Electronic Supplementary Material (ESI) for Dalton Transactions.

Ferrocenyl palladacycles derived from unsymmetrical pincer-type ligands: Evidences of Pd(0) nanoparticles generation during Suzuki-Miyaura reaction and applications in direct arylation of thiazole and isoxazole

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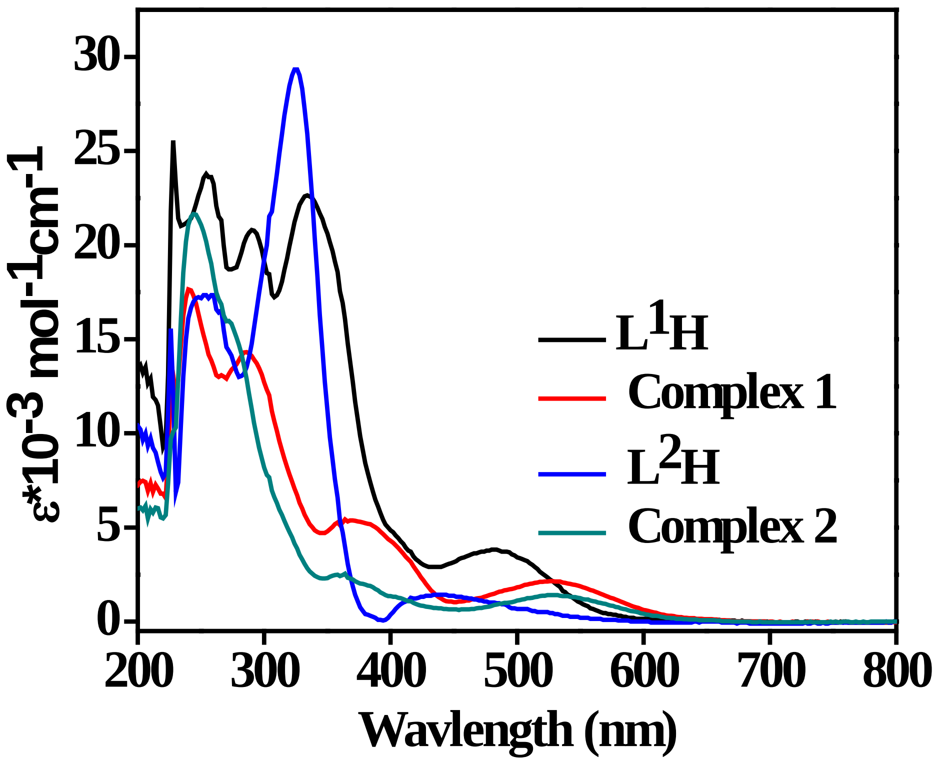


Figure S1. Electronic absorption spectra of ligands L[1]H, L[2]H and metal complexes **Pd1** and **Pd2** in dichloromethane solutions.

Table S1. Electronic spectral data in dichloromethane solution of ligands L[1]H, L[2]H and metal complexes **Pd1** and **Pd2**.

Compound	**λ_{max}/nm(Ɛ mol^{-1} cm^{-1})**
L[1]H	484(3825), 332(22690), 290(20850), 251 (23850)
Complex **1**	532(2150), 365(5420), 285(14320), 240 (17650)
L[2]H	435(1430), 325(29300), 255(17350)
Complex **2**	535(1350), 355(2590), 243(21700).

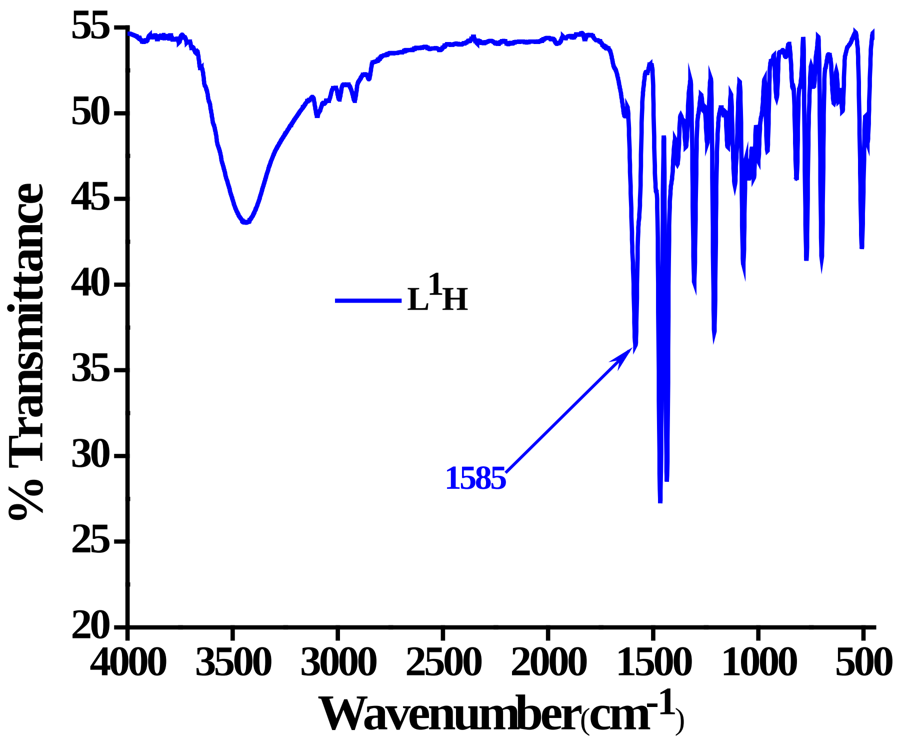


Figure S2. IR spectrum of ligand **L[1]H**.

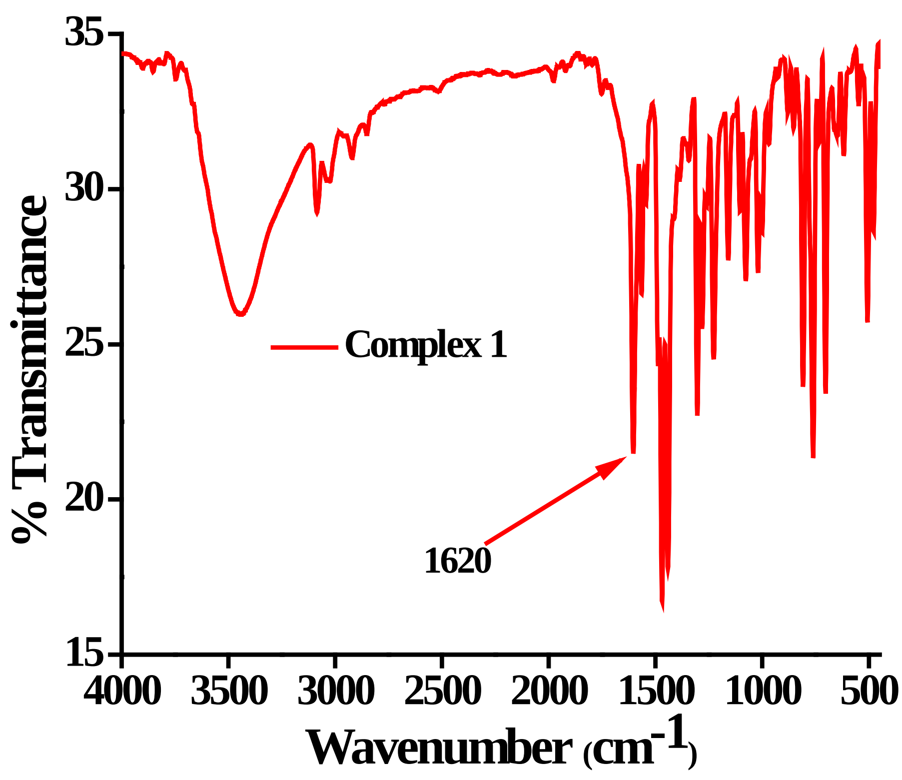


Figure S3. IR spectrum of complex **Pd1**.

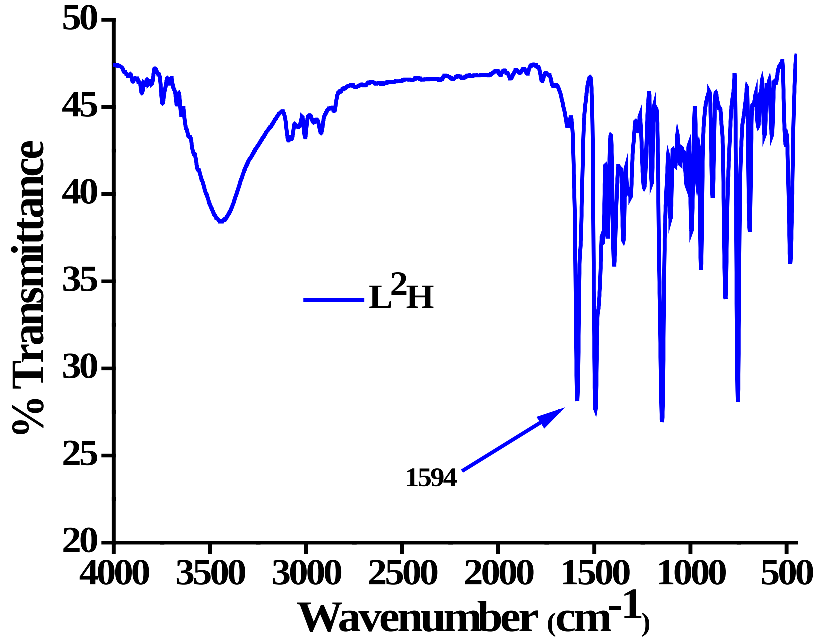


Figure S4. IR spectrum of ligand L^2H.

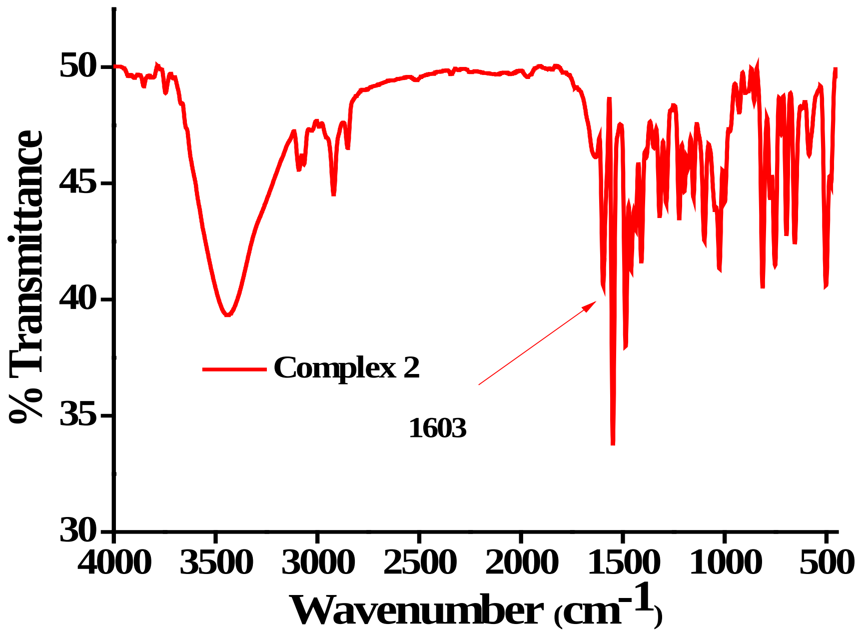


Figure S5. IR spectrum of complex **Pd2**.

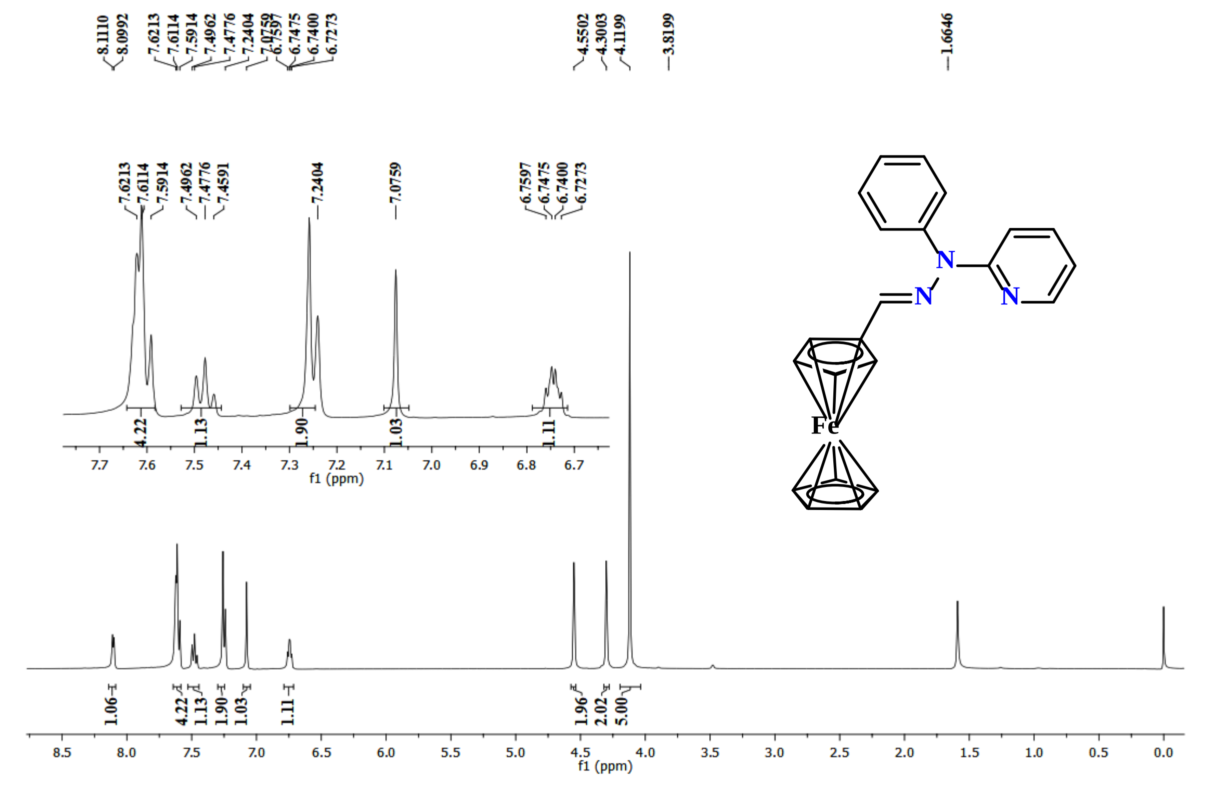


Figure S6. The ^{1}H-NMR spectrum of ligand $L^{1}H$ in $CDCl_3$.

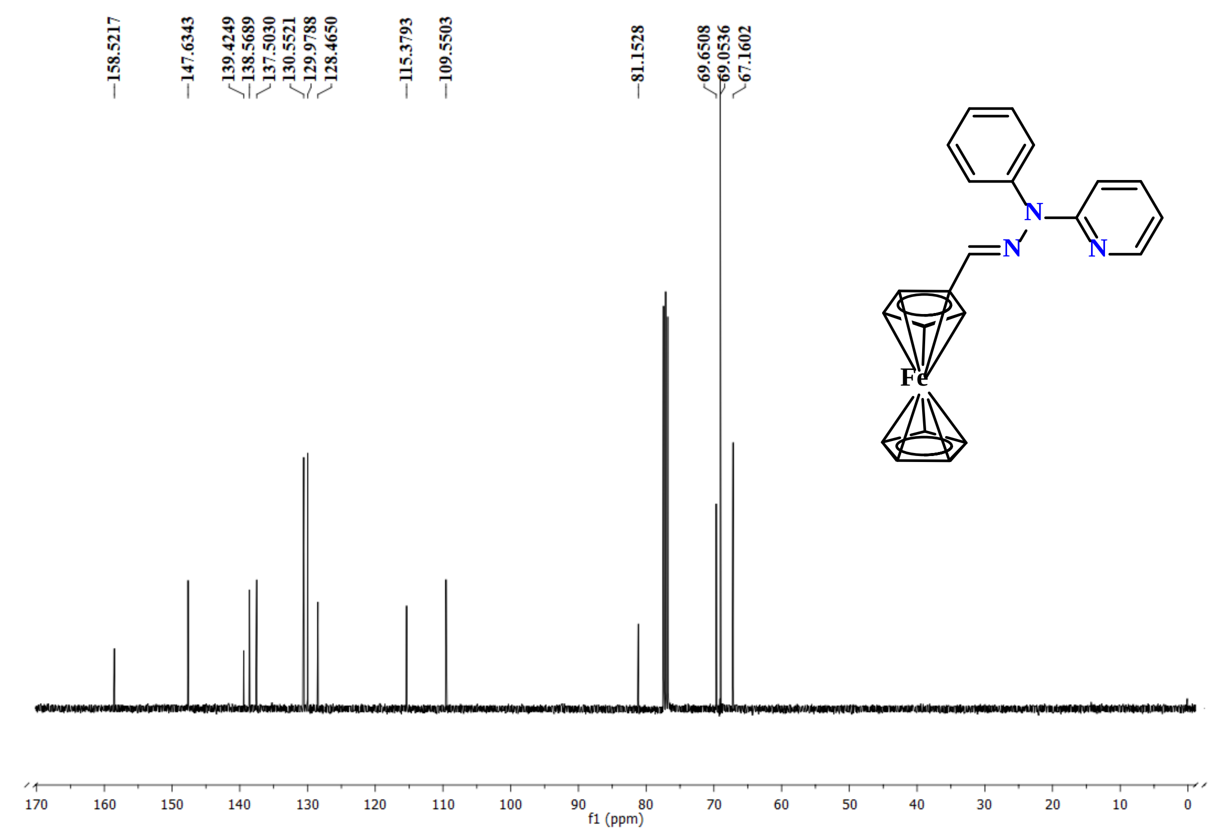


Figure S7. The ^{13}C-NMR spectrum of ligand $L^{1}H$ in $CDCl_3$.

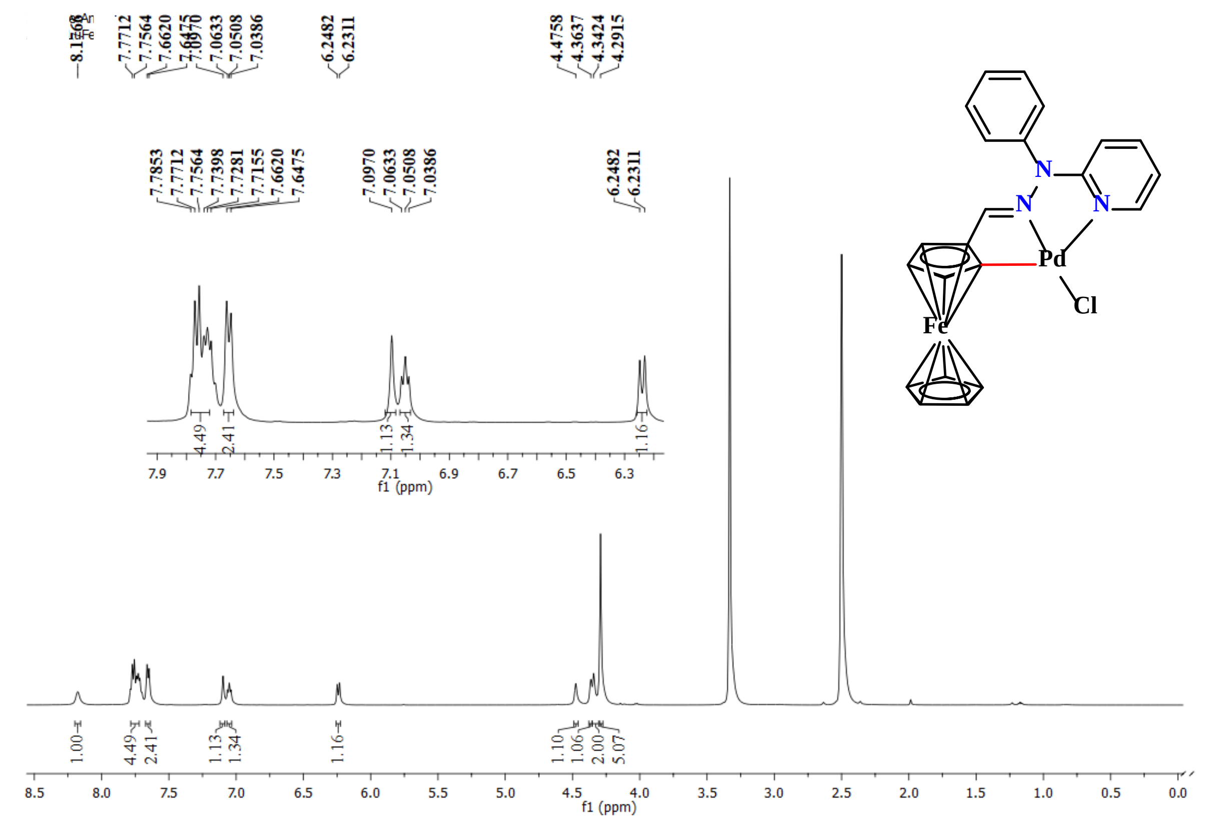


Figure S8. The ^{1}H-NMR spectrum of complex **Pd1** in d^6-DMSO.

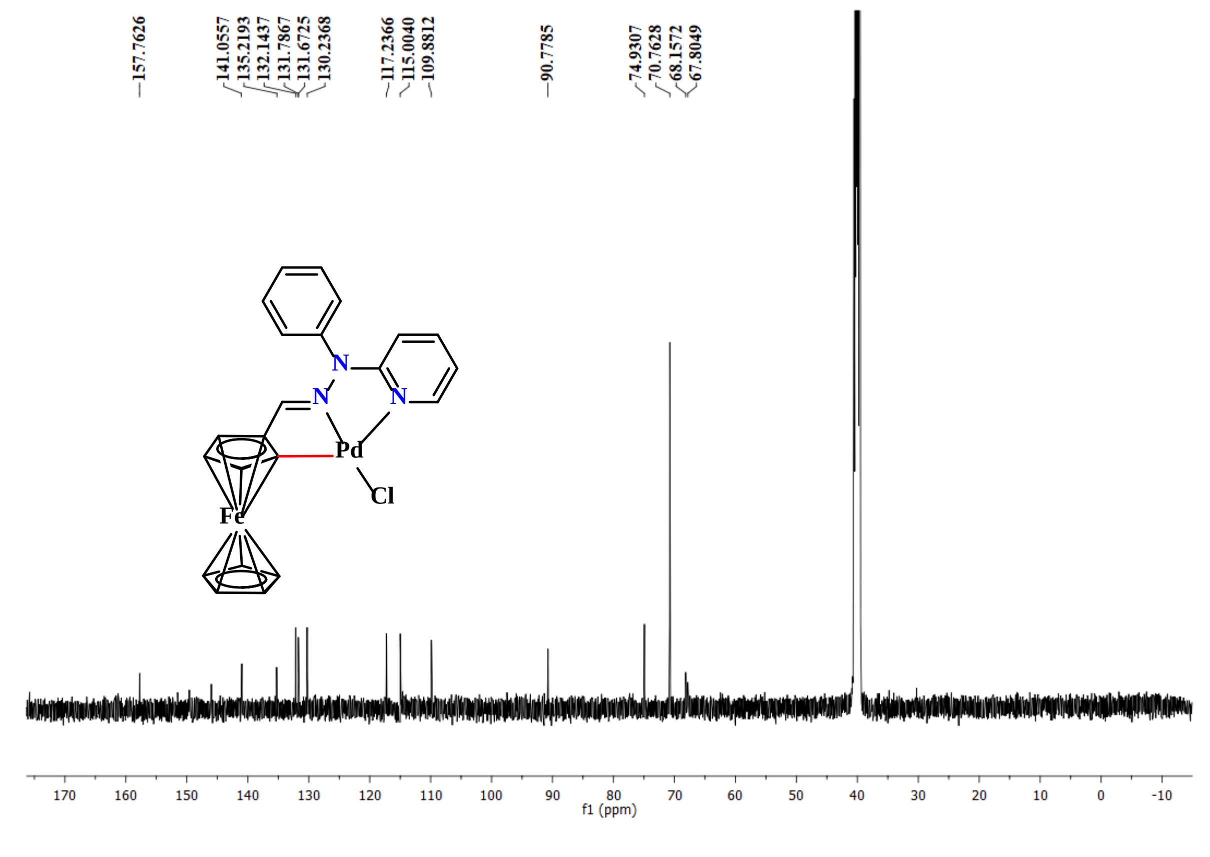


Figure S9. The ^{13}C-NMR spectrum of complex **Pd1** (**1)** in d^6-DMSO.

