Supporting Information

Well-defined Cu(I) complexes based on [N,P]-pyrrole ligands catalyzed a highly *endo*-selective 1,3-dipolar cycloaddition

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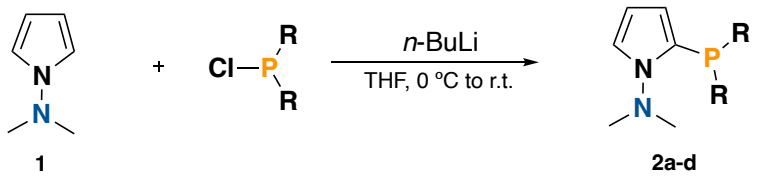
1. General Considerations

All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Anhydrous THF was obtained by distillation under an inert atmosphere over sodium and benzophenone. Column chromatography was performed using 70–230 mesh silica gel. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by IR spectra, recorded on a Perkin-Elmer 283B or 1420 spectrophotometer, by means of film and KBr techniques, and all data are expressed in wave numbers (cm^{-1}). Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. NMR spectra were measured with a JEOL Eclipse +300 and a Varian Gemini (200 MHz), using $CDCl_3$ as solvent. Chemical shifts are in ppm (δ), relative to TMS. The MS-FAB$^+$ and MS-EI spectra were obtained on a JEOL SX 102A, the values of the signals are expressed in mass/charge units (m/z), followed by the relative intensity with reference to a 100% base peak.

2. General synthesis of ligand bidentate [N,P] based on pyrrole.

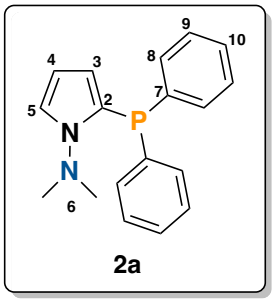
In a Schlenk flask, a solution of N,N-dimethyl-1H-pyrrol-1-amine (8.3 mmol, 1 equiv) in dry THF (15 ml) was prepared under a nitrogen atmosphere. The reaction mixture was cooled to -78 °C, and then n-butyl lithium (9.9 mmol, 1.2 equivalents of 2.5 M solution in n-hexane) was slowly added dropwise using a syringe. The temperature of the mixture was gradually raised to room temperature. After reaching this temperature, the reaction mixture was cooled to 0 °C, followed by the addition of various chlorophosphines (8.3 mmol, 1 equiv), and it was stirred at room temperature for 2 hours. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography using different hexane/ethyl acetate mixtures as eluents. (**Scheme S1**).[1]



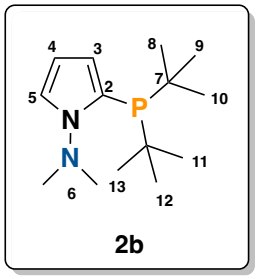
Scheme S1. General synthesis of bidentate [N,P] ligands based on pyrrole **2a-d**.

3. Characterization Data of ligand bidentate [N,P] based on pyrrole.

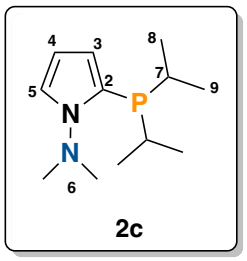
[1] Suarez-Meneses, J.V.; Oukhrib, A.; Gouygou, M.; Urrutigoïty, M.; Daran, J.-C.; Cordero-Vargas, A.; Ortega-Alfaro, M.C.; López-Cortés, J.G. *Dalton Trans*., **2016**, *23*, 9621–9630.



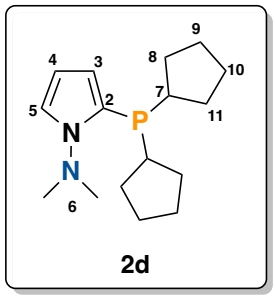
2-(diphenylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (2a). White powder, mp 106-108 ºC (90%).[1]H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.32 (*m*, 10H, H8, H9, H10); 7.16 (*m*, 1H, H5); 6.19 (*t*, J_{H-H}= 3.3 Hz, 1H, H4); 5.59 (*d*, J_{H-H}=2.66 Hz, 1H, H3); 2.66 (*s*, 6H, H6). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 137.5, 137.4 (*d*, J_{C-P}=.8.3 Hz) (C7); 133.5, 133.7 (*d*, J_{C-P}=20.1 Hz) (C8); 128.5 (C10); 128.2, 128.3 (*d*, J_{C-P}=16.7 Hz) (C9); 128.6, 116.5 (C5); 113.3 (C4); 108.4 (C3); 47.8 (C6). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) -29.2.



2-(di-*tert*-butylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (2b). Colorless oil, (92%). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.17 (*m*, 1H, H5); 6.38-6.36 (*dd*, J_{H-H}= 1.63 Hz, J_{H-H}= 3.95 Hz, 1H, H4); 6.25-6.23 (*t*, J_{H-H}= 2.91 Hz, J_{H-H}= 6.84 Hz, 1H, H3); 2.83 (*s*, 6H, H6); 1.21 (*s*, 9H, H8, H9, H10); 1.17 (*s*, 9H, H11, H12, H13). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm)127.0 (C2); 115.5 (C5); 113.3 (C3); 107.3 (C4); 48.3 (C6); 32.4-32.2 (*d*, J_{C-P}= 16.9 Hz, C7); 30.4-30.2 (*d*, J_{C-P}= 15.1 Hz, C8, C9, C10). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) 1.5.



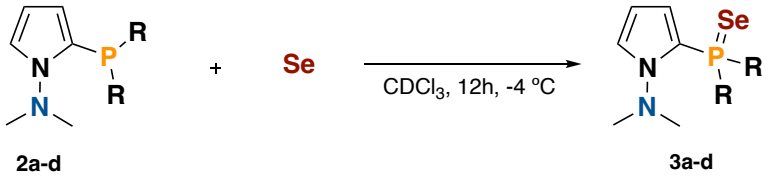
2-(diisopropylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (2c). Colorless oil (86 %). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.11 (*m*, 1H, H5); 6.22 (*t*, 1H, H4, J_{H-H}= 4.0 Hz, *J*=2.7 Hz); 6.13 (*m*, 1H, H3); 2.82 (*s*, 6H, H6); 2.05 (*hept*, 2H, H7, J_{H-H}= 6.9 Hz); 1.12 (*dd*, 6H, H8, J_{H-H}= 6.9 Hz, J_{H-H}= 8.1 Hz); 1.01 (*dd*, 6H, H9, J_{H-H}=5.1 Hz, J_{H-H}= 6.9 Hz). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 126.4 (C2); 115.8 (C5); 112.3 (C3); 107.6 (C4); 48.1 (C6); 23.7, 23.6 (*d*, J_{C-P}= 7.7 Hz, C7); 20.2, 20.0 (*d*, J_{C-P}= 18.1 Hz, C8); 19.3, 19.2 (*d*, J_{C-P}= 9.0 Hz). ^{31}P NMR (50 MHz, $CDCl_3$) δ -17.6.



2-(dicyclopentylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (2d). Colorless oil (60 %). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.06 (*m*, 1H, H5); 6.17 (*t*, J_{H-H} = 2.9 Hz, J_{H-H} = 9.2 Hz 1H, H3); 6.16 (s, 1H, H4); 2.82 (*s*, 6H, H6); 2.26–2.24 (*m*, 2H, H7); 1.93–1.90 (*m*, 2H, H8, 11); 1.67–1.24 (*m*, 14H, H,8,9,10,11). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 1129.0, 28.9 (d, J_{C-P} = 5.9 Hz, C2); 115.5 (C5); 112.3 (C3); 107.6 (C4); 48.1 (C6); 37.0-36.9 (*d*, J_{C-P}= 6.4 Hz, (C7); 31.2 (d, J_{C-P}= 5.2 Hz, (C8); 31.0 (C11); 26.8 (d, J_{C-P}= 7.9 Hz, (C9); 25.8 (*d*, J_{C-P}= 6.4 Hz, (C10). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) -25.6.

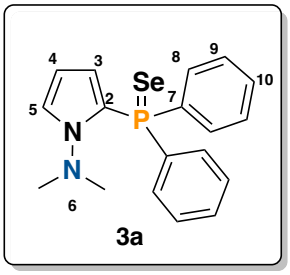
4. General procedure for synthesis of phosphine selenides.

To a ligand solution (0.5 mmol) in $CDCl_3$, was added the Molecular selenium (5 mmol) reaction mixture was stored under refrigeration for 12 hours, at the end of the time it was filtered and analyzed directly in ^{31}P NMR. (**Scheme S2**)

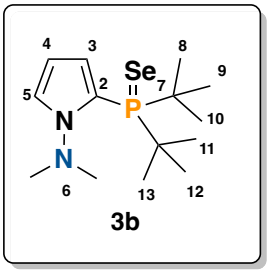


Scheme S2. General synthesis of pyrrole-based phosphorus selenides **3a-d**.

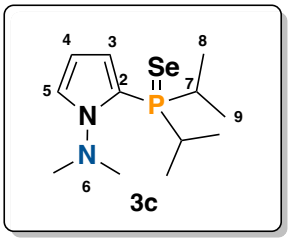
5. Characterization Data of phosphine selenides.



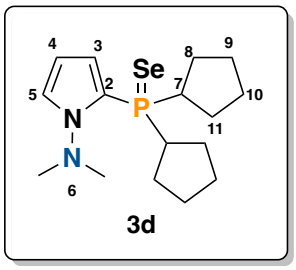
(1-(dimetilamino)-1*H*-pirrol-2-il)difenilfosfin selenuro (73a). NMR ^1H (300.0 MHz, $CDCl_3$) δ (ppm) 7.91-7.84 (*m*, 4H, H8); 7.46-7.43 (*m*, 6H, H9, H10), 7.20 (*m*, 1H, H5); 6.16-6.14 (*m*,1H, H4); 5.89-5.86 (*m*, 1H, H3); 2.56 (*s*, 6H, H6). ^{31}P NMR (50 MHz, $CDCl_3$) δ 16.2 (*t*, $J_{P\text{-}Se}$= 736 Hz).



di-*tert*-butyl(1-(dimethylamino)-1*H*-pyrrol-2-yl)phosphine selenide (3b). ^1H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.33 (*m*, 2H, H4,H5), 6.21 (*m*, 1H, H3), 2.86 (*s*, 6H, H6); 1.50 (*s*, 9H, H8, H9, H10), 1.45 (*s*, 9H, H11, H12, H13). ^{31}P NMR (50 MHz, $CDCl_3$, 323 ºK) δ -72.4 (*t*, $J_{P\text{-}Se}$= 707 Hz).



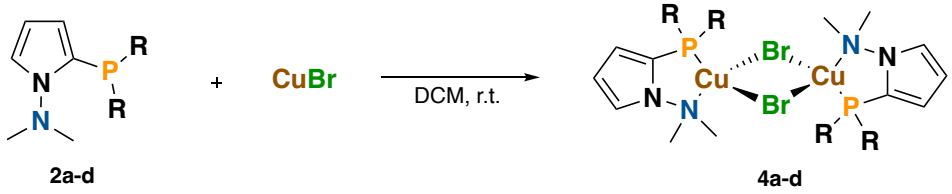
(1-(dimethylamino)-1*H*-pyrrol-2-yl)diisopropylphosphine selenide (3c). ^1H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.25 (*dd*, $J_{H\text{-}H}$= 1.91 Hz, $J_{H\text{-}H}$= 2.81 Hz, 1H, H5); 6.90 (*dt*, $J_{H\text{-}H}$= 0.95 Hz, $J_{H\text{-}H}$= 4.5 Hz, 1H, H4); 6.20 (*m*, 1H, H3); 2.83 (*s*, 6H, H6); 2.84-2.78 (*m*, 1H, H7); 1.32-1.23 (*dd*, 6H, H8, $J_{H\text{-}H}$= 6.79 Hz, $J_{H\text{-}H}$= 23.76 Hz), 1.04-0.95 (*dd*, 6H, H9, $J_{H\text{-}H}$= 6.98 Hz, $J_{H\text{-}H}$= 18.84 Hz). ^{31}P NMR (50 MHz, $CDCl_3$) δ 56.4 (*t*, $J_{P\text{-}Se}$= 704 Hz).



dicyclopentyl(1-(dimethylamino)-1*H*-pyrrol-2-yl)phosphine selenide (3d). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.21-7.19 (*dd*, J_{H-H}= 2.84 Hz, J_{H-H}= 4.73 Hz, 1H, H5), 6.93-691 (*dd*, J_{H-H}= 1.84 Hz, J_{H-H}= 4.35 Hz, 1H, H4,), 6.21-6.18 (*m*, 1H, H3), 2.95-2.91 (m, 2H, H7)2.09-1.40 (*m*, 19H, H8, H9, H10, H11). ^{31}P NMR (50 MHz, $CDCl_3$) δ 50.2 (*t*, J_{P-Se}= 705 Hz).

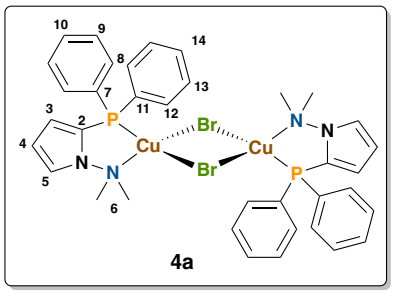
6. General procedure for complexation reaction.

In a Schlenk flask, the corresponding ligand (0.5 mmol, 1 eq.) is weighed and then CuBr (0.5 mmol, 1 eq.) is added. The flask is brought to anhydrous conditions with N2, and anhydrous CH2Cl2 (5 ml) is added. The reaction mixture is stirred for approximately 1 hour at room temperature. At the end of the reaction, the solvent is removed under vacuum, leaving a white residue that is washed with hexane to obtain the pure complexes. (**Scheme S3**).[2]



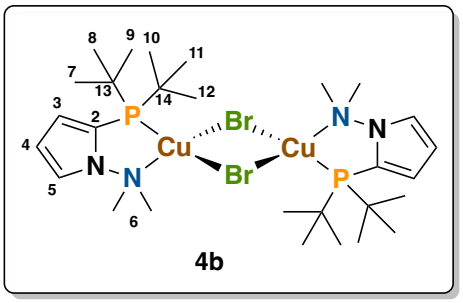
Scheme S3. General synthesis of dinuclear Cu(I) complexes **4a-d**.

7. Characterization Data of dinuclear Cu(I) complexes.

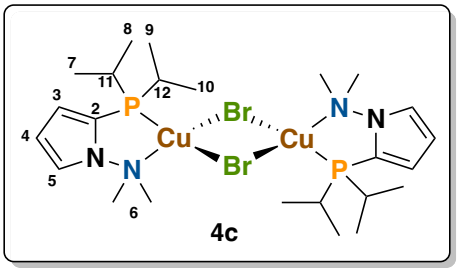


2-(diphenylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine copper(I) bromide (4a). solid white (80%). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.65.-7.59 (*m*, 4H, H8, H12); 7.45-7.42 (*m*, 6H, H13, H9, H14, H10); 7.32 (*m*, 1H, H5); 6.35-6.33 (*t*, *J*= 3.6 Hz, 1H, H4); 6.16-6.15 (*d*, *J*= 4.0 Hz, 1H, H3); 2.96 (*s*, 6H, H6). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ(ppm) 133.5-133.4 (*d*, J_{C-P}= 15.9 Hz C8,C12); 132.8-132.3 (*d*, J_{C-P}= 38.5 Hz C7,C11); 129.8 (C10, C14); 128.6-128.5 (*d*, J_{C-P}= 10.1 Hz C9,C13); 124.6-123.8 (*d*, J_{C-P}= 59.0 Hz C2); 117.4 (C5), 114.5 (C3), 109.7-109.6 (*d*, J_{C-P}= 5.3 Hz C4); 50.6 (C6). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) -34.26. IR (ATR, cm^{-1}) νmax: 3129.2 (=C-H); 2964.0 (-CH); 1811.6-1660.0 (C=C); 742.0-692.0 (C-H_{pyrrol}). HRMS (MALDI-TOF): calc. for $C_{36}H_{38}Br_2Cu_2N_4P_2$ [M^+] 875.5755; found 796.505 [M^+ -Br].

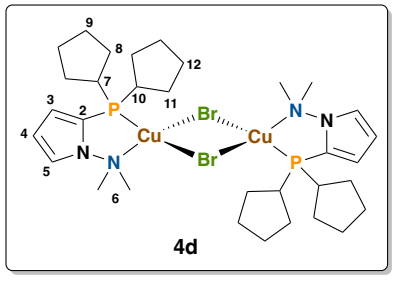
[2] Harutyunyan, S. R.; López, F.; Browne, W. R.; Correa, A.; Peña, D.; Badorrey, R.; Meetsma, A.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.*, **2006**, *128*, 9103-9118.



2-(di-*tert*-butylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine copper(I) bromide (4b). solid white (54%). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.30 (*m*, 1H, H5), 6.43 (*d*, *J*= 2.51 Hz, 1H, H4), 6.33-6.32 (*t*, *J*= 3.15 Hz 1H, H3), 3.01 (*s*, 6H, H6), 1.31 (*s*, 18H, H7, H8, H9, H10, H11, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ(ppm) 121.7 (C2), 117.5 (C5), 113.8 (C4), 109.4 (C3), 50.4 (C6), 34.2 (C13, C14), 29.9 (C7, C8, C9, C10, C11, C12). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) 11.53. IR (ATR, cm^{-1}) νmax: 3098.7 (=C-H); 2998.7-2866.0 (-CH); 1720.7-1653.6 (C=C); 742.2 (C-H_{pyrrol}). HRMS (MALDI-TOF): calc. for $C_{28}H_{54}Br_2Cu_2N_4P_2$ [M^+] 792.0782; found 717.142 [M^+ -Br].
X-Ray data or complex **4a**.



2-(diisopropylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine copper(I) bromide (4c). solid white (68 %). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.27 (*m*, 1H, H5), 6.31 (*m*, 1H, H4), 6.26 (*m*, 1H, H3), 3.01 (*s*, 6H, H6), 2.24–2.26 (*m*, 2H, H11,12), 1.22–1.17 (*d*,*d*, *J*= 6.7 Hz, *J*= 18.4 Hz 6H, H7,8), 1.10–1.06 (*d*,*d*, *J*= 6.9 Hz *J*= 14.8 Hz 6H, H9,10). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 121.6-121.1 (*d*, $J_{C\text{-}P}$= 48.6 Hz C2), 117.6 (C5), 112.9 (C4), 109.6 (*d*, $J_{C\text{-}P}$= 4.0 Hz C3), 50.6 (C6), 24.4-24.1 (*d*, $J_{C\text{-}P}$= 23.4 Hz C11,C12), 19.7-19.5 (*d*, $J_{C\text{-}P}$= 10.0 Hz C8,C10), 18.3 (C7, C9). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) -9.75. IR (ATR, cm^{-1}) νmax: 3069.7 (=C-H); 2955.0 – 2862.9 (-CH); 733.1 (C-H_{pyrrol}). HRMS (MALDI-TOF): calcd. for $C_{24}H_{46}Br_2Cu_2N_4P_2$ [M^+] 736.0156; found 661.395 [M^+ -Br].



2-(dicyclopentylphosphaneyl)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine copper(I) bromide (4d). solid white (60 %). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ (ppm) 7.19 (*s*, 1H, H5), 6.27 (*m*, 2H, H3, H4), 3.01 (*s*, 6H, H6), 2.53-2.27 (m, 1H, H7), 2.07-1.96 (m, 1H, H10), 1.74–1.48 (*m*, 18H, H7, H8, H9, H10, H11, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm)124.8-124.2 (*d*, $J_{C\text{-}P}$= 49.8 Hz C2), 116.9 (C5), 112.2 (C4), 109.5-109.4 (*d*, $J_{C\text{-}P}$= 4.3 Hz C3), 50.6 (C6), 37.4-37.1 (*d*, $J_{C\text{-}P}$= 25.7 Hz C7), 30.7-30.9 (*d*, $J_{C\text{-}P}$= 12.6 Hz C10), 30.6-30.5 (*d*, $J_{C\text{-}P}$= 4.9 Hz C8, C11), 26.7-26.5 (*d*, $J_{C\text{-}P}$= 10.0 Hz C12), 25.7-25.6 (*d*, $J_{C\text{-}P}$= 8.8 Hz C9). ^{31}P NMR (50 MHz, $CDCl_3$) δ (ppm) -17.86. IR (ATR, cm^{-1}) νmax: 3106.9 (=C-H); 2999.9 – 2862.6 (-CH); 717.0 - 705.4 (C-H_{pyrrol}). HRMS (MALDI-TOF): calc. for $C_{32}H_{54}Br_2Cu_2N_4P_2$ [M^+] 840.0782; found 764.922 [M^+ -Br].

8. X-Ray diffraction data for complex 4a-d

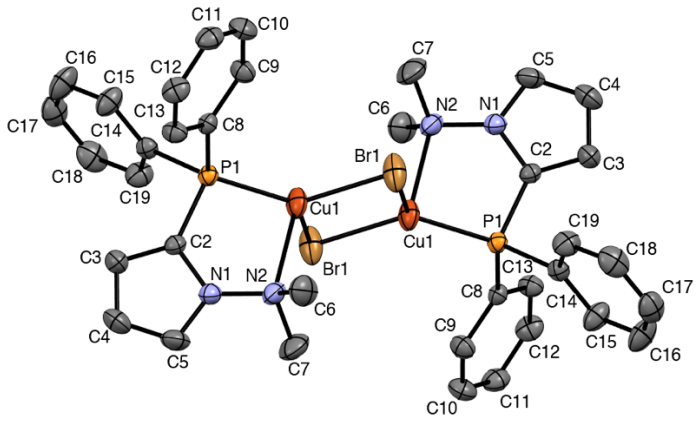


Figure S1. Crystal structure of complex **4a**. Hydrogen atoms are omitted for clarity.

Table S1. Distances [Å] and angles [°] of **4a**.

Br(1)-Cu(1), 2.4374(9)	C(3)-C(4), 1.406(4)
Br(1)-Cu(1), 2.4437(8)	C(4)-C(5), 1.360(4)
Cu(1)-P(1), 2.1910(9)	C(8)-C(13), 1.384(3)
Cu(1)-N(2), 2.559(2)	C(8)-C(9), 1.404(3)
Cu(1)-Cu(1), 2.8441(10)	C(9)-C(10), 1.383(4)
P(1)-C(2), 1.808(3)	C(10)-C(11), 1.377(4)
P(1)-C(8), 1.822(2)	C(11)-C(12), 1.374(4)
P(1)-C(14), 1.836(2)	C(12)-C(13), 1.380(4)
N(1)-C(5), 1.371(3)	C(14)-C(15), 1.374(4)
N(1)-C(2), 1.373(3)	C(14)-C(19), 1.387(4)
N(1)-N(2), 1.422(3)	C(15)-C(16), 1.387(4)
N(2)-C(7), 1.480(4)	C(16)-C(17), 1.354(5)
N(2)-C(6), 1.481(4)	C(17)-C(18), 1.367(5)
C(2)-C(3), 1.380(4)	C(18)-C(19), 1.393(4)

Cu(1)-Br(1)-Cu(1), 71.28(2)	C(2)-P(1)-Cu(1), 104.20(8)
P(1)-Cu(1)-Br(1), 126.82(3)	C(8)-P(1)-Cu(1), 116.57(8)
P(1)-Cu(1)-Br(1), 122.39(3)	C(14)-P(1)-Cu(1), 123.67(8)
Br(1)- Cu(1)-Br(1), 108.72(2)	C(5)-N(1)-C(2), 110.3(2)
P(1)-Cu(1)-N(2), 80.63(6)	C(5)-N(1)-N(2), 127.4(2)
Br(1)-Cu(1)-N(2), 100.31(6)	C(2)-N(1)-N(2), 122.3(2)
Br(1)-Cu(1)-N(2), 105.38(6)	N(1)-N(2)-C(7), 110.3(2)
P(1)-Cu(1)-Cu(1), 166.86(3)	N(1)-N(2)-C(6), 109.7(2)
Br(1)-Cu(1)-Cu(1), 54.46(2)	C(7)-N(2)-C(6), 111.5(2)
Br(1)-Cu(1)-Cu(1), 54.26(2)	N(1)-N(2)-Cu(1), 105.55(14)
N(2)-Cu(1)-Cu(1), 112.42(6)	C(7)-N(2)-Cu(1), 105.2(2)

C(2)-P(1)-C(8), 105.70(11)	C(6)-N(2)-Cu(1), 114.38(19)
C(2)-P(1)-C(14), 100.56(11)	N(1)-C(2)-C(3), 106.0(2)
C(8)-P(1)-C(14), 103.72(11)	N(1)-C(2)-P(1), 121.09(18)
C(3)-C(2)-P(1), 132.9(2)	C(2)-C(3)-C(4), 108.5(2)
C(5)-C(4)-C(3), 107.4(3)	C(4)-C(5)-N(1), 107.7(2)
C(13)-C(8)-C(9), 117.8(2)	C(13)-C(8)-P(1), 124.51(19)
C(9)-C(8)-P(1), 117.65(19)	C(10)-C(9)-C(8), 120.7(3)
C(11)-C(10)-C(9), 120.2(3)	C(12)-C(11)-C(10), 119.5(3)
C(11)-C(12)-C(13), 120.7(3)	C(12)-C(13)-C(8), 121.0(3)
C(15)-C(14)-C(19), 118.3(2)	C(15)-C(14)-P(1), 123.2(2)
C(19)-C(14)-P(1), 118.4(2)	C(14)-C(15)-C(16), 120.5(3)
C(17)-C(16)-C(15), 120.9(3)	C(16)-C(17)-C(18), 119.8(3)
C(17)-C(18)-C(19), 120.0(3)	C(14)-C(19)-C(18), 120.4(3)

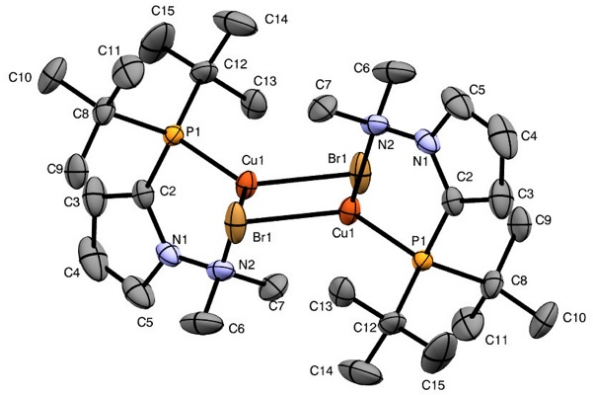


Figure S2. Crystal structure of complex **4b**. Hydrogen atoms are omitted for clarity.

Table S2. Distances [Å] and angles [°] of **4b**.

Br(1)-Cu(1), 2.4460(8)	N(2)-C(6), 1.475(8)
Br(1)-Cu(1), 2.4591(8)	C(2)-C(3), 1.385(7)
Cu(1)-P(1), 2.1888(13)	C(3)-C(4), 1.413(11)
Cu(1)-N(2), 2.368(4)	C(4)-C(5), 1.337(12)
P(1)-C(2), 1.809(5)	C(8)-C(9), 1.521(9)
P(1)-C(8), 1.880(5)	C(8)-C(11), 1.526(8)
P(1)-C(12), 1.886(6)	C(8)-C(10), 1.527(8)
N(1)-C(5), 1.350(7)	C(12)-C(13), 1.510(8)
N(1)-C(2), 1.388(7)	C(12)-C(15), 1.522(9)
N(1)-N(2), 1.412(6)	C(12)-C(14), 1.523(10)

N(2)-C(7), 1.462(7)	

Cu(1)-Br(1)-Cu(1), 77.35(3)	C(7)-N(2)-Cu(1), 110.9(4)
P(1)-Cu(1)-N(2), 84.97(12)	C(6)-N(2)-Cu(1), 108.2(4)
P(1)-Cu(1)-Br(1), 124.61(4)	C(3)-C(2)-N(1), 106.0(5)
N(2)-Cu(1)-Br(1), 106.04(11)	C(3)-C(2)-P(1), 134.9(5)
P(1)-Cu(1)-Br(1), 127.33(5)	N(1)-C(2)-P(1), 119.0(4)
N(2)-Cu(1)-Br(1), 104.59(12)	C(2)-C(3)-C(4), 106.5(7)
Br(1)-Cu(1)-Br(1), 102.65(3)	C(5)-C(4)-C(3), 109.4(6)
C(2)-P(1)-C(8), 104.6(2)	C(4)-C(5)-N(1), 107.5(7)
C(2)-P(1)-C(12), 103.9(3)	C(9)-C(8)-C(11), 108.7(6)
C(8)-P(1)-C(12), 114.5(3)	C(9)-C(8)-C(10), 108.4(5)
C(2)-P(1)-Cu(1), 103.22(19)	C(11)-C(8)-C(10), 109.9(6)
C(8)-P(1)-Cu(1), 114.74(19)	C(9)-C(8)-P(1), 105.7(4)
C(12)-P(1)-Cu(1), 114.0(2)	C(11)-C(8)-P(1), 107.6(4)
C(5)-N(1)-C(2), 110.6(6)	C(10)-C(8)-P(1), 116.2(4)
C(5)-N(1)-N(2), 125.5(6)	C(13)-C(12)-C(15), 108.1(6)
C(2)-N(1)-N(2), 123.8(4)	C(13)-C(12)-C(14), 107.8(6)
N(1)-N(2)-C(7), 109.5(5)	C(15)-C(12)-C(14), 111.3(7)
N(1)-N(2)-C(6), 107.7(5)	C(13)-C(12)-P(1), 105.3(4)
C(7)-N(2)-C(6), 111.7(5)	C(15)-C(12)-P(1), 116.7(5)
N(1)-N(2)-Cu(1), 108.6(3)	C(14)-C(12)-P(1), 107.2(5)

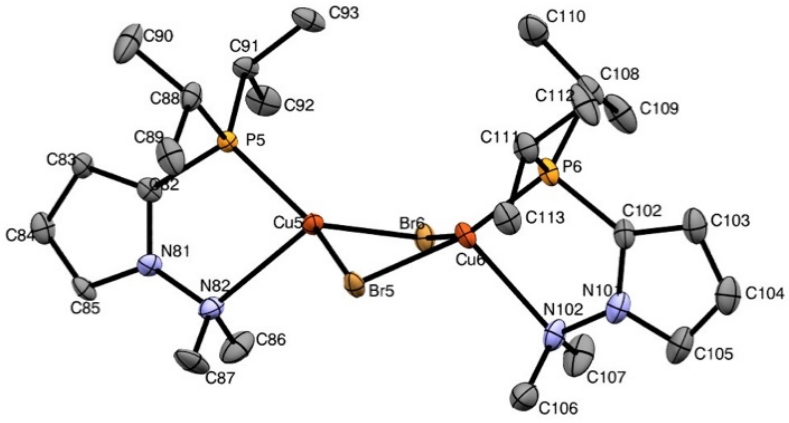


Figure S3. Crystal structure of complex **4c**. Hydrogen atoms are omitted for clarity.

Table S3. Distances [Å] and angles [°] of **4c**.

Br(5)-Cu(5), 2.4364(12)	C(82)-C(83), 1.387(11)
Br(5)-Cu(6), 2.4644(12)	C(83)-C(84), 1.408(12)
Br(6)-Cu(6), 2.4419(13)	C(84)-C(85), 1.360(13)
Br(6)-Cu(5), 2.4677(13)	C(88)-C(90), 1.525(12)
Cu(5)-P(5), 2.189(2)	C(88)-C(89), 1.532(14)
Cu(5)-N(82), 2.523(8)	C(91)-C(92), 1.520(12)
Cu(5)-Cu(6), 2.9686(14)	C(91)-C(93), 1.535(12)
Cu(6)-P(6), 2.193(2)	N(101)-C(105), 1.361(12)
Cu(6)-N(102), 2.450(7)	N(101)-C(102), 1.388(12)
P(5)-C(82), 1.810(8)	N(101)-N(102), 1.452(11)
P(5)-C(91), 1.842(8)	N(102)-C(106), 1.457(14)
P(5)-C(88), 1.846(8)	N(102)-C(107), 1.478(12)
P(6)-C(102), 1.794(9)	C(102)-C(103), 1.401(12)
P(6)-C(111), 1.839(9)	C(103)-C(104), 1.410(15)
P(6)-C(108), 1.848(9)	C(104)-C(105), 1.365(15)
N(81)-C(85), 1.375(10)	C(108)-C(110), 1.518(14)
N(81)-C(82), 1.376(10)	C(108)-C(109), 1.548(14)
N(81)-N(82), 1.411(10)	C(111)-C(112), 1.536(13)
N(82)-C(86), 1.459(11)	C(111)-C(113), 1.541(13)
N(82)-C(87), 1.477(11)	

Cu(5)-Br(5)-Cu(6), 74.56(4)	C(91)-P(5)-C(88), 106.4(4)
Cu(6)-Br(6)-Cu(5), 74.40(4)	C(82)-P(5)-Cu(5), 105.9(3)
P(5)-Cu(5)-Br(5), 130.50(7)	C(91)-P(5)-Cu(5), 117.7(3)
P(5)-Cu(5)-Br(6), 125.96(7)	C(88)-P(5)-Cu(5), 116.5(3)
Br(5)-Cu(5)-Br(6), 98.64(4)	C(102)-P(6)-C(111), 104.0(4)
P(5)-Cu(5)-N(82), 81.81(17)	C(102)-P(6)-C(108), 103.1(4)
Br(5)-Cu(5)-N(82), 101.58(17)	C(111)-P(6)- C(108), 107.2(4)
Br(6)-Cu(5)-N(82), 112.58(17)	C(102)-P(6)-Cu(6), 103.9(3)
P(5)-Cu(5)-Cu(6), 139.73(7)	C(111)-P(6)-Cu(6), 116.2(3)
Br(5)-Cu(5)-Cu(6), 53.15(3)	C(108)-P(6)-Cu(6), 120.3(3)
Br(6)-Cu(5)-Cu(6), 52.40(3)	C(85)-N(81)-C(82), 109.2(7)
N(82)-Cu(5)-Cu(6), 138.33(17)	C(85)-N(81)-N(82), 127.3(7)
P(6)-Cu(6)-Br(6), 133.86(8)	C(82)-N(81)-N(82), 123.2(7)
P(6)-Cu(6)-N(102), 84.1(2)	N(81)-N(82)-C(86), 110.6(7)
Br(6)-Cu(6)-N(102), 105.00(18)	N(81)-N(82)-C(87), 109.4(7)
P(6)-Cu(6)-Br(5), 123.38(7)	C(86)-N(82)-C(87), 109.6(8)
Br(6)-Cu(6)-Br(5), 98.58(4)	N(81)-N(82)-Cu(5), 108.0(5)
N(102)-Cu(6)-Br(5), 104.1(2)	C(86)-N(82)-Cu(5), 107.7(6)
P(6)-Cu(6)-Cu(5), 140.93(8)	C(87)-N(82)-Cu(5), 111.5(5)
P(6)-Cu(6)-Cu(5), 140.93(8)	N(81)-C(82)-C(83), 107.5(7)

P(6)-Cu(6)-Cu(5), 140.93(8)	N(81)-C(82)-P(5), 120.5(6)
N(102)-Cu(6)-Cu(5), 134.50(19)	C(83)-C(82)-P(5), 131.9(7)
Br(5)-Cu(6)-Cu(5), 52.29(3)	C(82)-C(83)-C(84), 106.9(7)
C(82)-P(5)-C(91), 104.5(4)	C(85)-C(84)-C(83), 108.5(8)
C(82)-P(5)-C(88), 104.4(4)	C(84)-C(85)-N(81), 107.8(7)
C(90)-C(88)-C(89), 112.1(9)	C(90)-C(88)-P(5), 114.4(6)
C(89)-C(88)-P(5), 108.2(6)	C(92)-C(91)-C(93), 112.1(8)
C(92)-C(91)-P(5), 109.7(6)	C(93)-C(91)-P(5), 109.1(5)
C(105)-N(101)-C(102), 111.6(8)	C(105)-N(101)-N(102), 126.3(8)
C(102)-N(101)-N(102), 121.5(7)	N(101)-N(102)-C(106), 108.2(7)
N(101)-N(102)-C(107), 108.4(7)	C(106)-N(102)-C(107), 113.1(9)
N(101)-N(102)-Cu(6), 107.7(5)	C(106)-N(102)-Cu(6), 111.0(6)
C(107)-N(102)-Cu(6), 108.2(6)	N(101)-C(102)-C(103), 105.6(8)
N(101)-C(102)-P(6), 121.6(6)	C(103)-C(102)-P(6), 132.6(8)
C(102)-C(103)-C(104), 106.9(9)	C(105)-C(104)-C(103), 109.5(9)
N(101)-C(105)-C(104), 106.5(10)	C(110)-C(108)-C(109), 110.8(8)
C(110)-C(108)-P(6), 109.8(6)	C(109)-C(108)-P(6), 107.2(7)
C(112)-C(111)-C(113), 109.3(8)	C(112)-C(1119)-P(6), 116.3(7)
C(113)-C(111)-P(6), 109.2(7)	

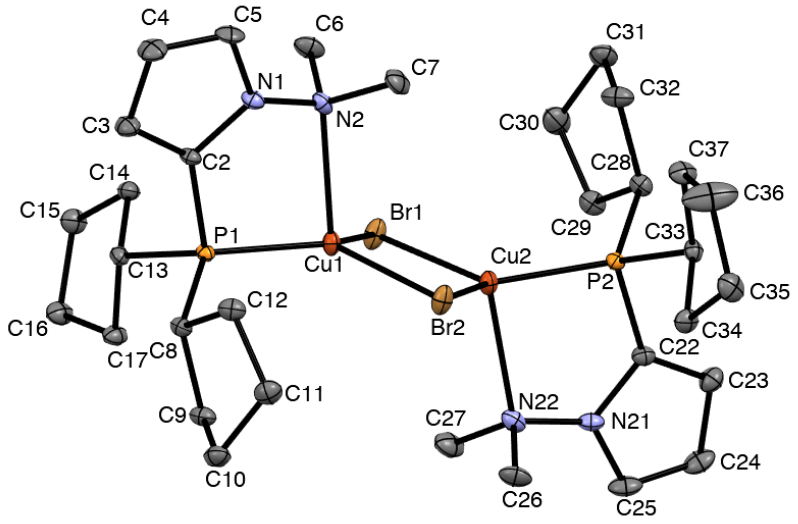


Figure S4. Crystal structure of complex **4d**. Hydrogen atoms are omitted for clarity.

Table S4. Distances [Å] and angles [°] of **4d**.

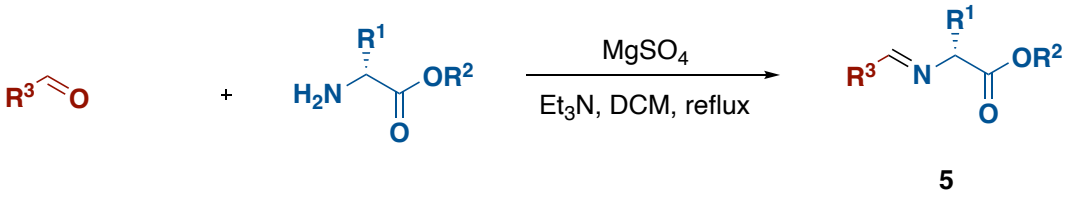
Br(1)-Cu(1), 2.4297(3)	C(2)-C(3), 1.380(2)
Br(1)-Cu(2), 2.4572(3)	C(3)-C(4) 1.413(2)
Br(2)-Cu(2), 2.4359(3)	C(4)-C(5) 1.370(3)
Br(2)-Cu(1), 2.4560(3)	C(8)-C(9), 1.545(2)
Cu(1)-P(1), 2.1867(4)	C(8)-C(12), 1.557(2)
Cu(1)-N(2), 2.4157(15)	C(9)-C(10), 1.529(3)
Cu(1)-Cu(2), 2.8055(3)	C(10)-C(11), 1.529(3)
Cu(2)-P(2), 2.1868(5)	C(11)-C(12), 1.540(2)
Cu(2)-N(22), 2.4056(15)	C(13)-C(17), 1.537(2)
P(1)-C(2), 1.8010(16)	C(13)-C(14), 1.540(2)
P(1)-C(13), 1.8377(16)	C(14)-C(15), 1.541(2)
P(1)-C(8), 1.8386(17)	C(15)-C(16), 1.540(3)
P(2)-C(22), 1.8007(17)	C(16)-C(17), 1.535(2)
P(2)-C(33), 1.8361(17)	N(21)-C(25), 1.371(2)
P(2)-C(28), 1.8366(17)	N(21)-C(22) 1.380(2)
N(1)-C(5), 1.375(2)	N(21)-N(22) 1.423(2)
N(1)-C(2), 1.382(2)	N(22)-C(27), 1.474(2)
N(1)-N(2), 1.4250(19)	N(22)-C(26), 1.476(2)
N(2)-C(7), 1.470(2)	C(22)-C(23), 1.381(2)
N(2)-C(6), 1.475(2)	C(23)-C(24), 1.414(3)
C(24)-C(25), 1.355(3)	C(28)-C(32), 1.542(2)
C(28)-C(32), 1.542(2)	C(28)-C(29), 1.549(2)
C(29)-C(30), 1.536(3)	C(30)-C(31), 1.525(3)
C(31)-C(32), 1.529(3)	C(33)-C(34), 1.541(2)
C(33)-C(37), 1.543(2)	C(34)-C(35), 1.524(2)
C(35)-C(36), 1.519(3)	C(36)-C(37), 1.525(3)

Cu(1)-Br(1)-Cu(2), 70.069(8)	C(8)-P(1)-Cu(1), 119.12(6)
Cu(2)-Br(2)-Cu(1), 69.989(8)	C(22)-P(2)-C(33), 102.99(8)
P(1)-Cu(1)-N(2), 84.56(3)	C(22)-P(2)-C(28), 102.13(8)
P(1)-Cu(1)-Br(1), 126.495(15)	C(33)-P(2)-C(28) 106.17(8)
N(2)-Cu(1)-Br(1), 105.07(3)	C(22)-P(2)-Cu(2), 102.90(6)
P(1)-Cu(1)-Br(2), 118.902(15)	C(33)-P(2)-Cu(2), 118.75(5)
N(2)-Cu(1)-Br(2), 102.97(3)	C(28)-P(2)-Cu(2), 120.88(6)
Br(1)-Cu(1)-Br(2), 110.001(9)	C(5)-N(1)-C(2), 109.92(14)
P(1)-Cu(1)-Cu(2), 162.624(15)	C(5)-N(1)-N(2), 126.38(14)
N(2)-Cu(1)-Cu(2), 112.21(3)	C(2)-N(1)-N(2), 122.46(13)
Br(1)-Cu(1)-Cu(2), 55.425(7)	N(1)-N(2)-C(7), 110.75(14)
Br(2)-Cu(1)-Cu(2), 54.670(7)	N(1)-N(2)-C(6), 109.02(13)
P(2)-Cu(2)-N(22), 84.76(4)	C(7)-N(2)-C(6), 110.92(14)
P(2)-Cu(2)-Br(2), 124.487(15)	N(1)-N(2)-Cu(1), 106.11(9)

N(22)-Cu(2)-Br(2), 103.31(4)	C(7)-N(2)-Cu(1). 109.39(11)
P(2)-Cu(2)-Br(1), 120.919(15)	C(6)-N(2)-Cu(1), 110.54(11)
N(22)-Cu(2)-Br(1), 105.24(4)	C(3)-C(2)-N(1), 106.66(14)
Br(2)-Cu(2)-Br(1), 109.755(10)	C(3)-C(2)-P(1), 132.72(13)
P(2)-Cu(2)-Cu(1), 157.047(15)	N(1)-C(2)-P(1), 120.27(12)
N(22)-Cu(2)-Cu(1), 118.13(4)	C(2)-C(3)-C(4), 108.10(16)
Br(2)-Cu(2)-Cu(1), 55.342(7)	C(5)-C(4)-C(3), 107.66(16)
Br(1)-Cu(2)-Cu(1), 54.506(7)	C(4)-C(5)-N(1), 107.65(15)
C(2)-P(1)-C(13), 102.83(8)	C(9)-C(8)-C(12), 104.44(14)
C(2)-P(1)-C(8) 102.21(7)	C(9)-C(8)-P(1), 113.71(11)
C(13)-P(1)-C(8), 106.30(8)	C(12)-C(8)-P(1), 111.00(11)
C(2)-P(1)-Cu(1), 102.81(5)	C(10)-C(9)-C(8), 103.05(14)
C(13)-P(1)-Cu(1), 120.51(5)	C(9)-C(10)-C(11), 102.83(14)
C(10)-C(11)-C(12), 104.55(15)	C(17)-C(13)-C(14), 101.84(13)
C(11)-C(12)-C(8), 106.43(14)	C(17)-C(13)-P(1), 113.90(11)
C(14)-C(13)-P(1), 111.69(11)	C(13)-C(14)-C(15), 104.86(13)
C(16)-C(15)-C(14), 106.25(14)	C(17)-C(16)-C(15), 105.52(14)
C(16)-C(17)-C(13), 103.91(14)	C(25)-N(21)-C(22), 109.75(15)
C(25)-N(21)-N(22), 126.71(15)	C(22)-N(21)-N(22), 123.54(14)
N(21)-N(22)-C(27), 109.71(14)	N(21)-N(22)-C(26), 109.55(14)
C(27)-N(22)-C(26), 111.23(15)	N(21)-N(22)-Cu(2), 107.36(9)
C(27)-N(22)-Cu(2), 108.89(11)	C(26)-N(22)-Cu(2), 110.02(11)
N(21)-C(22)-C(23), 106.59(15)	N(21)-C(22)-P(2), 120.43(12)
C(23)-C(22)-P(2), 132.98(14)	C(22)-C(23)-C(24), 107.77(17)
C(25)-C(24)-C(23), 107.83(16)	C(24)-C(25)-N(21), 108.06(17)
C(32)-C(28)-C(29), 104.74(14)	C(32)-C(28)-P(2), 113.94(12)
C(29)-C(28)-P(2), 109.96(11)	C(30)-C(29)-C(28), 106.44(15)
C(31)-C(30)-C(29), 105.19(15)	C(30)-C(31)-C(32), 103.11(15)
C(31)-C(32)-C(28), 103.22(15)	C(34)-C(33)-C(37), 103.62(14)
C(34)-C(33)-P(2), 110.71(11)	C(37)-C(33)-P(2), 113.31(12)
C(35)-C(34)-C(33), 103.31(14)	C(36)-C(35)-C(34), 104.60(16)
C(35)-C(36)-C(37), 107.75(17)	C(36)-C(37)-C(33), 105.56(15)

9. General synthesis of Imino Esters

A mixture of aminoacid methyl ester hydrochloride (1.0 g, 7.96 mmol), 4-chlorobenzaldehyde (1.120 g, 7.96 mmol), triethylamine (0.806 g, 7.96 mmol), and anhydrous magnesium sulfate (1.5 g, 12.5 mmol) was refluxed for 2 h in dichloromethane. After the reaction mixture was cooled to room temperature, the undissolved materials were removed by filtration, washed with dichloromethane, and discarded. The filtrate was concentrated to dryness on a rotatory evaporator to give a white solid. The white solid was dissolved in benzene and filtered, and the resulting solution was concentrated to dryness on a rotatory evaporator to give compound **Imino Esters**.[3]



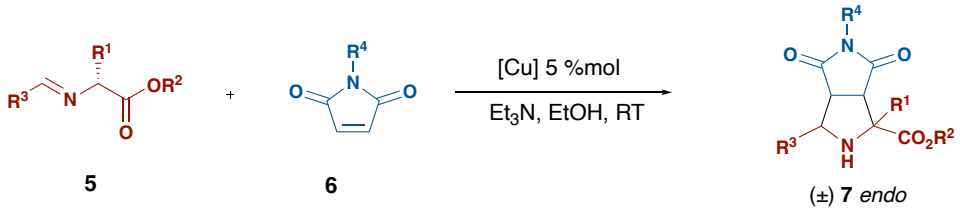
Scheme S4. General synthesis of imino esters **5**.

note: due to their easy oxidation to the corresponding aldehyde all imino esters were prepared *in-situ*

10. General Procedure for the 1,3-Dipolar Cycloaddition of Imino Esters and Dipolarophiles

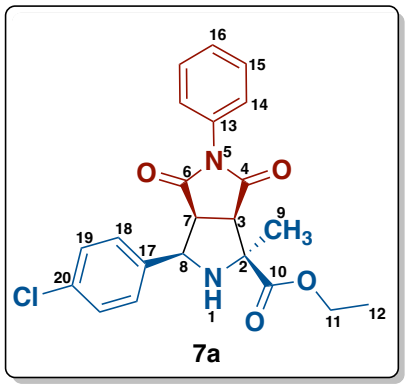
Typical procedure for asymmetric 1,3-dipolar cycloaddition of azomethine ylides: To a solution of the appropriate imino ester **5** (1.2 mmol) in 3.0 mL of ethanol (EtOH), were added 0.17 mL of triethylamine (Et_3N, 1.2 mmol) and *N*-phenyl maleimide (174 mg, 1 mmol). Then, 0.03 mmol (27 mg) of **4a** are added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 3 hours. Then, the reaction mixture was evaporated under vacuum and crude was redissolved with 5 mL of CH_2Cl_2 and washed with H_2O (3 × 15 mL). The organic phase was dried with anhydrous sodium sulfate and then filtered through a pad of celite and alumina, using 5.0 mL of CH_2Cl_2. Subsequently, the solvent was removed under reduced pressure. The crude was further purified through silica gel chromatography (eluent: 7:3 hexanes/EtOAc) to obtain the corresponding adducts **7** (**Scheme S5**).

[3] Albert, J.; Crespo, M.; Granell, J.; Rodríguez, J.; Zafrilla, J.; Calvet, T.; Font-Bardia, M.; Solans, X. *Organometallics*, **2010**, *29*, 214–225



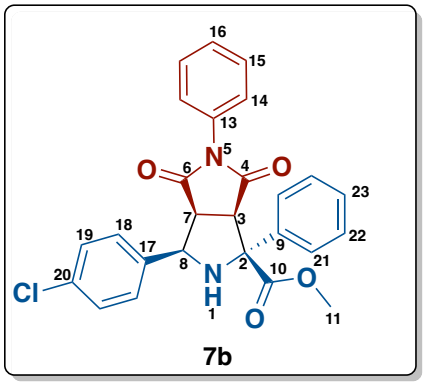
Scheme S5. 1,3-dipolar cycloaddition reaction between imino ester **5** and *N*-phenyl maleimide **6**.

11. Characterization Data of Pyrrolidine derivatives.



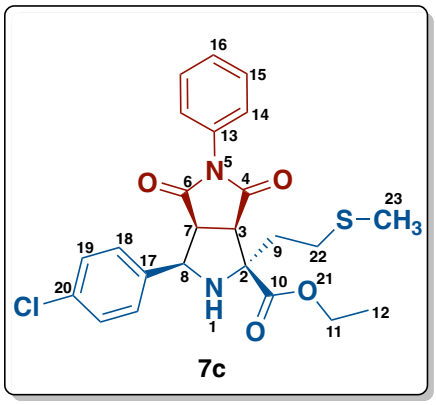
7a

(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-3-(4-chlorophenyl)-1-methyl-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7a). solid white (95 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.40-7.36 (*m*, 4H, H19, H14), 7.33-7.30 (*m*, 3H, H15, H16), 7.08-7.06 (*d*, *J*= 7.47 Hz, 2H, H18), 4.85–4.81 (*t*, *J*= 8.12 Hz, 1H, H8), 4.35–4.30 (*q*, *J*= 7.1 Hz, *J*= 14.3 Hz, 2H, H11), 3.69–3.65 (*dd*, *J*= 7.8 Hz, *J*= 8.8 Hz, 1H, H3), 3.45-3.43 (*d*, *J*= 7.7 Hz, 1H, H7), 2.57-2.55 (*d*, *J*= 7.0 Hz, 1H, NH) 1.65 (*s*, 3H, H9) 1.38-1.34 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (100.0 MHz, $CDCl_3$) δ (ppm) 174.6 (C4), 173.5 (C6), 172.2 (C10), 135.6 (C13), 134.1 (C17), 129.2 (C19), 128.7 (C14), 128.6 (C15), 128.6 (C16), 126.1 (C18), 67.5 (C11), 62.0 (C2), 61.6 (C8), 55.3 (C7), 50.0 (C3), 24.0 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3342.9 (N-H); 2990.0 (-CH); 1729.6 (O=C-CH_2CH_3); 1691.9 (O=C-NPh); 1599.7 (C=C); 1383.9 (C-O). MS (DART): m/z: 413.8700 [M+1]. HRMS (DART): calc. for $C_{22}H_{21}ClN_2O_4$ [M+] 412.1190; found 413.1251.



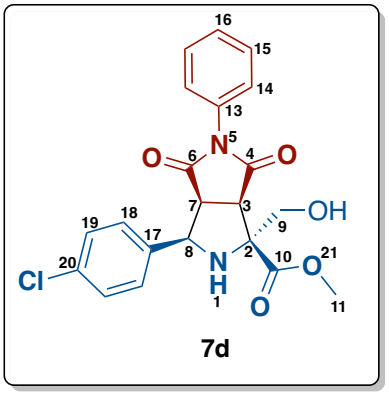
7b

(±)- methyl (1*R*,3*R*,3a*S*,6a*R*)-3-(4-chlorophenyl)-4,6-dioxo-1,5-diphenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7b). solid white (75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.57-7.55 (*d*, *J*= 8.0 Hz, 2H, H19), 7.29-7.48 (*m*, 10H, H14, H15, H16, H21, H22, H23), 7.12-7.10 (*d*, *J*= 8.0 Hz, 2H, H18), 4.37–4.33 (*dd*, *J*= 5.78 Hz, *J*= 9.24 Hz, 1H, H8), 4.24–4.22 (*dd*, *J*= 1.31 Hz, *J*= 7.37 Hz, 1H, H3), 3.78 (*s*, 3H, H11), 3.52–3.48 (*dd*, *J*= 7.4 Hz, *J*= 9.21 Hz, 1H, H7), 3.19 (*d*, *J*= 5.28 Hz, 1H, NH). ^{13}C NMR (100.0 MHz, $CDCl_3$) δ (ppm) 175.0 (C4), 173.5 (C6), 170.9 (C10), 138.3 (C13), 135.3 (C17), 134.2 (C20), 131.5 (C9), 129.2 (C23, C16), 128.7 (C14), 128.6 (C21), 128.6 (C22), 128.5 (C15), 126.0 (C19, 125.9 (C18), 72.6 (C2), 60.7 (C8), 53.1 (C3), 52.9 (C11), 49.6 (C7). IR (ATR, cm^{-1}) νmax: 3357.2 (N-H); 3057.3 (=C-H); 1746.1 (O=C-CH_3); 1711.4 (O=C-NPh); 1595.7 (C=C); 1381.2 (C-O). MS (DART): m/z: 461.9140 [M+1]. HRMS (DART): calc. for $C_{26}H_{21}ClN_2O_4$ [M+] 460.1190; found 461.1267 [M+1].



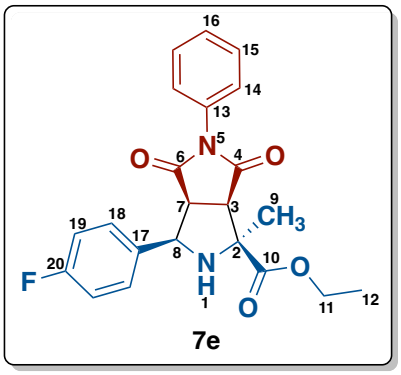
7c

(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-3-(4-chlorophenyl)-1-(2-(methylthio)ethyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7c). solid white (85 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.41-7.31 (*m*, 7H, H14, H15, H16, H19), 7.07-7.04 (*d*, *J*= 7 Hz, 2H, H18), 4.76–4.70 (*t*, *J*= 8.6 Hz, 1H, H8), 4.39–4.29 (*m*, 2H, H11), 3.67-3.62 (*dd*, J= 7.7 Hz J= 9 Hz, 1H, H3), 3.45–3.42 (*d*, *J*= 7.7 Hz, 1H, H7), 2.90-2.87 (*d*, *J*= 9.4 Hz, 1H, NH). 2.59-2.39 (*m*, 4H, H9, H22) 2.14 (*s*, 3H, H23), 2.39.2.35 (*t*, *J*= 7.2 Hz 3H, H12) ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.3 (C4), 173.4 (C6), 171.0 (C10), 135.3 (C13), 134.2 (C17), 131.4 (C20), 129.1 (C19), 128.8 (C14), 128.7 (C15), 128.5 (C16), 126.0 (C18), 71.1 (C11) 62.2 (C22), 61.7 (C23), 55.7 (C2), 50.3 (C8), 34.9 (C7), 28.7 (C3), 15.9 (C9), 14.1 (C12). IR (ATR, cm^{-1}) vmax: 3330.9 (N-H); 2986.2 (=C-H); 2923.7 (-CH); 1707.5 (O=C-NPh); 1597.8 (C=C); 1376.9 (C-O). MS (DART): m/z: 472.9840 [M+1]. HRMS (DART): calc. for $C_{24}H_{25}ClN_2O_4S$ [M+] 472.1224; found 473.1295 [M+1].

