

Supporting Information of synthesis, structures, NMR and EPR
spectroscopy and computations

**Synthesis of a heterobimetallic arsenic triple-decker
complex and its fragmentation chemistry**

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1. Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds $[(\text{Cp}''\text{Co})_2(\mu,\eta^4:\eta^4-\text{C}_7\text{H}_8)]$ (**2**)^[1], $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$ (**1b**)^[2] and $[(\text{Cp}''\text{CoCl})_2]$ ^[3] were prepared according to literature procedures.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^1H : 400.13 MHz, ^{31}P : 161.976 MHz). The chemical shifts are given in ppm referenced to external SiMe_4 (^1H) and H_3PO_4 (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. All mass spectra were recorded with a Finnigan MAT 95 mass spectrometer (LIFDI-MS). The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magrettech GmbH.

1.1 Synthesis of $[(\text{Cp}^*\text{Fe})(\text{Cp}''\text{Co})(\mu,\eta^5:\eta^4\text{-As}_5)]$ (**3**)

A solution of $[(\text{Cp}''\text{Co})_2(\mu,\eta^4:\eta^4-\text{C}_7\text{H}_8)]$ (**2**) (598 mg, 0.884 mmol, 1 eq) in 50 mL pentane was added dropwise to a stirred solution of $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$ (**1b**) (1.00 g, 1.768 mmol, 2 eq) in 200 mL pentane. The color changed to dark green after one hour. The ^1H NMR spectrum of the reaction mixture reveals the clean formation of **3** beside unused **1b** in a ratio of 91:9. Further **2** (51 mg, 0.075 mmol) in pentane was added and stirred for another hour. The solvent was removed *in vacuo*. **3** can be obtained as a dark green solid. Very few crystals of **3** suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C after a few days beside decomposition products (vide infra).

Yield: 1.373 g (91 %).

$^1\text{H NMR}$ (C_6D_6 , 293 K): δ [ppm] = 3.67 (s, 2H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 1.43 (s, 18H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 1.40 (s, 15H, C_5Me_5), 1.33 (s, 9H, $\text{C}_5\text{H}_2^t\text{Bu}_3$).

LIFDI-MS (toluene): m/z = 932.6 (4 %, $[\text{M+As}]^+$), 857.7 (100 %, $[\text{M}]^+$), 782.8 (4 %, $[\text{M-As}]^+$), 707.9 (15 %, $[\text{M-2As}]^+$).

EA: $\text{C}_{27}\text{H}_{44}\text{CoFeAs}_5$: calc [%]: C: 37.79; H: 5.17; found [%]: C: 37.32; H: 5.17.

1.2 Synthesis of $[(\text{Cp}^*\text{Fe})(\text{Cp}'''\text{Co})(\mu,\eta^3:\eta^3\text{-As}_3)]$ (4) and $[(\text{Cp}^*\text{Fe})_2(\text{Cp}'''\text{Co})_2(\mu_4,\eta^4:\eta^4:\eta^4:\eta^3\text{-As}_{11})]$ (5)

10 mL MeCN were added to a solution of **3** (1.00 g, 1.166 mmol) in 50 mL CH_2Cl_2 and stirred for three days. The color changed from dark green to brown green. The ^1H NMR spectrum reveals a mixture of **3**, $[(\text{Cp}^*\text{Fe})(\text{Cp}'''\text{Co})(\mu,\eta^3:\eta^3\text{-As}_3)]$ (**4**) and $[(\text{Cp}^*\text{Fe})_2(\text{Cp}'''\text{Co})_2(\mu_4,\eta^4:\eta^4:\eta^4:\eta^3\text{-As}_{11})]$ (**5**). The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 , SiO_2 added and dried *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2 , pentane, 25 x 3 cm). Using pentane a dark green fraction can eluted containing a mixture of **3** and **4** in a ratio of 22:78 which cannot be separated further from each other (using alumina for column chromatography and using thin layer chromatography with silica and alumina, respectively were not successful). Using toluene, a strong dark brown fraction of **5** can be eluted. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 and layered with MeCN at room temperature. After a few days **3** can be obtained as dark brown blocks. The supernatant was decanted off and the remaining crystals dried *in vacuo*. The mixture of **3** and **4** was dissolved in hexane and stored at -30 °C. After a few days two kind of slightly different shaped crystals were obtained, which were separated under the microscope yielding a few mg on analytically pure **4**.

Compound **4**:

Yield: 10 mg

$^1\text{H NMR}$ (C_6D_6 , 293 K): δ [ppm] = 5.31 (s, 2H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 1.60 (s, 15H, C_5Me_5), 1.30 (s, 18H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 0.66 (s, 9H, $\text{C}_5\text{H}_2^t\text{Bu}_3$).

LIFDI-MS (toluene): m/z = 708.0 (100 %, $[\text{M}]^+$).

EA: $\text{C}_{27}\text{H}_{44}\text{CoFeAs}_3$: calc [%]: C: 45.79; H: 6.26; found [%]: C: 45.62; H: 6.05.

Compound **5**:

Yield : 366 mg (0.204 mmol, 44 % related to **3** using the stoichiometry of 5 $[(\text{Cp}^*\text{Fe})(\text{Cp}'''\text{Co})\text{As}_5] \rightarrow [(\text{Cp}^*\text{Fe})(\text{Cp}'''\text{Co})\text{As}_3 + 2[(\text{Cp}^*\text{Fe})_2(\text{Cp}'''\text{Co})_2\text{As}_{11}]]$).

$^1\text{H NMR}$ (C_6D_6 , 293 K): δ [ppm] = 9.84 (br, 2H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 4.27 (s, 2H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 2.36 (br, 36H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 1.53 (s, 9H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), -0.51 (br, 9H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), -1.14 (br, 15H, C_5Me_5), -18.25 (br, 15H, C_5Me_5).

Evans-NMR (C_6D_6 , 293 K): $\mu_{\text{eff}} = 2.27 \mu_B$ corresponding to 1.48 unpaired electrons.

LIFDI-MS (toluene): m/z = 1224.9 (20 %, $[\text{M-Cp}^*\text{Fe-5As}]^+$), 1123.9 (11 %, $[\text{M-Cp}'''\text{Co-5As}]^+$), 1007.7 (7 %, $[\text{M-Cp}^*\text{Fe-Cp}'''\text{Co-4As}]^+$), 932.8 (70 %, $[\text{M-Cp}^*\text{Fe-Cp}'''\text{Co-5As}]^+$), 857.9 (100 %, $[\text{M-Cp}^*\text{Fe-Cp}'''\text{Co-6As}]^+$).

EA: $\text{C}_{54}\text{H}_{88}\text{Co}_2\text{Fe}_2\text{As}_{11} \times 0.85 \text{ CH}_2\text{Cl}_2$: calc [%]: C: 35.38; H: 4.85; found [%]: C: 35.44; H: 4.66.

EPR (X-band): (solid, 77 K) $g_x = 2.29632$, $g_y = 2.16718$, $g_z = 2.07149$, $g_{\text{iso}} = 2.17833$.

1.3 Synthesis of $[(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})(\mu_3,\eta^2:\eta^2:\eta^2\text{-As}_3)_2]$ (7)

A solution of **3** (1.05 g, 1.2237 mmol) in decaline was stirred under reflux for 3 h while the color changed to brown-green. The ^1H NMR of the reaction mixture reveals $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$ (**1b**), $[(\text{Cp}''\text{Co})_2(\text{As}_2)_2]$ (**6**) and $[(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})(\mu_3,\eta^2:\eta^2:\eta^2\text{-As}_3)_2]$ (**7**). The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 , SiO_2 was added and the solvent removed *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2 , hexane, 16x3 cm). Using hexane, a first dark green fraction (**6**) and a bright green fraction (**1b**) can be eluted. Using CH_2Cl_2 , a dark brown fraction (**7**) can be eluted. **1b** and **6** were disposed. The solvent was removed *in vacuo*. Compound **7** was dissolved in toluene and layered with acetonitrile at room temperature. After a few days, **7** can be obtained as dark brown blocks. The supernatant was decanted off and dried *in vacuo*.

Compound **7**:

Yield: 203 mg (90 % related to **1** using the stoichiometry of **3** $[(\text{Cp}^*\text{Fe})(\text{Cp}''\text{Co})\text{As}_5] \rightarrow [\text{Cp}^*\text{FeAs}_5] + [(\text{Cp}''\text{Co})_2(\text{As}_2)_2] + [(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})\text{As}_6]$).

$^1\text{H NMR}$ (C_6D_6 , 293 K): δ [ppm] = 5.13 (s, 2H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 1.84 (s, 30H, C_5Me_5), 1.54 (s, 18H, $\text{C}_5\text{H}_2^t\text{Bu}_3$), 1.39 (s, 9H, $\text{C}_5\text{H}_2^t\text{Bu}_3$).

LIFDI-MS (toluene): m/z = 1123.9 (100 %, $[\text{M}]^+$).

EA: $\text{C}_{37}\text{H}_{59}\text{CoFe}_2\text{As}_6$: calc [%]: C: 39.54; H: 5.29; found [%]: C: 39.79; H: 5.17.

1.4 Thermolysis reactions of $[(\text{Cp}^*\text{Fe})(\text{Cp}''\text{Co})(\mu,\eta^5:\eta^4\text{-As}_5)]$ (3)

a-c): A solution of 50 mg **3** were dissolved in toluene (a, b) and xylene (c), respectively, and stirred for 93 h at a) 60 °C, b) 115 °C and c) 140 °C. Samples were each taken after 1, 4, 7, 25, 45, 69 and 93 hours, the solvent was removed *in vacuo* and taken up in C₆D₆ for NMR investigations. Selected spectra and graphs are depicted in chapter 2.6-2.8.

2. NMR spectroscopic investigations

2.1 $[(\text{Cp}^*\text{Fe})(\text{Cp}''\text{Co})(\mu,\eta^5:\eta^4\text{-As}_5)]$ (3)

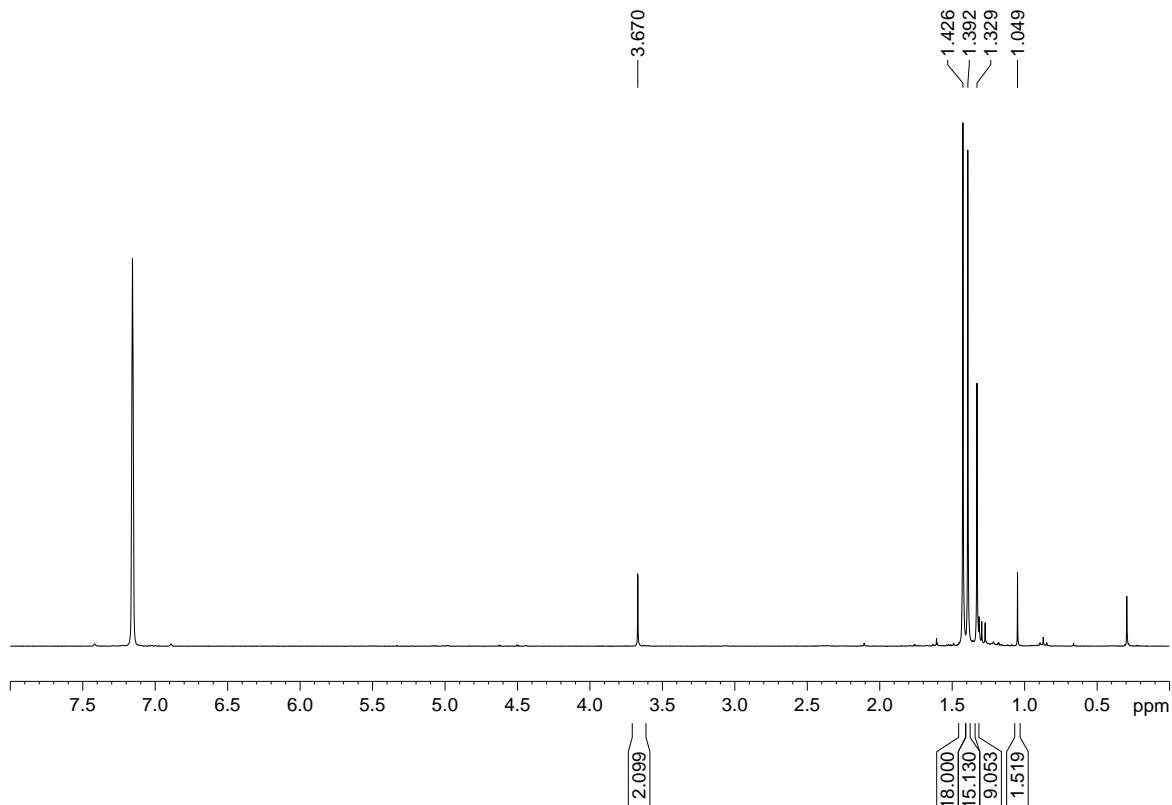


Figure S1: ${}^1\text{H}$ NMR spectrum in C_6D_6 at room temperature. Stoichiometric reaction of **1b** and **2**.

