Selective Hydrogenation of Fluorinated Arenes using Rhodium Nanoparticles on Molecularly Modified Silica

Souha Kacem,[a,b] Meike Emondts,[b,c] Alexis Bordet,[a] and Walter Leitner*[a,b]*

Supporting information

Safety Warning

High-pressure experiments with compressed H_2 must be carried out only with appropriate equipment and under rigorous safety precautions.

General

If not otherwise stated, the synthesis of the molecularly modified silica (Si-R) and the nanoparticles immobilized on Si-R (NPs@Si-R) were carried out under an inert atmosphere (Ar) using standard Schlenk techniques or inside a glovebox. All the synthesized materials were stored under inert atmosphere except from the Rh@Si-R that was stored under air. [Rh(allyl)$_3$] was synthesized according to a modified literature procedure.[1] Reaction mixtures were prepared under air, but were flushed with H_2 prior to catalysis. TMS-protected alcohol (**10a**) was prepared according to the literature.[2] All other chemicals and solvents were commercially available and used without further purification. High-pressure experiments were performed using in-house engineered 10 mL stainless steel finger autoclaves. Catalytic reactions were performed in glass inlets using a magnetic stirrer and an aluminium-heating block.

Analytics

Gas chromatography (GC) was performed on a Shimadzu GC2030 equipped with a FID-detector and a CP-WAX-52CB column from Agilent. Gas chromatography coupled with a mass spectrometer (GC-MS) were performed on a Shimadzu QP2020. The composition of the reaction mixture was identified either by injecting the pure products in the GC or through NMR of the isolated products. All TEM images were recorded on a Hitachi HF2000 operating at 200 kV. Grids were prepared by drop casting a colloidal solution containing as prepared Rh@Supports in toluene on a copper grid covered with amorphous carbon. NPs size distributions were determined by measuring at least 200 NPs. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were collected using a Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) operating at 200 kV. Elemental Analysis was measured externally in "Mikroanalytisches Laboratorium Kolbe, Oberhausen Germany". BET measurements were performed on a Quadrasorb SI from Quantachrom Instruments. The X-ray powder patterns for qualitative phase analysis were collected on a Stoe STADI P transmission diffractometer using Mo radiation (0.7093 Å). The instrument is equipped with a primary Ge (111) monochromator (MoKα_1) and a position sensitive Mythen1K detector.

Data were collected in the range between 3 and 70° 2θ with a step width of 0.015° 2θ. Measuring time per step was 40s. For each sample 8 scans were collected and summed after data collection. For the measurements, the samples were filled into glass capillaries (∅ 0.5 mm). The measured patterns were evaluated qualitatively by comparison with simulated data (crystal structure data were taken from the ICSD database). ^{29}Si solid-state NMR spectra were obtained using a Bruker AVIII-500 spectrometer.

Synthesis of Rh NPs on silica based supports

General procedure for the synthesis of molecularly modified silica supports (Si-R)

Under Ar, the alkyltriethoxysilane (4 mmol) was added to a suspension of dehydroxylated (500 °C overnight under high vacuum) SiO_2 (5 g in 30 mL toluene). The resulting mixture was refluxed under Ar for 18 h at 130 °C. After 18 h, the organic phase was removed and the resulting functionalized silica was washed with DCM (3 x 15 mL, dry and degassed) and dried *in vacuo* at 60°C overnight. The organic phases were combined and the solvent evaporated to determine the residual quantity of the alkyl-silane not grafted on the dehydroxylated SiO_2 (total alkyl-silane loading = theoretical loading - recovered residual alkyl-silane).

Synthesis of Rh NPs immobilized on silica based supports

A solution of [Rh(allyl)$_3$] (11.3 mg, 0.05 mmol) in 2 mL dry and degassed DCM was added to a suspension of 500 mg support (SiO_2 or Si-R) in 3 mL dry and degassed DCM. The reaction mixture was stirred for 1 h under Ar at room temperature and the support turned bright yellow. The solvent was carefully removed under reduced pressure and the impregnated support material was transferred to an autoclave. The metal precursor was reduced under the following conditions: 100 °C, 50 bar H_2, 16 h. A dark black powder was obtained and stored under air.

Catalytic study

The catalytic reactions were carried out in 10 mL stainless steel finger autoclaves. In a typical experiment, 5 mg of catalyst (1 wt% Rh), 750 mg of solvent and the chosen mass of the substrate were added to the glass inlet of the autoclave. When applicable, an amount of CaO proportional to the expected released amount of HF was added to the reaction mixture (typically 4.5 mol% as compared to substrate). After pressurizing with H_2, the reaction mixture was stirred at 500 rpm at the adequate temperature for 1 h. After the reaction, the autoclave was cooled to room temperature and depressurized carefully. The resulting mixture was filtered using a syringe filter and the solution was analyzed by GC-FID and GC-MS using tetradecane as an internal standard. See section “product isolation” p. 11 for a detailed example.

Recyclability study

For the recycling experiments, the first cycle was performed as described in section "catalytic study" starting from a fresh catalyst (Rh@Si-Dec 20 mg, 0.002 mmol Rh) with fluorobenzene (2 mmol, 192 mg, 1000 eq.), CaO (36 mg, 0.64 mmol), and n-heptane (1300 mg, ≈ 2 mL) under 10 bar H_2, 80 °C, 500 rpm for 1 h. At the end of this first reaction, the reaction mixture was centrifuged (4 min at 2000 rpm) and the supernatant removed with a syringe. The remaining powder (catalyst + CaO) was washed with n-heptane (1 mL) and dried under argon flow for 1 h. Then, a fresh substrate solution was introduced, and the reaction restarted under the same conditions.

Preparation of TMS-protected alcohol

The TMS-protection of 4-fluorophenol was carried out according to the literature.[2]
4-Fluorophenol (4.5 g, 0.04 mol) was weighed inside of a reaction flask. Tetramethyldisilazane (4 g, 0.025 mol) was added gradually at ambient temperature. After complete addition, the reaction mixture was stirred at 160°C for 2 hours under reflux. The obtained mixture was distilled under *vacuo* after cooling.

Catalysts characterization

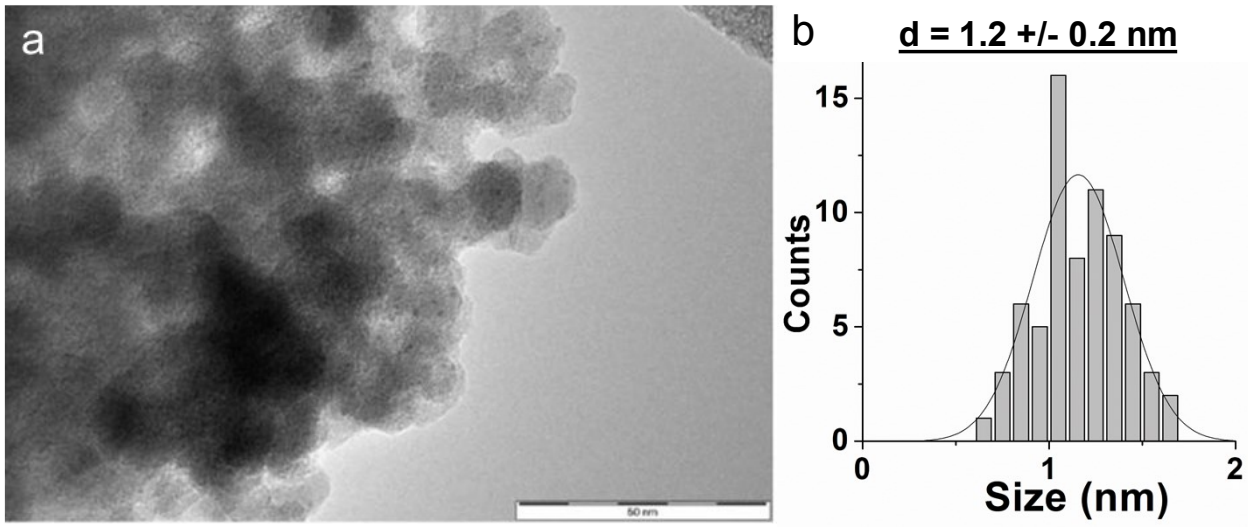


Figure S1: (a) Transmission electron microscopy (TEM) image of Rh@SiO_2 and (b) the corresponding particle size distribution histogram.

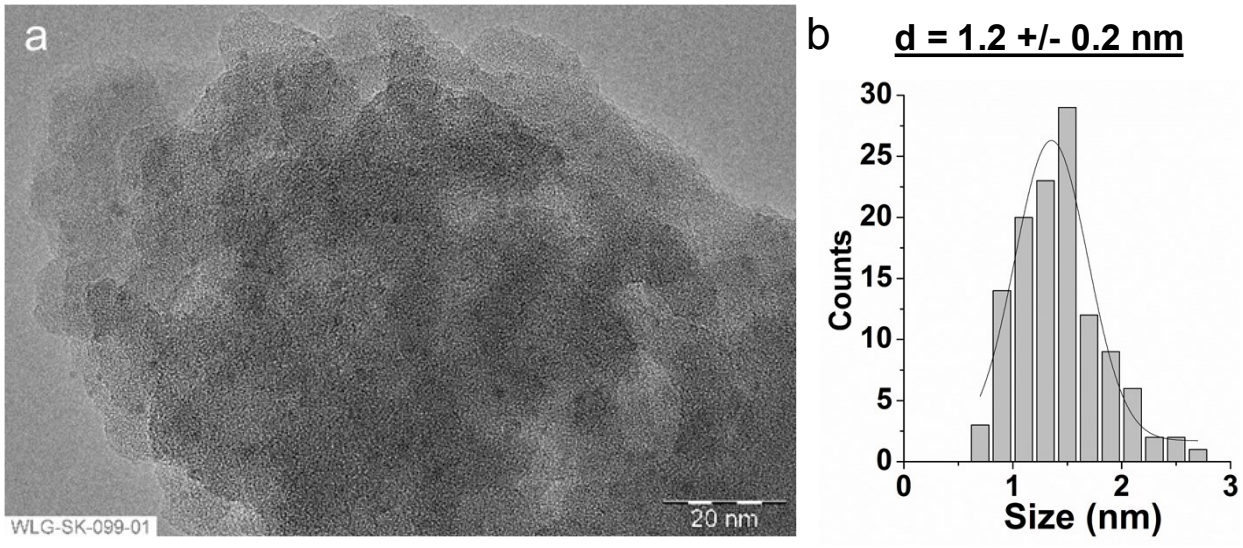


Figure S2: (a) Transmission electron microscopy (TEM) image of Rh@Si-Prop and (b) the corresponding particle size distribution histogram.

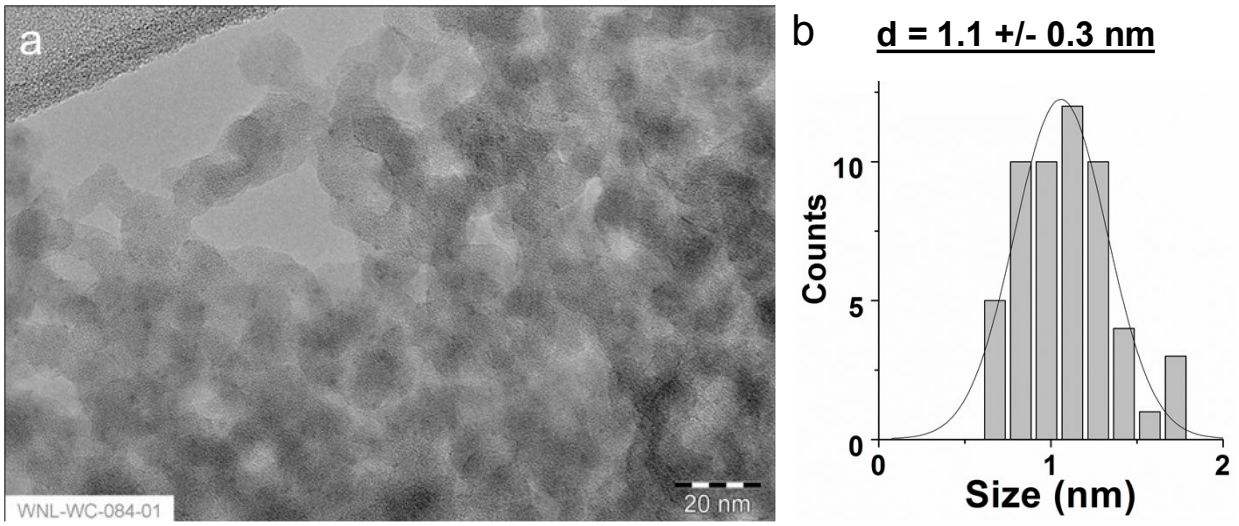


Figure S3: (a) Transmission electron microscopy (TEM) image of Rh@Si-Oct and (b) the corresponding particle size distribution histogram.

