6.689582	1.583835
H	0.420700	4.602596	1.120088
H	1.407562	6.425844	2.349094
H	3.156040	6.456343	2.000511
H	2.119505	7.784171	1.434009
H	3.762467	6.928961	-3.201452
H	3.988926	5.199144	-3.570079
H	2.577196	6.062406	-4.219244

Table S26: Internal energy and cartesian coordinates for **TS-1$_{2,1\text{-ins}}$**.

SCF Done: -1709.90656029 A.U.

Ni	-0.660987	-1.050031	-2.066999
N	-1.014655	0.091518	-0.587873
C	-2.269606	0.780795	-0.494575
C	-3.445750	0.077165	-0.136391
C	-2.370893	2.155499	-0.816214
C	-3.616402	2.810445	-0.795781
C	-4.763213	2.088886	-0.439023
C	-4.692136	0.726907	-0.110289
H	-5.589526	0.165748	0.163762
H	-5.735433	2.593716	-0.429516
H	-3.674874	3.868246	-1.066188
C	-0.131124	0.368771	0.352914
H	-0.443940	1.076086	1.139041
C	1.195031	-0.159172	0.473860
C	1.965381	0.263402	1.595749
H	1.518643	0.967199	2.306375
C	3.252702	-0.211968	1.778318
I	4.413299	0.429097	3.476264
C	3.827262	-1.122044	0.857982
H	4.843727	-1.495220	1.007519
C	3.082173	-1.535802	-0.239491
I	3.958928	-2.917852	-1.630820
C	1.739003	-1.086818	-0.496481
O	1.096291	-1.508578	-1.539852
C	-1.676904	-1.887168	-3.711295
H	-2.399999	-2.618664	-3.329250
H	-2.076085	-1.205567	-4.475393
C	-0.295093	-2.191670	-3.705557
H	-2.033834	-0.695785	-2.552326
H	0.021992	-3.134507	-3.240341
C	0.708216	-1.531226	-4.618693
H	0.929201	-2.184934	-5.487249
H	0.340479	-0.564383	-5.006183
H	1.657892	-1.363942	-4.081856
O	-3.282134	-1.272346	0.112546
O	-1.201052	2.762828	-1.237648
C	-4.191220	-1.946979	0.930669
C	-4.651985	-3.187207	0.475132
C	-5.495894	-3.965838	1.294615
C	-5.865413	-3.464103	2.554908
C	-5.401226	-2.214841	3.021692
C	-4.552941	-1.455322	2.198249
H	-4.342969	-3.539344	-0.515163
C	-5.984176	-5.319877	0.818631
H	-6.528645	-4.061333	3.194119
C	-5.804077	-1.708896	4.393333
H	-4.169826	-0.486617	2.536402
C	-0.984417	4.121094	-1.003152
C	-1.326420	4.743470	0.206911
C	-1.003957	6.101698	0.405059
C	-0.333803	6.799155	-0.616765
C	0.026272	6.172864	-1.828507
C	-0.313570	4.822163	-2.018020
H	-1.843353	4.175617	0.988240
C	-1.377582	6.790370	1.703647
H	-0.082267	7.856768	-0.465176
C	0.782220	6.935465	-2.898543
H	-0.058082	4.296962	-2.944777
H	-5.379065	-0.711609	4.598903
H	-6.903540	-1.633266	4.488100
H	-5.458781	-2.392460	5.191516
H	-6.778475	-5.715639	1.474491
H	-6.386799	-5.267530	-0.209516
H	-5.162051	-6.060779	0.805795
H	-1.000491	7.826873	1.731723
H	-2.474863	6.828080	1.841024
H	-0.961803	6.256719	2.578507
H	0.624728	6.495561	-3.898598
H	0.470744	7.994449	-2.936732
H	1.871876	6.923308	-2.702397

Table S27: Internal energy and cartesian coordinates for **3-β-C**.

SCF Done: -1709.92172895145 A.U.

C	-1.487362	-1.446414	-0.455021
C	-1.250684	-0.227075	0.292722
C	-2.223588	0.259136	1.214738
C	-3.409792	-0.425849	1.412318
C	-3.681768	-1.621590	0.706123
C	-2.739864	-2.103202	-0.194892
C	-0.043705	0.539021	0.167720
N	0.979894	0.260491	-0.617162
C	2.074002	1.178238	-0.604626
C	1.920900	2.527498	-1.017508
C	3.021004	3.403035	-1.053893
C	4.284639	2.937339	-0.666318
C	4.471026	1.607993	-0.260031
C	3.369626	0.735375	-0.233465
O	0.662364	2.888140	-1.465820
C	0.190030	4.186345	-1.266116
O	3.482525	-0.607437	0.086360
C	4.428234	-1.020013	1.028959
I	-4.872973	0.316553	2.809754
I	-3.163883	-3.920855	-1.258266
O	-0.659771	-1.966615	-1.315862
Ni	0.968407	-1.248337	-1.808689
C	1.297293	-2.598041	-3.134996
C	2.499855	-1.724698	-3.256917
H	2.586698	-1.174488	-4.209190
H	2.876711	4.433004	-1.391751
H	5.143218	3.616884	-0.698041
H	5.457597	1.240387	0.035519
H	0.025917	1.434735	0.807499
H	-2.011899	1.184877	1.760440
H	-4.619107	-2.160517	0.864371
H	3.453923	-2.210668	-2.988040
H	2.481371	-0.827571	-2.476246
H	0.545367	-2.482566	-3.931703
C	1.410574	-4.001241	-2.581129
H	1.674192	-4.734645	-3.372970
H	2.179039	-4.071914	-1.789715
H	0.442764	-4.312332	-2.149306
C	-0.591223	4.726634	-2.294457
C	-1.182984	5.996269	-2.131942
C	-0.962028	6.698092	-0.933430
C	-0.177264	6.157661	0.107892
C	0.399537	4.887384	-0.063976
H	-0.736203	4.145572	-3.211884
C	-2.043793	6.582493	-3.233549
H	-1.414153	7.689926	-0.803405
C	0.032012	6.933313	1.394165
H	1.009693	4.444579	0.730663
H	-2.314135	7.630537	-3.019077
H	-1.524798	6.558095	-4.209408
H	-2.984010	6.011676	-3.354372
H	0.661866	6.374512	2.107325
H	0.522139	7.906337	1.202612
H	-0.930486	7.151160	1.893642
C	5.144055	-2.186173	0.736221
C	6.044918	-2.712708	1.685673
C	6.209711	-2.038298	2.908044
C	5.489282	-0.861753	3.209586
C	4.588043	-0.354928	2.258272
H	4.988309	-2.680464	-0.229028
C	6.811537	-3.985534	1.384682
H	6.912855	-2.440000	3.649112
C	5.679222	-0.165292	4.543102
H	4.006550	0.548975	2.468572
H	5.023400	0.717014	4.637119
H	5.454232	-0.844087	5.386707
H	6.723484	0.175717	4.674297
H	7.561717	-4.198540	2.165241
H	6.133199	-4.857772	1.325066
H	7.339652	-3.921247	0.415378

Table S28: Internal energy and cartesian coordinates for **TS-3$_{coor}$**.

SCF Done: -1788.47150219 A.U.

Ni	1.210343	-0.965040	-1.482338
N	0.868975	0.478149	-0.216391
C	1.808663	1.531824	0.000507
C	1.535126	2.861362	-0.405179
C	3.059253	1.264749	0.618447
C	3.987112	2.295091	0.846845
C	3.685765	3.599752	0.425931
C	2.472531	3.891976	-0.208862
H	2.239099	4.904037	-0.551218
H	4.413641	4.400457	0.596361
H	4.927744	2.075819	1.358351
O	0.346599	3.061600	-1.091677
O	3.234869	-0.041498	1.039722
C	-0.382254	4.236379	-0.894900
C	4.496591	-0.501314	1.427744
C	-0.254905	0.550740	0.467778
H	-0.375178	1.393222	1.170607
C	-1.356065	-0.371706	0.417378
C	-2.480996	-0.051497	1.232146
H	-2.456028	0.875521	1.815168
C	-3.580529	-0.890919	1.281072
I	-5.277511	-0.383818	2.508092
C	-3.605924	-2.090291	0.530914
H	-4.473593	-2.753921	0.571460
C	-2.511173	-2.415224	-0.261144
I	-2.574845	-4.242656	-1.391522
C	-1.337225	-1.587660	-0.376332
O	-0.361648	-1.957792	-1.149849
C	2.014721	-2.404569	-2.498321
C	1.843010	-3.774862	-1.882020
H	1.673088	-2.343103	-3.544504
C	3.252550	-1.613593	-2.188679
H	3.941886	-2.119746	-1.492022
H	3.792759	-1.239019	-3.076330
H	2.416248	-4.543557	-2.443731
H	2.192475	-3.795257	-0.833483
H	0.779914	-4.069307	-1.891741
H	2.988959	-0.621698	-1.639370
C	0.194327	0.210839	-3.363952
H	-0.528664	0.716496	-2.715239
C	1.383424	0.790485	-3.666259
H	-0.154151	-0.698714	-3.865129
H	1.681854	1.744885	-3.219601
H	2.081515	0.335881	-4.379551
C	-1.053704	4.744213	-2.015900
C	-1.876695	5.878990	-1.883647
C	-1.993899	6.488361	-0.619315
C	-1.326872	5.978008	0.512494
C	-0.511695	4.839723	0.367490
H	-0.926059	4.245942	-2.983113
C	-2.628864	6.424170	-3.081620
H	-2.621658	7.382453	-0.512056
C	-1.504848	6.625232	1.872348
H	0.022857	4.427024	1.229961
H	-2.883290	7.489912	-2.947404
H	-2.039568	6.326775	-4.010647
H	-3.578008	5.876463	-3.240022
H	-0.628821	6.454791	2.522375
H	-1.658389	7.715178	1.783378
H	-2.388295	6.214137	2.398277
C	4.570588	-1.165426	2.657246
C	5.790158	-1.741543	3.070731
C	6.912468	-1.622650	2.231638
C	6.844111	-0.957405	0.988238
C	5.619280	-0.396117	0.585839
H	3.671861	-1.231712	3.280154
C	5.876790	-2.478489	4.392532
H	7.866729	-2.061234	2.551171
C	8.068256	-0.863639	0.098137
H	5.536294	0.127201	-0.372782
H	7.884008	-0.221678	-0.780253
H	8.933645	-0.447222	0.646011
H	8.372572	-1.860538	-0.273233
H	6.923110	-2.702464	4.661887
H	5.431822	-1.888964	5.214764
H	5.329039	-3.439290	4.351957

Table S29: Internal energy and cartesian coordinates for **3-Coor-C**.

SCF Done: -1788.43651828 A.U.

Ni	1.196269	-0.896591	-1.531948
N	0.815742	0.536771	-0.266001
C	1.726399	1.615635	-0.049103
C	1.416771	2.937234	-0.454789
C	2.983795	1.382702	0.568837
C	3.883263	2.437921	0.797235
C	3.546512	3.733895	0.376321
C	2.325774	3.992984	-0.258472
H	2.064879	4.998316	-0.600828
H	4.252323	4.554117	0.546751
H	4.829515	2.244334	1.308741
O	0.223233	3.105044	-1.141287
O	3.194905	0.081720	0.990112
C	-0.537328	4.259547	-0.944510
C	4.468676	-0.343579	1.378134
C	-0.309698	0.578741	0.418168
H	-0.452860	1.417637	1.120997
C	-1.385339	-0.373339	0.367768
C	-2.518570	-0.083871	1.182536
H	-2.518846	0.843483	1.765558
C	-3.594845	-0.952912	1.231462
I	-5.305002	-0.492195	2.458482
C	-3.587582	-2.152532	0.481304
H	-4.436863	-2.839535	0.521850
C	-2.484391	-2.447544	-0.310754
I	-2.498294	-4.276032	-1.441132
C	-1.333406	-1.588329	-0.425942
O	-0.348115	-1.931767	-1.199459
C	2.212743	-2.381007	-2.249428
C	1.699851	-3.743718	-1.840800
H	2.169459	-2.349810	-3.350402
C	3.510332	-2.587103	-1.087789
H	2.381795	-4.550534	-2.185781
H	1.606402	-3.829953	-0.742709
H	0.705581	-3.927437	-2.281982
C	0.982920	0.273513	-3.139847
H	0.224674	0.890145	-2.645820
C	2.296190	0.611371	-3.089784
H	0.611986	-0.526951	-3.789129
H	2.642045	1.467922	-2.501442
H	3.056947	0.052188	-3.647765
C	-1.222354	4.748915	-2.065510
C	-2.075931	5.860868	-1.933257
C	-2.209680	6.466823	-0.668925
C	-1.529007	5.974817	0.462884
C	-0.683145	4.859144	0.317880
H	-1.081192	4.254304	-3.032723
C	-2.842662	6.385372	-3.131230
H	-2.861545	7.343496	-0.561666
C	-1.724536	6.616956	1.822738
H	-0.137557	4.461150	1.180351
H	-3.126005	7.443793	-2.997014
H	-2.250933	6.304054	-4.060257
H	-3.776545	5.812031	-3.289632
H	-0.844194	6.470425	2.472765
H	-1.907690	7.702319	1.733768
H	-2.596465	6.181964	2.348667
C	4.560724	-1.005432	2.607636
C	5.795525	-1.548137	3.021121
C	6.914182	-1.398736	2.182028
C	6.827742	-0.735599	0.938628
C	5.588085	-0.207861	0.536229
H	3.664134	-1.096157	3.230544
C	5.902186	-2.282451	4.342922
H	7.880029	-1.811181	2.501561
C	8.048881	-0.608544	0.048527
H	5.490884	0.313004	-0.422392
H	7.847225	0.028163	-0.829863
H	8.902613	-0.168724	0.596401
H	8.380221	-1.596790	-0.322843
H	6.954215	-2.477861	4.612277
H	5.441335	-1.705257	5.165154
H	5.380792	-3.257807	4.302347
H	3.574954	-3.329898	-1.881516
H	4.411733	-1.976041	-1.088214
H	3.413281	-3.090189	-0.126848

Table S30: Internal energy and cartesian coordinates for **TS-3$_{ins}$**.

SCF Done: -1788.46857397 A.U.

