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Electronic Supplementary Information

Synthesis and characterization of new square planar heteroleptic cationic complexes [Ni(II) β-oxodithioester-dppe]$^{+}$; their use as catalyst for Chan–Lam coupling

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Figure S1. Simulated (in red, generated from single crystal data) and experimental (in black) PXRD patterns of **2-5**

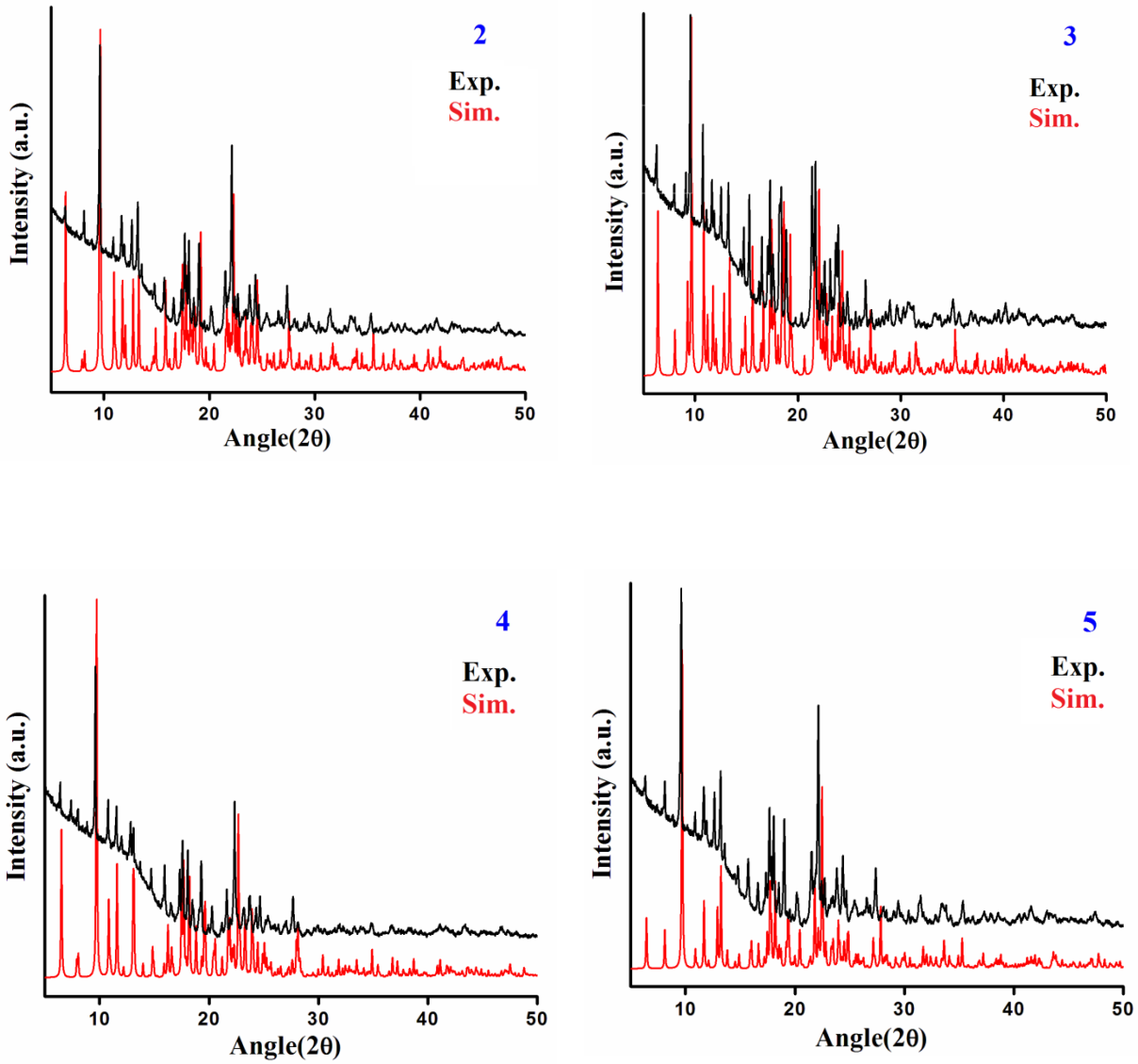
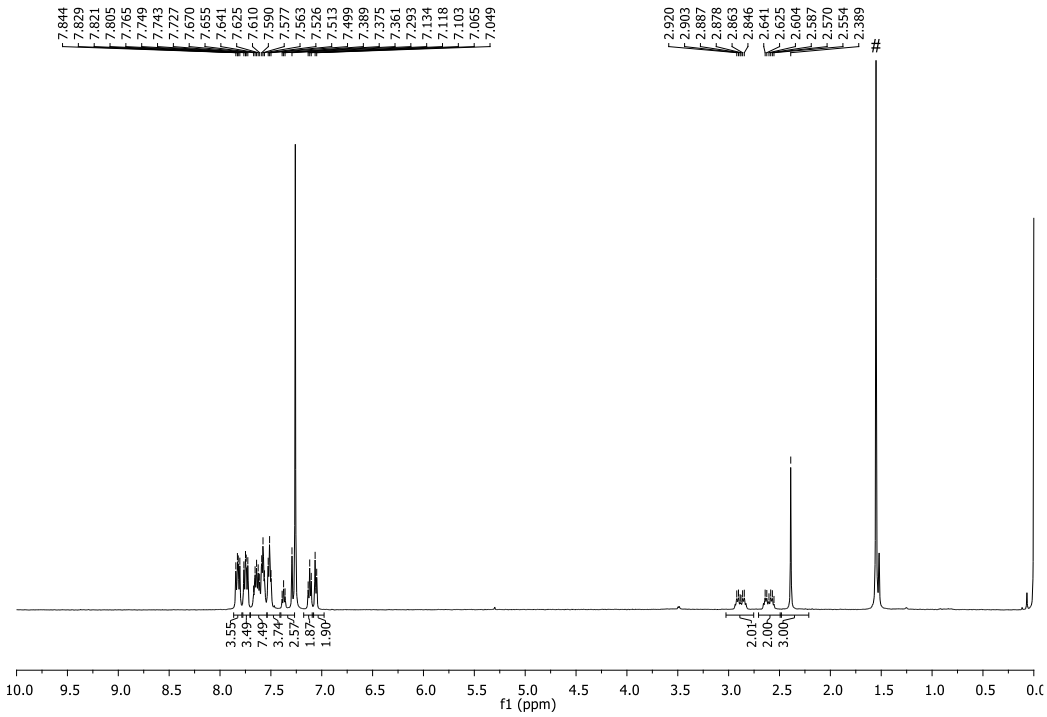
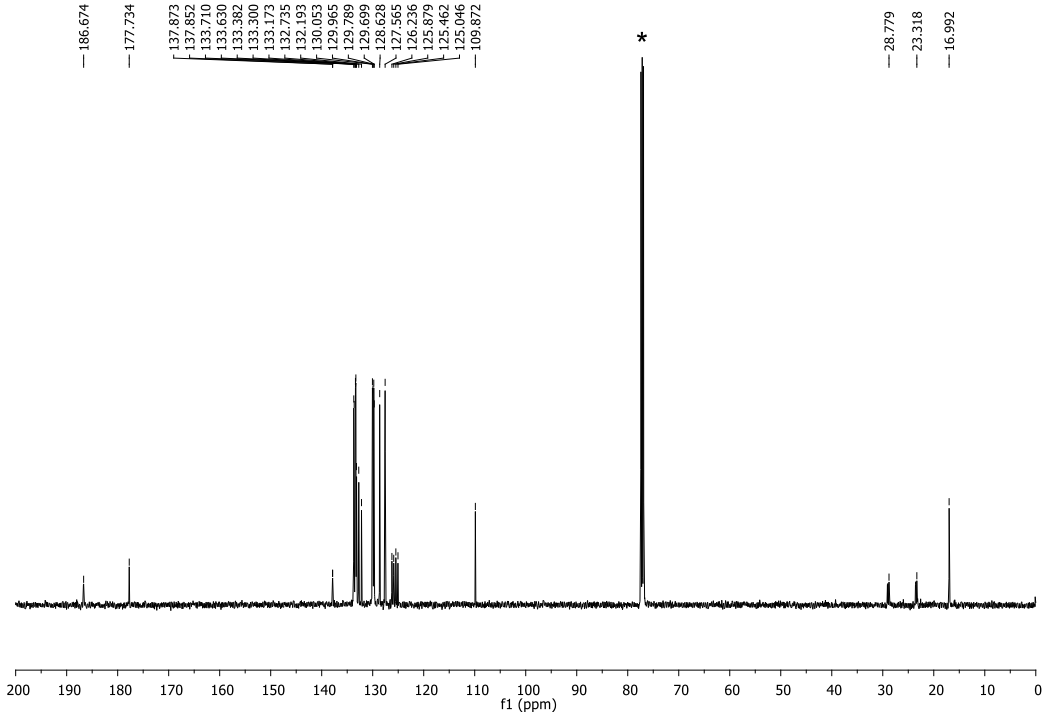


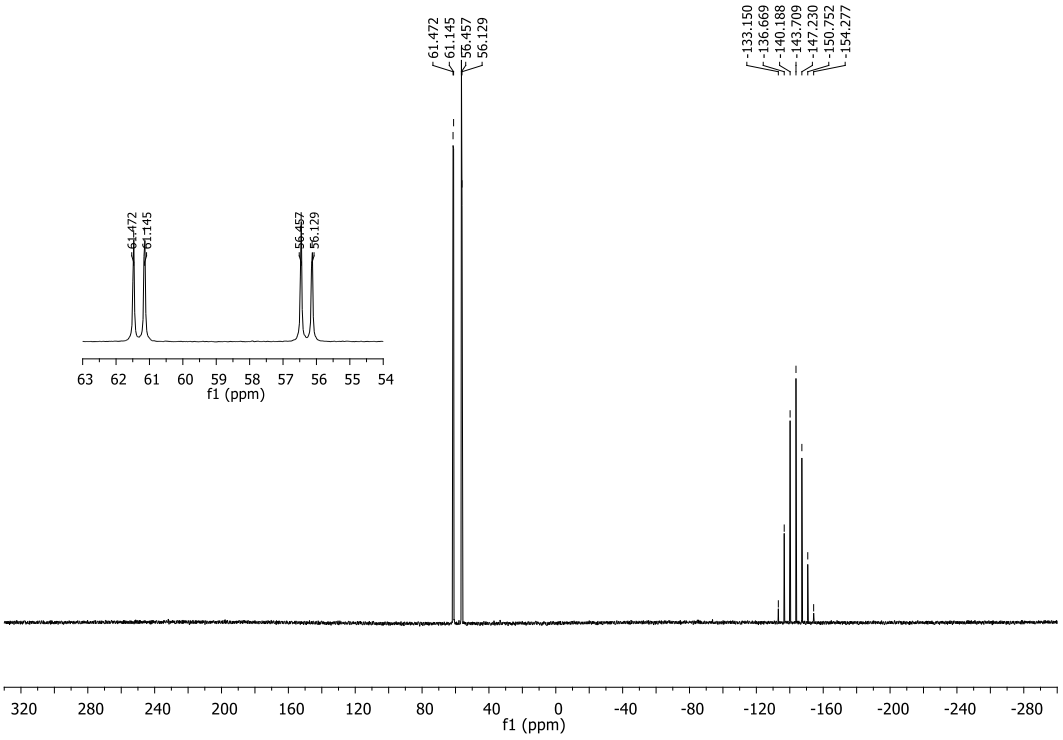
Figure S2. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra of complexes **1**-**6**.



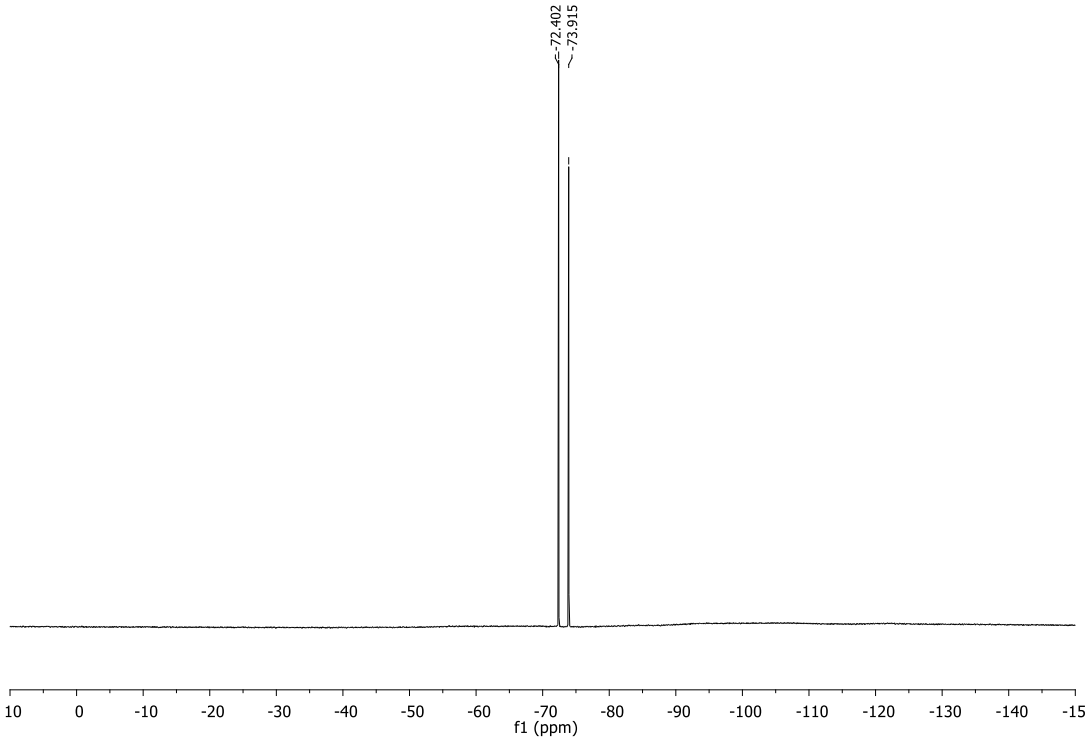
Spectrum 1: 500 MHz ^{1}H NMR spectrum of Complex **1** in $CDCl_3$. # represents the solvent impurity H_2O.



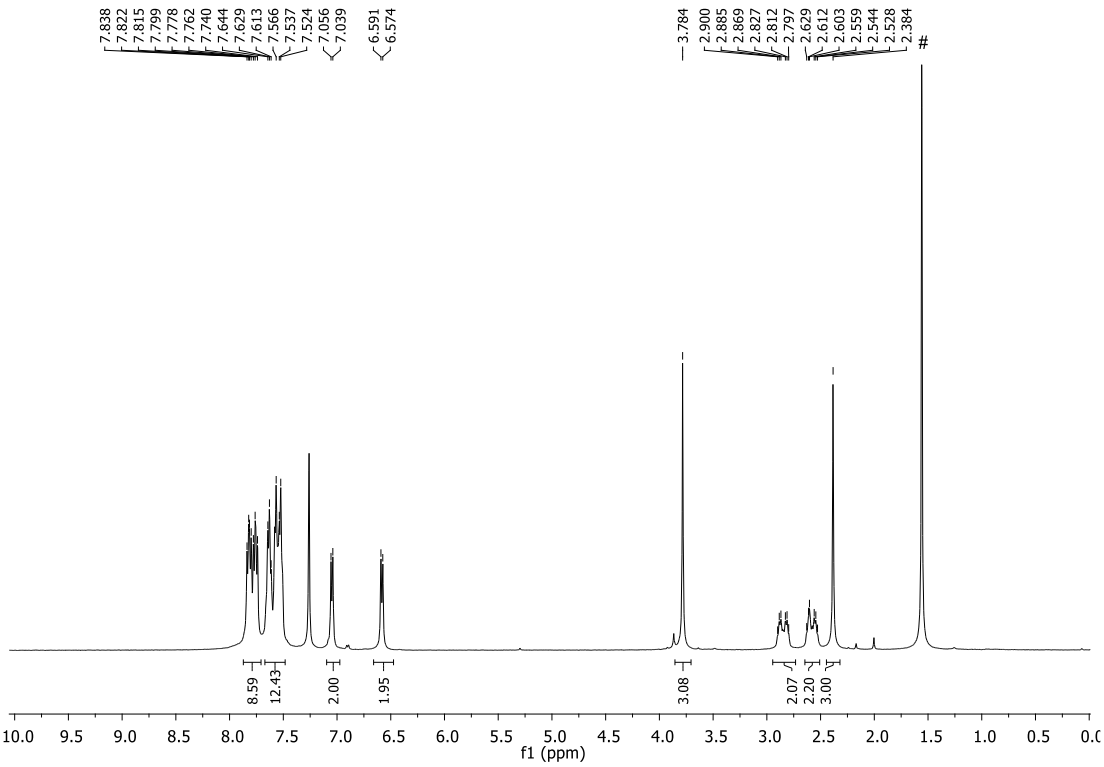
Spectrum 2: 125 MHz ^{13}C NMR spectrum of Complex **1** in $CDCl_3$ (*).



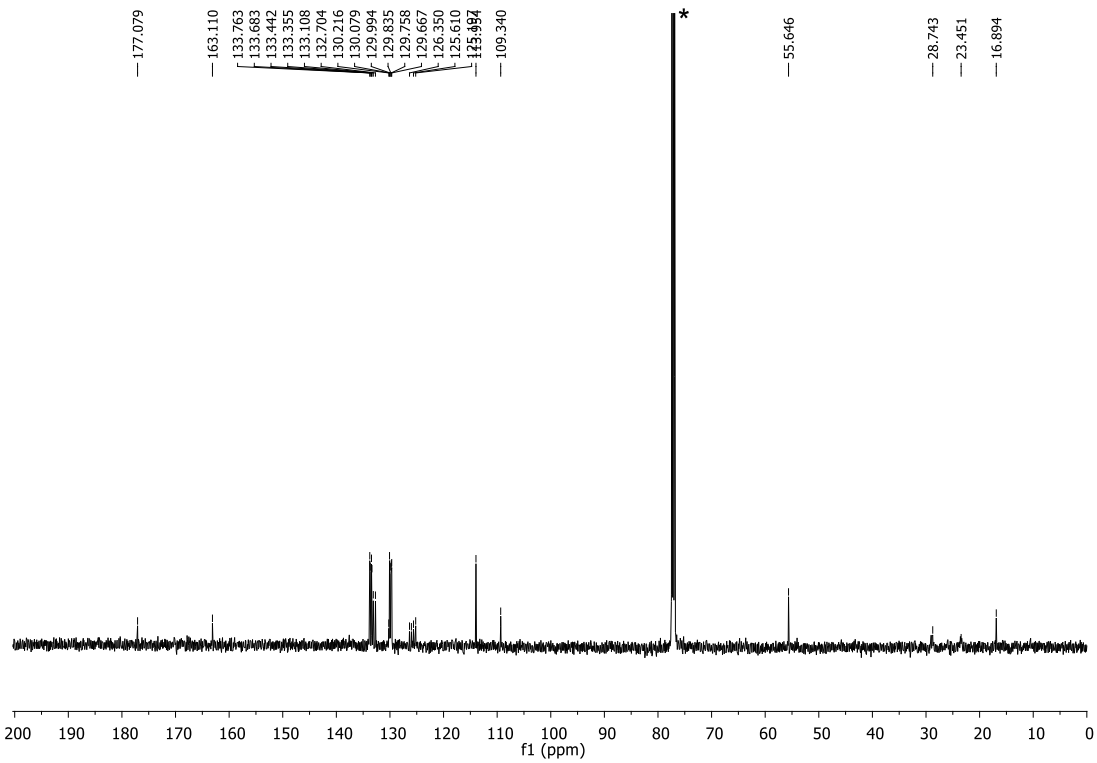
Spectrum 3: 202 MHz ^{31}P NMR spectrum of Complex **1** in $CDCl_3$.



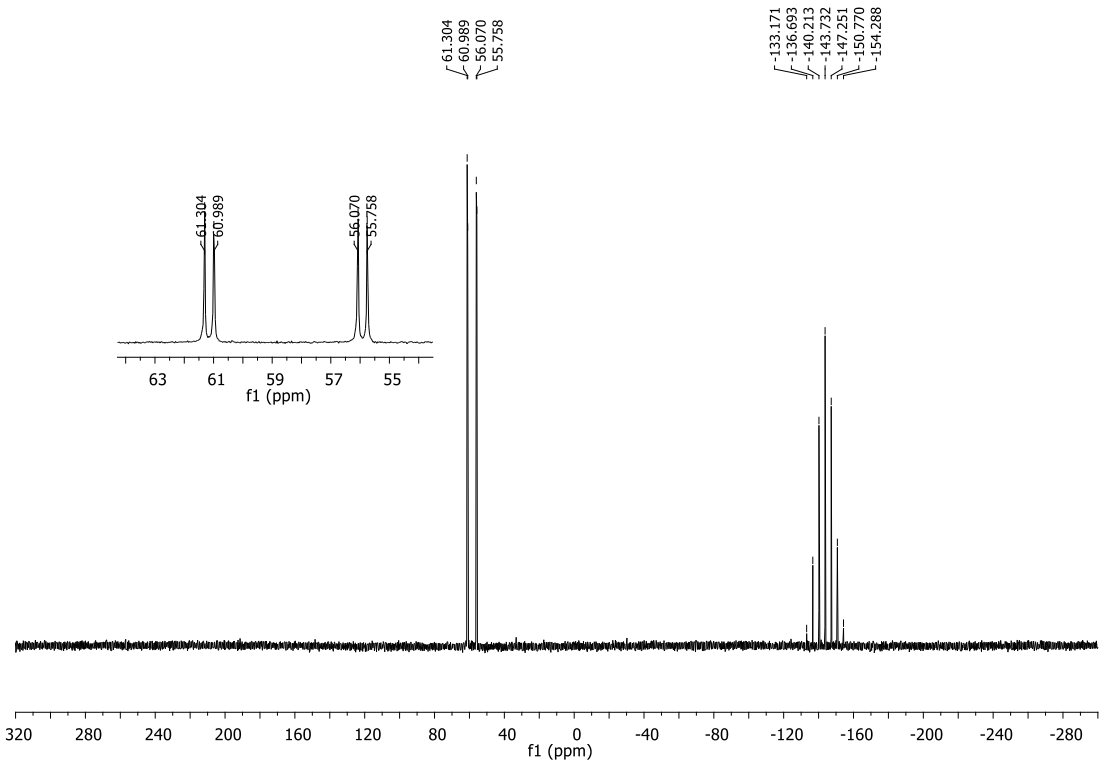
Spectrum 4: 470 MHz ^{19}F NMR spectrum of Complex **1** in $CDCl_3$.



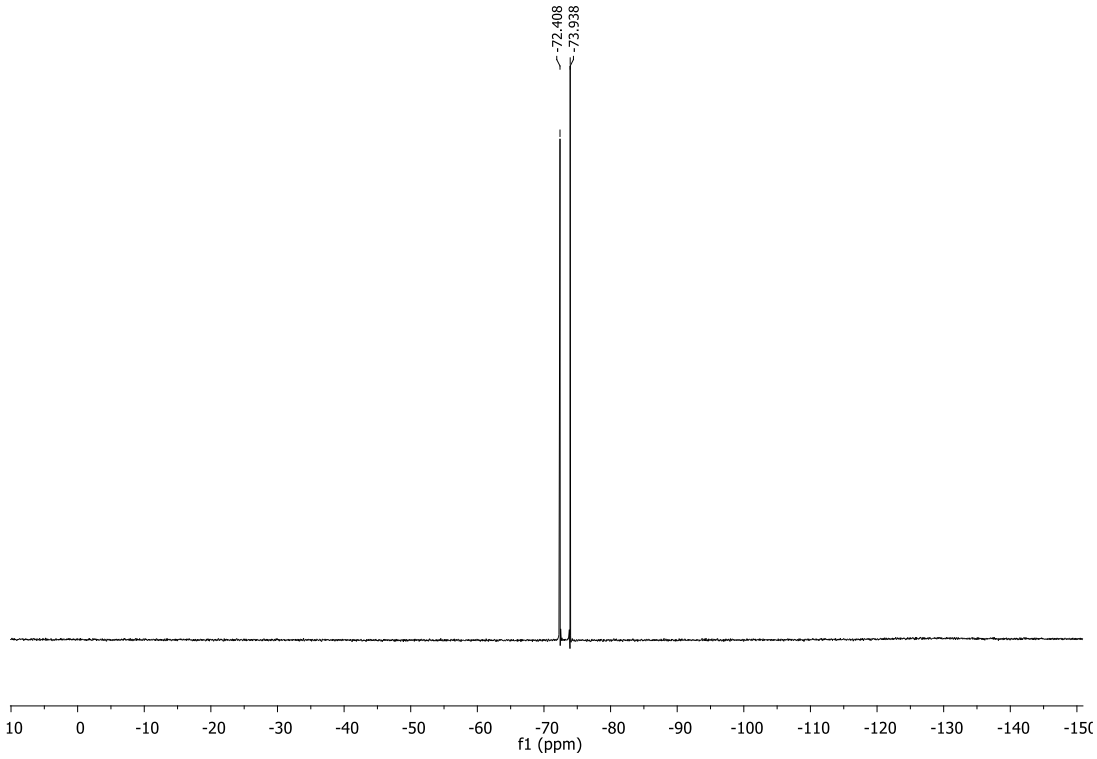
Spectrum 5: 500 MHz ^{1}H NMR spectrum of Complex **2** in $CDCl_3$. # represents the solvent impurity H_2O.



