Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Bis(silylenyl)-substituted ferrocene-stabilized η^6-arene iron(0) complexes: synthesis, structure and catalytic application

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Table of Content

1 General Considerations

All experiments and manipulations were carried out under dry nitrogen using standard Schlenk techniques or inside an MBraun glovebox. Solvents were dried by standard methods and freshly distilled prior to use. The NMR spectra were recorded on a Bruker spectrometers AV200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) or AV400 (^{1}H, 400.13 MHz; ^{13}C {^{1}H}, 100.61 MHz; ^{29}Si, 79.49 MHz) Spectrometer. The ^{1}H and ^{13}C {^{1}H} spectra were referenced to residual solvent signals as internal standards (^{1}H NMR: benzene-d_6, 7.16 ppm, THF-d_8, 1.72; 3.58 ppm and ^{13}C {^{1}H} NMR: benzene-d_6, 128.1 ppm, THF-d_8, 77.2 ppm). ^{29}Si {^{1}H} spectra were referenced by using $SiMe_4$ as external standard. Concentrated solutions of samples in deuterated solvent were sealed off in a NMR tube for measurements. Abbreviations: s = singlet; t = triplet; m = multiplet; br = broad. Signals were assigned by employing a combination of 2D NMR H,H-COSY, H,C-COSY (HMBC, HMQC) experiments and additional to DEPT experiments. High resolution APCI (atmospheric-pressure chemical ionization) or ESI (electrospray ionization) mass spectra were recorded on an Orbitrap LTQ XL of Thermo Scientific mass spectrometer. Elemental analyses were recorded in a Thermo FlashEA 1112 Organic elemental analyzer. Commercially available reagents were purchased from SIGMA-Aldrich, Acros, Alfa-Assar or ABCR and used as received. *N,N'*-di-*tert*-butyl(phenylamidinato)-chlorosilylene[S1] and the corresponding ferrocene bridged bis(silylene) ligand[S2] were synthesized according to reported procedures.

Single crystal X-ray structure analyses: Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on an Agilent Technologies SuperNova (single source) at 150 K (Cu-K_α radiation, λ = 1.5418 Å). All structures were solved by direct methods and refined on F^2 with the SHELX-97 software [4]. The positions of the H atoms were calculated and considered isotopically according to a riding model. Crystal structure of **1** was treated using the SQUEEZE routine in PLATON because of disordered co-crystallized benzene molecules. The CCDC numbers 1575933 (compound **1**), 1575932 (compound **2**), 1575930 (compound **3**), and 1575931 (compound **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

ATR/IR-spectroscopic Measurements: The ATR/IR-spectroscopic Measurements were recorded on a Firma Thermo Fisher Scientific spectrometer inside a glovebox. Vibration Modes are given in wavenumbers (cm^{-1}). Abbreviations: (vs) very strong, (s) strong, (m) middle, (w) weak and (br) broad.

^{57}Fe Mössbauer Measurement: ^{57}Fe Mössbauer spectra were recorded at the HU Berlin, in the group of Prof. Dr. Limberg (Adlershof) on a SooCo MS6 Spectrometer at 13 K. The minimum experimental line width is 0.28 mms^{-1}. The temperature of the samples was held constant in a Janis CCS-850 closed cycle cryostat with sample in exchange gas (helium). ^{57}Co/Rh was used as the radiation source. Isomer shifts were determined relative to α-iron at 298 K. The zero-field splitting spectrum was simulated by using Lorenzian doublets, simulated with WMOSS4 software.

Cyclic Voltammetry Measurement: Cyclic Voltammetry (CV) measurements were carried out at 295 K by using a Biologic SP-150 potentiostat and a three electrode set-up. Pt-wire was used as an auxiliary electrode. A freshly polished glassy carbon disc (3 mm diameter) as a working electrode and a pseudo reference electrode Ag/Ag^+ was used. All cyclic voltammograms were referenced against the Cp_2Fe/Cp_2Fe^+ redox couple which was used as an internal standard. As an electrolyte, 0.1 M solutions of $TBAPF_6$ in THF was used. The iR-drop was determined and compensated by using the impedance measurement technique implemented in the EC-Lab Software V10.

2 Synthesis

2.1 General procedure for the synthesis of Fe(II)-dihalide complexes 1 and 2 (GP1)

A 100 ml Schlenk flask was charged with a stoichiometric amount of the free bis(silylene) ligand **A** and $FeCl_{2.}(thf)_{1.5}$ or $FeBr_{2.}(thf)_2$ in a glovebox. THF (50 ml) was added under rapid stirring to the mixture via cannula at room temperature, affording an orange/yellow solution. The reaction mixture was stirred over night at room temperature. After all volatiles were removed, the obtained crude product was washed with hexane (2 x 10 ml) and the resulted Fe(II)-dihalide complex was dried for several hours under reduced pressure. The complex is good soluble in benzene, toluene and THF. The Fe(II)-dihalide complexes are paramagnetic.

2.1.1 Synthesis of Iron(II)-dichloride complex 1

Prepared from **A** (1.50 g, 2.13 mmol) and $FeCl_{2.}(thf)_{1.5}$ (500 mg, 2.13 mmol) according to **GP 1**. The desired compound **1** (1.62 g, 92%) was obtained as a yellow slid. **1**·$(C_6H_6)_5$ can be crystallized from a concentrated benzene solution at room temperature affording orange crystals of the desired complex **1**·$(C_6H_6)_5$ (1.34 g, 76%) suitable for X-ray diffraction analysis. **^{1}H NMR** (400 MHz, THF-d_8, 298 K): δ (ppm) = 12.36 (s, br), 9.39 (s, br), 7.34 (s, br), 6.32 (s, br). Elemental analysis of $C_{40}H_{54}N_4Si_2Fe_2Cl_2$: Calculated: C 57.91, H 6.56, N 6.75. Found: C 57.89, H 7.12, N 6.35. ^{57}Fe Mößbauer 13 K (zero field, mm·s^{-1}): δ = 0.661 , ΔE_Q = 3.267; ferrocene-backbone: δ = 0.539, ΔE_Q = 2.331. Melting Point: T > 105 °C (decomp.).

2.1.2 Synthesis of Iron(II)-bromide complex 2

Prepared from **A** (1.50 g, 2.13 mmol) and $FeBr_{2.}(thf)_2$ (450 mg, 2.13 mmol) according to **GP 1**. The desired compound **2** (1.70 g, 87%) was obtained as an orange solid. **2**·(C_6H_6) can be crystallized from a concentrated benzene solution at room temperature affording orange crystals of the desired complex **2**·(C_6H_6) (1.41 g, 72%) suitable for X-ray diffraction analysis. **^{1}H NMR** (400 MHz, THF-d_8, 298 K): δ (ppm) = 13.15 (s, br), 9.25 (s, br), 7.29 (s, br), 6.62 (s, br). Elemental analysis of $C_{40}H_{54}N_4Si_2Fe_2Br_2$·$(C_6H_6)$: Calculated: C 55.43, H 6.07, N 5.62. Found: C 55.69, H 6.51, N 5.85. ^{57}Fe Mößbauer 13 K (zero field, mm·s^{-1}): δ = 0.656, ΔE_Q = 3.459; ferrocene-backbone: δ = 0.539, ΔE_Q = 2.327. Melting Point: T > 107 °C (decomp.).

2.2 General procedure for the synthesis of Fe(0)-(η_6-arene) complexes 3 and 4 (GP 2)

A 100 ml Schlenk tube was charged with 500 mg (1.0 equiv.) of Fe(II)-dihalide complex **1** (0.603 mmol) or **2** (0.544 mmol) and 2.6 equiv. KC_8 (211 mg or 191 mg) in a glovebox. A solution of THF/arene (arene = benzene, toluene; 50.0 ml, 1:1) was added under rapid stirring to the mixture via cannula at room temperature. The suspension was stirred at room temperature and the consumption of **1** or **2** can be observed by *in situ* ^{1}H NMR(C_6D_6) forming a new diamagnetic Fe(0) species; changing from orange/yellow to red/violet respectively. (Reaction-times: **2**, 3 h; **1**, 5 h). After the reaction is completed, all volatiles were removed under reduced pressure and the desired Fe(0)-arene complex could be extracted from diethyl ether (2 x 20.0 mL). After drying under reduced pressure, the Fe(0)-arene complex could be obtained as red/brown solid. Complex **3**, **4** showed low solubility in deuterated solvents such as C_6D_6 and THF-d_8. The conduction of ^{13}C- and ^{29}Si-NMR spectra for further discussion was not possible

2.2.1 Benzene iron(0) complex 3

Prepared from either **1** (500 mg, 0.603 mmol) or **2** (500 mg, 0.544 mmol) by following GP 2. The desired product **3** (327 mg, 63%; starting from **1**) was isolated as red/brown solid and **3** (214 mg, 47%, 0.256 mmol; starting from **2**). **3**·(C_6H_6) can be crystallized from a concentrated benzene solution at room temperature affording red crystals of the desired complex suitable for X-ray diffraction analysis. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.38 (s, 36H, NC(C*H*$_3$)$_3$), 4.42 (m, 4H, FeC*H*), 4.59 (m, 4H, FeC*H*), 5.16 (s, 6H, η^6(C_6H_6)), 6.77–7.38 (m, 10H, arom. *H*). ESI-MS (THF), m/z: calcd for [$C_{46}H_{60}Fe_2N_4Si_2$ + H]$^+$: 837.3127, found: 837.3128. Elemental analysis of $C_{46}H_{60}Fe_2N_4Si_2$. Calculated: C 66.02, H 7.23, N 6.69. Found: C 65.12, H 7.08, N 6.23. ^{57}Fe Mößbauer 13 K (zero field, mm·s^{-1}): δ = 0.368, ΔE_Q = 1.334; ferrocene-backbone: δ = 0.531, ΔE_Q = 2.301. Melting Point: T > 145 °C (decomp.). CV: $E^{1/2}$ (fc/fc$^+$) = -1.56 eV (revers.).

2.2.2 Toluene iron(0) complex 4

Prepared from **1** (500 mg, 0.603 mmol), the desired product **3** (318 mg, 62%, 0.374 mmol) was isolated as red/brown solid. **4**·(Et_2O)$_2$ can be crystallized from a concentrated diethyl ether solution at -30 °C, affording red crystals of the desired complex suitable for X-ray diffraction analysis. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ(ppm) = 1.38 (s, 36H, NC(C*H*$_3$)$_3$), 2.71 (s, 3H, Ph-C*H*$_3$), 4.42 (m, 4H, FeC*H*), 4.61 (m, 4H, FeC*H*), 4.94-5.09 (m, 4H, η^6(C_6H_5-Me)), 5.26 (s, 1H,

η^6(C_6H_5-Me)), 6.77-7.38 (m, 10H, arom. *H*). ESI-MS (THF), m/z: calculated for $[C_{47}H_{62}Fe_2N_4Si_2 + H]^+$: 851.3285, found: 851.3283. Elemental analysis of $C_{47}H_{63}Fe_2N_4Si_2$. Calculated: C 66.34, H 7.34, N 6.58. Found: C 65.92, H 7.51, N 6.43. ^{57}Fe Mößbauer 13 K (zero field, $mm \cdot s^{-1}$): δ = 0.406, ΔE_Q = 2.294; ferrocene-backbone: δ = 0.537, ΔE_Q = 2.294. Melting Point: T > 143 °C (decomp.). CV: $E^{1/2}$ (fc/fc$^+$) = -1.58 eV (revers.).

2.3 General procedure for carbonyl Fe(0) complex 5

2.3.1 By reduction

A 100 ml Schlenk tube was charged with 100 mg of **1** (0.121 mmol, 1.0 equiv.) and 2.6 equiv. of KC_8 (0.313 mmol, 42.3 mg) in a glovebox. THF (10.0 ml) was added to the mixture via cannula at room temperature. The N_2-atmosphere was changed to CO through three freeze-pump-thaw cycles. The suspension was stirred for 1 h at room temperature and the consumption of **1** can be observed by *in situ* ^{1}H NMR(C_6D_6), forming a new diamagnetic Fe(0) species (color changes from orange/yellow to slight yellow). After the reaction is completed, all volatiles were removed under reduced pressure and the desired Fe(0)-carbonyl complex **5** could be extracted from diethyl ether (2 x 5 ml). After drying under reduced pressure for several hours, the Fe(0)-carbonyle complex **5** (70 mg, 72%)could be obtained as slight yellow solid with.

2.3.2 By Arene/ CO ligand exchange

A 100 ml Schlenk tube was charged with 10 mg of Fe(0)η^6(arene) complexes (**3**, **4**) and dissolved in 10.0 ml THF. The N_2-atmosphere was changed to CO through three freeze-pump-thaw cycles. After allowing the solution to warm up to room temperature, a color change from red to yellow was observed indicating the arene/ CO ligand exchange. After 5 min, all volatiles were removed under reduced pressure and **5** could be obtained quantitatively as slight orange solid.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ(ppm) = 1.33 (s, 36H, NC(CH_3)$_3$), 4.39 (m, 4H, Fe*CH*), 4,65 (m, 4H, Fe*CH*), 6.99–7.12 (m, 8H, arom. *H*), 7.36–7.39 (m, 2H, C_{arom}.*H*). ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ(ppm) = 1.17 (s, 36H, NC(CH_3)$_3$), 4.65 (m, 4H, Fe*CH*), 4.83 (m, 4H, Fe*CH*), 7.50–7.62 (m, 10H, C_{arom}.*H*). ^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ(ppm) = 31.4 (NC(CH_3)$_3$), 54.2 (N*C*(CH_3)$_3$), 70.7 (Fe*C*H), 74.5 (Fe*C*H), 82.3 (Si*C*), 121.0, 128.7, 130.3, 130.8 ($C_{arom.}$),167.9 (N*C*N), 225.5 (*C*O). ^{13}C {^{1}H} NMR (100 MHz, THF-d_8, 298 K): δ(ppm) = 31.78

(NC(CH_3)$_3$), 55.8 (N*C*(CH_3)$_3$), 74.2 (Fe*C*H), 75.0 (Fe*C*H), 77.6 (Si*C*), 129.1, 129.3 129.7, 129.8, 131.8, 131.9 ($C_{arom.}$),171.2 (N*C*N), 217.50 (*C*O). ^{29}Si {^{1}H} NMR (79.5 MHz, THF-d_8, 298 K): δ(ppm) = 104.2 ppm. ESI-MS (THF), m/z: calculated for $[C_{43}H_{54}N_4Si_2Fe_2O_3 + H]^+$: 842.2428, found. 842.2430; $[M - CO + H]^+$: 814.2479, found. 814.2478. Melting Point: T > 94 °C (decomp.). IR (ATR): ν_{CO}(cm^{-1}) = 1941, 1900, 1862 (s).

2.4 Characterisation

2.4.1 Dihalido Fe(II) complexes 1 and 2

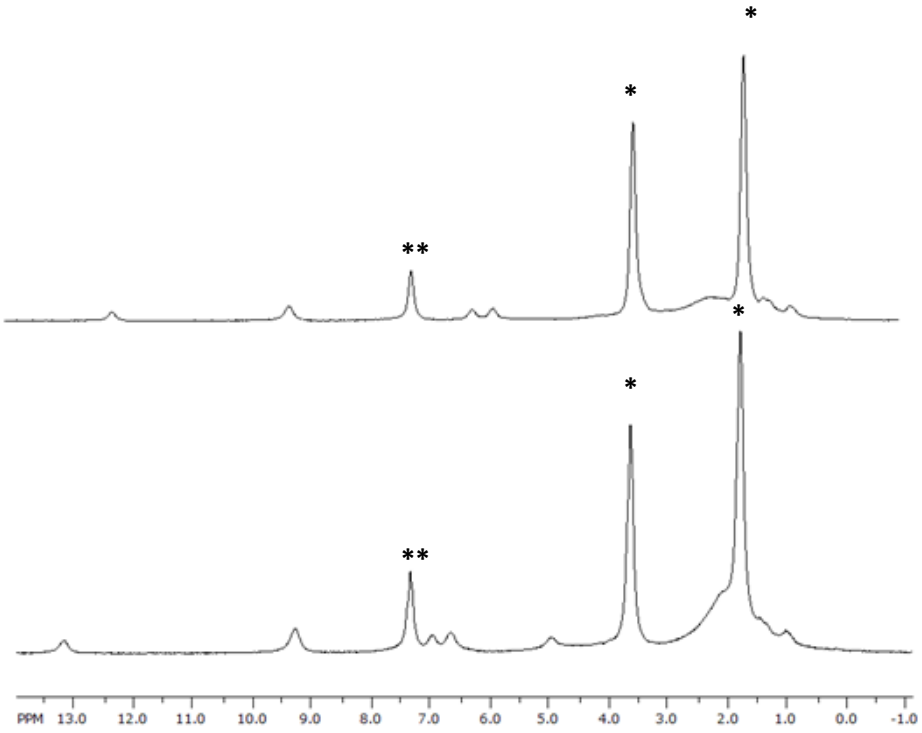


***Figure S1*:** Paramagnetic ^{1}H NMR spectra of both Fe(II)-dihalide complexes **1** (top) and **2** (bottom) in THF-d8 (*) at 298 K with co-crystallized benzene (**, 7.15 ppm).

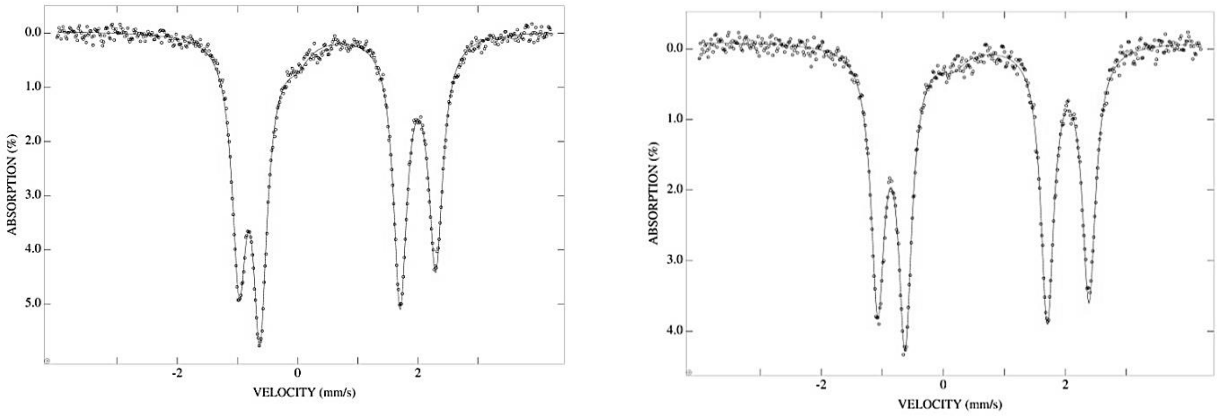


***Figure S2*:** ^{57}Fe Mössbauer spectra of **1** (left) and **2** (right).

2.4.2 Fe(0)-Arene complexes 3 and 4

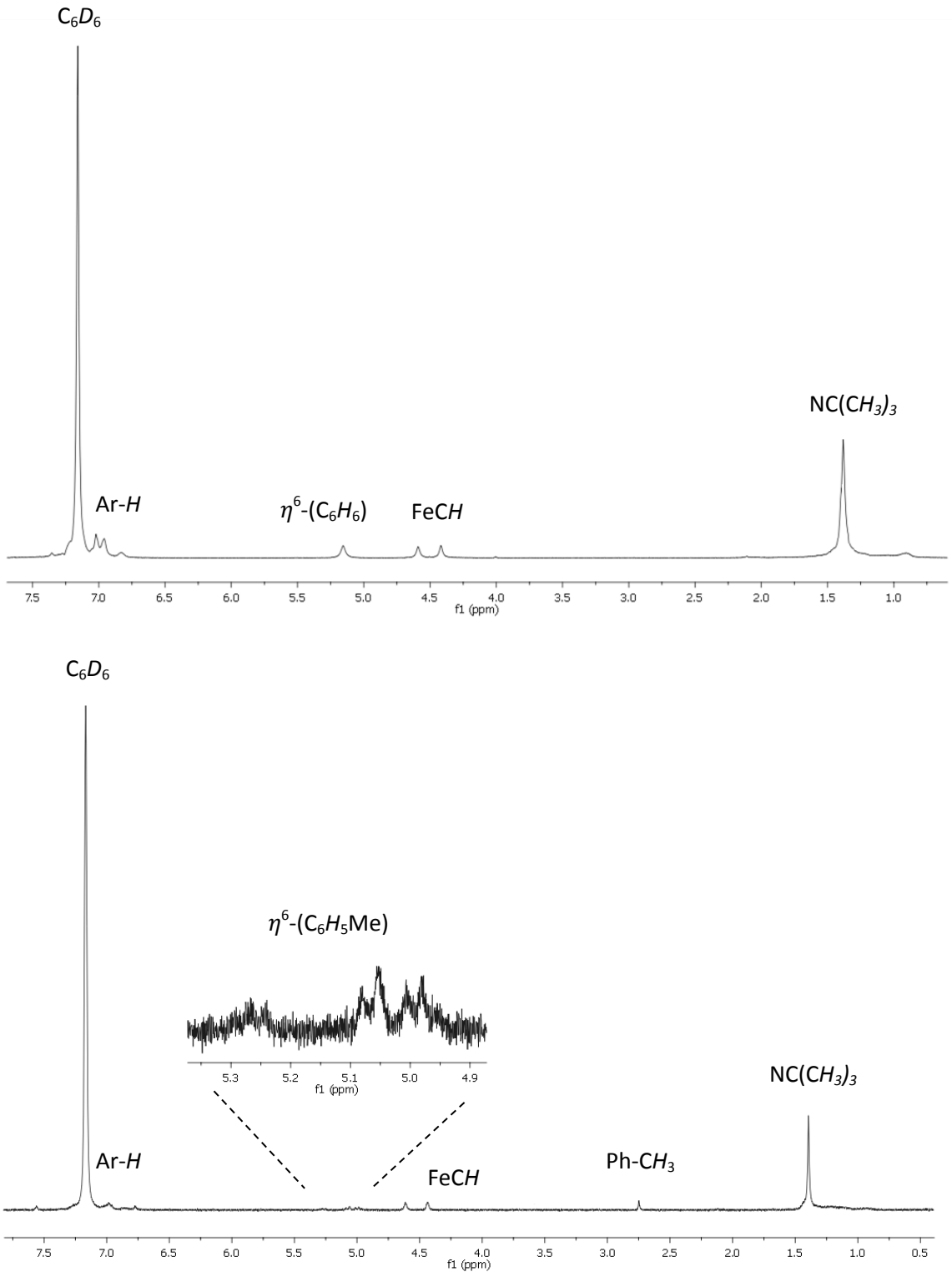


***Figure S3*:** ^{1}H NMR spectra of **3** (top) and **4** (bottom) in C_6D_6 at 298 K.

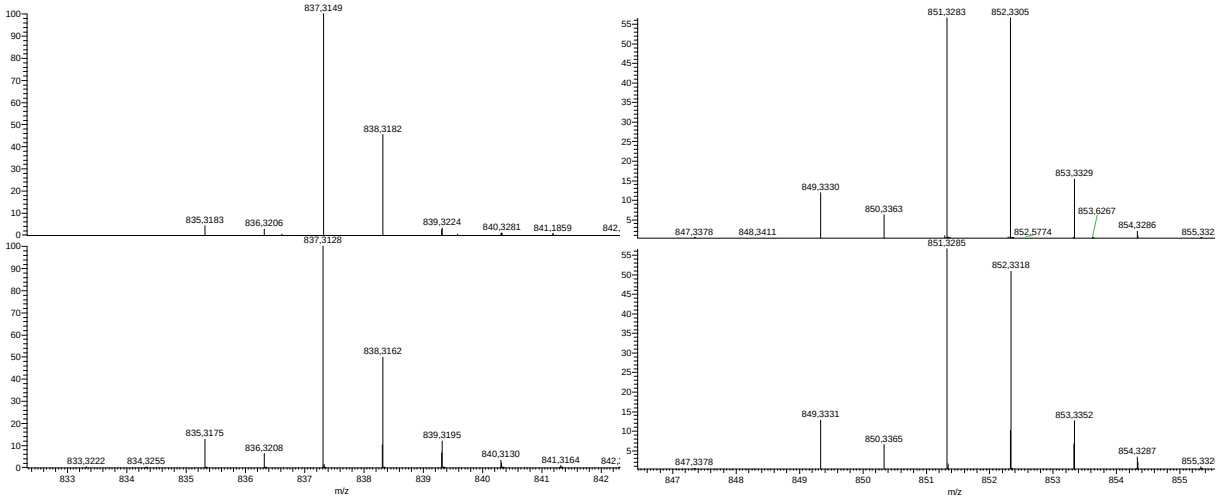


***Figure S4*:** ESI-mass spectrum (THF) $[M+H]^+$ **3** (left) and **4** (right). (top: expt.; bottom: calculated).

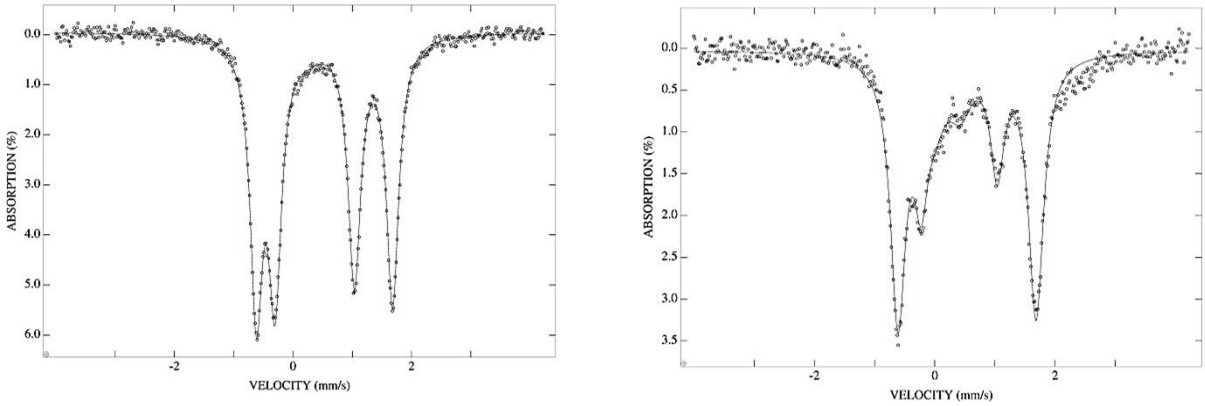


***Figure S5*:** ^{57}Fe Mössbauer spectra **3** (left) and **4** (right). Spectra show a Fe(III) impurity which might come from $FeCl_2$.