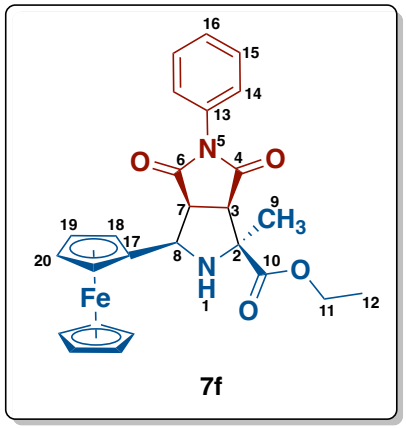


7d

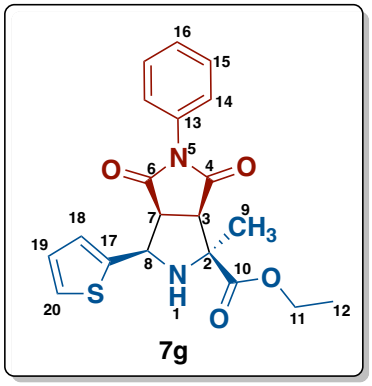
(±)- methyl (1*R*,3*R*,3a*S*,6a*R*)-3-(4-chlorophenyl)-1-(hydroxymethyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7d). solid white (80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.50-7.38 (*m*, 7H, H14, H15, H16, H19), 7.13-7.10 (*d*, *J*= 8.1 Hz, 2H, H18), 5.36 (m, 1H, OH), 4.84–4.80 (*d*, *J*= 10.2 Hz, 1H, H8), 4.10–4.06 (*d*, *J*= 14.0 Hz, 1H, H9), 3.86 (*s*, 3H, H11), 3.80-3.76 (*d*, *J*= 11.1 Hz, 1H, H9),3.70-3.65 (*d,d*, *J*= 7.9 Hz, *J*= 9.0 Hz, 1H, H3) 3.51-3.48 (*d*, *J*= 8.0 Hz, 1H, H7), 3.08 (*s*, 1H, NH). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.5 (C4), 173.4 (C6), 171.6 (C10), 136.0 (C13), 133.9 (C17), 131.7 (C19), 129.5 (C14), 128.6 (C15), 128.3 (C16), 126.7 (C18),125.9 (C20), 72.5 (C9), 64.0 (C11), 63.1 (C2), 61.9 (C8), 61.5 (C7), 51.3 (C3). IR (ATR, cm^{-1}) vmax: 3468.5 (-O-H); 3330.9 (N-H); 2958.2 (-C-H); 1707.5 (O=C-NPh); 1597.8 (C=C); 1376.9 (C-O); 1280.5 (C-OH). MS (DART): m/z: 415.8420 [M+1]. HRMS (DART): calc. for $C_{21}H_{19}ClN_2O_5$ [M+] 414.0982; found 415.1057 [M+1] .



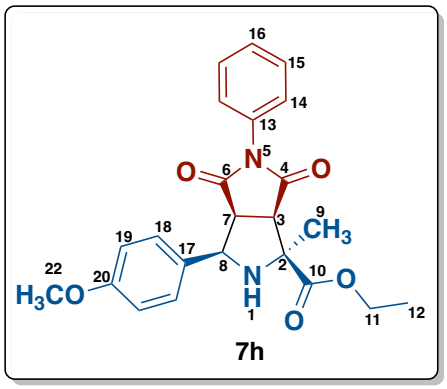
(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-3-(4-fluorophenyl)-1-methyl-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7e). solid white (74 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.43-7.31 (*m*, 5H, H19, H14, H16), 7.09-7.01 (*m*, 4H, H15, H18), 4.86–4.83 (*d*, *J*= 9.0 Hz, 1H, H8), 4.36–4.29 (*q*, *J*= 7.0 Hz, *J*= 14.1 Hz, 2H, H11), 3.67–3.63 (*dd*, *J*= 7.7 Hz, *J*= 9.1 Hz, 1H, H3), 3.44-3.42 (*d*, *J*= 7.7 Hz, 1H, H7), 2.56 (*s*, 1H, NH) 1.64 (*s*, 3H, H9) 1.38-1.36 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.7 (C4), 173.6 (C6), 172.3 (C10), 164.2 (C20), 160.9 (C17), 132.8 (C13), 131.5 (C19), 129.1 (C14), 128.9 (C15), 128.8 (C16), 126.1 (C18), 67.5 (C11), 61.9 (C2), 61.5 (C8), 55.4 (C7), 50.0 (C3), 24.0 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3337.1 (N-H); 2982.3 (-CH); 1729.8 (O=C-CH_2CH_3); 1703.9 (O=C-NPh); 1604.2 (C=C); 1390.1 (C-O). MS (DART): m/z: 397.4184 [M+1]. HRMS (DART): calc. for $C_{22}H_{21}FN_2O_4$ [M+] 396.1485; found 397.1576 [M+1].



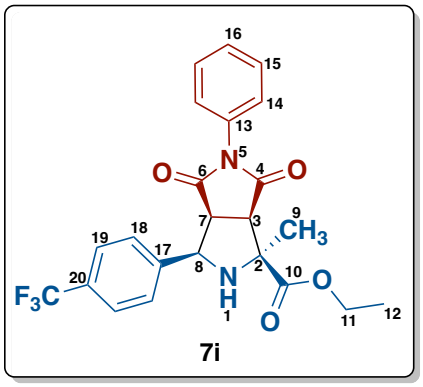
(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-1-methyl-4,6-dioxo-5-phenyl-3-(1-ferrocenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7f). solid yellow (56 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.38-7.28 (*m*, 3H, H15, H16), 7.08-7.05 (*m*, 2H, H14), 4.67-4.61 (*t, J= 8.3* Hz 1H, H8) 4.35–4.33 (*m*, 2H, H11), 4.22-4.17 (*m*, 8H, H18, H19, H20, Cp), 3.55-3.50 (*t*, *J*= 6.9Hz, 1H, H7), 3.43-3.41 (*d*, *J*= 7.7 Hz, 1H, H3) 2.90-2.88 (*d*, *J*= 7.7 Hz, 1H, NH), 1.62 (*s*, 3H, H9) 1.40-1.35 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.9 (C4), 173.8 (C6), 172.6 (C10), 131.6 (C13), 128.9 (C15), 128.3 (C16), 126.1 (C14), 84.7 (C2), 69.0 (CCp), 68.6 (C20), 68.1 (C19), 67.4 (C2), 64.7 (C18), 62.0 (C11), 59.7 (C8), 57.2 (C3), 50.7 (C7), 25.0 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3341.8 (N-H); 3074.8 (=C-H); 2981.1 (-CH); 1711.4 (O=C-NPh); 1597.7 (C=C); 1375.3 (C-O). MS (DART): m/z: 487.3490 [M+1]. HRMS (DART): calc. for $C_{26}H_{26}FeN_2O_4$ [M+] 486.1242; found 487.1324 [M+1].



(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-1-methyl-4,6-dioxo-5-phenyl-3-(thien-2-yl)octahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7g). solid white (%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.41-7.31 (*m*, 3H, H20, H14), 7.24-7.22 (*d,d, J*= 5.1 Hz, *J*= 1.2 Hz, 1H, H19), 7.16-7.11 (*m*, 3H, H15, H16), 7.01-6.98 (*d,d, J*= 5.1 Hz, *J*= 4.0 Hz, 1H, H18), 5.16-5.11 (*d,d, J*= 8.8 Hz, *J*= *7.5* Hz 1H, H8) 4.34–4.27 (*q*, *J*= 14.0 Hz, *J*= 6.7 Hz, 2H, H11), 3.67–3.61 (*dd*, *J*= 9.1 Hz, *J*= 7.7 Hz, 1H, H3), 3.44-3.41 (*d*, *J*= 8.3 Hz, 1H, H7), 2.78-2.76 (*d*, *J*= 7.3 Hz, 1H, NH) 1.60 (*s*, 3H, H9) 1.37-1.32 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.6 (C4), 173.3 (C6), 171.9 (C10), 141.1 (C17), 131.7 (C20), 129.0 (C14), 129.5 (C19), 127.1 (C18), 126.3 (C15), 125.4 (C16), 125.1 (C13), 67.2 (C11), 61.9 (C2), 58.2 (C8), 55.4 (C7), 50.1 (C3), 23.9 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3333.4 (N-H); 3119.6 (=C-H); 2987.7 (-CH); 1738.8 (O=C-CH_2CH_3); 1712.9 (O=C-NPh); 1598.6 (C=C); 1385.0 (C-O). MS (DART): m/z: 385.4500 [M+1]. HRMS (DART): calc. for $C_{20}H_{20}N_2O_4S$ [M+] 384.1144; found 385.1208 [M+1].

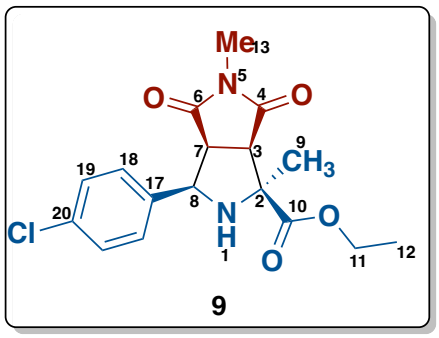


(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-3-(4-methoxyphenyl)-1-methyl-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (7h). solid white (79 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.40-7.30 (*m*, 5H, H14, H15, H16), 7.12-7.08 (*d, J*= 10.4 Hz, 2H, H18), 6.89-6.86 (*d*, *J*= 8.8 Hz, 2H, H19), 4.84-4.81 (*d, J*= *9.1* Hz 1H, H8) 4.36–4.27 (*q*, *J*= 14.3 Hz, *J*= 7.1 Hz, 2H, H11), 3.77 (*s*, 3H, H23) 3.66-3.60 (*d,d*, *J*= 9.1 Hz, *J*= 7.7 Hz, 1H, H7), 3.44-3.41 (*d*, *J*= 7.7 Hz, 1H, H3) 2.64 (s, 1H, NH), 1.63 (*s*, 3H, H9) 1.38-1.33 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.9 (C4), 173.8 (C6), 172.4 (C10), 159.5 (C17), 131.6 (C13), 129.0 (C14), 128.9 (C19), 128.5 (C18), 128.3 (C15), 126.1 (C16), 113.9 (C20), 67.5 (C11), 62.1 (C22), 61.9 (C2), 55.8 (C8), 55.2 (C7), 50.4 (C3), 24.0 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3258.7 (N-H); 3034.1 (=C-H); 2987.8 (-CH); 1747.1 (O=C-CH_2CH_3); 1707.1 (O=C-NPh); 1610.8 (C=C); 1383.6 (C-O). MS (DART): m/z: 409.4540 [M+1]. HRMS (DART): calc. for $C_{23}H_{24}N_2O_5$ [M+] 408.1685; found 409.1747 [M+1].



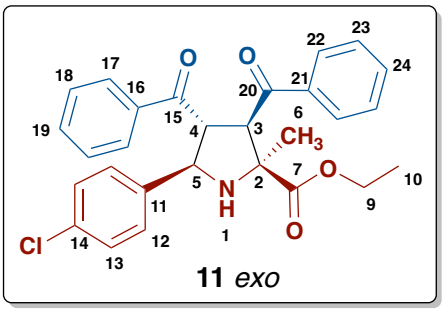
7i

(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-1-methyl-4,6-dioxo-5-phenyl-3-(4-(trifluoromethyl) phenyl) octahydropyrrolo [3,4-*c*]pyrrole-1-carboxylate (7i). solid white (85 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.62-7.58 (*m*, 4H, H19, H14), 7.55-7.38 (*m*, 3H, H15, H16), 7.06-7.03 (*m*, 2H, H18), 4.92–4.87 (*t*, *J*= 8.1 Hz, 1H, H8), 4.36–4.29 (*q*, *J*= 15.3 Hz, *J*= 7.1 Hz, 2H, H11), 3.75–3.72 (*dd*, *J*= 8.9 Hz, *J*= 7.7 Hz, 1H, H3), 3.46-3.44 (*d*, *J*= 7.7 Hz, 1H, H7), 2.61-2.59 (*d*, *J*= 7.0 Hz, 1H, NH) 1.66 (*s*, 3H, H9) 1.39-1.34 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ (ppm) 174.6 (C4), 173.4 (C6), 172.2 (C10), 141.1 (C20), 131.4 (C17), 130.6 (C13), 130.2 (C19), 129.1 (C14), 128.7 (C15), 127.7 (C16), 126.1 (C18), 125.6-125.3 (CF_3), 67.7 (C11), 62.0 (C2), 61.7 (C8), 55.3 (C7), 50.0 (C3), 24.0 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3334.2 (N-H); 3075.3 (=C-H); 2984.8 (-CH); 1737.6 (O=C-CH_2CH_3); 1716.8 (O=C-NPh); 1620.7 (C=C); 1370.1 (C-O). MS (DART): m/z: 447.4262 [M+1]. HRMS (DART): calc. for $C_{23}H_{21}F_3N_2O_4$ [M+] 446.1453; found 447.1543 [M+1].

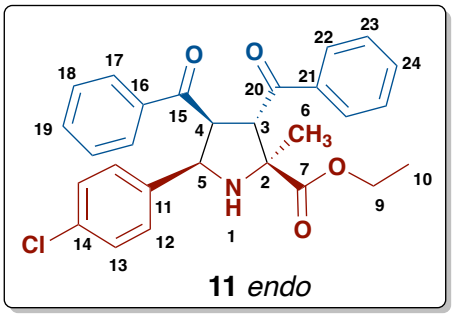


9

(±)- ethyl (1*S*,3*R*,3a*S*,6a*R*)-3-(4-chlorophenyl)-1,5-dimethyl-4,6-dioxooctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (9) solid white (90 %). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ(ppm) 7.32-7.30 (*d*, *J*= 8.7 Hz, 2H, H19), 7.27-7.24 (*d*, *J*= 8.9 Hz, 2H, H18), 4.75–4.70 (*t*, *J*= 8.5 Hz, 1H, H8), 4.36–4.31 (*q*, *J*= 5.7Hz, *J*= 14.4 Hz, 2H, H11), 3.55–3.50 (*dd*, *J*= 7.7 Hz, *J*= 8.8 Hz, 1H, H3), 3.28-3.26 (*d*, *J*= 7.5 Hz, 1H, H7), 2.81 (s, 3H, H13), 2.46-2.44 (*d*, *J*= 7.3 Hz, 1H, NH) 1.60 (*s*, 3H, H9) 1.41-1.36 (*t*, *J*= 7.2 Hz, 3H, H12). ^{13}C NMR (100.0 MHz, $CDCl_3$) δ (ppm) 175.6 (C4), 174.6 (C6), 172.2 (C10), 135.7 (C17), 133.9 (C20), 128.6 (C19), 67.1 (C11), 61.9 (C2), 61.2 (C8), 55.3 (C7), 50.1 (C3), 24.9 (C13), 23.9 (C9), 14.1 (C12). IR (ATR, cm^{-1}) νmax: 3342.9 (N-H); 2990.3 (-CH); 1743.5 (O=C-CH_2CH_3); 1692.8 (O=C-NPh); 1600.1 (C=C); 1384.0 (C-O). MS (DART): m/z: 351.7990 [M+1]. HRMS (DART): calc. for $C_{17}H_{19}ClN_2O_4$ [M+] 350.1033; found 351.1107 [M+1].



(±)- ethyl (2*S*,3*S*,4*S*,5*R*)-3,4-dibenzoil-5-(4-clorophenyl)-2-methylpirrolidin-2-carboxylate (11). Solid white (45 %). NMR ^{1}H (300 MHz, $CDCl_3$) δ(ppm) 8.10-8.07 (*d*, *J*= 8.3 Hz, 2H, H13), 7.59 (*m*, 3H, H19, H18), 7.32-7.26 (*m*, 2H, H22), 7.04 (*s*, 4H, H12, H17), 5.16–5.0 (*m*, 3H, H5, H9), 4.16–4.05 (*m*, 1H, H3), 3.9–3.86 (*m*, 1H, H4), 3.17 (*s*, 1H, NH), 3.0 (*s*, 3H, H6) 1.0-0.95 (*t*, *J*= 7.2 Hz, 3H, H10). NMR ^{13}C (75.0 MHz, $CDCl_3$) δ (ppm) 198.8 (C20), 198.5 (C15), 174.8 (C7), 138.1 (C21), 138.0 (C16), 137.1 (C11), 133.4 (C14), 133.3 (C13), 133.1 (C22), 129.0 (C17), 128.6 (C18), 128.4 (C24), 128.3 (C23), 128.2 (C19), 67.8 (C3), 63.4 (C2), 61.8 (C5), 56.7 (C4), 54.8 (C9), 21.9 (C6), 13.6 (C10).



(±)- ethyl (2*S*,3*R*,4*R*,5*R*)-3,4-dibenzoil-5-(4-clorophenyl)-2-methylpirrolidin-2-carboxylate (11). Solid white (40 %). NMR ^{1}H (300 MHz, $CDCl_3$) δ(ppm) 7.93-7.91 (*d*, *J*= 7.1 Hz 2H, H13), 7.57-7.54 (*m*, 3H, H19, H18), 7.47-7.39 (*m*, 5H, H22, H23, H24), 7.27-7.19 (m, 4H, H12, H17) 4.71–4.69 (*d*, *J*= 7.3 Hz, 1H, H5), 4.56–4.48 (*q*, *J*= 6.3 Hz, 2H, H9), 4.08–3.98 (*m*, 1H, H4), 3.92-3.88 (*m*, 1H, H3), 1.72 (*s*, 3H, H6) 1.03-0.98 (*t*, *J*= 7.1 Hz, 3H, H10). NMR ^{13}C (75.0 MHz, $CDCl_3$) δ (ppm) 200.3 (C20), 199.6 (C15), 173.6 (C7), 138.4 (C21), 137.0 (C16), 136.3 (C11), 133.8 (C14), 133.6 (C13), 129.0 (C22), 128.7 (C17), 128.7 (C18), 128.4 (C24), 70.6 (C3), 66.7 (C2), 61.7 (C5), 60.6 (C4), 60.2 (C9), 20.3 (C6), 13.7 (C10).

12. NMR spectra of the compounds synthesized.

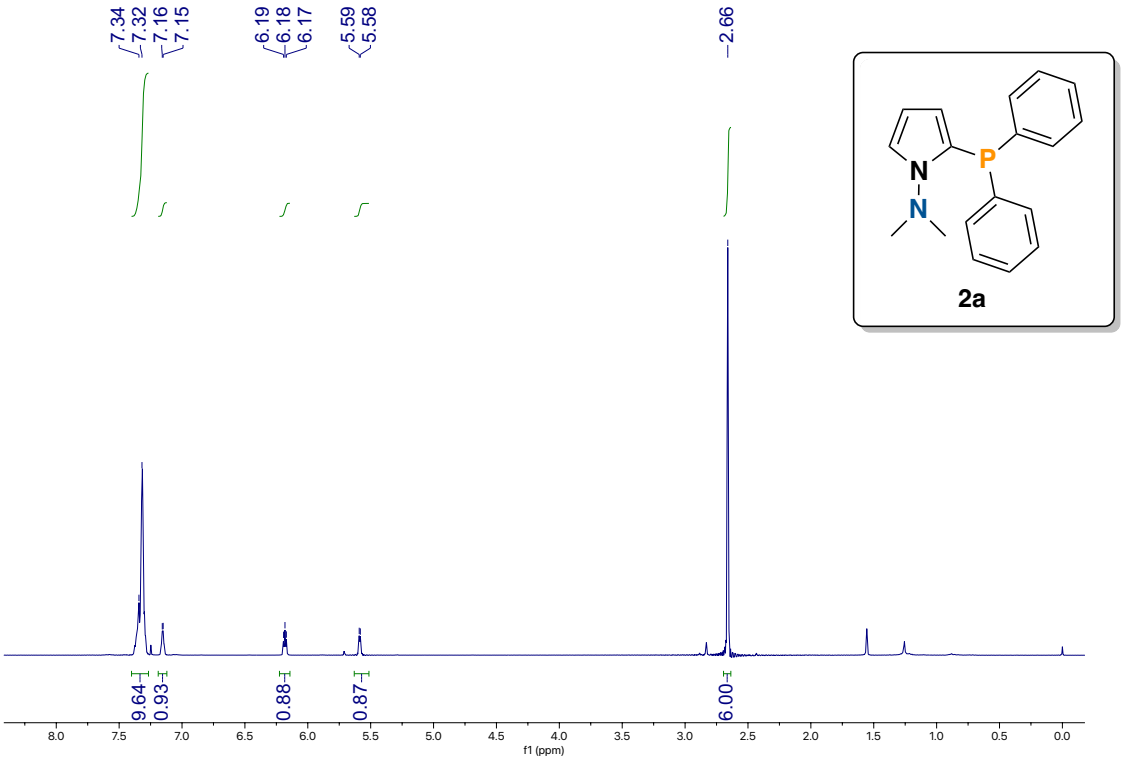


Figure S5. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **2a**.

