Supporting Information

Phosphoresecent Emitters from Natural Products: *Cinchonine* Derived Iridium (III) Complexes

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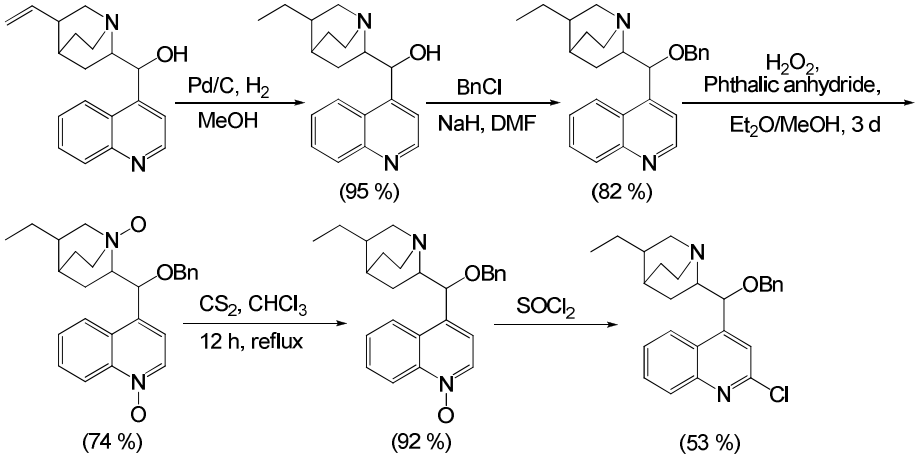
Synthetic procedure for 2'-chloro-9-*O*-benzyl-10,11-dihydrocinchonine.



Synthesis of 10,11-Dihydrocinchonine. Cinchonine (5.0 g) and Pd/C catalyst (10 %, 0.5 g) were added to MeOH (250 mL) in a double-necked round-bottom flask. The air was replaced by H_2 and the mixture stirred for 5 h and then filtered. The solvent was evaporated to give a white solid of 10,11-dihydrocinchonine. Yield (4.8 g, 95 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (d, J = 4.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.67–7.70 (m, 1H), 7.59 (d, J = 4.4 Hz, 1H), 7.49–7.52 (m, 1H), 5.66 (d, J = 4.9 Hz, 1H), 5.30 (s, 1H), 3.06–3.11 (m, 1H), 2.84–2.95 (m, 3H), 2.70–2.76 (m, 1H), 1.88–1.92 (m, 1H), 1.45–1.53 (m, 2H), 1.17–1.21 (m, 1H), 1.37–1.39 (m, 3H), 1.24–1.27 (m, 1H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (125

MHz, $CDCl_3$): δ 150.9, 149.7, 149.0, 131.1, 129.7, 127.3, 126.6, 123.8, 119.0, 72.8, 60.9, 51.9, 50.9, 38.1, 27.9, 27.0, 25.9, 22.1, 12.7. MS (ESI): 297.3 $[M+H]^+$.

Synthesis of 9-*O*-benzyl-10,11-dihydrocinchonine. To a solution of 10,11-dihydrocinchonine (2.96 g, 10 mmol) in dry DMF was added NaH (1.0 g, 60% suspension in mineral oil, 2.5 eq.). The resulting mixture was stirred for 2 h at room temperature. Benzylchloride (1.38 g, 11 mmol) was added dropwise via a syringe over 10 min and then stirred overnight. Brine (20 mL) was added carefully to quench the reaction and the resulting mixture was extracted with EtOAc (100 mL). The organic phase was washed with brine (3 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent was removed. The crude product was purified by chromatography on silica. (EA/MeOH = 10/1) to give colorless oil (3.28 g, 82 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.86 (d, J = 4.4 Hz, 1H), 8.14 (br, 1H), 8.12 (br, 1H), 7.61–7.64 (m, 1H), 7.47–7.51 (m, 2H), 7.26 (br, 4H), 7.20–7.23 (m, 1H), 5.30 (br, 1H), 4.31–4.40 (AB–system, J_{AB} = 11.4 Hz, 2H), 3.01 (br, 1H), 2.93 (br, 1H), 2.79–2.83 (m, 1H), 2.70–2.74 (m, 1H), 2.59–2.66 (m, 1H), 1.97–2.00 (m, 1H), 1.59 (br, 1H), 1.29–1.42 (m, 5H), 1.21 (br, 1H), 0.80 (t, J = 7.2 Hz, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 150.1, 148.6, 146.6, 137.9, 130.5, 129.0, 128.3, 127.8, 127.7, 126.6, 126.5, 123.4, 118.8, 81.0, 71.4, 60.6, 50.9, 50.2, 37.5, 27.4, 26.4, 25.3, 22.1, 12.0. MS (ESI): 387.3 $[M+H]^+$.

Synthesis of 9-*O*-benzyl-10,11-dihydrocinchonine-N,N'-dioxide. Phthalic acid anhydride (12 g, 81 mmol) was dissolved in Et_2O (150 mL) and cooled to 0 °C. Hydrogen peroxide (35 %, 10 mL, 53.6 mmol) was added and the solution stirred for

10 min. 9-O-benzyl-10,11-dihydrocinchonine (3.86 g, 10 mmol) was dissolved in a mixture of MeOH (50 mL) and HOAc (10 mL) and added dropwise to the ether solution. The resulting mixture was stirred for 3 d. When the reaction was judged to be complete by TLC, the pH was adjusted to 6 – 7 with aqueous NaOH (10 %). The solvent was then evaporated and the crude product extracted with $CHCl_3$ and washed 3 times with brine. The organic phase was dried (anhydrous Na_2SO_4), condensed and the product purified by chromatography on silica. (EA/MeOH = 4/1) to give a yellow oily product (2.60 g, 74 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80–8.81 (m, 1H), 8.59–8.61 (m, 1H), 8.54 (d, J = 6.3 Hz, 1H), 7.77–7.82 (m, 2H), 7.54 (d, J = 6.3 Hz, 1H), 7.32–7.42 (m, 5H), 6.93 (s, 1H), 4.48–4.78 (AB quartet, 2H), 3.82–3.86 (m, 1H), 3.53–3.60 (m, 1H), 3.36–3.42 (m, 2H), 3.25–3.29 (m, 1H), 2.59–2.69 (m, 2H), 1.88–1.99 (m, 3H), 1.35–1.50 (m, 3H), 0.77 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.8, 137.5, 135.3, 135.2, 130.9, 130.1, 128.9, 128.6, 128.5, 128.3, 125.0, 120.8, 118.8, 73.6, 72.3, 72.1, 66.3, 66.2, 39.2, 27.4, 26.1, 25.4, 20.9, 11.8. MS (ESI): 419.2 $[M+H]^+$.

Synthesis of 9-*O*-benzyl-10,11-dihydrocinchonine-N'-monoxide. 9-*O*-benzyl-10,11-dihydrocinchonine-N,N'-dioxide (4.18 g, 10 mmol) was dissolved in 30 mL of $CHCl_3$ at 0 °C. CS_2 (20 mL) was added and the mixture was stirred for 30 min and then refluxed overnight. The solvent was removed and the product was purified by chromatography on silica (EA/MeOH = 4/1) to give a yellowish oily product (3.70 g, 92 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83–8.85 (m, 1 H), 8.50 (d, J = 6.3 Hz, 1 H), 8.21 (d, J = 7.5 Hz, 1 H), 7.77–7.80 (m, 1 H), 7.66–7.69 (m, 1 H),

7.39 (d, J = 6.2 Hz, 1 H), 7.29–7.36 (m, 5 H), 5.19 (br, 1 H), 4.38–4.48 (AB quartet, 2 H), 3.06 (br, 1 H), 2.69–2.87 (m, 4 H), 1.93–1.98 (m, 1 H), 1.34–1.54 (m, 7 H), 7.39 (t, J = 7.3 Hz, 3 H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.5, 137.5, 136.8, 135.0, 130.1, 128.8, 128.7, 128.5, 128.0, 127.9, 124.1, 120.7, 119.4, 80.4, 71.6, 60.7, 50.8, 50.1, 37.4, 27.2, 26.3, 25.3, 22.6, 11.9. MS (ESI): 403.2 $[M+H]^+$.

Synthesis of 9-*O*-benzyl-2'-chloro-10,11-dihydrocinchonine. 9-*O*-benzyl-10,11-dihydrocinchonine-N'-monoxide (4.02 g, 10 mmol) and $SOCl_2$ (10 mL) were stirred and heated at 60 °C for 5 h. The mixture was cooled to room temperature and diluted with CH_2Cl_2 (80 mL). Water (15 mL) was carefully added and the mixture stirred for 1 h. The organic phase was washed with water (3 × 50 mL) dried (anhydrous Na_2SO_4) and condensed to a black residue which was purified by chromatography on silica (EA/MeOH = 20/1) to give a light brown solid (2.23 g, 53 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (d, J = 8.1 Hz, 1H), 8.06–8.08 (m, 1H), 7.74–7.81 (m, 2H), 7.55 (s, 1H), 7.31–7.42 (m, 5H), 6.72 (br, 1H), 4.54–4.78 (AB quartet, 2H), 3.73–3.77 (m, 1H), 3.30–3.44 (m, 3H), 3.08–3.14 (m, 1H), 2.39–2.44 (m, 1H), 1.68–1.87 (m, 4H), 1.39–1.49 (m, 2H), 1.21–1.27 (m, 1H), 0.79 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.2, 149.1, 147.3, 137.2, 131.7, 130.1, 129.3, 129.2, 129.1, 129.0, 125.0, 124.5, 119.9, 75.7, 73.2, 60.6, 50.5, 49.9, 35.9, 26.2, 25.1, 24.7, 19.1, 11.9. MS (ESI): 421.2 $[M+H]^+$.

Infred Data for **1–8**

IR (KBr pellet) for **1**: 3059 (m), 2931 (s), 2868 (s), 2021 (w), 1603 (s), 1580 (m), 1539 (s), 1517 (m), 1452 (s), 1370 (m), 1287 (m), 1204 (w), 1161 (w), 1116 (m), 1064 (w), 1046 (w), 1027 (w), 994 (w), 937 (w), 893 (w), 833 (w), 762 (s), 738 (s), 699 (s), 604 (w), 555 (w), 527 (w), 505 (w), 489 (w), 447 (w) cm^{-1}.

IR (KBr pellet) for **2**: 2956 (s), 2933 (s), 2870 (s), 2040 (s), 1599 (s), 1575 (w), 1544 (s), 1515 (w), 1499 (w), 1455 (m), 1425 (w), 1405 (w), 1363 (m), 1327 (w), 1289 (m), 1252 (m), 1200 (w), 1158 (w), 1116 (m), 1104 (w), 1063 (w), 1042 (w), 1027 (w), 990 (m), 937 (w), 906 (w), 847 (w), 833 (m), 811 (w), 762 (m), 699 (s), 612 (w), 530 (w), 498 (w) cm^{-1}.

IR (KBr pellet) for **3**: 3059 (w), 2931 (m), 2865 (m), 1726 (w), 1602 (s), 1580 (s), 1538 (m), 1517 (s), 1451 (s), 1398 (m), 1364 (m), 1288 (m), 1260 (m), 1201 (w), 1159 (w), 1046 (m), 1025 (m), 932 (w), 803 (w), 762 (s), 737 (m), 698 (m) cm^{-1}.

IR (KBr pellet) for **4**: 3029 (w), 2931 (s), 2865 (m), 1599 (s), 1546 (s), 1517 (s), 1480 (s), 1452 (s), 1401 (s), 1372 (m), 1287 (m), 1261 (w), 1227 (m), 1158 (m), 1115 (m), 1071 (m), 1026 (m), 936 (m), 892 (w), 788 (w), 760 (s), 736 (m), 697 (s), 635 (m), 445 (w) cm^{-1}.

IR (KBr pellet) for **5**: 3059 (w), 2930 (s), 2862 (m), 1651 (s), 1635 (s), 1560 (s), 1538 (m), 1516 (w), 1450 (s), 1354 (s), 1288 (m), 1260 (m), 1203 (w), 1162 (m), 1111 (m), 1025 (w), 937 (w), 843 (m), 797 (m), 762 (s), 738 (m), 699 (s), 436 (w) cm^{-1}.

IR (KBr pellet) for **6**: 3060 (w), 2974 (m), 2927 (m), 2863 (m), 1722 (m), 1643 (s), 1601 (m), 1580 (m), 1539 (s), 1497 (w), 1451 (s), 1367 (m), 1355 (m), 1305 (m), 1260 (m), 1225 (w), 1202 (w), 1144 (m), 1114 (m), 1045 (w), 1025 (m), 936 (w), 878 (w), 833 (m), 795 (m), 762 (s), 738 (s), 699 (m), 665 (w) cm^{-1}.

IR (KBr pellet) for **7a**: 2931 (m), 2867 (m), 1601 (s), 1581 (m), 1542 (s), 1517 (m), 1497 (w), 1453 (m), 1431 (w), 1417 (w), 1395 (w), 1369 (w), 1310 (w), 1289 (w), 1261 (w), 1203 (w), 1162 (w), 1115 (m), 1095 (m), 1067 (w), 1048 (w), 1028 (w), 991 (w), 937 (w), 841 (s), 791 (w), 764 (m), 738 (m), 699 (m), 648 (w), 613 (w), 557 (s), 489 (w) cm^{-1}; **7b**: 2931 (s), 2868 (s), 1601 (s), 1581 (m), 1542 (s), 1516 (m), 1431 (w), 1414 (w), 1395 (m), 1368 (m), 1310 (w), 1289 (w), 1261 (s), 1203 (w), 1163 (w), 1096 (s), 1027 (s), 938 (w), 841 (s), 800 (m), 764 (m), 739 (m), 699 (s), 648 (w), 613 (w), 557 (s) cm^{-1}.

IR (KBr pellet) for **8**: 2930 (s), 2868 (m), 1598 (s), 1579 (m), 1545 (m), 1516 (m), 1454 (m), 1414 (w), 1363 (w), 1289 (w), 1255 (w), 1201 (w), 1163 (w), 1110(m), 1067 (m), 993 (m), 937 (w), 842 (s), 759 (m), 738 (m), 699 (m), 612 (w), 557 (m), 529 (w), 498 (w) cm^{-1}.

ESI-Mass Spectra

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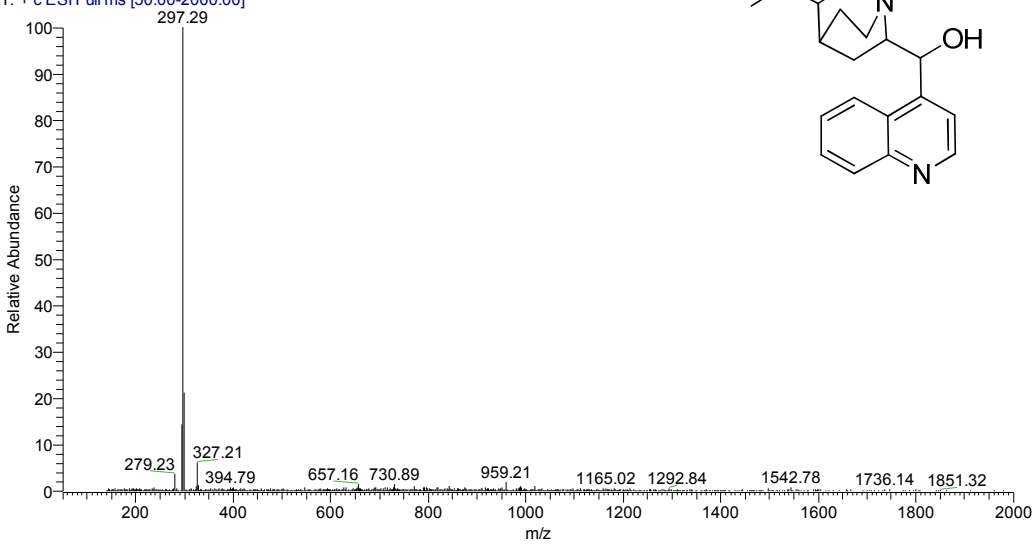

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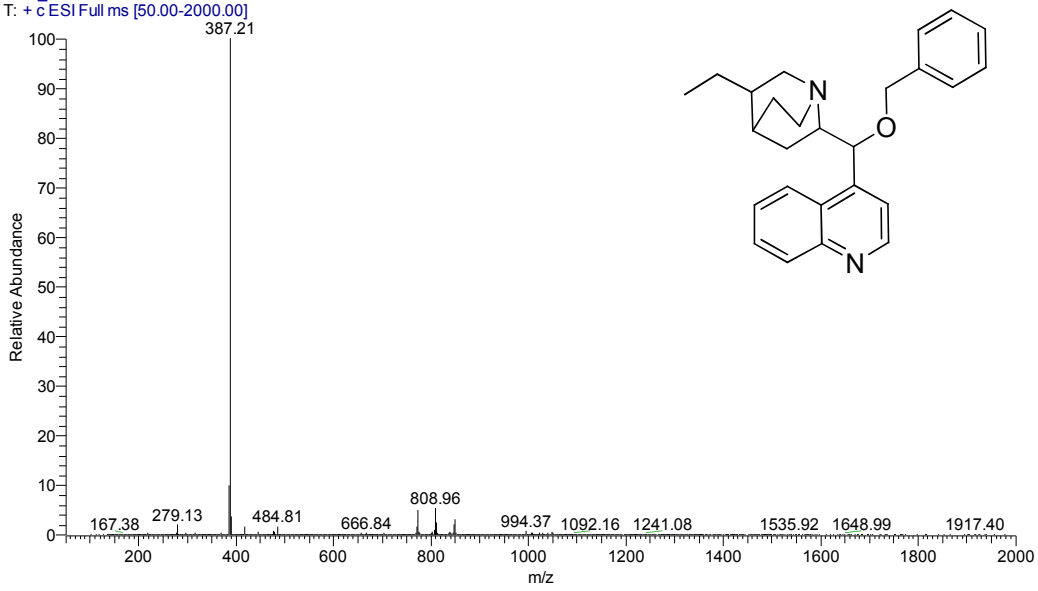

