

Supporting information for:
**Oxazaphospholidine-oxide as an efficient *ortho*-directing group for the
diastereoselective deprotonation of ferrocene**

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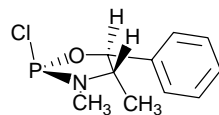
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General Conditions

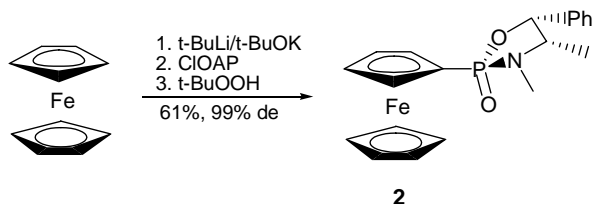
All reactions were carried out under a nitrogen atmosphere with standard Schlenk techniques. All glassware was oven-dried for a minimum of two hours before use. THF, dioxane and Et₂O were distilled under nitrogen atmosphere from a deep blue solution of sodium-benzophenone ketyl prior to use. Toluene, CH₂Cl₂, and NEt₃ were freshly distilled over powdered CaH₂ prior to use. Flash-chromatography was performed using silica gel 60 Å (37-70 nm). Analytical TLC was carried out utilizing 0.25 mm precoated plates (silica gel 60 UV₂₅₄) and spots were visualized by use of UV light and silica-I₂ revelation. For NMR spectra samples were dissolved in CDCl₃ and run at room temperature. ¹H (400 MHz), ¹³C (100 MHz), ³¹P (162 MHz) and ¹⁹F (376 MHz) NMR spectra were recorded on a 400 MHz Bruker spectrometer. Chemical shifts for protons are reported using TMS (0.05%) as internal reference (δ 0). Carbon signals are referenced to the shift from the ¹³C signal of CDCl₃ (δ 77.0). Mass spectra were measured at 50 eV (EI). Elemental analysis was performed by the Microanalysis Laboratory, Department of Chemistry, University of Liverpool. Melting points are reported as their uncorrected values.

(2*R*,4*S*,5*R*)-2-Chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine (1)



A 1 L Schlenk flask, equipped with magnetic stirrer bar and septum, was charged with toluene (250 mL) and *N*-methylmorpholine (26.6 mL, 242.0 mmol). Addition of PCl_3 (10.5 mL, 121 mmol) was smoky and resulted in a cloudy solution that was subsequently cooled to $-78\text{ }^\circ\text{C}$. A second Schlenk flask, equipped with a magnetic stirrer bar and septum, was charged with (1*R*,2*S*)-(-)-ephedrine and 150 mL of toluene and the solution was transferred via cannula to the first Schlenk flask. The reaction was allowed to reach room temperature overnight and the mixture was then filtered from the morpholine hydrochloride salt over previously oven-dried Celite. The yellowish solution was then evaporated under vacuum and the resulting oil solidified upon overnight cooling in the freezer ($-30\text{ }^\circ\text{C}$). The desired product was recovered as a yellowish waxy solid in 75% yield (20.8 g, 91.0 mmol). No further purification of the product was necessary before being used for the next step. ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.71 (d, $J = 6.5\text{ Hz}$, 3H), 2.69 (d, $J = 15.9\text{ Hz}$, 3H), 3.59-3.67 (m, 1H), 5.82 (d, $J = 7.8\text{ Hz}$ 1H), 7.14-7.36 (m, 5H). ^{31}P -NMR (CDCl_3 , 162 MHz) δ (ppm): 172.4.

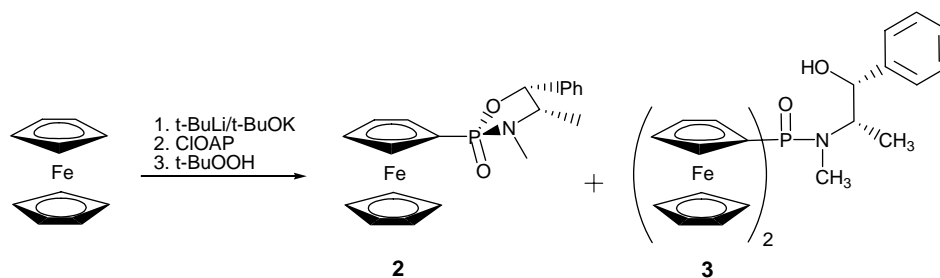
(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (2)



A Schlenk flask equipped with magnetic stirrer bar and septum was charged with ferrocene (8.00 g, 43.0 mmol) and *t*-BuOK (0.77 g, 6.9 mmol). The powder mixture was degassed using vacuum-nitrogen cycles before dry THF (100 mL) was added. The flask was cooled to $-78\text{ }^\circ\text{C}$ with a bath of dry ice and acetone and then *t*-BuLi (27.8 mL, 47.3 mmol) was added. After 1 hour stirring at room temperature a fine red-brick precipitate

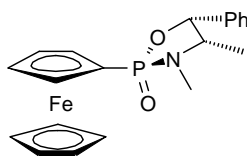
was formed. The slurry was transferred via cannula to a second Schlenk flask (500 mL), also equipped with magnetic stirrer bar and septum, containing a solution of oxazaphospholidine chloride (14.80 g, 64.5 mmol) in dry THF (150 mL) and previously cooled to -78 °C. The reaction was allowed to reach slowly room temperature. After overnight stirring the mixture was cooled to 0 °C with an ice bath and t-BuOOH (11 mL, 64.5 mmol) was added. After another 4 hours stirring the mixture was washed with a saturated solution of Na₂S₂O₃, extracted with EtOAc and dried over MgSO₄. The solution was filtrated from the salt on a sintered funnel and the solvent evaporated under vacuum. The crude mixture was then purified by flash chromatography on silica gel using EtOAc as eluent to afford (2*R*,4*S*,5*R*)-3,4-dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide **2** in 61% yield (10.3 g, 26.1 mmol).

When only one equivalent of oxazaphospholidine chloride was used (43.0 mmol) the ¹H-NMR of the crude mixture showed two products containing ferrocene. After purification by flash chromatography on silica gel using EtOAc/MeOH (9:1) as eluent, **2** was isolated in 43% yield (7.3 g, 18.5 mmol) and **3** in 28.5% yield (7.2 g, 12.2 mmol).



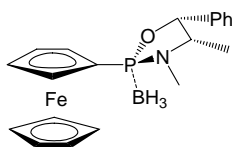
Analytical data

(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (**2**)



Mp: 160-162 °C. $[\alpha]_D^{20} = 140.1^\circ$ ($c = 0.81$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.83 (d, $J = 6.5$ Hz, 3H), 2.56 (d, $J = 10.3$ Hz, 3H), 3.60 (doublet of quintets, $J = 6.5$ Hz, 12.8 Hz, 1H), 4.34 (s, 5H), 4.35 (m, 1H), 4.44 (m, 2H), 4.70 (m, 1H), 5.47 (t, $J = 6.7$ Hz, 1H), 7.49-7.32 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.6, 28.8, 58.8, 69.9, 69.9, 71.3, 71.7, 82.3, 126.7, 128.2, 128.4, 136.7. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 40.8. HRMS calcd for C₂₀H₂₂FeNO₂P [M+Na]⁺: found: 418.0616, calculated: 418.0635. Anal. Calcd for C₂₀H₂₂FeNO₂P: C 60.78, H, 5.61, N, 3.54. Found: C, 60.44, H, 5.49, N, 3.38;

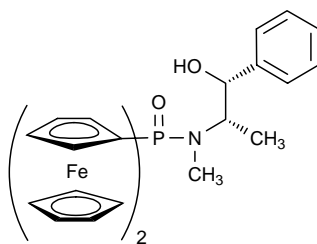
(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]oxazaphospholidine 2-borane (2a)



The procedure was the same as for **2** except BH₃S(CH₃)₂ was used instead of t-BuOOH.

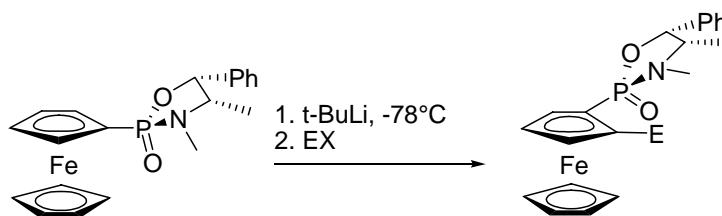
Mp: 162-163 °C. $[\alpha]_D^{20} = 95.4^\circ$ ($c = 0.65$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.75 (d, $J = 6.0$ Hz, 3H), 2.64 (d, $J = 12.0$ Hz, 3H), 3.54 (m, 1H), 4.34 (s, 6H), 4.48 (m, 2H), 4.59 (m, 1H), 5.51 (dd, $J = 4.9$ Hz, 6.3 Hz, 1H), 7.32-7.43 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.0, 29.4, 58.3, 69.7, 69.7, 72.1, 74.0, 84.6, 127.1, 128.31, 136.8. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 138.5. Anal. Calcd for C₂₀H₂₅BFeNOP: C, 61.12, H, 6.41, N, 3.56. Found: C, 61.30, H, 6.45, N, 3.47.

***N*-((1*R*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl)-*N*-methyl-*P,P*-diferrocenylphosphinic amide (3)**



Mp: 190-192 °C. $[\alpha]_D^{20} = -10.9^\circ$ ($c = 1.1$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 1.37 (d, $J = 7.2$ Hz, 3H), 1.93 (d, $J = 10.6$ Hz, 3H), 3.84 (m, 1H), 4.27-4.29 (m, 3H), 4.36 (s, 5H), 4.40 (s, 5H), 4.41 (m, 1H), 4.45 (m, 1H), 4.50 (m, 1H), 4.55 (m, 1H), 4.60 (m, 1H), 4.76 (m, 1H), 7.22-7.44 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 15.4, 32.0, 57.3, 70.1, 70.1, 70.7, 70.8, 70.8, 71.4, 71.5, 71.9, 72.3, 73.9, 74.2, 75.6, 77.6, 127.4, 127.5, 128.7, 142.5. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 44.2. HRMS calcd for C₃₀H₃₂Fe₂NO₂P $[M+Na]^+$: 604.2458. Found: 604.0801. Anal. Calcd for C₃₀H₃₂Fe₂NO₂P: C, 61.99, H, 5.55, N, 2.41. Found: C, 61.96, H, 5.55, N, 2.40.

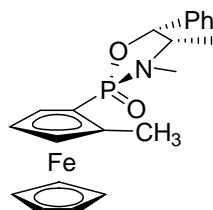
General Procedure for the *ortho*-Lithiation Reactions



A Schlenk tube, equipped with magnetic stirrer bar and septum, was charged with (2*R*,4*S*,5*R*)-3,4-dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide **2** (0.20 g, 0.51 mmol). The tube was degassed using vacuum-nitrogen cycles and then THF was added. The mixture was cooled to -78°C with a bath of dry ice and acetone for 30 minutes before *t*-BuLi was added. The reaction was stirred at -78°C for another hour before the electrophile was added. After overnight stirring at room temperature the crude product was analyzed with ¹H and ³¹P NMR, extracted with EtOAc (2 x 50 mL), washed with brine and dried over MgSO₄. Evaporation of the solvent under reduced pressure and purification by flash chromatography on silica gel afforded the pure products.

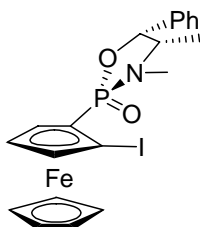
Analytical data

(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{Fe})-methyl-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (**4**)



The compound was purified by flash chromatography using EtOAc as eluent and recrystallized from the same solvent to afford orange needle crystals in 95% yield (199 mg, 0.48 mmol). Mp: 148 °C. $[\alpha]_D^{20} = 218.9^\circ$ ($c = 0.66$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.74 (d, $J = 6.5$ Hz, 3H), 2.23 (s, 3H), 2.41 (d, $J = 10.6$ Hz, 3H), 3.50 (doublet of quintets, $J = 6.5$ Hz, 15.2 Hz, 1H), 4.07 (s, 1H), 4.14 (s, 5H), 4.15 (s, 1H), 4.22 (s, 1H), 5.33 (dd, $J = 6.8$ Hz, 8.12 Hz, 1H), 7.14-7.41 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.8, 28.9, 58.9, 66.6, 70.0, 70.3, 70.8, 70.9, 73.7, 83.2, 90.5, 127.4, 128.6, 128.71, 137.2. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 41.5. HRMS calcd for C₂₁H₂₄FeNO₂P $[M+Na]^+$: 432.0792. Found: 432.0778, calculated: Anal. Calcd for C₂₁H₂₄FeNO₂P: C, 61.63, H, 5.91, N, 3.42. Found: C, 61.39, H, 5.84, N, 3.28.

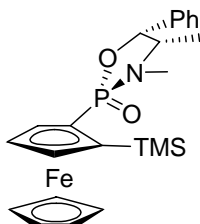
(2R,4S,5R)-3,4-Dimethyl-2-(α -(S_{Fc})-iodo-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (5)



The compound was purified by flash chromatography using EtOAc as eluent and the pure product was recovered as an orange solid in 76% yield (201 mg, 0.39 mmol). Mp: 75-76 °C. $[\alpha]_D^{20} = 4.9^\circ$ ($c = 1.15$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.85 (d, $J = 6.5$ Hz, 2H), 2.75 (d, 10.2 Hz, 3H), 3.64 (doublet of quintets, $J = 6.5$ Hz, 19.4 Hz, 1H), 4.37(s, 5H), 4.44-4.46 (m, 1H), 4.48-4.50 (m, 1H), 4.70-4.71 (m, 1H), 5.52 (t, $J = 6.36$, 1H), 7.30-7.47 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.8, 29.4, 59.1, 72.3, 72.9, 73.3, 80.3, 82.4, 127.0, 128.6, 128.7, 136.9. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 36.6. HRMS

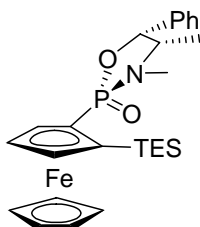
calcd for $C_{20}H_{21}FeINO_2P$ $[M+Na]^+$: 543.9602. Found: 543.9605. Anal. Calcd for $C_{20}H_{21}FeINO_2P$: C, 46.05, H, 4.15, N, 2.55. Found: C, 46.45, H, 4.22, N, 2.55.

(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{Fe})-trimethylsilylanyl-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (6)



The compound was purified by flash chromatography using EtOAc/Hexane (1:1) and the pure product was recovered as an orange solid in 95% yield (224 mg, 0.48 mmol). Mp: 137-138 °C. $[\alpha]_D^{20} = 254.0^\circ$ ($c = 0.88$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.41 (s, 9H), 0.83 (d, $J = 6.5$ Hz, 3H), 2.48 (d, $J = 10.32$ Hz, 3H), 3.61-3.70 (m, 1H), 4.30 (s, 5H), 4.42 (s, 1H), 4.49 (s, 1H), 4.56 (s, 1H), 5.57 (t, $J = 6.5$ Hz, 1H), 7.33-7.54 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 0.0, 13.6, 27.9, 58.2, 69.0, 72.4, 73.5, 77.7, 78.2, 81.7, 125.9, 127.3, 127.5, 135.9. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 42.9. HRMS calcd for $C_{23}H_{30}FeNO_2PSi$ $[M+Na]^+$: 490.1031. Found: 490.1008. Anal. Calcd for $C_{23}H_{30}FeNO_2PSi$: C, 59.10, H, 6.47, N, 3.00. Found: C, 59.05, H, 6.38, N, 2.98.

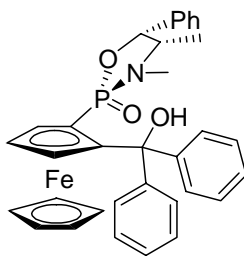
(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{Fe})-triethylsilylanyl-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (7)



The compound was purified by flash chromatography using EtOAc/Hexane (1:1) and the pure product was recovered as an orange solid in 70% yield (182 mg, 0.36 mmol). Mp: 137-138 °C. $[\alpha]_D^{20} = 303.8^\circ$ ($c = 0.52$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.76

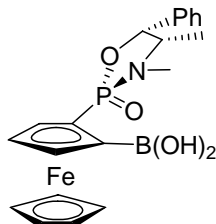
(d, $J = 6.5$ Hz, 3H), 0.82-1.09 (m, 15 H), 2.40 (d, $J = 10.36$ Hz, 3H), 3.54-3.64 (m, 1H), 4.22 (s, 5H), 4.33 (m, 1H), 4.41 (m, 1H), 4.52 (m, 1H), 5.50 (t, $J = 6.5$ Hz, 1H), 7.25-7.46 (m, 5H). ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 5.2, 8.5, 15.0, 28.9, 59.5, 70.3, 73.8, 74.6, 79.3, 82.8, 127.1, 128.5, 128.8, 137.2. ^{31}P -NMR (CDCl_3 , 162 MHz) δ (ppm): 43.0. HRMS calcd for $\text{C}_{26}\text{H}_{36}\text{FeNO}_2\text{PSi}$ $[\text{M}+\text{Na}]^+$: 532.1500. Found: 532.1488. Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{FeNO}_2\text{PSi}$: C, 61.29, H, 7.12, N, 2.75. Found: C, 61.28, H, 7.10, N, 2.77.

$[\alpha-(R_{\text{Fc}})-((2R,4S,5R)\text{-}3,4\text{-Dimethyl-2-oxo-5-phenyl-2-lambda}^5\text{-[1,3,2]oxazaphospholidin-2-yl)-ferrocenyl]diphenylmethanol (8)$



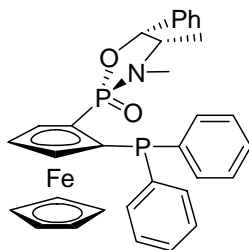
The compound was purified by flash chromatography using EtOAc as eluent and recrystallized from the same solvent to afford orange needles crystals (179 mg, 0.31 mmol, 61% yield). Mp: 181-182 °C. $[\alpha]_{\text{D}}^{20} = 77.2^\circ$ ($c = 1.84$ CHCl_3). ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 0.60 (d, $J = 6.5$ Hz, 3H), 1.46 (d, $J = 10.5$ Hz, 3H), 3.53 (doublet of quintets, $J = 6.5$ Hz, 9.2 Hz), 3.70-3.72 (m, 1H), 4.22-4.24 (m, 1H), 4.31 (dd, $J = 2.6$ Hz, 4.92 Hz, 1H), 4.40 (s, 5H), 5.37 (dd, $J = 6.5$ Hz, 8.9 Hz, 1H), 7.05-7.93 (m, 15H). ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 14.7, 27.2, 58.6, 70.2, 71.6, 71.9, 76.5, 77.6, 83.33, 106.9, 127.1, 127.2, 127.6, 128.0, 128.2, 128.7, 128.8, 136.8, 146.0, 150.0. ^{31}P -NMR (CDCl_3 , 162 MHz) δ (ppm): 45.0. HRMS calcd for $\text{C}_{33}\text{H}_{32}\text{FeNO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 600.1367. Found: 600.1340. Anal. Calcd for $\text{C}_{33}\text{H}_{32}\text{FeNO}_3\text{P}$: C, 67.98, H, 5.70, N, 2.48. Found: C, 67.98, H, 5.71, N, 2.49.

$[\alpha-(R_{\text{Fc}})-((2R,4S,5R)\text{-}3,4\text{-Dimethyl-2-oxo-5-phenyl-2-lambda}^5\text{-[1,3,2]oxazaphospholidin-2-yl)-ferrocenyl]boronic acid (9)$



The compound was purified by flash chromatography using EtOAc as eluent and the pure product was recovered as an orange solid in 73% yield (162 mg, 0.37 mmol). Mp: 114-115 °C. $[\alpha]_D^{20} = 162.7^\circ$ ($c = 0.75$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.82 (d, $J = 6.5$ Hz, 3H), 2.45 (d, $J = 10.8$ Hz, 3H), 3.62-3.71 (m, 1H), 4.34 (s, 5H), 4.50 (m, 1H), 4.68 (m, 1H), 4.88 (m, 1H), 5.56 (dd, $J = 6.6$ Hz, 9.36 Hz, 1H), 7.36-7.53 (m, 5H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.7, 28.3, 58.5, 70.8, 74.4, 75.1, 79.3, 83.6, 126.9, 128.5, 128.5, 136.2. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): 47.7.