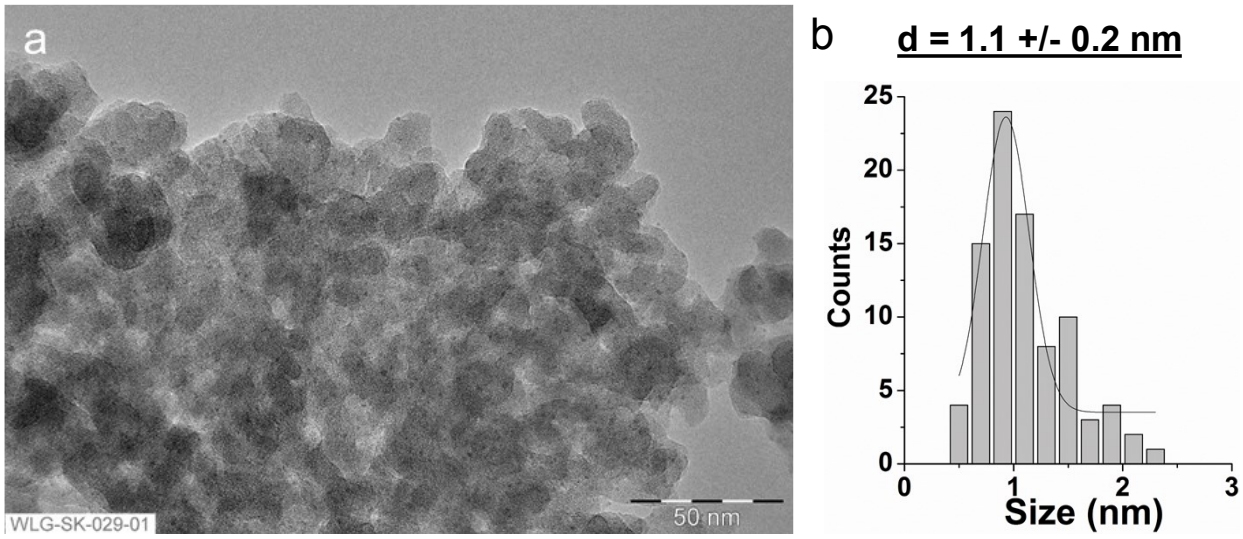


Figure S4: (a) Transmission electron microscopy (TEM) image of Rh@Si-FDec and (b) the corresponding particle size distribution histogram.

Table S1: BET and ICP-AAS data for the different catalysts synthesized.

Entry	Catalyst	BET Surface area (m^2/g)	Pore diameter [nm]	NPs size [nm]	Rh loading by ICP [wt. %]
1	$Rh@SiO_2$	342.3	8.8	1.2 +/- 0.2	0.98
2	Rh@Si-Prop	243.6	-	1.4 +/- 0.2	0.82
3	Rh@Si-Oct	290.4	-	1.1 +/- 0.3	0.62
4	Rh@Si-Fdec	295.3	7.5	1.1 +/- 0.2	0.81
5	Rh@Si-Dec	311.9	7.8	0.9 +/- 0.1	0.92
6	Rh@Si-Dec (after catalysis, 5 cycles)	-	-	1.8 +/- 0.6	0.92[a]

[a]Calculated by subtracting the amount of Rh leaching in solution after catalysis (very low, 1-4 ppm).

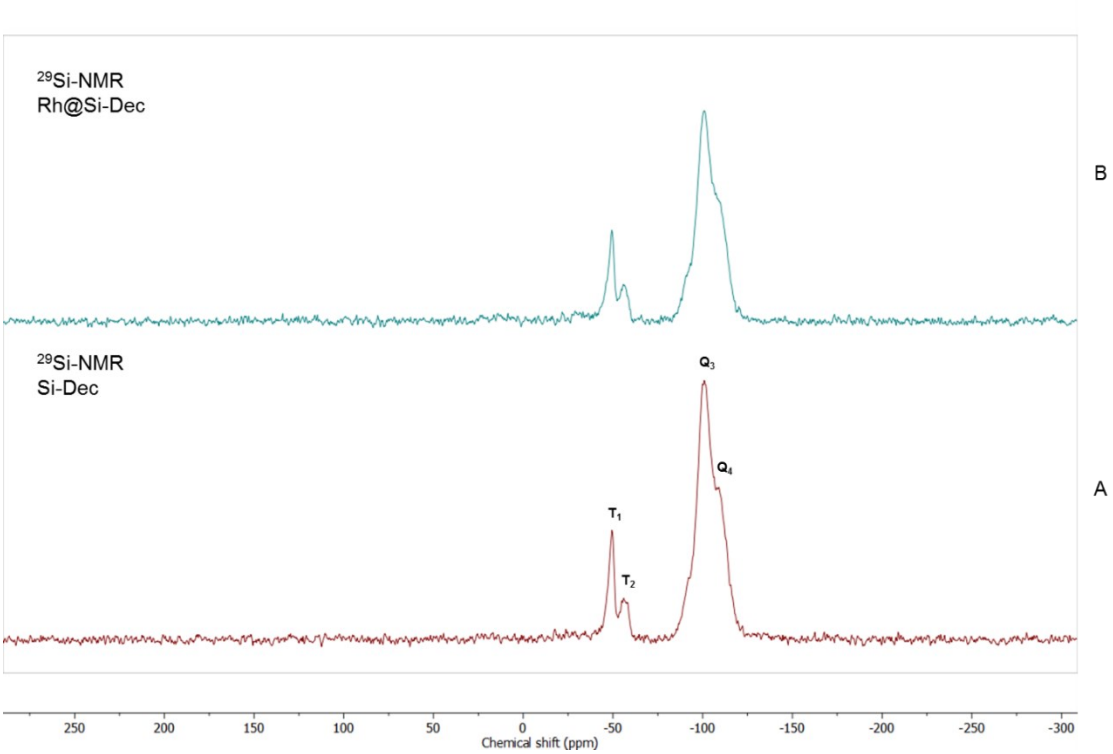


Figure S5: CP-MAS Solid state NMR (^{29}Si) of Si-Dec (A, red) and Rh@Si-Dec (B, green).

Determination of TOFs

Turn over frequencies were determined using the following equation:

$$TOF = \frac{n(product_{/h})}{n(Rh) * \%(surface\ Rh)}$$

The %(surface Rh) were estimated for each catalyst by calculating the volume of the Rh NPs as well as the volume of the shell containing the first layer of Rh atoms (approximation: spherical NPs):

$$V_{NPs} = \frac{4}{3}\pi * r^3{}_{NPs}$$

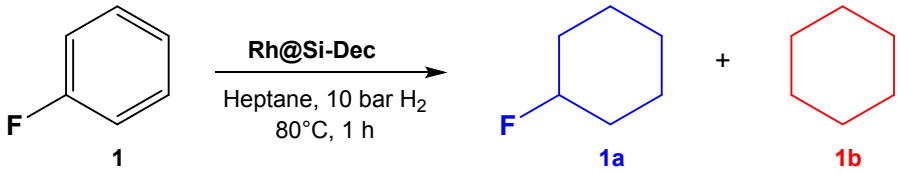
$$V_{shell} = \frac{4}{3}\pi * (r^3{}_{NPs} - (r_{NPs} - r_{at\ Rh})^3)$$

$$\%_{surface\ Rh} = \frac{V_{shell}}{V_{NPs}}$$

Screening of reaction parameters

Stirring speed

Table S2: Influence of the stirring speed on the hydrogenation of fluorobenzene.

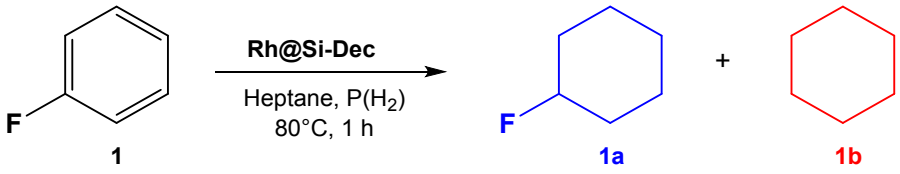


Stirring speed (rpm)	X (%)	S_{1a} (%)
250	>99	87
500	>99	92
750	>99	83
1000	>99	85

Reaction conditions: Rh@Si-Dec (5 mg, 0.0005 mmol Rh), fluorobenzene (1000 eq.), n-heptane (750 mg, ≈ 1 mL), 80 °C, 1 h. Conversion and selectivity determined by GC-FID using tetradecane as an internal standard. (X: Conversion / S: Selectivity).

H_2 Pressure

Table S3: Influence of the H_2 pressure on the hydrogenation of fluorobenzene.

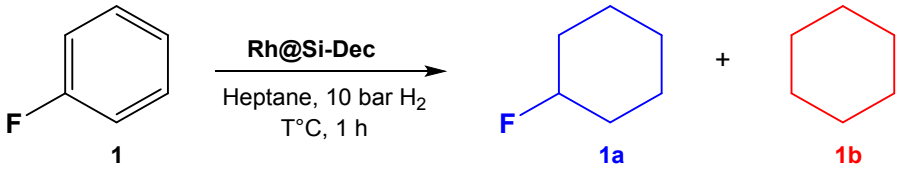


$P(H_2)$ (bar)	X (%)	S_{1a} (%)
10	>99	88
30	>99	84
55	>99	83
80	>99	86

Reaction conditions: Rh@Si-Dec (5 mg, 0.0005 mmol Rh), fluorobenzene (1100 eq.), n-heptane (750 mg, ≈ 1 mL), 80 °C, 1 h, 500 rpm. Conversion and selectivity determined by GC-FID using tetradecane as an internal standard. (X: Conversion / S: Selectivity).

Temperature

Table S4: Influence of the temperature on the hydrogenation of fluorobenzene.

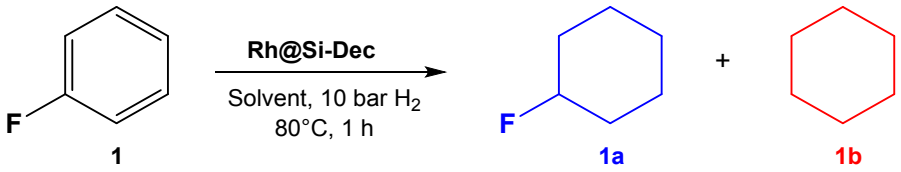


T°C	X (%)	S_{1a} (%)
25	62	77
50	>99	77
80	>99	86
100	>99	83
120	>99	52

Reaction conditions: Rh@Si-Dec (5 mg, 0.0005 mmol Rh), fluorobenzene (400 eq.), n-heptane (750 mg, ≈ 1 mL), 10 bar H_2, 1 h, 500 rpm. Conversion and selectivity determined by GC-FID using tetradecane as an internal standard. (X: Conversion / S: Selectivity).

Solvent

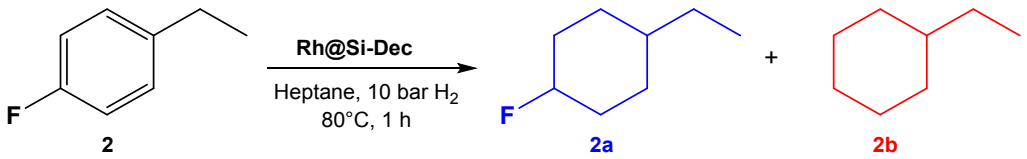
Table S5: Influence of the solvent on the hydrogenation of fluorobenzene.



Solvent	X (%)	S_{1a} (%)	Y_{1a} (%)
Methanol	81	37	30
DCM	79	63	50
HMDSO (Hexamethyldisiloxane)	34	87	30
Heptane	>99	92	92

Reaction conditions: Rh@Si-Dec (5 mg, 0.0005 mmol Rh), fluorobenzene (1000 eq.), solvent (750 mg, ≈ 1 mL), 10 bar H_2, 1 h, 80 °C, 500 rpm. Conversion and selectivity determined by GC-FID using tetradecane as an internal standard. (X: Conversion / S: Selectivity / Y: Yield).

