ANEXOS

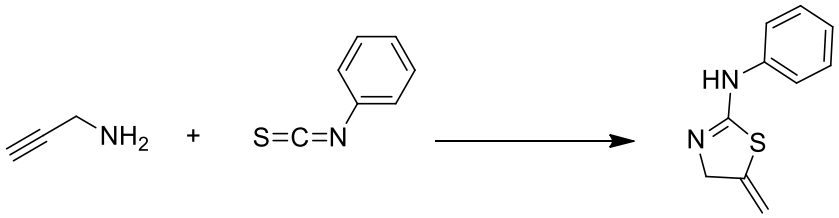
Capítulo 1

Syntheses

Synthesis of compound 1

To a solution of propargylamine (6.4 µl, 0.1 mmol) in ethanol/water mixture (1/1) (10 ml), phenyl isothiocyanate was added (11.9 µl, 0.1 mmol) and the solution stirred for 24 h. A light brown precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 70%



Scheme 1.2. Synthesis of compound **1**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.28 (m, 2H, C_{ortho}Ph); 7.17 (m, 2H, C_{meta}Ph); 7.07 (tt, 1H, C_{para}Ph, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 2.4 Hz); 5.20 (m, 1H, CH_2); 5.12 (m, 1H, CH_2); 4.58 (t, 2H, CH_2-N, $^4J_{HH}$ = 2.3 Hz)

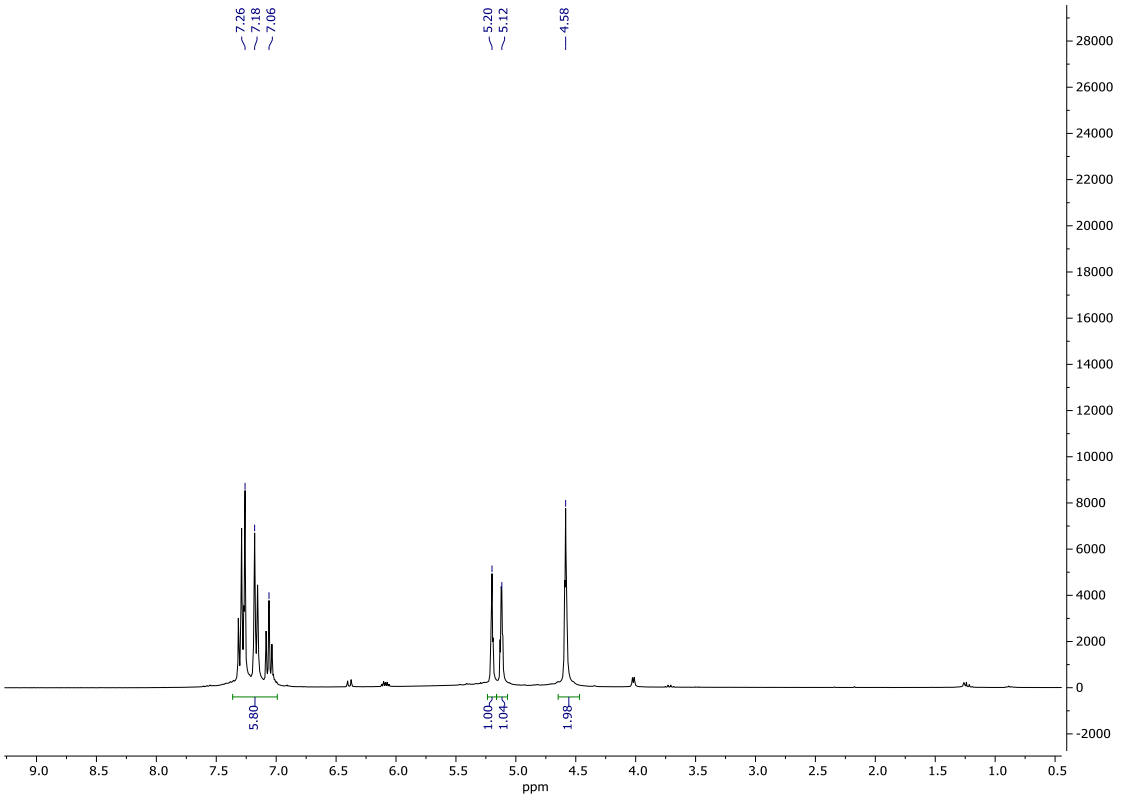


Figure 1.1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 158.4 (s, 1C, N-*C*=N); 145.1 (s, 1C, C_{ipso}Ph-NH); 144.2 (s, 1C, *C*=CH_2); 129.1 (s, 2C, C_{ortho}Ph) 123.5 (s, 1C, C_{para}Ph); 120.9 (s, 2C, C_{meta}Ph); 104.2 (s, 1C, CH_2); 59.3 (s, 1C, CH_2-N)

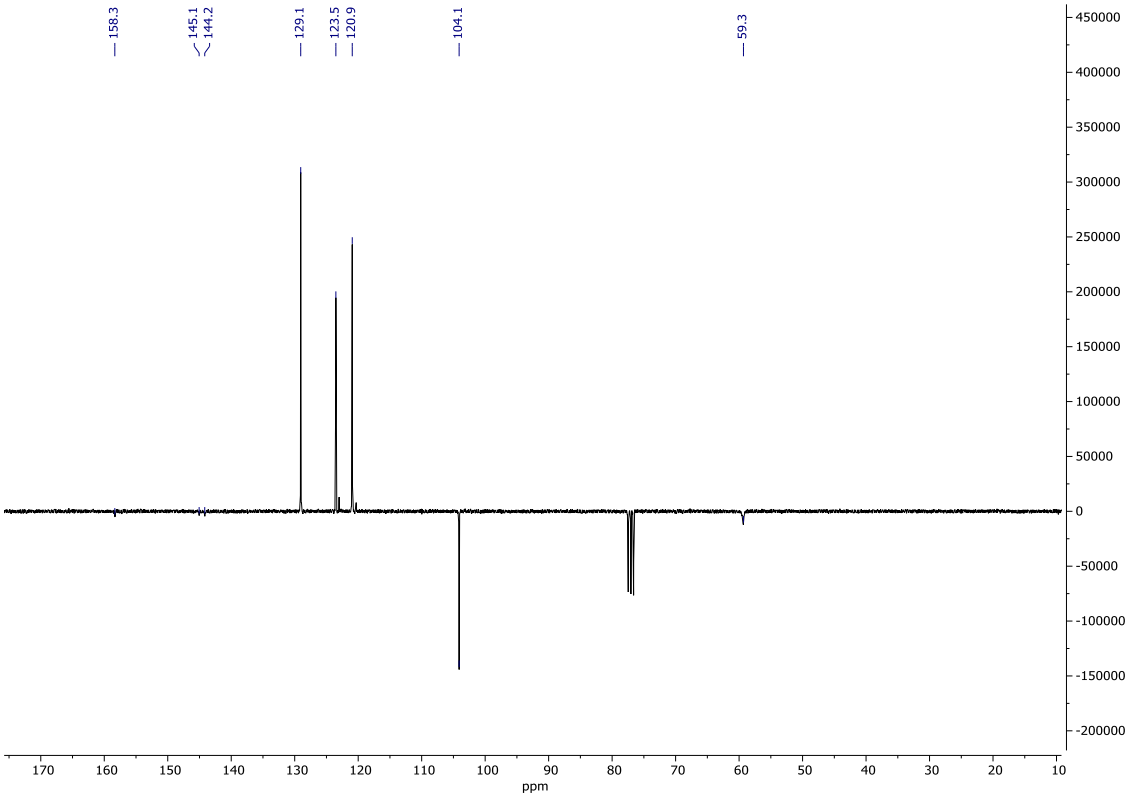
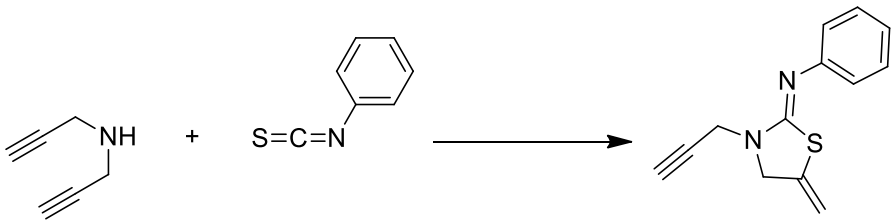


Figure 1.2. ^{13}C APT spectrum of compound **1** in $CDCl_3$ solution.

Synthesis of compound 2

To a solution of dipropargylamine (10.3 µl, 0.1 mmol) in ethanol (10 ml), phenyl isothiocyanate was added (11.9 µl, 0.1 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure and a yellow oil was collected and vacuum dried to give the product.

Yield: 64%



Scheme 1.2. Synthesis of compound **2**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.26 (m, 2H, C_{ortho}Ph); 7.06 (m, 1H, C_{para}Ph); 6.94 (m, 2H, C_{meta}Ph); 5.26 (m, 1H, CH_2); 5.10 (m, 1H, CH_2); 4.38 (d, 2H, $CH_2 - C \equiv CH$, $^{4}J_{HH}$ = 2.5 Hz); 4.37 (t, 2H, CH_2-N, $^{4}J_{HH}$ = 2.3 Hz); 2.33 (t, 1H, CH, $^{4}J_{HH}$ = 2.5 Hz).

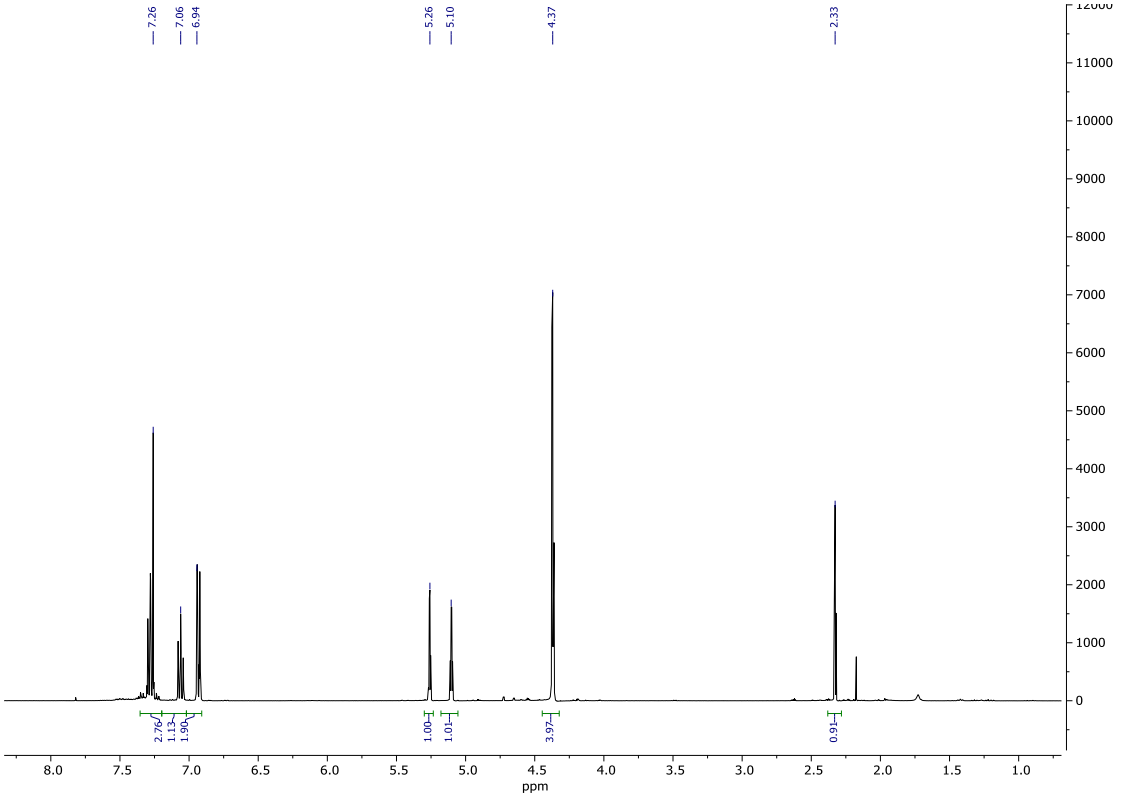


Figure 1.3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 156.3 (s, 1C, N-*C*=N); 151.2 (s, 1C, C_{ipso}Ph-NH); 137.0 (s, 1C, *C*-CH_2); 129.0 (s, 2C, C_{ortho}Ph) 123.6 (s, 1C, C_{para}Ph); 121.9 (s, 2C, C_{meta}Ph); 106.0 (s, 1C, CH_2); 77.4 (s, 1C, $C \equiv CH$); 72.9 (s, 1C, *CH*); 55.1 (s, 1C, CH_2-N); 33.3 (s, 1C, $CH_2 - C \equiv CH$).

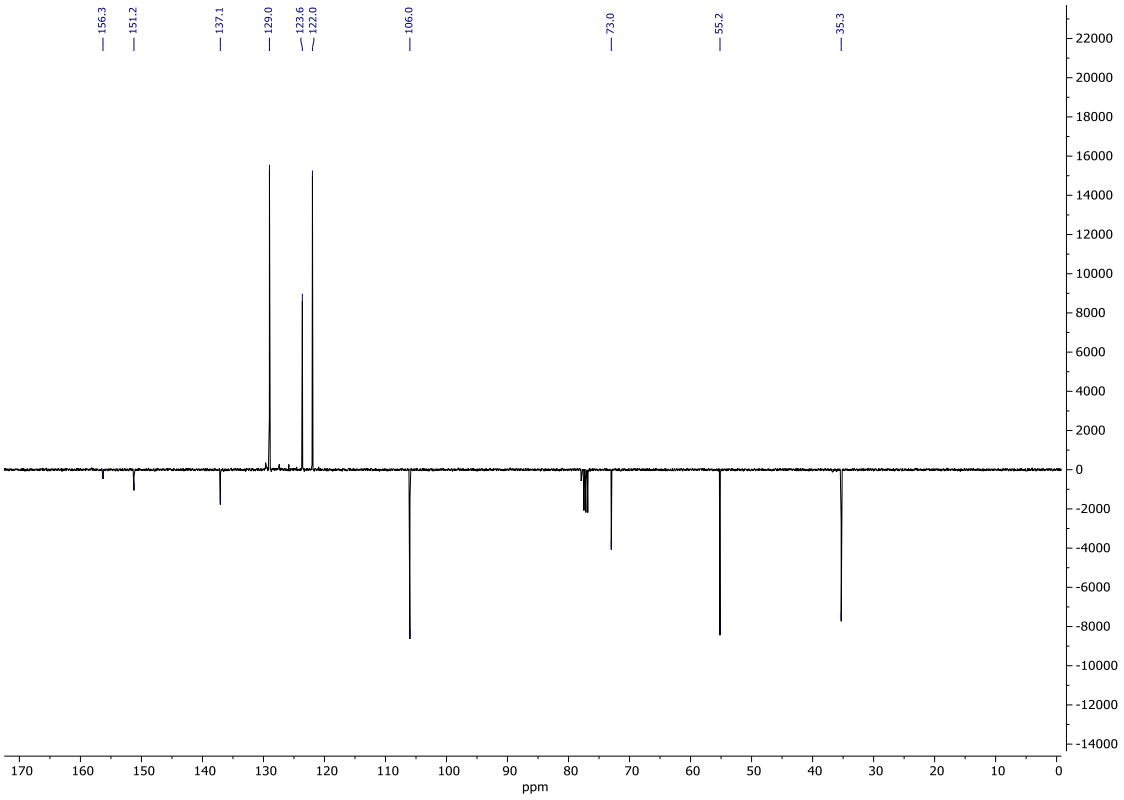
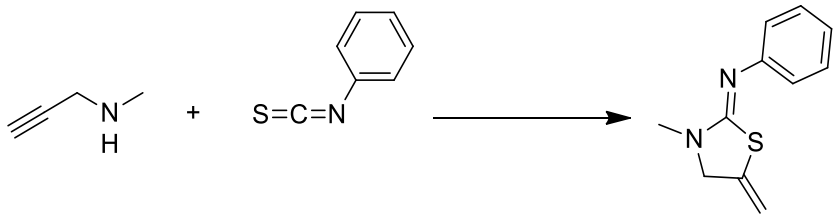


Figure 1.4. ^{13}C APT spectrum of compound **2** in $CDCl_3$ solution.

Synthesis of compound 3

To a solution of N-methyl-propargylamine (8.2 µl, 0.1 mmol) in ethanol/water mixture (1/1) (10 ml), phenyl isothiocyanate was added (11.9 µl, 0.1 mmol) and the solution stirred for 24 h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 50%



Scheme 1.3. Synthesis of compound **3**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.27 (m, 2H, C_{ortho}Ph); 7.05 (m, 1H, C_{para}Ph); 6.93 (m, 2H, C_{meta}Ph); 5.20 (m, 1H, CH_2); 5.07 (m, 1H, CH_2); 4.28 (t, 2H, CH_2-N, $^4J_{HH}$ = 2.3 Hz); 3.09 (s, 1H, CH_3).

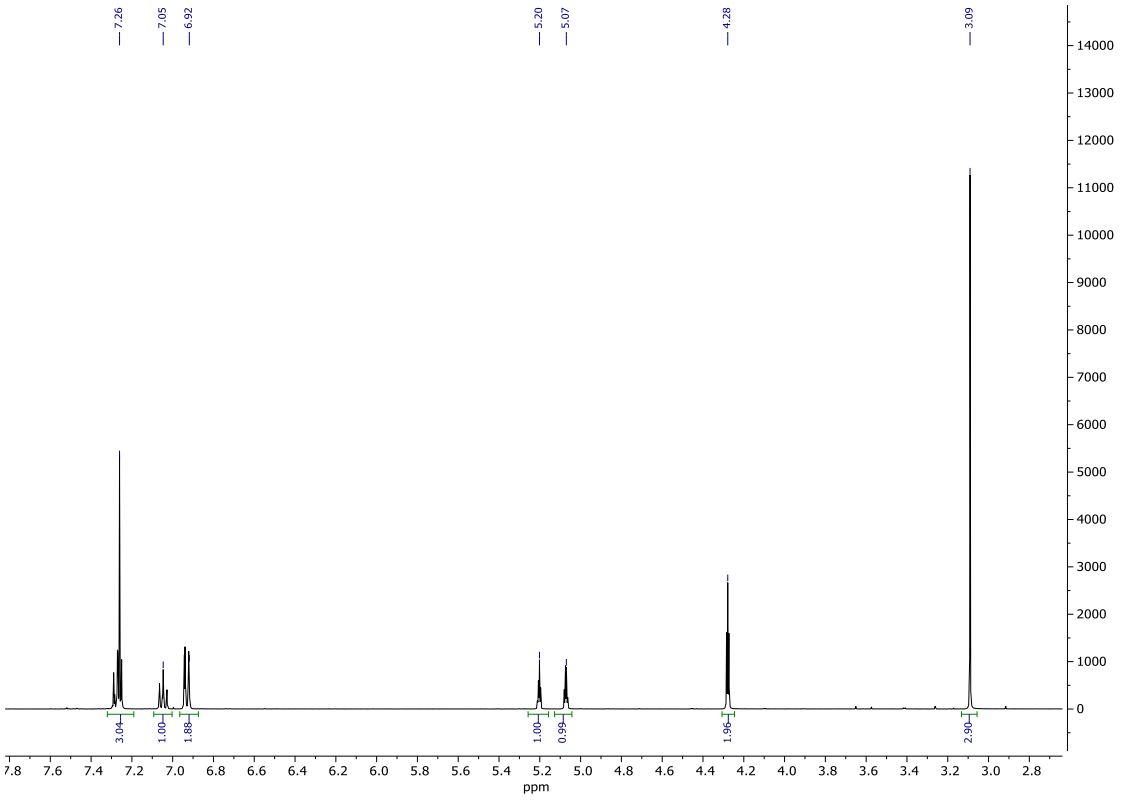


Figure 1.5. ^{1}H NMR spectrum of compound **3** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 151.8 (s, 1C, C_{ipso}Ph-NH); 137.6 (s, 1C, C=CH_2); 129.0 (s, 2C, C_{ortho}Ph) 123.4 (s, 1C, C_{para}Ph); 122.2 (s, 2C, C_{meta}Ph); 105.3 (s, 1C, CH_2); 58.1 (s, 1C, CH_2-N); 33.2 (s, 1C, CH_3).

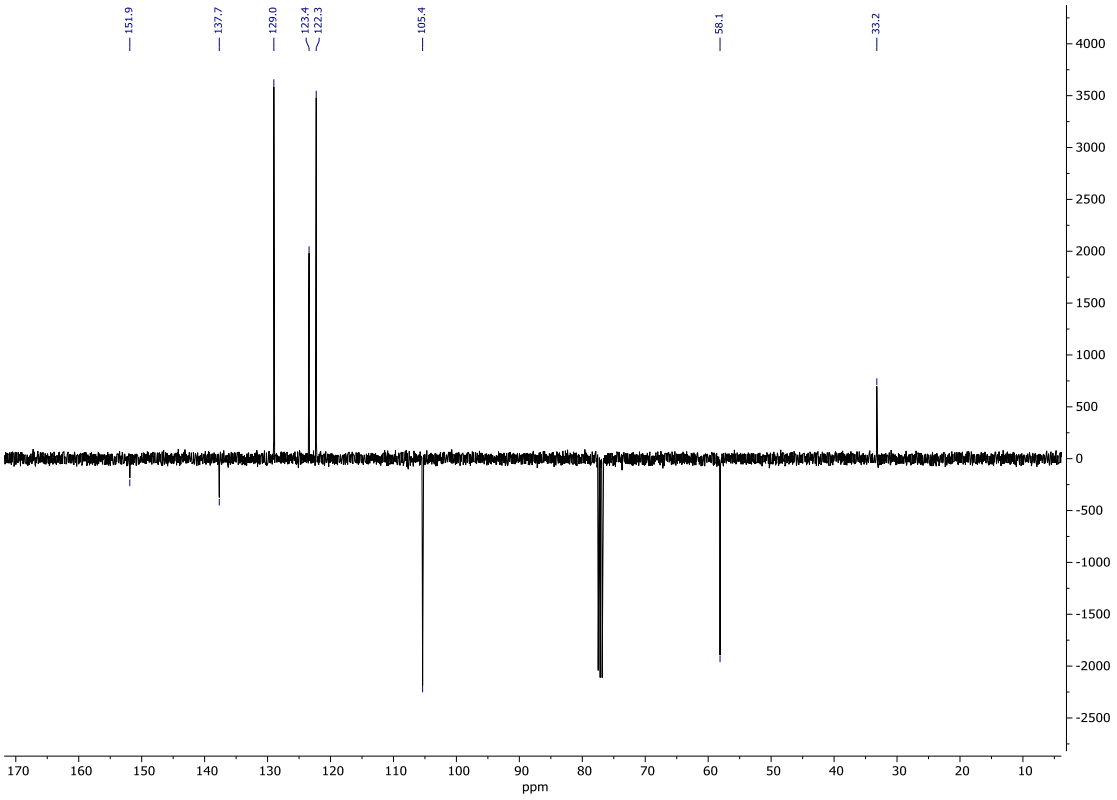
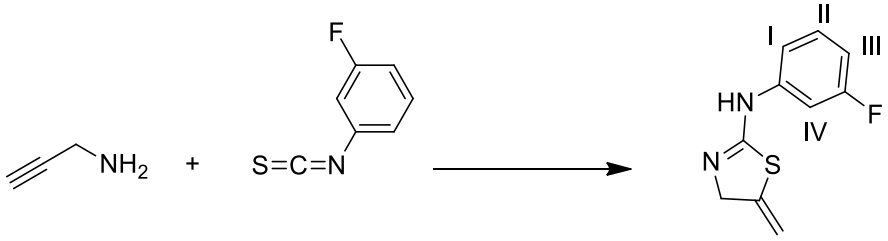


Figure 1.6. ^{13}C APT spectrum of compound **2** in $CDCl_3$ solution.

Synthesis of compound 4

To a solution of dipropargylamine (10.3 µl, 0.1 mmol) in ethanol/water mixture (1/1) (10 ml), 3-fluorophenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the solution stirred for 24 h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 60%



Scheme 1.4. Synthesis of compound **4**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.23 (m, 1H, *II*); 6.98 (td, 1H, *IV*, $^4J_{HH}$= 10.2 Hz, $^5J_{HH}$= 2.1 Hz); 6.87 (ddd, 1H, *I*, $^3J_{HH}$= 8.0 Hz, $^4J_{HH}$= 2.0 Hz, $^4J_{HH}$= 0.9 Hz); 6.75 (tdd, 1H, *III*, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$= 2.5 Hz, $^4J_{HH}$= 0.9 Hz); 5.23 (m, 1H, CH_2); 5.14 (m, 1H, CH_2); 4.56 (t, 2H, CH_2-N, $^3J_{HH}$= 2.4Hz).

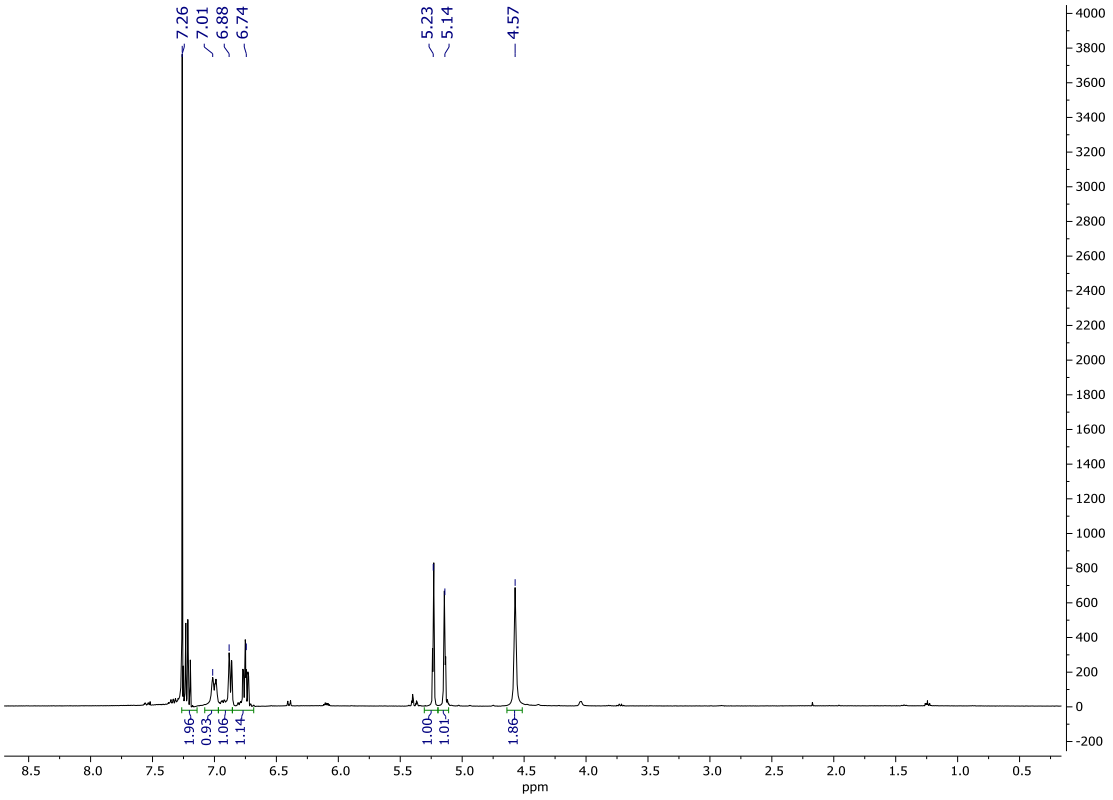


Figure 1.7. ^{1}H NMR spectrum of compound **4** in $CDCl_3$ solution.

^{19}F NMR (ppm) (376 MHz, $CDCl_3$): δ = -108.5 (m, 1F, *Ph-F*)

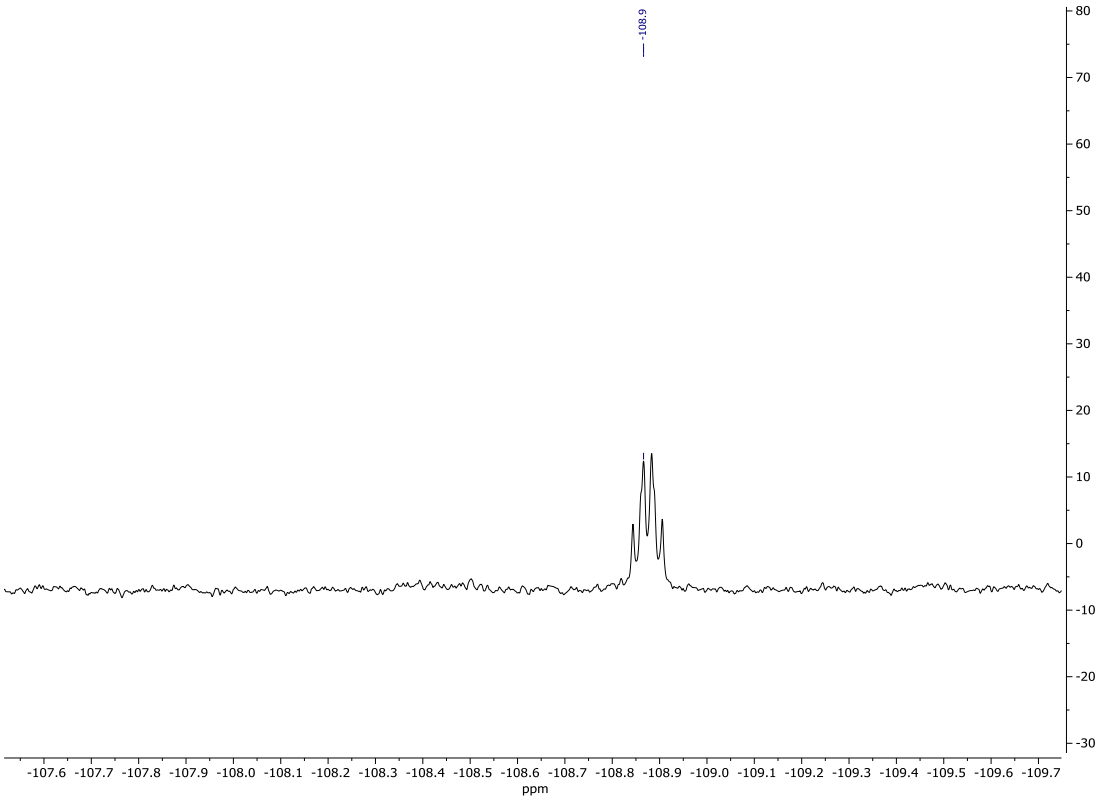


Figure 1.8. ^{19}F NMR spectrum of compound **4** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 163.3 (d, 1C, C_{ipso}Ph, $^1J_{CF}$ = 243.7 Hz); 130.2 (d, 1C, *II*, $^3J_{CF}$ = 9.6 Hz); 116.4 (d, 1C, *I*, $^4J_{CF}$ = 2.5 Hz); 110.2 (d, 1C, *III*, $^2J_{CF}$ = 21.12 Hz); 108.2 (d, 1C, *IV*, $^2J_{CF}$ = 23.8 Hz); 104.8 (s, 1C, CH_2); 60.44 (s, 1C, CH_2-N).

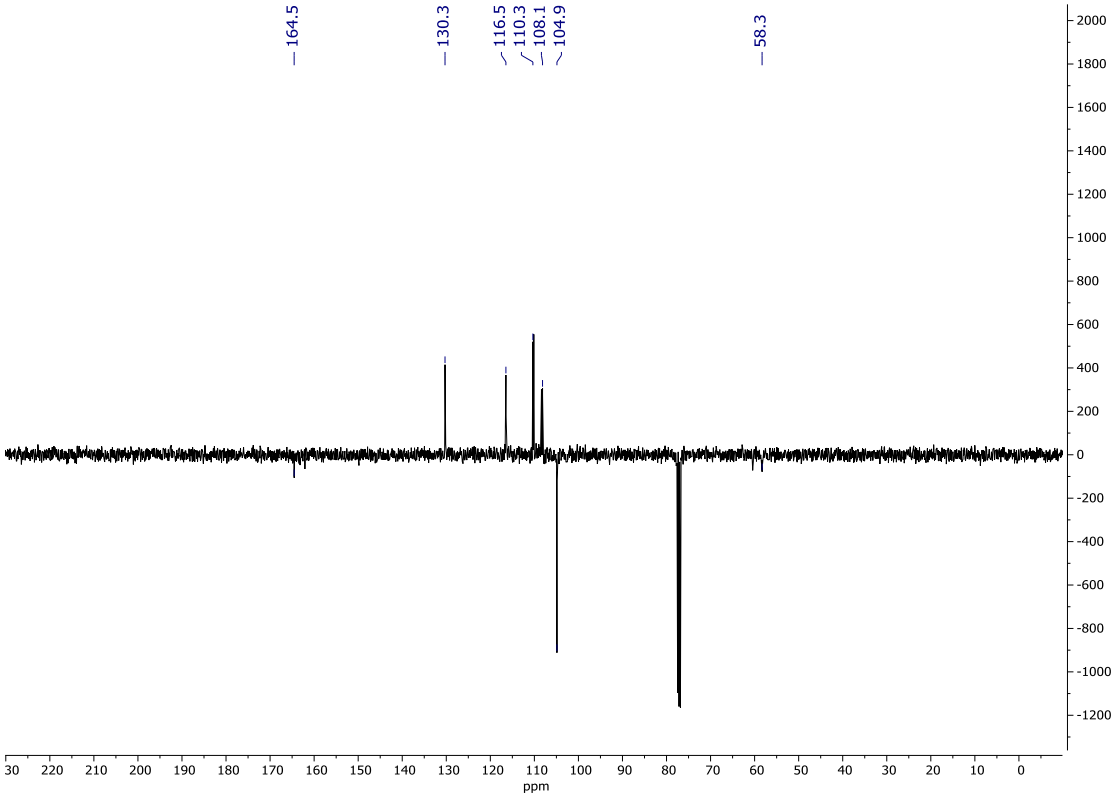
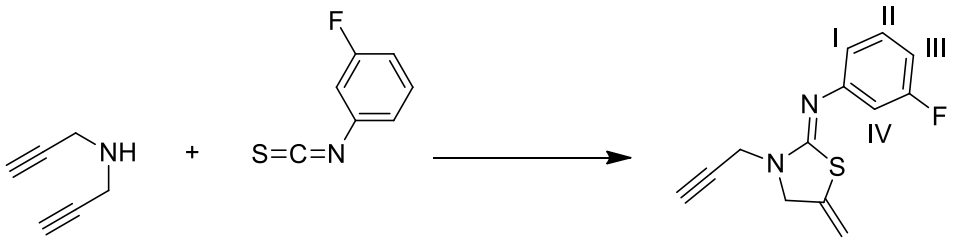


Figure 1.9. ^{13}C APT spectrum of compound 4 in $CDCl_3$ solution.

Synthesis of compound 5

To a solution of dipropargylamine (10.3 µl, 0.1 mmol) in ethanol/water mixture (1/1) (10 ml), 3-fluorophenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure and a yellow oil was collected and vacuum dried to give the product.

Yield: 58%



Scheme 1.5. Synthesis of compound **5**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.22 (m, 1H, *II*); 6.72 (m, 3H, *I*+*III*+*IV*); 5.27 (m, 1H, CH_2); 5.12 (m, 1H, CH_2); 4.38 (t, 2H, CH_2-N, $^{4}J_{HH}$ = 2.3 Hz); 4.36 (d, 2H, $CH_2 - C \equiv CH_2$);, $^{4}J_{HH}$= 2.5Hz); 2.33 (t, 1H, *CH*, $^{4}J_{HH}$ = 2.5 Hz).

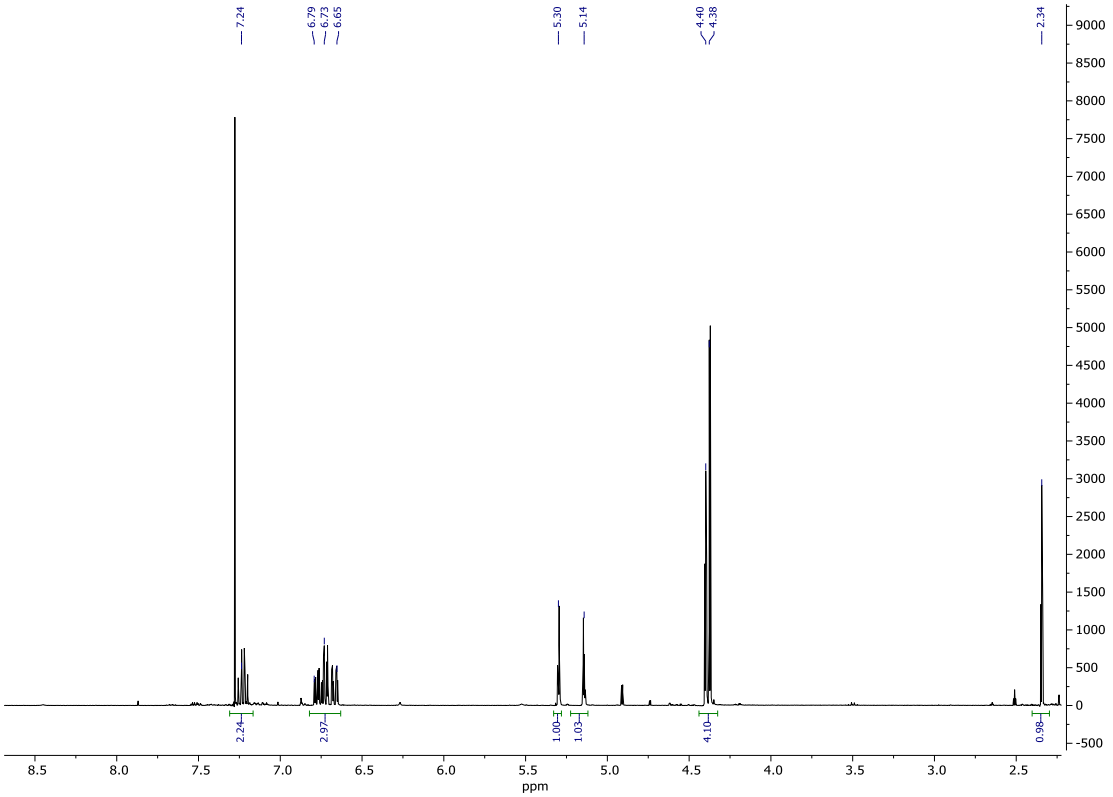


Figure 1.10. ^{1}H NMR spectrum of compound **5** in $CDCl_3$ solution.

^{19}F NMR (ppm) (376 MHz, $CDCl_3$): δ = -112.9 (m, 1F, *Ph-F*).

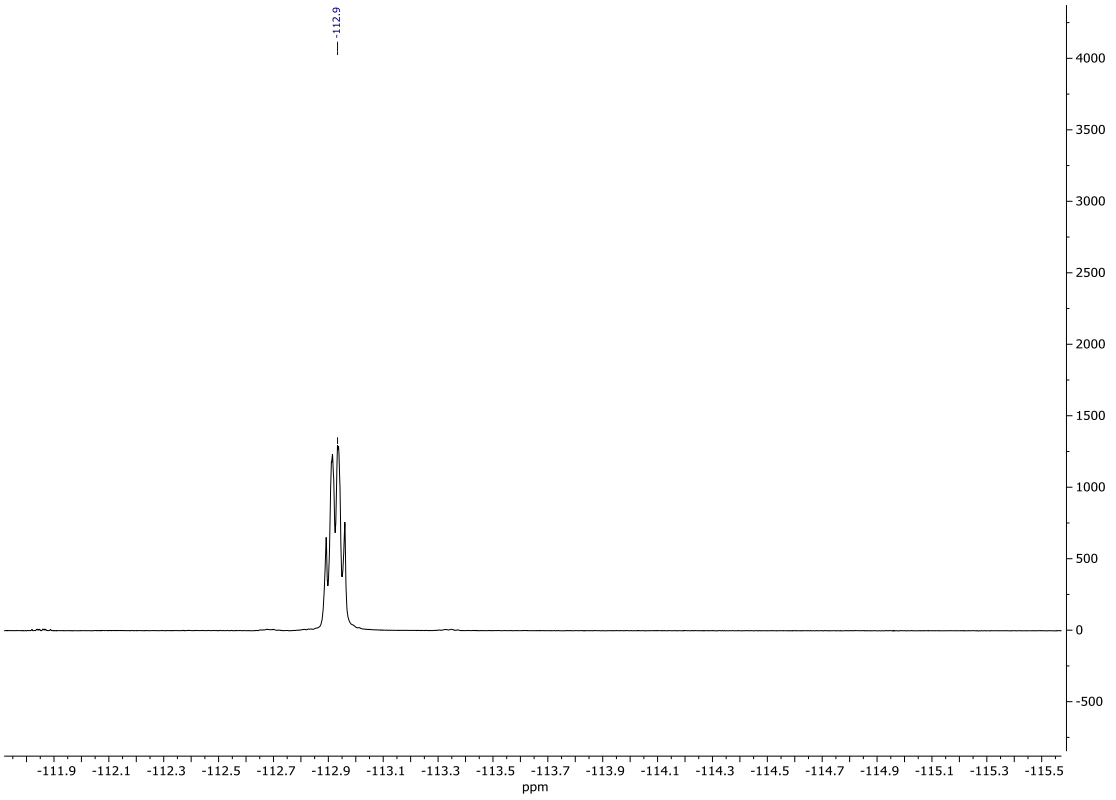


Figure 1.11. ^{19}F NMR spectrum of compound **5** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 164.5 (d, 1C, C_{ipso}Ph, $^{1}J_{CF}$ = 243.7 Hz); 156.8 (s, 1C, N-*C*=N); 152.9 (d, 1C, C_{ipso}Ph-NH, $^{3}J_{CF}$ = 9.6 Hz); 136.7 (s, 1C, *C*=CH_2); 130.1 (d, 1C, *II*, $^{3}J_{CF}$ = 9.6 Hz); 117.8 (d, 1C, *I*, $^{4}J_{CF}$ = 2.7 Hz); 110.4 (d, 1C, *III*, $^{2}J_{CF}$ = 21.1 Hz); 109.2 (d, 1C, *IV*, $^{2}J_{CF}$ = 22.0 Hz); 106.4 (s, 1C, CH_2); 77.5 (s, 1C, $C \equiv CH$); 73.1 (s, 1C, *CH*); 55.2 (s, 1C, CH_2-N); 35.3 (s, 1C, $CH_2 - C \equiv CH$).

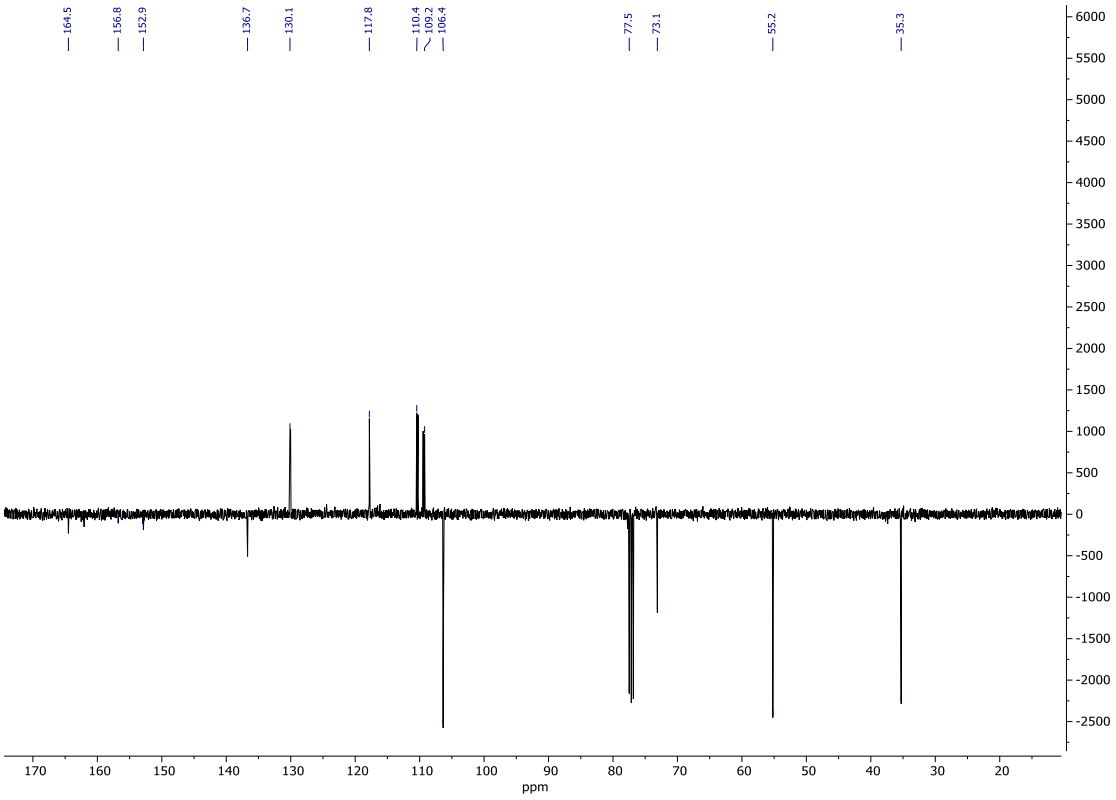
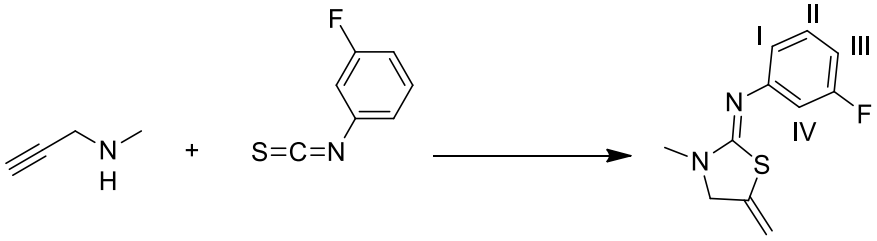


Figure 1.12. ^{13}C APT spectrum of compound **5** in $CDCl_3$ solution.

Synthesis of compound 6

To a solution of N-methyl-propargylamine (8.2 µl, 0.1 mmol) in ethanol (10 ml), 3-fluorophenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure and a transparent oil was collected and vacuum dried to give the product.

Yield: 60%



Scheme 1.6. Synthesis of compound **6**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.20 (m, 1H, *II*); 6.74 (m, 1H, *IV*); 6.71 (m, 1H, *I*); 6.65 (m, 1H, *III*); 5.21 (m, 1H, CH_2); 5.09 (m, 1H, CH_2); 4.28 (t, 2H, CH_2-N, $^4J_{HH}$ = 2.3 Hz); 3.07 (s, 3H, CH_3).

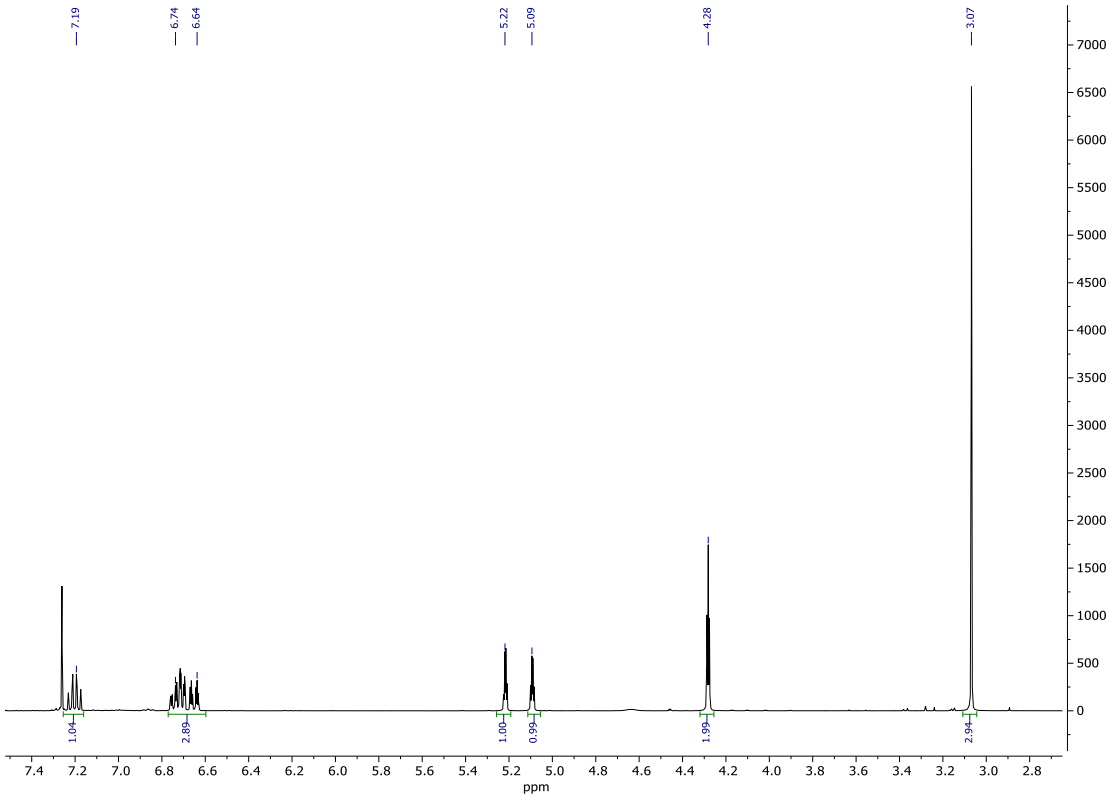


Figure 1.13. ^{1}H NMR spectrum of compound **6** in $CDCl_3$ solution.

^{19}F NMR (ppm) (376 MHz, $CDCl_3$): δ = -113.0 (m, 1F, *Ph-F*).

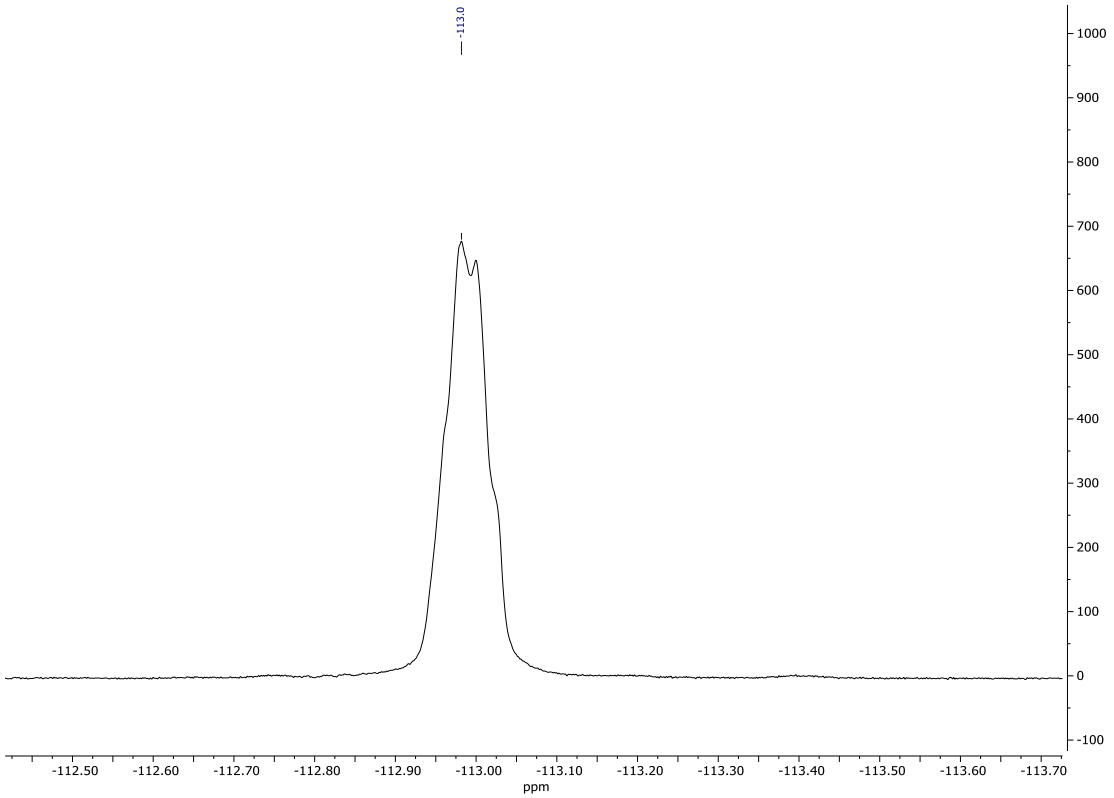


Figure 1.14. ^{19}F NMR spectrum of compound **6** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 163.8 (d, 1C, C_{ipso}Ph, $^1J_{CF}$ = 245.3 Hz); 157.8 (s, 1C, N-*C*=N); 154.0 (d, 1C, C_{ipso}Ph-NH, $^3J_{CF}$ = 9.6 Hz); 137.6 (s, 1C, *C*=CH_2); 130.3 (d, 1C, *II*, $^3J_{CF}$ = 9.7 Hz); 118.3 (d, 1C, *I*, $^4J_{CF}$ = 2.7 Hz); 110.2 (d, 1C, *III*, $^2J_{CF}$ = 21.3 Hz); 109.7 (d, 1C, *IV*, $^2J_{CF}$ = 22.0 Hz); 105.9 (s, 1C, CH_2); 57.9 (s, 1C, CH_2-N); 32.8 (s, 1C, CH_3).

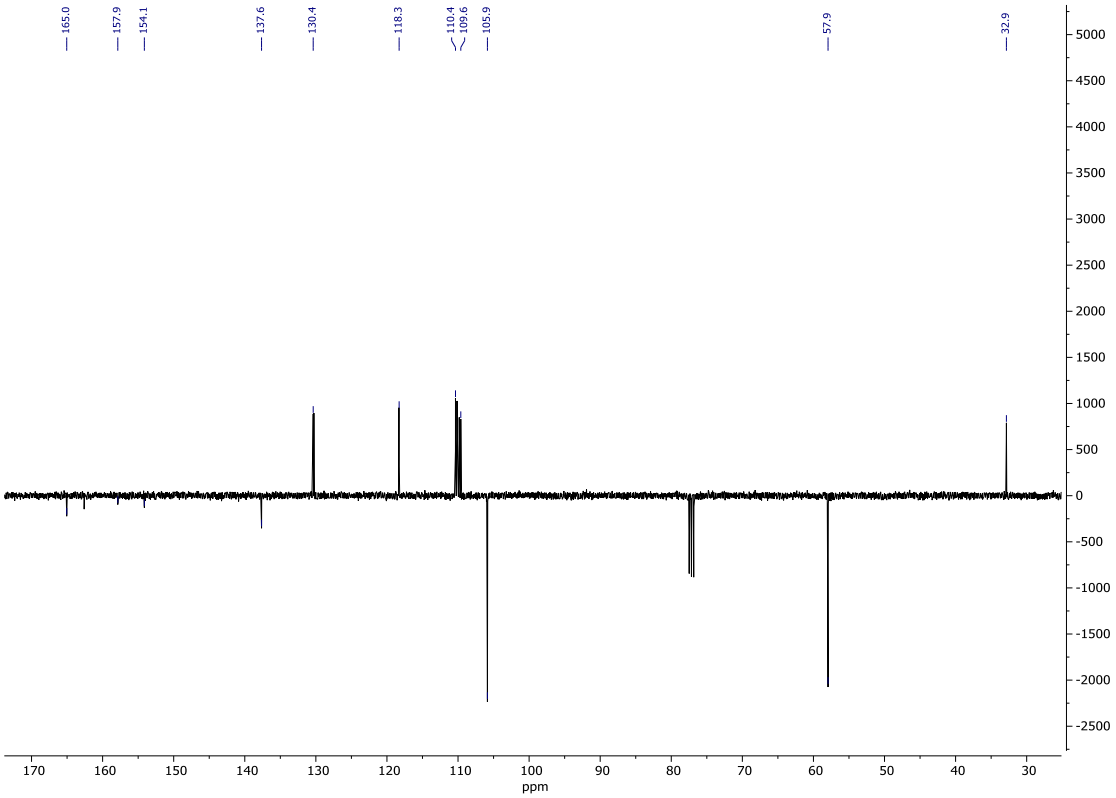
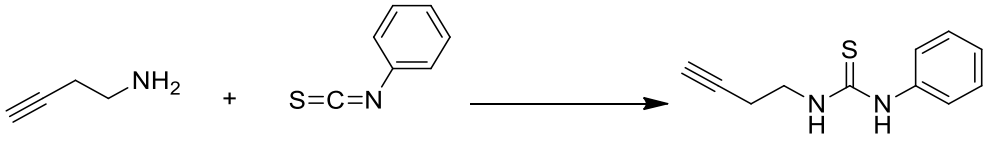


Figure 1.15. ^{13}C APT spectrum of compound **6** in $CDCl_3$ solution.

Synthesis of compound 7

To a solution of 1-amino-3-butyne (8.2 µl, 0.1 mmol) in ethanol/water mixture (1/1) (10 ml), isothiocyanate was added (12.0 µl, 0.1 mmol) and the solution stirred for 24 h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 58%



Scheme 1.7. Synthesis of compound **7**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 7.82 (s, 1H, *NH*-Ph); 7.44 (m, 2H, H_{ortho}Ph); 7.32 (tt, 1H, H_{para}Ph, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.1 Hz); 7.25 (m, 2H, H_{meta}Ph); 6.41 (s br, 1H, *NH*-CH_2); 3.81 (m, 2H, CH_2-CH_2-NH); 2.55 (td, 2H, CH_2-CH_2-NH, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 2.6 Hz); 1.93 (t, 1H, *CH*, $^{4}J_{HH}$ = 2.6 Hz).

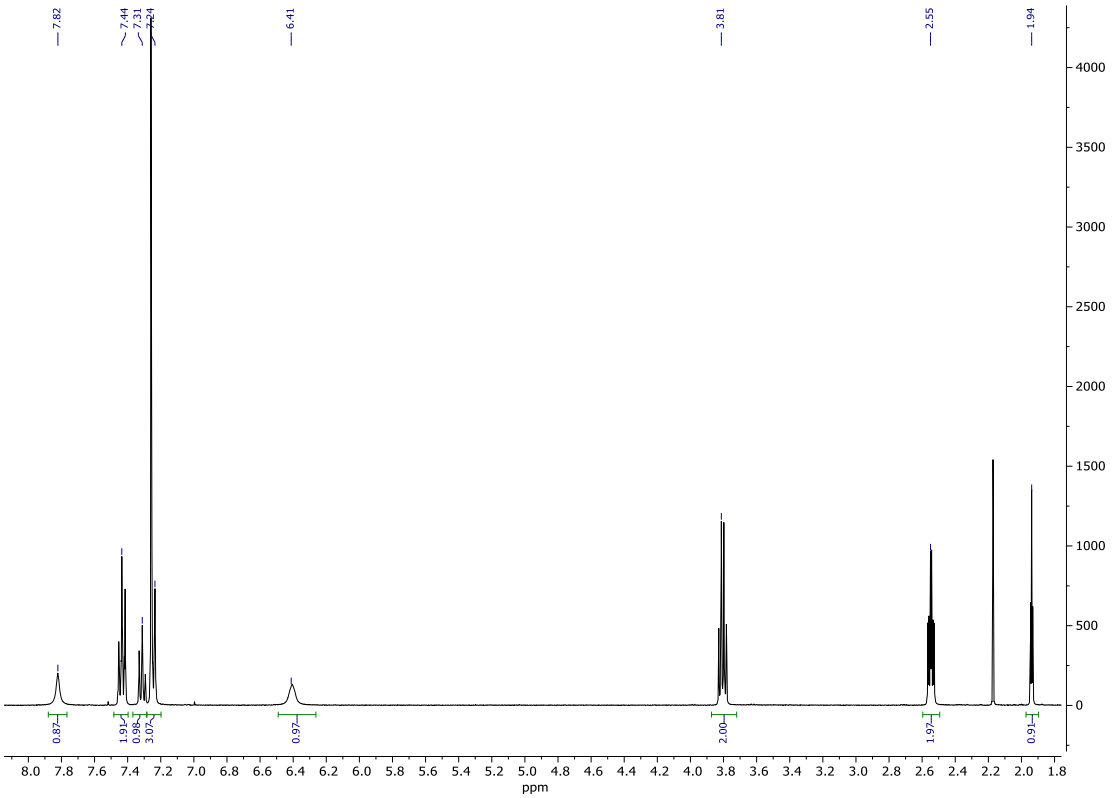


Figure 1.16. ^{1}H NMR spectrum of compound **7** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 180.8 (s, 1C, *C*=*S*); 135.9 (s, 1C, C_{ipso}Ph=; 130.3 (s, 2C, C_{ortho}Ph); 127.6 (s, 1C, C_{para}Ph); 125.4 (s, 2C, C_{meta}Ph); 81.5 (s, 1C, *C* ≡ CH); 70.4 (s, 1C, *CH*); 43.7 (s, 1C, CH_2-CH_2-NH); 18.9 (s, 1C, CH_2-CH_2-NH).

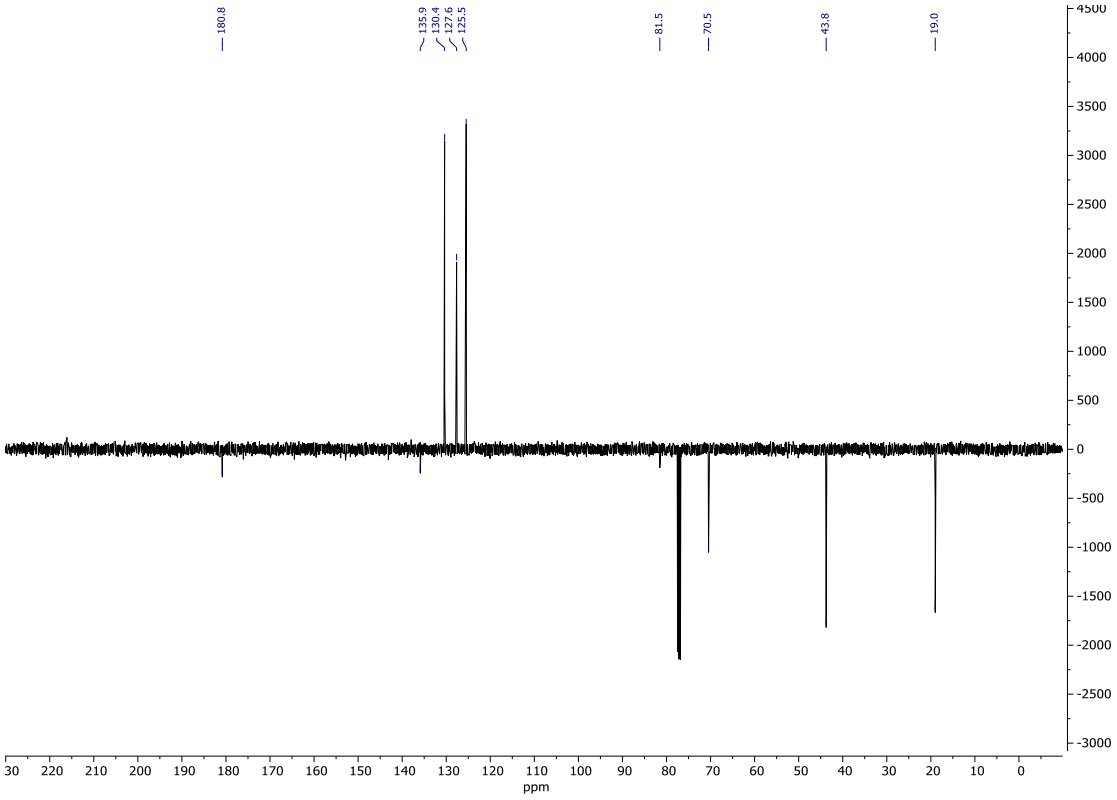
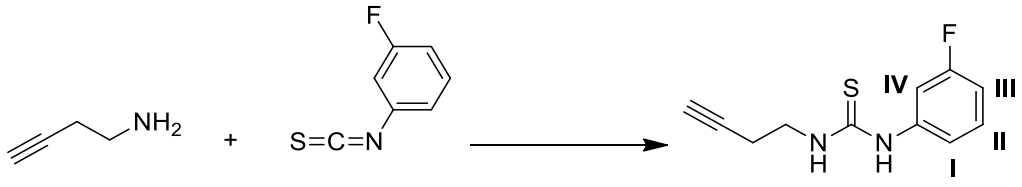


Figure 1.17. ^{13}C APT spectrum of compound **7** in $CDCl_3$ solution.

Synthesis of compound 8

To a solution of 1-amino-3-butyne (8.2 µl, 0.1 mmol) in ethanol (10 ml), 3-fluorophenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure and a white solid was collected and vacuum dried to give the product.

Yield: 62%



Scheme 1.8. Synthesis of compound **8**.

^{1}H NMR (ppm) (400 MHz, $CDCl_3$): δ = 8.07 (s br, 1H, *NH*-Ph); 7.39 (m, 1H, *II*), 7.01 (m, 3H, *I+III+IV*), 6.52 (s broad, 1H, *NH*-CH_2); 3.82 (m, 2H, CH_2-*CH_2*-NH); 2.57 (td, 2H, *CH_2*-CH_2-NH, ^{3} J_{HH} = 6.2, ^{4} J_{HH} = 2.6 Hz); 2.00 (t, 1H, *CH*, $^4J_{HH}$ = 2.6 Hz).

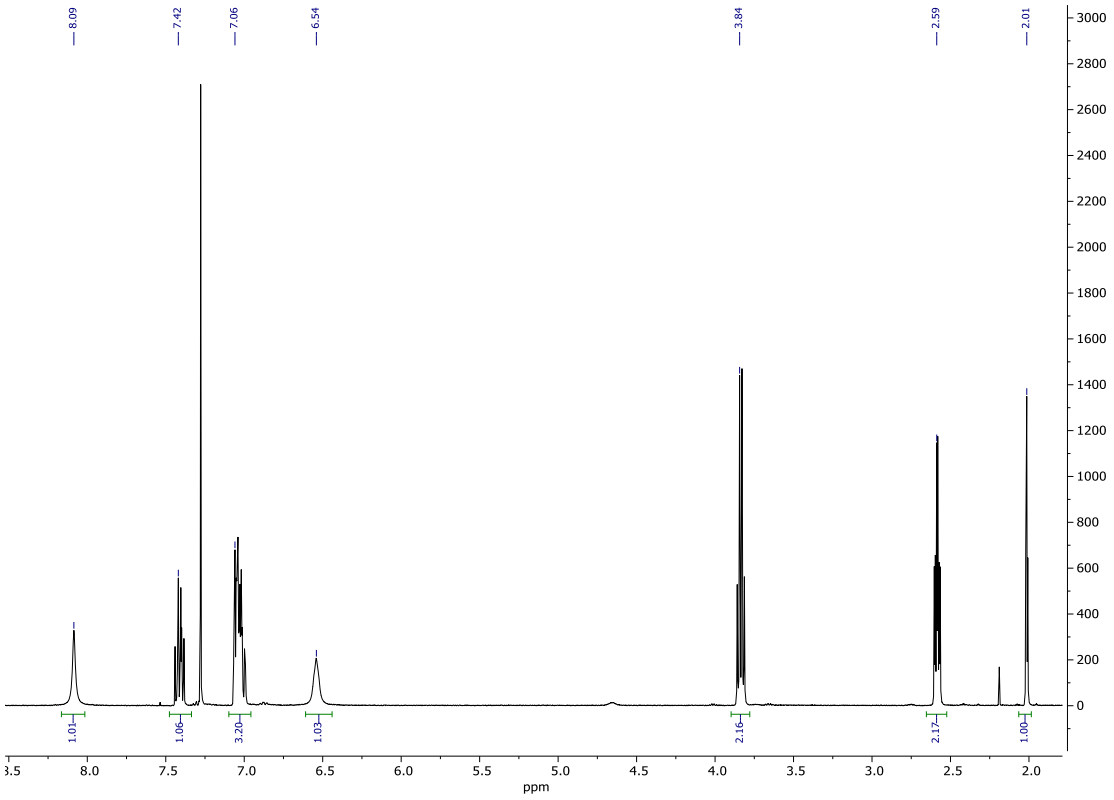


Figure 1.18. ^{1}H NMR spectrum of compound **8** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, $CDCl_3$): δ = 180.5 (s, 1C, *C*=*S*), 163.5 (d, 1C, C_{ipso}Ph-F, $^{1}J_{CF}$ = 247.8 Hz); 137.6 (d, 1C, C_{ipso}Ph-F, $^{3}J_{CF}$ = 9.4 Hz); 131.7 (d, 1C, *II*, $^{3}J_{CF}$ = 9.2 Hz); 120.5 (d, 1C, *I*, $^{4}J_{CF}$ = 3.2 Hz); 114.3 (d, *III*, $^{2}J_{CF}$ = 20.9 Hz); 112.3 (d, *IV*, $^{2}J_{CF}$ = 23.3 Hz); 81.5 (s, 1C, *C* ≡ CH); 70.7 (s, 1C, *CH*); 43.7 (s, 1C, CH_2-*CH_2*-NH); 18.9 (s, 1C, *CH_2*-CH_2-NH).

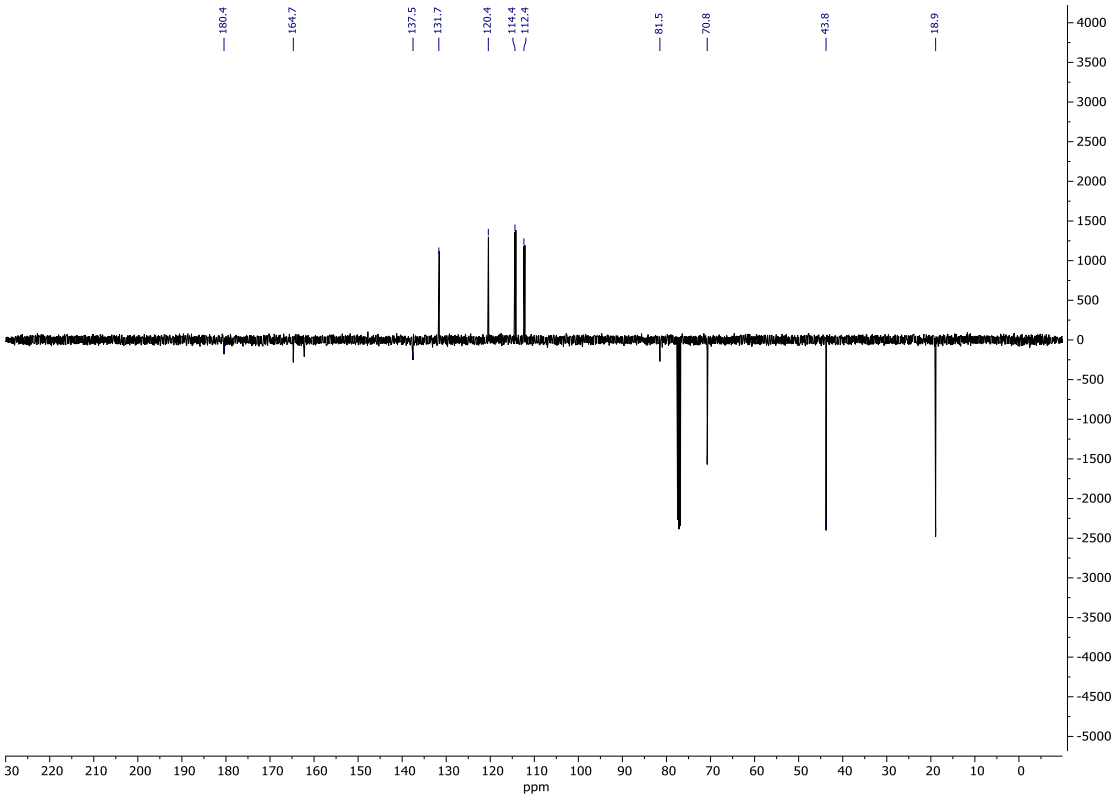
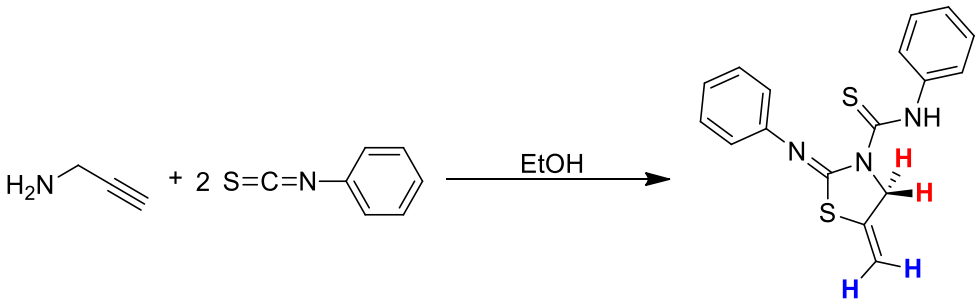


Figure 1.19. ^{13}C APT spectrum of compound **8** in $CDCl_3$ solution.

Synthesis of compound 9

To a solution of propargylamine (12.8 µl, 0.2 mmol) in ethanol (20 ml) was added some excess of phenyl isothiocyanate (71.5 µl, 0.6 mmol) and the solution stirred for 72 h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 75%



Scheme 1.9. Synthesis of compound **9**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.67 (m, 2H, *Ph*); 7.42 (m, 4H, *Ph*); 7.23 (m, 2H, *Ph*); 7.13 (m, 2H, *Ph*); 5.52 (m, 1H, CH_2); 5.38 (t, 2H, CH_2-N, $^4J_{HH}$ = 2.4 Hz); 5.24(dt, 1H, CH_2, $^2J_{HH}$ = 2.7 Hz, $^4J_{HH}$ = 2.2 Hz).

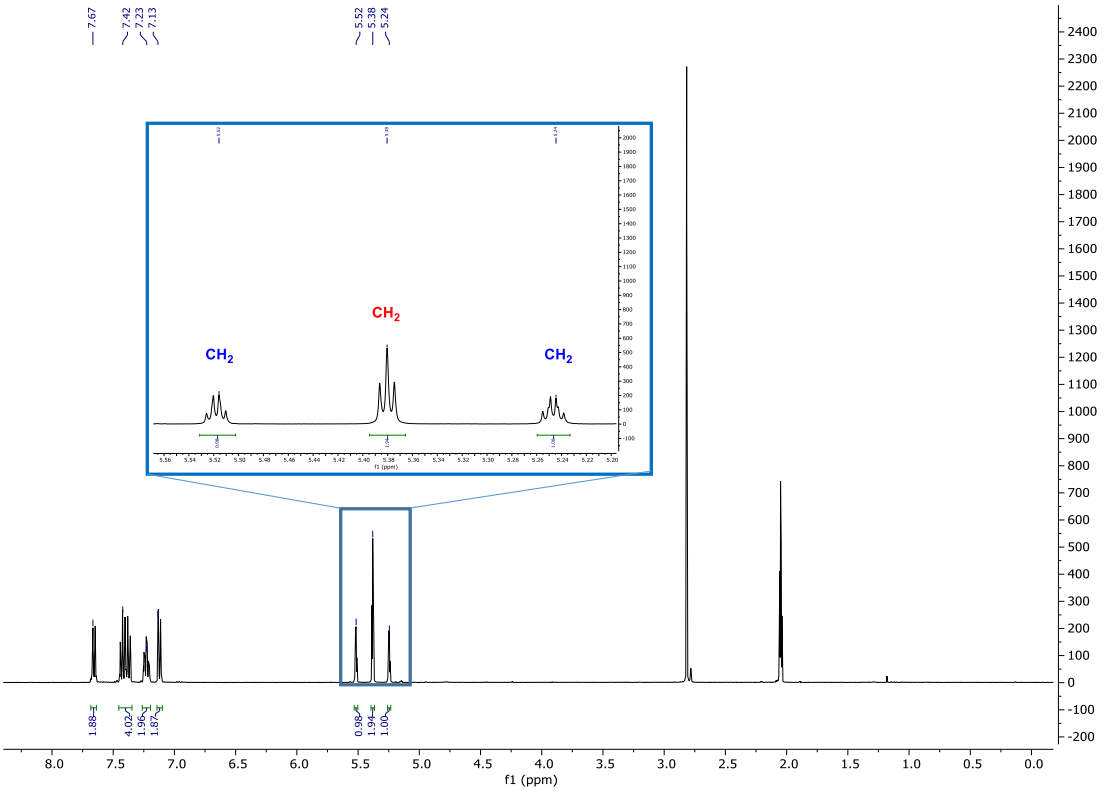


Figure 1.20. ^{1}H NMR spectrum of compound **9** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 178.6 (s, 1C, *C*=O); 158.6 (s, 1C, N=*C*-N); 149.2 (s, 1C, C_{ipso}Ph-N); 139.9 (s, 1C, C_{ipso}Ph-NH); 132.8 (s, 1C, CH_2=*C*); 130.3 (s, 2C, *Ph*); 129.4 (s, 2C, *Ph*); 126.8 (s, 2C, *Ph*); 126.3 (s, 1C, *Ph*); 125.2 (s, 1C, *Ph*); 122.3 (s, 2C, *Ph*); 107.9 (s, 1C, CH_2); 60.9 (s, 1C, CH_2-N).

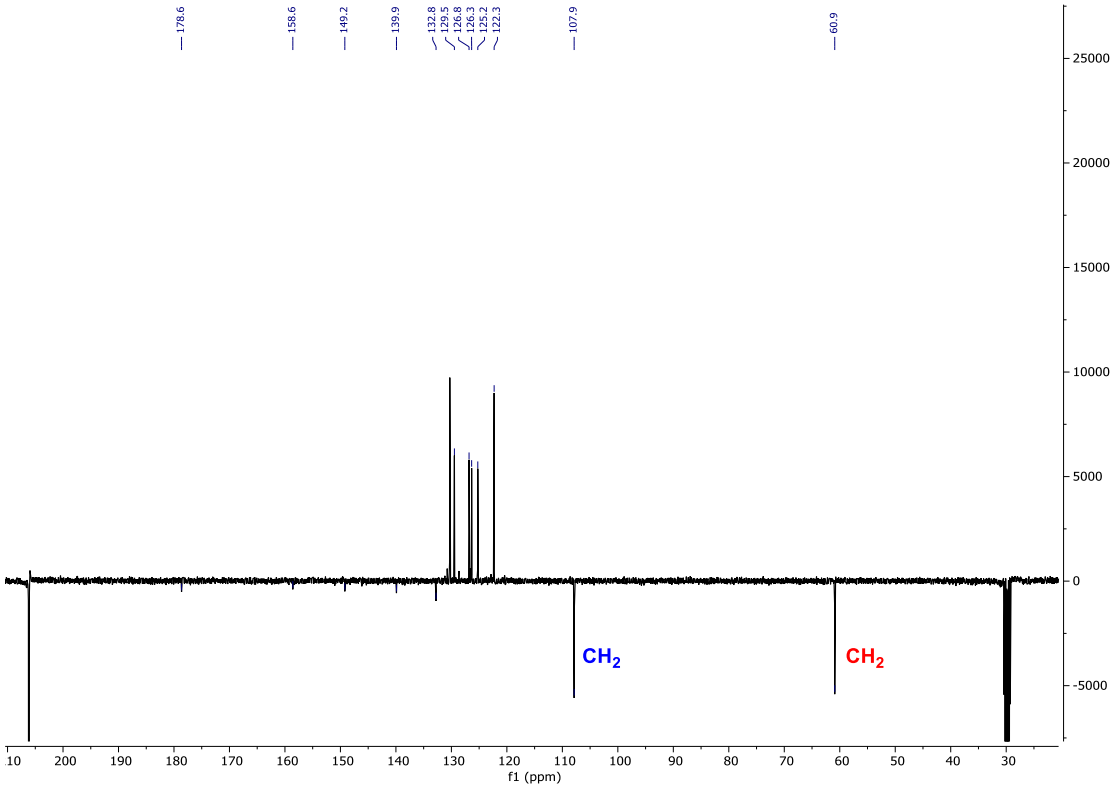
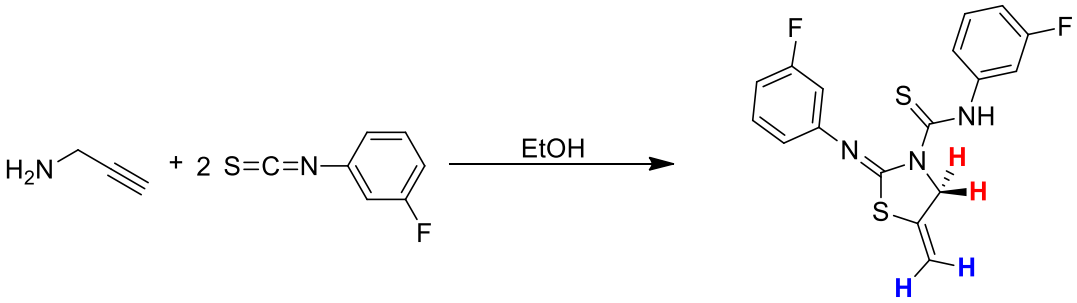


Figure 1.21. ^{13}C APT spectrum of compound **9** in $(CD_3)_2CO$ solution.

Synthesis of compound 10

To a solution of propargylamine (12.8 µl, 0.2 mmol) in ethanol (20 ml) was added some excess of 3-fluorophenyl isothiocyanate (72.0 µl, 0.6 mmol) and the solution stirred for 72 h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 73%



Scheme 1.10. Synthesis of compound **10**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.79-6.97 (m, 8H, *arom.*); 5.54 (m, 1H, CH_2); 5.38 (t, 2H, CH_2-N; J_{HH} = 2.4 Hz); 5.28 (m, 1H, CH_2).

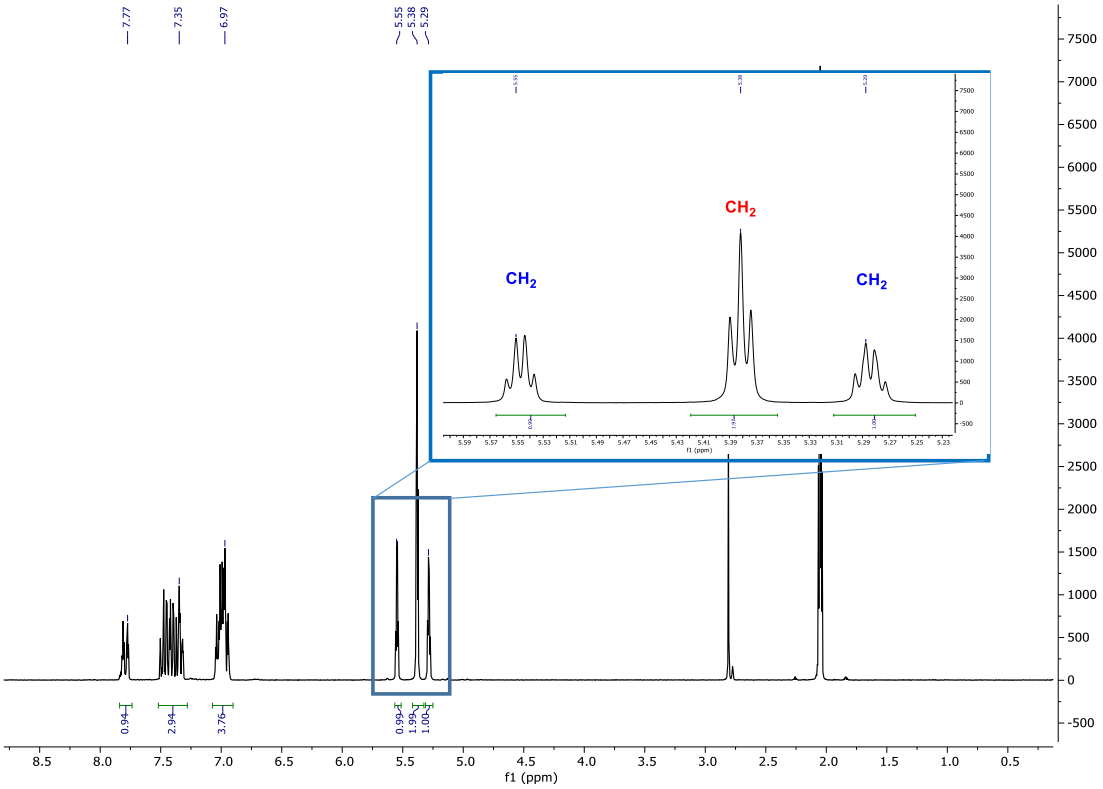


Figure 1.22. ^{1}H NMR spectrum of compound **10** in $(CD_3)_2CO$ solution.

^{19}F NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -110.99 (m, 1F, *Ph-F*); -111.50 (m, 1F, *Ph-F*).

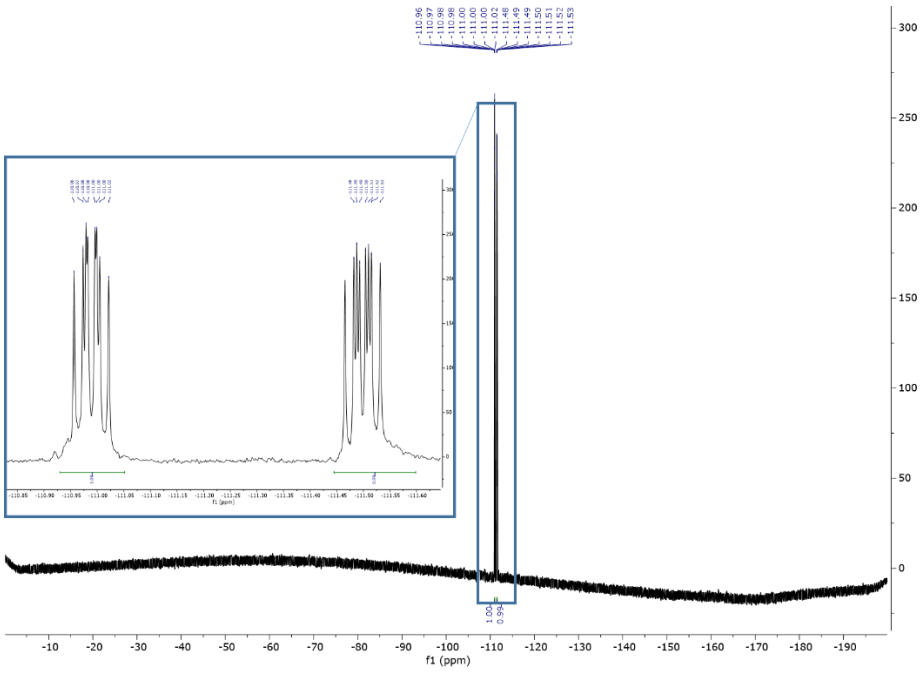


Figure 1.23. ^{19}F NMR spectrum of compound **10** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 165.5 (s, 1C, *C*=*S*); 157.9 (s, 1C, N=*C*-N); 150.0 (s, 1C, $C_{ipso}Ph$); 140.9 (s, 1C, $C_{ipso}Ph$); 131.2 (s, 1C, CH_2=*C*-CH_2); 131.9 (d, 1C, $C_{meta}Ph$, $^3J_{CF}$= 9.5Hz); 130.9 (d, 1C, $C_{meta}Ph$, $^3J_{CF}$= 9.4Hz); 120.8 (d, 1C, $C_{para}Ph$, $^4J_{CF}$= 3.0Hz); 118.4 (d, 1C, $C_{para}Ph$, $^4J_{CF}$= 3.0Hz); 113.3 (d, 1C, $C_{ortho}Ph$, $^2J_{CF}$= 21.4Hz); 112.9 (d, 1C, $C_{ortho}Ph$, $^2J_{CF}$= 21.3Hz); 112.0 (d, 1C, $C_{ortho}Ph$, $^2J_{CF}$= 25.6Hz); 109.8 (d, 1C, $C_{ortho}Ph$, $^2J_{CF}$= 23.3Hz); 108.3 (s, 1C, CH_2); 61.0 (s, 1C, CH_2-N).

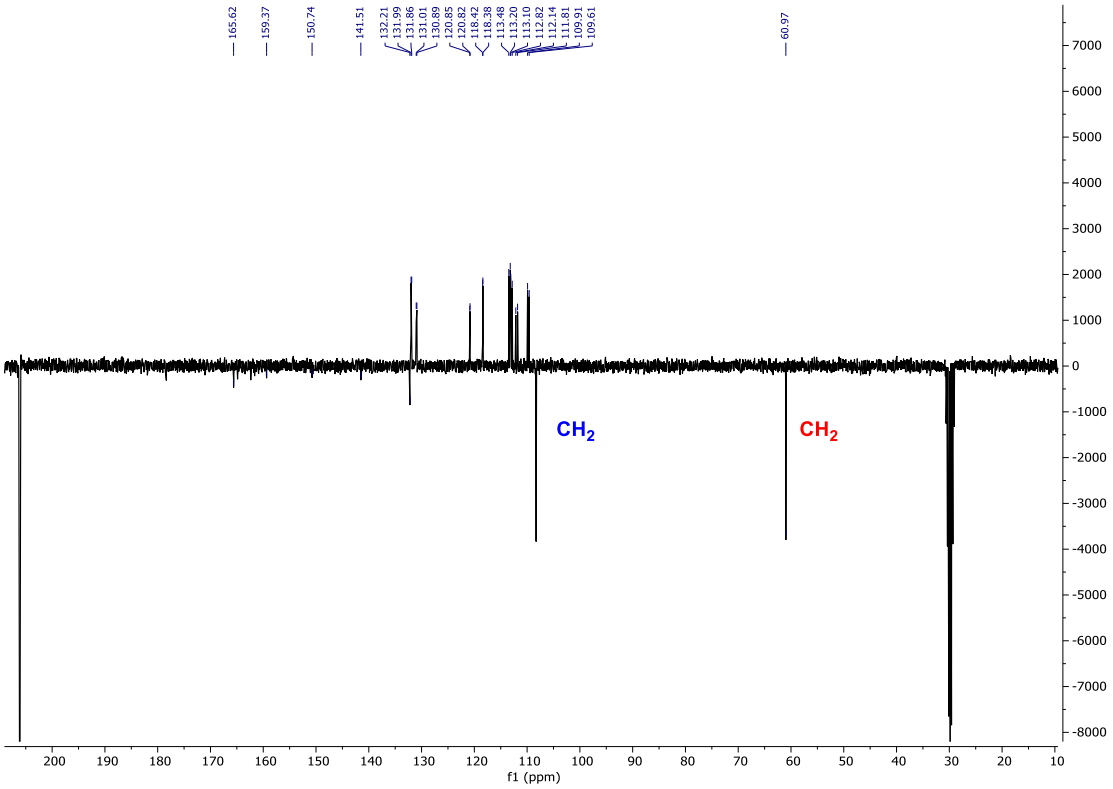
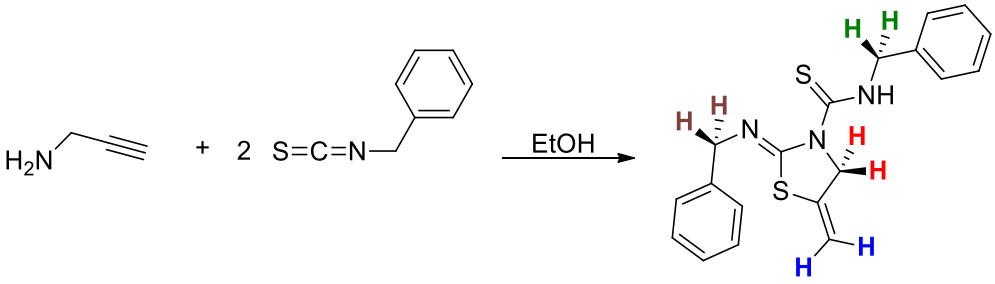


Figure 1.24. ^{13}C APT spectrum of compound **10** in $(CD_3)_2CO$ solution.

Synthesis of compound 11

To a solution of propargylamine (12.8 µl, 0.2 mmol) in ethanol (20 ml) was added some excess of bencyl isothiocyanate (78 µl, 0.6 mmol) and the solution stirred for 72 h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 75%



Scheme 1.11. Synthesis of compound **11**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 12.71 (s br, 1H, *NH*); 7.32-7.29 (m, 5H, *Ph*); 7.25-7.23 (m, 3H, *Ph*); 7.16-7.13 (m, 2H, *Ph*); 5.52 (m, 1H, CH_2); 5.30 (m, 1H, CH_2); 5.26 (t, 2H, CH_2-*N*, $^{4}J_{HH}$ = 2.3 Hz); 4.81 (d, 2H, NH-CH_2 , $^{3}J_{HH}$ = 4.9 Hz); 4.41 (s, 2H, N-CH_2-Ph).

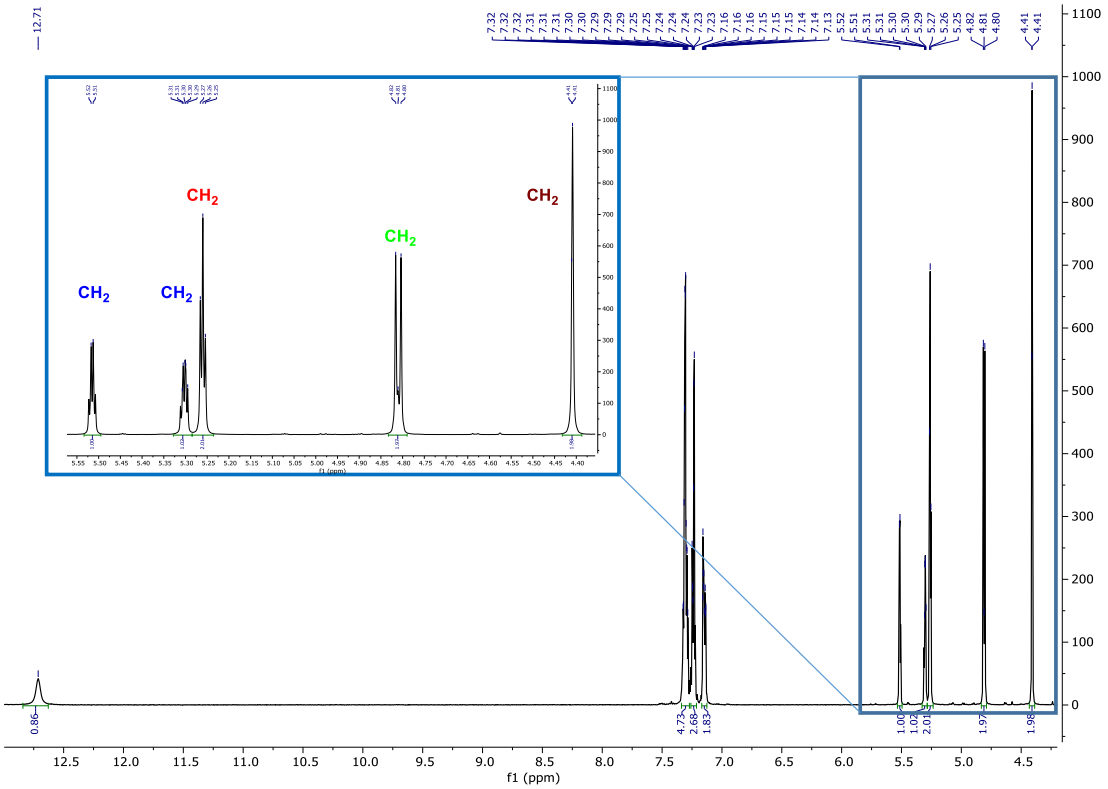


Figure 1.25. ^{1}H NMR spectrum of compound **11** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 180.2 (s, 1C, *C*=*S*); 156.9 (s, 1C, N-*C*=N); 139.5 (s, 1C, C_{ipso}Ph-CH_2-N); 138.2 (s, 1C, C_{ipso}Ph-CH_2-NH); 133.2 (s, 1C, *C*=CH_2); 129.5-127.8 (s, 10C, *Ph*); 107.8 (s, 1C, CH_2); 60.4 (s, 1C, CH_2-*N*); 59.0 (s, 1C, N-CH_2-Ph); 50.2 (s, 1C, NH-CH_2).

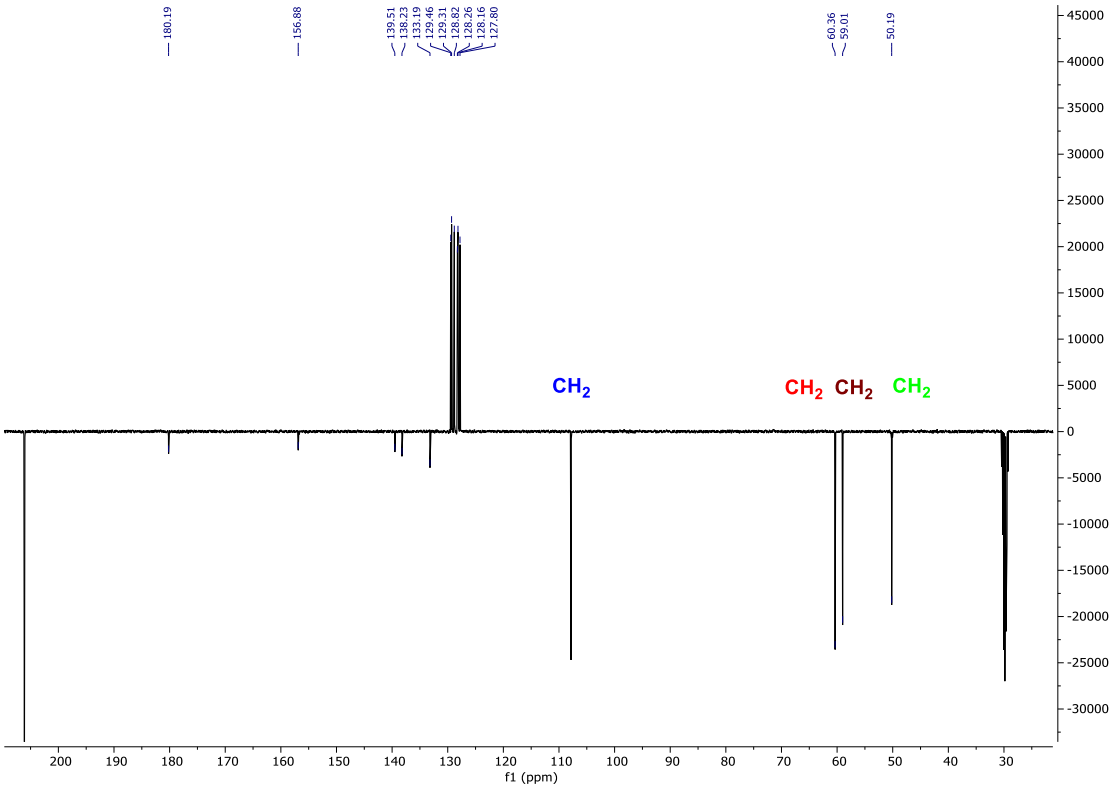
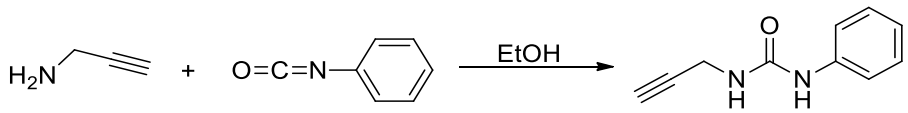


Figure 1.26. ^{13}C APT spectrum of compound **11** in $(CD_3)_2CO$ solution.

Synthesis of compound 12

To a solution of propargylamine (6.4 µl, 0.1 mmol) in ethanol (5 ml), phenyl isocyanate (10.8 µl, 0.1 mmol) was added and the solution stirred for 24h. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 99%



Scheme 1.12. Synthesis of compound **12**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.99 (s, 1H, *NH*-Ph); 7.47 (m, 2H, H_{ortho}Ph); 7.22 (m, 2H, H_{meta}Ph); 6.93 (tt, 1H, H_{para}Ph, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.1 Hz) 6.04 (s br, 1H, *NH*-CH_2); 4.00 (dd, 2H, CH_2, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 2.5 Hz); 2.64 (t, 1H, *CH*, $^4J_{HH}$ = 2.5 Hz).

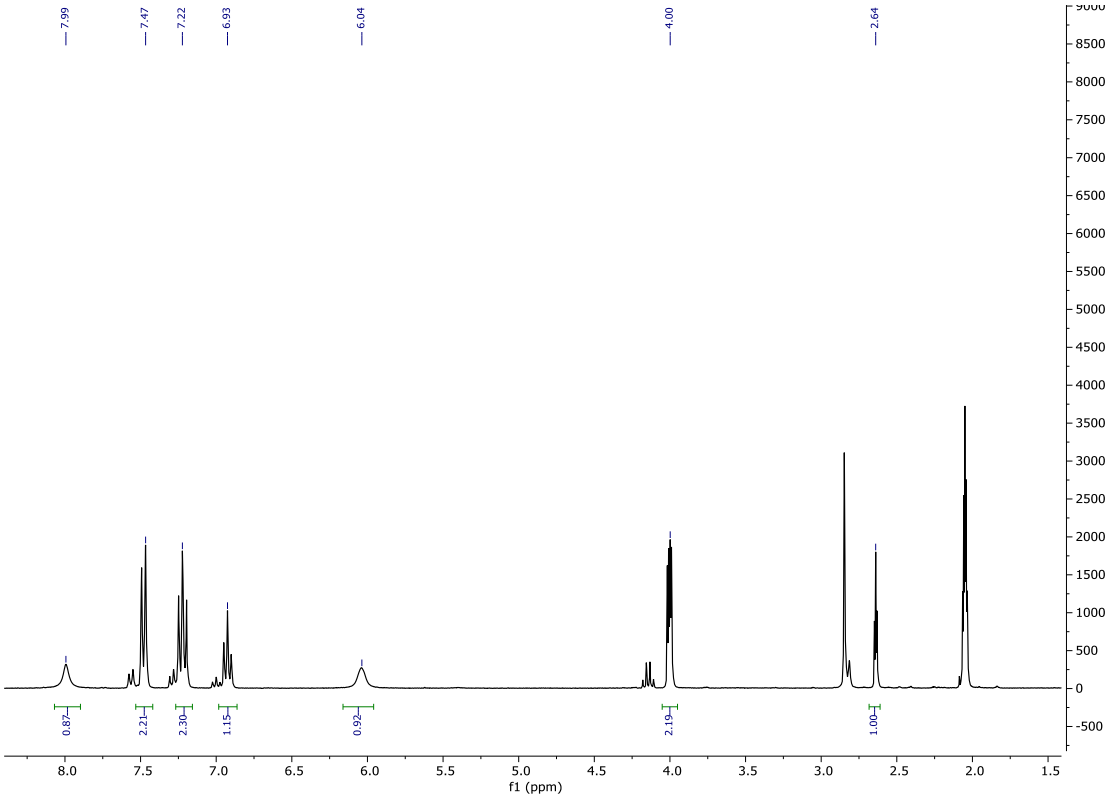


Figure 1.27. ^{1}H NMR spectrum of compound **12** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 155.6 (s, 1C, *CO*); 141.3 (s, 1C, C_{ipso}Ph); 129.5 (s, 2C, C_{ortho}Ph); 122.5 (s, 1C, C_{para}Ph); 119.2 (s, 2C, C_{meta}Ph); 82.3 (s, 1C, $C \equiv$ CH); 71.8 (s, 1C, *CH*); 29.8 (s, 1C, CH_2).

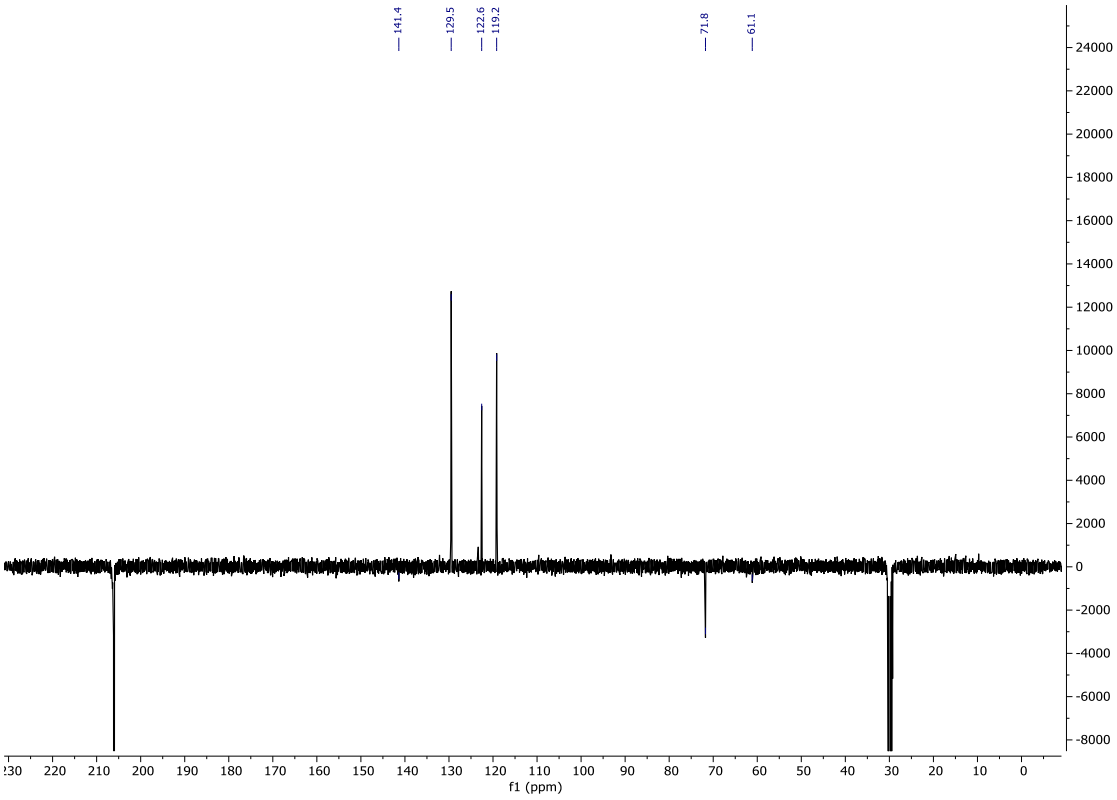
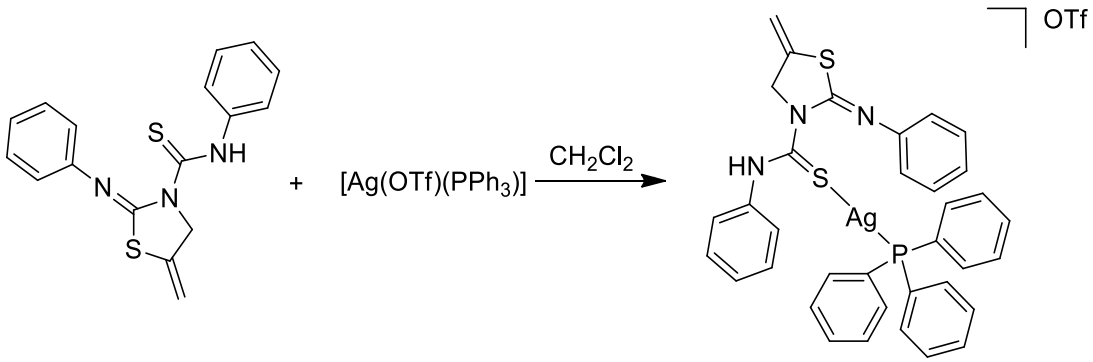


Figure 1.28. ^{13}C APT spectrum of compound **12** in $(CD_3)_2CO$ solution.

Synthesis of compound 13

To a solution of compound **9** (32.5 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added [Ag(OTf)(PPh_3)] (51.9 mg, 0.1 mmol) and the solution stirred for 2 h at room temperature with the exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 64%



Scheme 1.13. Synthesis of compound **13**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.54 (m, 21H, *Ph*); 7.26 (m, 1H, *Ph*); 7.20 (m, 1H, *Ph*); 7.12 (m, 2H, *Ph*); 5.59 (s br, 1H, CH_2); 5.46 (t br, 2H, CH_2-N); 5.35 (s br, 1H, CH_2).

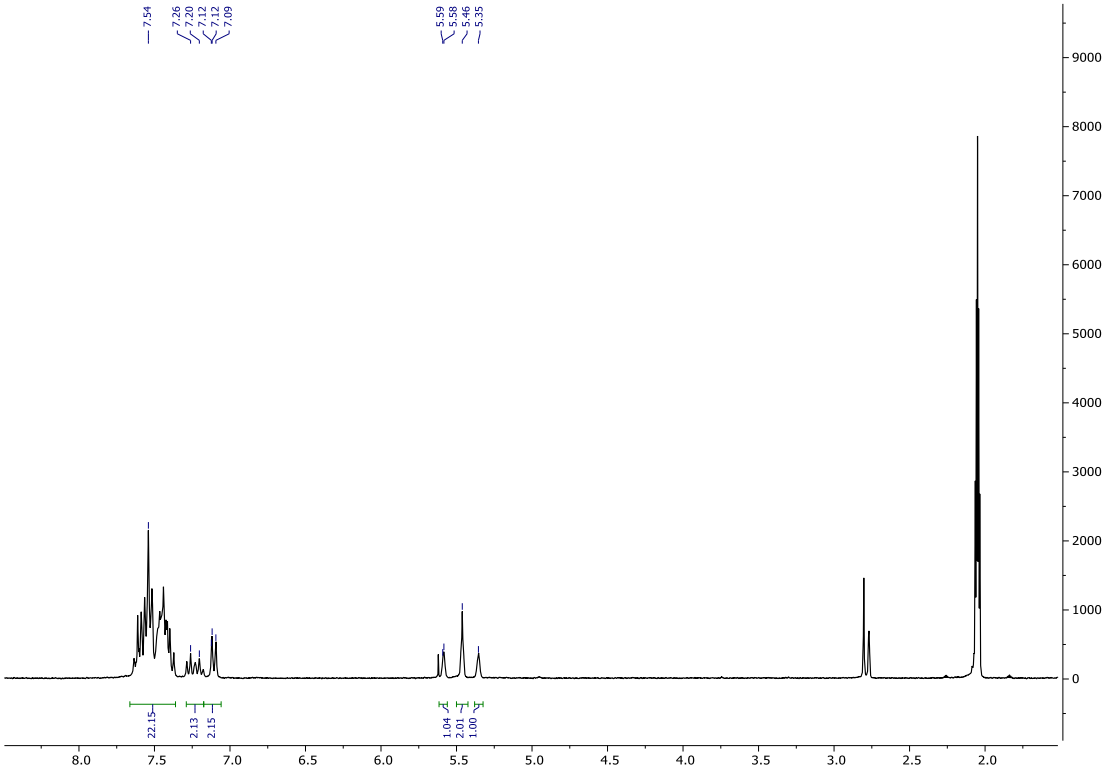


Figure 1.29. ^{1}H NMR spectrum of compound **13** in $(CD_3)_2CO$ solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, $(CD_3)_2CO$): δ = 12.0 (s br, 1P, PPh_3).

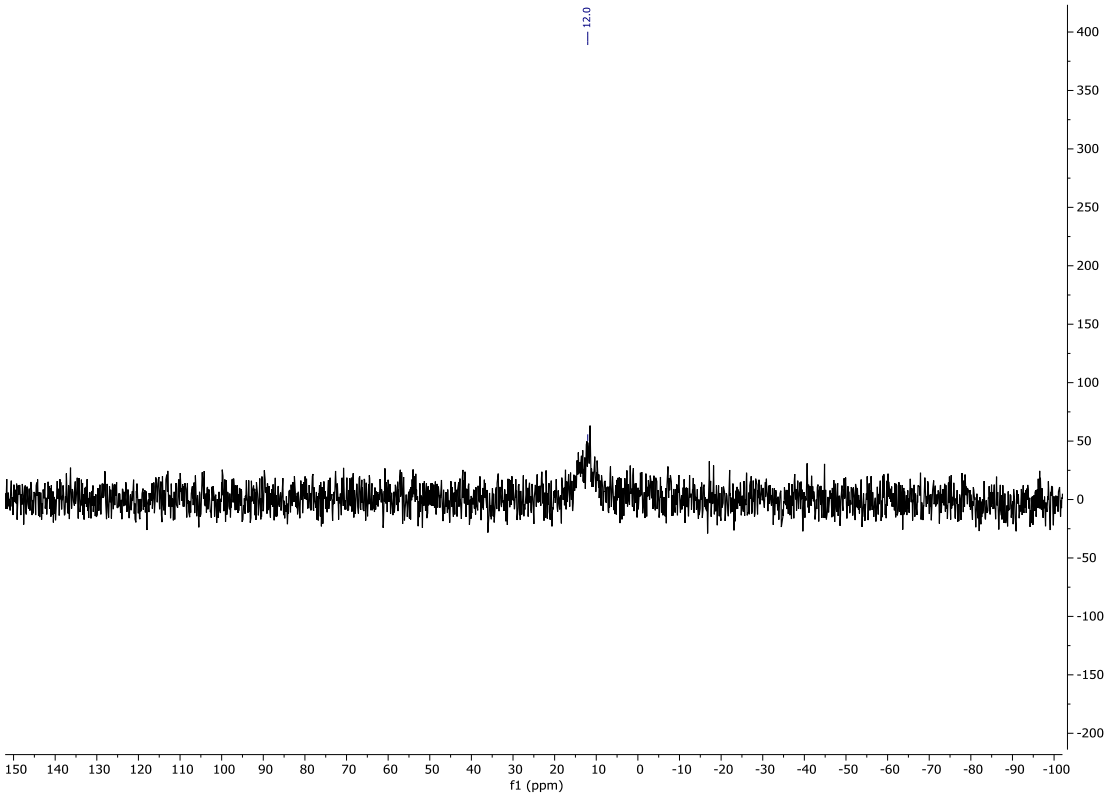


Figure 1.30. $^{31}P\{^{1}H\}$ NMR spectrum of compound **13** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 134.8 (d, 6C, $C_{ortho}PPh_3$, $^{3}J_{H\text{-}P}$= 15.6 Hz); 130.2 (d, 6C, $C_{meta}PPh_3$, $^{3}J_{H\text{-}P}$= 9.6 Hz); 132.2-122.1 (s, 13C, $C_{para}PPh_3$ + *Ph*); 109.0 (s, 1C, CH_2); 60.8 (s, 1C, CH_2-N).

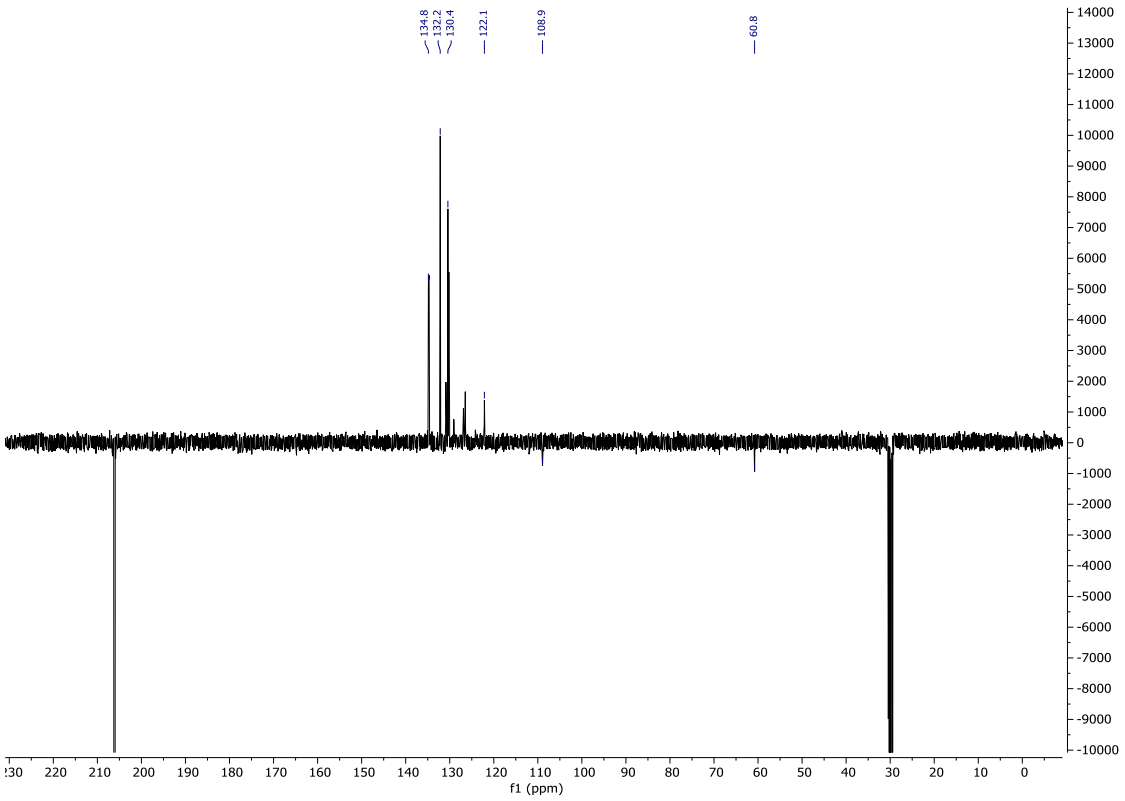


Figure 1.31. ^{13}C APT spectrum of compound **13** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{35}H_{30}AgN_3PS_2]^+$ 694.0664. Found 694.0647.

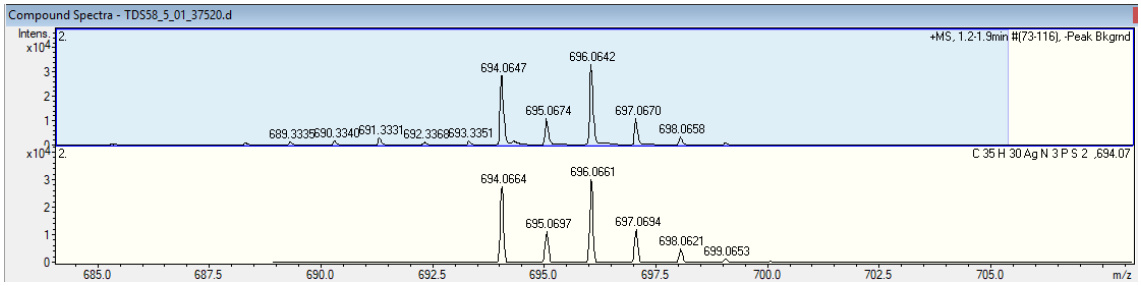
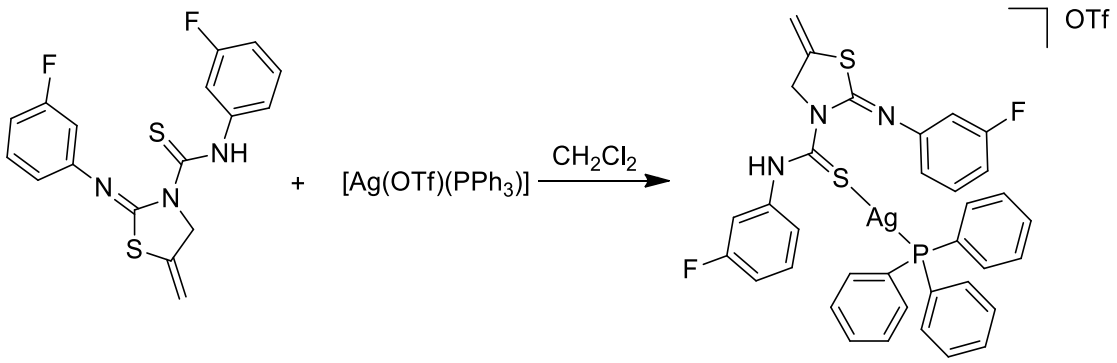


Figure 1.32. MS (ESI+ µ-TOF) compound **12**.