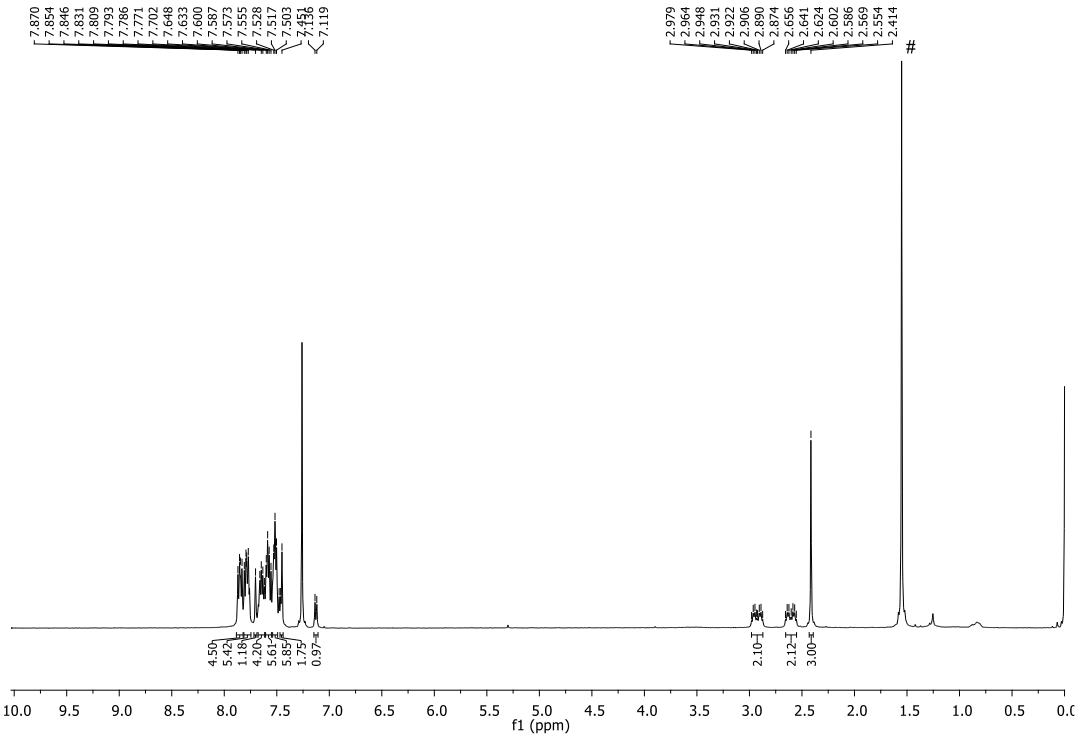
Spectrum 6: 125 MHz ^{13}C NMR spectrum of Complex **2** in $CDCl_3$ (*).



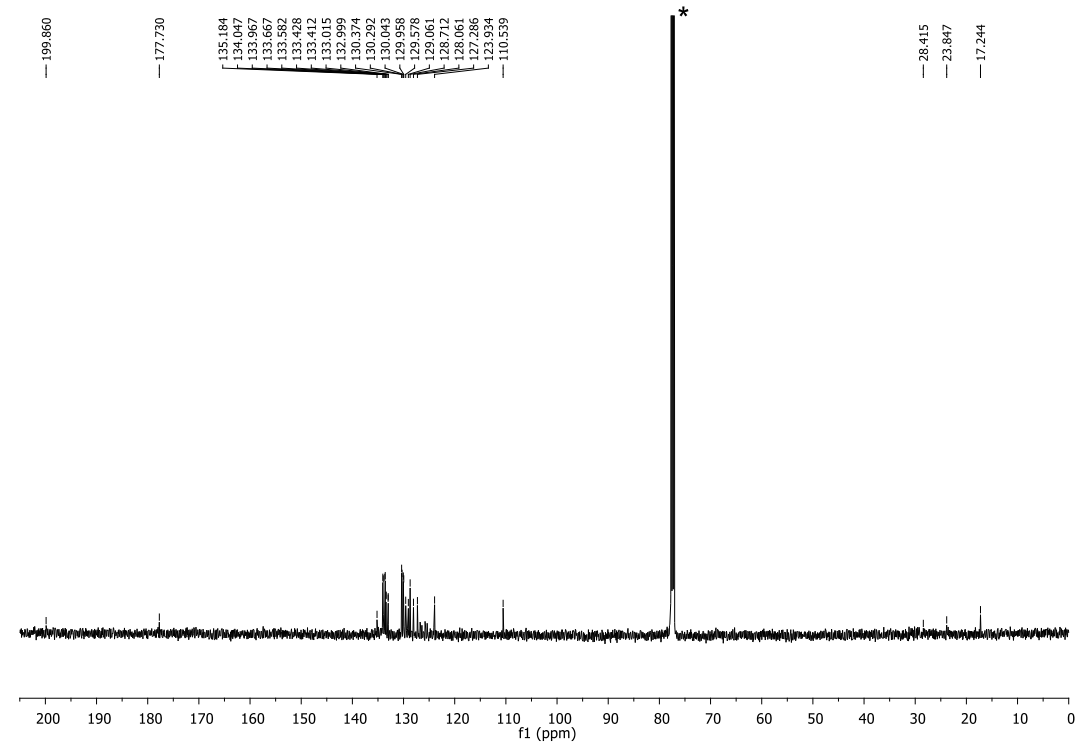
Spectrum 7: 202 MHz ^{31}P NMR spectrum of Complex **2** in $CDCl_3$.



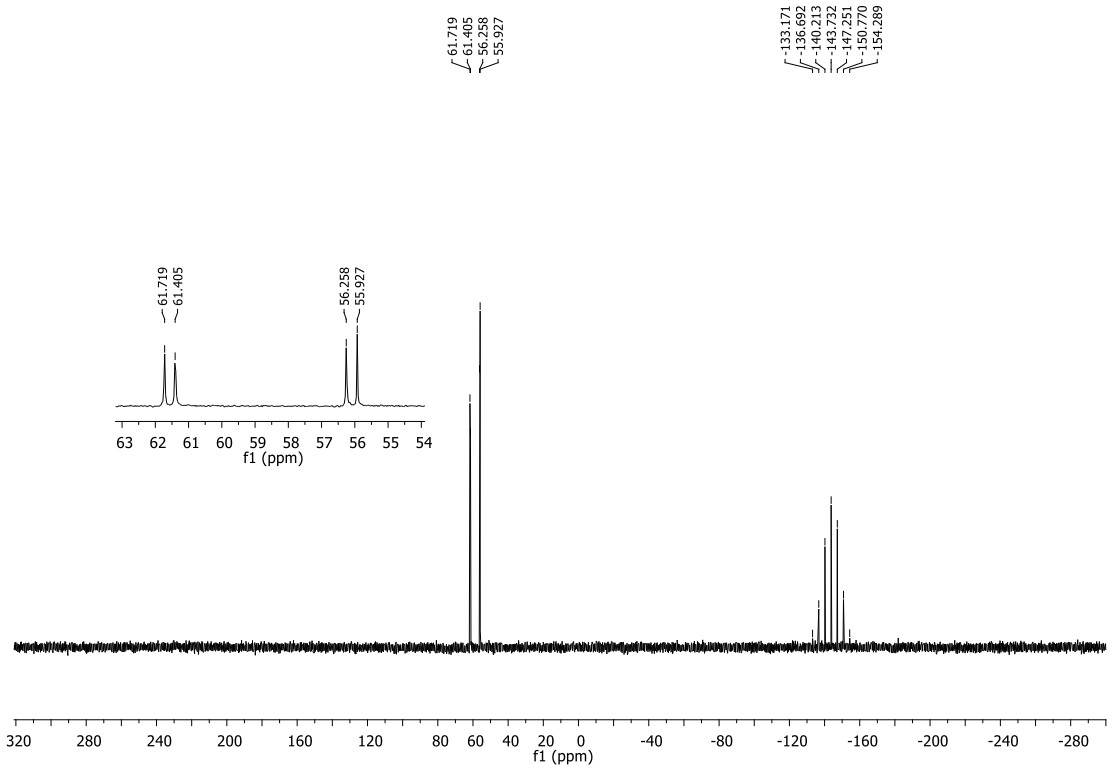
Spectrum 8: 470 MHz ^{19}F NMR spectrum of Complex **2** in $CDCl_3$.



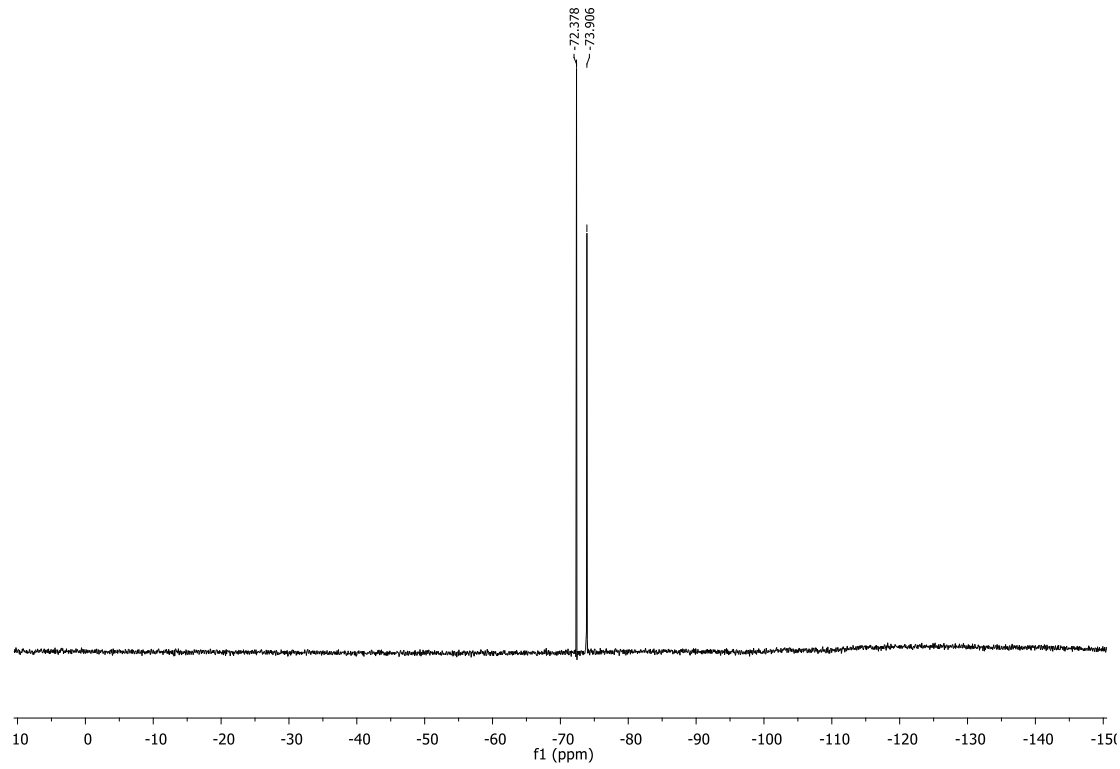
Spectrum 9: 500 MHz ^{1}H NMR spectrum of Complex **3** in $CDCl_3$. # represents the solvent impurity H_2O.



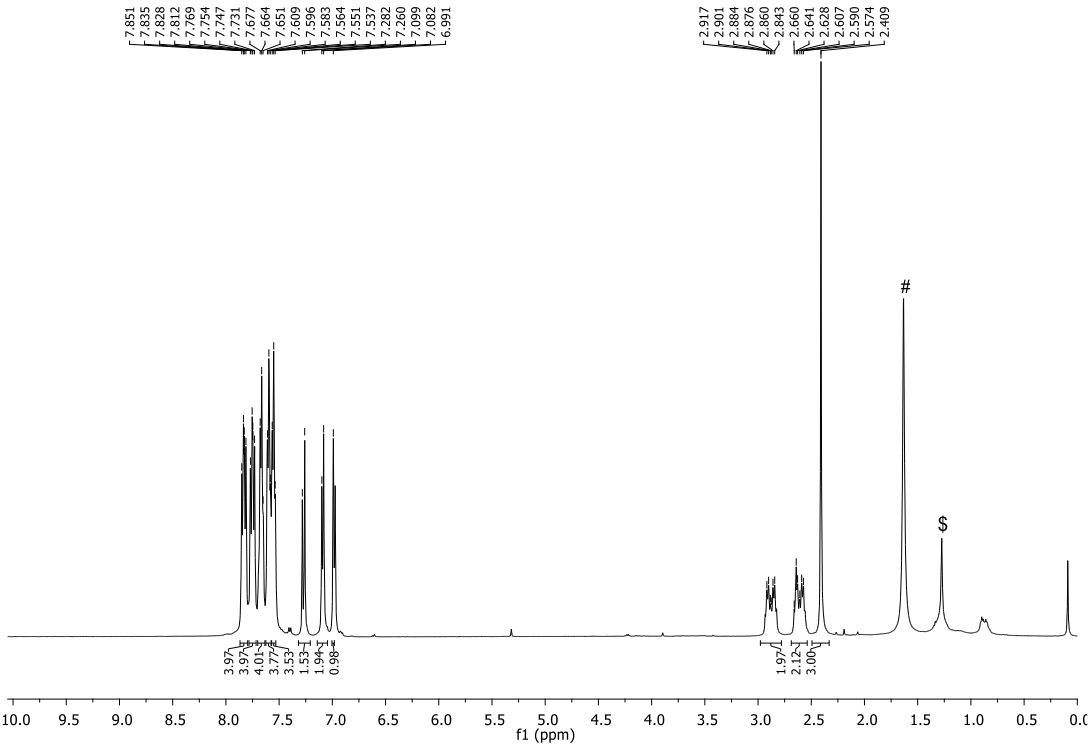
Spectrum 10: 125 MHz ^{13}C NMR spectrum of Complex **3** in $CDCl_3$ (*).



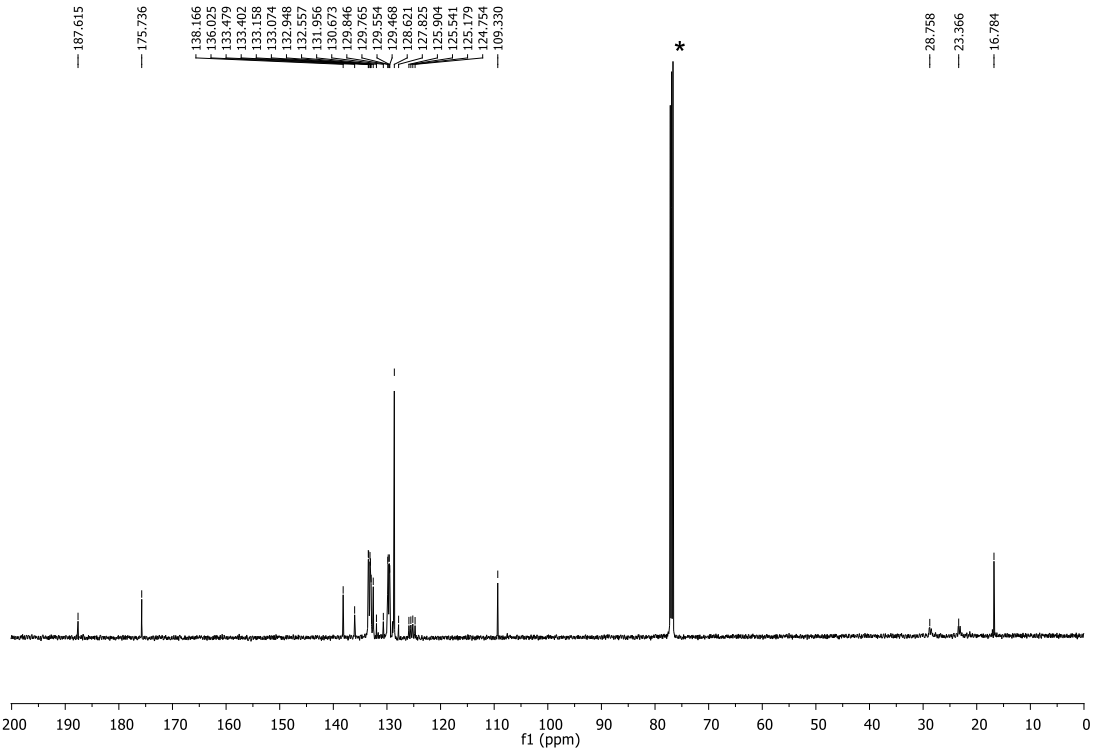
Spectrum 11: 202 MHz ^{31}P NMR spectrum of Complex **3** in $CDCl_3$.



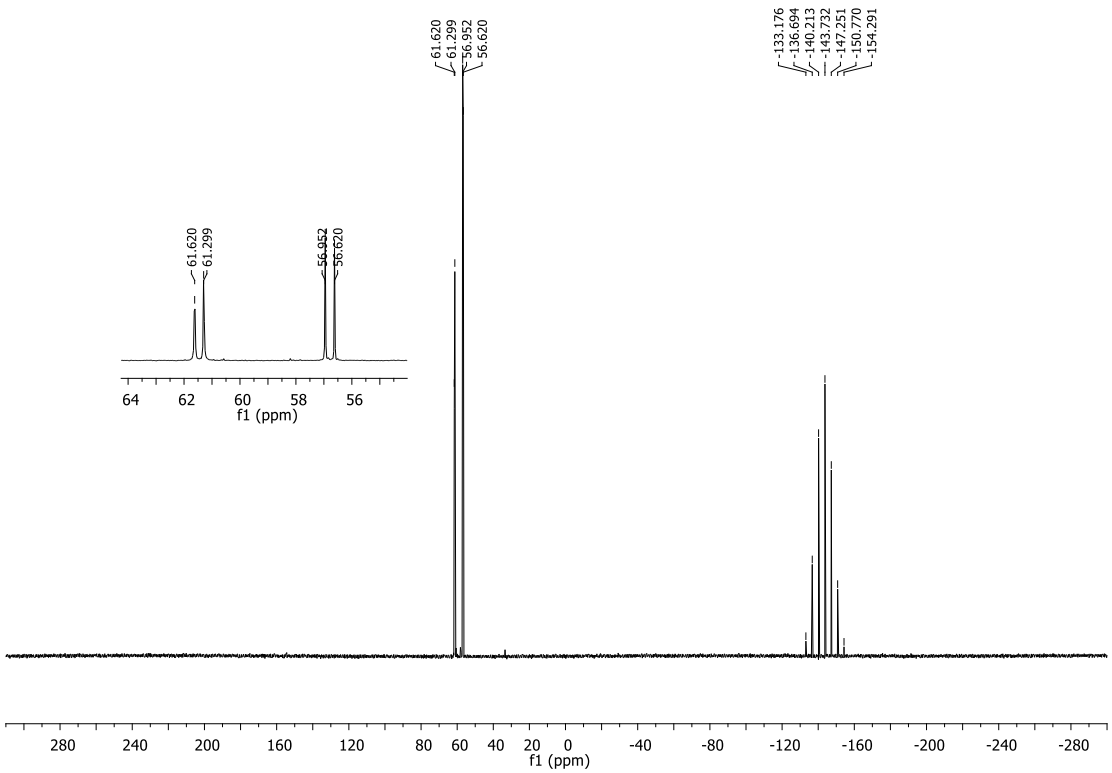
Spectrum 12: 470 MHz ^{19}F NMR spectrum of Complex **3** in $CDCl_3$.



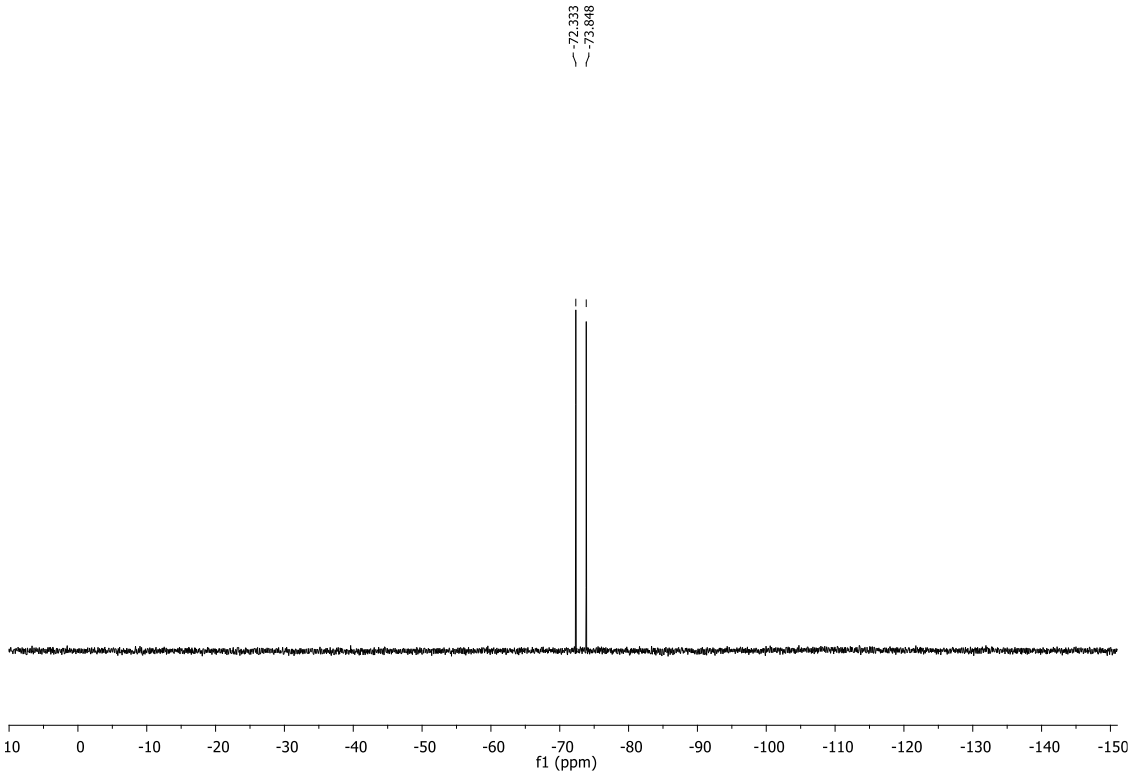
Spectrum 13: 500 MHz ^{1}H NMR spectrum of Complex **4** in $CDCl_3$. # and $ represent the solvent impurity H_2O and grease respectively.



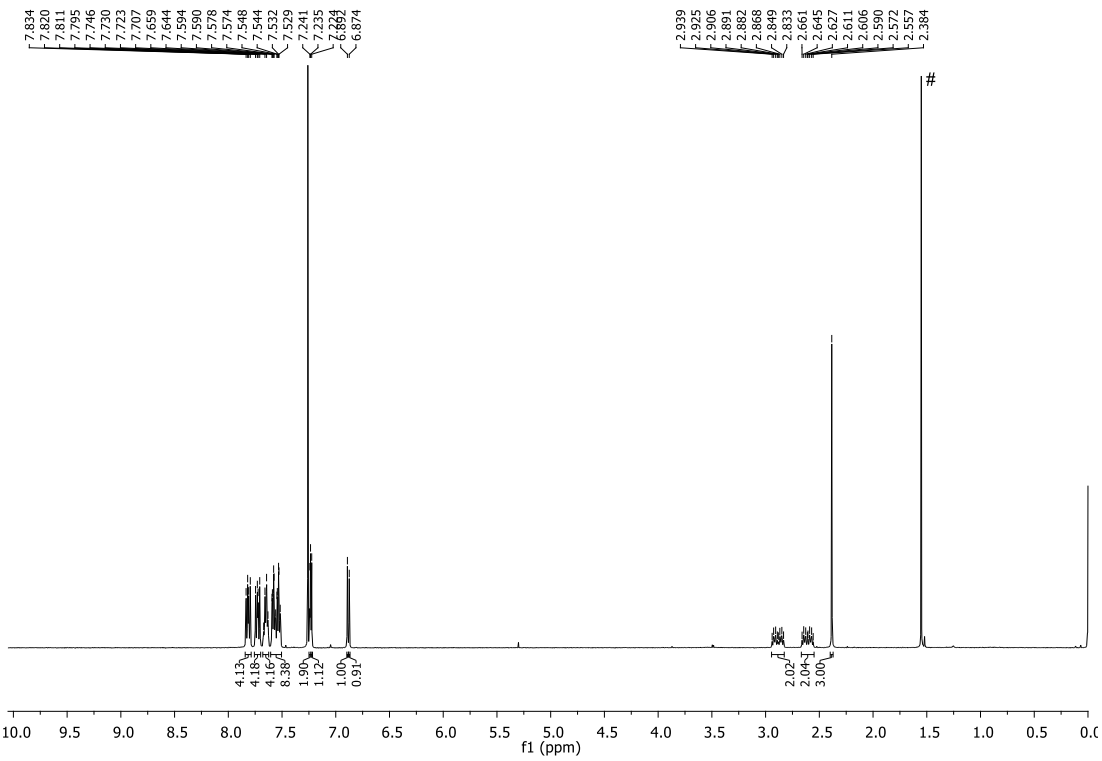
Spectrum 14: 125 MHz ^{13}C NMR spectrum of Complex **4** in $CDCl_3$ (*).



