# Supporting Information

# Assessing the reactivity of sodium zincate

# [(TMEDA)Na(TMP)Zn$^{t}$Bu$_2$] towards benzoylferrocene: deprotonative metalation vs alkylation reactions

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**General Experimental Conditions**

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Toluene and hexane were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for $^{1}$H, 150.32 MHz and 100.62 MHz for $^{13}$C{$^{1}$H}.

**General Crystallography**: All data was collected at 123 K on Oxford-Diffraction CCD diffractometers using $Mo_{K\alpha}$ radiation, $\lambda$ = 0.71073 Å. All refinements were to convergence on $F^2$ and used all unique reflections and the program SHELXL-97.[37] Selected crystallographic parameters are given in table S1 and full data has been deposited, see CCDC reference numbers 838243–838246. See http://www.rsc.org/

**Table S1:** Crystallographic Data

| **Compound** | **3** | **4/6** | **5** | **8** |
|---|---|---|---|---|
| **Formula** | $C_{36}H_{56}FeN_3NaOZn$ | $0.95(C_{21}H_{23}FeIO)$ $0.05(C_{21}H_{22}FeI_2O)$ | $C_{21}H_{22}FeO$ | $C_{43}H_{64}FeN_3NaOZn$ |
| ***Fw*** | 691.05 | 474.14 / 600.05 | 346.24 | 783.18 |
| **Crystal system** | monoclinic | monoclinic | monoclinic | triclinic |
| **Space group** | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | P-1 |
| ***a*, Å** | 16.5928(8) | 9.6150(3) | 10.9164(6) | 11.0692(8) |
| ***b*, Å** | 11.8192(4) | 11.7549(4) | 25.1685(13) | 14.4319(10) |
| ***c*, Å** | 19.0005(8) | 17.2226(5) | 18.3340(11) | 14.6345(7) |
| **α, deg** | 90 | 90 | 90 | 102.227(5) |
| **β, deg** | 111.772(5) | 105.283(3) | 91.060(5) | 111.723(5) |
| **γ, deg** | 90 | 90 | 90 | 100.148(6) |
| ***V*, Å$^3$** | 3460.5(3) | 1877.72(10) | 5036.4(5) | 2037.4(2) |
| ***Z*** | 4 | 4 | 12 | 2 |
| **$D_{calcd}$, g cm$^{-3}$** | 1.326 | 1.677 | 1.370 | 1.277 |
| **μ, mm$^{-1}$** | 1.157 | 2.452 | 0.900 | 0.991 |
| ***T*, K** | 123 | 123 | 123 | 123 |
| **Crystal size, mm** | 0.1 × 0.1 × 0.1 | 0.1 × 0.1 × 0.1 | 0.3 × 0.05 × 0.05 | 0.1 × 0.1 × 0.1 |
| **Measured reflns** | 20669 | 27212 | 45919 | 20067 |
| **Unique reflns** | 8165 | 5212 | 10967 | 8608 |
| **$R_{int}$** | 0.0648 | 0.0547 | 0.1130 | 0.0562 |
| **No of parameters** | 395 | 206 | 631 | 486 |
| ***R* ($F$, $F^2 > 2\sigma$)** | 0.0464 | 0.0505 | 0.0580 | 0.0430 |
| **$R_w$ ($F^2$, all data)** | 0.0771 | 0.1161 | 0.1252 | 0.1091 |
| **Goodness of fit** | 0.787 | 1.128 | 0.990 | 1.027 |
| **Max, min Δρ, e Å$^{-3}$** | 0.818, –0.479 | 1.336, -0.621 | 0.502, –0.618 | 0.748, –0.814 |

**Figure S1**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of [(TMEDA)Na(μ-TMP)Zn{OC($^{t}$Bu)(Ph)($\eta^5$-$C_5H_3$)Fe($\eta^5$-$C_5H_5$)}] (3) in $d_6$-benzene.