Table S6: Comparison of the catalytic activity of different Rh@Si-R catalysts for the selective hydrogenation of ethylfluorobenzene (**2**).



Entry	Catalyst	X (%)	S_{2a} (%)	Y_{2a} (%)
1	$Rh@SiO_2$	94	65	61
2	Rh@Si-Oct	>99	75	75
3	Rh@Si-Dec	>99	85	85
4	Rh@Si-Fdec	>99	85	85
5	Ru@Si-Dec	80	83	66

Reaction conditions: Catalyst (5 mg, 0.0005 mmol Rh), 4-ethylfluorobenzene (400 eq.), n-heptane (750 mg, ≈ 1 mL), 10 bar H_2 , 500 rpm, 1 h. Conversion and selectivity determined by GC-FID using tetradecane as an internal standard. (X: Conversion / S: Selectivity / Y: Yield).

Table S7: Comparison between the catalytic results obtained for the hydrogenation of fluorobenzene with and without the addition of CaO.

Entry	CaO (mg)	X (%)	S_{1b} (%)
1	0	>99	93
2	10	>99	94

Reaction conditions: Rh@Si-Dec (10 mg, 0.001 mmol Rh), fluorobenzene (400 eq.), n-heptane (750 mg, ≈ 1 mL), 10 bar H_2, 80 °C, 500 rpm, 1 h. Conversion and selectivity determined by GC-FID using tetradecane as an internal standard. (X: Conversion / S: Selectivity).

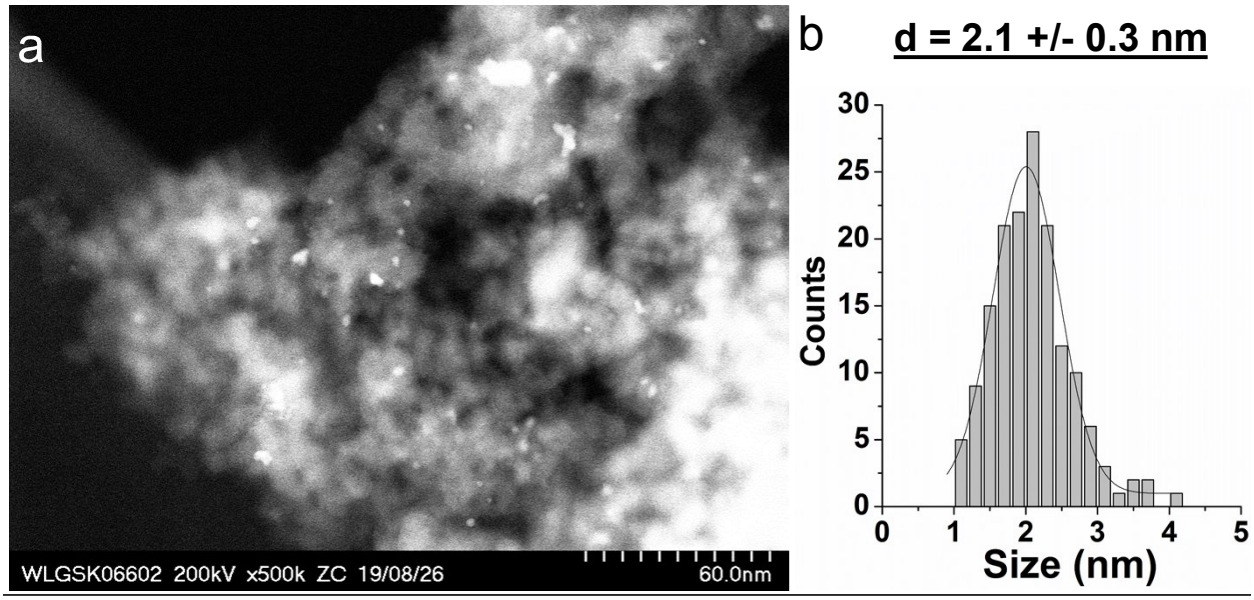


Figure S6: (a) STEM-HAADF of Rh@Si-Dec after 2 cycles with (b) the corresponding particle size distribution histogram.

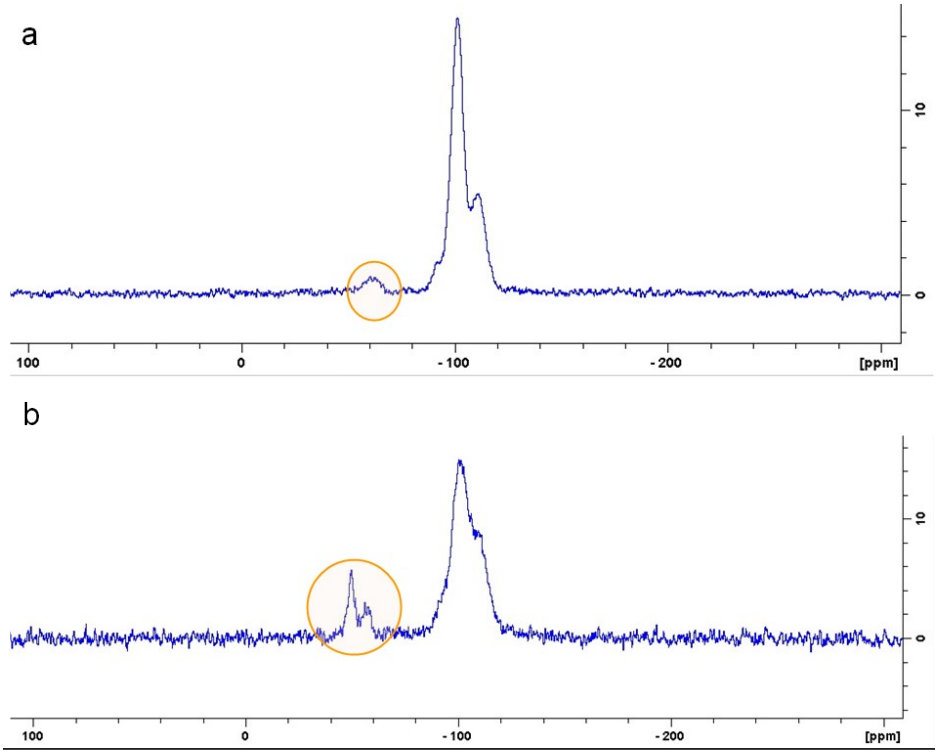


Figure S7: CP-MAS Solid state NMR (^{29}Si) of Rh@Si-Dec. a) after catalysis without CaO, b) after catalysis in the presence of CaO.

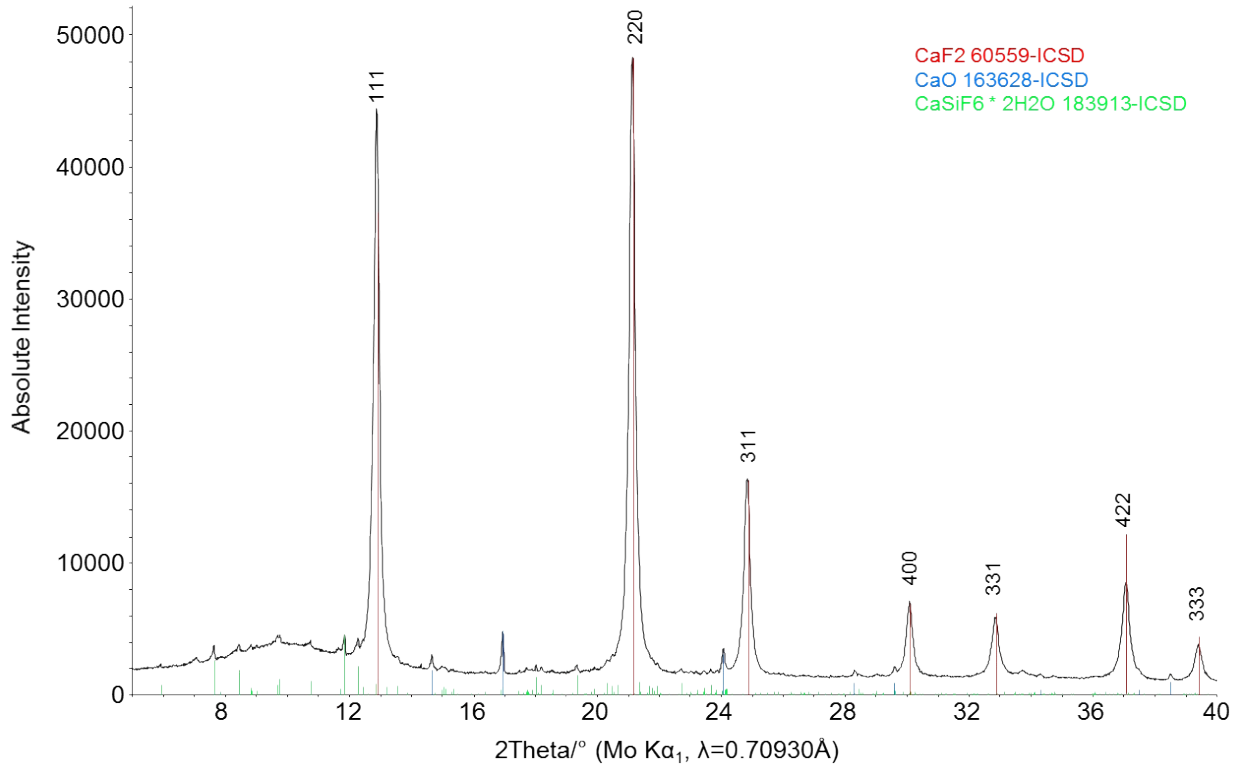


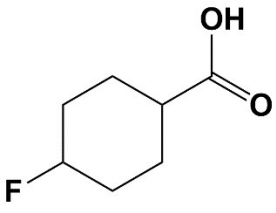
Figure S8: XRD pattern of the Rh/Si-Dec catalyst with CaO after catalysis (recycled for 5 runs) demonstrating the presence of CaF_2 formed by the reaction between CaO and HF released during the reaction.

Product isolation

General procedure

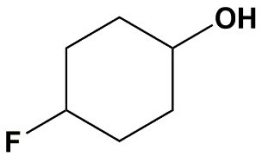
The substrate (1.0 mmol), Rh@Si-Dec (10 mg, 0.001 mmol Rh), CaO (25 mol% relative to substrate, 0.25 mmol) and n-heptane (750 mg) were mixed in a glass inlet and placed in a high pressure autoclave. The reactor was first purged (3 times) with H_2 then pressurized at 55 bar. The autoclave was brought to reaction temperature (80 - 100 °C) using a preheated aluminum cone. The reaction mixture was left under stirring at 500 rpm using a magnetic stirrer bar for 2h. After the reaction was finished, the autoclave was cooled to room temperature and carefully

depressurized. The obtained reaction mixture was purified by column chromatography. The isolated products (**9a**, **10a** and **11a**) were then analyzed by ^{1}H and ^{13}C NMR.



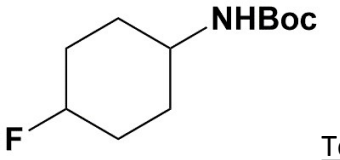
4-fluorocyclohexane-1-carboxylic acid (**9a**): purified by column chromatography on silica gel eluting with hexane then hexane/ethyl acetate (70:30 to 60:40 to 30:70, v/v), 40% isolated yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.84 – 4.78 (m, 1H), 2.34 (m, 1H), 1.95 – 1.39 (m, 8H). **^{13}C** NMR (126 MHz, $CDCl_3$) δ (ppm): 182.2, 90.3, 42.3, 31.8, 28.3. **HRMS/ESI(-)** (MeOH): m/z = 145.067034, calcd for $[C_7H_{10}FO_2]^-$ = 145.067180.



4-fluorocyclohexanol (**10a**): purified by column chromotagraphy on silica gel eluting with pentane/diethyl ether (99.95:0.05 to 99:1, v/v), 43% isolated yield as a colorless oil. A deprotection of the alcohol occurred on the column during the purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 4.82 – 4.53 (m, 1H), 3.86 – 3.57 (m, 1H), 2.10 – 1.35 (m, 8H). **^{13}C** NMR (126 MHz, $CDCl_3$) δ (ppm): 89.3, 68.5, 30.1, 28.7.

