Supplementary information

1 Table of contents

2 General Specifications

All manipulations with air and moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk and glovebox techniques (nitrogen glovebox, mBraun Uni Lab plus).

$B(C_6F_5)_3$ was synthesized from Boron trifluoride etherate, according to literature procedures.[1]

$MeB(C_6F_5)_2$ was synthesized from $ClB(C_6F_5)_2$ according to literature procedures.[2]

All dry, non-deuterated solvents were purchased by Acros Organics or Sigma Aldrich in a sealed bottle with a septum and stored (except benzene) over molecular sieves.

Deuterated solvents were distilled under inert conditions and kept in the glovebox over 4 Å molecular sieves.

NMR spectra were recorded on Bruker Avance II 200 MHz, Bruker Avance III HD 400 MHz, Bruker Avance II 400 MHz and Bruker Avance III HD 600 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are referenced to residual solvent resonance peaks.

Mass spectra were recorded on an APCI-MS-Bruker Mikro-TOF mass spectrometer. In positive ion detection mode, the capillary current was set to 1500 V with the end plate offset of –500 V.

Elemental analysis was performed with a Thermo FlashEA 1112 instrument.

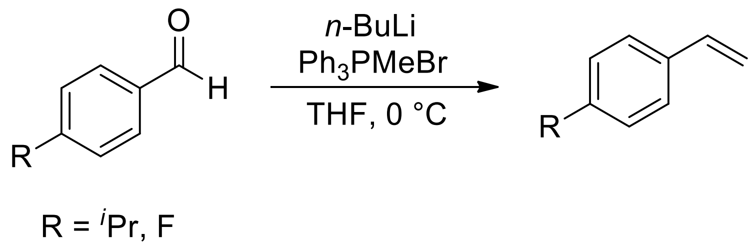
3 Synthesis of allenes

Allenes were synthesized via the Doering-LaFlamme route starting from the respective olefins.[3] Styrene, *p*-Cl-styrene, *p*-Me-styrene and 1-vinylnaphthalene were purchased commercially. *p*-F-styrene and *p*-isopropylstyrene were synthesized from the corresponding aldehydes. *p*-F-benzaldehyde and *p*-isopropylbenzaldehyde were purchased commercially.

3.1 Wittig reaction

p-Isopropylstyrene was synthesized from *p*-isopropylbenzaldehyde via a Wittig reaction according to the literature known procedure (Scheme SI 1).[4]

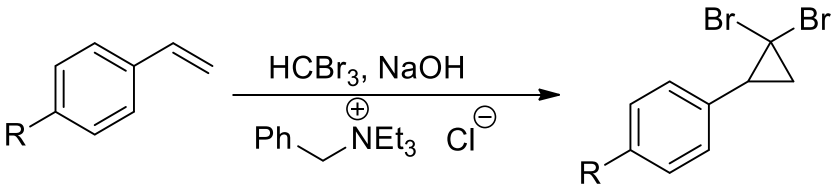
p-F-styrene was synthesized analogous to a literature known procedure using *p*-F-benzaldehyde (5.86 g, 47.2 mmol, 1 eq.), Ph_3PMeBr (18.5 g, 51.8 mmol, 1.1 eq.) and *n*-butyllithium (32.5 mL of a 1.6 M solution in *n*-hexane, 52.0 mmol, 1.1 eq.) in 62 % (3.6 g, 0.029 mmol) yield.[4]



Scheme SI 1: Wittig reaction for the synthesis of the styrene derivatives starting from the corresponding benzaldehydes.

3.2 Dibromocyclopropanation

The dibromocyclopropanation was done by phase-transfer catalysis with bromoform and NaOH (Scheme SI 2). The dibromocyclopropane derivatives from styrene, *p*-Me-styrene, *p*-Cl-styrene, 1-vinylnaphthalene and *p*-F-styrene were synthesized according to reported procedures.[5]



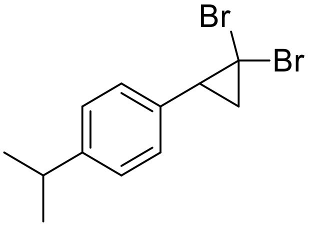
Scheme SI 2: Dibromocyclopropation of olefins.

The synthesis starting from *p*-isopropylstyrene was done analogous to the literature reported procedure.[5]

3.2.1 Synthesis of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene

In 250 mL two-necked flask with a large stirring bar, reflux condenser and gas hose *p*-isopropylstyrene (5.7 g, 40.0 mmol, 1.0 eq.), bromoform (5.1 mL, 58.3 mml, 1.5 eq.) and triethylethylbenzylammoniumchloride (TEBAC) were suspended in DCM (10 mL). A solution of NaOH in water (6.3 g in 6.0 mL ,158 mmol, 4.0 eq.) was added slowly and the reaction mixture was heated overnight to 70 °C under nitrogen flow. The next day the reaction mixture was transferred to a separation funnel, water was added and the aqueous phase was extracted three times with DCM. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure.

The crude product was distilled under oil-pump vacuum yielding the pure product as a yellowish oil in 60 % yield (7.6 g, 23.9 mmol).



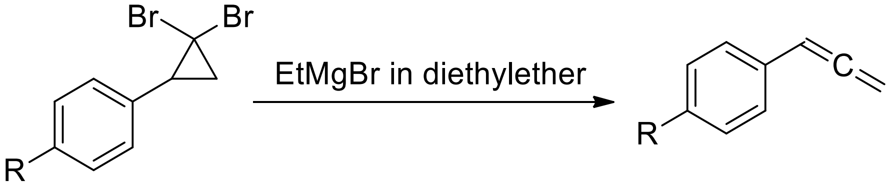
^{1}H NMR (400 MHz, chloroform-*d*) δ 7.25-7.16 (m, 4H, Ar-*H*), 2.99 – 2.87 (m, 2H, $(H_3C)_2CH$, H_2C-C*H*), 2.12 (dd, *J* = 10.5, 7.7 Hz, 1H, CH_2), 2.00 (t, *J* = 8.0 Hz, 1H, CH_2), 1.27 (d, *J* = 6.9 Hz, 6H, $(H_3C)_2CH$).

^{13}C NMR (101 MHz, chloroform-*d*) δ 148.41 ($C_{Ar,q}$), 133.44 ($C_{Ar,q}$), 128.93 (C_{Ar}), 126.47 (C_{Ar}), 35.82 (H*C*-CH_2), 33.92 ($(H_3C)_2CH$), 29.04 (CBr_2), 27.47 (CH_2), 24.07 ($(H_3C)_2CH$), 24.1 ($(H_3C)_2CH$).

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{12}H_{14}Br_2H^+$: 316.9541; found: 316.9368.

3.3 Skattebøl rearrangement

Phenylallene, *p*-Me-phenylallene, *p*-F-phenylallene, *p*-Cl-phenylallene and 1-naphtylallene were synthesized according to literature known procedures (Scheme SI 3).[6] The spectroscopic data agree with those reported in the literature.[6a, 7]



Scheme SI 3: Skattebøl rearrangement of dibromocyclopropanes.

p-Isopropylphenylallene was synthesized according to a reported procedure.[6a]

3.3.1 Synthesis of *p*-isopropylphenylallene

In a flame dried three-necked 250 mL flask with stirring bar, gas hose, reflux condenser and dropping funnel 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene (7.60 g, 23.9 mmol, 1.0 eq.) was dissolved in dry THF (50 mL) and cooled to 0 °C with an ice bath under nitrogen gas flow. EtMgBr (17 mL of a 3 M solution in diethylether, 51.0 mmol, 2.1 eq.) was transferred to the dropping funnel and slowly added to the reaction solution. Afterwards, the reaction mixture was warmed to room temperature and stirred overnight. Water was added to quench any excess of EtMgBr. The reaction mixture was transferred to a separation funnel and extracted three times with *n*-pentane. The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure.

The crude product was distilled under oil-pump vacuum to yield the product as a colourless liquid in 59 % yield (2.25 g, 14.2 mmol). The spectroscopic data are identical to the literature.[8]

3.4 Additional NMR spectra of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene

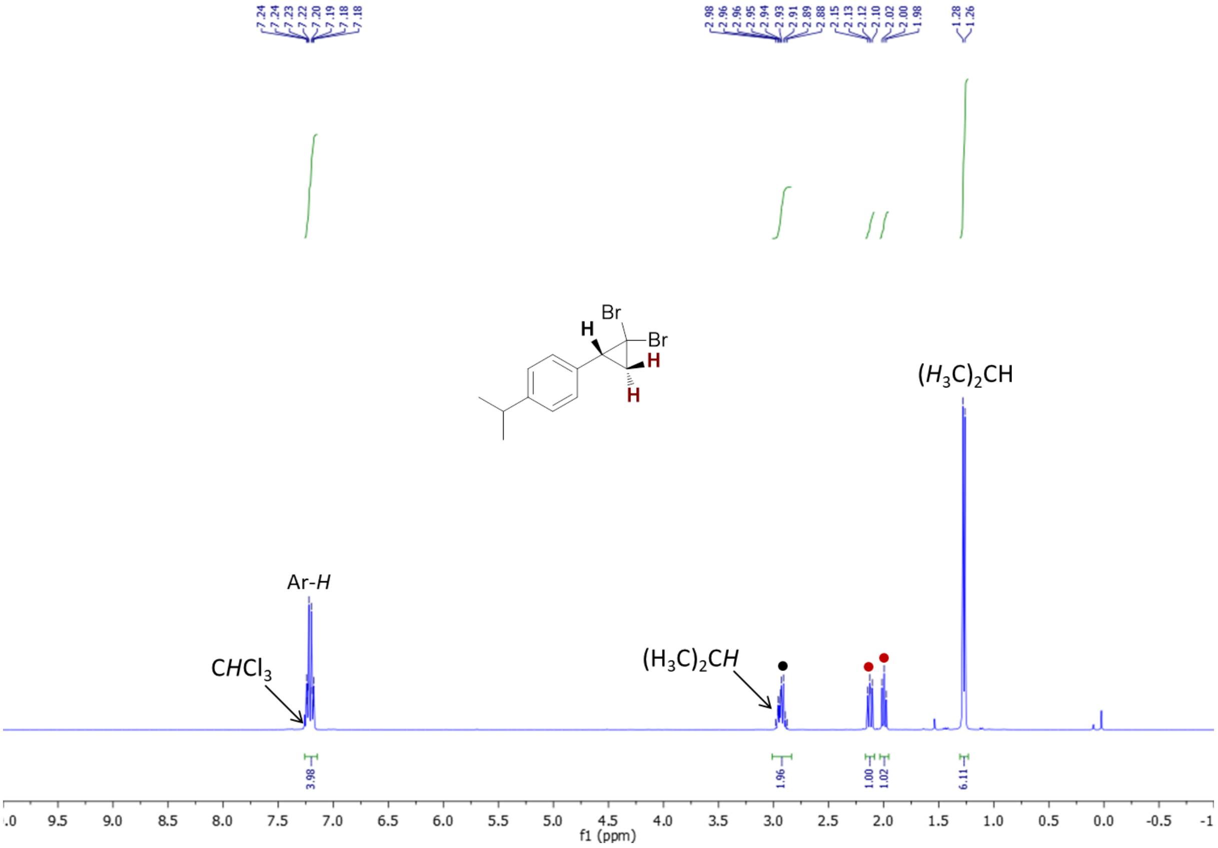


Figure SI 1: ^{1}H NMR spectrum of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene (400 MHz, chloroform-*d*).

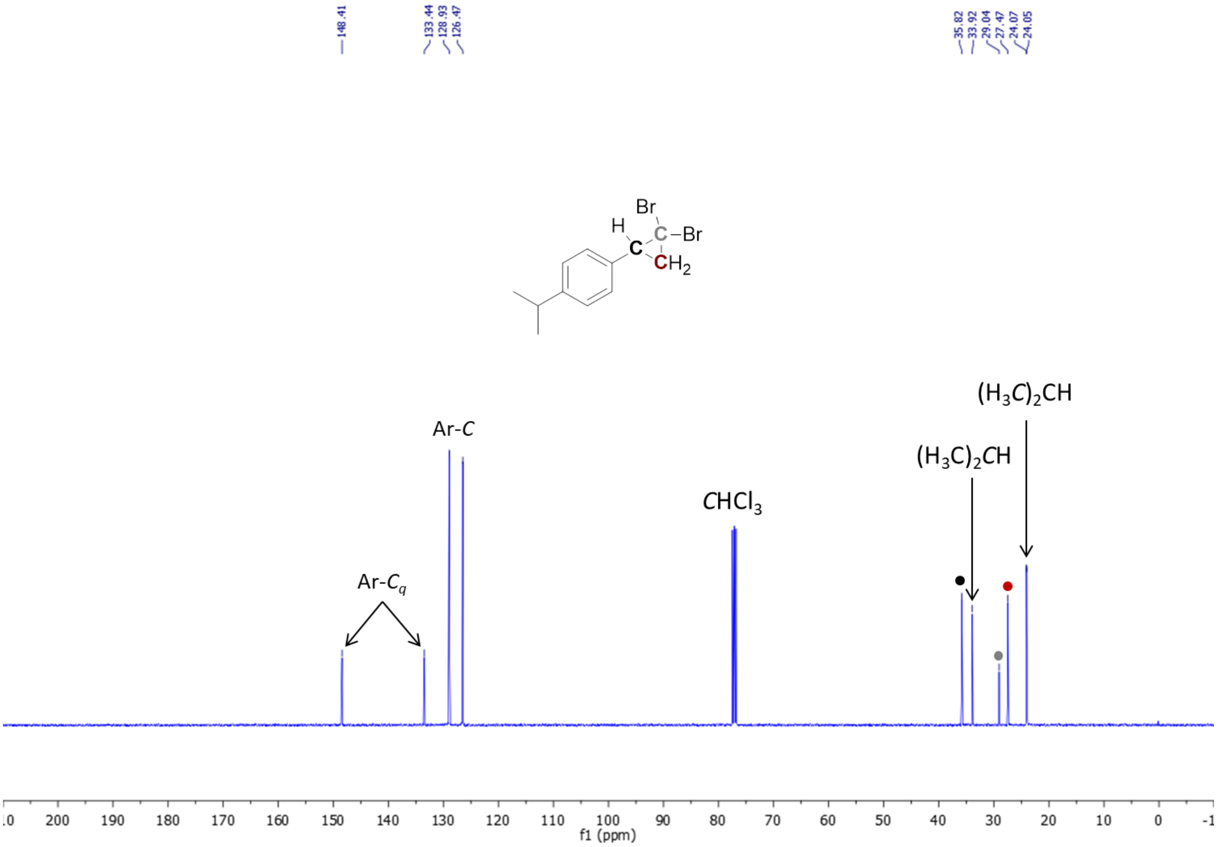


Figure SI 2: ^{13}C NMR spectrum of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene (101 MHz, chloroform-*d*).

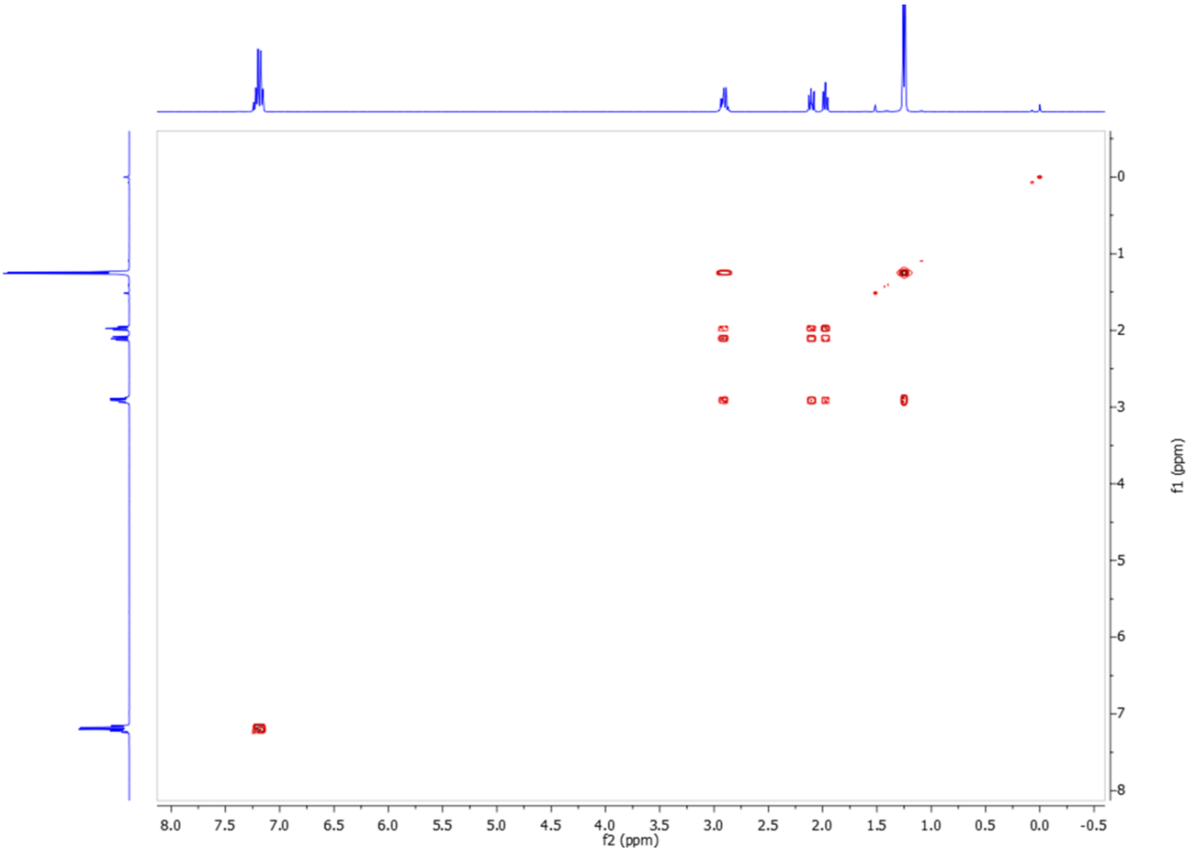


Figure SI 3: HH COSY NMR spectrum of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene (400 MHz, chloroform-*d*).

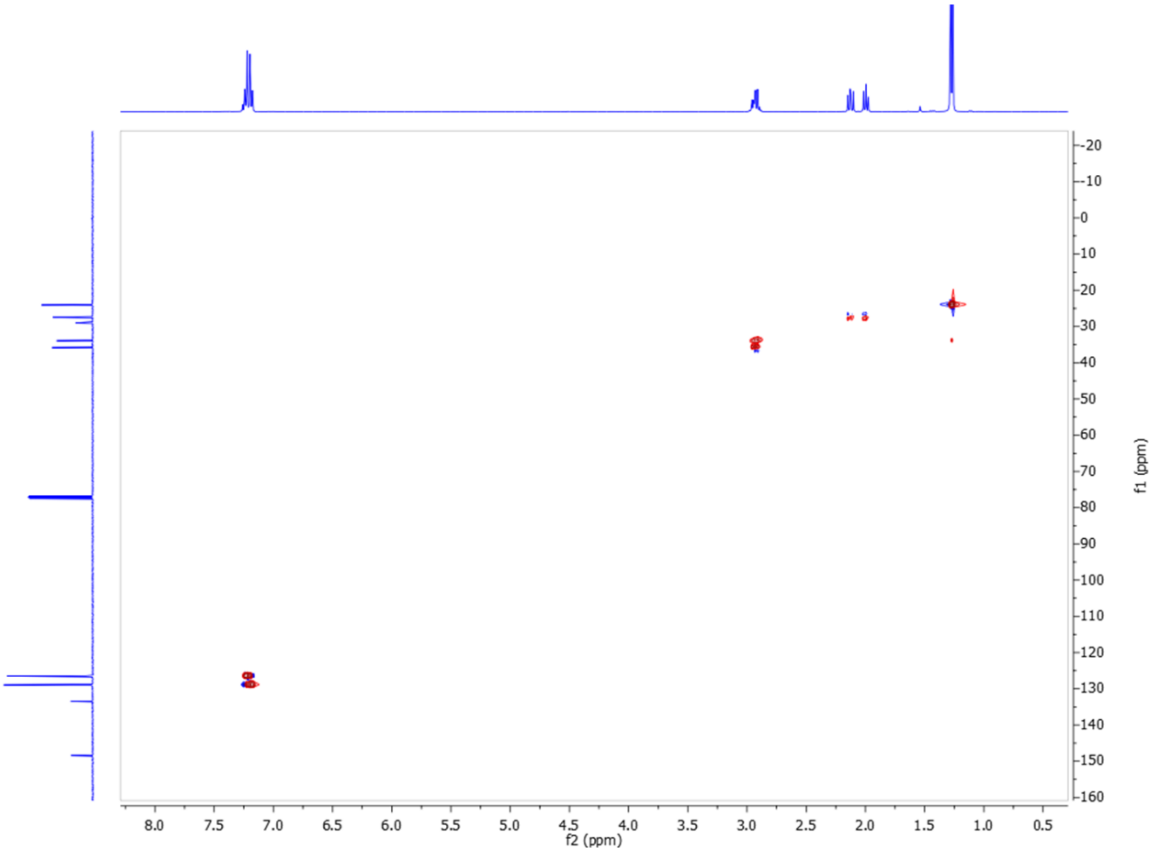


Figure SI 4: ^{1}H-^{13}C HSQC NMR spectrum of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene (101 MHz, chloroform-*d*).

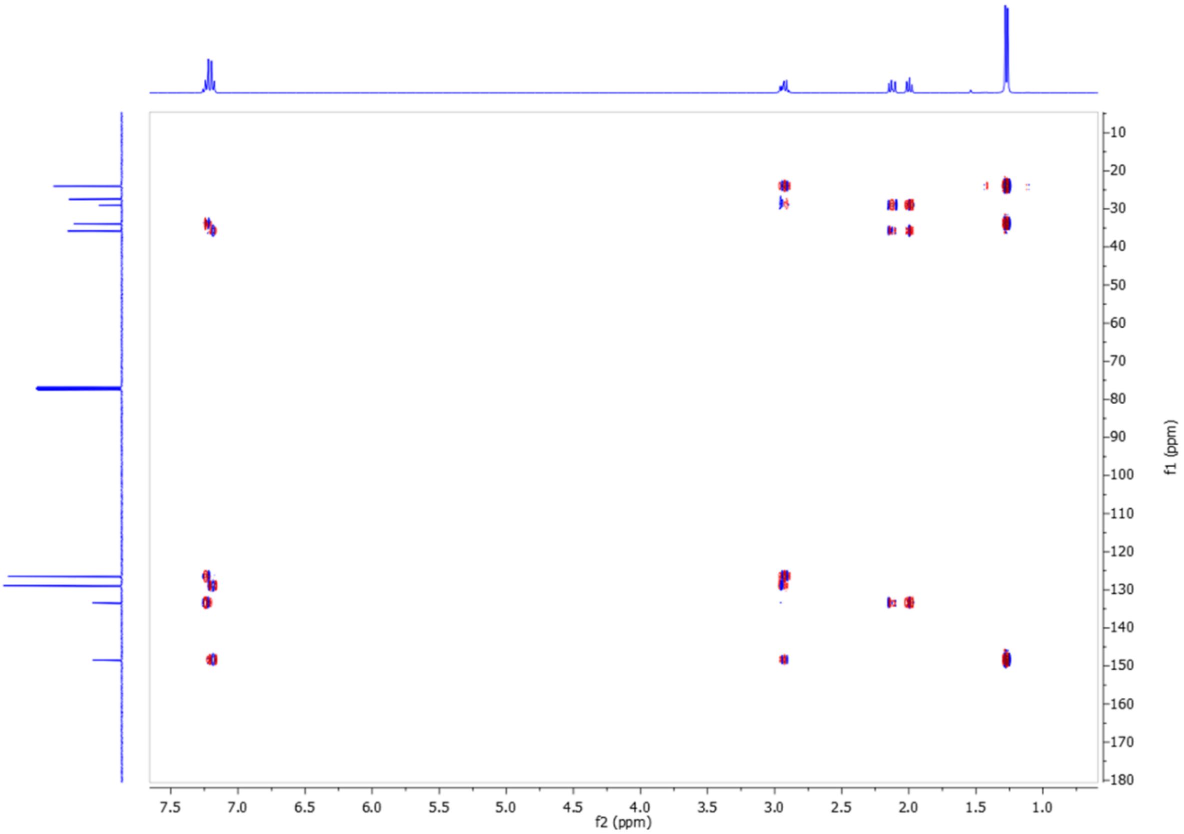


Figure SI 5: ^{1}H-^{13}C HMBC NMR spectrum of 1-(2,2-dibromocyclopropyl)-4-isopropylbenzene (400 MHz, chloroform-*d*).

4 Initial NMR reaction of phenylallene and $B(C_6F_5)_3$

Inside a nitrogen filled glovebox $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol, 1.0 eq.) was dissolved in DCM-d_2 (0.5 mL) in a 10 mL glass vial. Phenylallene (6.4 µL, 0.91 g/mL, 0.05 mmol, 1.0 eq.) was added, the reaction mixture was transferred to an NMR tube with J Young valve and left for 45 min at room temperature.

A ^1H and ^{11}B NMR spectrum were measured (Figure SI 6, Figure SI 7). The spectra show a complex reaction mixture where all phenylallene has reacted and 2-pentafluorophenylindene is the main component. Further products are two regioisomers of the hydroboration of phenylallene by Piers borane and a dimerization product of phenylallene resulting from the reaction of the corresponding allylborane with an additional equivalent of phenylallene as was reported and characterized by Erker *et al.*[9] This is in accordance with our mechanistic proposal where Piers borane is released by a retrohydroboration reaction in the last reaction step.

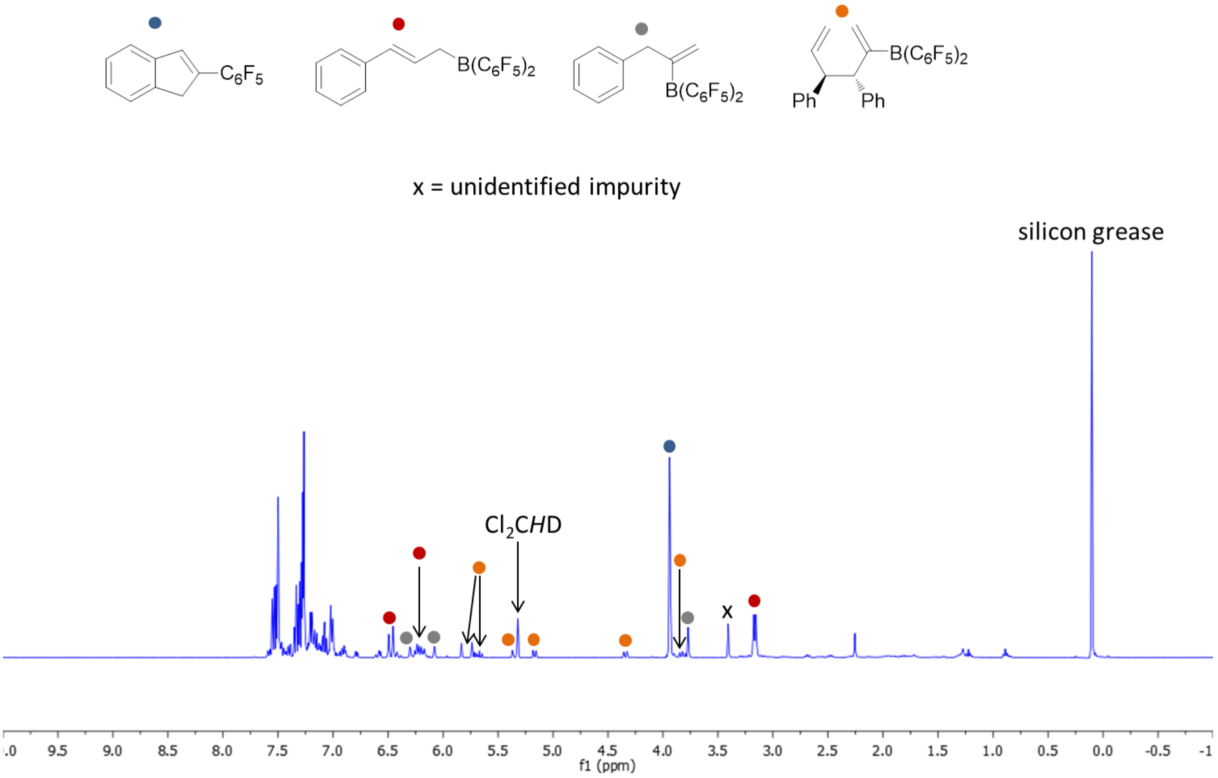


Figure SI 6: ^1H NMR spectrum of the reaction of $B(C_6F_5)_3$ with phenylallene after 45 min at room temperature (400 MHz, DCM-d_2).

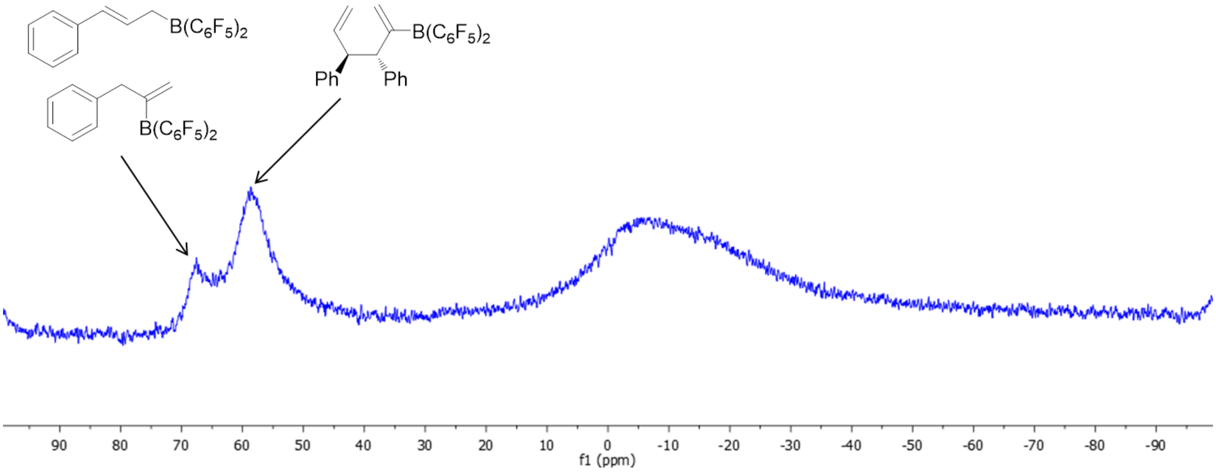


Figure SI 7: ^{11}B NMR spectrum of the reaction of $B(C_6F_5)_3$ with phenylallene after 45 min at room temperature (128 MHz, DCM-d_2).

For *in situ* quantification by qNMR, 1,3,5-trimethoxybenzene (100 µL of a 0.25 M stock solution in benzene-d_6, 0.025 mmol) was added to the reaction mixture inside a glovebox. The respective ^{1}H NMR spectrum showed that the yield of 2-pentafluorophenylindene is 48 % and 22 % regarding the allylborane (Figure SI 8, Figure SI 9).

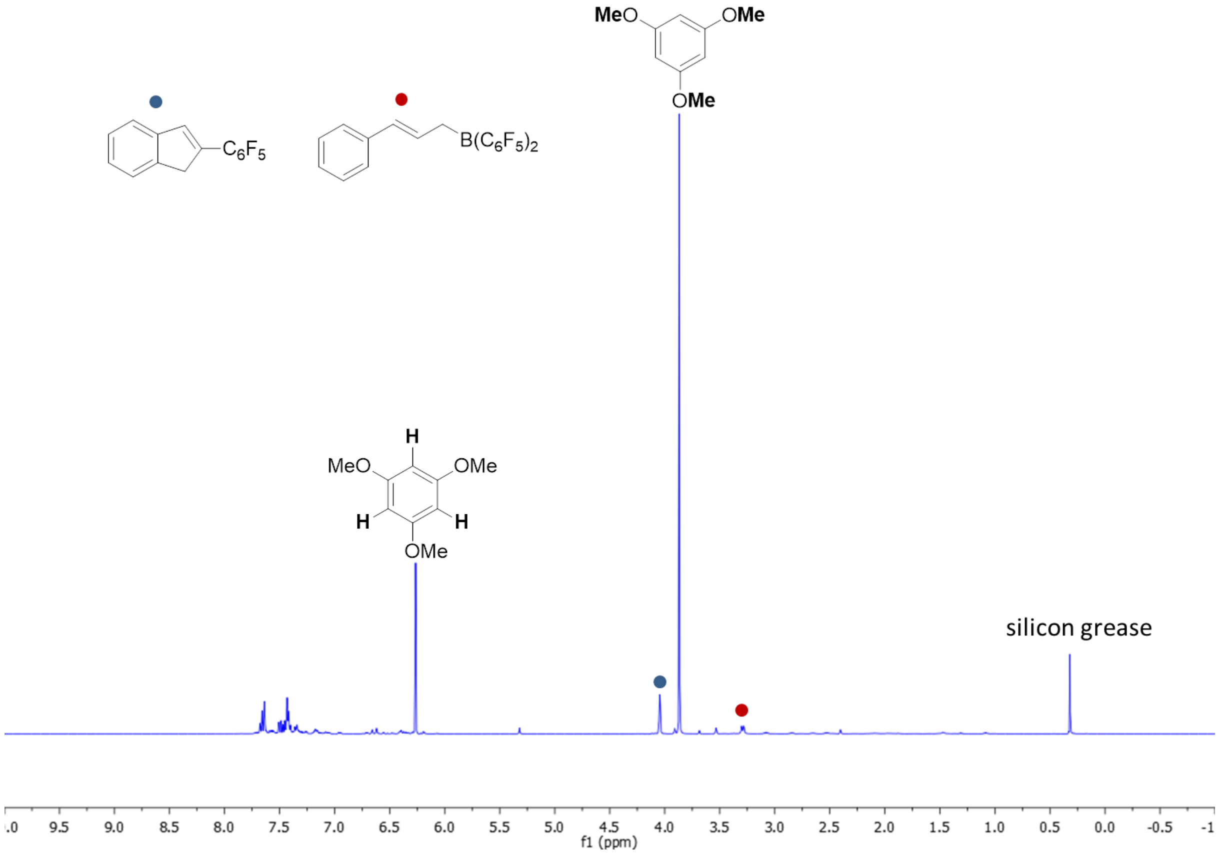


Figure SI 8: ^{1}H NMR spectrum of the reaction of $B(C_6F_5)_3$ with phenylallene with 1,3,5-trimethoxybenzene (100 µL of a 0.25 M stock solution in benzene-*d*$_6$, 0.025 mmol) as internal standard (400 MHz, DCM-*d*$_2$).

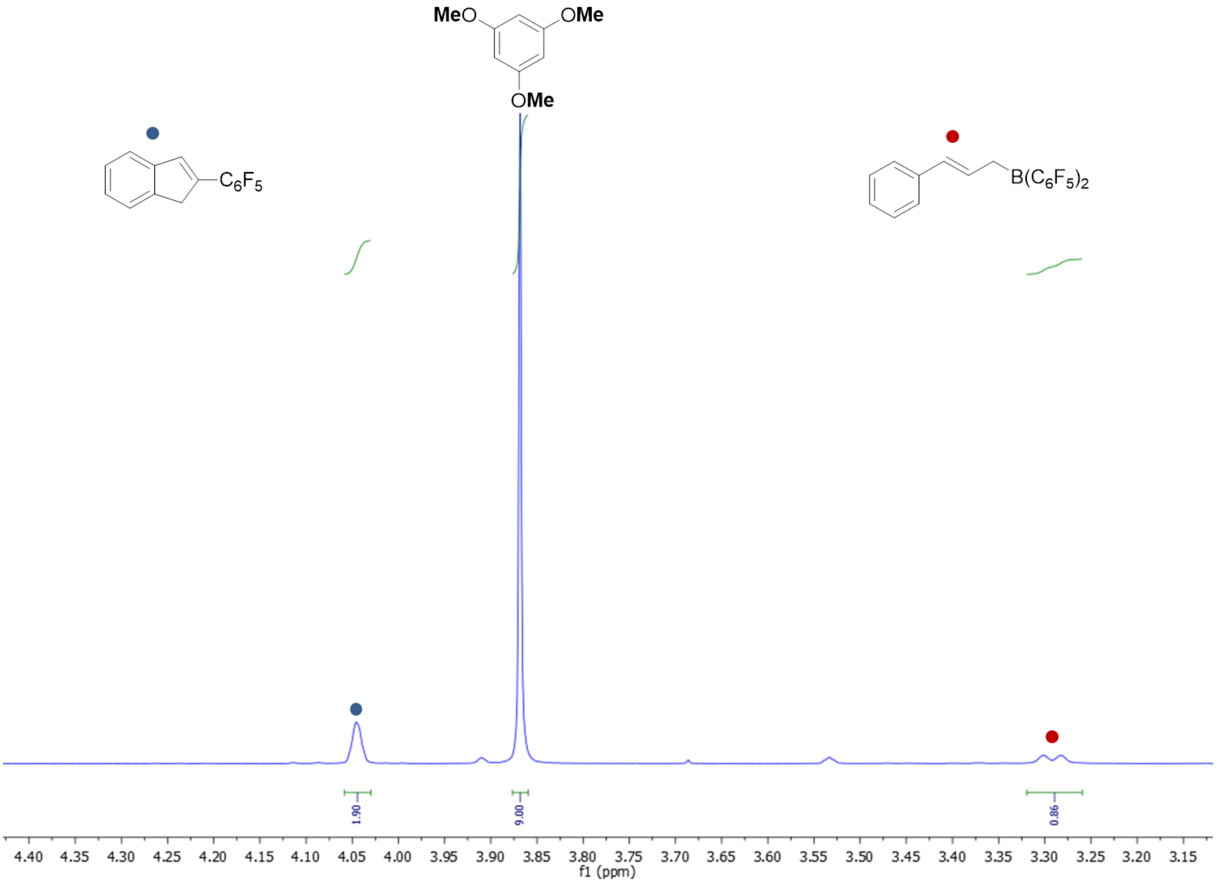


Figure SI 9: Excerpt of the ^{1}H NMR spectrum of the reaction of $B(C_6F_5)_3$ with phenylallene with 1,3,5-trimethoxybenzene (100 µL of a 0.25 M stock solution in benzene-d_6, 0.025 mmol) as internal standard (400 MHz, DCM-d_2).

5 Synthesis and characterization of indene derivatives

The indene derivatives were synthesized according to three similar general procedures at different temperatures.

5.1 General synthesis procedures

General procedure A

Inside a nitrogen-filled glovebox $B(C_6F_5)_3$ (256.0 mg, 0.50 mmol, 1.0 eq.) was dissolved in dry DCM (5 mL) in a 10 mL vial with a stirring bar. The respective allene (1.00 mmol, 2.0 eq.) was added and the reaction mixture was stirred at room temperature for 45 min. Pyridin (80.7 µL, 0.98 g/mL, 1.00 mmol, 2.0 eq.) was added. The reaction mixture was taken out of the glovebox and the solvent was evaporated under reduced pressure. The crude product was purified via column chromatography using SiO_2 and *n*-hexane as eluent.

General procedure B

Inside a nitrogen-filled glovebox $B(C_6F_5)_3$ (256.0 mg, 0.50 mmol, 1.0 eq.) was dissolved in dry DCM (4 mL) in a small Schlenk tube with a stirring bar. The allene (1.00 mmol, 2.0 eq.) was dissolved in another Schlenk tube in DCM (1 mL) with a stirring bar. Both tubes were taken out of the glovebox and cooled with an ice bath to 0 °C under nitrogen gas flow. After one hour the solution of $B(C_6F_5)_3$ in DCM was transferred with a syringe to the allene solution. The reaction mixture was stirred for 45 min at 0 °C. Pyridine (80.7 µL, 0.98 g/mL, 1.00 mmol, 2.0 eq.) was added. The solvent was evaporated under reduced pressure. The crude product was purified via column chromatography using SiO_2 and *n*-hexane as eluent.

General procedure C

Inside a nitrogen-filled glovebox $B(C_6F_5)_3$ (256.0 mg, 0.50 mmol, 1.0 eq.) was dissolved in dry DCM (5 mL) in a 10 mL Schlenk tube with J Young valve. Allene (1.00 mmol, 2.0 eq.) was added, the tube was closed, taken out of the glovebox and put in an oil-bath preheated to 60 °C for 45 min. (*Caution: pressure builds up. A blast shield has to be used.)*. Pyridine (80.7 µL, 0.98 g/mL, 1.00 mmol, 2.0 eq.) was added and the solvent was evaporated under reduced pressure. The crude product was purified via column chromatography using SiO_2 and *n*-hexane as eluent.

5.2 Optimization of reaction temperature

To establish the optimal reaction temperature the different substrates were tested at different reaction temperatures. This revealed that more electron-rich substrates give better yields at 0 °C while electron-poor substrates need higher temperatures (Table SI 1).

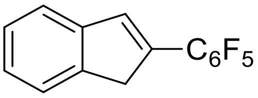
Table SI 1: Optimization of the reaction temperature for the different substrates.[a] 60 °C oil bath temperature with a closed reaction vessel.

Substrate	Yield		
	Gen. proc. A (r.t.)	**Gen. proc. B (0° C)**	**Gen. proc. C (60 °)[a]**
phenylallene	68%	-	-
1-naphtylallene	65%	-	-
4-Me-phenylallene	46%	53%	-
4-*i*Pr-phenylallene	56%	62%	-
4-Cl-phenylallene	37%	-	45%
4-F-phenylallene	47%	-	58%

5.3 Characterization of indene products

5.3.1 2-pentafluorophenylindene

2-Pentafluorophenylindene was synthesized according to general procedure A with phenylallene (127.6 µL, 0.91 g/mL, 1.0 mmol, 2.0 eq.). The product was isolated in 68 % yield (95.8 mg, 0.34 mmol) as a colourless solid.



^{1}H NMR (400 MHz, chloroform-*d*) δ 7.57 – 7.47 (m, 3H, Ar-*H*, H_{sp2}), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-*H*), 7.29 (td, *J* = 7.4, 1.3 Hz, 1H, Ar-*H*), 3.92 (br, 2H, CH_2).

