

## Supporting Information

### Manipulating Pre-equilibria in Olefin Polymerization Catalysis: Backbone-Stiffening Converts a Living into a Highly Active Salan-type Catalyst.

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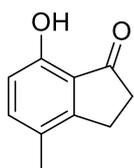
# 1. Synthesis of the Ligands and Complexes

## 1.1 General Information

All manipulations with air- or moisture-sensitive compounds were performed in a glovebox under controlled atmosphere of purified argon ( $\leq 1$  ppm  $O_2$ ,  $\leq 1$  ppm water). Toluene, diethyl ether and THF were distilled from sodium/benzophenone.  $ZrCl_4$  was purchased from Strem. Other commercial reagents were purchased from Sigma-Aldrich, Merck, ABCR and Acros and were used as received. All new compounds were characterized by means of GC,  $^1H$ -NMR,  $^{13}C$ -NMR, and HRMS. GC/MS analysis was performed on an Agilent Technologies 7890A GC/5975C MSD system. GC runs were performed with the following method: GC; HP-5MSI column; inlet temperature 300 °C; column temperature 70 °C for 5 min, then 50 °C/min to 240 °C, then 240 °C for 15 min. NMR spectra were recorded on Bruker AVANCE (400 MHz) or Agilent Technologies 400-MR (400 MHz) NMR spectrometers and can be found at the end of the document. High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6530 Q-TOF LC/MS system paired with an Agilent 1260 HPLC and using Agilent JetStream ion source. All  $^1H$ -NMR data are reported in  $\delta$  units, parts per million (ppm), and were calibrated relative to residual resonances of the deuterated solvents. All  $^{13}C$ -NMR data are reported in ppm relative to residual resonances of the deuterated solvents and were obtained with  $^1H$  decoupling.

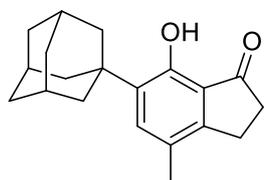
## Experimental Procedures and Characterization Data

### 7-Hydroxy-4-methyl-2,3-dihydro-1H-inden-1-one (3a)



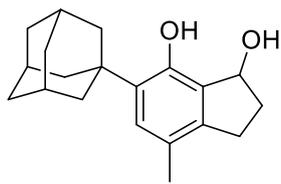
A mixture of 20.0 g of p-cresol (185 mmol) and 19.4 ml of 3-chloropropionyl chloride (203 mmol) was stirred at 80 °C for 2 h, after that the reaction mixture was cooled to room temperature and 90.0 g of  $AlCl_3$  (675 mmol) was added in one portion. The resulting mixture was stirred at 135 °C for 2 h and at 175 °C for another 2 h. The resulting brown-colored mixture was cooled to room temperature, frozen with liquid nitrogen and crushed thoroughly while still cold. The powder thus obtained was poured into mixture of 1000 ml of dichloromethane, 1500 ml of crushed ice and 500 ml of 4N HCl. The mixture was stirred until the suspended powder was completely dissolved. The organic phase was separated, the aqueous phase was additionally extracted with dichloromethane (3 x 400 ml); the combined organic extract was dried over  $Na_2SO_4$  and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63  $\mu m$ , eluent: dichloromethane-hexane = 4:1, vol.  $\rightarrow$  dichloromethane). Yield 19.4 g (65%) of a yellow solid.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.93 (s, 1H), 7.27 (d,  $J = 8.3$  Hz, 1H), 6.69 (d,  $J = 8.3$  Hz, 1H), 2.96 – 3.00 (m, 2H), 2.70 – 2.74 (m, 2H), 2.24 (s, 3H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  210.3, 155.4, 153.4, 138.1, 126.1, 122.3, 113.4, 35.9, 24.9, 16.7. HRMS (ESI):  $[M+H]^+$  Calcd. for  $C_{10}H_{11}O_2^+$ : 163.0754; Found: 163.0759. The NMR spectra match the literature data.<sup>1</sup>

### 6-(Adamantan-1-yl)-7-hydroxy-4-methyl-2,3-dihydro-1H-inden-1-one (3b)



To a solution of 7.00 g of **3a** (43.2 mmol) and 6.88 g of adamantan-1-ol (45.3 mmol) in 70 ml of dichloromethane a mixture of 2.5 ml of conc.  $H_2SO_4$  and 4.9 ml of acetic acid was added dropwise for 1 h. The resulting solution was stirred at 40 °C for 2 days, after that the reaction mixture was cooled to room temperature. The precipitate was filtered off on a glass frit (G4), washed with 10 ml of cold dichloromethane and 2 x 30 ml of water. The filter cake was washed off with dichloromethane, the filtrate thus obtained was dried over  $Na_2SO_4$  and evaporated to dryness. Yield 7.49 g (59%) of a colorless crystalline solid.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  9.82 (s, 1H), 7.23 (s, 1H), 2.90 – 2.96 (m, 2H), 2.69 – 2.76 (m, 2H), 2.24 (s, 3H), 2.12 (br.s, 6H), 2.09 (br.s, 3H), 1.77 – 1.81 (m, 6H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  211.2, 155.0, 150.5, 135.7, 135.0, 125.1, 122.5, 40.5, 37.0, 36.5, 36.2, 28.9, 24.0, 17.1. HRMS (ESI):  $[M+H]^+$  Calcd. for  $C_{20}H_{25}O_2^+$ : 297.1849; Found: 297.1858.

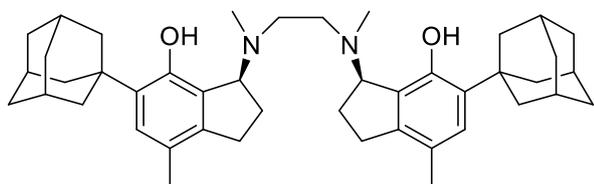
### 6-(Adamantan-1-yl)-4-methyl-2,3-dihydro-1H-indene-1,7-diol (**3c**)



To a solution of 4.00 g of **3b** (13.5 mmol) in a mixture of 120 ml of THF and 50 ml of methanol 1.40 g of sodium borohydride (36.8 mmol) was added portionwise at 0°C. The resulting suspension was stirred at room temperature overnight, then evaporated to near dryness. To the residue 100 ml of boiling water was added, the resulting suspension was cooled to room temperature and the precipitate was filtered off on a glass frit (G4). The powder thus obtained was washed with 2 x 30 ml

of water and dried in vacuo. Yield 4.00 g (near quant.) of a white powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.02 (s, 1H), 6.94 (s, 1H), 5.52 (q,  $J = 7.7$  Hz, 1H), 2.82 – 2.93 (m, 1H), 2.58 – 2.72 (m, 2H), 2.18 (s, 3H), 2.06 – 2.20 (m, 9H), 1.94 (d,  $J = 8.6$  Hz, 1H), 1.80 – 1.92 (m, 1H), 1.75 – 1.80 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  151.2, 139.4, 135.0, 128.7, 128.2, 124.7, 40.7, 37.1, 36.5, 36.4, 29.1, 27.9, 18.0. HRMS (ESI):  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{20}\text{H}_{27}\text{O}_2^+$ : 299.2006; Found: 299.2003.

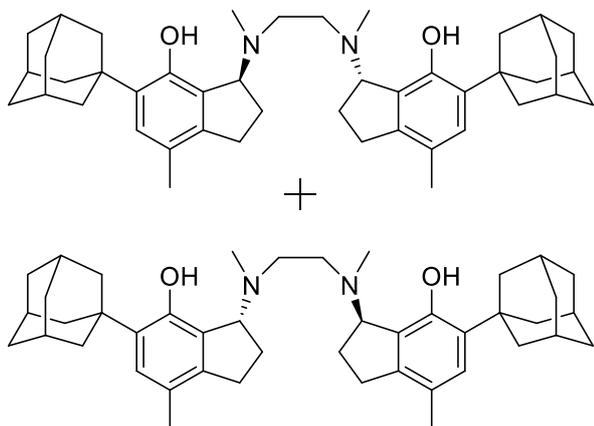
### *meso*-3,3'-(Ethane-1,2-diylbis(methylazanediyl))bis(5-(adamantan-1-yl)-7-methyl-2,3-dihydro-1H-inden-4-ol) (*meso*-**3d**)



A mixture of 4.09 g of **3c** (13.7 mmol), 0.57 g of *N,N'*-dimethylethylenediamine (6.44 mmol) and 13 ml of DIPEA in 13 ml of toluene was stirred in a pressure vessel at 105°C for 4 days. After cooling to room temperature, the reaction mixture was filtered through a glass frit (G4); the powder thus obtained was washed with 2 x 10 ml of

toluene and dried in vacuo. Yield 3.01 g (72%) of an off-white powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.70 (br.s, 2H), 6.87 (s, 2H), 4.60 (broad, 2H), 2.63 – 2.88 (m, 6H), 2.02 – 2.50 (m, 36H), 1.78 (br.s, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz, signals marked with asterisk are very broad and non-representative):  $\delta$  152.2, 139.4, 134.1, 127.1, 126.4, 123.5, 70.5\*, 54.5\*, 47.8\*, 40.7, 37.2, 36.3, 29.1, 28.5, 21.7 (broad), 18.1. HRMS (ESI):  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{44}\text{H}_{61}\text{N}_2\text{O}_2^+$ : 649.4728; Found: 649.4721.