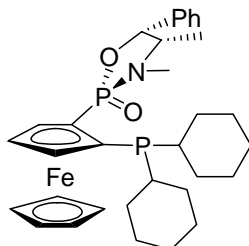
(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{Fe})-diphenyl-phosphanyl-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (10)



The compound was purified by flash chromatography using EtOAc as eluent and the pure product was recovered as an orange solid in 65% yield (191 mg, 0.33 mmol). Mp: 113-114 °C. $[\alpha]_D^{20} = 196.7^\circ$ ($c = 0.30$ CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.74 (d, $J = 6.5$ Hz, 3H), 2.82 (d, $J = 10.0$ Hz, 3H), 3.35 (doublet of quintets, $J = 6.5$ Hz, 22.1 Hz, 1H), 3.89 (s, 1H), 4.27 (s, 5H), 4.47 (dd, $J = 3.4$ Hz, 6.20 Hz, 1H), 4.58 (dd, $J = 2.0$ Hz, 4.4 Hz, 1H), 4.9 (s, 1H), 8.08-7.00 (m, 15H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.6, 29.7, 59.3, 71.5, 73.5, 75.8, 75.9, 77.1, 80.7, 126.5, 128.2, 128.4, 128.5, 128.6, 128.8, 128.9, 128.9, 129.0, 129.5, 133.3, 133.5, 135.2, 135.4, 137.0, 138.2, 140.8. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): -19.4, 41.0. HRMS calcd for C₃₂H₃₁FeNO₂P₂ $[M+H]^+$: 580.1258.

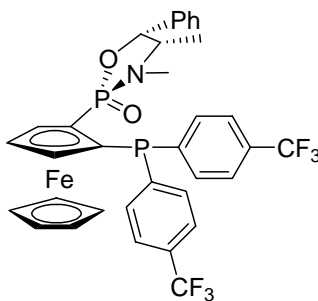
Found: 580.1284. Anal. Calcd for $C_{32}H_{31}FeNO_2P_2$: C, 66.34, H, 5.39, N, 2.42. Found: C, 66.34, H, 5.27, N, 2.31.

(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{FC})-dicyclohexyl-phosphanyl-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (11)



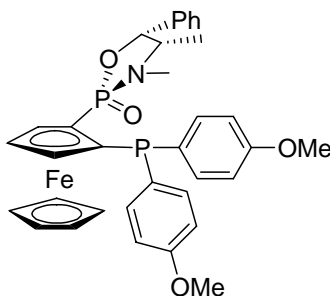
The compound was purified by flash chromatography using EtOAc as eluent and the pure product was recovered as an orange solid in 68 % yield (207 mg, 0.35 mmol). Mp: 89-90 °C. $[\alpha]_D^{20} = 27.5^\circ$ ($c = 0.40$ $CHCl_3$). 1H -NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.84 (d, $J = 6.5$ Hz, 3H), 0.99-2.36 (m, 22H), 2.73 (d, $J = 10.0$ Hz, 3H), 3.73-3.82 (m, 1H), 4.34 (s, 5H), 4.41-4.43 (m, 1H), 4.58-4.59 (m, 1H), 4.63-4.65 (m, 1H), 5.58 (t, $J = 6.7$ Hz, 1H), 7.30-7.49 (m, 5H). ^{13}C -NMR ($CDCl_3$, 100 MHz) δ (ppm): 15.7, 26.9, 71.3, 72.7, 74.0, 74.1, 75.6, 75.7, 82.1, 127.1, 128.4, 128.7, 137.5. ^{31}P -NMR ($CDCl_3$, 162 MHz) δ (ppm): -10.8, 39.5. HRMS calcd for $C_{32}H_{43}FeNO_2P_2$ $[M+H]^+$: 592.2197. Found: 592.2210. Anal. Calcd for $C_{32}H_{43}FeNO_2P_2$: C, 64.98, H, 7.33, N, 2.37. Found: C, 64.93, H, 7.37, N, 2.42.

(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{FC})-[bis(4-trifluoromethylphenyl)-phosphanyl]-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (12)

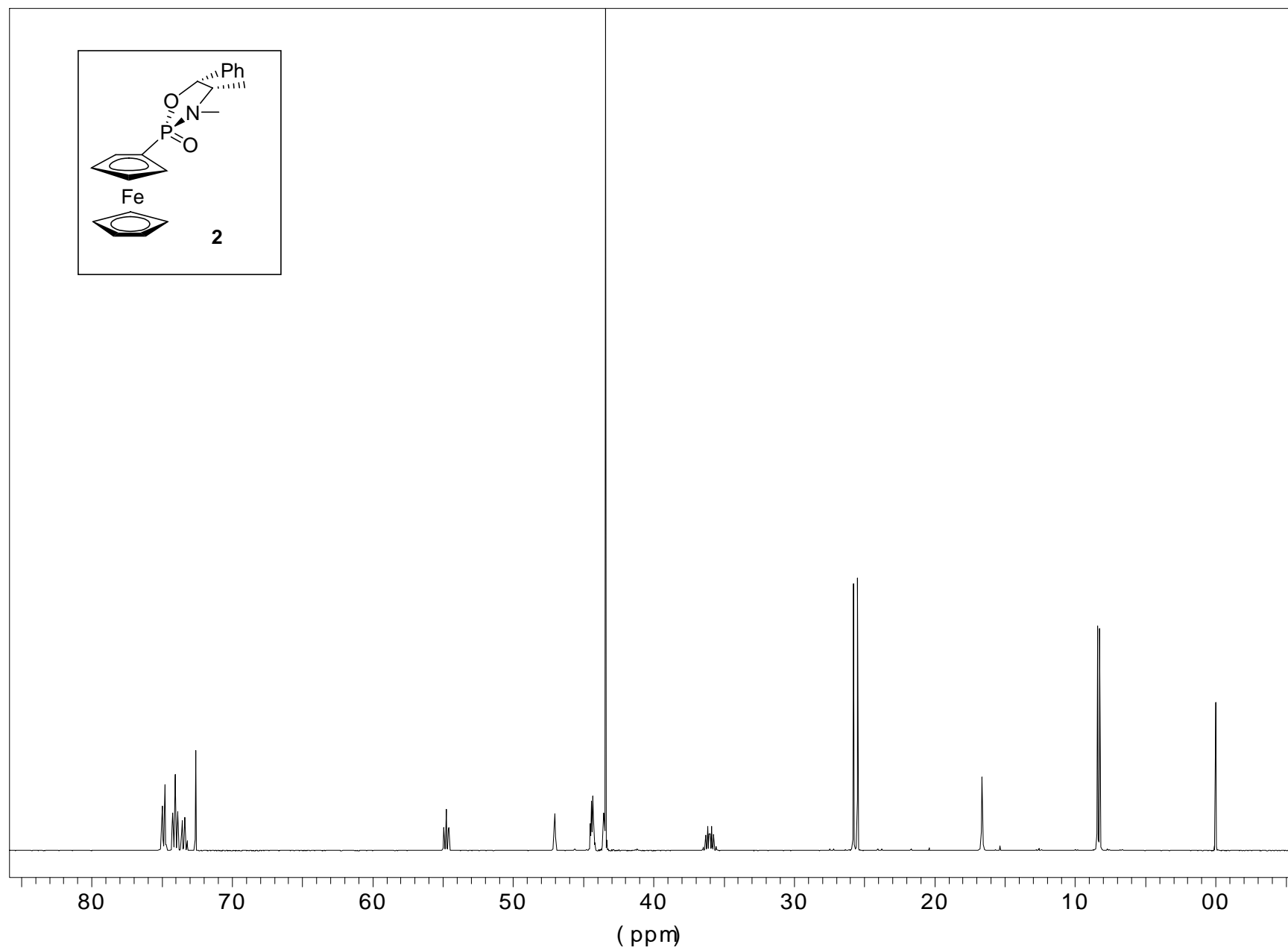


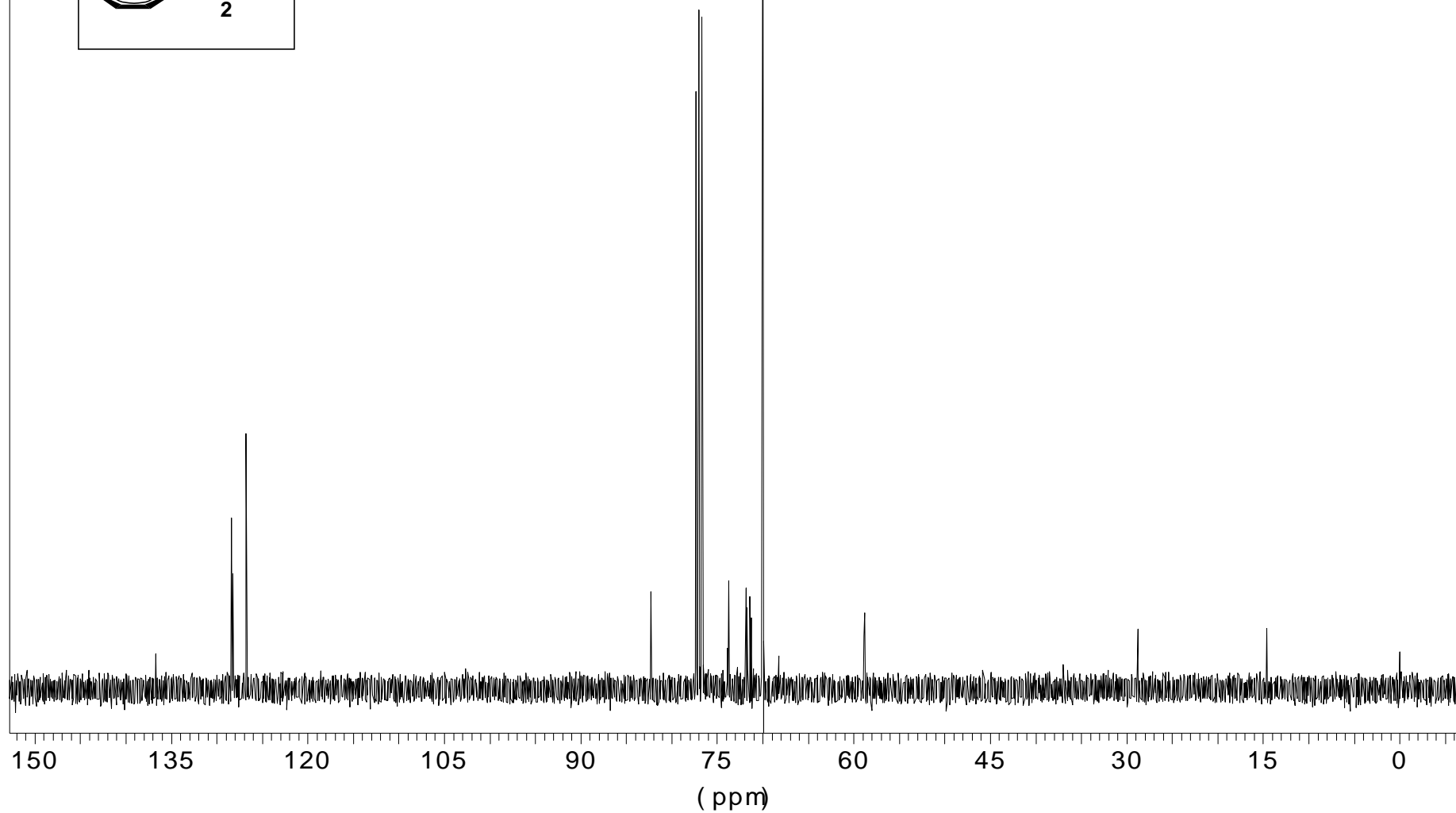
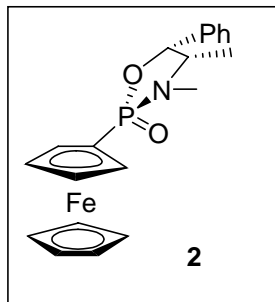
The compound was purified with flash chromatography (100% EtOAc) to afford an orange solid (265 mg, 0.37 mmol, 73% yield). Mp: 111-112 °C. $[\alpha]_D^{20} = -36.1^\circ$ (c = 0.72 CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.77 (d, *J* = 6.5 Hz, 3H), 2.57 (d, *J* = 10.14 Hz, 3H), 3.42-3.48 (m, 1H), 3.87 (s, 1H), 4.29 (s, 5H), 4.64 (m, 1H), 4.84-4.87 (m, 2H), 7.14-7.67 (m, 14 H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.7, 29.3, 59.4, 71.6, 81.7, 125.6, 126.6, 128.6, 133.5, 135.6, 190.4. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): -18.6, 38.2. ¹⁹F-NMR (CDCl₃, 376 MHz) δ (ppm): -63.2. HRMS calcd for C₃₄H₂₉F₆FeNO₂P₂ [M+H]⁺: 716.1005. Found: 716.1030. Anal. Calcd for C₃₄H₂₉F₆FeNO₂P₂: C, 57.08, H, 4.09, N, 1.96. Found C, 57.01, H, 4.09, N, 1.93.

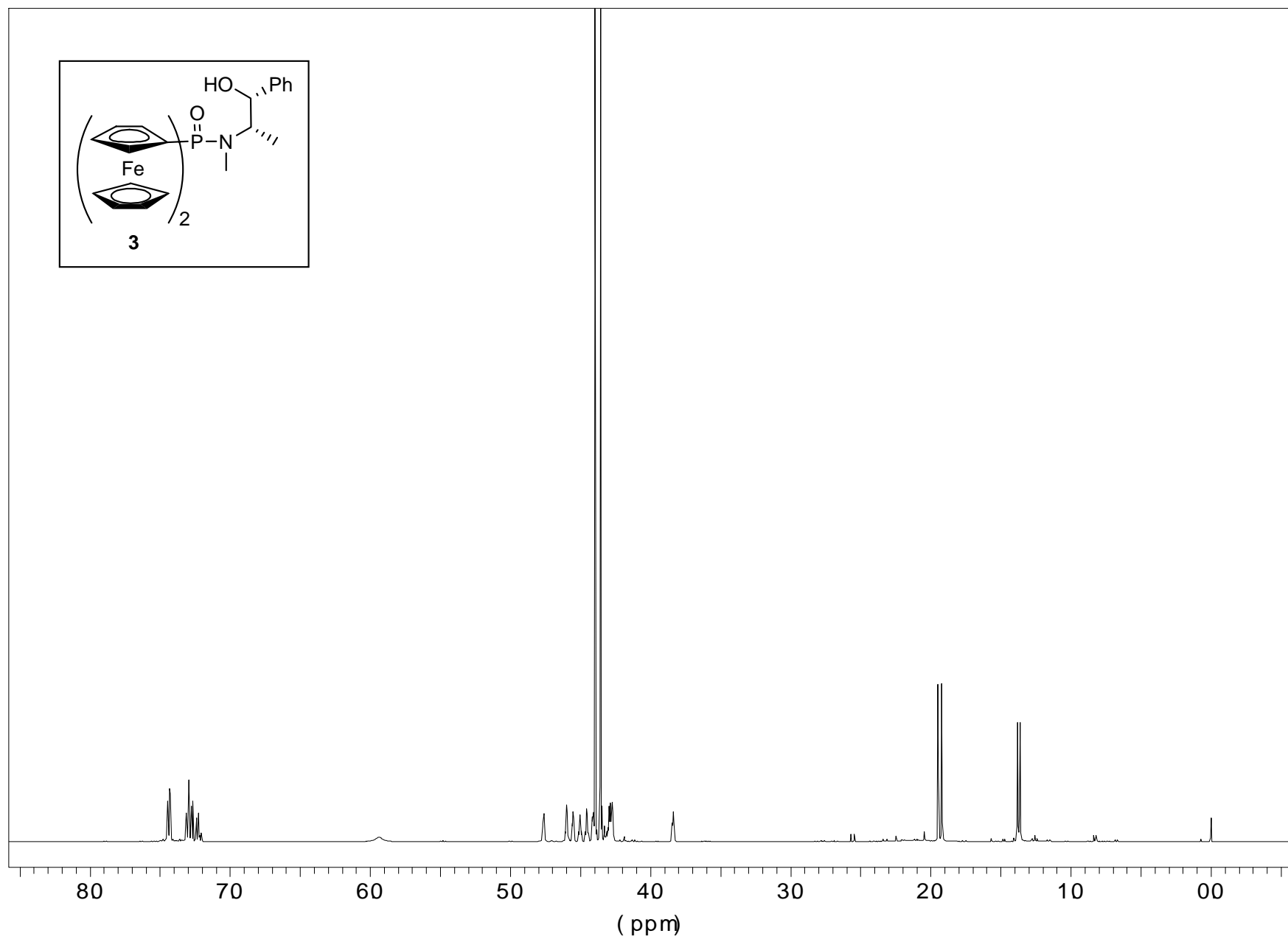
(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(α -(*R*_{Fe})-[bis(4-methoxyphenyl)-phosphanyl]-ferrocenyl)-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (13)