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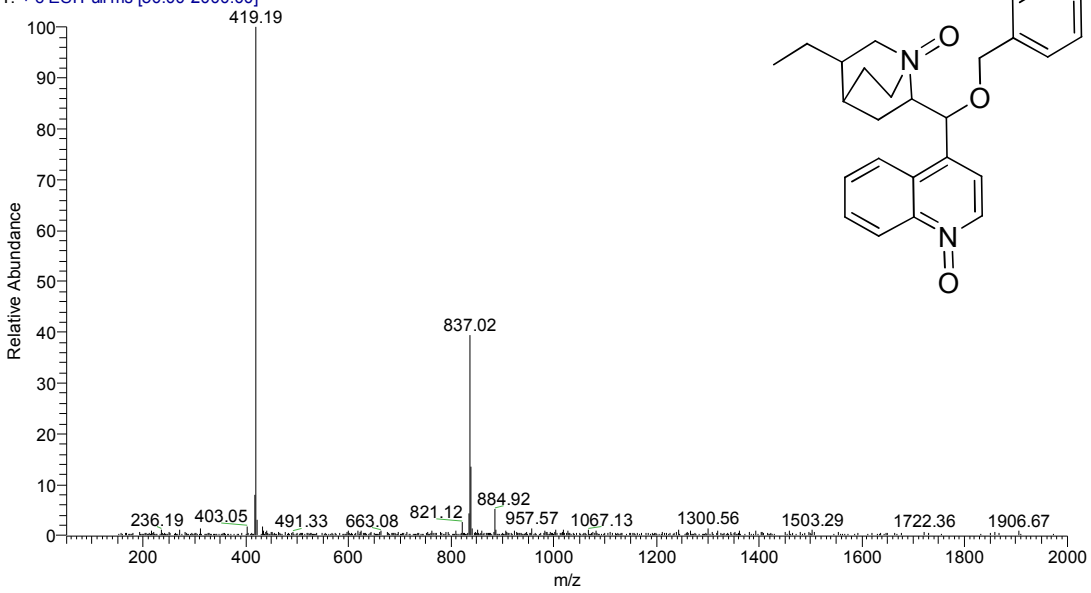

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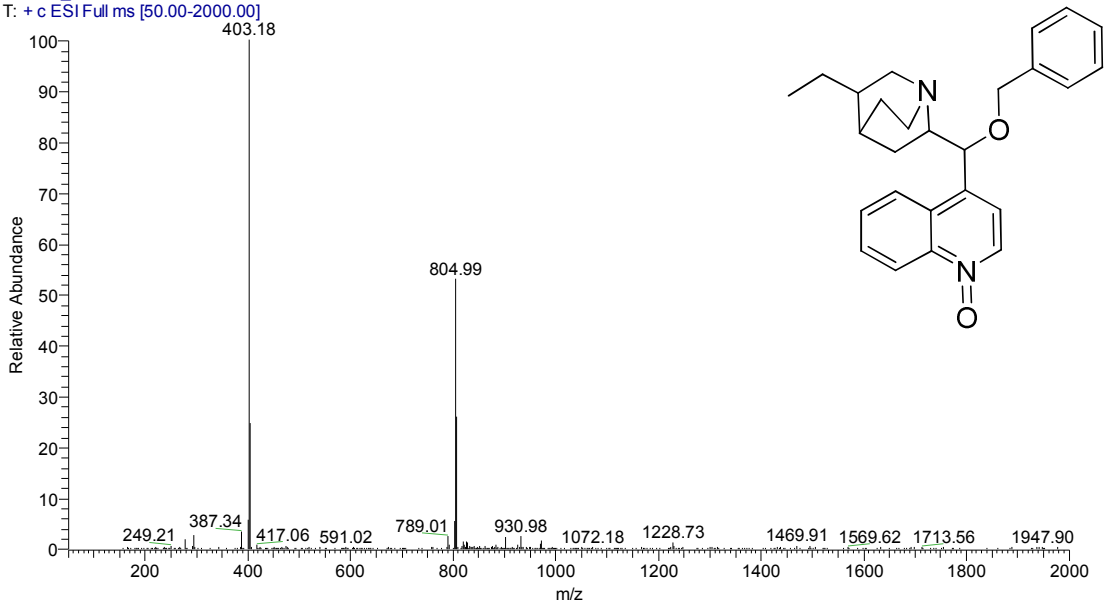

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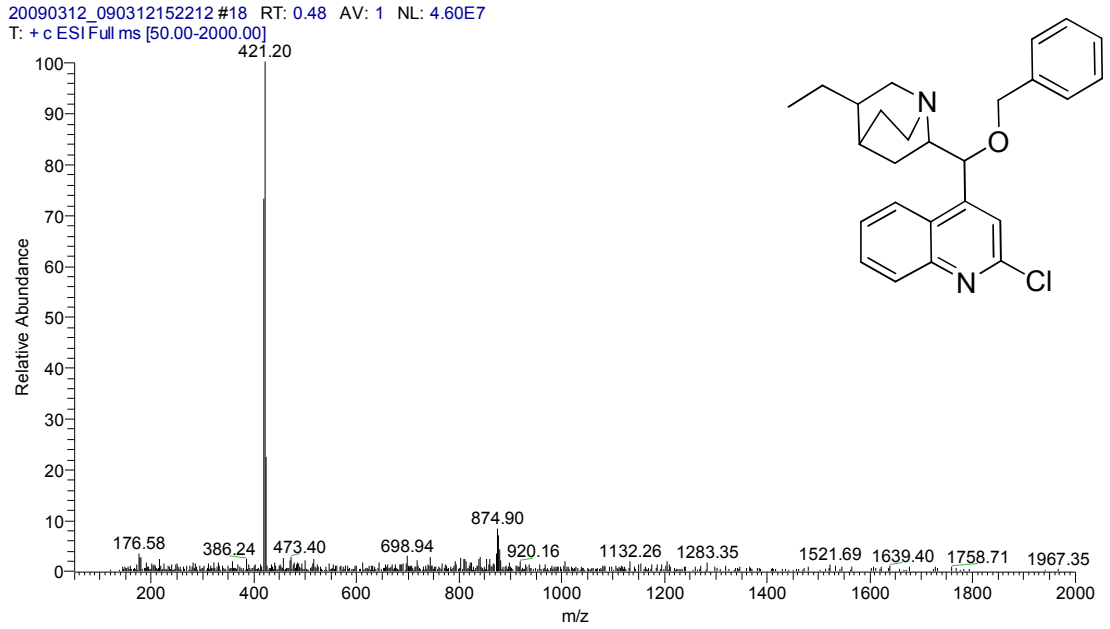

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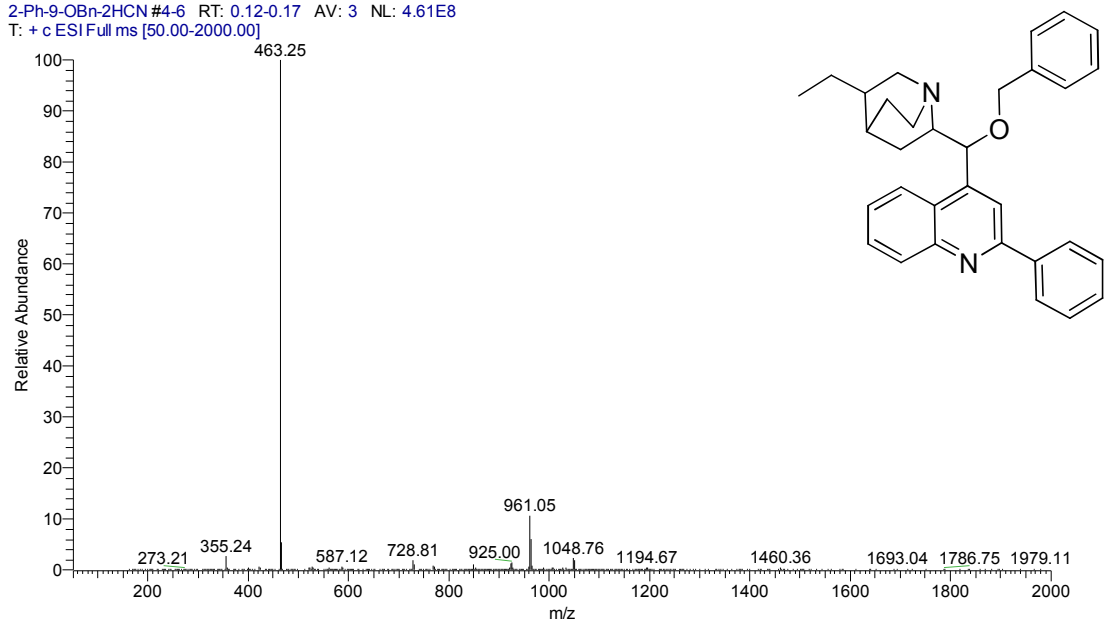

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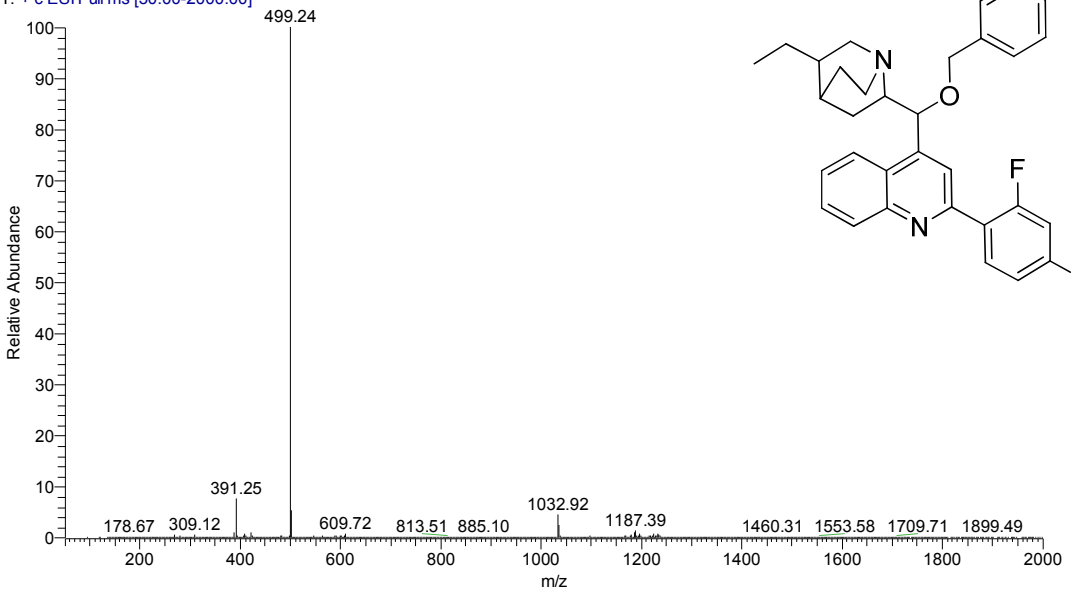

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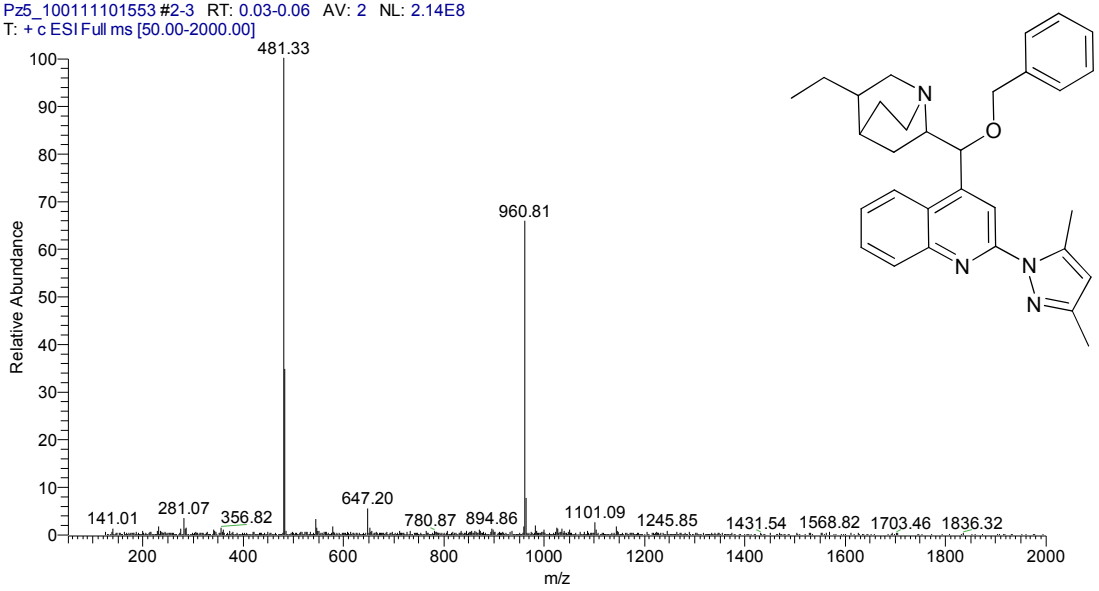

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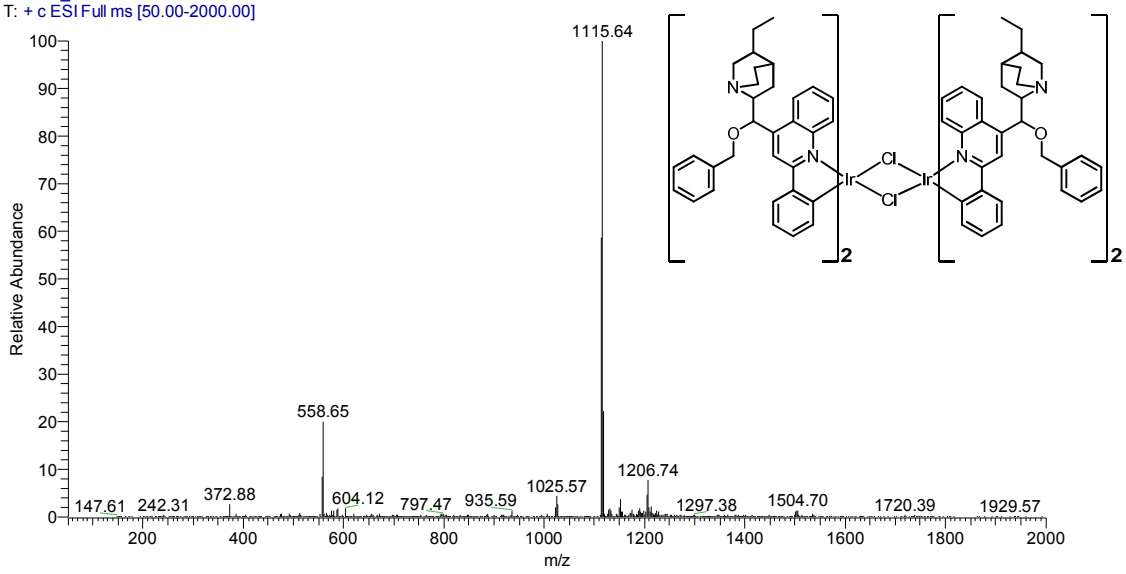

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MeOH

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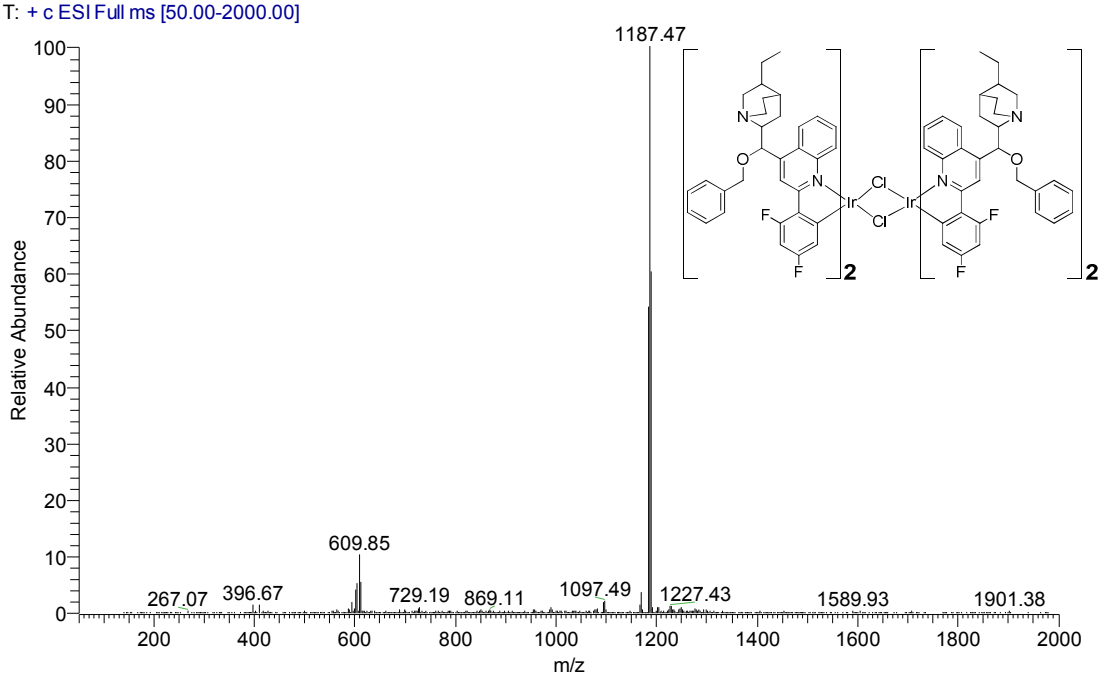

Ir(2-ph-9OBn)dimer 3rd with acac 1/20/2010 12:23:10 PM WH-1-0
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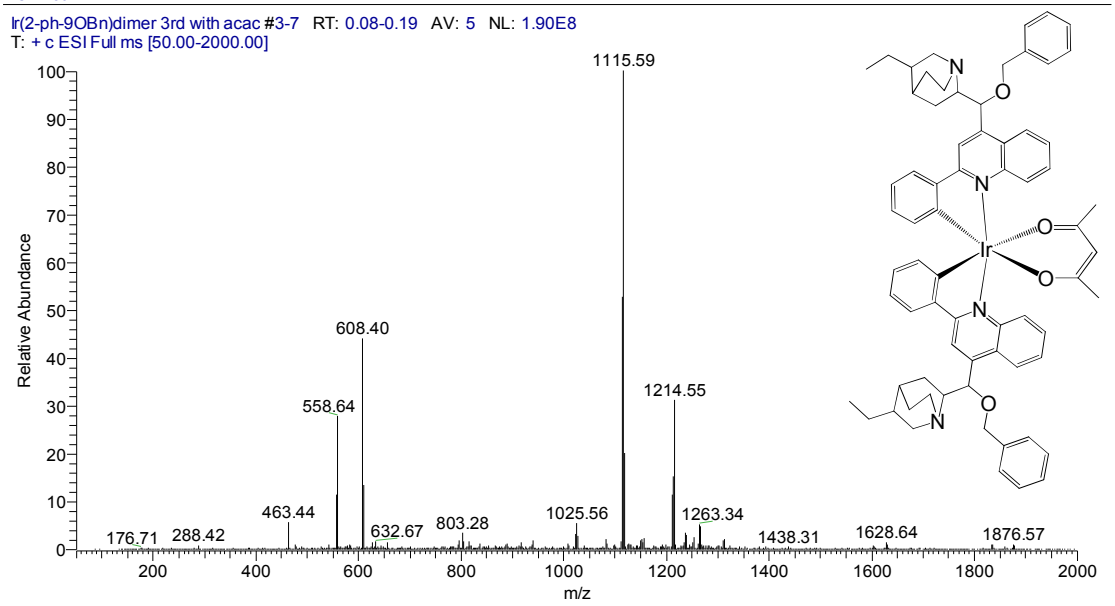