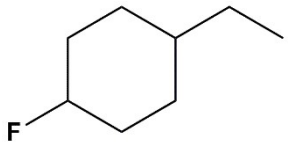


Tert-butyl(4-fluorocyclohexyl)carbamate (**11a**): purified by column chromatography on silica gel eluting with pentane then pentane/diethyl ether (9:1 to 4:1, v/v), 59% isolated yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.69 (ddt, J = 48.4, 4.7, 2.4 Hz, 1H), 4.54 – 4.30 (m, 1H), 3.42 (s, 1H), 1.95 (m, 2H), 1.78 – 1.60 (m, 2H), 1.52 – 1.41 (m, 4H), 1.38 (s, 9H). **^{13}C** NMR (126 MHz, $CDCl_3$) δ (ppm): 155.27, 87.9 (d, J = 134 Hz), 79.24, 48.2, 29.7 (d, J = 16.0 Hz), 28.40, 28.37.

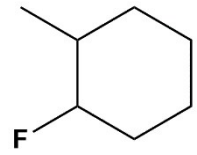
Product characterization:

The experiments were performed in deuterated heptane and the crude mixtures were directly analyzed with NMR after filtration.



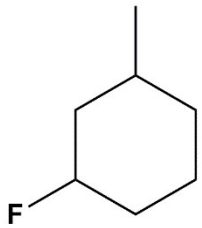
1-ethyl-4-fluorocyclohexane (**2a**): Only the signals of the major diastereomer are listed.

^{1}H NMR (400 MHz, Heptane-d_{16}) δ (ppm): 5.59-5.46 (d, *J* = 48.7 Hz, 1H), 2.86-2.78 (m, 2H), 2.72 – 2.50 (m, 2H), 2.40-2.36 (m, 2H), 2.26-2.21 (m, 2H), 2.17 (m, 1H), 2.05 (m, 2H), 1.78 (s, 3H). **^{13}C** NMR (126 MHz, Heptane-d_{16}) δ (ppm): 86.62 (d, *J* = 172.6 Hz, 39.72, 38.74, 33.14, 30.92, 29.58, 26.81, 10.95 (d, *J* = 2.52 Hz). **^{19}F** NMR (470 MHz, Heptane-d_{16}) δ (ppm): -170.90 (d, *J* = 49.4 Hz) (minor), -185.36 (major).



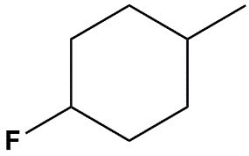
1-fluoro-2-methylcyclohexane (**4a**): Only the signals of the major diastereomer are listed.

^{1}H NMR (500 MHz, Heptane-d_{16}) δ (ppm): 4.64 (d, *J* = 49.3 Hz, 1H), 2.17 (m, 1H), 1.74 (m, 8H), 1.19 (d, *J* = 19.3 Hz, 3H). **^{13}C** NMR (126 MHz, Heptane-d_{16}) δ (ppm): 90.60 (d, *J* = 175.1 Hz), 32.89, 31.08, 28.69, 25.27, 20.07, 17.31. **^{19}F** NMR (470 MHz, Heptane-d_{16}) δ (ppm): -175.05 (d, *J* = 49.2 Hz) (major), -199.88 (minor).



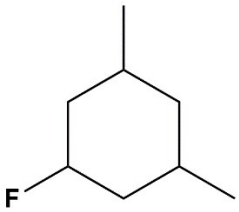
1-fluoro-3-methylcyclohexane (**5a**): Only the signals of the major diastereomer are listed.

^{1}H NMR (500 MHz, Heptane-d_{16}) δ (ppm): 4.66 (d, *J* = 48.5 Hz, 1H), 2.23 – 1.45 (m, 9H), 1.11 (d, *J* = 6.6 Hz, 3H). **^{13}C** NMR (126 MHz, Heptane-d_{16}) δ (ppm): 89.74 (d, *J* = 176.4 Hz), 41.64, 35.50, 34.04, 26.46, 23.28, 20.21. **^{19}F** NMR (470 MHz, Heptane-d_{16}) δ (ppm): -168.44 (d, *J* = 48.6 Hz) (major), -183.27 (d, *J* = 43.8 Hz) (minor).



1-fluoro-4-methylcyclohexane (**6a**): Only the signals of the major diastereomer are listed.

^{1}H NMR (400 MHz, Heptane-d_{16}) δ (ppm): 5.57-5.45 (d, J = 48.2 Hz, 1H), 2.84 (m, 2H), 2.55 (m, 2H), 2.34 (m, 5H), 1.79 (d, J = 4.7 Hz, 3H). **^{13}C** NMR (126 MHz, Heptane-d_{16}) δ (ppm): 86.22 (d, J = 171.36 Hz), 32.54, 31.89, 28.98, 21.96. **^{19}F** NMR (470 MHz, Heptane-d_{16}) δ (ppm): -171.69 (minor), -185.50 (major).



1-fluoro-3,5-dimethylcyclohexane (**7a**): Only the signals of the major diastereomer are listed.

^{1}H NMR (400 MHz, Heptane-d_{16}) δ (ppm): 5.20 (d, J = 48.9 Hz, 1H), 2.88 (m, 2H), 2.37 (m, 6H), 1.83 (m, 6H), 1.42 (m, 1H). **^{13}C** NMR (126 MHz, Heptane-d_{16}) δ (ppm): 89.49 (d, J = 176.4 Hz), 44.56, 43.16, 26.41, 21.69. **^{19}F** NMR (470 MHz, heptane-d_{16}) δ (ppm): -170.19 (major), -174.71 (minor), -181.57 (minor).

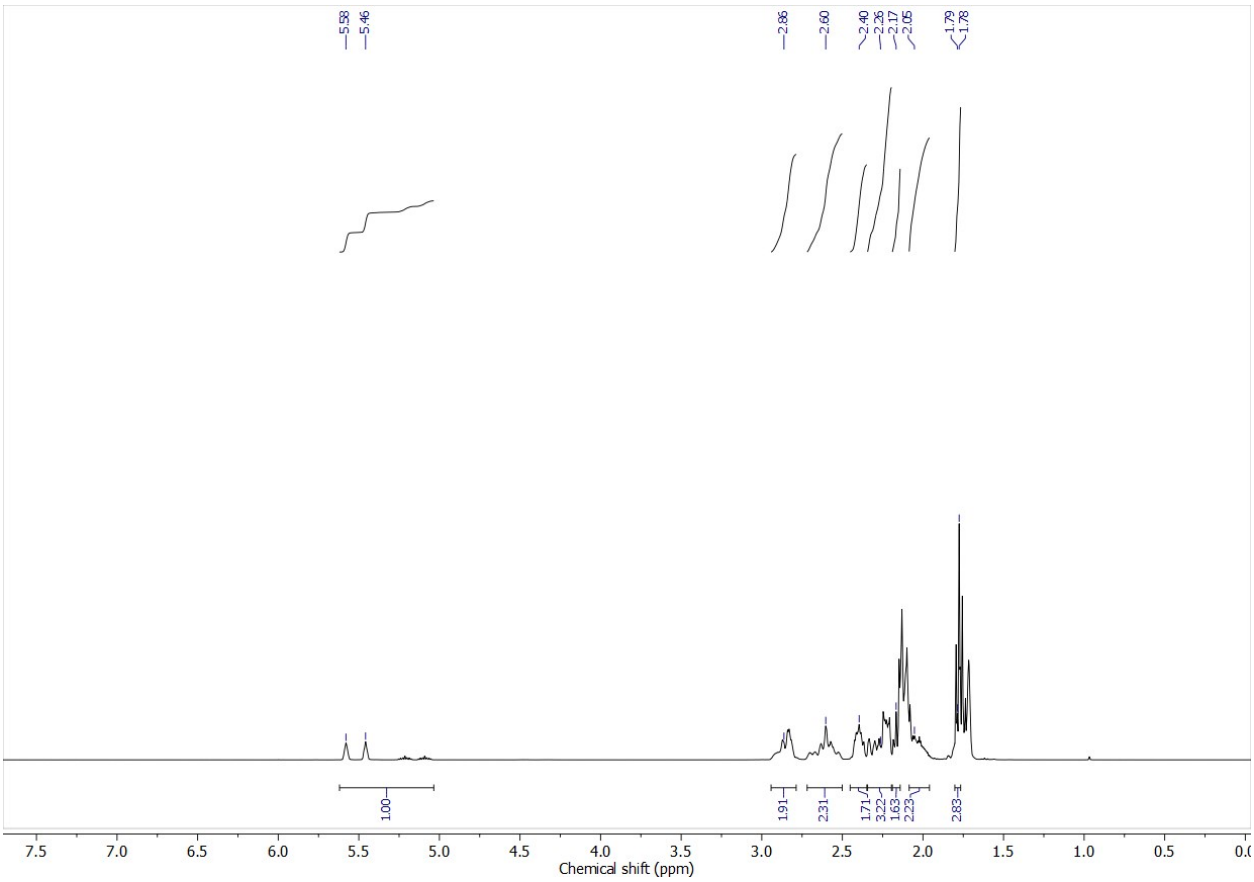


Figure S9: **^{1}H**-NMR of the crude mixture of 1-ethyl-4-fluorocyclohexane (**2a**) and ethylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 2.10-2.13, 1.71)

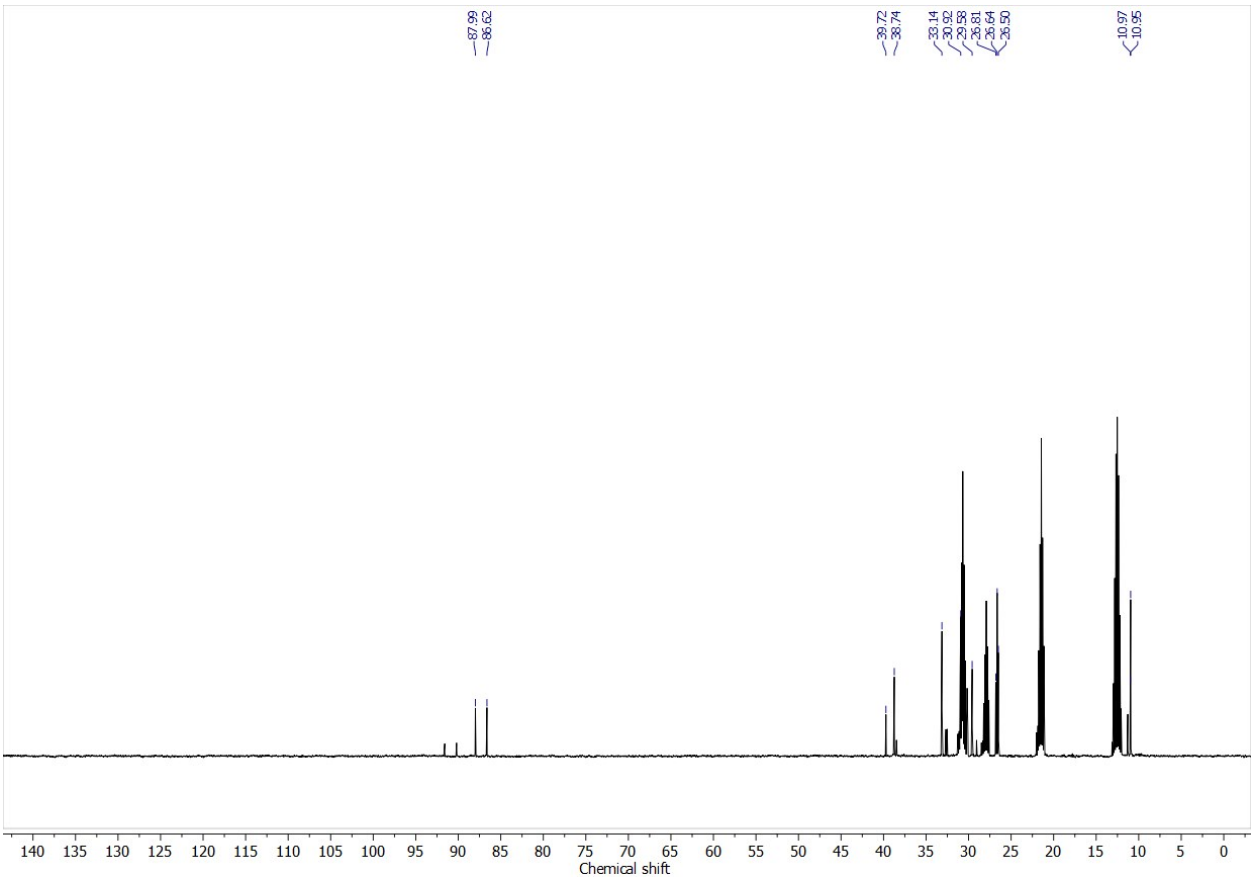


Figure S10: **$^{13}C\{^{1}H\}$**-NMR of the crude mixture of 1-ethyl-4-fluorocyclohexane (**2a**) and ethylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 30.64 (m), 27.85 (m), 21.38 (m), 12.49 (m))

