Electronic Supporting Information

Knölker-Type Iron Complexes Bearing an N-Heterocyclic Carbene Ligand: Synthesis, Characterization, and Catalytic Dehydration of Primary Amides

Saravanakumar Elangovan,[a] Samuel Quintero-Duque,[a] Vincent Dorcet,[b] Thierry Roisnel,[b] Lucie Norel,[a] Christophe Darcel,[a]* Jean-Baptiste Sortais[a]*

[a] UMR 6226 CNRS-Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Team Organometallics: Materials and Catalysis, Centre for Catalysis and Green Chemistry, Campus de Beaulieu, 263 av. du Général Leclerc, 35042 Rennes Cedex, France.

[b] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Centre de Diffractométrie X, Campus de Beaulieu, 263 av. du Général Leclerc, 35042 Rennes Cedex, France.

E-mail: christophe.darcel@univ-rennes1.fr, jean-baptiste.sortais@univ-rennes1.fr

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Synthesis of 1-mesityl-3-((*R*)-1-phenylethyl)imidazolium chloride salt

The imidazolium salt was prepared following the procedure described by Baslé and Maudit,[1] starting from *R*-(+)-α-methylbenzylamine (1.41 mL, 10 mmol). Pure compound was obtained after purification by column chromatography on silica gel (CH_2Cl_2/MeOH, 9/1 as the eluant). 900 mg, yield 28%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.85 (s, 1H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.36-7.29 (m, 3H), 7.19 (s, 1H), 6.92 (s, 1H, CH_{Im}), 6.91 (s, 1H, CH_{Im}), 6.67 (q, *J* = 7.0 Hz, 1H), 2.27 (s, 3H, CH_{3Mes}), 2.03 (s, 3H, CH_{3Mes}), 2.02 (d, *J* = 7.0 Hz, 3H), 1.95 (s, 3H, CH_{3Mes}).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.9, 138.1, 137.8, 134.0, 133.9, 130.7, 129.6, 129.2, 129.0, 127.1, 123.4, 120.9, 59.1 (CH), 20.9 (CH_{3Mes}), 20.6 (CH_3), 17.5 (CH_{3Mes}), 17.4 (CH_{3Mes}).

Anal. calc for $C_{20}H_{23}N_2Cl$: C, 73.49; H, 7.09; N, 8.57. Found: C, 73.31; H, 7.02; N, 8.32.

Electrochemical studies

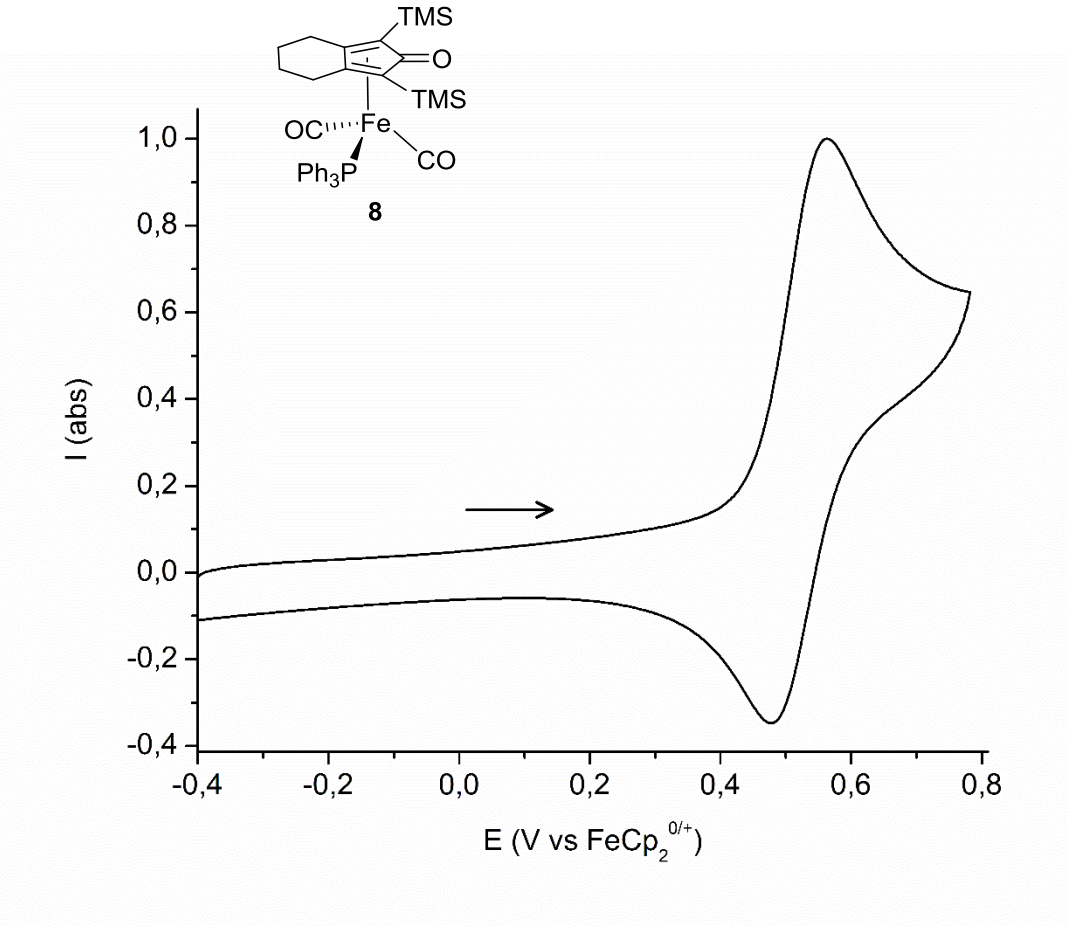


Figure S1. Normalized CV traces of the complex **8** in CH_2Cl_2 (0.2 M Bu_4NPF_6, v = 100 mV·s^{-1}).

Dehydration of primary amides

1. General procedure for the dehydration of the primary amides

A Schlenk tube containing a stirring bar was loaded with the primary amide (1.0 mmol), followed by the addition of the iron complex (0.05-0.08 mmol), the solvent (dry toluene or 1,4-dioxane : THF, 4 mL) and finally PMHS (5.0 mmol). The mixture was stirred for 24 h at 100 °C. After completion of reaction, the reaction mixture was cooled to r.t. The cooled reaction mixture was diluted with ethyl acetate (5 mL) and concentrated under reduced pressure (850 mbar, 40 °C). The residue was purified by silica gel column chromatography and gave the corresponding nitrile derivatives.

2. Optimization of the parameters of the reaction.

Table S1: Optimization of parameters of the dehydration of benzamide with the complex 2[a]

Entry	*PMHS (equiv.)*	*Solvent*	*Temp (°C)*	*Yield (%)[b]*
1	5	Toluene	100	97
2	5	CPME	100	97
3	5	1,4 dioxane	100	94
4	5	THF	70	13
5	5	DMC	100	0
6	5	EtOH	100	0
7	5	Toluene	70	12
8 [c]	5	CPME	100	51
9	3	CPME	100	87
10	2	CPME	100	35
11	5	CPME	UV	6

[a] Typical conditions: catalyst (5 mol%), benzamide (0.25 mmol), toluene (2 mL), and PMHS (5 equiv.) were added in this order under argon atmosphere and the solution was heated at 100 °C for 24 h. [b] Determined by GC using dodecane as the internal standard. [c] 3 mol% of catalyst **2** was used.

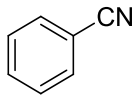
Table S2: Screening of the complexes[a]

Entry	*Catalyst (5 mol%)*	*PMHS (equiv.)*	*Solvent*	*Temp (°C)*	*Yield(%)* [b]
1	2	3	CPME	80	18
		5	toluene	100	97
2	3	3	CPME	80	24
		5	toluene	100	97
3	4	3	CPME	80	29
		5	toluene	100	97
4	5	3	CPME	80	0
		5	toluene	100	97
5	6	3	CPME	80	0
		5	toluene	100	97
6	**1**	5	toluene	100	2
7	(IMes) $Fe(CO)_4$	5	toluene	100	57

[a] catalyst (5 mol%), benzamide (0.25 mmol), solvent (2 mL), and PMHS (3-5 equiv.) were added in this order under argon atmosphere and the solution was heated to 80-100 °C for 24 h.
[b] Determined by GC using dodecane as the internal standard.

3. Characterization data of the nitrile products.

Benzonitrile [2]

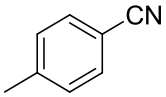


The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), colorless oil, 75 mg, 72% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 112.4, 118.8, 129.0, 132.1, 132.7.

4-Methylbenzonitrile [2]

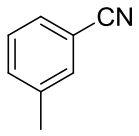


The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), colorless oil, 98 mg, 84% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 21.7, 109.1, 119.0, 129.7, 131.9, 143.6.

3-Methylbenzonitrile [3]

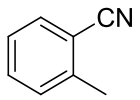


The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), colorless oil, 90 mg, 77% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.32-7.46 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 21.1, 112.2, 119.0, 128.9, 129.2, 132.5, 133.6, 139.2.

2-Methylbenzonitrile [2]

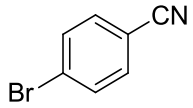


The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), colorless oil, 85 mg, 72% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3 H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 20.4, 112.8, 118.0, 126.2, 130.2, 132.5, 132.6, 141.9.

4-Bromobenzonitrile [3]

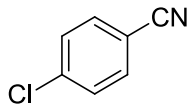


The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), white powder, 96 mg, 53% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 111.2, 118.0, 127.9, 132.6, 133.4.

***p*-Chlorobenzonitrile** [2]

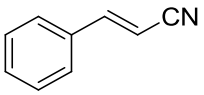


The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), white powder, 71 mg, 52% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.6 Hz, 2 H), 7.60 (d, *J* = 8.6 Hz, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 110.8, 118.0, 129.7, 133.3, 139.5.

Cinnamonitrile [3]



The compound was prepared as described in the general procedure. Purification by flash chromatography (Petroleum ether/ethyl acetate: 80:20), white powder, 80 mg, 61% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (d, *J* = 16.7 Hz, 1H), 7.39-7.46 (m, 6H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 96.3, 118.1, 127.3, 129.1, 131.2, 133.5, 150.5.

References

1. Queval, P.; Jahier, C.; Rouen, M. ; Artur, I. ; Legeay, J.-C. ; Falivene, L. ; Toupet, L. ; Crévisy, C. ; Baslé, O. ; Maudit M. *Angew. Chem. Int. Ed.* **2013**, *52*, 14103-14107.
2. Hanada, S.; Motoyama, Y.; Nagashima, H. *Eur. J. Org. Chem*., **2008**, 4097-4100.
3. Zhou, S.; Addis, D.; Das, S.; Junge, K.; Beller, M.; *Chem. Commun*. **2009**, 4883-4885.

^{1}H NMR and ^{13}C{^{1}H} NMR data for the compounds

^{1}H and ^{13}C{^{1}H} Spectra of the new NHC salt

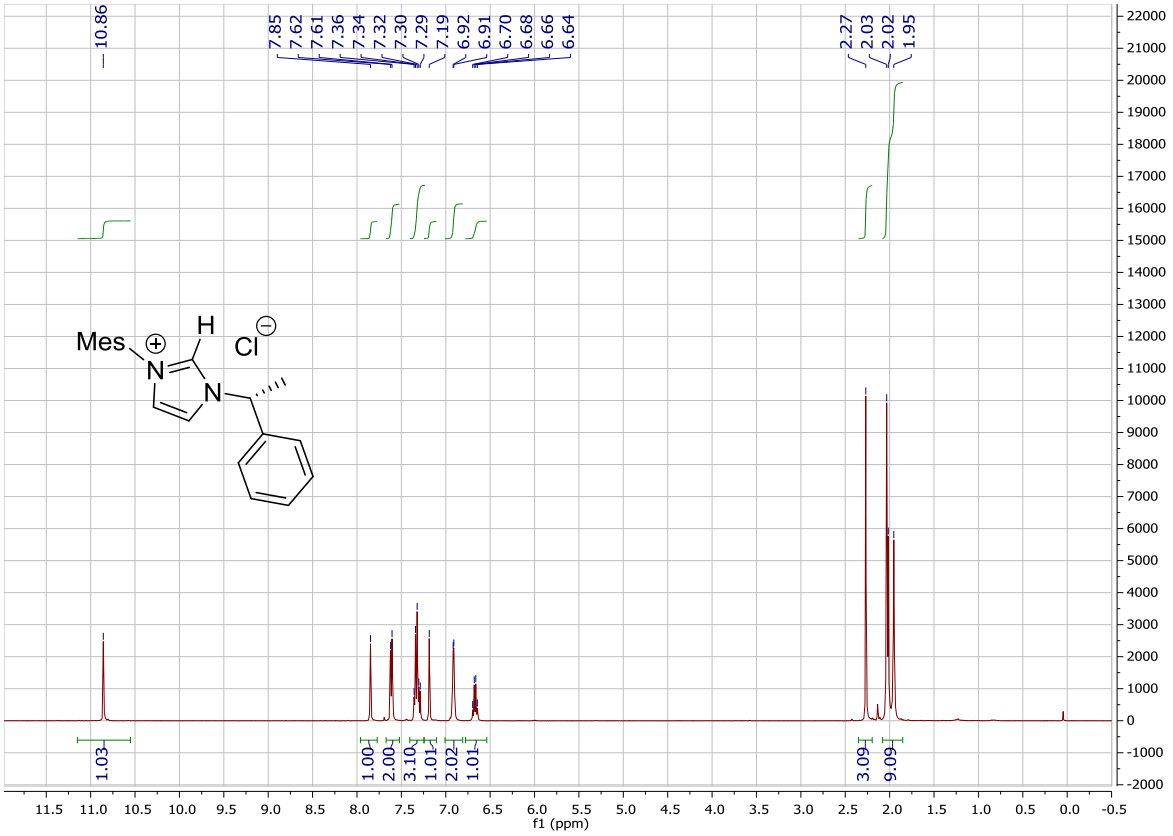


Figure S2: ^{1}H NMR spectrum of 1-mesityl-3-((*R*)-1-phenylethyl)imidazolium chloride salt in $CDCl_3$ recorded at 400 MHz.