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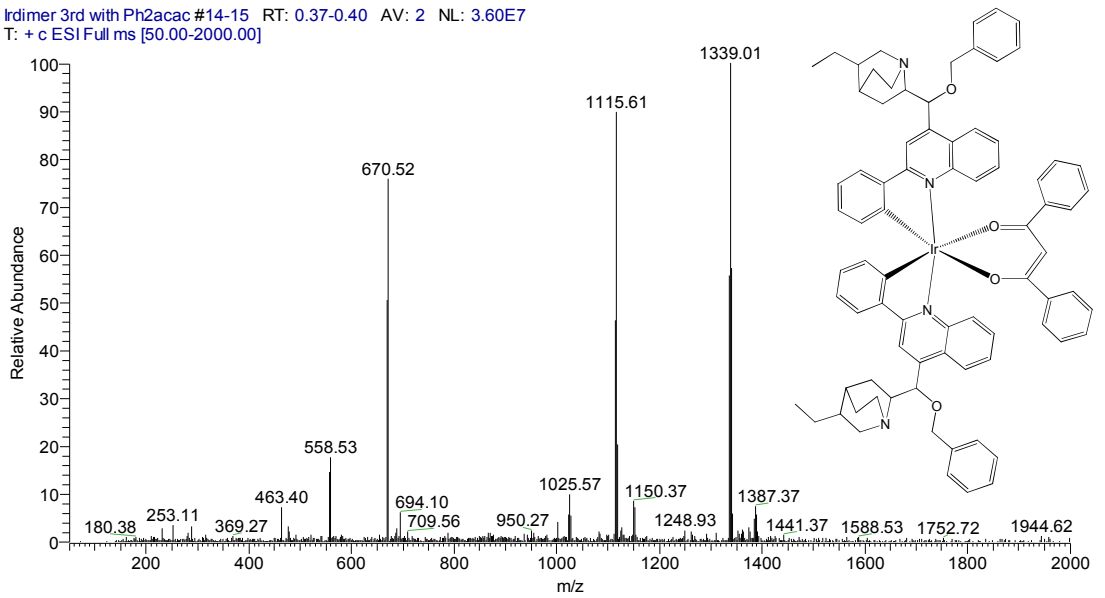

Irdimer 3rd pic 1st com 1/19/2010 9:58:17 AM WH-1-00
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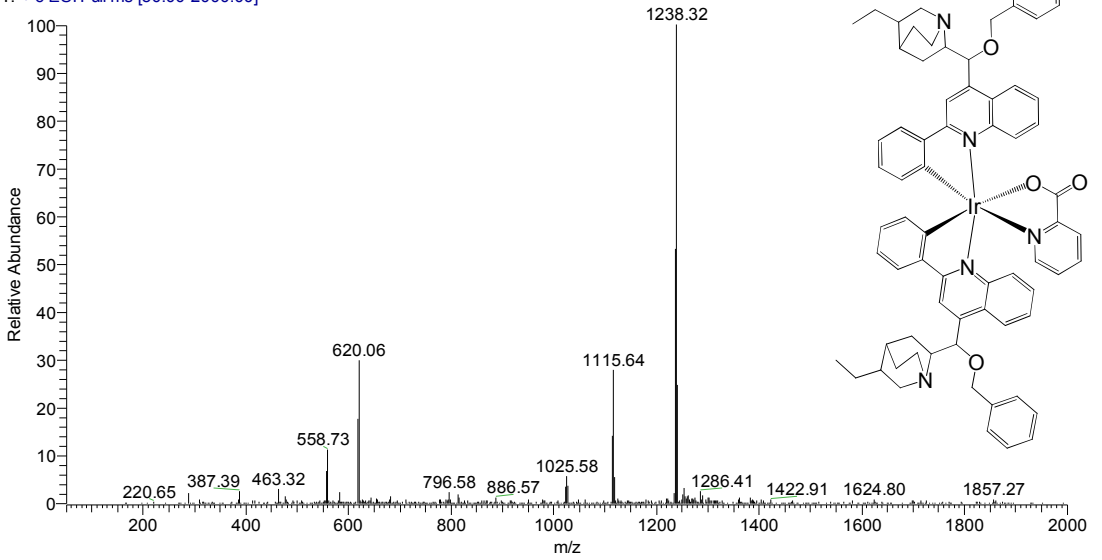

Ir dimer 3rd with isoq 1/15/2010 9:59:37 AM WH-1-005 major product
DCM 200

Ir dimer 3rd with isoq #6-7 RT: 0.15-0.18 AV: 2 NL: 1.09E8
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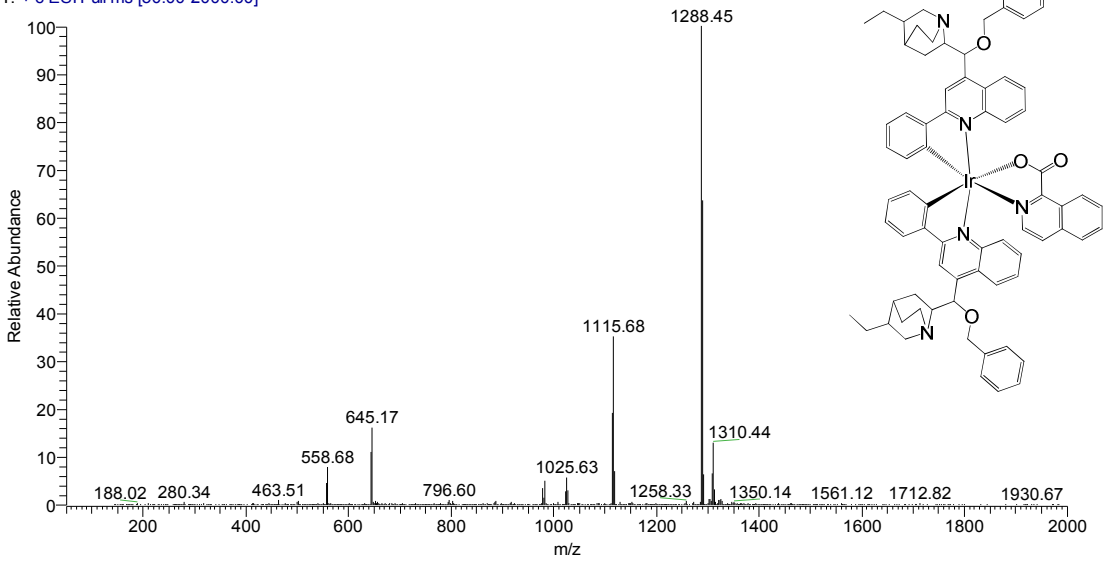

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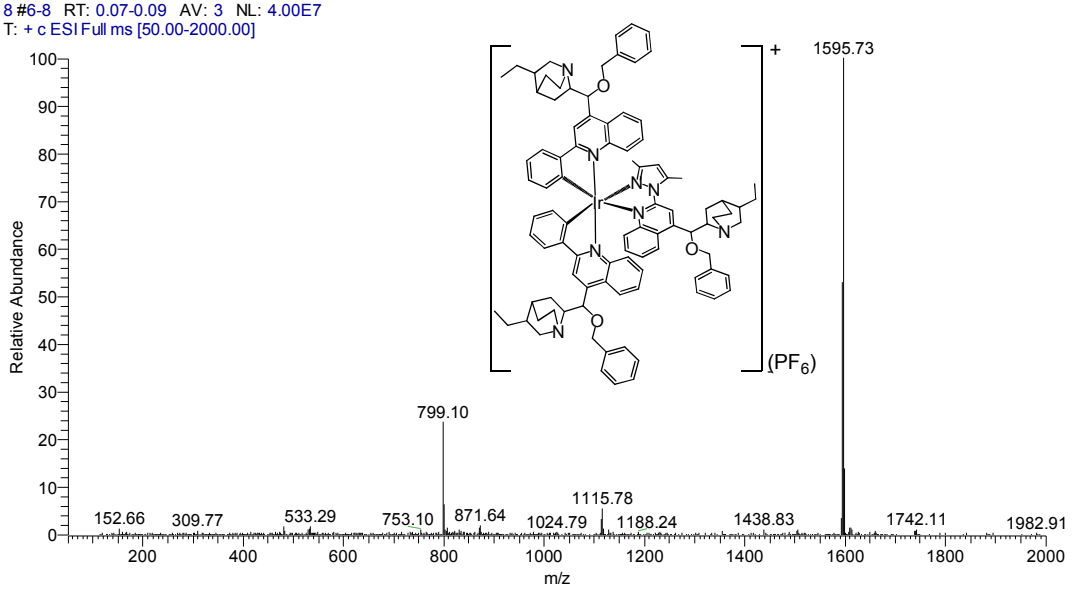

D:\Student\...\F2Ir dimer with Pz 2nd2 5/12/2010 9:40:41 AM F2Ir dimer with Pz 2nd2
DCM, 180

F2Ir dimer with Pz 2nd2 #87-88 RT: 2.38-2.41 AV: 2 NL: 3.00E8
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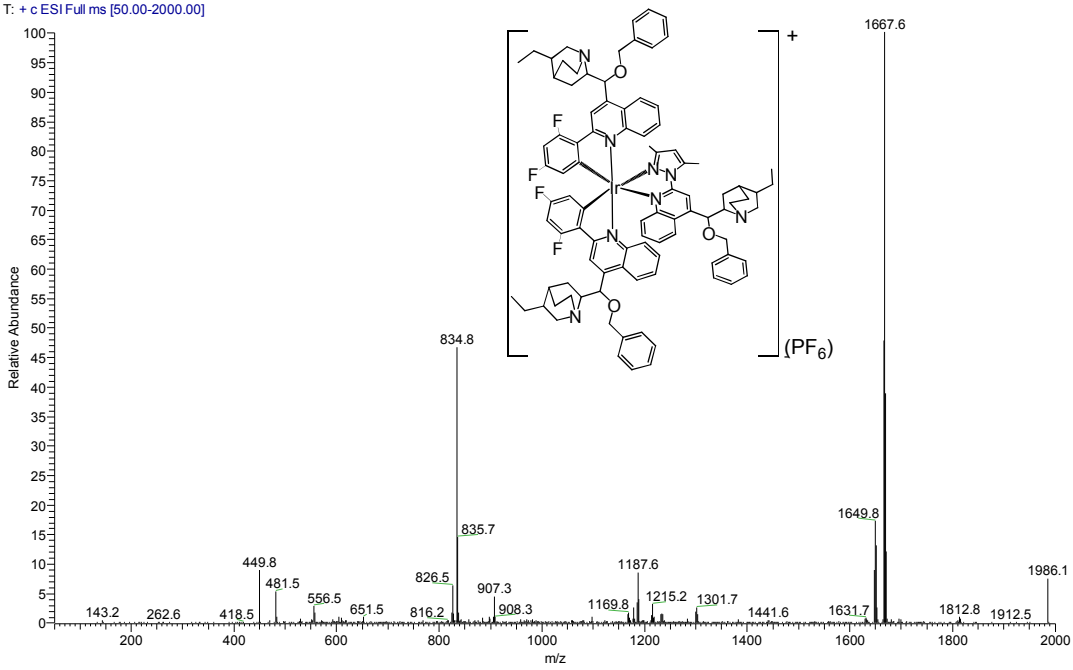
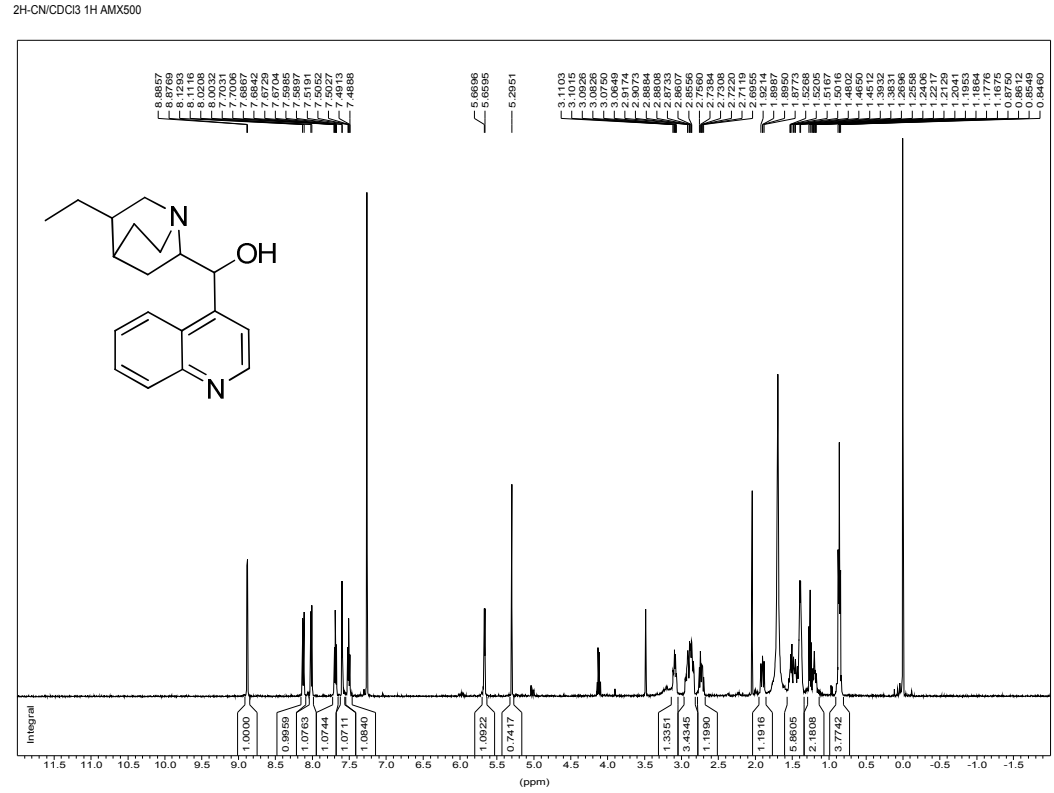
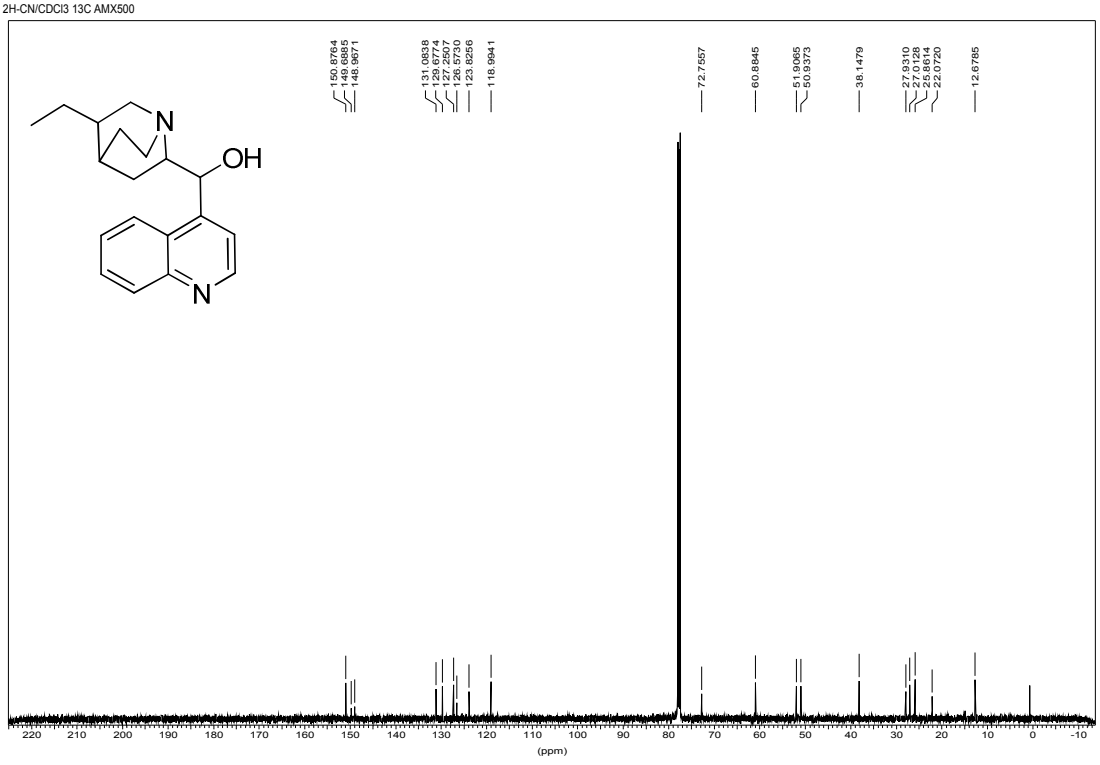


