Deprotonative metallation of ferrocenes using mixed lithium-zinc and lithium-cadmium combinations

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General Methods

All reactions were performed under argon atmosphere. THF was freshly distilled over sodium/benzophenone. 2,2,6,6-Tetramethylpiperidine was stored over KOH pellets. $CdCl_2$·TMEDA[1] and $ZnCl_2$·TMEDA[2] were prepared as described. Commercially available starting materials were used without further purification. Liquid chromatography separations were achieved on silica gel Merck-Geduran Si 60 (63-200 µm).

Melting points were measured on a Kofler apparatus.

High resolution mass spectra measurements (using either a Micromass ZabSpec TOF or a Varian MAT311 instrument) and elemental analyses (using a Thermo-Finnigan Flash EA 1112 CHNS analyzer) were performed at the CRMPO in Rennes (Centre Régional de Mesures Physiques de l'Ouest).

Nuclear magnetic resonance (NMR) spectra were acquired on Bruker AC-300 (300 MHz and 75 MHz for ^{1}H and ^{13}C respectively) or Avance 500 (500 MHz and 125 MHz for ^{1}H and ^{13}C respectively) spectrometer. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak, and ^{13}C chemical shifts relative to the central peak of the solvent signal.[3] Coupling constants are given in Hz.

Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer with ATR.

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[2] M. Isobe, S. Kondo, N. Nagasawa, T. Goto, *Chem. Lett.* **1977**, 679-682.
[3] H. E.Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512-7515.

Typical Procedures and Compound Characterizations

2-Ferrocenyl-1,3-dioxane (3) was prepared by acid-catalyzed acetalization of ferrocenecarboxaldehyde as previously described.[4]

Methyl ferrocenecarboxylate (9) and **methyl ferrocenedicarboxylate (17)** were prepared as previously described.[5]

Cyanoferrocene (13) was prepared as described previously.[6]

***N*,*N*-Diethyl ferrocenecarboxamide (14)** was prepared by adapting a described procedure.[7] Compound **14** was isolated (eluent: hexane/EtOAc 75/25) as an orange powder (yield: 96%): mp 68 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 1.21 (t, 6H, *J* = 7.1 Hz), 3.51 (br s, 4H), 4.21 (s, 5H), 4.29 (s, 2H), 4.61 (s, 2H). ^{13}C NMR (125 MHz, C_6D_6, 340K) 14.1 (2C), 41.8 (2C), 69.1 (2C), 70.2 (5C), 70.6 (2C), 81.1, 168.9. HRMS (ESI): calcd for $C_{15}H_{19}{}^{56}FeNNaO$ ($[M+Na]^+$) and $C_{15}H_{20}{}^{56}FeNO$ ($[M+H]^+$) 308.0714 and 286.0894, found: 308.0716 and 286.0894.

General procedure for the deprotonation using $(TMP)_3CdLi$ (1 equiv) in pentane (reflux) followed by trapping using I_2. To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (1.1 mL, 6.0 mmol) in pentane (5 mL) were successively added BuLi (1.6 M hexanes solution, 6.0 mmol) and, 5 min later, $CdCl_2$·TMEDA (0.60 g, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (2.0 mmol). After 3 h at 35-40 °C, a solution of I_2 (1.5 g, 6.0 mmol) in THF (5 mL) was added. The mixture was stirred overnight before addition of an aqueous saturated solution of $Na_2S_2O_3$ (10 mL) and extraction with EtOAc

[4] W. Steffen, M. Laskoski, G. Collins, U. H. F. Bunz, *J. Organomet. Chem.* **2001**, *630*, 132-138.
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[6] A. Kivrak, M. Zora, *J. Organomet. Chem.* **2007**, *692*, 2346-2349.
[7] R. S. Dothager, K. S. Putt, B. J. Allen, B. J. Leslie, V. Nesterenko, P. J. Hergenrother, *J. Am. Chem. Soc.* **2005**, *127*, 8686-8696.

(3 x 20 mL). After drying over anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure, and the iodide was isolated by purification by flash chromatography on silica gel.

Iodoferrocene (2a) was isolated (eluent: heptane) as an orange powder (yield: 86%). The physical and spectroscopic data were found identical to those previously described.[8]

Racemic 2-(2-iodoferrocenyl)-1,3-dioxane (*rac*-4a) was isolated (eluent: heptane/Et_3N 90/10) as a red powder (yield: 76%): mp 87 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 1.40 (d, 1H, *J* = 13.5 Hz), 2.08-2.25 (m, 1H), 3.91-4.05 (m, 2H), 4.14-4.17 (m, 6H), 4.22 (t, 1H, *J* = 2.7 Hz), 4.26-4.32 (m, 1H), 4.40-4.44 (m, 2H), 5.37 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) 25.8, 41.4, 66.0, 67.6, 67.7, 68.9, 72.0 (5C), 75.0, 86.5, 101.3. Anal. Calcd for $C_{14}H_{15}FeIO_2$ (398.02): C, 42.25; H, 3.80. Found: C, 41.99; H, 3.78.

General procedure for the deprotonation using $(TMP)_3CdLi$ (1 equiv) in THF followed by trapping using I_2. To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (1.1 mL, 6.0 mmol) in THF (5 mL) were successively added BuLi (1.6 M hexanes solution, 6.0 mmol) and, 5 min later, $CdCl_2$·TMEDA (0.60 g, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (2.0 mmol). After 2 h at room temperature, a solution of I_2 (1.5 g, 6.0 mmol) in THF (5 mL) was added. The mixture was stirred overnight before addition of an aq saturated solution of $Na_2S_2O_3$ (10 mL) and extraction with EtOAc (3 x 20 mL). After drying over anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure, and the iodide was isolated by purification by flash chromatography on silica gel.

2-(2,5-Diiodoferrocenyl)-1,3-dioxane (4b) was isolated (eluent: heptane/Et_3N 90/10) as a red powder (yield: 10%): mp 111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 1.39 (d, 1H, *J* = 13.4 Hz), 2.18-2.33 (m, 1H), 3.91-4.01 (m, 2H), 4.21 (s, 5H), 4.26-4.32 (m, 2H), 4.51 (s, 2H), 5.43 (s, 1H). ^{13}C NMR

[8] F. S. Kamounah, J. B. Christensen, *J. Chem. Res. (S)* **1997**, 150.

(75 MHz, $CDCl_3$) 25.8, 39.6 (2C), 67.8 (2C), 72.0, 75.0 (5C), 76.9, 85.1, 101.5. Anal. Calcd for $C_{14}H_{14}FeI_2O_2$ (523.91): C, 32.10; H, 2.69. Found: C, 32.42; H, 2.67.

Racemic 2-iodoferrocenecarboxaldehyde (*rac*-5a). Before chromatography, the crude was dissolved in THF (5 mL) containing water (0.3 mL) and PTSA (0.38 g, 2.0 mmol), and the mixture was heated to reflux for 1 h.[9] After cooling to room temperature, Et_2O (40 mL) was added, and the reaction mixture was poured over aqueous saturated $NaHCO_3$ (40 mL). The organic phase was washed with aqueous saturated $NaHCO_3$ (2 x 20 mL) and with water (20 mL). 2-Iodoferrocenecarboxaldehyde was isolated (eluent: heptane/EtOAc 92/8) as a red oil (overall yield: 51%). The spectroscopic data were found identical to those previously described.[10]

Methyl 2,5-diiodoferrocenecarboxylate (10b) was isolated (eluent: heptane/EtOAc 95/5) as a red powder (yield: 82%): mp 85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 3.91 (s, 3H), 4.24 (s, 5H), 4.75 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) 38.9 (2C), 51.9, 74.0, 75.9 (5C), 80.5 (2C), 169.4. Anal. Calcd for $C_{12}H_{10}FeI_2O_2$ (495.86): C, 29.07; H, 2.03. Found: C, 29.12; H, 2.05. The structure was identified unequivocally by X-ray structure analysis from crystals obtained by slowly evaporating a CH_2Cl_2 solution.

(2*R*)-2-(*tert*-Butyldiphenylsilyloxy)prop-1-yl 2,5-diiodoferrocenecarboxylate (12b) was isolated (eluent: pentane/Et_2O 96/4) as a red oil (yield: 68%). ^{1}H NMR (300 MHz, $CDCl_3$) 1.10 (s, 9H), 1.34 (d, 3H, *J* = 6.0 Hz), 4.10-4.29 (m, 8H), 4.75 (s, 2H), 7.35-7.47 (m, 6H), 7.71-7.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) 19.3, 21.3, 27.1 (3C), 38.9-39.1 (2C), 67.5, 69.7, 73.8, 75.9 (5C), 80.5 (2C), 127.7-127.8 (4C), 129.8-129.9 (2C), 133.8-134.1 (2C), 136.0 (4C), 168.7. $[\alpha]_D$ = +3.05 (CH_2Cl_2, *c* = 2.2, 20 °C). Anal. Calcd for $C_{30}H_{32}FeI_2O_3Si$ (778.31): C, 46.30; H, 4.14. Found: C, 46.65; H, 4.32.

[9] A. Bueno, M. Rosol, J. García, A. Moyano, *Adv. Synth. Catal.* **2006**, *348*, 2590-2596.
[10] O. Riant, O. Samuel, T. Flessner, S. Taudien, H. B. Kagan, *J. Org. Chem.* **1997**, *62*, 6733-6745.

Racemic methyl 2,2'-diiodoferrocene-1,1'-dicarboxylate (*rac*-18b1) was isolated (eluent: heptane/EtOAc 90/10) as an orange oil (yield: 20%). ^{1}H NMR (300 MHz, $CDCl_3$) 3.89 (s, 6H), 4.41 (dd, 2H, *J* = 2.7 and 3.0), 4.69 (dd, 2H, *J* = 1.5 and 2.7), 4.82 (dd, 2H, *J* = 1.5 and 3.0). ^{13}C NMR (75 MHz, $CDCl_3$) 40.9 (2C), 52.0 (2C), 74.3 (2C), 74.8 (2C), 77.8 (2C), 83.8 (2C), 168.6 (2C). HRMS (ESI): calcd for $C_{14}H_{12}O_4I_2Na^{56}Fe$ ($[M+Na]^+$) 576.8072, found: 576.8074.

Meso methyl 2,2'-diiodoferrocene-1,1'-dicarboxylate (18b2) was isolated (eluent: heptane/EtOAc 90/10) as a red powder (yield: 15%): mp 97-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 3.89 (s, 6H), 4.44 (dd, 2H, *J* = 2.4 and 2.7), 4.65 (dd, 2H, *J* = 1.5 and 2.4), 4.84 (dd, 2H, *J* = 1.5 and 2.7). ^{13}C NMR (75 MHz, $CDCl_3$) 41.3 (2C), 52.0 (2C), 74.4 (2C), 74.8 (2C), 77.3 (2C), 83.9 (2C), 168.6 (2C). HRMS (ESI): calcd for $C_{14}H_{12}O_4I_2Na^{56}Fe$ ($[M+Na]^+$) 576.8072, found: 576.8066.

Methyl 2,5,2'-triiodoferrocene-1,1'-dicarboxylate (*rac*-18c) was isolated (eluent: heptane/EtOAc 90/10) as a red powder (yield: 30%): mp 96-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 3.91 (s, 3H), 3.92 (s, 3H), 4.47 (dd, 1H, *J* = 2.4 and 2.7), 4.60 (dd, 1H, *J* = 1.5 and 2.4), 4.64 (d, 1H, *J* = 2.5), 4.70 (d, 1H, *J* = 2.5), 4.82 (dd, 1H, *J* = 1.5 and 2.7). ^{13}C NMR (125 MHz, $CDCl_3$) 41.2, 41.3, 42.7, 52.0, 52.1, 76.4, 77.7, 80.2, 85.3, 85.4, 87.1, 87.8, 167.4, 167.5. HRMS (ESI): calcd for $C_{14}H_{11}O_4I_3Na^{56}Fe$ ($[M+Na]^+$) 702.7039, found: 702.7037.

General procedure for the deprotonation using $(TMP)_3CdLi$ (0.5 equiv) in THF followed by trapping using I_2. To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (1.1 mL, 6.0 mmol) in THF (5 mL) were successively added BuLi (1.6 M hexanes solution, 6.0 mmol) and, 5 min later, $CdCl_2$·TMEDA (0.60 g, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (4.0 mmol). After 2 h at room temperature, a solution of I_2 (1.5 g, 6.0 mmol) in THF (5 mL) was added. The mixture was stirred overnight before addition of an aq saturated solution of $Na_2S_2O_3$ (10 mL) and extraction with EtOAc (3 x 20 mL). After drying over

anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure, and the iodide was isolated by purification by flash chromatography on silica gel.

Racemic 2-iodoferrocenyl phenyl ketone (*rac*-8a) was isolated (eluent: heptane/Et_2O 92/8) as a red oil (yield: 36%). ^{1}H NMR (300 MHz, $CDCl_3$) 4.23 (s, 5H), 4.53 (t, 1H, *J* = 2.6 Hz), 4.61 (dd, 1H, *J* = 2.7, 1.4 Hz), 4.85 (dd, 1H, *J* = 2.4, 1.4 Hz), 7.42-7.48 (m, 2H), 7.53-7.58 (m, 1H), 7.84-7.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) 41.1, 71.6, 72.5, 73.4 (5C), 77.7, 80.2, 128.3 (2C), 128.8 (2C), 132.1, 139.3, 197.9. Anal. Calcd for $C_{17}H_{13}FeIO$ (416.03): C, 49.08; H, 3.15. Found: C, 48.88; H, 3.15. **2,5-Diiodoferrocenyl phenyl ketone** (**8b**) was isolated similarly in 2% yield as a yellow oil, and was identified by NMR. ^{1}H NMR (300 MHz, $CDCl_3$) 4.38 (s, 5H), 4.68 (s, 2H), 7.42 (t, 2H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.3 Hz), 7.71 (d, 2H, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 39.6 (2C), 76.1 (5C), 76.6 (2C), 92.6, 128.6 (2C), 130.0 (2C), 133.5, 136.8, 195.6.

Racemic methyl 2-iodoferrocenecarboxylate (*rac*-10a)[11] was isolated (eluent: heptane/EtOAc 95/5) as a red oil (yield: 73%). ^{1}H NMR (300 MHz, $CDCl_3$) 3.84 (s, 3H), 4.22 (s, 5H), 4.44 (t, 1H, *J* = 2.6 Hz), 4.69 (dd, 1H, *J* = 2.4, 1.6 Hz), 4.84 (dd, 1H, *J* = 2.7, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 39.8, 51.8, 70.3, 71.1, 72.4, 72.9 (5C), 79.8, 170.9. Anal. Calcd for $C_{12}H_{11}FeIO_2$ (369.96): C, 38.96; H, 3.00. Found: C, 39.21; H, 3.13.

General procedure for the deprotonation using the in situ prepared mixture of $ZnCl_2$·TMEDA (0.5 equiv) and LiTMP (1.5 equiv) in THF followed by trapping using I_2. To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (1.1 mL, 6.0 mmol) in THF (5 mL) were successively added BuLi (1.6 M hexanes solution, 6.0 mmol) and, 5 min later, $ZnCl_2$·TMEDA (0.50 g, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (4.0 mmol). After 2 h at room temperature, a solution of I_2 (1.5 g, 6.0 mmol) in THF (5 mL) was added. The mixture was stirred overnight before addition of an aq saturated

[11] A. Brunner, S. Taudien, O. Riant, H. B. Kagan, *Chirality* **1997**, *9*, 478-486.

solution of $Na_2S_2O_3$ (10 mL) and extraction with EtOAc (3 x 20 mL). After drying over anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure, and the iodide was isolated by purification by flash chromatography on silica gel.

Racemic 1-cyano-2-iodoferrocene (*rac*-15a) was isolated (eluent: heptane/EtOAc 95 to 5) as an orange powder (yield: 87%): mp 135 °C. IR (ATR): ν 817, 827, 948, 1000, 1030, 1106, 1239, 1362, 1378, 1408, 2227, 2922, 3112 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) 4.34 (s, 5H), 4.41 (t, 1H, *J* = 2.65 Hz), 4.65 (dd, 1H, *J* = 2.6, 1.3 Hz), 4.70 (dd, 1H, *J* = 2.7, 1.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 41.6, 59.1, 71.7, 72.1, 73.7 (5C), 77.4, 119.5. HRMS (ESI): calcd for $C_{11}H_8{}^{56}FeINNa$ ($[M+Na]^+$) 359.8949, found: 359.8950.

