New iron(II) α-iminopyridine complexes and their catalytic activity in the oxidation of activated methylene groups and secondary alcohols to ketones

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Supporting information - Submitted to Dalton Transactions

1. Experimental details and characterization data for the catalysis products in Table 6

Experimental section for the isolated yields in Table 6.

General. The solvents (including pyridine) and the substrates utilized for catalysis (all Aldrich) were used as received. The oxidant *t*-BuOOH (70 wt% in H_2O, Aldrich) was used as received. NMR spectra were obtained at room temperature on a Bruker Avance 300 MHz or a Varian Unity Plus 300 MHz instrument and referenced to a residual solvent signal; all assignments are tentative. IR spectra were recorded on a Thermo Nicolet 360 FT-IR spectrometer and GC/MS spectra were recorded on a Hewlett Packard GC/MS System Model 5988A.

Benzophenone. The substrate diphenylmethane (0.100 g, 0.595 mmol) and the catalyst **8a** (0.013 g, 0.018 mmol) were dissolved in pyridine (1.0 mL). The oxidant *t*-BuOOH (0.62 mL, 70 wt% in H_2O, 2.4 mmol) was slowly added within 20 to 30 minutes, and the tan solution was shaken for 4 h at room temperature. The pyridine solvent was removed under vacuum. The product benzophenone was isolated by column chromatography as a colorless liquid (0.080 g, 0.439 mmol, 74%, TOF 6.1), using silica gel and CH_2Cl_2 as eluent.

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.81-7.78 (4H, m, aromatic), 7.57-7.55 (2H, m, aromatic), 7.49-7.44 (4H, m, aromatic). ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 196.9 (s, *C*O), 137.7 (s, aromatic), 132.6 (s, aromatic), 130.2 (s, aromatic), 128.4 (s, aromatic). MS (EI): *m*/*z* 182 (20%, M), 105 (100, M – Ph), 77 (70, M – 2Ph – CO).

Anthraquinone. The substrate 9,10-Dihydroanthracene (0.200 g, 1.11 mmol), utilizing the oxidant *t*-BuOOH (1.15 mL, 70 wt% in H_2O, 4.4 mmol) and catalyst **8a** (0.024 g, 0.033 mmol), was converted to anthraquinone (yellow solid, 0.118 g, 0.569 mmol, 51%) as described above for benzophenone, using CH_2Cl_2 / hexanes 7/3 as eluent.

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 8.34-8.31 (4H, m, aromatic), 7.83-7.80 (4H, m, aromatic). ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 183.4 (s, *C*O), 134.3 (s, aromatic), 133.8 (s, aromatic), 127.5 (s, aromatic). IR (neat) ν_{max}/cm^{-1} 1673s (C=O), 1589m, 1574w, 1282s.

9-Fluorenone. The substrate fluorene (0.100 g, 0.602 mmol), utilizing the oxidant *t*-BuOOH (0.62 mL, 70 wt% in H_2O, 2.4 mmol), was converted to 9-fluorenone (0.099 g, 0.548 mmol, 91%, TOF 7.6) as described above for benzophenone.

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.64-7.61 (2H, m, aromatic), 7.46-7.44 (4H, m, aromatic), 7.28-7.23 (2H, m, aromatic). ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 193.9 (s, *C*O), 144.5 (s, aromatic), 134.8 (s, aromatic), 134.2 (s, aromatic), 129.2 (s, aromatic), 124.3 (s, aromatic), 120.4 (s, aromatic); IR (neat) ν_{max}/cm^{-1} 1711s (C=O), 1610s, 1598s.

2-Undecanone. The substrate 2-undecanol (0.100 g, 0.580 mmol), utilizing the oxidant t-BuOOH (0.61 mL, 70 wt% in H_2O, 2.3 mmol) and catalyst **8a** (0.013 g, 0.018 mmol) was converted to 2-undecanone (0.047 g, 0.274 mmol, 47%, TOF 4), as described above for benzophenone, using CH_2Cl_2/hexanes as eluent.

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 2.40 (2H, t, $^1J_{HH}$ = 7 Hz, CH_2C=O), 2.1 (3H, s, CH_3), 1.55 (2H, t, $^1J_{HH}$ = 7.4 Hz, CH_2), 1.25 (12H, m, 6CH_2), 0.87 (3H, t,

$^1J_{HH}$ = 7.4 Hz, C*H*$_3$). ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 209.5 (s, *C*O), 43.9 (s), 32.0, 29.9, 29.6, 29.5, 29.4, 29.3, 24.1, 22.8, 14.3; IR (neat) ν_{max}/cm^{-1} 2924s, 2854s, 1717s (C=O), 1358m.

3,4-dihydronaphthalen-1(2*H*)-one. The substrate tetrahydronaphthalene (0.100 g, 0.767 mmol), utilizing the oxidant *t*-BuOOH (0.55 mL, 70 wt% in H_2O, 3.0 mmol) and catalyst **8a** (0.016 g, 0.023 mmol), was converted to 2-undecanone (0.024 g, 0.164 mmol, 22%, TOF 1.8), as described above for benzophenone, using CH_2Cl_2/hexanes 95/5 as eluent.

NMR (δ, $CDCl_3$) 2.47-2.39 (m, 2H), 2.97-2.93 (m, 2H), 3.28-3.24 (m, 2H), 8.32 (1H, d, $^1J_{HH}$ = 7.8 Hz), 7.76 (1H, dt, $^1J_{HH}$ = 7.5 Hz, $^2J_{HH}$ = 1.5 Hz), 7.61-7.53 (2H, m); ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 198.6 (*C*=O), 144.7, 133.6, 132.8, 128.9, 127.4, 126.8, 39.3, 29.9, 23.5. MS (EI): *m*/*z* 146 (50%, M), 118 (100, M – C_2H_4), 90 (80, M – $(CH_2)_2CO$).

Acetophenone. The substrate ethylbenzene (0.100 g, 0.734 mmol), utilizing the oxidant t-BuOOH (0.53 mL, 70 wt% in H_2O, 2.9 mmol) and catalyst **8a** (0.015 g, 0.022 mmol), was converted to acetophenone (0.053 g, 0.444 mmol, 47%, TOF 5.1), as described above for benzophenone, using $CHCl_3$/ hexanes 80/20 as eluent.

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 7.96-7.94 (2H, m), 7.59-7.53 (1H, m), 7.48-7.43 (2H, m), 2.59 (3H, s). ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 198.3 (s, *C*O), 137.3, 133.3, 128.7, 128.5, 26.7.[1]

Cyclooctanone. The substrate cyclooctanol (0.100 g, 0.779 mmol), utilizing the oxidant *t*-BuOOH (0.4 mL, 70 wt% in H_2O, 3.12 mmol) and catalyst **8a** (0.017 g, 0.024

mmol), was converted to cyclooctanone (0.022 g, 0.177 mmol, 23%, TOF 1.9), as described above for acetophenone, using hexanes/diethyl ether 90/10 as eluent.

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 2.50-2.39 (2H, m), 1.98-1.84 (2H, m), 1.65-1.51 (4H, m), 1.41-1.32 (2H, m), 1.26-1.14 (2H, m), 0.93-0.86 (2H, m); ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 218.6 (s, *C*O), 42.2, 27.4, 25.9, 24.9 (all s).

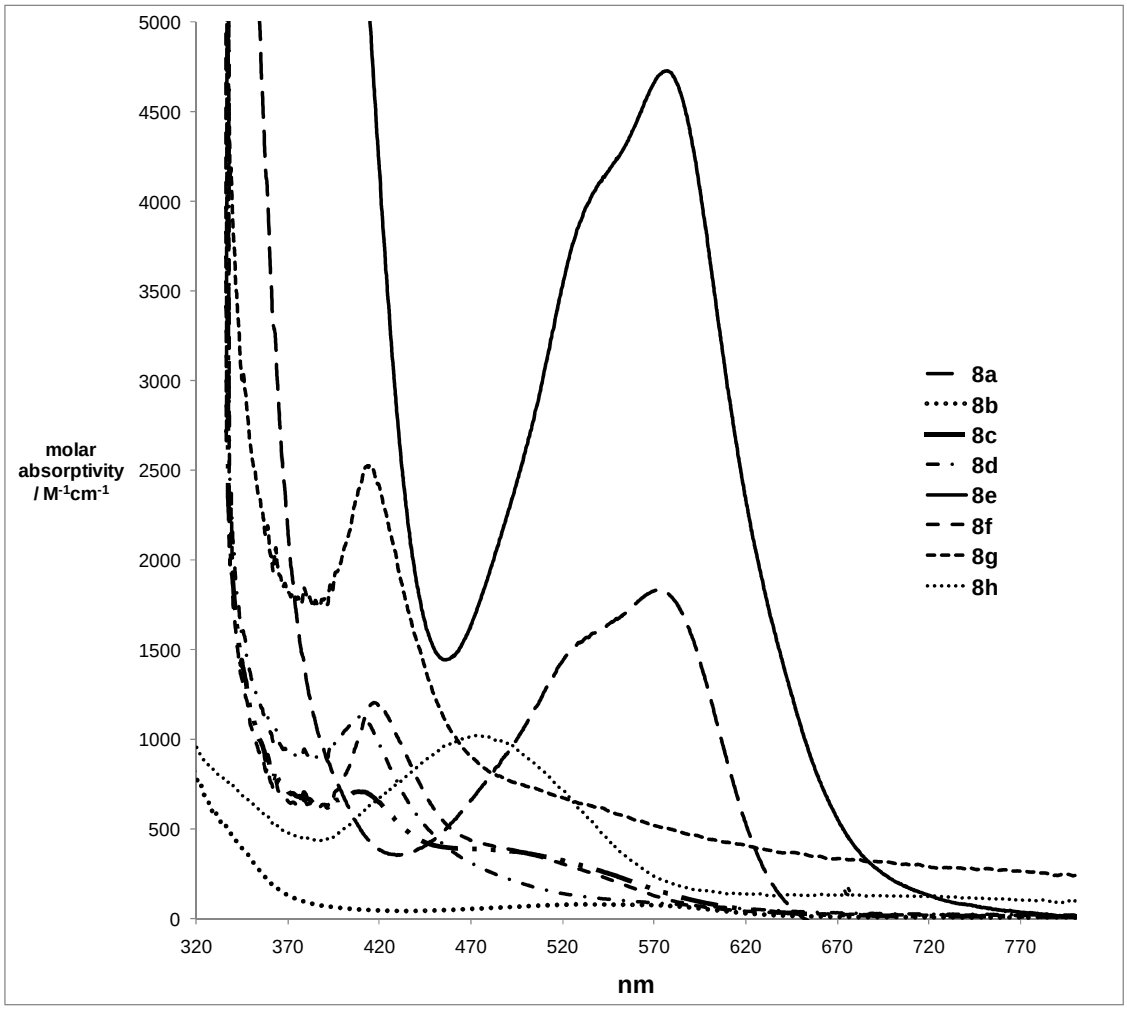
4-Phenyl-2-butanone. The substrate 4-phenyl-2-butanol (0.100 g, 0.667 mmol), utilizing the oxidant *t*-BuOOH (0.34 mL, 70 wt% in H_2O, 2.66 mmol) and catalyst **8a** (0.014 g, 0.020 mmol), was converted to 4-phenyl-2-butanone (0.037 g, 0.252 mmol, 38%, TOF 1.9) as described above for acetophenone, using hexanes/diethyl ether 90/10 as eluent.[2]