^{1}H, ^{13}C, ^{19}F NMR spectra

^{1}H NMR, 500 MHz, $CDCl_3$

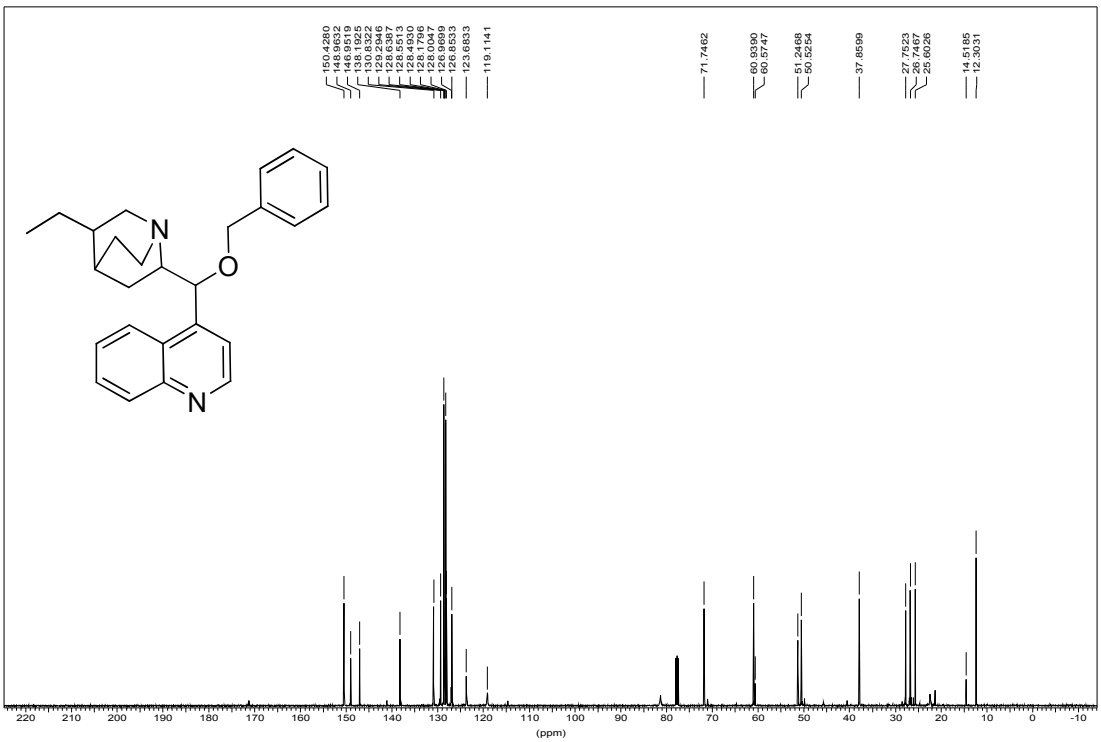


^{13}C NMR, 125 MHz, $CDCl_3$

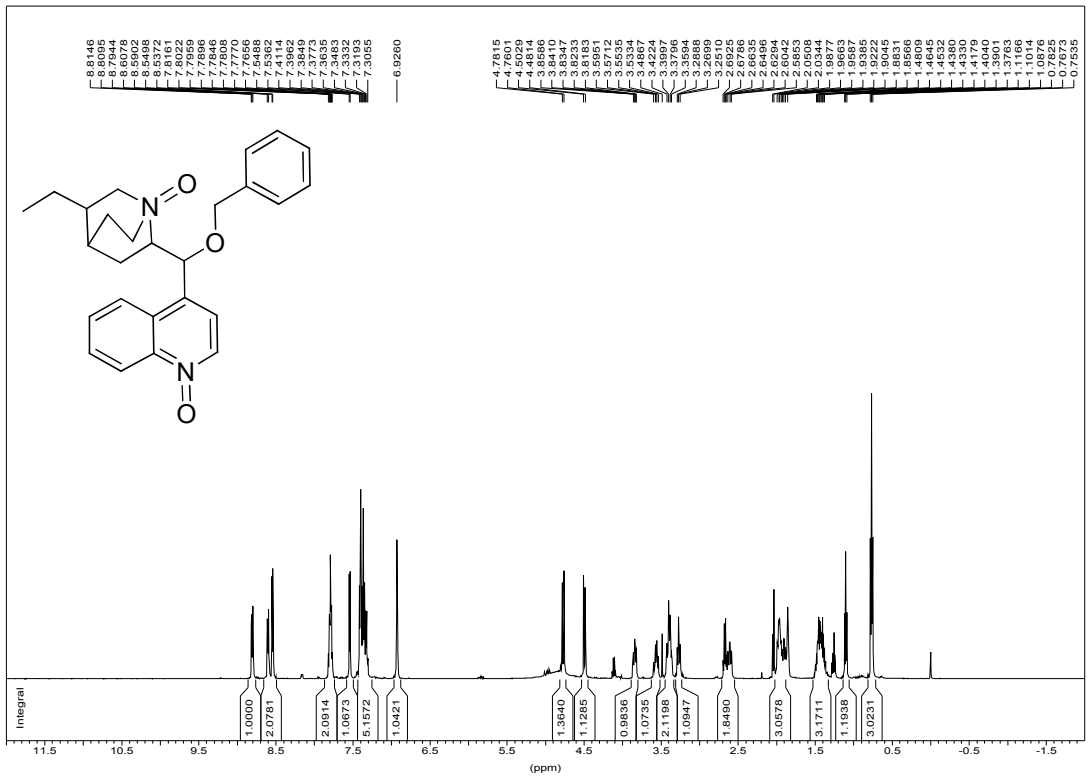


^{1}H NMR, 500 MHz, $CDCl_3$

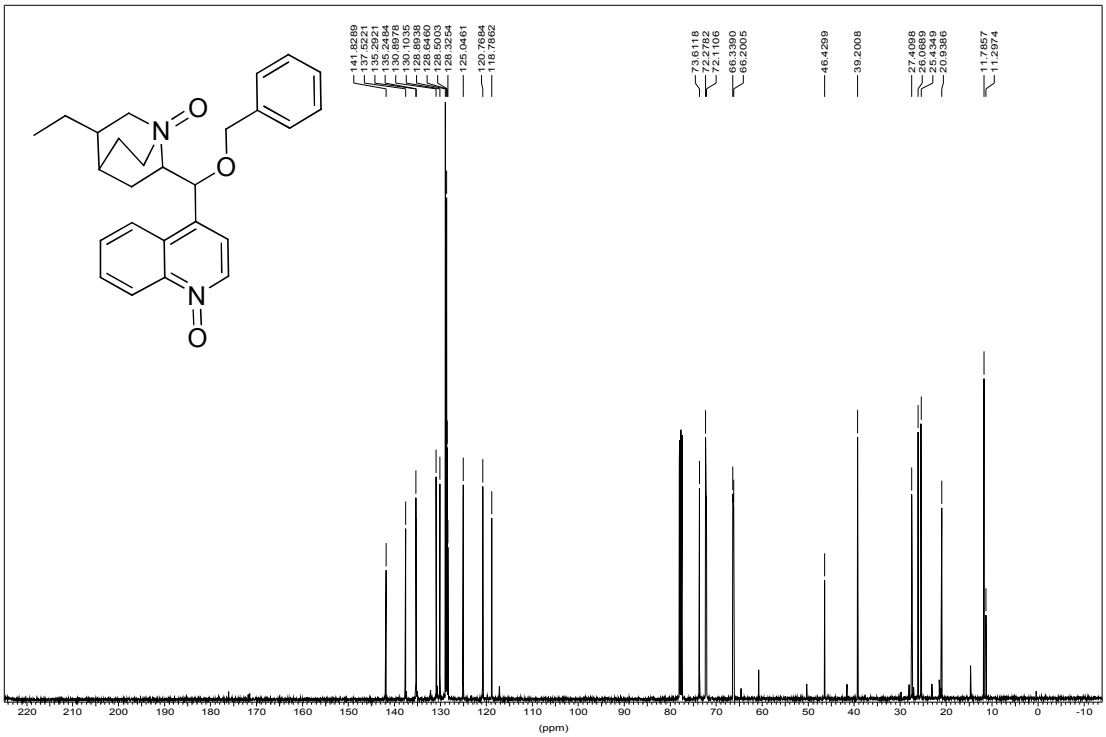
^{13}C NMR, 125 MHz, $CDCl_3$



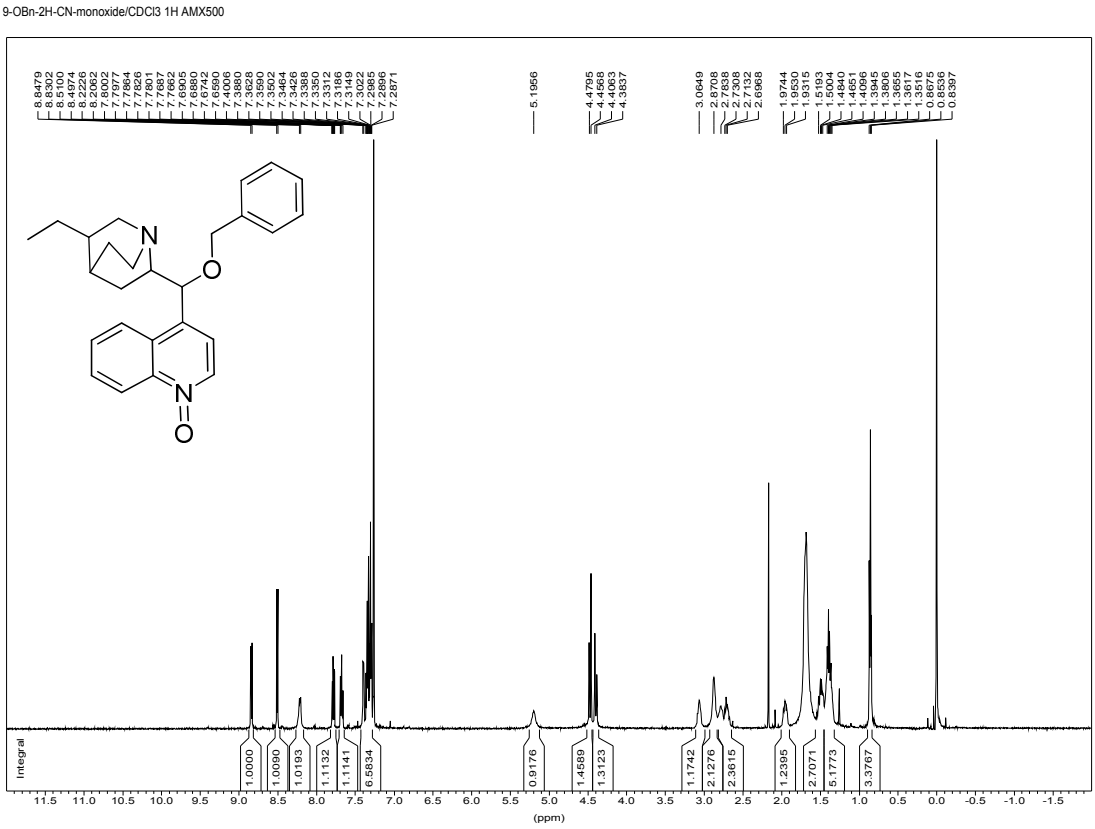
^{1}H NMR, 500 MHz, $CDCl_3$



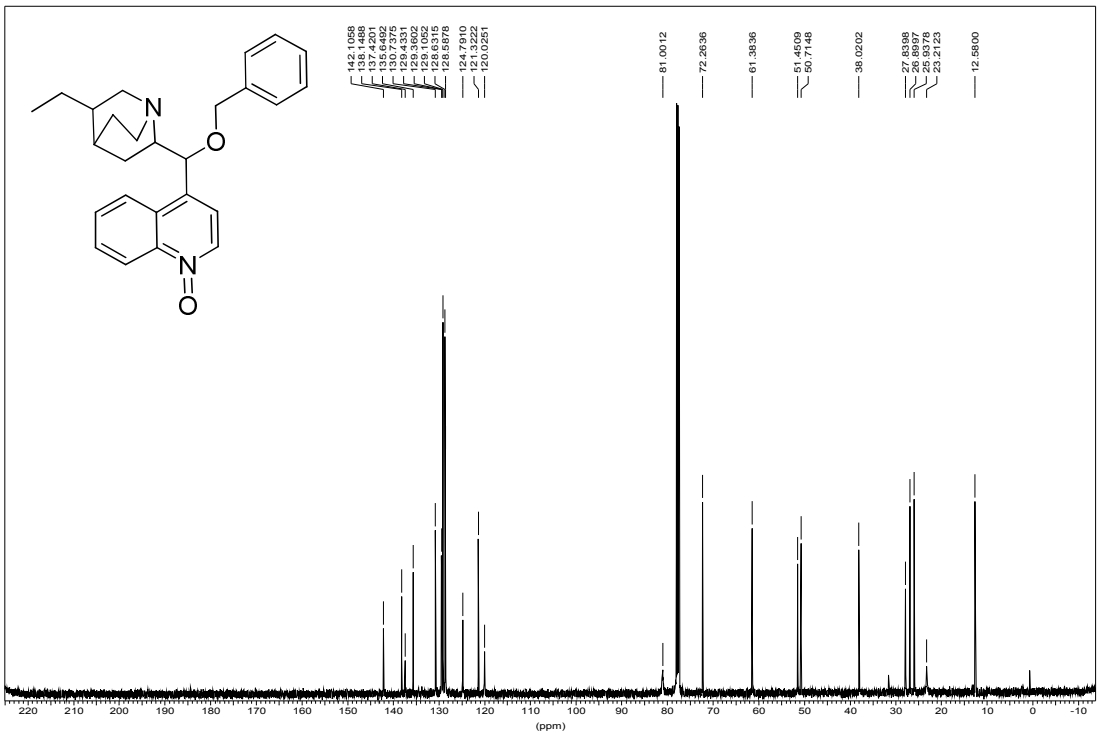
^{13}C NMR, 125 MHz, $CDCl_3$



^{1}H NMR, 500 MHz, $CDCl_3$

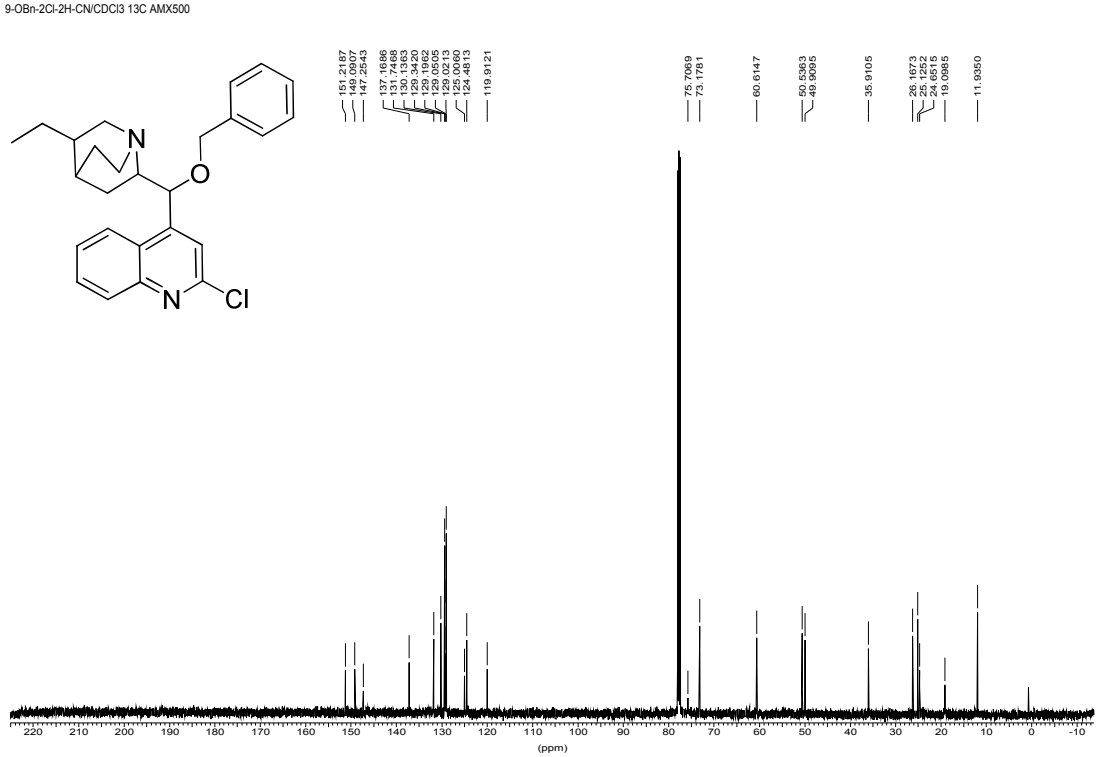


^{13}C NMR, 125 MHz, $CDCl_3$

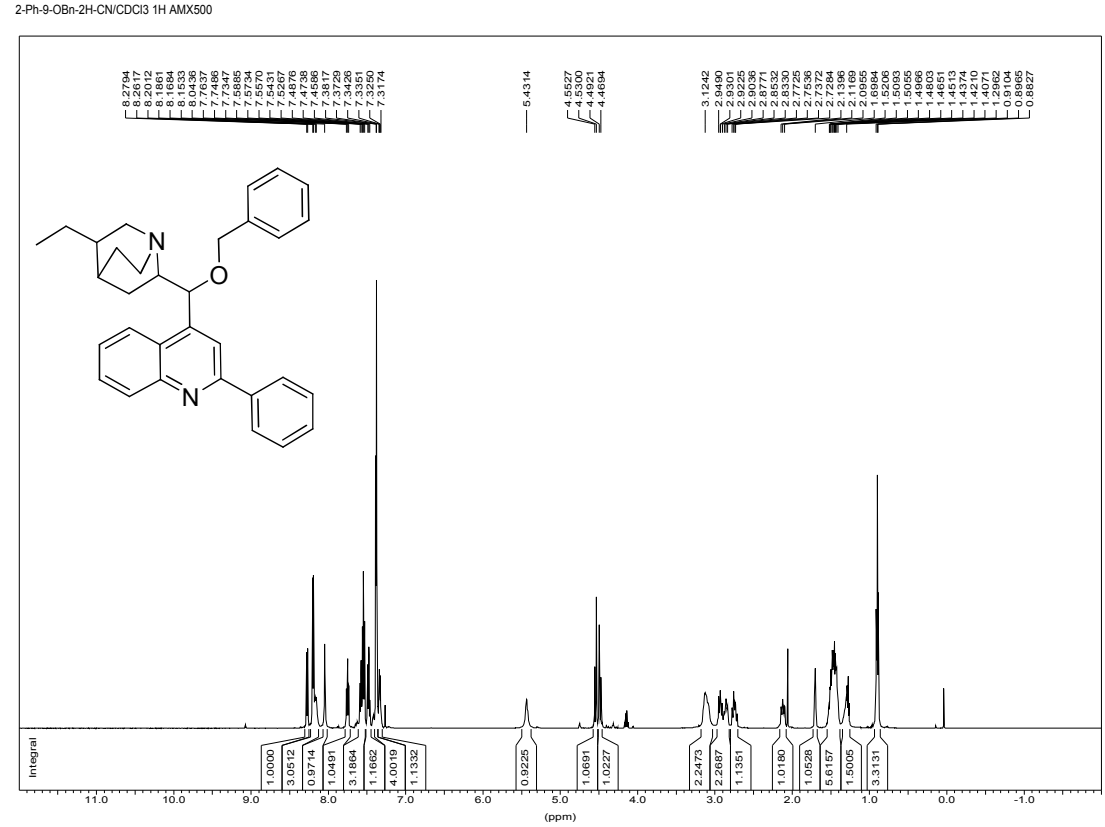