Racemic *N*,*N*-diethyl 2-iodoferrocenecarboxamide (*rac*-16a) was isolated (eluent: heptane/EtOAc 92.5/7.5 to 90/10) as an orange oil (yield: 91%). ^1H NMR (500 MHz, $CDCl_3$, 340K) 0.91 (br s, 6H), 3.00 (br s, 2H), 3.26 (br s, 2H), 3.85 (br s, 1H), 4.13 (br s, 1H), 4.25 (br s, 1H), 4.31 (br s, 5H). ^{13}C NMR (125 MHz, C_6D_6, 340K) 13.8 (2C), 41.5 (3C), 68.1 (2C), 73.4 (5C), 74.5, 91.0, 166.4. HRMS (ESI): calcd for $C_{15}H_{18}{}^{56}FeINNaO$ ($[M+Na]^+$) 433.9680, found: 433.9673.

Racemic methyl 2-iodoferrocene-1,1'-dicarboxylate (*rac*-18a) was isolated (eluent: heptane/EtOAc 80/20) as an orange powder (yield: 72%): mp 65-67 °C. ^1H NMR (300 MHz, $CDCl_3$) 3.85 (s, 3H), 3.85 (s, 3H), 4.39-4.42 (m, 2H), 4.46 (t, 1H, *J* = 2.7 Hz), 4.69 (dd, 1H, *J* = 2.4, 1.5 Hz), 4.78-4.82 (m, 2H), 4.86 (dd, 1H, *J* = 3.0, 1.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 40.2, 51.8, 51.8, 71.7, 73.6, 73.9, 74.2, 74.9, 75.6, 76.1, 81.0, 169.4, 169.8. HRMS (ESI): calcd for $C_{14}H_{13}O_4INa^{56}Fe$ ($[M+Na]^+$) 450.9106, found: 450.9106.

Racemic 1-bromo-2-iodoferrocene (*rac*-20a)[12] was purified (eluent: heptane) as an orange powder (yield: 64%), and identified by its NMR data: mp 54-55 °C. ^1H NMR (300 MHz, C_6D_6)

[12] I. R. Butler, *Inorg. Chem. Commun.* **2008**, *11*, 15-19.

4.19 (t, 1H, *J* = 2.7 Hz), 4.22 (s, 5H), 4.43 (dd, 1H, *J* = 2.7, 1.5 Hz), 4.52 (dd, 1H, *J* = 2.7, 1.5 Hz). ^{1}H NMR (300 MHz, C_6D_6) 3.60 (t, 1H, *J* = 2.6 Hz), 3.92 (s, 5H), 4.07 (dd, 1H, *J* = 2.7, 1.5 Hz), 4.15 (dd, 1H, *J* = 2.4, 1.2 Hz). ^{13}C NMR (75 MHz, C_6D_6) 46.4, 68.6, 69.9, 73.8 (5C), 73.9, 85.0. HRMS (ESI): calcd for $C_{10}H_8{}^{79}Br^{56}FeI$ ($M^{+\bullet}$) 389.8203, found: 389.8203. The structure was confirmed by X-ray structure analysis from crystals obtained by slowly evaporating a CH_2Cl_2 solution.

Racemic 1-bromo-3-iodoferrocene (*rac*-20b) was isolated (eluent: heptane) as an orange oil (yield: 7%). ^{1}H NMR (300 MHz, C_6D_6) 3.93 (s, 5H), 3.97 (dd, 1H, *J* = 2.1, 1.2 Hz), 4.02 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.41 (t, 1H, *J* = 1.2 Hz). ^{13}C NMR (75 MHz, C_6D_6) 38.1, 70.9, 71.3, 73.8 (5C), 76.3, 77.7. HRMS (ESI): calcd for $C_{10}H_8{}^{79}Br^{56}FeI$ ($M^{+\bullet}$) 389.8203, found: 389.8199.

General procedure for the deprotonation using the in situ prepared mixture of $ZnCl_2$·TMEDA (0.5 equiv) and LiTMP (1.5 equiv) in THF followed by palladium-catalyzed cross coupling. To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (1.1 mL, 6.0 mmol) in THF (10 mL) were successively added BuLi (1.6 M hexanes solution, 6.0 mmol) and, 5 min later, $ZnCl_2$·TMEDA (0.50 g, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (4.0 mmol). After 2 h at room temperature, 2-chloropyridine (0.55 g, 4.8 mmol), palladium(II) chloride (14 mg, 80 μmol), and 1,1'-diphenylphosphinoferrocene (44 mg, 80 μmol) were added to the reaction mixture, and the latter was heated at THF reflux for 24 h. After addition of water (0.5 mL) and EtOAc (50 mL), and drying over anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure, and the coupled product was isolated by purification by flash chromatography on silica gel.

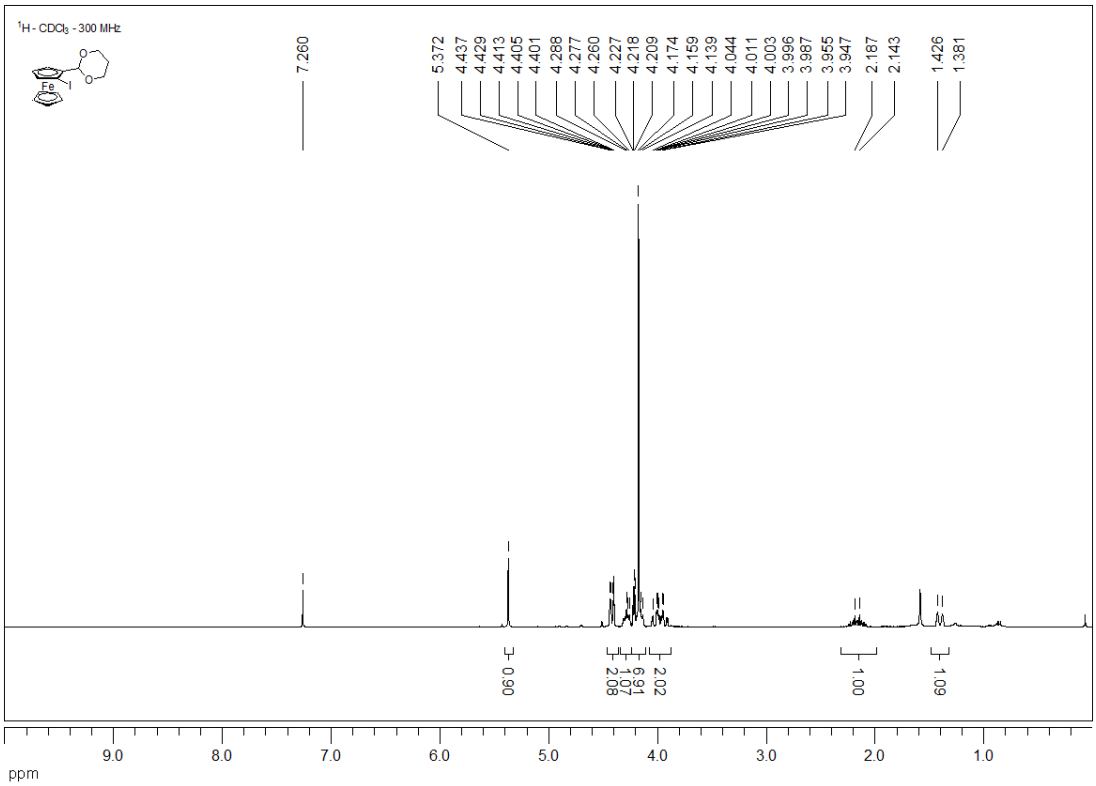
Racemic 2-(2-cyanoferrocenyl)pyridine (*rac*-15c) was isolated (eluent: heptane/EtOAc 90/10) as an orange-red powder (yield: 67%): mp 104-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 4.25 (s, 5H), 4.59 (t, 1H, *J* = 2.7 Hz), 4.87 (dd, 1H, *J* = 2.7, 1.5 Hz), 5.20 (dd, 1H, *J* = 2.7, 1.5 Hz), 7.19 (ddd,

1H, *J* = 7.5, 4.8, 1.2 Hz), 7.68 (td, 1H, *J* = 7.7, 1.8 Hz), 8.60 (ddd, 1H, *J* = 5.1, 1.8, 0.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 51.0, 71.0, 71.5, 72.3 (5C), 74.2, 86.9, 120.7, 120.9, 122.1, 136.6, 149.8, 155.9. HRMS (ESI): calcd for $C_{16}H_{12}N_2Na^{56}Fe$ ($[M+Na]^+$) 311.0248, found: 311.0245. The structure was identified unequivocally by X-ray structure analysis from crystals obtained by slowly evaporating a CH_2Cl_2 solution.

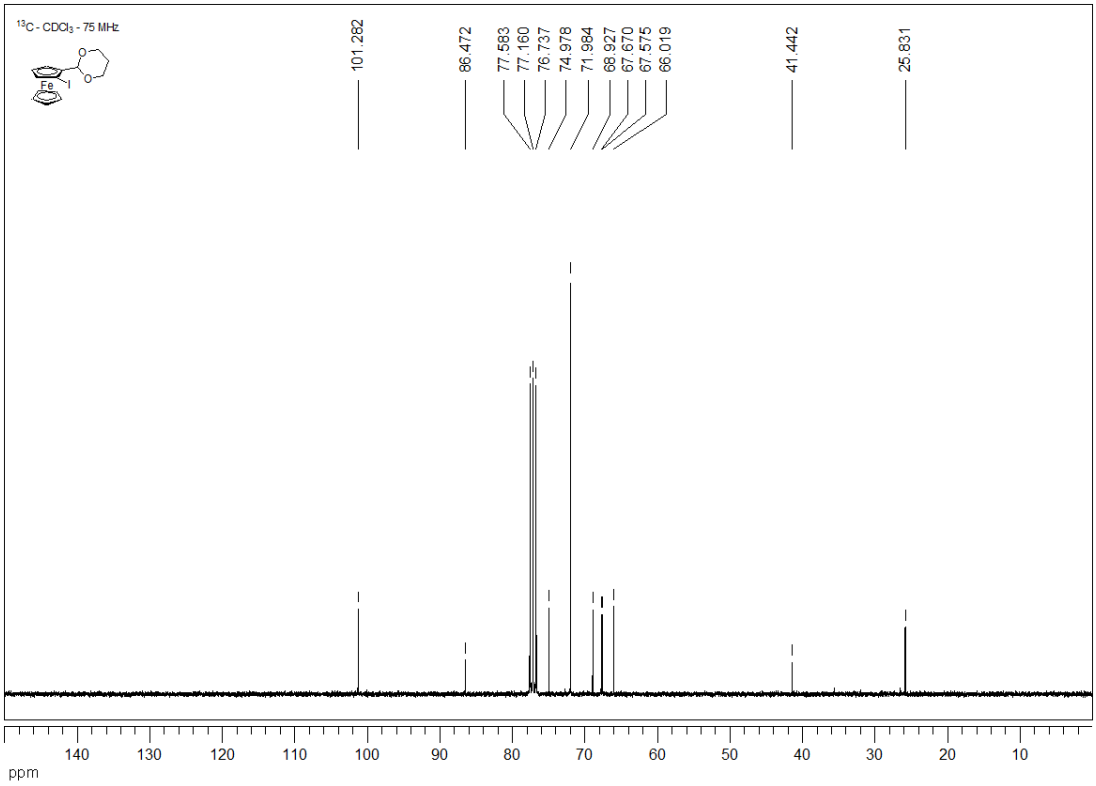
Racemic *N*,*N*-diethyl 2-(2-pyridyl)ferrocenecarboxamide (*rac*-16c) was isolated (eluent: heptane/EtOAc 75/25) as an orange-red oil (yield: 80%). ^{1}H NMR (300 MHz, $CDCl_3$) 0.70-0.88 (m, 3H), 1.14-1.26 (m, 3H), 2.83 (m, 1H), 2.98 (m, 1H), 3.21 (m, 1H), 3.72 (m, 1H), 4.25 (s, 5H), 4.39 (s, 1H), 4.53 (s, 1H), 4.92 (s, 1H), 7.10 (m, 1H), 7.5-7.7 (m, 2H), 8.47 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) 12.4, 13.4, 39.4, 42.7, 66.3, 67.9, 70.7, 71.3 (5C), 82.6, 87.8, 120.9, 121.8, 135.8, 149.0, 158.1, 168.5. HRMS (ESI): calcd for $C_{20}H_{23}N_2O^{56}Fe$ ($[M+H]^+$) 363.1160, found: 363.1168.