2.4.3 Fe(0)-Carbonyl complex 5

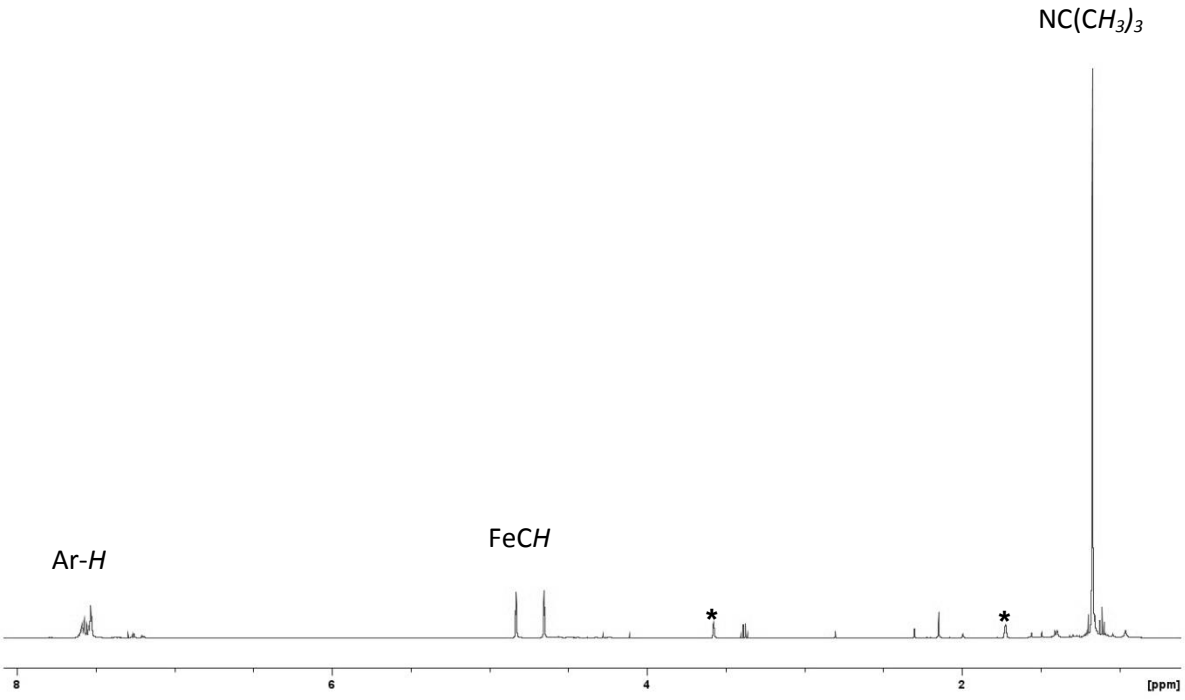


***Figure S6*:** ^{1}H NMR spectra of **5** in THF-d_8(*) at 298 K.

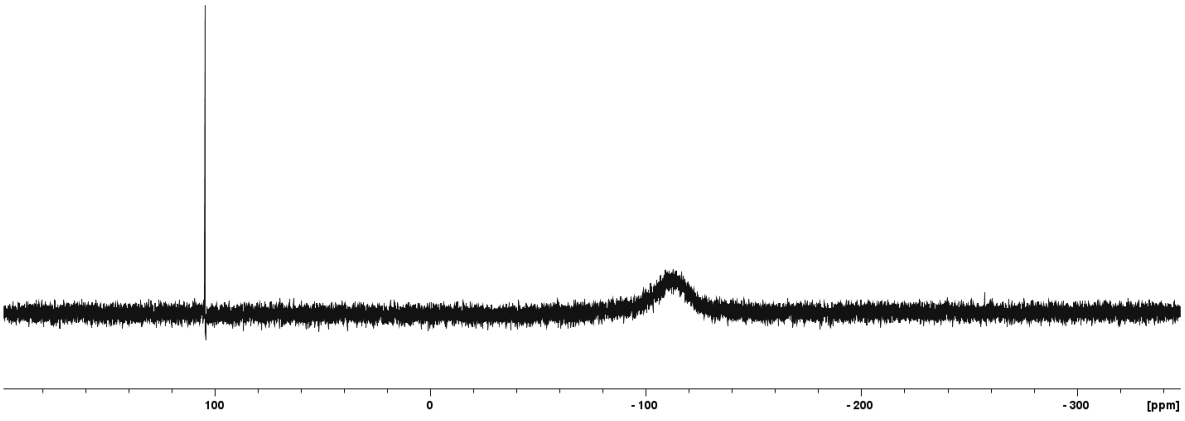


***Figure S7*:** ^{29}Si NMR spectra of **5** in THF-d_8 at 298 K.

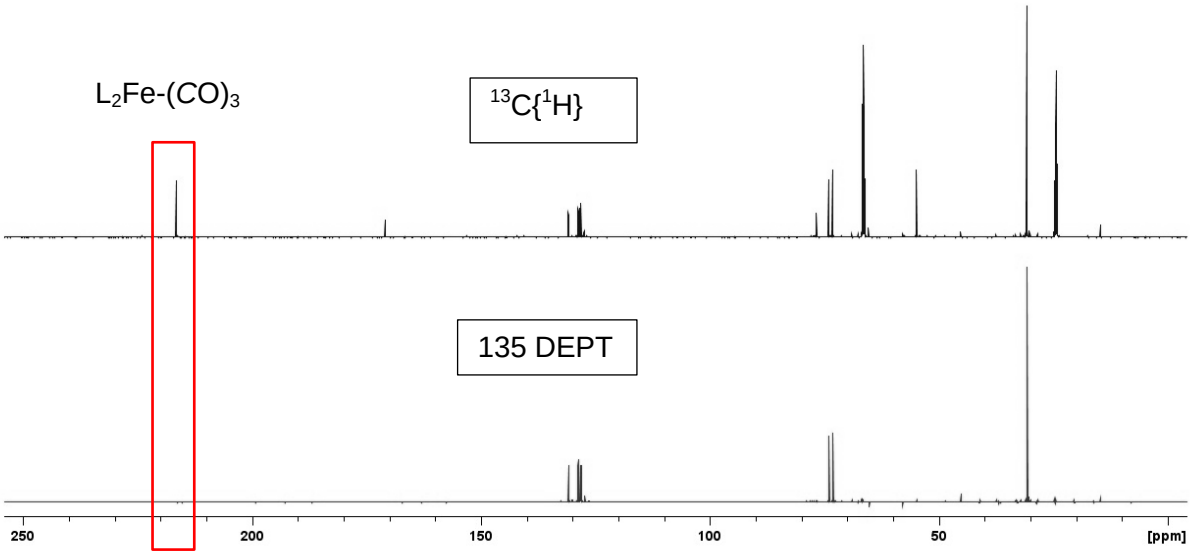


***Figure S8*:** ^{13}C NMR spectra of **5** in THF-d_8 at 298 K.

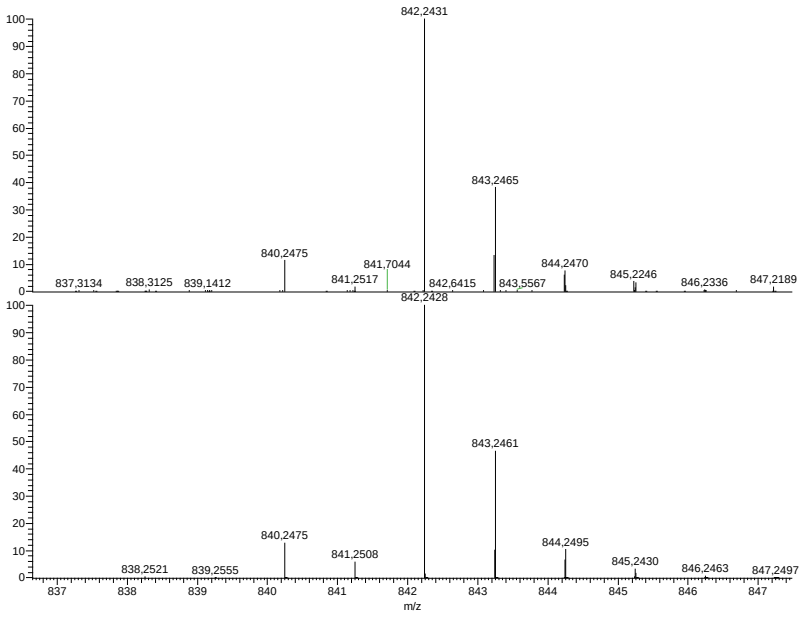


***Figure S9*:** ESI-mass spectrum (THF) $[M + H]^+$ of **5** (top: expt.; bottom: calculated).

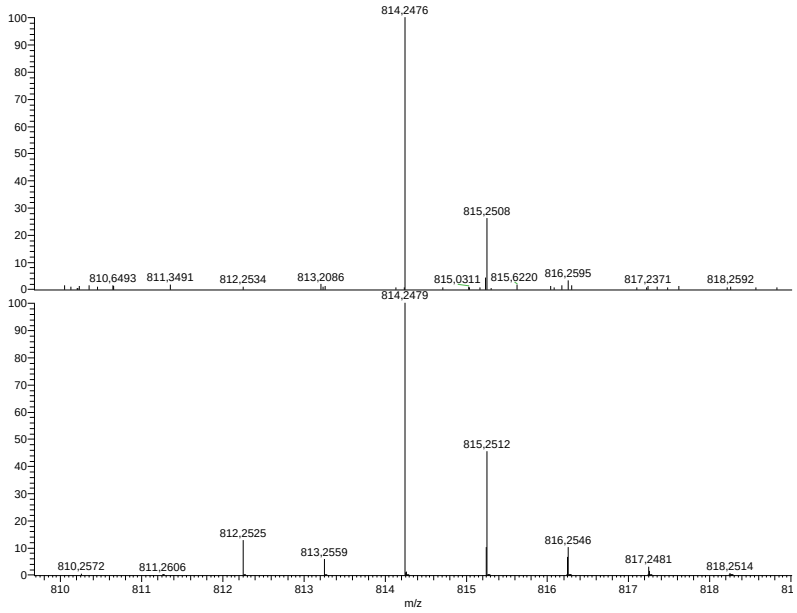


Figure S10: ESI-mass spectrum (THF) $[M\text{-}CO + H]^+$ of **5** (top: expt.; bottom: calculated).

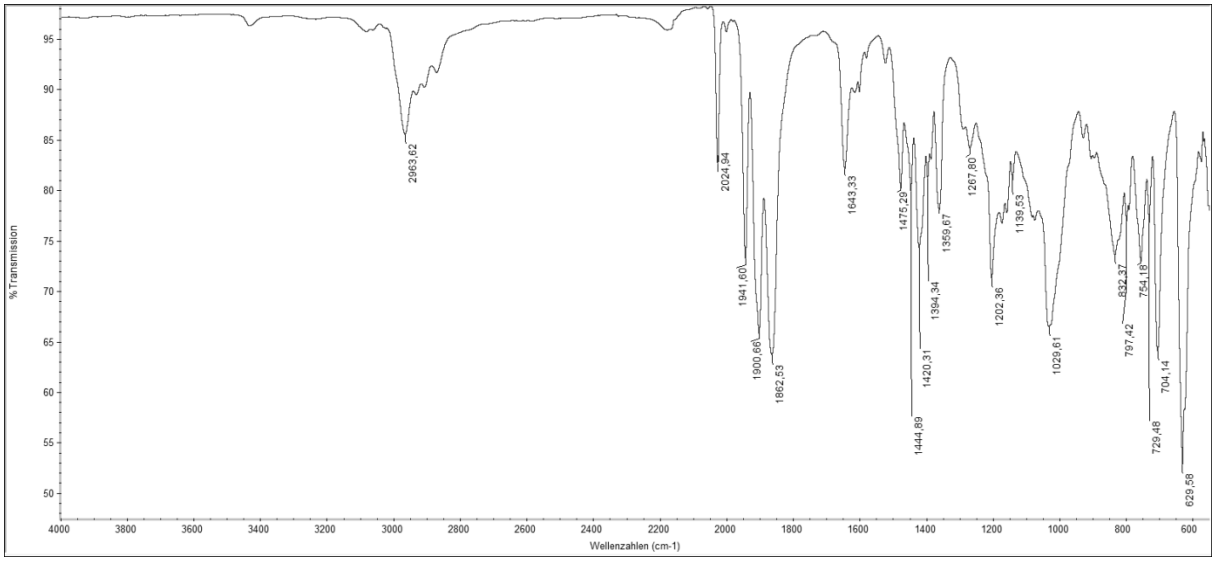


Figure S11: ATR-IR spectra of **4**. Typical for cis-$L_2M(CO)_3$ with 2A` und 1A`` IR active modes.

2.4.4 Electrochemistry of 3 and 4

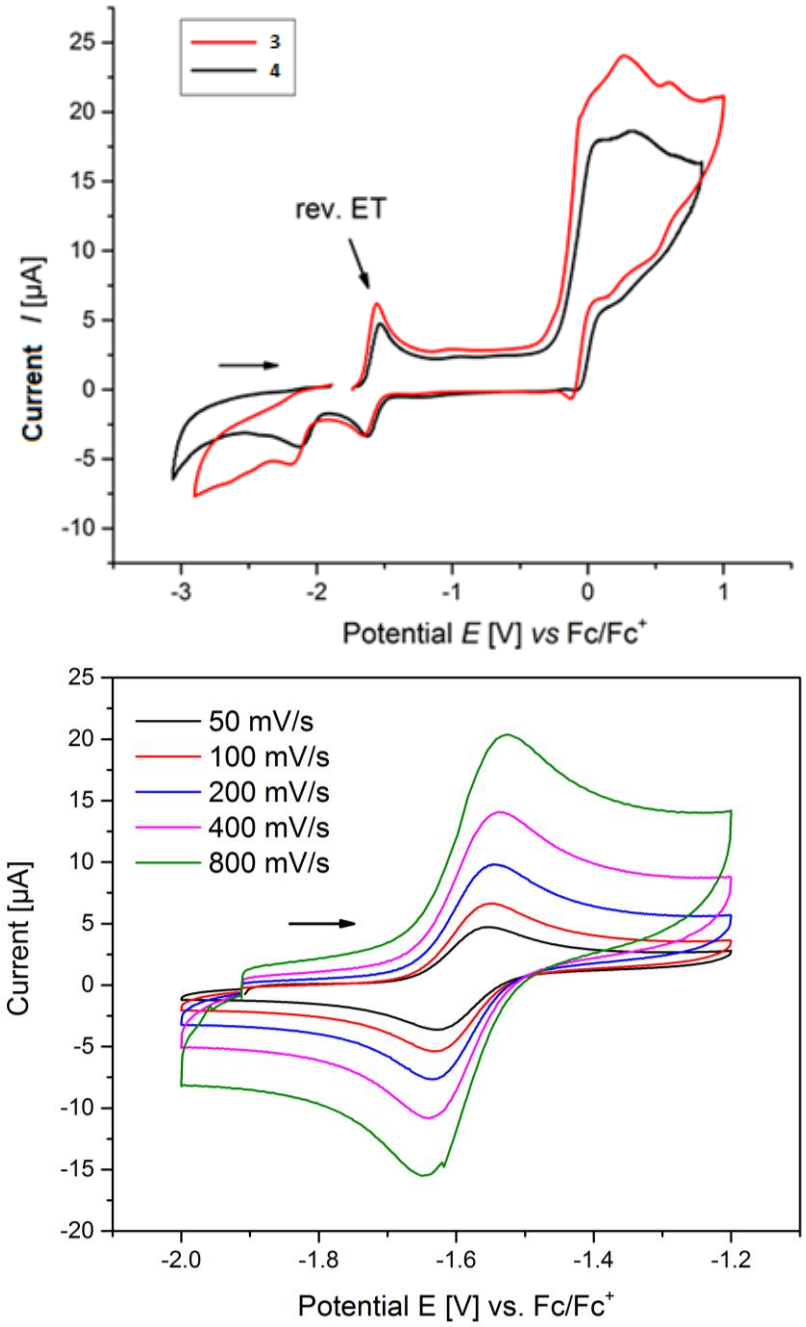


***Figure S12*:** Top: CV of **3** (red) and **4** (black) (1mM in THF/ 0.1M $TBAPF_6$) recorded at a scan rate v = 100 $mV \cdot s^{-1}$ showed one reversible redox event for both complexes. Bottom: Reversible redox event at $E^{1/2}$ = -1.56 V (*vs* Fc/Fc^+) measured with scan rates v = 50-800 mVs^{-1} for **3**.

Table S 1: Data for the reversible ET at $E^{1/2}$ = -1.56 V (*vs* Fc/Fc^{+}) for **3**.

v [mV·s^{-1}]	E_{pc} [V]	E_{pa} [V]	ΔE_p [mV]	i_{pc} [µA]	i_{pa} [µA]	i_{pa}/i_{pc}	$i_{pc}/(v^{1/2})$
50	-1.359	-1.423	64	4	4	1.0	0.5
100	-1.358	-1.424	66	5	5	1.0	0.5
200	-1.347	-1.430	83	7	7	1.0	0.5
400	-1.339	-1.439	100	10	10	1.0	0.5
800	-1.335	-1.437	102	13	13	1.0	0.5

Furthermore, a linear dependence of the forward peak current i_{pc} on the square-root of the scan rate $v^{1/2}$ implied diffusion control for the redox processes at $E^{1/2}$ = -1.56 V (*vs* Fc/Fc^{+}).

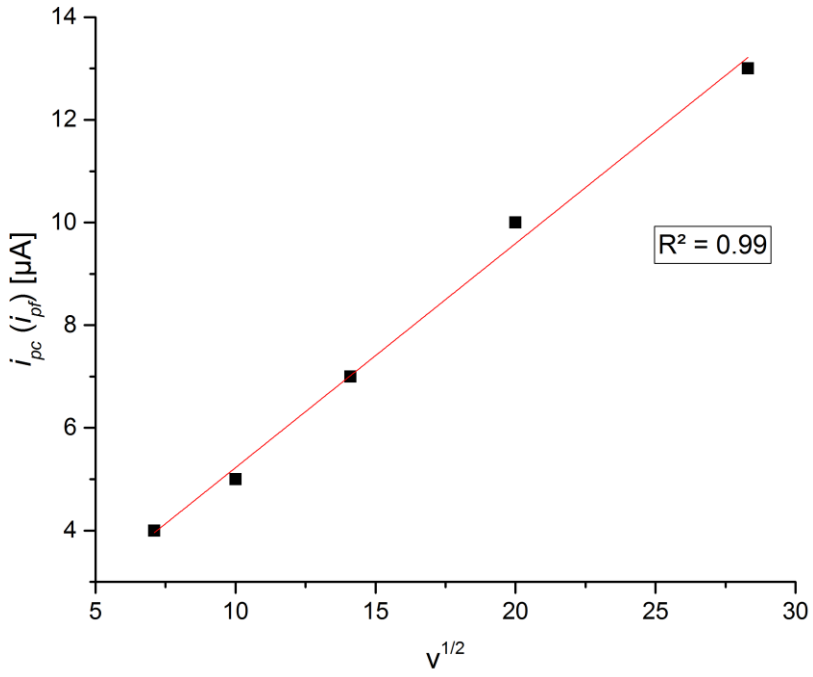


***Figure S13*:** Linear dependence of the forward peak current i_{pc} on the square-root of the scan rate v indicates diffusion control for the redox process at $E^{1/2}$ = -1.56 V. The linearfit (*red*) was calculated by the least square approach using the model function y = a + bx.