^{13}C {^{1}H} NMR (101 MHz, chloroform-*d*) δ 143.70 (Ar-C_q), 143.46 (Ar-C_q), 136.05 (td, *J* = 7.3, 2.3 Hz, C_{sp2}), 131.90 (C_q-C_6F_5), 126.94 (Ar-*C*), 126.29 (Ar-*C*), 123.70 (Ar-*C*), 122.11 (Ar-*C*), 41.76 (t, *J* = 4.8 Hz, CH_2).

Remark: The $^{13}C\{^1H\}$ NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups.

^{19}F NMR (377 MHz, chloroform-*d*) δ -139.98 – -140.11 (m, 2F, o-*F*), -156.51 (t, *J* = 21.1 Hz, 1F, p-*F*), -162.61 – -162.77 (m, 2F, m-*F*).

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{15}H_7F_5H^+$: 283.0541; found: 283.0539

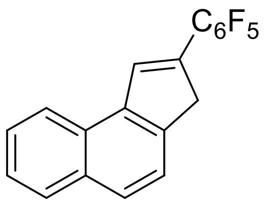
Anal. Calcd for $C_{15}H_7F_5$: C, 63.73; H, 2.63. Found: C, 63.84; H, 2.50.

5.3.2 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene

2-Pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene were synthesized according to general procedure A from 1-naphtylallene (166.2 mg, 1.0 mmol, 2.0 eq.). The product was isolated in 65 % yield (108.8 mg, 0.33 mmol) in a 1 : 0.56 ratio as a colourless solid.

Major isomer

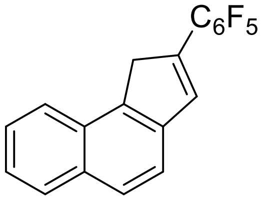
ratio 1



2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene

Minor isomer

0.56



2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene

The product is a mixture of two isomers that could not be separated by column chromatography. The isomers were assigned using 1D and 2D NMR spectroscopy (see 5.3.2.4).

5.3.2.1 NMR data of the major isomer, 2-pentafluorophenyl-3H-cyclopenta[a]naphthalene

^1H NMR (400 MHz, chloroform-*d*) δ 8.18 (dd, *J* = 8.2, 1.1 Hz, 1H, H_4C_6), 8.10 (br, 1H, C_{sp2}-H), 7.93 (d, *J* = 8.1 Hz, 1H, H_4C_6), 7.79 (d, *J* = 8.5 Hz, 1H, C_6H_2), 7.67 (d, *J* = 8.2 Hz, 1H C_6H_2), 7.58 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H, H_4C_6), 7.51 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H, H_4C_6), 4.07 (d, *J* = 1.8 Hz, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (101 MHz, chloroform-*d*) δ 141.71 (t, *J* = 2.8 Hz, Ar-C_q), 139.95 (s, Ar-C_q), 133.45 (td, *J* = 7.5, 1.7 Hz, C_{sp2}-H), 132.80 (s, Ar-C_q), 132.06 - 131.91 (m, Ar-C_q), 128.72 (s, H_4C_6), 128.05 (s, Ar-C_q), 126.78 (s, C_6H_2), 126.41 (s, H_4C_6), 125.58 (s, H_4C_6), 123.67 (s, H_4C_6), 122.08 (s, C_6H_2), 43.04 (t, *J* = 5.0 Hz, C_{sp3}-H_2).

Remark: The $^{13}C\{^1H\}$ NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -140.03 – -140.13 (m, 2F, o-*F*), -156.87 (t, *J* = 21.0 Hz, 1F, p-*F*), -162.62 – -162.81 (m, 2F, p-*F*)

5.3.2.2 NMR data of the minor isomer, 2-pentafluorophenyl-1H-cyclopenta[a]naphthalene

^1H NMR (400 MHz, chloroform-*d*) δ 8.01 (d, *J* = 8.3 Hz, 1H, H_4C_6), 7.89 (d, *J* = 8.1 Hz, 1H, H_4C_6), 7.82 (d, *J* = 8.3 Hz, 1H, C_6H_2), 7.64 (d, *J* = 8.4 Hz, 1H, C_6H_2), 7.62 (br, 1H, C_{sp2}-*H*), 7.54 (t, *J* = 7.2 Hz, 1H, H_4C_6), 7.46 (t, *J* = 7.6 Hz, 1H, H_4C_6), 4.24 (br, 2H, CH_2).

^{13}C NMR (101 MHz, chloroform-*d*) δ 141.24 (s, Ar-C_q), 140.53 (t, *J* = 2.8 Hz, Ar-C_q), 136.64 (td, *J* = 7.7, 2.1 Hz, C_{sp2}-H), 132.31 (s, Ar-C_q), 131.62 – 131.45 (m, Ar-C_q), 129.75 (s, Ar-C_q), 129.10 (s, H_4C_6), 127.92 (s, C_6H_2), 126.78 (s, C_6H_2), 125.55 (s, H_4C_6), 123.74 (s, H_4C_6), 120.79 (s, H_4C_6), 40.86 (t, *J* = 4.9 Hz, C_{sp3}-H_2).

Remark: The $^{13}C\{^1H\}$ NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups.

^{19}F NMR (377 MHz, chloroform-*d*) δ -140.03 – -140.13 (m, 2F, o-*F*), -156.90 (t, *J* = 21.0 Hz, 1F, p-*F*), -162.62 – -162.81 (m, 2F, p-*F*)

5.3.2.3 APCI-HRMS and elemental analysis of a mixture of the major and minor isomer

HRMS (APCI) m/z [$M+H^+$] calc. for $C_{19}H_9F_5H^+$: 333.0697; found: 333.0698

Anal. Calcd for $C_{19}H_9F_5$: C, 68.68; H, 2.73. Found: C, 68.74; H, 2.83.

5.3.2.4 Assignment of the two isomers using NMR spectra

The assignment of both isomers can be done using the 2D NMR spectra. The HH COSY NMR spectrum shows long-range coupling between the CH_2 groups, the C_{sp2}-H and an aromatic hydrogen (Figure SI 10).

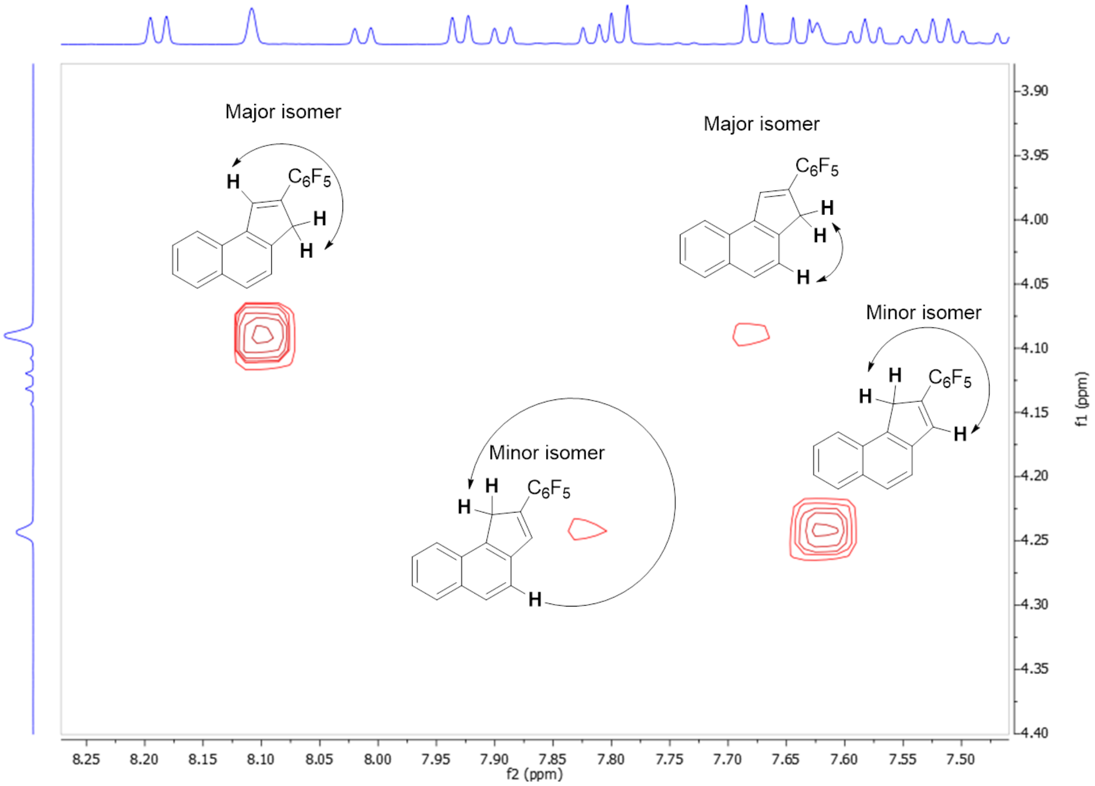


Figure SI 10: Excerpt of a HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1H-cyclopenta[a]naphthalene showing long-range couplings of the CH_2 group (400 MHz, chloroform-*d*).

The aromatic region shows only a coupling of the C_{sp2}-H to an aromatic hydrogen for the minor isomer (Figure SI 11).

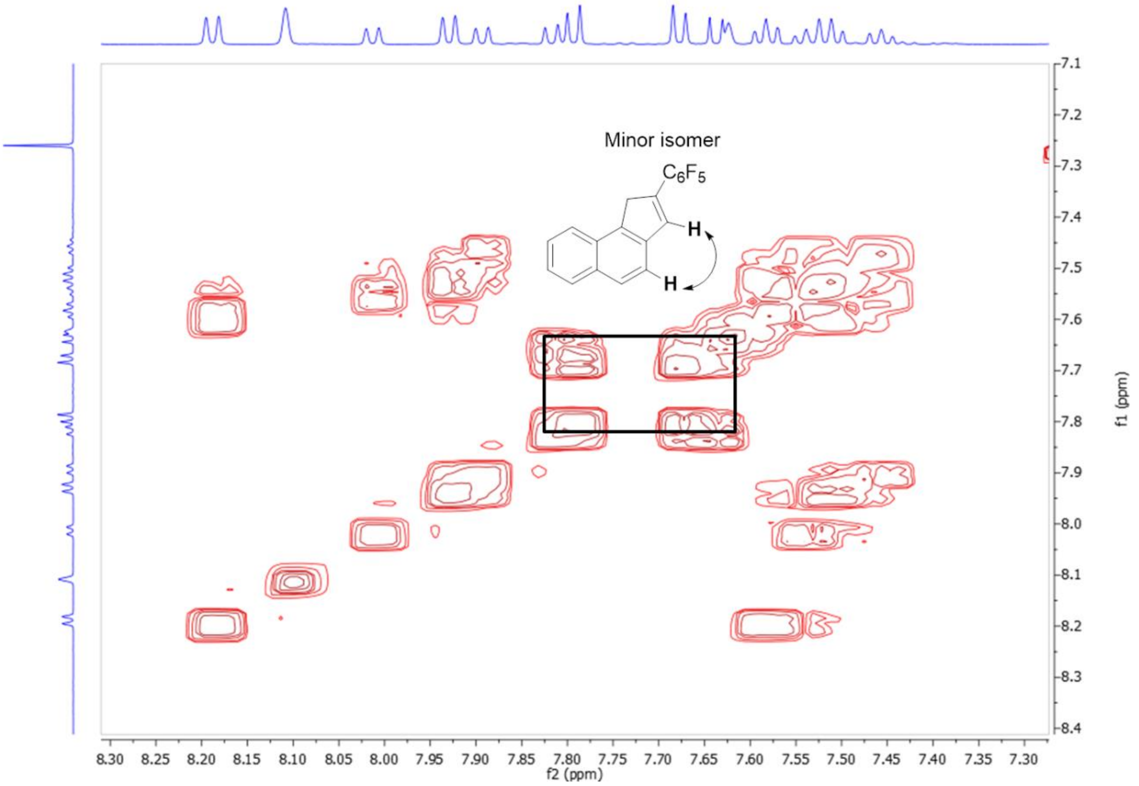


Figure SI 11: Low field **e**xcerpt of a HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene showing the C_{sp2}-H – Ar-H long-range coupling of the minor isomer (400 MHz, chloroform-*d*).

The ^{1}H ^{13}C HMBC NMR spectrum shows the coupling between an aromatic CH group and the aliphatic CH_2 group, which is not visible for the minor isomer (Figure SI 12, Figure SI 13).

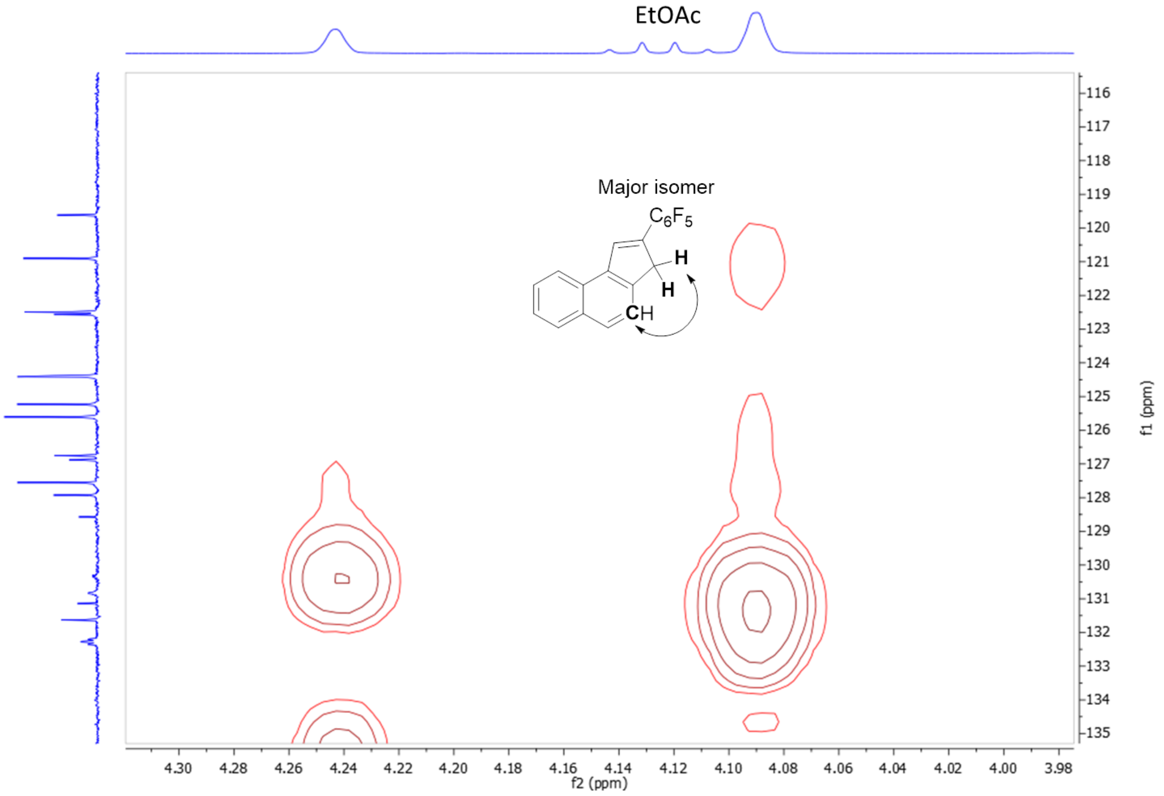


Figure SI 12: Excerpt of a ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene showing coupling between the CH_2 group and an aromatic carbon (101 MHz, chloroform-*d*).

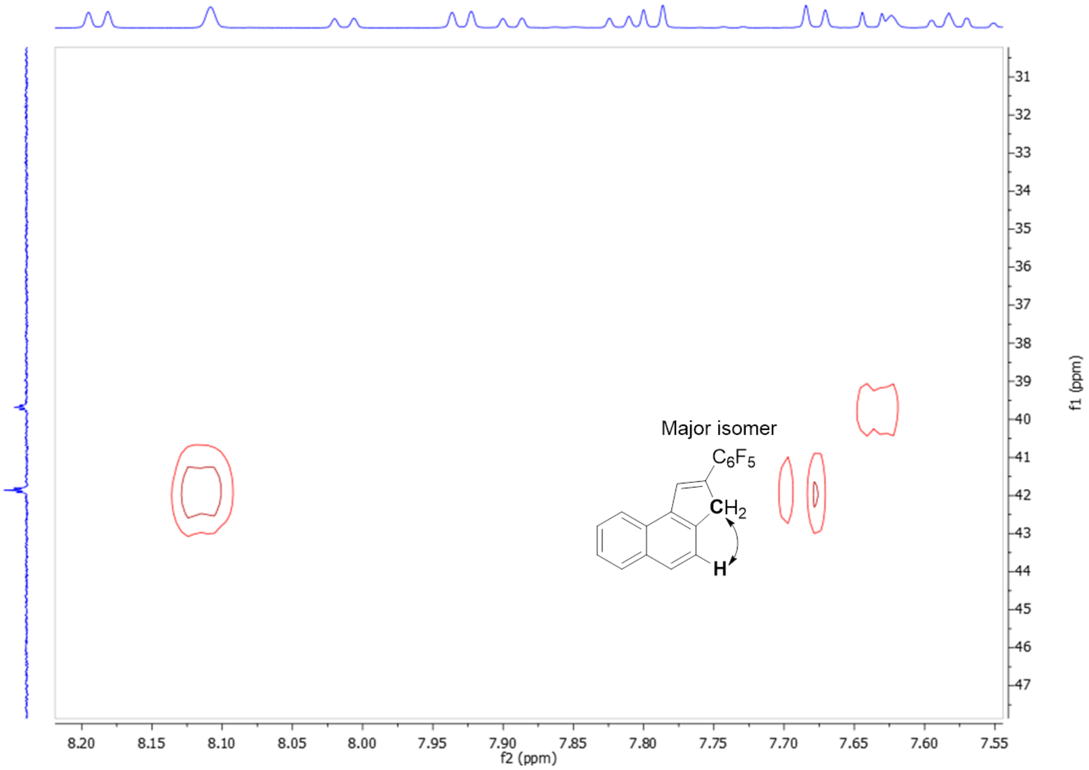
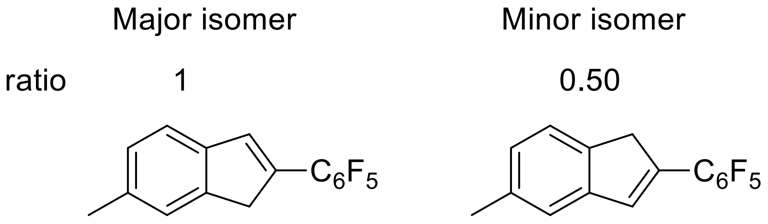


Figure SI 13: Excerpt of a ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene showing coupling between the CH_2 group and an aromatic hydrogen (101 MHz, chloroform-*d*).

5.3.3 2-Pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene

2-Pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene were synthesized according to general procedure B from 4-methylphenylallene (130.2 mg, 1.0 mmol, 2.0 eq.). The product was isolated in 53 % yield (78.7 mg, 0.27 mmol) as a 1 : 0.50 mixture of regioisomers as a colourless solid.



2-pentafluorophenyl-6-methyl-1*H*-indene   2-pentafluorophenyl-5-methyl-1*H*-indene

The product is a mixture of two isomers which could not be separated by column chromatography. The isomers were assigned using 1D and 2D NMR spectroscopy (see 5.3.3.4).

5.3.3.1 NMR data of the major isomer, 2-pentafluorophenyl-6-methyl-1H-indene

^{1}H NMR (600 MHz, chloroform-*d*) δ 7.45 (br, 1H, C_{sp2}-*H*), 7.38 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.34 (s, 1H, Ar-*H*), 7.15 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 3.87 (br, 2H, CH_2), 2.43 (s, 3H, CH_3).

^{13}C NMR (101 MHz, chloroform-*d*) δ 143.83 (t, *J* = 2.4 Hz, Ar-C_q), 141.13 (s, Ar-C_q), 136.30 (s, Ar-C_q-CH_3), 135.89 (dt, *J* = 7.3, 2.0 Hz, C_{sp2}), 130.92 – 130.74 (m, Ar-C_q), 127.75 (s, Ar-*C*), 124.52 (s, Ar-*C*), 121.75 (s, Ar-*C*), 41.54 (t, *J* = 4.8 Hz, CH_2), 21.77 (s, CH_3).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups.

^{19}F NMR (377 MHz, chloroform-*d*) δ -140.15 – -140.26 (m, 2F, o-*F*), -157.04 (t, *J* = 20.9 Hz, 1F, p-*F*), -162.71 – -163.00 (m, 2F, m-*F*).

5.3.3.2 NMR data of the major isomer, 2-pentafluorophenyl-5-methyl-1H-indene

^{1}H NMR (600 MHz, chloroform-*d*) δ 7.43 (br, 1H, C_{sp2}-*H*), 7.40 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.32 (s, 1H, Ar-*H*), 7.10 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 3.87 (br, 2H, CH_2), 2.42 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) δ 143.95 (s, Ar-C_q), 140.58 (t, J = 2.4 Hz, Ar-C_q), 136.60 (s, Ar-C_q-CH_3), 136.06 (dt, J = 8.0, 2.0 Hz, C_{sp2}), 132.15 – 131.90 (m, Ar-C_q), 127.22 (s, Ar-*C*), 123.35 (s, Ar-*C*), 122.69 (s, Ar-*C*), 41.39 (t, J = 4.8 Hz, CH_2), 21.56 (s, CH_3).

Remark: The $^{13}C\{^{1}H\}$ NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups.

^{19}F NMR (377 MHz, chloroform-*d*) δ -140.15 – -140.26 (m, 2F, o-*F*), -156.77 (t, J = 20.9 Hz, 1F, p-*F*), -162.71 – -163.00 (m, 2F, m-*F*).

5.3.3.3 APCI-HRMS and elemental analysis of a mixture of the major and minor isomer

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{16}H_9F_5H^+$: 297.0697; found: 297.0695

Anal. Calcd for $C_{16}H_9F_5$: C, 64.87; H, 3.06. Found: C, 64.58; H, 2.99.

5.3.3.4 Assignment of the two isomers using NMR spectra

The isomers can be assigned using 2D NMR spectroscopy. The assignment of the isomers of the other indene derivatives was done analogously. The HH COSY NMR spectrum shows the long-range coupling between the CH_2 groups to the C_{sp2}-H for both isomers (Figure SI 14). Additionally, for the major isomer, a coupling between the CH_2 group and the aromatic singlet is visible while for the minor isomer coupling to the aromatic doublet is visible.

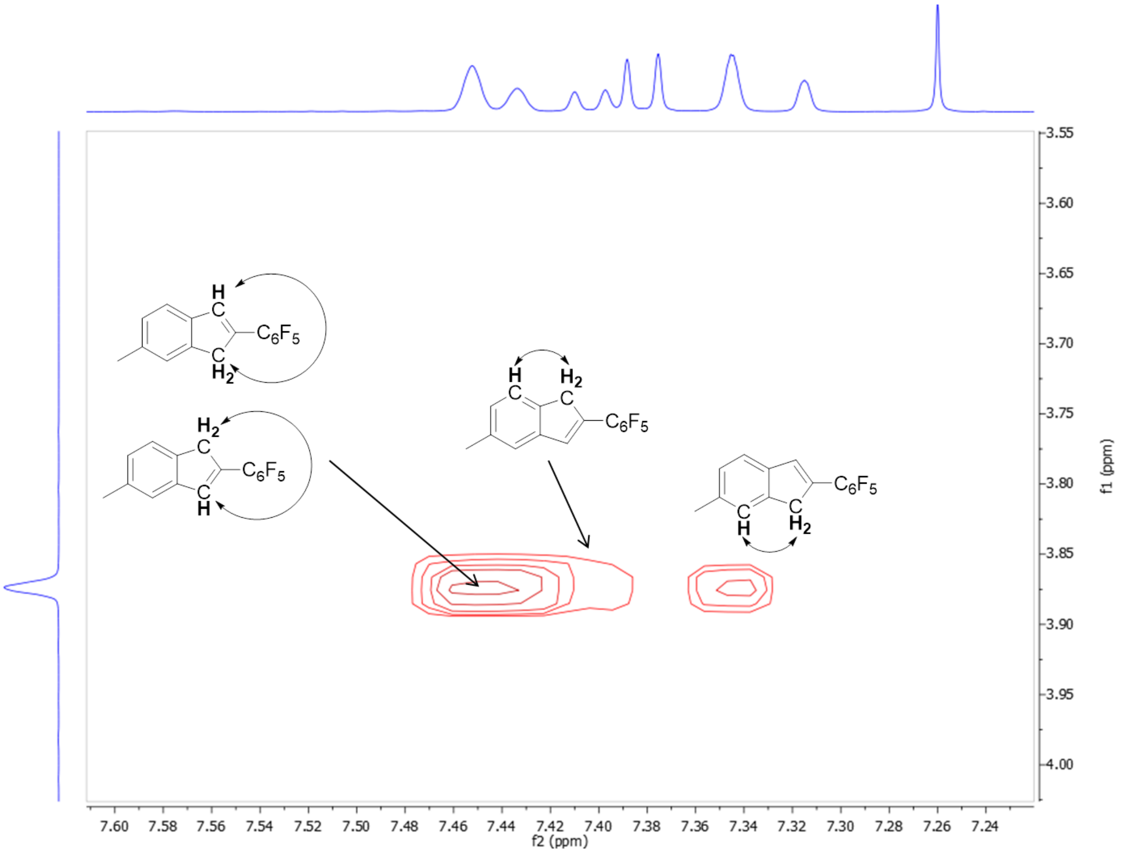


Figure SI 14: Excerpt of a HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene showing different long-range couplings (600 MHz, chloroform-*d*).

Additional proof for the assignment of the two isomers comes from the ^{1}H ^{13}C NMR HMBC spectrum (Figure SI 15, Figure SI 16) that show characteristic ^3J couplings between the CH_2 group and aromatic carbons and hydrogens.

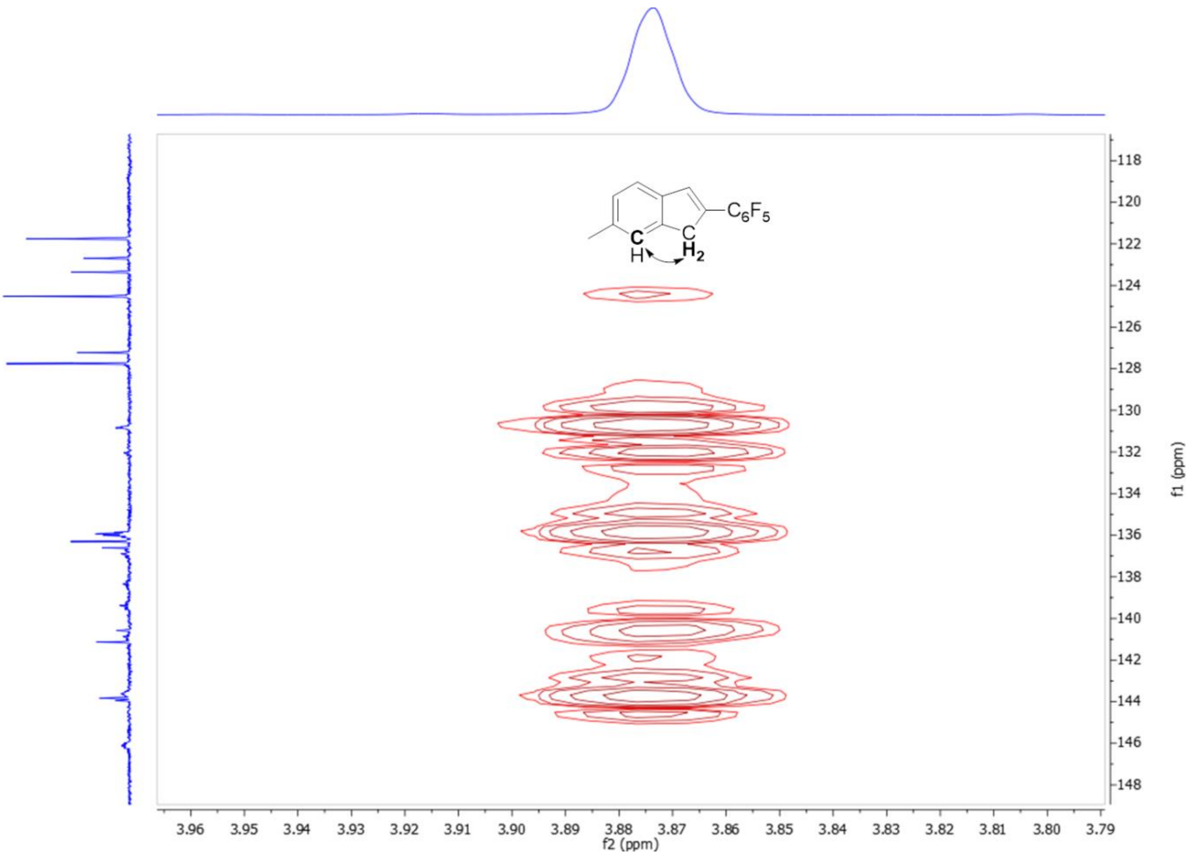


Figure SI 15: Excerpt of a ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene showing coupling between the hydrogens of the CH$_2$ group with an aromatic carbon (101 MHz, chloroform-*d*).

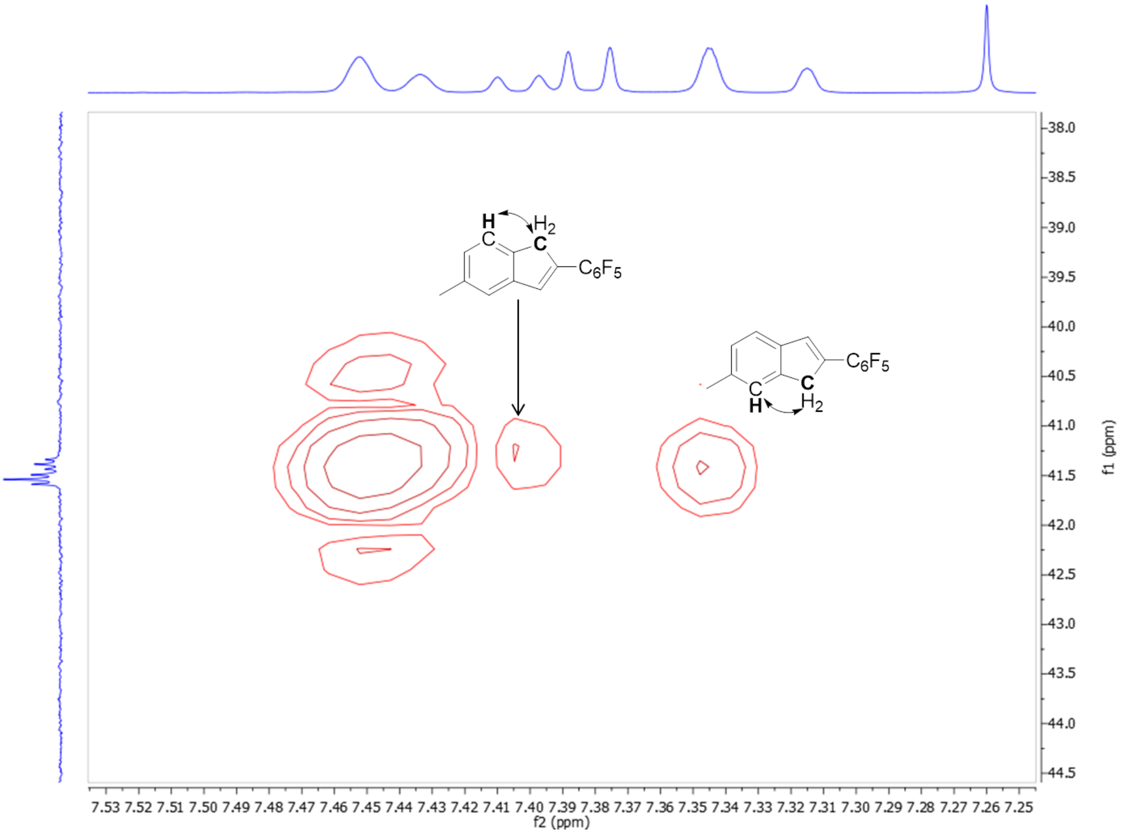
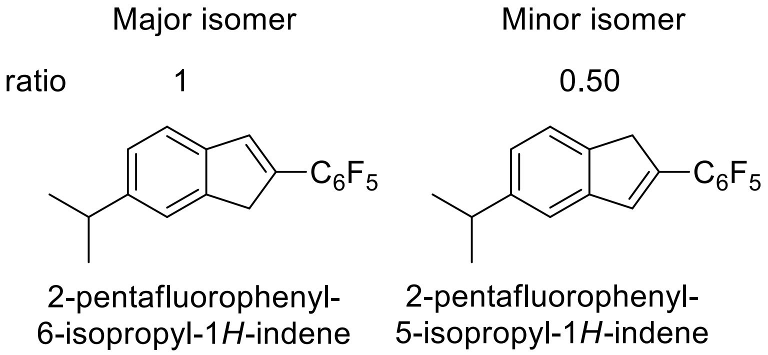


Figure SI 16: Excerpt of a ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene showing coupling between the carbon of the CH_2 group with an aromatic hydrogen (101 MHz, chloroform-*d*).

5.3.1 2-Pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene

2-Pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene were synthesized using general procedure B from 4-isopropylphenylallene (158.2 mg, 1.0 mmol, 2.0 eq.). The product was isolated in 62 % yield (100.6 mg, 0.31 mmol) as a 1 : 0.50 mixture as a colourless solid.



The product is a mixture of two isomers which could not be separated by column chromatography. The assignment of the isomers was done using 1D and 2D NMR spectroscopy analogous as described in chapter 5.3.3.4.

5.3.1.1 NMR data of the major isomer, 2-pentafluorophenyl-6-isopropyl-1H-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.47 – 7.46 (br, 1H, C_{sp2}-*H*), 7.44 – 7.41 (m, 2H, Ar-*H*), 7.23 (dd, *J* = 7.9, 1.5 Hz, 1H, Ar-*H*), 3.90 (br, 2H, C*H*$_2$), 3.01 (hept, *J* = 6.9 Hz, 1H, *H*C(CH$_3$)$_2$), 1.33 (d, *J* = 6.9 Hz, 6H, HC(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 147.57 (s, Ar-*C*$_q$-CH(CH$_3$)$_2$), 143.82 (t, *J* = 2.5 Hz, Ar-*C*$_q$), 141.56 (s, Ar-*C*$_q$), 135.91 (td, *J* = 7.2, 2.1 Hz, *C*$_{sp2}$H), 131.02 (q, *J* = 2.9 Hz, Ar-*C*$_q$), 125.33 (s, Ar-*C*), 121.85 (s, Ar-*C*), 121.78 (s, Ar-*C*), 41.65 (t, *J* = 4.8 Hz, *C*H$_2$) , 34.49 (s, H*C*(CH$_3$)$_2$), 24.35 (s, HC(*C*H$_3$)$_2$).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively to the carbons of the pentafluorophenyl group.

^{19}F NMR (377 MHz, chloroform-*d*) δ -140.18 – -140.31 (m, 2F, o-*F*), -157.05 (t, *J* = 21.0 Hz, 1F, p-*F*), -162.82 – -162.97 (m, 2F, m-*F*).

5.3.1.2 NMR data of the major isomer, 2-pentafluorophenyl-5-isopropyl-1H-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.48 – 7.44 (m, 2H, C$_{sp2}$-*H*, Ar-*H*), 7.40 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 7.19 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar-*H*), 3.88 (br, 2H, C*H*$_2$), 3.01 (hept, *J* = 6.9 Hz, 1H, *H*C(CH$_3$)$_2$), 1.33 (d, *J* = 6.9 Hz, 6H, HC(C*H*$_3$)$_2$).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups.

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 147.99 (s, Ar-*C*$_q$-CH(CH$_3$)$_2$), 143.94 (s, Ar-*C*$_q$), 141.02 (t, *J* = 2.5 Hz, Ar-*C*$_q$), 136.19 (td, *J* = 7.1, 1.9 Hz, *C*$_{sp2}$H), 131.99 (q, *J* = 2.8 Hz, Ar-*C*$_q$), 124.85 (s, Ar-*C*), 123.47 (s, Ar-*C*), 119.98 (s, Ar-*C*), 41.40 (t, *J* = 4.8 Hz, *C*H$_2$), 34.34 (s, H*C*(CH$_3$)$_2$), 24.41 (s, *H*C(*C*H$_3$)$_2$)

^{19}F NMR (377 MHz, Chloroform-*d*) δ -140.06 – -140.19 (m, 2F, *o*-F), -156.81 (t, *J* = 21.0 Hz, 1F, *p*-F), -162.74 – -162.88 (m, 2F, *m*-F).

5.3.1.3 APCI-HRMS and elemental analysis of a mixture of the major and minor isomer

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{18}H_{13}F_5H^+$: 325.1010; found: 325.1012

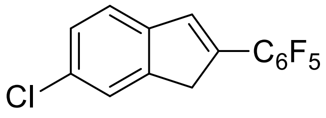
Anal. Calcd for $C_{18}H_{13}F_5$: C, 66.26; H, 4.11. Found: C, 66.67; H, 4.04.

5.3.2 2-Pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene

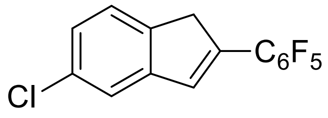
2-Pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene were synthesized according to general procedure C from 4-chlorophenylallene (150.6 mg, 1.0 mmol, 2.0 eq.). The product was isolated in 45 % yield (71.5 mg, 0.23 mmol) as a 1 : 0.24 mixture as a colourless solid.

Major isomer Minor isomer

ratio 1 0.24



2-pentafluorophenyl-6-chloro-1*H*-indene



2-pentafluorophenyl-5-chloro-1*H*-indene

The product is a mixture of two isomers, which could not be separated by column chromatography. The assignment of the isomers was done using 1D and 2D NMR spectroscopy analogous as described in chapter 5.3.3.4.

5.3.2.1 NMR data of the major isomer, 2-pentafluorophenyl-6-chloro-1H-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.48 (br, 1H, Ar-*H*), 7.43 (br, 1H, $C_{sp2}H$), 7.39 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 7.24 (dd, *J* = 7.9, 1.9 Hz, 1H, Ar-*H*), 3.89 (br, 2H, CH_2).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 144.99 (t, *J* = 2.6 Hz, Ar-C_q), 142.15 (s, Ar-C_q), 135.09 (td, *J* = 7.4, 2.2 Hz, $C_{sp2}H$), 132.37 (Ar-C_q), 127.27 (s, Ar-*C*), 124.10 (s, Ar-*C*), 122.81 (s, Ar-*C*), 41.64 (t, *J* = 5.0 Hz, CH_2).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively to the carbons of the pentafluorophenyl group. The quarternary aromatic carbon bound to the chlorine could not be unequivocally identified in the ^{13}C{^{1}H} NMR spectrum.

^{19}F NMR (377 MHz, chloroform-*d*) δ -139.83 – -139.95 (m, 2F, o-*F*), -155.89 (t, *J* = 21.0 Hz, 1F, p-*F*), -162.36 – -162.51 (m, 2F, m-*F*).

5.3.2.2 NMR data of the major isomer, 2-pentafluorophenyl-5-chloro-1H-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.45 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.42 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.40 (br, 1H, $C_{sp2}H$), 7.24 (dd, *J* = 7.9, 1.9 Hz, 1H, Ar-*H*), 3.88 (br, 2H, CH_2).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 145.28 (s, Ar-C_q), 141.52 (t, *J* = 2.5 Hz, Ar-C_q), 134.89 (td, *J* = 7.2, 1.8 Hz), 132.93 (s, Ar-C_q), 126.21 (s, Ar-*C*), 124.58 (s, Ar-*C*), 122.10 (s, Ar-*C*), 41.36 (t, *J* = 5.1 Hz, CH_2).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups. The quaternary aromatic carbon bound to the chlorine could not be unequivocally identified in the ^{13}C{^{1}H} NMR spectrum.

^{19}F NMR (377 MHz, chloroform-*d*) δ -139.68 – -139.79 (m, 2F, o-*F*), -155.60 (t, *J* = 21.0 Hz, 1F, p-*F*), -162.38 (t, *J* = 6.9 Hz, 2F, m-*F*).

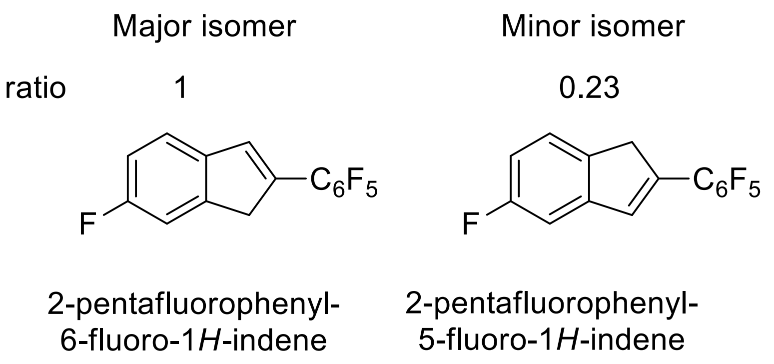
5.3.2.3 APCI-HRMS and elemental analysis of a mixture of the major and minor isomer

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{15}H_6ClF_5H^+$: 317.0151; found: 317.0153

Anal. Calcd for $C_{15}H_6ClF_5H^+$: C, 56.90; H, 1.91. Found: C, 57.22; H, 1.92.

5.3.1 2-Pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene

2-Pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene were synthesized according to general procedure C from 4-fluorophenylallene (134.2 mg, 1.0 mmol, 2.0 eq.). The product was isolated in 58 % yield (87.8 mg, 0.29 mmol) as a 1 : 0.23 mixture as a colourless solid.



The product is a mixture of two isomers, which could not be separated by column chromatography. The assignment of the isomers was done using 1D and 2D NMR spectroscopy analogous as described in chapter 5.3.3.4.