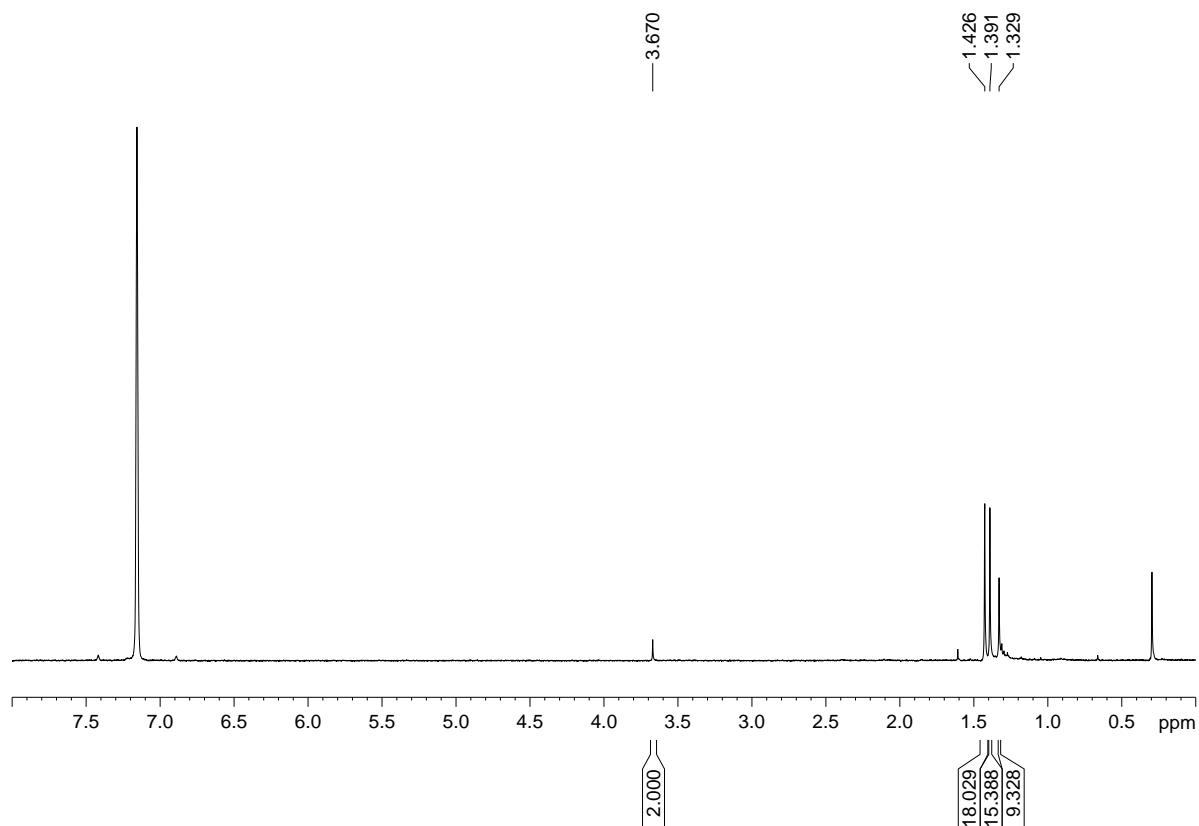


Figure S2: ${}^1\text{H}$ NMR spectrum of isolated dark green solid in C_6D_6 at room temperature.

2.1 $[(\text{Cp}^*\text{Fe})(\text{Cp}'''\text{Co})(\mu,\eta^3:\eta^3\text{-As}_3)]$ (4)

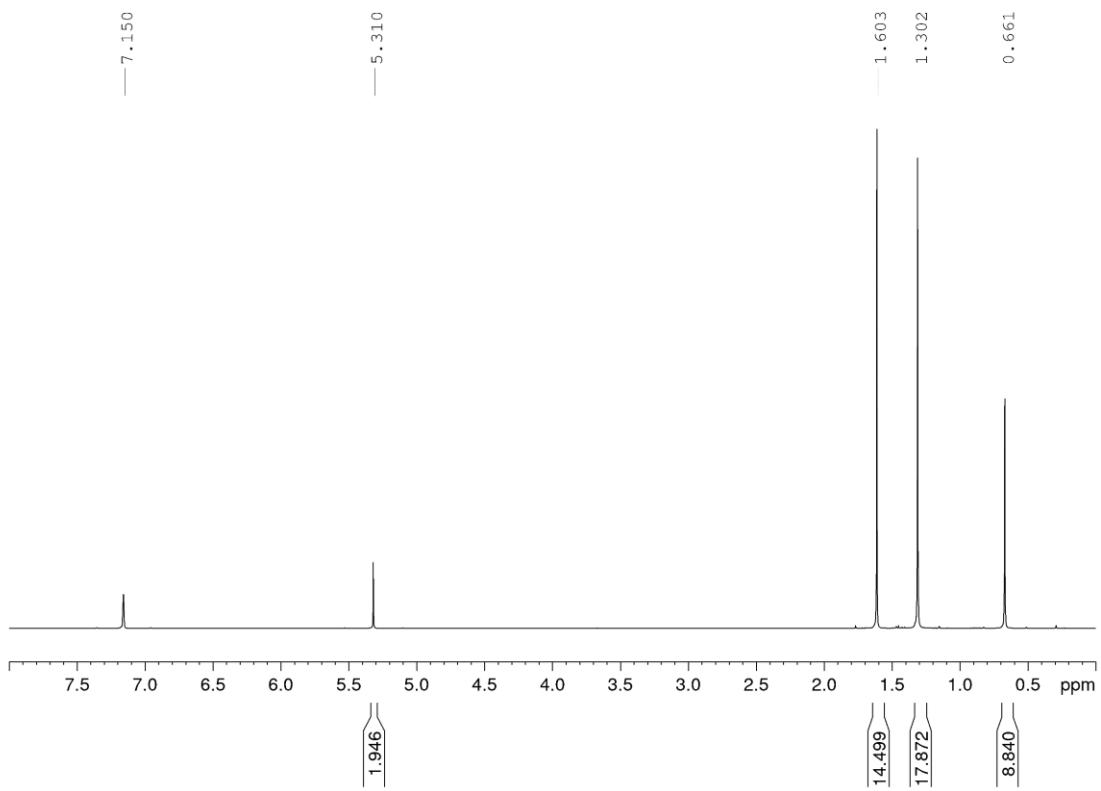


Figure S3: ^1H NMR spectrum of **4** in C_6D_6 at room temperature.

2.3 $[(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})_2(\mu_4,\eta^4:\eta^4:\eta^4:\eta^3\text{-As}_{11})] \text{ (5)}$

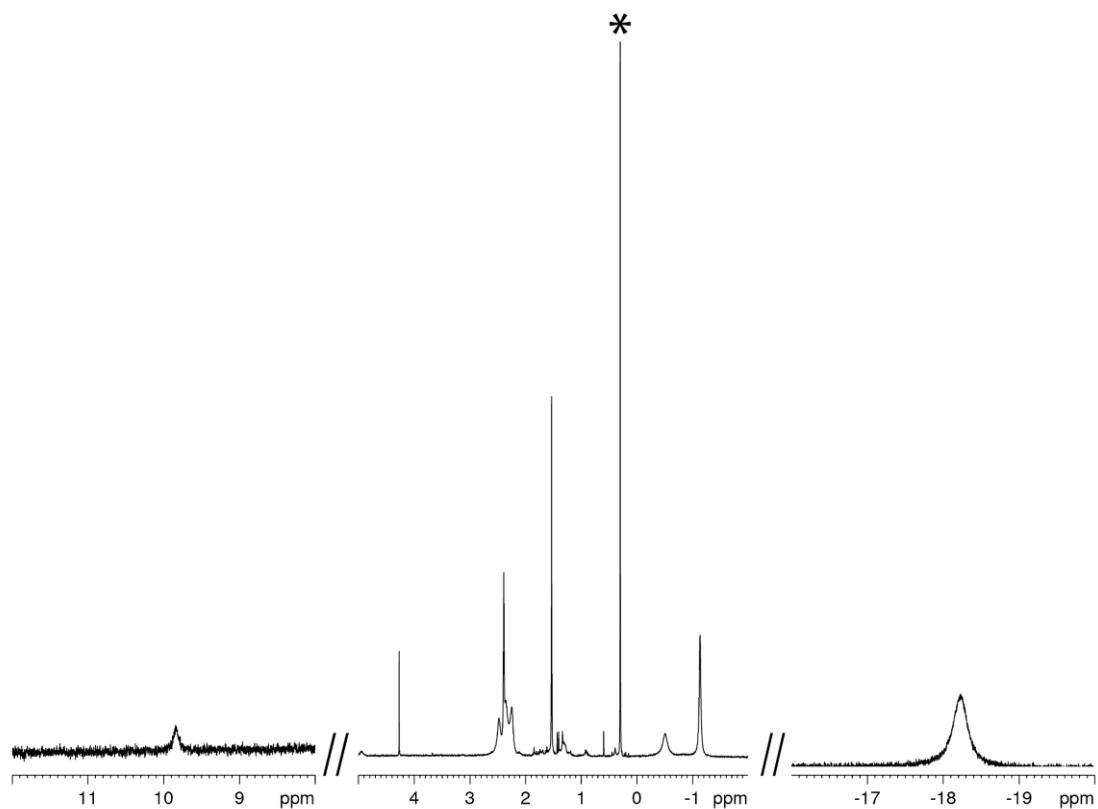


Figure S4: ¹H NMR spectrum of **5** in C₆D₆ at room temperature. Left and right part magnified for overview. Impurity of silicon grease (*).

2.4 $[(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})(\mu_3,\eta^2:\eta^2:\eta^2\text{-As}_3)_2]$ (7)

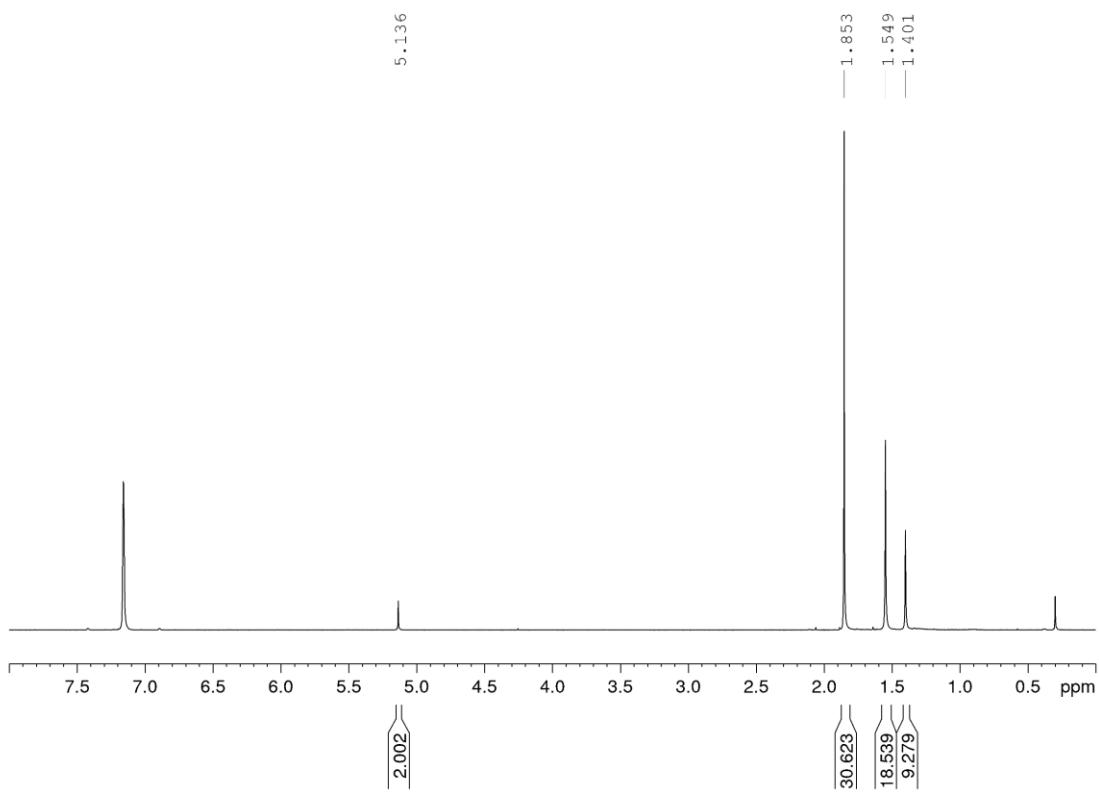


Figure S5: ^1H NMR spectrum of 7 in C_6D_6 at room temperature.

2.5 Fragmentation of 3 with acetonitrile

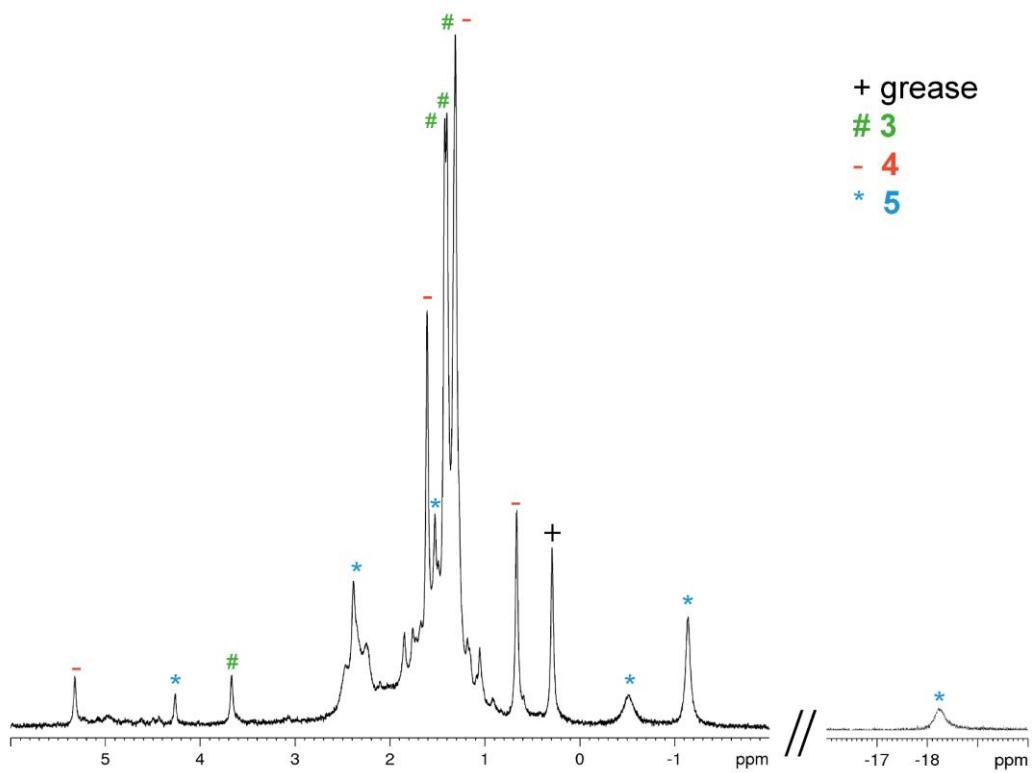


Figure S6: ¹H NMR spectrum of the reaction mixture three days after the addition of MeCN in C₆D₆ at room temperature.