2.4.5 ORTEP representations

2.4.5.1 Fe(II)-dihalide complexes 1 and 2

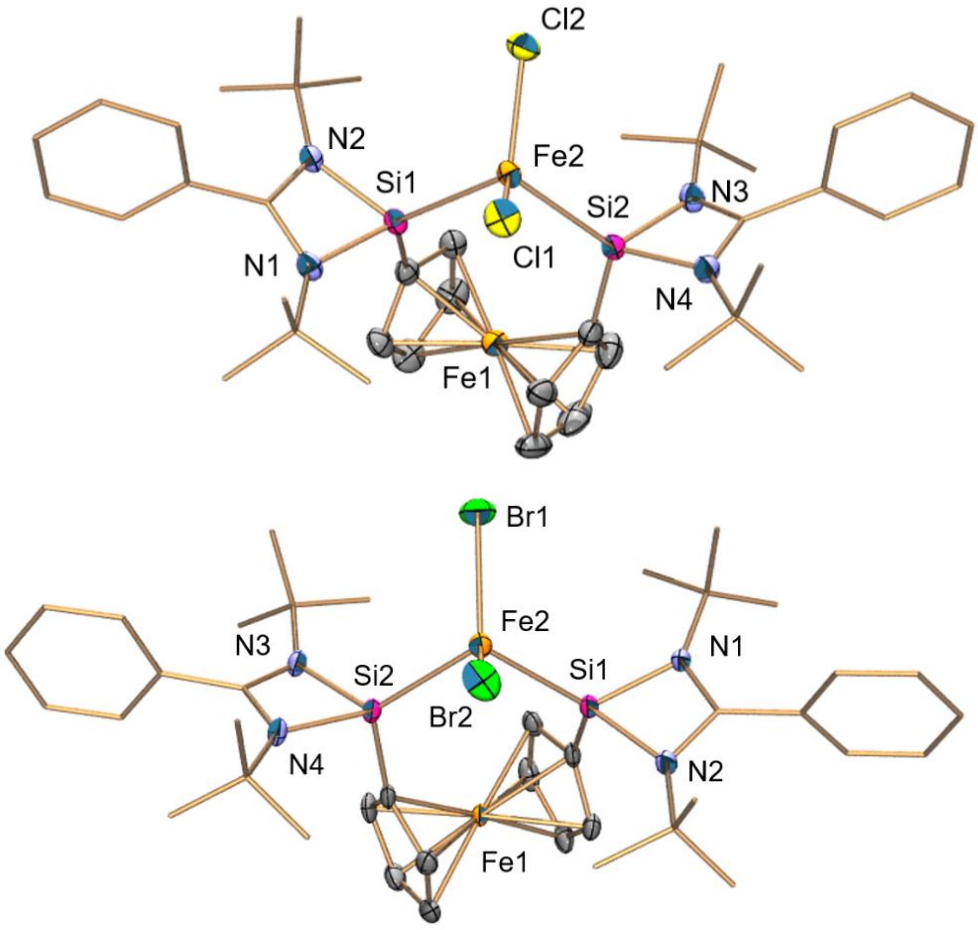


***Figure S14**:* ORTEP representation of **1** (top) and **2** (bottom) in the solid-state at 50 % probability level. Hydrogen and solvent atoms are omitted for clarity. Selected bond lengths [Å]: **1**: Fe2-Cl1 2.255(6), Fe2-Cl2 2.2553(4), Si1-Fe2 2.4923(4), Si2-Fe2 2.4823(4), Si2-N3 1.8438(11), Si2-N4 1.8543(11), Si1-N2 1.8490(11), Si1-N1 1.856(12). Selected bond angle [°]: Cl1-Fe2-Cl2 119.94(2), Si1-Fe2-Si2 100.341(13), Cl2-Fe2-Si1 109.481(14), Cl1-Fe2-Si1 108.269(14), Cl2-Fe2-Si2 107.609(15), Cl1-Fe2-Si2 109.442(15). **2**: Selected bond lengths [Å]: Fe2-Br1 2.402(5), Fe2-Br2 2.397(5), Si1-Fe2 2.498(8), Si2-Fe(2) 2.504(8), Si2-N3 1.850(2) , Si2-N4 1.863(2), Si1-N2 1.853(2), Si1-N1 1.859(2). Selected bond angle [°]: Br1-Fe2-Br2 117.04(2), Si1-Fe2-Si2 100.90(3), Br2-Fe2-Si1 108.40(2), Br1-Fe2-Si1 109.82(2), Br2-Fe2-Si2 109.97, Br1-Fe2-Si2 109.48(2).

2.4.5.2 Fe(0)-(arene) complexes 3 and 4

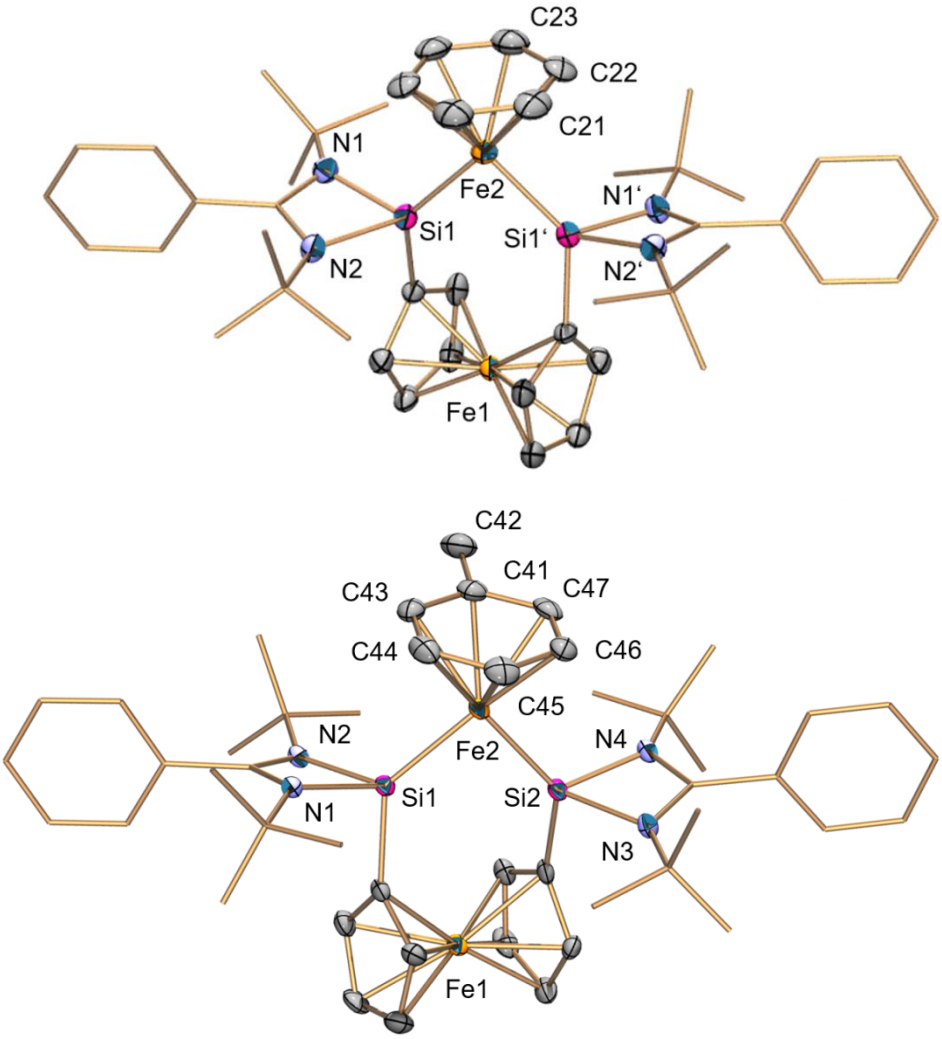
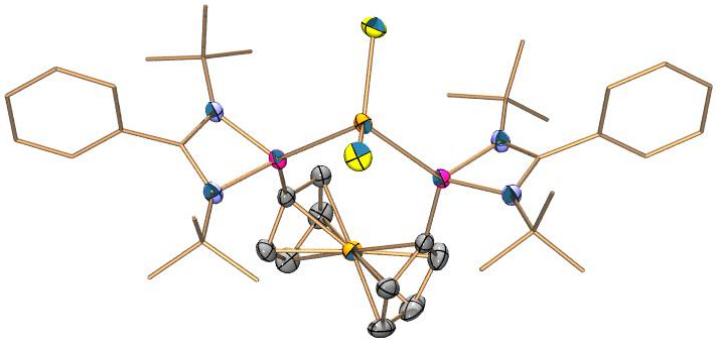


***Figure S15**:* ORTEP representation of the solid-state structure of **3** (top) and **4** (bottom) at 50% probability level. Hydrogen and solvent atoms are omitted for clarity. **3**: Symmetry transformations used to generate equivalent atoms (`): 1-x, -y,z. Selected bond lengths [Å]: Fe2-C22 2.084(5), Fe2-C23 2.089(6), Fe2-C21 2.089(6), C21-C22 1.426(9), Fe2-Si1 2.178216, Si1-C16 1.899(5), Si1-N1 1.917(4), Si1-N2 1.914(4). Selected bond angle [°]:Si1-Fe2-Si1` 89.27(8), N1-Si1-N2 68.16(7). **4**: Selected bond lengths [Å]: Fe2-Si2 2.1752(8), Fe2-Si1 2.1707(8), Si1-C31 1.890(3), Si1-N1 1.913(2), Si1-N2 1.912(2), Fe2-C44 2.078(3), Fe2-C46 2.079(3), Fe2-C45 2.085(3), Fe2-C43 2.096(3), Fe2-C47 2.103(3), Fe2-C41 2.130(3).C41-C42 1.505(4). C41-C43 1.408(4). Selected bond angle [°]:Si1-Fe2)-Si1` 89.27(8), N1-Si1-N2 68.16(7).

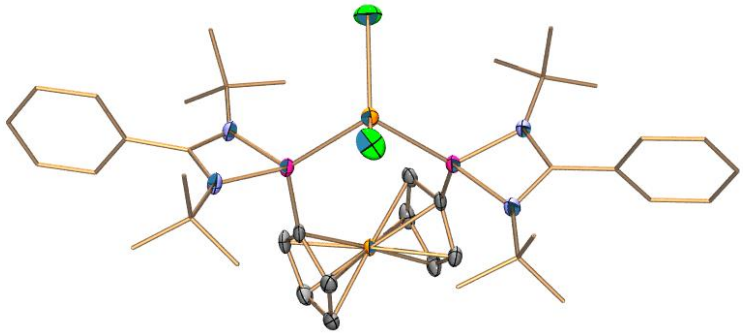
2.5 Crystallographic data

2.5.1 Crystallographic data of 1



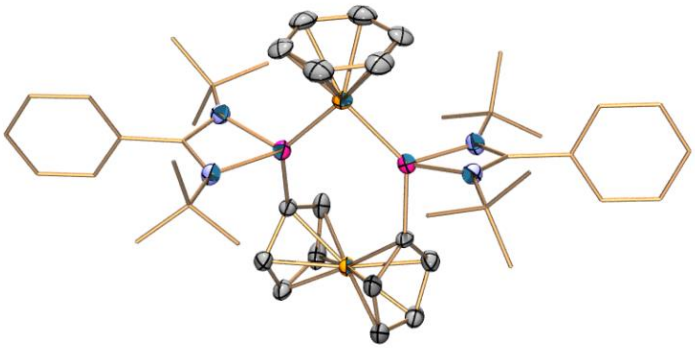
Empirical formula	$C_{40}\ H_{54}\ Fe_2\ N_4\ Si_2\ Cl_2$	
Formula weight	829.65	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.8818(3) Å	α = 78°
	b = 14.0127(4) Å	β = 78°
	c = 17.8488(5) Å	γ = 71°
Volume	3181.94(14) $Å^3$	
Z	2	
Density (calculated)	0.866 Mg/m^3	
Absorption coefficient	4.949 mm^{-1}	
F(000)	872	
Crystal size	0.38 x 0.27 x 0.18 mm^3	
Theta range for data collection	2.56 to 67.50°.	
Index ranges	-15<=h<=16, -13<=k<=16, -21<=l<=21	
Reflections collected	22070	
Independent reflections	11452 [R(int) = 0.0256]	
Completeness to theta = 67.50°	98.7%	
Max. and min. transmission	1.00000 and 32292	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11452 / 0 / 464	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0723	
R indices (all data)	R1 = 0.0313, wR2 = 0.0737	
Largest diff. peak and hole	0.231 and -0.302 $e.Å^{-3}$	

2.5.2 Crystallographic data of 2



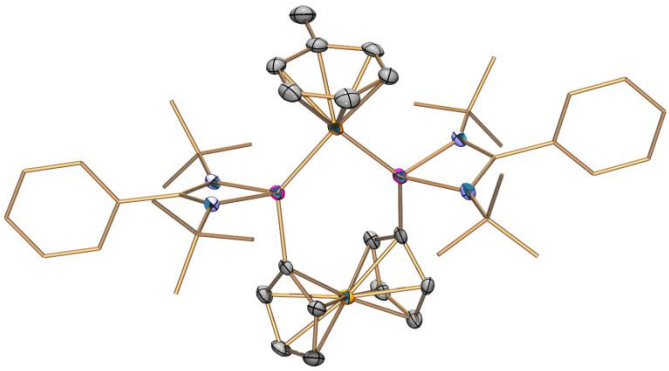
Empirical formula	$C_{40}\ H_{54}\ Fe_2\ N_4\ Si_2\ Br_2$	
Formula weight	996.68	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 25.8064(2) Å	α = 90 °
	b = 14.18970(10) Å	β = 90 °
	c = 26.0933(3) Å	γ = 90 °
Volume	9554.98(15) $Å^3$	
Z	8	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	7.569 mm^{-1}	
F(000)	4112	
Crystal size	0.29 x 0.17 x 0.11 mm^3	
Theta range for data collection	3.39 to 67.50°.	
Index ranges	-30<=h<=25, -17<=k<=11, -31<=l<=29	
Reflections collected	34624	
Independent reflections	8590 [R(int) = 0.0438]	
Completeness to theta = 67.50°	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.24995	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8590 / 0 / 517	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0864	
R indices (all data)	R1 = 0.0466, wR2 = 0.0930	
Largest diff. peak and hole	0.930 and -0.579 $e.Å^{-3}$	

2.5.3 Crystallographic data of 3



Empirical formula	$C_{46}\ H_{60}\ Fe_2\ N_4\ Si_2$	
Formula weight	993.08	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 63.1351(12) Å	α = 90 °
	b = 15.0398(3) Å	β = 90 °
	c = 10.8191(2) Å	γ = 90 °
Volume	10273.2(3) $Å^3$	
Z	8	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	5.287 mm^{-1}	
F(000)	4224	
Crystal size	0.23 x 0.18 x 0.07 mm^3	
Theta range for data collection	2.80 to 67.42°.	
Index ranges	-54<=h<=75, -18<=k<=18, -11<=l<=12	
Reflections collected	17151	
Independent reflections	4345 [R(int) = 0.0438]	
Completeness to theta = 67.42°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.31245	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4345 / 1 / 305	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R_1 = 0.0605, wR_2 = 0.1557	
R indices (all data)	R_1 = 0.0640, wR_2 = 0.1583	
Absolute structure parameter	0.393(8)	
Largest diff. peak and hole	0.584 and -0.632 e.$Å^{-3}$	

2.5.4 Crystallographic data of 4



Empirical formula	$C_{47}\ H_{62}\ Fe_2\ N_4\ Si_2$	
Formula weight	999.13	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	C12/c1	
Unit cell dimensions	a = 24.4147(3) Å	α = 90°
	b = 13.4021(2) Å	β =100°
	c = 33.7053(5) Å	γ = 90°
Volume	10846.0(3) $Å^3$	
Z	8	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	5.033 mm^{-1}	
F(000)	4288	
Crystal size	0.36 x 0.20 x 0.09 mm^3	
Theta range for data collection	2.67 to 61.49°.	
Index ranges	-27<=h<=24, -15<=k<=9, -38<=l<=36	
Reflections collected	18380	
Independent reflections	8401 [R(int) = 0.0518]	
Completeness to theta = 61.49°	99.8%	
Max. and min. transmission	0.6545 and 0.2616	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8401 / 0 / 603	
Goodness-of-fit on F^2	0.976	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.0858	
R indices (all data)	R1 = 0.0579, wR2 = 0.0925	
Largest diff. peak and hole	0.409 and -0.441 $e.Å^{-3}$	

3 Catalysis

3.1 General Information

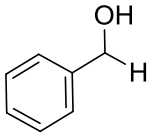
Reactions were performed in flame-dried glassware using an MBraun glovebox or conventional Schlenk techniques under a static pressure of nitrogen gas unless otherwise stated. Liquids and solutions were transferred with syringes. All ketones were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by Merck using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker AV400 and AV500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplett, q = quartet, sept = septet, m = multiplet, br = broad signal), coupling constants (Hz), and integration. Gas-liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph equipped with a FS-SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by CSChromatographie Service using the following program: N2 carrier gas, injection temperature 240 °C, detector temperature 300 °C, flow rate: 1.74 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

3.2 General Procedure for the Hydrogenation of Ketones (GP)

In a glove box with argon atmosphere, a glass vial (50 x 14 mm, Schütt) is charged with the ketone (0.10 mmol, 1.0 equiv), Fe(0)-η^6(arene) complex (2.2 mg, 2.5 mol%), and toluene (2 mL). The vial is sealed with a rubber septum and transferred to a nitrogen-purged stainless-steel BR-100 or BR-300 autoclave (including the appropriate metal heating block, Berghof) under a counterflow of nitrogen gas. A needle (0.90 x 50 mm, Braun) is pierced through the rubber septum at a constant counterflow, and the autoclave is sealed. The autoclave is then purged with nitrogen gas (3 x) and hydrogen gas (3 x). The hydrogen pressure is adjusted to 50 bar and the reaction mixture is maintained for 20 h at 50 °C. The reaction mixture is then filtered through a small plug of silica gel using CH_2Cl_2 as eluent to afford the reduced product. Wherever necessary flash column chromatography using cyclohexane/ethyl acetate mixtures as eluent is performed to obtain the desired product.

3.3 Experimental Details

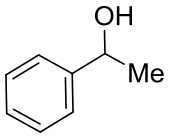
3.3.1 Phenylmethanol (c2a)



c2a
C_7H_8O
M = 108.14 g/mol

Prepared from benzaldehyde (**c1a**, 9.0 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by filtering the reaction mixture through a small pad of silica gel using CH_2Cl_2 as eluent afforded desired alcohol **c2a** (10 mg, 90%) as a clear liquid.
GLC (SE-54): t_R = 7.1 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.71 (s, 1H), 4.70 (s, 2H), 7.29–7.39 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 65.5, 127.1, 127.8, 128.7, 141.0 ppm.
The spectroscopic data are in accordance with those reported.[S1]

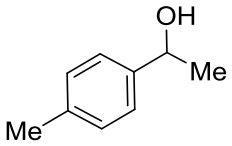
3.3.2 1-Phenylethan-1-ol (c2b)



c2b
$C_8H_{10}O$
M = 122.17 g/mol

Prepared from acetophenone (**c1b**, 12 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by filtering the reaction mixture through a small pad of silica gel using CH_2Cl_2 as eluent afforded desired alcohol **c2b** (12 mg, 92%) as a light yellow oil.
GLC (SE-54): t_R = 7.6 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 6.5 Hz, 3H), 4.79 (q, *J* = 6.7, 1H), 7.14–7.19 (m, 1H), 7.22–7.29 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 25.3, 70.6, 125.5, 127.6, 128.7, 145.9 ppm.
The spectroscopic data are in accordance with those reported.[S3]

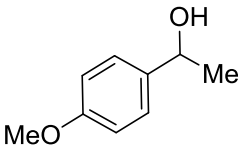
3.3.3 1-(*p*-Tolyl)ethan-1-ol (c2c)



c2c
$C_9H_{12}O$
M = 136.19 g/mol

Prepared from 4-methylacetophenone (**c1c**, 14 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by filtering the reaction mixture through a small pad of silica gel using CH_2Cl_2 as eluent afforded desired alcohol **c2c** (12 mg, 90%) as yellow oil.
GLC (SE-54): t_R = 8.3 min. **1H NMR** (400 MHz, $CDCl_3$): δ = 1.49 (d, *J* = 6.3 Hz, 3H), 1.63 (s, 1H), 2.34 (s, 3H), 4.87 (q, *J* = 6.6 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 21.2, 25.2, 70.4, 125.5, 129.3, 137.3, 143.7 ppm.
The spectroscopic data are in accordance with those reported.[S3]

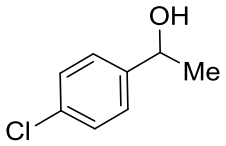
3.3.4 1-(4-methoxyphenyl)ethan-1-ol (c2d)



c2d
$C_9H_{12}O_2$
M = 152.19 g/mol

Prepared from 4-methylacetophenone (**c1d**, 15 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 3**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2d** (7 mg, 44%) as clear oil.
GLC (SE-54): t_R = 8.9 min. **1H NMR** (400 MHz, $CDCl_3$): δ = 1.47 (d, *J* = 6.6 Hz, 3H), 1.76 (s, 1H), 3.80 (s, 3H), 4.86 (q, *J* = 6.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 25.1, 55.4, 70.1, 114.0, 126.8, 138.1, 159.1 ppm.
The spectroscopic data are in accordance with those reported.[S5]

3.3.5 1-(4-Chlorophenyl)ethan-1-ol (c2e)



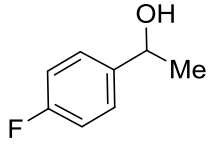
c2e
C_8H_9ClO
M = 156.61 g/mol

Prepared from 1-(4-chlorophenyl)ethan-1-one (**c1e**, 16 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2e** (14 mg, 87%) as transparent oil.

GLC (SE-54): t_R = 9.9 min. **1H NMR** (400 MHz, C_6D_6): δ = 1.24 (d, *J* = 6.3 Hz, 3H), 1.63 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 1H), 6.98–7.02 (d, 2H), 7.19–7.22 (d, 2H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = 25.4, 69.3, 127.0, 128.6, 133.0, 145.1 ppm.

The spectroscopic data are in accordance with those reported.[S3]

3.3.6 1-(4-fluorophenyl)ethan-1-ol (c2f)

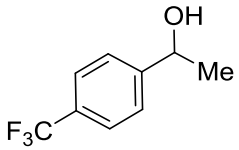


c2f
C_8H_9FO
M = 140.16 g/mol

Prepared from 1-(4-fluorophenyl)ethan-1-one (**c1f**, 14 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 1:1 as eluent afforded the desired alcohol **c2f** (9 mg 61%) as transparent oil.

GLC (SE-54): t_R = 9.4 min. **1H NMR** (400 MHz, C_6D_6): δ = 1.48 (d, *J* = 6.6 Hz, 3H), 1.84 (s, 1H), 4.89 (q, *J* = 6.3 Hz, 1H), 7.01–7.04 (m, 2H), 7.30–7.35 (m, 2H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = 25.4, 69.9, 115.4 (*J* = 21.2 Hz), 127.2 (*J* = 8.7 Hz), 141.6 (*J* = 2.8 Hz), 162.2 (*J* = 245.7 Hz) ppm. The spectroscopic data are in accordance with those reported.[S1]

3.3.7 1-(4-(Trifluoromethyl)phenyl)ethan-1-ol (c2g)



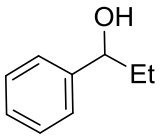
c2g
$C_9H_9F_3O$
M = 190.17 g/mol

Prepared from 1-(4-(trifluoromethyl)phenyl)ethan-1-one (**c1g**, 19 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 1:1 as eluent afforded the desired alcohol **c2g** (12 mg, 64%) as a white powder.

GLC (SE-54): t_R = 10.4 min. **1H NMR** (400 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.3 Hz, 3H), 1.86 (s, 1H), 4.97 (q, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ= 25.6, 70.0, 124.6 (*J* = 357 Hz), 125.6 (*J* = 3.9 Hz), 125.7, 130.2, 149.8 ppm.

The spectroscopic data are in accordance with those reported.[S3]

3.3.8 1-Phenylpropan-1-ol (c2h)



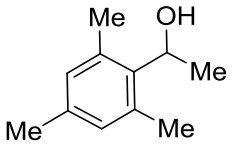
c2h
$C_9H_{12}O$
M = 136.19 g/mol

Prepared from propiophenone (**c1h**, 14 mg, 0.10 mmol, 1.0 equiv), and F e(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2h** (11 mg, 80%) as transparent oil.

GLC (SE-54): t_R = 8.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.4 Hz, 3H), 1.70–1.72 (m, 2H), 4.53 (t, *J* = 6.8 Hz, 1H), 7.18–7.23 (m, 1H), 7.26–7.30 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 10.3, 32.0, 76.2, 126.1, 127.6, 128.5, 144.7 ppm.

The spectroscopic data are in accordance with those reported.[S4

3.3.9 1-Mesitylethan-1-ol (c2i)



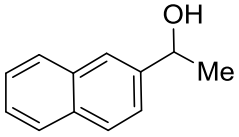
c2i
$C_{11}H_{16}O$
M = 164.25 g/mol

Prepared from 1-mesitylethan-1-one (**c1i**, 17 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 1:1 as eluent afforded the desired alcohol **c2i** (7.0 mg, 42%) as an oil.

GLC (SE-54): t_R = 11.3 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 6.7 Hz, 3H), 1.7 (s, 1H), 2.26 (s, 3H), 2.42 (s, 6H), 5.26 (q, *J* = 6.7 Hz, 1H), 6.74 (s, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 20.6, 20.8, 21.7, 67.6, 130.2, 135.8, 136.5, 137.8, ppm.