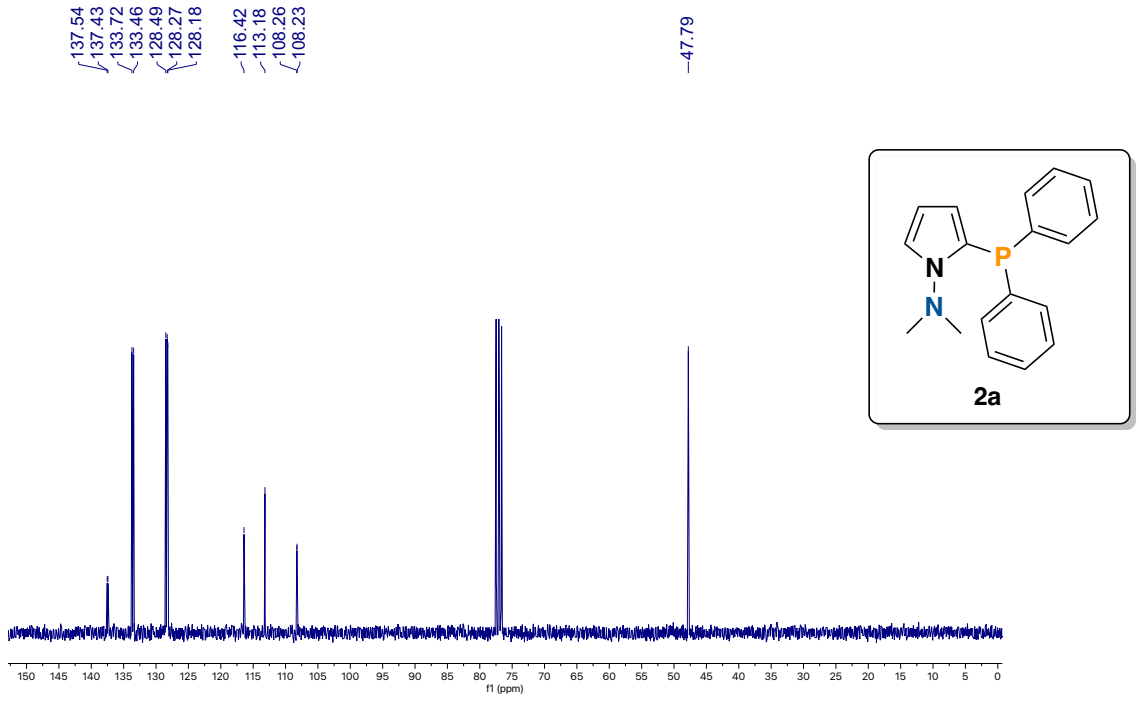


Figure S6. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **2a**

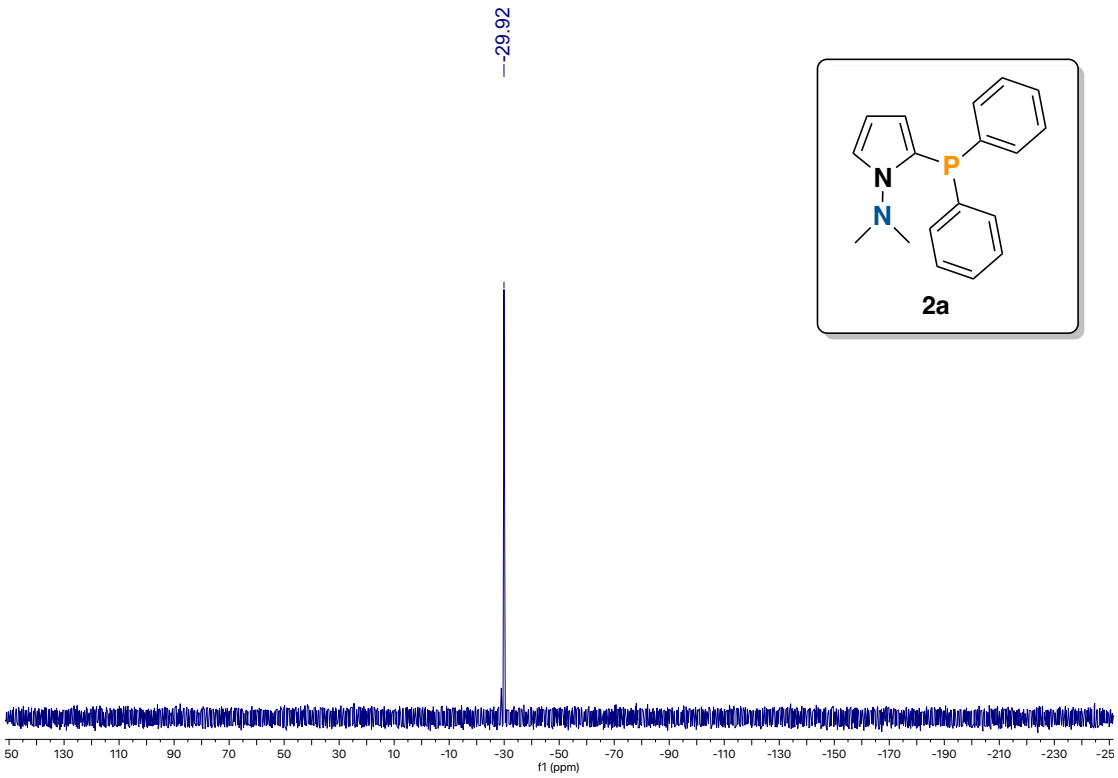


Figure S7. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **2a**

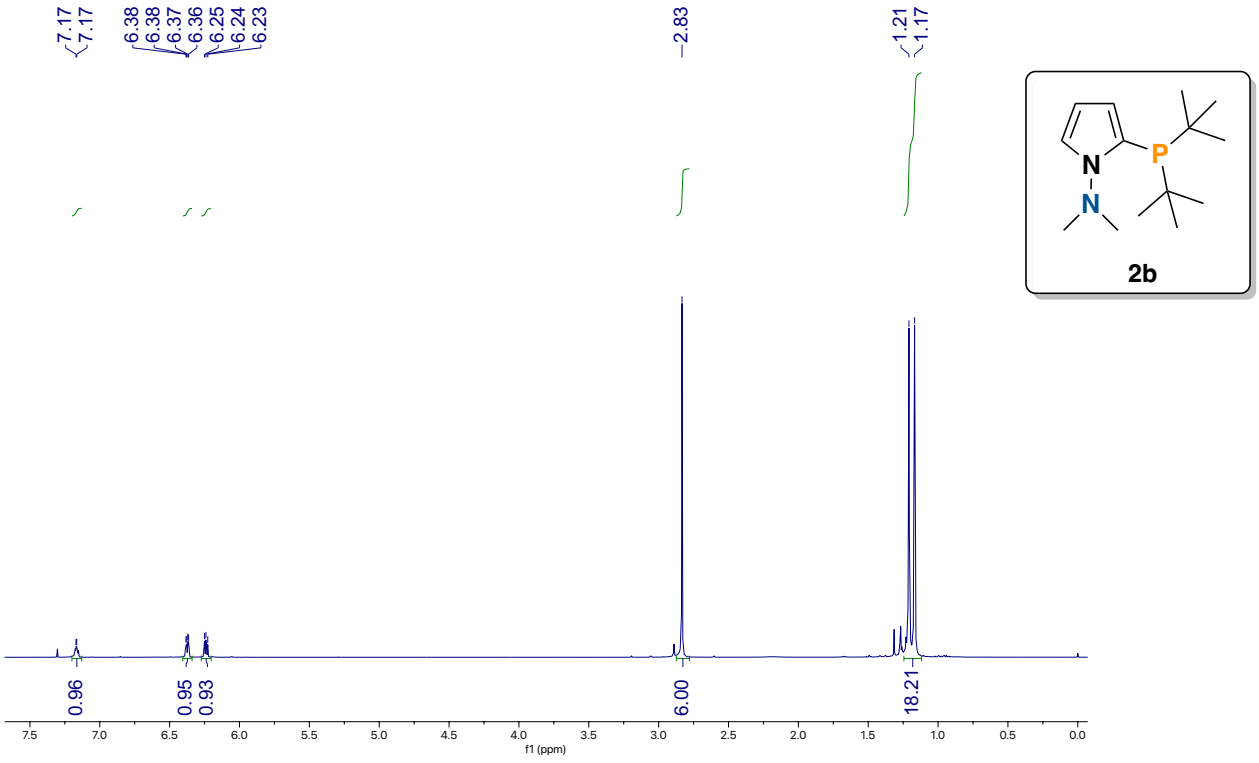


Figure S8. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **2b.**

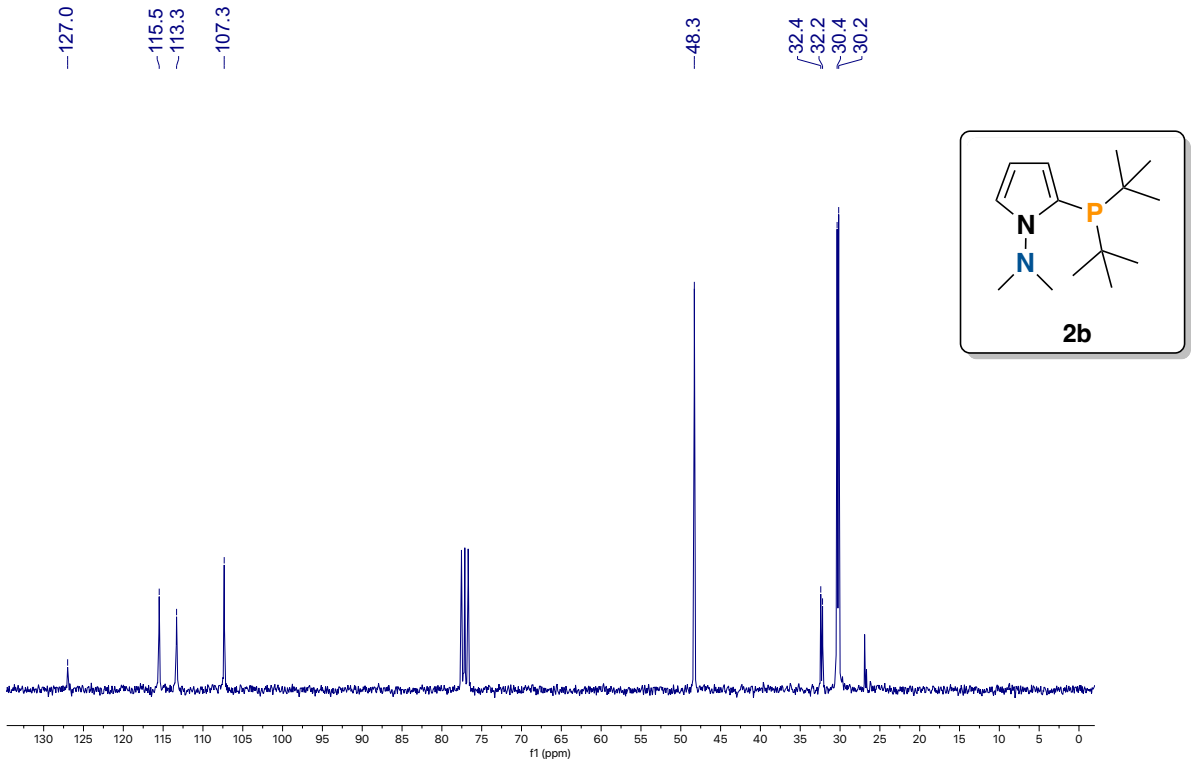


Figure S9. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **2b**

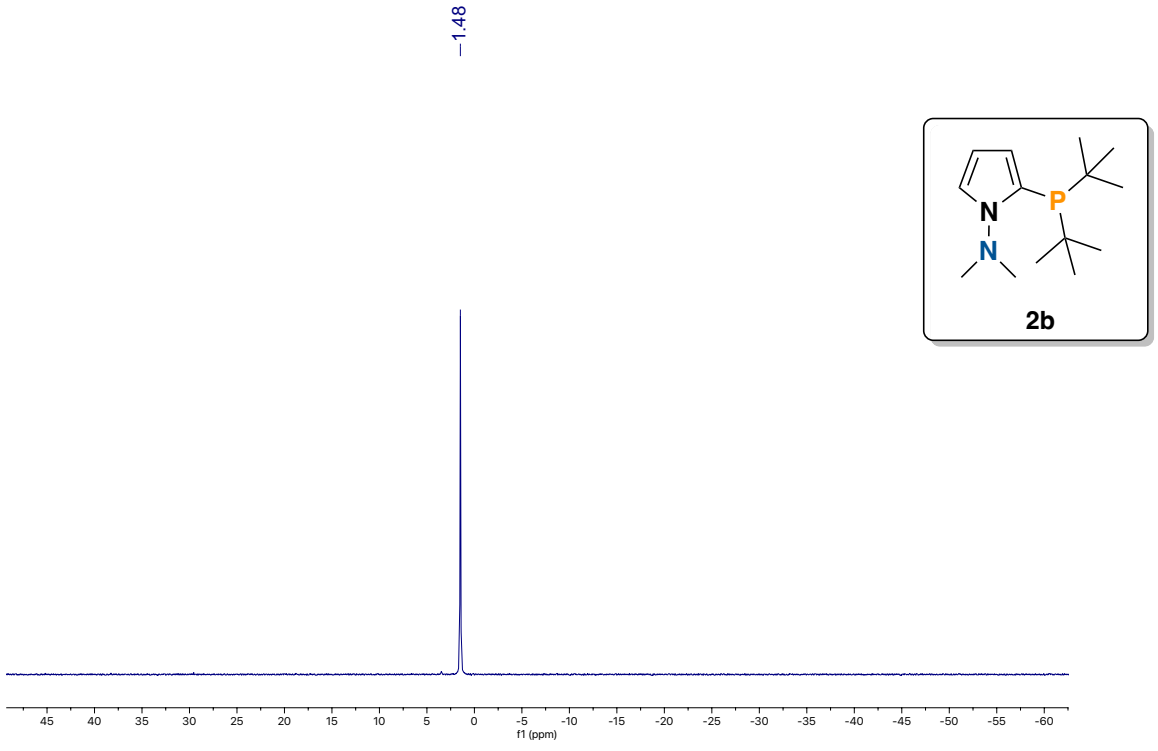


Figure S10. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **2b**

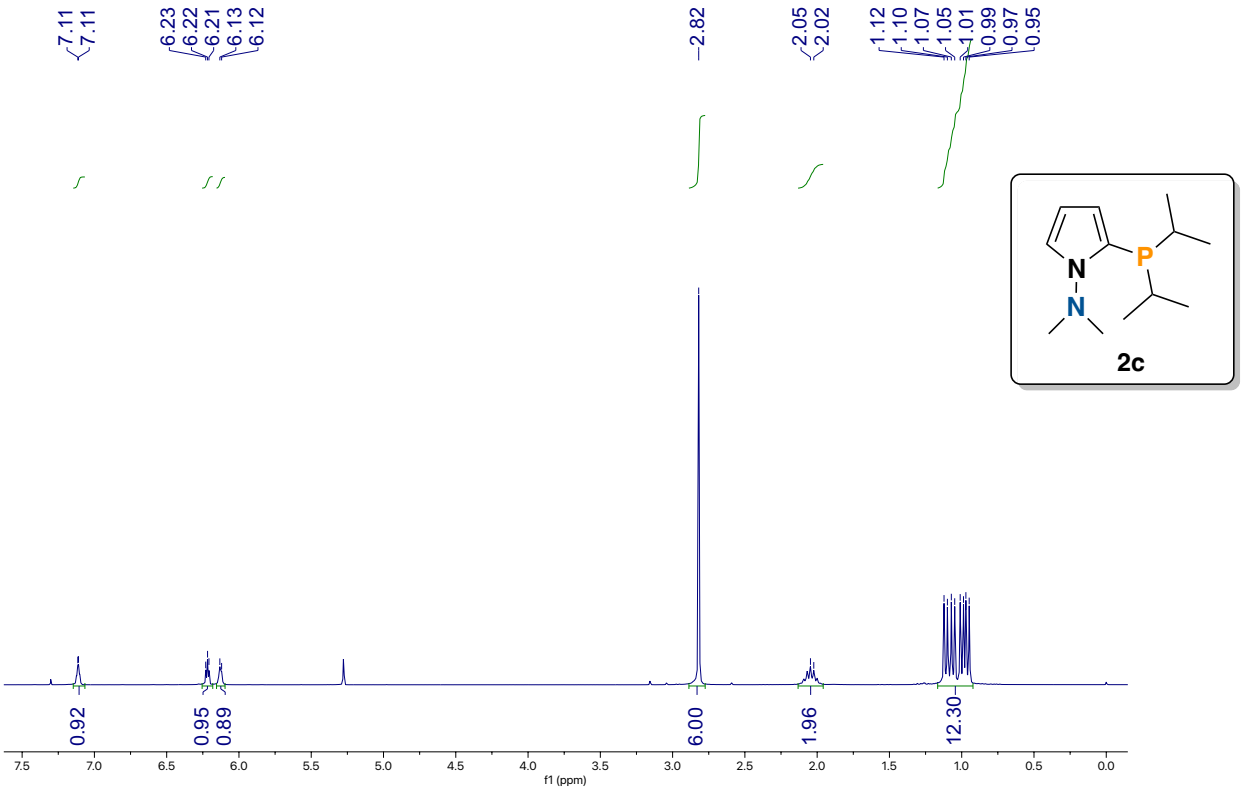


Figure S11. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **2c**

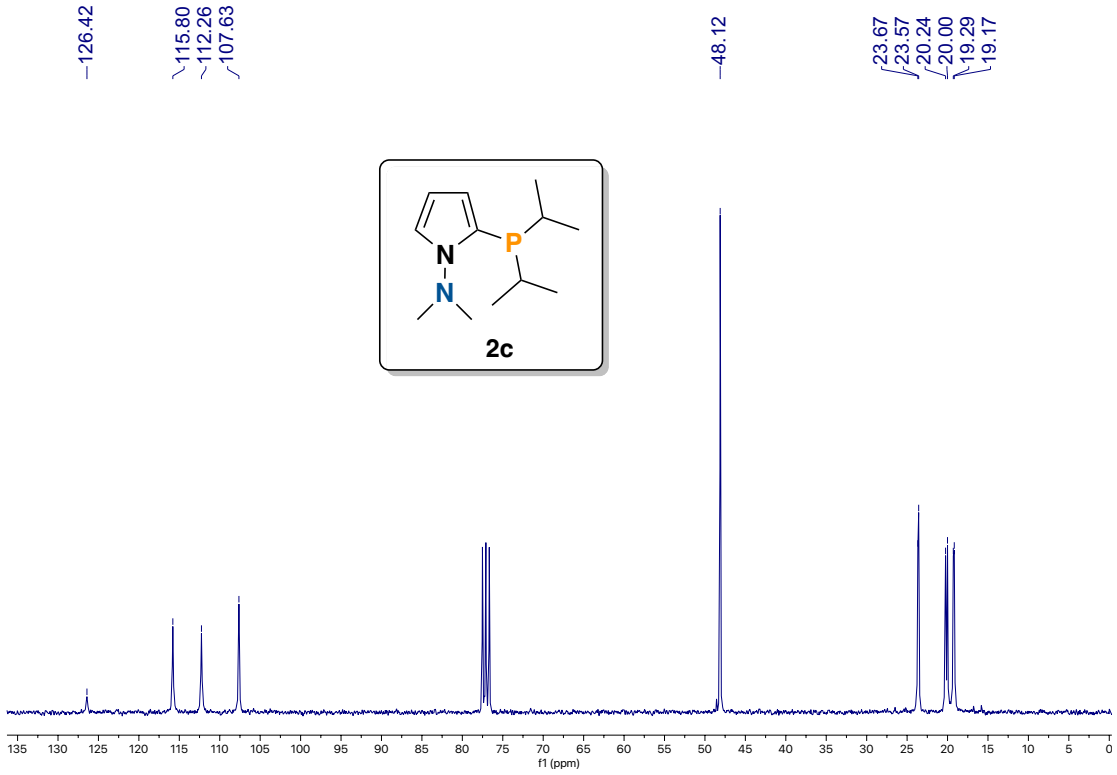


Figure S12. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **2c**

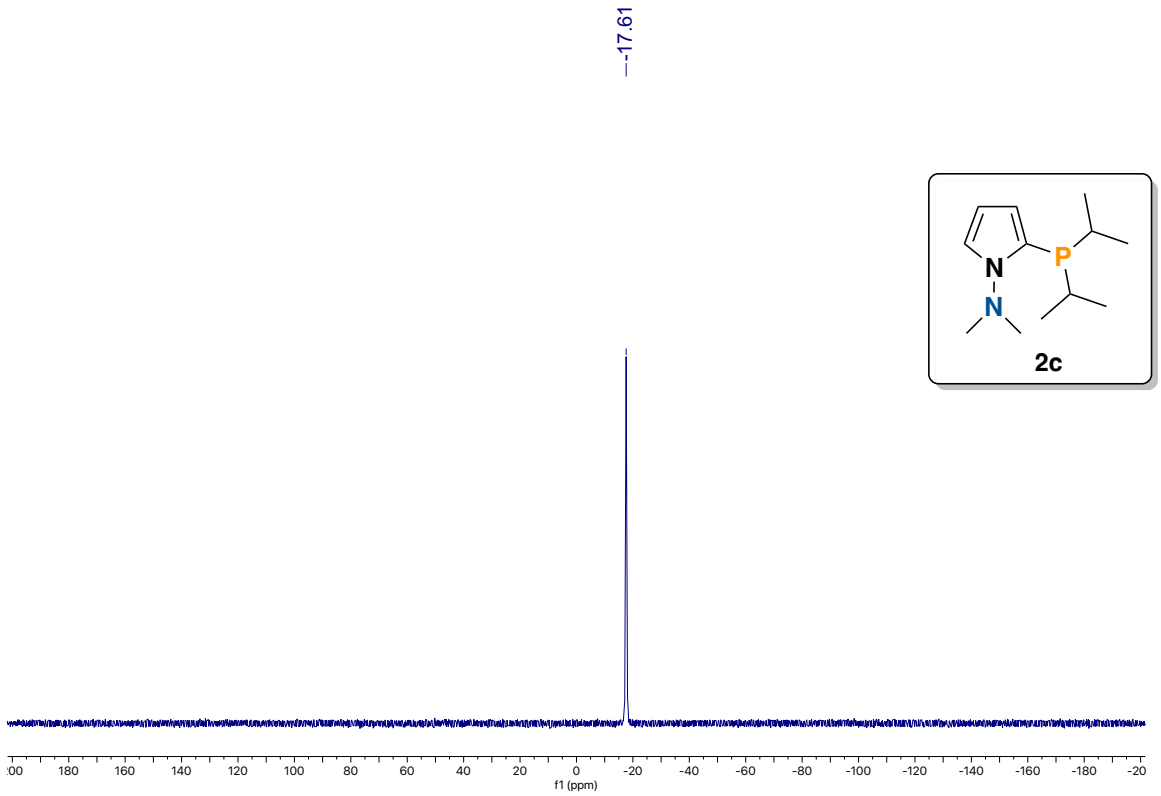


Figure S13. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **2c**

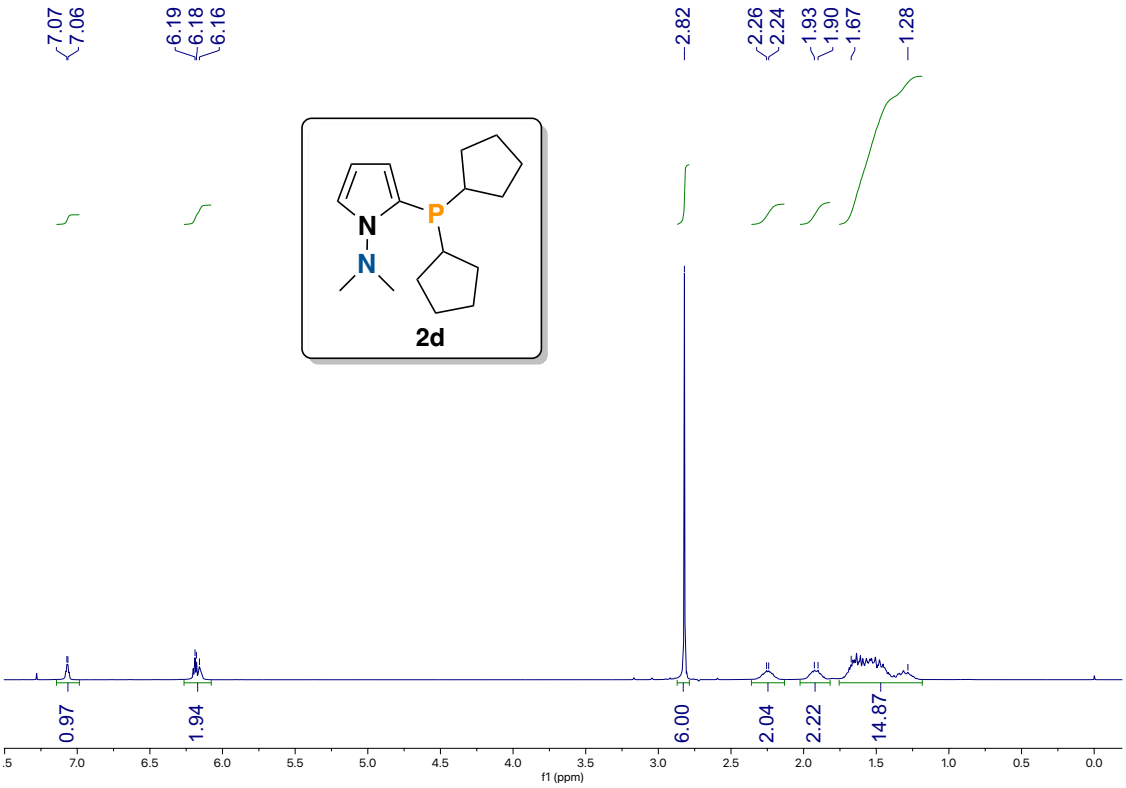


Figure S14. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **2d**

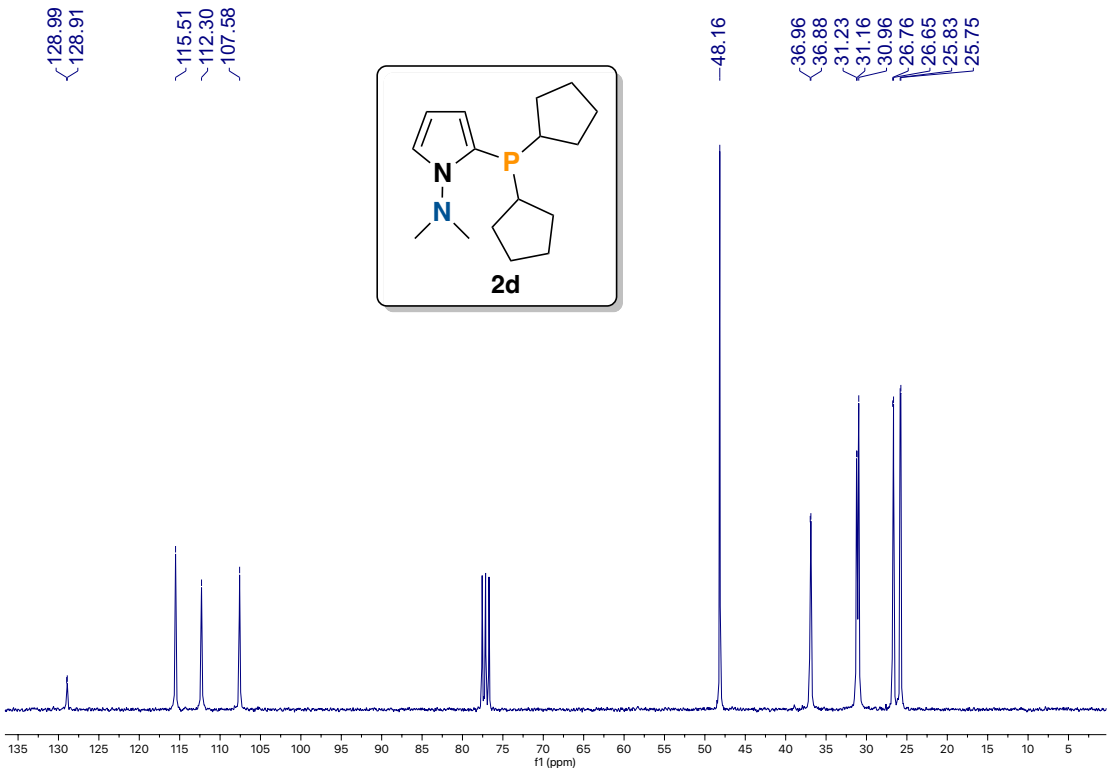


Figure S15. ^{13}C NMR Spectrum (300 MHz, $CDCl_3$) of compound **2d**

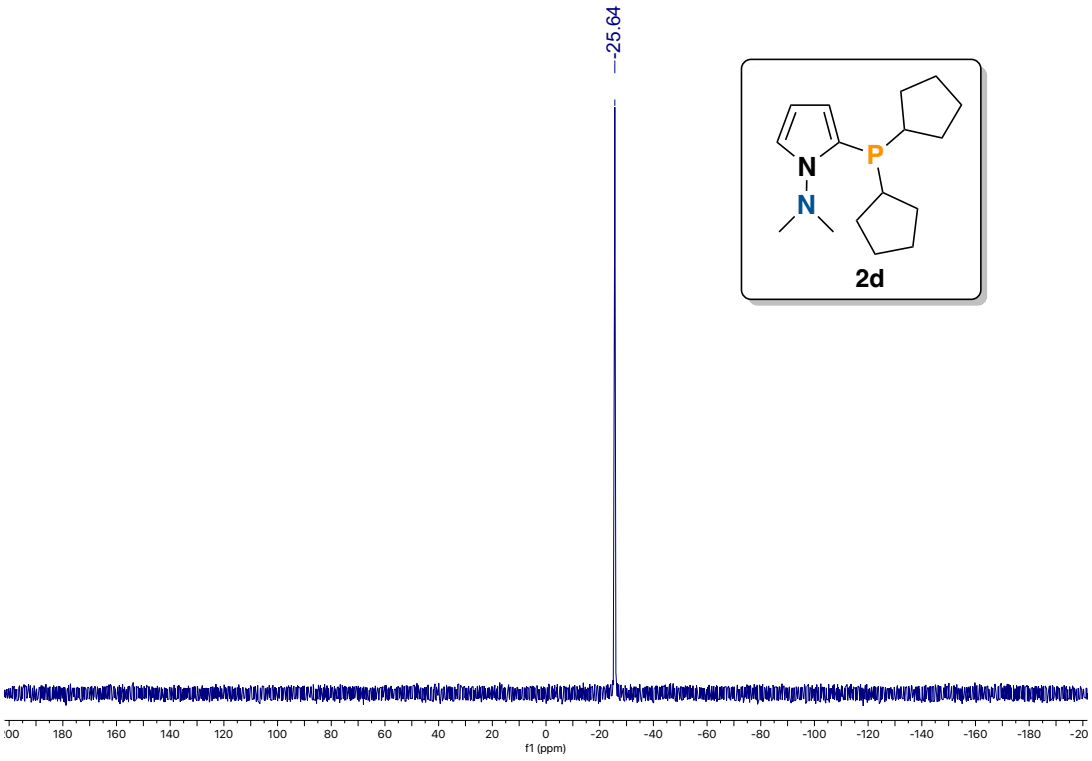


Figure S16. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **2d**

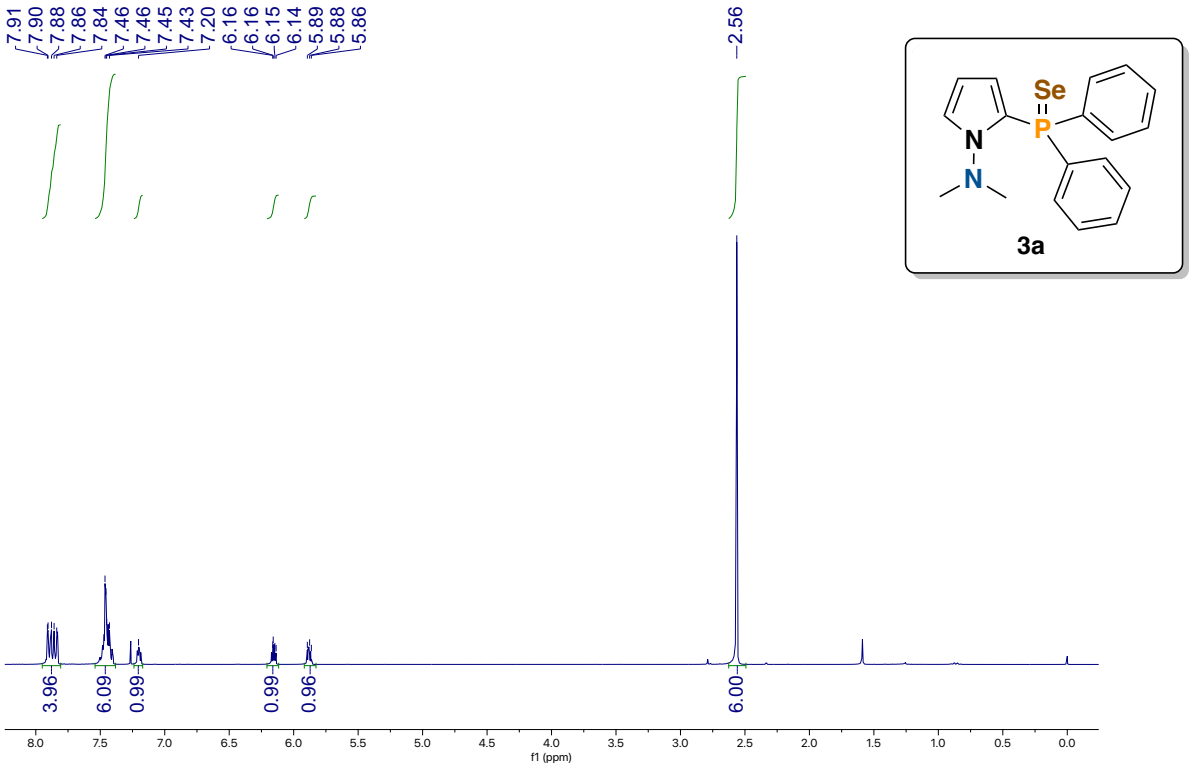


Figure S17. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **3a**

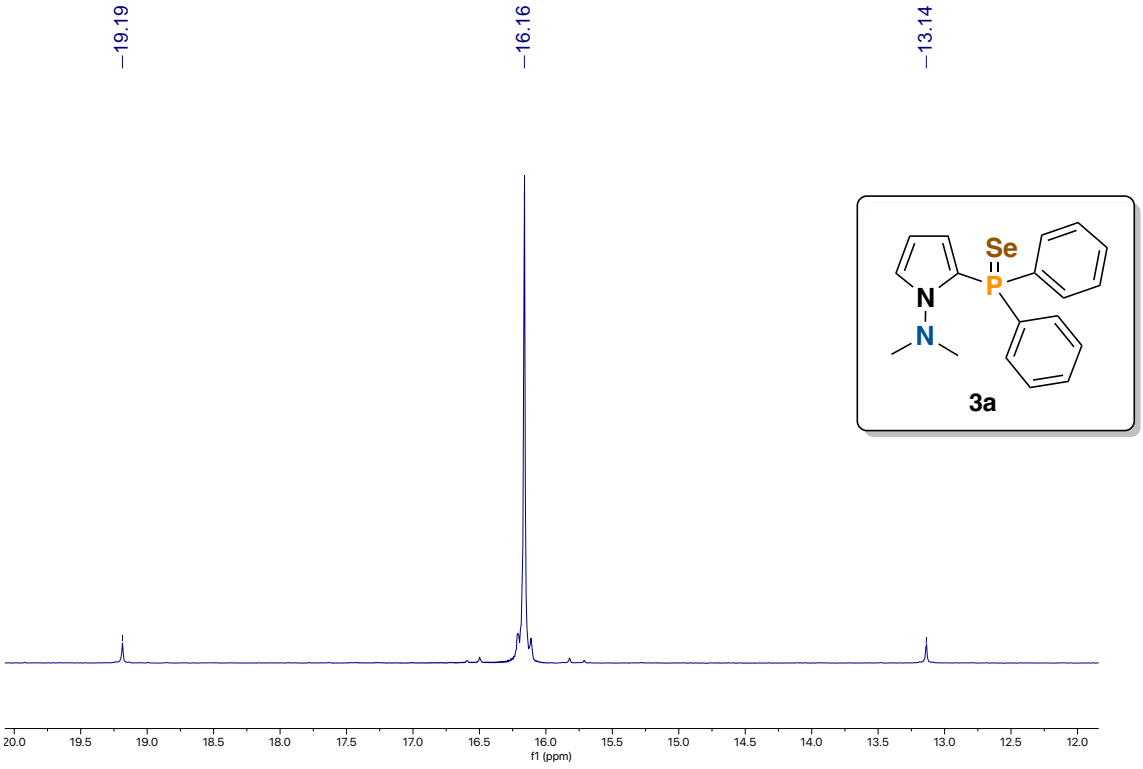


Figure S18. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **3a**

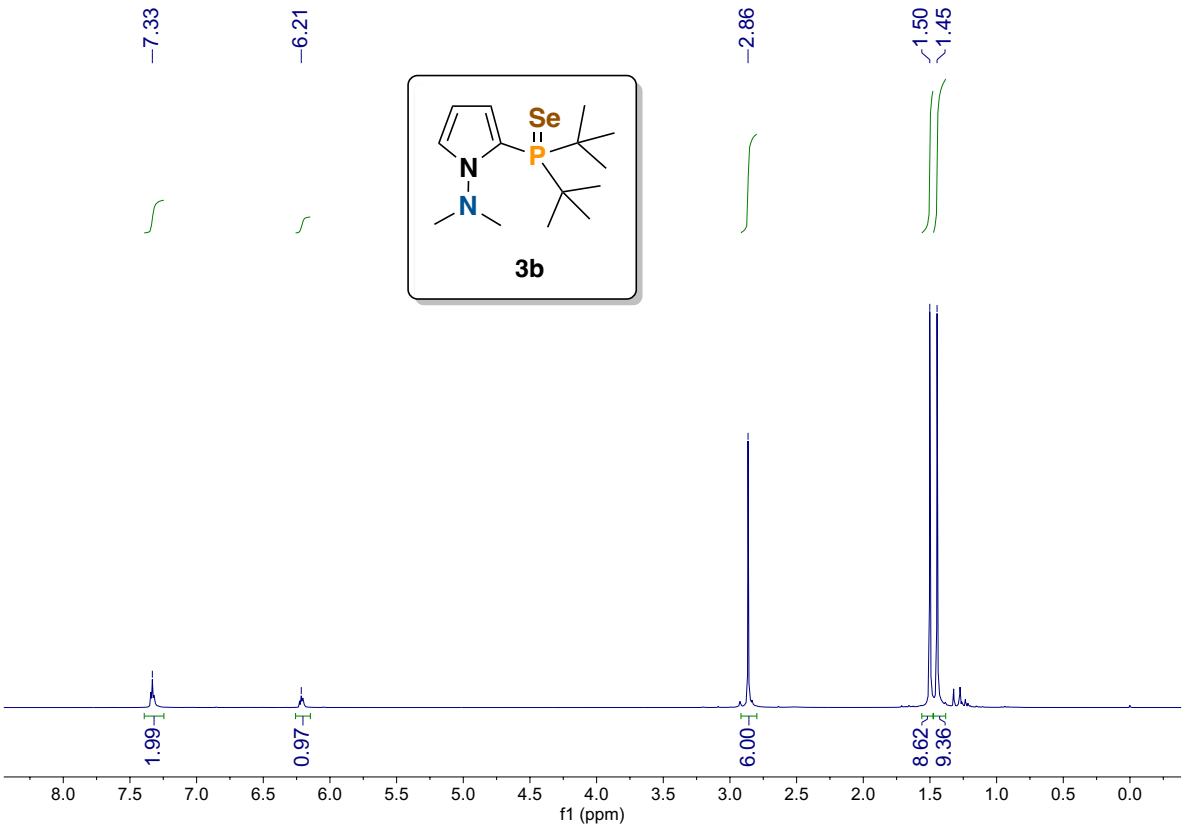


Figure S19. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **3b**

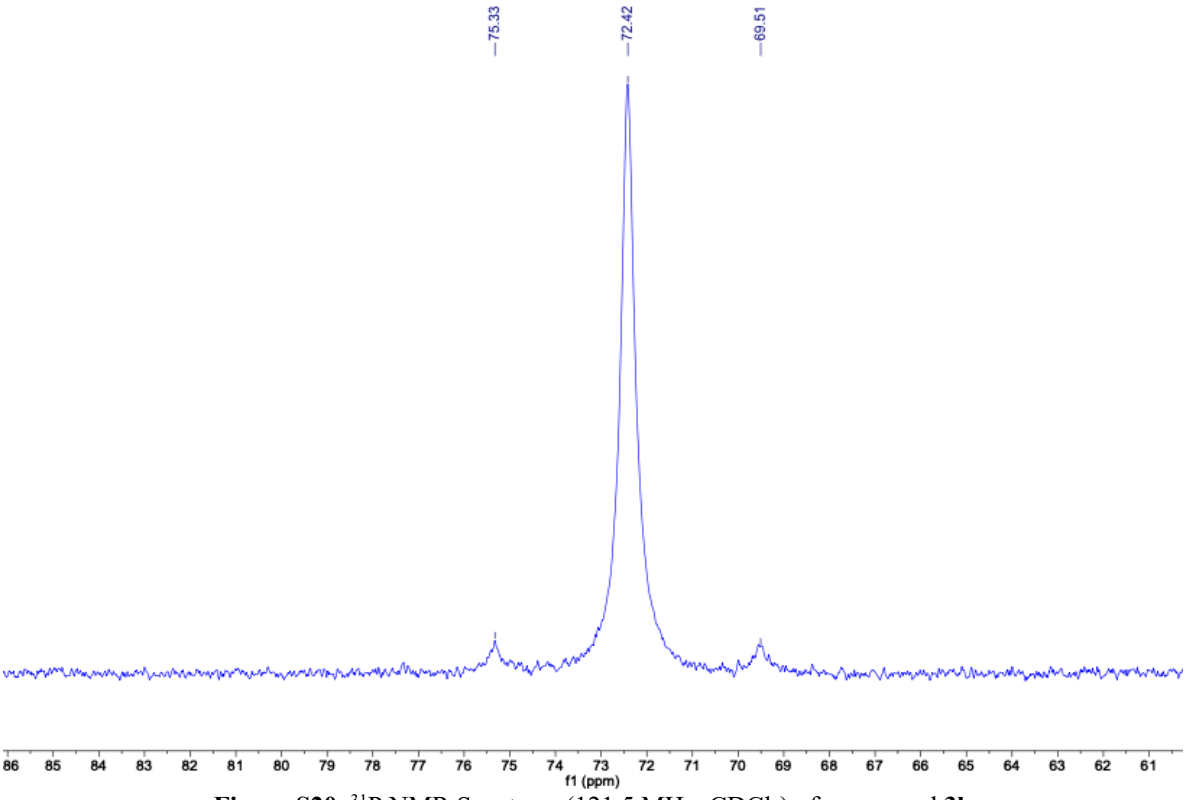


Figure S20. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **3b**

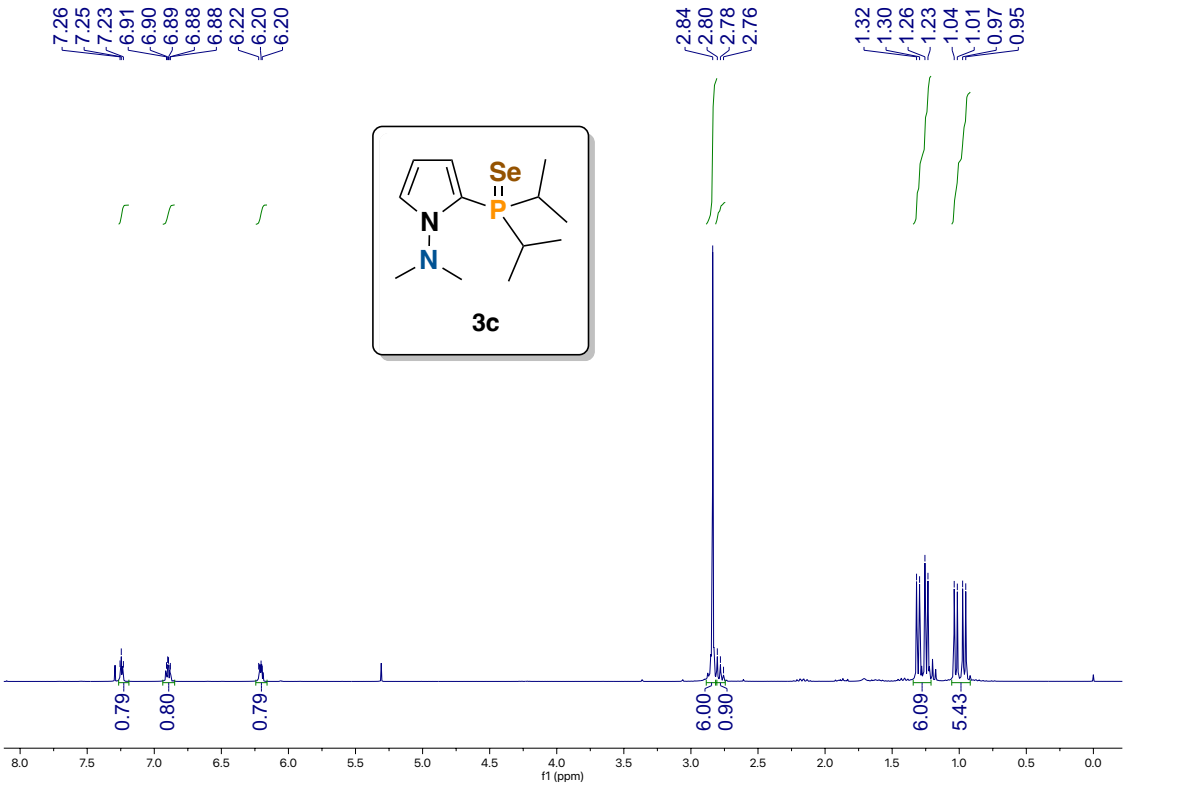


Figure S21. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **3c**

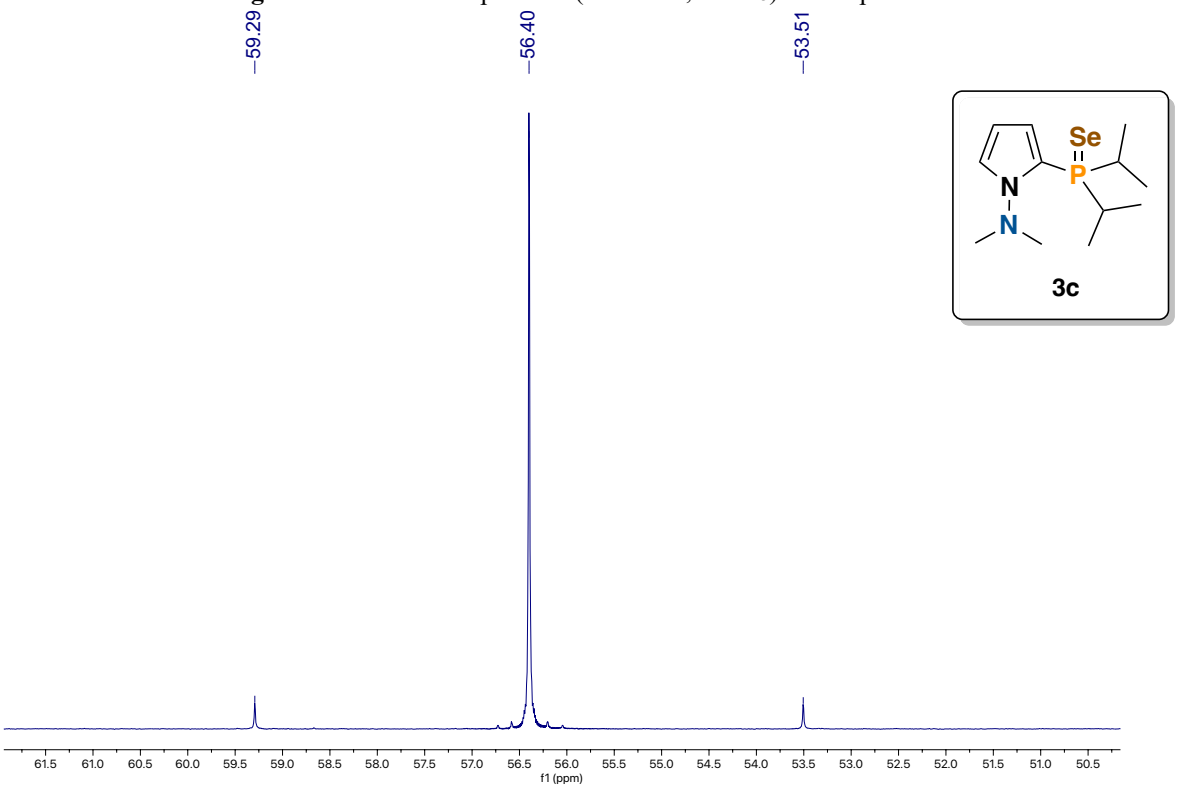


Figure S22. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **3c**

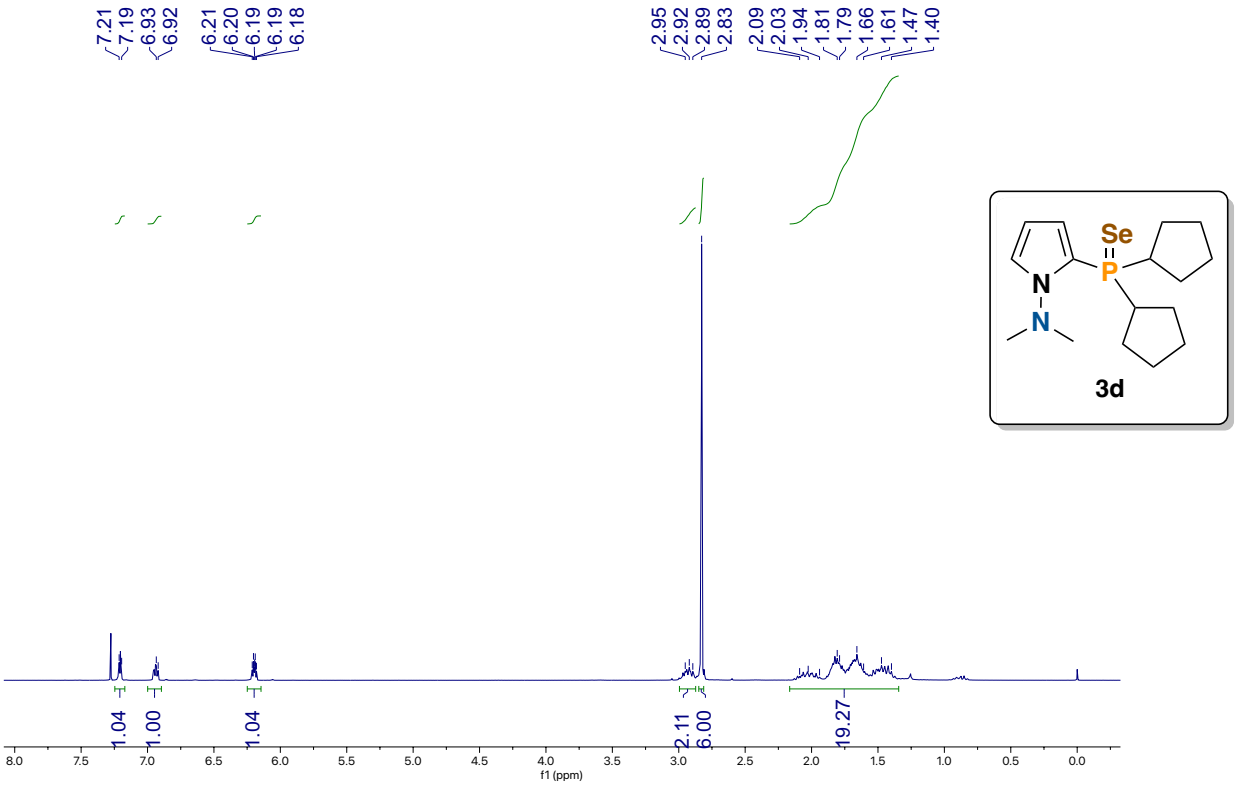


Figure S23. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **3d**

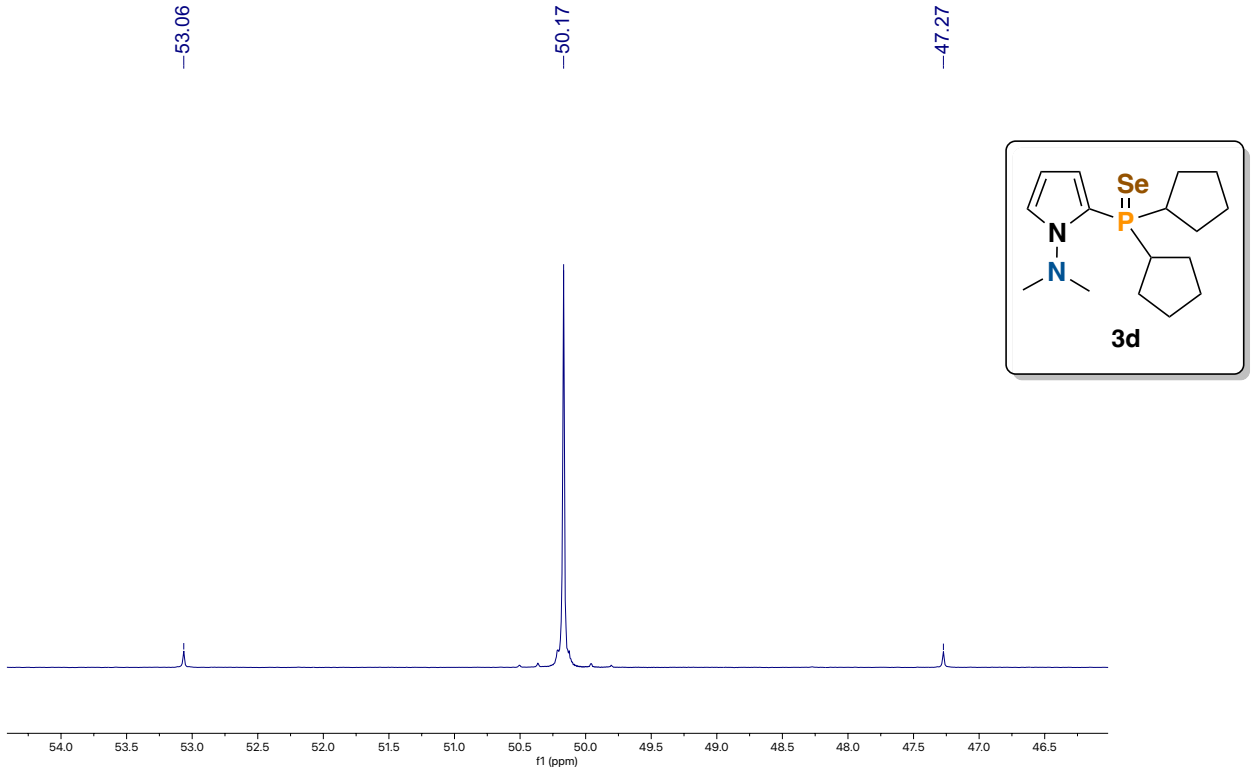


Figure S24. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **3d**

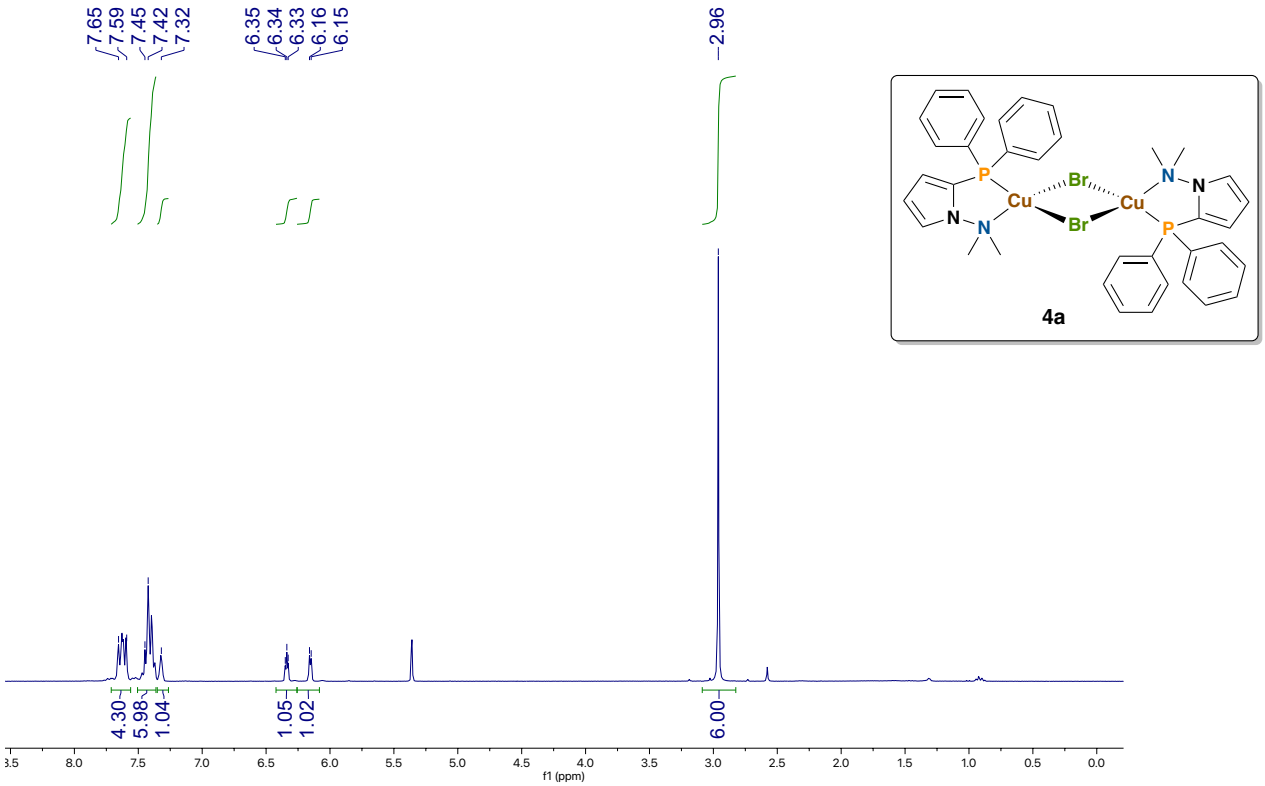


Figure S25. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **4a**

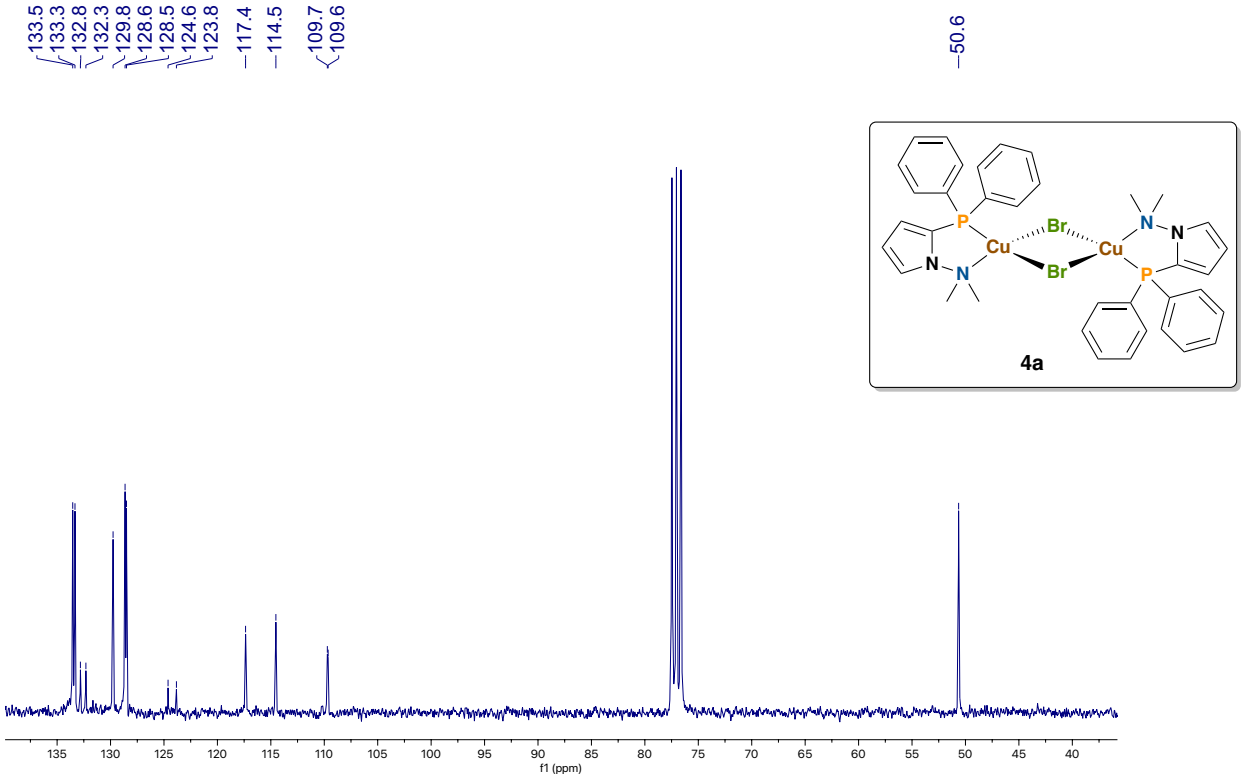


Figure S26. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **4a**

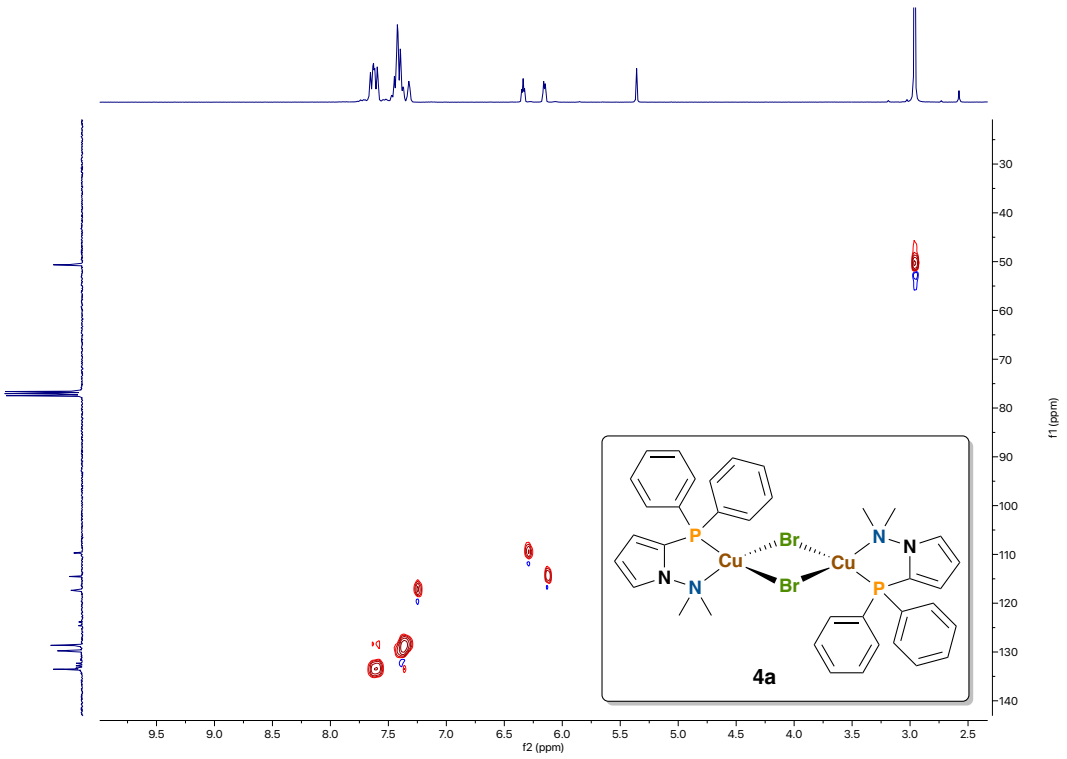


Figure S27. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound **4a**

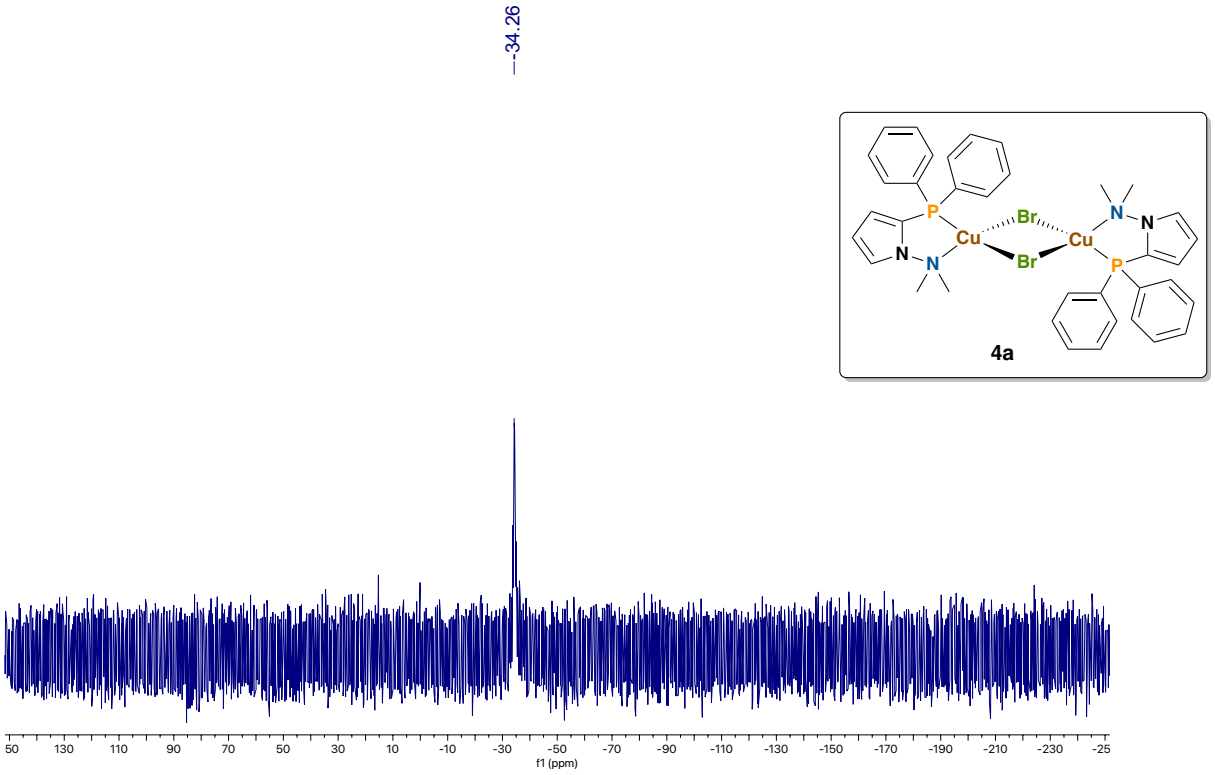


Figure S28. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **4a**

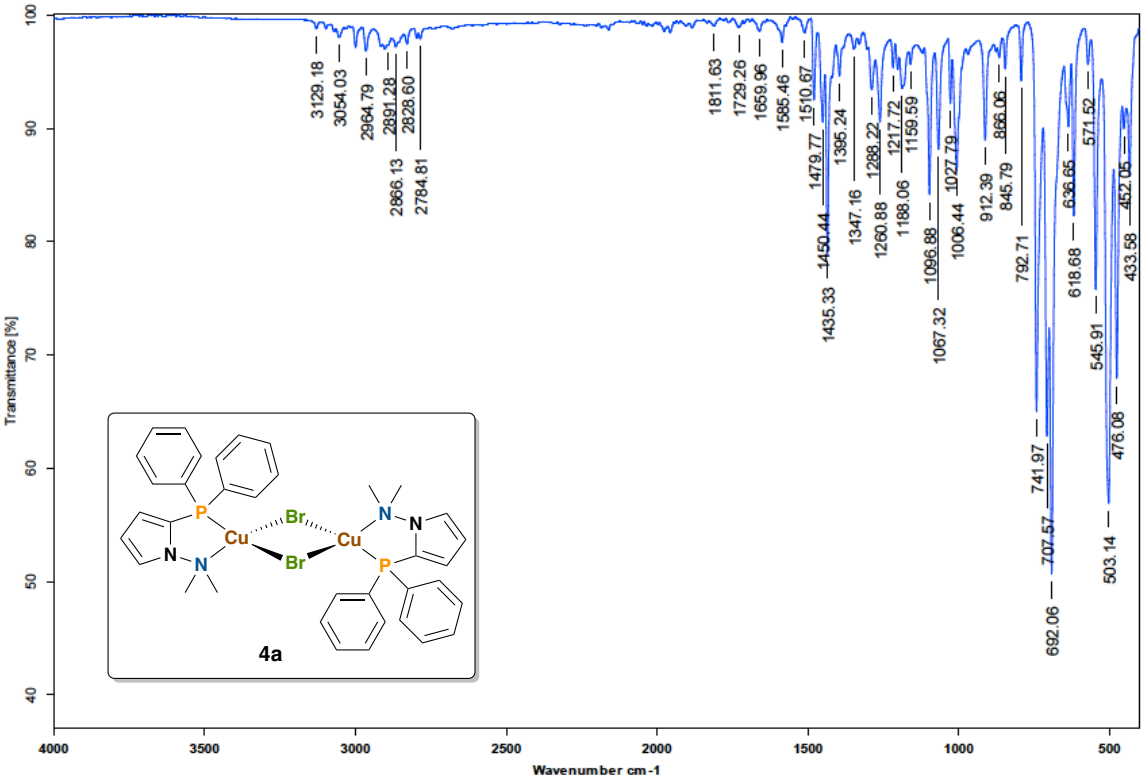


Figure S29. IR Spectrum of compound **4a**

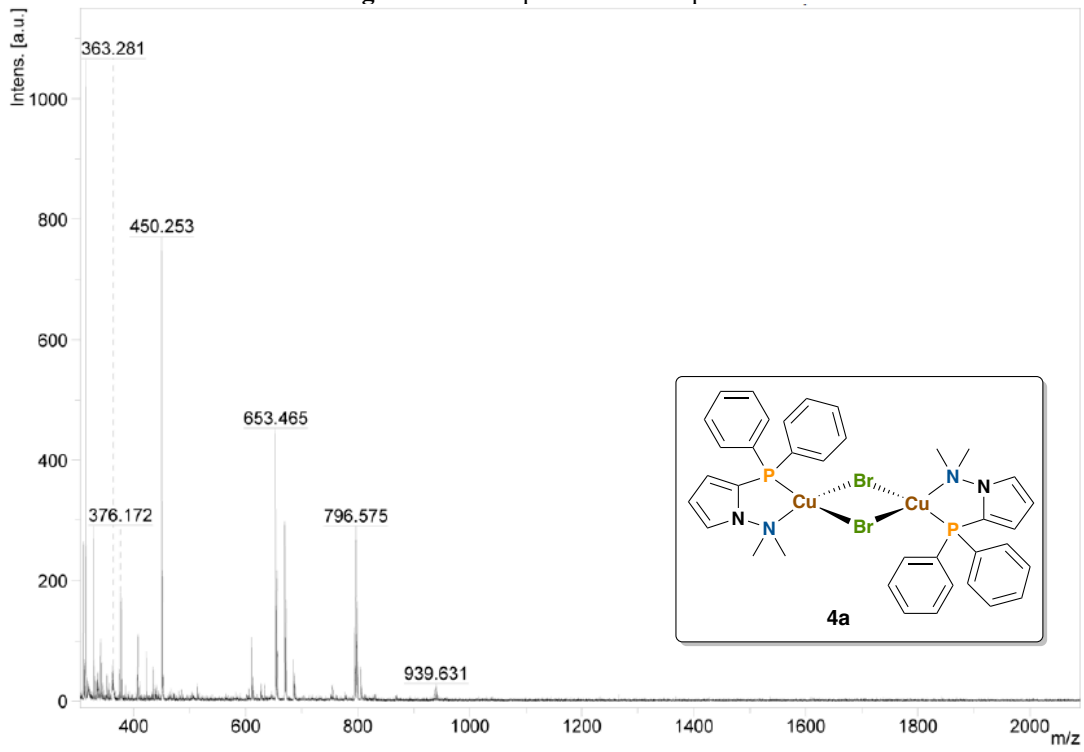


Figure S30. ERSM Spectrum (MALDI-TOF) of compound **4a**

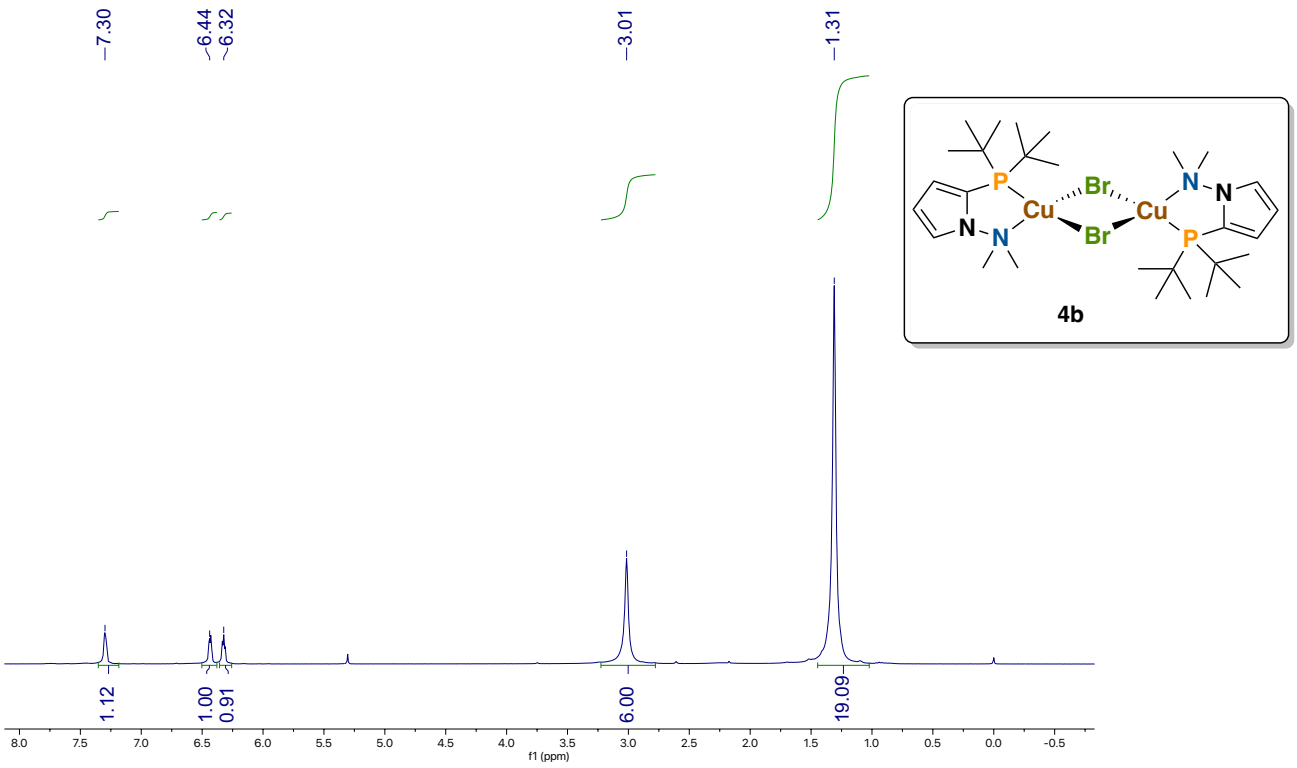


Figure S31. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **4b**

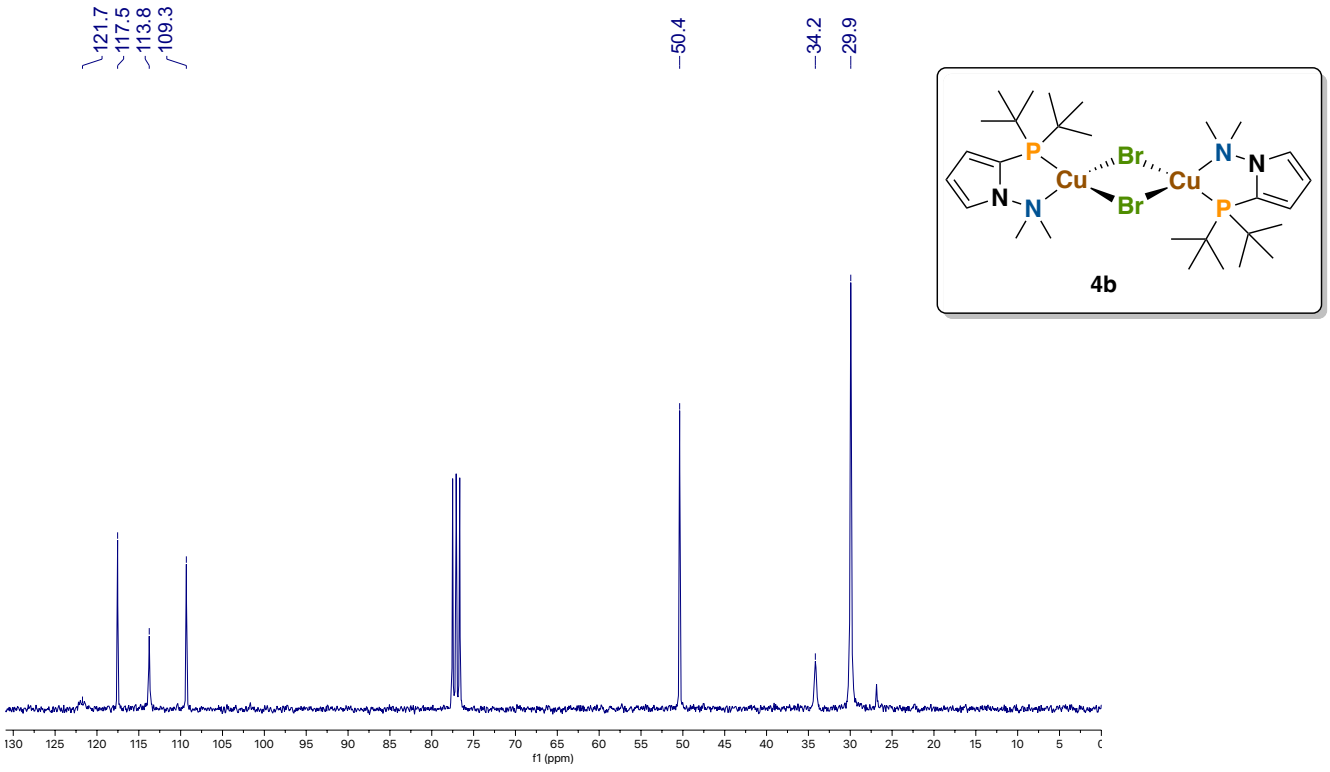


Figure S32. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **4b**

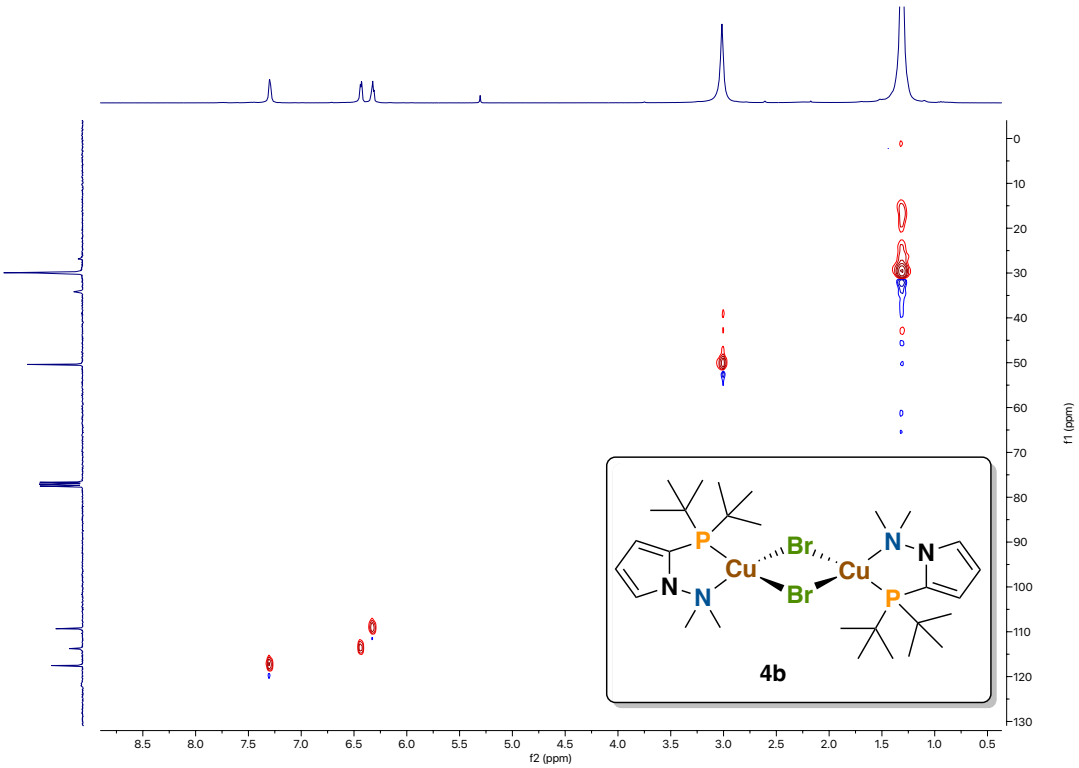