5.3.1.1 NMR data of the major isomer, 2-pentafluorophenyl-6-fluoro-1H-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.46 – 7.39 (m, 2H, C_{sp2}-*H*, Ar-*H*), 7.22 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-*H*), 7.04 (ddd, *J* = 10.6, 8.4, 2.4 Hz, 1H, Ar-*H*), 3.90 (br, 2H, CH_2).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 162.26 (d, *J* = 245.2 Hz, Ar-C_q-F), 145.54 (dt, *J* = 9.0, 2.6 Hz, Ar-C_q), 139.69 (s, Ar-C_q), 135.12 (t, *J* = 7.4 Hz, C_{sp2}H), 131.62 (d, *J* = 3.9 Hz, Ar-C_q), 122.83 (d, *J* = 8.8 Hz, Ar-*C*), 114.12 (d, *J* = 23.1 Hz, Ar-*C*), 111.34 (d, *J* = 23.5 Hz, Ar-*C*), 41.86 (td, *J* = 5.0, 2.6 Hz, *C*H_2).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively to the carbons of the pentafluorophenyl group.

^{19}F NMR (377 MHz, chloroform-*d*) δ -115.78 (s, 1F, C*F*), -140.13 – -140.26 (m, 2F, o-*F*), -156.38 (t, *J* = 21.0 Hz, 1F, p-*F*), -162.51 – -162.68 (m, 2F, m-*F*).

5.3.1.2 NMR data of the major isomer, 2-pentafluorophenyl-5-fluoro-1*H*-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.46 – 7.41 (m, 2H, C_{sp2}-*H*, Ar-*H*), 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H, Ar-*H*), 6.98 (ddd, *J* = 9.5, 8.2, 2.4 Hz, 1H, Ar-*H*), 3.87 (d, *J* = 1.6 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 162.55 (d, *J* = 242.9 Hz, Ar-C_q-F), 145.32 (d, *J* = 9.4 Hz, Ar-C_q), 138.82 – 138.66 (m, Ar-C_q), 135.42 - 135.16 (m, C_{sp2}H), 134.28 – 134.03 (m, Ar-C_q), 124.48 (d, *J* = 9.0 Hz, Ar-*C*), 113.16 (d, *J* = 23.2 Hz, Ar-*C*), 108.88 (d, *J* = 23.2 Hz, Ar-*C*), 41.15 (t, *J* = 4.9 Hz, CH_2).

Remark: The ^{13}C{^{1}H} NMR spectrum shows broad signals with low intensity in the aromatic region which can be tentatively assigned to the pentafluorophenyl groups. The quaternary aromatic carbon bound to the chlorine could not be unequivocally identified in the ^{13}C{^{1}H} NMR spectrum.

^{19}F NMR (377 MHz, chloroform-*d*) δ -116.48 (s, 1F, C*F*), -139.70 – -139.97 (m, 2F, o-*F*), -155.79 (t, *J* = 21.0 Hz, 1F, p-*F*)), -162.34 – -162.51 (m, 2F, m-*F*).

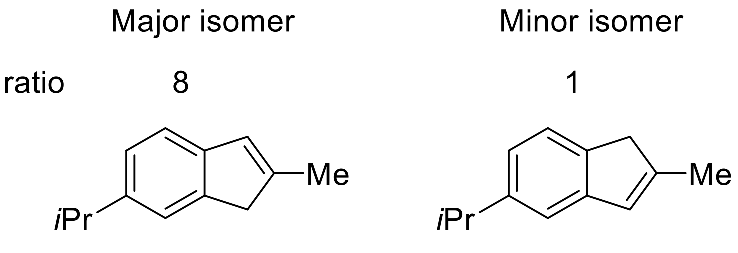
5.3.1.3 APCI-HRMS and elemental analysis of a mixture of the major and minor isomer

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{15}H_6F_6H^+$: 301.0446; found: 301.0449

Anal. Calcd for $C_{15}H_6F_6H^+$: C, 56.90; H, 1.91. Found: C, 60.01; H, 2.01.

5.3.2 2-Methyl-6-(isopropyl)-1*H*-indene and 2-methyl-5-(isopropyl)-1*H*-indene

Inside a nitrogen-filled glovebox $MeB(C_6F_5)_2$ (90.0 mg, 0.25 mmol, 1.0 eq.) was dissolved in dry DCM (3 mL) in a vial. *p*-Isopropylallene (79.1 mg, 0.50 mmol, 2.0 eq.) was added and the reaction mixture was transferred to a Schlenk tube with J. Young valve. The mixture was heated to 60 °C in an oil-bath for 72 h. Pyridine (40.3 µL, 0.98 g/mL, 0.50 mmol, 2.0 eq.) was added and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using SiO_2 and *n*-hexane as eluent. The product was obtained as a colorless oil (13 mg, 0.075 mmol, 30 %).



2-methyl-
6-(isopropyl)-1*H*-indene

2-methyl-
5-(isopropyl)-1*H*-indene

The product is a mixture of two isomers that could not be separated by column chromatography. The major product was identified using the 1D and 2D spectra. Only the NMR shifts of the major isomer are assigned.

5.3.2.1 NMR data of the major isomer2-methyl-6-(isopropyl)-1H-indene

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.24 (m, 1H, Ar-*H*), 7.16 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.07 (dd, *J* = 7.7, 2.2 Hz, 1H, Ar-*H*), 6.44 (s, 1H, C*H*), 3.25 (s, 2H, CH_2), 2.91 (h, *J* = 7.0 Hz, 1H, C*H*), 2.12 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.25 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, chloroform-*d*) δ 145. 17 (Ar-C_q), 144.38 (Ar-C_q), 143.76 (Ar-C_q), 143.62 (Ar-C_q), 126.87 (*C*H), 124.37 (Ar-*C*H), 121.57 (Ar-*C*H), 119.37 (Ar-*C*H), 42.64 (CH_2), 34.12 ($CH(CH_3)_2$), 24.37 ($CH(CH_3)_2$), 16.77 (CH_3).

5.3.2.2 APCI-HRMS of a mixture of the major and minor isomer

HRMS (APCI) m/z [$M+H^+$] calc. for $C_{13}H_{16}H^+$: 173.1325; found: 173.1322

5.4 Reaction of phenylallene and BCF with norbornene as Piers' borane scrambler

Inside the glovebox BCF (256.0 mg, 0.50 mmol, 1.0 eq.) and norbornene (47.1 mg, 0.50 mmol, 1.0 eq.) were dissolved in DCM (5 mL) in a 10 mL glass vial with a small stirring rod. Phenylallene (63.8 µL, 0.91 g/mL, 0.50 mmol, 1.0 eq.) was added and the reaction mixture was stirred for 45 min at room temperature. Pyridine (80.5 µL, 0.98 g/mL, 1.0 mmol, 2.0 eq.) was added. The vial was taken out of the glovebox and the crude product was purified by column chromatography using SiO_2 and *n*-hexane as eluent. The product was obtained as a colorless solid (81.2 mg, 0.28 mmol, 58 %).

The spectroscopic data agree with the ones reported in chapter 5.5.1. In spite of repeated column chromatography, trace amounts of an unknown impurity could not be removed from the product (Figure SI 17).

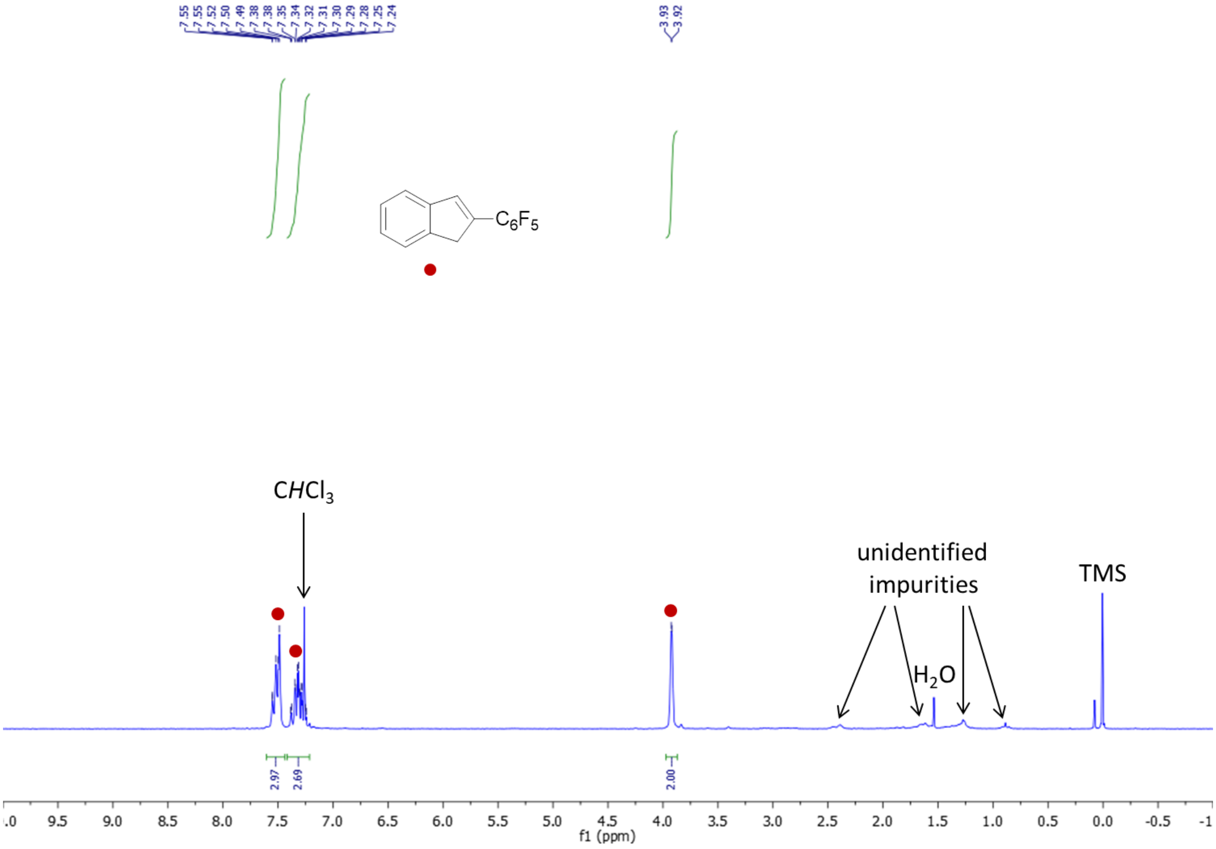


Figure SI 17: ^1H NMR spectrum of 2-pentafluorophenylindene obtained after column chromatography of the reaction of phenylallene, BCF and norbornene as Piers' borane scrambler (200 MHz, chloroform-*d*).

5.5 Additional NMR spectra

5.5.1 NMR spectra of 2-pentafluorophenylindene

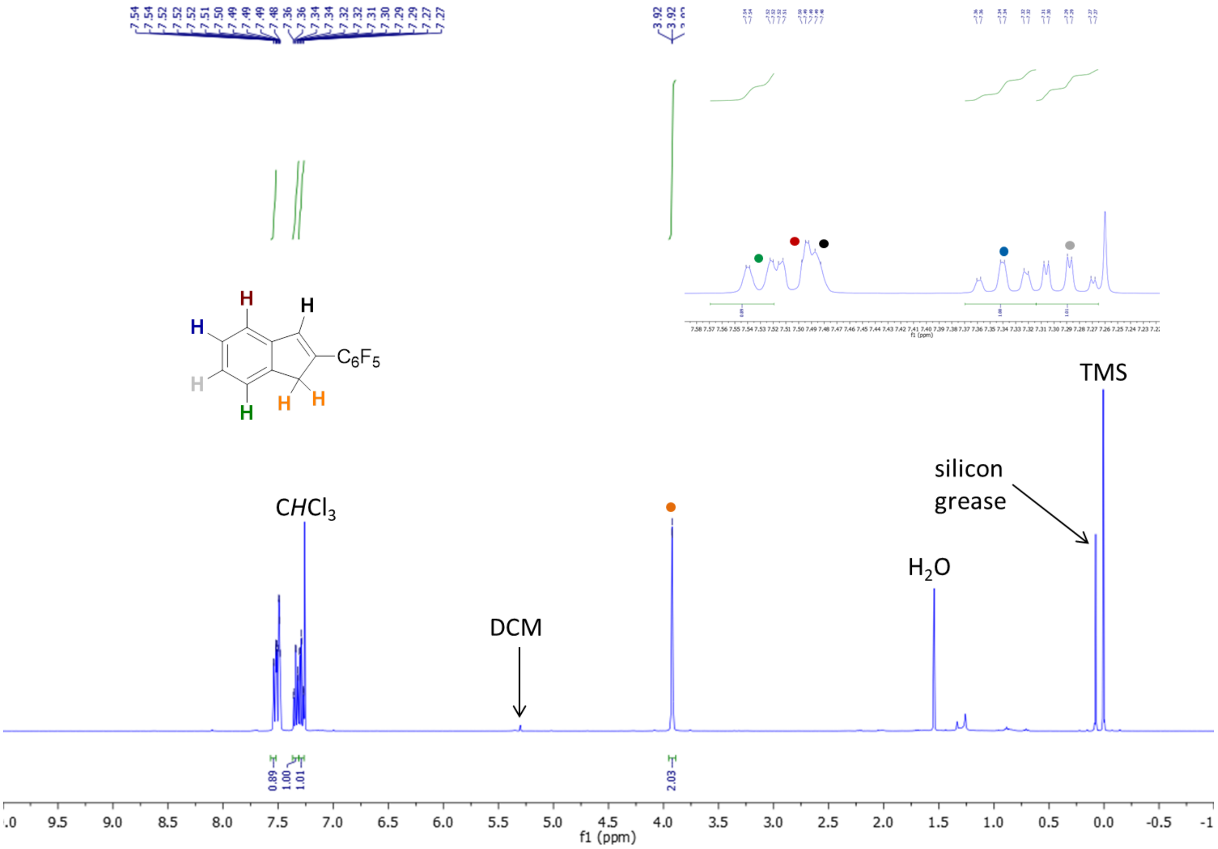


Figure SI 18: ^1H NMR spectrum of 2-(pentafluorobenzene)indene with low field excerpt (400 MHz, chloroform-*d*).

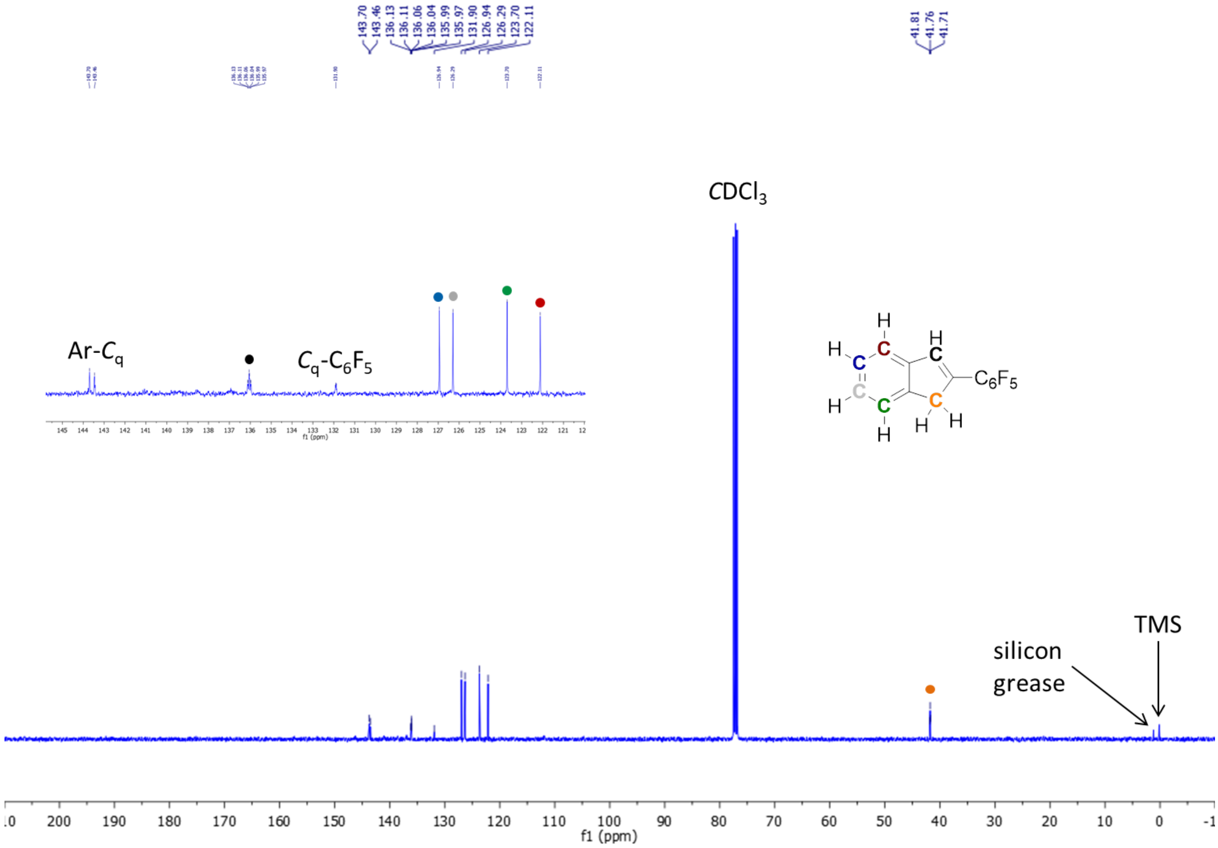


Figure SI 19: ^{13}C NMR spectrum of 2-(pentafluorobenzene)indene with low field excerpt (101 MHz, chloroform-*d*).

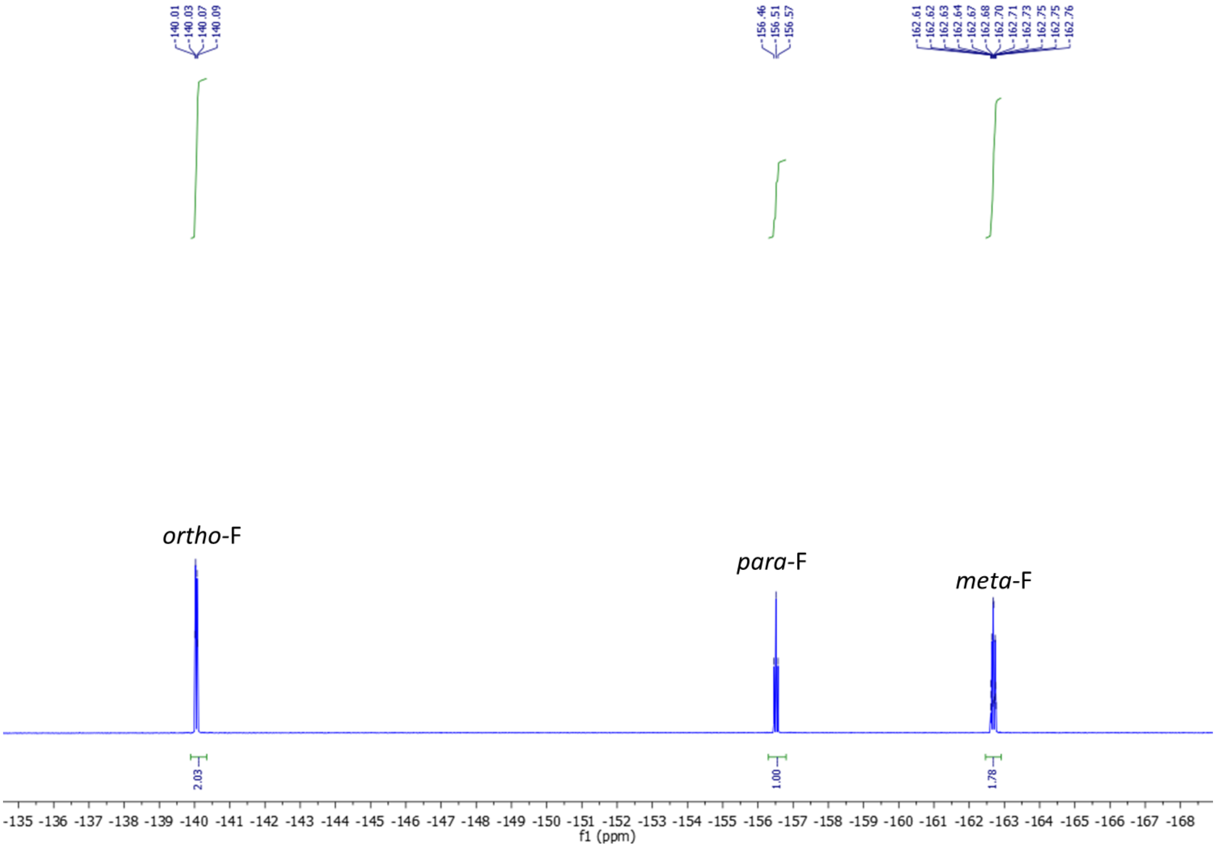


Figure SI 20: ^{19}F NMR spectrum of 2-(pentafluorobenzene)indene (377 MHz, chloroform-*d*).

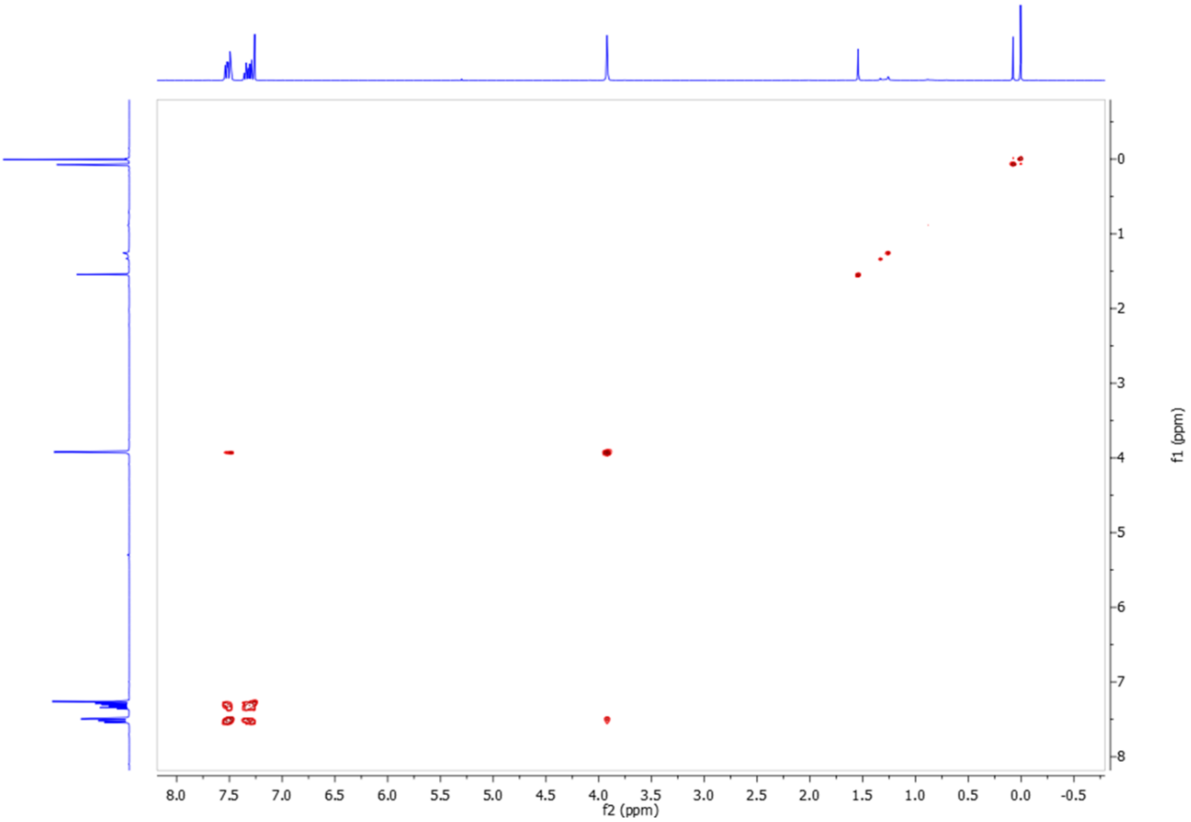


Figure SI 21: HH COSY NMR spectrum of 2-(pentafluorobenzene)indene (400 MHz, chloroform-*d*).

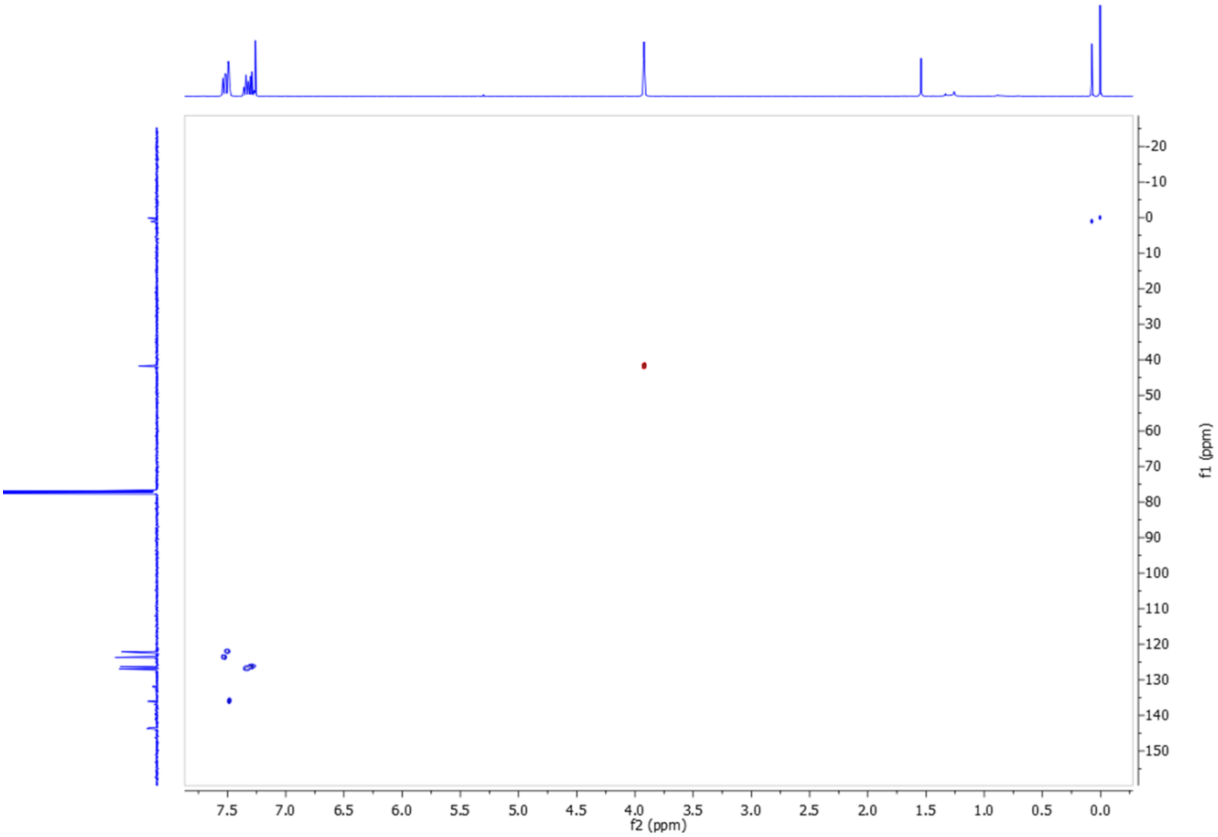


Figure SI 22: $^1H^{13}C$-HSQC spectrum of 2-(pentafluorobenzene)indene (101 MHz, chloroform-*d*).

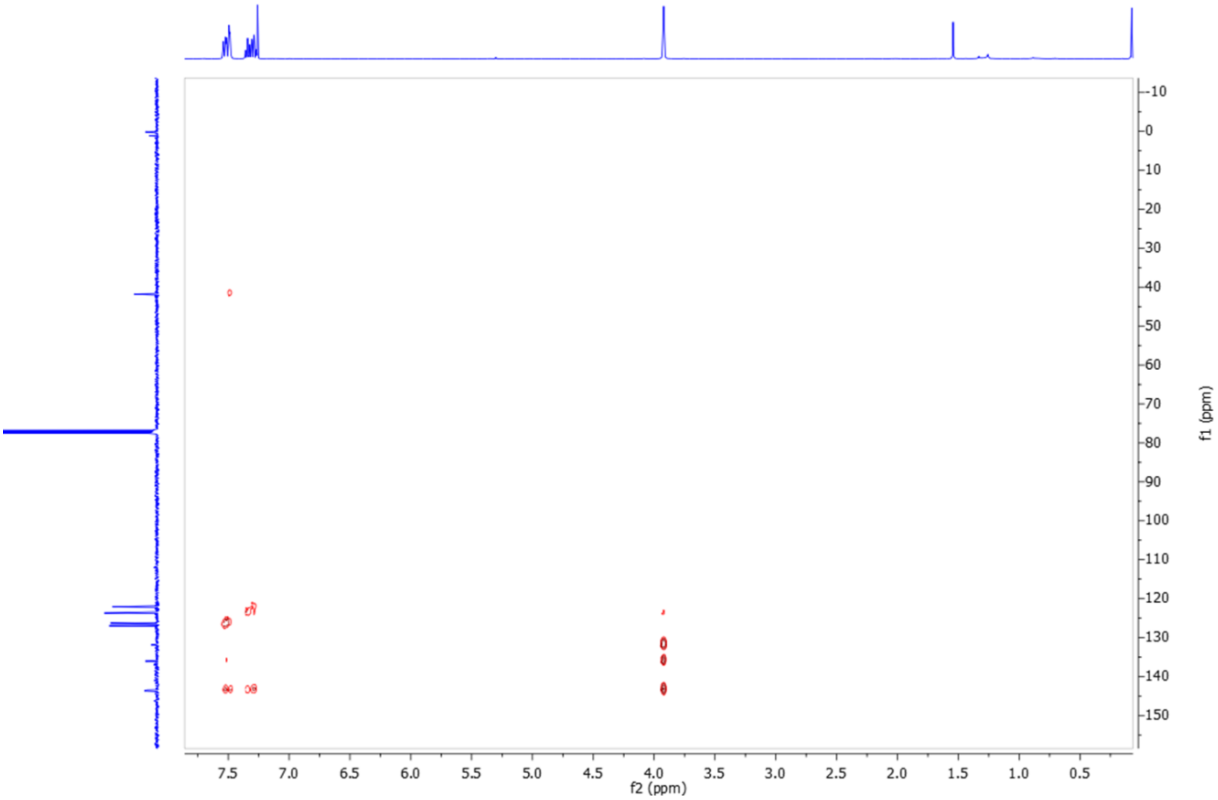


Figure SI 23: ^{1}H ^{13}C HMBC spectrum of 2-(pentafluorobenzene)indene (101 MHz, chloroform-*d*).

5.5.2 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene

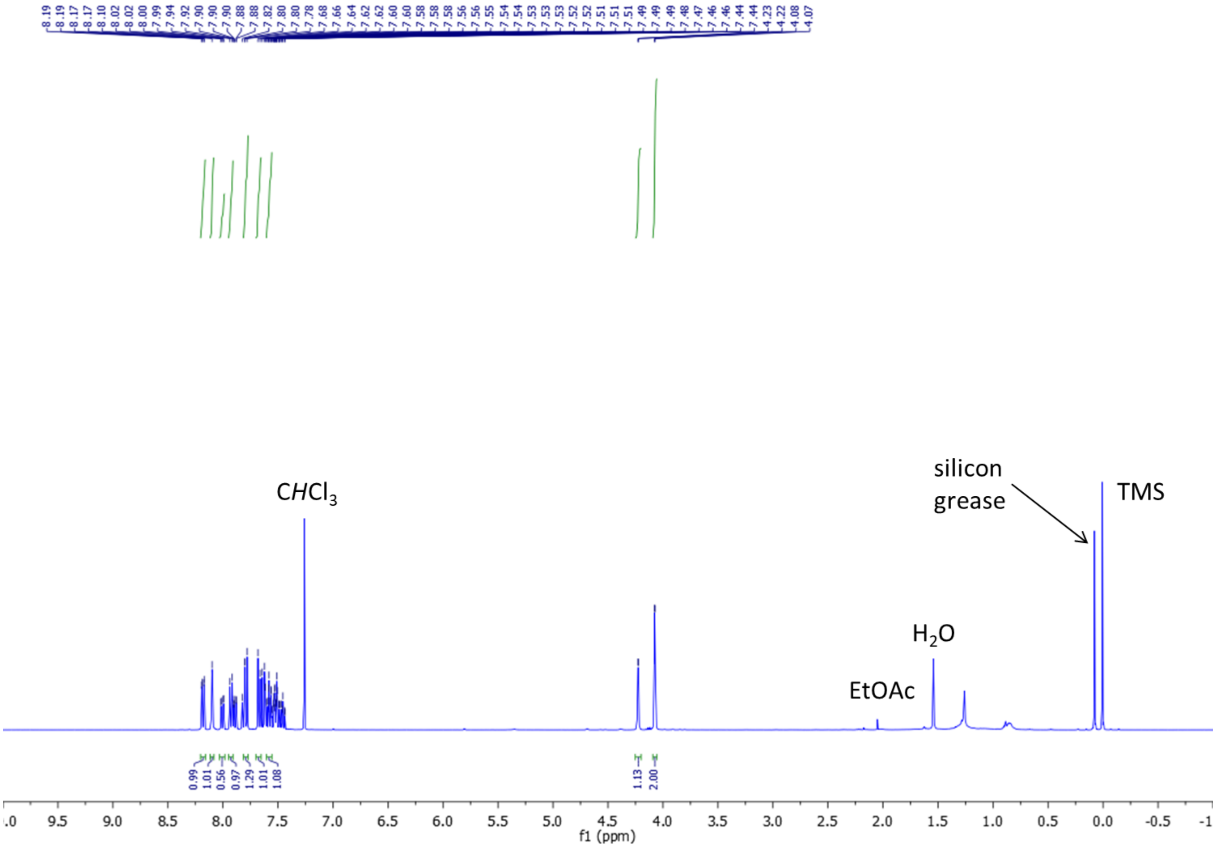


Figure SI 24: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene (400 MHz, chloroform-*d*).

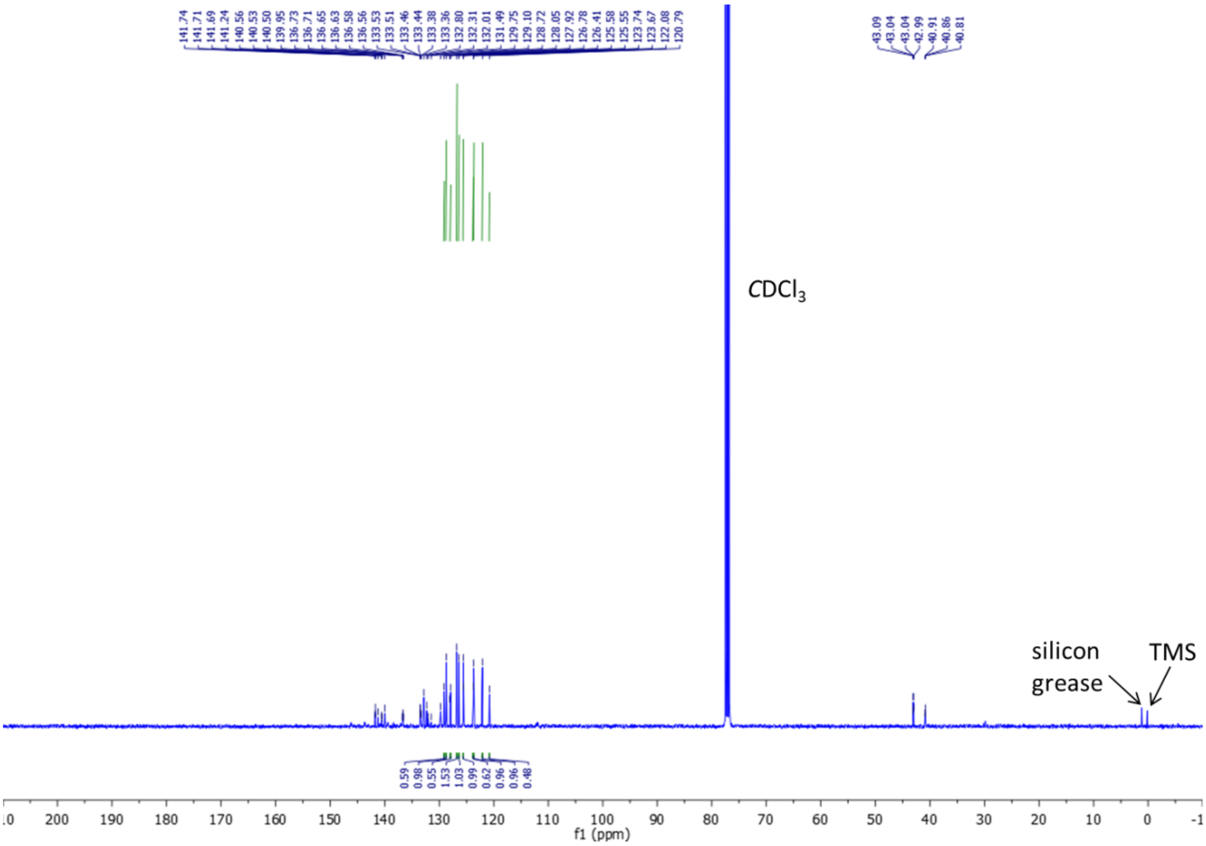


Figure SI 25: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene (101 MHz, chloroform-*d*).

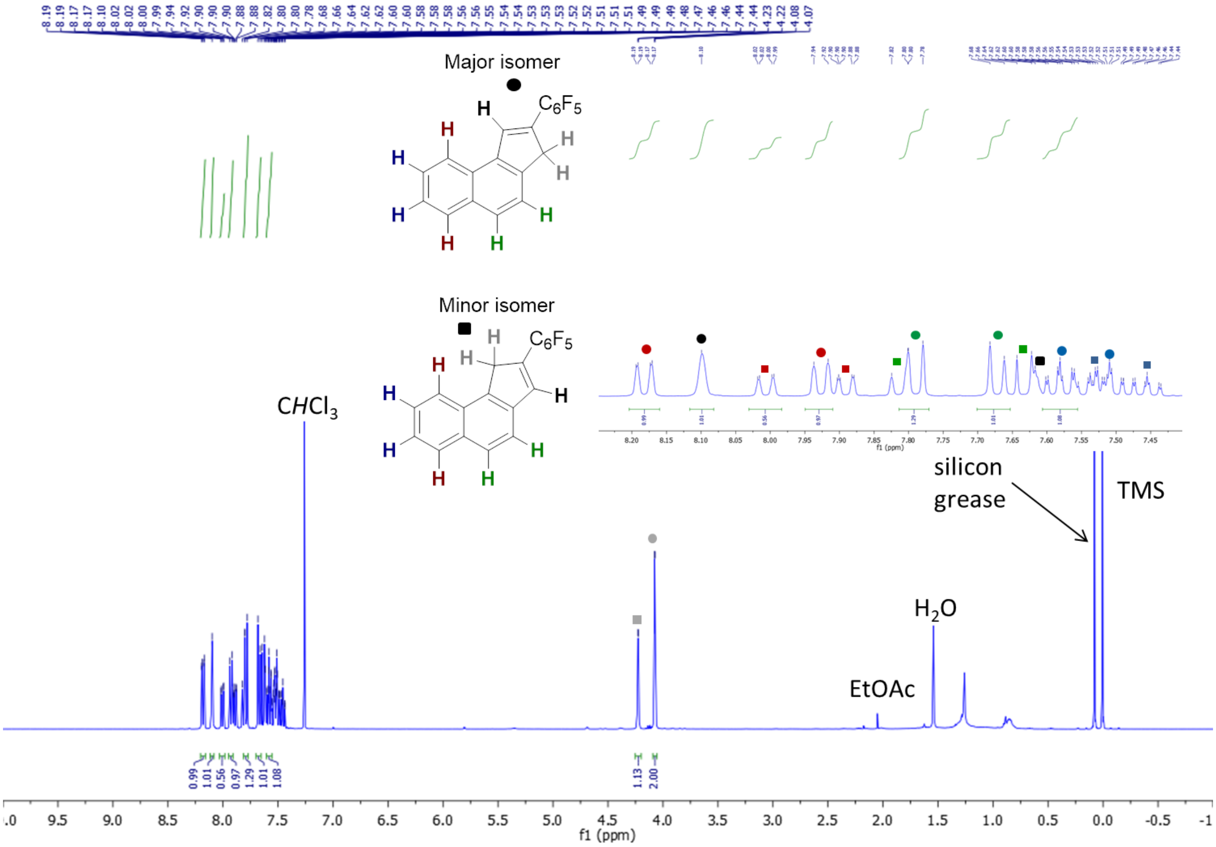


Figure SI 26: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene with low field excerpt and peak assignment (400 MHz, chloroform-*d*).