Ni	0.937720	-1.092728	-1.877441
N	0.985662	0.307050	-0.590882
C	2.147078	1.135963	-0.460965
C	2.136934	2.490466	-0.874542
C	3.350794	0.599409	0.057545
C	4.504582	1.393677	0.174749
C	4.461907	2.734137	-0.235501
C	3.290331	3.289062	-0.768273
O	3.335807	-0.747915	0.370379
C	4.062099	-1.212438	1.469319
C	-0.016271	0.602277	0.219474
H	0.136510	1.451500	0.906258
C	-1.276163	-0.068290	0.339856
C	-2.208484	0.473312	1.272022
C	-1.577506	-1.278880	-0.403433
O	-0.768749	-1.807260	-1.261369
C	-2.854702	-1.878093	-0.109919
C	1.242212	-3.048286	-2.712537
C	-3.426470	-0.149016	1.484341
C	-3.761743	-1.338993	0.794179
I	-3.374228	-3.696473	-1.129355
H	-4.721222	-1.831126	0.972515
I	-4.837553	0.675068	2.889234
H	-1.942938	1.389033	1.811407
C	1.489830	-1.287473	-3.845114
C	2.259131	-0.328247	-3.091486
H	3.317981	-0.537872	-2.888030
H	2.005597	-2.002697	-4.496055
H	2.004925	0.736796	-3.157861
H	0.539326	-0.951423	-4.288306
C	0.171690	-3.714280	-3.563952
C	2.650638	-3.619912	-2.853113
H	0.949478	-3.128980	-1.646293
O	0.965697	2.934843	-1.465866
C	0.545648	4.254742	-1.293728
C	-0.096699	4.846952	-2.389737
C	-0.627549	6.146180	-2.272660
C	-0.485822	6.828484	-1.049150
C	0.152871	6.235521	0.058827
C	0.673869	4.934547	-0.070273
H	-0.177275	4.283377	-3.325742
C	-1.346472	6.787341	-3.443195
H	-0.884869	7.846631	-0.954473
C	0.251175	6.973983	1.379729
H	1.178981	4.454256	0.774740
C	4.709112	-2.445493	1.318242
C	5.387283	-3.019250	2.412521
C	5.407281	-2.325192	3.636307
C	4.753276	-1.085370	3.795948
C	4.076073	-0.527453	2.697164
H	4.676699	-2.948483	0.345544
C	6.074615	-4.362647	2.267096
H	5.943347	-2.760890	4.489393
C	4.754748	-0.380086	5.138341
H	3.558193	0.432888	2.792425
H	-1.384176	7.885702	-3.341305
H	-0.853490	6.549192	-4.402616
H	-2.390536	6.426368	-3.516556
H	-0.659286	6.822099	1.991350
H	1.110179	6.624869	1.979040
H	0.360680	8.062164	1.226427
H	6.768280	-4.553088	3.104022
H	5.338522	-5.189310	2.251137
H	6.650495	-4.424983	1.325947
H	5.732542	-0.475337	5.643655
H	4.527871	0.695039	5.033309
H	3.995295	-0.812522	5.818044
H	5.363042	3.351756	-0.155072
H	3.259637	4.327929	-1.108383
H	5.419688	0.955540	0.582985
H	2.670222	-4.641114	-2.422370
H	2.977873	-3.706527	-3.907180
H	3.395951	-3.017428	-2.304407
H	0.096812	-4.786565	-3.293152
H	-0.814913	-3.259362	-3.378259
H	0.405343	-3.663211	-4.644841

Table S31: Internal energy and cartesian coordinates for **4-β-T**.

SCF Done: -1788.51289169 A.U.

Ni	0.533875	-2.233211	-0.266688
N	1.035220	-0.638345	0.514882
C	2.310926	-0.488740	1.149060
C	3.382682	0.154266	0.478164
C	4.652373	0.241308	1.078885
C	4.855735	-0.303212	2.355241
C	3.809827	-0.941064	3.038905
C	2.548565	-1.032974	2.430687
O	1.533871	-1.749440	3.052506
C	0.647228	-1.078967	3.894280
H	3.952321	-1.377722	4.031817
H	5.846601	-0.235690	2.817098
H	5.470889	0.725187	0.538752
O	3.108258	0.594746	-0.801943
C	3.887036	1.599343	-1.384031
C	4.141201	2.814540	-0.724812
C	4.321868	1.377413	-2.696075
C	5.029793	2.387580	-3.378462
C	5.293803	3.597548	-2.710170
C	4.852357	3.829145	-1.390449
C	5.114654	5.159642	-0.711971
H	5.058076	5.074402	0.387086
H	6.111976	5.555959	-0.973413
H	4.372094	5.919965	-1.022244
H	3.784632	2.966416	0.299956
H	4.099067	0.417674	-3.175004
H	5.910076	1.159058	-4.948755
H	4.642336	2.269090	-5.516110
H	6.254382	2.905925	-5.101789
C	5.486770	2.169813	-4.807283
H	5.855472	4.383837	-3.231040
H	2.206109	-3.558376	1.107560
H	2.965338	-2.965889	-0.458055
C	2.054729	-3.334314	0.041597
C	1.200582	-4.283788	-0.744871
H	0.874974	-5.159603	-0.148523
H	0.151116	-3.790814	-0.954856
C	1.707843	-4.710586	-2.145720
H	2.059181	-3.790599	-2.655666
C	2.900766	-5.674734	-1.998566
H	3.715763	-5.223589	-1.405109
H	2.590692	-6.609325	-1.492767
H	3.307730	-5.949633	-2.988411
C	0.580554	-5.334492	-2.989200
H	0.180960	-6.246303	-2.505200
H	-0.258297	-4.628029	-3.128489
H	0.949319	-5.623356	-3.989750
O	-1.157595	-1.715483	-0.903403
C	-1.686309	-0.538708	-0.795883
C	-1.023878	0.572090	-0.136604
C	-1.655225	1.848576	-0.051824
H	-1.127464	2.665545	0.451726
C	-2.912179	2.043423	-0.596706
I	-3.863431	3.972271	-0.462777
H	-4.591432	1.148319	-1.671638
C	-2.989919	-0.259216	-1.335682
I	-4.022335	-1.862921	-2.320301
H	0.672428	1.350044	0.938966
C	0.270644	0.443490	0.459726
C	-3.597336	0.986656	-1.246650
C	-0.432116	-1.846006	4.365869
C	-1.369925	-1.272267	5.239281
C	-1.200877	0.072202	5.634712
C	-0.125113	0.844870	5.164183
C	0.811057	0.257809	4.286107
H	-0.523270	-2.888250	4.040955
C	-2.556917	-2.077315	5.730486
H	-1.925811	0.524113	6.323955
C	0.027619	2.296318	5.576634
H	1.669601	0.835709	3.928168
H	1.089288	2.572890	5.707572
H	-0.394723	2.977940	4.812744
H	-0.498032	2.503379	6.524882
H	-2.806768	-1.830666	6.777930
H	-3.458756	-1.868773	5.123054
H	-2.364500	-3.162537	5.670378

Table S32: Internal energy and cartesian coordinates for **TS-1**$_{\textbf{Transf-1}}$.

SCF Done: -1788.45889573 A.U.

Ni	-0.197961	-1.943052	-1.829046
N	0.912497	-1.168124	-0.453394
C	2.212882	-1.706228	-0.192667
C	3.389487	-1.007448	-0.561154
C	2.354172	-2.985932	0.394898
C	3.616763	-3.560858	0.594565
C	4.766574	-2.856608	0.203953
C	4.659209	-1.584736	-0.374137
H	5.548903	-1.032729	-0.691181
H	5.755873	-3.304463	0.345722
H	3.677344	-4.553154	1.051378
O	3.210157	0.207488	-1.206044
O	1.215496	-3.711887	0.718316
C	4.107038	1.256728	-0.989860
C	0.645421	-3.534965	1.978061
C	0.568252	-0.106393	0.250728
H	1.298021	0.260521	0.991908
C	-0.665731	0.620377	0.188923
C	-0.793652	1.734579	1.069244
H	0.053008	1.995747	1.713319
C	-1.967297	2.466727	1.107863
I	-2.155751	4.146713	2.441860
C	-3.064341	2.117294	0.283482
H	-3.992188	2.694069	0.322341
C	-2.950329	1.030765	-0.574729
I	-4.631760	0.514871	-1.808170
C	-1.757155	0.228711	-0.686668
O	-1.697175	-0.761233	-1.515416
H	0.907990	-2.860975	-2.135202
C	-1.425997	-3.535808	-2.069185
C	-1.184582	-3.026982	-3.353988
H	-0.864790	-4.394652	-1.685767
H	-2.342623	-3.260650	-1.532370
C	-2.170178	-2.201458	-4.143122
H	-0.377224	-3.493051	-3.935312
H	-2.769125	-2.869415	-4.796207
H	-2.853733	-1.643971	-3.485145
H	-1.657054	-1.481575	-4.805558
C	1.384873	-0.738332	-4.043342
H	1.051153	-1.356606	-4.885214
C	0.668245	0.313220	-3.603967
H	2.344317	-1.005653	-3.588365
H	-0.289900	0.593778	-4.056183
H	1.018854	0.928331	-2.768400
C	4.353074	2.093680	-2.086999
C	5.178547	3.224339	-1.932811
C	5.751902	3.478556	-0.672073
C	5.502653	2.643804	0.436158
C	4.670891	1.520706	0.269984
H	3.894593	1.852567	-3.052369
C	5.433189	4.152030	-3.104392
H	6.408000	4.349824	-0.548670
C	6.097431	2.963830	1.793837
H	4.467214	0.853559	1.114457
H	4.592334	4.858615	-3.244077
H	6.346372	4.752886	-2.952002
H	5.545194	3.591621	-4.049624
H	6.189251	2.060299	2.421612
H	7.099937	3.417110	1.698511
H	5.465999	3.685681	2.347275
C	-0.573475	-4.203329	2.188234
C	-1.216458	-4.115253	3.433324
C	-0.614685	-3.356023	4.459672
C	0.602873	-2.683914	4.255635
C	1.239884	-2.779548	3.000061
H	-1.002347	-4.792258	1.370258
C	-2.545702	-4.807408	3.662822
H	-1.107445	-3.289829	5.438164
C	1.225423	-1.852763	5.361085
H	2.201767	-2.283917	2.831944
H	-2.638110	-5.169798	4.702125
H	-3.392002	-4.116681	3.482151
H	-2.676443	-5.670012	2.986378
H	2.326425	-1.946375	5.369898
H	0.991310	-0.777523	5.236605
H	0.849596	-2.156056	6.353619

Table S33: Internal energy and cartesian coordinates for **1-Transf-1**.

SCF Done: -1788.41880525 A.U.

C	-1.808746	-0.852323	-0.441541
C	-0.884017	0.106873	0.130522
C	-1.351349	1.153395	0.982471
C	-2.694126	1.253912	1.296945
C	-3.633143	0.335548	0.762969
C	-3.194463	-0.672151	-0.085009
C	0.519638	0.095203	-0.155423
N	1.222915	-0.825896	-0.795645
C	2.603665	-0.484646	-1.022004
C	2.952475	0.538087	-1.958153
C	4.313629	0.732707	-2.286640
C	5.327841	-0.024335	-1.692451
C	4.991283	-0.946129	-0.697534
C	3.645689	-1.175152	-0.332084
O	1.979853	1.512547	-2.550622
C	1.837411	2.938479	-2.329422
O	3.406599	-2.074318	0.836586
C	3.374008	-1.771510	2.254242
I	-3.388888	2.813553	2.605618
I	-4.623875	-2.045612	-0.901972
O	-1.463622	-1.811288	-1.237880
Ni	0.270766	-2.428938	-1.786812
C	-0.691262	-3.238621	-3.296480
C	-0.898285	-2.108440	-4.287528
C	1.896772	-3.554974	-2.112440
C	0.927163	-4.309409	-1.405119
C	0.878995	-4.525603	0.087874
H	4.566119	1.493608	-3.033383
H	6.374492	0.133471	-1.972506
H	5.780141	-1.478906	-0.154871
H	1.068824	0.977901	0.220242
H	-0.625406	1.866964	1.387277
H	-4.693887	0.423075	1.011771
H	0.052322	-1.726519	-4.704132
H	2.053544	-3.742703	-3.182437
H	2.739915	-3.092285	-1.590275
H	0.335634	-5.036256	-1.976078
H	1.526361	-5.383399	0.363490
H	1.231630	-3.649844	0.653863
H	-0.147759	-4.765041	0.413925
H	-1.486127	-2.485322	-5.153402
H	-1.469400	-1.274216	-3.852979
H	-0.129493	-4.077888	-3.738995
H	-1.625924	-3.587714	-2.829323
C	2.811368	3.822087	-2.809676
C	2.673838	5.198848	-2.596102
C	1.562351	5.692002	-1.902275
C	0.588394	4.808393	-1.422022
C	0.725923	3.431632	-1.635595
H	3.675947	3.438484	-3.349374
C	3.682579	6.114014	-3.093509
H	1.455372	6.762926	-1.736147
C	-0.562790	5.319159	-0.703415
H	-0.031675	2.744311	-1.262025
H	3.406263	7.134865	-2.833828
H	4.644751	5.872884	-2.644060
H	3.754323	6.021614	-4.176207
H	-1.205136	4.489960	-0.410601
H	-0.228693	5.851196	0.186100
H	-1.119119	5.999925	-1.346047
C	2.168256	-1.405488	2.864312
C	2.136789	-1.113122	4.233082
C	3.311076	-1.186780	4.991782
C	4.516829	-1.552802	4.381711
C	4.548296	-1.845168	3.012941
H	1.254828	-1.348193	2.274152
C	0.887974	-0.734026	4.864941
H	3.286599	-0.959360	6.056490
C	5.733055	-1.629091	5.167507
H	5.486199	-2.129882	2.538394
H	6.561384	-1.926958	4.526362
H	5.944613	-0.654321	5.604530
H	5.606594	-2.363287	5.961789
H	1.059222	-0.546518	5.923920
H	0.502406	0.169059	4.394096
H	0.164387	-1.539907	4.751356

Table S34: Internal energy and cartesian coordinates for **TS-1$_{\text{Transf-2}}$**.

Done: -1788.47851058 A.U.