Figure S33. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound **4b**

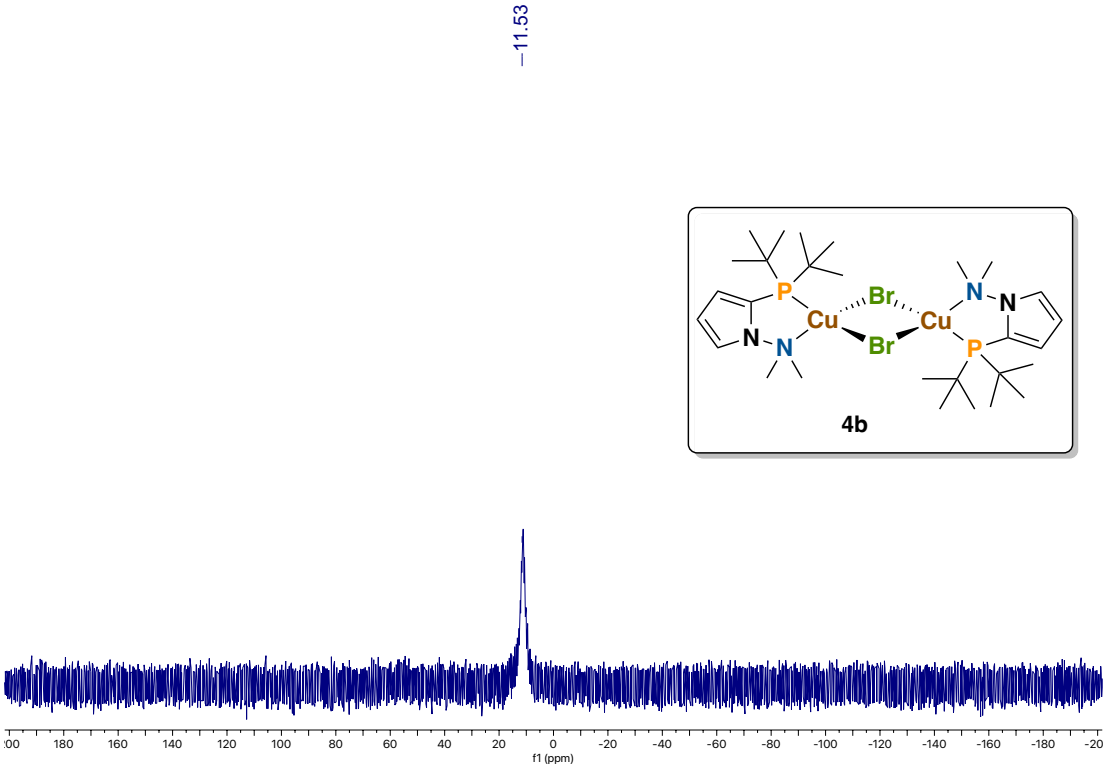


Figure S34. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **4b**

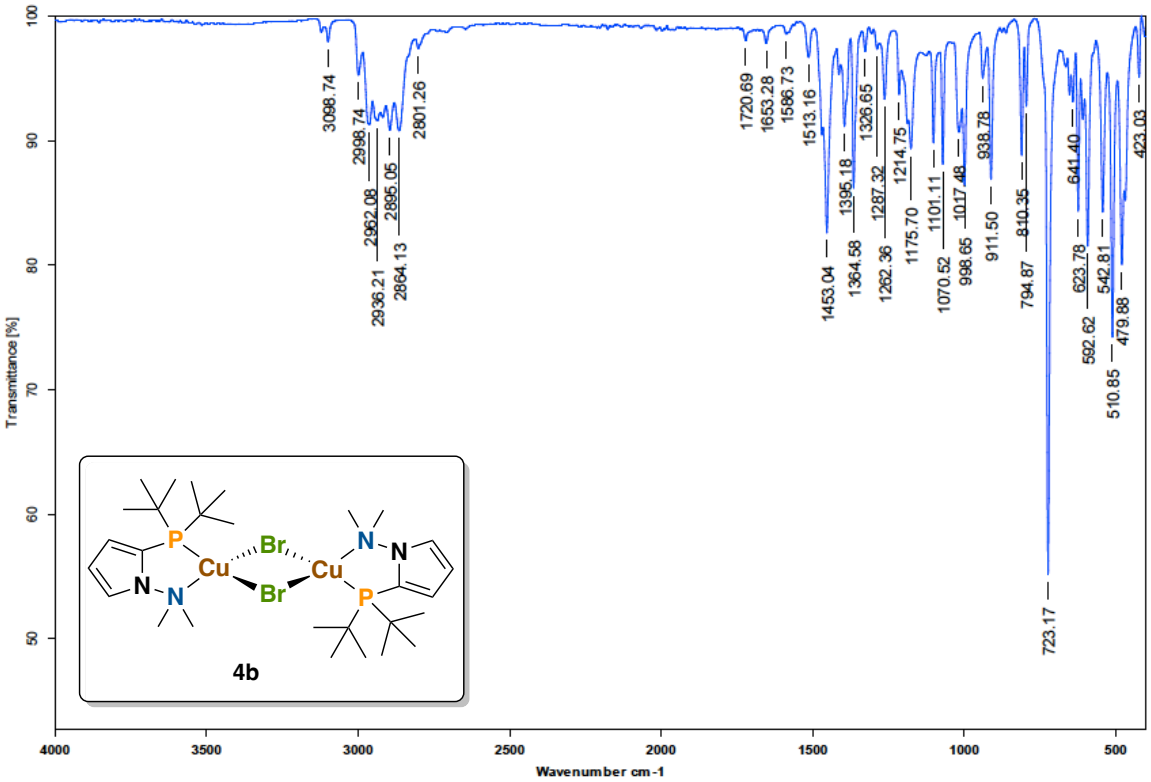


Figure S35. IR Spectrum of compound **4b**

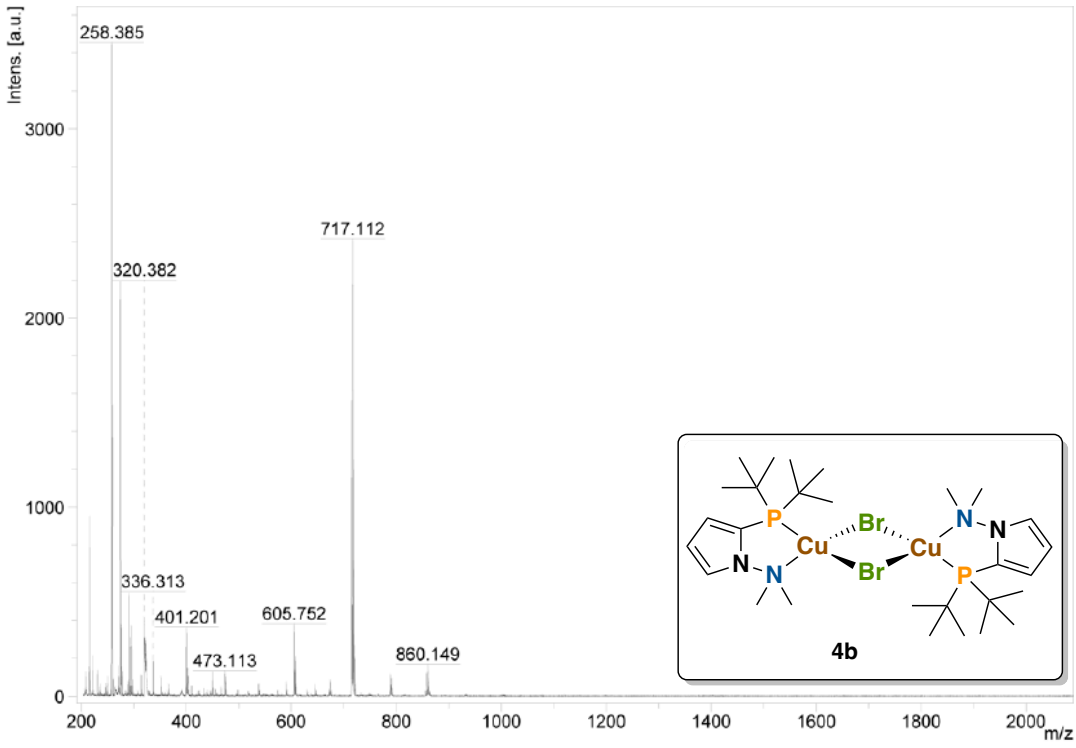


Figure S36. ERSM Spectrum (MALDTI-TOF) of compound **4b**

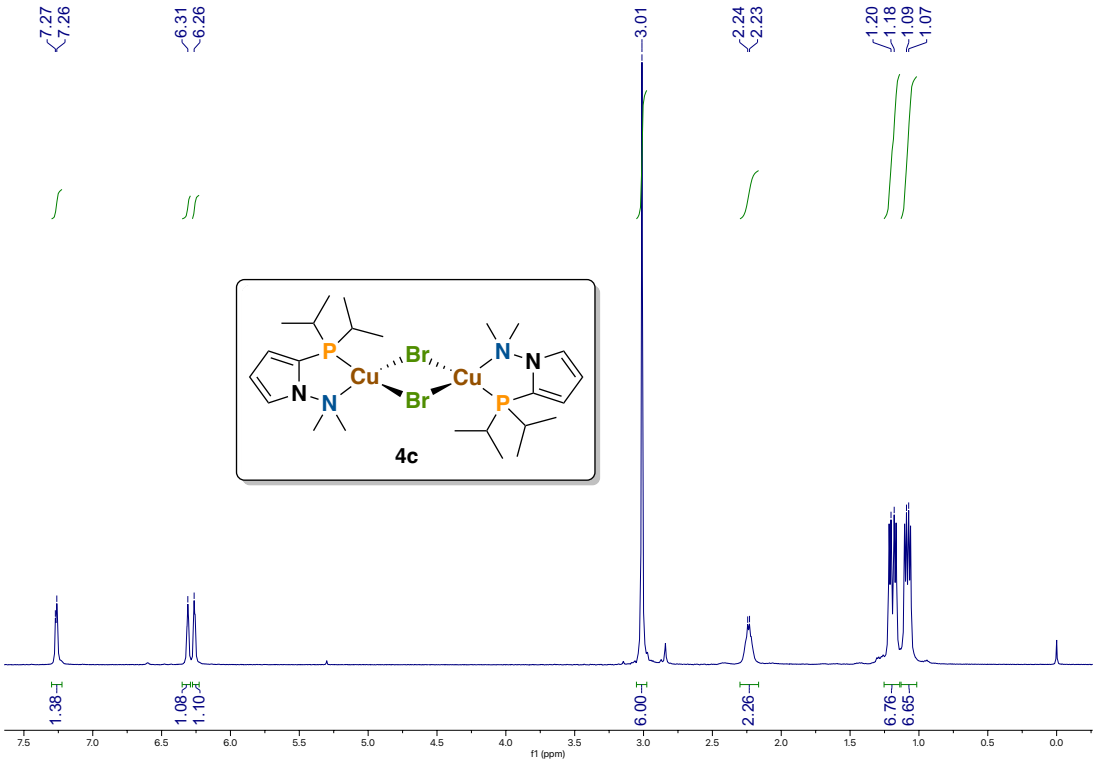


Figure S37. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **4c**

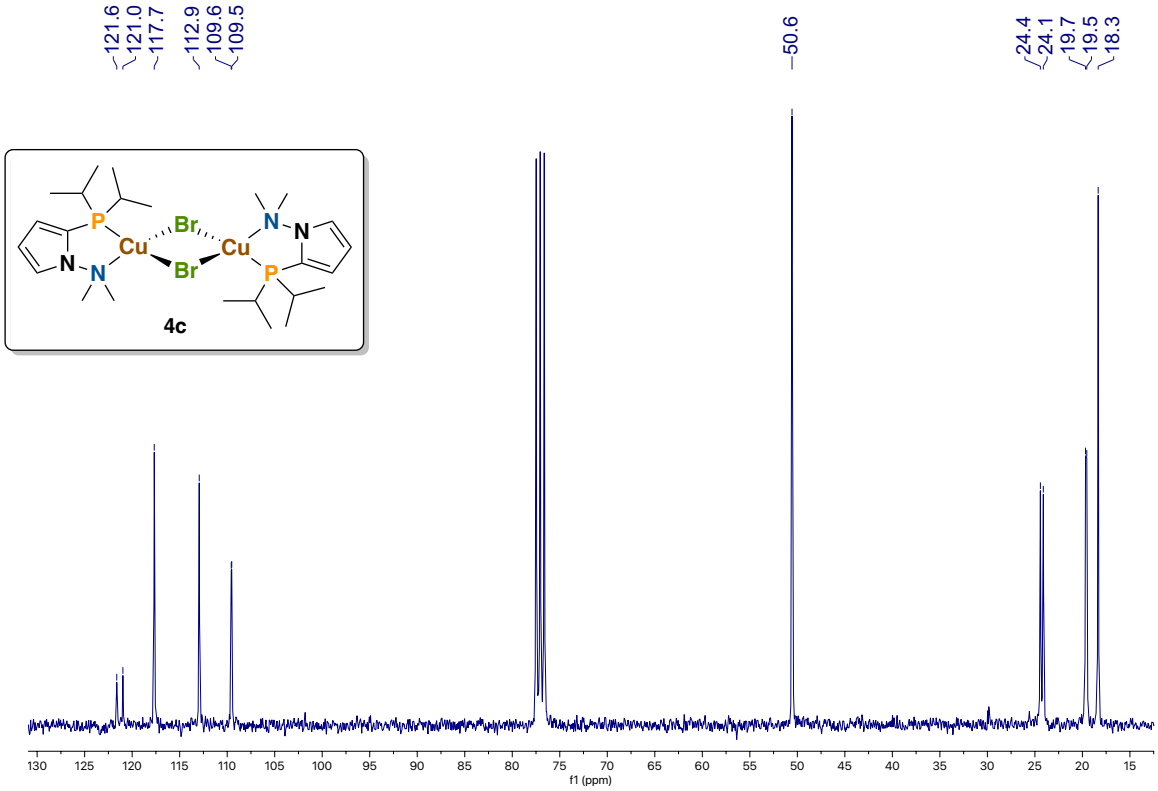


Figure S38. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **4c**

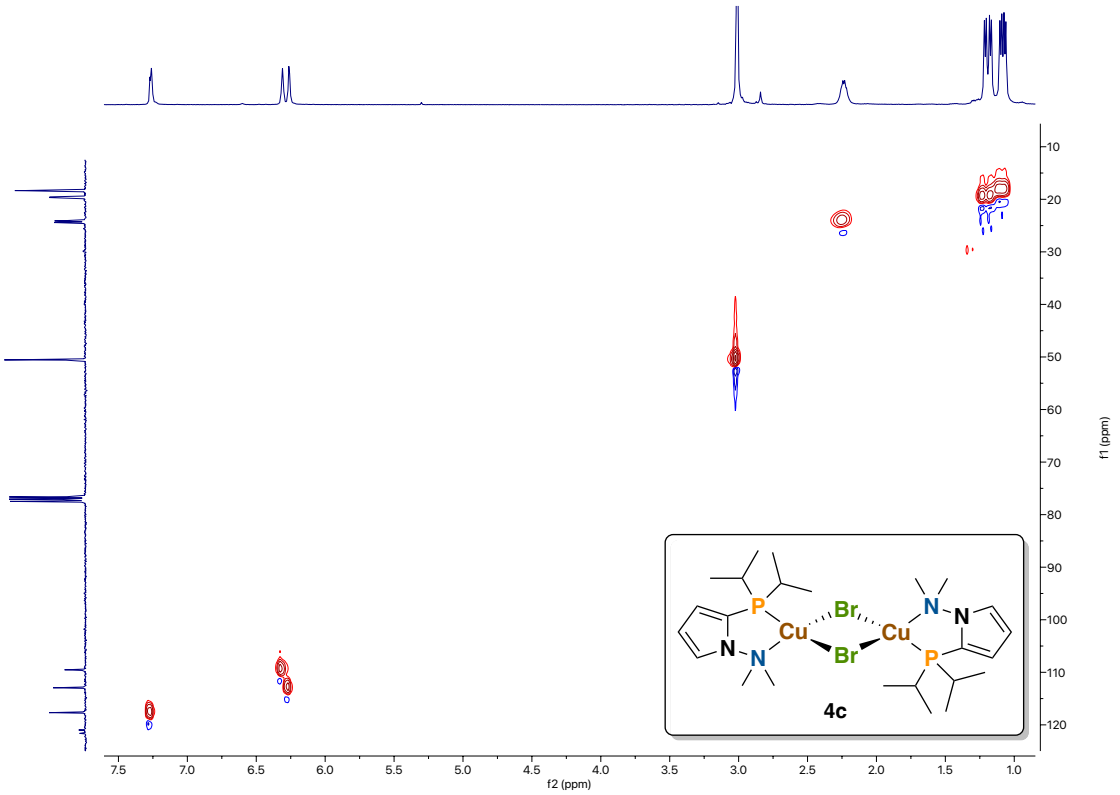


Figure S39. NMR HMQC Spectrum (300 MHz, $CDCl_3$) of compound **4c**

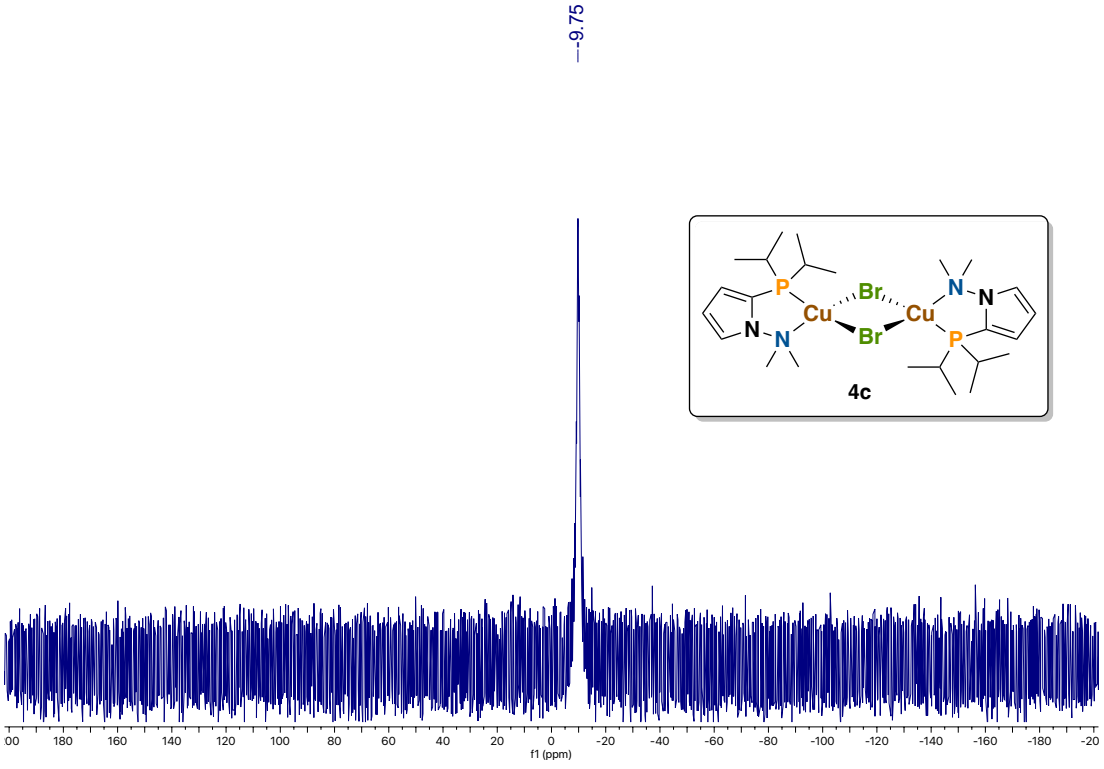


Figure S40. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **4c**

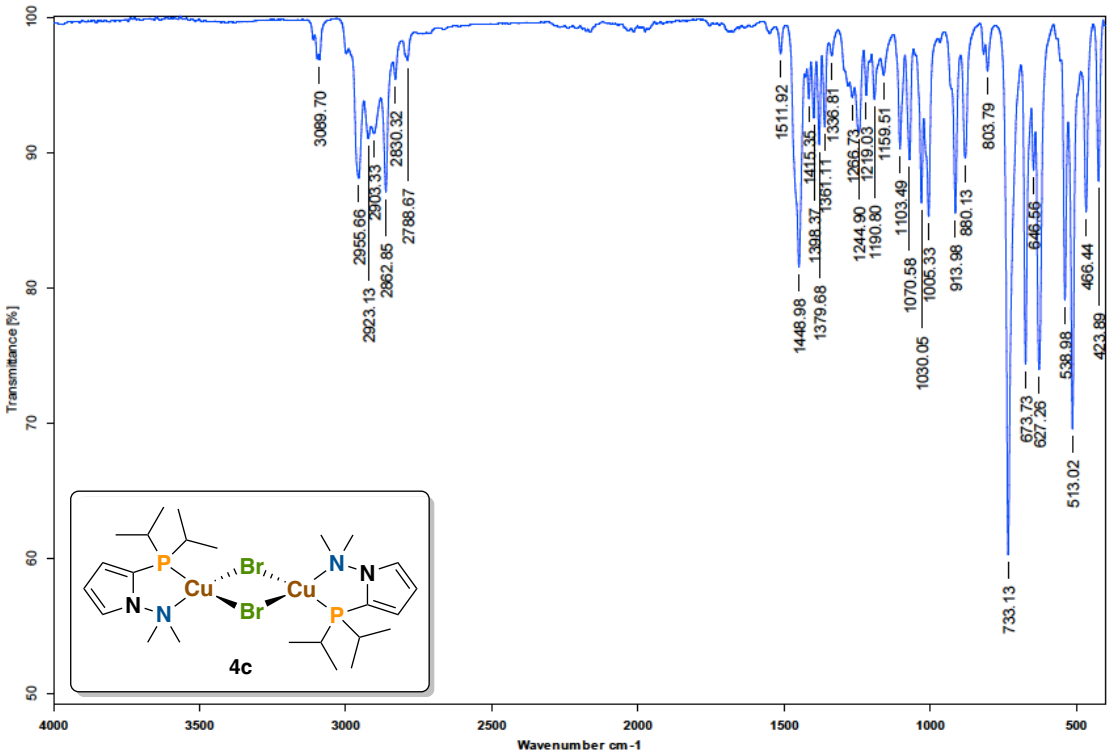


Figure S41. IR Spectrum of compound **4c**

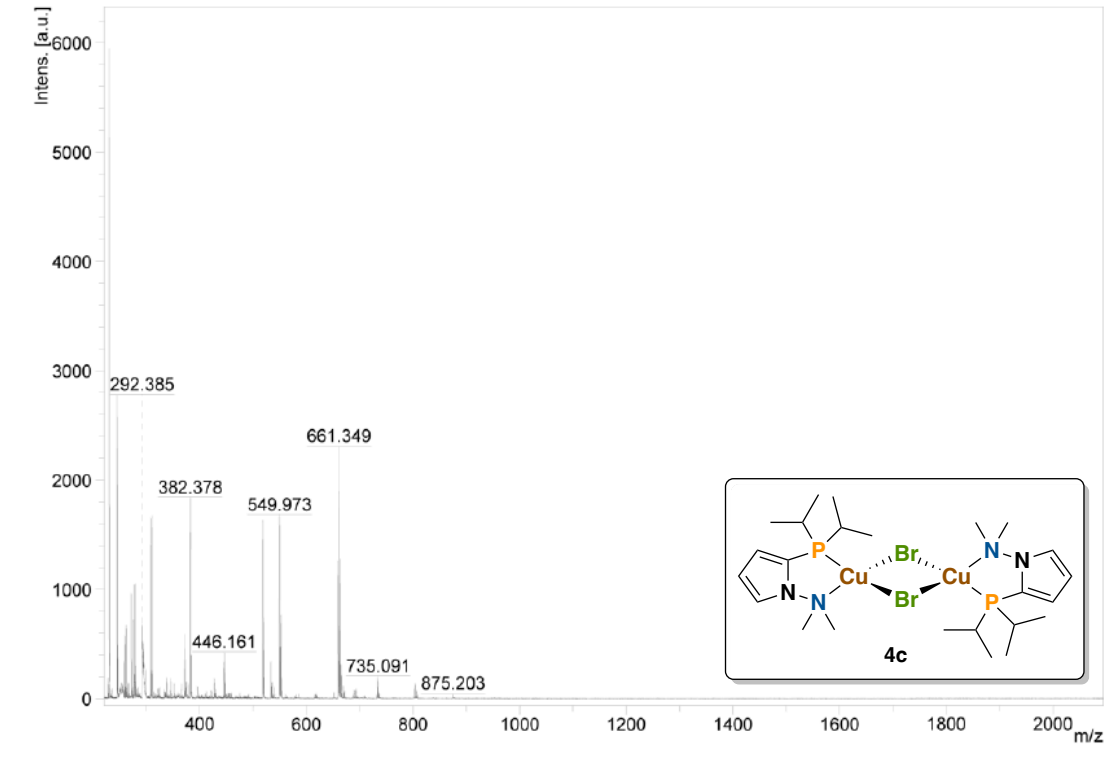


Figure S42. ERSM Spectrum (MALDI-TOF) of compound **4c**

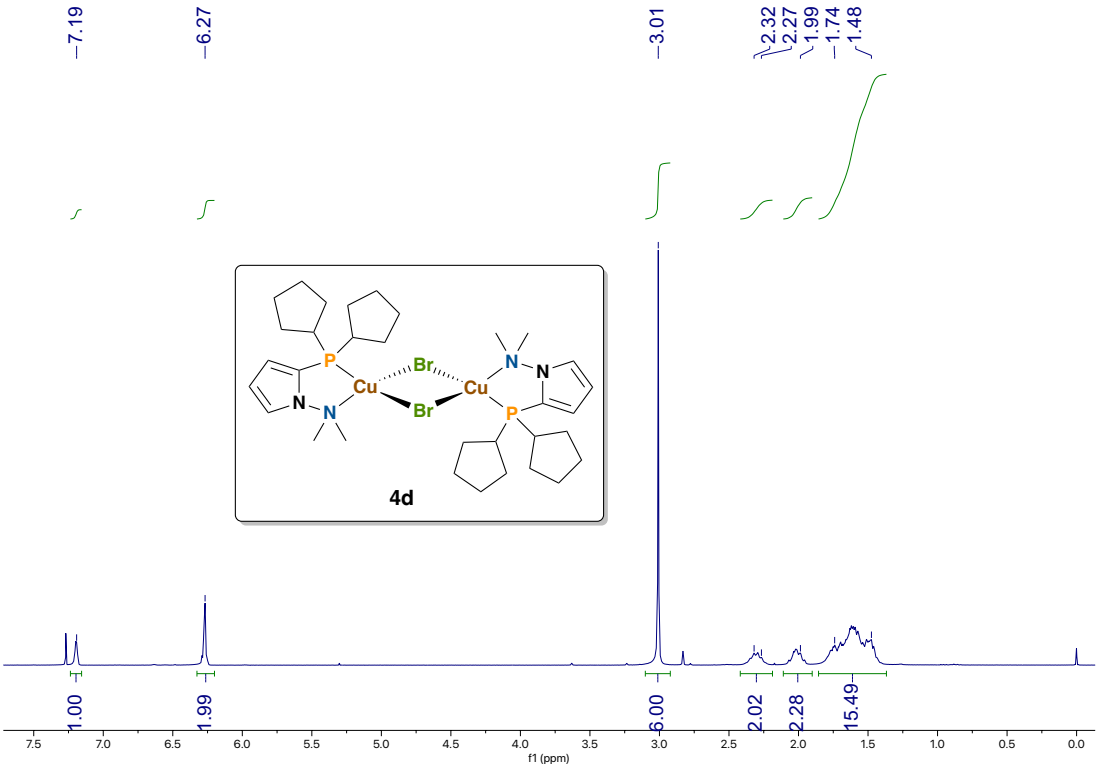


Figure S43. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound **4d**

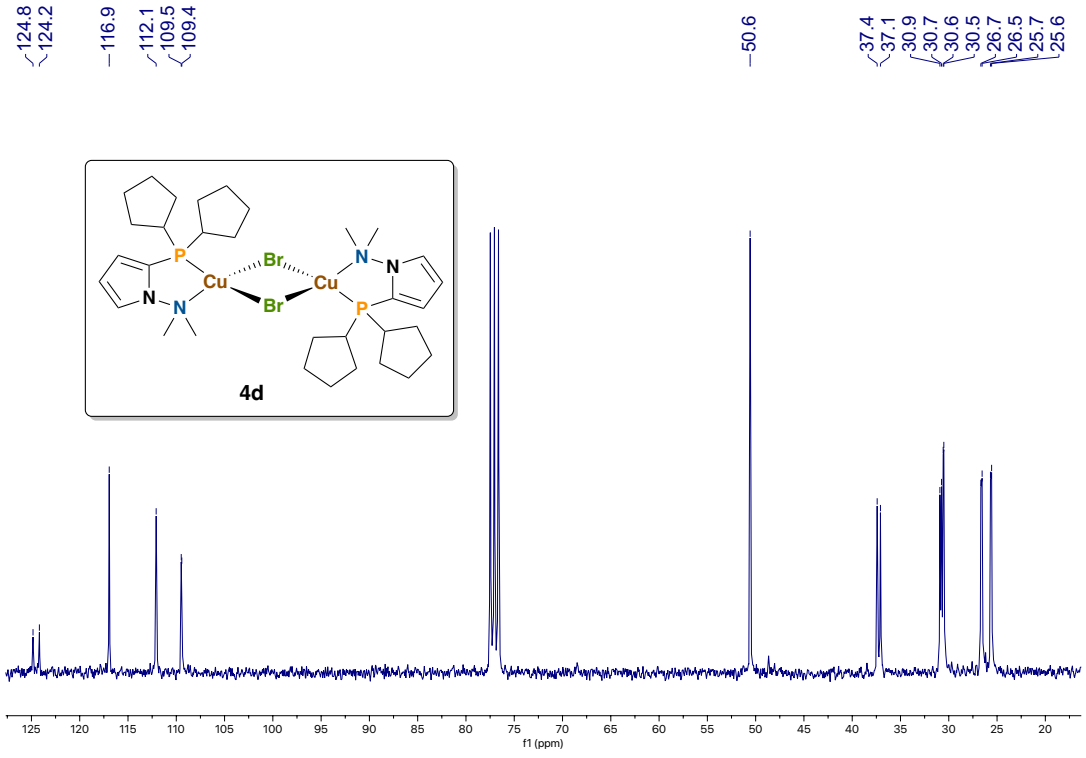


Figure S44. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound **4d**

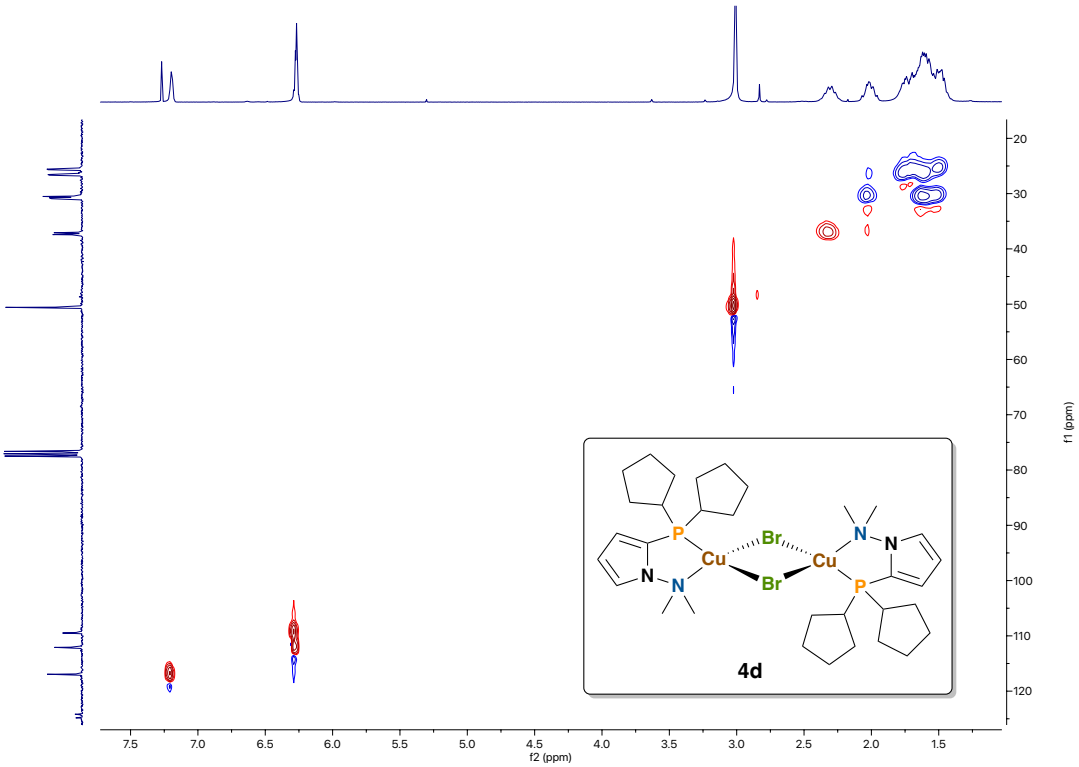


Figure S45. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound **4d**

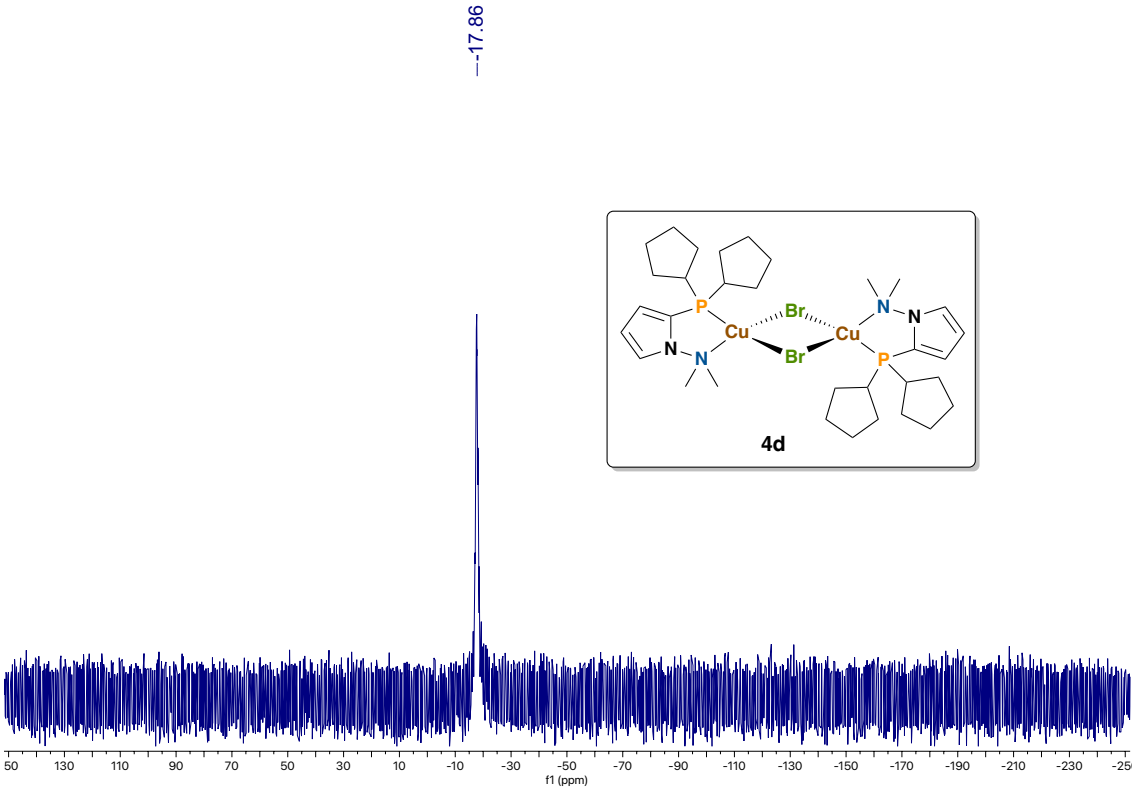


Figure S46. ^{31}P NMR Spectrum (121.5 MHz, $CDCl_3$) of compound **4d**

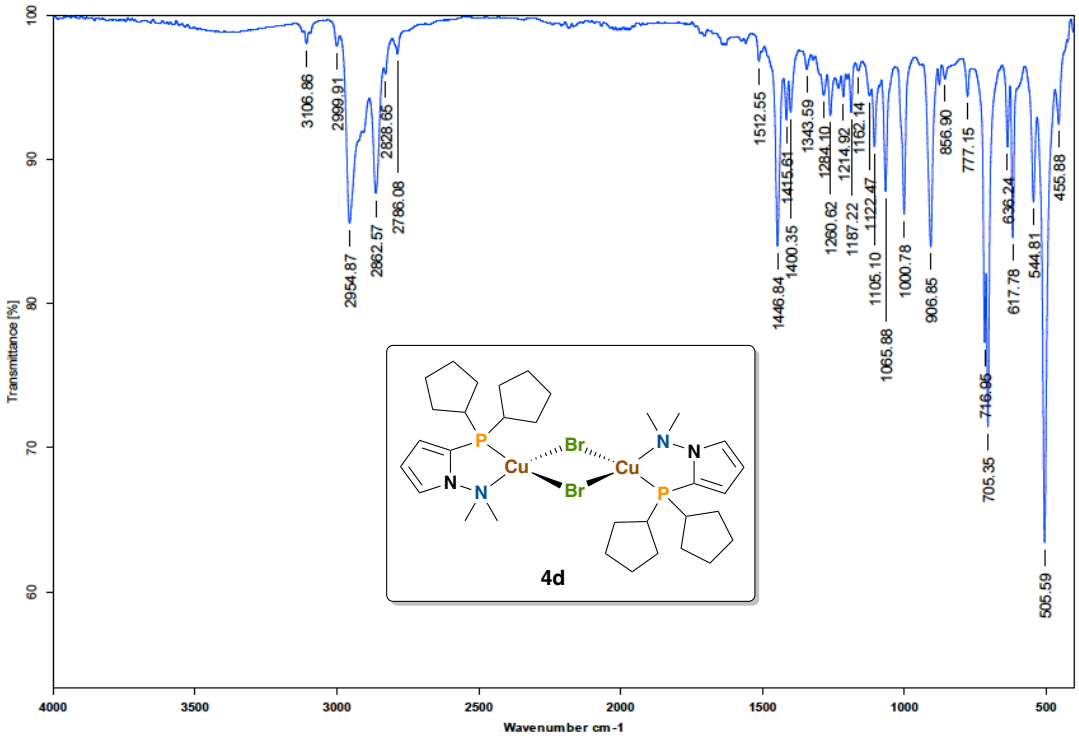


Figure S47. IR Spectrum of compound **4d**

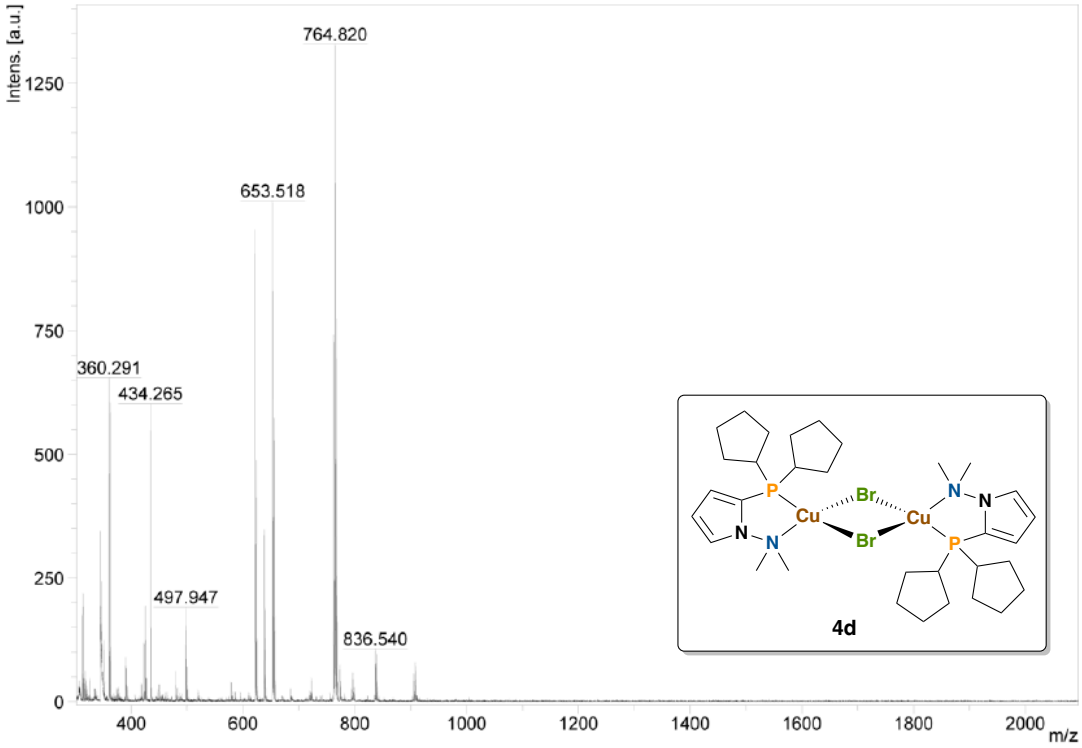


Figure S48. ERSM Spectrum (MALDI-TOF) of compound **4d**

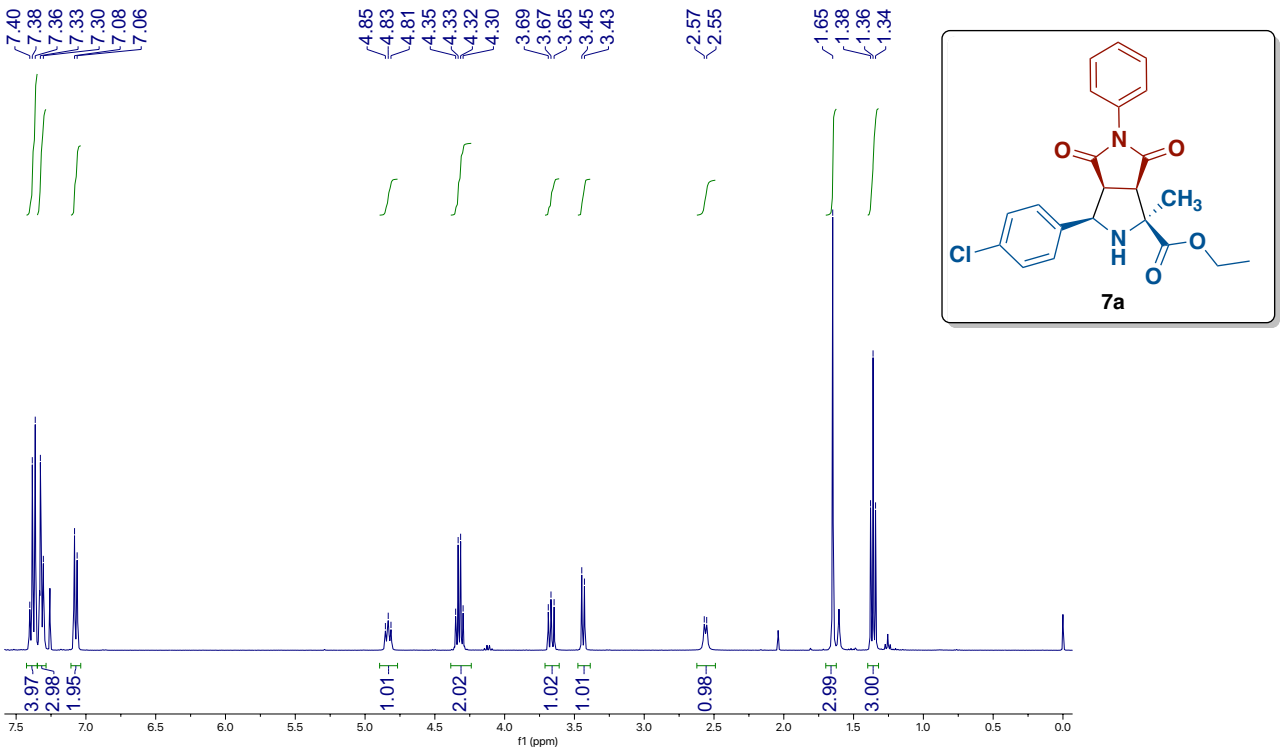


Figure S49. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of compound (±) **7a**

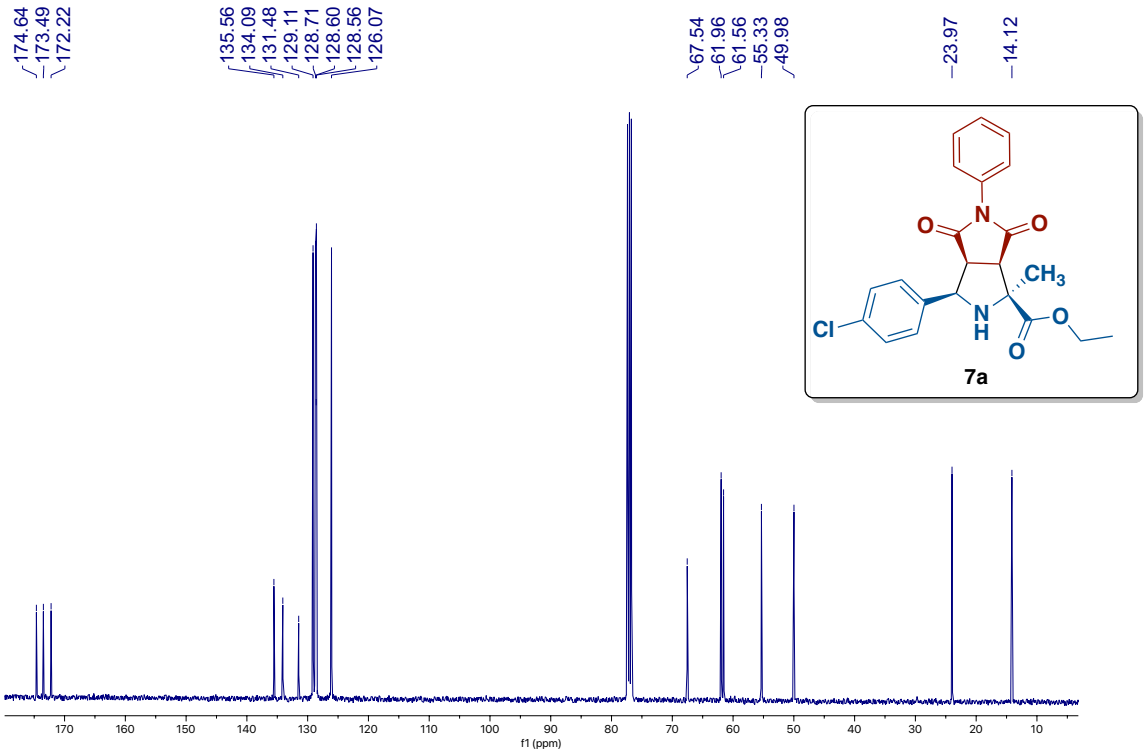


Figure S50. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of compound (±) **7a**

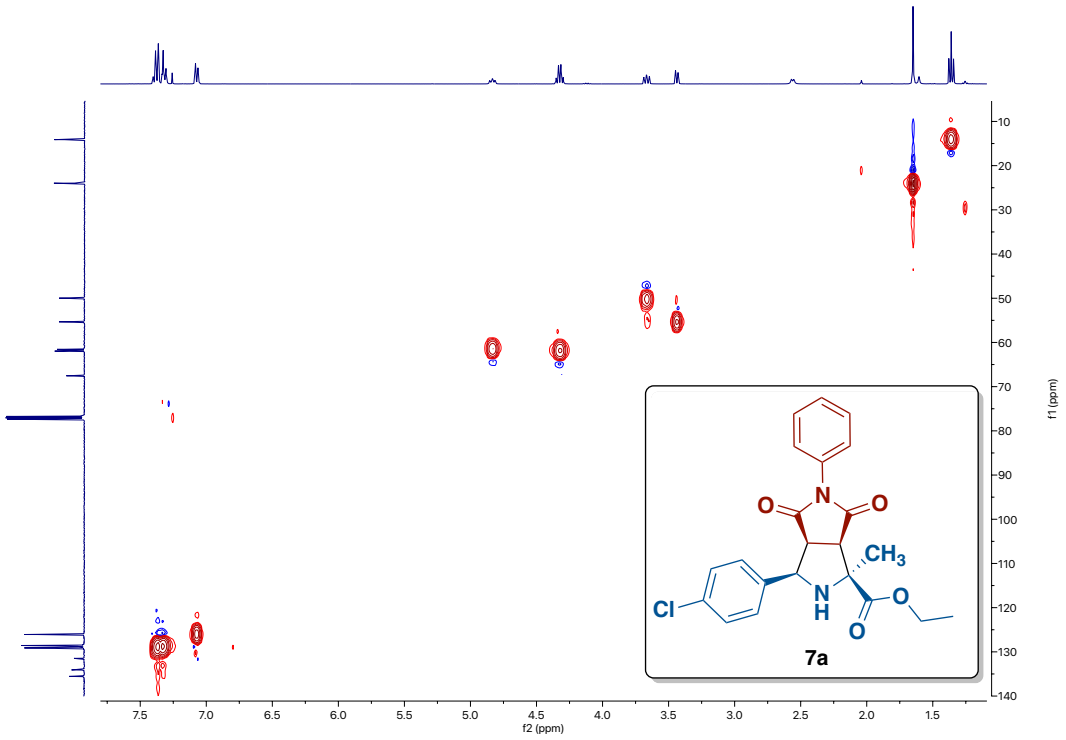


Figure S51. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7a**

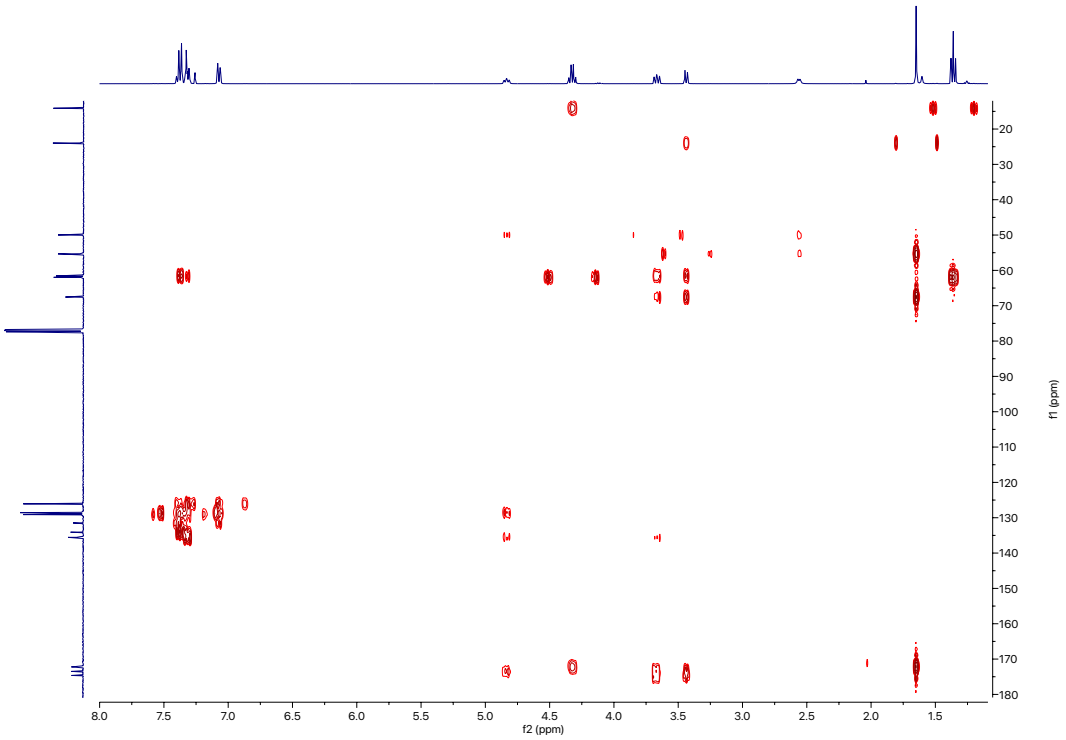


Figure S52. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7a**

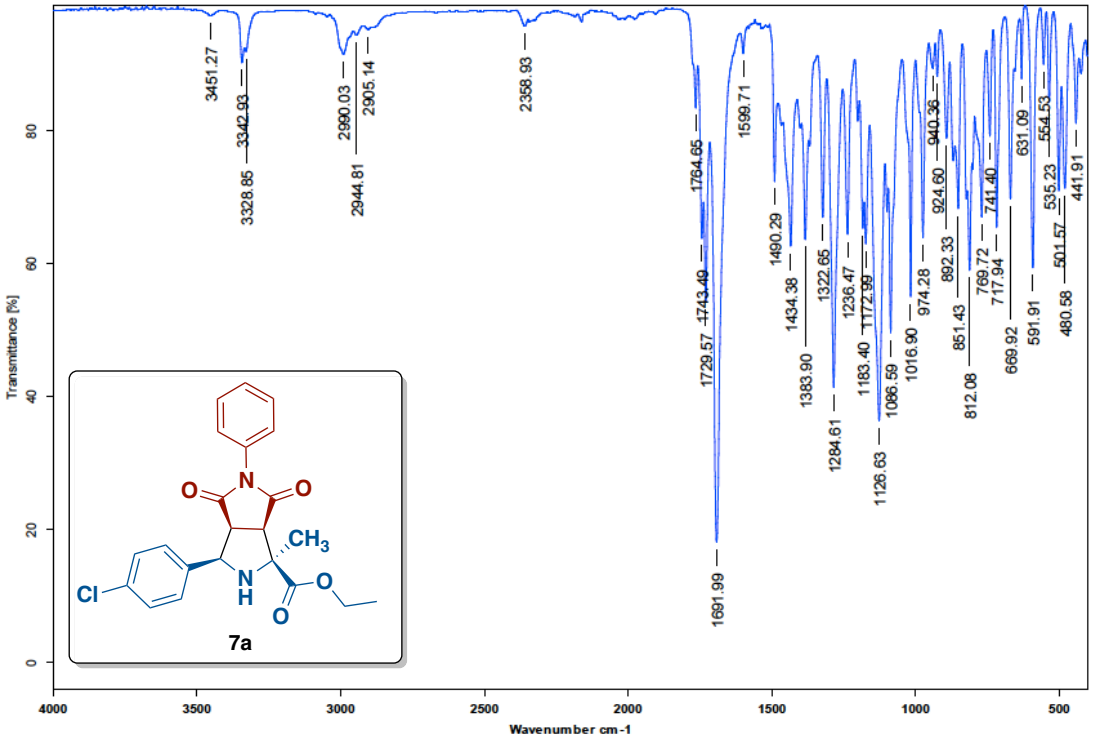
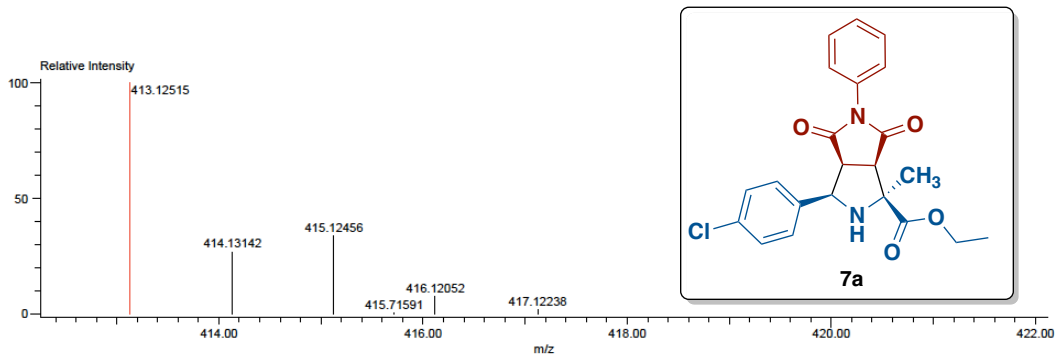


Figure S53. IR Spectrum of compound (±) **7a**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
413.12515	31880.51	413.12681	-1.66	-4.02	$^{12}C_{22}{}^{1}H_{22}{}^{35}Cl_{1}{}^{14}N_{2}{}^{16}O_{4}$	12.5

Figure S54. ERSM Spectrum (DART+) of compound (±) **7a**

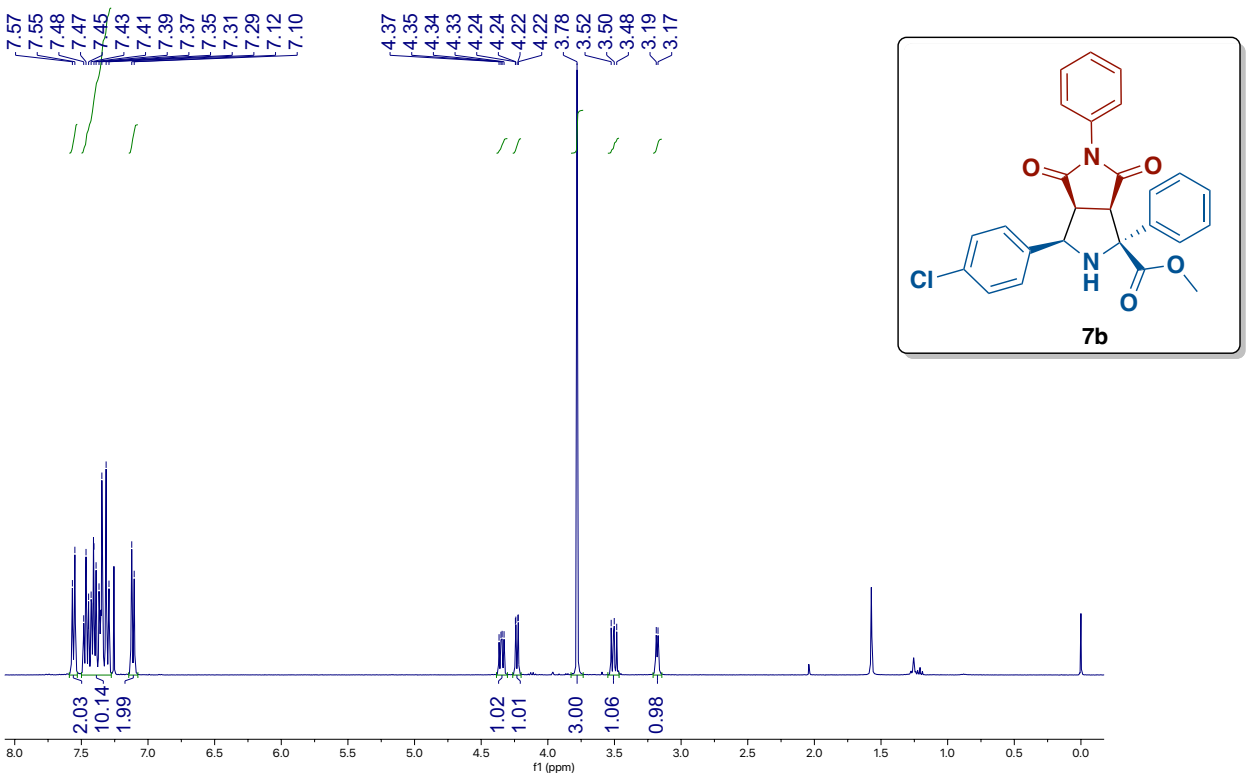


Figure S55. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7b**

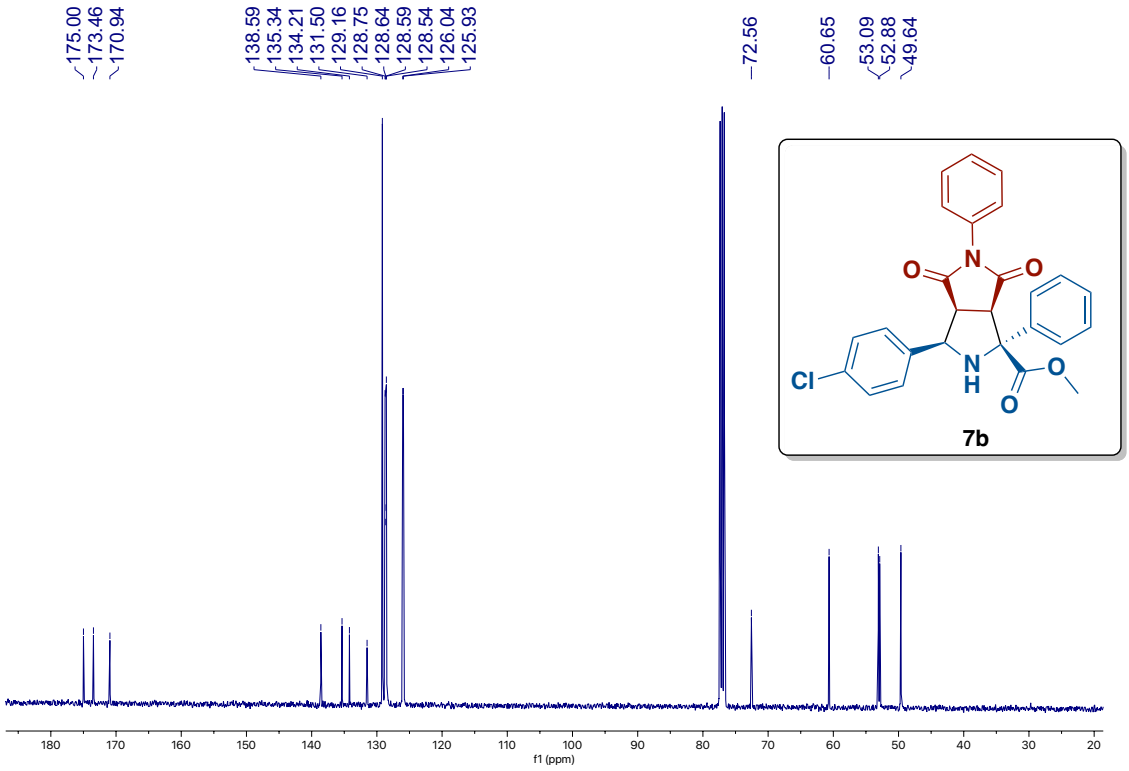


Figure S56. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7b**

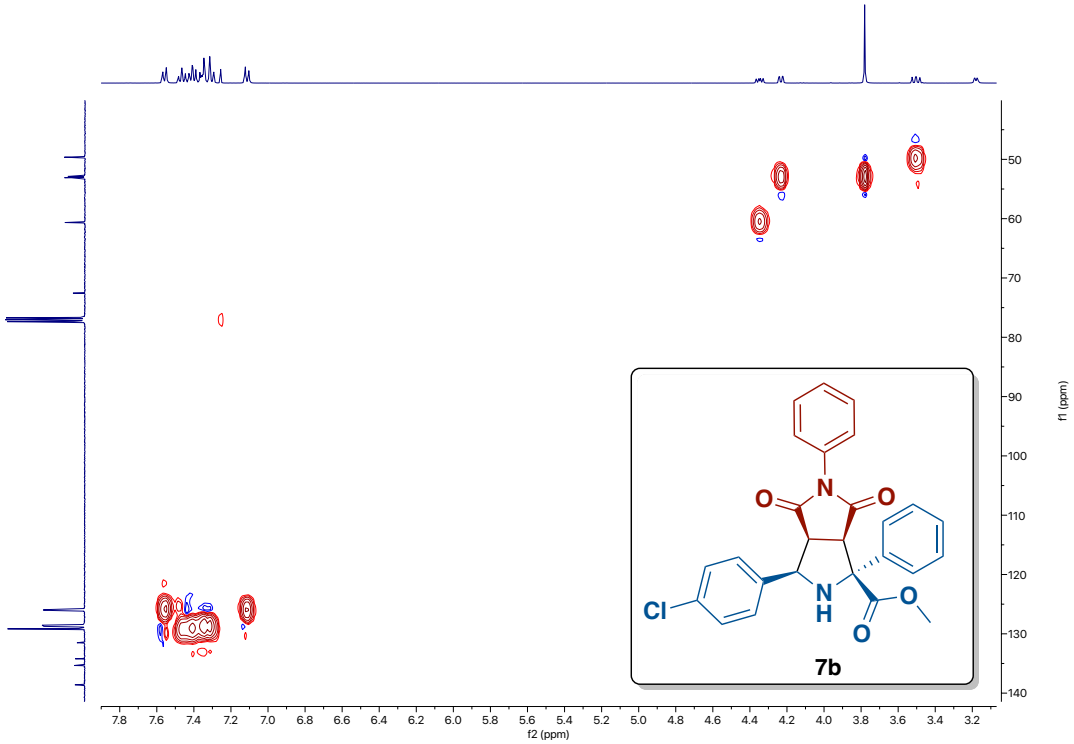


Figure S57. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7b**

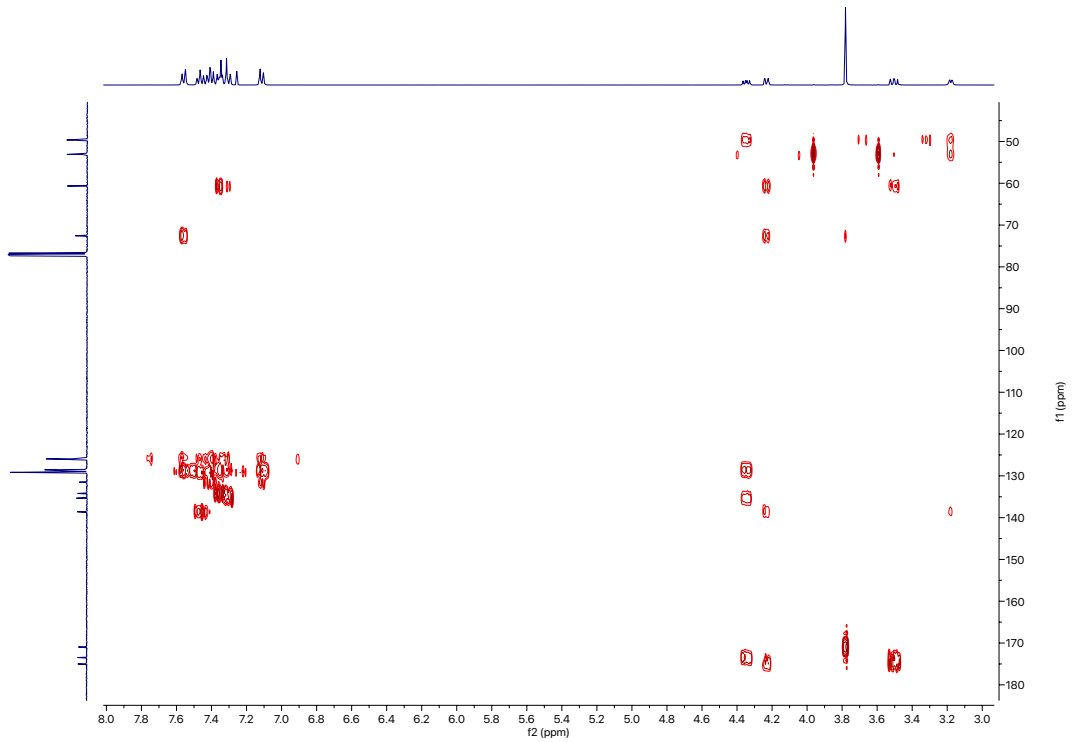


Figure S58. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7b**

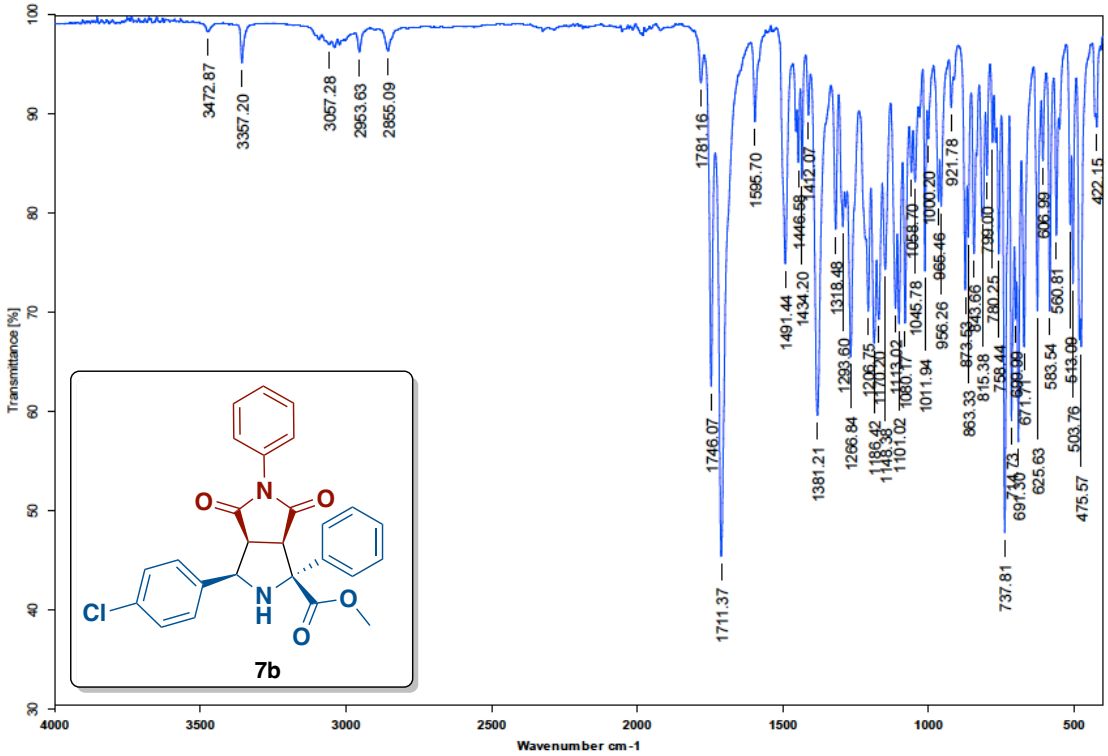
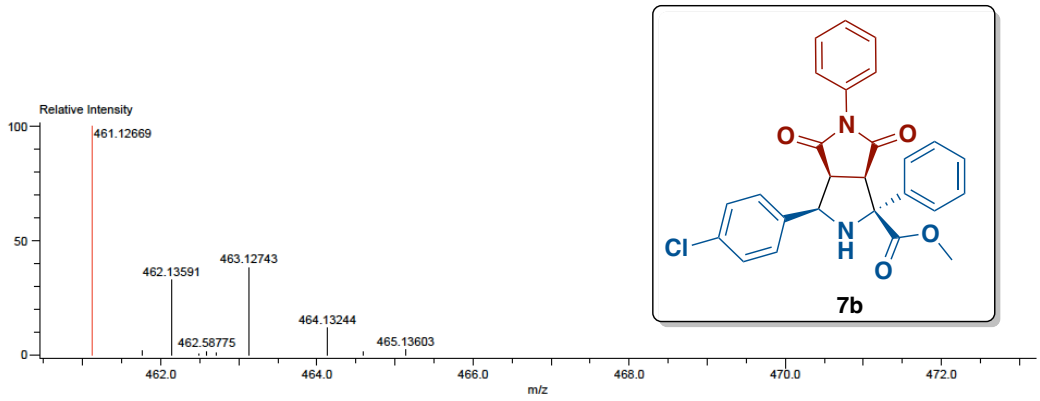