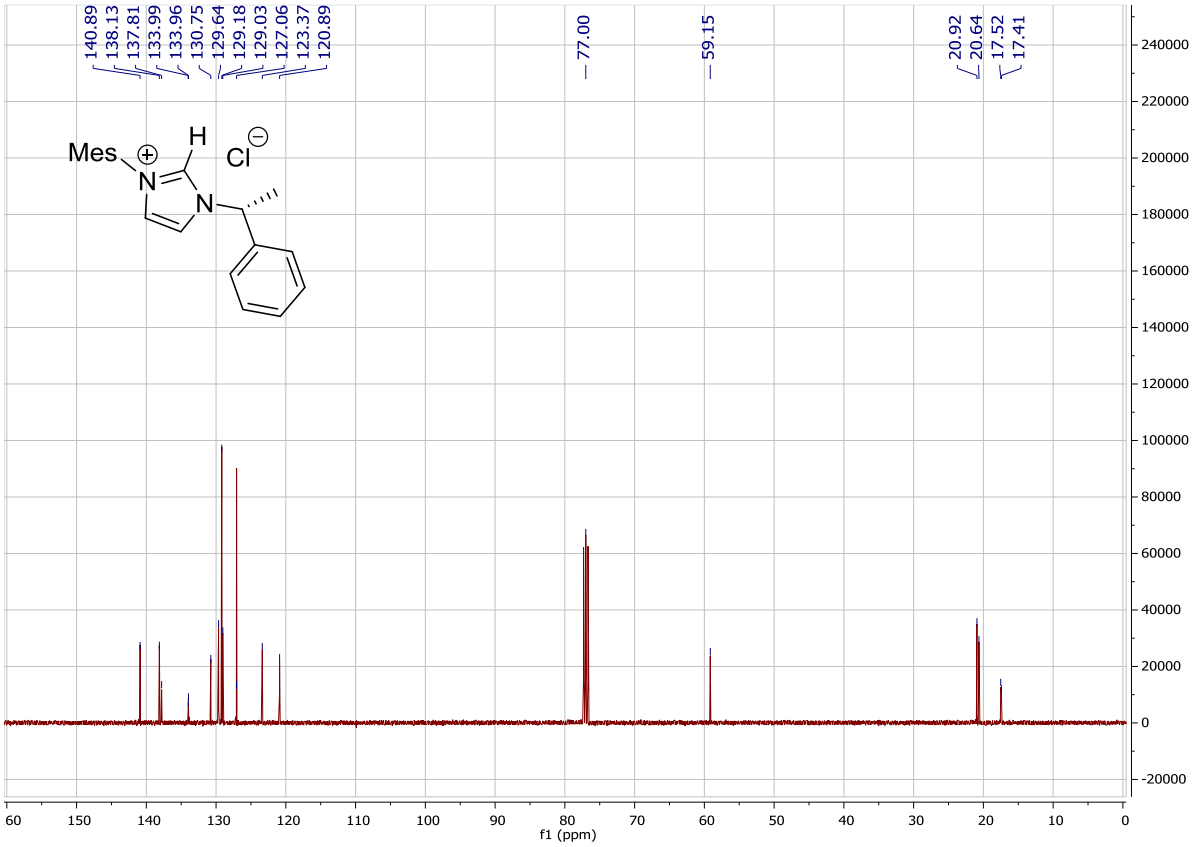


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of 1-mesityl-3-((*R*)-1-phenylethyl)imidazolium chloride salt in $CDCl_3$ recorded at 101 MHz.

^{1}H and $^{13}C\{^{1}H\}$ Spectra of the complexes 2-7

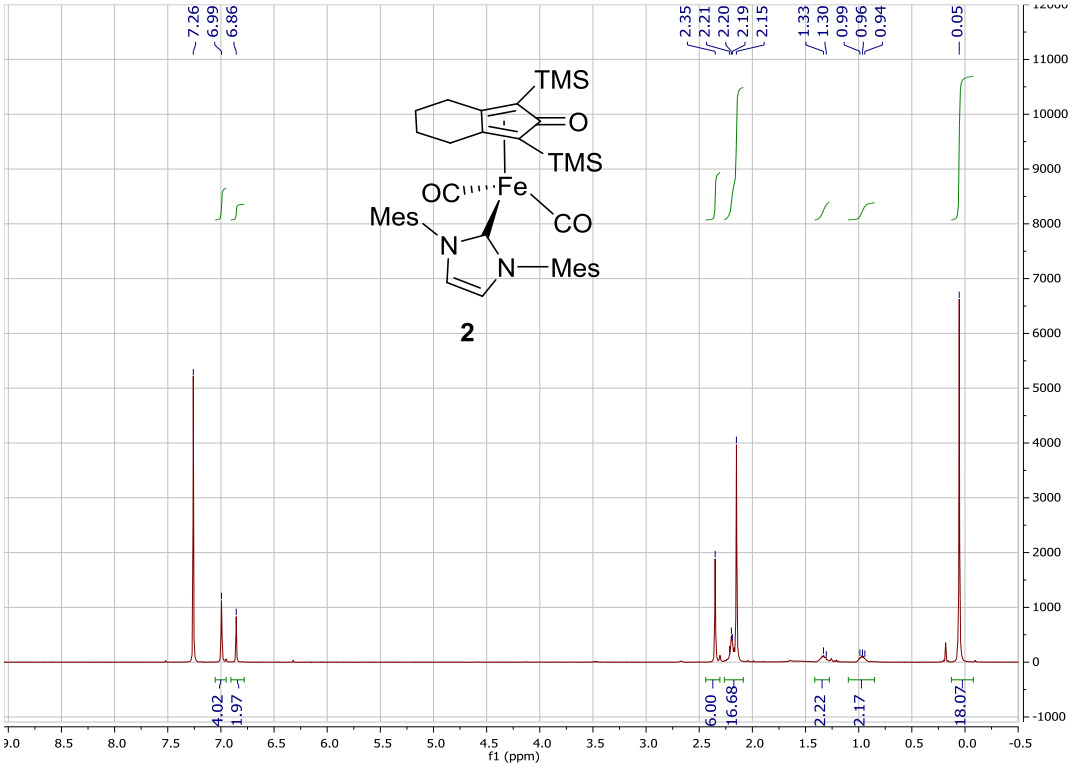


Figure S4: ^{1}H NMR spectrum of the complex **2** in $CDCl_3$ recorded at 400MHz.

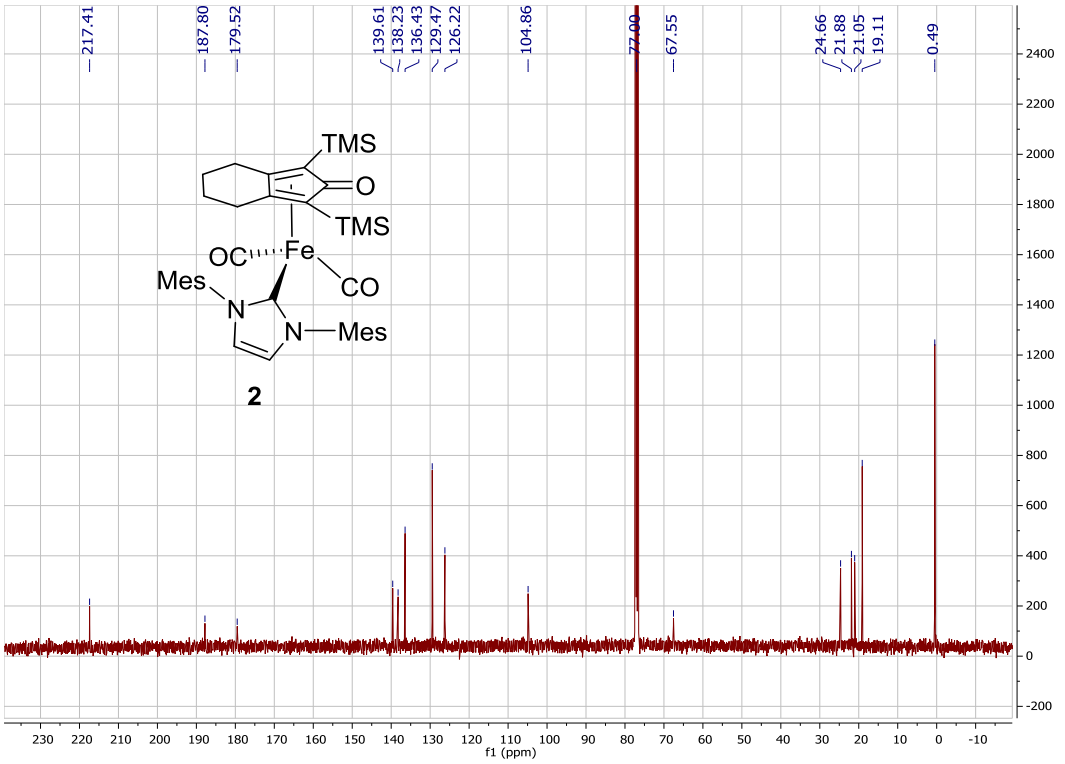


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **2** in $CDCl_3$ recorded at 101 MHz.

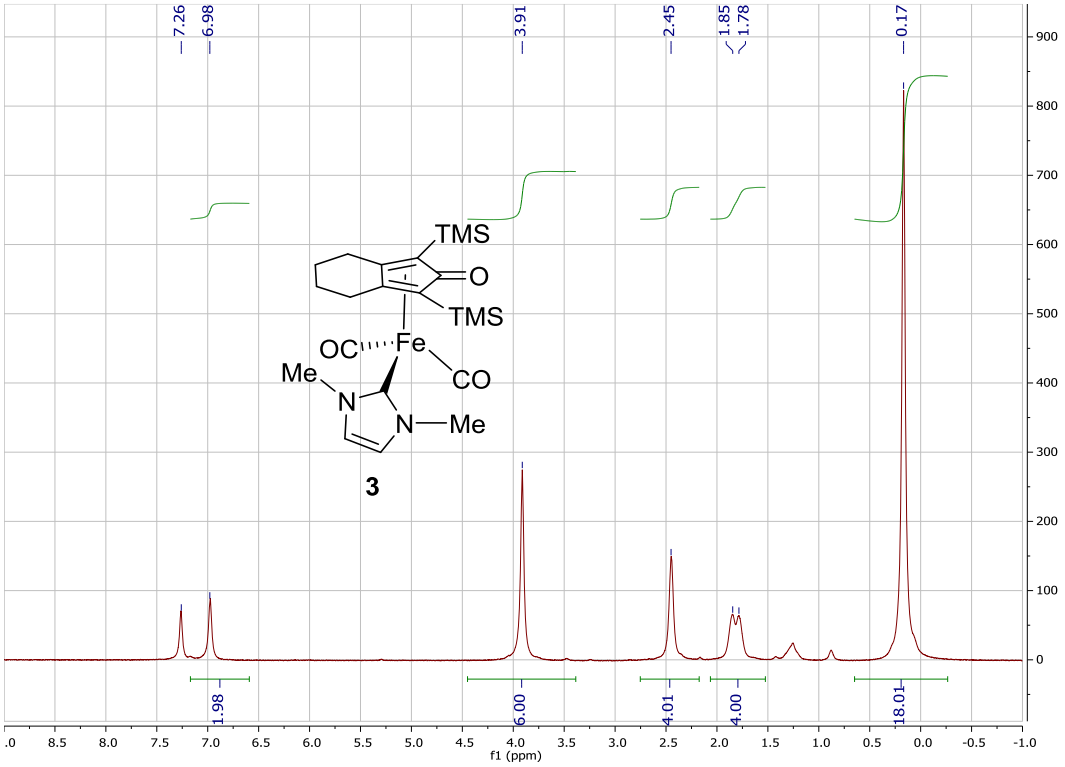


Figure S6: ^{1}H NMR spectrum of the complex **3** in $CDCl_3$ recorded at 500MHz.

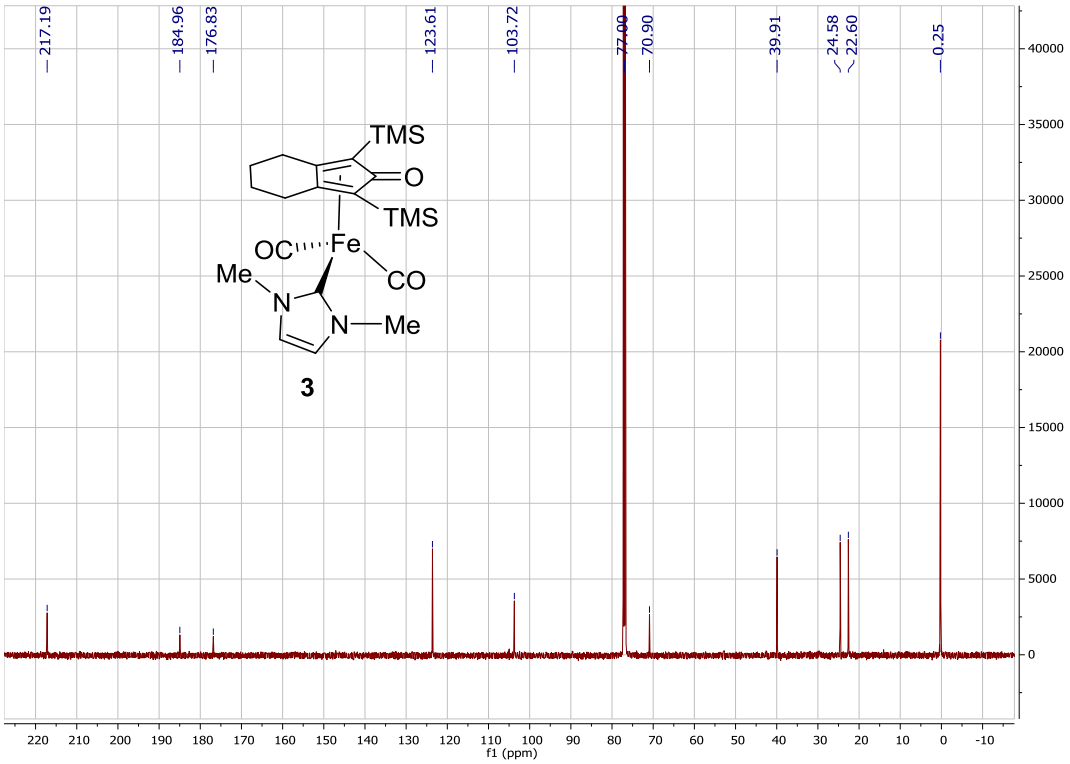


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **3** in $CDCl_3$ recorded at 125 MHz.