Ni	-1.720939	-0.927800	-0.715740
N	-0.636859	0.686811	-0.402411
C	-1.351620	1.907039	-0.390353
C	-2.755861	1.814357	-0.183854
C	-0.830107	3.217663	-0.596600
C	-1.661156	4.350243	-0.538659
C	-3.027997	4.206430	-0.272001
C	-3.591145	2.932711	-0.098254
H	-4.661343	2.804882	0.081720
H	-3.669336	5.092828	-0.227576
H	-1.223208	5.336633	-0.716217
O	-3.247016	0.505918	-0.104295
O	0.502540	3.320784	-0.963789
C	-4.497243	0.300604	0.523324
C	1.265816	4.413761	-0.540572
C	0.635805	0.635408	-0.042589
H	1.148455	1.568023	0.227558
C	1.433313	-0.553253	0.057316
C	2.805700	-0.358919	0.400672
H	3.168238	0.665532	0.537497
C	3.659049	-1.437809	0.546664
I	5.732647	-1.122290	1.045140
C	3.189601	-2.762366	0.371928
H	3.864960	-3.613527	0.489732
C	1.853968	-2.965412	0.050522
I	1.149478	-4.979044	-0.211421
C	0.904737	-1.895214	-0.132899
O	-0.322526	-2.180937	-0.441080
H	-3.441385	-2.287144	1.396405
C	-2.460179	-0.148883	-3.035875
C	-1.491853	-1.058933	-3.321532
H	-3.507593	-0.449440	-2.930431
H	-2.245327	0.926058	-3.001477
C	-0.057387	-0.735183	-3.637370
H	-1.776048	-2.116461	-3.407047
H	0.164979	-0.978240	-4.695758
H	0.169549	0.332203	-3.473698
H	0.631158	-1.341442	-3.021395
C	-3.035425	-3.026021	0.680241
H	-3.721478	-3.901679	0.699727
C	-2.909271	-2.456993	-0.724578
H	-2.053305	-3.369282	1.049021
H	-3.868787	-2.066500	-1.119565
H	-2.476639	-3.189291	-1.427720
C	2.182066	4.927929	-1.467694
C	3.047801	5.971976	-1.087401
C	2.958819	6.482612	0.221992
C	2.043647	5.963801	1.160431
C	1.188748	4.916253	0.769146
H	2.208891	4.506988	-2.478724
C	4.059627	6.524986	-2.071344
H	3.621019	7.305587	0.520160
C	1.998263	6.502572	2.577081
H	0.463951	4.495965	1.474967
H	2.690117	5.946347	3.238840
H	2.296201	7.565047	2.614003
H	0.988024	6.414993	3.014008
H	4.402888	7.530932	-1.774155
H	4.953905	5.875203	-2.132260
H	3.639657	6.593634	-3.090707
C	-5.609066	0.023644	-0.276226
C	-6.853411	-0.234759	0.339079
C	-6.931179	-0.192667	1.743055
C	-5.806885	0.086340	2.550317
C	-4.573175	0.337813	1.922637
H	-5.504670	0.015544	-1.366193
C	-8.070041	-0.561474	-0.503292
H	-7.897292	-0.386310	2.226776
C	-5.920507	0.084100	4.061625
H	-3.673455	0.555084	2.508428
H	-5.101609	0.655267	4.531549
H	-6.878933	0.519880	4.395417
H	-5.874906	-0.947192	4.461077
H	-8.996787	-0.521061	0.093952
H	-8.178369	0.140415	-1.350078
H	-7.994518	-1.578281	-0.933609

Table S35: Internal energy and cartesian coordinates for **1-Transf-2**.

Done: -1670.62434805 A.U.

Ni	0.165185	1.832786	-1.959829
N	-0.918747	1.082930	-0.561901
C	-2.229506	1.594320	-0.324327
C	-3.395715	0.814212	-0.550678
C	-2.399324	2.947293	0.059286
C	-3.672373	3.512877	0.216727
C	-4.807154	2.723444	-0.023882
C	-4.675673	1.381848	-0.409347
H	-5.558078	0.769487	-0.614984
H	-5.806868	3.157780	0.082916
H	-3.751407	4.561471	0.518316
O	-3.181841	-0.472855	-1.007297
O	-1.275756	3.755661	0.198606
C	-4.167090	-1.450495	-0.838513
C	-0.577041	3.735510	1.408992
C	-0.522912	0.052934	0.162219
H	-1.211422	-0.335066	0.930379
C	0.745158	-0.608788	0.060903
C	0.974116	-1.698001	0.952549
H	0.177714	-1.981363	1.649207
C	2.178719	-2.378876	0.935661
I	2.516346	-4.017641	2.292940
C	3.207166	-2.009979	0.035583
H	4.157738	-2.549363	0.024964
C	2.993296	-0.950489	-0.837404
I	4.555869	-0.395298	-2.200895
C	1.768757	-0.197350	-0.878498
O	1.657758	0.782330	-1.730038
H	-1.080542	2.910522	-2.431330
C	-0.461796	3.403265	-3.319290
H	-0.486984	4.463612	-3.017542
C	0.893966	2.803175	-3.435317
H	-1.134755	3.211891	-4.172127
H	1.755448	3.409215	-3.122927
H	1.096665	2.146000	-4.291652
C	-4.455565	-2.251793	-1.948329
C	-5.370638	-3.318074	-1.821673
C	-5.981477	-3.540499	-0.574825
C	-5.691920	-2.736513	0.549190
C	-4.770207	-1.684782	0.410603
H	-3.957471	-2.041007	-2.901030
C	-5.678485	-4.204773	-3.012029
H	-6.699505	-4.364487	-0.471925
C	-6.361570	-3.008792	1.882090
H	-4.520043	-1.048585	1.266703
C	0.652302	4.413600	1.410241
C	1.411049	4.483549	2.591184
C	0.910669	3.872687	3.759723
C	-0.318553	3.188655	3.762420
C	-1.071038	3.125177	2.571342
H	1.002039	4.883688	0.484653
C	2.756690	5.181774	2.598494
H	1.494873	3.930782	4.687089
C	-0.825138	2.511425	5.021277
H	-2.040908	2.616792	2.556475
H	-6.525973	-4.879628	-2.803044
H	-5.931450	-3.607445	-3.907112
H	-4.807832	-4.833279	-3.279470
H	-6.004648	-2.317442	2.664441
H	-7.459900	-2.897387	1.810331
H	-6.164986	-4.040574	2.228062
H	-1.928739	2.510017	5.067390
H	-0.494175	1.455646	5.069468
H	-0.446175	3.012674	5.929068
H	2.987075	5.604157	3.592405
H	3.571915	4.476848	2.344879
H	2.793481	6.001946	1.860122

4.2.2 8-CH_3-I2

Table S36: Internal energy and cartesian coordinates for **1-β-T**.

SCF Done: -1638.10632613 A.U.

Ni	-0.841768	-1.529516	0.881803
N	-1.172125	-0.194553	-0.350711
C	-2.480100	0.007041	-0.934513
C	-3.432156	0.818828	-0.271056
C	-4.694333	0.996764	-0.873013
C	-5.007343	0.389909	-2.094122
C	-4.052472	-0.413349	-2.735276
C	-2.780615	-0.625776	-2.171636
C	-1.779531	-1.533981	-2.880863
C	2.025989	1.543043	-1.072163
C	1.188227	0.566097	-0.456647
C	1.741416	-0.401203	0.474618
C	3.153298	-0.291427	0.725256
C	3.959264	0.668746	0.126079
C	3.378409	1.588598	-0.781664
I	4.634139	3.067276	-1.716901
H	5.027793	0.712807	0.352204
I	4.031986	-1.686385	2.099041
H	-0.497113	1.333892	-1.562827
C	-0.201796	0.582645	-0.811207
C	-2.592628	-2.200643	1.217305
C	-3.139237	1.481172	1.074878
C	-3.345647	2.991600	1.081949
C	-4.423097	3.564577	1.777924
H	-5.114243	2.913127	2.330471
C	-4.633018	4.960944	1.789289
H	-3.889146	6.865648	1.079431
C	-3.735720	5.777936	1.082352
C	-2.638474	5.234892	0.378710
C	-1.673232	6.142790	-0.358293
H	-1.612546	3.407187	-0.159575
C	-2.460236	3.841950	0.386268
C	-5.791409	5.559225	2.563658
H	-5.427221	1.642360	-0.374588
H	-5.990490	0.547290	-2.551588
H	-4.289541	-0.881423	-3.698765
H	1.578775	2.253613	-1.775438
O	1.027995	-1.317262	1.051085
C	-1.807351	-3.076372	2.149141
C	-2.096569	-2.929489	3.653830
H	-1.806722	-4.131246	1.819199
H	-3.262887	-1.464501	1.689175
H	-3.026608	-2.682629	0.329301
H	-0.661076	-2.834850	2.044126
H	-3.100090	-3.330393	3.880744
H	-1.359932	-3.476036	4.268425
H	-2.074581	-1.867814	3.955554
H	-5.949706	6.619132	2.299319
H	-6.734641	5.016329	2.369166
H	-5.612989	5.513070	3.655379
H	-0.950995	5.563656	-0.959043
H	-2.205095	6.831882	-1.040409
H	-1.093109	6.770499	0.344769
C	-1.651156	-2.923901	-2.255828
C	-0.441305	-3.333405	-1.666781
C	-0.305706	-4.609328	-1.075819
C	-1.419939	-5.467964	-1.076814
C	-2.645746	-5.089086	-1.666395
C	-2.747026	-3.810289	-2.245220
H	0.419058	-2.652691	-1.674741
C	1.013880	-5.028120	-0.458243
H	-1.331237	-6.462115	-0.617587
C	-3.819343	-6.049165	-1.692456
H	-3.700499	-3.495681	-2.690024
H	-4.779651	-5.513300	-1.791143
H	-3.746303	-6.751015	-2.546202
H	-3.863297	-6.662221	-0.774396
H	0.896311	-5.917859	0.185006
H	1.759067	-5.281018	-1.237168
H	1.447395	-4.213767	0.150446
H	-0.779480	-1.065226	-2.905380
H	-2.101438	-1.636660	-3.934936
H	-2.108370	1.237400	1.385836
H	-3.805343	1.032233	1.838210

Table S37: Internal energy and cartesian coordinates for **TS-2$_{Coor}$**.

SCF Done: -1716.65001098 A.U.

Ni	1.045187	-1.338462	-1.533805
N	0.968957	0.367516	-0.796056
C	2.048991	1.318804	-0.937662
C	2.006569	2.281876	-1.973870
C	3.143299	1.244679	-0.036115
C	4.204373	2.154382	-0.198614
C	4.185254	3.107923	-1.227134
C	3.094806	3.167338	-2.105450
H	3.077876	3.909942	-2.912817
H	5.023895	3.803475	-1.343902
H	5.054253	2.102376	0.489793
C	0.816013	2.378880	-2.910932
C	3.127171	0.198507	1.078866
C	-0.374865	3.178613	-2.371621
C	4.436756	0.000727	1.821893
C	-0.053495	0.757000	-0.047151
H	-0.009967	1.791515	0.328055
C	-1.206192	0.000070	0.349987
C	-2.178184	0.670857	1.148695
H	-2.027421	1.729710	1.383736
C	-3.292378	-0.009932	1.610807
I	-4.759701	1.007882	2.817314
C	-3.486784	-1.379797	1.309138
H	-4.366539	-1.911252	1.681230
C	-2.543662	-2.041020	0.531386
I	-2.834741	-4.118311	0.071094
C	-1.371226	-1.399087	0.002348
O	-0.527789	-2.043045	-0.739473
C	2.767794	-1.291222	-2.355784
H	2.706046	-0.918502	-3.393636
H	3.534996	-0.752821	-1.779944
C	2.756706	-2.798131	-2.214095
H	1.689781	-3.138297	-1.957453
C	3.148317	-3.600408	-3.472703
H	3.348480	-3.122582	-1.339365
C	-0.405625	-2.683396	-3.846420
H	-1.031408	-3.239513	-3.140354
C	-0.381727	-1.333763	-3.846527
H	0.201670	-3.269218	-4.546571
H	-1.038366	-0.754418	-3.188395
H	0.224302	-0.766109	-4.563141
H	3.007839	-4.686080	-3.325326
H	2.543228	-3.287381	-4.341318
H	4.209503	-3.418332	-3.717483
C	-0.197374	4.294663	-1.533500
C	-1.299202	5.049065	-1.078906
C	-2.593038	4.658347	-1.469654
C	-2.804548	3.543065	-2.305961
C	-1.684167	2.814815	-2.746063
H	0.815689	4.583323	-1.225768
C	-1.087994	6.269057	-0.202715
H	-3.458451	5.232245	-1.111373
C	-4.209327	3.125473	-2.694642
H	-1.834509	1.940586	-3.393741
C	4.634599	0.566296	3.093852
C	5.845443	0.390999	3.796146
C	6.866966	-0.362924	3.191853
C	6.700767	-0.947824	1.918947
C	5.481299	-0.753234	1.246824
H	3.828696	1.156796	3.550576
C	6.029633	0.988450	5.177530
H	7.817177	-0.501469	3.725470
C	7.806747	-1.782364	1.302991
H	5.339765	-1.195478	0.251297
H	-1.964687	6.464107	0.439783
H	-0.204643	6.151971	0.449986
H	-0.921886	7.178375	-0.812882
H	-4.197973	2.344291	-3.474214
H	-4.763362	2.720833	-1.826505
H	-4.793661	3.981289	-3.079997
H	7.685751	-1.871284	0.209234
H	8.802390	-1.345995	1.501091
H	7.815810	-2.809042	1.717986
H	7.095809	1.033093	5.460164
H	5.618524	2.012570	5.235502
H	5.508861	0.387726	5.948263
H	2.793387	-0.763840	0.637128
H	2.333624	0.462429	1.806418
H	1.155433	2.844358	-3.858525
H	0.469630	1.361284	-3.168363

Table S38: Internal energy and cartesian coordinates for **2-Coor-T.**

SCF Done: -1716.66121232 A.U.

C	2.317364	-0.231067	0.790895
C	1.826135	0.163096	-0.510848
C	2.723732	0.472146	-1.575142
C	4.090835	0.406892	-1.369993
C	4.618499	0.025813	-0.110280
C	3.750782	-0.285539	0.928062
C	0.424592	0.228254	-0.791715
N	-0.606040	0.026434	0.015808
C	-1.880107	0.137781	-0.665534
C	-2.469760	1.416260	-0.836315
C	-3.695829	1.495327	-1.523288
C	-4.315182	0.340304	-2.020289
C	-3.720207	-0.916149	-1.838461
C	-2.495104	-1.040923	-1.158013
C	-1.755842	2.659003	-0.296523
C	-2.577469	3.936940	-0.290958
C	-1.797648	-2.390939	-0.976043
I	5.456475	0.884165	-2.963984
I	4.557908	-0.863882	2.829494
O	1.535791	-0.525233	1.773437
Ni	-0.414005	-0.435432	1.926176
C	0.004849	-0.582632	3.959634
C	-0.244153	-1.842023	3.411513
C	-2.356581	-0.262466	2.208145
H	-4.162551	2.475774	-1.663063
H	-5.269151	0.419879	-2.553827
H	-4.204451	-1.818336	-2.226103
H	0.177243	0.472823	-1.839434
H	2.312312	0.761329	-2.548582
H	5.699435	-0.023937	0.042454
H	-1.206648	-2.347828	3.543397
H	0.590150	-2.457386	3.056354
H	1.033241	-0.213254	4.022007
H	-0.752119	-0.053423	4.543538
C	-3.037391	-0.188355	3.575918
H	-2.573747	0.661247	1.642046
H	-2.750941	-1.115351	1.620310
C	-4.575611	-0.129230	3.432400
H	-2.783004	-1.058403	4.212593
H	-2.701551	0.712980	4.125251
H	-5.064848	-0.065041	4.422132
H	-4.888680	0.749846	2.840167
H	-4.961550	-1.028994	2.919112
C	-3.529484	4.173647	0.722371
C	-4.304639	5.346479	0.738825
C	-4.116377	6.291322	-0.291671
C	-3.172104	6.089629	-1.313708
C	-2.410986	4.901938	-1.299800
H	-3.670750	3.424480	1.512919
C	-5.309579	5.602467	1.845012
H	-4.720435	7.208834	-0.294758
C	-2.960660	7.130036	-2.396369
H	-1.673352	4.726749	-2.094847
H	-6.250114	6.025848	1.448145
H	-5.557359	4.674809	2.389457
H	-4.917649	6.325888	2.586048
H	-2.815221	6.662286	-3.386884
H	-3.819875	7.819396	-2.467958
H	-2.061610	7.744027	-2.194102
C	-2.635548	-3.615075	-1.302293
C	-3.595200	-4.093214	-0.384507
C	-4.379564	-5.224080	-0.668155
C	-4.191537	-5.880225	-1.903619
C	-3.242574	-5.433096	-2.838751
C	-2.472224	-4.293570	-2.521937
H	-3.733451	-3.568594	0.570431
C	-5.396631	-5.740803	0.330731
H	-4.800194	-6.763844	-2.139392
C	-3.034392	-6.163116	-4.151289
H	-1.727910	-3.930113	-3.243531
H	-2.988290	-5.460910	-5.003796
H	-2.083622	-6.730317	-4.150042
H	-3.848138	-6.882578	-4.347753
H	-6.377897	-5.920350	-0.146054
H	-5.074350	-6.702331	0.774624
H	-5.548728	-5.027378	1.159126
H	-1.432135	-2.455502	0.069084
H	-0.879535	-2.405718	-1.597666
H	-1.401889	2.438464	0.731117
H	-0.831324	2.829853	-0.883669

Table S39: Internal energy and cartesian coordinates for **TS-2$_{ins-T}$**.