Figure S59. IR Spectrum of compound (±) **7b**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
461.12669	44179.02	461.12681	-0.12	-0.26	$^{12}C_{28}{}^{1}H_{22}{}^{35}Cl_{1}{}^{14}N_{2}{}^{16}O_{4}$	16.5

Figure S60. ERSM Spectrum (DART+) of compound (±) **7b**

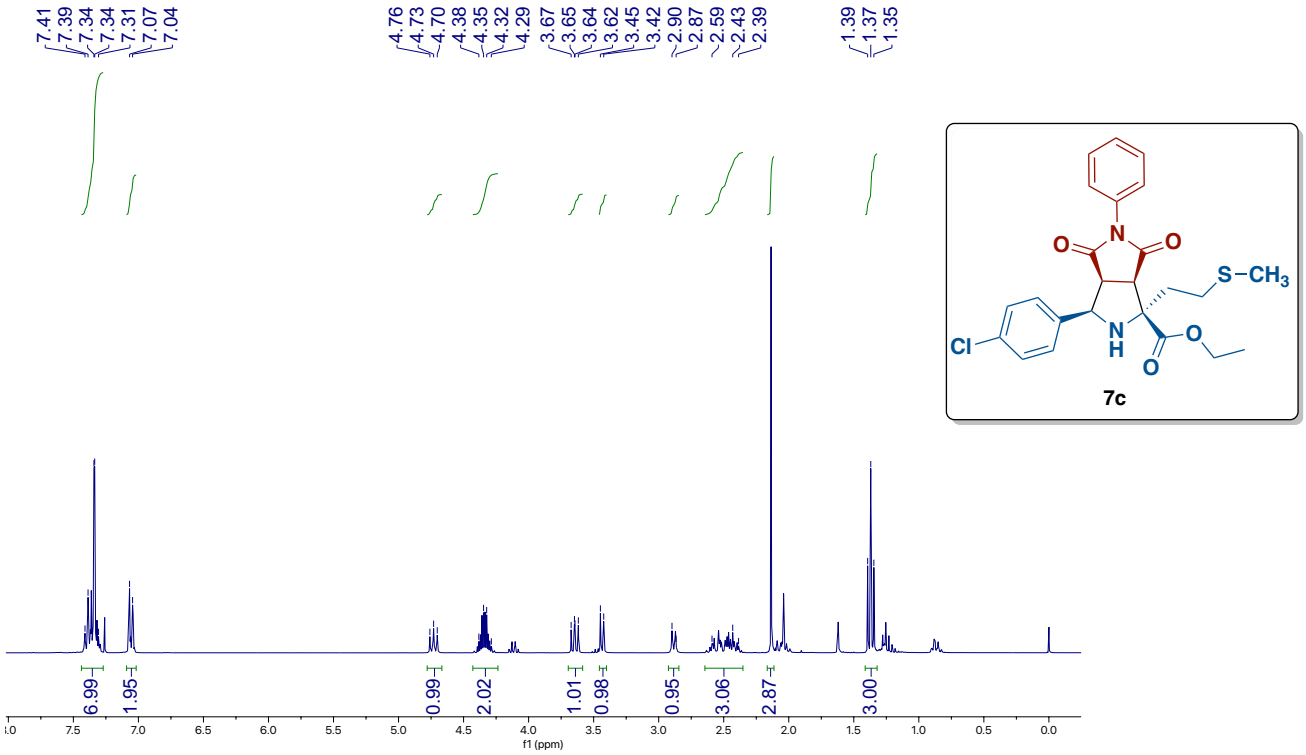


Figure S61. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7c**

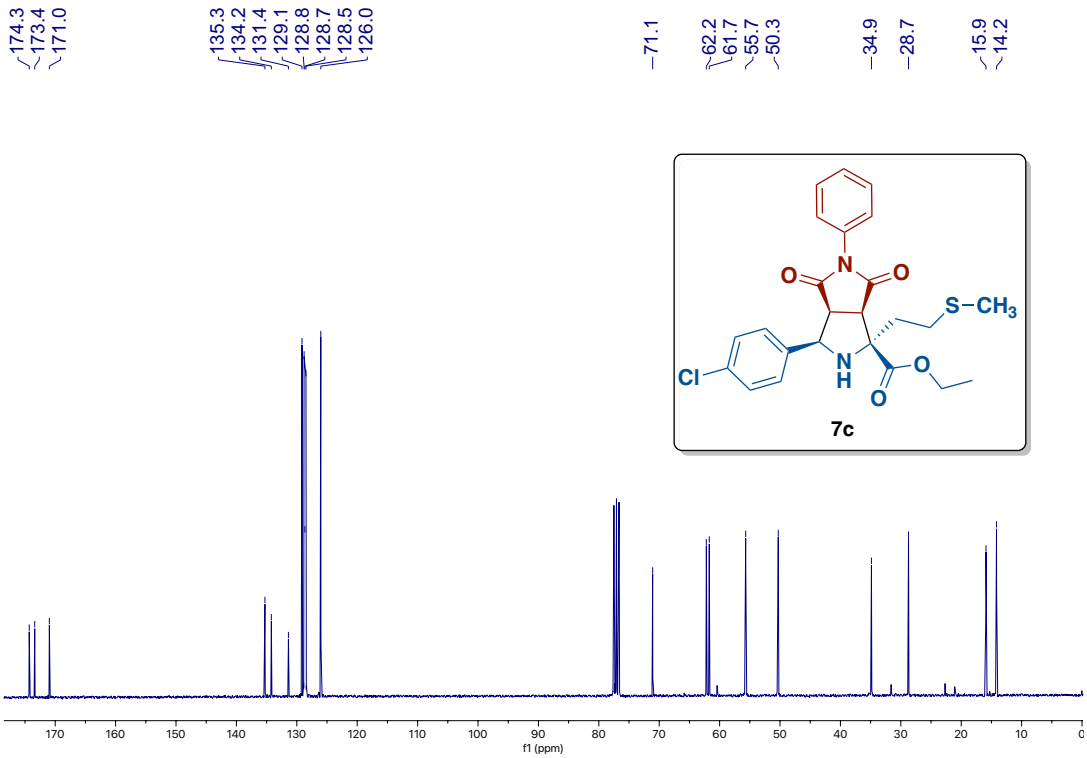


Figure S62. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7c**

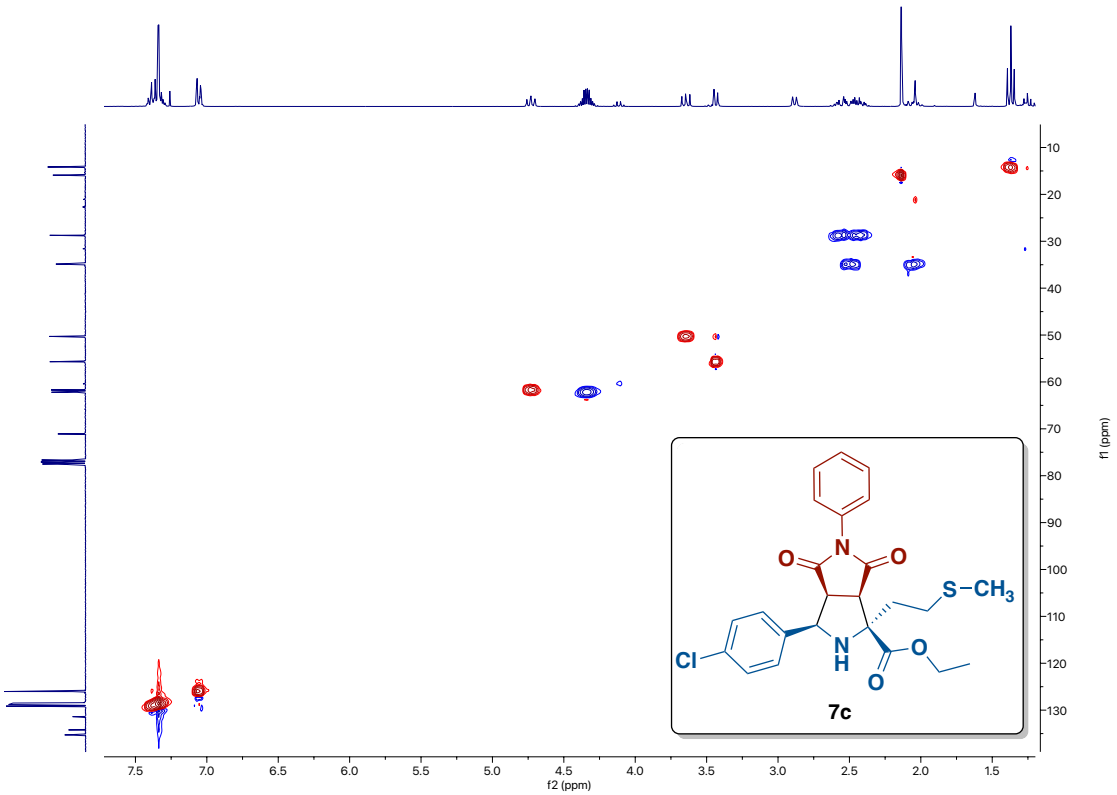


Figure S63. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7c**

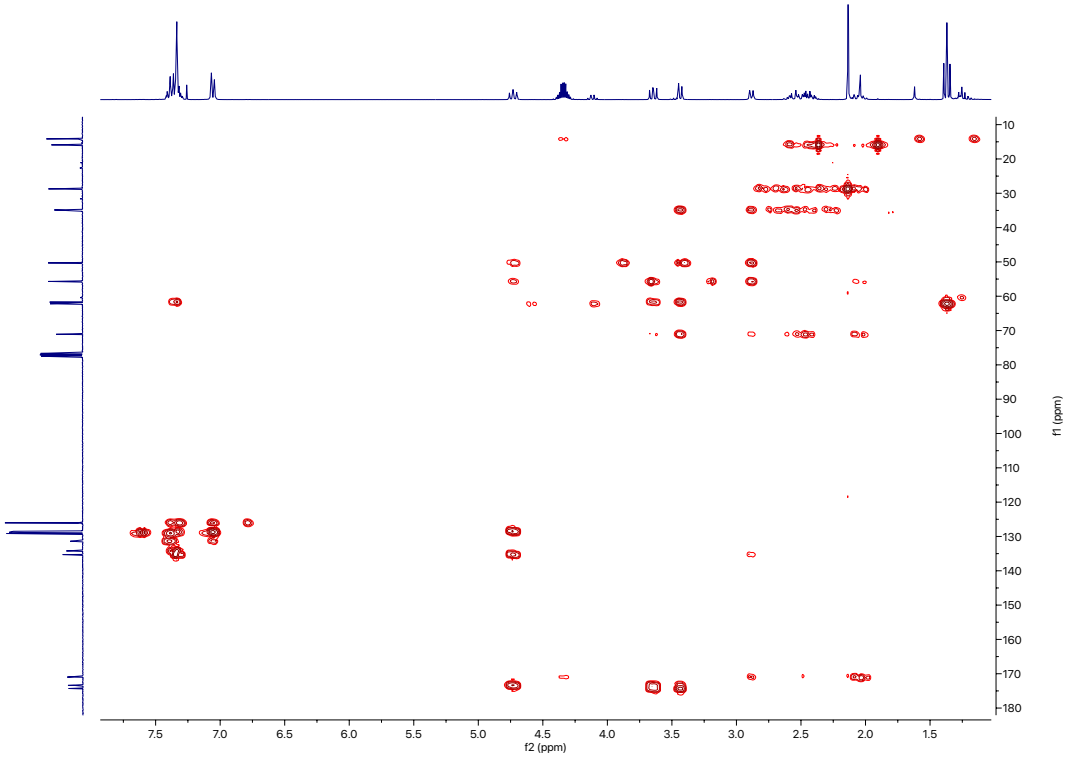


Figure S64. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7c**

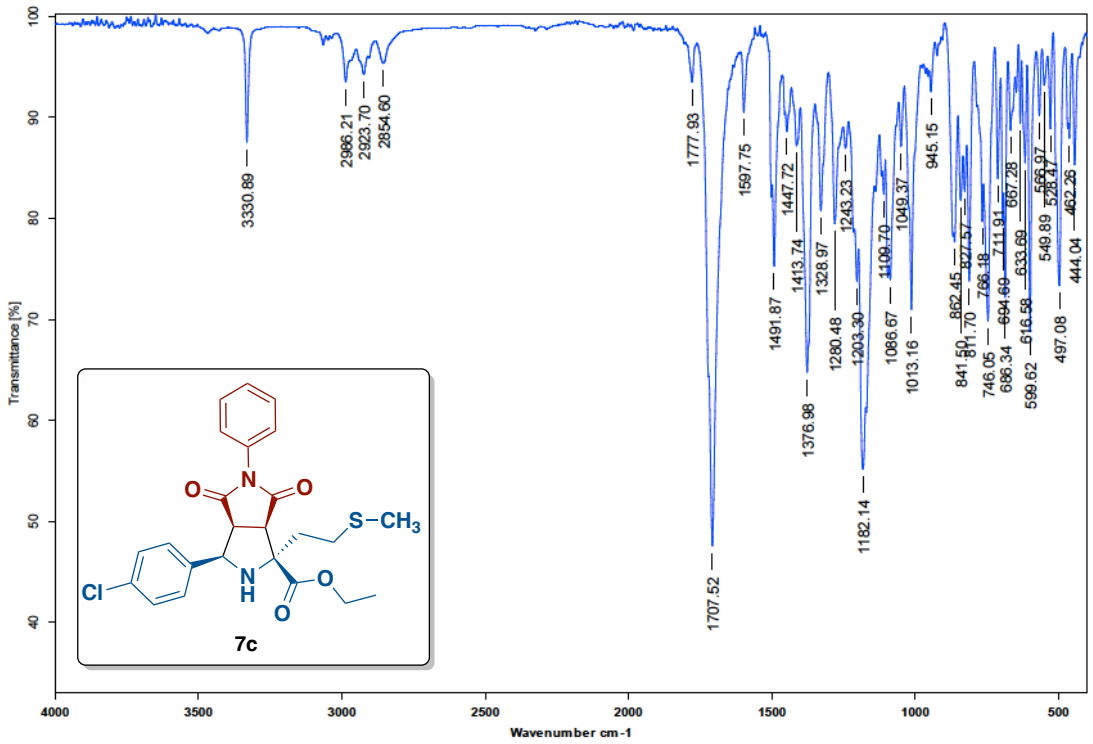
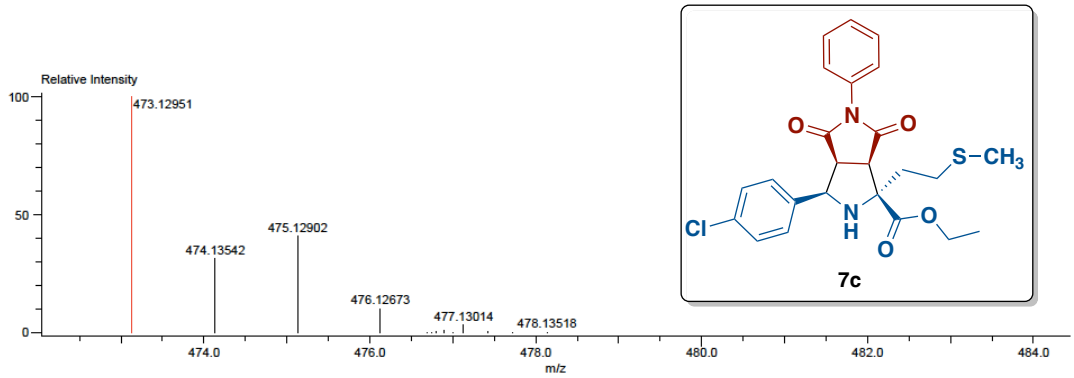


Figure S65. IR Spectrum of compound (±) **7c**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
473.12951	21255.25	473.13018	-0.67	-1.41	$^{12}C_{24}{}^{1}H_{26}{}^{35}Cl{}^{14}N_{2}{}^{16}O_{4}{}^{32}S_{1}$	13.5

Figure S66. ERSM Spectrum (DART+) of compound (±) **7c**

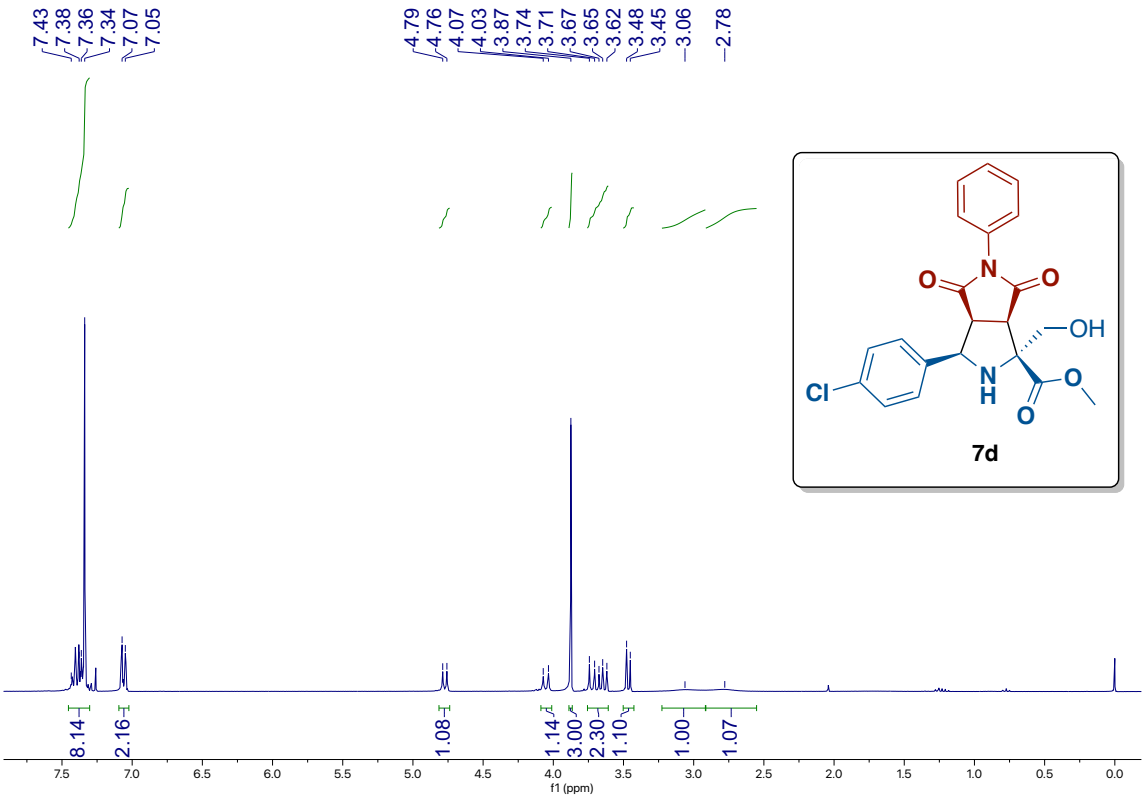


Figure S67. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7d**

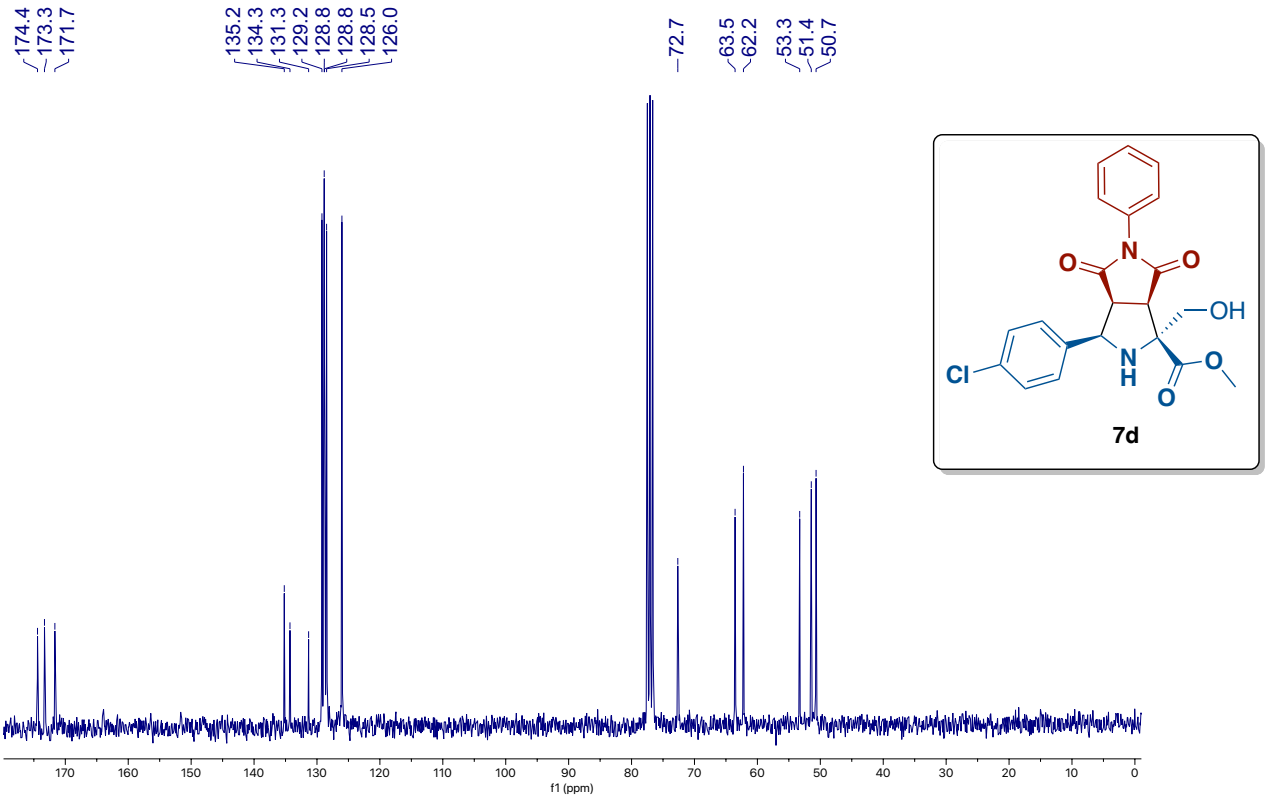


Figure S68. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7d**

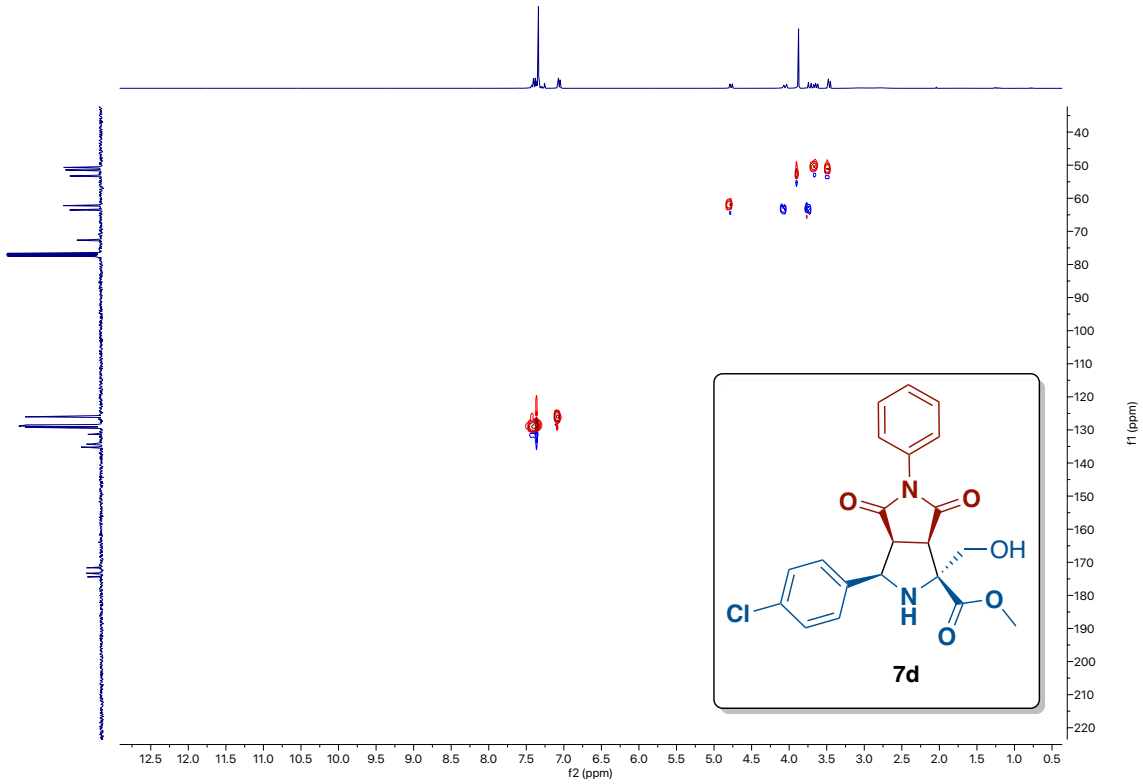


Figure S69. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7d**

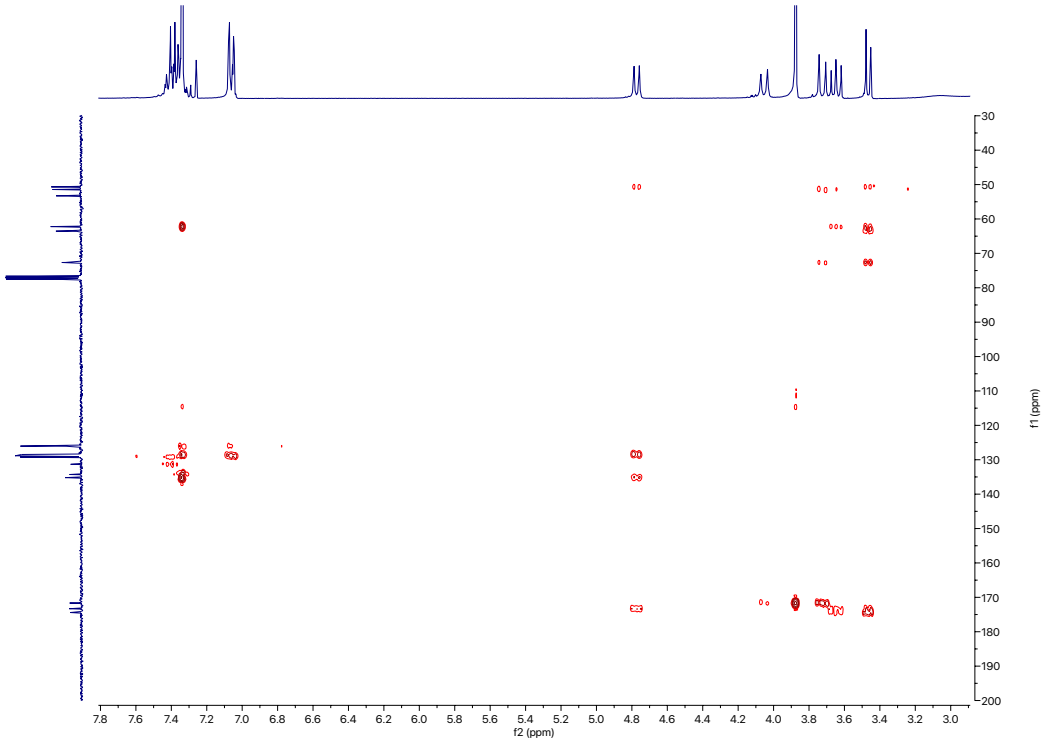


Figure S70. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7d**

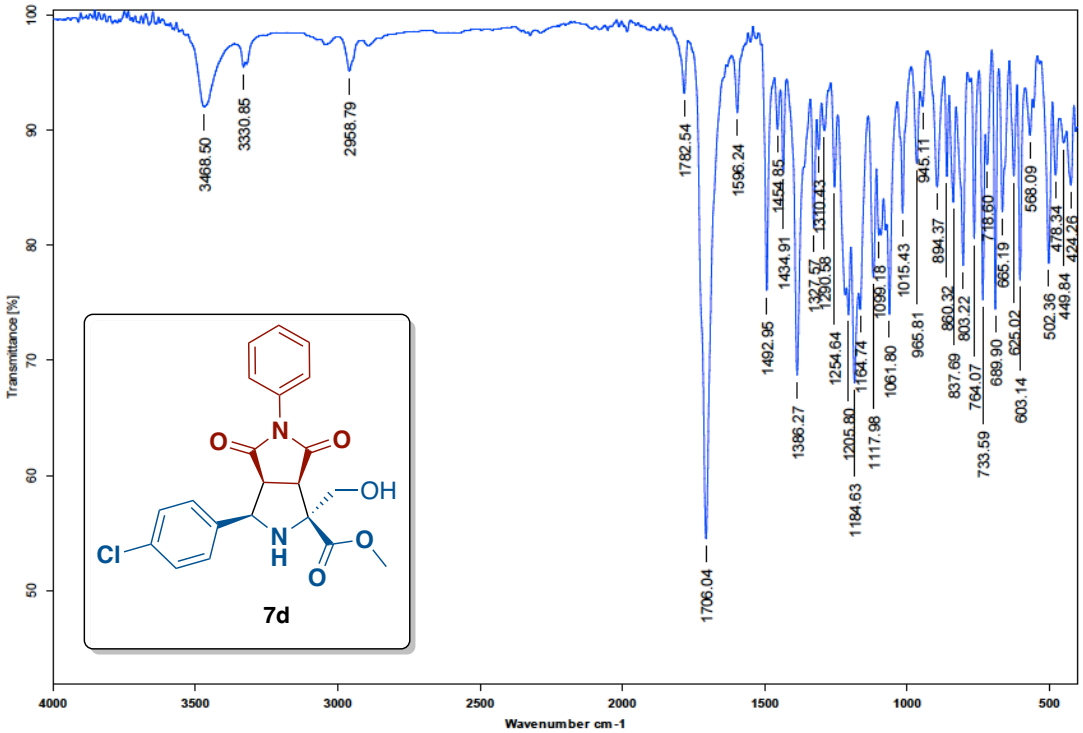
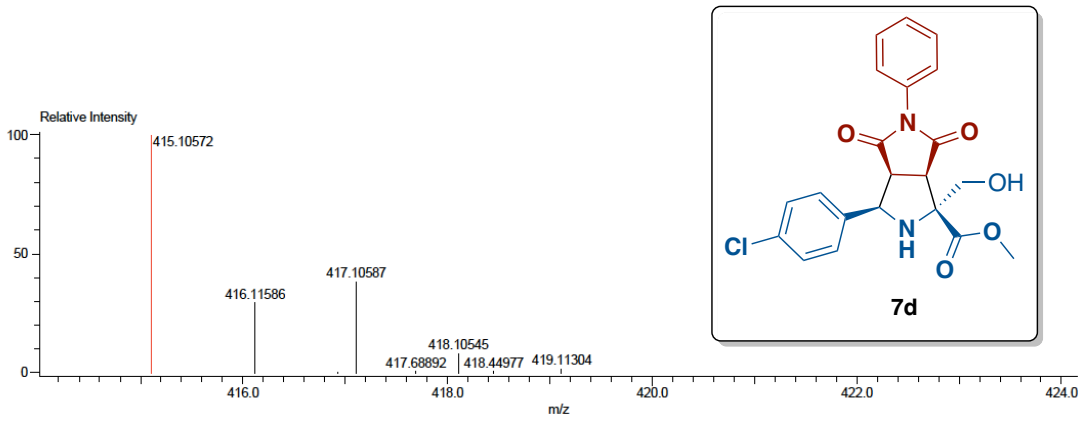


Figure S71. IR Spectrum of compound (±) **7d**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
415.10572	62259.89	415.10607	-0.35	-0.85	$^{12}C_{21}{}^{1}H_{20}{}^{35}Cl_{1}{}^{14}N_{2}{}^{16}O_{5}$	12.5

Figure S72. ERSM Spectrum (DART+) of compound (±) **7d**

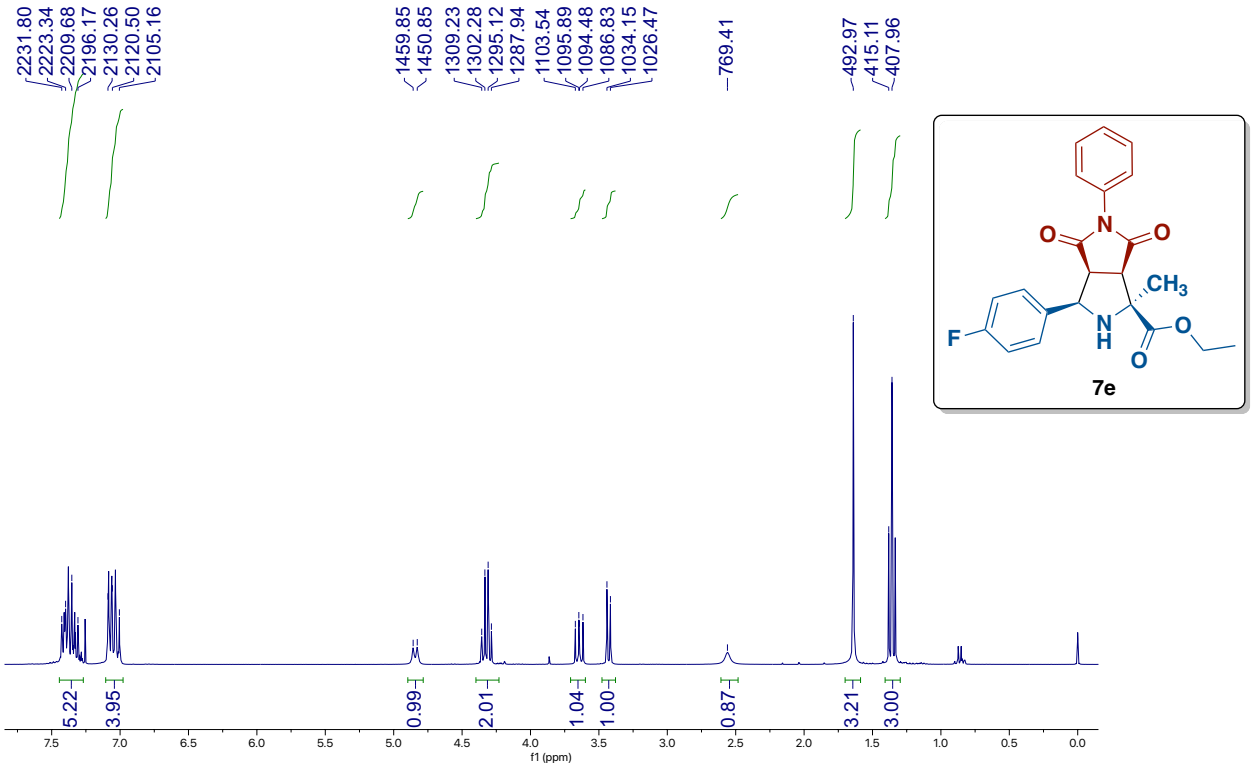


Figure S73. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7e**

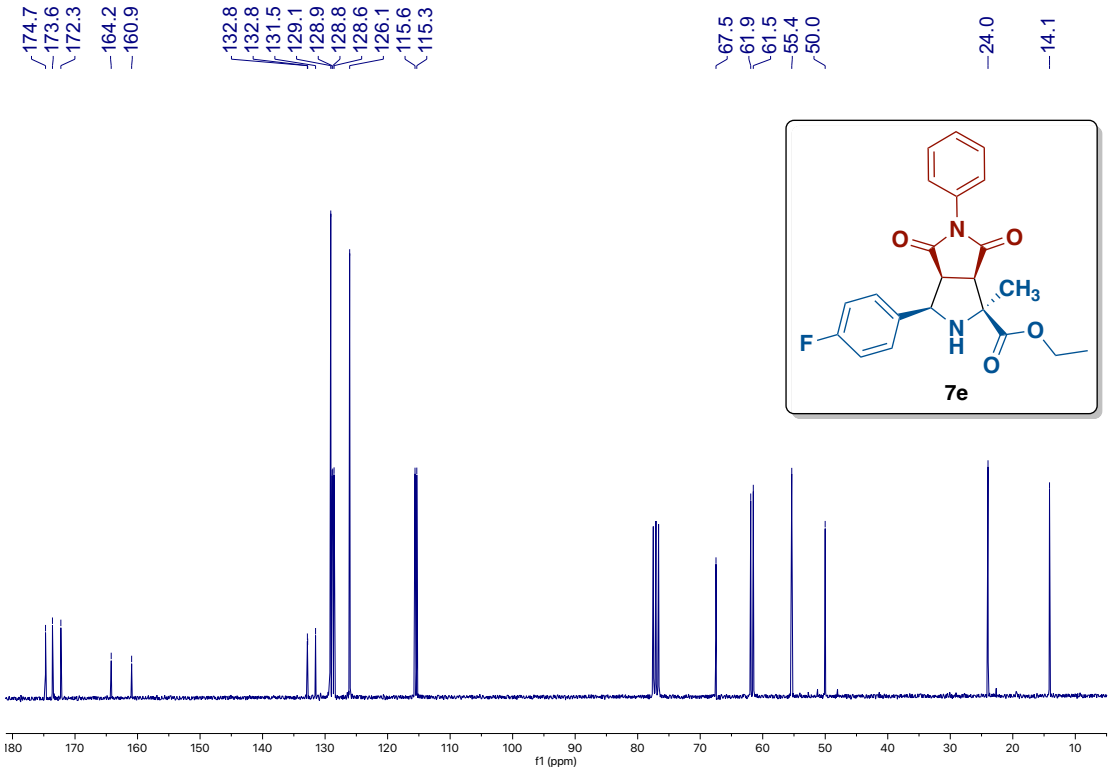


Figure S74. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7e**

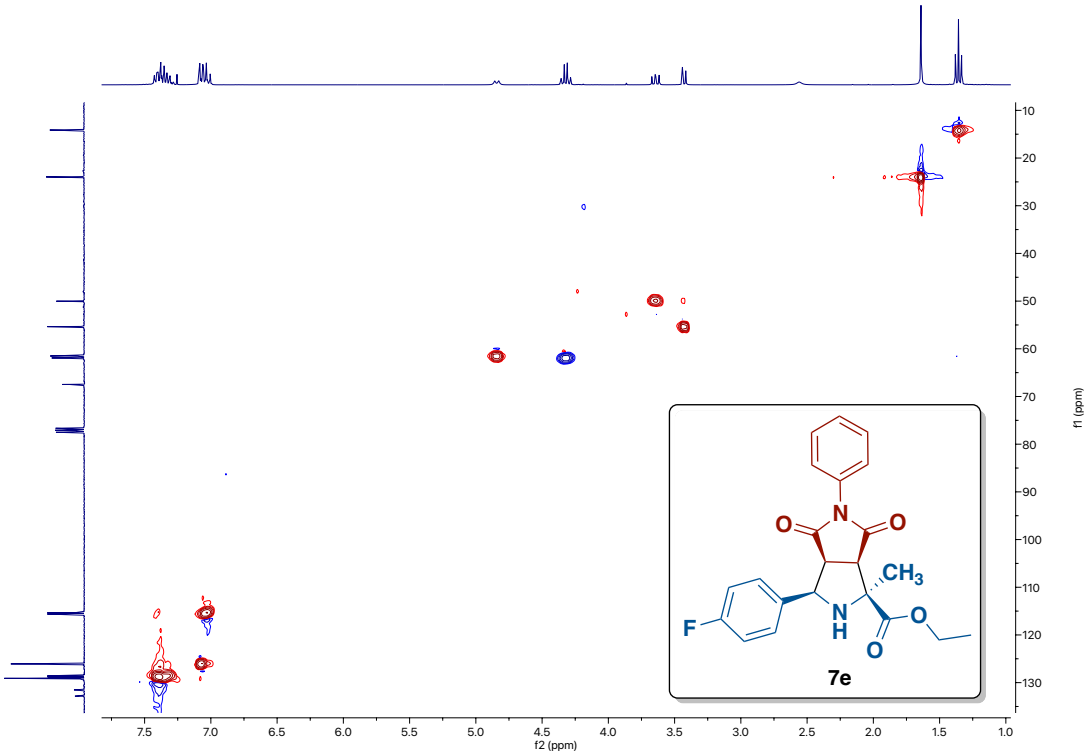


Figure S75. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7e**

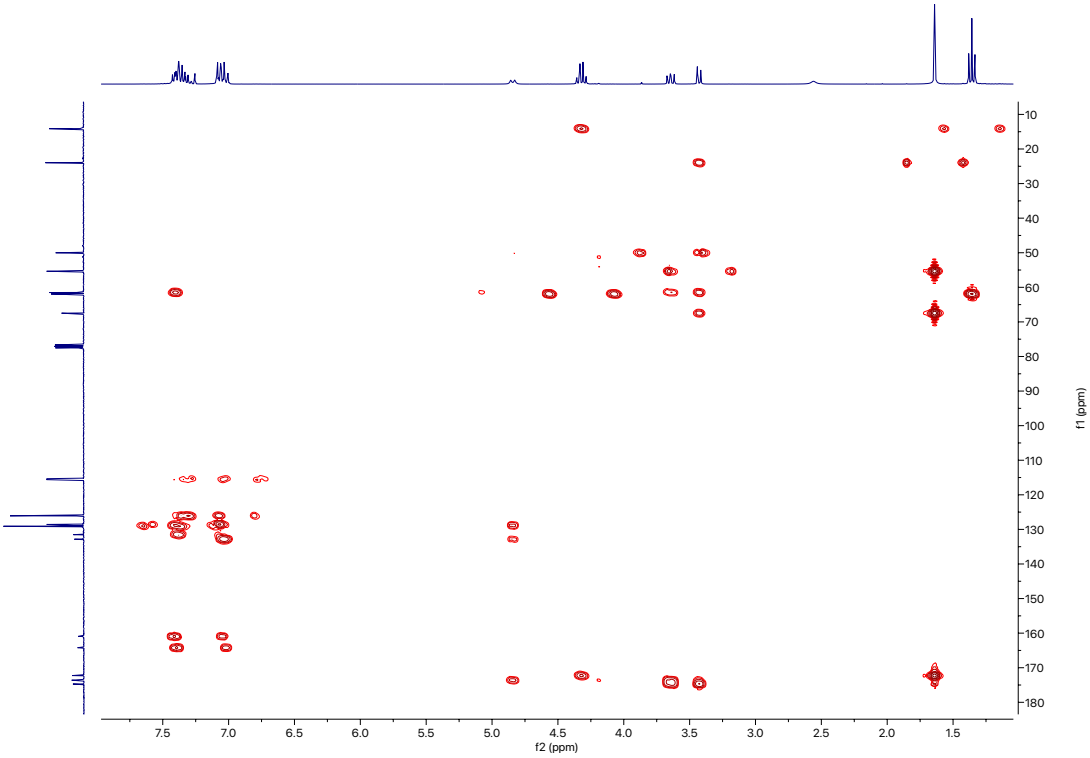


Figure S76. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7e**

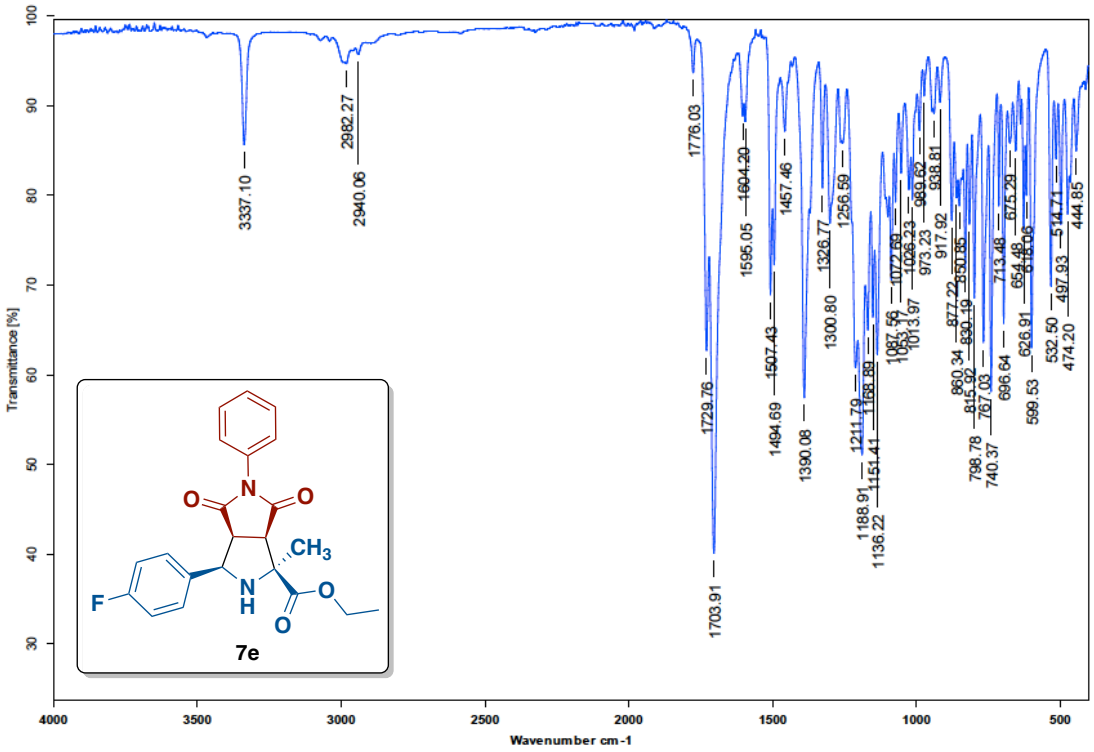
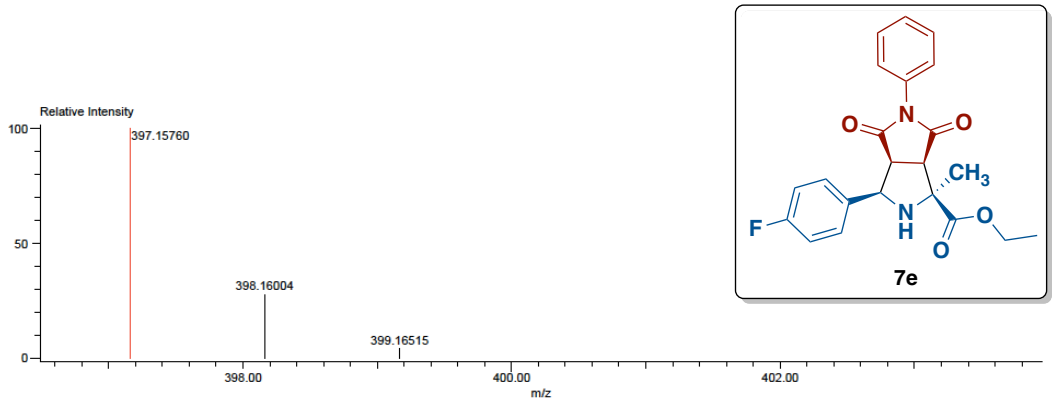


Figure S77. IR Spectrum of compound (±) **7e**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
397.15760	101266.35	397.15636	1.24	3.11	$^{12}C_{22}{}^{1}H_{22}{}^{19}F_{1}{}^{14}N_{2}{}^{16}O_{4}$	12.5