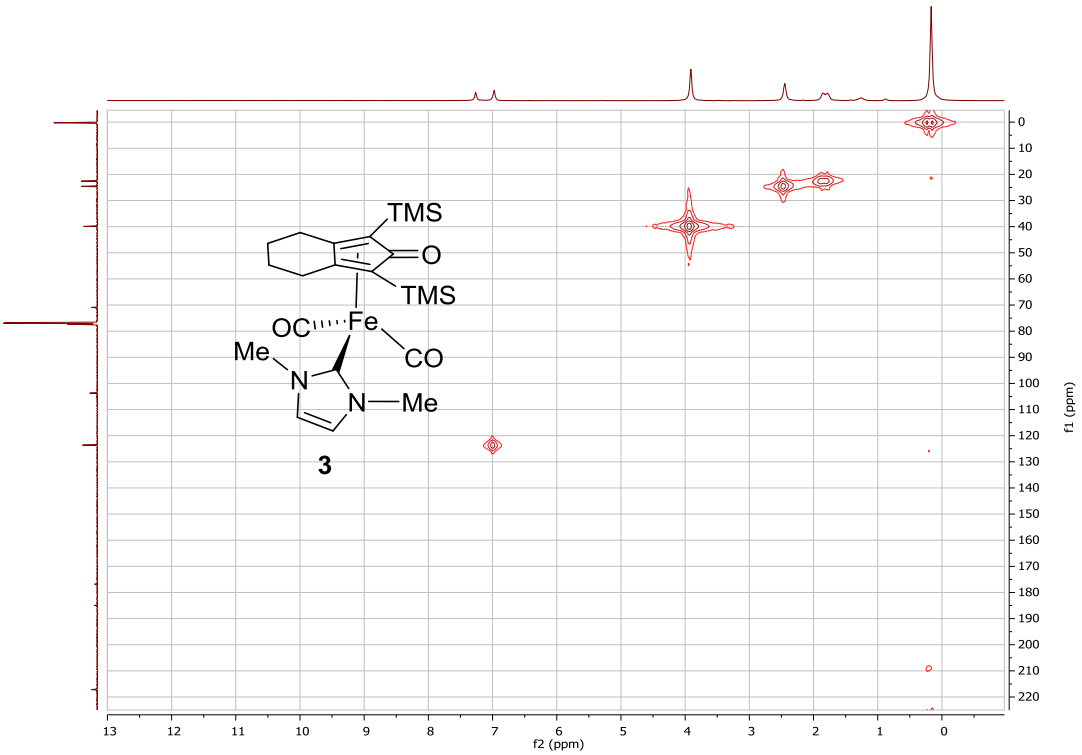


Figure S8: ^{1}H ^{13}C HSQC NMR spectrum of the complex **3** in $CDCl_3$ recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

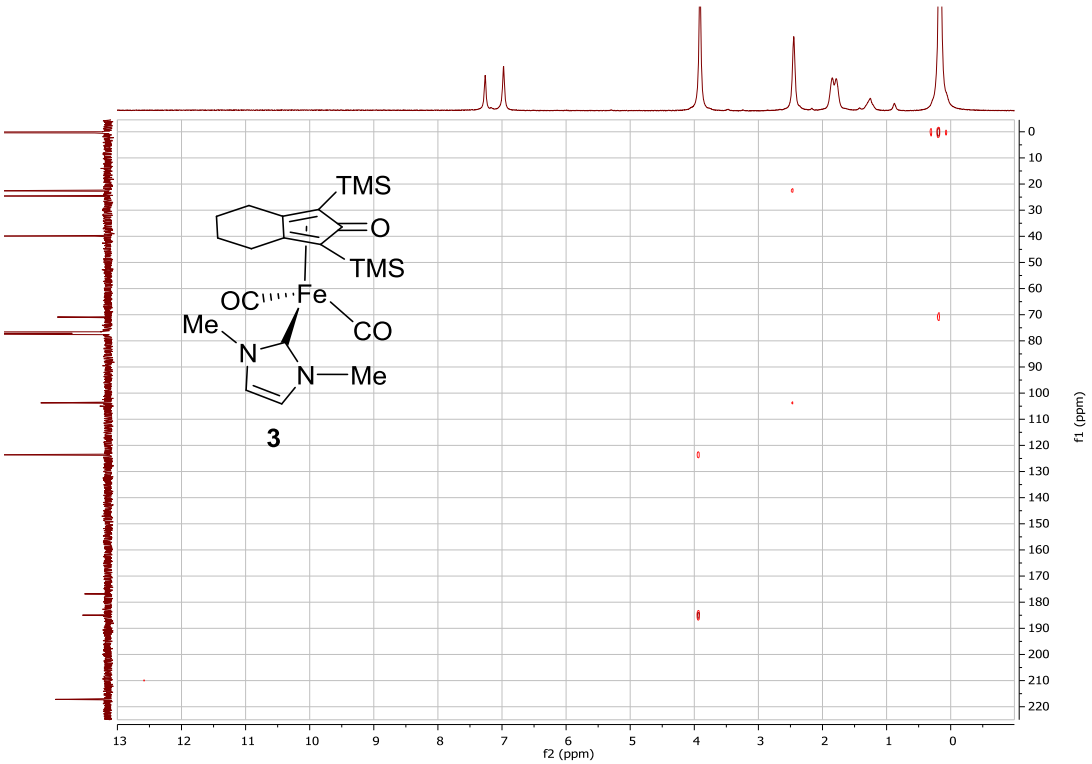


Figure S9: ^{1}H ^{13}C HMBC NMR spectrum of the complex **3** in $CDCl_3$ recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

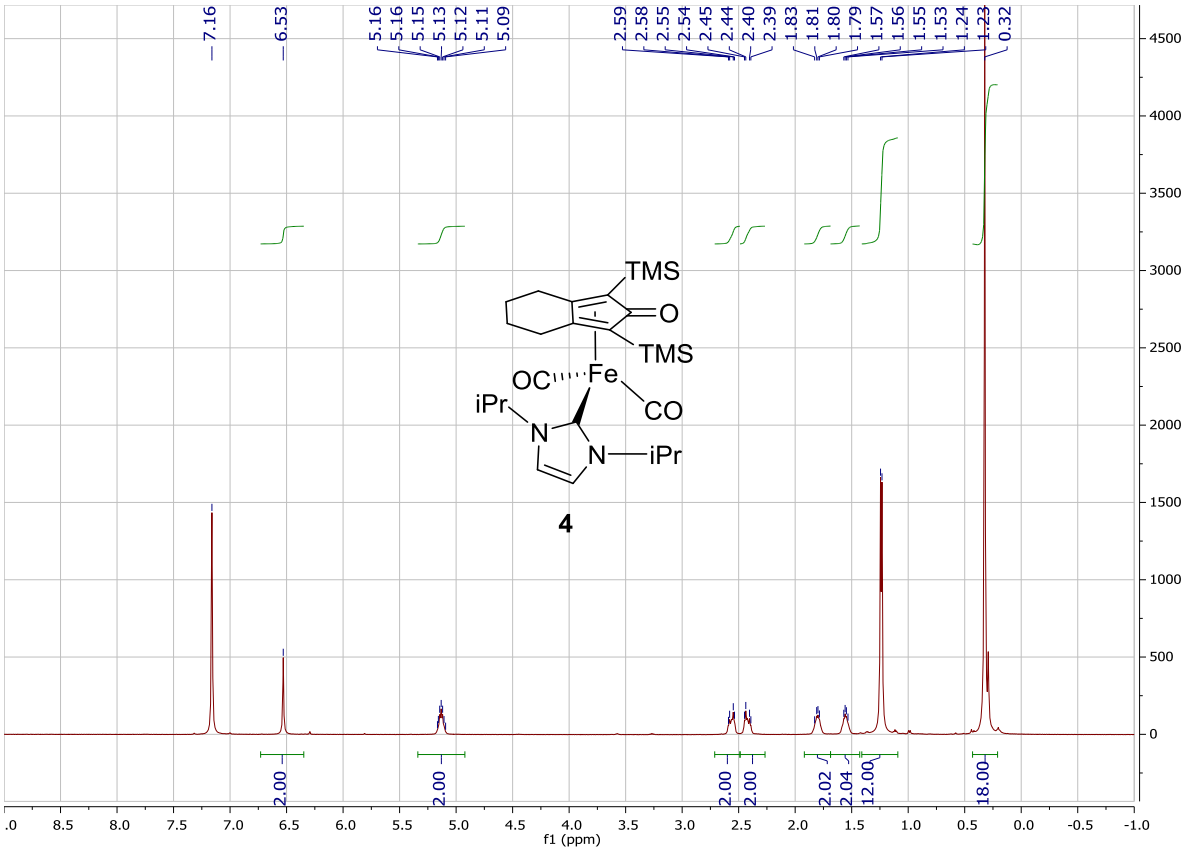


Figure S10: ^{1}H NMR spectrum of the complex **4** in C_6D_6 recorded at 500MHz.

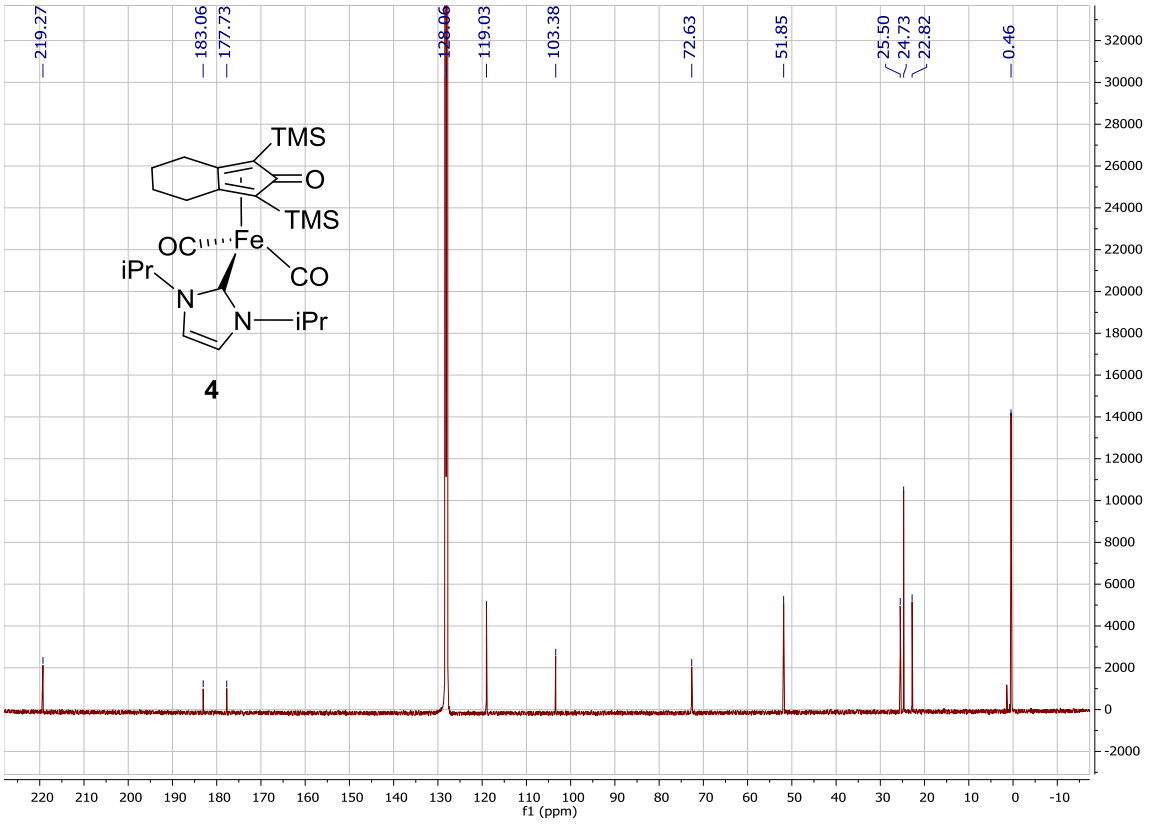


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **4** in C_6D_6 recorded at 125 MHz.

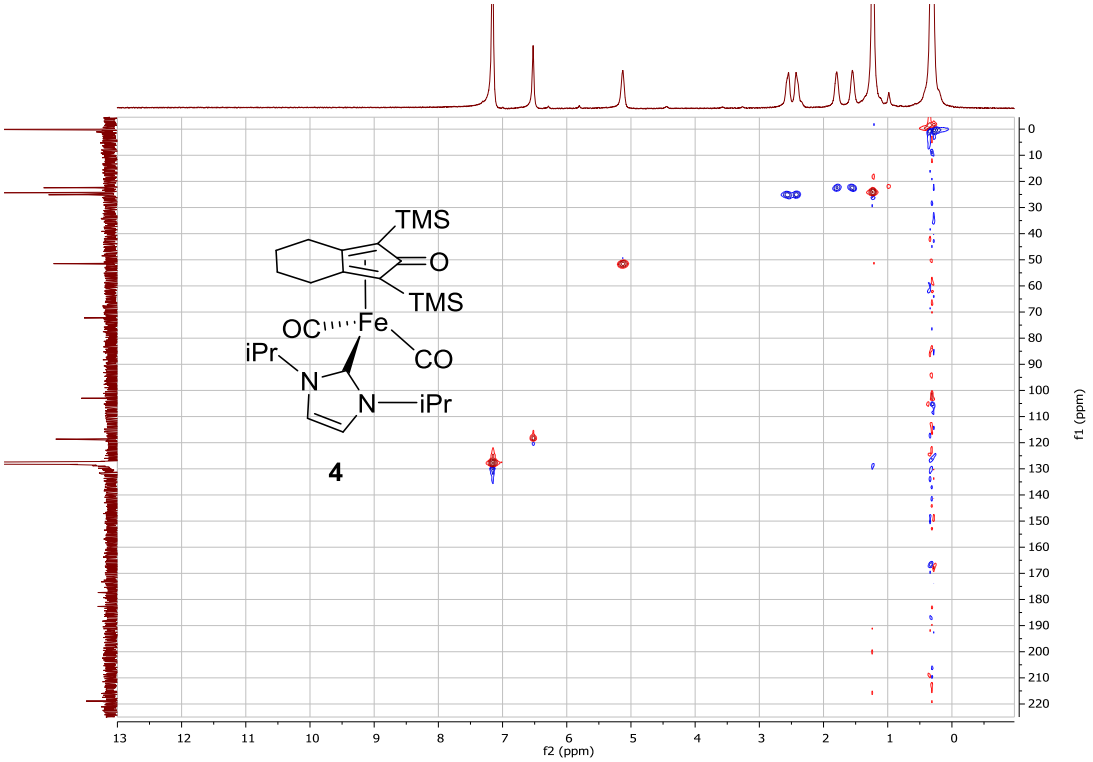


Figure S12: $^{1}H\,^{13}C$ HSQC NMR spectrum of the complex **4** in C_6D_6 recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