^{1}H NMR, 500 MHz, $CDCl_3$

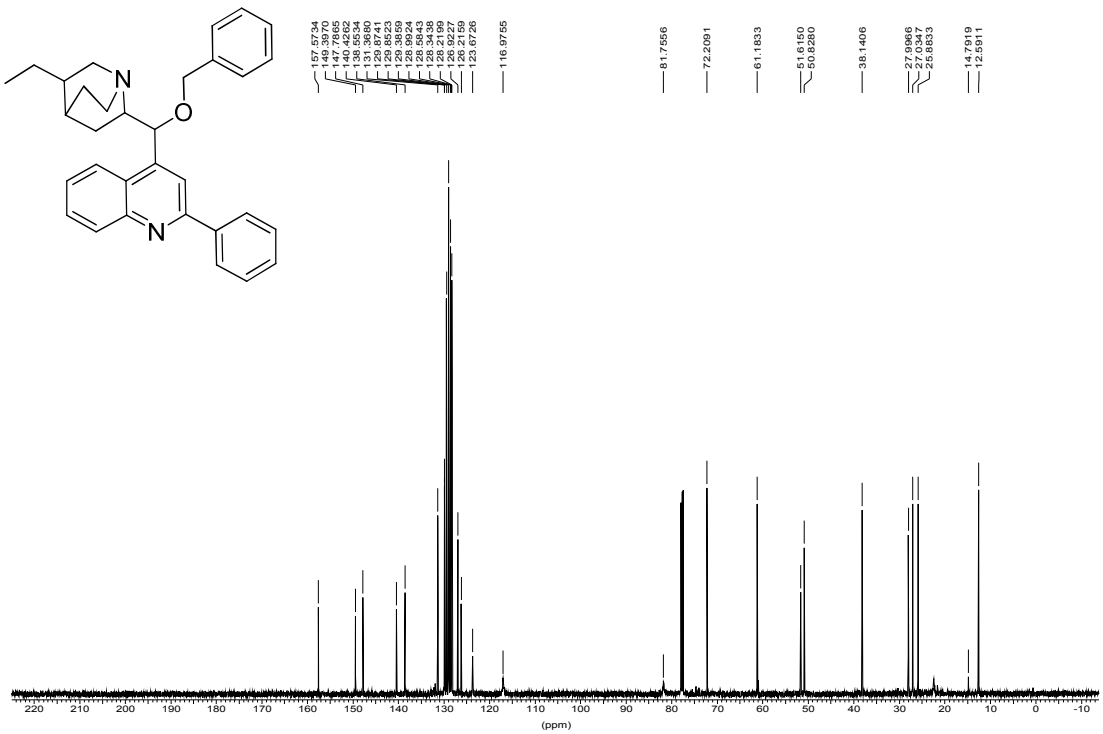
^{13}C NMR, 125 MHz, $CDCl_3$



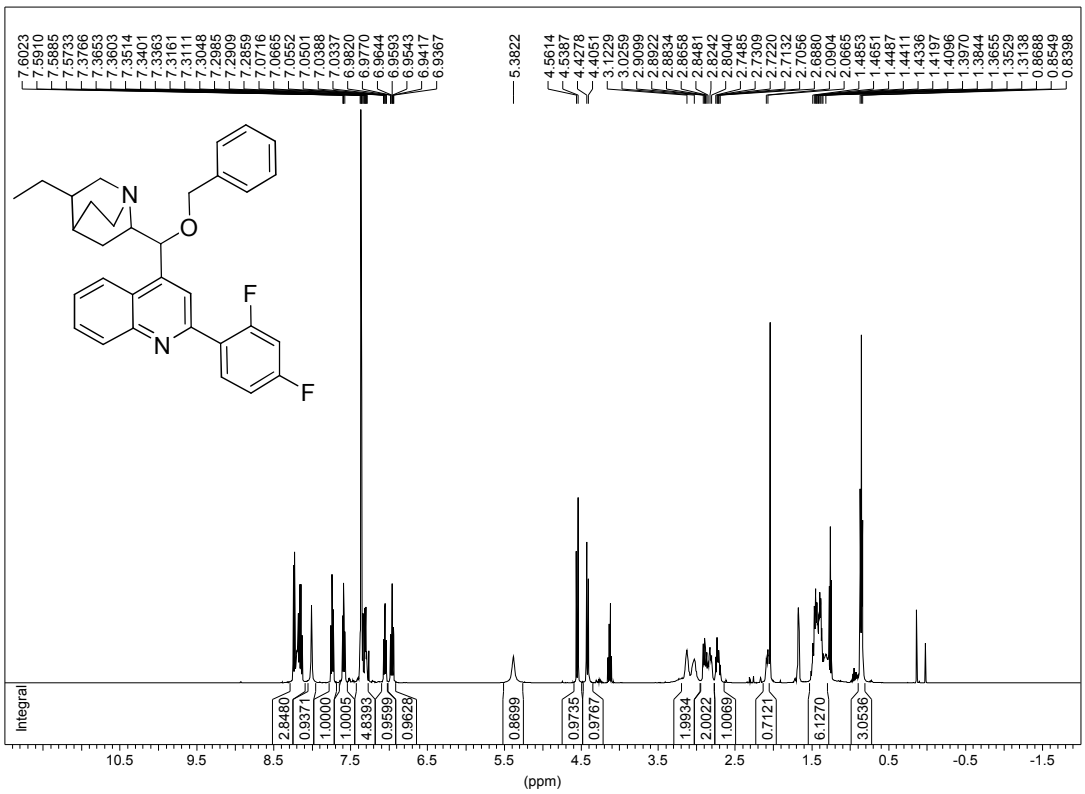
^{1}H NMR, 500 MHz, $CDCl_3$



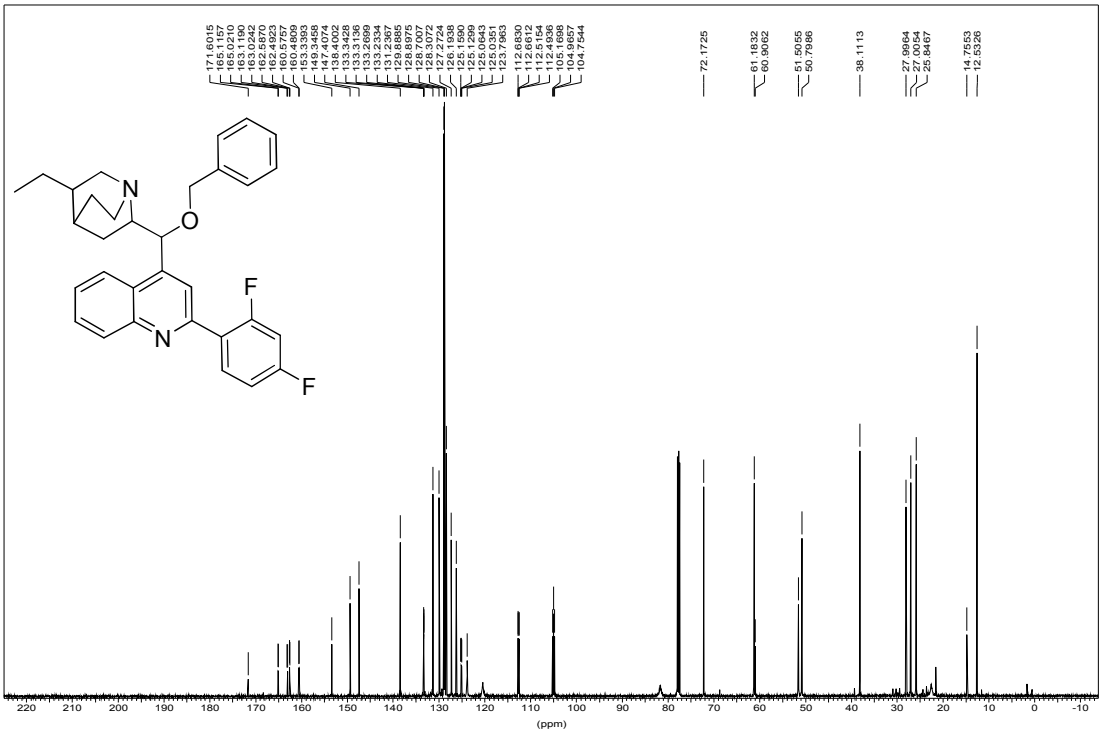
^{13}C NMR, 125 MHz, $CDCl_3$



^{1}H NMR, 500 MHz, $CDCl_3$

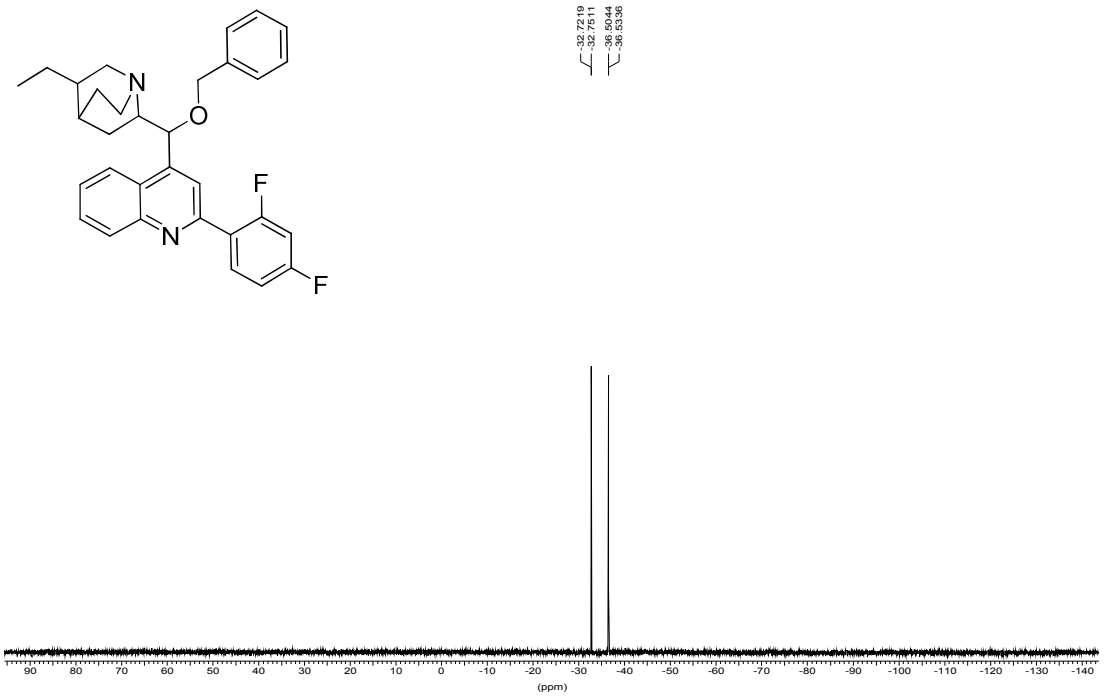


^{13}C NMR, 125 MHz, $CDCl_3$

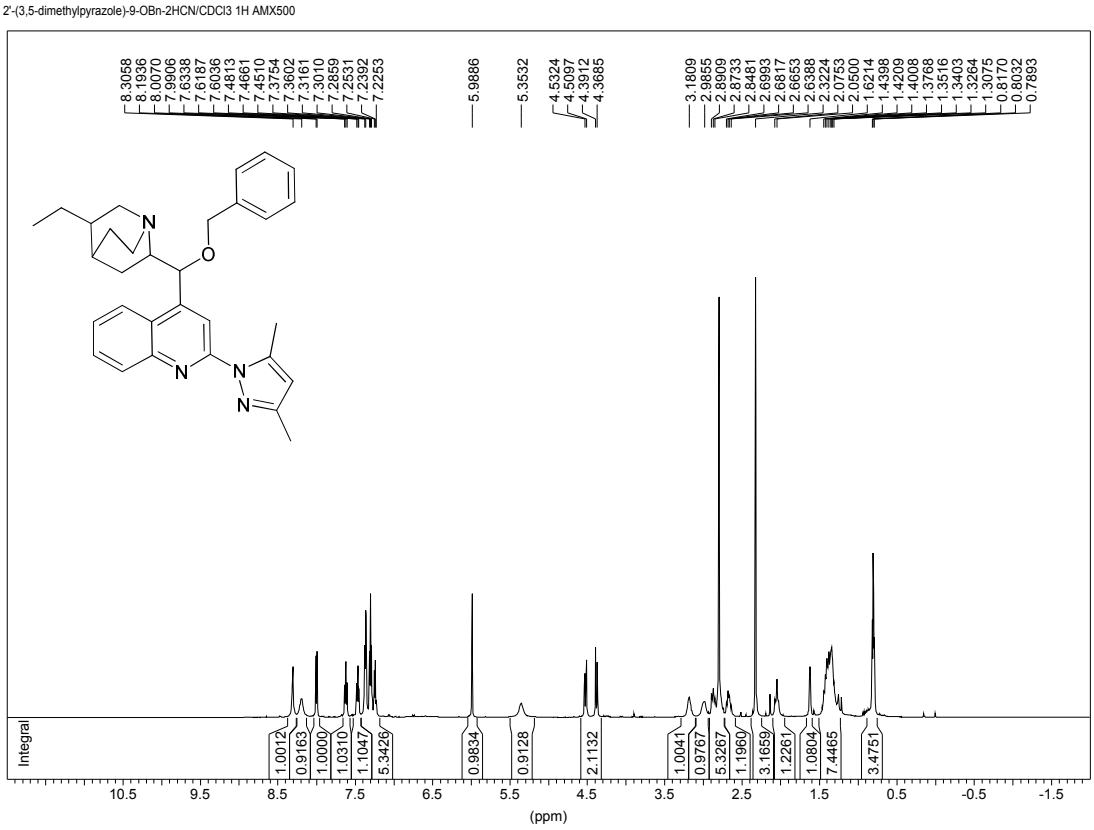


^{19}F NMR, 282 MHz, $CDCl_3$

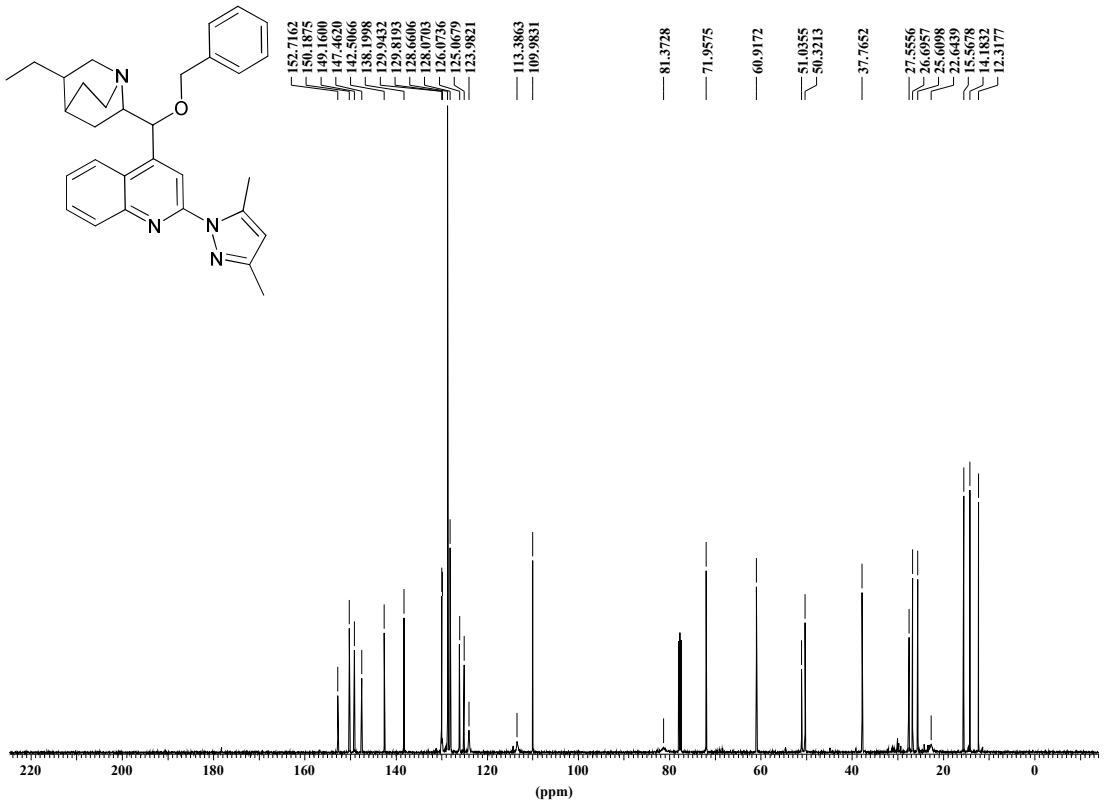
9-O-benzyl-2-(2,4-difluorophenyl)-dihydrocinchonine/CDCl3 F19 decoupled