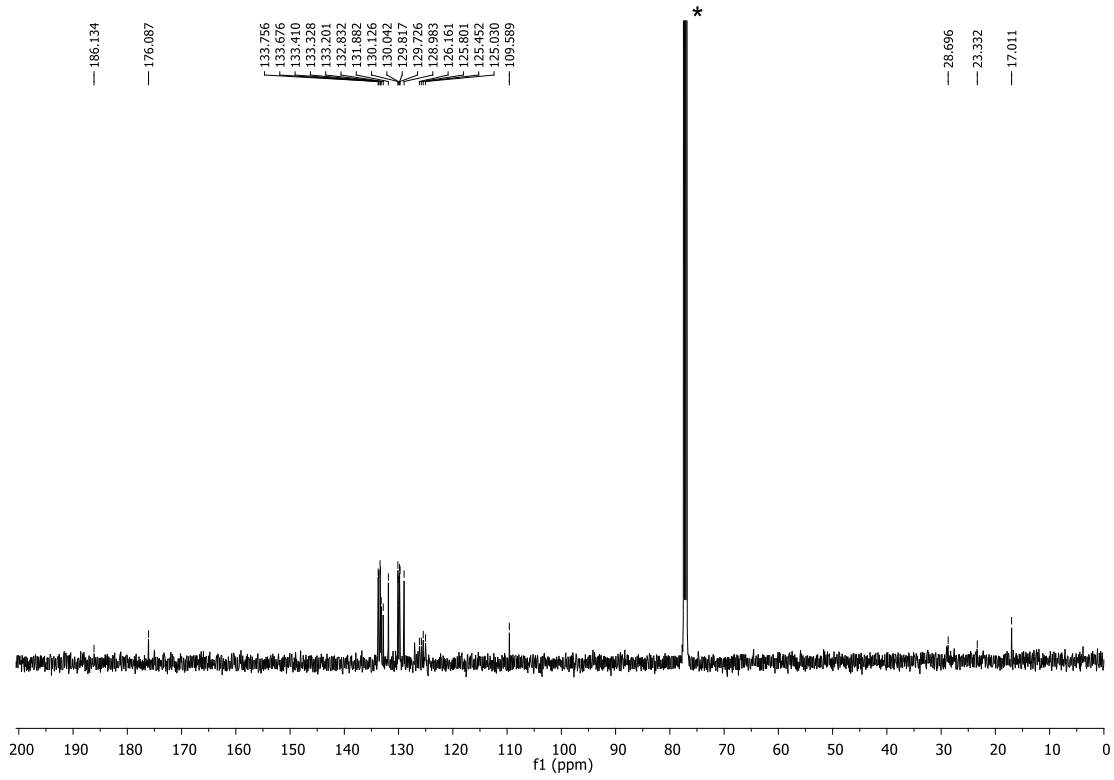
Spectrum 15: 202 MHz ^{31}P NMR spectrum of Complex **4** in $CDCl_3$.



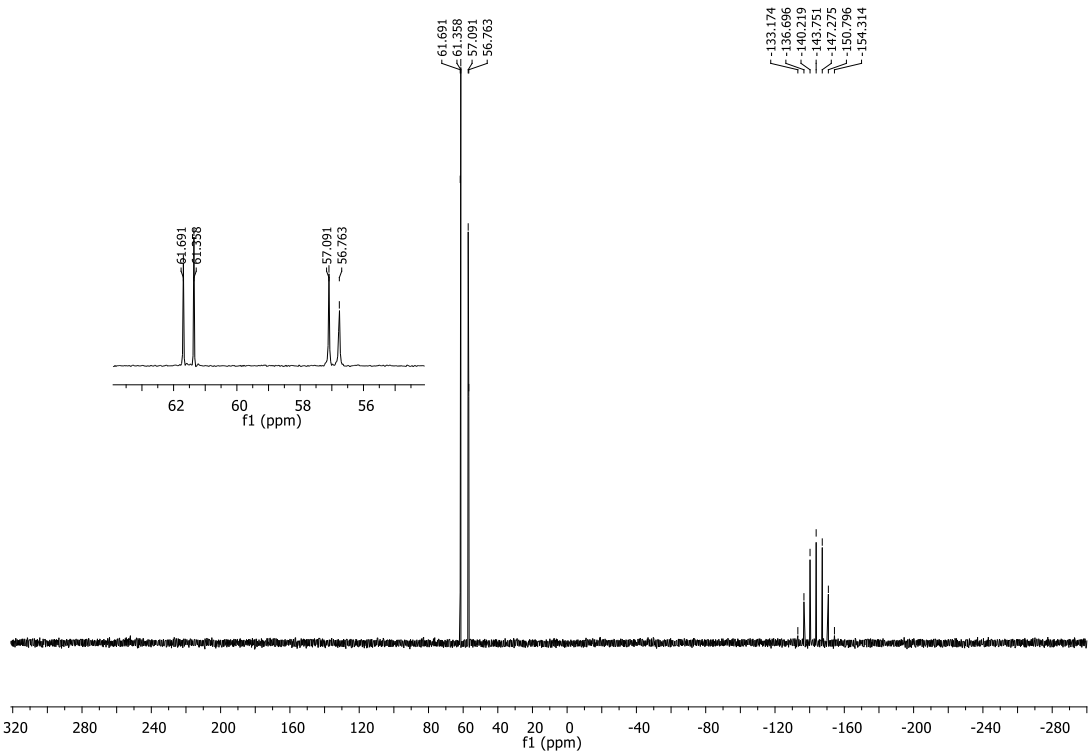
Spectrum 16: 470 MHz ^{19}F NMR spectrum of Complex **4** in $CDCl_3$.



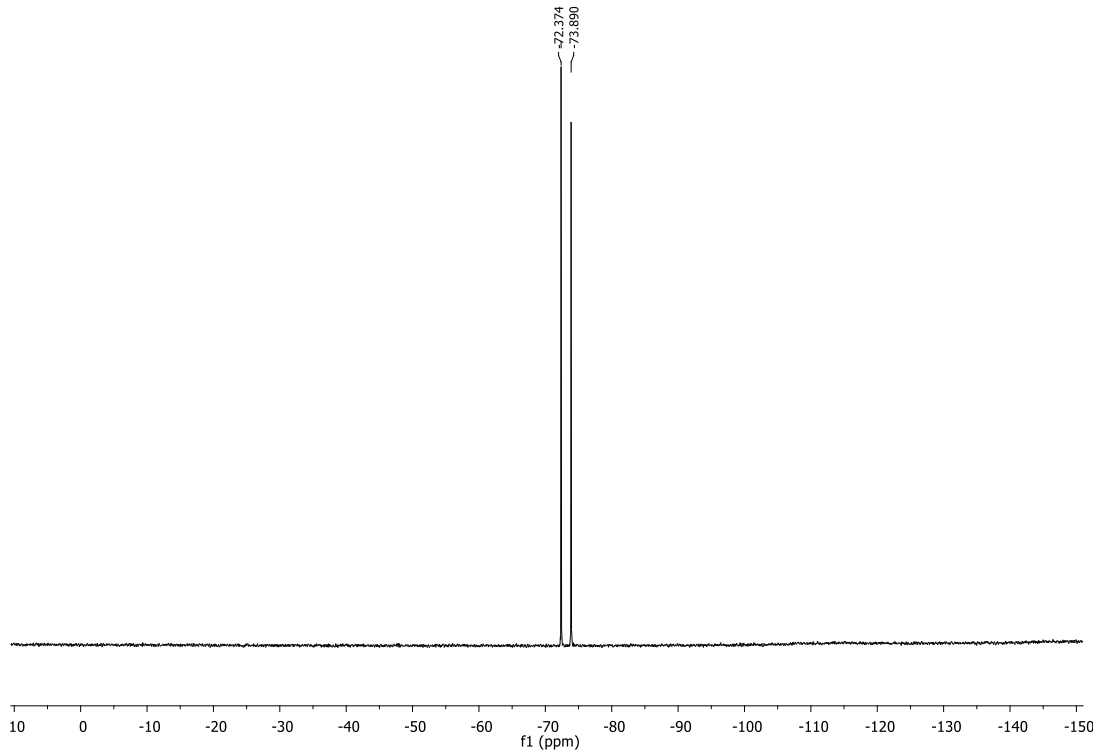
Spectrum 17: 500 MHz ^{1}H NMR spectrum of Complex **5** in $CDCl_3$. # represents the solvent impurity H_2O.



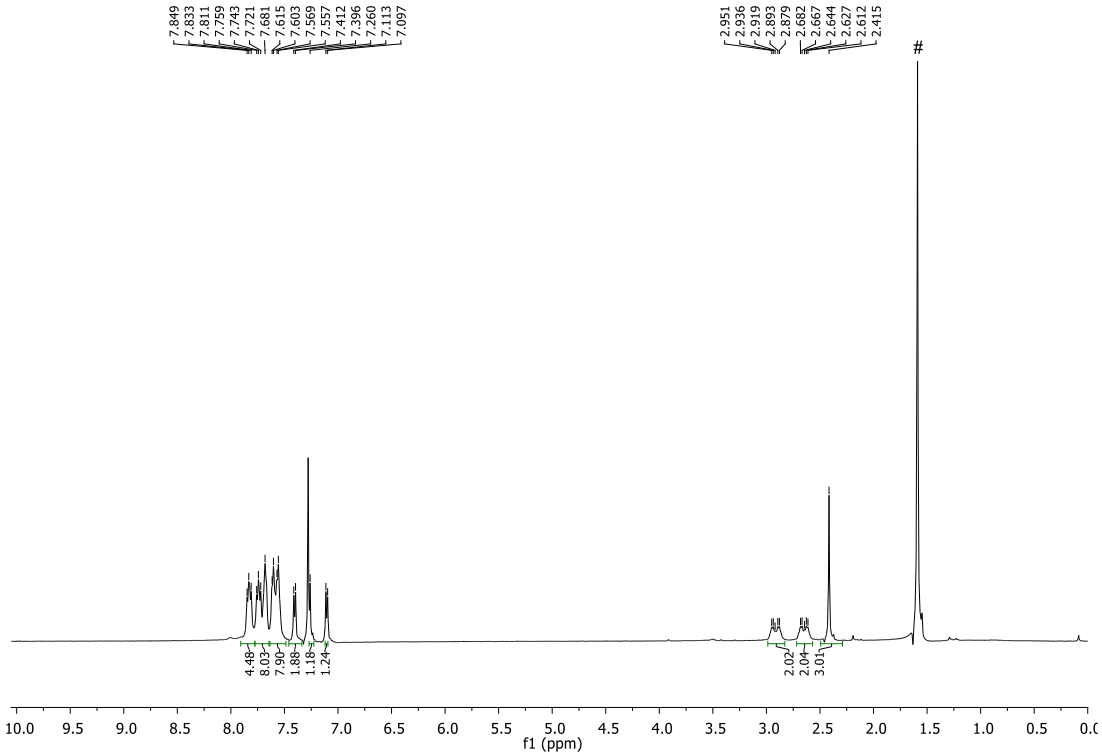
Spectrum 18: 125 MHz ^{13}C NMR spectrum of Complex **5** in $CDCl_3$ (*).



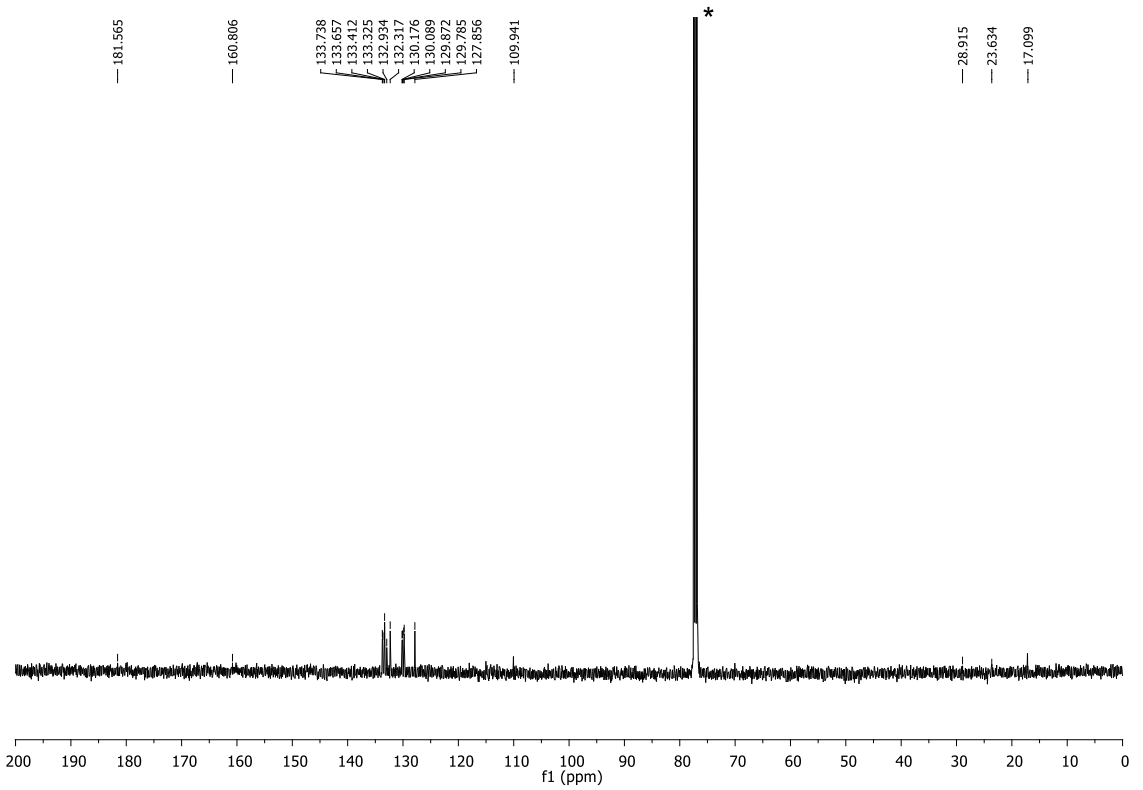
Spectrum 19: 202 MHz ^{31}P NMR spectrum of Complex **5** in $CDCl_3$.



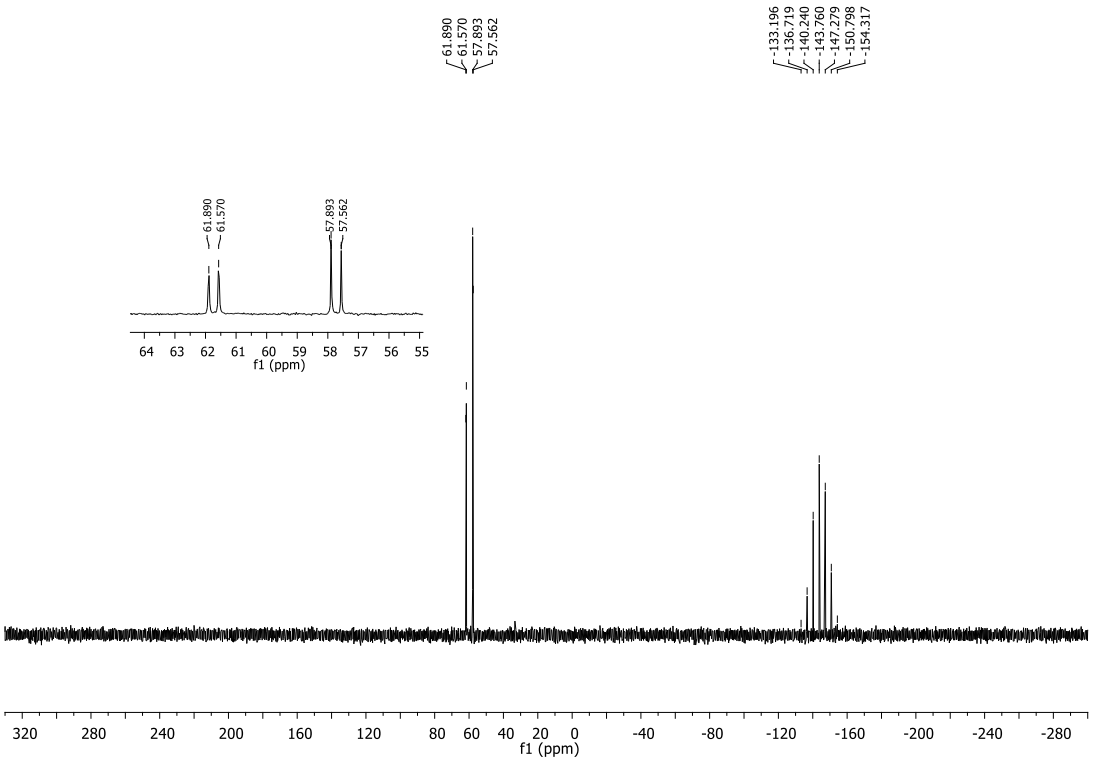
Spectrum 20: 470 MHz ^{19}F NMR spectrum of Complex **5** in $CDCl_3$.



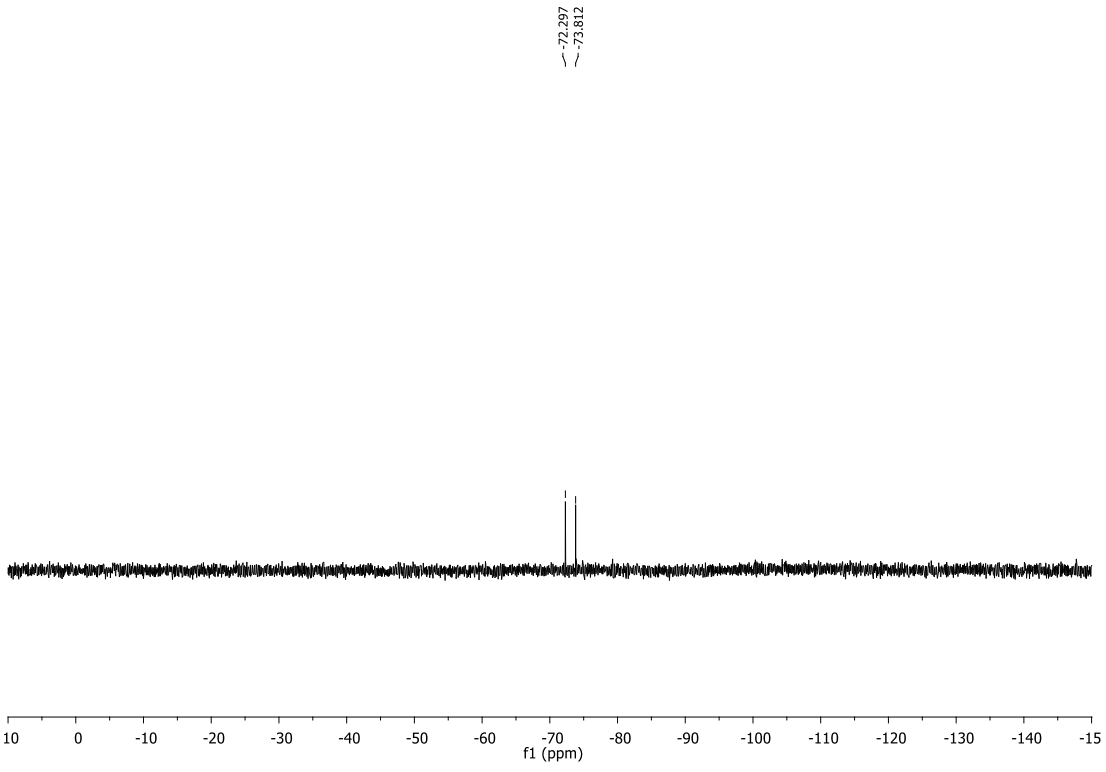
Spectrum 21: 500 MHz ^{1}H NMR spectrum of Complex **6** in $CDCl_3$. # represents the solvent impurity H_2O.



Spectrum 22: 125 MHz ^{13}C NMR spectrum of Complex **6** in $CDCl_3$ (*).



Spectrum 23: 202 MHz ^{31}P NMR spectrum of Complex **6** in $CDCl_3$.



Spectrum 24: 470 MHz ^{19}F NMR spectrum of Complex **6** in $CDCl_3$.

Figure S3. ESI-MS spectrum of complex **1**. Experimental (bottom) and simulated (top) isotopic peak patterns corresponding to cation $[M\text{-}PF_6]^{+1}$.

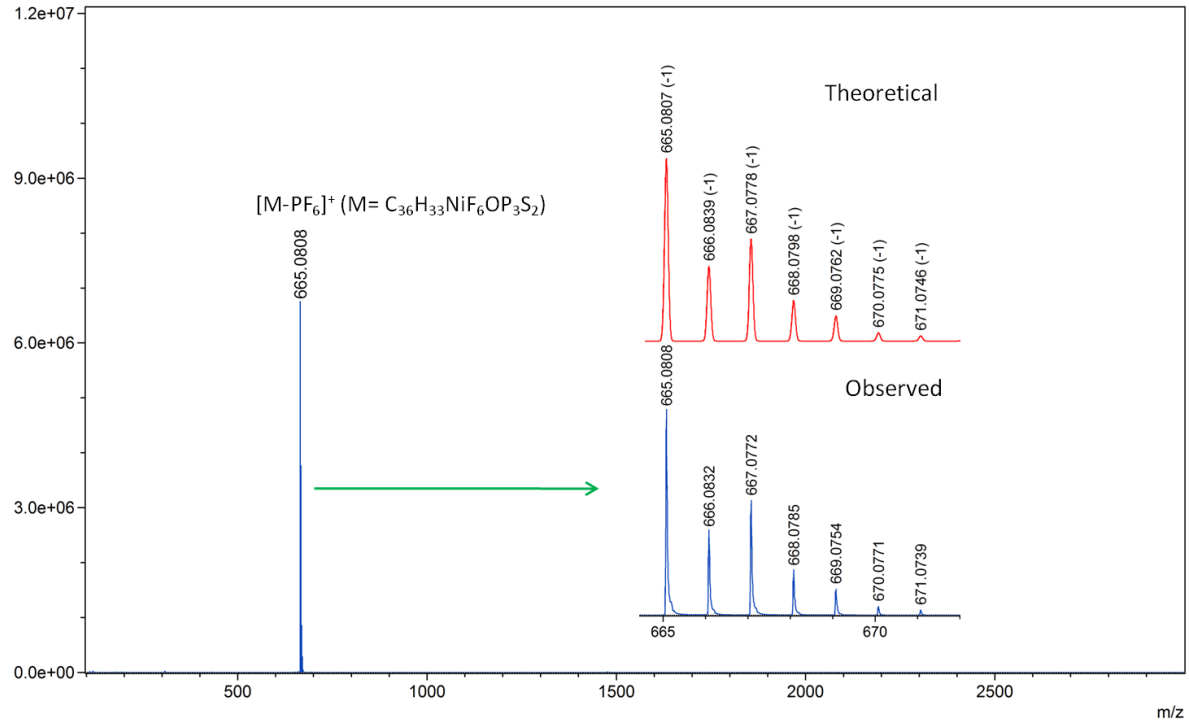


Figure S4. ESI-MS spectrum of complex **2**. Experimental (bottom) and simulated (top) isotopic peak patterns corresponding to cation $[M\text{-}PF_6]^{+1}$.

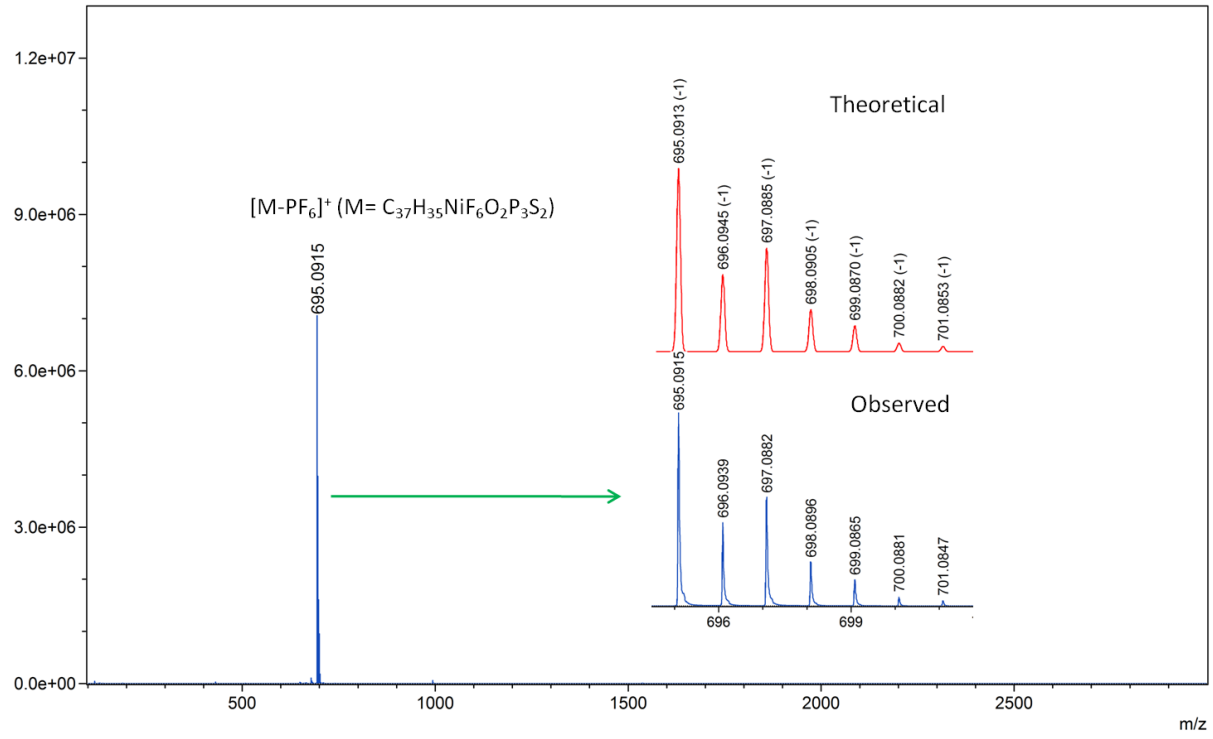


Figure S5. ESI-MS spectrum of complex **3**. Experimental (bottom) and simulated (top) isotopic peak patterns corresponding to cation $[M\text{-}PF_6]^{+1}$.