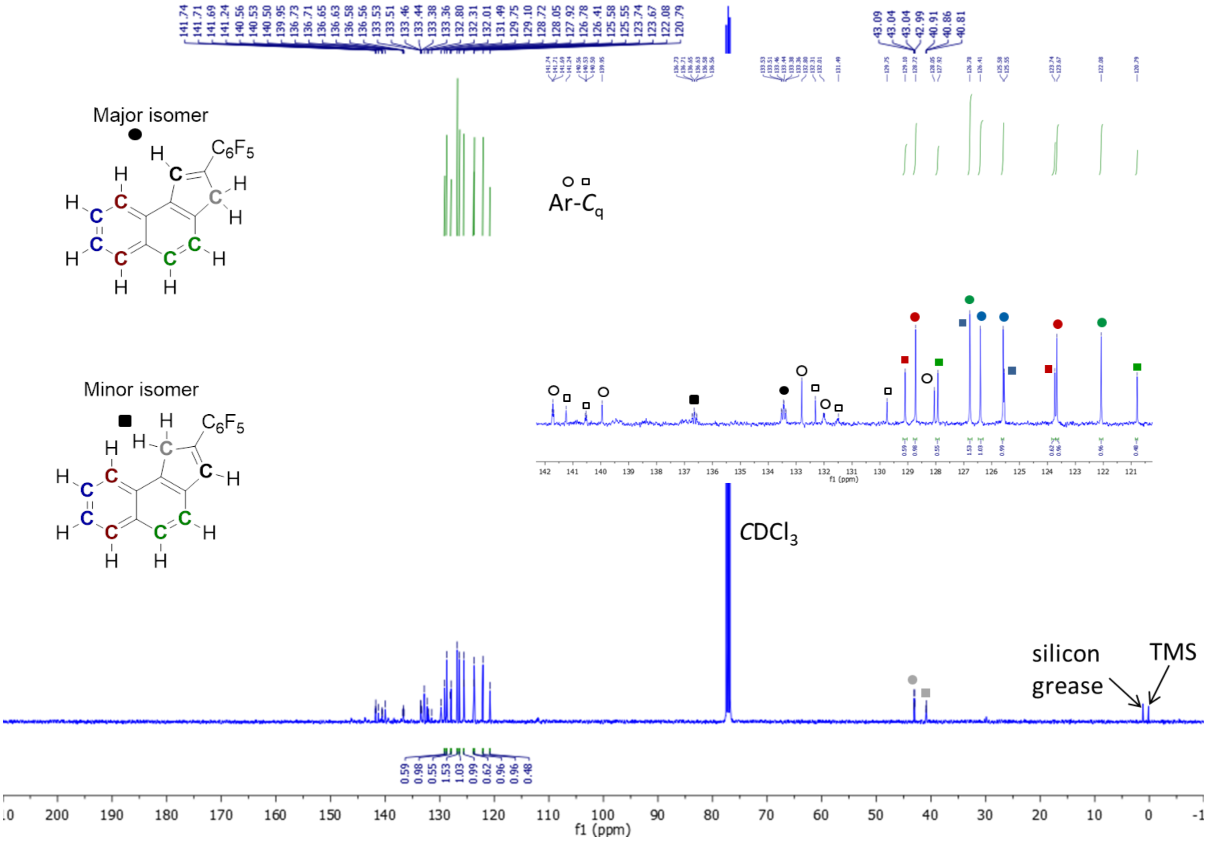


Figure SI 27: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene with low field excerpt and peak assignment (101 MHz, chloroform-*d*).

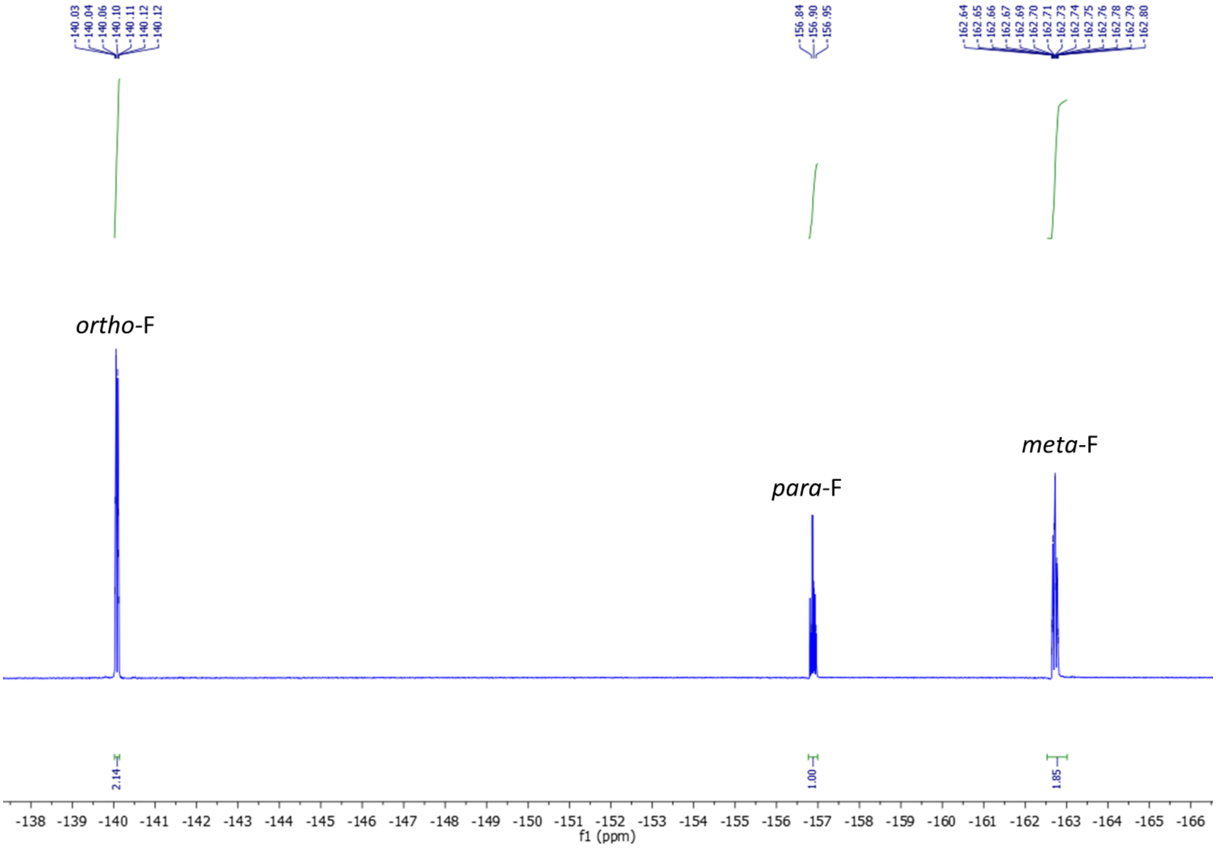


Figure SI 28: ^{19}F NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene (377 MHz, chloroform-*d*).

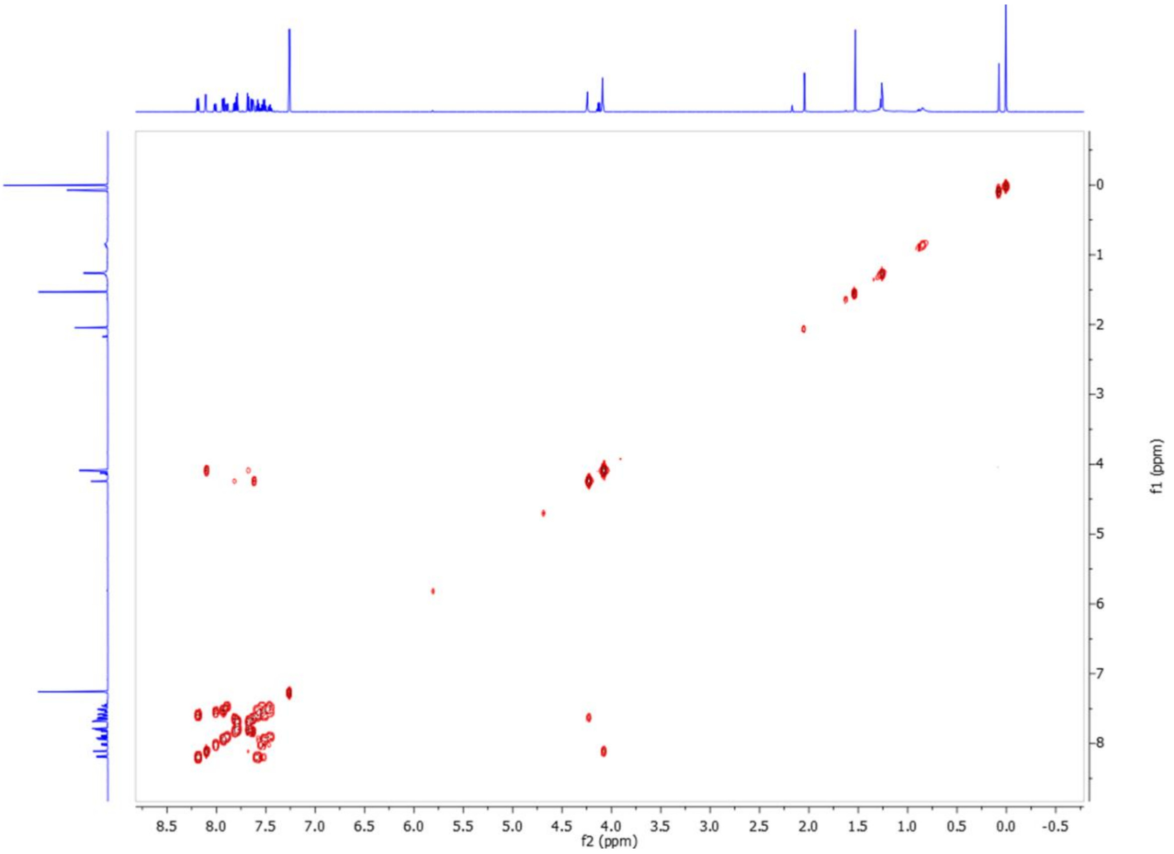


Figure SI 29: HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene (400 MHz, chloroform-*d*).

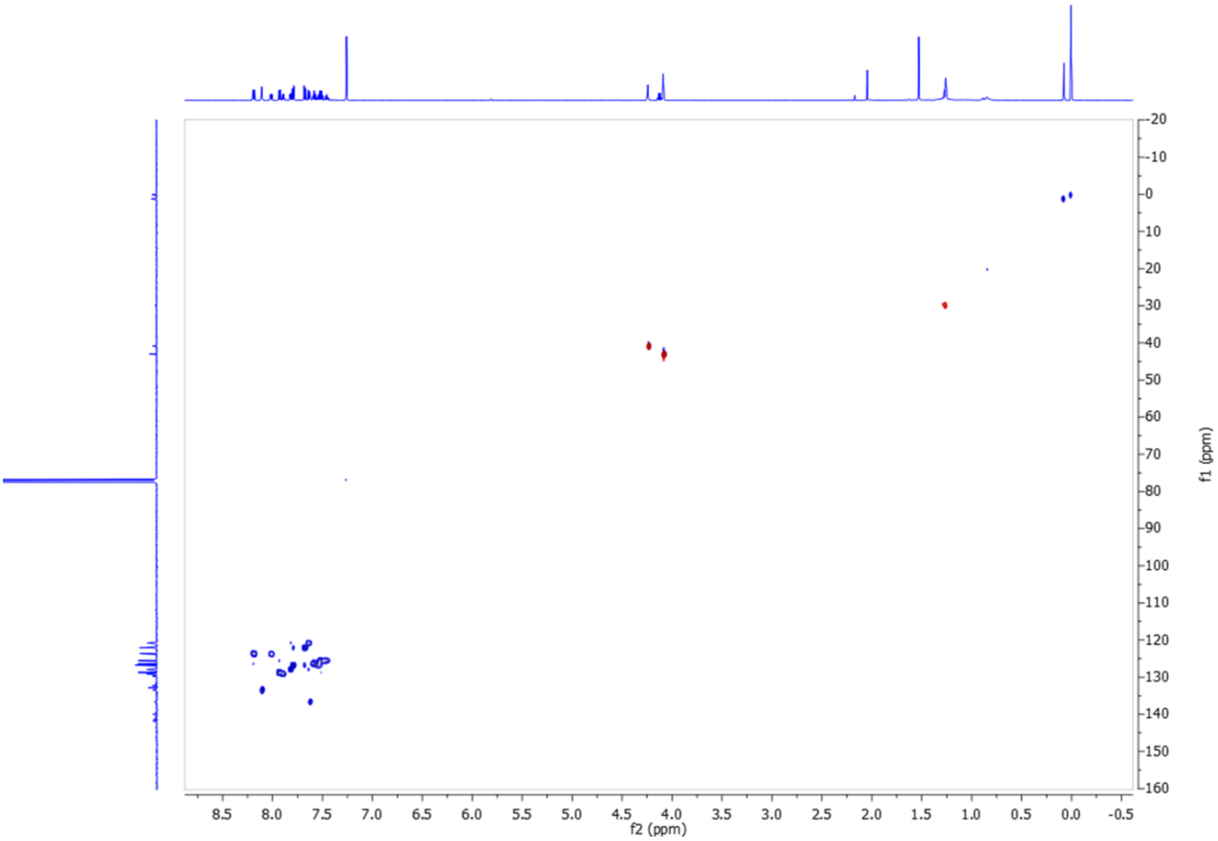


Figure SI 30: $^1H^{13}C$-HSQC spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene (101 MHz, chloroform-*d*).

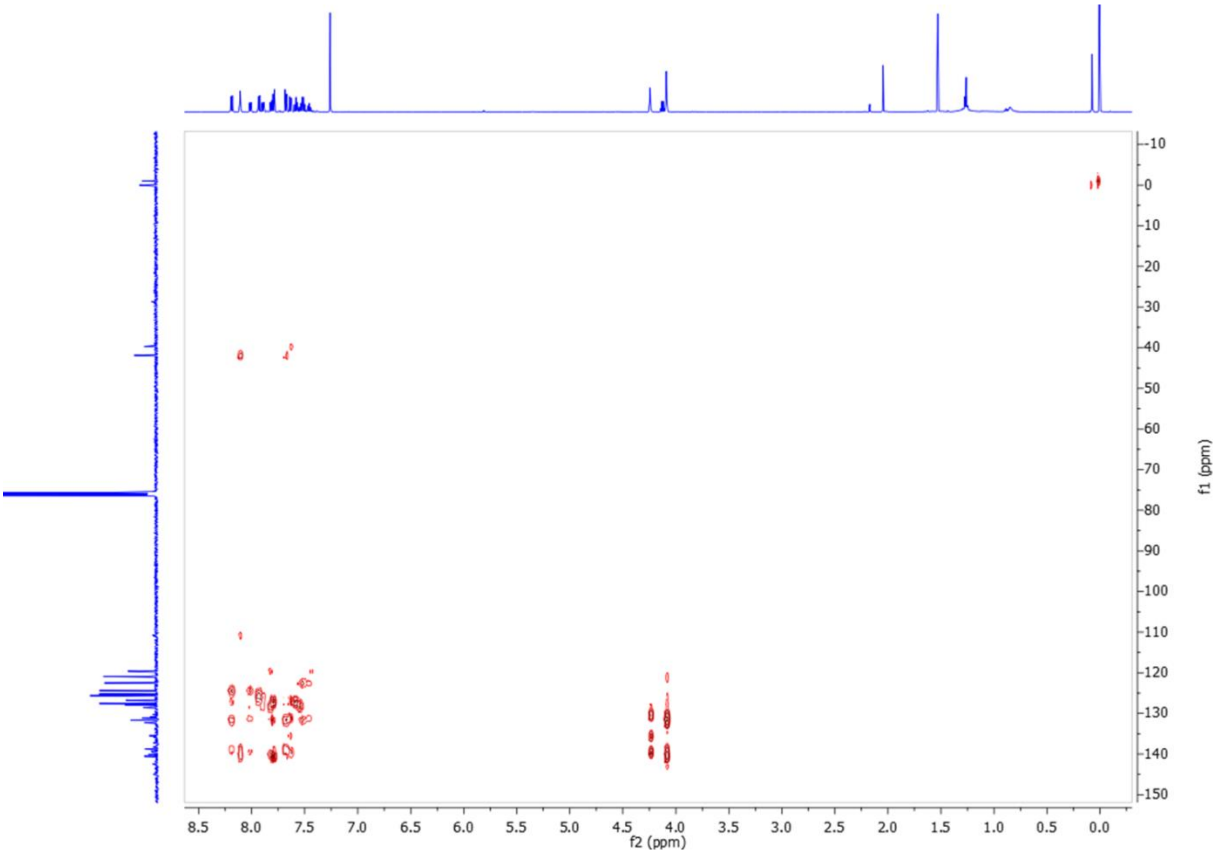


Figure SI 31: ^{1}H ^{13}C HMBC spectrum of a mixture of 2-pentafluorophenyl-3*H*-cyclopenta[a]naphthalene and 2-pentafluorophenyl-1*H*-cyclopenta[a]naphthalene (101 MHz, chloroform-*d*).

5.5.3 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene

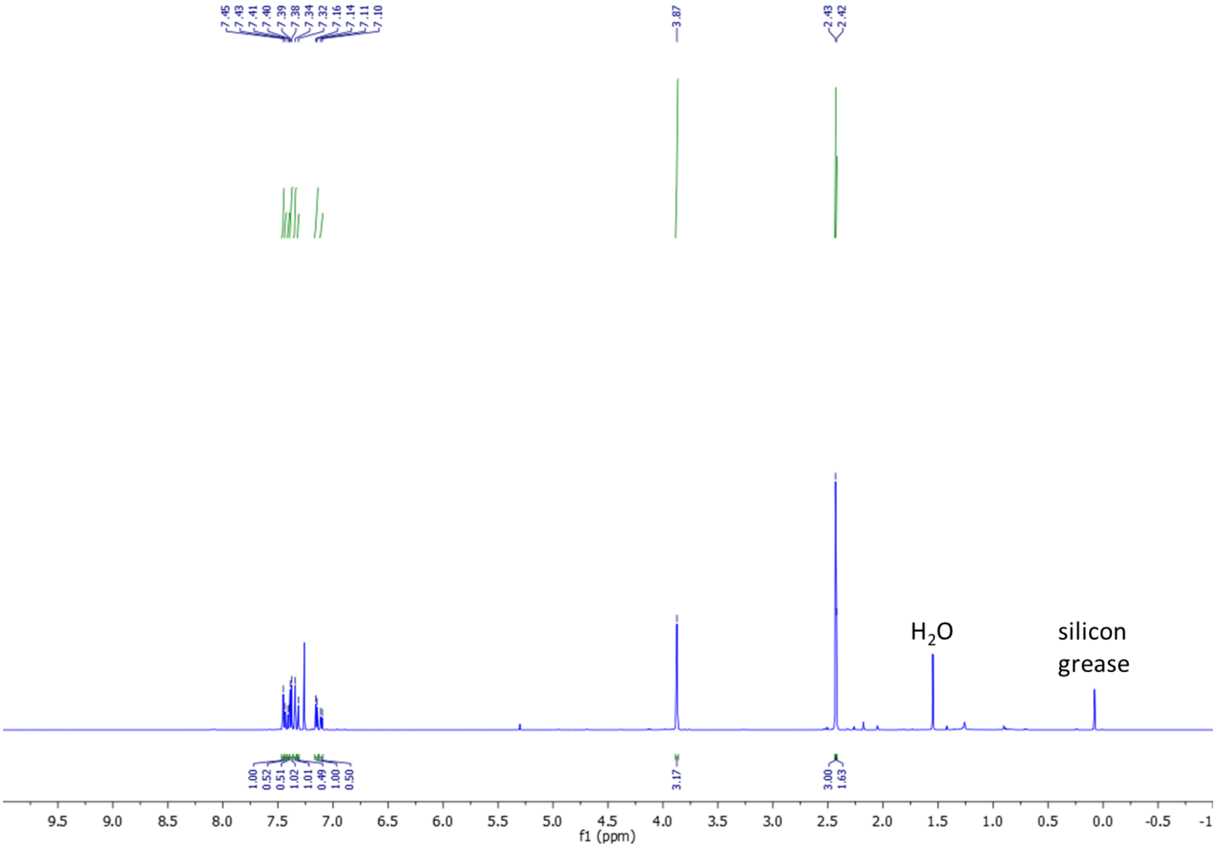


Figure SI 32: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene (600 MHz, chloroform-*d*).

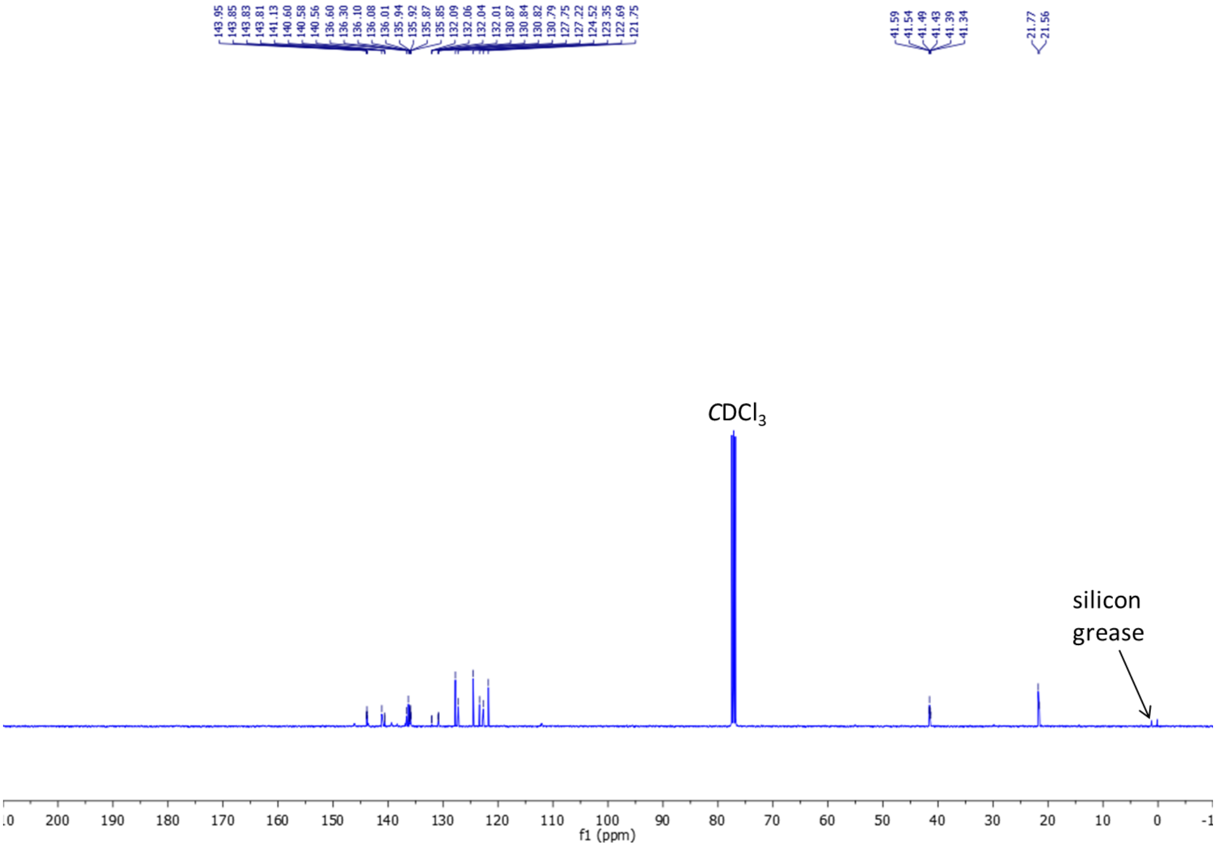


Figure SI 33: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene (101 MHz, chloroform-*d*).

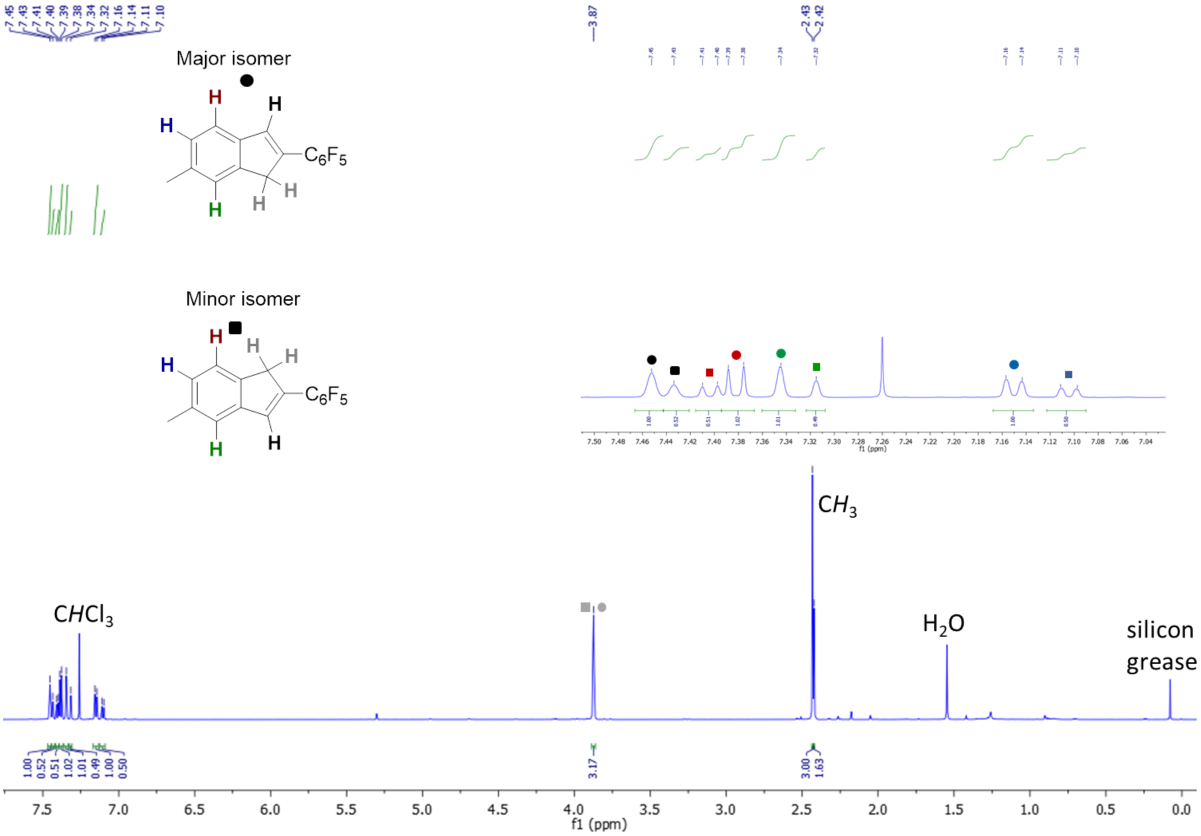


Figure SI 34: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene with low field excerpt and assignment of peaks (600 MHz, chloroform-*d*).

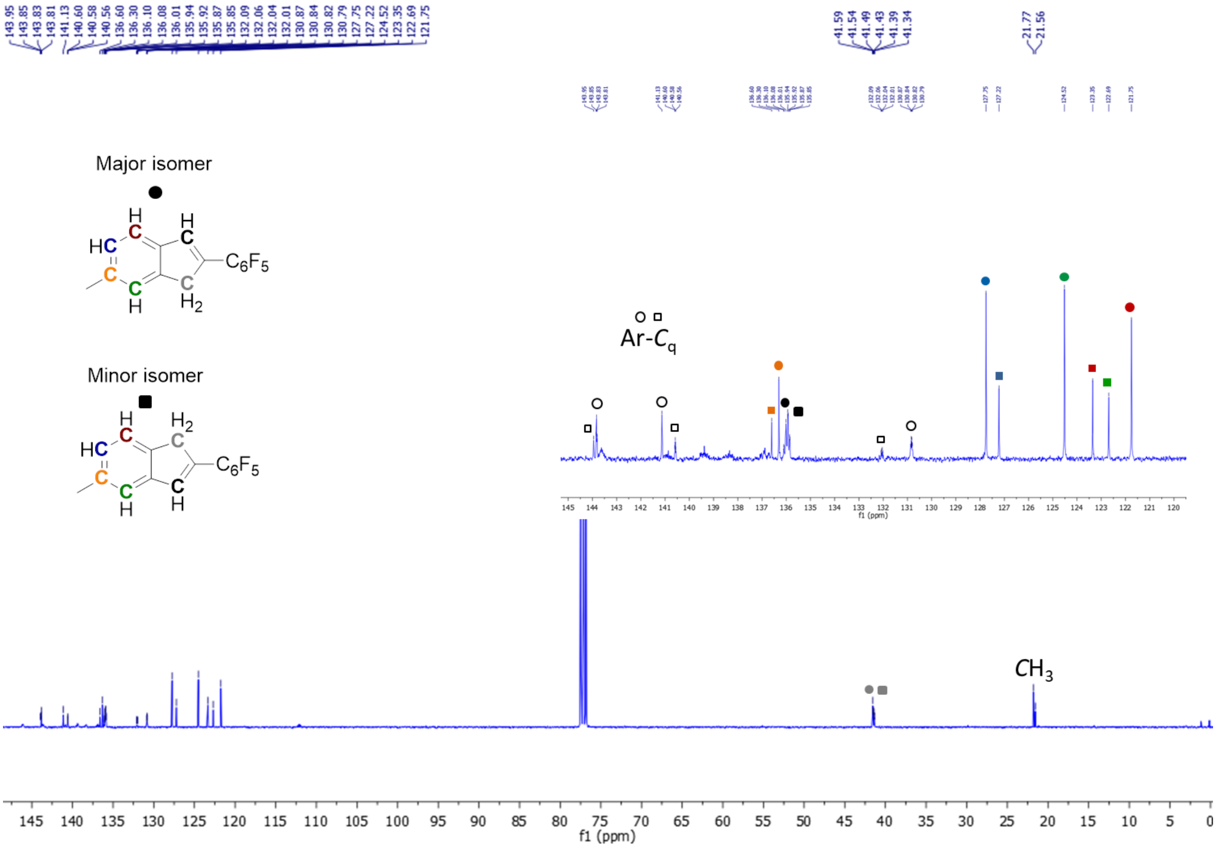


Figure SI 35: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene with low field excerpt and assignment of peaks (101 MHz, chloroform-*d*).

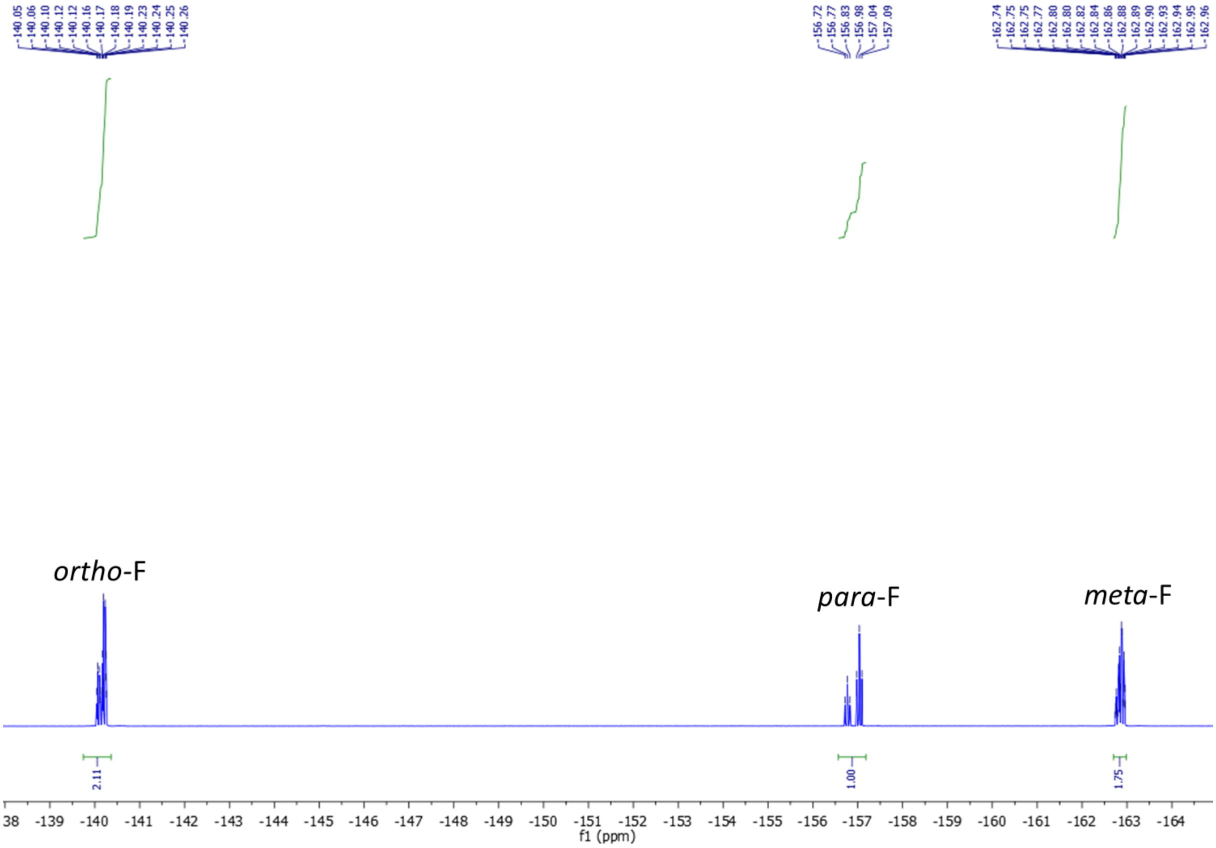


Figure SI 36: ^{19}F NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene (377 MHz, chloroform-*d*).

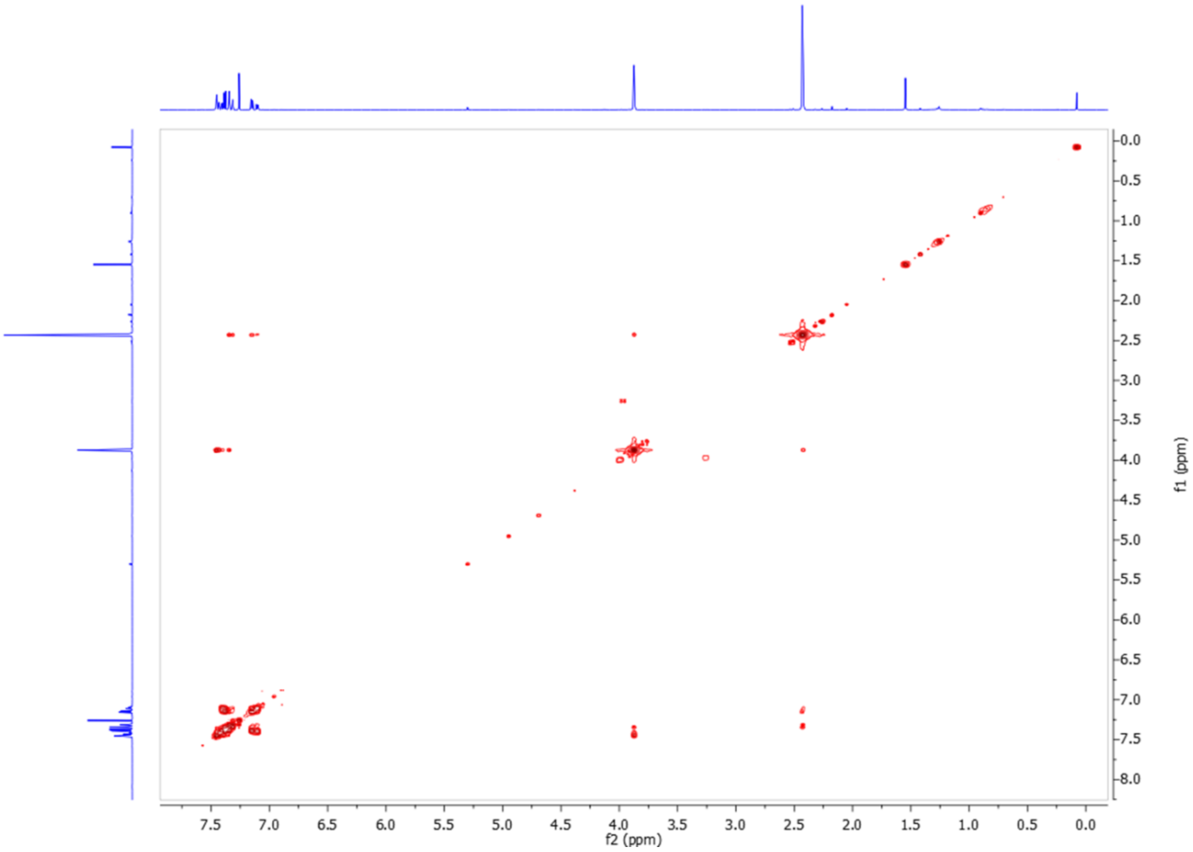


Figure SI 37: HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene (600 MHz, chloroform-*d*).

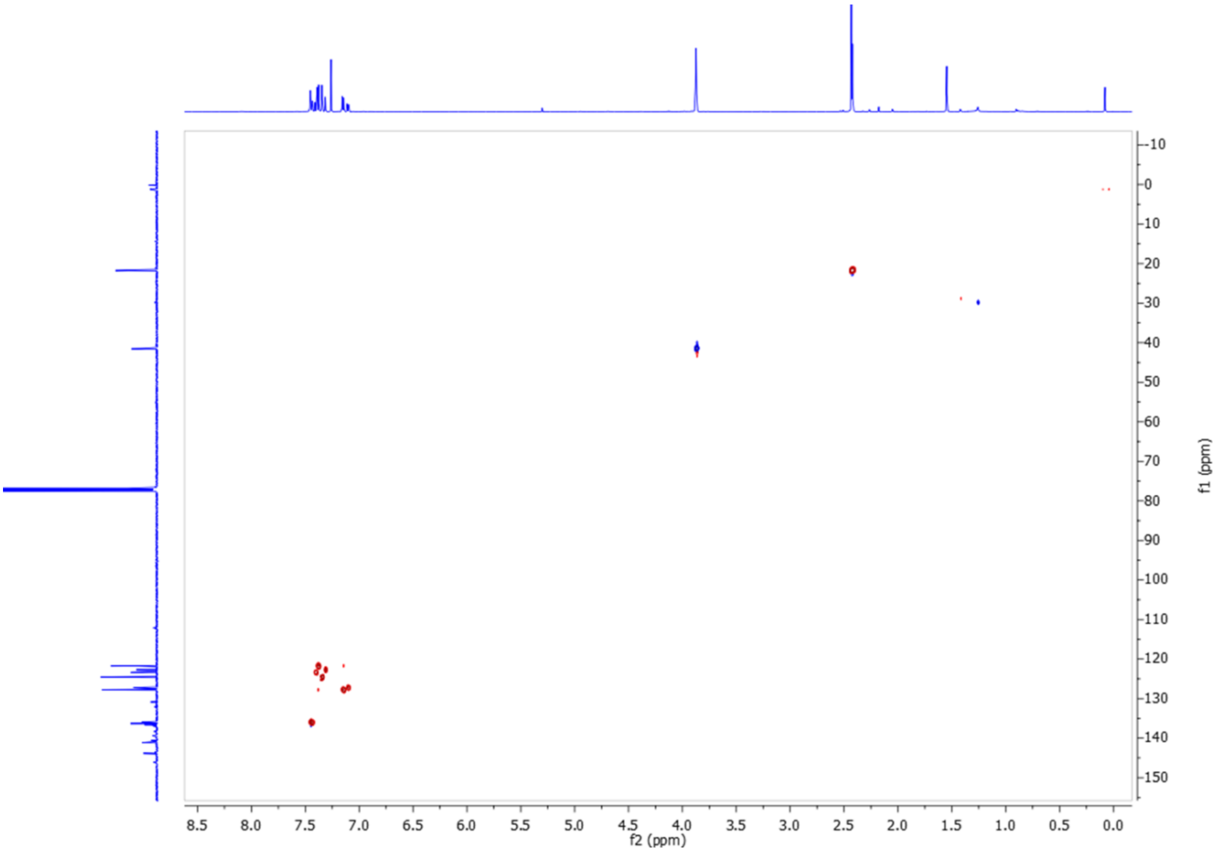


Figure SI 38: ^{1}H ^{13}C HSQC NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene (101 MHz, chloroform-*d*).

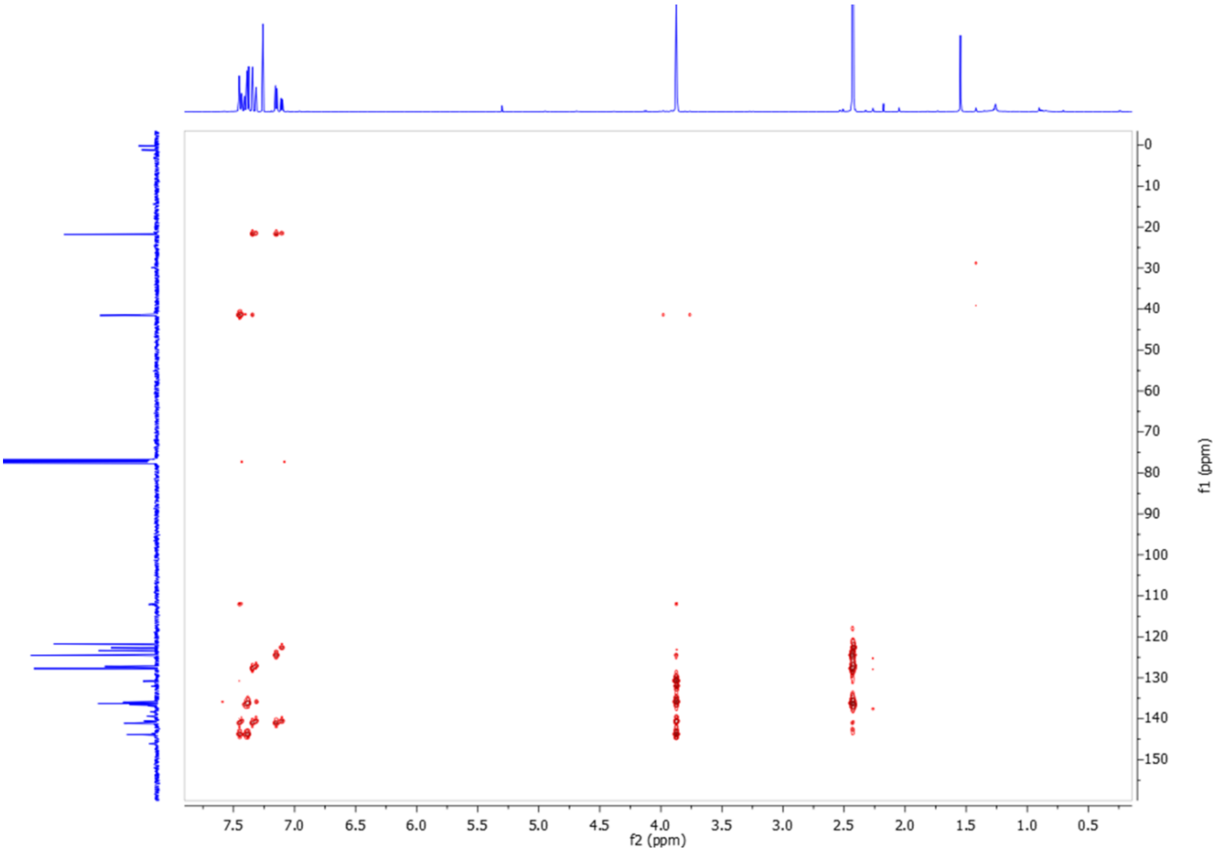


Figure SI 39: ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-6-methyl-1*H*-indene and 2-pentafluorophenyl-5-methyl-1*H*-indene (101 MHz, chloroform-*d*).