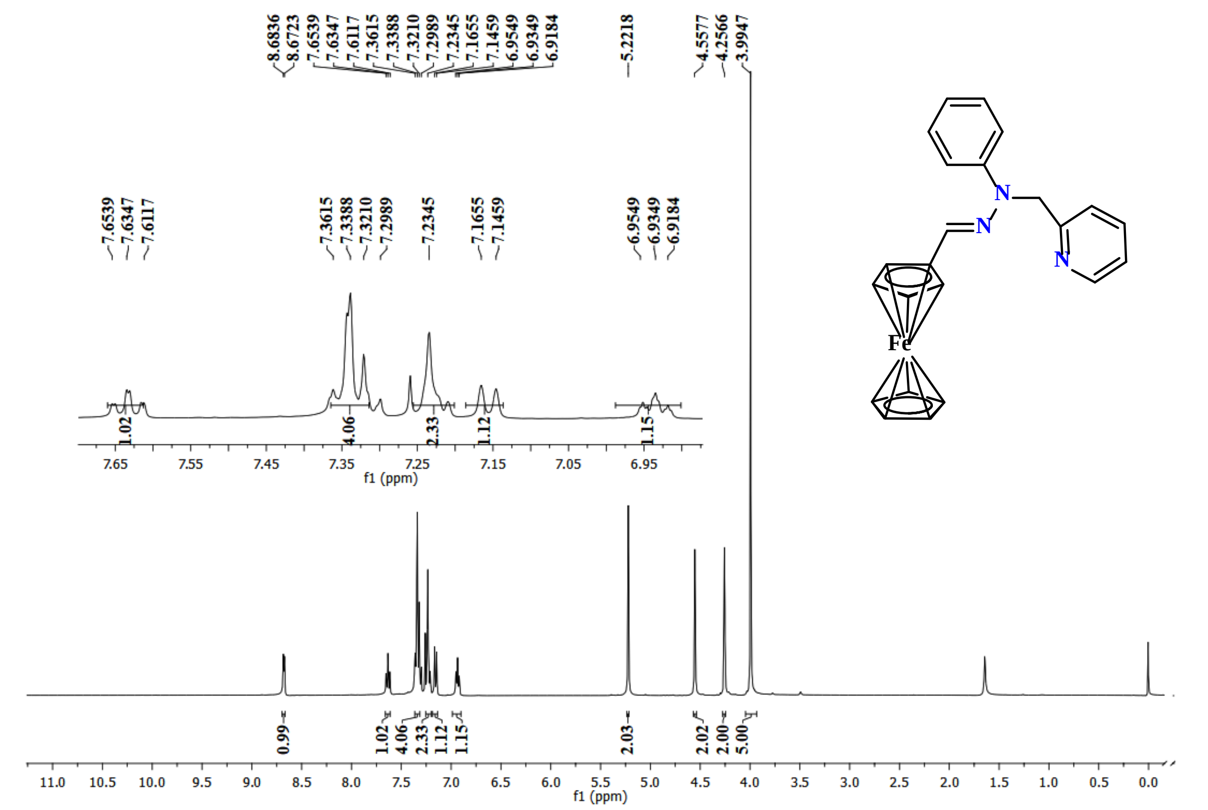


Figure S10. The ^{1}H-NMR spectrum of ligand L^2H in $CDCl_3$.

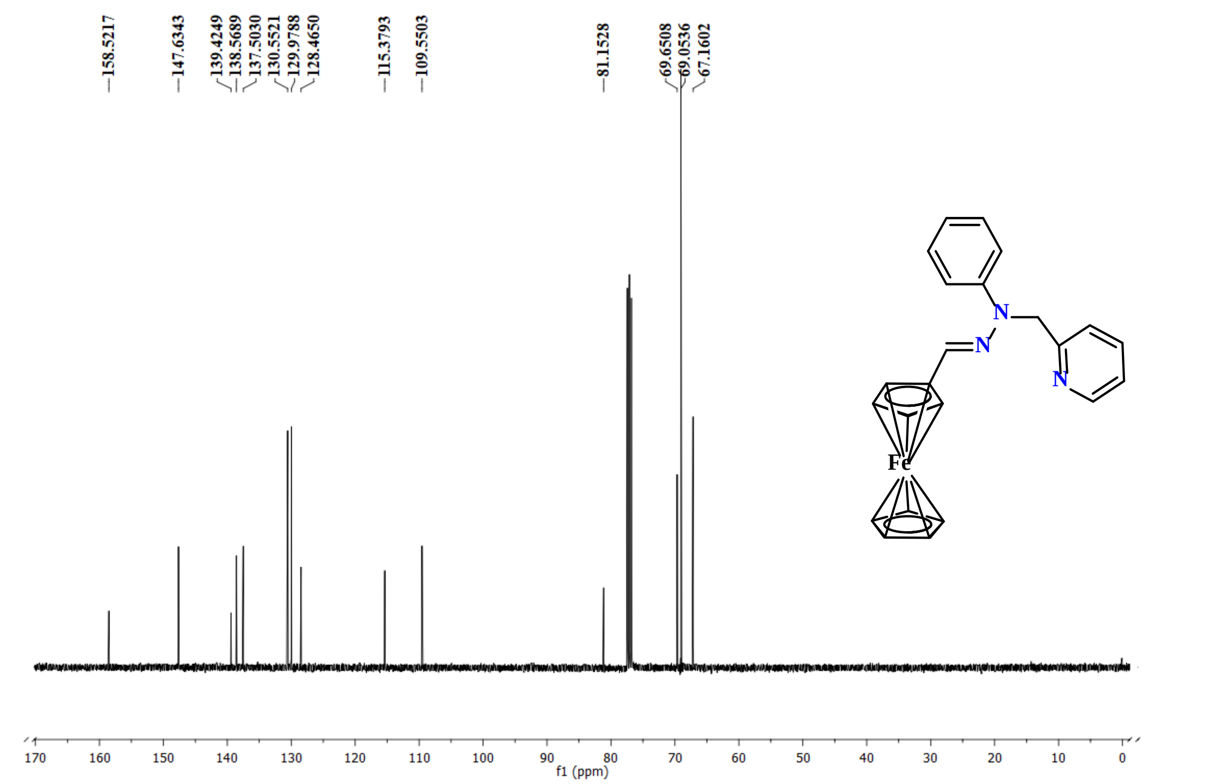


Figure S11. The ^{13}C-NMR spectrum of ligand L^2H in $CDCl_3$.

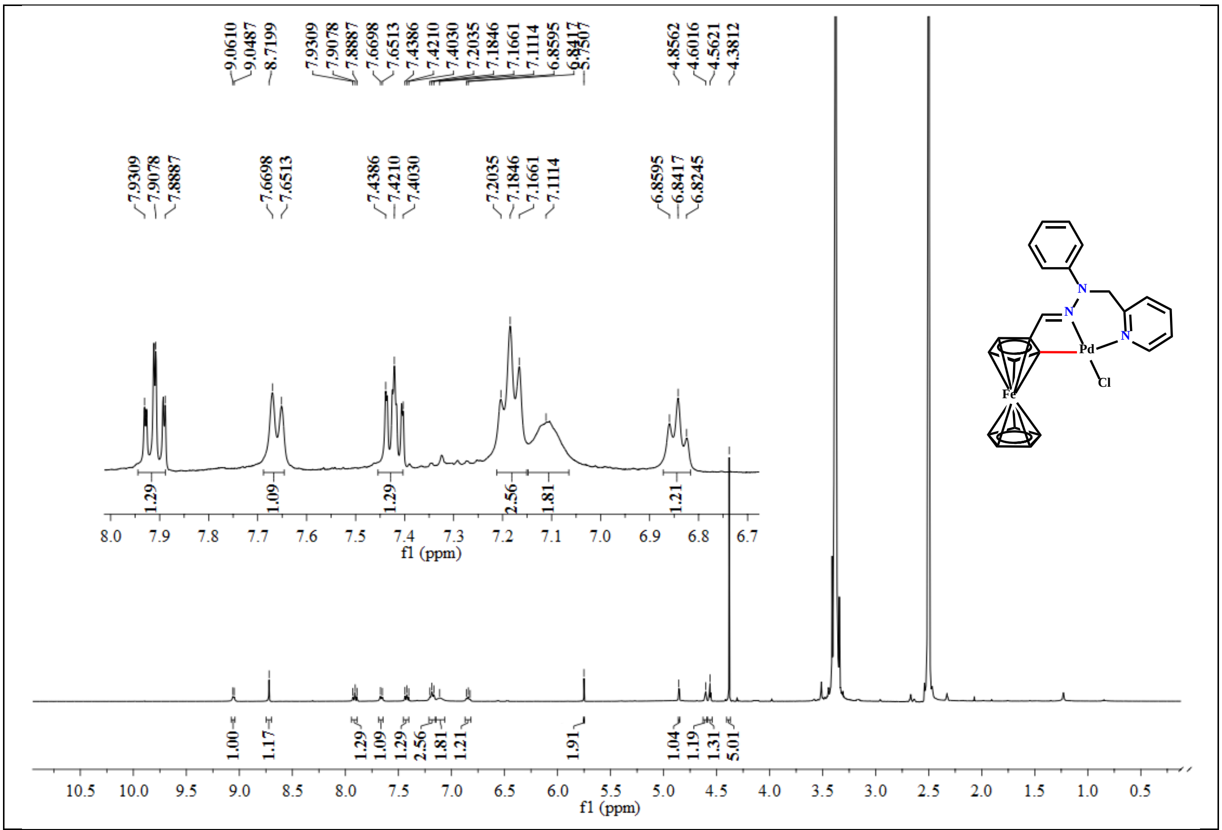


Figure S12. The [1]H-NMR spectrum of complex **Pd2 (2)** in d[6]-DMSO.

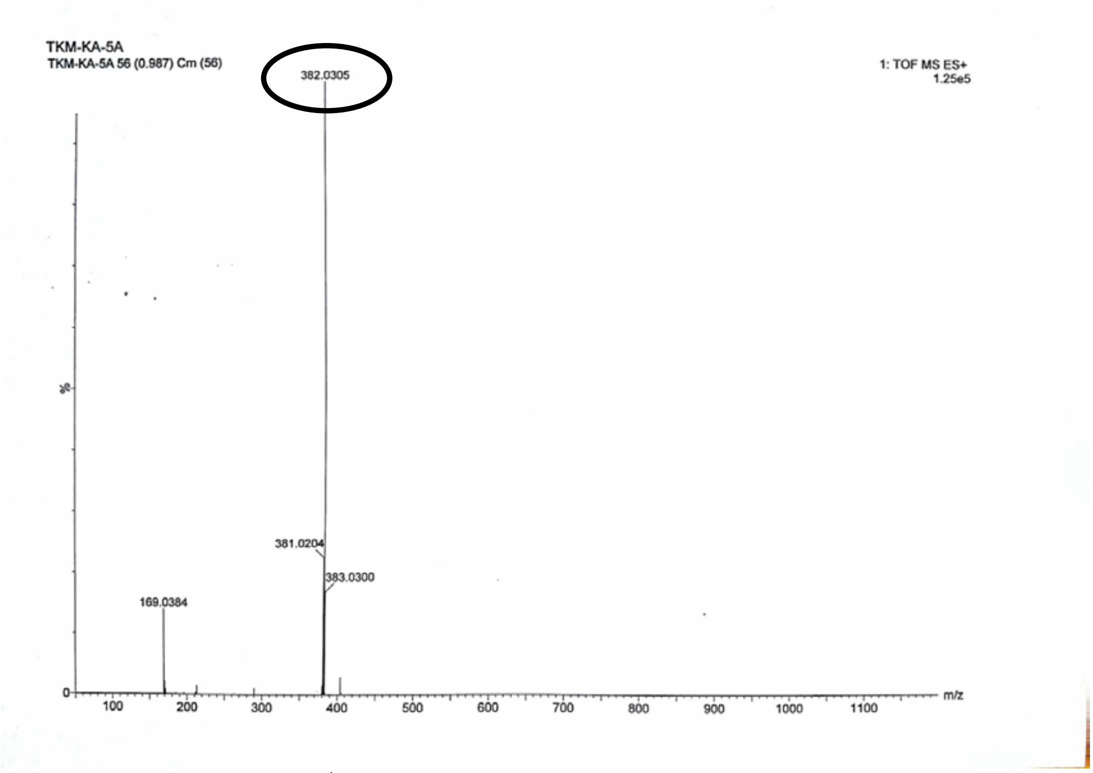


Figure S13. ESI-MS analysis of L[1]H in acetonitrile.

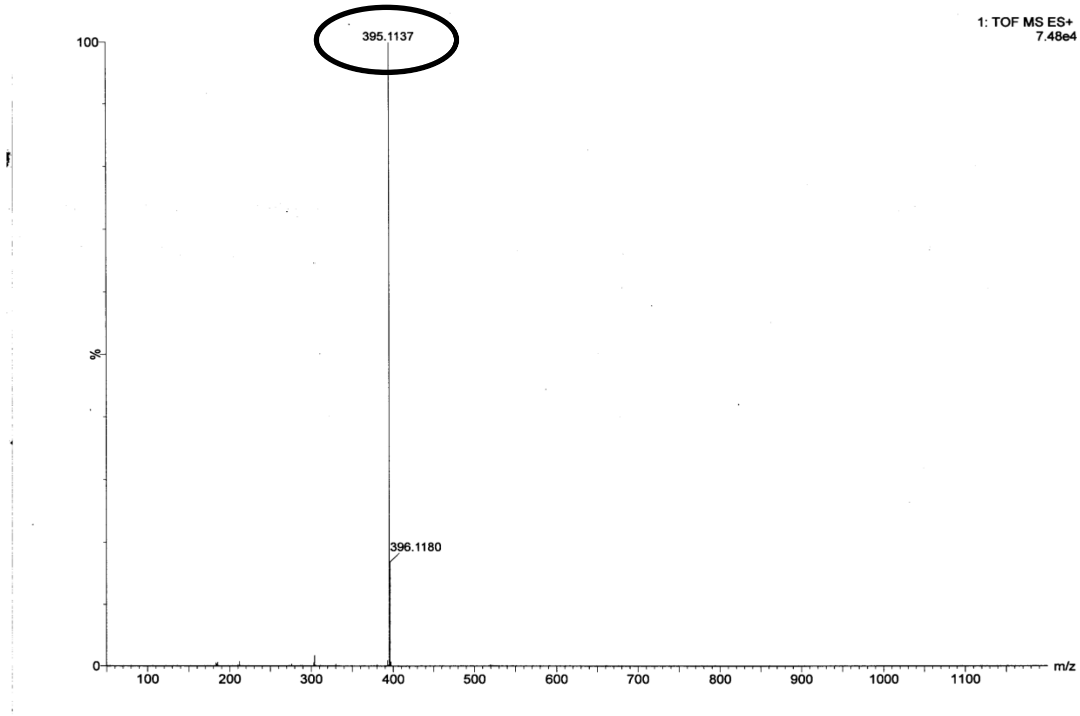


Figure S14. ESI-MS analysis of L^2H in acetonitrile.

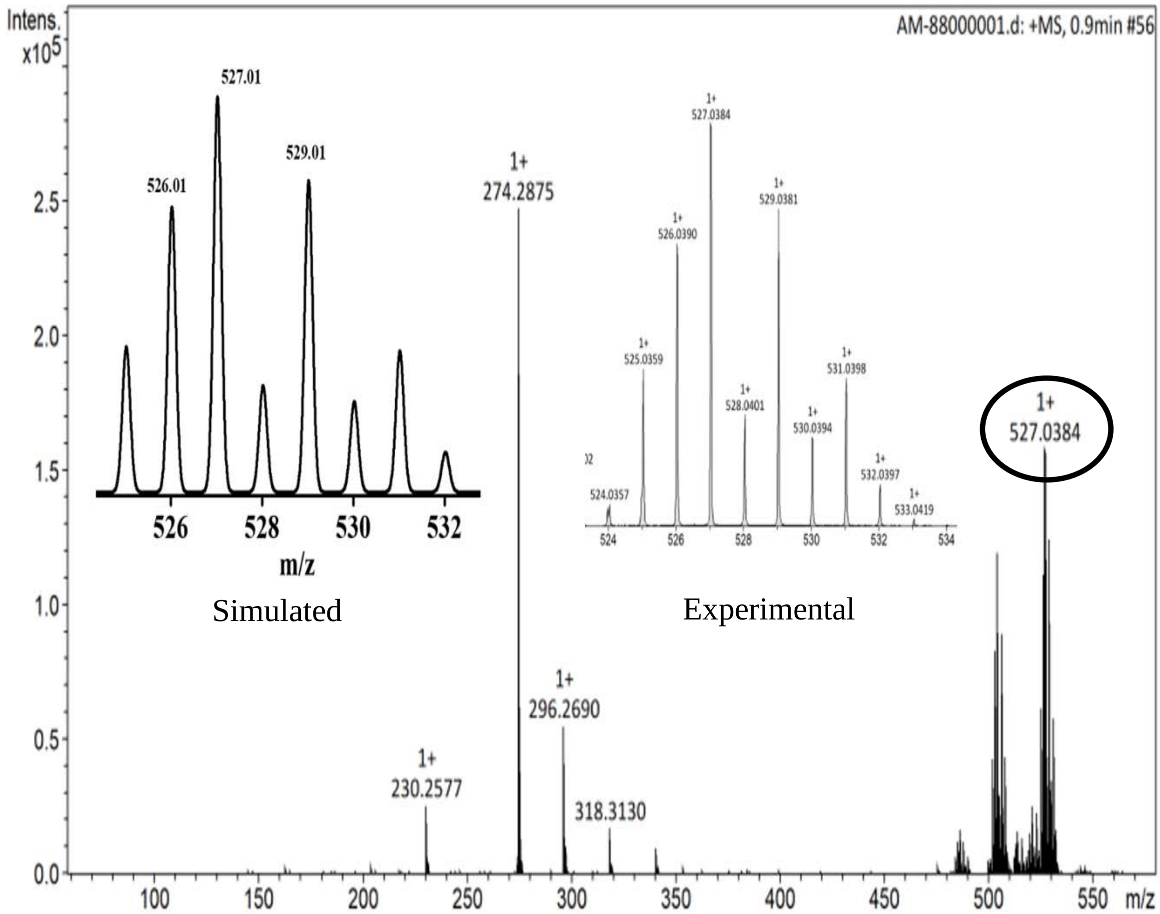


Figure S15. ESI-MS analysis of **Pd1** in acetonitrile.

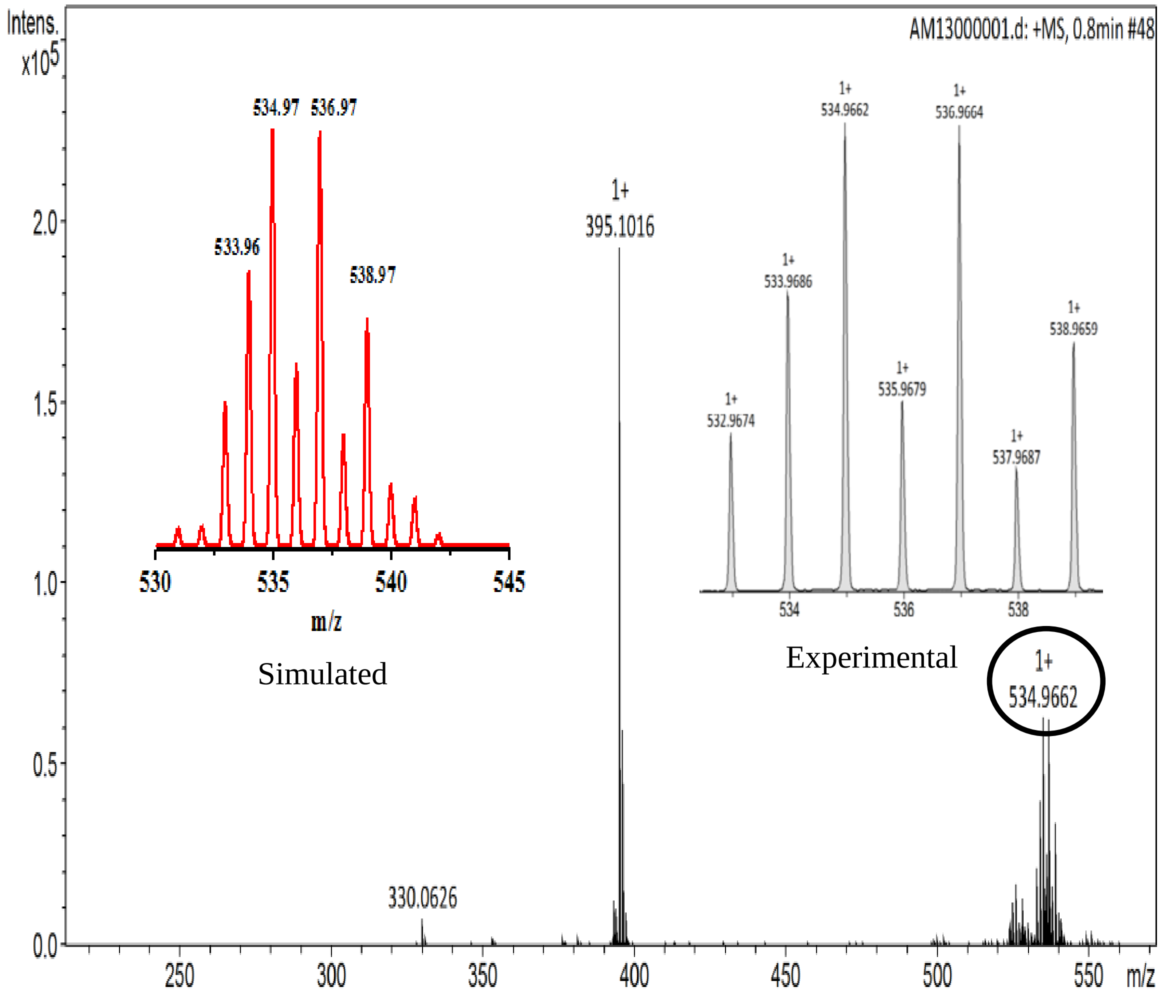


Figure S16. ESI-MS analysis of **Pd2** in acetonitrile.

Table S2. Crystal data and structural refinement parameters for complexes **Pd1** and **Pd2**.