2.6 Thermolysis of 3 in toluene at 60 °C

Since **1b** is the only compound which is present in all spectra, it was chosen to be the reference.

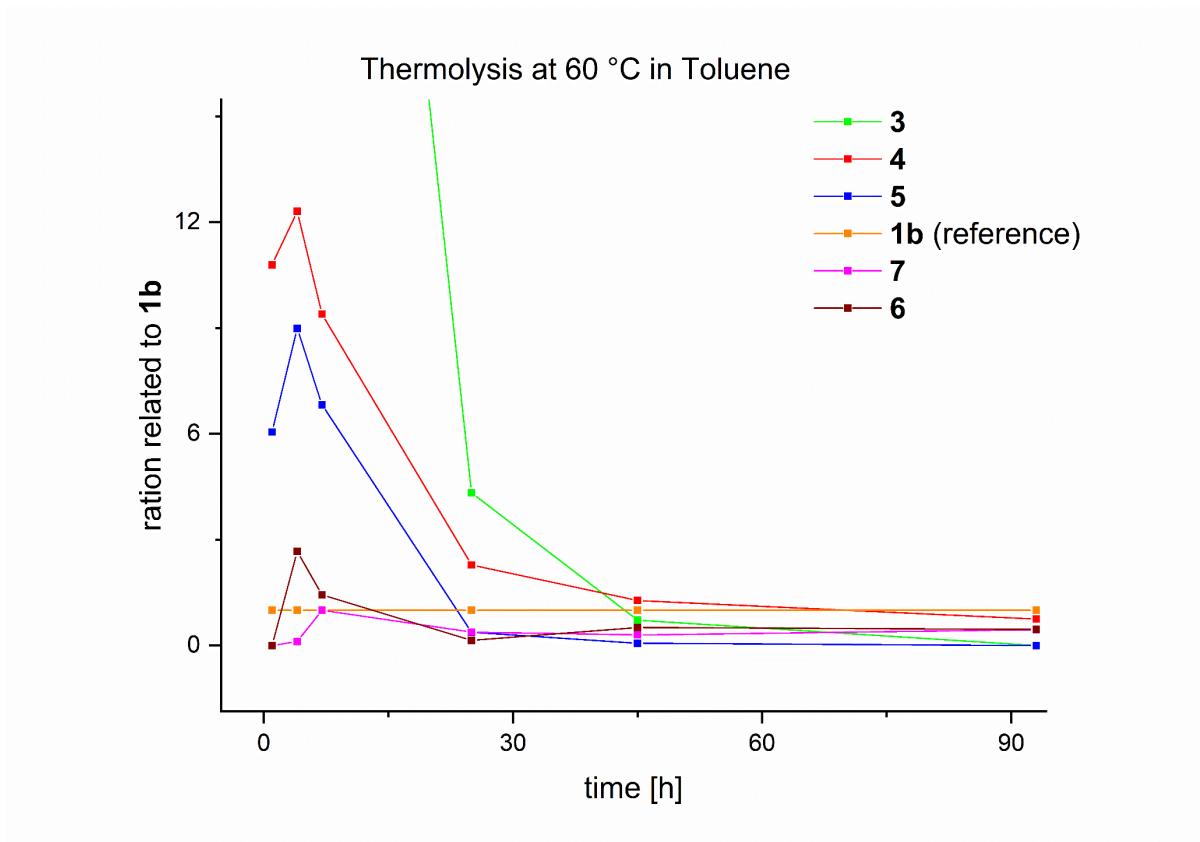


Figure S7: Plotted relative integrals for all compounds referenced to **1b**.

Table S1: Integral ratios of all compounds related to **1b**.

Time [h]	3	4	5	7	1b	6
1	131.579	10.789	6.053	0	1	0
4	96.154	12.308	8.99	0.115	1	2.663
7	43.478	9.391	6.822	1	1	1.435
25	4.329	2.281	0.377	0.381	1	0.146
45	0.715	1.276	0.061	0.299	1	0.511
93	0	0.745	0	0.445	1	0.454

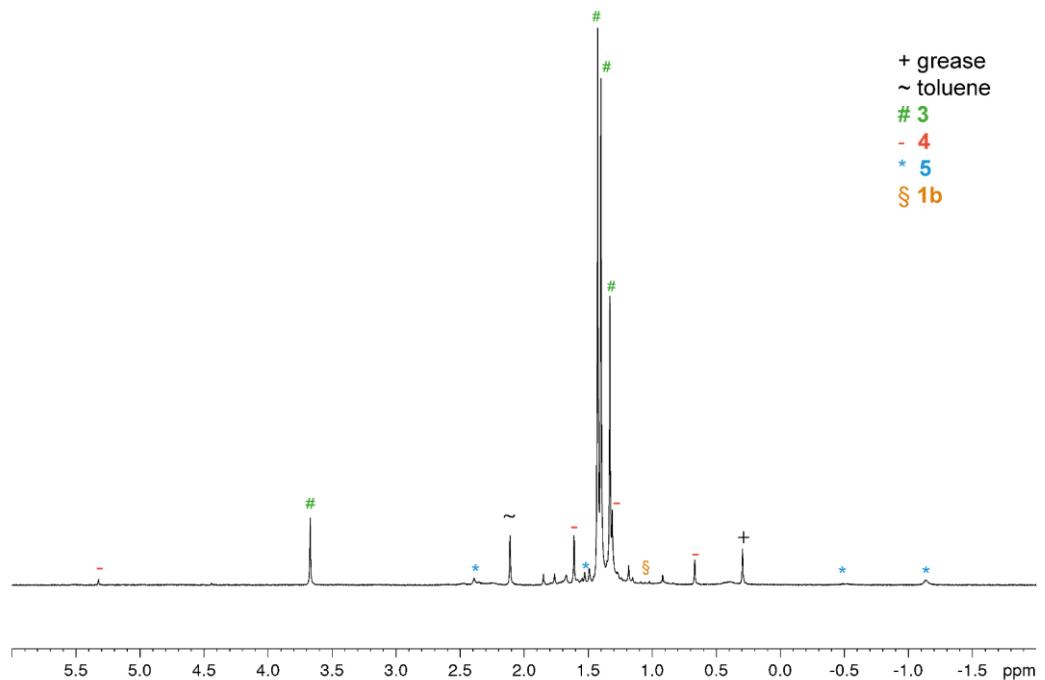


Figure S8: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 1h.

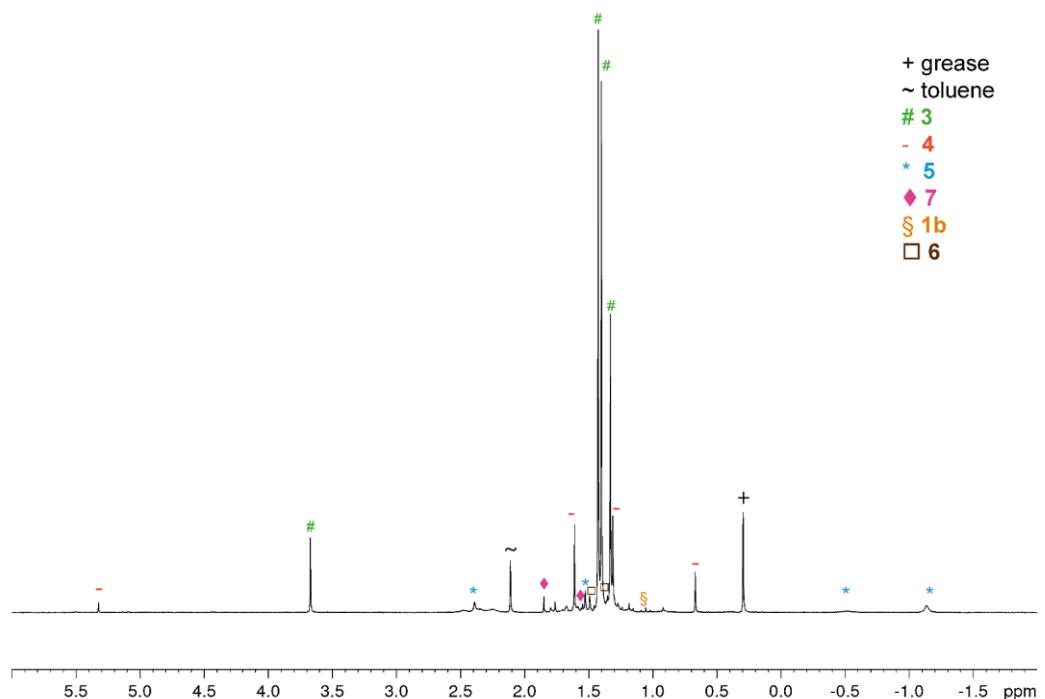


Figure S9: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 4h.

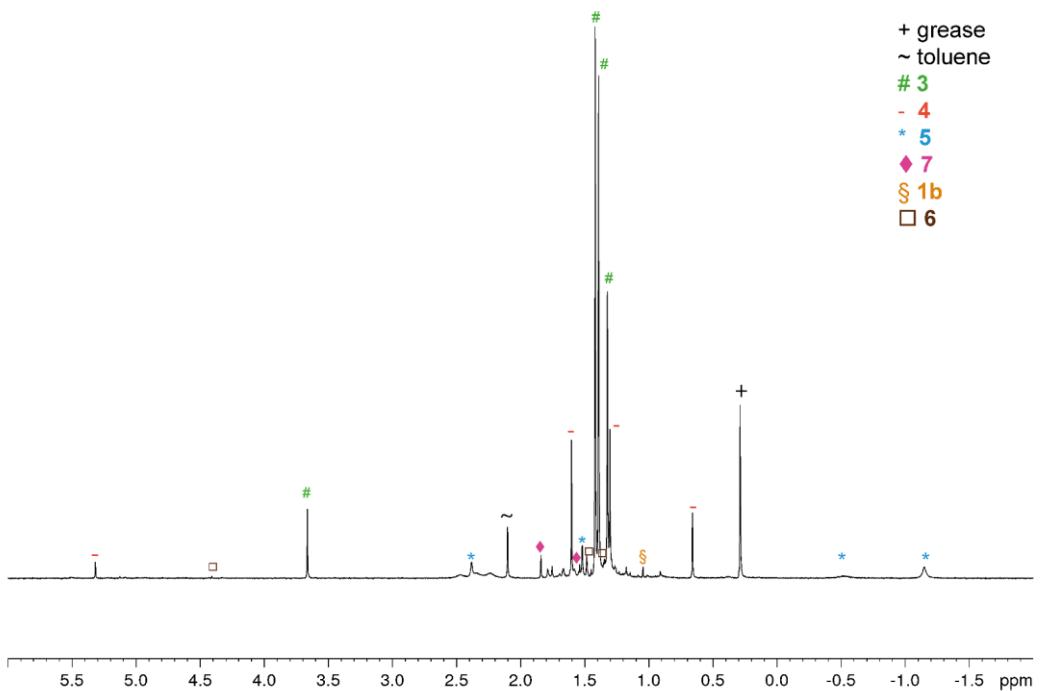


Figure S10: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 7h.

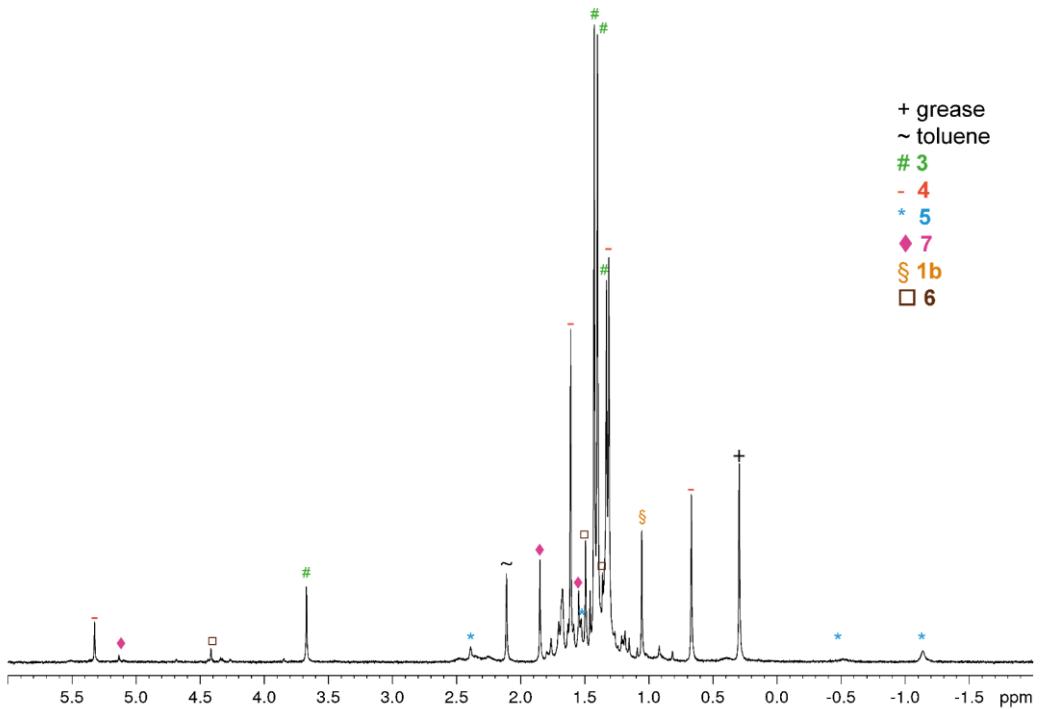


Figure S11: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 25h.