SCF Done: -1716.63573880 A.U.

C	-0.894994	4.241697	1.861676
C	-2.384067	3.558802	0.656616
C	-2.852563	4.868317	0.014907
C	-4.136614	4.669242	-0.815554
C	0.250661	4.472347	1.014963
Ni	-0.447318	2.711653	0.531893
O	1.220690	2.285260	-0.222521
C	1.725101	1.113375	-0.467364
C	3.037541	1.006835	-1.047298
C	3.652388	-0.209446	-1.321353
C	2.968565	-1.411028	-1.018194
C	1.700426	-1.383845	-0.461821
C	1.060773	-0.140747	-0.188377
C	-0.263484	-0.199154	0.366545
N	-1.053579	0.818530	0.648056
C	-2.354464	0.474690	1.168027
C	-3.451885	0.292247	0.288097
C	-4.722747	0.032751	0.843472
C	-4.911334	-0.030249	2.228046
C	-3.814078	0.146105	3.086266
C	-2.525350	0.387808	2.577048
C	-1.338400	0.511364	3.518560
C	-3.304574	0.386729	-1.230301
H	-3.952562	0.089242	4.173255
H	-5.908311	-0.221385	2.640529
H	-5.567685	-0.128099	0.163506
H	-0.745851	3.637363	2.770145
H	-1.606030	5.055670	2.050841
H	0.197095	5.258518	0.250303
H	1.261623	4.225900	1.358018
H	1.168249	-2.311546	-0.226152
I	3.928097	-3.294520	-1.437329
I	4.079110	2.828564	-1.501214
H	-0.648549	-1.212957	0.568543
H	4.653048	-0.234807	-1.760893
H	-4.477574	5.628795	-1.244651
H	-3.969057	3.968780	-1.654212
H	-4.957096	4.264775	-0.195311
H	-2.056118	5.269931	-0.640488
H	-3.043633	5.639042	0.788129
H	-3.039110	3.199951	1.466075
H	-2.378361	2.785113	-0.141199
H	-3.790316	1.319759	-1.580236
H	-2.235330	0.483735	-1.490942
C	-3.914052	-0.784664	-1.993603
H	-1.712703	0.828949	4.512736
C	-0.513501	-0.769260	3.688166
H	-0.662590	1.311781	3.162834
C	-4.929423	-0.570037	-2.940220
C	-5.495310	-1.639614	-3.667773
C	-5.025283	-2.939708	-3.419394
C	-4.005728	-3.189554	-2.475061
C	-3.464132	-2.103033	-1.768911
H	-5.288921	0.452278	-3.121376
C	-6.575171	-1.382428	-4.700705
H	-5.462222	-3.782596	-3.971991
C	-3.507000	-4.601864	-2.238845
H	-2.681451	-2.285342	-1.020961
C	0.886230	-0.687433	3.802490
C	1.675883	-1.837979	4.003081
C	1.030777	-3.085333	4.091988
C	-0.369532	-3.201218	3.980616
C	-1.128594	-2.034488	3.770303
H	1.376005	0.292913	3.728122
C	3.186265	-1.733644	4.081242
H	1.633816	-3.990440	4.245555
C	-1.045677	-4.553154	4.105085
H	-2.218277	-2.112745	3.667429
H	-2.842288	-4.654527	-1.359429
H	-4.344344	-5.304914	-2.074006
H	-2.937080	-4.979103	-3.109560
H	-7.095699	-2.314220	-4.982254
H	-7.332657	-0.668713	-4.328252
H	-6.151355	-0.947983	-5.626807
H	3.630717	-2.631846	4.544065
H	3.631099	-1.625917	3.073581
H	3.502505	-0.853742	4.670075
H	-2.022160	-4.566791	3.589756
H	-0.422489	-5.359652	3.678932
H	-1.231764	-4.814117	5.165280

Table S40: Internal energy and cartesian coordinates for **2-Coor-C**.

SCF Done: -1717.55219903 A.U.

Ni	-0.189946	-2.899360	0.109277
N	0.954569	-1.241771	0.515924
C	2.293100	-1.341350	1.050175
C	3.411738	-1.384397	0.178082
C	2.460954	-1.432982	2.460343
C	3.758518	-1.611727	2.974351
C	4.872600	-1.674474	2.123248
C	4.695055	-1.548467	0.741478
H	5.562372	-1.564818	0.071096
H	5.876686	-1.813067	2.539221
H	3.890769	-1.697711	4.060038
C	3.271114	-1.264224	-1.340395
C	1.272899	-1.310028	3.402501
C	4.205700	-0.238298	-1.973042
C	0.810024	0.125423	3.670962
C	0.514669	-0.006706	0.382260
H	1.184584	0.809260	0.703427
C	-0.747821	0.419888	-0.155870
C	-0.970106	1.823346	-0.247119
H	-0.194237	2.505021	0.117092
C	-2.149258	2.308071	-0.789524
I	-2.479308	4.430590	-0.949416
C	-3.147001	1.422364	-1.260810
H	-4.072689	1.809393	-1.694980
C	-2.938068	0.050732	-1.164976
I	-4.456084	-1.283950	-1.885309
C	-1.743196	-0.523283	-0.605628
O	-1.614855	-1.813620	-0.527499
C	1.337484	-4.194460	-0.201343
C	-1.484642	-4.352956	-0.198016
H	1.011383	-4.952983	-0.921725
H	2.200047	-3.589336	-0.499648
C	0.954489	-4.242973	1.146116
H	1.528097	-3.686796	1.895699
H	0.315201	-5.045668	1.528638
C	-2.559031	-4.308270	0.884175
H	-1.876671	-4.075763	-1.191648
H	-0.990072	-5.340362	-0.247584
C	-3.676983	-5.344862	0.618728
H	-2.116493	-4.506306	1.881641
H	-3.003951	-3.297911	0.917279
H	-4.449493	-5.302074	1.408742
H	-4.170213	-5.148671	-0.350198
H	-3.274028	-6.374303	0.592180
C	5.152239	-0.631612	-2.933362
C	6.016441	0.305359	-3.541114
C	5.917319	1.653051	-3.158372
C	4.976993	2.081282	-2.195713
C	4.132067	1.123772	-1.611361
H	5.219124	-1.689793	-3.221247
C	7.016333	-0.138864	-4.590845
H	6.588385	2.391430	-3.617855
C	4.884553	3.544752	-1.810162
H	3.405551	1.441297	-0.852066
H	4.201226	3.695798	-0.956721
H	5.873088	3.952751	-1.528696
H	4.509957	4.160590	-2.650022
H	7.771485	0.642021	-4.786821
H	7.549012	-1.056964	-4.282069
H	6.516786	-0.364975	-5.552713
C	-0.563540	0.408775	3.776694
C	-1.025634	1.709581	4.064254
C	-0.076594	2.731195	4.250925
C	1.307359	2.479754	4.152751
C	1.735722	1.172656	3.854455
H	-1.292478	-0.399420	3.628827
C	-2.511330	2.003554	4.130857
H	-0.423112	3.749355	4.474047
C	2.312888	3.591433	4.383781
H	2.809795	0.966044	3.764225
H	3.302622	3.335014	3.967222
H	1.983554	4.540266	3.922851
H	2.452088	3.789690	5.464347
H	-2.715128	2.936079	4.685303
H	-2.939551	2.121455	3.117052
H	-3.065605	1.184435	4.623263
H	1.544914	-1.783966	4.367197
H	0.415472	-1.883379	3.002185
H	2.223405	-1.024720	-1.594610
H	3.476866	-2.249715	-1.804706

Table S41: Internal energy and cartesian coordinates for **TS-2$_{ins}$**.

SCF Done: -1716.65258546 A.U.

Ni	0.438314	-2.745191	-1.075654
N	1.469552	-1.180944	-0.519124
C	2.909285	-1.234179	-0.373182
C	3.740982	-0.723072	-1.400706
C	3.461067	-1.834582	0.787264
C	4.862375	-1.929131	0.892724
C	5.701679	-1.439592	-0.118945
C	5.138652	-0.842646	-1.254567
C	2.566887	-2.364811	1.896143
C	1.993164	-1.296416	2.830572
C	0.948790	-0.010185	-0.191854
H	1.655447	0.772892	0.123254
C	-0.431443	0.373243	-0.187180
C	-0.737183	1.728363	0.121479
C	-1.473449	-0.590751	-0.445377
O	-1.237308	-1.831330	-0.730787
C	-2.819569	-0.090953	-0.352666
C	-0.934702	-4.388032	-1.171524
C	-2.057373	2.145621	0.175234
C	-3.116600	1.235875	-0.059439
I	-4.431482	-1.465349	-0.710612
H	-4.156470	1.570186	-0.011914
I	-2.526233	4.199186	0.633650
H	0.086472	2.426050	0.303109
C	1.063820	-4.559702	-2.054343
C	2.079290	-3.634357	-1.718527
H	2.757909	-3.851914	-0.884944
H	1.054612	-5.521210	-1.529494
H	2.481482	-2.960247	-2.484844
H	0.691548	-4.599878	-3.085240
H	-1.025991	-5.258089	-1.839462
C	-1.000152	-4.809082	0.292988
H	-1.702410	-3.652805	-1.454509
C	3.156540	-0.055643	-2.635741
C	2.815767	1.429842	-2.473042
C	1.689460	1.961597	-3.125768
C	1.364268	3.330758	-3.032912
C	2.197652	4.166813	-2.267846
C	3.334485	3.664452	-1.601388
C	3.628099	2.292462	-1.709012
H	1.045412	1.296134	-3.716269
C	0.124963	3.876257	-3.714385
H	1.954041	5.234539	-2.184284
C	4.229448	4.589403	-0.799075
H	4.503272	1.887620	-1.185235
C	0.645894	-1.356304	3.223609
C	0.099653	-0.413916	4.121286
C	0.936459	0.600072	4.617288
C	2.293344	0.689429	4.239437
C	2.806155	-0.263068	3.341918
H	0.003388	-2.150799	2.820639
C	-1.360702	-0.490437	4.521347
H	0.522110	1.344235	5.310940
C	3.174552	1.791670	4.795022
H	3.856537	-0.198441	3.030106
H	0.161997	4.975928	-3.801396
H	0.002522	3.456823	-4.729400
H	-0.788339	3.619760	-3.144518
H	3.640306	5.270529	-0.158127
H	4.918304	4.022346	-0.149104
H	4.847674	5.225913	-1.461343
H	-1.625882	0.307903	5.235694
H	-2.023674	-0.388941	3.642095
H	-1.600512	-1.460839	4.995448
H	3.328130	1.675796	5.885088
H	4.169468	1.793555	4.317032
H	2.722497	2.789034	4.639957
H	6.789531	-1.530121	-0.024990
H	5.787350	-0.465129	-2.054740
H	5.294737	-2.402729	1.782935
H	1.723820	-2.927926	1.450161
H	3.151653	-3.090896	2.496055
H	3.885259	-0.162895	-3.464709
H	2.240849	-0.590387	-2.951102
C	-2.262690	-5.655819	0.579397
H	-0.100661	-5.396257	0.568831
H	-1.012040	-3.913002	0.940019
H	-2.302276	-5.954074	1.643084
H	-3.180025	-5.085281	0.351173
H	-2.273525	-6.577224	-0.031969

Table S42: Internal energy and cartesian coordinates for **2-β-T**.

SCF Done: -1717.57505210 A.U.

Ni	-0.664335	-1.135208	0.252452
N	-0.684119	0.228854	-0.994053
C	-1.858368	0.513530	-1.785586
C	-2.841433	1.392131	-1.262492
C	-3.986377	1.649891	-2.038934
C	-4.148190	1.060279	-3.300614
C	-3.160404	0.203879	-3.805218
C	-2.000887	-0.089759	-3.061079
C	-0.943859	-1.031062	-3.632073
C	2.655078	1.845287	-1.018510
C	1.675073	0.892704	-0.609822
C	1.992866	-0.114783	0.386495
C	3.329029	-0.070748	0.916012
C	4.274545	0.865559	0.516271
C	3.922809	1.827223	-0.462639
I	5.393319	3.277453	-1.074920
H	5.276566	0.859316	0.952492
I	3.861061	-1.528638	2.398914
H	0.265993	1.765140	-1.992476
C	0.382853	0.978606	-1.227969
C	-2.471888	-1.739621	0.229018
C	-2.613851	2.050285	0.099186
C	-3.816116	2.760976	0.696311
C	-4.847789	2.028344	1.318165
H	-4.774072	0.933582	1.369092
C	-5.972833	2.669050	1.868013
H	-6.934170	4.585691	2.197057
C	-6.056395	4.073812	1.779486
C	-5.042510	4.836139	1.171318
C	-5.133800	6.348596	1.114930
H	-3.132228	4.741791	0.145058
C	-3.928735	4.161513	0.630375
C	-7.062930	1.872363	2.558166
H	-4.752210	2.325998	-1.645043
H	-5.042548	1.277190	-3.895472
H	-3.278590	-0.243083	-4.800210
H	2.384236	2.589491	-1.775276
O	1.143817	-1.008784	0.787472
C	-1.922268	-2.630752	1.303519
C	-2.478567	-2.436498	2.729121
H	-1.911683	-3.694486	0.998015
H	-3.203746	-0.980608	0.549775
H	-2.732975	-2.215351	-0.727523
H	-0.763824	-2.449419	1.413989
H	-3.538027	-2.761051	2.725302
C	-1.702882	-3.205557	3.813637
H	-2.480472	-1.354546	2.966597
H	-8.061672	2.307328	2.374145
H	-7.079044	0.823728	2.212877
H	-6.915014	1.854439	3.655560
H	-4.689897	6.748221	0.185644
H	-6.181451	6.693116	1.168490
H	-4.591549	6.815893	1.959964
C	-0.939417	-2.428323	-3.013191
C	0.161628	-2.875204	-2.261373
C	0.184061	-4.163675	-1.682743
C	-0.933078	-4.998481	-1.867174
C	-2.051068	-4.581990	-2.622415
C	-2.041261	-3.291045	-3.182758
H	1.027540	-2.214512	-2.128620
C	1.388250	-4.617706	-0.881691
H	-0.931501	-6.002571	-1.421387
C	-3.225254	-5.516067	-2.844181
H	-2.910652	-2.948838	-3.759944
H	-4.157998	-4.956958	-3.035934
H	-3.054539	-6.176764	-3.716622
H	-3.393604	-6.171591	-1.971070
H	1.184377	-5.557313	-0.339032
H	2.261952	-4.796559	-1.537571
H	1.689969	-3.849970	-0.145558
H	0.063523	-0.590973	-3.516198
H	-1.121053	-1.117635	-4.721251
H	-1.775041	2.769928	0.012888
H	-2.246855	1.271580	0.799117
C	-2.295423	-3.015741	5.219781
H	-1.689800	-4.284382	3.558814
H	-0.645624	-2.872849	3.809637
H	-1.716811	-3.572832	5.977774
H	-2.292463	-1.949566	5.512945
H	-3.341190	-3.372593	5.266169

Table S43: Internal energy and cartesian coordinates for **TS-2$_{decoor}$**.