5.5.1 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl -1*H*-indene

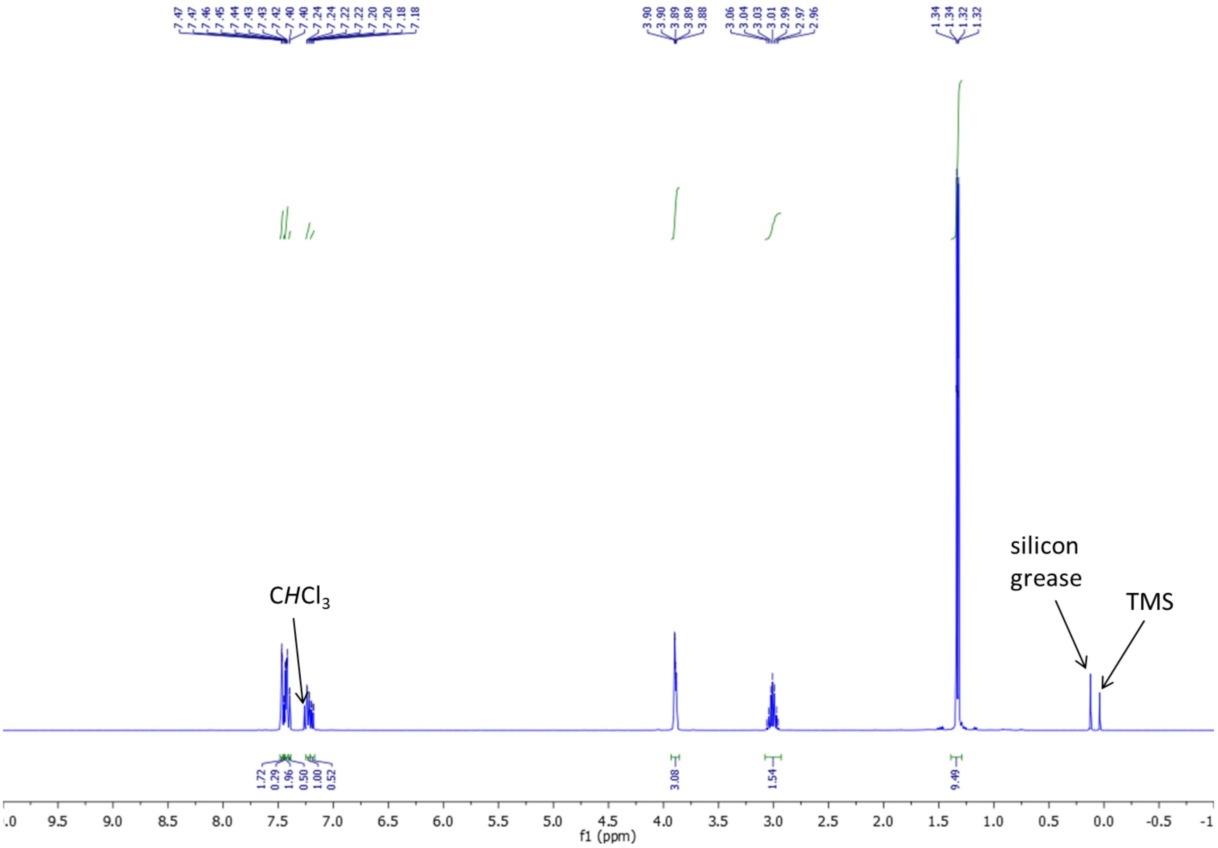


Figure SI 40: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene (400 MHz, chloroform-*d*).

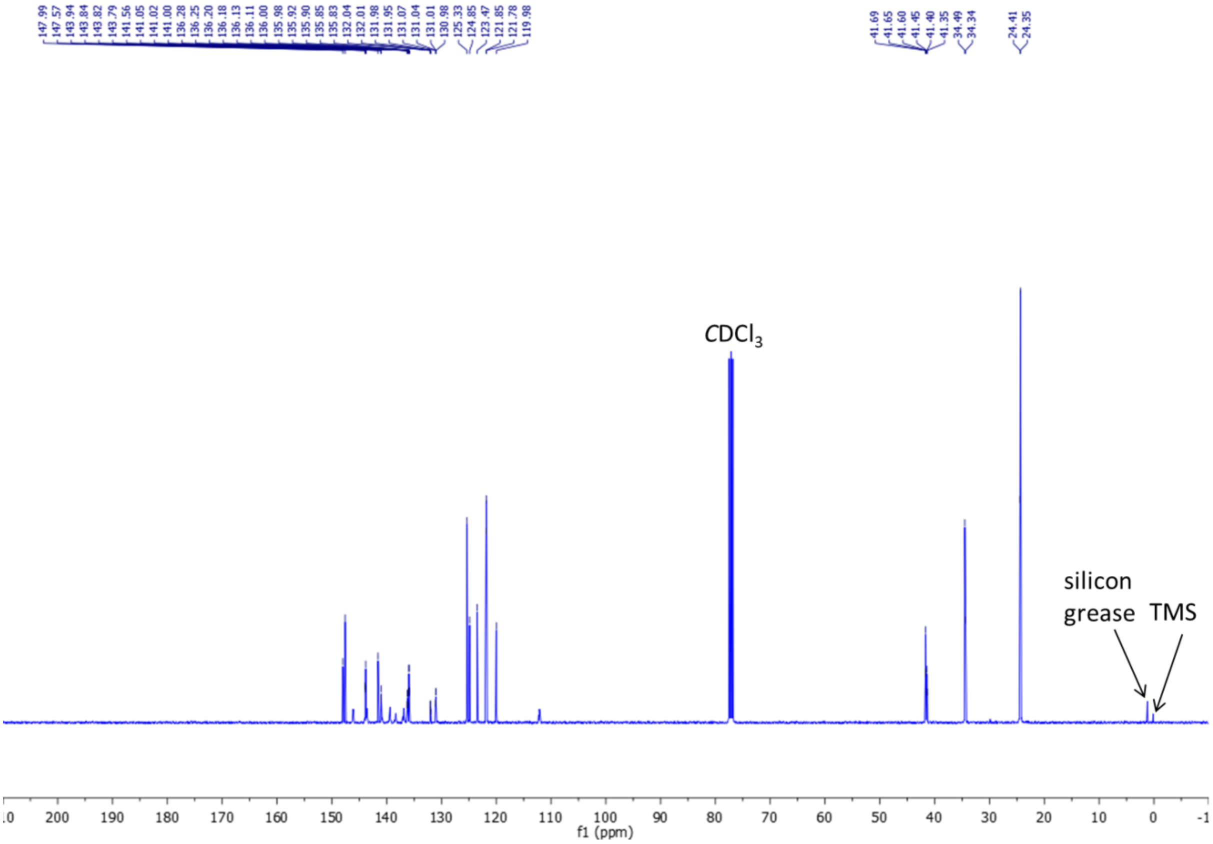


Figure SI 41: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene (101 MHz, chloroform-*d*).

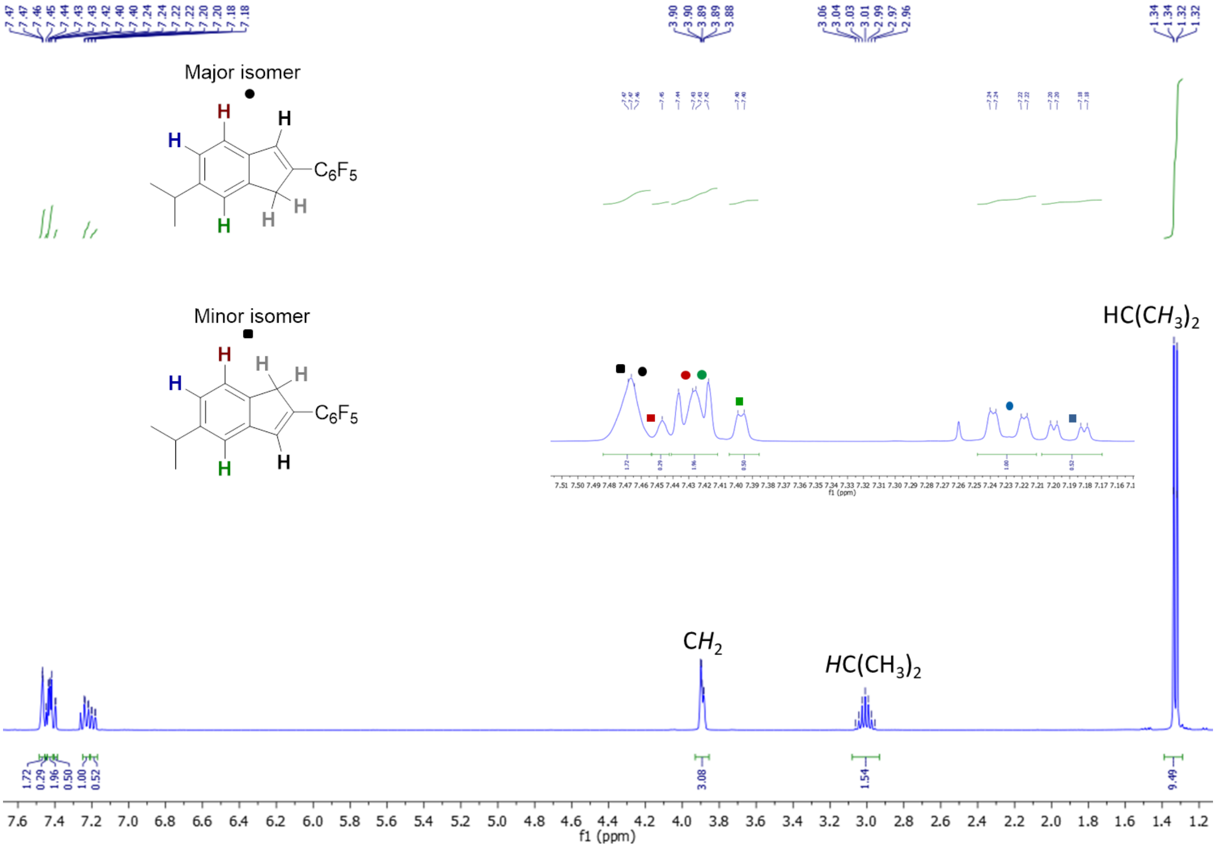


Figure SI 42: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene with low field excerpt and assignment of peaks (400 MHz, chloroform-*d*).

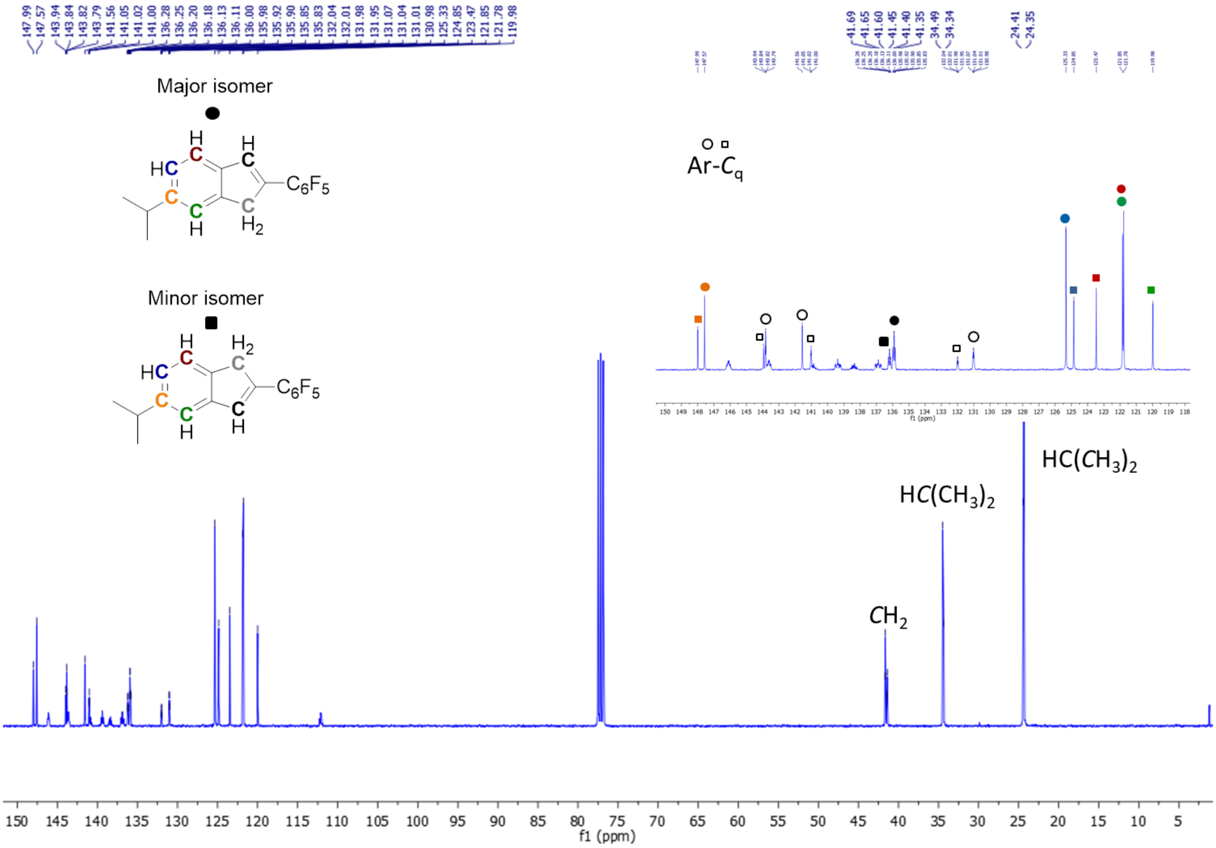


Figure SI 43: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene with low field excerpt and assignment of peaks (101 MHz, chloroform-*d*).

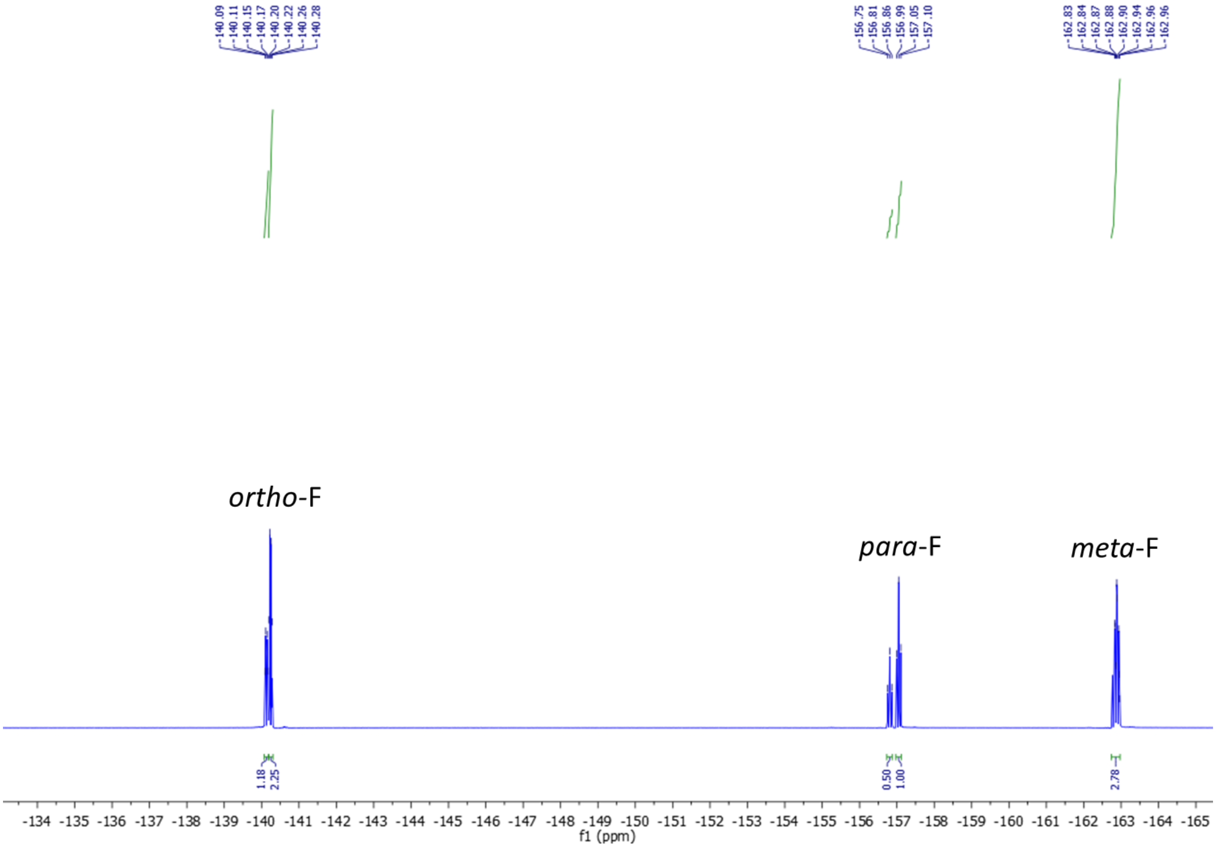


Figure SI 44: ^{19}F NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene (377 MHz, chloroform-*d*).

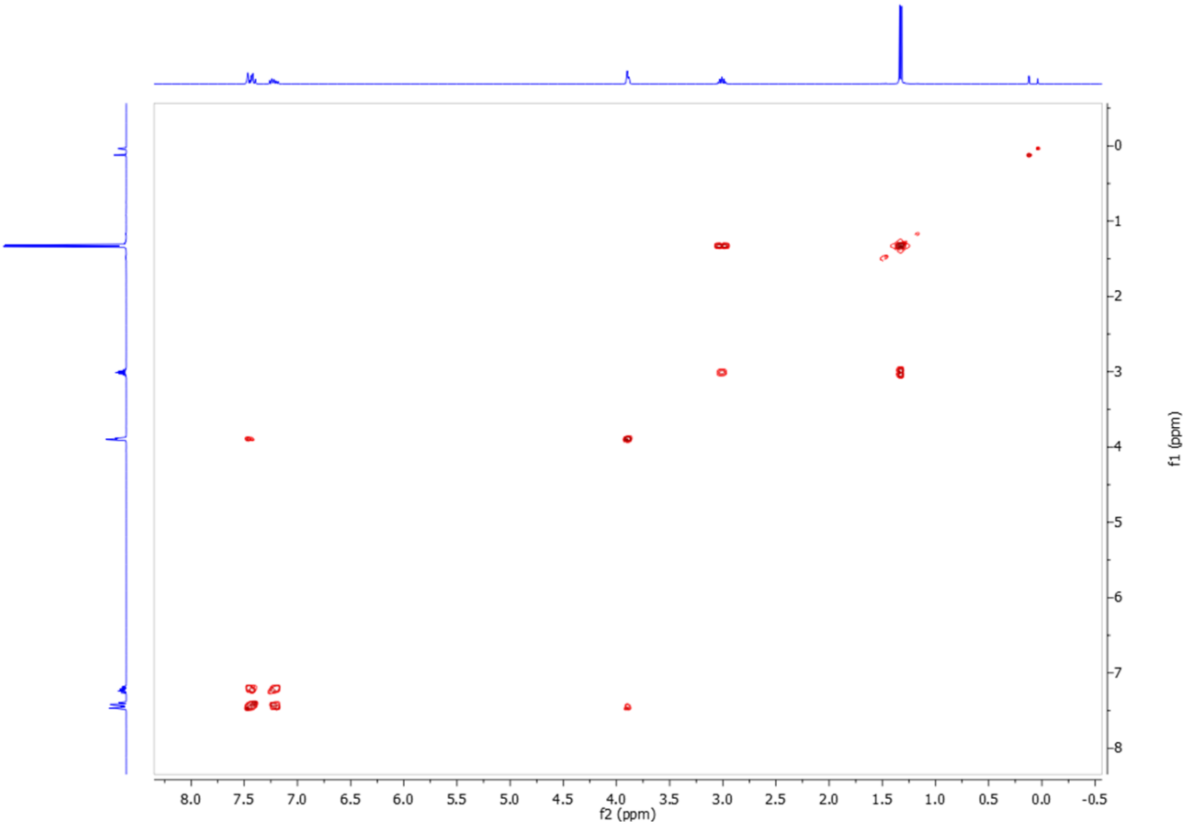


Figure SI 45: HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene (400 MHz, chloroform-*d*).

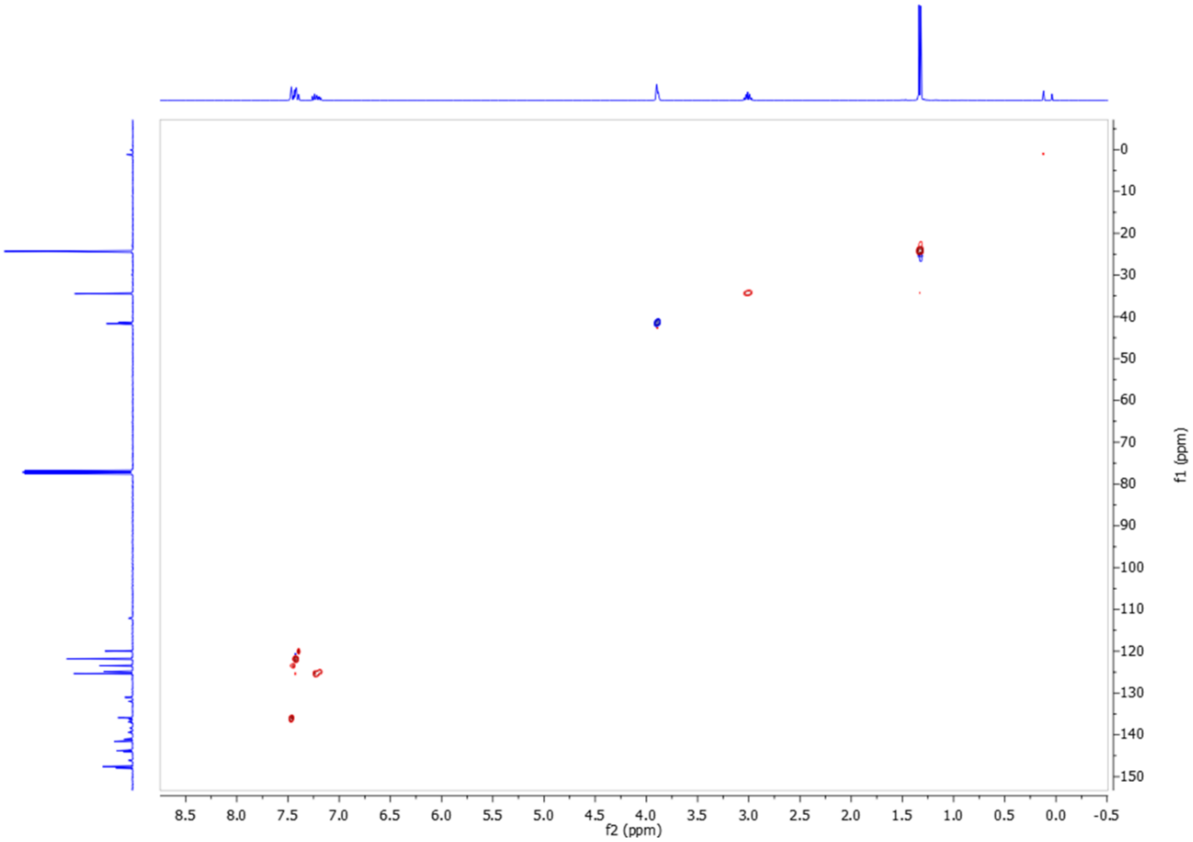


Figure SI 46: ^{1}H ^{13}C HSQC NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene (101 MHz, chloroform-*d*).

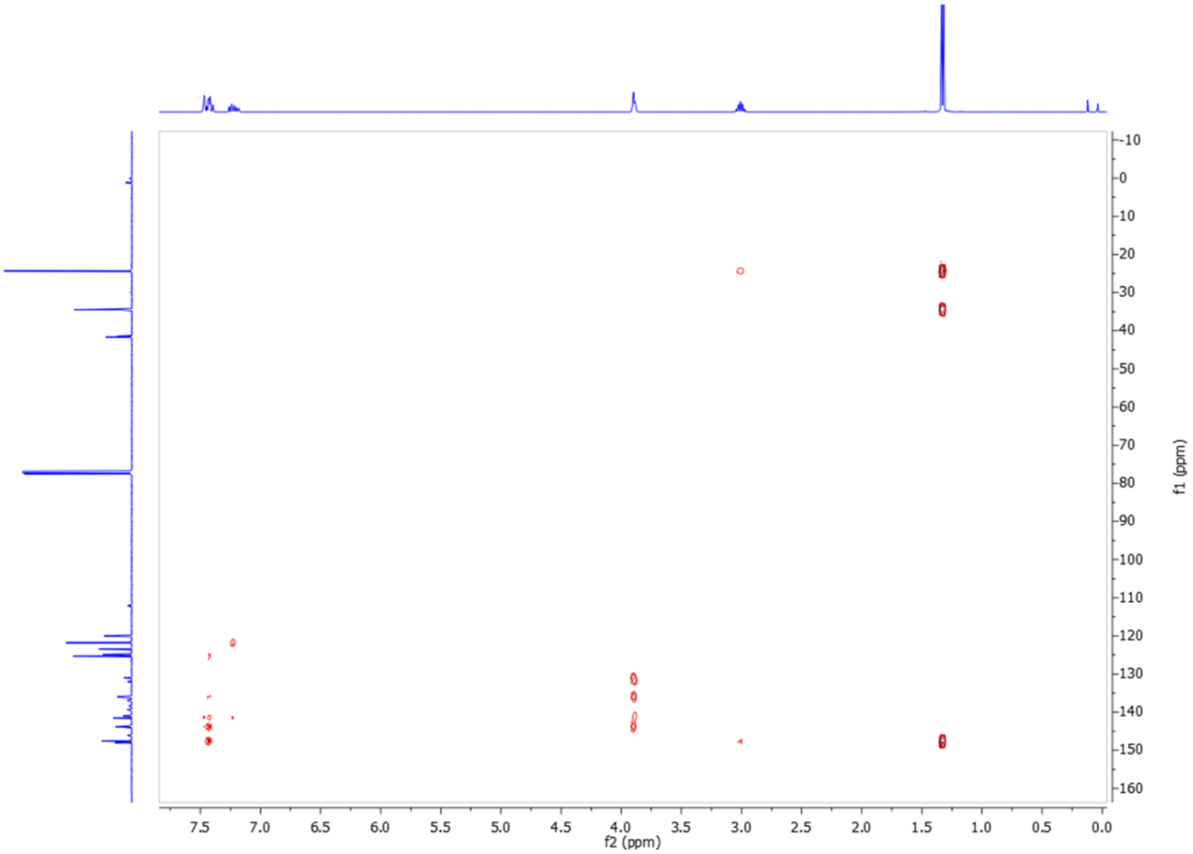


Figure SI 47: ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-6-isopropyl-1*H*-indene and 2-pentafluorophenyl-5-isopropyl-1*H*-indene (101 MHz, chloroform-*d*).

5.5.2 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5- chloro-1*H*-indene

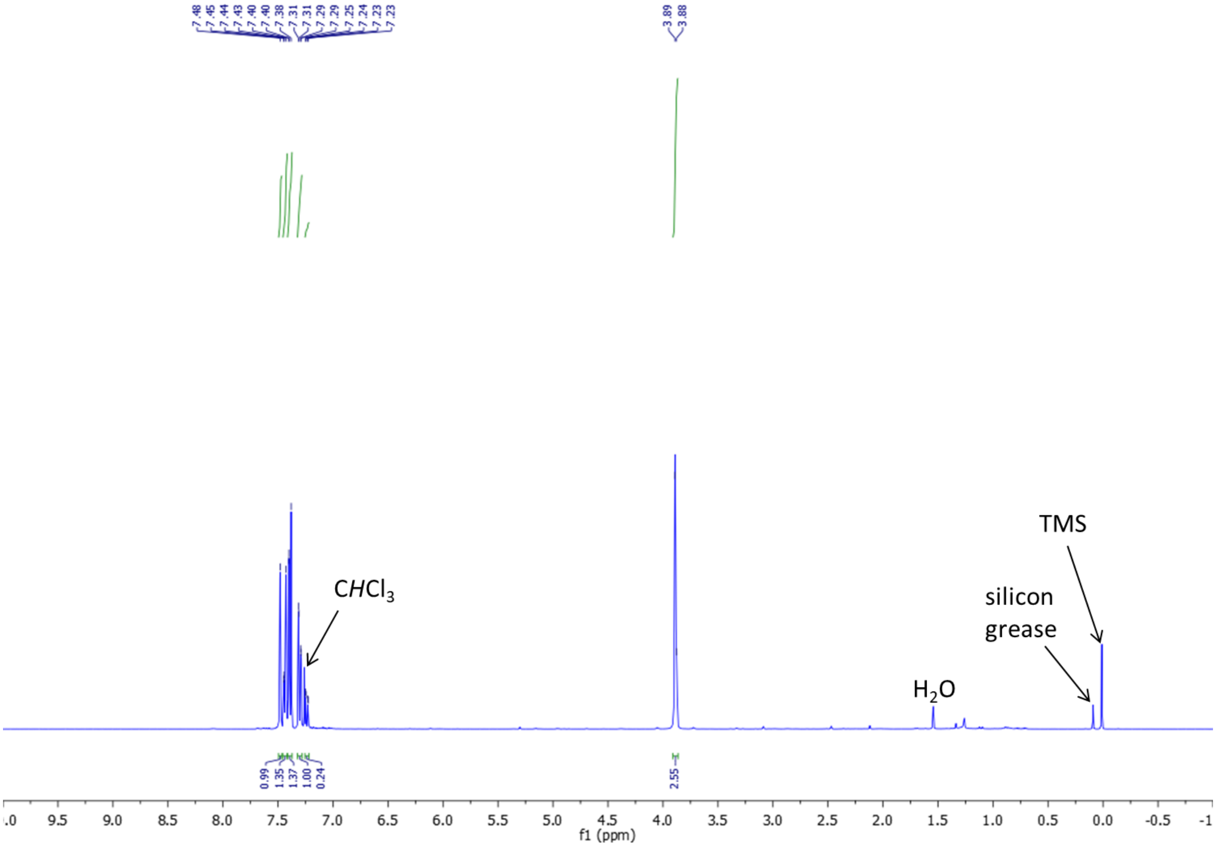


Figure SI 48: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene (400 MHz, chloroform-*d*).

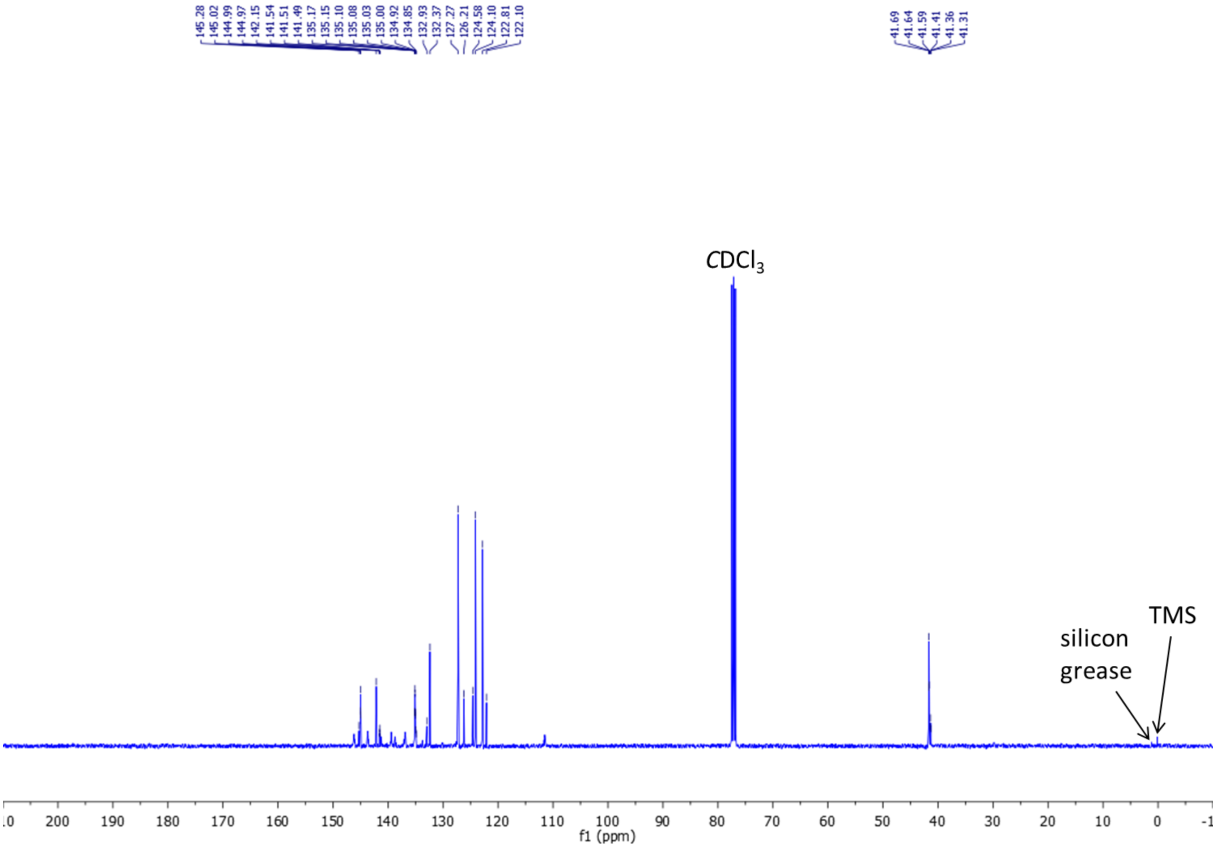


Figure SI 49: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene (101 MHz, chloroform-*d*).

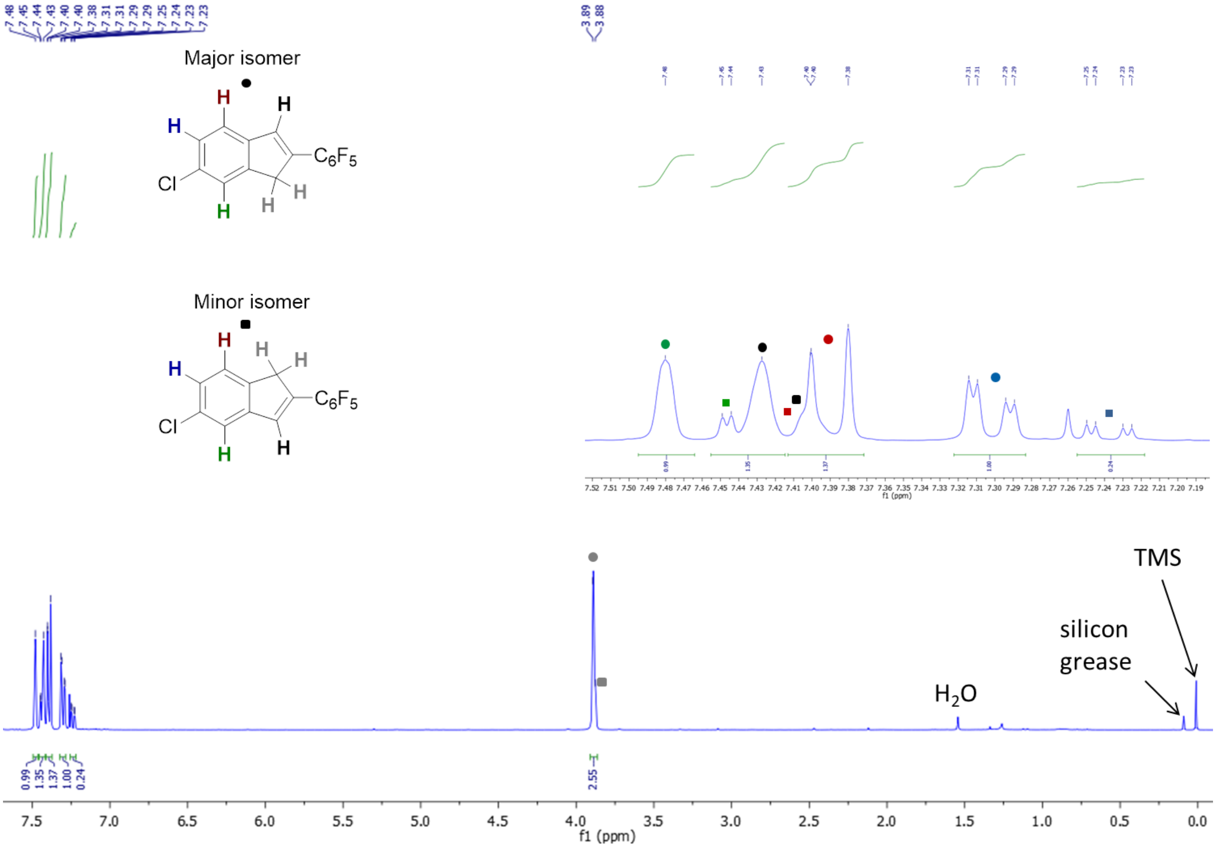


Figure SI 50: ^1H NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene with low field excerpt and assignment of peaks (400 MHz, chloroform-*d*).

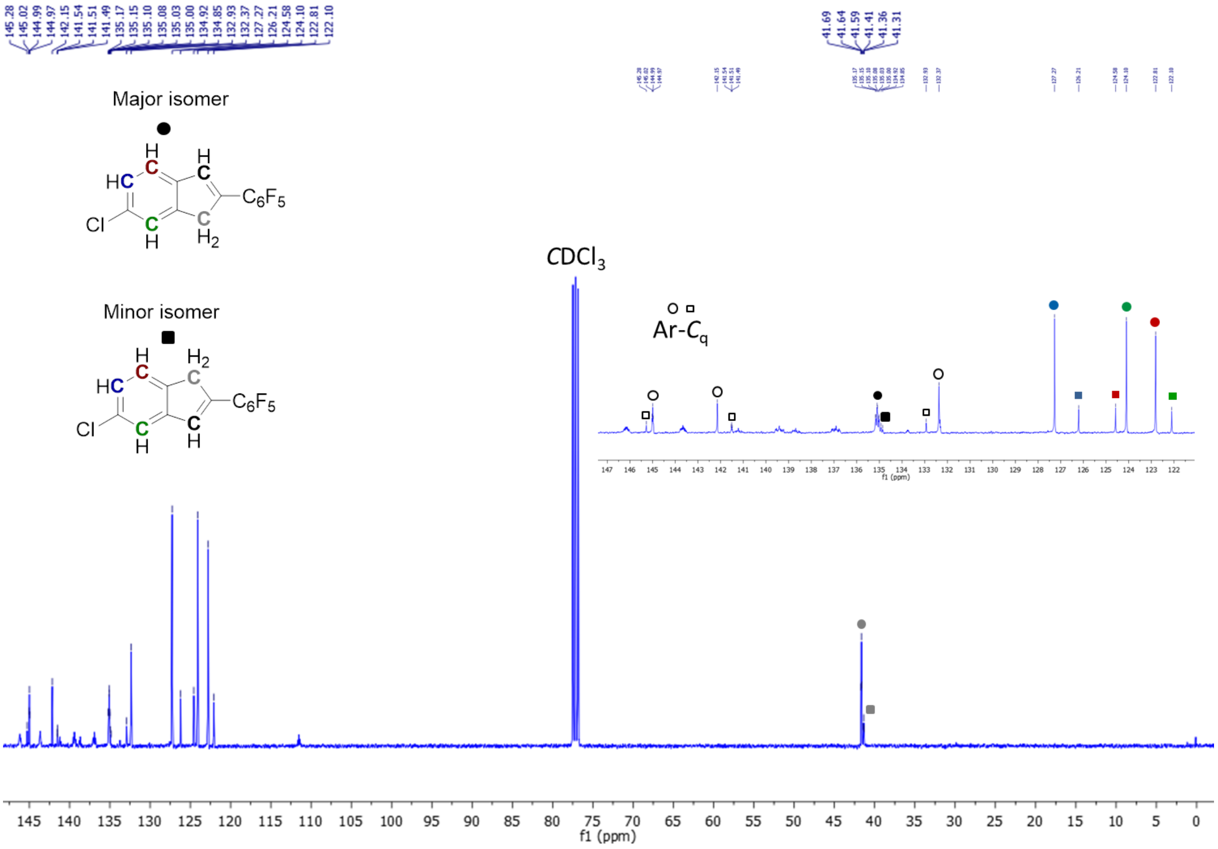


Figure SI 51: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene with low field excerpt and assignment of peaks (101 MHz, chloroform-*d*).