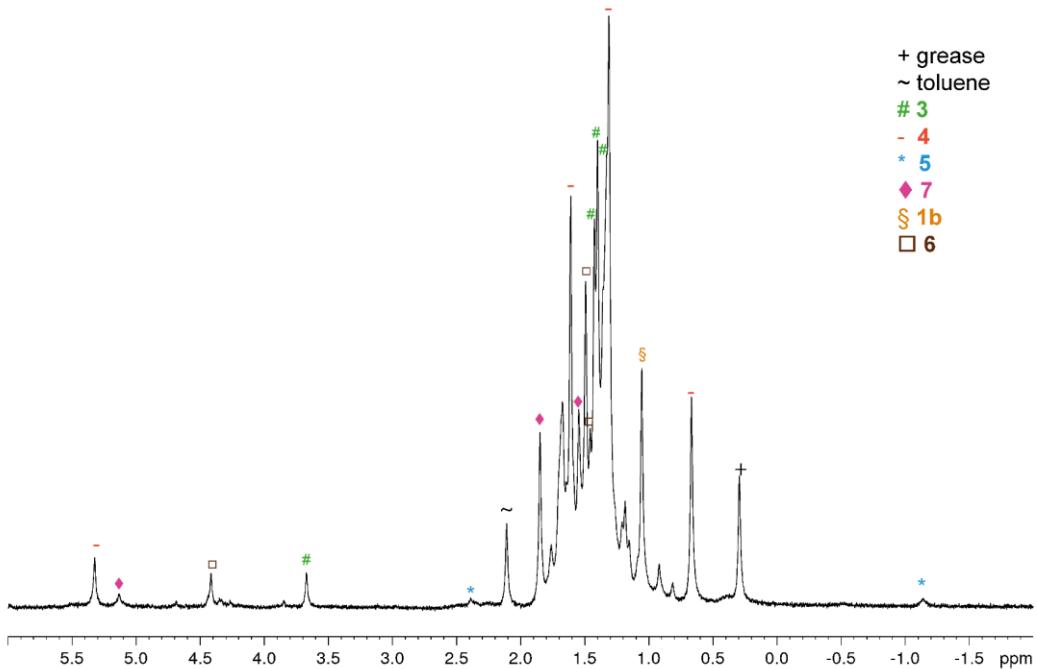


Figure S12: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 45h.

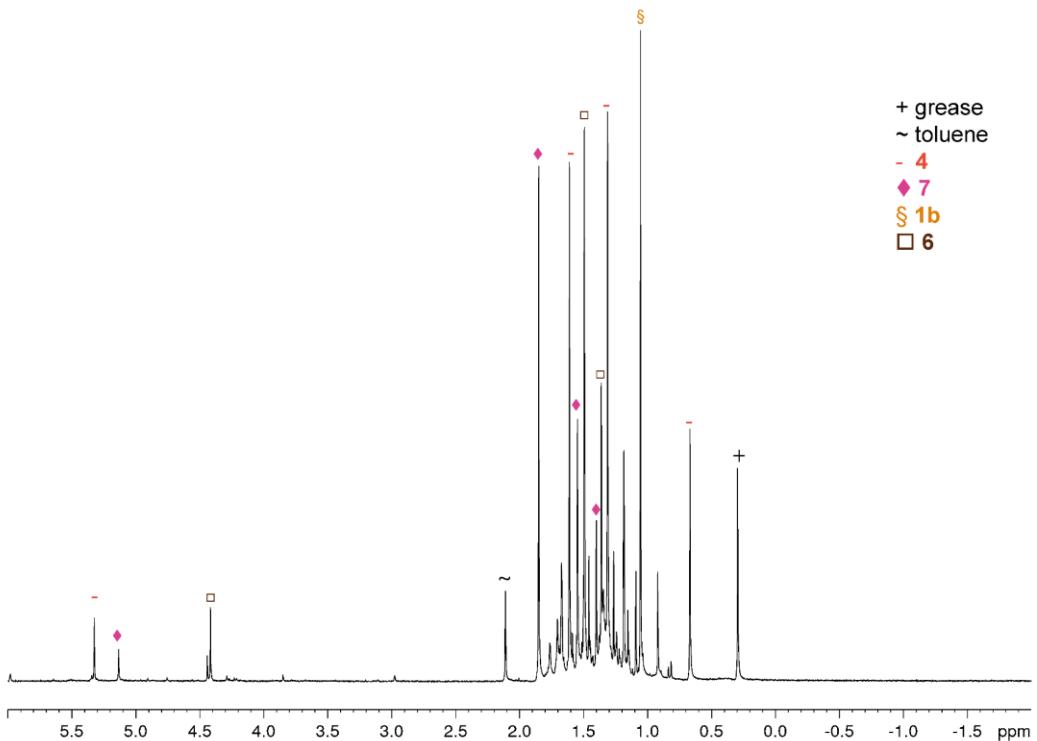


Figure S13: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 93h.

2.7 Thermolysis of 3 in toluene at 115 °C

Since **1b** is the only compound which is present in all spectra, it was chosen to be the reference.

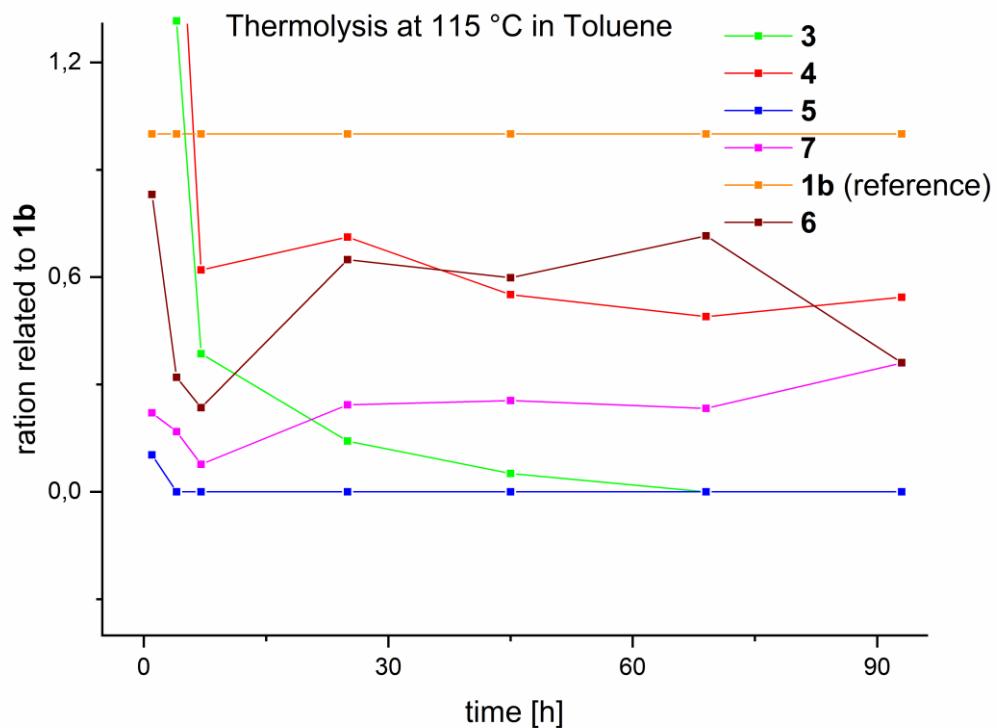


Figure S14: Plotted relative integrals for all compounds referenced to **1b**.

Table S2: Integral ratios of all compounds related to **1b**.

Time [h]	3	4	5	7	1b	6
1	4.329	3.281	0.103	0.221	1	0.831
4	1.316	1.845	0	0.168	1	0.32
7	0.386	0.62	0	0.077	1	0.235
25	0.142	0.712	0	0.243	1	0.649
45	0.051	0.551	0	0.255	1	0.598
69	0	0.4894	0	0.2331	1	0.7154
93	0	0.5438	0	0.3601	1	0.361

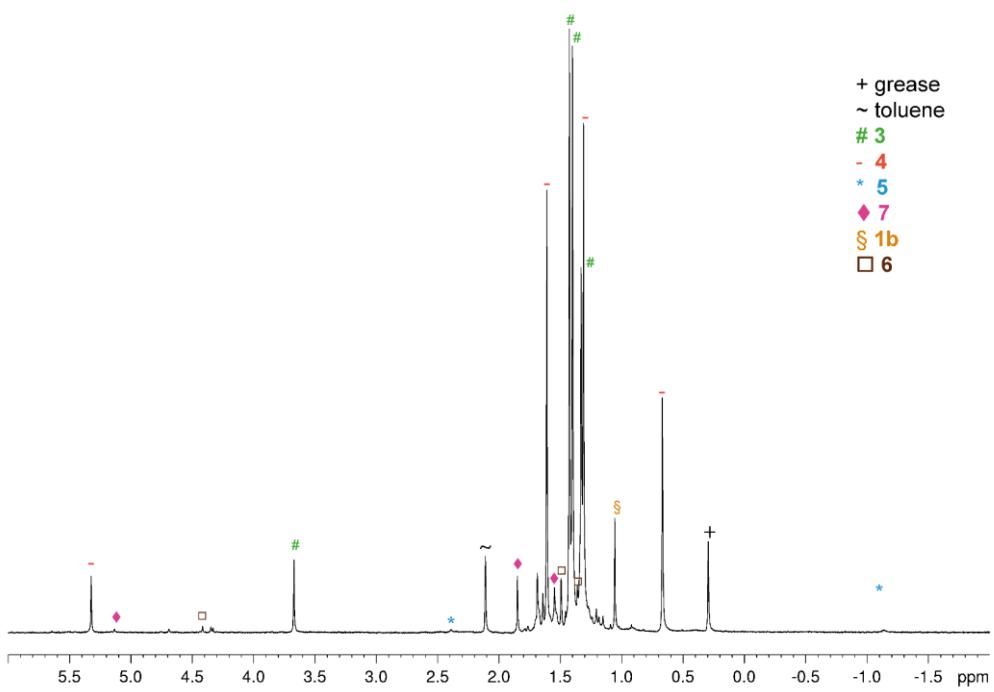


Figure S15: 1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 1h.

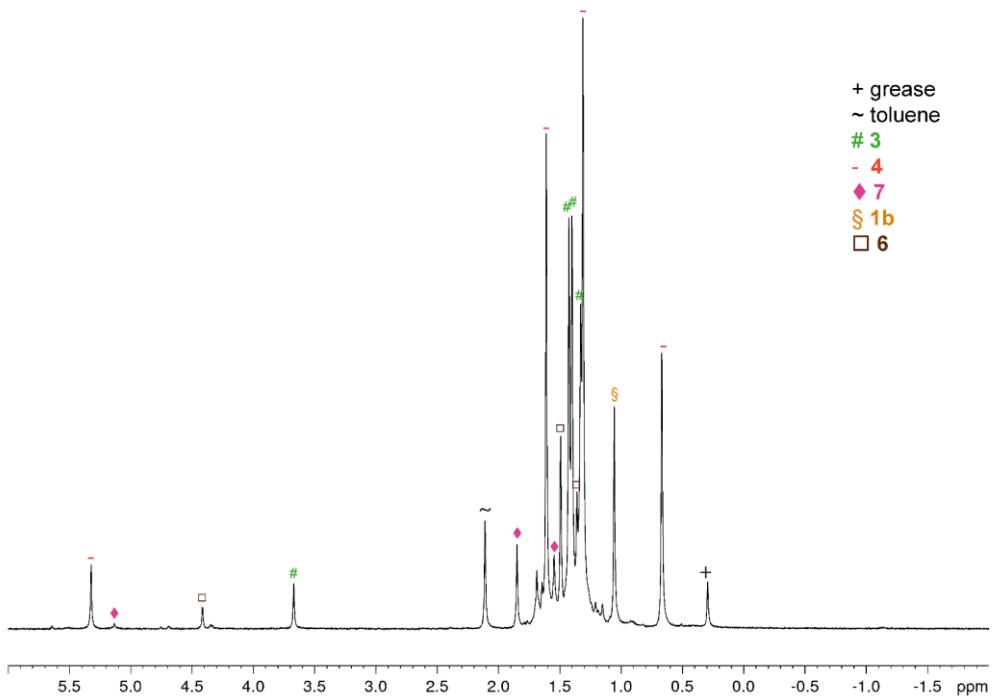


Figure S16: 1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 4h.

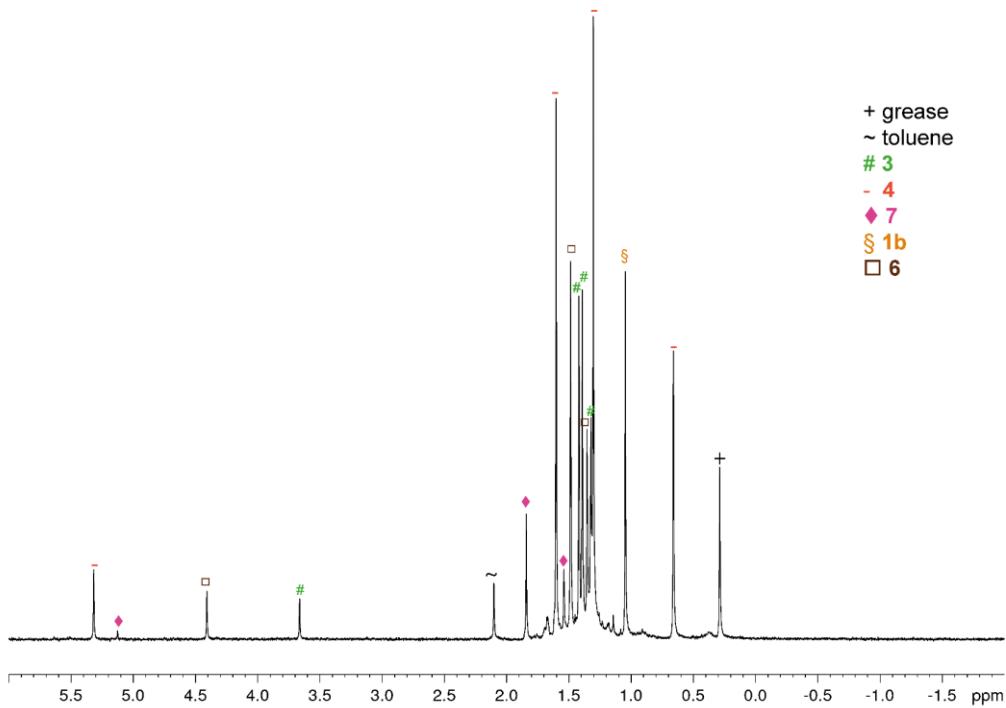


Figure S17: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 7h.