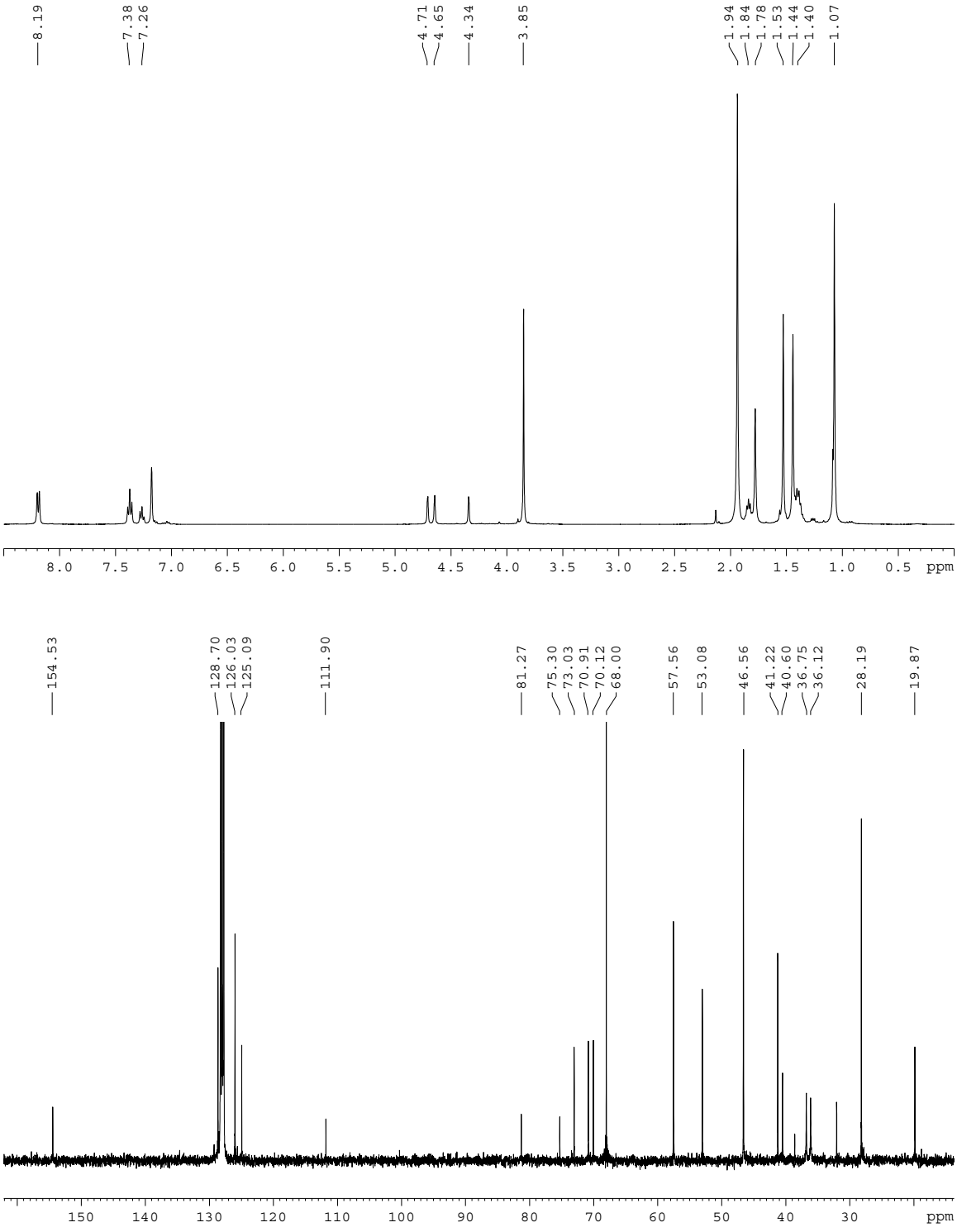
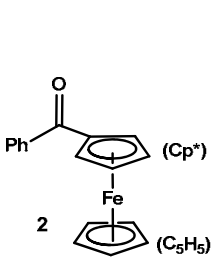
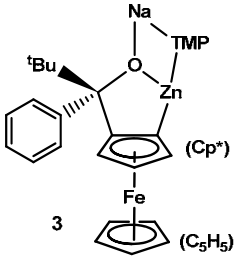