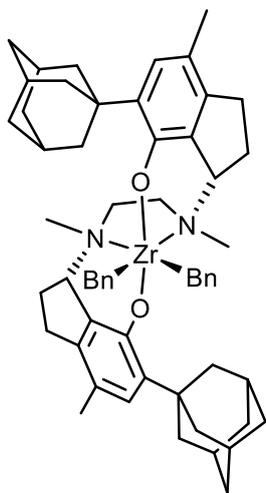
### *rac*-3,3'-(Ethane-1,2-diylbis(methylazanediyl))bis(5-(adamantan-1-yl)-7-methyl-2,3-dihydro-1H-inden-4-ol) (*rac*-**3d**)



A solution of 700 mg of *meso*-**3d** (1.08 mmol) in 55 ml of degassed toluene was stirred at 105°C for 12 h. The reaction vessel was rapidly cooled to room temperature using water bath and stirring, and the reaction mixture was additionally stirred at room temperature for 2 h. The obtained suspension was filtered on glass frit (G4). The filtrate was evaporated and the residue was triturated with 3 ml of *n*-hexane. The solids obtained were filtered off on a glass frit (G4), washed with 1 ml of *n*-hexane and dried in vacuo. Yield 345 mg (99% assuming that the 1:1 *rac/meso* mixture had been formed) of an off-white powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.68 (br.s, 2H), 6.86 (s, 2H), 4.64 (br.s, 2H), 2.60 – 2.85 (m, 6H), 1.95 – 2.50

(m, 36H), 1.77 (br.s, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  151.8, 138.9, 133.7, 126.8, 126.1, 123.1, 40.2, 36.8, 35.9, 28.7, 28.2, 21.1, 17.7. HRMS (ESI):  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{44}\text{H}_{61}\text{N}_2\text{O}_2^+$ : 649.4728; Found: 649.4725.

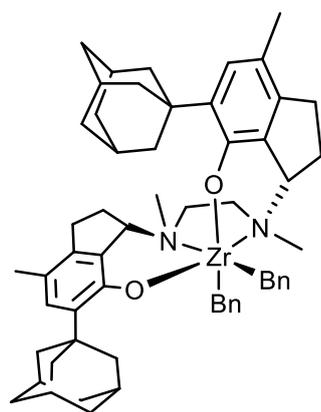
***fac/fac*-Dibenzylzirconium[*rac*-3,3'-(ethane-1,2-diylbis(methylazanediyl))bis(5-(adamantan-1-yl)-7-methyl-2,3-dihydro-1*H*-inden-4-olate)] (*rac*-3FF)**



To a solution of 100 mg of ***rac*-3d** (0.154 mmol) in 40 ml of toluene a solution of 70.2 mg of tetrabenzylzirconium (0.154 mmol) in 20 ml of toluene was added dropwise for 10 min at 60°C. The resulting yellow solution was stirred at room temperature overnight and then evaporated to dryness. The residue was triturated with 5 ml of n-hexane and the resulting suspension was filtered through a glass frit (G4). The obtained yellow powder was washed with 5 ml of n-hexane and dried in vacuo, yielding 84 mg (61%) of a product as a *ca.*3:2 mixture of the *fac-fac* isomer and a  $C_1$ -symmetric (presumably *fac-mer*) isomer, respectively. This powder was redissolved in 10 ml of toluene and the obtained solution was carefully layered with 10 ml of n-hexane. After three days, the precipitated yellow crystals were filtered through a glass frit (G4) and dried in vacuo. Yield 29 mg (19%, *fac-fac*,  $\times 0.75$ PhMe solvate) of small yellow crystals.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz):  $\delta$  7.00 (s, 2H), 6.80 – 6.90 (m, 8H), 6.65 (t,  $J = 6.5$  Hz, 2H), 4.08 (t,  $J = 8.2$  Hz, 2H), 2.74 (d,  $J = 9.0$  Hz, 2H), 2.67 – 2.76 (m, 2H), 2.59 (d,  $J = 10.1$  Hz, 2H), 2.39 – 2.50 (m, 4H), 2.36 (br.s, 12H), 2.32 (s, 6H), 2.19 (br.s, 6H), 2.17 (s, 6H), 2.11 (d,  $J = 10.1$  Hz, 2H), 2.06 (d,  $J = 9.1$  Hz, 2H), 1.94 – 2.02 (m, 6H),

1.80 – 1.92 (m, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz):  $\delta$  155.5, 148.7, 141.1, 136.2, 130.9, 128.7, 128.5, 127.0, 124.2, 121.0, 71.4, 68.0, 47.9, 42.9, 41.7, 37.7, 37.2, 30.0, 28.6, 22.8, 18.5.

**Dibenzylzirconium[*meso*-3,3'-(ethane-1,2-diylbis(methylazanediyl))bis(5-(adamantan-1-yl)-7-methyl-2,3-dihydro-1*H*-inden-4-olate)] (*meso*-3)**



To a solution of 100 mg of ***meso*-3d** (0.154 mmol) in 40 ml of toluene a solution of 70.2 mg of tetrabenzyl zirconium (0.154 mmol) in 20 ml of toluene was added dropwise for 10 min at 60°C. The resulting yellow solution was stirred at room temperature overnight and then evaporated to dryness. The residue was triturated with 5 ml of n-hexane and the resulting suspension was filtered through a glass frit (G4). The obtained yellow powder was washed with 5 ml of n-hexane and dried in vacuo. Yield 104 mg (74%, *fac-mer*) of a yellow powder.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  7.24 – 7.26 (m, 2H), 7.08 – 7.16 (m, 6H), 6.97 (t,  $J = 7.64$  Hz, 2H), 6.85 – 6.90 (m, 1H), 6.79 (t,  $J = 7.2$  Hz, 1H), 4.08 (t,  $J = 8.7$  Hz, 1H), 3.29 (d,  $J = 8.9$  Hz, 1H), 3.09 – 3.14 (m, 2H), 2.86 – 2.93 (m, 2H), 2.65 – 2.74 (m, 2H), 2.45 – 2.59 (m, 12H), 2.29 – 2.42 (m, 14H), 2.10 – 2.25 (m, 9H), 1.93 – 2.02 (m, 6H), 1.84 – 1.89 (m, 6H), 1.40 – 1.69 (m, 5H).

## 1.2 X-ray Crystallography Data

X-ray experiments were carried out using Bruker D8 Quest with Photon III detector diffractometer ( $\lambda(\text{Mo-K}\alpha)=0.71073 \text{ \AA}$ , graphite monochromator,  $\omega$ -scans) at 100 K. Structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions and included in the refinement using riding approximation. The details of data collection and crystal structure refinement for which we used SAINT Plus, SADABS and SHELXL-2018/3 program packages, are summarized in **Table S1**. Crystallographic data for ***rac-3<sub>FF</sub>*** have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 2283479. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

**Table S1.** Crystal data and structure refinement for ***rac-3<sub>FF</sub>***.

Identification code	<b><i>rac-3<sub>FF</sub></i></b>
Empirical formula	C <sub>58</sub> H <sub>72</sub> Zr N <sub>2</sub> O <sub>2</sub>
Formula weight	920.39
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 <sub>1</sub> /n
Unit cell dimensions	a = 14.971(3) Å $\alpha = 90^\circ$ . b = 24.564(4) Å $\beta = 116.848(4)^\circ$ . c = 15.027(3) Å $\gamma = 90^\circ$ .
Volume	4930.4(15) Å <sup>3</sup>
Z	4
Density (calculated)	1.240 Mg/m <sup>3</sup>
Absorption coefficient	0.267 mm <sup>-1</sup>
F(000)	1960
Crystal size	0.362 x 0.284 x 0.190 mm <sup>3</sup>
Theta range for data collection	1.730 to 27.500°.
Index ranges	-19 ≤ h ≤ 19, -31 ≤ k ≤ 31, -19 ≤ l ≤ 19
Reflections collected	41151
Independent reflections	11333
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.494 and 0.540
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	0.979
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0611, wR <sub>2</sub> = 0.1734
Extinction coefficient	n/a

## 2. NMR Studies

### 2.1 General considerations.

All manipulations and synthesis of air- and moisture sensitive chemicals and preparation of NMR samples were performed under rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware interfaced to a high-vacuum line ( $10^{-5}$  Torr), or in a nitrogen-filled MBraun glovebox ( $<0.5$  ppm  $O_2$  and  $H_2O$ ). Molecular sieves (4 Å, MS) were activated for 24 h at ca. 200–230 °C under dynamic vacuum. Chlorobenzene- $d^5$  (Apollo Scientific) and 1-hexene (Sigma-Aldrich) used in the studies of the activated complexes were freeze-pump-thaw degassed on the high vacuum line, dried over  $CaH_2$  and vacuum transferred into dry storage Schlenk flasks equipped with PTFE valves.  $[CPh_3][B(C_6F_5)_4]$  was obtained from Boulder Scientific Company and used as received.