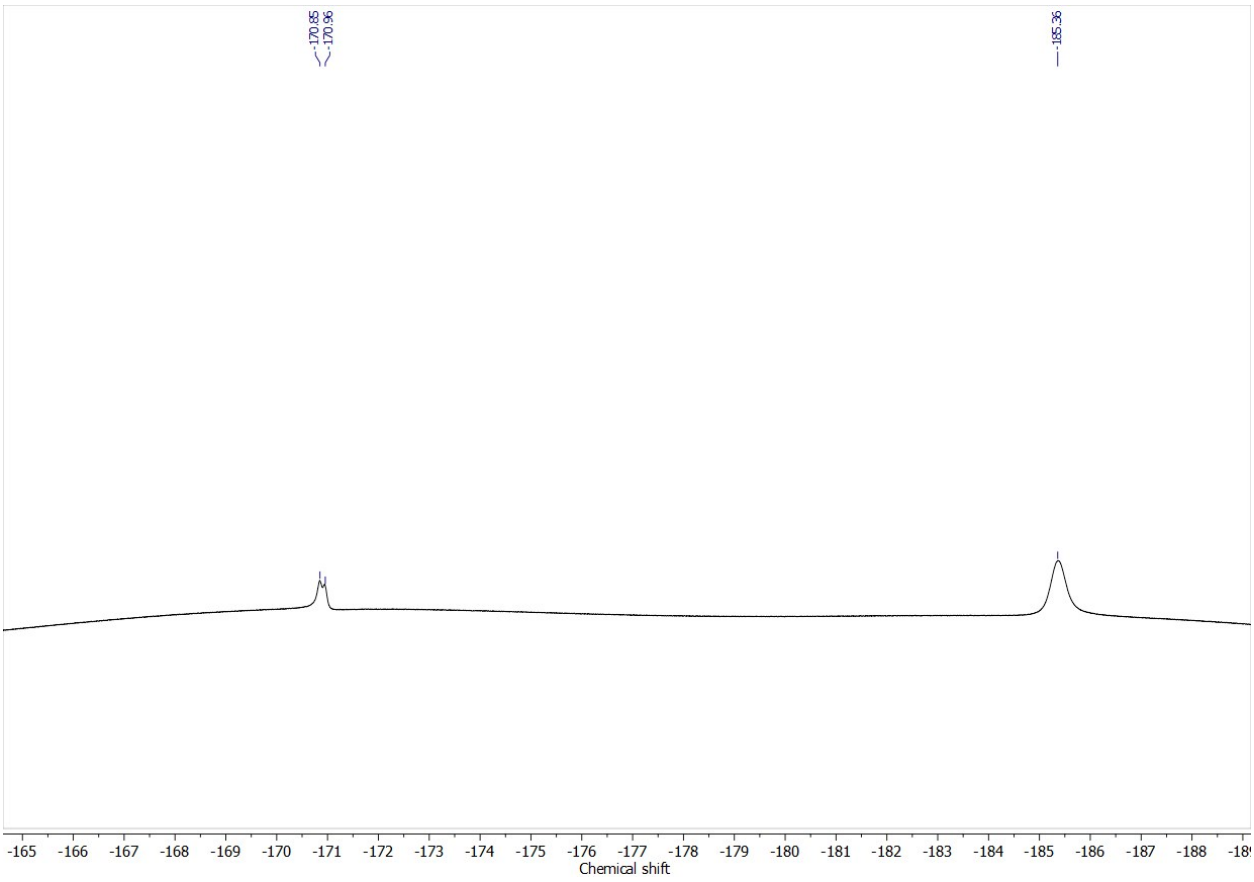


Figure S11: ^{19}**F-**NMR of the crude mixture of 1-ethyl-4-fluorocyclohexane (**2a**) and ethylcyclohexane in heptane-d_{16}.

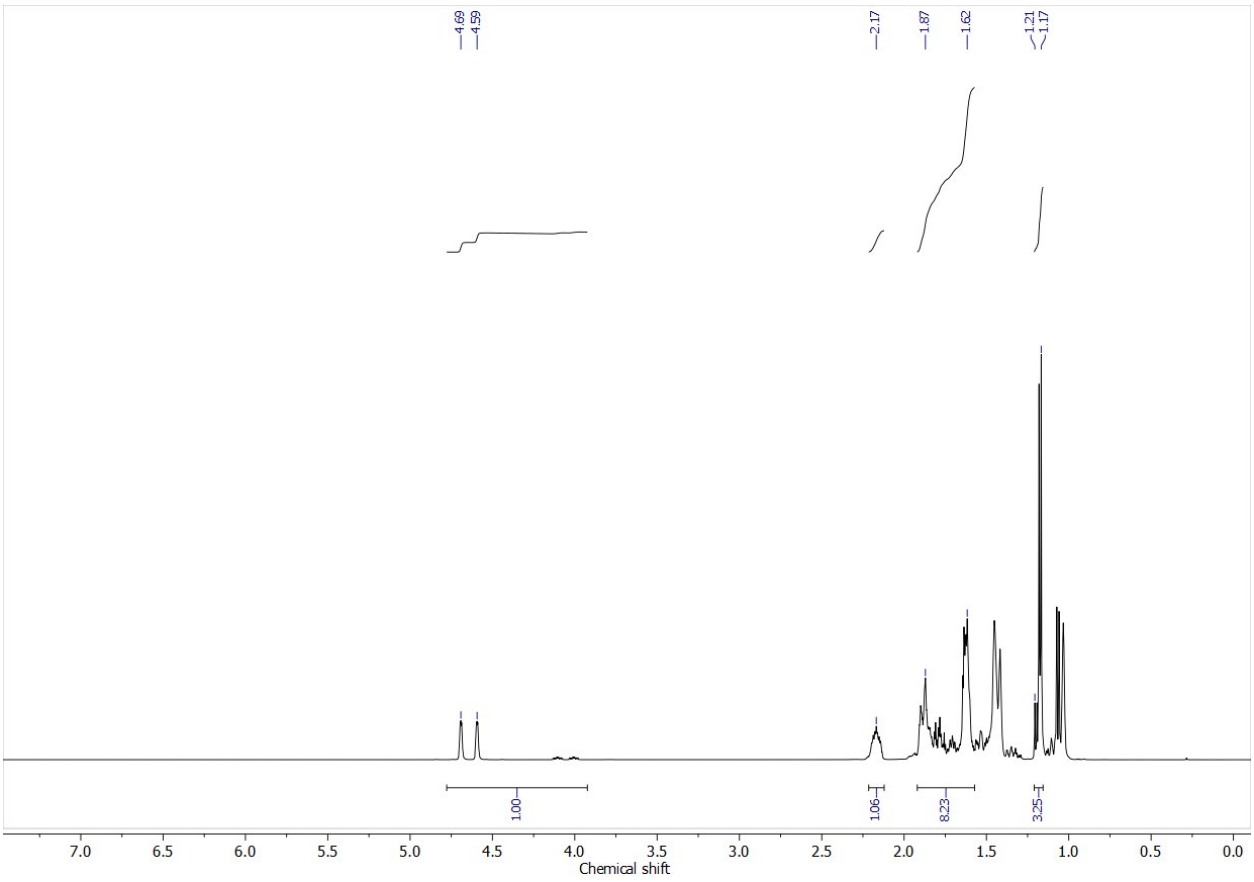


Figure S12: **^{1}H-**NMR of the crude mixture of 1-fluoro-2-methylcyclohexane (**4a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 1.45-1.42, 1.03)

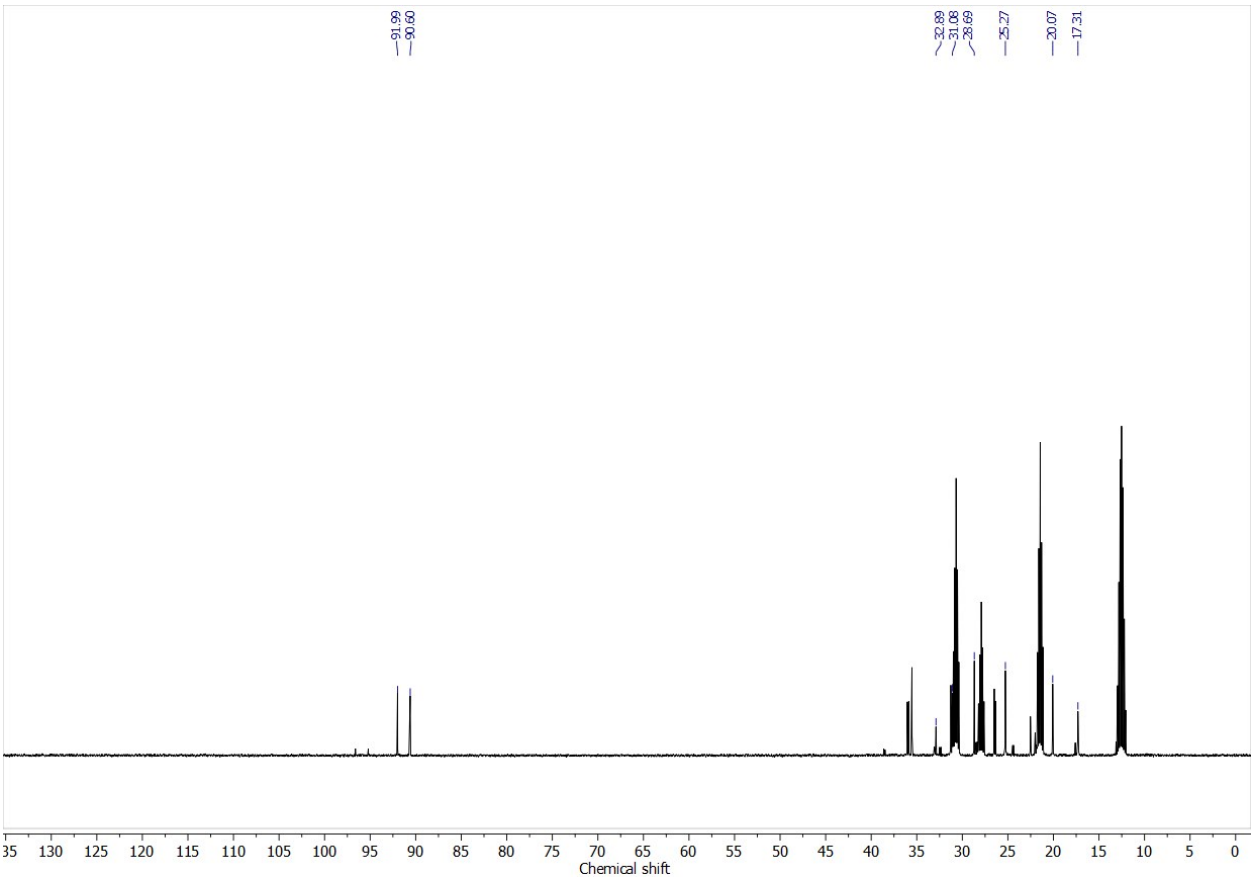


Figure S13: **$^{13}C\{^{1}H\}$-**NMR of the crude mixture of 1-fluoro-2-methylcyclohexane (**4a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 30.64 (m), 27.85 (m), 21.38 (m), 12.49 (m))