**Table S2**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR resonances of 2 and 3 in $d_6$-benzene solutions.




2




3

| | δ $^{1}H$(3) (ppm) | δ $^{13}C\{^{1}H\}$(3) (ppm) | δ $^{1}H$(2)(ppm) | δ $^{13}C\{^{1}H\}$(2) (ppm) |
|---|---|---|---|---|
| **Ph ($C_{ipso}$)** | - | 154.5 | - | 140.5 |
| **Ph($CH_{ortho}$)** | 8.19 | 128.7 | 7.94 | 131.3 |
| **Ph($CH_{meta}$)** | 7.36 | 126.0 | 7.12 | 128.5 |
| **Ph($CH_{para}$)** | 7.26 | 124.9 | 7.18 | 128.3 |
| **C-O** | - | 81.3 | - | 197.3 |
| **Cp*(*CH*)** | 4.70, 4.63, 4.33 | 73.0, 70.8, 70.0 | 4.84, 4.13 | 72.3, 71.8 |
| **Cp*(*C*-CO)** | - | 75.3 | - | 79.2 |
| **Cp* (*C*-Zn)** | - | 111.8 | - | - |
| **$C_5H_5$** | 3.84 | 68.0 | 3.91 | 70.3 |
| **TMEDA** | 1.94 (NC$H_3$), 1.78 (NC$H_2$) | 57.5, 46.6 | - | - |
| **TMP** | 1.78 (β-H), 1.39 (γ-H) | 53.0 (Cα), 41.2 (Cβ), 19.8 (Cγ) | - | - |
| **α-Me TMP** | 1.52, 1.44 | 36.8, 36.1 | - | - |
| **$^{t}$Bu** | 1.06 | 40.5 ($CH_3$), 28.2 (*C*) | - | - |

**Figure S2**. X-ray crystallographic structure of [(TMEDA)Na(μ-TMP)Zn{OC($^{t}$Bu)($\eta^5$-$C_5H_3$)Fe($\eta^5$-$C_5H_5$)}.$C_7H_8$] (8) with selective atom labelling and 40% probability ellipsoids. Hydrogen atoms and minor disordered component of TMEDA have been omitted for clarity.

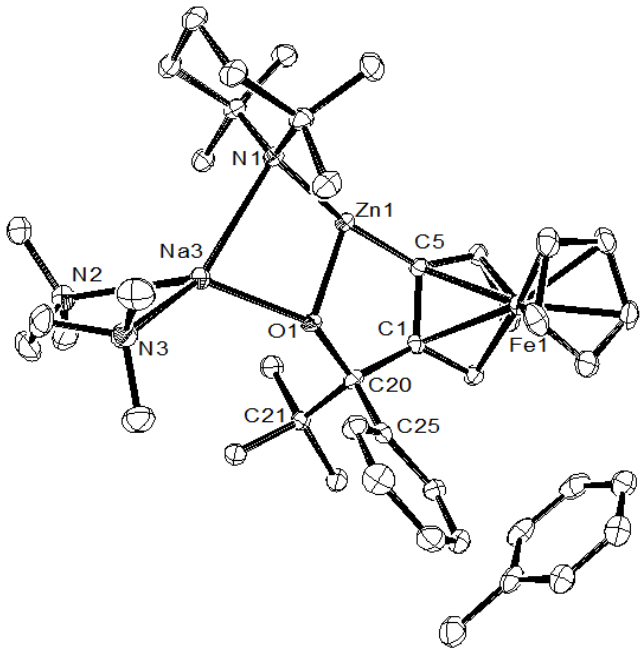


**Figure S3**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of [PhC(OH)($^{t}$Bu)($\eta^5$-$C_5H_3I$)Fe($\eta^5$-$C_5H_5$)] (**4**)in $CDCl_3$ (spectra contains traces of [PhC(OH)($^{t}$Bu)($\eta^5$-$C_5H_3I$)Fe($\eta^5$-$C_5H_4I$)] (**6**)).