Synthesis of compound 14

To a solution of compound **10** (36.1 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added $[Ag(OTf)(PPh_3)]$ (51.9 mg, 0.1 mmol) and the solution stirred for 2 h at room temperature with the exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 61%



Scheme 1.14. Synthesis of compound **14**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.51-7.34 (m, 20H, *arom.* + *PPh_3*); 7.06-6.95 (m, 3H, *Ph*); 5.57 (s, 1H, *CH_2*); 5.46 (s, 2H, *CH_2*); 5.36 (m, 1H, *CH_2*-N).

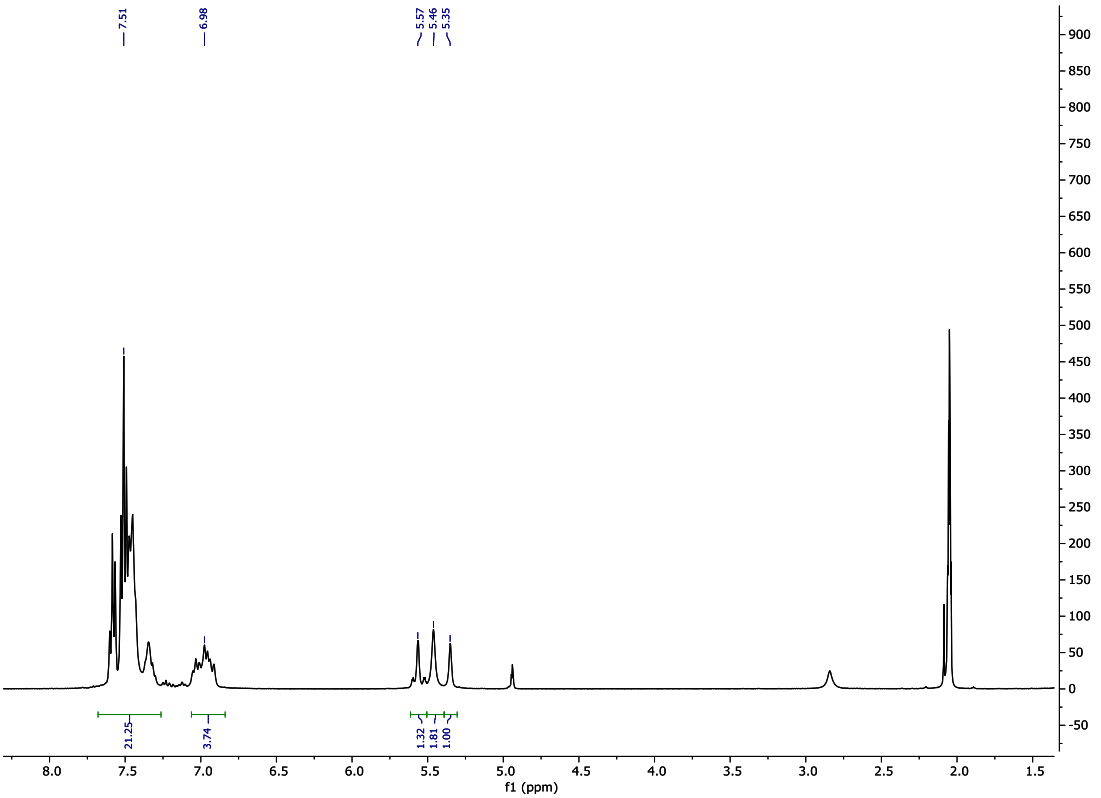


Figure 1.33. ^{1}H NMR spectrum of compound **14** in $(CD_3)_2CO$ solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -79.92 (s, 1F, *OTf*); -113.81(m, 1F, *Ph*); -114.25 (m, 1F, *Ph*).

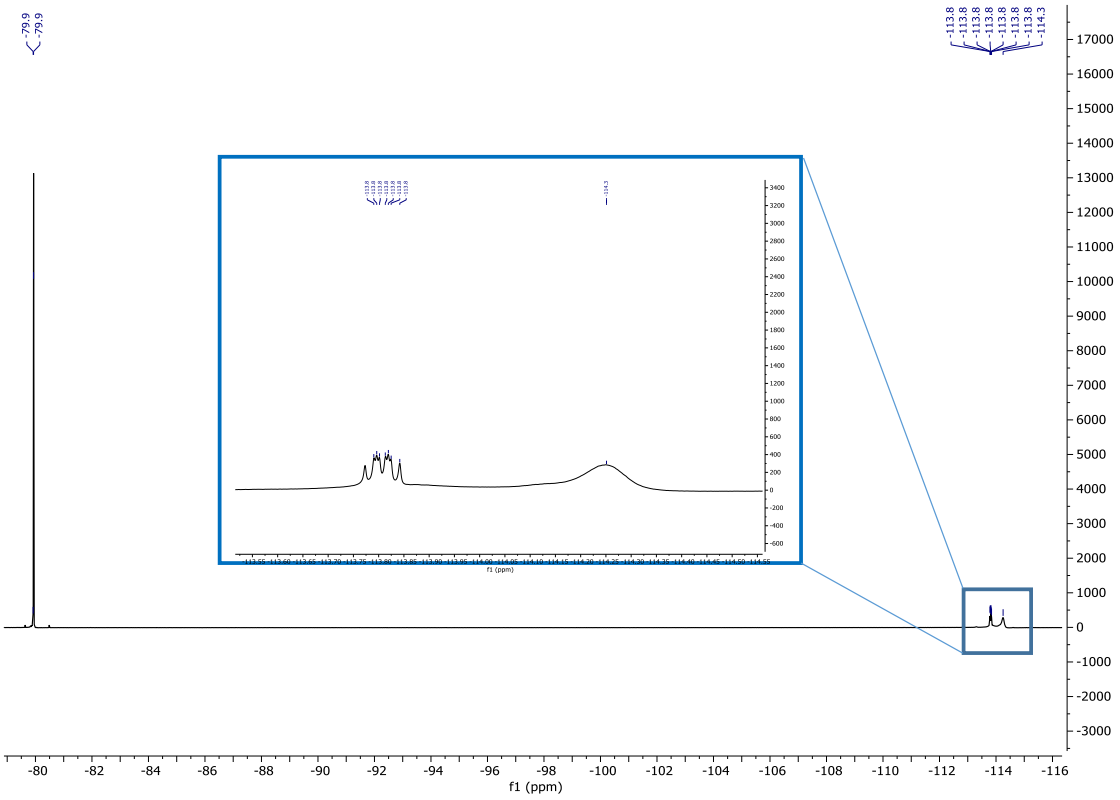


Figure 1.34. $^{19}F\{^{1}H\}$ NMR spectrum of compound **14** in $(CD_3)_2CO$ solution.

^{31}P {^{1}H} NMR (ppm) (162 MHz, $(CD_3)_2CO$): δ = 12.20 (s, 1P, *PPh_3*).

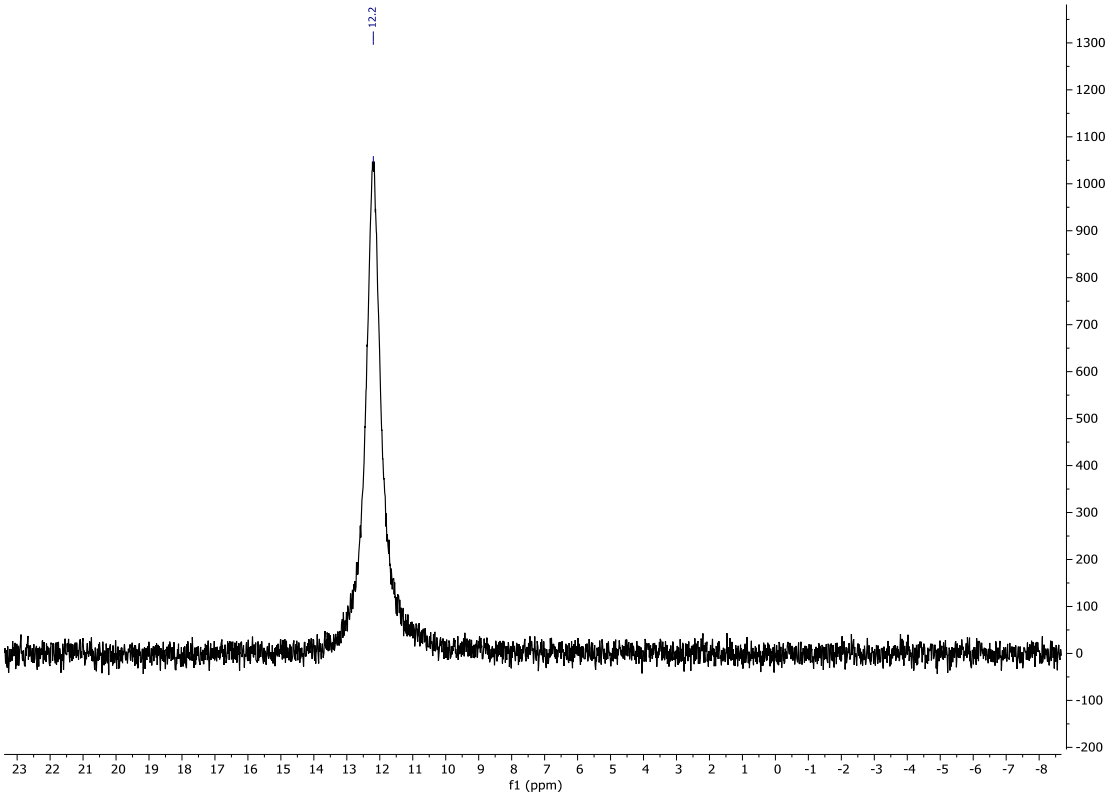


Figure 1.35. $^{31}P\{^{1}H\}$ NMR spectrum of compound **14** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 165.2 (s, 1C, *C*=*S*); 162.7 (s, 1C, $C_{quaternary}$); 134.7 (d, 6C, $C_{ortho}PPh_3$, $^2J_{CP}$ = 15.3Hz); 132.1 (s, 3C, $C_{para}PPh_3$); 131.4 (d, 3C, $C_{ipso}PPh_3$, $^1J_{CP}$ = 35.1Hz); 130.2 (d, 6C, $C_{meta}PPh_3$, $^3J_{CP}$= 8.6 Hz); 118.3-109.6 (m, 10C, *Ph-F*); 109.5 (s, 2C, CH_2); 61.0 (s, 1C, CH_2-N).

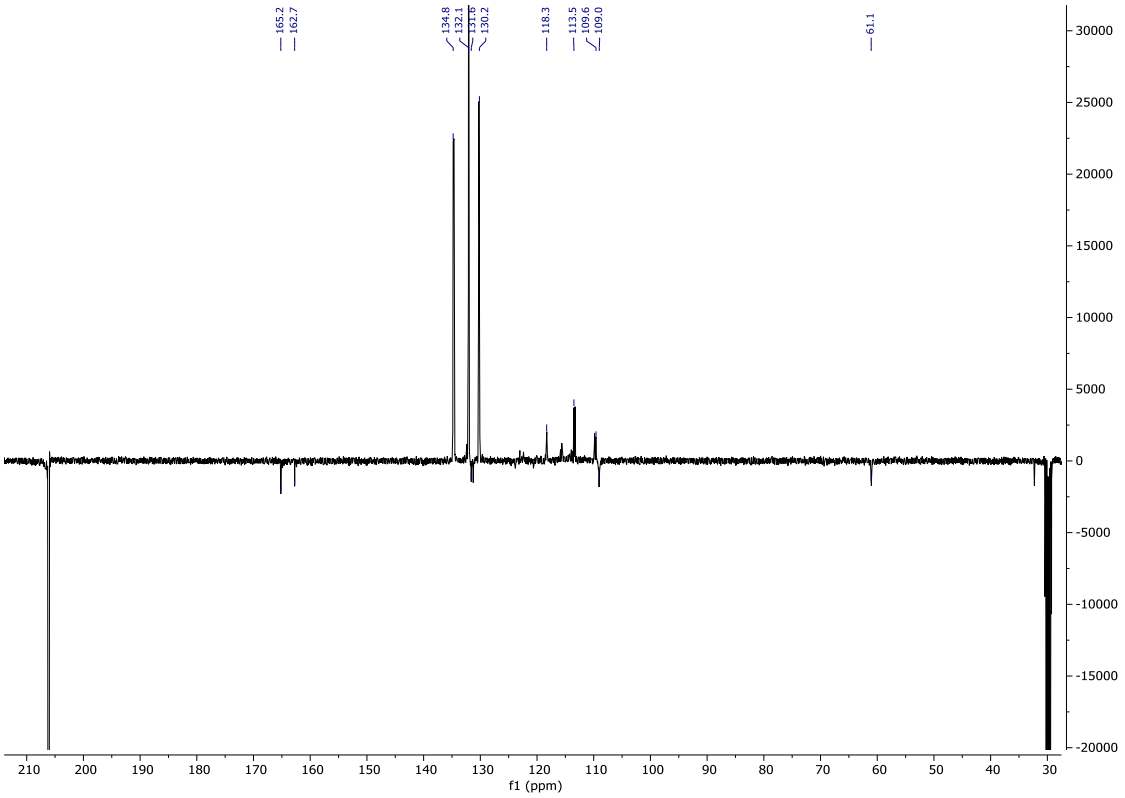
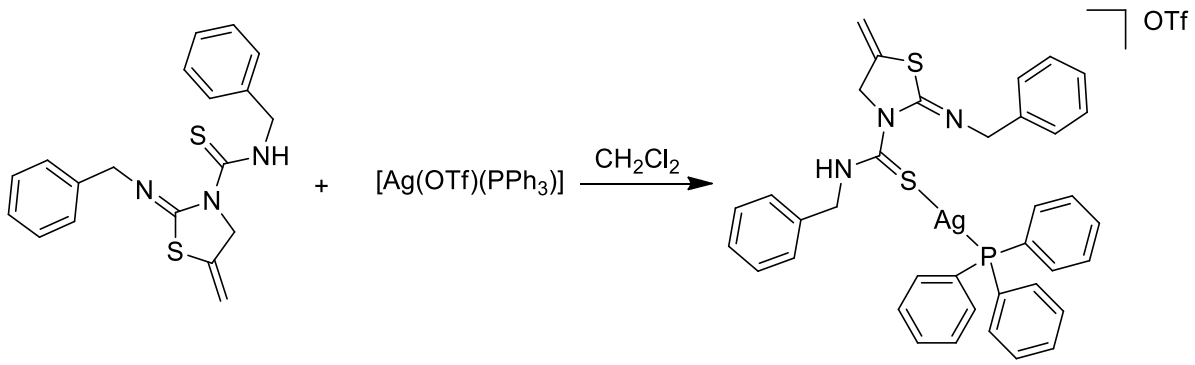


Figure 1.36. ^{13}C APT spectrum of compound **14** in $(CD_3)_2CO$ solution.

Synthesis of compound 15

To a solution of compound **11** (35.3 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added [Ag(OTf)(PPh_3) (51.9 mg, 0.1 mmol) and the solution stirred for 2 h at room temperature with the exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 60%



Scheme 1.15. Synthesis of compound **15**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.55-7.26 (m, 25H, *Ph*); 5.46 (m, 1H, CH_2); 5.38 (t, 2H, CH_2-N); 5.34 (m, 1H, CH_2); 4.95 (d, 2H, NH-CH_2, J_{HH} = 4.8 Hz); 4.44 (s, 2H, N-CH_2).

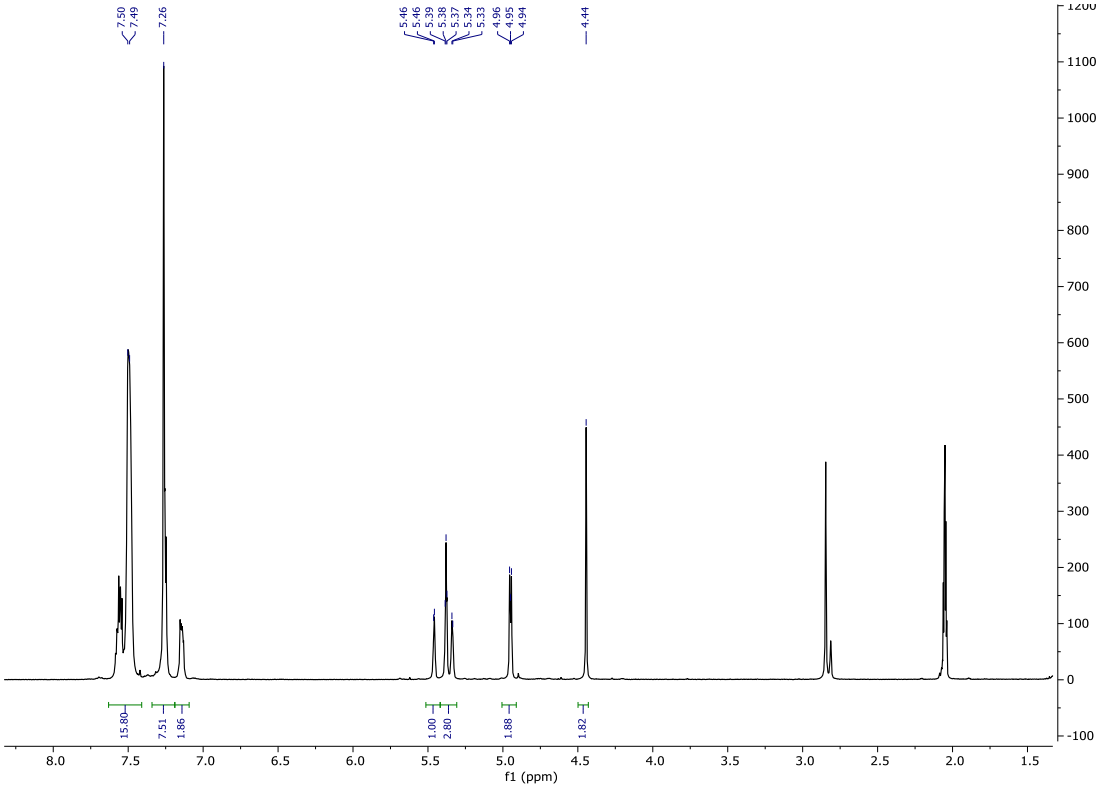


Figure 1.37. ^{1}H NMR spectrum of compound **15** in $(CD_3)_2CO$ solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, $(CD_3)_2CO$): δ = 11.5 (s, 1P, PPh_3).

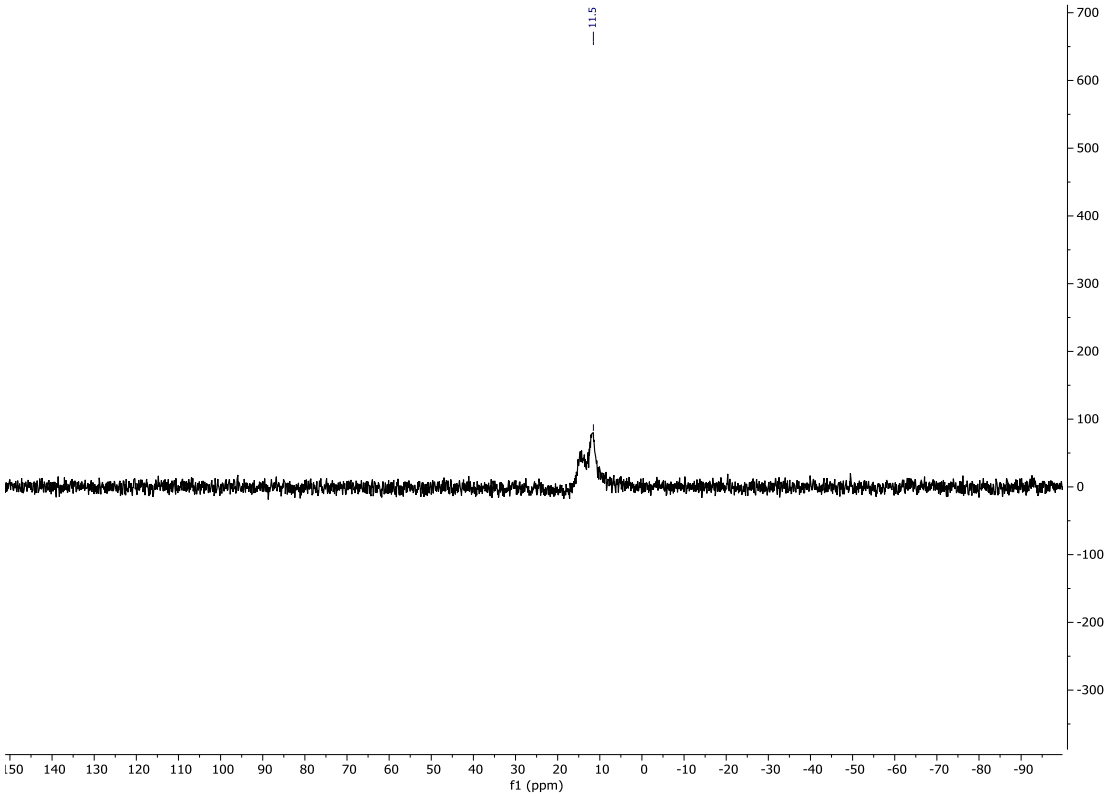


Figure 1.38. $^{31}P\{^{1}H\}$ NMR spectrum of compound **15** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 177.9 (s, 1C, *C*=*S*); 158.2 (s, 1C, N-*C*=N); 138.8 (s, 1C, C_{ipso}Ph-CH_2-N); 136.5 (s, 1C, C_{ipso}Ph-CH_2-NH); 133.2 (s, 1C, *C*=CH_2); 134.7 (d, 6C, $C_{ortho}PPh_3$, $^{2}J_{HP}$= 15.3 Hz); 132.1 (s, 3C, $C_{para}PPh_3$); 131.6 (d, 3C, $C_{ipso}PPh_3$, $^{1}J_{HP}$= 31.5 Hz); 130.2 (d, 6C, $C_{meta}PPh_3$, $^{3}J_{HP}$= 8.4 Hz);129.8-128.1 (m, 10C, *Ph*); 108.9 (s, 1C, CH_2); 60.6 (s, 1C, CH_2-N); 59.2 (s, 1C, Ph-CH_2-N=C); 51.3 (s, 1C, Ph-CH_2-NH).

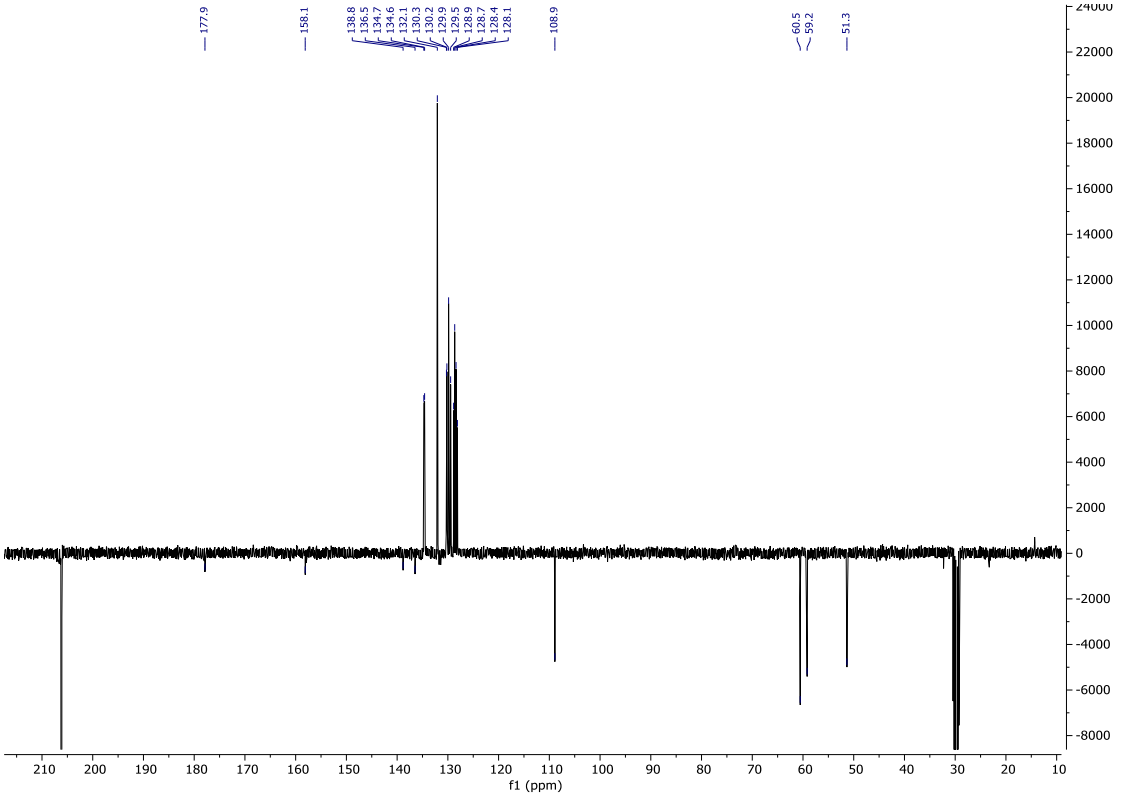


Figure 1.39. ^{13}C APT spectrum of compound **15** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{37}H_{34}AgN_3PS_2]^+$ 724.0975. Found 724.0977.

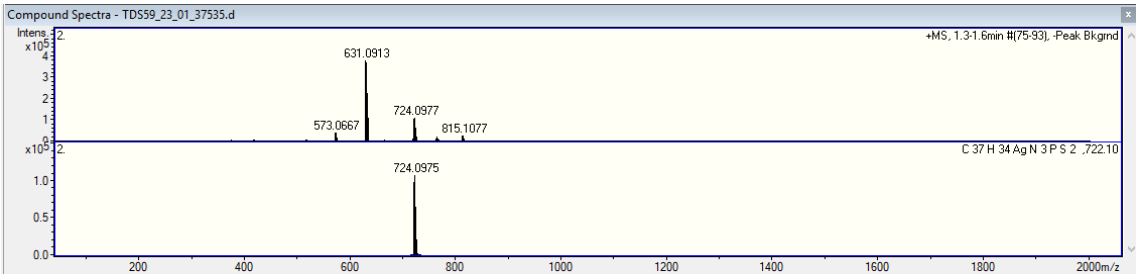
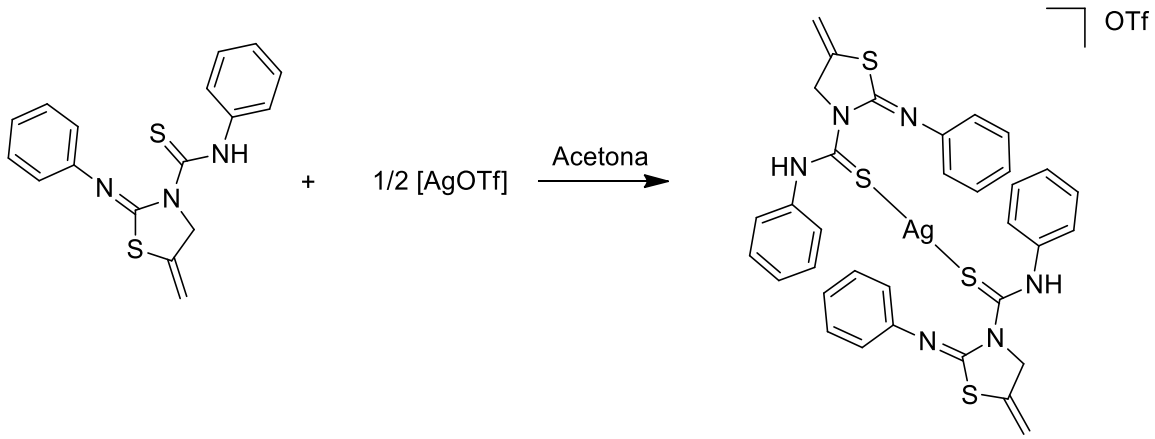


Figure 1.40. MS (ESI+ µ-TOF) compound **12**.

Synthesis of compound 16

To a solution of compound **9** (65.0 mg, 0.2 mmol) in CH_2Cl_2 (10 ml) was added AgOTf (25.7 mg, 0.1 mmol) and the solution stirred for 1 h at room temperature with the exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 87%



Scheme 1.16. Synthesis of compound **16**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.61 (m, 4H, *Ph*); 7.41 (m, 10H, *Ph*); 7.26 (t br, 2H, *Ph*); 7.11 (d br, 4H, *Ph*); 5.64 (s br, 2H, CH_2); 5.42 (s br, 4H, CH_2-N); 5.39 (s br, 2H, CH_2).

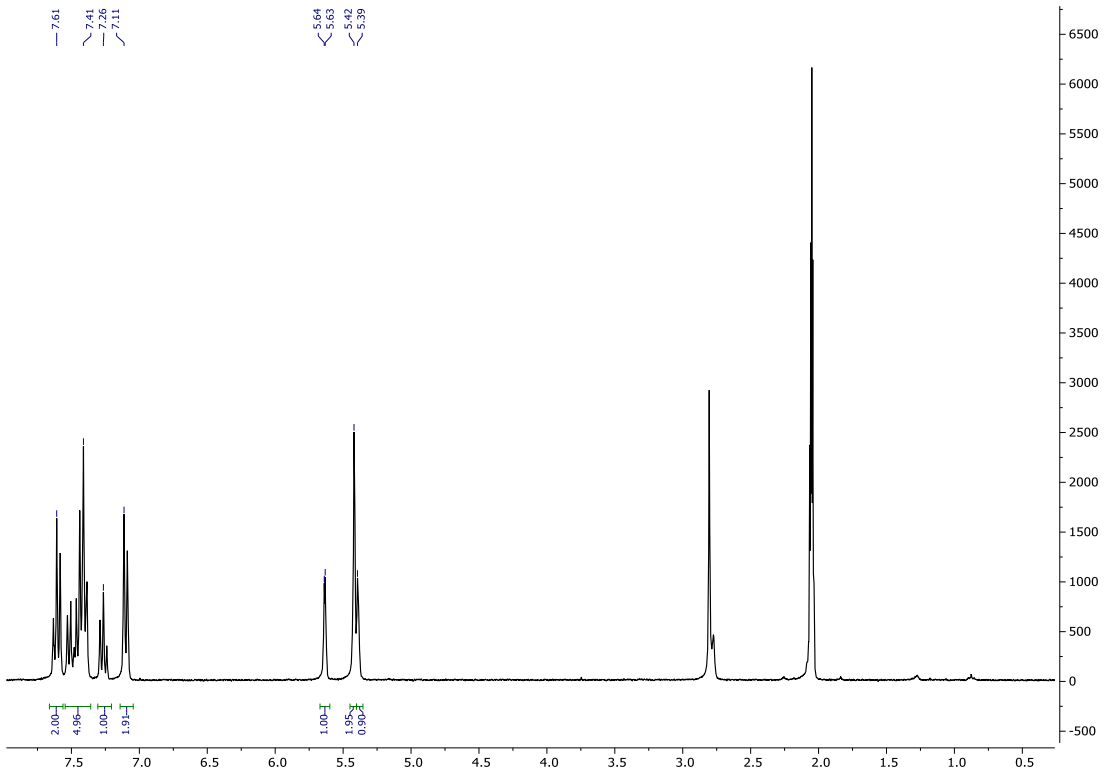


Figure 1.41. ^{1}H NMR spectrum of compound **16** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 178.8 (s, 2C, *C*=*S*); 160.1 (s, 2C, $C_{quaternary}$); 148.1 (s, 2C, C_{ipso}); 137.5 (s, 2C, C_{ipso}); 132.0 (s, 2C, $C_{quaternary}$); 131.1-122.1 (s, 20C, *Ph*); 109.1 (s, 2C, CH_2); 60.7 (s, 2C, CH_2-N).

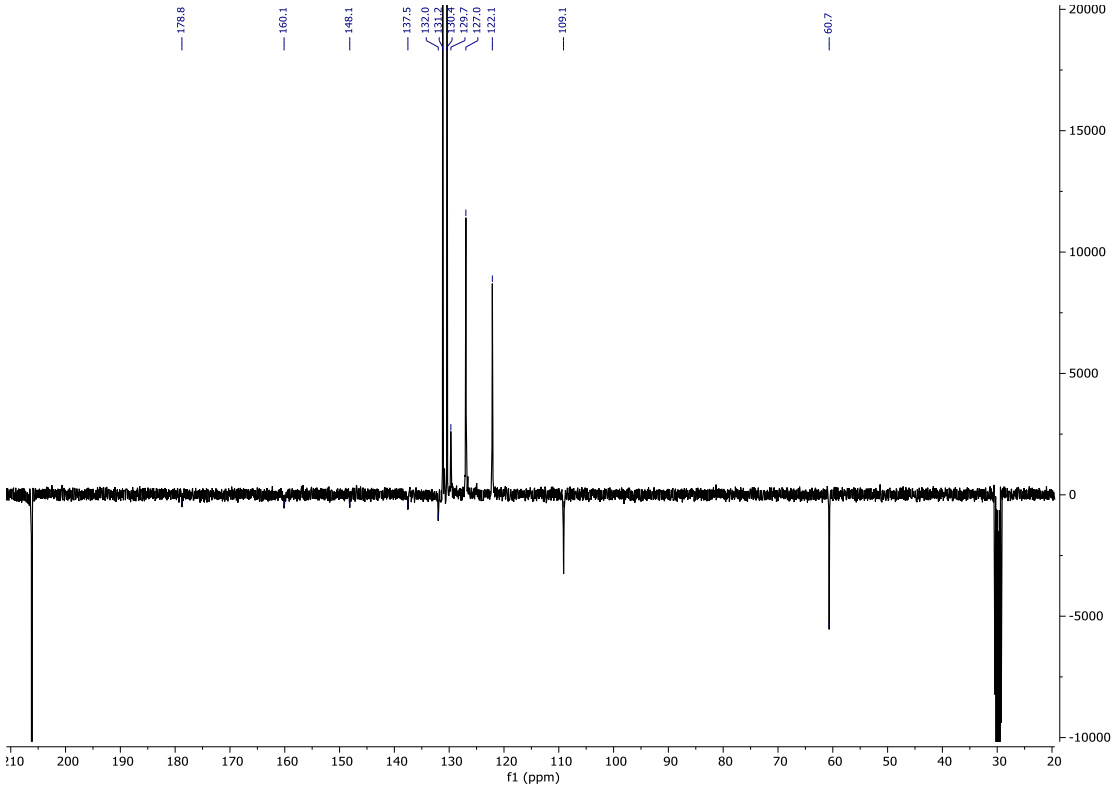
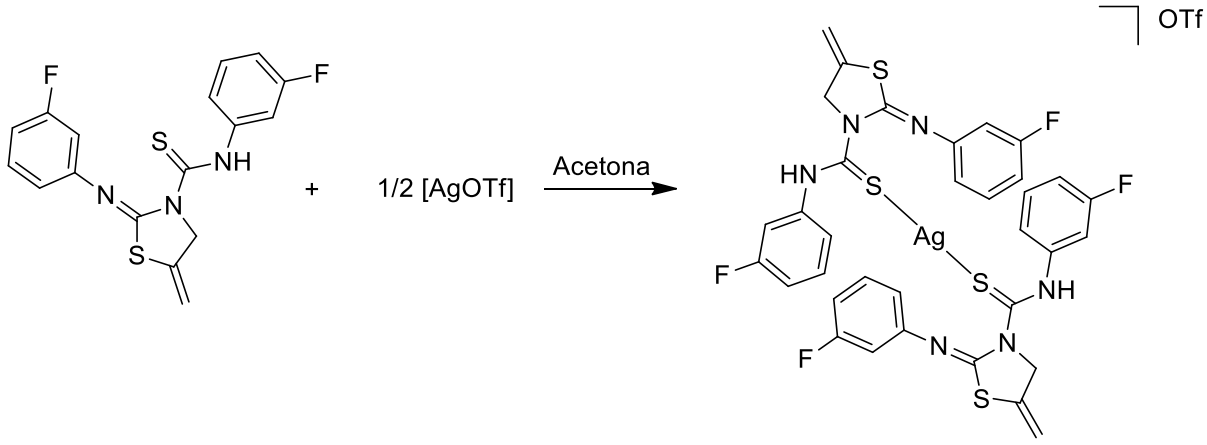


Figure 1.42. ^{13}C APT spectrum of compound **16** in $(CD_3)_2CO$ solution.

Synthesis of compound 17

To a solution of compound **10** (72.0 mg, 0.2 mmol) in CH_2Cl_2 (10 ml), AgOTf was added (25.7 mg, 0.1 mmol) and the solution stirred for 1 h at room temperature with the exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield; 90%



Scheme 1.17. Synthesis of compound **17**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.61-6.92 (m, 16H, *arom.*), 5.64 (s br, 2H, CH_2); 5.44 (s br, 4H, CH_2-N); 5.42 (s br, 2H, CH_2).

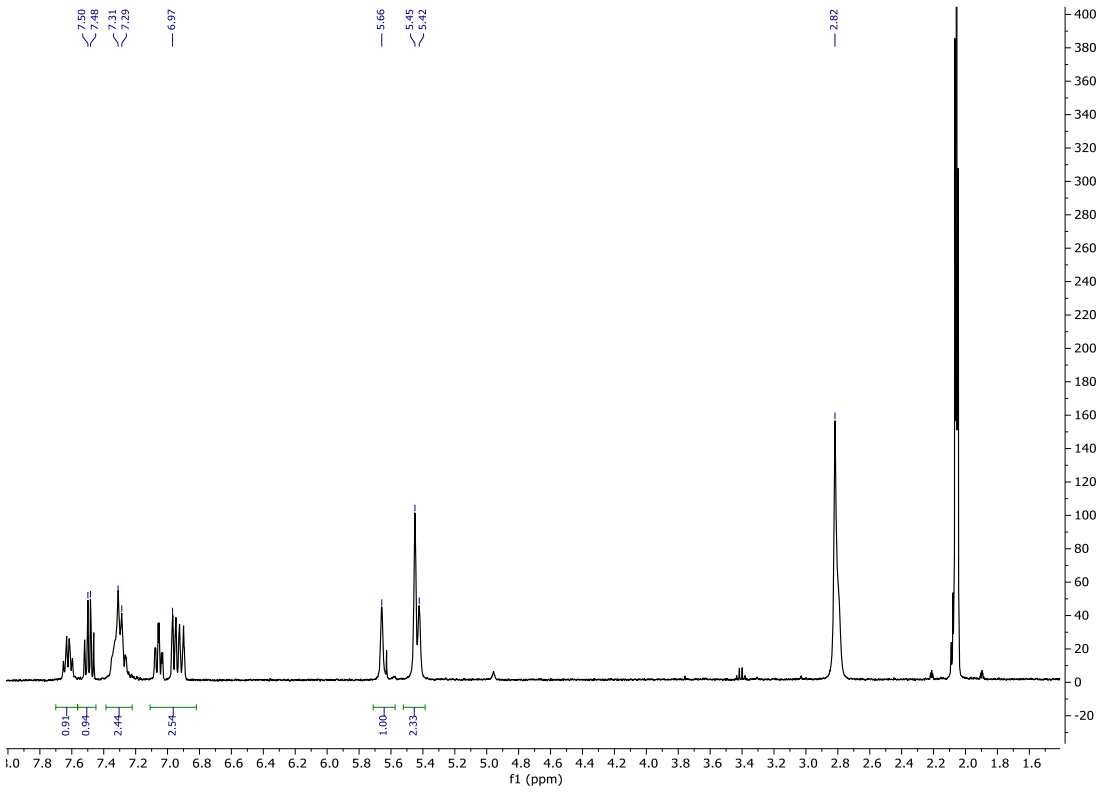


Figure 1.43. ^{1}H NMR spectrum of compound **17** in $(CD_3)_2CO$ solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -79.9 (s, 1F, OTf); -112.24 (m, 2F, *Ph*); -114.15 (m, 2F, *Ph*).

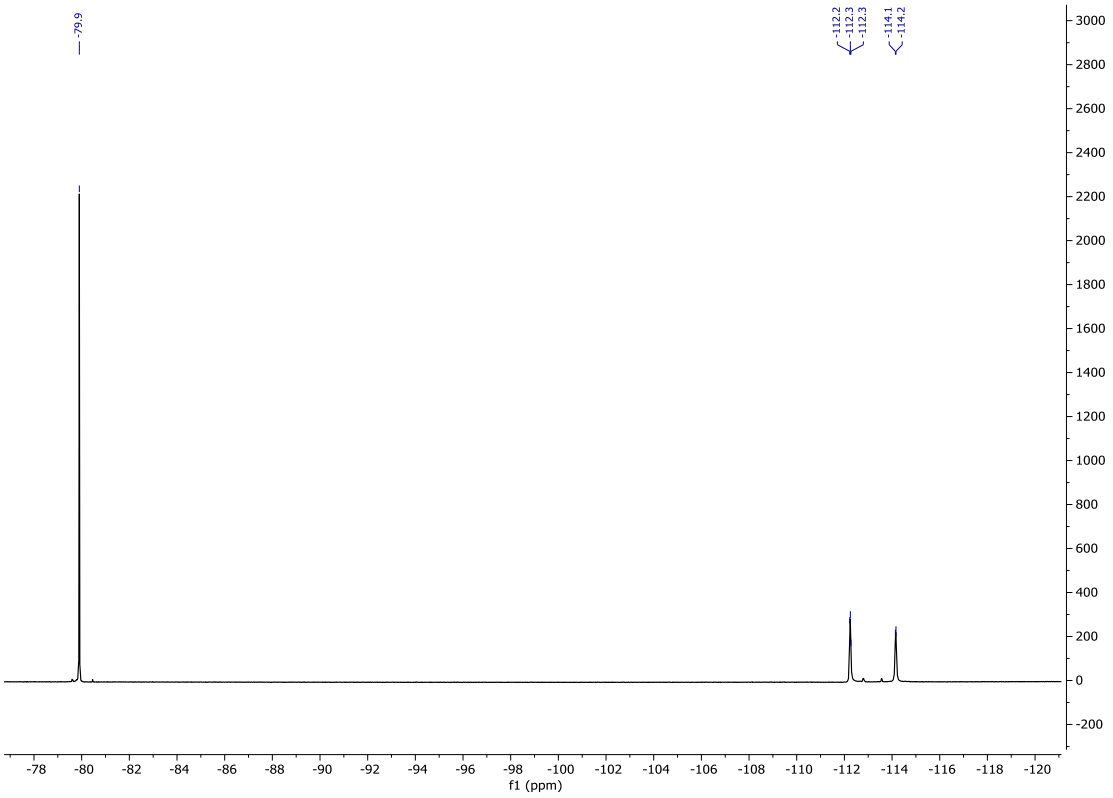


Figure 1.44. ^{19}F NMR spectrum of compound **17** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 168.1 (s, 2C, *C*=*S*); 132.5 (d, 4C, *II*, $^3J_{HF}$ = 9.2Hz); 132.2 (d, 4C, *II*, $^3J_{HF}$ = 9.3Hz); 123.1 (s, 2C, *I*); 118.2 (s, 2C, *I*); 116.4 (d, 2C, *III*, $^2J_{HF}$ = 21.9Hz); 114.6 (d, 2C, *IV*, $^2J_{HF}$ = 24.8Hz); 113.6 (d, 2C, *III*, $^2J_{HF}$ = 22.1Hz); 109.7(d, 2C, *IV*, $^2J_{HF}$ = 23.9Hz); 109.5 (s, 2C, CH_2); 60.8 (s, 2C, CH_2-N).

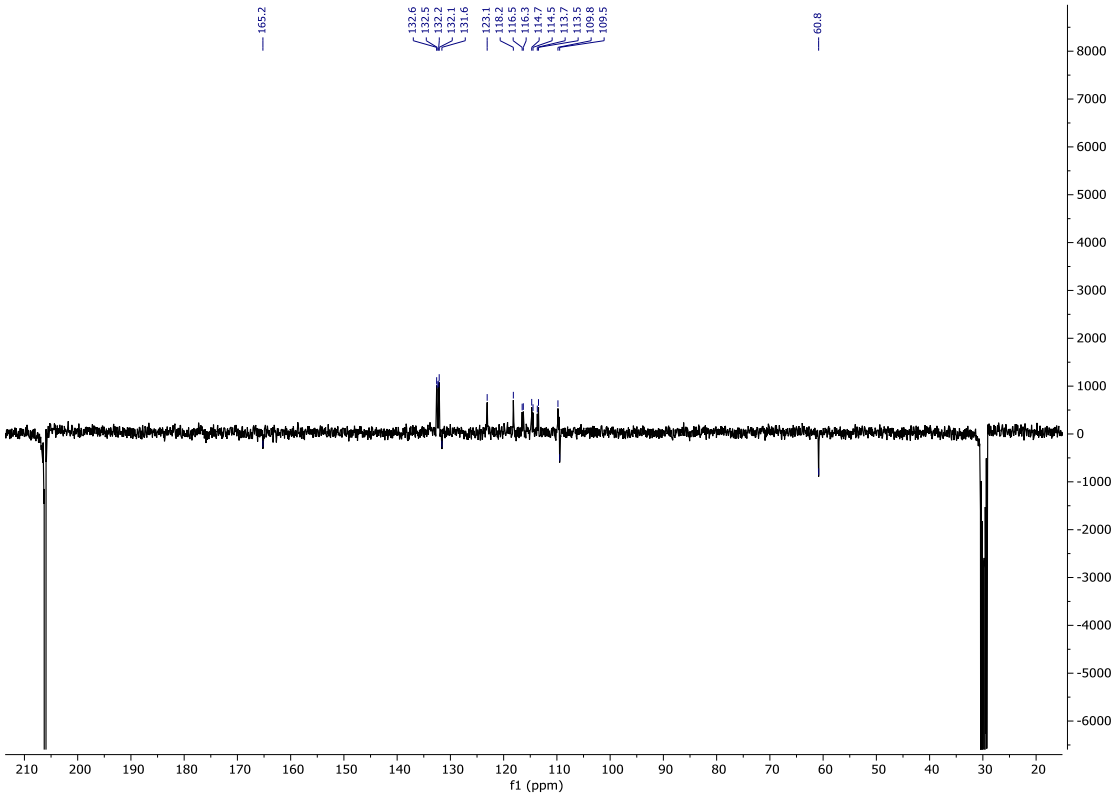


Figure 1.45. ^{13}C APT spectrum of compound **17** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{34}H_{26}AgF_4N_6S_4]^+$ 831.0079. Found 831.0056.

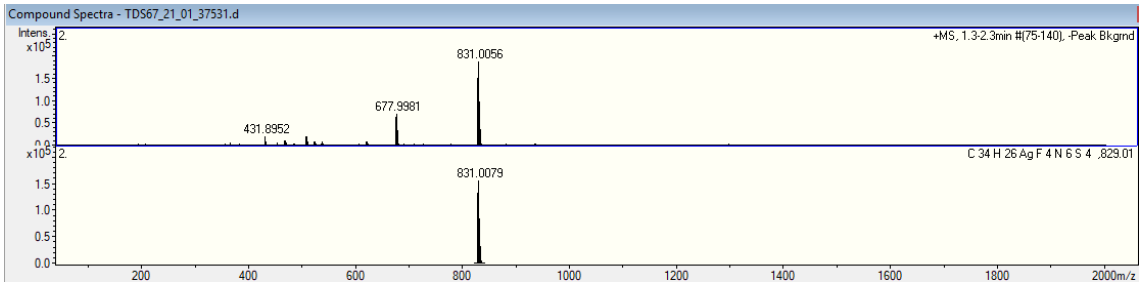
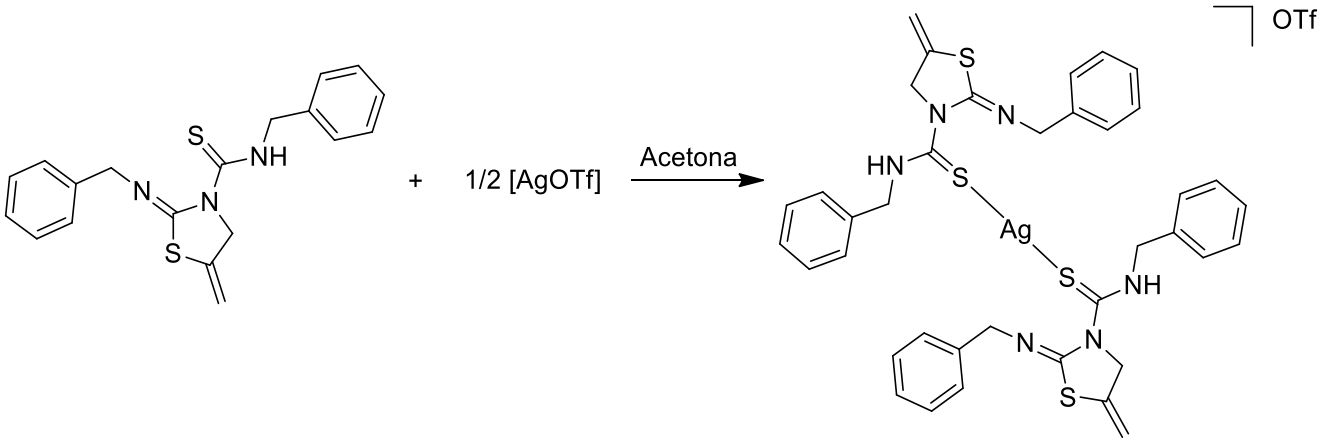


Figure 1.46. MS (ESI+ µ-TOF) compound **17**.

Synthesis of compound 18

To a solution of compound **11** (72.0 mg, 0.2 mmol) in CH_2Cl_2 (10 ml) was added AgOTf (25.7 mg, 0.1 mmol) and the solution stirred for 1 h at room temperature with the exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 88%



Scheme 1.18. Synthesis of compound **18**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.33 (m, 10H, *Ph*); 7.24 (m, 6H, *Ph*); 7.13 (m,4H, *Ph*); 5.52 (m, 2H, CH_2); 5.39 (m, 4H, CH_2-N); 5.35 (m, 2H, CH_2); 4.98 (m, 4H, NH-CH_2); 4.43 (s, 4H, N-CH_2).

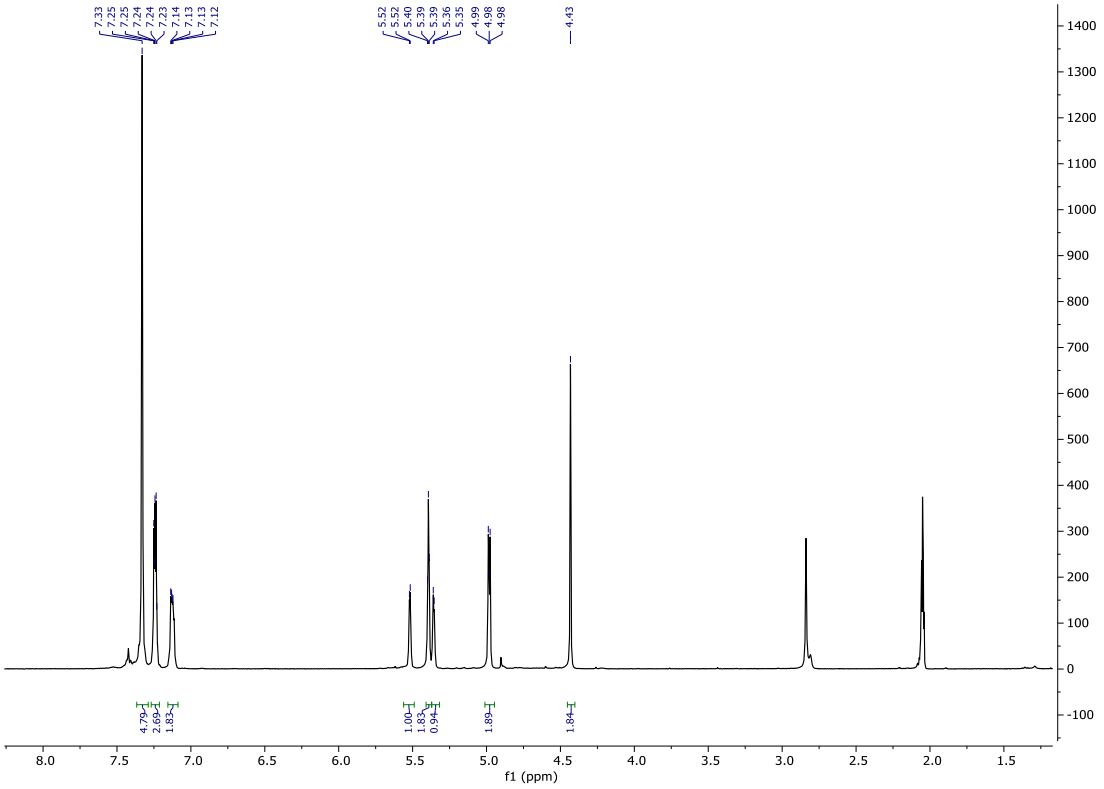


Figure 1.47. ^{1}H NMR spectrum of compound **18** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 176.5 (s, 2C, *C*=*S*); 156.5 (s, 2C, *N*-*C*=*N*); 138.7 (s, 2C, C_{ipso}Ph-CH_2-N); 136.0 (s, 2C, C_{ipso}Ph-CH_2-NH); 132.0 (s, 2C, CH_2=*C*); 130.0-128.1 (s, 20C, *Ph*); 109.0 (s, 2C, CH_2); 60.5 (s, 2C, CH_2-N); 59.2 (s, 1C, Ph-CH_2-N=C); 51.5 (s, 1C, Ph-CH_2-NH).

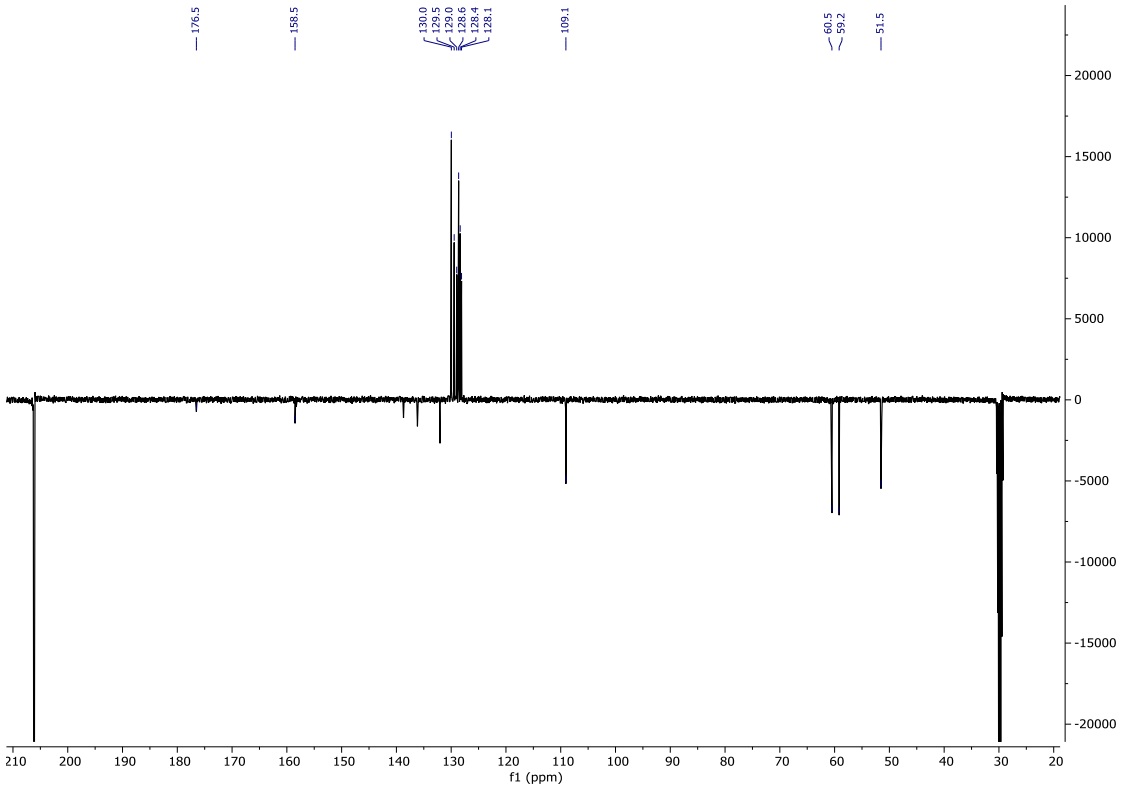


Figure 1.48. ^{13}C APT spectrum of compound **18** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= [$M]^+$ Calcd for $[C_{38}H_{38}AgN_6S_4]^+$ 815.1083. Found 815.1099.

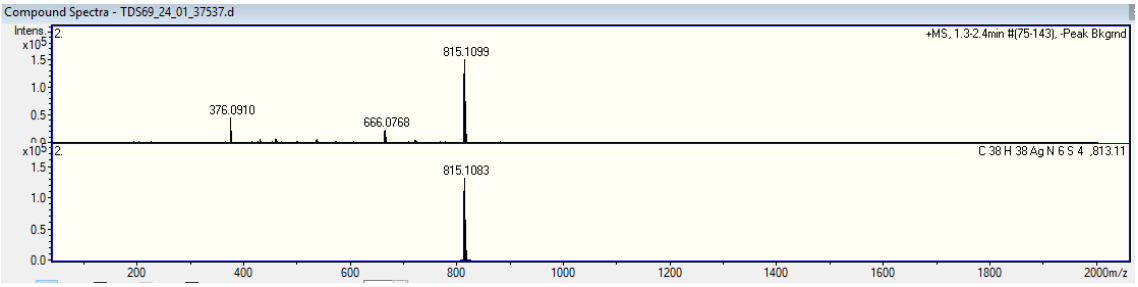
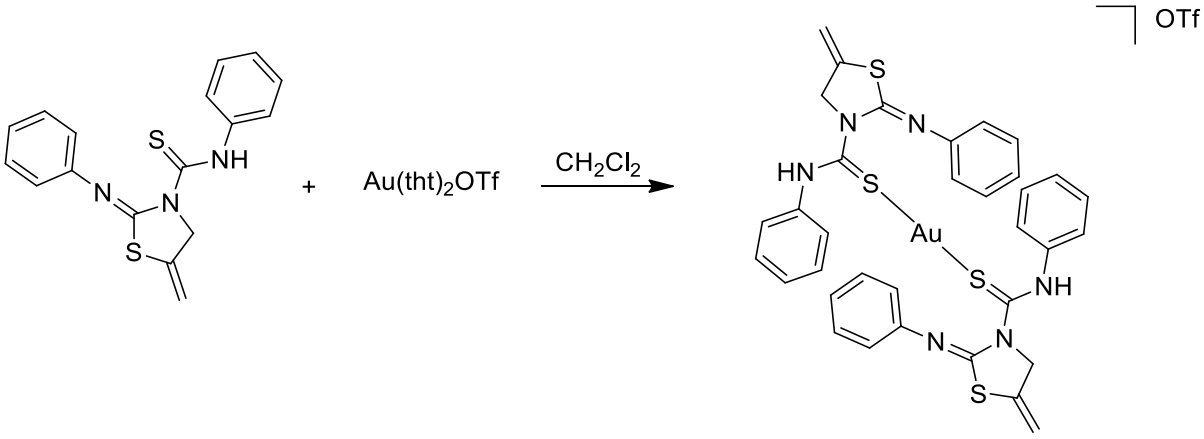


Figure 1.49. MS (ESI+ µ-TOF) compound **18**.

Synthesis of compound 22

To a solution of $Au(tht)_2OTf$ (52.2 mg, 0.1 mmol) which has been prepared *in situ* in CH_2Cl_2 (10 ml) was added compound **9** (65.0 mg, 0.2 mmol) and the solution stirred for 3 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 50%



Scheme 1.22. Synthesis of compound **22**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.59-7.11(m, 20H, *Ph*); 5.67 (s br, 2H, *CH_2*); 5.43 (s br, 6H, *CH_2*-N + *CH_2*).

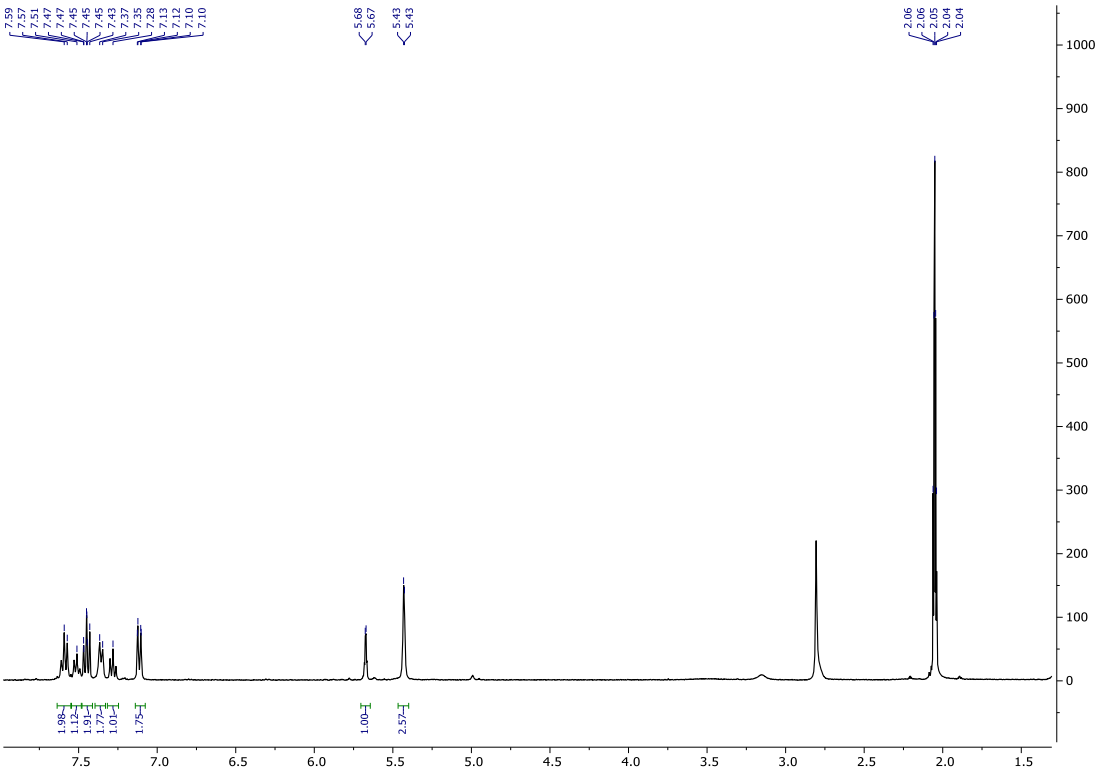


Figure 1.50. ^{1}H NMR spectrum of compound **22** in $(CD_3)_2CO$ solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -80.1 (s, 3F, *OTf*).

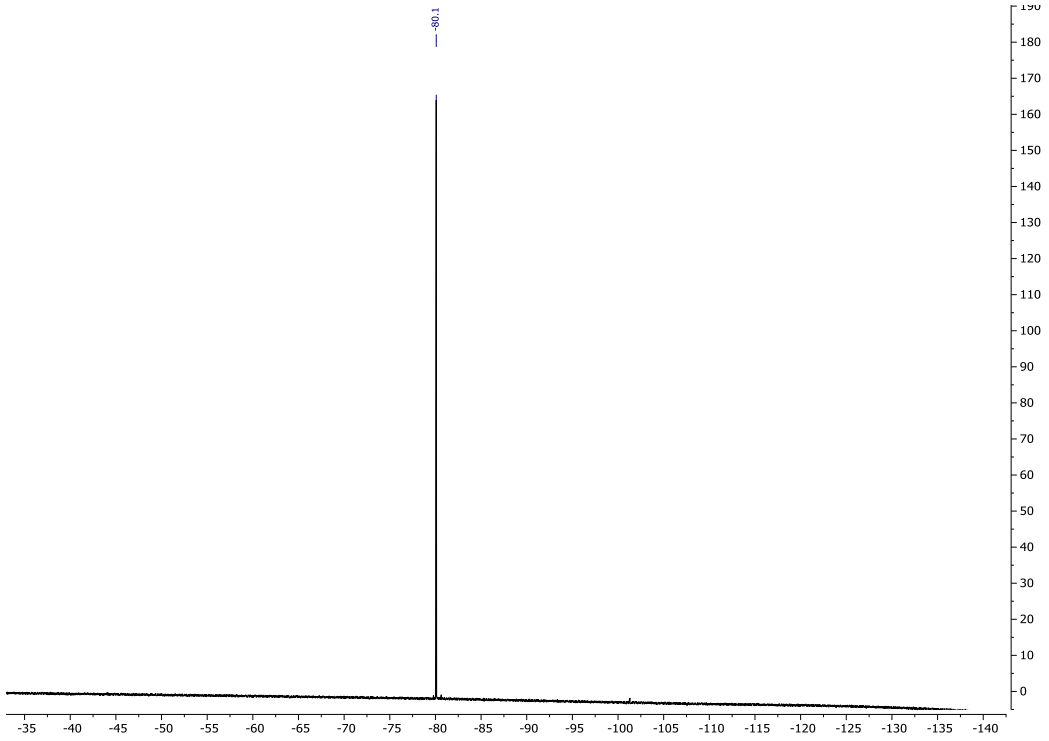


Figure 1.51. $^{19}F\{^{1}H\}$ NMR spectrum of compound **22** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (400 MHz, $(CD_3)_2CO$): 138.8-131.8 (s, 4C, *$C_{quaternary}$*); 130.6-122.1 (s, 20C, *Ph*); 109.5 (s, 2C, *CH_2*); 60.2 (s, 2C, *CH_2*-N).

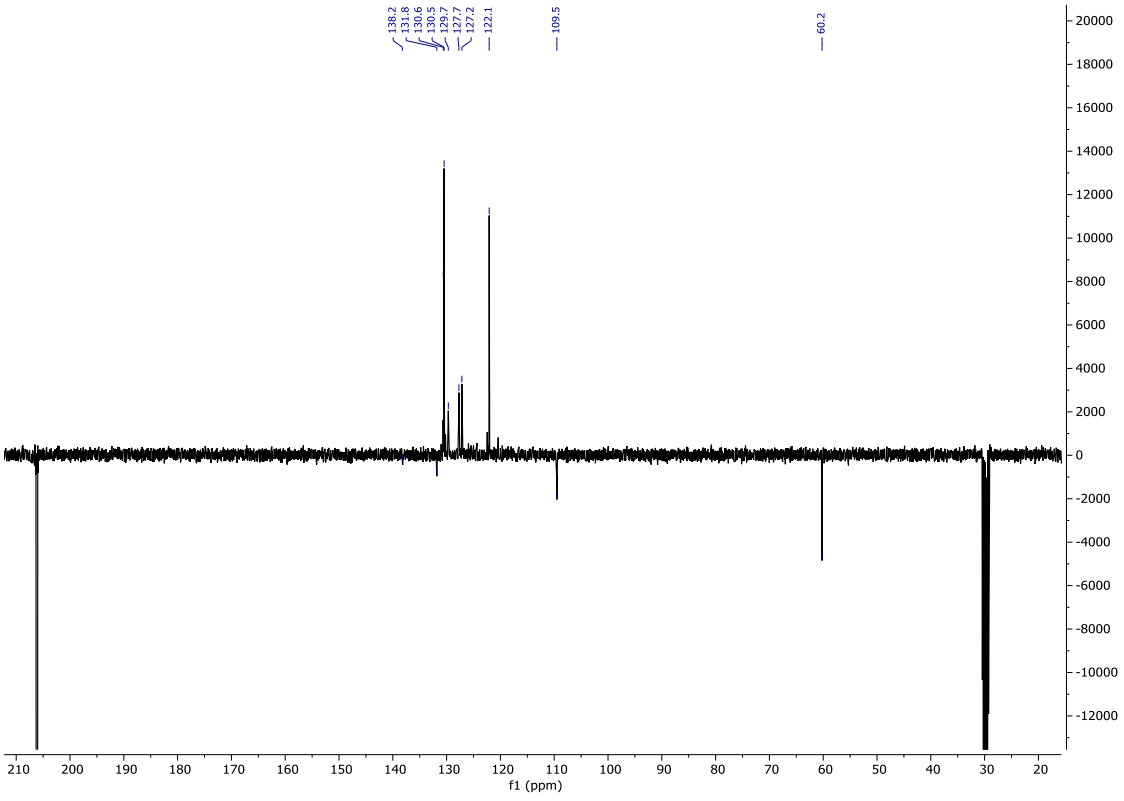
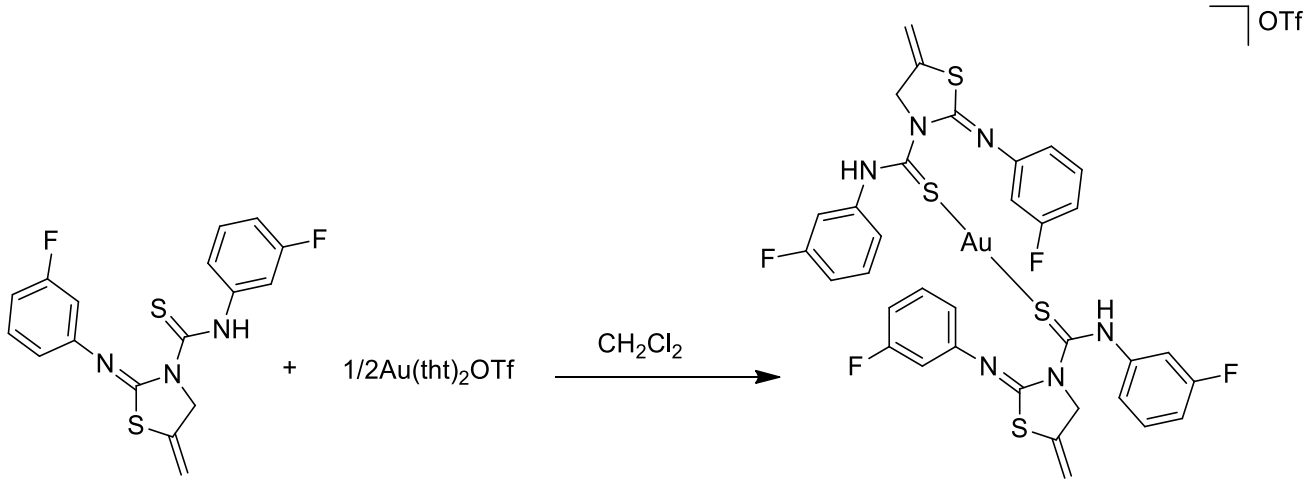


Figure 1.52. ^{13}C APT spectrum of compound **22** in $(CD_3)_2CO$ solution..

Synthesis of compound 23

To a solution of $Au(tht)_2OTf$ (52.2 mg, 0.1 mmol) which has been prepared *in situ* in CH_2Cl_2 (10 ml) was added compound **10** (72.0 mg, 0.2 mmol) and the solution stirred for 3 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 50%



Scheme 1.23. Synthesis of compound **23**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.64-6.92 (m, 16H, *arom*), 5.70 (d br, 2H, *CH_2*); 5.47 (d br, 6H, *CH_2*-N + *CH_2*).

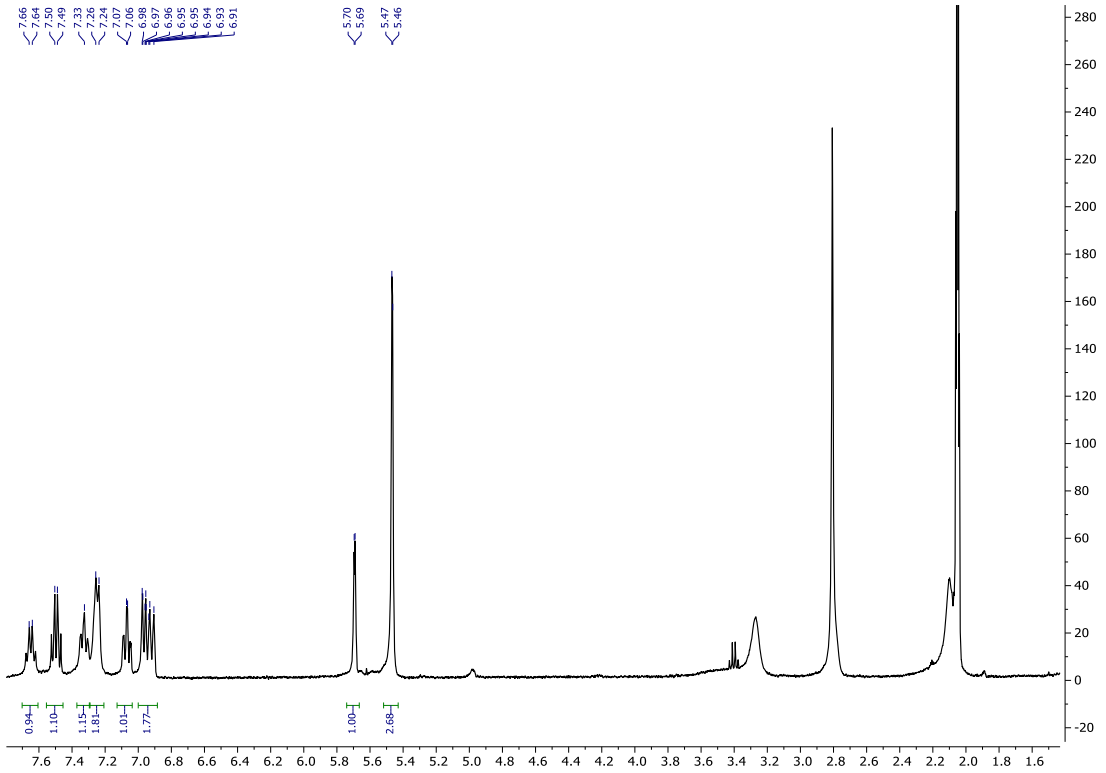


Figure 1.53. ^{1}H NMR spectrum of compound **23** in $(CD_3)_2CO$ solution.

^{19}F NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -73.5 (s, 1F, OTf); -106.4 (m, 1F, *Ph*); -107.5 (m, 1F, *Ph*).

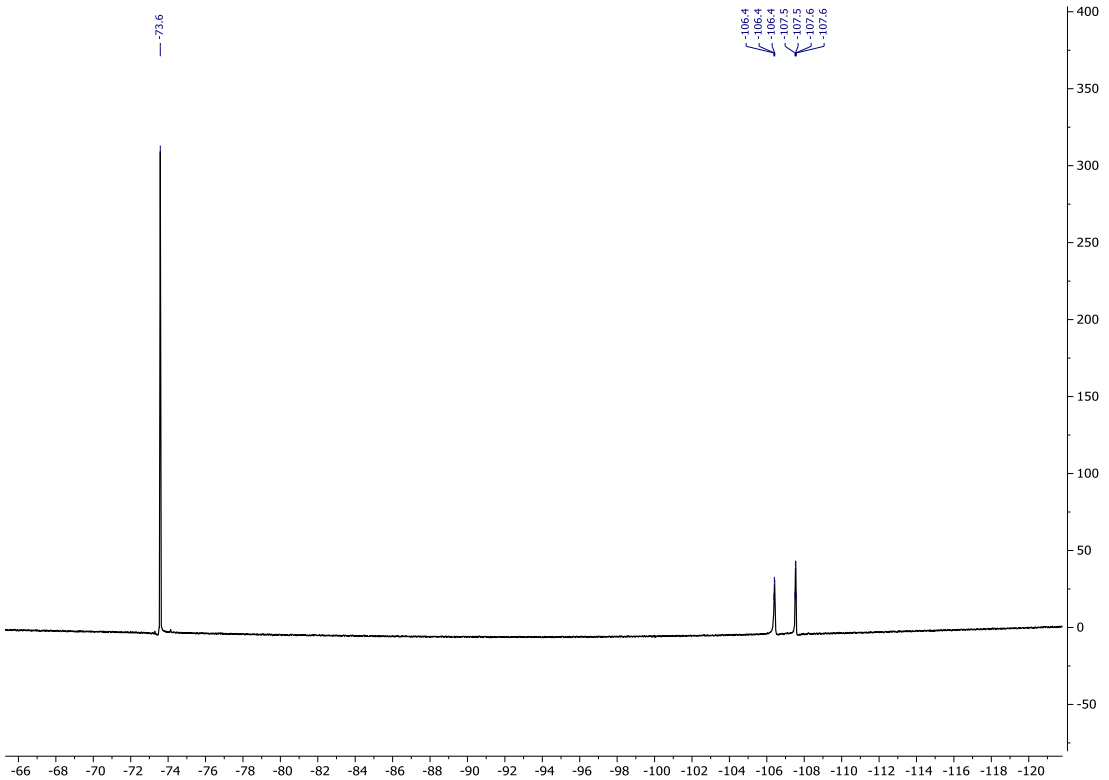


Figure 1.54. ^{19}F NMR spectrum of compound **23** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 166.2 (s, 2C, *C*=*S*); 162.8 (s, 1C, $C_{quaternary}$); 132.1 (d, 4C, *II*, $^3J_{CF}$ = 9.3Hz); 132.1 (d, 4C, *II*, $^3J_{CF}$ = 9.4Hz); 118.3 (s, 4C, *I*); 113.4 (d, 4C, *III*, $^2J_{CF}$ = 21.2Hz); 109.7 (d, 4C, *IV*, $^2J_{CF}$ = 23.5Hz); 109.2 (s, 2C, CH_2); 60.9 (s, 1C, CH_2-N).

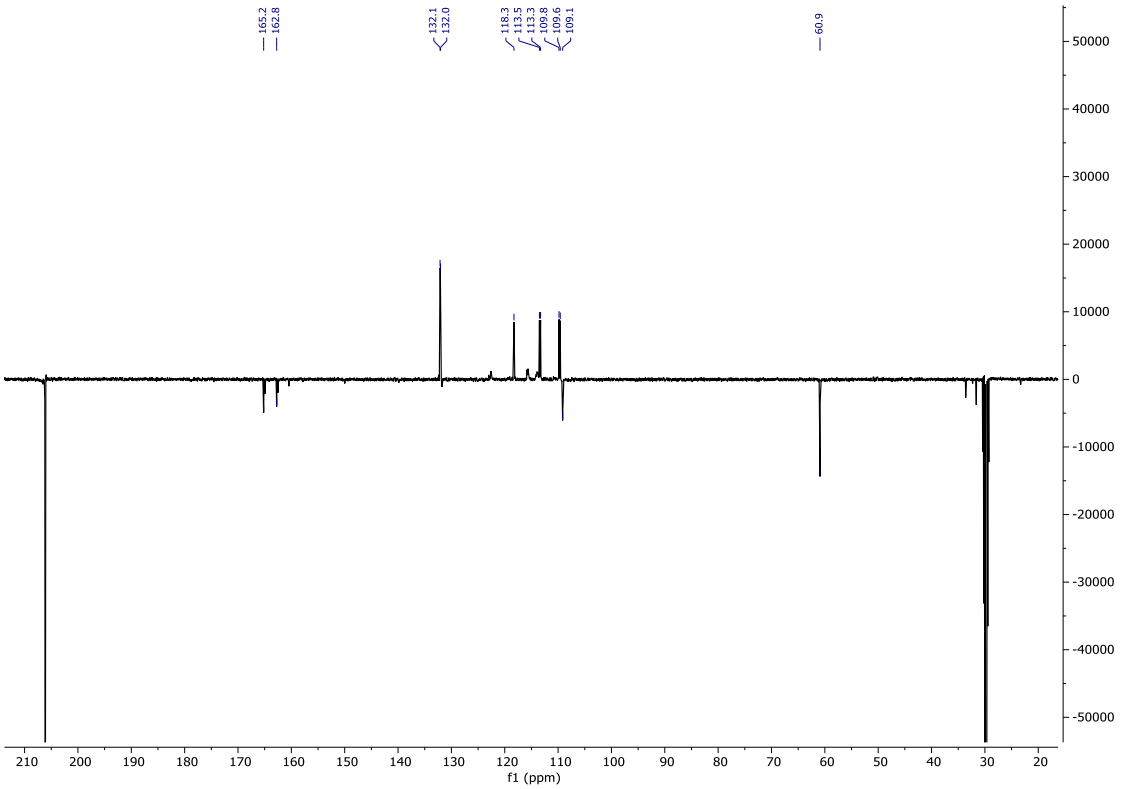
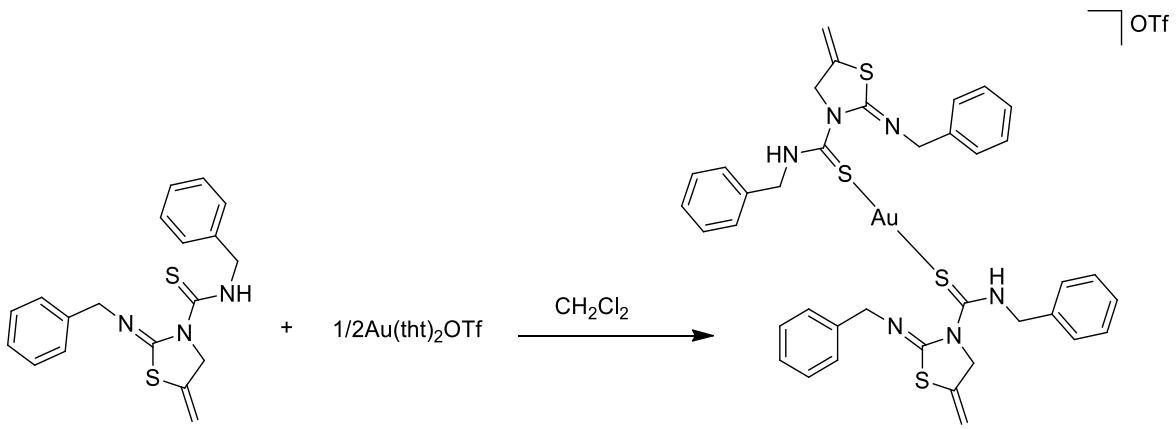


Figure 1.55. ^{13}C APT spectrum of compound **23** in $(CD_3)_2CO$ solution.

Synthesis of compound 24

To a solution of $Au(tht)_2OTf$ (52.2 mg, 0.1 mmol) which has been prepared *in situ* in CH_2Cl_2 (10 ml) was added compound **11** (72.0 mg, 0.2 mmol) and the solution stirred for 3 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) was added to precipitated a white solid which was collected and vacuum dried to give the product.

Yield: 64%



Scheme 1.24. Synthesis of compound **24**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.32-7.14 (m, 20H, *Ph*); 5.60 (s br, 2H, CH_2); 5.42 (m, 6H, CH_2-N, CH_2); 5.08 (m, 2H, NH-CH_2); 4.48 (s, 2H, N-CH_2).

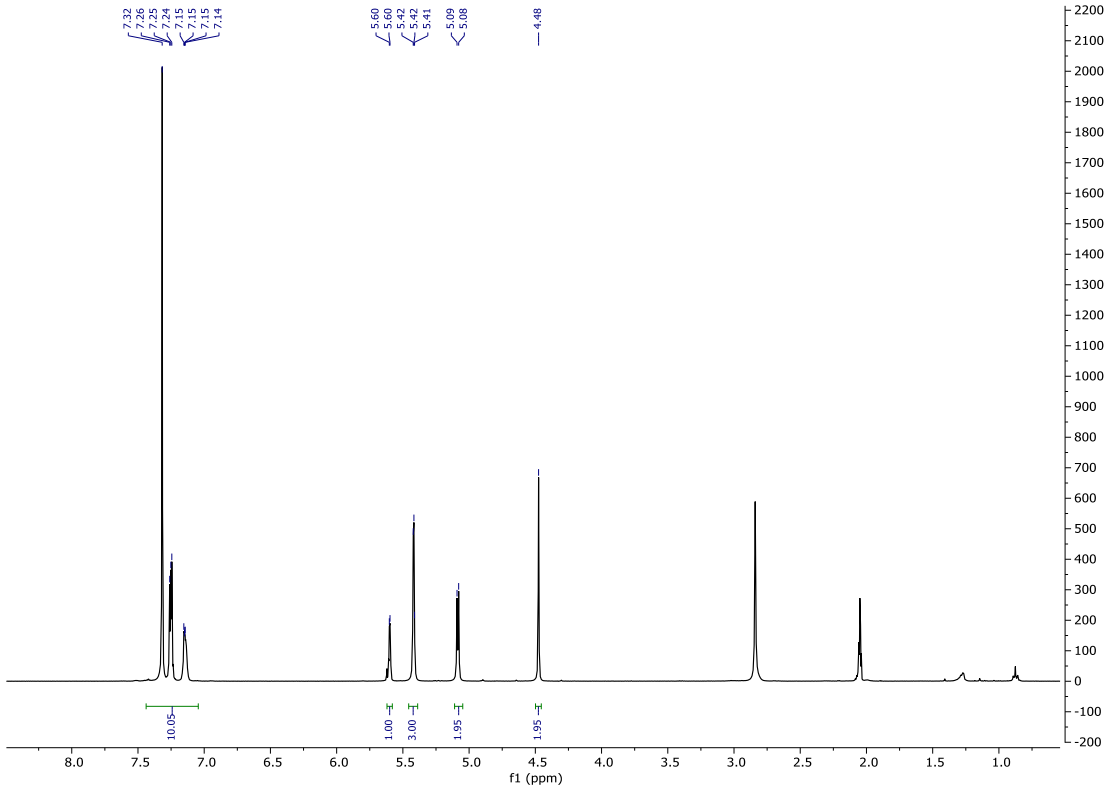


Figure 1.56. ^{1}H NMR spectrum of compound **24** in $(CD_3)_2CO$ solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -79.8 (s, 1F, *OTf*).

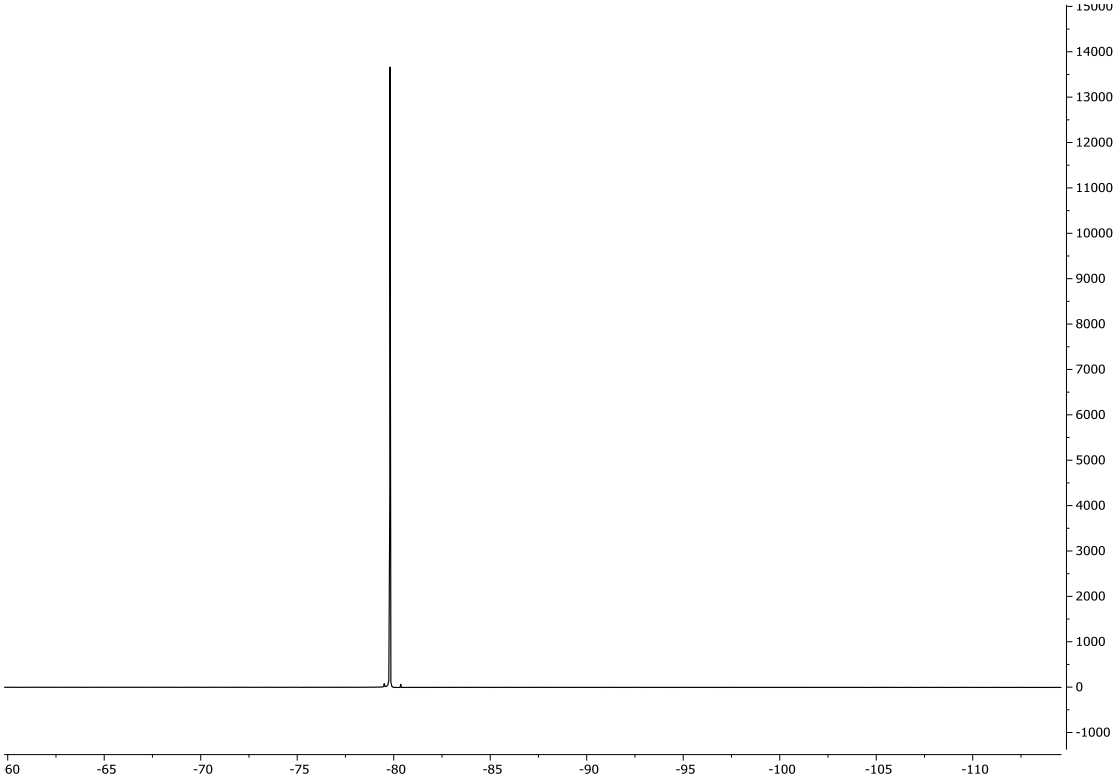


Figure 1.57. $^{19}F\{^{1}H\}$ NMR spectrum of compound **24** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 176.1 (s, 2C, *C*=*S*); 158.2 (s, 2C, N-*C*=N); 138.9 (s, 2C, C_{ipso}Ph-CH_2-N); 136.9 (s, 2C, C_{ipso}Ph-CH_2-NH); 133.3 (s, 2C, CH_2=*C*); 129.7-128.1 (s, 20C, *Ph*); 108.9 (s, 2C, *C*=CH_2); 60.4 (s, 2C, CH_2); 59.1 (s, 2C, Ph-CH_2-N=C); 51.2 (s, 2C, Ph-CH_2-NH).

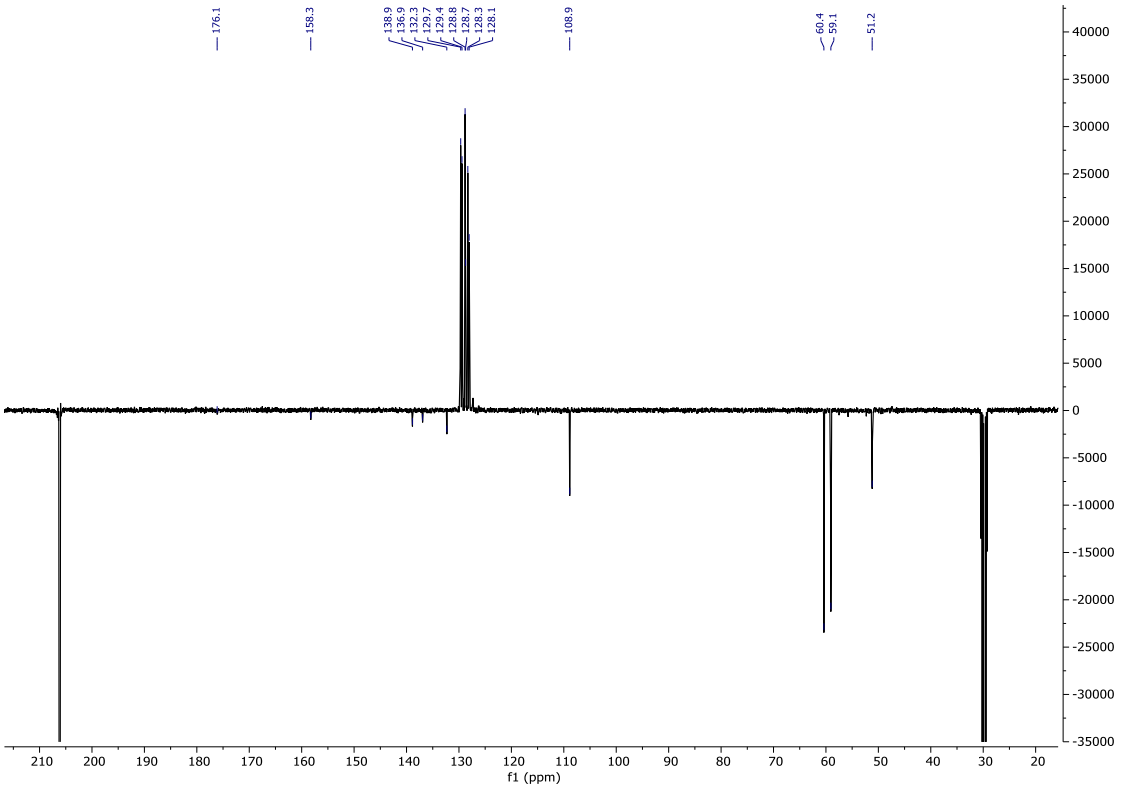
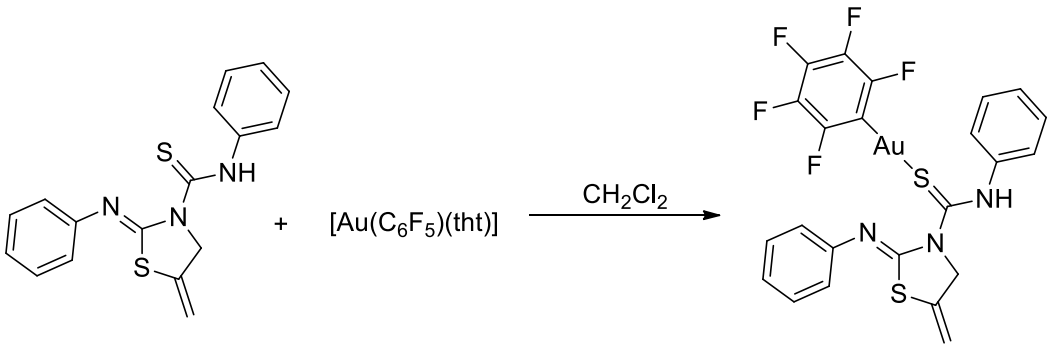


Figure 1.58. ^{13}C APT spectrum of compound **24** in $(CD_3)_2CO$ solution.

Synthesis of compound 25

To a solution of compound **9** (32.5 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added $[Au(C_6F_5)(tht)]$ (45.3 mg, 0.1 mmol) and the solution stirred for two hours and half at room temperature. The solution was concentrated under reduced pressure to approximately 1 ml and a white solid was precipitating which was collected and vacuum dried to give the product.

Yield: 80%



Scheme 1.25. Synthesis of compound **25**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.39-7.12 (m, 10H, *Ph*); 5.67 (s br, 1H, CH_2); 5.55 (t br, 2H, CH_2-N); 5.40 (s br, 1H, CH_2).

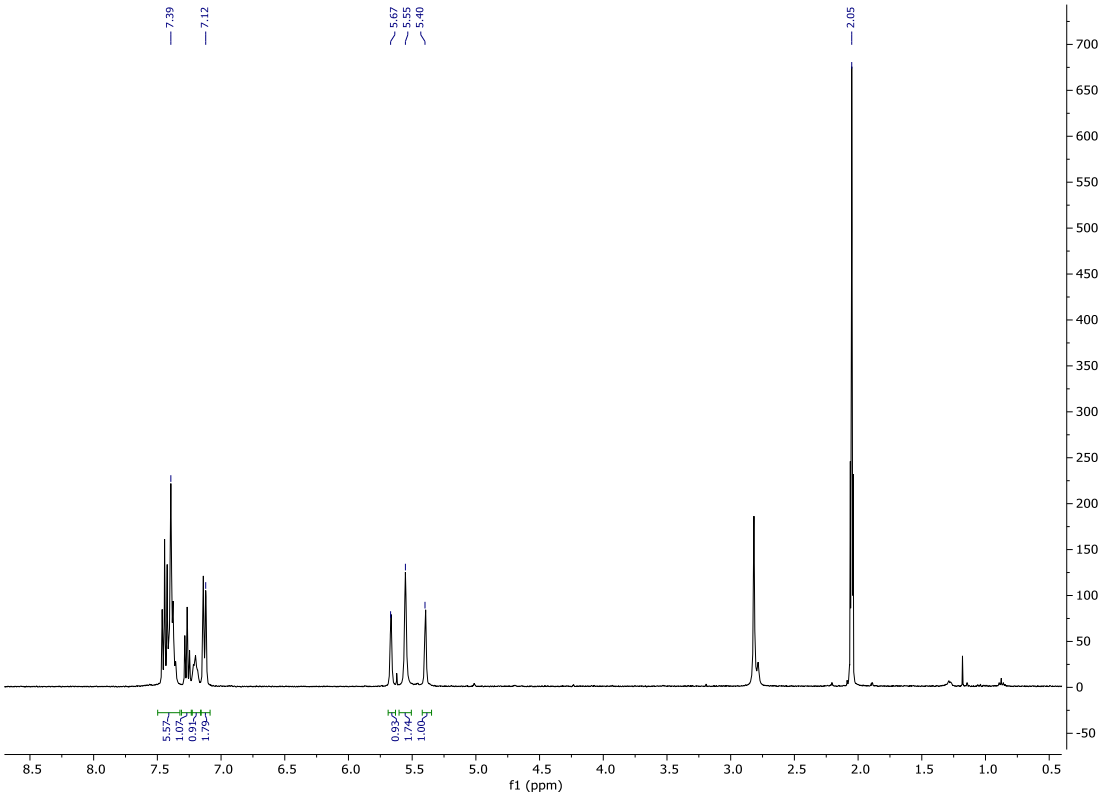


Figure 1.59: ^{1}H NMR spectrum of compound **25** in $(CD_3)_2CO$ solution.

^{19}F NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -116.4 (m, 2F, $F_{ortho}C_6F_5$); -164.1 (t, 1F, $F_{para}C_6F_5$, $^{3}J_{FF}$ = 19.7 Hz); -166.3 (m, 2F, $F_{meta}C_6F_5$).

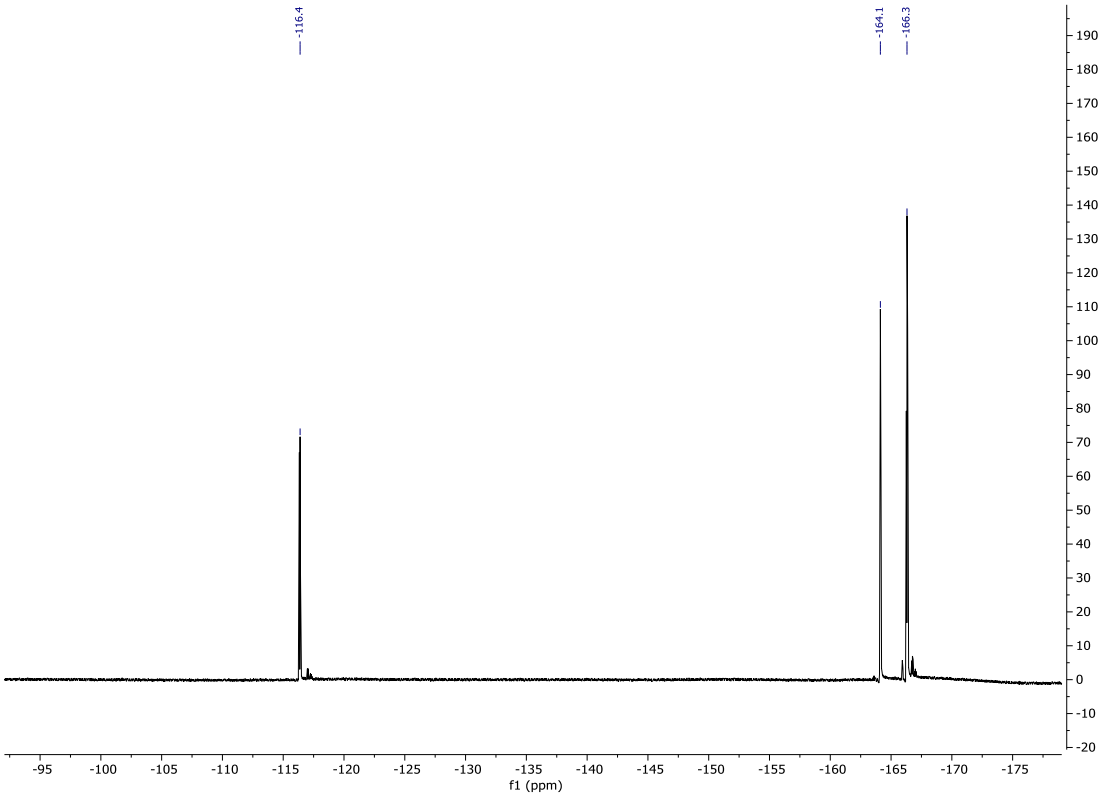


Figure 1.60: ^{19}F $\{^{1}H\}$ NMR spectrum of compound **25** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 148.1 (s, 1C, *C*$_{ipso}$Ph); 138.2 (s, 1C, *C*$_{ipso}$Ph); 132.1 (s, 1C, CH_2=*C*); 130.4 (s, 4C, *C*$_{ortho}$Ph); 129.3 (s, 1C, *C*$_{para}$Ph); 127.4 (s, 2C, *C*$_{meta}$Ph); 127.0 (s, 1C, *C*$_{para}$Ph); 121.1 (s, 2C, *C*$_{meta}$Ph); 109.2 (s, 1C, *CH*$_2$); 60.5 (s, 1C, *CH*$_2$-N).

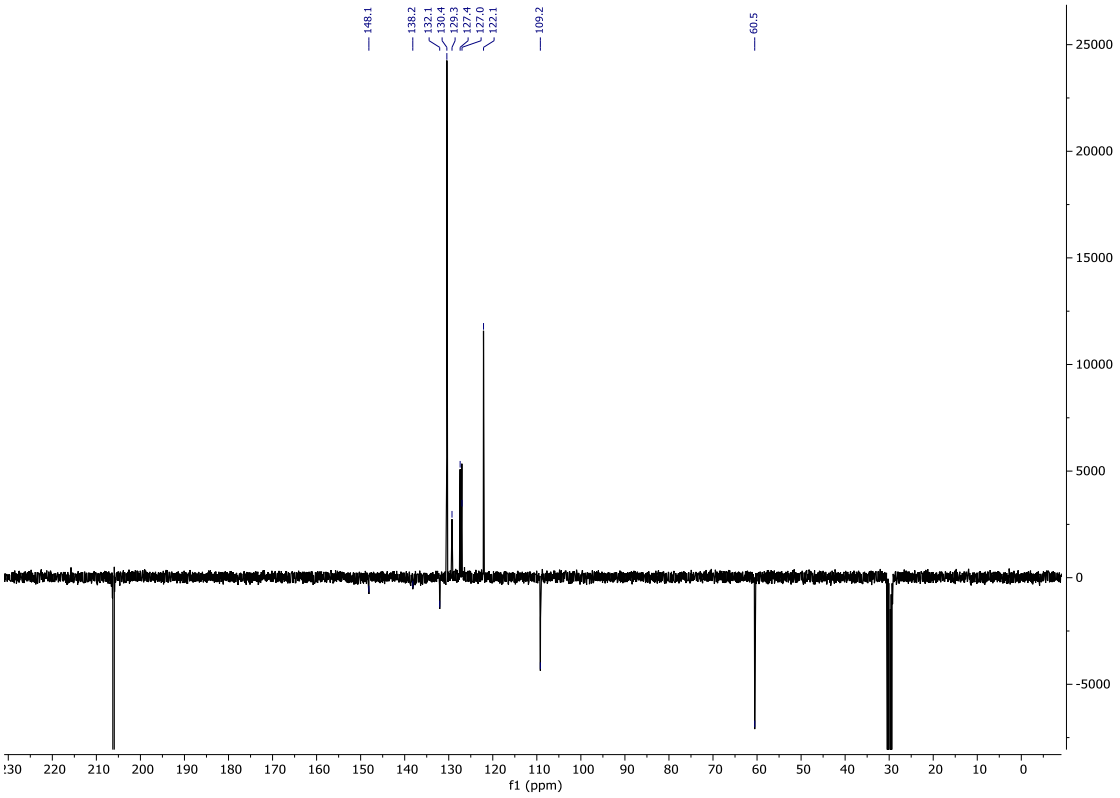
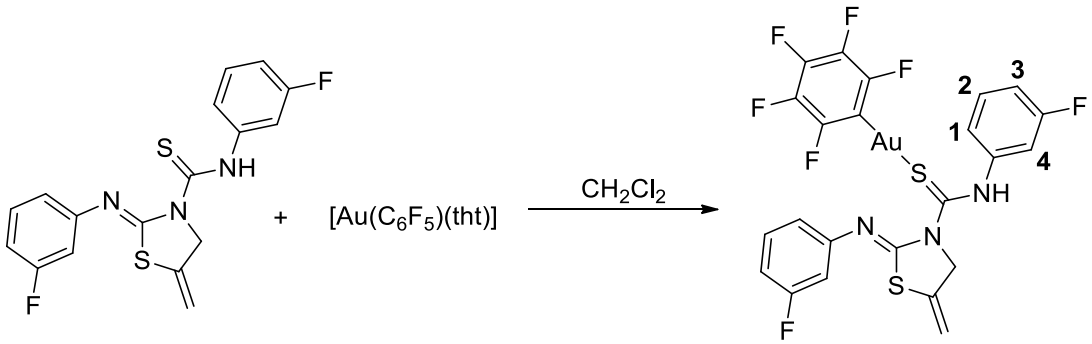


Figure 1.61: ^{13}C APT spectrum of compound **25** in $(CD_3)_2CO$ solution.

Synthesis of compound 26

To a solution of compound **10** (36.1 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added $[Au(C_6F_5)(tht)]$ (45.3 mg, 0.1 mmol) and the solution stirred for two hours and half at room temperature. The solution was concentrated under reduced pressure to approximately 1 ml and a white solid was precipitating which was collected and vacuum dried to give the product.

Yield: 52%



Scheme 1.26. Synthesis of compound **26**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.48 (m, 2H, *Ph-F*); 7.25 (m, 2H, *Ph-F*); 6.99 (m, 4H, *Ph-F*); 5.70 (s br, 1H, CH_2); 5.55 (t br, 2H, CH_2-N); 5.43 (s br, 1H, CH_2).

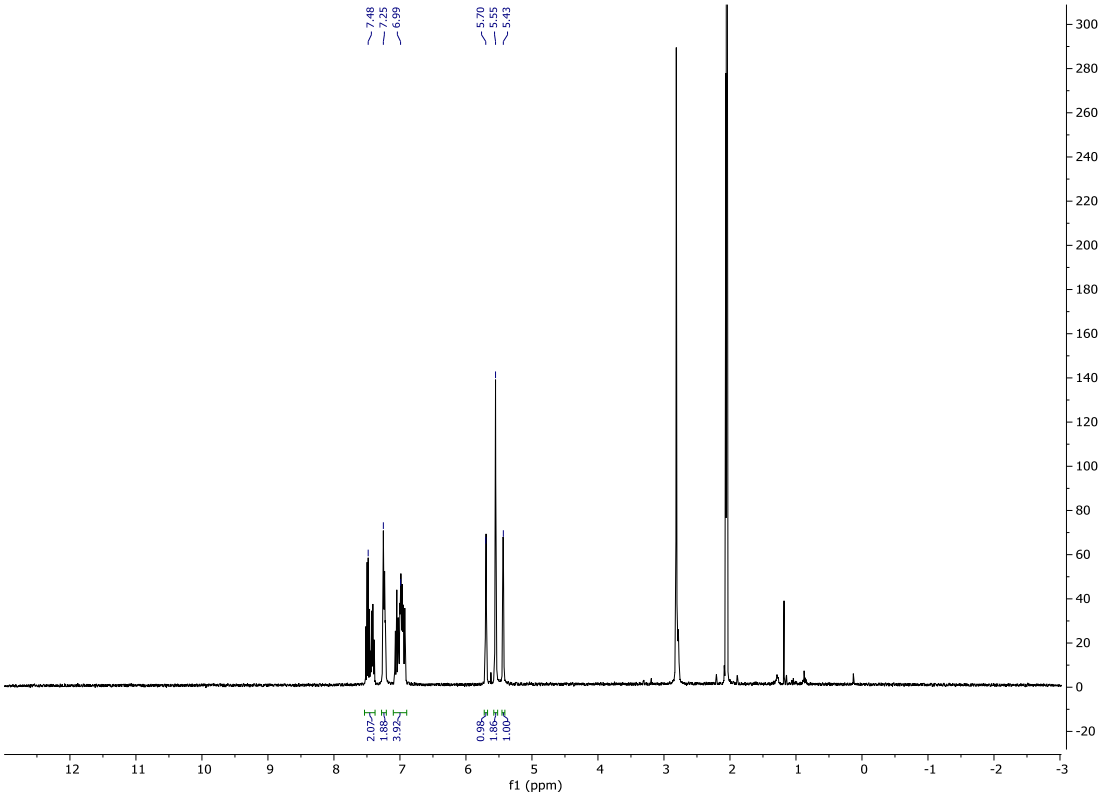


Figure 1.62. ^{1}H NMR spectrum of compound **26** in $(CD_3)_2CO$ solution.

^{19}F NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -114.0 (m, 1F, *Ph-F*); -114.0 (m, 1F, *Ph-F*); -116.6 (m, 2F, $F_{ortho}C_6F_5$); -163. (t, 1F, $F_{para}C_6F_5$, $^{3}J_{FF}$ = 19.7 Hz); -166.2 (m, 2F, $F_{meta}C_6F_5$).

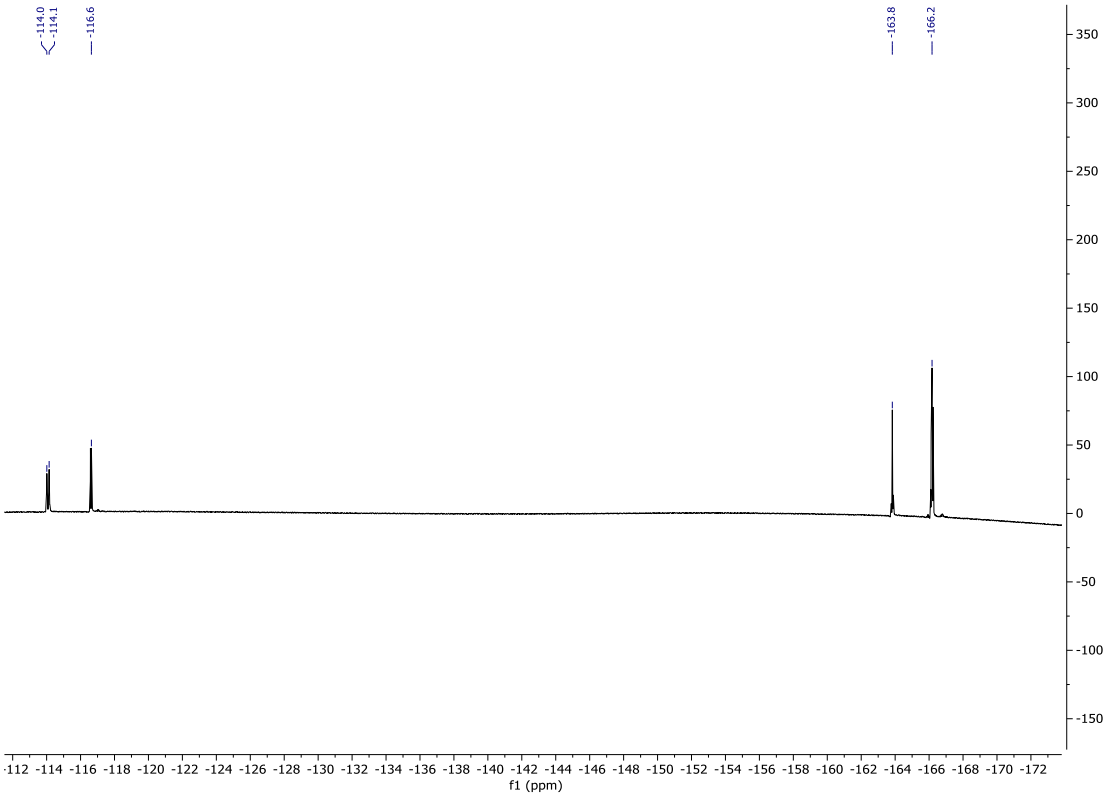


Figure 1.63. ^{19}F $\{^{1}H\}$ NMR spectrum of compound **26** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 165.1 (d, 1C, C_{ipso}Ph-F, $^{3}J_{CF}$ = 15.3 Hz); 162.7 (d, 1C, C_{ipso}Ph-F, $^{3}J_{CF}$ = 15.8 Hz); 132.2 (d, 1C, *II*, $^{3}J_{HF}$ = 9.4 Hz); 132.0 (d, 1C, *II*, $^{3}J_{CF}$ = 9.4 Hz); 131.6 (s, 1C, CH_2=*C*); 123.8 (s, 1C, *I*); 118.2 (s, 1C, *I*); 116.2 (d, 1C, *III*, $^{2}J_{CF}$ = 21.3 Hz); 115.3 (d, 1C, *IV*, $^{2}J_{CF}$ = 28.5 Hz); 113.6 (d, 1C, *III*, $^{2}J_{CF}$ = 21.3 Hz); 109.7 (d, 1C, *IV*, $^{2}J_{CF}$ = 23.7 Hz); 109.6 (s, 1C, CH_2); 60.6 (s, 1C, CH_2-N).

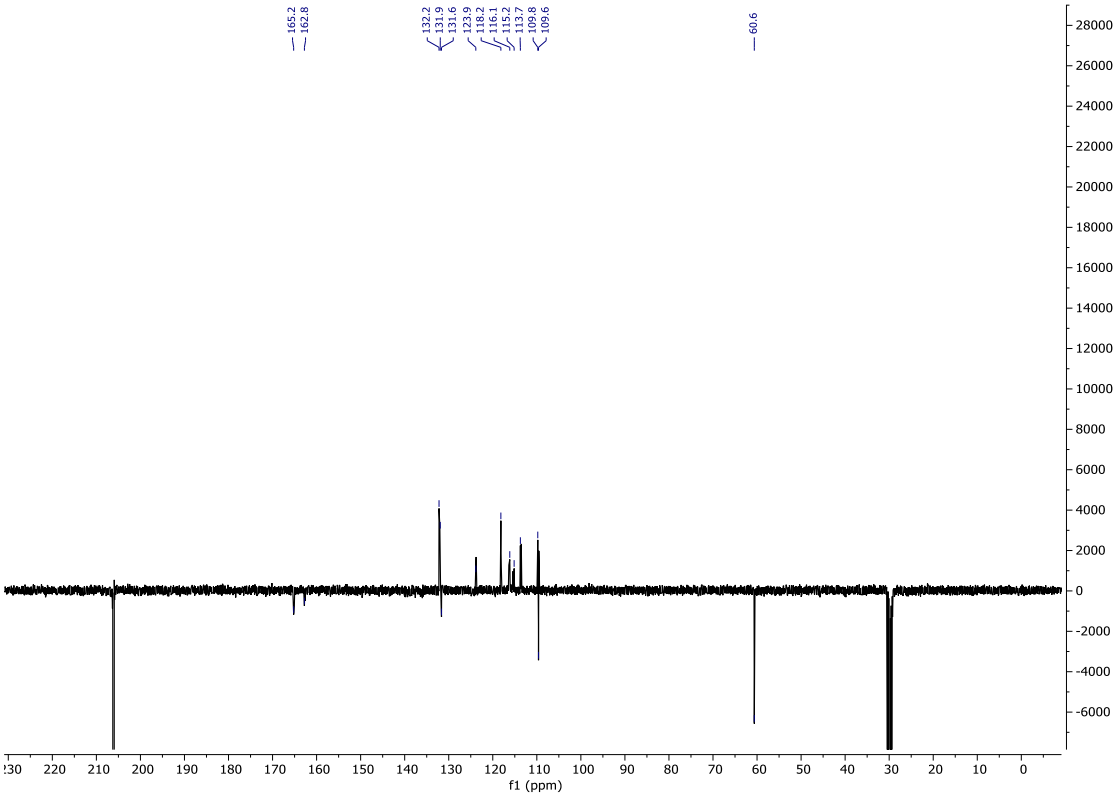
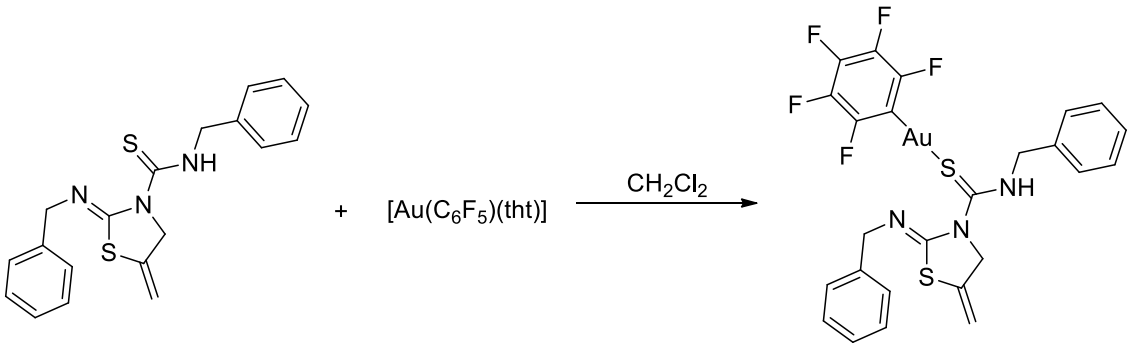


Figure 1.64. ^{13}C APT spectrum of compound **26** in $(CD_3)_2CO$ solution.

Synthesis of compound 27

To a solution of compound **11** (35.3 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was added $[Au(C_6F_5)(tht)]$ (45.3 mg, 0.1 mmol) and the solution stirred for two hours and half at room temperature. The solution was concentrated under reduced pressure to approximately 1 ml and a white solid was precipitating which was collected and vacuum dried to give the product.

Yield: 75%



Scheme 1.27. Synthesis of compound **27**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.37-7.11 (m, 10H, *Ph*); 5.67 (s br, 1H, CH_2); 5.57 (m, 2H, CH_2-N) 5.45 (m, 1H, CH_2); 5.34 (m, 2H, NH-CH_2); 4.48 (s, 2H, N-CH_2).

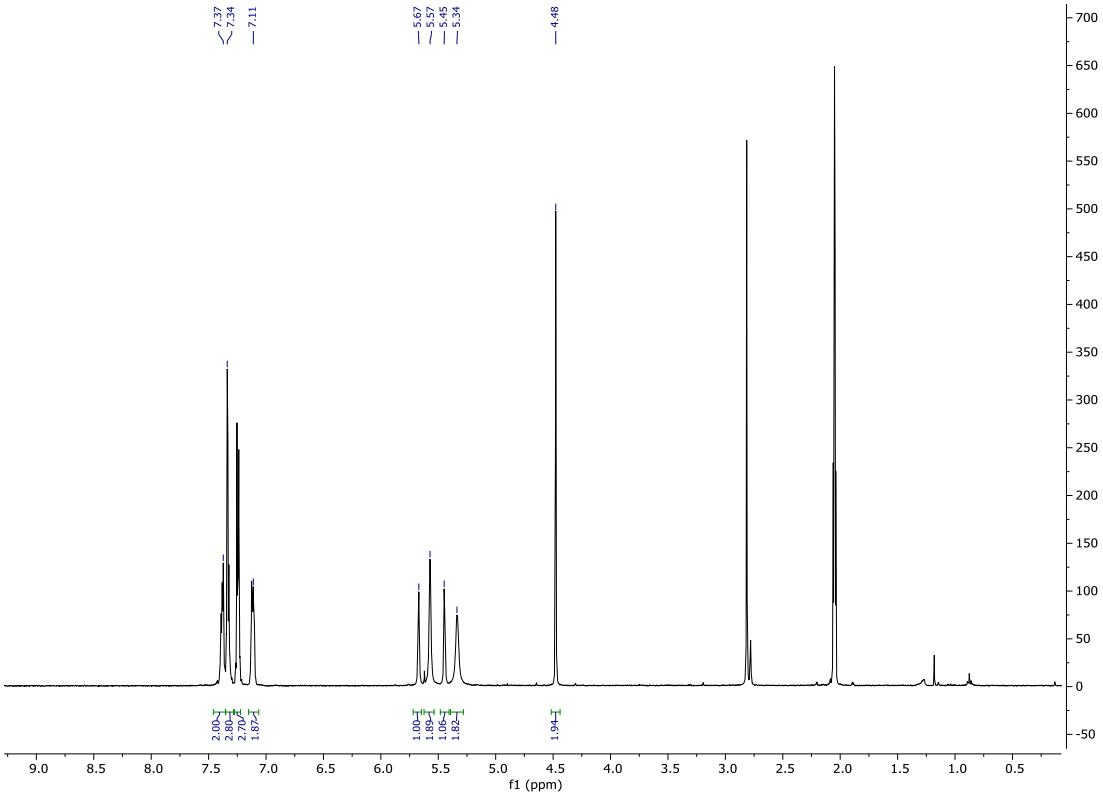


Figure 1.65. ^{1}H NMR spectrum of compound **27** in $(CD_3)_2CO$ solution.