Empirical formula	C22 H18 Cl Fe N3 Pd	C23 H20 Cl Fe N3 Pd	**Z**	4	2
Color	red	red	**ρ_{calc}(gcm^{-3})**	1.757	1.782
Formula weight	522.09	536.12	**F(000)**	1040	536
Temperature (K)	296(2)	293(2)	***θ* range for data collection**	2.125 - 30.043	1.808-28.397
λ (Å) (Mo-Kα)	0.71073	0.71073	**Index ranges**	-14<h<14, -17<k<17 -22<l<22	-11<h<11, -14<k<13 -15<l<12
Crystal system	'monoclinic'	'triclinic'	**Refinement method**	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Space group	P 21/n	P- 1	**Data/restraint/ parameters**	5599/0/ 254	4886/0/262
a(Å)	10.4053(7)	8.8740(7)	**GOF[a] on F^2**	1.277	1.193

b(Å)	12.1239(8)	10.5965(8)	**R_1[b] [I > 2σ(I)]**	0.0412	0.0306
c(Å)	15.8095(11)	11.6557(9)	**R_1 (all data)**	0.0504	0.0375
α(°)	90	85.319(4)	**wR_2[c] (I > 2σ(I))**	0.1408	0.0908
β(°)	98.272(2)	75.046(4)	**wR_2 (all data)**	0.1571	0.1116
γ(°)	90	70.671(4)			

[a]GOF = $[\Sigma[w(F_o^2–F_c^2)^2] /M–N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R_1 = \Sigma\|F_o│–│F_c\|/\Sigma│F_o│$, [c] $wR_2 = [\Sigma[w(F_o^2–F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$

Table S3. Selected bond lengths and bond angles of complex **Pd1** and their theoretical comparison.

Bond lengths (Å)			**Bond angles (°)**		
	Experimental	**Theoretical**		**Experimental**	**Theoretical**
Pd1—C11	1.968(6)	1.98675	C11—Pd1—N3	81.29(22)	81.901
Pd1—N3	1.986(5)	2.03894	C11—Pd1—N1	160.27(22)	158.600
Pd1—N1	2.125(5)	2.19720	N3—Pd1—N1	78.99(21)	76.699
Pd1—Cl1	2.290(2)	2.33925	C11—Pd1—Cl1	97.01(19)	98.803
			N3—Pd1—Cl1	176.48(15)	178.784
			N1—Pd1—Cl1	102.70(17)	102.593

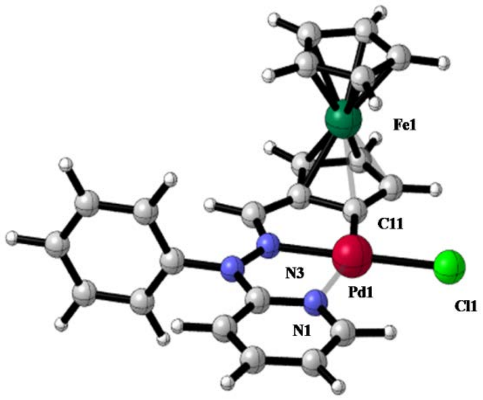
Table S4. Selected bond lengths and bond angles of complex **Pd2** and their theoretical comparison.

Bond lengths (Å)			**Bond angles (°)**		
	Experimental	**Theoretical**		**Experimental**	**Theoretical**
Pd1—C11	1.972(4)	1.98745	C11—Pd1—N3	80.82(14)	80.475
Pd1—N3	2.015(6)	2.08000	C11—Pd1—N1	171.53(12)	170.708
Pd1—N1	2.155(4)	2.22064	N3—Pd1—N1	90.83(11)	90.321
Pd1—Cl1	2.306(7)	2.35950	C11—Pd1—Cl1	92.72(11)	93.950
			N3—Pd1—Cl1	173.13(8)	174.126
			N1—Pd1—Cl1	95.69(8)	95.206

DFT calculation

Optimized structure:

Complexes **Pd1** and **Pd2** are diamagnetic at room temperature indicating their singlet ground state. The geometry optimization of these complexes was performed using their crystallographic coordinates in gas phase in their singlet spin state without any ligand simplification by DFT method using the (R)B3LYP hybrid functional[1] approach incorporated in GAUSSIAN 09 program package.[2] In the ground state (S_0), HOMO of all the complexes mainly on metal centre (Fe-71% for **Pd1** and Fe-80% for **Pd2**) and ligand moity (L-26% for Pd1 and L-15% for **Pd2**). Ongoing to the more stabilized H-1 contribution iron Fe-76% for **Pd1** and Fe-71% for **Pd2**). But going to H-2 state its mainly contribute ligand orbital l (L-65% for **Pd1** and L-69% for **Pd2**) and d orbital of Pd (15%). On the other hand, first vacant orbital LUMO mainly composed of π* orbital delocalized mainly ligands (L-84% for **Pd1** and L-79% for **Pd2)** But on the other hand L+1 composed π* orbital delocalized L (L-45% for **Pd1** and L-69% for **Pd2)** and d orbital of Pd (Pd-43% for **Pd1** and Pd-24% for **Pd2**). The energy difference between HOMO and LUMO are ~3.72 eV (Complex **Pd1**) and 3.82 eV (Complex **Pd2**).



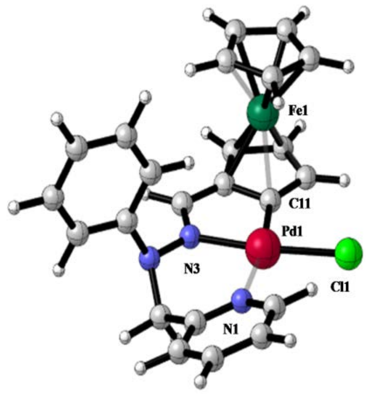


Figure S17. Optimized molecular structures of complex **Pd1** and **Pd2**. (Pd: Deep red, cyan, Fe: Blue Cl: green, N: blue, O: red, C: grey.

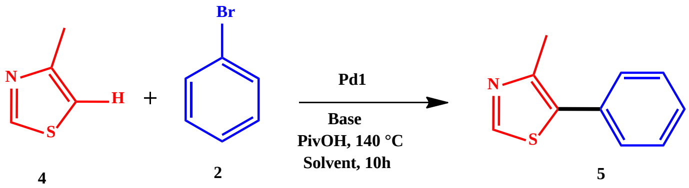
Table S5. Frontier Molecular Orbital Composition (%) in the ground state for complex **Pd1**.

Complex 1						
Orbital	**Energy(eV)**	**Pd**	**Fe**	**Cl**	**L**	**Main orbital contribution**
L+5	-0.33	7	54	0	40	dz2(Fe)
L+4	-0.49	0	3	0	97	π*(L)
L+3	-0.72	5	1	1	94	π*(L)
L+2	-1.03	1	4	0	95	π*(L)
L+1	-1.52	43	2	10	45	dxy (Pd) + π*(L)
L	**-1.75**	**6**	**10**	**0**	**84**	π*(L)
H	**-5.47**	**2**	**71**	**1**	**26**	dx2-y2(Fe)+ π(L)
H-1	-5.55	4	76	0	19	dx2-y2(Fe)
H-2	-5.81	9	26	0	65	dx2-y2(Fe)+ π(L)

H-3	-6.38	42	31	8	19	dz2 (Fe) +dz2 (Pd)
H-4	-6.48	26	8	11	55	dyz (Pd)_ π(L)
H-5	-6.69	34	53	4	10	dz2 (Fe) +dz2 (Pd)

Table S6. Frontier Molecular Orbital Composition (%) in the ground state for complex **Pd2**.

Complex 2						
Orbital	**Energy(eV)**	**Pd**	**Fe**	**Cl**	**L**	**Main orbital contribution**
L+5	-0.29	1	14	0	85	π*(L)
L+4	-0.41	7	52	0	42	dz2(Fe)+π*(L)
L+3	-0.75	2	0	0	98	π*(L)
L+2	-1.24	24	5	5	67	π*(L)
L+1	-1.46	24	2	6	69	dx2-y2 (Pd) + π*(L)
L	**-1.74**	**7**	**13**	**1**	**79**	π*(L)
H	**-5.56**	**4**	**80**	**1**	**15**	dxy(Fe)
H-1	-5.62	4	71	0	25	dx2-y2(Fe)
H-2	-5.87	9	21	2	69	π(L)
H-3	-6.4	48	11	4	38	dyz (Pd)
H-4	-6.46	35	16	5	45	dyz (Pd)+π(L)
H-5	-6.56	36	6	28	31	dz2 (Fe) +dz2 (Pd)



Scheme 1. Screening of reaction conditions for the direct arylation reaction of 4-methylthiazole with bromobenzene.

Table S7.Optimization of arylation reaction .

Entry	Base	Solvent	% Yield
1	NaOAc	DMA	80
2	KF	DMA	22
3	K_3PO_4	DMA	41
4	KOH	DMA	55
5	Na^tOBu	DMA	12
6	K^tOBu	DMA	25
7	K_2CO_3	DMA	94
8	Na_2CO_3	DMA	90
9	KOAc	DMA	12
10	$NaHCO_3$	DMA	62
11	K_2CO_3	Toluene	75
12	K_2CO_3	NMP	65
13	K_2CO_3	DMF	55
14	K_2CO_3	Dioxane	60
15	K_2CO_3	DMSO	74
16	K_2CO_3	DMA	NR[a,b]
17	K_2CO_3	DMA	NR[c]
18	K_2CO_3	DMA	43[d]

Reaction conditions: **Pd1** (0.1 mol%), 2a (1.0 mmol), 3a (1.2 mmol), base (2 mmol), 0.3 mol% PivOH, sovent (2.0 mL), 140 °C, 10 h. [a]only ligand L^1H, [b]No base, [c]In presence of Na_2PdCl_4 [d]In the absence of PivOH

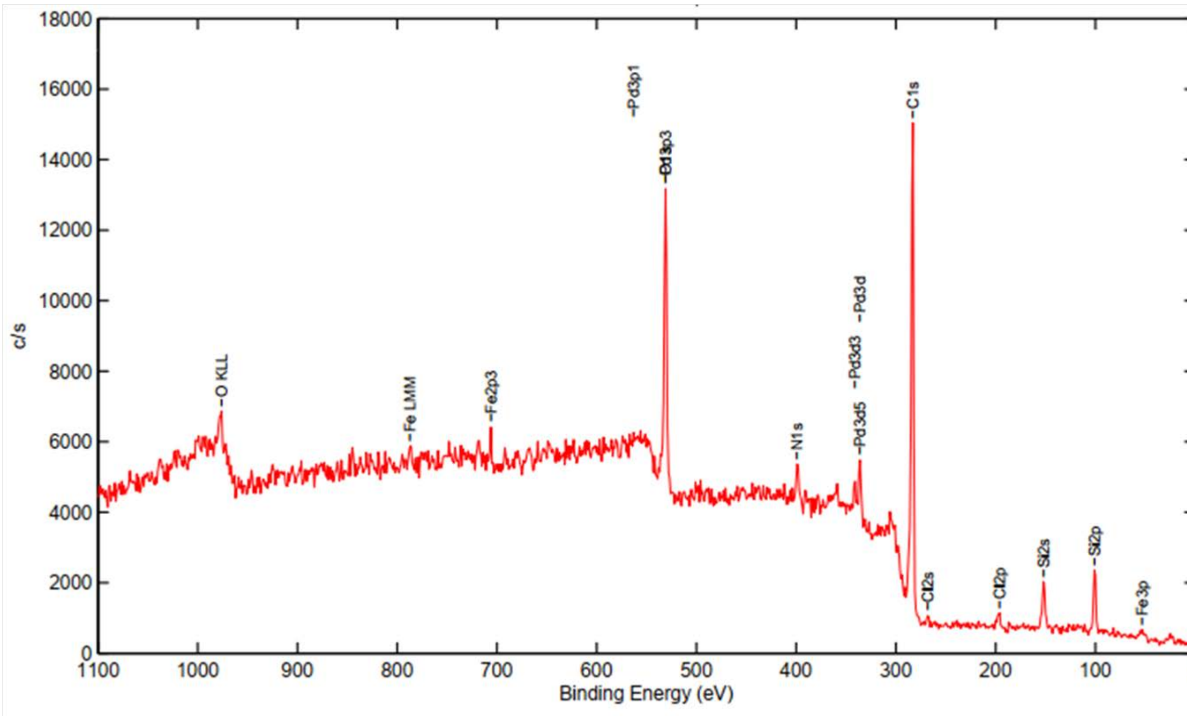


Figure S18. XPS survey scan of **Pd1**.

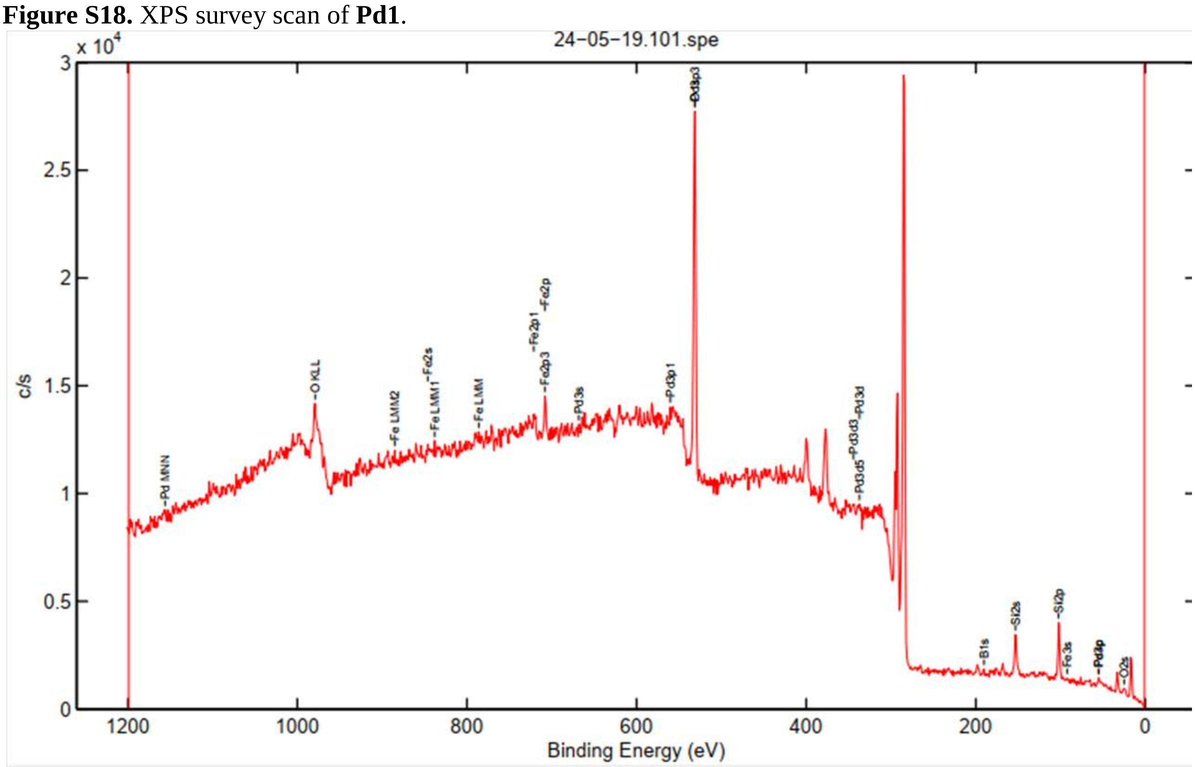


Figure S19. XPS survey scan of SMC reaction mixture in the presence of **Pd1**.

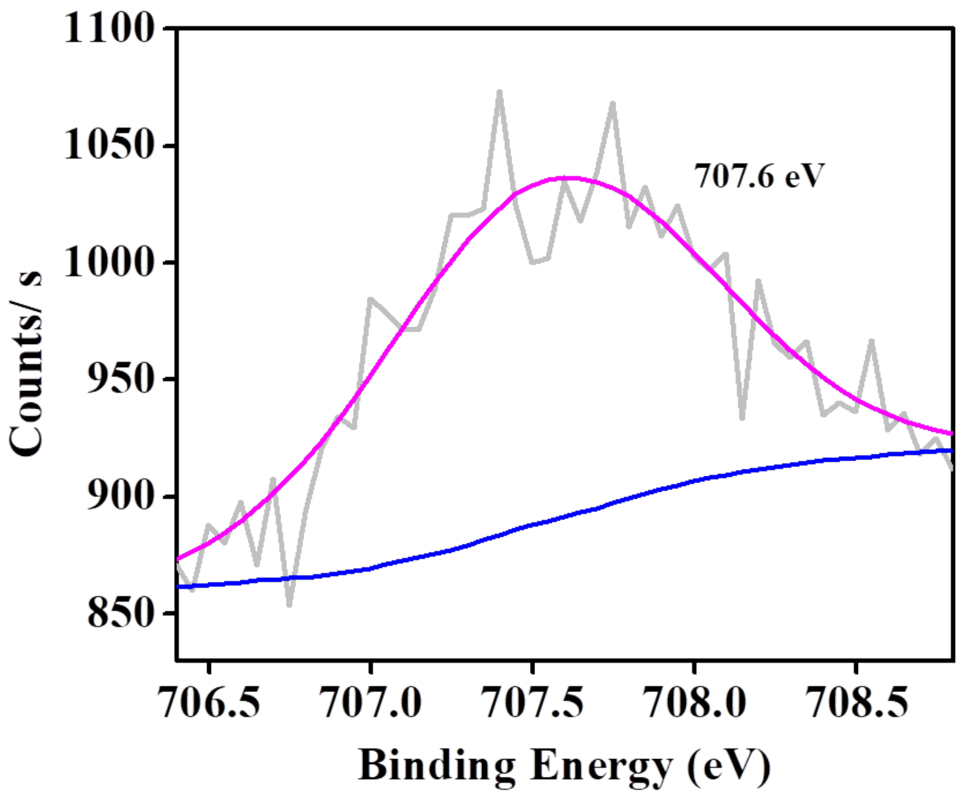


Figure S20. XPS spectrum of 2p3/2 of iron(II) of catalyst **Pd1**.

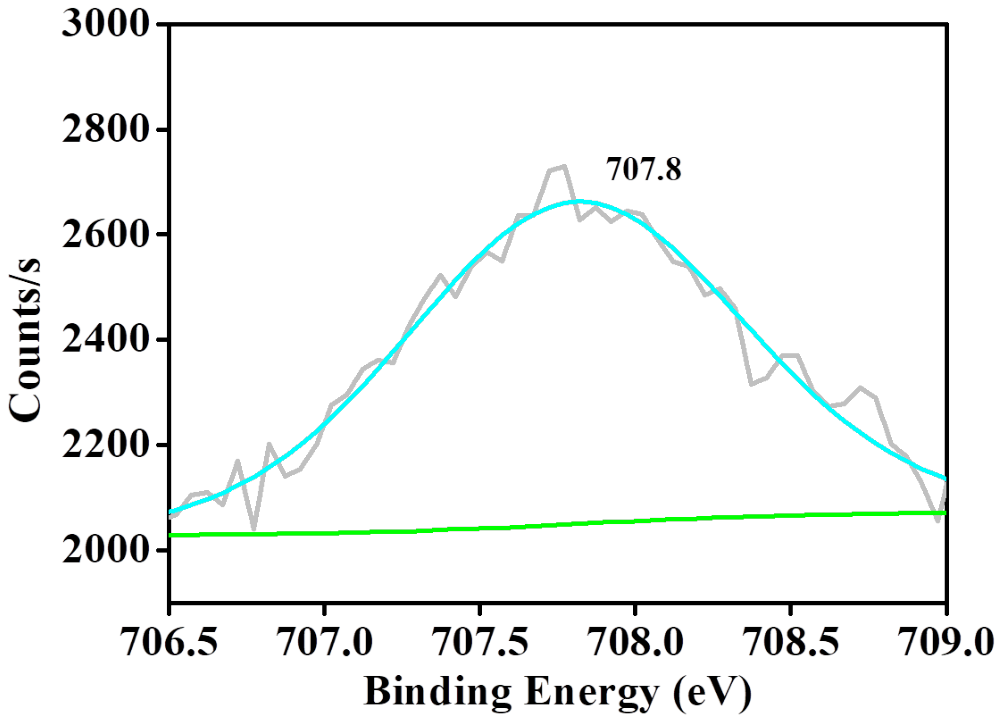


Figure S21. XPS spectrum of 2p3/2 of iron(II) of catalyst **Pd1** during SMC reaction.

[1,1'-biphenyl]-4-carbaldehyde][3]**(3aa)** White colored solid, Yield 167.6 mg 92% (Complex **Pd1**), 173 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ 192.15, 147.29, 139.78, 135.23, 130.41, 129.15, 128.60, 127.80, 127.48.

1-([1,1'-biphenyl]-4-yl)ethanone (3ab) White colored solid, Yield 184.4 mg 92% (Complex **Pd1**), 188.4 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 2.62 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ 198.01, 145.87, 139.92, 135.86, 129.07, 129.03, 128.35, 127.37, 127.32, 26.85.

4-nitro-1,1'-biphenyl (3ac) Off-white colored solid, Yield 181.3 mg 91% (Complex **Pd1**), 185.2 mg 93% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.46 (dt, *J* = 13.6, 7.1 Hz, 3H) ^{13}C-NMR (500 MHz, $CDCl_3$) δ 129.25, 129.01, 127.90, 127.48, 127.47, 124.21, 124.20.

2-nitro-1,1'-biphenyl (3ad) Off-white colored solid, Yield 151.4 mg 76% (Complex **Pd1**), 151.4 mg 76% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 4H), 7.40 – 7.37 (m, 1H), 7.19 (dd, *J* = 17.0, 7.8 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 143.50, 139.53, 130.47, 129.11, 128.83, 128.51, 127.66, 127.18, 118.67, 115.62.

[1,1'-biphenyl]-4-carbonitrile[4] **(3ae)** White colored solid, Yield 167.6 mg 92% (Complex **Pd1**), 170.1 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69 (q, *J* = 8.6 Hz, 4H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 6.6 Hz, 1H).^{13}C-NMR (101 MHz, $CDCl_3$) δ 145.77, 139.27, 132.68, 129.19, 128.74, 127.82, 127.31, 119.02, 111.00.

2-phenylquinoline (3af) White colored solid, Yield 133.40 mg 65% (Complex **Pd1**), 158.0 mg 77% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.15 (t, *J* = 8.5 Hz, 3H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 3H), 7.45 (t, *J* = 7.3 Hz, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 157.40, 148.32, 139.72,136.76, 129.76, 129.64, 129.31, 128.83, 127.58, 127.45, 127.20, 126.28, 119.01.

2-phenylpyridine[3] **(3ag)** Oil liquid, Yield 116.4 mg 75% (Complex **Pd1**), 121.1 mg 78% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66(d, J= 4.81H), 8.00-7.98 (m,2H), 7.65-7.59 (m, 2H), 7.46-7.42 (m, 2H) 7.38-7.36 (m, 1H) 7.14- 7.10 (m, 1H) ^{13}C-NMR (126 MHz, $CDCl_3$) δ 157.47, 149.66, 139.40, 136.80, 128.99, 128.78, 126.95, 122.13, 120.60.

2,6-diphenylpyridine (3ah) White colored solid, Yield 152.6 mg 66% (Complex **Pd1**), 164.2 mg 71% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.9 Hz, 4H), 7.84 (t, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 4H), 7.52 – 7.48 (m, 2H).^{13}C- NMR (126 MHz, $CDCl_3$) δ 156.85, 139.54, 137.48, 129.00,128.71,127.02, 118.67

1-phenylnaphthalene(**3ak**) White colored liquid Yield 176.5 mg 86% (Complex **Pd1**), 194 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 9.4 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.53 (m, 6H), 7.49 (t, *J* = 6.9 Hz, 3H).^{13}C-NMR (101 MHz, $CDCl_3$) δ 140.94, 140.44, 133.98, 131.80, 130.27, 128.46, 127.83, 127.42, 127.12, 126.22, 125.96, 125.57

4'-ethyl-[1,1'-biphenyl]-4-carbaldehyde] **(3al)** White colored solid, Yield 176.5 mg 84% (Complex **Pd1**), 180.7 mg 86% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.07, 147.22, 144.98, 137.09, 135.06, 130.40, 128.76, 128.66, 127.52, 127.41, 28.70, 15.68.