^{1}H and ^{13}C NMR spectra

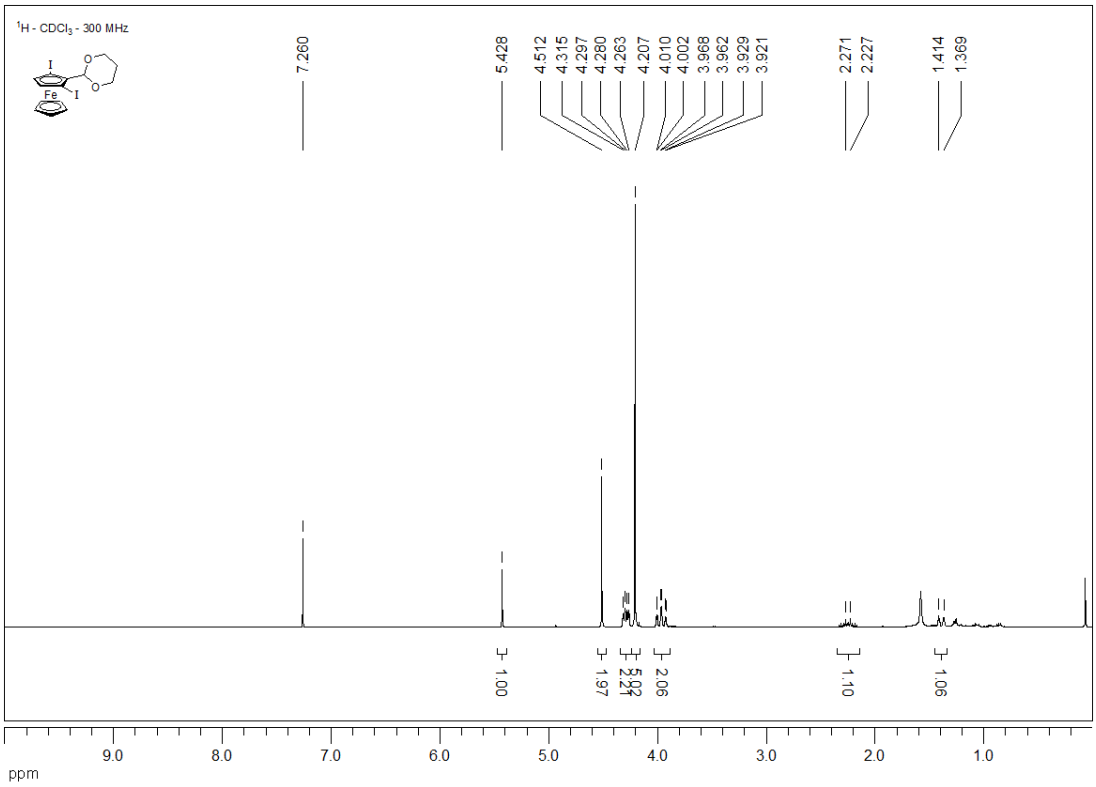
rac-4a ^{1}H



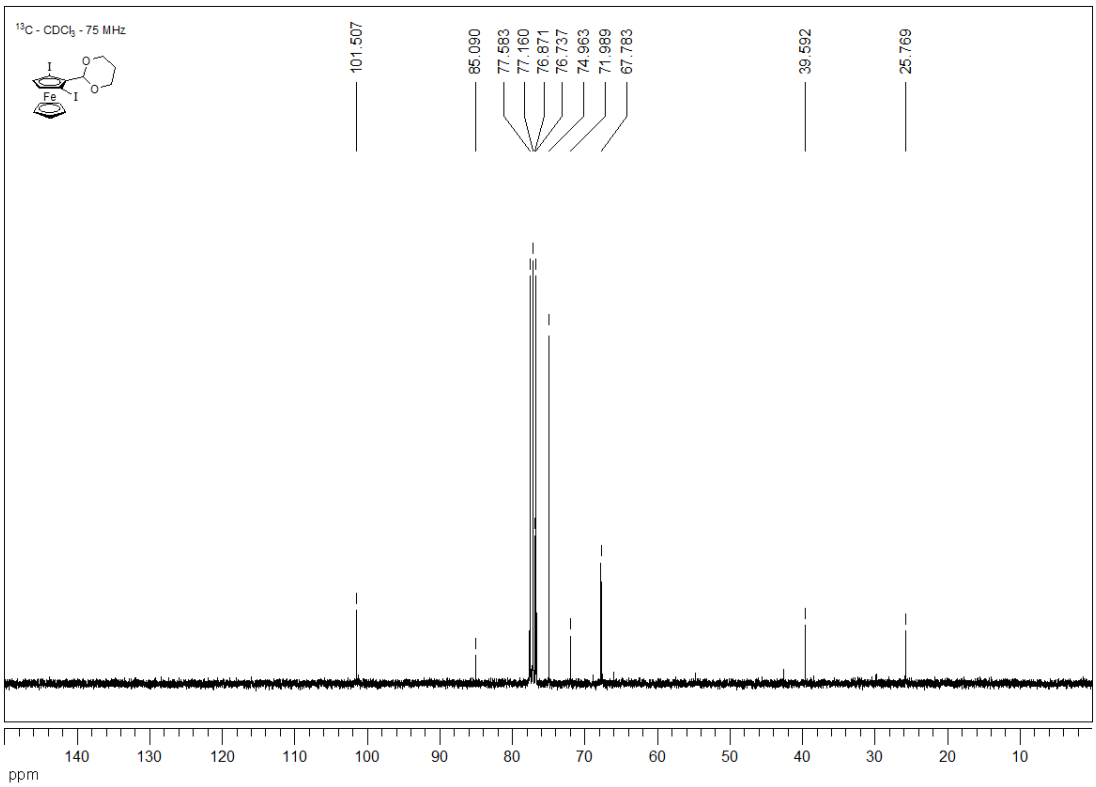
rac-4a ^{13}C



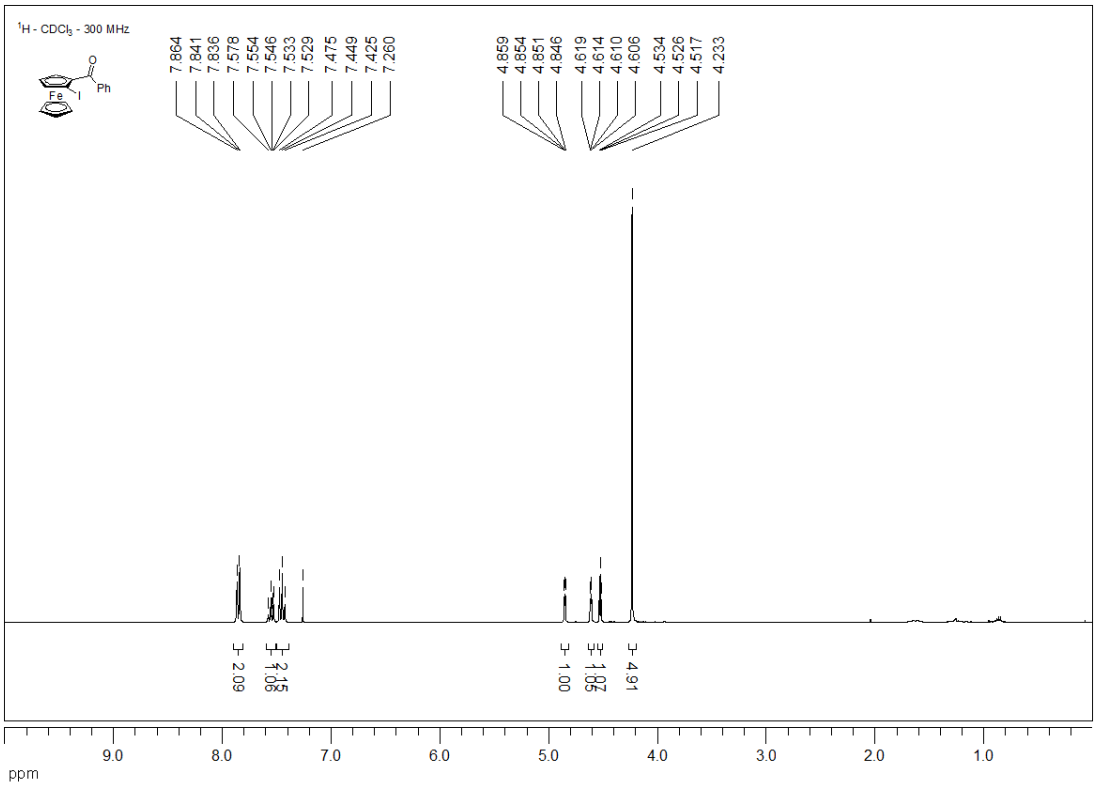
4b ^{1}H


1H - CDCl3 - 300 MHz
7.260
5.428
4.512
4.315
4.297
4.280
4.263
4.207
4.010
4.002
3.968
3.962
3.929
3.921
2.271
2.227
1.414
1.369
1.00
1.67
5.21
2.06
1.10
1.06
ppm

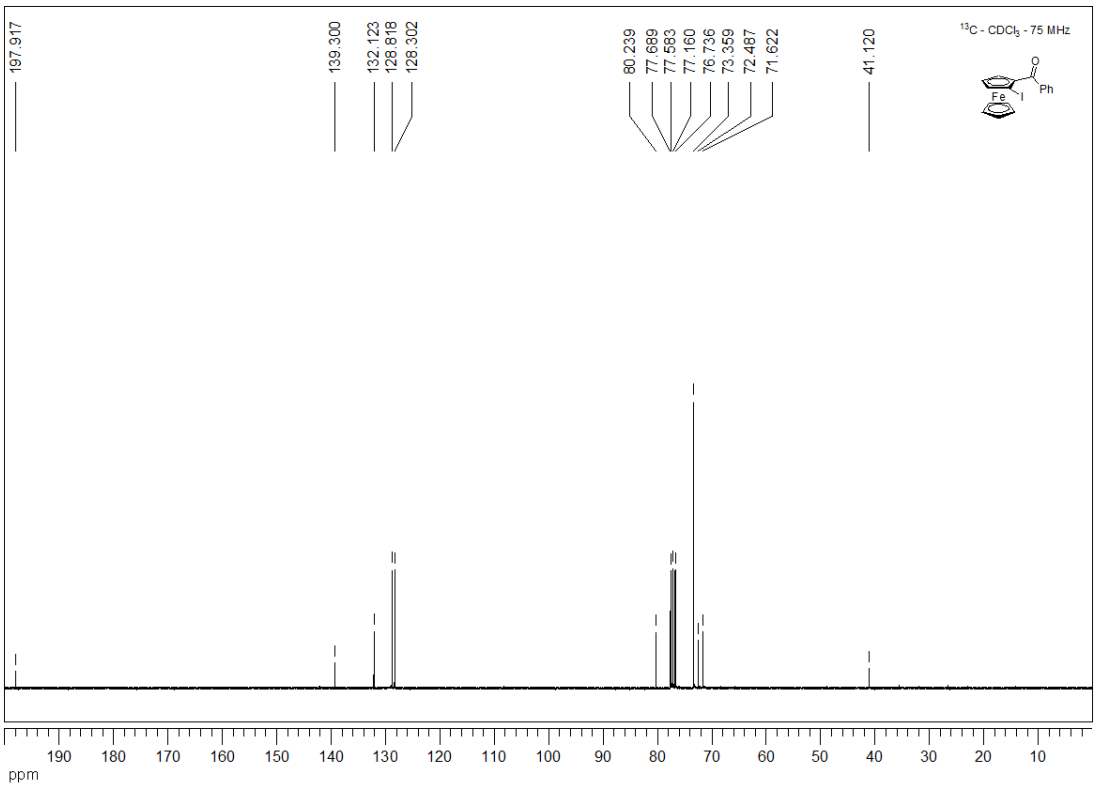
4b ^{13}C


13C - CDCl3 - 75 MHz
101.507
85.090
77.583
77.160
76.871
76.737
74.963
71.989
67.783
39.592
25.769
ppm

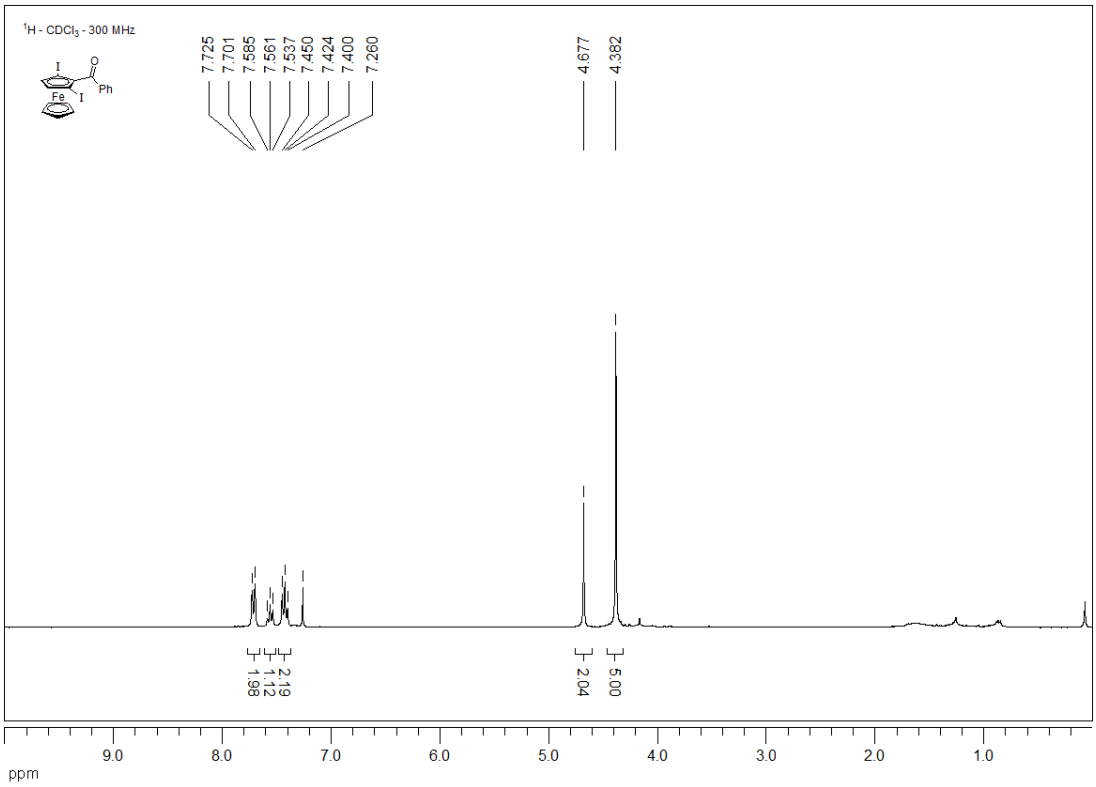
rac-8a ^{1}H



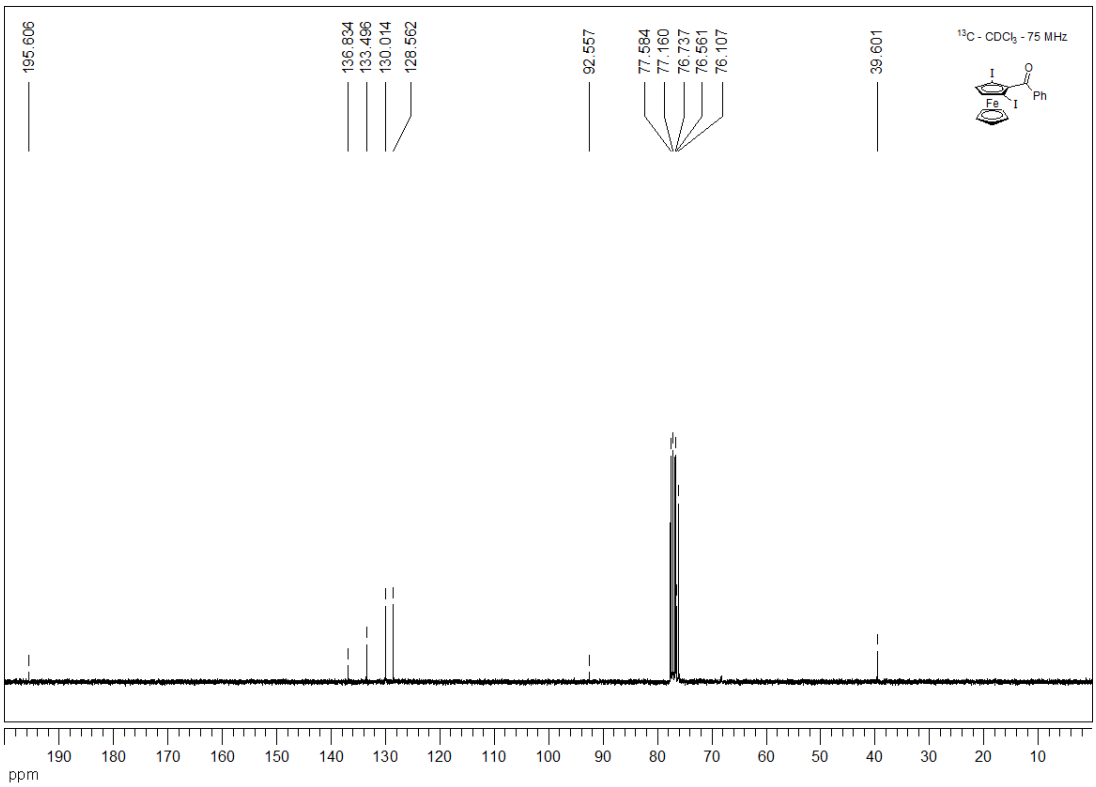
rac-8a ^{13}C



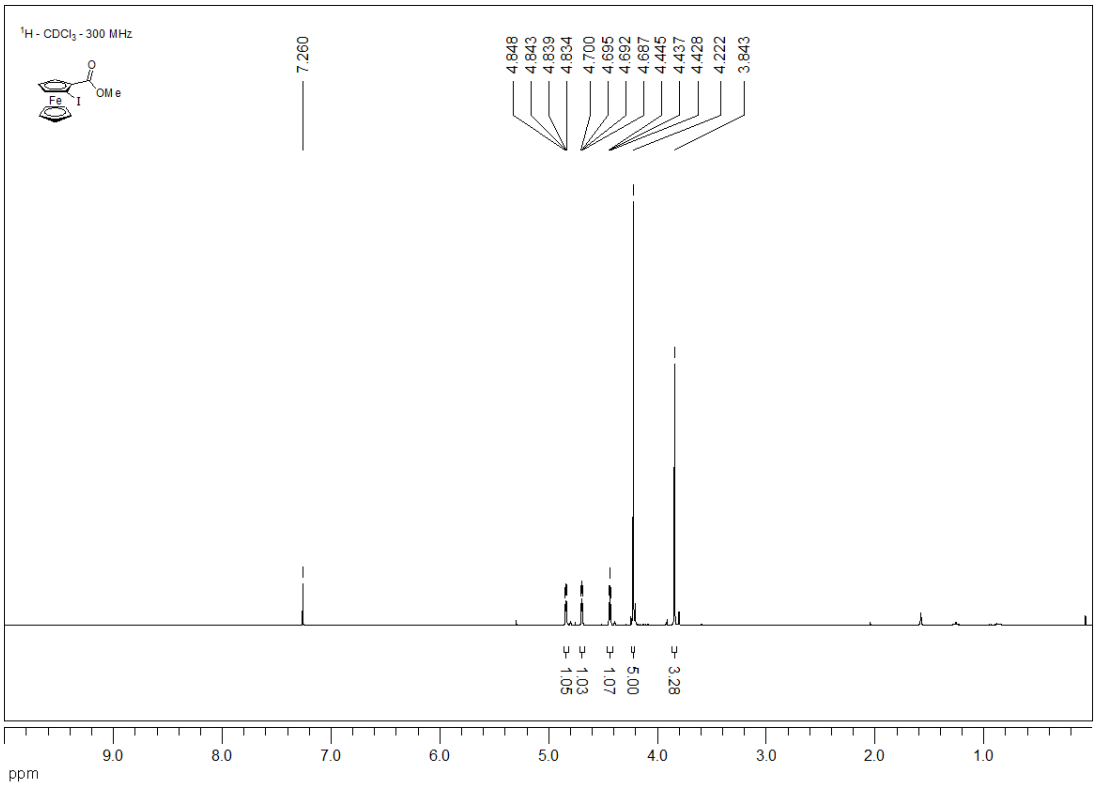
8b ^{1}H


1H - CDCl3 - 300 MHz
7.725
7.701
7.585
7.561
7.537
7.450
7.424
7.400
7.260
4.677
4.382
1.98
2.19
1.12
2.04
5.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm