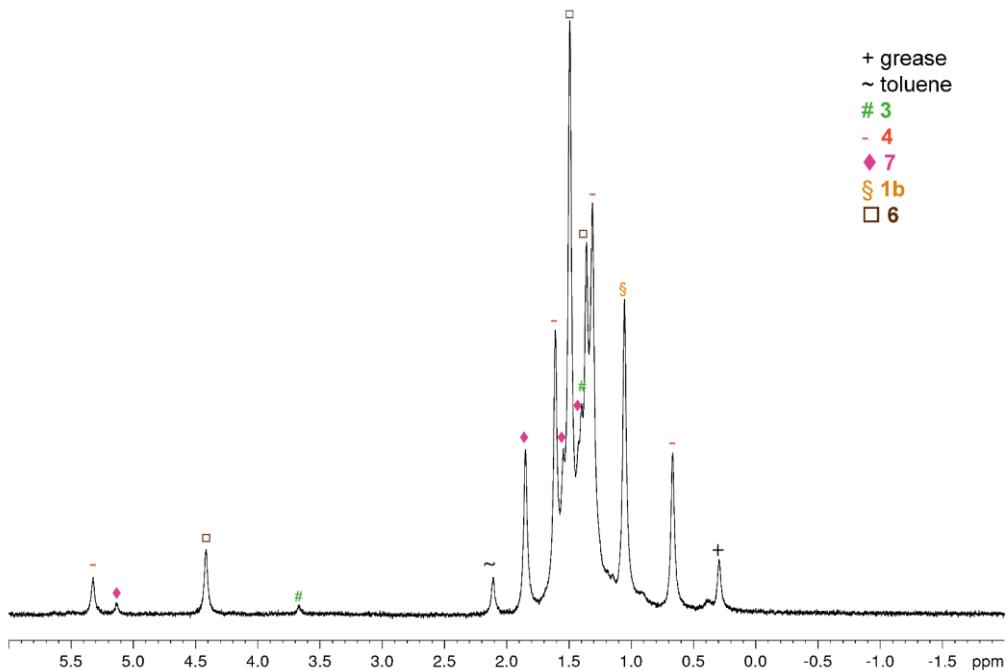


Figure S18: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 25h.

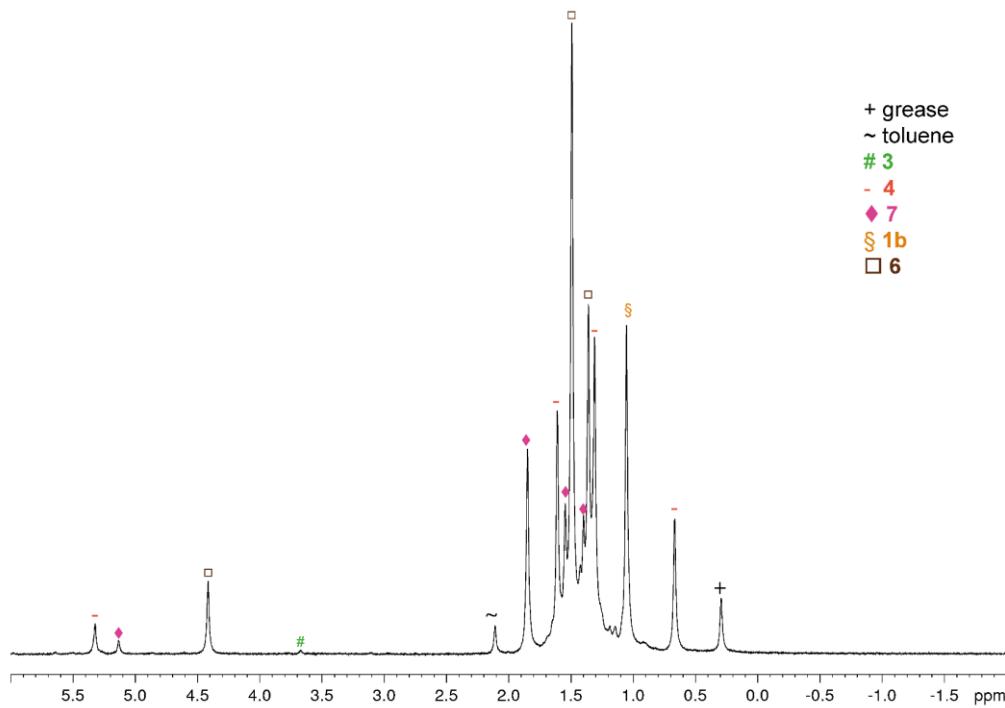


Figure S19: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 45h.

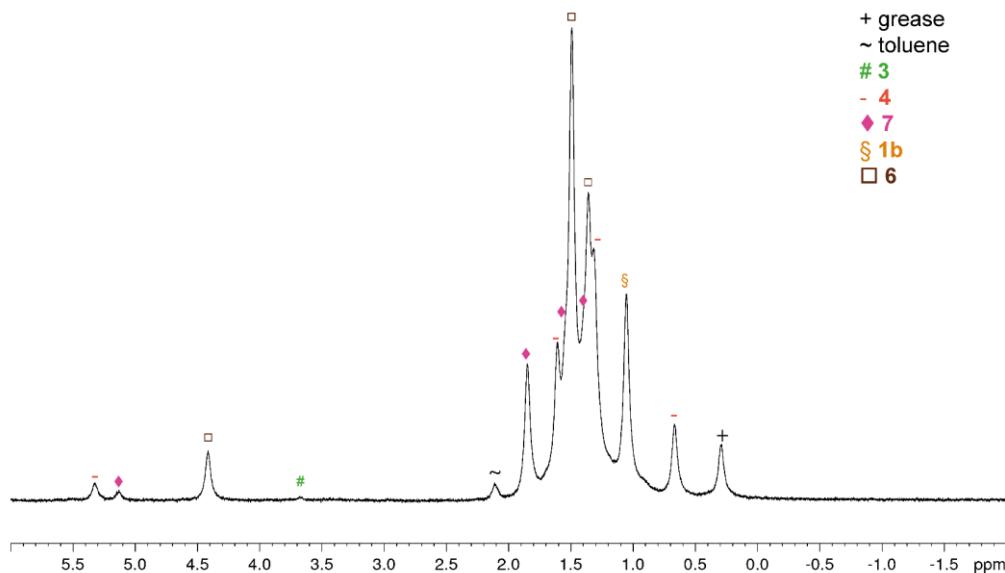


Figure S20: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 69h.

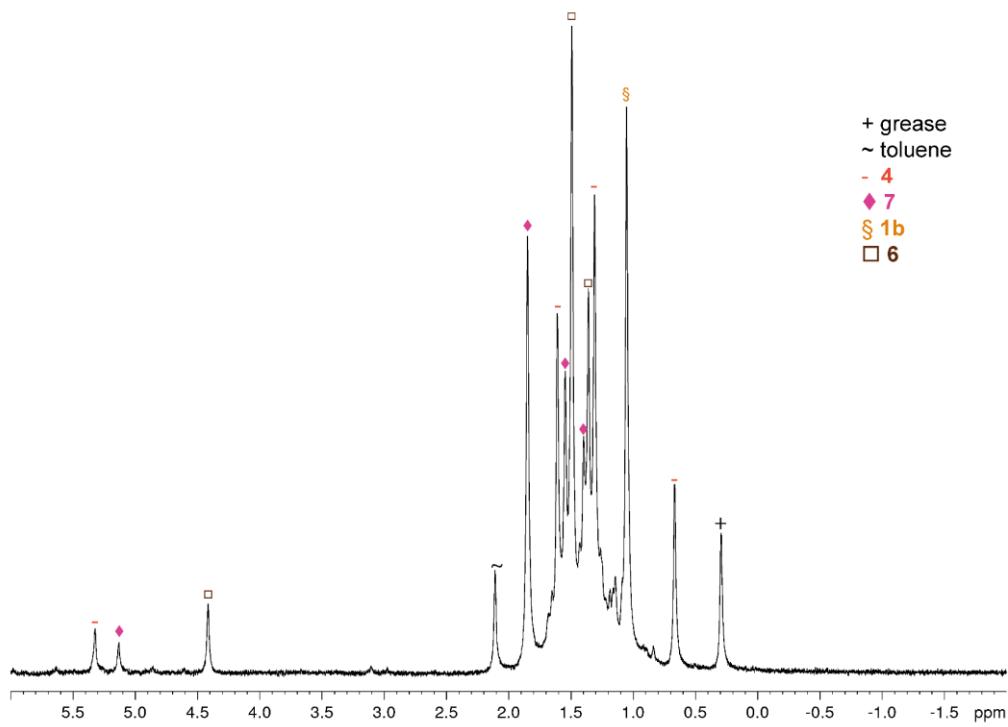


Figure S21: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 93h.

2.8 Thermolysis of 3 in xylene at 140 °C

Since **1b** is the only compound which is present in all spectra, it was chosen to be the reference.

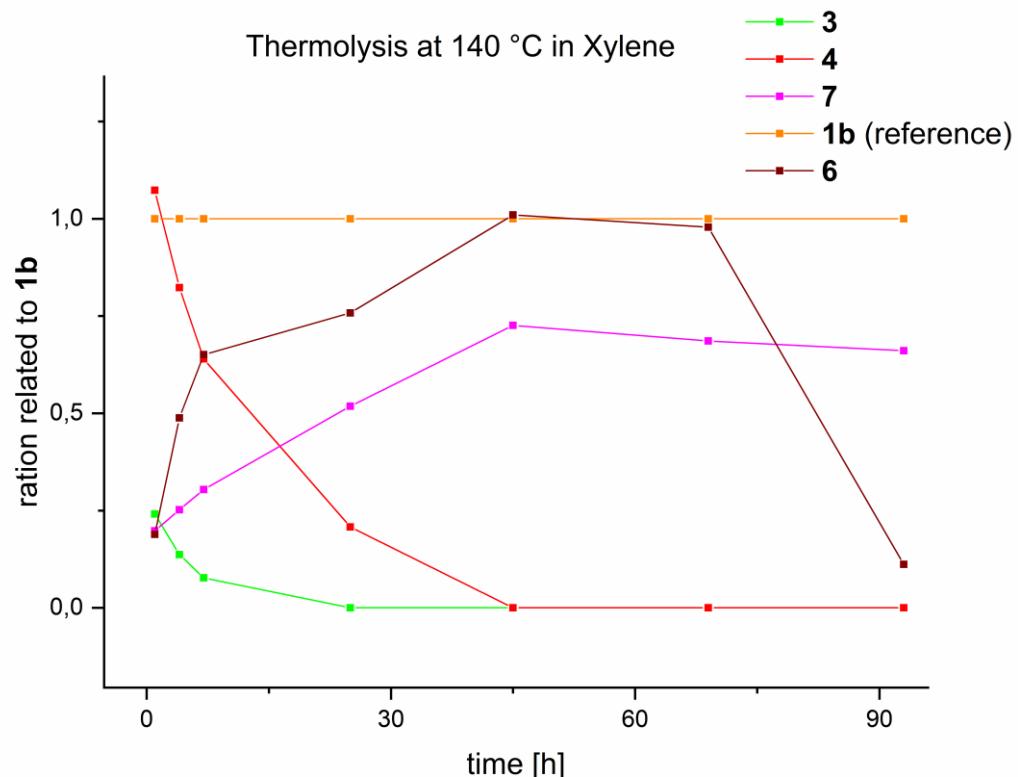


Figure S22: Plotted relative integrals for all compounds referenced to **1b**.

Table S3: Integral ratios of all compounds related to **1b**.

Time [h]	3	4	5	7	1b	6
1	0.241	1.073	0	0.198	1	0.189
4	0.137	0.823	0	0.252	1	0.488
7	0.077	0.64	0	0.304	1	0.651
25	0	0.208	0	0.518	1	0.758
45	0	0	0	0.726	1	1.01
69	0	0	0	0.686	1	0.9782
93	0	0	0	0.6606	1	0.112

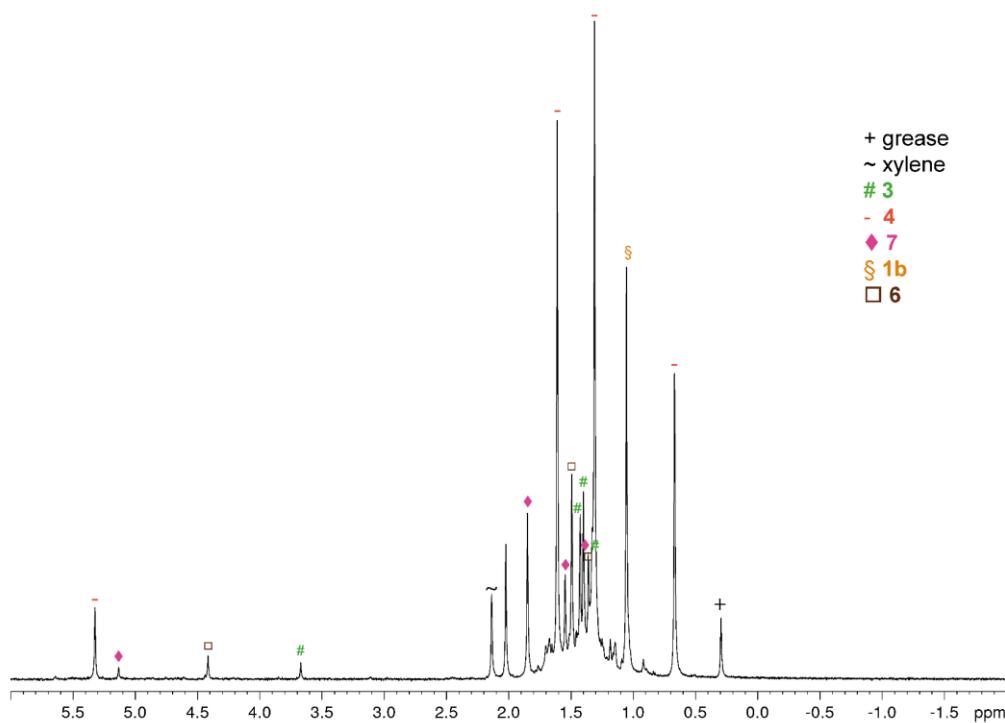


Figure S23: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 1h.