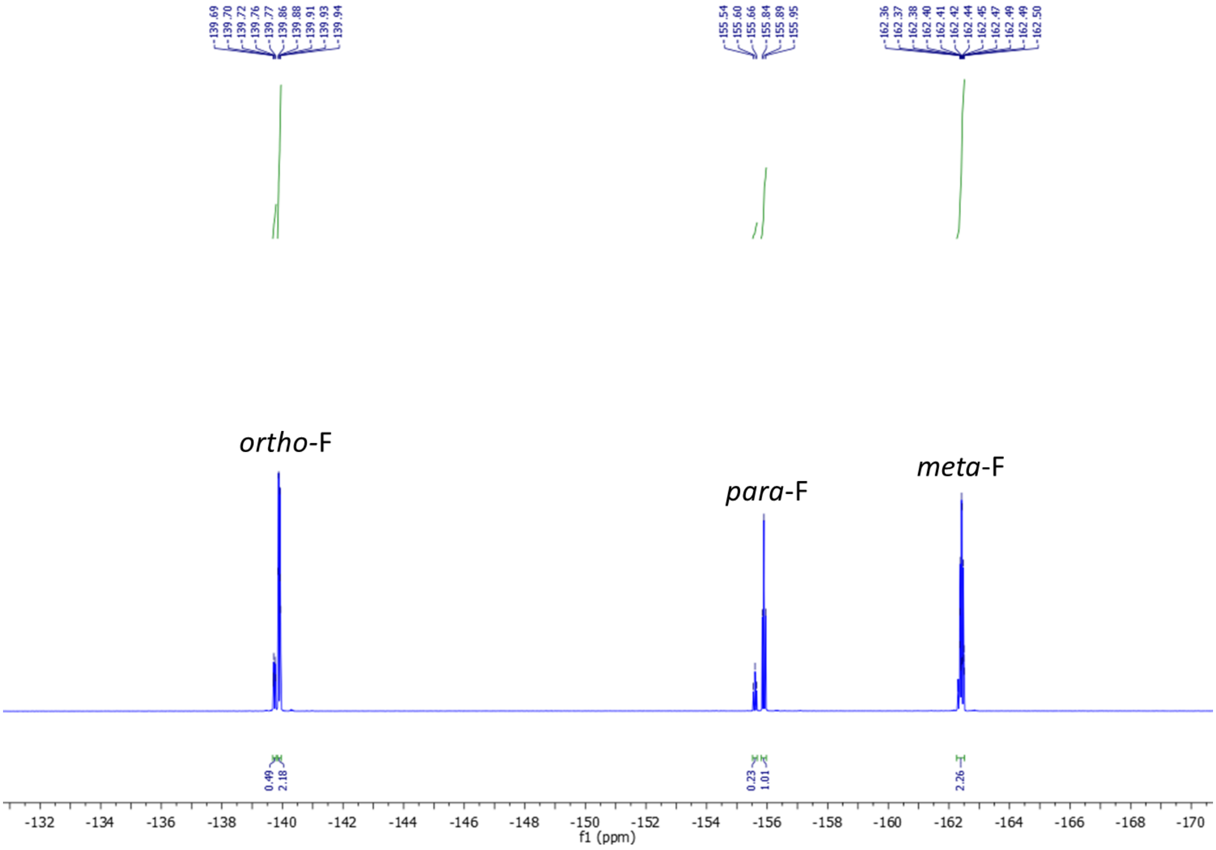


Figure SI 52: ^{19}F NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene (377 MHz, chloroform-*d*).

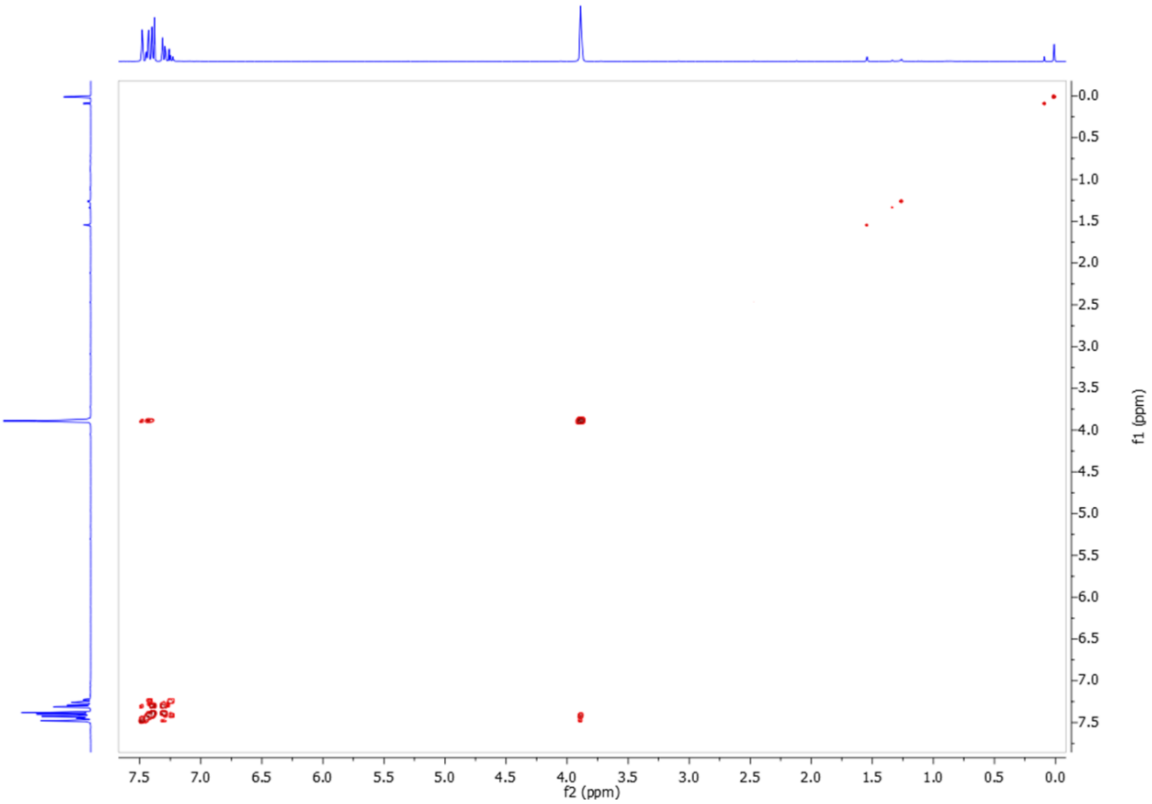


Figure SI 53: HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene (400 MHz, chloroform-*d*).

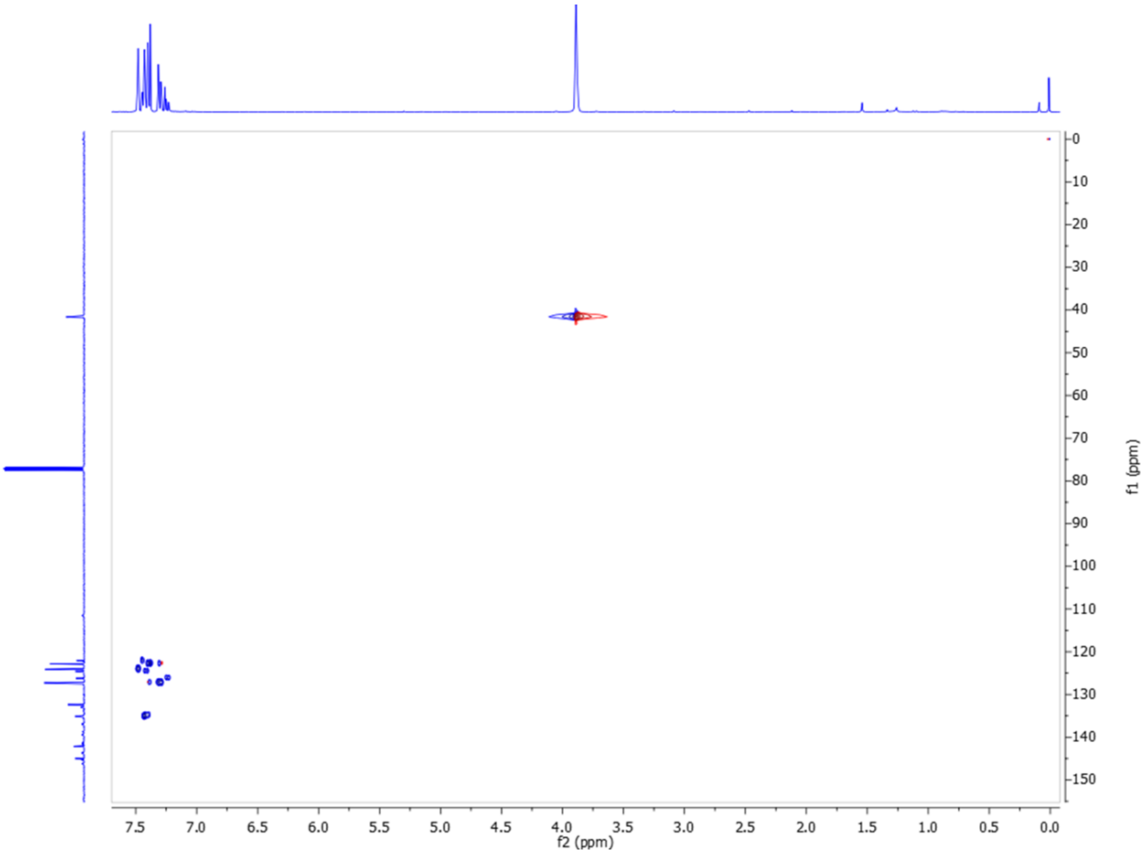


Figure SI 54: ^{1}H ^{13}C HSQC NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene (101 MHz, chloroform-*d*).

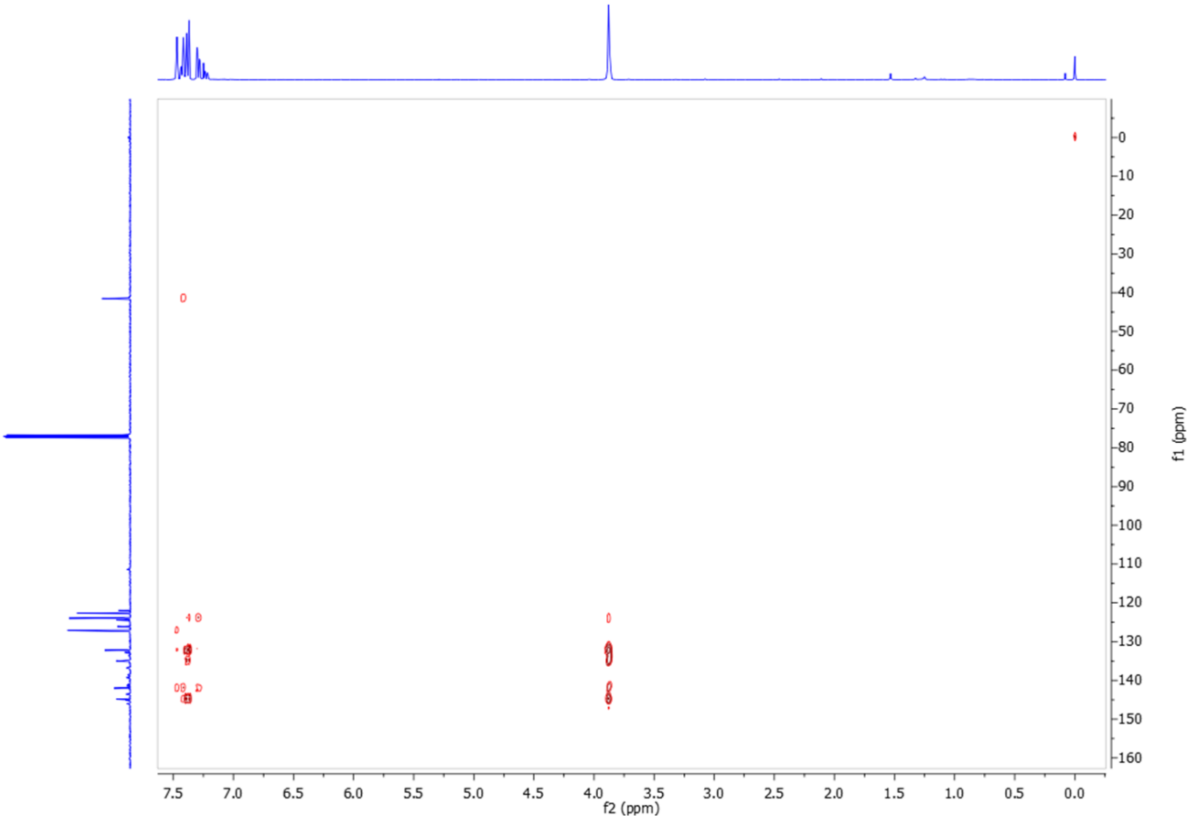


Figure SI 55: ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-6-chloro-1*H*-indene and 2-pentafluorophenyl-5-chloro-1*H*-indene (101 MHz, chloroform-*d*).

5.5.1 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5- fluoro-1*H*-indene

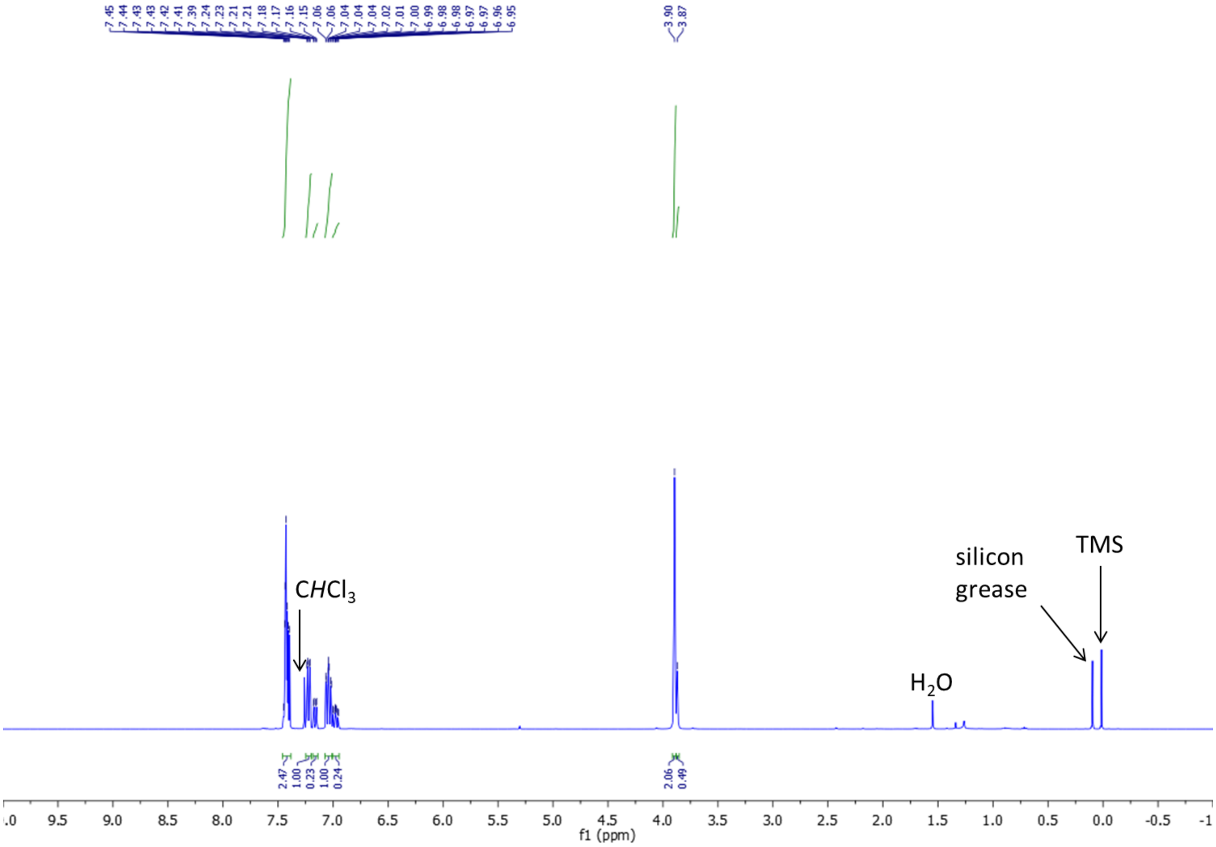


Figure SI 56: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene (400 MHz, chloroform-*d*).

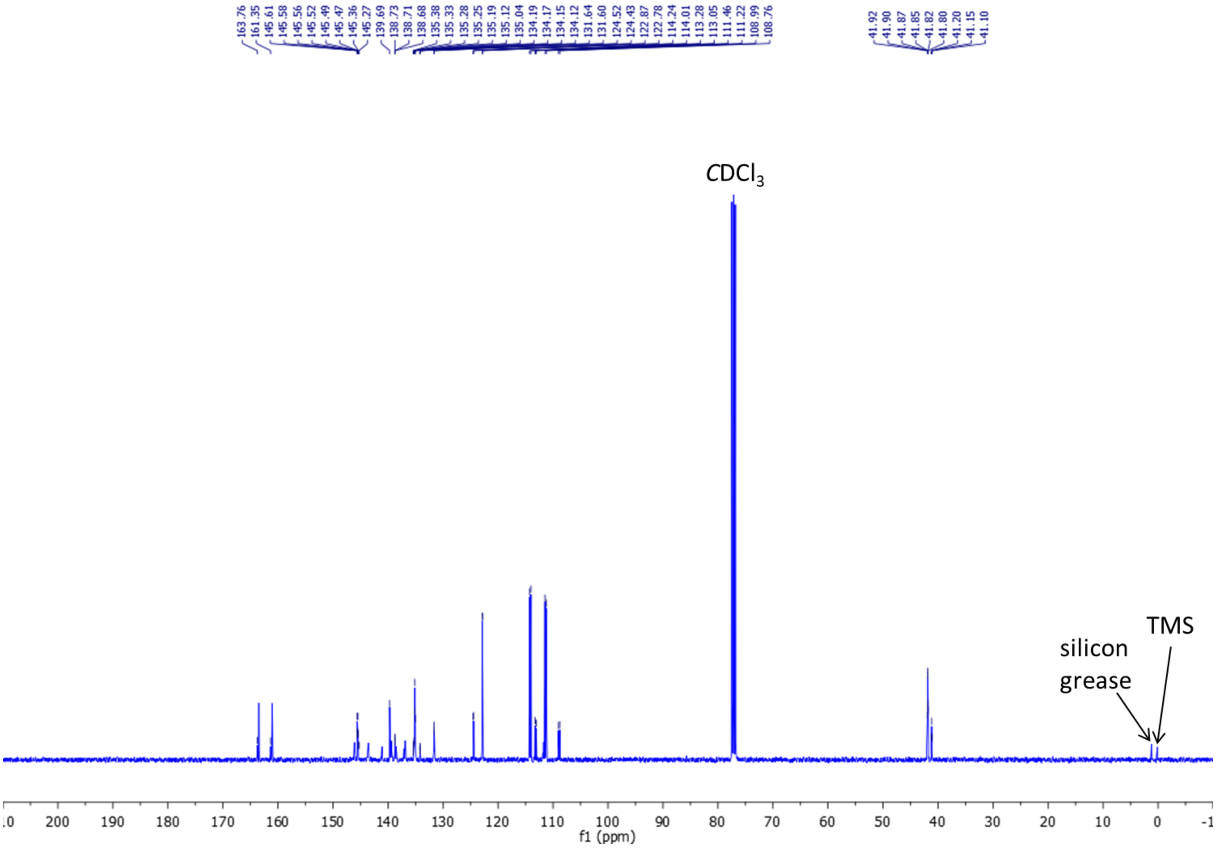


Figure SI 57: ^{13}C NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene (101 MHz, chloroform-*d*).

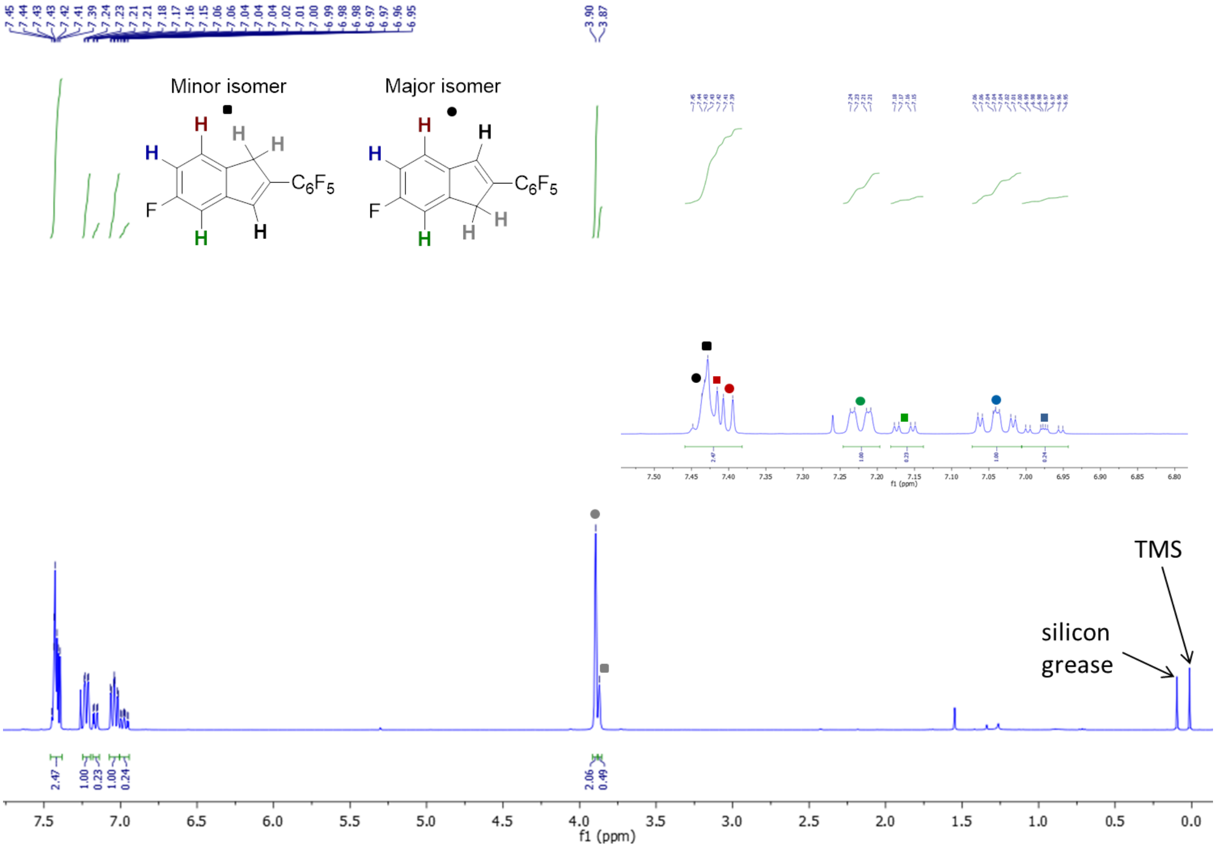


Figure SI 58: ^{1}H NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene with low field excerpt and assignment of peaks (400 MHz, chloroform-*d*).

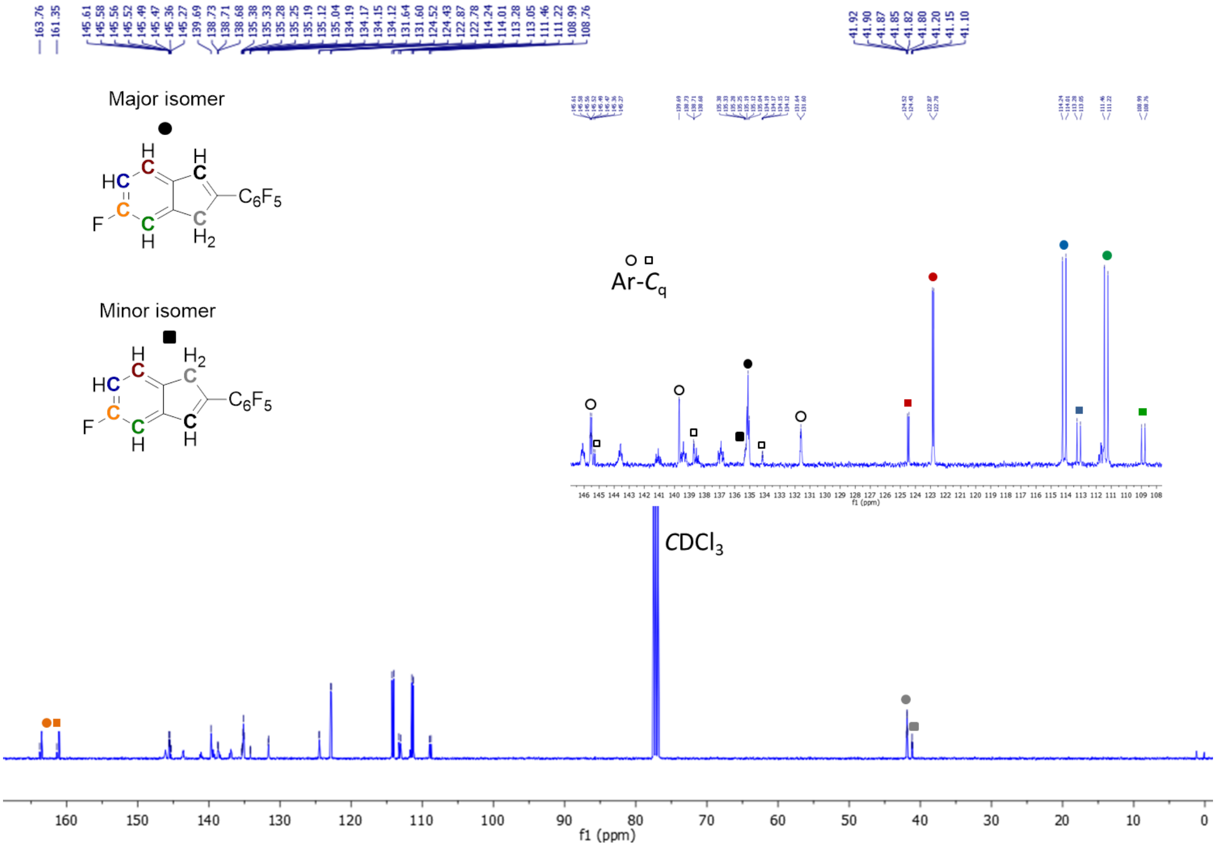


Figure SI 59: ^{13}C NMR spectrum of a mixture of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene with low field excerpt and assignment of peaks (101 MHz, chloroform-*d*).

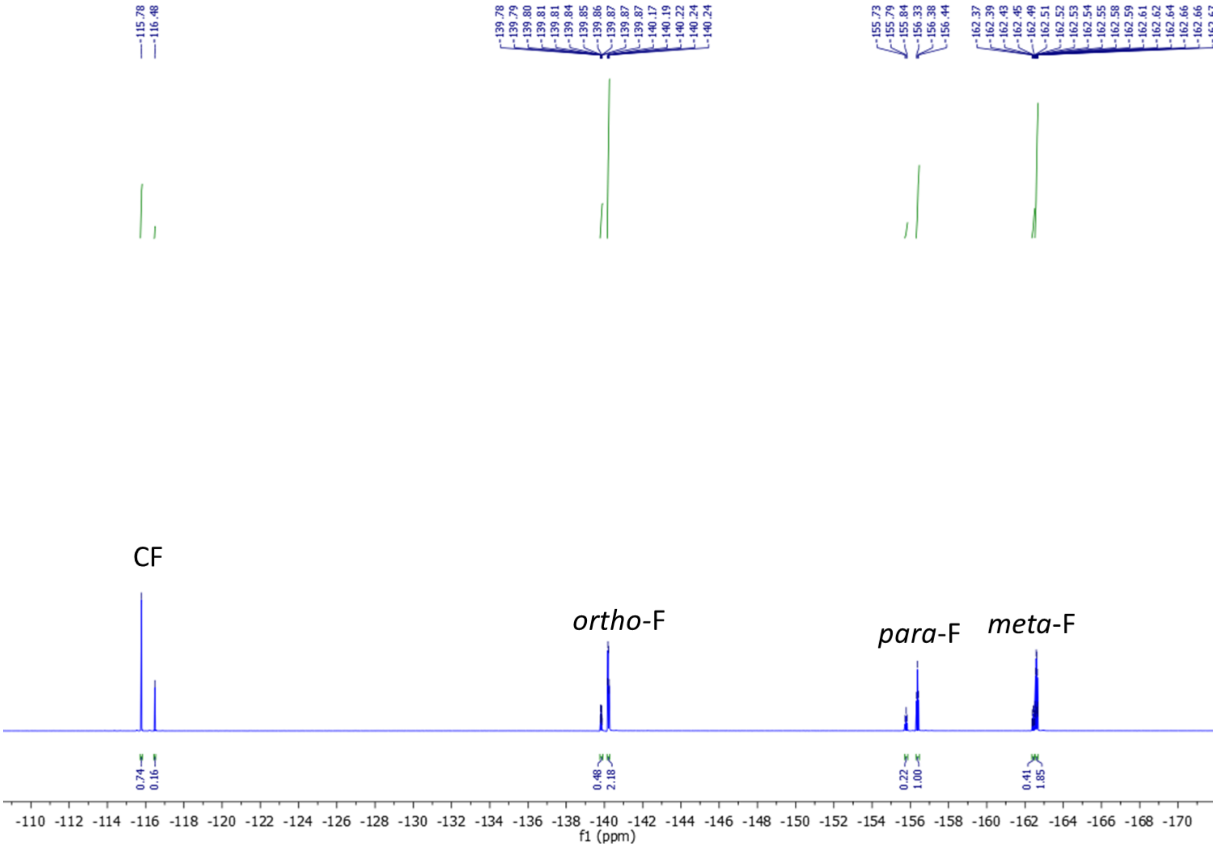


Figure SI 60: ^{19}F NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene (377 MHz, chloroform-*d*).

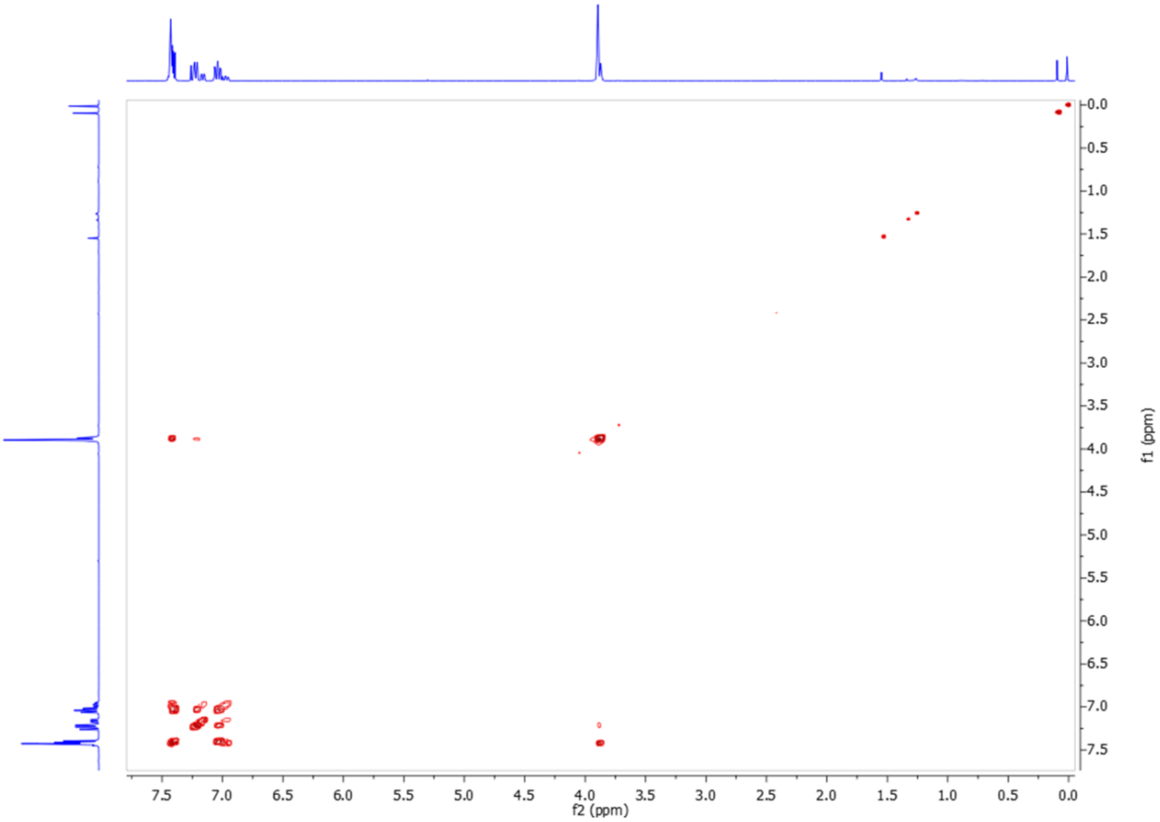


Figure SI 61: HH COSY NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene (400 MHz, chloroform-*d*).

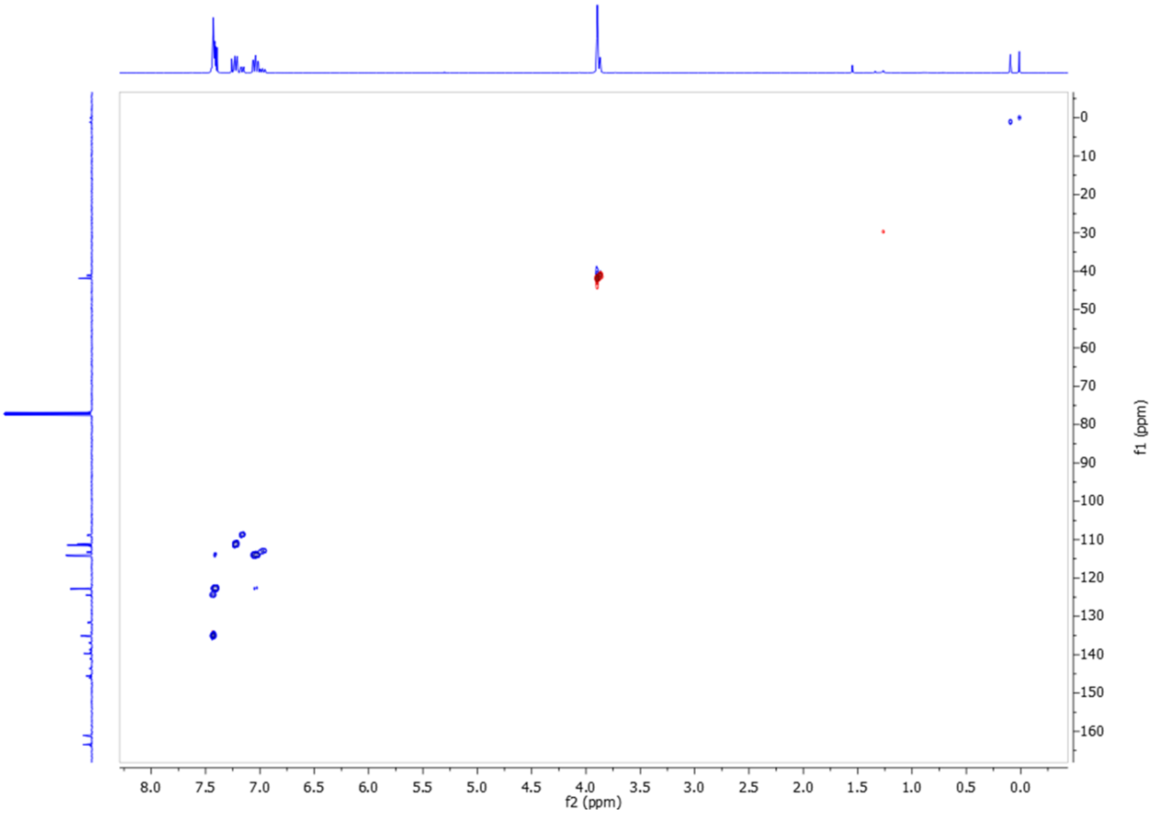


Figure SI 62: ^{1}H ^{13}C HSQC NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene (101 MHz, chloroform-*d*).

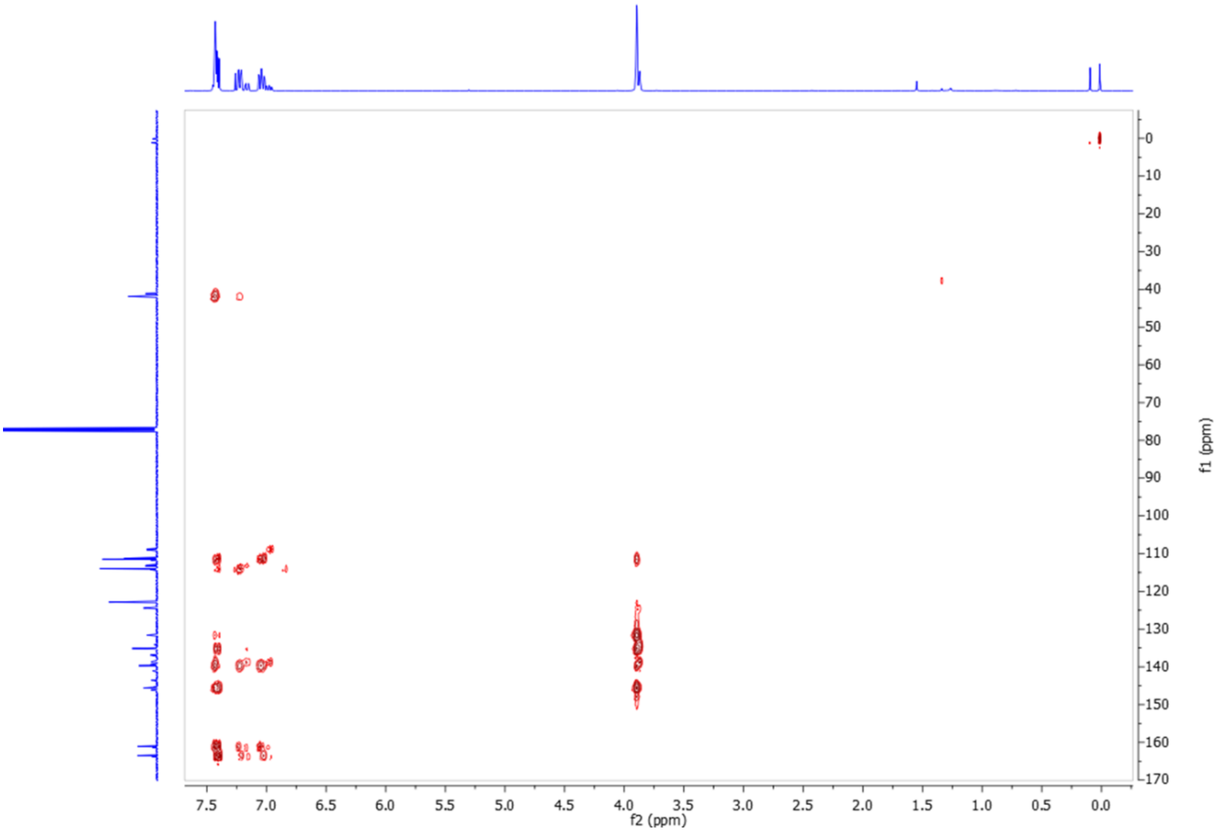


Figure SI 63: ^{1}H ^{13}C HMBC NMR spectrum of a mixture of 2-pentafluorophenyl-6-fluoro-1*H*-indene and 2-pentafluorophenyl-5-fluoro-1*H*-indene (101 MHz, chloroform-*d*).

5.5.2 NMR spectra of 2-methyl-6-(isopropyl)-1*H*-indene

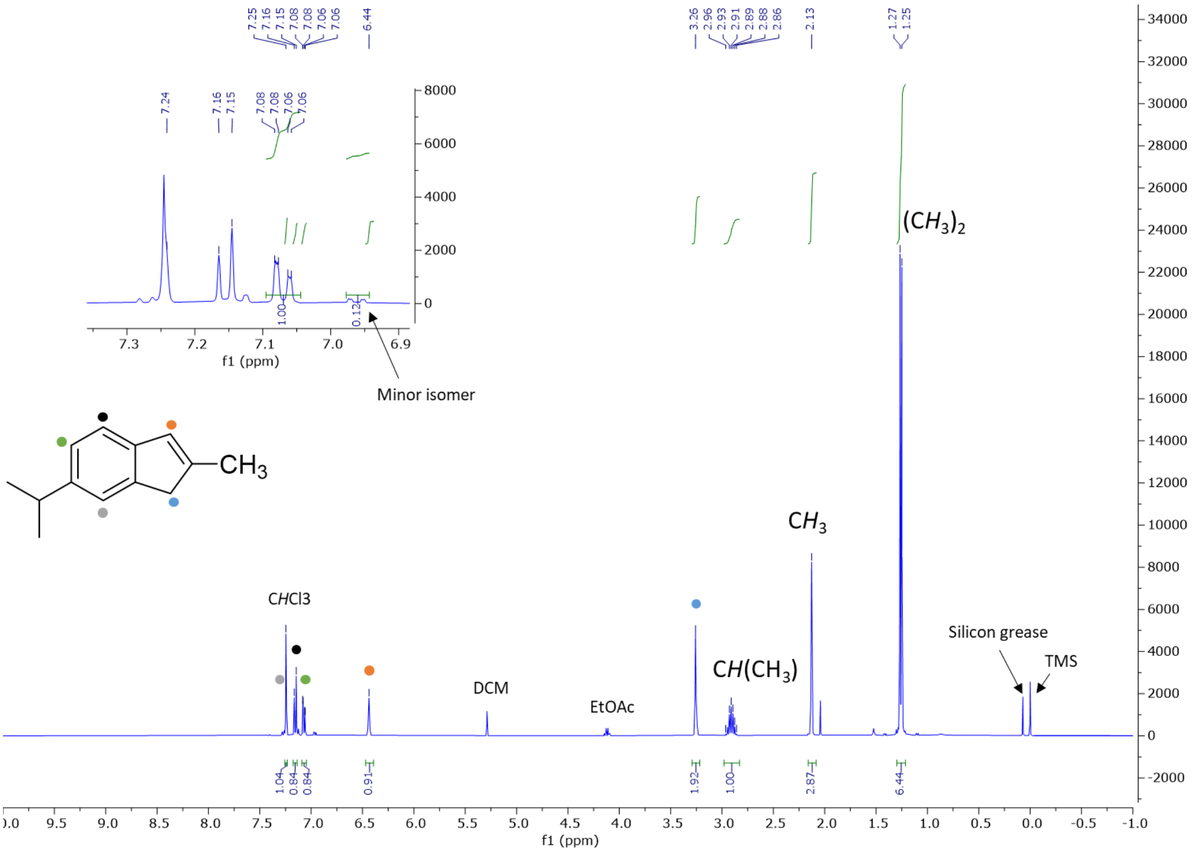


Figure SI 64: ^{1}H NMR spectrum of 2-methyl-6-(isopropyl)-1*H*-indene (400 MHz, chloroform-*d*).