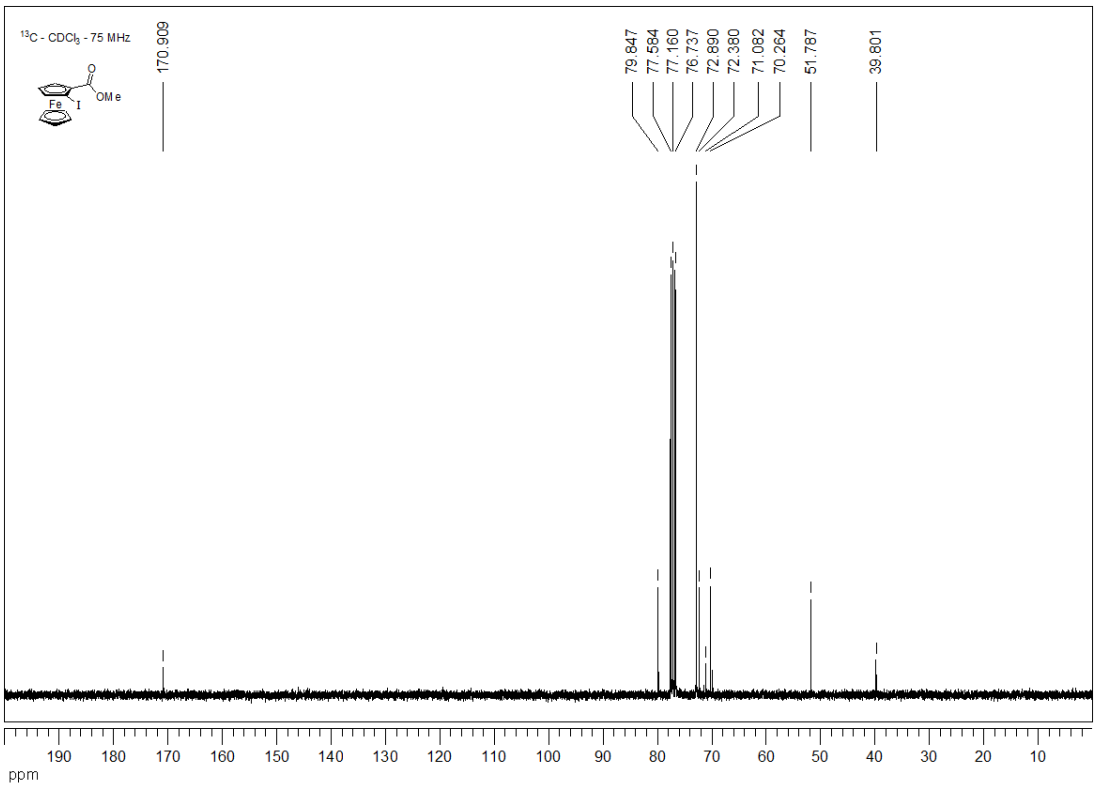
8b ^{13}C


195.606
136.834
133.496
130.014
128.562
92.557
77.584
77.160
76.737
76.561
76.107
39.601
13C - CDCl3 - 75 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