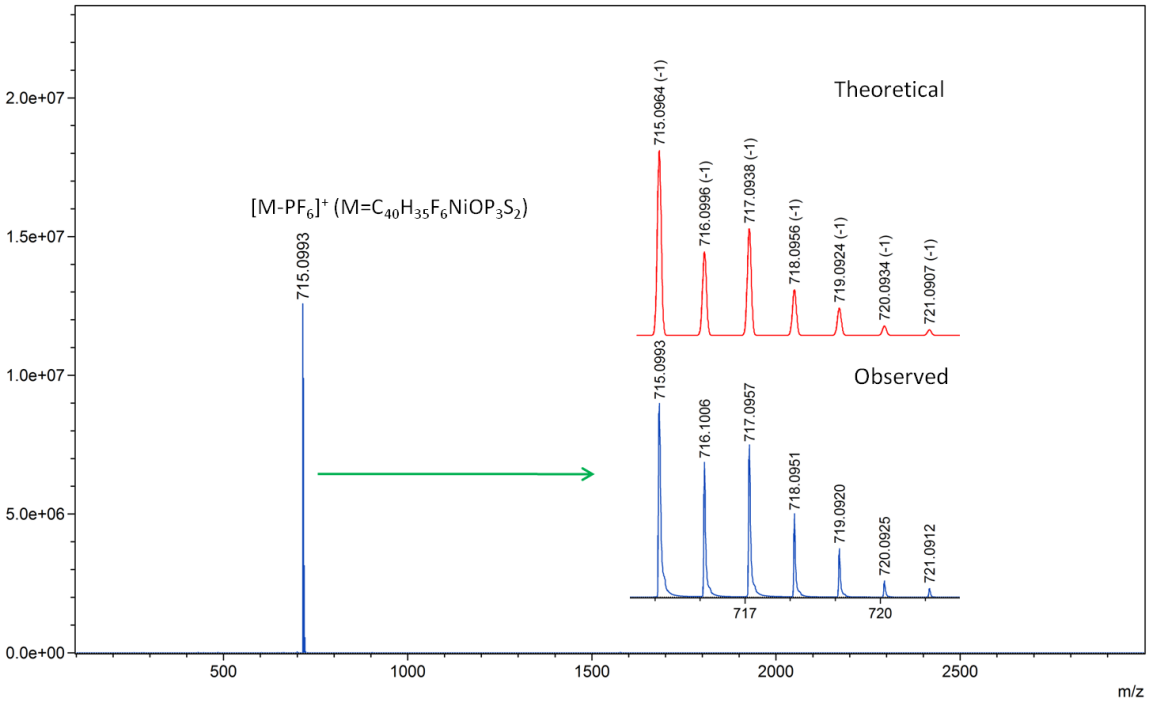


Figure S6. ESI-MS spectrum of complex **4**. Experimental (bottom) and simulated (top) isotopic peak patterns corresponding to cation $[M\text{-}PF_6]^{+1}$.

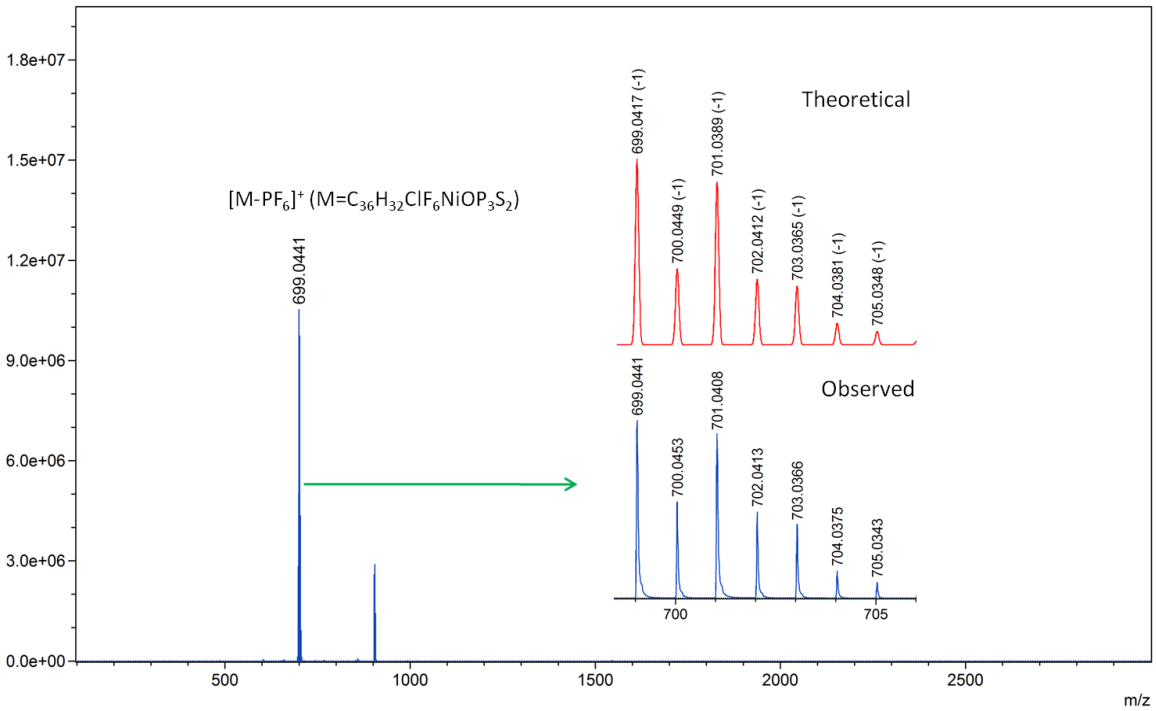


Figure S7. ESI-MS spectrum of complex **5**. Experimental (bottom) and simulated (top) isotopic peak patterns corresponding to cation $[M\text{-}PF_6]^{+1}$.

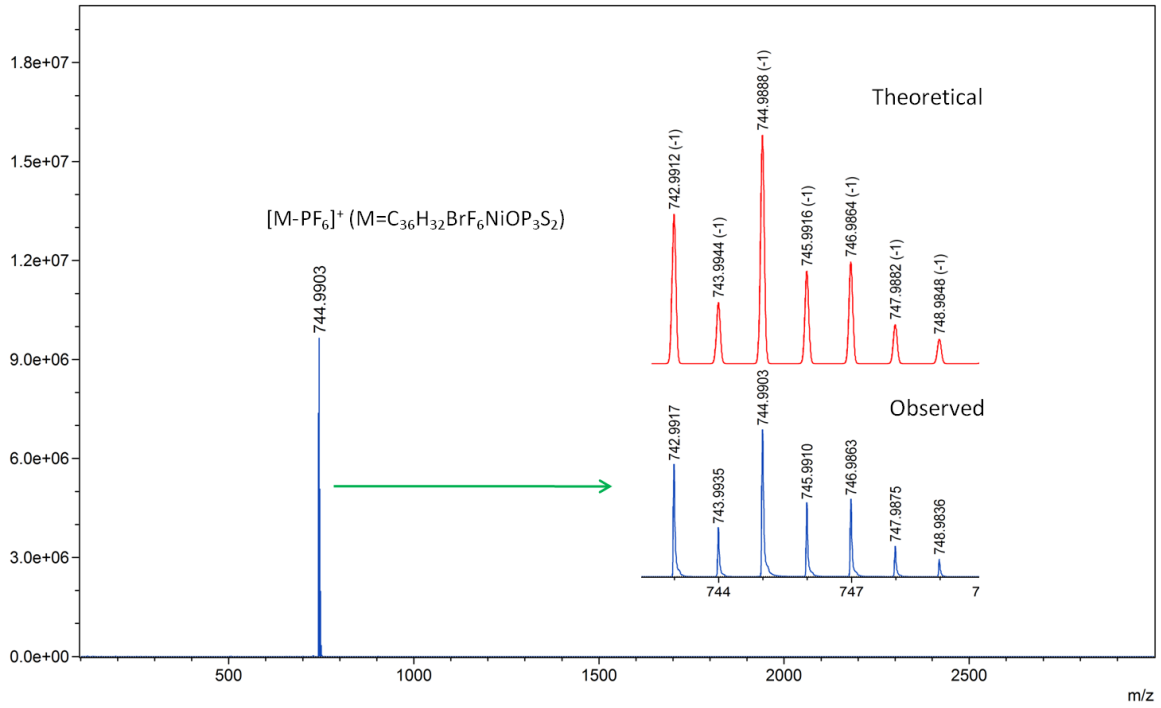


Figure S8. ESI-MS spectrum of complex **6**. Experimental (bottom) and simulated (top) isotopic peak patterns corresponding to cation $[M\text{-}PF_6]^{+1}$.

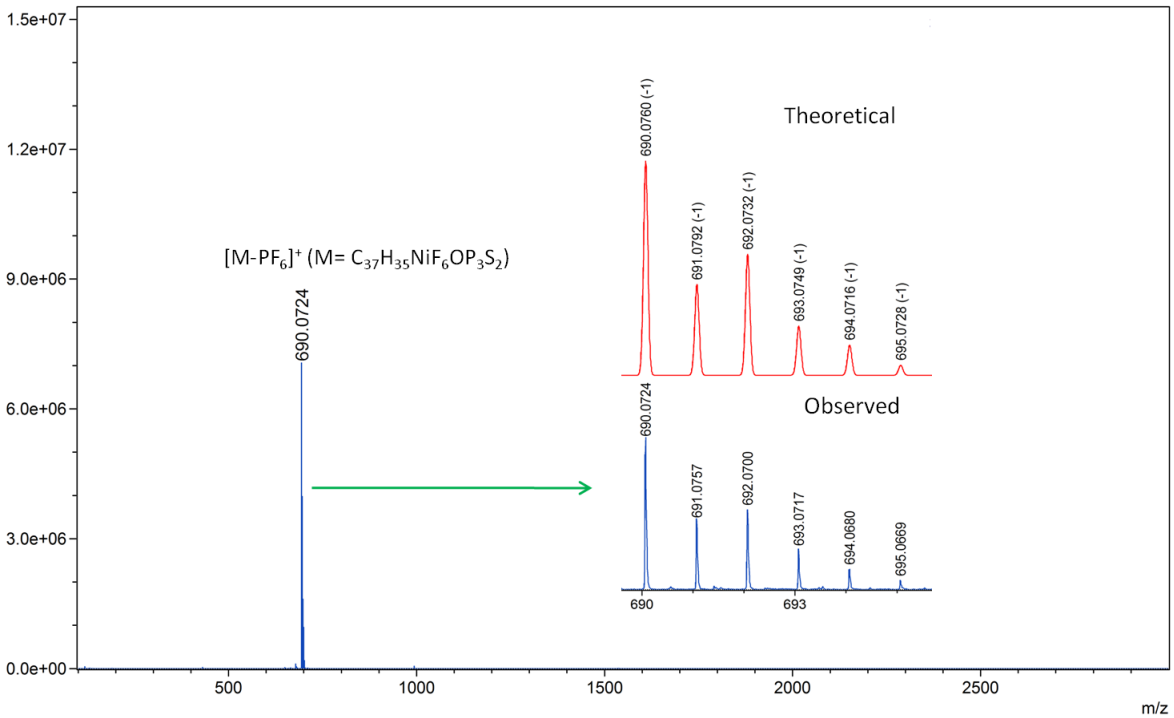
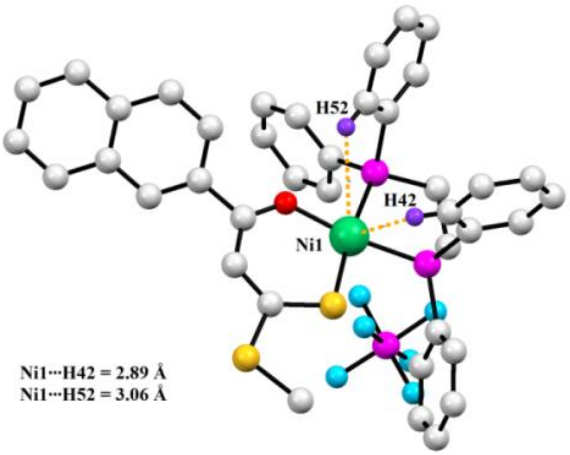
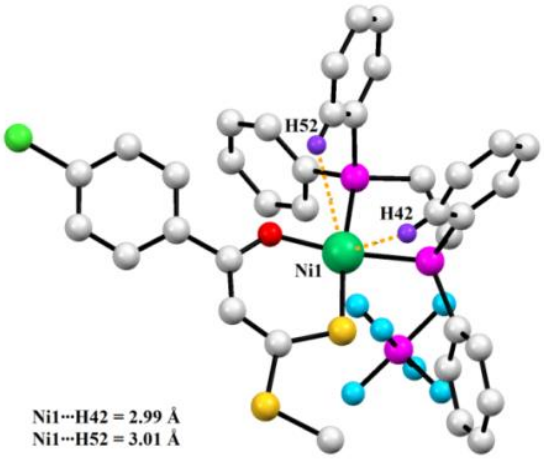


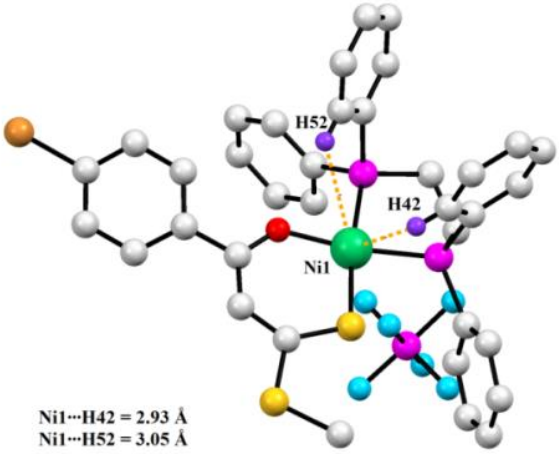
Figure S9. Intramolecular Ni···H−C anagostic interactions in **3**, **4** and **5**.



3



4



5

Figure S10. Noncovalent C-H···F interactions in **3**.

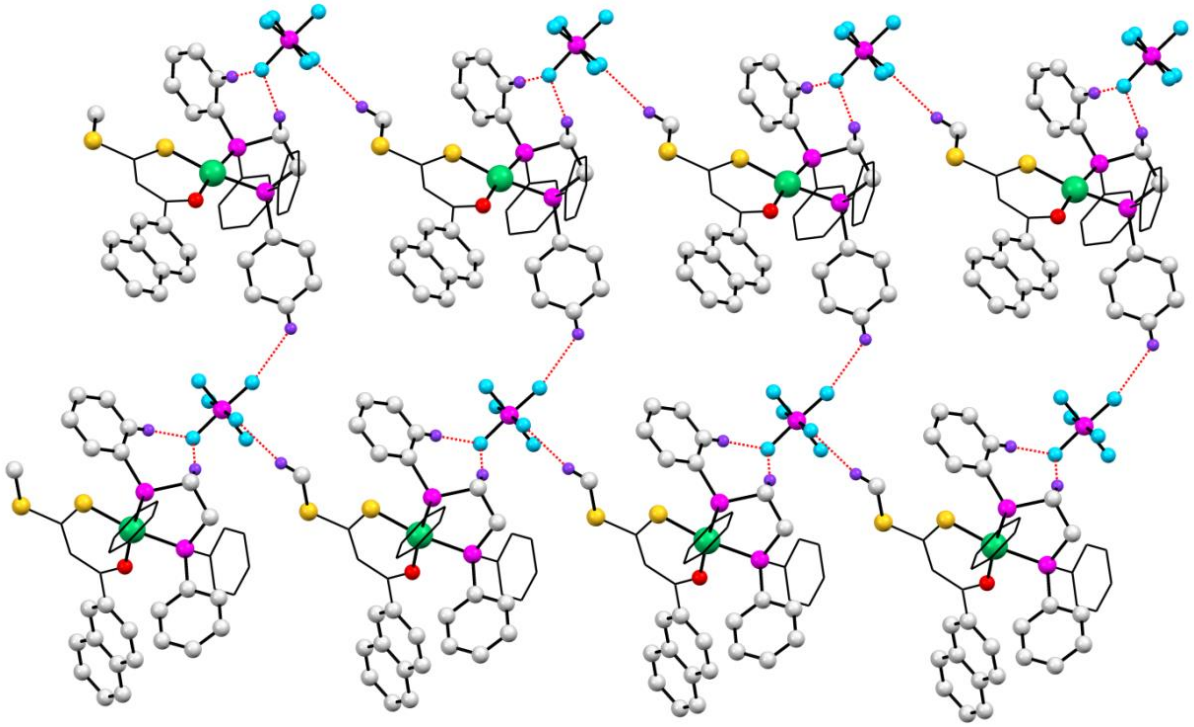


Figure S11. Noncovalent C-H···F interactions in **4**.

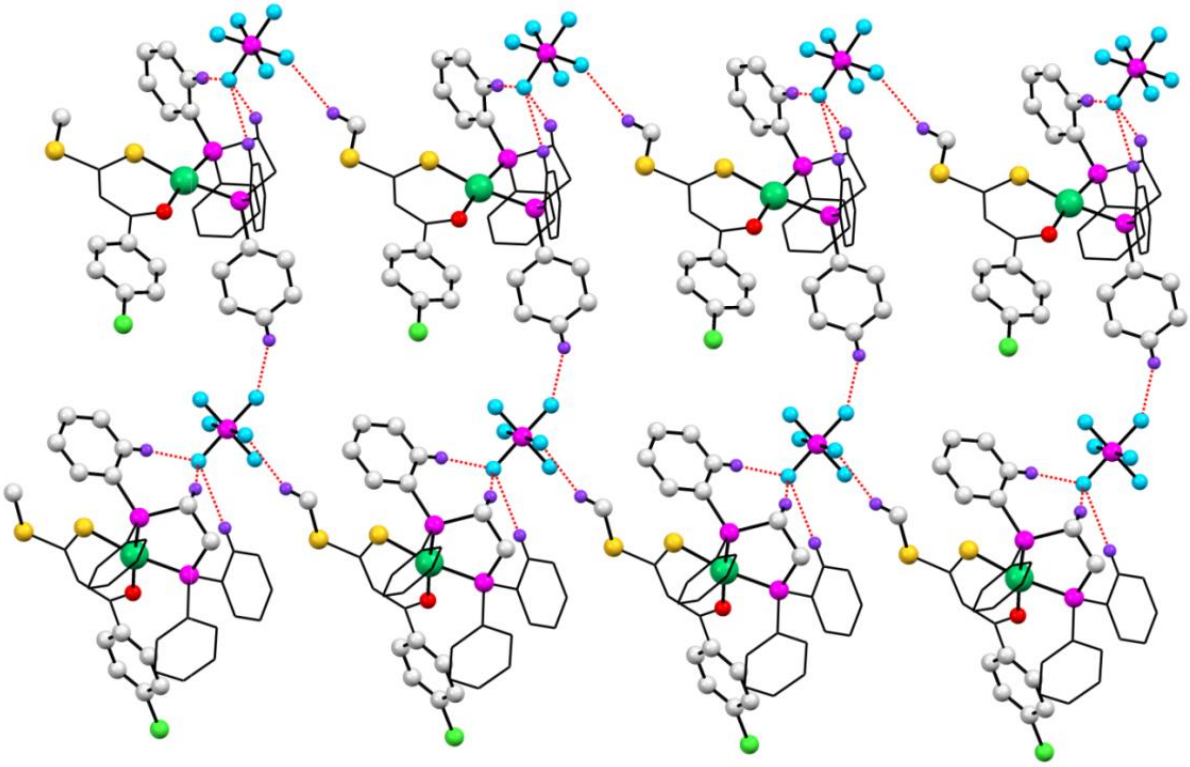


Figure S12. Noncovalent C-H···F interactions in **5**.

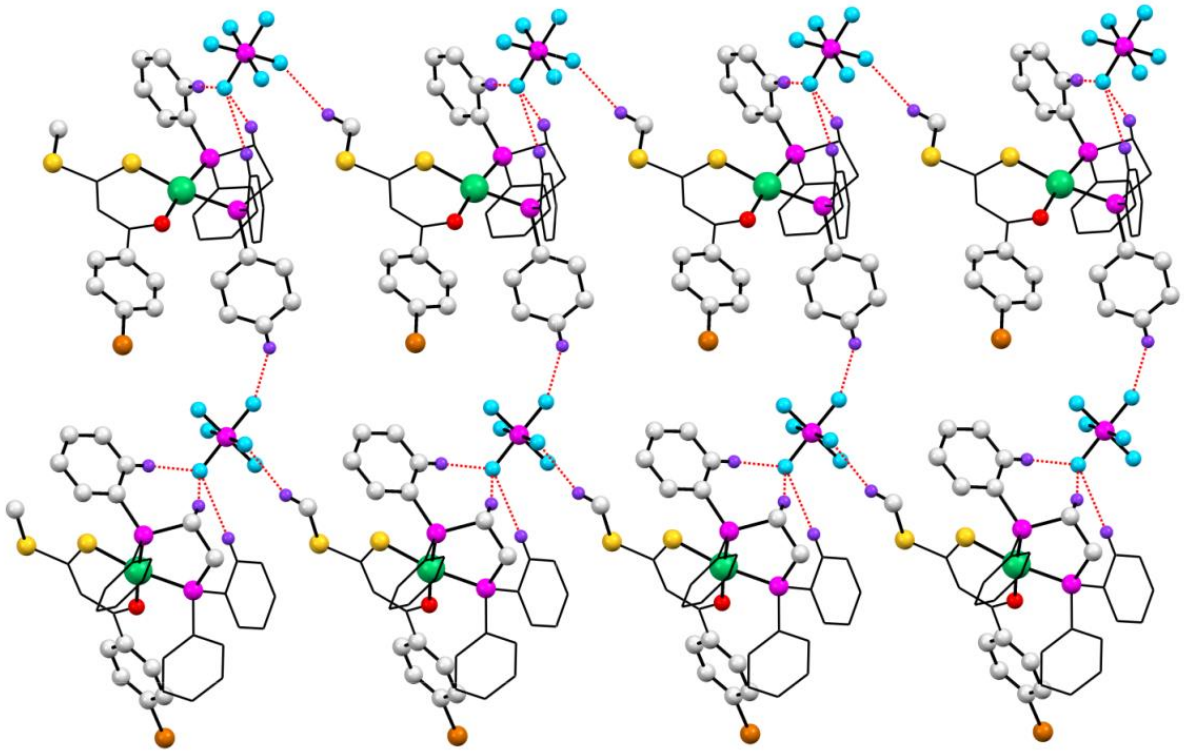


Table S13. Noncovalent C−H···F bonding interactions (distances [Å]) in **2-5**

In 2

Donor (D)···Acceptor (A)	D−H	H···A	D−H···A	D···A	Symmetry Element
C17-H17B···F71	0.96	2.60	159	3.512(5)	1+x,y,z
C17-H17C···F74	0.96	2.61	169	3.558(5)	1-x,-1/2+y,1/2+z
C28-H28B···F74	0.96	2.52	158	3.433(6)	x,3/2-y,z-1/2
C36-H36···F73	0.93	2.36	166	3.265(5)	
C52-H52···O11	0.93	2.65	131	3.337(5)	
C56-H56···O27	0.93	2.66	134	3.375(5)	-x,1-y,1-z
C62-H62···F73	0.93	2.64	153	3.539(4)	
C2-H2A···F75	0.97	2.47	132	3.207(4)	-x,-1/2+y,3/2-z
C2-H2B···F73	0.97	2.50	164	3.441(5)	
C3-H3B···F76	0.97	2.51	150	3.383(5)	-x,-1/2+y,3/2-z

In **3**

Donor (D)···Acceptor (A)	D−H	H···A	D−H···A	D···A	Symmetry Element
C17-H17C···F74	0.96	2.59	169	3.536(4)	-x+1, y-1/2, -z+3/2
C36-H36···F73	0.93	2.51	169	3.426(4)	x,y,z
C2-H2A···F75	0.97	2.63	131	3.352(4)	-x, y-1/2, -z+3/2

In **4**

Donor (D)···Acceptor (A)	D−H	H···A	D−H···A	D···A	Symmetry Element
C36-H36···F73	0.93	2.36	170	3.281(7)	x,y,z
C62-H62···F73	0.93	2.60	167	3.513(6)	x,y,z
C2-H2A···F75	0.97	2.57	128	3.260(6)	-x, y-1/2, -z+3/2
C2-H2B···F73	0.97	2.47	160	3.394(6)	x,y,z
C3-H3B···F76	0.97	2.48	158	3.398(6)	-x, y-1/2, -z+3/2

In **5**

Donor (D)···Acceptor (A)	D−H	H···A	D−H···A	D···A	Symmetry Element
C17-H17B···F71	0.96	2.57	158	3.479(5)	x+1, y, z
C36-H36···F73	0.93	2.37	170	3.285(4)	x,y,z
C2-H2A···F75	0.97	2.57	130	3.259(4)	-x, y-1/2, -z+3/2
C2-H2B···F73	0.97	2.49	163	3.429(4)	x,y,z
C3-H3B···F76	0.97	2.51	154	3.407(4)	-x, y-1/2, -z+3/2

Figure S14. Stacking interaction between benzene and metal-chelate ring in **3**.