The spectroscopic data are in accordance with those reported.[S3]

3.3.10 1-(Naphthalen-2-yl)ethan-1-ol (c2j)



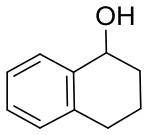
c2j
$C_{12}H_{12}O$
M = 172.23 g/mol

Prepared from 1-(naphthalen-2-yl)ethan-1-one (**c1j**, 17 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 1:1 as eluent afforded the desired alcohol **c2j** (9.0 mg, 50%) as clear oil.

GLC (SE-54): t_R = 16.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.52 (s, 3H), 1.59 (s, 1H), 5.01 (q, *J* = 6.6 Hz, 1H), 7.37–7.46 (m, 3H), 7.75–7.78 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 24.5, 67.3, 122.1, 123.3, 125.6, 125.7, 126.2, 128.1, 129.0, 130.4, 133.9, 141.5 ppm.

The spectroscopic data are in accordance with those reported.[S3]

3.3.11 1,2,3,4,4a,8a-Hexahydronaphthalen-1-ol (c2k)



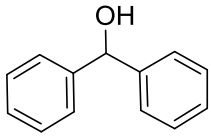
c2k
$C_{10}H_{12}O$
M = 148.21 g/mol

Prepared from 3,4-dihydronaphthalen-1(*2H*)-one (**c1k**, 15 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 7:3 as eluent afforded the desired alcohol **c2k** (4.0 mg, 28%) as light yellow oil.

GLC (SE-54): t_R = 17.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.75–1.84 (m, 1H), 1.89–2.03 (m, 3H), 2.69–2.87 (m, 2H), 4.79 (t, *J* = 4.8 Hz, 1H), 7.10–7.12 (m, 1H), 7.19–7.22 (m, 2H), 7.43–7.45 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 18.9, 29.4, 32.4, 68.3, 126.3, 127.7, 128.8, 129.2, 137.3, 139.0 ppm.

The spectroscopic data are in accordance with those reported.[S5]

3.3.12 Diphenylmethanol (c2l)



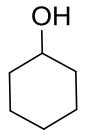
c2l
$C_{13}H_{12}O$
M = 184.24 g/mol

Prepared from benzophenone (**c1l**, 18 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 1:1 as eluent afforded the desired alcohol **c2l** (11 mg, 58%) as white solid.

GLC (SE-54): t_R = 16.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.11 (s, 1H), 5.78 (s, 1H), 7.17–7.21 (m, 2H), 7.24–7.33 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 76.4, 126.7, 127.7, 128.7, 143.9 ppm.

The spectroscopic data are in accordance with those reported.[S3

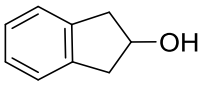
3.3.13 Cyclohexanol (c2m)



c2m
$C_6H_{12}O$
M = 100.16 g/mol

Prepared from cyclohexanone (**c1m**, 9.8 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to GP 1. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2m** (8.5 mg, 83%).
GLC (SE-54): t_R = 11.1 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.15–1.31 (m, 5H), 1.47 (s, 1H), 1.53–1.56 (m, 1H), 1.72–1.75 (s, 2H), 1.87–1.90 (s, 2H), 3.61 (q, *J* = 8.2 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 24.3, 25.6, 35.7, 70.5 ppm.
The spectroscopic data are in accordance with those reported.[S4]

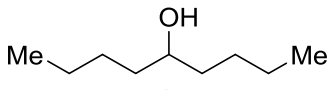
3.3.14 2,3-dihydro-1H-inden-2-ol (c2n)



c2n
$C_9H_{10}O$
M = 134.18 g/mol

Prepared from 1,3-dihydro-2*H*-inden-2-one (**c1n**, 14 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2n** (8.0 mg, 51%)
GLC (SE-54): t_R = 11.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.86 (s, 1H), 2.83 (dd, *J* = 3.1, 3.2 Hz, 2H), 3.14 (dd, *J* = 5.8, 5.7 Hz, 2H), 4.60–4.64 (m, 1H), 7.08–7.12 (m, 2H), 7.15–7.19 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 42.8, 73.3, 125.1, 126.8, 140.9 ppm.
The spectroscopic data are in accordance with those reported.[S6]

3.3.15 Nonan-5-ol (c2o)



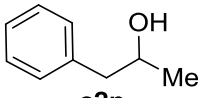
c2o
$C_9H_{20}O$
M = 232.41 g/mol

Prepared from nonan-5-one (**c1o**, 23 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to GP 1. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 7:3 as eluent afforded the desired alcohol **c2o** (13 mg, 56%).

GLC (SE-54): t_R = 11.3 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.2 Hz, 6H), 1.27–1.48 (m, 12H), 3.58 (s, 1H), 3.71 (q, *J* = 5.4 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 14.2, 22.9, 28.0, 37.3, 72.1 ppm.

The spectroscopic data are in accordance with those reported.[S4]

3.3.16 1-Phenylpropan-2-ol (c2p)



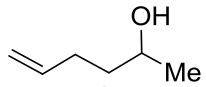
c2p
$C_9H_{12}O$
M = 136.19 g/mol

Prepared from 1-phenylpropan-2-one (**c1p**, 14 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by filtering the reaction mixture through a small pad of silica gel using CH_2Cl_2 as eluent afforded desired alcohol **c2p** (13 mg, 90%) as transparent oil.

GLC (SE-54): t_R = 8.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.18 (s, 3H), 1.46 (s, 1H), 2.59–2.75 (m, 2H), 3.92–3.99 (m, 1H), 7.13–7.27 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 22.9, 45.9, 69.0, 126.6, 128.7, 129.5, 138.6 ppm.

The spectroscopic data are in accordance with those reported.[S5]

3.3.17 Hex-5-en-2-ol (c2q)



c2q

$C_6H_{12}O$

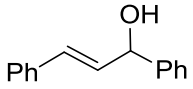
M = 100.16 g/mol

Prepared from hex-5-en-2-one (**c1q**, 10 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2q** (8.0 mg, 79%) as transparent oil.

GLC (SE-54): t_R = 9.1 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.0 Hz, 3H), 1.50–1.59 (m, 2H), 2.12–2.20 (m, 2H), 3.68–3.87 (m, 2H), 4.96–5.10 (m, 2H), 5.79–5.89 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 23.6, 30.3, 38.4, 67.8, 114.9, 138.6 ppm.

The spectroscopic data are in accordance with those reported.[S6]

3.3.18 1,3-Diphenylprop-2-en-1-ol (c2r)



c2r

$C_{15}H_{14}O$

M = 210.28 g/mol

Prepared from chalcone (**c1r**, 21 mg, 0.10 mmol, 1.0 equiv), and Fe(0)-η^6(arene) complex (2.2 mg, 2.5 µmol, 2.5 mol%) according to **GP 1**. The reaction mixture was stirred at a H_2 pressure of 50 bar at 50 °C. Purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate = 9:1 as eluent afforded the desired alcohol **c2r** (7.0 mg, 30%) as clear oil.

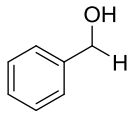
GLC (SE-54): t_R = 21.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.44 (d, *J* = 6.7 Hz, 1H), 6.44 (dd, *J* = 6.3, 6.4 Hz, 1H), 6.74 (d, *J* = 15.3 Hz, 1H), 7.29–7.50 (m, 10H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 79.3, 126.7, 127.1, 127.7, 128.6, 130.4, 130.5, 131.4, 131.6, 136.7, 141.3 ppm.

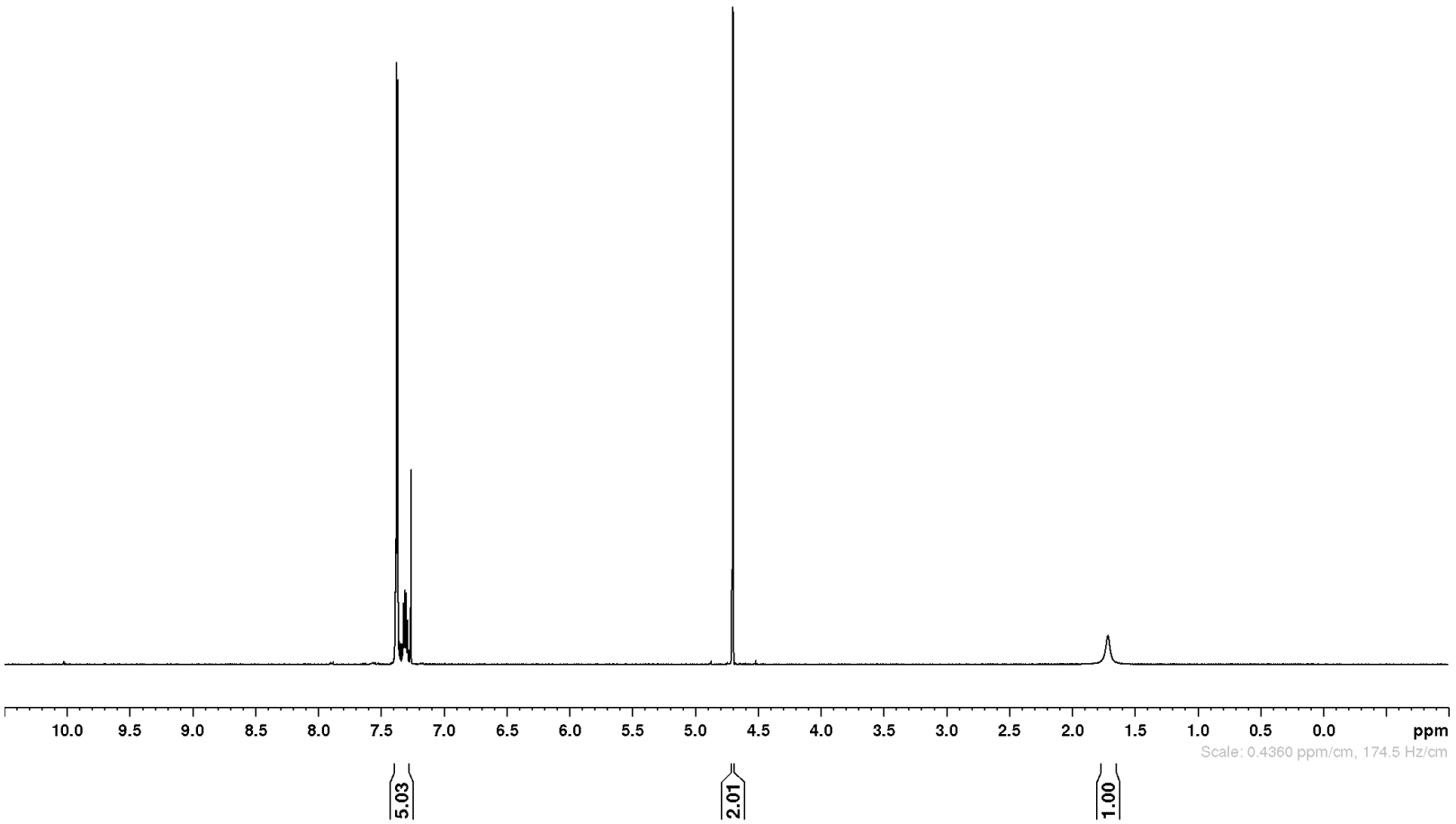
The spectroscopic data are in accordance with those report.[S6]

3.4 NMR Spectra

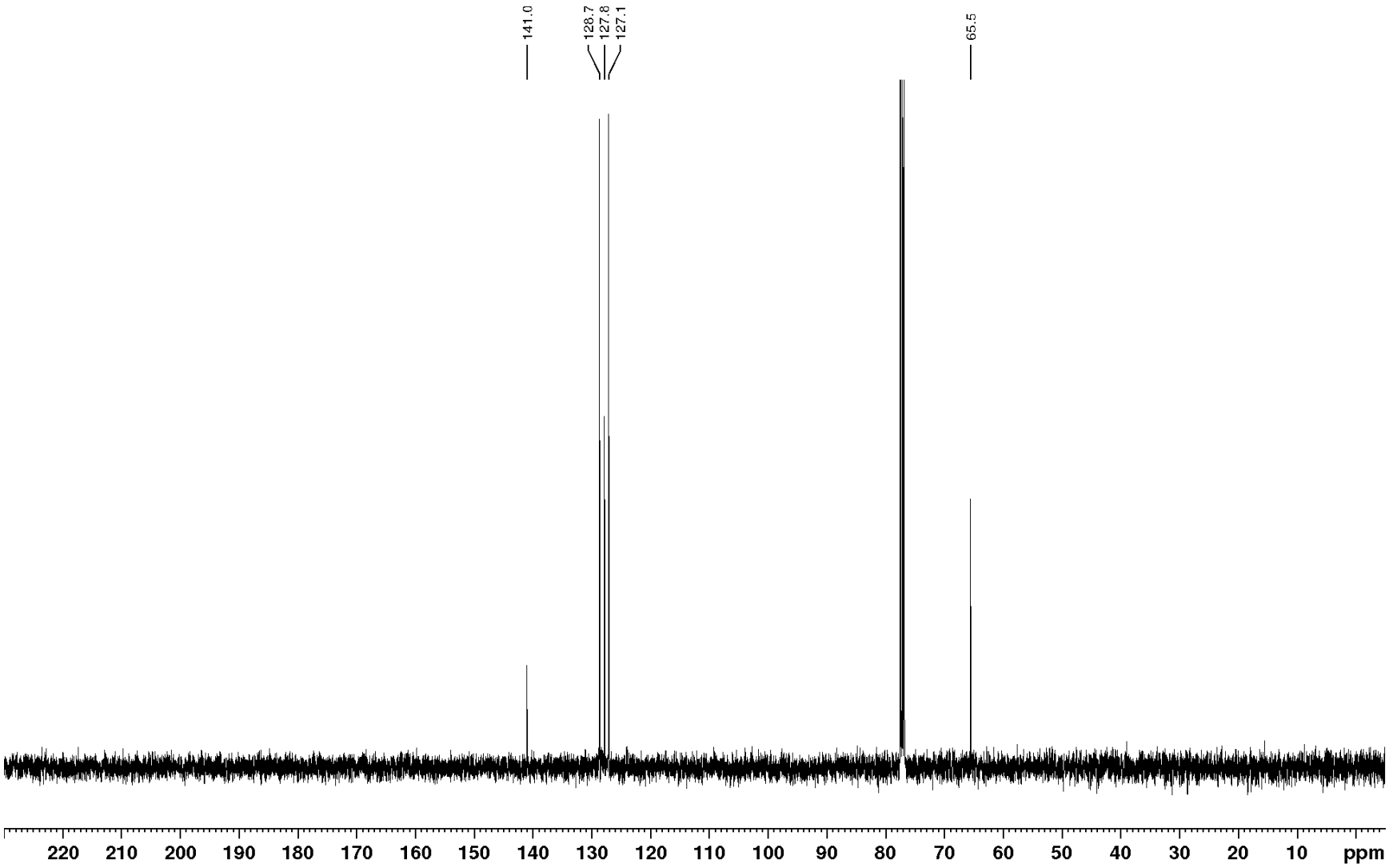
Phenylmethanol (c2a)

^{1}H NMR (400 MHz, $CDCl_3$):



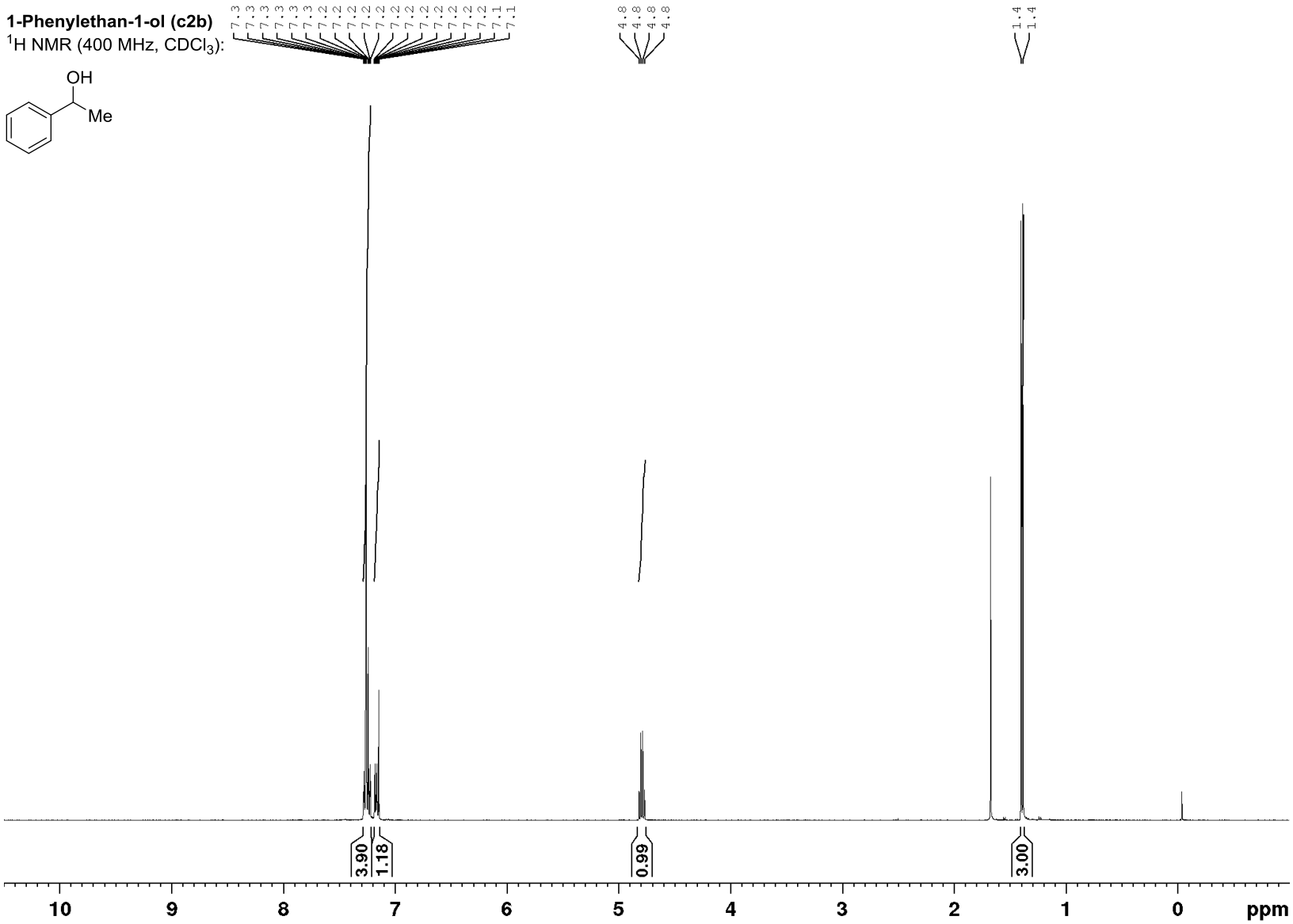


^{13}C NMR (101 MHz, $CDCl_3$):

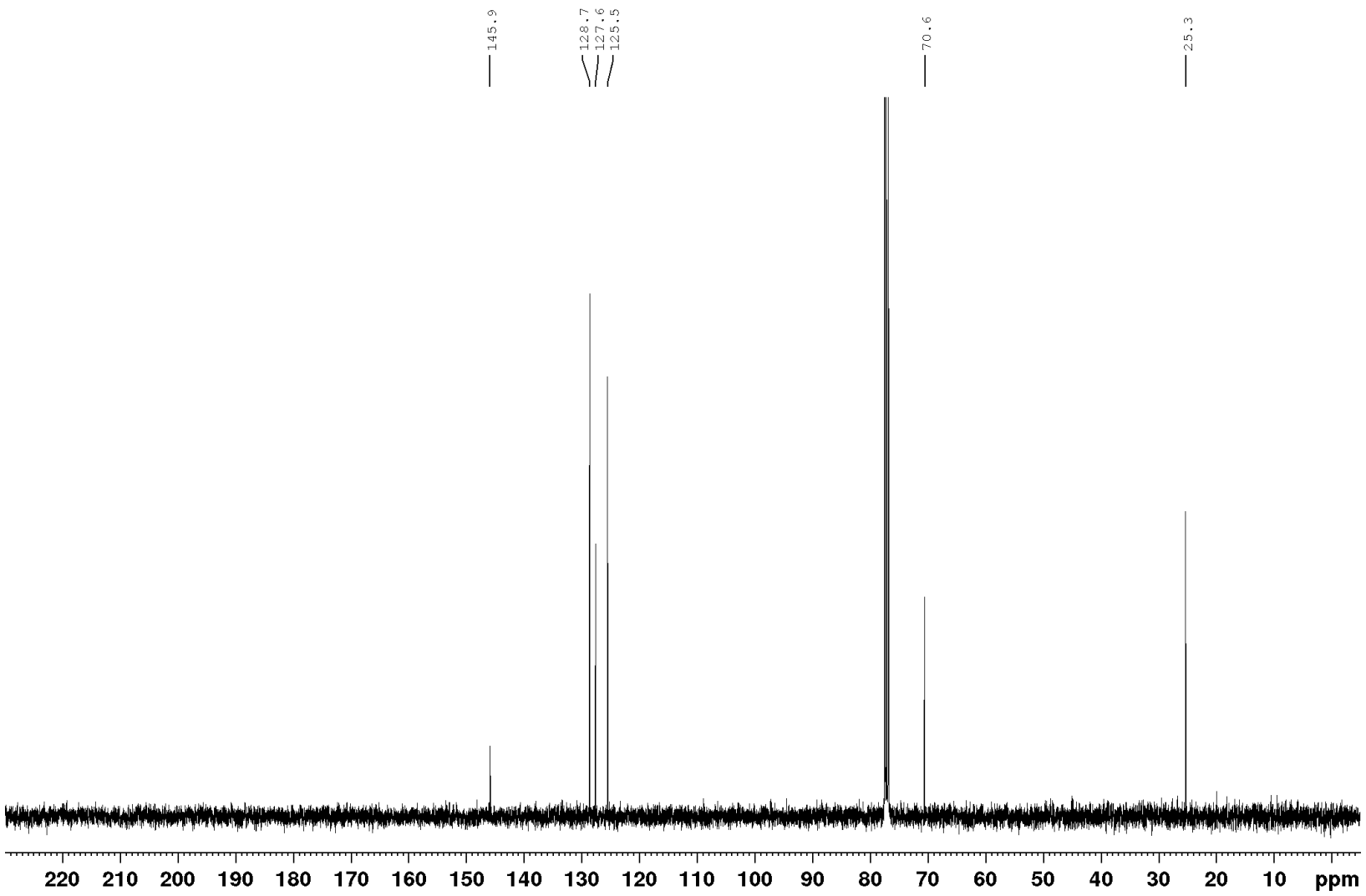


1-Phenylethan-1-ol (c2b)

^{1}H NMR (400 MHz, $CDCl_3$):

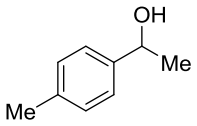


^{13}C NMR (101 MHz, $CDCl_3$):