^{19}F NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -117.7 (m, 2F, $F_{ortho}C_6F_5$); -163.4 (t, 1F, $F_{para}C_6F_5$, $^{3}J_{FF}$ = 19.6 Hz); -166.7 (m, 2F, $F_{meta}C_6F_5$).

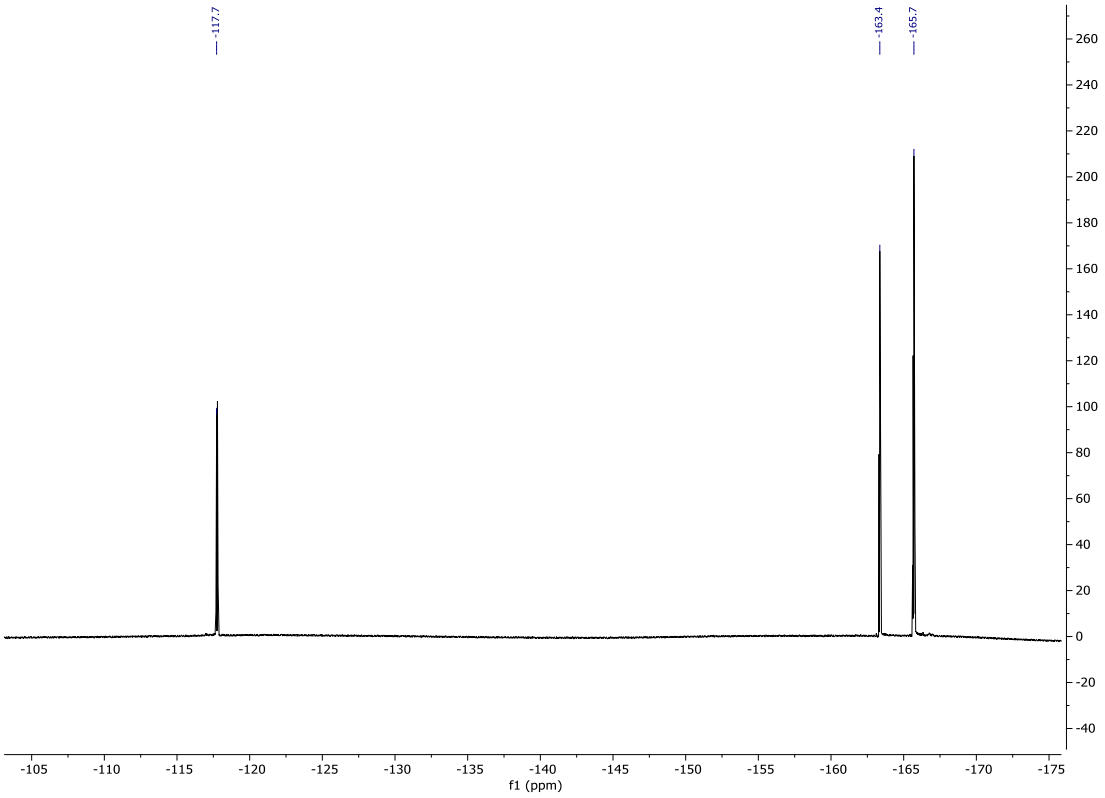


Figure 1.66. ^{19}F $\{^{1}H\}$ NMR spectrum of compound **27** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 157.9 (s, 1C, N-*C*=N); 138.5 (s, 1C, C_{ipso}Ph-F); 132.0 (s, 1C, CH_2=*C*); 129.8-128.1 (m, 10C, *Ph*); 109.3 (s, 1C, CH_2); 60.5 (s, 1C, CH_2-N); 59.1 (s, 1C, Ph-CH_2-N=C); 52.3 (s, 1C, Ph-CH_2-NH).

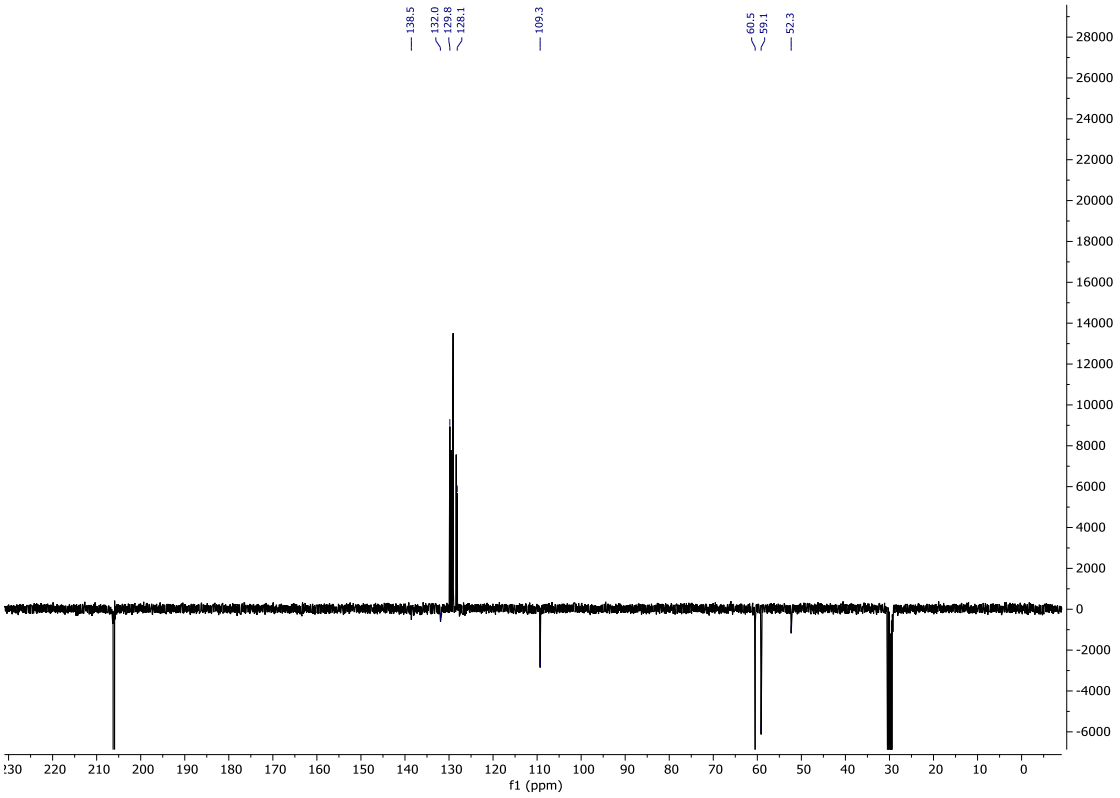
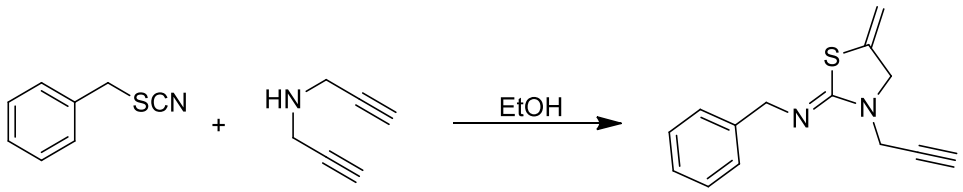


Figure 1.67. ^{13}C APT spectrum of compound **27** in $(CD_3)_2CO$ solution.

Synthesis of compound 28

To a solution of dipropargylamine (10.3 µl, 0.1 mmol) in ethanol (10 ml) was added bencylisothiocianate (13.2 µl, 0.1 mmol) and the mixture stirred for 24h. The solution was concentrated under reduced pressure and a yellow oil was collected and vacuum dried to give the product.

Yield: 99%



Scheme 1.28. Synthesis of compound **28**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.29 (m, 5H, *Ph*); 5.41 (m, 1H, CH_2); 5.25 (m, 1H, CH_2); 4.36 (s, 2H, N-CH_2-Ph); 4.31 (t, 2H, CH_2-N, $^4J_{HH}$ = 2.2 Hz); 4.28 (d, 2H, $CH_2 - C \equiv CH$, $^4J_{HH}$ = 2.5 Hz); 2.78 (t, 1H, *CH*, $^4J_{HH}$ = 2.5 Hz).

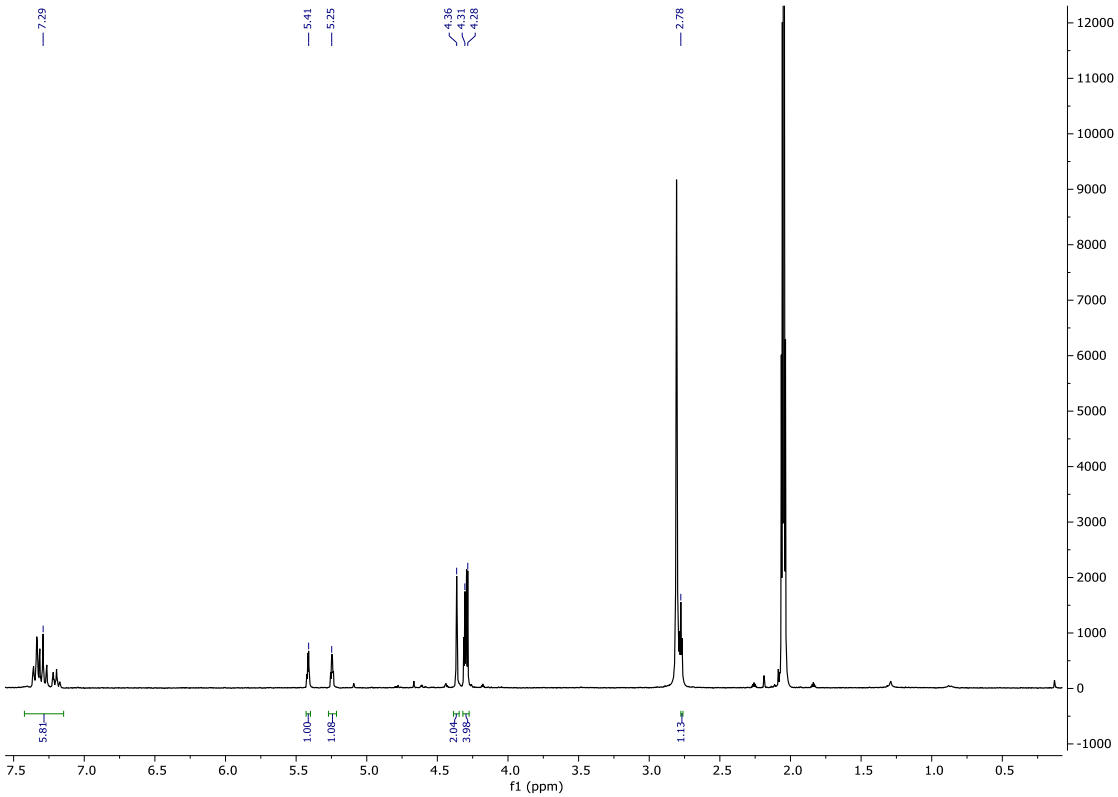


Figure 1.68. ^{1}H NMR spectrum of compound **28** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 140.9 (s, 1C, *$C_{ipso}Ph$*); 137.3 (s, 1C); 128.1 (s, 2C, *$C_{orto}Ph$*); 127.2 (s, 1C, *$C_{para}Ph$*); 126.3 (s, 2C, *$C_{meta}Ph$*); 105.9 (s, 1C, *CH_2*); 73.0 (s, 1C, *CH*); 57.9 (s, 1C, N-*CH_2*-Ph); 54.6 (s, 1C, *CH_2*-N); 34.6 (s, 1C, $CH_2 - C \equiv CH$).

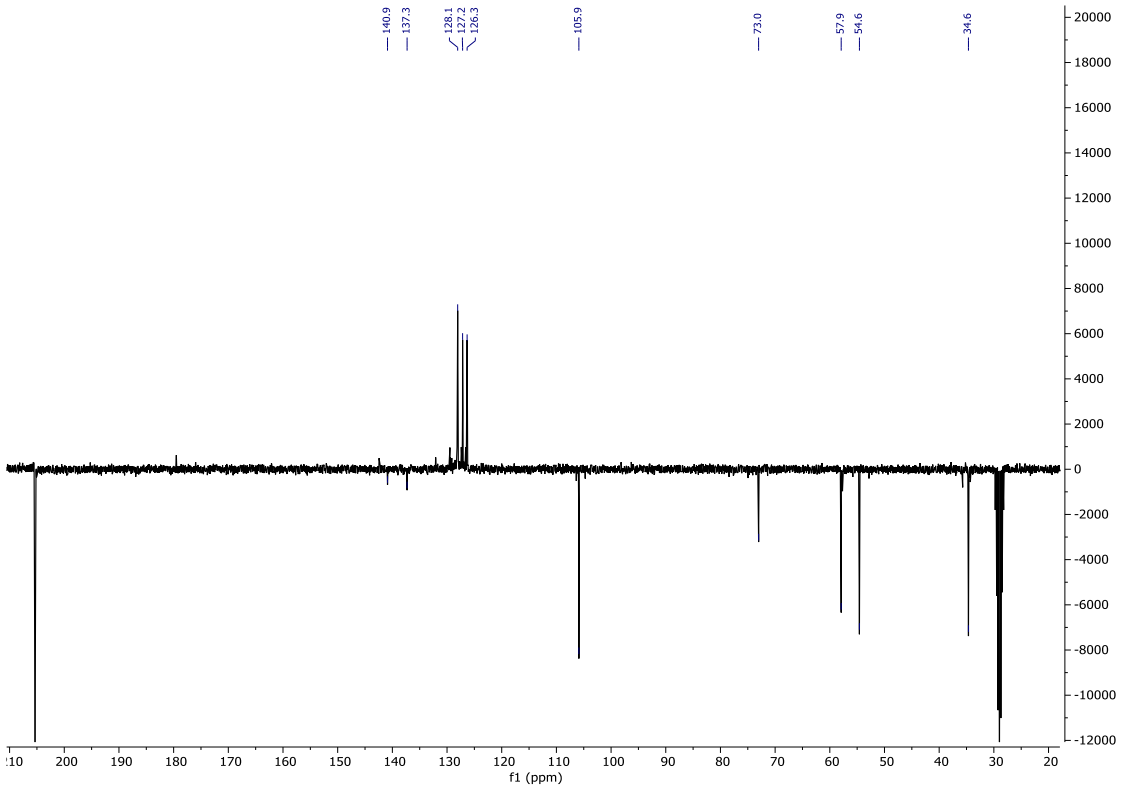
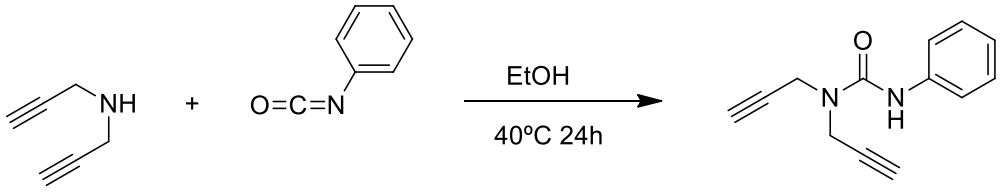


Figure 1.69. ^{13}C APT spectrum of compound **28** in $(CD_3)_2CO$ solution.

Synthesis of compound 32

To a solution of dipropargylamine (21.0 µl, 0.2 mmol) in ethanol (10 ml) was added phenylisocynate (22 µl, 0.2 mmol) and the mixture stirred for 24h at 40°C. The solution was concentrated under reduced pressure and a yellow oil was collected and vacuum dried to give the product.

Yield: 99%



Scheme 1.28. Synthesis of compound **32**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 8.04 (s br, 1H, *NH*); 7.55 (m, 2H, H_{meta}Ph); 7.25 (m, 2H, H_{ortho}Ph); 6.99 (tt, 1H, H_{para}Ph, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz); 4.35 (d, 4H, CH_2, $^4J_{HH}$ = 2.5 Hz); 2.83 (t, 1H, *CH*, $^4J_{HH}$ = 2.4 Hz).

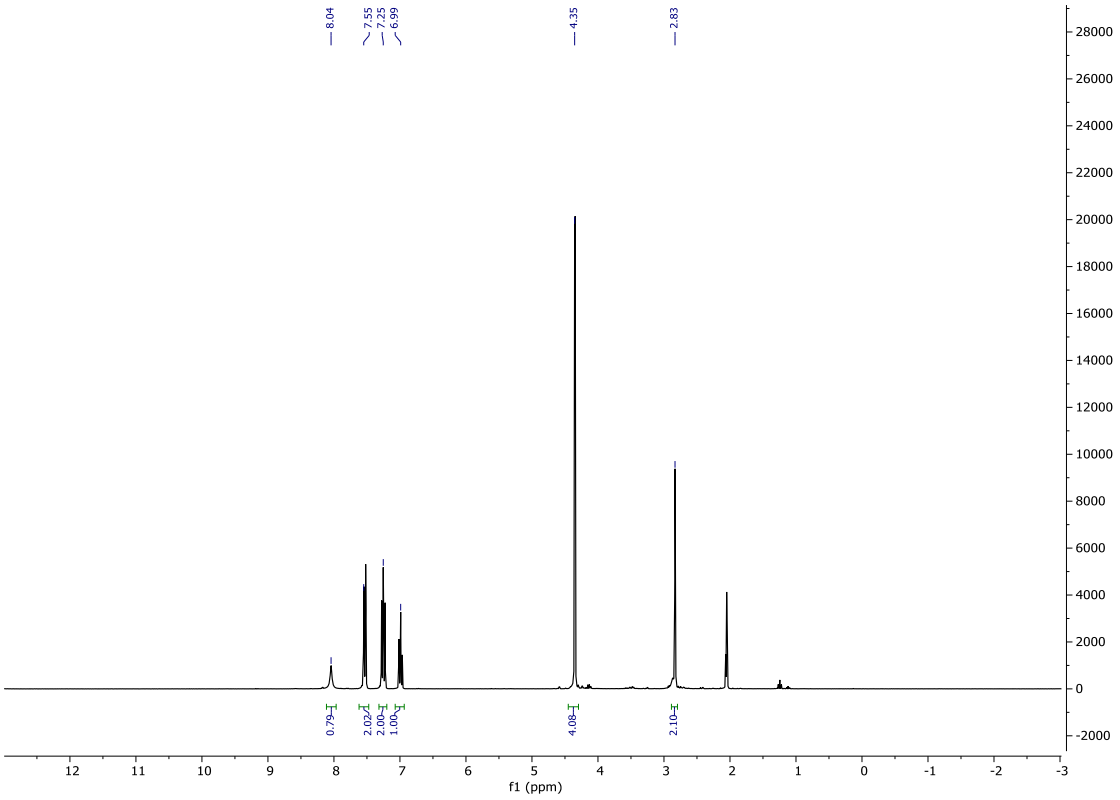


Figure 1.70 ^{1}H NMR spectrum of compound **32** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 155.1 (s, 1C, *CO*); 140.9 (s, 1C, C_{ipso}Ph); 129.3 (s, 2C, C_{ortho}Ph); 123.4 (s, 1C, C_{para}Ph); 120.7 (s, 2C, C_{meta}Ph); 79.8 (s, 2C, $CH_2 - C \equiv CH$); 74.1 (s, 2C, *CH*); 36.1 (s, 2C, CH_2).

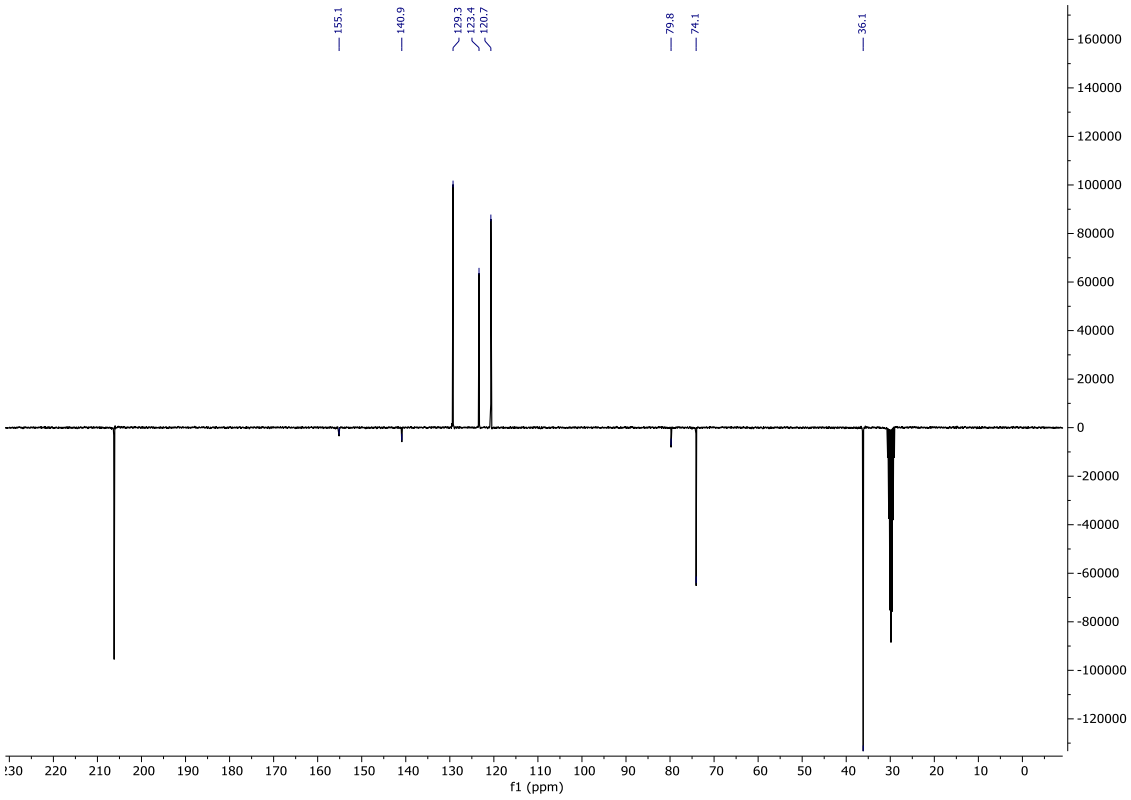
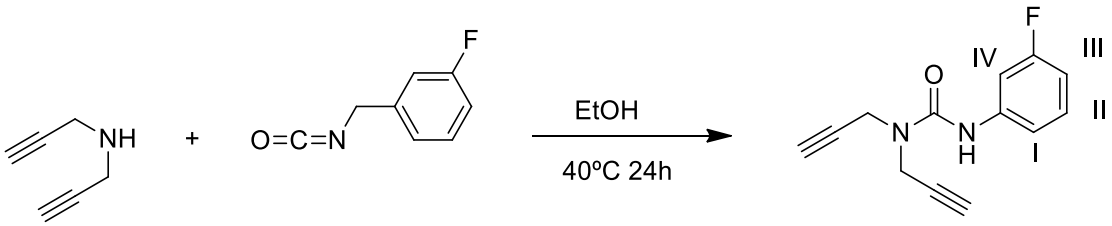


Figure 1.71 ^{13}C APT spectrum of compound **32** in $(CD_3)_2CO$ solution.

Synthesis of compound 33

To a solution of dipropargylamine (51.7 µl, 0.5 mmol) in ethanol (10 ml) was added 3-fluorophenylisocynate (57.1 µl, 0.5 mmol) and the mixture stirred for 24h at 40°C. The solution was concentrated under reduced pressure and a yellow oil was collected and vacuum dried to give the product.

Yield: 99%



Scheme 1.29. Synthesis of compound **33**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 8.24 (s br, 1H, NH); 7.53 (m, 1H, *IV*); 7.26 (m, 2H, *I+II*); 6.74 (m, 1H, *III*); 4.35 (d, 4H, CH_2, $^4J_{HH}$ = 2.4 Hz); 2.84 (t br, 2H, *CH*).

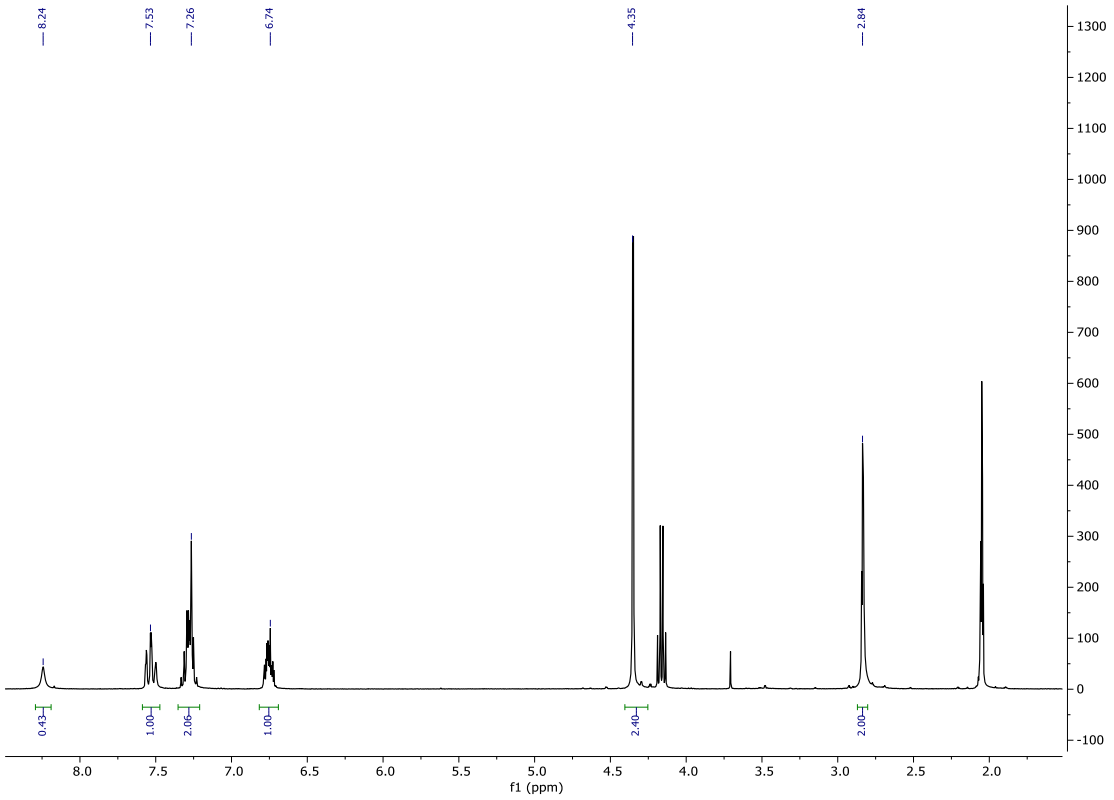


Figure 1.72 ^{1}H NMR spectrum of compound **33** in $(CD_3)_2CO$ solution.

^{19}F NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -115. (s, 1F, *Ph-F*).

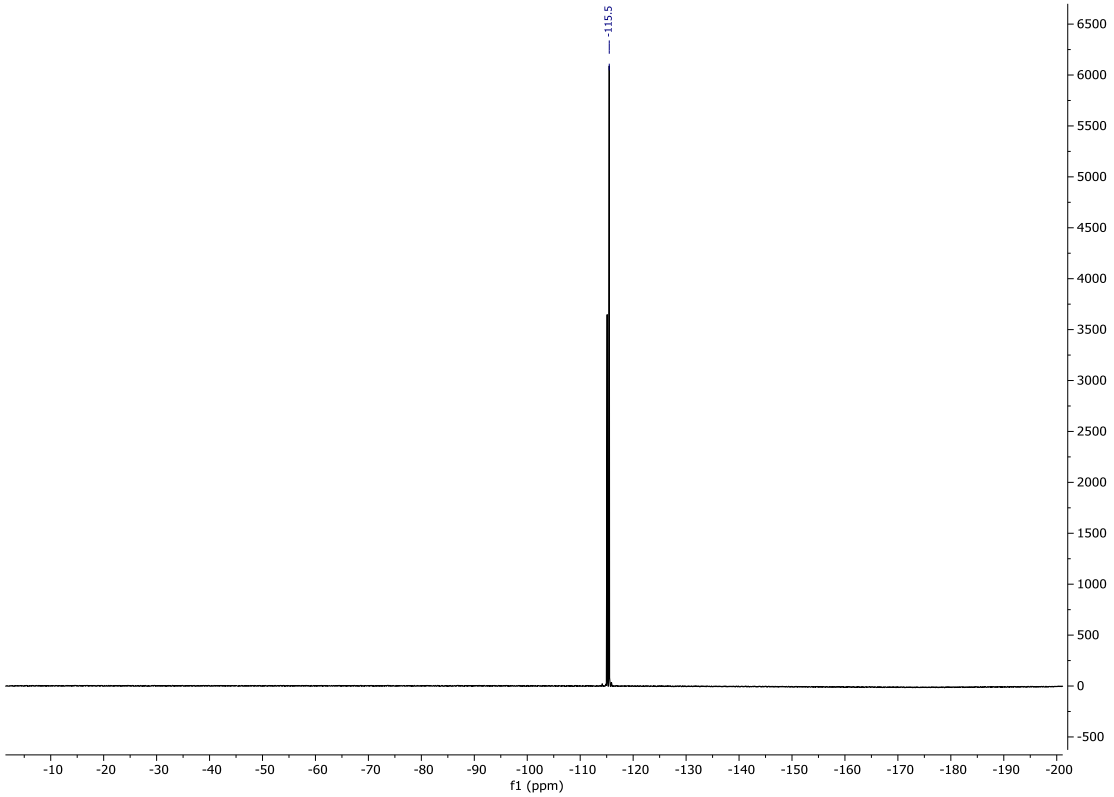


Figure 1.73 ^{19}F $\{^{1}H\}$ NMR spectrum of compound **33** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 165.1 (d, 1C, C_{ipso}Ph-F, $^{1}J_{CF}$ = 20.8 Hz); 154.9 (s, 1C, *CO*); 142.9 (d, 1C, C_{ipso}Ph-F-NH, $^{3}J_{CF}$ = 11.4 Hz); 130.7 (d, 1C, *II*, $^{3}J_{CF}$ = 9.6 Hz); 116.0 (d, 1C, *I*, $^{4}J_{CF}$ = 2.8 Hz); 109.6 (d, 1C, *III*, $^{2}J_{CF}$ = 21.5 Hz); 107.4 (d, 1C, *IV*, J_{CF} = 26.8 Hz); 79.6 (s, 2C, $CH_2 - C \equiv CH$);); 74.2 (s, 2C, *CH*); 36.1 (s, 2C, CH_2).

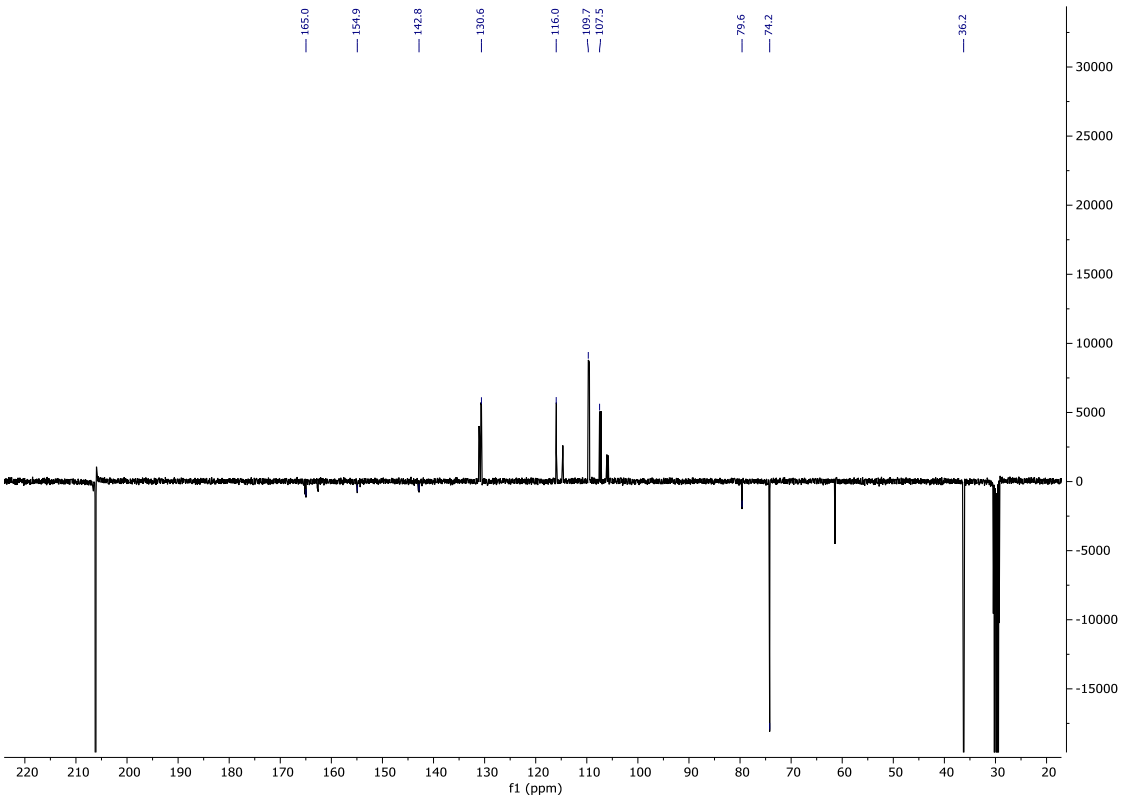
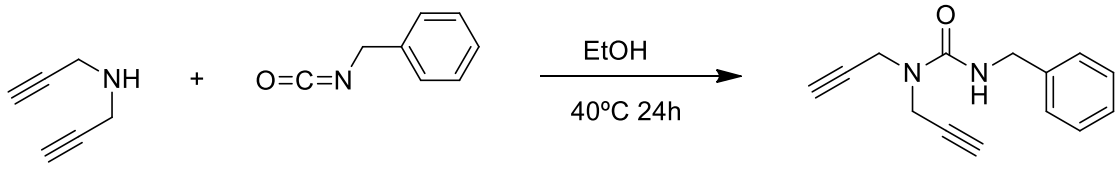


Figure 1.74 ^{13}C APT spectrum of compound **33** in $(CD_3)_2CO$ solution.

Synthesis of compound 34

To a solution of dipropargylamine (51.7 µl, 0.5 mmol) in ethanol (10 ml) was added benzylisocynate (61.8 µl, 0.2 mmol) and the mixture stirred for 24h at 40°C. The solution was concentrated under reduced pressure and a yellow oil was collected and vacuum dried to give the product.

Yield: 99%



Scheme 1.30. Synthesis of compound **34**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.32 (m, 5H, *Ph*); 6.55 (s br, 1H, *NH*); 4.41 (d, 2H, NH-*CH*$_2$-Ph, $^{3}J_{HH}$ = 5.8 Hz); 4.25 (d, 4H, *CH*$_2$, $^{4}J_{HH}$ = 2.4 Hz); 2.78 (t, 2H, *CH*, $^{4}J_{HH}$ = 2.4 Hz).

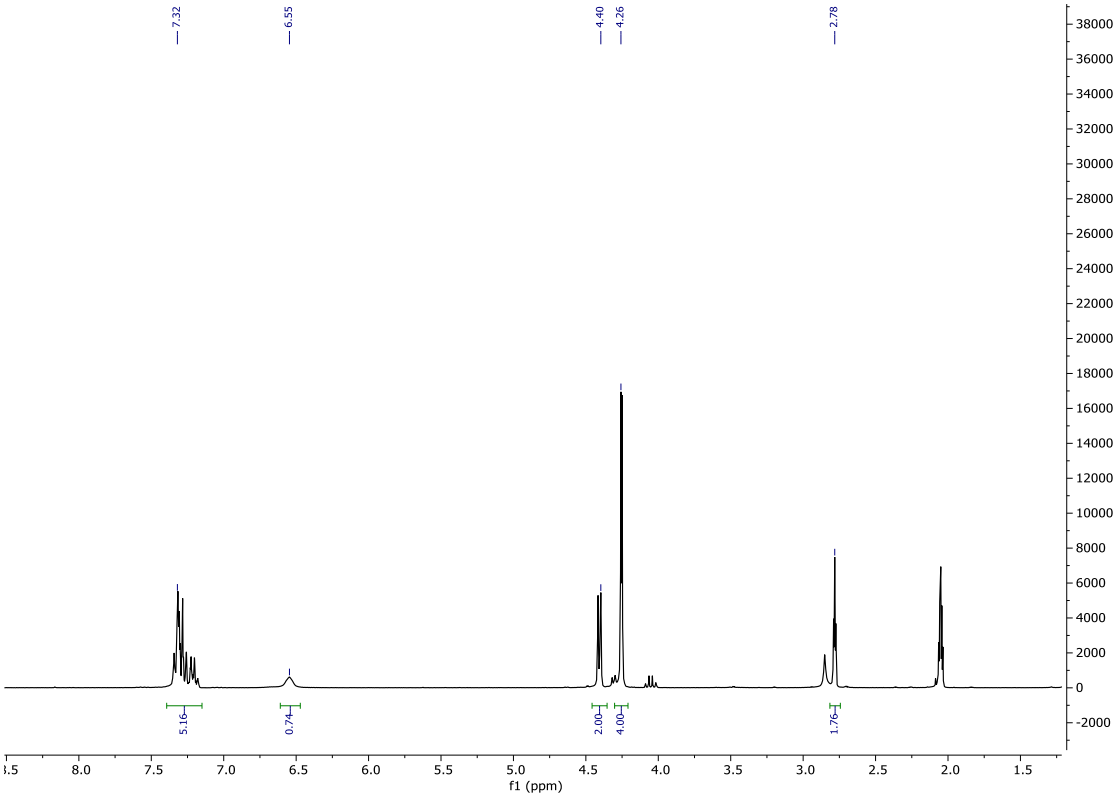


Figure 1.75. ^{1}H NMR spectrum of compound **34** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 157.4 (s, 1C, *CO*); 141.4 (s, 1C, *C*$_{ipso}$Ph); 129.0 (s, 2C, *C*$_{ortho}$Ph); 128.2 (s, 1C, *C*$_{para}$Ph); 127.5 (s, 2C, *C*$_{meta}$Ph); 80.1 (s, 2C, $CH_2 - C \equiv CH$); 73.7 (s, 2C, *CH*); 45.1 (s, 1C, NH-*CH*$_2$-Ph); 35.8 (s, 2C, *CH*$_2$).

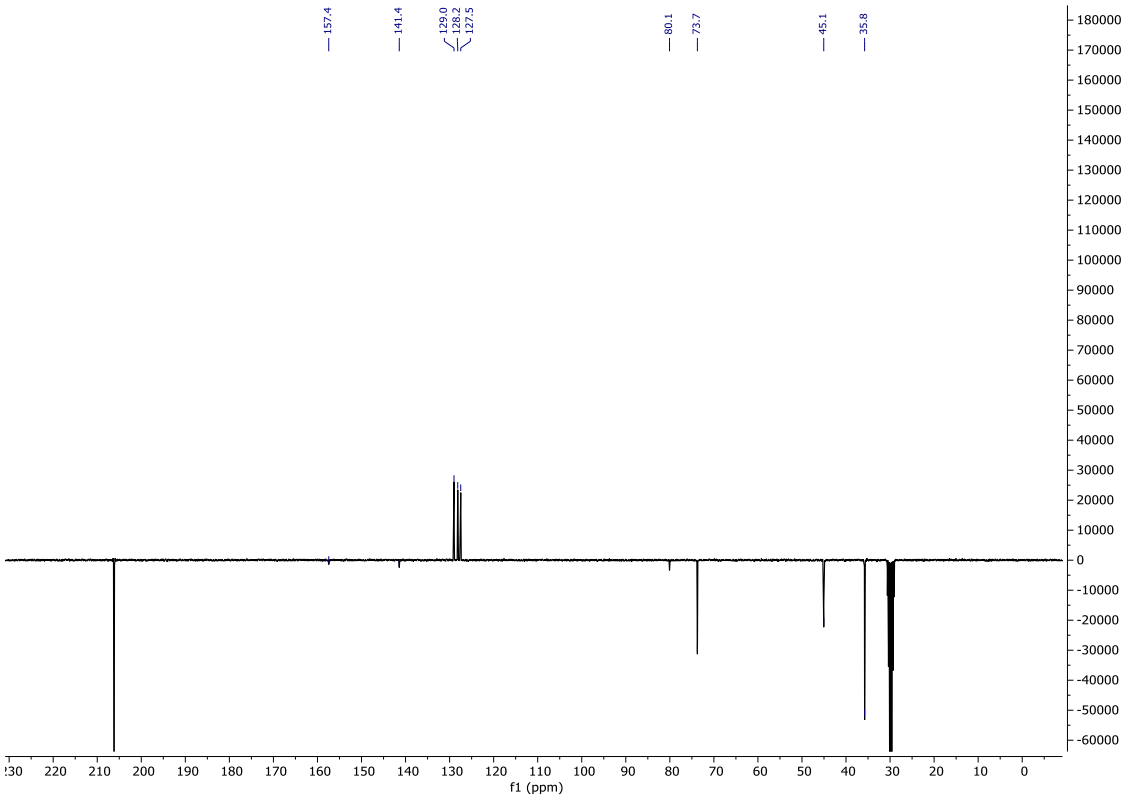
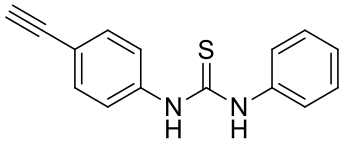


Figure 1.76. ^{13}C APT spectrum of compound **34** in $(CD_3)_2CO$ solution.

Synthesis of compound 35

To a solution of 4-ethynylaniline (12 mg, 0.1 mmol) in ethanol/water mixture (1/1), phenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the mixture was stirred for 24 hours. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 50 %



Scheme 1.31. Synthesis of compound **35**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 7.88 (s br, 1H, *NH*); 7.74 (s br, 1H, *NH*); 7.51-7.32 (m, 9H, *arom.*); 3.10 (s, 1H, *CH*).

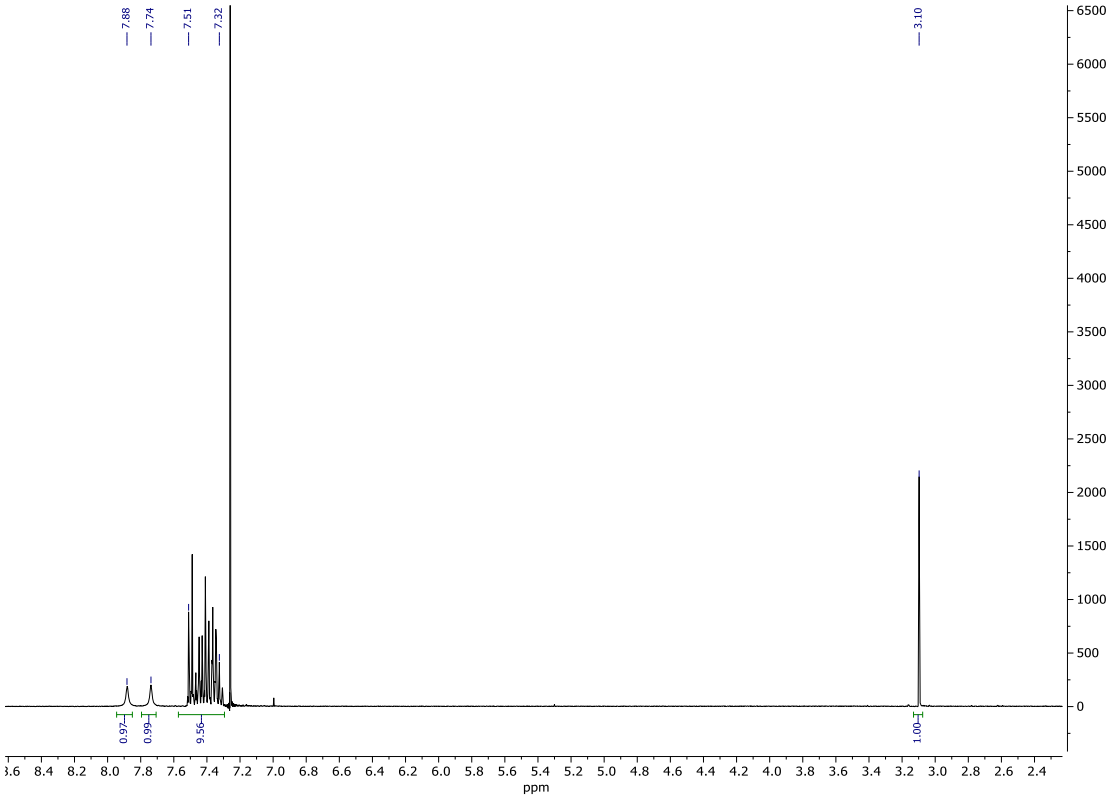


Figure 1.77. ^{1}H NMR spectrum of compound **35** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 179.8 (s, 1C, *C*=*S*); 147.1 (s, 1C, C_{ipso}); 137.9 (s, 1C, C_{ipso}); 133.2-124.4 (m, 10C, *arom.*); 120.4 (s, 1C, C_{ipso}); 83.0 (s, 1C, $C \equiv CH$); 78.0 (s, 1C, *CH*).

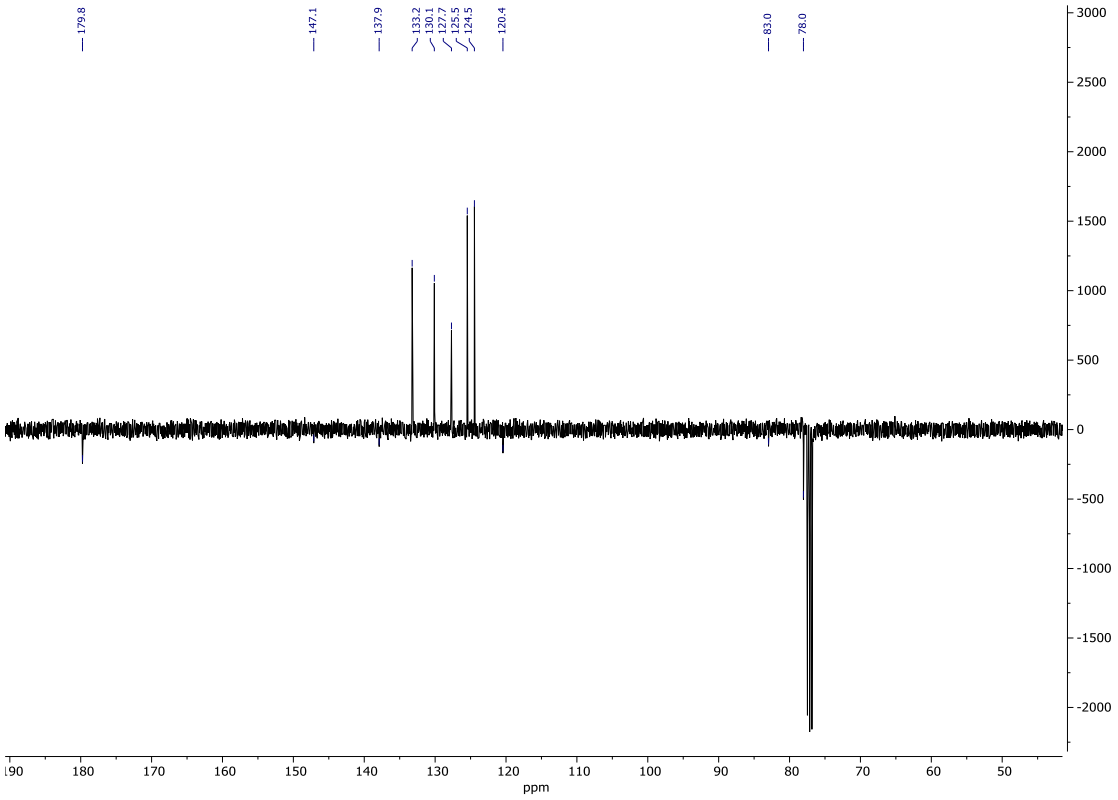
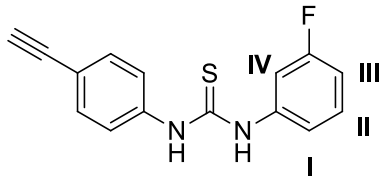


Figure 1.78. ^{13}C APT spectrum of compound **35** in $CDCl_3$ solution.

Synthesis of compound 36

To a solution of 4-ethynylaniline (12 mg, 0.1 mmol) in ethanol/water mixture (1/1), 3-fluorophenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the mixture was stirred for 24 hours. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 46 %



Scheme 1.32. Synthesis of compound **36**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 7.86 (s br, 1H, *NH*); 7.84 (s br, 1H, *NH*); 7.53-7.35 (m, 5H, *arom.+II*); 7.22 (dt, 1H, *IV*, $^3J_{HF}$ = 9.7 Hz, $^4J_{HH}$ = 2.2 Hz); 7.13 (m, 1H, *I*); 6.99 (m, 1H, *III*); 3.12 (s, 1H, *CH*).

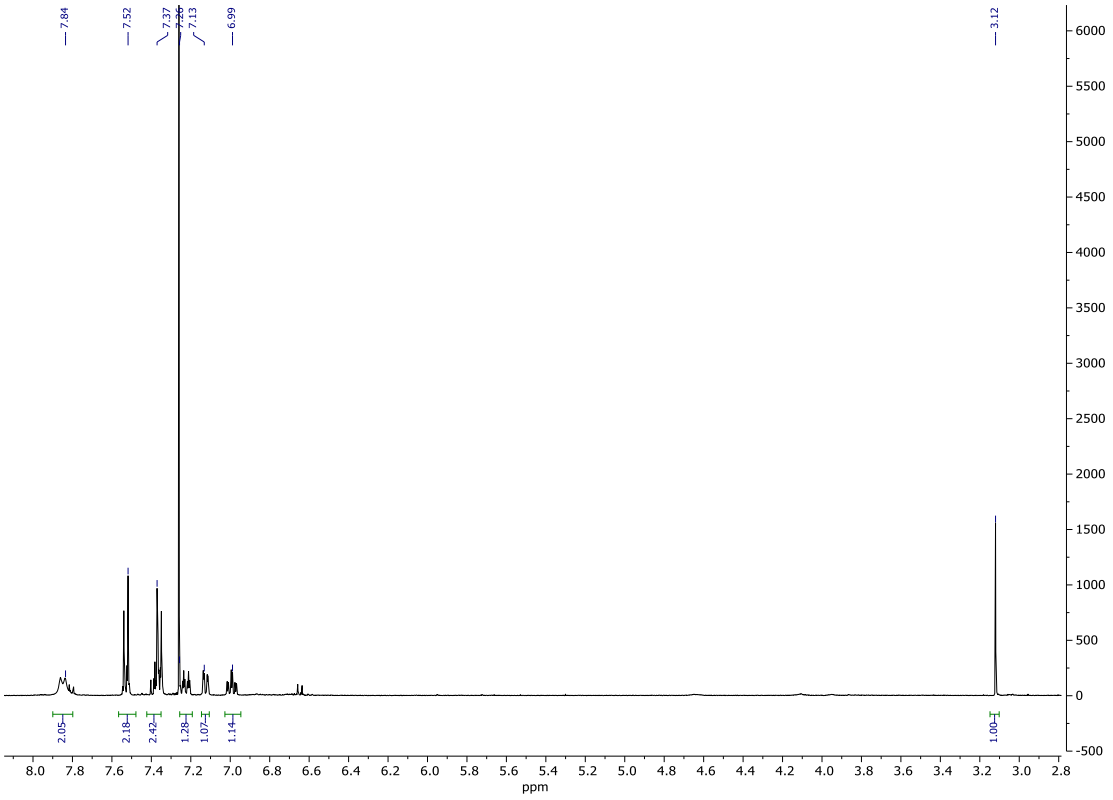


Figure 1.79. ^{1}H NMR spectrum of compound **36** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 179.6 (s, 1C, *C*=*S*); 133.5 (s, 2C, *arom.*); 131.0 (d, 1C, *II*. $^{3}J_{CF}$ = 9.2 Hz); 124.6 (s, 2C, *arom.*); 120.3 (d, 1C, *I*, $^{4}J_{CF}$ = 3.2 Hz); 114.1 (d, 1C, *III*, $^{2}J_{CF}$ = 20.9 Hz); 112.3 (d, 1C, *IV*, $^{2}J_{CF}$ = 24.1 Hz); 78.3 (s, 1C, *CH*).

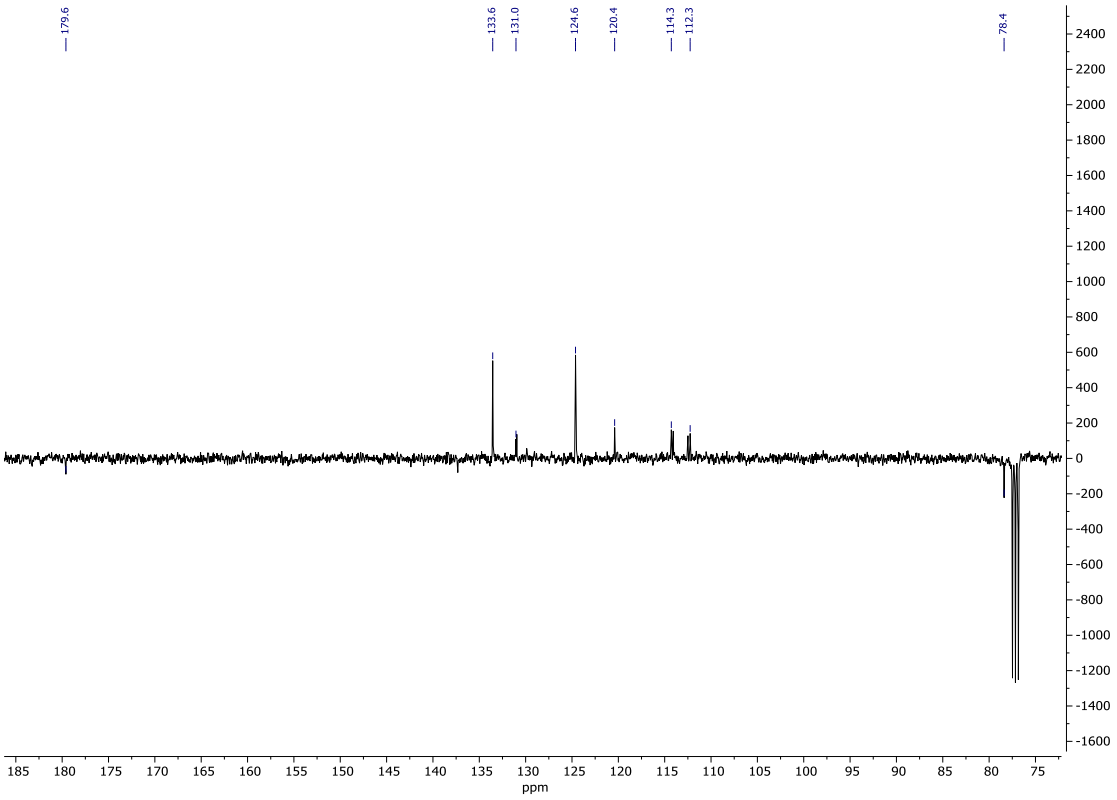
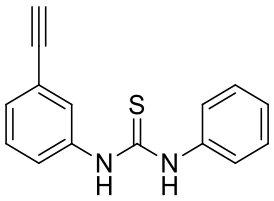


Figure 1.80. ^{13}C APT spectrum of compound **36** in $CDCl_3$ solution.

Synthesis of compound 37

To a solution of 3-ethynylaniline (11.3 µl, 0.1 mmol) in ethanol (10 mL), phenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the mixture was stirred for 24 hours. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 48 %



Scheme 1.33. Synthesis of compound **37**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 8.04 (s br, 1H, *NH*); 7.87 (s br, 1H, *NH*); 7.48-7.34 (m, 9H, *arom.*); 3.11 (s, 1H, *CH*).

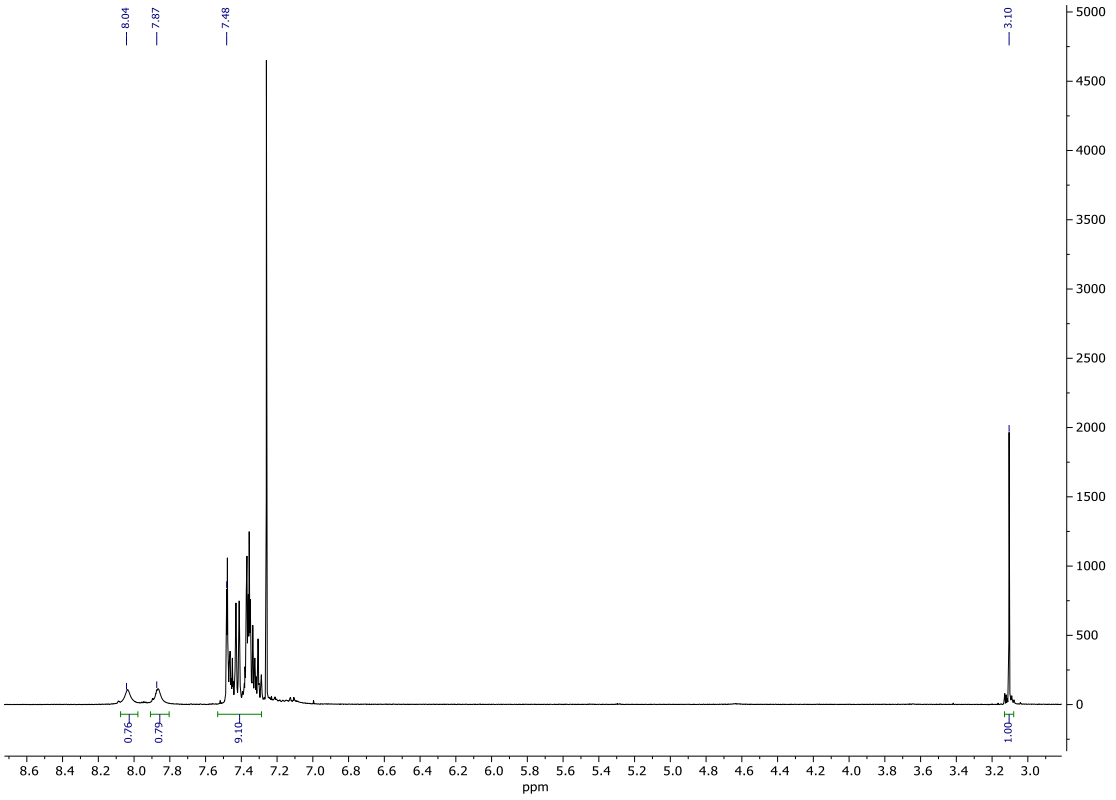


Figure 1.81. ^{1}H NMR spectrum of compound **37** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 138.2 (s, 1C, C_{ipso}); 137.4 (s, 1C, C_{ipso}); 131.1-124.1 (m, 10C, *arom.*); 83.2 (s, 1C, $C \equiv CH$); 79.1 (s, 1C, *CH*).

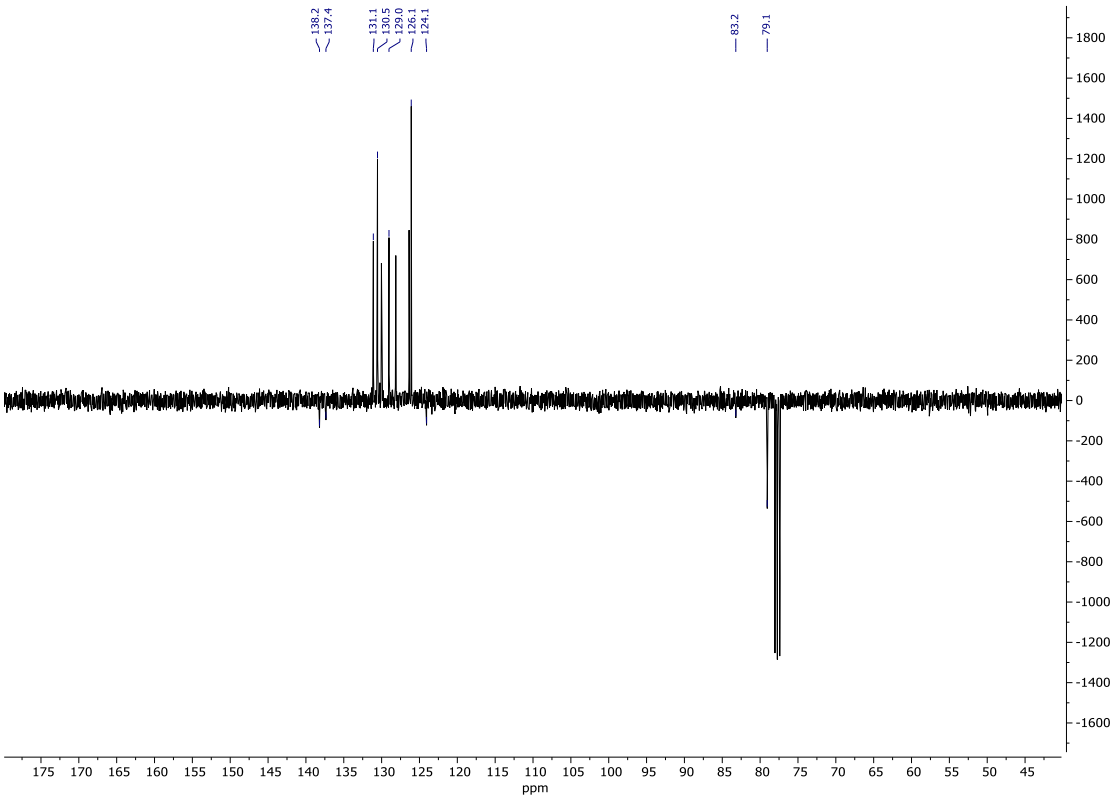
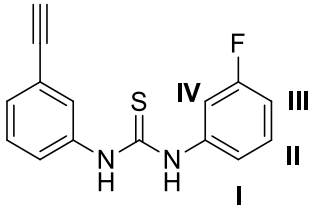


Figure 1.82. ^{13}C APT spectrum of compound **37** in $CDCl_3$ solution.

Synthesis of compound 38

To a solution of 3-ethynylaniline (11.2 µl, 0.1 mmol) in ethanol/water mixture (1/1), 3-fluorophenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the mixture was stirred for 24 hours. A white precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 46 %



Scheme 1.34. Synthesis of compound **38**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 8.06 (s br, 1H, *NH*); 8.04 (s br, 1H, *NH*); 7.46-7.7.33 (m, 5H, *arom.+II*); 7.20 (dt, 1H, *IV*, $^3J_{HF}$ = 9.7 Hz, $^4J_{HH}$ = 2.2 Hz); 7.11 (m, 1H, *I*); 6.98 (m, 1H, *III*); 3.13 (s, 1H, *CH*).

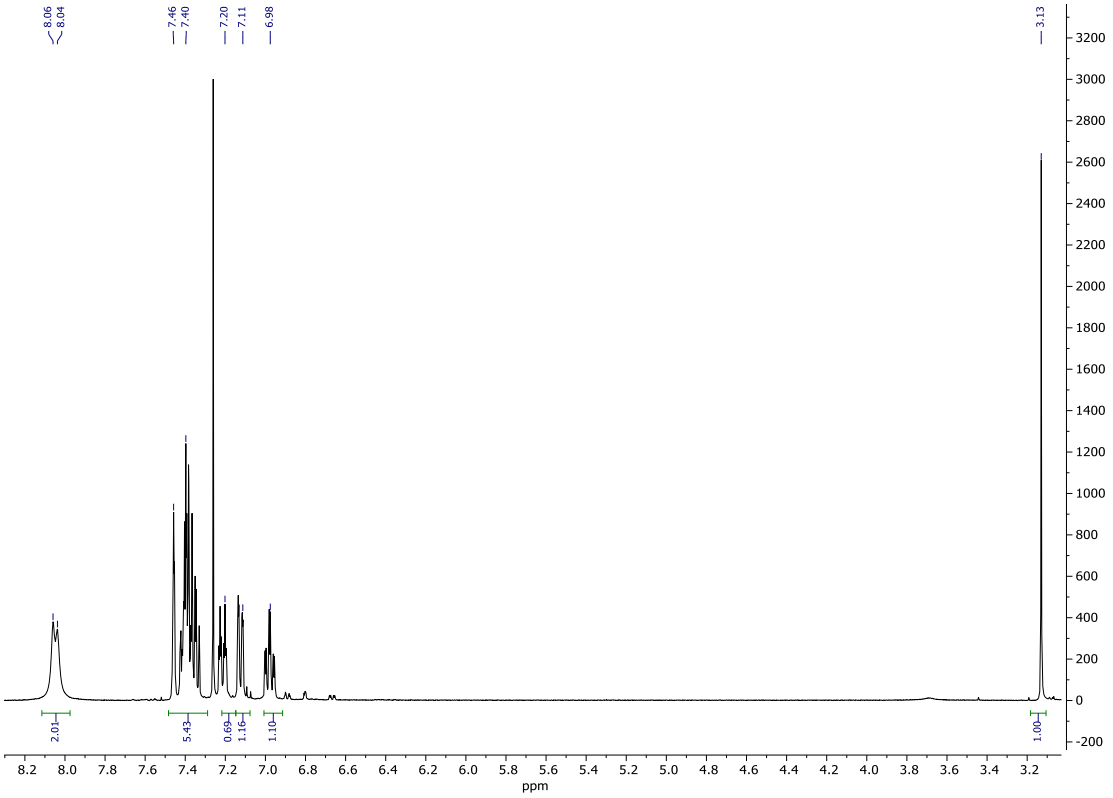


Figure 1.83. ^1H NMR spectrum of compound **38** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 179.8 (s, 1C, *C*=*S*); 163.0 (d, 1C, C_{ipso}Ph-F, $^1J_{CF}$ = 246.6 Hz); 138.6 (d, 1C, C_{ipso}Ph-F, $^3J_{CF}$ = 9.9 Hz); 137.7 (s, 1C, C_{ipso}Ph- $C \equiv CH_2$); 130.9, 129.8, 128.6, 125.9 (s, 4C, *arom.*); 130.8 (d, 1C, *II*. $^3J_{CF}$ = 9.9 Hz); 123.8 (s, 1C, $C \equiv CH$); 120.5 (d, 1C, *I*, $^4J_{CF}$ = 3.1 Hz); 114.1 (d, 1C, *III*, $^2J_{CF}$ = 21.0 Hz); 112.5 (d, 1C, *IV*, $^2J_{CF}$ = 24.0 Hz); 82.4 (s, 1C, $C \equiv CH$); 78.8 (s, 1C, *CH*).

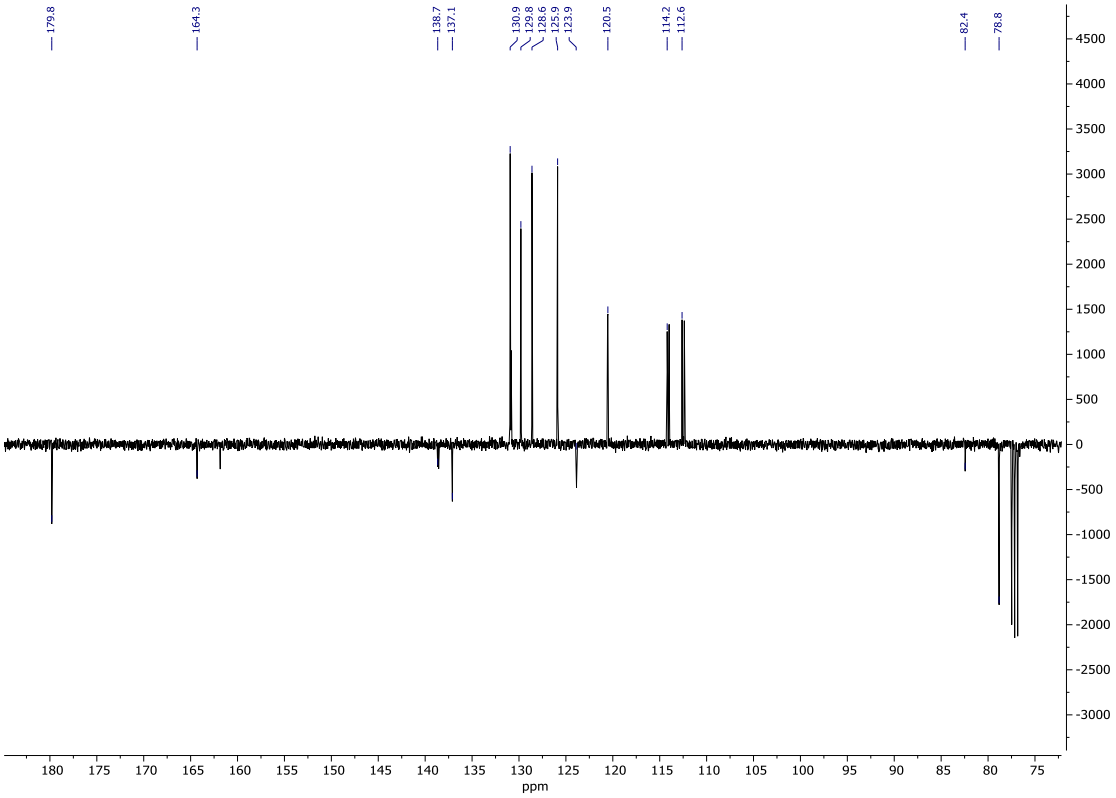
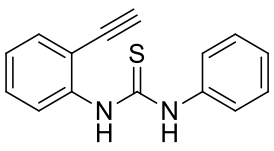


Figure 1.84. ^{13}C APT spectrum of compound **38** in $CDCl_3$ solution.

Synthesis of compound 39

To a solution of 2-ethynylaniline (11.2 µl, 0.1 mmol) in ethanol (10 mL), phenylisothiocyanate was added (12.0 µl, 0.1 mmol) and the mixture was stirred for 24 hours. A brown precipitated was formed which was filtered and vacuum dried to give the product.

Yield: 45 %



Scheme 1.35. Synthesis of compound **39**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 8.79 (s br, 1H, *NH*); 7.65 (s br, 1H, *NH*); 7.79-7.33 (m, 9H, *arom.*); 3.11 (s, 1H, *CH*).

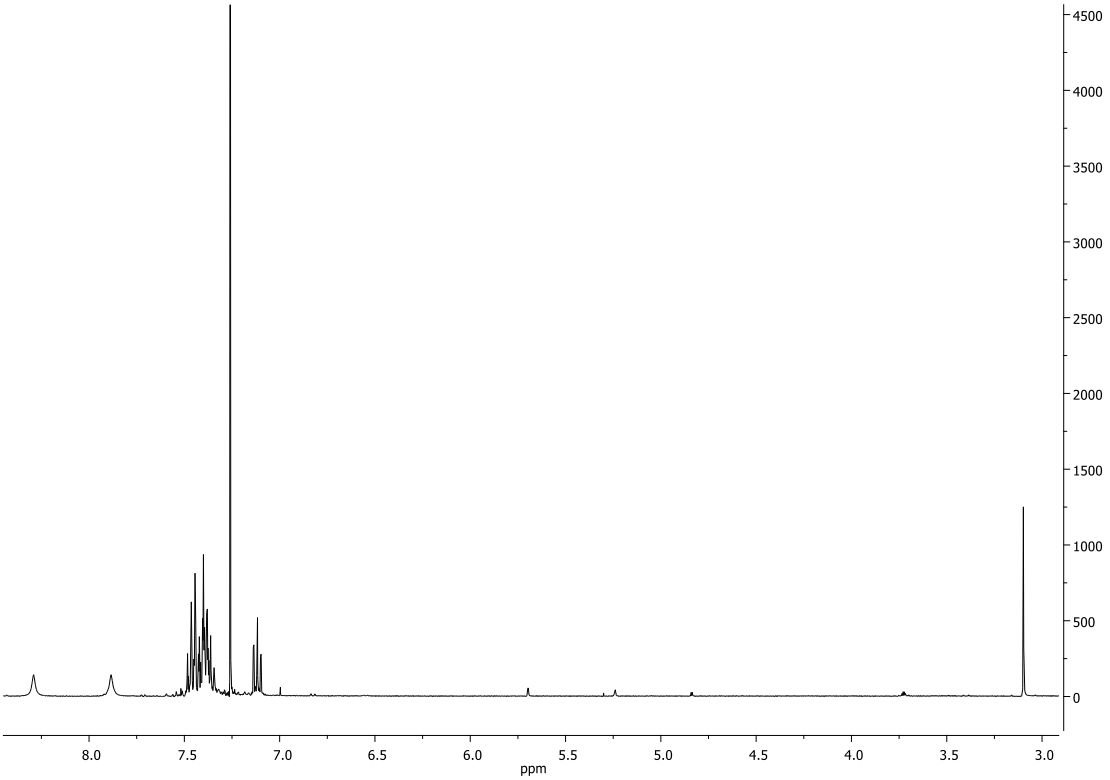


Figure 1.85. ^{1}H NMR spectrum of compound **39** in $CDCl_3$ solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 179.1 (s, 1C, *C*=*S*); 140.0 (s, 1C, C_{ipso}); 136.0 (s, 1C, C_{ipso});132.6-125.1 (m, 10C, *arom.*); 84.4 (s, 1C, $C \equiv CH_2$); 79.0 (s, 1C, *CH*).

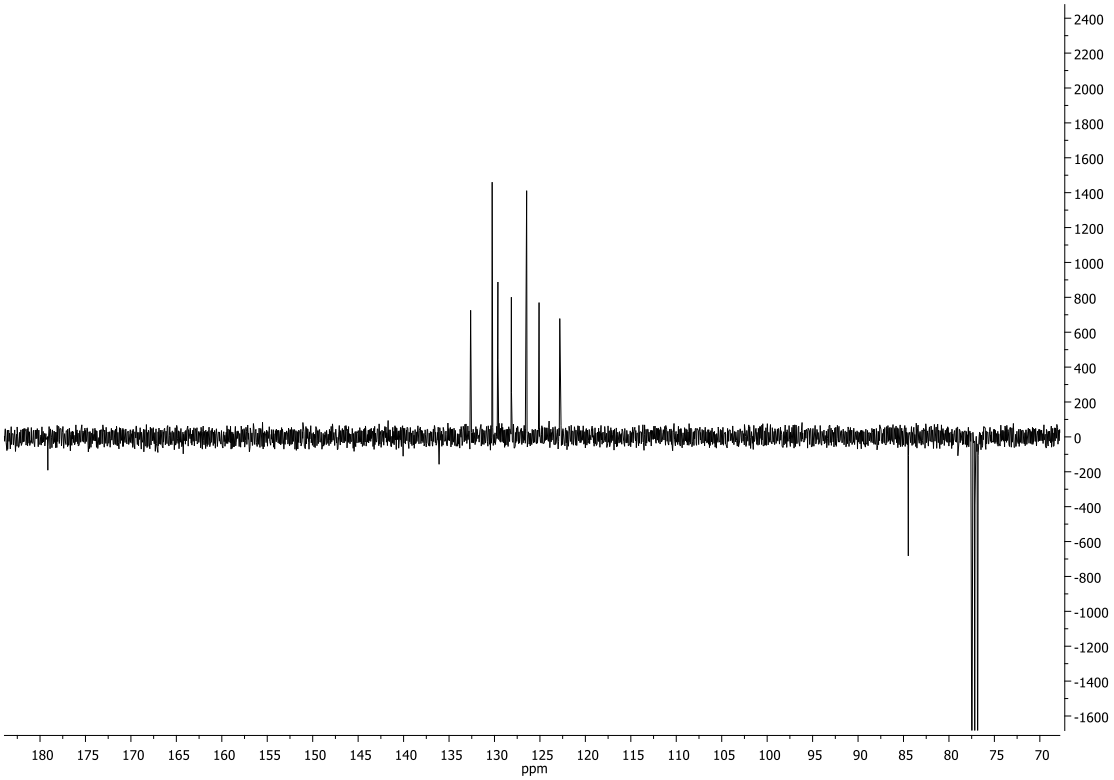
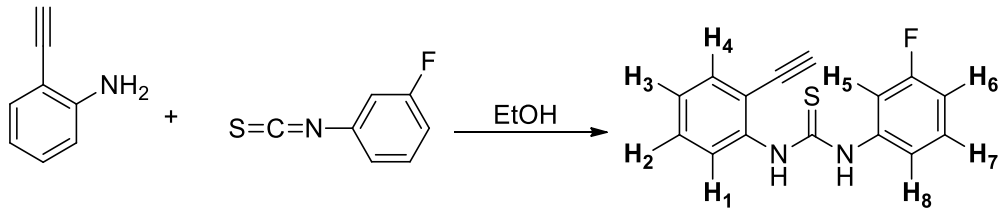


Figure 1.86. ^{13}C APT spectrum of compound **39** in $CDCl_3$ solution.

Synthesis of compound 40

To a solution of 2-ethynylaniline (56.0 µl, 0.5 mmol) and 1-fluoro-3-isothiocyanatobenzene (60.0 µl, 0.5 mmol) were mixed in ethanol (10 ml) and the mixture was stirred for 30 minutes. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 70 %



Scheme 1.36. Synthesis of compound **40**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 8.27 (s, 1H, *H*$_1$); 8.25 (s, 1H, *NH*); 8.07 (s br, 1H, *NH*); 7.52 (d, 1H, *H*$_4$, $^3J_{HH}$ = 7.5 Hz); 7.41 (m, 2H, *H*$_2$ + *H*$_7$); 7.26 (d, 1H, *H*$_5$, $^2J_{HF}$ =

9.8 Hz); 7.19 (m, 2H, $H_3 + H_8$); 7.05 (td, 1H, H_6, $^3J_{HF}$ = 8.4, $^3J_{HH}$ = 2.6 Hz); 3.35 (s, 1H, *CH*).

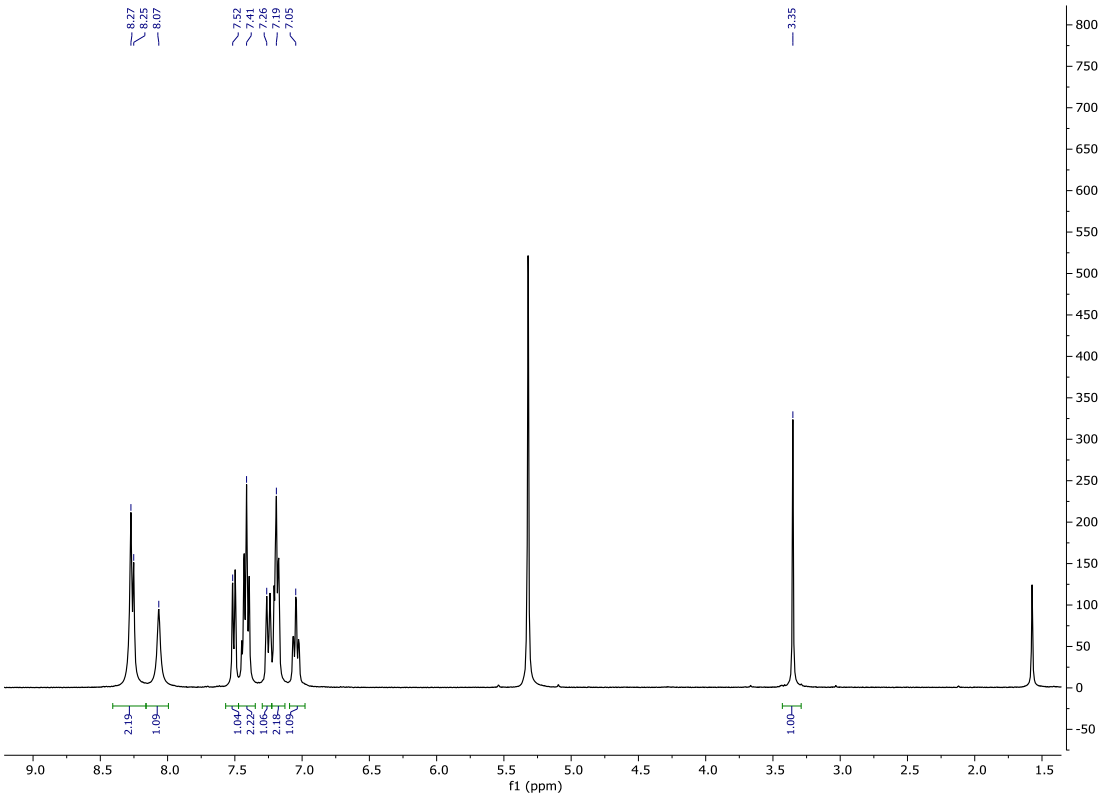


Figure 1.87. ^{1}H NMR spectrum of compound **40** in CD_2Cl_2 solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, CD_2Cl_2): δ = -111.0 (m, 1F, *F*).

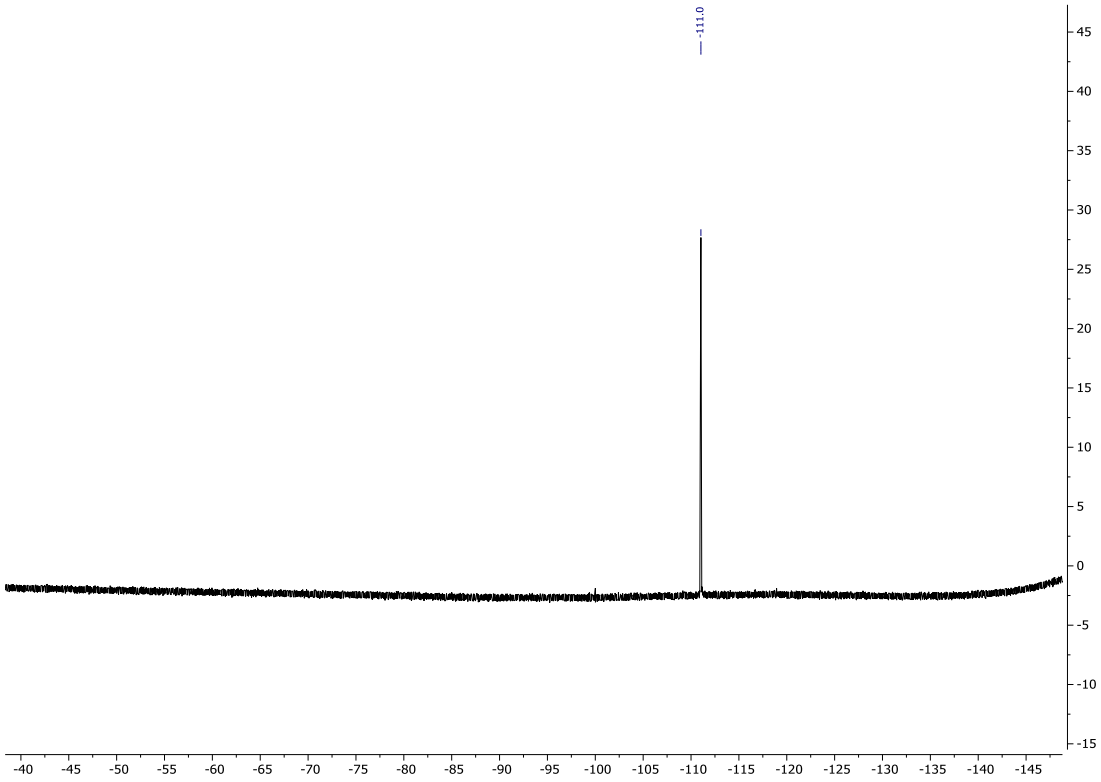


Figure 1.88. $^{19}F\{^{1}H\}$ NMR spectrum of compound **40** in CD_2Cl_2 solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 179.7 (s, 1C. *C*=*S*); 164.9 (d, 1C, C_{ipso}Ph-F, $^{1}J_{CF}$ = 247.7 Hz); 140.2 (s, 1C, C_{ipso}Ph); 138.7 (d, 1C, C_{ipso}Ph-F, $^{3}J_{CF}$ = 9.9 Hz); 133.4 (s, 1C, C_4); 131.7 (d, 1C, C_7, $^{3}J_{CF}$ = 9.3 Hz); 130.1 (s, 1C, C_2); 126.2 (s, 1C, C_3); 124.3 (s, 1C, C_1); 121.7 (d, 1C, C_8, $^{4}J_{CF}$ = 3.2 Hz); 116.3 (s, 1C, C_{ipso}Ph-CCH); 114.7 (d, 1C, C_6, $^{2}J_{CF}$ = 21.1 Hz); 113.4 (d, 1C, C_5, $^{2}J_{CF}$ = 23.7 Hz); 84.9 (s, 1C, $C \equiv CH$);); 79.5 (s, 1C, *CH*).

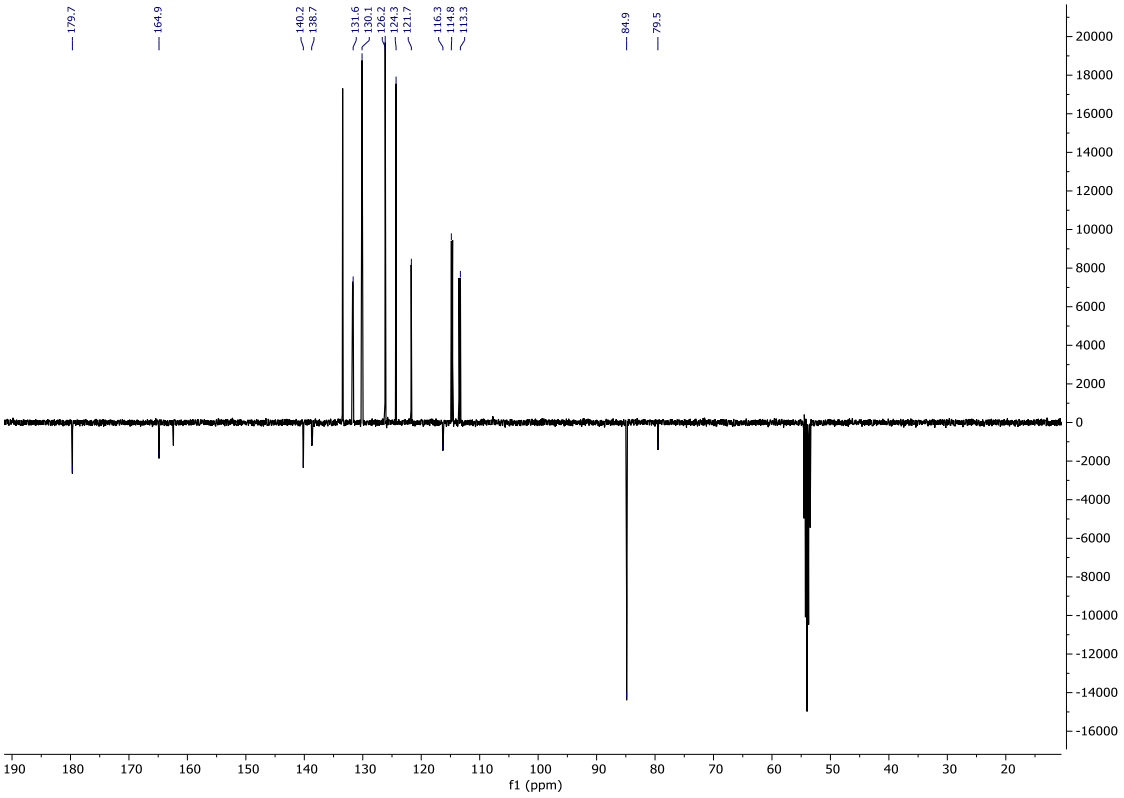
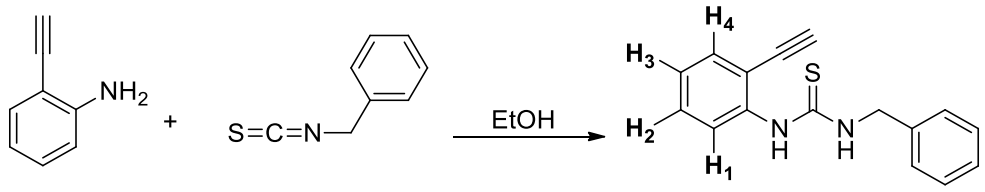


Figure 1.89. ^{13}C APT spectrum of compound **40** in CD_2Cl_2 solution.

Synthesis of compound 41

To a solution of 2-ethynylaniline (56.0 µl, 0.5 mmol) and benzylisocyanate(66.0 µl, 0.5 mmol) were mixed in ethanol (10 ml) and the mixture was stirred for 30 minutes. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 60 %



Scheme 1.37. Synthesis of compound **41**.

^{1}H NMR (ppm) (400 MHz, CD_2Cl_2): δ = 7.81 (s br, *NH*-Ph); 7.55 (d, 1H, H_1, $^3J_{HH}$ = 7.8 Hz); 7.39 (td, 1H, *H4*, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz); 7.34 (m, 5H, *Ph*); 7.29 (m, 1H, H_2),

7.21 (td, 1H, H_3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.1 Hz); 6.40 (s br, 1H, *NH*-CH_2); 4.84 (d, 2H, CH_2, $^3J_{HH}$ = 5.6 Hz); 3.47 (s, 1H, *CH*).

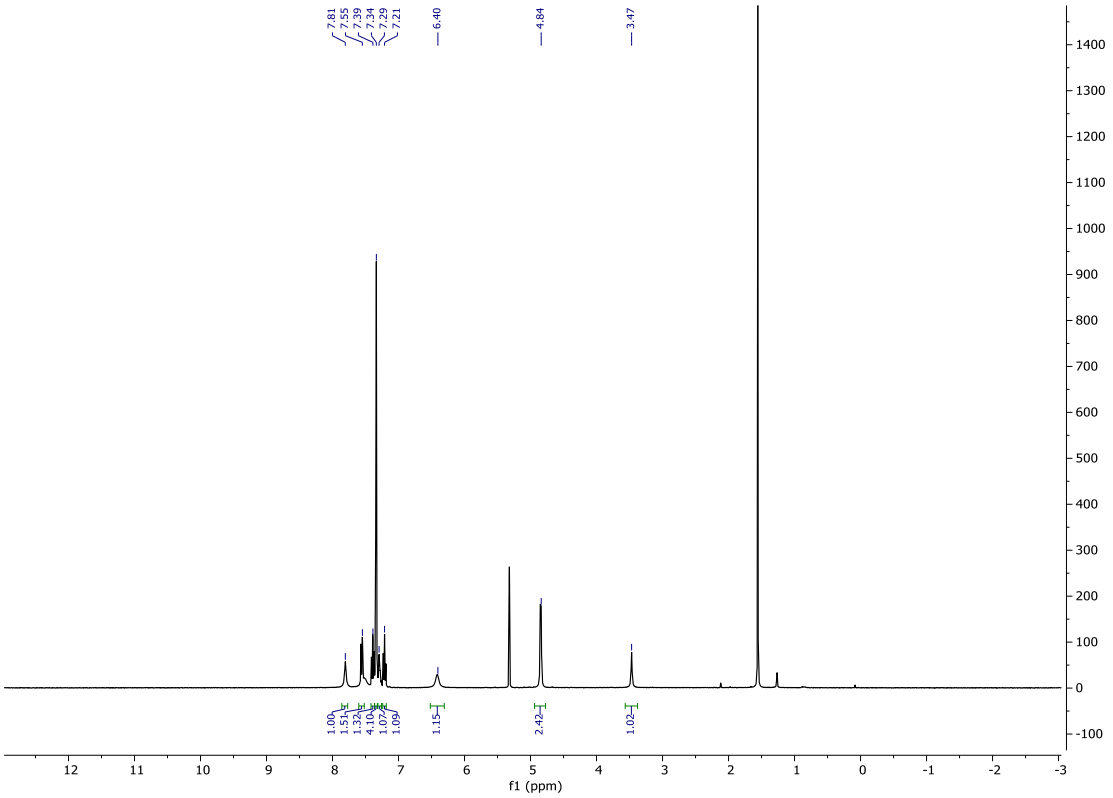


Figure 1.90. ^{1}H NMR spectrum of compound **41** in CD_2Cl_2 solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 181.67 (s, 1C. *C*=*S*); 134.4 (s, 1C, C_4); 130.7 (s, 1C, C_2); 129.3 (s, 2C, C_{ortho}Ph); 128.2 (s, 2C, C_{para}Ph + C_1); 126.8 (s, 1C, C_3); 124.9 (s, 2C, C_{meta}Ph); 84.7 (s, 1C, *CH*); 79.4 (s, 1C, $C \equiv CH$); 49.8 (s, 1C, CH_2).

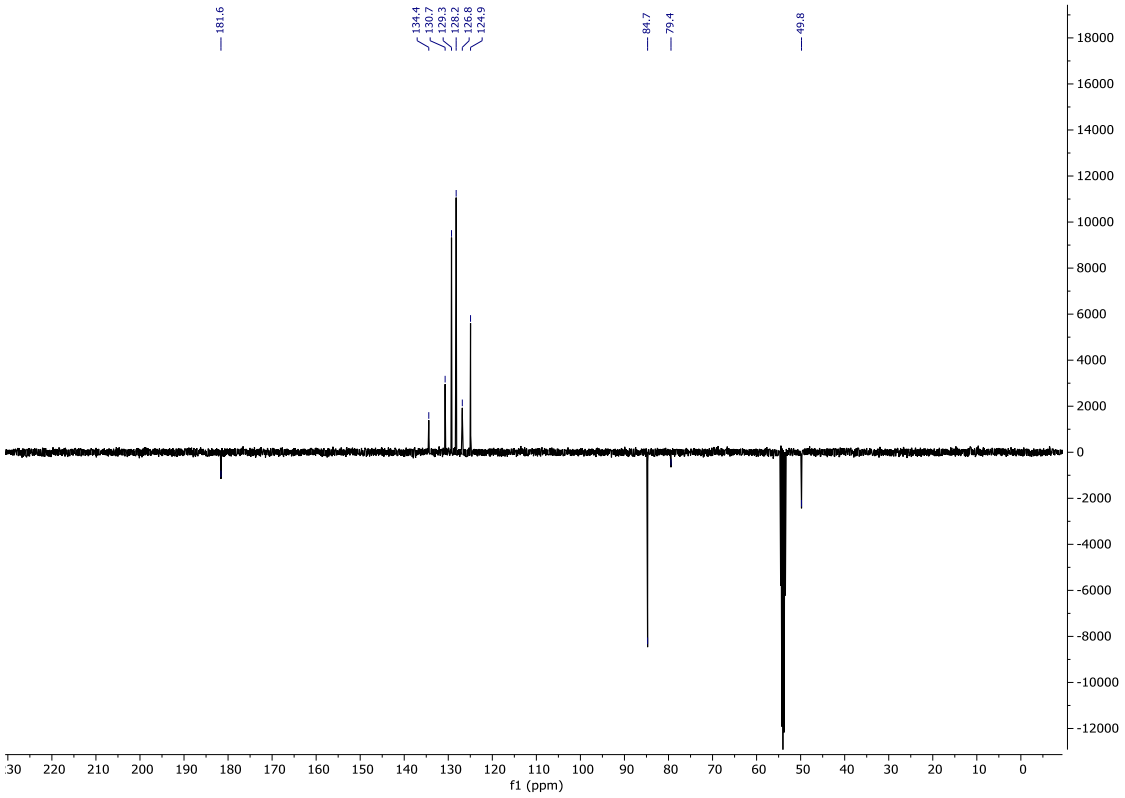
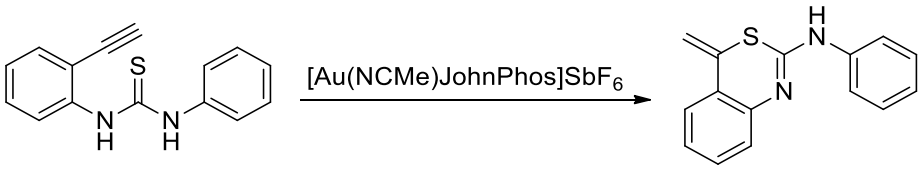


Figure 1.91. ^{13}C APT spectrum of compound **41** in CD_2Cl_2 solution.

Synthesis of compound 44

To a solution of compound **39** (25.2 mg, 0.1 mmol) in ethanol (5 ml), [Au(NCMe)JohnPhos]SbF_6 (2.6 mg, 0.005 mmol) was added and the mixture was stirred for 4 hours. The solution was concentrated under reduced pressure. Dichlorometano was added to solve the compound again (2ml), and hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 99%



Scheme 1.38. Synthesis of compound **44**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.77-7.05 (m, 9H, *arom.*); 5.80 (d, 1H, CH_2, $^2J_{HH}$ = 1.3 Hz); 5.26 (d, 1H, CH_2, $^2J_{HH}$ = 1.3 Hz).

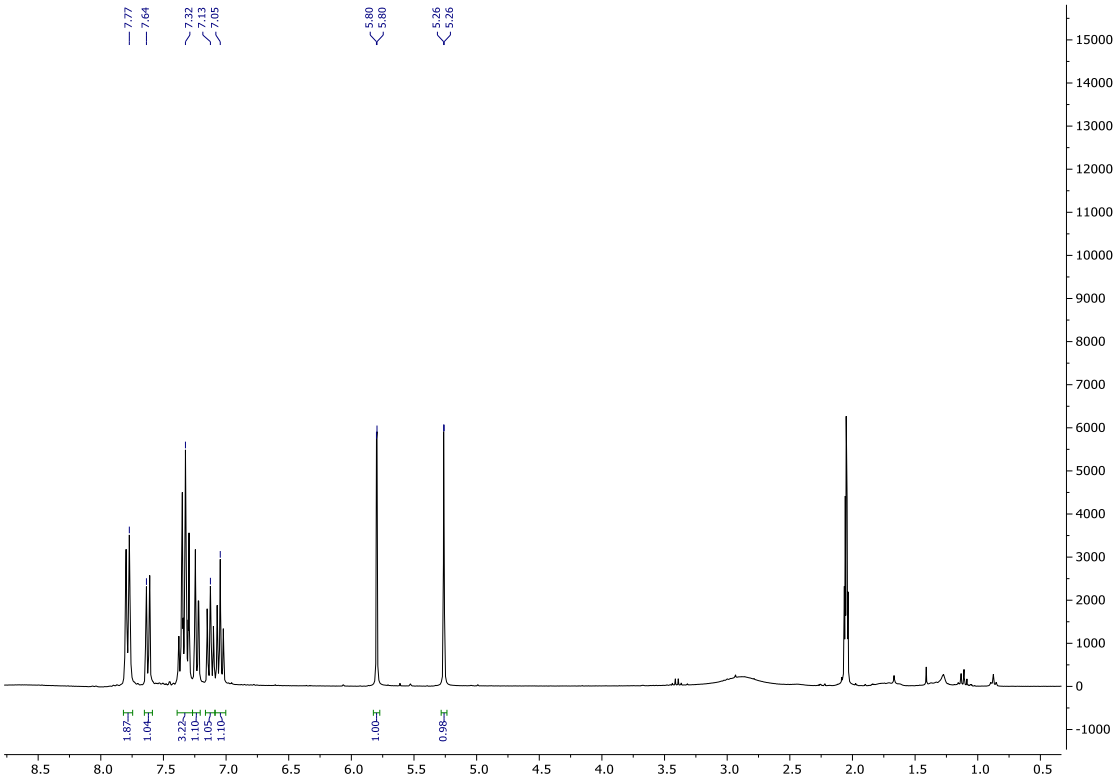


Figure 1.92: ^{1}H NMR spectrum of compound **44** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 131.0-121.1 (s, 9C, *arom*); 111.0 (s, 1C, *CH_2*).

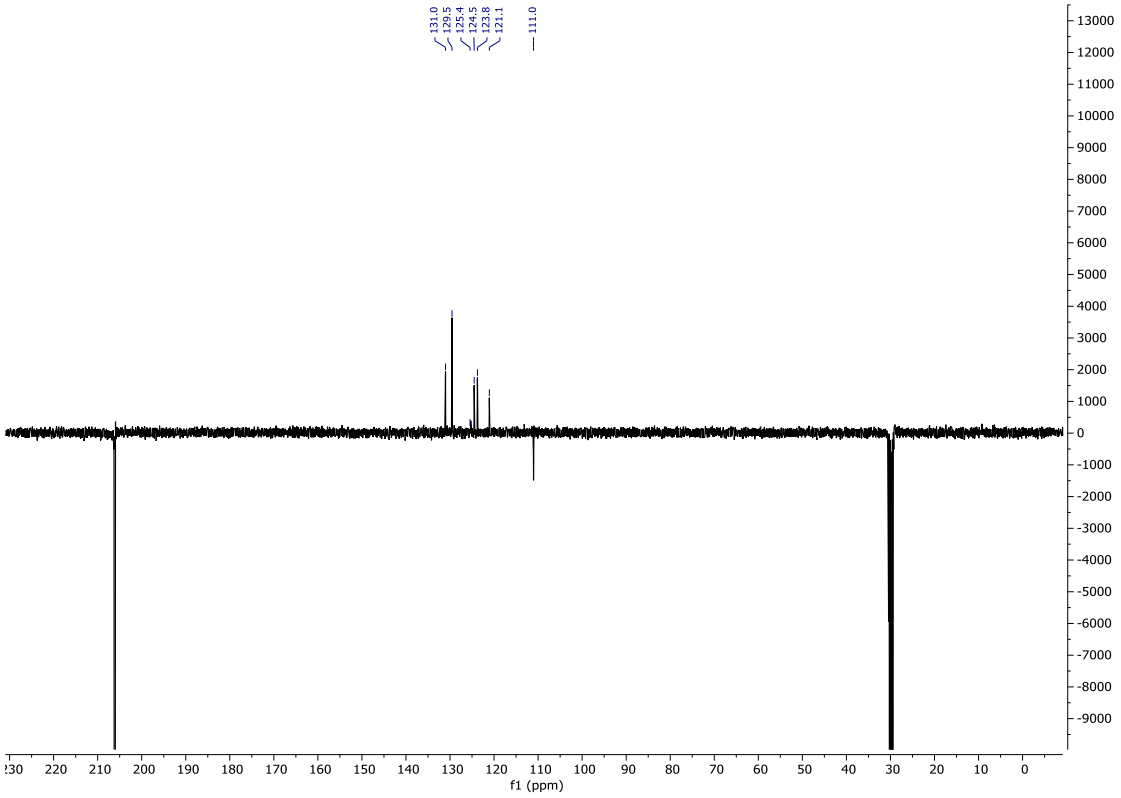
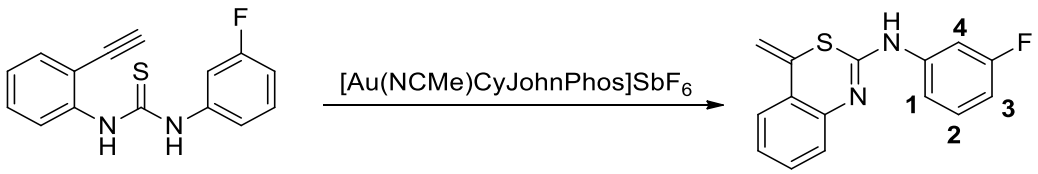


Figure 1.93. ^{13}C APT spectrum of compound **44** in CD_2Cl_2 solution.

Synthesis of compound 45

To a solution of compound **40** (27.0 mg, 0.1 mmol) in ethanol (5 ml), [Au(NCMe)CyJohnPhos]SbF_6 (2.9 mg, 0.005 mmol) was added and the mixture was stirred for 4 hours. The solution was concentrated under reduced pressure. Dichlorometano was added to solve the compound again (2ml), and hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 80 %



Scheme 1.39. Synthesis of compound **45**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.88 (s, 1H, *IV*); 7.66 (m, 6H, *I*+*II*+*arom.*); 6.81 (m, 1H, *III*); 5.83 (d, 1H, CH_2, $^2J_{HH}$ = 1.4 Hz); 5.26 (d, 1H, CH_2, $^2J_{HH}$ = 1.4 Hz).

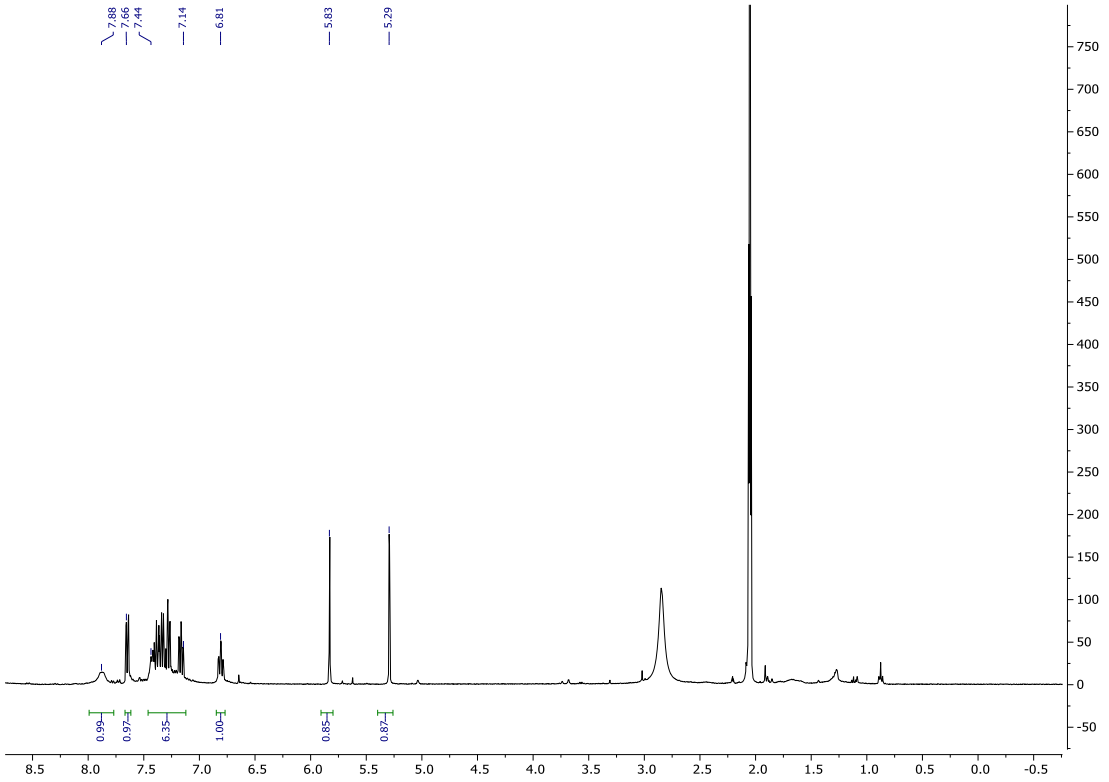


Figure 1.94. ^{1}H NMR spectrum of compound **45** in CD_2Cl_2 solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, CD_2Cl_2): δ = -114.8 (s, 1F, *F*).

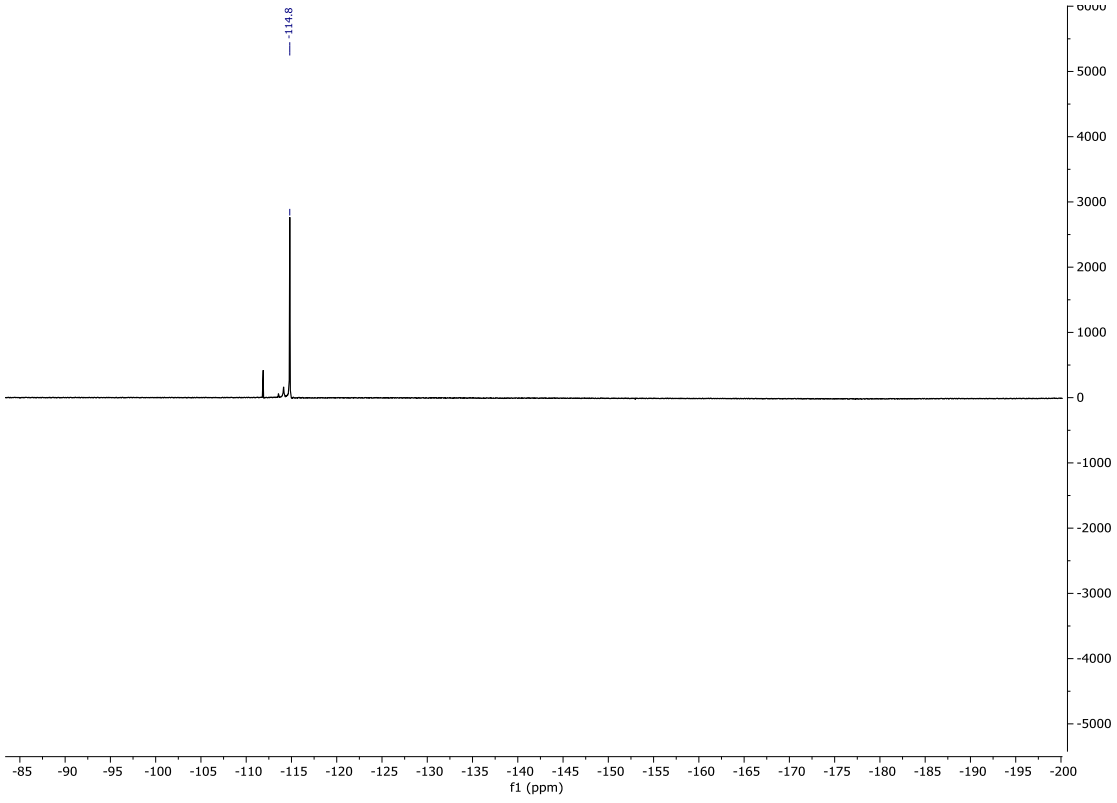


Figure 1.95. ^{19}1{^{1}H} NMR spectrum of compound **45** in CD_2Cl_2 solution.

^{13}C APT (ppm) (100 MHz, CD_2Cl_2): δ = 166.0 (s, 1C, $C_{quaternary}$); 162.6 (s, 1C, $C_{quaternary}$); 149.0 (s, 1C, N=*C*-NH); 142.5 (s, 1C, C_{ipso}Ph-F); 134.9 s, 1C, C_{ipso}Ph-F); 131.1 (s, 1C, *arom.*); 130.1 (d, 1C, *II*, $^3J_{CF}$ = 9.6 Hz); 125.7 (s, 1C, *arom.*); 124.9 (s, 1C, *arom.*); 124.6 (s, 1C, *arom.*); 120.6 (s, 1C, *C*=CH_2); 116.4 (s, 1C, *I*); 114.4 (s, 1C, CH_2); 109.9 (d, 1C, *III*, $^2J_{CF}$ = 21.5 Hz); 107.9 (d, 1C, *IV*, $^2J_{CF}$ = 26.6 Hz)

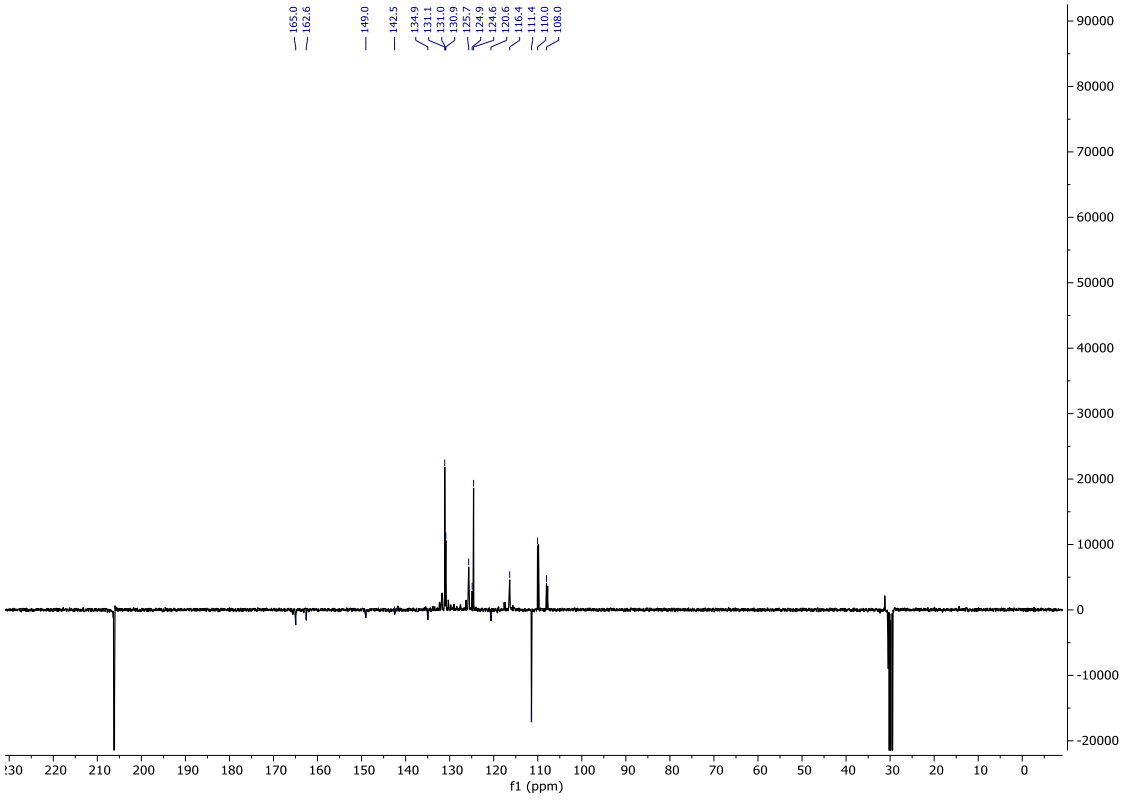
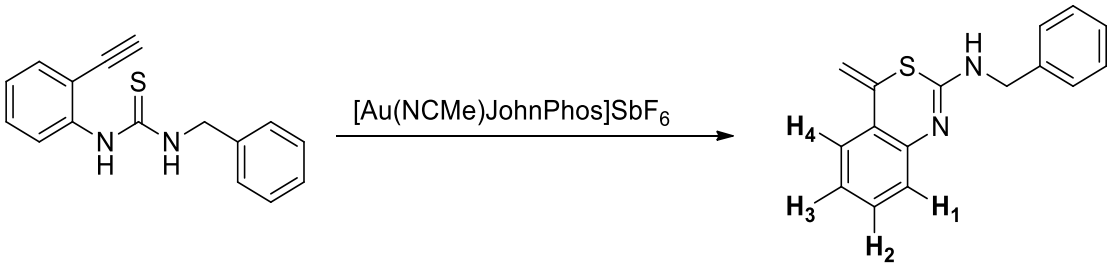


Figure 1.96. ^{13}C APT spectrum of compound **45** in CD_2Cl_2 solution.

Synthesis of compound 46

To a solution of compound **41** (26.6 mg, 0.1 mmol) in ethanol (5 ml), [Au(NCMe)JohnPhos]SbF_6 (2.6 mg, 0.005 mmol) was added and the mixture was stirred for 4 hours. The solution was concentrated under reduced pressure. Dichlorometano was added to solve the compound again (2ml), and hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 99%



Scheme 1.40. Synthesis of compound **46**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 7.58 (dd, 1H, *H*$_1$, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.5 Hz); 7.40 (m, 2H, *H*$_3$ + *NH*); 7.32-7.22 (m, 5H, *Ph*); 7.10 (dd, 1H, *H*$_4$, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.4 Hz); 7.03 (dt, 1H, *H*$_2$, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.4 Hz); 5.73 (d, 1H, *CH*$_2$, $^{2}J_{HH}$ = 1.2 Hz); 5.19 (d, 1H, *CH*$_2$, $^{2}J_{HH}$ = 1.2 Hz); 4.70 (s, 2H, *CH*$_2$-Ph).

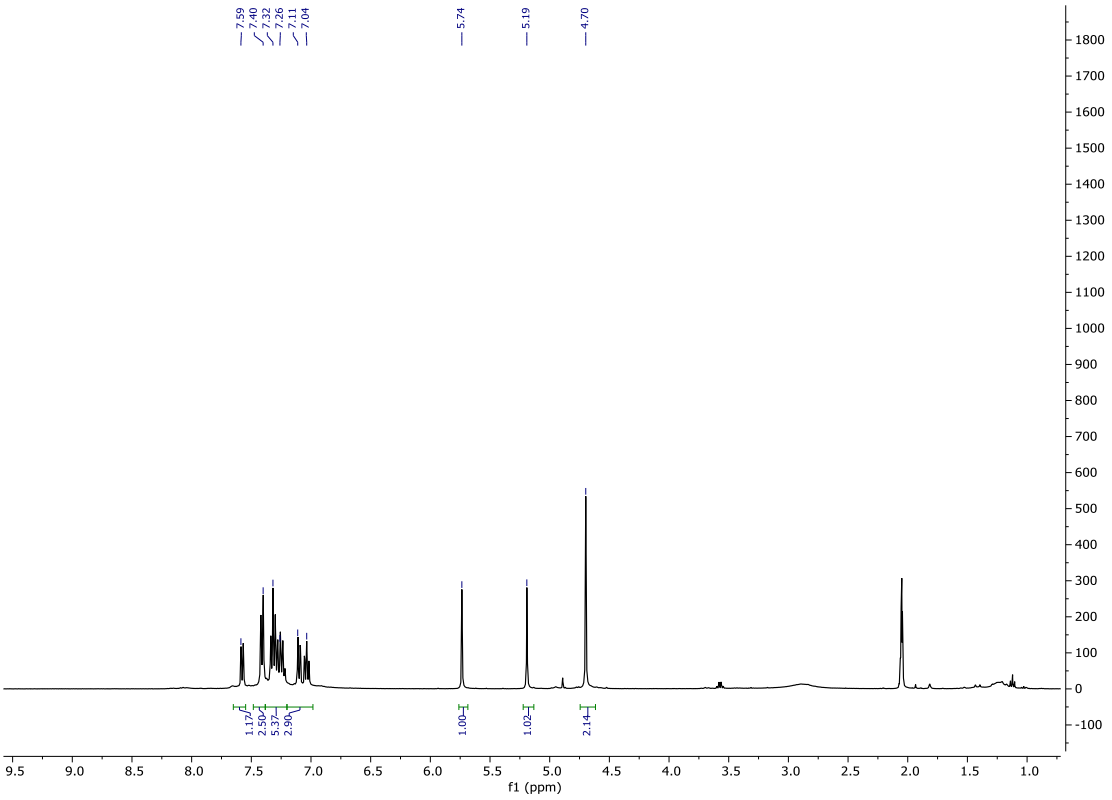


Figure 1.97. ^{1}H NMR spectrum of compound **46** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD)_3CO$): δ = 152.3 (s, 1C, N=*C*-NH); 146.0 (s, 1C, CH_1-*C*-N); 140.4 (s, 1C, *C*$_{ipso}$Ph); 135.9 (s, 1C, CH_4-*C*-C=CH_2); 130.8 (s, 2C, *C*$_{ortho}$Ph); 129.2 (s, 1C, *C*$_{para}$Ph); 128.7 (s, 1C, H_3); 127.8 (s, 2C, *C*$_{meta}$Ph); 127.3 (s, 1C, H_4); 124.3 (d, 2C, H_1+H_2); 120.4 (s, 1C, *C*=CH_2); 109.9 (s, 1C, C=*CH*$_2$); 46.1 (s, 1C, *CH*$_2$-Ph).