^{1}H-NMR δ_H (300.13 MHz; $CDCl_3$; Me_4Si) 2.13 (3H, s, C*H*$_3$), 2.77-2.73 (2H, m, C*H*$_2$), 2.92-2.87 (2H, m, C*H*$_2$), 7.21-7.16 (3H, m, aromatic), 7.31-7.25 (2H, m, aromatic); ^{13}C-NMR δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 208.1 (s, *C*O), 141.2, 128.8, 128.7, 128.6, 128.5, 126.3, 45.4, 26.6, 26.1 (all s).

2. UV-vis spectra for the complexes **8**

All UV-vis spectra were recorded at room temperature in CH_2Cl_2 except for complex **8e** (CH_3CN), concentrations range from 1.11×10^{-4} to 2.82×10^{-3} M.

Fig. S1 UV-vis spectra of all complexes **8**



3. UV-vis experiment analog to Figure 7 with H_2O_2

Analog to the experiment described in Figure 7 of the manuscript, H_2O_2 was added to complex **8c** and UV-vis spectra recorded in three minute intervals for 30 minutes. The rising band around 600 nm might be again a [Fe-O-O-H] species, but the band is broader and not as "distinct" than that one for the corresponding experiment with *t*-BuOOH.

Fig. S2 UV-vis spectra taken in three minute intervals for the reaction of **8c** with H_2O_2 in CH_3CN at room temperature.

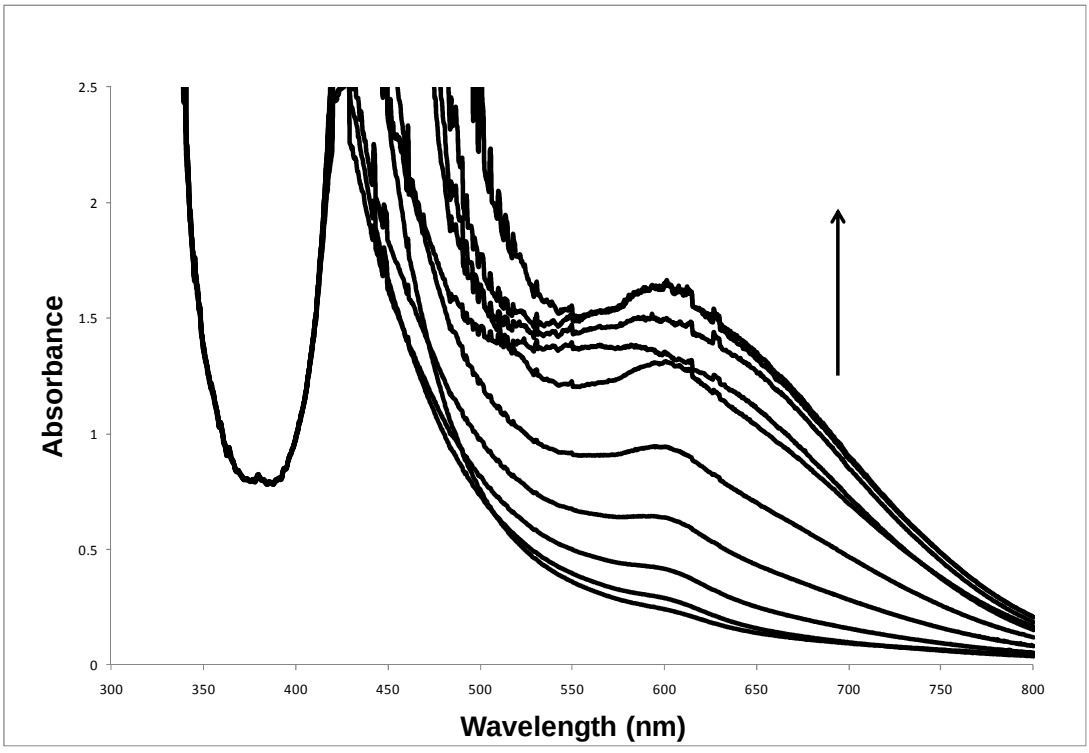
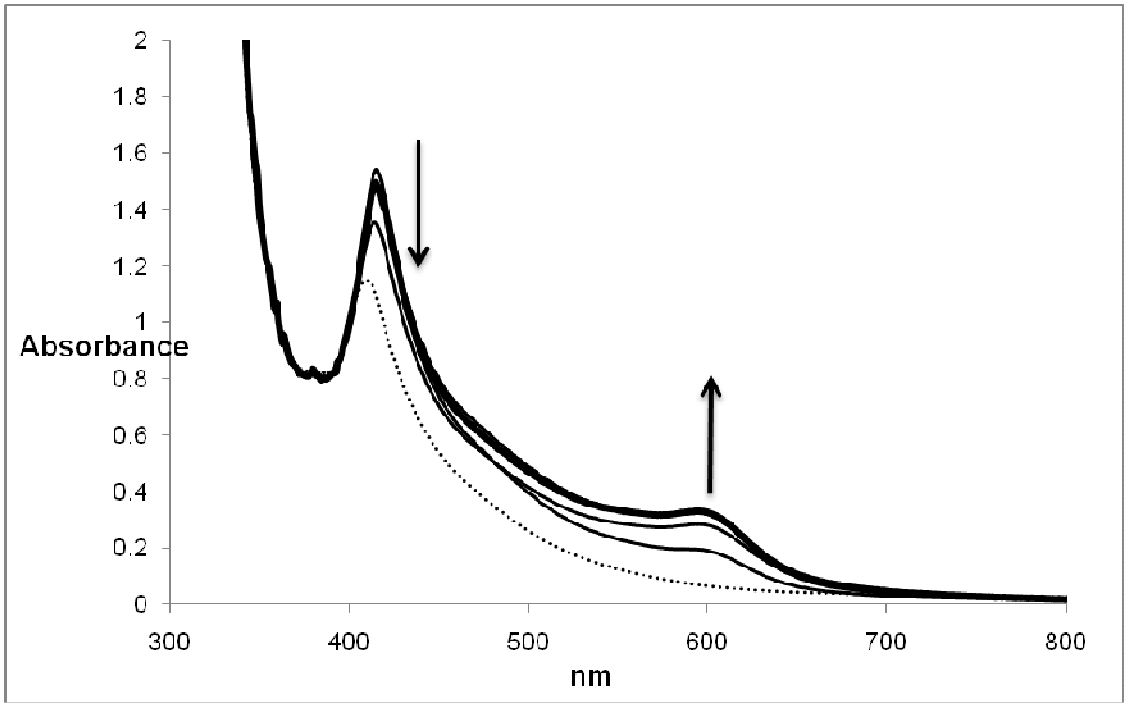


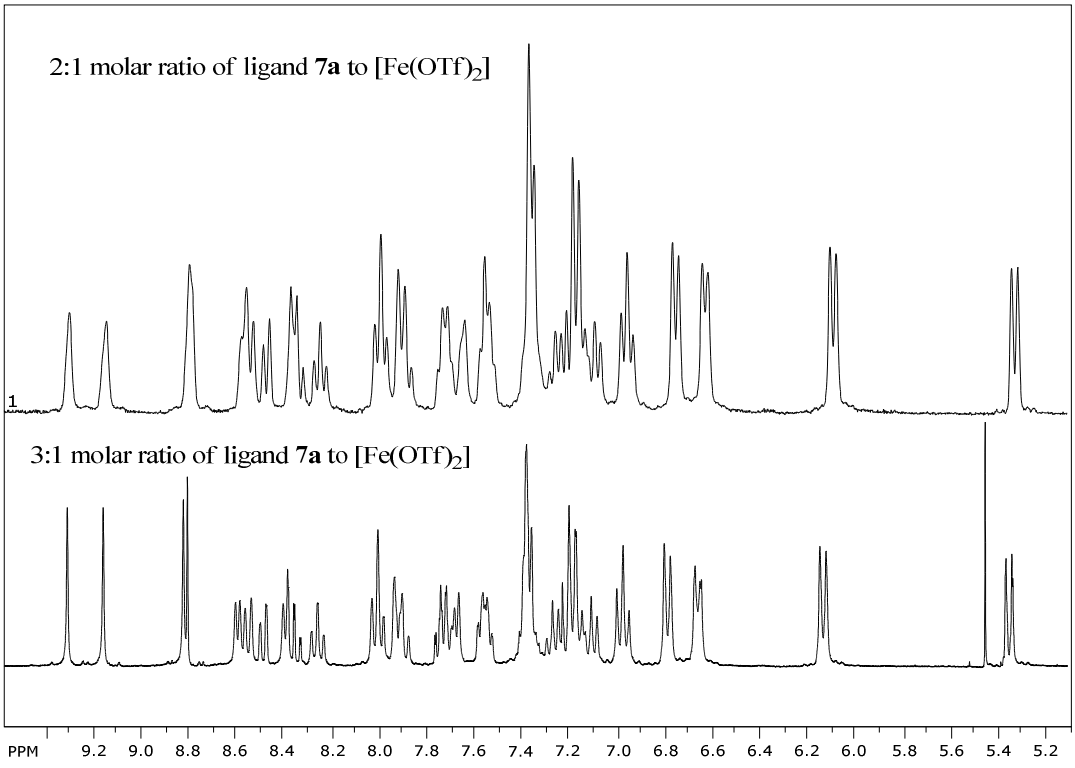
Fig. S3 Reaction of complex **8c** with *t*-BuOOH followed over 24 h. The band around 600 nm increases up to five hours after the reaction was started. After 24 h, the band has disappeared and the spectrum changed to that one originally obtained for **8c** (dotted line).