### 2.2 NMR Spectroscopy Experiments.

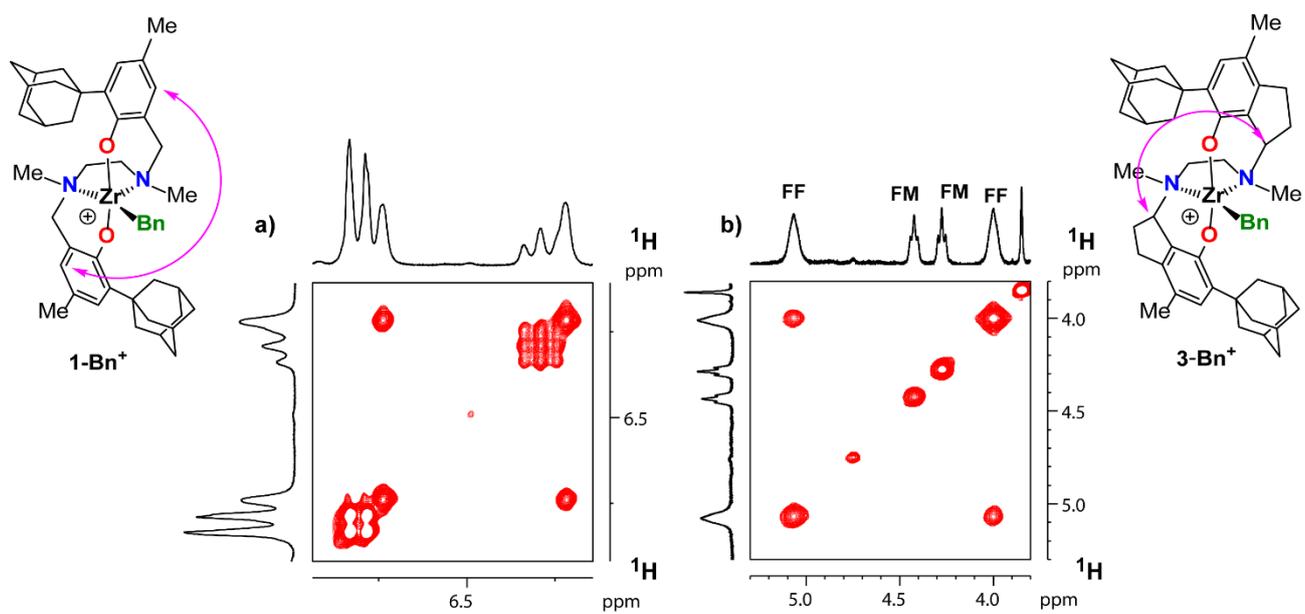
One- and two-dimensional, homo- and hetero-nuclear NMR spectra were recorded on a Bruker Avance III 400 spectrometer equipped with a smartprobe and using standard pulse sequences. Unless otherwise stated, referencing is relative to external TMS ( $^1H$  and  $^{13}C$ ) and  $CCl_3F$  ( $^{19}F$ ). Low temperature  $^1H$  EXSY NMR measurements were acquired at 223K for **3<sub>FF</sub>-Bn<sup>+</sup>** and at 228K for **1-Bn<sup>+</sup>** by using the PFG version of the NOESY sequence (noesygptp), setting a relaxation delay of 1 s, with mixing time values ( $\tau_m$ ) ranging between 2.7 and 800 ms depending on the rate of chemical exchange. Typically, a matrix of 1024x1024 data points was used for acquisition and the raw data were processed using zero-filling to 2048 data points in both spectral dimensions. The spectral window and the number of transients were optimized depending on distribution and of relevant resonances and the sample concentration. Typically, at least two experiments with different  $\tau_m$  values were acquired for each temperature, and the rate constant values were obtained from the average of all the values. For the Site Epimerization (SE) dynamical motions, rate constants ( $k_{SE}$ ,  $s^{-1}$ ) were evaluated by the method proposed by Perrin,<sup>1</sup> and were calculated from the integration of the 2D spectra by using the EXSYCALC software.

To describe the multiplicity of the signals, the following abbreviations are used: s, singlet; bs, broad singlet; d, doublet; bd, broad doublet; dd, doublet of doublets; t, triplet; br, broad; and m, multiplet. Buried is used whenever the signal of interest is covered by the NMR signals relevant to the adamantyl moiety of the ligand.

#### NMR characterization of **3-Bn<sup>+</sup>** (2:1 mixture of FF and FM)

**3<sub>FF</sub>-Bn<sup>+</sup>**:  $^1H$  NMR (233K,  $C_6D_5Cl$ ):  $\delta$  = 5.07 (br, 1H, CH Ind), 4.00 (br, 1H, CH Ind), 3.19 (br, 1H,  $CH_2$  Ind), 3.10 (br, 1H, CH Ind), 2.36 (s, buried,  $H_2/H_2'$ ), 2.18 (buried,  $CH_2$  Ind), 1.96 (s, buried,  $H_2/H_2'$ ), 1.56 (m,  $CH_2$  Ind);  $^{13}C$  NMR (233K,  $C_6D_5Cl$ ):  $\delta$  = 74.6 (CH Ind), 73.4 ( $CH_2$  Ind), 71.6 (CH Ind), 44.6 (C2/C2'), 44.4 ( $CH_2$  Ind), 43.4 (C2/C2').

**3<sub>FM</sub>-Bn<sup>+</sup>**:  $^1H$  NMR (233K,  $C_6D_5Cl$ ):  $\delta$  = 4.42 (t, 1H, CH Ind), 4.27 (t, 1H, CH Ind), 2.79 (d br,  $CH_2$  Ind), 2.58 (m,  $CH_2$  Ind), 2.08 (buried,  $CH_2$  Ind), 2.00 (s, buried,  $H_2/H_2'$ ), 1.55 (s, buried,  $H_2/H_2'$ ), 1.44 (buried,  $CH_2$  Ind);  $^{13}C$  NMR (233K,  $C_6D_5Cl$ ):  $\delta$  = 72.2 (CH Ind), 67.6 (CH Ind), 67.5 ( $CH_2$  Ind), 45.3 ( $CH_2$  Ind), 39.9 (C2/C2'), 39.6 (C2/C2').



**Figure S1.** Sections of  $^1\text{H}$ ,  $^1\text{H}$  EXSY NMR spectra ( $\text{C}_6\text{D}_5\text{Cl}$ ) of a) **1-Bn<sup>+</sup>**, exchange between protons marked with pink arrow, aromatic region (228K, 800 ms,  $k_{\text{SE}} = 0.4 \text{ s}^{-1}$ ), and b) **3<sub>FF</sub>-Bn<sup>+</sup>**, exchange between protons marked with pink arrow (223K, 500 ms,  $k_{\text{SE}} = 0.6 \text{ s}^{-1}$ ). No exchange observed between **3<sub>FF</sub>-Bn<sup>+</sup>** and **3<sub>FM</sub>-Bn<sup>+</sup>**.

### 3. Polymerization experiments and polymer characterization

Propene polymerization experiments were performed in a Freeslate Parallel Pressure Reactor setup with 48 reaction cells (PPR48), fully contained in a triple MBraun glovebox operating under nitrogen, following established experimental protocols (Table S2).<sup>2-4</sup>

All polymers were characterized by means of high-temperature gel permeation chromatography (GPC) and <sup>13</sup>C NMR spectroscopy. GPC curves were recorded with a Freeslate Rapid GPC setup, equipped with a set of two mixed-bed Agilent PLgel 10 μm columns and a Polymer Char IR4 detector. Calibration was performed with the universal method, using 10 monodisperse polystyrene samples ( $M_n$  between 1.3 and 3,700 kDa).

Quantitative <sup>13</sup>C NMR spectra were recorded using a Bruker Avance III 400 spectrometer equipped with a high-temperature cryoprobe for 5 mm OD tubes, on 45 mg mL<sup>-1</sup> polymer solutions in tetrachloroethane-*d*<sub>2</sub> (with BHT added as a stabilizer, [BHT] = 0.4 mg mL<sup>-1</sup>). Acquisition conditions were: 45° pulse; acquisition time, 2.7 s; relaxation delay, 5.0 s; 2 K transients. Broad-band proton decoupling was achieved with a modified WALTZ16 sequence (BI\_WALTZ16\_32 by Bruker).

**Table S2.** Detailed polymerization results.

# ID	Cat (nmol)	$t_p$ (s)	Yield (mg)	$R_p^*$	$M_n$ (kDa)	$M_w$ (kDa)	PDI	$\sigma$	[2,1] (%)
1	600	3608	106	0.18	7.1	15	1.8	0.998	0.52
	600	2482	84.5	0.20	7.9	13	1.9		
	600	2505	85.5	0.20	7.8	15	1.9		
2	15	1478	108	17	1.3	1.9	1.5	0.82	0.80
	15	1644	118	17	1.3	1.9	1.5		
	15	1720	115	16	1.3	2.1	1.5		
<i>rac</i> -3FF	15	453	67.9	36	103	237	2.3	0.994	0.53
	15	520	77.7	36	115	270	2.3		
	20	244	50.2	37	103	228	2.2		
	20	250	53.2	39	111	265	2.4		
	20	248	56.7	41	109	240	2.2		

Other experimental conditions: MAO, 5 μmol; [BHT]/[Al<sub>free</sub>-TMA] = 2;  $T_p$  = 60°C,  $p_{propene}$  = 6.6 bar.

\* in kg mmol<sup>-1</sup> h<sup>-1</sup>

## 4. Computational Conformer Sampling

Suitable guess structures were generated for a *fac-fac* and *mer-mer* isomer of the complex and optimized with Gaussian as detailed in the Experimental Section. The optimized structures were then both submitted to the CREST workflow with the following keywords: `--ethr 0.5 --cluster --noreftopo --subrmsd -alpb toluene`.

After completion, the clustered output was screened for duplicates and all unique structures were pre-optimized with TPSSh/cc-pVDZ(-PP) utilizing a smaller grid to reduce computational time (`int=grid=sg1`) and loose convergence criteria. The optimized structures were screened again for duplicates and only unique conformers were fully optimized and evaluated. Conformers are numbered as obtained from the CREST output and represent true minima as indicated by the absence of imaginary frequencies). After full optimization, at the TPSSh/cc-pVDZ(-PP) level, single point (SP) calculations were performed at the TPSSh(D<sub>zero</sub>/PCM)/cc-pVTZ(-PP) level of theory. Final energies, enthalpies and Gibbs free energies were determined combining the SP energies and corrections determined at the DZ level. The density-fitting approximation (Resolution of Identity, RI) and standard Gaussian16 quality settings were used at the optimization stage and SP calculations.

For Kol type salans, this workflow leads to both *fac-fac* and *mer-mer* structures (and *fac-mer* structures) regardless of which isomer is used as a starting point. For indanosalans, this crossover is not observed (**Table S3**). NOTE: The lowest identified conformer starting from a *fac-fac* structure is a *fac-mer* conformer for indanosalans.