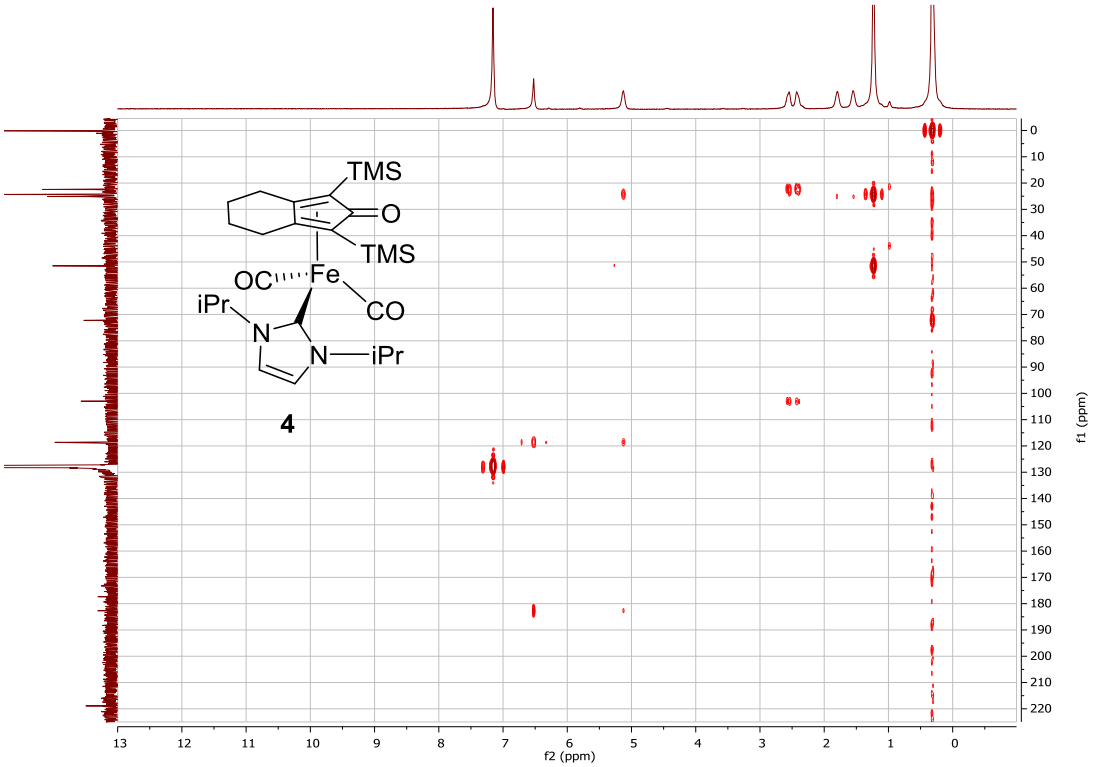


Figure S13: $^{1}H\,^{13}C$ HMBC NMR spectrum of the complex **4** in C6D6 recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

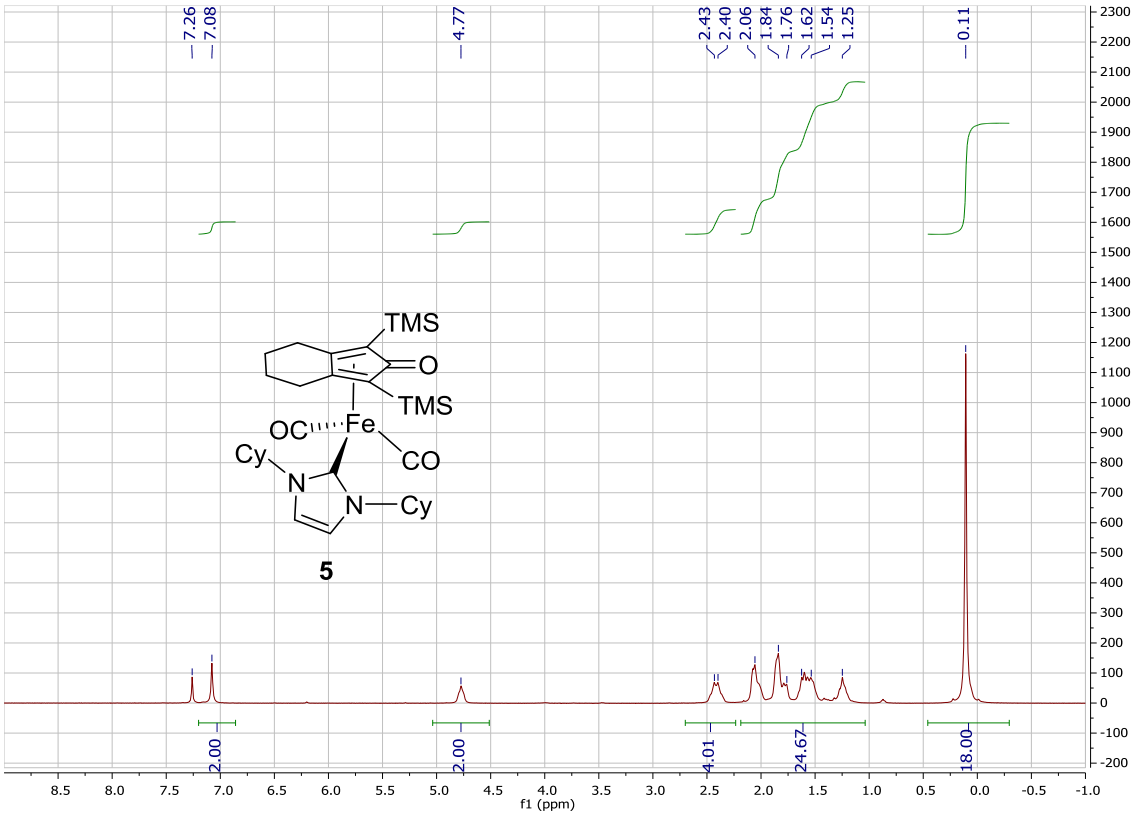


Figure S14: ^{1}H NMR spectrum of the complex **5** in $CDCl_3$ recorded at 500MHz.

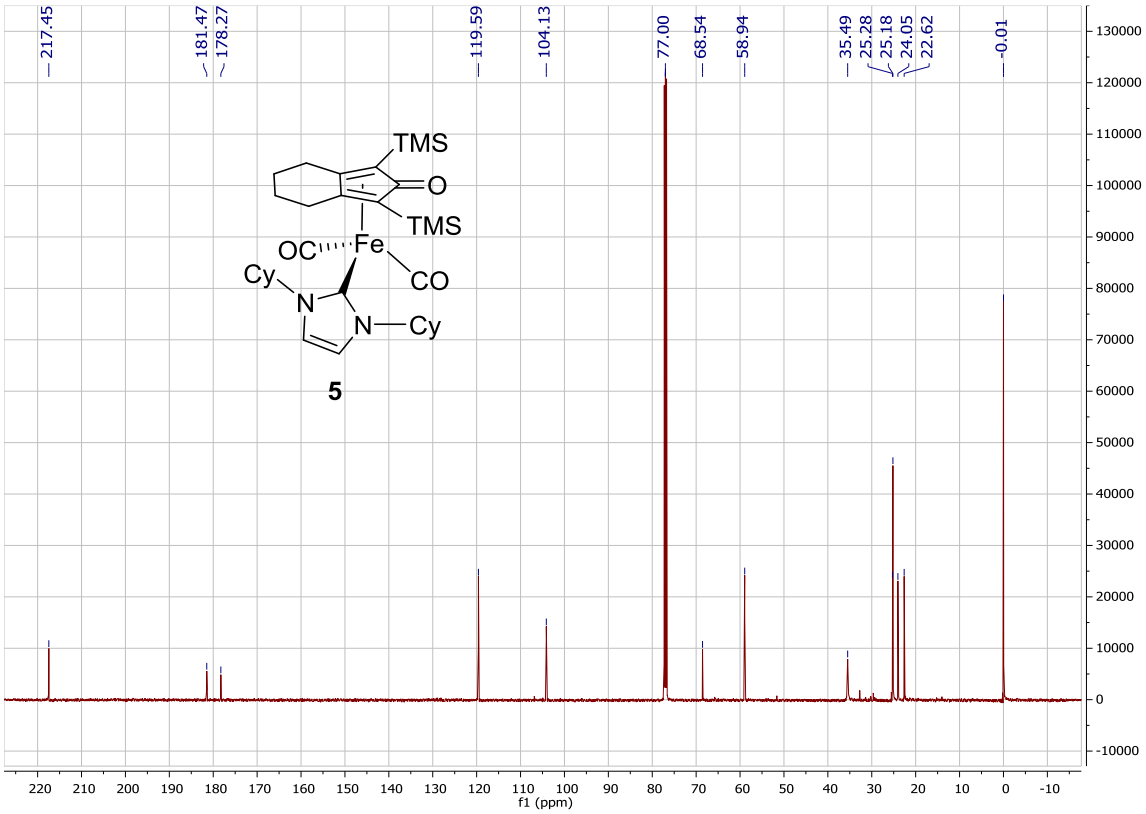


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **5** in $CDCl_3$ recorded at 125 MHz.

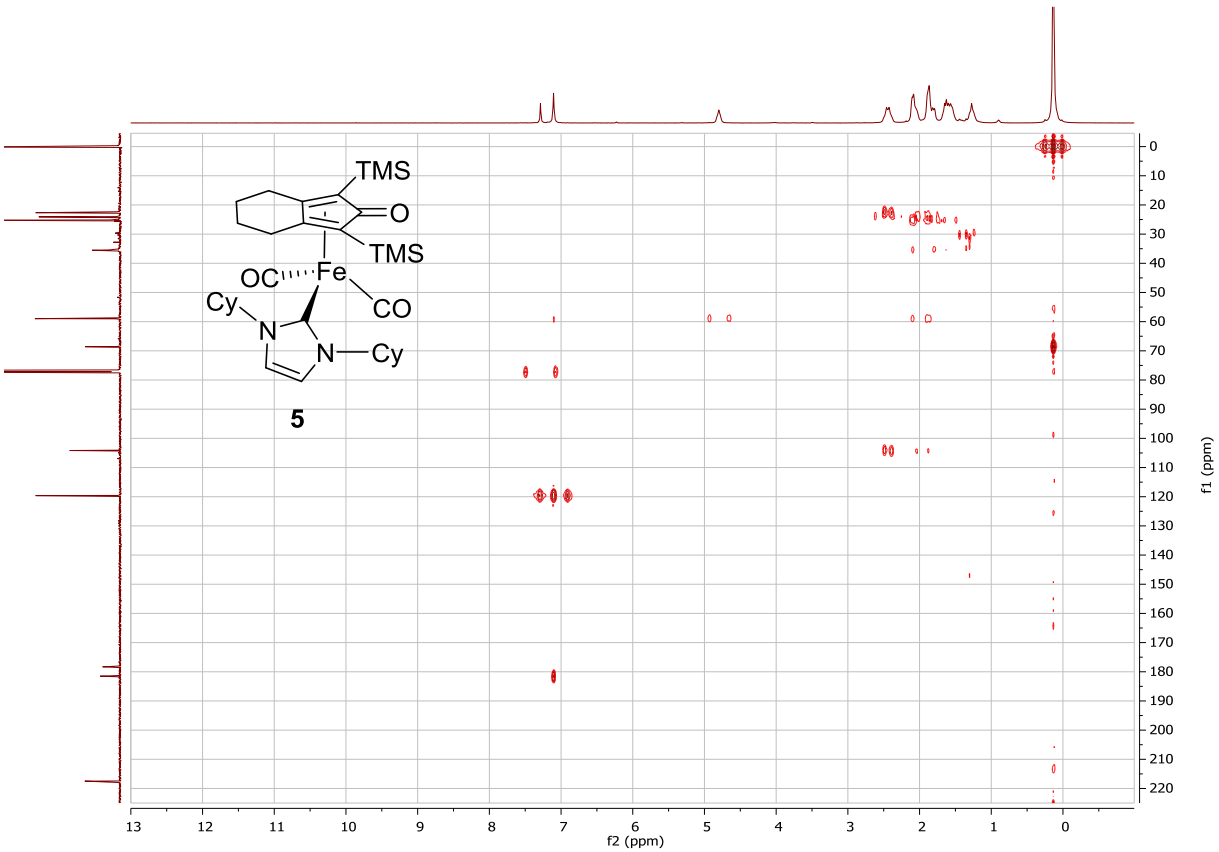


Figure S16: ^{1}H ^{13}C HMBC NMR spectrum of the complex **5** in $CDCl_3$ recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

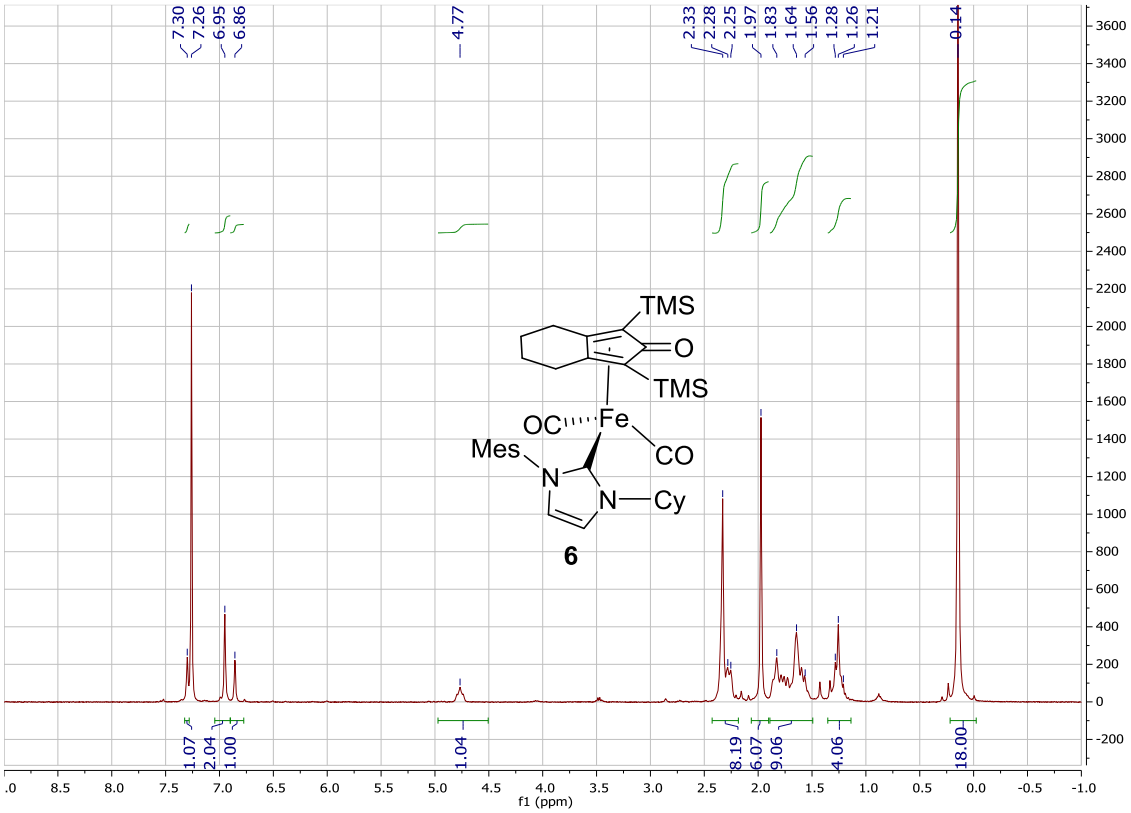


Figure S17: ^{1}H NMR spectrum of the complex **6** in $CDCl_3$ recorded at 400MHz.