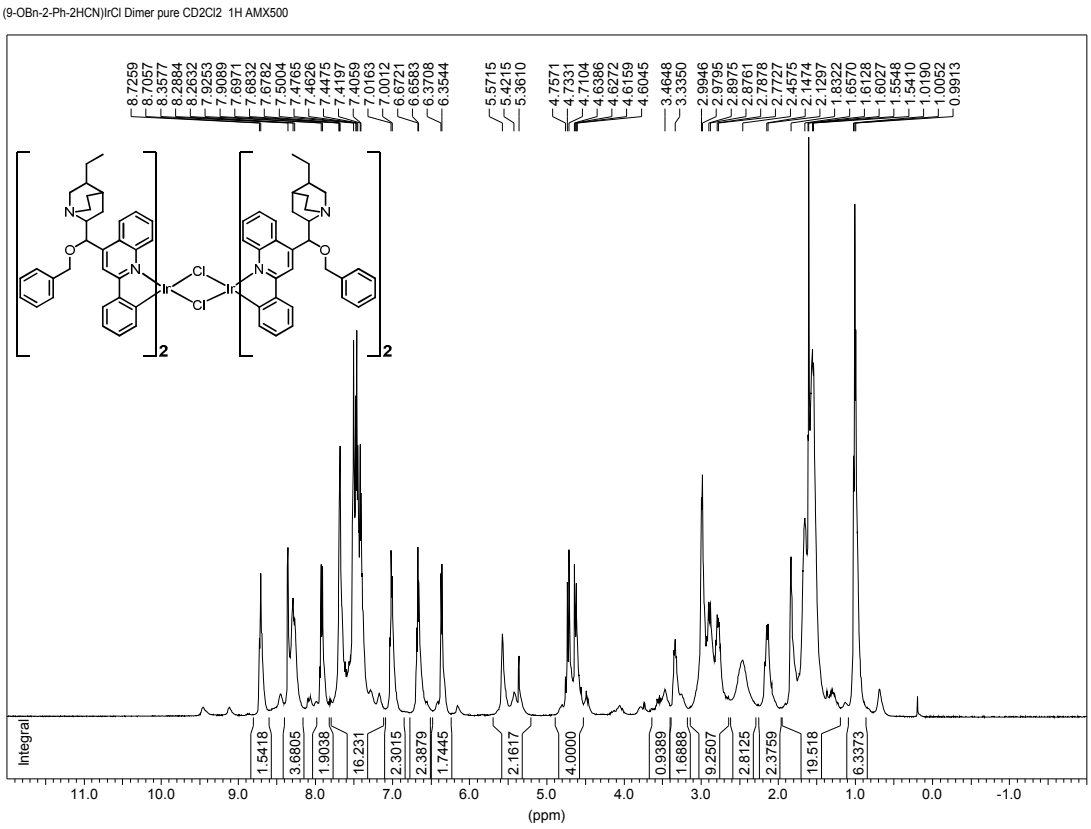
^{1}H NMR, 500 MHz, $CDCl_3$



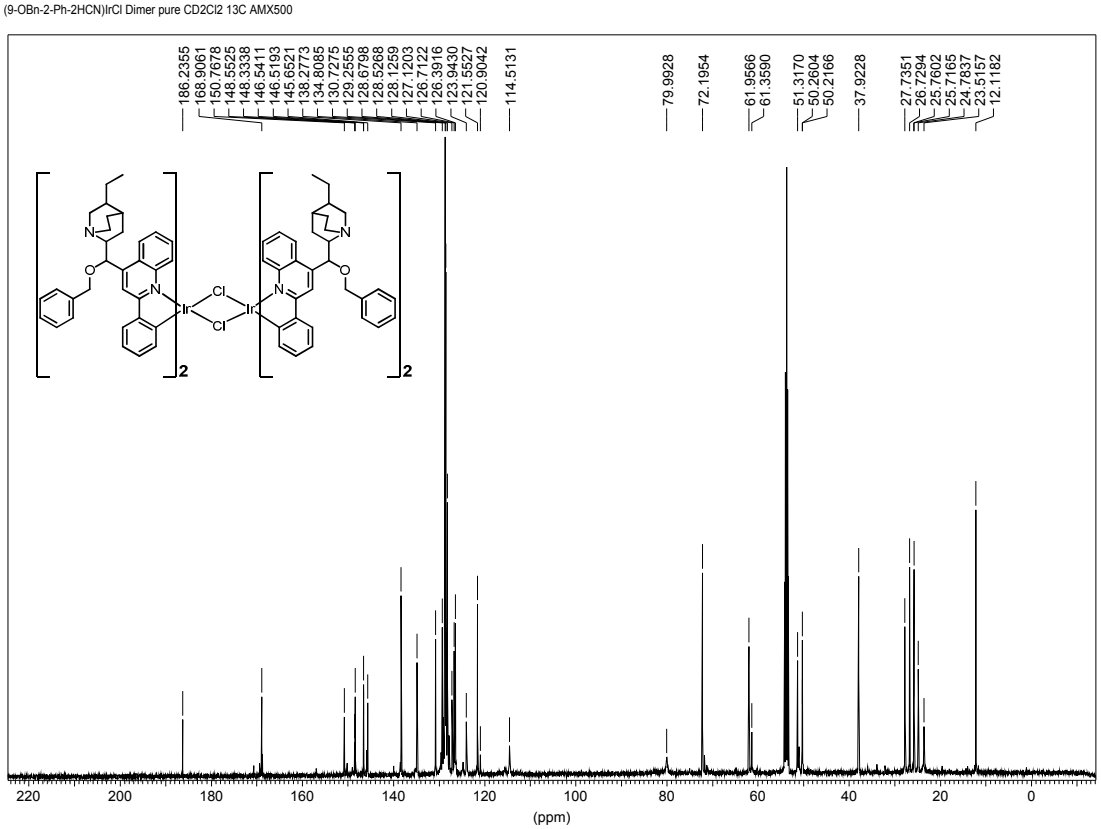
^{13}C NMR, 125 MHz, $CDCl_3$



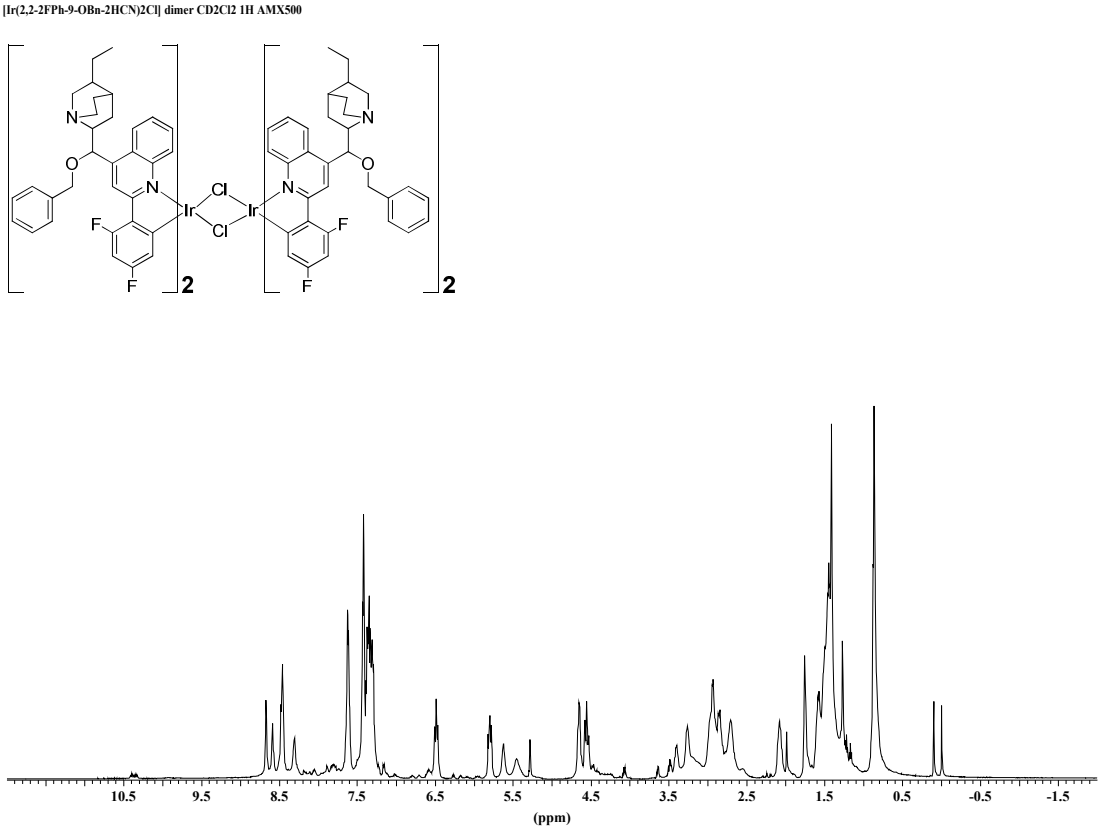
^{1}H NMR, 500 MHz, CD_2Cl_2



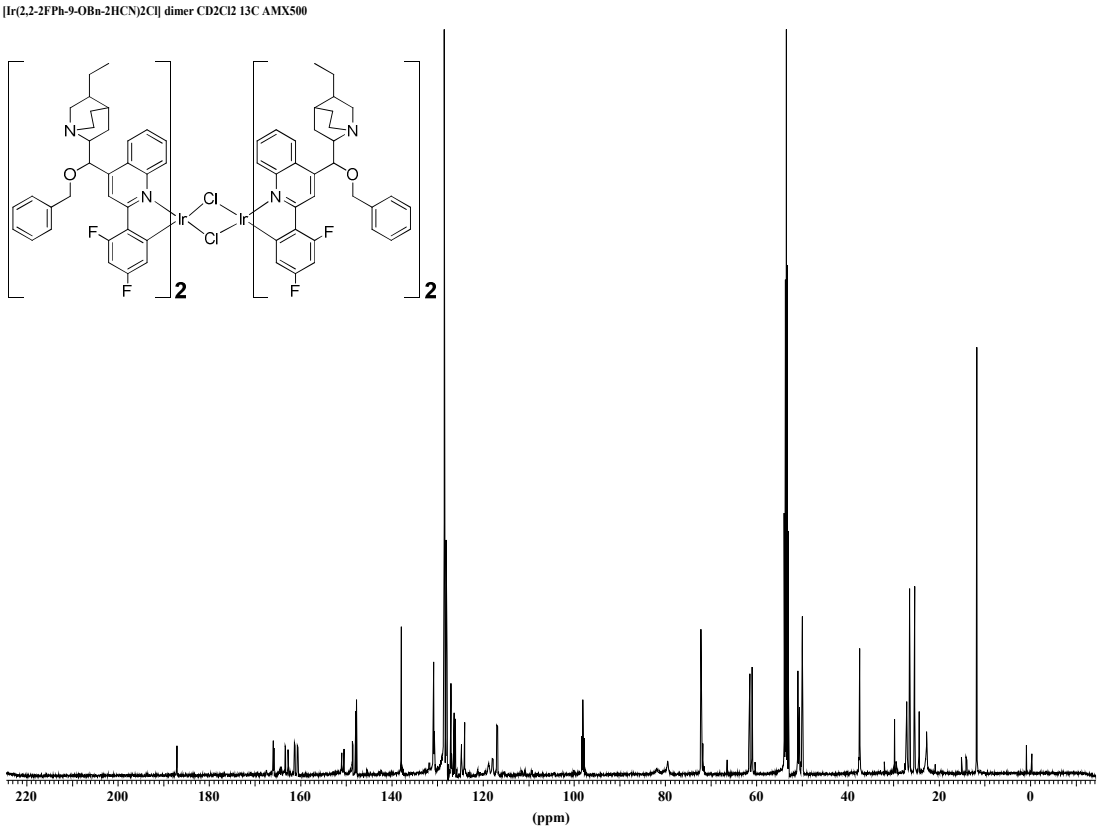
^{13}C NMR, 125 MHz, CD_2Cl_2



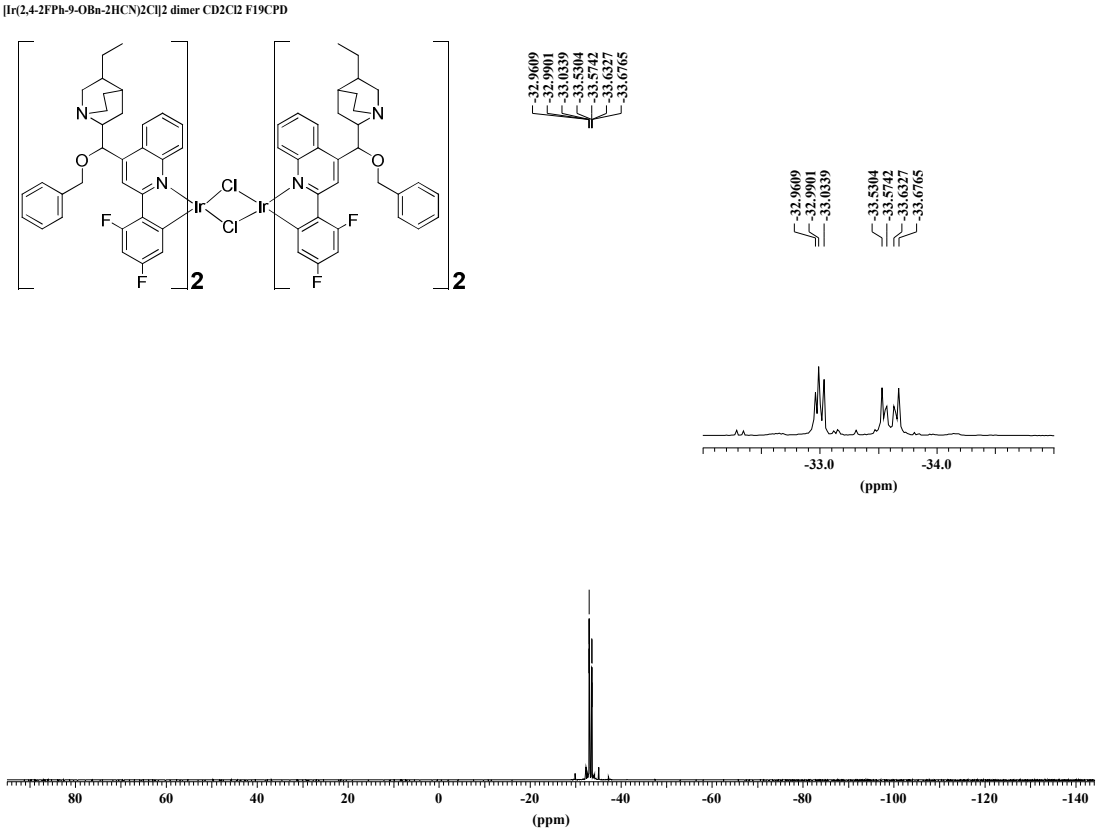
^{1}H NMR, 500 MHz, CD_2Cl_2



^{13}C NMR, 125 MHz, CD_2Cl_2

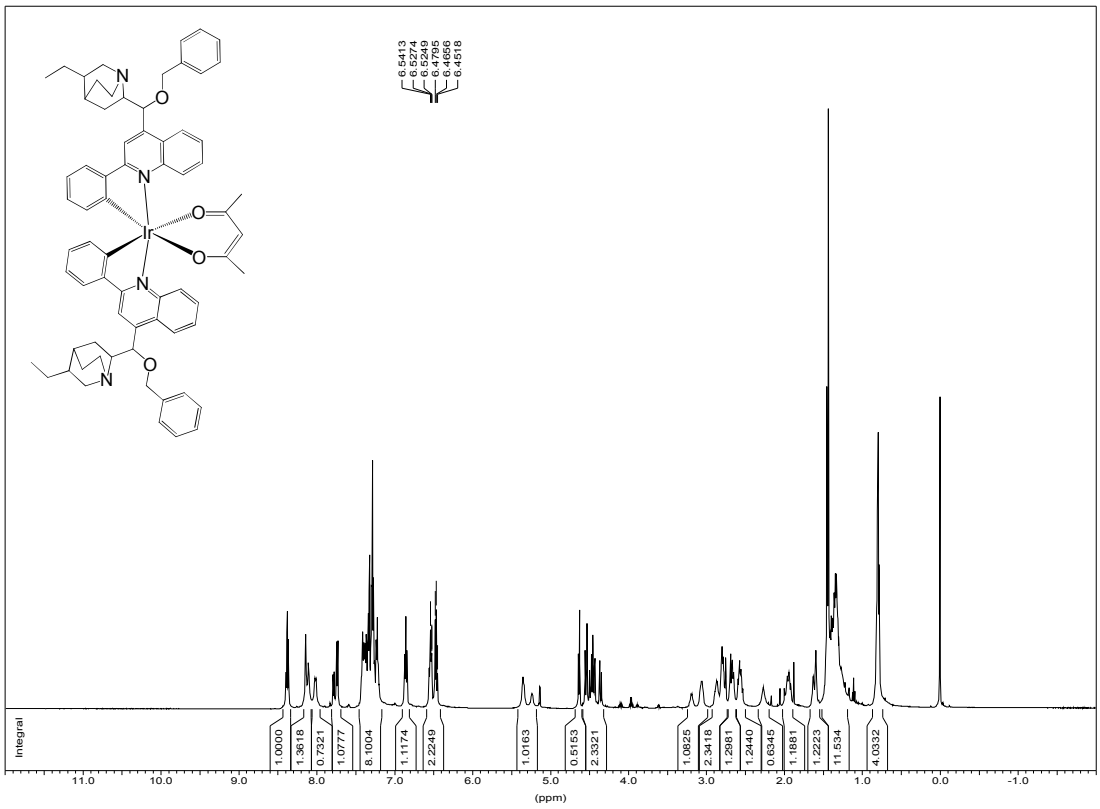


^{19}F NMR, 282 MHz, CD_2Cl_2



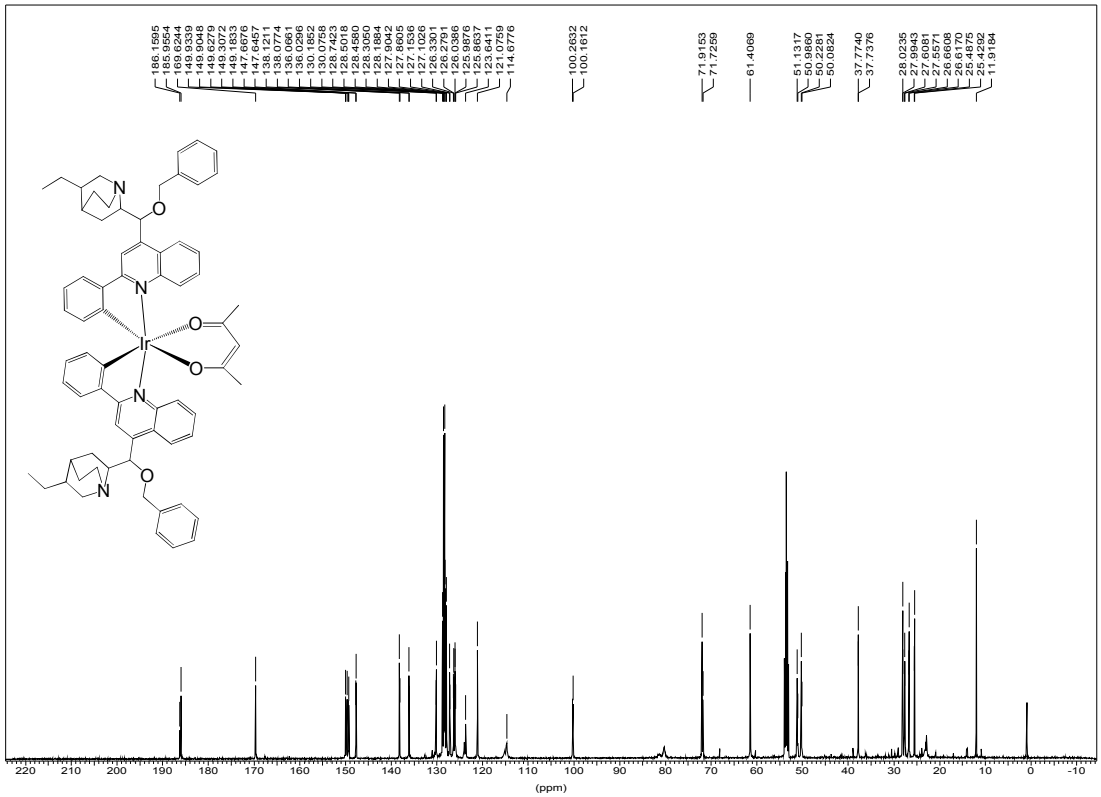
^{1}H NMR, 500 MHz, CD_2Cl_2

WH-1-011 Ir(9-OBn-2-Ph) dimer 3rd with acacH /CD2Cl2 1H AMX500

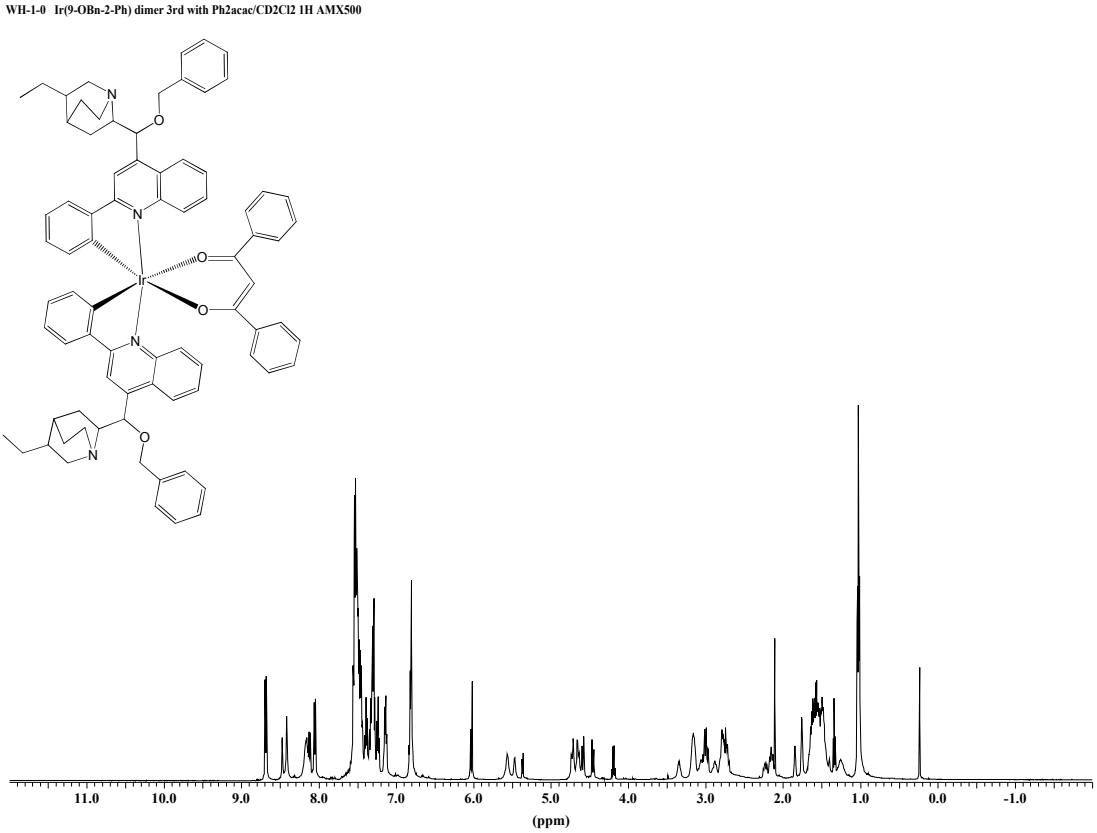


^{13}C NMR, 125 MHz, CD_2Cl_2

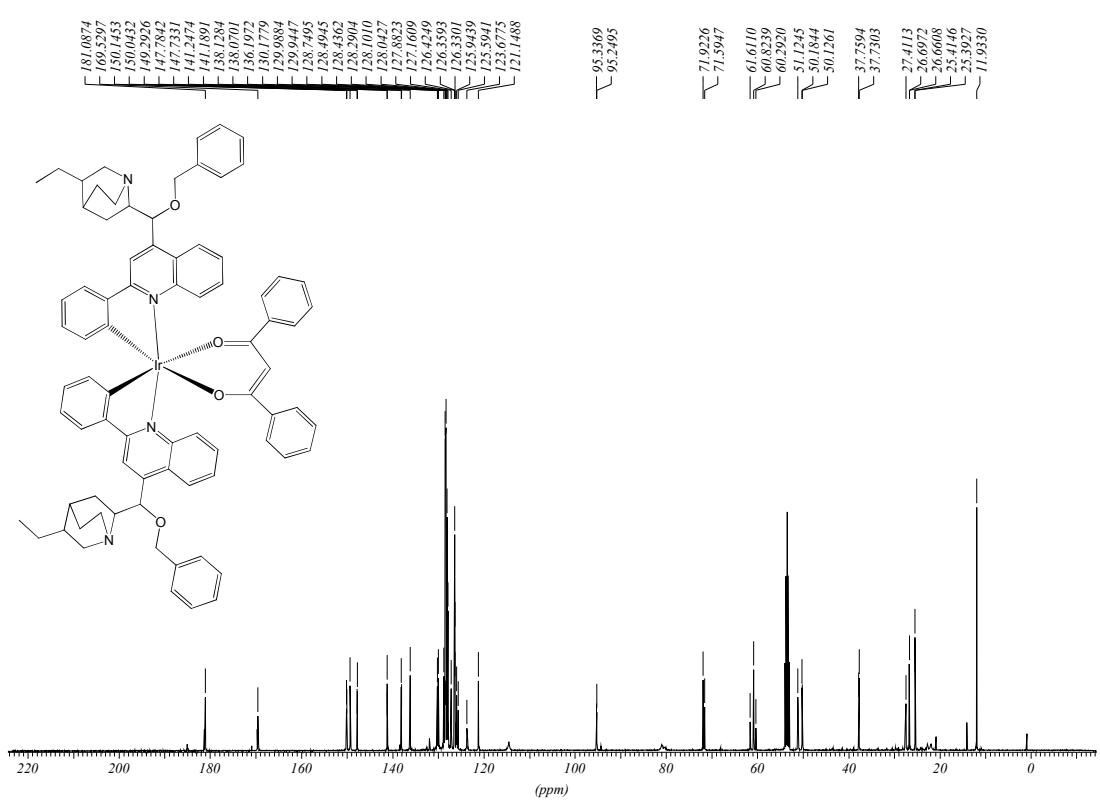
WH-1-011 Ir(9-OBn-2-Ph) dimer 3rd with acacH /CD2Cl2 13C AMX500