**Table S3.** Computational Results. Energies in Hartree, relative Energies in kcal/mol.

Name()	Formula()	Energy(DZ)	Energy(TZ)	DO	ZPE()	(t=298.15, p=1.0)		E	H	G	ΔE	ΔH	ΔG	conformer type
						EnthalpyCorr	EntropyCorr							
<b>Starting conformer (CREST) <i>rac</i>-3Bn<sup>+</sup><sub>FF</sub></b>														
FF-1	1H65N2O2	-2289.84769	-2290.4181	-0.16169	1.057570165	1.108204188	0.131417405	-2289.52226	-2289.47163	-2289.559679	2.0	1.8	2.4	FM
FF-3	1H65N2O2	-2289.841255	-2290.4134	-0.16489	1.058353727	1.1086154	0.130186728	-2289.51998	-2289.469722	-2289.556947	3.4	3.0	4.1	FF
FF-4	1H65N2O2	-2289.83751	-2290.4095	-0.16222	1.058522873	1.108668599	0.129474839	-2289.51318	-2289.463034	-2289.549782	7.7	7.2	8.6	FF
FF-5	1H65N2O2	-2289.84264	-2290.4149	-0.16348	1.058712697	1.108878322	0.129536325	-2289.51967	-2289.469505	-2289.556295	3.6	3.2	4.5	FF
FF-6	1H65N2O2	-2289.841255	-2290.4134	-0.16489	1.05835285	1.108614336	0.1301825	-2289.51999	-2289.469725	-2289.556948	3.4	3.0	4.1	FF
FF-7	1H65N2O2	-2289.842635	-2290.415	-0.16349	1.058697825	1.108869629	0.129559698	-2289.51978	-2289.469612	-2289.556417	3.6	3.1	4.4	FF
FF-8	1H65N2O2	-2289.841706	-2290.4139	-0.16226	1.058246388	1.108498458	0.129785215	-2289.51787	-2289.467619	-2289.554575	4.8	4.3	5.6	FF
FF-9	1H65N2O2	-2289.838382	-2290.4106	-0.16333	1.058224012	1.108494521	0.130195924	-2289.51568	-2289.465408	-2289.552639	6.1	5.7	6.8	FF
FF-10	1H65N2O2	-2289.841707	-2290.4139	-0.16226	1.058246899	1.108499321	0.129788054	-2289.51787	-2289.467619	-2289.554577	4.8	4.3	5.6	FF
FF-12	1H65N2O2	-2289.843982	-2290.4146	-0.16099	1.057543306	1.108132498	0.132626754	-2289.51806	-2289.46747	-2289.556329	4.6	4.4	4.5	FM
FF-14	1H65N2O2	-2289.830739	-2290.4025	-0.1642	1.058443801	1.108829377	0.130655973	-2289.50826	-2289.457878	-2289.545418	10.8	10.5	11.3	FF
FF-15	1H65N2O2	-2289.838746	-2290.4117	-0.16083	1.058190322	1.108406445	0.12963296	-2289.51439	-2289.46417	-2289.551024	6.9	6.5	7.8	FF
<b>Starting conformer (CREST) <i>rac</i>-3Bn<sup>+</sup><sub>MM</sub></b>														
MM-1	1H65N2O2	-2289.844408	-2290.4165	-0.1624	1.05771478	1.107491524	0.129046331	-2289.52118	-2289.471399	-2289.55786	2.7	2.0	3.5	FM
MM-2	1H65N2O2	-2289.840539	-2290.4114	-0.16134	1.057220759	1.108001058	0.13223522	-2289.5155	-2289.464724	-2289.553321	6.2	6.2	6.4	FM
MM-4	1H65N2O2	-2289.843983	-2290.4182	-0.16203	1.057460213	1.10826696	0.131989421	-2289.52278	-2289.471972	-2289.560404	1.7	1.6	1.9	FM
MM-5	1H65N2O2	-2289.846507	-2290.4218	-0.1609	1.05723947	1.108147933	0.132749226	-2289.52545	-2289.474538	-2289.56348	0.0	0.0	0.0	MM

## 5. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Organic Compounds and Metal Complexes

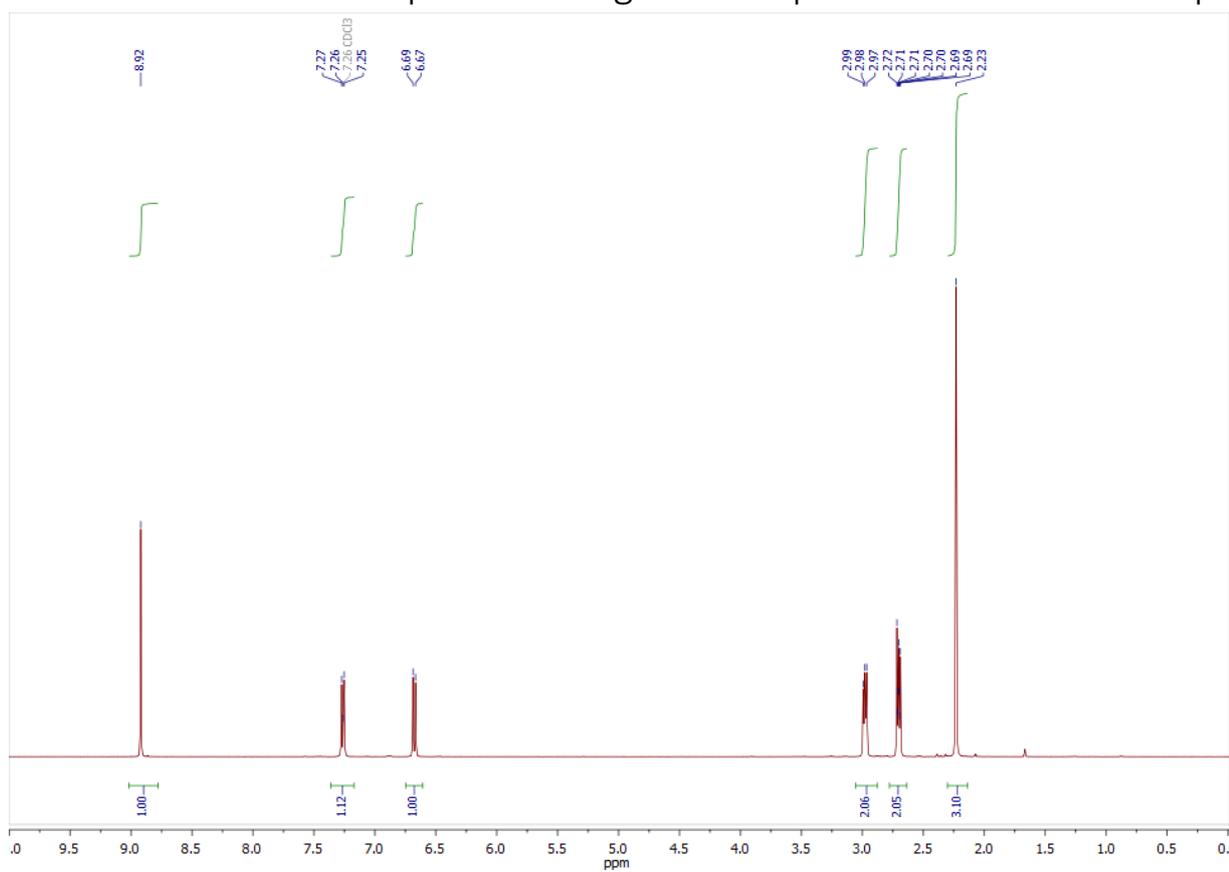


Figure S2.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3a**.

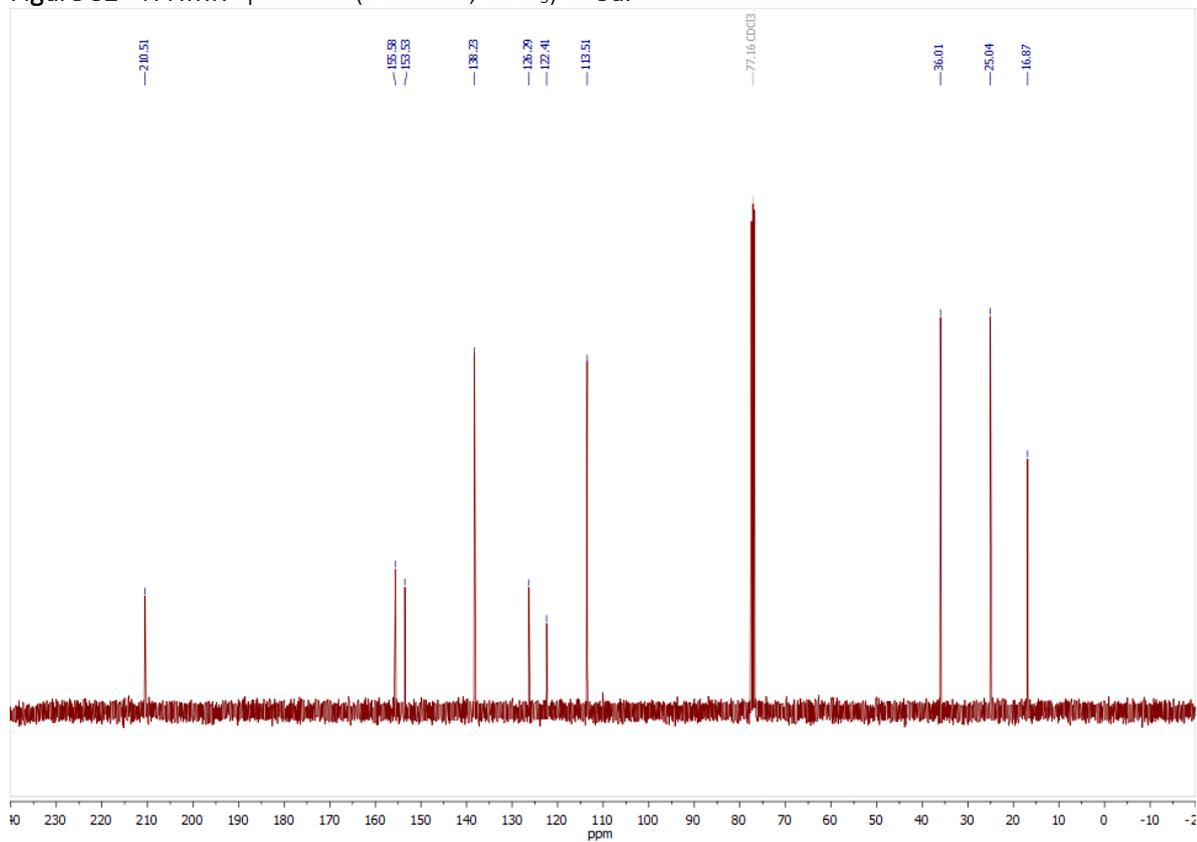


Figure S3.  $^{13}\text{C}\{^1\text{H}\}$  NMR-spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3a**.