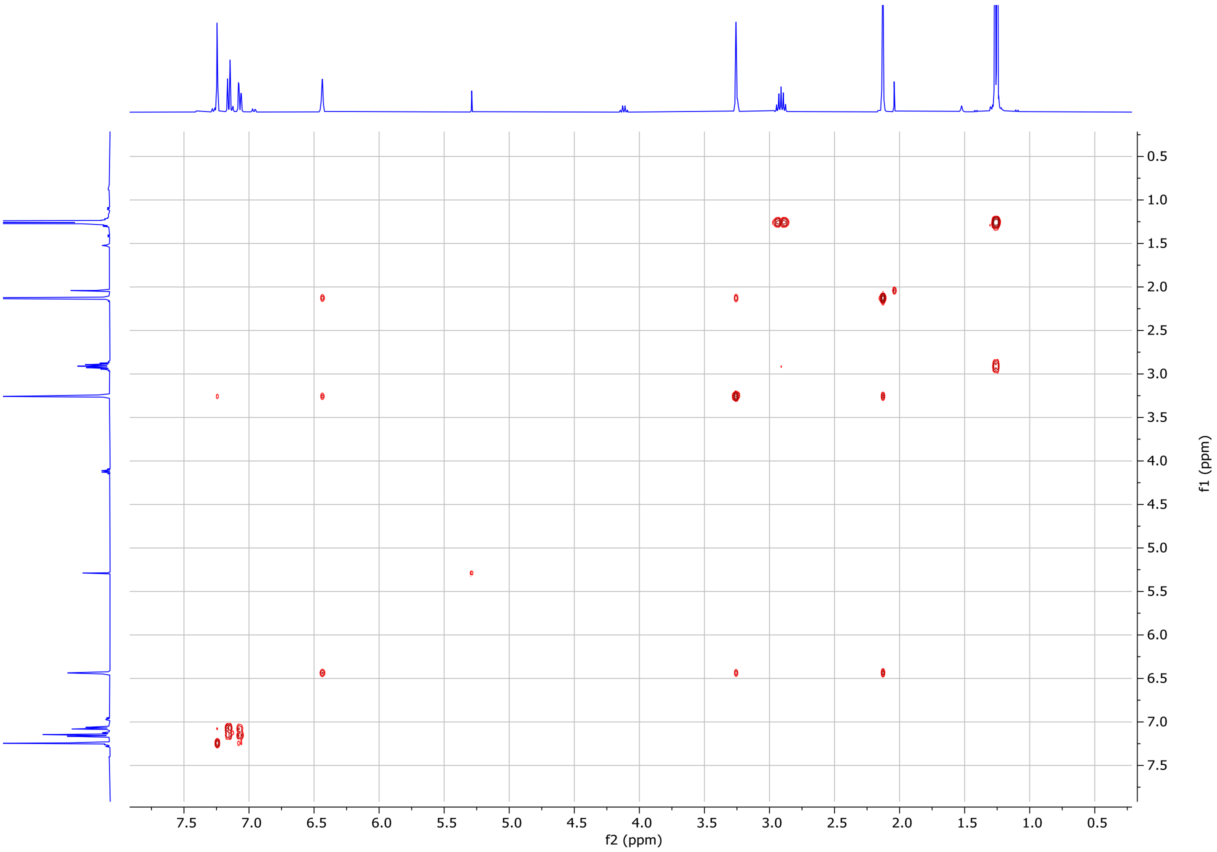


Figure SI 65: HH COSY NMR spectrum of 2-methyl-6-(isopropyl)-1*H*-indene (400 MHz, chloroform-*d*).

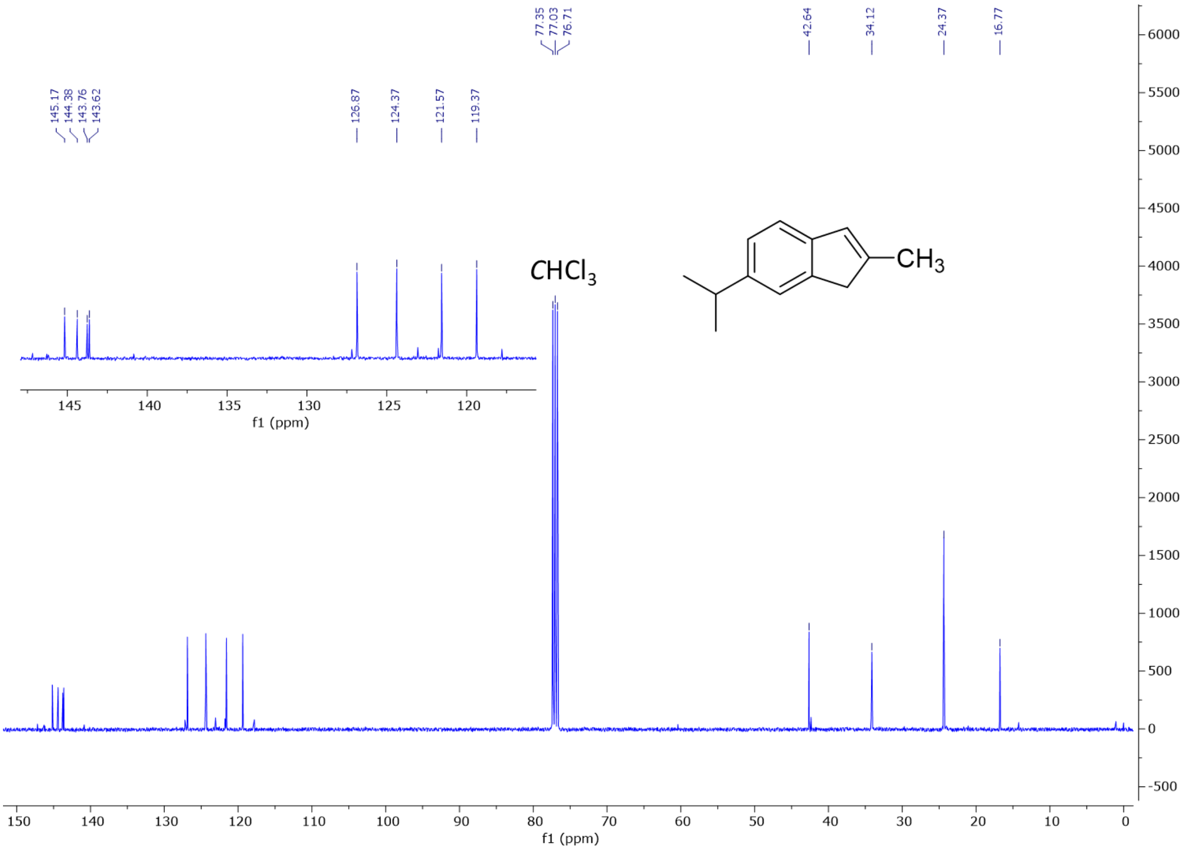


Figure SI 66: $^{13}C\{^1H\}$ NMR spectrum of 2-methyl-6-(isopropyl)-1*H*-indene (101 MHz, chloroform-*d*).

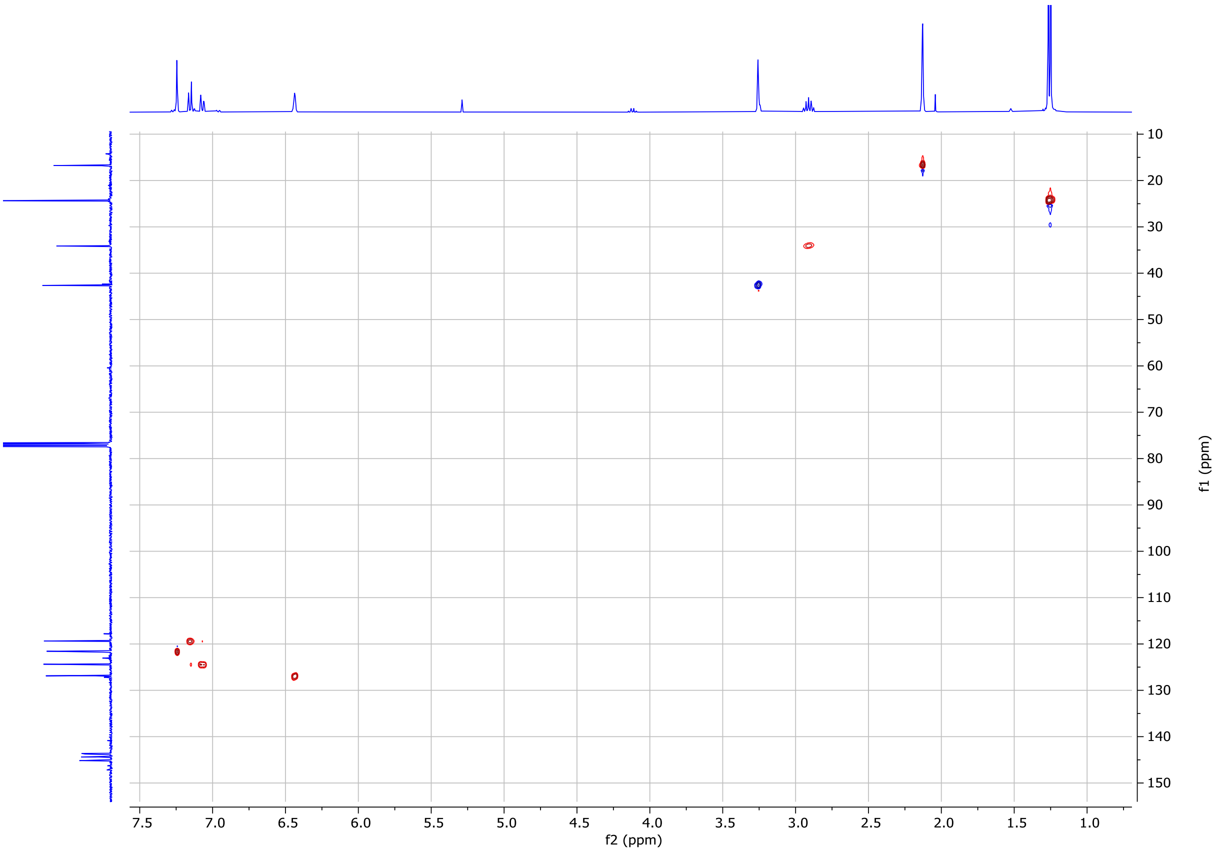


Figure SI 67: ^{1}H ^{13}C-HSQC spectrum of 2-methyl-6-(isopropyl)-1*H*-indene (400 MHz, 101 MHz, chloroform-*d*).

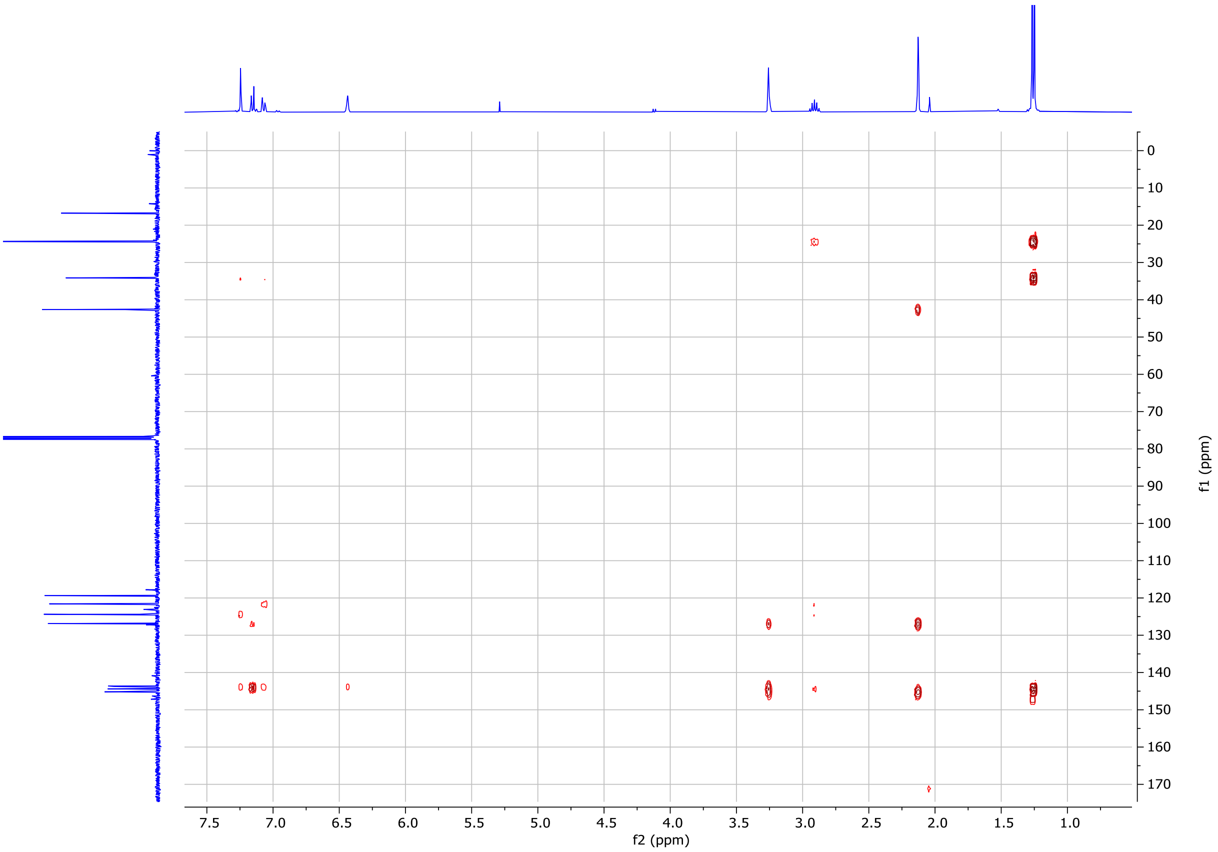


Figure SI 68: ^{1}H ^{13}C HMBC NMR spectrum of 2-methyl-6-(isopropyl)-1*H*-indene (400 MHz, 101 MHz, chloroform-*d*).

6 Kinetic measurements

6.1 General procedure

In a glovebox, tris(perfluorophenyl)borane (205 mg, 0.4 mmol, 1.0 eq.) was dissolved in dry DCM (5 mL) in a Schlenk flask. In a Schlenk tube, the respective allene (0.4 mmol, 1.0 eq.) was dissolved in dry DCM (3 mL). Both the Schlenk flask and the Schlenk tube were pre-cooled to 0 °C for 1 h using an ice bath. Using a syringe, the allene solution was quickly transferred to the tris(perfluorophenyl)borane solution resulting in a 0.05 M solution regarding both reaction compounds. An aliquot was taken at each time interval by transferring 0.90 mL of the solution to a vial filled with pyridine (8.0 µL, 0.1 mmol, 2.0 eq.) using a syringe. From this solution, 0.80 mL (0.04 mmol) were transferred to a second vial. After evaporation of the solvent in a stream of nitrogen, the residue was taken up in $CDCl_3$ and mesitylene (2.8 µL, 0.02 mmol) was added as an internal standard. The solution was then transferred to an NMR tube and analysed by ^1H NMR spectroscopy. The signals for the benzylic CH_2 groups of the indene products were integrated in the same ppm range, as well as the CH_3 signals of the internal standard for all samples. For each substrate, two runs were performed. The rate-constants were evaluated using the second-order rate law and plotting $1/n_0$-n vs. t. The slope of the resulting fit straight is then the second-order rate-constant k at 0 °C. The values for k were averaged from the two runs and the error is assumed as deviation from the average.

6.1.1 Quantitative NMR analysis for phenylallene

In the following, the general procedure for the data analysis of the kinetic experiments is shown exemplary for one experiment for phenylallene (Figure SI 63).

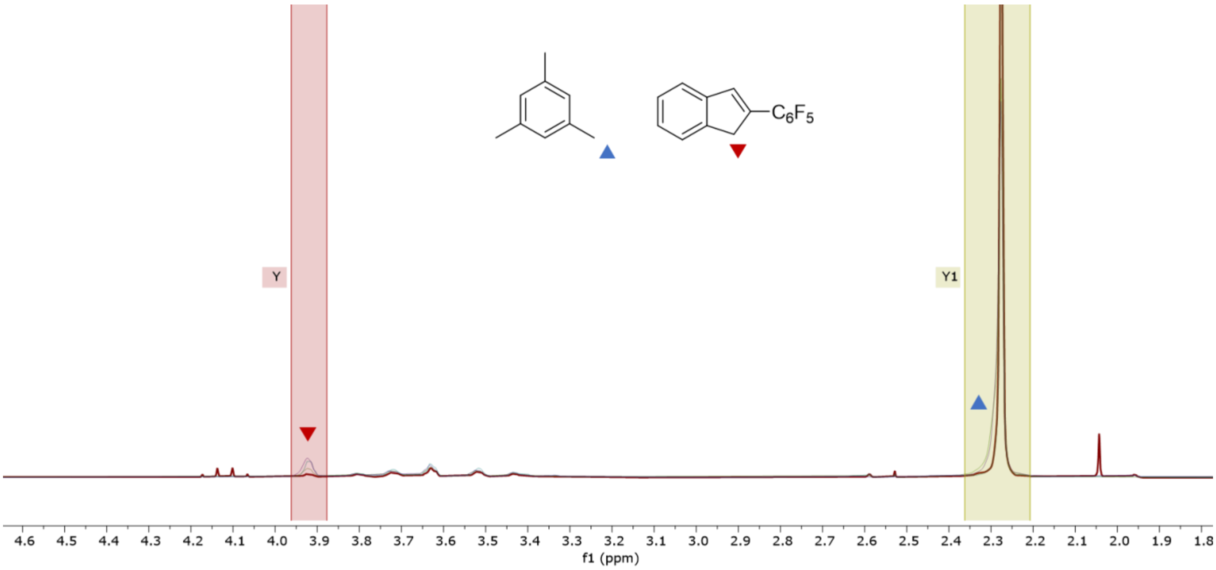


Figure SI 69: Stacked plot of the NMR spectra for the reaction of phenylallene and tris(perfluorphenyl)borane at 0 °C. NMR spectra recorded after 5 min, 10 min, 15 min and 20 min reaction time (chloroform-*d*, 200 MHz).

The data analysis was conducted using MestReNova 14.2 and the internal data analysis tool. The amount of product was then determined using equation 1.

$$n_\mathrm{P} = \frac{I_\mathrm{P} \cdot \#\mathrm{H}_\mathrm{Std.}}{I_\mathrm{Std} \cdot \#\mathrm{H}_\mathrm{P}} \cdot n_\mathrm{Std} \tag{1}$$

Where I_P is the absolute integral of the indene product, I_{Std} is the absolute integral of the methyl groups of mesitylene, #H are the respective number of hydrogens and *n* the amount of substance.

6.1.2 Measurements for phenylallene

Table SI 2: Data of the first kinetic experiment for phenylallene at 0 °C.

Absolute integral of product	Absolute integral of standard	$n_{Standard}$ [mmol]	$n_{Product}$ [mmol]	$1/n_0$-n [1/mmol]	*t* [min]
61465.3	1.05E+06	0.02	0.0053	28.8	10
65313.9	1.02E+06	0.02	0.0058	29.2	15
96636.7	1.17E+06	0.02	0.0074	30.7	20
97283.8	9.48E+05	0.02	0.0092	32.5	25

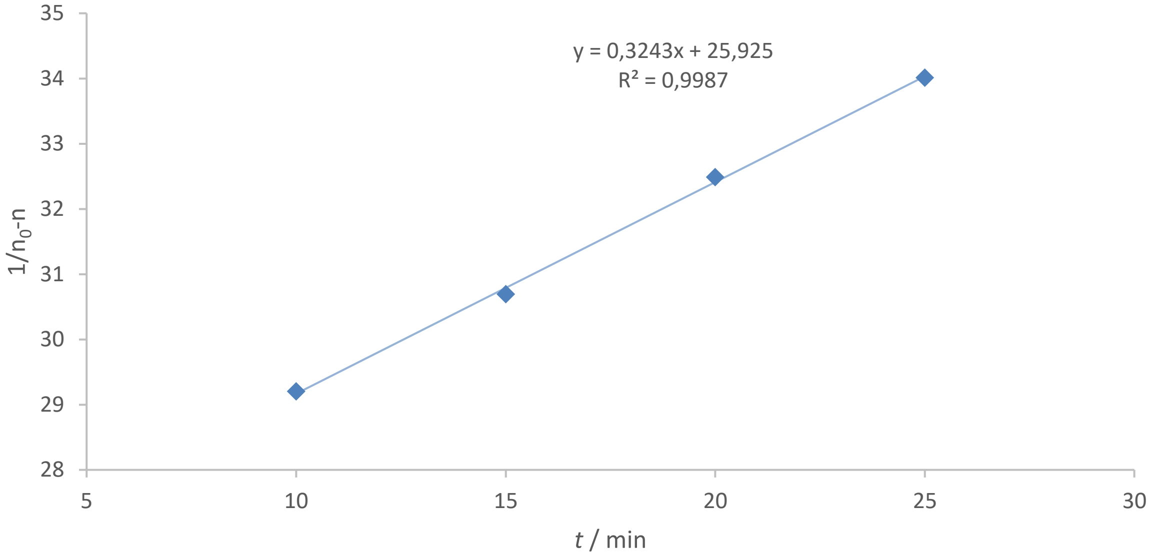


Figure SI 70: Second order rate law plot of the first run for phenylallene.

Table SI 3: Data of the second kinetic experiment for phenylallene.

Absolute integral of product	**Absolute integral of standard**	**$n_{Standard}$ [mmol]**	**$n_{Product}$ [mmol]**	**$1/n_0$-n [1/mmol]**	***t* [min]**
65380.2	9.73E+05	0.02	0.0060	29.4	10
43538.3	4.85E+05	0.02	0.0081	31.3	15
112853	1.05E+06	0.02	0.0097	33.0	20
137613	1.05E+06	0.02	0.0118	35.5	25

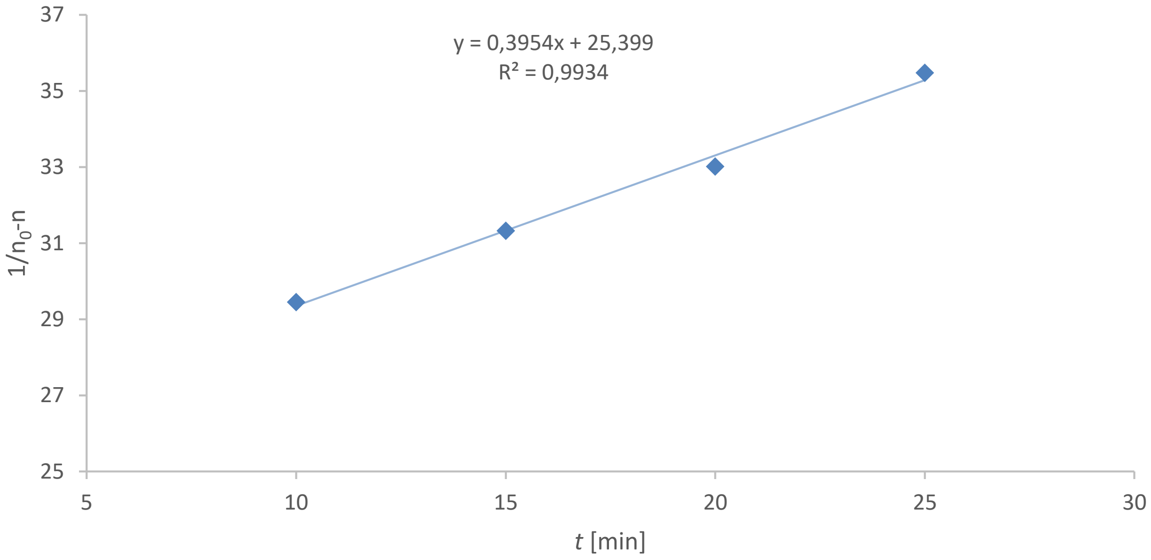


Figure SI 71: Second order rate law plot of the second run for phenylallene.

6.1.3 Measurements for (4-methyl)phenylallene

Table SI 4: Data of the first kinetic experiment for (4-methyl)phenylallene.

Absolute integral of product	Absolute integral of standard	$n_{Standard}$ [mmol]	$n_{Product}$ [mmol]	$1/n_0$-n [1/mmol]	*t* [min]
46420.9	6.64E+05	0.02	0.0063	29.7	5
87863.7	7.35E+05	0.02	0.0108	34.2	10
125700	8.09E+05	0.02	0.0140	38.4	15
126923	8.02E+05	0.02	0.0142	38.8	20
103736	4.73E+05	0.02	0.0197	49.3	25

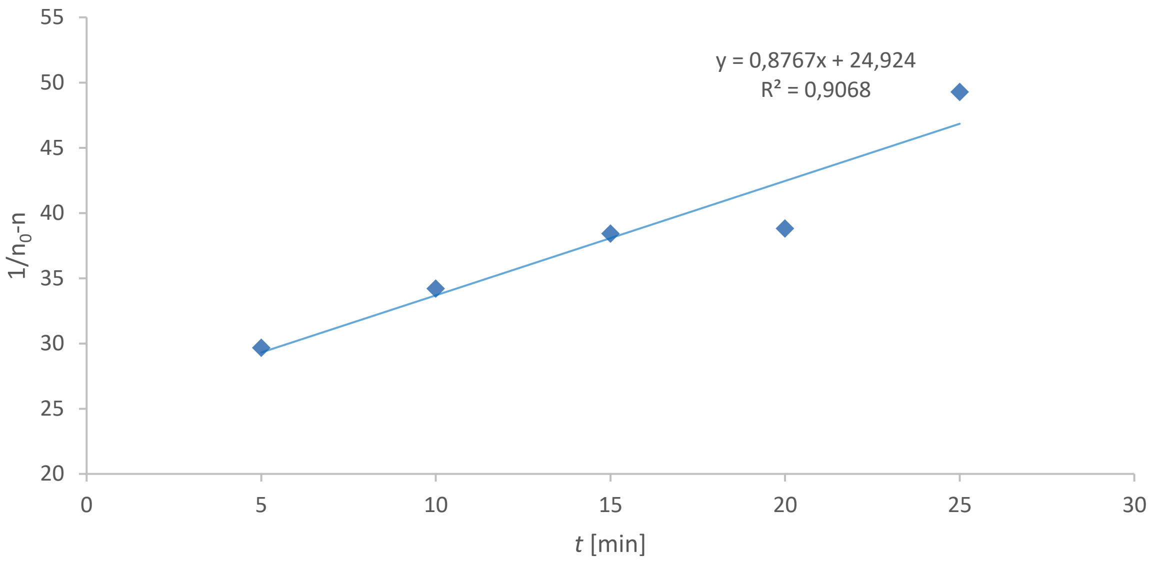


Figure SI 72: Second-order rate-law plot for the reaction of (4-methyl)phenylallene.

Table SI 5: Data of the second kinetic experiment for (4-methyl)phenylallene.

Absolute integral of product	**Absolute integral of standard**	**$n_{Standard}$ [mmol]**	**$n_{Product}$ [mmol]**	**$1/n_0$-n [1/mmol]**	***t* [min]**
54332.2	6.0E+05	0.02	0.0082	31.4	5
62630.8	4.71E+05	0.02	0.0119	35.6	10
78870.8	4.90E+05	0.02	0.0145	39.2	15
85048.8	4.87E+05	0.02	0.0157	41.2	20
108350	5.08E+05	0.02	0.0191	48.0	25

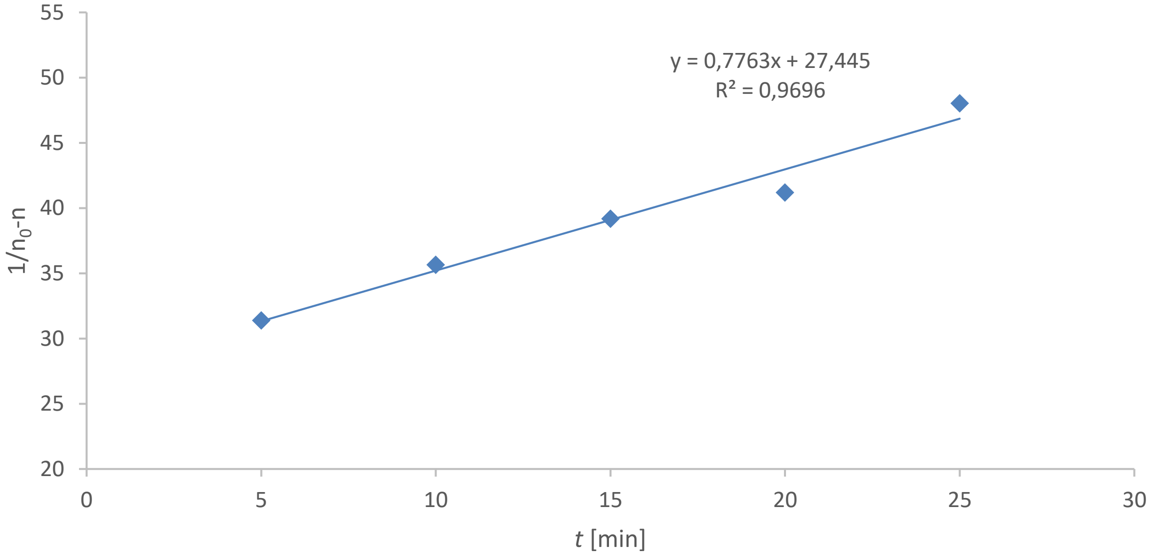


Figure SI 73: Second-order rate-law plot for the reaction of (4-methyl)phenylallene.

6.1.4 Measurements for (4-fluoro)phenylallene

Table SI 6: Data of the first kinetic experiment for (4-fluoro)phenylallene.

Absolute integral of product	Absolute integral of standard	$n_{Standard}$ [mmol]	$n_{Product}$ [mmol]	$1/n_0$-n [1/mmol]	*t* [min]
16485.1	6.59E+05	0.02	0.0022	26.5	30
44320.6	8.01E+05	0.02	0.0050	28.6	60
80881.3	8.14E+05	0.02	0.0089	32.2	95
109815	8.33E+05	0.02	0.0119	35.5	120

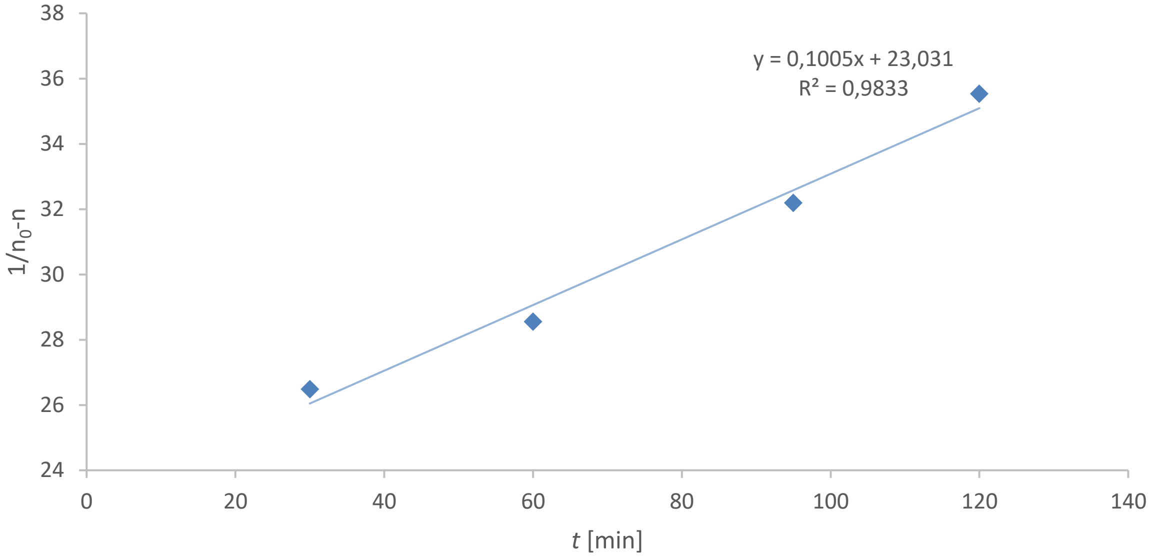


Figure SI 74: Second-order rate-law plot for the reaction of (4-fluoro)phenylallene.

Table SI 7: Data of the second kinetic experiment for (4-fluoro)phenylallene.

Absolute integral of product	Absolute integral of standard	$n_{Standard}$ [mmol]	$n_{Product}$ [mmol]	$1/n_0$-n [1/mmol]	*t* [min]
28098.1	9.14E+05	0.02	0.0028	26.8	30
65768.4	1.01E+06	0.02	0.0058	29.3	60
84704.5	9.17E+05	0.02	0.0083	31.6	95
127687	9.53E+05	0.02	0.0120	35.8	120

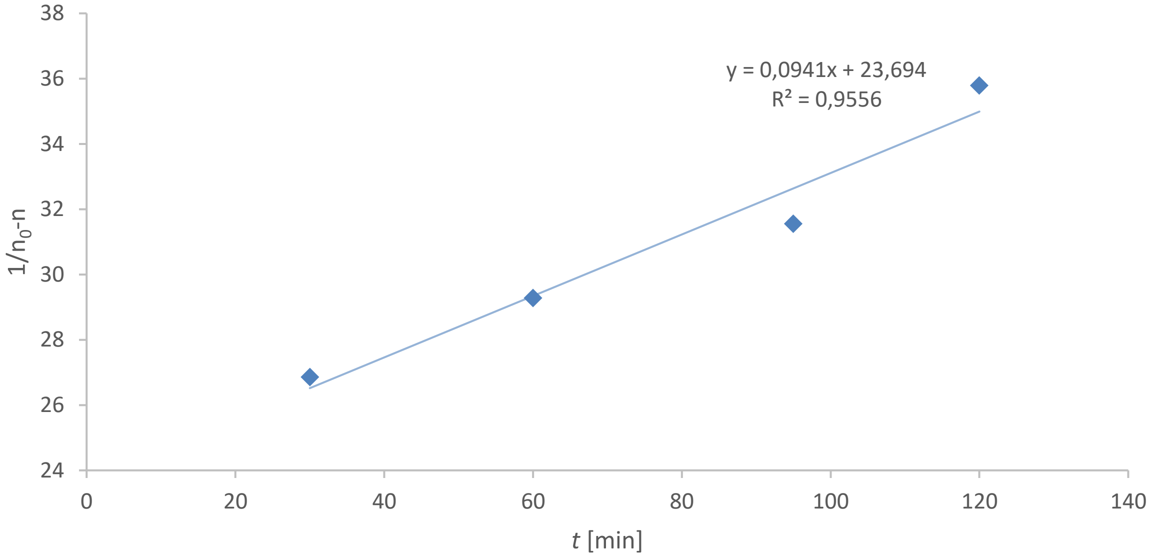


Figure SI 75: Second-order rate-law plot for the reaction of (4-fluoro)phenylallene.

6.1.5 Data for (4-chloro)phenylallene

Table SI 8: Data of the first kinetic experiment for (4-chloro)phenylallene.

Absolute integral of product	Absolute integral of standard	$n_{Standard}$ [mmol]	$n_{Product}$ [mmol]	$1/n_0$-n [1/mmol]	*t* [min]
8135.76	8.15E+05	0.02	0.0009	25.6	60
28658.7	8.42E+05	0.02	0.0031	27.1	120
47686.4	8.34E+05	0.02	0.0051	28.7	180
64194.1	8.21E+05	0.02	0.0070	30.3	240
83099.6	8.17E+05	0.02	0.0091	32.4	300

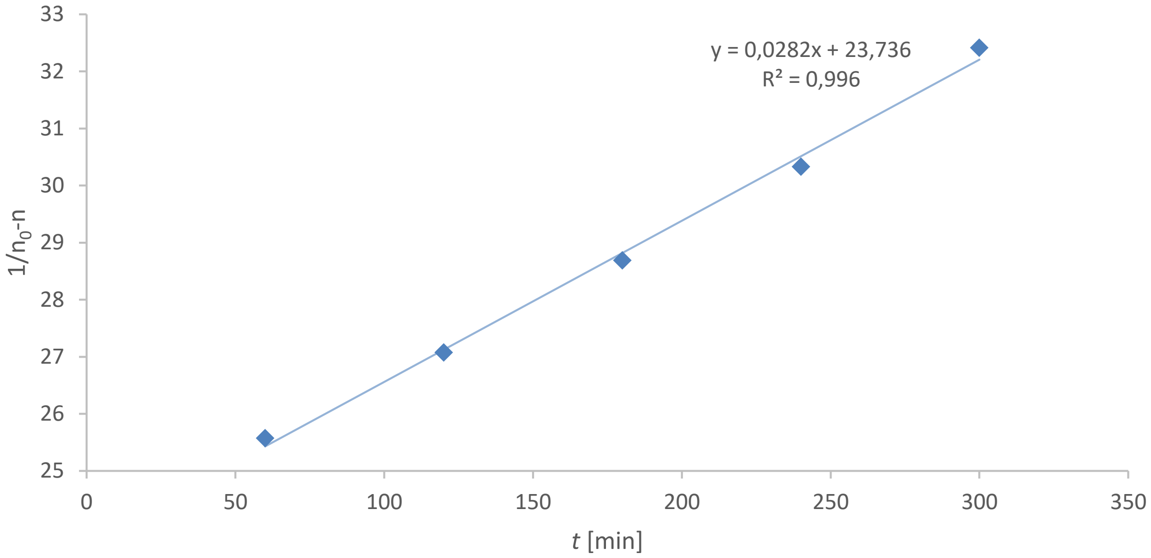


Figure SI 76: Second-order rate-law plot for the reaction of (4-chloro)phenylallene.

Table SI 9: Data of the second kinetic experiment for (4-chloro)phenylallene.

Absolute integral of product	**Absolute integral of standard**	**$n_{Standard}$ [mmol]**	**$n_{Product}$ [mmol]**	**$1/n_0$-n [1/mmol]**	***t* [min]**
15774	7.89E+05	0.02	0.0018	26.2	60
28865.3	7.97E+05	0.02	0.0032	27.2	120
42497.1	7.15E+05	0.02	0.0052	28.9	180
55488	6.77E+05	0.02	0.0074	30.6	240
75448.3	7.44E+05	0.02	0.0091	32.4	300

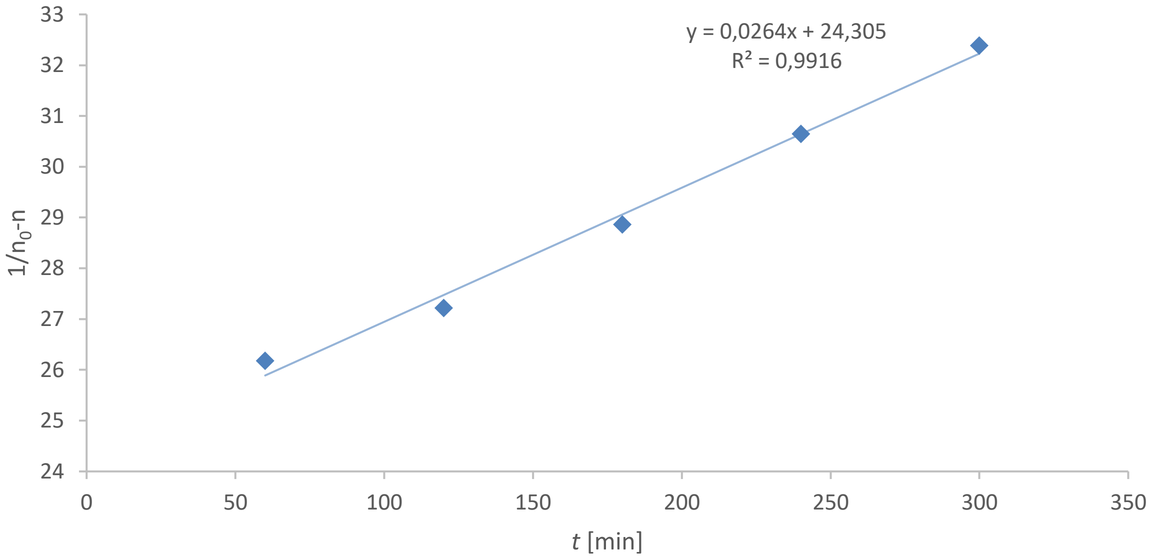


Figure SI 77: Second-order rate-law plot for the reaction of (4-chloro)phenylallene.

6.1.6 Hammett analysis

The following table shows the second-order rate-constants at 0 °C for the reaction of the different allenes (Table SI 10). The error is given as deviation from the average. The Hammett constants are taken from the literature.[10]

Table SI 10: Rate constants for the reaction of allenes with tris(perfluorphenyl)borane at 0 °C. Values displayed are the average of two runs. The errors for $\log(k_X/k_H)$ were determined by error propargation.

Subst.	***k***	**Δ*k***	σ_p	$\log(k_X/k_H)$	$\Delta\log(k_X/k_H)$
H	0.360	±0.036	0	0	-
Me	0.826	±0.050	-0.17	0.36	±0.017
F	0.097	±0.003	0.06	0.57	±0.012
Cl	0.027	±0.001	0.22	1.12	±0.002

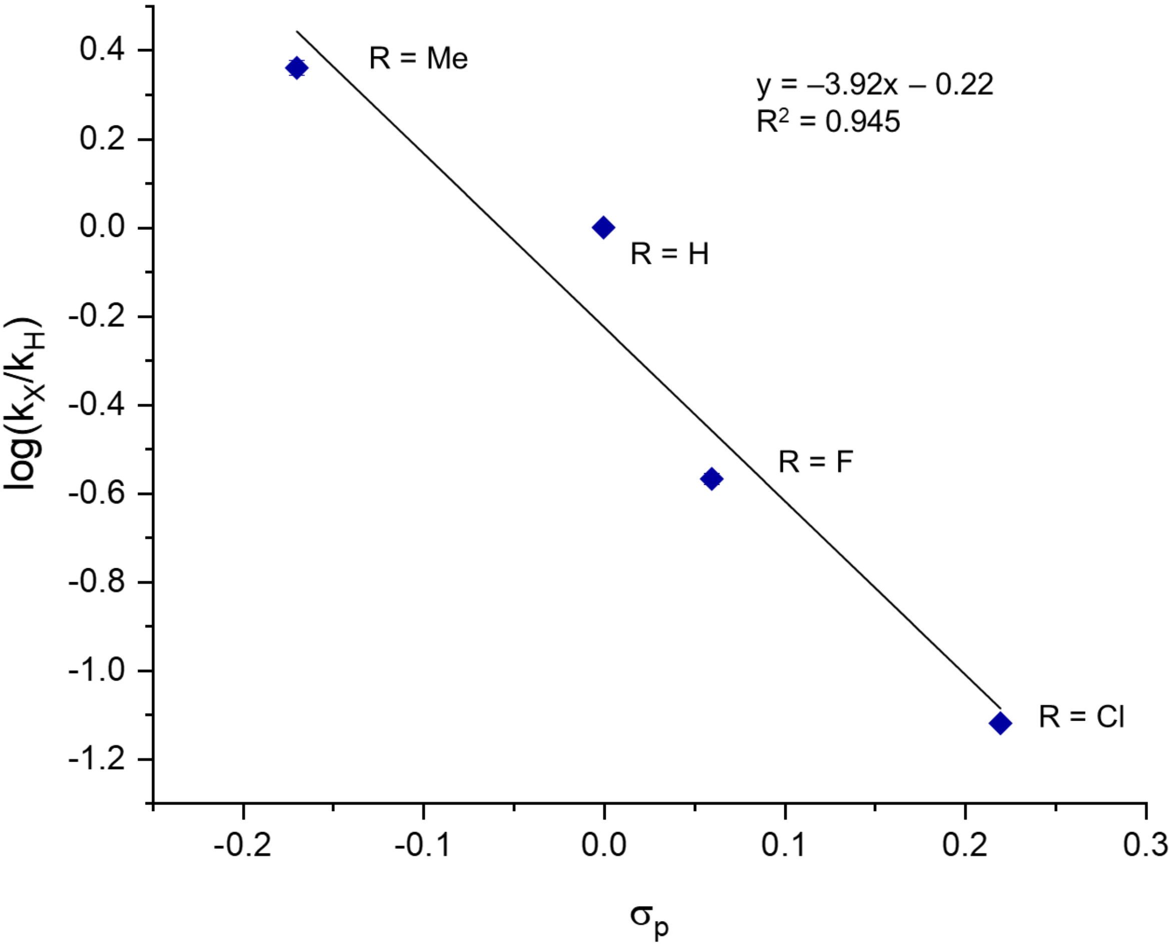


Figure SI 78: Hammett plot for the reaction of different *p*-substituted allenes with tris(perfluorphenyl)borane.