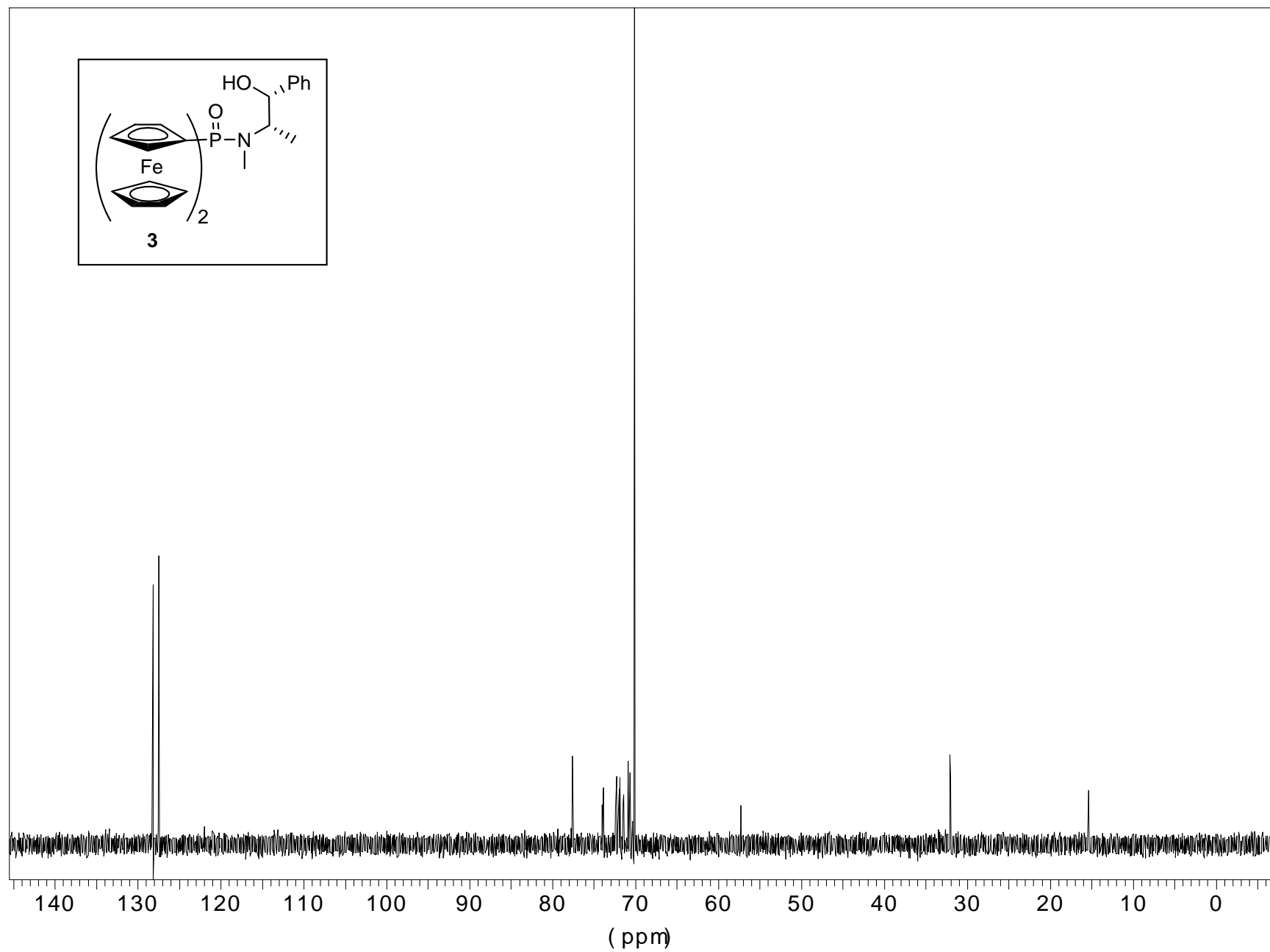


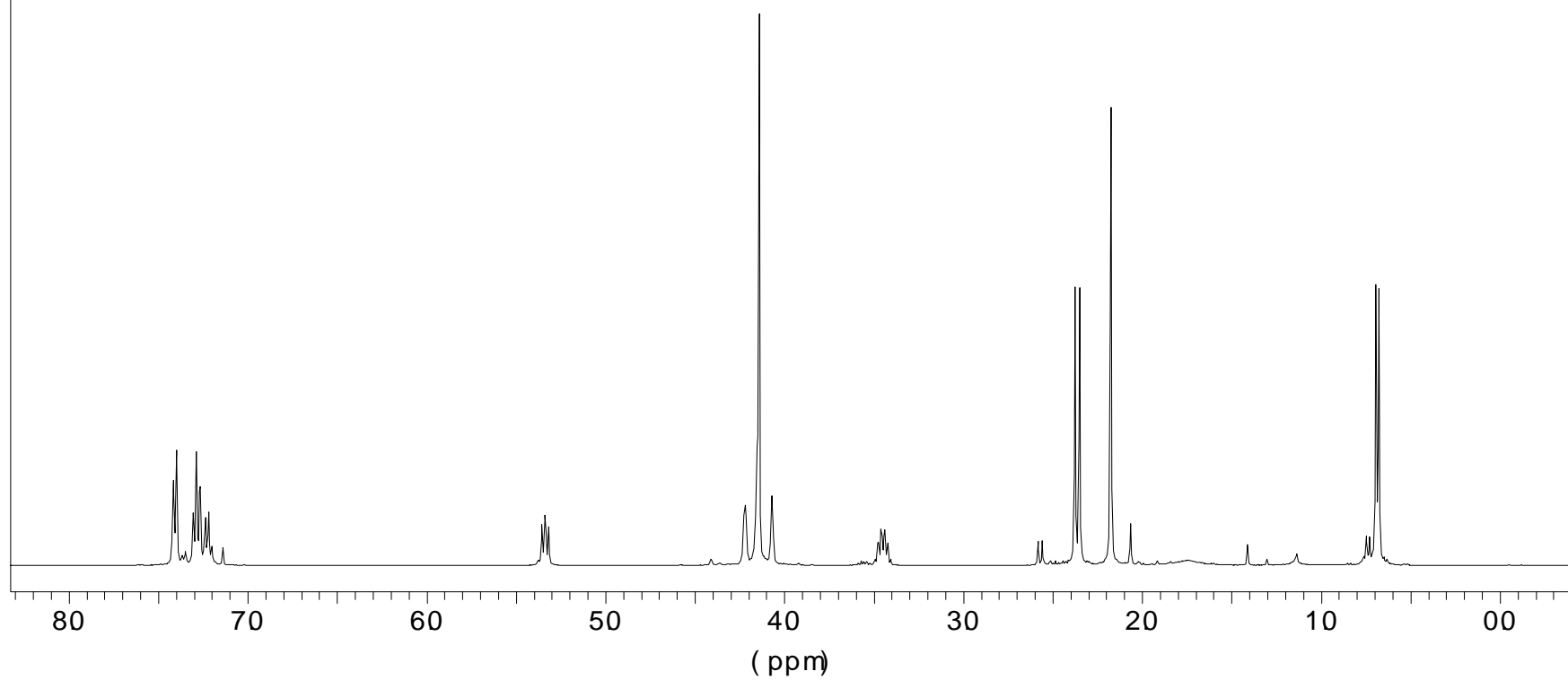
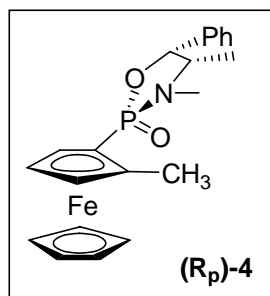
The compound was purified with flash chromatography (100% EtOAc) to afford an orange solid (145 mg, 0.23 mmol, 45% yield). Mp: 142-143 °C. $[\alpha]_D^{20} = -34.7^\circ$ (c = 0.59 CHCl₃). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 0.75 (d, *J* = 6.5 Hz, 3H), 2.85 (d, *J* = 9.9 Hz, 3H), 3.29 (m, 1H), 3.73 (s, 3H), 3.84 (s, 3H), 3.87 (s, 1H), 4.28 (s, 5H), 4.34 (m, 1H), 4.56 (m, 1H), 4.88 (s, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 6.5 Hz), 7.21-7.26 (m, 5H), 7.44 (dd, *J* = 7.2 Hz, 8.3 Hz, 2H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 14.6, 29.9, 55.6, 59.4, 71.4, 73.4, 80.5, 114.2, 114.6, 126.5, 128.1, 128.4, 134.8, 136.5, 137.0, 160.5, 160.8. ³¹P-NMR (CDCl₃, 162 MHz) δ (ppm): -22.9, 38.6. HRMS calcd for [M+H]⁺: 640.1469. Found: 640.1456. Anal. Calcd for C₃₄H₃₅FeNO₄P₂: C, 63.86, H, 5.52, N, 2.19. Found: C, 63.89, H, 5.46, N, 2.16.

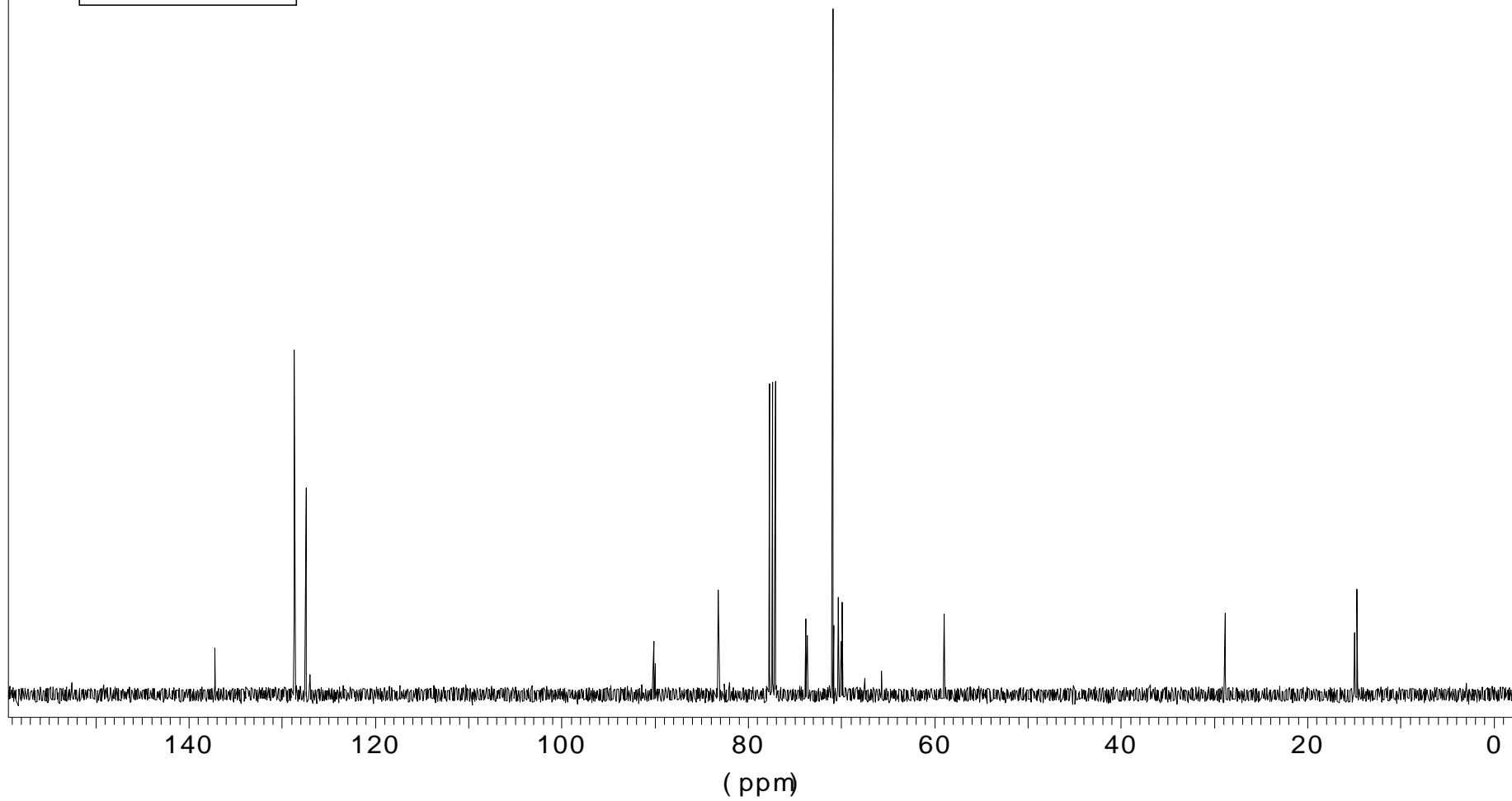
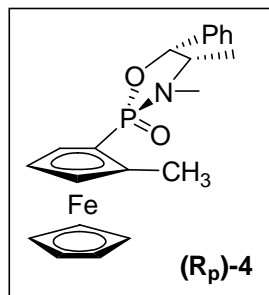


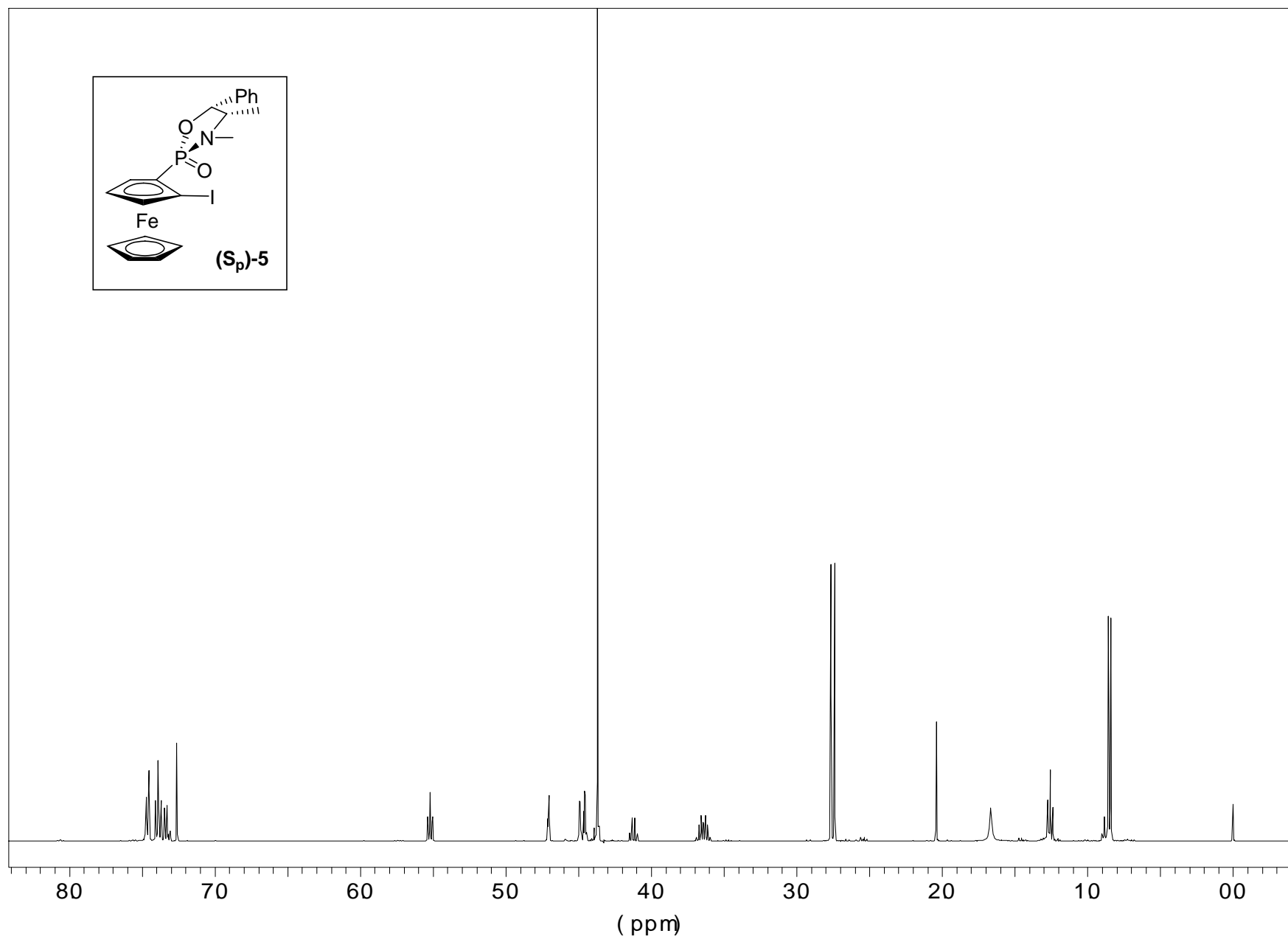


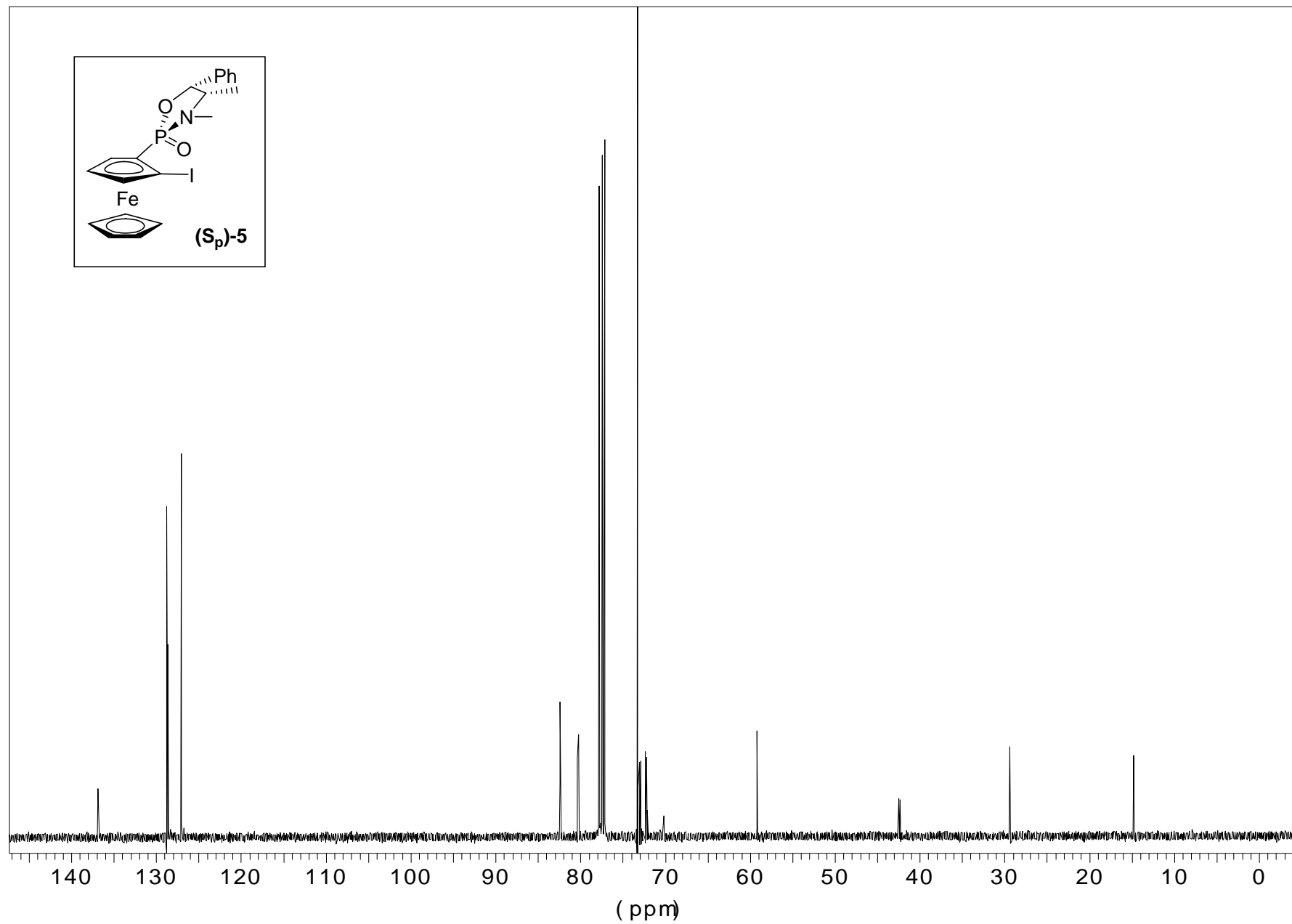


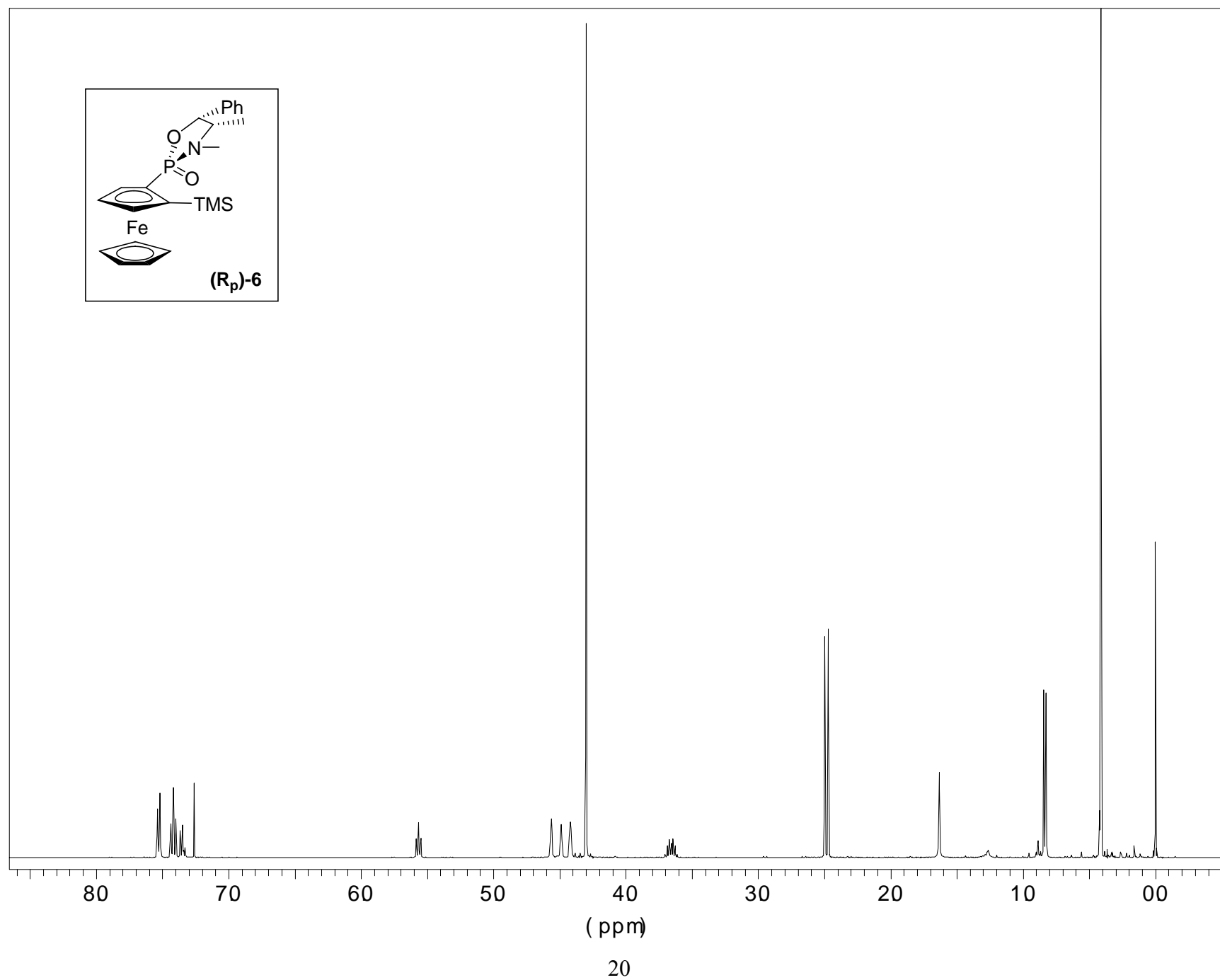
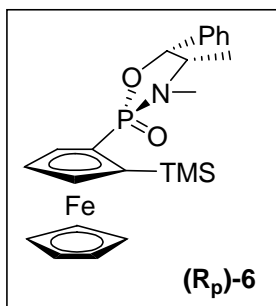