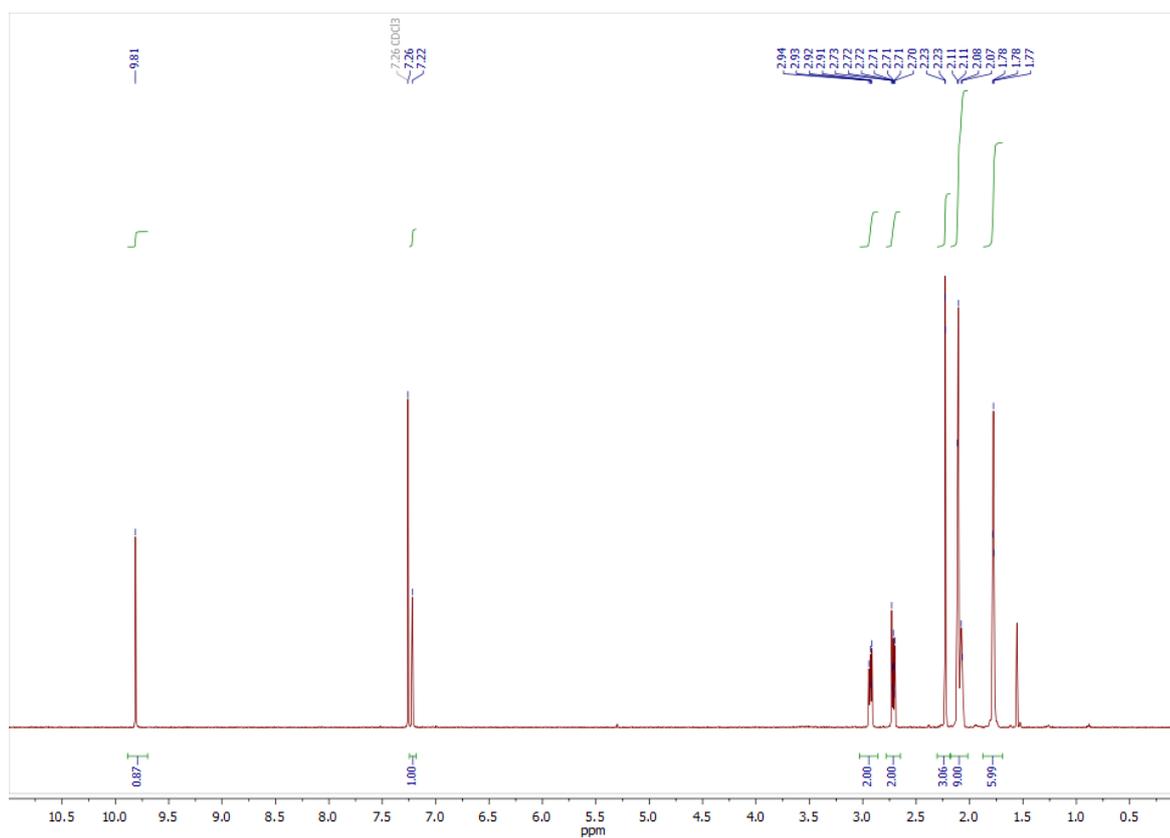


Figure S4.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3b**.

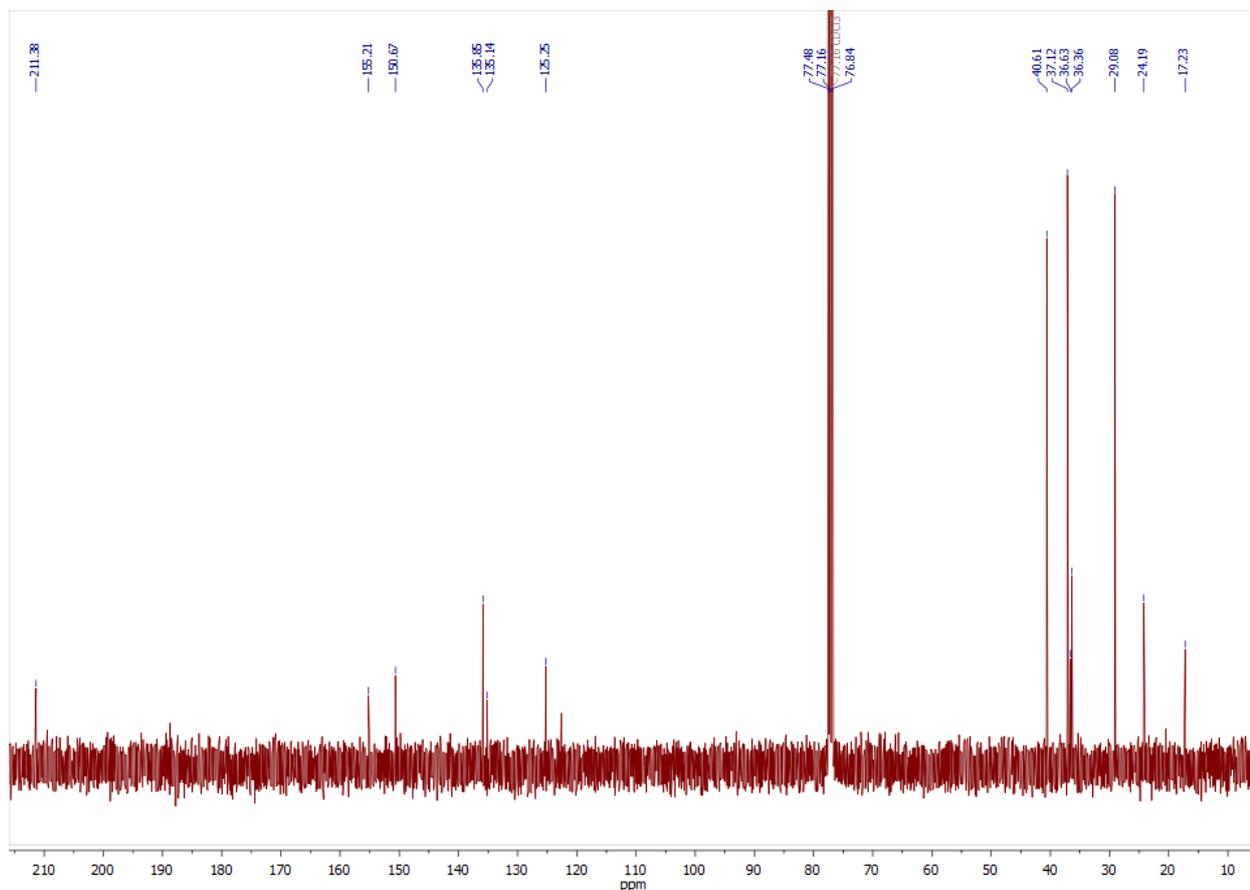


Figure S5.  $^{13}\text{C}\{^1\text{H}\}$  NMR-spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3b**.

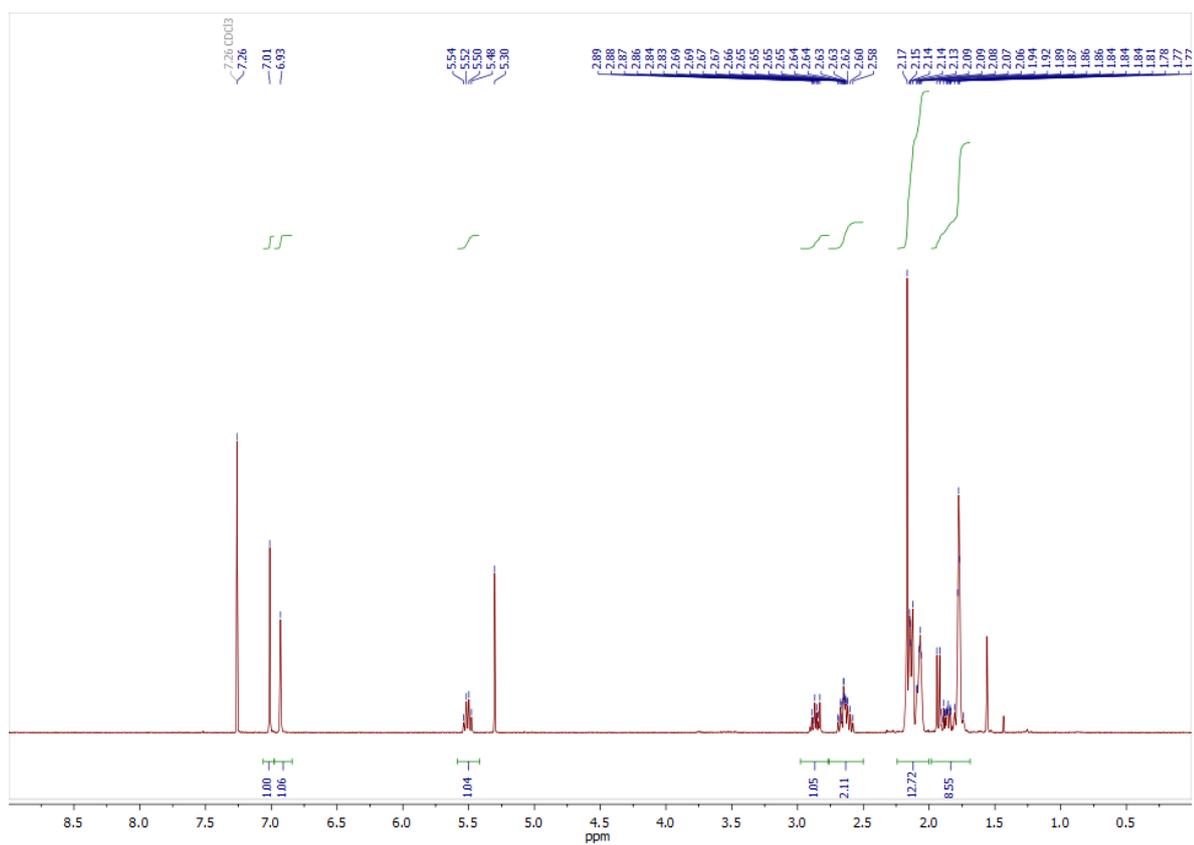


Figure S6.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3c** (residual dichloromethane).