SCF Done: -1716.64881242 A.U.

Ni	1.238991	-2.482348	-0.855190
N	1.665442	-0.602328	-0.500323
C	3.035505	-0.162697	-0.419735
C	3.606141	0.617444	-1.459161
C	3.812004	-0.568414	0.698384
C	5.176728	-0.225981	0.732643
C	5.765168	0.515144	-0.302437
C	4.977720	0.936484	-1.381932
H	6.831583	0.763895	-0.266690
H	5.782291	-0.551166	1.587837
C	2.782068	1.122829	-2.633106
C	3.178868	-1.324572	1.857911
C	2.358951	-0.451164	2.809750
C	0.734556	0.280966	-0.209333
H	1.055144	1.305222	0.039437
C	-0.686237	0.041527	-0.169980
C	-1.512781	1.183343	0.034971
H	-1.036781	2.167379	0.099259
C	-2.887700	1.046881	0.138016
I	-4.130739	2.784730	0.424406
C	-3.495869	-0.227946	0.063329
H	-4.580315	-0.333993	0.149428
C	-2.694305	-1.349085	-0.122719
I	-3.626207	-3.281674	-0.227637
C	-1.263365	-1.284933	-0.262725
O	-0.592816	-2.387932	-0.438791
C	2.676748	-4.287305	-0.735777
H	3.211400	-4.647344	-1.634494
C	3.295743	-4.855223	0.553619
C	1.189426	-4.404550	-0.871284
H	2.957890	-3.148515	-0.765987
H	0.791999	-4.816394	-1.809821
H	0.634910	-4.748287	0.014966
C	0.833635	-2.275880	-3.259527
H	0.079512	-3.068569	-3.304223
H	0.444720	-1.259163	-3.130891
C	2.140116	-2.512338	-3.539604
H	2.885212	-1.710040	-3.572609
H	2.504172	-3.524003	-3.753694
H	3.464413	1.274169	-3.494261
H	2.058211	0.349499	-2.945317
C	2.012113	2.425619	-2.387585
C	0.775325	2.628611	-3.029419
C	0.046077	3.821842	-2.860614
C	0.584481	4.823028	-2.029175
C	1.821090	4.652825	-1.376247
C	2.522566	3.444860	-1.560878
H	0.367127	1.838183	-3.673916
C	-1.301852	4.006196	-3.529558
H	0.025340	5.757433	-1.885324
C	2.397950	5.756257	-0.510515
H	3.480471	3.295070	-1.047235
H	-1.529448	5.074120	-3.693181
H	-1.341309	3.493971	-4.507287
H	-2.117664	3.588127	-2.909004
H	3.056666	5.350033	0.277101
H	3.003471	6.463021	-1.110974
H	1.602784	6.345803	-0.020741
C	1.017595	-0.768244	3.079804
C	0.247047	0.004490	3.975762
C	0.852912	1.109361	4.597289
C	2.198933	1.453721	4.346301
C	2.937351	0.667322	3.445835
H	0.556745	-1.627357	2.574158
C	-1.202005	-0.350993	4.243994
H	0.262551	1.723343	5.290985
C	2.830345	2.644010	5.042521
H	3.980691	0.932654	3.229938
H	3.984280	-1.829607	2.426729
H	2.515632	-2.119550	1.464702
H	3.804260	2.905414	4.593351
H	2.180579	3.536917	4.988310
H	3.004353	2.438762	6.116550
H	-1.684035	0.389595	4.905258
H	-1.784106	-0.397111	3.305353
H	-1.291978	-1.342419	4.727287
H	5.428259	1.521733	-2.193203
H	3.260697	-5.958636	0.527035
H	4.349277	-4.547455	0.674460
H	2.733580	-4.521856	1.442964

Table S44: Internal energy and cartesian coordinates for **TS-2-Deccor-η²**.

SCF Done: -1716.63699101 A.U.

Ni	-2.225300	0.116551	0.091456
N	-0.711525	1.430463	-0.244035
C	-0.970089	2.831360	-0.138815
C	-0.316642	3.670305	0.806514
C	-1.982845	3.352204	-0.983817
C	-2.352066	4.701066	-0.880053
C	-1.738854	5.536323	0.068136
C	-0.733997	5.017336	0.893634
H	-0.252991	5.664350	1.637750
H	-2.042155	6.584883	0.160891
H	-3.121415	5.099828	-1.552750
C	0.772391	3.181981	1.749924
C	-3.407033	1.241120	-1.603579
C	2.220508	3.358457	1.274845
C	-4.785471	1.444050	-1.287218
H	-5.114360	2.448961	-0.990327
C	-5.730151	0.429499	-1.444687
C	-7.195319	0.658209	-1.135829
C	-5.295989	-0.834838	-1.946971
H	-6.046439	-1.616164	-2.127585
C	-3.957650	-1.105837	-2.221525
C	-3.508294	-2.448786	-2.751436
C	-2.990043	-0.075226	-1.988505
H	-1.986766	-0.204019	-2.418688
C	0.534204	1.045059	-0.429116
H	1.291937	1.822280	-0.627372
C	1.026969	-0.305460	-0.379765
C	2.366871	-0.517663	-0.812910
H	2.928941	0.331591	-1.215670
C	2.941529	-1.774660	-0.720115
I	4.954506	-2.104939	-1.415519
C	2.222651	-2.857447	-0.161399
H	2.680687	-3.846878	-0.084513
C	0.924103	-2.650395	0.290312
I	-0.142670	-4.305811	1.146939
C	0.242391	-1.384220	0.191972
O	-0.973243	-1.264281	0.627848
C	-3.565166	-1.163729	0.752700
H	-2.907662	-2.338573	-3.674179
H	-2.867897	-2.970433	-2.014166
H	-4.367237	-3.103111	-2.978320
H	-7.400610	1.717901	-0.905689
H	-7.837909	0.363280	-1.986608
H	-7.522466	0.057538	-0.265336
H	-4.533837	-0.702476	0.489618
H	-3.385657	-2.056923	0.132090
C	-3.439522	-1.513042	2.229225
H	-2.379850	-1.707064	2.476294
H	-3.786023	-0.678966	2.866975
C	-4.265765	-2.775578	2.579078
H	-5.337538	-2.635906	2.344497
H	-3.904499	-3.649577	2.007675
H	-4.181832	-3.015162	3.655686
C	-2.486749	1.764571	2.867382
C	-3.492274	1.991598	2.000636
H	-2.467113	0.887316	3.522429
H	-1.645459	2.460069	2.953730
H	-4.355751	1.322496	1.925621
C	3.230600	2.574343	1.870987
C	4.580321	2.713887	1.503422
C	4.912617	3.665981	0.516753
C	3.930029	4.462091	-0.096632
C	2.582514	4.293866	0.289967
H	2.956628	1.834807	2.635582
C	5.651122	1.839779	2.125880
H	5.963049	3.784236	0.218289
C	4.305359	5.497935	-1.138759
H	1.806095	4.905216	-0.186508
H	6.582712	2.406375	2.304579
H	5.318390	1.416366	3.089407
H	5.908532	0.989913	1.464992
H	3.583084	5.512828	-1.975050
H	4.318587	6.517517	-0.706754
H	5.308231	5.305658	-1.558039
C	-2.563344	2.445553	-2.046722
H	-1.731393	2.053644	-2.662751
H	-3.188971	3.054806	-2.727056
H	-3.506282	2.885121	1.367352
H	0.660705	3.731725	2.707327
H	0.610748	2.115772	1.994940

Table S45: Internal energy and cartesian coordinates for **1-η²-C**.

SCF Done: -1638.08480161 A.U.

Ni	-2.318833	-0.037411	-0.078242
N	-0.866066	1.313640	-0.407194
C	-1.196662	2.702426	-0.349051
C	-3.764790	1.080393	-1.274325
C	-4.892117	1.547936	-0.519777
H	-4.909040	2.600015	-0.206398
C	-5.988569	0.729755	-0.259175
C	-7.189551	1.239214	0.510941
C	-5.978211	-0.612879	-0.753853
H	-6.861837	-1.243175	-0.585042
C	-4.885639	-1.146553	-1.431197
C	-4.872028	-2.573265	-1.931457
C	-3.742664	-0.307258	-1.654374
H	-2.994842	-0.643704	-2.387826
C	0.410500	0.984683	-0.496400
H	1.143572	1.798814	-0.629011
C	0.968897	-0.337058	-0.431338
C	2.372654	-0.444106	-0.664835
H	2.932214	0.463703	-0.914573
C	3.007132	-1.670707	-0.572565
I	5.121975	-1.838035	-0.950082
C	2.284709	-2.835875	-0.219005
H	2.792006	-3.800561	-0.140908
C	0.922660	-2.738251	0.034239
I	-0.157766	-4.514341	0.573885
C	0.183343	-1.505727	-0.076351
O	-1.095085	-1.502999	0.138539
C	-3.392540	-0.966607	1.248922
H	-4.421473	-0.591921	1.134078
H	-3.320884	-2.045827	1.037577
C	-2.748840	-0.565901	2.568530
H	-1.736328	-1.001112	2.643680
H	-2.641339	0.537731	2.628279
C	-3.599899	-1.034057	3.778953
H	-4.611053	-0.588879	3.752535
H	-3.712278	-2.132919	3.777724
H	-3.121201	-0.739426	4.731061
C	-0.577256	3.617701	0.548827
C	-1.026910	4.957088	0.543470
C	-2.040024	5.396382	-0.316276
C	-2.654862	4.476294	-1.181455
C	-2.255290	3.133303	-1.192362
C	0.486962	3.217763	1.559503
H	-0.565326	5.662745	1.245470
H	-2.362966	6.443037	-0.300178
H	-3.458901	4.800299	-1.853736
C	-2.935681	2.102492	-2.064305
H	-3.611603	2.616922	-2.776125
H	-2.188717	1.556541	-2.670370
H	0.287413	3.779038	2.495251
H	0.371999	2.150139	1.825184
C	1.947562	3.469919	1.164337
C	2.307664	4.303659	0.092705
C	3.664196	4.539659	-0.226020
C	4.656773	3.918454	0.548930
C	4.327060	3.073125	1.631184
C	2.970010	2.859342	1.923347
H	1.523095	4.781153	-0.507203
C	4.031439	5.457697	-1.375881
H	5.714013	4.091170	0.306065
C	5.417667	2.401119	2.441709
H	2.698351	2.199531	2.758521
H	5.103848	5.383436	-1.626041
H	3.452671	5.218692	-2.286980
H	3.819950	6.516230	-1.129962
H	5.004762	1.880389	3.322698
H	5.963915	1.652152	1.837793
H	6.164323	3.134160	2.799454
H	-8.126810	1.088318	-0.057409
H	-7.309362	0.703842	1.472394
H	-7.098181	2.315388	0.736857
H	-4.661209	-2.619624	-3.016936
H	-4.080107	-3.159275	-1.427631
H	-5.837487	-3.076003	-1.750592

Table S46: Internal energy and cartesian coordinates for **1-β-C**.

SCF Done: -1638.10639822 A.U.

Ni	1.839897	-0.459626	0.922729
N	1.140284	0.998527	-0.107604
C	1.975975	2.138006	-0.392785
C	2.794141	2.128413	-1.552112
C	2.009079	3.222602	0.520997
C	2.886935	4.293189	0.260912
C	3.695957	4.305813	-0.884071
C	3.637974	3.232318	-1.783783
H	4.257204	3.243309	-2.689354
H	4.366138	5.150913	-1.076673
H	2.926677	5.128608	0.970952
C	2.784231	0.955667	-2.524824
C	1.117481	3.237023	1.751935
C	-0.332803	3.659309	1.498841
C	-0.100100	1.027726	-0.552303
H	-0.432832	1.927410	-1.096544
C	-1.074222	-0.020301	-0.399409
C	-2.352428	0.199381	-0.990099
H	-2.534532	1.147302	-1.507525
C	-3.339671	-0.768642	-0.908868
I	-5.263478	-0.437903	-1.822691
C	-3.102031	-1.990851	-0.236998
H	-3.881748	-2.754155	-0.177193
C	-1.860516	-2.209737	0.348367
I	-1.505087	-4.068720	1.364025
C	-0.787780	-1.253726	0.304371
O	0.345020	-1.544310	0.881966
C	3.816391	-0.534731	1.858705
H	4.676542	-0.824145	1.228211
C	4.228073	0.271913	3.102338
C	2.845484	-1.641062	2.049303
H	3.337606	0.296258	1.130504
H	3.039091	-2.593567	1.539008
H	2.372829	-1.745404	3.037402
C	-1.375592	3.033363	2.204163
C	-2.719300	3.423974	2.028247
C	-3.001423	4.464449	1.125071
C	-1.978214	5.111637	0.401579
C	-0.648579	4.694086	0.594754
H	-1.139712	2.218832	2.902331
C	-3.831569	2.712951	2.773756
H	-4.044151	4.775920	0.975944
C	-2.306328	6.244477	-0.551973
H	0.156631	5.180314	0.029276
H	-1.465981	6.453492	-1.236698
H	-3.196610	6.014519	-1.165270
H	-2.526562	7.181323	-0.004228
H	-4.776447	3.281734	2.729466
H	-4.025648	1.712376	2.342762
H	-3.573861	2.561636	3.837802
H	1.113361	2.232309	2.216858
H	1.565323	3.926494	2.495975
H	4.896215	-0.340278	3.733194
H	4.762020	1.200079	2.833750
H	3.343726	0.542293	3.704969
H	3.176832	1.313078	-3.496585
C	3.610552	-0.248651	-2.069119
H	1.747774	0.621640	-2.709831
C	2.995605	-1.495247	-1.856375
C	3.745353	-2.630583	-1.475426
C	5.132180	-2.485742	-1.294693
C	5.779754	-1.246625	-1.498458
C	5.003522	-0.136471	-1.877685
H	1.912779	-1.593587	-2.003616
C	3.056955	-3.965039	-1.268725
H	5.727723	-3.358950	-0.995289
C	7.283487	-1.127881	-1.337342
H	5.493184	0.834417	-2.030165
H	7.595739	-0.077616	-1.201847
H	7.647095	-1.706945	-0.469179
H	7.815055	-1.516535	-2.227740
H	3.726170	-4.695222	-0.781110
H	2.150560	-3.855282	-0.645779
H	2.735044	-4.403272	-2.233146

Table S47: Internal energy and cartesian coordinates for **TS-1$_{BHE-C}$**.