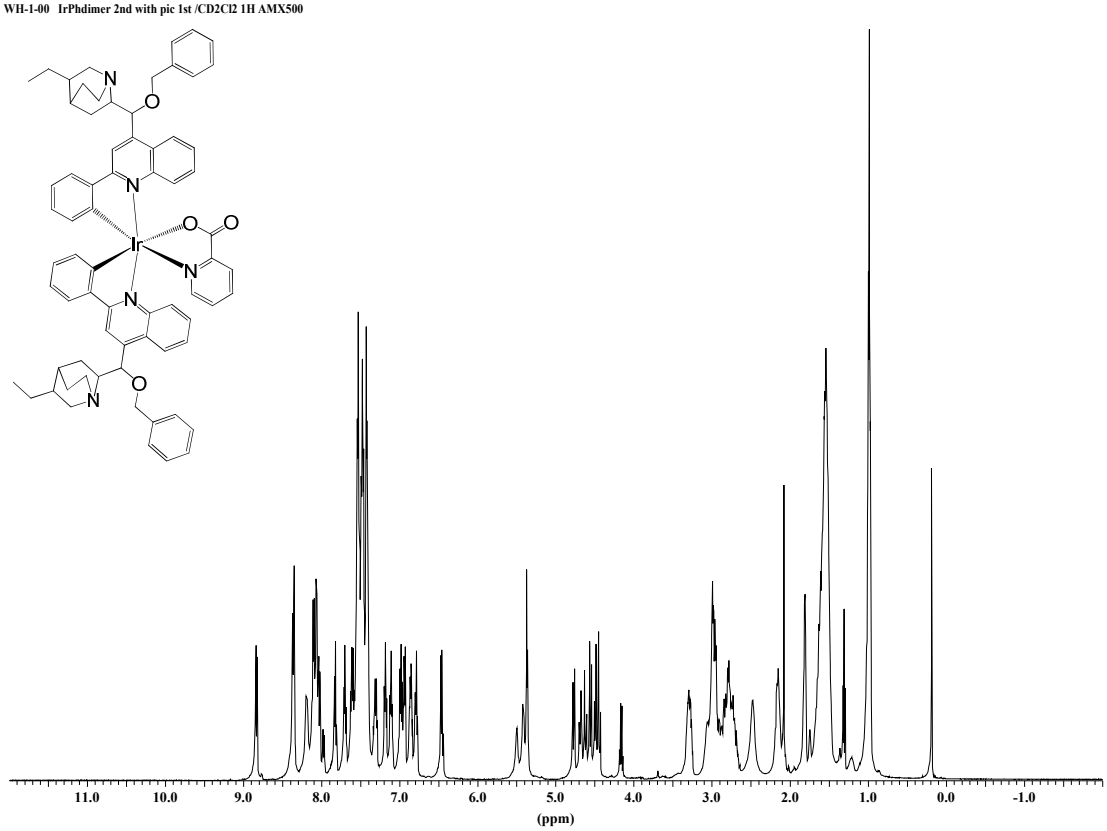
^{1}H NMR, 500 MHz, CD_2Cl_2



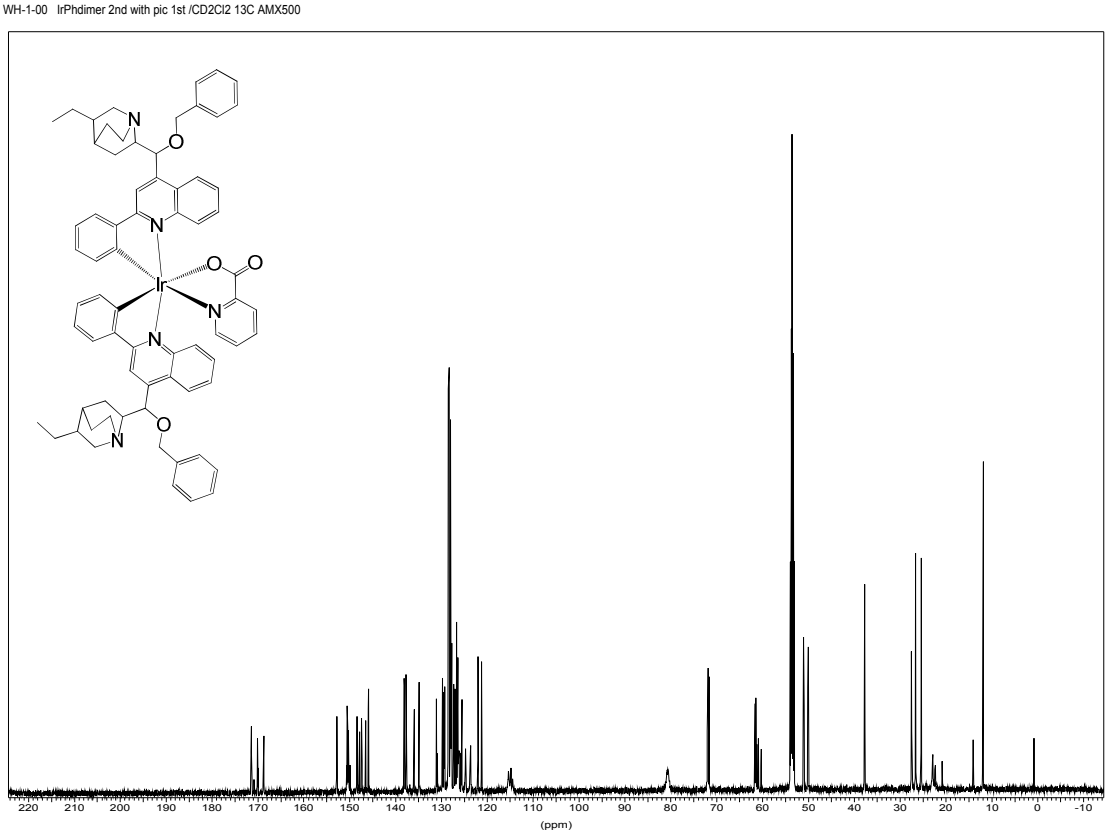
^{13}C NMR, 125 MHz, CD_2Cl_2



^{1}H NMR, 500 MHz, CD_2Cl_2

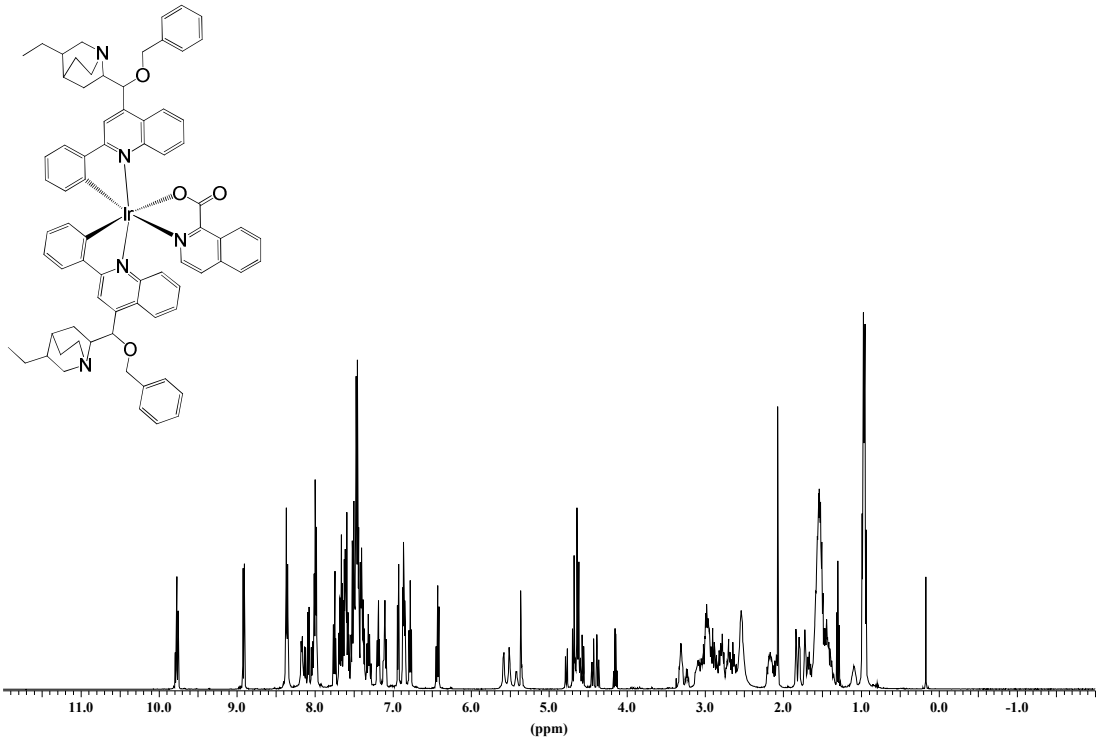


^{13}C NMR, 125 MHz, CD_2Cl_2



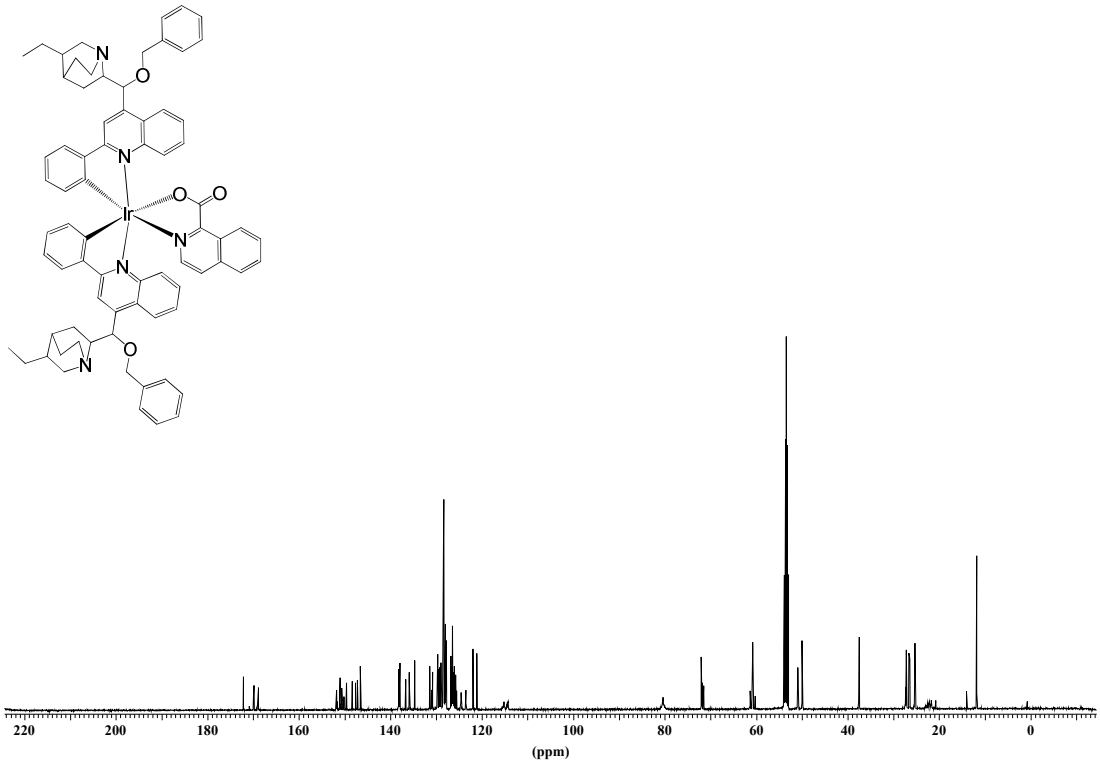
^{1}H NMR, 500 MHz, CD_2Cl_2

[Ir(9-OBn-2Ph2HCN)2(isoq)] without base CD2Cl2 1H AMX500

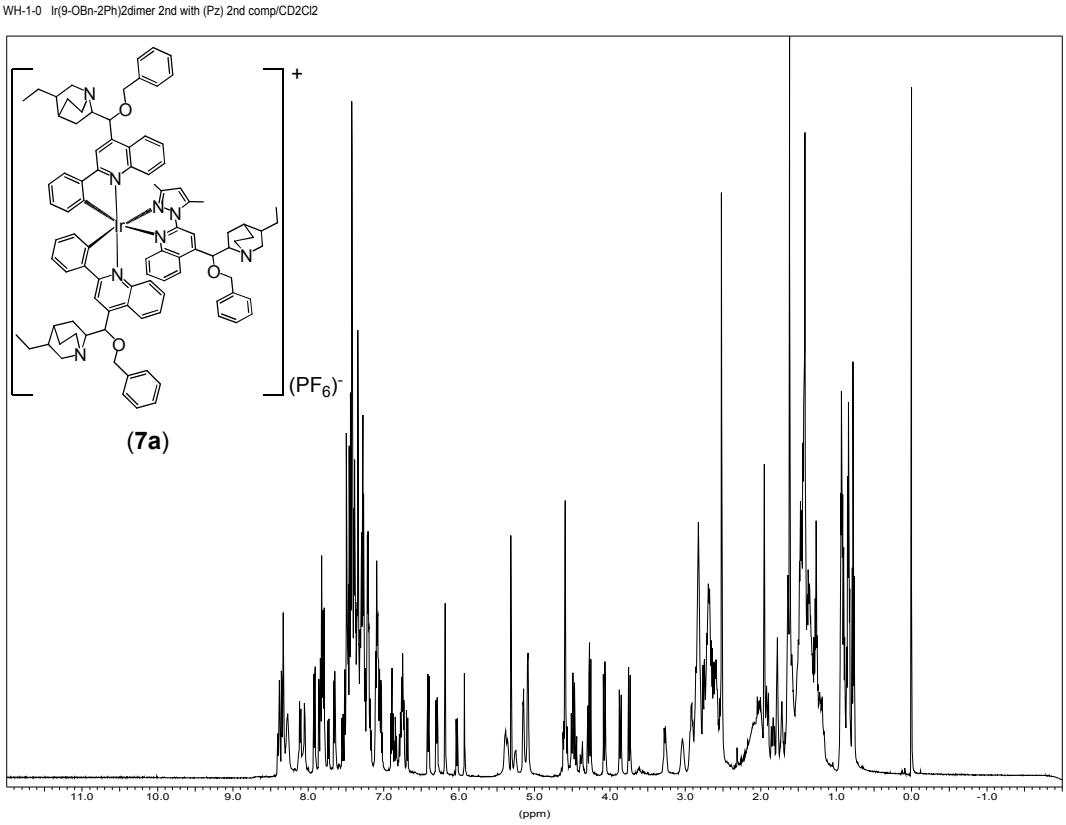


^{13}C NMR, 125 MHz, CD_2Cl_2

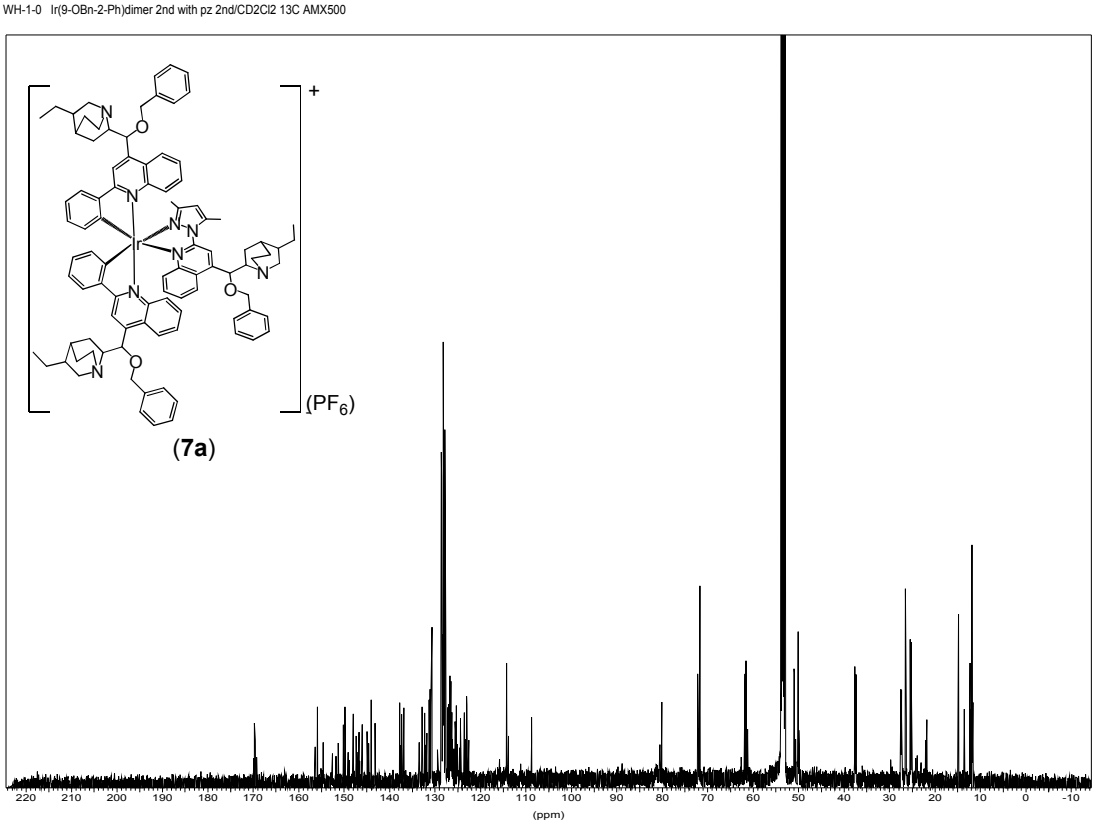
[Ir(9-OBn-2Ph2HCN)2(isoq)] without base CD2Cl2 13C AMX500