1-(4'-ethyl-[1,1'-biphenyl]-4-yl)ethanone) (3am) White colored solid, Yield 190.6 mg 85% (Complex **Pd1**), 195.1 mg 87% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 197.96, 145.86, 144.69, 137.27, 135.64, 129.01, 128.60, 127.29, 127.09, 28.65, 26.78, 15.65.

4'-ethyl-4-nitro-1,1'-biphenyl (3an) Yellow colored solid, Yield 171.1 mg 86% (Complex **Pd1**), 177.1 mg 89% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 146.32 (s), 145.76 (s),137.30, 133.25, 129.35, 128.18, 127.84, 119.73, 111.22, 29.23, 16.21.

4'-ethyl-2-nitro-1,1'-biphenyl (3ao) Yellow colored solid, Yield 195.4 mg 86% (Complex **Pd1**), 202.2 mg 89% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.17 (dd, *J* = 12.2, 7.6 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 2.72 (t, *J* = 6.5 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 143.58, 143.18, 136.74, 130.49, 129.01, 128.30, 127.70, 118.65, 115.56, 28.60, 15.57.

4'-ethyl-[1,1'-biphenyl]-4-carbonitrile (3ap) White colored solid, Yield 178.2 mg 86% (Complex **Pd1**), 188.6 mg 91% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68 (q, *J* = 8.7 Hz, 4H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.27

(t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 145.72, 145.16, 136.59, 132.65, 128.75, 127.58, 127.24, 119.11, 110.62, 28.66, 15.57.

2-(4-ethylphenyl)quinolone (3aq) White colored solid, Yield 158.6 mg 68% (Complex **Pd1**), 167.9 mg 72% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.2, 5.4 Hz, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 9.3 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H).^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.51, 148.37, 145.85, 137.24, 136.86, 128.40, 127.72, 127.53, 127.18, 119.04, 28.83, 15.73.

2-(4-ethylphenyl)pyridine (3ar) Off-white colored solid, Yield 130.0 mg 71% (Complex **Pd1**), 139.3 mg 76% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.20 (ddd, *J* = 6.8, 4.9, 2.2 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.60, 149.61, 145.39, 136.88, 128.52, 128.29, 126.97, 122.01, 120.44, 28.70, 15.61.

2,6-bis(4-ethylphenyl)pyridine (3as) White colored solid, Yield 186.8 mg 65% (Complex **Pd1**), 201.2 mg 70% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 4H), 7.79 – 7.74 (m, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 4H), 2.71 (q, *J* = 7.6 Hz, 4H), 1.28 (t, *J* = 7.6 Hz, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 156.87, 145.45, 137.43, 137.15, 128.31, 127.05, 118.21, 28.81, 15.74.

1-(4-ethylphenyl)naphthalene (**3at**) White colored liquid, Yield 197.0 mg 85% (Complex **Pd1**), 211.2 mg 91% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.97 (d, *J* = 10.3 Hz, 1H), 7.68 – 7.52 (m, 6H), 7.46 (d, *J* = 7.8 Hz, 2H), 2.93 – 2.85 (m, 2H), 1.47 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 143.45, 140.54, 138.30, 134.06, 131.99, 130.28, 128.51, 128.03, 127.70, 127.17, 126.40, 126.18, 125.97, 125.67, 28.90, 15.88.

3-phenylpyridine (**3au**) White colored liquid, Yield 122.6 mg 79% (Complex **Pd1**), 127.2 mg 82% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 3.1 Hz, 1H), 8.55 (dd, *J* s= 4.8, 1.6 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.53 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (dd, *J* = 8.6, 4.8 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 148.37, 137.85, 136.69, 134.43, 129.13, 128.17, 127.20, 123.71.

3-(4-ethylphenyl)pyridine (**3av**) White colored liquid, Yield 125.7 mg 81% (Complex **Pd1**), 131.9 mg 85% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 3.1 Hz, 1H), 8.54 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 8.1, 2.5 Hz, 3H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 148.29, 144.43, 136.63, 135.21, 134.21, 128.78, 127.10, 123.57, 28.51, 15.77.

1-(4'-chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (3ba) White colored solid, Yield 205.3 mg 89% (Complex **Pd1**), 209.9 mg 91% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 2.62 (s, 3H**).** ^{13}C-NMR (101 MHz, $CDCl_3$) δ 197.79, 144.55, 138.36, 136.15, 134.54, 129.28, 128.83, 127.14, 26.66.

4'-chloro-[1,1'-biphenyl]-4-carbonitrile (3bb) White colored solid, Yield 196.5 mg 92% (Complex **Pd1**), 202.9 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 144.48, 137.67, 135.05, 132.79, 129.40, 128.55, 127.65, 118.84, 111.35.

3-(4-chlorophenyl)pyridine (3bc) White colored liquid, Yield 162.1 mg 85% (Complex **Pd1**), 168.7 mg 89% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.61 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.34 (m, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 148.74, 148.07, 136.25, 135.52, 134.28, 129.29, 128.39, 123.63.

2-(4-chlorophenyl)quinoline (3bd) White colored solid, Yield 174.9 mg 73% (Complex **Pd1**), 184.56 mg 77% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 1H), 8.13 (dd, *J* = 14.3, 8.8 Hz, 3H), 7.83 (dd, *J* = 7.9, 3.6 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 20.7, 7.8 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 156.12, 148.31, 138.14, 137.06, 135.63, 129.77, 129.01, 127.57, 126.60, 118.67.

4'-chloro-3-nitro-1,1'-biphenyl (3be) Yellow colored solid, Yield 165.9 mg 71% (Complex **Pd1**), 179.9 mg 79% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 148.77, 141.61, 137.09, 134.85, 132.84, 129.90, 129.37, 128.42, 122.34, 121.76.

4'-chloro-2-nitro-1,1'-biphenyl (3bf) Yellow colored solid, Yield 163.55 mg 70% (Complex Pd1), 179.9 mg 77% (Complex **Pd2**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.41 – 7.38 (m, 3H), 7.24 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.15, 135.99, 135.31, 134.55, 132.57, 131.91, 129.37, 129.00, 128.64 124.36.

1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (3ca) White colored solid, Yield 197.1 mg 92% (Complex **Pd1**), 203.52 mg 95% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.18 (t, *J* = 8.1 Hz, 2H), 2.66 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 197.68, 144.75, 135.87, 128.98, 127.07, 116.01, 26.64.

4'-fluoro-[1,1'-biphenyl]-4-carbonitrile (3cb) White colored solid, Yield 183.4 mg 93% (Complex **Pd1**), 187.34 mg 95% (Complex **Pd2**);^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.55 (dd, *J* = 8.5, 4.9 Hz, 2H), 7.16 (t, *J* = 8.7 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.51, 162.04, 144.70, 135.37, 132.74, 129.09, 127.66, 118.92, 116.12, 111.03.

3-(4-fluorophenyl)pyridine (3cc) White colored oil, Yield 150.6 mg 87% (Complex **Pd1**), 155.87 mg 90% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.61 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.39 (s, 1H), 7.18 (t, *J* = 8.2 Hz, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 163.92, 161.95, 148.42, 135.81, 134.25, 133.92, 128.85, 123.64, 116.16.

2-(4-fluorophenyl)quinoline (3cd) White colored solid, Yield 167.43 mg 75% (Complex **Pd1**), 180.83 mg 81% (Complex **Pd2**);^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.13 (m, 4H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 6.9 Hz, 1H), 7.20 (t, *J* = 8.7 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.12, 162.65, 156.32, 148.30, 136.98, 135.91, 129.84, 127.57, 126.43, 118.72, 115.80.

4'-fluoro-3-nitro-1,1'-biphenyl (3ce) Yellow colored solid, Yield 175.23 mg 75% (Complex **Pd1**), 207.9 mg 79% (Complex **Pd2**) ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 14.5, 7.4 Hz, 3H), 7.21 (t, *J* = 8.2 Hz, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 141.92, 134.85, 132.87, 129.80, 128.87, 122.06, 121.83, 116.26, 116.09.

4'-fluoro-2-nitro-1,1'-biphenyl (3cf) Yellow colored solid, Yield 156.37mg 72% (Complex **Pd1**), 169.33 mg 78% (Complex **Pd2**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 2H).

4-methyl-5-phenylthiazole[5] **(6a)** Off-white colored solid, Yield 149 mg 85% (Complex **Pd1**), 156 mg 89% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.45 – 7.38 (m, 5H), 7.35 (dd, *J* = 5.9, 2.9 Hz, 1H), 2.52 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.46, 148.56, 132.02, 129.41, 128.79, 127.98, 126.39, 16.15.

5-(4-chlorophenyl)-4-methylthiazole[5] **(6b)** Off-white colored solid, Yield 186.6 mg 89% (Complex **Pd1**), 192.8 mg 92% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.45 – 7.30 (m, 4H), 2.50 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.73, 148.94, 134.07, 130.79, 130.49, 129.11, 128.99, 16.18.

5-(4-fluorophenyl)-4-methylthiazole[5] **(6c)** Off-white colored solid, Yield 175.8 mg 91% (Complex **Pd1**), 181.6 mg 94% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.39 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 2.49 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.75, 161.28, 150.40, 148.68, 131.13, 127.97, 115.91, 16.01.

1-(4-(4-methylthiazol-5-yl)phenyl)ethanone[5] **(6d)** Off-white colored solid, Yield 195.5 mg 90% (Complex **Pd1**), 206.4 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 2.62 (s, 3H), 2.55 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 197.51, 151.29, 149.66, 136.91, 136.21, 130.95, 129.37, 128.85, 26.77, 16.47.

5-(4-methoxyphenyl)-4-methylthiazole[5] **(6e)** Off-white colored solid, Yield 154 mg 75% (Complex **Pd1**), 162.1 mg 79% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.49 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.45, 149.80, 147.99, 131.82, 130.63, 124.25, 114.25, 55.43, 16.03.

4-methyl-5-(p-tolyl)thiazole[5] (**6f**) Off-white colored solid,Yield 145.7 mg 77% (Complex **Pd1**), 153.3 mg 81% (Complex **Pd2**);^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.32 (d, *J*= 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.52 (s, 3H), 2.38 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.07, 148.27, 137.94, 132.06, 129.50, 129.26, 129.05, 21.28, 16.12.

4-(4-methylthiazol-5-yl)benzaldehyde[5] (**6g**) White colored solid, Yield 181.2 mg 89% (Complex **Pd1**), 184.9 mg 91% (Complex **Pd2**);^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.74 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 2.57 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.61, 151.53, 149.97, 138.33, 135.47, 130.83, 130.17, 129.77, 16.53.

4-methyl-5-(pyridin-3-yl)thiazole[6] **(6h)** Off-white colored solid, Yield 155.0 mg 88% (Complex **Pd1**), 162.1 mg 92% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.67 (s, 1H), 8.56 (d, *J* = 4.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 3.9 Hz, 1H), 2.51 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.35, 149.79, 148.98, 136.52, 128.35, 128.13, 123.51, 21.60, 16.06.

5-(3-methoxyphenyl)-4-methylthiazole[5] **(6i)** Off-white colored solid, Yield 143.7 mg 70% (Complex **Pd1**), 153.9 mg 75% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.33 – 7.29 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.95 (s, 1H), 6.88 (d, *J* = 9.1 Hz, 1H), 3.81 (s, 3H), 2.52 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.76, 150.41, 148.68, 133.28, 131.84, 129.83, 121.86, 115.14, 113.43, 55.40, 16.25.

4-methyl-5-(3-nitrophenyl)thiazole[5] **(6j)** Off-white colored solid, Yield 165.2 mg 75% (Complex **Pd1**), 178.4 mg 81% (Complex **Pd2**); ^{1}H- NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.30 (t, *J* = 2.0 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 2.56 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.48, 150.10, 135.15, 133.92, 129.88, 129.48, 124.05, 122.76, 16.22.

4-(4-methylthiazol-5-yl)benzonitrile[5] **(6k)** White colored solid, Yield 176.2 mg 88% (Complex **Pd1**),190.2 mg 95% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 2.55 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.68, 150.13, 136.95, 132.60, 130.18, 129.80, 118.55, 111.58, 16.43.

4-methyl-5-(4-nitrophenyl)thiazole[5] **(6l)** Yellow colored solid, Yield 198.2 mg 90% (Complex **Pd1**), 211.4 mg 96% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.28 (d, *J* = 8.9 Hz, 2H), 7.61 (d, *J* = 8.9 Hz, 2H), 2.58 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.96, 150.46, 147.18, 138.87, 129.91, 126.33, 124.14, 16.50.

4-methyl-5-(naphthalen-1-yl)thiazole[5] **(6m)** White colored solid, Yield 193.7 mg 86% (Complex **Pd1**), 207.2 mg 92% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.90 (d, *J* = 10.6 Hz, 2H), 7.67 (d, *J* = 10.7 Hz, 1H), 7.48 (dt, *J* = 11.3, 8.5 Hz, 4H), 2.28 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.67, 150.92, 133.78, 132.57, 129.44, 129.30, 129.14, 128.94, 128.55, 126.82, 126.30, 125.66, 125.26, 15.85.

3,5-dimethyl-4-phenylisoxazole[7] **(8a)** Yellow colored solid, Yield 138.5 mg 80% (Complex **Pd1**),143.7 mg 83% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.26, 158.79, 130.56, 129.17, 128.86, 127.58, 116.73, 11.62, 10.87.

4-(4-chlorophenyl)-3,5-dimethylisoxazole (8b)[6] Off-white colored solid, Yield 176.5 mg 85% (Complex **Pd1**), 184.7 mg 89% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.45, 158.55, 133.69, 130.44, 129.15, 129.00, 11.60, 10.81.

4-(4-fluorophenyl)-3,5-dimethylisoxazole[7] **(8c)** Off-white colored solid, Yield 162.5 mg 85% (Complex **Pd1**), 174 mg 91% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.30, 163.52, 161.06, 158.70, 130.83, 115.83, 11.55, 10.78.

1-(4-(3,5-dimethylisoxazol-4-yl)phenyl)ethanone[7] **(8d)** Off-white colored solid Yield 180.8 mg 84% (Complex **Pd1**), 191.5 mg 89% (Complex **Pd2**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.61 (s, 3H), 2.41 (s, 3H), 2.27 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.10, 158.89, 137.42, 129.61, 129.08, 127.57, 116.64, 21.31, 11.63, 10.90.

4-(4-methoxyphenyl)-3,5-dimethylisoxazole[7] **(8e)** Off-white colored solid, Yield 142.2 mg 70% (Complex **Pd1**), 152.4 mg 75% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H). ^{13}C-NMR

(101 MHz, $CDCl_3$) δ 164.92, 159.07, 158.93, 130.34, 122.70, 116.34, 114.34, 55.40, 11.59, 10.87.

3,5-dimethyl-4-(p-tolyl)isoxazole[7] **(8f)** Off-white colored solid, Yield 121.7 mg 65% (Complex **Pd1**),136.7 mg 73% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.38 (d, *J* = 1.5 Hz, 6H), 2.25 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 165.10, 158.89, 137.42, 129.61, 129.08, 127.57, 116.64, 21.31, 11.63, 10.90.

4-(3,5-dimethylisoxazol-4-yl)benzaldehyde[7] **(8g)** Off-white colored solid, Yield 157 mg 78% (Complex **Pd1**), 163 mg 81% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.67, 166.11, 158.37, 137.00, 135.37, 130.24, 129.58, 115.93, 11.85, 10.98.

3,5-dimethyl-4-(pyridin-3-yl)isoxazole[6] **(8h)** Off-white colored solid, Yield 139.3 mg 80% (Complex **Pd1**), 144.6 mg 83% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.52 (d, *J* = 3.0 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.38-7.35 (1H), 2.41 (s, 3H), 2.26 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.24, 158.27, 148.69, 135.01, 132.45, 129.99, 123.86, 122.56, 114.98, 11.74, 10.85.

4-(3-methoxyphenyl)-3,5-dimethylisoxazole[7] **(8i)** Off-white colored solid, Yield 132.0 mg 65% (Complex **Pd1**), 144.3 mg 71% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 6.89 (d, *J* = 5.8 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 4.1 Hz, 1H), 3.83 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.38, 159.88, 158.76, 131.89, 129.90, 121.58, 116.63, 115.18, 112.68, 55.36, 11.66, 10.89.

3,5-dimethyl-4-(3-nitrophenyl)isoxazole[7] **(8j)** Off-white colored solid, Yield 154.9 mg 71% (Complex **Pd1**),165.8 mg 76% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.12 (t, *J* = 1.9 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.59 (dt, *J* = 7.7, 1.5 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.14, 158.59, 149.95, 148.89, 136.36, 126.68, 123.70, 113.56, 11.64, 10.80.

4-(3,5-dimethylisoxazol-4-yl)benzonitrile[7] **(8k)** Off-white colored solid, Yield 160.5 mg 81% (Complex **Pd1**), 170.5 mg 86% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.42 (s, 3H), 2.27 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.23, 158.22, 135.63, 132.75, 129.70, 118.60, 115.54, 111.52, 11.83, 10.93.

3,5-dimethyl-4-(4-nitrophenyl)isoxazole[7] **(8l)** Off-white colored solid, Yield 183.3 mg 84% (Complex **Pd1**),194.2 mg 89% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 2.44 (s, 3H), 2.29 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.35, 158.09, 147.06, 137.50, 129.68, 124.13, 115.16, 11.78, 10.86.

3,5-dimethyl-4-(naphthalen-1-yl)isoxazole[7] **(8m)** Off-white colored solid, Yield 176.3 mg 79% (Complex **Pd1**), 189.7 mg 85% (Complex **Pd2**); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 7.0 Hz, 2H), 7.60 – 7.44 (m, 4H), 7.32 (d, *J* = 7.0 Hz, 1H), 2.25 (s, 3H), 2.09 (s, 3H).). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.67, 166.11, 158.37, 137.00, 135.37, 130.24, 129.58, 115.93, 11.85, 10.98.

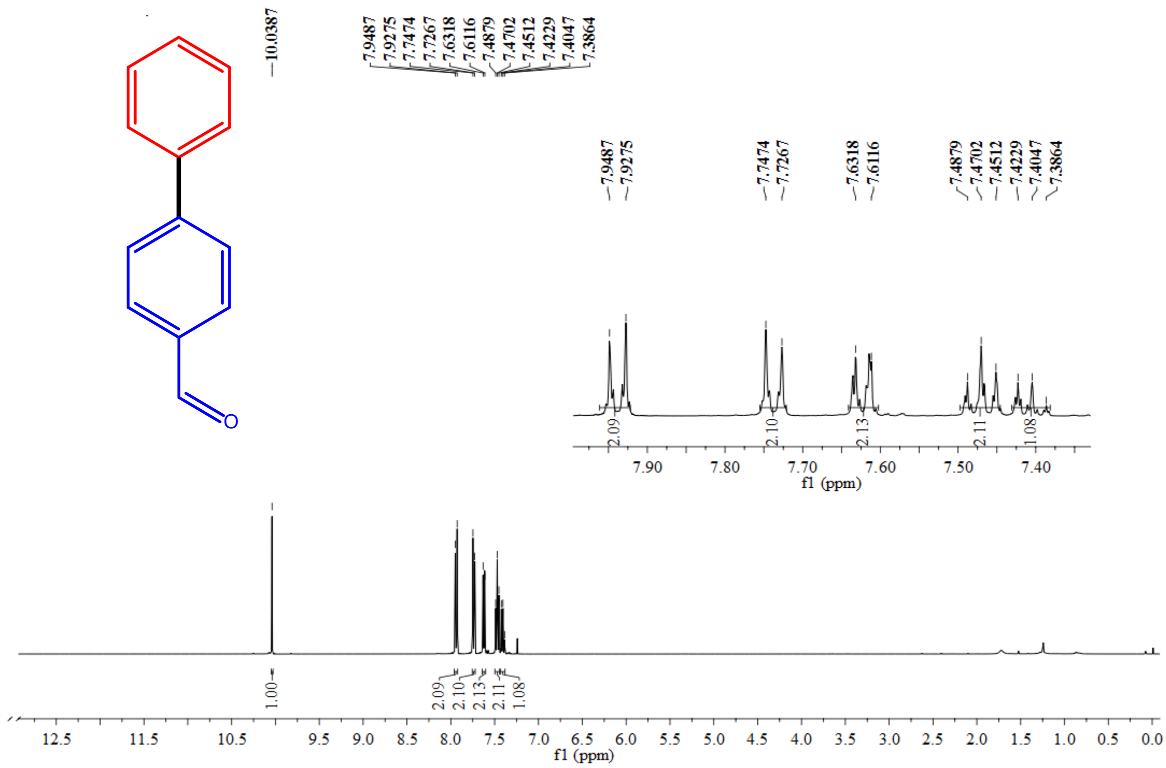


Figure S22. ^{1}H-NMR spectrum of 3aa in $CDCl_3$.

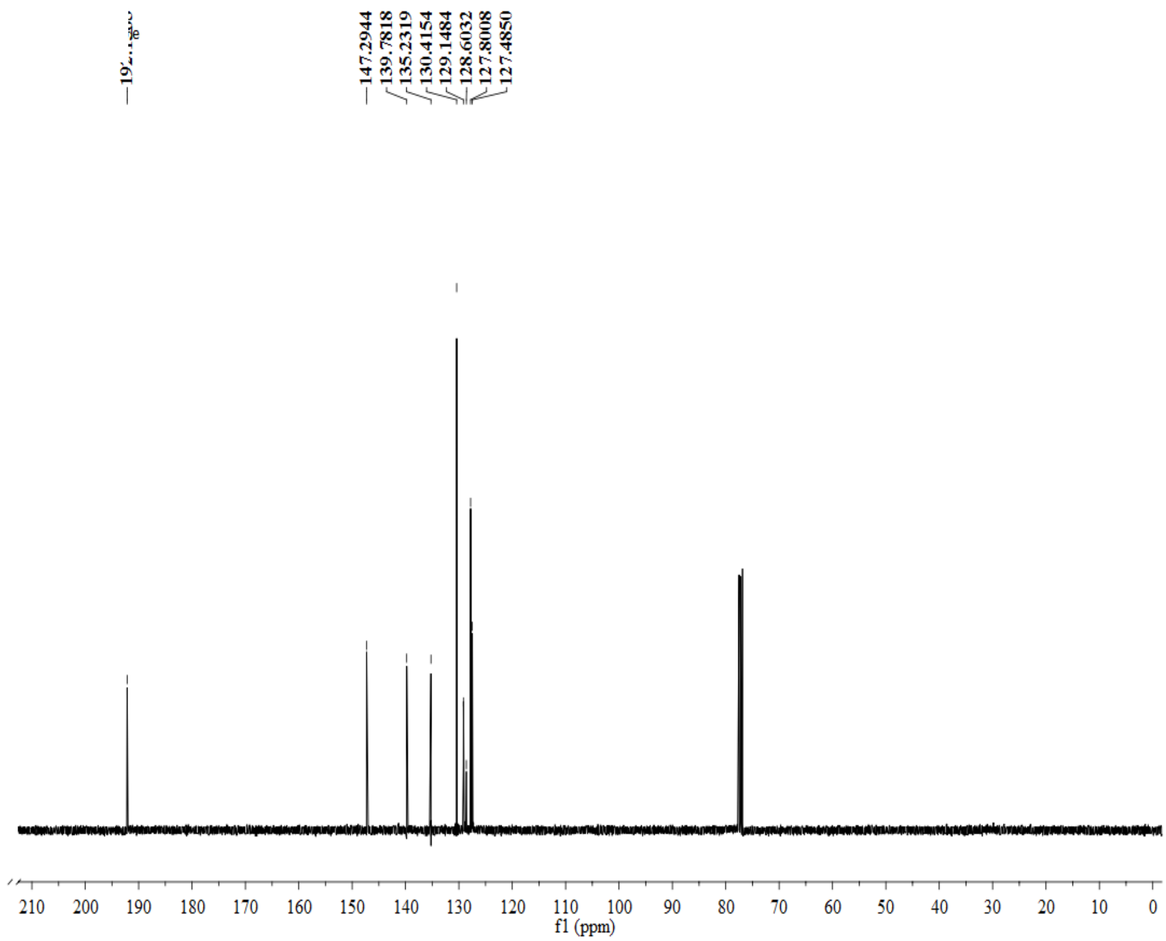


Figure S23. ^{13}C-NMR spectrum of 3aa in $CDCl_3$.