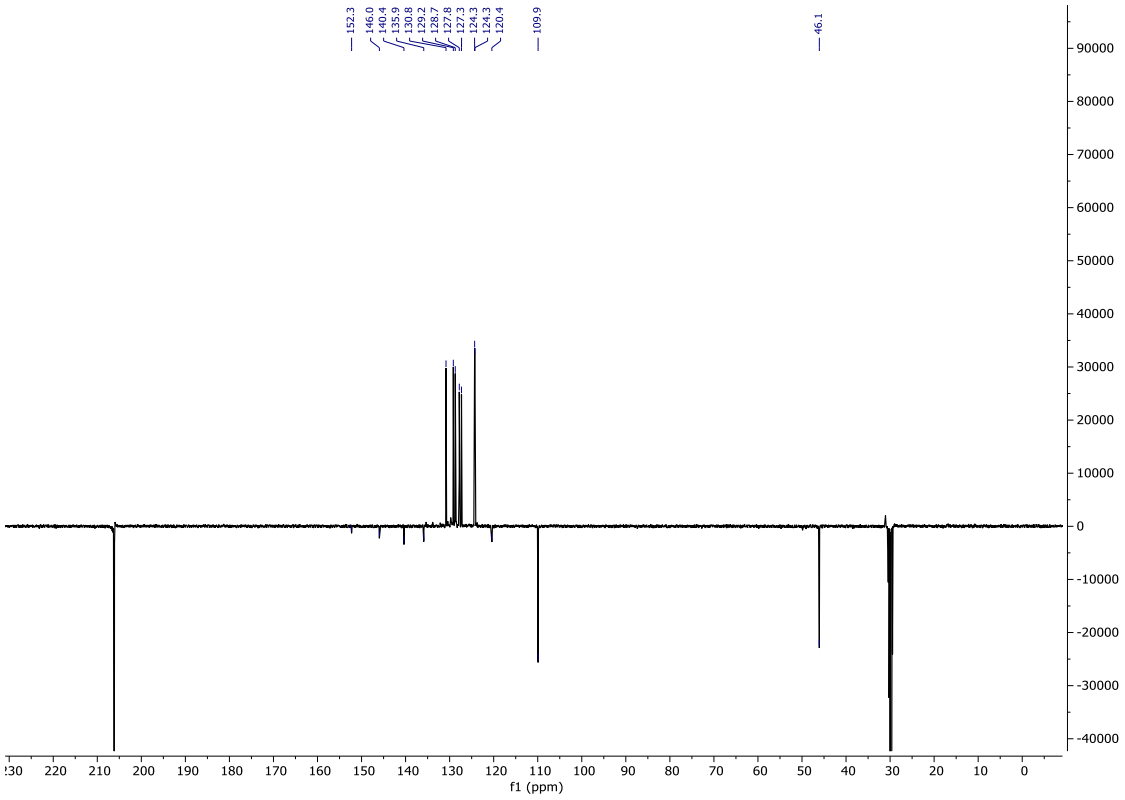


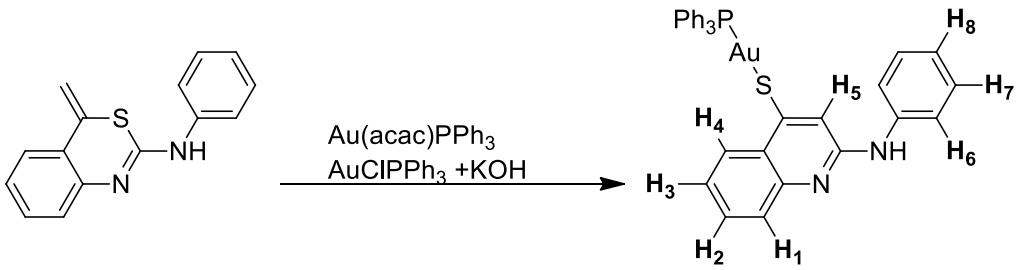
Figure 1.98. ^{13}C APT spectrum of compound **46** in $(CD_3)_2CO$ solution.

Synthesis of compound 47

a) To a solution of compound **44** (25.2 mg, 0.1 mmol) and Au(acac)PPh_3 (55.8 mg, 0.1 mmol) were mixed in CH_2Cl_2 (10 ml) and the mixture stirred 4h. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a light brown product which was collected and vacuum dried to give the product.

b) To a solution of compound **44** (25.2 mg, 0.1 mmol) and Au$ClPPh_3$ (49.5 mg, 0.1 mmol) were mixed in MeOH (20 ml) was added an excess of KOH (0.3 mmol, 16.8 mg) and the mixture stirred 5h. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a light brown product which was collected and vacuum dried to give the product.

Yield: 50%



Scheme 1.41. Synthesis of compound **47**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 8.53 (d, 1H, *H*$_4$, $^{3}J_{HH}$ = 8.0 Hz); 8.13 (s, 1H, *NH*); 7.90 (m, 2H, *H*$_6$); 7.59 (m, 16H, *PPh*$_3$ + *H*$_1$ + *H*$_5$); 7.51 (t, 1H, *H*$_2$, $^{3}J_{HH}$ = 8.0 Hz); 7.21 (m, 3H, *H*$_3$ + *H*$_7$); 6.88 (t, 1H, *H*$_8$, $^{3}J_{HH}$ = 7.3 Hz).

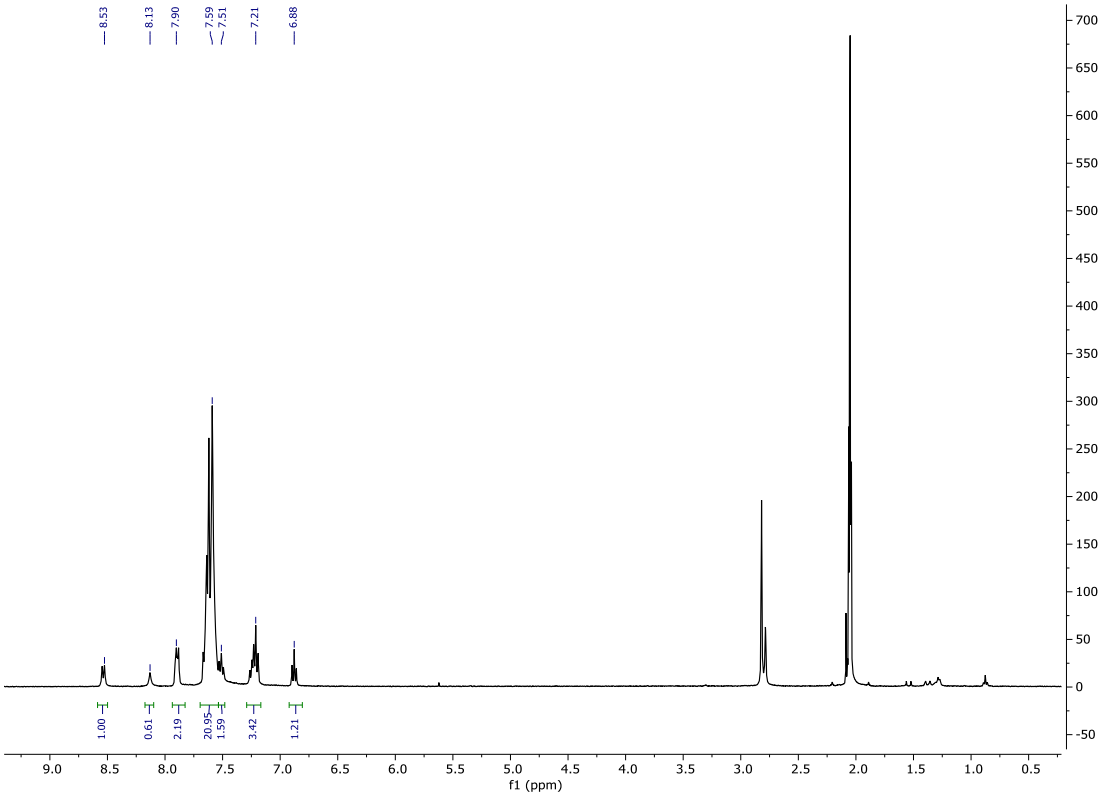


Figure 1.99. ^{1}H NMR spectrum of compound **47** in CD_2Cl_2 solution.

^{31}P{^{1}H} NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = 38.5 (s, 1P, *PPh*$_3$).

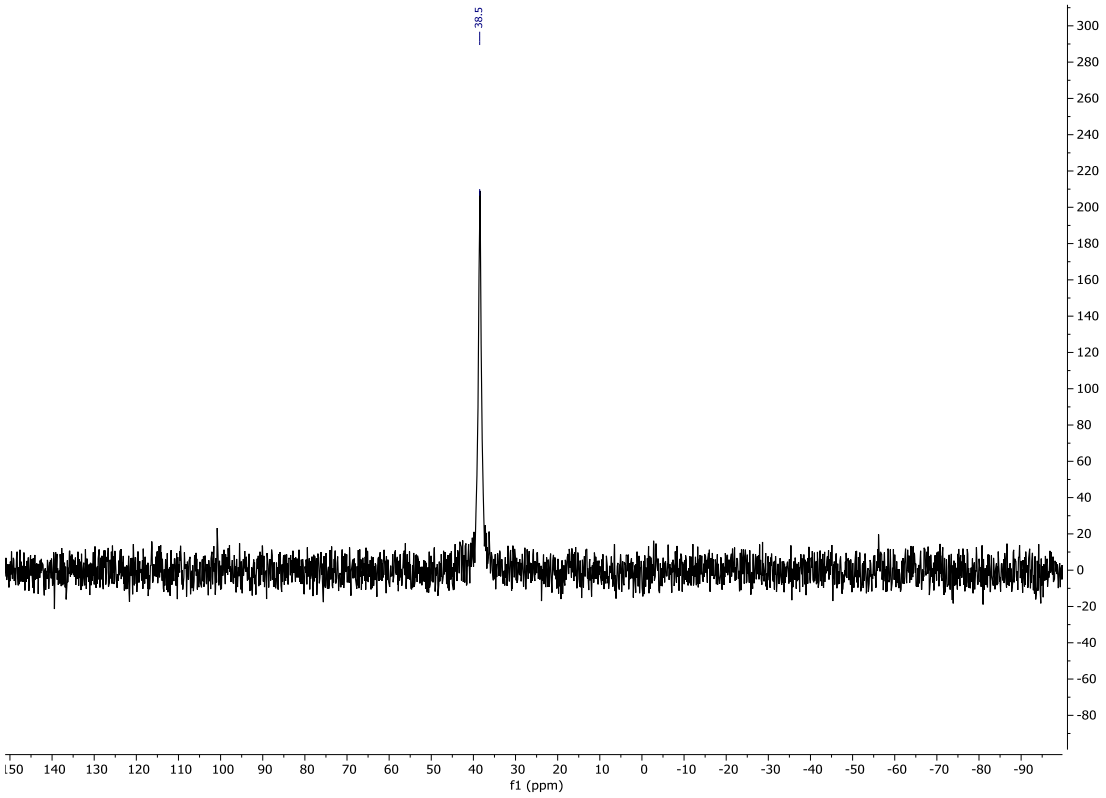


Figure 1.100. $^{31}P\{^{1}H\}$ NMR spectrum of compound **47** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 154.2, 148.6 142.9 (s, 3C, $C_{quaternary}$); 135.1 (d, 6C, $C_{ortho}PPh_3$, $^{2}J_{CP}$ = 13.8 Hz); 133.0 (d, 3C, $C_{para}PPh_3$, $^{4}J_{CP}$ = 1.8 Hz); 130.5 (d, 6C, $C_{meta}PPh_3$, $^{3}J_{CP}$ = 11.5 Hz); 129.8 (s, 1C, C_2); 129.8 (s, 3C, $C_{ipso}PPh_3$); 129.4 (s, 1C, C_7); 128.1 (s, 1C, C_1); 127.3 (s, 1C, C_4); 122.8 (s, 1C, C_3); 121.8 (s, 1C, C_8); 119.7 (s, 1C, C_6); 116.9 (s, 1C, C_5).

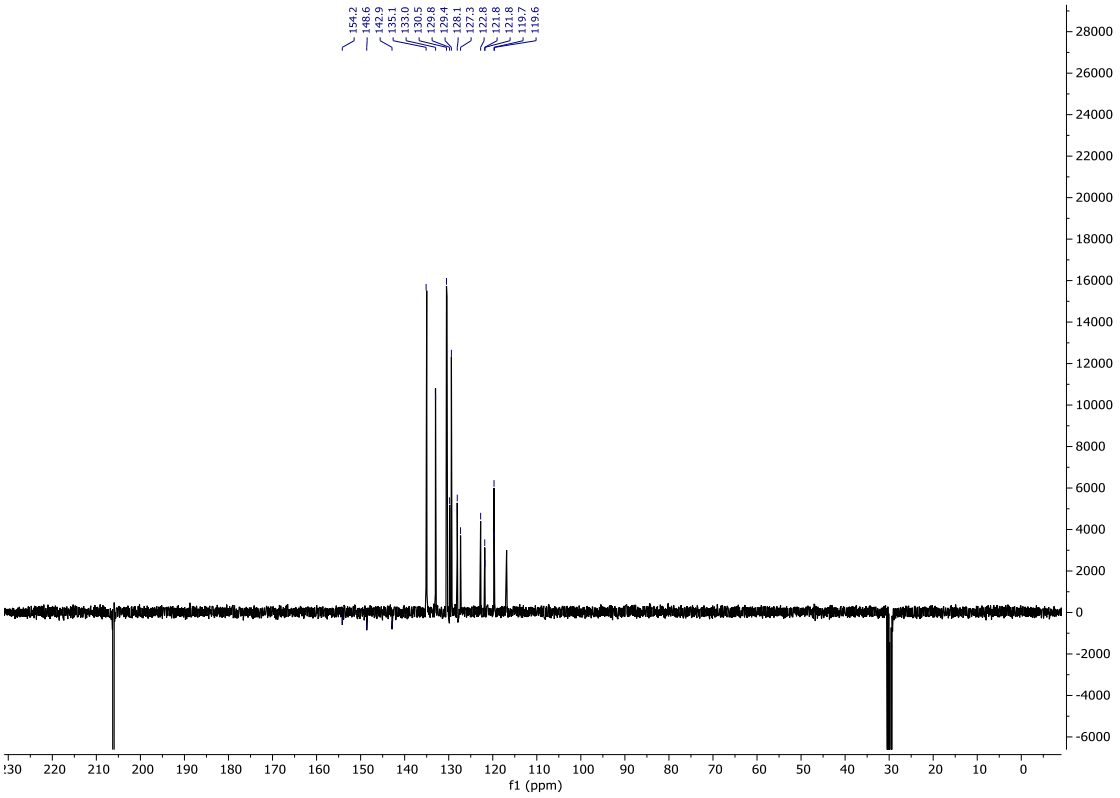


Figure 1.101. ^{13}C APT spectrum of compound **47** in CD_2Cl_2 solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{33}H_{27}AuN_2PS]^+$ 711.1293. Found 711.1261

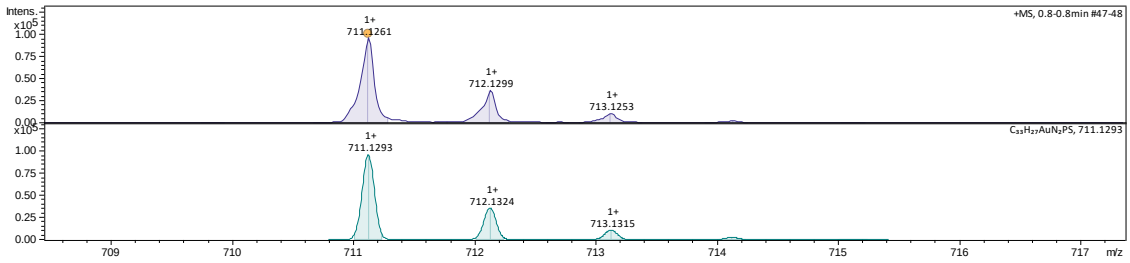
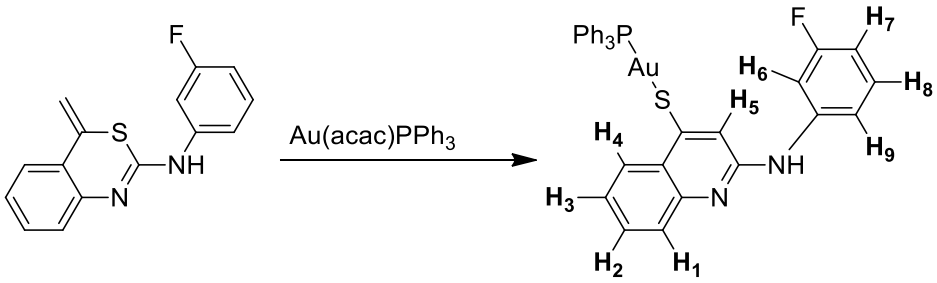


Figure 1.102. MS (ESI+ µ-TOF) compound **47**.

Synthesis of compound 48

To a solution of compound **45** (27.3 mg, 0.1 mmol) and $Au(acac)PPh_3$ (55.8 mg, 0.1 mmol) were mixed in CH_2Cl_2 (10 ml) and the mixture stirred 4h. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a light brown product which was collected and vacuum dried to give the product.

Yield: -%



Scheme 1.42. Synthesis of compound **48**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 8.54 (d, 1H, *H*$_4$, $^{3}J_{HH}$ = 8.8 Hz); 8.47(s br, 1H, *NH*); 8.27 (d, 1H, *H*$_6$, $^{3}J_{HF}$ = 14.3 Hz); 7.70 (d, 1H, *H*$_1$, $^{3}J_{HH}$ = 8.2 Hz); 7.56-7.45 (m, 18H, *PPh*$_3$ + *H*$_2$ + *H*$_8$ + *H*$_9$); 7.22 (m, 1H, *H*$_3$); 6.63 (m, 1H, *H*$_7$).

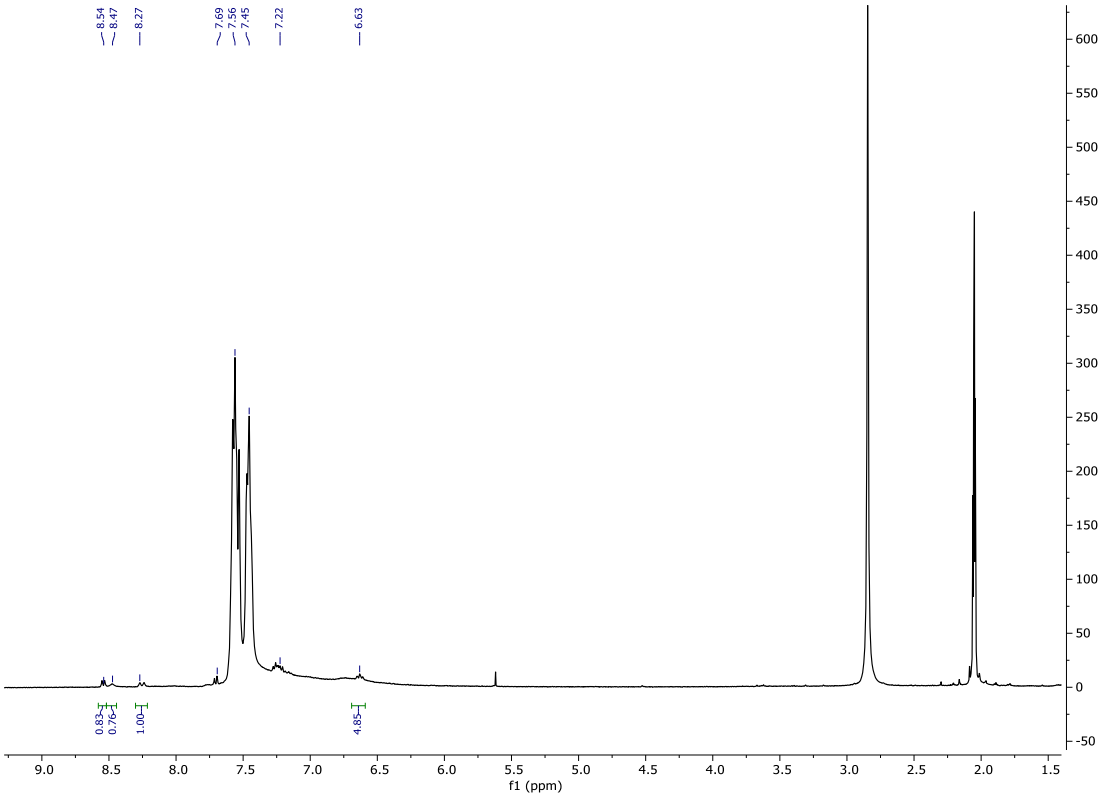


Figure 103. ^{1}H NMR spectrum of compound **48** in $(CD_3)_2CO$ solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, $(CD_3)_2CO$): δ = -115.1 (s, 1F, *F*).

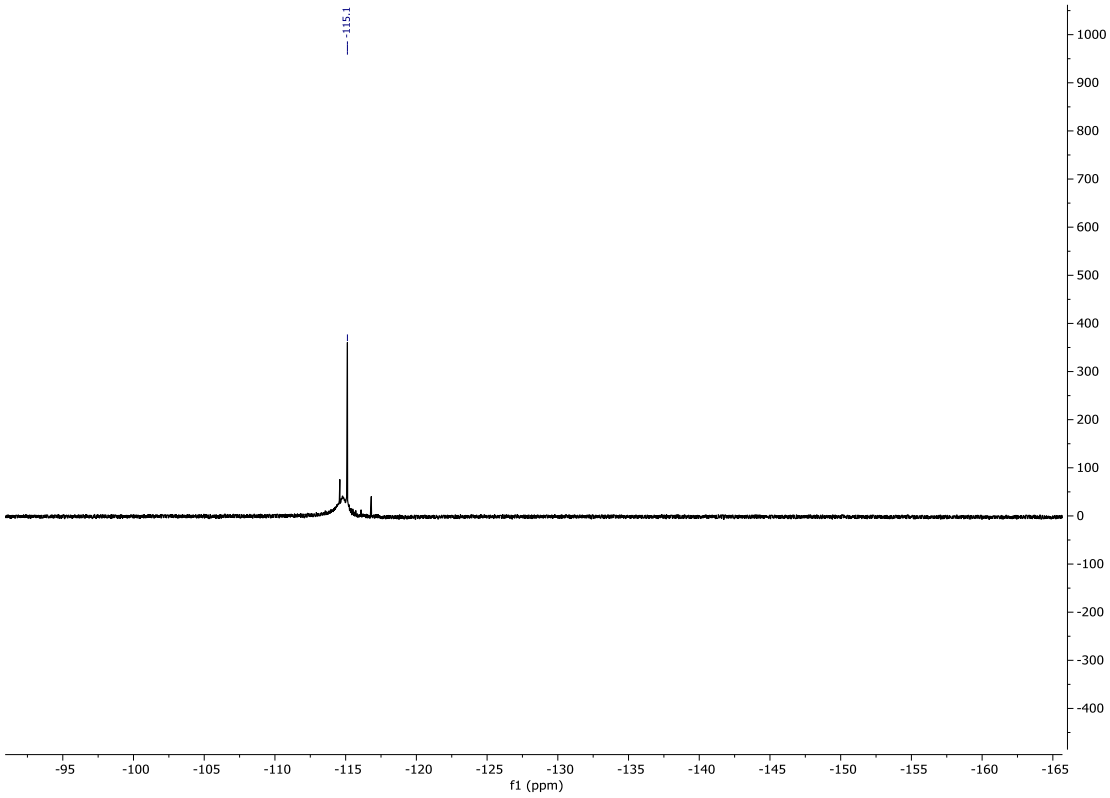


Figure 104.: ^{19}F $\{^{1}H\}$ NMR spectrum of compound **48** in $(CD_3)_2CO$ solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, $(CD_3)_2CO$): δ = 34.1 (s, 1P, *PPh_3*).

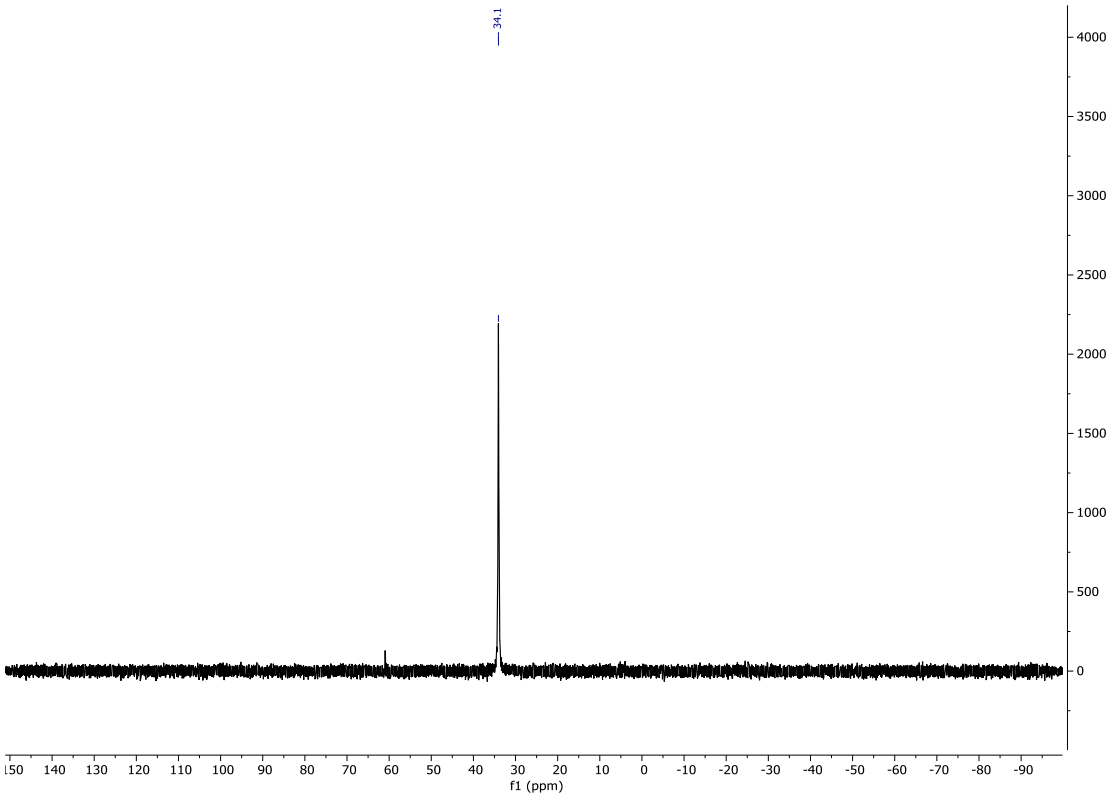


Figure 105.: ^{31}P $\{^{1}H\}$ NMR spectrum of compound **48** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 135.0 (d, 6C, $C_{ortho}PPh_3$, $^2J_{CP}$ = 13.8 Hz); 133.0 (d, 3C, $C_{para}PPh_3$, $^4J_{CP}$ = 2.6 Hz); 130.4 (d, 6C, $C_{meta}PPh_3$, $^3J_{CP}$ = 11.7 Hz); 129.9 (s, 1C, C_2); 129.8 (s, 3C, $C_{ipso}PPh_3$); 128.2 (s, 1C, C_1); 127.4 (s, 1C, C_4); 123.1 (s, 1C, C_3); 117.4 (s, 1C, C_8); 114.9 (s, 1C, C_9); 107.4 (d, 1C, C_7, $^2J_{CF}$ = 21.6 Hz); 106.3 (d, 1C, C_6, $^2J_{CF}$ = 27.5 Hz).

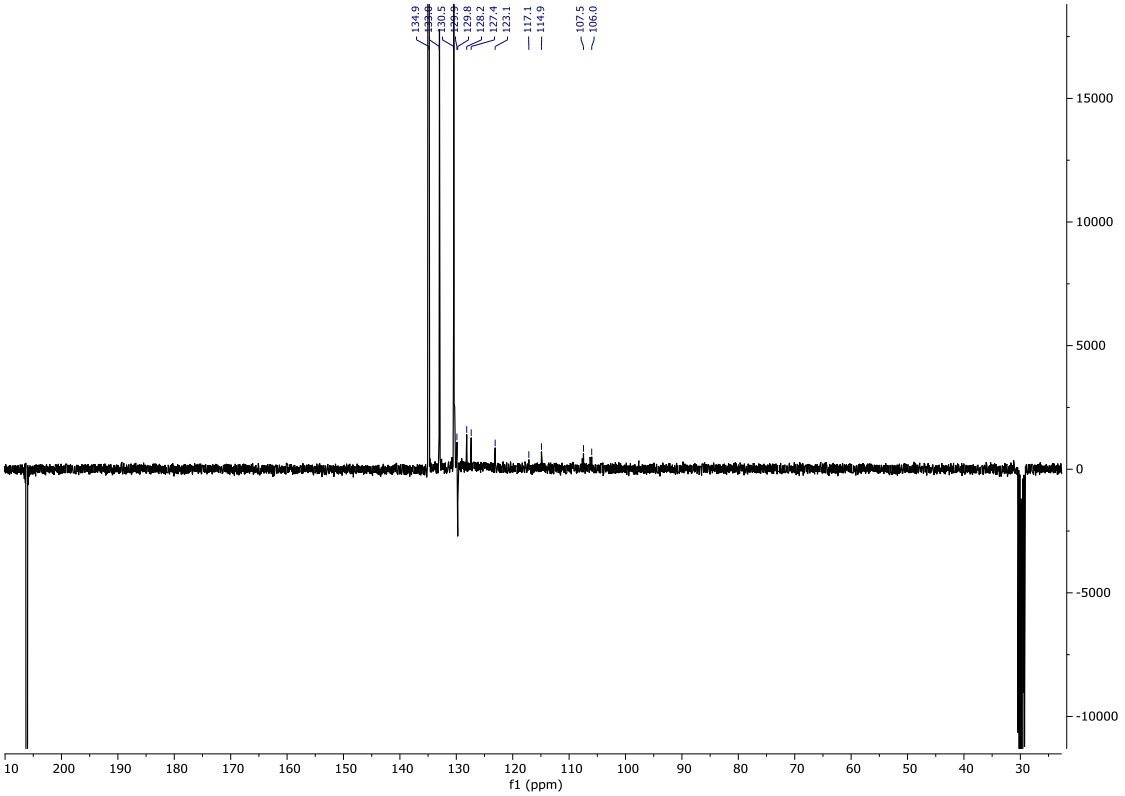


Figure 106. ^{13}C APT spectrum of compound **48** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{36}H_{30}AuP_2]^+$ 721.149. Found 721.1445; $[M]^+$ Calcd for $[C_{33}H_{26}AuFN_2PS]^+$ 729.1199. Found 729.1170; Calcd for $[C_{54}H_{46}Au_3P_3S]^+$ 1410.829. Found 1409.1120.

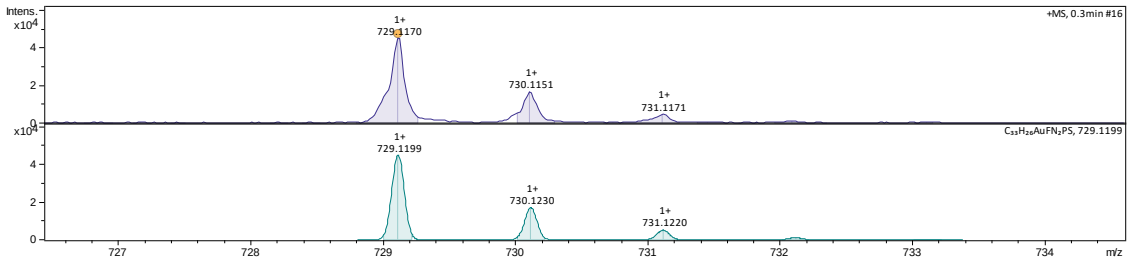


Figure1.107. MS (ESI+ µ-TOF) compound **48**.

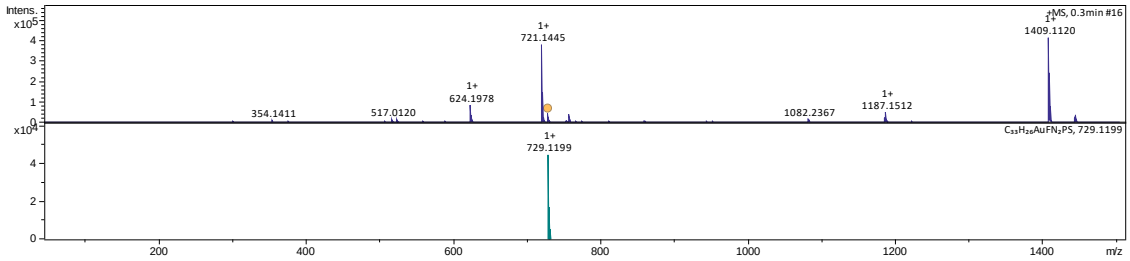
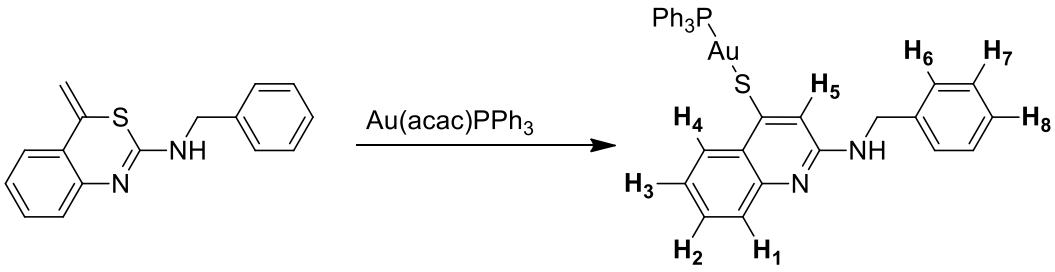


Figure1.108. MS (ESI+ µ-TOF) compound **48**.

Synthesis of compound 49

To a solution of compound **46** (26.6 mg, 0.1 mmol) and Au(acac)PPh_3 (55.8 mg, 0.1 mmol) were mixed in CH_2Cl_2 (10 ml) and the mixture stirred 4h. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a light brown product which was collected and vacuum dried to give the product.

Yield: -%



Scheme 1.43. Synthesis of compound **47**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 8.45 (d, 1H, *H_4*, *$^3J_{HH}$* = 8.0 Hz); 7.49-7.14 (m, 24H, *PPh_3* +*H_1* + *H_2* + *H_3* + *H_5* + *H_6* + *H_7* + *H_8* + *H_9*); 6.17 (s, 1H, *NH*); 4.67 (d, 2H, *CH_2*, *$^3J_{HH}$* = 5.9 Hz).

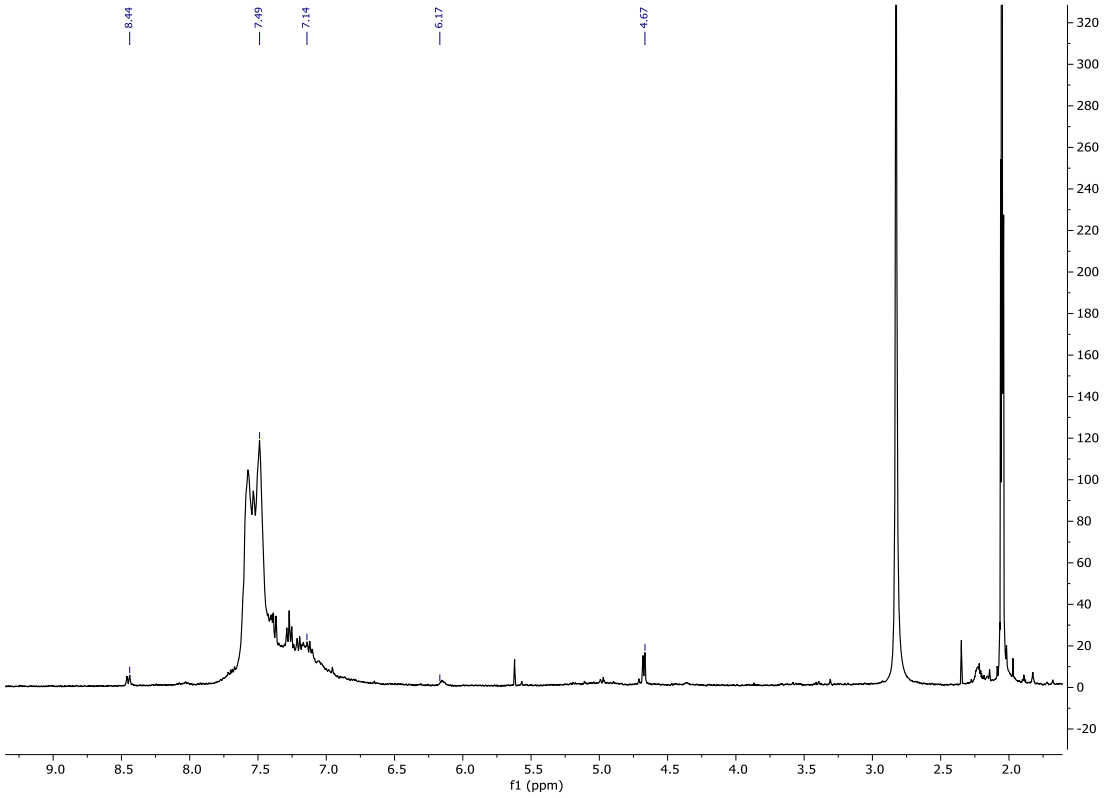


Figure 109. ^{1}H NMR spectrum of compound **49** in $(CD_3)_2CO$ solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, $(CD_3)_2CO$): δ = 33.9 (m, 1P, *PPh_3*).

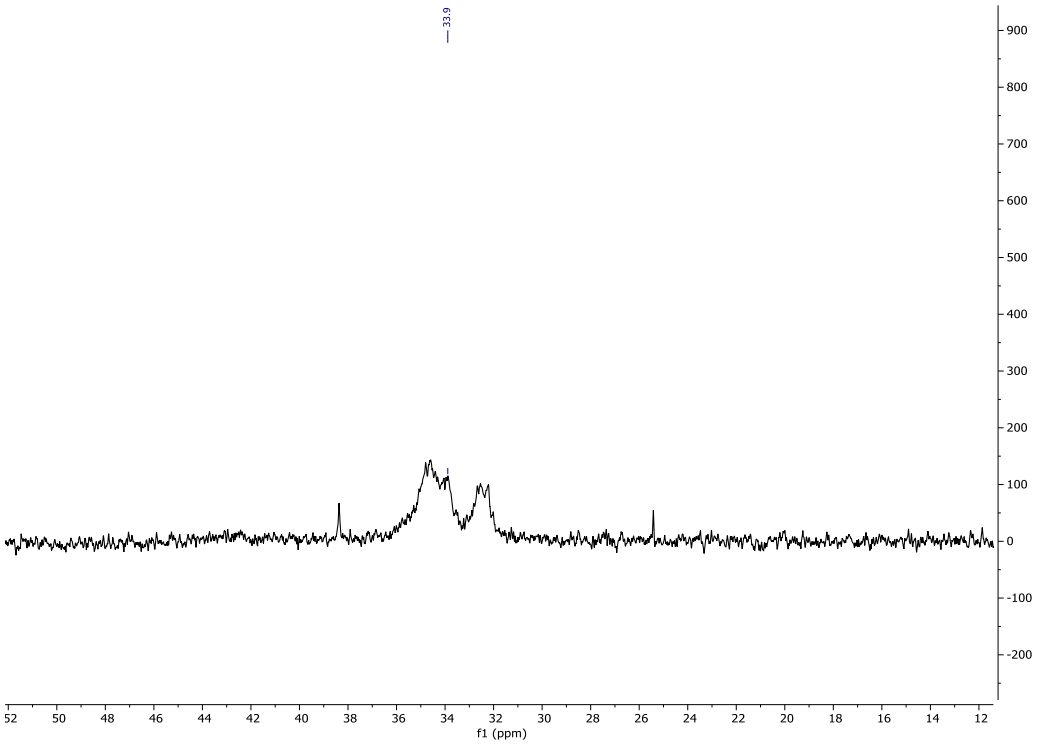


Figure 110. ^{31}P $\{^{1}H\}$ NMR spectrum of compound **49** in $(CD_3)_2CO$ solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 134.9 (d, 6C, $C_{ortho}PPh_3$, $^2J_{CP}$ = 13.9 Hz); 132.9 (s, 3C, $C_{para}PPh_3$); 130.4 (d, 6C, $C_{meta}PPh_3$, $^3J_{CP}$ = 11.5 Hz); 129.1 (s, 1C, C_2); 128.2 (s, 1C, C_1); 127.4 (s, 1C, C_4); 121.7 (s, 2C, C_6); 115.7 (s, 2C, C_7); 45.6 (s, 1C, CH_2).

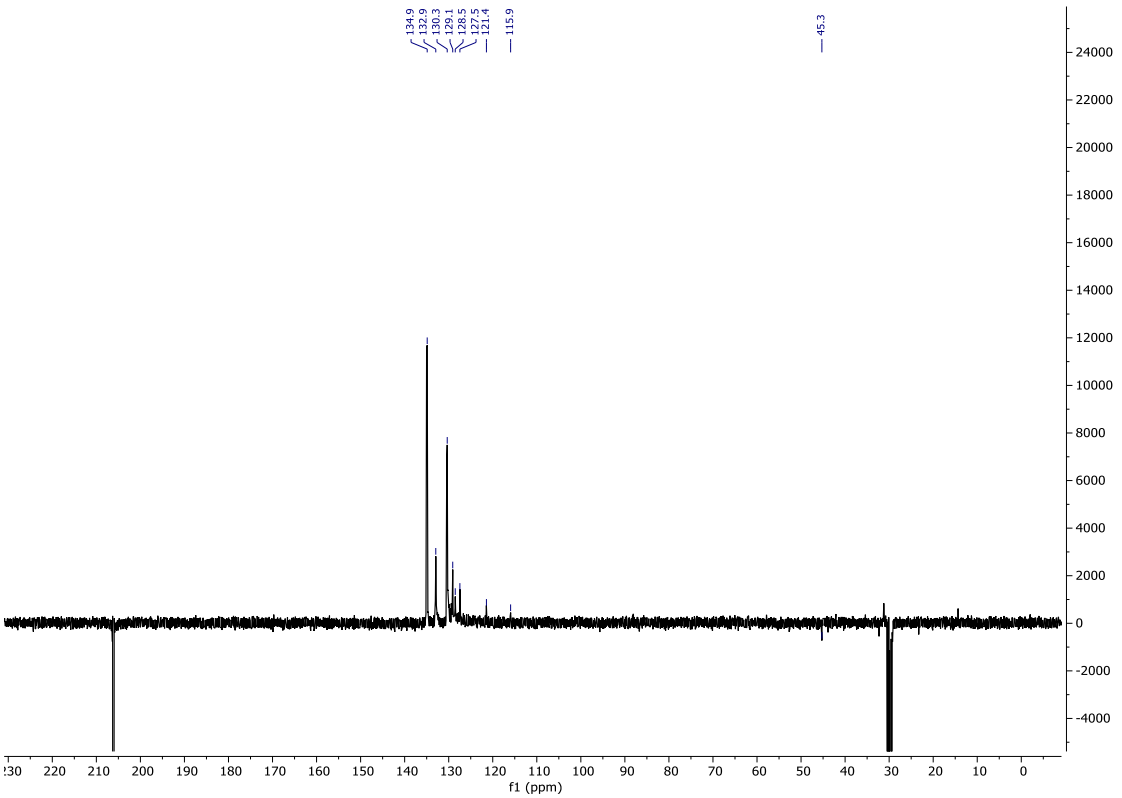


Figure 1.111. ^{13}C APT spectrum of compound **49** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{36}H_{30}AuP_2]^+$ 721.149. Found 721.1455; $[M]^+$ Calcd for $[C_{34}H_{28}AuN_2PS]^+$ 724.605. Found 725.1413; Calcd for $[C_{54}H_{46}Au_3P_3S]^+$ 1410.829. Found 1409.1146.

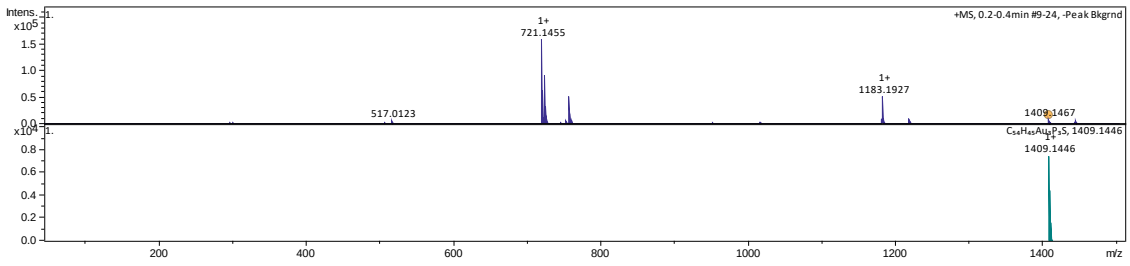
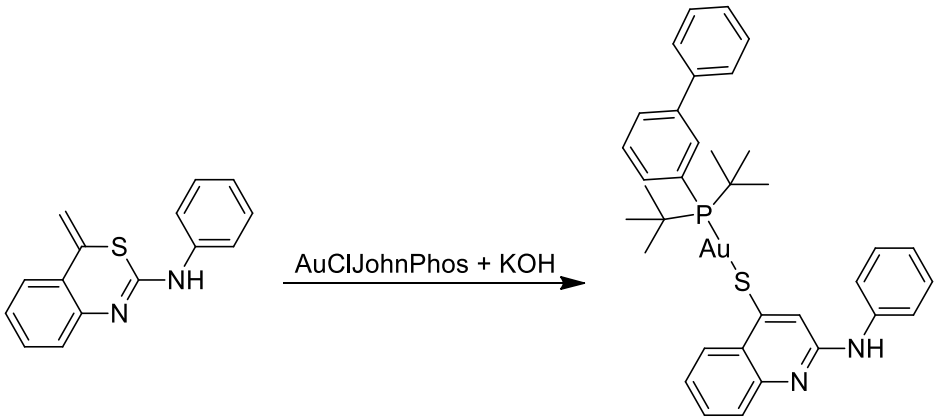


Figure1.112. MS (ESI+ µ-TOF) compound **49**.

Synthesis of compound 50

To a solution of compound **42** (25.2 mg, 0.1 mmol) and AuClJohnPhos (53.1 mg, 0.1 mmol) were mixed in MeOH (20 ml) was added an excess of KOH (0.3 mmol, 16.8 mg) and the mixture stirred 5h. The solution was concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a light brown product which was collected and vacuum dried to give the product.

Yield: %



Scheme 1.44. Synthesis of compound **50**.

^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$): δ = 8.49 (d, 1H, *H4*, $^{3}J_{HH}$ = 8.2 Hz); 8.08 (m, 1H, *JohnPhos*); 7.84 (m, 2H, *Ph*); 7.63 (m, 2H, *JohnPhos*); 7.46 (t, 1H, H_{para}, $^{3}J_{HH}$ = 7.9 Hz); 7.37-7.18 (m, 11H, *Ph* + *JohnPhos*); 6.92 (t, 1H, H_{para}, $^{3}J_{HH}$ = 7.3 Hz); 1.39 (d, 18H, CH_3, $^{3}J_{HH}$ = 15.3 Hz).

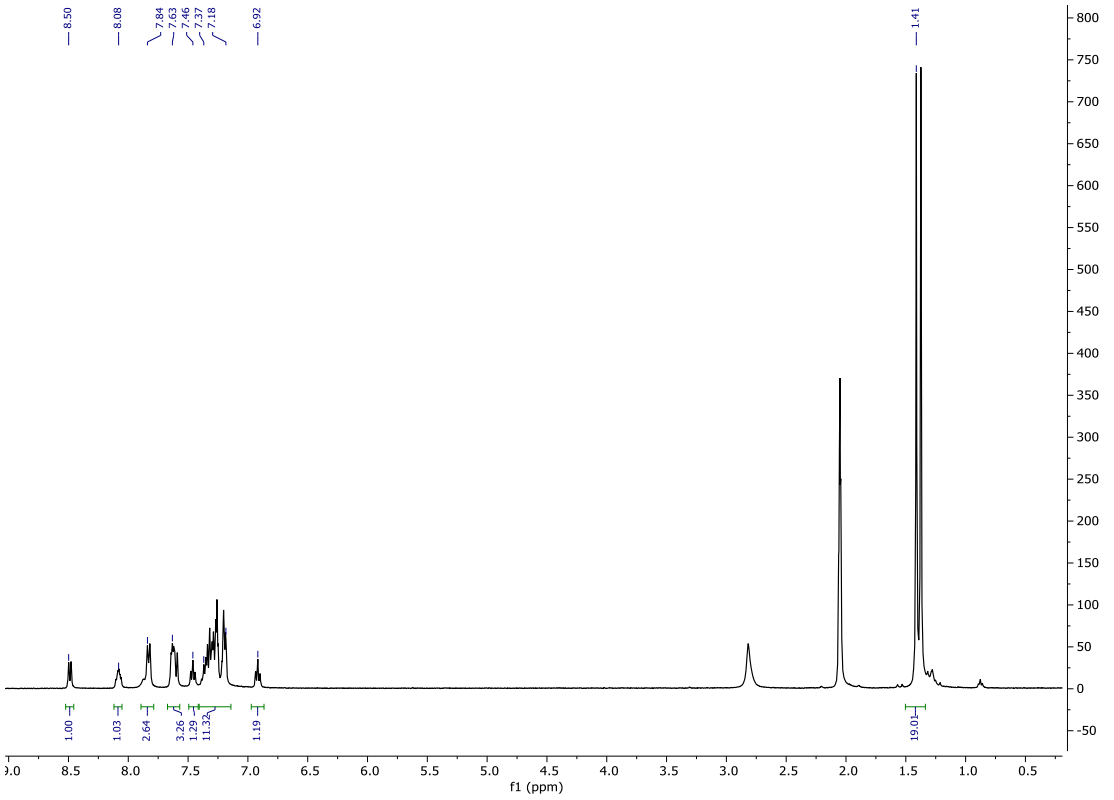


Figure 1.113. ^{1}H NMR spectrum of compound **50** in $(CD_3)_2CO$ solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, $(CD_3)_2CO$): δ = 64.4 (s, 1P, *JohnPhos*).

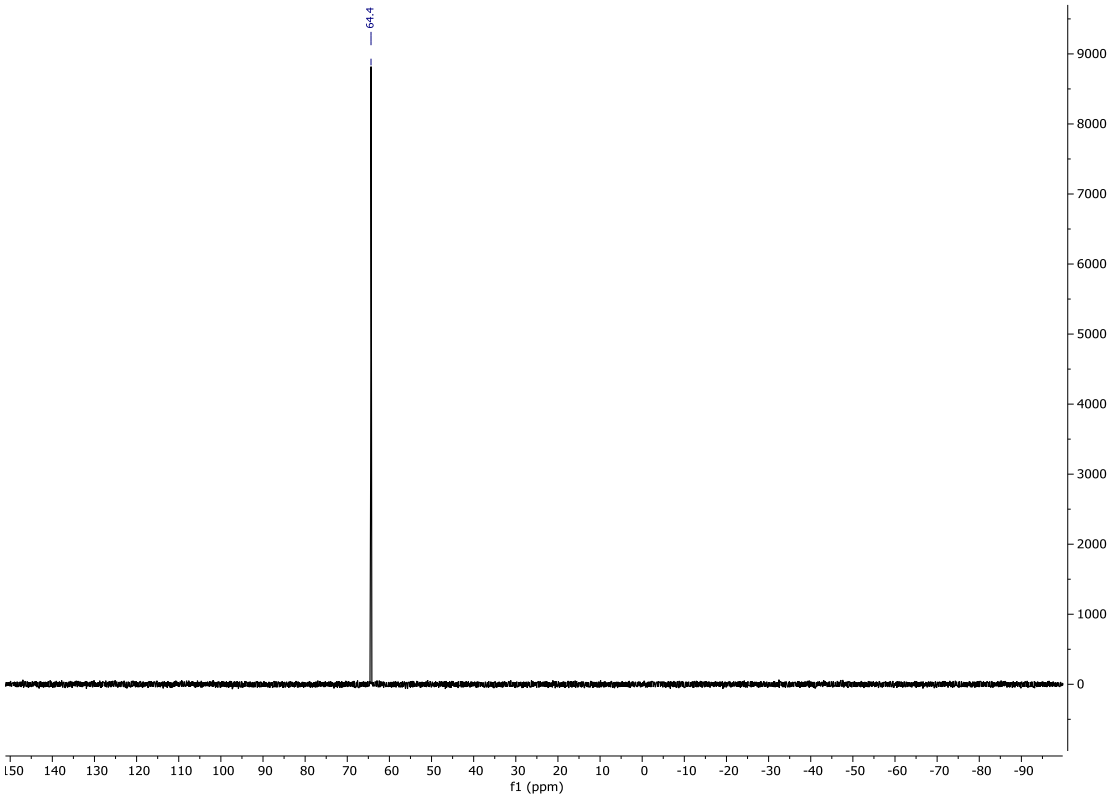


Figure 1.114.: ^{31}P {^{1}H} NMR spectrum of compound **50** in $(CD_3)_2$ CO solution.

^{13}C APT (ppm) (100 MHz, $(CD_3)_2CO$): δ = 154.1 (s, 1C, $C_{quaternary}$); 150.9 (s, 1C, $C_{quaternary}$); 148.4 (s, 1C, $C_{quaternary}$); 143.6 (s, 1C, $C_{quaternary}$); 135.7 (d, 1C, $C_{JohnPhos}$, $^3J_{CP}$ = 1.5 Hz); 133.8 (d, 1C, $C_{JohnPhos}$, $^2J_{CP}$ = 7.5 Hz); 131.6 (s br, 1C, $C_{JohnPhos}$); 130.1 (s, 2C, C_{ortho}Ph); 129.4 (s, 2C, C_{meta}Ph); 129.3 (s, 1C, C_{para}Ph); 128.5 (s, 1C, $C_{JohnPhos}$); 128.3 (s, 1C, C_{ipso}); 128.1 (d, 1C, $C_{JohnPhos}$, $^2J_{CP}$ = 6.2 Hz); 127.8 (s, 1C, *arom.*); 122.3 (s, 1C, *Ph*); 121.8 (s, 1C, C_{para}Ph); 119.9 (s, 1C, *Ph*); 116.3 (s, 1C, *Ph*); 38.3 (d, 2C. C_{ipso}^{t}Bu, $^1J_{CP}$ = 23.1 Hz); 31.2 (d, 2C, ^{t}*Bu*, $^1J_{CP}$ = 6.8 Hz).

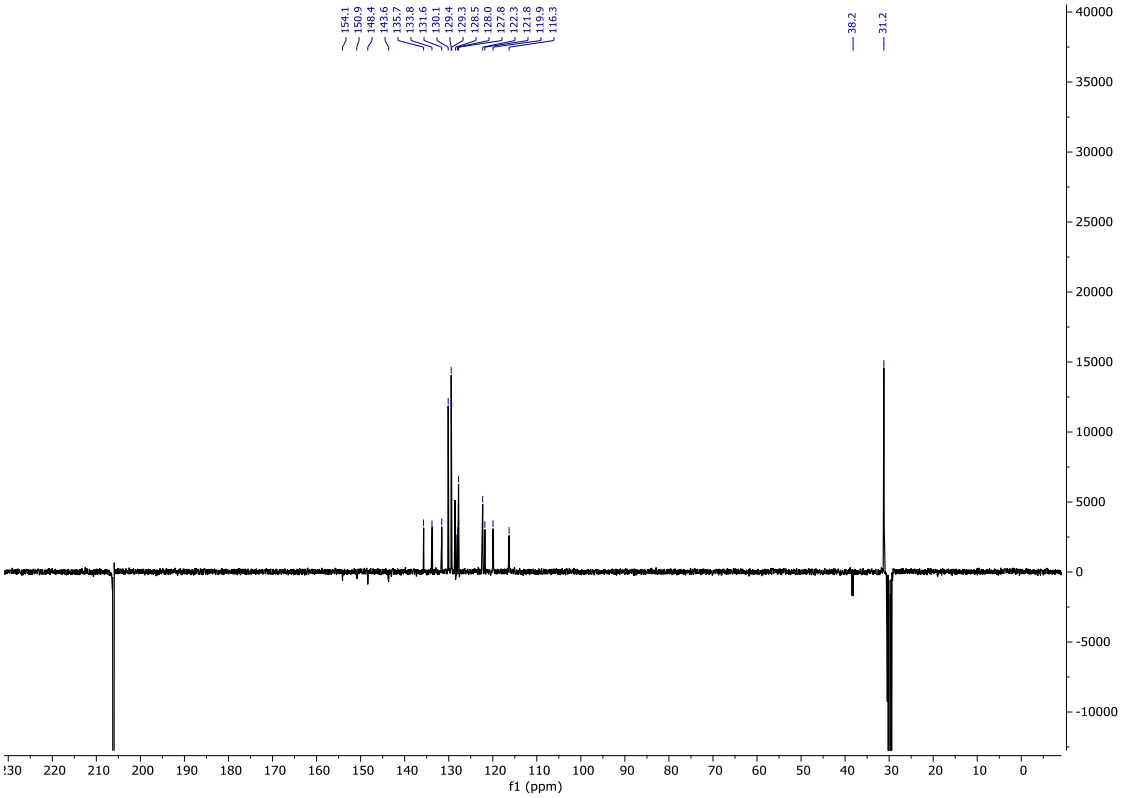


Figure 1.115. ^{13}C APT spectrum of compound **50** in $(CD_3)_2CO$ solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{35}H_{39}AuN_2PS]^+$ 747.2232. Found 747.2204.

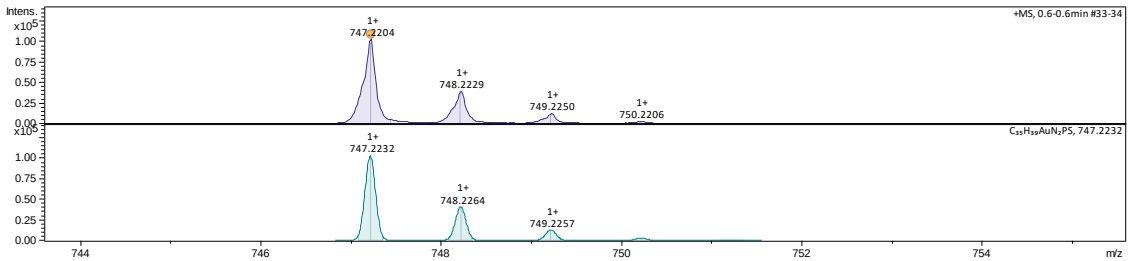


Figure 1.116. MS (ESI+ µ-TOF) compound **50**.

Anexos

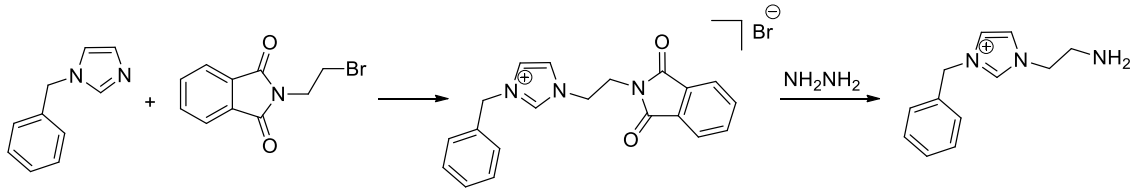
Capítulo 2

Syntheses

Synthesis of Compound 51

To a solution of 1-Benzylimidazole (282.0 mg, 1 mmol) in toluene (20 ml), N-(2-Bromoethyl)phthalimide was added (108 µL, 1 mmol) and the solution stirred for 72h (120°C). A white powder formed which was collected, and vacuum dried to give the product. Lately, this white powder was solved in ethanol (20 ml) and an excess of hydrazine was added. The solution stirred for 24 h. a white precipitated was formed and the solution was decanted and vacuum dried to give a transparent oil.

Yield: 99%



Scheme2.1. Synthesis of compound **51**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.30 (s, 1H, *imidazole*); 7.78 (m, 2H, *imidazole*); 7.42 (m, 5H, *Ph*-CH_2); 5.44 (s, 2H, Ph-*CH_2*-imidazole); 4.13 (m, 2H, NH_2-CH_2-*CH_2*); 2.91 (m, 2H, NH_2-*CH_2*-CH_2).

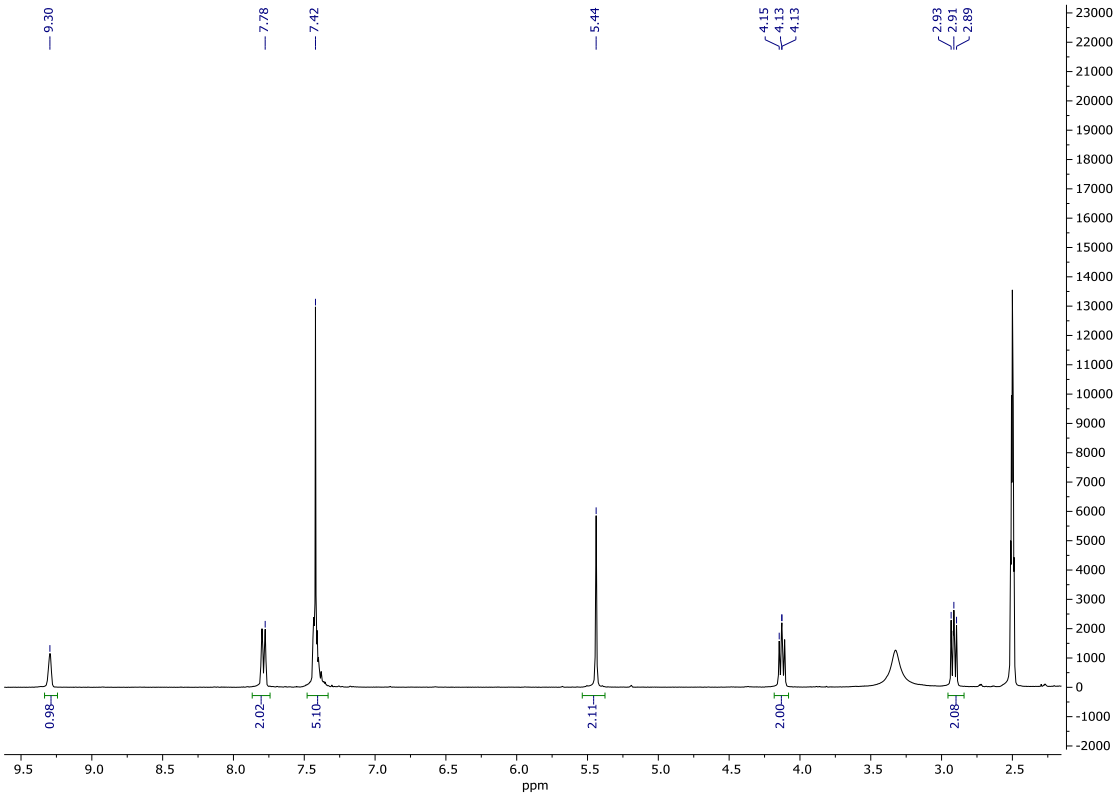
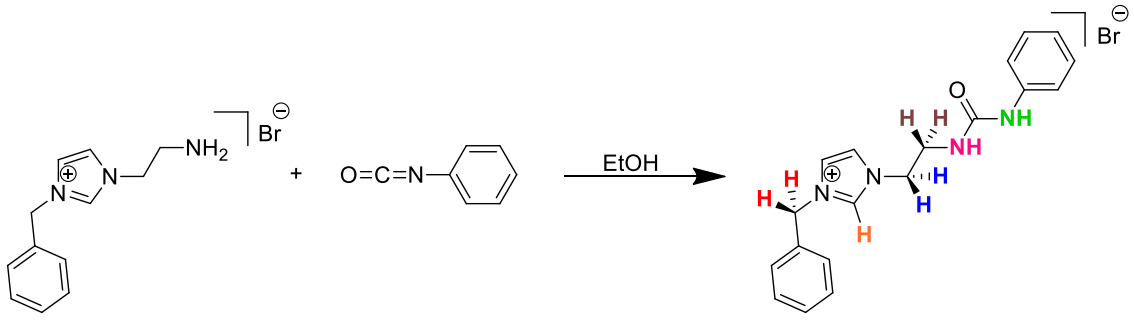


Figure 2.1. [1]H NMR spectrum of compound **52** in DMSO solution.

Synthesis of Compound 52

To a solution of aminoethyl-benzylimidazolium salt (282.0 mg, 1 mmol), phenyl isothiocyanate was added (108 µL, 1 mmol) and the solution stirred for 24h. A white precipitate formed which was collected, washed with acetonitrile and vacuum dried to give the product.

Yield: 84%



Scheme 2.2. Synthesis of compound **52**.

[1]H NMR (ppm) (400 MHz, DMSO): δ = 9.34 (s, 1H, *imidazole*); 8.72 (s, 1H, CO-*NH*-Ph); 7.80 (m, 2H, *imidazole*); 7.34 (m, 7H, CH_2-*Ph* + H_{ortho}PH-NH); 7.21 (m, 2H, H_{meta}Ph-NH); 6.90 (m, 1H, H_{para}Ph-NH); 6.40 (t, 1H, CH_2-*NH*-CO, $^3J_{H\text{-}H}$ = 5.9 Hz); 5.44

(s, 2H, Ph-*CH*$_2$-imidazole); 4.28 (t, 2H, NH-CH$_2$-*CH*$_2$, $^3J_{H\text{-}H}$ = 5.5 Hz); 3.55 (q, 2H, NH-*CH*$_2$-CH$_2$, $^3J_{H\text{-}H}$ = 5.7 Hz).

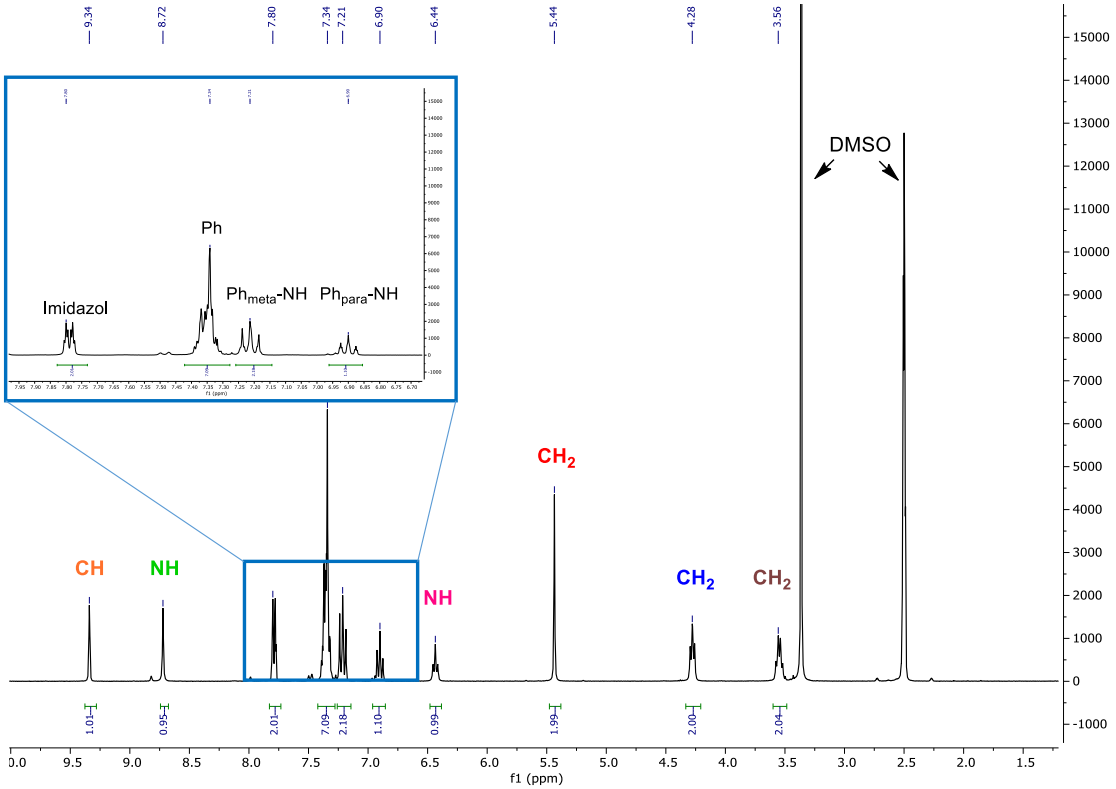


Figure 2.2. ^{1}H NMR spectrum of compound **52** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 155.3 (s, 1C, *CO*); 140.2 (s, 1C, *C$_{ipso}$Ph*-NH); 136.6 (s, 1C, *CH*-imidazole); 134.8 (s, 1C, *C$_{ipso}$Ph*-CH$_2$); 128.9 (s, 2C, *C$_{ortho}$Ph*-CH$_2$); 128.6 (s, 2C, *C$_{ortho}$Ph*-NH); 128.6 (s, 1C, *C$_{para}$Ph*-CH$_2$); 128.1(s, 2C, *C$_{meta}$Ph*-CH$_2$); 123.3 (s, 1C, *imidazole*); 122.4 (s, 1C, *imidazole*); 121.2 (s, 1C, *C$_{para}$Ph*-NH); 117,7 (s, 2C, *C$_{meta}$Ph*-NH); 51.8(s, 1C, Ph-*CH*$_2$-imidazole); 49.7 (s, 1C, NH-CH$_2$-*CH*$_2$); 40.0 (s, 1C, NH-*CH*$_2$-CH$_2$).

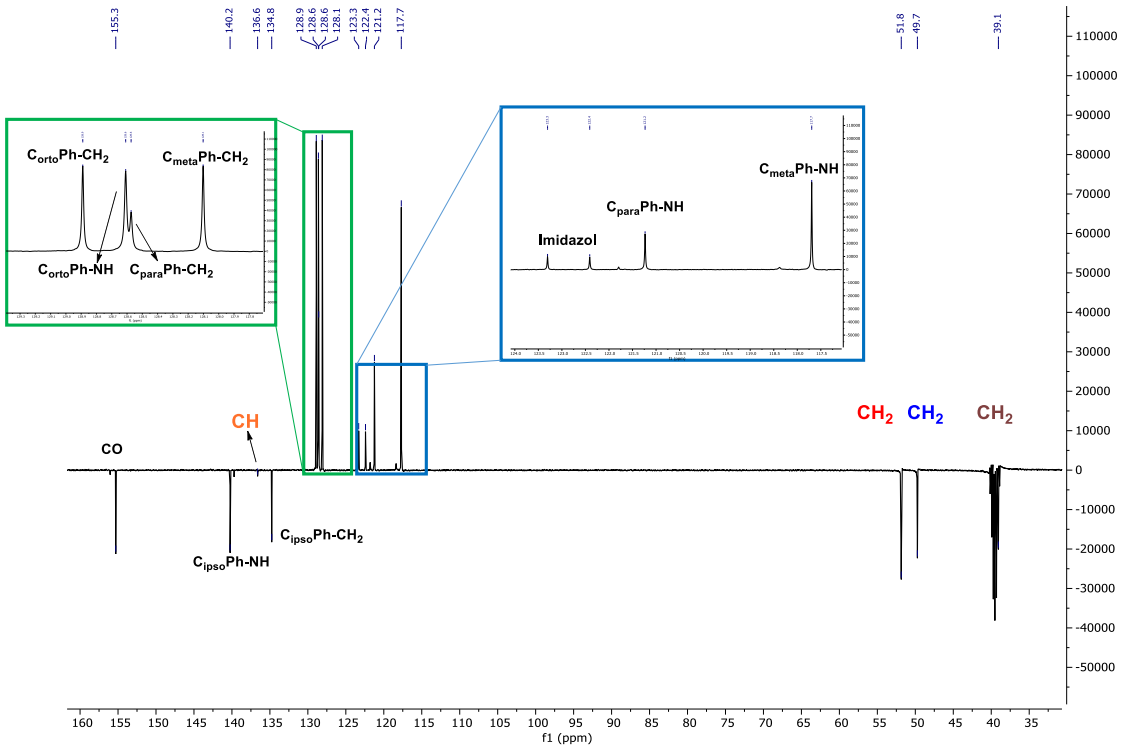
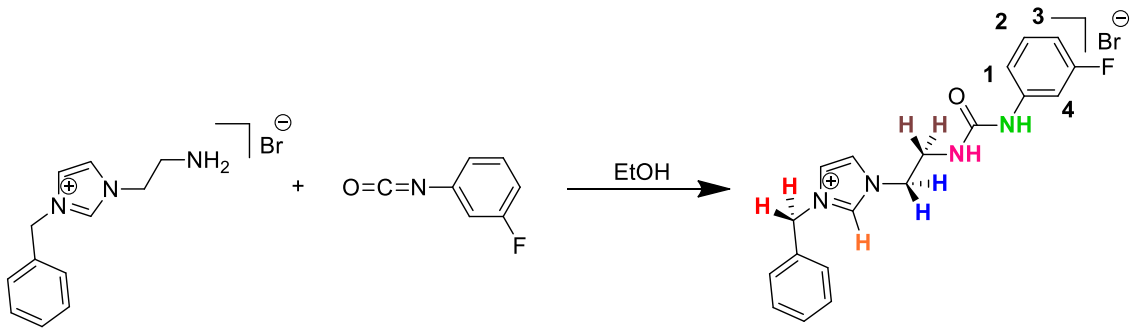


Figure 2.3. ^{13}C APT spectrum of compound **52** in DMSO solution.

Synthesis of compound 53

To a solution of aminoethyl-benzylimidazolium salt (282.0 mg, 1 mmol), 3-flurophenyl isothiocyanate was added (114 µL, 1 mmol) and the solution stirred for 24h. A white precipitate formed which was collected, washed with acetonitrile and vacuum dried to give the product.

Yield: 92%



Scheme 2.3. Synthesis of compound **53**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.31 (s, 1H, *imidazole*); 8.91 (s, 1H, CO-*NH*-Ph); 7.78 (m, 2H, *imidazole*); 7.44 (m, 1H, *4*); 7.35 (s, 5H, CH_2-*Ph*); 7.25 (m, 1H, *2*); 7.00 (m, 1H, *1*); 6.72 (m , 1H, *3*); 6.45 (t, 1H, CO-*NH*-CH_2, $^3J_{H\text{-}H}$ = 5.9 Hz); 5.43 (s, 2H, Ph-

CH₂-imidazole); 4.28 (t, 2H, NH-CH₂-*CH₂*, $^{3}J_{H\text{-}H}$ = 5.6 Hz); 3.55 (q, 2H, NH-*CH₂*-CH₂, $^{3}J_{H\text{-}H}$ = 5.8 Hz).

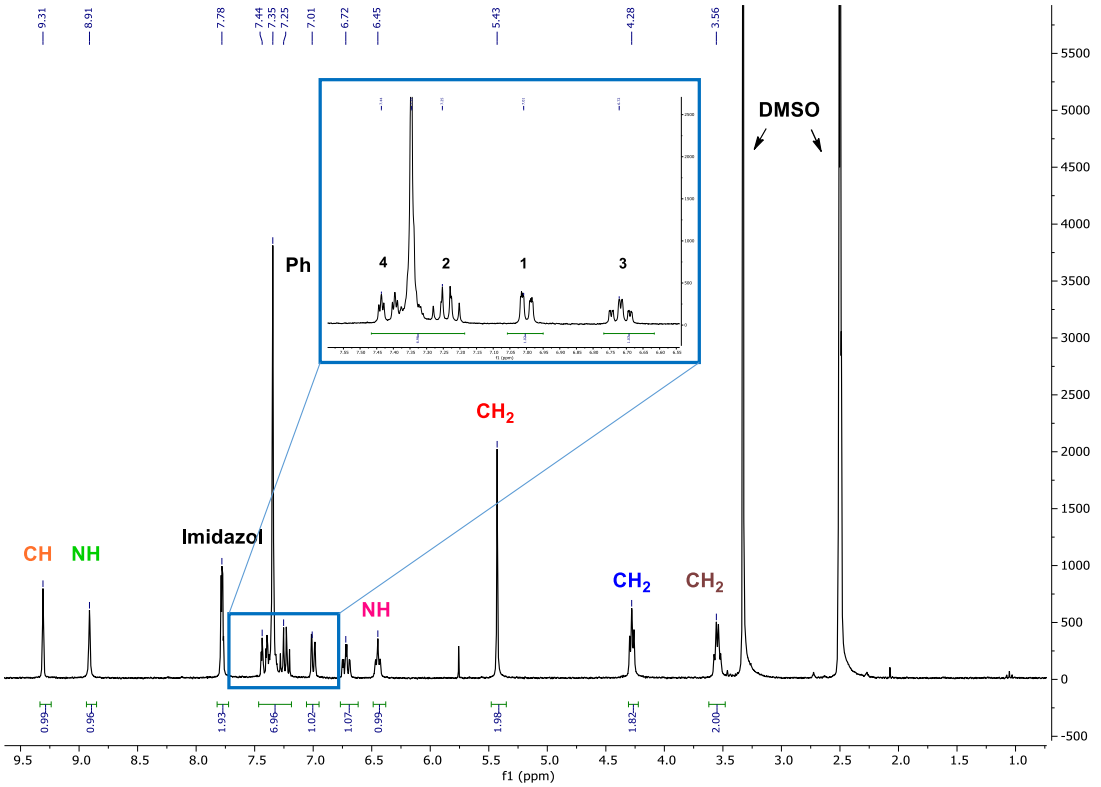


Figure 2.4. ^{1}H NMR spectrum of compound **53** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -112.3 (m, 1F, Ph-*F*).

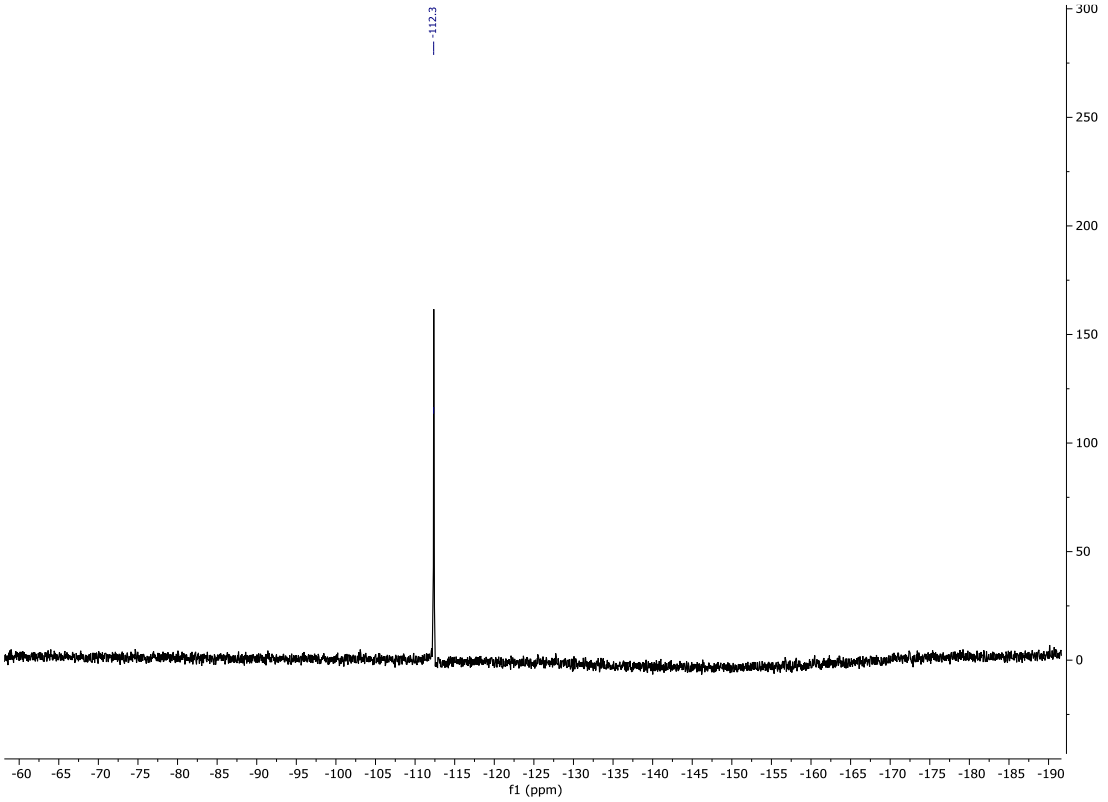


Figure 2.5. $^{19}F\{^{1}H\}$ NMR spectrum of compound **53** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 162.4 (d, 1C, *C_{ipso}Ph-F*, $^{1}J_{C\text{-}F}$ = 240.0 Hz); 155.5 (s, 1C, *CO*); 142.1 (d, 1C, *C_{ipso}Ph*-NH, $^{3}J_{C\text{-}F}$ = 11.5 Hz); 134.7 (s, 1C, *CH imidazole*); 130.1 (d, 1C, *2*, $^{3}J_{C\text{-}F}$ = 9.8 Hz); 128.8 (s, 2C, *C_{ortho}Ph*); 128.6 (s, 1C, *C_{para}Ph*); 128.0 (s, 2C, *C_{meta}Ph*); 123.4 (s, 1C, *imidazole*); 122.4 (s, 1C, *imidazole*); 113.4 (s, 1C, *1*); 107.5 (d, 1C, *3*, $^{2}J_{C\text{-}F}$ = 21.3 Hz); 104.4 (d, 1C, *4*, $^{2}J_{C\text{-}F}$ = 26.5 Hz); 51.8 (s, 1C, Ph-*CH_2*-imidazole); 49.6 (s, 1C, NH-CH_2-*CH_2*); 40.1 (s, 1C, NH-*CH_2*-CH_2).

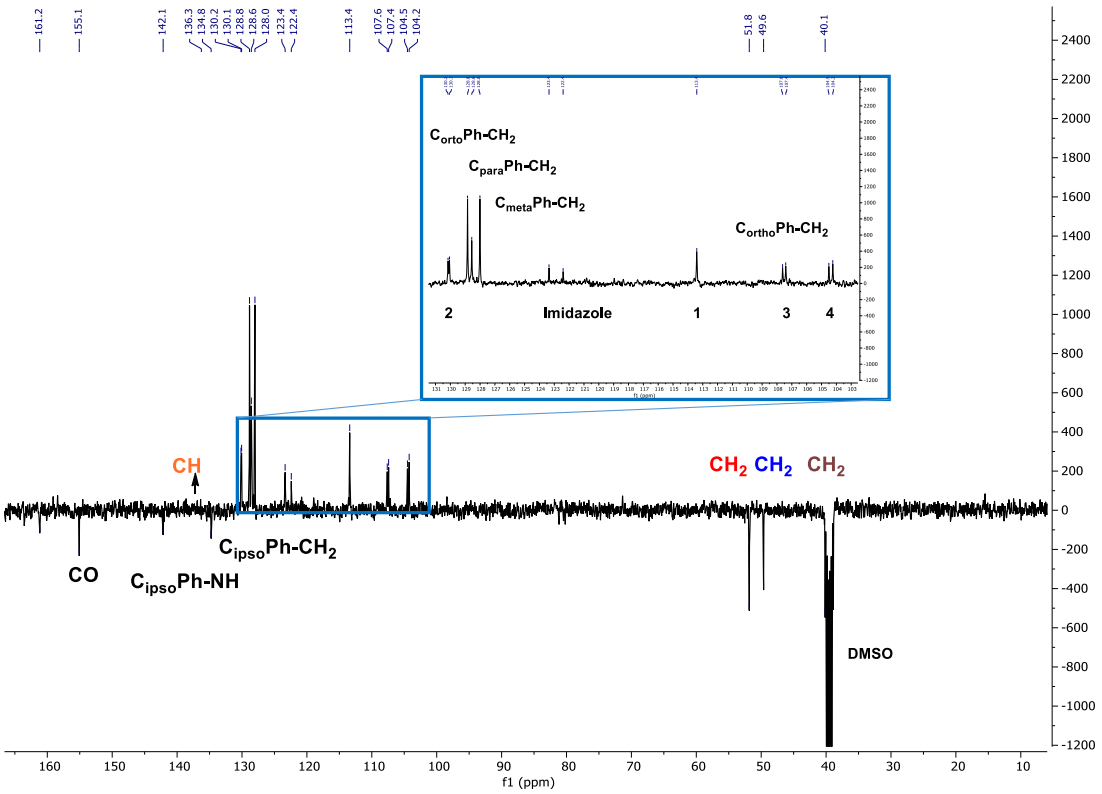
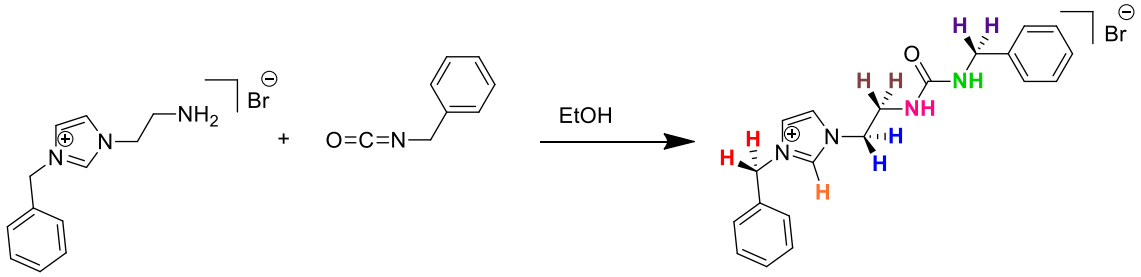


Figure 2.6. ^{13}C APT spectrum of compound **53** in DMSO solution.

Synthesis of compound 54

To a solution of aminoethyl-benzylimidazolium salt (282.0 mg, 1 mmol), benzyl isothiocyanate was added (123 µL, 1 mmol) and the solution stirred for 24h. A white precipitate formed which was collected, washed with acetonitrile and vacuum dried to give the product.

Yield: 73%



Scheme 2.4. Synthesis of compound **54**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.30 (s, 1H, *imidazole*); 7.77 (m, 2H, *imidazole*); 7.40-7.21 (m, 10H, CH_2-*Ph*); 6.55 (t, 1H, CO-*NH*-CH_2-Ph, $^{3}J_{H\text{-}H}$ = 6.0 Hz); 6.24 (t, 1H, CH_2-CH_2-*NH*-CO, $^{3}J_{H\text{-}H}$ = 5.9 Hz); 5.42 (s, 2H, Ph-*CH_2*-imidazole); 4.23 (t,

2H, *CH*$_2$-CH$_2$-NH-CO, $^3J_{H\text{-}H}$ = 5.6 Hz); 4.16 (d, 2H, NH-*CH*$_2$-Ph, $^3J_{H\text{-}H}$ = 6.0 Hz); 3.47 (q, 2H, CH$_2$-*CH*$_2$-NH-CO, $^3J_{H\text{-}H}$ = 5.6 Hz).

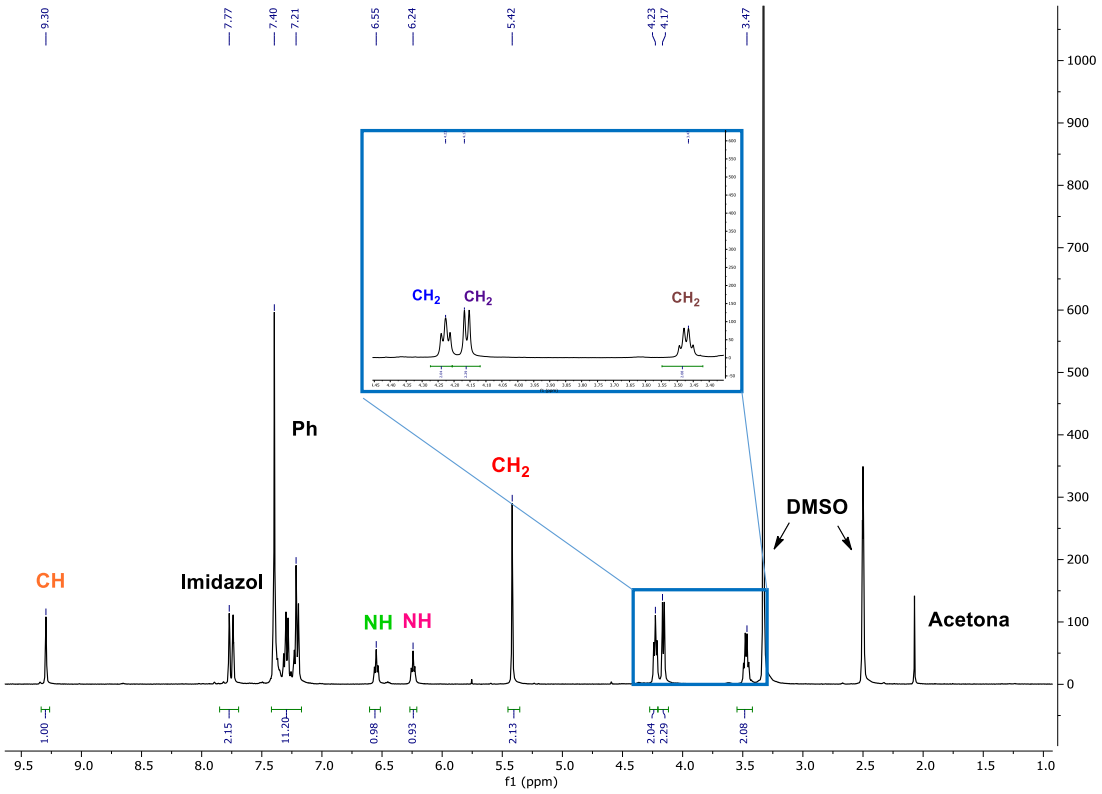


Figure 2.7. ^{1}H NMR spectrum of compound **54** in DMSO solution.

^{13}C APT (ppm) (100 MHz, (DMSO): δ = 157.9 (s, 1C, *CO*); 140.6 (s, 1C, *C$_{ipso}$*Ph-CH$_2$-NH); 136.5 (s, 1C, *imidazole*); 134.7 (s, 1C, *C$_{ipso}$Ph*-CH$_2$-imidazole); 128.9 (s, 2C, CH$_2$-*Ph*); 128.6 (s, 1C, *C$_{para}$Ph*CH$_2$); 128.2 (s, 2C, CH$_2$-*Ph*); 128.1 (s, 2C, CH$_2$-*Ph*); 127.0 (s, 2C, CH$_2$-*Ph*); 126.6 (s, 1C, *C$_{para}$Ph*-CH$_2$); 123.3 (s, 1C, *imidazole*-CH$_2$-CH$_2$); 122.3 (s, 1C, *imidazole*-CH$_2$-Ph); 51.8 (s, 1C, Ph-*CH*$_2$-imidazole); 49.8 (s, 1C, *CH*$_2$-CH$_2$-NH-CO); 42.9 (s, 1C, NH-*CH*$_2$-Ph); 39.5 (s, 1C, CH$_2$-*CH*$_2$-NH-CO).

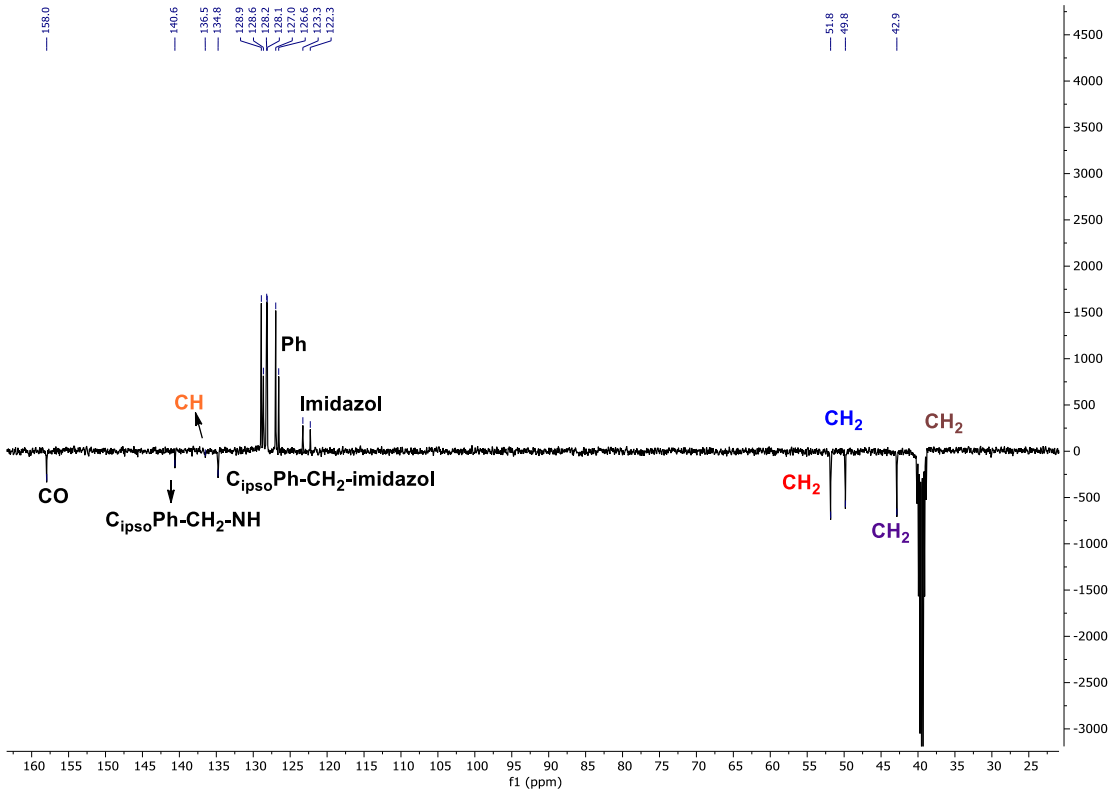
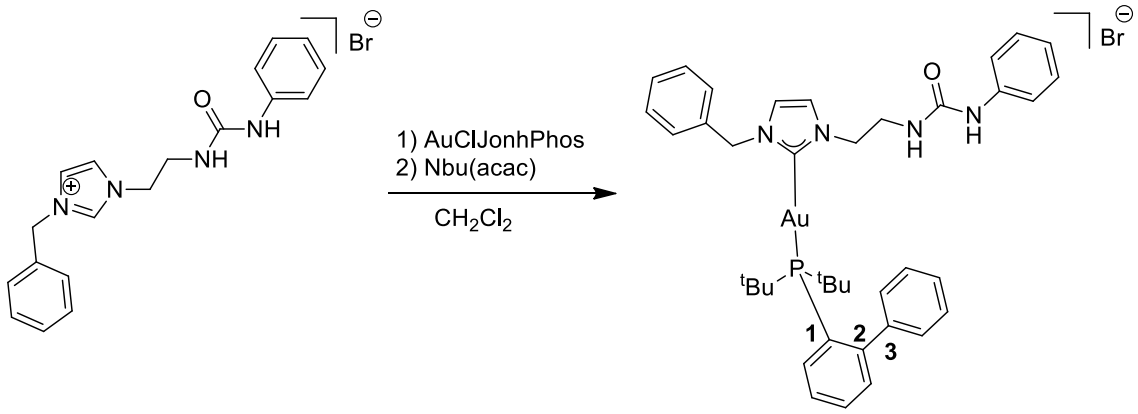


Figure 2.8. ^{13}C APT spectrum of compound **54** in DMSO solution.

Synthesis of compound 55

To a solution of compound **52** (80 mg, 0.2 mmol) and [AuCl(JohnPhos)] (106 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred for 2.5h. The solution washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 62%



Scheme 2.5. Synthesis of compound **55**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.57 (s br, 1H, CO-*NH*-Ph); 7.99-6.86 (m, 19H, CH_2-*Ph*+*Ph*); 7,57 (m, 2H, *imidazole*); 6.29 (t, 1H, CH_2-*NH*-CO, $^{3}J_{H\text{-}H}$ = 5.9 Hz); 5.18 (s, 2H, Ph-*CH_2*-imidazole); 4.06 (t, 2H, NH-CH_2-*CH_2*, $^{3}J_{H\text{-}H}$ = 6.0 Hz); 3.50 (m, 2H, NH-*CH_2*-CH_2); 1.29 (d, 18H, *^{t}Bu*, $^{3}J_{H\text{-}P}$ = 15.4 Hz).

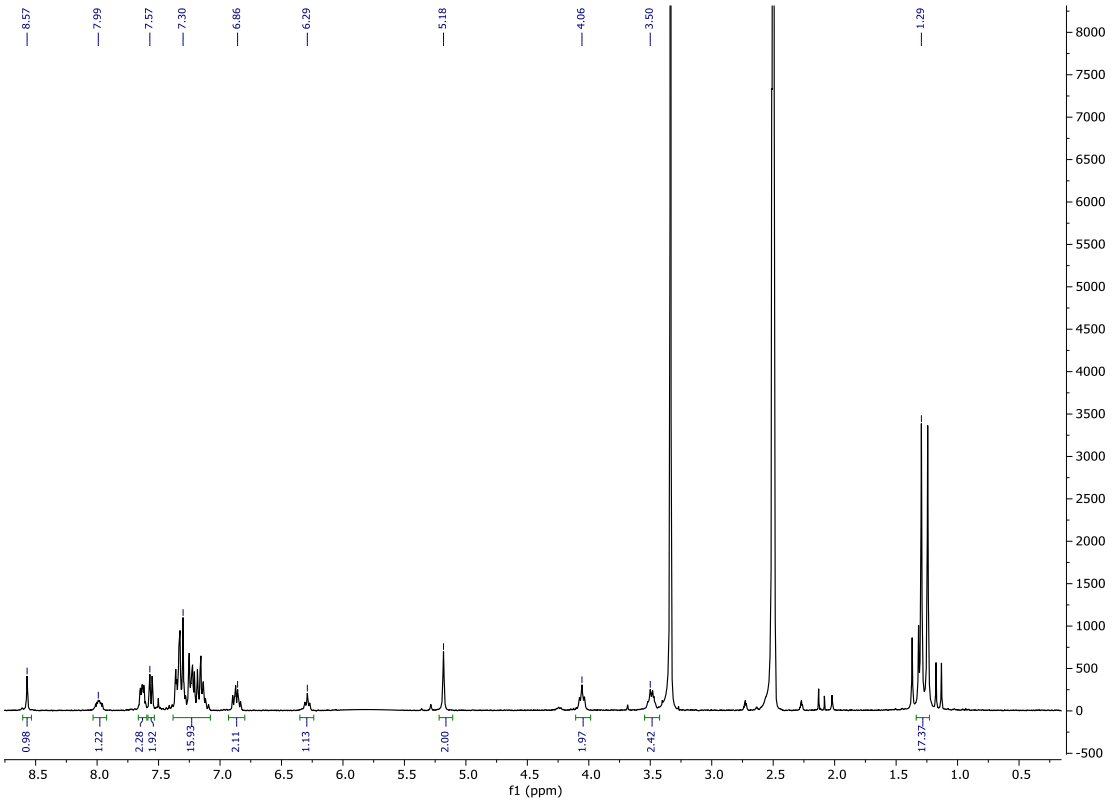


Figure 2.9. ^{1}H NMR spectrum of compound **55** in DMSO solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, DMSO): δ = 63.8 (s, 1P, *JohnPhos*).

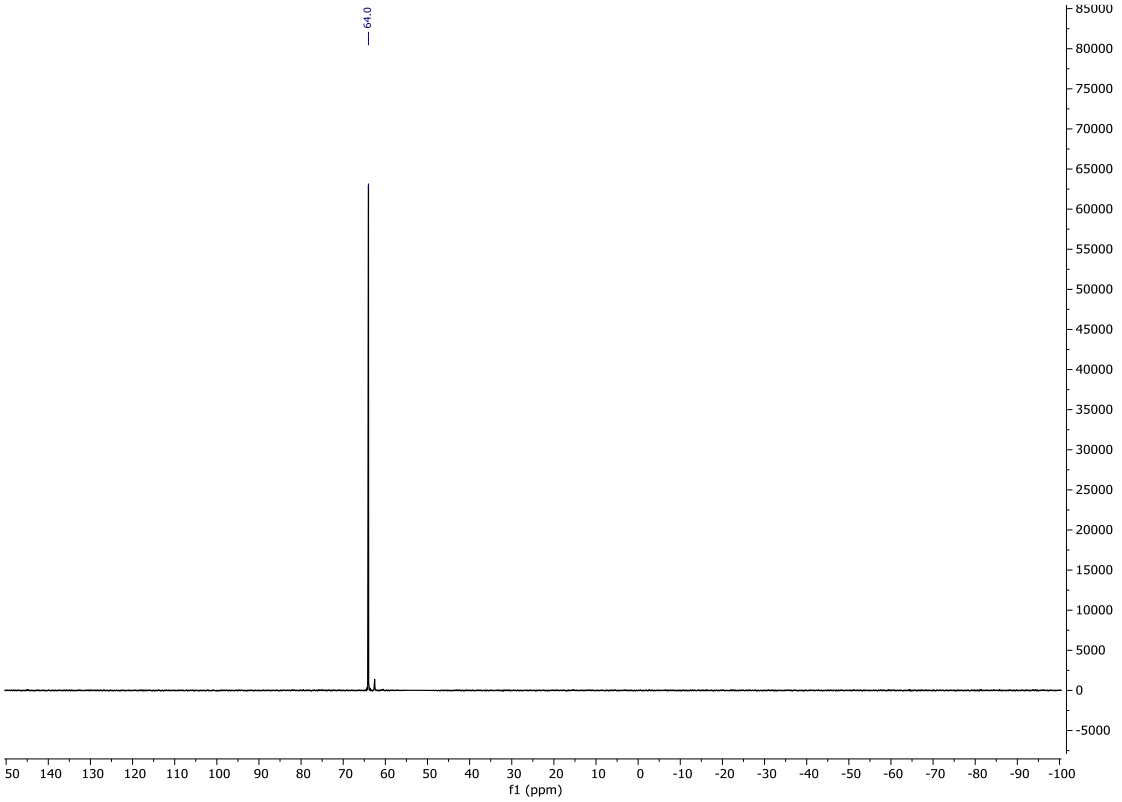


Figure 2.10. $^{31}P\{^{1}H\}$ NMR spectrum of compound **55** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 187.0 (d, 1C, *C*=Au, $^{2}J_{C\text{-}P}$ = 115.0 Hz); 155.1 (s, 1C, *CO*); 148.8 (d, 1C, C_{ipso}-*2*, $^{2}J_{C\text{-}P}$ = 14.3 Hz); 142.9 (d, 1C, C_{ipso}-*3*, $^{3}J_{C\text{-}P}$ = 6.1 Hz); 140.3 (s, 1C, C_{ipso}*Ph*-NH); 136.4 (s, 1C, C_{ipso}*Ph*-CH_2); 134.7-117.6 (m, 19C, CH_2-*Ph+Ph+JohnPhos*); 125.5 (d, 1C, C_{ipso}-*1*, $^{1}J_{C\text{-}P}$ = 42.5 Hz); 122.6 (s, 1C, *imidazole*); 122.3 (s, 1C, *imidazole*); 53.4 (s, 1C, Ph-CH_2-imidazole); 50.9 (s, 1C, NH-CH_2-CH_2); 39.8 (s, 1C, NH-CH_2-CH_2); 37.0 (d, 2C, $C_{ipso}{}^{t}Bu$, $^{1}J_{C\text{-}P}$ = 23.0 Hz); 30.3 (d, 6C, ^{t}Bu, $^{1}J_{C\text{-}P}$ = 6.4 Hz).

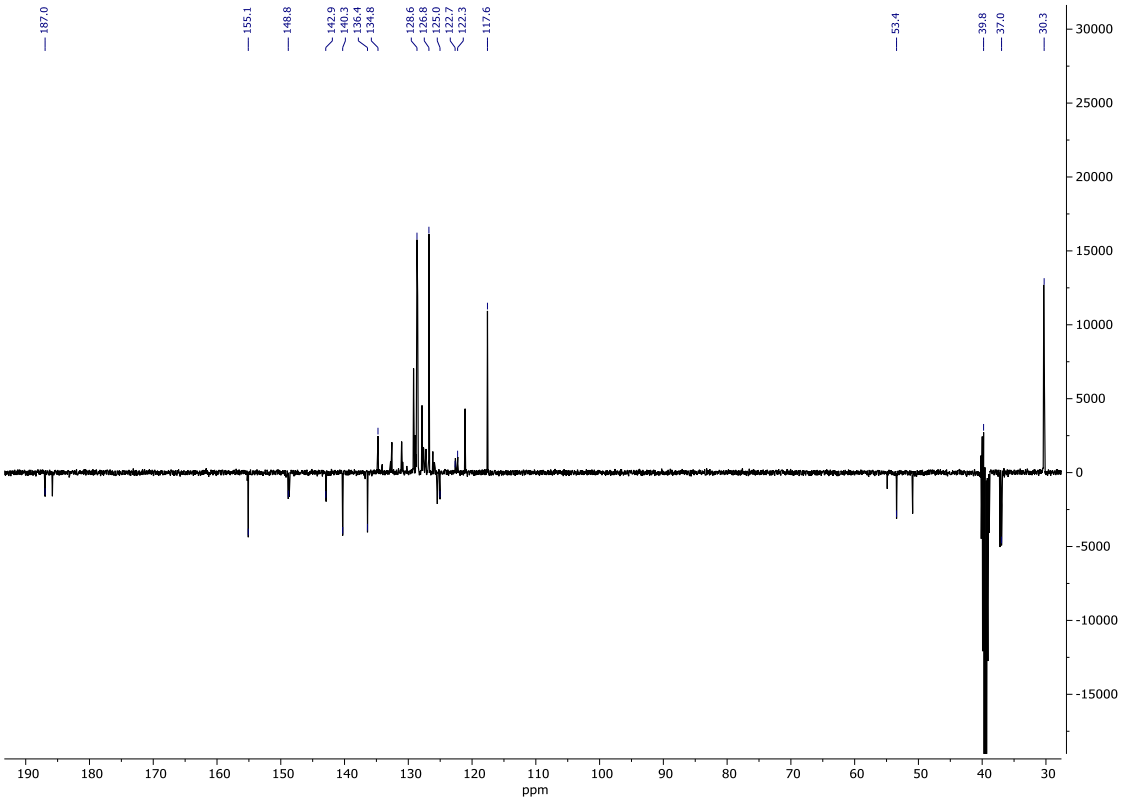


Figure 2.11. ^{13}C APT spectrum of compound **55** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{39}H_{47}AuN_4O_2]^+$ 815.3148. Found 815.3113.

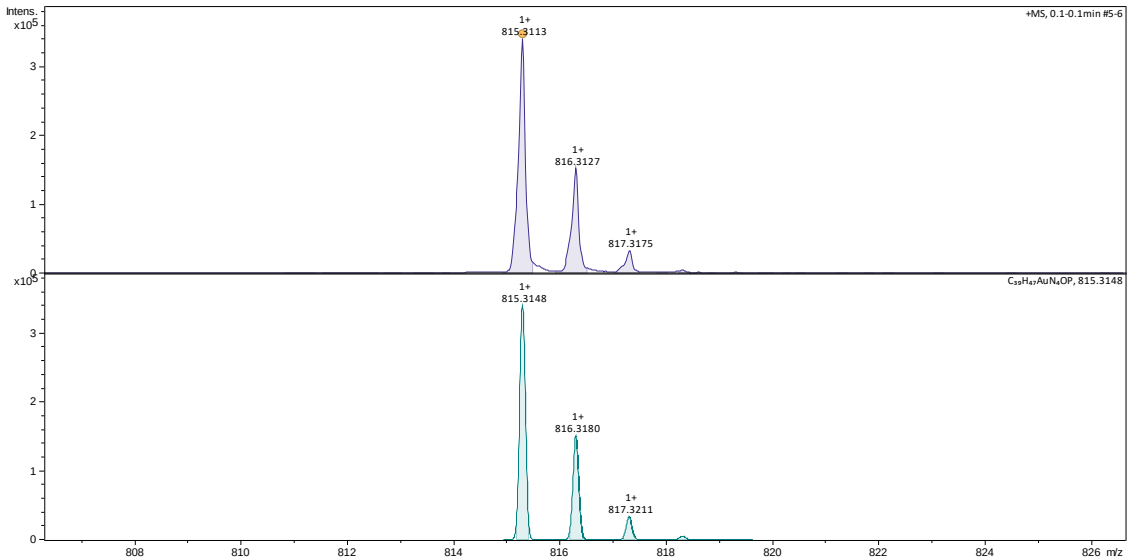
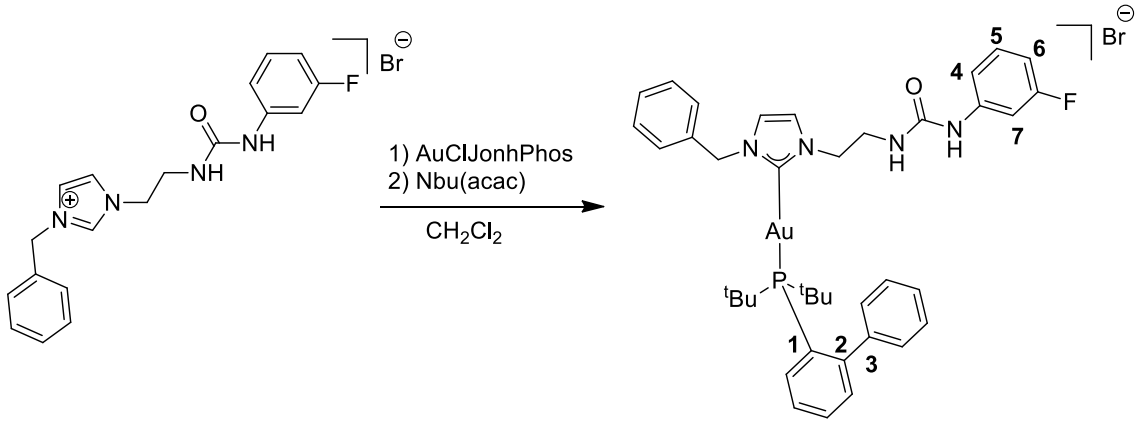


Figure 2.12. MS (ESI+ µ-TOF) compound **55**.

Synthesis of compound 56

To a solution of compound **53** (83.86 mg, 0.2 mmol) and [AuCl(JohnPhos)] (106 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred for 4.5h. The solution washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 60%



Scheme 2.6. Synthesis of compound **56**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.95 (s br, 1H, CO-*NH*-Ph); 7.00-6.68 (m, 13H, CH_2-*Ph+JohnPhos*); 7,56 (m, 2H, *imidazole*); 7.46 (m, 1H, *7*); 6.97 (m, 1H, *4*); 6.68 (m, 1H, *6*); 6.46 (t, 1H, CH_2-*NH*-CO, $^3J_{H-H}$ = 5.8 Hz); 5.18 (s, 2H, Ph-*CH_2*-imidazol); 4.06 (t, 2H, NH-CH_2-*CH_2*, $^3J_{H-H}$ = 6.0 Hz); 3.50 (m, 2H, NH-*CH_2*-CH_2); 1.29 (d, 18H, ^{t}*Bu*, $^3J_{H-P}$ = 15.4 Hz).

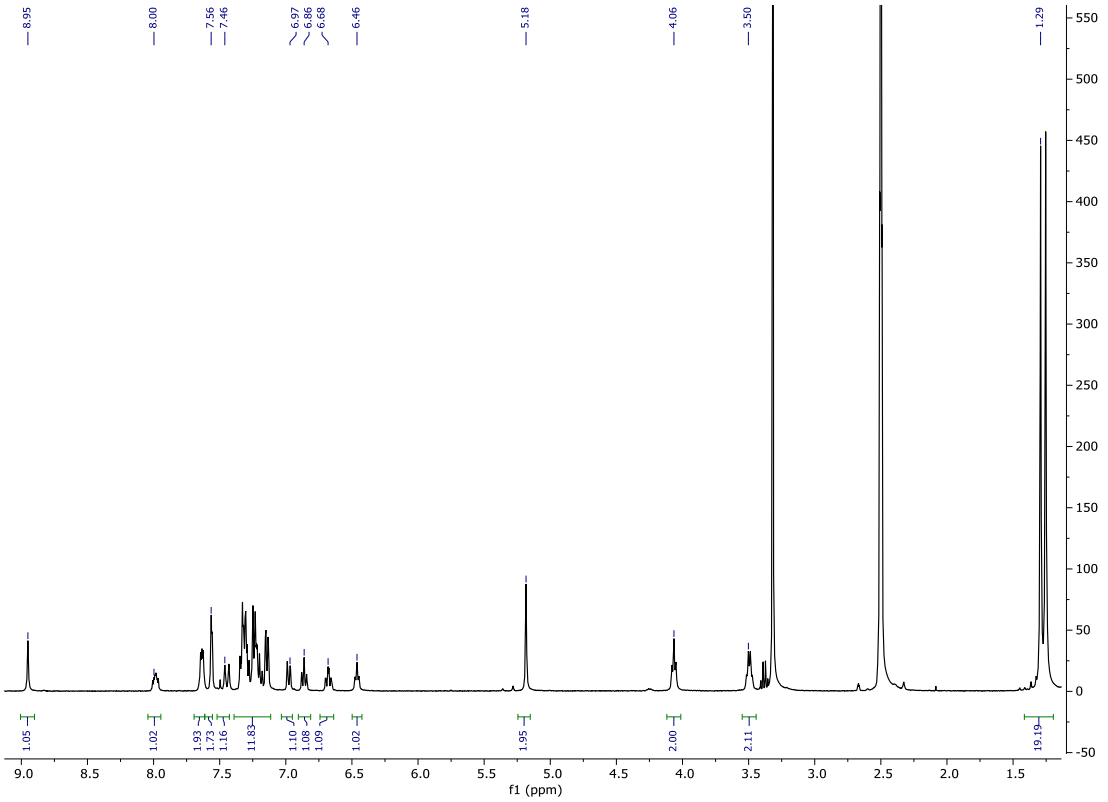


Figure 2.13. ^{1}H NMR spectrum of compound **56** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -112.5 (m, 1F, *Ph-F*).

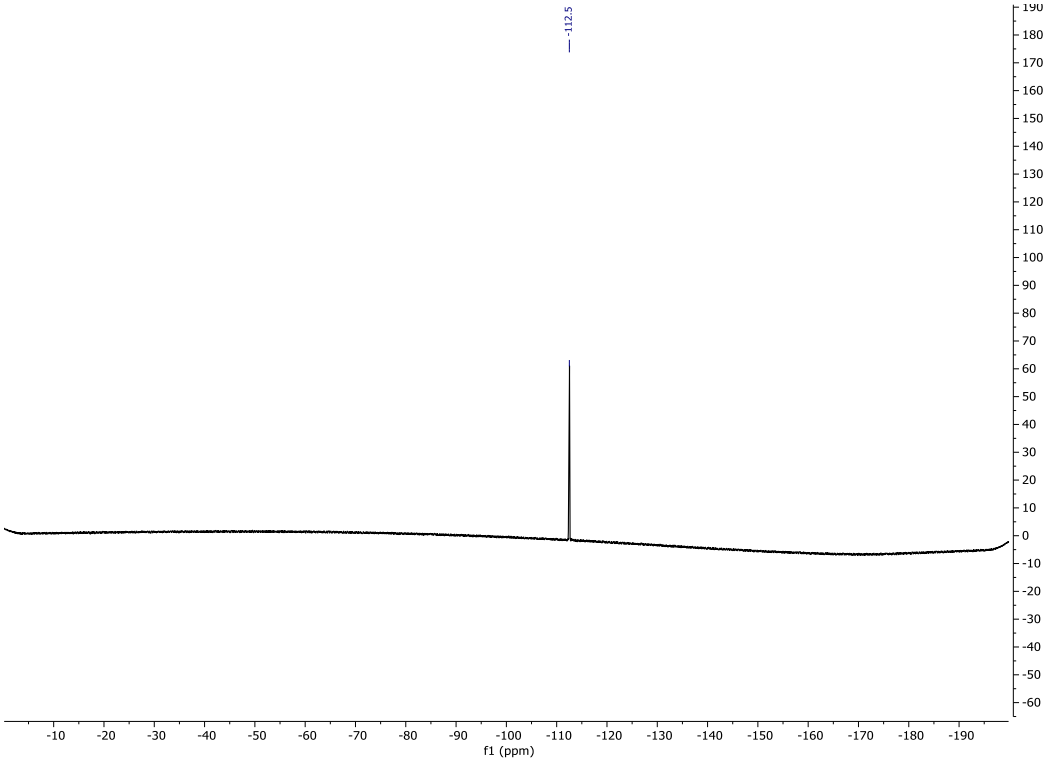


Figure 2.14. ^{19}F{^{1}H} NMR spectrum of compound **56** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 64.1 (s, 1P, *JohnPhos*).

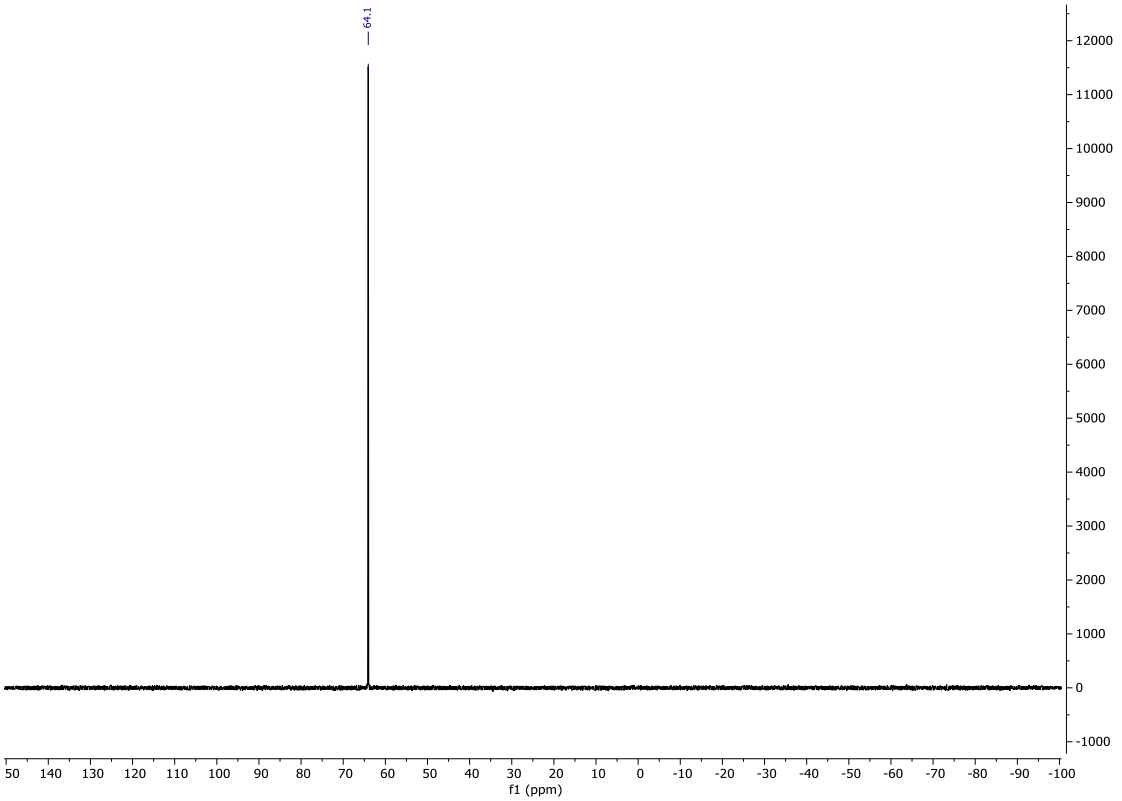


Figure 2.15. $^{31}P\{^{1}H\}$ NMR spectrum of compound **56** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 186.4 (d, 1C, *C*=Au, $^{2}J_{C-P}$ = 115.2 Hz); 162.3 (d, 1C, C_{ipso}*Ph-F*, $^{1}J_{C-F}$ = 240.1 Hz); 154.9 (s, 1C, *CO*); 148.7 (d, 1C, C_{ipso}*-2*, $^{2}J_{C-P}$ = 14.3 Hz); 142.9 (d, 1C, C_{ipso}*-3*, $^{3}J_{C-P}$ = 6.0 Hz); 142.9 (s, 1C, C_{ipso}*Ph*-NH); 136.4 (s, 1C, C_{ipso}*Ph*-CH_2); 134.8-127.3 (m, 10C, *5*+*JohnPhos*); 128.6 (s, 2C, C_{orto}*Ph*); 127.8 (s, 1C, C_{para}*Ph*); 126.7 (s, 2C, C_{meta}*Ph*); 125.2 (d, 1C, C_{ipso}*-1*, $^{1}J_{C-P}$ = 42.5 Hz); 122.6 (s, 1C, *imidazole*); 122.2 (s, 1C, *imidazole*); 113.2 (d, 1C, *4*, $^{4}J_{C-F}$ = 2.3 Hz); 107.3 (d, 1C, *6*, $^{2}J_{C-F}$ = 21.2 Hz); 104.2 (d, 1C, *7*, $^{2}J_{C-F}$ = 26.6 Hz); 53.4 (s, 1C, Ph-CH_2-imidazole); 50.8 (s, 1C, NH-CH_2-CH_2); 39.8 (s, 1C, NH-CH_2-CH_2); 37.1 (d, 2C, $C_{ipso}{}^{t}$*Bu*, $^{1}J_{C-P}$ = 23.0 Hz); 30.3 (d, 6C, ^{t}*Bu*, $^{1}J_{C-P}$ = 6.4 Hz).