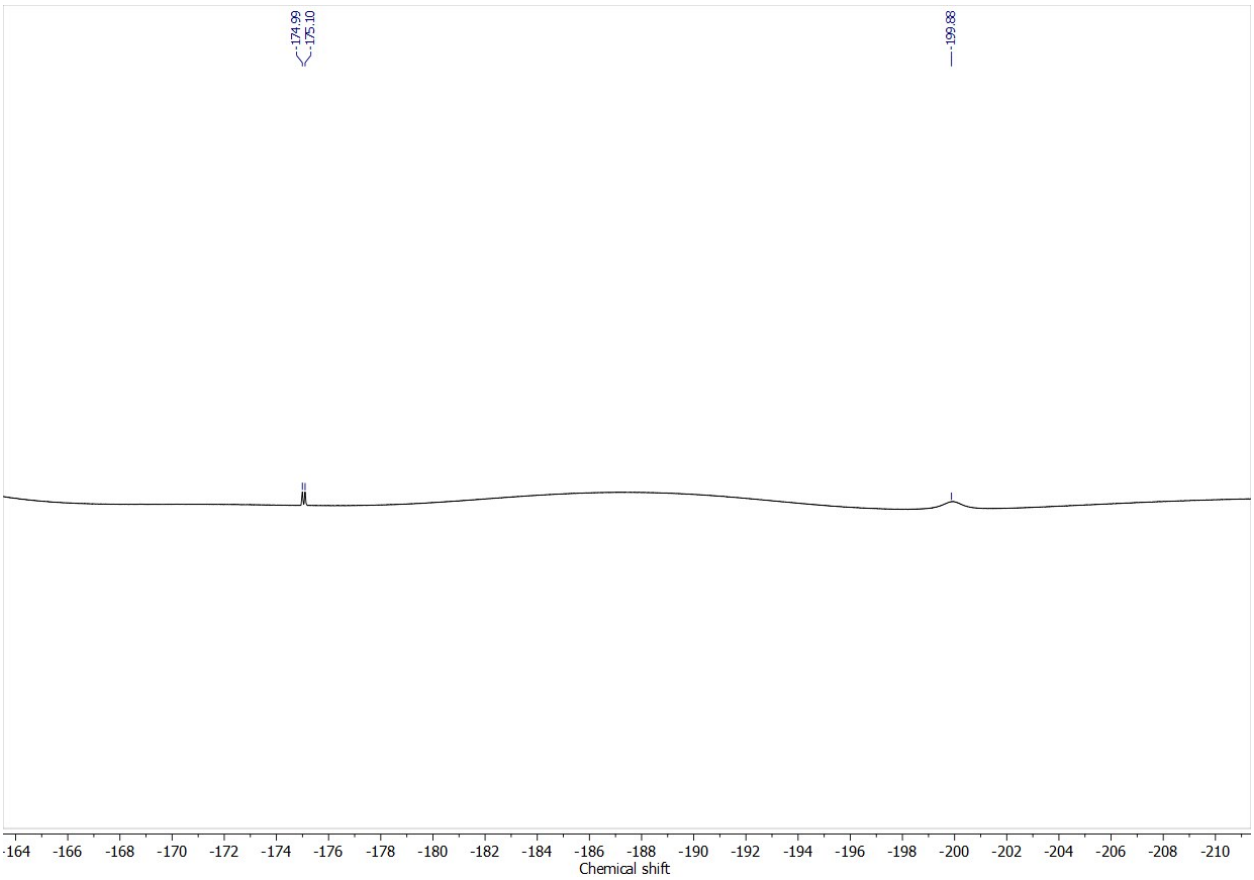


Figure S14: ^{19}**F-**NMR of the crude mixture of 1-fluoro-2-methylcyclohexane (**4a**) and methylcyclohexane in heptane-d_{16}.

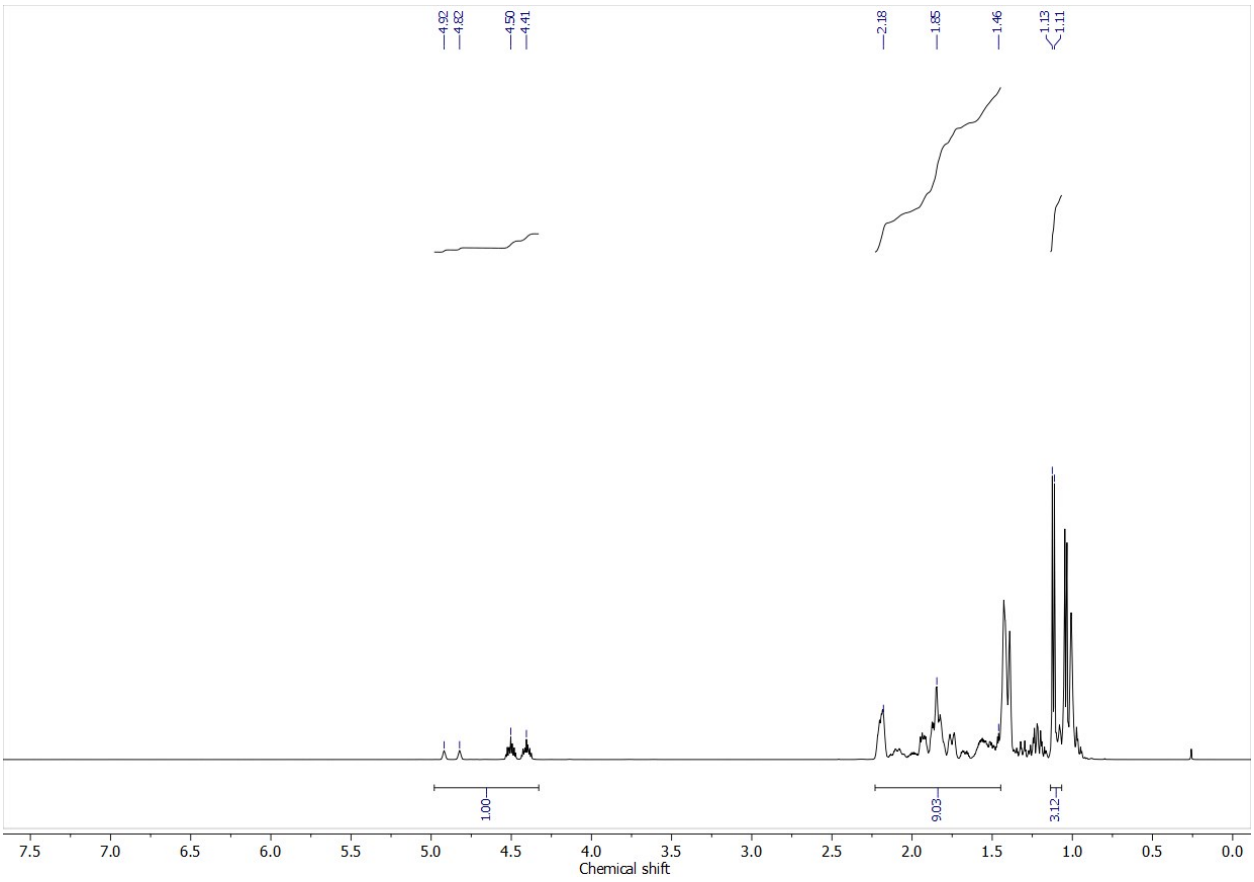


Figure S15: **^{1}H-**NMR of the crude mixture of 1-fluoro-3-methylcyclohexane (**5a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 1.42-1.39, 1.01)

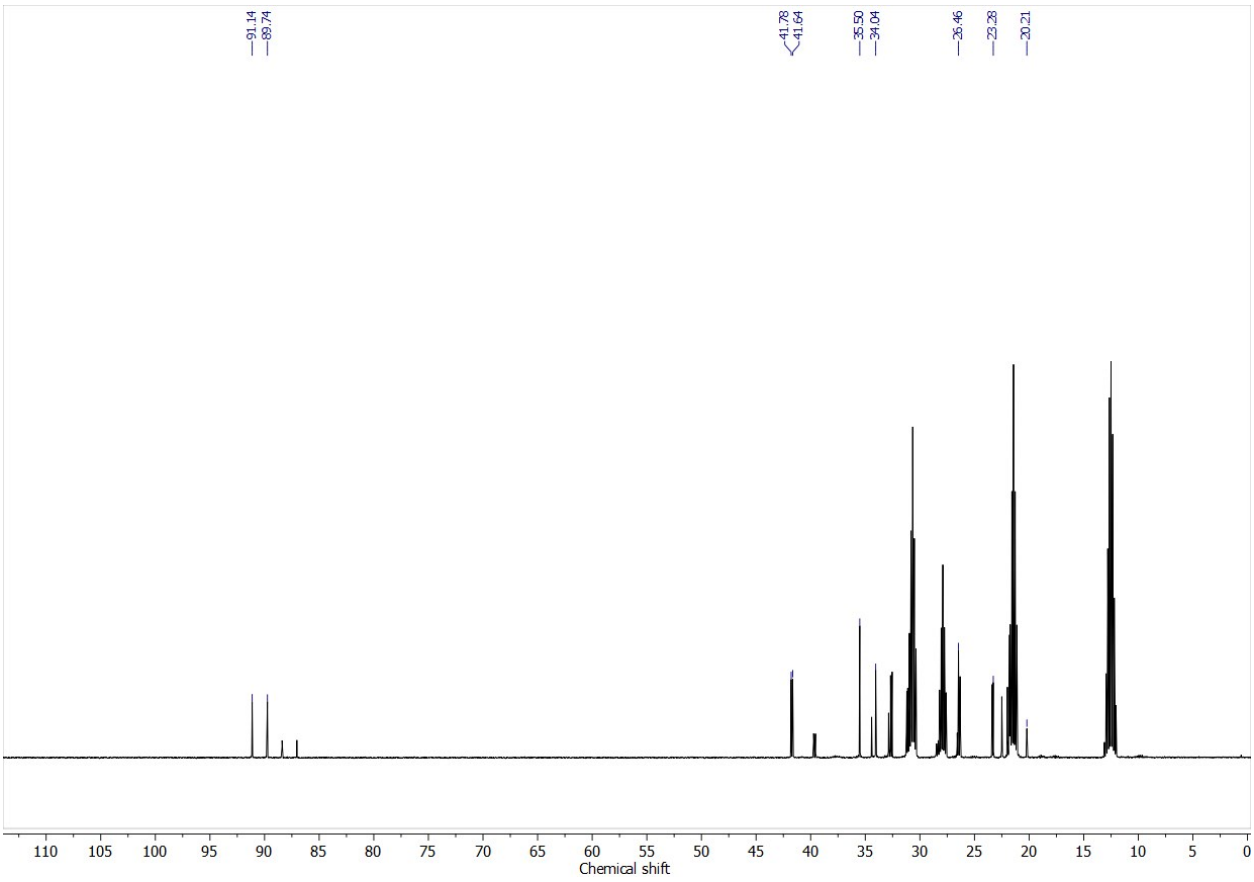


Figure S16: $^{13}C\{^{1}H\}$-NMR of the crude mixture of 1-fluoro-3-methylcyclohexane (**5a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 30.64 (m), 27.85 (m), 21.38 (m), 12.49 (m))

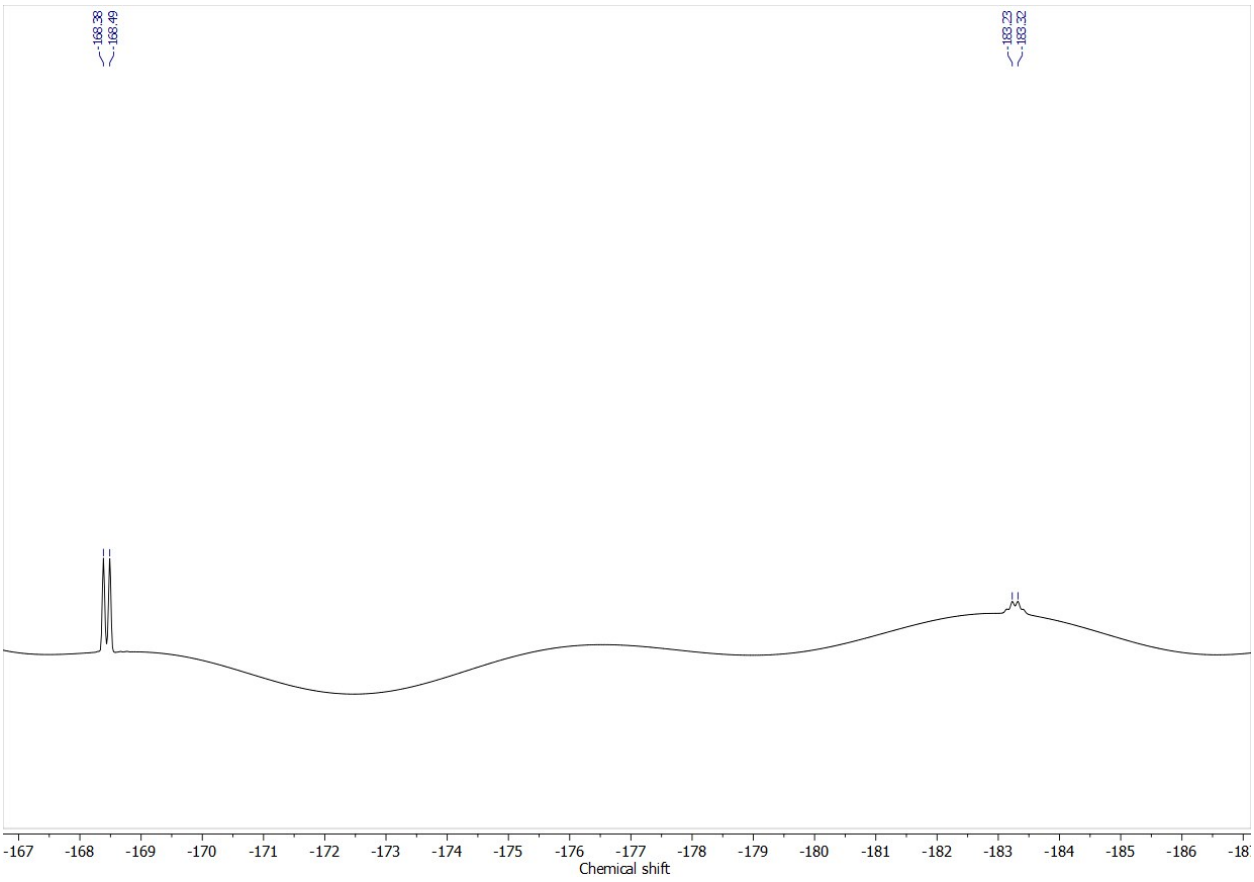


Figure S17: **^{19}F-**NMR of the crude mixture of 1-fluoro-3-methylcyclohexane (**5a**) and methylcyclohexane in heptane-d_{16}.