^{1}H NMR, 500 MHz, CD_2Cl_2

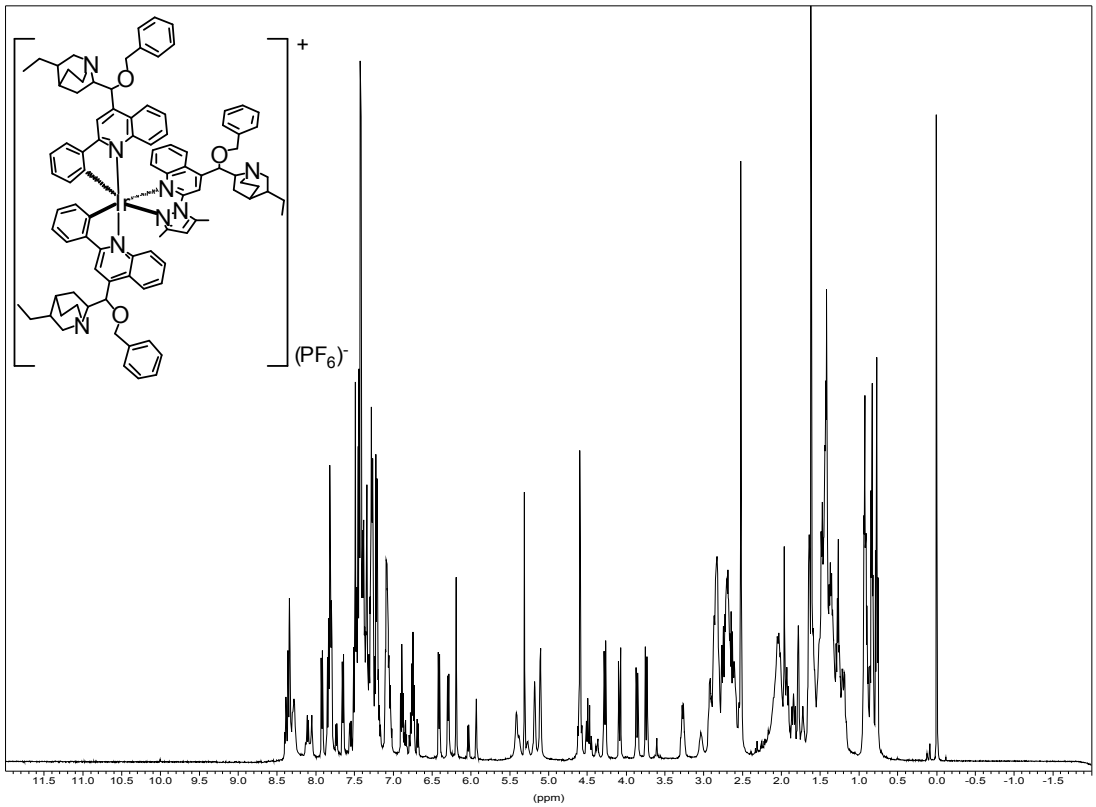


^{13}C NMR, 125 MHz, CD_2Cl_2



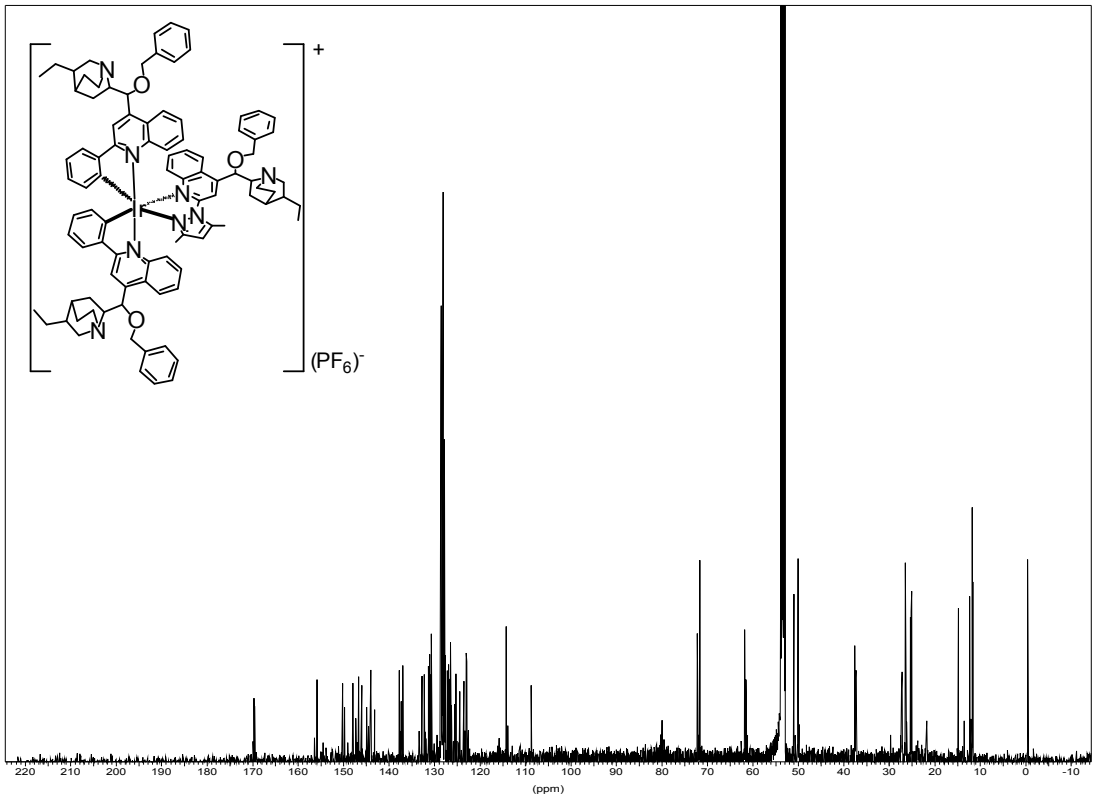
^{1}H NMR, 500 MHz, CD_2Cl_2

WH-1-0 Ir(9-OBn-2Ph)2dimer 2nd with (Pz) 3rd comp/CD2Cl2

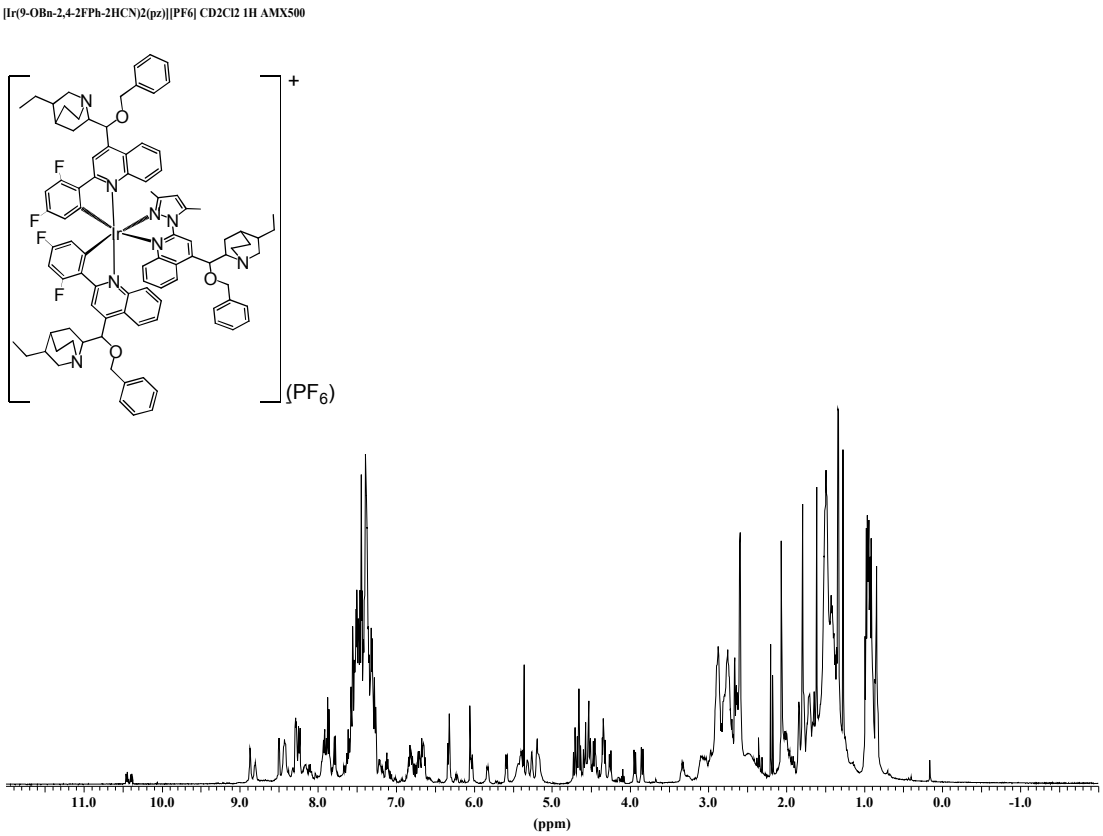


^{13}C NMR, 125 MHz, CD_2Cl_2

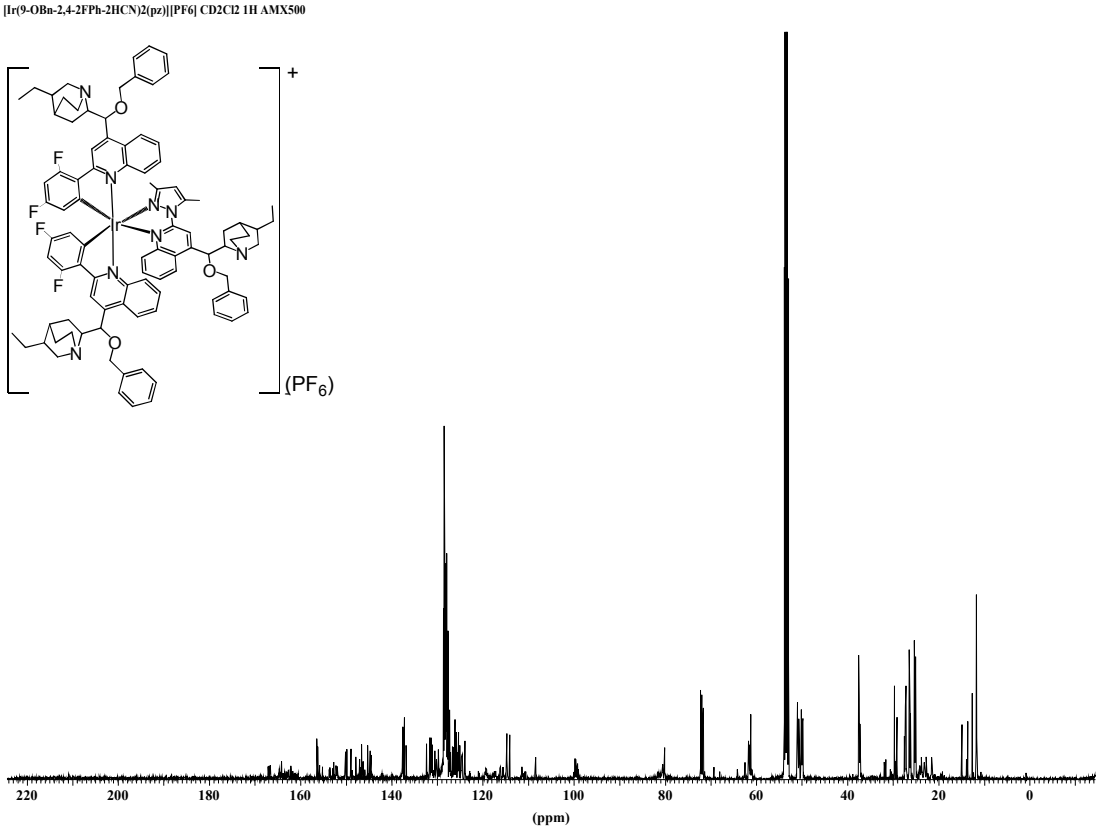
WH-1-0 Ir(9-OBn-2-Ph)dimer 2nd with pz 3rd/CD2Cl2 13C AMX500



^{1}H NMR, 500 MHz, CD_2Cl_2



^{13}C NMR, 125 MHz, CD_2Cl_2



^{19}F NMR, 282 MHz, CD_2Cl_2