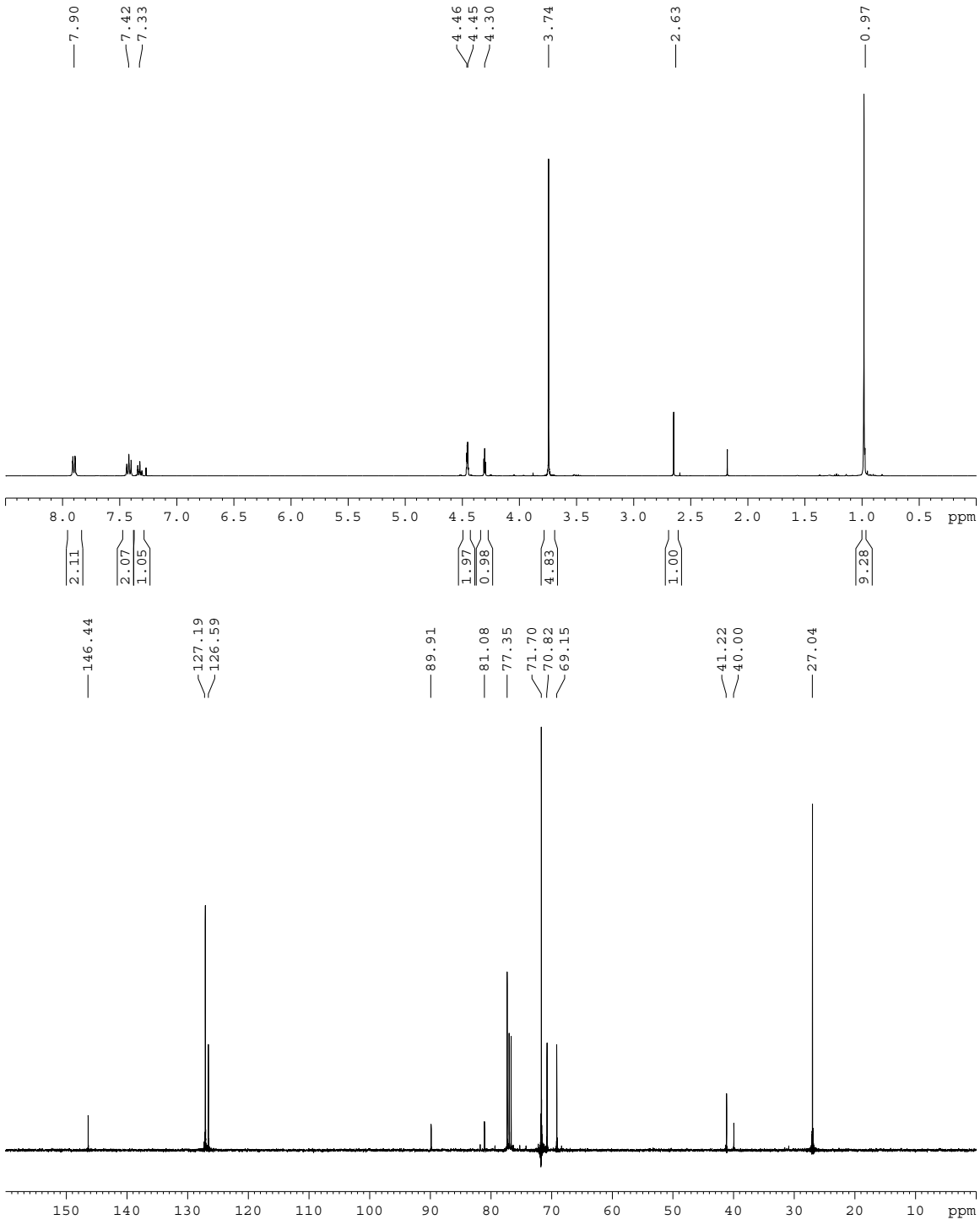


**Figure S4**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of [4-$^{t}$Bu-$C_6H_4C(=O)(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)$] (**5**) in $CDCl_3$.