4. Comparison of the ^{1}H NMR spectra of complex **8a** and **8e** with varying synthetic procedures

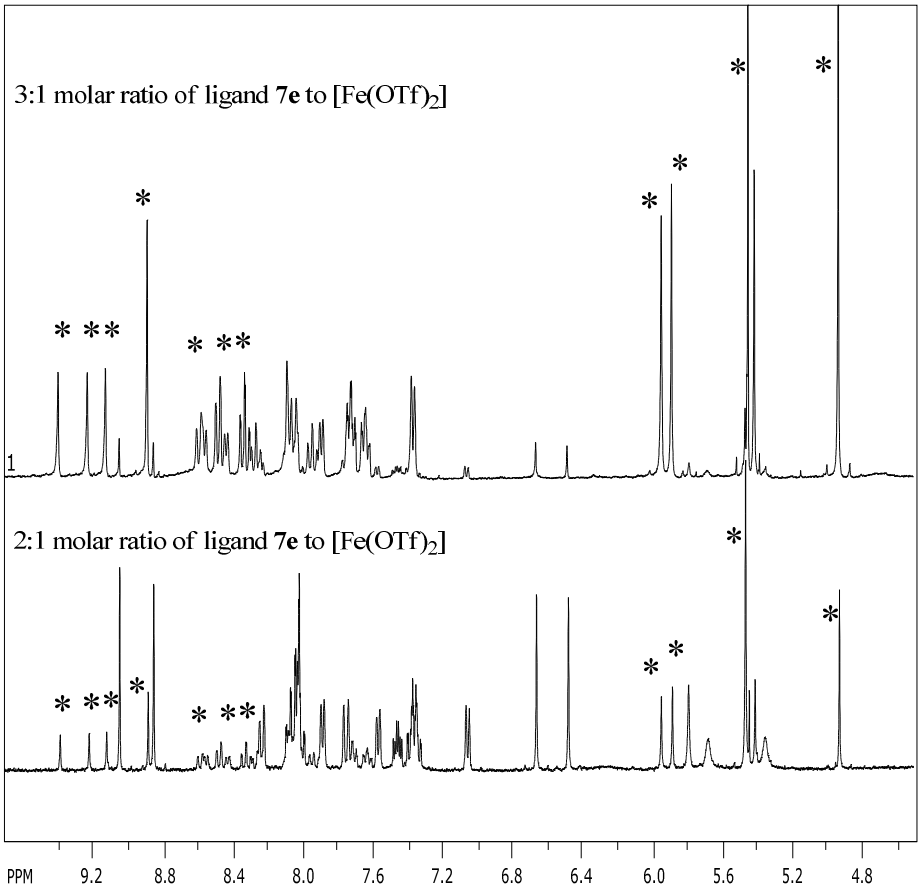
For the syntheses of the complexes **8**, a 2:1 molar ratio of ligand **7** to [Fe(OTf)$_2$] was employed. When a 3.5:1 molar ratio of ligand **7a** to [Fe(OTf)$_2$] was employed for the synthesis of complex **8a**, the ^{1}H NMR spectra of the isolated material were identical (see below), suggesting that only two ligands **7a** coordinate to the iron center.

Fig. S4 Comparison of ^{1}H NMR spectra of isolated material of **8a** (top) and of the isolated material when a 3.5:1 molar ratio of the ligand **7a** and [Fe(OTf)$_2$] was employed (bottom).



For complex **8e**, the ^{1}H NMR spectra differed significantly when a 3.5:1 molar ratio of ligand **7e** and [Fe(OTf)$_2$] was employed. The spectrum on bottom obtained from a 2:1 molar ratio of ligand to metal contained already signals for the tris-coordinated material [Fe(**7e**)$_3$](OTf)$_2$ (starred in the spectra below). These signals increased when a 3.5:1 molar ratio of **7e** and [Fe(OTf)$_2$] was employed (top).

Figure S5 Comparison of ^{1}H NMR spectra of isolated material of **8e** (bottom) and of the isolated material when a 3.5:1 molar ratio of the ligand **7e** and [Fe(OTf)$_2$] was employed (top). Starred (*) are the signals assigned to [Fe(**7e**)$_3$](OTf)$_2$



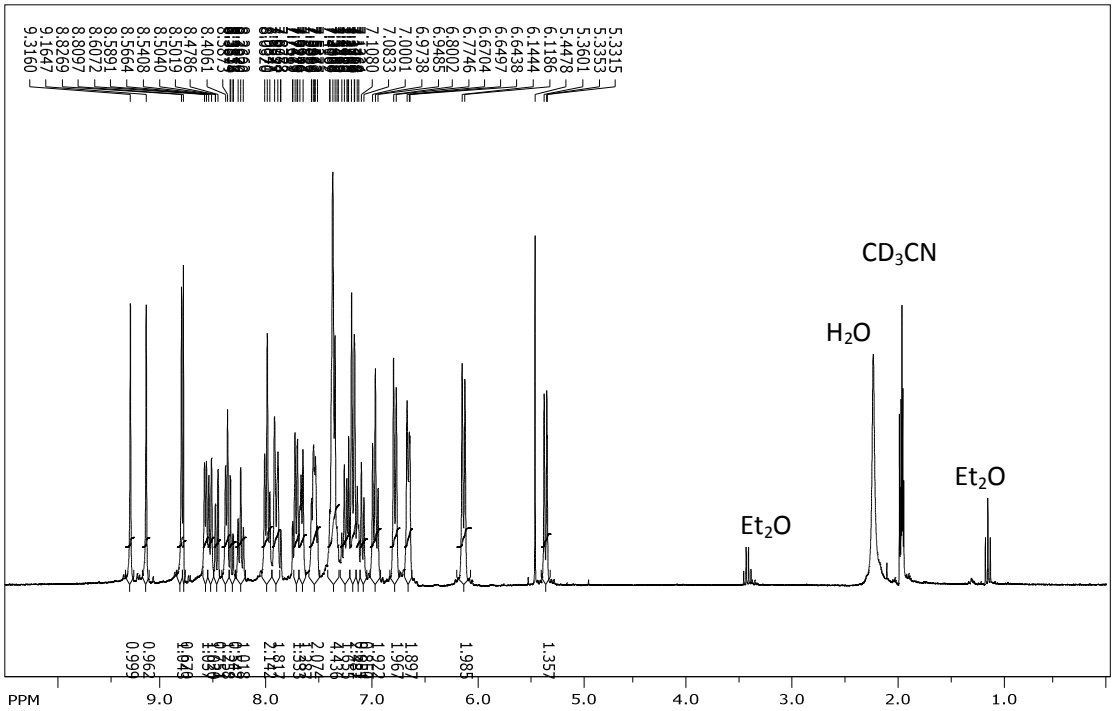
5. References

[1] The product contained about 10% of methylbenzyl alcohol.

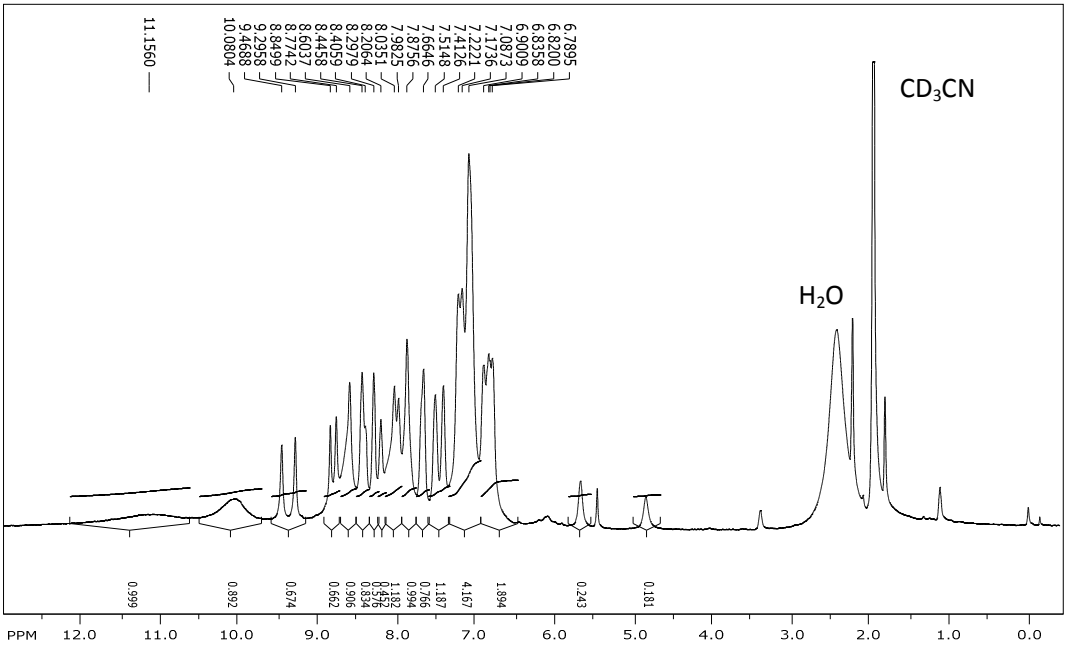
[2] The product contained about 5 mol% impurities, which we tentatively ascribed to 3-hydroxy-1-phenylbutan-1-one.