Figure S78. ERSM Spectrum (DART+) of compound **7e**

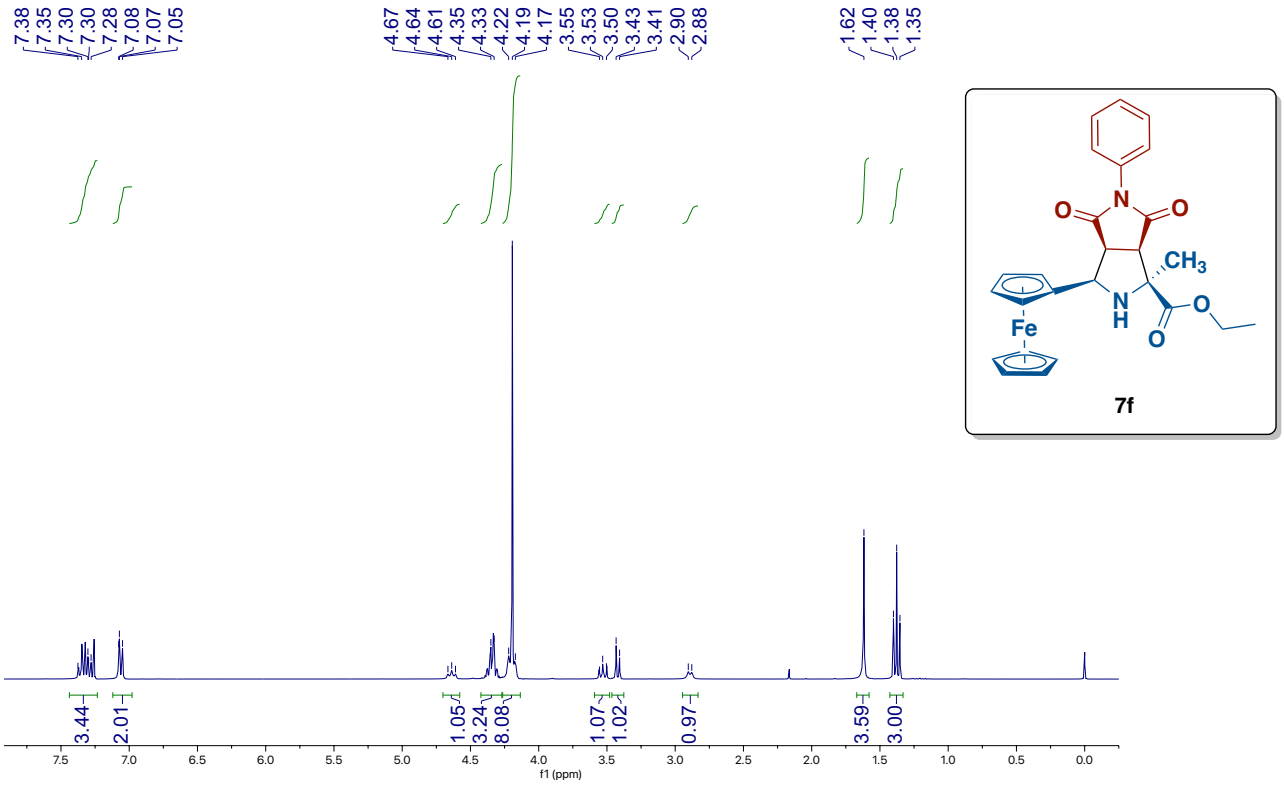


Figure S79. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7f**

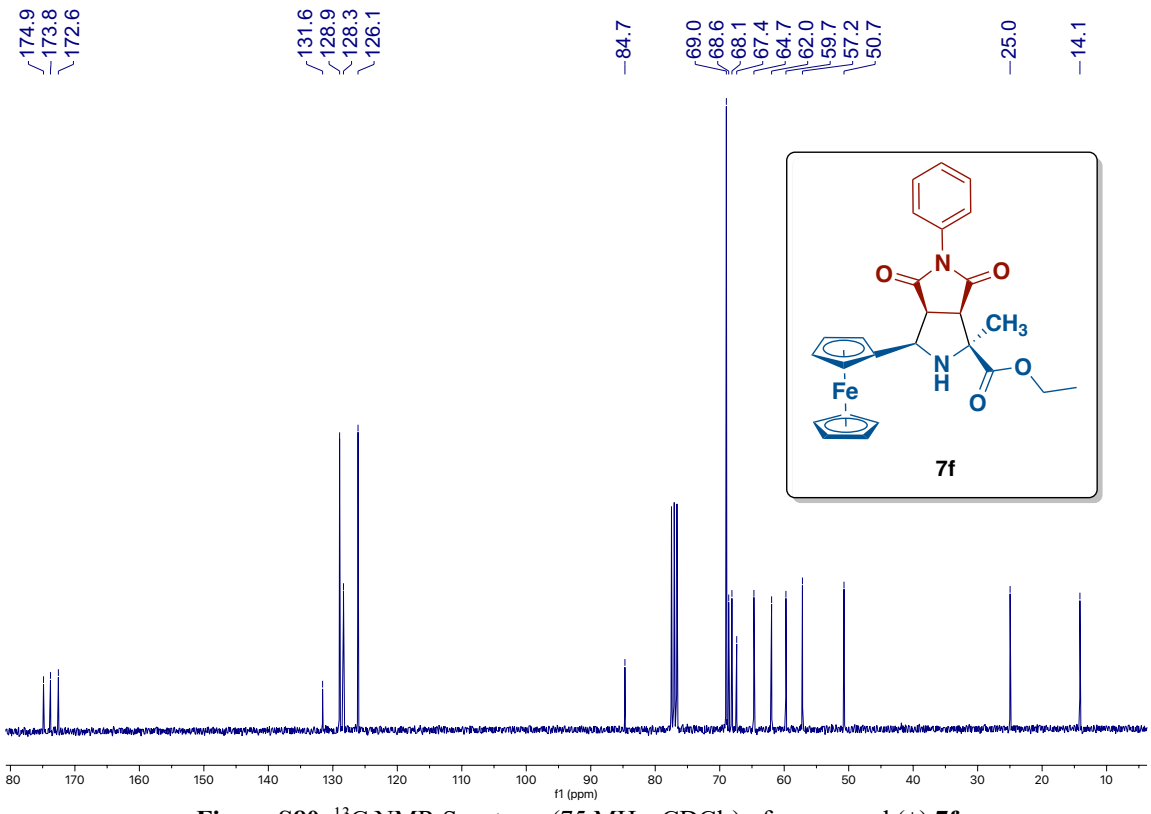


Figure S80. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7f**

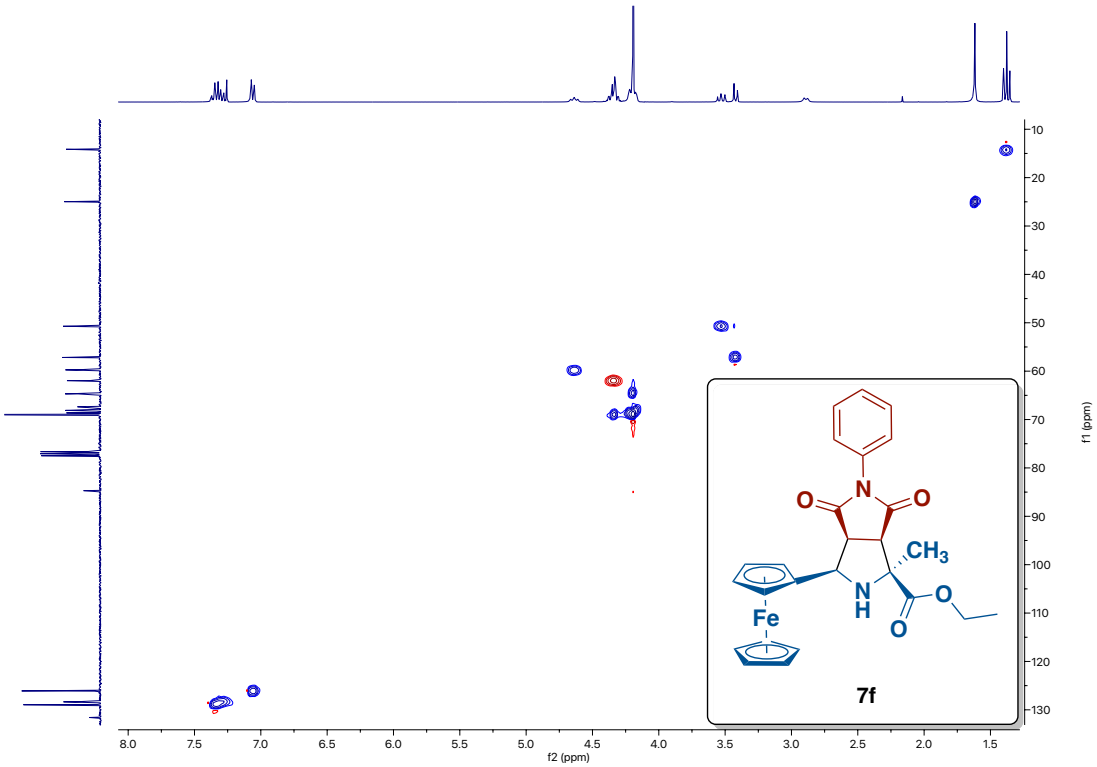


Figure S81. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7f**

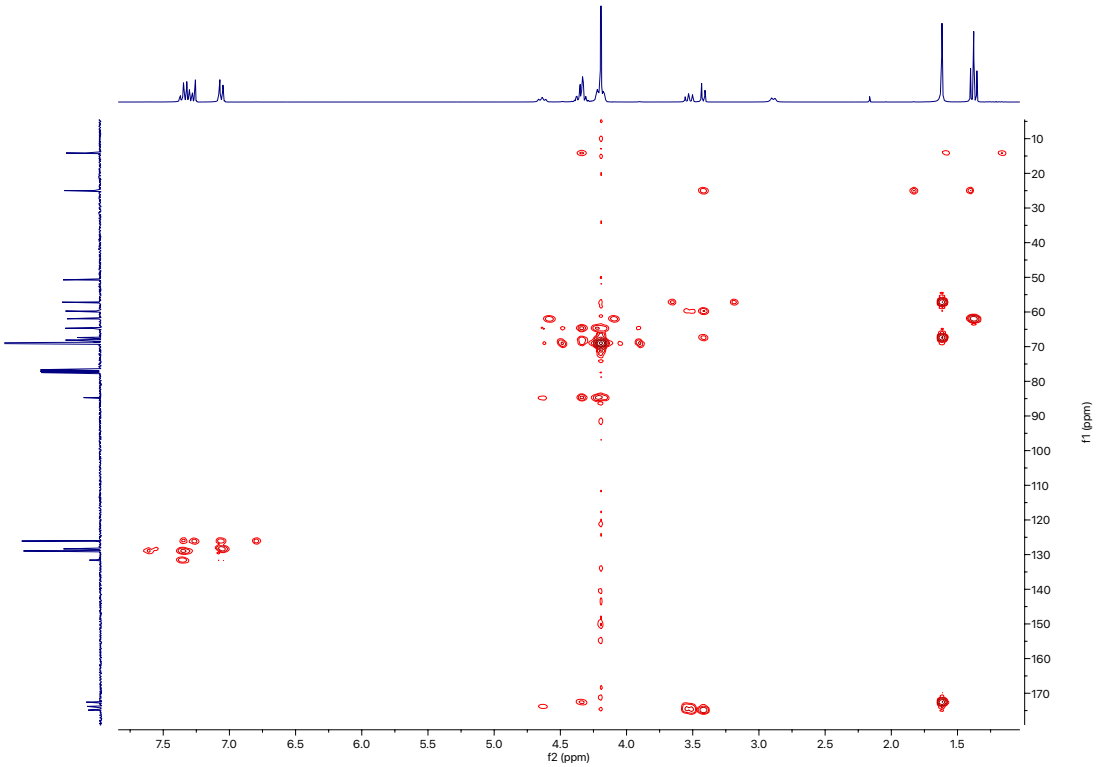


Figure S82. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7f**

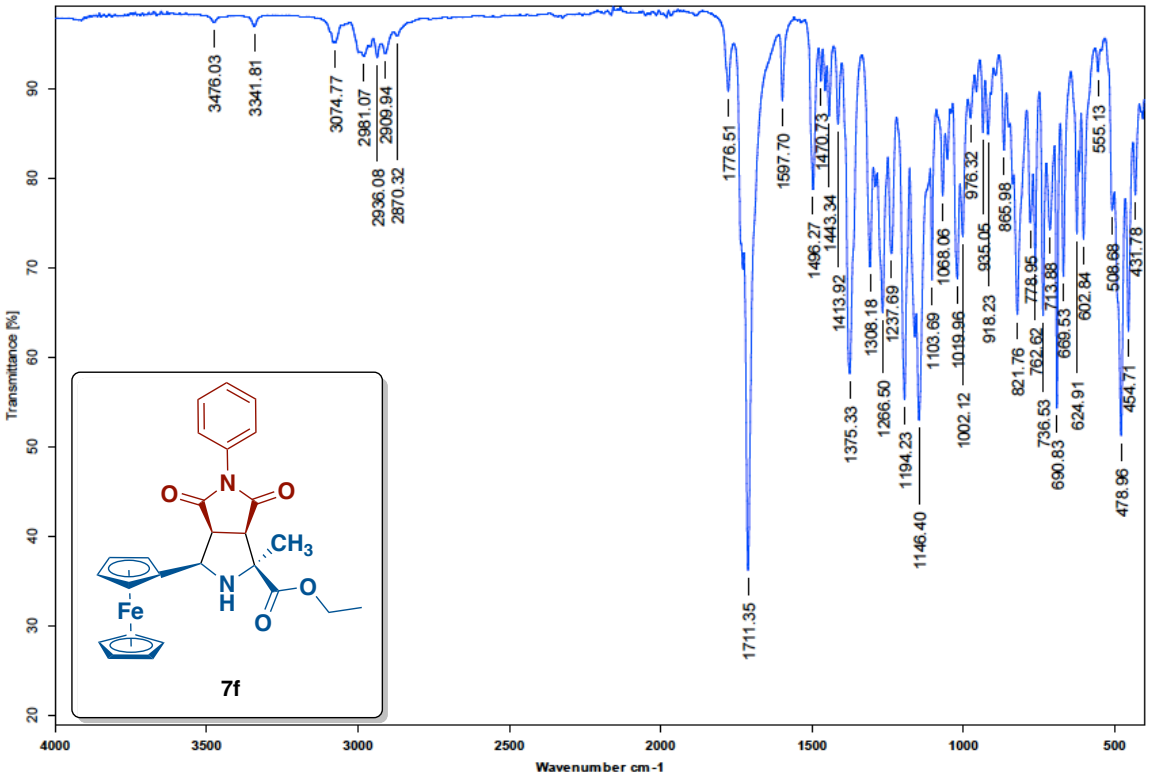
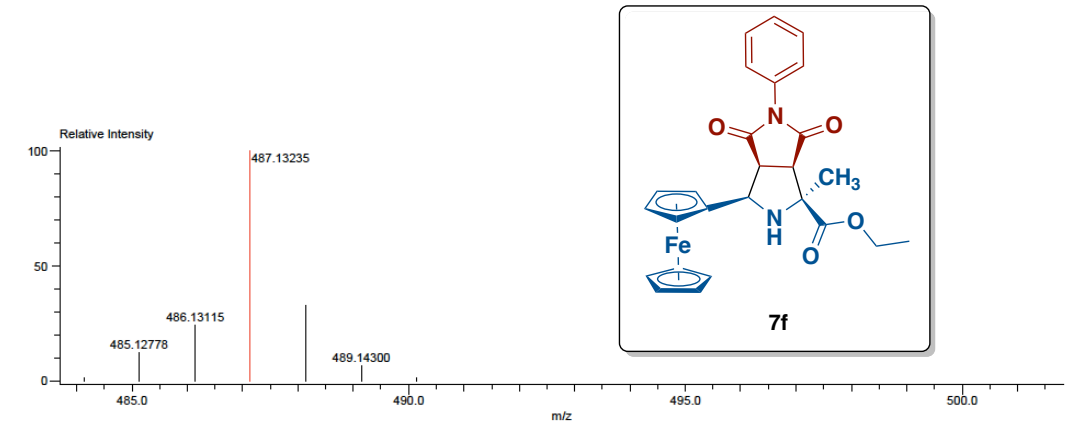


Figure S83. IR Spectrum of compound (±) **7f**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
487.13235	63913.93	487.13202	0.33	0.68	$^{12}C_{26}{}^{1}H_{27}{}^{56}Fe_{1}{}^{14}N_{2}{}^{16}O_{4}$	15.0

Figure S84. ERSM Spectrum (DART+) of compound (±) **7f**

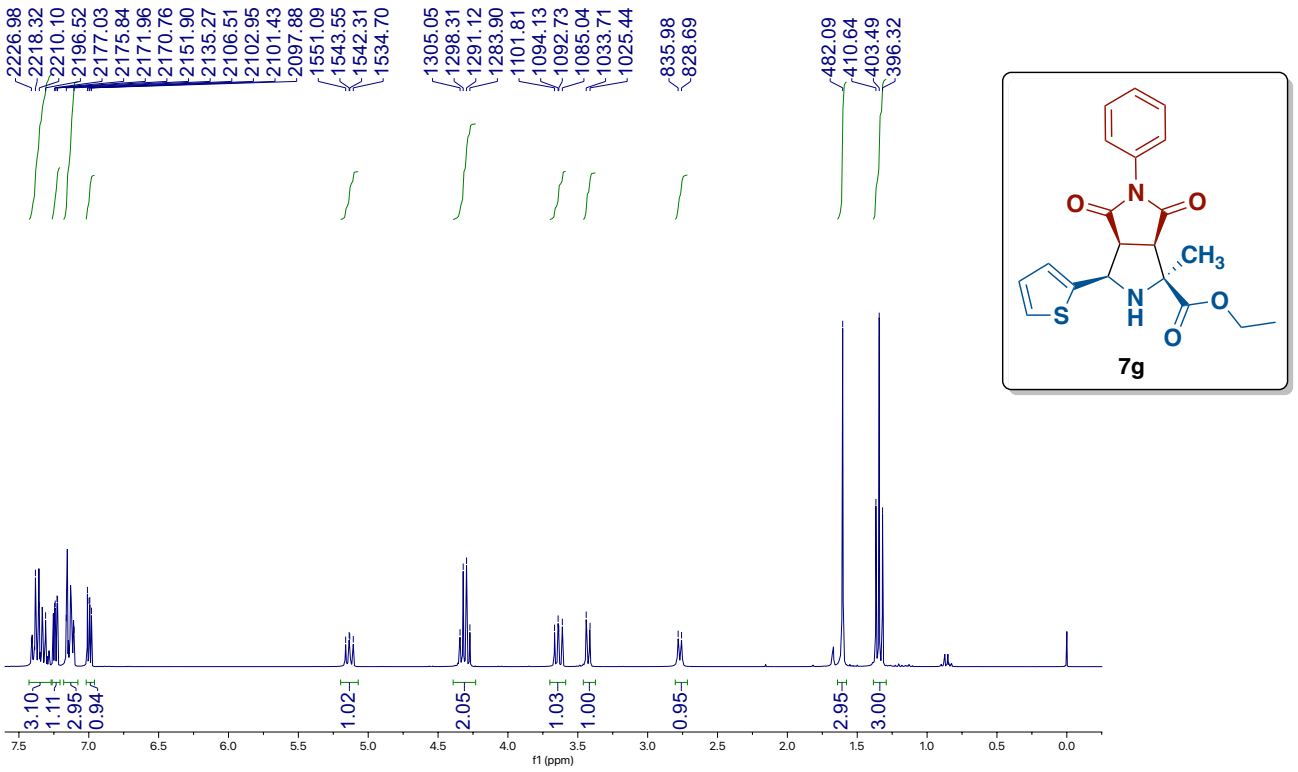


Figure S85. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7g**

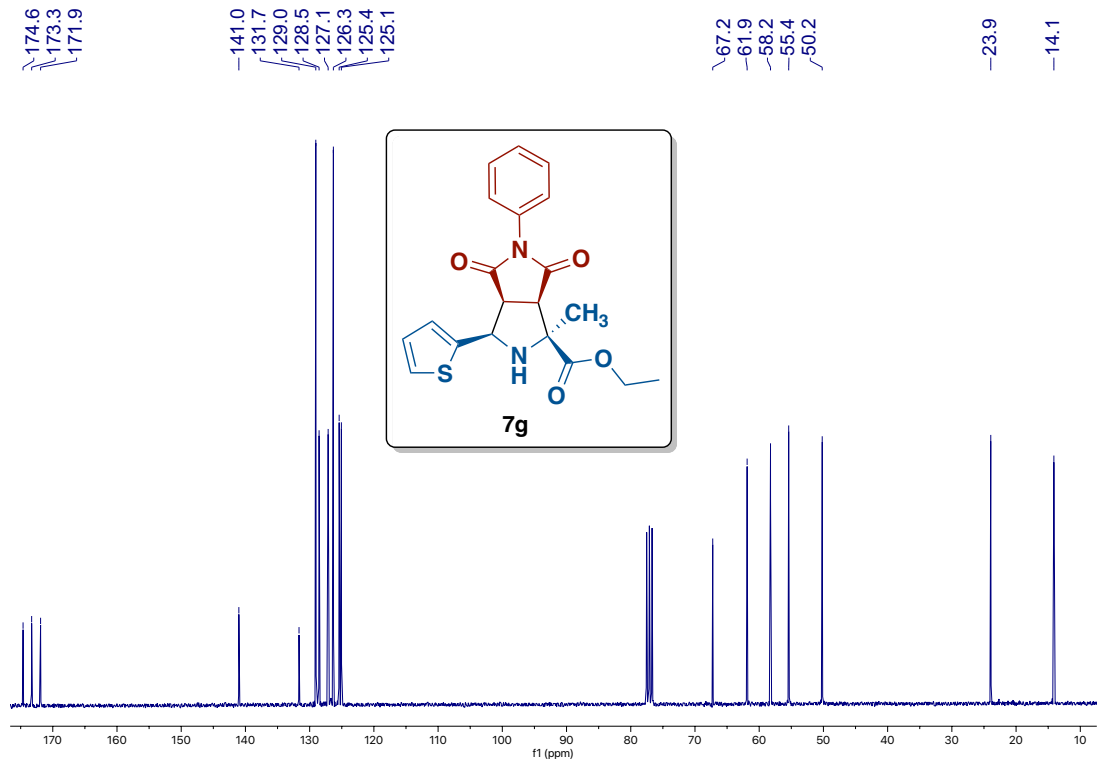


Figure S86. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7g**

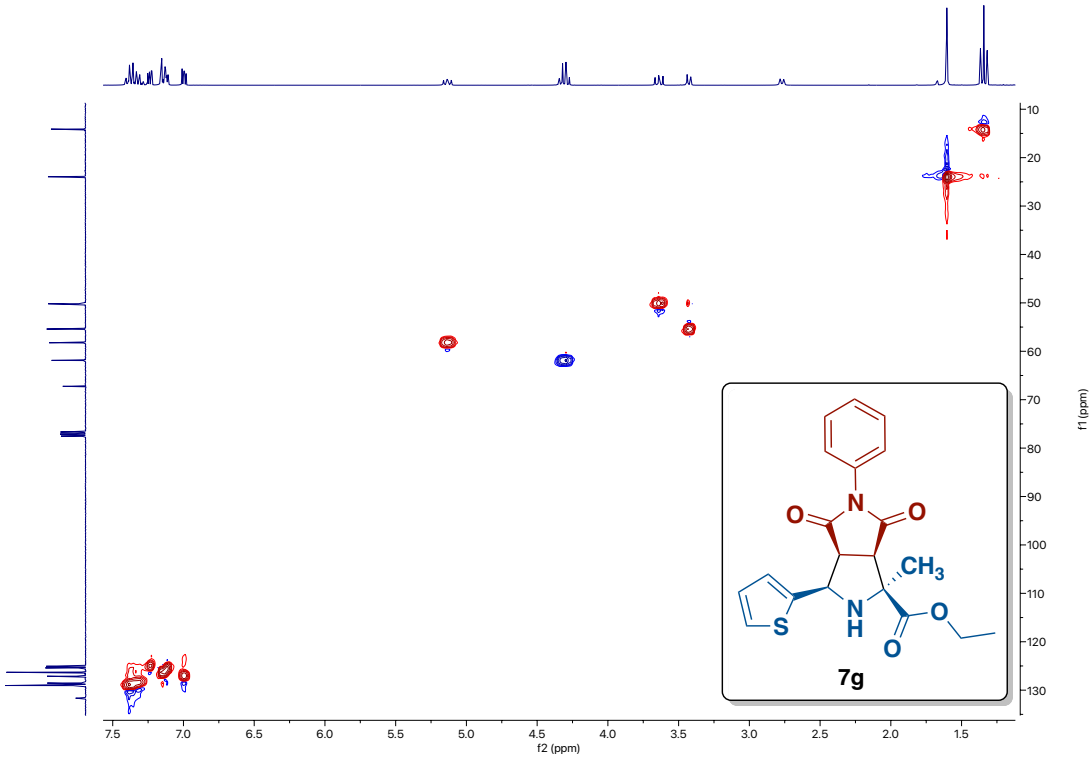


Figure S87. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7g**

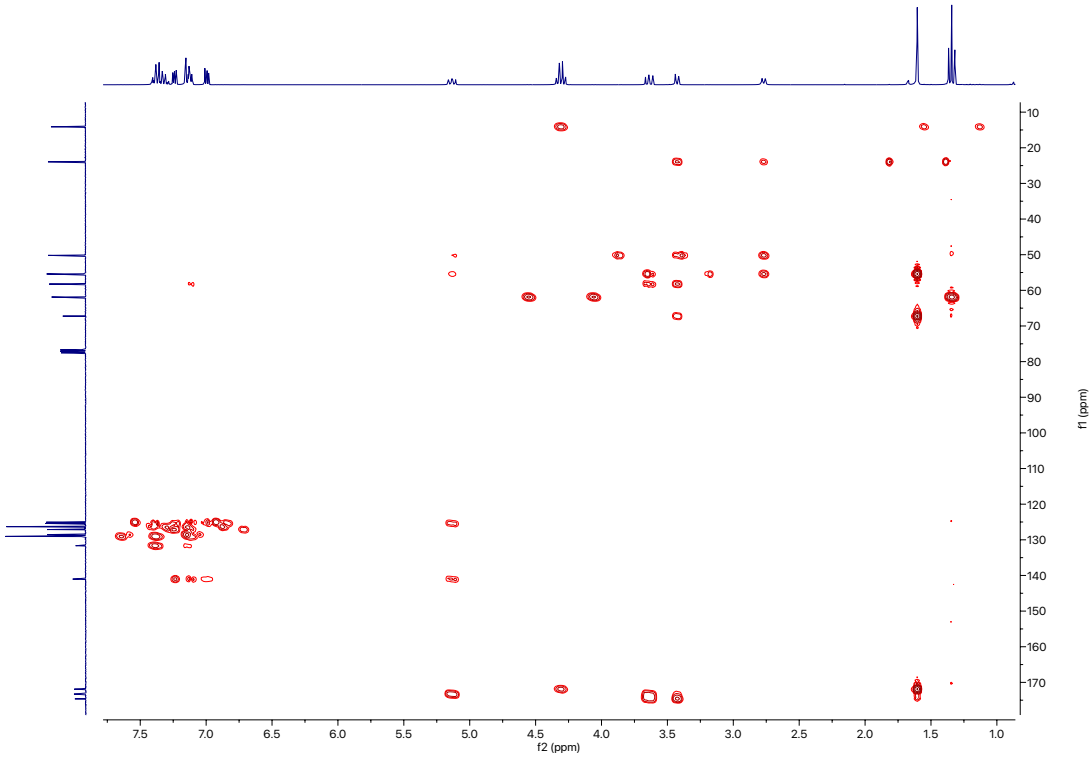


Figure S88. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7g**

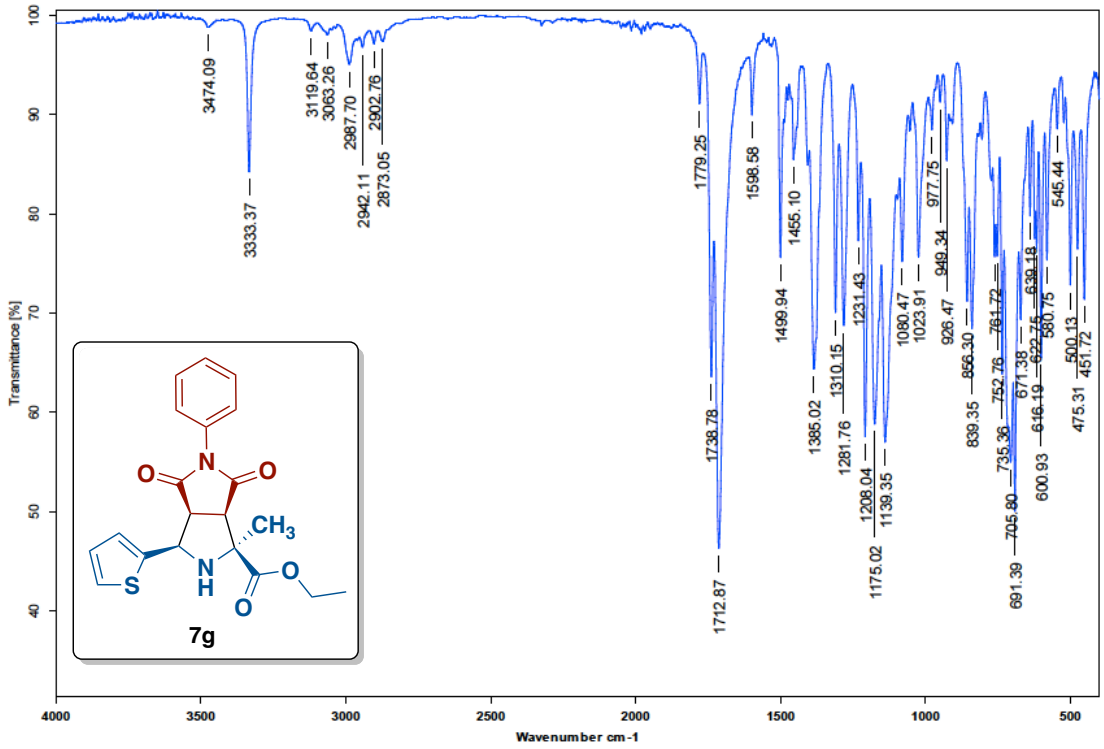
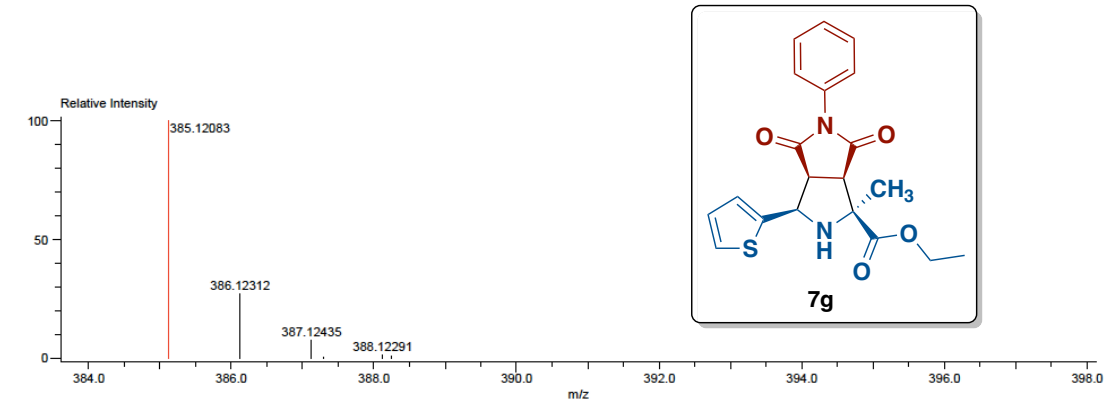


Figure S89. IR Spectrum of compound (±) **7g**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
385.12083	38558.11	385.12220	-1.37	-3.56	$^{12}C_{20}{}^{1}H_{21}{}^{14}N_{2}{}^{16}O_{4}{}^{32}S_{1}$	12.5

Figure S90. ERSM Spectrum (DART+) of compound (±) **7g**

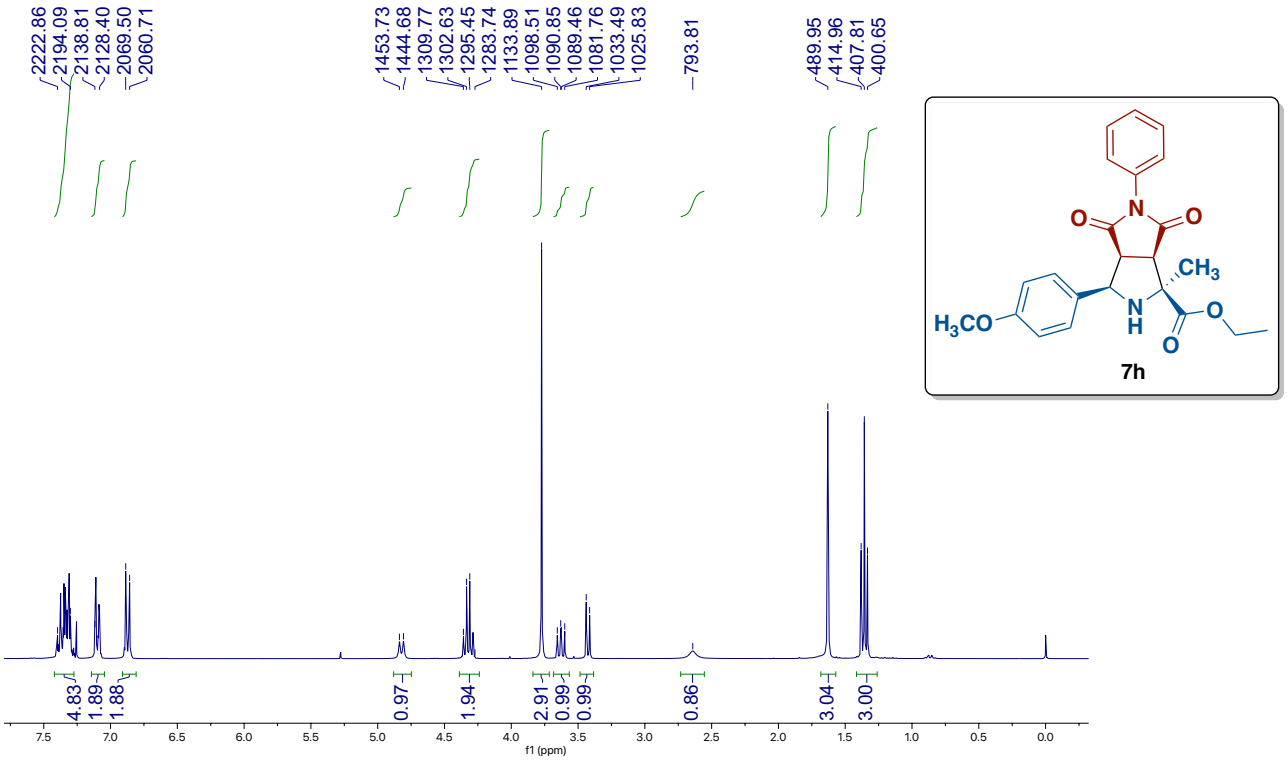


Figure S91. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7h**

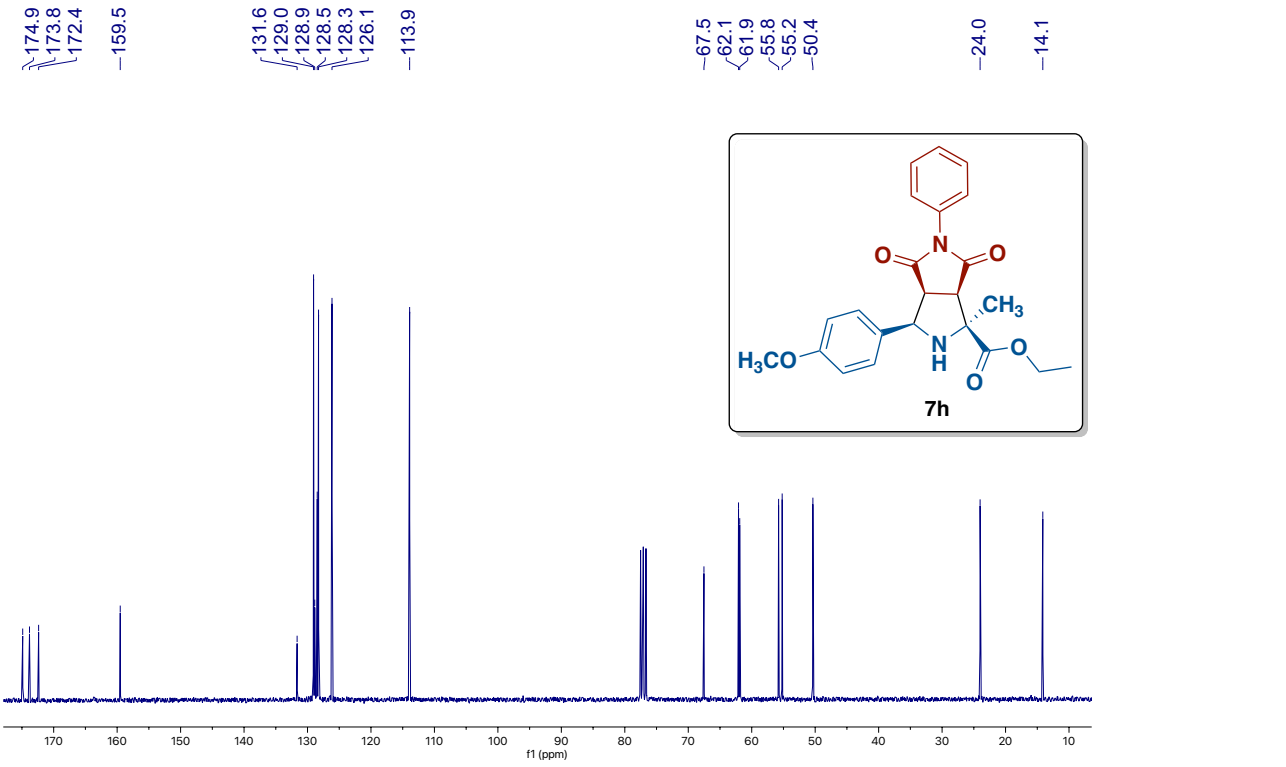


Figure S92. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7h**

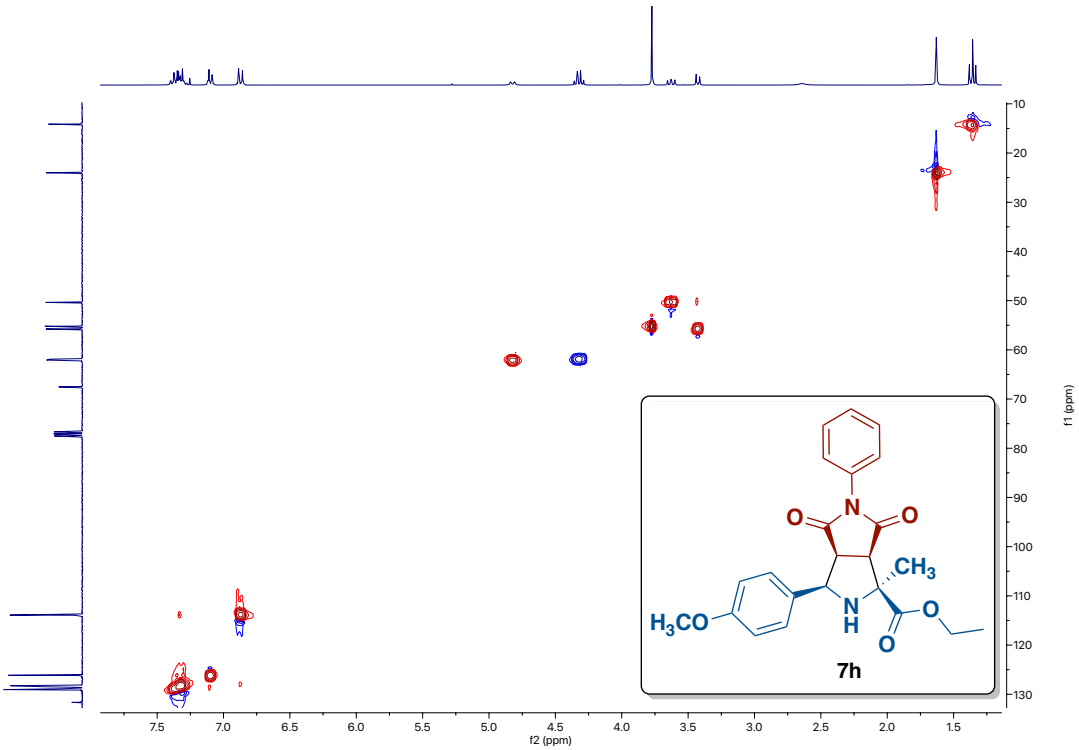


Figure S93. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7h**

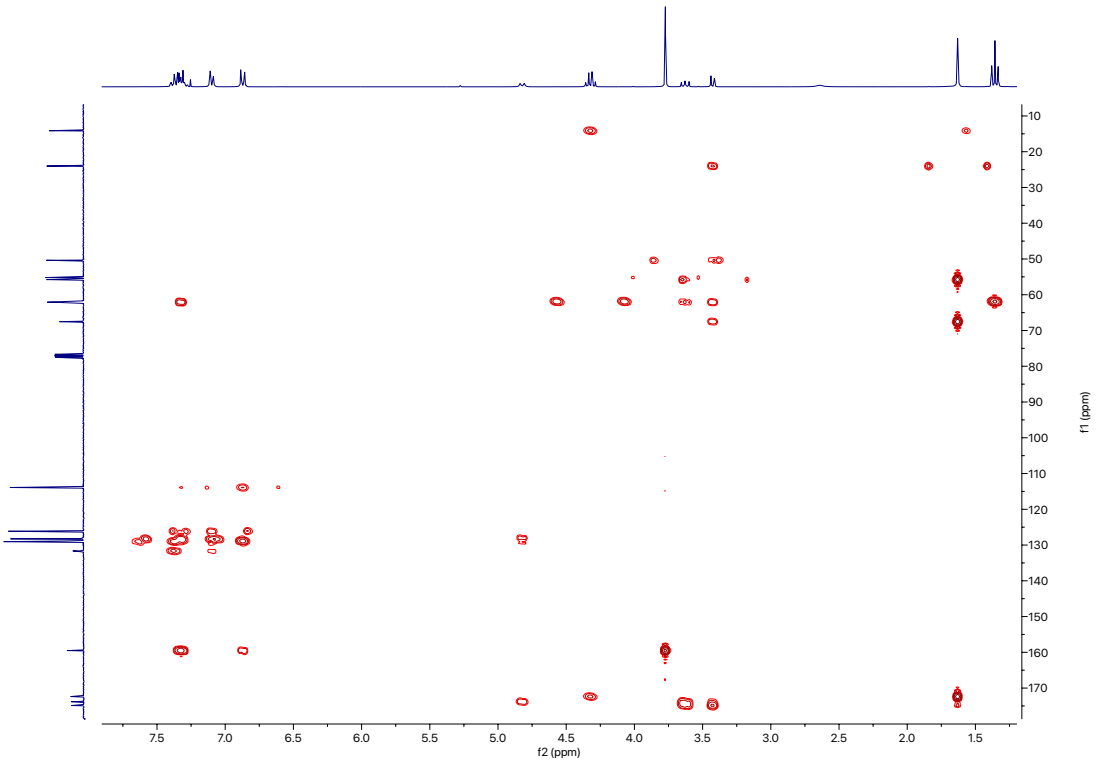


Figure S94. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7h**

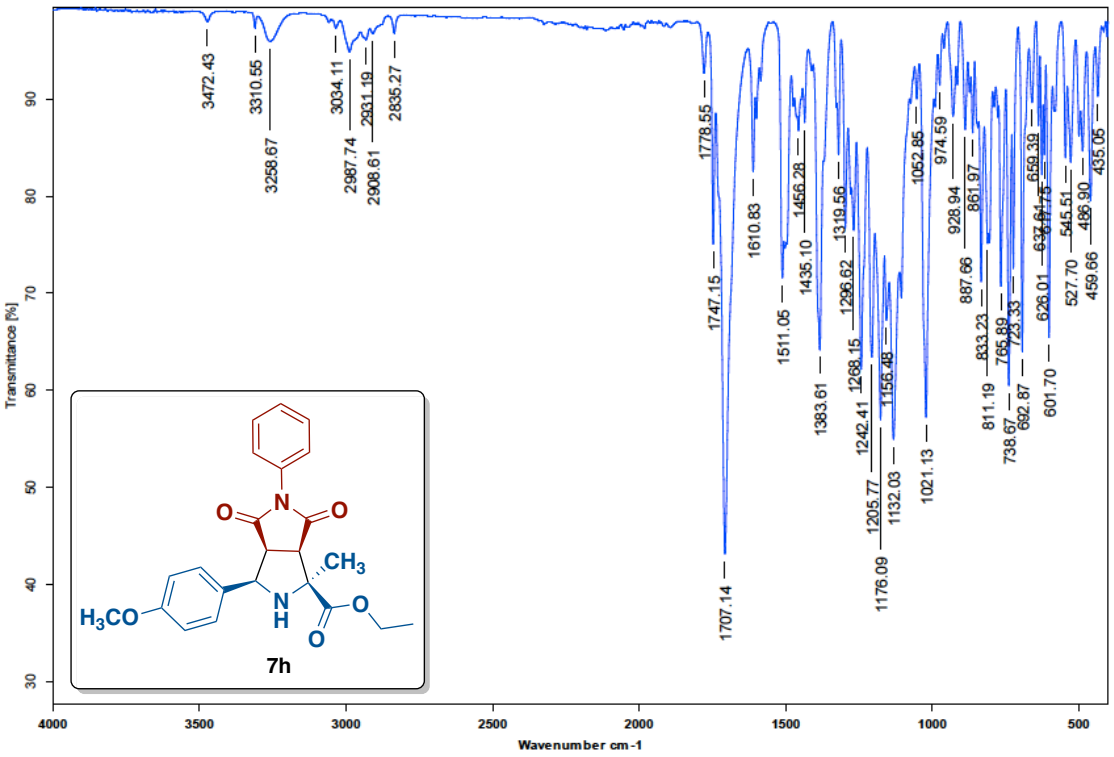
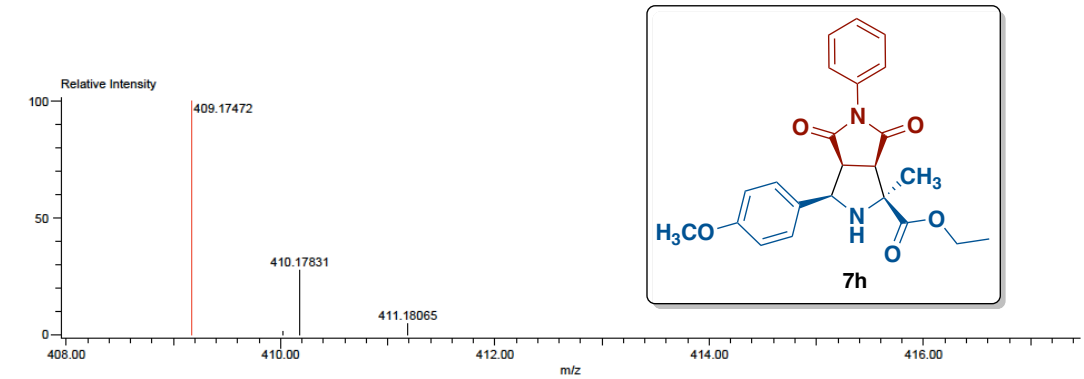


Figure S95. IR Spectrum of compound (±) **7h**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
409.17472	22665.65	409.17635	-1.63	-3.97	$^{12}C_{23}{}^{1}H_{25}{}^{14}N_{2}{}^{16}O_{5}$	12.5

Figure S96. ERSM Spectrum (DART+) of compound (±) **7h**

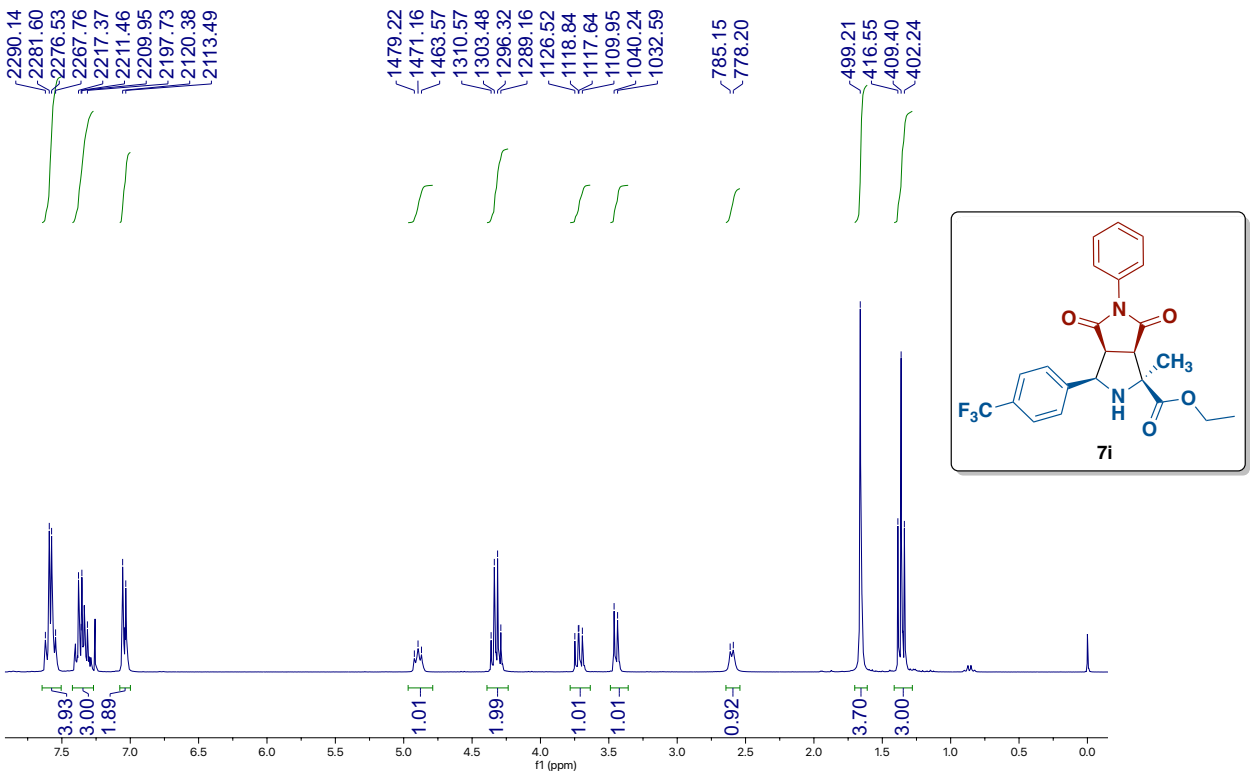


Figure S97. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7i**

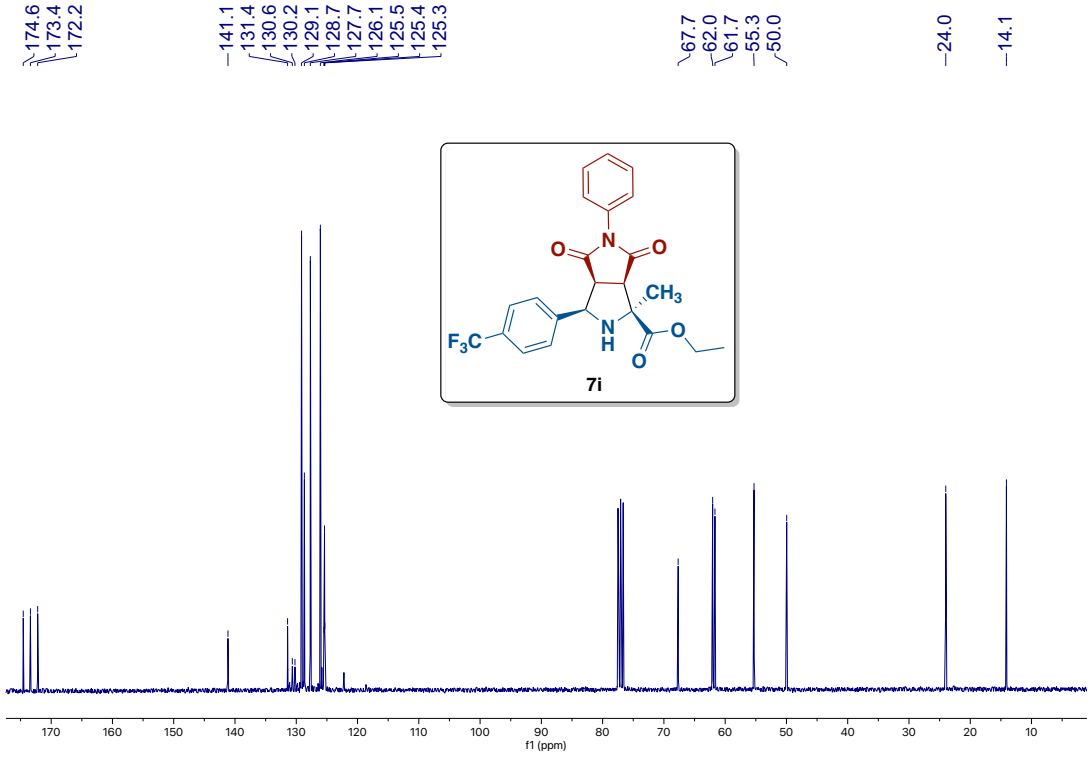


Figure S98. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **7i**

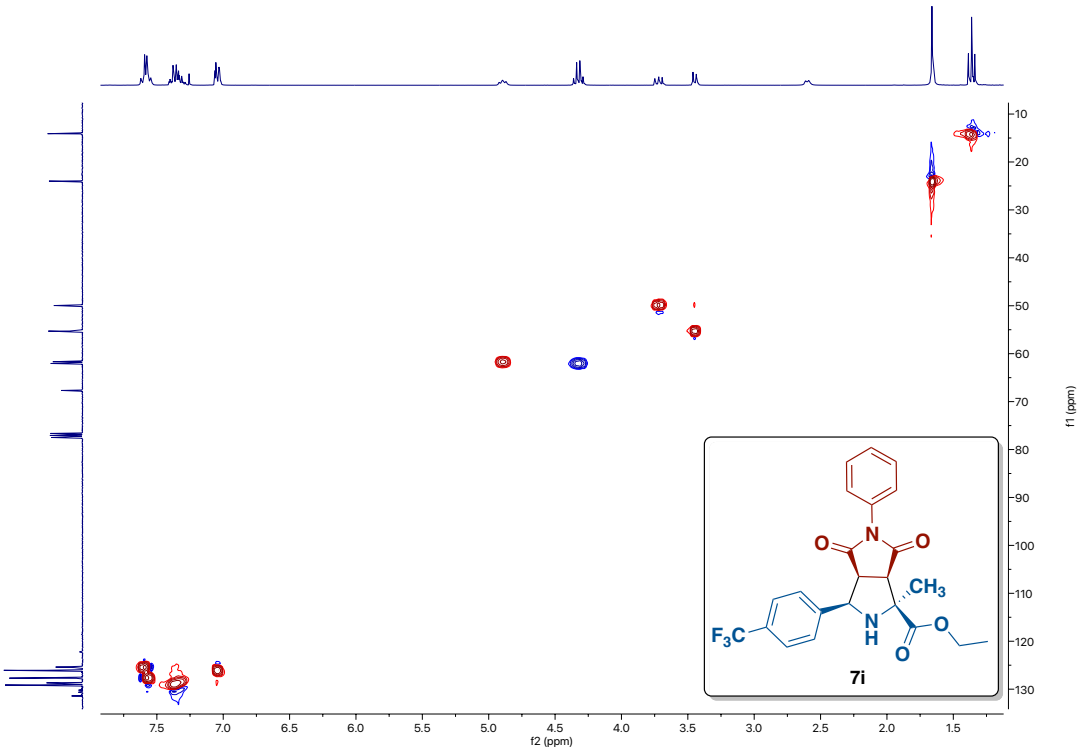


Figure S99. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7i**

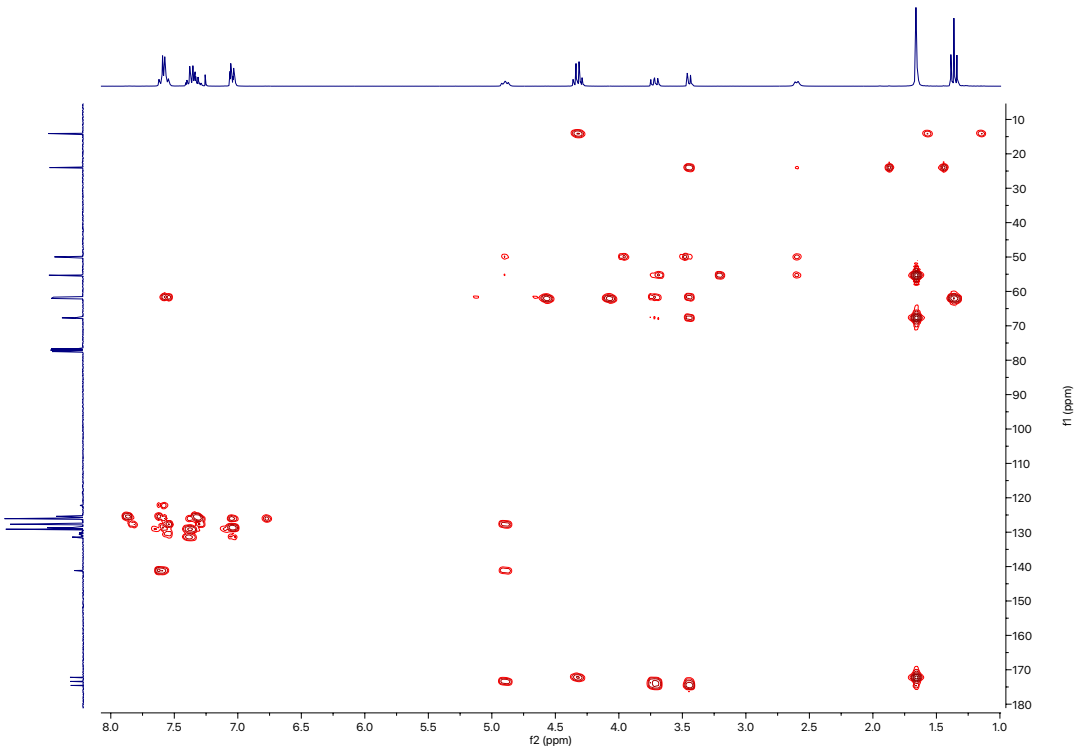


Figure S100. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7i**

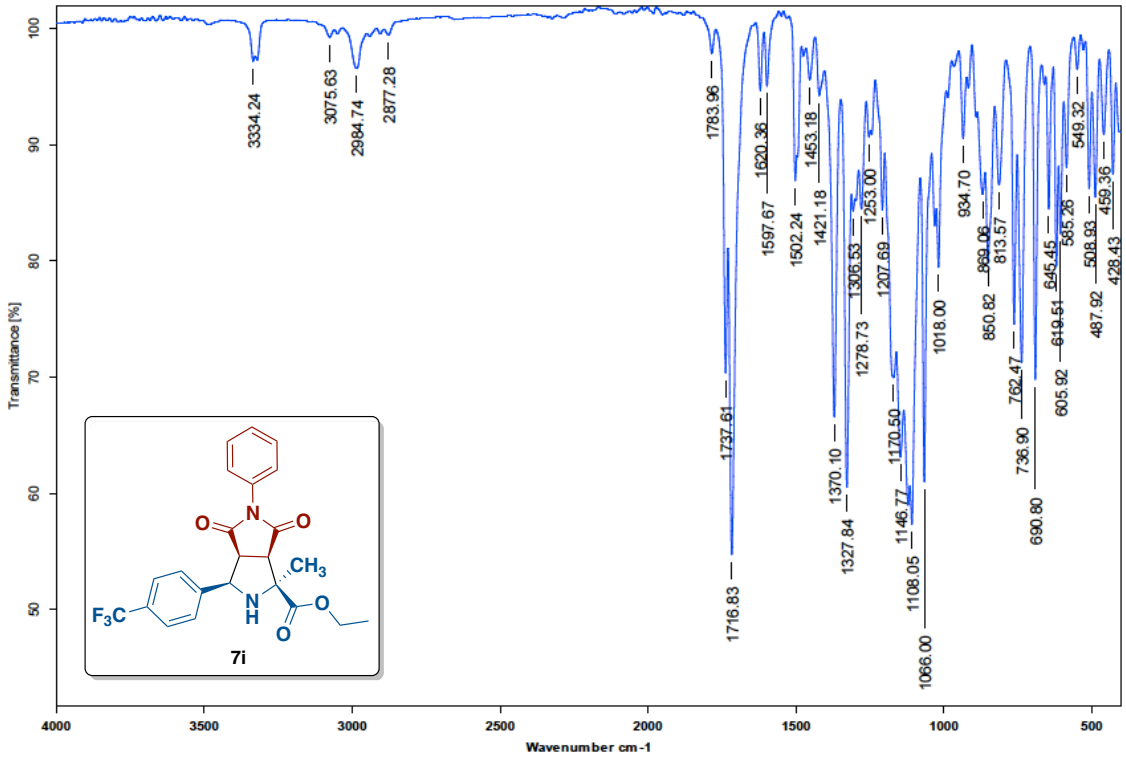
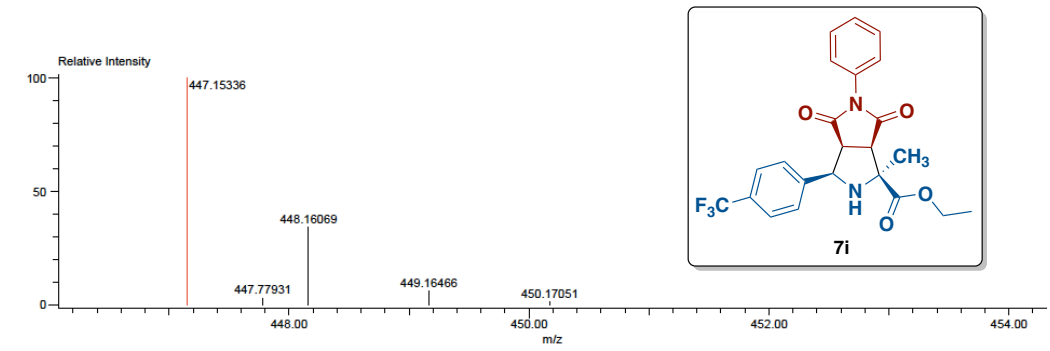


Figure S101. IR Spectrum of compound (±) **7i**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
447.15336	82080.24	447.15317	0.19	0.42	$^{12}C_{23}{}^{1}H_{22}{}^{19}F_{3}{}^{14}N_{2}{}^{16}O_{4}$	12.5