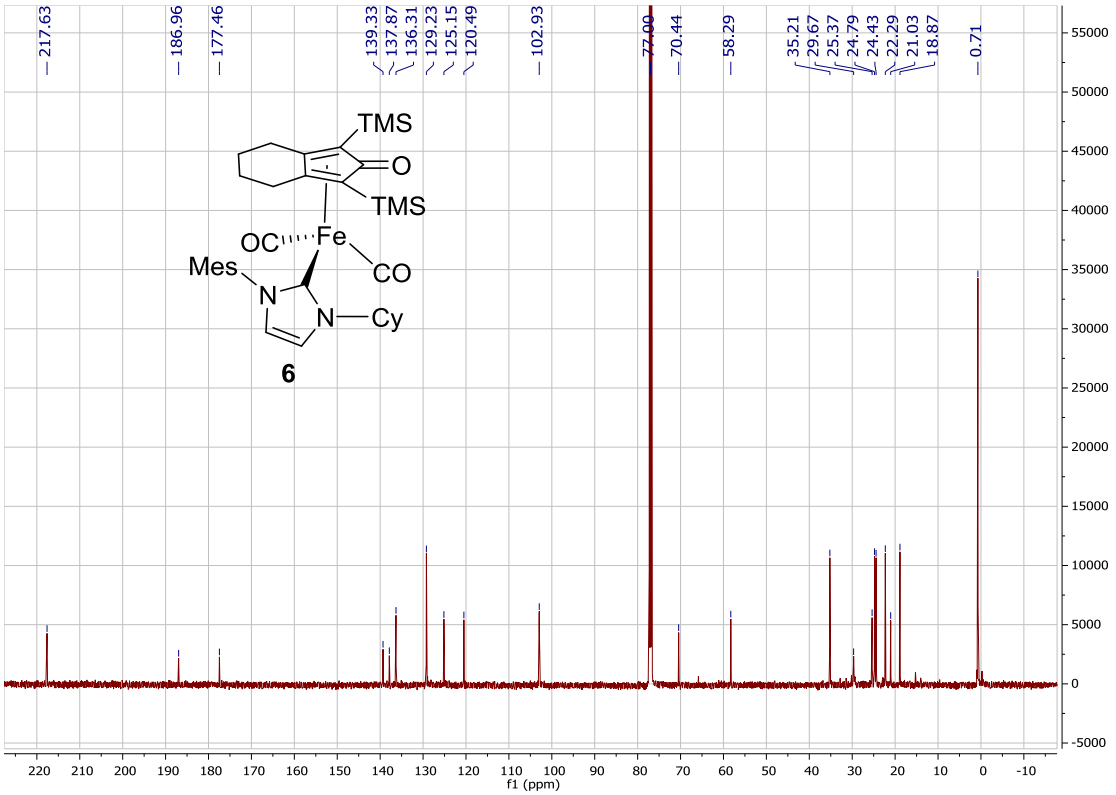


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **6** in $CDCl_3$ recorded at 125 MHz.

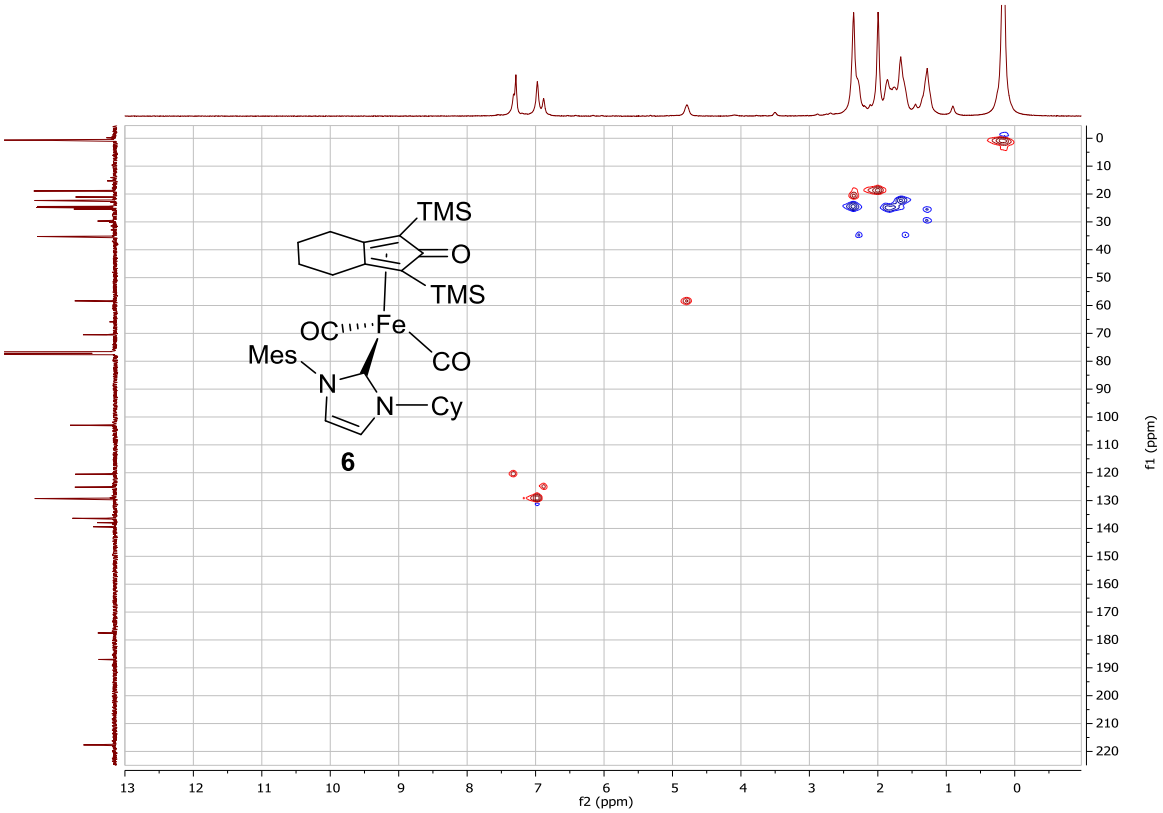


Figure S19: ^{1}H ^{13}C HSQC NMR spectrum of the complex **6** in $CDCl_3$ recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

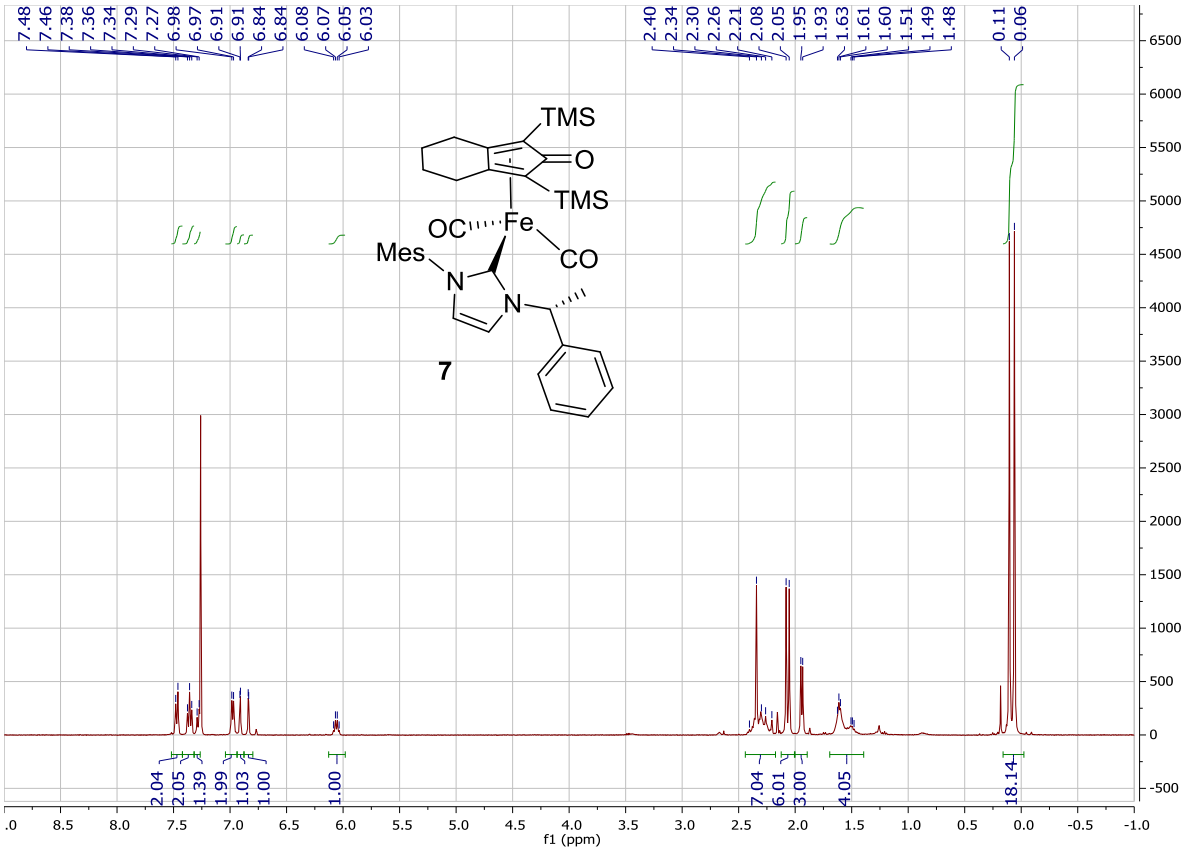


Figure S20: ^{1}H NMR spectrum of the complex **7** in $CDCl_3$ recorded at 400MHz.

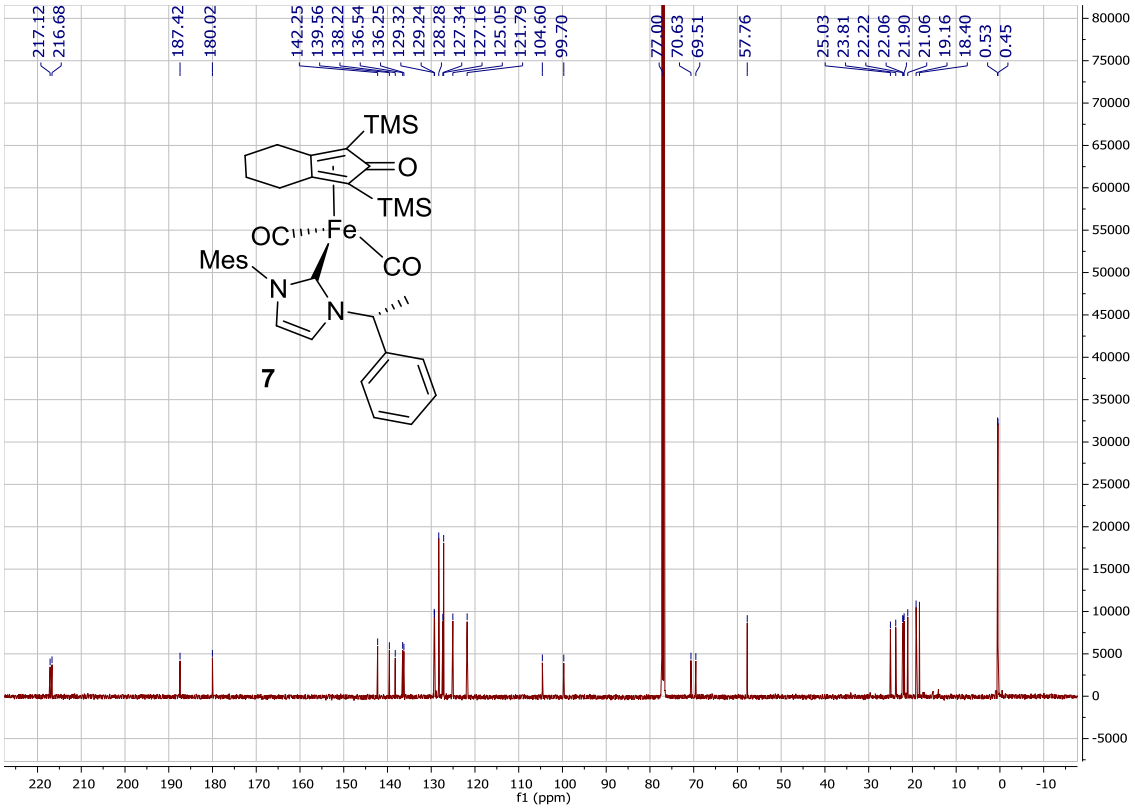


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **7** in $CDCl_3$ recorded at 125 MHz.

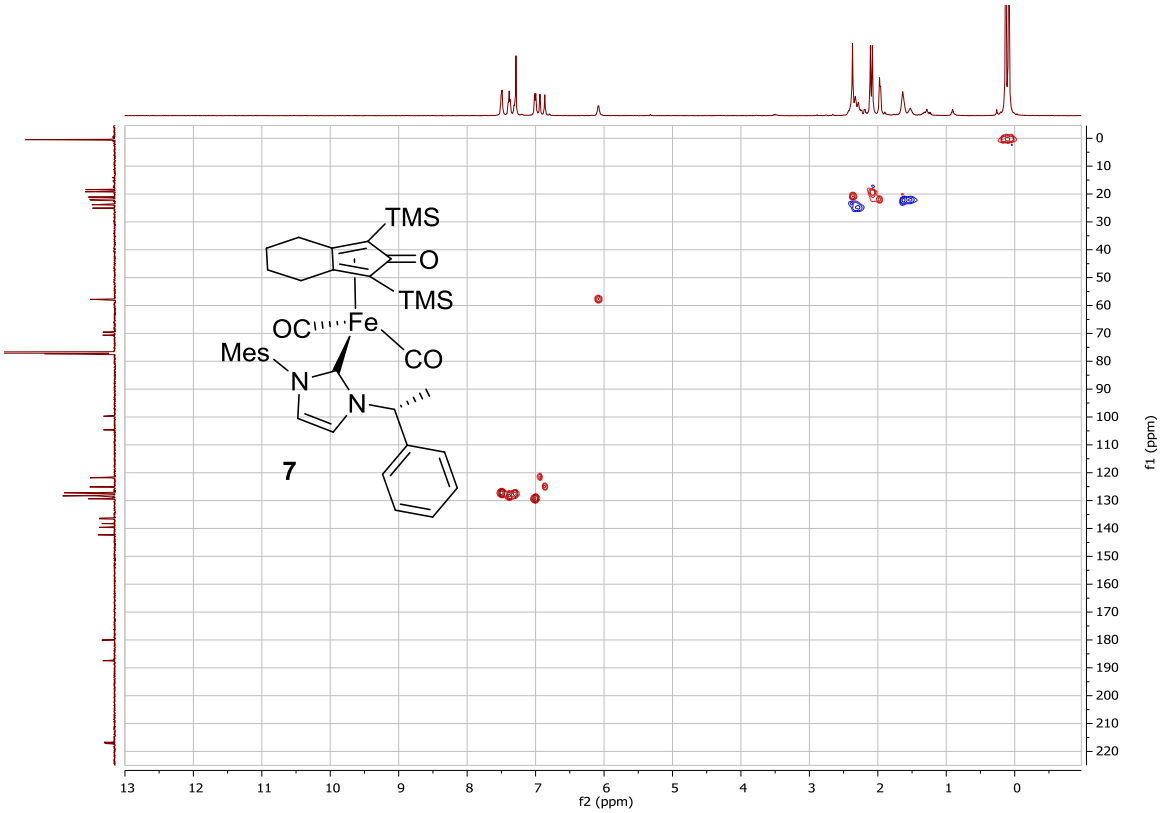


Figure S22: $^{1}H\,^{13}C$ HSQC NMR spectrum of the complex **7** in $CDCl_3$ recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