6. ^{1}H NMR spectra of the complexes **8**

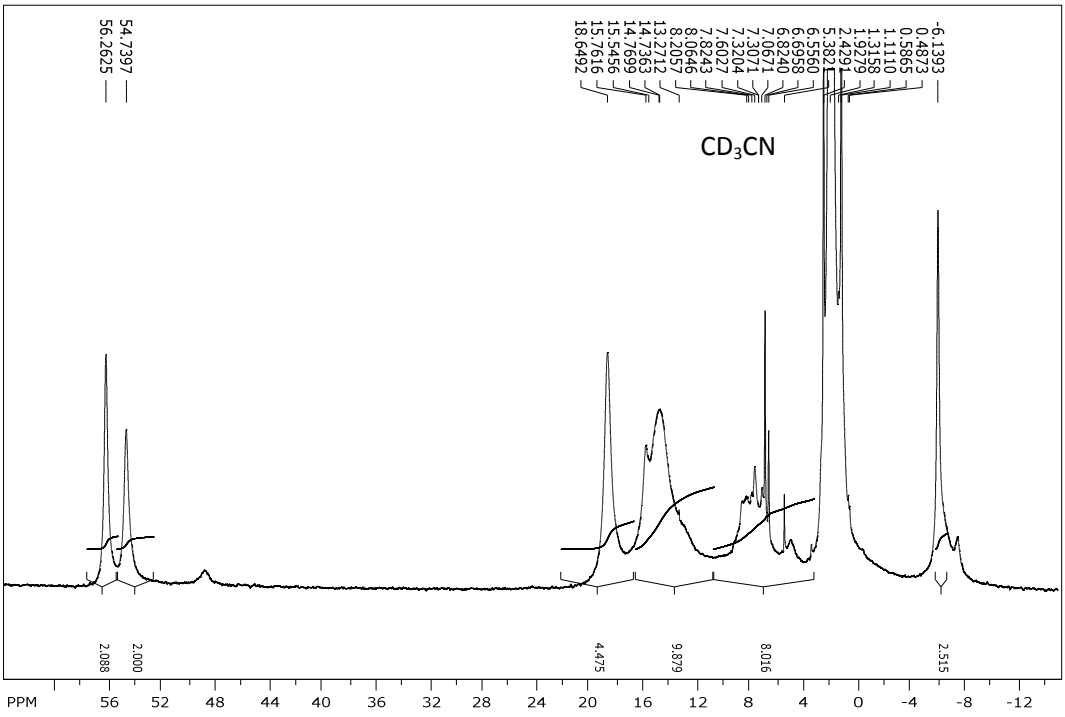
[Fe(OTf)$_2$(**7a**)$_2$] (**8a**), 298 K, CD$_3$CN.



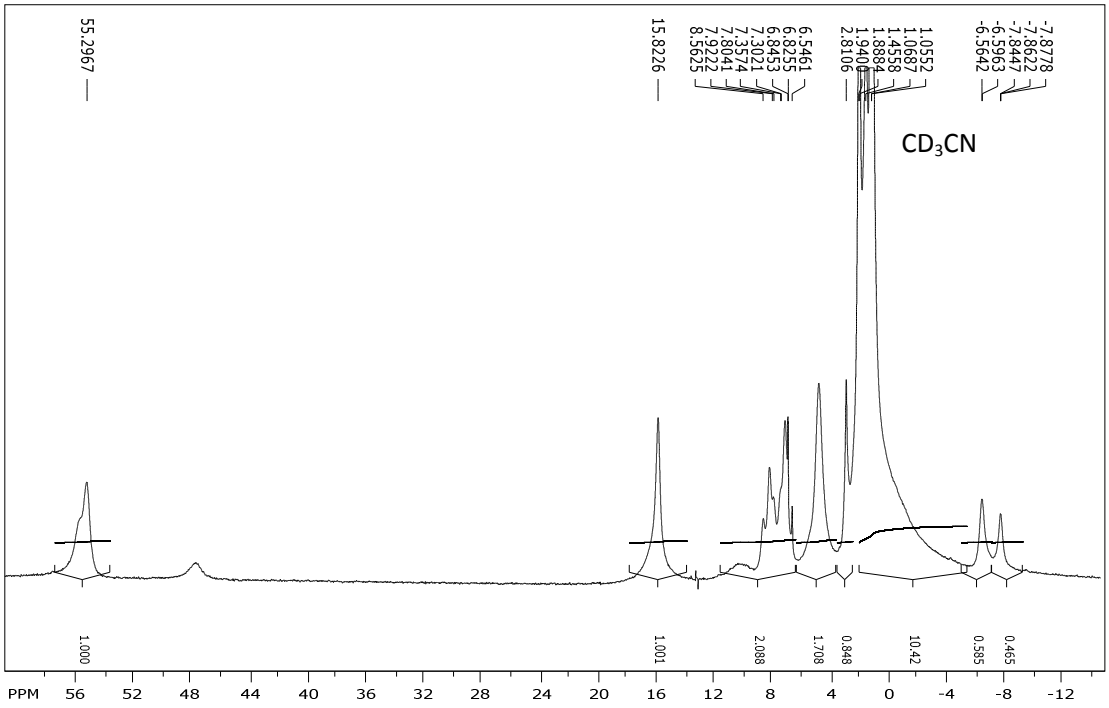
[Fe(OTf)$_2$(**7b**)$_2$] (**8b**), 243 K, CD$_3$CN.



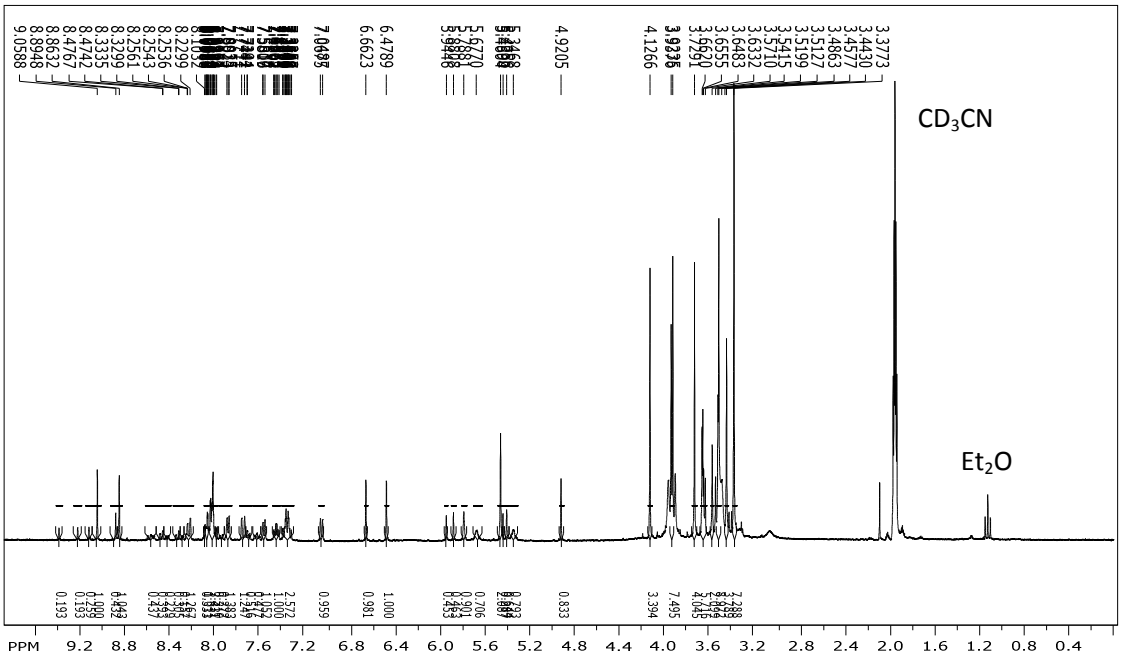
[$Fe(OTf)_2$(**7c**)$_2$] (**8c**), 298 K, CD_3CN.



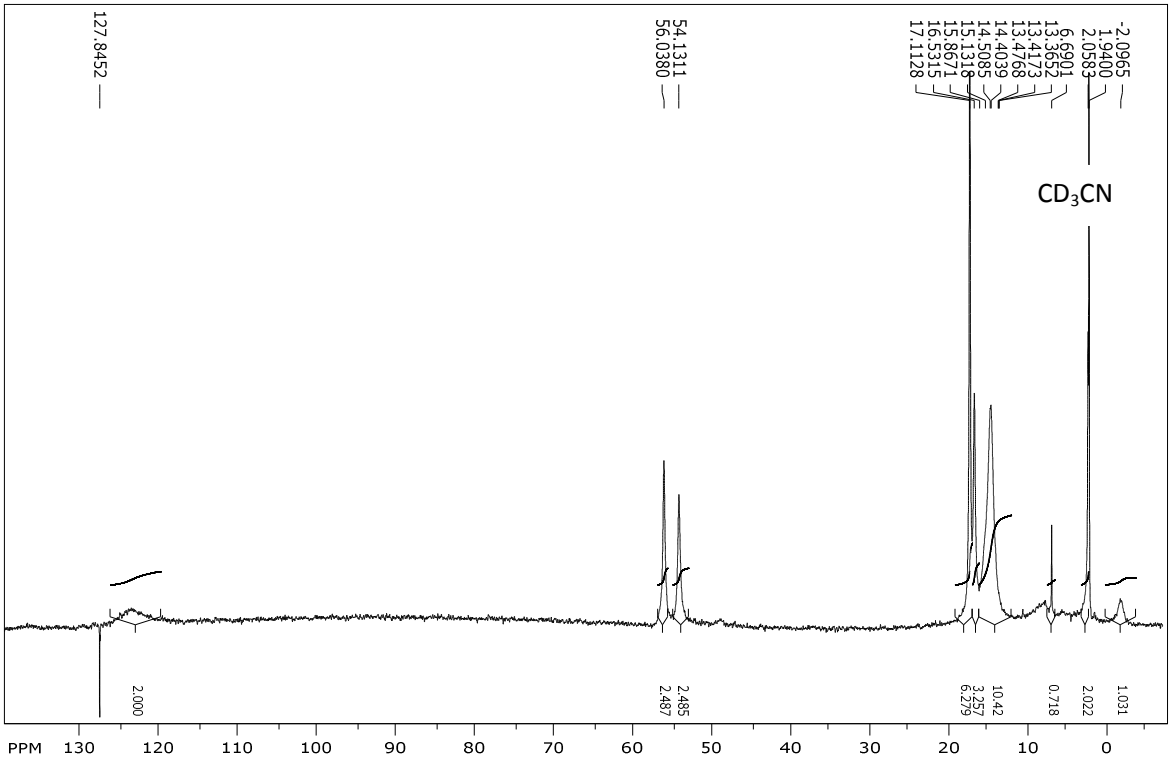
[$Fe(OTf)_2$(**7d**)$_2$] (**8d**), 298 K, CD_3CN.