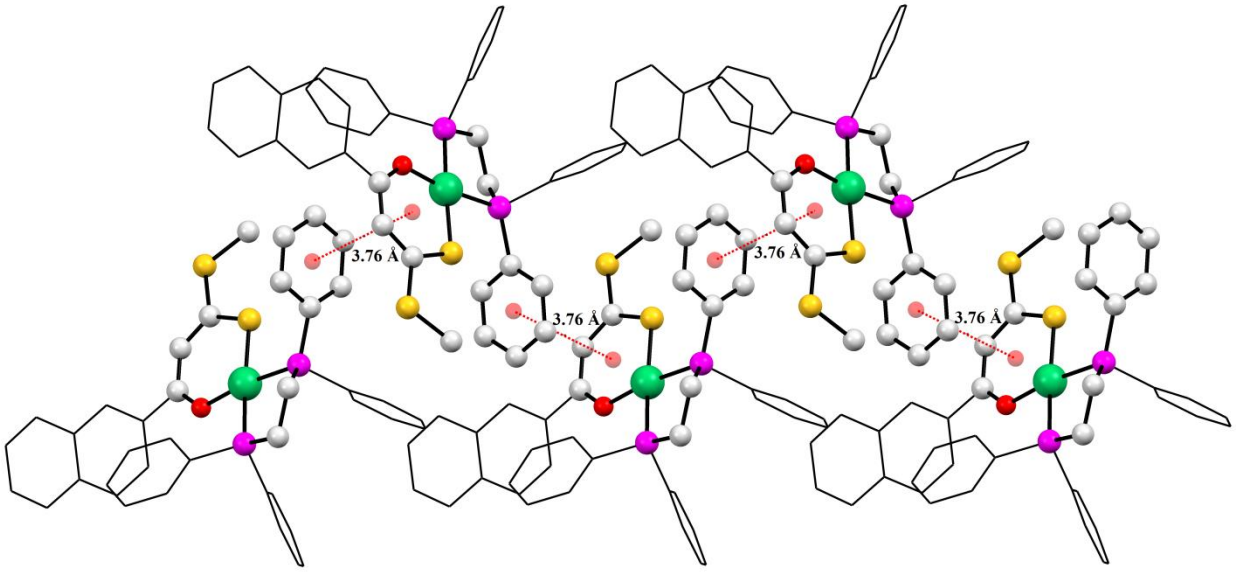


Figure S15. Stacking interaction between benzene and metal-chelate ring in **4**.

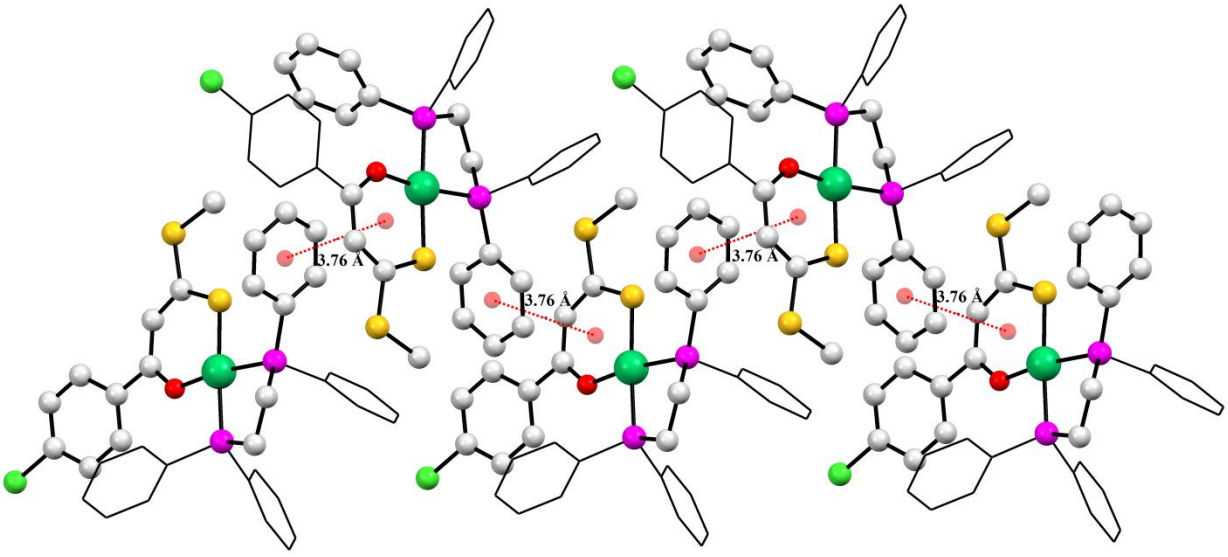
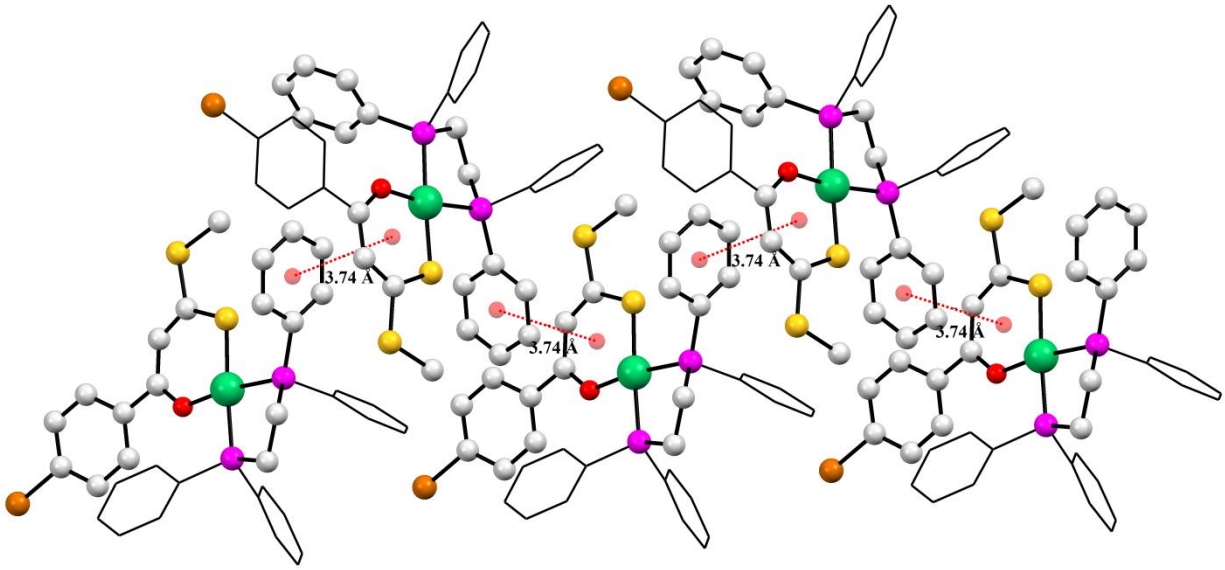
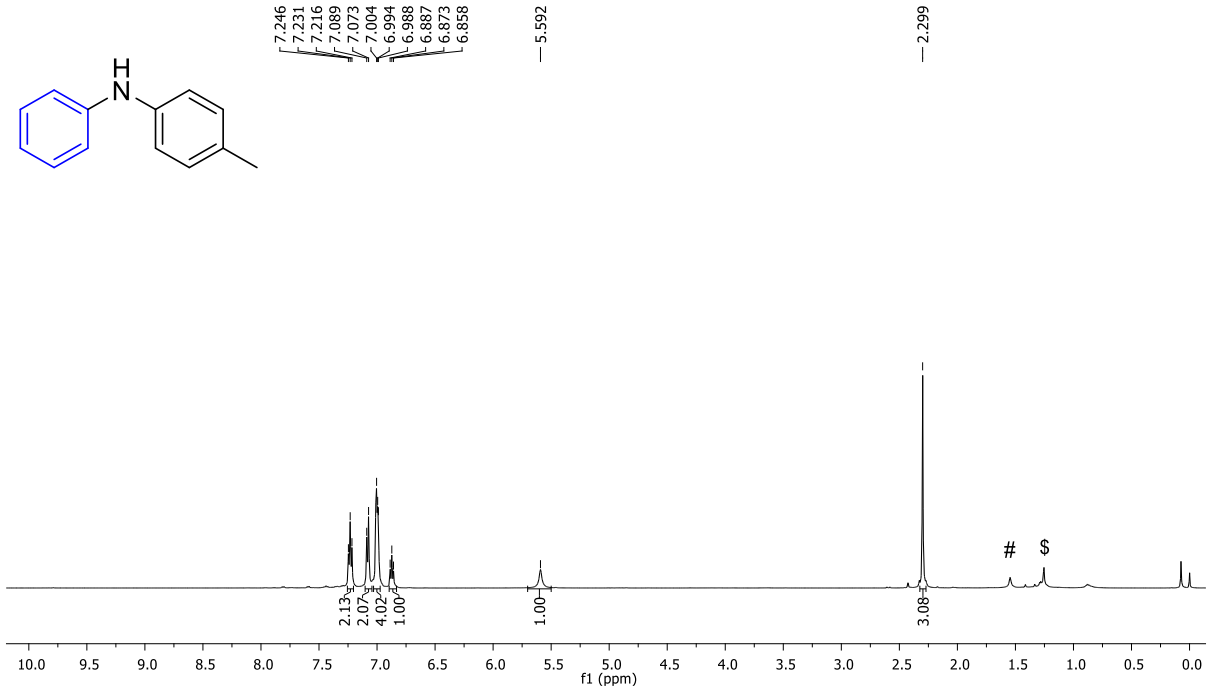


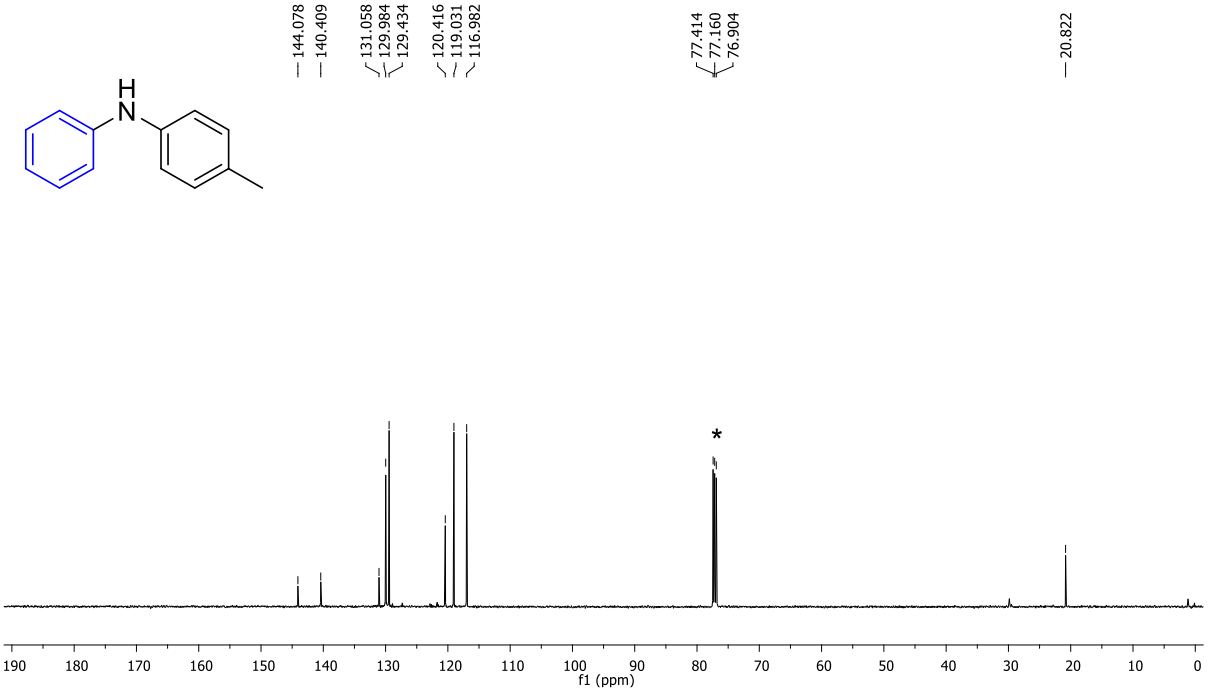
Figure S16. Stacking interaction between benzene and metal-chelate ring in **5**.



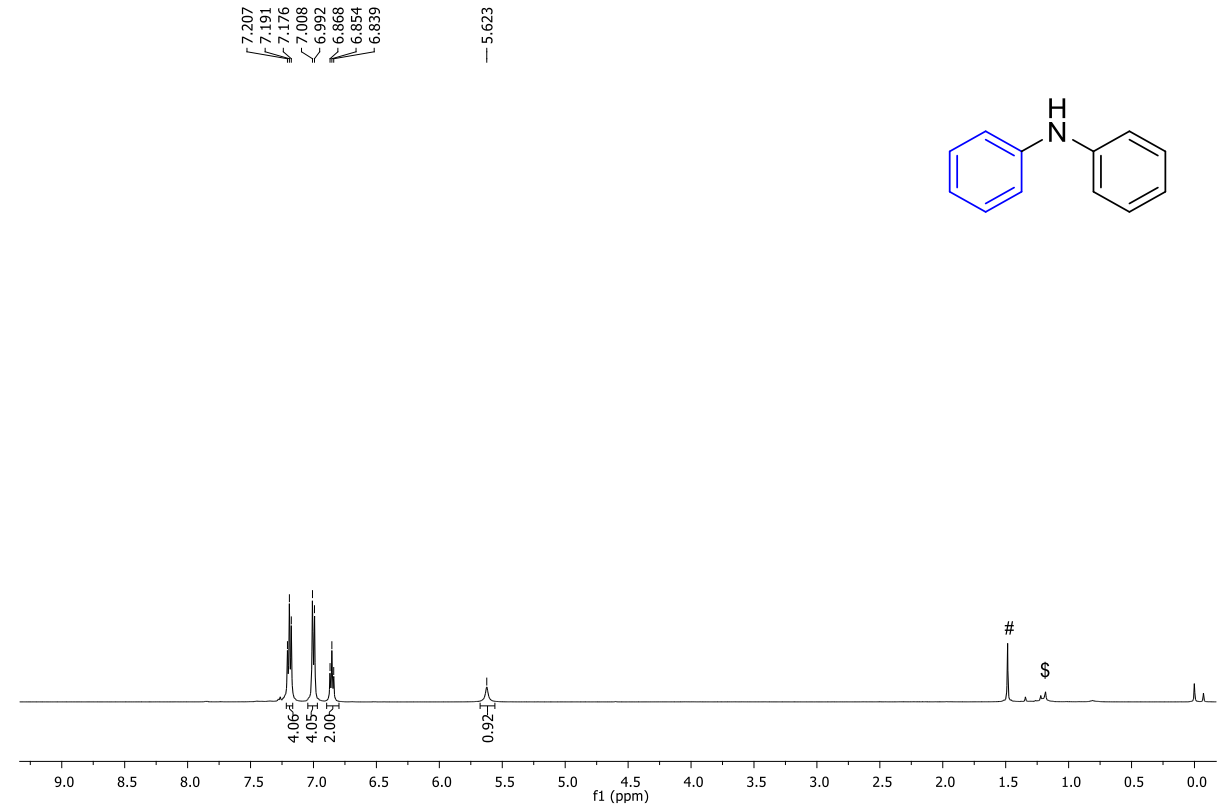
S17: ^{1}H and ^{13}C NMR spectra of arylated products (**9a-o**)



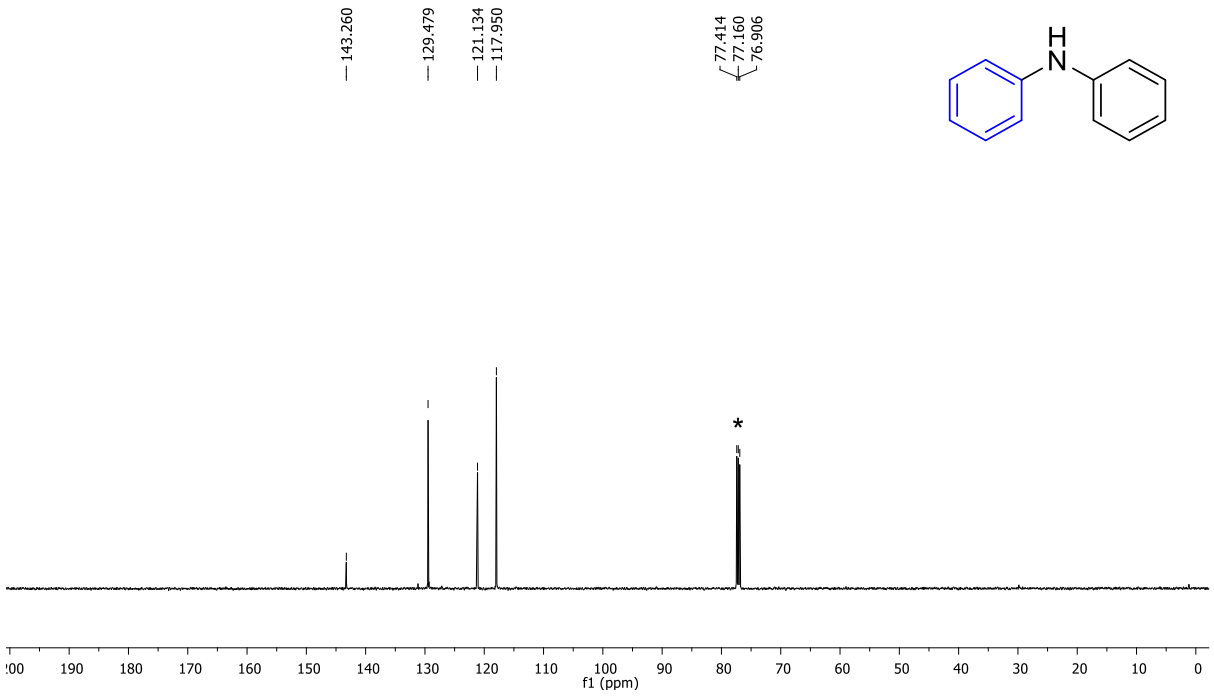
Spectrum 1: 500 MHz ^{1}H NMR spectrum of compound **9a** in $CDCl_3$. # and $ represent the solvent impurity H_2O and grease respectively.



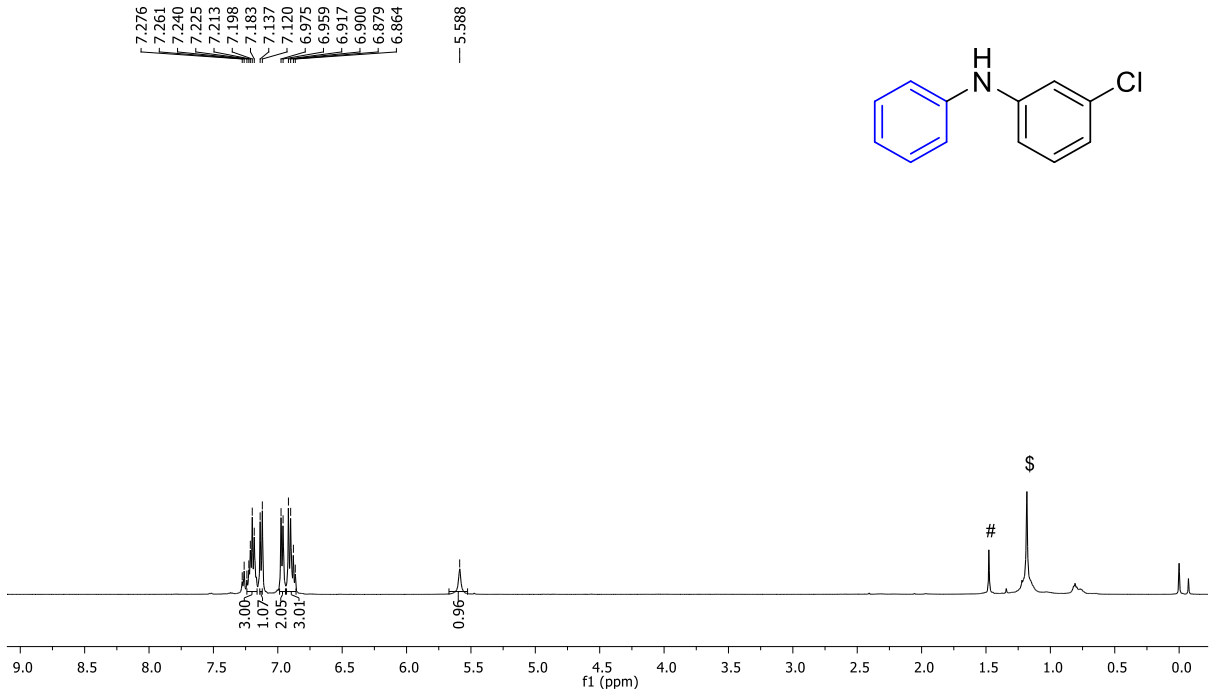
Spectrum 2: 125 MHz ^{13}C NMR spectrum of compound **9a** in $CDCl_3$ (*).



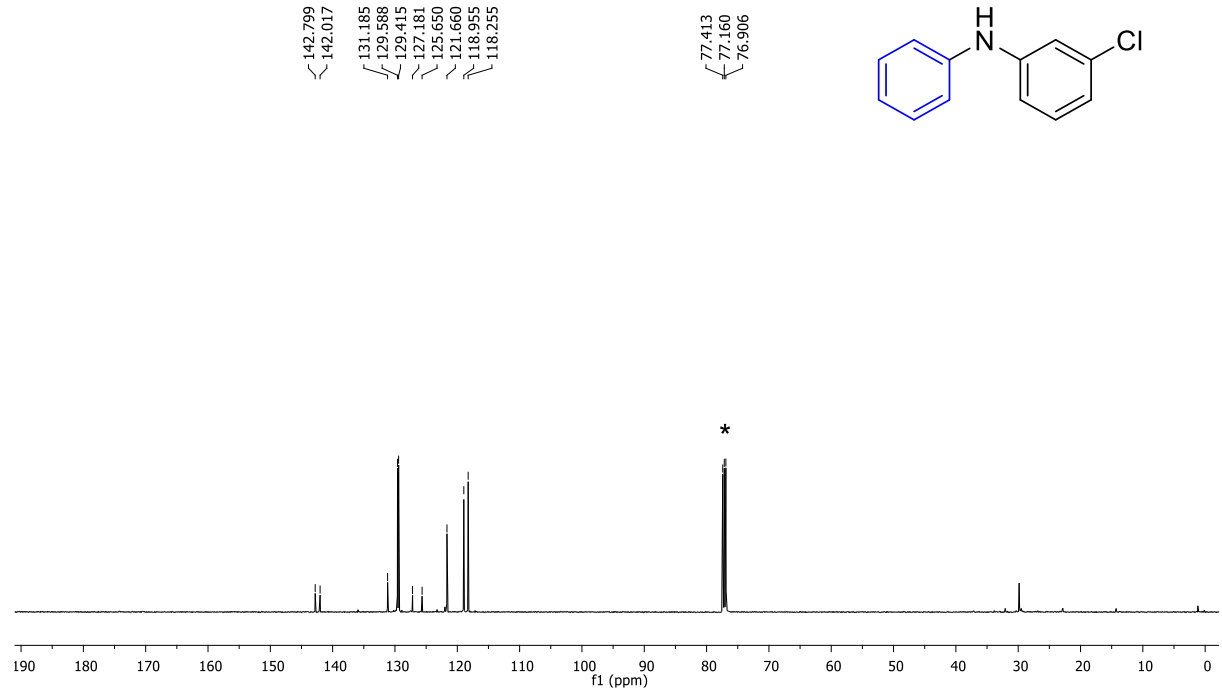
Spectrum 3: 500 MHz ^{1}H NMR spectrum of compound **9b** in $CDCl_3$. # and $ represent the solvent impurity H_2O and grease respectively.



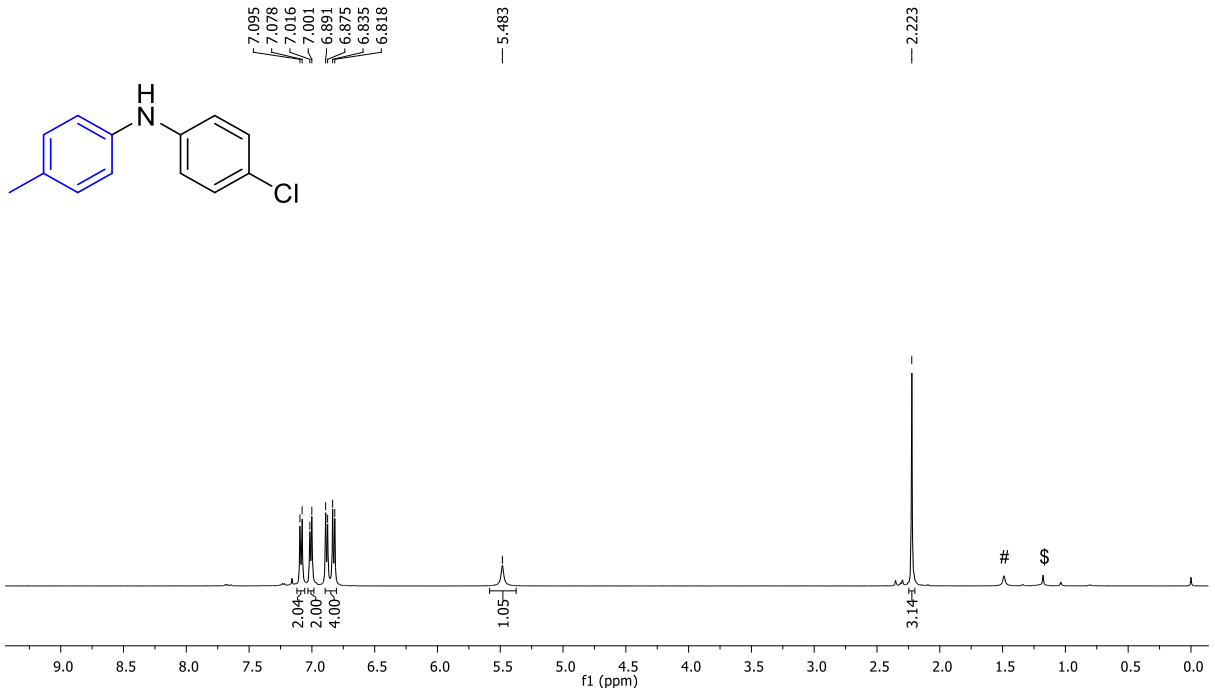
Spectrum 4: 125 MHz ^{13}C NMR spectrum of compound **9b** in $CDCl_3$ (*).