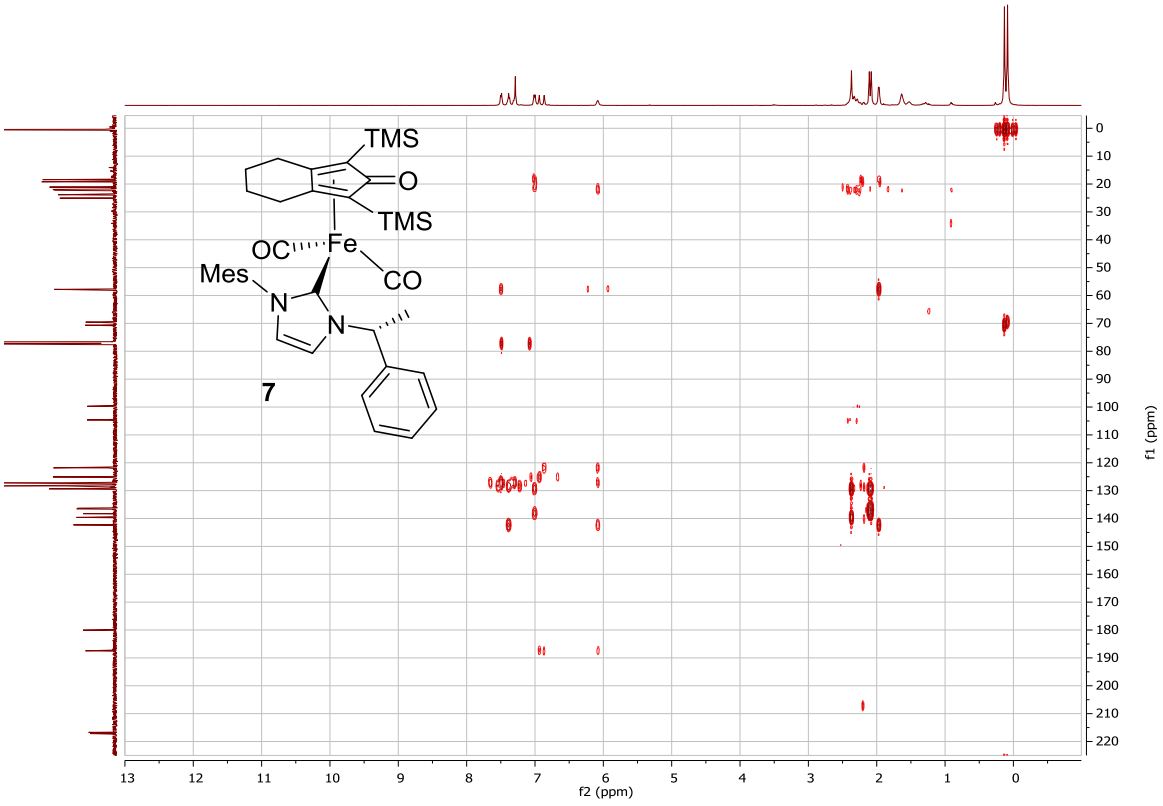


Figure S23: $^{1}H\,^{13}C$ HMBC NMR spectrum of the complex **7** in $CDCl_3$ recorded at 500 MHz, $^{13}C\{^{1}H\}$ 125 MHz.

^{1}H and $^{13}C\{^{1}H\}$ Spectra of the benzonitrile derivatives

Benzonitrile

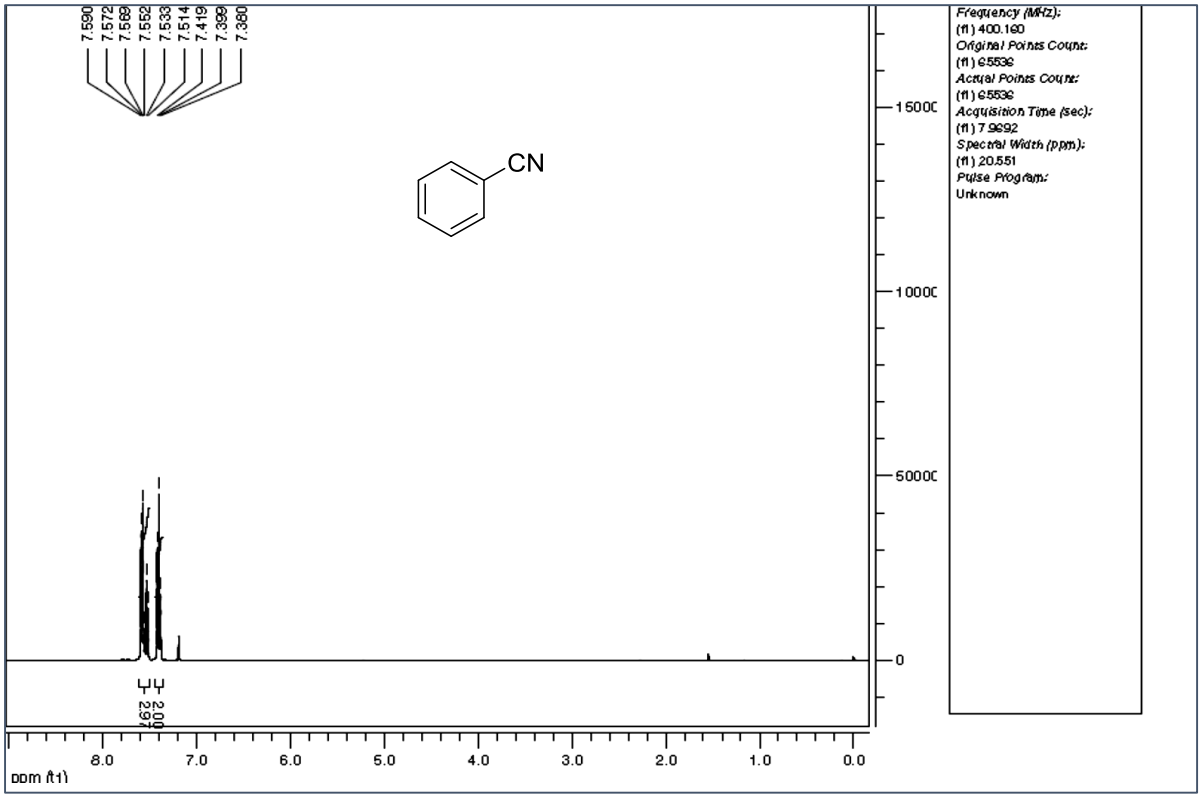


Figure S24: ^{1}H NMR spectrum of benzonitrile in $CDCl_3$ recorded at 400MHz.

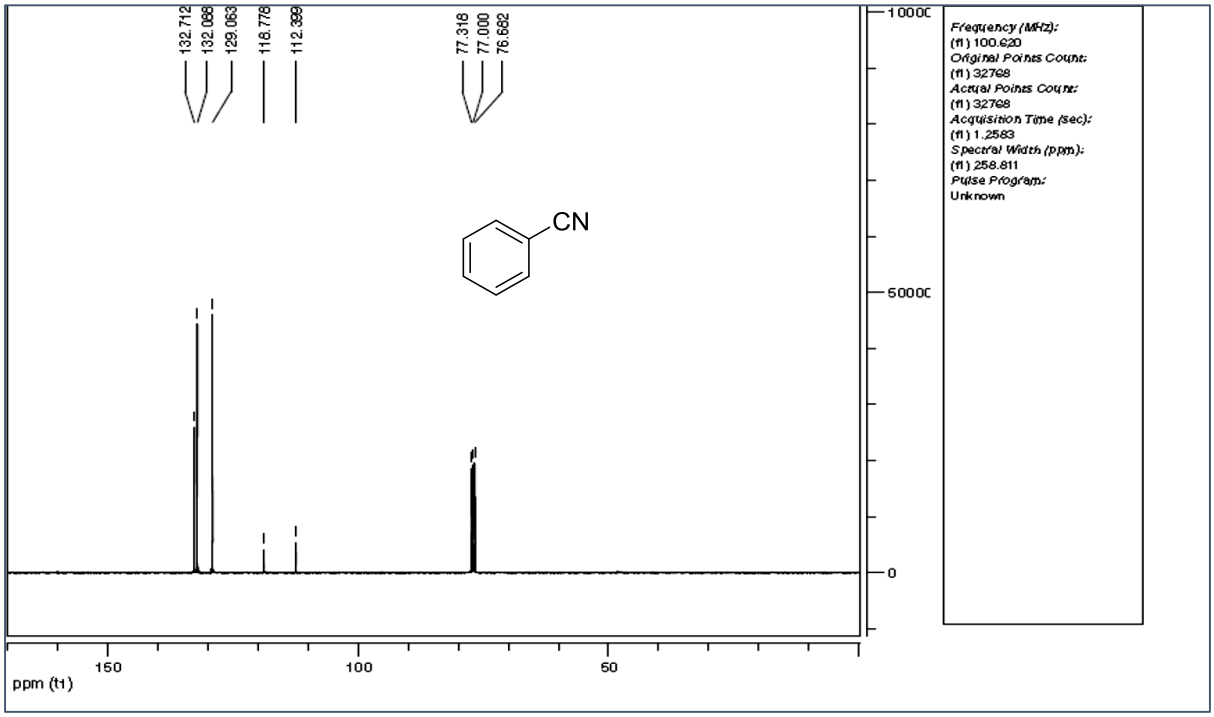


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of benzonitrile in $CDCl_3$ recorded at 100 MHz.

4-Methylbenzonitrile

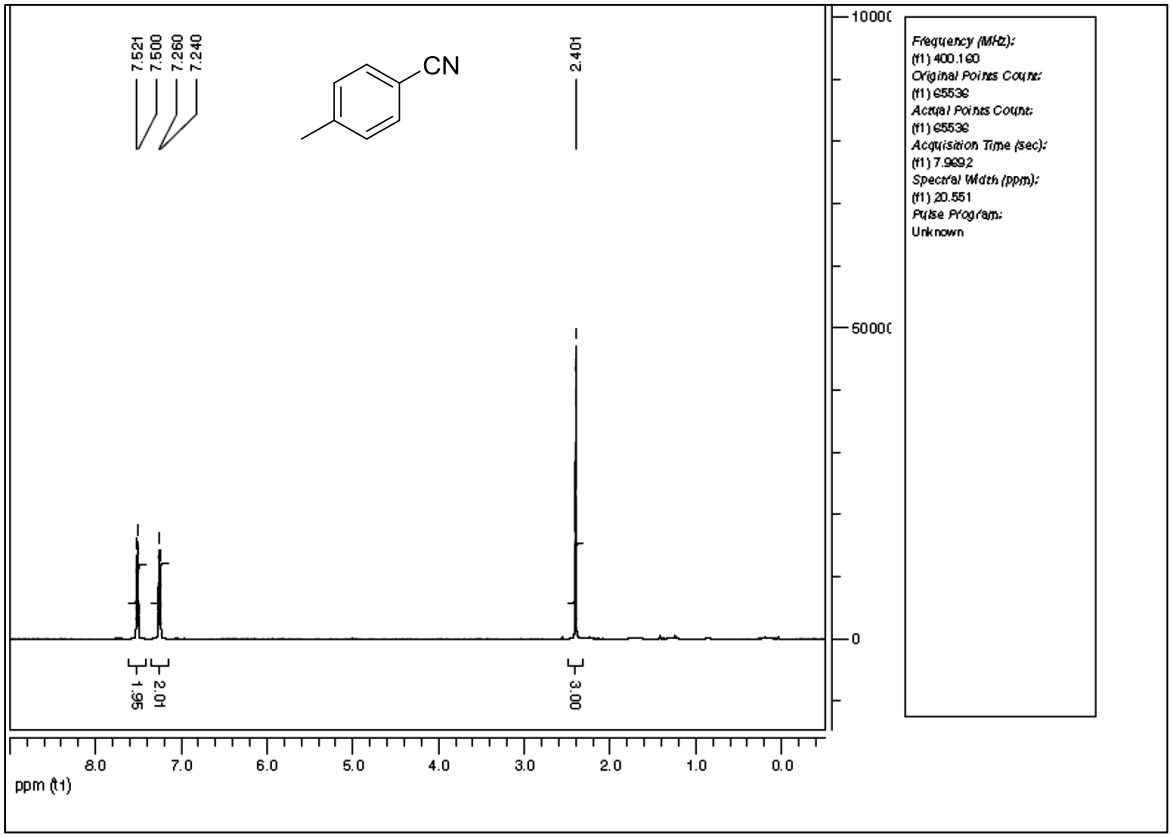


Figure S26: ^{1}H NMR spectrum of 4-methylbenzonitrile in $CDCl_3$ recorded at 400MHz.

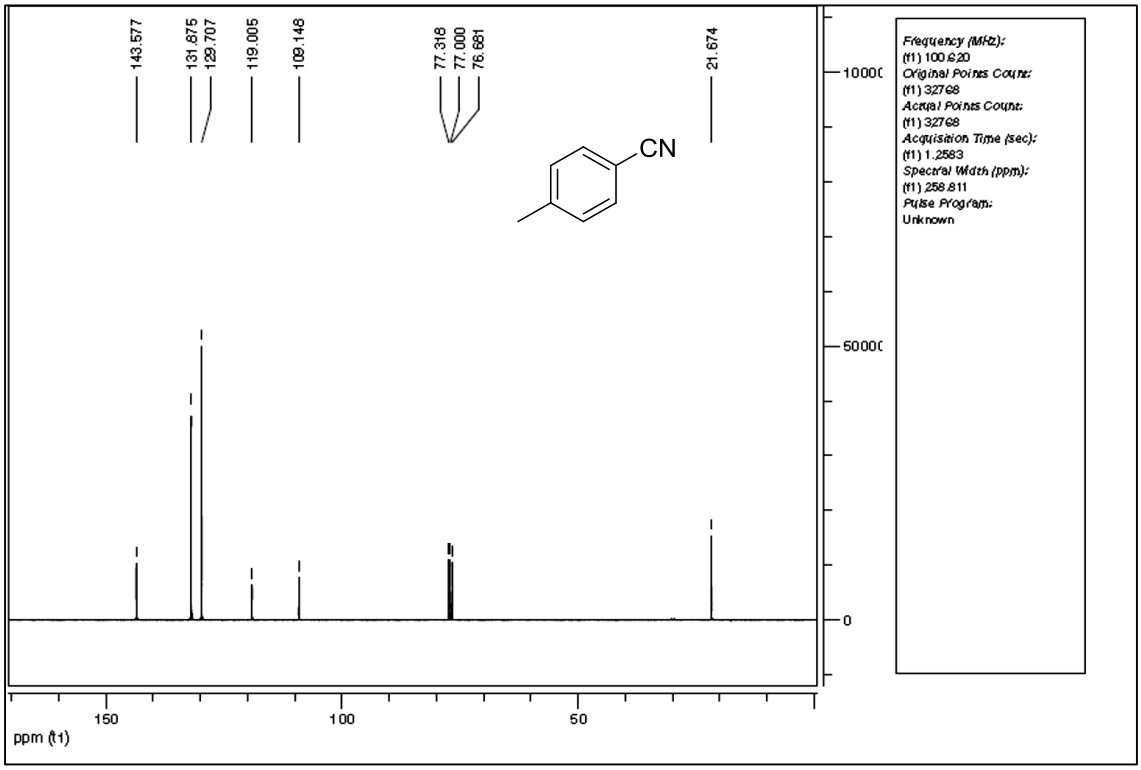


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of 4-methylbenzonitrile in $CDCl_3$ recorded at 100 MHz.