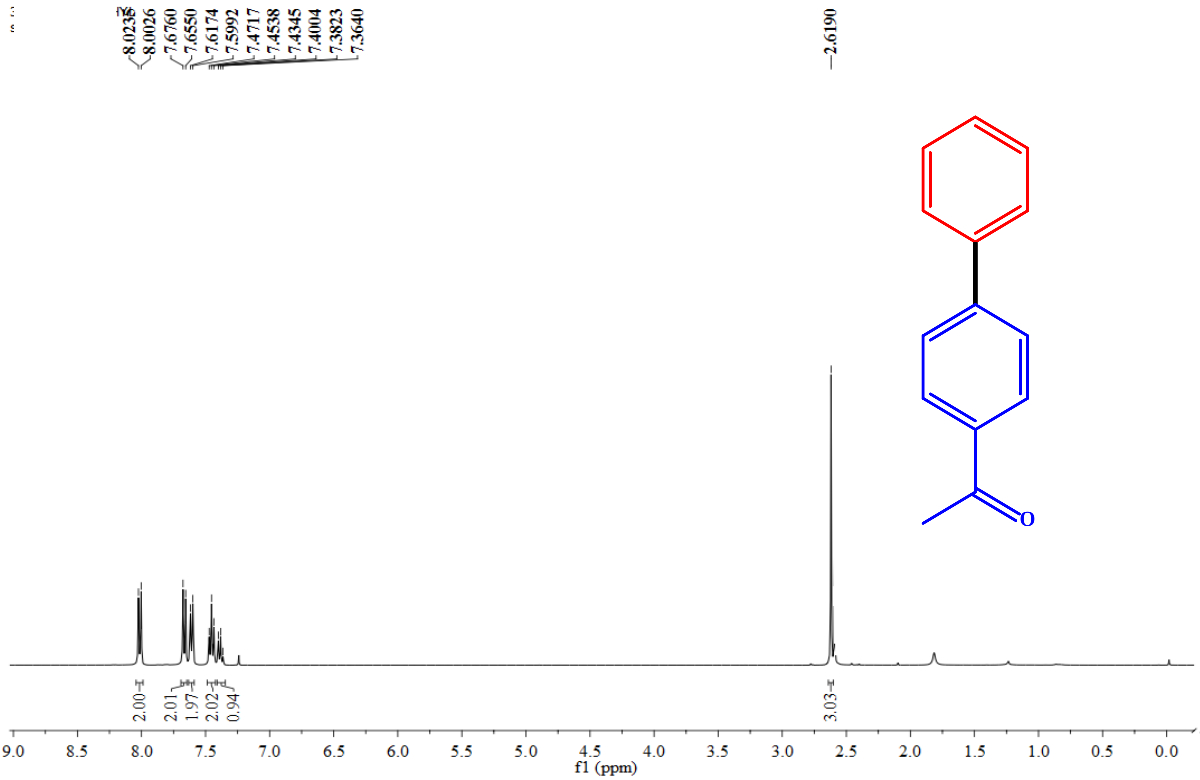


Figure S24. ^{1}H-NMR spectrum of 3ab in $CDCl_3$.

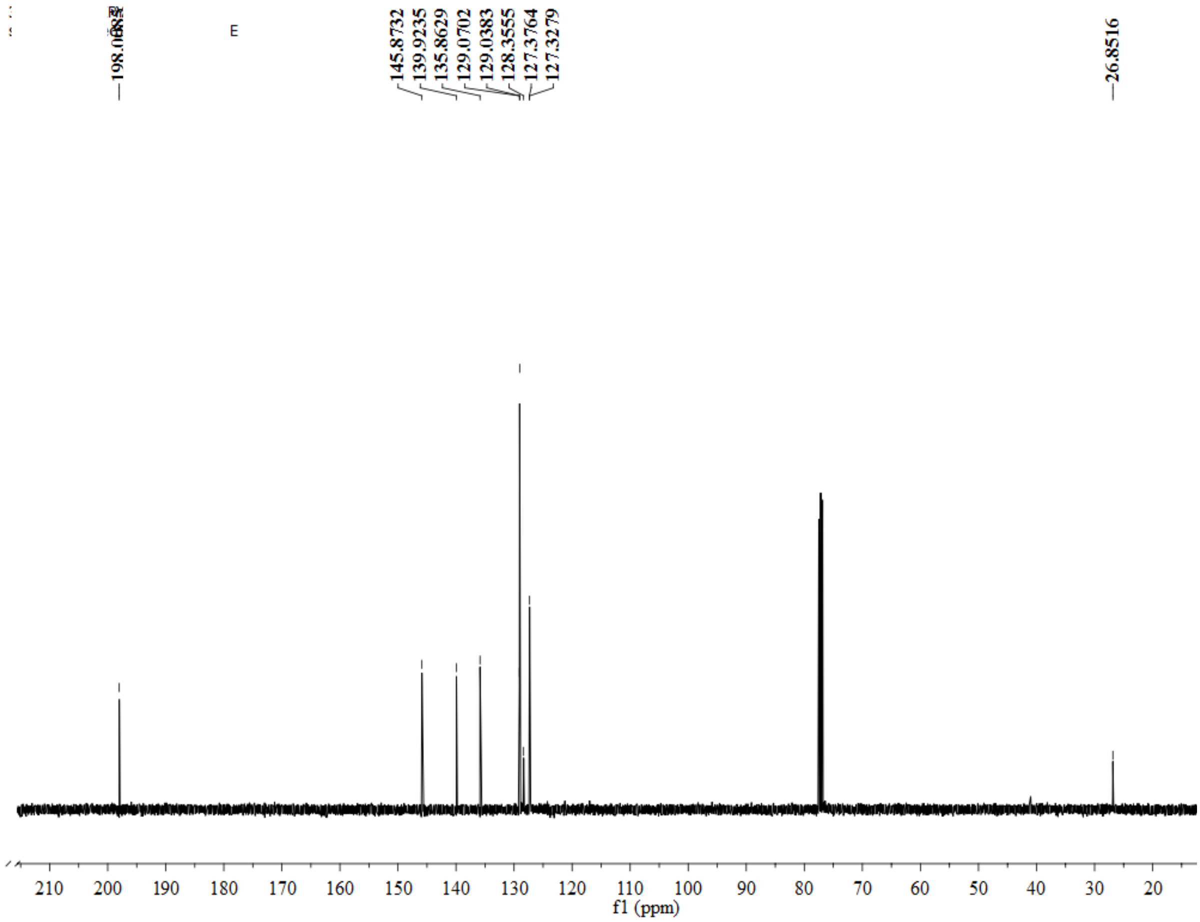


Figure S25. ^{13}C-NMR spectrum of 3ab in $CDCl_3$.

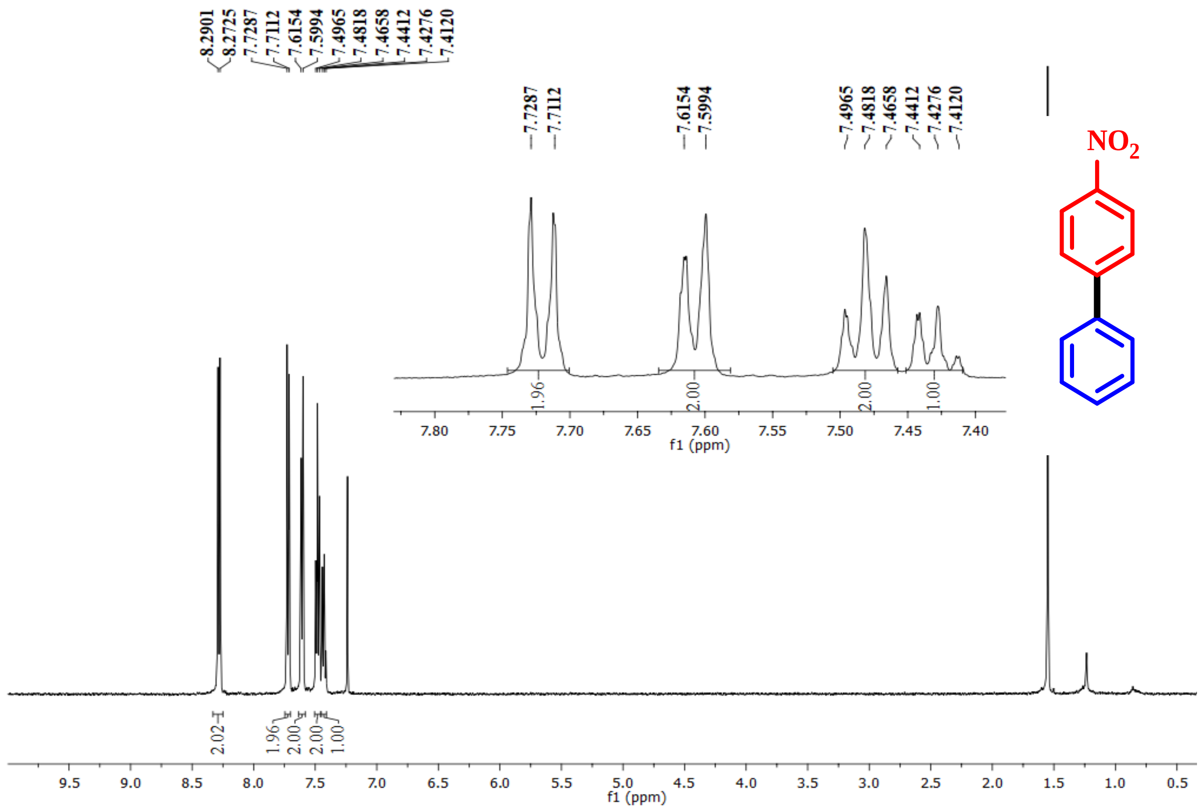


Figure S26. ^{1}H-NMR spectrum of 3ac in $CDCl_3$.

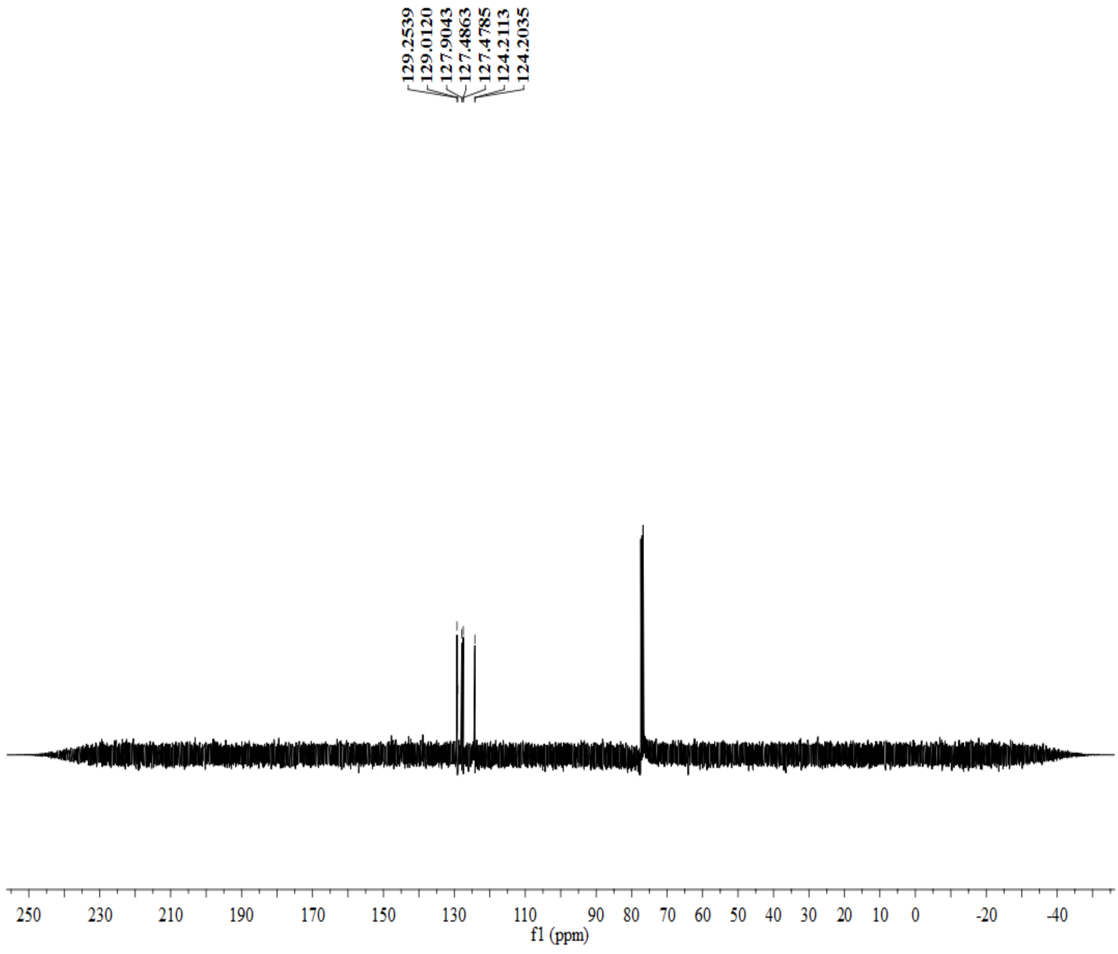


Figure S27. ^{13}C-NMR spectrum of 3acin $CDCl_3$.

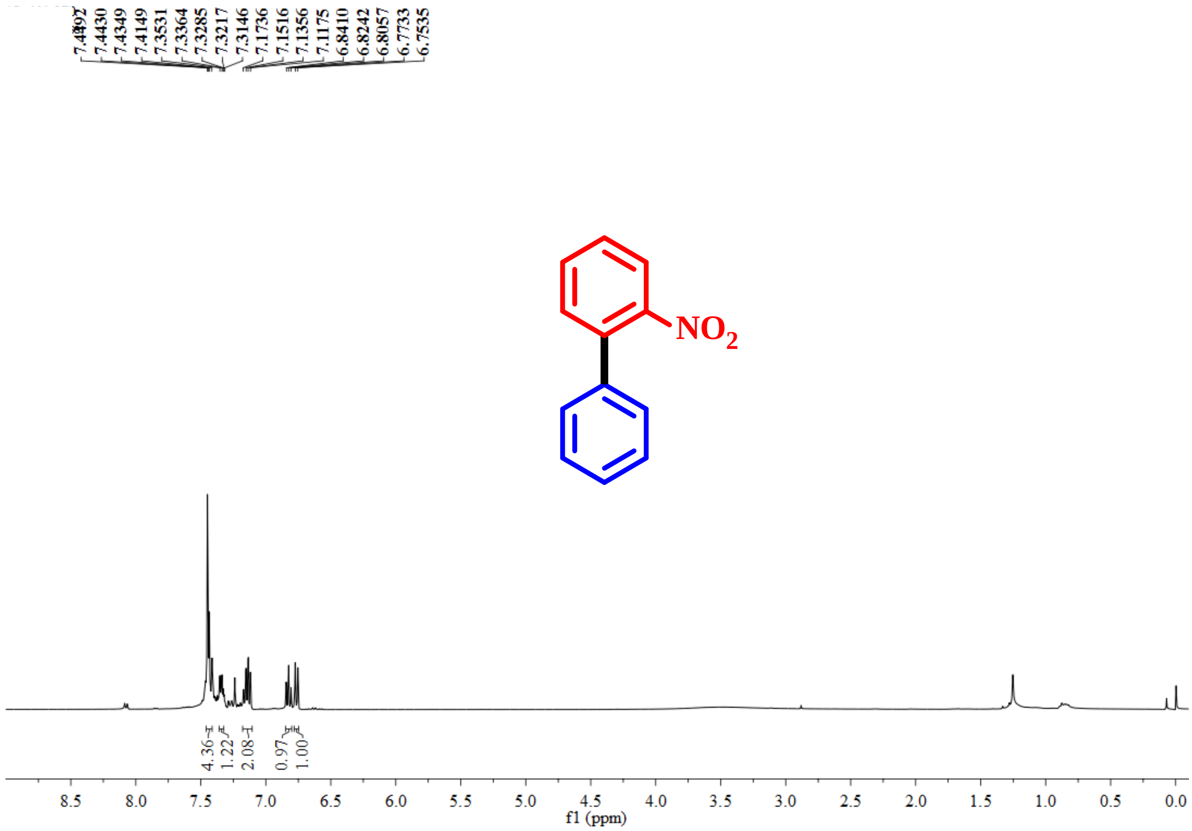


Figure S28. ^{1}H-NMR spectrum of 3ad in $CDCl_3$.

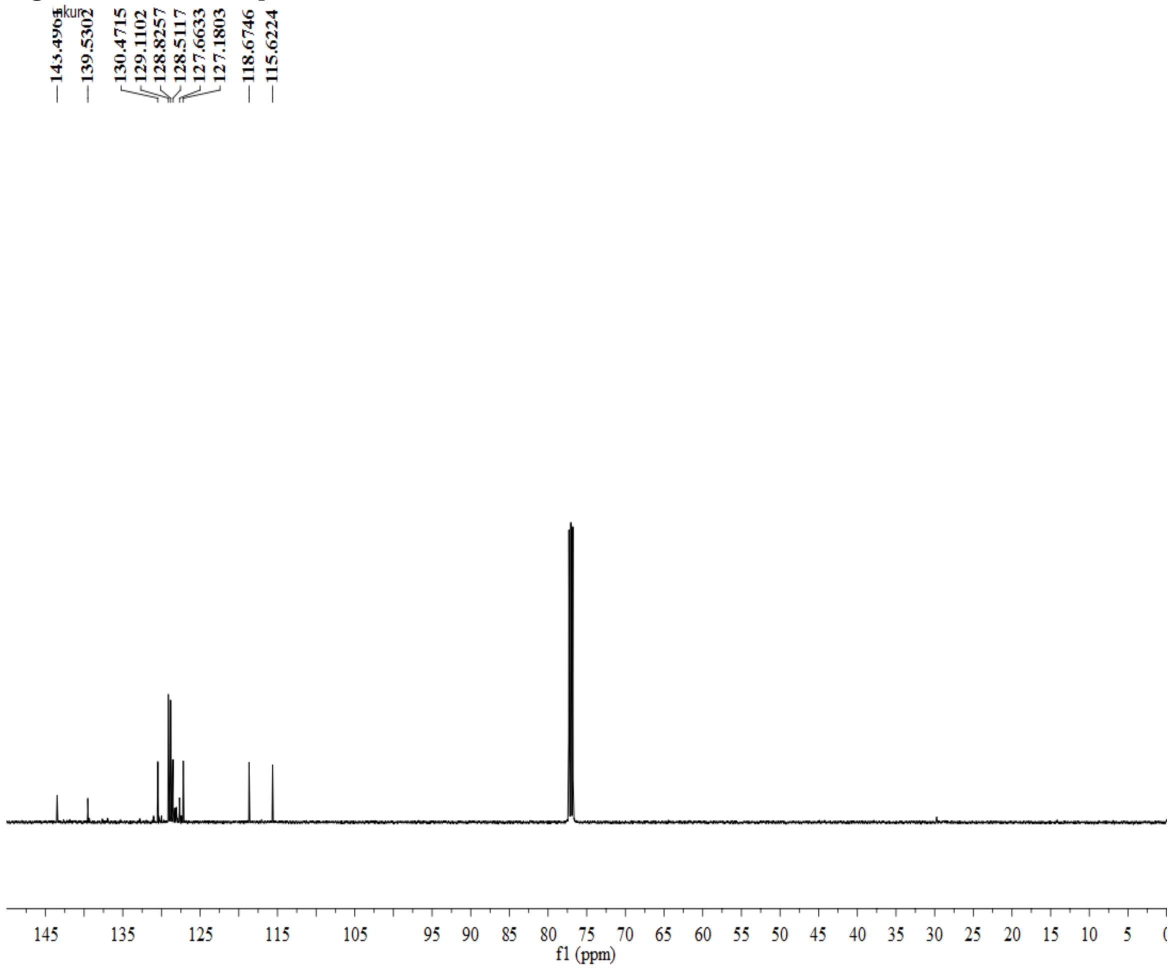


Figure S29. ^{13}C-NMR spectrum of 3ad in $CDCl_3$.

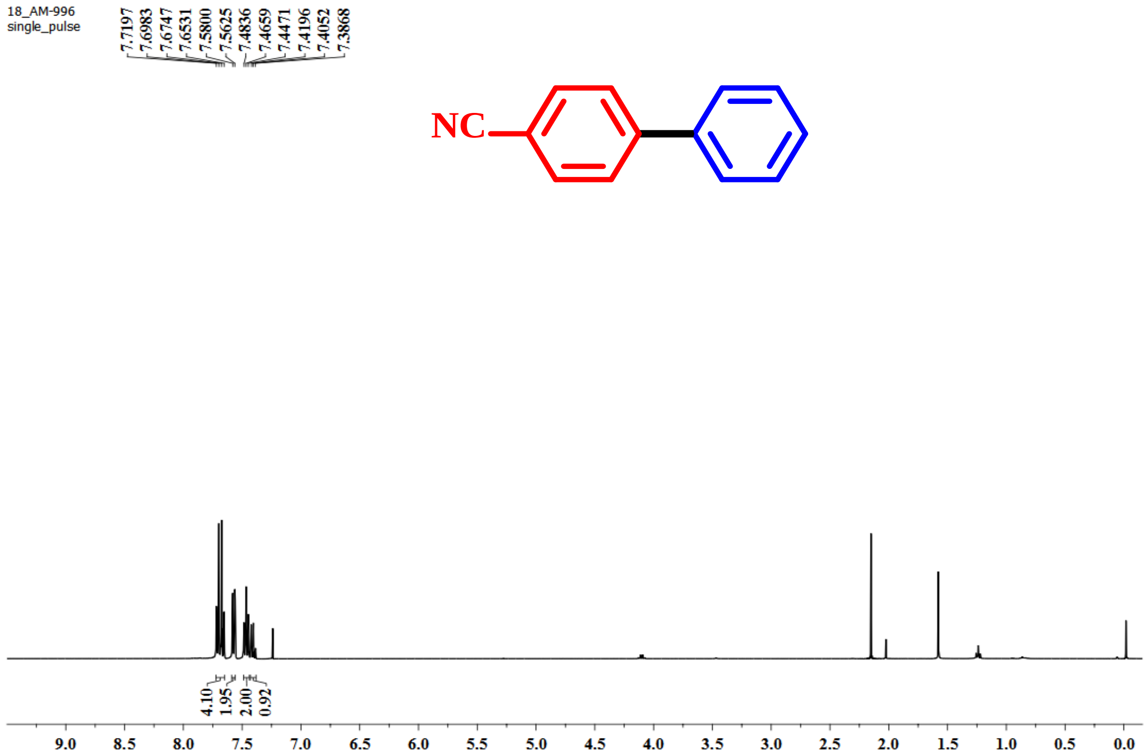


Figure S30. ^{1}H-NMR spectrum of 3ae in $CDCl_3$.