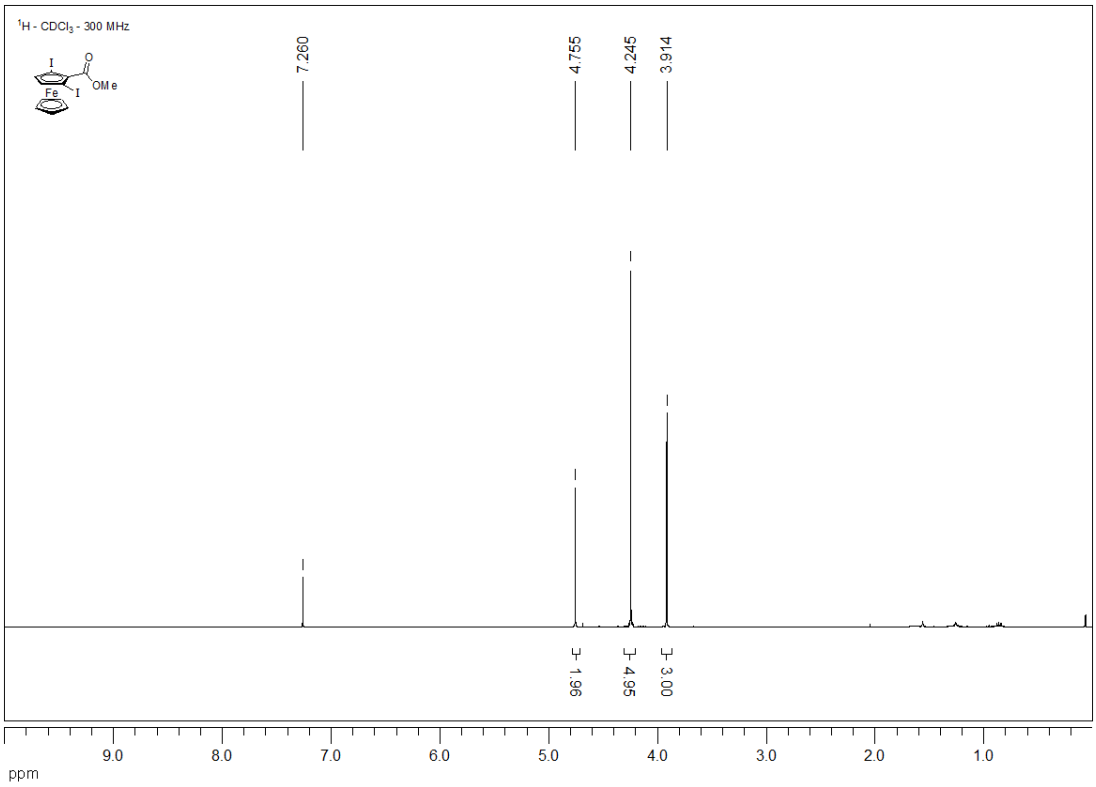
rac-10a ^{1}H



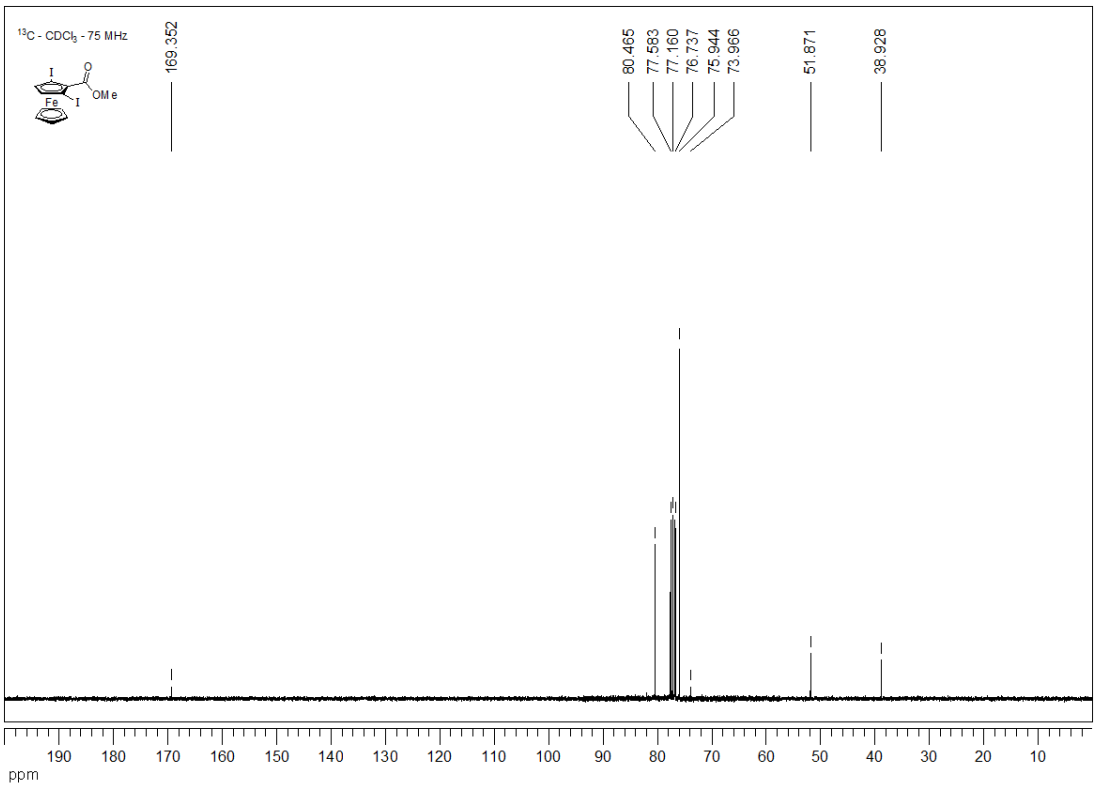
rac-10a ^{13}C



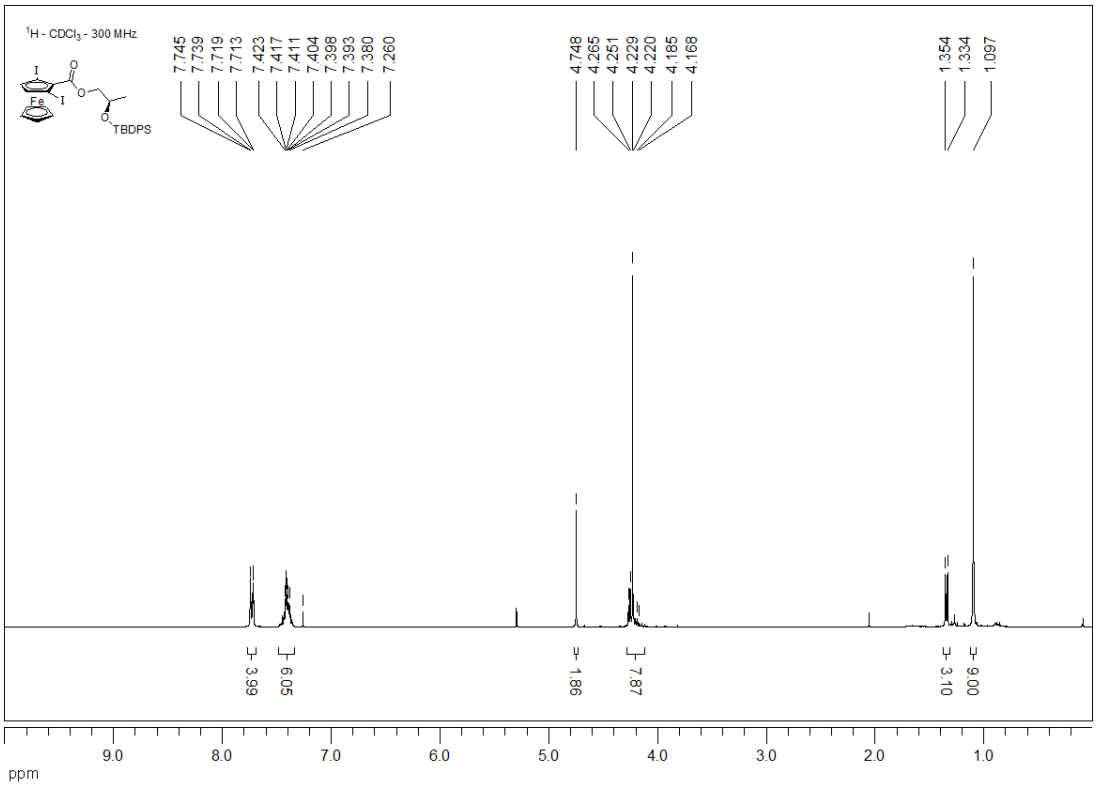
10b ^{1}H



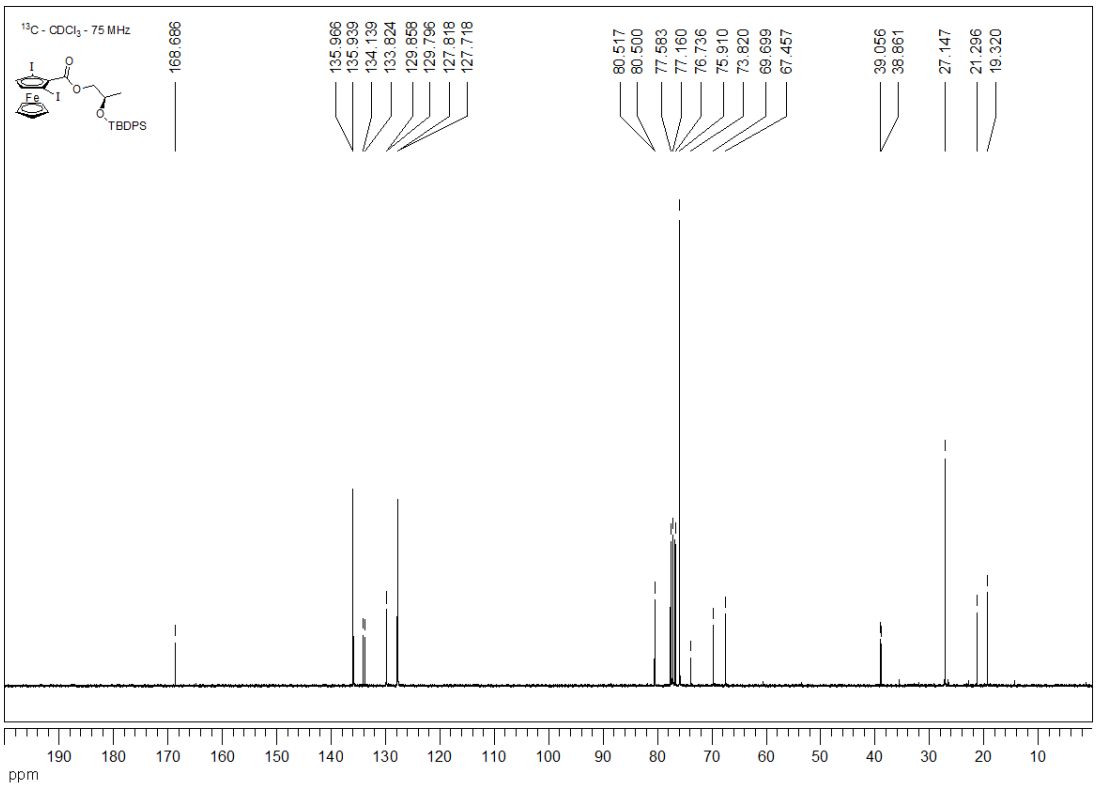
10b ^{13}C



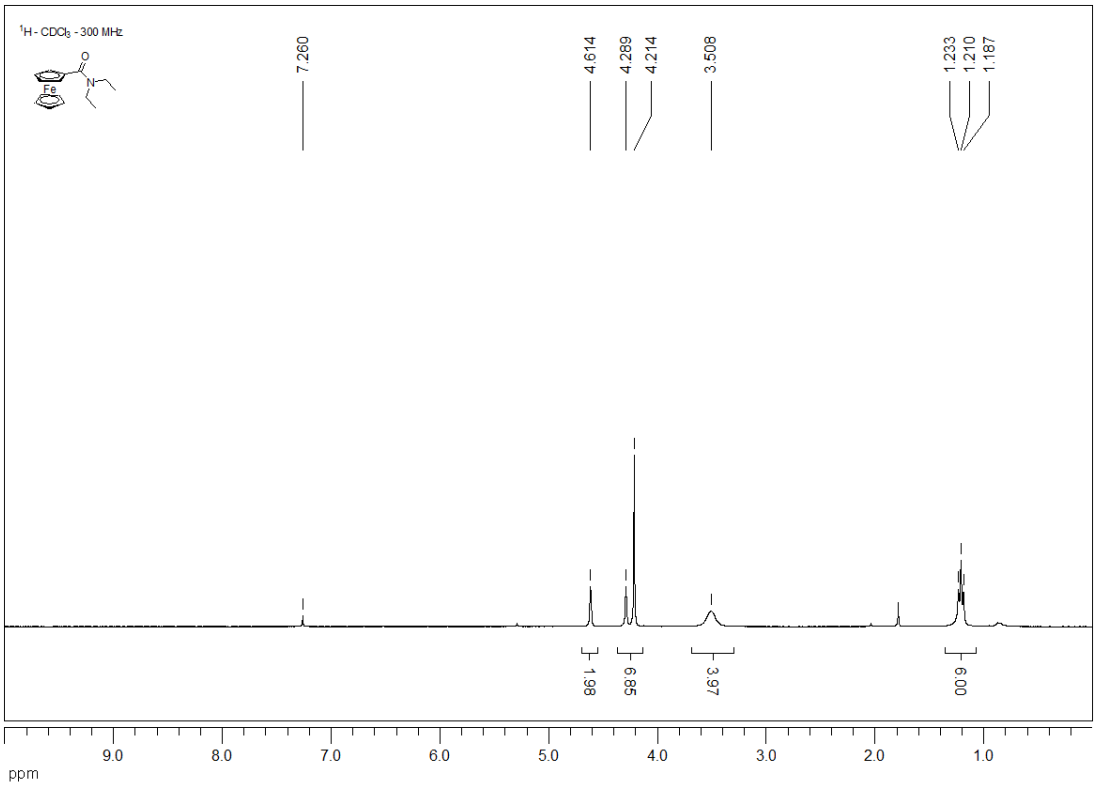
12b ^{1}H



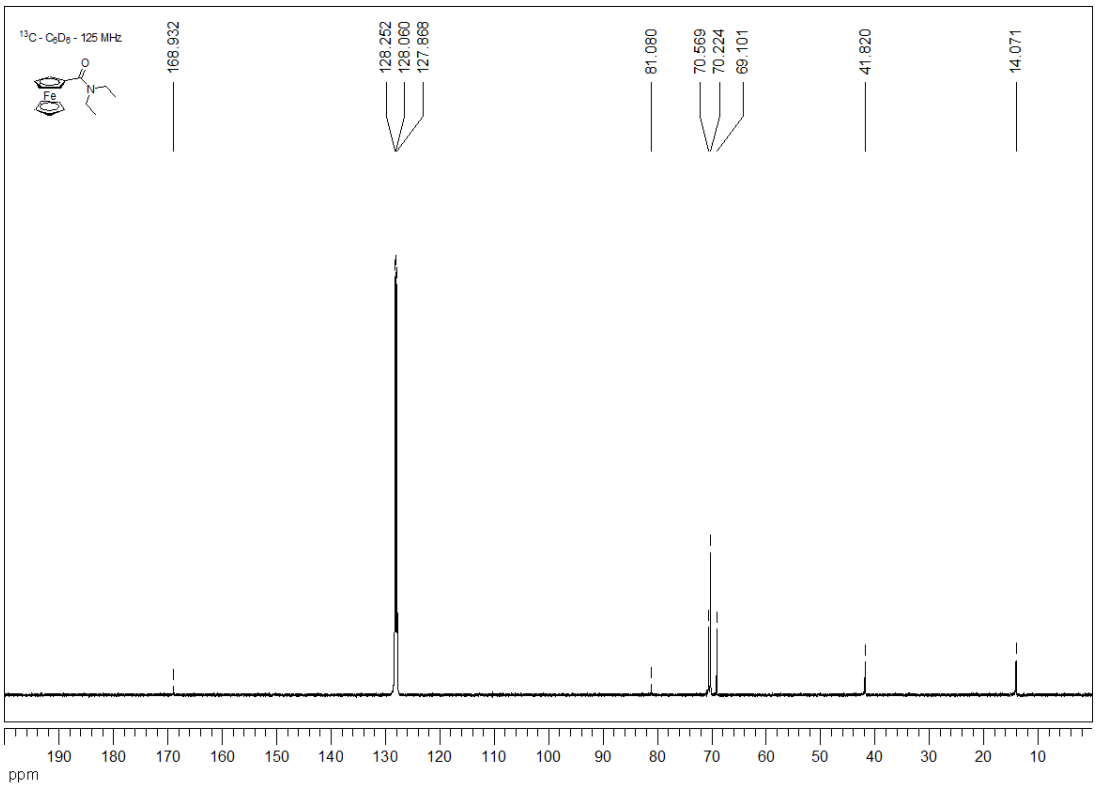
12b ^{13}C



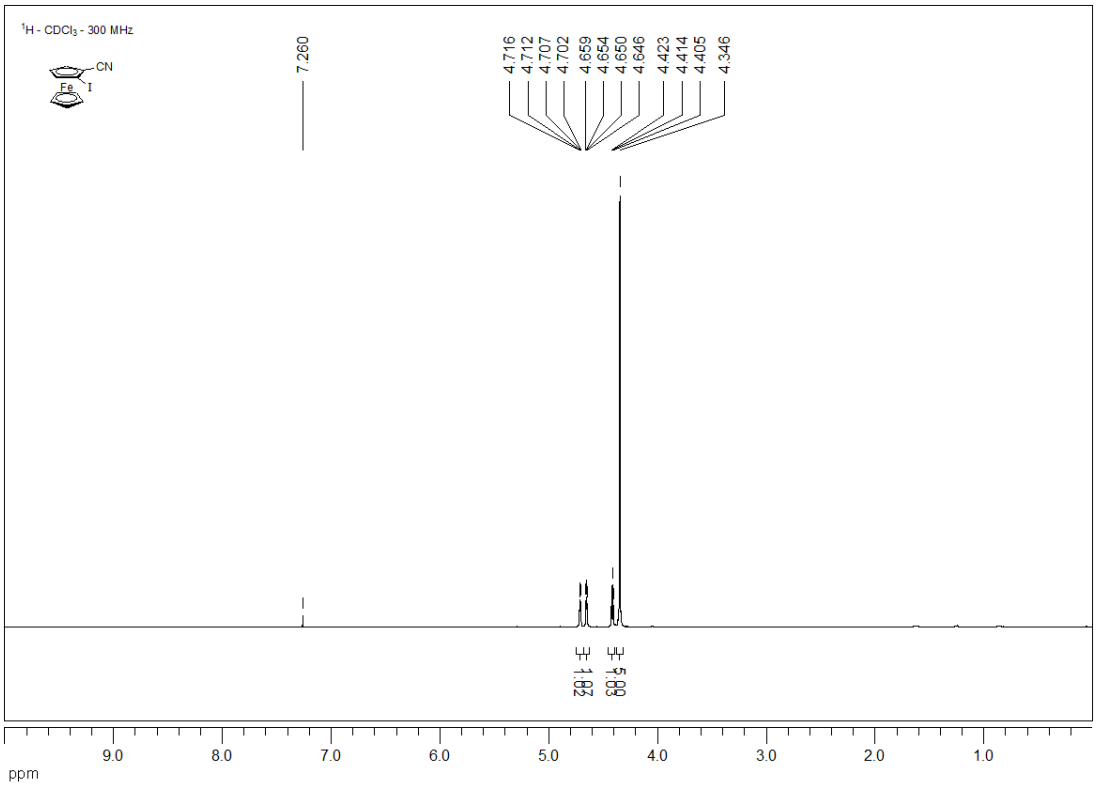
14 ^{1}H


1H - CDCl3 - 300 MHz
7.260
4.614
4.289
4.214
3.508
1.233
1.210
1.187
1.98
6.85
3.97
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm

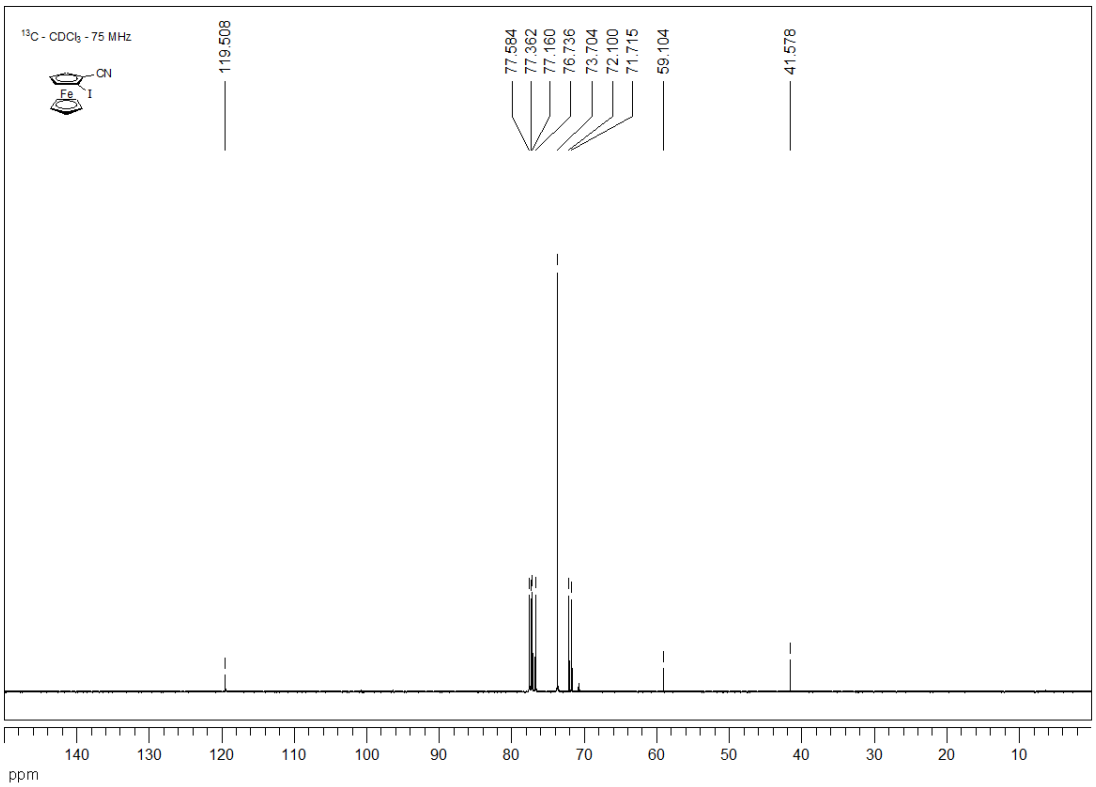
14 ^{13}C


13C - C6D6 - 125 MHz
168.932
128.252
128.060
127.868
81.080
70.569
70.224
69.101
41.820
14.071
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