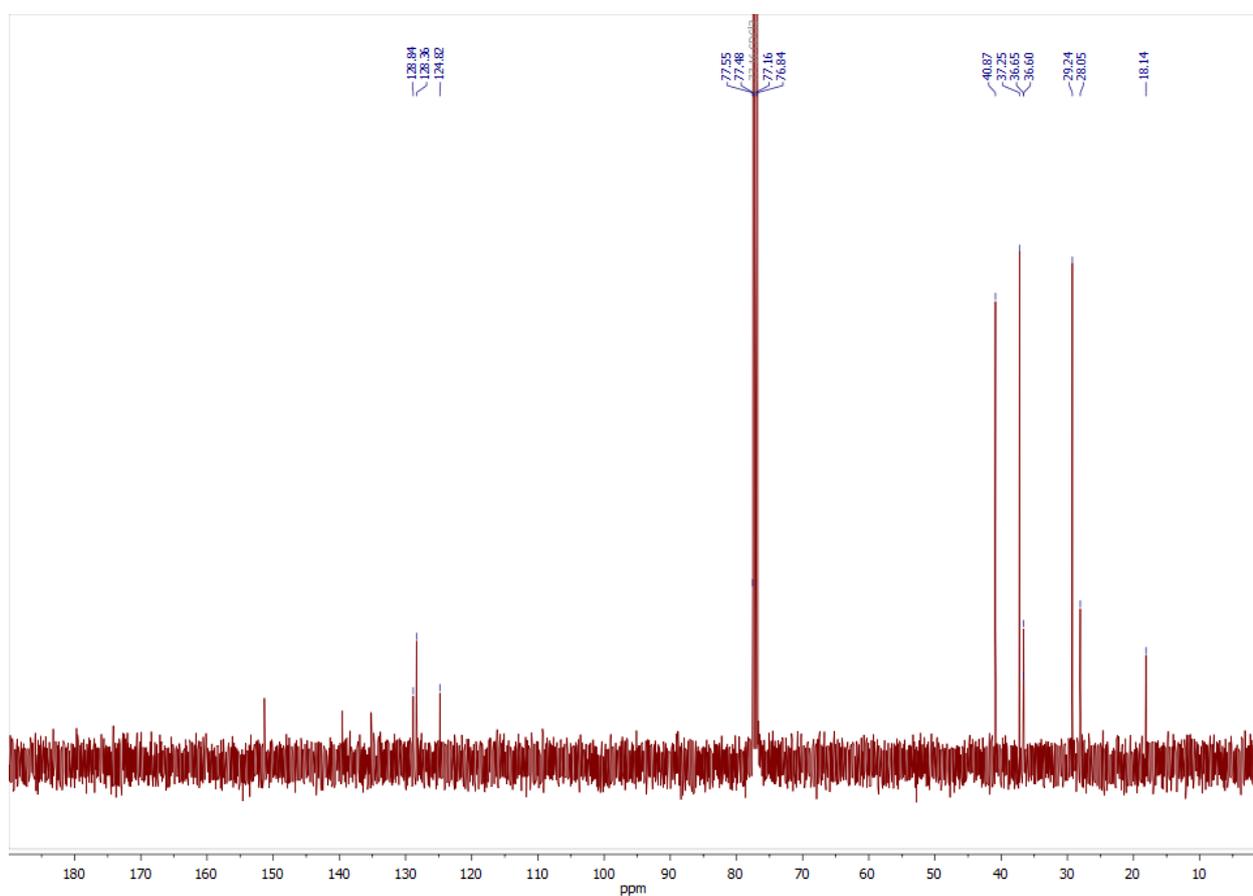


Figure S7.  $^{13}\text{C}\{^1\text{H}\}$  NMR-spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3c**.

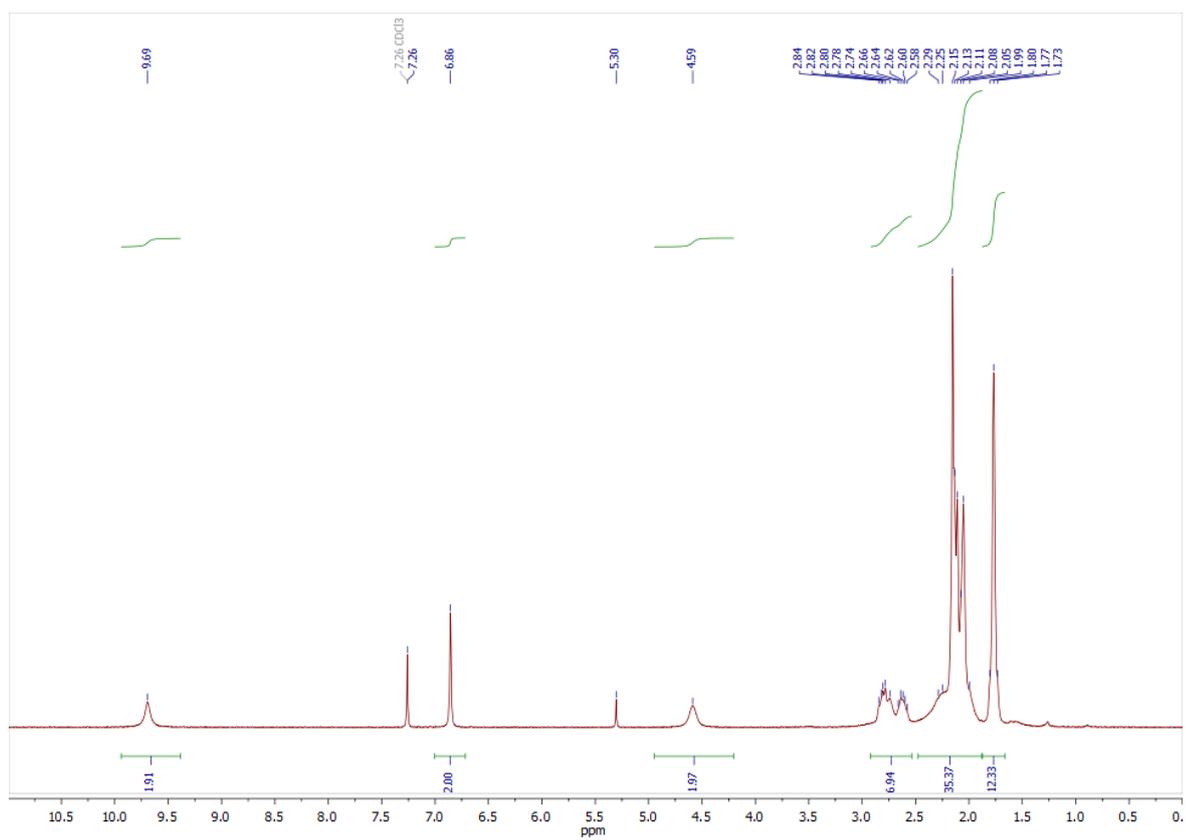


Figure S8.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of *meso*-3d (residual dichloromethane).