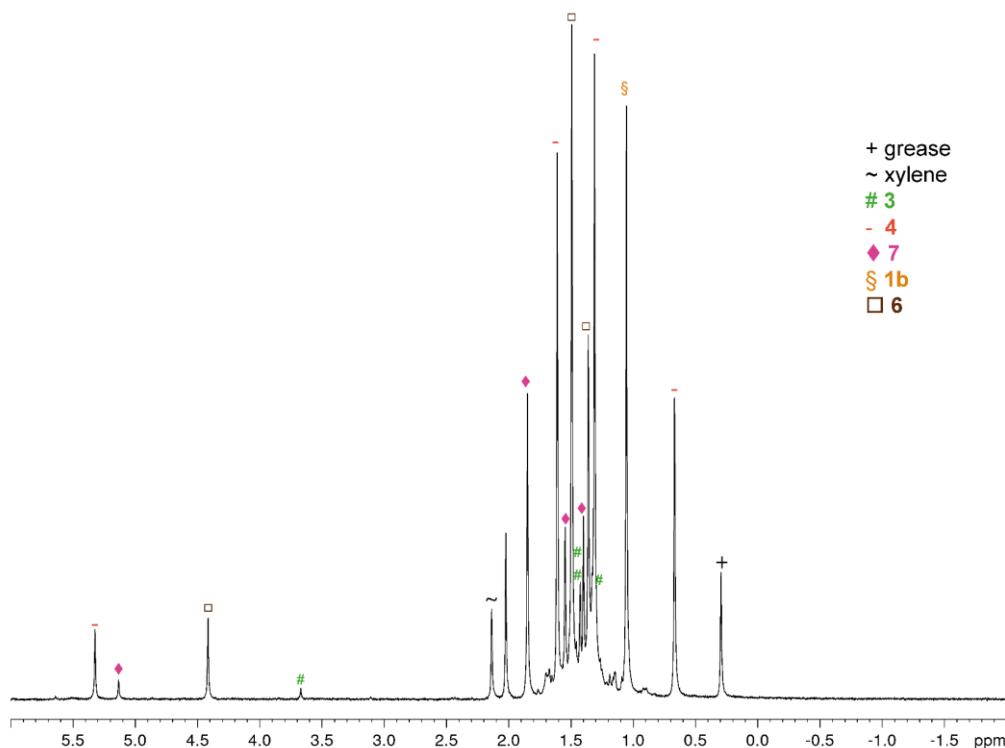


Figure S24: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 4h.

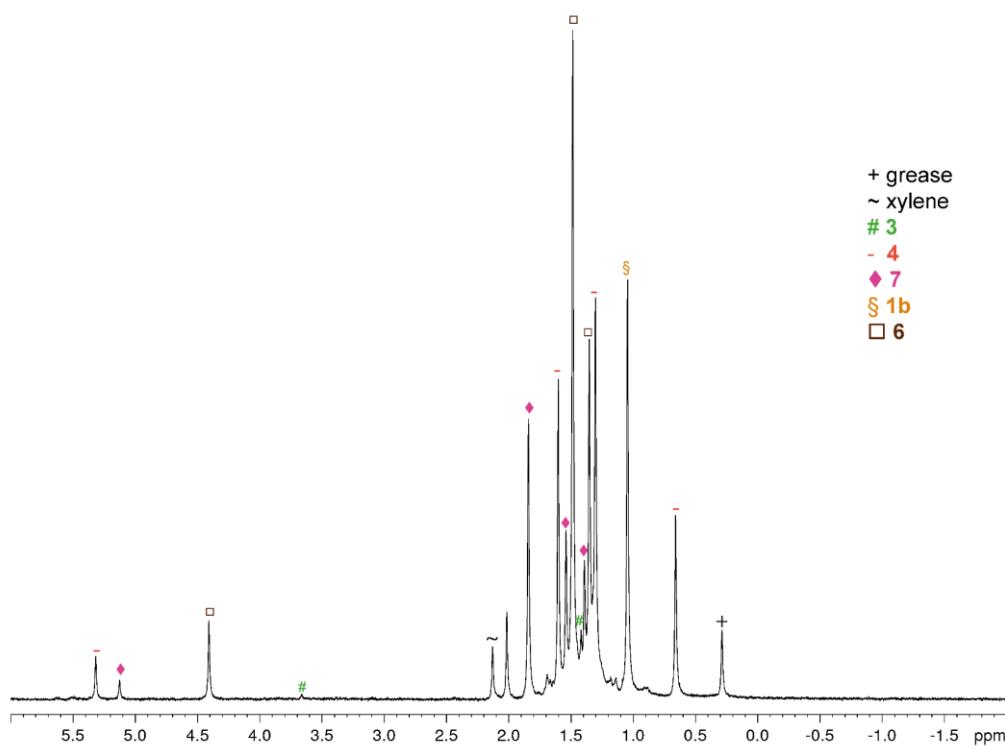


Figure S25: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 7h.

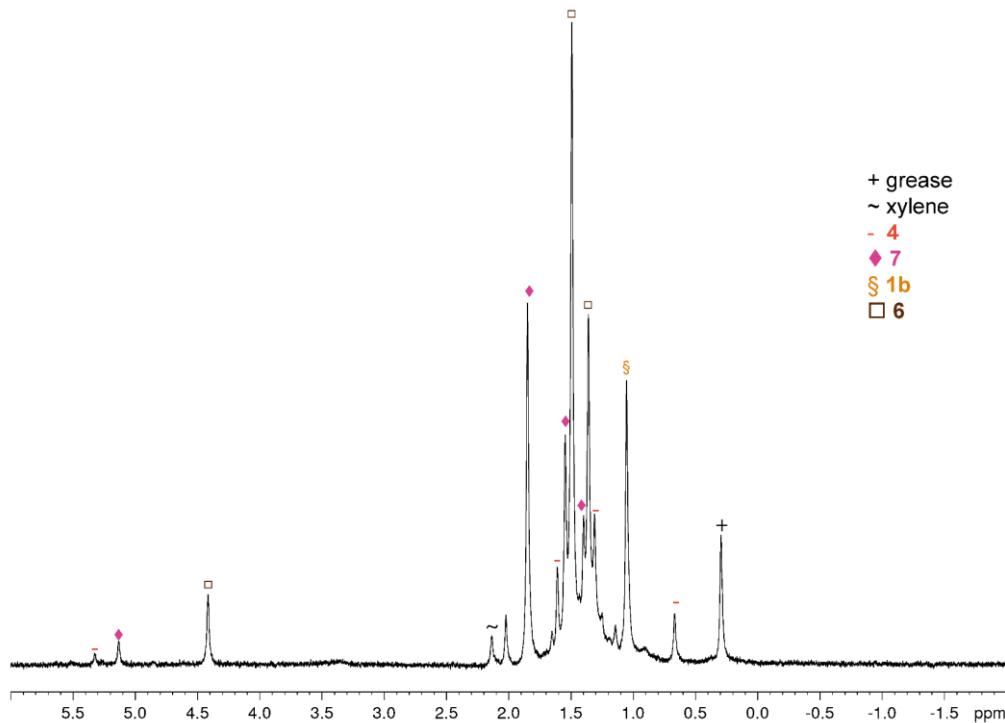


Figure S26: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 25h.

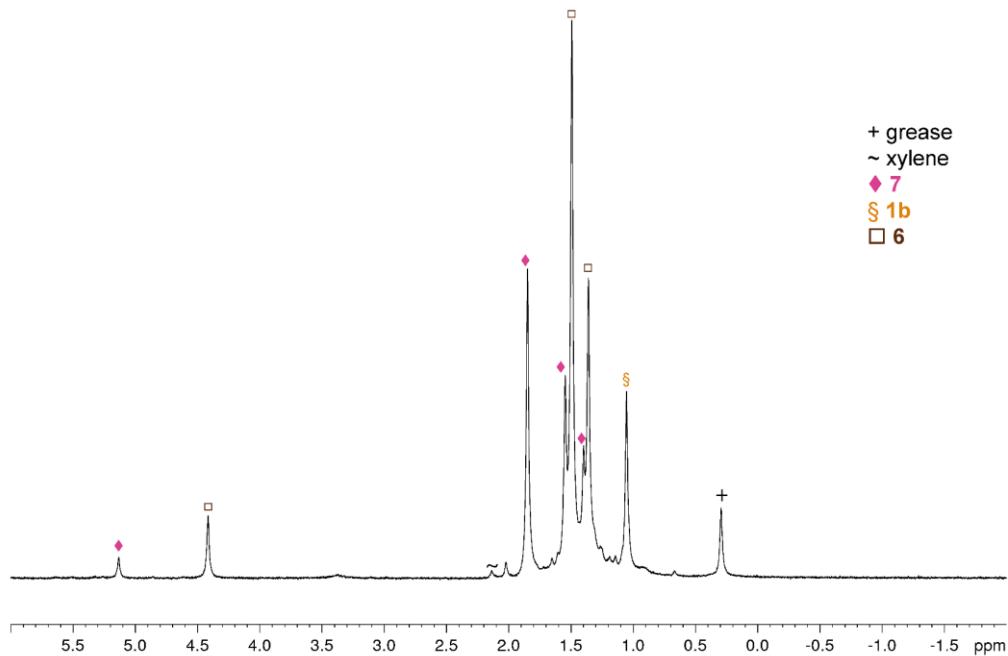


Figure S27: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 45h.

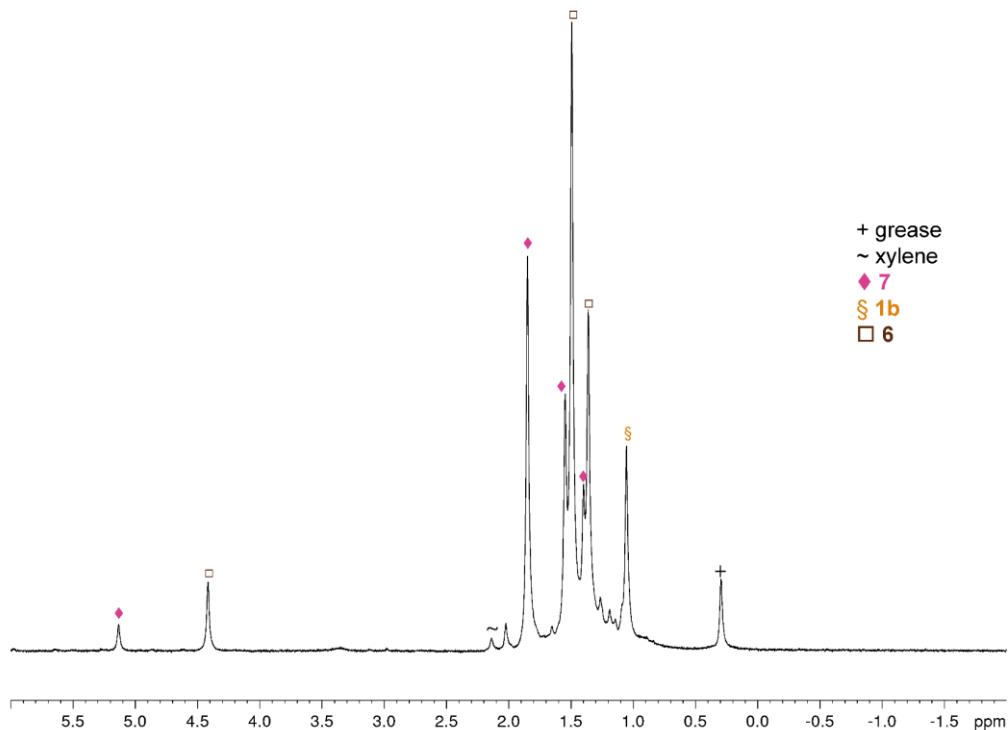


Figure S28: ^1H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 69h.