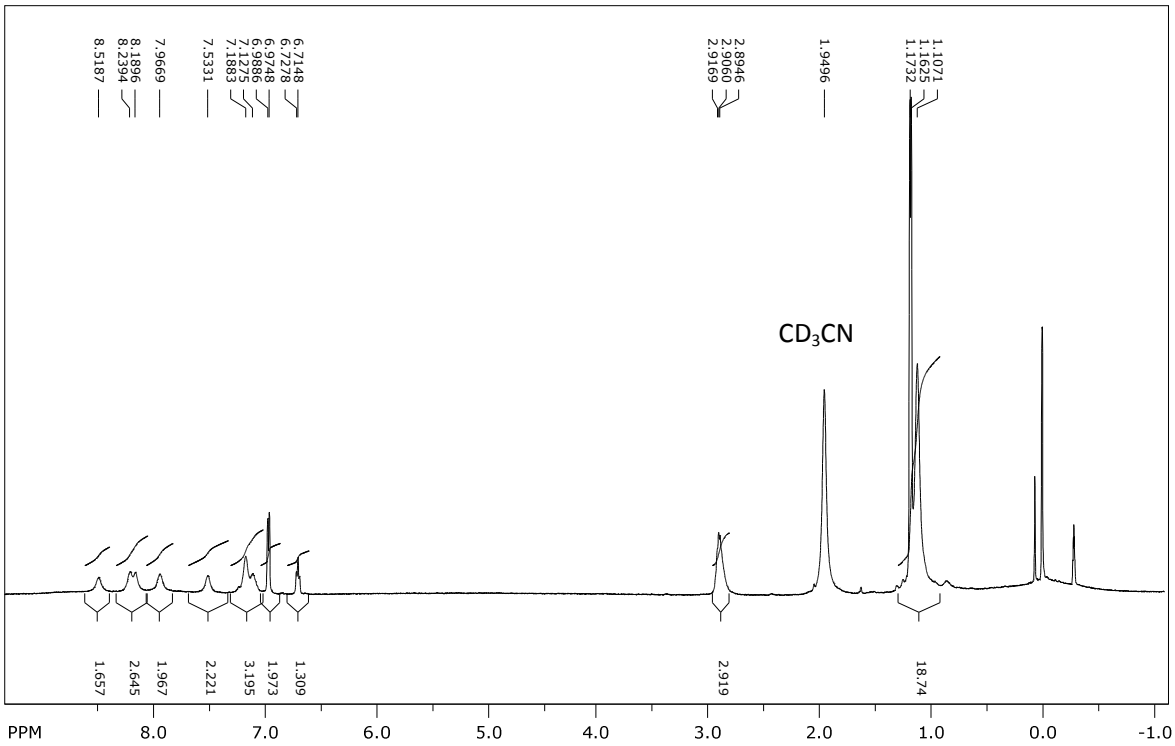
[Fe(OTf)$_2$(**7e**)$_2$] (**8e**), 298 K, CD_3CN, see also Figure S5).



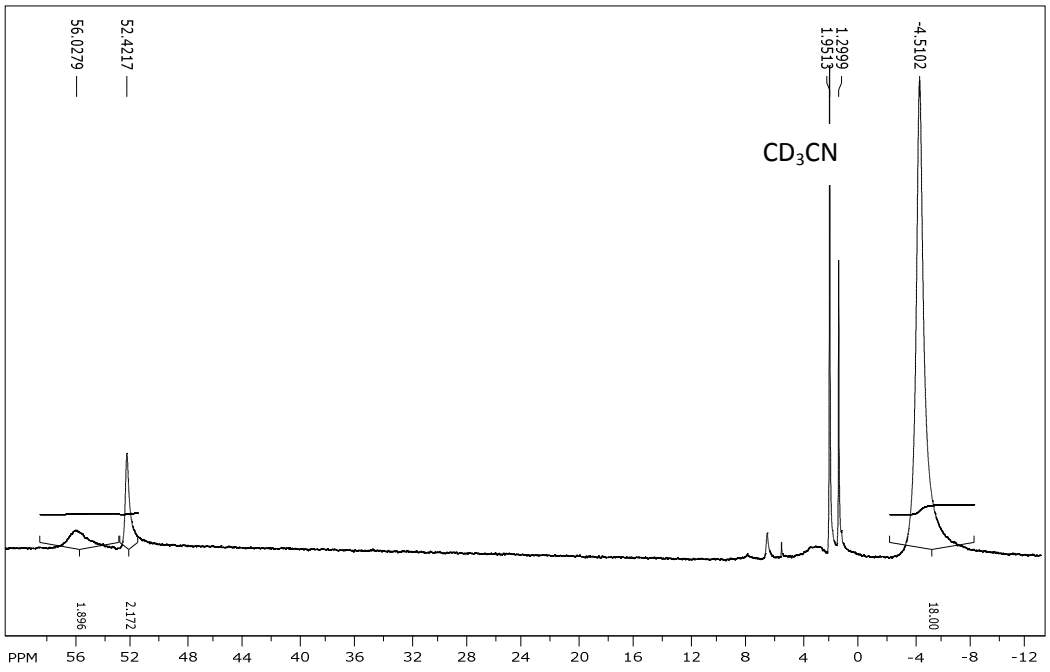
[Fe(OTf)$_2$(**7f**)$_2$] (**8f**), 298 K, CD_3CN



[Fe(OTf)$_2$(**7g**)$_2$] (**8g**), 253 K, CD_3CN

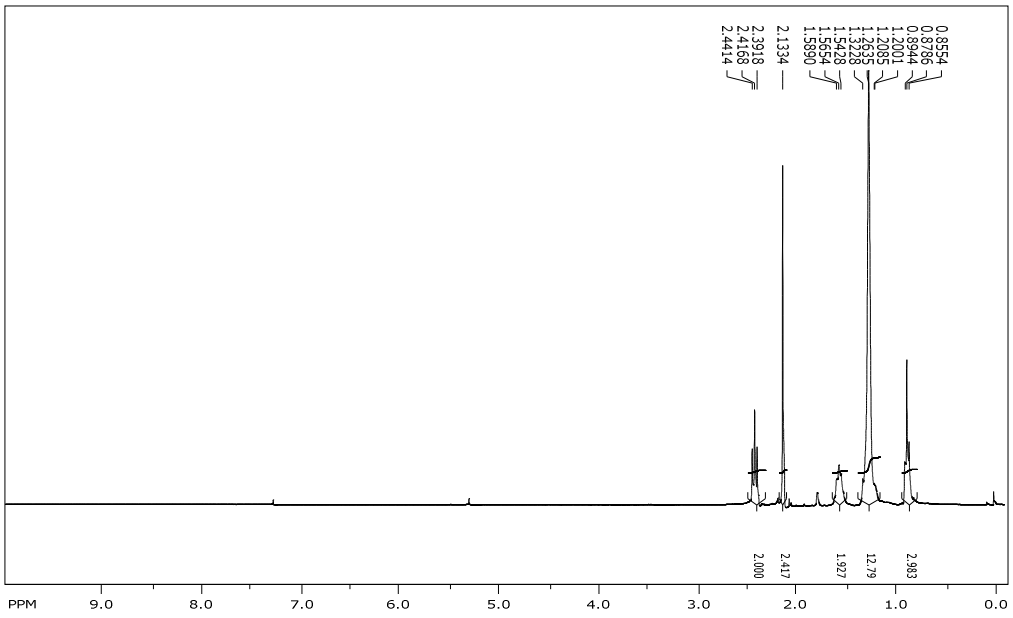


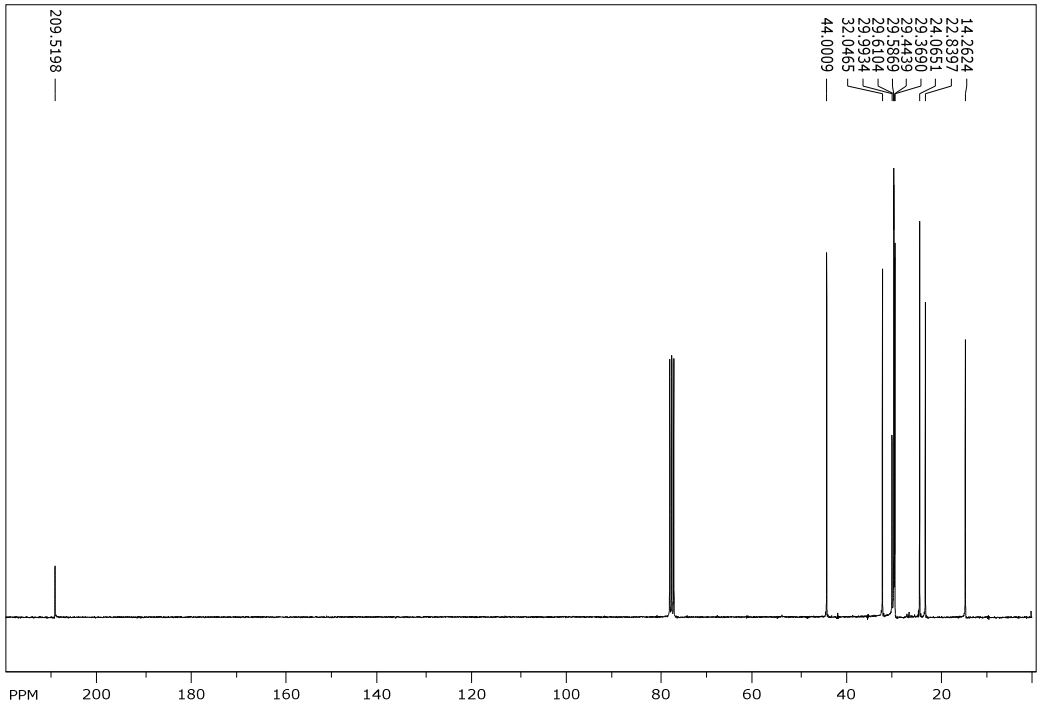
[Fe(OTf)$_2$(**7h**)$_2$] (**8h**), 298 K, CD_3CN