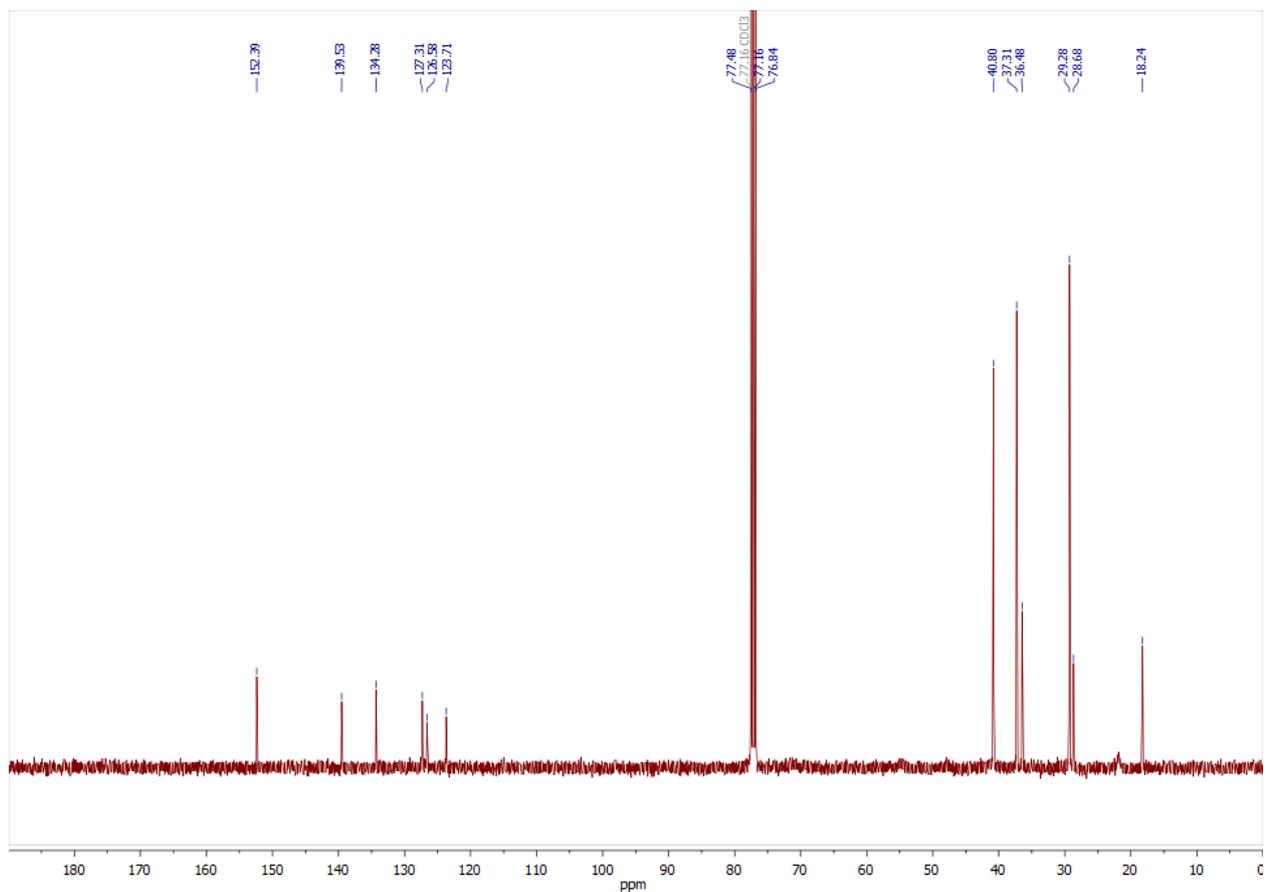


Figure S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR-spectrum (101 MHz,  $\text{CDCl}_3$ ) of *meso*-3d.

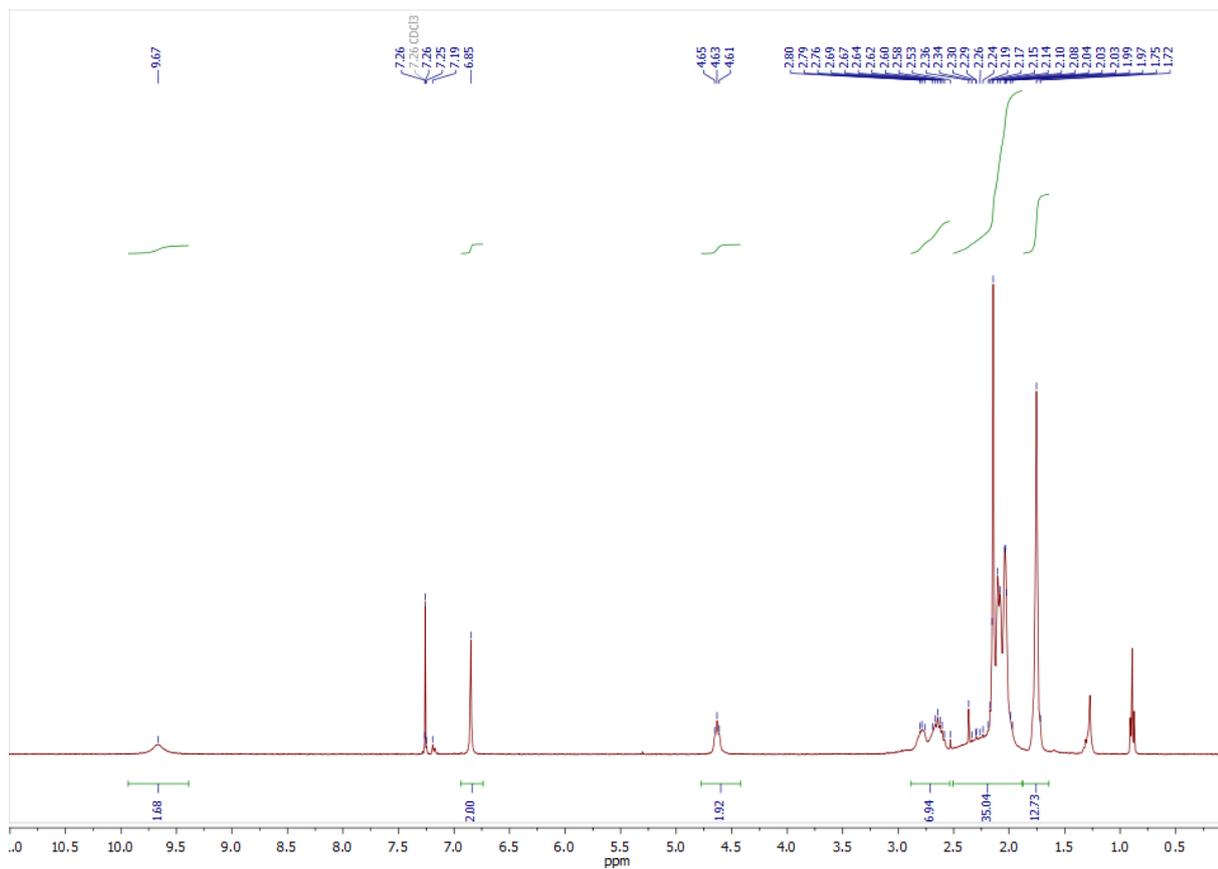


Figure S10.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of *rac*-3d (residual hexane and toluene).

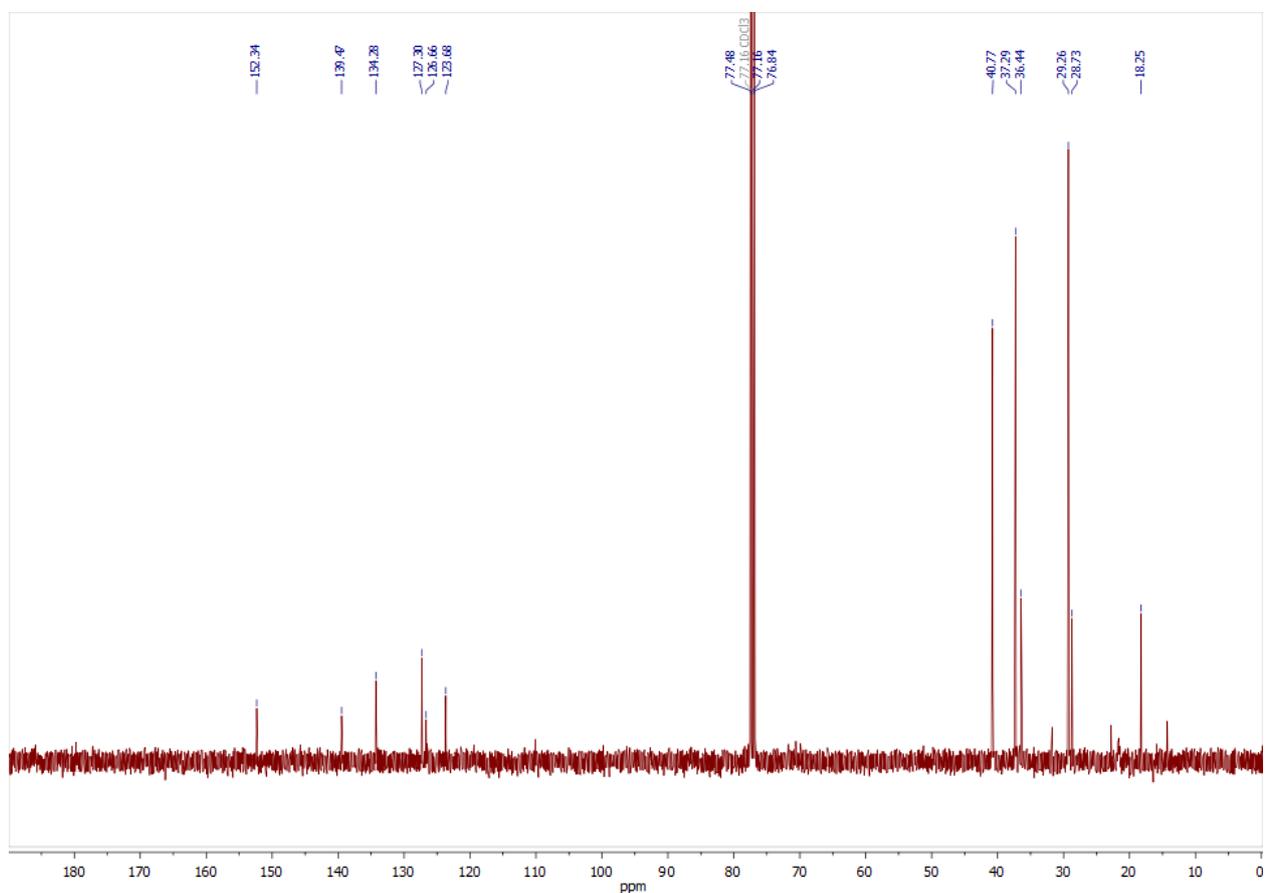


Figure S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR-spectrum (101 MHz,  $\text{CDCl}_3$ ) of *rac*-3d (residual hexane and toluene).