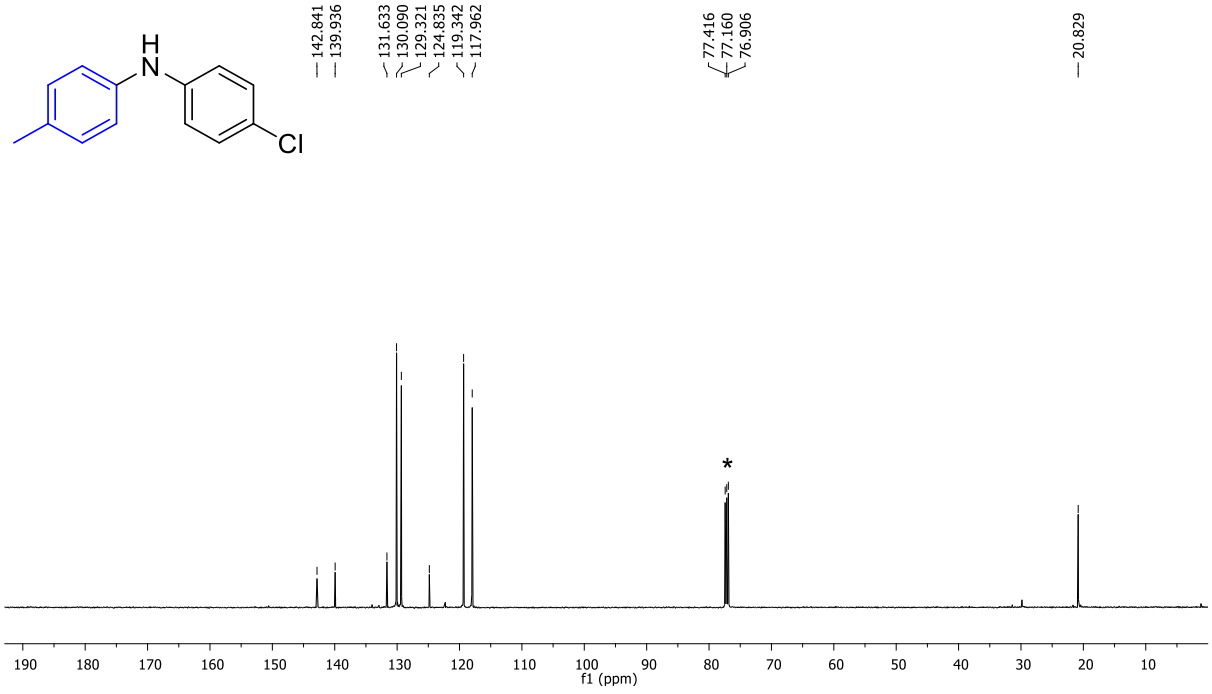
Spectrum 5: 500 MHz ^{1}H NMR spectrum of compound **9c** in $CDCl_3$. # and $ represent the solvent impurity H_2O and grease respectively.



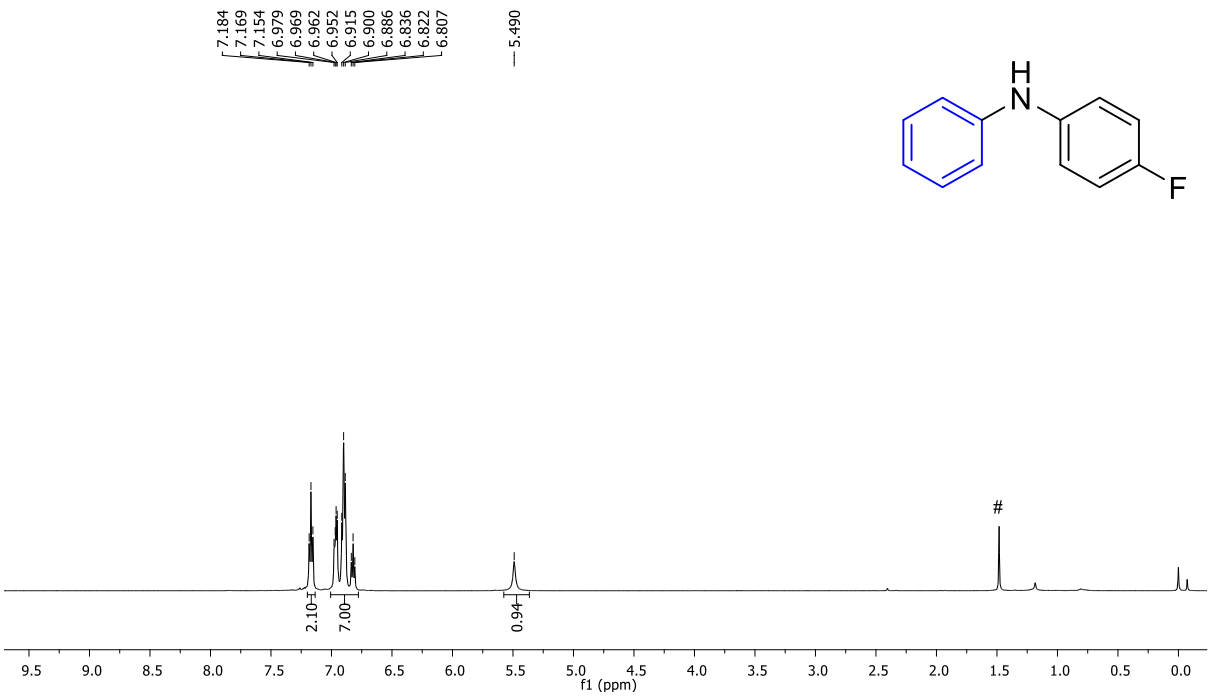
Spectrum 6: 125 MHz ^{13}C NMR spectrum of compound **9c** in $CDCl_3$ (*).



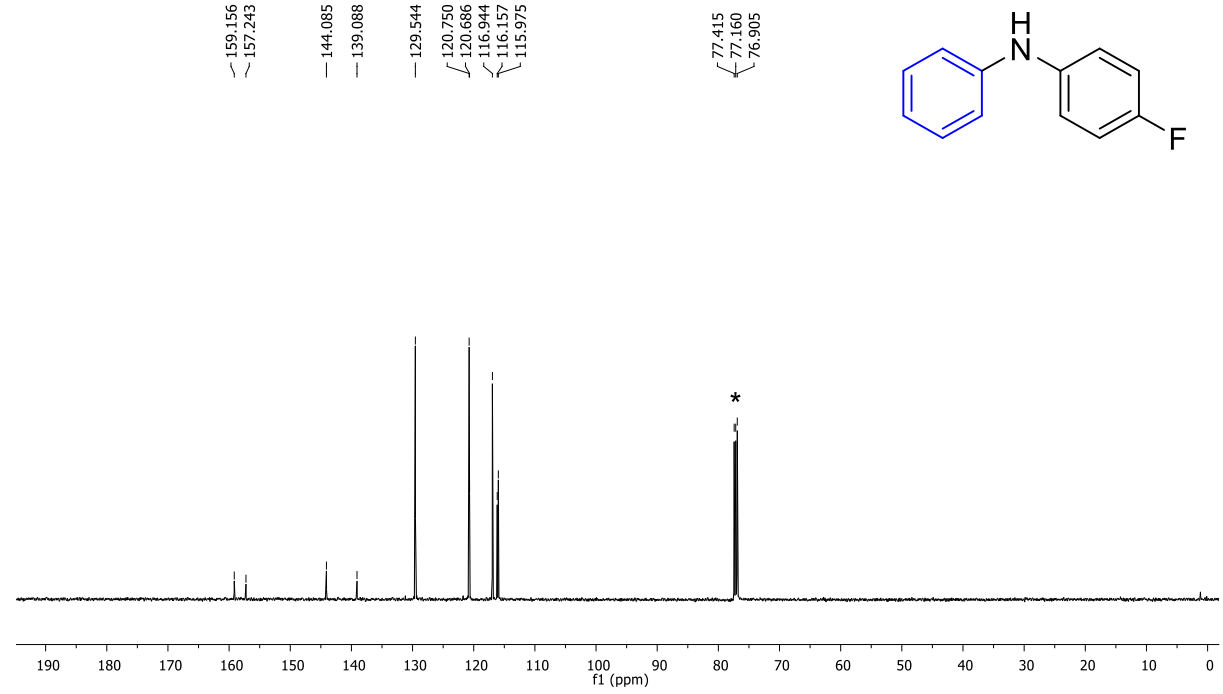
Spectrum 7: 500 MHz ^{1}H NMR spectrum of compound **9d** in $CDCl_3$. # and $ represents the solvent impurity H_2O and grease respectively.



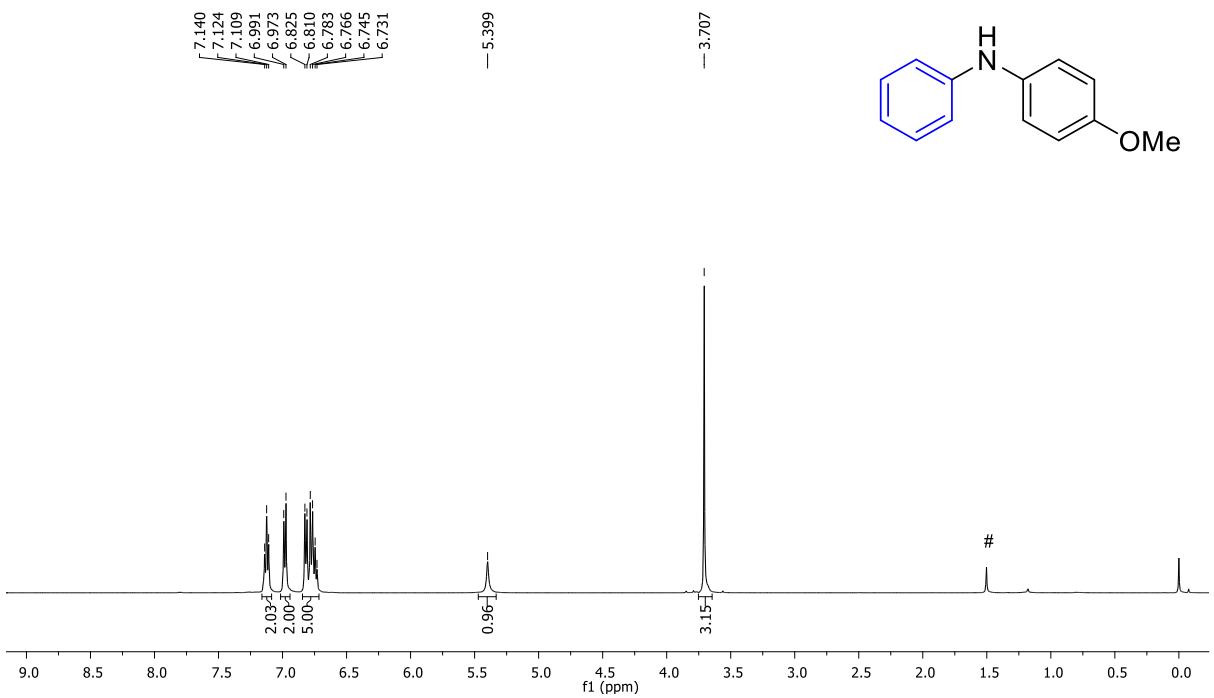
Spectrum 8: 125 MHz ^{13}C NMR spectrum of compound **9d** in $CDCl_3$ (*).



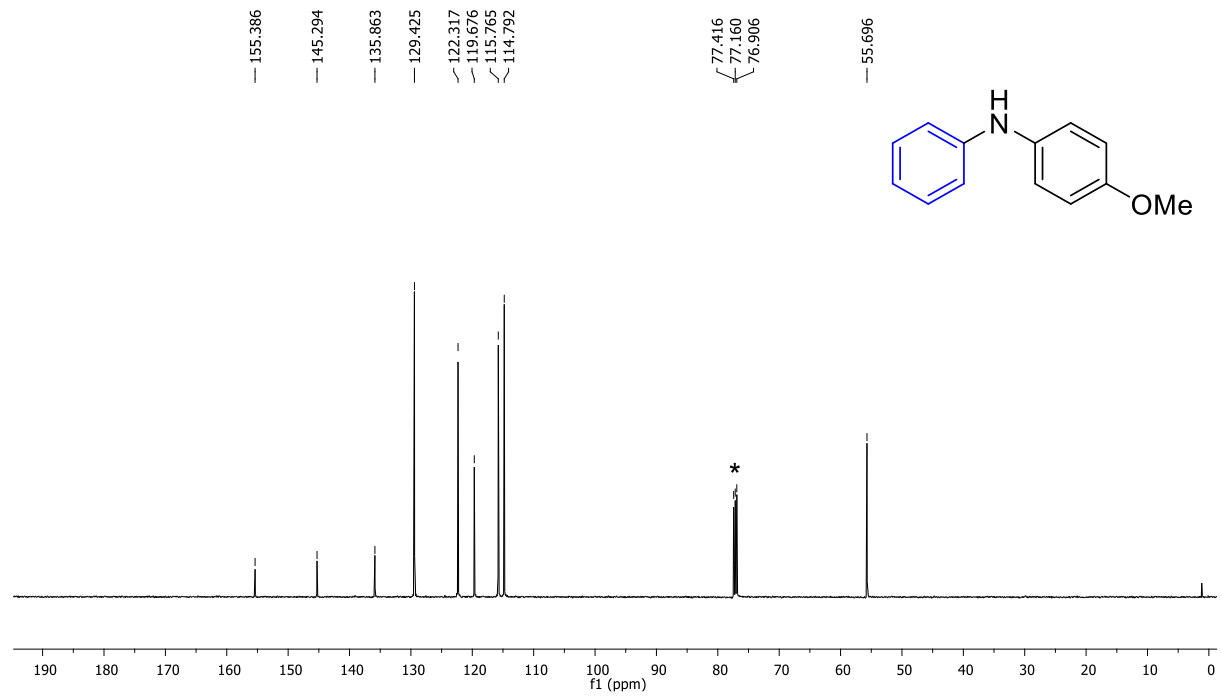
Spectrum 9: 500 MHz ^{1}H NMR spectrum of compound **9e** in $CDCl_3$. # represents the solvent impurity H_2O.



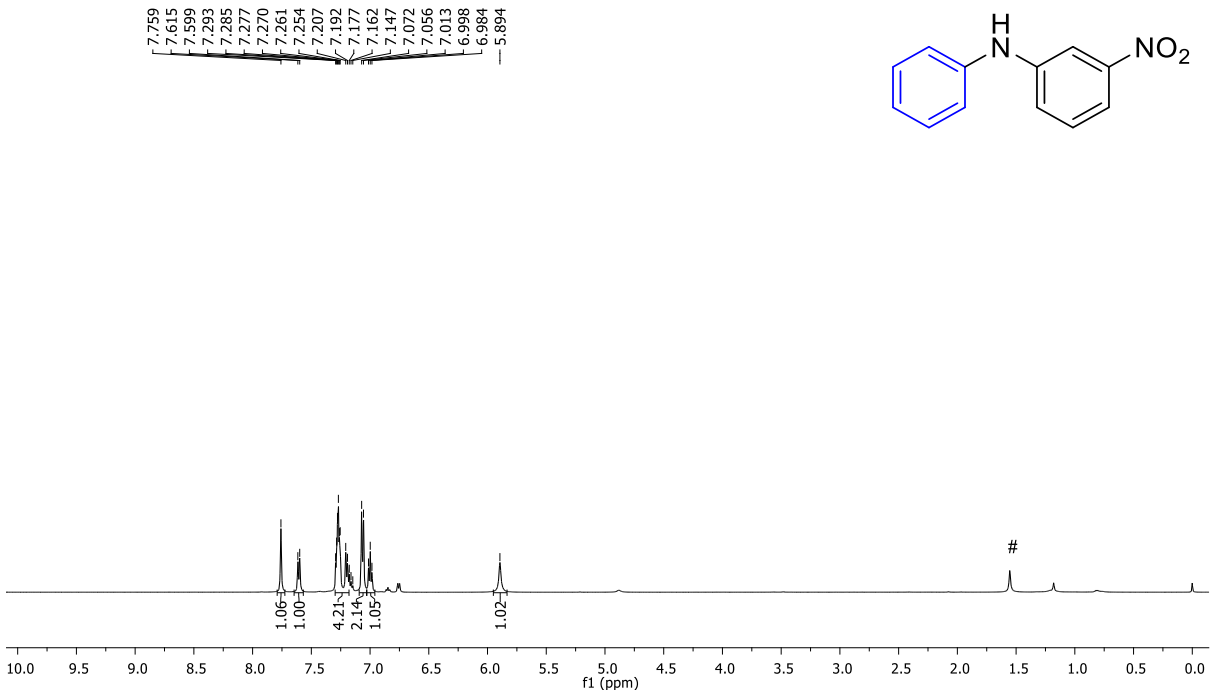
Spectrum 10: 125 MHz ^{13}C NMR spectrum of compound **9e** in $CDCl_3$ (*).



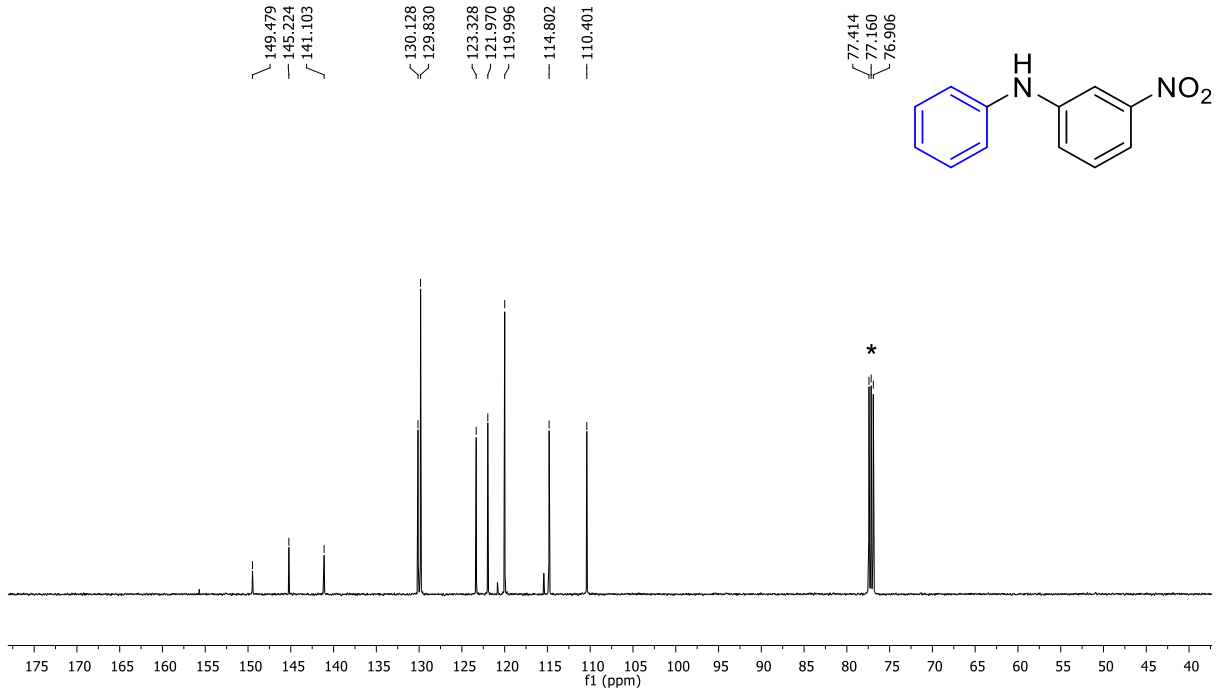
Spectrum 11: 500 MHz ^{1}H NMR spectrum of compound **9f** in $CDCl_3$. # represents the solvent impurity H_2O.



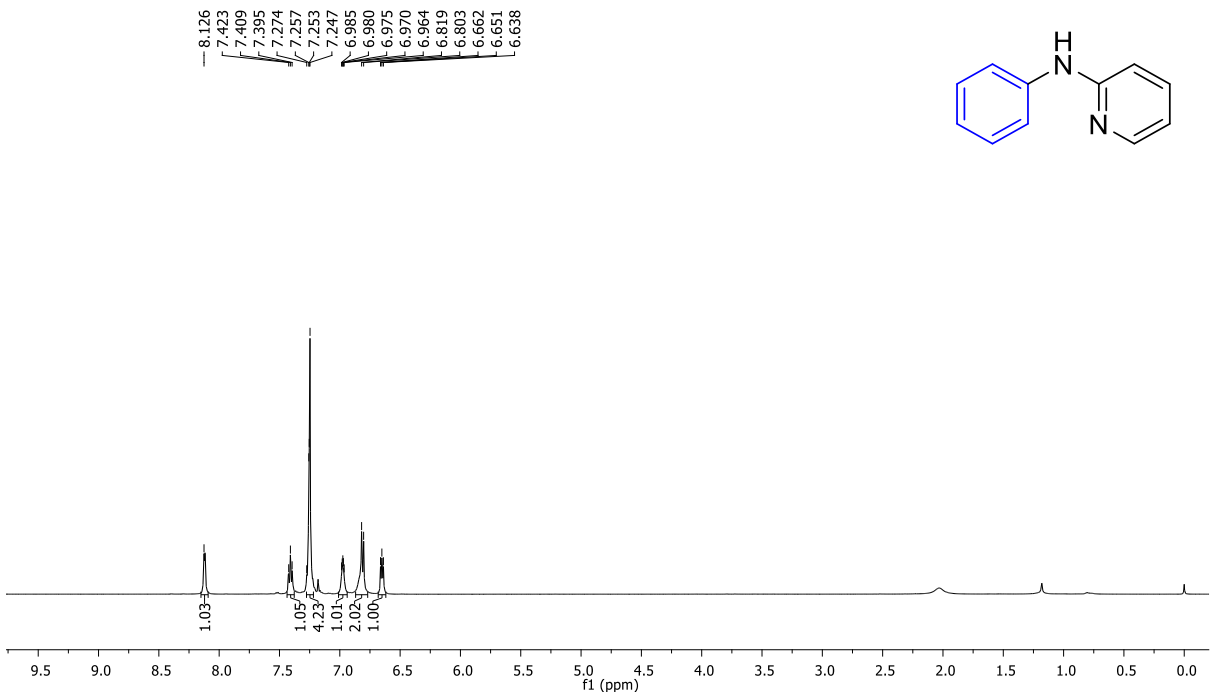
Spectrum 12: 125 MHz ^{13}C NMR spectrum of compound **9f** in $CDCl_3$ (*).



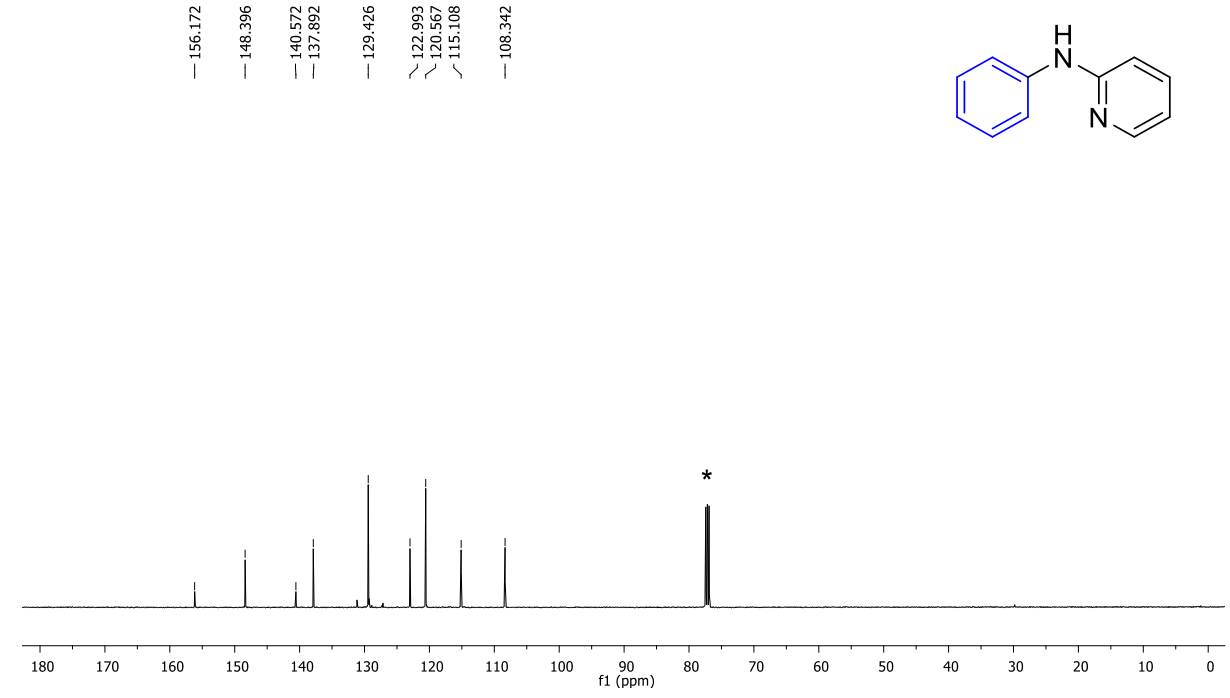
Spectrum 13: 500 MHz ^{1}H NMR spectrum of compound **9g** in $CDCl_3$. # represents the solvent impurity H_2O.