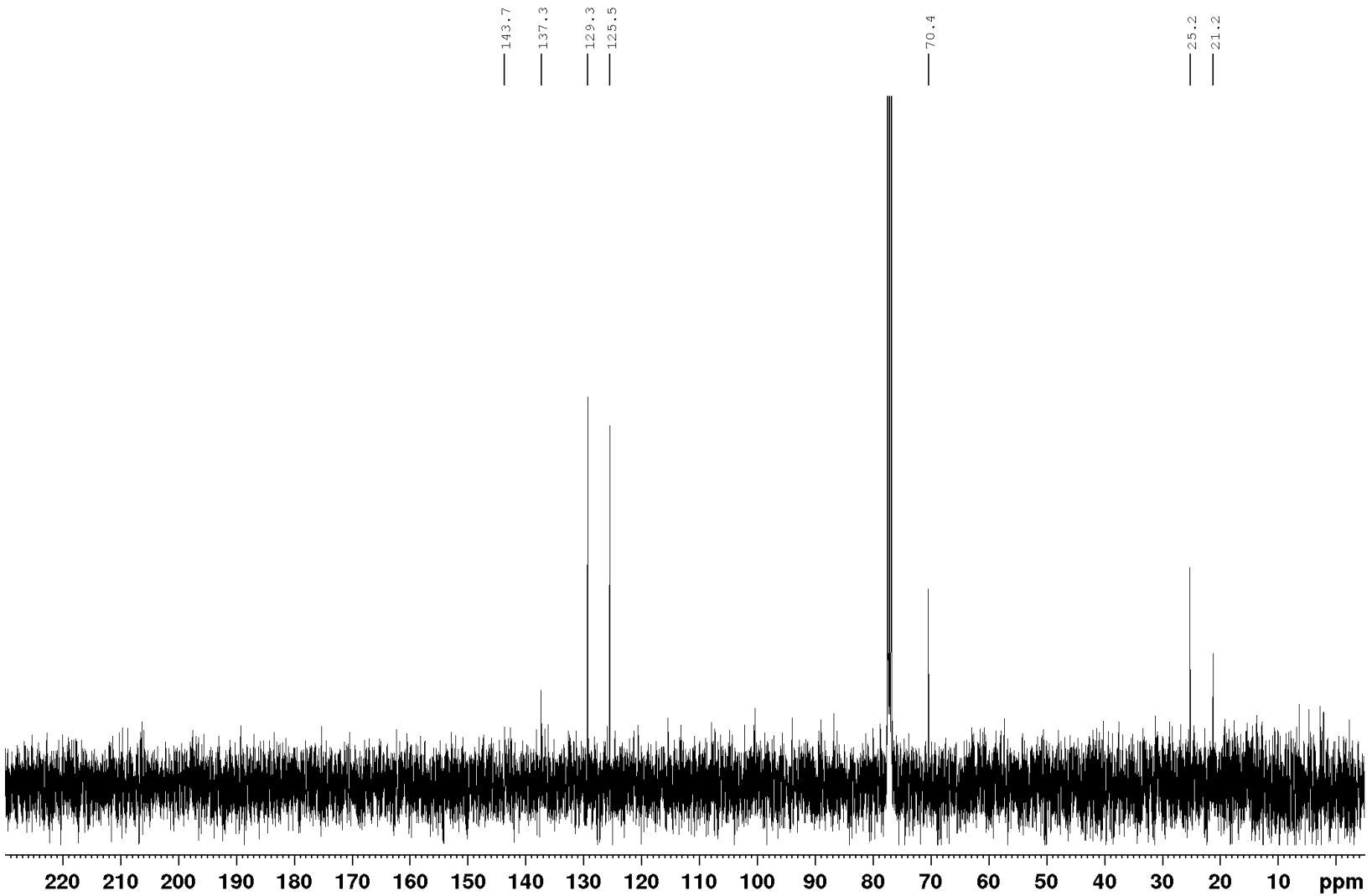


1-(*p*-Tolyl)ethan-1-ol (c2c)

^{1}H NMR (400 MHz, $CDCl_3$):

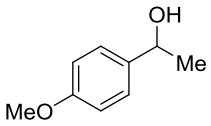


^{13}C NMR (101 MHz, $CDCl_3$):

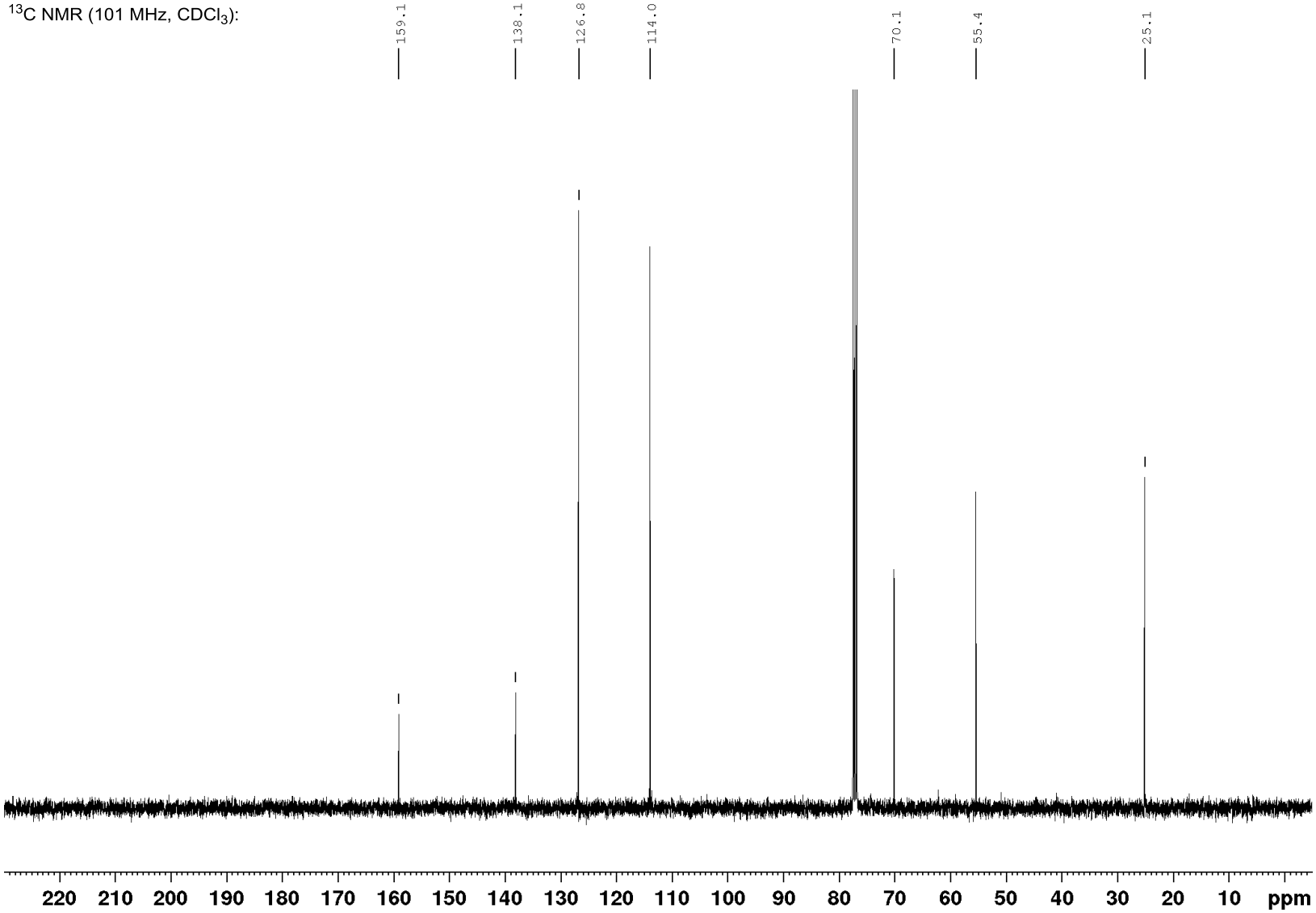


1-(4-Methoxyphenyl)ethan-1-ol (c2d)

^{1}H NMR (400 MHz, $CDCl_3$):

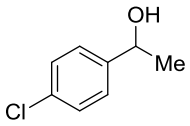


^{13}C NMR (101 MHz, $CDCl_3$):

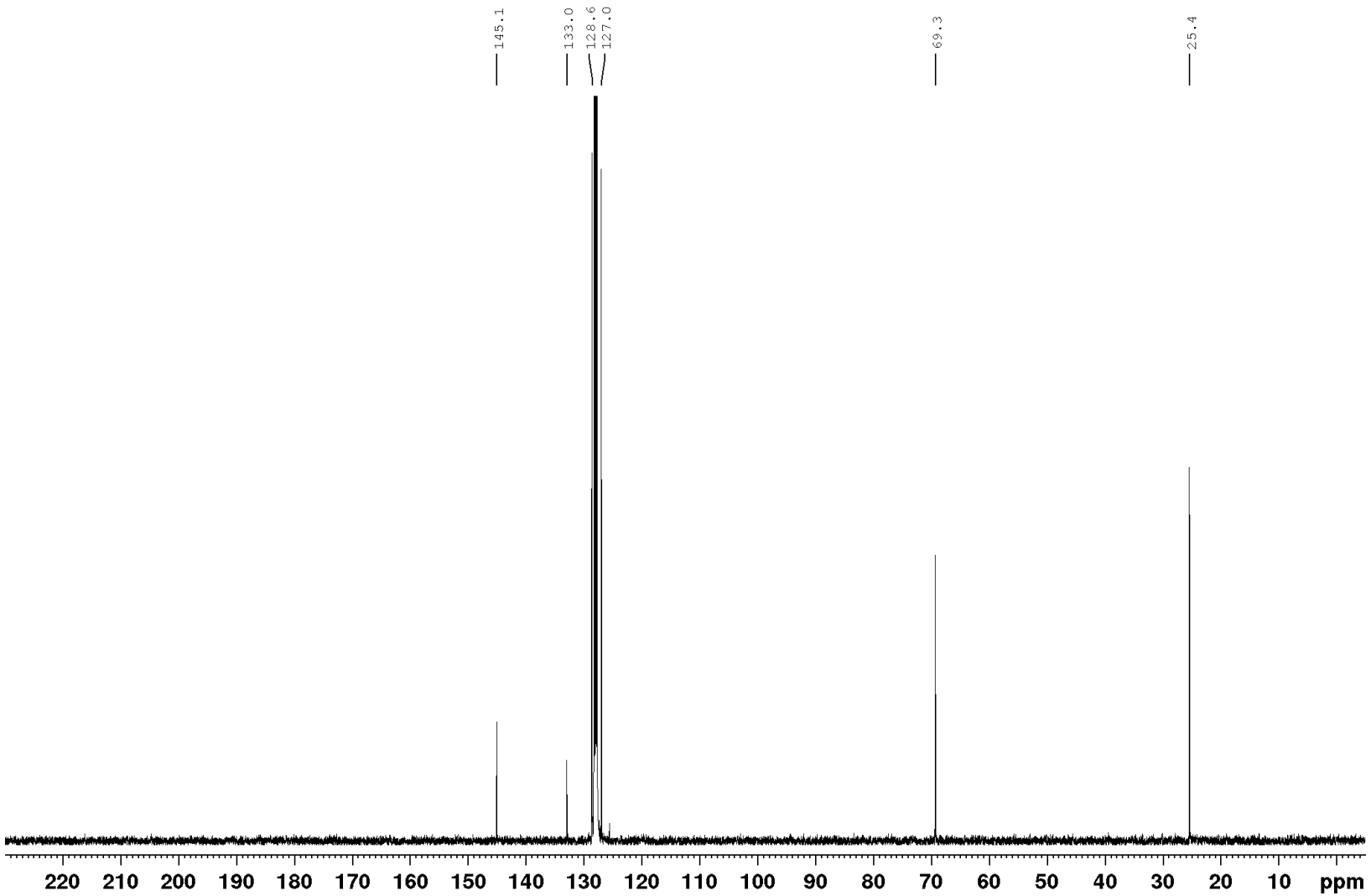


1-(4-chlorophenyl)ethan-1-ol (c2e)

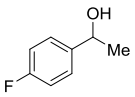
^{1}H NMR (400 MHz, $CDCl_3$):



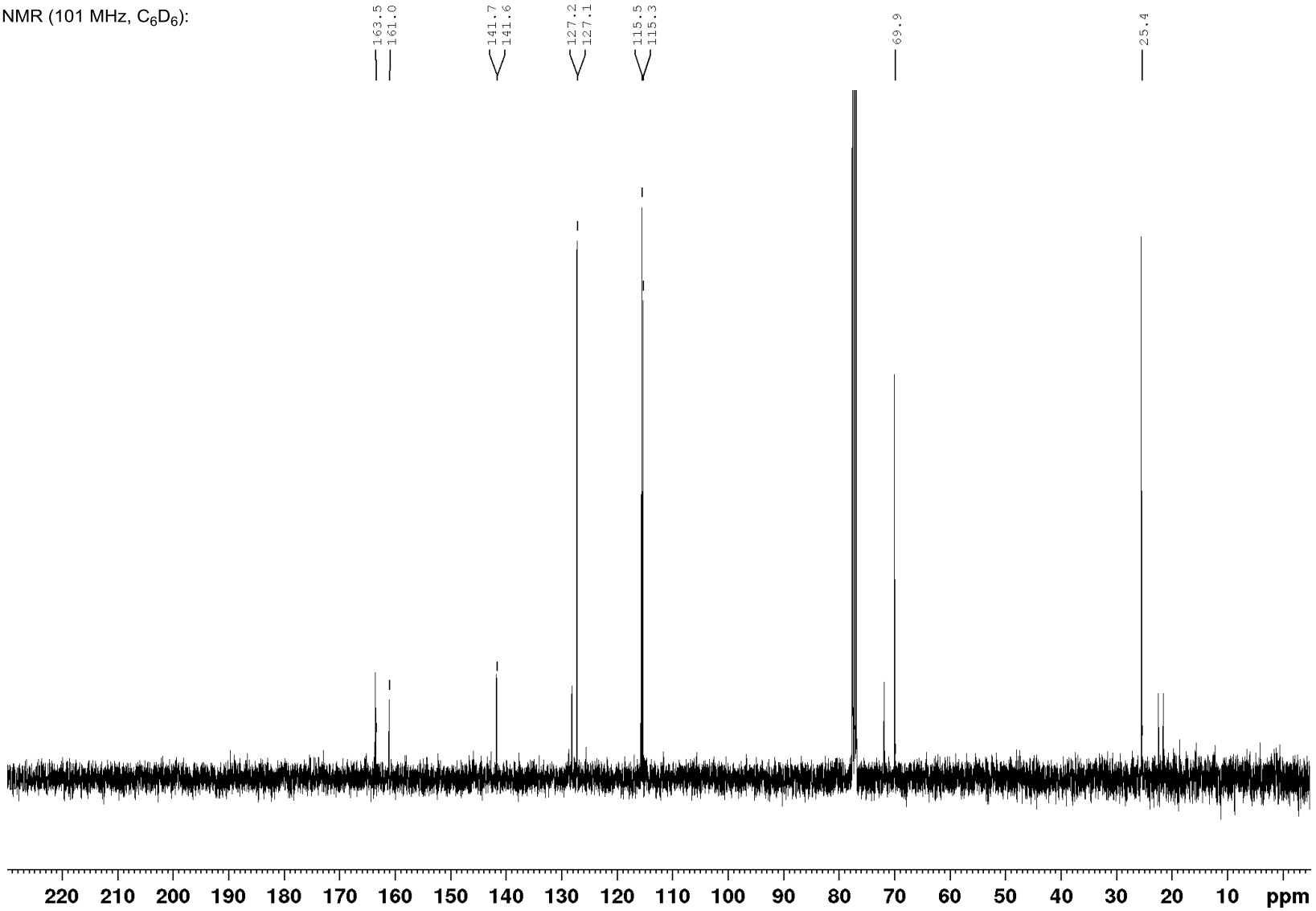
^{13}C NMR (101 MHz, C_6D_6):



1-(4-fluorophenyl)ethan-1-ol (c2f)
^{1}H NMR (400 MHz, $CDCl_3$):

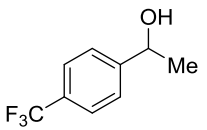


^{13}C NMR (101 MHz, C_6D_6):

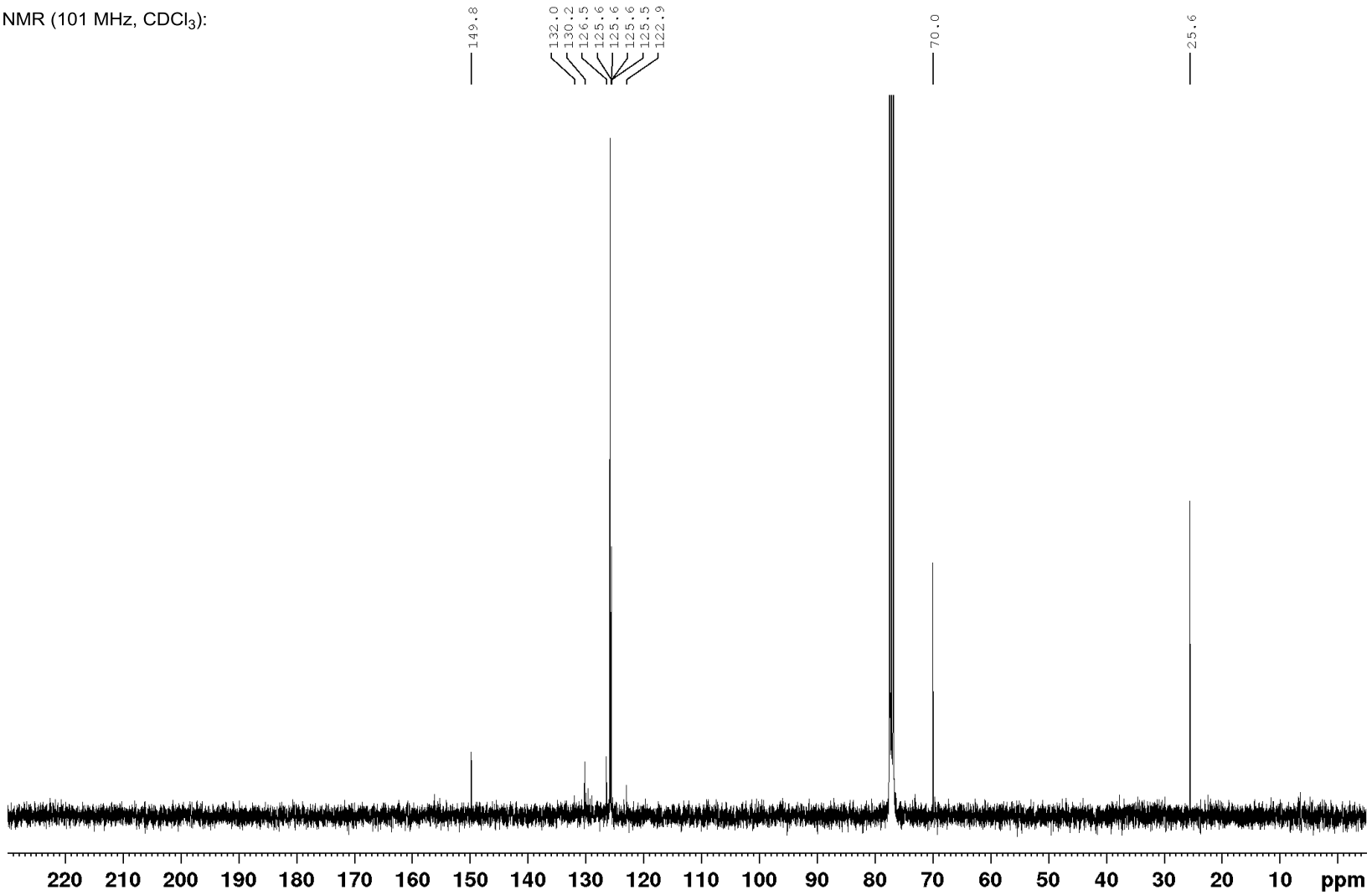


1-(4-(Trifluoromethyl)phenyl)ethan-1-ol (c2g)

^{1}H NMR (400 MHz, $CDCl_3$):

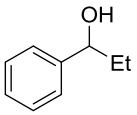


^{13}C NMR (101 MHz, $CDCl_3$):

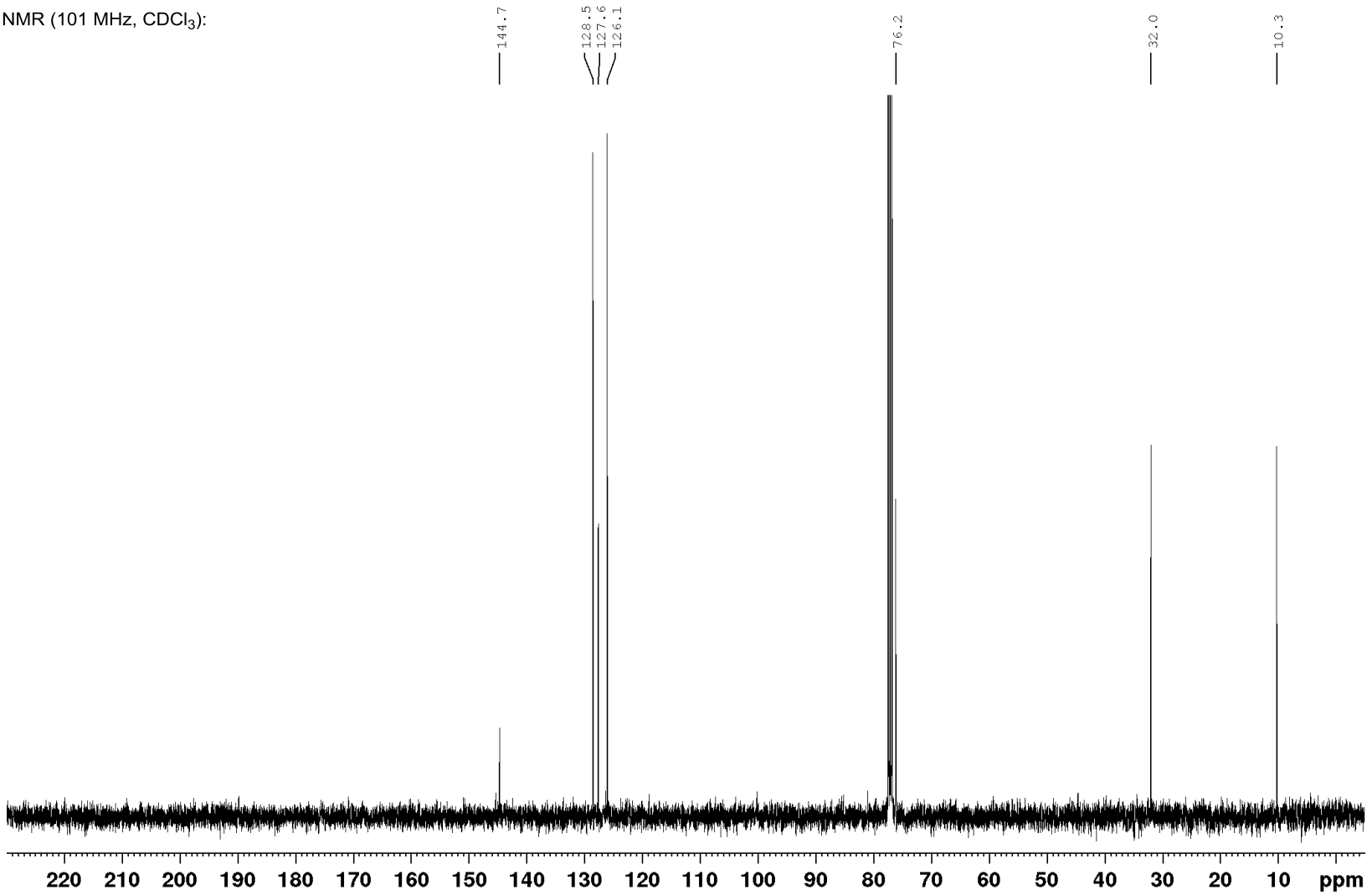


1-Phenylpropan-1-ol (c2h)

^{1}H NMR (400 MHz, $CDCl_3$):

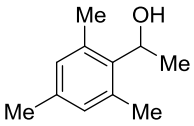


^{13}C NMR (101 MHz, $CDCl_3$):