SCF Done: -1638.08277223 A.U.

Ni	-0.984281	-1.344854	-1.813999
N	-1.009766	0.295949	-0.861609
C	-2.105800	1.226804	-1.040720
C	-3.253195	1.102302	-0.217058
C	-2.020872	2.212686	-2.053065
C	-3.116934	3.080272	-2.229380
C	-4.253587	2.983621	-1.415363
C	-4.317183	2.001150	-0.416399
H	-5.095648	3.669141	-1.562918
H	-3.070275	3.837306	-3.022097
C	-3.296556	0.004128	0.845593
C	-0.791792	2.329263	-2.938190
C	-0.041729	0.693808	-0.055664
H	-0.151987	1.694279	0.393787
C	1.144300	-0.029523	0.299087
C	2.034697	0.586947	1.225187
C	1.433760	-1.333124	-0.257580
O	0.669367	-1.945068	-1.108178
C	2.656854	-1.944216	0.189725
C	-4.645745	-0.232403	1.501752
C	3.193004	-0.063926	1.615475
C	3.517077	-1.342957	1.100564
I	3.150712	-3.881890	-0.593217
H	4.433544	-1.850723	1.412563
I	4.534651	0.861803	3.023990
H	1.785551	1.579086	1.616175
C	-0.875466	-2.959078	-3.035478
C	-2.245514	-2.734909	-2.817474
H	-0.315731	-3.678448	-2.428775
H	-2.834464	-2.325369	-3.650178
C	-3.048537	-3.490898	-1.778579
H	-0.400872	-2.627464	-3.967528
H	-2.294415	-0.942291	-2.376445
H	-3.555528	-4.348509	-2.263973
H	-2.406044	-3.883612	-0.972783
H	-3.831348	-2.859029	-1.325377
C	0.375733	3.119053	-2.339074
C	1.698553	2.735820	-2.627324
C	2.799163	3.466393	-2.136060
C	2.549646	4.602916	-1.344260
C	1.236733	5.012397	-1.036196
C	0.159101	4.255897	-1.534917
H	1.877606	1.845639	-3.245481
C	4.217512	3.014174	-2.422959
H	3.398257	5.180528	-0.953152
C	0.990485	6.254754	-0.201595
H	-0.868057	4.558767	-1.294975
C	-5.678680	-0.893225	0.801721
C	-6.929197	-1.133095	1.394994
C	-7.141124	-0.690697	2.718960
C	-6.136476	-0.028156	3.443680
C	-4.890593	0.194273	2.817186
H	-5.502216	-1.220181	-0.231996
C	-8.025647	-1.861164	0.642103
H	-8.114697	-0.870826	3.194639
C	-6.374349	0.436546	4.867184
H	-4.094173	0.709353	3.371419
H	-8.981830	-1.307282	0.681952
H	-7.761416	-2.002558	-0.420233
H	-8.216437	-2.862226	1.074323
H	-6.207098	1.525059	4.971248
H	-7.405763	0.221807	5.196058
H	-5.685993	-0.062555	5.575239
H	-0.028697	6.261766	0.222793
H	1.708996	6.332621	0.634473
H	1.100536	7.175207	-0.807534
H	4.928640	3.857655	-2.378671
H	4.553846	2.261634	-1.684156
H	4.300387	2.548559	-3.421117
H	-5.207029	1.915635	0.215841
H	-0.433775	1.315981	-3.204420
H	-1.095137	2.813216	-3.888739
H	-2.545636	0.226684	1.629706
H	-2.939920	-0.934464	0.372780

Table S48: Internal energy and cartesian coordinates for **1-BHE-C**.

SCF Done: -1638.09007180 A.U.

Ni	0.702621	-2.978226	-0.074383
N	1.589506	-1.304962	-0.056138
C	3.036647	-1.248788	-0.042737
C	3.738949	-1.127461	-1.265781
C	3.717187	-1.369084	1.193488
C	5.125210	-1.361639	1.183569
C	5.841856	-1.240652	-0.015726
C	5.147775	-1.128776	-1.228279
H	5.701136	-1.051047	-2.172455
H	6.937452	-1.245534	-0.006085
H	5.660784	-1.464185	2.135535
C	3.003912	-1.018576	-2.590948
C	2.951244	-1.523162	2.494871
C	2.493906	0.381513	-2.945977
C	2.373636	-0.229372	3.075401
C	0.961564	-0.142215	-0.034166
H	1.593931	0.759050	-0.012424
C	-0.453637	0.087588	-0.031267
C	-0.888456	1.443909	-0.002534
H	-0.134964	2.237647	0.003606
C	-2.240583	1.741091	0.018738
I	-2.900318	3.790974	0.076930
C	-3.211285	0.709629	0.014648
H	-4.276906	0.952087	0.036325
C	-2.794082	-0.615432	-0.015426
I	-4.274495	-2.171644	-0.010650
C	-1.408245	-1.001830	-0.043871
O	-1.065952	-2.250852	-0.075211
H	2.033302	-3.606168	-0.009168
C	-0.103395	-4.786088	0.462139
C	0.157163	-4.840126	-0.909905
H	0.601578	-5.219421	1.180898
H	-1.107631	-4.540199	0.826508
C	-0.877770	-4.654565	-1.991270
H	1.105729	-5.290366	-1.232335
H	-1.188113	-5.650960	-2.368507
H	-1.766091	-4.121005	-1.620701
H	-0.464642	-4.102535	-2.855094
C	3.241727	1.535214	-2.636630
C	2.799686	2.815750	-3.020221
C	1.584335	2.927328	-3.725040
C	0.809034	1.795471	-4.039566
C	1.279751	0.528099	-3.641984
H	4.187145	1.432601	-2.089047
C	3.605273	4.052941	-2.672083
H	1.232038	3.920741	-4.034544
C	-0.515748	1.938964	-4.762574
H	0.688476	-0.364825	-3.885442
H	3.654629	4.756368	-3.523062
H	3.153191	4.604667	-1.825098
H	4.639067	3.795168	-2.383453
H	-1.348492	2.076107	-4.046260
H	-0.516869	2.814471	-5.435688
H	-0.748413	1.043425	-5.365419
C	1.150384	-0.262291	3.774074
C	0.609769	0.895519	4.363215
C	1.323290	2.105437	4.242946
C	2.547424	2.171508	3.552743
C	3.058290	0.994980	2.966729
H	0.603834	-1.211439	3.856317
C	-0.725967	0.853552	5.079147
H	0.911597	3.018489	4.694136
C	3.315169	3.476248	3.456759
H	4.007720	1.035151	2.417496
H	3.841392	3.567337	2.489633
H	2.647130	4.348694	3.565783
H	4.083469	3.551153	4.251022
H	-0.707607	1.451958	6.008103
H	-1.533832	1.265048	4.444266
H	-1.010352	-0.179451	5.344539
H	2.146999	-1.719291	-2.593760
H	3.688421	-1.360191	-3.393565
H	2.124575	-2.245159	2.342956
H	3.629029	-1.979100	3.244649

Table S49: Internal energy and cartesian coordinates for **TS-1$_{2,1\text{-ins}}$**.

SCF Done: -1638.08932696 A.U.

Ni	1.134818	-1.420079	-1.632913
N	1.031546	0.315684	-0.851885
C	2.099878	1.269590	-1.054184
C	1.961559	2.277088	-2.040651
C	3.285306	1.143140	-0.283279
C	4.330879	2.055649	-0.511911
C	4.214559	3.056664	-1.487848
C	3.041599	3.158946	-2.247017
H	2.952706	3.931658	-3.020813
H	5.043235	3.752843	-1.659357
H	5.247065	1.969288	0.081325
C	0.012597	0.725674	-0.120169
H	0.055695	1.757244	0.265373
C	-1.158518	-0.029165	0.225004
C	-2.140541	0.627082	1.021502
H	-1.968173	1.667537	1.316401
C	-3.291618	-0.042799	1.401649
I	-4.773156	0.947152	2.613507
C	-3.515478	-1.382905	1.005332
H	-4.426894	-1.906254	1.305714
C	-2.562180	-2.026525	0.224753
I	-2.918675	-4.056557	-0.380922
C	-1.341791	-1.398676	-0.205103
O	-0.488780	-2.057885	-0.930742
C	2.426405	-2.408965	-2.981243
H	2.376627	-1.968989	-3.986370
H	3.446684	-2.649266	-2.648343
C	1.344459	-3.213304	-2.517537
H	2.469961	-1.000028	-2.224276
H	0.449456	-3.270904	-3.152463
C	1.504583	-4.318537	-1.501713
H	1.593732	-5.301608	-2.008042
H	2.403872	-4.177879	-0.875613
H	0.616816	-4.361895	-0.846754
C	0.696761	2.404680	-2.874290
C	3.381277	0.034797	0.765776
H	0.325801	1.396659	-3.140723
C	-0.448562	3.186920	-2.222901
H	0.963202	2.900444	-3.829836
C	-0.205174	4.284378	-1.375002
C	-1.266949	5.025187	-0.817553
C	-2.588391	4.639944	-1.114382
C	-2.864696	3.543242	-1.954770
C	-1.781799	2.828868	-2.501943
H	0.829361	4.568240	-1.143496
C	-0.988880	6.227371	0.064467
H	-3.423352	5.204105	-0.677249
C	-4.293622	3.118663	-2.230730
H	-1.981855	1.968901	-3.155238
H	2.624446	0.219920	1.553731
H	3.059776	-0.914132	0.285854
C	4.743122	-0.151054	1.410568
C	5.007451	0.359084	2.692464
C	6.268205	0.190879	3.305576
C	7.266792	-0.504339	2.603146
C	7.035042	-1.030462	1.313693
C	5.769502	-0.844079	0.732892
H	4.214581	0.896193	3.230588
C	6.529895	0.749799	4.690563
H	8.250540	-0.646009	3.070878
C	8.127774	-1.786532	0.583161
H	5.573392	-1.246187	-0.270110
H	-4.376117	2.572587	-3.186772
H	-4.671125	2.447038	-1.436056
H	-4.973815	3.987886	-2.273178
H	-1.792931	6.382575	0.805533
H	-0.035925	6.116911	0.611723
H	-0.913987	7.156406	-0.533910
H	7.536977	0.479640	5.052356
H	6.454448	1.853777	4.702397
H	5.794983	0.370460	5.424977
H	7.801990	-2.092172	-0.426166
H	9.040417	-1.171659	0.470374
H	8.423276	-2.701214	1.131330

Table S50: Internal energy and cartesian coordinates for **3-β-C**.

SCF Done: -1638.09640274 A.U.

C	2.155324	-0.190948	0.720211
C	1.682720	0.020262	-0.632987
C	2.603754	0.140747	-1.714144
C	3.967405	0.059805	-1.487655
C	4.472193	-0.144158	-0.181870
C	3.581859	-0.263542	0.878729
C	0.285020	0.119646	-0.956197
N	-0.716894	0.043201	-0.104203
C	-2.052128	0.184166	-0.635064
C	-2.609303	1.482020	-0.771779
C	-3.927744	1.591157	-1.251706
C	-4.669616	0.447906	-1.580329
C	-4.107163	-0.827810	-1.430346
C	-2.792860	-0.983579	-0.953505
C	-1.771114	2.708718	-0.401368
C	-2.539598	4.012605	-0.271614
C	-2.140150	-2.357395	-0.783830
C	-3.076162	-3.549013	-0.884711
I	5.356446	0.245533	-3.122802
I	4.364886	-0.567819	2.854657
O	1.390088	-0.317768	1.769430
Ni	-0.453250	-0.231133	1.774100
C	-0.588335	-0.478932	3.677644
C	-2.013746	-0.350026	3.259759
H	-2.531466	0.554634	3.620938
H	-4.371330	2.586595	-1.358365
H	-5.695594	0.551437	-1.951431
H	-4.689413	-1.720884	-1.680457
H	0.042116	0.275409	-2.022474
H	2.209750	0.298638	-2.724235
H	5.548773	-0.206681	-0.006201
H	-2.627400	-1.252536	3.427284
H	-2.129346	-0.219094	2.079700
H	-0.154488	0.411163	4.160272
C	-0.045139	-1.795165	4.187382
H	-0.216366	-1.912186	5.278652
H	-0.512090	-2.659904	3.681238
H	1.044817	-1.842730	4.016177
C	-3.267253	4.301438	0.902572
C	-3.984680	5.501184	1.043009
C	-3.969018	6.422919	-0.026211
C	-3.254477	6.167647	-1.208754
C	-2.543546	4.952601	-1.315749
H	-3.271513	3.572544	1.724031
C	-4.751541	5.811328	2.313716
H	-4.526465	7.364566	0.069733
C	-3.232246	7.174013	-2.342689
H	-1.978833	4.738695	-2.233430
H	-5.802170	6.080352	2.097294
H	-4.759434	4.948824	3.002505
H	-4.306177	6.667339	2.855740
H	-3.499127	6.704169	-3.307491
H	-3.939734	8.001890	-2.163068
H	-2.225820	7.616977	-2.469036
C	-3.864469	-3.937286	0.219456
C	-4.735867	-5.037132	0.147327
C	-4.813938	-5.753808	-1.066258
C	-4.042669	-5.395317	-2.184930
C	-3.177089	-4.285399	-2.077184
H	-3.794808	-3.367481	1.155806
C	-5.565456	-5.457966	1.344654
H	-5.491064	-6.615860	-1.137522
C	-4.123200	-6.185674	-3.476399
H	-2.567169	-3.992098	-2.942432
H	-4.294122	-5.525084	-4.346493
H	-3.183036	-6.736374	-3.671142
H	-4.941802	-6.925366	-3.447389
H	-5.221872	-6.427279	1.754048
H	-5.507100	-4.714289	2.158258
H	-6.630840	-5.582602	1.076197
H	-1.619669	-2.372435	0.196375
H	-1.331075	-2.466712	-1.533577
H	-1.241107	2.490606	0.548113
H	-0.965654	2.838291	-1.151866

Table S51: Internal energy and cartesian coordinates for **TS-3$_{coor}$**.