3-Methylbenzonitrile

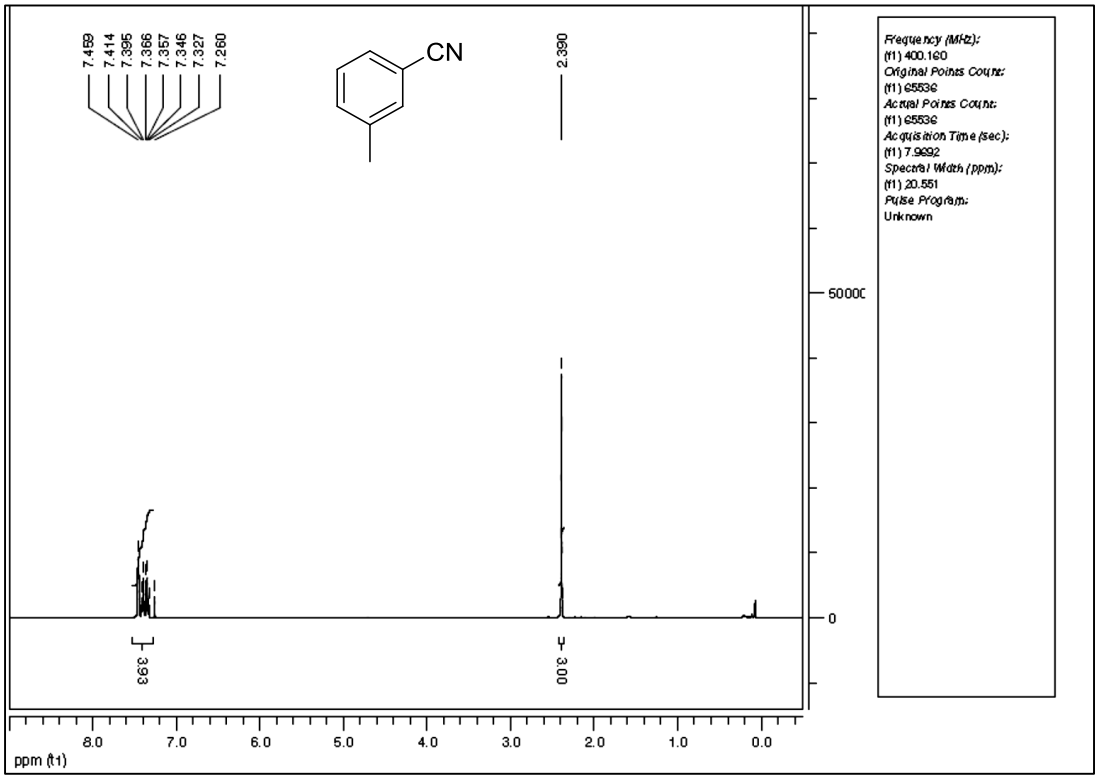


Figure S28: ^{1}H NMR spectrum of 3-methylbenzonitrile in $CDCl_3$ recorded at 400MHz.

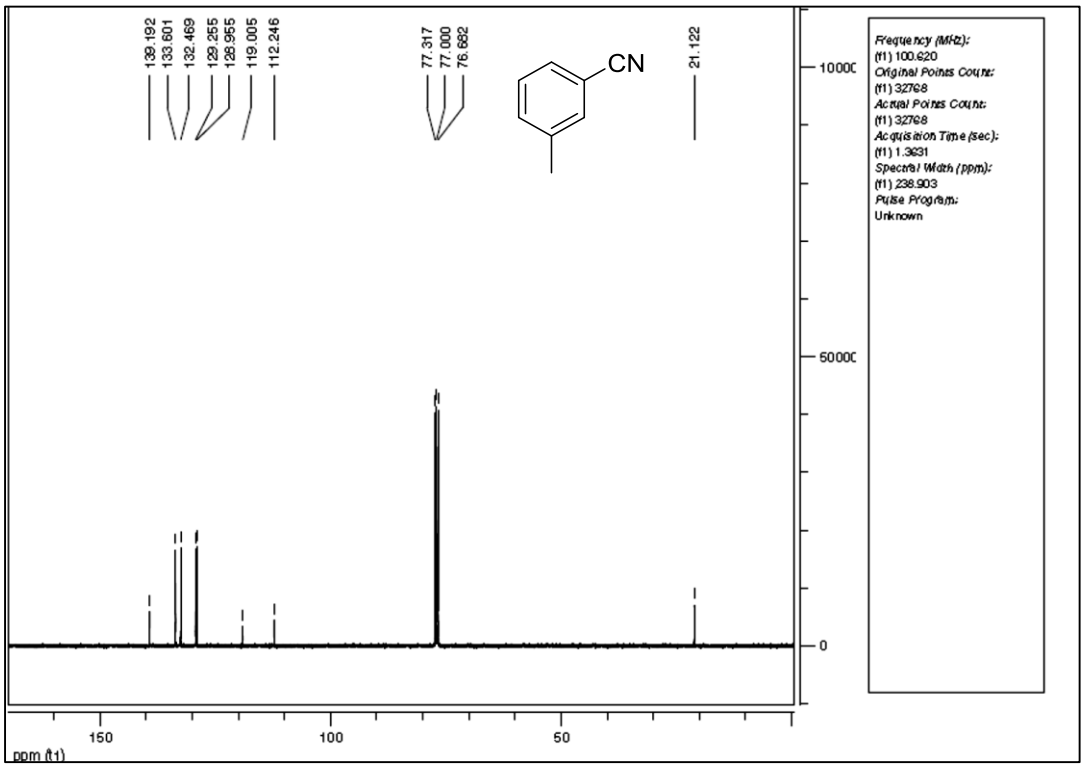


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of 3-methylbenzonitrile in $CDCl_3$ recorded at 100 MHz.

2-Methylbenzonitrile

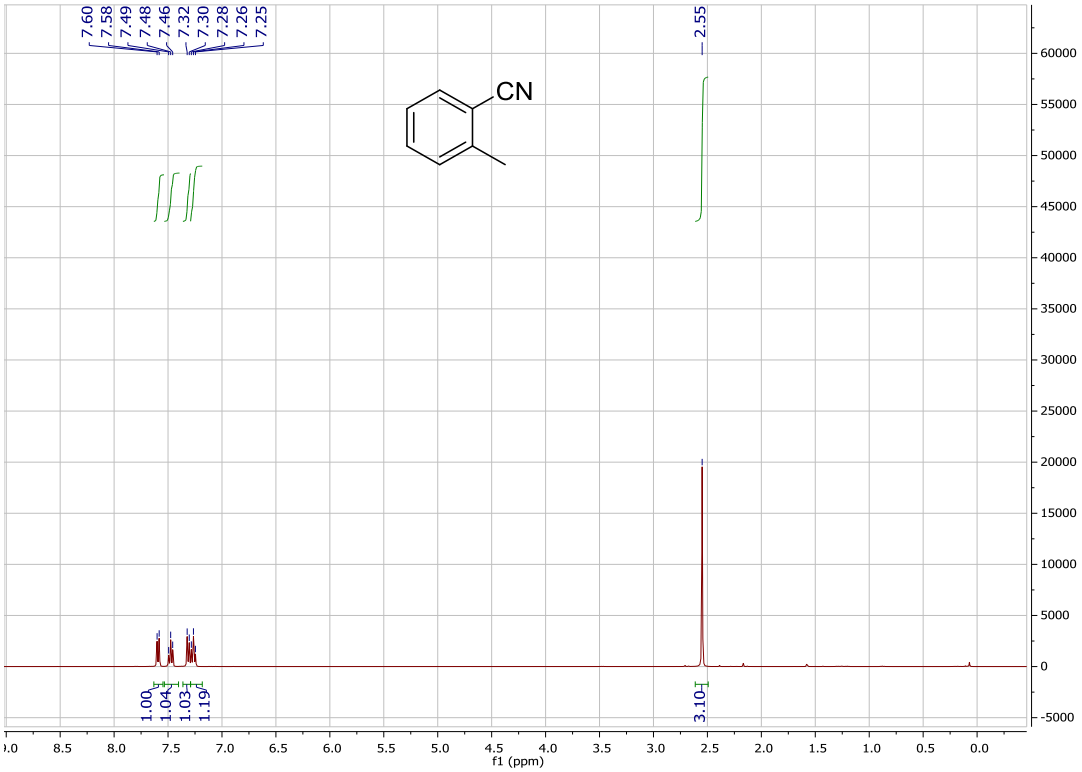


Figure S30: ^{1}H NMR spectrum of 2-methylbenzonitrile in $CDCl_3$ recorded at 400MHz.

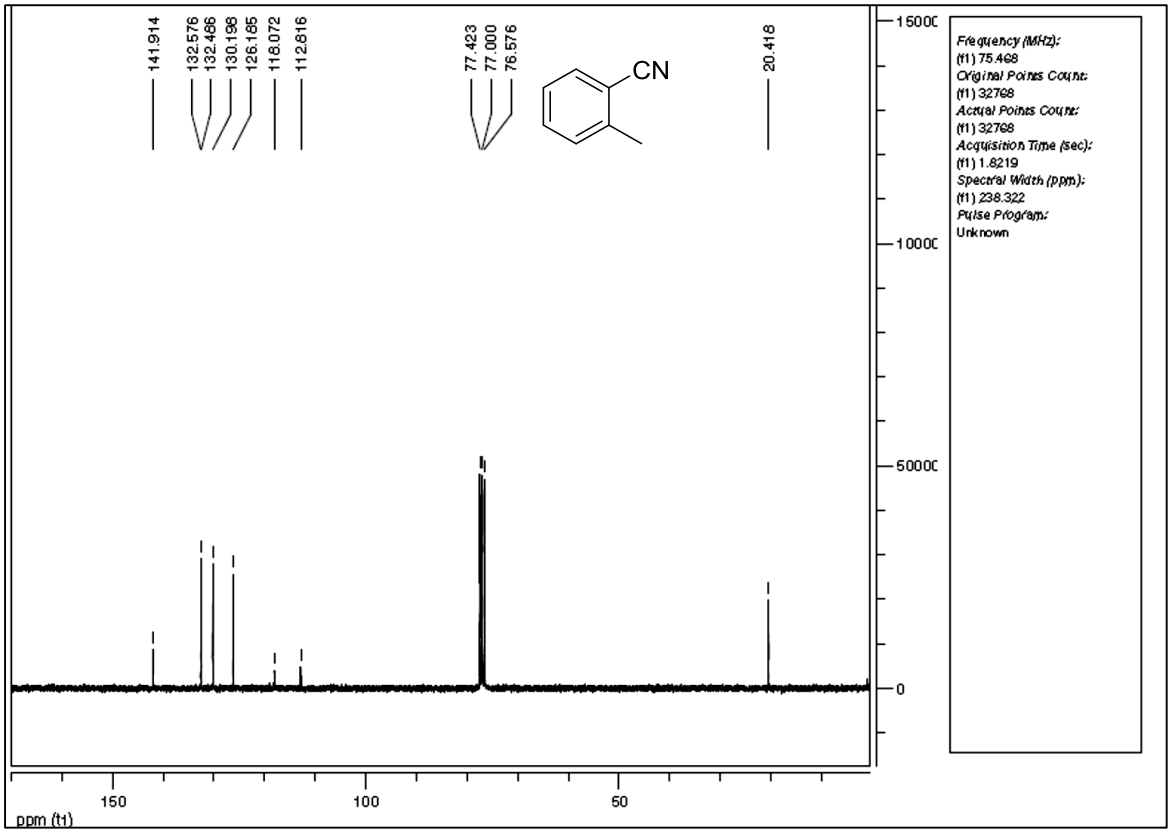


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of 2-methylbenzonitrile in $CDCl_3$ recorded at 75 MHz.

4-Bromobenzonitrile

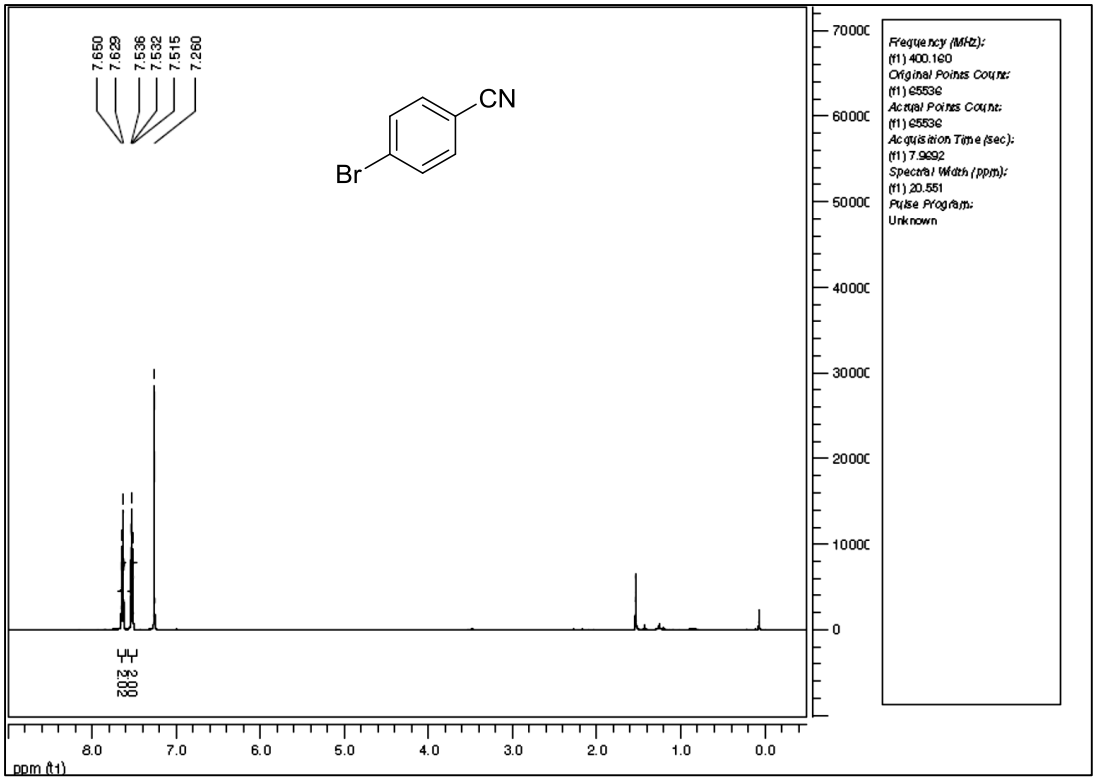


Figure S32: ^{1}H NMR spectrum of 4-bromobenzonitrile in $CDCl_3$ recorded at 400MHz.