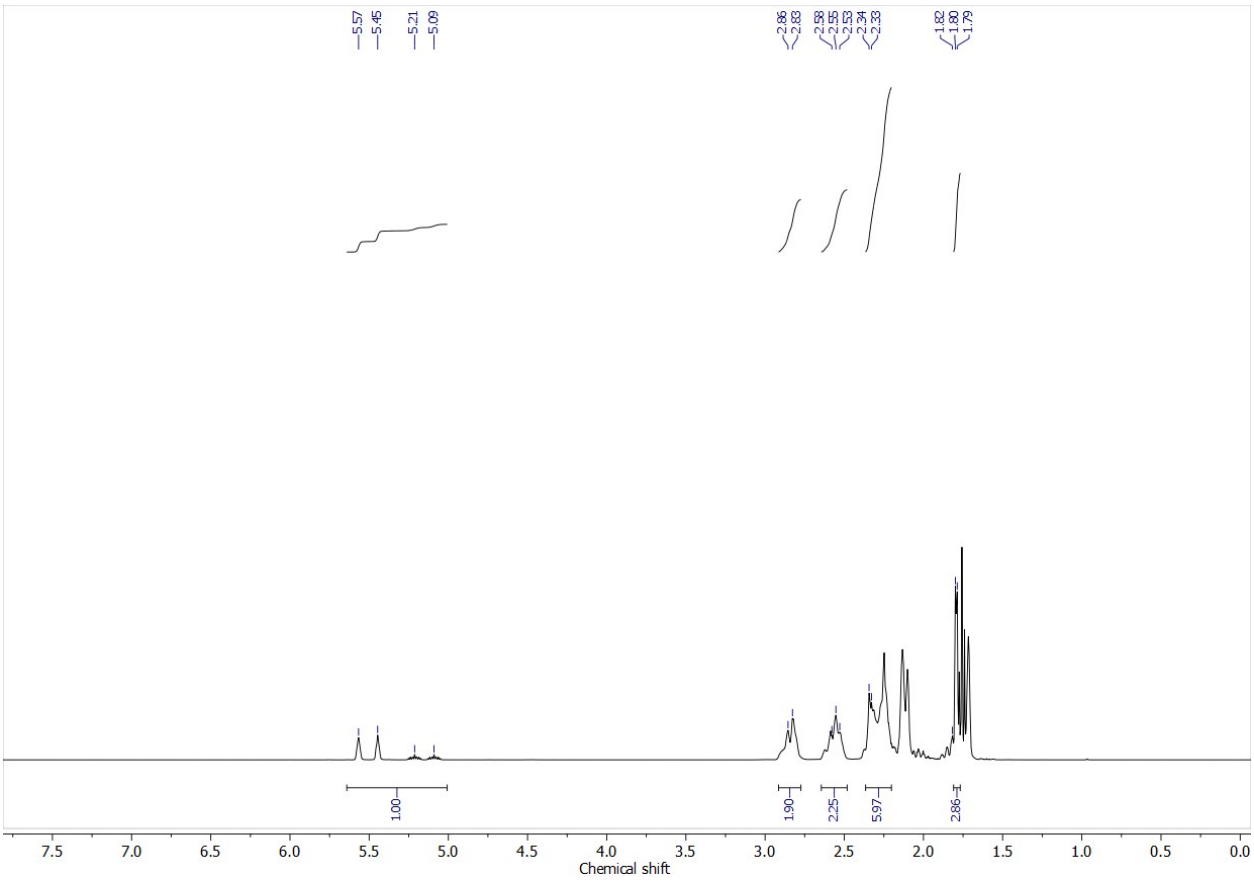


Figure S18: **^{1}H-**NMR of the crude mixture of 1-fluoro-4-methylcyclohexane (**6a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 2.10-2.13, 1.71)

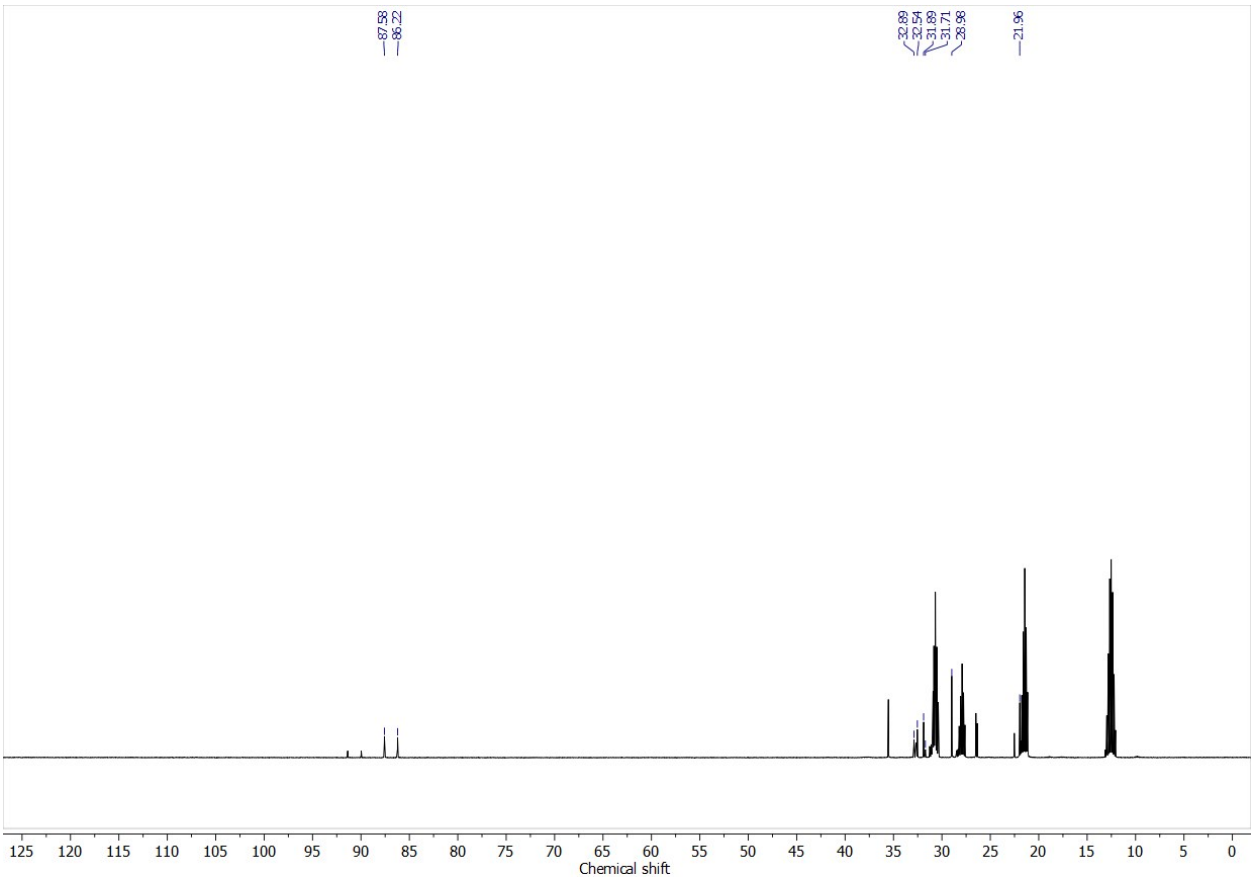


Figure S19: $^{13}C\{^{1}H\}$-NMR of the crude mixture of 1-fluoro-4-methylcyclohexane (**6a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 30.64 (m), 27.85 (m), 21.38 (m), 12.49 (m))

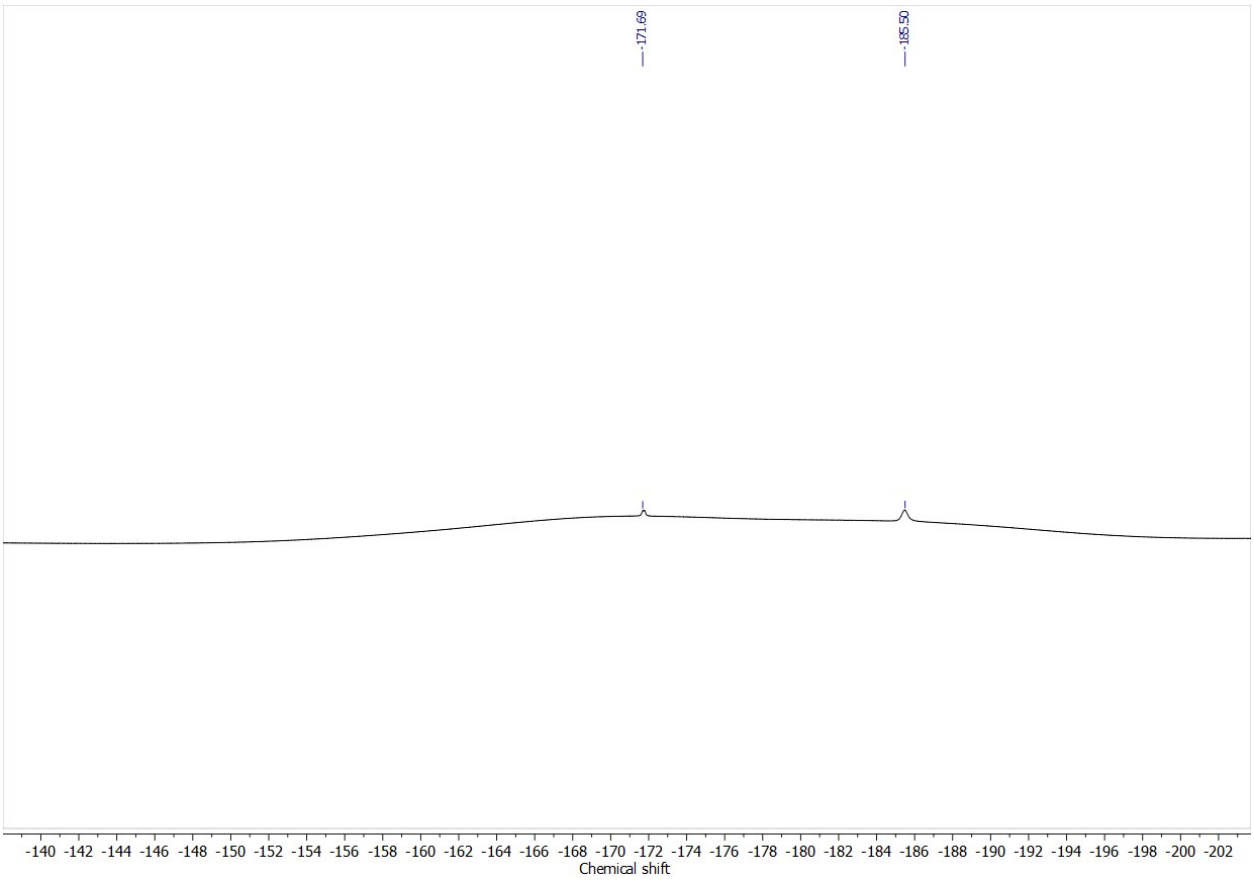


Figure S20: **^{19}F-**NMR of the crude mixture of 1-fluoro-4-methylcyclohexane (**6a**) and methylcyclohexane in heptane-d_{16}.