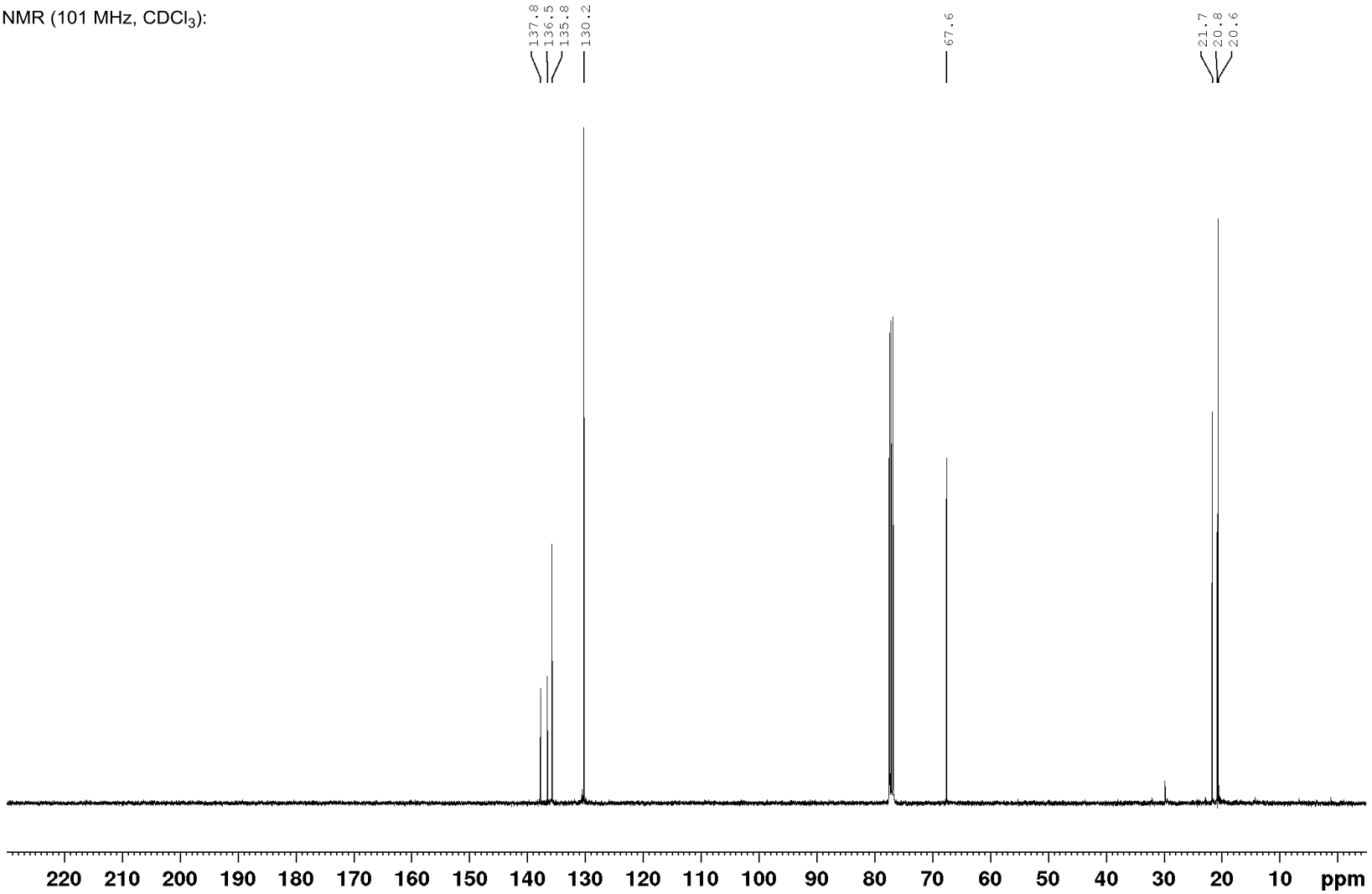


1-Mesitylethan-1-ol (c2i)

^{1}H NMR (400 MHz, $CDCl_3$):

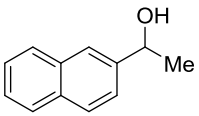


^{13}C NMR (101 MHz, $CDCl_3$):

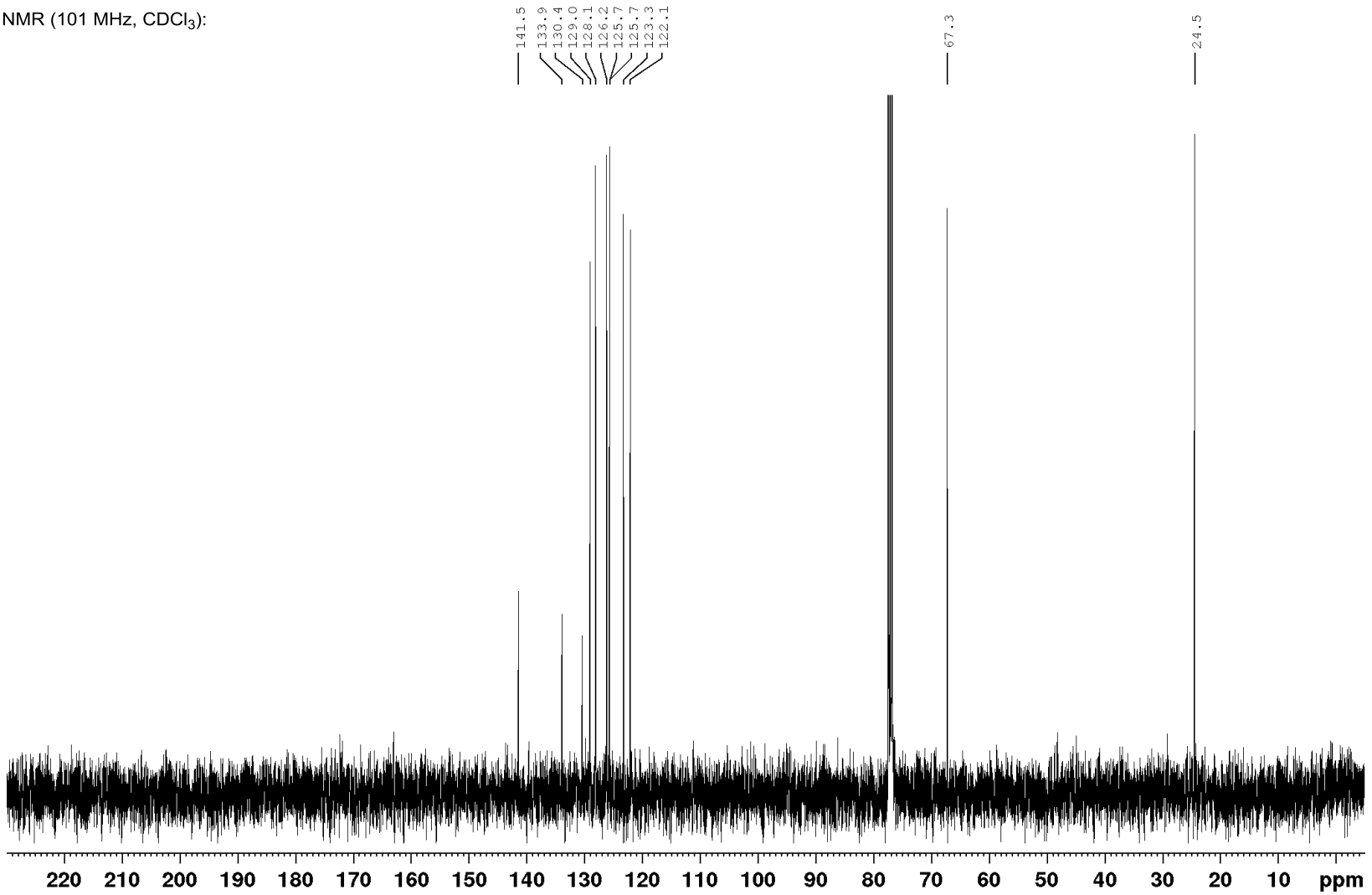


1-(Naphthalen-2-yl)ethan-1-ol (c2j)

^{1}H NMR (400 MHz, $CDCl_3$):

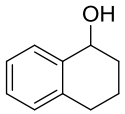


^{13}C NMR (101 MHz, $CDCl_3$):

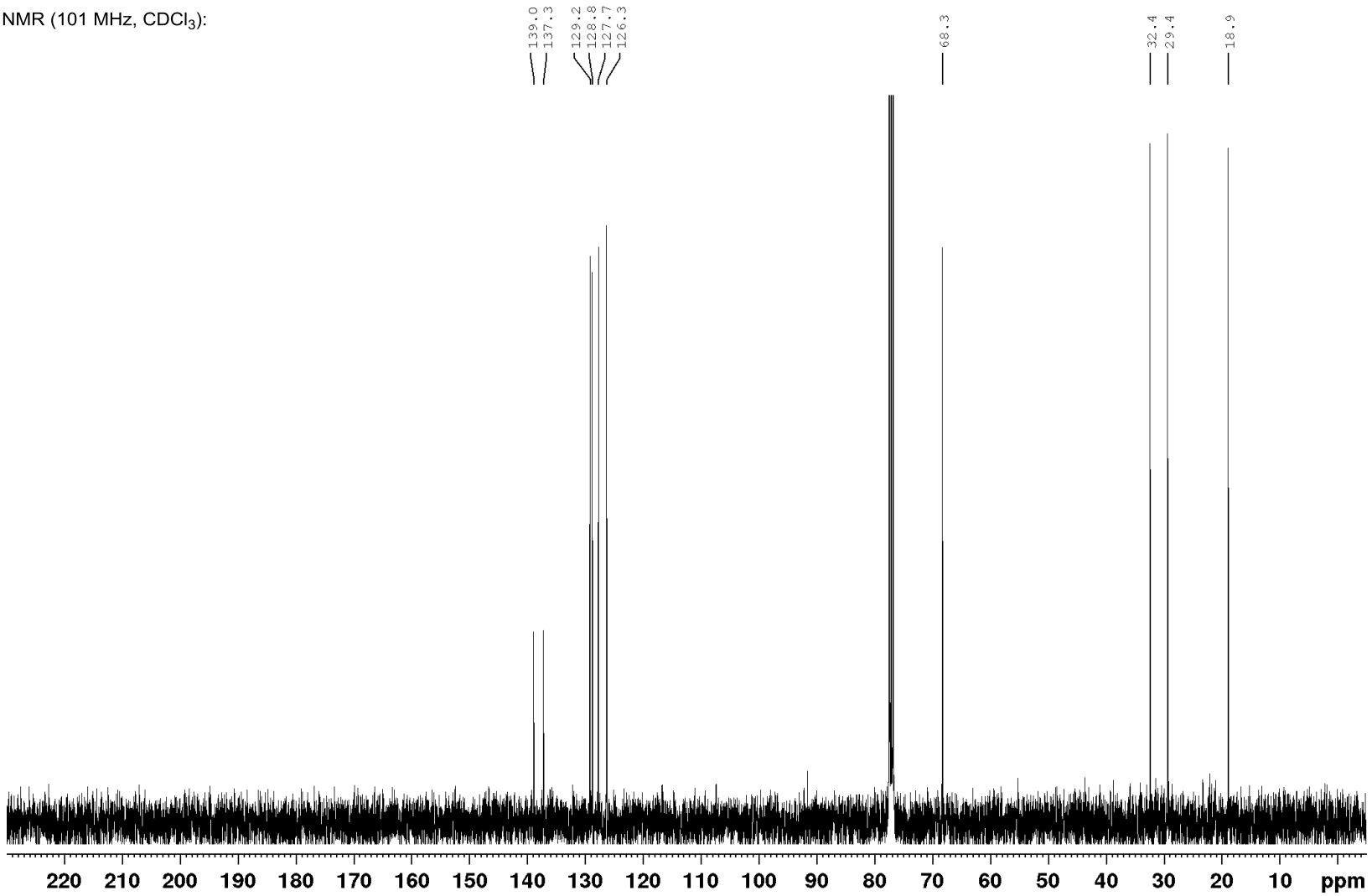


1,2,3,4-tetrahydronaphthalen-1-ol (c2k)

^{1}H NMR (400 MHz, $CDCl_3$):

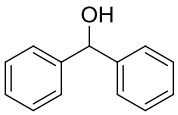


^{13}C NMR (101 MHz, $CDCl_3$):

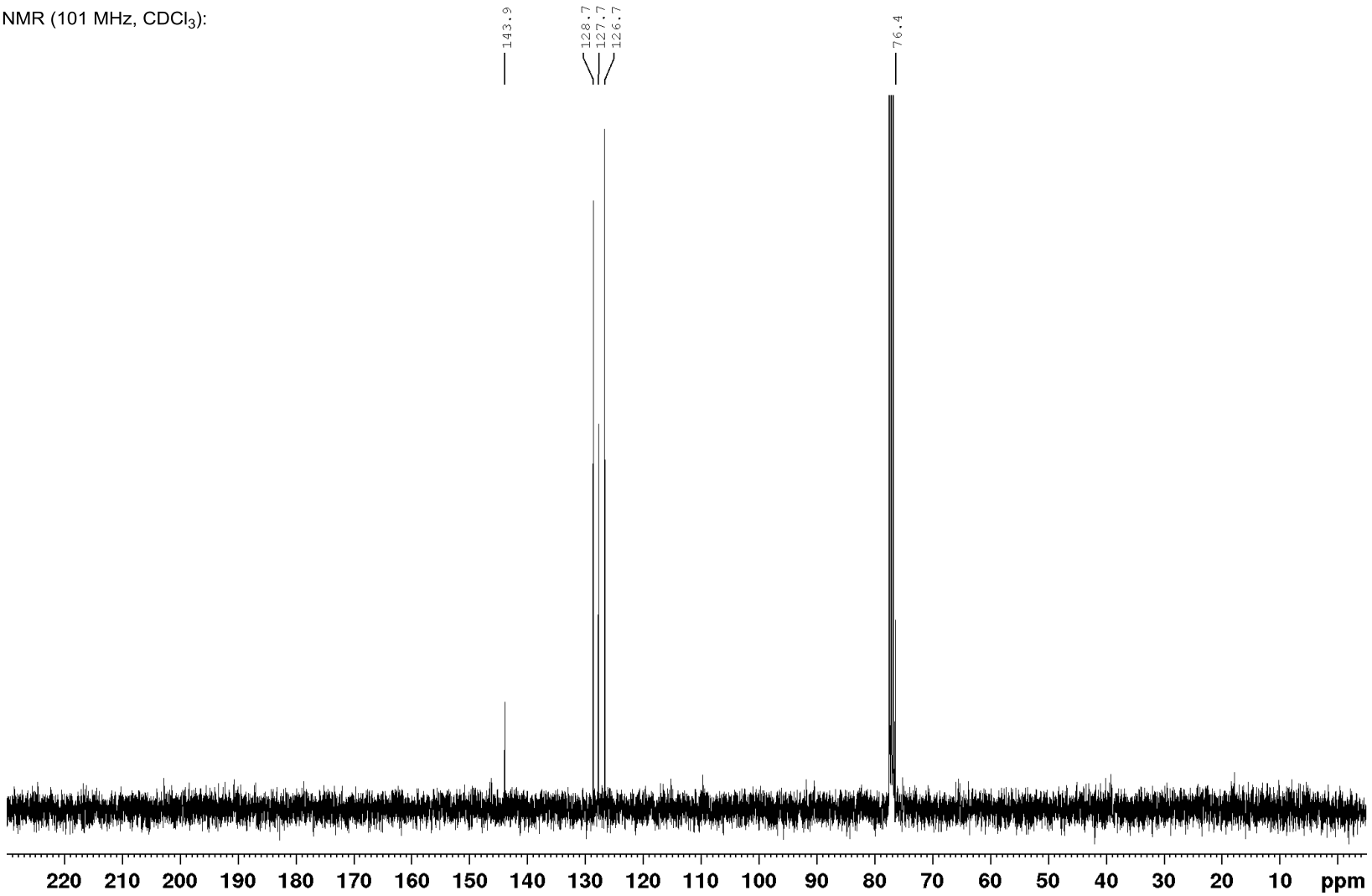


Diphenylmethanol (c2l)

^{1}H NMR (400 MHz, $CDCl_3$):

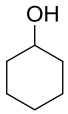


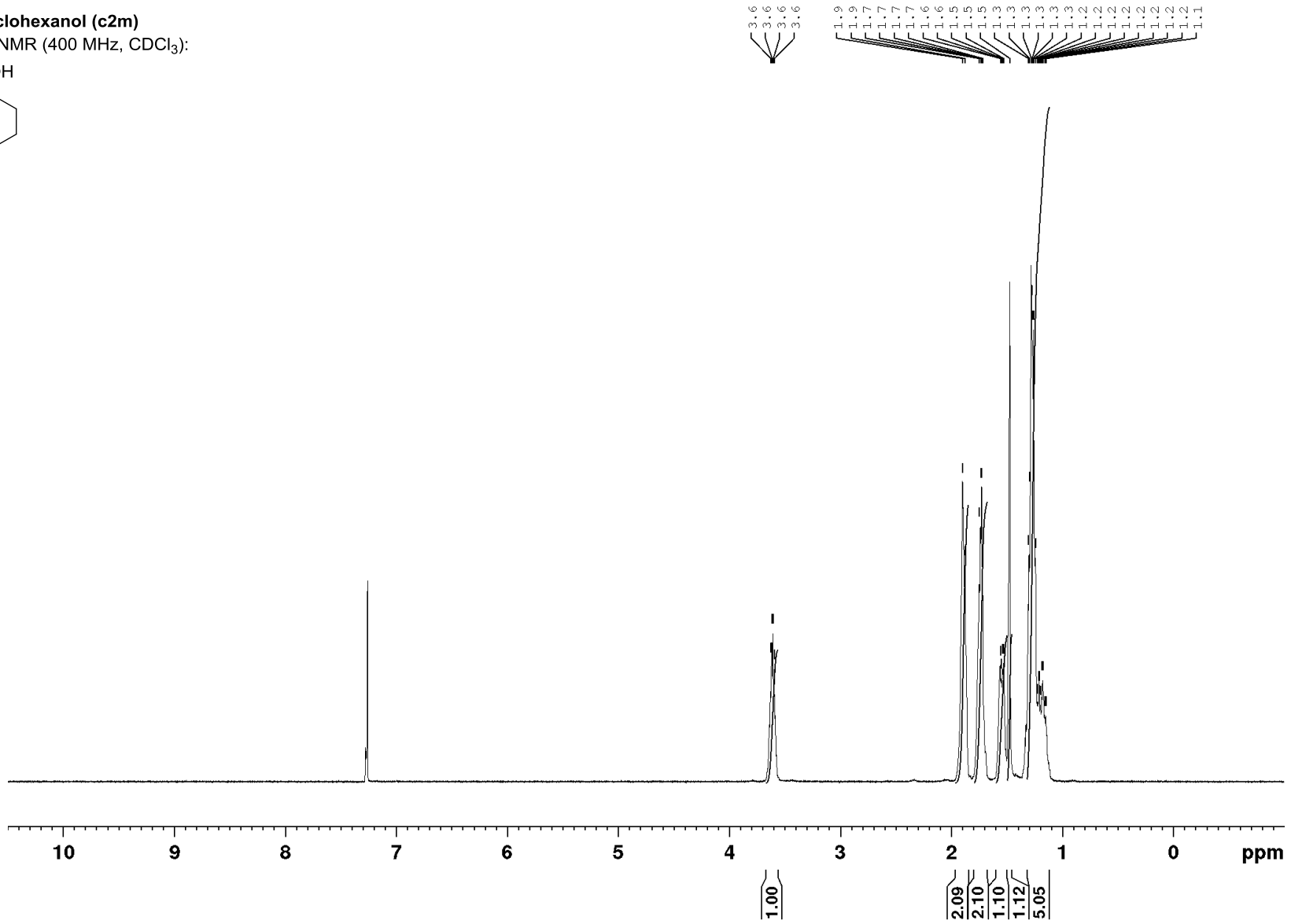
^{13}C NMR (101 MHz, $CDCl_3$):



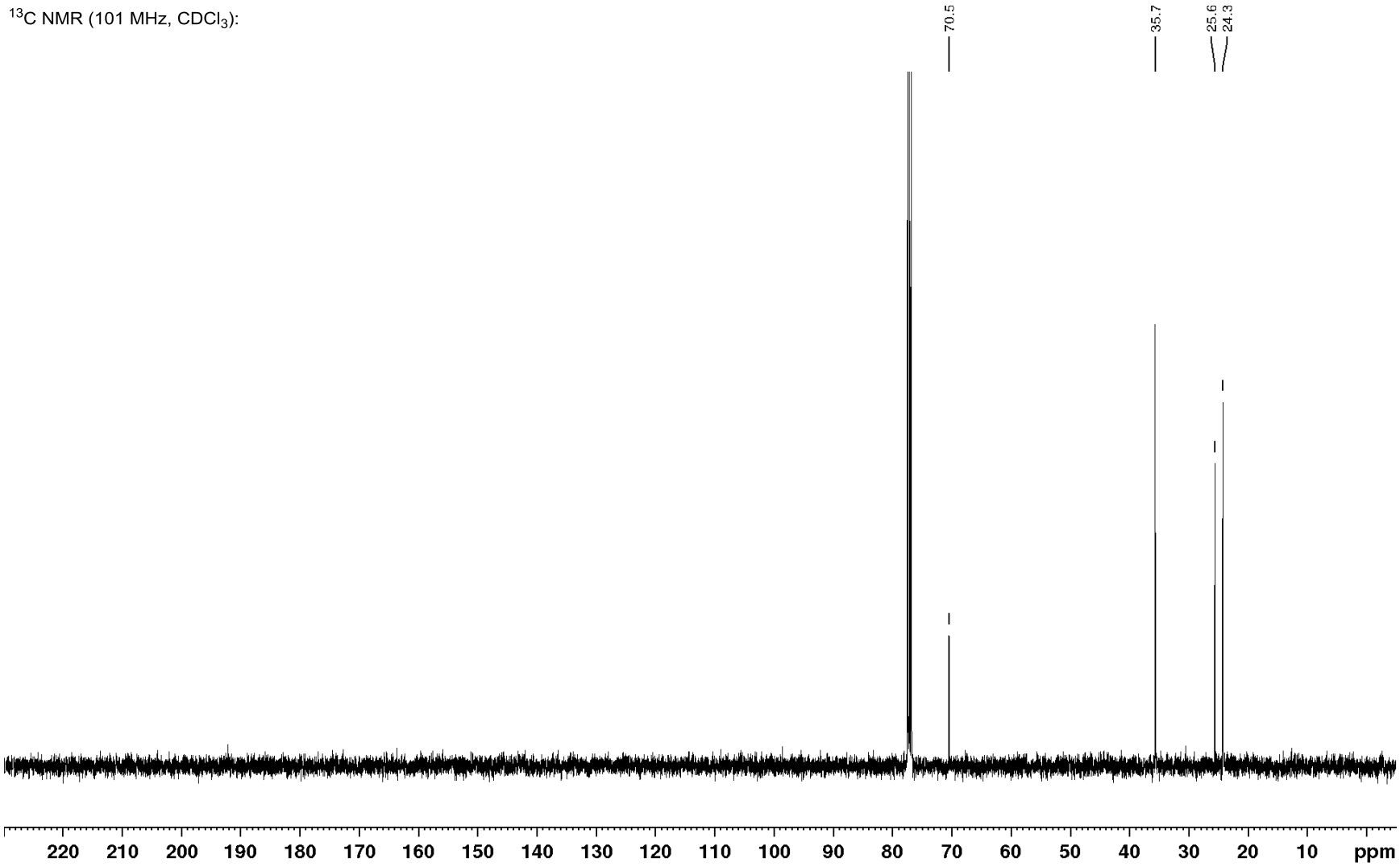
Cyclohexanol (c2m)

^{1}H NMR (400 MHz, $CDCl_3$):



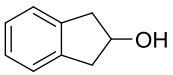


^{13}C NMR (101 MHz, $CDCl_3$):