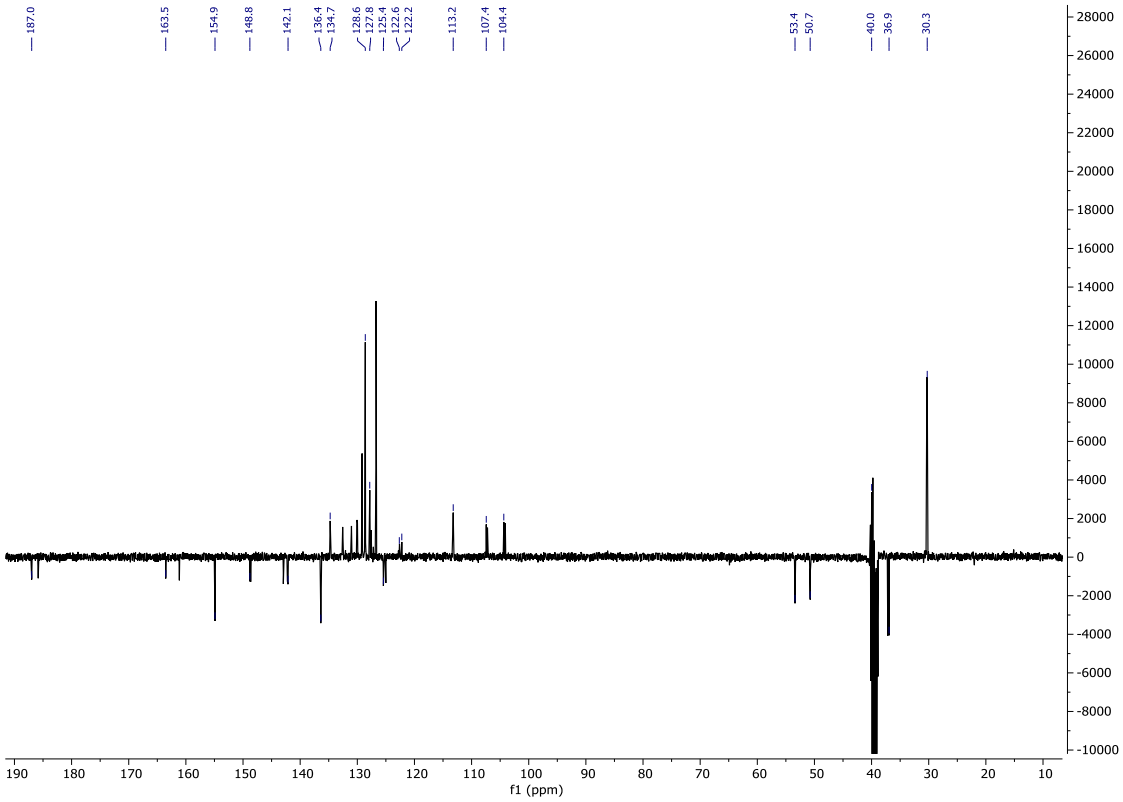


Figure 2.16. ^{13}C APT spectrum of compound **56** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{39}H_{46}AuFN_4OP]^+$ 833.3053. Found 833.3034.

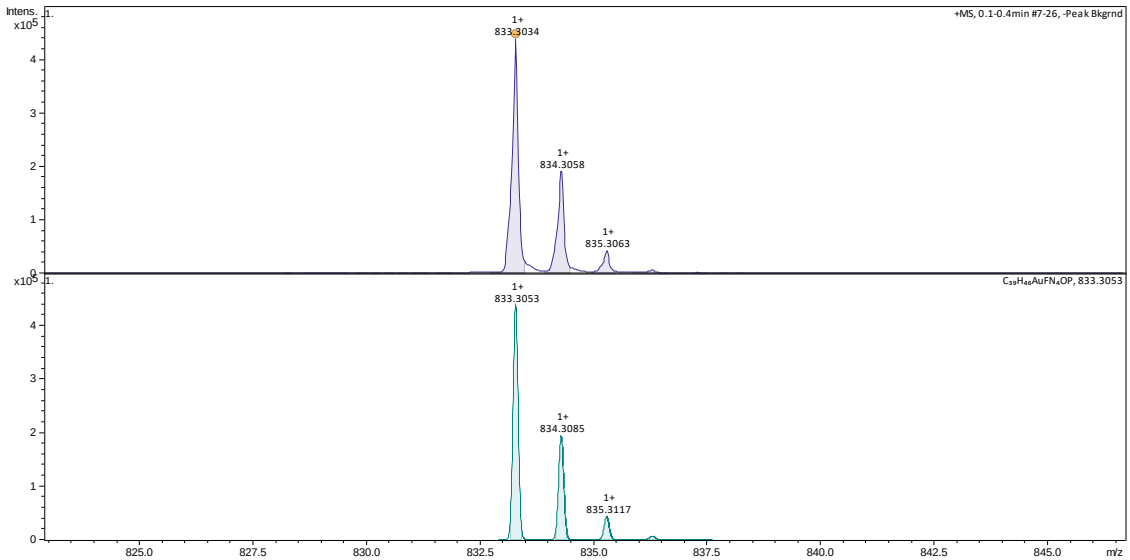
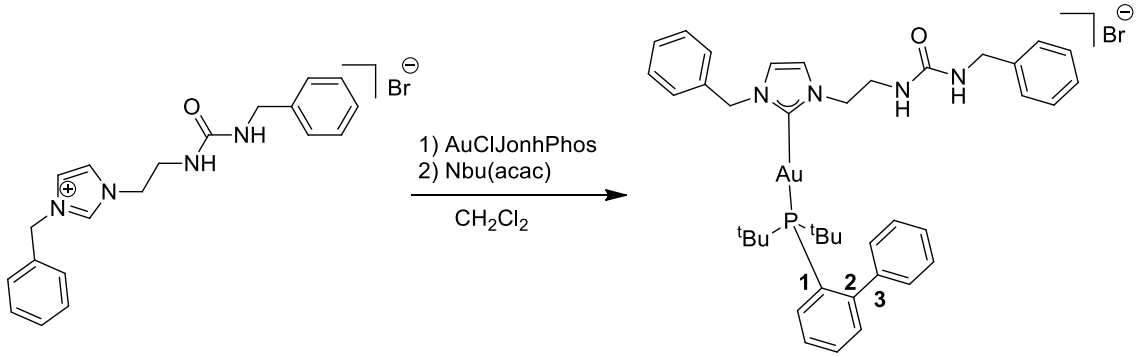


Figure 2.17. MS (ESI+ µ-TOF) compound **56**.

Synthesis of compound 57

To a solution of compound **54** (83 mg, 0.2 mmol) and [AuCl(JohnPhos)] (106 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred for 2.5h. The solution washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 52%



Scheme 2.7. Synthesis of compound **57**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.00-6.85 (m, 21H, CH_2-*Ph+JohnPhos*); 6.45 (t, 1H, CO-*NH*-CH_2-Ph, $^3J_{H\text{-}H}$ = 6.0 Hz); 6.10 (t, 1H, CH_2-CH_2-*NH*-CO, $^3J_{H\text{-}H}$ = 5.8 Hz); 5.18 (s, 2H, Ph-*CH_2*-imidazole); 4.16 (d, 2H, NH-*CH_2*-Ph, $^3J_{H\text{-}H}$ = 6.0 Hz); 4.01 (t, 2H, *CH_2*-CH_2-NH-CO, $^3J_{H\text{-}H}$ = 6.1 Hz); 3.42 (m, 2H, CH_2-*CH_2*-NH-CO); 1.28 (d, 18H, ^{t}*Bu*, $^3J_{H\text{-}P}$ = 15.4 Hz).

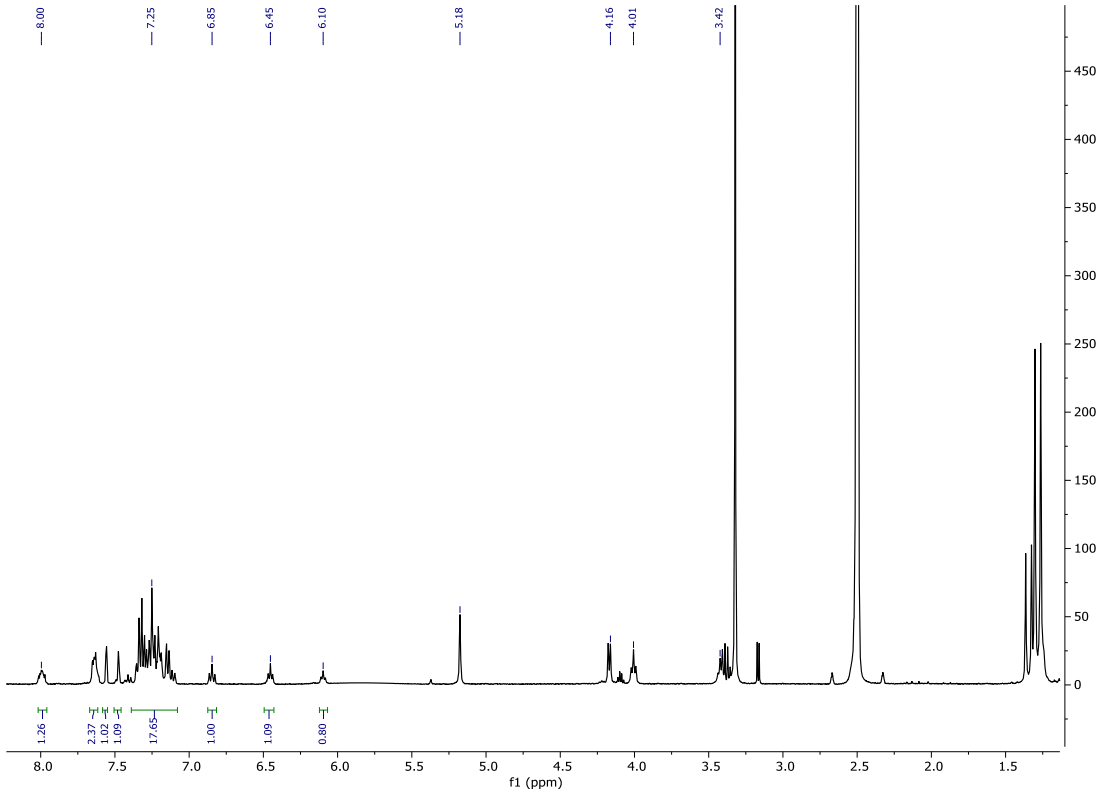


Figure 2.18. ^{1}H NMR spectrum of compound **57** in DMSO solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, DMSO): δ = 64.1 (s, 1P, *JohnPhos*).

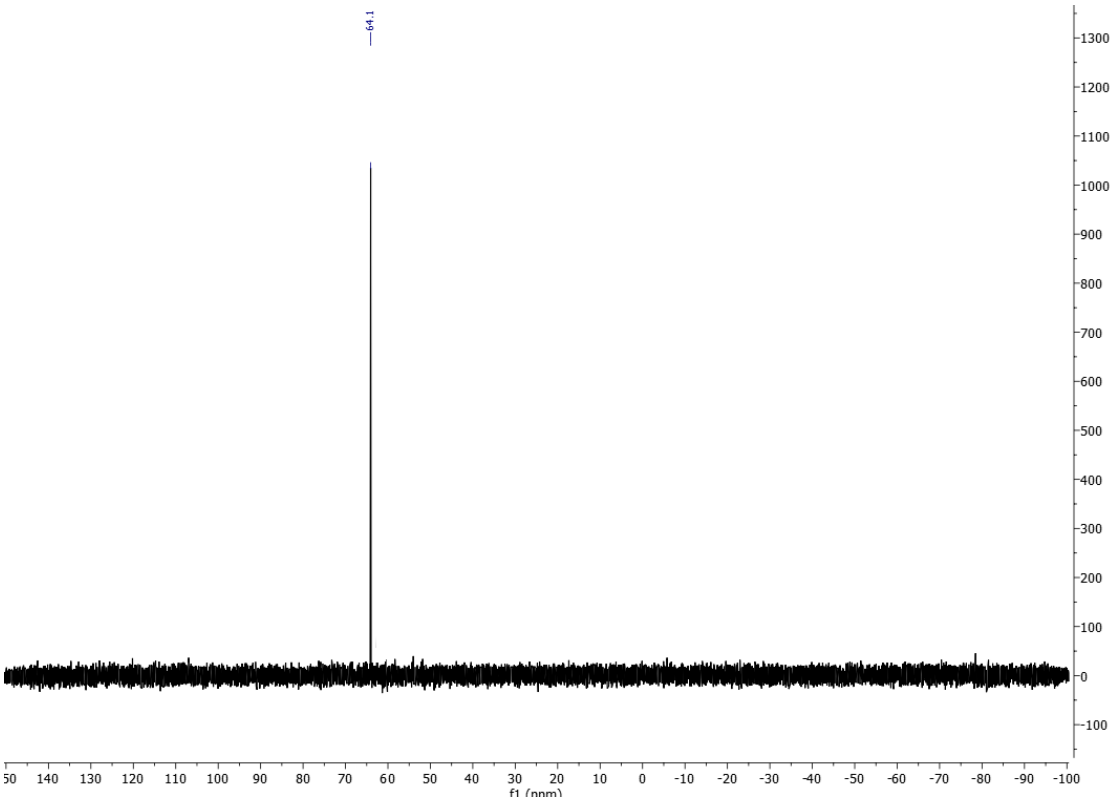


Figure 2.19. ^{31}P{^{1}H} NMR spectrum of compound **57** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 186.3 (d, 1C, *C*=Au, $^{2}J_{C\text{-}P}$ = 115.2 Hz); 157.8 (s, 1C, *CO*); 148.7 (d, 1C, C_{ipso}-*2*, $^{2}J_{C\text{-}P}$ = 14.3 Hz); 142.9 (d, 1C, C_{ipso}-*3*, $^{3}J_{C\text{-}P}$ = 6.1 Hz); 140.7 (s, 1C, C_{ipso}*Ph*-CH_2-NH); 136.4 (s, 1C, C_{ipso}*Ph*-CH_2-imidazole); 134.7-126.5 (m, 19C, CH_2-*Ph*+*JohnPhos*); 125.5 (d, 1C, C_{ipso}-*1*, $^{1}J_{C\text{-}P}$ = 42.5 Hz); 122.4 (s, 1C, *imidazole*); 122.2 (s, 1C, *imidazole*); 53.9 (s, 1C, Ph-CH_2-imidazole); 50.9 (s, 1C, NH-CH_2-CH_2); 42.8 (s, 1C, NH-CH_2-Ph); 39.8 (s, 1C, NH-CH_2-CH_2); 37.1 (d, 2C, C_{ipso}^{t}*Bu*, $^{1}J_{C\text{-}P}$ = 23.0 Hz); 30.3 (d, 6C, ^{t}*Bu*, $^{1}J_{C\text{-}P}$ = 6.4 Hz).

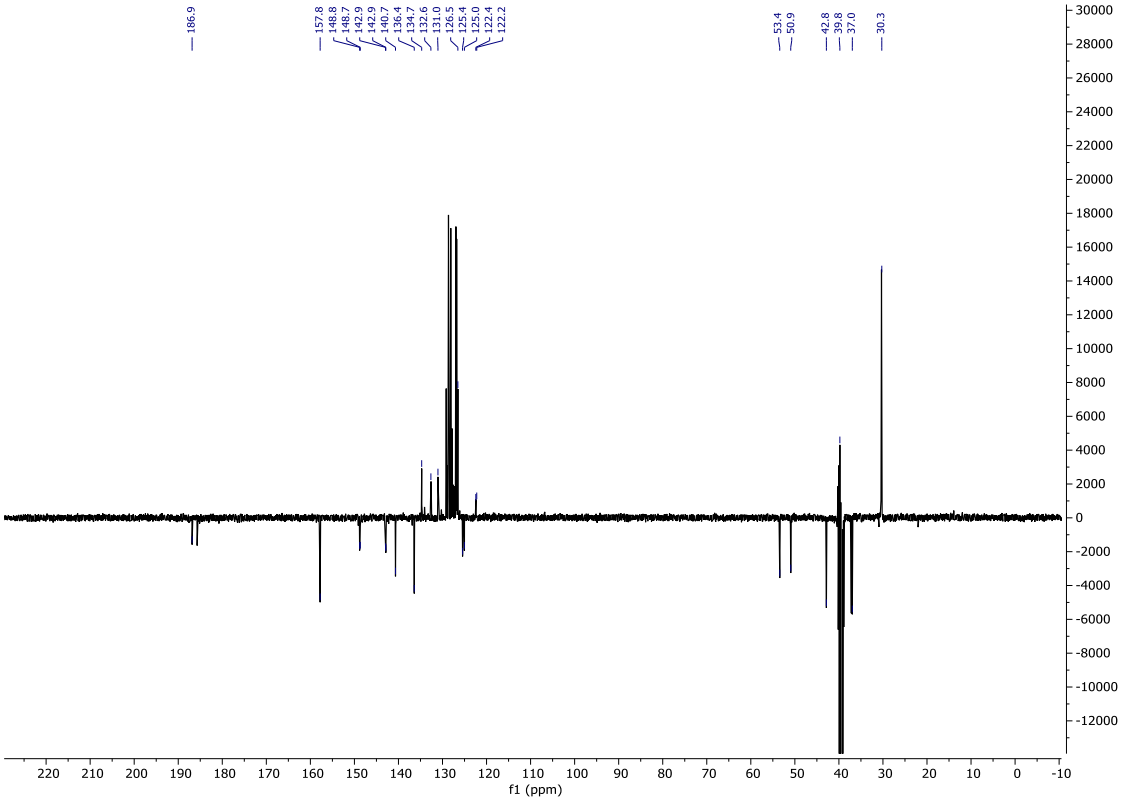


Figure 2.20. ^{13}C APT spectrum of compound **57** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{40}H_{49}AuN_4OP]^+$ 829.3304. Found 829.3274.

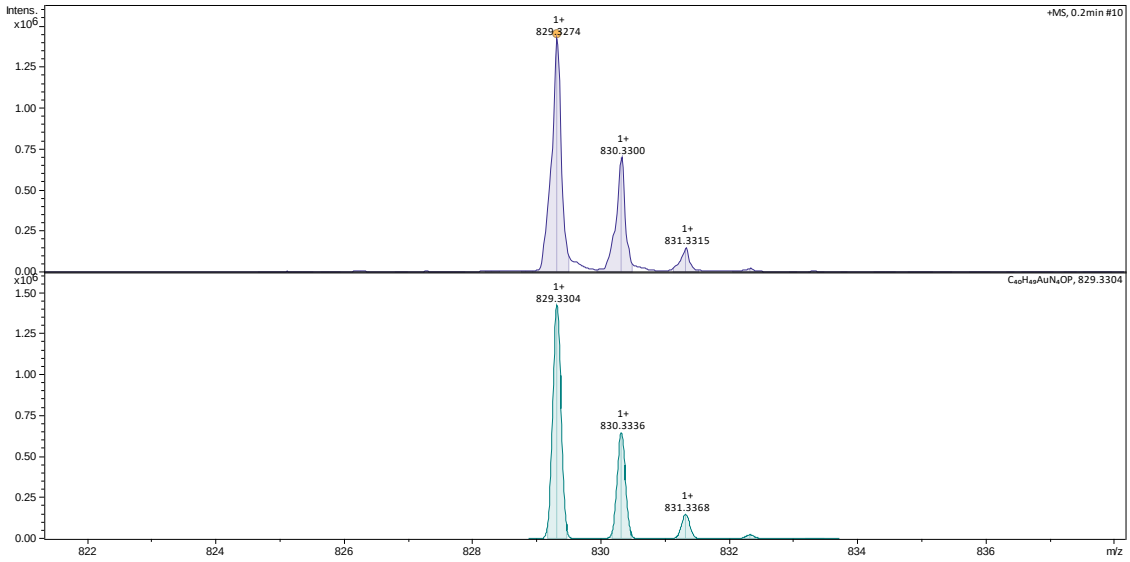
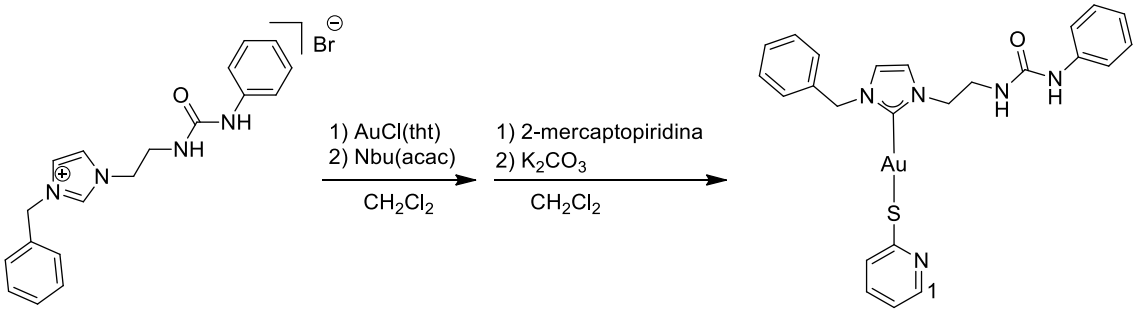


Figure 2.21. MS (ESI+ µ-TOF) compound **57**.

Synthesis of compound 58

To a solution of compound **52** (80 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 4.5h later, 2-mercaptopyridine was added (22 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 55%



Scheme 2.8. Synthesis of compound **58**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.58 (s br, 1H, CO-*NH*-Ph); 8.13 (s, 1H, *1*); 7,53 (m, 2H, *imidazole*); 7.32-6.88 (m, 13H, *Ph*+CH_2-*Ph*+*arom*); 6.32 (t, 1H, CH_2-*NH*-CO, $^3J_{H\text{-}H}$ = 5.9 Hz); 5.42 (s, 2H, Ph-*CH_2*-imidazole); 4.27 (t, 2H, NH-CH_2-*CH_2*, $^3J_{H\text{-}H}$ = 5.7 Hz); 3.59 (m, 2H, NH-*CH_2*-CH_2).

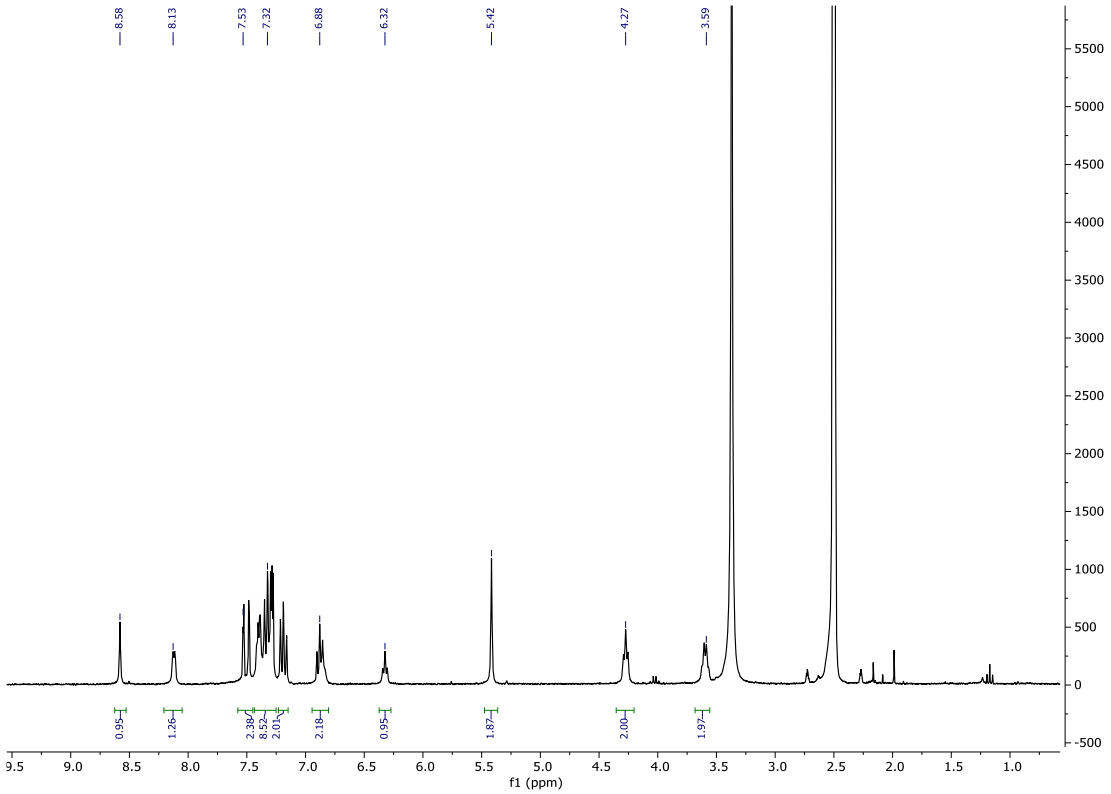


Figure 2.22. ^{1}H NMR spectrum of compound **58** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 155.1 (s, 1C, *CO*); 148.0 (s, 1C, *1*); 140.3 (s, 1C, C_{ipso}*Ph*-NH); 136.8 (s, 1C, C_{ipso}*Ph*-CH_2); 136.6 (s, 1C, *arom*); 128.6 (s, 2C, C_{ortho}*Ph*-CH_2); 128.5 (s, 2C, C_{ortho}*Ph-NH*); 127.9 (s, 1C, C_{para}*Ph*-CH_2); 127.6 (s, 2C, C_{meta}*Ph*-CH_2); 126.8 (s, 1C, *arom*); 122.3 (s, 1C, *imidazole*); 121.6 (s, 1C, *imidazole*); 121.1 (s, 1C, C_{para}*Ph-NH*); 117.8 (s, 2C, C_{meta}*Ph-NH*); 117.7 (s, 1C, *2*); 53.5 (s, 1C, Ph-CH_2-imidazole); 50.7 (s, 1C, NH-CH_2-CH_2); 40.0 (s, 1C, NH-CH_2-CH_2).

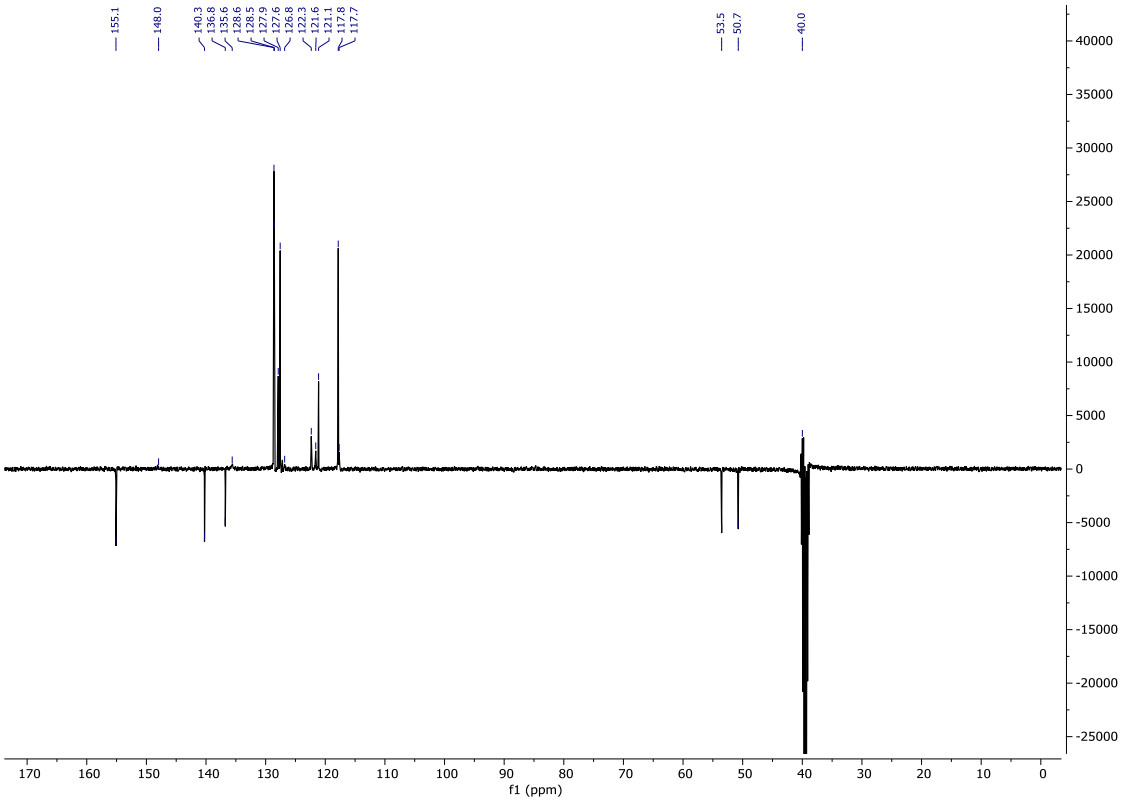


Figure 2.23. ^{13}C APT spectrum of compound **58** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{24}H_{25}AuN_5OS]^+$ 628.1440. Found 628.1412.

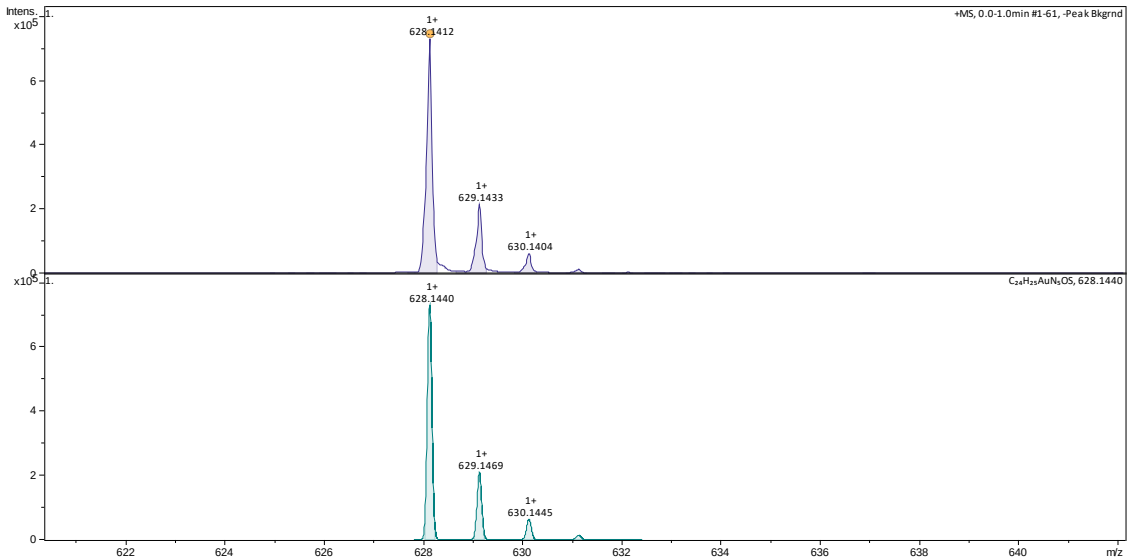


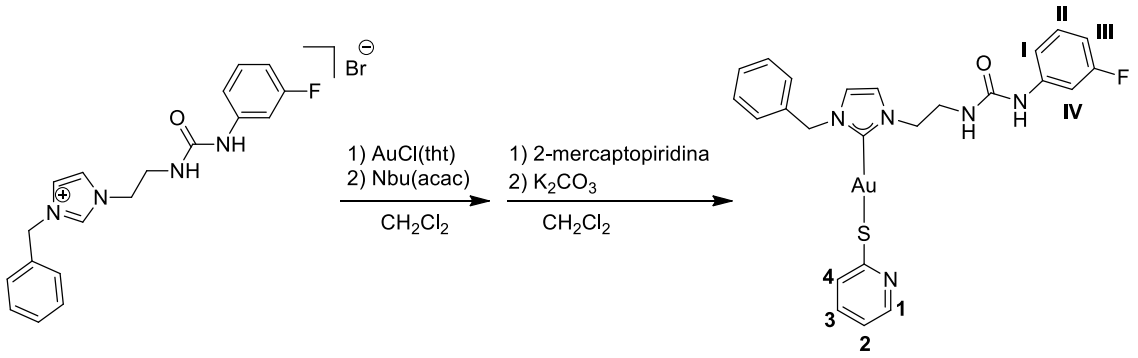
Figure 2.24. MS (ESI+ µ-TOF) compound **58**.

Synthesis of compound 59

To a solution of compound **53** (83.86 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added NBu_4(acac) (64 mg, 0.2 mmol) and the mixture

stirred. 4.5h later, 2-mercaptopyridine was added (22 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 53%



Scheme 2.9. Synthesis of compound **59**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.88 (s br, 1H, CO-*NH*-Ph); 8.12 (s, 1H, *1*); 7.51 (m, 2H, *imidazole*); 7.39-7.28 (m, 9H, CH_2-*Ph+3+4+ IV*); 7.21 (m, 1H, *II*); 6.96 (m, 1H, *I*); 6.84 (m, 1H, *2*); 6.68 (m, 1H, *III*); 6.43 (t br, 1H, CH_2-*NH*-CO); 5.41 (s, 2H, Ph-*CH_2*-imidazole); 4.27 (t br, 2H, NH-CH_2-*CH_2*); 3.59 (m, 2H, NH-*CH_2*-CH_2).

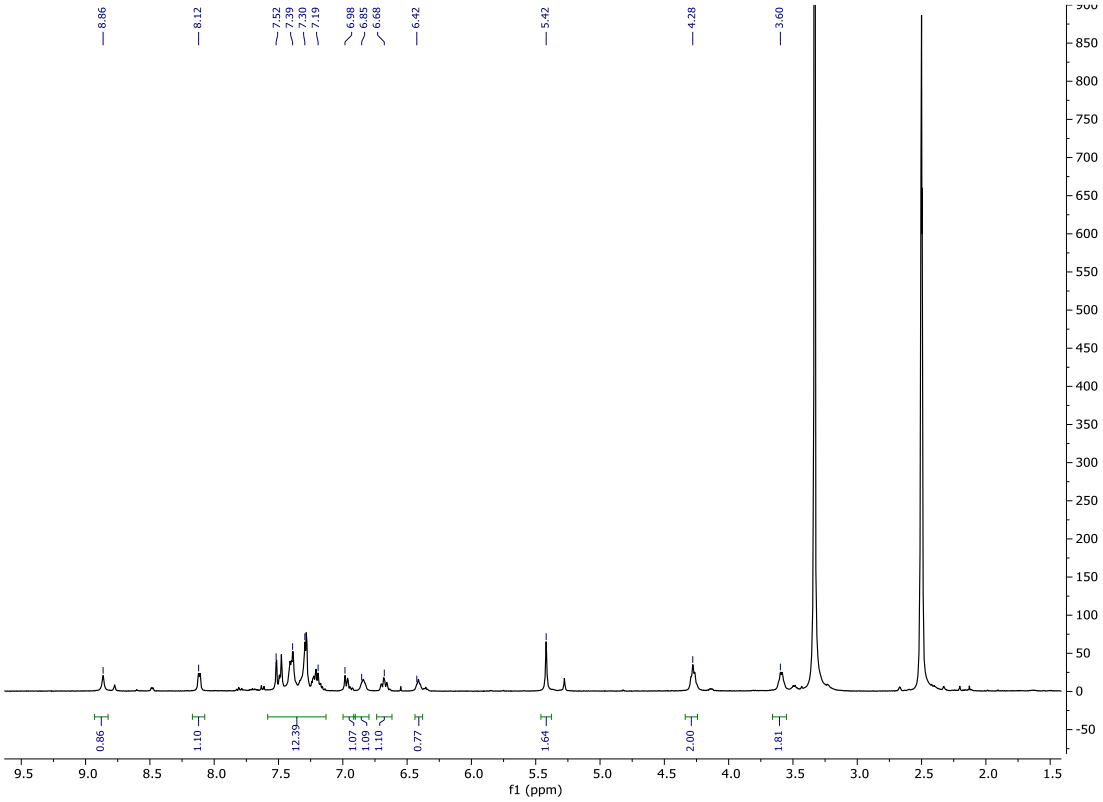


Figure 2.25. [1]H NMR spectrum of compound **59** in DMSO solution.

^{19}F ^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -112.5 (m, 1F, *Ph-F*).

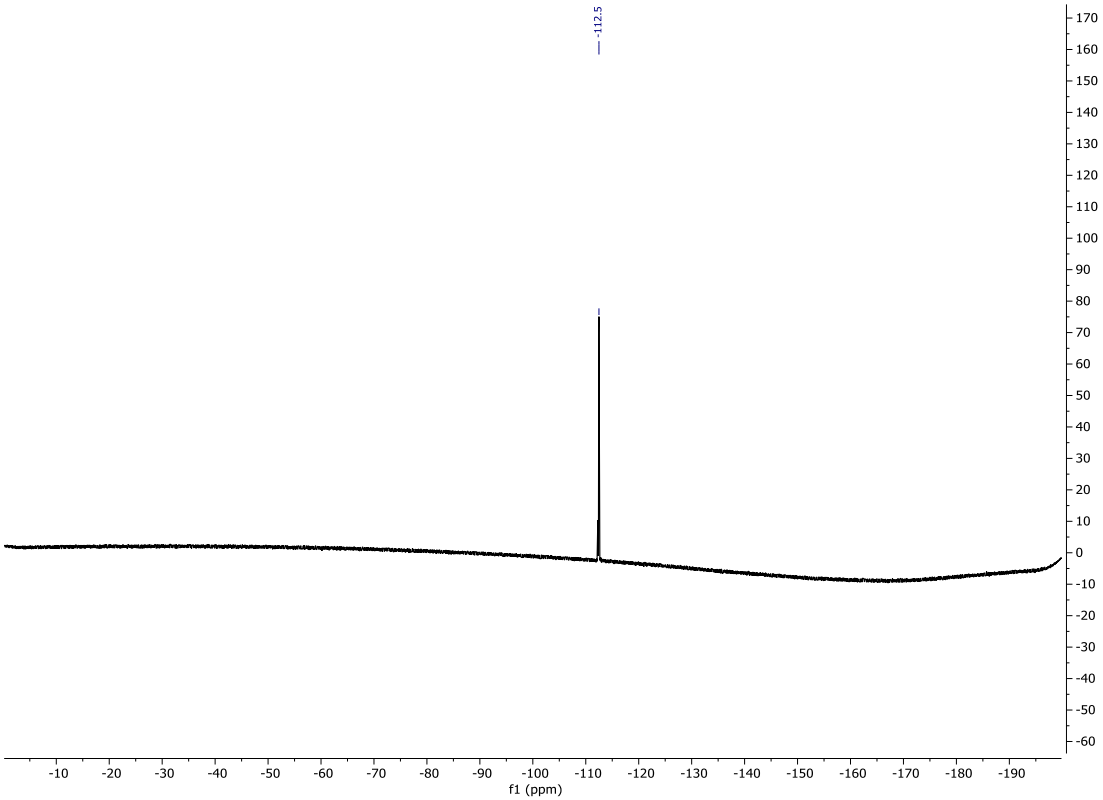


Figure 2.26. [19] F{[1]H} NMR spectrum of compound **59** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 183.2 (s, 1C, *C*=Au); 162.3 (d, 1C, C_{ipso}*Ph-F*, $^{1}J_{C\text{-}F}$ = 240.1 Hz); 154.9 (s, 1C, *CO*); 149.7 (s, 1C, *1*); 142.2 (d, 1C, C_{ipso}*Ph*-NH, $^{3}J_{C\text{-}F}$ = 11.5 Hz); 138.1 (s, 1C, *arom*); 136.8 (s, 1C, C_{ipso}*Ph*-CH_2); 136.1 (d, 1C, *II*, $^{3}J_{C\text{-}F}$ = 9.9 Hz); 128.6 (s, 2C, C_{ortho}*Ph*); 127.9 (s, 1C, C_{para}*Ph*); 127.6 (s, 2C, C_{meta}*Ph*); 127.2 (s, 1C, *arom*); 122.4 (s, 1C, *imidazole*); 121.8 (s, 1C, *imidazole*); 119.6 (s, 1C, *2*); 113.4 (s, 1C, *I*); 107.5 (d, 1C, *III*, $^{2}J_{C\text{-}F}$ = 21.2 Hz); 104.2 (d, 1C, *IV*, $^{2}J_{C\text{-}F}$ = 26.5 Hz); 53.5 (s, 1C, Ph-CH_2-imidazole); 50.7 (s, 1C, NH-CH_2-CH_2); 39.8 (s, 1C, NH-CH_2-CH_2).

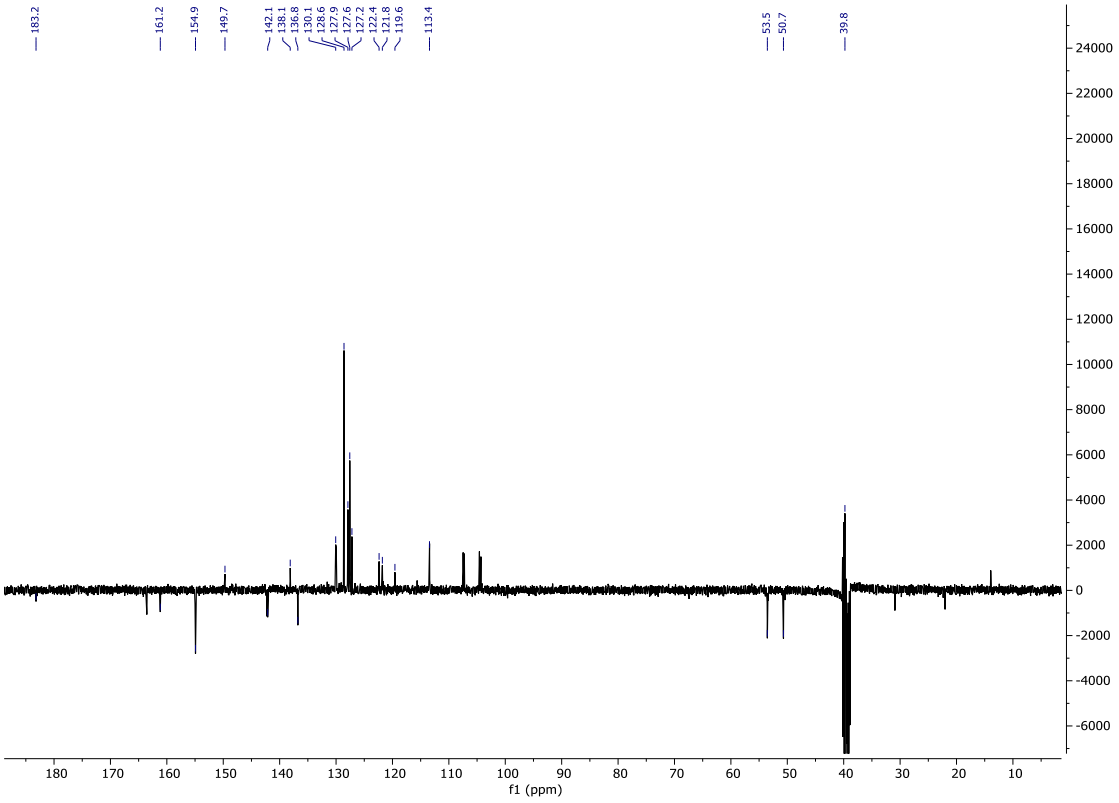


Figure 2.27. ^{13}C APT spectrum of compound **59** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= [$M]^+$ Calcd for $[C_{24}H_{24}AuFN_5OS]^+$ 646.1346. Found 646.1329.

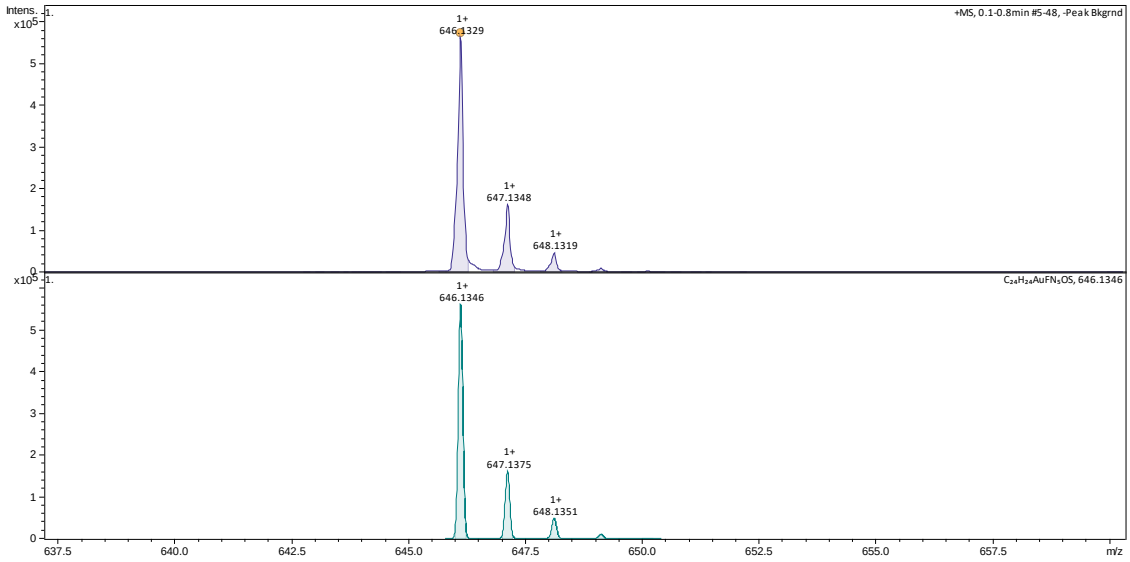
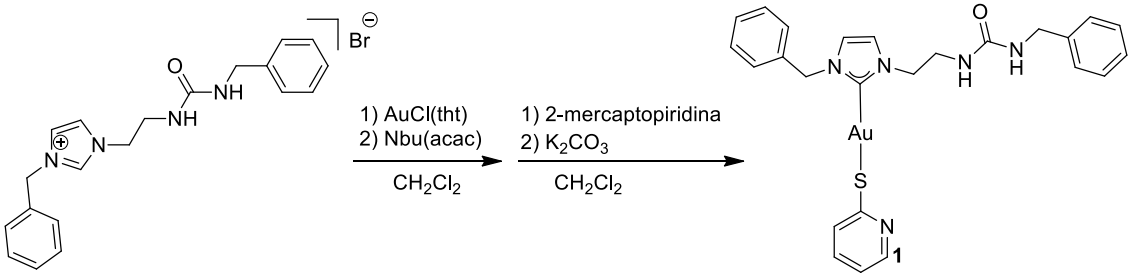


Figure 2.28. MS (ESI+ µ-TOF) compound **59**.

Synthesis of compound 60

To a solution of compound **54** (83.0 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 4.5h later, 2-mercaptopyridine was added (22 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 60%



Scheme 2.10. Synthesis of compound **60**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.11 (s, 1H, *1*); 7.54-7.23 (m, 14H, CH_2-*Ph* + *imidazole* + *arom*); 6.83 (s, 1H, *2*); 6.42 (t, 1H, CO-*NH*-CH_2-Ph, $^3J_{H\text{-}H}$ = 5.9 Hz); 6.17 (t, 1H, CO-*NH*-CH_2-Ph, $^3J_{H\text{-}H}$ = 5.6 Hz); 5.42 (s, 2H, Ph-*CH_2*-imidazole); 4.23 (t, 2H, imidazole-*CH_2*-CH_2, $^3J_{H\text{-}H}$ = 5.4 Hz); 4.18 (d, 2H, CO-NH-*CH_2*-Ph, $^3J_{H\text{-}H}$ = 5.8 Hz); 3.53 (m, 2H, imidazole-CH_2-*CH_2*-NH).

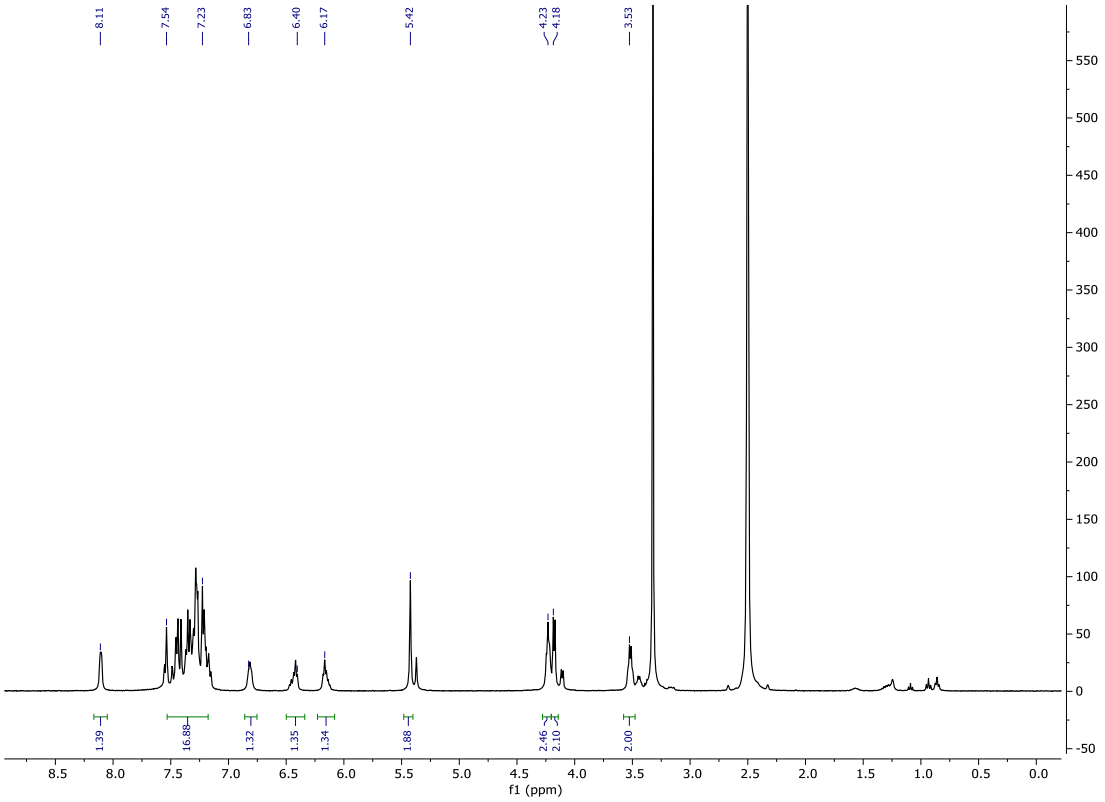


Figure 2.29. ^{1}H NMR spectrum of compound **60** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 183.1 (s, 1C, *C=Au*); 157.9 (s, 1C, *CO*); 148.3 (s, 1C, *1*); 140.7 (s, 1C, C_{ipso}*Ph*-CH_2-NH); 136.8 (s, 1C, C_{ipso}*Ph*-CH_2-imidazole); 136.0 (s, 1C, *arom*); 128.6-126.4 (m, 11C, CH_2-*Ph* + *arom*); 122.2 (s, 1C, *imidazole*); 121.4 (s, 1C, *imidazole*); 117.3 (s, 1C, *2*); 53.5 (s, 1C, Ph-*CH_2*-imidazole); 50.8 (s, 1C, imidazole-*CH_2*-CH_2-NH); 42.9 (CO-NH-*CH_2*-Ph); 40.1 (s, 1C, imidazole-CH_2-*CH_2*-NH)

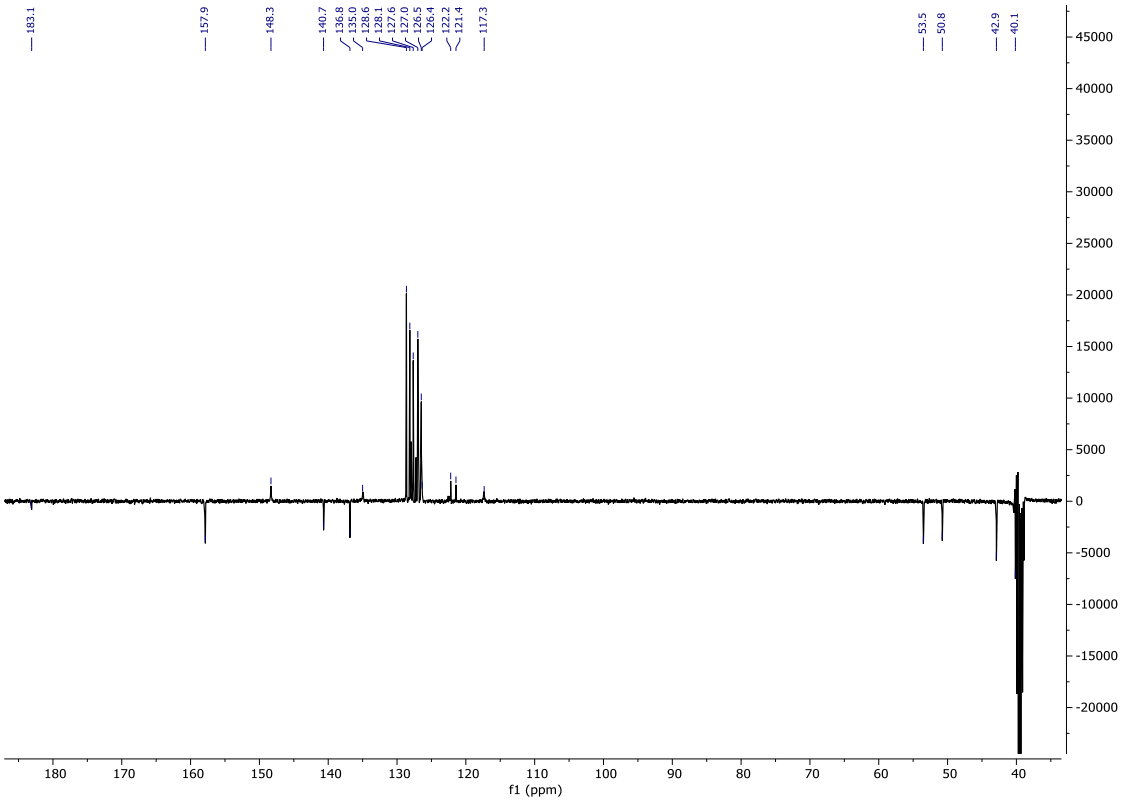


Figure 2.30. ^{13}C APT spectrum of compound **60** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{25}H_{27}AuN_5OS]^+$ 642.1597. Found 642.1582.

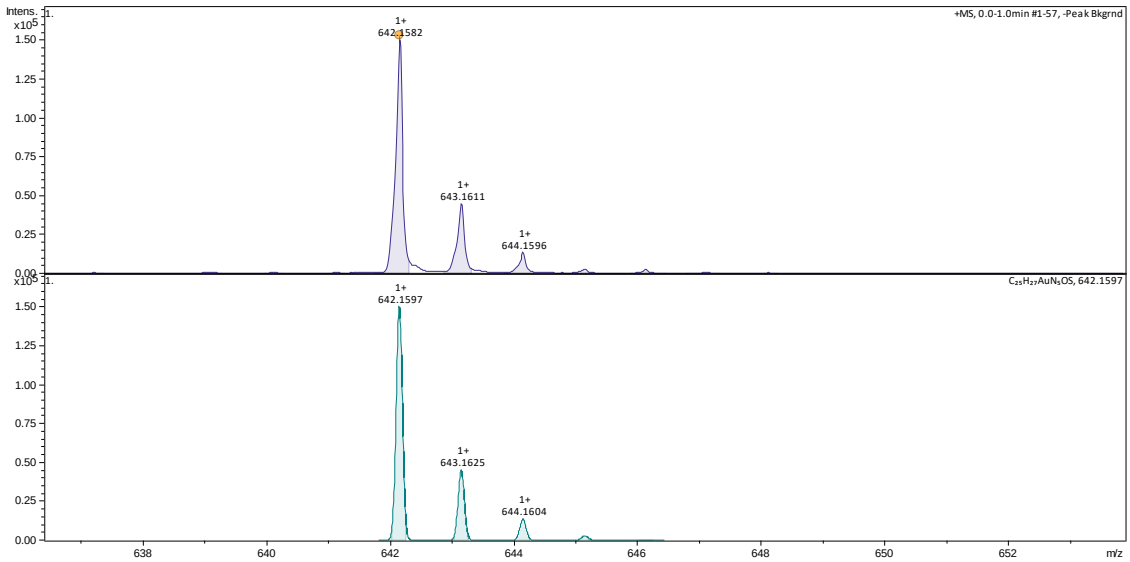


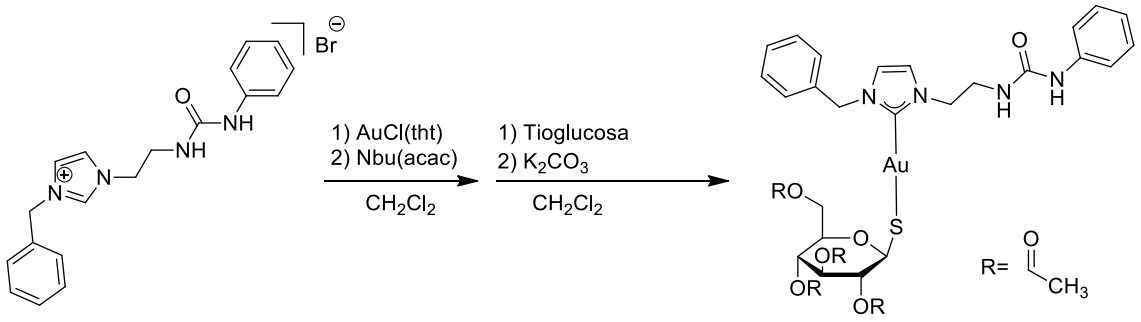
Figure 2.31. MS (ESI+ µ-TOF) compound **60**.

Synthesis of compound 61

To a solution of compound **52** (80.0 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added NBu_4(acac) (64 mg, 0.2 mmol) and the mixture

stirred. 4.5h later, 1-Thio-beta-D-glucose tetraacetate was added (73 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 58%



Scheme 2.11. Synthesis of compound **61**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.47 (s br, 1H, CO-*NH*-Ph); 7.51-6.89 (m, 12H, CH_2-*Ph + imidazole*); 6.24 (t, 1H, CH_2-*NH*-CO, $^3J_{H\text{-}H}$ = 5.8 Hz); 5.39 (m, 2H, Ph-*CH_2*-imidazol); 5.12; 4.84; 3.91 (m, 5H, *thioglucose*); 4.05 (m, 2H, CH_3COO-*CH_2*-6-member ring thioglucose); 4.23 (t, 2H, NH-CH_2-*CH_2*, $^3J_{H\text{-}H}$ = 5.9 Hz); 3.57 (m, 2H, NH-*CH_2*-CH_2); 1.96 (m, 12H, *CH_3*).

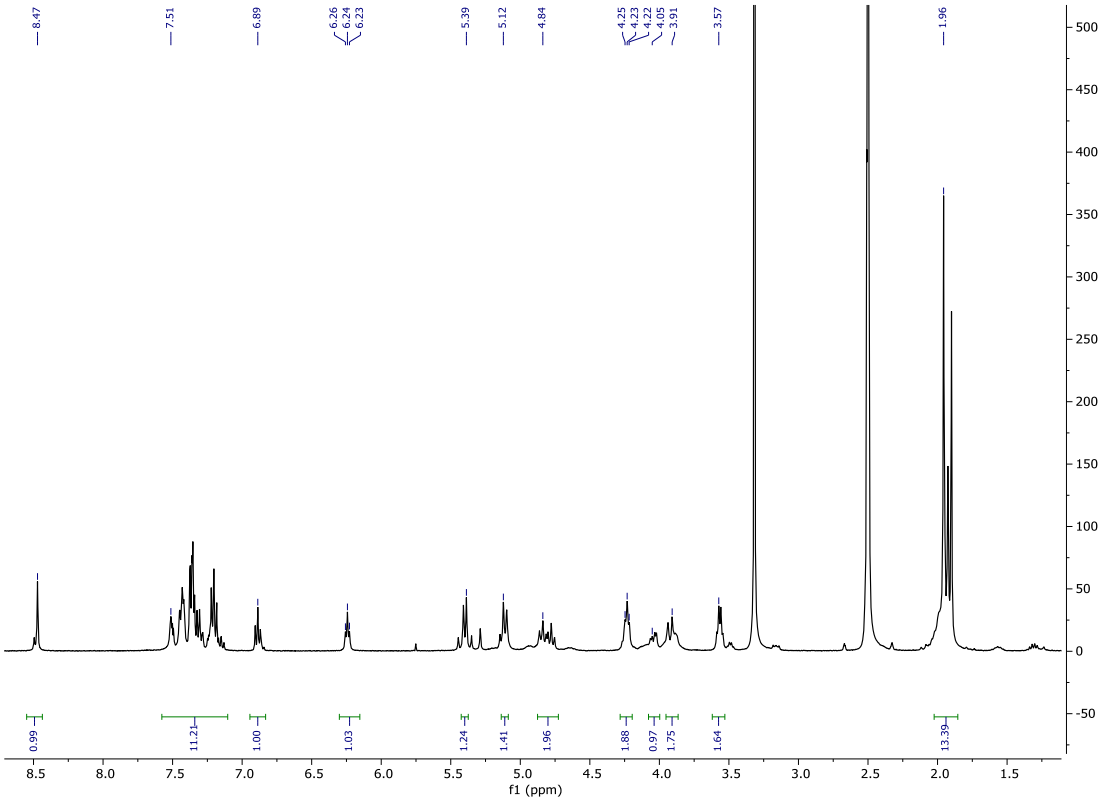


Figure 2.32. ^{1}H NMR spectrum of compound **61** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 183.2 (s, 1C, *C*=Au); 170.0 (s, 4C, *CO-thioglucose*); 155.0 (s, 1C, *CO*); 140.2 (s, 1C, C_{ipso}*Ph*-NH); 136.8 (s, 1C, C_{ipso}*Ph*-CH_2); 128.6-117.8 (m, 12C, CH_2-*Ph+imidazole*); 81.7; 77.0; 74.3; 73.5; 68.6 (s, 5C, *thioglucose-ring*); 62.4 (s, 1C, CH_3COO-CH_2-6-member ring thioglucose); 53.4 (s, 1C, Ph-CH_2-imidazol); 50.5 (s, 1C, NH-CH_2-CH_2); 39.8 (s, 1C, NH-CH_2-CH_2); 20.3 (s, 4C, CH_3).

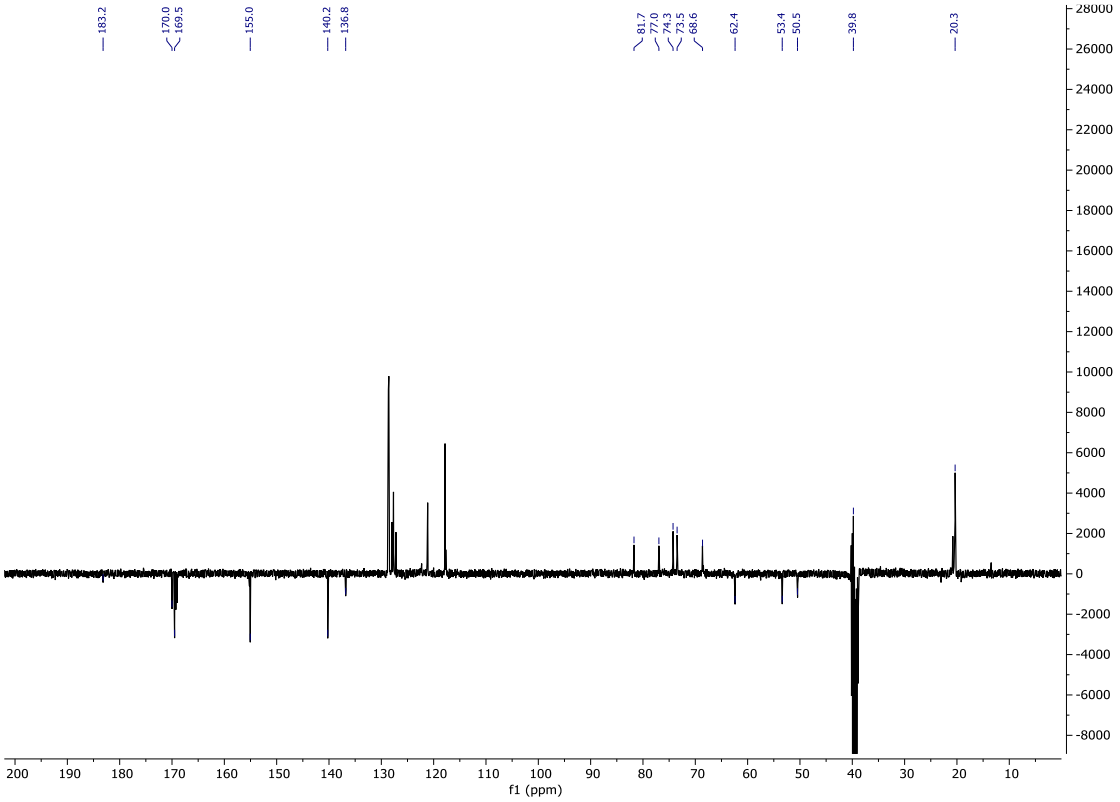


Figure 2.33. ^{13}C APT spectrum of compound **61** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{33}H_{40}AuN_4O_{10}S]$ 881.72. Found 903.1889 $[C_{33}H_{40}AuN_4O_{10}S + Na]^+$.

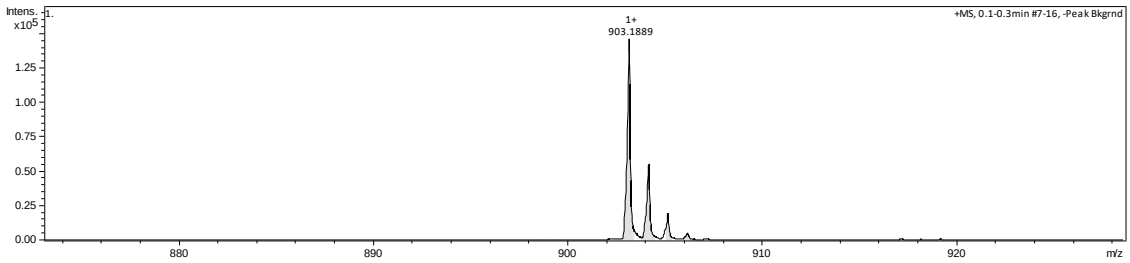
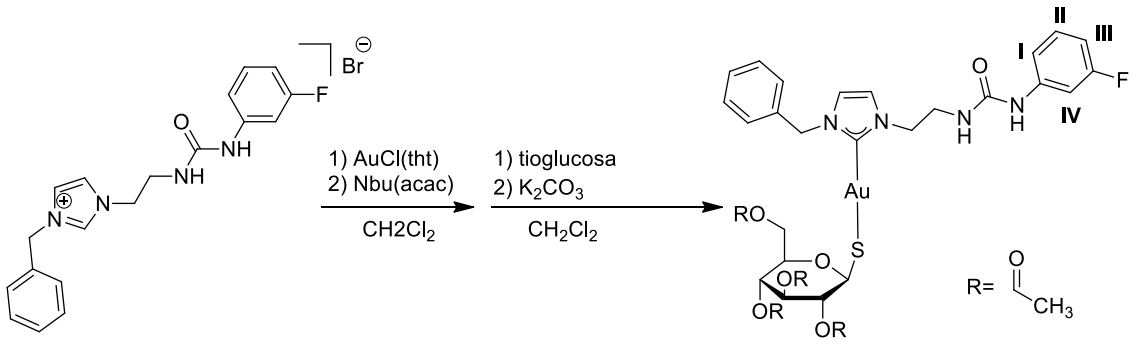


Figure 2.3. MS (ESI+ µ-TOF) compound **61**.

Synthesis of compound 62

To a solution of compound **53** (83.86 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 4.5h later, 1-Thio-beta-D-glucose tetraacetate was added (73 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 54%



Scheme 2.12. Synthesis of compound **62**.

^{1}H NMR (ppm) (400 MHz, (DMSO): δ = 8.75 (s br, 1H, CO-*NH*-Ph); 7.51-7.23 (m, 9H, CH_2-*Ph + imidazole + II + IV*); 7.02 (m, 1H, *I*); 6.69 (m, 1H, *III*); 6.34 (t, 1H, CH_2-*NH*-CO, $^{3}J_{H-H}$ = 5.9 Hz); 5.39 (m, 2H, Ph-CH_2-imidazol); 5.09; 4.78; 3.90 (m, 5H, *thioglucose*); 4.05 (m, 2H, CH_3COO-CH_2-6-member ring thioglucose); 4.23 (t, 2H, NH-CH_2-CH_2, $^{3}J_{H-H}$ = 5.9 Hz); 3.57 (m, 2H, NH-CH_2-CH_2); 1.96 (m, 12H, CH_3).

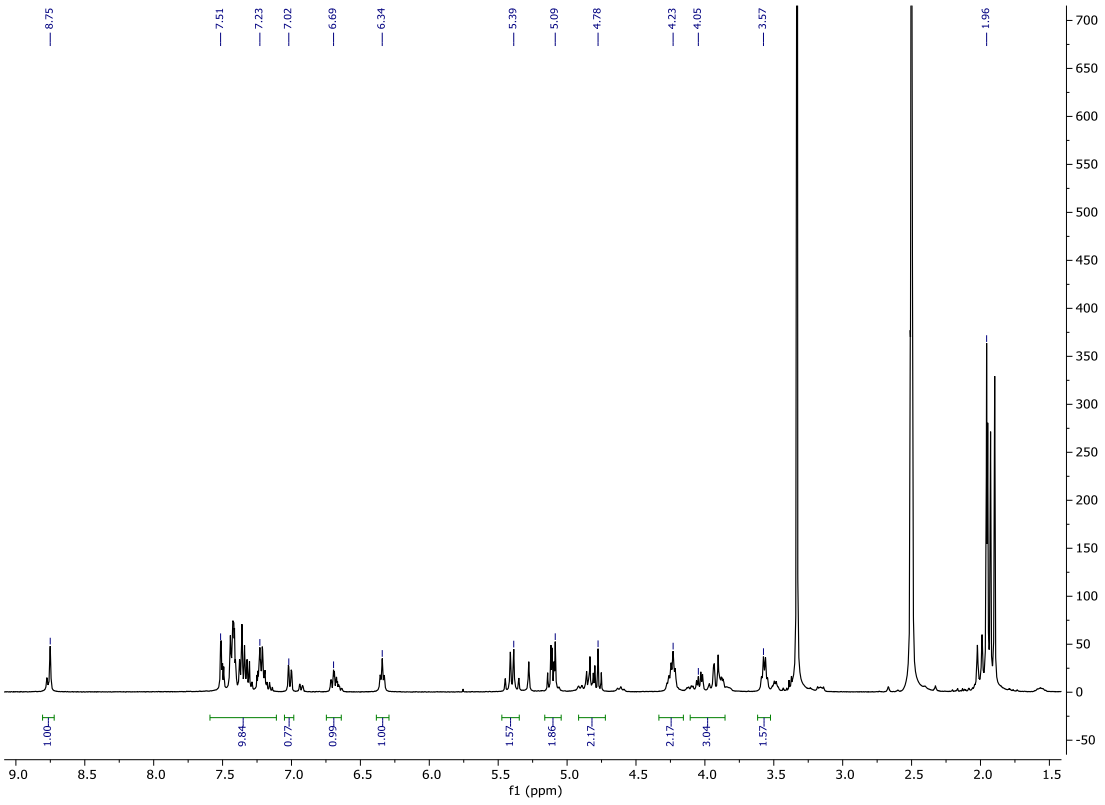


Figure 2.35. ^{1}H NMR spectrum of compound **62** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -112.5 (s, 1F, *Ph*).

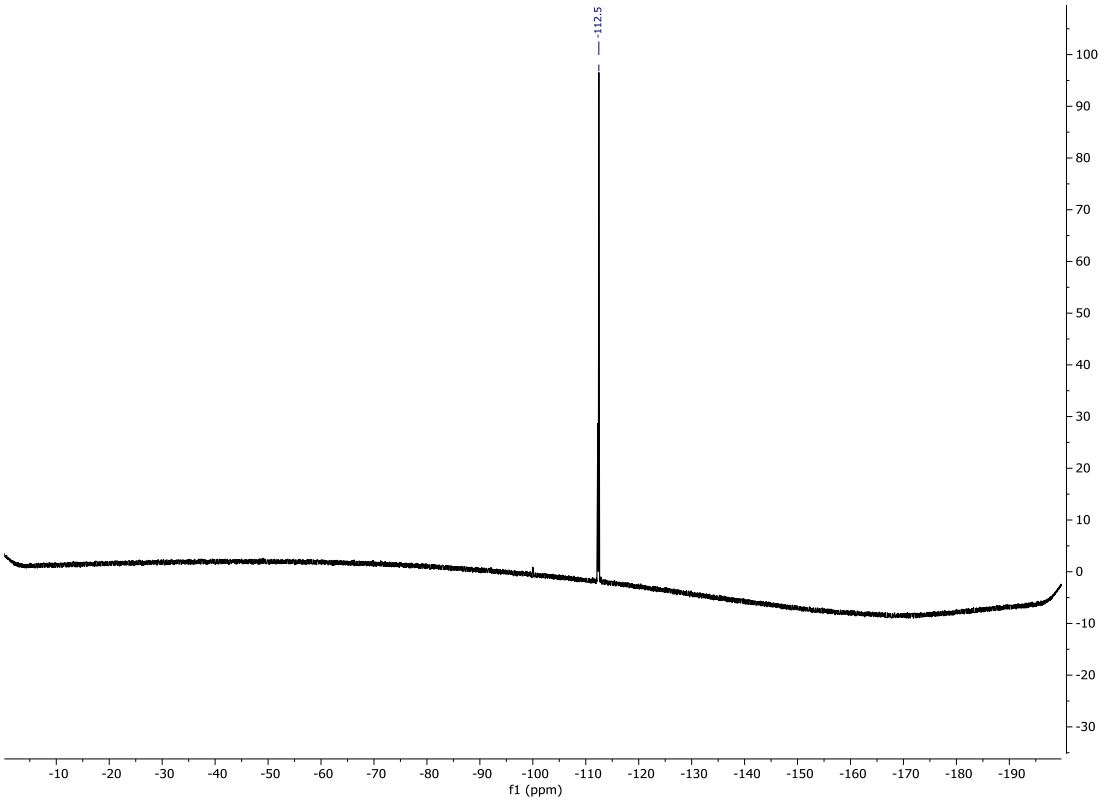


Figure 2.36. $^{19}F\{^{1}H\}$ NMR spectrum of compound **62** in DMSO solution.

^{13}C APT (ppm) (100 MHz, (DMSO): δ = 181.1 (s, 1C, *C*=Au); 169.5 (s, 4C, *CO-thioglucose*); 162.4 (d, 1C, C_{ipso}*Ph-F*, $^{1}J_{C\text{-}F}$ = 240.2 Hz); 154.9 (s, 1C, *CO*); 142.2 (d, 1C, C_{ipso}*Ph-F*, $^{3}J_{C\text{-}F}$ = 11.5 Hz); 136. 9(s, 1C, C_{ipso}*Ph*-CH_2); 130.1 (d, 1C, *II*, $^{3}J_{C\text{-}F}$ = 9.8 Hz); 128.6 (s, 2C, C_{ortho}*Ph*); 128.0 (s, 1C, C_{para}*Ph*); 127.7 (s, 2C, C_{meta}*Ph*); 122.3 (s, 1C, *imidazole*); 121.3 (s, 1C, *imidazole*); 113.5 (s, 1C, *I*); 107.4 (d, 1C, *III*, $^{2}J_{C\text{-}F}$ = 21.1 Hz); 104.5 (d, 1C, *IV*, $^{3}J_{C\text{-}F}$ = 26.4 Hz); 81.7; 77.0; 74.3; 73.5; 68.6 (s, 5C, *thioglucose-ring*); 62.4 (s, 1C, CH_3COO-CH_2-6-member ring thioglucose); 53.4 (s, 1C, Ph-CH_2-imidazole); 50.4 (s, 1C, NH-CH_2-CH_2); 39.8 (s, 1C, NH-CH_2-CH_2); 20.3 (s, 4C, CH_3).

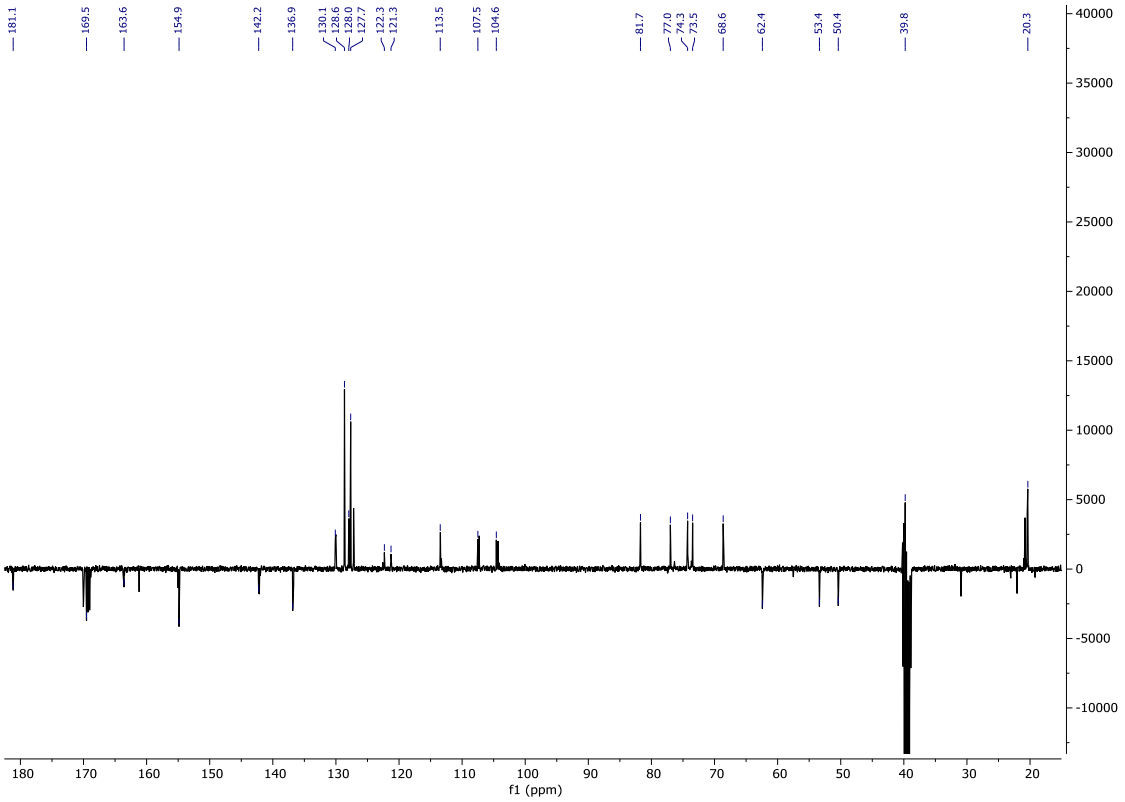


Figure 2.37. ^{13}C APT spectrum of compound **62** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{33}H_{39}AuFN_4O_{10}S]$ 899.714. Found 921.1815 $[C_{33}H_{39}AuFN_4O_{10}S + Na]^+$.

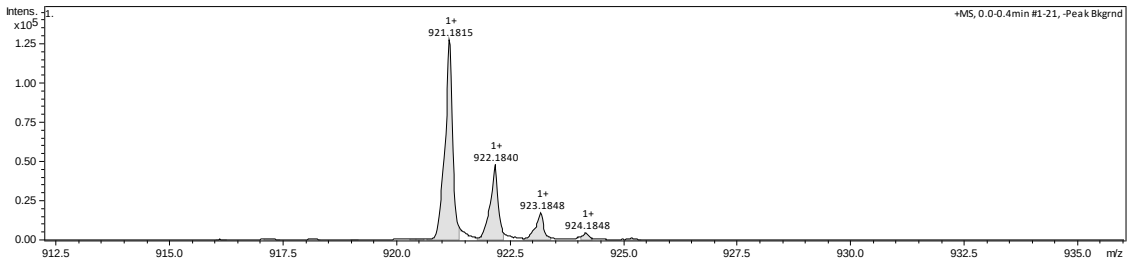
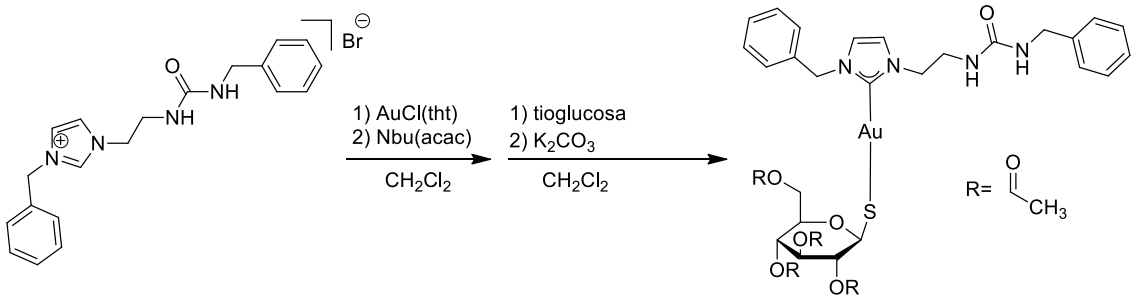


Figure 2.38. MS (ESI+ µ-TOF) compound **62**.

Synthesis of compound 63

To a solution of compound **54** (83.0 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 2.5h later, 1-Thio-beta-D-glucose tetraacetate was added (73 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 50%



Scheme 2.13. Synthesis of compound **63**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.51-7.28 (m, 12H, CH_2-*Ph* + *imidazole*); 6.39 (t, 1H, CO-*NH*-CH_2-Ph, $^{3}J_{H\text{-}H}$ = 5.9 Hz); 6.07 (t, 1H, CH_2-CH_2-*NH*-CO, $^{3}J_{H\text{-}H}$ = 5.7 Hz); 5.38 (m, 2H, Ph-*CH_2*-imidazol); 5.11; 4.84; 3.91 (m, 5H, *thioglucose*); 4.20 (m, 2H, NH-*CH_2*-Ph + NH-CH_2-*CH_2*); 4.05 (m, 2H, CH_3COO-*CH_2*-6-member ring thioglucose); 3.48 (m, 2H, CH_2-*CH_2*-NH-CO); 1.95 (m, 12H, *CH_3*).

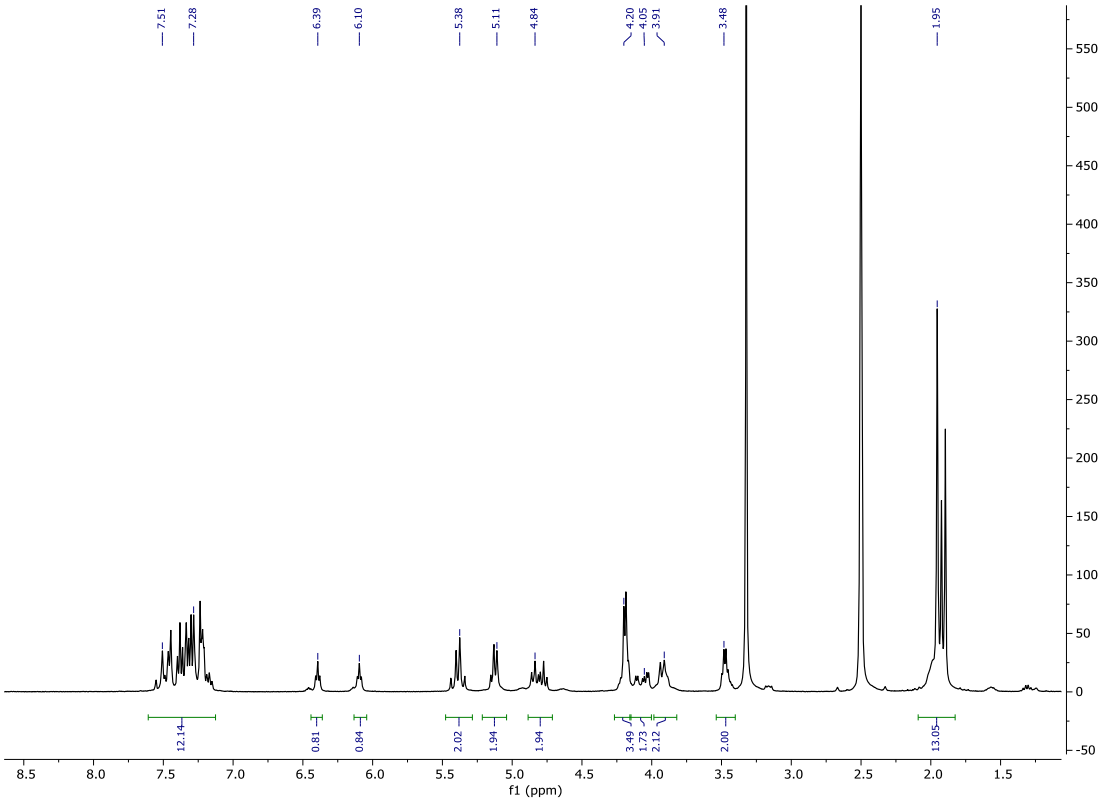


Figure 2.39. ^{1}H NMR spectrum of compound **63** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 181.0 (s, 1C, *C*=Au); 169.5 (s, 4C, *CO-thioglucose*); 157.8 (s, 1C, *CO*); 140.7 (s, 1C, C_{ipso}*Ph*-CH_2); 136. 8 (s, 1C, C_{ipso}*Ph*-CH_2); 128.7-126.5 (m, 10C, *Ph*); 122.1 (s, 1C, *imidazole*); 121.1 (s, 1C, *imidazole*); 81.7; 77.0;

74.3; 73.5; 68.6 (s, 5C, *thioglucose-ring*); 62.4 (s, 1C, CH_3COO-*CH_2*-6-member ring thioglucose); 53.4 (s, 1C, Ph-*CH_2*-imidazole); 50.4 (s, 1C, NH-CH_2-*CH_2*); 42.9 (s, 1C, NH-*CH_2*-Ph); 39.8 (s, 1C, NH-*CH_2*-CH_2); 20.4 (s, 4C, *CH_3*).

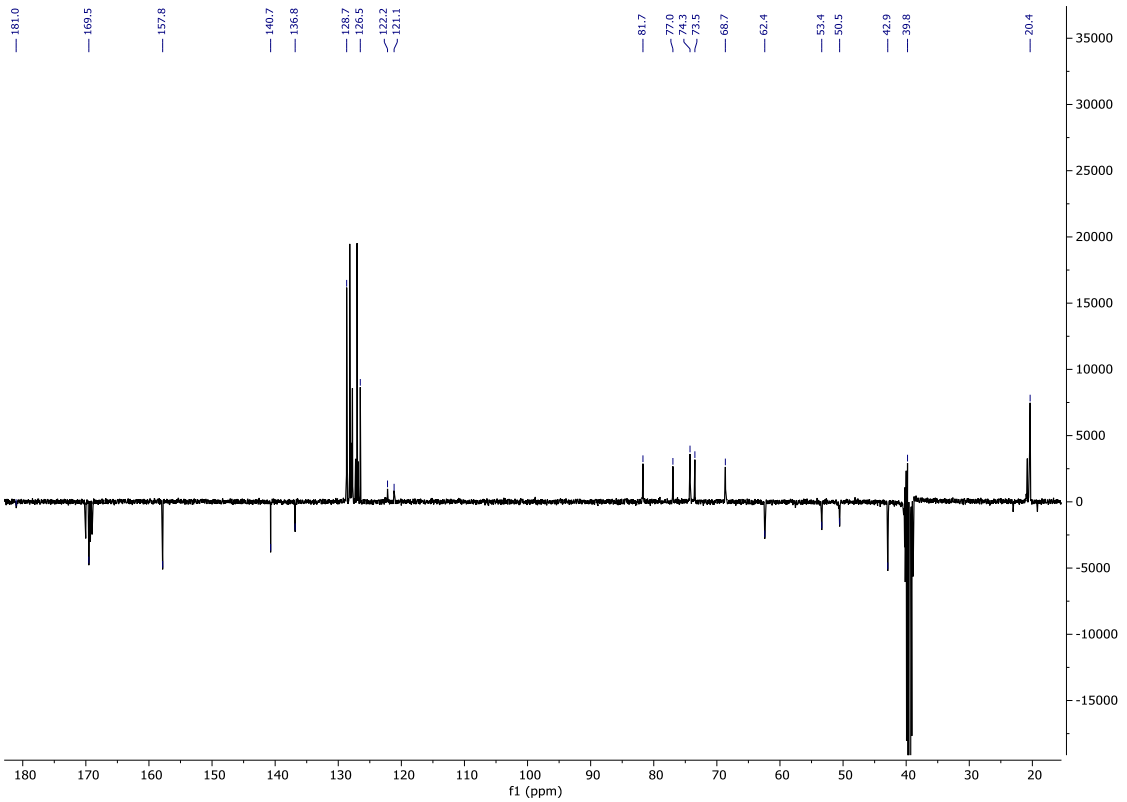


Figure 2.40. ^{13}C APT spectrum of compound **63** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{34}H_{42}AuN_4O_{10}S]$ 895.229. Found 917.1920 $[C_{34}H_{42}AuN_4O_{10}S + Na]^+$,

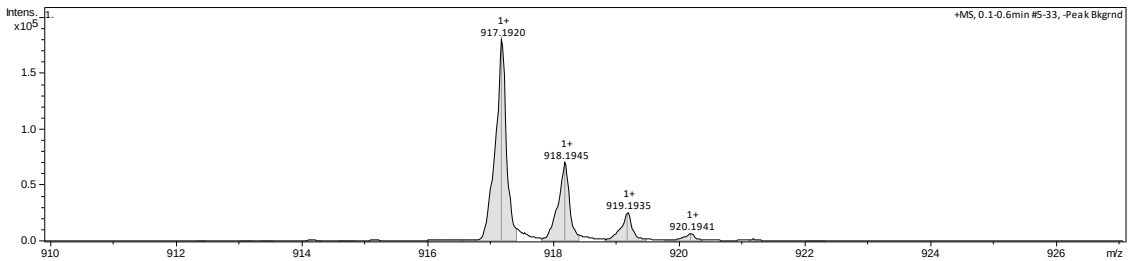


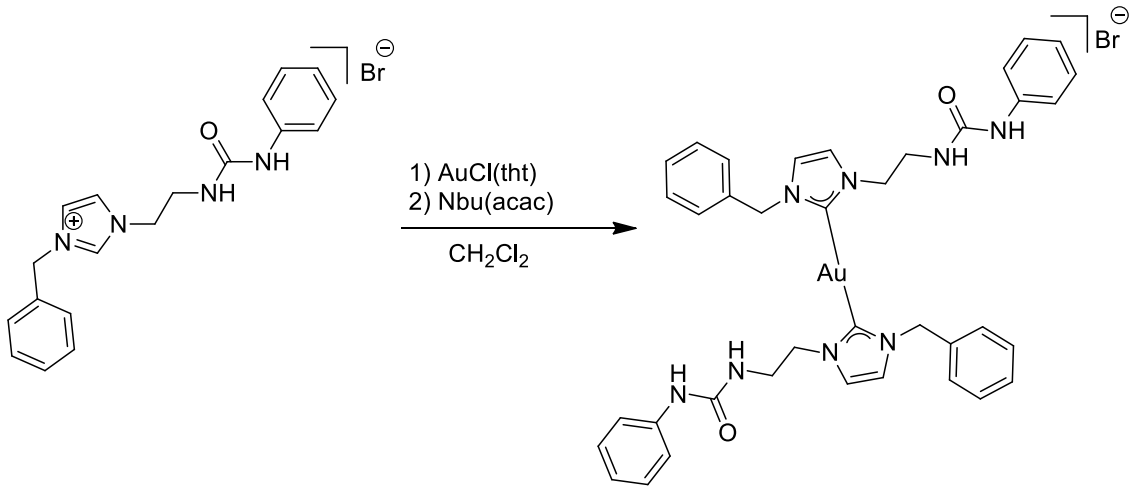
Figure 2.41. MS (ESI+ µ-TOF) compound **62**.

Synthesis of compound 64

To a solution of compound **52** (160.0 mg, 0.4 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). NBu_4(acac) (128 mg, 0.4 mmol) was added and the mixture stirred for 2.5h. The solution was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure

to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 63%



Scheme 2.14. Synthesis of compound **64**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.64 (s br, 2H, CO-*NH*-Ph); 7,57 (s br, 4H, *imidazole*); 7.30 (m, 4H, H_{orto}*Ph*-NH); 7.22 (m, 10H, *Ph*-CH_2); 7.15 (m, 4H, H_{meta}*Ph*-NH); 6.86 (d, 2H, H_{para}Ph-NH); 6.35 (t, 2H, CH_2-*NH*-CO, $^{3}J_{H\text{-}H}$ = 5.9 Hz); 5.29 (s, 4H, Ph-*CH_2*-imidazole); 4.25 (t, 4H, NH-CH_2-*CH_2*, $^{3}J_{H\text{-}H}$ = 5.8 Hz); 3.50 (m, 4H, NH-*CH_2*-CH_2).

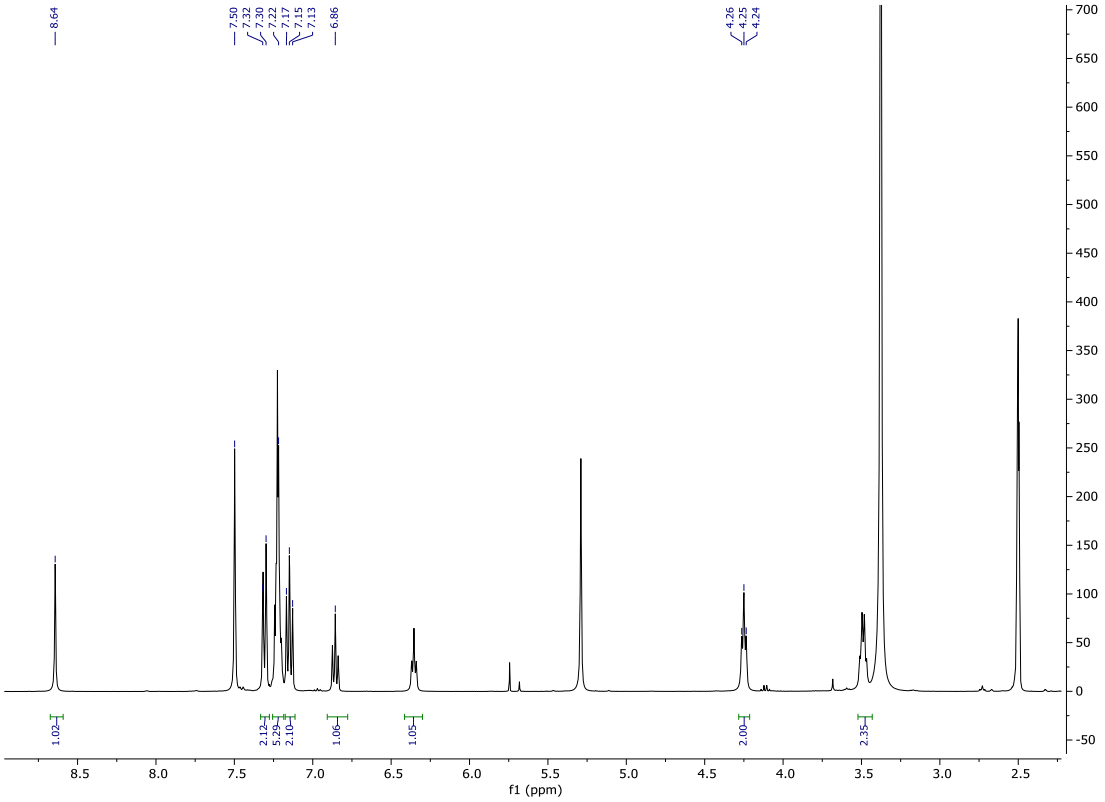


Figure 2.42. ^{1}H NMR spectrum of compound **64** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 183.2 (s, 2C, *C*=Au); 155.3 (s, 2C, *CO*); 140.2 (s, 2C, C_{ipso}*Ph*-NH); 136.8 (s, 2C, C_{ipso}*Ph*-CH_2); 128.6 (s, 4C, C_{orto}*Ph*-CH_2); 128.6 (s, 4C, C_{orto}*Ph*-NH); 127.8 (s, 2C, C_{para}*Ph*-CH_2); 127.2 (s, 4C, C_{meta}*Ph*-CH_2); 122.5 (s, 2C, *imidazole*); 122.4 (s, 2C, *imidazole*); 121.1 (s, 2C, C_{para}*Ph*-NH); 117.7 (s, 4C, C_{meta}*Ph*-CH_2); 53.4 (s, 2C, Ph-*CH_2*-imidazole); 50.6 (s, 2C, NH-CH_2-*CH_2*); 40.2 (s, 2C, NH-*CH_2*-CH_2).

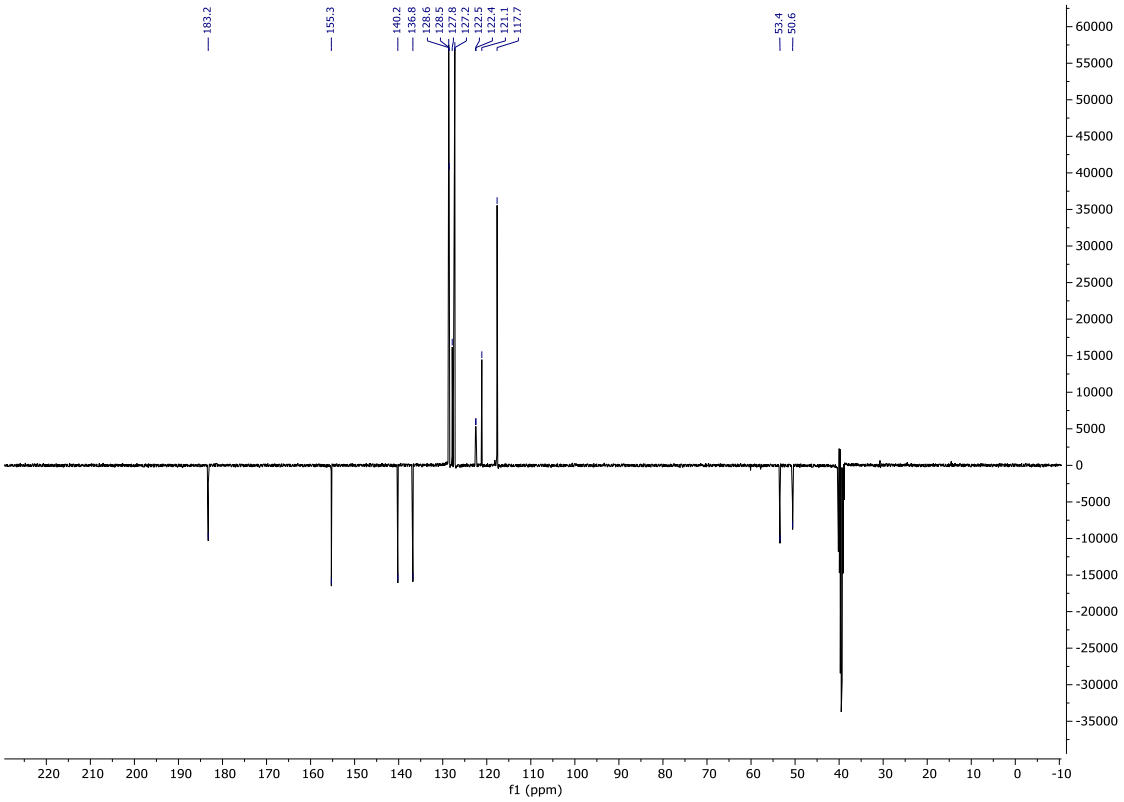


Figure 2.43. ^{13}C APT spectrum of compound **64** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= [$M]^+$ Calcd for $[C_{38}H_{40}AuN_8O_2]^+$ 837.759. Found 837.2942.

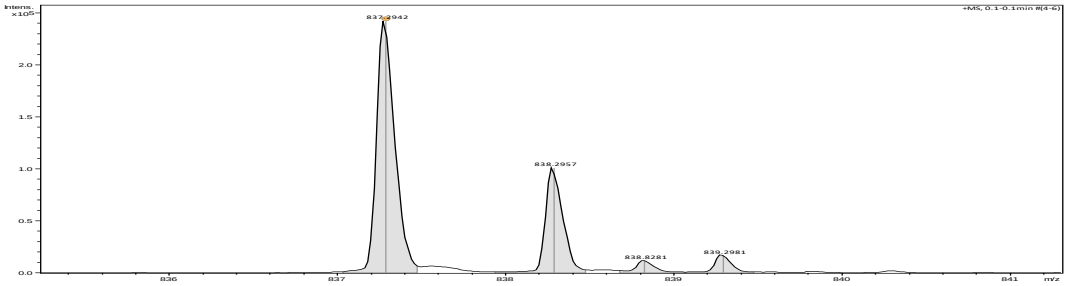
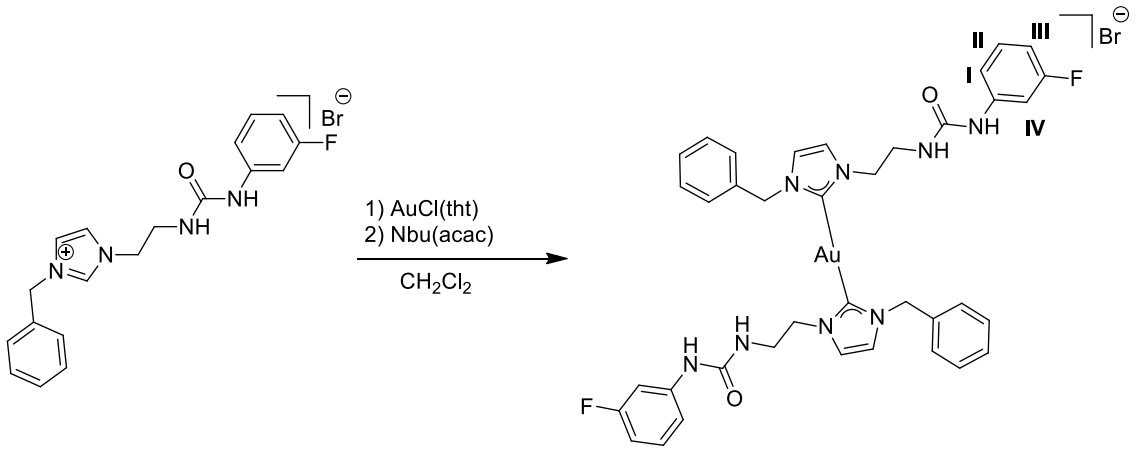


Figure 2.44. MS (ESI+ µ-TOF) compound **64**.

Synthesis of compound 65

To a solution of compound **53** (167.7 mg, 0.4 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). NBu_4(acac) (128 mg, 0.4 mmol) was added and the mixture stirred for 2.5h. The solution was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 61%



Scheme 2.15. Synthesis of compound **65**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.87 (s br, 2H, CO-*NH*-Ph); 7.50 (s, 4H, *imidazole*); 7.34 (dt, 2H, *IV*, $^{3}J_{F\text{-}H}$ = 12.3 Hz, $^{4}J_{H\text{-}H}$ = 2.3 Hz); 7.23 (m, 10H, *Ph*-CH_2); 7.16 (m, 2H, *II*); 6.96 (d, 2H, *I*, $^{5}J_{F\text{-}H}$ = 9.3 Hz); 6.66 (m, 2H, *III*); 6.40 (t, 2H, CH_2-*NH*-CO, $^{3}J_{H\text{-}H}$ = 5.9 Hz); 5.29 (s, 4H, Ph-*CH_2*-imidazole); 4.26 (t, 4H, NH-CH_2-*CH_2*, $^{3}J_{H\text{-}H}$ = 5.9 Hz); 3.50 (m, 4H, NH-*CH_2*-CH_2);

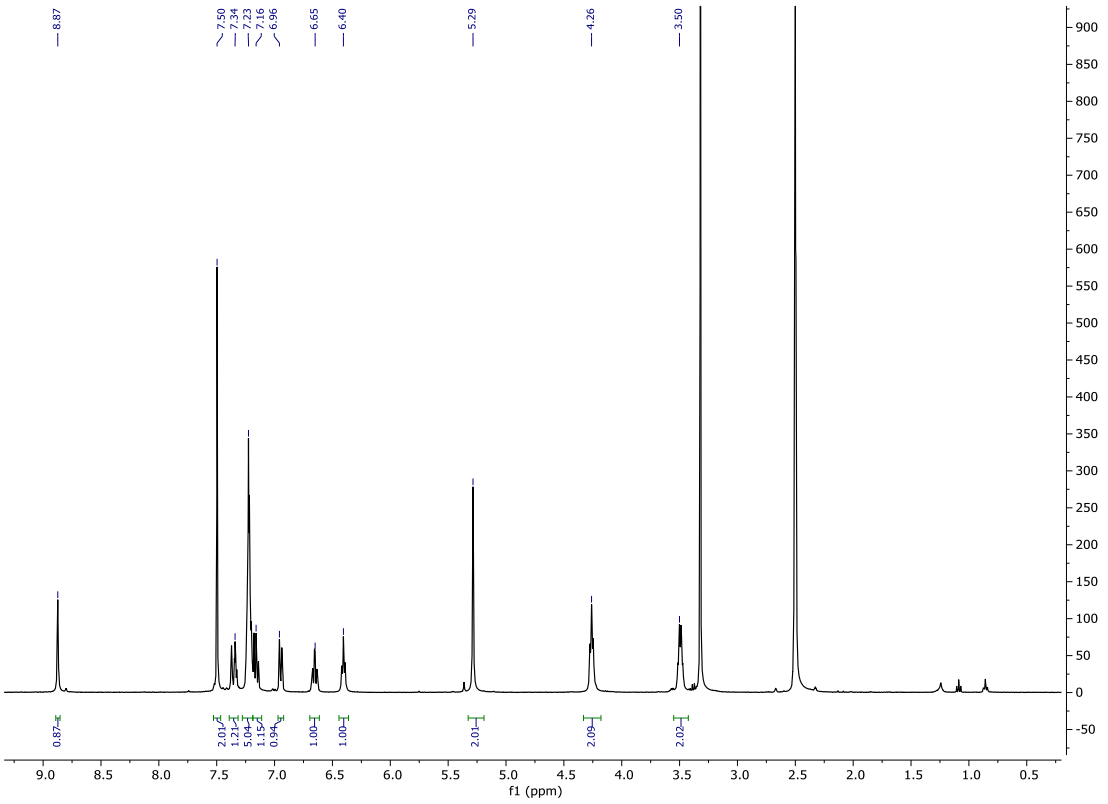


Figure 2.45. ^{1}H NMR spectrum of compound **65** in DMSO solution.

^{19}F{^{1}H} RMN (ppm) (376 MHz, DMSO): δ = -112.3 (m, 1F, *Ph-F*).

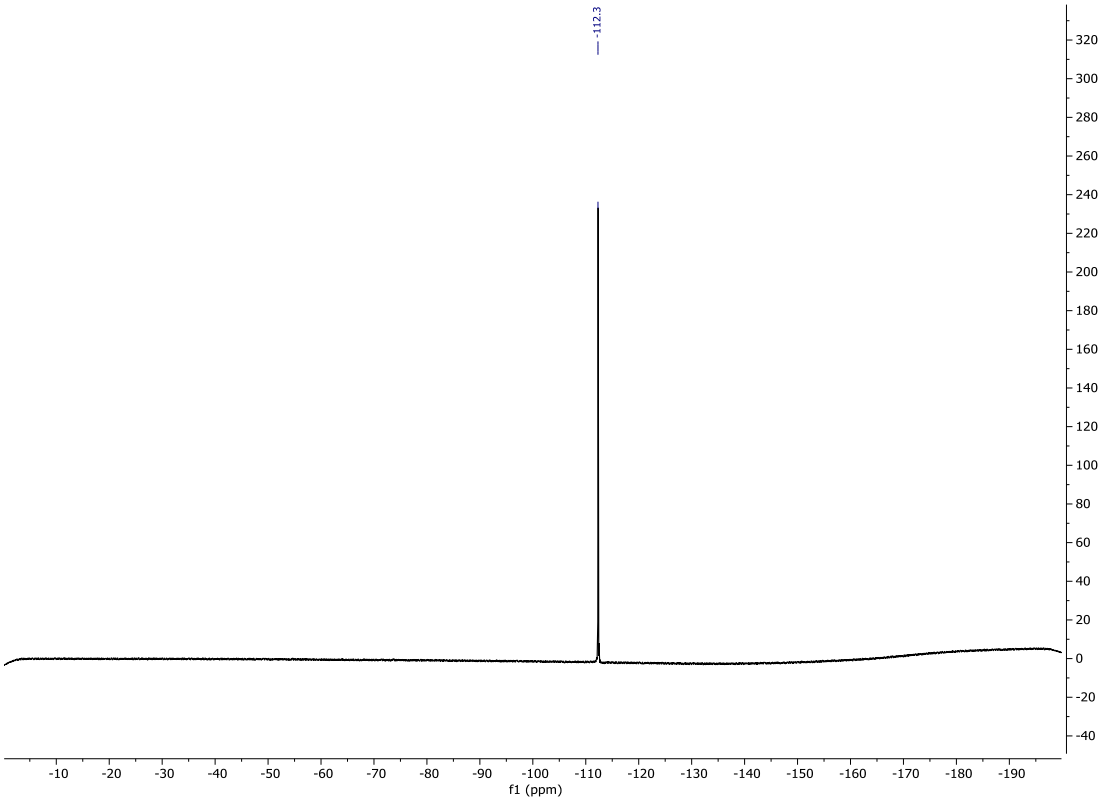


Figure 2.46. ^{19}F{^{1}H} NMR spectrum of compound **65** in DMSO solution.

^{13}C APT (ppm) (400 MHz, DMSO): δ = 183.2 (s, 2C, *C*=Au); 162.3 (d, 2C, C_{ipso}*Ph-F*, $^{1}J_{C\text{-}F}$ = 240.2 Hz); 155.0 (s, 2C, *CO*); 142.1 (d, 2C, C_{ipso}*Ph-F*, $^{3}J_{C\text{-}F}$ = 11.5 Hz); 136.7 (s, 2C, C_{ipso}*Ph*-CH_2) 129.9 (d, 2C, *II*, $^{3}J_{C\text{-}F}$ = 9.8 Hz); 128.6 (s, 4C, C_{ortho}*Ph*); 127.8 (s, 2C, C_{para}*Ph*); 127.2 (s, 4C, C_{meta}*Ph*); 122.5 (s, 2C, *imidazole*); 122.4 (s, 2C, *imidazole*); 113.2 (d, 2C, *I*, $^{3}J_{C\text{-}F}$ = 2.1 Hz); 107.3 (d, 2C, *III*, $^{2}J_{C\text{-}F}$ = 21.2 Hz); 104.2 (d, 2C, *IV*, $^{3}J_{C\text{-}F}$ = 26.7 Hz); 53.4 (s, 2C, Ph-CH_2-imidazole); 50.4 (s, 2C, NH-CH_2-CH_2); 40.0 (s, 2C, NH-CH_2-CH_2).

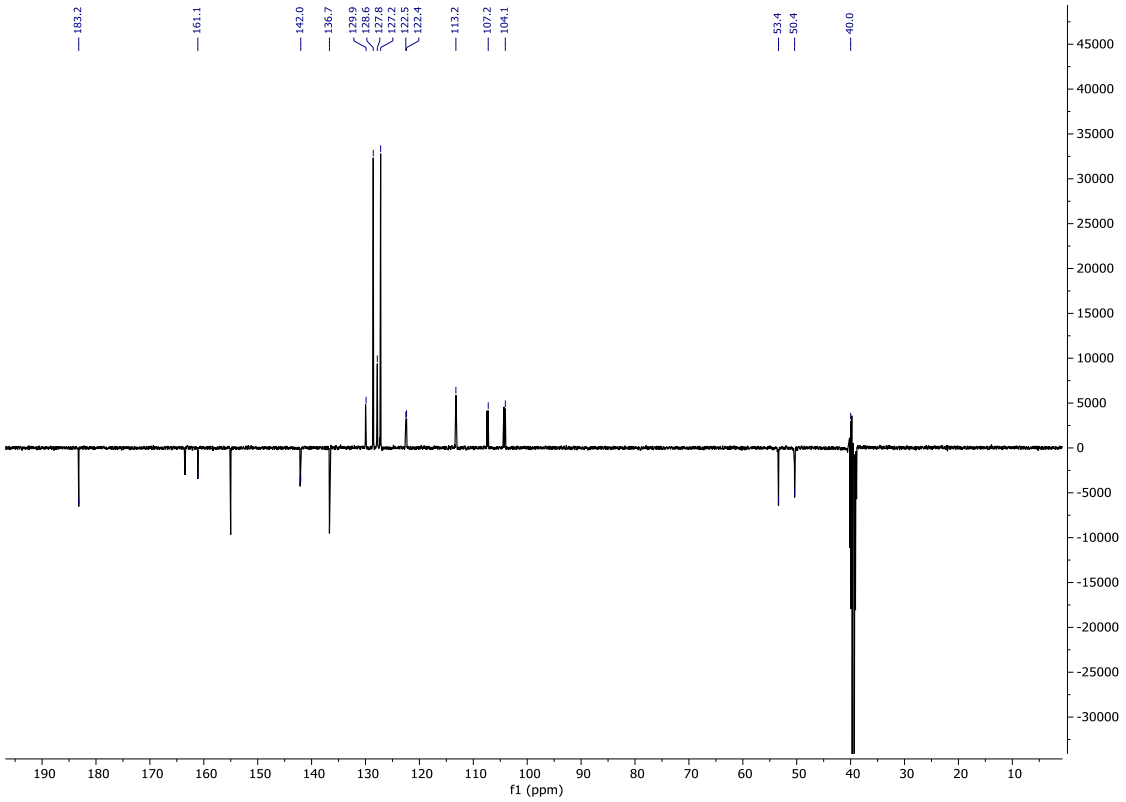


Figure 2.47. ^{13}C APT spectrum of compound **65** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= [$M]^+$ Calcd for $[C_{38}H_{38}AuF_2N_8O_2]^+$ 873.2746. Found 873.2784.

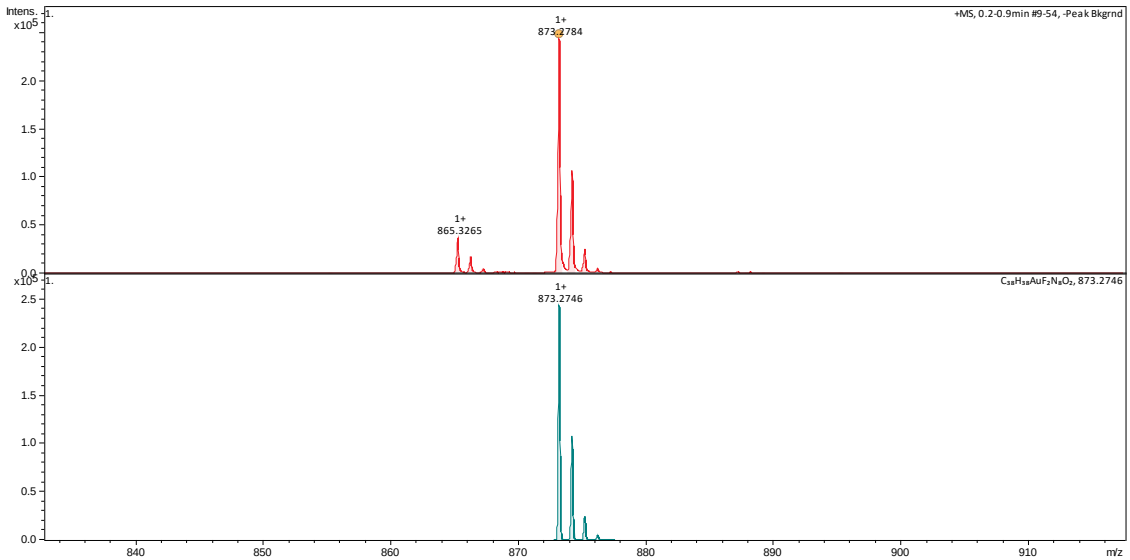
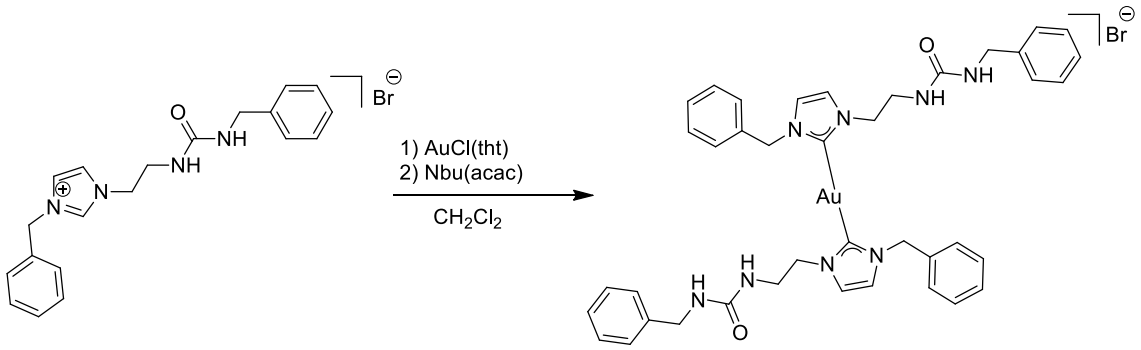


Figure 2.48. MS (ESI+ µ-TOF) compound **65**.

Synthesis of compound 66

To a solution of compound **54** (166 mg, 0.4 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). NBu_4(acac) (128 mg, 0.4 mmol) was added and the mixture stirred for 2.5h. The solution was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 62%



Scheme 2.16. Synthesis of compound **66**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.05 (m, 4H, *imidazole*); 6.83 (m, 20H, CH_2-*Ph*); 6.08 (t, 2H, CO-*NH*-CH_2-Ph, $^3J_{H\text{-}H}$ = 5.9 Hz); 5.77 (t, 2H, CH_2-CH_2-*NH*-CO, $^3J_{H\text{-}H}$ = 5.6 Hz); 4.92 (s, 4H, Ph-*CH_2*-imidazole); 3.77 (t, 4H, *CH_2*-CH_2-NH-CO, $^3J_{H\text{-}H}$ = 5.9 Hz); 3.66 (d, 4H, CH_2-*CH_2*-NH-CO, $^3J_{H\text{-}H}$ = 5.9 Hz); 3.00 (m, 4H, CH_2-*CH_2*-NH-CO).