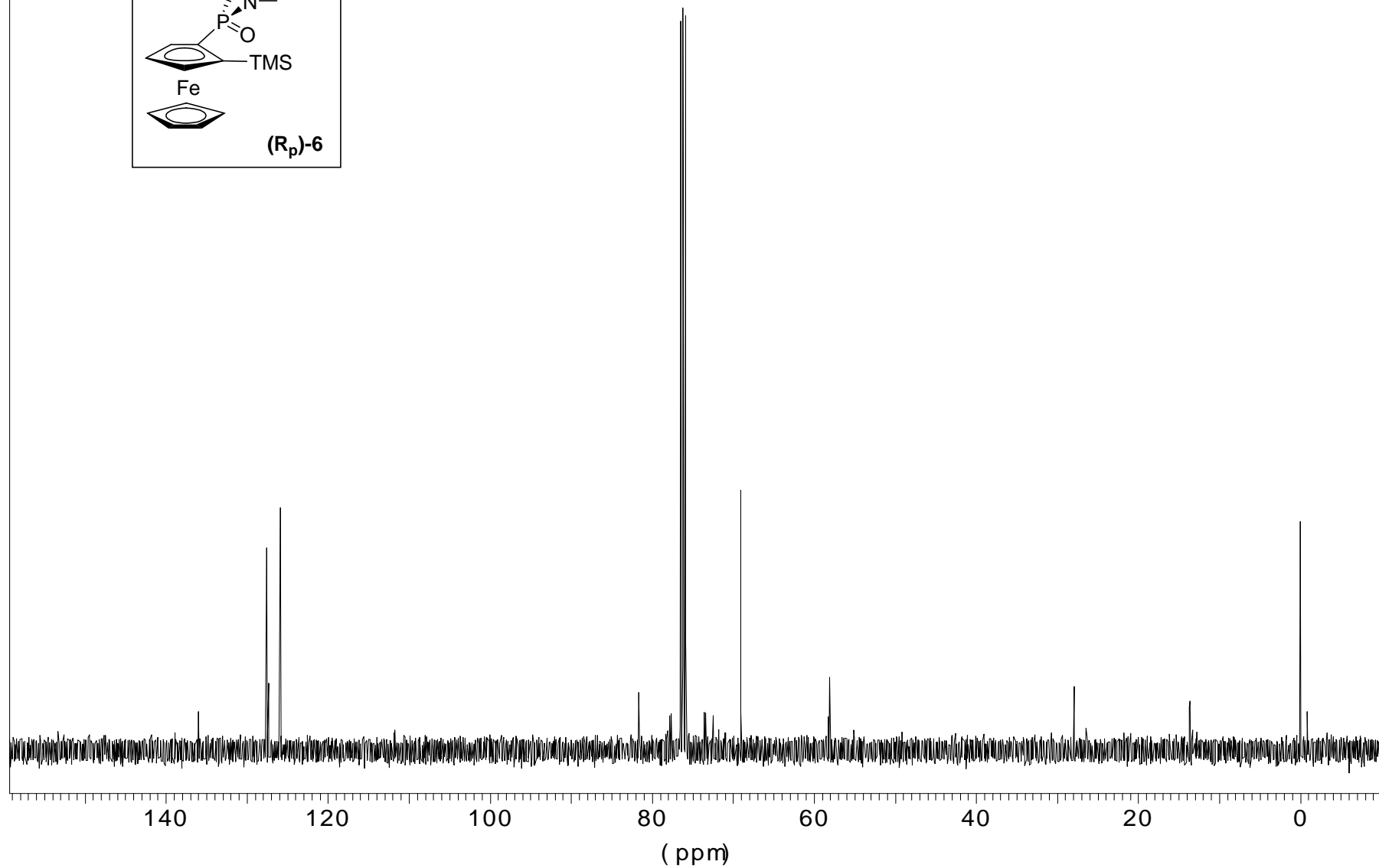
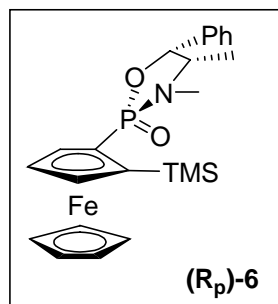


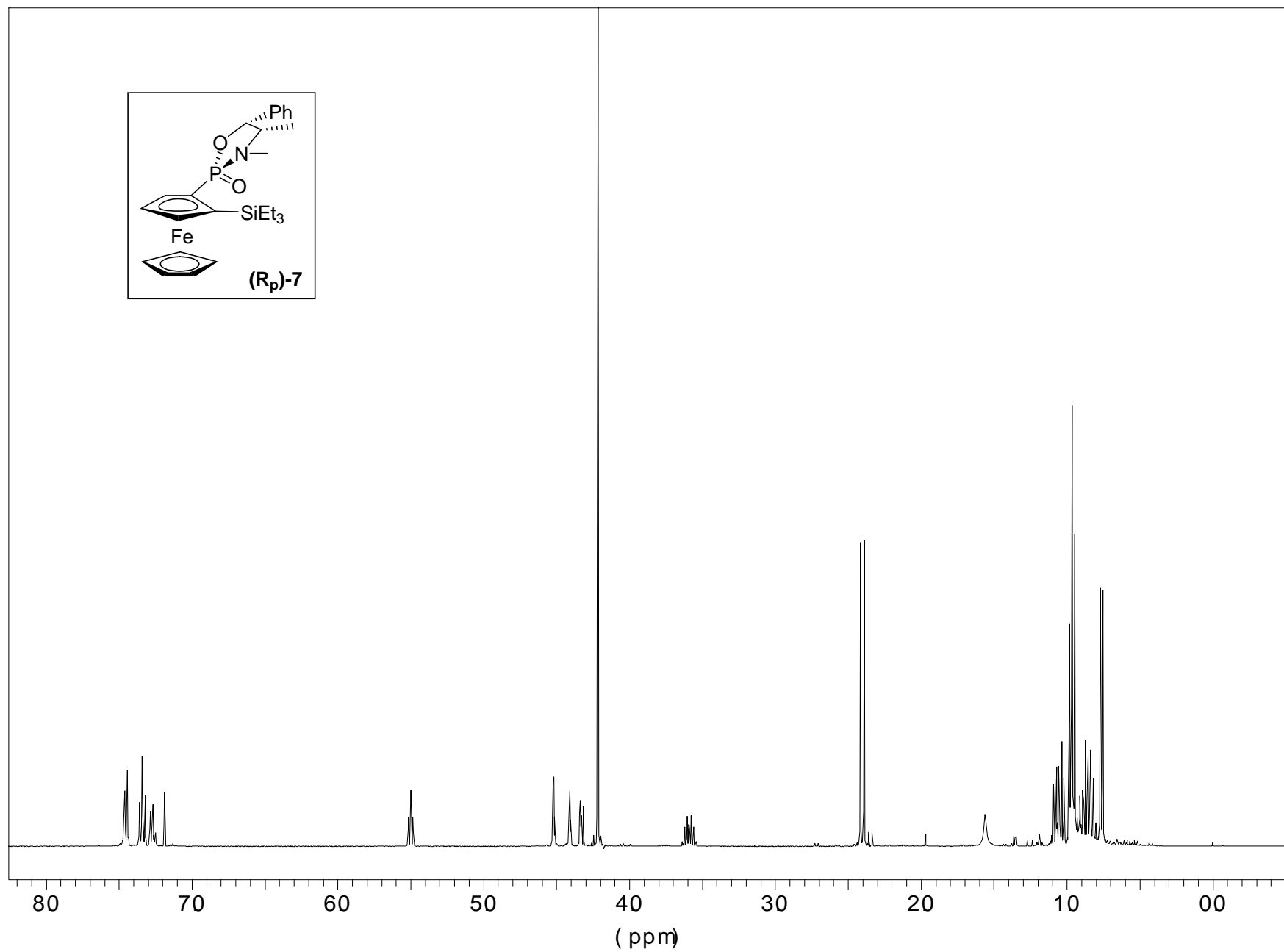


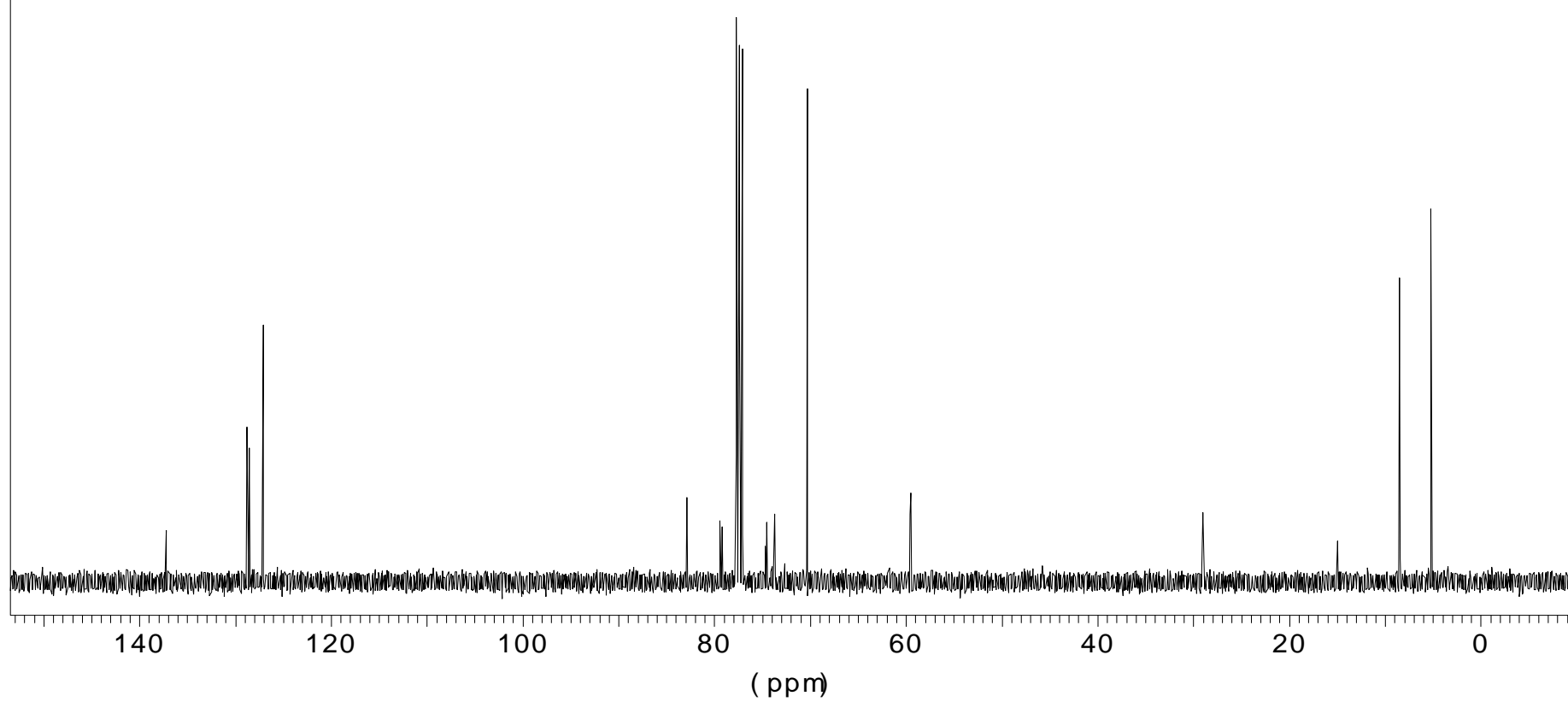
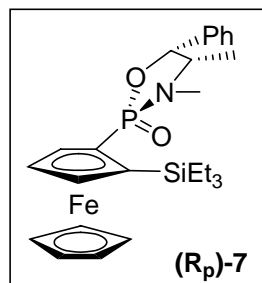


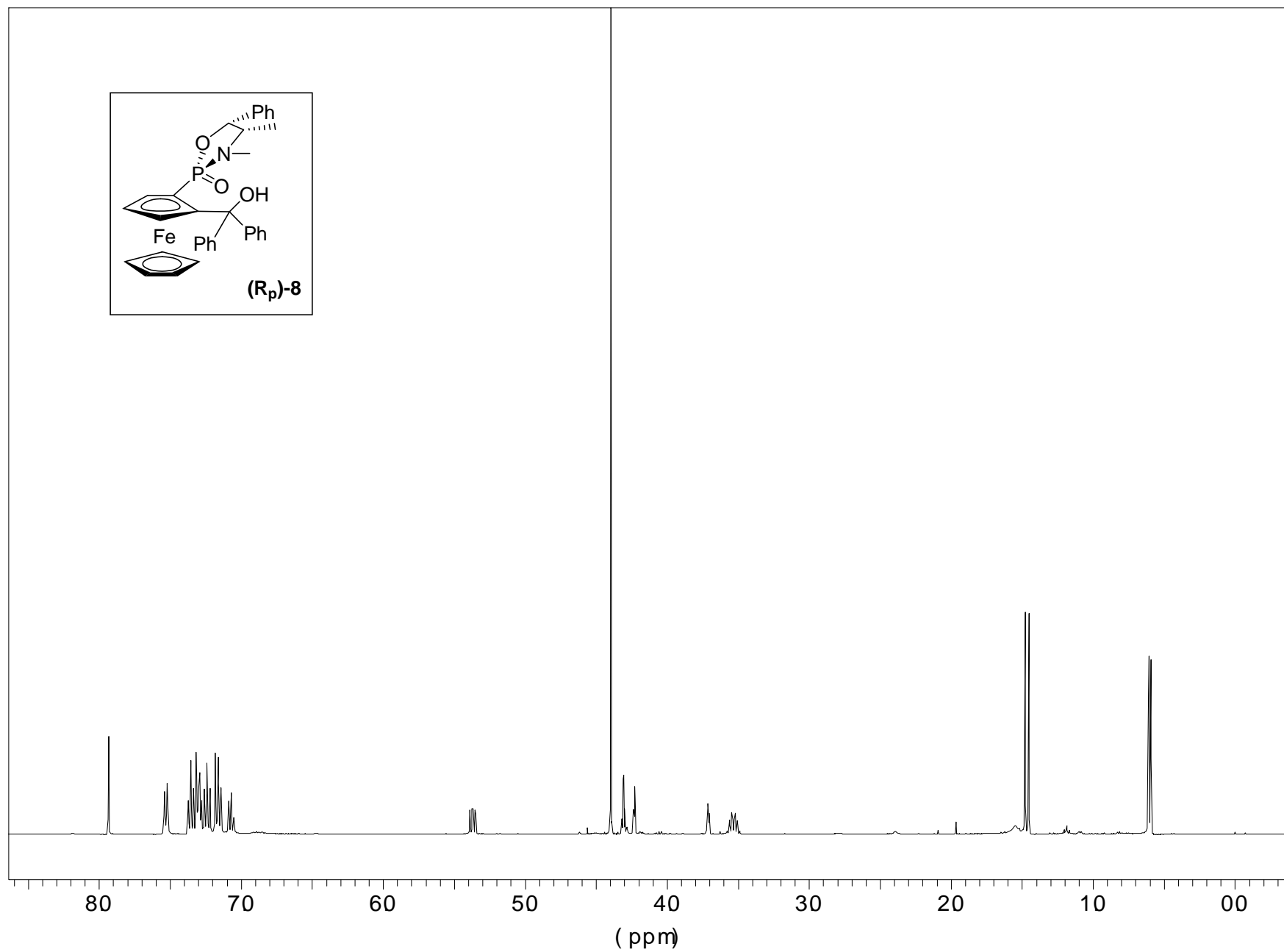
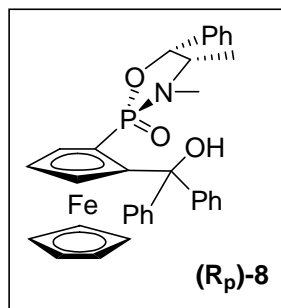


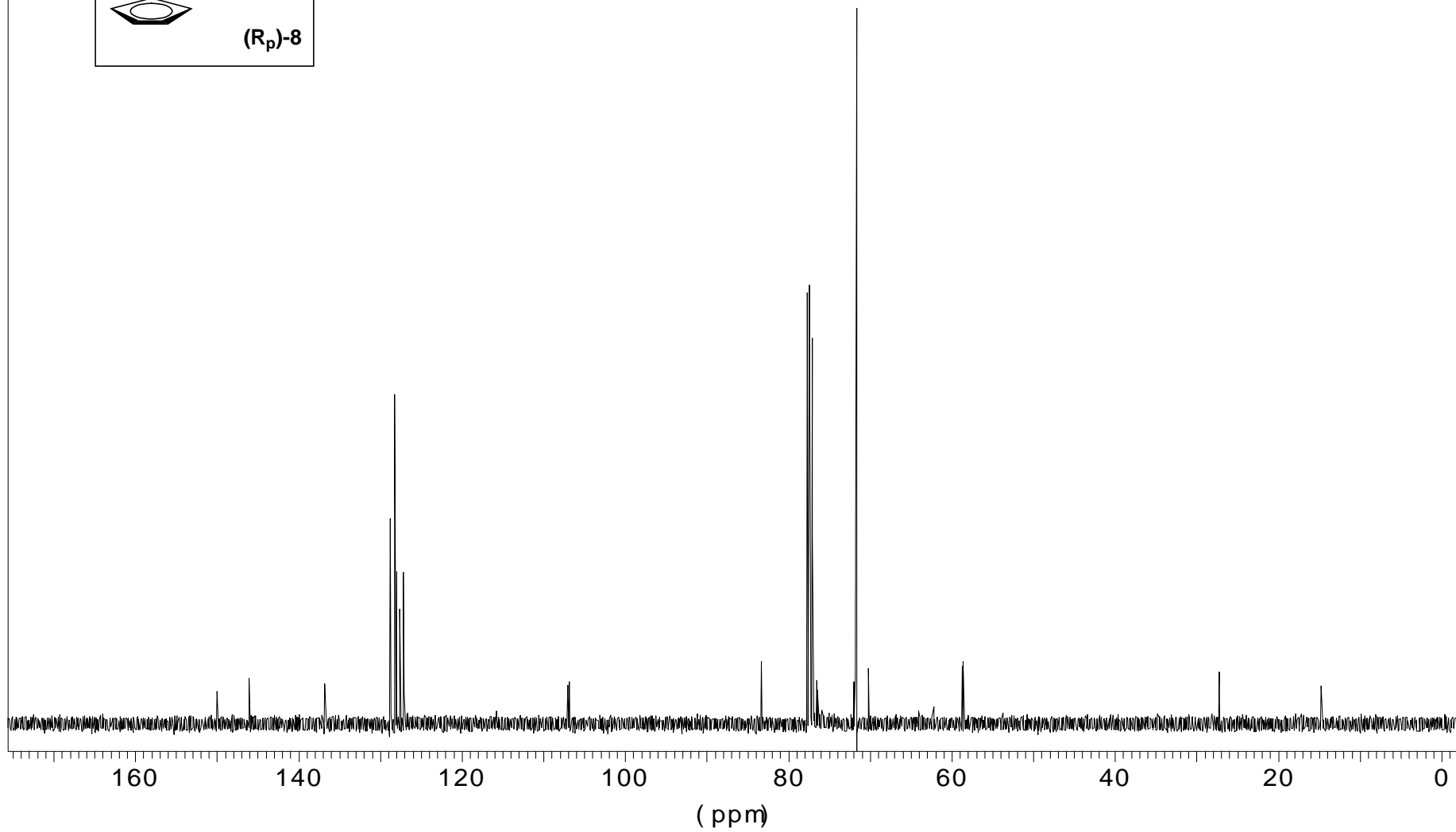
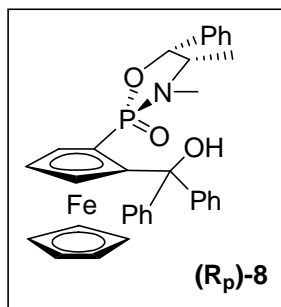