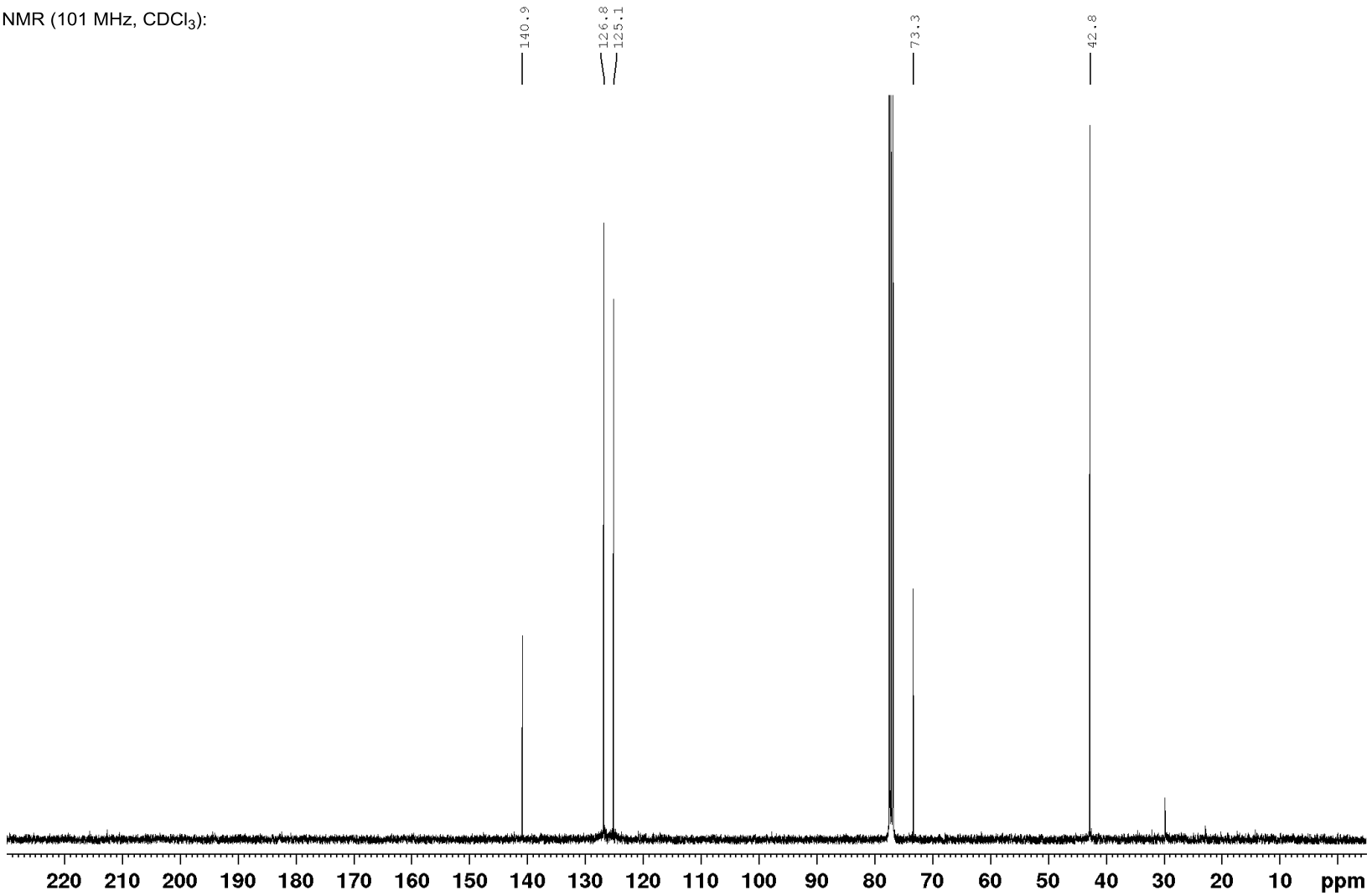


2,3-dihydro-1*H*-inden-2-ol (c2n)

^{1}H NMR (400 MHz, $CDCl_3$):

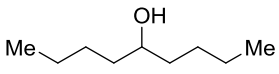


^{13}C NMR (101 MHz, $CDCl_3$):

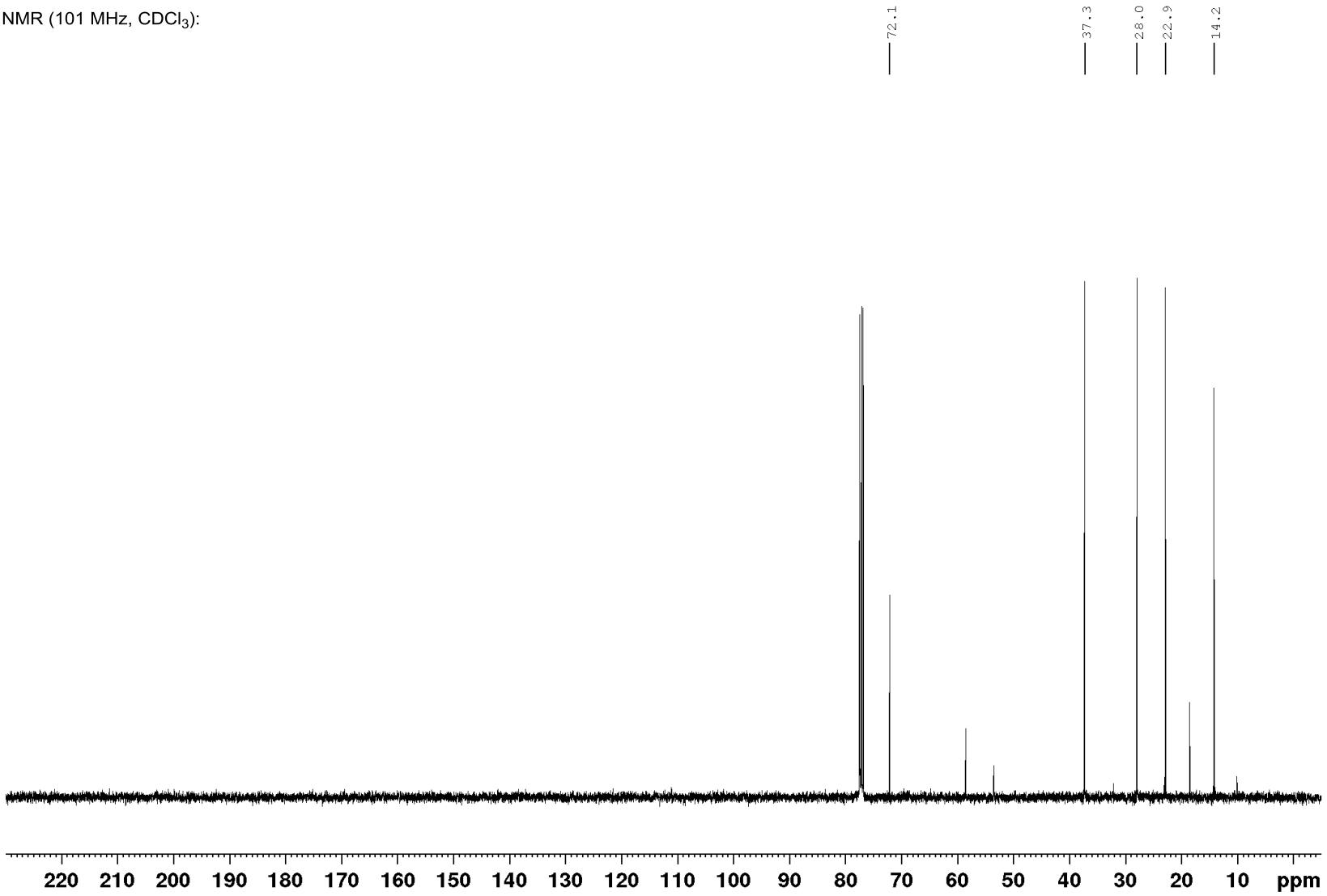


Nonan-5-ol (c2o)

^{1}H NMR (400 MHz, $CDCl_3$):

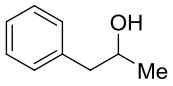


^{13}C NMR (101 MHz, $CDCl_3$):

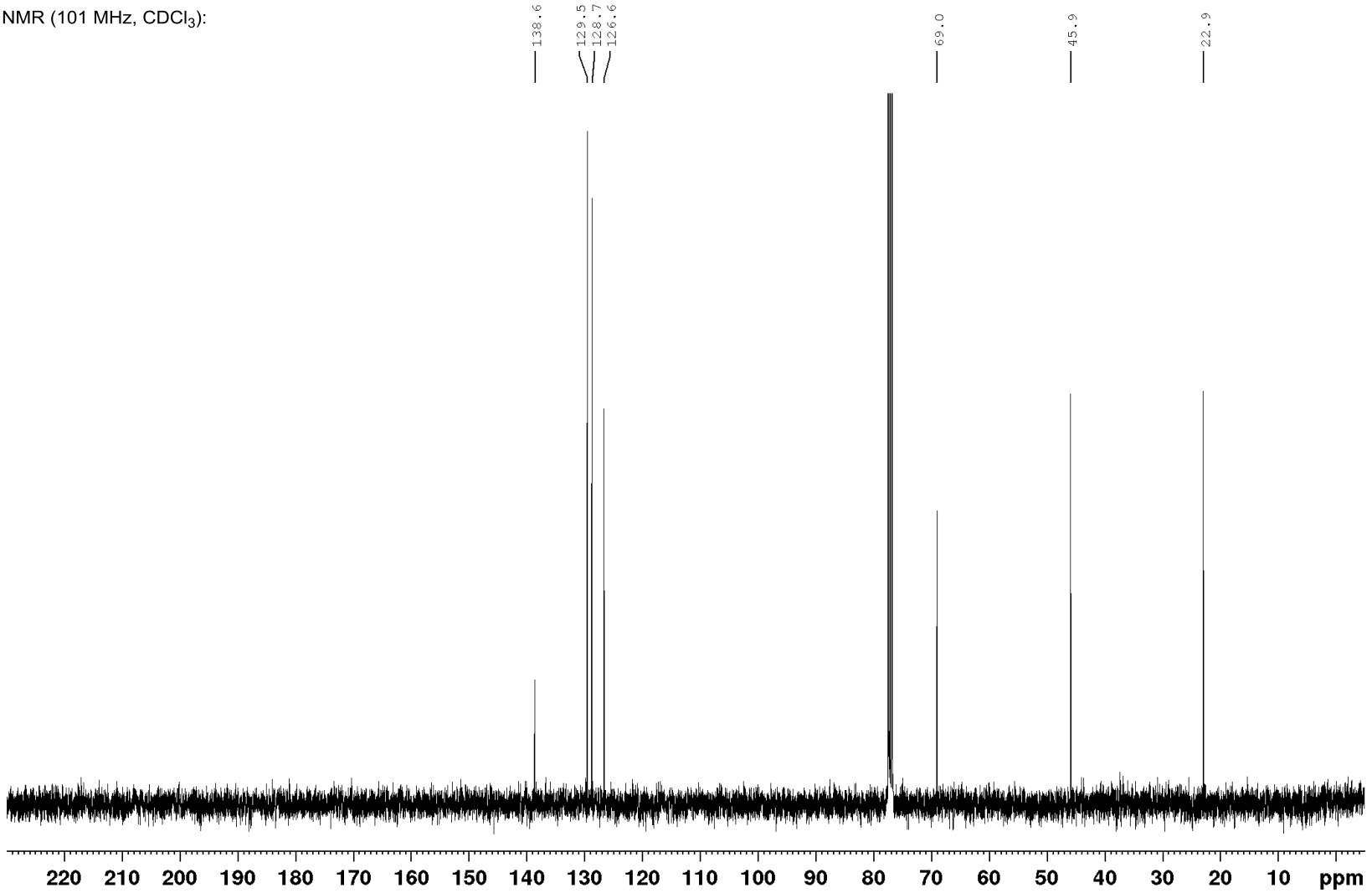


1-Phenylpropan-2-ol (c2p)

^{1}H NMR (400 MHz, $CDCl_3$):

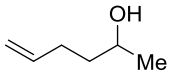


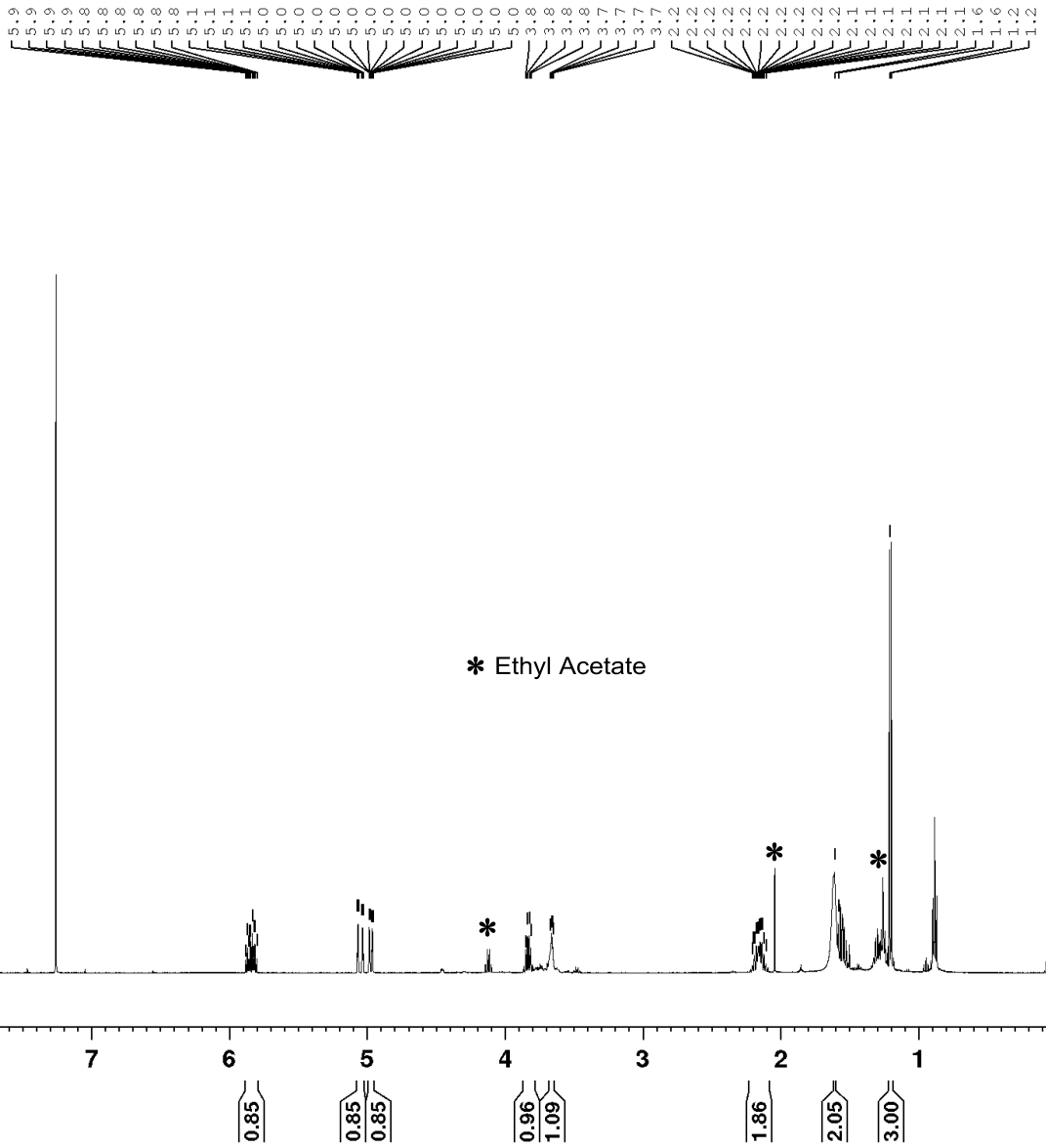
^{13}C NMR (101 MHz, $CDCl_3$):



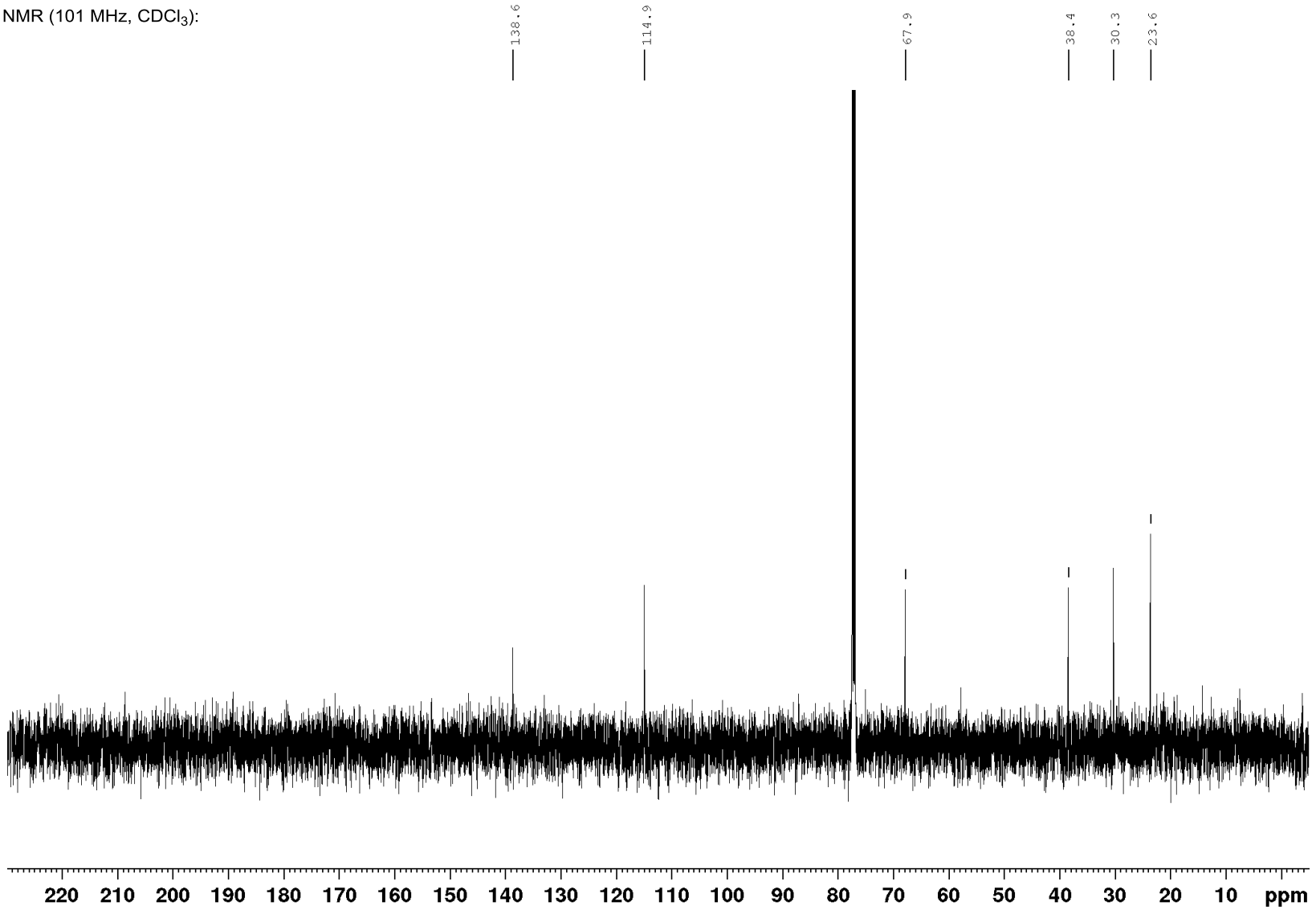
Hex-5-en-2-ol (c2q)

^{1}H NMR (400 MHz, $CDCl_3$):



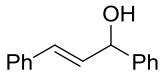


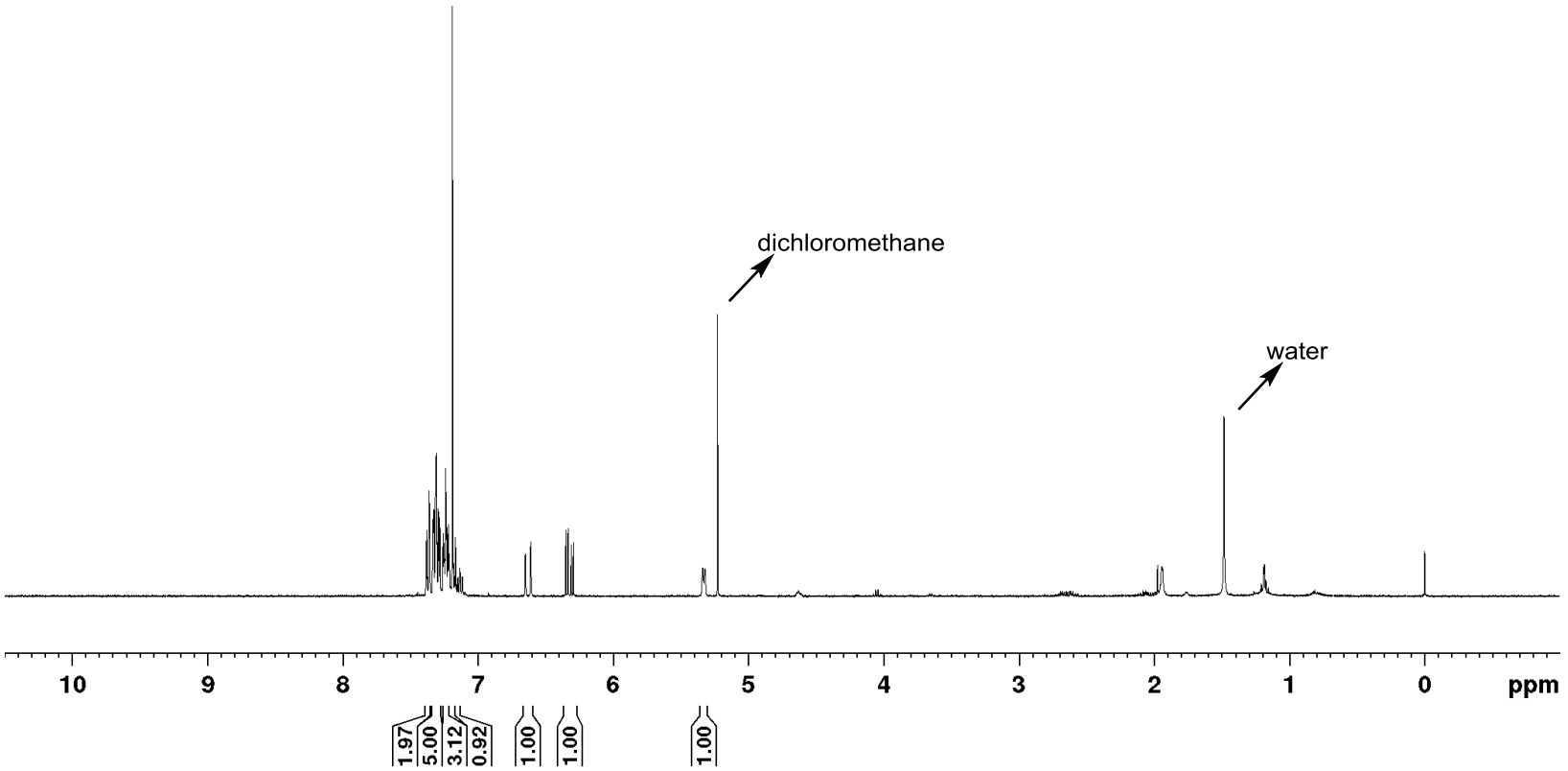
^{13}C NMR (101 MHz, $CDCl_3$):