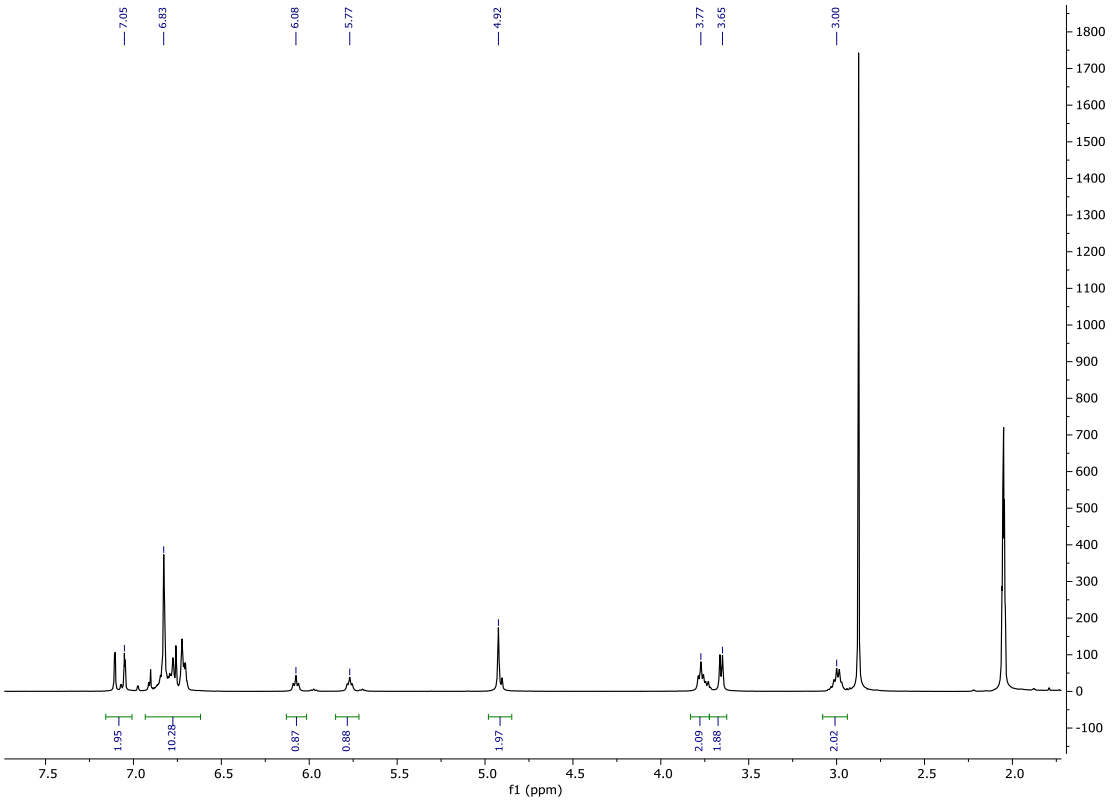


Figure 2.49. ^{1}H NMR spectrum of compound **66** in DMSO solution.

^{13}C APT (ppm) (400 MHz, DMSO): δ = 183.1 (s, 2C, *C*=Au); 158.0 (s, 2C, *CO*); 140.6 (s, 2C, *C$_{ipso}$Ph*-CH$_2$-NH); 136.9 (s, 2C, *C$_{ipso}$Ph*-CH$_2$-imidazole); 128.6-126.4 (m, 20C, *Ph*);122.6 (s, 2C, *imidazole*); 122.4 (s, 2C, *imidazole*); 53.4 (s, 2C, Ph-*CH$_2$*-imidazole); 50.7 (s, 2C, NH-CH$_2$-*CH$_2$*); 42.8 (s, 2C, Ph-*CH$_2$*-NH-CO); 39.8 (s, 2C, NH-*CH$_2$*-CH$_2$).

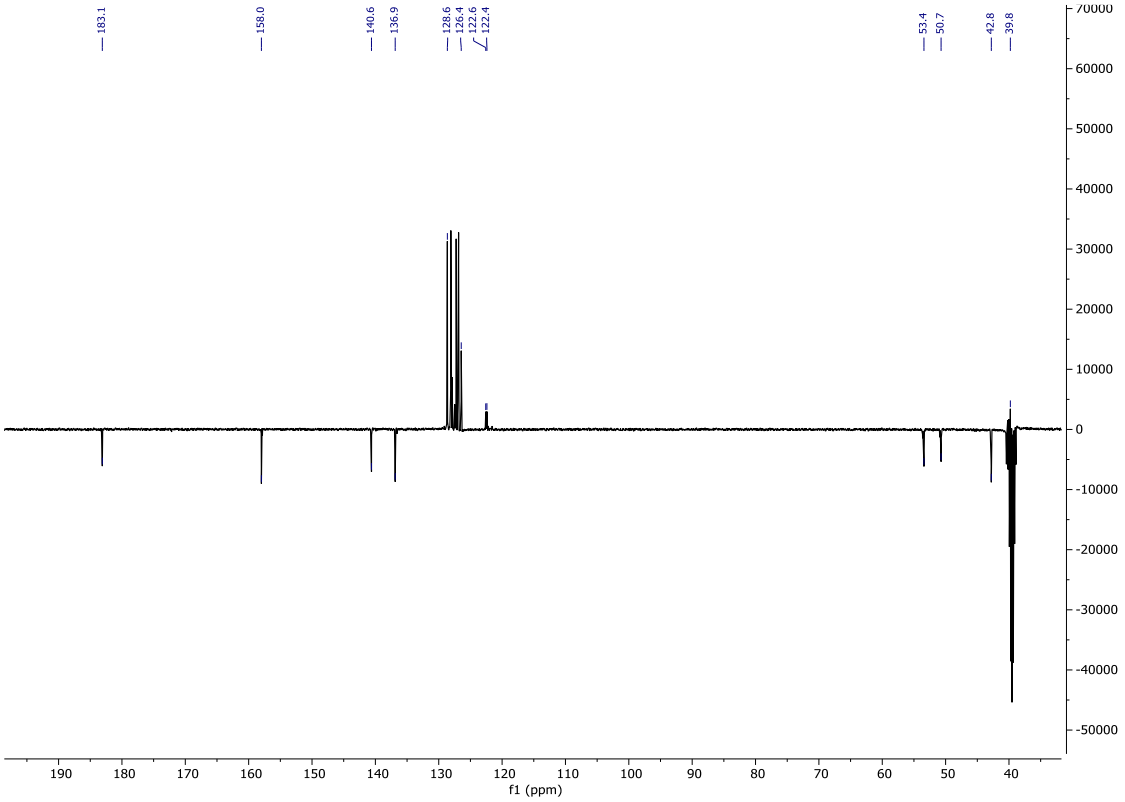


Figure 2.50. ^{13}C APT spectrum of compound **66** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{40}H_{44}AuN_8O_2]^+$ 865.3247. Found 865.3229.

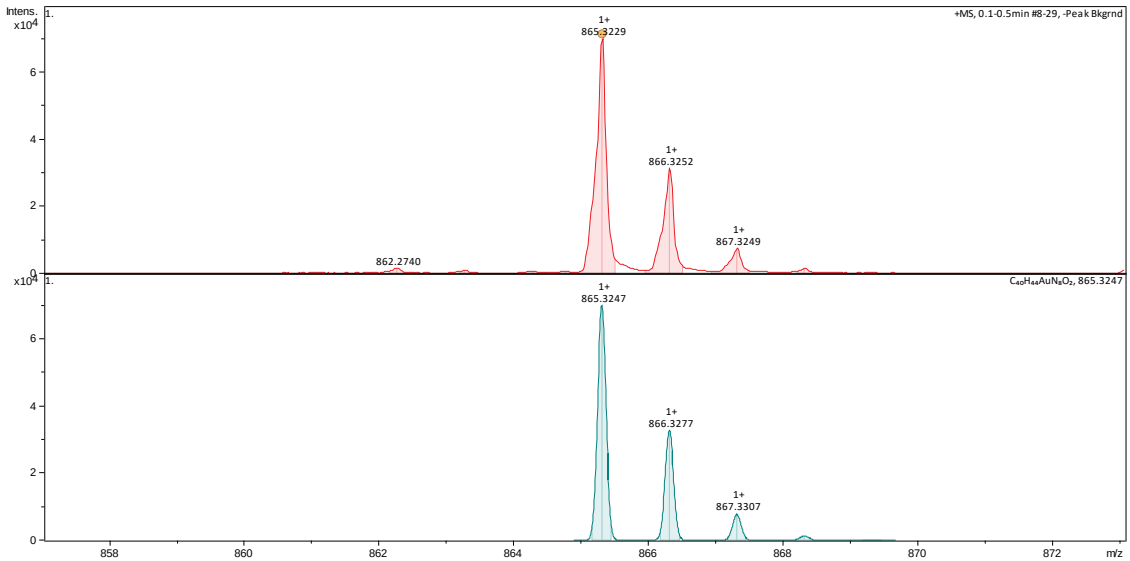
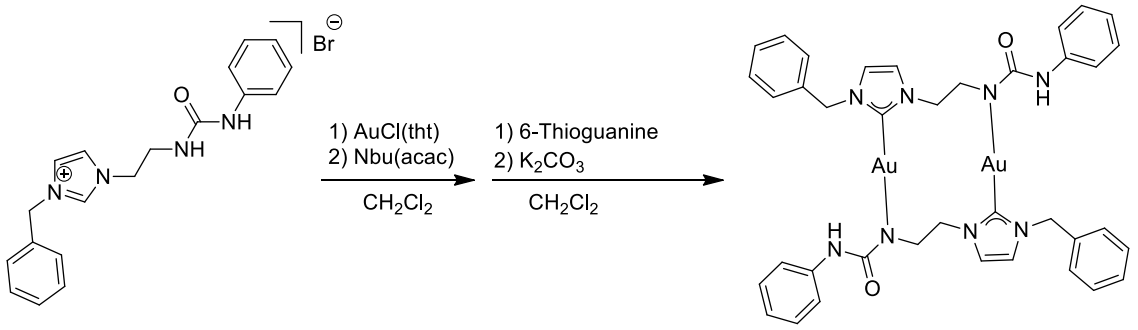


Figure 2.51. MS (ESI+ µ-TOF) compound **66**.

Synthesis of compound 67

To a solution of compound **52** (80.0 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 2h later, 6-thioguanine was added (33 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 84%



Scheme 2.17. Synthesis of compound **67**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.53 (m, 2H, *imidazole*); 7.43 (s, 2H, *imidazole*); 7.15-6.71 (m, 20H, *arom*); 5.44 (s, 4H, Ph-*CH$_2$*-imidazole); 4.44 (t, 4H, NH-CH$_2$-*CH$_2$*, $^3J_{H\text{-}H}$ = 5.4 Hz); 3.88 (t, 4H, NH-*CH$_2$*-CH$_2$, $^3J_{H\text{-}H}$ = 5.4 Hz).

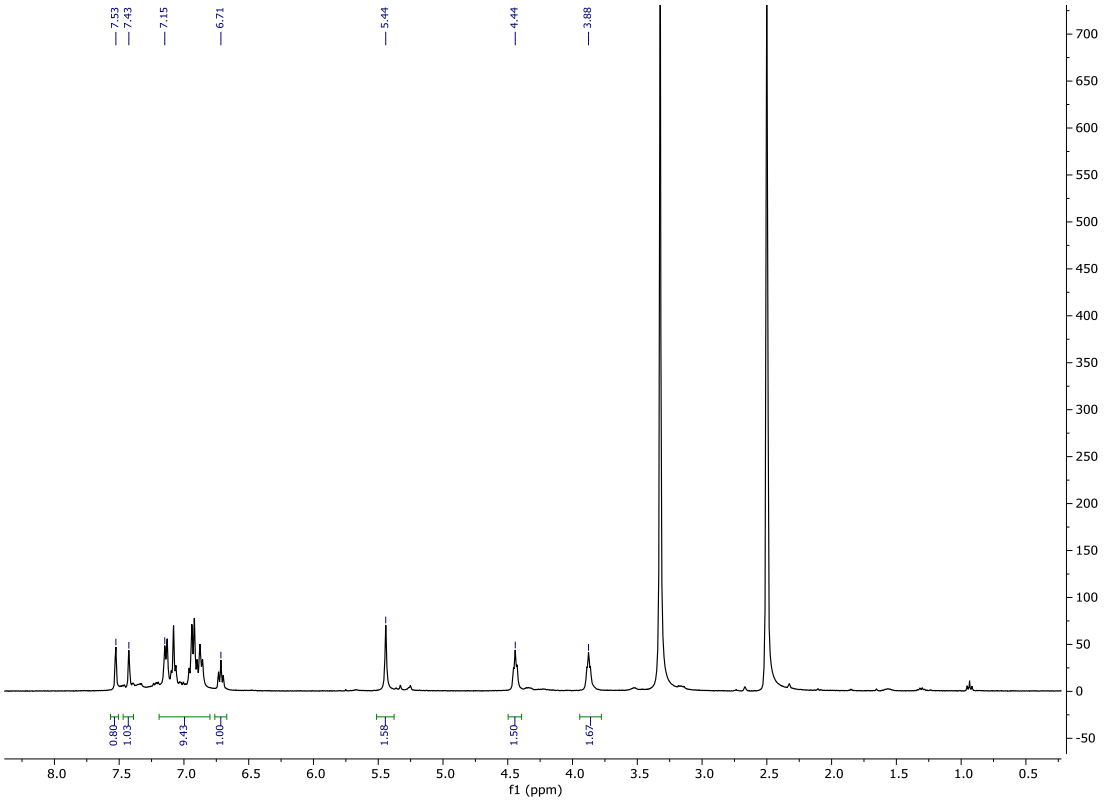


Figure 2.52. ^{1}H NMR spectrum of compound **67** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 171.4 (s, 2C, *C*=Au); 160.7 (s, 2C, *CO*); 141.6 (s, 2C, $C_{ipso}Ph$-NH); 137.0 (s, 2C, $C_{ipso}Ph$-CH_2); 128.6 (s, 4C, Ph_{ortho}-NH); 127.3 (s, 2C, Ph_{para}-CH_2); 126.3(s, 4C, Ph_{meta}-CH_2); 124.2 (s, 2C, *imidazole*); 122.2 (s, 2C, *imidazole*); 119.4 (s, 2C, Ph_{para}-NH); 117,2 (s, 4C, Ph_{meta}-NH); 53.1 (s, 2C, Ph-CH_2-imidazole); 45.9 (s, 2C, NH-CH_2-CH_2); 39.8 (s, 2C, NH-CH_2-CH_2).

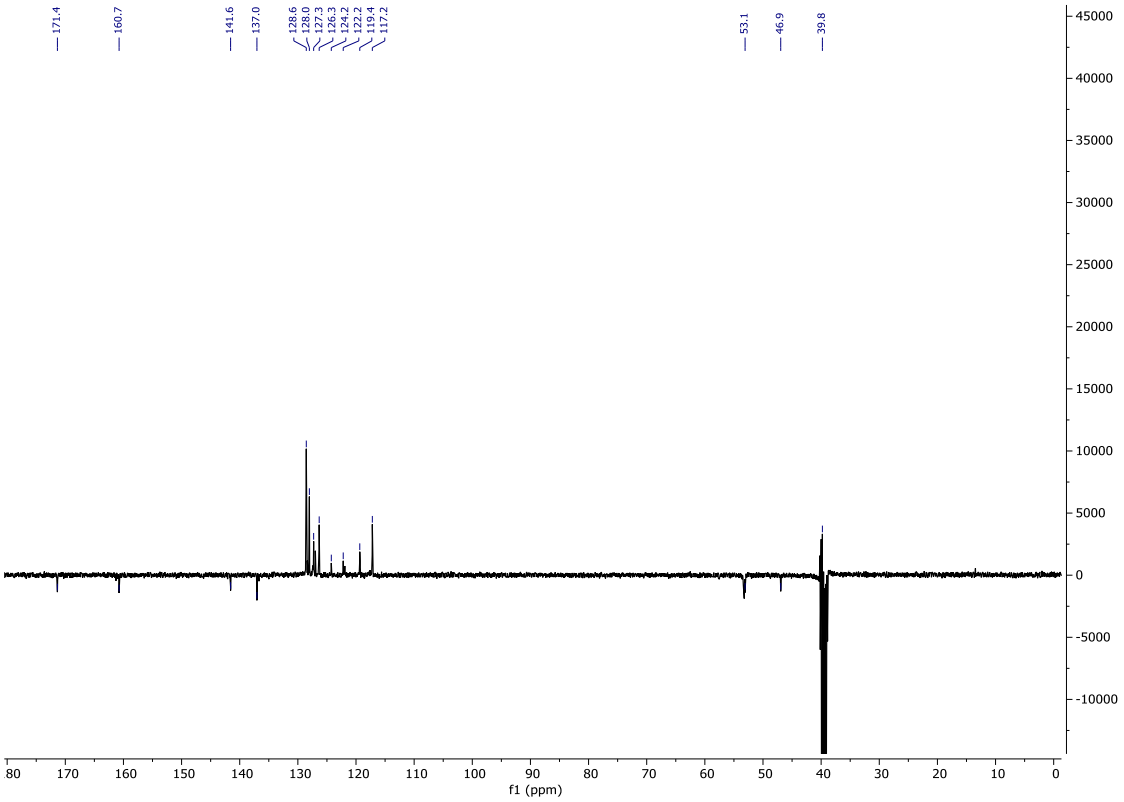
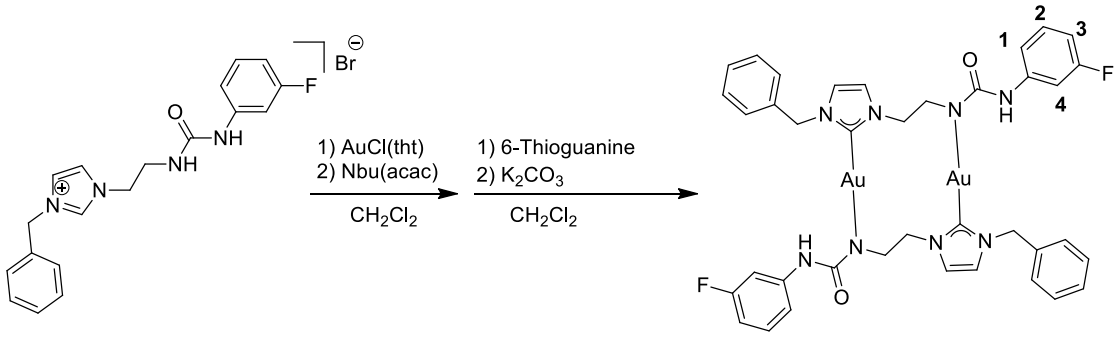


Figure 2.53. ^{13}C APT spectrum of compound **67** in DMSO solution.

Synthesis of compound 68

To a solution of compound **53** (83.86 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 2h later, 6-thioguanine was added (33 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 65%.



Scheme 2.18. Synthesis of compound **68**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.53 (s, 2H, *imidazole*); 7.44 (s, 2H, *imidazole*); 7.32-6.96 (m, 14H, CH_2-*Ph + 2 + 4*); 6.51 (m, 2H, *1*); 6.37 (m , 2H, *3*); 5.45 (s, 4H, Ph-*CH_2*); 4.44 (t, 4H, *CH_2*-CH_2-NH-CO, $^{3}J_{H\text{-}H}$ = 5.6 Hz); 3.86 (t, 4H, NH-*CH_2*-CH_2, $^{3}J_{H\text{-}H}$ = 5.2 Hz).

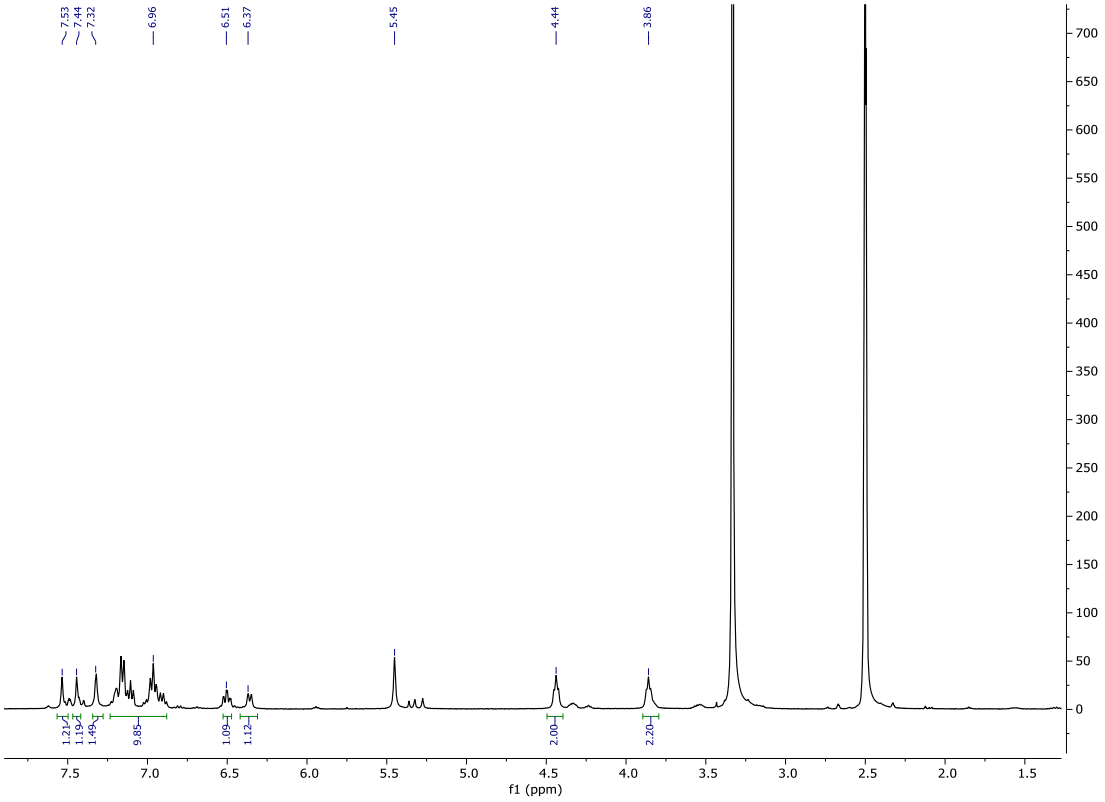


Figure 2.54. ^{1}H NMR spectrum of compound **68** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -113.3 (m, 1F, Ph-*F*).

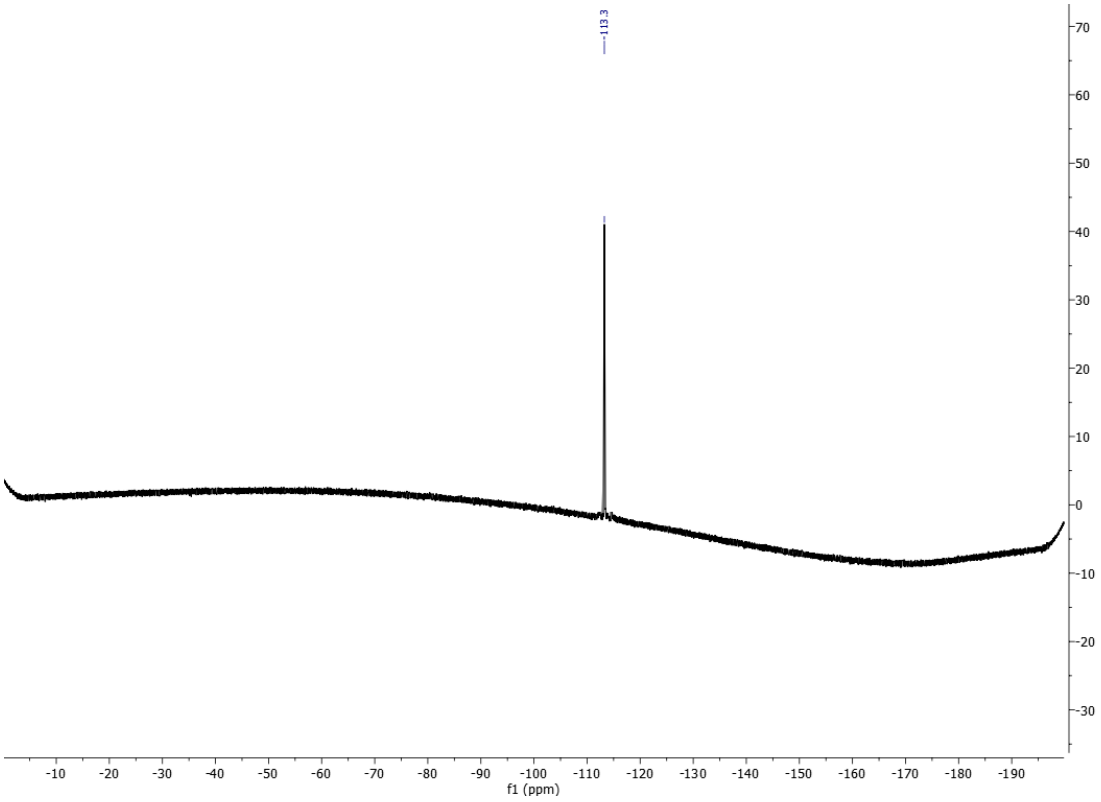


Figure 2.55. $^{19}F\{^{1}H\}$ NMR spectrum of compound **68** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 171.1 (s, 2C, *C=Au*); 162.4 (d, 2C, C_{ipso}*Ph-F*, $^{1}J_{C\text{-}F}$ = 238.8 Hz); 160.5 (s, 2C, *CO*); 143.5 (d, 2C, C_{ipso}Ph-NH, $^{3}J_{C\text{-}F}$ = 11.8 Hz); 137.1 (s, 2C, C_{ipso}*Ph-*CH_2); 129.3 (d, 2C, *2*, $^{3}J_{C\text{-}F}$ = 10.7 Hz); 128.5 (s, 2C, C_{ortho}Ph); 127.4 (s, 2C, C_{para}Ph); 126.5 (s, 4C, C_{meta}Ph); 122.2 (s, 4C, *imidazole*); 112.9 (s, 4C, *1*); 105.5 (d, 2C, *3*, $^{2}J_{C\text{-}F}$ = 20.9 Hz); 103.7 (d, 2C, *4*, $^{2}J_{C\text{-}F}$ = 26.3 Hz); 53.2 (s, 1C, Ph-CH_2-imidazole); 47.0 (s, 2C, NH-CH_2-CH_2); 39.8 (s, 2C, NH-CH_2-CH_2).

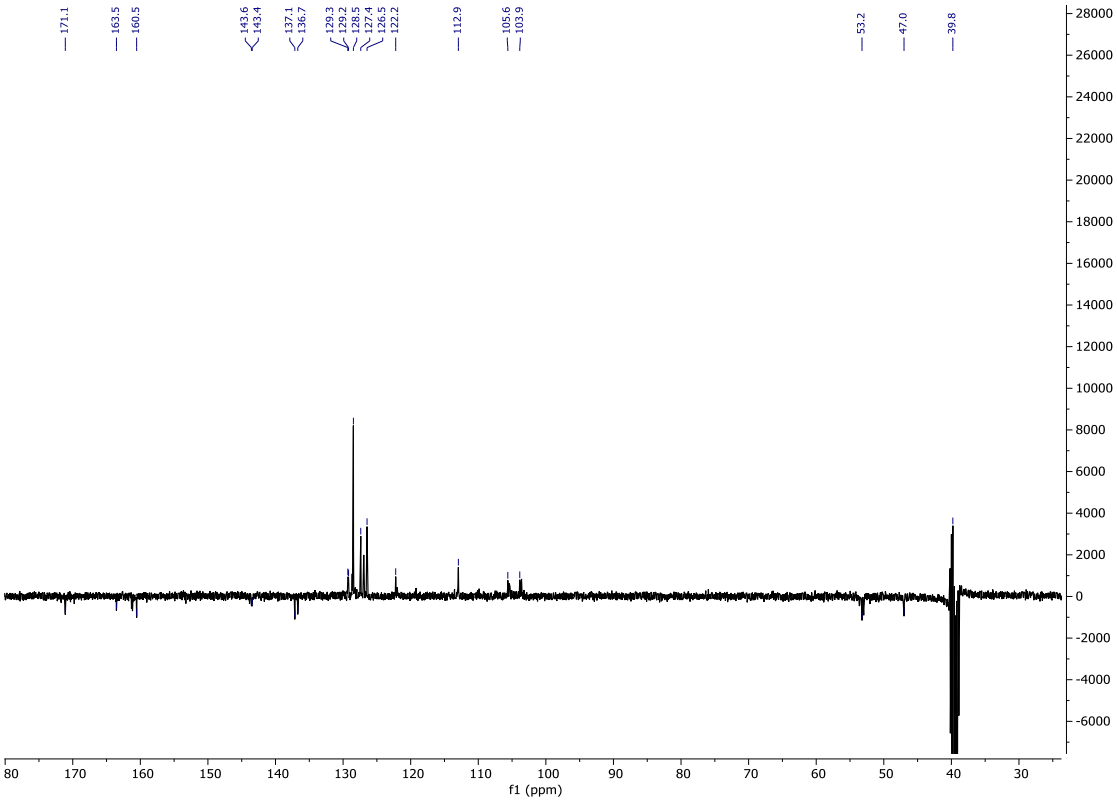
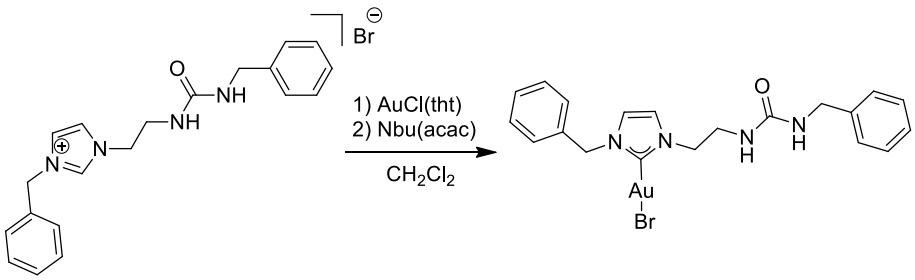


Figure 2.56. ^{13}C APT spectrum of compound **68** in DMSO solution.

Synthesis of compound 69

To a solution of compound **54** (83.0 mg, 0.2 mmol) and [AuCl(tht)] (64 mg, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) was added $NBu_4(acac)$ (64 mg, 0.2 mmol) and the mixture stirred. 2h later, 6-thioguanine was added (33 mg, 0.2 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate was washed with H_2O (3 x 25 ml), dried over Na_2SO_4 and then concentrated under reduced pressure to approximately 1 ml. Hexane (10 ml) was added to precipitate a white product which was collected and vacuum dried to give the product.

Yield: 73%



Scheme 2.19. Synthesis of compound **69**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.52-7.42 (m, 2H, *imidazole*); 7.35-7.22 (m, 10H, CH_2-*Ph*); 6.41 (t, 1H, CO-*NH*-CH_2-Ph, $^{3}J_{H\text{-}H}$ = 6.1 Hz); 6.12 (t, 1H, CH_2-CH_2-*NH*-CO, $^{3}J_{H\text{-}H}$ = 6.0 Hz); 5.35 (s, 2H, Ph-*CH_2*-imidazol); 4.18 (m, 4H, *CH_2*-CH_2-NH-CO + CH_2-*CH_2*-NH-CO); 3.48 (m, 2H, CH_2-*CH_2*-NH-CO).

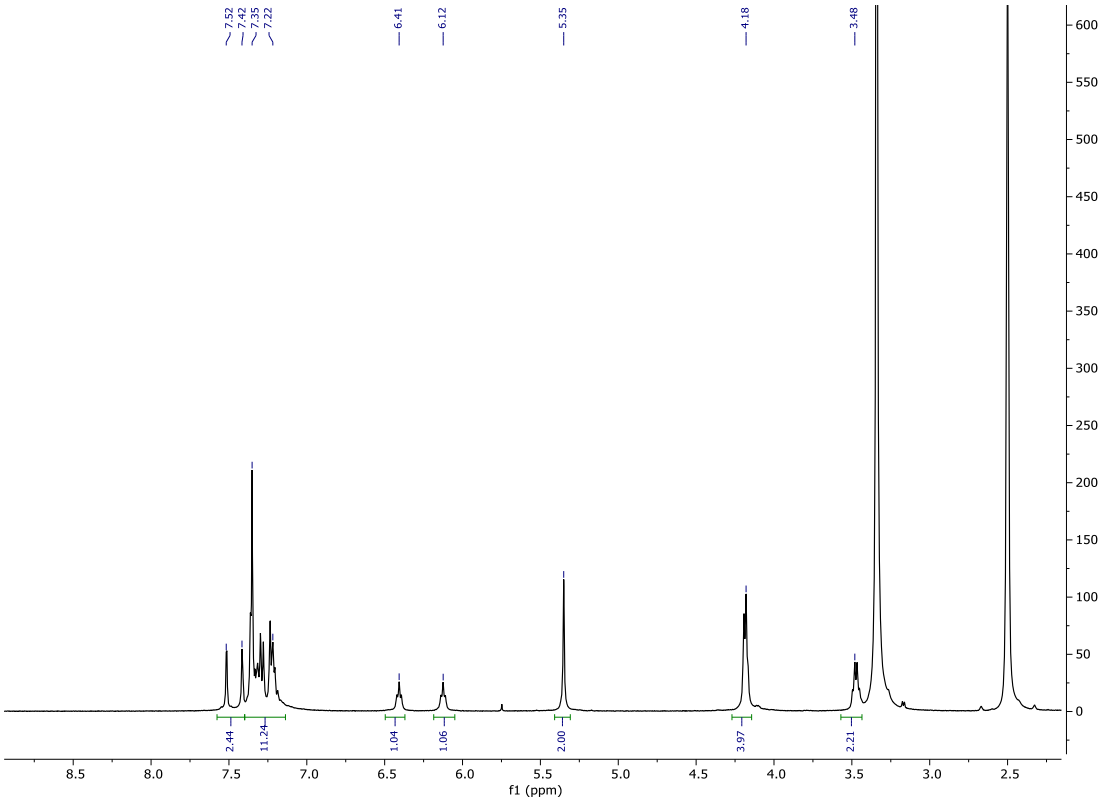


Figure 2.57. ^{1}H NMR spectrum of compound **69** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 172.2 (s, 1C, *C*=Au); 157.8 (s, 1C, *CO*); 140.7 (s, 1C, *C_{ipso}Ph*-CH_2-NH); 136.6 (s, 1C, *C_{ipso}Ph*-CH_2-imidazole); 128.7-126.5 (m, 10C, CH_2-*Ph*);122.2 (s, 1C, *imidazole*); 121.6 (s, 1C, *imidazole*); 53.7 (s, 1C, Ph-*CH_2*-imidazole); 50.9 (s, 1C, NH-CH_2-*CH_2*); 42.9 (s, 1C, Ph-*CH_2*-NH-CO); 39.8 (s, 1C, NH-*CH_2*-CH_2).

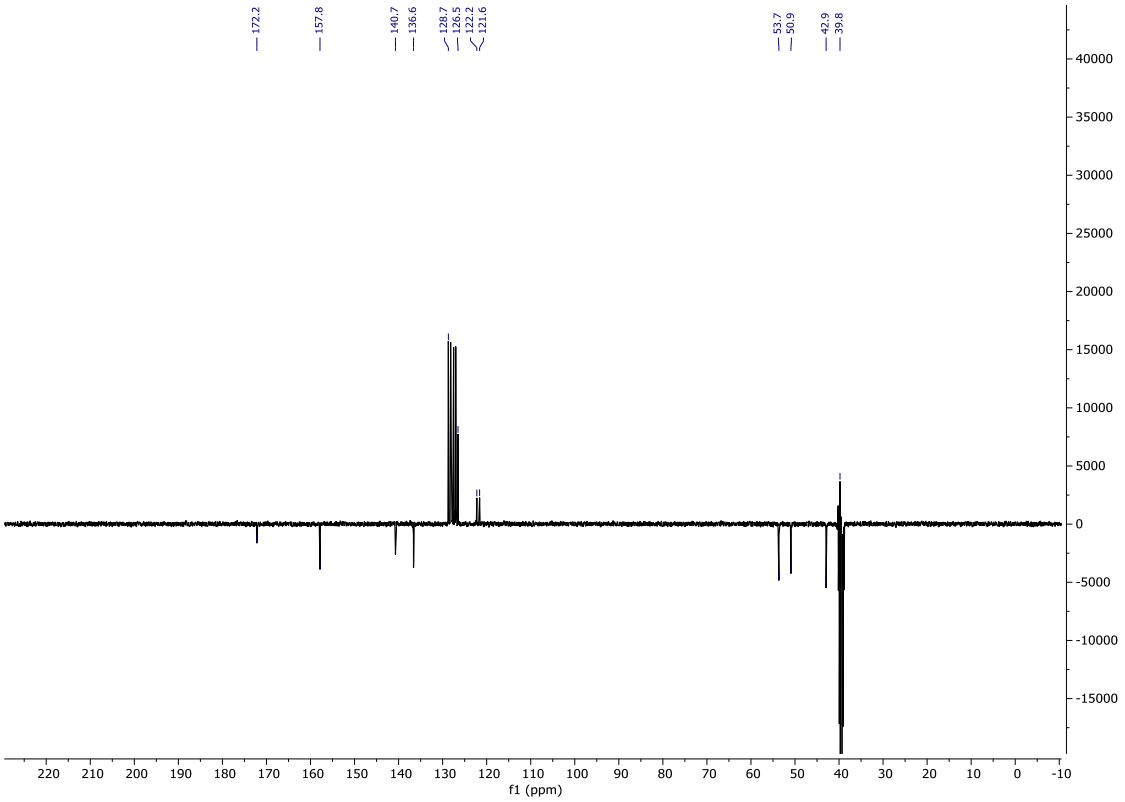


Figure 2.58. ^{13}C APT spectrum of compound **69** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{20}H_{23}AuBrN_4O]$ 611.2934. Found 633.0501 $[C_{20}H_{23}AuBrN_4O + Na]^+$.

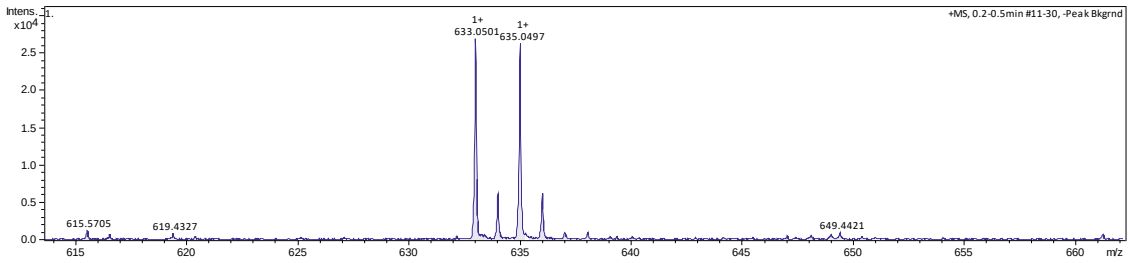


Figure 2.59. MS (ESI+ µ-TOF) compound **69**.

ANEXOS

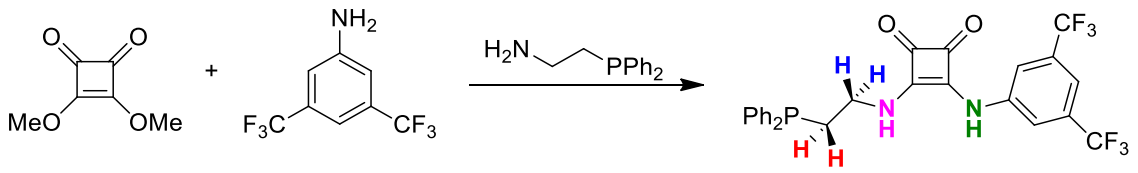
Capítulo 3

Syntheses

Synthesis of compound 70

To a solution of 3,4-Dimethoxy-3-cyclobutene-1,2-dione (29 mg, 0.2 mmol) in methanol (5 ml) was added 3,5-Bis(trifluoromethyl)aniline (32 µL, 0.2 mmol) and the solution stirred. 80 hours later, 2-(diphenylphosphino)ethylamine was added (46 µL, 0.2 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 77 %.



Scheme 3.1. Synthesis of compound **70**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 10.04 (s, 1H, *NH*-Ph); 7.96 (s, 2H, H_{ortho}Ph-CF_3);7.79 (s, 1H, *NH*-CH_2); 7.60 (s, 1H, H_{para}Ph-CF_3); 7.41(m, 4H, $H_{ortho}$$PPh_2$); 7.31 (m, 6H, H_{meta}+$H_{para}$$PPh_2$); 3.72 (s br, 2H, PPh_2-CH_2-*CH_2*); 2.47 (s br, 2H, PPh_2-*CH_2*-CH_2).

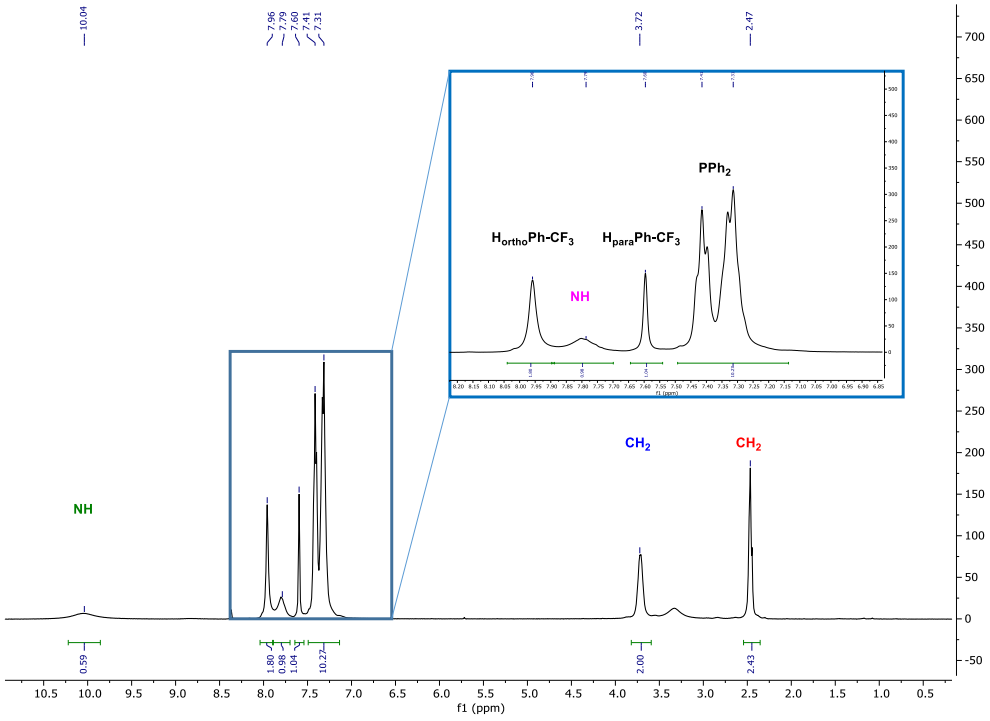


Figure 3.1. ^{1}H NMR spectrum of compound **70** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -61.8 (s, 3F, CF_3).

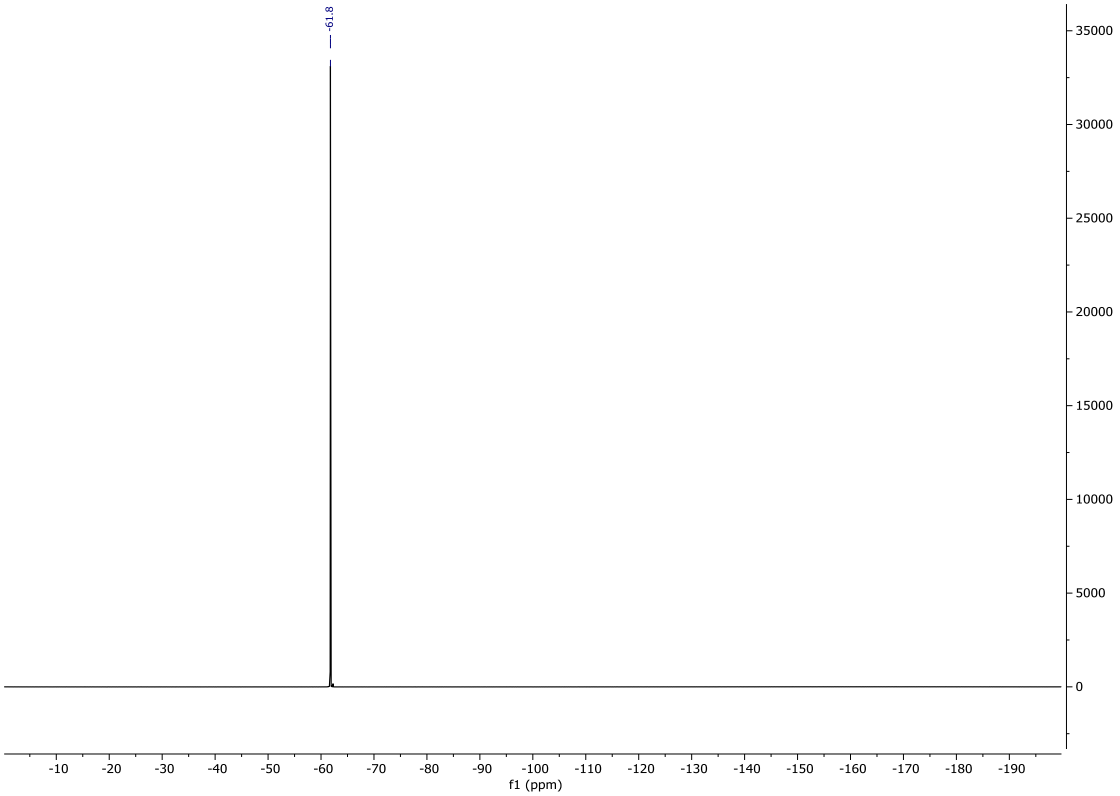


Figure 3.2. $^{19}F\{^{1}H\}$ NMR spectrum of compound **70** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -22.6 (s, 1P, PPh_2).

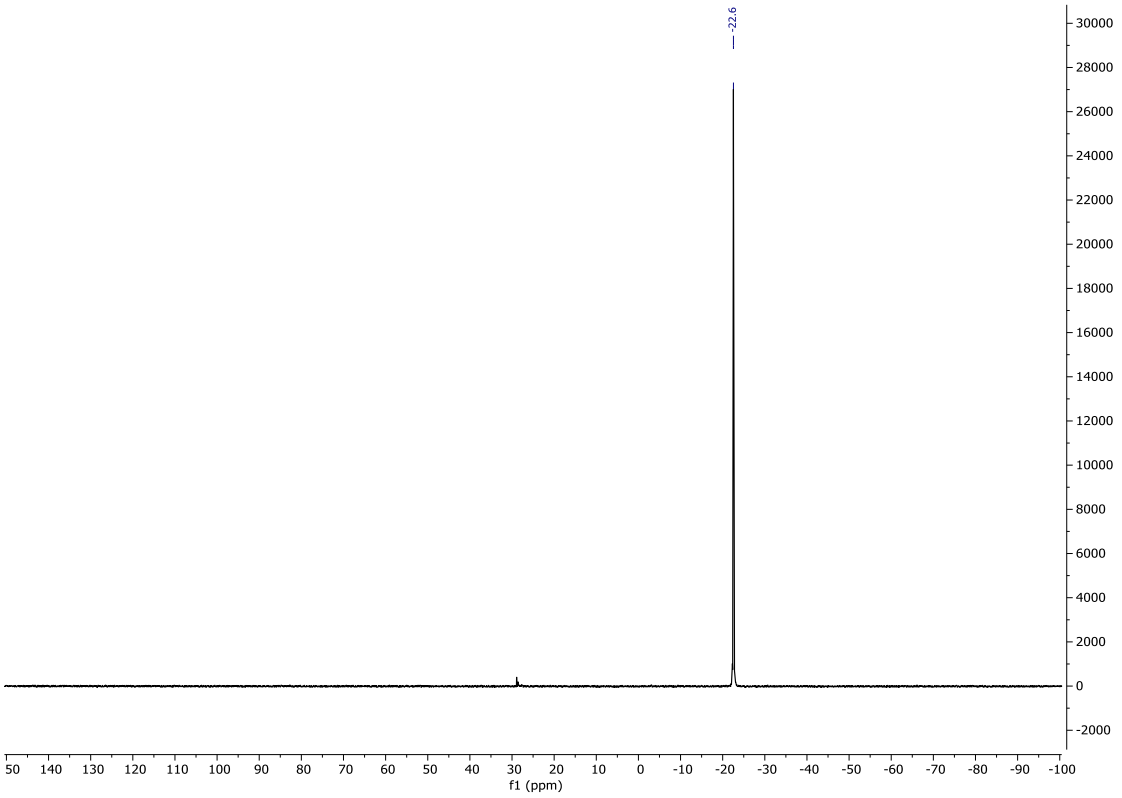


Figure 3.3. $^{31}P\{^{1}H\}$ NMR spectrum of compound **70** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.7 (s, 1C, *C*=*O*); 180.5 (s, 1C, *C*=*O*); 169.6 (s, 1C, Ph-C=*C*-*NH*-*CH*$_2$); 162.7 (s, 1C, *Ph*-*NH*-*C*=C-CH$_2$); 141.1 (s, 1C, C_{ipso}-Ph-CF$_3$); 137.5 (d, 2C, C_{ipso}-PPh$_2$, $^{1}J_{CP}$ = 12.8 Hz); 132.4 (d, 4C, C_{ortho}PPh$_2$, $^{2}J_{CP}$ = 19.0 Hz); 131.3 (q, 1C, C_{ipso}-Ph-CF$_3$, $^{2}J_{CP}$ = 32.2 Hz); 128.8 (s, 2C, C_{para}PPh$_2$); 128.6 (d, 4C, C_{meta}PPh$_2$, $^{2}J_{CP}$ = 6.8 Hz); 123.2 (q, 2C, CF_3, $^{1}J_{CF}$ = 272.9 Hz); 118.0 (s, 2C, C_{ortho}Ph-CF$_3$); 114.4 (s, 1C, C_{para}Ph-CF$_3$); 41.4 (d, 1C, PPh$_2$-CH$_2$-*CH*$_2$, $^{2}J_{CP}$ = 22.6 Hz); 28.4 (d, 1C, PPh$_2$-*CH*$_2$-CH$_2$, $^{2}J_{CP}$ = 13.1 Hz).

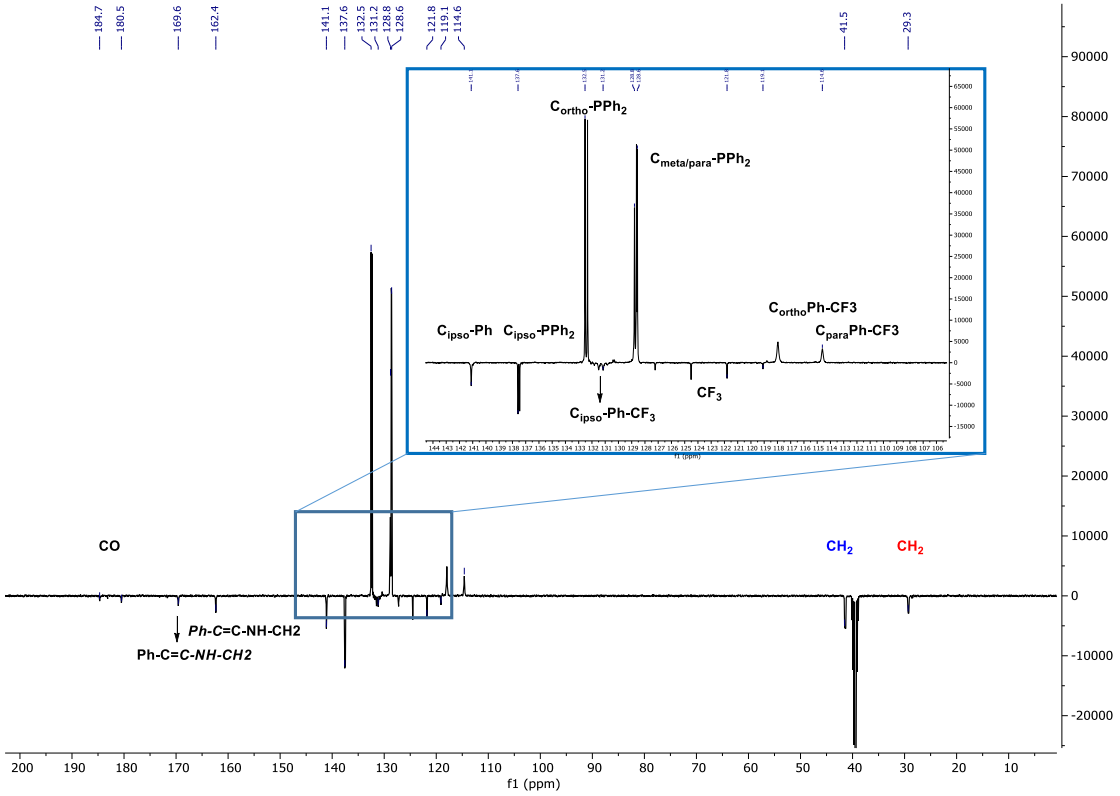


Figure 3.4. ^{13}C APT spectrum of compound **70** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{26}H_{19}F_6N_2O_2P]$ 536.1083. Found 559.0960 $[C_{26}H_{19}F_6N_2O_2P + Na]^+$.

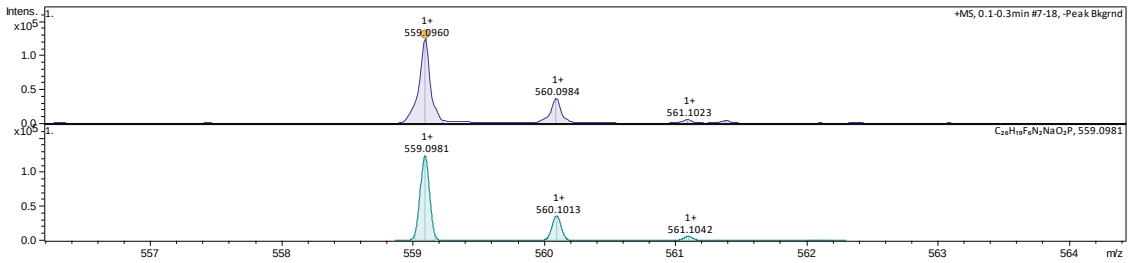
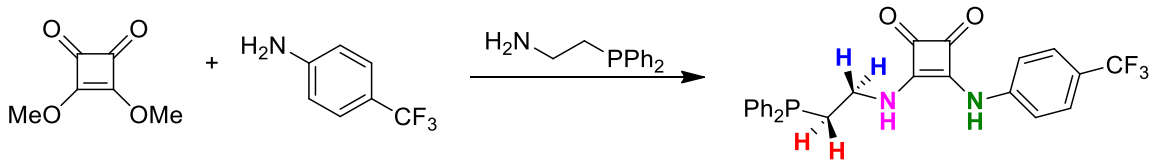


Figure 3.5. MS (ESI+ µ-TOF) compound **70**.

Synthesis of compound 71

To a solution of 3,4-Dimethoxy-3-cyclobutene-1,2-dione (29 mg, 0.2 mmol) in methanol (5 ml) was added 4-(trifluoromethyl)aniline (25 µL, 0.2 mmol) and the solution stirred. 64 hours later, 2-(diphenylphosphino)ethylamine was added (46 µL, 0.2 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 98 %.



Scheme 3.2. Synthesis of compound **71**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.88 (s, 1H, *NH*-Ph); 7.85 (s, 1H, *NH*-CH_2); 7.66 (s, 2H, H_{ortho}Ph-CF_3); 7.58 (s, 1H, H_{meta}Ph-CF_3); 7.45 (m, 4H, $H_{ortho}$$PPh_2$); 7.34 (m, 6H, H_{meta}+$H_{para}$$PPh_2$); 3.74 (m, 2H, PPh_2-CH_2-*CH_2*); 2.50 (m, 2H, PPh_2-*CH_2*-CH_2).

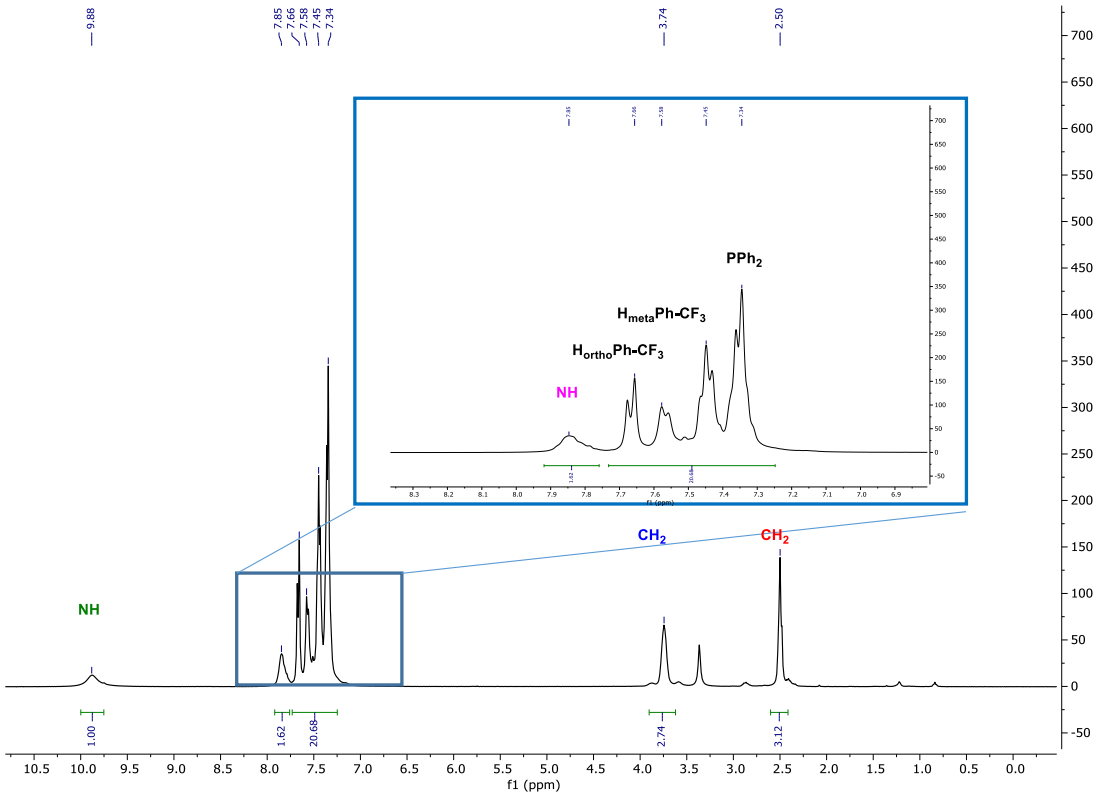


Figure 3.6. ^{1}H NMR spectrum of compound **71** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.2 (s, 3F, *CF_3*).

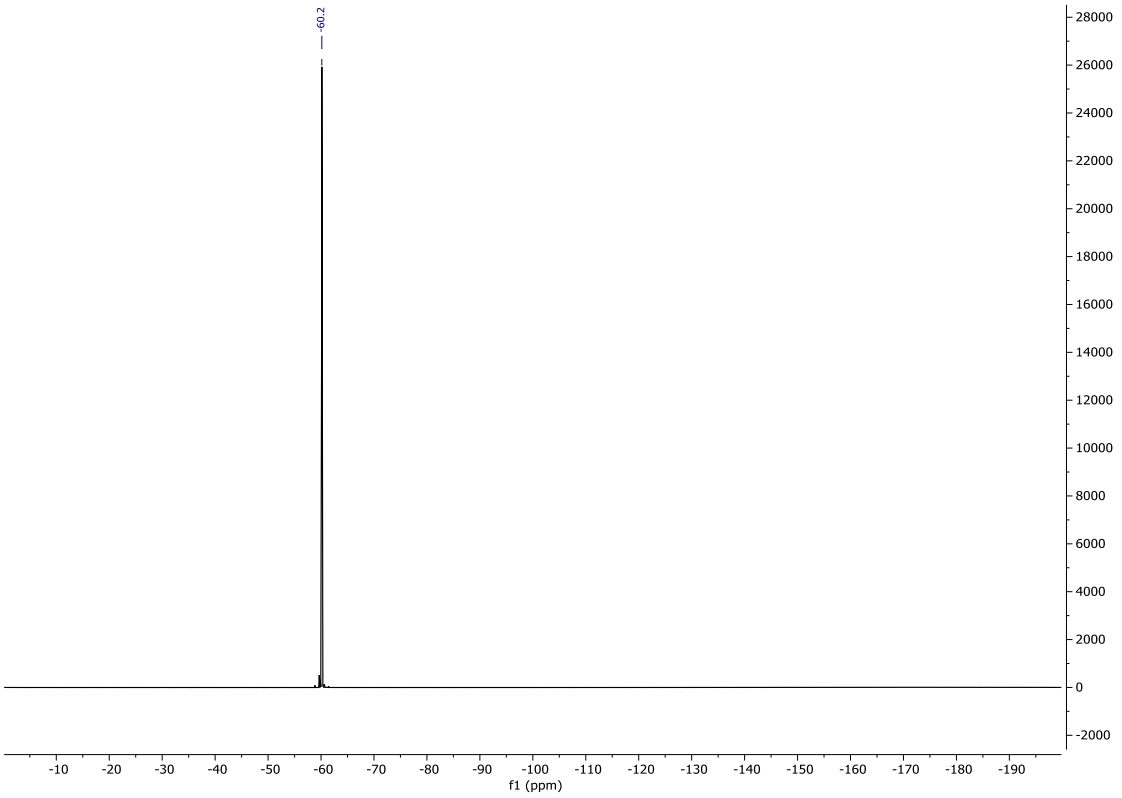


Figure 3.7.: $^{19}F\{^{1}H\}$ NMR spectrum of compound **71** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -22.4 (s, 1P, *PPh_2*).

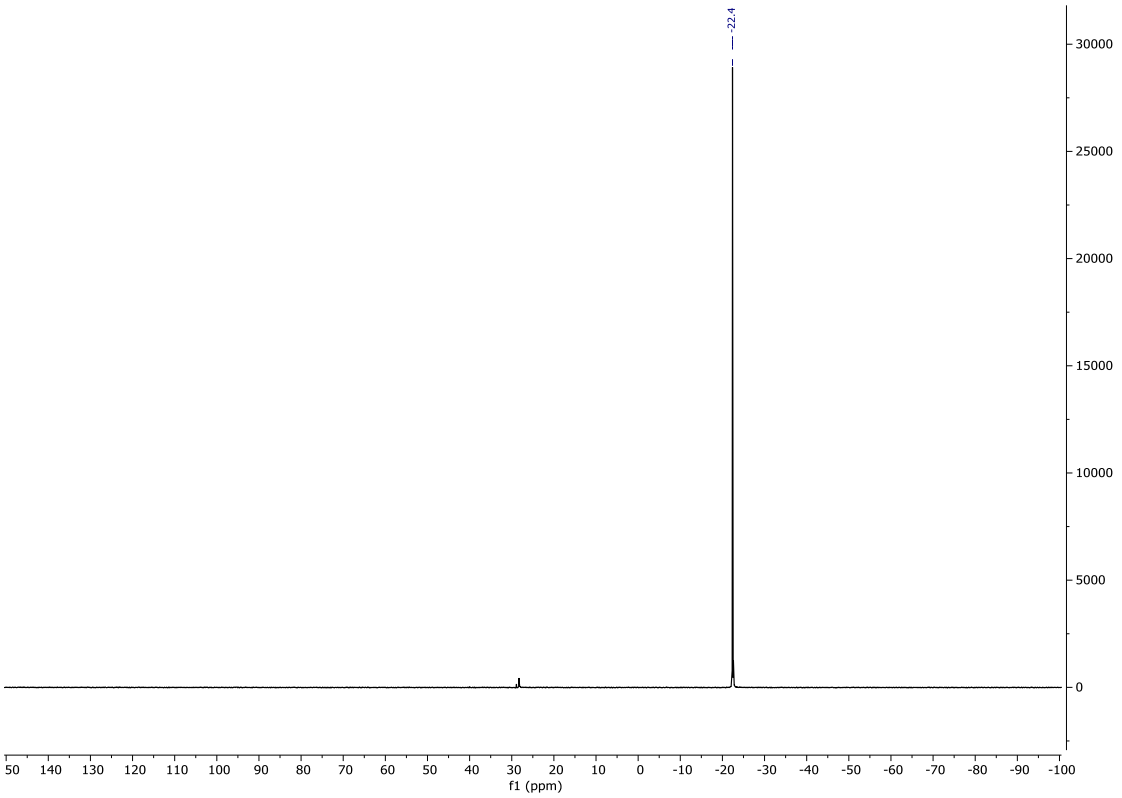


Figure 3.8.: $^{31}P\{^{1}H\}$ NMR spectrum of compound **71** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.6 (s, 1C, *C*=*O*); 180.2 (s, 1C, *C*=*O*); 169.4 (s, 1C, Ph-C=*C*-*NH*-*CH*$_2$); 162.9 (s, 1C, *Ph*-*NH*-*C*=C-CH$_2$); 142.5 (s, 1C, C_{ipso}-Ph-CF$_3$); 137.5 (d, 2C, C_{ipso}-PPh$_2$, $^1J_{CP}$ = 12.8 Hz); 132.4 (d, 4C, C_{ortho}PPh$_2$, $^2J_{CP}$ = 19.0 Hz); 128.8 (s, 2C, C_{para}PPh$_2$); 128.6 (d, 4C, C_{meta}PPh$_2$, $^2J_{CP}$ = 6.8 Hz); 126.6 (s, 2C, C_{ortho}Ph-CF$_3$); 123.6 (m, 2C, *CF*$_3$); 122.3 (q, 1C, C_{ipso}-Ph-CF$_3$, $^2J_{CP}$ = 32.0 Hz); 117.9 (s, 2C, C_{meta}Ph-CF$_3$); 41.3 (d, 1C, PPh$_2$-CH$_2$-*CH*$_2$, $^2J_{CP}$ = 22.6 Hz); 29.3 (d, 1C, PPh$_2$-*CH*$_2$-CH$_2$, $^2J_{CP}$ = 13.2 Hz).

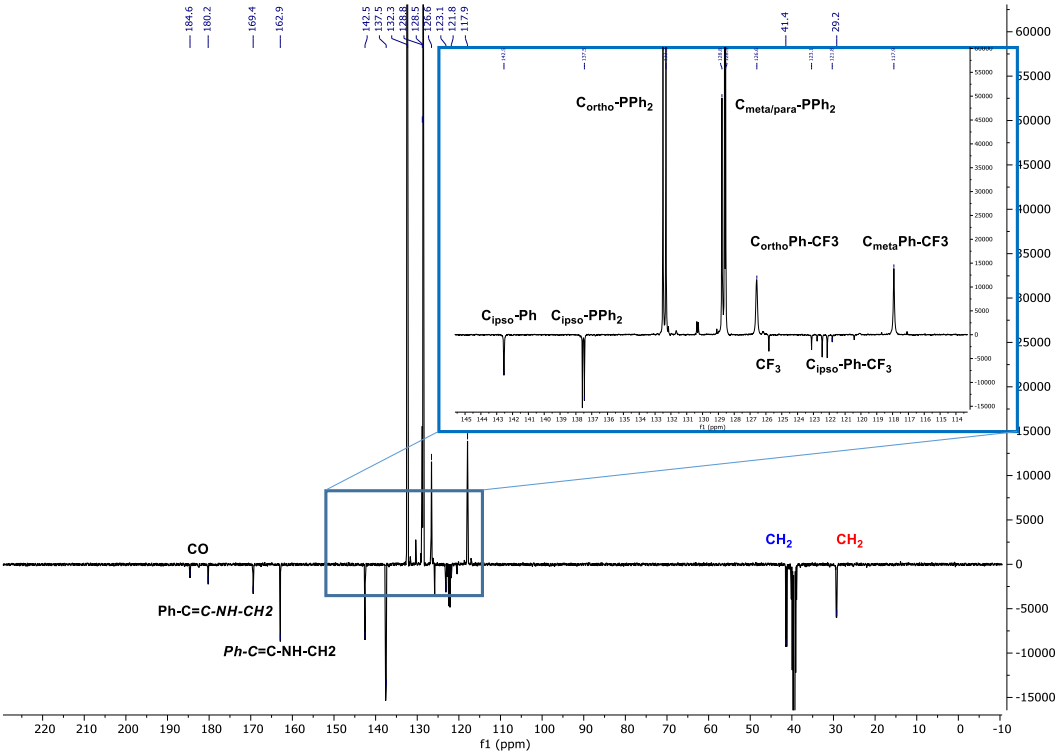


Figure 3.9. ^{13}C APT spectrum of compound **71** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= [M]$^+$ Calcd for [$C_{25}H_{20}F_3N_2O_2P$] 468.1209. Found 491.1090 [$C_{25}H_{20}F_3N_2O_2P$ + Na]$^+$.

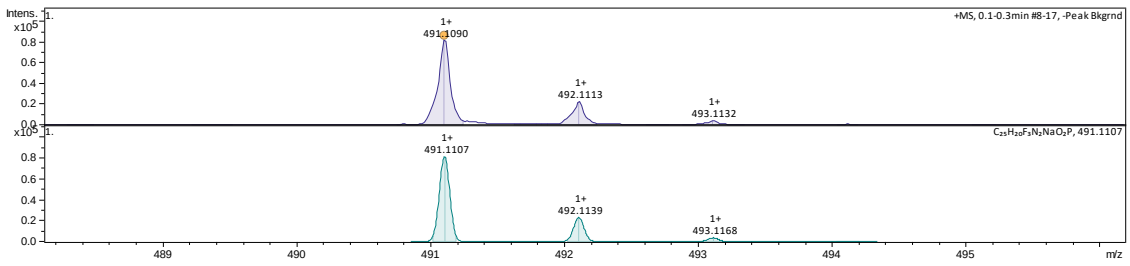
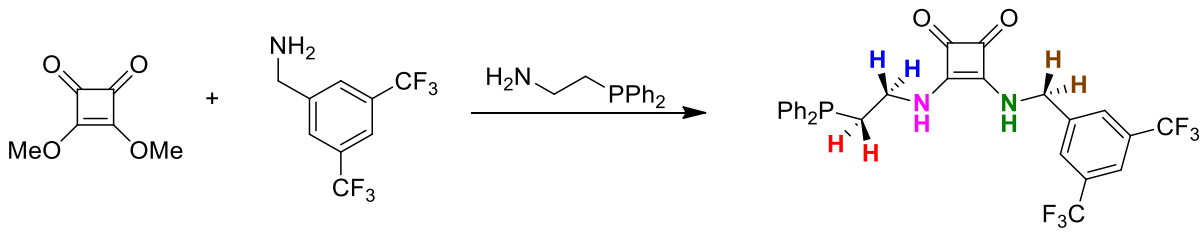


Figure 3.10. MS (ESI+ µ-TOF) compound **71**.

Synthesis 72

To a solution of 3,4-Dimethoxy-3-cyclobutene-1,2-dione (29 mg, 0.2 mmol) in methanol (5 ml) was added 3,5-Bis(trifluoromethyl)benzylamine (50 mg, 0.2 mmol) and the solution stirred. 21 hours later, 2-(diphenylphosphino)ethylamine was added (46 µL, 0.2 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 95%.



Scheme 3.3. Synthesis of compound **72**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.06 (m, 3H, H_{ortho}Ph-CF_3+H_{para}Ph-CF_3); 7.33 (m, 10H, *PPh*$_2$); 4.86 (s, 2H, NH-*CH*$_2$-Ph-CF_3); 3.63(t, 2H, PPh_2-CH_2-*CH*$_2$, $^3J_{H\text{-}H}$ = 7.3 Hz); 2.42 (s, 2H, PPh_2-*CH*$_2$-CH_2).

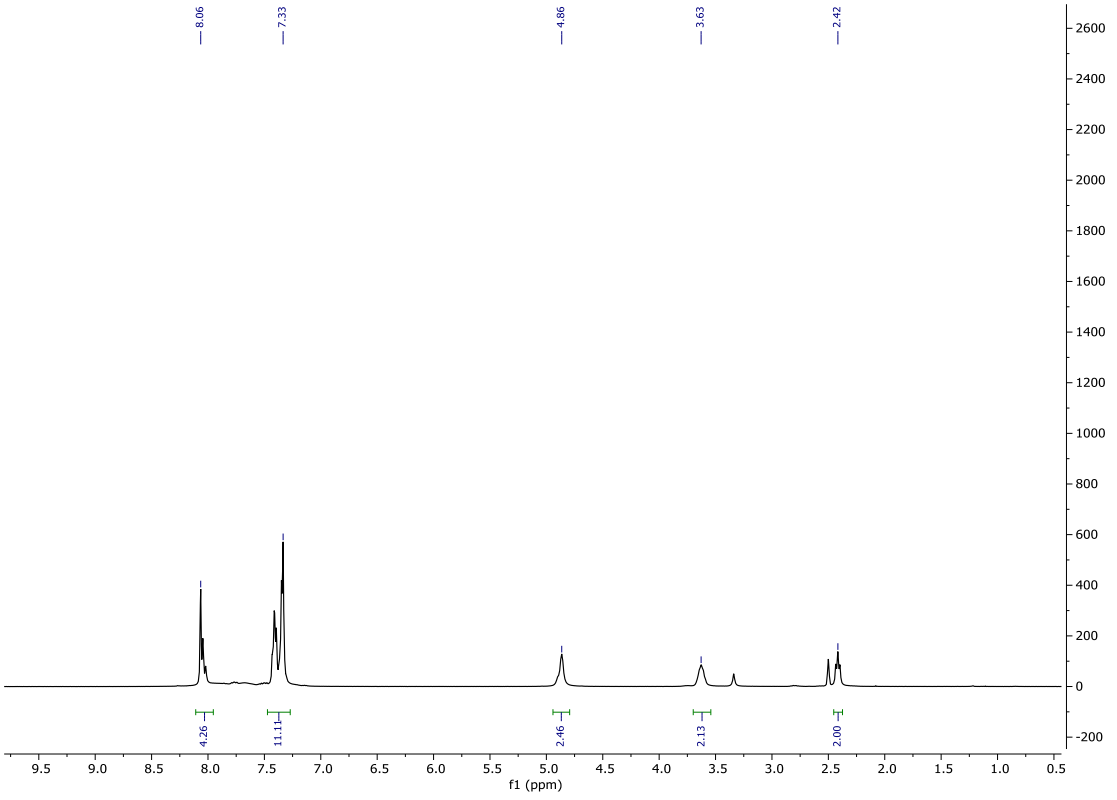


Figure 3.11. ^{1}H NMR spectrum of compound **72** in DMSO solution.

^{1}H NMR (ppm) (400 MHz, CD_3CN): δ = 7.97 (s, 2H, H_{ortho}Ph-CF_3); 7.46-7.36 (m, 11H, H_{para}Ph-CF_3+PPh_2); 6.30 (s, 1H, *NH*); 6.12 (s, 1H, *NH*); 4.86 (d, 2H, NH-CH_2-Ph-CF_3, $^{3}J_{H-H}$ = 6.0 Hz); 3.72 (m, 2H, PPh_2-CH_2-CH_2, $^{3}J_{H-H}$ = 6.6 Hz); 2.45 (m, 2H, PPh_2-CH_2-CH_2).

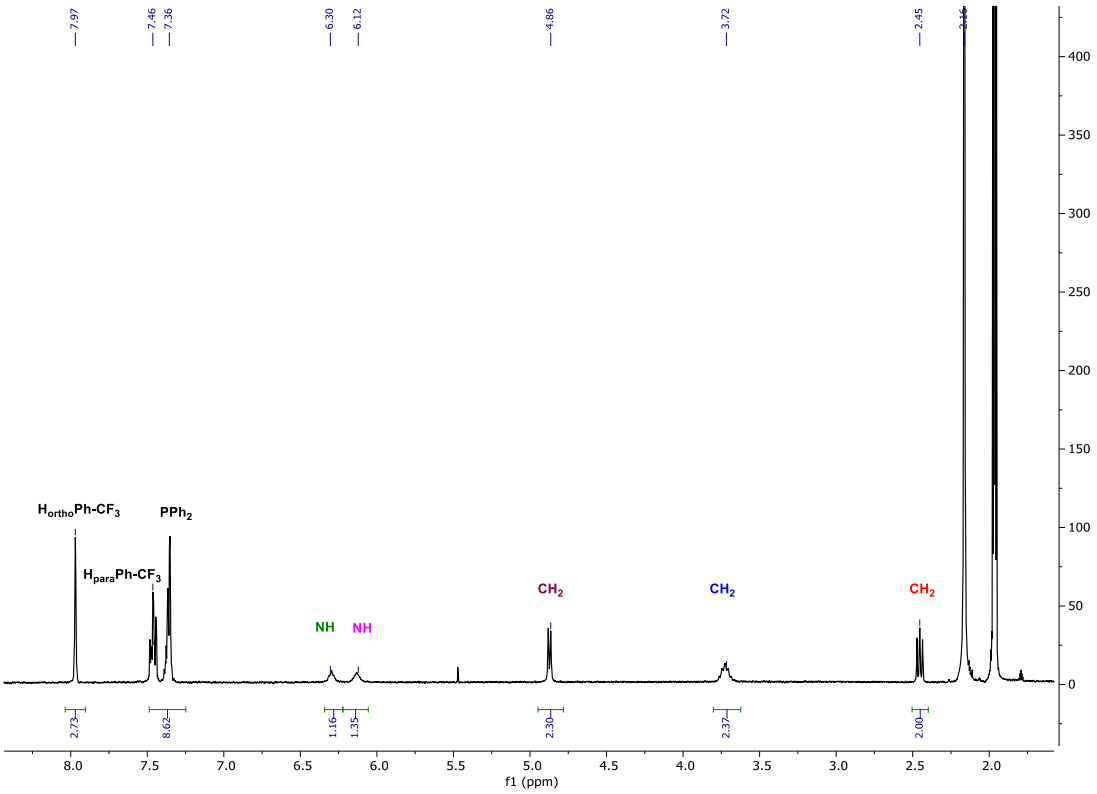


Figure 3.12. ^{1}H NMR spectrum of compound **72** in CD_3CN solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -61.3 (s, 6F, CF_3).

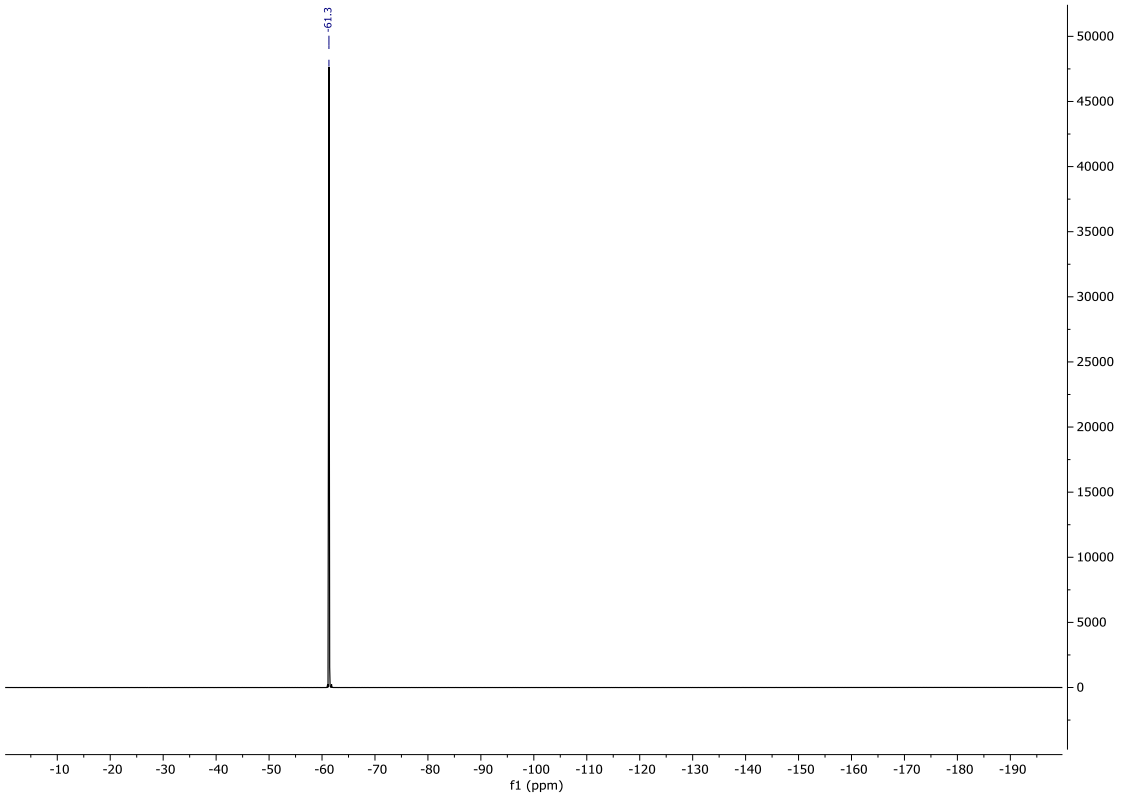


Figure 3.13. $^{19}F\{^{1}H\}$ NMR spectrum of compound **72** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -22.4 (s br, 1P, *PPh_2*).

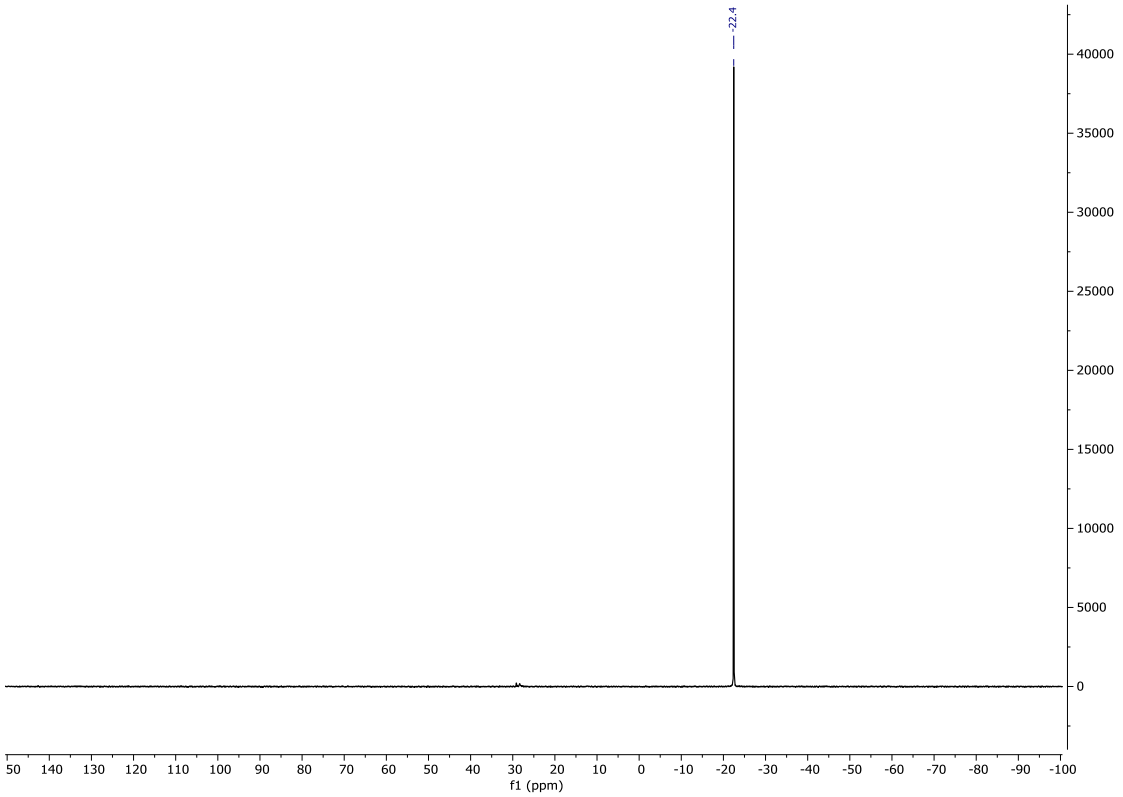


Figure 3.14. $^{31}P\{^{1}H\}$ NMR spectrum of compound **72** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 182.8 (s, 1C, *C*=*O*); 182.5 (s, 1C, *C*=*O*); 167.9 (s, 1C, Ph-C=*C*-*CH*$_2$); 167.2 (s, 1C, *Ph*-*C*=C-CH$_2$); 142.6 (s, 1C, *C*$_{ipso}$-*Ph*); 137.6 (d, 2C, *C*$_{ipso}$PPh$_2$, $^{1}J_{CP}$ = 12.9 Hz); 132.3 (d, 4C, *C*$_{ortho}$PPh$_2$, $^{2}J_{CP}$ = 18.9 Hz); 130.4 (q, 2C, *C*$_{ipso}$*C*-*CF*$_3$, $^{2}J_{CF}$ = 32.7 Hz); 128.7 (s, 1C, *C*$_{para}$PPh$_2$); 128.5 (s br, 4C, *C*$_{meta}$PPh$_2$, $^{3}J_{CP}$ = 6.7 Hz); 128.3 (s, 2C, *C*$_{ortho}$Ph-CF$_3$); 123.3 (q, 2C, *CF*$_3$, $^{1}J_{CF}$ = 272.9 Hz); 121.9 (s, 1C, *C*$_{para}$Ph-CF$_3$); 45.7 (s, 1C, NH-*CH*$_2$-Ph-CF$_3$); 40.9 (s, 1C, PPh$_2$-CH$_2$-*CH*$_2$, $^{2}J_{CP}$ = 23.1 Hz); 29.47 (s, 1C, PPh$_2$-*CH*$_2$-CH$_2$, $^{1}J_{CP}$ = 13.2 Hz).

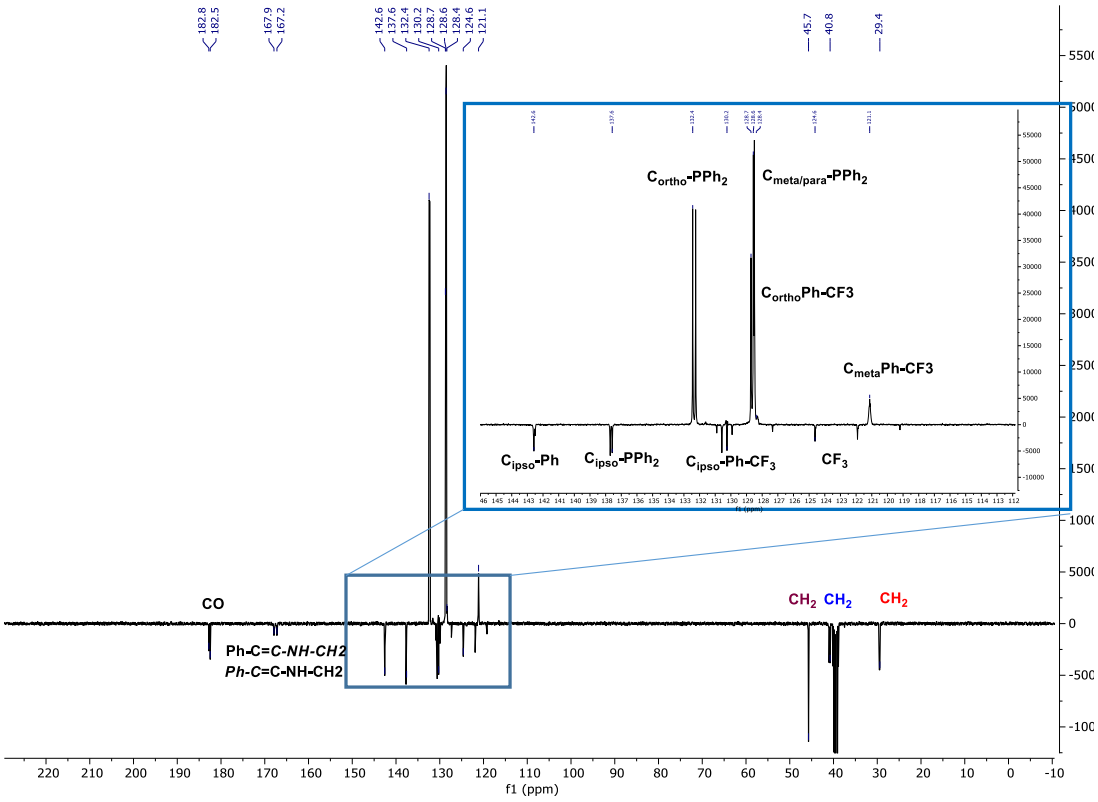


Figure 3.15: ^{13}C APT spectrum of compound **72** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{27}H_{21}F_6N_2O_2P]$ 550.1239. Found 573.1115 $[C_{27}H_{21}F_6N_2O_2P + Na]^+$.

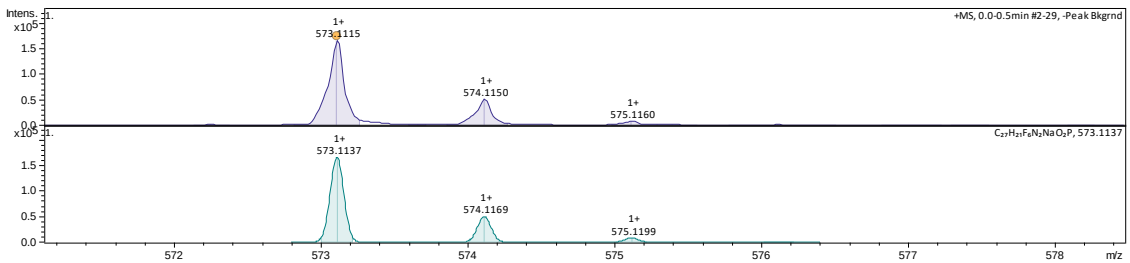
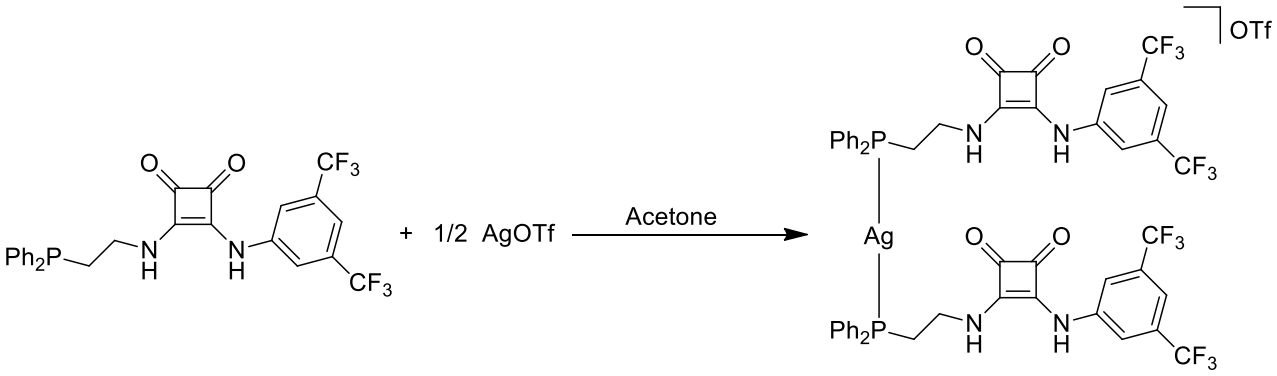


Figure 3.16. MS (ESI+ µ-TOF) compound **72**.

Synthesis of compound 73

To a solution of compound **70** (53 mg, 0.1 mmol) in acetone (5 ml) was added [AgOTf] (12 mg, 0.05 mmol) and the solution stirred for 2 hours with exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 40%.



Scheme 3.4. Synthesis of compound **73**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 10.20 (s, 2H, *NH*-PPh_2); 7.98 (s, 4H, H_{ortho}Ph-CF_3); 7.72 (m, 10H, $H_{ortho}PPh_2$ + *NH*-CH_2); 7.50 (m, 14H, H_{para}Ph-CF_3 + H_{meta}+$H_{para}PPh_2$); 3.83(m, 4H, PPh_2-CH_2-*CH_2*); 2.93(m, 4H, PPh_2-*CH_2*-CH_2).

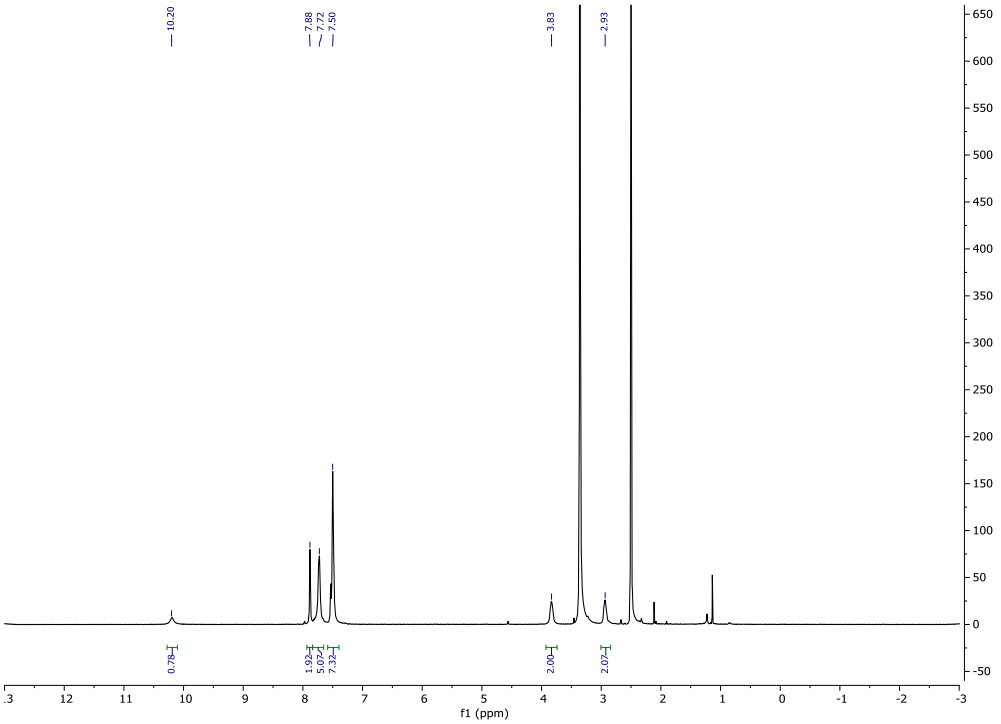


Figure 3.17. ^{1}H NMR spectrum of compound **73** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -61.8 (s, 12F, *CF_3*); -77.7 (s, 3F, *OTf*).

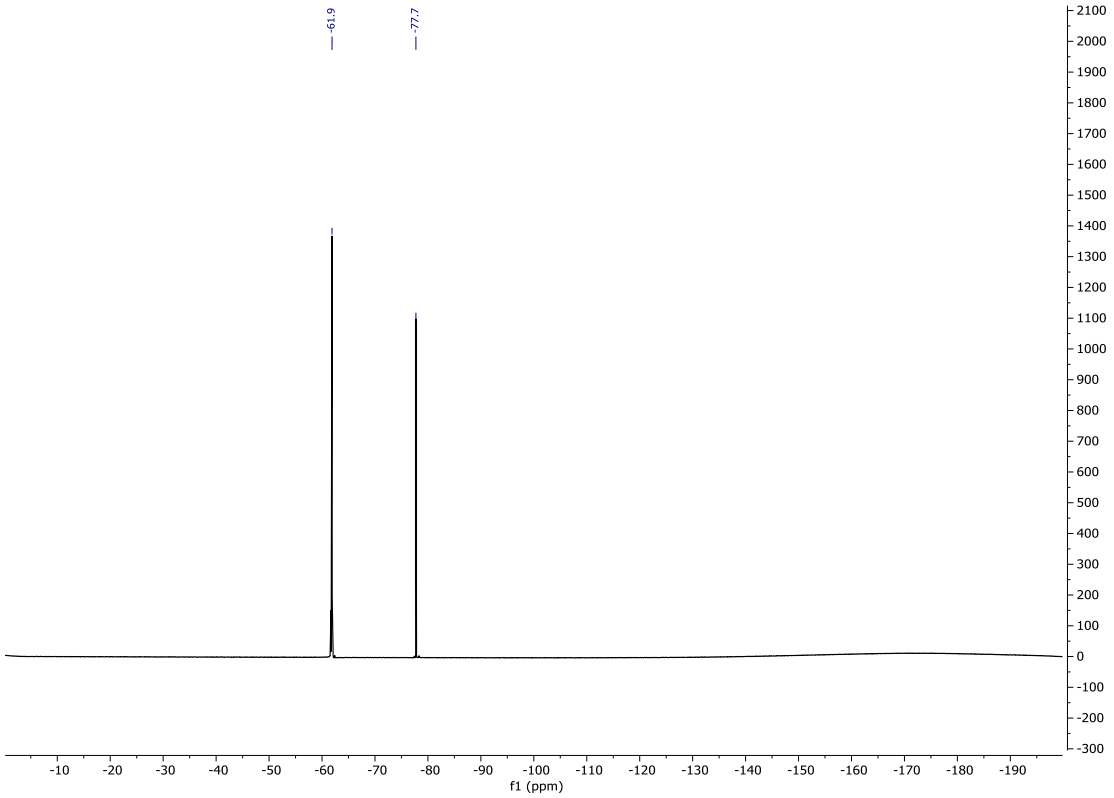


Figure 3.18. $^{19}F\{^{1}H\}$ NMR spectrum of compound **73** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -1.7 (d, 2P, *PPh_2*, $^{1}J_{Ag\text{-}P}$ = 394.8Hz).

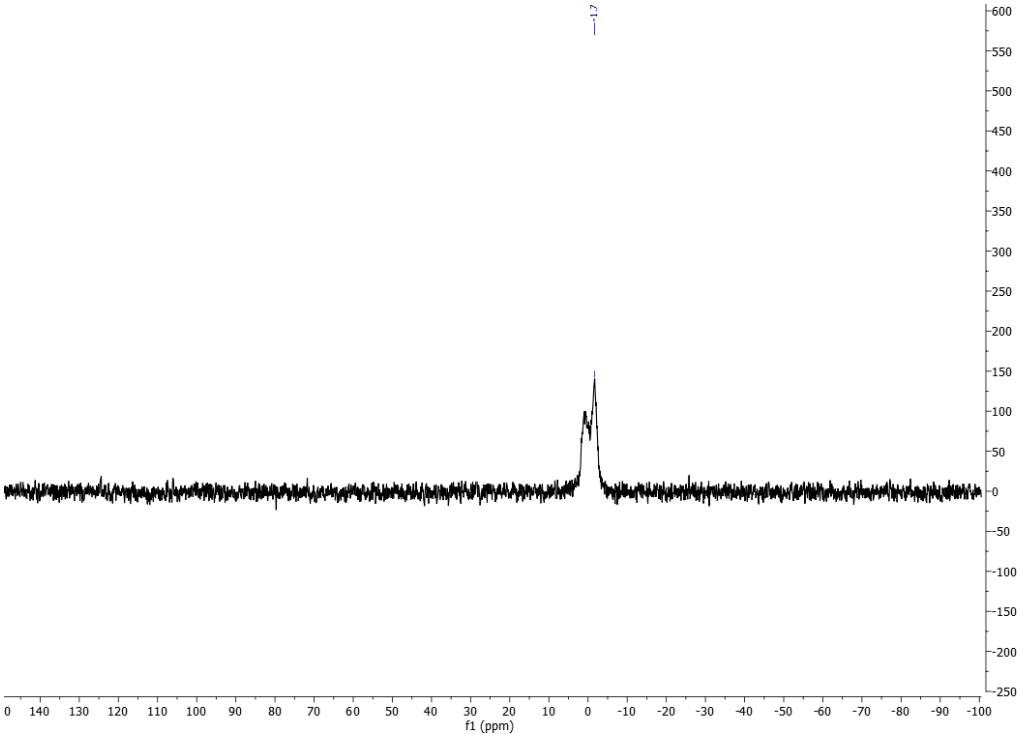


Figure 3.19. $^{31}P\{^{1}H\}$ NMR spectrum of compound **73** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.8 (s, 2C, *C*=*O*); 180.2 (s, 2C, *C*=*O*); 169.0 (s, 2C, Ph-C=*C*-*CH*$_2$); 162.8 (s, 2C, *Ph*-*C*=C-CH$_2$); 140.8 (s, 2C, *C$_{ipso}$*-*Ph*); 133.0 (s br, 8C, *C$_{ortho}$*PPh$_2$); 131.2 (d, 4C, *C$_{ipso}$*PPh$_2$, $^1J_{CP}$ = 33.2 Hz); 130.9 (s br, 2C, *C$_{para}$*PPh$_2$); 129.1 (s br, 8C, *C$_{meta}$*PPh$_2$); 123.1 (q, 4C, *CF$_3$*, $^1J_{CF}$ = 272.7 Hz); 117.8 (s, 4C, *C$_{ortho}$*Ph-CF$_3$); 114.7 (s, 2C, *C$_{para}$*Ph-CF$_3$); 40.0 (m, 2C, PPh$_2$-CH$_2$-*CH$_2$*); 29.6 (s, 2C, PPh$_2$-*CH$_2$*-CH$_2$).

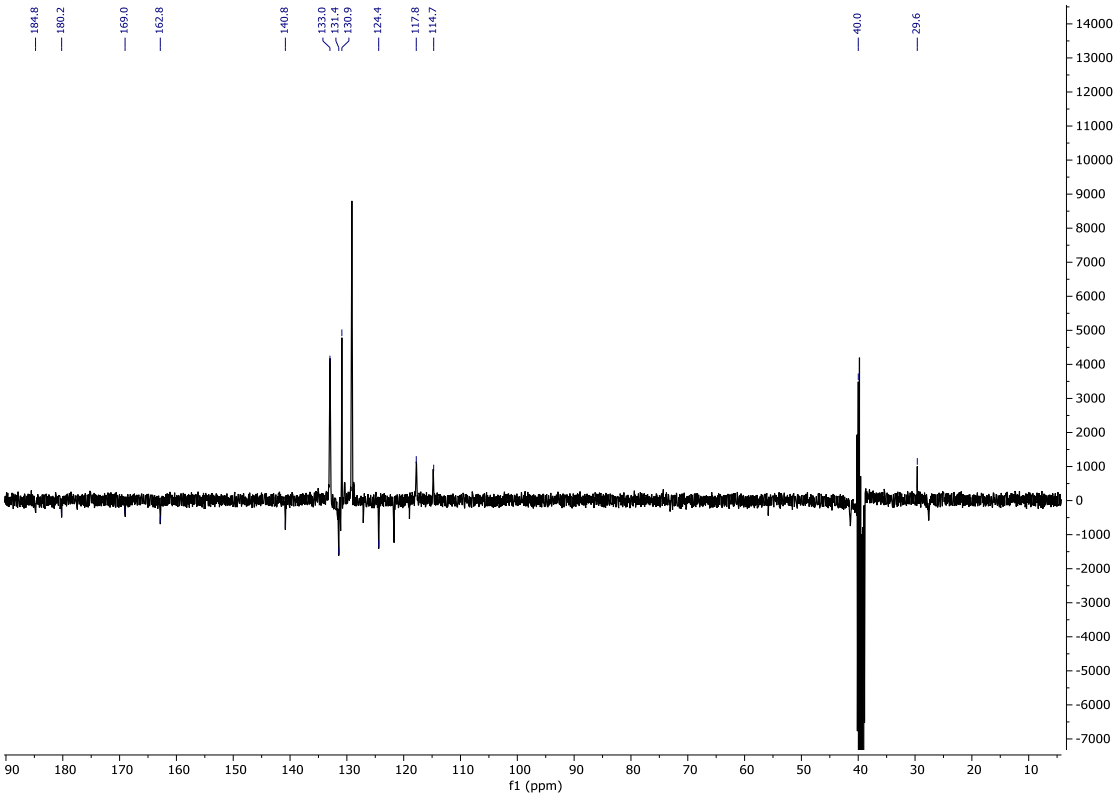


Figure 3.20.: ^{13}C APT spectrum of compound **73** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= [M]$^+$ Calcd for [$C_{52}H_{38}AgF_{12}N_4O_4P_2$] 1179.1222. Found 1179.1188.

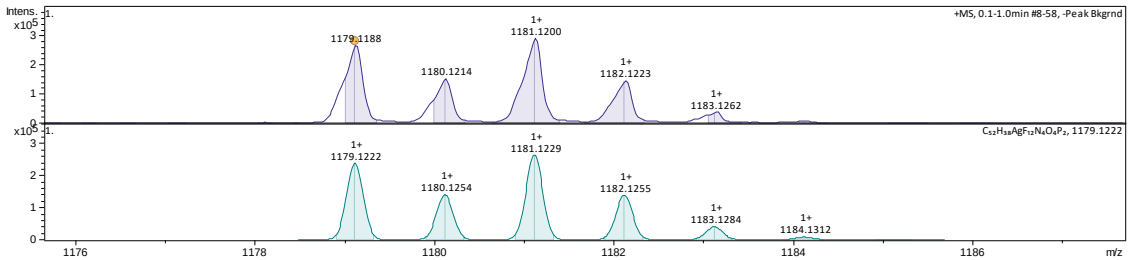
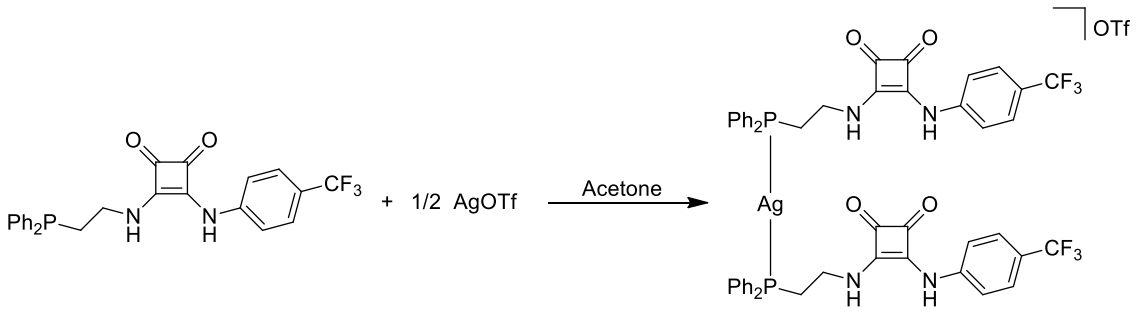


Figure 3.21. MS (ESI+ µ-TOF) compound **73**.

Synthesis of compound 74

To a solution of compound **71** (46 mg, 0.1 mmol) in acetone (5 ml) was added [AgOTf] (12 mg, 0.05 mmol) and the solution stirred for 2 hours with exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 46%.



Scheme 3.5. Synthesis of compound **74**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.90 (s, 2H, *NH*-PPh_2); 7.70 (m, 10H, $H_{ortho}PPh_2$ + *NH*-CH_2); 7.57 (s, 4H, H_{ortho}Ph-CF_3); 7.48 (m, 16H, H_{meta}Ph-CF_3 + H_{meta}+$H_{para}PPh_2$); 3.84 (s br, 4H, PPh_2-CH_2-*CH_2*,); 2.93 (s br, 4H, PPh_2-*CH_2*-CH_2).

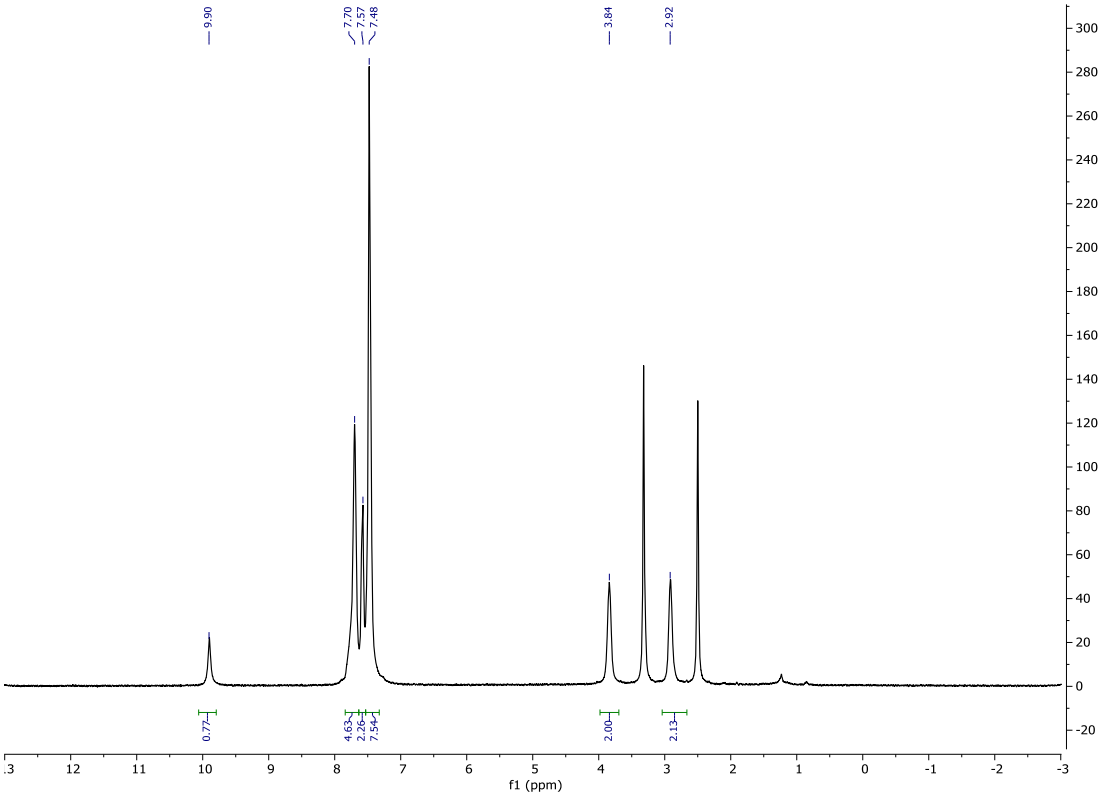


Figure 3.22. ^{1}H NMR spectrum of compound **74** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.3 (s, 6F, *CF_3*); -77.7 (s, 3F, *OTf*).

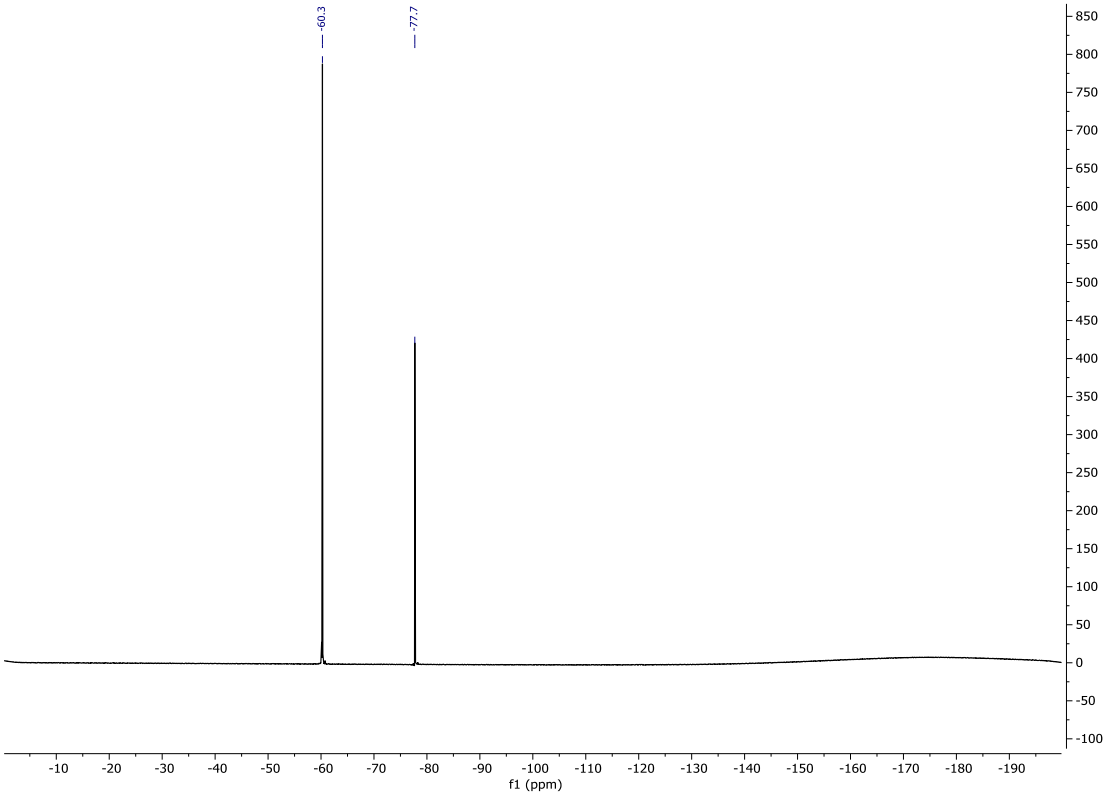


Figure 3.23. ^{19}F{^{1}H} NMR spectrum of compound **74** in DMSO solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, DMSO): δ = -1.1 (s br, 2P, *PPh_2*).

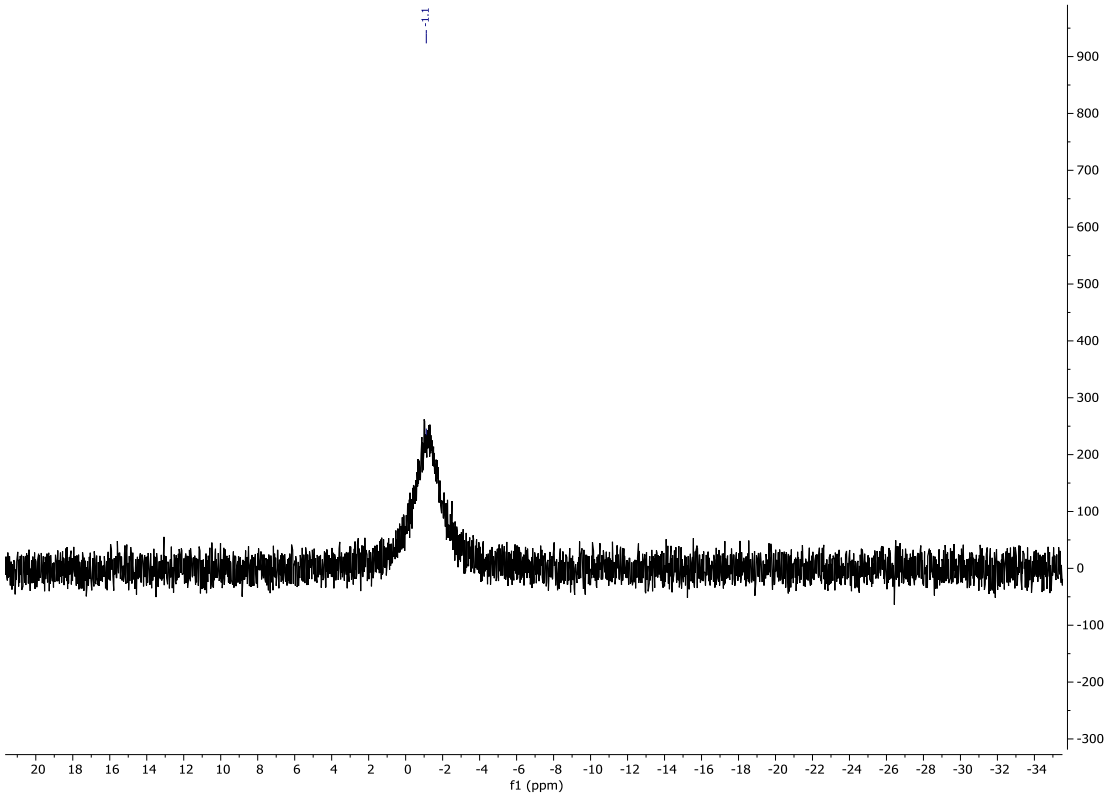


Figure 3.24. $^{31}P\{^{1}H\}$ NMR spectrum of compound **74** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.8 (s, 2C, *C*=*O*); 179.9 (s, 2C, *C*=*O*); 168.8 (s, 2C, *C*=*C*); 163.4 (s, 2C, *C*=*C*); 142.82 (s, 2C, $C_{ipso}Ph$); 132.8 (d, 8C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 13.8 Hz); 131.6 (d, 4C, $C_{ipso}PPh_2$, $^{1}J_{CP}$ = 29.5 Hz); 130.7 (s br, 2C, $C_{para}PPh_2$); 129.0 (s br, 8C, $C_{meta}PPh_2$, $^{3}J_{CP}$ = 5.1 Hz); 126.5 (s, 4C, C_{ortho}Ph-CF_3); 122.6 (m, 2C, CF_3); 118.0 (s, 4C, C_{meta}Ph-CF_3); 41.1 (m, 2C, PPh_2-CH_2-CH_2); 27.8 (s, 2C, PPh_2-CH_2-CH_2).

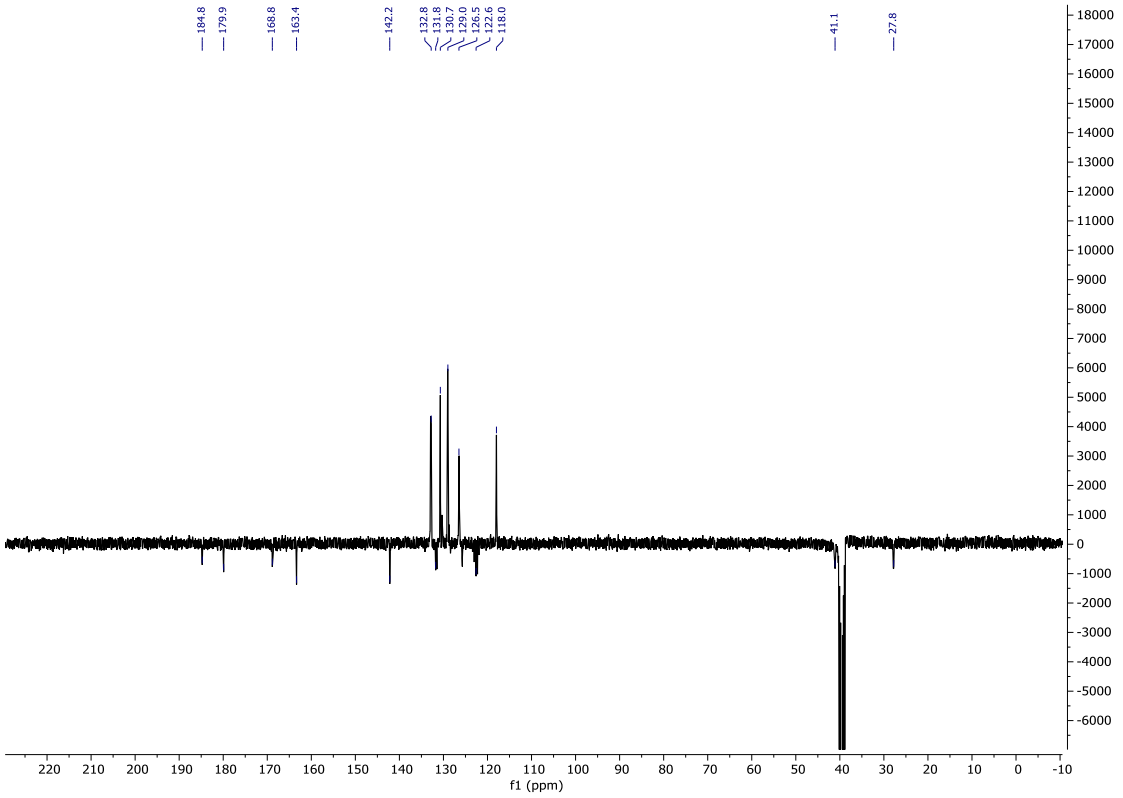


Figure 3.25. ^{13}C APT spectrum of compound **74** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{50}H_{40}AgF_6N_4O_4P_2]$ 1043.1474. Found 1043.1491.