7 Single crystal X-ray diffraction analysis

Diffraction data for **2** was collected at low temperatures (100K) using ϕ- and ω-scans on a BRUKER D8 Venture system equipped with dual IµS microfocus sources, a PHOTON100 detector and an OXFORD CRYOSYSTEMS 700 low temperature system. Mo-K_α radiation with wavelength 0.71073 Å and a collimating Quazar multilayer mirror were used. Semi-empirical absorption correction from equivalents was applied using SADABS-2016/2[11] and the structure was solved in the monoclinic space group $P2_1/n$ by direct methods using SHELXT2014/5.[12] Refinement was performed against F^2 on all data by full-matrix least squares using SHELXL2018/3.[13] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2x the U_{eq} value of the atoms they are linked to. Upon closer inspection of the anisotropic displacement parameters and the hydrogen atom positions, the structure was found to exhibit whole molecule disorder. The disorder was modelled with the help of same distance restraints, similarity restraints on the anisotropic displacement parameters[14] and advanced rigid bond restraints.[15] The anisotropic displacement parameters of three atoms, where the disorder refined to very similar positions, were set to the same parameters. The disorder ratio was allowed to refine freely and converged to 0.49(1).

The crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 2059168 and can be obtained free of charge (https://www.ccdc.cam.ac.uk/structures/).

Table SI 11: Crystal data and structure refinement for 2-pentafluorophenylindene 2.

CCDC No	2059168	
Empirical formula	$C_{15} H_7 F_5$	
Formula weight	282.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 6.7868(3) Å	α= 90°.
	b = 24.2929(10) Å	β= 102.298(2)°.
	c = 6.8686(3) Å	γ = 90°.
Volume	1106.45(8) Å^3	
Z	4	
Density (calculated)	1.694 Mg/m^3	

Absorption coefficient	0.157 mm^{-1}
$F(000)$	568
Crystal size	0.365 x 0.163 x 0.055 mm^3
Theta range for data collection	1.677 to 32.574°.
Index ranges	$-10 \le h \le 10$, $-36 \le k \le 36$, $-10 \le l \le 10$
Reflections collected	137261
Independent reflections	4026 [R(int) = 0.0640]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4026 / 1033 / 345
Goodness-of-fit on F^2	1.065
Final R indices [I>2σ(I)]	R1 = 0.0381, wR2 = 0.0980
R indices (all data)	R1 = 0.0563, wR2 = 0.1118
Extinction coefficient	0.0131(19)
Largest diff. peak and hole	0.332 and -0.283 e.$Å^{-3}$

Table SI 12: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 2-pentafluorophenylindene **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	8211(14)	4271(4)	8683(13)	18(1)
F(2)	7372(9)	3210(3)	8570(8)	18(1)
F(3)	3546(7)	2821(2)	7324(8)	16(1)
F(4)	455(8)	3546(3)	6207(8)	19(1)
F(5)	1242(16)	4611(5)	6340(20)	24(1)
C(1)	5080(40)	5109(4)	7500(70)	15(1)
C(2)	3767(15)	5542(4)	7081(15)	18(1)
C(3)	4856(17)	6061(4)	7330(30)	14(1)
C(4)	4040(14)	6634(4)	7028(19)	18(2)
C(5)	5300(20)	7021(5)	7340(30)	20(2)
C(6)	7360(20)	6937(4)	7970(20)	20(2)
C(7)	8170(18)	6355(4)	8210(30)	16(1)
C(8)	6907(16)	5946(4)	7920(20)	14(1)
C(9)	7203(12)	5335(3)	8113(12)	11(1)
C(10)	4753(11)	4507(2)	7479(15)	12(1)
C(11)	6283(11)	4130(2)	8079(14)	9(1)
C(12)	5879(18)	3567(4)	7960(70)	18(1)
C(13)	3954(18)	3357(4)	7400(70)	18(1)
C(14)	2382(13)	3717(3)	6820(30)	18(2)
C(15)	2853(13)	4267(3)	6900(17)	22(2)
F(1A)	8055(14)	4281(5)	8613(15)	29(2)
F(2A)	7370(11)	3212(3)	8514(11)	37(2)
F(3A)	3519(10)	2832(3)	7303(11)	36(2)
F(4A)	449(11)	3571(4)	6216(11)	35(2)
F(5A)	1060(16)	4644(4)	6246(17)	21(1)
C(1A)	5110(40)	5117(4)	7520(70)	15(1)
C(2A)	6942(13)	5379(3)	7975(13)	18(1)
C(3A)	6627(15)	5972(3)	7861(19)	13(1)
C(4A)	8160(16)	6417(4)	8300(20)	19(1)
C(5A)	7563(19)	6912(4)	8050(20)	18(1)
C(6A)	5520(20)	7043(5)	7500(30)	17(1)
C(7A)	3985(14)	6587(4)	7091(17)	18(1)
C(8A)	4578(16)	6077(4)	7280(30)	13(1)

C(9A)	3458(13)	5539(3)	6998(13)	12(1)
C(10A)	4625(11)	4529(3)	7453(15)	16(1)
C(11A)	6110(13)	4114(3)	7950(17)	22(2)
C(12A)	5801(17)	3557(4)	8010(70)	18(1)
C(13A)	3847(17)	3375(4)	7340(60)	18(1)
C(14A)	2323(12)	3760(3)	6800(30)	17(1)
C(15A)	2665(10)	4318(3)	6840(12)	9(1)

Table SI 13: Bond lengths [Å] and angles [°] for 2-pentafluorophenylindene **2**.

F(1)-C(11)	1.330(8)
F(2)-C(12)	1.333(9)
F(3)-C(13)	1.330(9)
F(4)-C(14)	1.350(8)
F(5)-C(15)	1.365(9)
C(1)-C(2)	1.37(2)
C(1)-C(10)	1.478(8)
C(1)-C(9)	1.51(2)
C(2)-C(3)	1.454(12)
C(2)-H(2)	0.9500
C(3)-C(8)	1.393(9)
C(3)-C(4)	1.495(14)
C(4)-C(5)	1.259(18)
C(4)-H(4)	0.9500
C(5)-C(6)	1.390(9)
C(5)-H(5)	0.9500
C(6)-C(7)	1.512(17)
C(6)-H(6)	0.9500
C(7)-C(8)	1.301(15)
C(7)-H(7)	0.9500
C(8)-C(9)	1.500(11)
C(9)-H(9A)	0.9900
C(9)-H(9AB)	0.9900
C(10)-C(11)	1.379(7)
C(10)-C(15)	1.393(8)
C(11)-C(12)	1.394(8)
C(12)-C(13)	1.379(9)
C(13)-C(14)	1.371(9)
C(14)-C(15)	1.374(8)
F(1A)-C(11A)	1.363(9)
F(2A)-C(12A)	1.343(9)
F(3A)-C(13A)	1.337(8)
F(4A)-C(14A)	1.331(8)
F(5A)-C(15A)	1.338(8)
C(1A)-C(2A)	1.37(2)
C(1A)-C(10A)	1.463(8)
C(1A)-C(9A)	1.51(2)
C(2A)-C(3A)	1.456(10)
C(2A)-H(2A)	0.9500

C(3A)-C(8A)	1.386(8)
C(3A)-C(4A)	1.487(14)
C(4A)-C(5A)	1.268(17)
C(4A)-H(4A)	0.9500
C(5A)-C(6A)	1.397(9)
C(5A)-H(5A)	0.9500
C(6A)-C(7A)	1.505(16)
C(6A)-H(6A)	0.9500
C(7A)-C(8A)	1.300(14)
C(7A)-H(7A)	0.9500
C(8A)-C(9A)	1.504(11)
C(9A)-H(9AA)	0.9900
C(9A)-H(9AC)	0.9900
C(10A)-C(15A)	1.404(7)
C(10A)-C(11A)	1.416(8)
C(11A)-C(12A)	1.369(9)
C(12A)-C(13A)	1.380(9)
C(13A)-C(14A)	1.385(8)
C(14A)-C(15A)	1.375(7)

C(2)-C(1)-C(10)	131.8(19)
C(2)-C(1)-C(9)	108.5(7)
C(10)-C(1)-C(9)	119.7(17)
C(1)-C(2)-C(3)	110.5(11)
C(1)-C(2)-H(2)	124.8
C(3)-C(2)-H(2)	124.8
C(8)-C(3)-C(2)	108.1(10)
C(8)-C(3)-C(4)	123.1(10)
C(2)-C(3)-C(4)	128.8(9)
C(5)-C(4)-C(3)	117.0(11)
C(5)-C(4)-H(4)	121.5
C(3)-C(4)-H(4)	121.5
C(4)-C(5)-C(6)	123.0(13)
C(4)-C(5)-H(5)	118.5
C(6)-C(5)-H(5)	118.5
C(5)-C(6)-C(7)	119.3(11)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-H(6)	120.3
C(8)-C(7)-C(6)	119.1(11)

C(8)-C(7)-H(7)	120.4
C(6)-C(7)-H(7)	120.4
C(7)-C(8)-C(3)	118.3(11)
C(7)-C(8)-C(9)	132.3(10)
C(3)-C(8)-C(9)	109.4(9)
C(8)-C(9)-C(1)	103.5(9)
C(8)-C(9)-H(9A)	111.1
C(1)-C(9)-H(9A)	111.1
C(8)-C(9)-H(9AB)	111.1
C(1)-C(9)-H(9AB)	111.1
H(9A)-C(9)-H(9AB)	109.0
C(11)-C(10)-C(15)	113.6(6)
C(11)-C(10)-C(1)	123.4(11)
C(15)-C(10)-C(1)	123.0(12)
F(1)-C(11)-C(10)	123.3(7)
F(1)-C(11)-C(12)	116.1(7)
C(10)-C(11)-C(12)	120.5(7)
F(2)-C(12)-C(13)	117.3(8)
F(2)-C(12)-C(11)	119.6(8)
C(13)-C(12)-C(11)	122.9(8)
F(3)-C(13)-C(14)	118.1(8)
F(3)-C(13)-C(12)	123.4(8)
C(14)-C(13)-C(12)	118.5(8)
F(4)-C(14)-C(13)	122.5(7)
F(4)-C(14)-C(15)	120.9(8)
C(13)-C(14)-C(15)	116.7(7)
F(5)-C(15)-C(14)	114.7(8)
F(5)-C(15)-C(10)	117.6(8)
C(14)-C(15)-C(10)	127.7(7)
C(2A)-C(1A)-C(10A)	130.4(18)
C(2A)-C(1A)-C(9A)	109.3(6)
C(10A)-C(1A)-C(9A)	120.3(16)
C(1A)-C(2A)-C(3A)	109.4(10)
C(1A)-C(2A)-H(2A)	125.3
C(3A)-C(2A)-H(2A)	125.3
C(8A)-C(3A)-C(2A)	108.9(9)
C(8A)-C(3A)-C(4A)	122.7(9)
C(2A)-C(3A)-C(4A)	128.4(9)
C(5A)-C(4A)-C(3A)	118.2(11)

C(5A)-C(4A)-H(4A)	120.9
C(3A)-C(4A)-H(4A)	120.9
C(4A)-C(5A)-C(6A)	121.6(12)
C(4A)-C(5A)-H(5A)	119.2
C(6A)-C(5A)-H(5A)	119.2
C(5A)-C(6A)-C(7A)	119.3(11)
C(5A)-C(6A)-H(6A)	120.4
C(7A)-C(6A)-H(6A)	120.4
C(8A)-C(7A)-C(6A)	119.8(10)
C(8A)-C(7A)-H(7A)	120.1
C(6A)-C(7A)-H(7A)	120.1
C(7A)-C(8A)-C(3A)	118.3(10)
C(7A)-C(8A)-C(9A)	132.7(9)
C(3A)-C(8A)-C(9A)	109.0(9)
C(8A)-C(9A)-C(1A)	103.3(9)
C(8A)-C(9A)-H(9AA)	111.1
C(1A)-C(9A)-H(9AA)	111.1
C(8A)-C(9A)-H(9AC)	111.1
C(1A)-C(9A)-H(9AC)	111.1
H(9AA)-C(9A)-H(9AC)	109.1
C(15A)-C(10A)-C(11A)	113.0(6)
C(15A)-C(10A)-C(1A)	124.0(11)
C(11A)-C(10A)-C(1A)	122.9(11)
F(1A)-C(11A)-C(12A)	115.3(8)
F(1A)-C(11A)-C(10A)	117.2(8)
C(12A)-C(11A)-C(10A)	127.2(7)
F(2A)-C(12A)-C(11A)	120.5(8)
F(2A)-C(12A)-C(13A)	122.5(8)
C(11A)-C(12A)-C(13A)	116.7(8)
F(3A)-C(13A)-C(12A)	117.9(8)
F(3A)-C(13A)-C(14A)	123.3(8)
C(12A)-C(13A)-C(14A)	118.8(7)
F(4A)-C(14A)-C(15A)	119.5(7)
F(4A)-C(14A)-C(13A)	117.4(7)
C(15A)-C(14A)-C(13A)	123.2(7)
F(5A)-C(15A)-C(14A)	117.0(7)
F(5A)-C(15A)-C(10A)	122.2(7)
C(14A)-C(15A)-C(10A)	120.8(6)

Table SI 14: Anisotropic displacement parameters (Å^{2}x 10^3) for 2-pentafluorophenylindene **2**. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	8(1)	14(2)	28(2)	-2(1)	-2(1)	-2(1)
F(2)	16(2)	12(3)	27(2)	1(2)	7(2)	4(2)
F(3)	18(2)	8(2)	25(2)	-3(2)	12(2)	-3(2)
F(4)	11(2)	20(2)	24(2)	-1(2)	3(2)	-6(1)
F(5)	11(2)	16(2)	43(3)	5(1)	-1(1)	1(1)
C(1)	18(1)	13(1)	14(1)	0(1)	4(1)	-2(1)
C(2)	13(3)	25(2)	17(2)	0(1)	3(2)	-1(1)
C(3)	16(3)	10(2)	18(2)	0(1)	4(3)	1(2)
C(4)	23(3)	10(2)	24(3)	4(1)	10(2)	9(2)
C(5)	18(2)	18(3)	23(3)	1(2)	1(2)	4(2)
C(6)	26(4)	7(2)	26(3)	0(2)	2(2)	0(2)
C(7)	22(2)	6(2)	20(3)	1(2)	3(2)	4(1)
C(8)	7(2)	22(2)	13(2)	3(1)	2(1)	6(1)
C(9)	10(2)	5(1)	17(2)	0(1)	3(1)	-1(1)
C(10)	16(2)	6(2)	14(3)	-3(2)	2(2)	-6(2)
C(11)	12(2)	2(1)	12(2)	-2(1)	1(1)	0(1)
C(12)	19(1)	14(1)	21(2)	-1(1)	6(1)	1(1)
C(13)	21(1)	12(1)	20(2)	-1(1)	6(2)	-2(1)
C(14)	22(3)	11(2)	20(3)	-3(2)	5(3)	-9(2)
C(15)	20(2)	21(2)	25(2)	8(1)	6(2)	12(1)
F(1A)	18(2)	17(2)	49(3)	2(2)	2(2)	3(1)
F(2A)	28(3)	17(3)	63(3)	0(2)	2(3)	3(2)
F(3A)	43(3)	16(2)	47(3)	-1(2)	6(3)	-6(2)
F(4A)	26(3)	22(2)	55(3)	-1(2)	4(2)	-8(2)
F(5A)	12(2)	19(2)	30(2)	7(1)	0(1)	5(1)
C(1A)	18(1)	13(1)	14(1)	0(1)	4(1)	-2(1)
C(2A)	16(2)	21(2)	17(2)	6(1)	2(1)	8(1)
C(3A)	15(3)	6(1)	18(2)	0(1)	4(2)	1(2)
C(4A)	17(2)	18(3)	23(2)	-5(2)	4(2)	-7(2)
C(5A)	15(2)	22(3)	18(2)	2(2)	3(1)	-2(2)
C(6A)	23(3)	8(2)	20(3)	-2(1)	2(2)	-6(2)
C(7A)	18(2)	16(2)	19(2)	0(2)	0(2)	-7(2)
C(8A)	6(2)	19(2)	14(2)	0(1)	2(1)	1(1)

C(9A)	10(2)	7(1)	19(2)	-1(1)	2(1)	-2(1)
C(10A)	15(2)	22(2)	14(3)	4(2)	7(2)	7(1)
C(11A)	14(2)	31(3)	21(3)	-2(2)	3(2)	-6(1)
C(12A)	19(1)	14(1)	21(2)	-1(1)	6(1)	1(1)
C(13A)	21(1)	12(1)	20(2)	-1(1)	6(2)	-2(1)
C(14A)	13(2)	19(2)	20(3)	3(2)	4(2)	4(2)
C(15A)	7(1)	6(1)	12(2)	0(1)	0(1)	-1(1)

Table SI 15: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for 2-pentafluorophenylindene **2**.

	x	y	z	U(eq)
H(2)	2344	5508	6680	22
H(4)	2634	6702	6619	22
H(5)	4819	7388	7125	24
H(6)	8255	7241	8259	24
H(7)	9581	6290	8551	19
H(9A)	7827	5230	9500	13
H(9AB)	8063	5200	7216	13
H(2A)	8217	5202	8311	22
H(4A)	9549	6334	8749	23
H(5A)	8532	7200	8239	22
H(6A)	5094	7417	7386	21
H(7A)	2589	6670	6699	22
H(9AA)	2707	5494	5604	15
H(9AC)	2501	5512	7899	15

8 Computational chemistry

8.1 Computational details

All structures were fully optimized with the composite method PBEh-3c.[16] Thermodynamic properties were obtained at the same level of theory from a frequency computation. The computed free energies were corrected regarding the standard state by adding RT ln(c0s/c0g) (i.e., about 1.89 kcal mol^{-1}) to energies of all structures. For final single point energy computations, the revDSD-PBEP86 functional with Grimme's D4 dispersion correction and the def2-QZVPP basis set was used in combination with the RIJK approximation.[17] Solvent effects were considered implicitly for the structure optimizations and the single point computations using the SMD model for dichloromethane.[18]

8.2 Cartesian coordinates and energies

1

C	8.854042000	-3.361249000	-0.787783000
C	7.947582000	-4.186169000	-1.219120000
H	7.722542000	-4.275055000	-2.276595000
H	7.382802000	-4.812336000	-0.536692000
C	9.770521000	-2.534209000	-0.354428000
C	11.192383000	-2.857582000	-0.178381000
C	11.711607000	-4.122662000	-0.465428000
C	13.058616000	-4.388344000	-0.286823000
C	13.915453000	-3.397776000	0.181601000
C	13.410251000	-2.138247000	0.469574000
C	12.060005000	-1.870899000	0.291033000
H	11.674398000	-0.884124000	0.518370000
H	14.066955000	-1.359006000	0.834412000
H	14.967767000	-3.608755000	0.320148000
H	13.443559000	-5.374204000	-0.513969000
H	11.056609000	-4.904535000	-0.831035000
H	9.465821000	-1.521833000	-0.102539000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.1091851	68.51468751

E revDSD-PBEP86-D4/def2-QZVPP -347.2227472 -217885.5725

$B(C_6F_5)_3$

B	0.611886000	-0.077680000	-0.729698000
C	2.140354000	-0.313680000	-0.544817000
C	3.067363000	0.693863000	-0.775830000
C	2.644833000	-1.542332000	-0.140235000
C	4.425094000	0.498474000	-0.627848000
C	3.994453000	-1.765664000	0.038763000
C	4.885336000	-0.738141000	-0.213142000
C	-0.037174000	1.243726000	-0.222049000
C	-0.985374000	1.927054000	-0.971586000
C	0.304970000	1.798977000	1.003719000
C	-1.559684000	3.105502000	-0.541379000
C	-0.265852000	2.963567000	1.474112000
C	-1.198499000	3.619190000	0.690992000
F	1.810052000	-2.543317000	0.124800000
F	2.654291000	1.887987000	-1.191334000
F	5.287922000	1.475232000	-0.876431000
F	6.182222000	-0.938960000	-0.056877000
F	4.444187000	-2.945287000	0.447050000
F	1.187207000	1.181592000	1.784364000
F	0.066466000	3.457731000	2.659667000
F	-1.747331000	4.741332000	1.122530000
F	-2.447675000	3.747064000	-1.289812000
F	-1.339894000	1.464537000	-2.167174000
C	-0.264613000	-1.162420000	-1.422350000
C	0.174772000	-1.844291000	-2.549475000
C	-1.523532000	-1.499555000	-0.943055000
C	-0.590999000	-2.802899000	-3.180263000
C	-2.306001000	-2.468892000	-1.536044000
C	-1.834915000	-3.116858000	-2.663518000
F	-1.995448000	-0.904445000	0.148706000
F	-3.495780000	-2.784945000	-1.041369000
F	-2.576488000	-4.040654000	-3.249339000
F	-0.151608000	-3.422451000	-4.268077000

F	1.360044000	-1.552112000	-3.077173000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.10671141	66.96242353
E revDSD-PBEP86-D4/def2-QZVPP	-2206.211244	-1384418.515

TS-1

B	7.586403000	-2.527593000	0.187419000
C	8.808218000	-3.397994000	-1.547706000
C	8.040270000	-4.029516000	-2.403645000
H	8.291843000	-3.994032000	-3.459161000
H	7.122180000	-4.539662000	-2.150312000
C	9.995558000	-2.888634000	-1.208103000
C	11.236474000	-3.639940000	-1.150805000
C	11.308780000	-4.993967000	-1.493306000
C	12.525808000	-5.649244000	-1.480510000
C	13.684473000	-4.967534000	-1.119845000
C	13.621780000	-3.625195000	-0.770614000
C	12.403666000	-2.966118000	-0.781163000
H	12.354533000	-1.918739000	-0.508882000
H	14.520590000	-3.093489000	-0.488310000
H	14.634125000	-5.486145000	-1.108098000
H	12.575525000	-6.696729000	-1.746507000
H	10.409080000	-5.533088000	-1.761560000
H	10.069839000	-1.841138000	-0.938085000
C	6.309330000	-3.484231000	0.156440000
C	6.433145000	-4.853957000	0.347533000
C	5.353856000	-5.708103000	0.452584000
C	4.075537000	-5.188289000	0.398608000
C	3.900684000	-3.828091000	0.244310000
C	5.006106000	-3.005099000	0.131594000
F	4.760986000	-1.699428000	0.030795000
F	2.673258000	-3.319134000	0.214944000
F	3.025093000	-5.989060000	0.502156000
F	5.533300000	-7.015305000	0.610459000

F	7.645950000	-5.400594000	0.422488000
C	7.576634000	-1.130228000	-0.564070000
C	8.319992000	-0.032774000	-0.135464000
C	8.322557000	1.187358000	-0.784456000
C	7.570105000	1.348952000	-1.929131000
C	6.834669000	0.284946000	-2.413289000
C	6.851318000	-0.916977000	-1.736059000
F	6.138943000	-1.899978000	-2.277263000
F	6.121550000	0.426757000	-3.525281000
F	7.562470000	2.508956000	-2.565441000
F	9.049646000	2.198166000	-0.321547000
F	9.107889000	-0.119769000	0.936261000
C	8.273900000	-2.637876000	1.637300000
C	7.640205000	-1.897545000	2.628192000
C	9.305917000	-3.444298000	2.082462000
C	8.005718000	-1.912803000	3.956595000
C	9.707336000	-3.484482000	3.408888000
C	9.058962000	-2.715918000	4.350424000
F	9.977235000	-4.237801000	1.253043000
F	6.606966000	-1.118703000	2.287932000
F	7.360486000	-1.172223000	4.852191000
F	9.435320000	-2.751110000	5.621745000
F	10.714507000	-4.270803000	3.778465000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.24115753	151.3286411
E revDSD-PBEP86-D4/def2-QZVPP	-2553.422134	-1602296.646

INT-1

B	7.737822000	-2.669132000	0.168412000
C	8.836748000	-3.405157000	-0.823385000
C	8.503503000	-4.240764000	-1.837437000
H	9.192040000	-4.483120000	-2.638198000
H	7.497826000	-4.619848000	-1.963436000
C	10.163898000	-2.927285000	-0.801528000
C	11.334293000	-3.628893000	-1.163893000

C	11.375622000	-5.034688000	-1.284268000
C	12.529421000	-5.652208000	-1.716964000
C	13.653563000	-4.888092000	-2.019880000
C	13.642475000	-3.502617000	-1.870772000
C	12.500140000	-2.877007000	-1.424523000
H	12.477084000	-1.802173000	-1.298499000
H	14.528824000	-2.925637000	-2.094002000
H	14.557604000	-5.380514000	-2.353060000
H	12.569854000	-6.729283000	-1.798441000
H	10.523684000	-5.630566000	-0.986832000
H	10.324593000	-1.907139000	-0.460096000
C	6.317414000	-3.490379000	0.157986000
C	6.331795000	-4.840776000	0.480877000
C	5.200427000	-5.628331000	0.571538000
C	3.964189000	-5.056058000	0.350643000
C	3.890614000	-3.711614000	0.052517000
C	5.050672000	-2.959798000	-0.030430000
F	4.876160000	-1.661938000	-0.293845000
F	2.701450000	-3.145218000	-0.146688000
F	2.859091000	-5.789449000	0.430814000
F	5.289957000	-6.922298000	0.873937000
F	7.498102000	-5.448198000	0.735753000
C	7.683314000	-1.167213000	-0.492500000
C	8.255991000	-0.025763000	0.046437000
C	8.265007000	1.203353000	-0.593516000
C	7.697133000	1.326064000	-1.842804000
C	7.139773000	0.211786000	-2.439465000
C	7.153708000	-0.992066000	-1.765409000
F	6.624838000	-2.036654000	-2.411464000
F	6.602945000	0.309613000	-3.654188000
F	7.696802000	2.495844000	-2.471999000
F	8.827109000	2.263244000	-0.015238000
F	8.876418000	-0.058998000	1.232102000
C	8.160505000	-2.668309000	1.755240000
C	7.351541000	-1.993409000	2.659596000
C	9.197916000	-3.373931000	2.336409000
C	7.550305000	-1.991648000	4.024446000

C	9.438770000	-3.401628000	3.700884000
C	8.609495000	-2.705410000	4.552383000
F	10.052587000	-4.087703000	1.588430000
F	6.311800000	-1.285042000	2.206148000
F	6.739622000	-1.313589000	4.834595000
F	8.823071000	-2.719519000	5.863889000
F	10.461198000	-4.099045000	4.193934000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.24258515	152.2244862
E revDSD-PBEP86-D4/def2-QZVPP	-2553.443398	-1602309.99

TS-2

B	7.868661000	-2.601400000	0.308618000
C	9.137518000	-3.179535000	-0.559415000
C	9.019212000	-4.095471000	-1.623089000
H	9.431596000	-3.847428000	-2.593261000
H	8.228562000	-4.835174000	-1.668492000
C	10.428165000	-2.719594000	-0.388038000
C	11.418097000	-3.537887000	-0.968403000
C	11.021554000	-4.874919000	-1.284602000
C	11.777538000	-5.620226000	-2.213839000
C	12.931076000	-5.086153000	-2.723081000
C	13.385454000	-3.813297000	-2.309953000
C	12.660747000	-3.055400000	-1.429333000
H	12.983634000	-2.059133000	-1.157678000
H	14.308736000	-3.425514000	-2.718740000
H	13.534667000	-5.661394000	-3.412267000
H	11.477665000	-6.629335000	-2.459976000
H	10.422419000	-5.436126000	-0.574861000
H	10.683721000	-1.822524000	0.163731000
C	6.532354000	-3.543020000	0.167403000
C	6.631943000	-4.888236000	0.491683000
C	5.568673000	-5.769564000	0.490946000
C	4.311484000	-5.301004000	0.167294000

C	4.150682000	-3.966167000	-0.140654000
C	5.245992000	-3.118851000	-0.128211000
F	4.988001000	-1.839987000	-0.414104000
F	2.939494000	-3.501910000	-0.442209000
F	3.268610000	-6.124114000	0.158460000
F	5.741729000	-7.052550000	0.802088000
F	7.824360000	-5.394265000	0.839732000
C	7.754704000	-1.129695000	-0.408444000
C	8.201897000	0.065684000	0.129999000
C	8.179659000	1.267934000	-0.557975000
C	7.715838000	1.304298000	-1.855517000
C	7.293491000	0.132012000	-2.452045000
C	7.332160000	-1.041853000	-1.728479000
F	6.951978000	-2.152548000	-2.373232000
F	6.863040000	0.146261000	-3.711991000
F	7.688317000	2.448661000	-2.529661000
F	8.612387000	2.386540000	0.020632000
F	8.717510000	0.115204000	1.363722000
C	8.122592000	-2.546607000	1.928392000
C	7.206155000	-1.868019000	2.720858000
C	9.100309000	-3.222867000	2.638508000
C	7.255419000	-1.822727000	4.098397000
C	9.189893000	-3.203977000	4.022007000
C	8.264025000	-2.498490000	4.758264000
F	10.033185000	-3.956484000	2.018378000
F	6.200614000	-1.206447000	2.137599000
F	6.347460000	-1.141924000	4.795254000
F	8.334664000	-2.472313000	6.084956000
F	10.161071000	-3.870666000	4.644840000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.2428718	152.4043618
E revDSD-PBEP86-D4/def2-QZVPP	-2553.434191	-1602304.213

INT-2

B	7.882807000	-2.687237000	0.349697000
C	9.264671000	-3.248040000	-0.272842000
C	9.388296000	-3.615861000	-1.723092000
H	9.448210000	-2.693425000	-2.306313000
H	8.553130000	-4.185523000	-2.125734000
C	10.509065000	-3.311265000	0.308608000
C	11.447871000	-3.819039000	-0.599558000
C	10.752177000	-4.322682000	-1.800229000
C	11.559859000	-4.393696000	-3.029851000
C	12.900933000	-4.288631000	-2.955866000
C	13.539789000	-4.040256000	-1.697522000
C	12.849404000	-3.823704000	-0.535959000
H	13.365833000	-3.555780000	0.375516000
H	14.620740000	-3.981700000	-1.681634000
H	13.516627000	-4.400239000	-3.837258000
H	11.063934000	-4.627536000	-3.963220000
H	10.545579000	-5.388475000	-1.577331000
H	10.759165000	-2.986599000	1.308371000
C	6.674502000	-3.789999000	0.262406000
C	6.847468000	-5.148003000	0.067137000
C	5.809430000	-6.064528000	0.113038000
C	4.530222000	-5.628732000	0.382526000
C	4.308946000	-4.283064000	0.608198000
C	5.373033000	-3.407004000	0.551116000
F	5.107743000	-2.119681000	0.794765000
F	3.078706000	-3.851454000	0.879315000
F	3.520723000	-6.491539000	0.431493000
F	6.039015000	-7.360633000	-0.092656000
F	8.063370000	-5.659824000	-0.172268000
C	7.674527000	-1.362214000	-0.602752000
C	8.535338000	-0.282057000	-0.464392000
C	8.507360000	0.835160000	-1.274460000
C	7.591907000	0.896004000	-2.306944000
C	6.737740000	-0.166868000	-2.510953000
C	6.801493000	-1.268818000	-1.673756000
F	5.976074000	-2.275976000	-1.979592000
F	5.866810000	-0.130417000	-3.517812000

F	7.545574000	1.959581000	-3.101738000
F	9.354383000	1.843918000	-1.078895000
F	9.470352000	-0.300043000	0.492696000
C	7.980798000	-2.353035000	1.956917000
C	7.546842000	-1.191647000	2.579625000
C	8.413973000	-3.339131000	2.832756000
C	7.585233000	-0.998997000	3.950224000
C	8.472691000	-3.189197000	4.205327000
C	8.056992000	-2.001630000	4.770956000
F	8.790003000	-4.532630000	2.356396000
F	7.043113000	-0.174103000	1.874894000
F	7.162802000	0.145925000	4.484599000
F	8.100066000	-1.830448000	6.088044000
F	8.913393000	-4.177423000	4.982216000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.24583296	154.2625178
E revDSD-PBEP86-D4/def2-QZVPP	-2553.4578	-1602319.027

INT-4

B	7.616696000	-3.255436000	0.796783000
C	8.750193000	-2.892278000	-0.250710000
C	8.774772000	-3.648851000	-1.614675000
H	8.291527000	-3.091951000	-2.417040000
H	8.258406000	-4.607909000	-1.568799000
C	10.968537000	-3.707249000	-0.691469000
C	10.240470000	-3.860017000	-1.864501000
C	10.879396000	-4.185663000	-3.050787000
C	12.259863000	-4.353666000	-3.047318000
C	12.986389000	-4.202008000	-1.870813000
C	12.342905000	-3.879240000	-0.681070000
H	12.911510000	-3.758739000	0.232905000
H	14.061218000	-4.329678000	-1.883017000
H	12.773726000	-4.599241000	-3.967797000
H	10.317606000	-4.303074000	-3.969552000

C	6.587542000	-4.435714000	0.630940000
C	6.922577000	-5.757736000	0.386359000
C	5.976307000	-6.757942000	0.282368000
C	4.638600000	-6.441520000	0.423656000
C	4.261380000	-5.137563000	0.682005000
C	5.236734000	-4.167736000	0.795934000
F	4.846782000	-2.921376000	1.060861000
F	2.977388000	-4.833513000	0.823593000
F	3.719871000	-7.388006000	0.316705000
F	6.338725000	-8.014598000	0.056234000
F	8.203354000	-6.113314000	0.282188000
C	8.741000000	-1.408358000	-0.587164000
C	9.799249000	-0.511972000	-0.564800000
C	9.658523000	0.801727000	-0.989657000
C	8.450374000	1.256607000	-1.469168000
C	7.372267000	0.392293000	-1.513439000
C	7.542258000	-0.900831000	-1.077545000
F	6.478419000	-1.712879000	-1.101620000
F	6.195010000	0.813358000	-1.959256000
F	8.319197000	2.510212000	-1.877826000
F	10.701089000	1.624010000	-0.946207000
F	11.013675000	-0.854940000	-0.143702000
C	7.606147000	-2.552119000	2.219005000
C	7.287774000	-1.236771000	2.511915000
C	7.954896000	-3.343796000	3.304445000
C	7.325529000	-0.729957000	3.797389000
C	8.019126000	-2.870788000	4.598804000
C	7.700379000	-1.549132000	4.843695000
F	8.268192000	-4.625940000	3.098607000
F	6.882243000	-0.408093000	1.552395000
F	6.998804000	0.535005000	4.032885000
F	7.748103000	-1.071773000	6.077207000
F	8.379312000	-3.665575000	5.598470000
C	10.055430000	-3.384914000	0.454618000
H	9.865311000	-4.307455000	1.014084000
H	10.452882000	-2.682658000	1.183215000

	Hatree	kcal mol−1
G-E(el) PBEh-3c	0.24675165	154.8390045
E revDSD-PBEP86-D4/def2-QZVPP	-2553.497765	-1602344.106

TS-3

B	8.254043000	-3.045979000	0.614492000
C	9.037013000	-1.967220000	-0.952072000
C	8.783155000	-2.610905000	-2.313628000
H	9.197103000	-1.939592000	-3.074508000
H	7.747813000	-2.775023000	-2.588206000
C	10.345308000	-3.894202000	-1.101047000
C	9.580006000	-3.869815000	-2.262817000
C	9.637458000	-4.924054000	-3.158609000
C	10.486256000	-5.985126000	-2.870606000
C	11.260779000	-6.000122000	-1.709814000
C	11.193494000	-4.953481000	-0.805113000
H	11.777833000	-4.966927000	0.105760000
H	11.910904000	-6.842044000	-1.513007000
H	10.549868000	-6.817416000	-3.559531000
H	9.041747000	-4.926160000	-4.062435000
C	7.372507000	-4.236665000	-0.002678000
C	7.706825000	-5.538466000	0.377073000
C	7.056659000	-6.666289000	-0.086348000
C	6.004041000	-6.530584000	-0.966993000
C	5.622322000	-5.267501000	-1.365398000
C	6.298532000	-4.161446000	-0.882142000
F	5.868634000	-2.991155000	-1.348145000
F	4.610953000	-5.120203000	-2.216902000
F	5.367826000	-7.599826000	-1.422954000
F	7.431868000	-7.878099000	0.313808000
F	8.698748000	-5.770373000	1.237812000
C	8.749721000	-0.533386000	-0.729152000
C	9.466177000	0.265731000	0.163288000
C	9.173048000	1.596054000	0.386201000

C	8.139589000	2.198452000	-0.302481000
C	7.413626000	1.451153000	-1.205862000
C	7.718187000	0.117572000	-1.405775000
F	6.966256000	-0.526513000	-2.289064000
F	6.419261000	2.012417000	-1.880975000
F	7.853661000	3.473697000	-0.101673000
F	9.888500000	2.298185000	1.255212000
F	10.481798000	-0.233338000	0.862781000
C	7.748713000	-1.928701000	1.650911000
C	6.592487000	-1.165678000	1.547217000
C	8.501308000	-1.676932000	2.796850000
C	6.204852000	-0.225472000	2.483695000
C	8.150398000	-0.741787000	3.754072000
C	6.991349000	-0.010213000	3.597303000
F	9.636361000	-2.338029000	3.030970000
F	5.788130000	-1.303258000	0.498033000
F	5.085688000	0.472820000	2.318108000
F	6.636276000	0.886761000	4.504934000
F	8.916156000	-0.546235000	4.822906000
C	10.042270000	-2.704327000	-0.324329000
H	9.157260000	-3.591327000	1.175731000
H	10.686209000	-2.373345000	0.472304000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.24604874	154.3979218
E revDSD-PBEP86-D4/def2-QZVPP	-2553.470471	-1602326.979

2

C	9.283519000	-1.834664000	-1.163133000
C	9.119318000	-2.440394000	-2.534198000
H	9.622818000	-1.836151000	-3.295486000
H	8.074935000	-2.517089000	-2.845788000
C	10.199324000	-3.929721000	-1.055256000
C	9.744832000	-3.790493000	-2.372779000
C	9.900424000	-4.819331000	-3.282509000

C	10.520975000	-5.993462000	-2.863007000
C	10.973160000	-6.132051000	-1.553352000
C	10.816990000	-5.101093000	-0.635242000
H	11.169549000	-5.212246000	0.382582000
H	11.451599000	-7.053792000	-1.248315000
H	10.652877000	-6.808382000	-3.563012000
H	9.550714000	-4.720579000	-4.302947000
C	8.874743000	-0.468541000	-0.825937000
C	9.748432000	0.417277000	-0.202918000
C	9.386551000	1.714707000	0.103185000
C	8.120025000	2.165632000	-0.212984000
C	7.226368000	1.313635000	-0.832267000
C	7.608632000	0.020282000	-1.127548000
F	6.709705000	-0.775709000	-1.701626000
F	6.003620000	1.739177000	-1.129448000
F	7.762892000	3.408212000	0.078700000
F	10.251441000	2.533773000	0.691446000
F	10.984617000	0.033847000	0.099906000
C	9.906334000	-2.698298000	-0.340352000
H	10.146906000	-2.528013000	0.700056000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.14445209	90.64505877
E revDSD-PBEP86-D4/def2-QZVPP	-1073.811222	-673826.743

HB(C_6F_5)$_2$

B	0.690411000	0.014162000	-0.664502000
C	2.192682000	-0.307254000	-0.447627000
C	3.197529000	0.654164000	-0.486152000
C	2.607894000	-1.626283000	-0.293340000
C	4.534368000	0.335328000	-0.370250000
C	3.934982000	-1.978183000	-0.155275000
C	4.899191000	-0.988064000	-0.197551000
C	-0.001065000	1.340078000	-0.247493000
C	-1.080524000	1.821512000	-0.980558000

C	0.340609000	2.060321000	0.892062000
C	-1.767217000	2.966180000	-0.630748000
C	-0.337019000	3.196578000	1.282107000
C	-1.391673000	3.650877000	0.510205000
F	1.706168000	-2.600443000	-0.249260000
F	2.888855000	1.932387000	-0.678109000
F	5.470082000	1.275261000	-0.426284000
F	6.175659000	-1.306984000	-0.075153000
F	4.294970000	-3.244904000	0.011475000
F	1.331210000	1.639535000	1.672061000
F	0.004860000	3.854361000	2.383462000
F	-2.043621000	4.744024000	0.866189000
F	-2.778336000	3.411175000	-1.366785000
F	-1.465778000	1.184094000	-2.080655000
H	0.021735000	-0.811456000	-1.194718000

	Hatree	kcal mol^{-1}
G-E(el) PBEh-3c	0.07245461	45.46595609
E revDSD-PBEP86-D4/def2-QZVPP	-1479.663107	-928502.6565

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