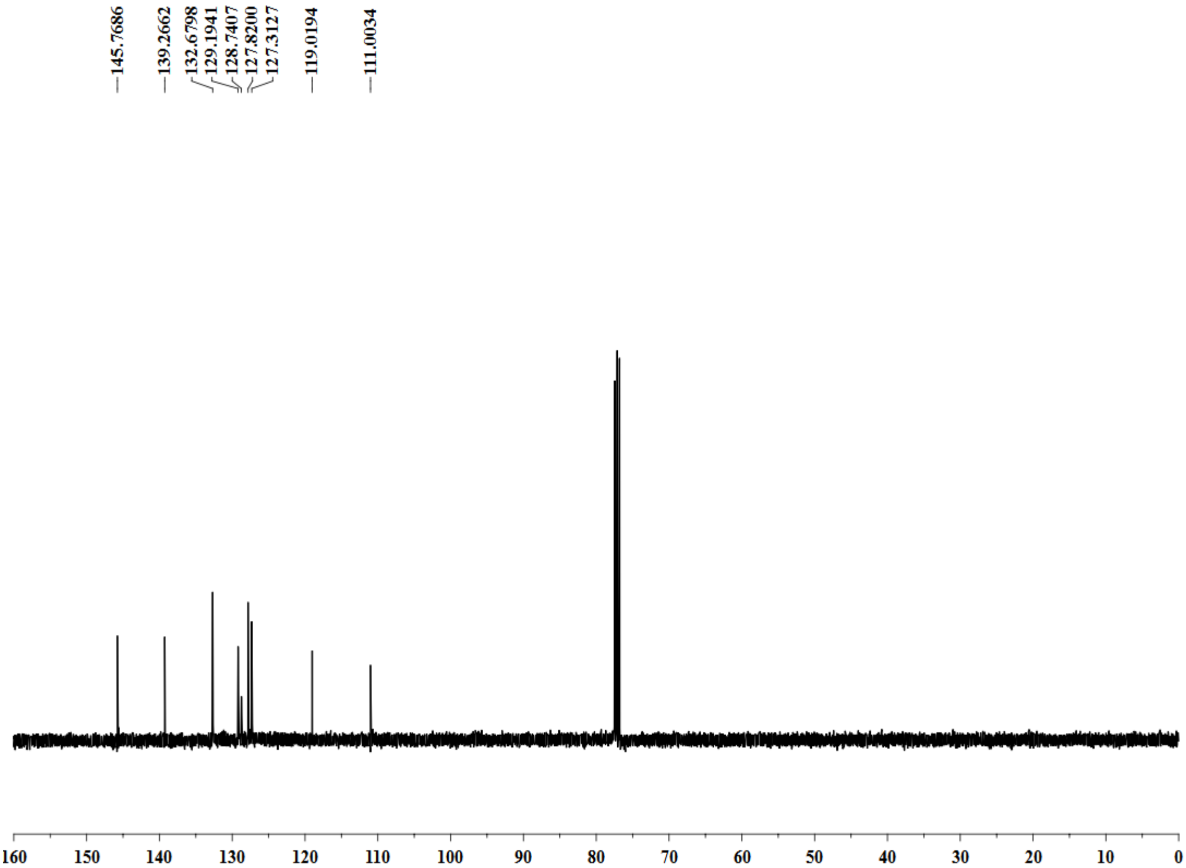


Figure S31. ^{13}C-NMR spectrum of 3ae in $CDCl_3$.

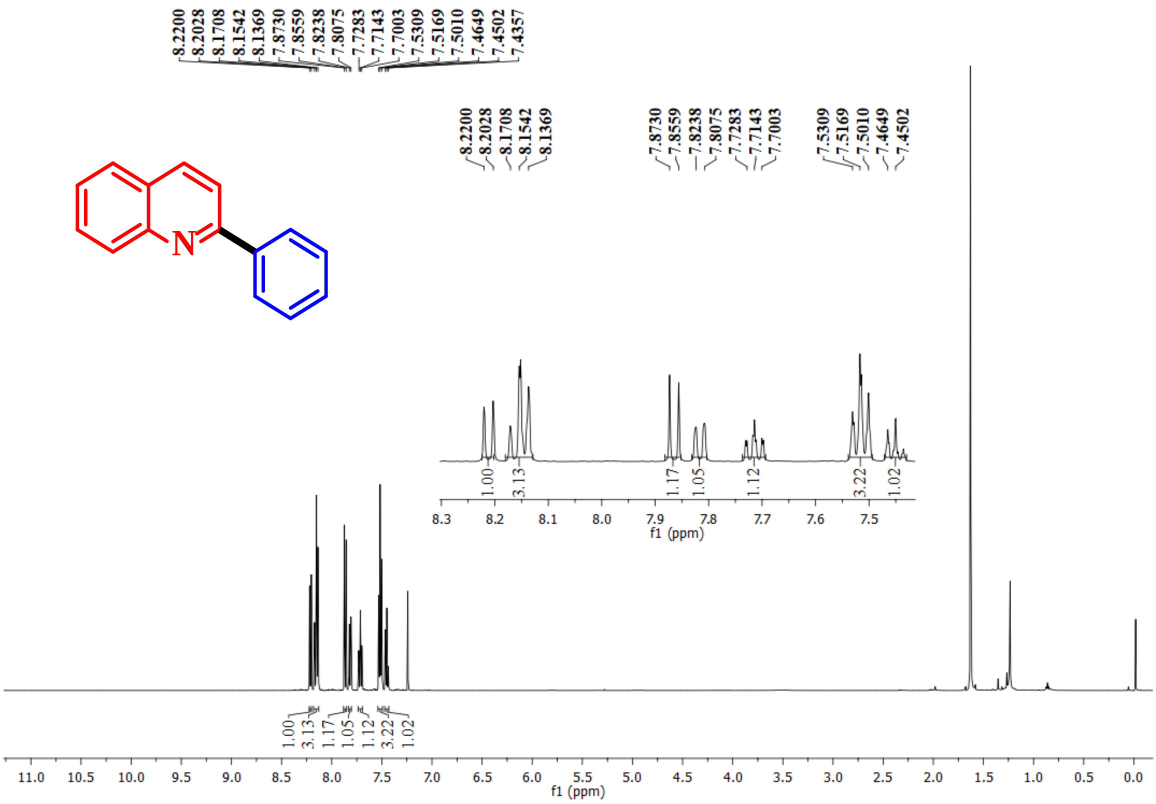


Figure S32. ^{1}H-NMR spectrum of 3af in $CDCl_3$.

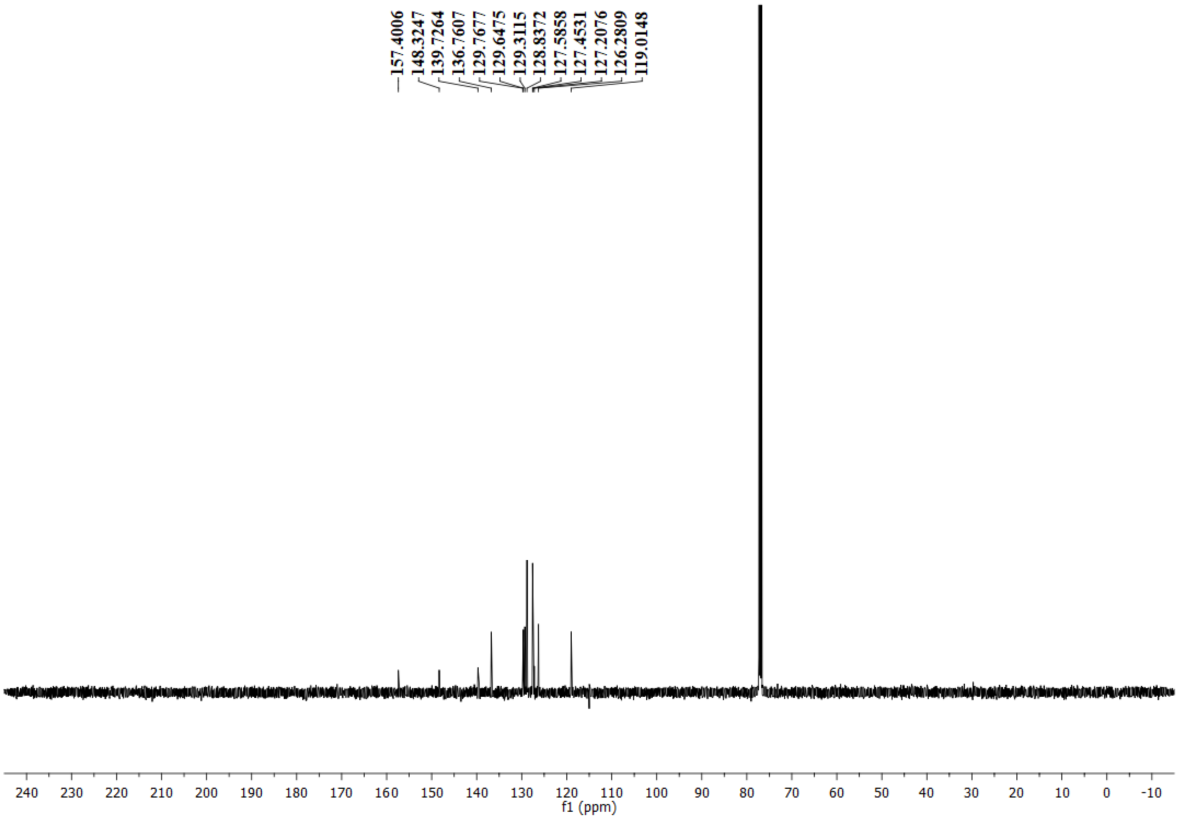


Figure S33. ^{13}C-NMR spectrum of 3af in $CDCl_3$.

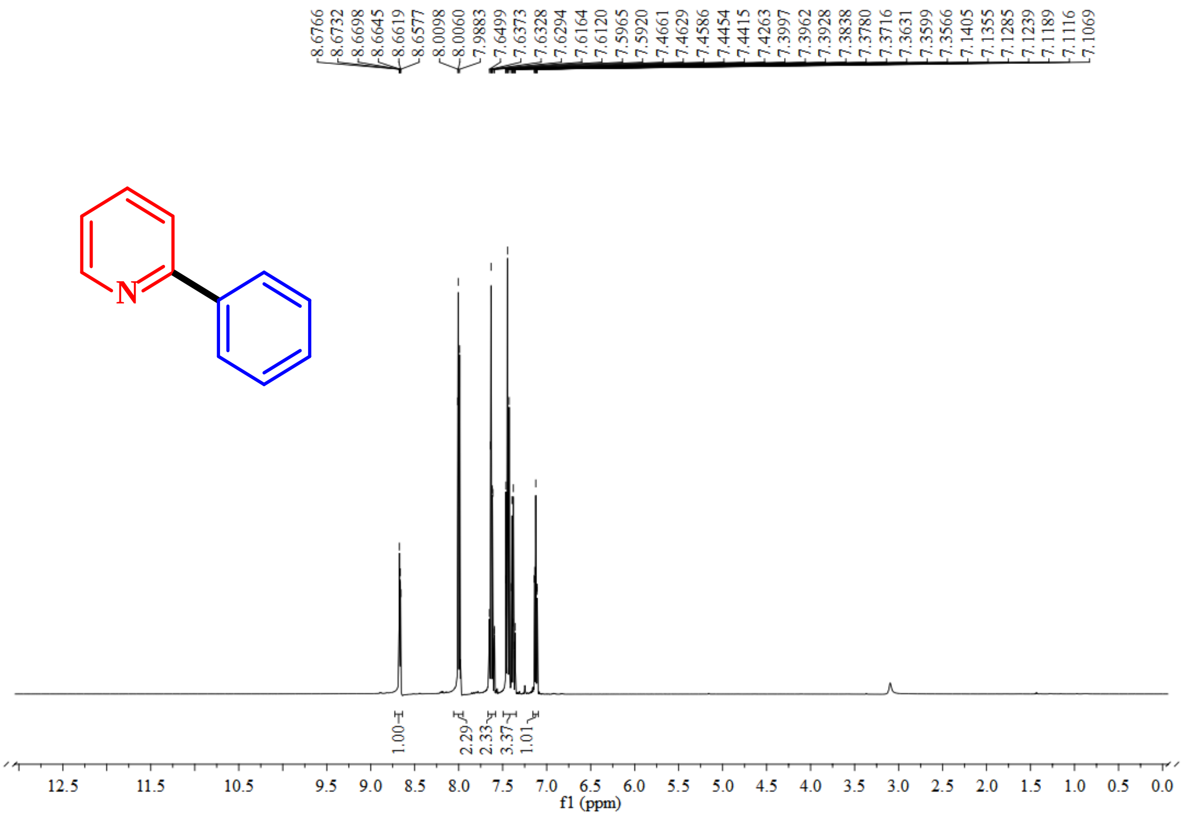


Figure S34. ^{1}H-NMR spectrum of 3ag in $CDCl_3$.

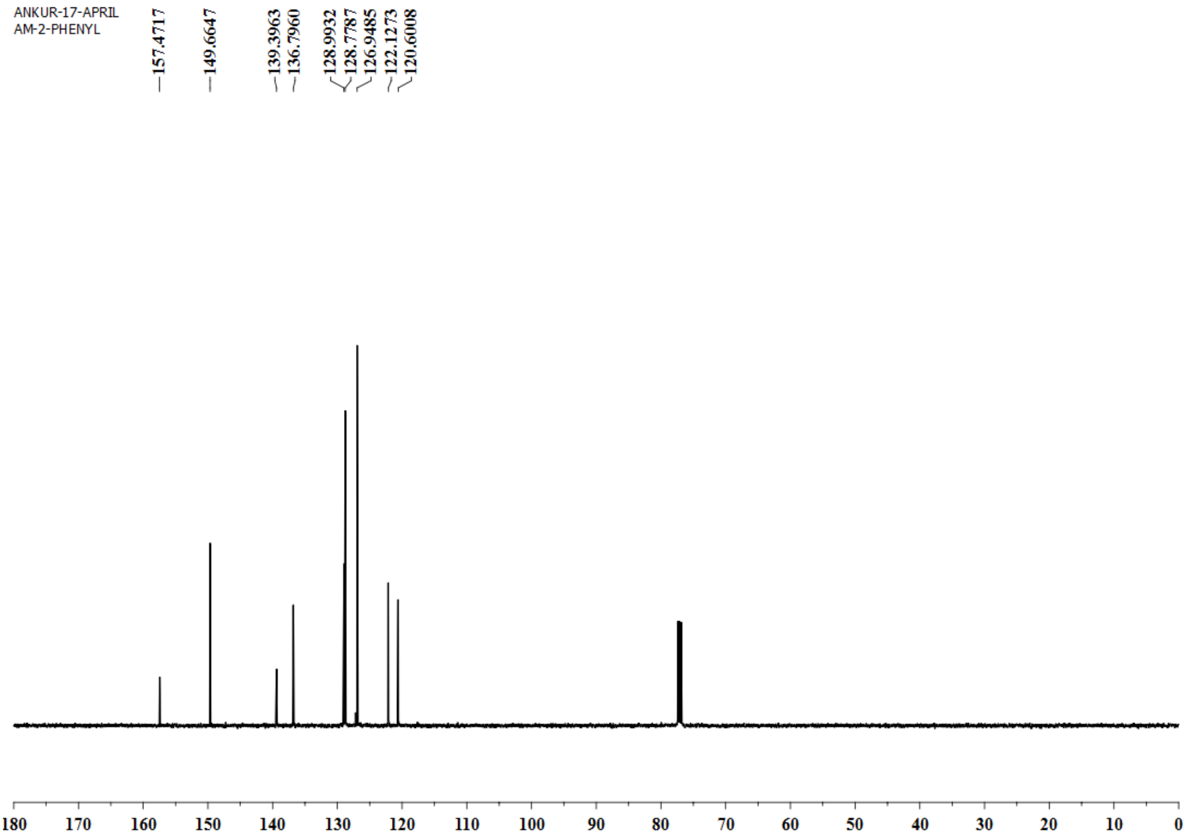


Figure S35. ^{13}C-NMR spectrum of 3ag in $CDCl_3$.

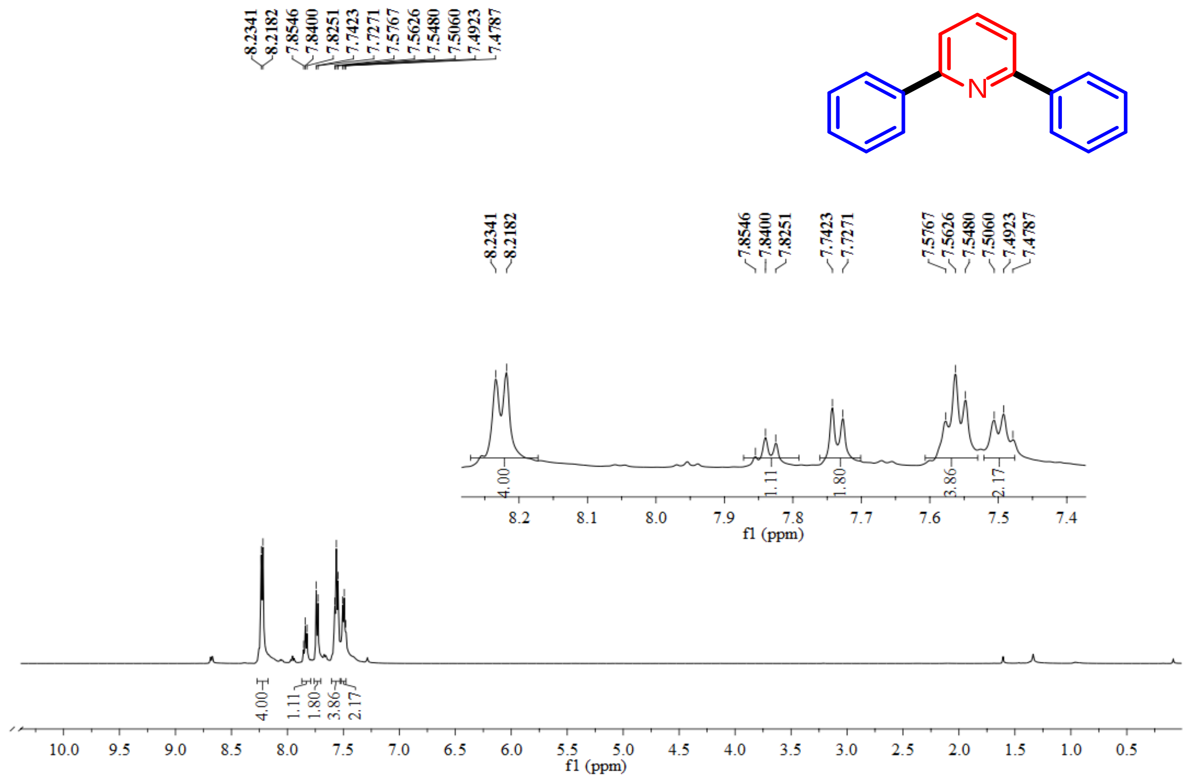


Figure S36. ^{1}H-NMR spectrum of 3ah in $CDCl_3$.

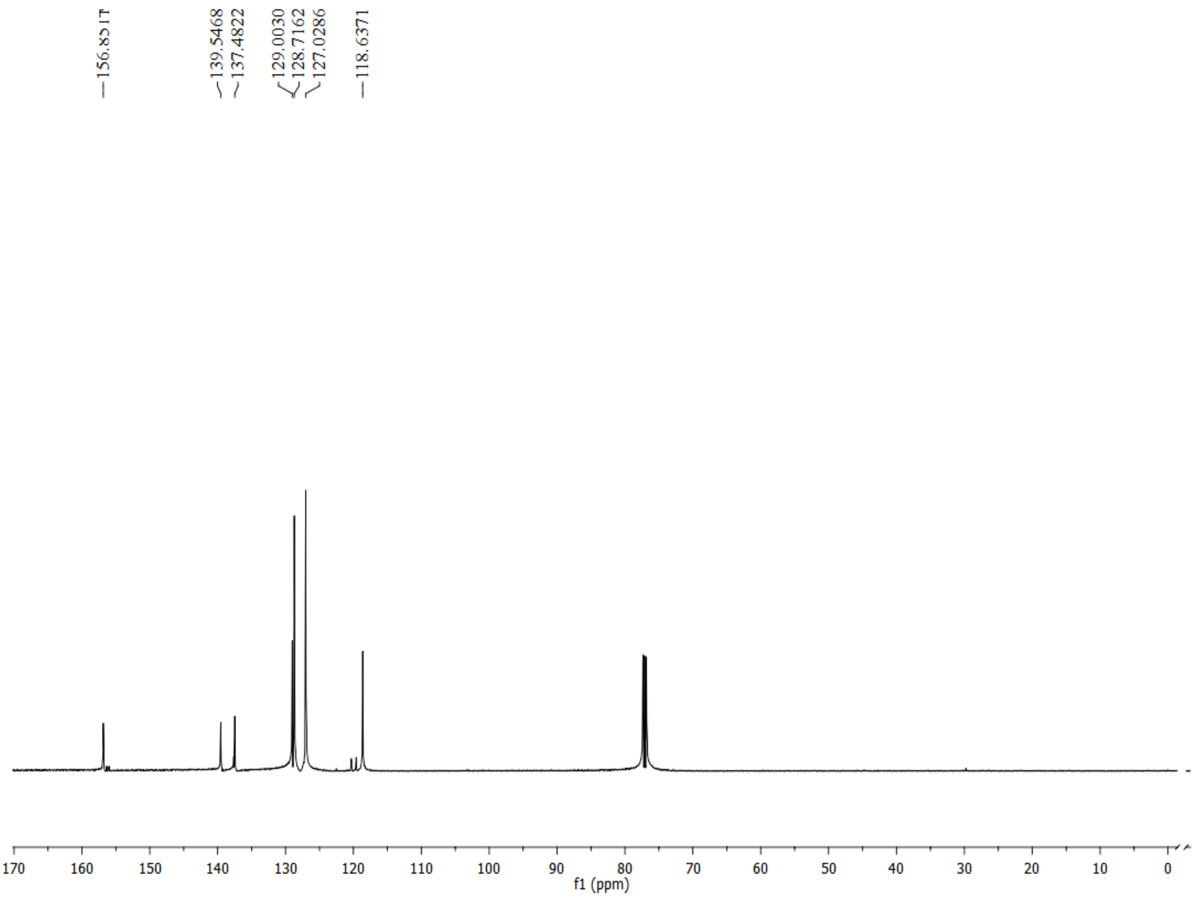


Figure S37. ^{13}C-NMR spectrum of 3ah in $CDCl_3$.