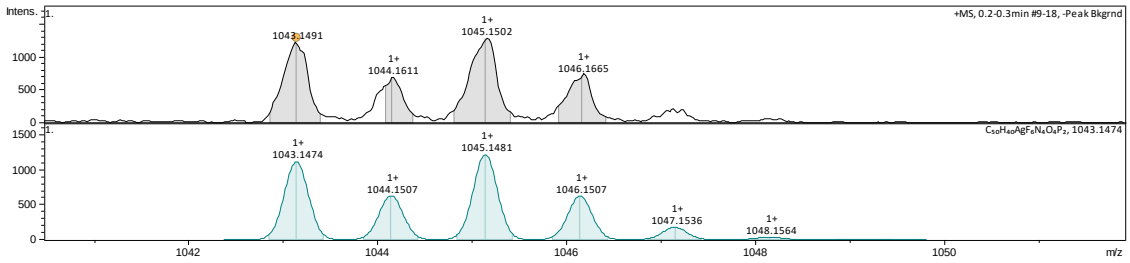
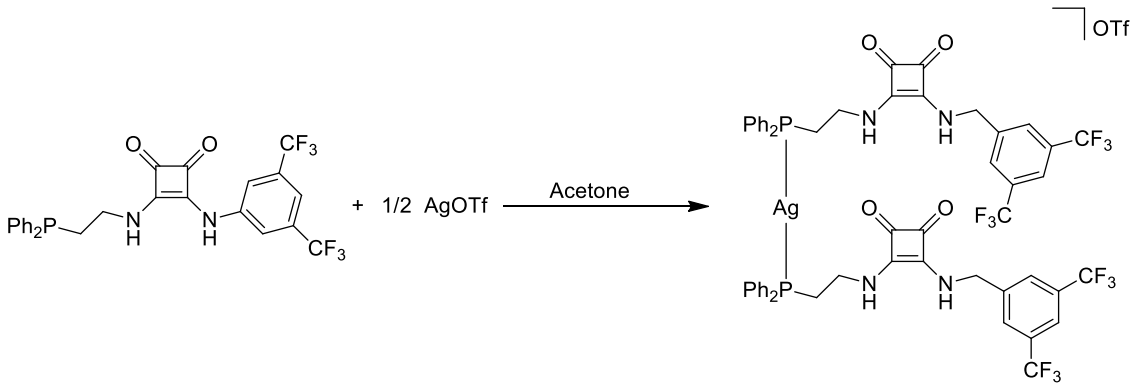


Figure 3.26. MS (ESI+ µ-TOF) compound **74**.

Synthesis of compound 75

To a solution of compound **72** (56 mg, 0.1 mmol) in acetone (5 ml) was added [AgOTf] (12 mg, 0.05 mmol) and the solution stirred for 2 hours with exclusion of light. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 38%.



Scheme 3.6. Synthesis of compound **75**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.06 (s, 2H, H_{para}Ph-CF_3); 8.04 (s, 4H, H_{ortho}Ph-CF_3); 7.66 (s, 8H, $H_{ortho}$$PPh_2$); 7.43 (s, 12H, H_{meta}+$H_{para}$$PPh_2$); 4.81 (s, 4H, NH-$CH_2$-Ph-$CF_3$); 3.78 (s, 4H, PPh_2-CH_2-CH_2); 2.82(s, 4H, PPh_2-CH_2-CH_2).

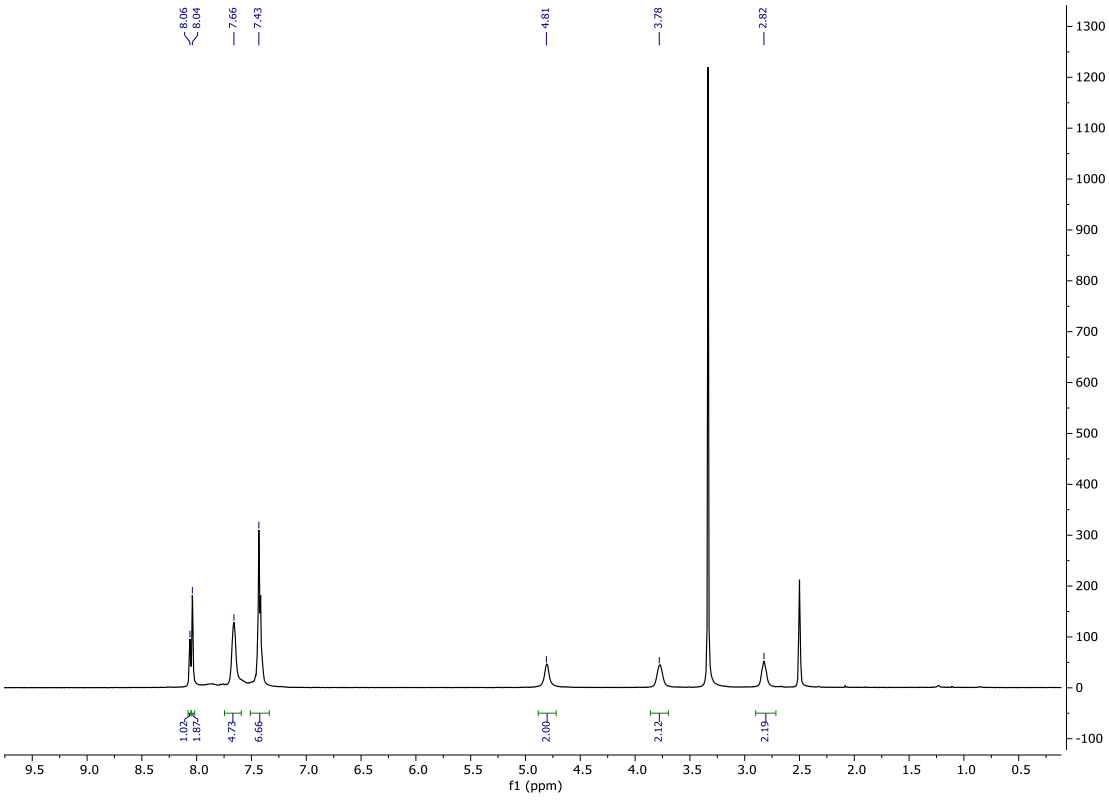


Figure 3.27. ^{1}H NMR spectrum of compound **75** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -61.3 (s, 12F, CF_3); -77.7 (s, 3F, *OTf*).

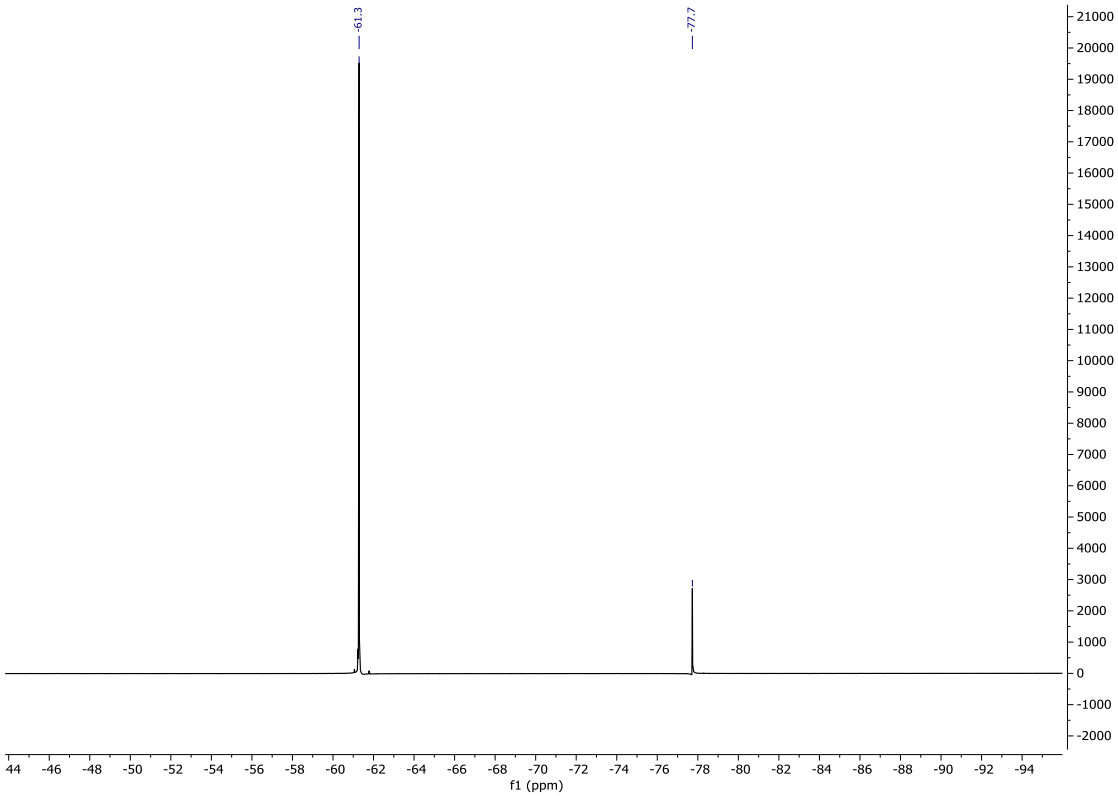


Figure 3.28. $^{19}F\{^{1}H\}$ NMR spectrum of compound **75** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -0.2 (s br, 2P, *PPh_2*).

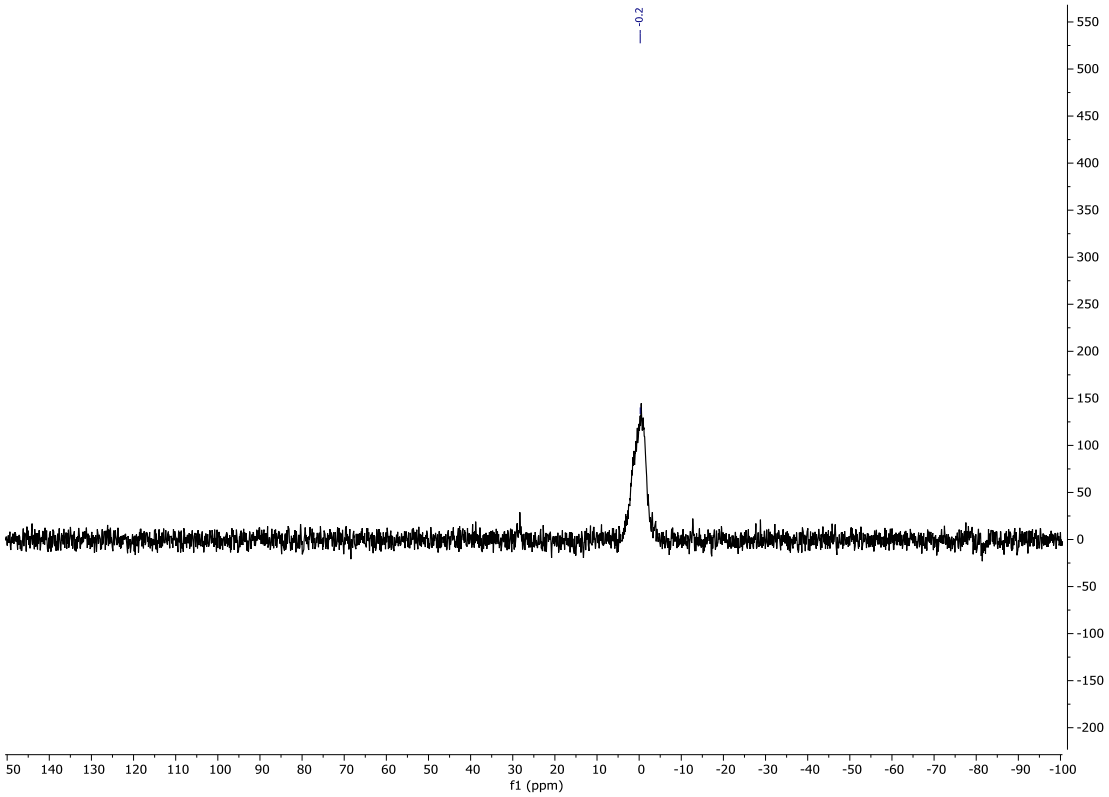


Figure 3.29. $^{31}P\{^{1}H\}$ NMR spectrum of compound **75** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 183.0 (s, 2C, *C*=*O*); 182.1 (s, 2C, *C*=*O*); 167.7 (s, 2C, *C*=*C*); 167.3 (s, 2C, *C*=*C*); 142.3 (s, 2C, $C_{ipso}Ph$); 132.9 (d, 8C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 9.2 Hz); 131.7 (d, 4C, $C_{ipso}PPh_2$, $^{1}J_{CP}$ = 28.1 Hz); 130.7 (s br, 2C, $C_{para}PPh_2$); 130.4 (q, 4C, $C_{ipso}C\text{-}CF_3$, $^{2}J_{CF}$ = 33.0 Hz); 129.0 (s br, 8C, $C_{meta}PPh_2$); 128.6 (s, 4C, C_{ortho}Ph-CF_3); 123.3 (q, 4C, CF_3, $^{1}J_{CF}$ = 272.7 Hz); 121.2 (s, 2C, C_{para}Ph-CF_3); 45.8 (s, 2C, NH-CH_2-Ph-CF_3); 40.9 (s, 2C, PPh_2-CH_2-CH_2); 28.3(s, 2C, PPh_2-CH_2-CH_2).

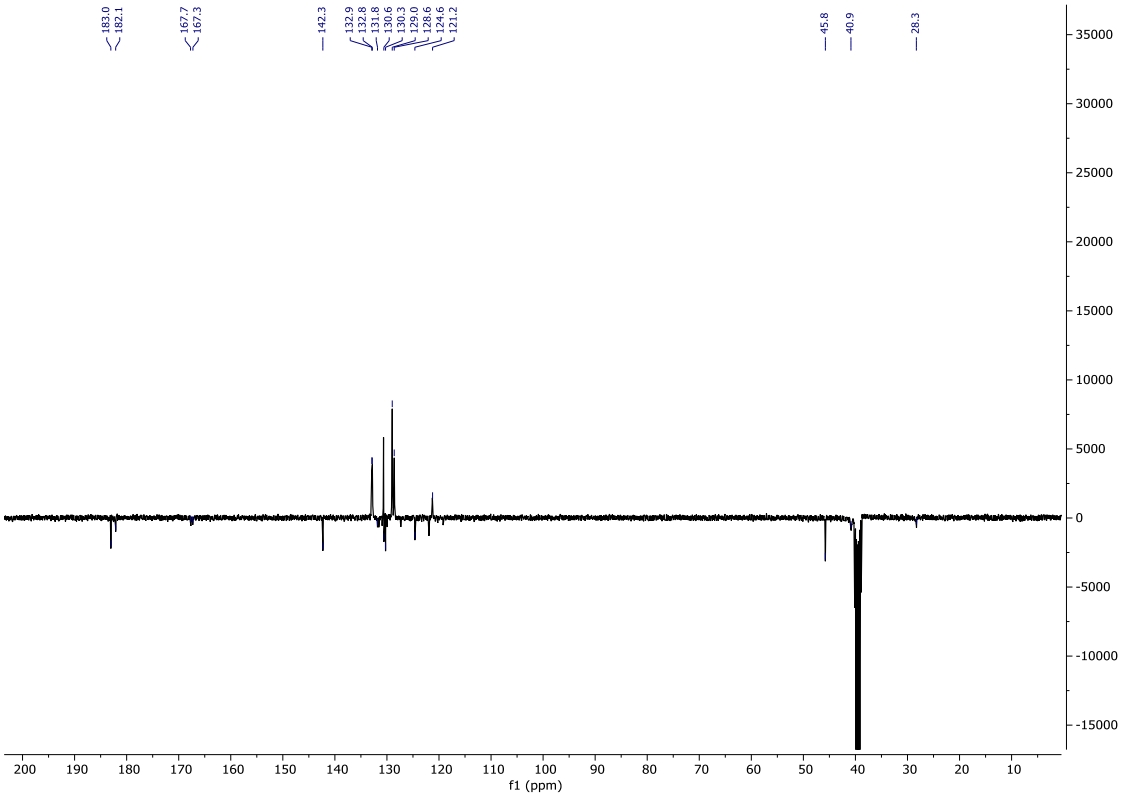


Figure 3.30. ^{13}C APT spectrum of compound **75** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{54}H_{42}AgF_{12}N_4O_4P_2]$ 1207.1535 Found 1207.1570.

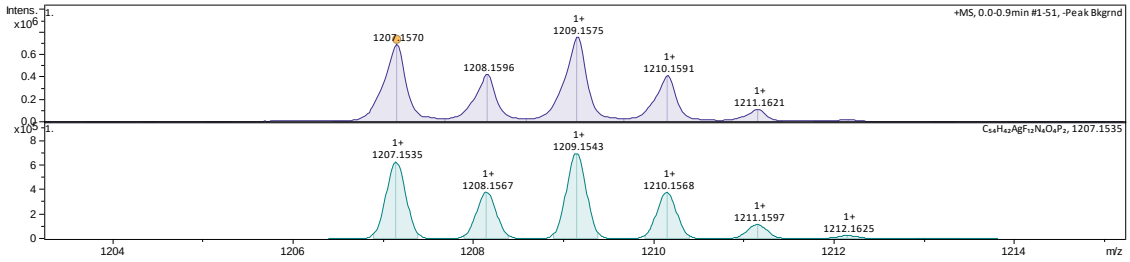
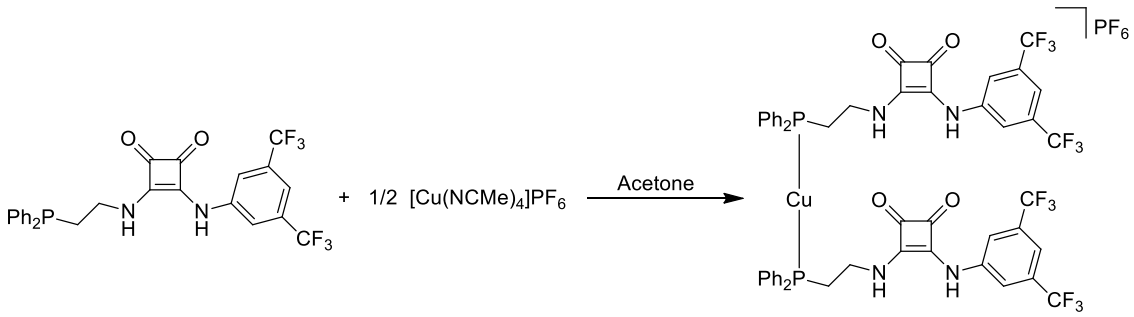


Figure 3.31. MS (ESI+ µ-TOF) compound **75**.

Synthesis of compound 76

To a solution of compound **70** (53 mg, 0.2 mmol) in acetonitrile (50 ml) was added $[Cu(NCMe)_4]PF_6$ (18.6 mg, 0.05 mmol) and the solution stirred for 2 hours. The solution was concentrated under reduced pressure to approximately 1 ml and pentane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 38%.



Scheme 3.7. Synthesis of compound **76**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 10.17 (s, 2H, *NH*-PPh_2); 7.87 (s, 4H, H_{ortho}Ph-CF_3); 7.73 (s, 2H, *NH*-CH_2); 7.57 (m, 8H, $H_{ortho}PPh_2$); 7.52 (s, 2H, H_{para}Ph-CF_3); 7.43 (m, 12H, H_{meta}+$H_{para}PPh_2$); 3.71 (m, 4H, PPh_2-CH_2-*CH_2*); 2.76 (m, 4H, PPh_2-*CH_2*-CH_2).

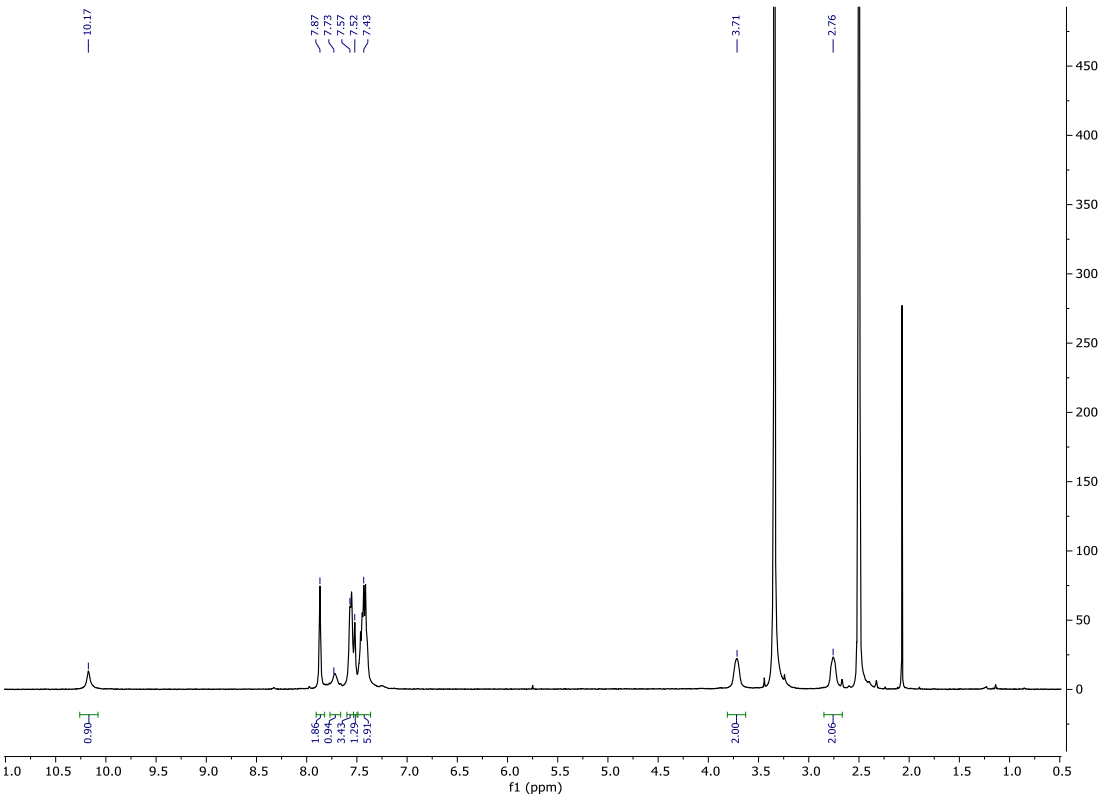


Figure 3.32. ^{1}H NMR spectrum of compound **76** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -61.9 (s, 12F, CF_3); -69.2, -71.1 (s, 6F, PF_6).

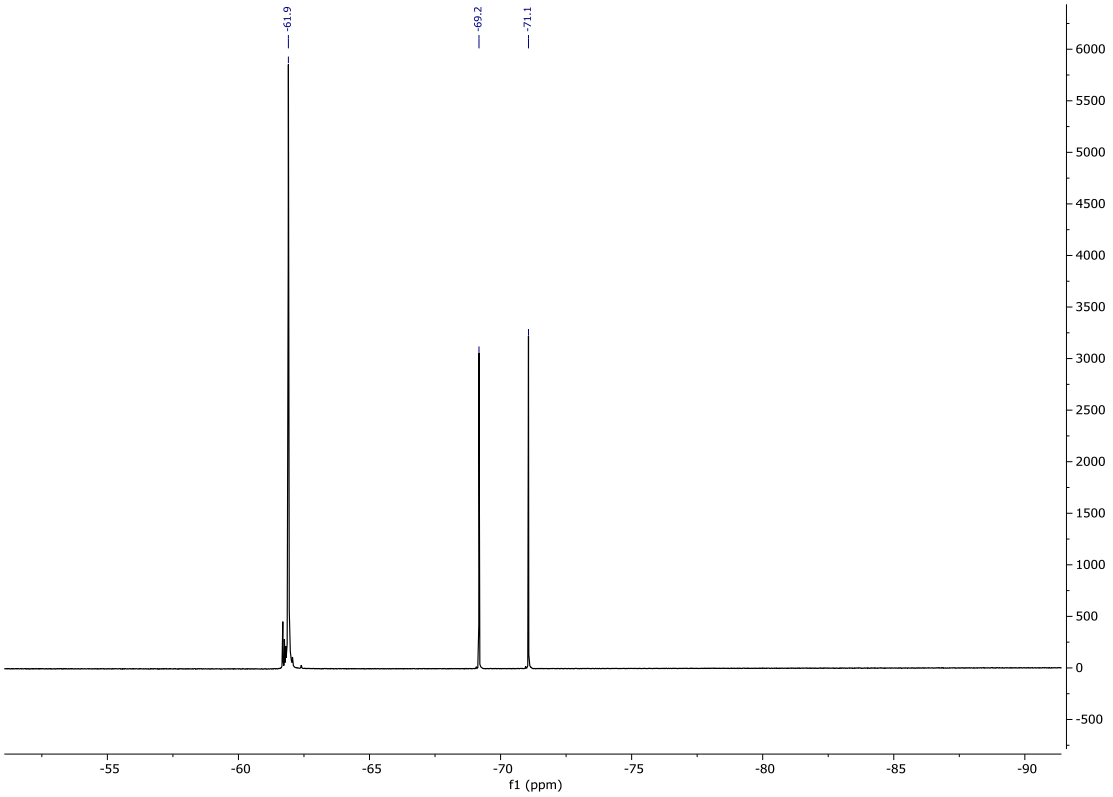


Figure 3.33. $^{19}F\{^{1}H\}$ NMR spectrum of compound **76** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -15.8 (s, 2P, PPh_2).

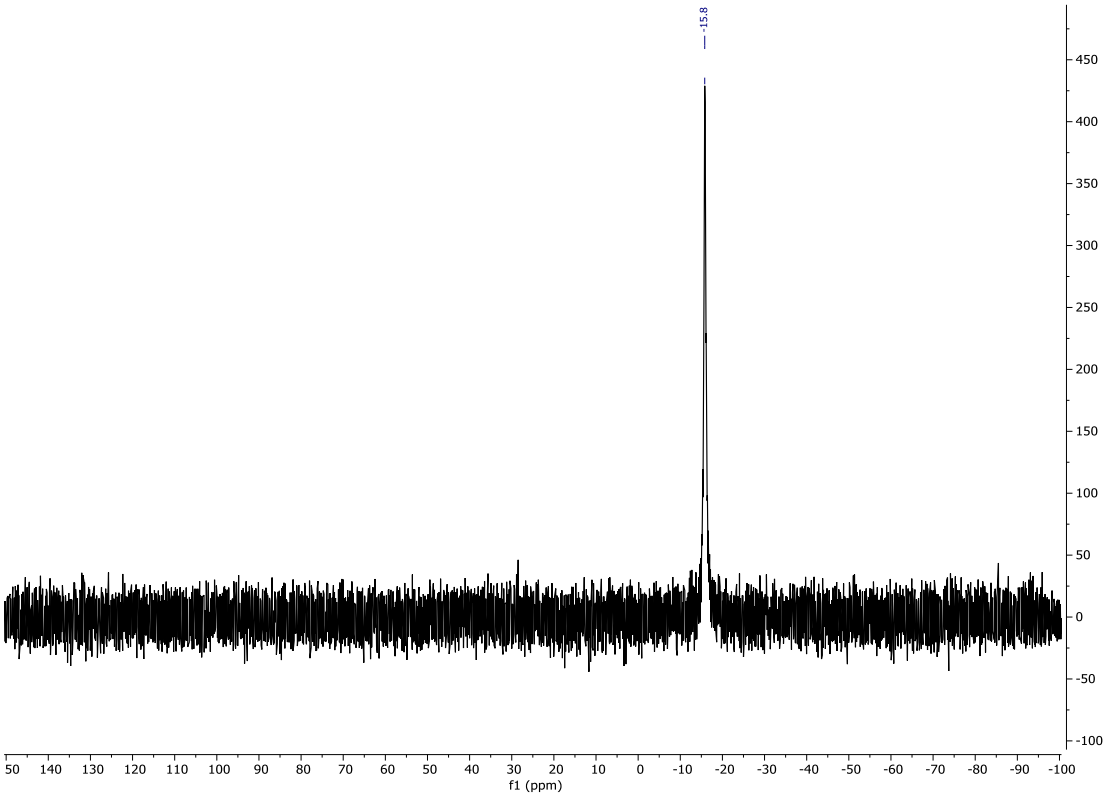


Figure 3.34. $^{31}P\{^{1}H\}$ NMR spectrum of compound **76** in DMSO solution.

^{13}C APT (100 MHz, DMSO): δ = 184.7 (s, 2C, *C=O*); 180.2 (s, 2C, *C=O*); 169.0 (s, 2C, Ph-C=*C*-*CH*$_2$); 162.7 (s, 2C, *Ph*-*C*=C-CH$_2$); 140.8 (s, 2C, *C*$_{ipso}$*Ph*); 132.5 (s br, 8C, *C*$_{ortho}$PPh$_2$); 131.2 (d, 4C, *C*$_{ipso}$PPh$_2$, $^{1}J_{CP}$ = 33.1 Hz); 130.2 (s br, 2C, *C*$_{para}$PPh$_2$); 128.8 (s br, 8C, *C*$_{meta}$PPh$_2$); 123.0 (q, 4C, *CF*$_3$, $^{1}J_{CF}$ = 272.7 Hz); 117.8 (s, 4C, *C*$_{ortho}$Ph-CF$_3$); 114.7 (s, 2C, *C*$_{para}$Ph-CF$_3$); 40.1 (s, 2C, PPh$_2$-CH$_2$-*CH*$_2$); 27.5 (m, 2C, PPh$_2$-*CH*$_2$-CH$_2$).

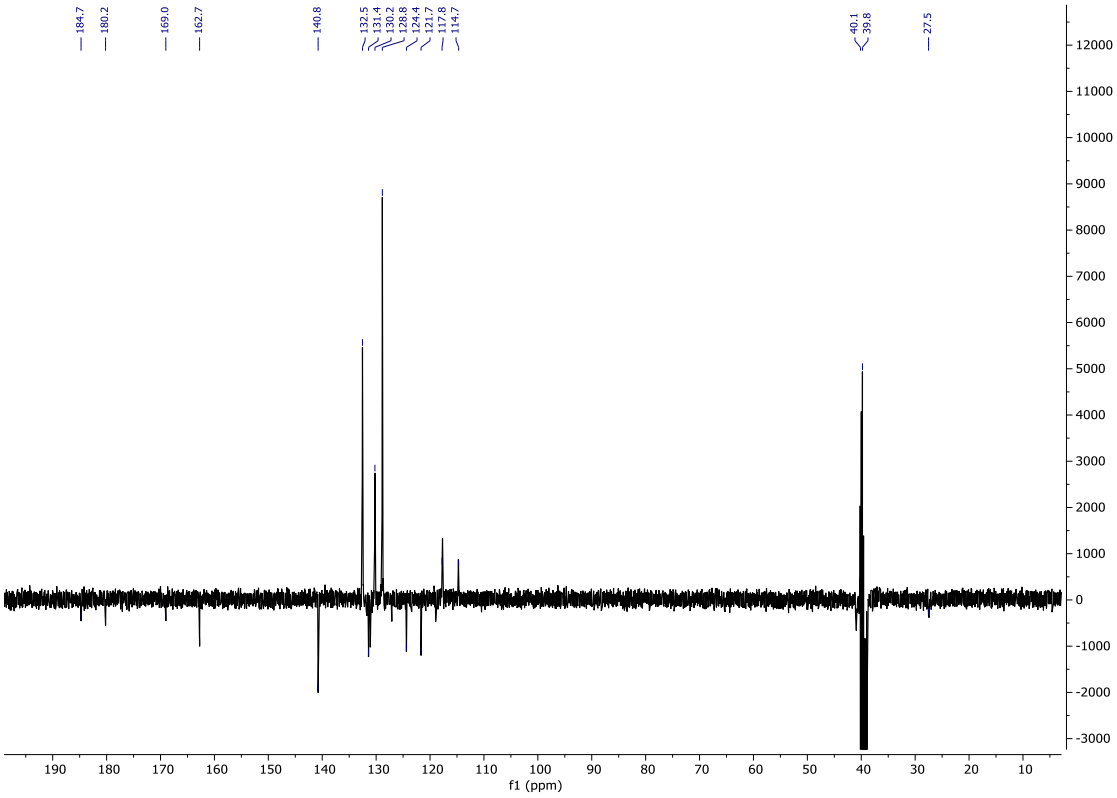


Figure 3.35. ^{13}C APT spectrum of compound **76** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{52}H_{38}CuF_{12}N_4O_4P_2]$ 1135.1467. Found 1135.1499.

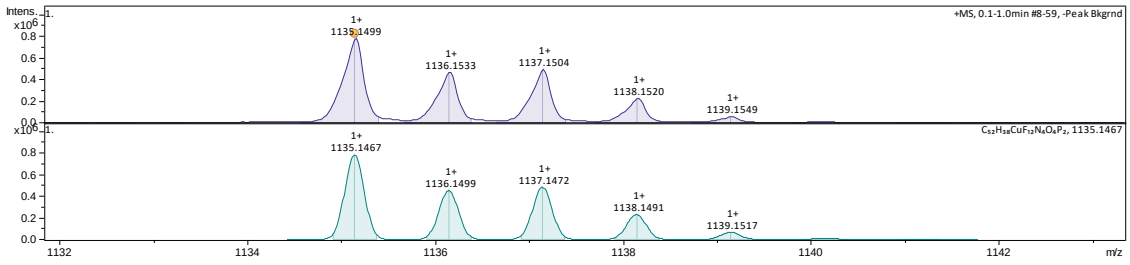


Figure 3.36. MS (ESI+ µ-TOF) compound **76**.

Synthesis of compound 77

To a solution of compound **71** (46 mg, 0.2 mmol) in acetonitrile (50 ml) was added $[Cu(NCMe)_4]PF_6$ (18.6 mg, 0.05 mmol) and the solution stirred for 2 hours. The solution was concentrated under reduced pressure to approximately 1 ml and pentane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 30%.

Scheme 3.8. Synthesis of compound **77**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.91 (s, 2H, *NH*-Ph-CF_3); 7.72-7.56 (m, 30H, H_{ortho}Ph-CF_3 + H_{meta}Ph-CF_3 + $H_{ortho}PPh_2$ + $H_{meta}PPh_2$ +$H_{para}PPh_2$ + *NH*-CH_2); 3.72 (m, 4H, PPh_2-CH_2-*CH_2*); 2.73(m, 4H, PPh_2-*CH_2*-CH_2).

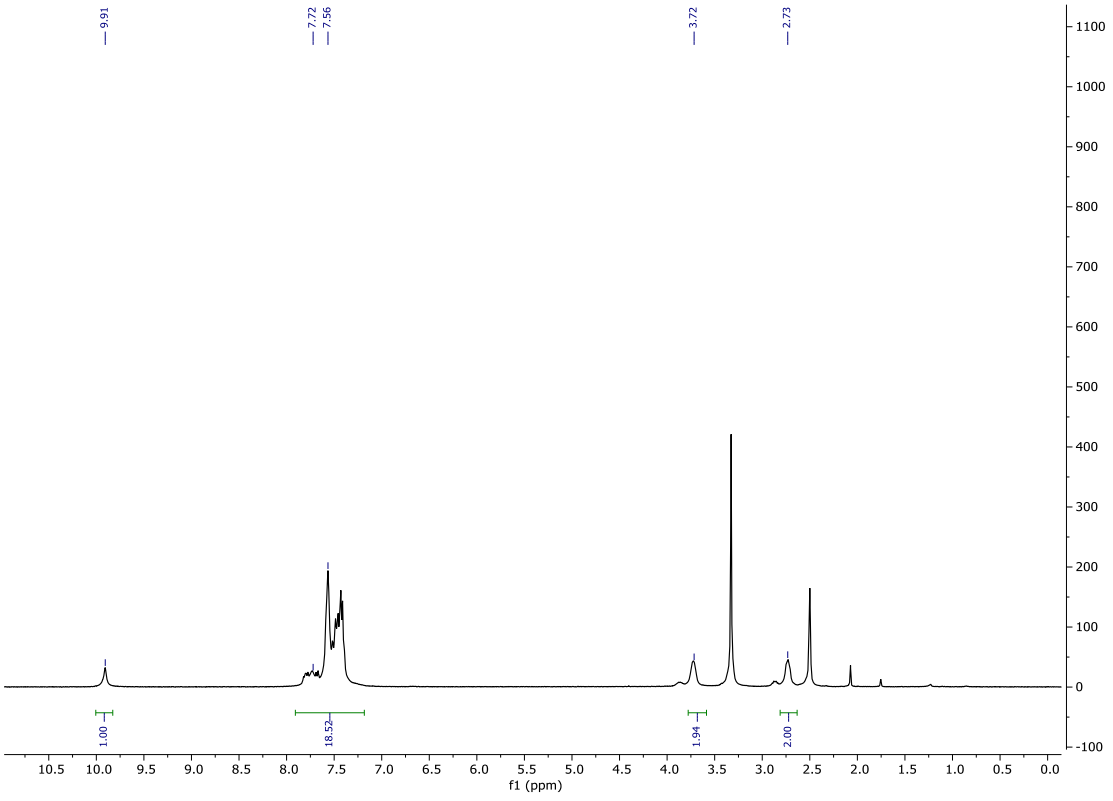


Figure 3.37. ^{1}H NMR spectrum of compound **77** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.3 (s, 12F, *CF_3*); -69.2, -71.1 (s, 6F, *PF_6*).

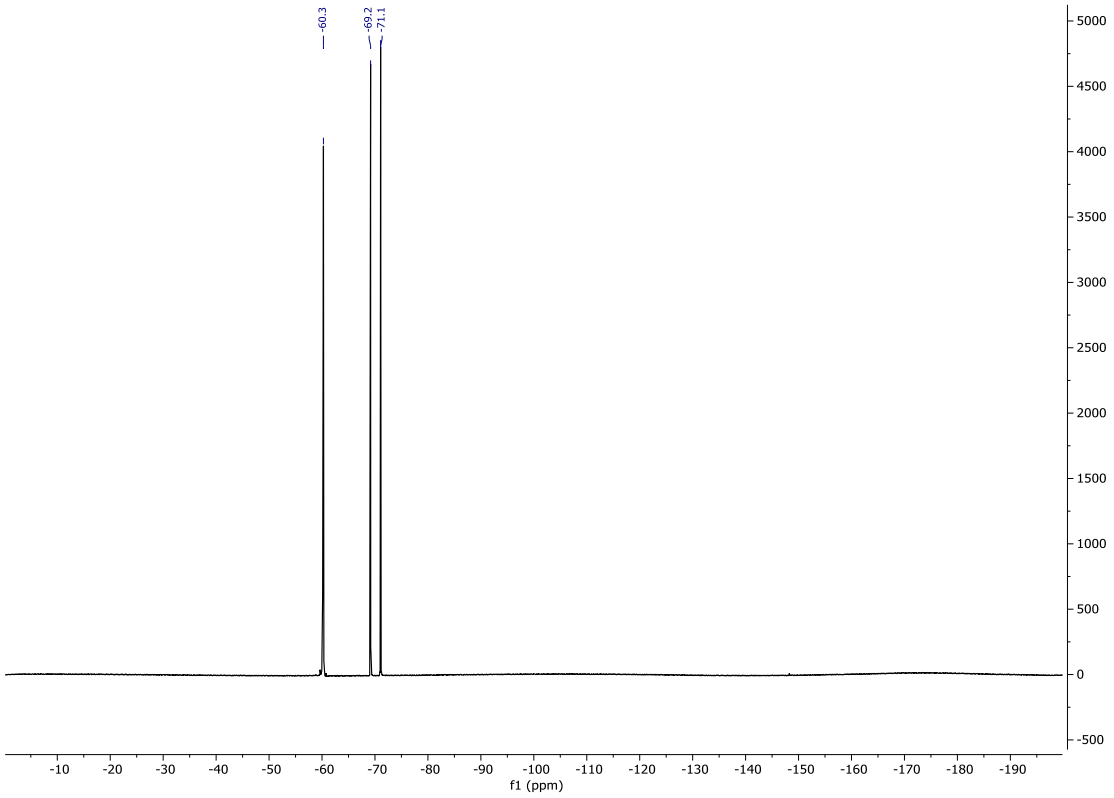


Figure 3.38. $^{19}F\{^{1}H\}$ NMR spectrum of compound **77** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (400MHz, DMSO): δ = -15.4 (s, 2P, *PPh_2*).

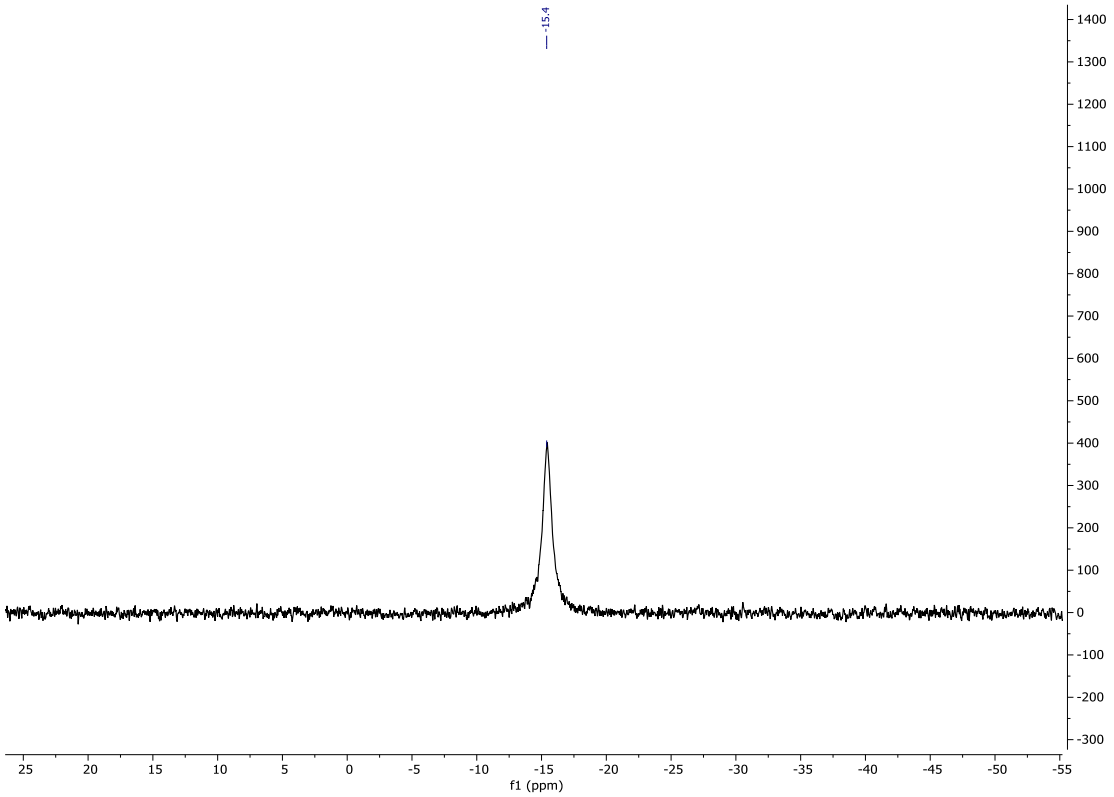


Figure 3.39. $^{31}P\{^{1}H\}$ NMR spectrum of compound **77** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.7 (s, 2C, *C*=*O*); 179.9 (s, 2C, *C*=*O*); 168.9 (s, 2C, *C*=*C*); 163.3 (s, 2C, *C*=*C*); 142.3 (s, 2C, C_{ipso}-*Ph*); 132.5 (s br, 8C, $C_{ortho}PPh_2$); 130.2 (s br, 2C, $C_{para}PPh_2$); 128.8 (s br, 8C, $C_{meta}PPh_2$); 126.5 (s, 4C, C_{para}Ph-CF_3); 123.0 (m, 4C, CF_3); 118.0 (s, 4C, C_{ortho}Ph-CF_3); 40.7(s, 2C, PPh_2-CH_2-CH_2); 27.8 (s, 2C, PPh_2-CH_2-CH_2).

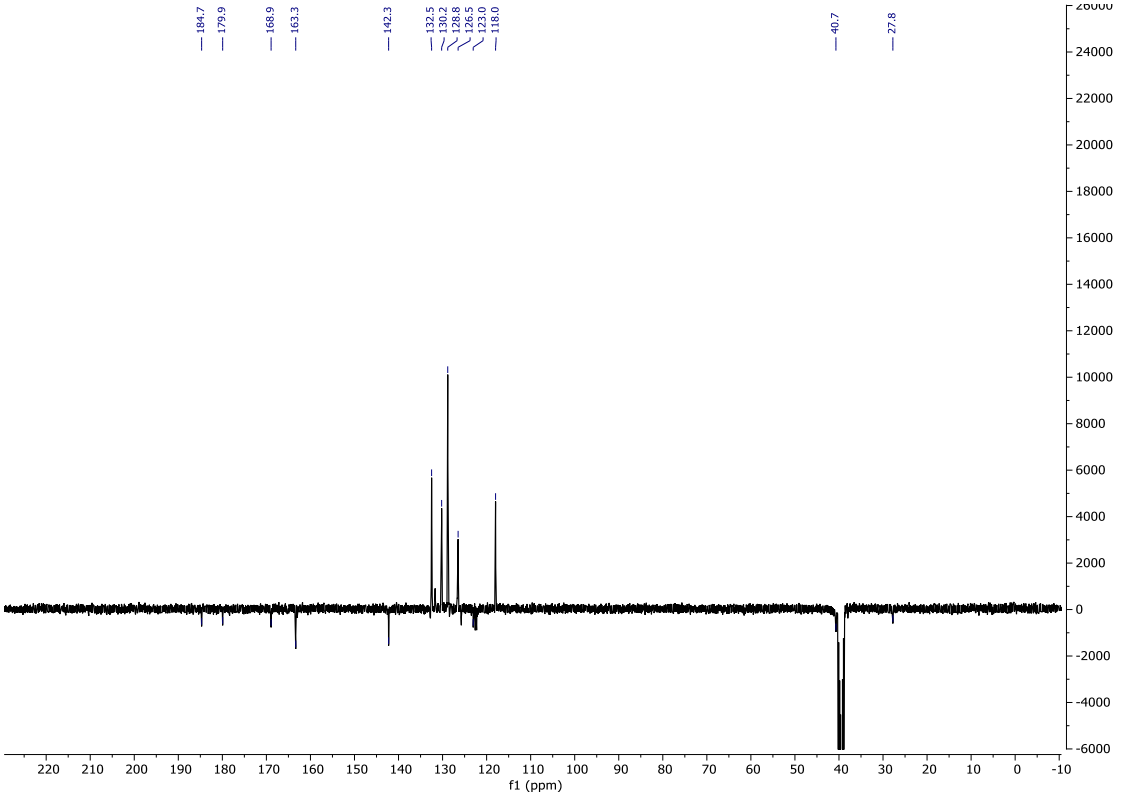


Figure 3.40. ^{13}C APT spectrum of compound **77** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{50}H_{40}CuF_6N_4O_4P_2]$ 999.1719. Found 999.1731.

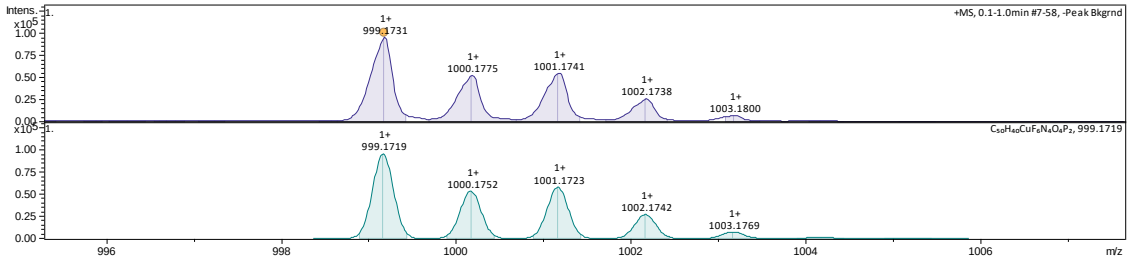
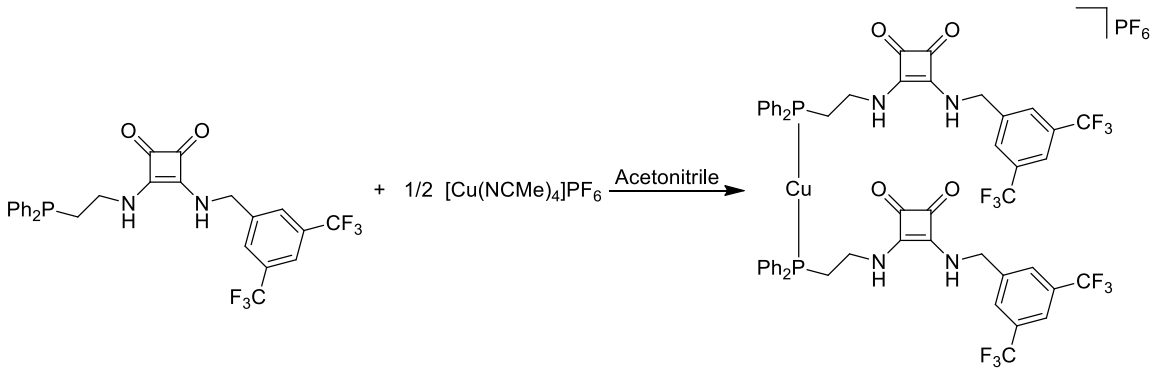


Figure 3.41. MS (ESI+ µ-TOF) compound **77**.

Synthesis of compound 78

To a solution of compound **72** (55 mg, 0.1 mmol) in acetonitrile (50 ml) was added $[Cu(NCMe)_4]PF_6$ (18.6 mg, 0.05 mmol) and the solution stirred for 2 hours. The solution was concentrated under reduced pressure to approximately 1 ml and pentane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 35%.



Scheme 3.9. Synthesis of compound **78**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.05 (m, 6H, H_{ortho}Ph-CF_3 + H_{para}Ph-CF_3); 7.50 (s, 8H, H_{ortho}PPh_2); 7.37 (s, 2H, H_{para}Ph-CF_3); 4.82 (s, 4H, NH-*CH_2*-Ph-CF_3); 3.64(s, 4H, PPh_2-CH_2-*CH_2*); 2.59(s, 4H, PPh_2-*CH_2*-CH_2).

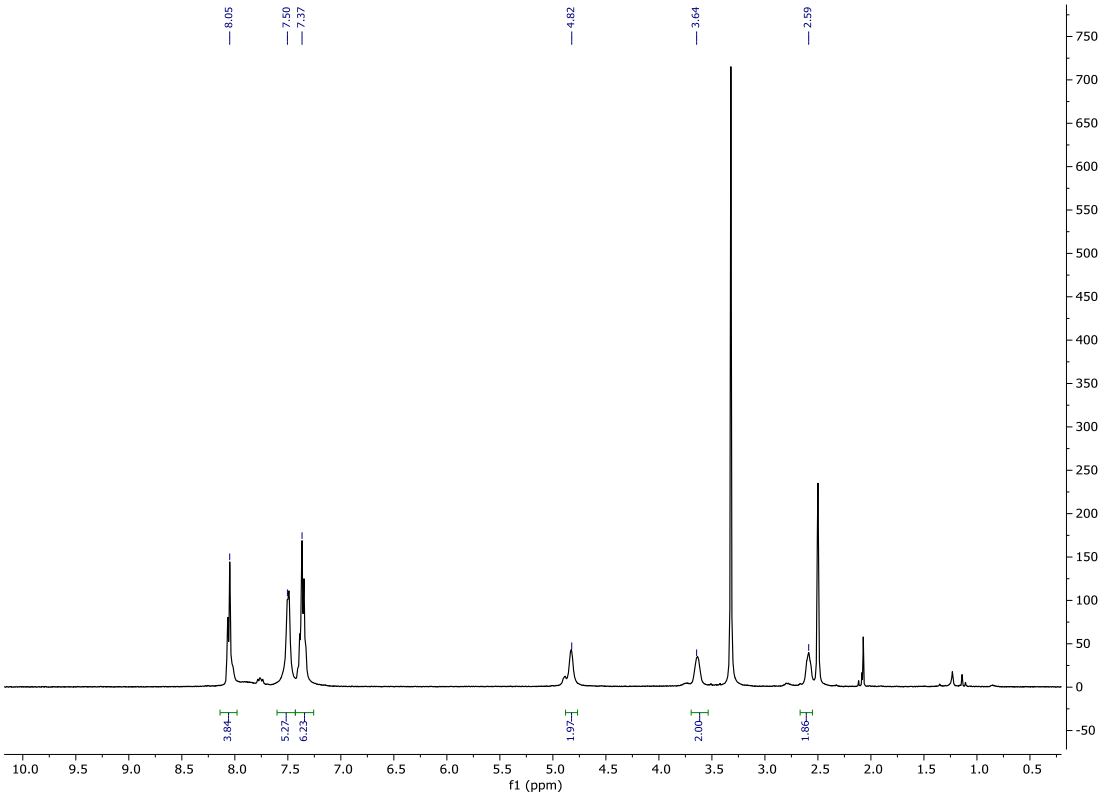


Figure 3.42. ^{1}H NMR spectrum of compound **78** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -61.9 (s, 12F, CF_3); -69.2, -71.1 (s, 6F, PF_6).

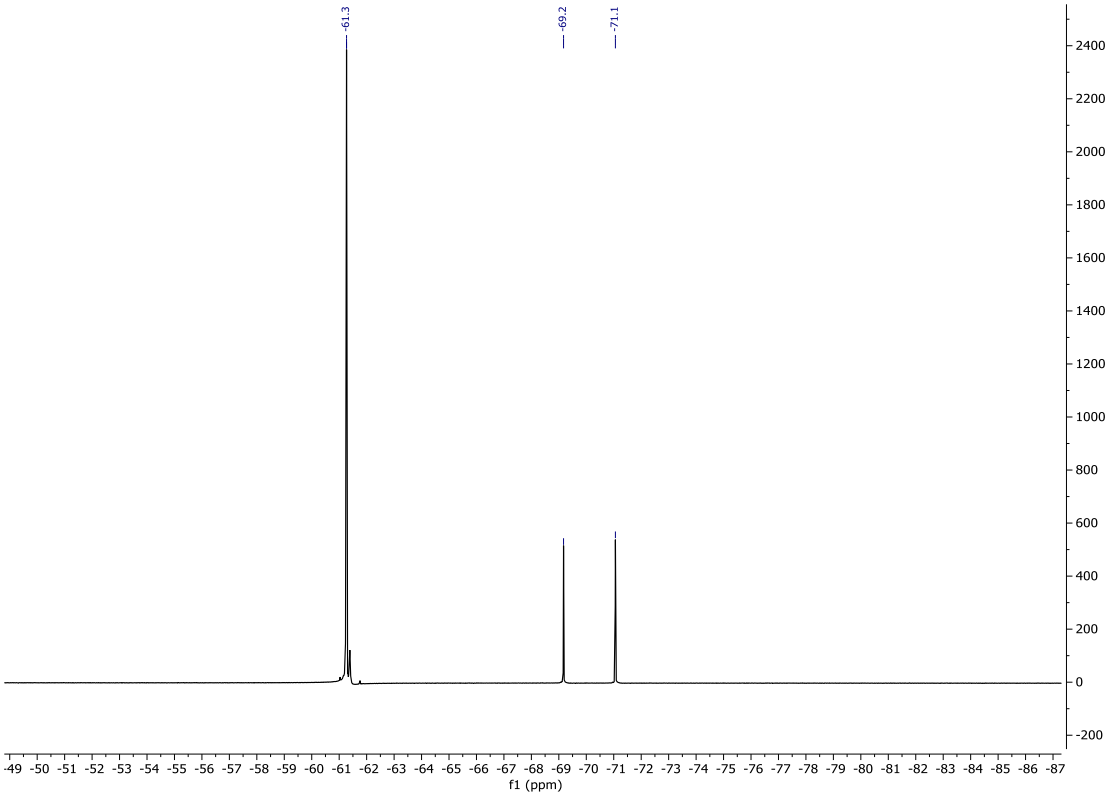


Figure 3.43. $^{19}F\{^{1}H\}$ NMR spectrum of compound **78** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = -14.8 (s, 2P, PPh_2).

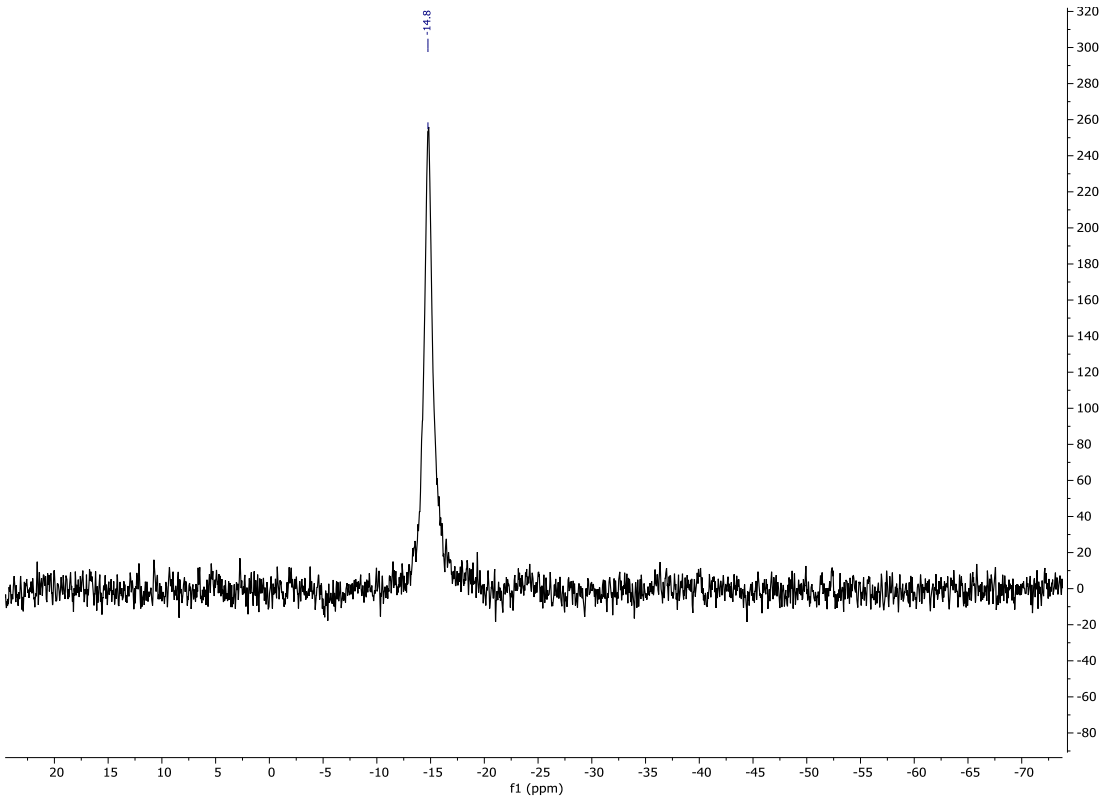


Figure 3.44. $^{31}P\{^{1}H\}$ NMR spectrum of compound **78** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 183.1(s, 2C, *C=O*); 142.3 (s, 2C, $C_{ipso}Ph$); 132.4 (s br, 8C, $C_{ortho}PPh_2$); 130.6 (m, 4C, $C_{ipso}C\text{-}CF_3$); 130.1 (s, 2C, $C_{para}PPh_2$); 128.7 (s br, 8C, $C_{meta}PPh_2$); 128.6 (s, 4C, $C_{ortho}Ph\text{-}CF_3$); 123.3 (q, 4C, CF_3, $^{1}J_{CF}$ = 273.0 Hz); 121.3 (s, 2C, $C_{para}Ph\text{-}CF_3$); 45.8 (s, 2C, NH-CH_2-Ph-CF_3); 40.3(s, 2C, $PPh_2\text{-}CH_2\text{-}CH_2$); 28.2 (m, 2C, $PPh_2\text{-}CH_2\text{-}CH_2$).

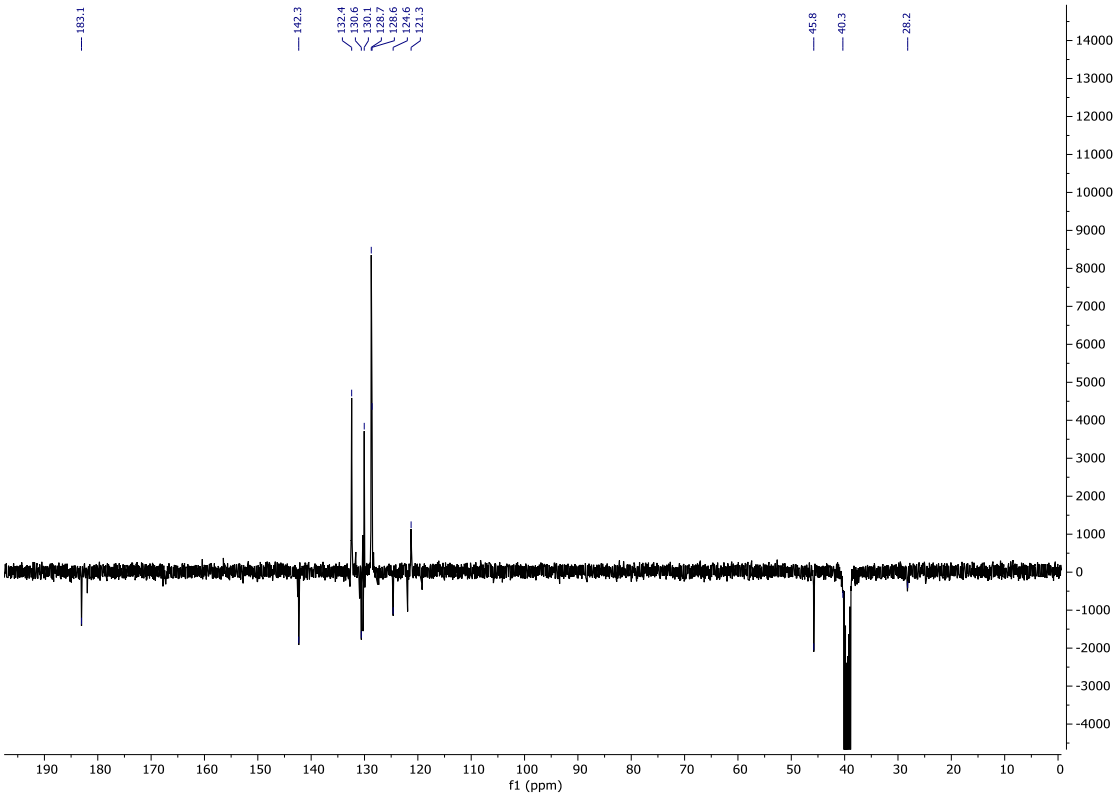


Figure 3.45. ^{13}C APT spectrum of compound **78** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{54}H_{42}CuF_{12}N_4O_4P_2]$ 1163.1780. Found 1163.1799.

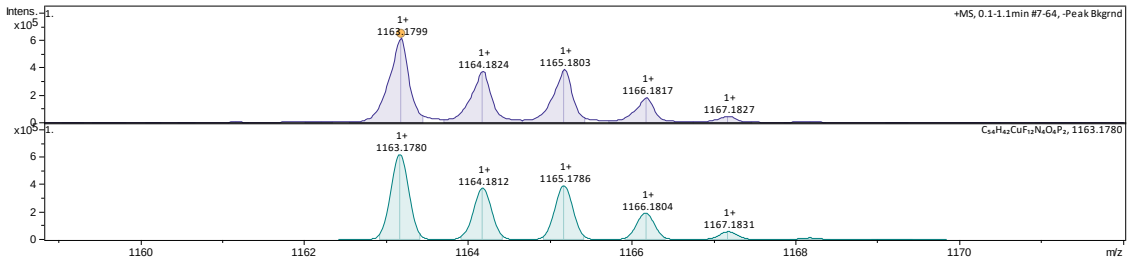
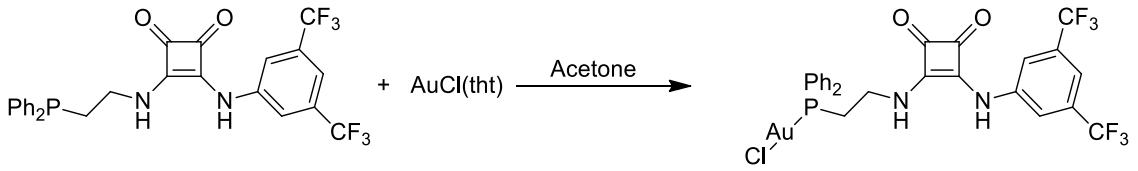


Figure 3.46. MS (ESI+ µ-TOF) compound **78**.

Synthesis of compound 79

To a solution of compound **70** (53 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred for 2 hours. The solution was concentrated under reduced pressure to approximately 1 ml and pentane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 27%.



Scheme 3.10. Synthesis of compound **79**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 10.14 (s, 1H, *NH*-Ph-CF_3); 7.98 (s, 2H, H_{ortho}Ph-CF_3); 7.81 (m, 5H, $H_{ortho}PPh_2$ + *NH*-CH_2); 7.68 (s, 1H, H_{para}Ph-CF_3); 7.56 (s, 6H, H_{meta}+$H_{para}PPh_2$); 3.18 (m, 2H, PPh_2-CH_2-*CH_2*); 3.94 (m, 2H, PPh_2-*CH_2*-CH_2).

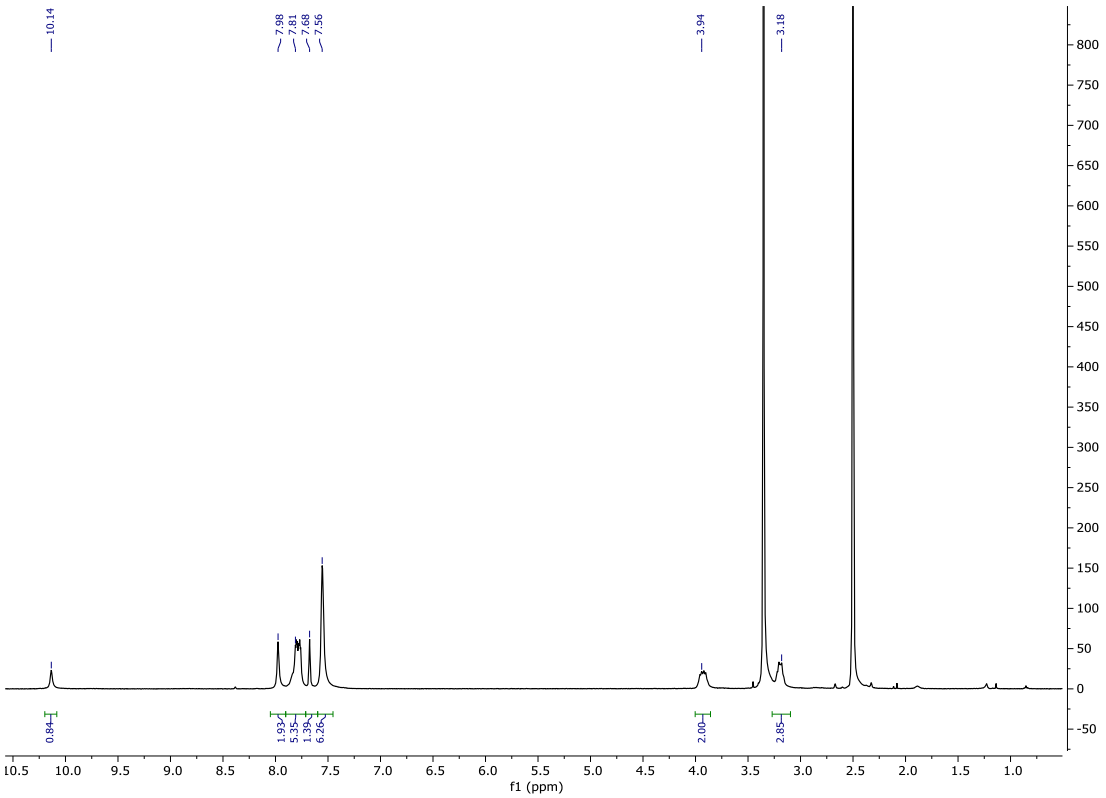


Figure 3.47. ^{1}H NMR spectrum of compound **79** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -63.6 (s, 3F, *CF_3*).

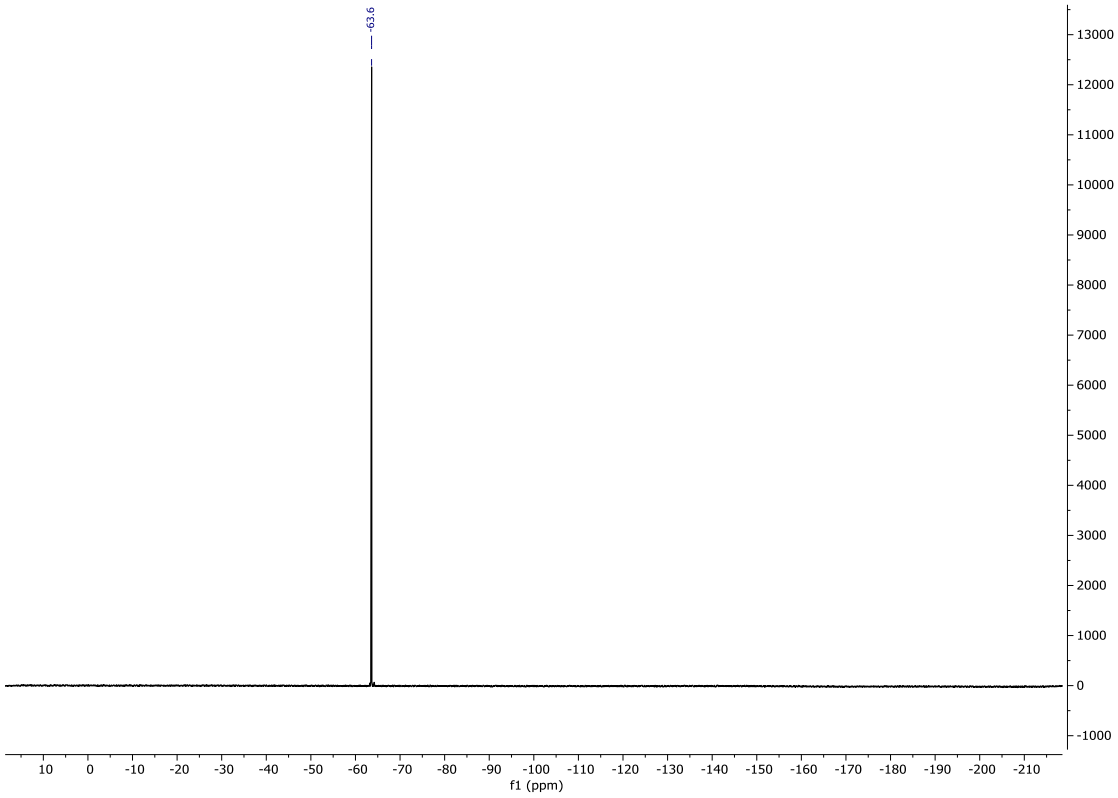


Figure 3.48. $^{19}F\{^{1}H\}$ NMR spectrum of compound **79** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 24.2 (s, 1P, *PPh_2*).

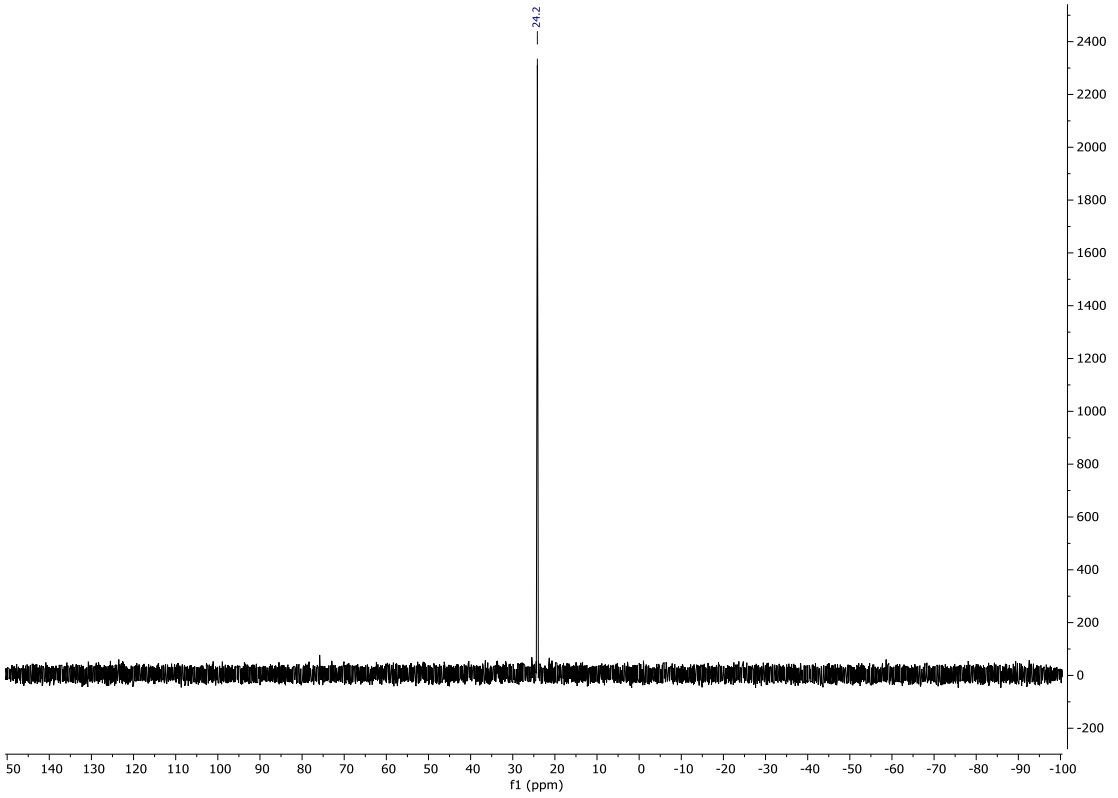


Figure 3.49. $^{31}P\{^{1}H\}$ NMR spectrum of compound **79** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.5 (s, 1C, *C*=*O*); 180.7 (s, 1C, *C*=*O*); 169.5 (s, 1C, Ph-C=*C*-*CH*$_2$); 162.7 (s, 1C, *Ph*-*C*=C-CH$_2$); 140.9 (s, 1C, *C$_{ipso}$*-*Ph*); 133.2 (d, 4C, *C$_{ortho}$*PPh$_2$, $^2J_{CP}$ = 13.5 Hz); 132.1 (d, 2C, *C$_{para}$*PPh$_2$, $^2J_{CP}$ = 2.2 Hz); 131.3 (q , 1C, *C$_{ipso}$*-*Ph*-*CF*$_3$); 129.4 (d, 4C, *C$_{meta}$*PPh$_2$, $^2J_{CP}$ = 11.6 Hz); 129.0 (d, 2C, *C$_{ipso}$*PPh$_2$, $^2J_{CP}$ = 60.8 Hz); 123.2 (q, 2C, *CF*$_3$, $^1J_{CF}$ = 272.8 Hz); 118.3 (s, 2C, *C$_{ortho}$*Ph-CF$_3$); 114.9 (s, 1C, *C$_{para}$*Ph-CF$_3$); 39.8 (m, 1C, PPh$_2$-CH$_2$-*CH*$_2$); 28.4 (d, 1C, PPh$_2$-*CH*$_2$-CH$_2$, $^2J_{CP}$ = 37.7Hz).

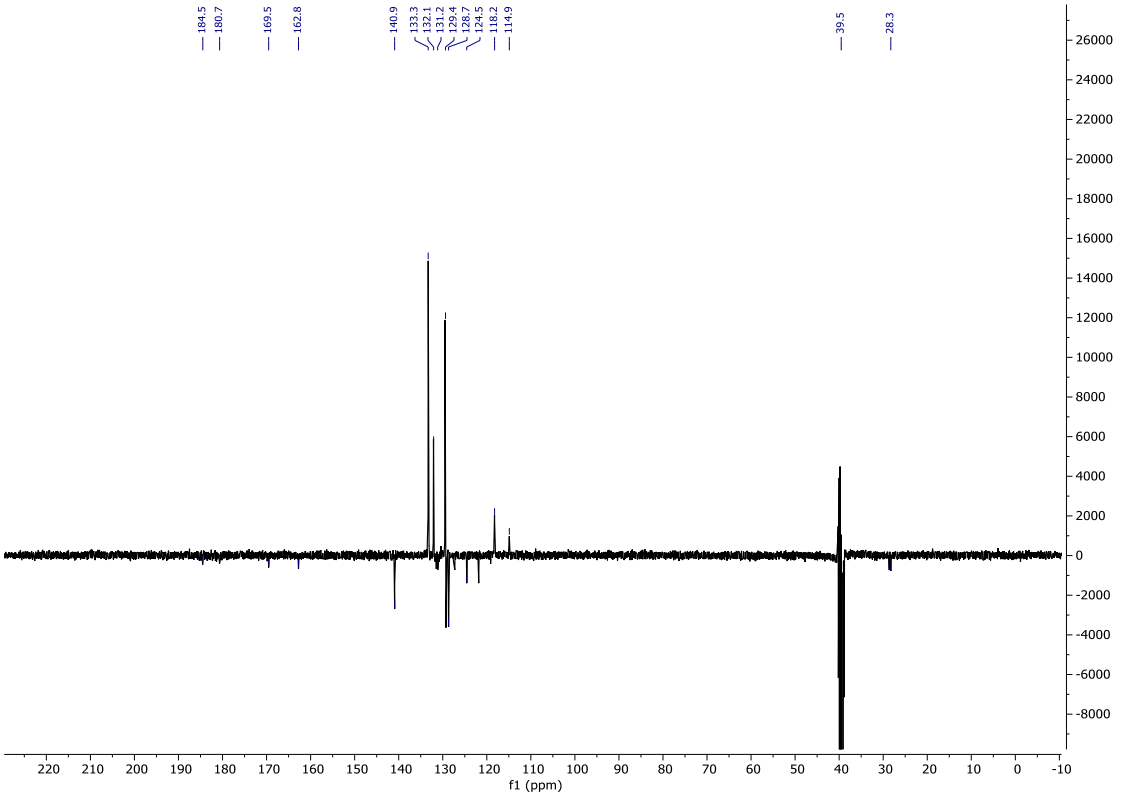


Figure 3.50. ^{13}C APT spectrum of compound **79** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= [M]$^+$ Calcd for [C$_{26}$H$_{19}$AuClF$_6$N$_2$O$_2$P] 768.0137. Found 791.0318 [C$_{26}$H$_{19}$AuClF$_6$N$_2$O$_2$P + Na]$^+$.

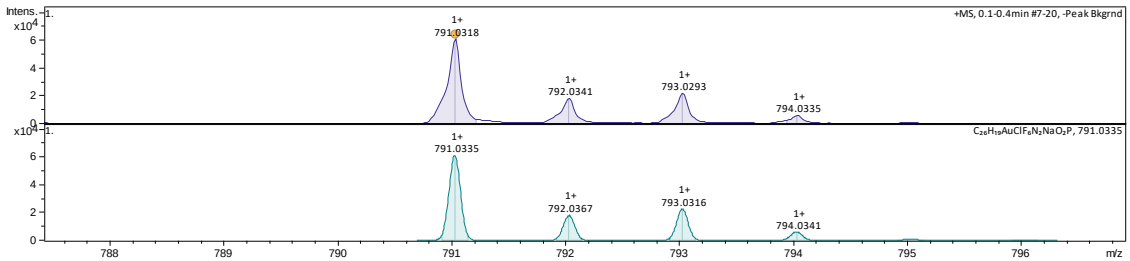
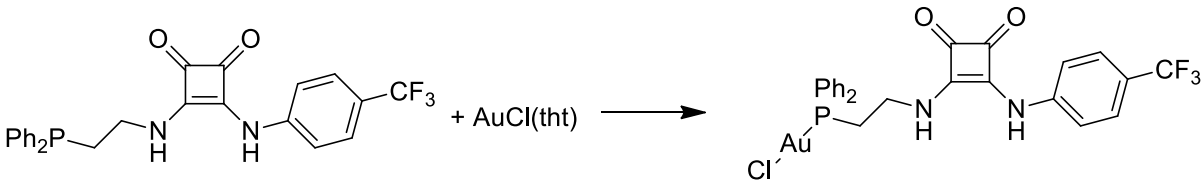


Figure 3.51. MS (ESI+ µ-TOF) compound **79**.

Synthesis of compound 80

To a solution of compound **71** (46 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred for 2 hours. The solution was concentrated under reduced pressure to approximately 1 ml and pentane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 32%.



Scheme 3.11. Synthesis of compound **80**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.87 (s, 1H, *NH*-Ph-CF_3); 7.89 (s, 1H, *NH*-CH_2); 7.78 (m, 4H, H_{ortho}Ph-CF_3); 7.67-7.54 (m, 10H, H_{meta}+$H_{para}$$PPh_2$+ H_{ortho}Ph-CF_3+ H_{meta}Ph-CF_3); 3.96 (m, 2H, PPh_2-CH_2-*CH_2*), 3.18 (m, 2H, PPh_2-*CH_2*-CH_2).

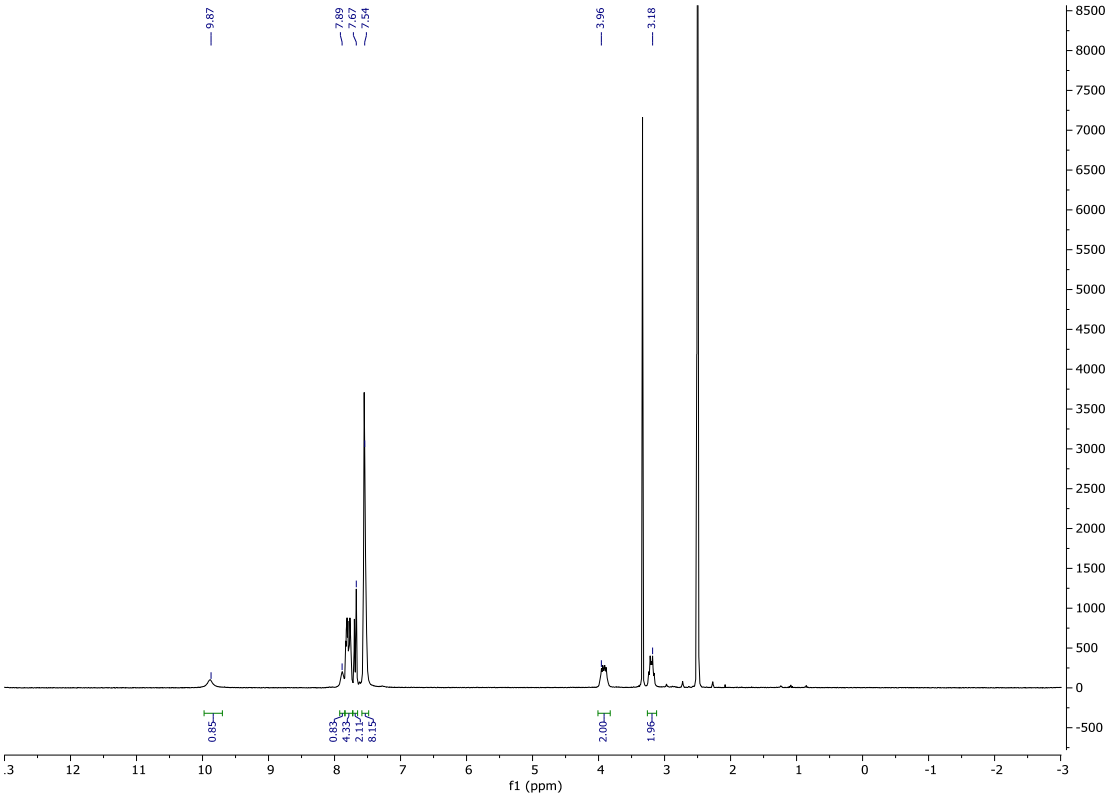


Figure 3.52. ^{1}H NMR spectrum of compound **80** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -57.3 (s, 3F, CF_3).

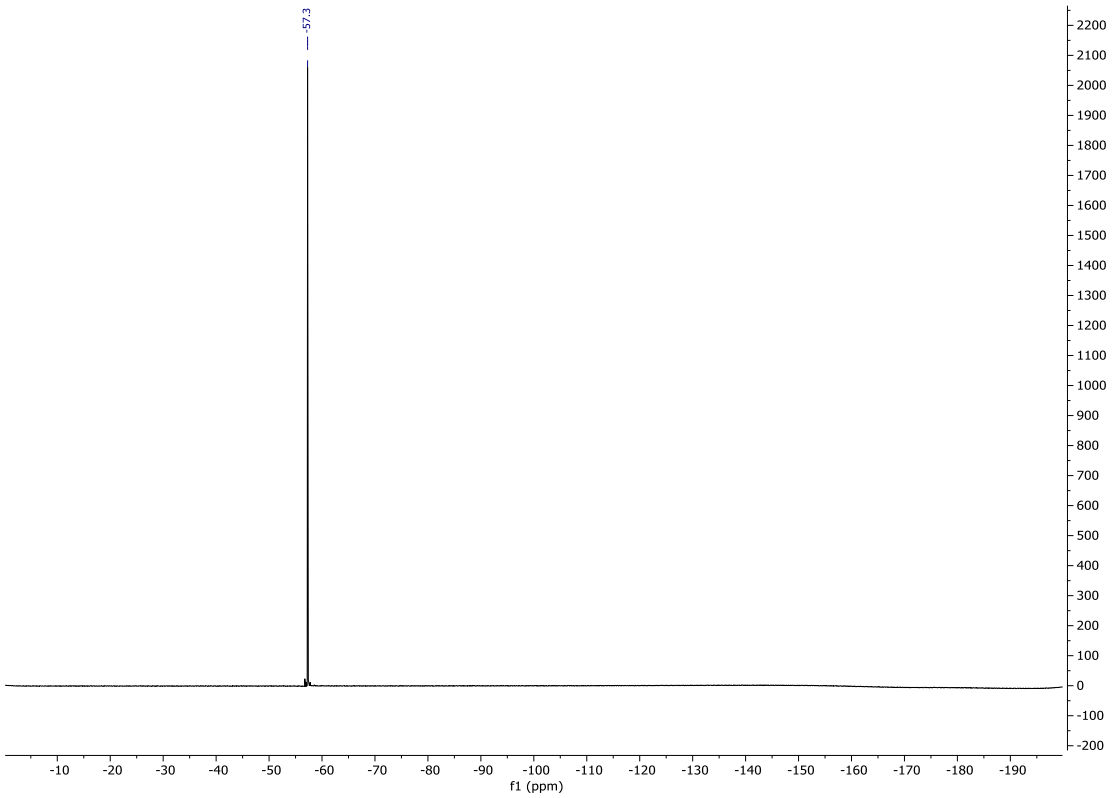


Figure 3.53. $^{19}F\{^{1}H\}$ NMR spectrum of compound **80** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 27.5 (s, 1P, PPh_2).

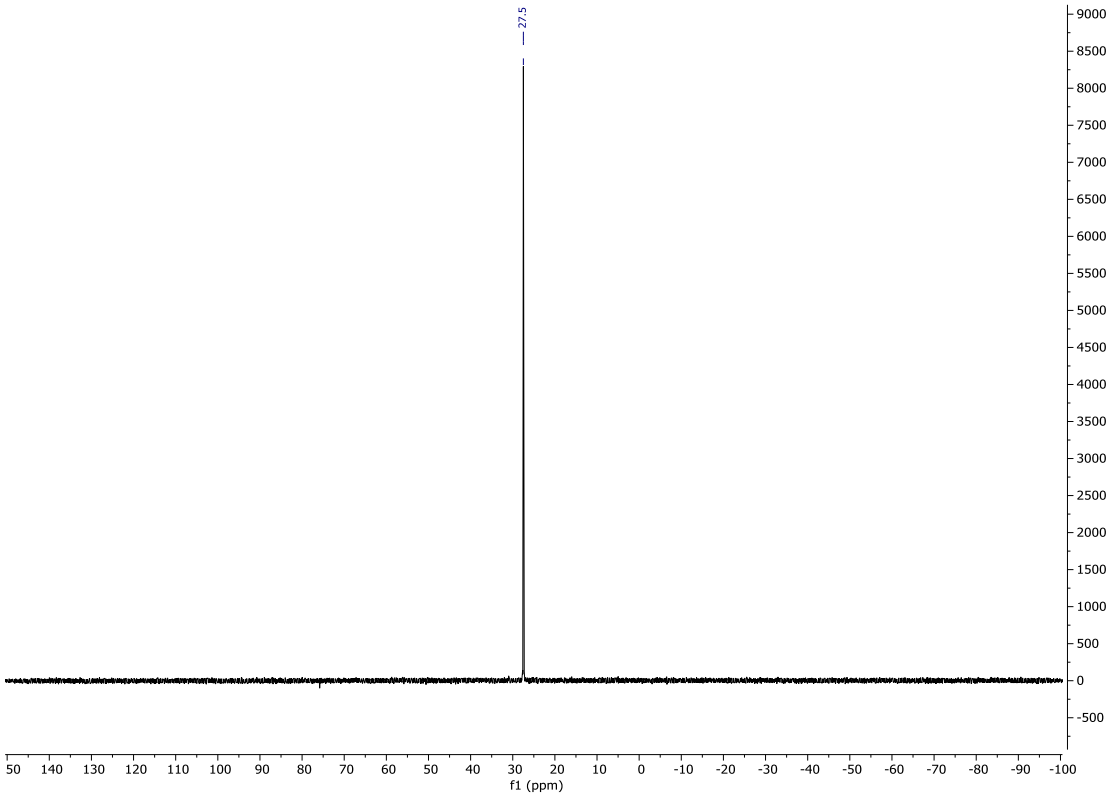


Figure 3.54. $^{31}P\{^{1}H\}$ NMR spectrum of compound **80** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ =184.4 (s, 1C, *C=O*); 180.4 (s, 1C, *C=O*); 169.3 (s, 1C, *C=C*); 163.3 (s, 1C, *C=C*); 142.4 (s, 1C, C_{ipso}-*Ph*); 133.2 (d, 4C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 13.5 Hz); 132.0 (d, 2C, $C_{para}PPh_2$, $^{2}J_{CP}$ = 2.7 Hz); 131.3 (d, 1C, $C_{ipso}PPh_2$, $^{1}J_{CP}$ = 34.3 Hz); 129.4 (d, 4C, $C_{meta}PPh_2$, $^{2}J_{CP}$ = 11.7 Hz); 128.7 (s, 2C, C_{ipso}-*Ph*-CF_3); 126.6 (s, 2C, C_{ortho}Ph-CF_3); 122.5 (m, 1C, CF_3); 118.1 (s, 2C, C_{meta}Ph-CF_3); 39.8 (m, 1C, PPh_2-CH_2-CH_2); 28.7 (d, 1C, PPh_2-CH_2-CH_2, $^{2}J_{CP}$ = 32.2 Hz).

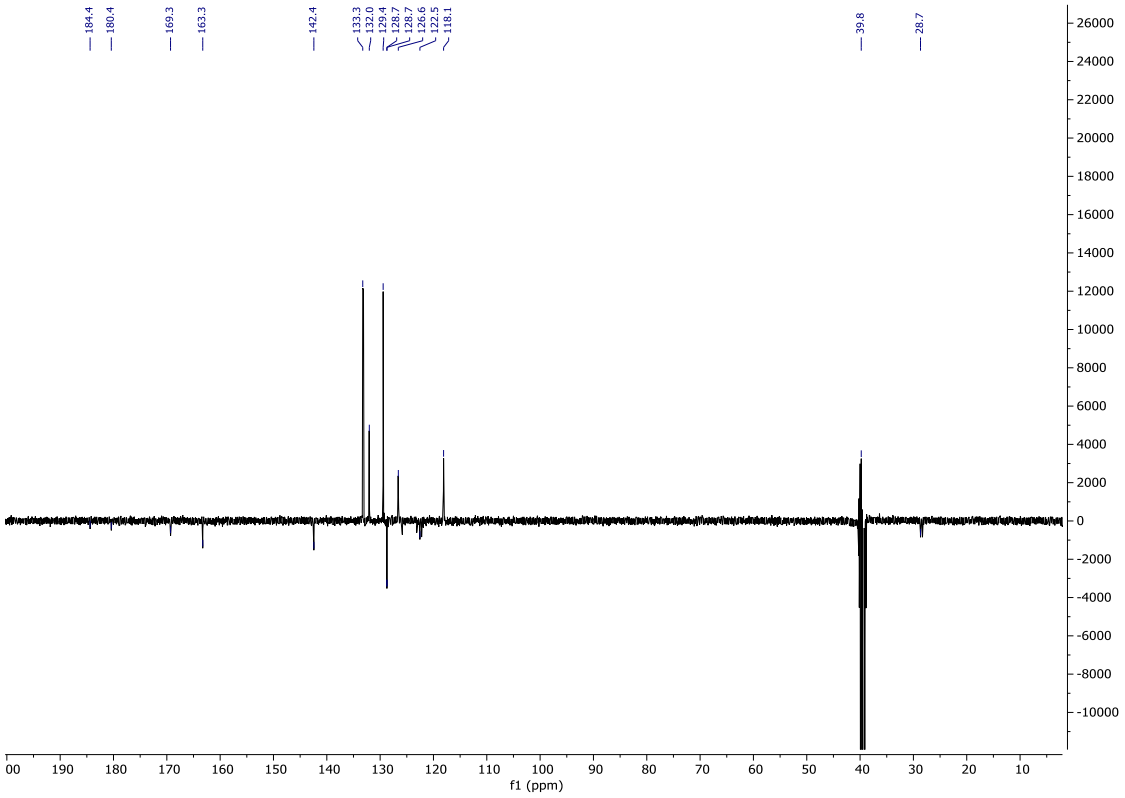


Figure 3.55. ^{13}C APT spectrum of compound **80** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{25}H_{20}AuClF_3N_2O_2P]$ 700.0584. Found 723.0442 $[C_{25}H_{20}AuClF_3N_2O_2P + Na]^+$.

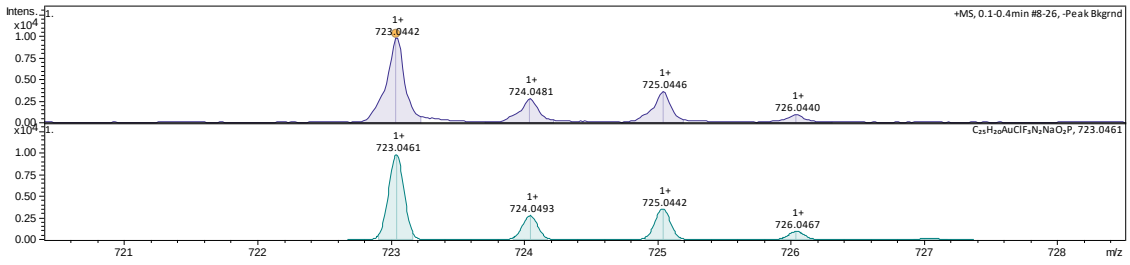
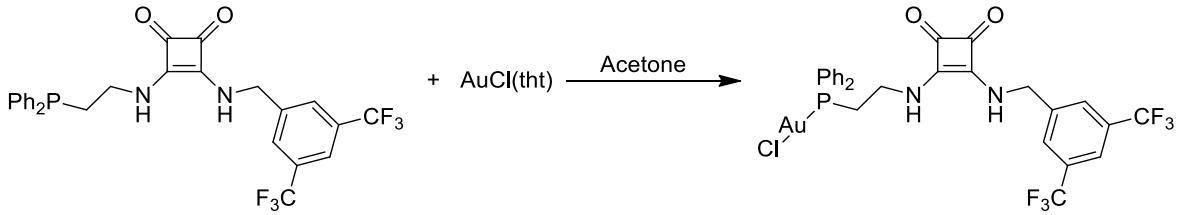


Figure 3.56. MS (ESI+ µ-TOF) compound **80**.

Synthesis of compound 81

To a solution of compound **72** (55 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred for 2 hours. The solution was concentrated under reduced pressure to approximately 1 ml and pentane (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 38%.



Scheme 3.12 Synthesis of compound **81**.

^{1}H NMR (ppm) (400 MHz, CD_3CN): δ = 7.95 (m, 3H, *Ph-CF_3*); 7.73 (m, 4H, *ortho PPh_2*); 7.49 (m, 6H, *meta*, *para PPh_2*); 6.69 (s br, 1H, *NH*-CH_2-Ph-CF_3); 6.53 (s br, 1H, *NH*-CH_2-CH_2); 4.83 (d, 2H, NH-*CH_2*-PH-CF_3, $^{3}J_{HH}$= 6.3 Hz); 3.90 (m, 2H, NH-*CH_2*-CH_2); 3.01 (m, 2H, PPh_2-*CH_2*-CH_2).

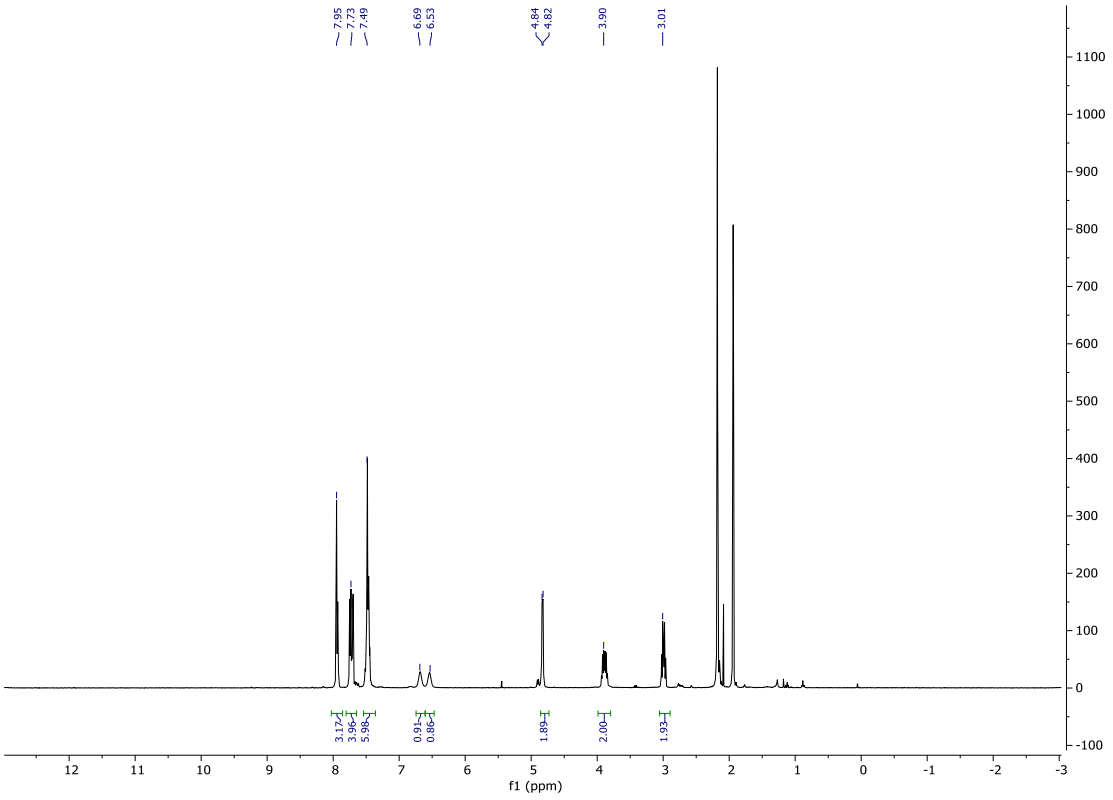


Figure 3.57. ^{1}H NMR spectrum of compound **81** in CD_3CN solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -63.2 (s, 1P, *CF_3*).

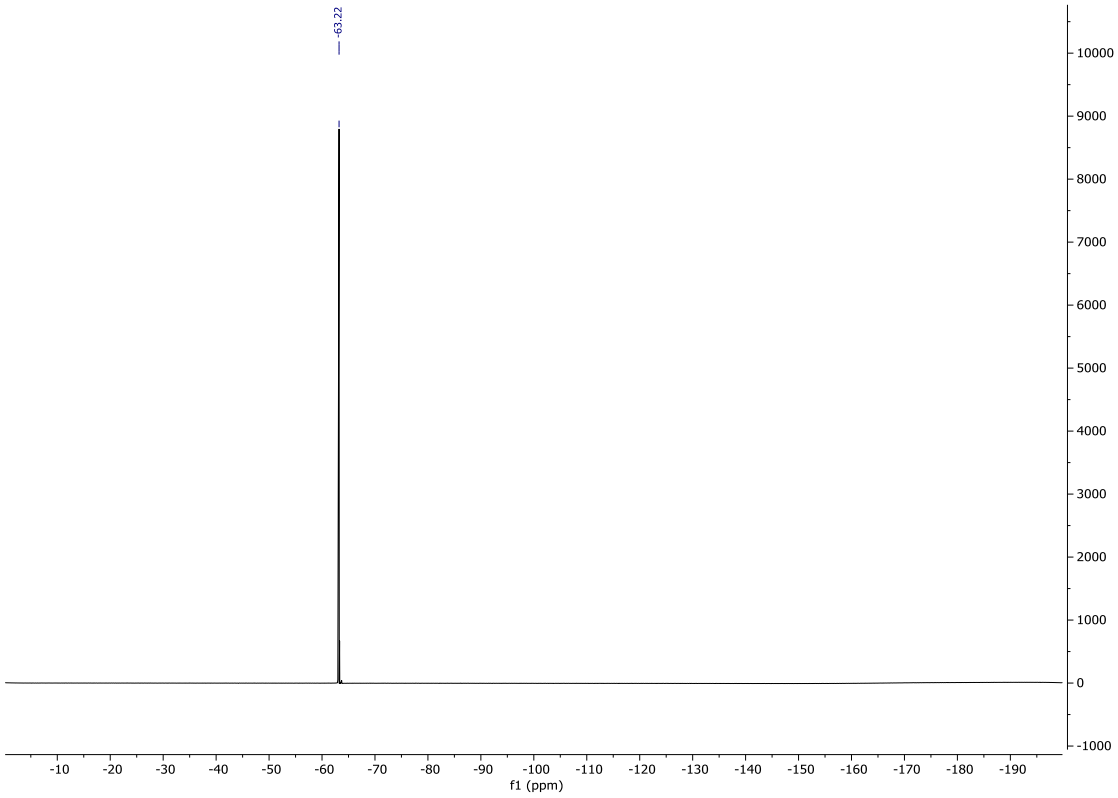


Figure 3.58. $^{19}F\{^{1}H\}$ NMR spectrum of compound **81** in CD_3CN solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 24.6 (s, 1P, *PPh_2*).

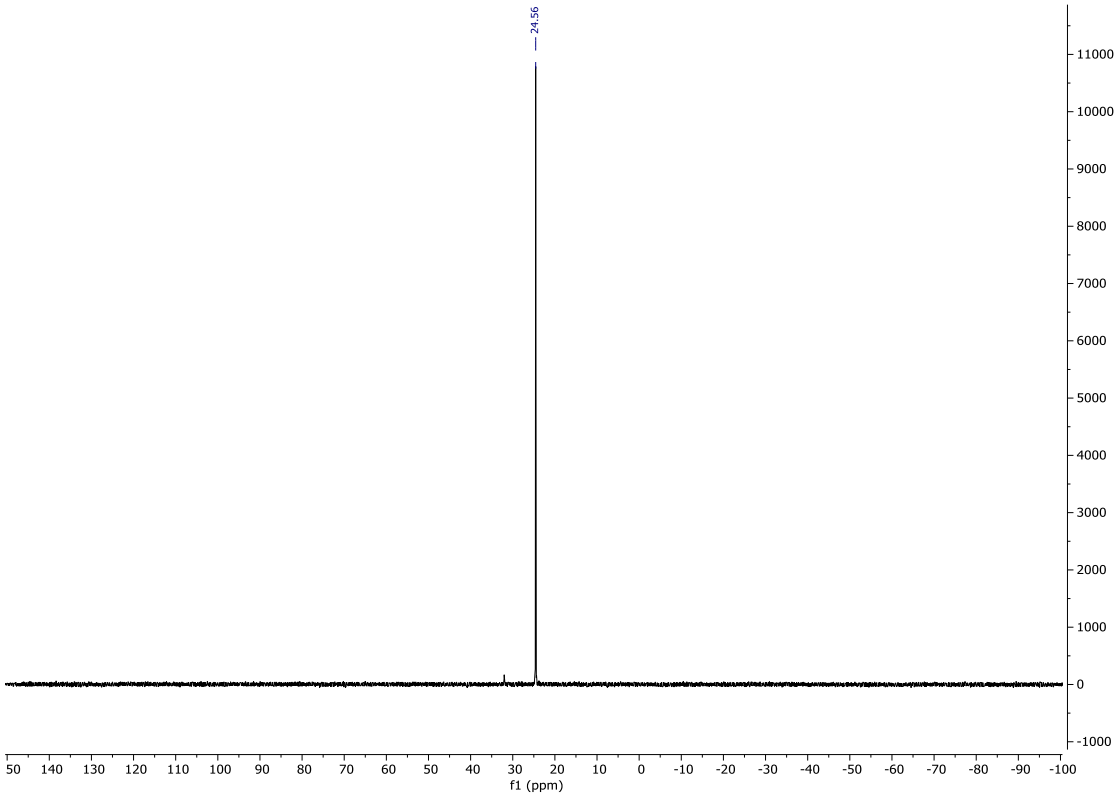


Figure 3.59. $^{31}P\{^{1}H\}$ NMR spectrum of compound **81** in CD_3CN solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.2 (s, 1C, *C*=*O*); 168.7 (s, 1C, *C*=*C*); 142.9 (s, 1C, C_{ipso}-*Ph*); 134.3 (d, 4C, $C_{ortho}PPh_2$, $^2J_{CP}$= 13.5 Hz); 133.0 (d, 2C, $C_{para}PPh_2$, $^4J_{CP}$= 2.6 Hz); 132.2 (d, $C_{ipso}PPh_2$); 130.3 (d, 4C, $C_{meta}PPh_2$, $^3J_{CP}$= 11.7 H); 129.9 (m, 2C, CF_3); 129.5 (s, 2C, $C_{ortho}Ph$-CF_3); 122.5 (s, 1C, $C_{para}Ph$-CF_3); 47.4 (s, 1C, NH-CH_2-Ph-CF_3); 43.4 (s, 1C, PPh_2-CH_2-CH_2); 30.7 (s, 1C, PPh_2-CH_2-CH_2).

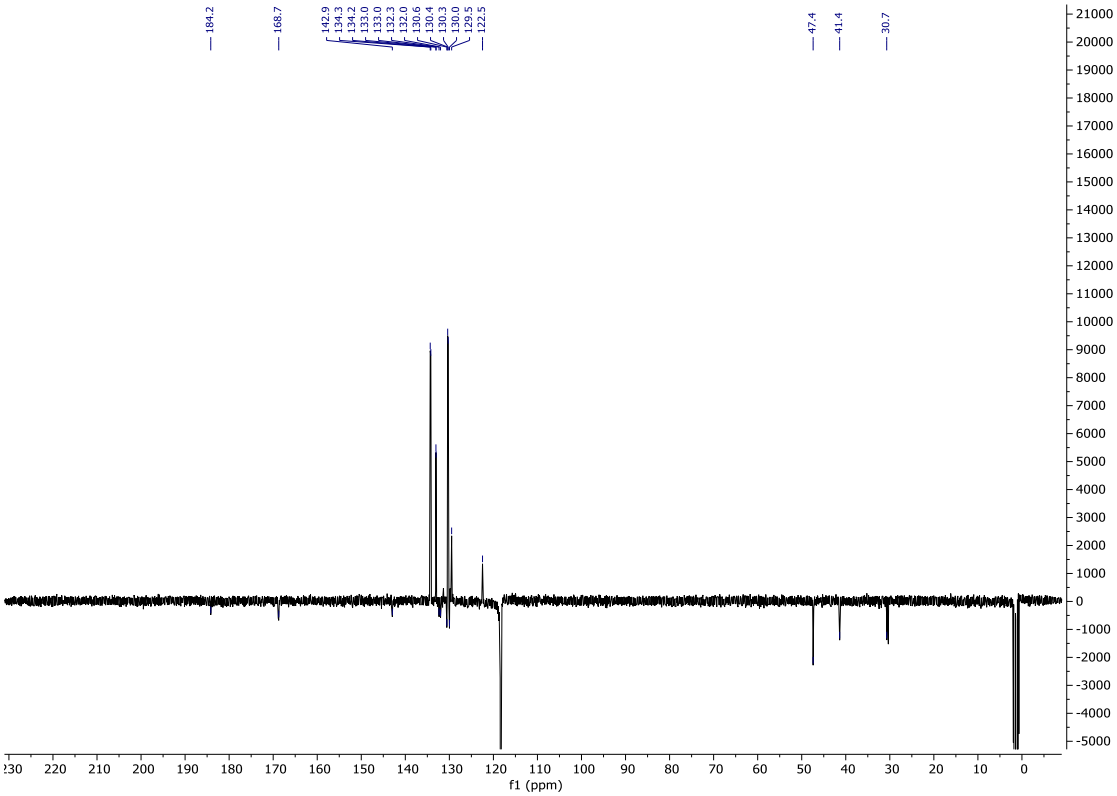


Figure 3.60. ^{13}C APT spectrum of compound **81** in CD_3CN solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{27}H_{21}AuClF_6N_2O_2P]$ 782.0593. Found 805.0477 $[C_{27}H_{21}AuClF_6N_2O_2P + Na]^+$.

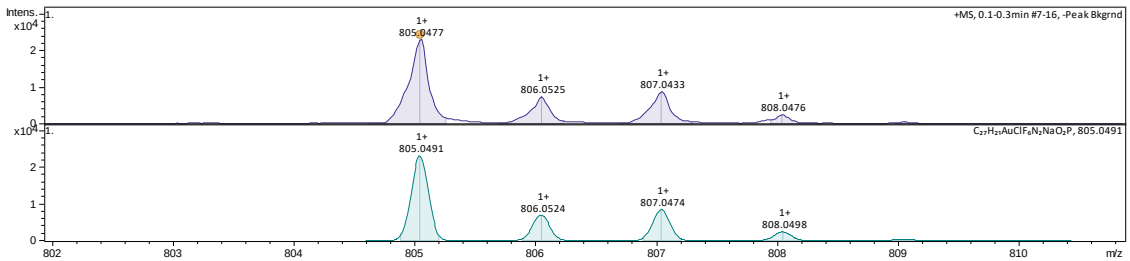


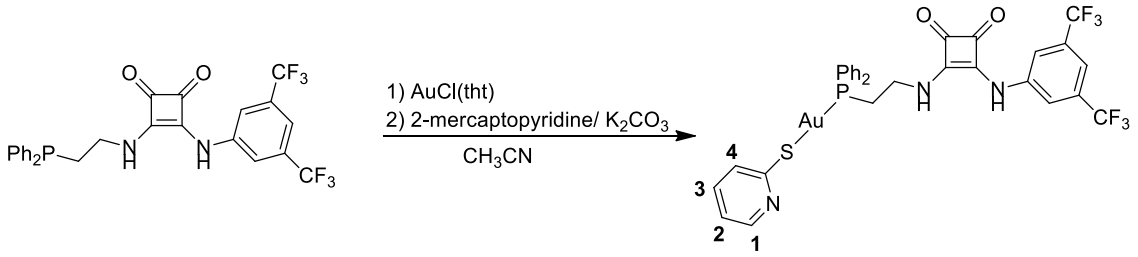
Figure 3.61. MS (ESI+ µ-TOF) compound **81**.

Synthesis of compound 82

To a solution of compound **70** (53 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred. 2 hours later, 2-mercaptopyridine

was added (11 mg, 0.1 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 40%.



Scheme 3.13. Synthesis of compound **82**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.22 (d, 1H, *1*, $^1J_{HH}$ = 4.2 Hz); 7.91 (m, 4H, $H_{ortho}PPh_2$); 7.56 (m, 8H, H_{meta}+$H_{para}PPh_2$+ H_{ortho}Ph-CF_3); 7.33 (m, 3H, *3*+*4*+ H_{para}Ph-CF_3); 6.89 (t, 1H, *2*, $^1J_{HH}$ = 6.4 Hz); 3.71 (m, 2H, PPh_2-CH_2-*CH_2*); 3.17 (m, 2H, PPh_2-*CH_2*-CH_2).

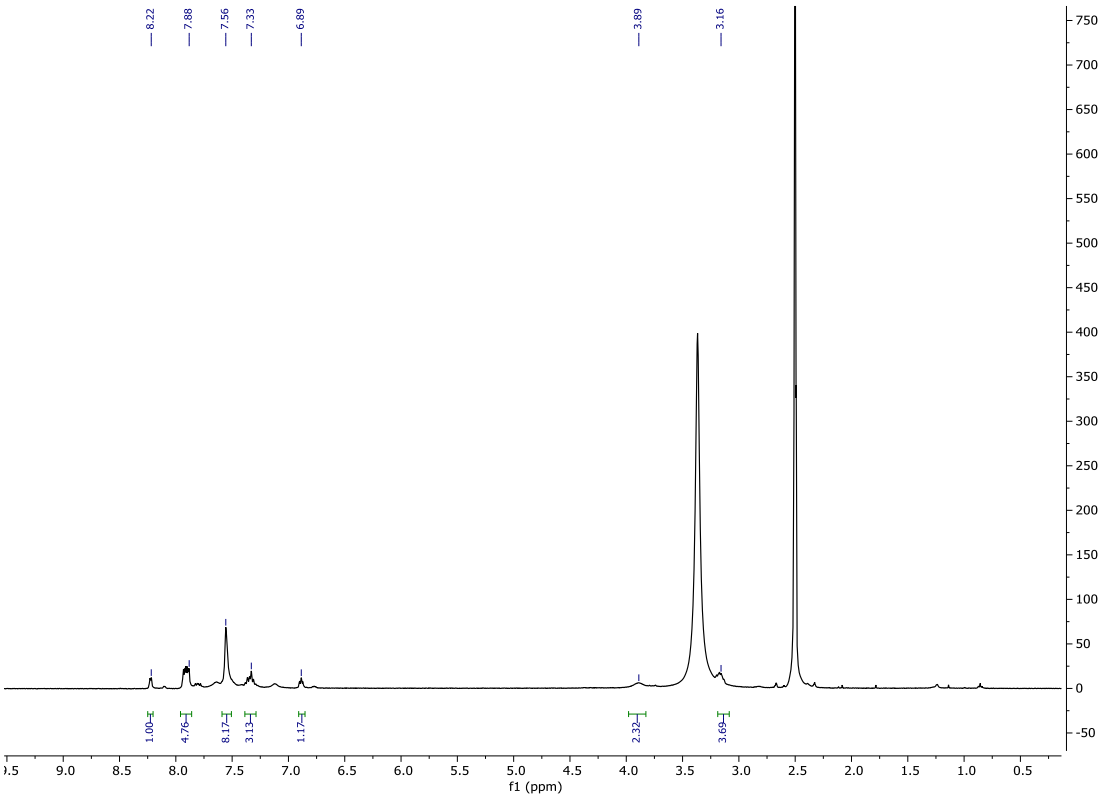


Figure 3.62. ^{1}H NMR spectrum of compound **82** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -61.5 (s, 1F, CF_3).

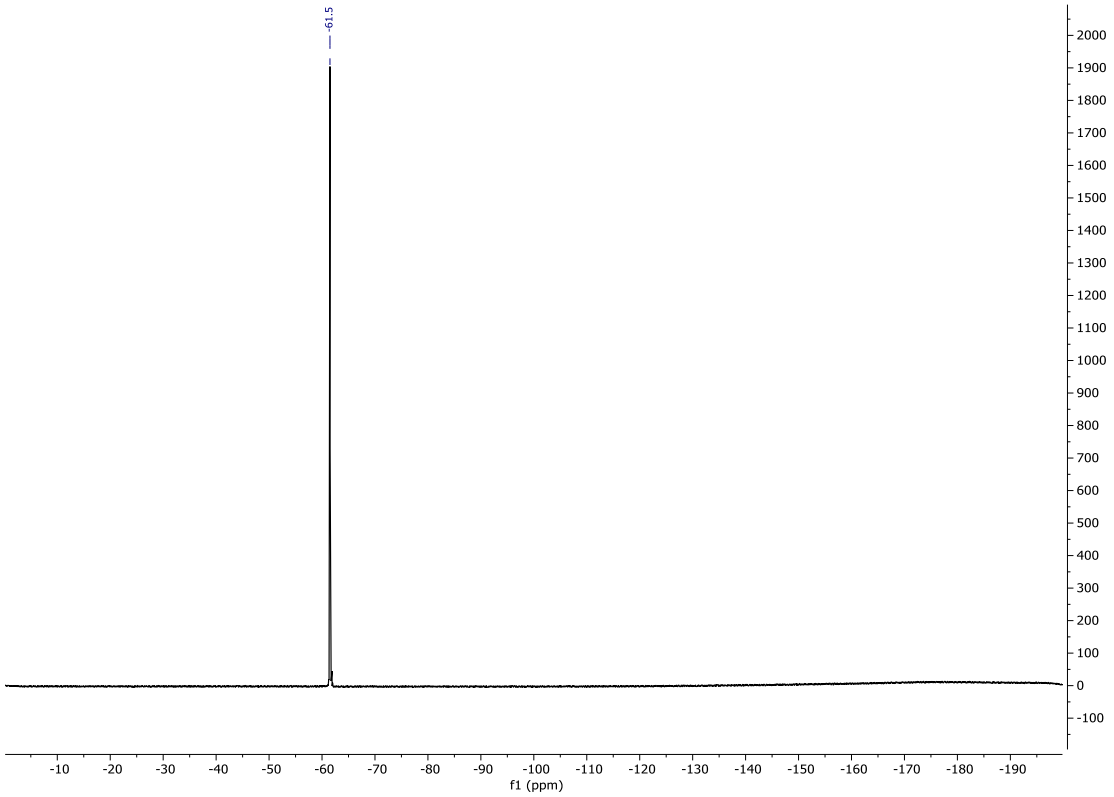


Figure 3.63. $^{19}F\{^{1}H\}$ NMR spectrum of compound **82** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (400 MHz, DMSO): δ = 29.3 (s, 1P, PPh_2).