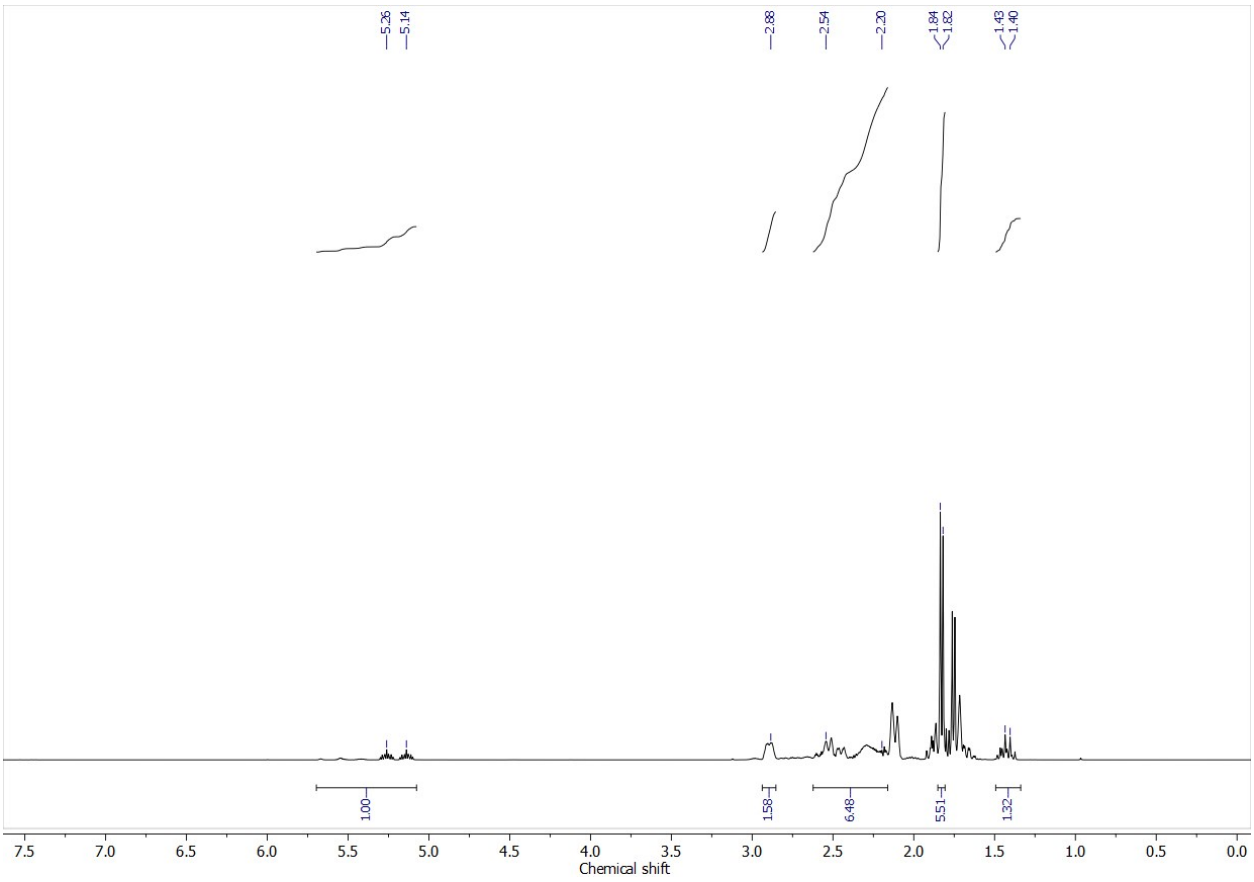


Figure S21: **^{1}H-**NMR of the crude mixture of 1-fluoro-3,5-dimethylcyclohexane (**7a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 2.10-2.13, 1.71)

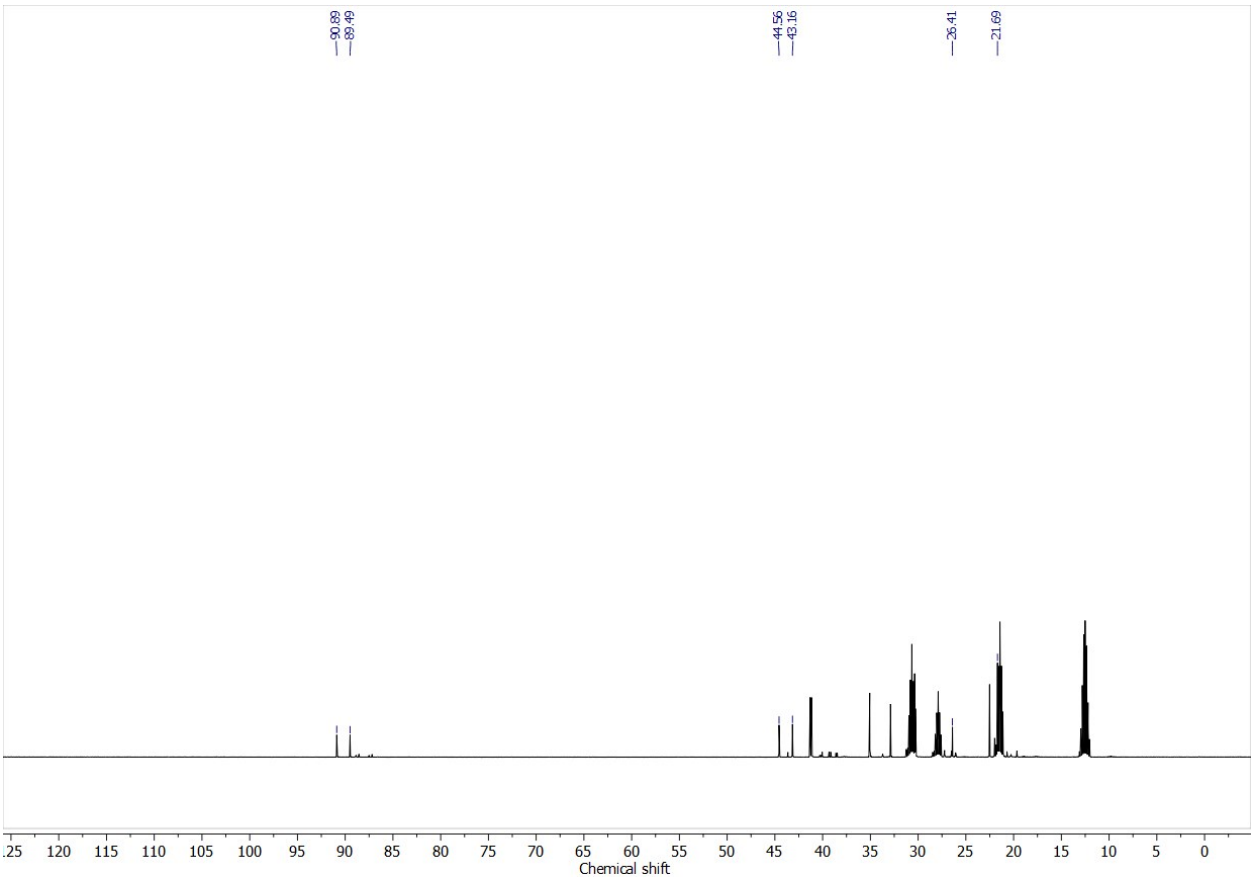


Figure S22: $^{13}C\{^{1}H\}$-NMR of the crude mixture of 1-fluoro-3,5-dimethylcyclohexane (**7a**) and methylcyclohexane in heptane-d_{16}. (Solvent traces δ (ppm): 30.64 (m), 27.85 (m), 21.38 (m), 12.49 (m))

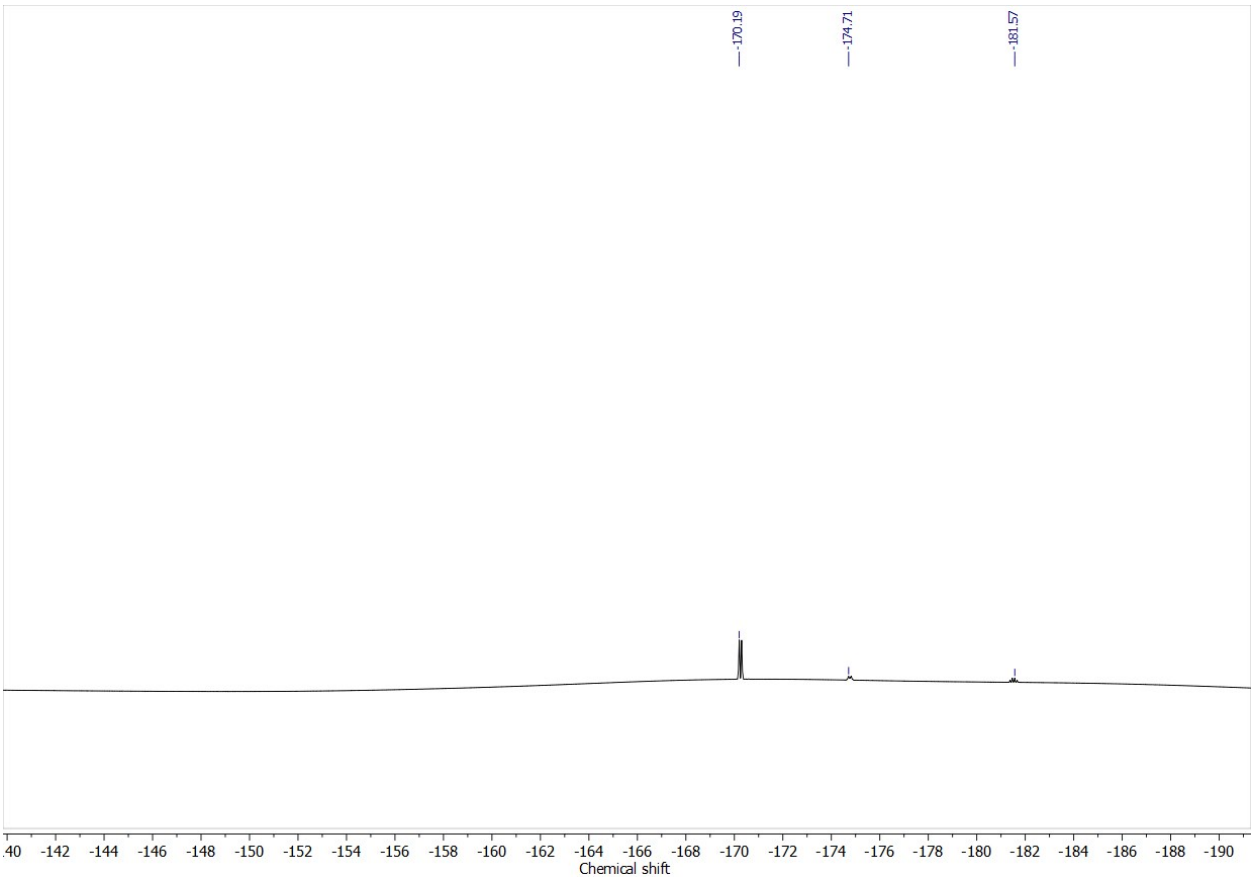


Figure S23: **^{19}F-**NMR of the crude mixture of 1-fluoro-3,5-dimethylcyclohexane (**7a**) and methylcyclohexane in heptane-d_{16}.

References

1. John, K.D.; Eglin, J.L.; Salazar, K.V.; Baker, R.T.; Sattelberger, A.P.; Serra, D.; White, L.M. Tris(Allyl)Iridium and -Rhodium. *Inorganic Syntheses vol. 36,* **2014***.*
2. Blechta, V.; Šabata, S.; Sýkora, J.; Hetflejš, J.; Soukupová, L.; Schraml, J. The effect of solvent accessible surface on Hammett-type dependencies of infinite dilution ^{29}Si and ^{13}C NMR shifts in ring substituted silylated phenols dissolved in chloroform and acetone. *Magn. Reson. Chem*. **2012**, *50*, 128-134.