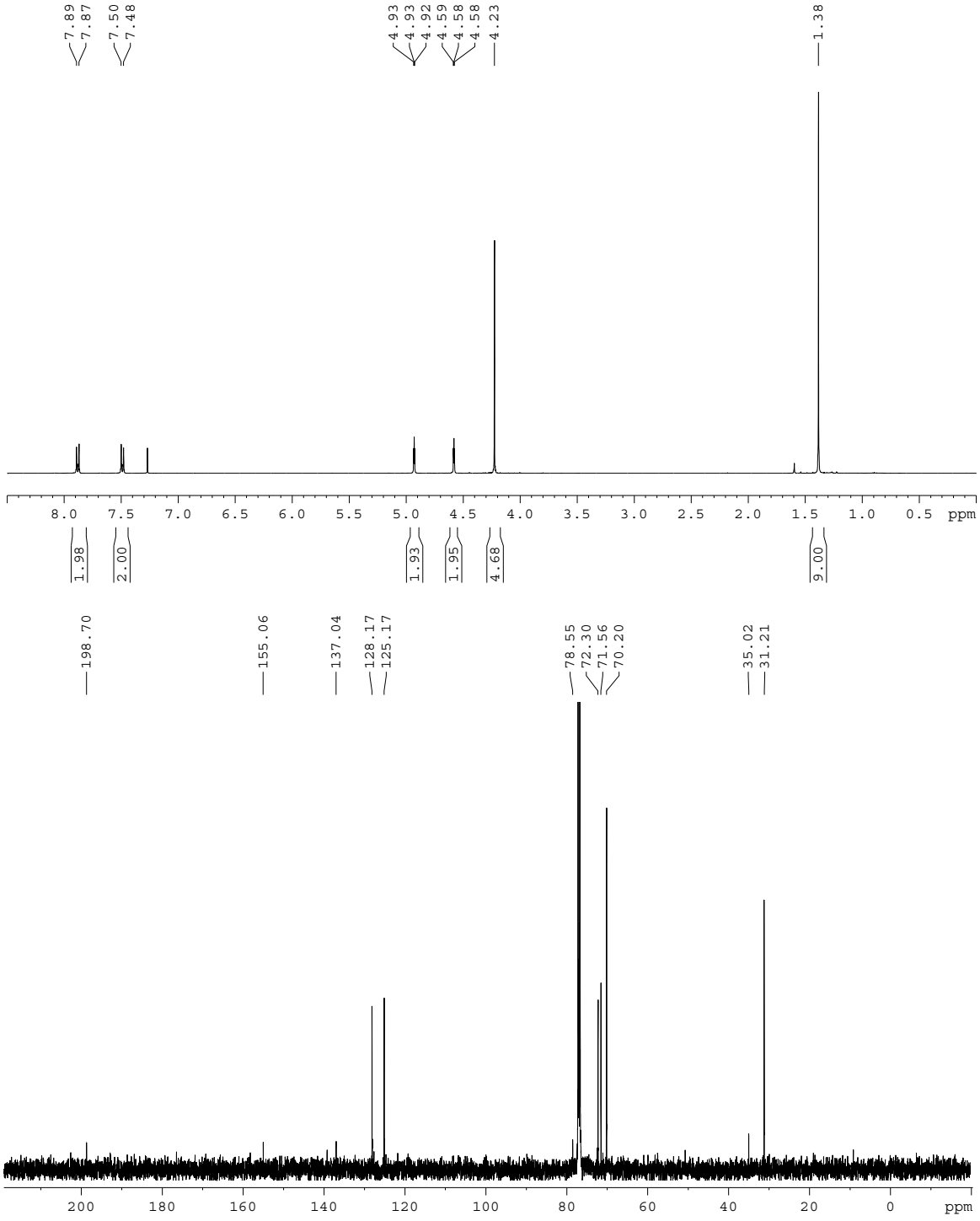


**Figure S5**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of [PhC(OH)($^{t}$Bu)($\eta^5$-$C_5H_3D$)Fe($\eta^5$-$C_5H_5$)] (**7**-D) in $CDCl_3$, and $^{2}D$ NMR spectra in $CHCl_3$.