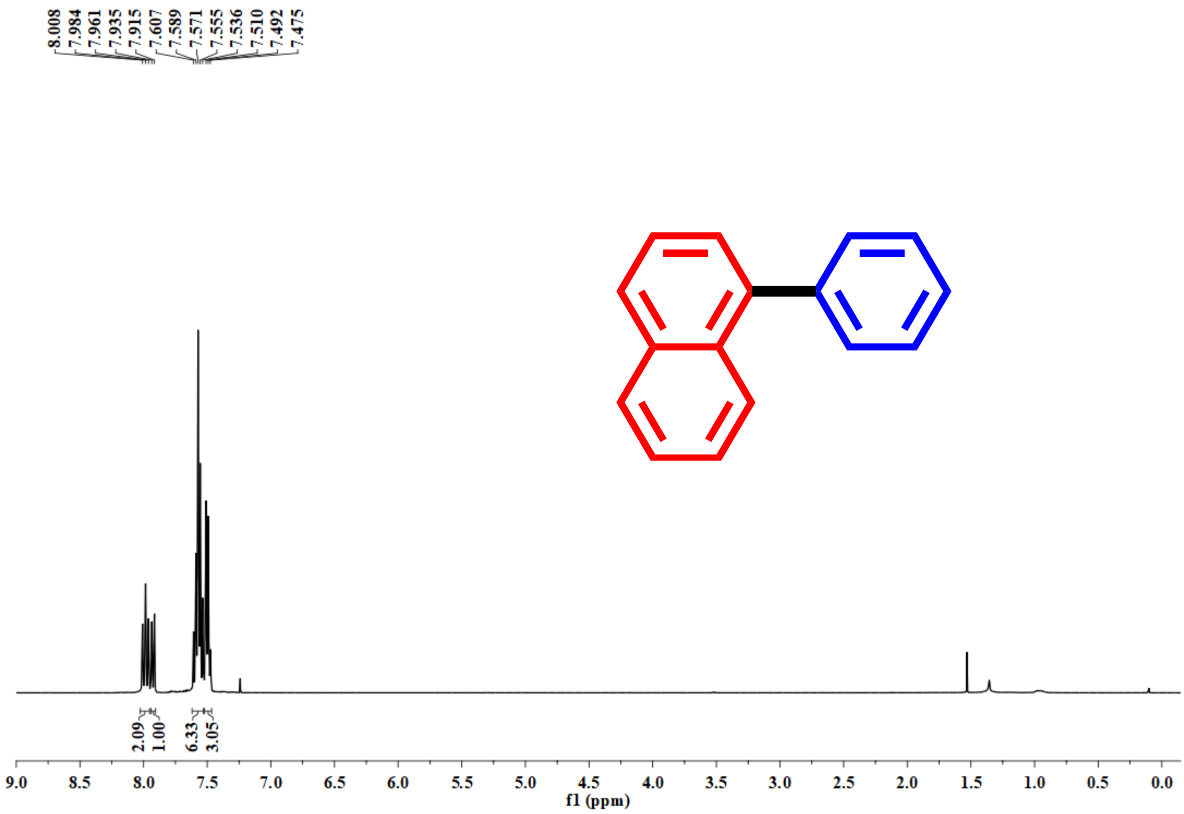


Figure S38. ^{1}H-NMR spectrum of 3ak in $CDCl_3$.

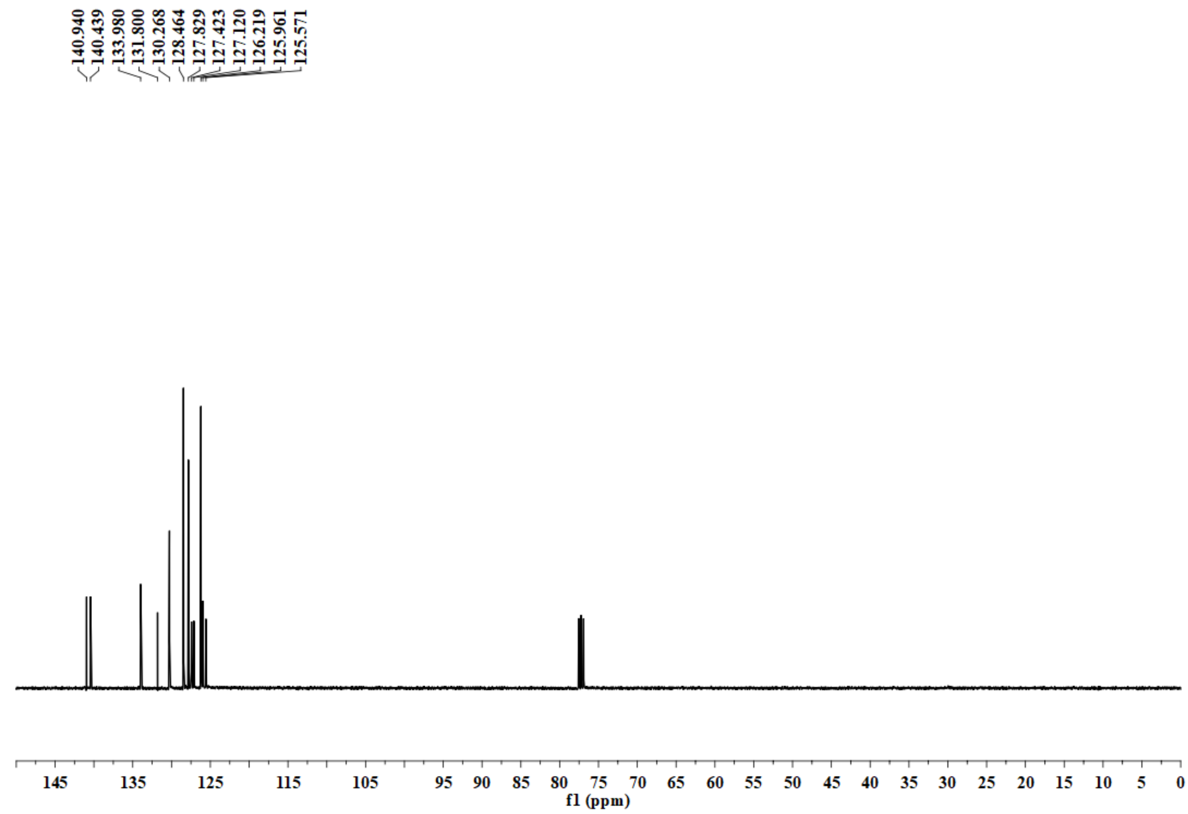


Figure S39. ^{13}C-NMR spectrum of 3ak in $CDCl_3$.

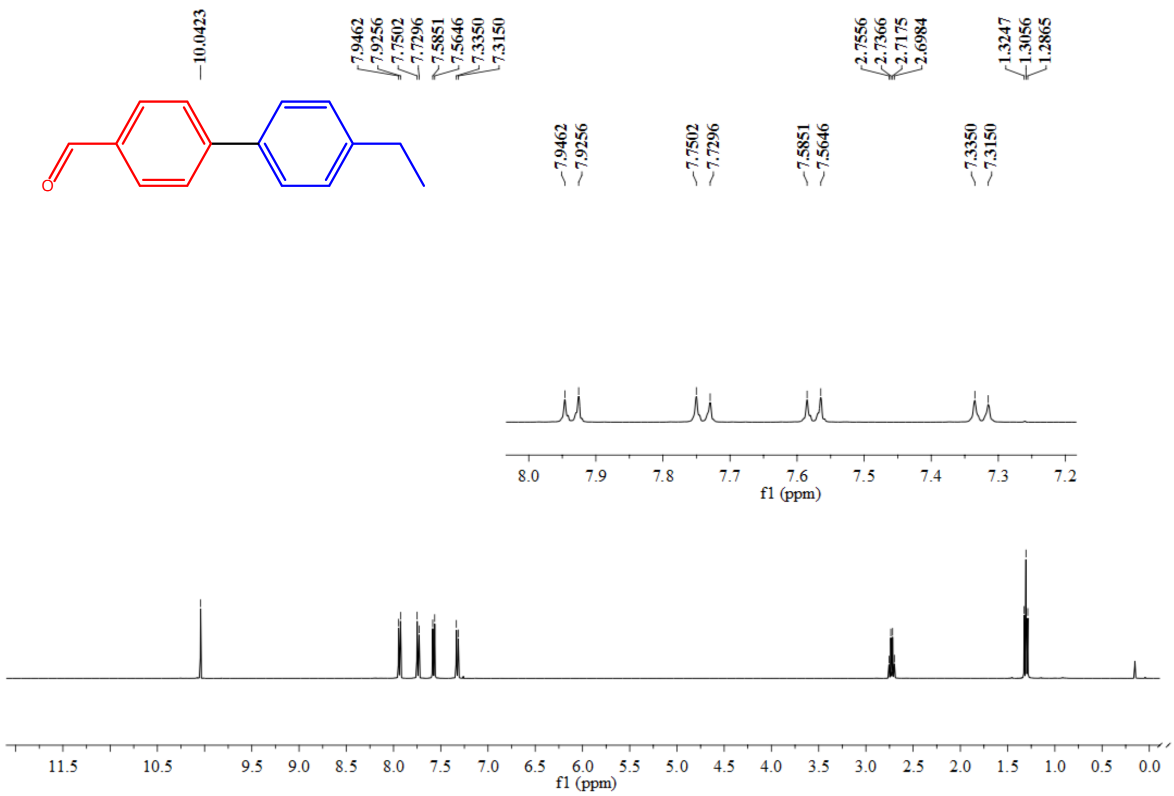


Figure S40. ^{1}H-NMR spectrum of 3al in $CDCl_3$.

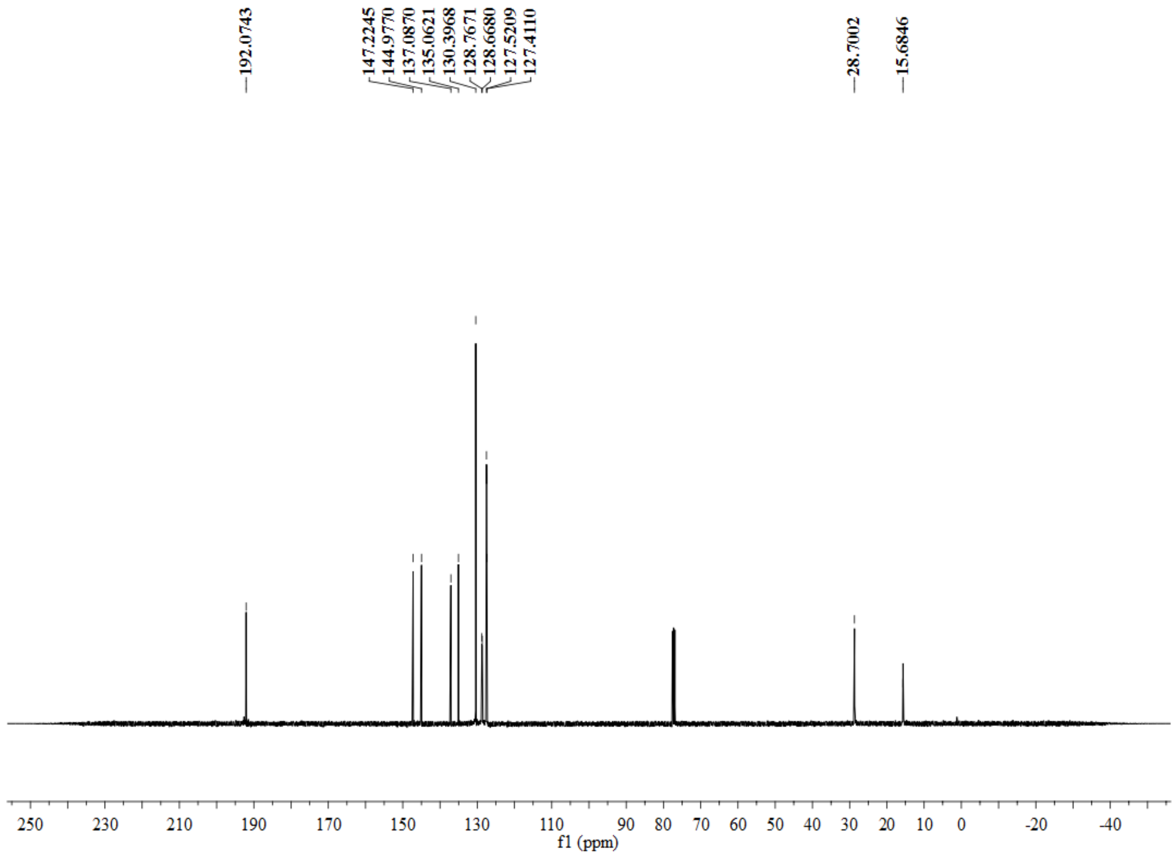


Figure S41. ^{13}C-NMR spectrum of 3al in $CDCl_3$.

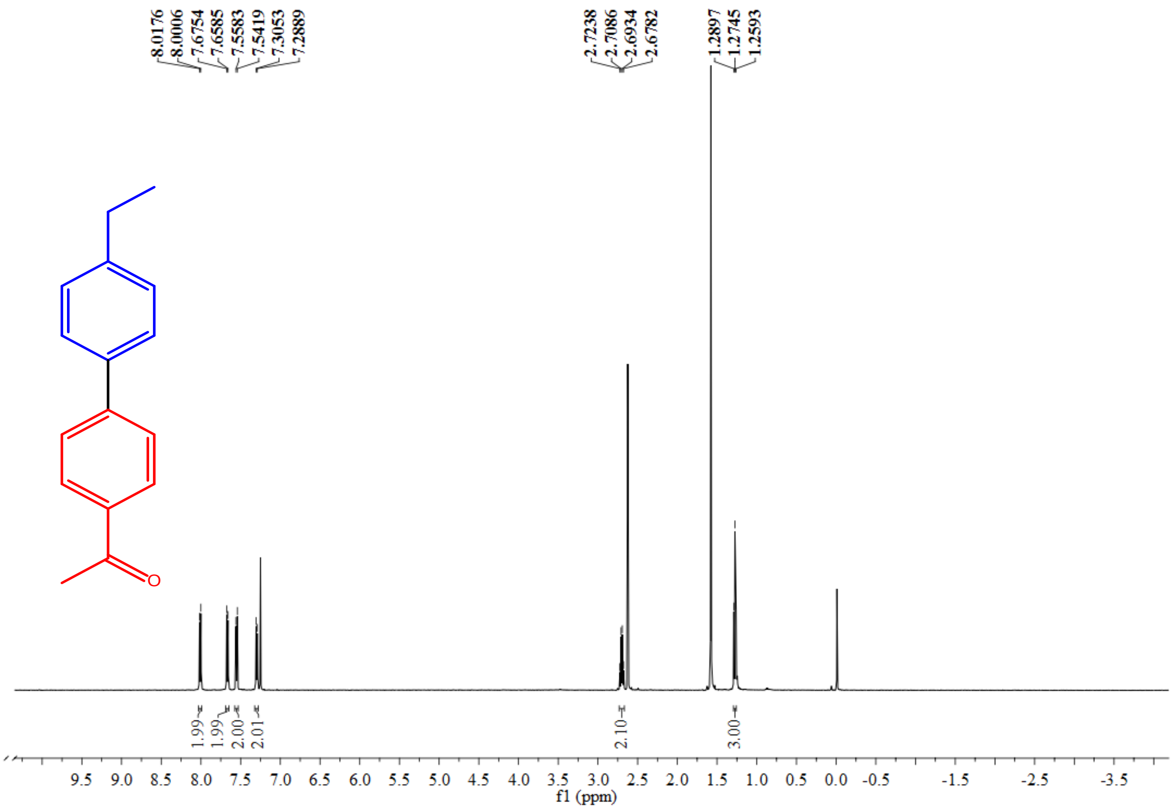


Figure S42. ^{1}H-NMR spectrum of 3am in $CDCl_3$.

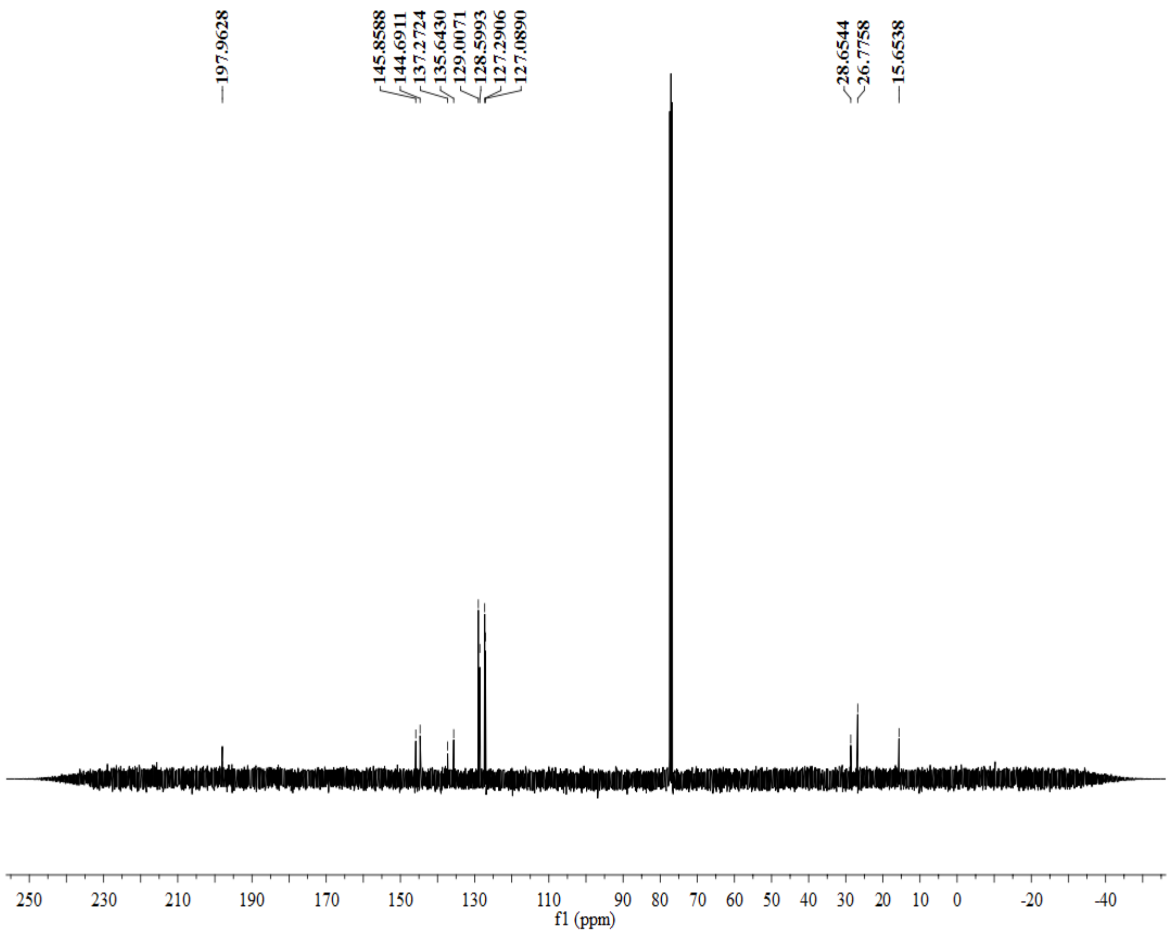


Figure S43. ^{13}C-NMR spectrum of 3am in $CDCl_3$.

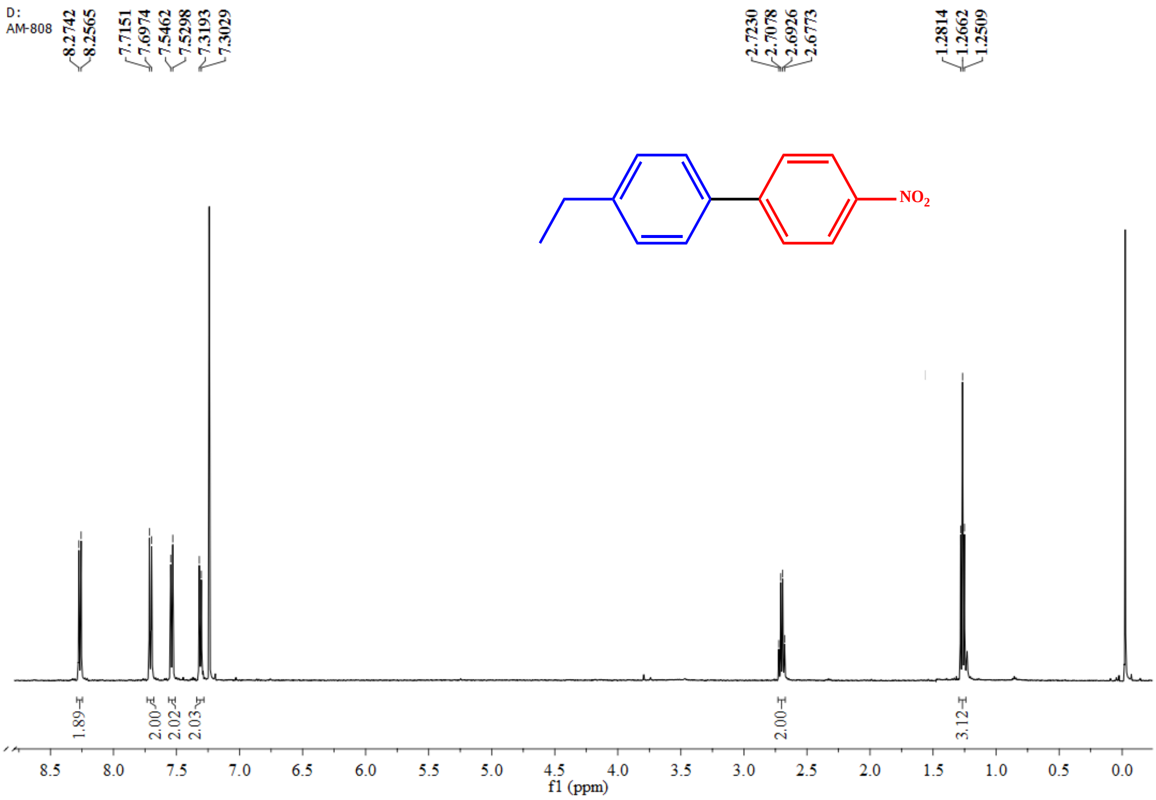


Figure S44. ^{1}H-NMR spectrum of 3an in $CDCl_3$.

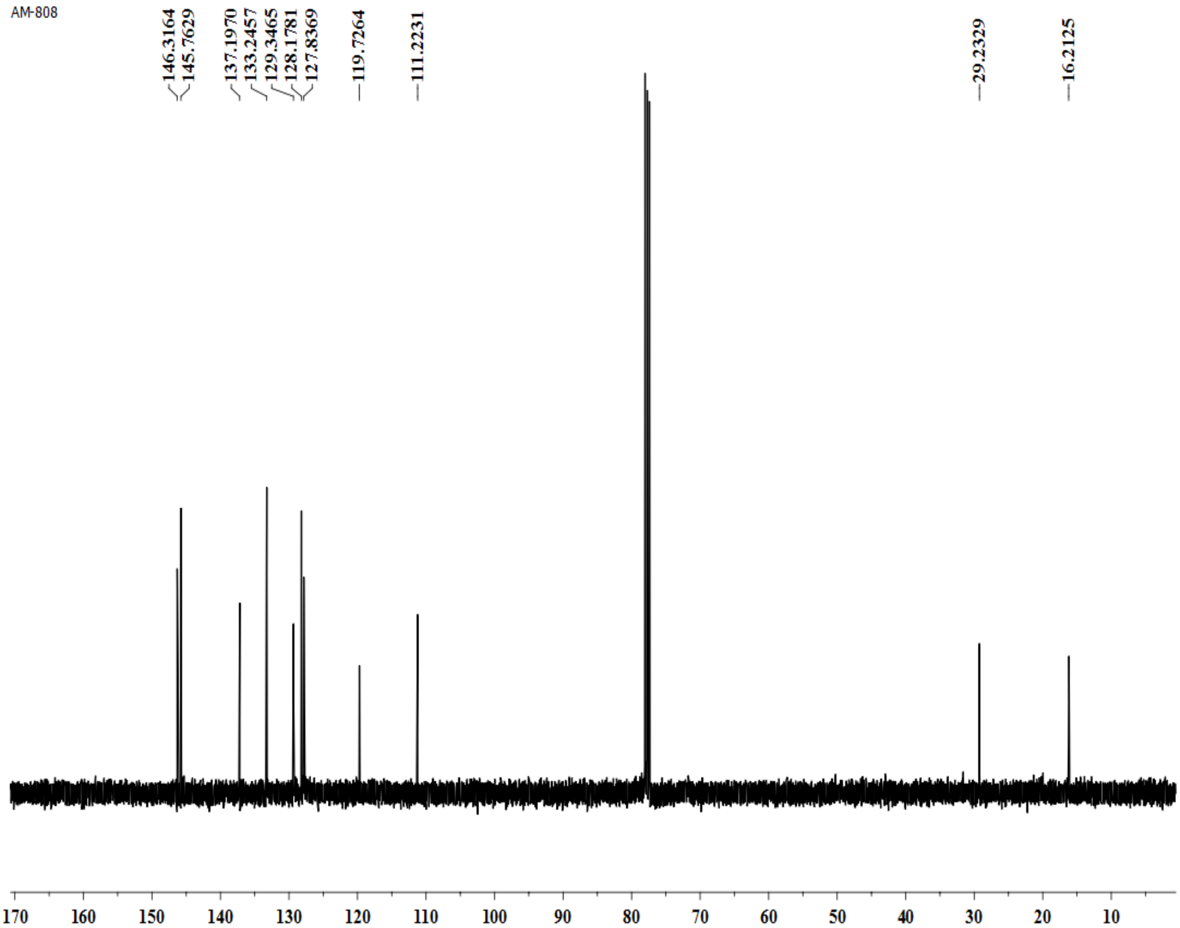


Figure S45. ^{13}C-NMR spectrum of 3anin $CDCl_3$.