SCF Done: -1716.64966201 A.U.

Ni	1.206787	-1.314041	-1.559565
N	0.925819	0.471911	-0.813587
C	1.946675	1.484061	-0.923260
C	1.781884	2.582014	-1.807290
C	3.131465	1.337183	-0.148708
C	4.158467	2.285123	-0.303258
C	4.027513	3.351573	-1.205022
C	2.846514	3.496695	-1.943425
H	2.734086	4.335972	-2.641113
H	4.843712	4.072992	-1.323594
H	5.069340	2.179126	0.295009
C	0.491802	2.812203	-2.578592
C	3.224990	0.199257	0.870109
C	-0.603390	3.567468	-1.814823
C	4.573798	0.008698	1.541486
C	-0.143583	0.772634	-0.106209
H	-0.209966	1.788837	0.317054
C	-1.253549	-0.098898	0.185153
C	-2.352695	0.491519	0.873409
H	-2.315881	1.563638	1.093226
C	-3.446705	-0.274630	1.240341
I	-5.115285	0.629309	2.263044
C	-3.487648	-1.658580	0.953419
H	-4.348856	-2.263219	1.248062
C	-2.416041	-2.244072	0.288880
I	-2.507770	-4.348812	-0.139769
C	-1.252090	-1.513090	-0.139519
O	-0.291808	-2.136956	-0.758357
C	1.964683	-3.020239	-2.090280
C	1.923516	-4.074427	-1.008006
H	1.504951	-3.339712	-3.039214
C	3.174663	-2.147602	-2.236929
H	3.964202	-2.354695	-1.494229
H	3.597284	-2.107769	-3.256378
H	2.424853	-5.010131	-1.335790
H	2.424057	-3.731642	-0.083921
H	0.876588	-4.320311	-0.758460
H	2.912888	-1.020231	-2.061025
C	-0.104586	-0.991748	-3.639675
H	-0.786347	-0.279967	-3.160365
C	1.030903	-0.587665	-4.257977
H	-0.456497	-2.027433	-3.689495
H	1.351483	0.459930	-4.264509
H	1.671144	-1.296497	-4.796535
C	-1.955315	3.312304	-2.111581
C	-2.995313	4.006925	-1.461327
C	-2.654317	4.975112	-0.498105
C	-1.310494	5.251831	-0.175410
C	-0.295205	4.540005	-0.842979
H	-2.207729	2.557817	-2.869060
C	-4.446475	3.695620	-1.770759
H	-3.454880	5.526534	0.013462
C	-0.967942	6.287648	0.878158
H	0.754436	4.745497	-0.599387
H	-5.097289	4.565882	-1.575139
H	-4.581524	3.397553	-2.825634
H	-4.818396	2.861216	-1.145404
H	0.109539	6.526557	0.874827
H	-1.525326	7.228694	0.717133
H	-1.226391	5.931541	1.894040
H	0.073745	1.847178	-2.916438
H	0.735983	3.382699	-3.497935
C	4.769073	0.401047	2.876214
C	6.010936	0.220405	3.523156
C	7.063773	-0.364094	2.799446
C	6.903045	-0.770465	1.457096
C	5.654135	-0.574690	0.843982
H	3.935320	0.854700	3.429074
C	6.193738	0.642912	4.967820
H	8.034990	-0.510736	3.291202
C	8.050964	-1.416053	0.705823
H	5.517737	-0.876334	-0.203186
H	2.453757	0.364035	1.648891
H	2.912467	-0.743809	0.373083
H	7.823008	-1.521097	-0.369123
H	8.980205	-0.824101	0.798533
H	8.273419	-2.426529	1.099265
H	7.232440	0.486679	5.306449
H	5.948563	1.711828	5.111863
H	5.531340	0.068471	5.642830

Table S52: Internal energy and cartesian coordinates for **3-Coor-C**.

SCF Done: -1716.57082118 A.U.

Ni	0.382988	-1.566037	-2.300654
N	1.239211	-0.379323	-0.831677
C	2.657626	-0.148131	-0.779776
C	3.286543	1.015394	-1.329941
C	3.469022	-1.150802	-0.182137
C	4.870546	-1.010933	-0.163544
C	5.484122	0.106838	-0.733513
C	4.694070	1.107678	-1.306936
H	5.168262	1.980346	-1.768530
H	6.574819	0.201520	-0.726656
H	5.475737	-1.780983	0.323775
C	2.608873	2.141642	-1.942175
C	2.875239	-2.328526	0.420264
C	2.392596	3.463978	-1.421130
C	2.969019	-2.761620	1.784222
C	0.526507	0.320059	0.031929
H	1.076516	0.979972	0.725280
C	-0.896511	0.300038	0.217324
C	-1.426663	1.106835	1.267795
H	-0.735815	1.706108	1.870299
C	-2.788786	1.121419	1.517544
I	-3.593479	2.332067	3.103253
C	-3.673888	0.338397	0.737322
H	-4.748065	0.353921	0.938684
C	-3.166764	-0.452404	-0.286219
I	-4.522413	-1.633447	-1.451563
C	-1.763415	-0.513664	-0.603595
O	-1.347450	-1.267439	-1.571516
C	1.885665	-1.342006	-3.664922
C	-0.634433	-2.657010	-3.593174
H	1.443904	-1.317634	-4.667542
H	2.476056	-0.461444	-3.384163
C	2.048430	-2.541247	-2.959414
H	2.744387	-2.591319	-2.116417
H	1.750212	-3.505738	-3.382660
C	-1.107804	-3.939521	-2.918634
C	-1.725673	-1.751225	-3.895249
H	-0.043982	-2.858027	-4.505437
H	-1.756181	-4.517916	-3.576789
H	-0.244176	-4.568339	-2.623214
H	-1.660540	-3.687361	-1.996690
C	3.388479	4.424708	-1.635664
C	3.220949	5.735835	-1.164346
C	2.044455	6.074887	-0.480819
C	1.038019	5.117798	-0.268891
C	1.216569	3.806182	-0.740255
H	4.298599	4.150993	-2.172431
C	4.273190	6.743522	-1.389789
H	1.907265	7.094143	-0.114128
C	-0.196374	5.496279	0.441096
H	0.437822	3.061746	-0.586689
H	-0.869518	4.638965	0.514690
H	0.042516	5.847450	1.450107
H	-0.707747	6.299817	-0.098471
H	3.974286	7.702945	-0.957969
H	5.209467	6.421515	-0.922496
H	4.443732	6.876158	-2.463058
C	1.792727	-2.886082	2.531044
C	1.852027	-3.317221	3.865951
C	3.097107	-3.619586	4.440373
C	4.280494	-3.496639	3.692700
C	4.211582	-3.065921	2.359321
H	0.830639	-2.648257	2.073834
C	0.613369	-3.448942	4.654209
H	3.145932	-3.954616	5.478384
C	5.582771	-3.818593	4.304185
H	5.124960	-2.971524	1.771780
H	6.388490	-3.666735	3.580059
H	5.760307	-3.174213	5.171221
H	5.595568	-4.862519	4.633588
H	0.846046	-3.793303	5.665933
H	0.102892	-2.482586	4.717857
H	-0.059334	-4.170915	4.180249
H	-2.396147	-2.218015	-4.615314
H	-2.273979	-1.526032	-2.981701
H	-1.326453	-0.829353	-4.315600
H	3.019233	2.601540	-2.839960
H	1.586239	2.032653	-2.300314
H	1.793687	-2.455609	0.416363
H	3.130017	-3.318884	0.045830

Table S53: Internal energy and cartesian coordinates for **TS-3$_{ins}$**.

SCF Done: -1716.65377115 A.U.

Ni	-1.479708	2.364064	-0.774373
N	-1.779519	0.503023	-0.449047
C	-3.123735	-0.025973	-0.428387
C	-3.615377	-0.744373	-1.547254
C	-3.944844	0.230418	0.699325
C	-5.271575	-0.240024	0.683452
C	-5.778115	-0.949087	-0.415772
C	-4.951662	-1.194430	-1.520244
C	-3.404743	0.985612	1.903159
C	-2.506993	0.153408	2.821013
C	-0.821647	-0.367655	-0.184445
H	-1.136717	-1.402758	0.019289
C	0.592942	-0.130804	-0.126088
C	1.423611	-1.263491	0.108822
C	1.156327	1.197220	-0.262637
O	0.441440	2.256433	-0.472250
C	2.588053	1.275630	-0.131949
C	-1.211543	4.466625	-0.343747
C	2.796882	-1.111163	0.210931
C	3.395279	0.165747	0.092927
I	3.516050	3.206125	-0.301319
H	4.478877	0.280826	0.178188
I	4.058171	-2.822308	0.569312
H	0.956160	-2.249787	0.194734
C	-2.275151	3.766663	-2.045642
C	-3.193674	2.735927	-1.634914
H	-4.039604	3.008766	-0.988825
H	-2.590693	4.815806	-2.028891
H	-3.387969	1.883414	-2.296303
H	-1.608795	3.558600	-2.897634
C	-2.742983	-1.015945	-2.762861
C	-1.832752	-2.244851	-2.665427
C	-0.580760	-2.231731	-3.311085
C	0.272825	-3.350260	-3.280644
C	-0.154324	-4.500693	-2.587287
C	-1.399972	-4.546402	-1.933259
C	-2.228210	-3.405911	-1.975517
H	-0.259533	-1.326019	-3.842698
C	1.636841	-3.305806	-3.940348
H	0.503025	-5.379926	-2.552190
C	-1.854018	-5.802654	-1.215083
H	-3.196244	-3.423147	-1.458885
C	-1.216326	0.599227	3.148693
C	-0.382778	-0.138548	4.017537
C	-0.872711	-1.341701	4.552738
C	-2.164092	-1.818778	4.239709
C	-2.966870	-1.062795	3.369021
H	-0.844324	1.534847	2.710078
C	1.012954	0.354582	4.344493
H	-0.232517	-1.927849	5.225979
C	-2.671247	-3.116666	4.838552
H	-3.968269	-1.428797	3.106734
H	1.902573	-4.279915	-4.388515
H	1.677550	-2.540549	-4.735023
H	2.426376	-3.058823	-3.204988
H	-2.464014	-5.563483	-0.325783
H	-2.476141	-6.439983	-1.873507
H	-0.995613	-6.414131	-0.885872
H	1.519503	-0.313869	5.061834
H	1.641181	0.411793	3.436144
H	0.991054	1.369074	4.784974
H	-2.848179	-3.018313	5.926962
H	-3.622310	-3.430607	4.374605
H	-1.941836	-3.937146	4.705839
H	-6.816120	-1.299813	-0.414902
H	-5.344209	-1.735562	-2.390152
H	-5.915629	-0.036280	1.547973
H	-2.831182	1.866146	1.551945
H	-4.263602	1.371979	2.486992
H	-3.407038	-1.138828	-3.642566
H	-2.111129	-0.131543	-2.971627
C	-0.158722	5.286481	-1.073446
C	-2.331629	5.265540	0.315956
H	-0.711655	3.860499	0.436362
H	-0.595835	5.907193	-1.878986
H	0.335569	5.973983	-0.358096
H	0.622677	4.633646	-1.494541
H	-1.912180	5.840805	1.165736
H	-2.800727	5.997095	-0.369516
H	-3.124801	4.613919	0.723543

Table S54: Internal energy and cartesian coordinates for **4-β-T**.

SCF Done: -1716.69371761 A.U.

Ni	1.011070	1.387297	-1.327206
N	0.866938	-0.377402	-0.808264
C	1.905785	-1.336004	-1.108917
C	2.991608	-1.474312	-0.207050
C	4.006215	-2.396242	-0.524739
C	3.952956	-3.148229	-1.707480
C	2.877476	-2.988206	-2.591971
C	1.833342	-2.085959	-2.307610
C	0.662526	-1.924143	-3.262249
C	-0.608191	-2.685634	-2.872339
H	2.839385	-3.566440	-3.523592
H	4.756277	-3.855721	-1.941869
H	4.848459	-2.514838	0.164730
C	3.022075	-0.629799	1.067701
C	4.309734	-0.696662	1.869773
C	4.422598	-1.555285	2.977528
C	5.422180	0.091405	1.508625
C	6.627174	0.033695	2.230856
C	6.707996	-0.842715	3.333245
C	5.616746	-1.638987	3.723790
C	5.711315	-2.555190	4.928392
H	5.229824	-3.530948	4.735342
H	6.761384	-2.744034	5.211778
H	5.205815	-2.114926	5.809691
H	3.563046	-2.175157	3.266742
H	5.346167	0.762304	0.642347
H	7.706595	1.296944	0.822024
H	7.907308	1.771888	2.527325
H	8.759843	0.342080	1.903830
C	7.809150	0.902876	1.848128
H	7.645675	-0.903605	3.902324
H	2.644955	0.787732	-3.186199
H	3.533147	1.164872	-1.631878
C	2.664058	1.396343	-2.269290
C	2.292909	2.845526	-2.395237
H	2.073017	3.140140	-3.440857
H	1.236502	3.026432	-1.909718
C	3.210765	3.883437	-1.699045
H	3.430267	3.493051	-0.684467
C	4.536614	4.009833	-2.473886
H	5.046625	3.034597	-2.568082
H	4.358593	4.398896	-3.494705
H	5.223733	4.709328	-1.964578
C	2.512198	5.248256	-1.554898
H	2.260671	5.671051	-2.546459
H	1.576016	5.164717	-0.972955
H	3.166660	5.974199	-1.039992
O	-0.586921	2.035844	-0.582254
C	-1.464461	1.338540	0.069899
C	-1.325594	-0.085183	0.309105
C	-2.328998	-0.804356	1.023039
H	-2.197510	-1.880362	1.177673
C	-3.447950	-0.146809	1.505212
I	-4.954345	-1.231928	2.599735
H	-4.508016	1.755241	1.684354
C	-2.651534	1.951334	0.600284
I	-2.915465	4.057320	0.281484
H	-0.188473	-1.905053	0.090515
C	-0.186619	-0.828828	-0.143614
C	-3.621884	1.243941	1.299425
C	-1.869407	-2.107353	-3.111401
C	-3.061638	-2.790903	-2.803093
C	-2.969302	-4.081973	-2.248016
C	-1.723131	-4.688664	-1.997148
C	-0.549053	-3.974510	-2.307735
H	-1.924956	-1.097812	-3.540523
C	-4.410874	-2.135517	-3.022817
H	-3.890752	-4.626043	-1.999940
C	-1.645751	-6.091376	-1.425126
H	0.428425	-4.430916	-2.105572
H	-0.706291	-6.250204	-0.866732
H	-2.488854	-6.299155	-0.742390
H	-1.681603	-6.855428	-2.226213
H	-5.185695	-2.878985	-3.281247
H	-4.752379	-1.611178	-2.109744
H	-4.370676	-1.386820	-3.833343
H	2.806228	0.421396	0.784059
H	2.173402	-0.925843	1.715894
H	0.411903	-0.849636	-3.354607
H	0.985857	-2.260879	-4.267963

Table S55: Internal energy and cartesian coordinates for **TS-1$_{\text{Transf-1}}$**.