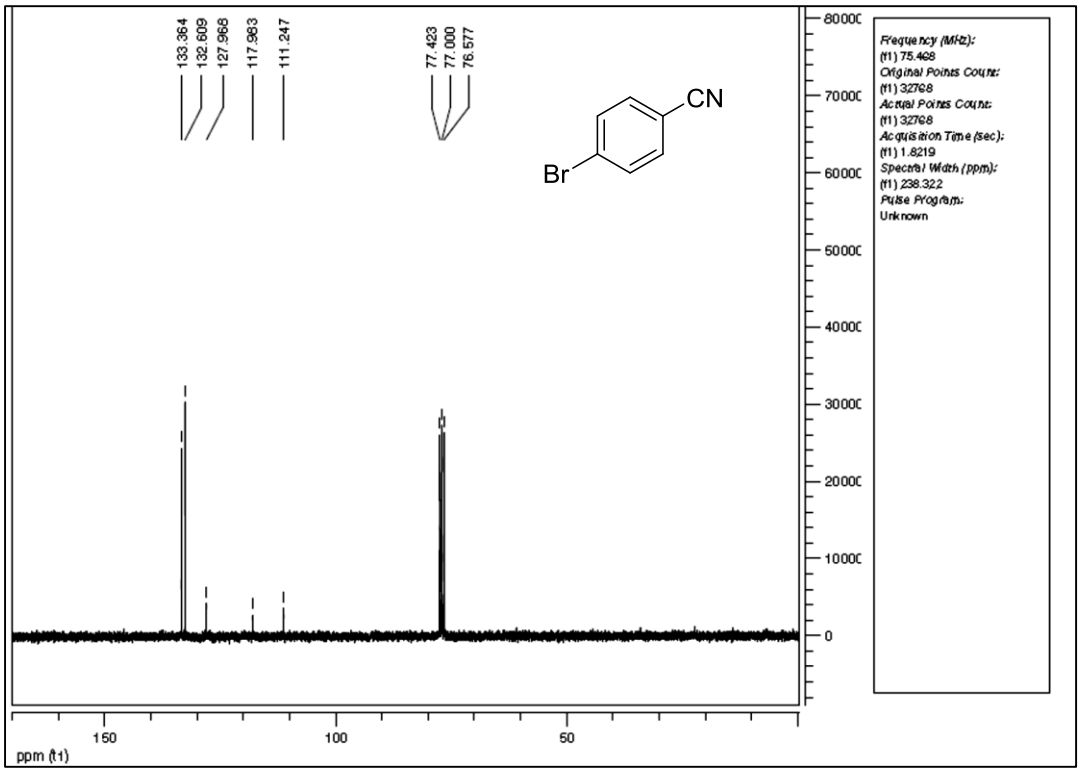


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of 4-bromobenzonitrile in $CDCl_3$ recorded at 75 MHz.

p-Chlorobenzonitrile

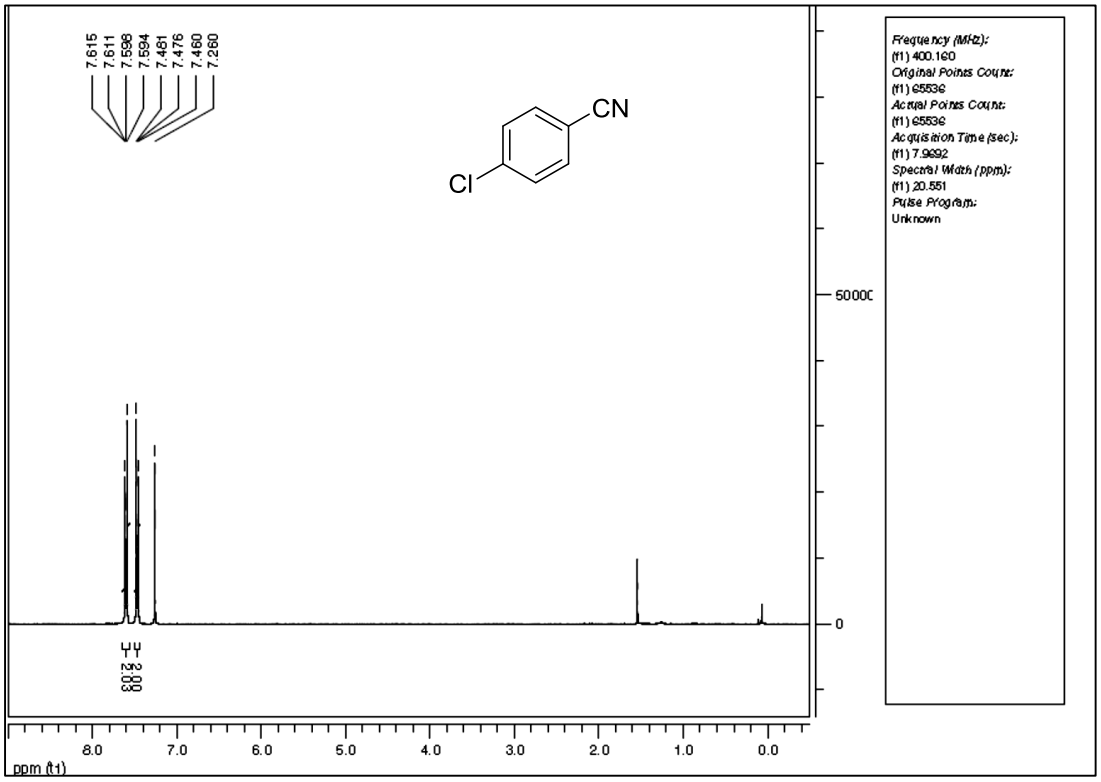


Figure S34: ^{1}H NMR spectrum of 4-chlorobenzonitrile in $CDCl_3$ recorded at 400MHz.

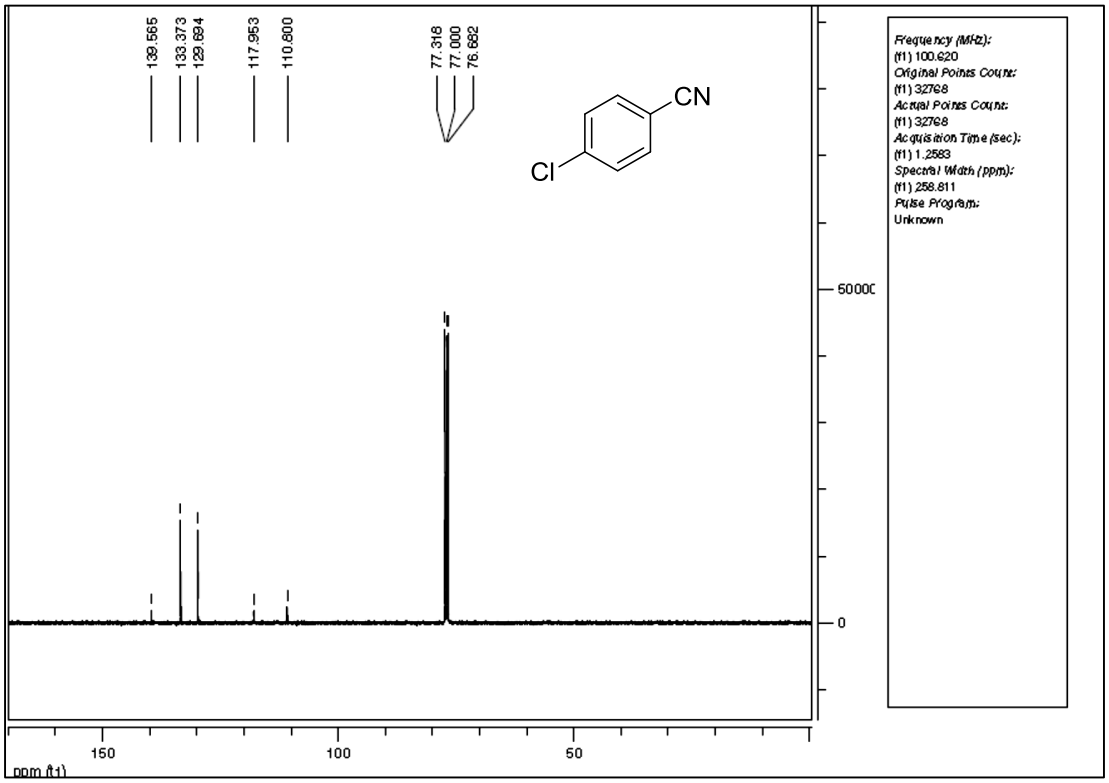


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum of 4-chlorobenzonitrile in $CDCl_3$ recorded at 100 MHz.

Cinnamonitrile

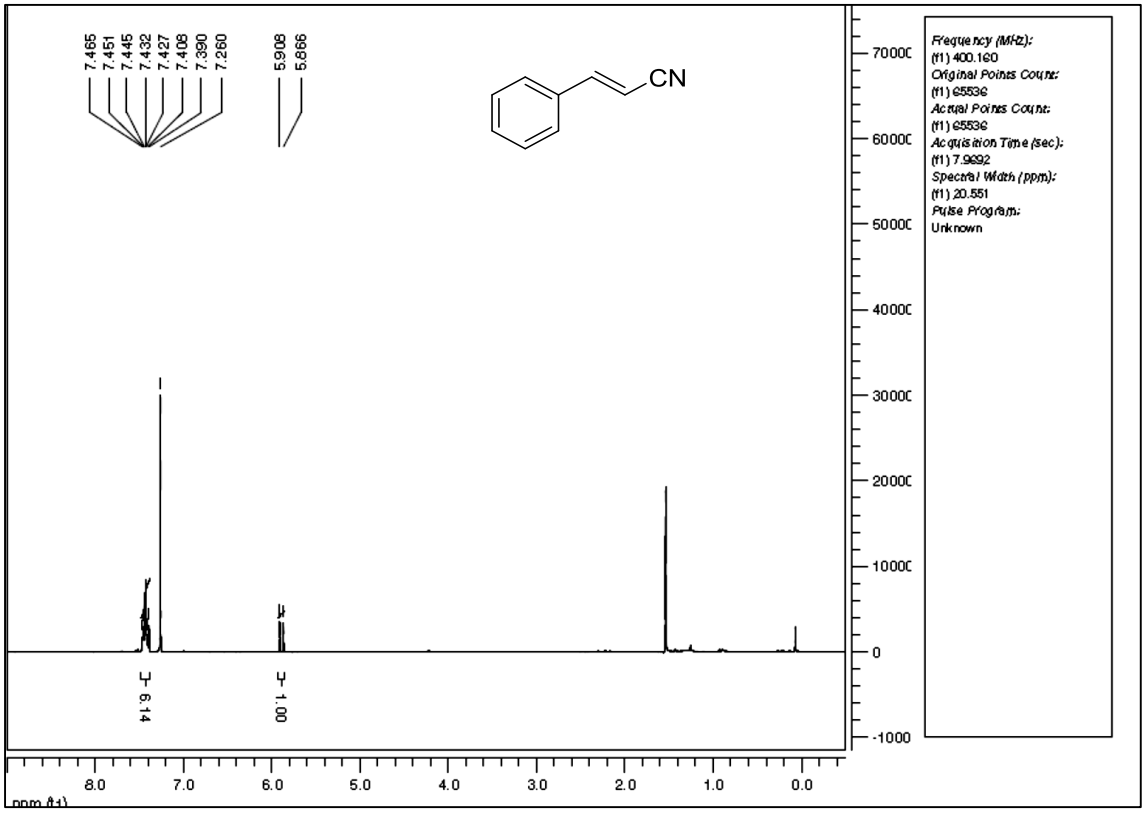


Figure S36: ^{1}H NMR spectrum of cinnamotrile in $CDCl_3$ recorded at 400MHz.

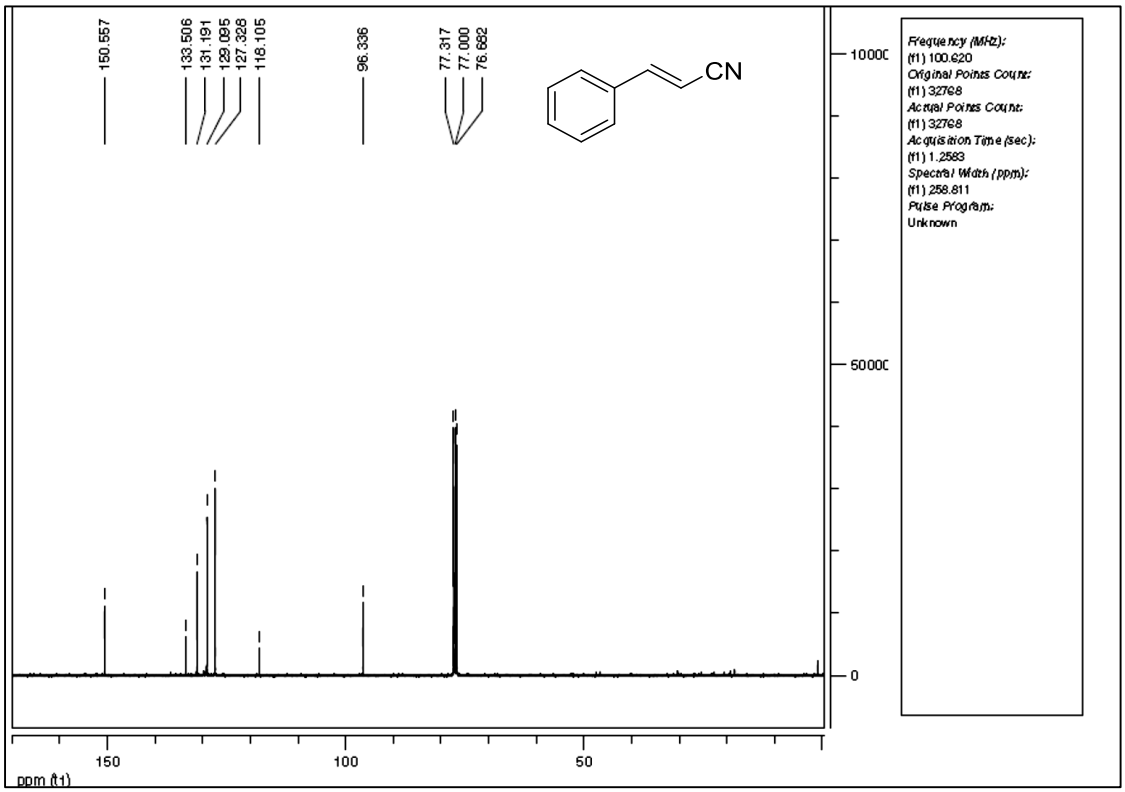


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of cinnamonitrile in $CDCl_3$ recorded at 100 MHz.