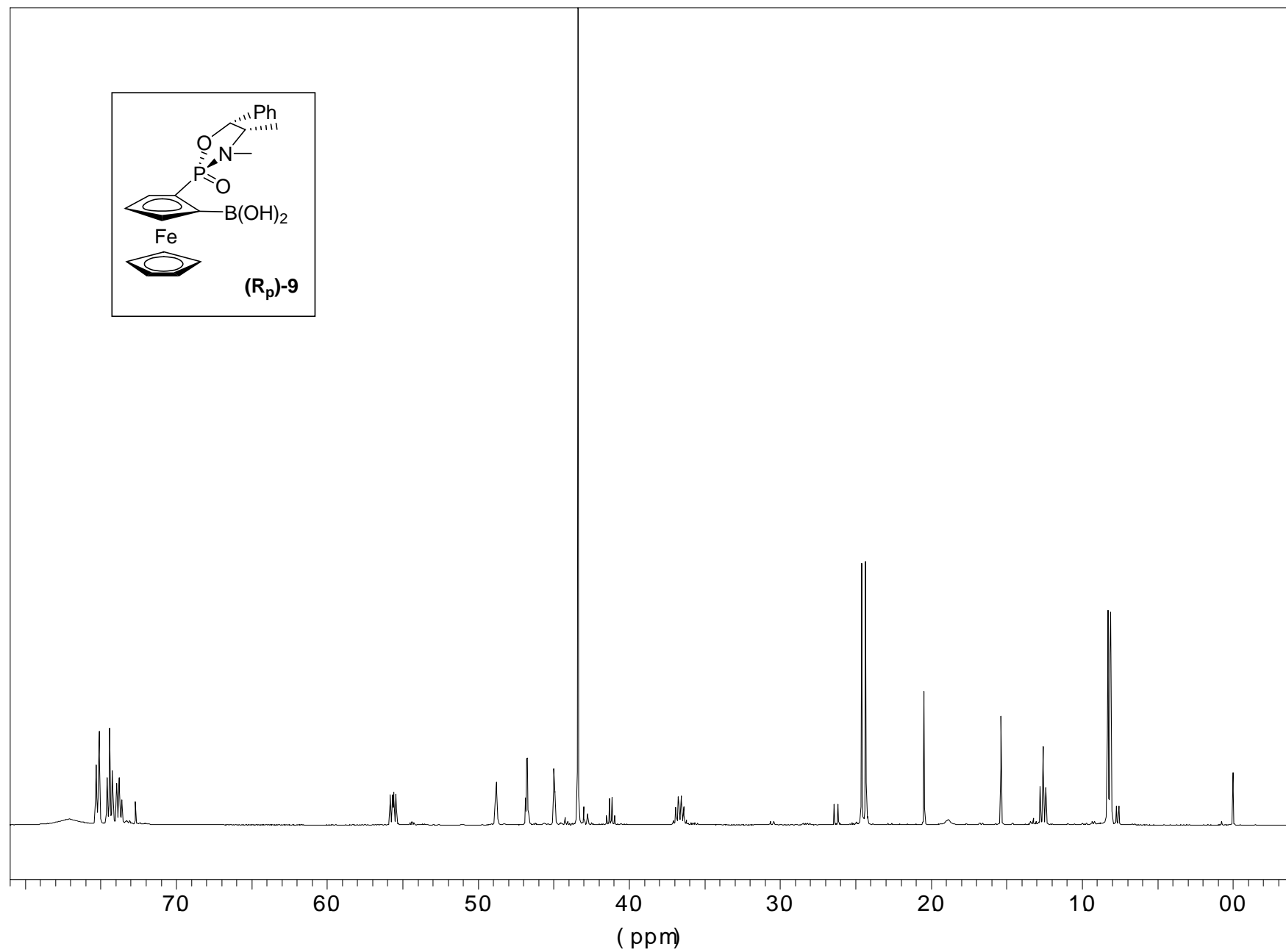
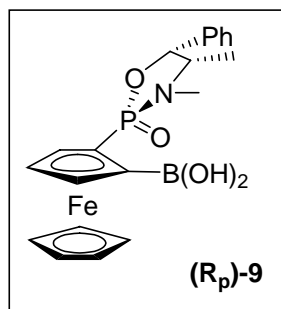


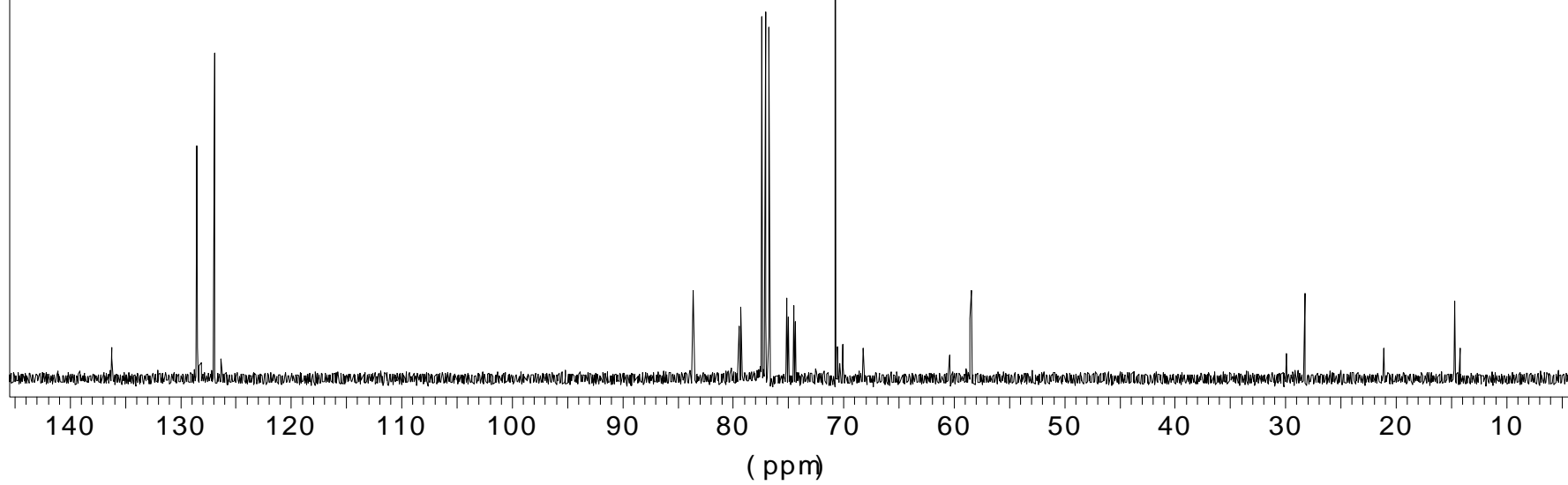
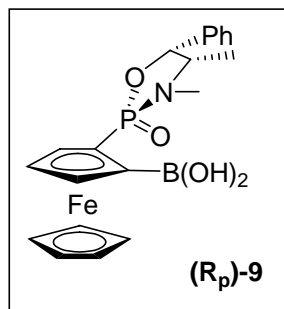


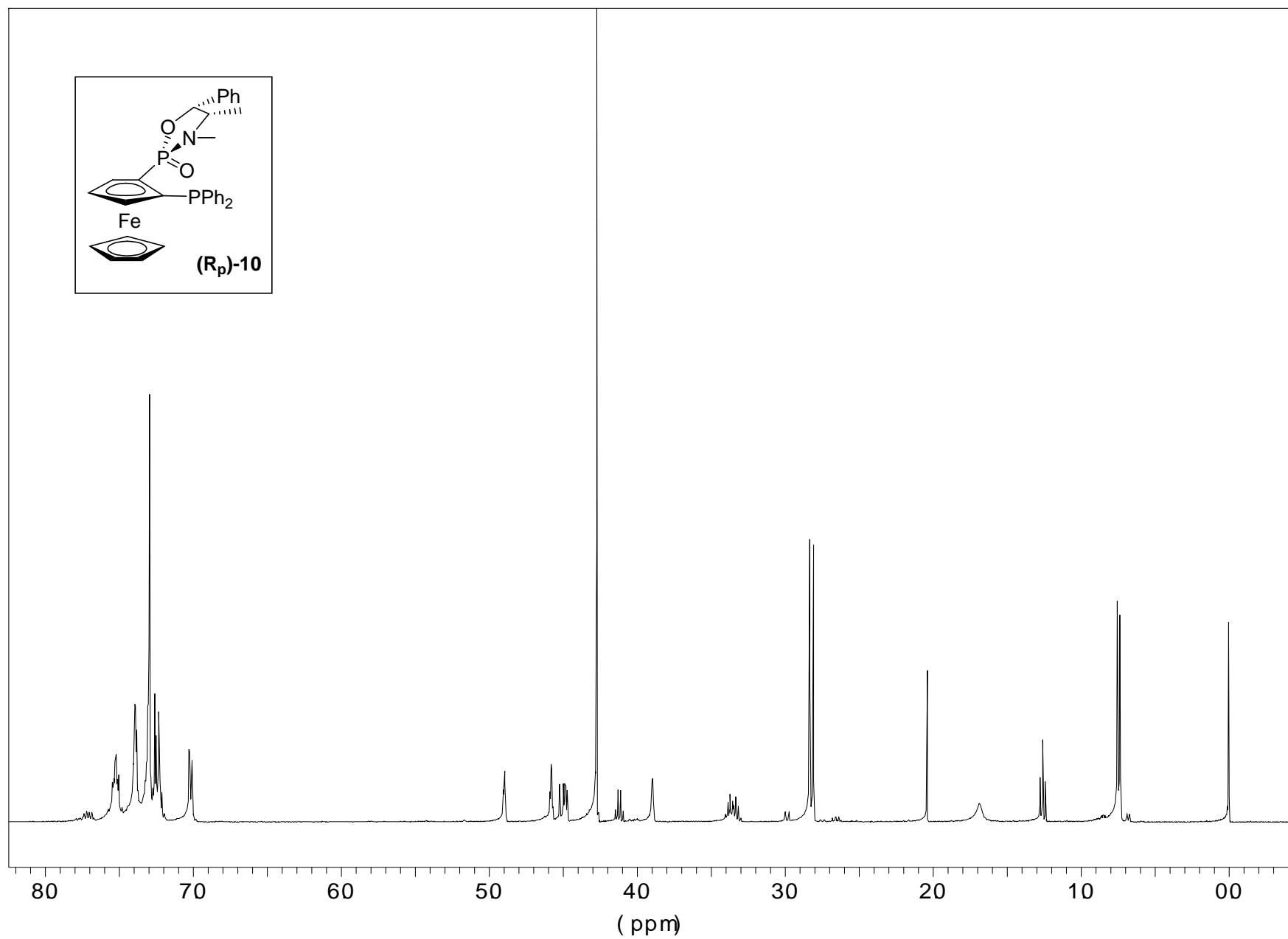


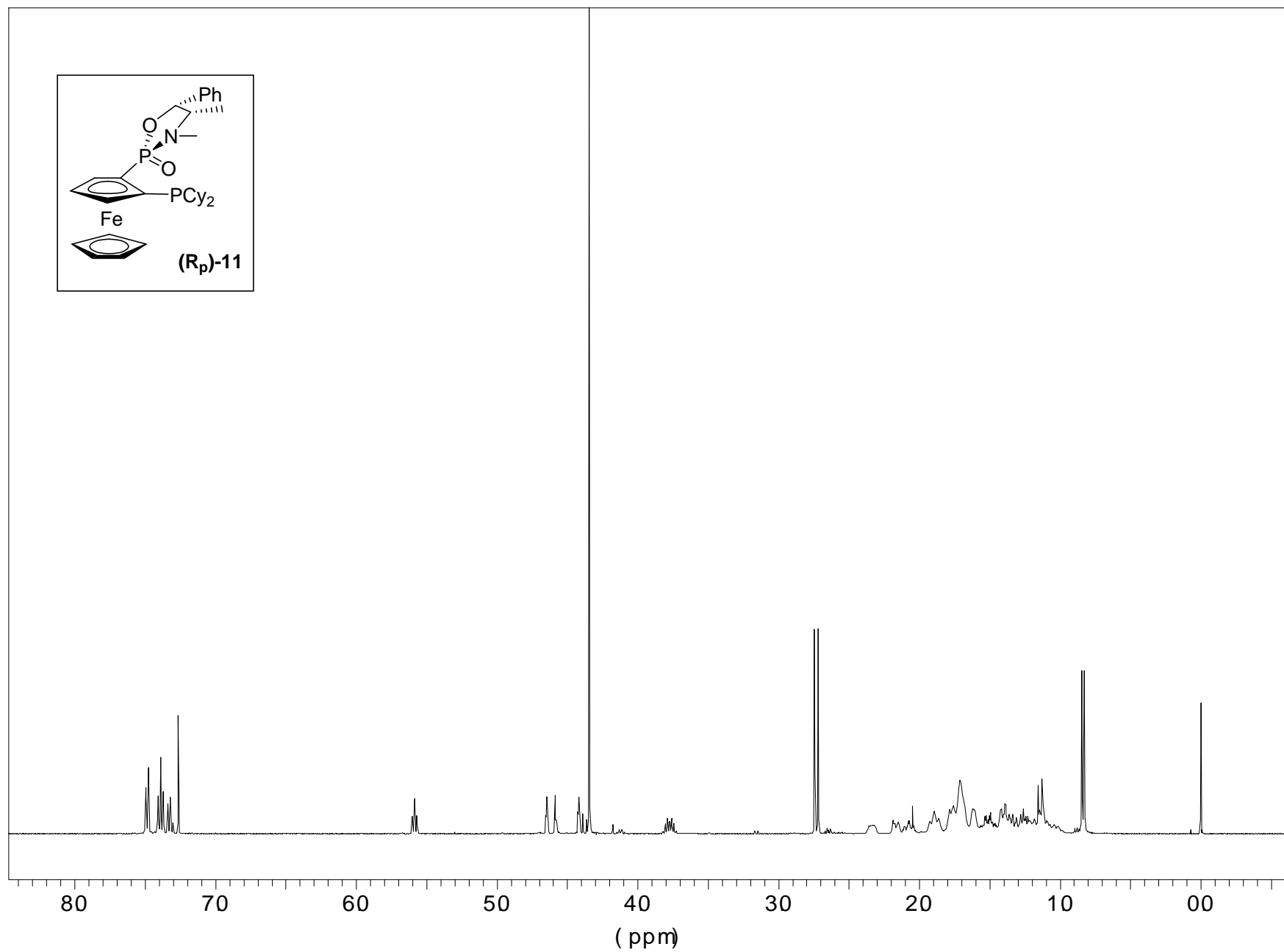
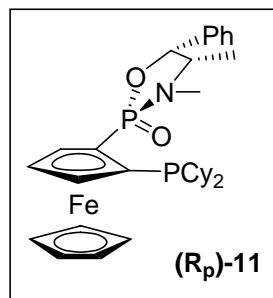