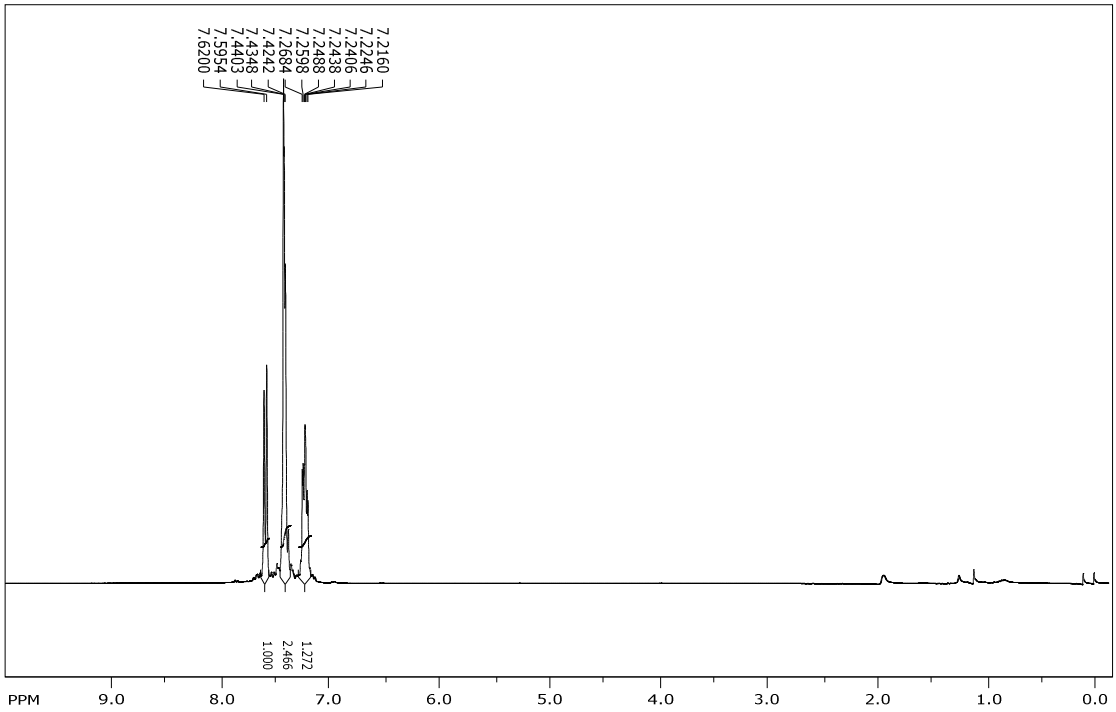
7. NMR spectra of the isolated oxidation products in Table 6.

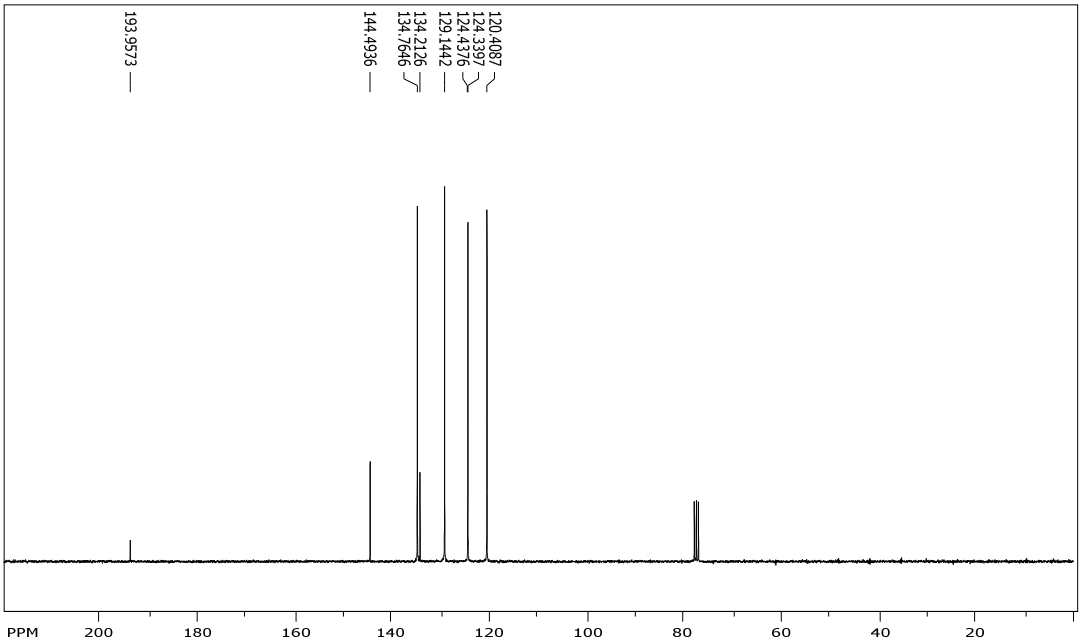
2-Undecanone ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



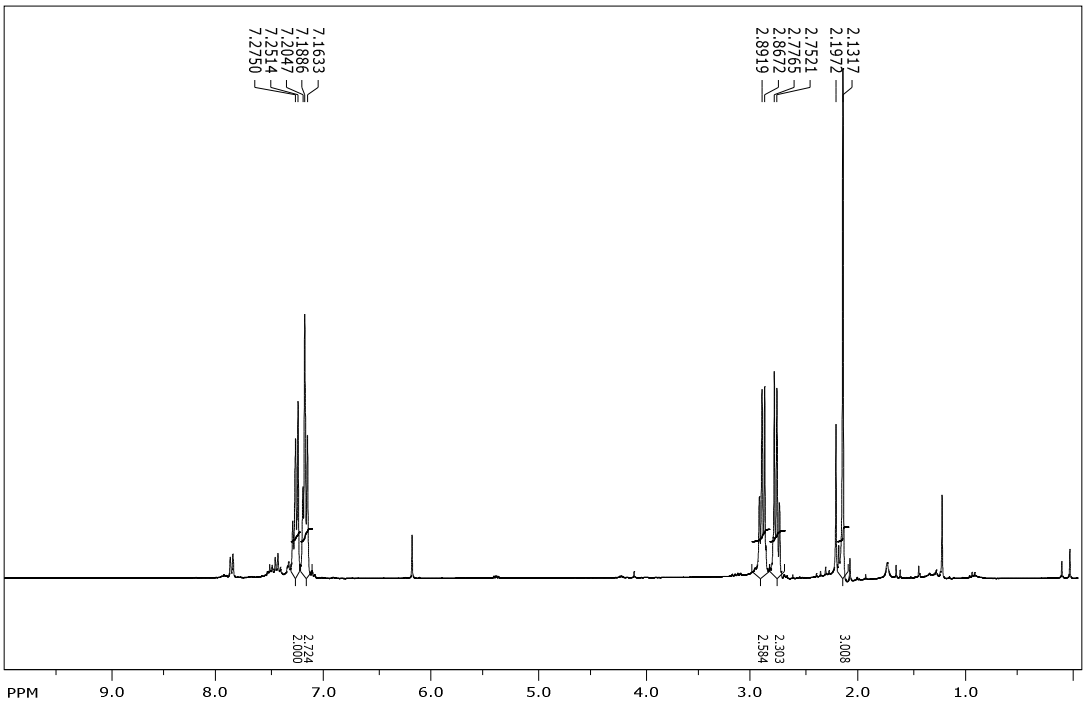


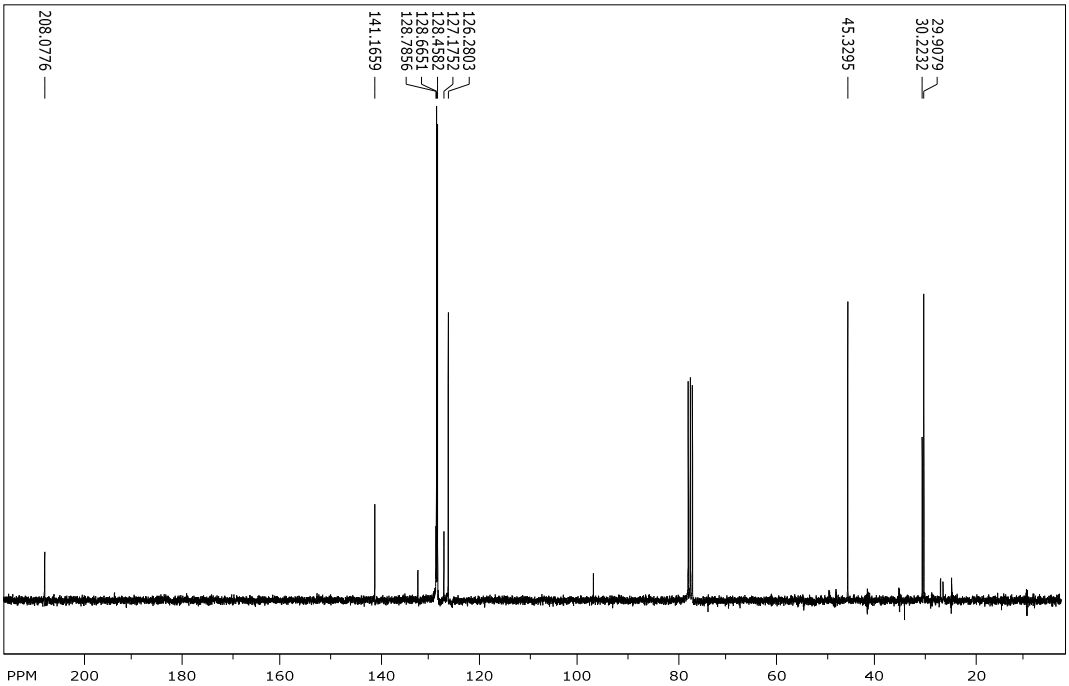
Fluorenone, ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