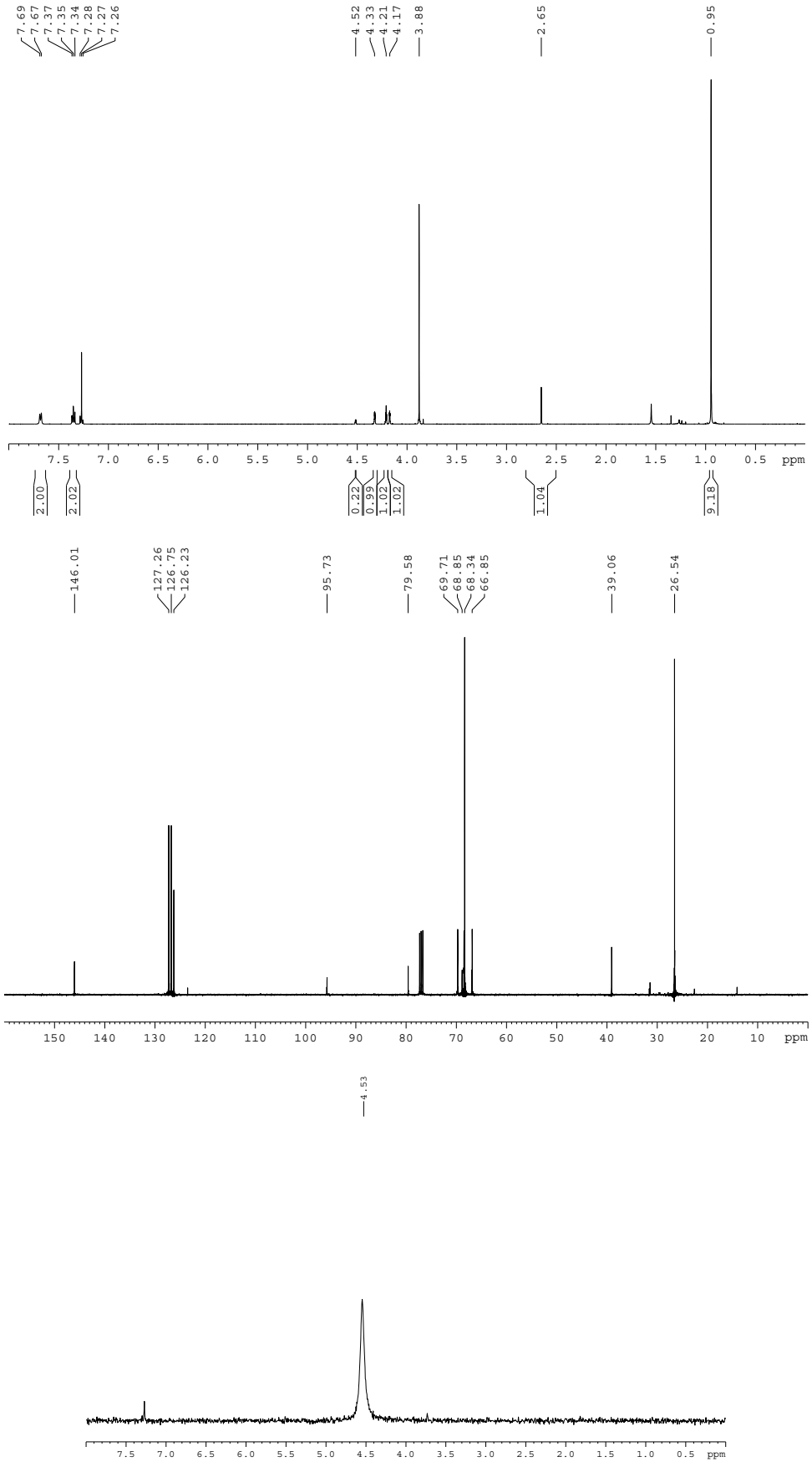


**Figure S6.** $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of [PhC(OH)($^{t}$Bu)($\eta^5$-$C_5H_4$)Fe($\eta^5$-$C_5H_5$)] (**7**) in $CDCl_3$.