SCF Done: -1716.63940807 A.U.

Ni	0.048003	-2.955525	-0.617375
N	1.266983	-1.455126	-0.343227
C	2.693071	-1.681494	-0.237963
C	3.553040	-1.376780	-1.322742
C	3.201544	-2.249712	0.958864
C	4.571922	-2.561965	1.027174
C	5.431495	-2.303157	-0.050172
C	4.919950	-1.705564	-1.208598
H	5.584827	-1.490278	-2.054365
H	6.493586	-2.564263	0.014450
H	4.963462	-3.020464	1.943838
C	3.052311	-0.697944	-2.586200
C	2.301273	-2.483073	2.160571
C	2.984320	0.833105	-2.529951
C	2.008496	-1.220093	2.975080
C	0.857603	-0.213099	-0.186822
H	1.633922	0.554239	-0.036586
C	-0.499353	0.267962	-0.166899
C	-0.669164	1.677759	-0.051864
H	0.221556	2.314940	-0.053725
C	-1.938108	2.223862	0.056437
I	-2.198819	4.355998	0.227193
C	-3.082629	1.393154	0.076019
H	-4.081098	1.826264	0.175464
C	-2.923946	0.016017	-0.030743
I	-4.677256	-1.226443	0.025624
C	-1.643043	-0.625596	-0.179636
O	-1.557433	-1.912637	-0.298268
H	1.231578	-3.800043	-0.837480
C	-0.601821	-4.461262	0.589030
C	-1.010656	-4.797610	-0.711462
H	0.281222	-4.932156	1.034816
H	-1.306716	-3.979392	1.278231
C	-2.424419	-4.666960	-1.221065
H	-0.356779	-5.475925	-1.276789
H	-2.958999	-5.627675	-1.070762
H	-2.974985	-3.870776	-0.697581
H	-2.450434	-4.455307	-2.305604
C	0.240740	-3.257507	-3.388475
H	-0.162136	-4.269976	-3.502926
C	-0.567191	-2.195103	-3.192987
H	1.327917	-3.157765	-3.478484
H	-1.654603	-2.302120	-3.119817
H	-0.176417	-1.174476	-3.107843
C	2.058406	1.513544	-3.347680
C	1.975367	2.917460	-3.353737
C	2.848366	3.644745	-2.517463
C	3.786146	2.996866	-1.694021
C	3.839200	1.586546	-1.706247
H	1.384995	0.934947	-3.994760
C	0.954912	3.635840	-4.214604
H	2.792177	4.741641	-2.507228
C	4.738979	3.792588	-0.822802
H	4.558237	1.070037	-1.058260
H	1.412743	4.475724	-4.768655
H	0.495089	2.954235	-4.950908
H	0.138653	4.060658	-3.599837
H	4.906280	3.298458	0.150994
H	5.729966	3.899115	-1.305614
H	4.357753	4.810297	-0.628719
C	0.686132	-0.871719	3.295373
C	0.394564	0.269950	4.073975
C	1.463003	1.061926	4.526126
C	2.803063	0.740156	4.219346
C	3.058828	-0.400028	3.439505
H	-0.137993	-1.497134	2.927189
C	-1.041881	0.633456	4.394511
H	1.249911	1.955242	5.128903
C	3.937671	1.608293	4.728639
H	4.095170	-0.653871	3.181264
H	-1.098784	1.537282	5.025337
H	-1.621283	0.828776	3.473086
H	-1.556874	-0.185739	4.930707
H	4.906739	1.299574	4.299586
H	3.778972	2.673239	4.475733
H	4.027751	1.551186	5.830466
H	3.718332	-0.988727	-3.423916
H	2.049464	-1.080837	-2.844575
H	1.342733	-2.916753	1.821820
H	2.783392	-3.234300	2.817386

Table S56: Internal energy and cartesian coordinates for **1-Transf-1**.

SCF Done: -1717.55361389 A.U.

C	1.501032	-1.071896	-0.281248
C	0.679352	0.110223	-0.152920
C	1.259257	1.383067	0.118970
C	2.631943	1.506915	0.259726
C	3.477732	0.378381	0.144861
C	2.916286	-0.866974	-0.112502
C	-0.752949	0.068028	-0.270248
N	-1.511684	-0.964184	-0.585002
C	-2.921791	-0.672378	-0.655975
C	-3.780822	-1.169967	0.361801
C	-5.169140	-0.978006	0.230075
C	-5.708122	-0.293140	-0.868579
C	-4.847243	0.228597	-1.842011
C	-3.448751	0.062723	-1.752741
C	-3.221191	-1.852233	1.600652
C	-2.681929	-0.876353	2.650022
C	-2.558775	0.695818	-2.811796
C	-2.065402	2.115376	-2.500654
I	3.519877	3.429166	0.663792
I	4.210160	-2.573493	-0.275166
O	1.037478	-2.259022	-0.520744
Ni	-0.755825	-2.884333	-0.781989
C	0.019120	-4.615538	-0.267327
C	0.113069	-4.578306	1.251047
C	-2.483000	-3.803843	-1.317314
C	-1.572805	-3.824897	-2.395297
C	-1.656696	-2.894446	-3.579763
H	-5.833651	-1.379186	1.005380
H	-6.792110	-0.164868	-0.962839
H	-5.257458	0.777817	-2.698554
H	-1.259156	1.027172	-0.072469
H	0.600355	2.254107	0.198326
H	4.559578	0.481123	0.260506
H	-0.878197	-4.508182	1.738218
H	-2.625433	-4.691643	-0.689750
H	-3.305616	-3.080118	-1.314348
H	-0.970431	-4.727303	-2.563450
H	-2.092083	-3.440496	-4.442362
H	-2.299807	-2.025056	-3.371105
H	-0.658760	-2.540209	-3.895628
H	0.582243	-5.515666	1.622196
H	0.743353	-3.741573	1.596459
H	-0.584964	-5.467339	-0.625156
H	1.004161	-4.596455	-0.760204
C	-3.506579	0.139852	3.177524
C	-3.035702	1.021186	4.165057
C	-1.705612	0.880057	4.616765
C	-0.857152	-0.116689	4.106790
C	-1.363672	-0.990956	3.120103
H	-4.534320	0.248464	2.807235
C	-3.934595	2.097151	4.743292
H	-1.322881	1.568460	5.382476
C	0.575670	-0.246292	4.584739
H	-0.713129	-1.774164	2.709059
H	-3.429526	3.080540	4.762275
H	-4.864311	2.204646	4.158000
H	-4.223670	1.865181	5.786568
H	1.291323	-0.043322	3.766146
H	0.793791	0.460832	5.403534
H	0.789177	-1.267034	4.953143
C	-2.781968	2.994842	-1.671197
C	-2.325495	4.310382	-1.435526
C	-1.133694	4.731792	-2.049633
C	-0.389116	3.870802	-2.884067
C	-0.869830	2.567373	-3.098175
H	-3.710853	2.655165	-1.196434
C	-3.107777	5.240901	-0.528687
H	-0.771243	5.753488	-1.873368
C	0.911071	4.335994	-3.509045
H	-0.300922	1.885519	-3.744620
H	1.230776	3.665378	-4.325313
H	0.819178	5.357041	-3.922087
H	1.727136	4.360033	-2.761726
H	-2.701983	6.266863	-0.555136
H	-4.173215	5.290011	-0.820538
H	-3.078875	4.897485	0.523062
H	-2.410800	-2.548203	1.311545
H	-4.023554	-2.466866	2.054206
H	-1.675216	0.059946	-2.998403
H	-3.124155	0.725255	-3.765661

Table S57: Internal energy and cartesian coordinates for **TS-1**$_{\textbf{Transf-2}}$.

SCF Done: -1716.65155379 A.U.

Ni	-0.363849	-2.956972	-0.276627
N	-1.339230	-1.257080	-0.314585
C	-2.780841	-1.259603	-0.334294
C	-3.476831	-1.664617	0.837235
C	-3.486157	-0.917179	-1.517671
C	-4.888436	-1.065835	-1.531246
C	-5.583660	-1.519347	-0.402689
C	-4.876591	-1.802553	0.774952
H	-5.415561	-2.136790	1.670353
H	-6.671624	-1.643968	-0.437255
H	-5.434899	-0.821728	-2.450669
C	-2.743663	-1.883191	2.154441
C	-2.775910	-0.367229	-2.743022
C	-2.457294	-0.589959	2.922858
C	-2.530438	1.147022	-2.740047
C	-0.741376	-0.092930	-0.171840
H	-1.375665	0.805911	-0.110723
C	0.677922	0.133068	-0.071044
C	1.095436	1.492660	0.007296
H	0.333902	2.276963	-0.054526
C	2.437441	1.810271	0.144961
I	3.059440	3.871854	0.252420
C	3.416963	0.792738	0.221398
H	4.474751	1.044226	0.333712
C	3.015742	-0.536883	0.155333
I	4.512669	-2.075179	0.271871
C	1.644225	-0.946211	-0.002536
O	1.361952	-2.214914	-0.068010
H	-1.841858	-3.996091	0.175893
C	-1.113945	-3.843213	-2.543710
C	0.218827	-3.686716	-2.764301
H	-1.520724	-4.799418	-2.196486
H	-1.844423	-3.080676	-2.834805
C	0.882489	-2.493655	-3.392825
H	0.890292	-4.522021	-2.522471
H	1.348605	-2.779420	-4.356566
H	0.168761	-1.674875	-3.586867
H	1.691296	-2.112370	-2.743969
C	-1.226871	-4.881554	0.611005
H	-1.671153	-5.744949	0.082935
C	0.233833	-4.678703	0.347867
H	-1.502504	-4.897698	1.678371
H	0.696314	-5.315605	-0.419244
C	-3.502017	0.286850	3.284259
C	-3.248358	1.458763	4.016136
C	-1.915664	1.755053	4.376259
C	-0.852313	0.906670	4.025702
C	-1.142488	-0.268257	3.297672
H	-4.531886	0.054194	2.983679
C	-4.378197	2.386875	4.419052
H	-1.704068	2.672916	4.941526
C	0.577576	1.245538	4.397307
H	-0.322711	-0.941713	3.014452
C	-1.447885	1.666447	-3.481031
C	-1.196053	3.047604	-3.544389
C	-2.054536	3.918876	-2.840314
C	-3.141951	3.433627	-2.093934
C	-3.366762	2.040199	-2.049144
H	-0.783376	0.976370	-4.018386
C	-0.021719	3.593071	-4.332904
H	-1.865679	5.000440	-2.872927
C	-4.068055	4.382748	-1.358044
H	-4.206253	1.650078	-1.460342
H	-4.165219	3.433680	4.132922
H	-5.330918	2.093885	3.944754
H	-4.535777	2.380369	5.514759
H	1.194329	1.417516	3.495352
H	0.628886	2.156432	5.018379
H	1.055561	0.423031	4.961360
H	-4.289054	4.022679	-0.336776
H	-3.630334	5.392661	-1.275704
H	-5.038822	4.484240	-1.880899
H	-0.349367	4.338094	-5.081999
H	0.707342	4.098820	-3.672490
H	0.513892	2.790034	-4.867672
H	-1.779627	-2.393500	1.970391
H	-3.353497	-2.557258	2.788031
H	-1.800384	-0.870295	-2.869094
H	-3.376431	-0.623617	-3.639617
H	0.888187	-4.512874	1.214448

Table S58: Internal energy and cartesian coordinates for **1-Transf-2**.

SCF Done: -1598.80131378 A.U.

Ni	0.626766	-2.399375	-1.569392
N	1.165501	-0.614992	-1.127679
C	2.459741	-0.134301	-1.549414
C	2.554129	0.680971	-2.710863
C	3.620781	-0.545924	-0.845907
C	4.877267	-0.111802	-1.313959
C	4.989556	0.687347	-2.457341
C	3.832085	1.073457	-3.150641
H	3.914380	1.688348	-4.055517
H	5.976020	1.006002	-2.812239
H	5.774872	-0.407352	-0.757617
C	1.315035	1.109372	-3.481523
C	3.548867	-1.449916	0.383519
C	0.584915	2.335190	-2.923150
C	4.205074	-0.856651	1.625743
C	0.385213	0.220947	-0.471886
H	0.762877	1.238956	-0.282121
C	-0.929294	-0.074475	0.029159
C	-1.604397	0.974668	0.718219
H	-1.104791	1.944599	0.811480
C	-2.867113	0.767088	1.247467
I	-3.873762	2.353026	2.303967
C	-3.512260	-0.485315	1.113812
H	-4.508746	-0.645995	1.533537
C	-2.862819	-1.511907	0.437959
I	-3.844361	-3.410085	0.236852
C	-1.553760	-1.369277	-0.138031
O	-1.023138	-2.387277	-0.760050
H	2.100333	-2.687316	-2.393416
C	1.820528	-3.800715	-2.713347
H	2.662549	-4.358233	-2.269563
C	0.471475	-4.190958	-2.223633
H	1.923789	-3.730197	-3.809441
H	0.410016	-4.916897	-1.401644
H	-0.338905	-4.278639	-2.959810
C	-0.817442	2.407590	-3.001738
C	-1.522955	3.533332	-2.528770
C	-0.790464	4.597857	-1.972392
C	0.616129	4.555815	-1.878671
C	1.290045	3.415618	-2.354637
H	-1.376423	1.567914	-3.436117
C	-3.037271	3.574909	-2.585384
H	-1.327883	5.480062	-1.598797
C	1.383733	5.722292	-1.286629
H	2.383445	3.365250	-2.277892
C	5.331791	-1.464314	2.202910
C	5.944745	-0.929206	3.357625
C	5.401115	0.234594	3.924772
C	4.266702	0.867944	3.370657
C	3.684304	0.312628	2.220352
H	5.740978	-2.378357	1.750596
C	7.157708	-1.604314	3.967811
H	5.869406	0.661648	4.822049
C	3.692405	2.115201	4.013472
H	2.807294	0.799704	1.774309
H	-3.415459	4.611212	-2.545309
H	-3.421528	3.104928	-3.508305
H	-3.482376	3.027695	-1.732456
H	2.446110	5.468644	-1.127885
H	1.348562	6.606877	-1.951232
H	0.960184	6.035635	-0.314499
H	2.879736	2.545930	3.403705
H	3.277970	1.898093	5.016424
H	4.465227	2.894966	4.147237
H	7.557395	-1.023466	4.816785
H	6.912085	-2.616811	4.341007
H	7.971358	-1.723832	3.227999
H	0.599421	0.266750	-3.530189
H	1.617511	1.322330	-4.526810
H	4.046626	-2.411724	0.148897
H	2.492222	-1.693456	0.597203

5. References

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