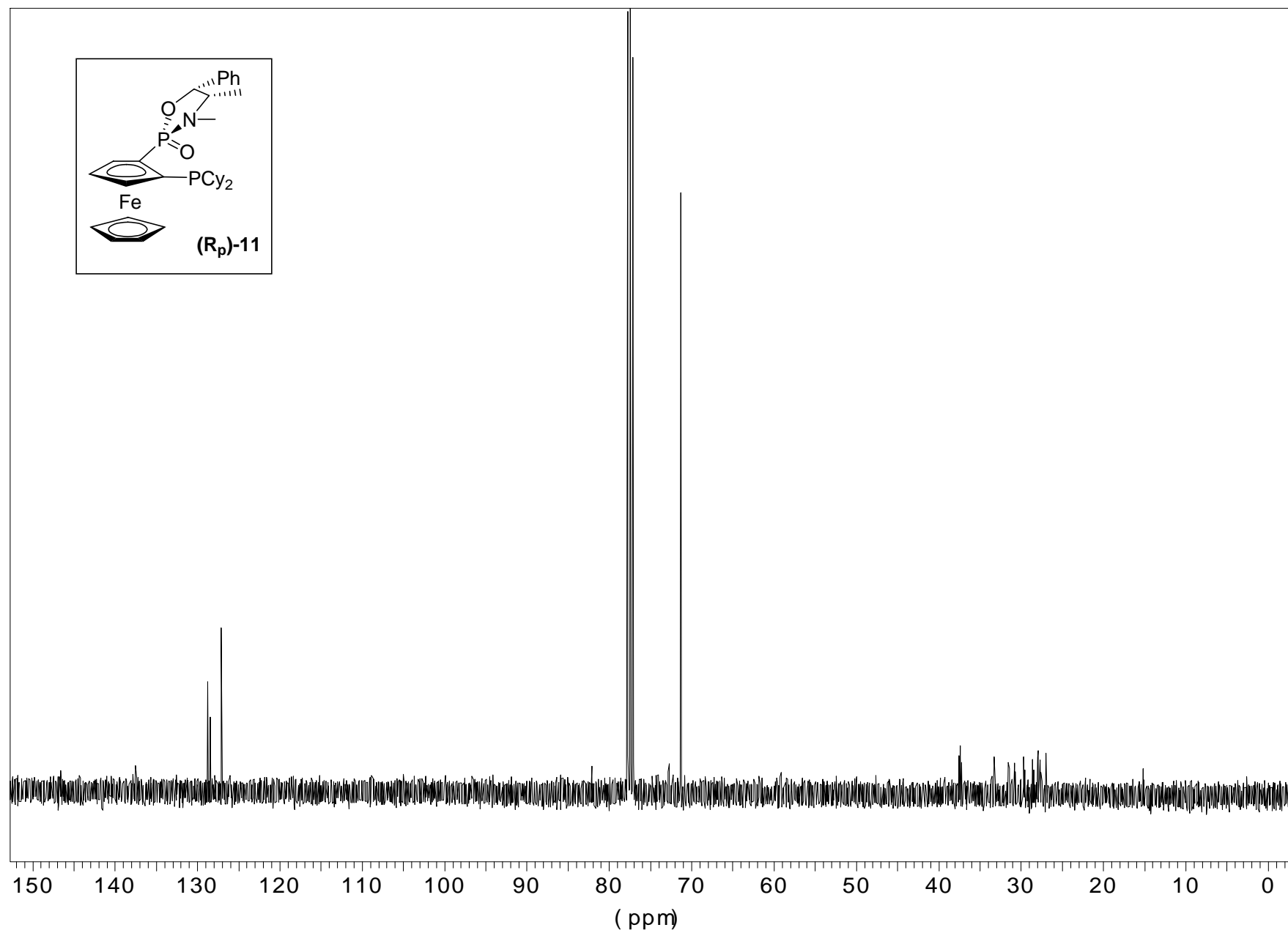


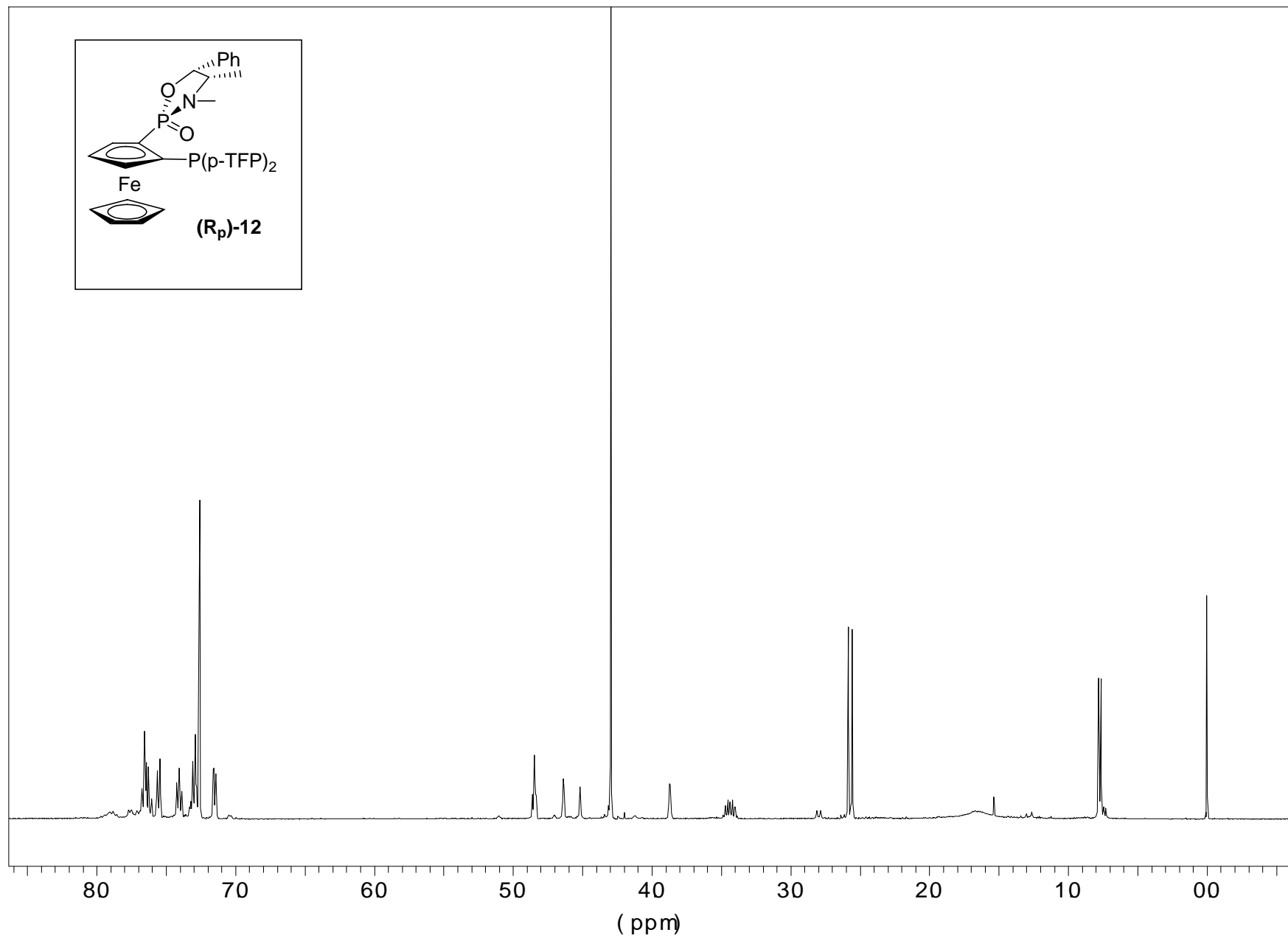
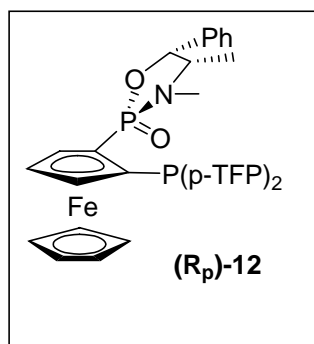


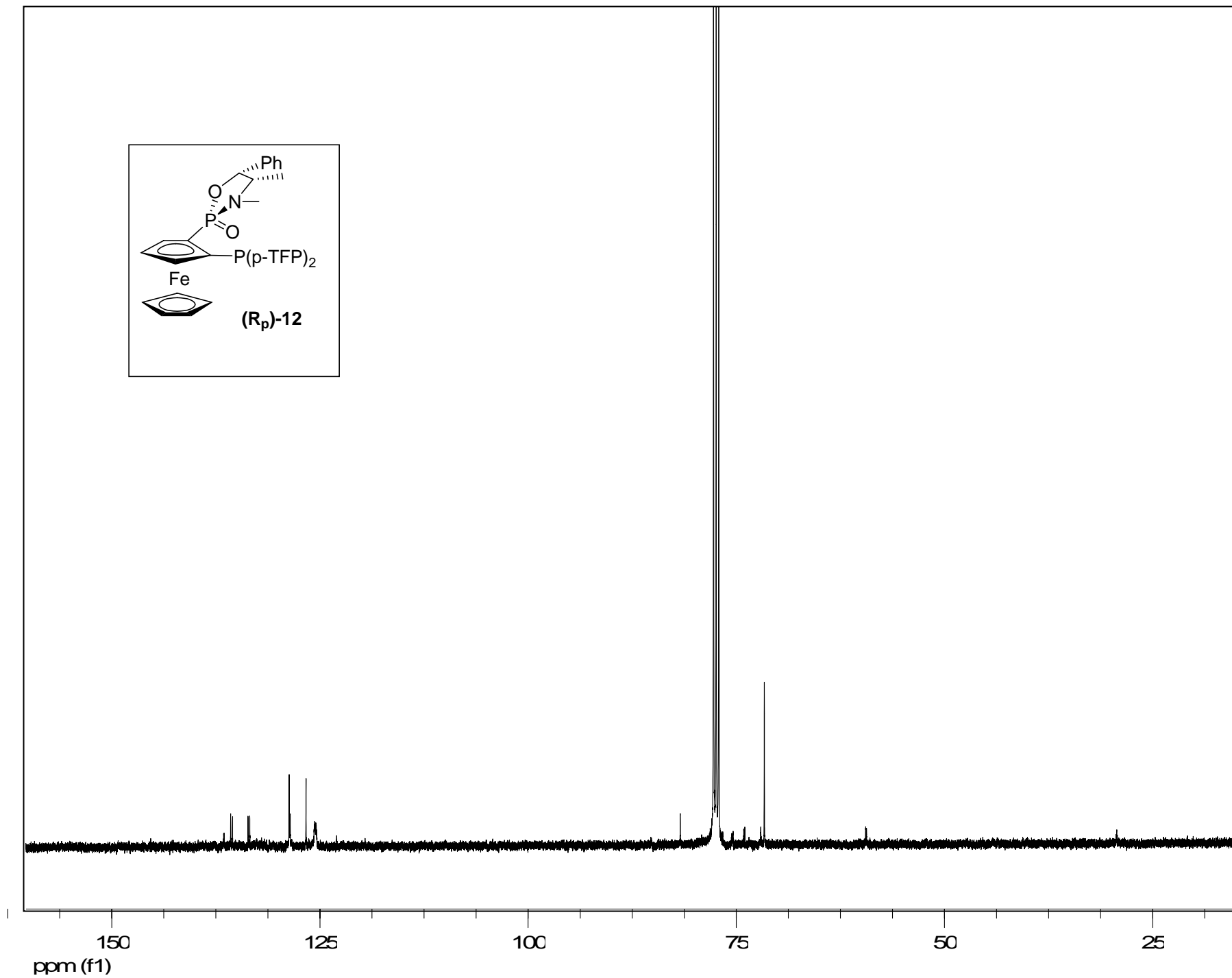
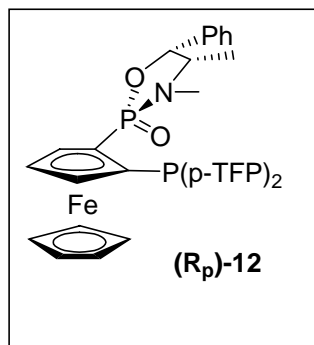


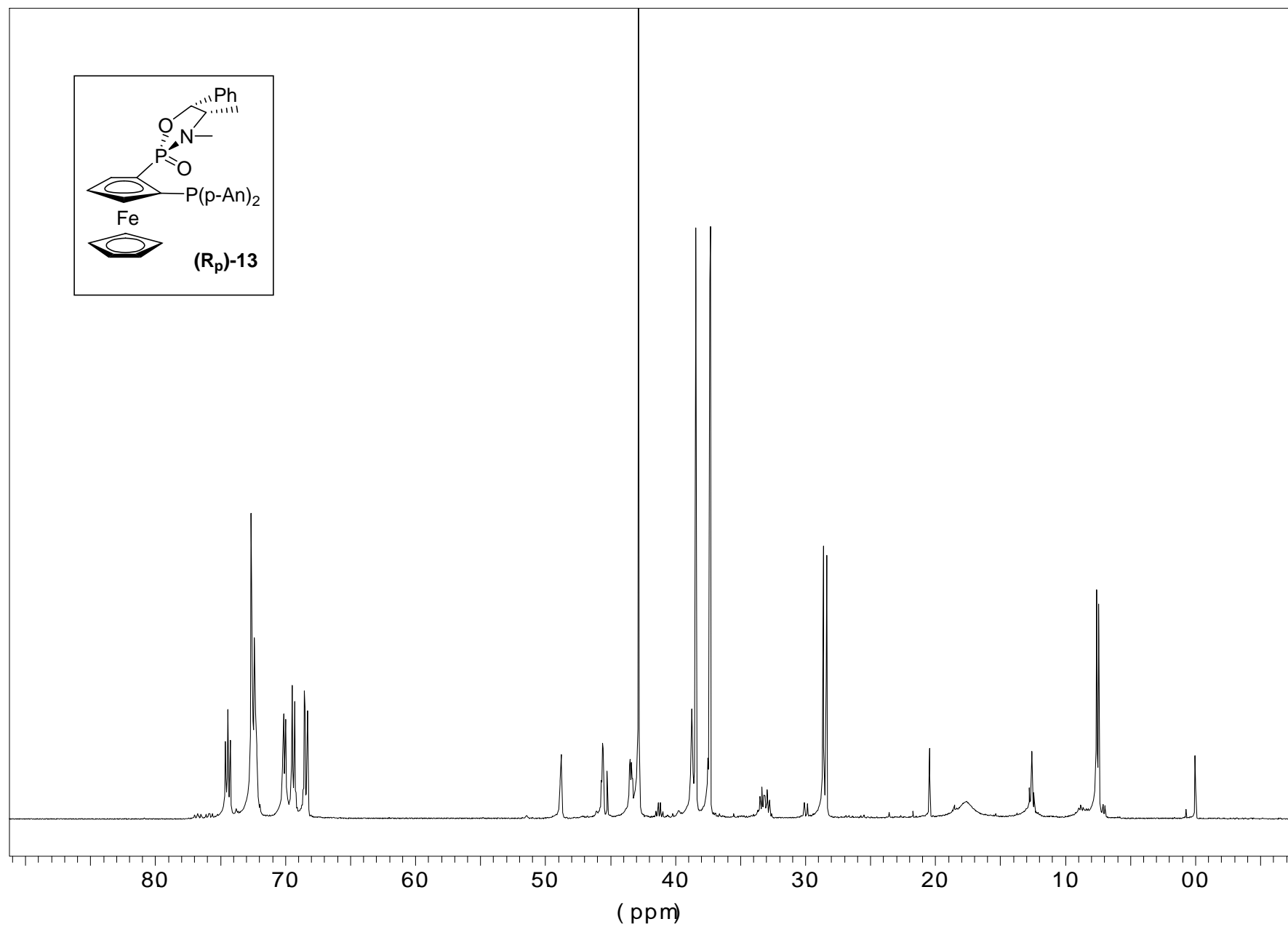


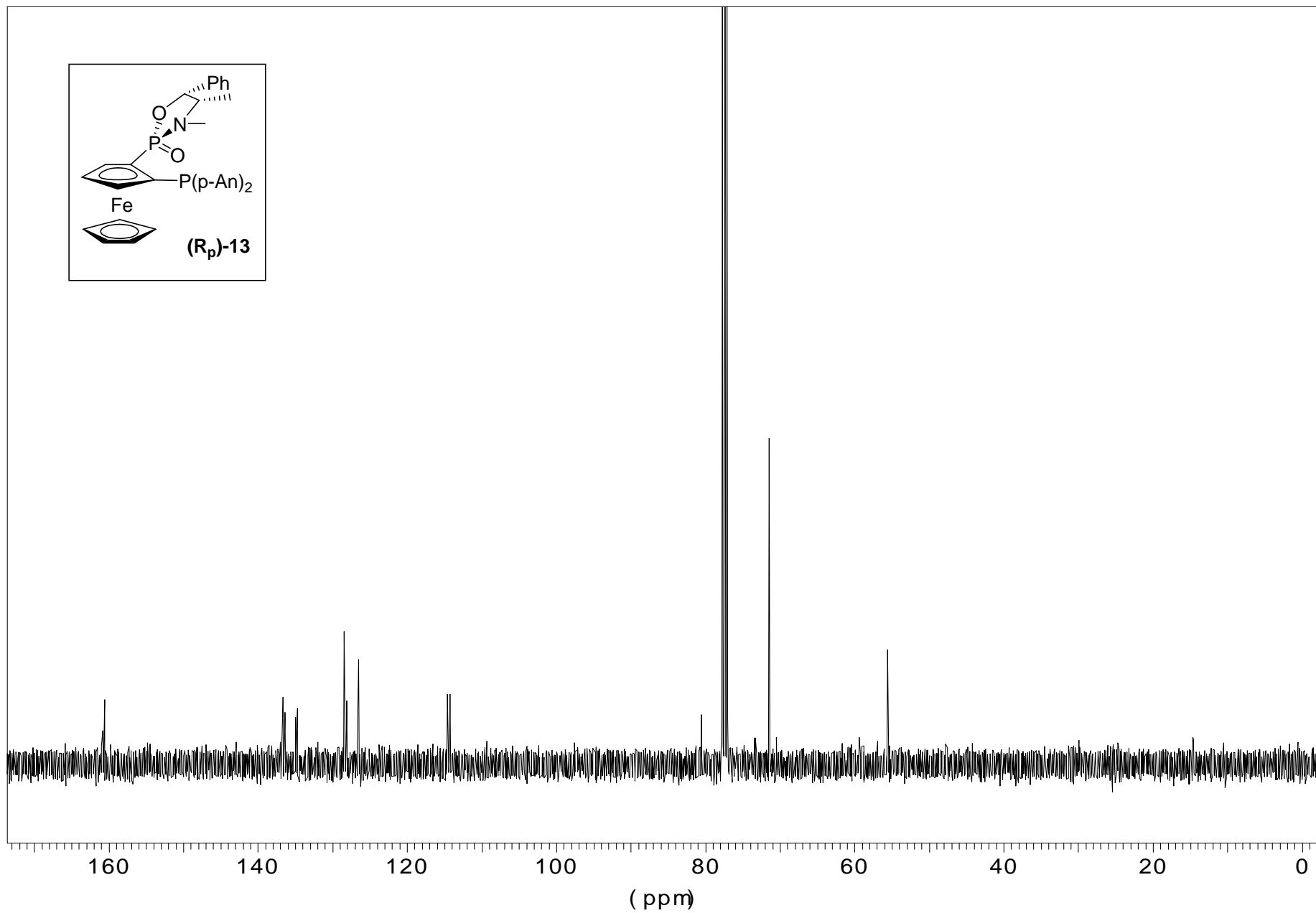










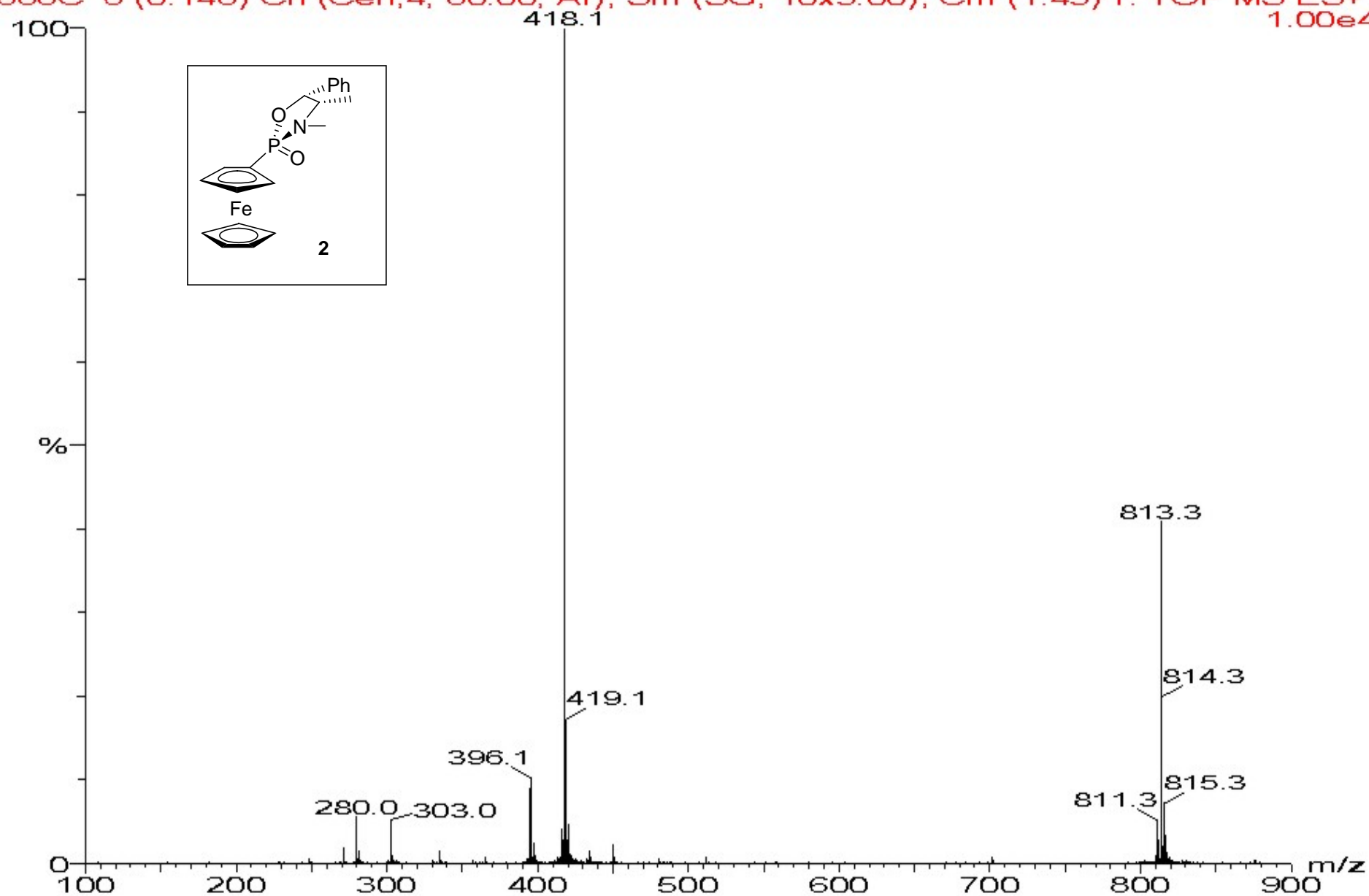


Sample: DV62 in CH₃OH/0.1% Formic Cone = 50V

D. Vinci / JX

Operator: AJM

688C 6 (0.148) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:43) 1: TOF MS ES+
1.00e4