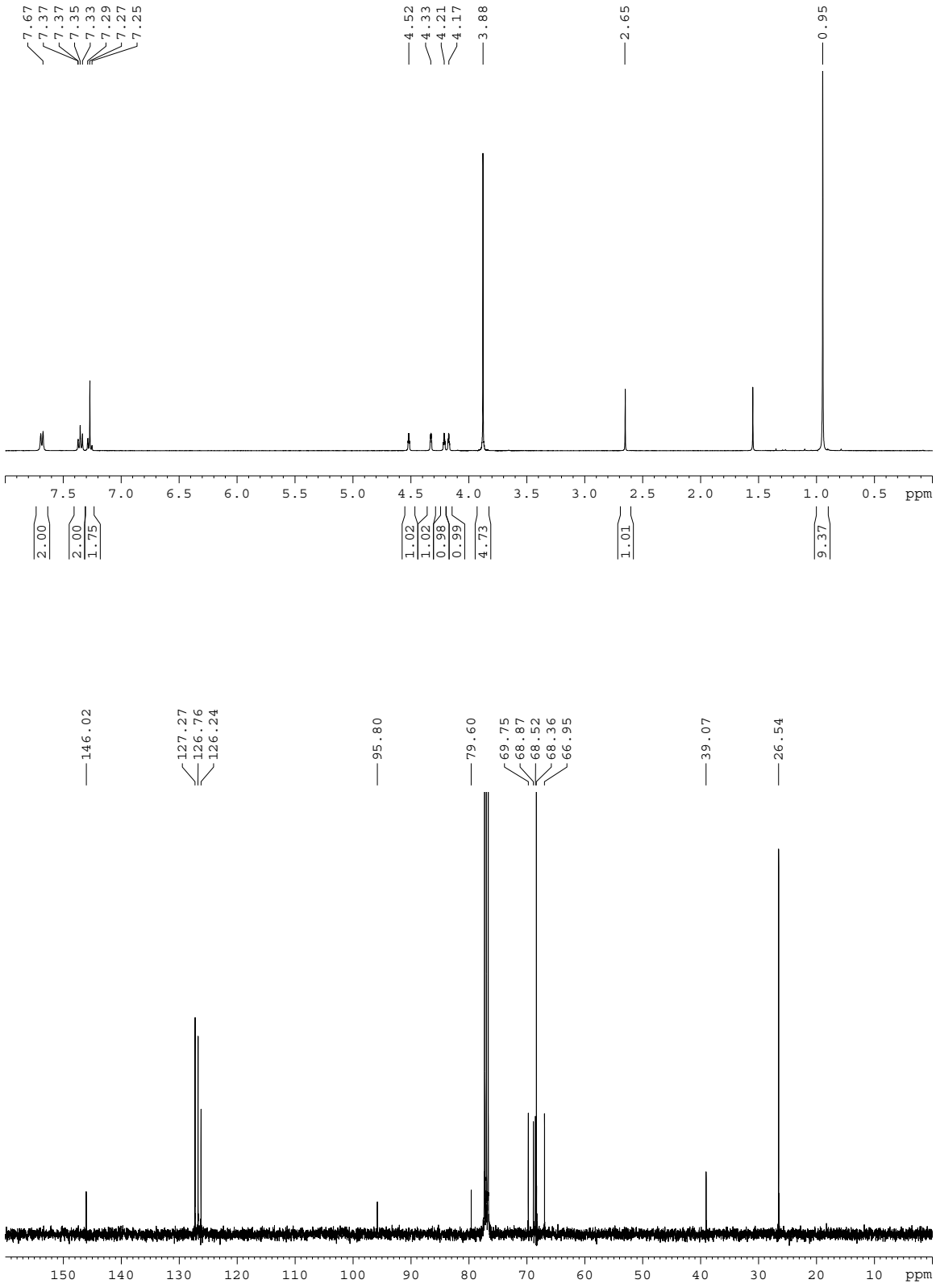
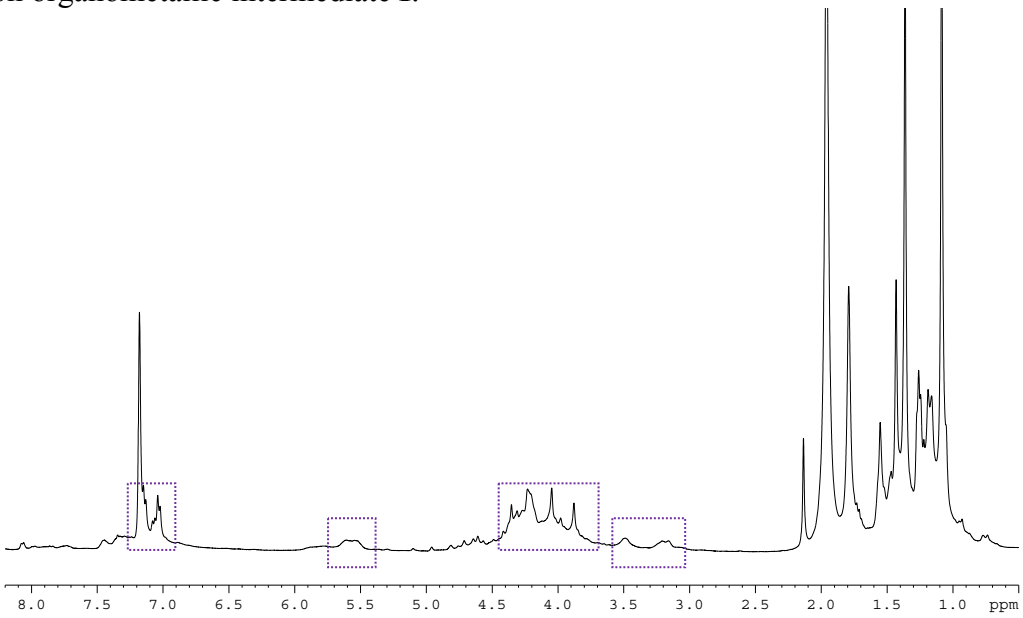