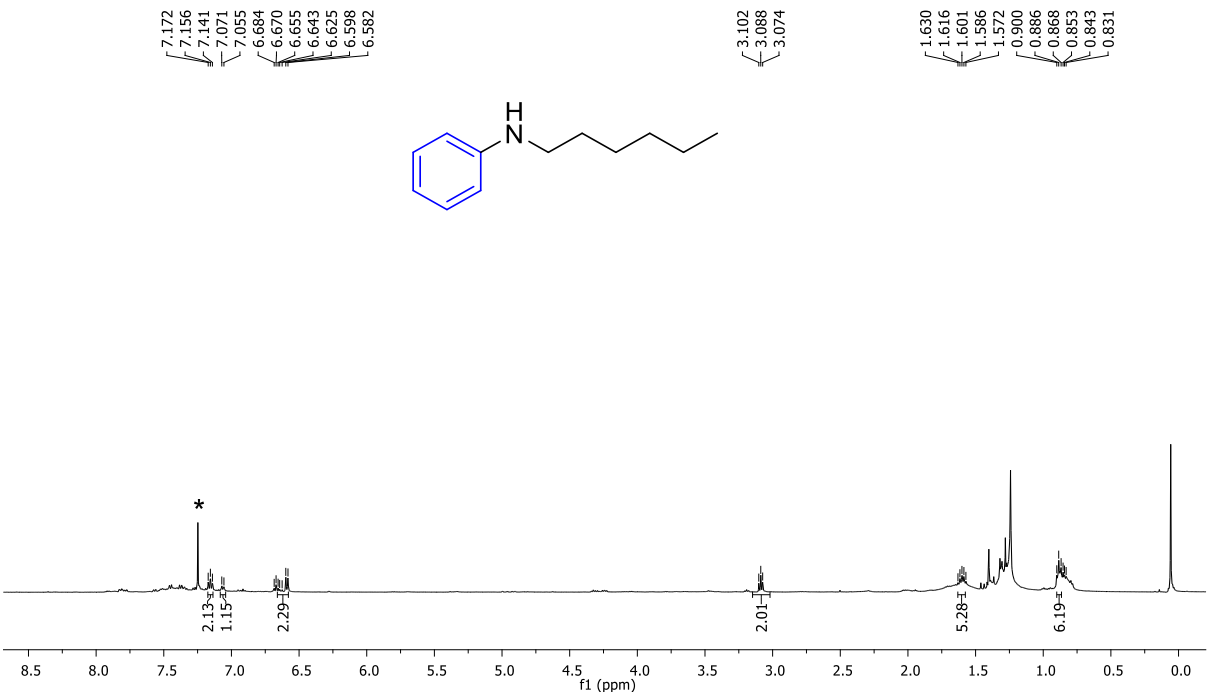
Spectrum 14: 125 MHz ^{13}C NMR spectrum of compound **9g** in $CDCl_3$ (*).



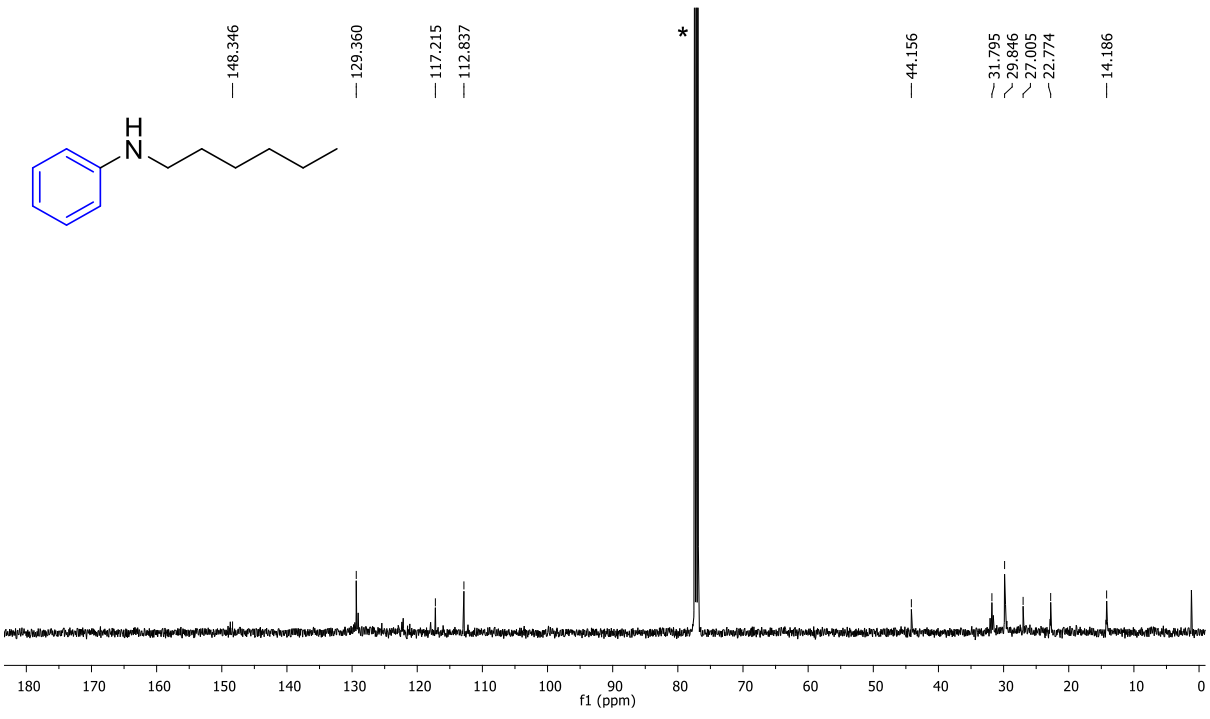
Spectrum 15: 500 MHz ^{1}H NMR spectrum of compound **9h** in $CDCl_3$.



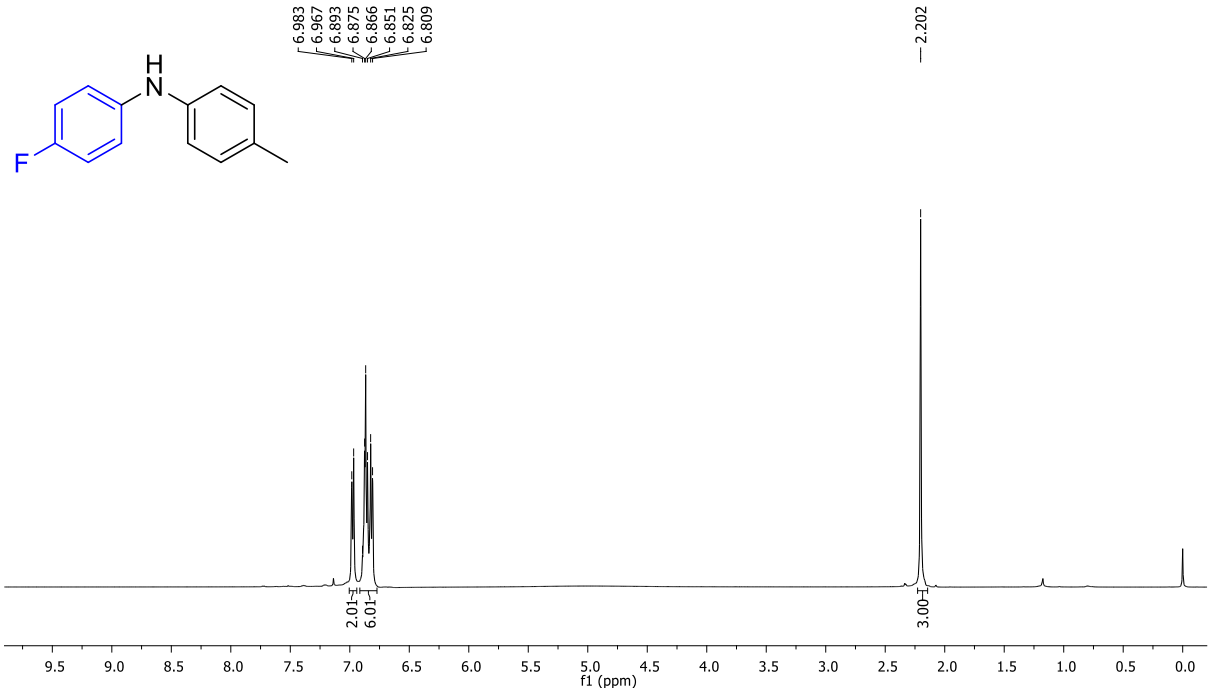
Spectrum 16: 125 MHz ^{13}C NMR spectrum of compound **9h** in $CDCl_3$ (*).



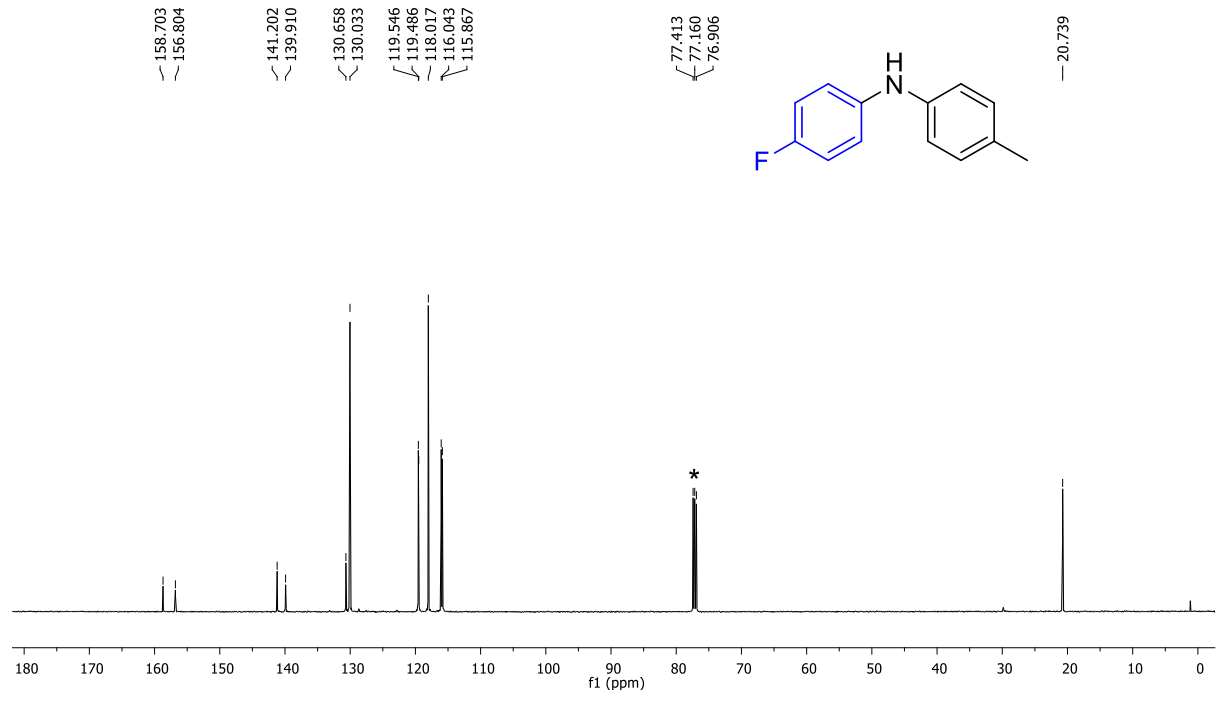
Spectrum 17: 500 MHz ^{1}H NMR spectrum of compound **9i** in $CDCl_3$ (*). Aromatic region has extra resonances due to presence of trace of undetectable impurities.



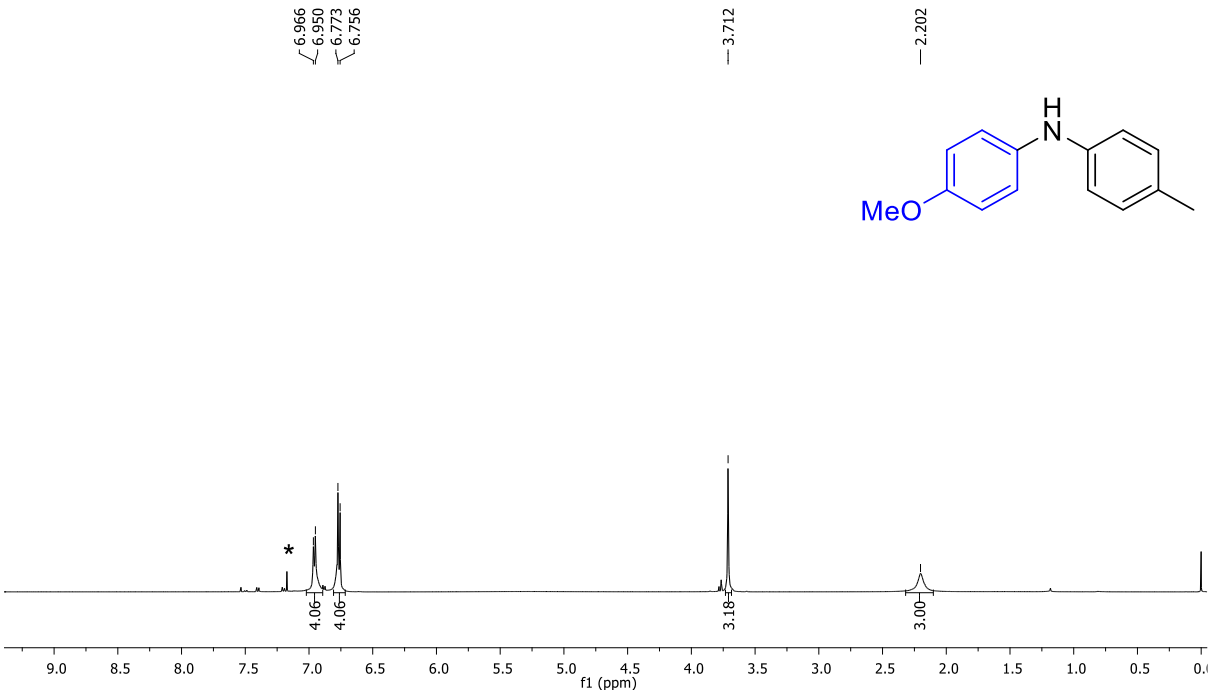
Spectrum 18: 125 MHz ^{13}C NMR spectrum of compound **9i** in $CDCl_3$ (*).



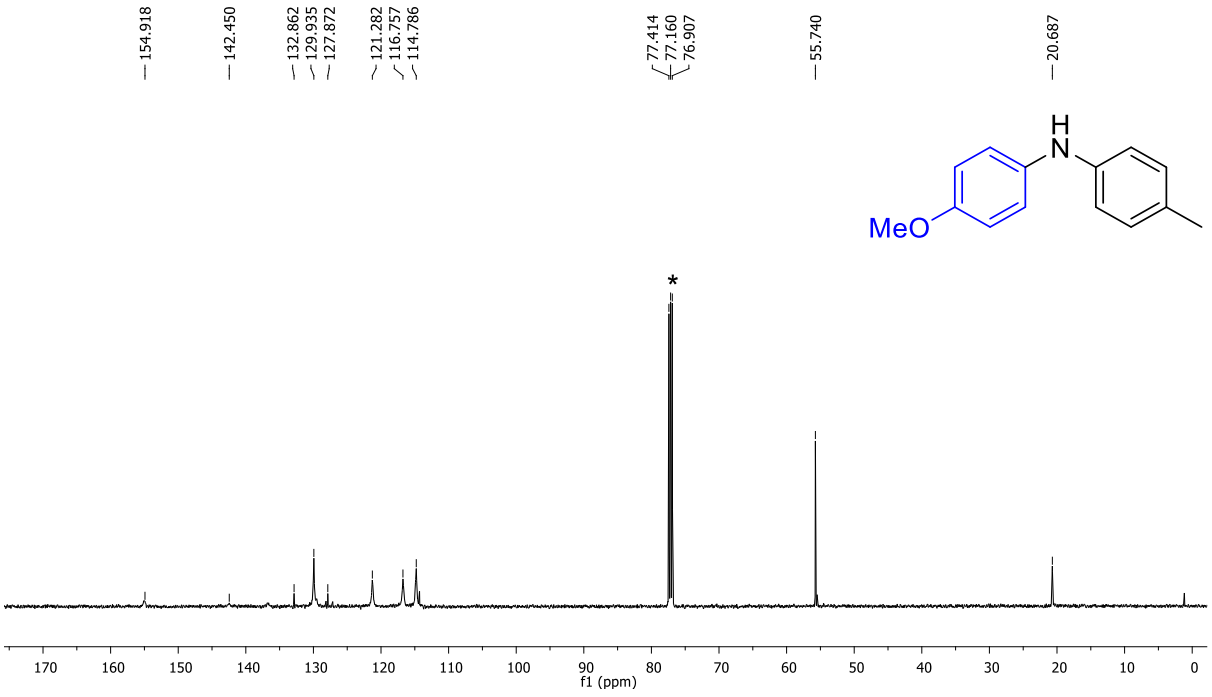
Spectrum 19: 500 MHz ^{1}H NMR spectrum of compound **9j** in $CDCl_3$.



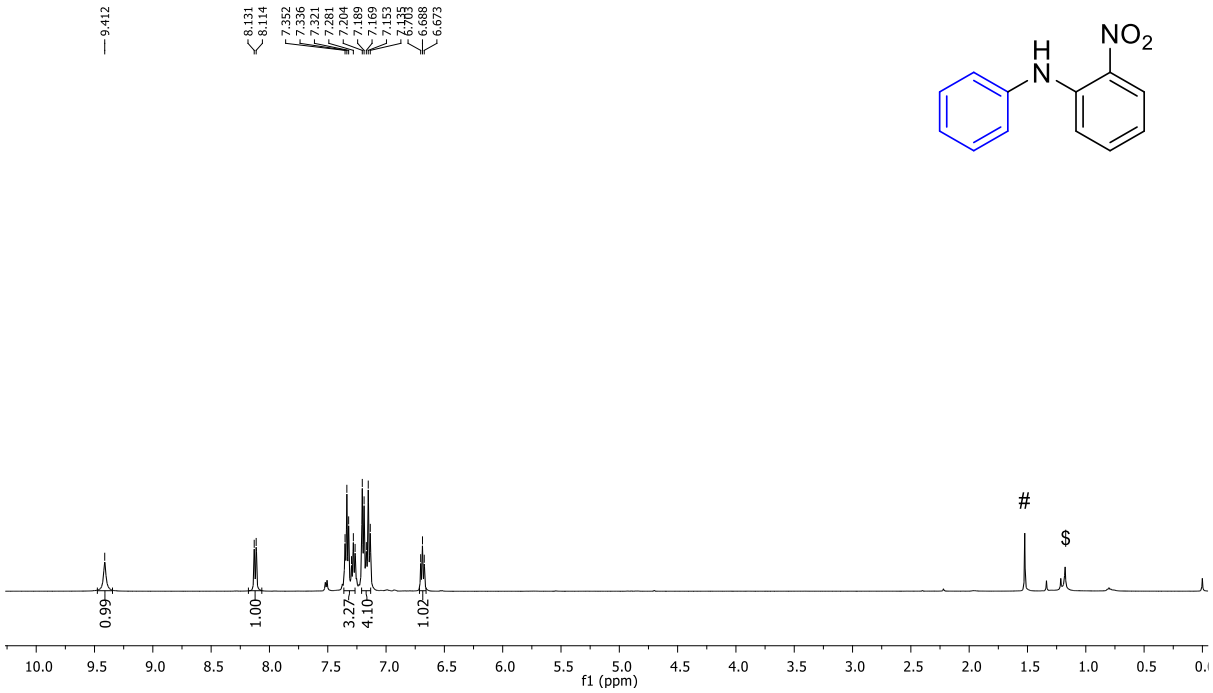
Spectrum 20: 125 MHz ^{13}C NMR spectrum of compound **9j** in $CDCl_3$ (*).



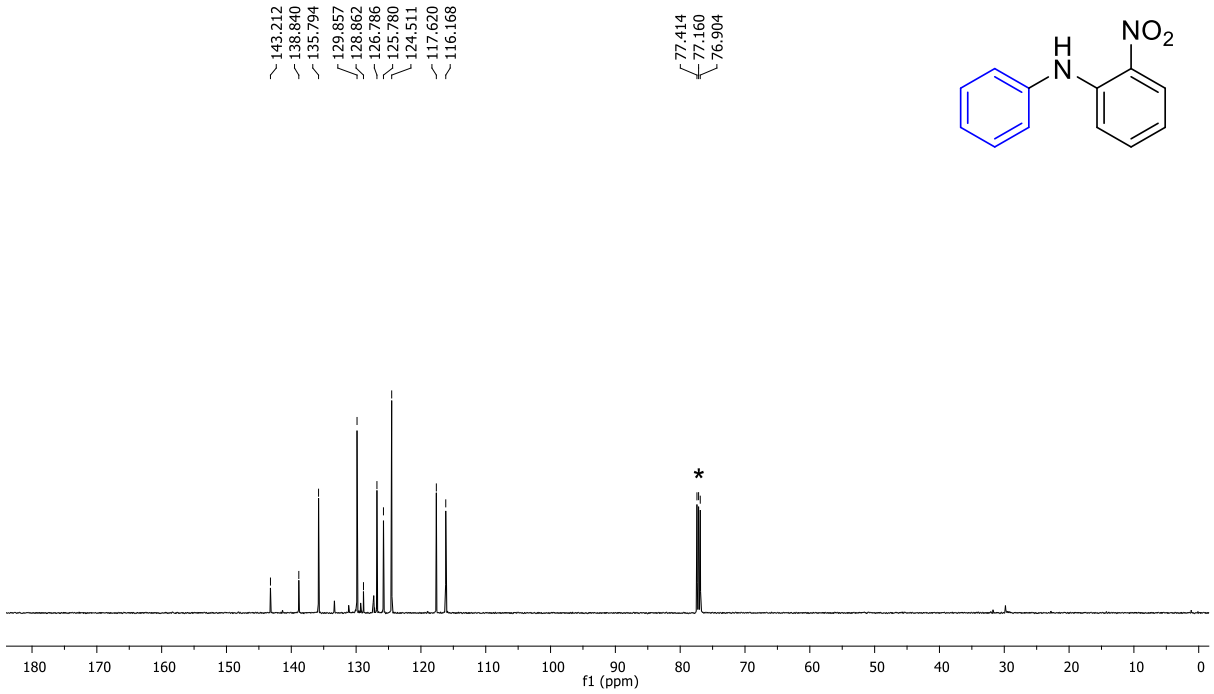
Spectrum 21: 500 MHz ^{1}H NMR spectrum of compound **9k** in $CDCl_3$ (*).



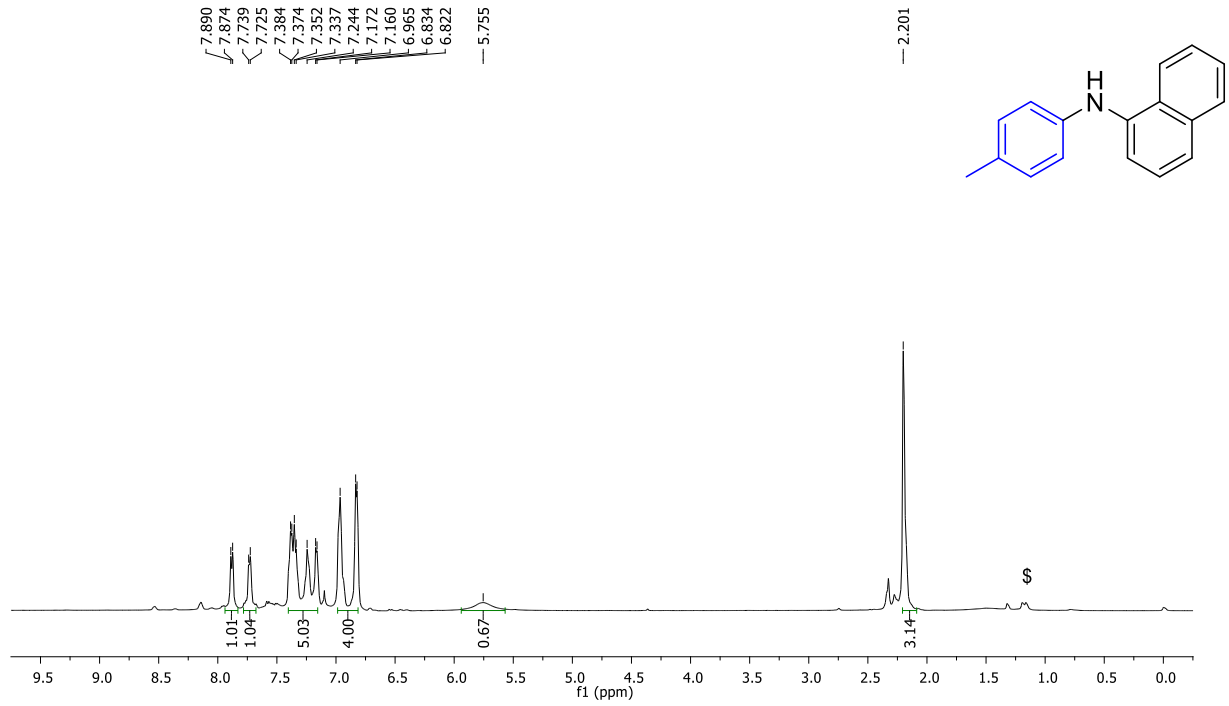
Spectrum 22: 125 MHz ^{13}C NMR spectrum of compound **9k** in $CDCl_3$ (*).