Sample: DV372 in CH3OH

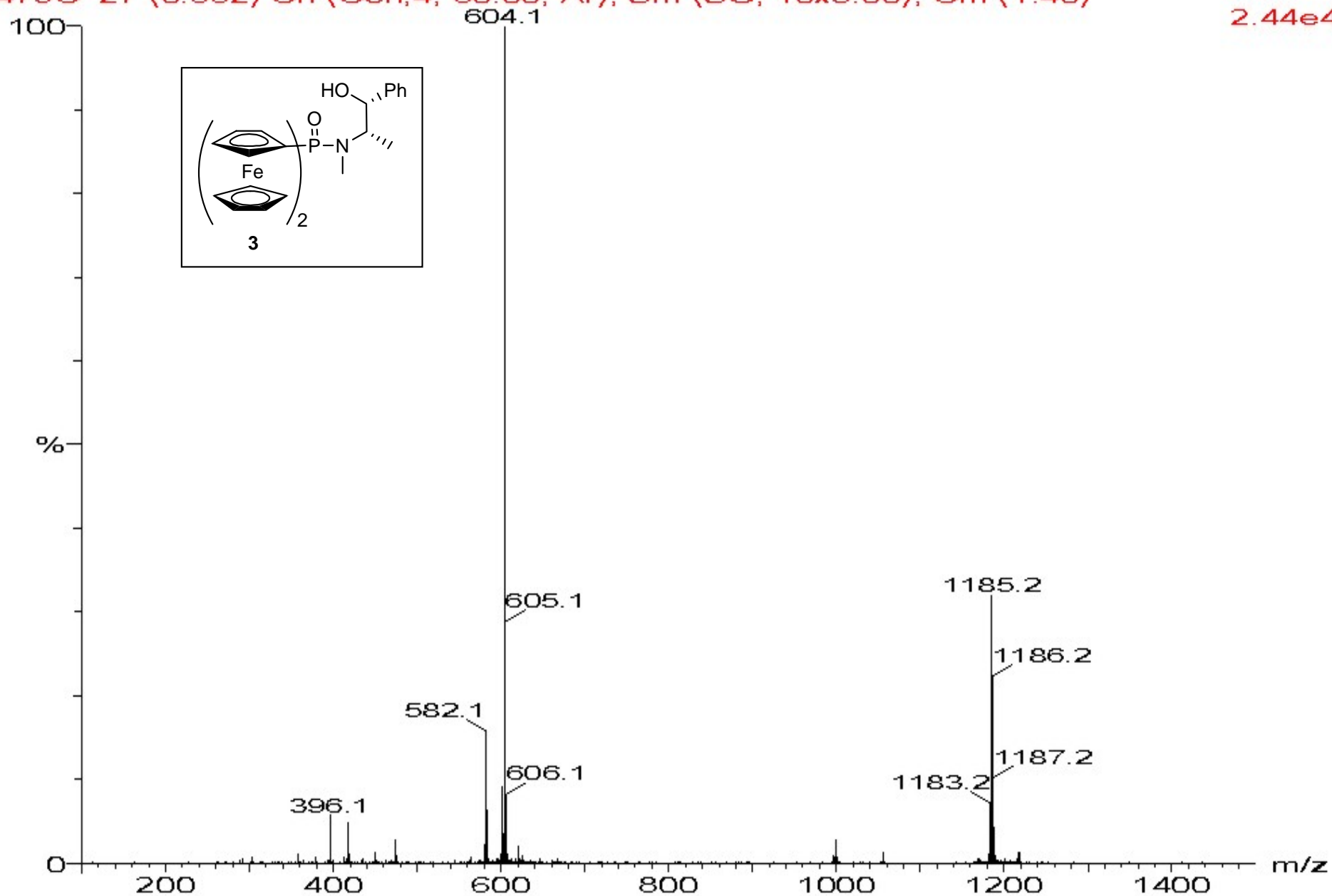
Cone = 50V

D. Vinci / JX

Operator: AJM

479C 27 (0.662) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40)

2.44e4



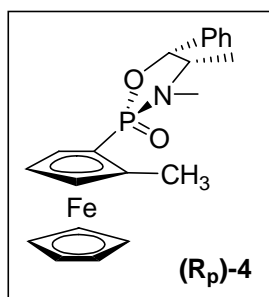
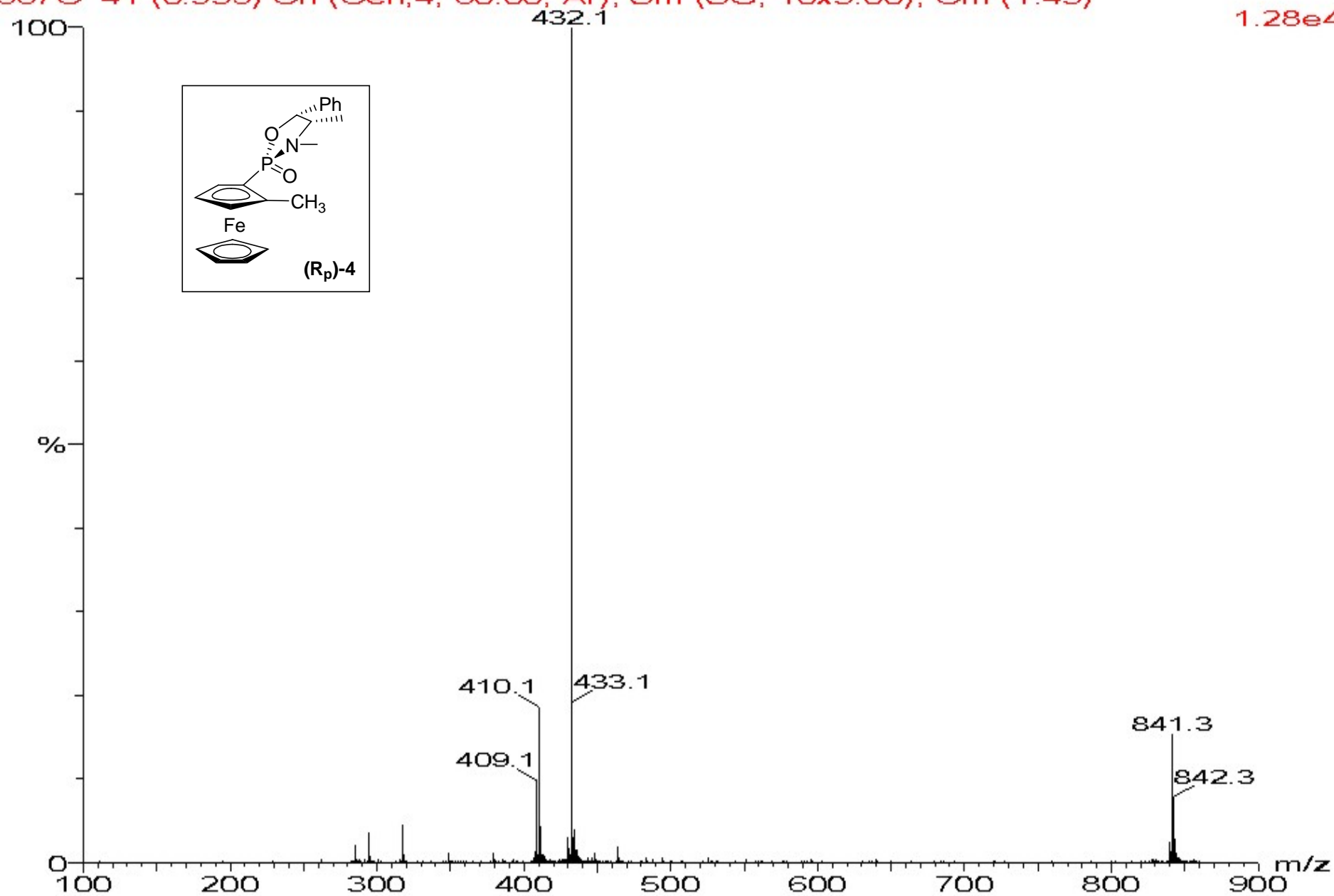
Sample: DV410 in CH₃OH/0.1% Formic Cone = 50V

D. Vinci / JX

Operator: AJM

687C 41 (0.956) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:43)

1.28e4



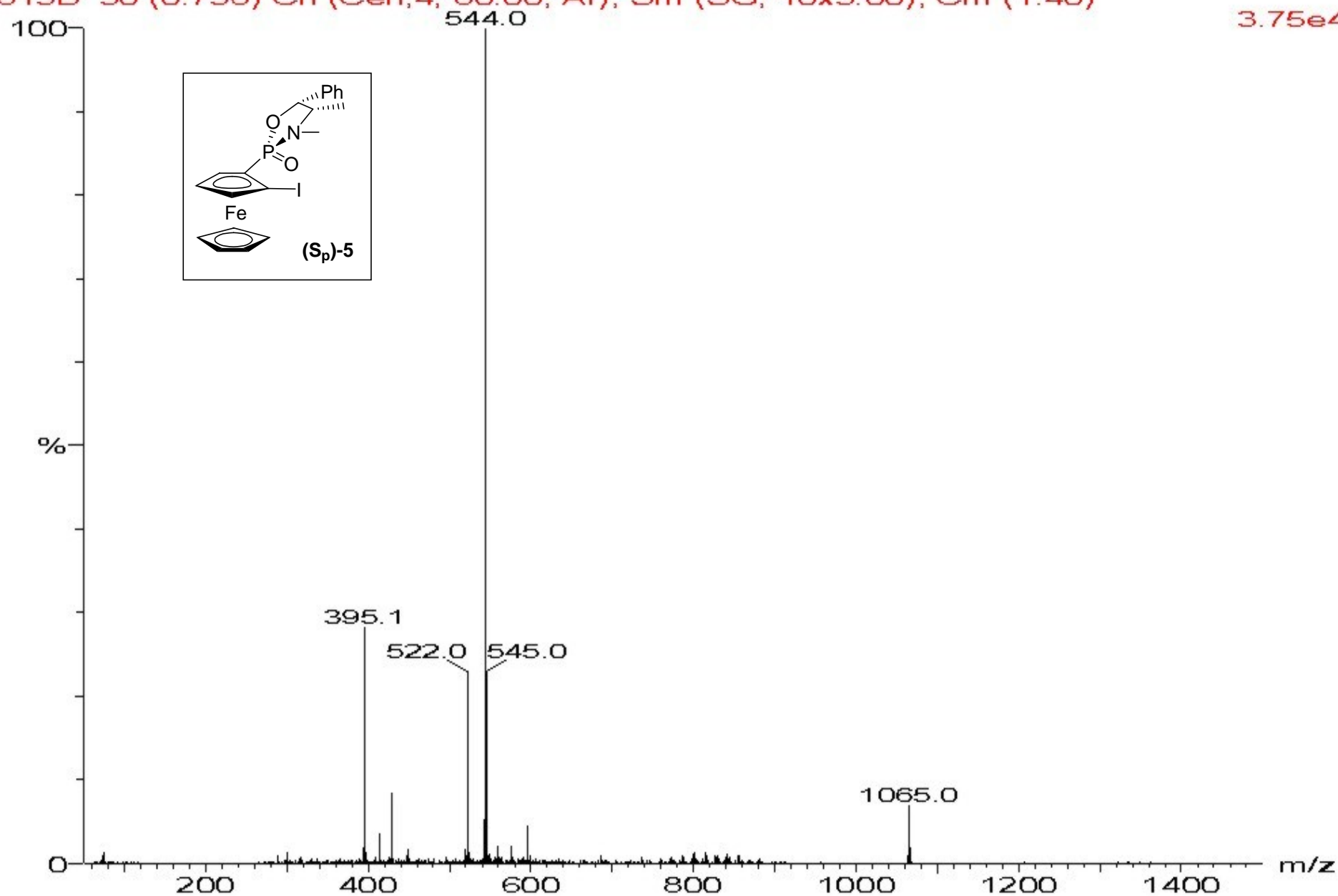
Sample: DV 64-E in CH₃OH Cone = 50V

D. Vinci / JX

Operator: AJM

613B 30 (0.736) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40)

3.75e4



Sample: DV472 in CH₃OH

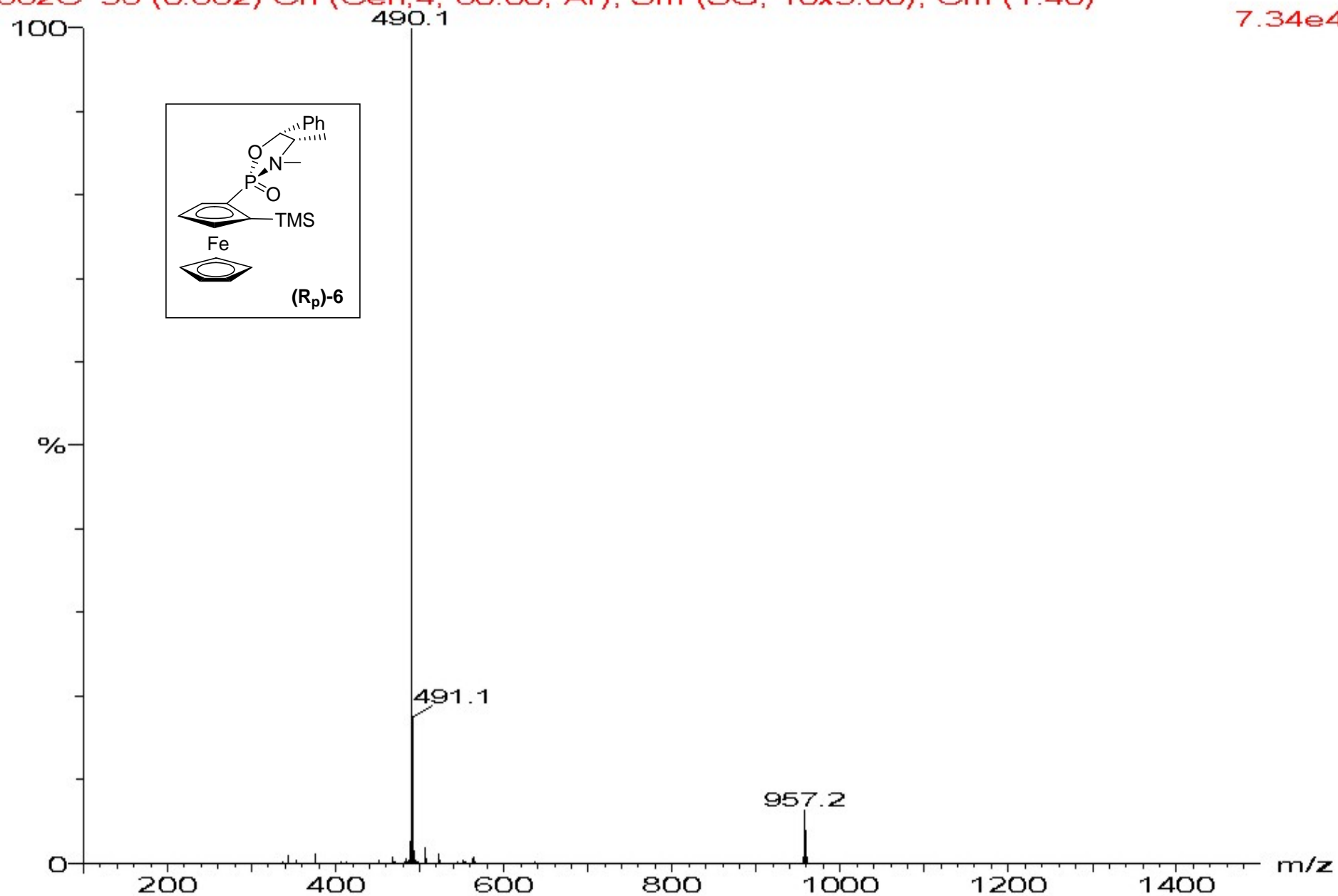
Cone = 50V

D. Vinci / JX

Operator: AJM

882C 36 (0.882) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40)

7.34e4



Sample: DV413 in CH₃OH

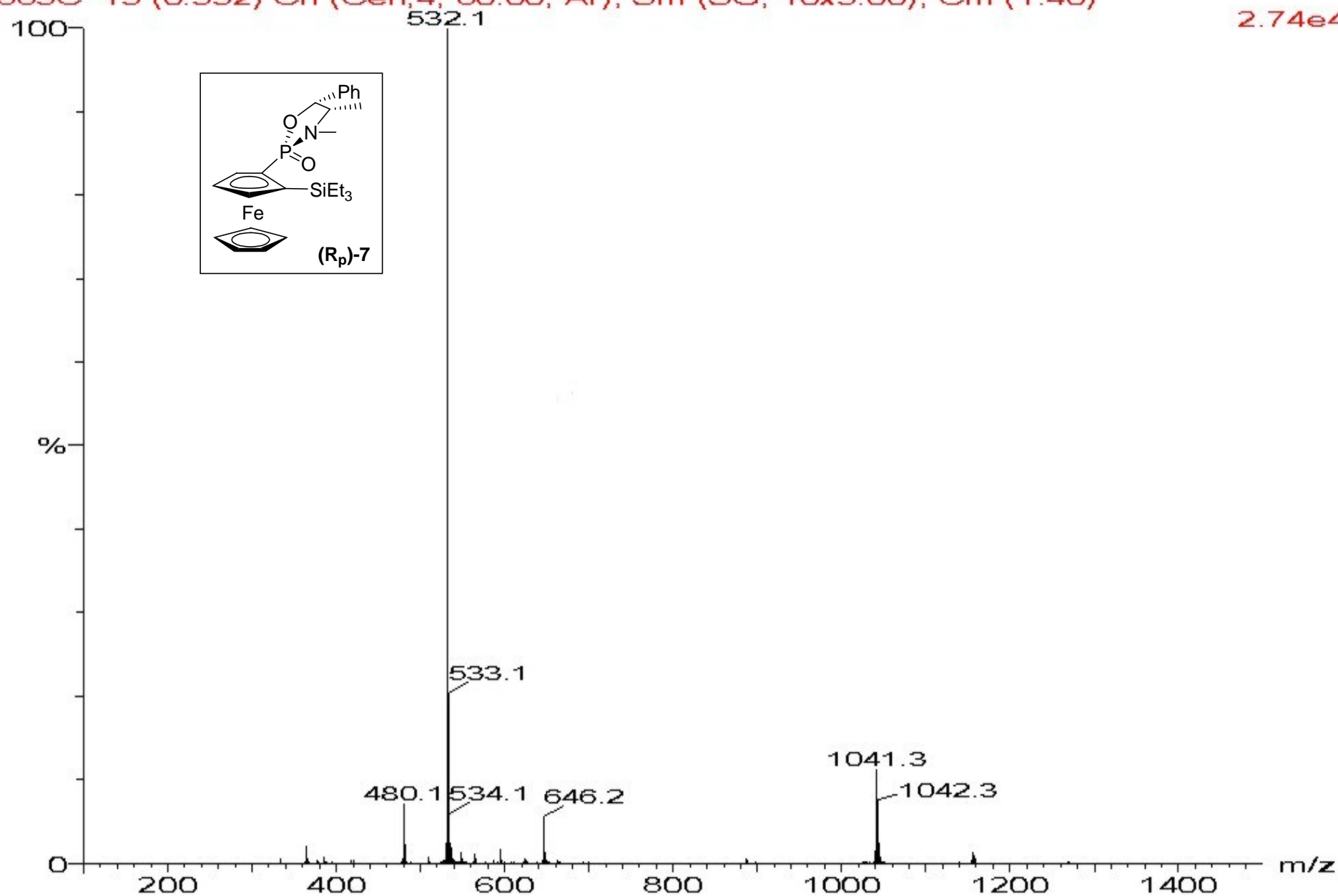
Cone = 50V

D. Vinci / JX

Operator: AJM

683C 13 (0.332) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40)