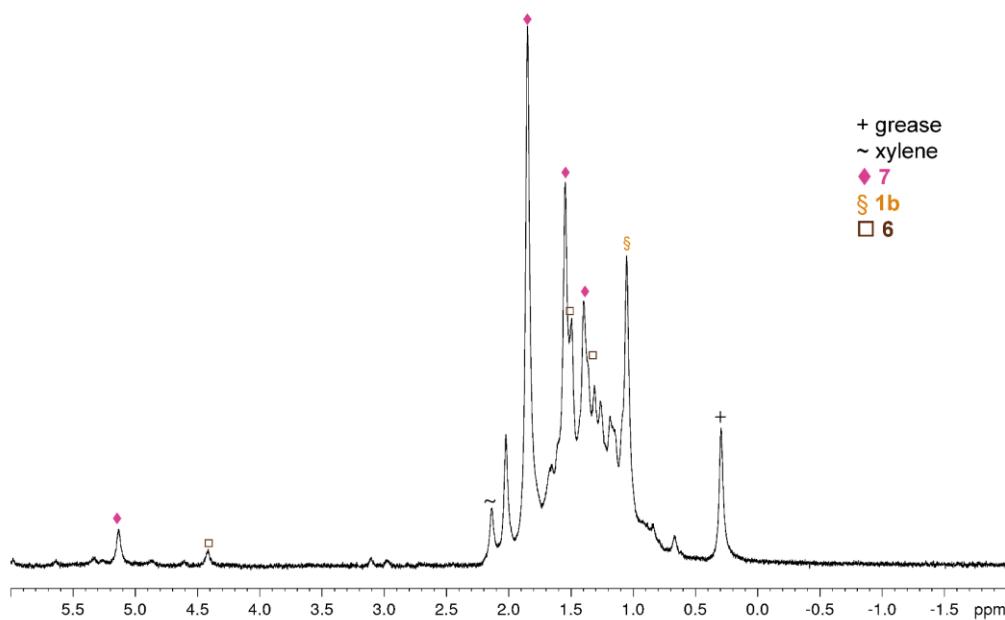


Figure S29: ¹H NMR spectrum of the reaction mixture in C₆D₆ at room temperature after 93h.

3. EPR spectroscopic investigations

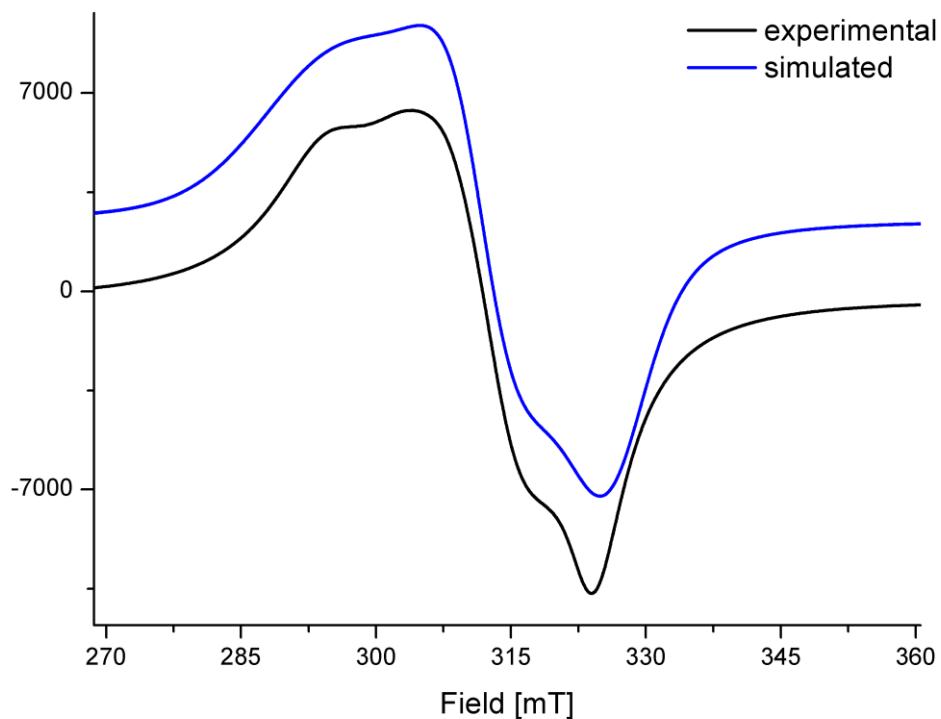


Figure S30: X-band EPR spectrum of **5** (crystalline solid at 77 K) experimental (black) and simulated (blue) $g_x = 2.29632$, $g_y = 2.16718$, $g_z = 2.07149$, $g_{iso} = 2.17833$.

The simulation has been performed using the EasySpin program.^[4]

```
Sys.S = 1/2;
Sys.g = [ 2.16718 2.29632 2.07149 ];
Sys.lwpp = [ 4.3 4.3 ];
Sys.HStrain = [ 80 469 99 ];
Exp.mwFreq = 9.440920;
Exp.Range = [264.0235 364.8285];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;
```

4. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation ($\lambda = 0.71073 \text{ \AA}$) (5), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying applying Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) (4) or Cu-K β radiation ($\lambda = 1.39222 \text{ \AA}$) (3, 7). All measurements were performed at 123 K. For the compounds (3, 4, 5, 7) a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was applied. All structures were solved by direct methods with ShelXT^[7] and Olex2^[8] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL^[7]. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-1994413 (3), CCDC-1994415 (4), CCDC-1994414 (5) and CCDC-1994416 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.1 $[(\text{Cp}^*\text{Fe})(\text{Cp}''\text{Co})(\mu,\eta^5:\eta^4\text{-As}_5)]$ (3)

Compound **3** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains five molecules **3** while four of them are heavily disordered (in one case even four times). Bond lengths and distances are given for the one non-disordered molecule. The structure in solid state is depicted in Figure SX and SX.

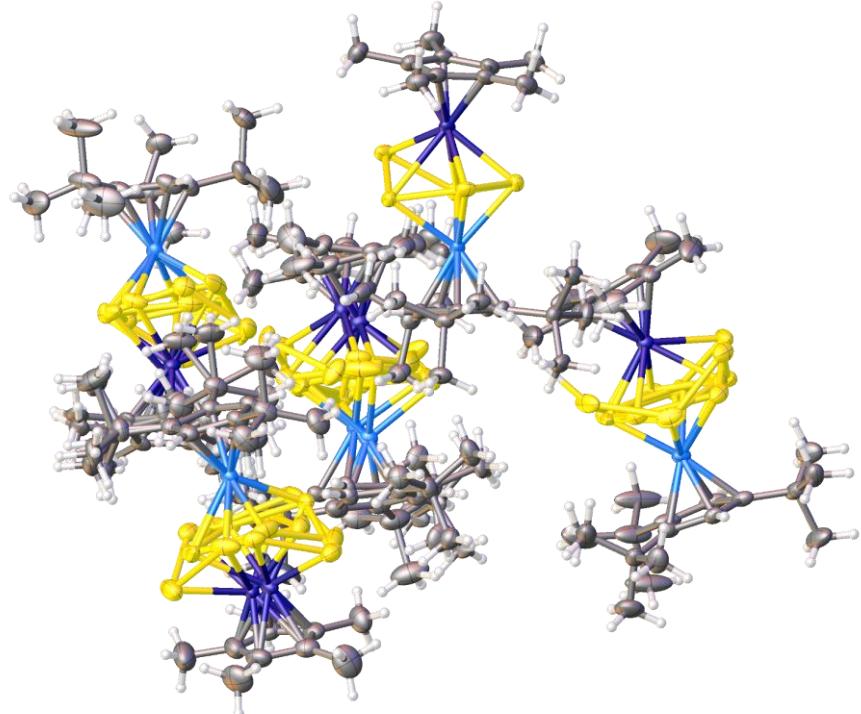


Figure S31: Molecular structure of **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

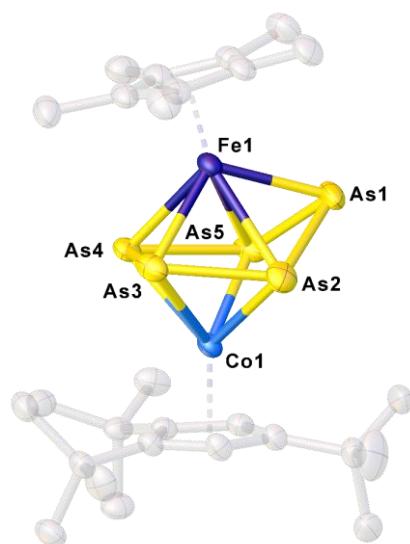


Figure S32: Molecular structure of one independent molecule **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.4241(5), As1-As2 2.3716(6), As2-As3 2.4383(6), As3-As4 2.3401(5), As4-As5 2.4627(5), As1-As5 2.3682(5), Co1-As1 3.6236(5), Co1-As2 2.4259(5), Co1-As3 2.4694(5), Co1-As4 2.4421(6), Co1-As5 2.4383(6), Fe1-As1 2.4095(6), Fe1-As2 2.7108(6), Fe1-As3 2.5026(5), Fe1-As4 2.4824(5), Fe1-As5 2.6514(5), As5-As1-As2-As3 130.722, Cp*Fe-Cp''Co 164.996.

4.3 $[(\text{Cp}^*\text{Fe})(\text{Cp}'''\text{Co})(\mu,\eta^3:\eta^3\text{-As}_3)]$ (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30°C in the monoclinic space group $I2_1/a$ as dark green blocks. The asymmetric unit contains one molecule **4**. Two ' Bu ' groups of the Cp''' ligand are disordered over two positions. The structure in solid state is depicted in Figure S33 and S34.

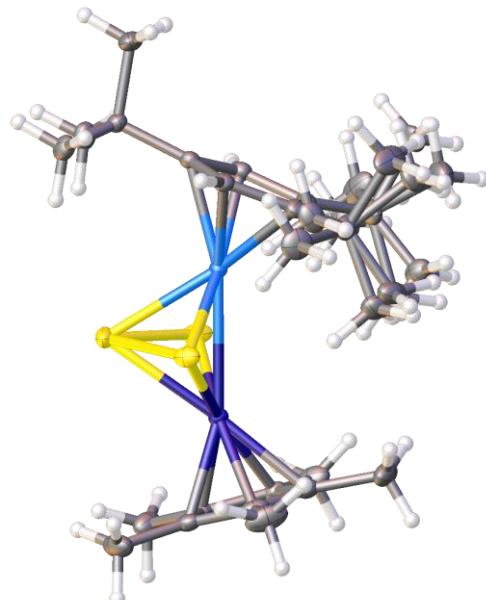


Figure S33: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

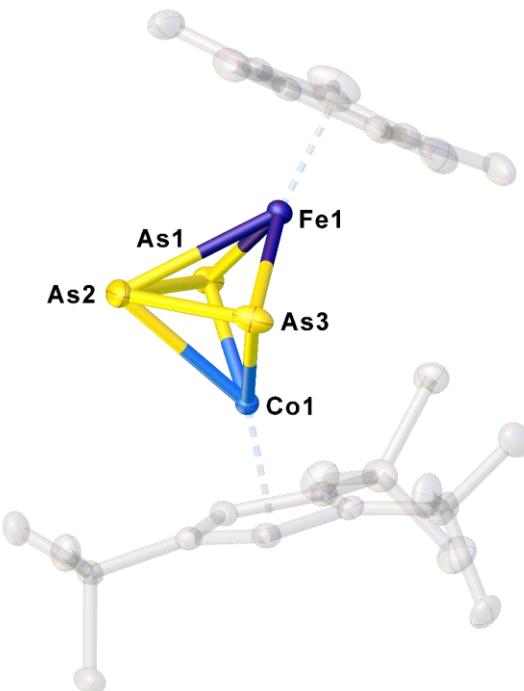


Figure S34: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is the part of highest occupation. Selected bond lengths [\AA] and angles [$^\circ$]: As1-As2 2.3933(3), As2-As3 2.3879(3), As1-As3 3.5123(3), Fe1-Co1 2.7744(4), Fe1-As1 2.2632(3), Fe1-As2 2.5757(3), Fe1-As3 2.2652(3), Co1-As1 2.3131(3), Co1-As2 2.4739(3), Co1-As3 2.3251(3), $\text{Cp}^*\text{Fe-Cp}'''\text{Co}$ 141.827.

4.3 $[(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})_2(\mu_4,\eta^4:\eta^4:\eta^4:\eta^3\text{-As}_{11})] \text{ (5)}$

Compound **5** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30°C in the monoclinic space group $P2_1/c$ as dark brown blocks. The asymmetric unit contains one molecule **5** and 0.85 molecules CH_2Cl_2 . One Cp^* and one Cp'' ligand are disordered over two positions, the CH_2Cl_2 molecule is disordered over four positions. The structure in solid state is depicted in Figure S35 and S36.

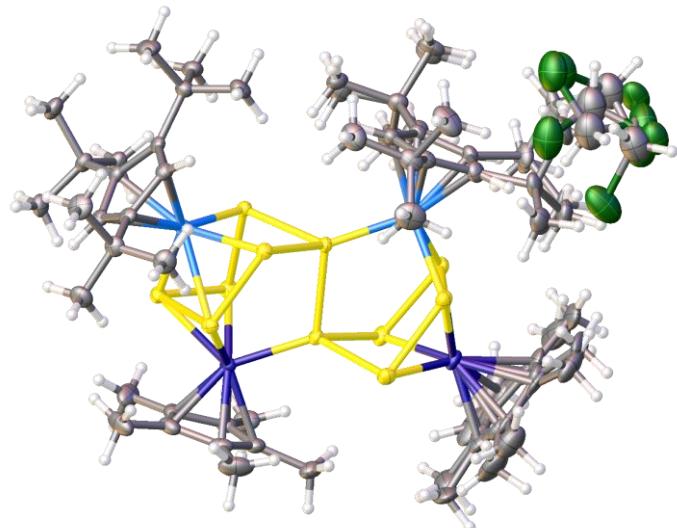


Figure S35: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

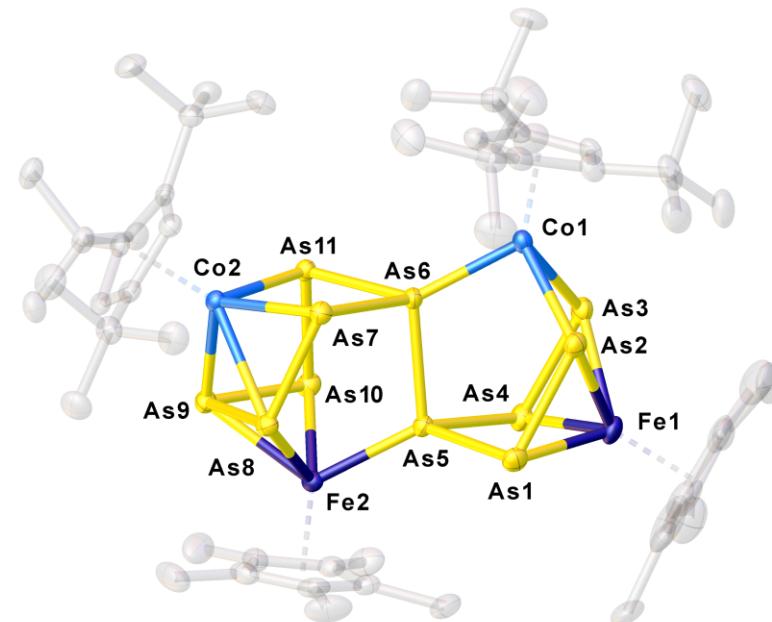


Figure S36: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is the part of highest occupation. Solvent molecules are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: As1-As2 2.3812(5), As2-As3 2.7746(5), As3-As4 2.3915(5), As4-As5 2.4316(4), As1-As5 2.4404(5), As5-As6 2.4123(4), As6-As7 2.4208(8), As7-As8 2.3843(4), As8-As9 2.5816(5), As9-As10 2.3812(5), As10-As11 2.4563(4), As6-As11 2.4628(4), Fe1-As1 2.4198(6), Fe1-As2 2.4539(6), Fe1-As3 2.4445(6), Fe1-As4 2.4231(6), Fe2-As5 2.2952(5), Fe2-As8 2.3842(5), Fe2-As9 2.4620(5), Fe2-As10 2.4648(5), Co1-As2 2.35802(5), Co1-As3 2.3646(5), Co1-As6 2.2793(5), Co2-As7 2.4126(5), Co2-As8 2.5740(5), Co2-As9 2.4053(5), Co2-As11 2.4175(5).