Figure S102. ERSM Spectrum (DART+) of compound (±) **7i**

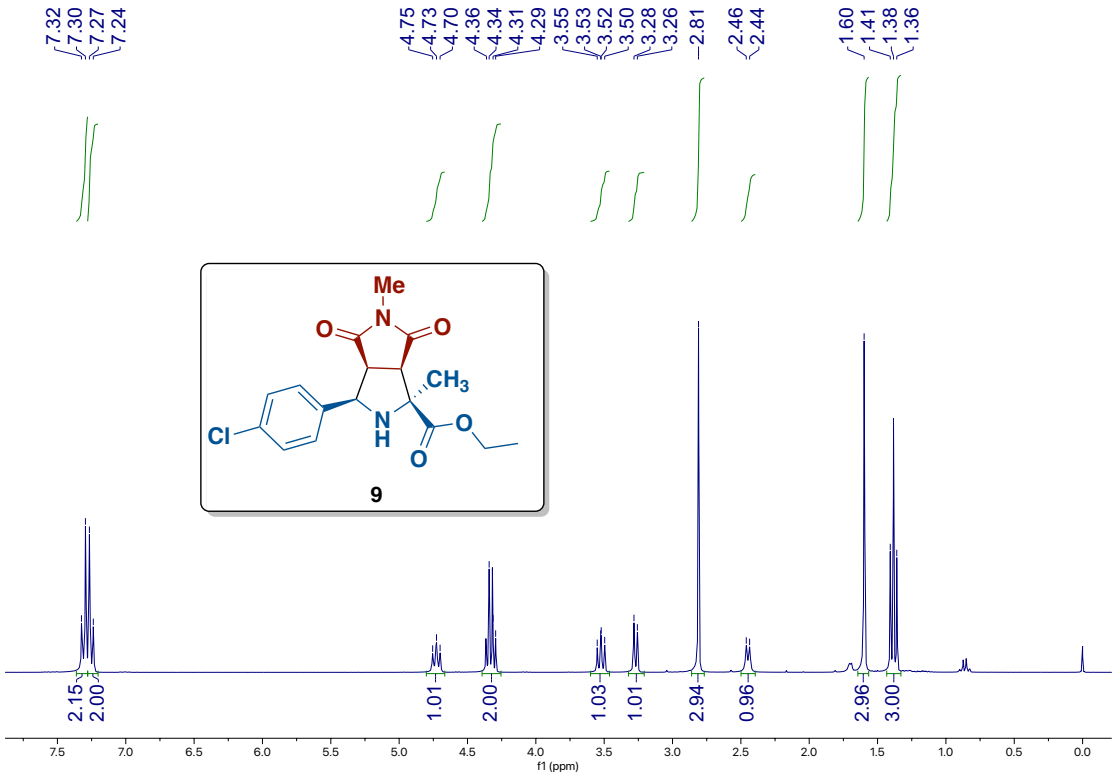


Figure S103. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **9**

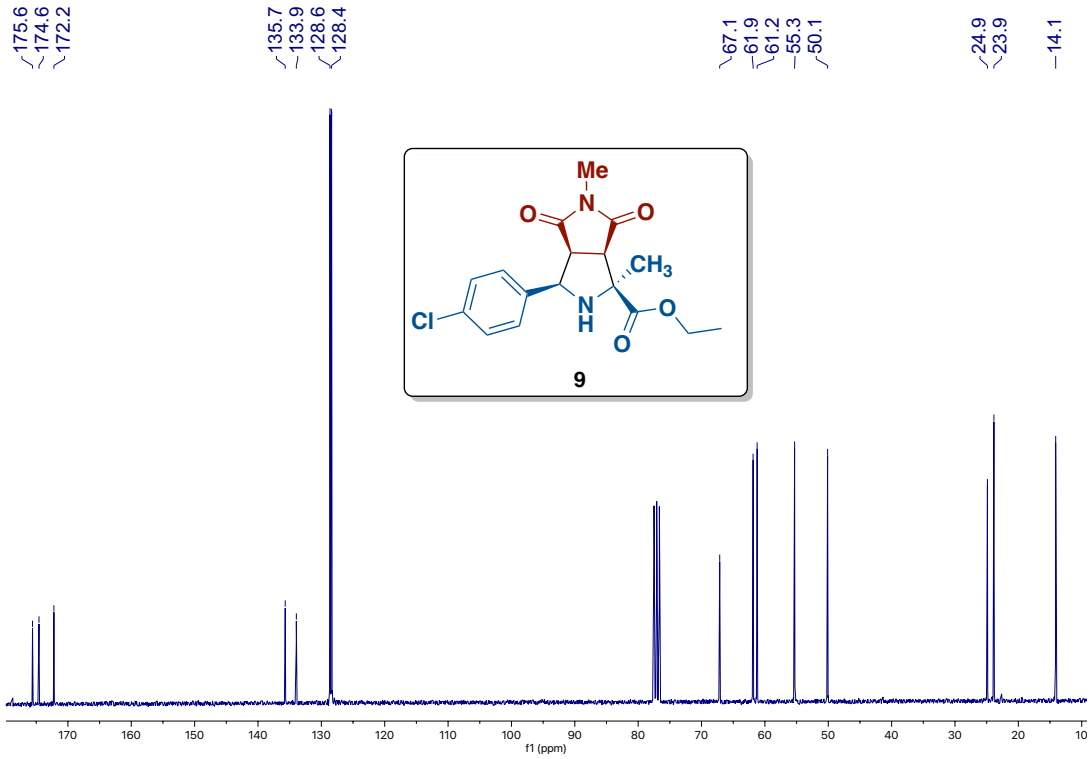


Figure S104. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **9**

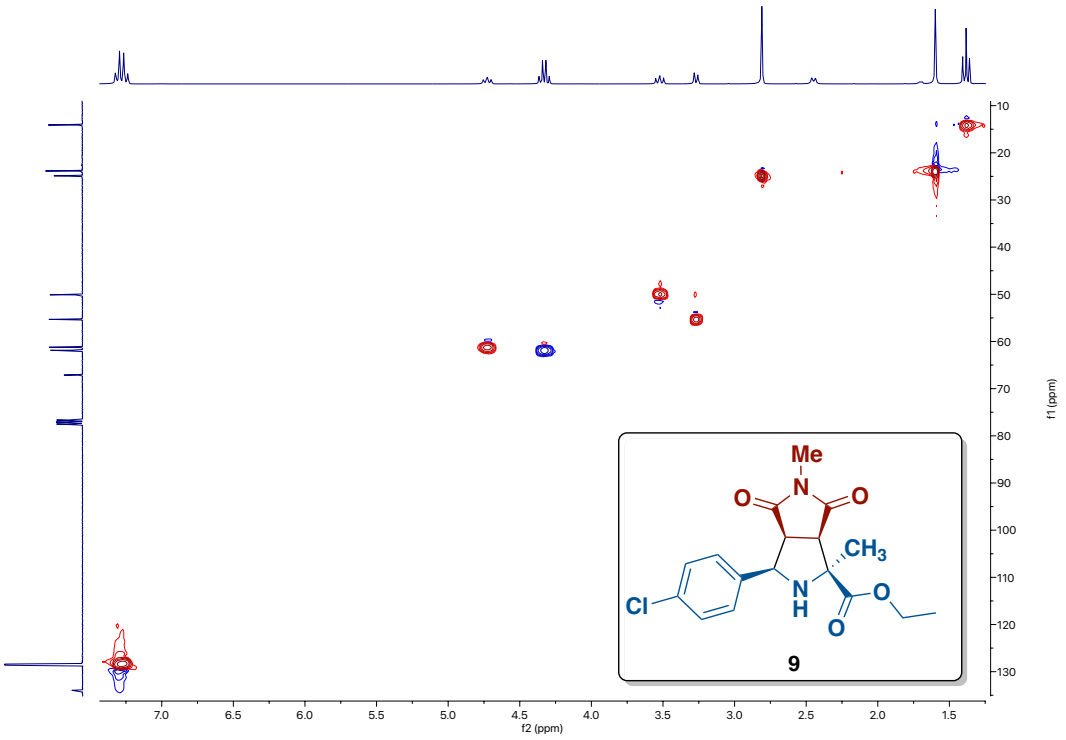


Figure S105. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **9**

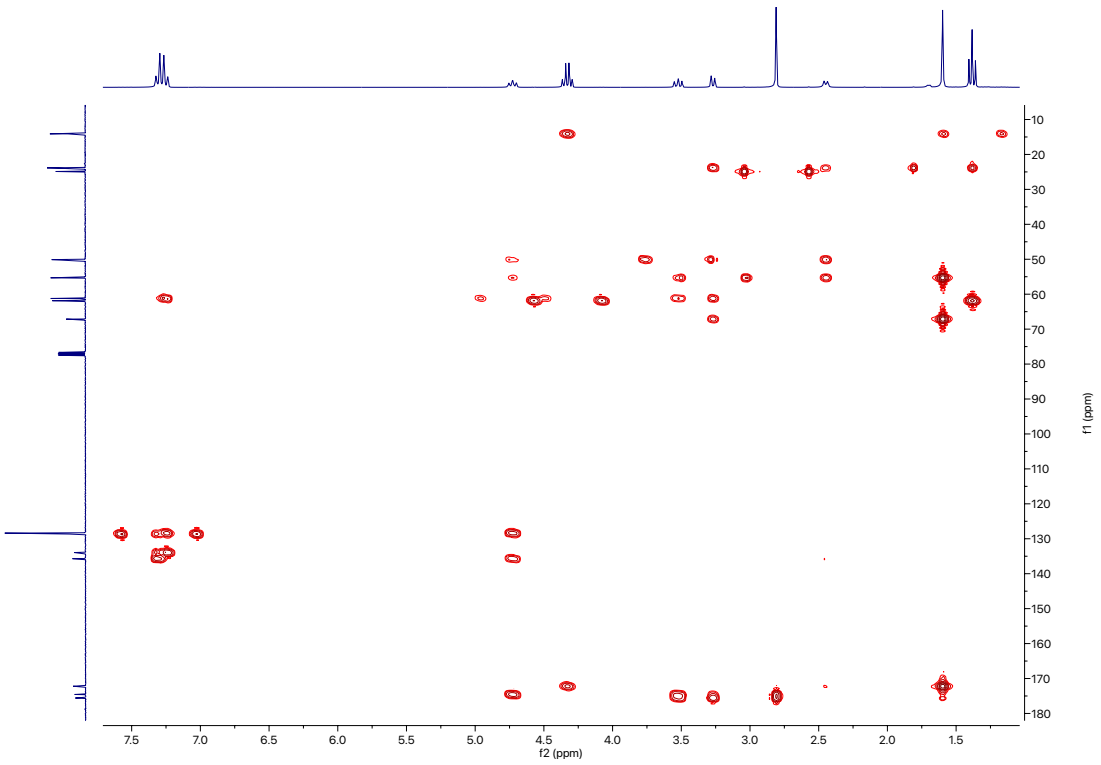


Figure S106. HMBC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **9**

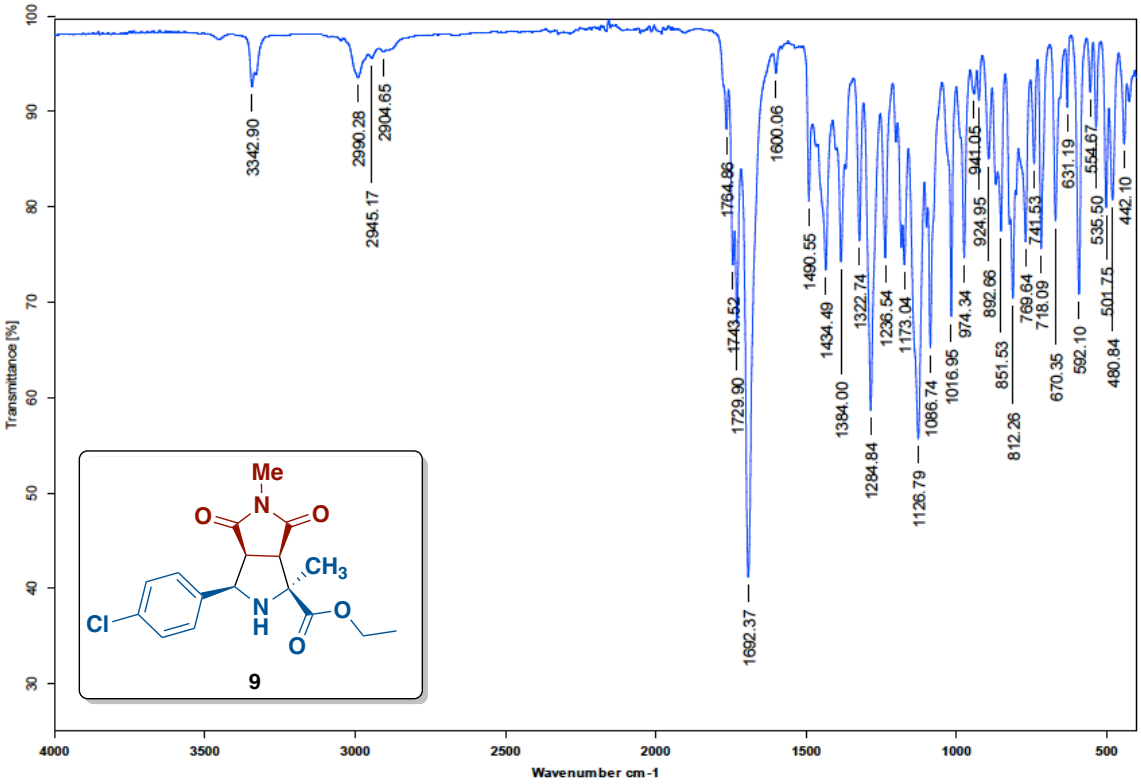
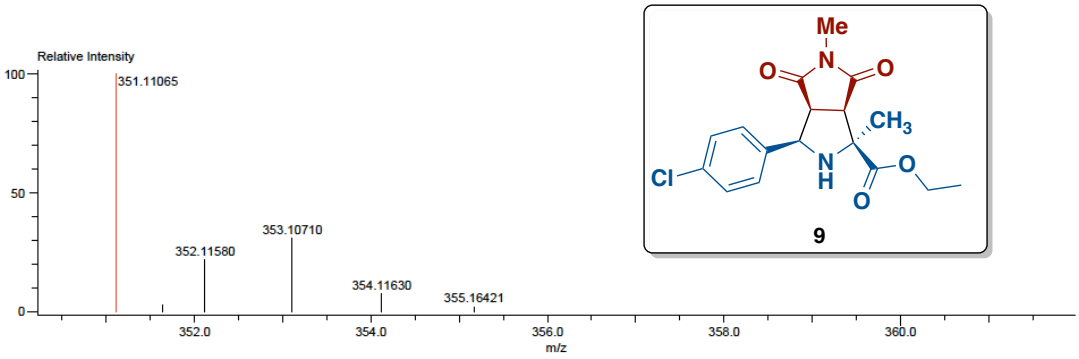


Figure S107. IR Spectrum of compound (±) **9**



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
351.11065	94314.43	351.11116	-0.51	-1.45	$^{12}C_{17}{}^{1}H_{20}{}^{35}Cl_{1}{}^{14}N_{2}{}^{16}O_{4}$	8.5

Figure S108. ERSM Spectrum (DART+) of compound (±) **9**

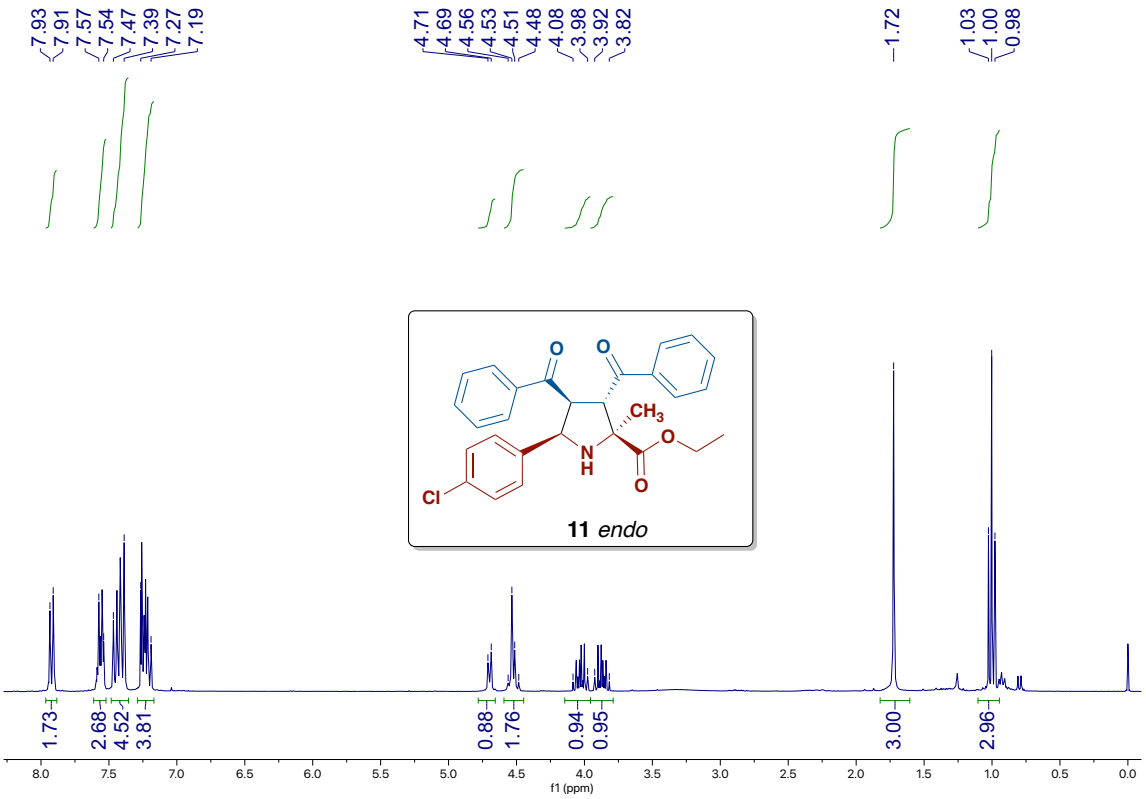


Figure S109. ^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **11** ***endo***

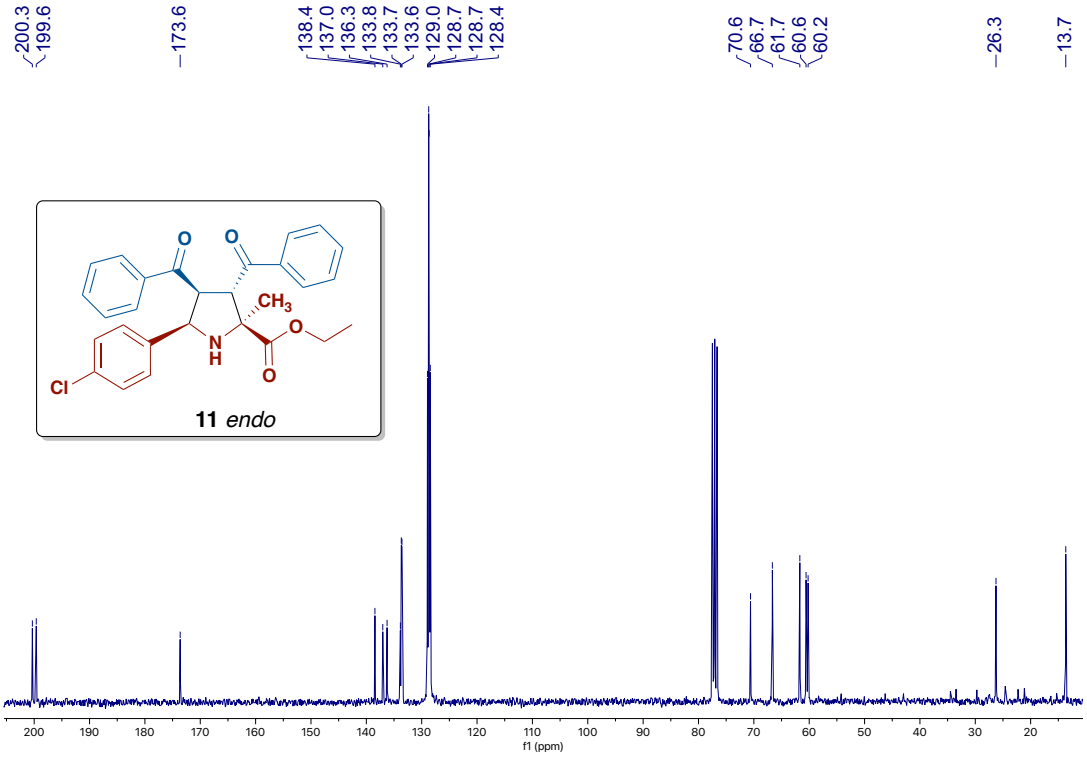


Figure S110. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **11** ***endo***

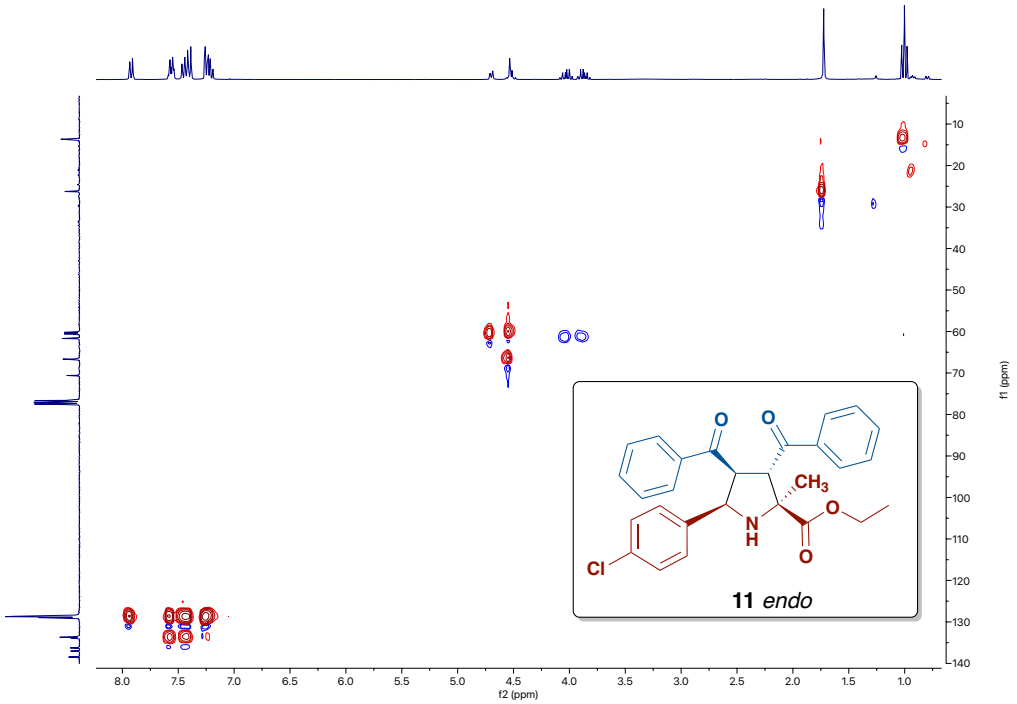


Figure S111. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **11** ***endo***

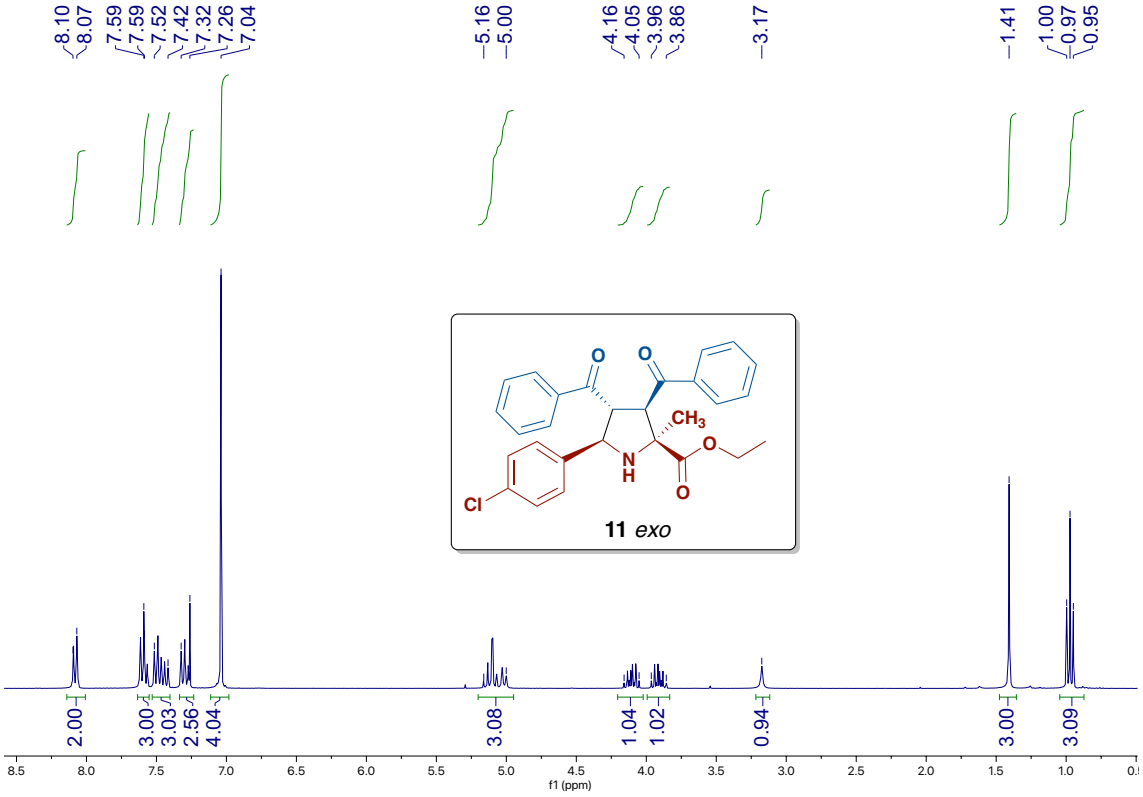


Figure S112. ^1H NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **11** ***exo***

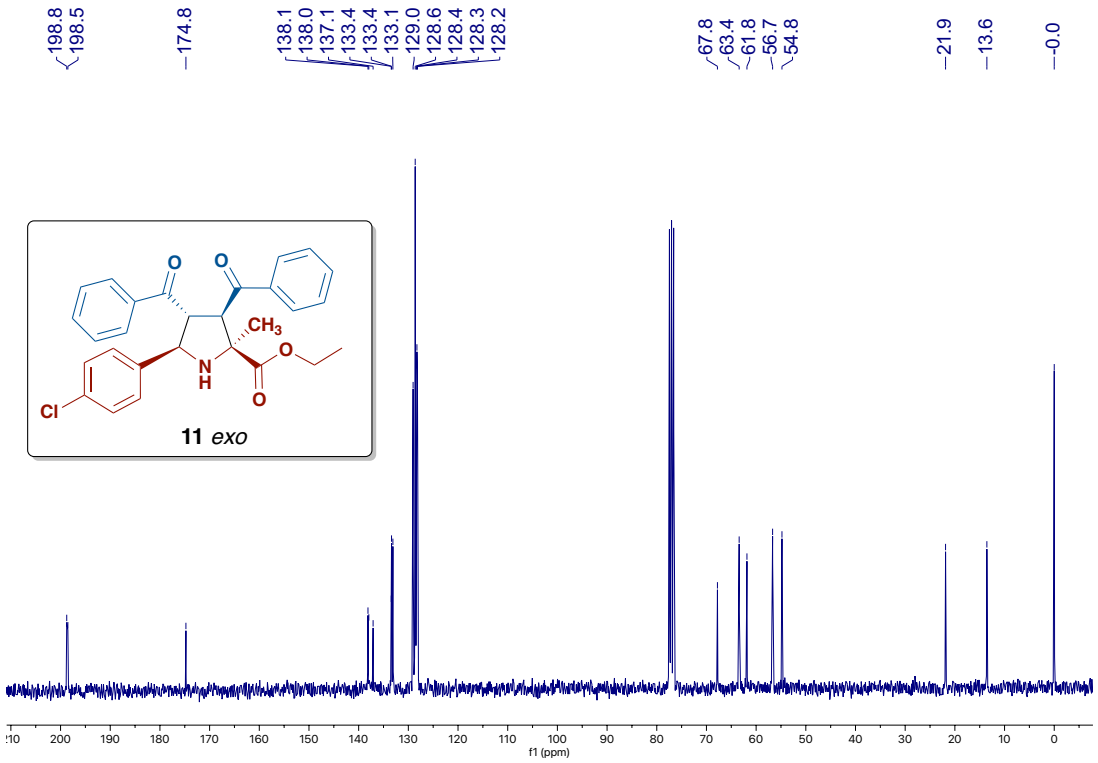


Figure S113. ^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of compound (±) **11** ***exo***

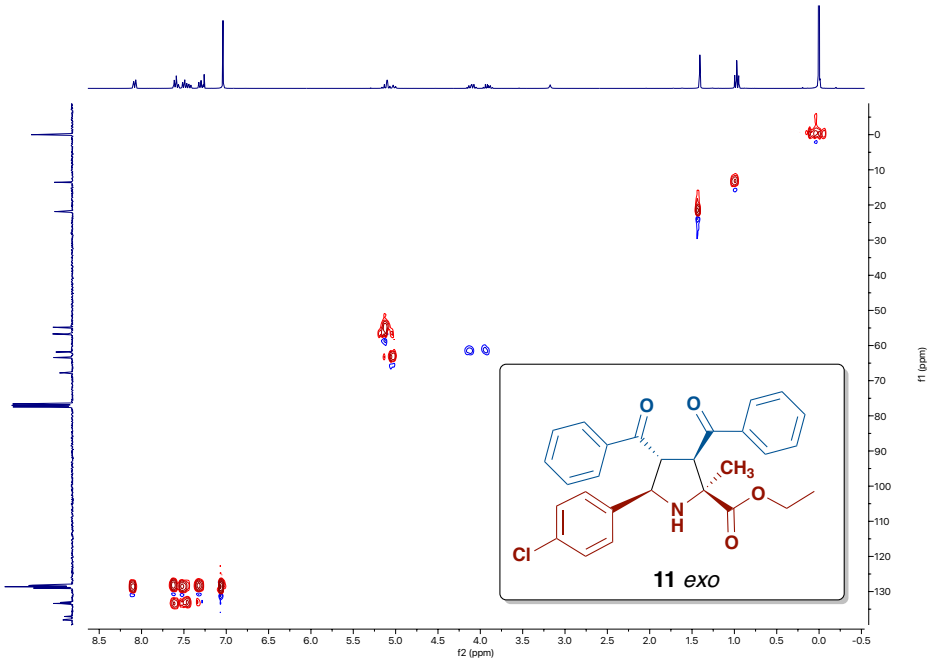


Figure S114. HMQC NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **11** ***exo***

RMN-nOe.

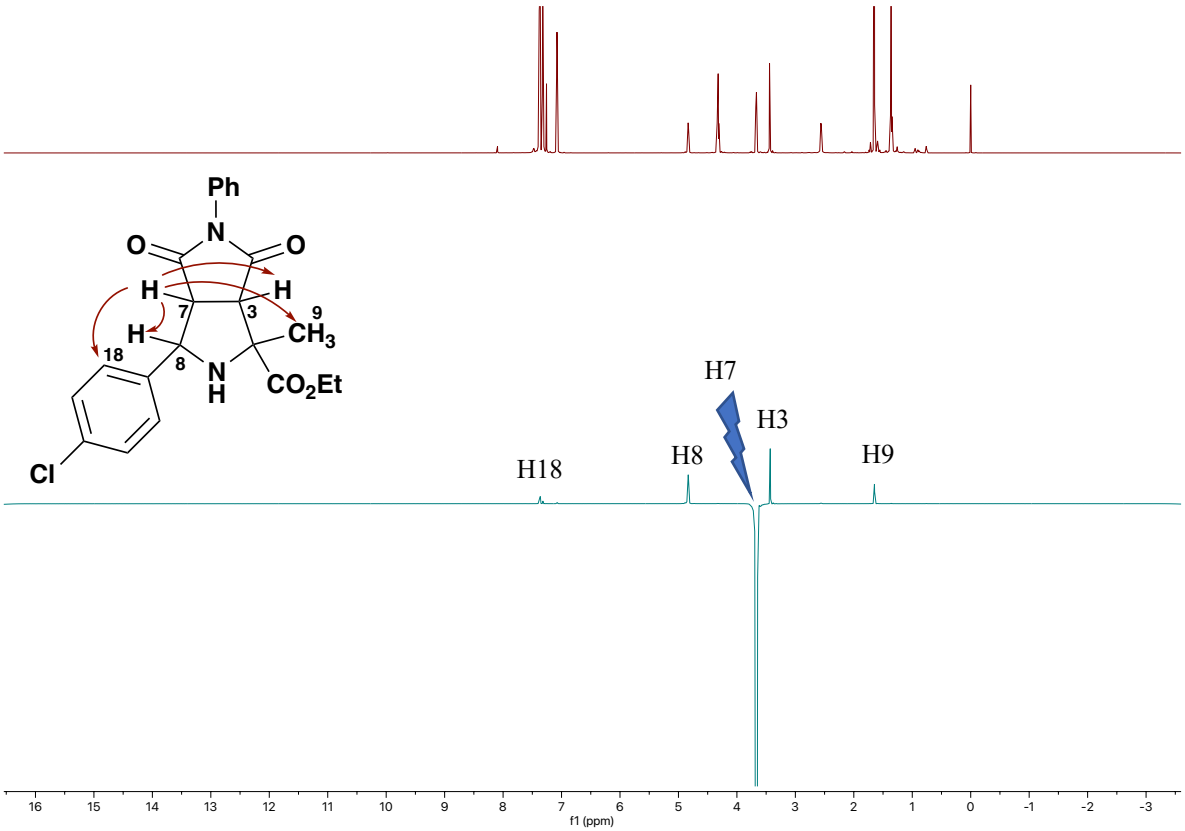


Figure S115. nOe NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **7a**

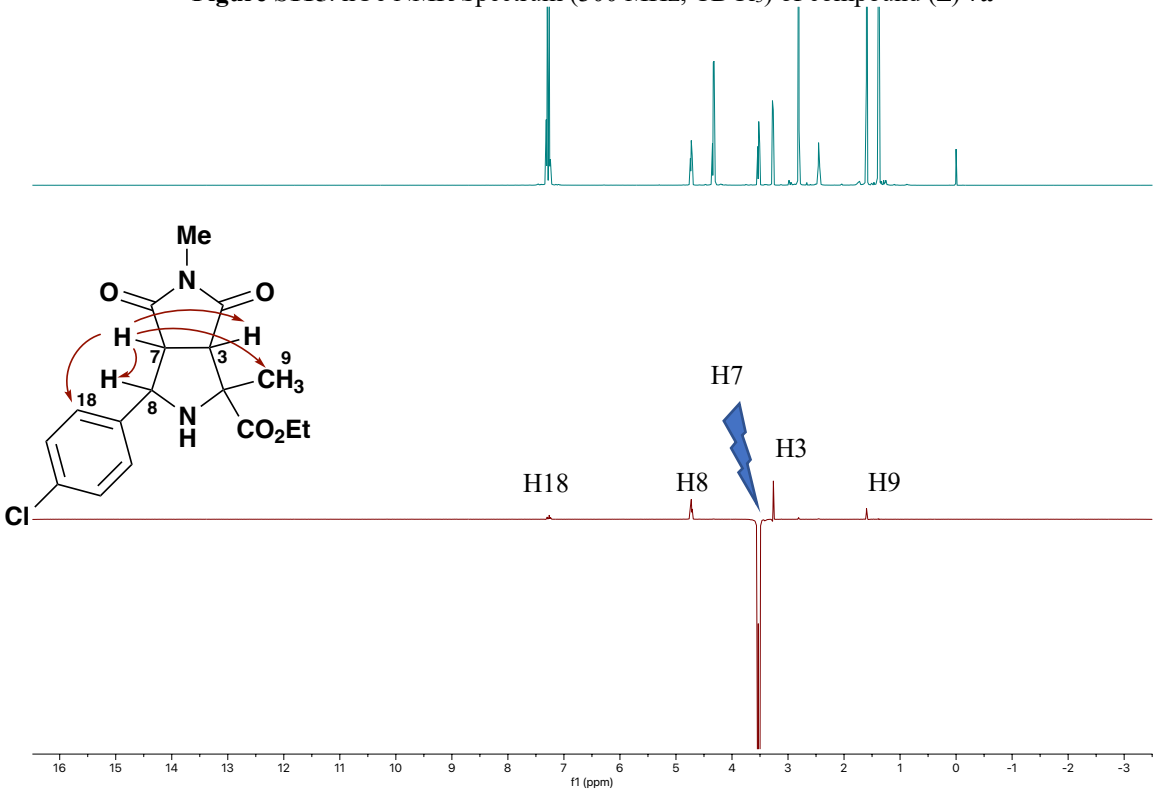


Figure S116. nOe NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **9**

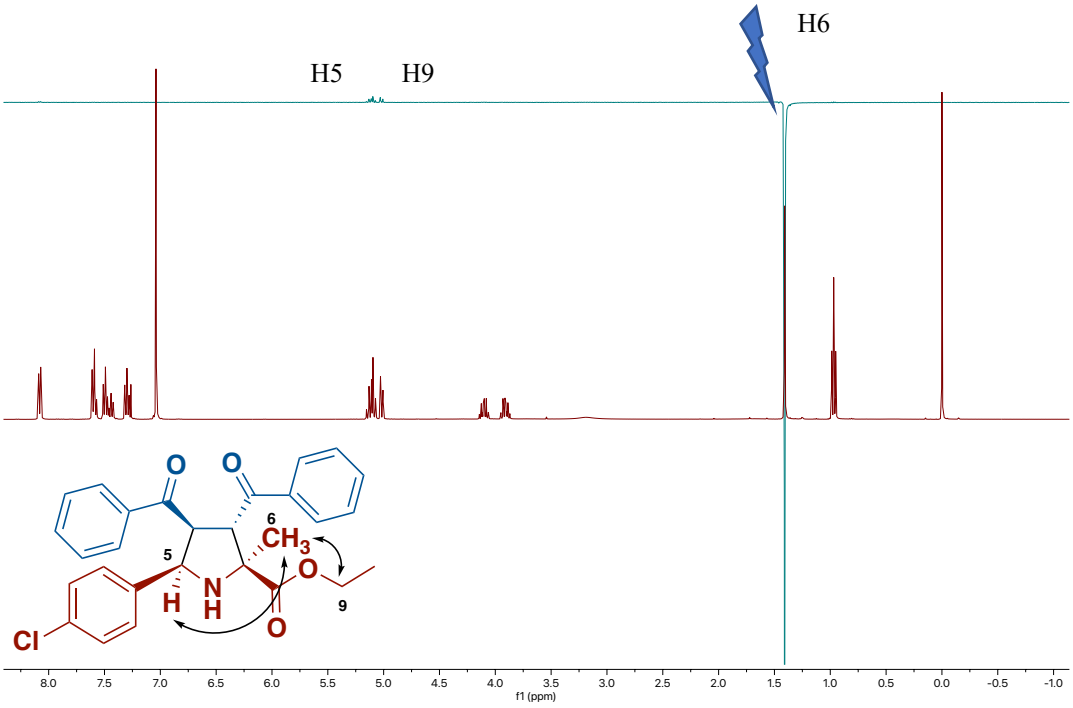
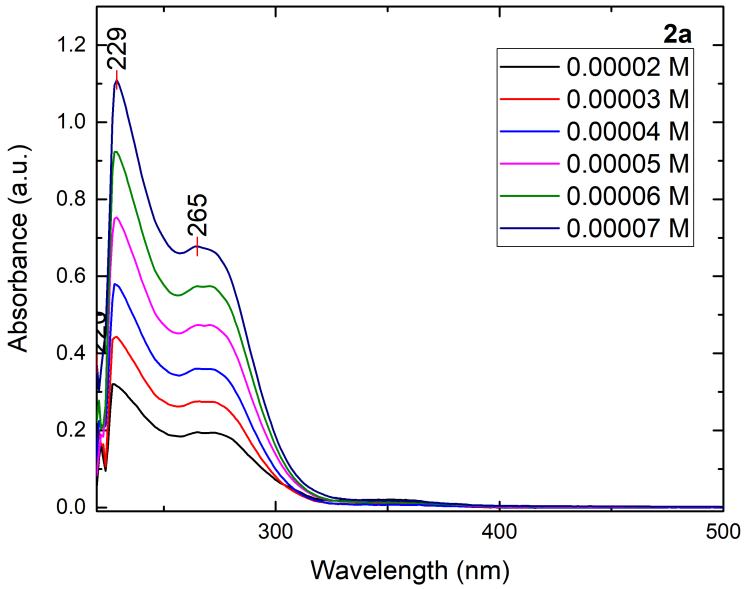


Figure S117. nOe NMR Spectrum (300 MHz, $CDCl_3$) of compound (±) **11**

13. UV-Vis Spectroscopy.



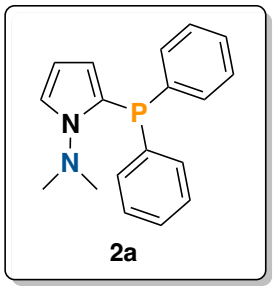


Figure S118. UV/Vis Spectrum in CH_2Cl_2 of compound **2a**

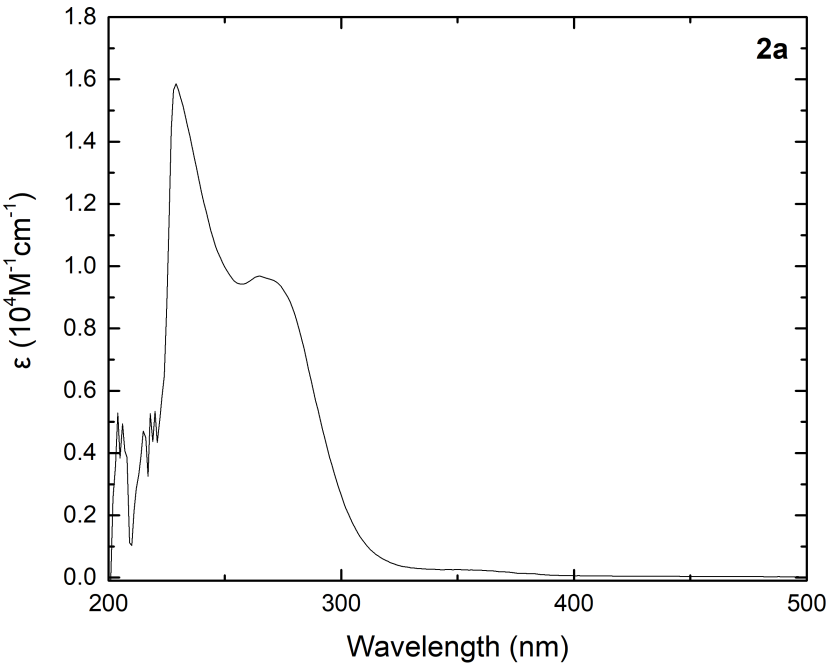


Figure S119. UV/Vis Spectrum in CH_2Cl_2 of compound **2a**

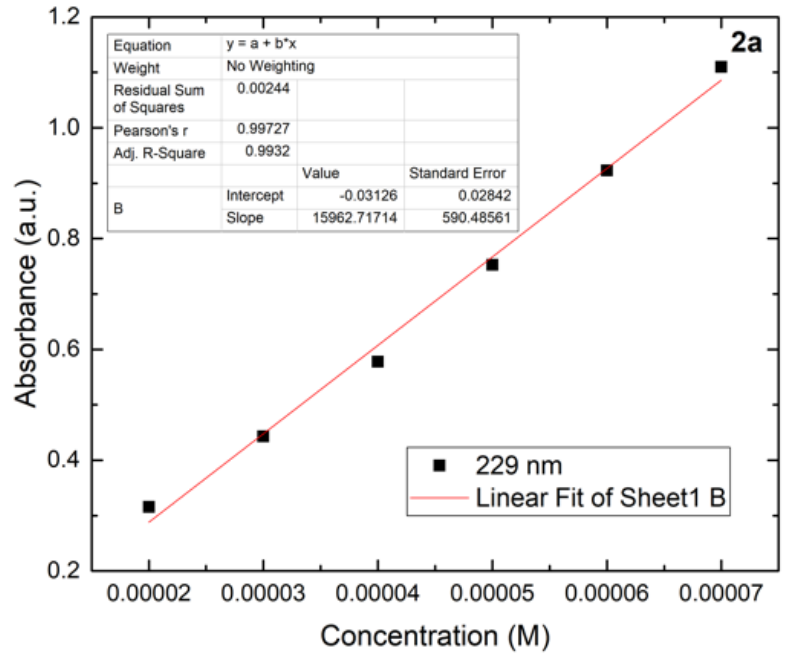


Figure S120. Graph of the absorption maxima of the compound **2a**

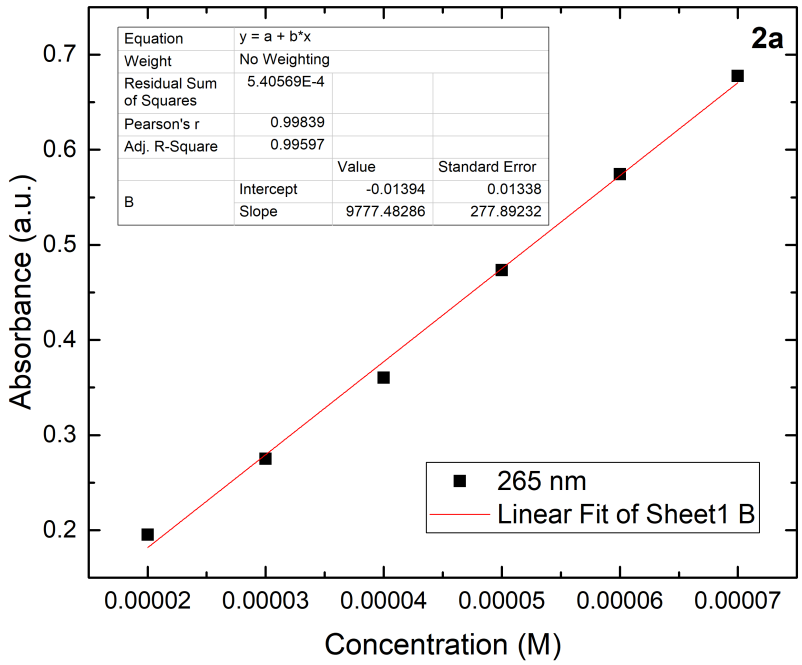
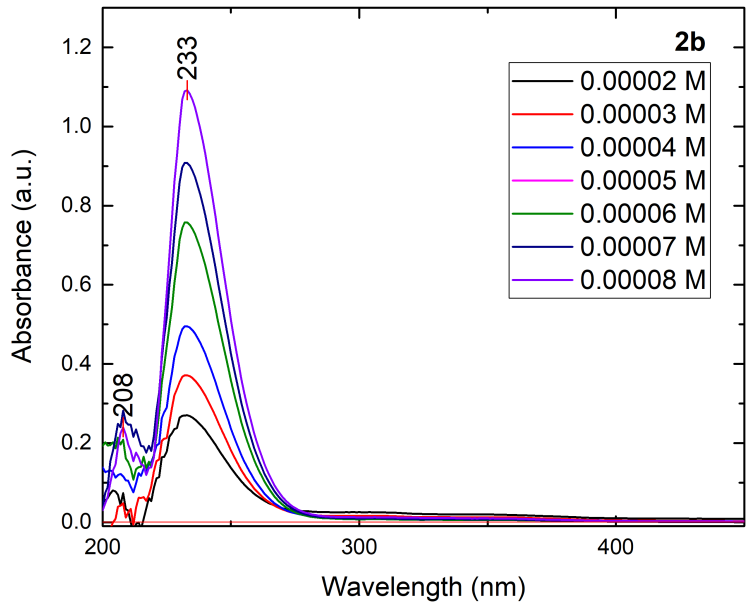


Figure S121. Graph of the absorption maxima of the compound **2a**



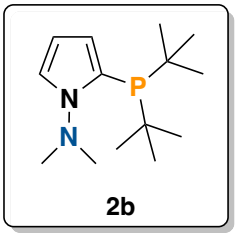


Figure S122. UV/Vis Spectrum in CH_2Cl_2 of compound **2b**

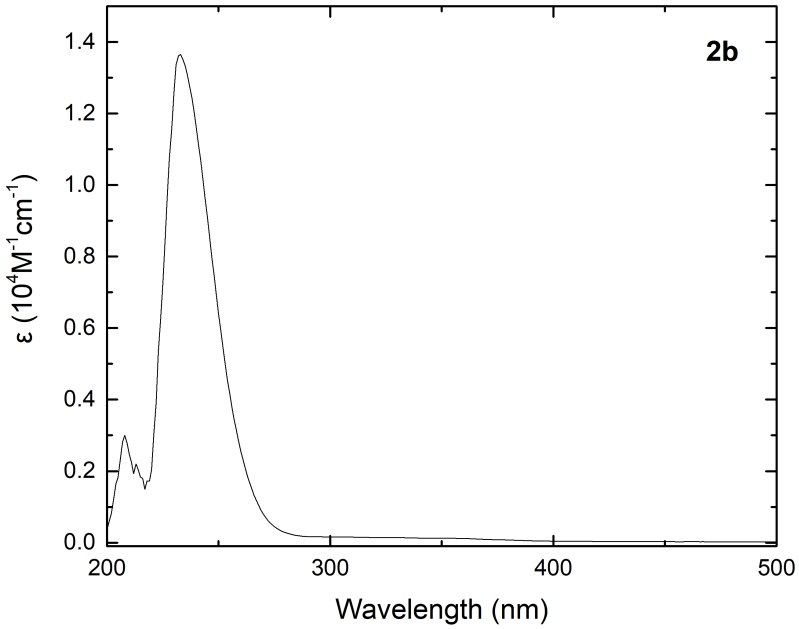


Figure S123. UV/Vis Spectrum in CH_2Cl_2 of compound **2b**

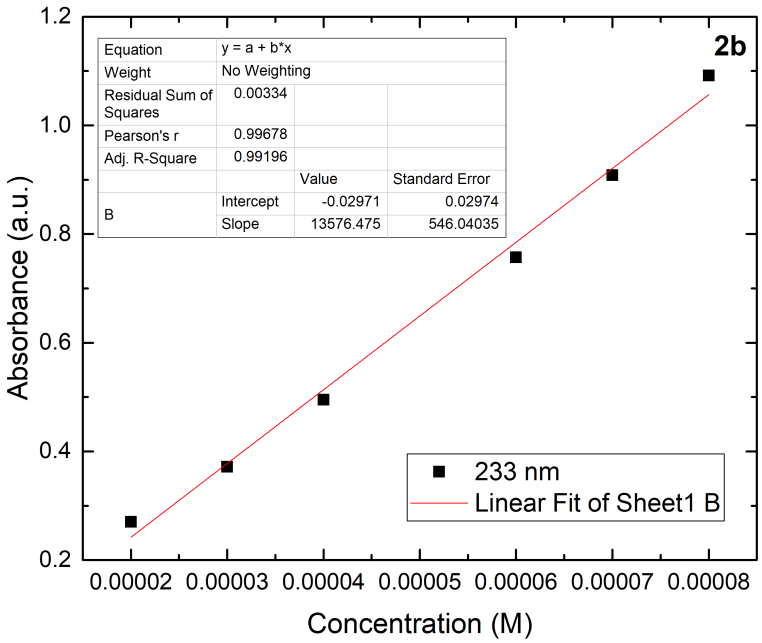
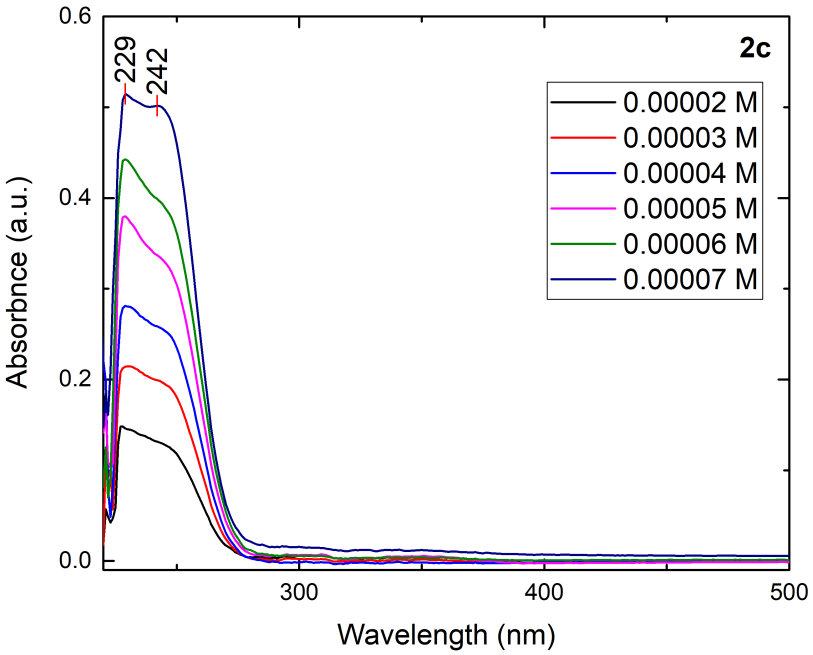


Figure S124. Graph of the absorption maxima of the compound **2b**



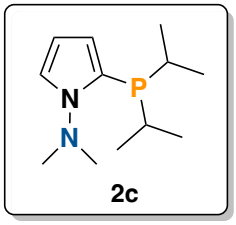


Figure S125. UV/Vis Spectrum in CH_2Cl_2 of compound **2c**

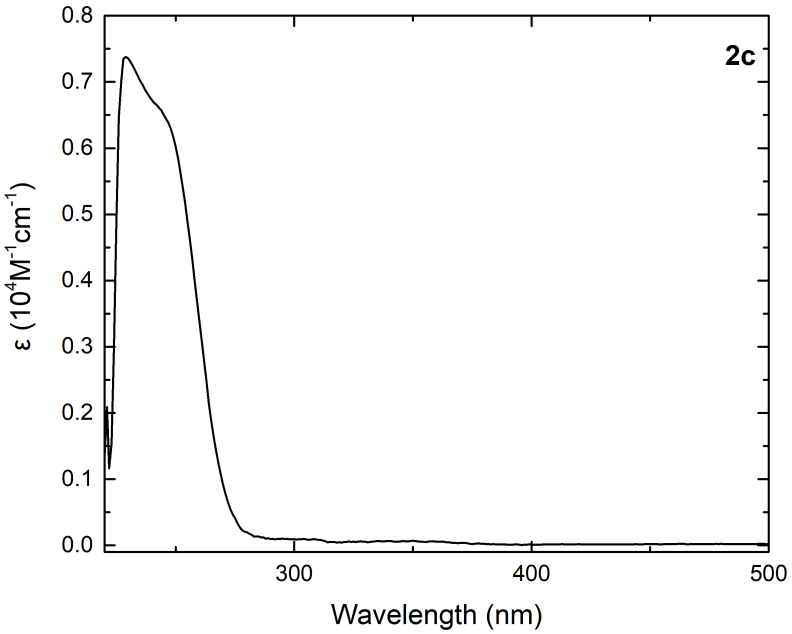


Figure S126. UV/Vis Spectrum in CH_2Cl_2 of compound **2c**

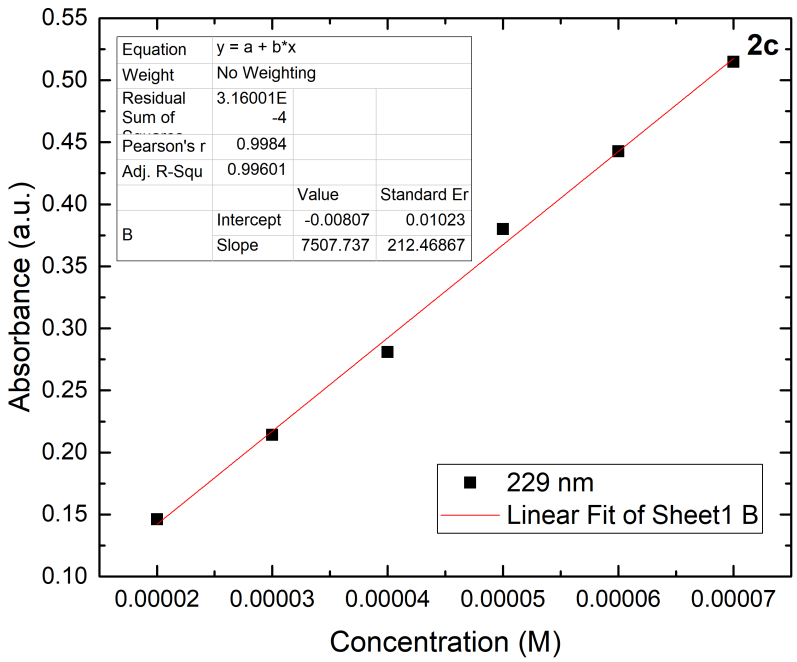


Figure S127. Graph of the absorption maxima of the compound **2c**

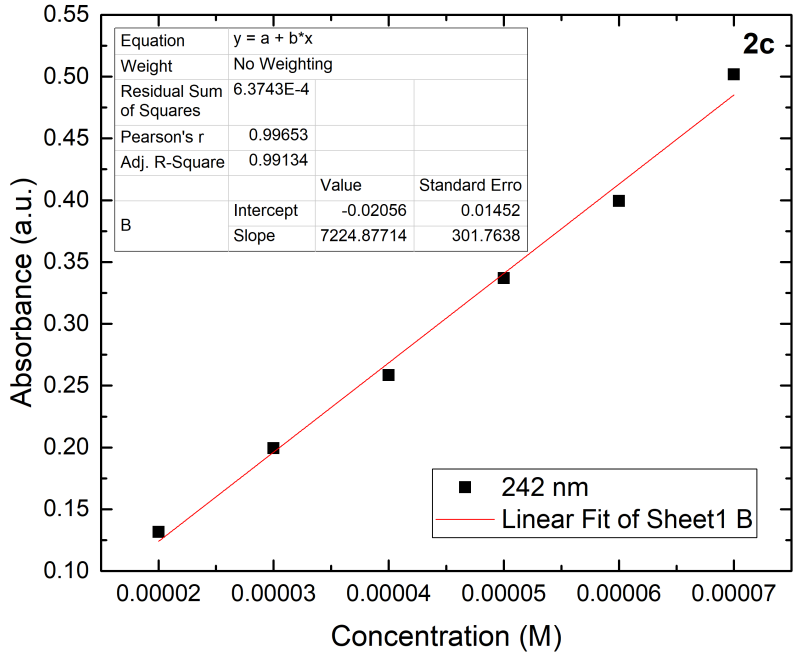
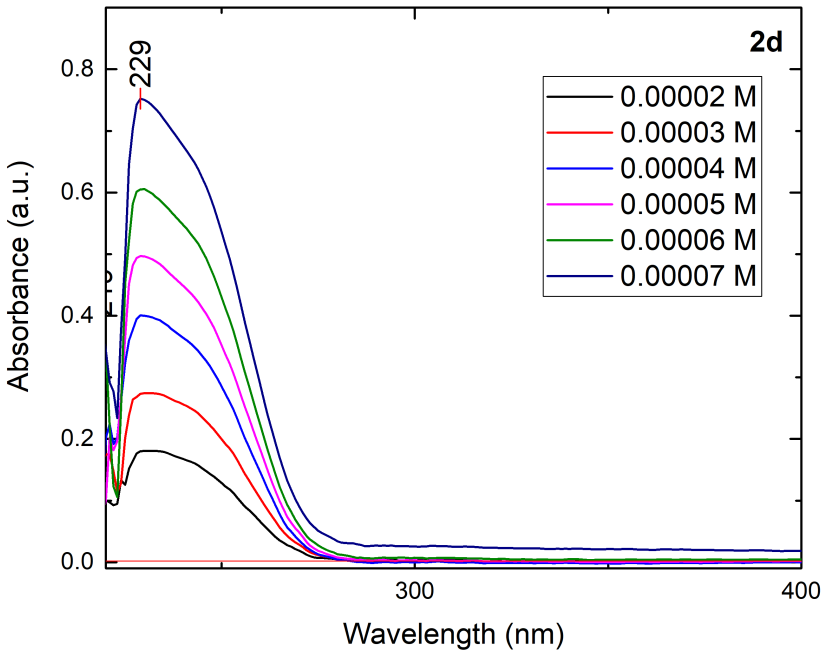