2.74e4



Sample: DV411 in CH₃OH

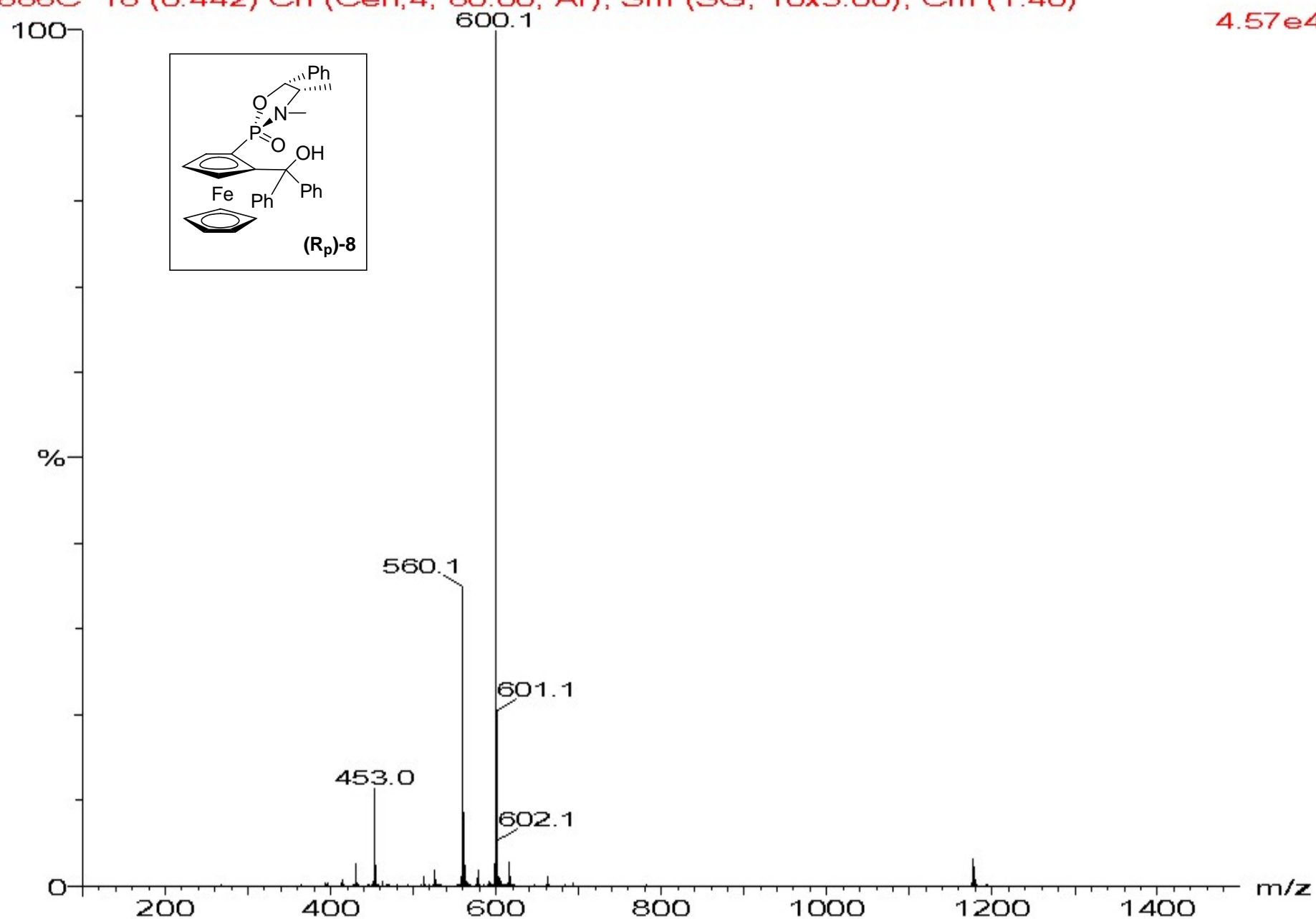
Cone = 50V

D. Vinci / JX

Operator: AJM

686C 18 (0.442) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40)

4.57e4



Sample: DV473 in CH₃OH

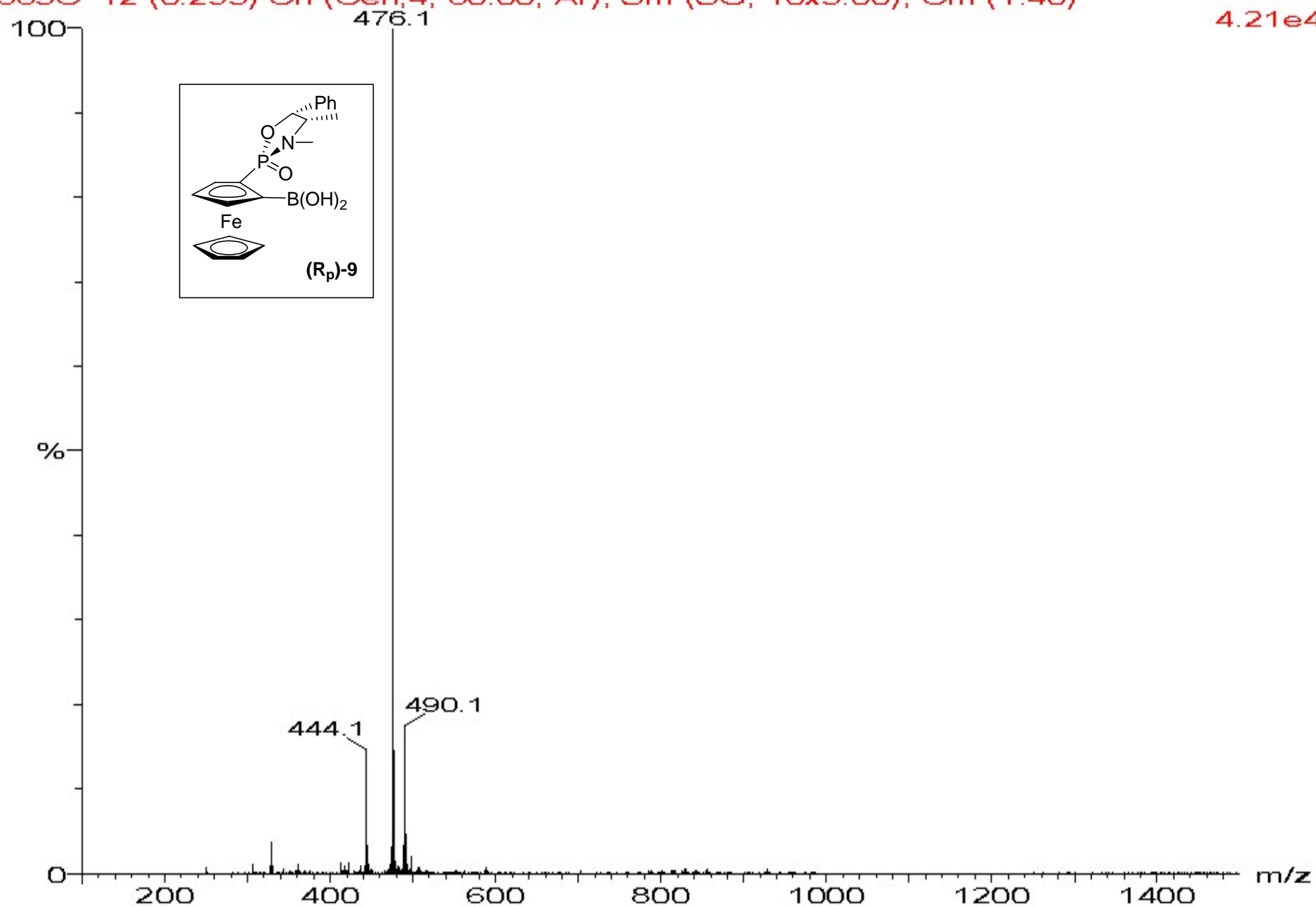
Cone = 50V

D. Vinci / JX

Operator: AJM

883C 12 (0.295) Cn (Cen, 4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40)

4.21e4

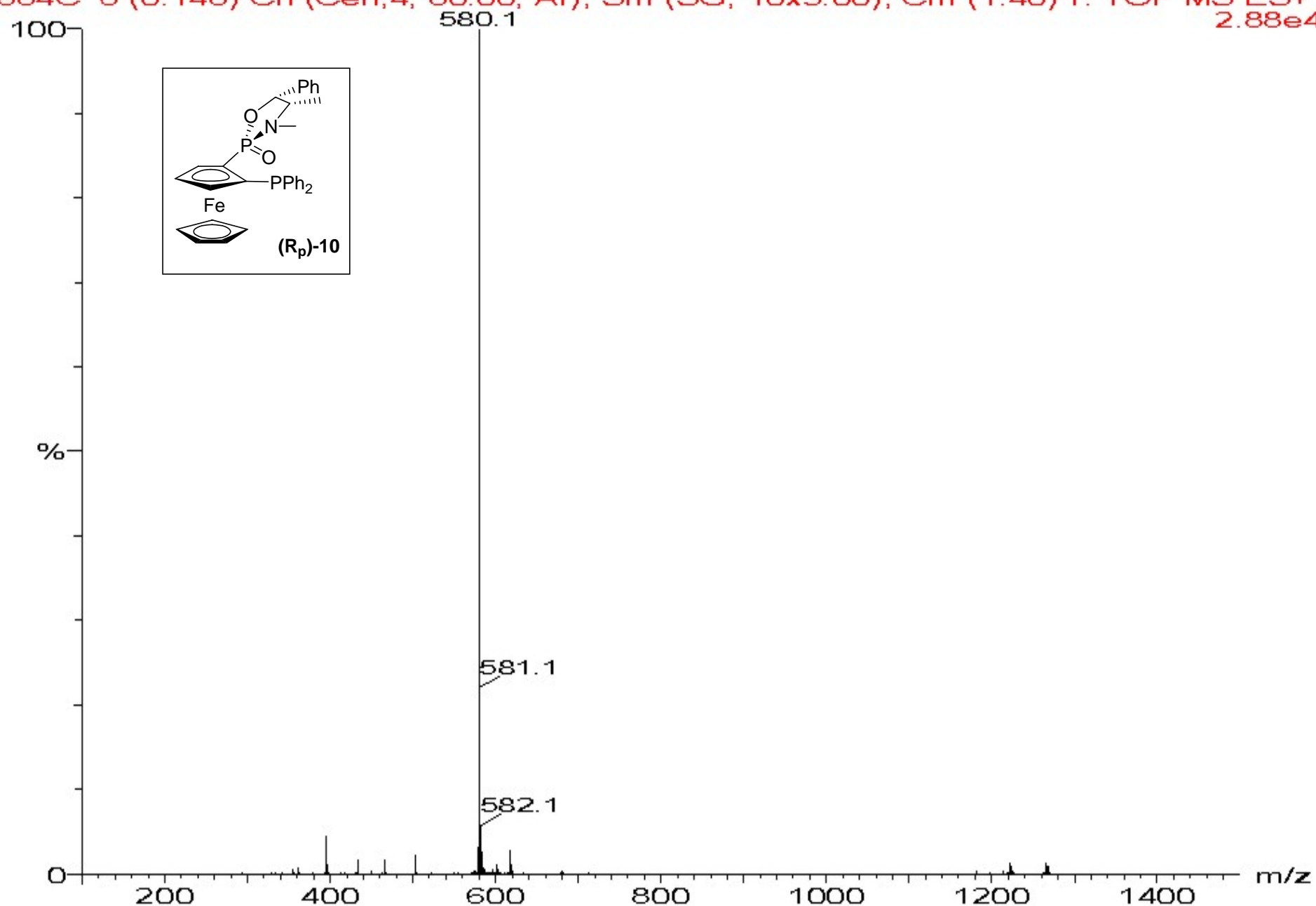


Sample: DV300 in CH₃OH/0.1% Formic Cone = 50V

D. Vinci / JX

Operator: AJM

684C 6 (0.148) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:40) 1: TOF MS ES+
2.88e4



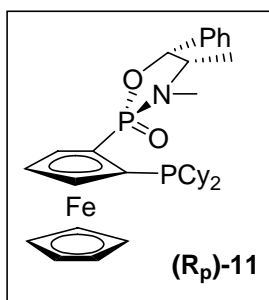
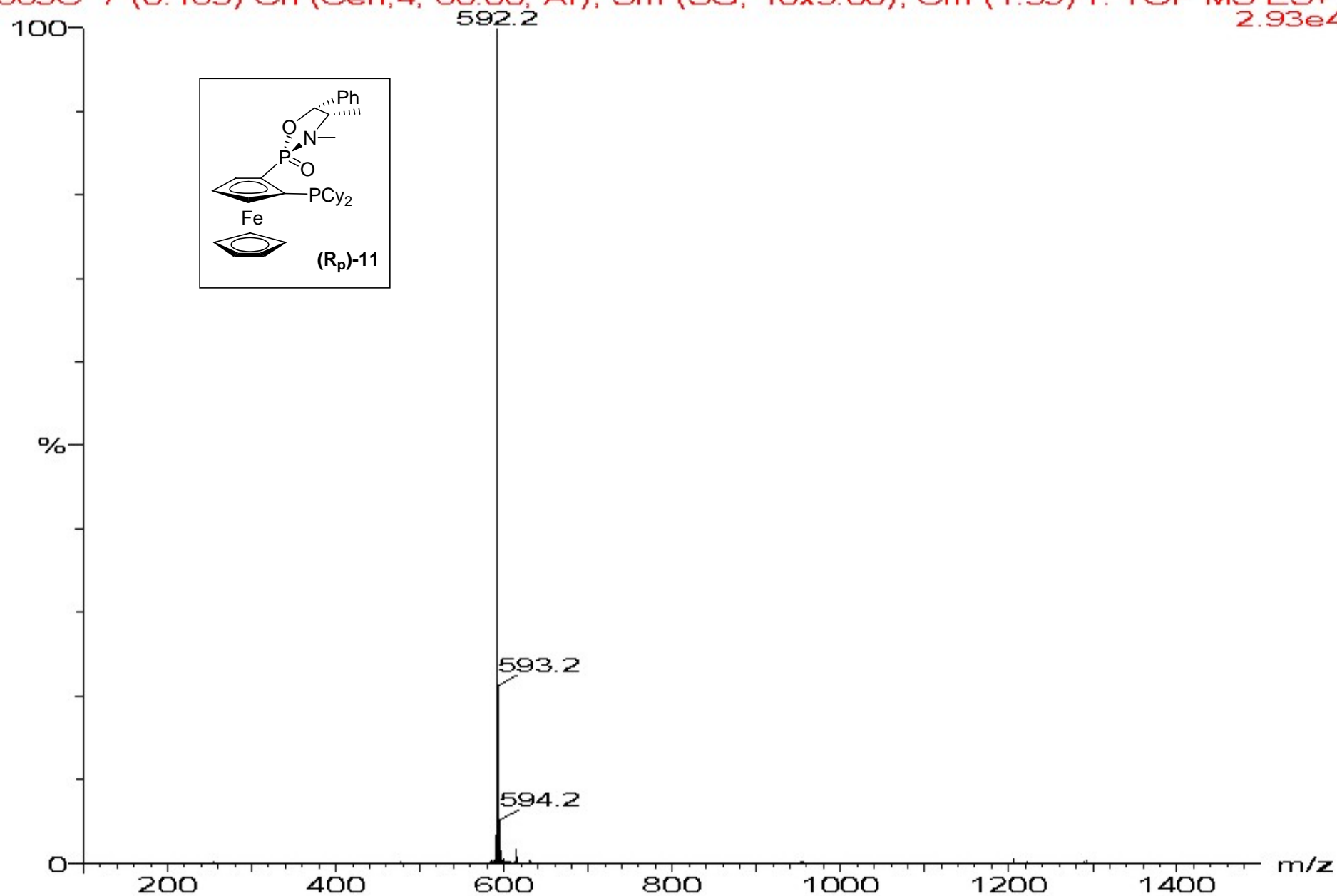
Sample: DV326 in CH₃OH

Cone = 50V

D. Vinci / JX

Operator: AJM

685C 7 (0.185) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x3.00); Cm (1:39) 1: TOF MS ES+
2.93e4

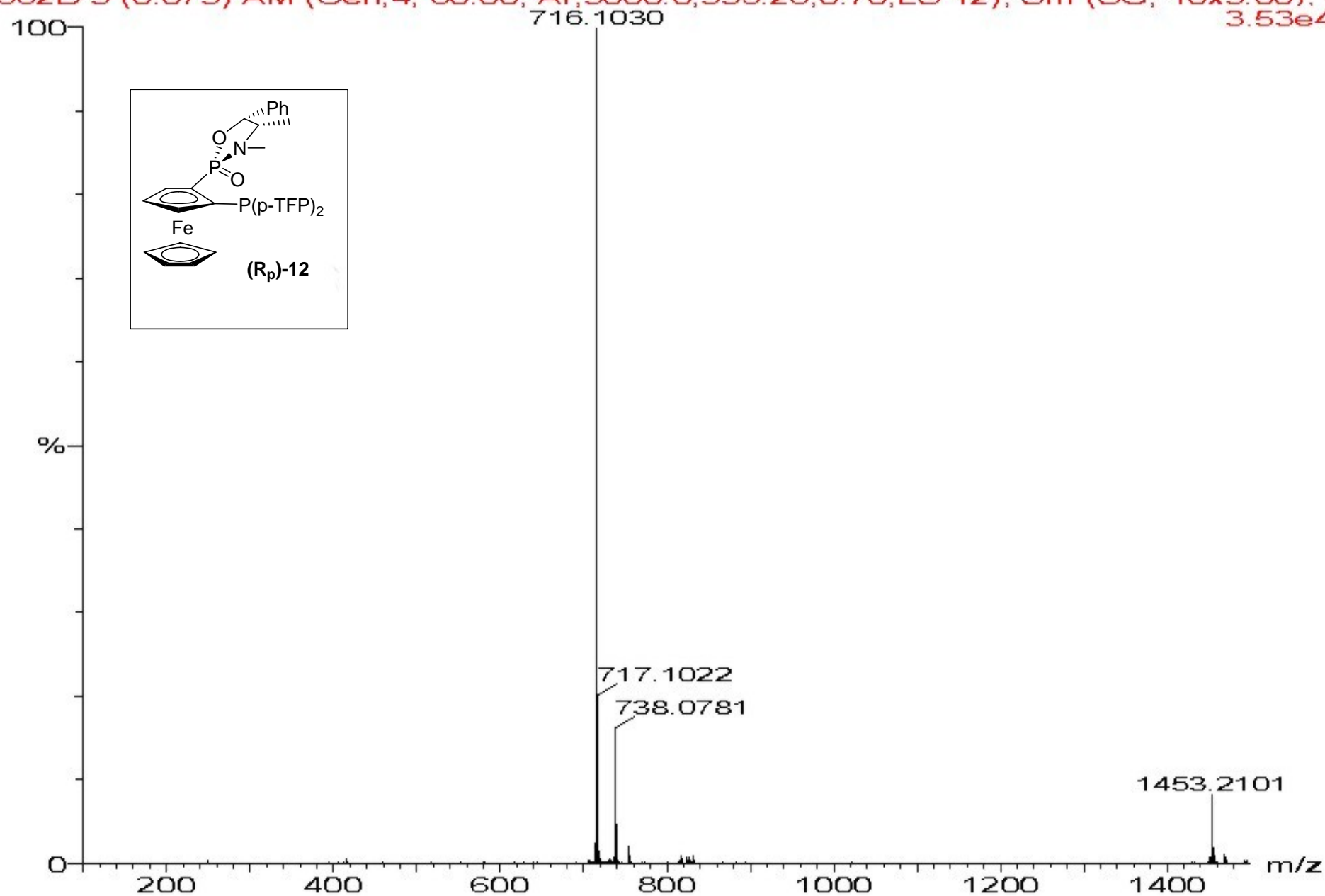


Sample: DV-601 in CH₃OH + 0.1% Formic Acid Cone = 35V

D. Vinci / JX

Operator: AJM

682D 3 (0.075) AM (Cen, 4, 80.00, Ar, 5000.0, 556.28, 0.70, LS 12); Sm (SG, 10x3.00); C 3.53e4



Sample: DV-606 in CH₃OH + 0.1% Formic Acid Cone = 35V

D. Vinci / JX

Operator: AJM

681D 8 (0.204) AM (Cen,4, 80.00, Ar,5000.0,556.28,0.70,LS 12); Sm (SG, 10x3.00); C
2.29e4