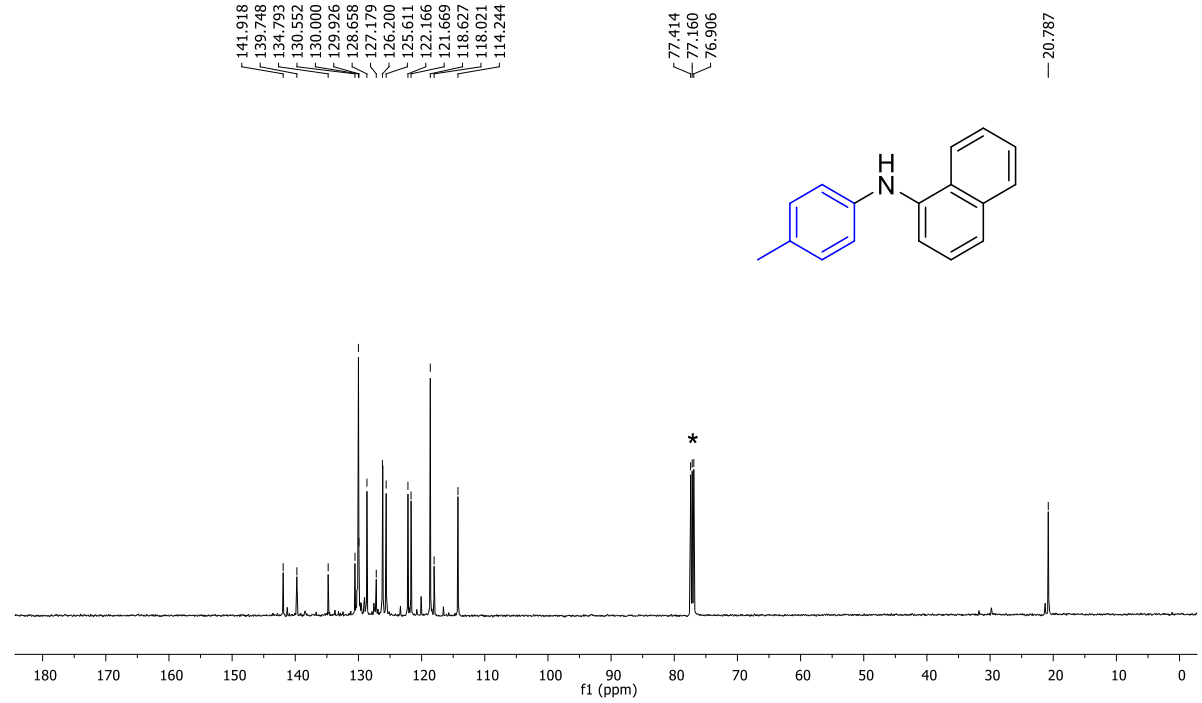
Spectrum 23: 500 MHz ^{1}H NMR spectrum of compound **9l** in $CDCl_3$. # and $ represent the solvent impurity H_2O and grease respectively.



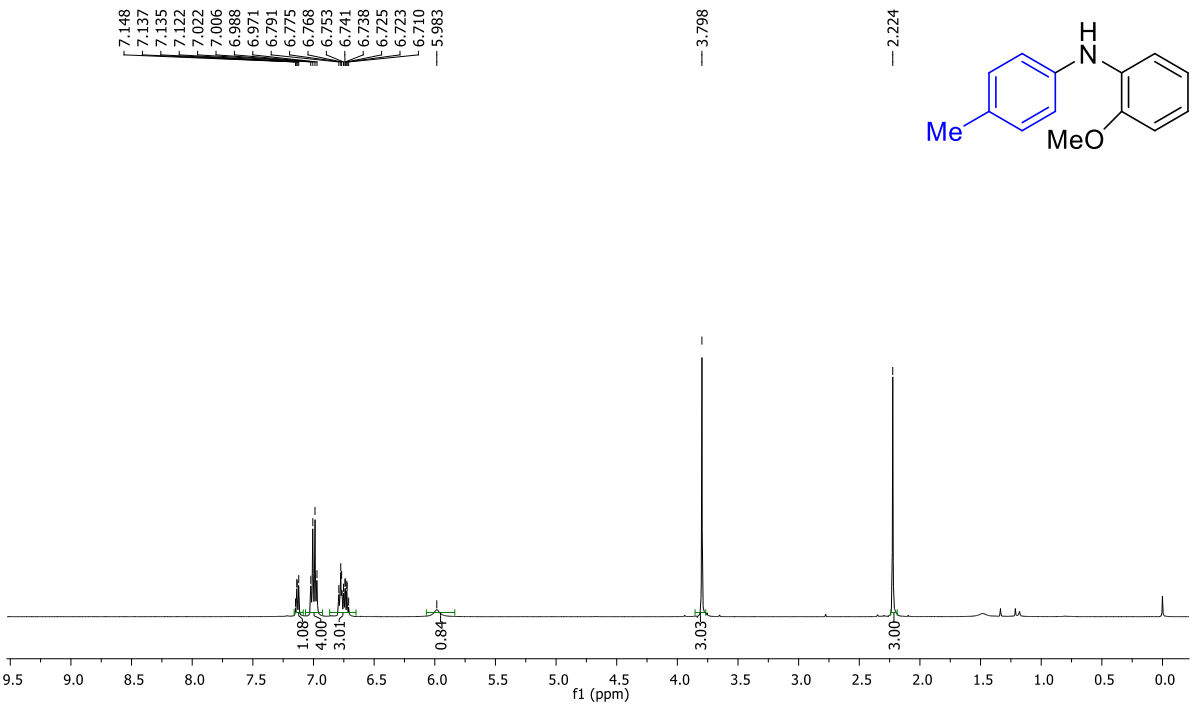
Spectrum 24: 125 MHz ^{13}C NMR spectrum of compound **9l** in $CDCl_3$ (*).



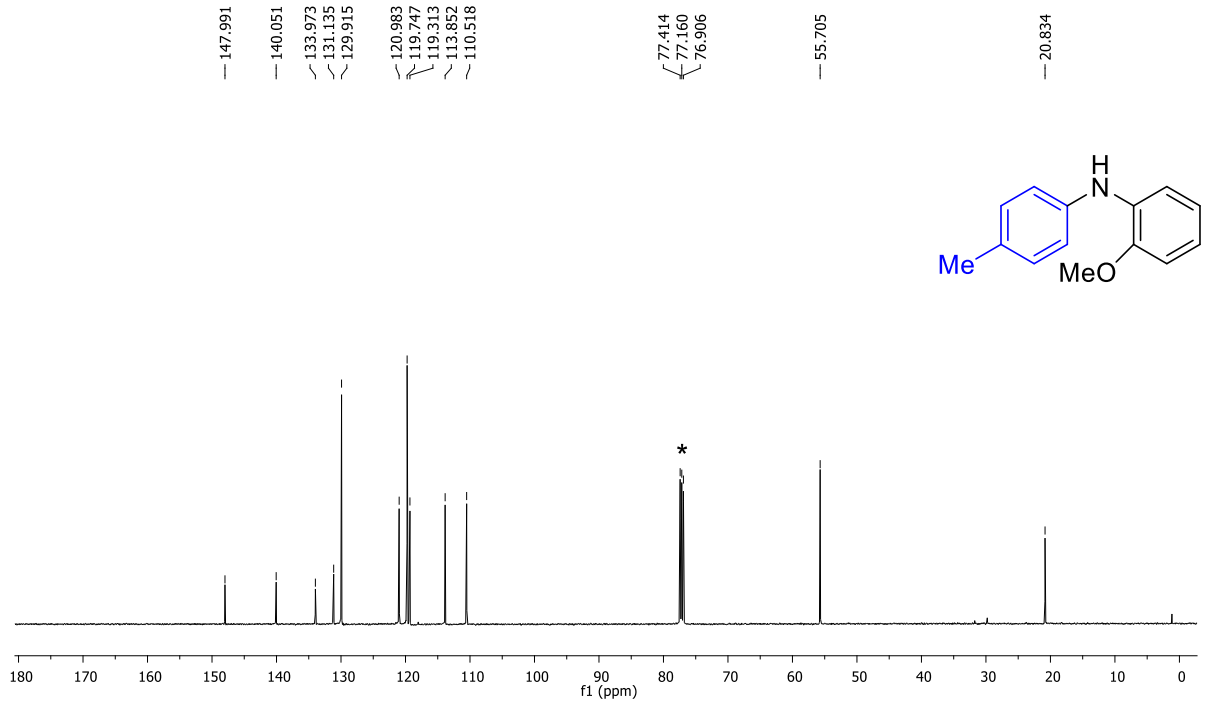
Spectrum 25: 500 MHz ^{1}H NMR spectrum of compound **9m** in $CDCl_3$. $ represents the grease impurity.



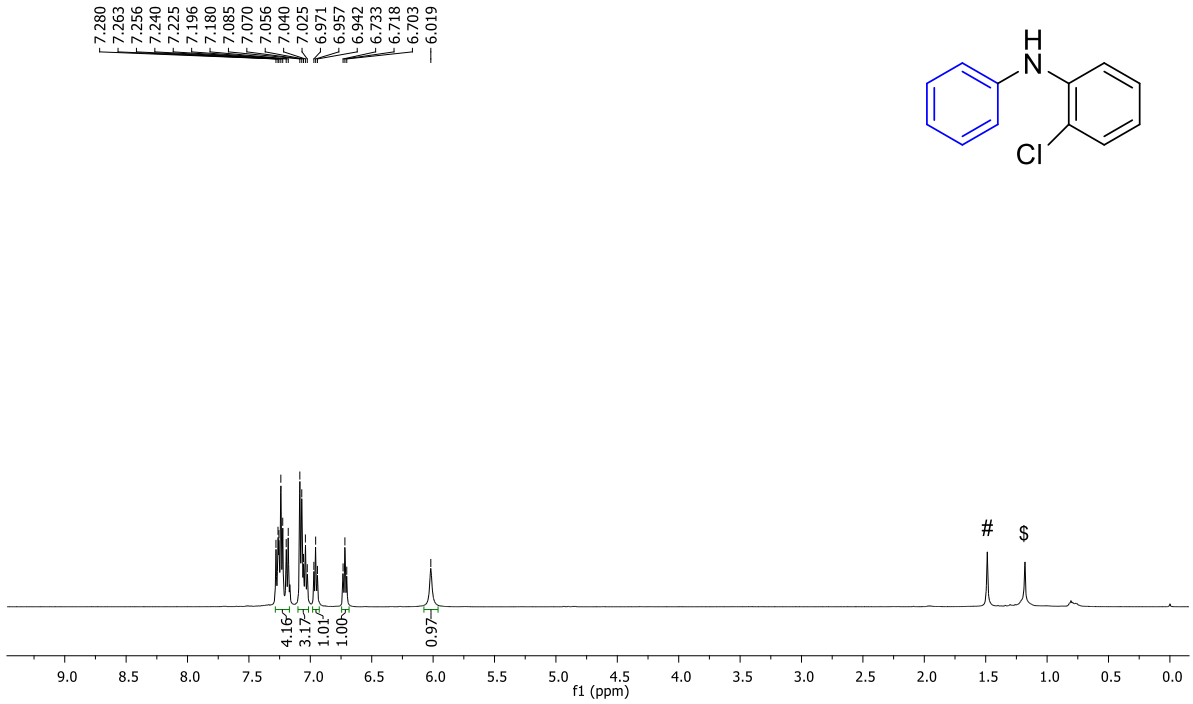
Spectrum 26: 125 MHz ^{13}C NMR spectrum of compound **9m** in $CDCl_3$ (*).



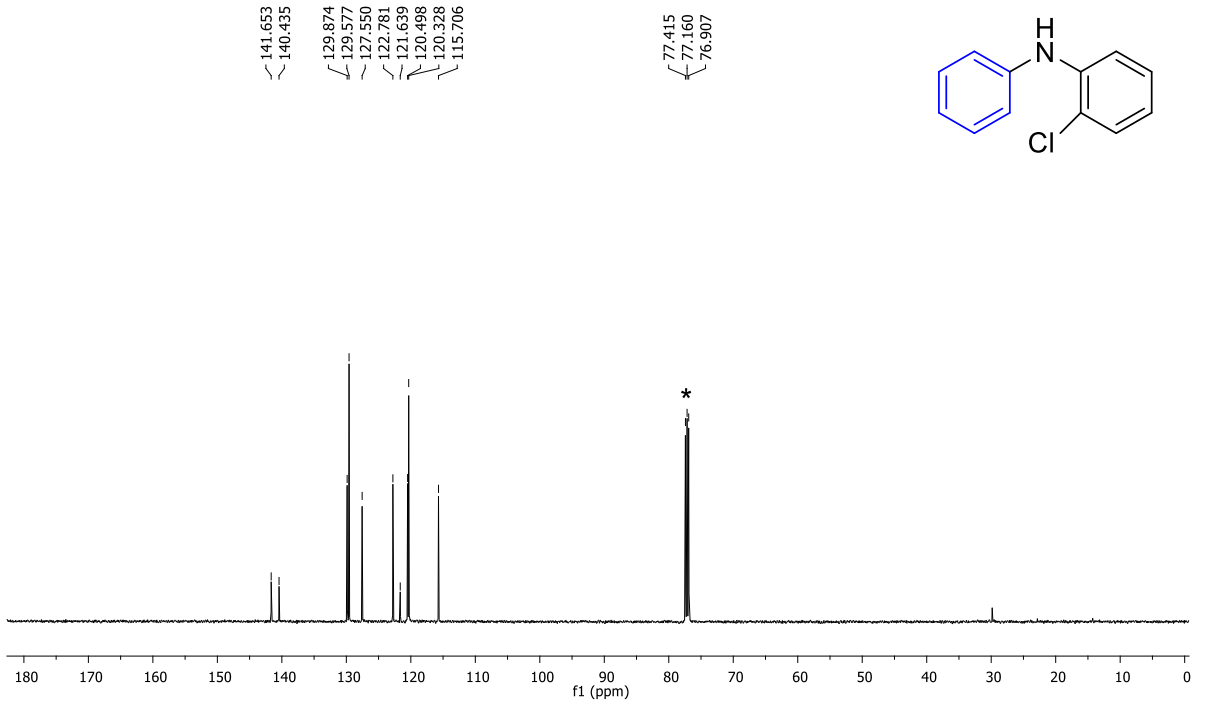
Spectrum 27: 500 MHz ^{1}H NMR spectrum of compound **9n** in $CDCl_3$.



Spectrum 28: 125 MHz ^{13}C NMR spectrum of compound **9n** in $CDCl_3$ (*).



Spectrum 29: 500 MHz ^{1}H NMR spectrum of compound **9o** in $CDCl_3$. # and $ represent the solvent impurity H_2O and grease respectively.



Spectrum 30: 125 MHz ^{13}C NMR spectrum of compound **9o** in $CDCl_3$ (*).

S18: NMR Data of Arylated Products.

4-Methyl-*N*-phenylaniline (9a).[1] Colorless solid (161 mg, 88%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.25 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00 - 6.99(m, 4H), 6.89 (t, *J* = 7.0 Hz, 2H), 5.59 (brs, 1H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 144.1, 140.4, 131.1, 130.0, 129.4, 120.4, 119.0, 117.0, 20.8.

Diphenylamine (9b).[1] Colorless solid (144 mg, 85%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.21 - 7.18 (m, 4H), 7.01 - 6.99 (m, 4H), 6.87 (t, *J* = 7.5 Hz, 2H), 5.62 (brs, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 143.3, 129.5, 121.1, 118.0.

N-(3-Chlorophenyl)benzenamine (9c).[2] Yellow oil (146 mg, 72%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.28 - 7.18 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.92 - 6.86 (m, 3H), 5.59 (brs, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 142.8, 142.0, 131.2, 129.6, 129.4, 127.2, 125.7, 121.7, 119.0, 118.3.

4-Chloro-*N*-(*p*-tolyl)aniline (9d).[3] White solid (169 mg, 78%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.10 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.89 - 6.82 (m, 4H), 5.48 (brs, 1H), 2.22 (s, 1H). $^{13}C\ \{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 142.8, 139.9, 131.6, 130.1, 129.3, 124.8, 119.3, 118.0, 20.8.

4-Fluoro-*N*-phenylaniline (9e).[1] White solid (138 mg, 74%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.18 (t, *J* = 7.0 Hz, 2H), 6.98 - 6.81 (m, 7H), 5.49 (brs, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 159.2 (d, *J* = 252.0), 144.1, 139.1, 129.5, 120.8, 120.7, 116.9, 116.2, 116.0.

4-Methoxy-*N*-phenylaniline (9f).[1] White solid (171 mg, 86%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.14 - 7.11, 6.99 (d, *J* = 7.0 Hz, 2H), 6.83 - 6.73 (m, 5H), 5.40 (brs, 1H), 3.71 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 155.4, 145.3, 135.9, 129.4, 122.3, 119.7, 115.8, 114.8, 55.70.

N-(3-Nitrophenyl)benzenamine (9g).[1] Yellow solid (146 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.76 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.15 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 5.89 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 149.5, 145.2, 141.1, 130.1, 129.8, 123.33, 122.0, 120.0, 114.8, 110.4.

N-Phenylpyridin-2-amine (9h).[2] Light yellow solid (143 mg, 84%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.13 (s, 1H), 7.42 - 7.40 (m, 1H), 7.27 - 7.25 (m, 4H), 6.99 - 6.96 (m, 1H), 6.82 (d, *J* = 8.0, 2H), 6.66 (d, *J* = 8.0, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 156.2, 148.4, 140.6, 137.9, 129.4, 123.0, 120.6, 115.1, 108.3.

N-Hexylaniline (9i).[1] Yellow liquid (117 mg, 66%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.17 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.68 - 6.58 (m, , 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 1.63 - 1.57 (m, 5H), 0.90 - 0.83 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 148.4, 129.4, 117.2, 112.8, 44.2, 31.8, 29.9, 27.0, 22.8, 14.2.

4-Fluoro-*N*-(*p*-tolyl)aniline (9j).[4] White solid (153 mg, 76%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.98 (d, *J* = 8.0 Hz, 2H), 6.89 - 6.81 (m, 6H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 158.7 (d, *J* = 239.4), 141.2, 139.9, 130.7, 130.0, 119.6, 119.5, 118.0, 116.0, 115.9, 20.7.

4-Methoxy-4'-methyldiphenylamine (9k).[1] White solid (153 mg, 72%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.97-6.95 (m, 4H), 6.77-6.76 (m, 4H), 3.71 (s, 3H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 154.92, 142.45, 132.86, 129.94, 127.87, 121.28, 116.76, 114.79, 77.41, 77.16, 76.91, 55.74, 20.69.

2-nitro-*N*-phenylaniline (9l).[5] Yellow solid (139 mg, 65%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.41 (brs, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.11 - 7.27 (m, 3H), 7.20 - 7.14 (m, 4H), 6.70 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 143.2, 138.8, 135.8, 129.9, 128.9, 126.8, 125.8, 124.5, 117.6, 116.2.

N-(*p*-Tolyl)naphthalen-1-amine (9m).[6] Light brown solid (196 mg, 84%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.89 (d, *J* = 8.0 Hz), 7.74 (d, *J* = 7.0 Hz), 7.38 - 7.16 (m, 5H), 6.96 - 6.82 (m, 4H), 5.76 (brs, 1H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 141.9, 139.8, 134.8, 130.6, 130.0, 129.9, 128.7, 127.2, 126.2, 125.6, 122.2, 121.7, 118.6, 118.0, 114.2, 20.8.

2-methoxy-*N*-(*p*-tolyl)aniline (9n).[3] Yellow liquid (162 mg, 76%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.15 - 7.12 (m, 1H), 7.02 - 6.97 (m, 4H), 6.79 - 6.71 (m, 3H), 5.98 (s, 1H), 3.80 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 148.0, 140.1, 134.0, 131.1, 129.9, 121.0, 119.8, 119.3, 113.9, 110.5, 55.71, 20.83.

N-(2-Chlorophenyl)-aniline (9o).[2] Yellow oil (144 mg, 71%).
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.28 - 7.18 (m, 4H), 7.09 - 7.02 (m, 3H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.02 (brs, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 141.7, 140.4, 129.9, 129.6, 127.6, 122.8, 121.6, 120.5, 120.3, 115.7.

S19: Characterization data of the synthesized ligands **HL1**–**HL6**

[**HL1**] Yield: (0.183 g, 87%). Anal. Calcd for $C_{10}H_{10}O_1S_2$ (210.31): C 57.11, H 4.79%. Found: C 57.02, H 4.84%, IR (KBr, cm^{-1}): 1159 ($\nu_{C–OH}$), 1590 ($\nu_{C=C}$), 1238 ($\nu_{C=S}$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.58 (s, 3H, –SC*H*$_3$), 6.94 (s, 1H, =C*H*–C(S)–), 7.42-7.94 (m, 5H, –C$_6$*H*$_5$), 15.08 (s, 1H, –C(O*H*)–). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 17.24 (–S*C*H$_3$), 107.93 (–*C*H=C–), 126.77, 128.86, 131.98, 133.19 (–*C*$_6$H$_5$), 169.29 (–*C*(OH) –), 217.33 (–*C*=S).

[**HL2**] Yield: (0.197 g, 82%). Anal. Calcd for $C_{11}H_{12}O_2S_2$ (240.34): C 54.97, H 5.03%. Found: C 54.89, H 5.09%, IR (KBr, cm^{-1}): 1177 ($\nu_{C–OH}$), 1603 ($\nu_{C=C}$), 1232 ($\nu_{C=S}$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.65 (s, 3H, –SC*H*$_3$), 3.87 (s, 3H, –OC*H*$_3$), 6.94 (s, 1H, =C*H*–C(S)–), 6.96-7.87 (m, 4H, –C$_6$*H*$_4$OCH$_3$), 15.18 (s, 1H, –C(O*H*)–). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 17.03 (–S*C*H$_3$), 55.56 (–O*C*H$_3$), 107.20 (–*C*H=C–), 114.26, 128.76, 130.68, 162.93 (–*C*$_6$H$_4$OCH$_3$), 169.63 (–*C*(OH)–), 215.75 (–*C*=S).

[**HL3**] Yield: (0.232 g, 89%). Anal. Calcd for $C_{14}H_{12}O_1S_2$ (260.37): C 64.58, H 4.65%. Found: C 64.49, H 4.74%, IR (KBr, cm^{-1}): 1130 ($\nu_{C–OH}$), 1579 ($\nu_{C=C}$), 1245 ($\nu_{C=S}$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.67 (s, 3H, –SC*H*$_3$), 7.10 (s, 1H, =C*H*–C(S)–), 7.53–8.46 (m, 7H, –C$_{10}$*H*$_7$), 15.18 (s, 1H, –C(O*H*)–). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ 17.27 (–S*C*H$_3$), 108.34 (–*C*H=C–), 122.83, 123.99, 126.87, 126.94, 127.88, 127.92, 130.31, 131.46, 132.99, 135.06 (–*C*$_{10}$H$_7$), 169.19 (–*C*(OH) –), 217.14 (–*C*=S).

[**HL4**] Yield: (0.215 g, 88%). Anal. Calcd for: $C_{10}H_9Cl_1O_1S_2$ (244.75): C 49.07, H 3.71%. Found: C 48.95, H 3.85%. IR (KBr, cm^{-1}): ν = 1121 ($\nu_{C–OH}$), 1582 ($\nu_{C=C}$), 1234 ($\nu_{C=S}$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.64 (s, 3H, –SC*H*$_3$), 6.88 (s, 1H, =C*H*–C(S)–), 7.39–7.80 (m, 4H, –C$_6$*H*$_4$Cl), 15.03 (s, 1H, –C(O*H*)–) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 17.13 (–S*C*H$_3$), 107.53 (–*C*H=C–), 127.84, 128.96, 132.57, 137.88, (–*C*$_6$H$_4$Cl), 167.58 (–*C*(OH)–), 217.44 (–*C*=S) ppm.

[**HL5**] Yield: (0.243 g, 84%). Anal. Calcd for $C_{10}H_9Br_1O_1S_2$ (289.31): C 41.53, H 3.14%. Found: C 41.45, H 3.24%, IR (KBr, cm^{-1}): 1178 ($\nu_{C–OH}$), 1584 ($\nu_{C=C}$), 1236 ($\nu_{C=S}$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.66 (s, 3H, –SC*H*$_3$), 6.90 (s, 1H, =C*H*–C(S)–), 7.57–7.83 (m, 4H, –C$_6$*H*$_4$Br), 15.04 (s, 1H, –C(O*H*)–). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 17.33 (–S*C*H$_3$), 107.69 (–*C*H=C–), 126.57, 128.17, 129.93, 132.13 (–*C*$_6$H$_4$Br), 167.84 (–*C*(OH) –), 217.73 (–*C*=S).

[**HL6**] Yield: (0.169 g, 72%). Anal. Calcd for $C_{11}H_9N_1O_1S_2$ (235.32): C 56.15, H 3.86%. Found: C 56.02, H 3.98%, IR (KBr, cm^{-1}): 1118 ($\nu_{C–OH}$), 1583 ($\nu_{C=C}$), 1229 ($\nu_{C=S}$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.61 (s, 3H, –SC*H*$_3$), 6.84 (s, 1H, =C*H*–C(S)–), 7.67–7.91 (m, 4H, –C$_6$*H*$_4$CN), 14.89(s, 1H, –C(O*H*)–). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 17.43 (–S*C*H$_3$), 108.38 (–*C*H=C–), 118.17 (–*C*N), 114.77, 127.02, 132.46, 138.69 (–*C*$_6$H$_4$CN), 165.77 (–*C*(OH)–), 218.80 (–*C*=S).

S20: References

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