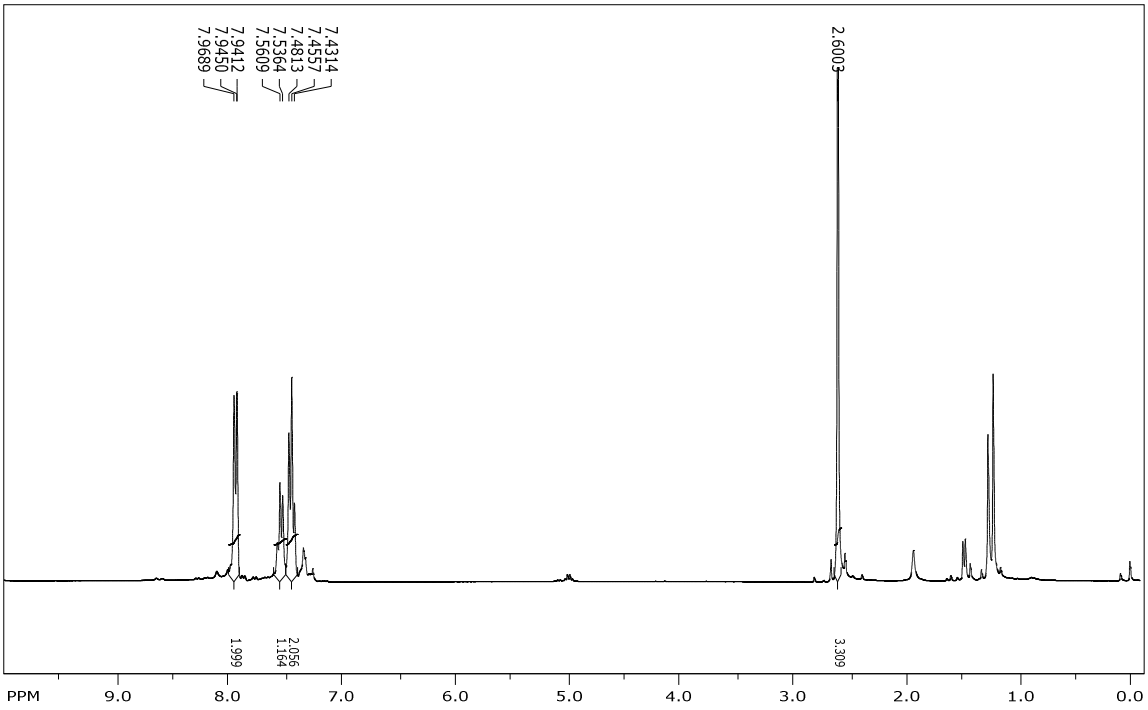


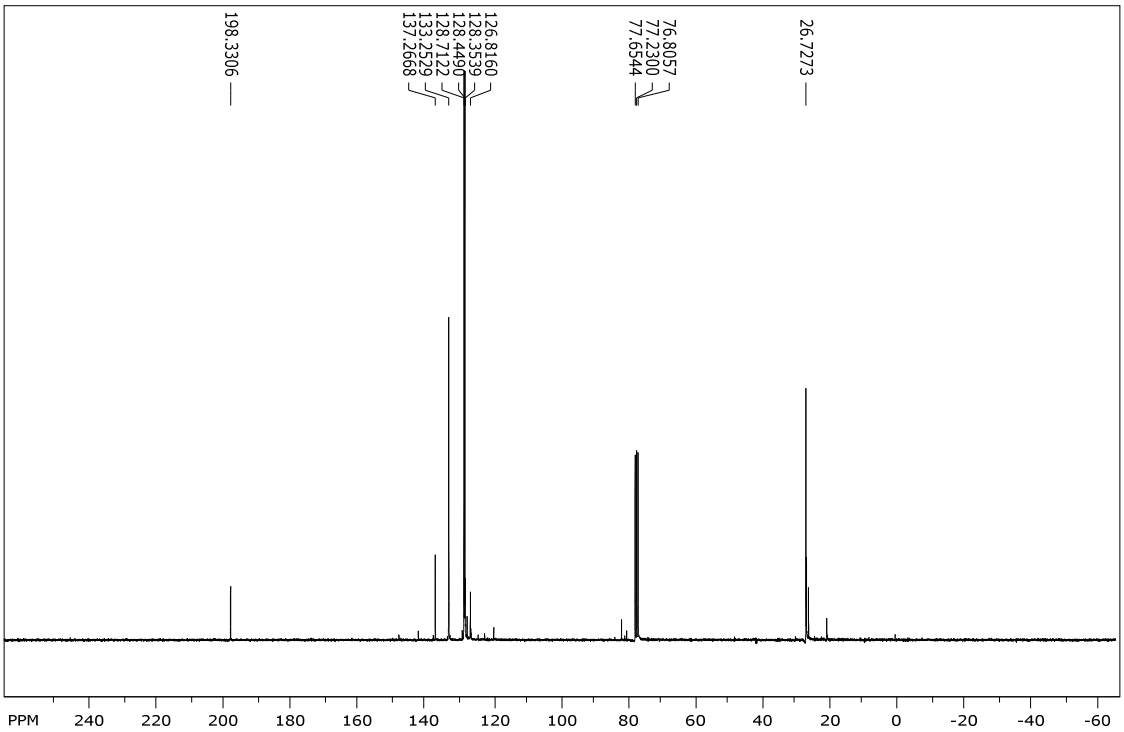
4-Phenyl-2-butanone, ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



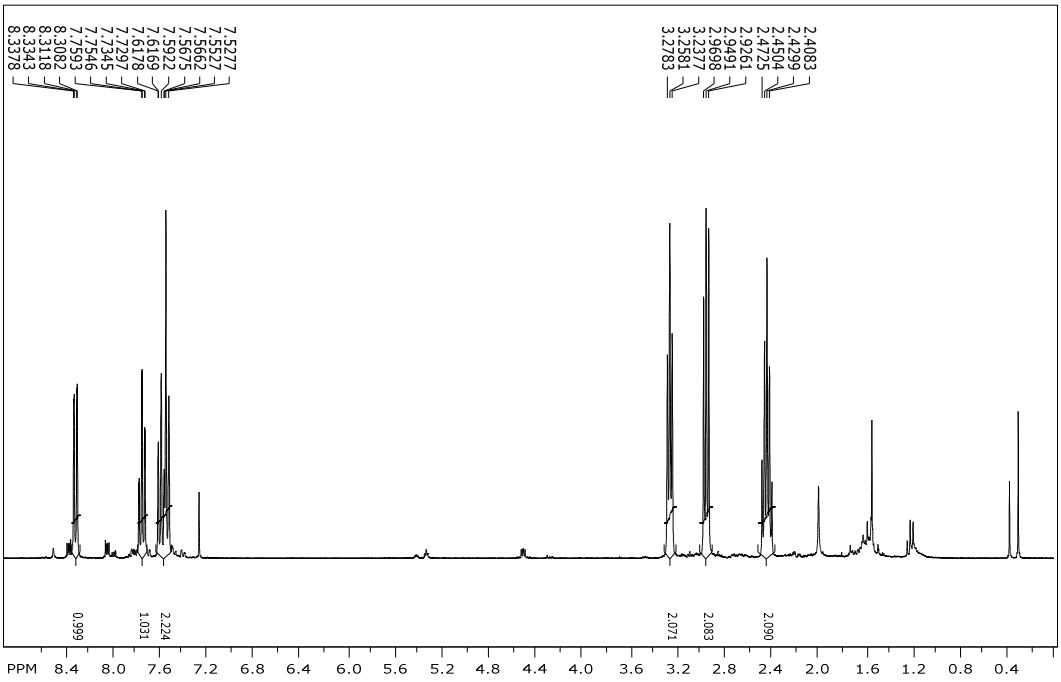


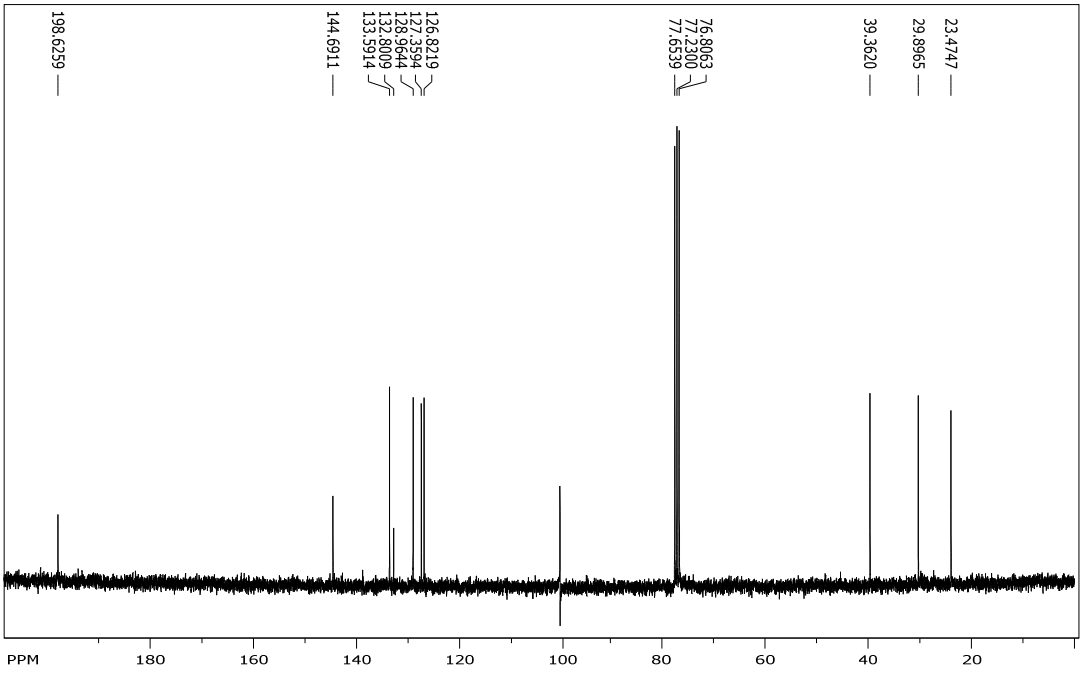
Acetophenone ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