**Figure S7**: $^{1}H$ NMR in $d_6$-benzene of the filtrate solution from the reaction of **1** with **2**. Highlighted in purple appear the resonances which are suggested to belong to the 1,6 addition organometallic intermediate **I**.




**[$C_6H_5C(OH)^tBu(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)$] (7) and [$^t$Bu-$C_6H_4CO(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)$] (5)**. Benzoylferrocene (0.290 g, 1 mmol) was dissolved in Toluene (7 mL) and added via cannula to a second Schlenk tube containing isolated crystals of **1** (0.460 g, 1 mmol, prepared as described above). The resulting deep red solution was stirred for 2 hours at room temperature, after which time TEMPO (0.468 g, 3 mmol) was added, and the reaction stirred for a further 20 hours at room temperature. The reaction was quenched with saturated $NH_4Cl$ solution (5 mL) and then extracted with EtOAc (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified by column chromatography (eluent: hexane/diethyl ether, 1:0 – 9:1) giving **7** (0.1185 g, 34%) as an orange solid and **5** (0.1415g, 41%) as a red solid.

NMR data for [$C_6H_5C(OH)^tBu(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)$] (**7**)**.** $^{1}H$ NMR (400.13 MHz, 298K, $CDCl_3$) δ 7.67 (2H, doublet, $CH_{ortho}$), 7.35 (2H, triplet, $CH_{meta}$), 7.27 (1H, triplet, $CH_{para}$), 4.52 (1H, multiplet, $C_5H_4$), 4.33 (1H, multiplet, $C_5H_4$), 4.21 (1H, multiplet, $C_5H_4$), 4.17 (1H, multiplet, $C_5H_4$), 3.88 (5H, singlet, $C_5H_5$), 2.65 (1H, singlet, OH), 0.95 (9H, singlet, $C(CH_3)_3$, $^t$Bu). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298K, $CDCl_3$) δ 146.0 ($C_{ipso}$), 127.3 ($C_{ortho}$), 126.8 ($C_{meta}$), 126.2 ($C_{para}$), 95.8 (*C*-O), 79.6 (OC-$C_{Cp*}$), 69.8 ($C_5H_4$), 68.9 ($C_5H_4$), 68.5 ($C_5H_4$), 68.4 ($C_5H_5$), 67.0 ($C_5H_4$), 39.0 ($C(CH_3)_3$, $^t$Bu), 26.5 ($C(CH_3)_3$, $^t$Bu).