4.4 $[(\text{Cp}^*\text{Fe})_2(\text{Cp}''\text{Co})(\mu_3,\eta^2:\eta^2:\eta^2\text{-As}_3)_2]$ (7)

Compound **7** crystallizes from a concentrated solution in toluene layered with acetonitrile at room temperature in the monoclinic space group *Cc* as dark brown blocks. The asymmetric unit contains one molecule **7**. The $\text{Cp}''\text{Co}$ fragment disordered over two positions. The structure in solid state is depicted in Figure S37 and S38.

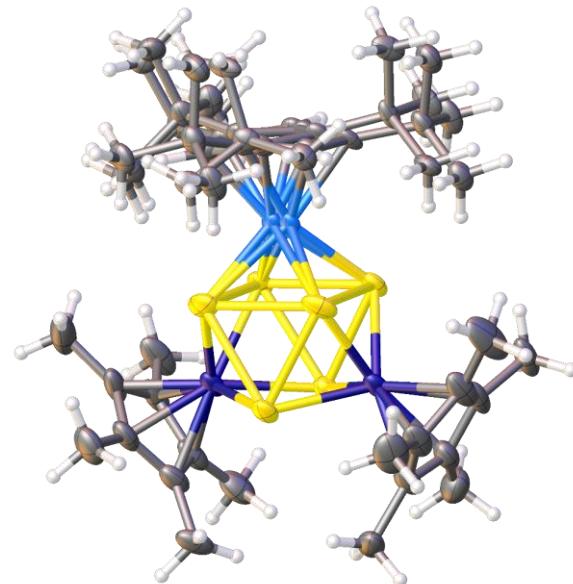


Figure S37: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

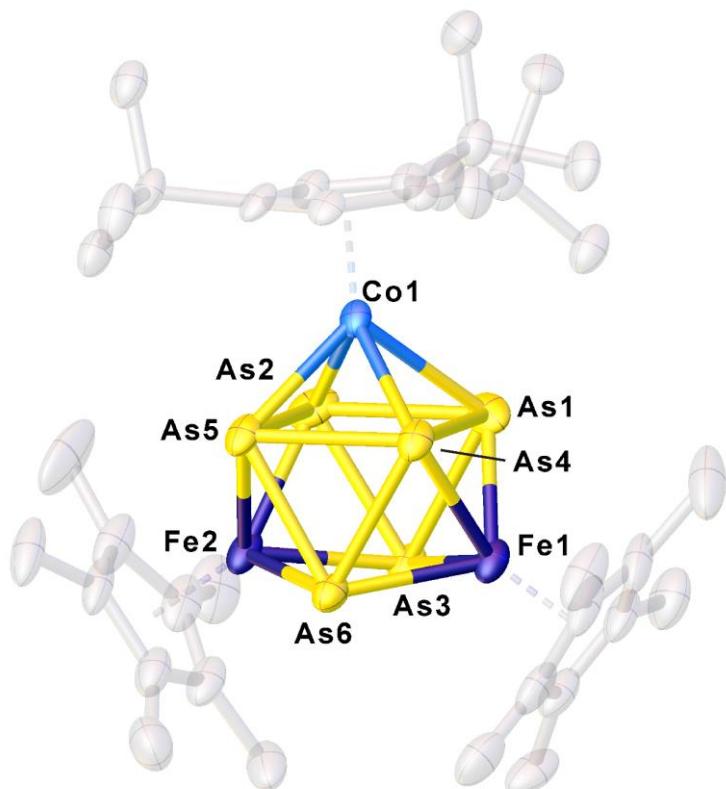


Figure S38: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is the part of **7** with the highest occupation (70%). Selected bond lengths [\AA] and angles [$^\circ$]: As1-As2 2.6224(15), As2-As3 2.5446(13), As1-As3 2.5285(13), As1-As4 2.7570(12), As2-As5 2.7544(13), As3-As6 2.9347(12), As4-As5 2.5853(11), As5-As6 2.5270(12), As4-As6 2.5334(12).

4.5 Crystallographic information

Table S4: Crystallographic data for all compounds

	3	4	5
CCDC	1994413	1994415	1994414
Formula	C ₁₃₅ H ₂₂₀ As ₂₅ Co ₅ Fe ₅	C ₂₇ H ₄₄ As ₃ CoFe	C _{54.85} H _{89.7} As ₁₁ Cl _{1.7} Co ₂ Fe ₂
D _{calc.} / g cm ⁻³	1.845	1.644	1.862
μ/mm ⁻¹	10.647	12.547	6.455
Formula Weight	4290.00	708.193	1863.11
Colour	clear dark green	clear dark green	clear dark brown
Shape	block	block	block
Size/mm ³	0.14×0.13×0.08	0.35×0.21×0.13	0.62×0.43×0.32
T/K	122.95(16)	296.78(10)	123(1)
Crystal System	triclinic	monoclinic	monoclinic
Space Group	P-1	I2/a	P2 ₁ /c
a/Å	12.02431(7)	17.54679(9)	12.8284(2)
b/Å	22.74711(14)	9.14890(5)	14.5804(2)
c/Å	29.66301(15)	35.63932(17)	35.7022(6)
α/°	72.6118(5)	90	90
β/°	86.0155(5)	90.5219(4)	95.551(2)
γ/°	89.9742(5)	90	90
V/Å ³	7722.14(8)	5721.08(5)	6646.54(18)
Z	2	8	4
Z'	1	1	1
Wavelength/Å	1.39222	1.54184	0.71073
Radiation type	Cu K _β	Cu K _α	Mo K _α
θ _{min} /°	3.520	4.96	3.364
θ _{max} /°	73.857	67.07	32.251
Measured Refl.	129880	56873	38659
Independent Refl.	41988	5105	20993
Reflections with I > 2(I)	36616	5088	16754
R _{int}	0.0458	0.0430	0.0232
Parameters	2427	364	921
Restraints	471	0	552
Largest Peak	1.322	0.4739	0.875
Deepest Hole	-0.962	-0.4008	-0.700
GooF	1.072	1.0695	1.085
wR ₂ (all data)	0.1087	0.0461	0.0801
wR ₂	0.1040	0.0460	0.0744
R ₁ (all data)	0.0510	0.0195	0.0561
R ₁	0.0435	0.0194	0.0386

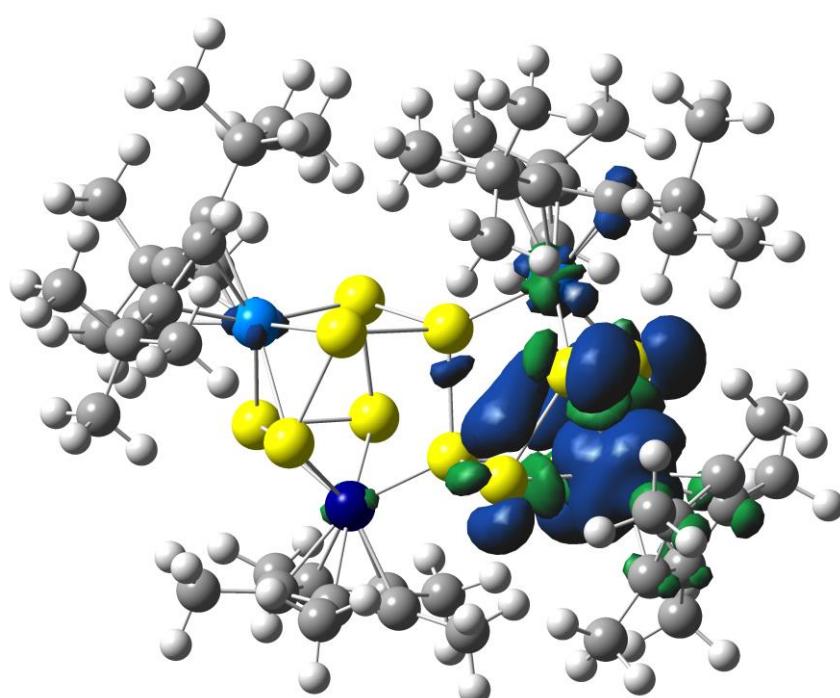
CCDC	7
	1994416
Formula	C ₃₇ H ₅₉ As ₆ CoFe ₂
D _{calc.} / g cm ⁻³	1.877
μ/mm ⁻¹	11.146
Formula Weight	1123.99
Colour	clear dark brown
Shape	block
Size/mm ³	0.31×0.23×0.14
T/K	123(1)
Crystal System	monoclinic
Flack Parameter	0.035(5)
Hooft Parameter	0.051(4)
Space Group	Cc
a/Å	19.6842(4)
b/Å	15.7329(2)
c/Å	12.8445(2)
α/°	90
β/°	91.174(2)
γ/°	90
V/Å ³	3976.97(11)
Z	4
Z'	1
Wavelength/Å	1.39222
Radiation type	Cu K _β
θ _{min} /°	3.247
θ _{max} /°	74.066
Measured Refl.	23082
Independent Refl.	7704
Reflections with I > 2(I)	7476
R _{int}	0.0350
Parameters	606
Restraints	128
Largest Peak	1.441
Deepest Hole	-2.008
GooF	1.050
wR ₂ (all data)	0.1117
wR ₂	0.1104
R ₁ (all data)	0.0416
R ₁	0.0405

5. Computational Details

Gaussian 09 program^[9] was used throughout. Density functional theory (DFT) in form of or BP86^[10] (Becke's exchange and Perdew 86 correlation functional) with def2-TZVP all electron basis set was employed. The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.^[11] The long range dispersion correction GD3BJ was applied.^[12] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.^[13]

Table S5: Total energies for all optimized geometries (BP86/def2-TZVP level of theory).

	total energy [Ha]
3 [(Cp*Fe)(Cp''Co)(μ,η ⁵ :η ⁴ -As ₅]	-14884.0016082
4 [(Cp*Fe)(Cp''Co) (μ,η ³ :η ³ -As ₃)]	-10411.5930462
5 [(Cp*Fe) ₂ (Cp''Co) ₂ (μ ₄ ,η ⁴ :η ⁴ :η ⁴ :η ³ -As ₁₁)]	-32004.3018793
7 [(Cp*Fe) ₂ (Cp''Co)(μ ₃ ,η ² :η ² :η ² -As ₃) ₂]	-18774.5846073
1b [Cp*Fe(η ⁵ -As ₅)]	-12835.2862475
6 [(Cp''Co) ₂ (As ₂) ₂]	-13042.1875737



1	As	-0,002194	52	C	-0,000136
2	As	0,007662	53	C	0,000346
3	As	0,003689	57	C	0,013922
4	As	0,018743	58	C	-0,000028
5	As	0,001518	62	C	-0,000019
6	As	0,001741	66	C	0,000128
7	As	-0,001139	67	C	0,000679
8	As	0,03719	68	C	-0,00001
9	As	0,03218	72	C	-0,000005
10	As	0,02579	76	C	-0,013028
11	As	0,024174	77	C	0,000143
12	Co	0,007323	81	C	0,000096
13	Co	-0,011191	85	C	-0,000031
14	Fe	-0,007745	89	C	-0,014973
15	Fe	0,898029	90	C	0,000174
16	C	-0,000179	94	C	-0,016562
17	C	0,000363	95	C	0,000006
19	C	-0,00053	99	C	0,002493
20	C	0,000038	103	C	-0,000252
22	C	-0,000323	107	C	-0,011837
23	C	-0,000185	108	C	-0,001009
24	C	0,000453	112	C	-0,009888
25	C	-0,000873	113	C	-0,000365
26	C	0,000169	117	C	-0,000152
27	C	-0,004621	121	C	-0,000772
28	C	0,0001	122	C	-0,001133
32	C	0,005812	126	C	0,001244
34	C	0,000677	130	C	0,004344
35	C	0,000091	134	C	0,001547
39	C	-0,000518	138	C	0,001928
40	C	-0,00259	142	C	0,002985
42	C	-0,000685	146	C	0,002714
43	C	0,000051	150	C	0,001647
47	C	-0,000025	154	C	0,002793
51	C	0,000013			

Figure S39. Isosurface of the spin density in **5** and spin densities with hydrogens summed into heavy atoms.

6. References

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