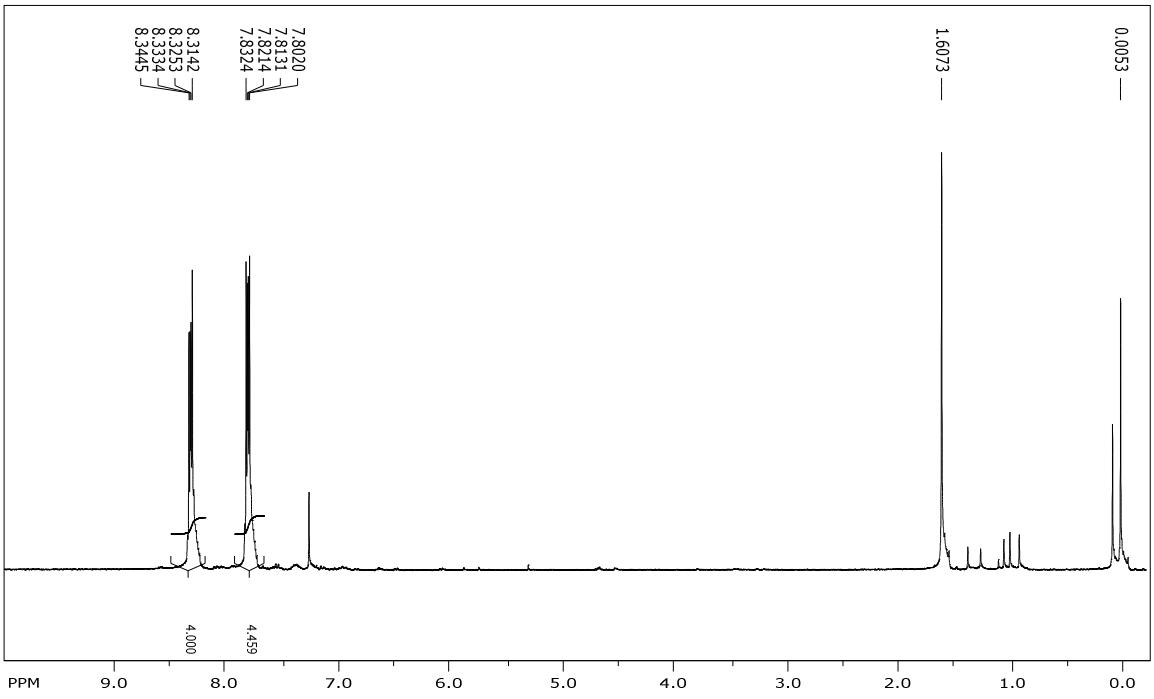


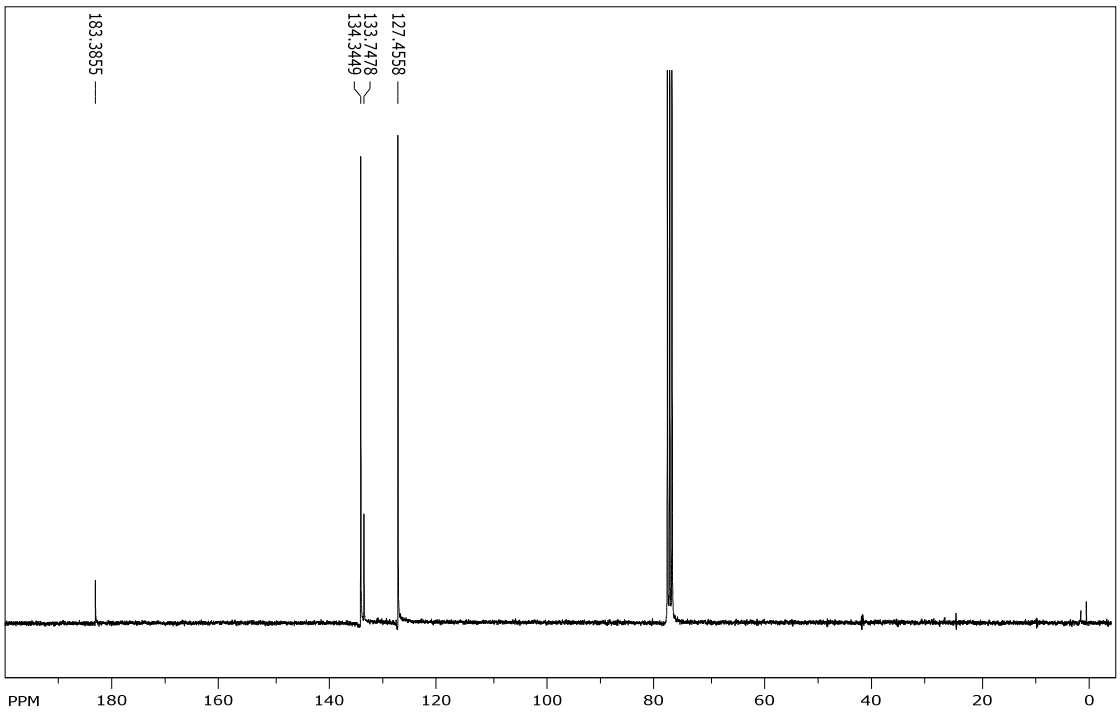
3,4-dihydronaphthalen-1(2H)-one, ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



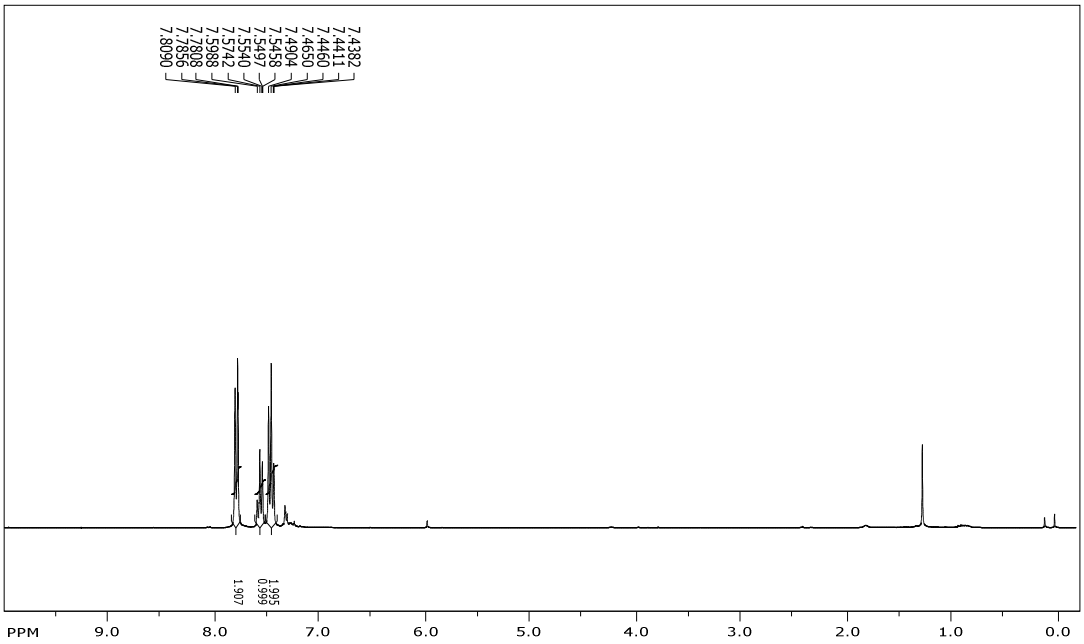


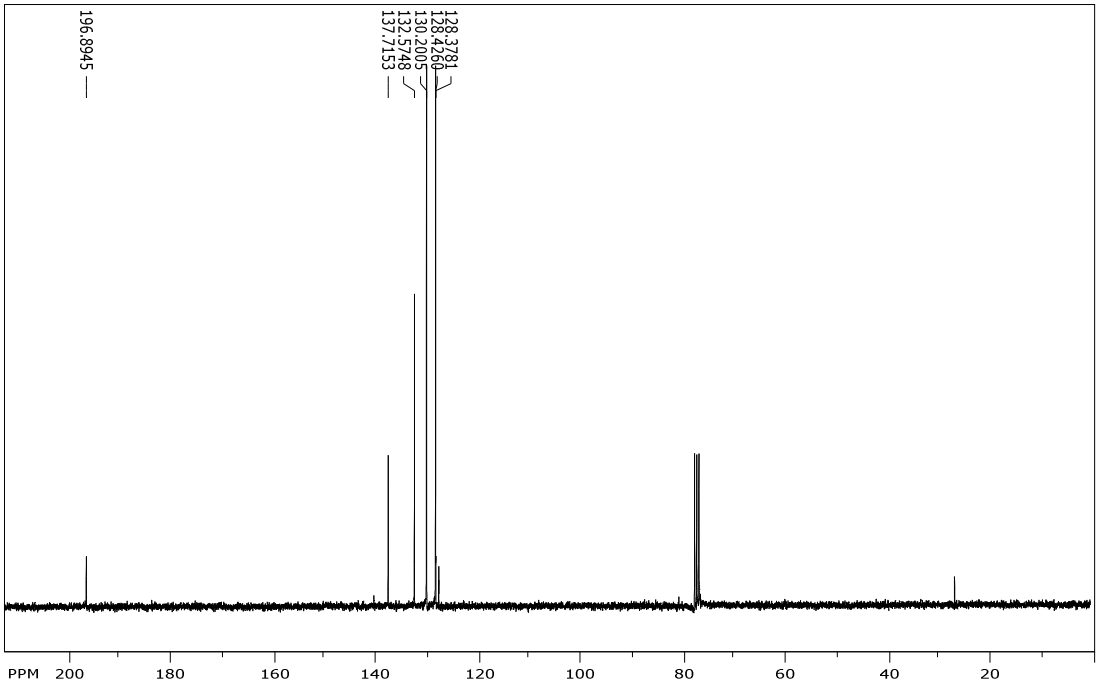
Anthraquinone, ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$





Benzophenone, ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$





Cyclooctanone, ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$