Figure S128. Graph of the absorption maxima of the compound **2c**



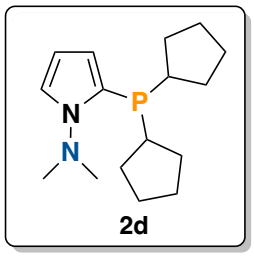


Figure S129. UV/Vis Spectrum in CH_2Cl_2 of compound **2d**

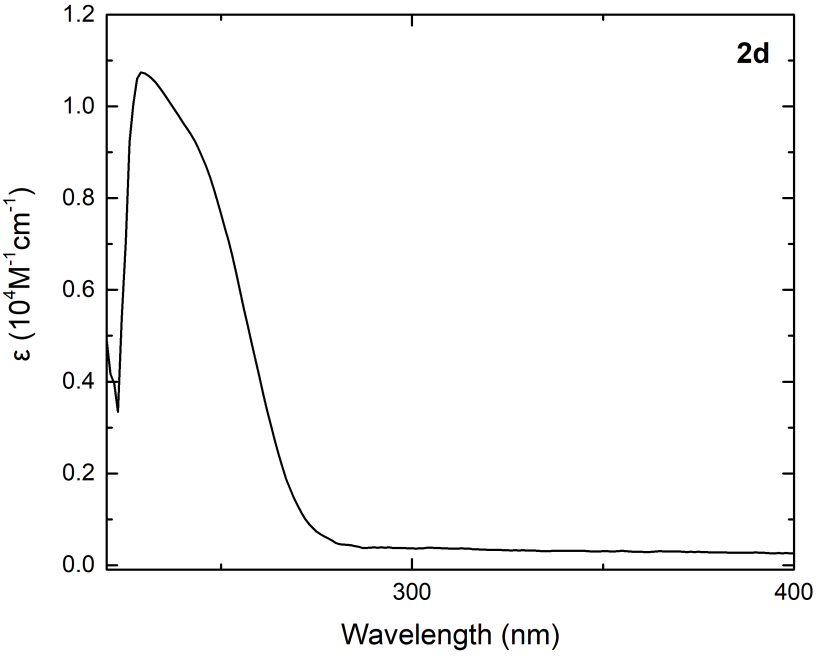


Figure S130. UV/Vis Spectrum in CH_2Cl_2 of compound **2d**

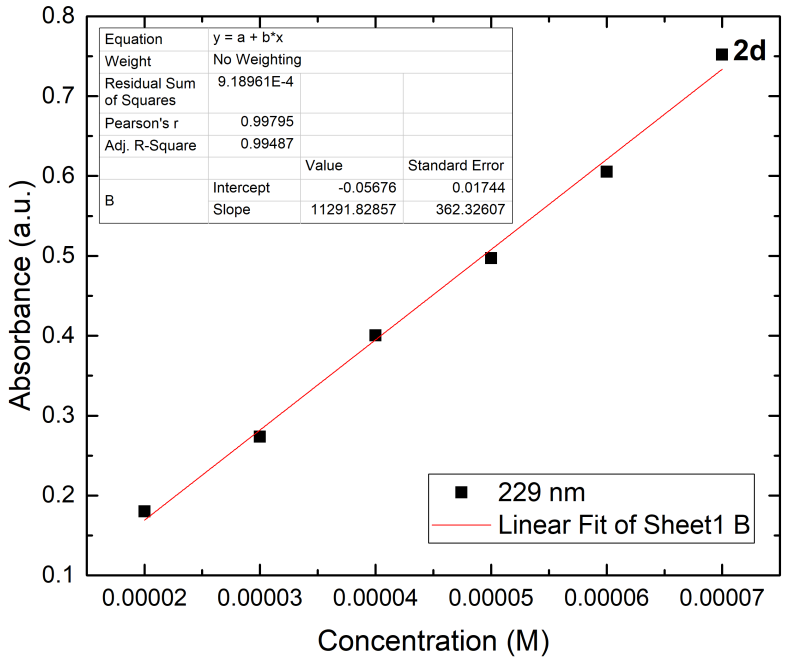
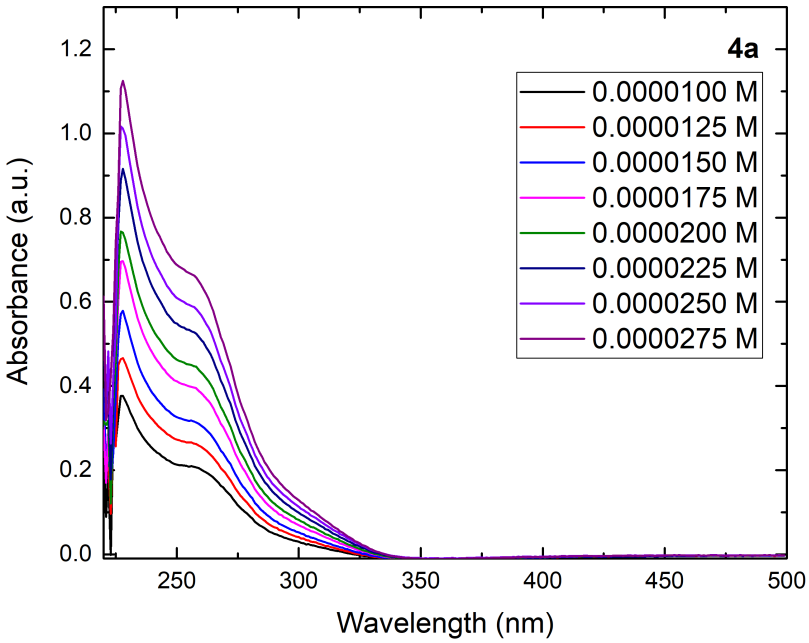


Figure S131. Graph of the absorption maxima of the compound **2d**



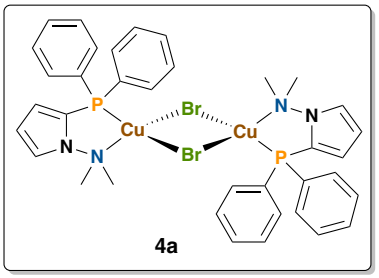


Figure S132. UV/Vis Spectrum in CH_2Cl_2 of compound **4a**

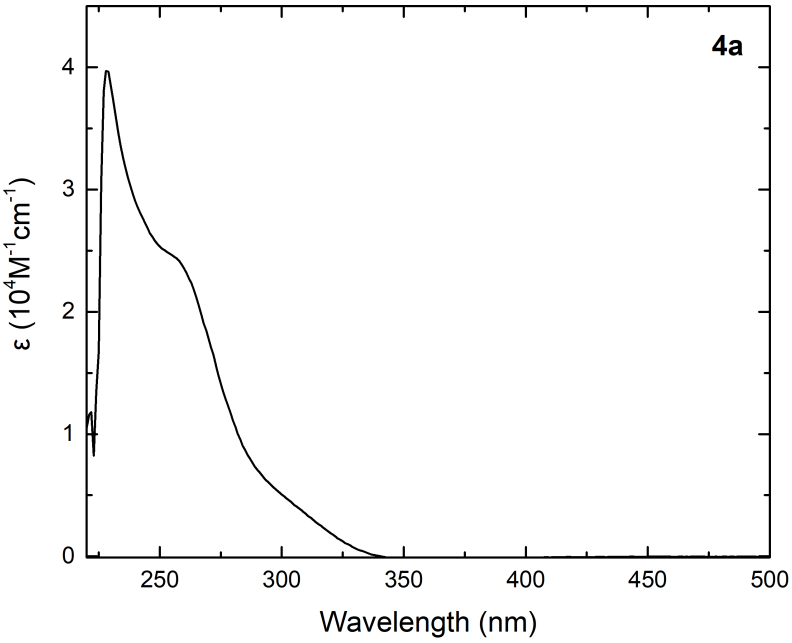


Figure S133. UV/Vis Spectrum in CH_2Cl_2 of compound **4a**

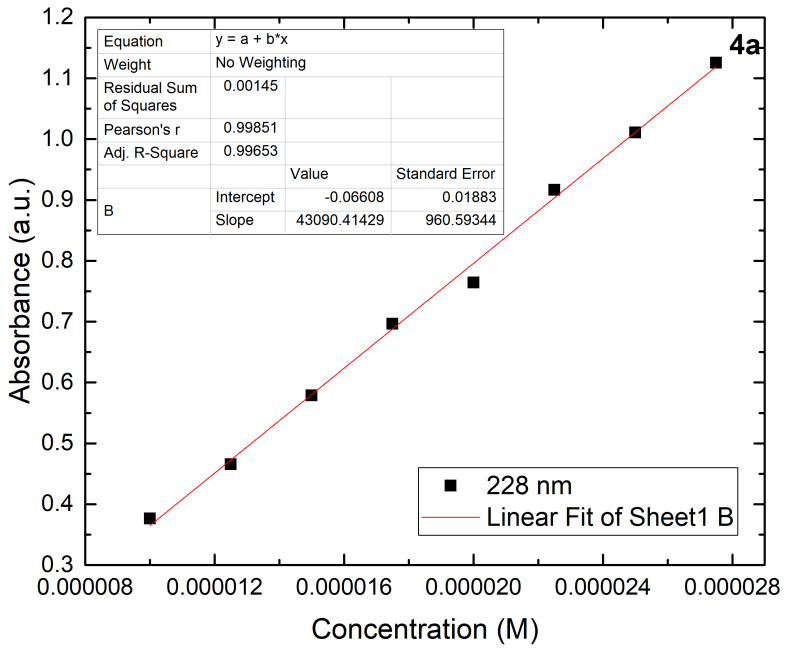


Figure S134. Graph of the absorption maxima of the compound **4a**

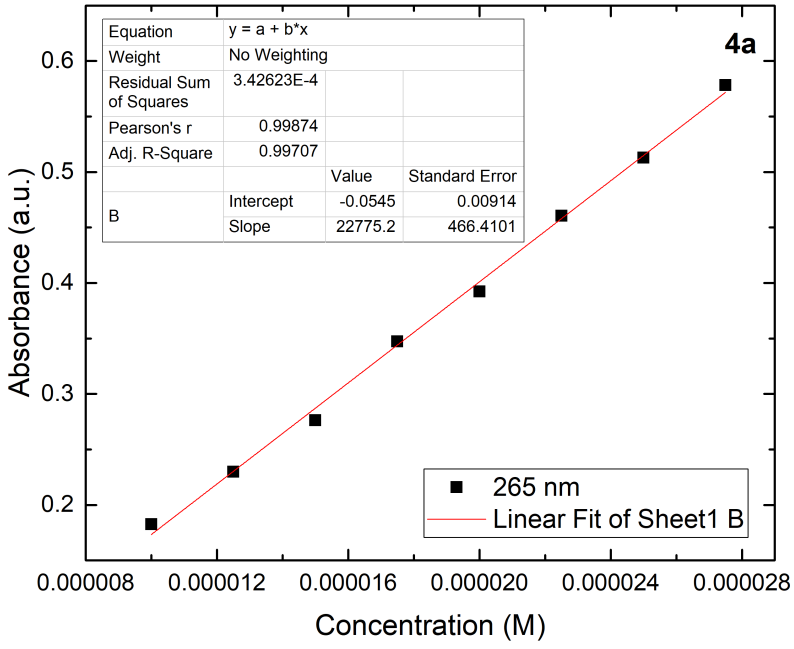


Figure S135. Graph of the absorption maxima of the compound **4a**

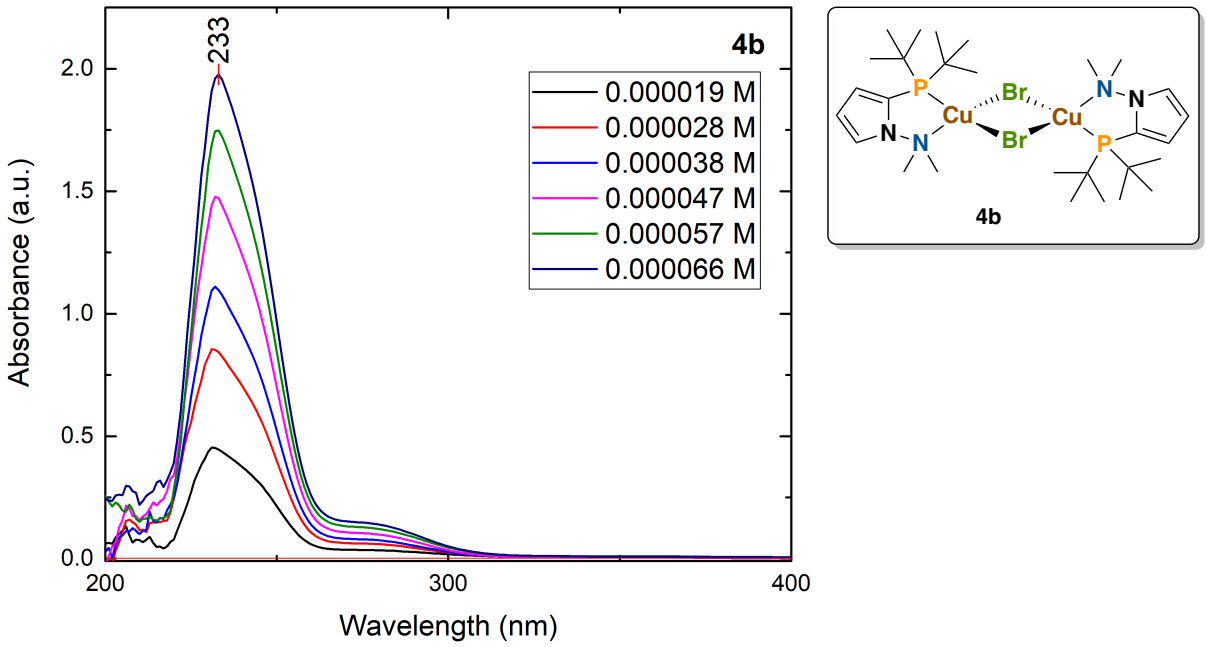


Figure S136. UV/Vis Spectrum in CH_2Cl_2 of compound **4b**

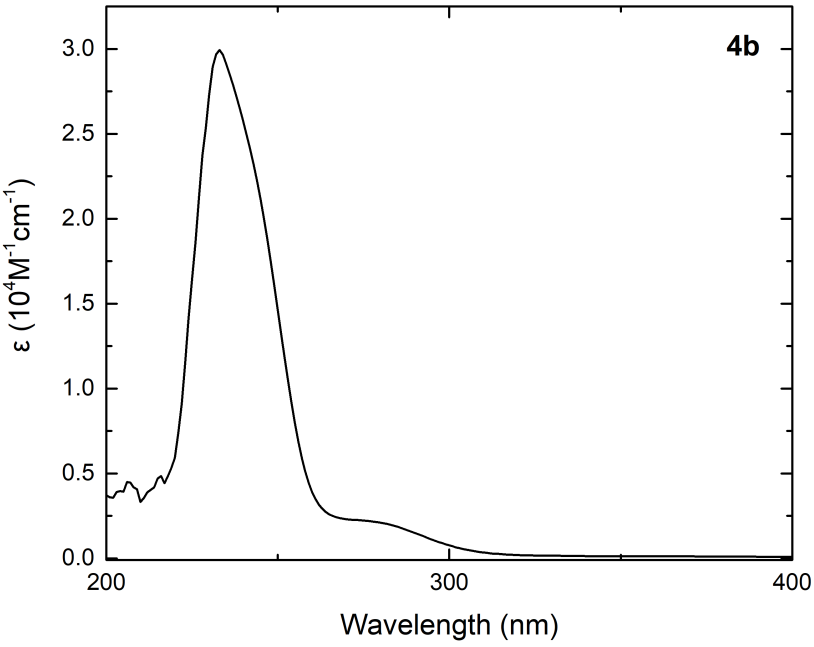


Figure S137. UV/Vis Spectrum in CH_2Cl_2 of compound **4b**

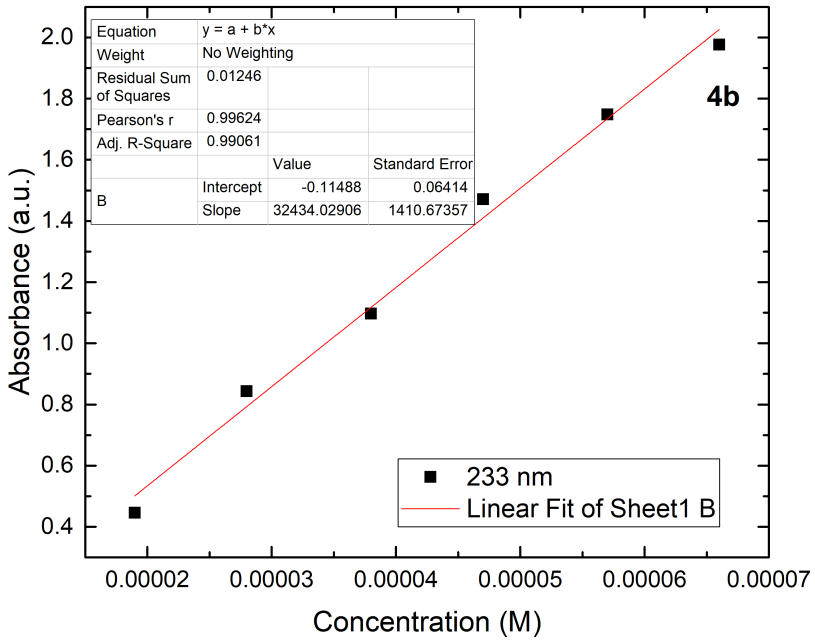


Figure S138. Graph of the absorption maxima of the compound **74b**

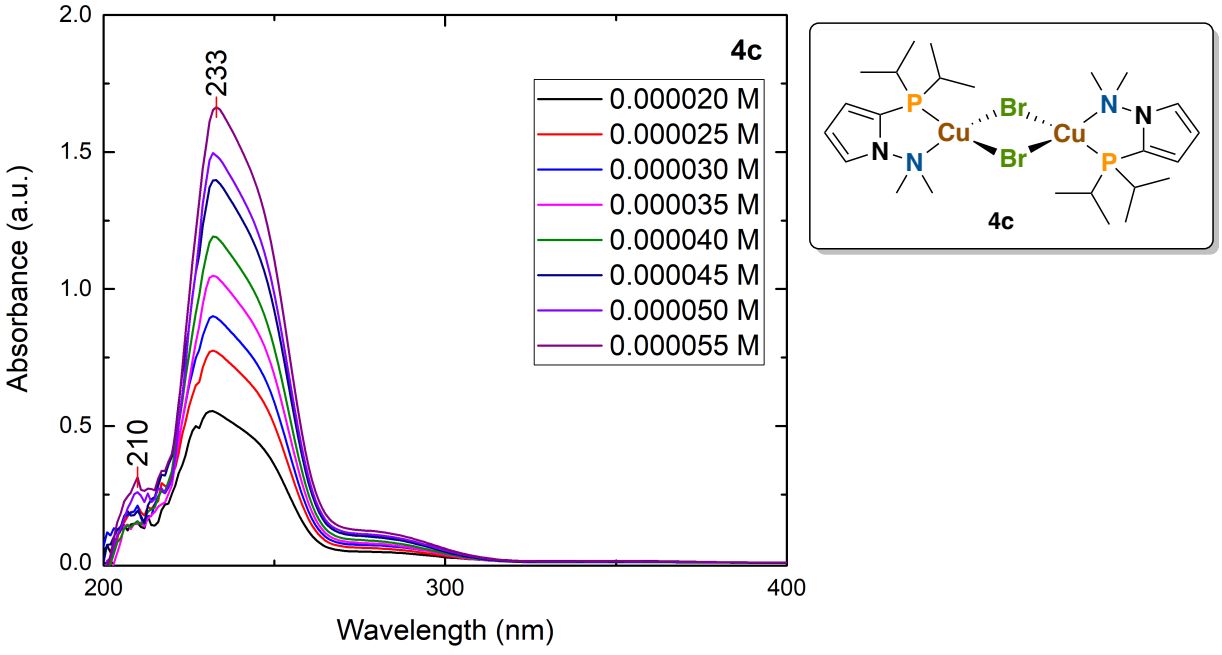


Figure S139. UV/Vis Spectrum in CH_2Cl_2 of compound **4c**

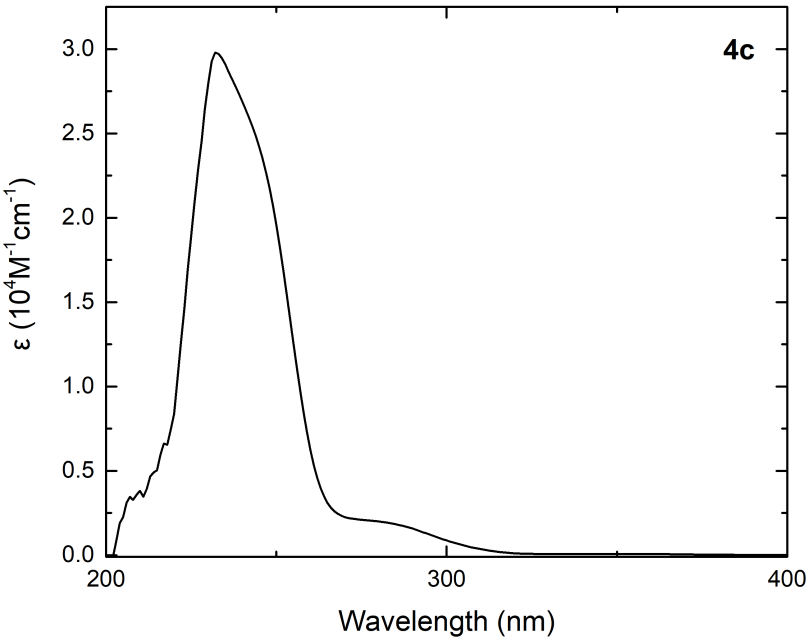


Figure S140. UV/Vis Spectrum in CH_2Cl_2 of compound **4c**

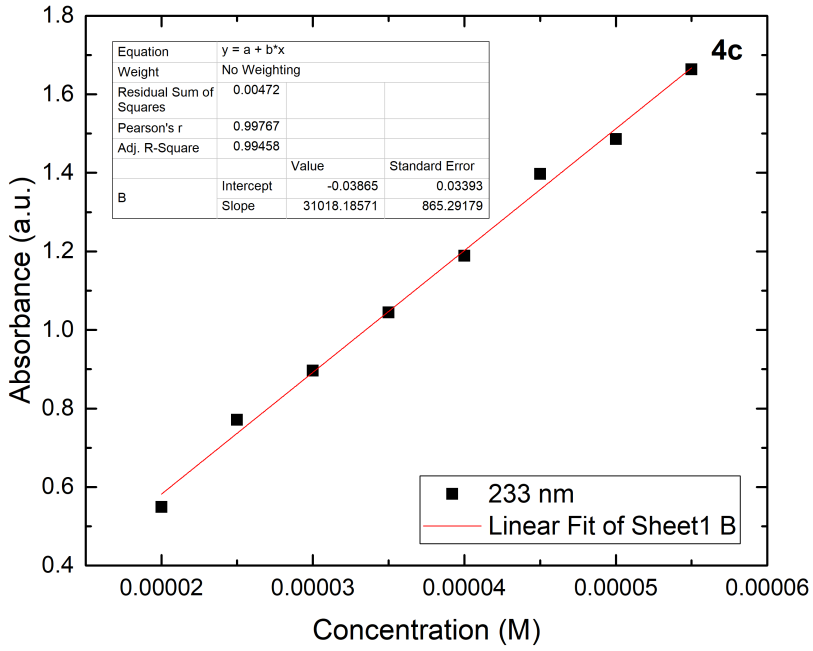


Figure S141. Graph of the absorption maxima of the compound **4c**

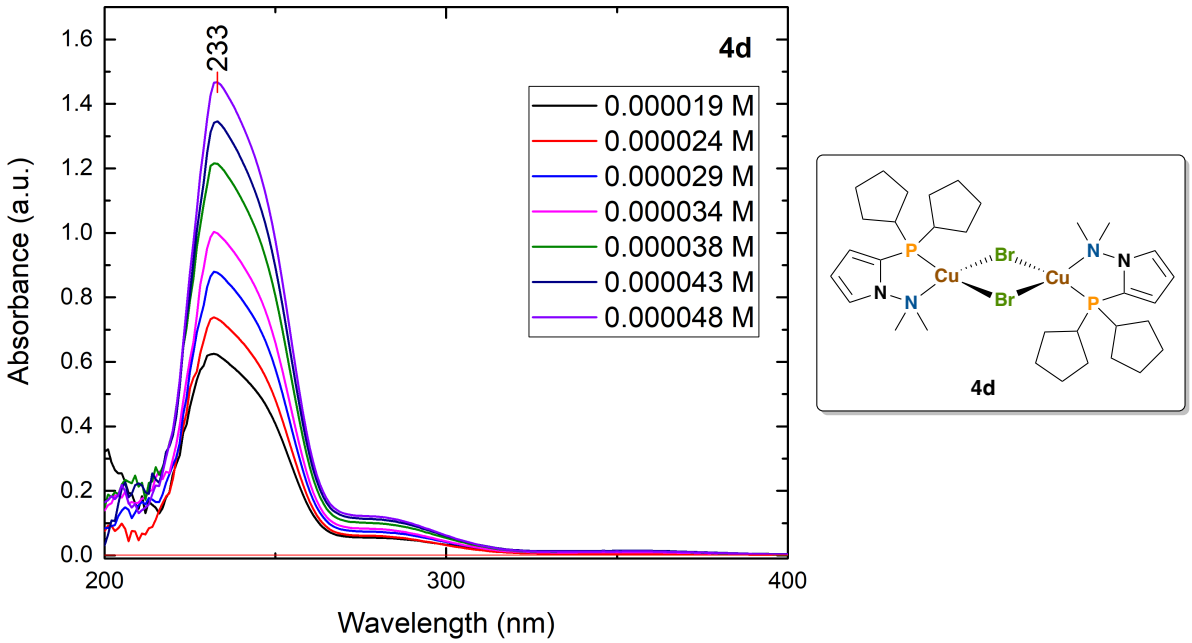


Figure S142. V/Vis Spectrum in CH_2Cl_2 of compound **4d**

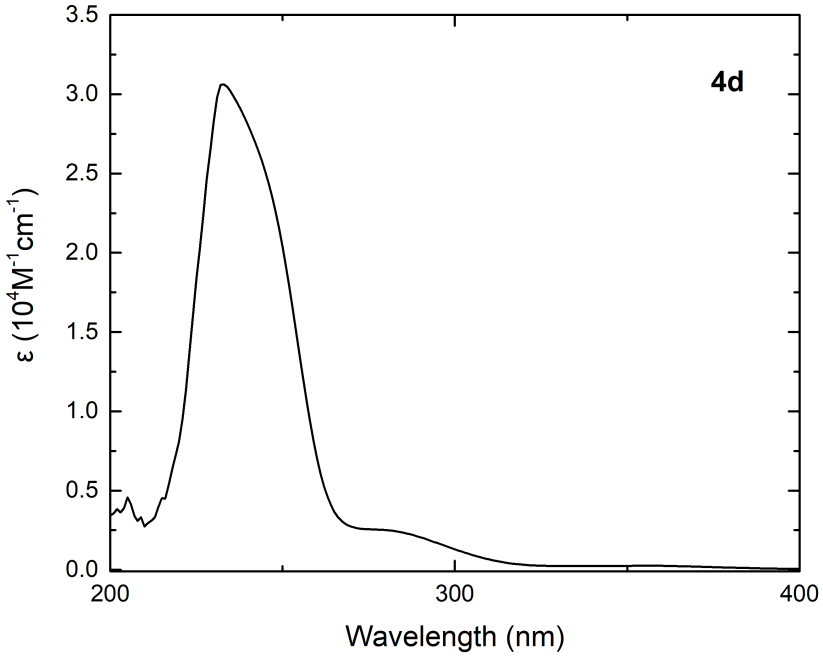


Figure S143. UV/Vis Spectrum in CH_2Cl_2 of compound **4d**

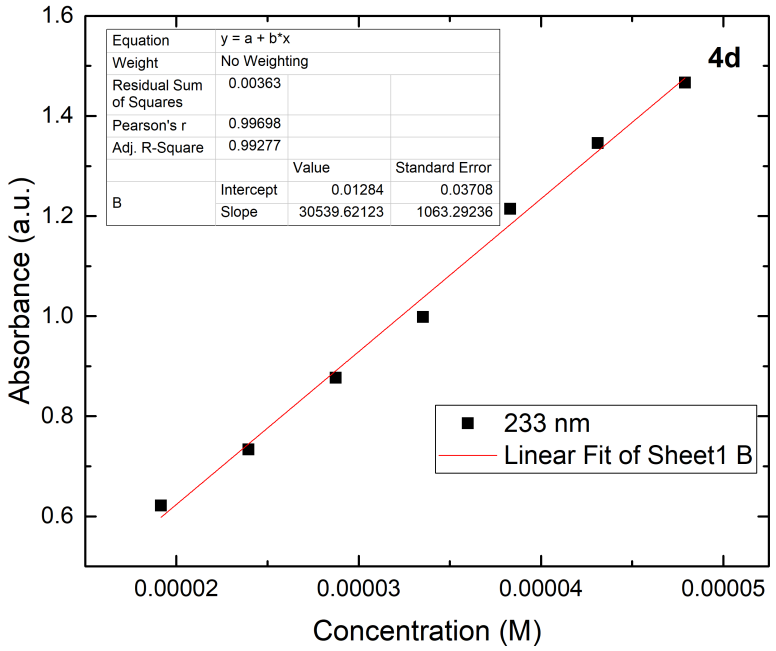


Figure S144. Graph of the absorption maxima of the compound **4d**

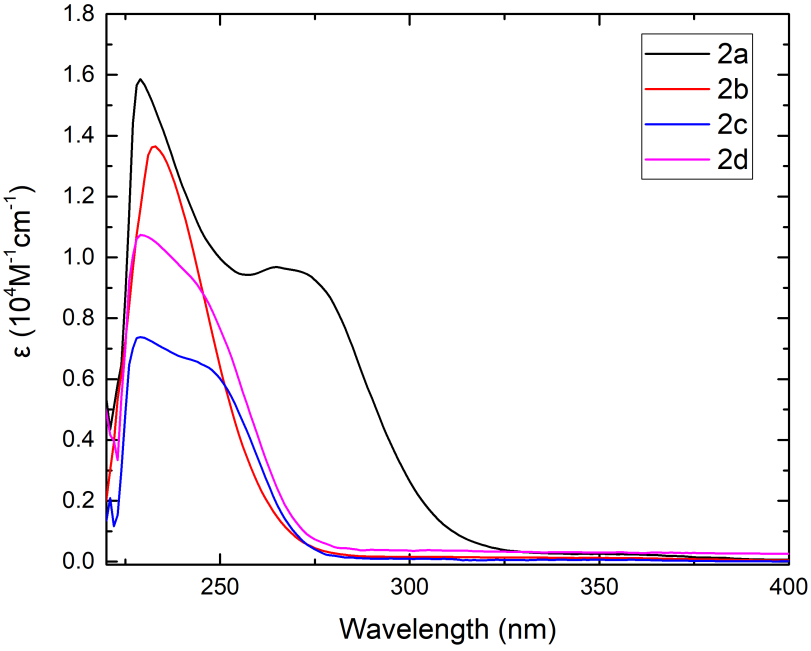


Figure S145. UV/Vis spectra of compounds **2a-d** acquired in CH_2Cl_2

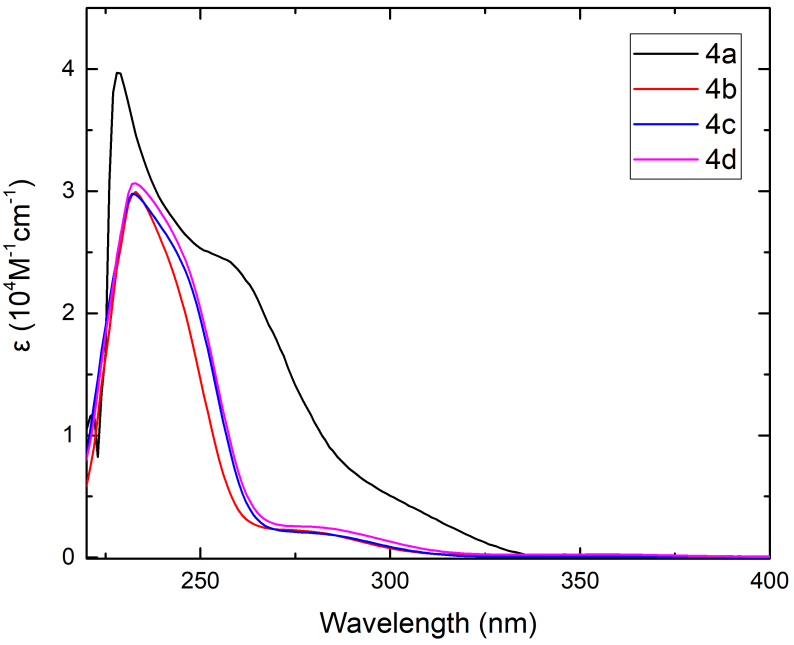


Figure S146. UV/Vis spectra of compounds **4a-d** acquired in CH_2Cl_2

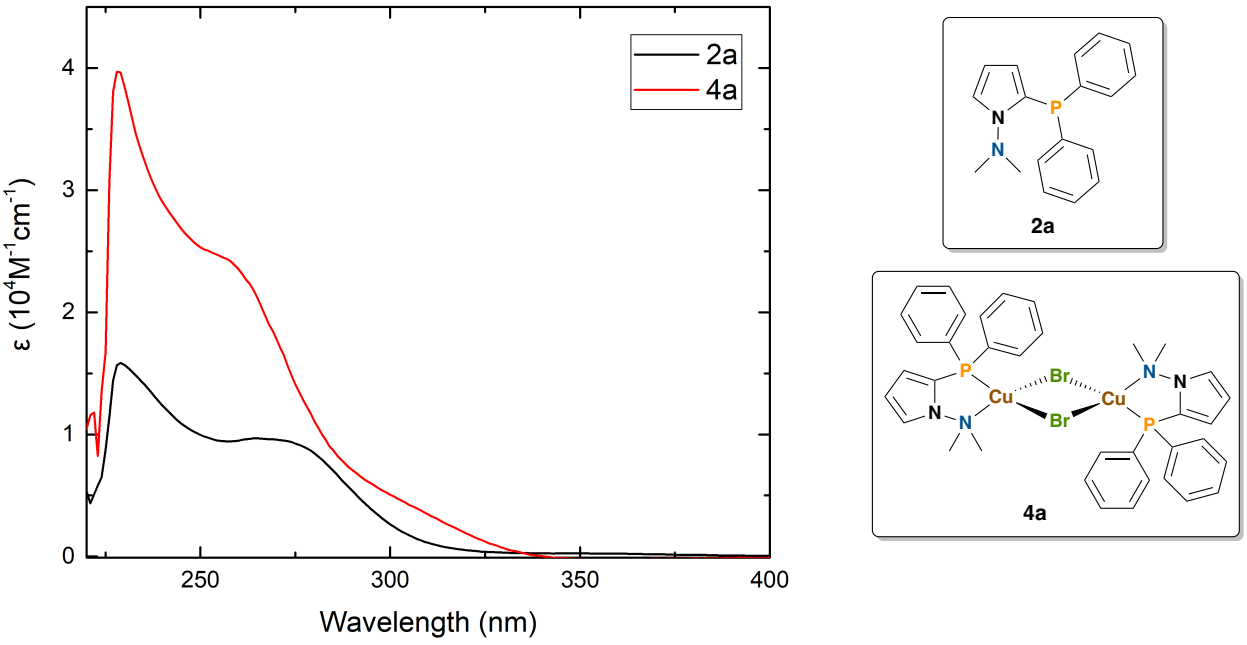


Figure S147. UV/Vis spectra of compounds **2a** and **4a,** acquired in CH_2Cl_2

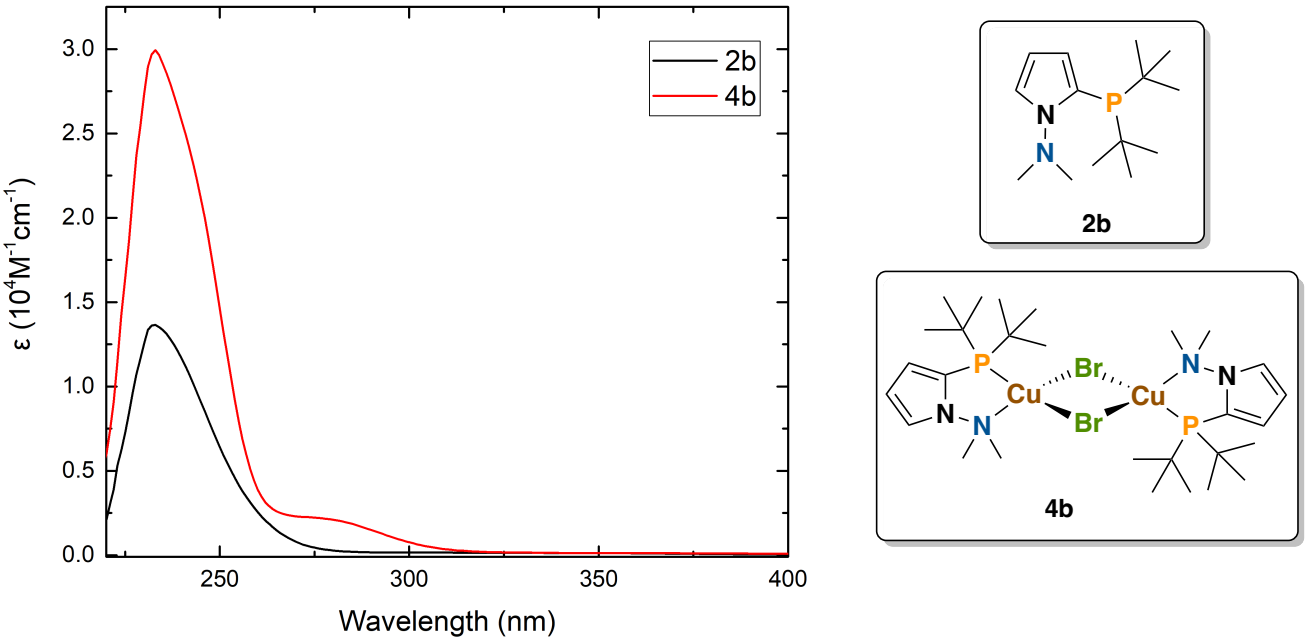


Figure S148. UV/Vis spectra of compounds **2b** and **4b,** acquired in CH_2Cl_2

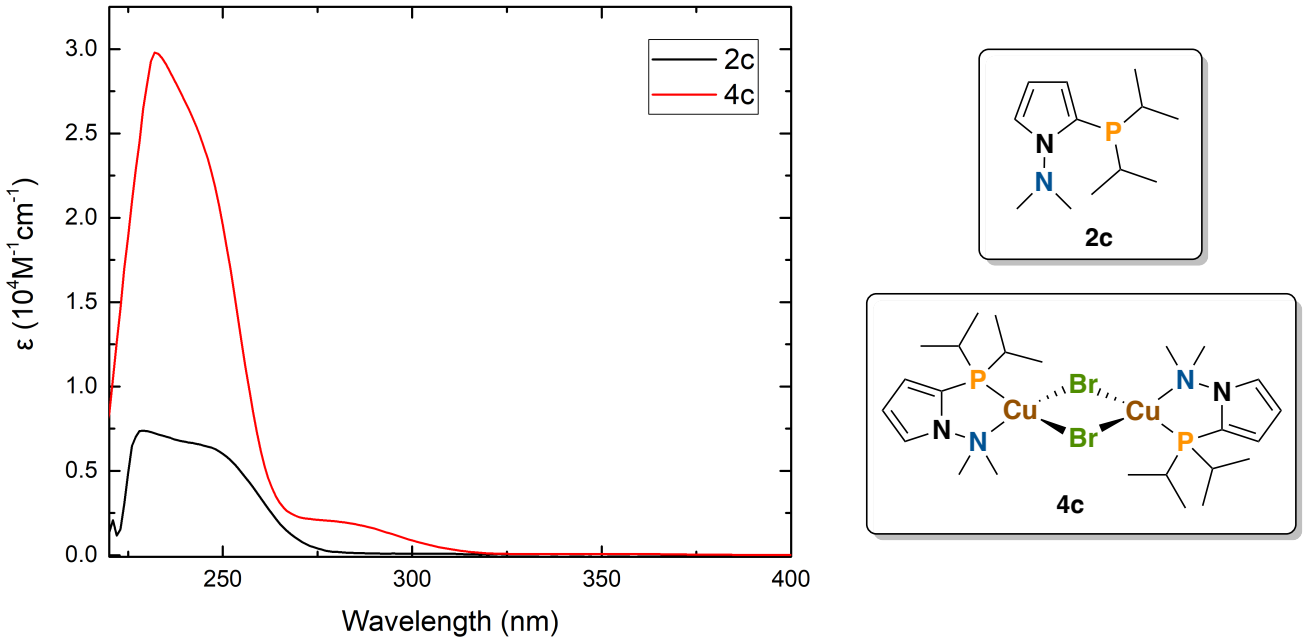


Figure S149. UV-vis spectra of compounds **2c** and **4c,** acquired in CH_2Cl_2

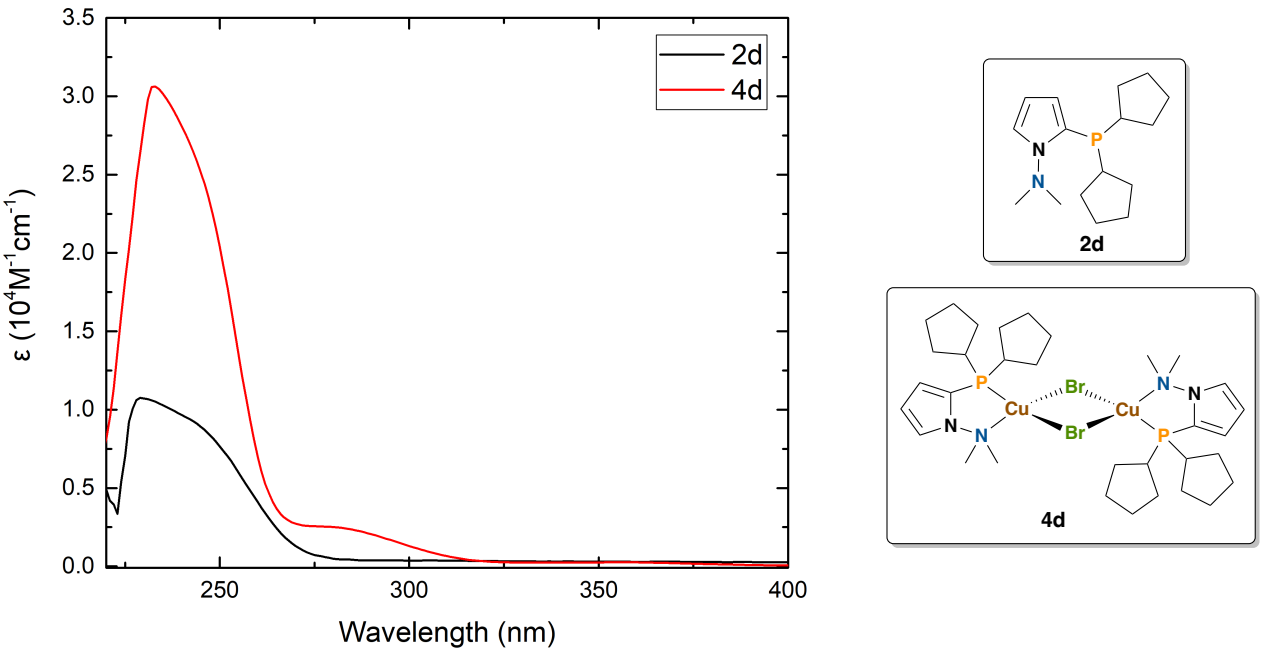


Figure S150. UV-vis spectra of compounds **2d** and **4d,** acquired in CH_2Cl_2

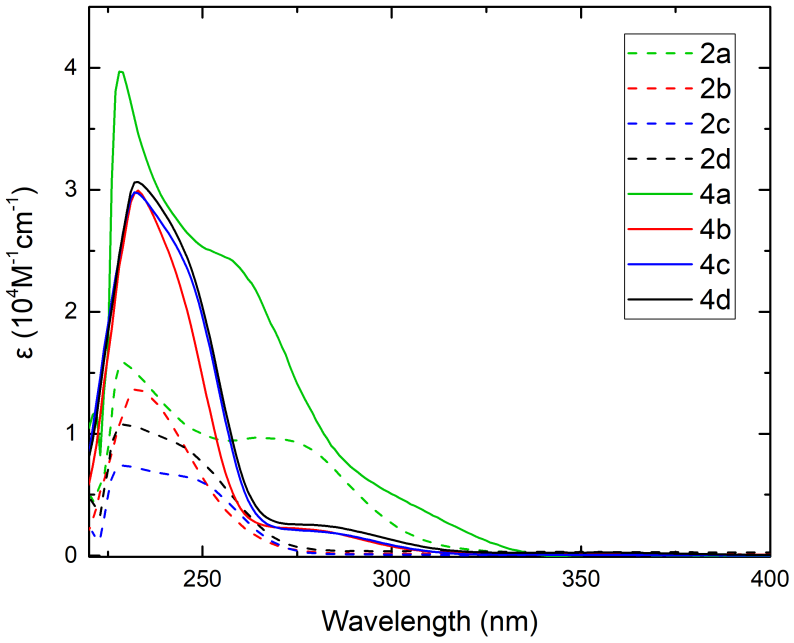


Figure S151. UV-vis spectra of compounds **2a-d** and **4a-d,** acquired in CH_2Cl_2

14. Follow-up of the 1,3-dipolar cycloaddition by 31P NMR

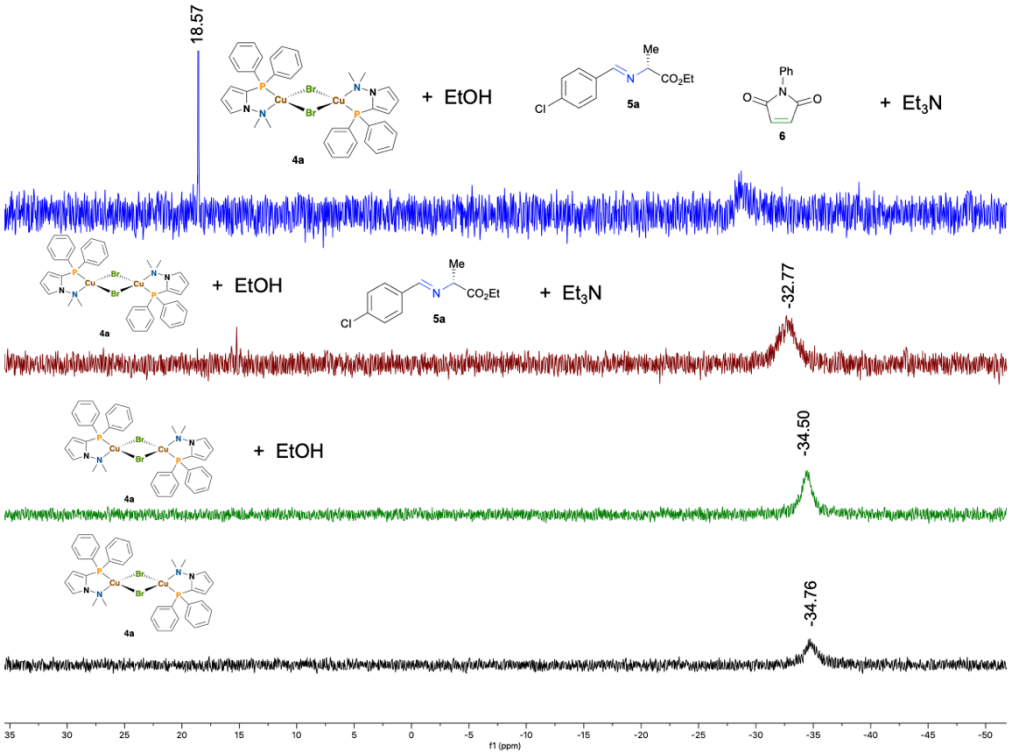


Figure S152. Follow-up of the 1,3-dipolar cycloaddition catalyzed for **4a** by ^{31}P NMR in CD_2Cl_2

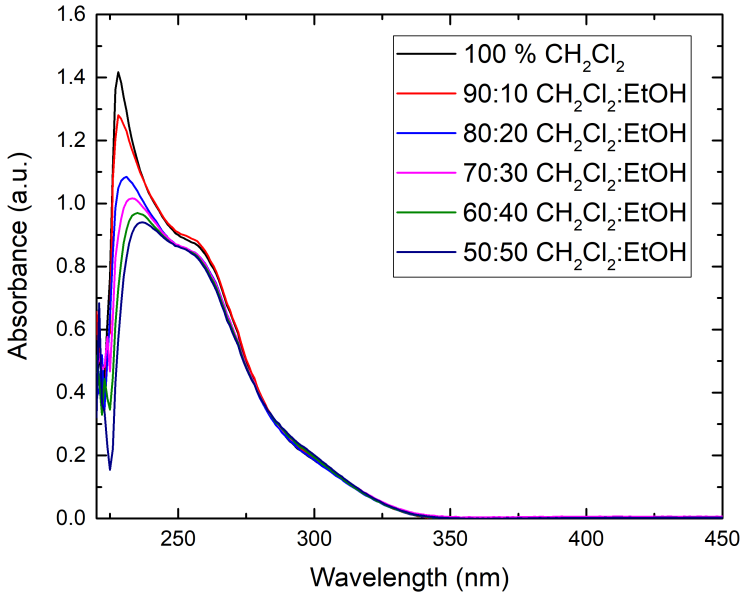


Figure S153. UV-visible spectra of **4a** in different ratios of CH_2Cl_2/EtOH

15. Theoretical data

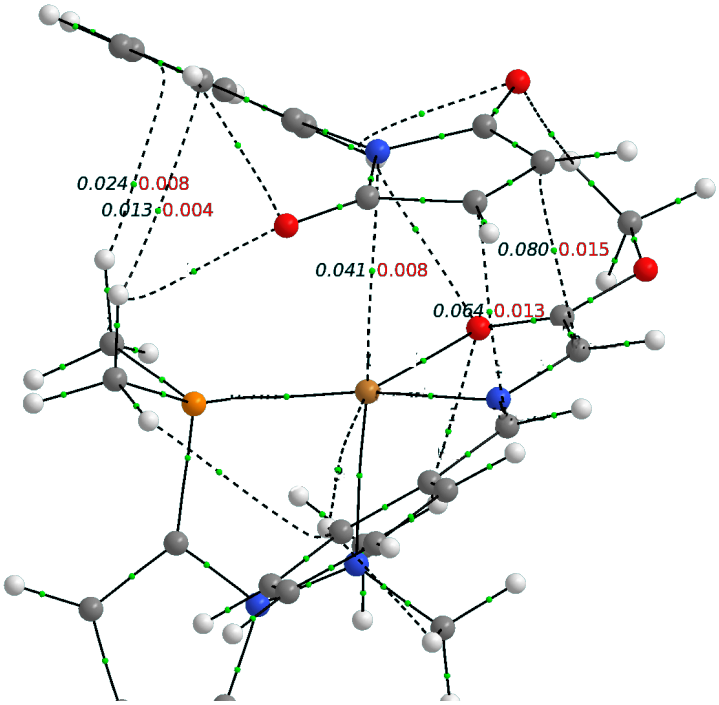


Figure S154. QTAIM molecular graph of the interaction between specie **C** and the maleimide. The density at the bond critical point (red) and the delocalization indices between the atoms liked by the bond paths (black) are shown for the intermolecular interactions.

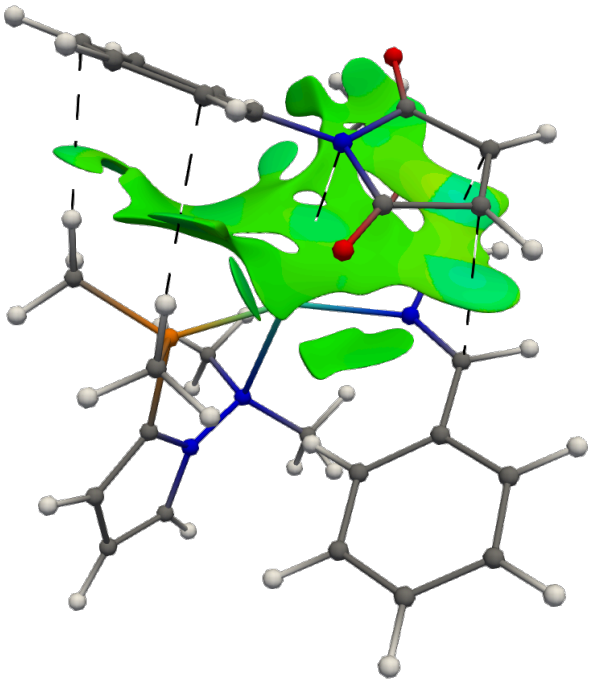


Figure S155. Intermolecular RDG surface of the interaction between specie **C** and the maleimide. The $sign(\lambda_2)\rho$ is plotted over the isosurface. $sign(\lambda_2)\rho$ color code: ≤ -5.0 x 10^{-2} a.u. (dark blue), 0.0 a.u. (green) and ≥ 5.0 x 10^{-2} a.u. (red).