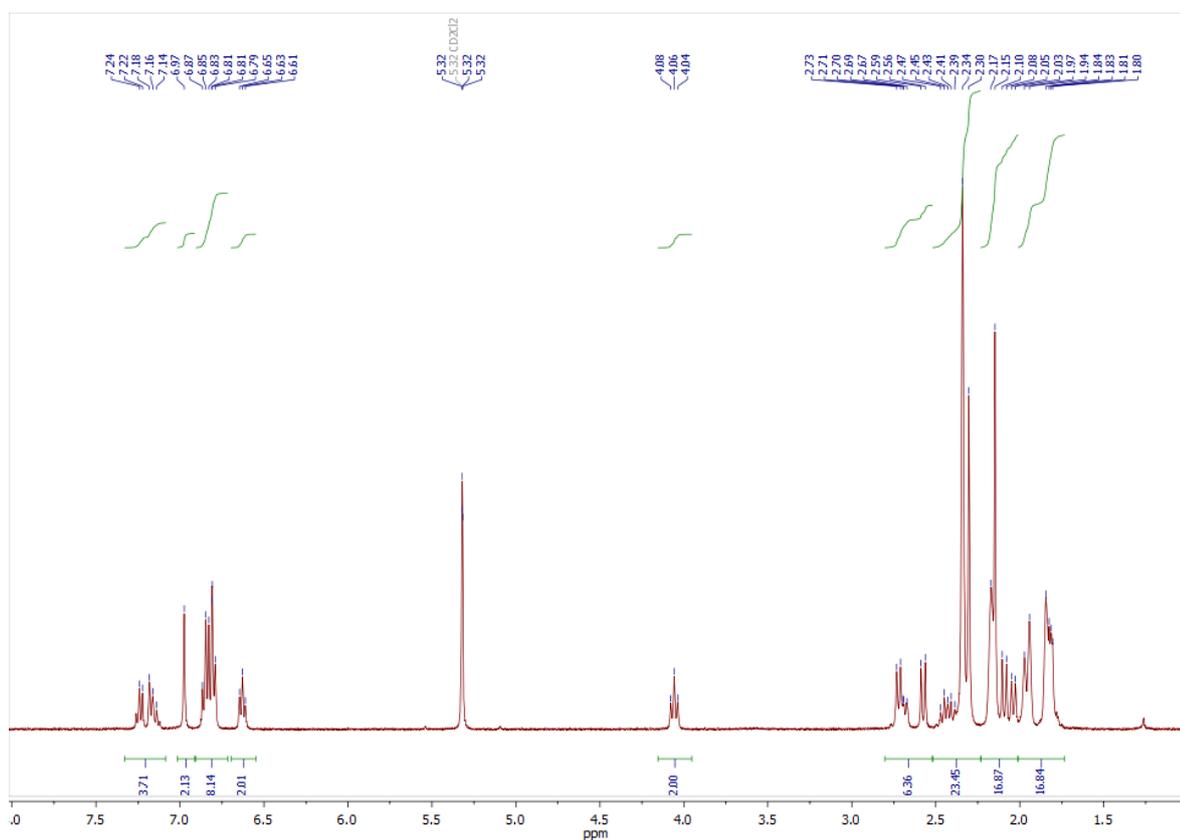


Figure S12.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of *rac*-**3FF** (toluene solvate).

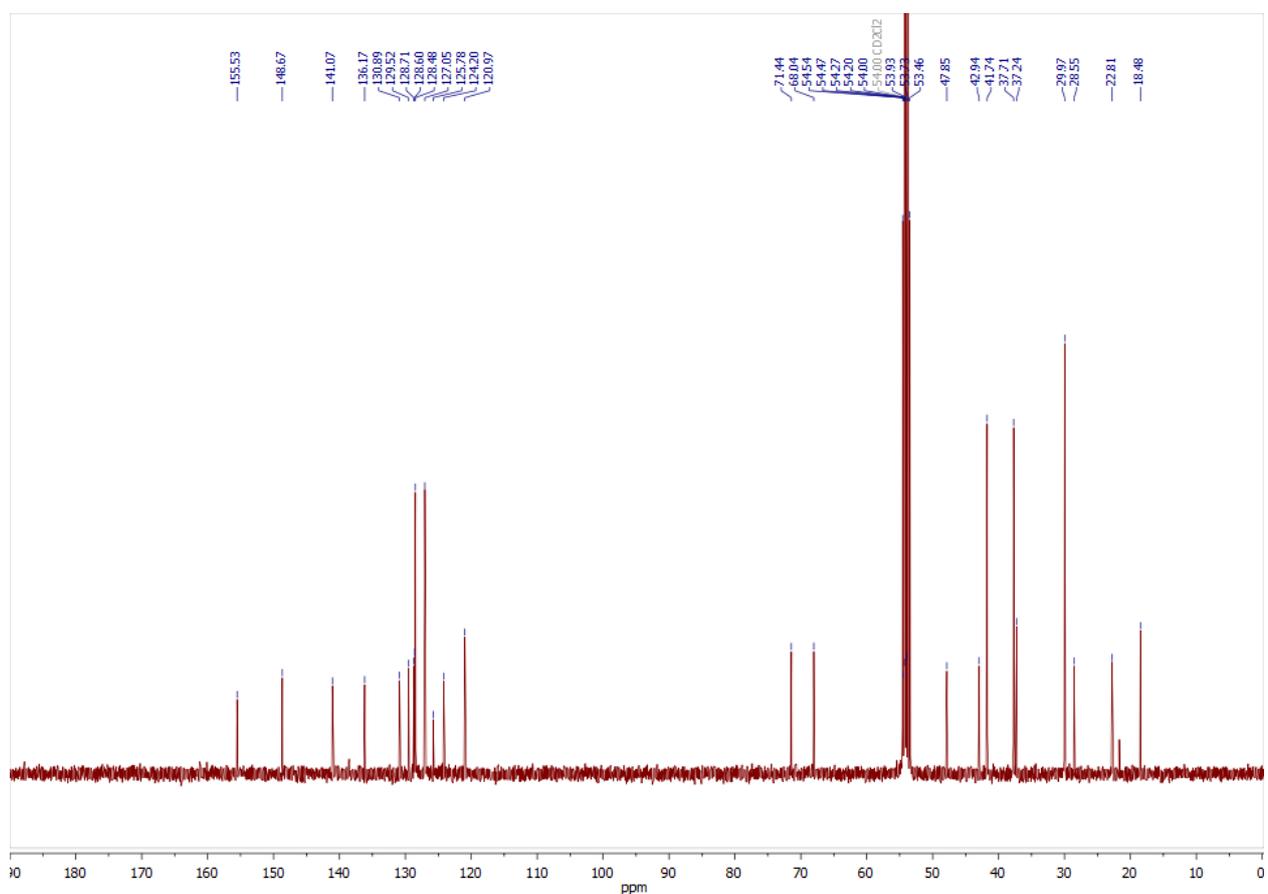


Figure S13.  $^{13}\text{C}\{^1\text{H}\}$  NMR-spectrum (101 MHz,  $\text{CD}_2\text{Cl}_2$ ) of *rac*-**3FF** (toluene solvate).

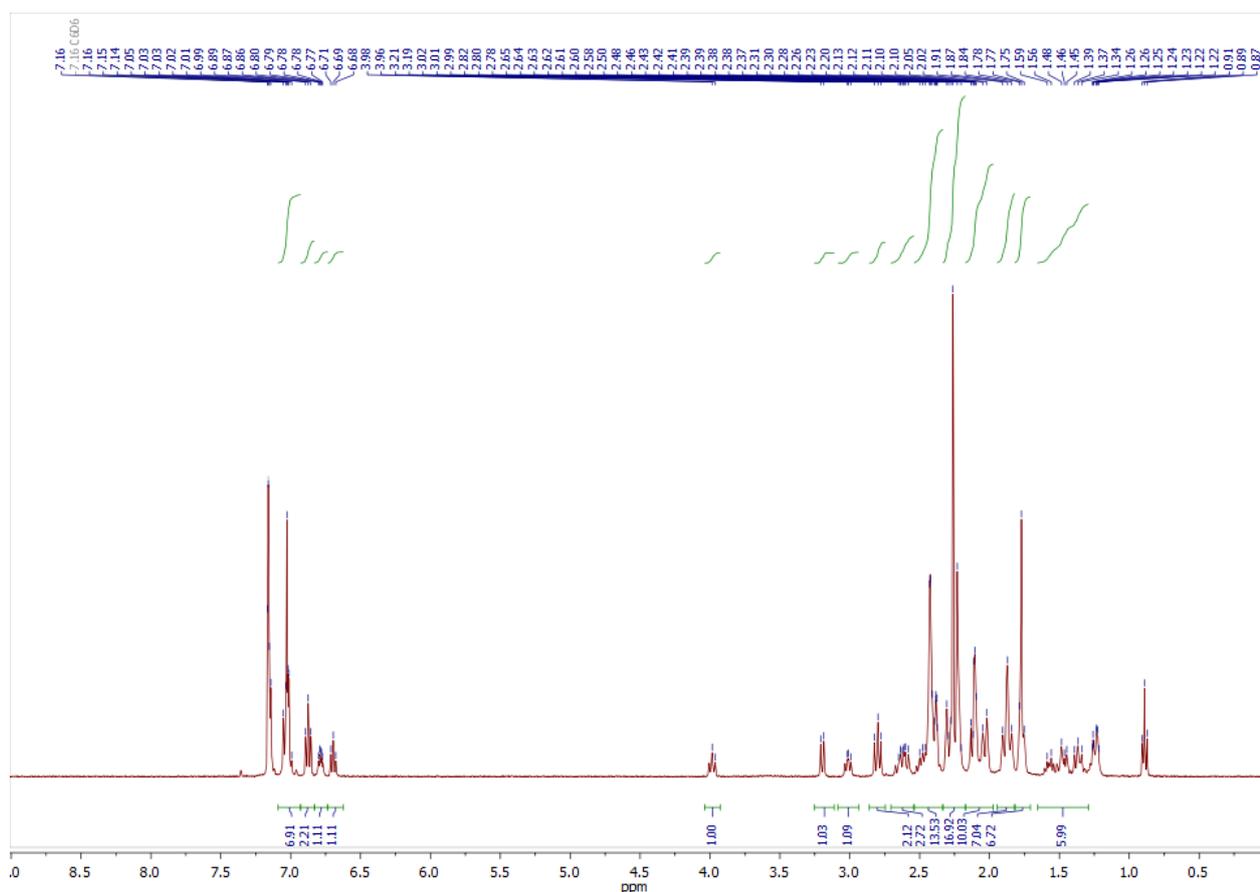


Figure S14.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{C}_6\text{D}_6$ ) of *meso*-3.

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