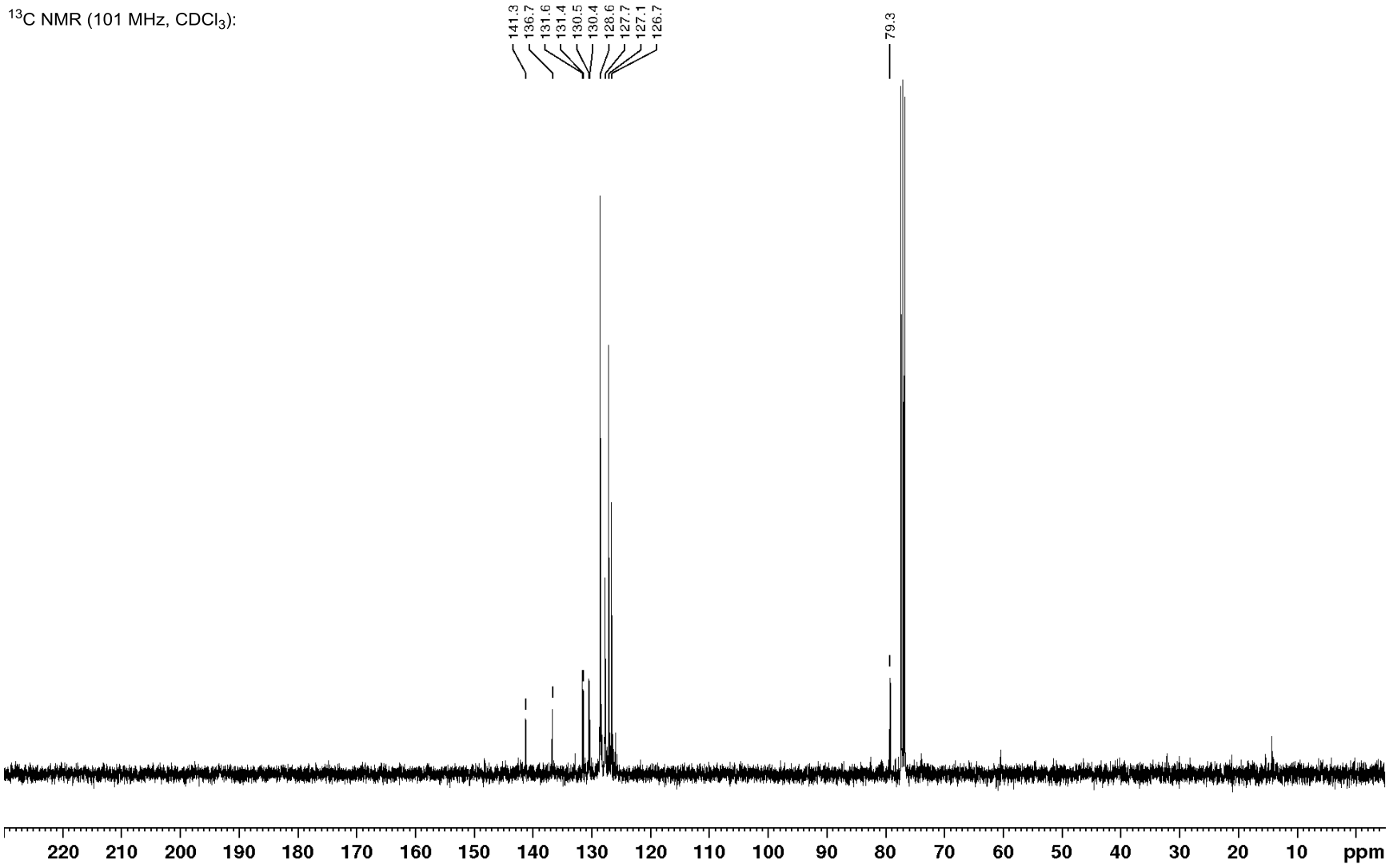
1,3-Diphenylprop-2-en-1-ol (c2r)

^{1}H NMR (400 MHz, $CDCl_3$):





^{13}C NMR (101 MHz, $CDCl_3$):



4 DFT-Calculations

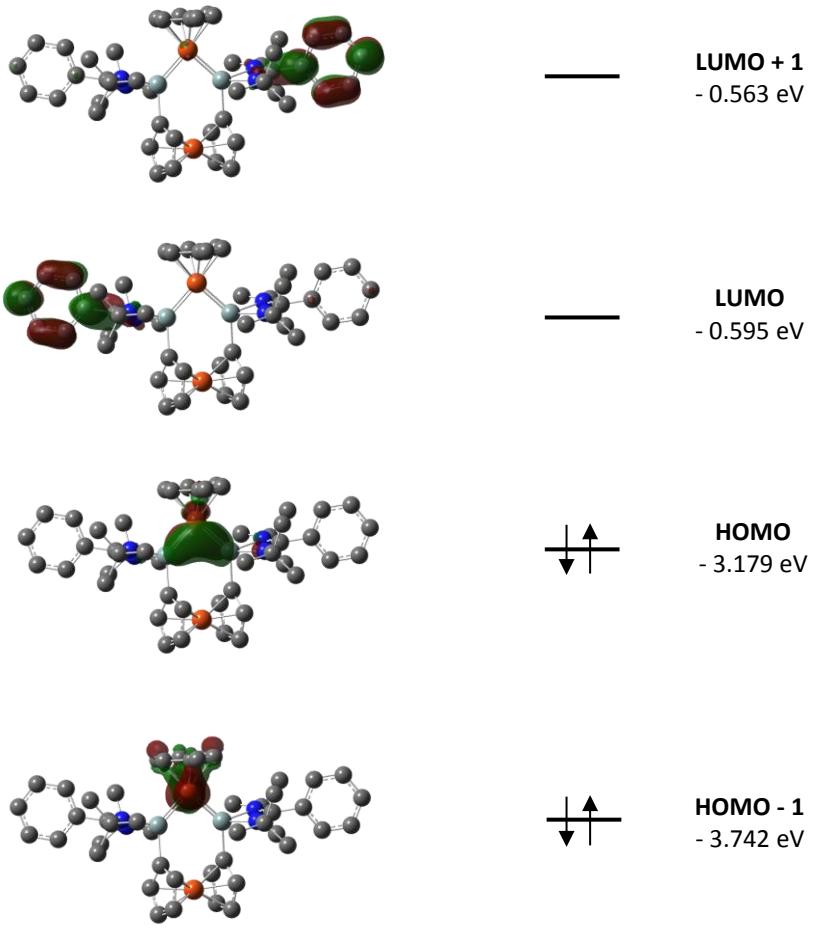
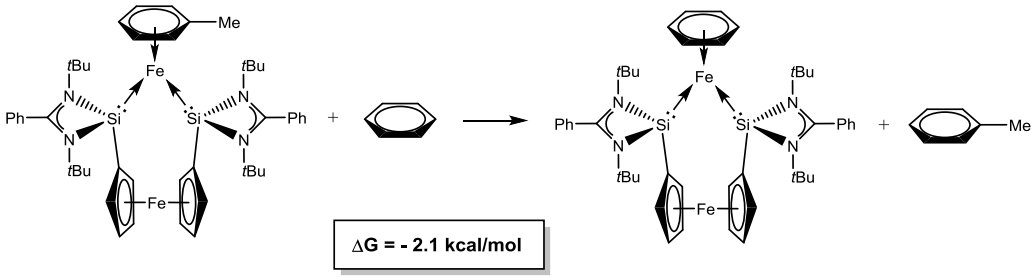


Figure S16: Frontier molecular orbitals of **4** at the B3LYP-D3 level with s6-31G* basis set for Fe and 6-31G* basis set for all other atoms (orange = iron, blue = nitrogen, green = silicon).



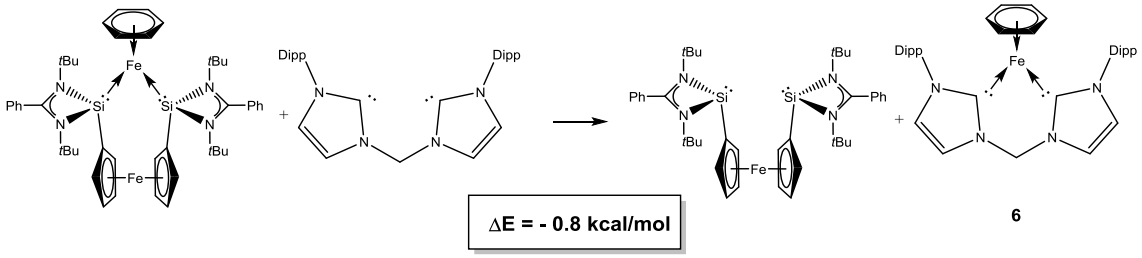
Scheme S1: Calculated Gibbs-energy at room temperature for arene-exchange reaction.

***Table S2*:** Selected geometric parameters [Å]: experimental and calculated for **3**.

Parameter	Experimental (X-ray)	Theoretical (DFT)
Fe-Si1	2.177	2.164
Fe-Si2	2.177	2.164
Si1-Fe-Si2	89.0	89.2
Fe-benzene	1.535	1.540

Table S3: Selected geometric parameters [Å]: experimental and calculated for **4**.

Parameter	Experimental (X-ray)	Theoretical (DFT)
Fe-Si1	2.175	2.171
Fe-Si2	2.171	2.172
Si1FeSi2	89.5	89.7
Fe-toluene	1.549	1.574



Scheme S2: Calculated Gibbs-energy at room temperature for Silylene-carbene ligand exchange reaction.

Table S4: Calculated frontier molecular orbitals of **6** at the B3LYP-D3 level with s6-31G* basis set for Fe and 6-31G* basis set for all other atoms.

	LUMO+1	LUMO	HOMO	HOMO-1
3	- 0.586	- 0.601	- 3.200	- 3.765
6	- 0.037	- 0.0930	- 2.803	- 3.505

Cartesian coordinates of the optimized structure of **3**.

C	-1.43833	-5.02056	0.87301
C	-2.35527	-2.76710	0.27404
C	-1.64631	-4.34192	-1.54366
C	-3.95994	1.15485	-0.52153
C	-1.32935	-3.84468	-0.11961
C	-4.03381	3.21920	0.89891
C	-4.14277	3.38850	-1.62525
C	-3.52558	2.63007	-0.43341
C	-1.83448	0.51799	3.88707
C	-1.91414	0.33298	2.47345
C	2.20618	-7.80185	-1.04960
C	1.97102	-6.95543	-2.13596
C	2.11185	-7.30500	0.25257
C	-1.17770	-0.81706	-3.11544
C	1.64634	-5.61560	-1.92159
C	1.77883	-5.96729	0.46903
C	-0.88549	1.55290	4.13503
C	0.39869	-2.00479	2.87249
C	1.54558	-5.11403	-0.61724
C	-1.01820	1.25068	1.81621
C	-1.28077	0.59455	-3.14668
C	1.20278	-3.68135	-0.38209
C	0.88549	-1.55290	4.13503
C	0.11567	-1.40467	-3.13983
C	-0.39869	2.00479	2.87249
C	1.01820	-1.25068	1.81621
C	-1.77883	5.96729	0.46903
C	-1.20278	3.68135	-0.38209
C	-2.11185	7.30500	0.25257
C	-1.54558	5.11403	-0.61724
C	-2.20618	7.80185	-1.04960
C	-1.64634	5.61560	-1.92159
C	-0.11567	1.40467	-3.13983
C	1.83448	-0.51799	3.88707
C	-1.97102	6.95543	-2.13596
C	1.28077	-0.59455	-3.14668
C	1.91414	-0.33298	2.47345
C	1.17770	0.81706	-3.11544

C	3.52558	-2.63007	-0.43341
C	4.03381	-3.21920	0.89891
C	4.14277	-3.38850	-1.62525
C	1.32935	3.84468	-0.11961
C	1.43833	5.02056	0.87301
C	3.95994	-1.15485	-0.52153
C	2.35527	2.76710	0.27404
C	1.64631	4.34192	-1.54366
H	-2.47623	-5.37074	0.91714
H	-3.37083	-3.17156	0.19953
H	-2.65859	-4.76148	-1.57818
H	-5.05304	1.09022	-0.48543
H	-5.12294	3.11333	0.97083
H	-0.81177	-5.86474	0.57642
H	-2.19031	-2.44143	1.30592
H	-5.22605	3.22243	-1.64617
H	-1.14094	-4.70746	1.87930
H	-3.55793	0.57613	0.31276
H	-2.26374	-1.88889	-0.37411
H	-2.37217	-0.04965	4.63598
H	-0.94937	-5.12338	-1.85845
H	-3.61347	0.69138	-1.44847
H	-1.59436	-3.51639	-2.25753
H	-2.52365	-0.41055	1.97952
H	-3.57452	2.69501	1.74293
H	-3.79436	4.28381	0.97477
H	-2.06980	-1.43347	-3.08658
H	-3.72285	3.02580	-2.57042
H	2.46276	-8.84416	-1.21742
H	-3.97132	4.46492	-1.56215
H	-0.35720	-2.76408	2.72945
H	2.04368	-7.33648	-3.15078
H	2.29520	-7.95841	1.10095
H	-2.25225	1.07181	-3.08863
H	0.56903	-1.91032	5.10681
H	1.47649	-4.95057	-2.76328
H	1.69461	-5.57732	1.47900
H	-0.56903	1.91032	5.10681
H	0.22665	-2.48105	-3.05972
H	-1.69461	5.57732	1.47900

H	-2.29520	7.95841	1.10095
H	-2.46276	8.84416	-1.21742
H	0.35720	2.76408	2.72945
H	-1.47649	4.95057	-2.76328
H	-2.04368	7.33648	-3.15078
H	-0.22665	2.48105	-3.05972
H	2.37217	0.04965	4.63598
H	3.79436	-4.28381	0.97477
H	3.97132	-4.46492	-1.56215
H	2.25225	-1.07181	-3.08863
H	3.57452	-2.69501	1.74293
H	2.52365	0.41055	1.97952
H	3.72285	-3.02580	-2.57042
H	1.14094	4.70746	1.87930
H	2.06980	1.43347	-3.08658
H	2.19031	2.44143	1.30592
H	0.81177	5.86474	0.57642
H	2.26374	1.88889	-0.37411
H	3.55793	-0.57613	0.31276
H	0.94937	5.12338	-1.85845
H	5.12294	-3.11333	0.97083
H	3.61347	-0.69138	-1.44847
H	1.59436	3.51639	-2.25753
H	5.22605	-3.22243	-1.64617
H	2.47623	5.37074	0.91714
H	5.05304	-1.09022	-0.48543
H	3.37083	3.17156	0.19953
H	2.65859	4.76148	-1.57818
N	0.00000	-3.20094	-0.05281
N	-2.04907	2.64958	-0.47104
N	2.04907	-2.64958	-0.47104
N	0.00000	3.20094	-0.05281
Si	-0.65864	1.36937	-0.05322
Si	0.65864	-1.36937	-0.05322
Fe	0.00000	0.00000	3.09046
Fe	0.00000	0.00000	-1.59442

Cartesian coordinates of the optimized structure of **4**.

C	-7.17138	-2.04211	0.84267
C	-8.08188	-0.98291	0.80759
C	-4.74559	-1.75886	-2.55378
C	-5.81384	-1.80468	0.62690
C	-7.62936	0.31528	0.55971
C	0.37736	-3.52586	-2.63325
C	-1.17593	-3.17035	-0.64398
C	-5.35445	-0.50299	0.38446
C	-1.41535	-2.98921	0.74228
C	0.13952	-3.25625	-1.16915
C	-3.78331	-0.56786	-2.37484
C	-6.27046	0.55593	0.35262
C	-2.57753	-0.77258	-3.30922
C	-4.48725	0.75149	-2.75343
C	1.21187	-3.19771	-0.23685
C	-0.33502	-2.88968	1.65595
C	-3.90125	-0.26042	0.14939
C	-3.43693	-1.05395	3.18553
C	0.98170	-3.02435	1.15217
C	-3.14448	0.30321	2.51610
C	-4.24057	1.31723	2.90286
C	3.95969	-1.72355	-2.68697
C	2.13940	-0.05027	-3.14094
C	-1.79051	0.82455	3.02337
C	3.44808	-0.30366	-2.37033
C	-1.50131	1.79824	-0.82995
C	-0.87164	2.27950	-2.03374
C	4.33917	-1.33827	3.14332
C	5.91957	-1.82298	0.21946
C	2.10327	-0.25770	3.42902
C	3.88318	-0.35192	0.14172
C	-2.01083	2.96746	-0.16621
C	4.50300	0.72481	-2.83066
C	3.42811	-0.19819	2.64563
C	7.30486	-1.98869	0.22929
C	5.36339	-0.53913	0.14909
C	-0.98777	3.70130	-2.09521
C	1.52036	1.87651	0.31290

C	-1.68904	4.12918	-0.92933
C	0.94094	2.66261	1.37201
C	8.14432	-0.87299	0.17640
C	2.05375	2.83167	-0.62109
C	6.20856	0.57663	0.09344
C	4.09678	1.16842	2.90174
C	7.59383	0.40931	0.11052
C	1.10690	4.05124	1.08569
C	1.79346	4.15624	-0.15890
H	-7.51782	-3.05398	1.03354
H	-9.13964	-1.16878	0.97179
H	-4.99676	-1.87235	-3.61467
H	-4.27626	-2.68844	-2.21219
H	-5.67819	-1.62157	-2.00307
H	-5.10414	-2.62686	0.63519
H	0.43543	-4.60591	-2.83025
H	-2.02182	-3.15936	-1.32270
H	-0.43228	-3.12142	-3.24825
H	-8.33320	1.14233	0.53009
H	-2.43457	-2.84279	1.08265
H	-2.92294	-0.86662	-4.34464
H	1.31186	-3.07680	-2.97945
H	-4.38067	-1.48014	2.83432
H	-4.78744	0.73404	-3.80800
H	-2.02251	-1.67413	-3.04160
H	-5.38752	0.90322	-2.15083
H	-2.63058	-1.76184	2.98103
H	2.23515	-3.21286	-0.59825
H	-0.50898	-2.72783	2.71451
H	-5.91259	1.56498	0.17182
H	-3.51102	-0.92663	4.27205
H	-1.88861	0.07367	-3.25681
H	-5.24273	0.93753	2.69327
H	1.83302	-2.90402	1.81225
H	-3.81165	1.59783	-2.59498
H	3.24871	-2.47597	-2.33834
H	4.08614	-1.84666	-3.76904
H	1.34325	-0.71235	-2.78858
H	2.29744	-0.20957	-4.21325
H	-4.17976	1.53185	3.97619

H	4.92630	-1.91535	-2.21371
H	-4.10616	2.25830	2.35881
H	-0.98036	0.16597	2.69350
H	3.90974	-2.31463	2.89161
H	-1.79249	0.87710	4.11775
H	1.57303	-1.19563	3.24788
H	5.26262	-2.68615	0.27220
H	1.80114	0.98044	-2.99457
H	-0.34993	1.66422	-2.75502
H	-1.59768	1.82663	2.62968
H	4.60151	0.68716	-3.92200
H	-2.51896	2.96640	0.78805
H	7.72761	-2.98815	0.28124
H	5.34091	-1.28160	2.71299
H	4.43929	-1.28010	4.23323
H	1.43917	0.55881	3.13858
H	2.30414	-0.16730	4.50227
H	5.48483	0.51999	-2.39805
H	0.42990	2.26860	2.23737
H	4.20959	1.74091	-2.54993
H	-0.58267	4.34180	-2.86834
H	2.53090	2.58430	-1.55792
H	-1.91126	5.15364	-0.65808
H	9.22299	-1.00248	0.18681
H	5.07433	1.22469	2.41449
H	3.46588	1.97516	2.51616
H	4.24726	1.32281	3.97699
H	5.77387	1.57005	0.03334
H	0.74756	4.87430	1.69036
H	8.24200	1.28029	0.07012
H	2.04415	5.07392	-0.67593
Fe	-0.04917	-1.55102	0.07992
Fe	0.03067	3.09995	-0.40275
N	-3.25135	-0.48439	-0.99848
N	-3.01553	0.17631	1.04794
N	3.12160	-0.15341	-0.93734
N	3.08841	-0.34498	1.21615
Si	-1.54292	-0.00544	-0.22626
Si	1.49850	-0.02898	0.14469

Cartesian coordinates of the optimized structure of **6**.

Fe	-0.01948	-0.74288	-0.52374
N	2.57483	-0.16735	1.04378
N	1.13931	-1.39635	2.07876
N	-1.19337	-1.62124	2.01705
N	-2.68929	-0.46610	0.99909
C	3.09300	-0.44024	2.31643
C	2.19057	-1.20543	2.96499
C	1.31112	-0.75381	0.85470
C	0.04627	-2.31289	2.24177
C	-2.30081	-1.61327	2.85162
C	-3.24623	-0.89432	2.20974
C	-1.37438	-0.91947	0.83426
C	3.44596	0.39187	0.04826
C	4.42230	-0.45386	-0.51912
C	5.34508	0.10994	-1.40891
C	5.28729	1.46094	-1.73416
C	4.30036	2.27295	-1.17765
C	3.36162	1.76103	-0.27296
C	4.49307	-1.94334	-0.19249
C	4.53049	-2.82183	-1.45688
C	5.70419	-2.24780	0.71052
C	2.28577	2.64732	0.35016
C	2.65375	3.04426	1.79439
C	2.00250	3.91175	-0.47607
C	-3.44443	0.39026	0.13182
C	-3.14963	1.76983	0.09885
C	-3.94923	2.58181	-0.71342
C	-5.01282	2.05172	-1.44412
C	-5.29065	0.69025	-1.38518
C	-4.50724	-0.16959	-0.60440
C	-4.80842	-1.66525	-0.57959
C	-4.87473	-2.27501	-1.99272
C	-6.11238	-1.95007	0.19054
C	-2.02143	2.34621	0.94907
C	-2.45401	2.48119	2.42421
C	-1.50311	3.69856	0.44573
C	0.60426	-1.93617	-2.13799

C	1.36043	-0.73378	-2.14754
C	0.74376	0.53491	-2.05754
C	-0.66598	0.62117	-2.01845
C	-1.42150	-0.57212	-2.12548
C	-0.80570	-1.84744	-2.14864
H	4.04958	-0.05110	2.62668
H	2.19257	-1.61596	3.96346
H	0.05896	-2.73210	3.25083
H	0.14314	-3.11024	1.48872
H	-2.31505	-2.11626	3.80666
H	-4.24972	-0.62186	2.49450
H	6.11112	-0.51781	-1.85525
H	6.00775	1.88454	-2.42911
H	4.26570	3.32022	-1.45558
H	3.58744	-2.21249	0.35767
H	3.67322	-2.62444	-2.10765
H	4.50551	-3.88113	-1.17540
H	5.44318	-2.65891	-2.04146
H	6.64266	-1.98487	0.20737
H	5.74139	-3.31509	0.95993
H	5.65417	-1.68233	1.64660
H	1.36444	2.05133	0.38735
H	2.78070	2.16779	2.43495
H	1.86130	3.66554	2.22991
H	3.58600	3.62269	1.81195
H	2.85950	4.59605	-0.47652
H	1.15818	4.45725	-0.04859
H	1.75747	3.67520	-1.51761
H	-3.74796	3.64572	-0.77381
H	-5.62376	2.70504	-2.06162
H	-6.11819	0.28489	-1.96064
H	-3.99066	-2.16368	-0.05094
H	-5.70351	-1.85956	-2.57738
H	-5.02981	-3.35831	-1.92576
H	-3.94953	-2.09991	-2.55065
H	-6.06077	-1.57510	1.21832
H	-6.30966	-3.02795	0.23135
H	-6.96794	-1.46804	-0.29774
H	-1.18536	1.63771	0.89536
H	-3.29964	3.17453	2.51764

H	-1.62497	2.87475	3.02506
H	-2.75003	1.52070	2.85341
H	-1.18333	3.65000	-0.60065
H	-0.64101	3.99982	1.04929
H	-2.25468	4.49218	0.53962
H	1.10562	-2.89765	-2.14580
H	2.43799	-0.78772	-2.09302
H	1.35829	1.42425	-2.00737
H	-1.17266	1.57690	-1.94694
H	-2.49679	-0.51187	-2.05681
H	-1.41944	-2.74196	-2.13626

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