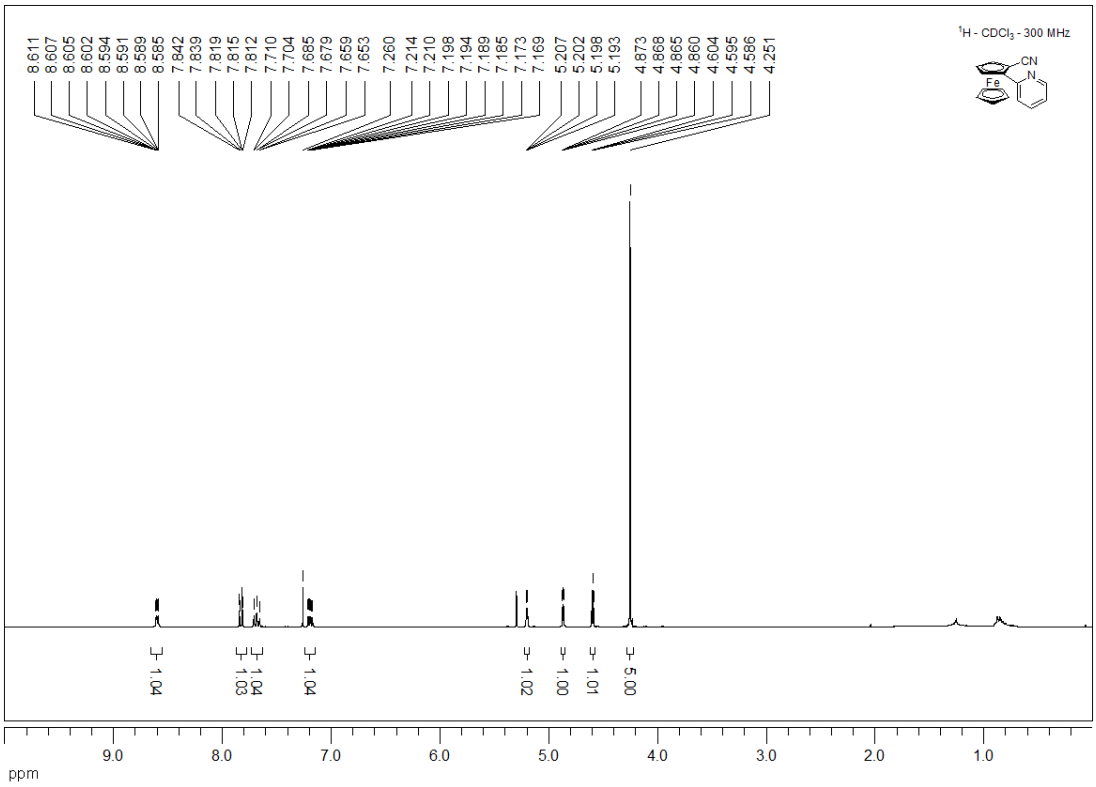
rac-15a ^{1}H



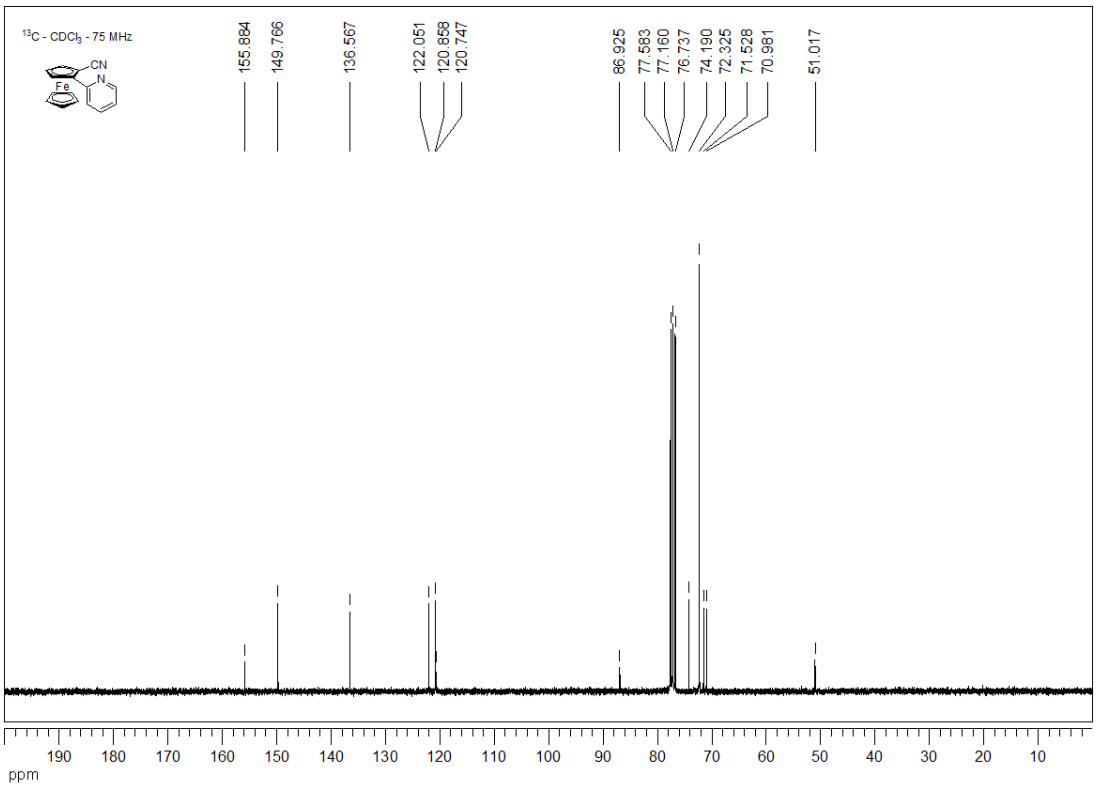
rac-15a ^{13}C



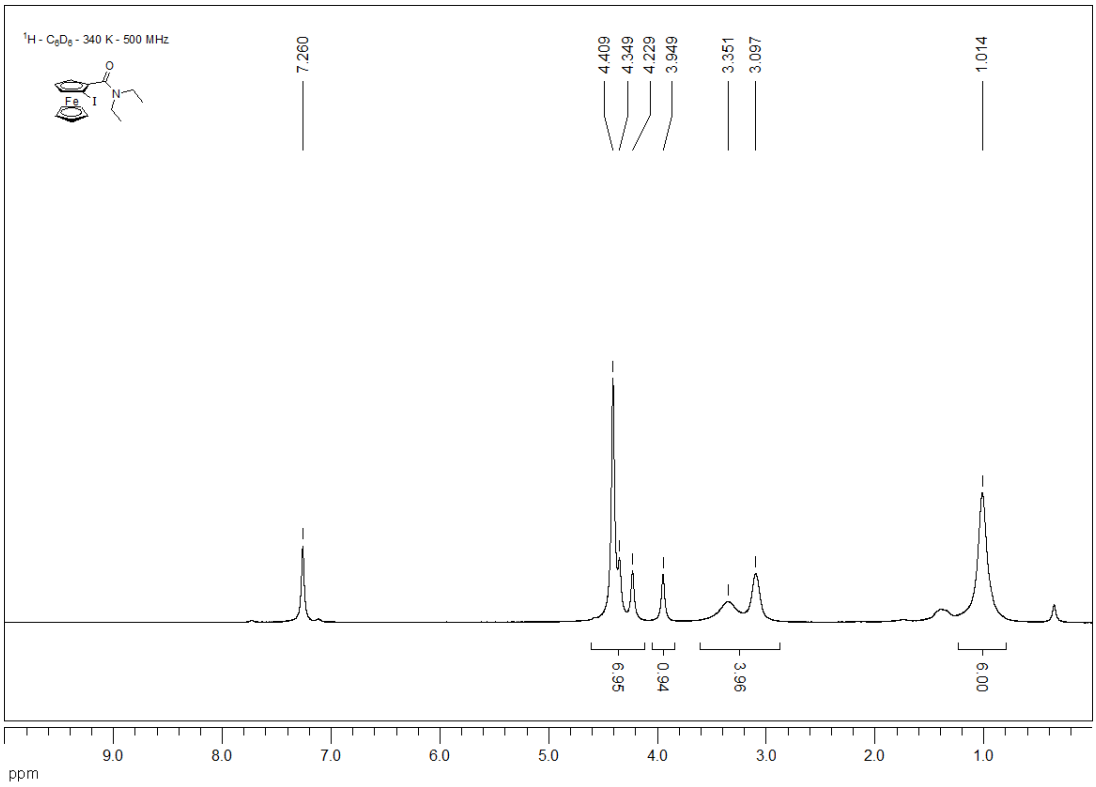
rac-15c ^{1}H



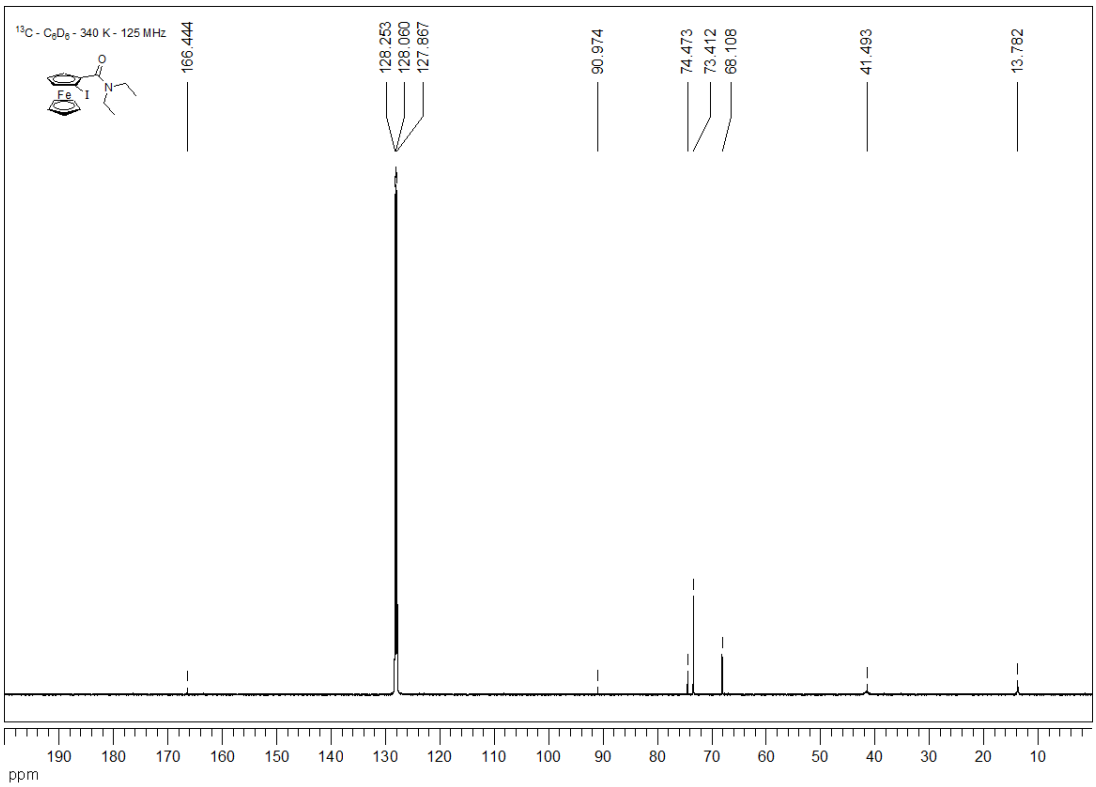
rac-15c ^{13}C



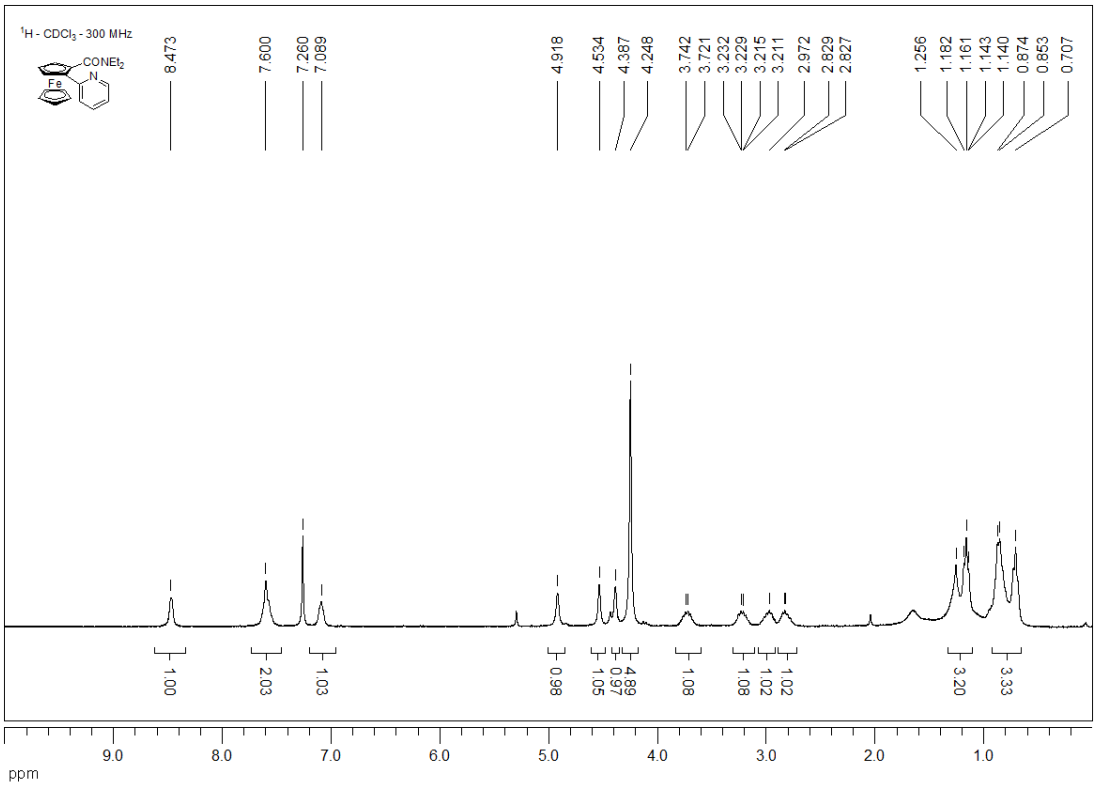
rac-16a ^{1}H



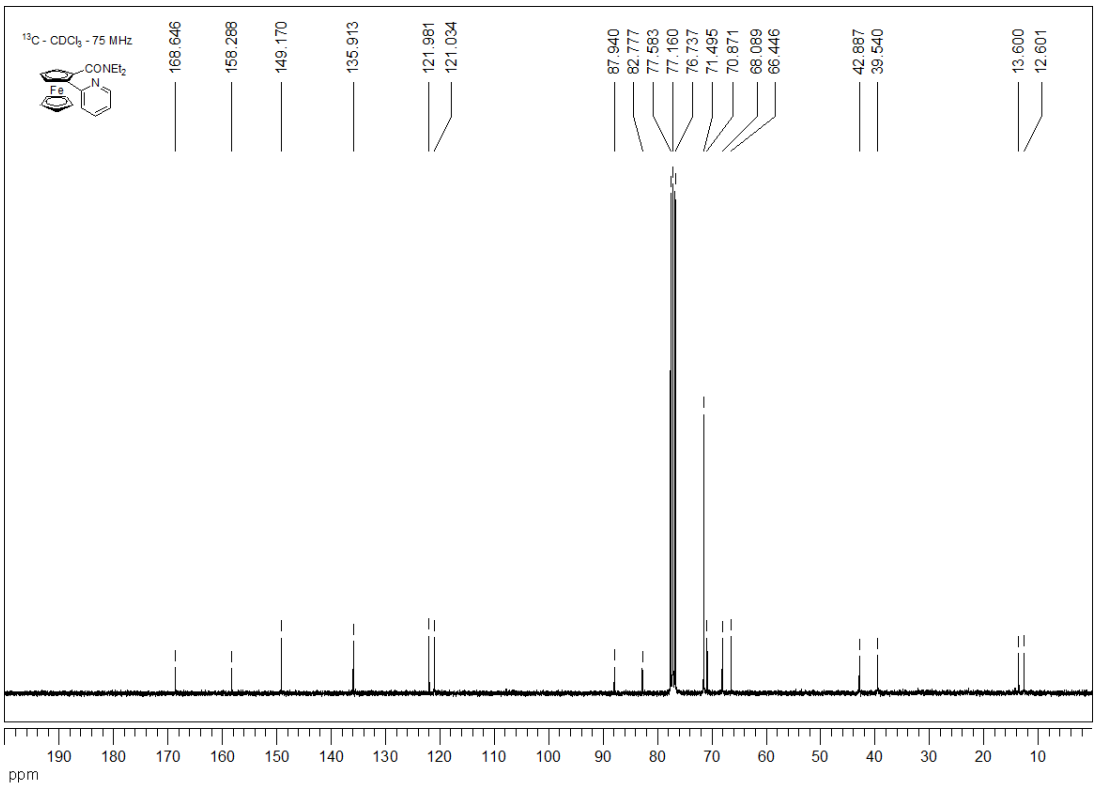
rac-16a ^{13}C



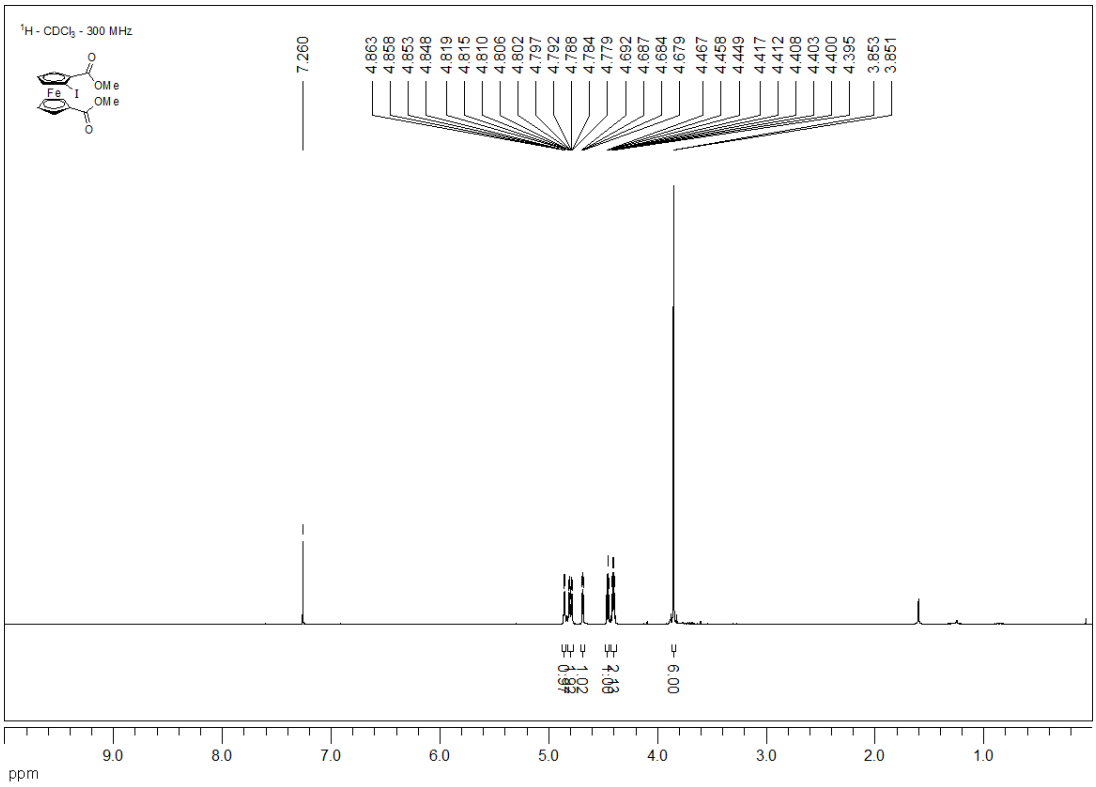
rac-16c ^{1}H



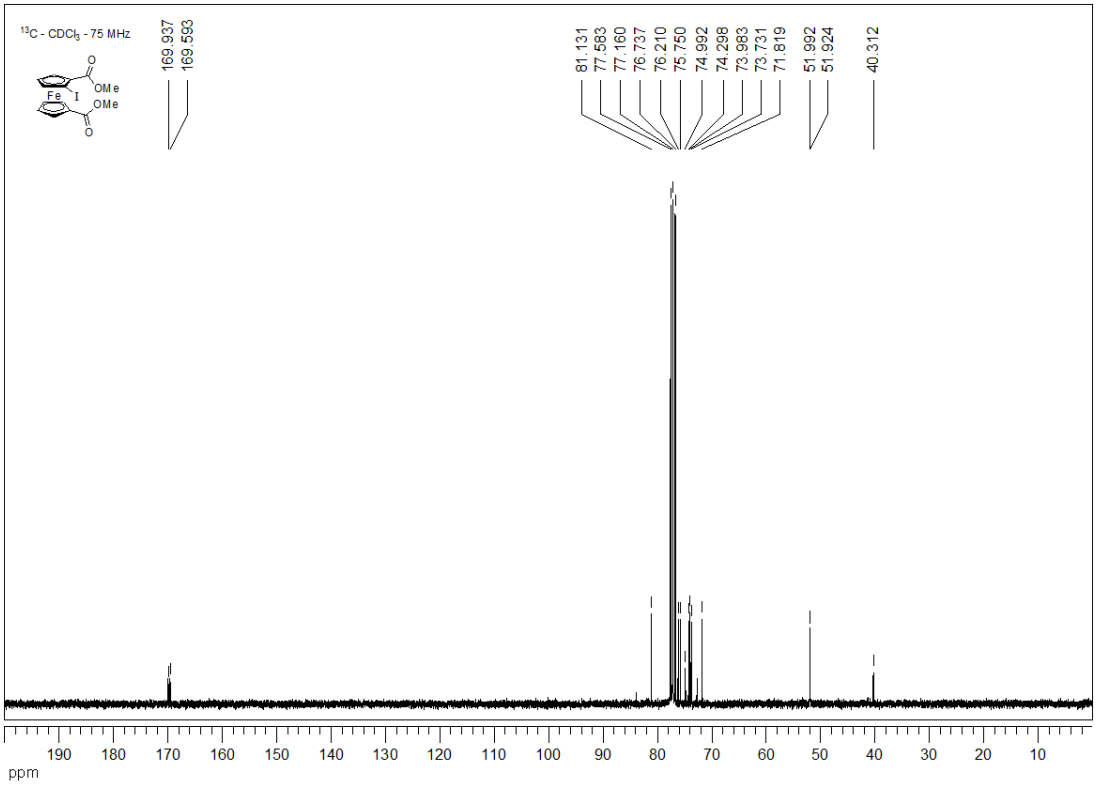
rac-16c ^{13}C



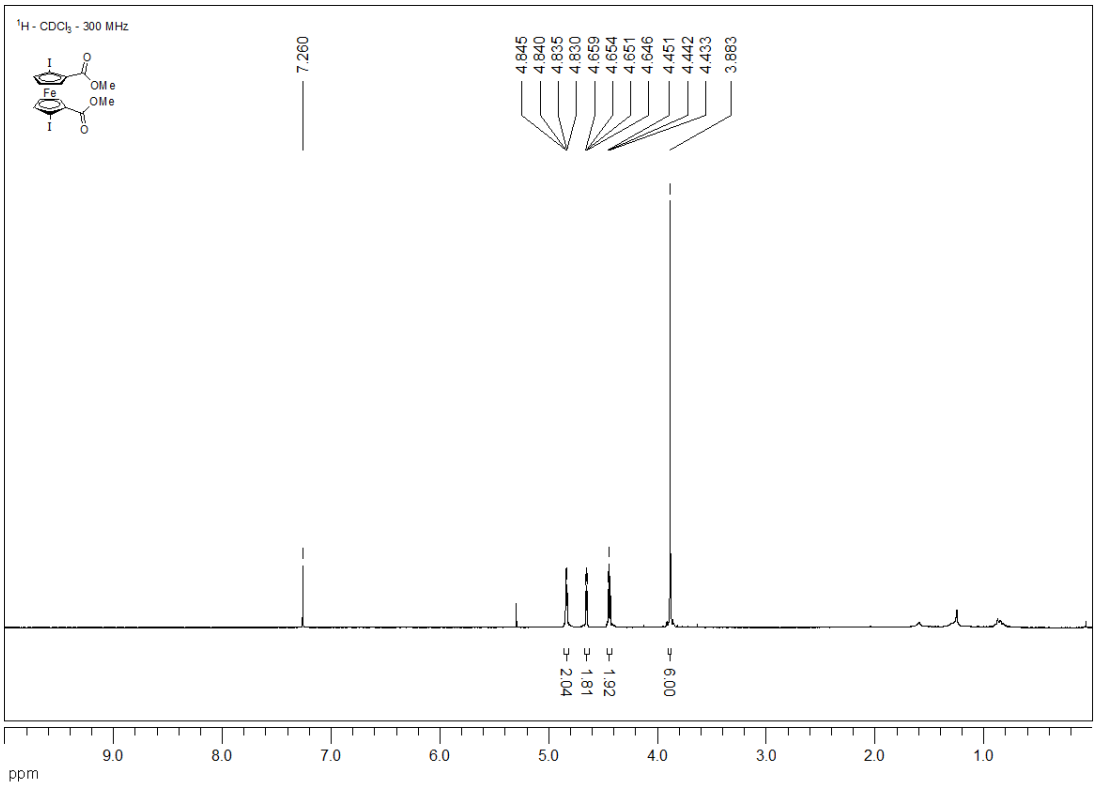
***rac*-18a** ^{1}H



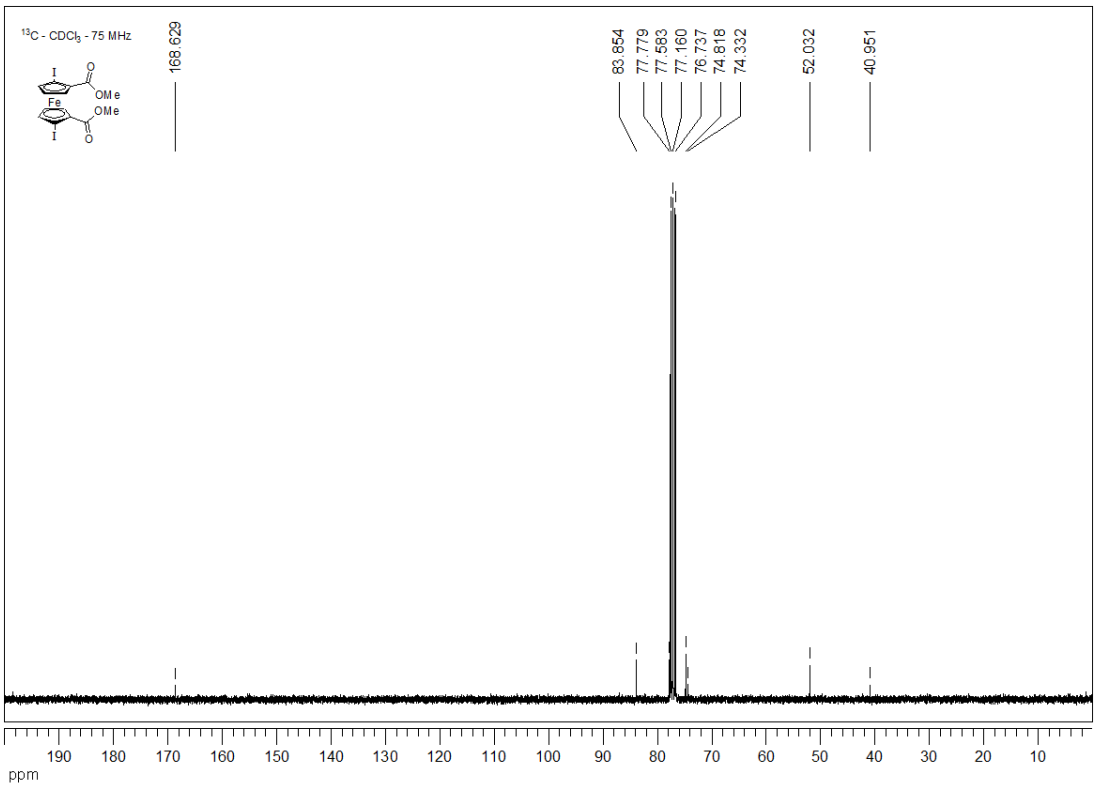
***rac*-18a** ^{13}C



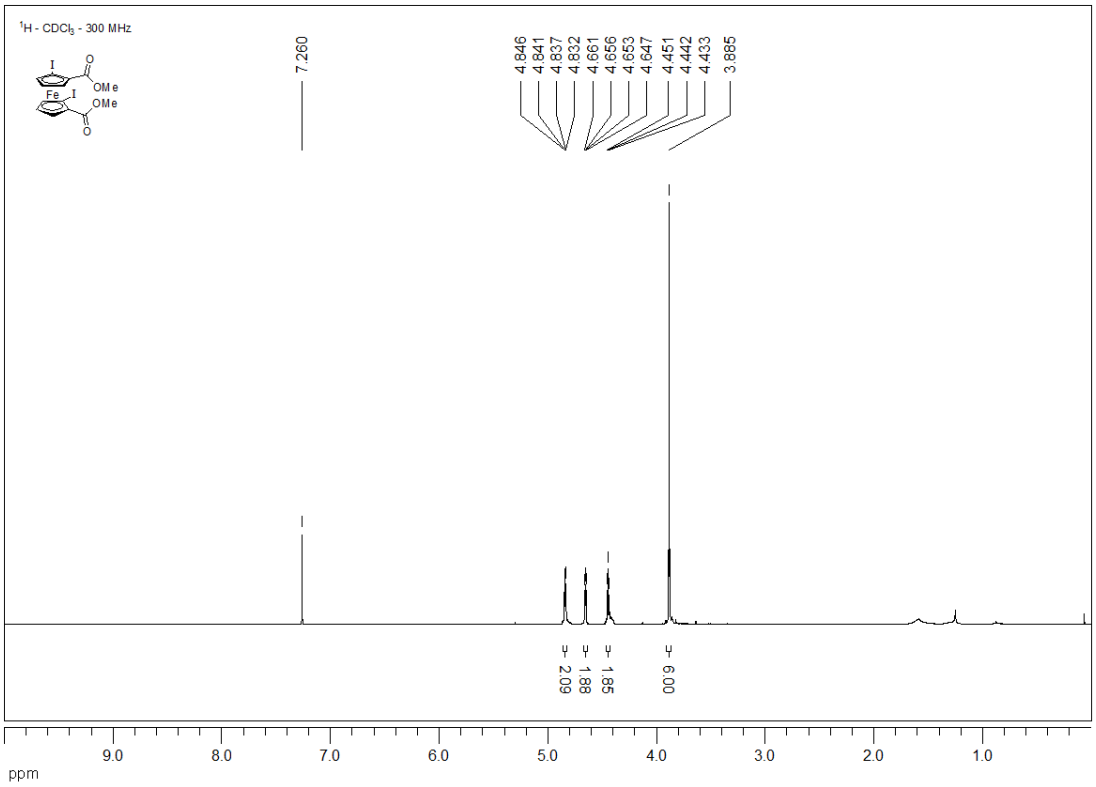
***rac*-18b1** ^{1}H



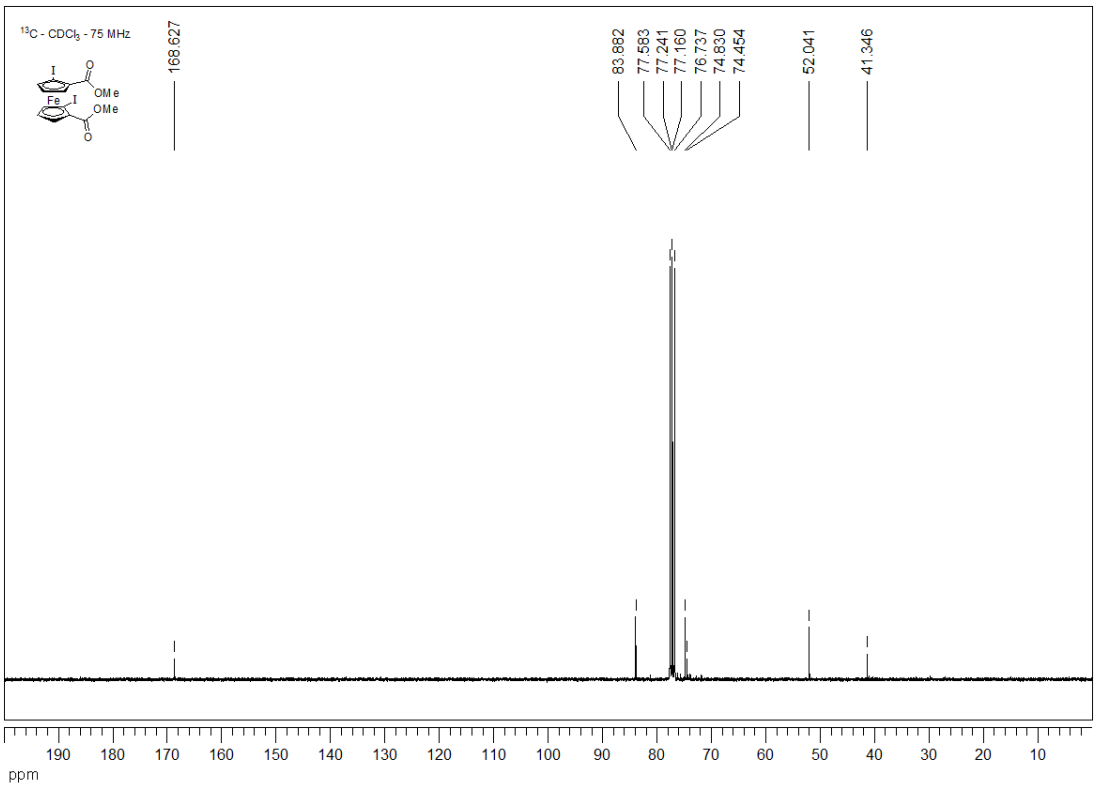
***rac*-18b1** ^{13}C



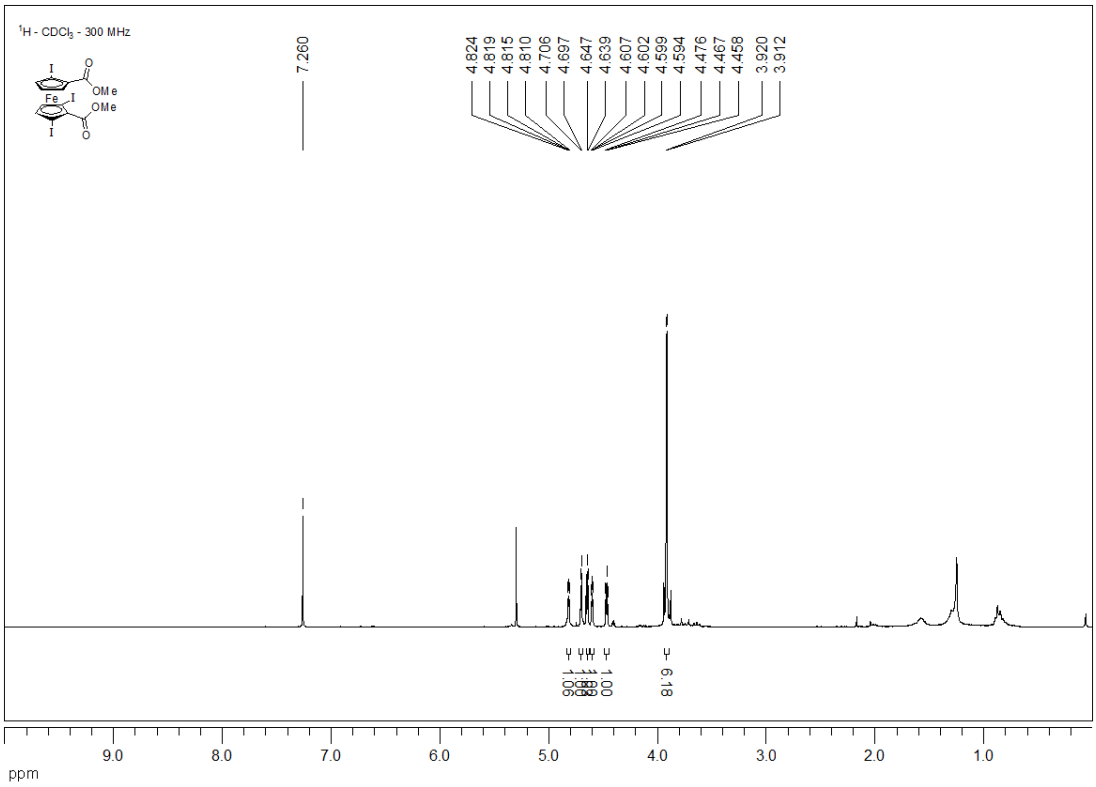
18b2 ^{1}H



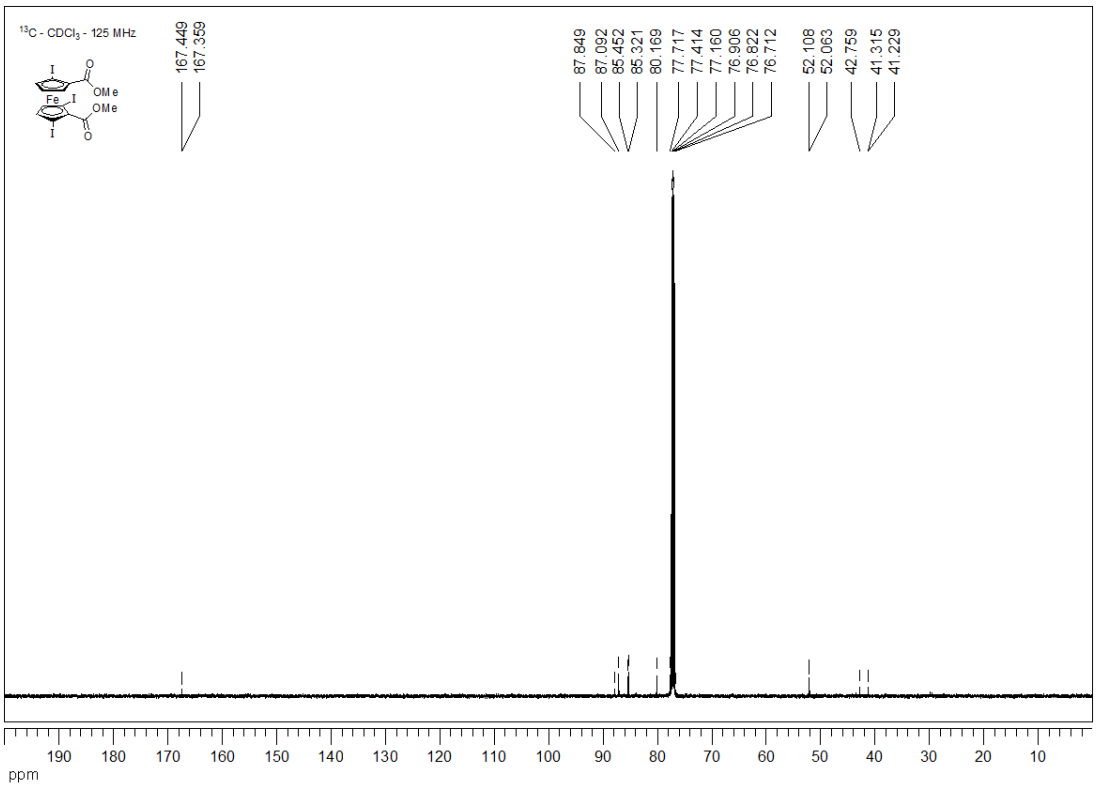
18b2 ^{13}C



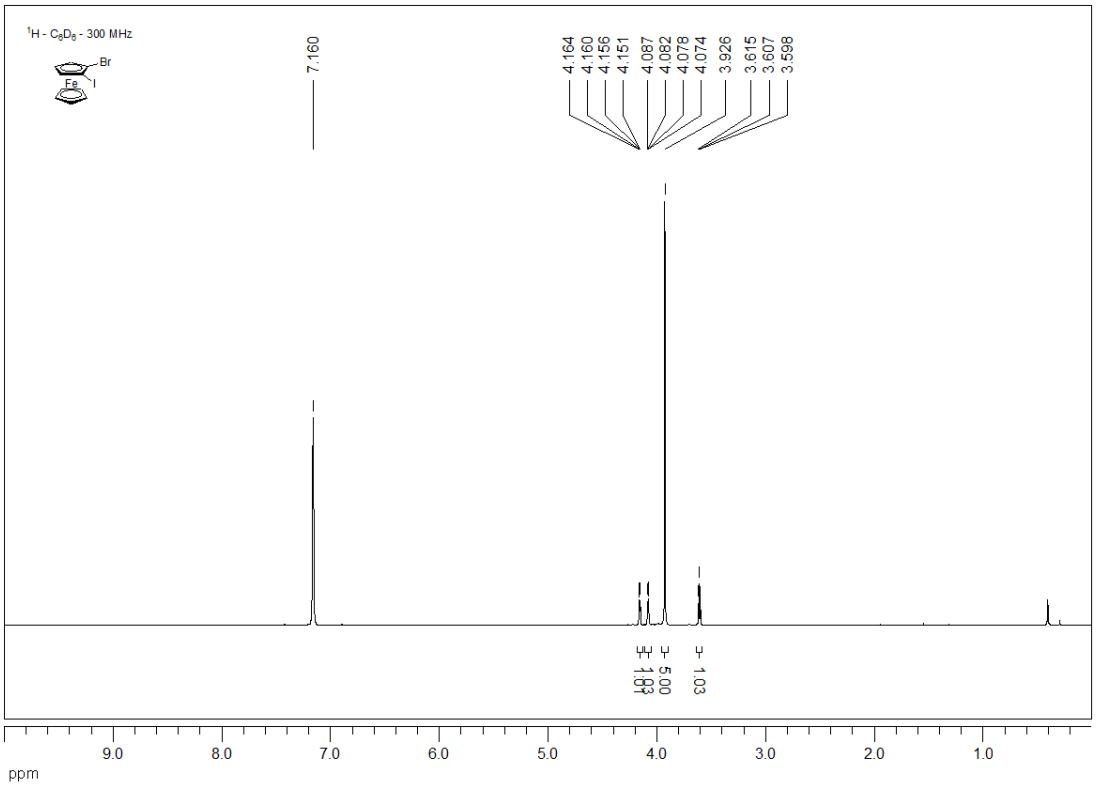
***rac*-18c** ^{1}H



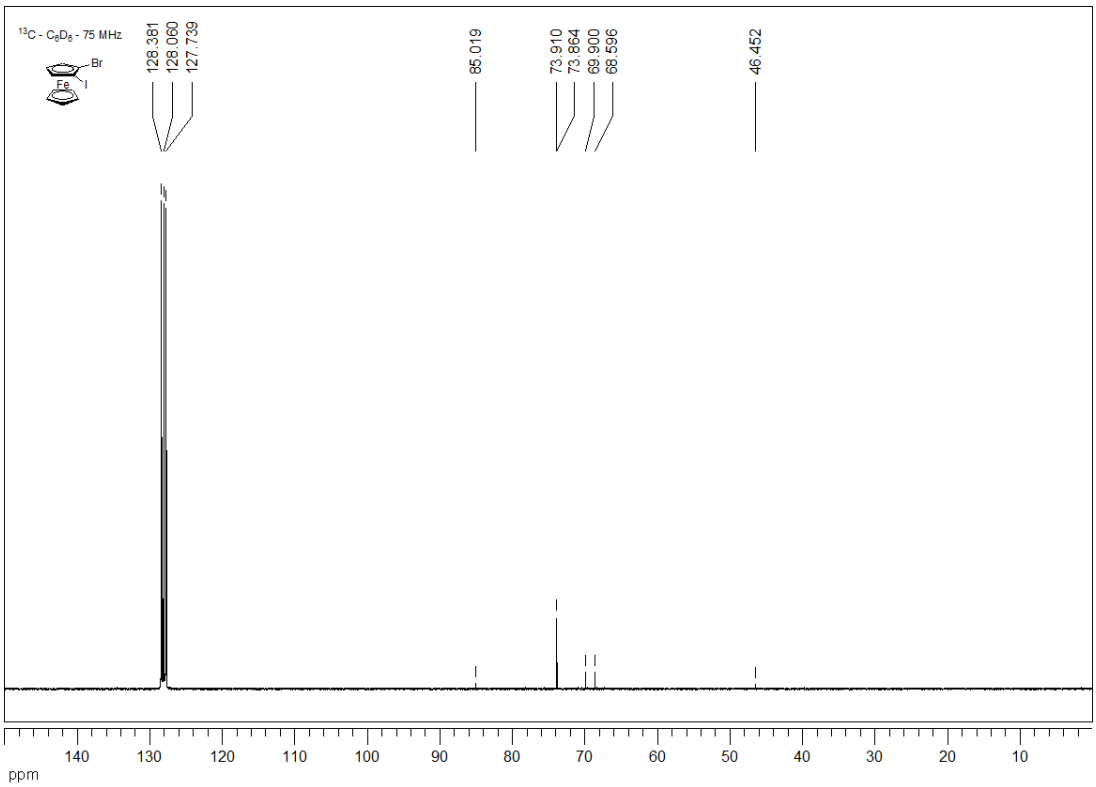
***rac*-18c** ^{13}C



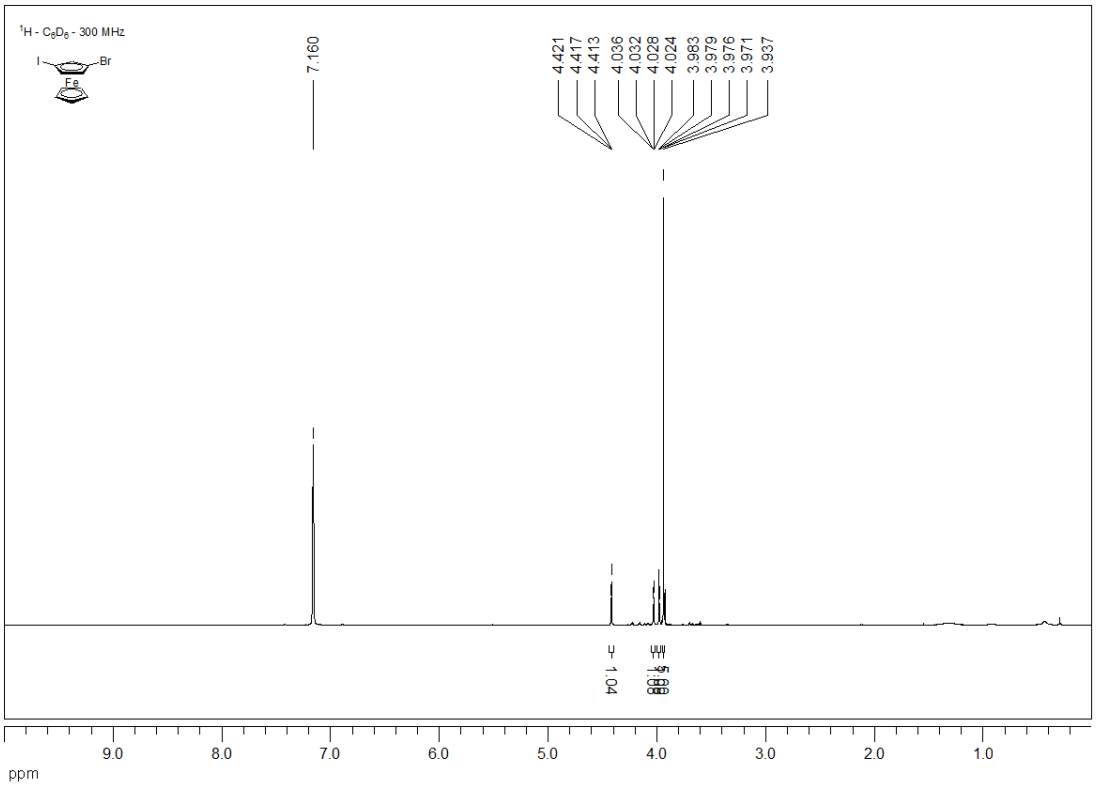
rac-20a ^{1}H



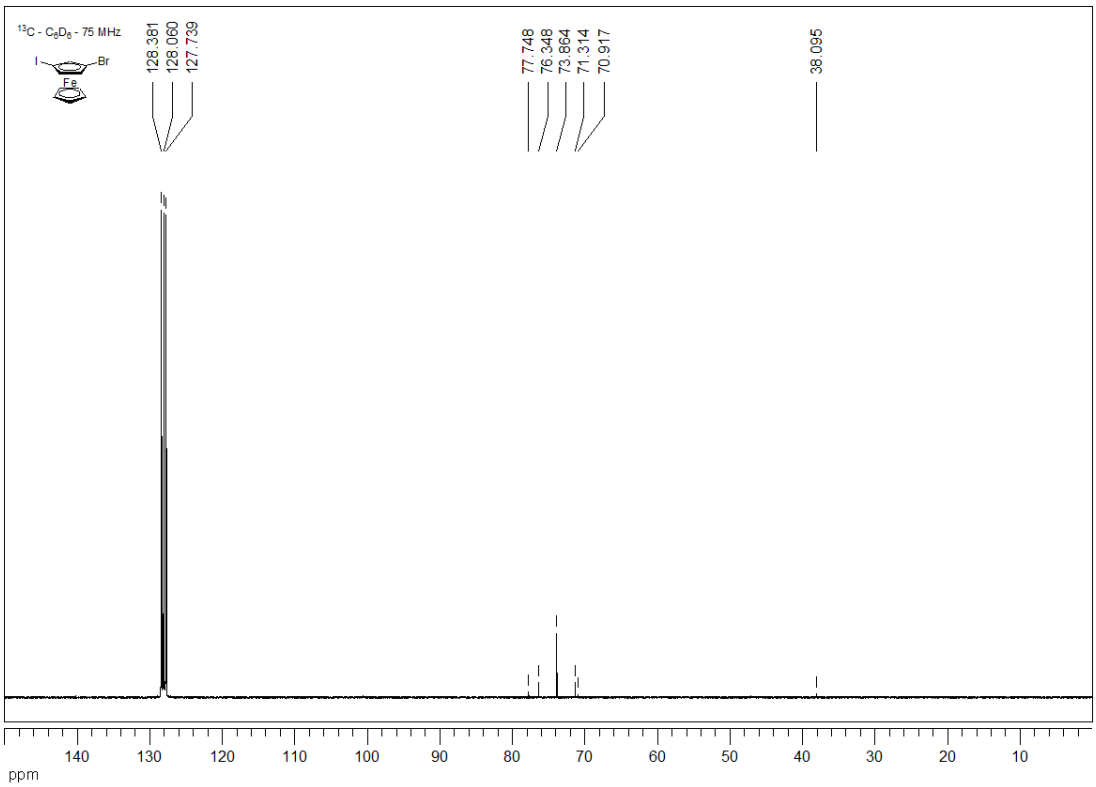
rac-20a ^{13}C



***rac*-20b** ^{1}H



***rac*-20b** ^{13}C



Crystal Data