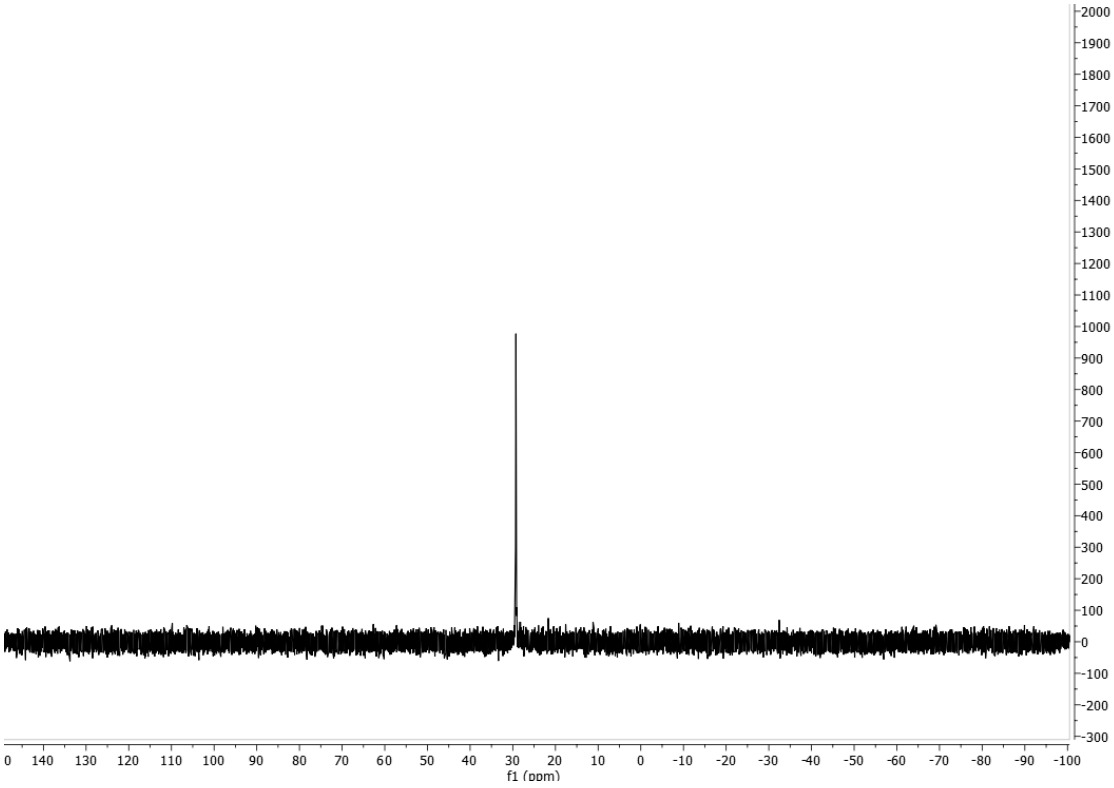


Figure 3.64. $^{31}P\{^{1}H\}$ NMR spectrum of compound **82** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 148.4 (s, 1C, *1*); 136.6;125.8 (s, 2C, *3*,*4*); 133.3 (d, 4C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 33.1 Hz); 131.7 (s, 2C, $C_{para}PPh_2$); 130.0 (m, 2C, CF_3); 129.4 (d, 4C, $C_{meta}PPh_2$, $^{3}J_{CP}$ = 11.3 Hz); 118.0 (s, 1C, *2*); 39.6 (s, 1C, PPh_2-CH_2-CH_2); 29.6 (m, 1C, PPh_2-CH_2-CH_2).

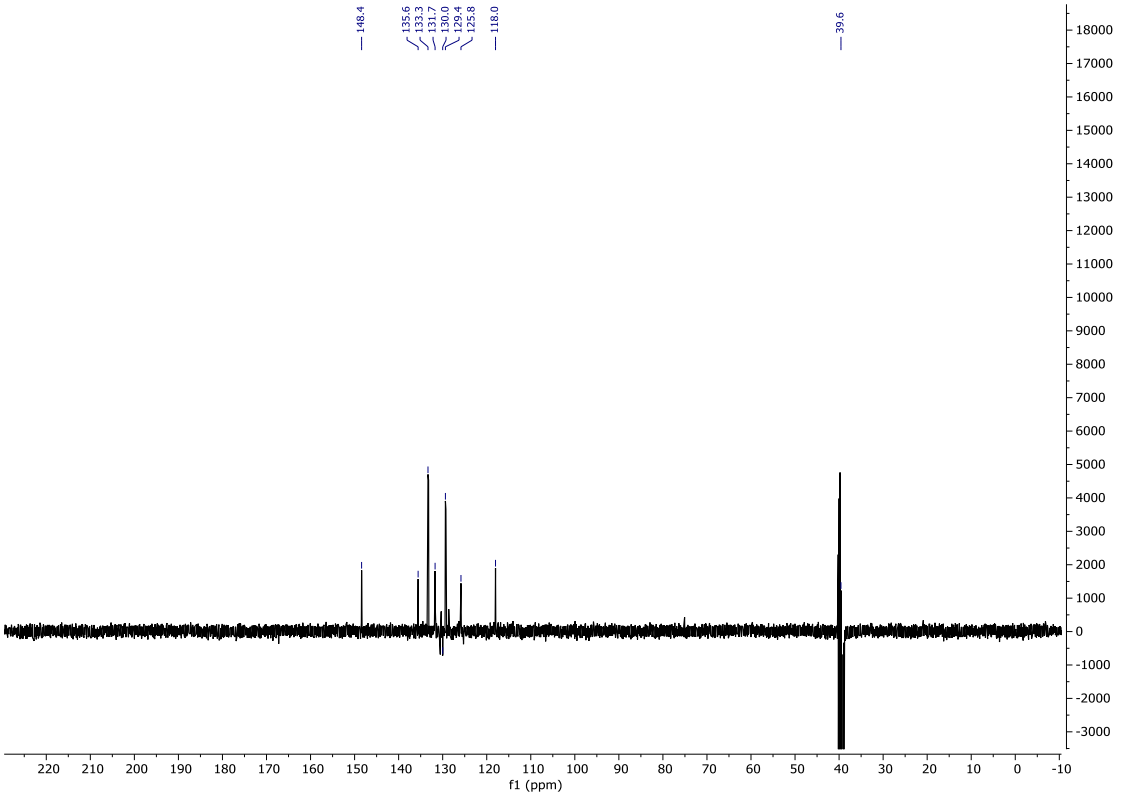


Figure 3.65. ^{13}C APT spectrum of compound **82** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{31}H_{24}AuF_6N_3O_2PS]$ 844.0891. Found 844.0856.

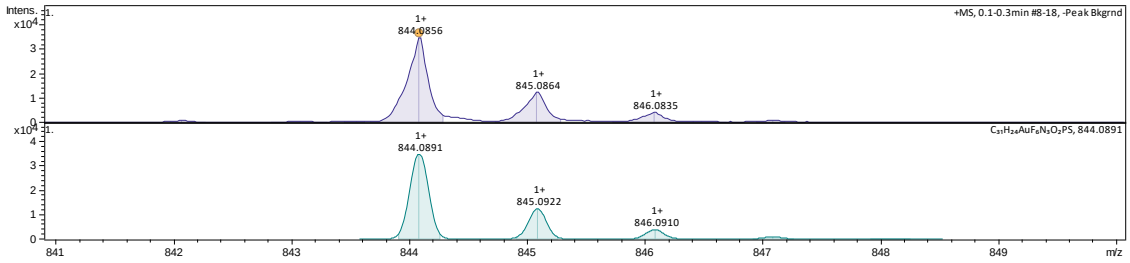
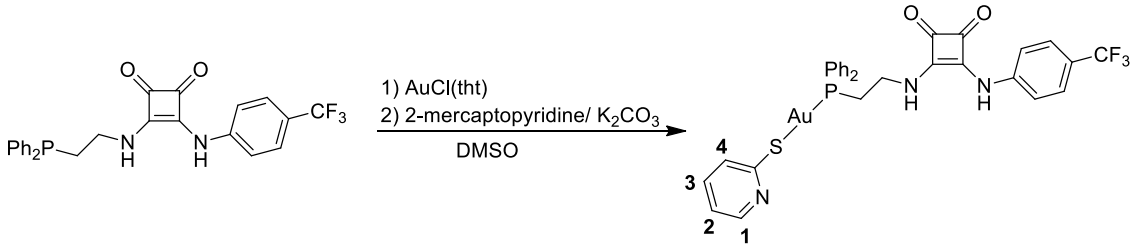


Figure 3.66. MS (ESI+ µ-TOF) compound **82**.

Synthesis of compound 83

To a solution of compound **71** (46 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred. 2 hours later, 2-mercaptopyridine was added (11 mg, 0.1 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite and concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 52%.



Scheme 3.14. Synthesis of compound **83**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.21 (m, 1H, *1*); 7.94 (m, 4H, $H_{ortho}PPh_2$); 7.55 (m, 8H, $H_{meta}PPh_2$ + H_{ortho}Ph-CF_3 + H_{meta}Ph-CF_3); 7.31 (m, 2H, *3+4*); 6.88 (m, 1H, *2*); 3.94 (m, 2H, PPh_2-CH_2-CH_2); 3.19 (m, 2H, PPh_2-CH_2-CH_2).

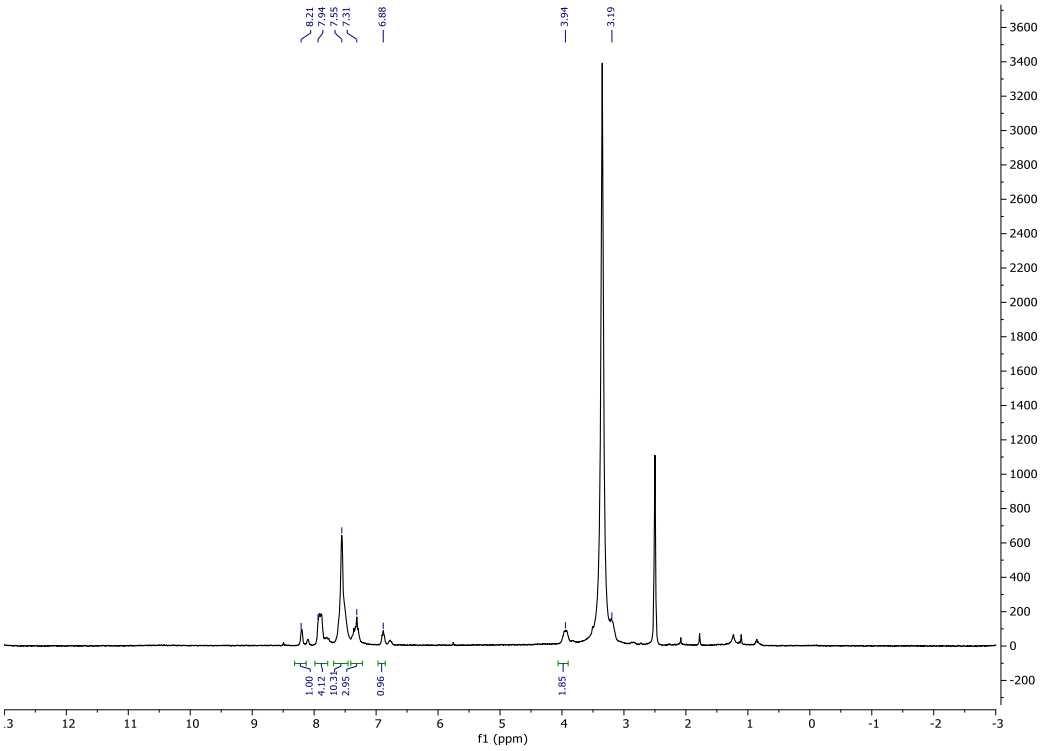


Figure 3.67. ^{1}H NMR spectrum of compound **83** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -59.9 (s, 3F, CF_3).

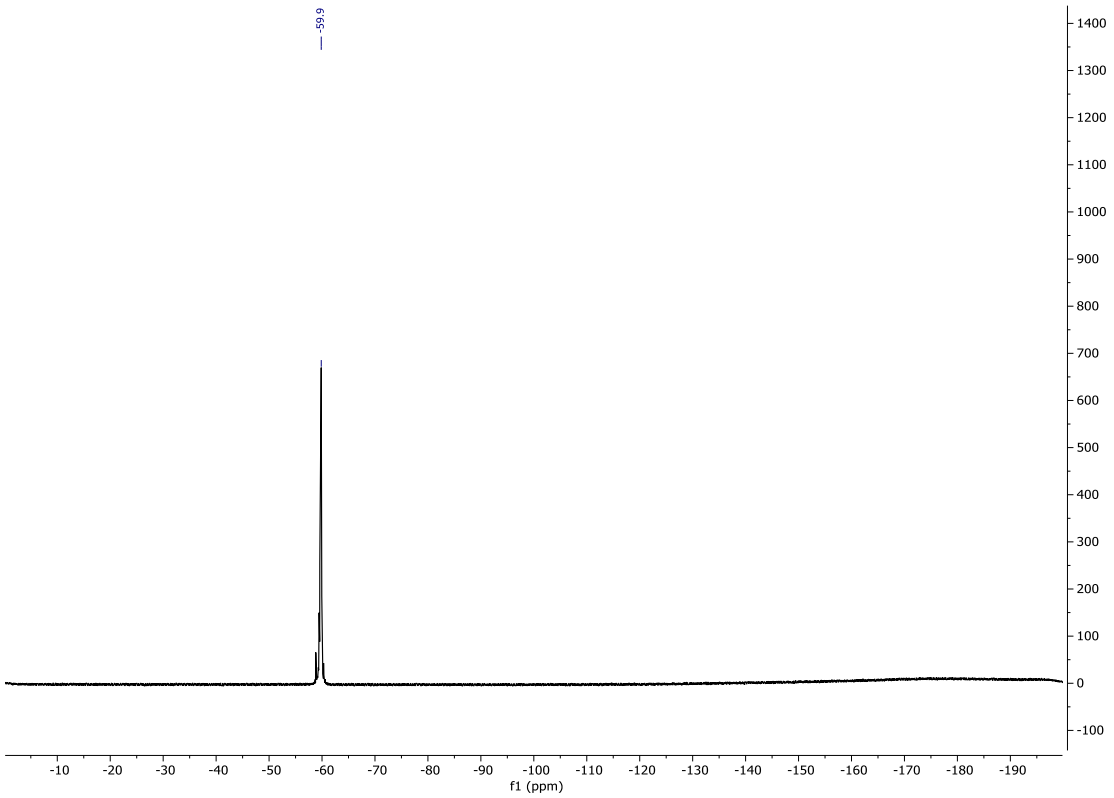


Figure 3.68. $^{19}F\{^{1}H\}$ NMR spectrum of compound **83** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 29.4 (s, 1P, PPh_2).

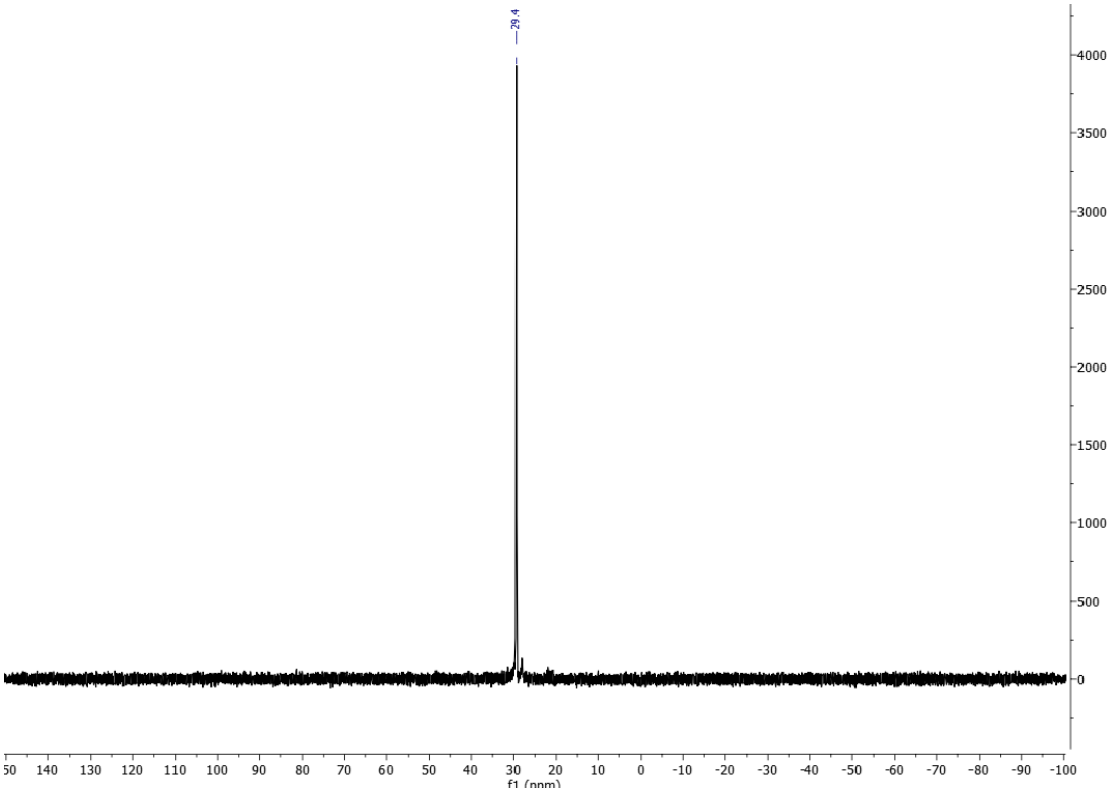


Figure 3.69. $^{31}P\{^{1}H\}$ NMR spectrum of compound **83** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 148.3 (s, 1C, *1*); 136.6;125.8 (s, 2C, *3*,*4*); 133.4 (d, 4C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 13.7 Hz); 131.8 (s, 2C, $C_{para}PPh_2$); 130.3 (s, 2C, C_{ortho}Ph-CF_3); 129.8 (s, 1C, $C_{ipso}PPh_2$); 129.3 (d, 4C, $C_{meta}PPh_2$, $^{3}J_{CP}$ = 11.3 Hz); 128.6 (s, 2C, C_{meta}Ph-CF_3); 118.0 (s, 1C, *2*); 41.1 (s, 1C, PPh_2-CH_2-CH_2); 28.6 (m, 1C, PPh_2-CH_2-CH_2).

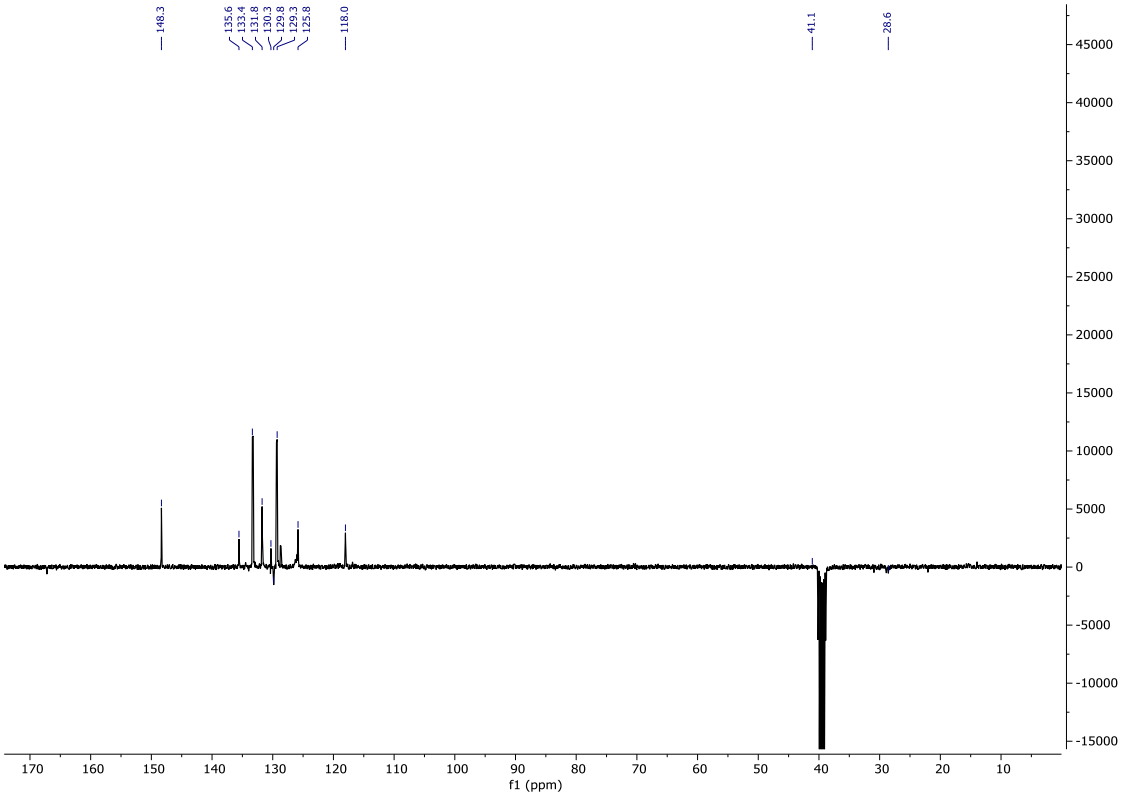


Figure 3.70. ^{13}C APT spectrum of compound **83** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{30}H_{24}AuF_3N_3O_2PS]$ 775.0939. Found 798.0804 $[C_{30}H_{24}AuF_2N_3O_2PS + Na]^+$.

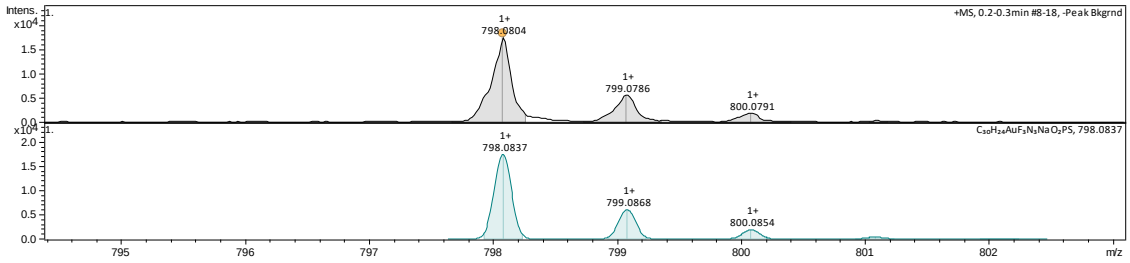
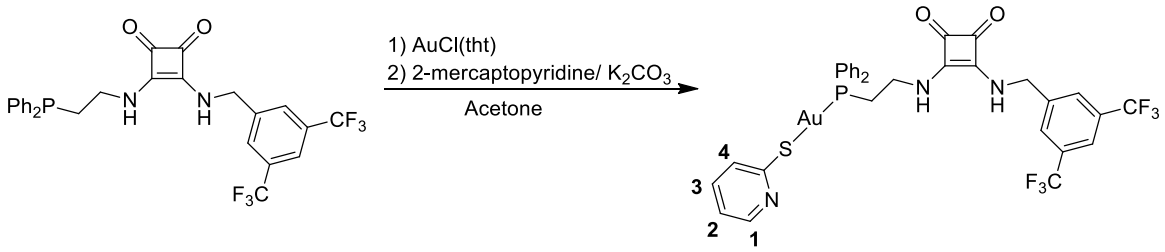


Figure 3.71. MS (ESI+ µ-TOF) compound **83**.

Synthesis of compound 84

To a solution of compound **72** (55 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred. 2 hours later, 2-mercaptopyridine was added (11 mg, 0.1 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite and concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 39%.



Scheme 3.15. Synthesis of compound **84**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.20 (s, 1H, *1*); 8.04 (m, 3H, H_{ortho}Ph-CF_3+ H_{para}Ph-CF_3); 7.90 (m, 4H, $H_{ortho}PPh_2$); 7.54 (m, 6H, H_{meta}+$H_{para}PPh_2$); 7.33 (m, 2H, *3*+*4*); 6.90 (s, 1H, *2*); 4.81 (s, 2H, NH-CH_2-Ph-CF_3); 3.89 (m, 2H, PPh_2-CH_2-CH_2); 3.12 (m, 2H, PPh_2-CH_2-CH_2).

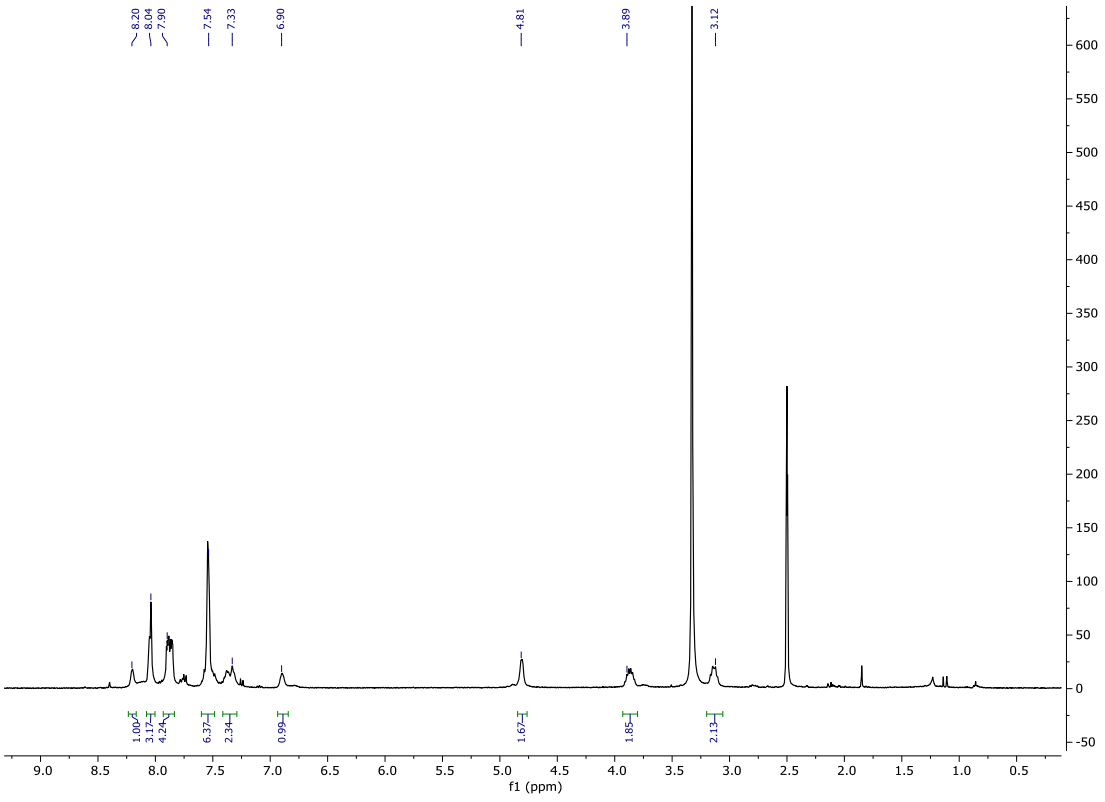


Figure 3.72. ^{1}H NMR spectrum of compound **84** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -61.2 (s, 1F, *CF_3*).

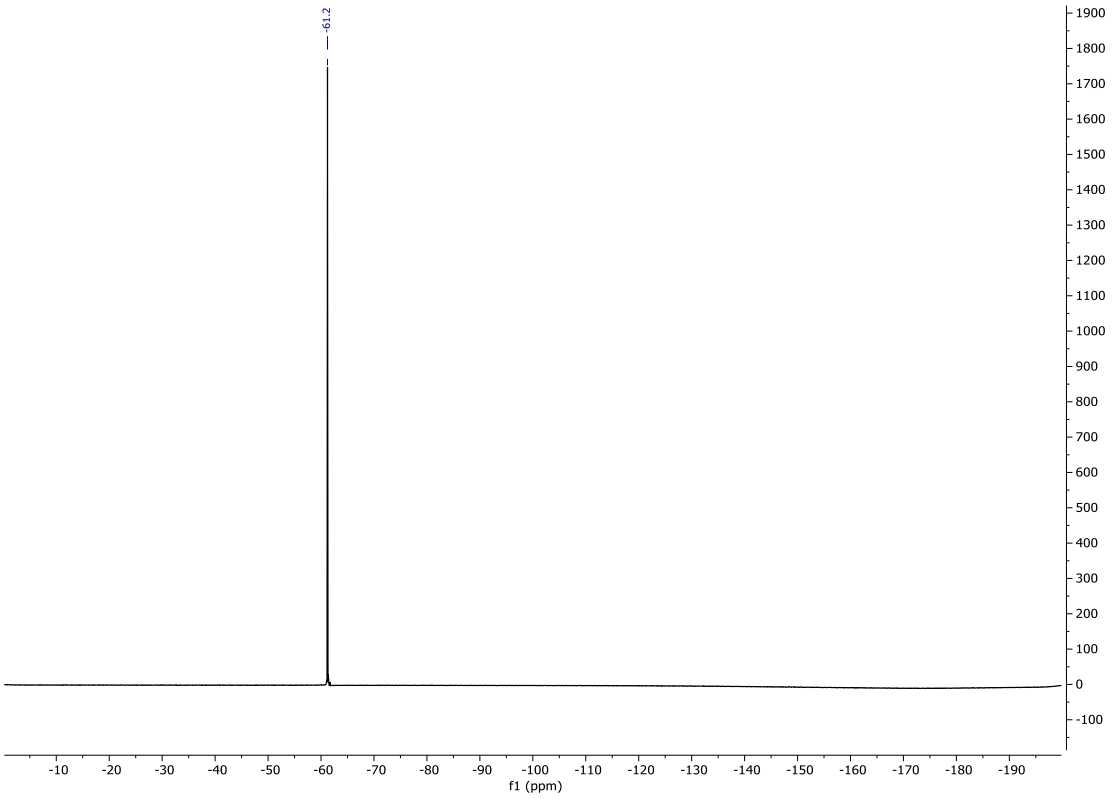


Figure 3.73. ^{19}F{^{1}H} NMR spectrum of compound **84** in DMSO solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, DMSO): δ = 29.7 (s, 1P, *PPh_2*).

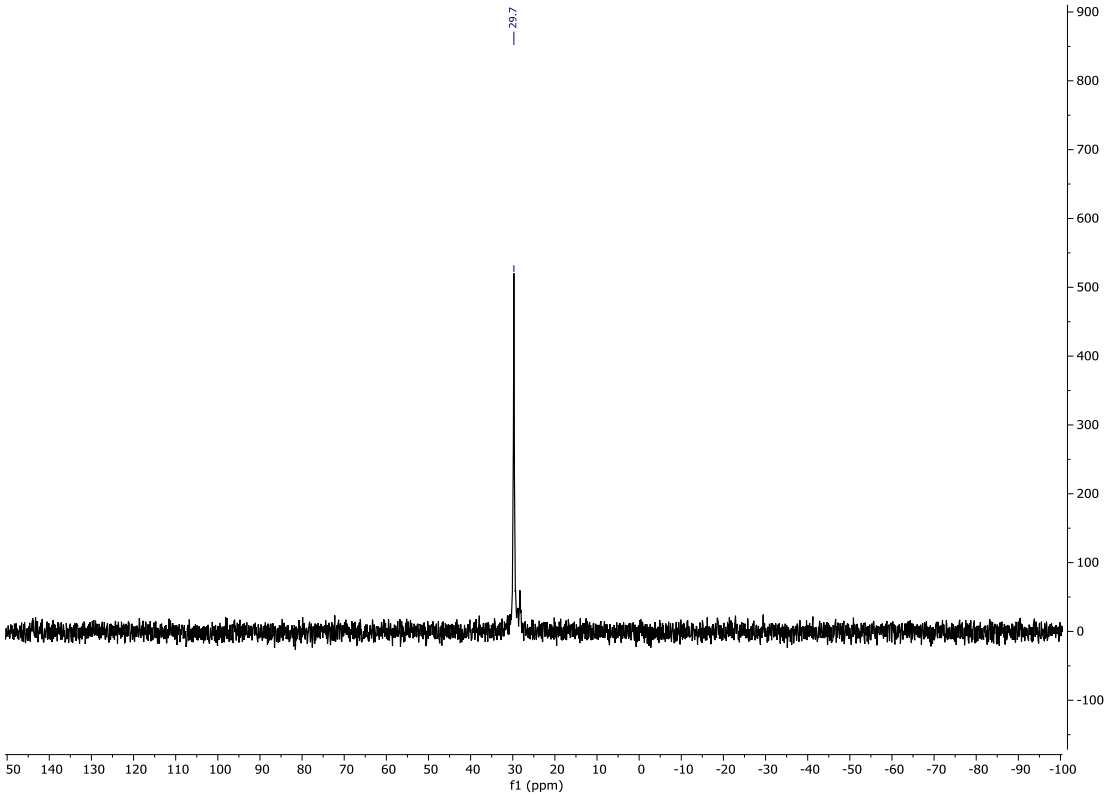


Figure 3.74. $^{31}P\{^{1}H\}$ NMR spectrum of compound **84** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 182.6 (s, 1C, *C=O*); 148.3 (s, 1C, *1*); 142.4 (s, 1C, C_{ipso}-*Ph*); 136.6; 125.8 (s, 2C, *3,4*); 133.3 (d, 4C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 13.7 Hz); 131.7(s, 2C, $C_{para}PPh_2$); 130.4 (m, 2C, $C_{ipso}C$-CF_3); 129.3 (d, 4C, $C_{meta}PPh_2$, $^{3}J_{CP}$ = 11.2 Hz); 128.6 (s, 2C, C_{ortho}Ph-CF_3); 124.6 (m, 2C, CF_3); 121.3 (s, 1C, C_{para}Ph-CF_3); 118.1 (s, 1C, *2*); 45.8 (s, 2H, NH-CH_2-Ph-CF_3); 40.1 (s, 1C, PPh_2-CH_2-CH_2); 28.7 (s, 1C, PPh_2-CH_2-CH_2).

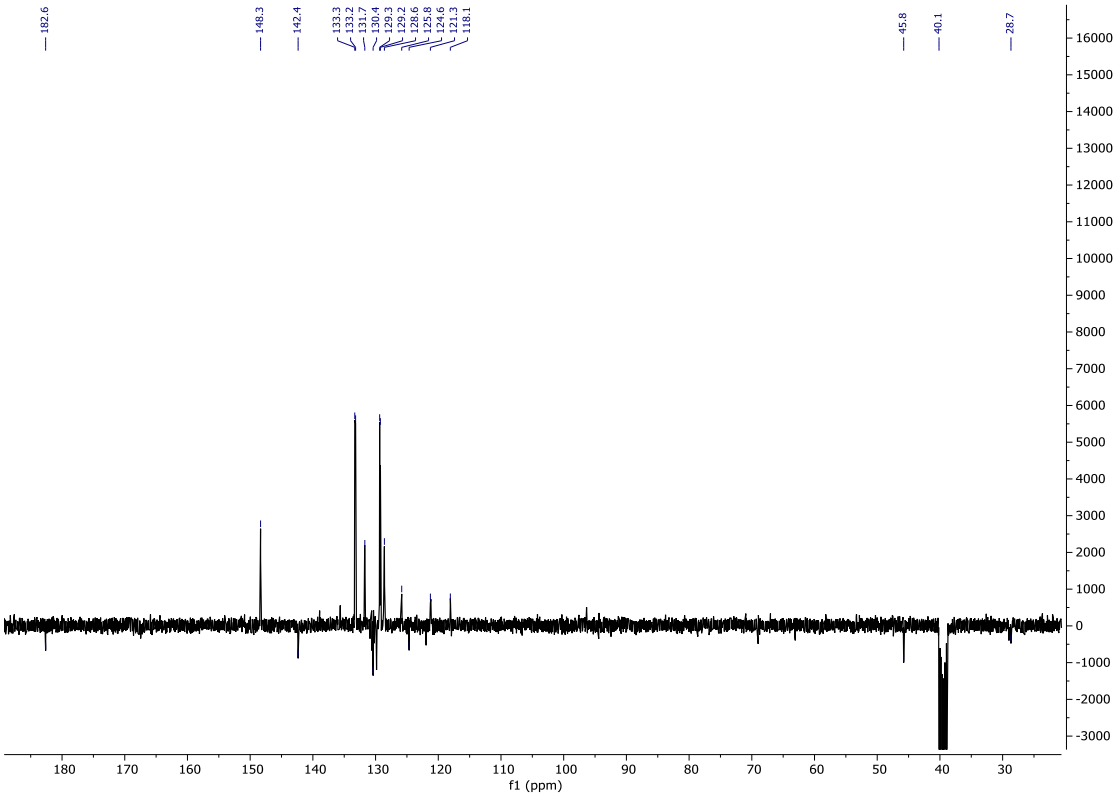


Figure 3.75. ^{13}C APT spectrum of compound **84** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{32}H_{26}AuF_6N_3O_2PS]$ 858.1048. Found 858.1013.

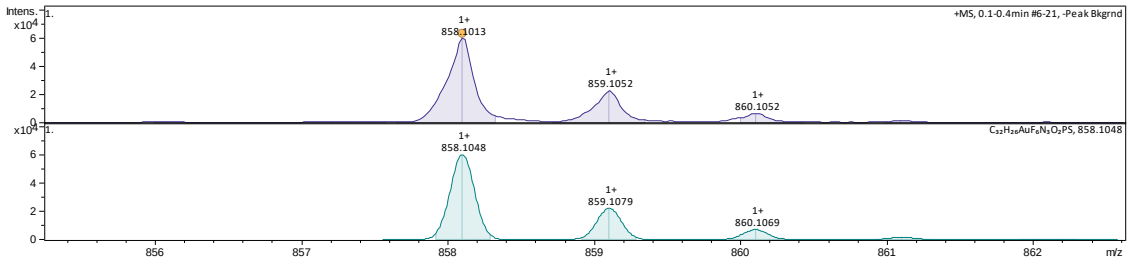
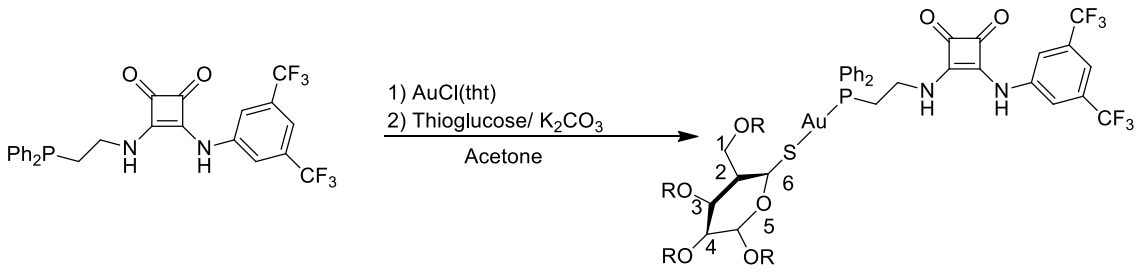


Figure 3.76. MS (ESI+ µ-TOF) compound **84**.

Synthesis of compound 85

To a solution of compound **70** (53 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred. 2 hours later, thioglucose was added (36 mg, 0.1 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 52%.



Scheme 3.16. Synthesis of compound **85**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.88 (m, 4H, H_{ortho}PPh); 7.83 (s br, 2H, H_{ortho}Ph-CF_3); 7.55 (s br, 6H, H_{meta}+$H_{para}$$PPh_2$); 7.22 (s br, 1H, H_{para}Ph-CF_3); 5.30 (d, 1H, *6*, $^{3}J_{H\text{-}H}$ = 9.2 Hz); 5.15 (t, 1H, *4*, $^{3}J_{H\text{-}H}$ = 9.5 Hz); 4.90 (t, 1H, *3*, $^{3}J_{H\text{-}H}$ = 9.7 Hz); 4.83 (t, 1H, *5*, $^{3}J_{H\text{-}H}$ = 9.5 Hz); 4.09 (dt, 1H, *2*, $^{3}J_{H\text{-}H}$ = 9.1, 12.5 Hz); 3.98 (d, 2H, *1*, $^{3}J_{H\text{-}H}$ = 11.2 Hz); 3.85 (s br, 2H, PPh_2-CH_2-CH_2); 3.12 (m, 2H, PPh_2-CH_2-CH_2), 1.97-1.83 (m, 12H, CH_3).

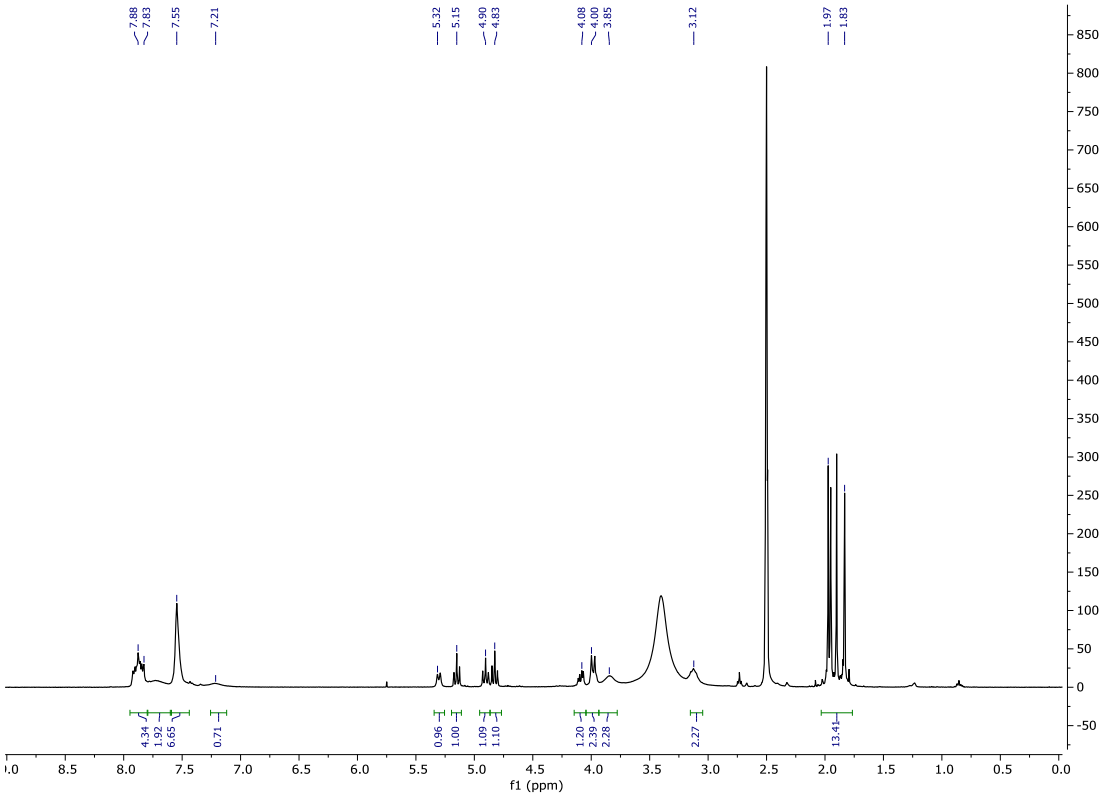


Figure 3.77. ^{1}H NMR spectrum of compound **85** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -61.5 (s, 1F, CF_3).

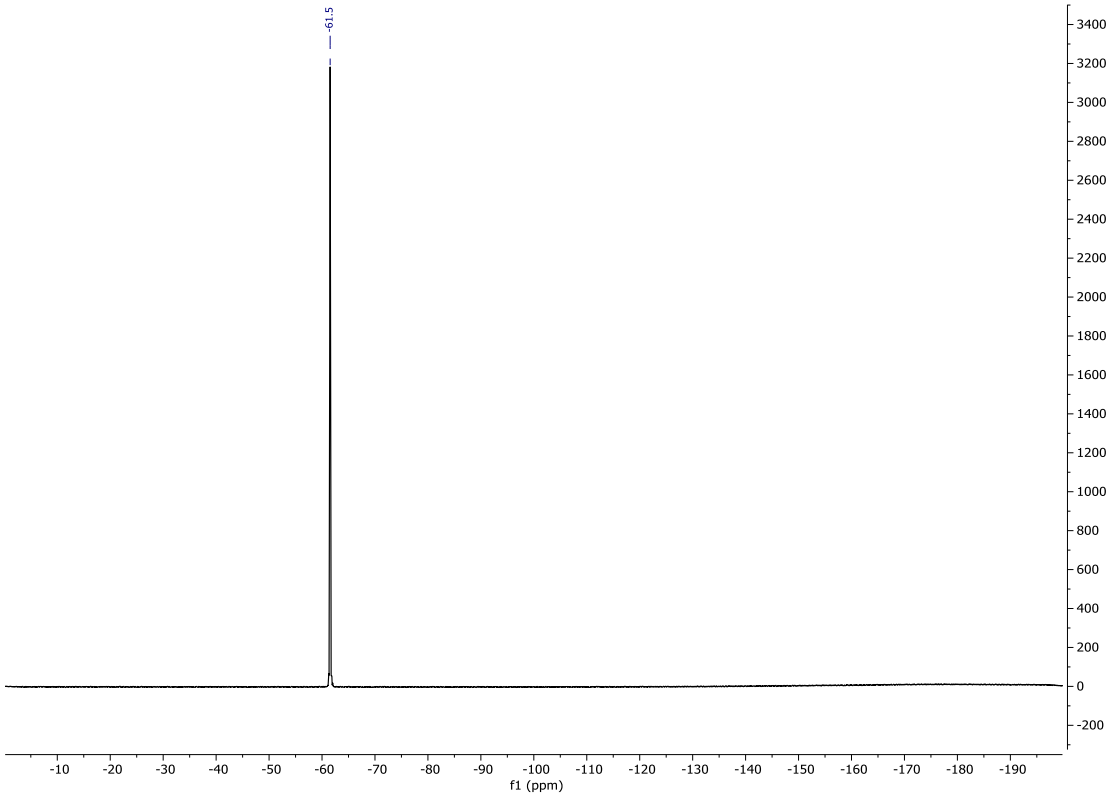


Figure 3.78. $^{19}F\{^{1}H\}$ NMR spectrum of compound **85** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 29.8 (s, 1P, *PPh_2*).

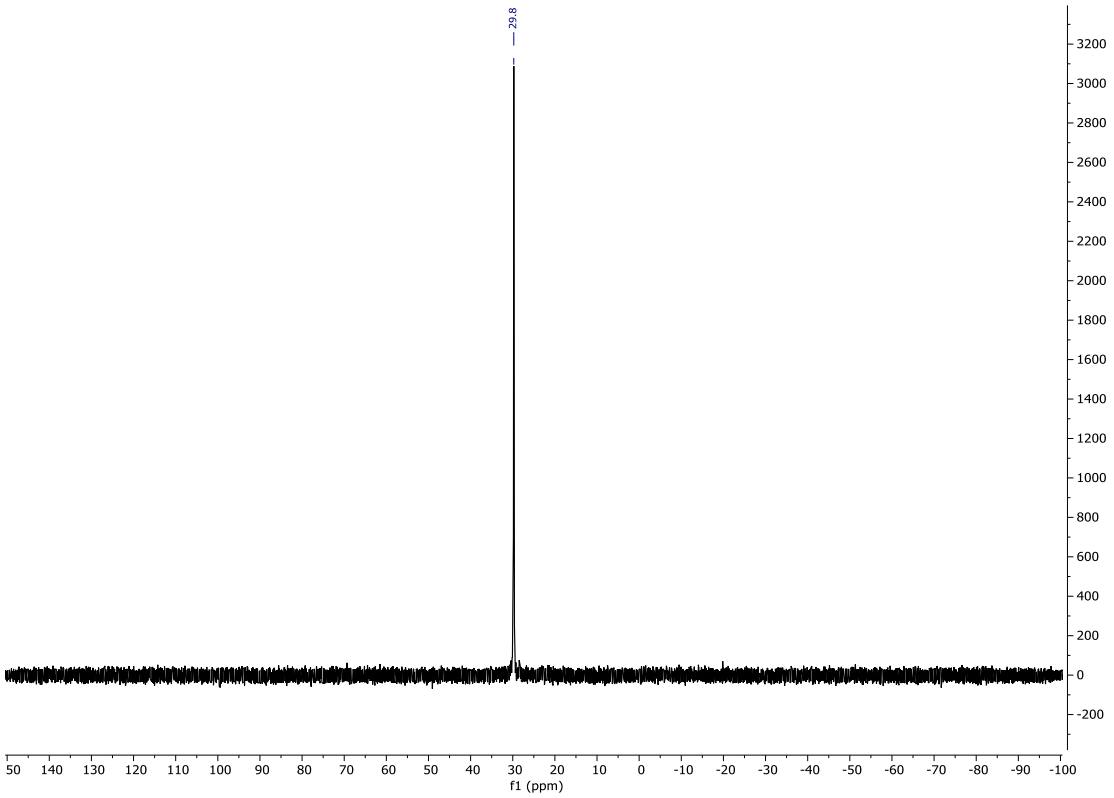


Figure 3.79. $^{31}P\{^{1}H\}$ NMR spectrum of compound **85** in DMSO solution.

^{13}C APT (ppm) (400 MHz, DMSO): δ = 170.0-169.0 (s, 4C, *OC=O*); 133.4 (m, 4C, $C_{ortho}PPh_2$); 131.7 (s, 2C, $C_{para}PPh_2$); 130.2 (m, 1C, $C_{ipso}PPh_2$); 129.2 (d, 4C, $C_{meta}PPh_2$, $^2J_{CP}$ = 11.2 z); 125.3 (m, 2C, CF_3); 81.7 (s, 1C, *6*); 77.1 (s, 1C, *5*); 74.3 (s, 1C, *2*); 73.3 (s, 1C, *4*); 68.6 (s, 1C, *3*); 62.3 (s, 1C, *1*); 39.8 (m, 1C, PPh_2-CH_2-CH_2); 31.1 (d, 1C, PPh_2-CH_2-CH_2, $^2J_{CP}$ = 43.5 Hz); 20.7-20.3 (s, 4C, CH_3).

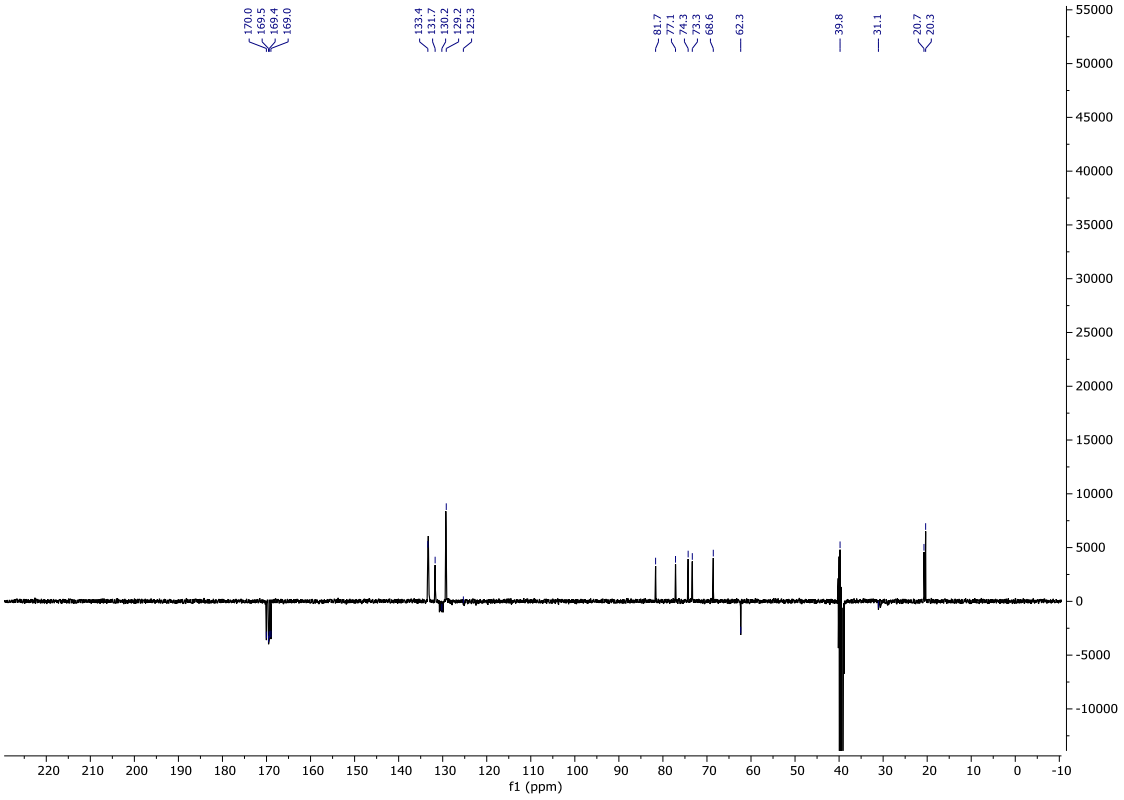


Figure 3.80. ^{13}C APT spectrum of compound **85** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{40}H_{38}AuF_6N_2O_{11}PS]$ 775.0939. Found 1096.1498 $[C_{40}H_{38}AuF_6N_2O_{11}PS + Na]^+$.

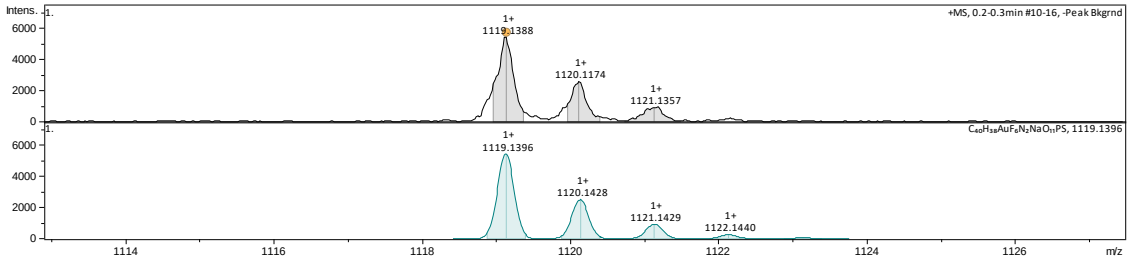
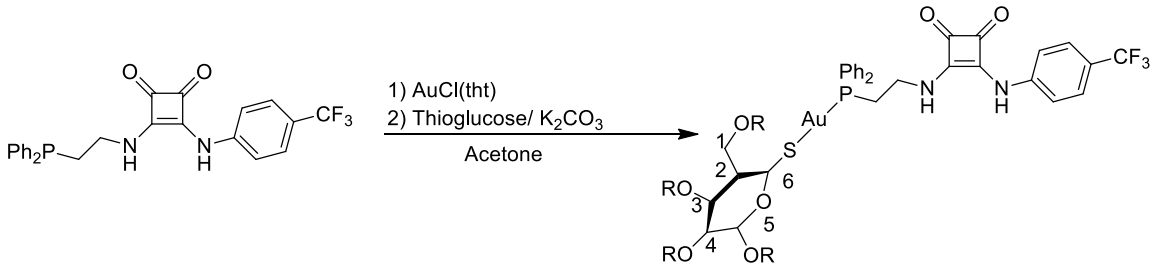


Figure 3.81. MS (ESI+ µ-TOF) compound **85**.

Synthesis of compound 86

To a solution of compound **71** (46 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred. 2 hours later, thioglucose was added (36 mg, 0.1 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite and concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 56%.



Scheme 3.17. Synthesis of compound **86**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 7.87-7.55 (m, 14H, *PPh_2 + Ph-CF_3*); 5.32 (d, 1H, *6*, $^3J_{H\text{-}H}$ = 9.3 Hz); 5.16 (t, 1H, *4*, $^3J_{H\text{-}H}$ = 9.5 Hz); 4.90 (m, 2H, *5 + 3*); 4.10 (m, 1H, *2*); 4.00 (m, 2H, *1*); 3.90 (m, 2H, PPh_2-CH_2-*CH_2*); 3.16 (s br, 2H, PPh_2-*CH_2*-CH_2); 1.97-1.83 (m, 12H, *CH_3*).

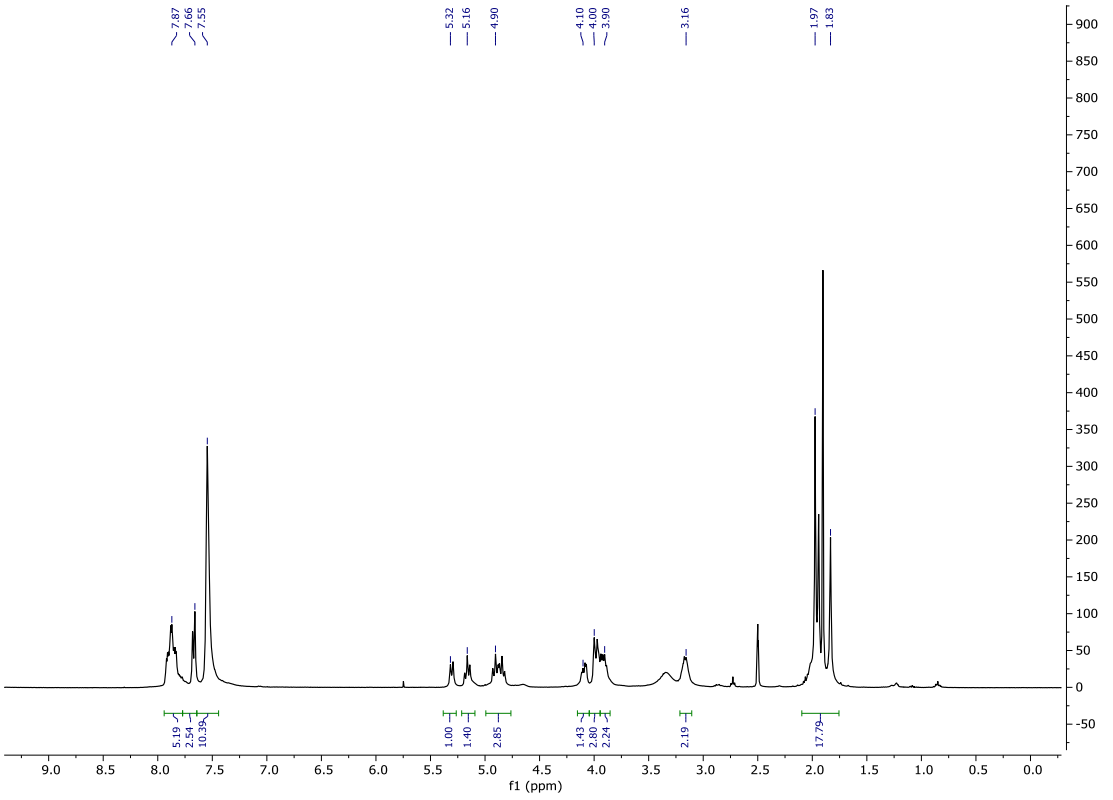


Figure 3.82. ^{1}H NMR spectrum of compound **86** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.1 (s, 1F, *CF_3*).

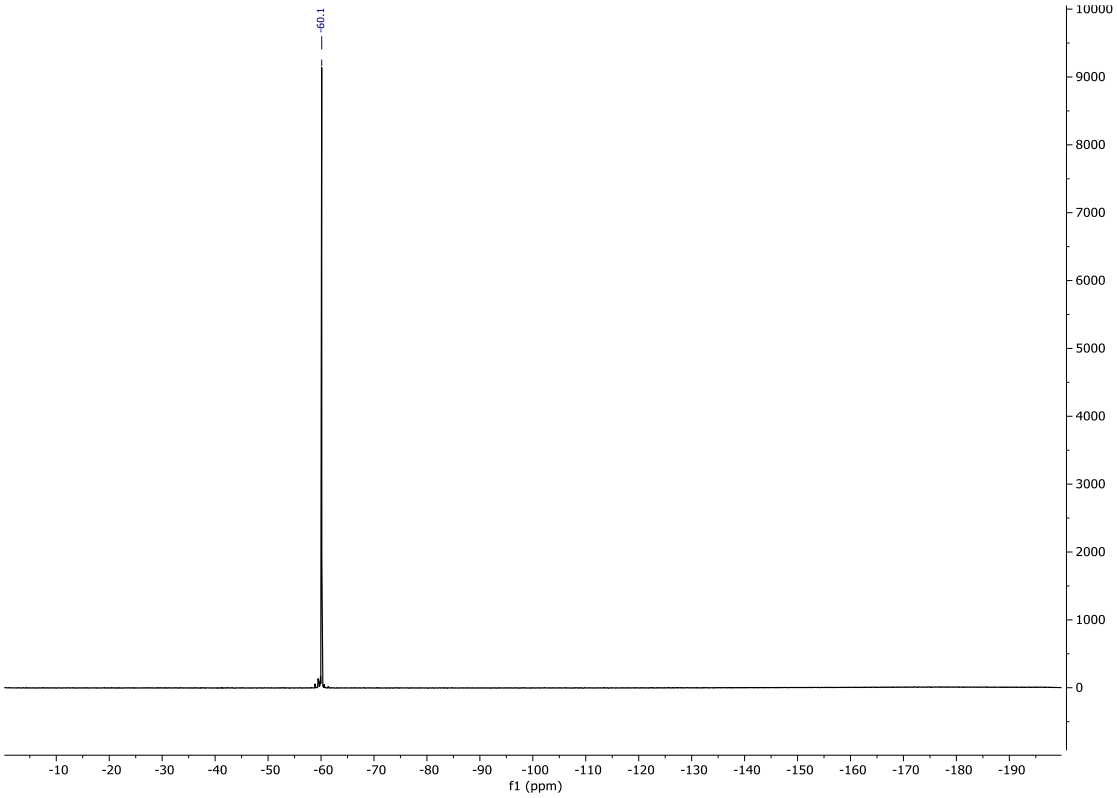


Figure 3.83. ^{19}F{^{1}H} NMR spectrum of compound **86** in DMSO solution.

^{31}P{^{1}H} NMR (ppm) (162 MHz, DMSO): δ = 29.9 (s, 1P, *PPh_2*).

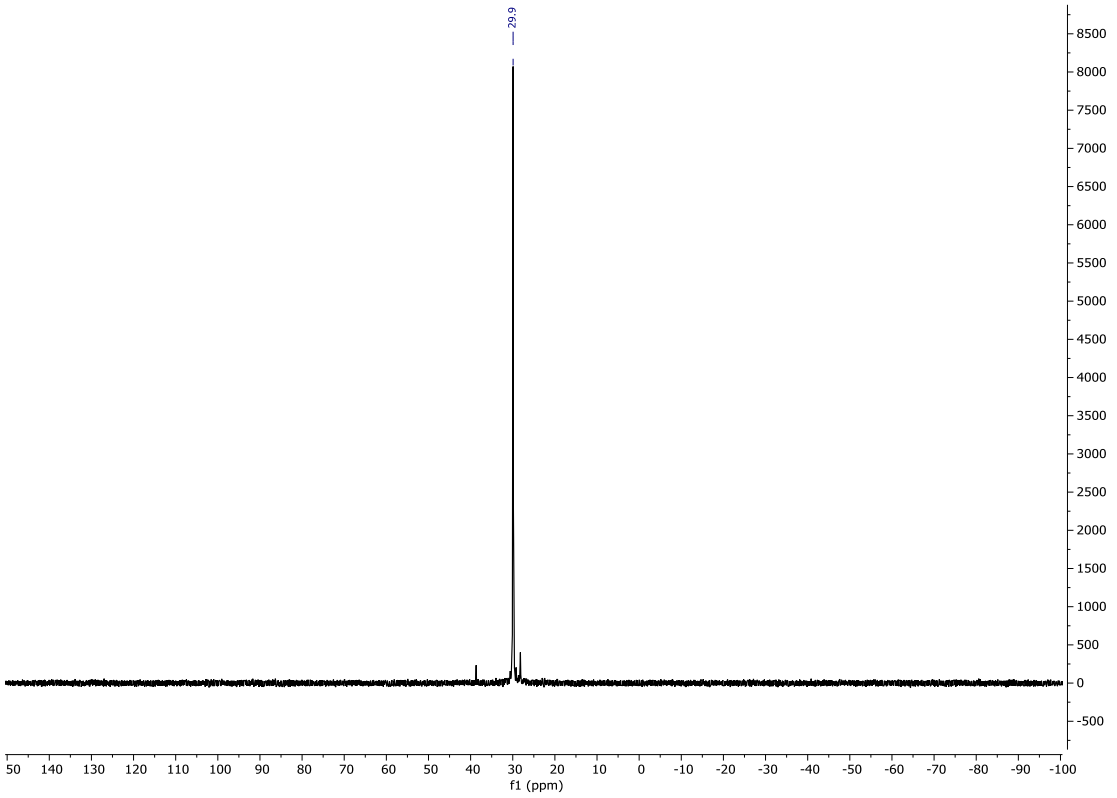


Figure 3.84. $^{31}P\{^{1}H\}$ NMR spectrum of compound **86** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.4 (s, 1C, *C*=*O*); 180.4 (s, 1C, *C*=*O*); 169.5 (s, 4C, *OC*=*O*); 163.5 (s, 1C, *C*=*C*); 142.6 (s, 1C, $C_{ipso}Ph$); 133.3 (m, 4C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 24.9 Hz); 131.8 (s, 2C, $C_{para}PPh_2$); 130.3 (m, 1C, $C_{ipso}PPh_2$); 129.2 (d, 4C, $C_{meta}PPh_2$, $^{3}J_{CP}$ = 11.2 Hz); 126.6 (s, 2C, C_{ortho}Ph-CF_3); 125.8 (m, 1C, CF_3); 118.2 (s, 2C, C_{meta}Ph-CF_3); 81.7 (s, 1C, *6*); 77.1 (s, 1C, *5*); 74.3 (s, 1C, *2*); 73.3 (s, 1C, *4*); 68.6 (s, 1C, *3*); 62.4 (s, 1C, *1*); 40.1 (m, 1C, PPh_2-CH_2-CH_2); 28.4 (d, 1C, PPh_2-CH_2-CH_2, $^{2}J_{CP}$ = 33.9 Hz); 20.4 (s, 4C, CH_3).

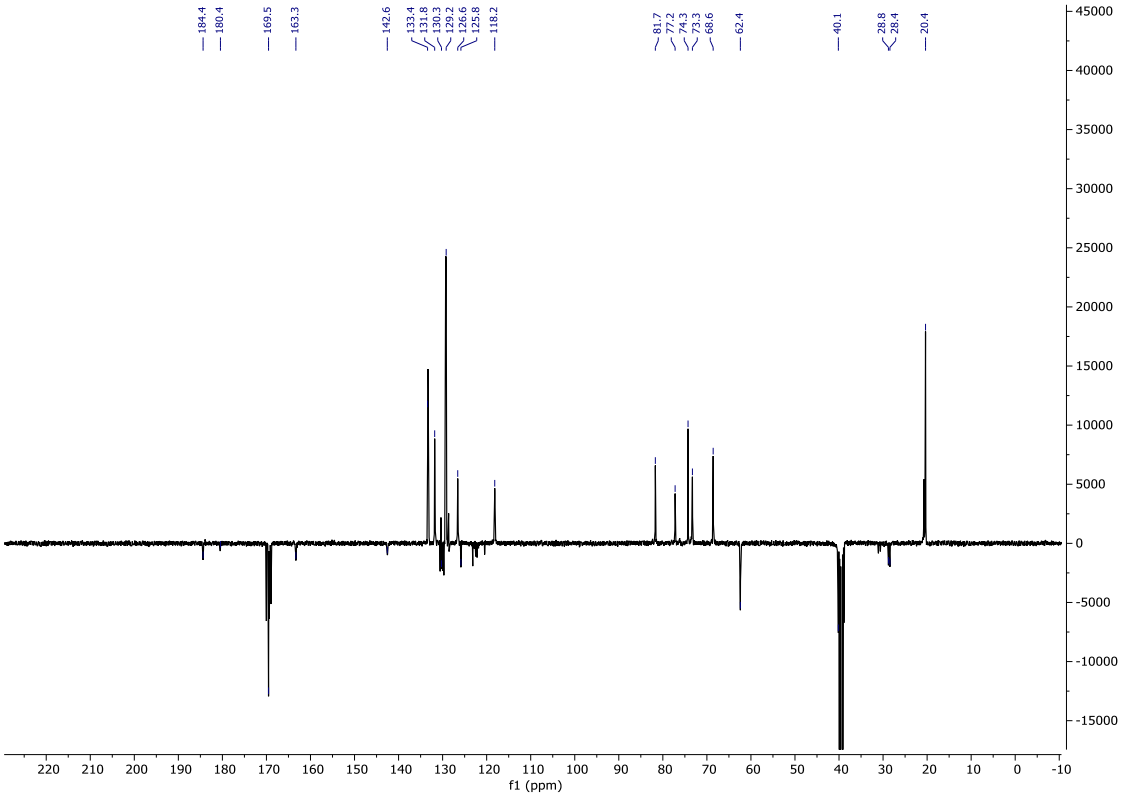


Figure 3.85. ^{13}C APT spectrum of compound **86** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{39}H_{39}AuF_3N_2O_{11}PS]$ 1028.1624. Found 1051.1557 $[C_{39}H_{39}AuF_3N_2O_{11}PS + Na]^+$.

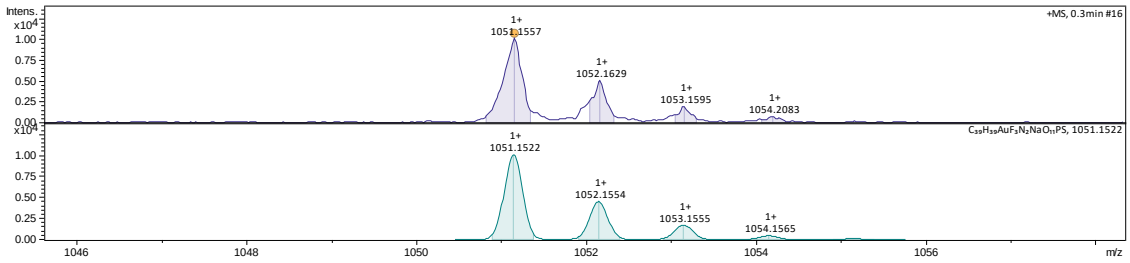


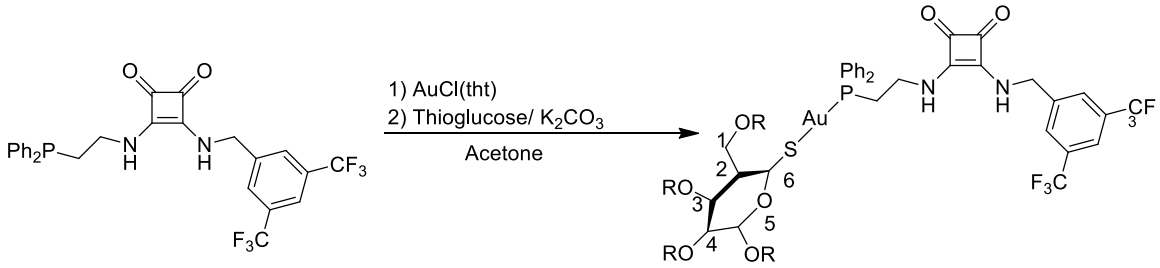
Figure 3.86. MS (ESI+ µ-TOF) compound **86**.

Synthesis of compound 87

To a solution of compound **72** (55 mg, 0.1 mmol) in acetone (20 ml) was added [AuCl(tht)] (32 mg, 0.1 mmol) and the solution stirred. 2 hours later, thioglucose was added (36 mg, 0.1 mmol) with an excess of K_2CO_3 and the solution stirred overnight. The solution was filtered through celite and concentrated under reduced pressure to

approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 53%.



Scheme 3.18. Synthesis of compound **87**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 8.05 (s, 3H, H_{ortho}Ph-CF_3+ H_{para}Ph-CF_3); 7.84 (m, 4H, H_{ortho}PPh); 7.54 (s, 6H, H_{meta}+H_{para}PPh_2); 5.33 (m, 1H, *6*); 5.17 (t, 1H, *4*, $^3J_{H\text{-}H}$ = 9.5 Hz); 4.90 (m, 4H, *3*+*5*+ NH-CH_2-Ph-CF_3); 4.10 (m, 1H, *2*,); 3.99 (d, 2H, *1*, $^3J_{H\text{-}H}$ = 10.5 Hz); 3.84(s br, 2H, PPh_2-CH_2-CH_2); 3.11 (m, 2H, PPh_2-CH_2-CH_2), 1.98 (m, 12H, CH_3).

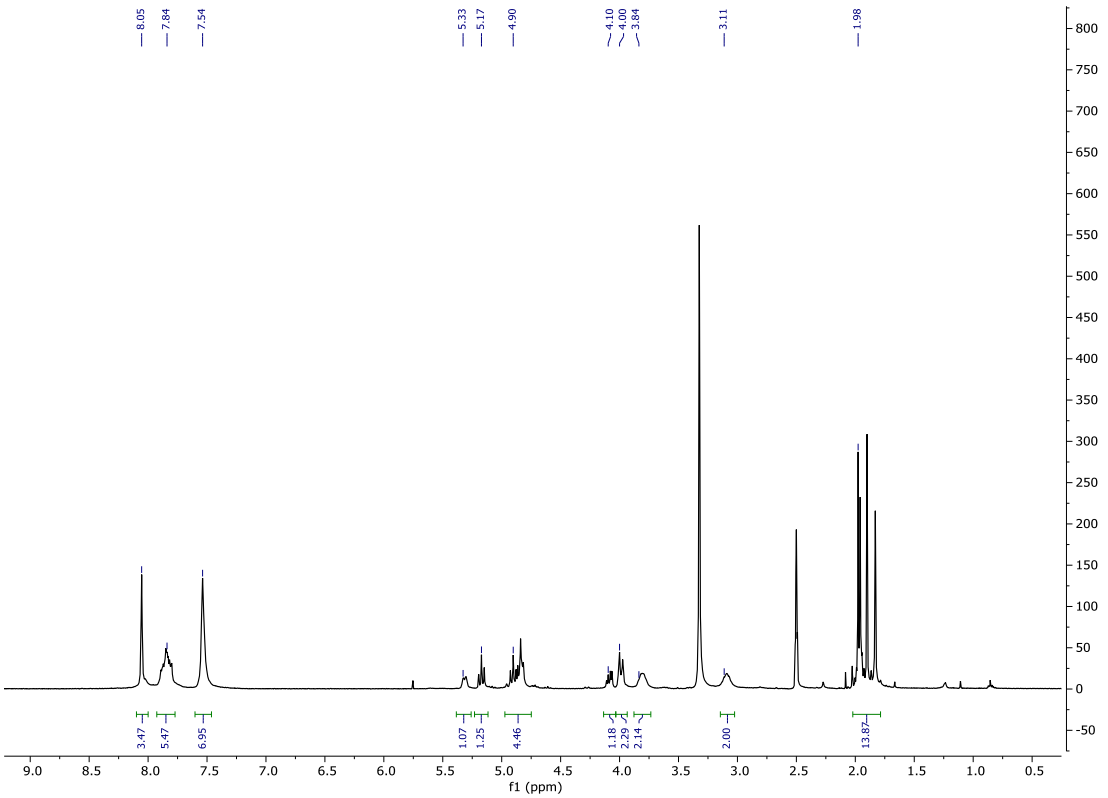


Figure 3.87. ^{1}H NMR spectrum of compound **87** in DMSO solution.

$^{19}F\{^{1}H\}$ NMR (ppm) (376 MHz, DMSO): δ = -61.2 (s, 1F, CF_3).

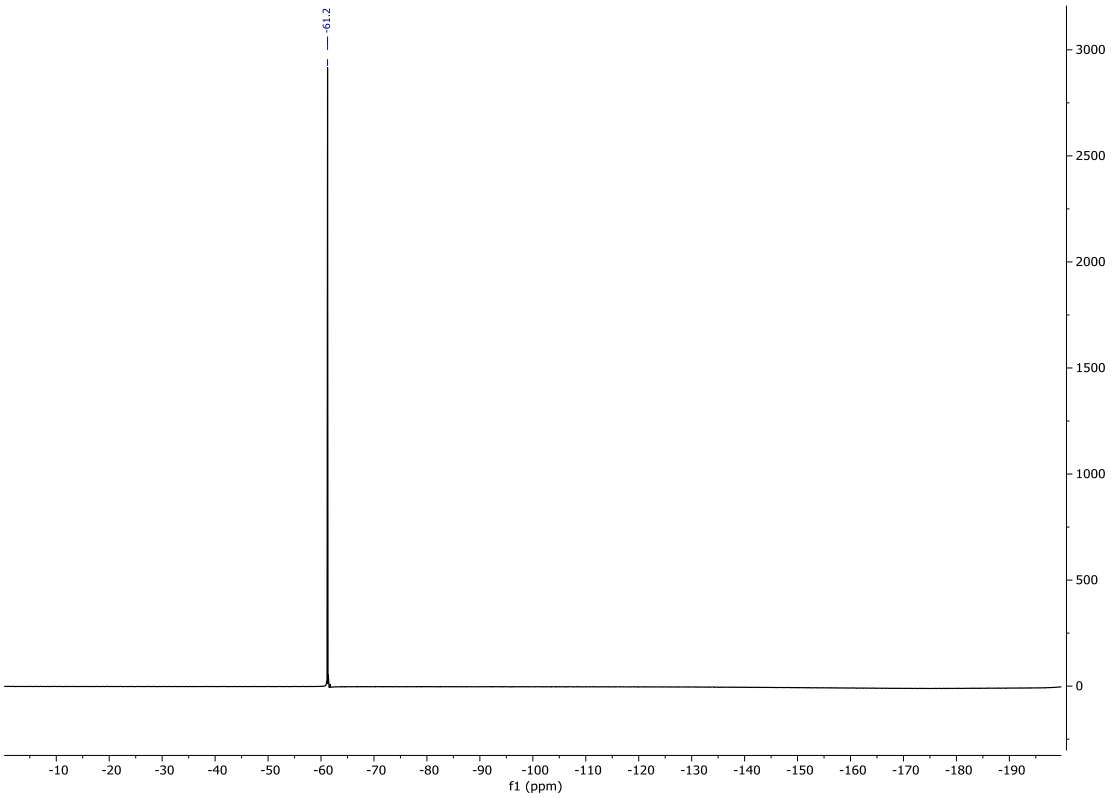


Figure 3.88. $^{19}F\{^{1}H\}$ NMR spectrum of compound **87** in DMSO solution.

$^{31}P\{^{1}H\}$ NMR (ppm) (162 MHz, DMSO): δ = 30.2 (s, 1P, PPh_2).

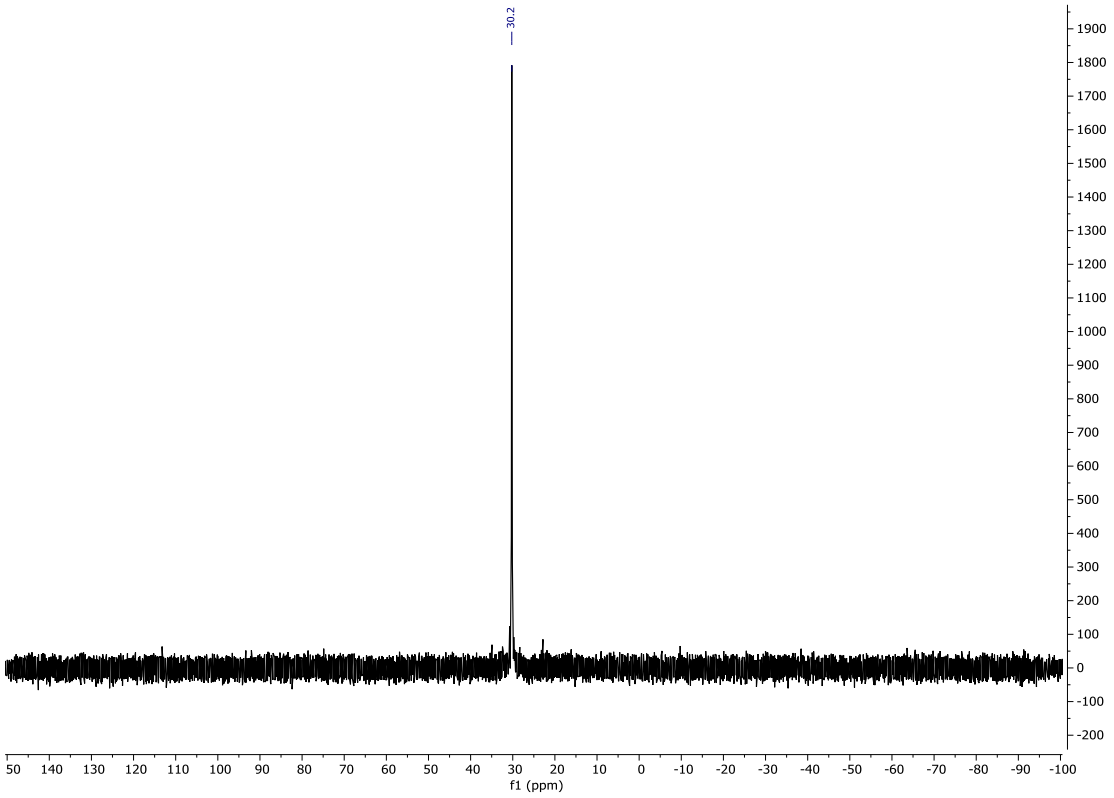


Figure 3.89. $^{31}P\{^{1}H\}$ NMR spectrum of compound **87** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 182.6 (s, 1C, *C=O*); 170.0 (s, 4C, *OC=O*); 142.4 (s, 1C, C_{ipso}-*Ph*); 133.2 (m, 4C, $C_{ortho}PPh_2$, $^{2}J_{CP}$ = 24.7 Hz); 131.7 (s, 2C, $C_{para}PPh_2$); 130.2 (m, 3C, $C_{ipso}PPh_2$+ $C_{ipso}C$-CF_3); 129.2 (d, 4C, $C_{meta}PPh_2$, $^{2}J_{CP}$ = 11.2 z); 128.6 (s, C_{ortho}Ph-CF_3); 123.3 (q, 2C, CF_3, $^{1}J_{CF}$ = 272.9 Hz); 121.3 (s, 1C, C_{para}Ph-CF_3); 81.7 (s, 1C, *6*); 77.2 (s, 1C, *5*); 74.3 (s, 1C, *2*); 73.3 (s, 1C, *4*); 68.6 (s, 1C, *3*); 62.3 (s, 1C, *1*); 45.7 (s, 2H, NH-CH_2-Ph-CF_3); 38.9 (m, 1C, PPh_2-CH_2-CH_2); 31.1 (d, 1C, PPh_2-CH_2-CH_2, $^{2}J_{CP}$ = 38.7 Hz); 20.4(s, 4C, CH_3).

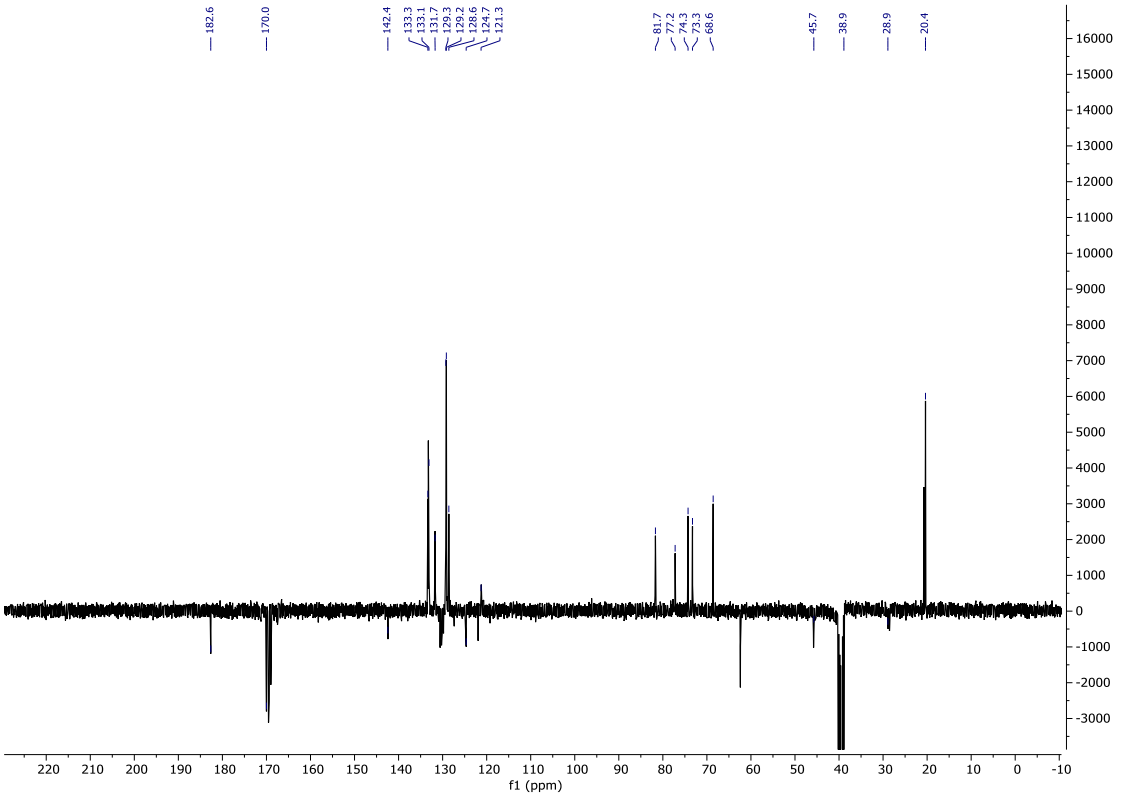


Figure 3.90. ^{13}C APT spectrum of compound **87** in DMSO solution.

MS (ESI+ µ-TOF): m/z (%)= $[M]^+$ Calcd for $[C_{41}H_{40}AuF_6N_2O_{11}PS]$ 1110.1651. Found 1133.1549 $[C_{41}H_{40}AuF_6N_2O_{11}PS + Na]^+$.

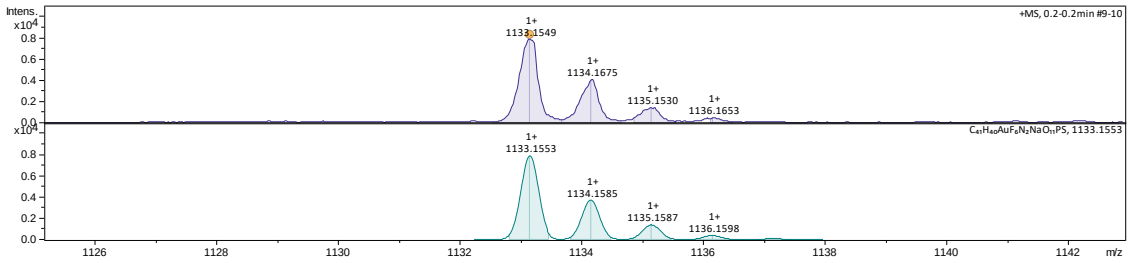
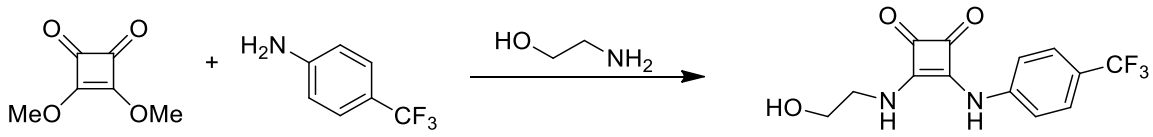


Figure 3.91. MS (ESI+ µ-TOF) compound **87**.

Synthesis of compound 88

To a solution of 3,4-Dimethoxy-3-cyclobutene-1,2-dione (29 mg, 0.2 mmol) in methanol (5 ml) was added 4-(trifluoromethyl)aniline (25 µL, 0.2 mmol) and the solution stirred. 21 hours later, 2-aminoethanol was added (12 µL, 0.2 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 70%.



Scheme 3.19. Synthesis of compound **88**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 10.01 (s, 1H, *NH*-Ph); 7.91 (s, 1H, *NH*-CH_2); 7.67-7.61 (m, 4H, *Ph*); 5.03 (s, 1H, *OH*); 3.67 (m, 2H, OH-CH_2-*CH_2*-NH); 3.58 (m, 2H, OH-*CH_2*-CH_2-NH).

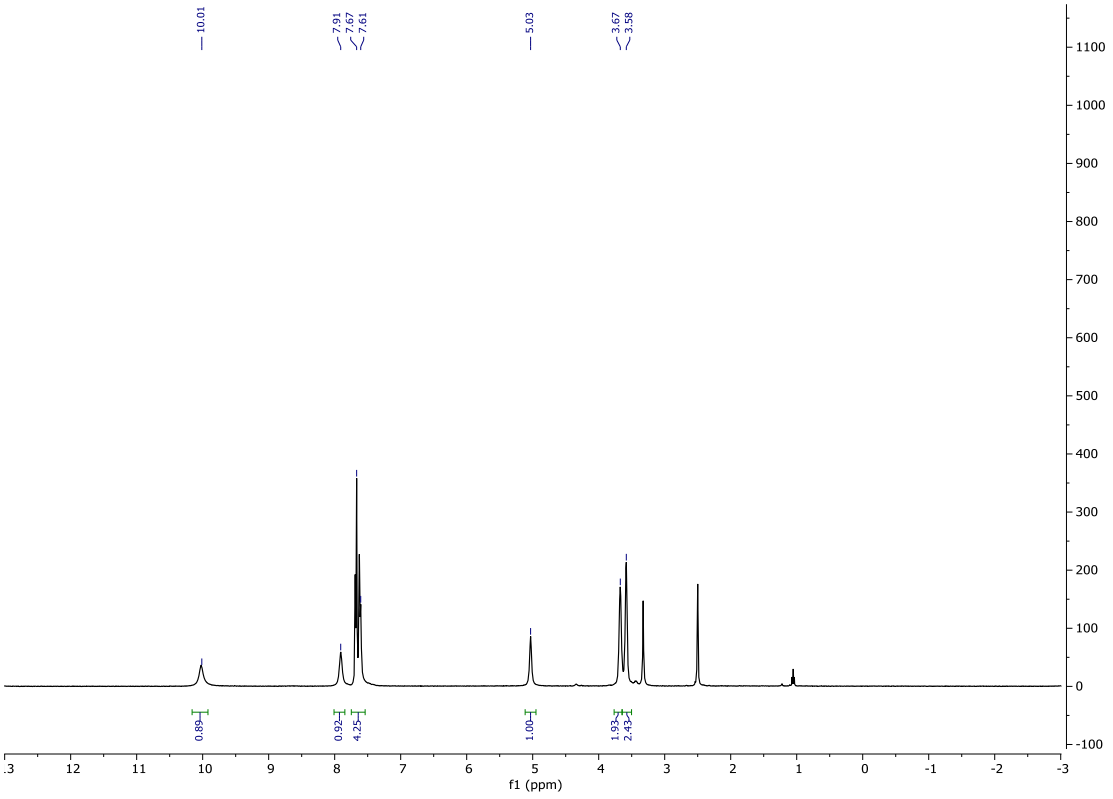


Figure 3.92. ^{1}H NMR spectrum of compound **88** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.1 (s, 3F, *CF_3*).

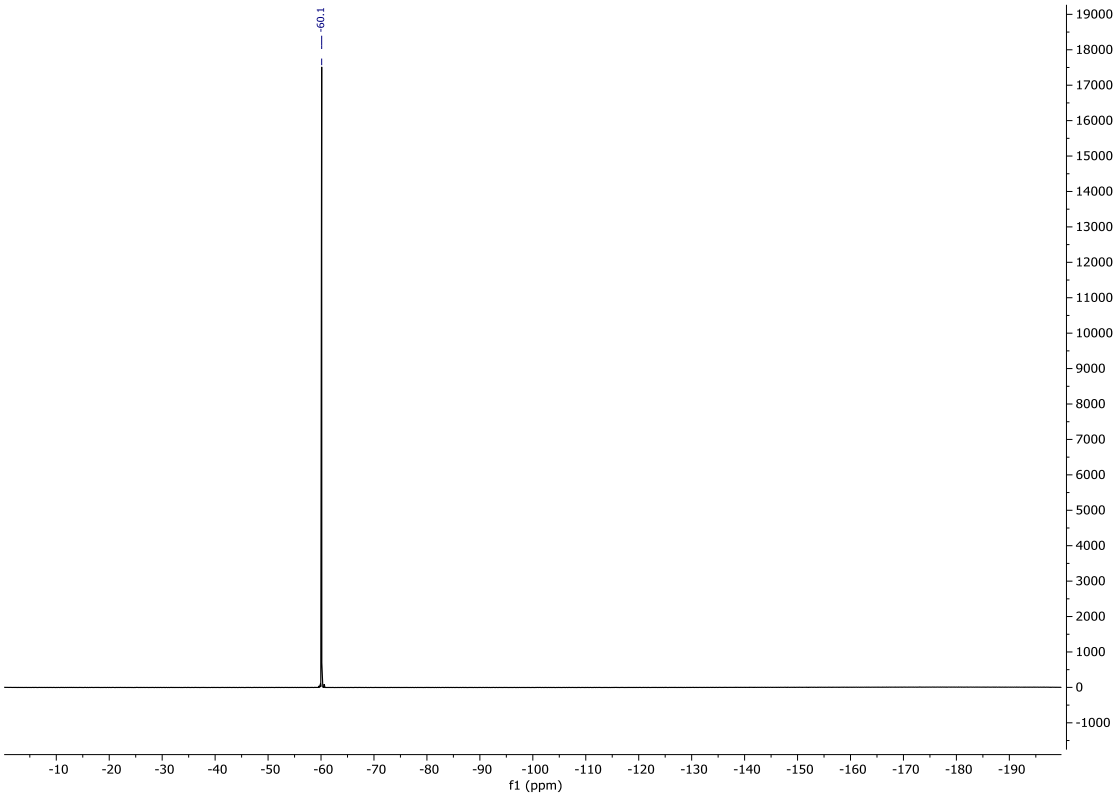


Figure 3.93. $^{19}F\{^{1}H\}$ NMR spectrum of compound **88** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.8 (s, 1C, *C*=*O*); 180.1 (s, 1C, *C*=*O*); 169.8 (s, 1C, Ph-C=*C*-*CH*$_2$); 162.9 (s, 1C, *Ph*-*C*=C-CH$_2$); 142.7 (s, 1C, *C*$_{ipso}$-*Ph*); 126.6 (s, 2C, *C*$_{ortho}$Ph-CF$_3$); 124.5 (q, 2C, *CF*$_3$, $^{1}J_{CF}$ = 271.2 Hz); 122.2 (q, 1C, *C*$_{ipso}$-*Ph*-*CF*$_3$, $^{2}J_{CP}$ = 32.1 Hz); 117.8 (s, 2C, *C*$_{meta}$Ph-CF$_3$); 60.5 (s, 2H, OH-*CH*$_2$-CH$_2$-NH); 46.3 (s, 2H, OH-CH$_2$-*CH*$_2$-NH).

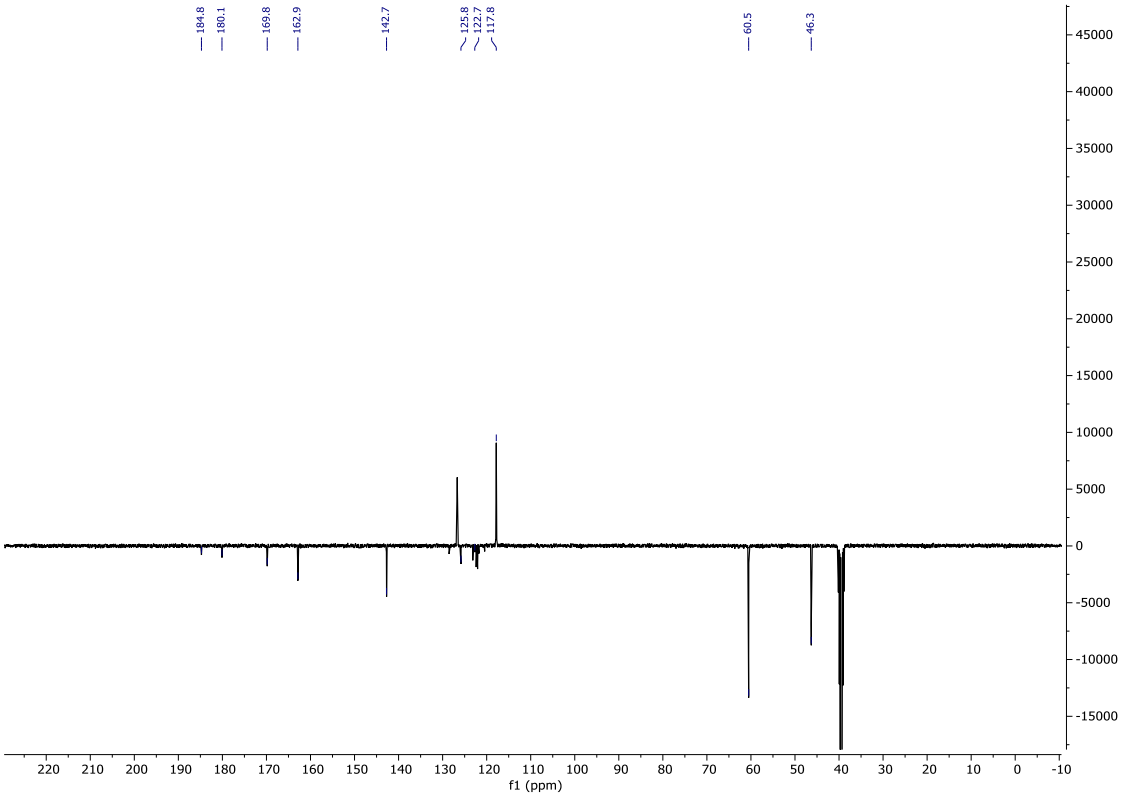
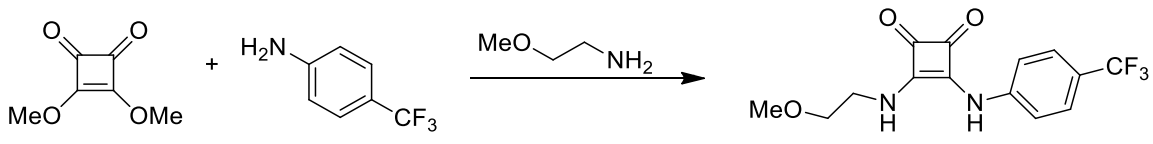


Figure 3.94. ^{13}C APT spectrum of compound **88** in DMSO solution.

Synthesis of compound 89

To a solution of 3,4-Dimethoxy-3-cyclobutene-1,2-dione (29 mg, 0.2 mmol) in methanol (5 ml) was added 4-(trifluoromethyl)aniline (25 µL, 0.2 mmol) and the solution stirred. 21 hours later, 2-methoxyethylamine was added (17 µL, 0.2 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 65%.



Scheme 3.20. Synthesis of compound **89**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.99 (s, 1H, *NH*-Ph); 7.88 (s, 1H, *NH*-CH_2); 7.67-7.62 (m, 4H, *Ph*); 3.78 (s, 2H, MeO-CH_2-*CH_2*-NH); 3.52 (t, 2H, MeO-*CH_2*-CH_2-NH, $^{3}J_{CP}$ = 5.0 Hz); 3.32 (s, 3H, *OMe*).

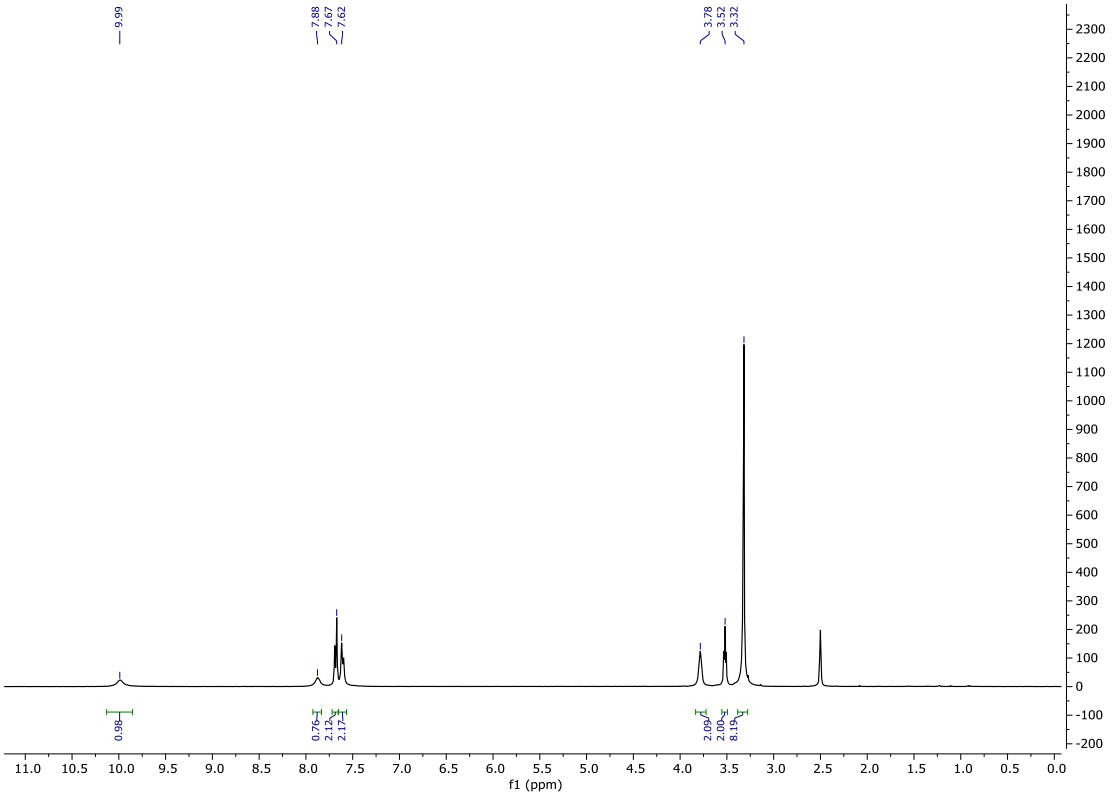


Figure 3.95. ^{1}H NMR spectrum of compound **89** in DMSO solution.

^{19}F ^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.1 (s, 3F, *CF_3*).

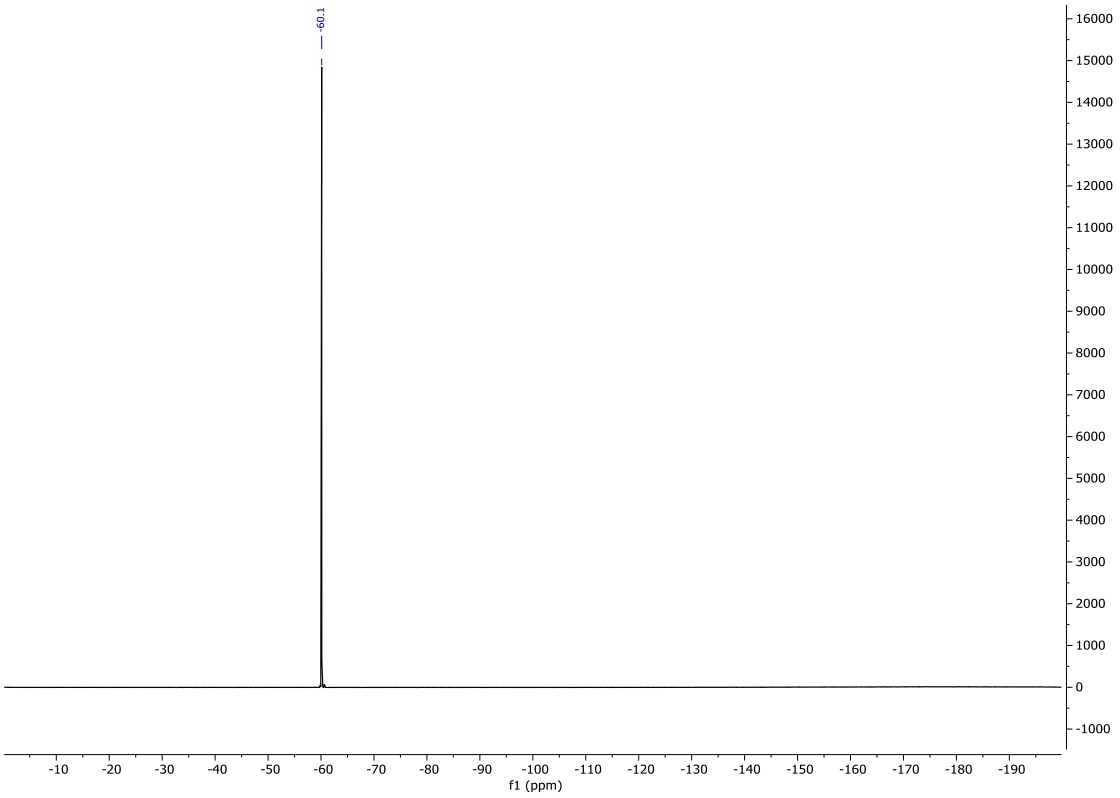


Figure 3.96. $^{19}F\{^{1}H\}$ NMR spectrum of compound **89** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.7 (s, 1C, *C*=*O*); 180.2 (s, 1C, *C*=*O*); 169.7 (s, 1C, Ph-C=*C*-*CH*$_2$); 162.9 (s, 1C, *Ph*-*C*=C-CH$_2$); 142.7 (s, 1C, *C*$_{ipso}$*Ph*); 126.7 (s, 2C, *C*$_{ortho}$Ph-CF$_3$); 124.5 (q, 2C, *CF*$_3$, $^{1}J_{CF}$ = 271.2 Hz); 122.3 (q, 1C, *C*$_{ipso}$*Ph*-*CF*$_3$, $^{2}J_{CP}$ = 31.9 Hz); 117.9 (s, 2C, *C*$_{meta}$Ph-CF$_3$); 71.3 (s, 2H, OMe-*CH*$_2$-CH$_2$-NH); 58.0 (s, 1C, *OMe*); 43.5 (s, 2H, OMe-CH$_2$-*CH*$_2$-NH).

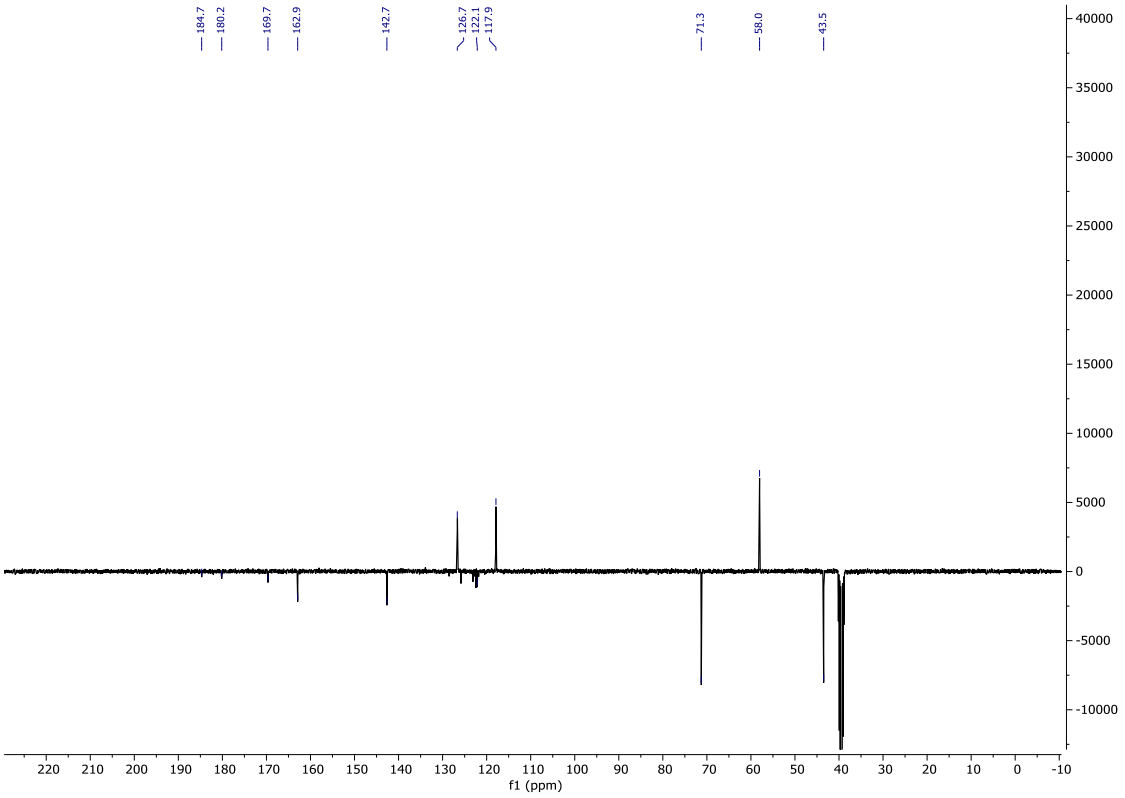
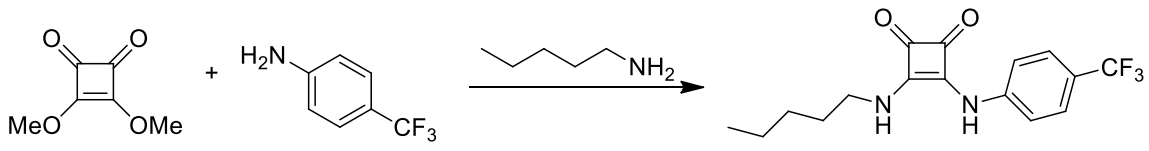


Figure 3.97. ^{13}C APT spectrum of compound **89** in DMSO solution.

Synthesis of compound 90

To a solution of 3,4-Dimethoxy-3-cyclobutene-1,2-dione (29 mg, 0.2 mmol) in methanol (5 ml) was added 4-(trifluoromethyl)aniline (25 µL, 0.2 mmol) and the solution stirred. 21 hours later, 1-pentamine was added (23 µL, 0.2 mmol) and the solution stirred for 24 h. The solution was concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid was collected and vacuum dried to give the product.

Yield: 84%.



Scheme 3.21. Synthesis of compound **90**.

^{1}H NMR (ppm) (400 MHz, DMSO): δ = 9.88 (s, 1H, *NH*-Ph); 7.72 (s, 1H, *NH*-CH_2); 7.66-7.61 (m, 4H, *Ph*); 3.59 (m, 2H, CH_3-CH_2-CH_2-CH_2-*CH_2*-NH); 1.57 (m, 2H, CH_3-

CH_2-CH_2-*CH_2*-CH_2-NH); 1.31 (m, 4H, CH_3-*CH_2*-*CH_2*-CH_2-CH_2-NH); 0.88 (t, 3H, *CH_3*-CH_2-CH_2-CH_2-CH_2-NH, $^3J_{HH}$ = 6.5 Hz).

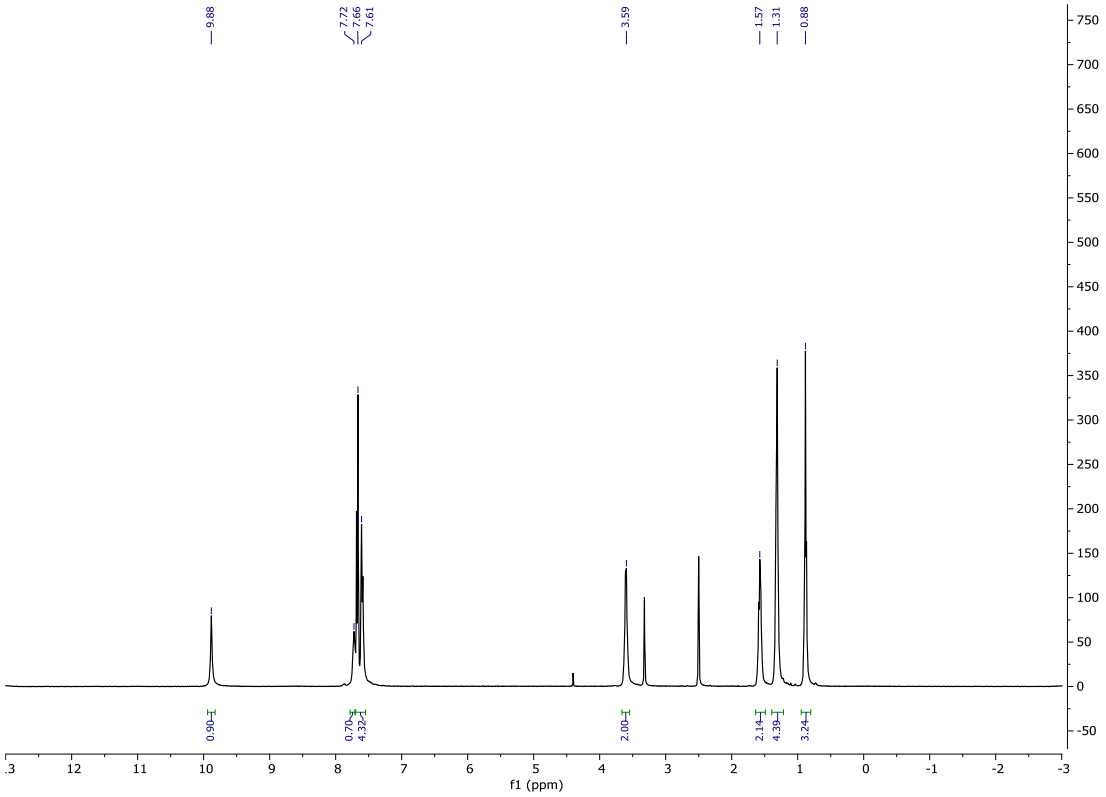


Figure 3.98. ^{1}H NMR spectrum of compound **90** in DMSO solution.

^{19}F{^{1}H} NMR (ppm) (376 MHz, DMSO): δ = -60.1 (s, 3F, *CF_3*).

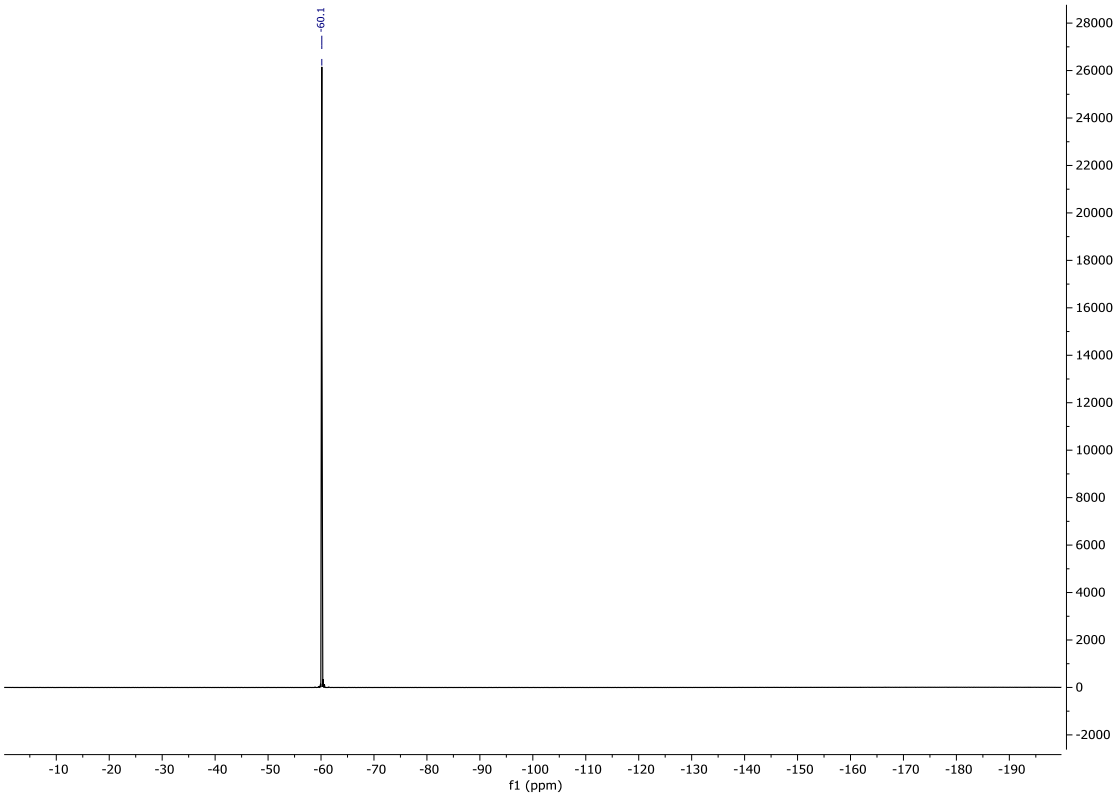


Figure 3.99. ^{19}F {^{1}H} NMR spectrum of compound **90** in DMSO solution.

^{13}C APT (ppm) (100 MHz, DMSO): δ = 184.7 (s, 1C, *C*=*O*); 180.0 (s, 1C, *C*=*O*); 169.7 (s, 1C, Ph-C=*C*-*CH*$_2$); 162.8 (s, 1C, *Ph*-*C*=C-CH$_2$); 142.6 (s, 1C, *C*$_{ipso}$-*Ph*); 126.6 (s, 2C, *C*$_{ortho}$Ph-CF$_3$); 124.5 (q, 2C, *CF*$_3$, $^{1}J_{CF}$ = 271.1 Hz); 122.3 (q, 1C, *C*$_{ipso}$-*Ph*-*CF*$_3$, $^{2}J_{CP}$ = 32.1 Hz); 117.9 (s, 2C, *C*$_{meta}$Ph-CF$_3$); 43.7 (s, 1C, CH$_3$-CH$_2$-CH$_2$-CH$_2$-*CH*$_2$-NH); 30.2 (s, 1C, CH$_3$-CH$_2$-CH$_2$-*CH*$_2$-CH$_2$-NH); 28.0, 21.7 (s, 2C, CH$_3$-*CH*$_2$-*CH*$_2$-CH$_2$-CH$_2$-NH); 13.8 (s, 1C, *CH*$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH).

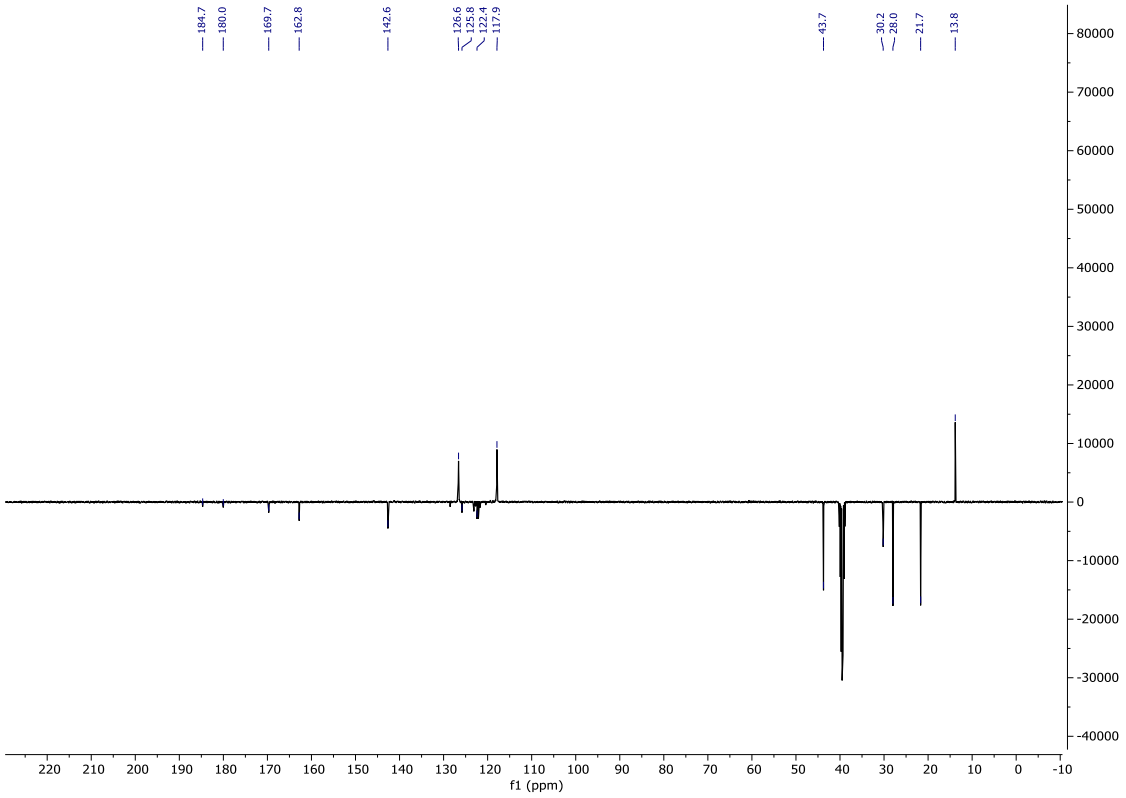


Figure 3.100.: ^{13}C APT spectrum of compound **90** in DMSO solution.