Single crystals suitable for X-ray diffraction were grown after slow evaporation (several days at room temperature) of solutions of **10b**, **15c** and **20a** in CH_2Cl_2.

The samples were studied with graphite monochromatized $Mo_{K\alpha}$ radiation (λ = 0.71073 Å).

The structure was solved by direct methods using the SIR97 program,[13] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[14] with the aid of the WINGX program.[15] All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions.

Compound **10b**.

The X-ray diffraction data were collected using APEXII, Bruker-AXS diffractometer at T = 100(2) K.

$2(C_{12}H_{10}Fe_1I_2O_2)$, M_r = 991.70, monoclinic; space group P21/n (I.T.#14), a = 14.781(2) Å, b = 8.0884(14) Å, c = 22.871(4) Å, β = 101.820(5), V = 2676.4(8) Å^3, Z = 4, ρ_{calcd} = 2.461 g.cm^{-3}, μ = 5.727 mm^{-1}. A final refinement on F^2 with 6132 unique intensities and 309 parameters converged at $\omega R(F^2)$ = 0.1091 (R(F) = 0.0462) for 5085 observed reflections with $I > 2\sigma(I)$.

Compound **15c**.

The X-ray diffraction data were collected using KappaCCD diffractometer at T = 150(2) K.

$2(C_{16}H_{12}FeN_2)$, M_r = 576.25, monoclinic; space group P21/c (I.T.#14), a = 16.3522(6) Å, b = 8.7529(4) Å, c = 17.9951(6) Å, β = 102.168(3)°, V = 2517.76(17) Å^3, Z = 4, ρ_{calcd} = 1.52 g.cm^{-3}, μ

[13] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115-119.
[14] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
[15] L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837-838.

= 1.182 mm^{-1}. A final refinement on F^2 with 5773 unique intensities and 343 parameters converged at $\omega R(F^2)$ = 0.0755 (R(F) = 0.0318) for 4303 observed reflections with $I > 2\sigma(I)$.

Compound **20a**.

The X-ray diffraction data were collected using APEXII, Bruker-AXS diffractometer at T = 150(2) K.

($C_{10}H_8BrFeI$, $C_{10}H_8BrFeI$), M_r = 781.65, triclinic; space group P-1 (I.T.#2), a = 9.8917(4) Å, b = 10.0527(5) Å, c = 10.8535(5) Å, α = 81.390(2)°, β = 82.628(2)°, γ = 84.345(2)°, V = 1054.8(8) $Å^3$, Z = 2, ρ_{calcd} = 2.461 $g.cm^{-3}$, μ = 8.093 mm^{-1}. A final refinement on F^2 with 4746 unique intensities and 235 parameters converged at $\omega R(F^2)$ = 0.1182 (R(F) = 0.0451) for 4184 observed reflections with $I > 2\sigma(I)$.

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).