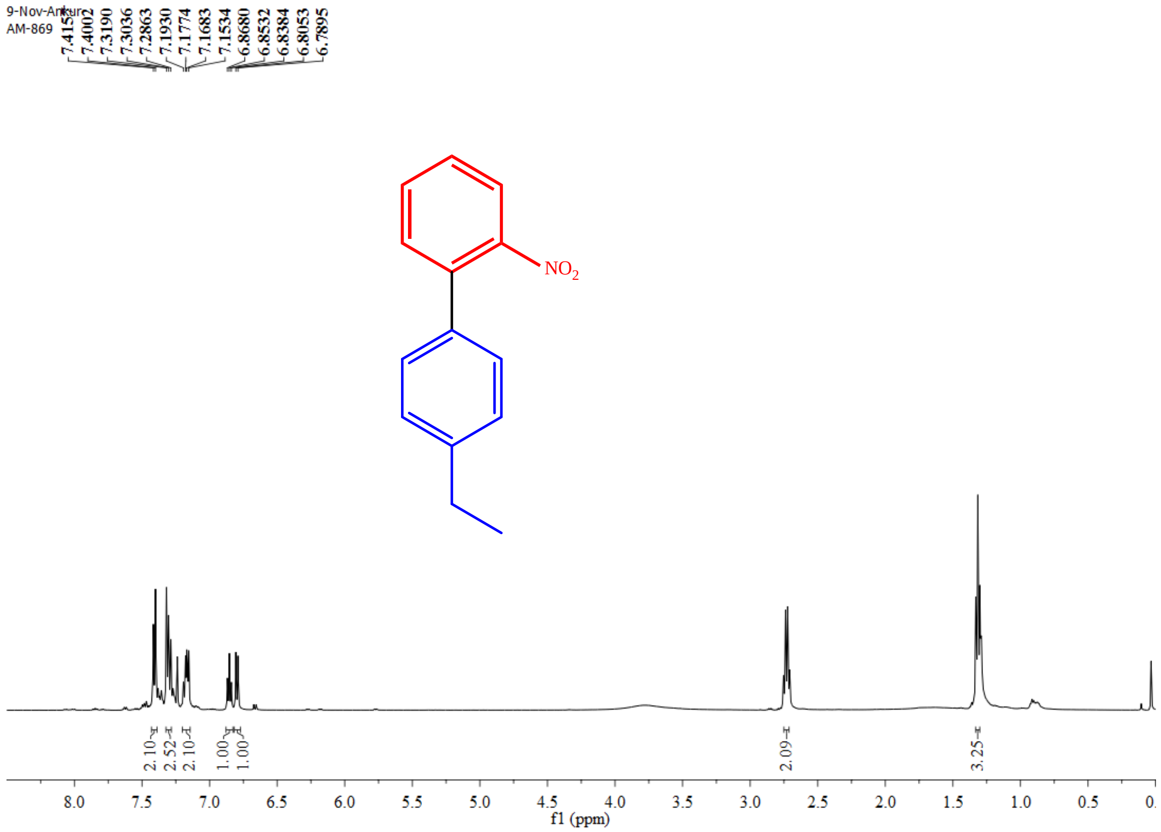


Figure S46. ^{1}H-NMR spectrum of 3ao in $CDCl_3$.

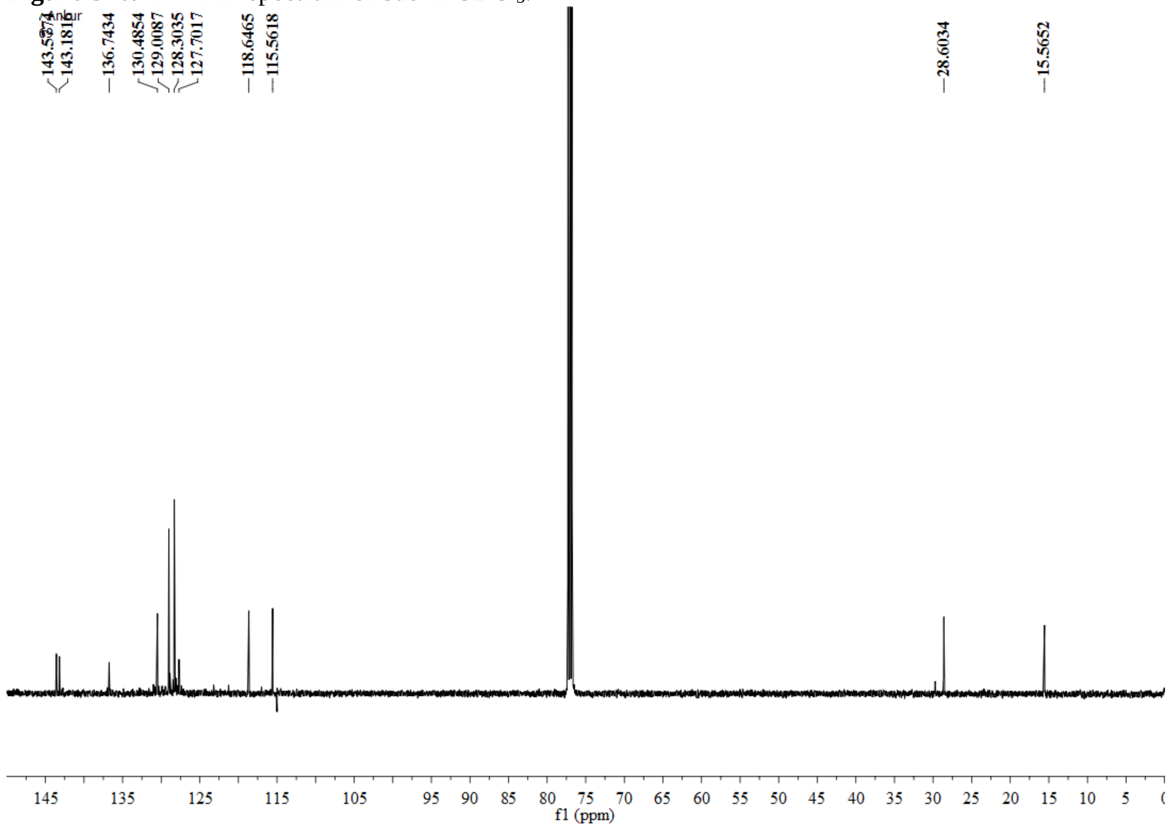


Figure S47. ^{13}C-NMR spectrum of 3ao in $CDCl_3$.

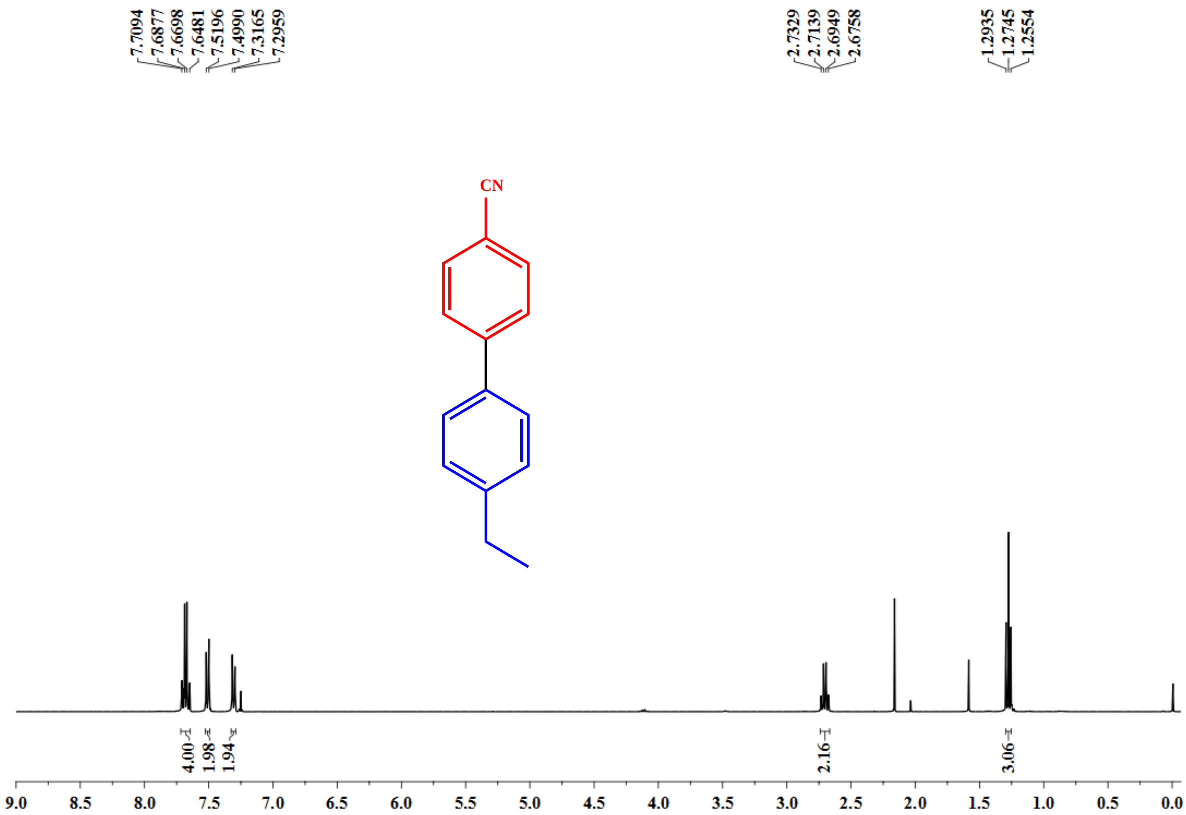


Figure S48. ^{1}H-NMR spectrum of 3ap in $CDCl_3$.

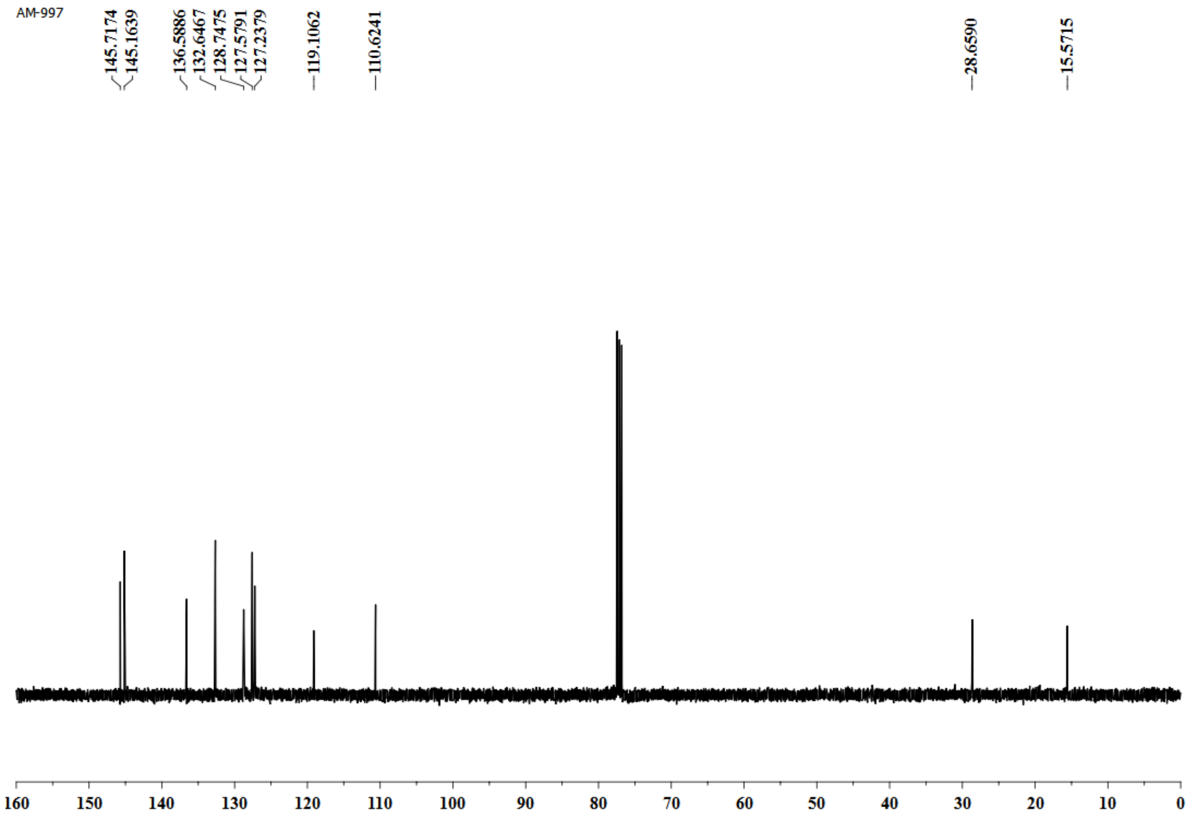


Figure S49. ^{13}C-NMR spectrum of 3ap in $CDCl_3$.

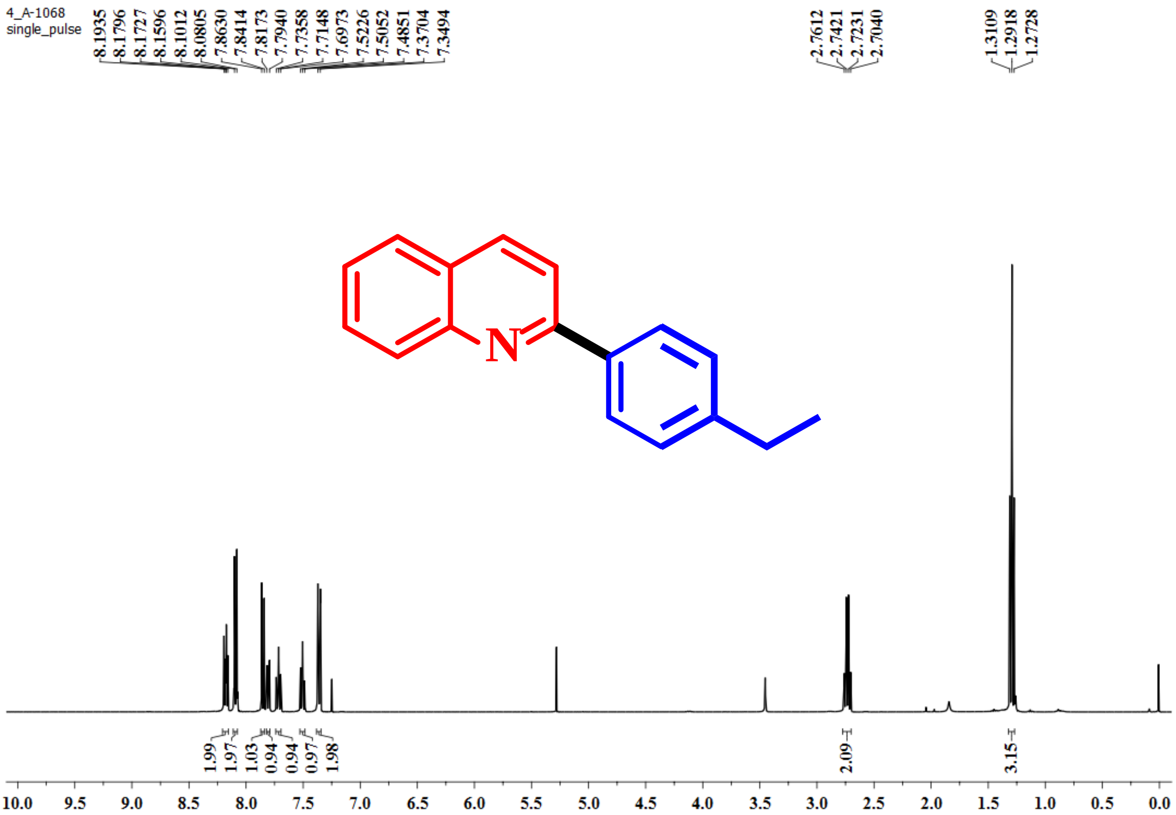


Figure S50. ^{1}H-NMR spectrum of 3aq in $CDCl_3$.

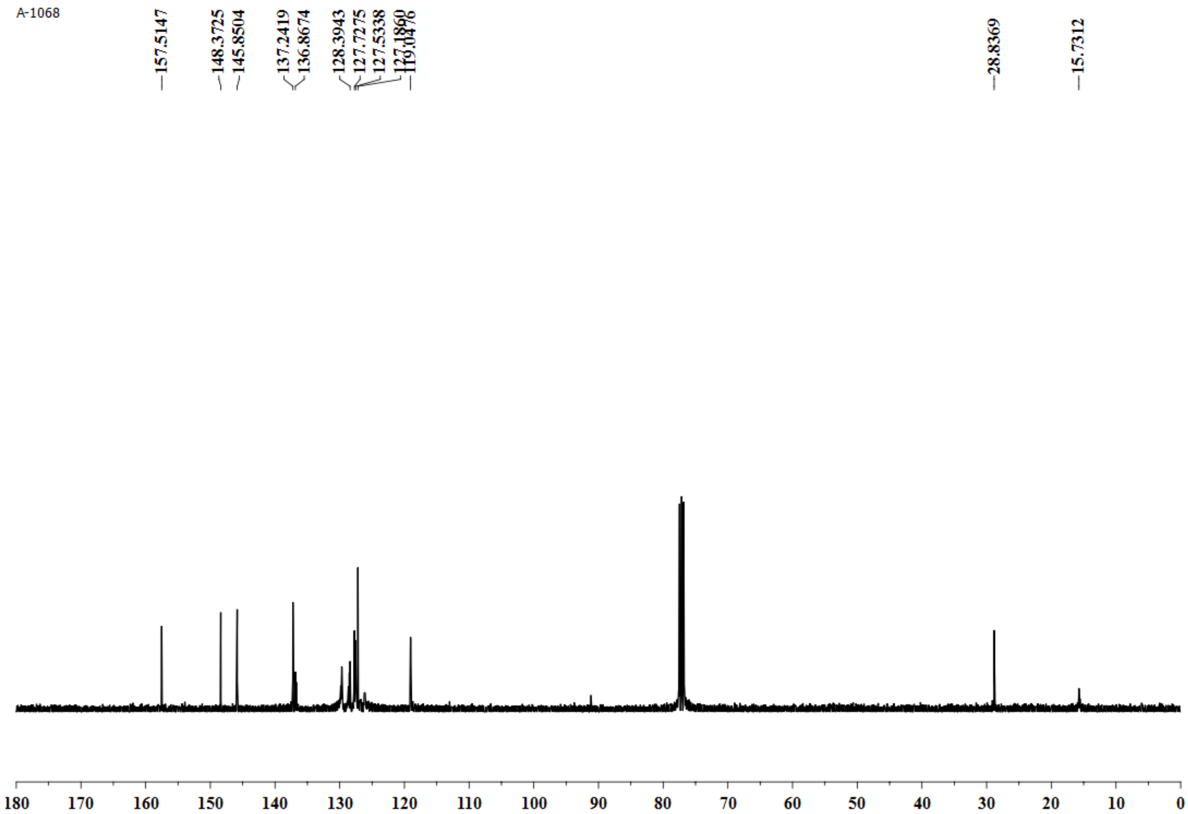


Figure S51. ^{13}C-NMR spectrum of 3aq in $CDCl_3$.

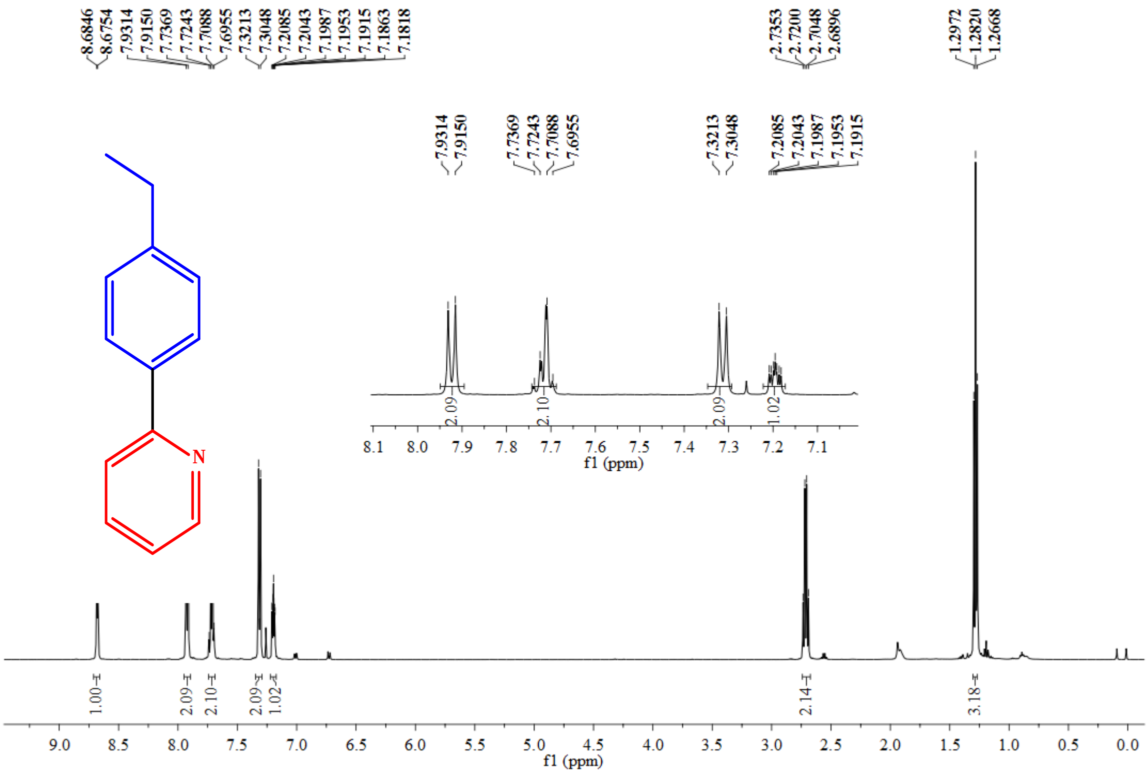


Figure S52. ^{1}H-NMR spectrum of 3ar in $CDCl_3$.

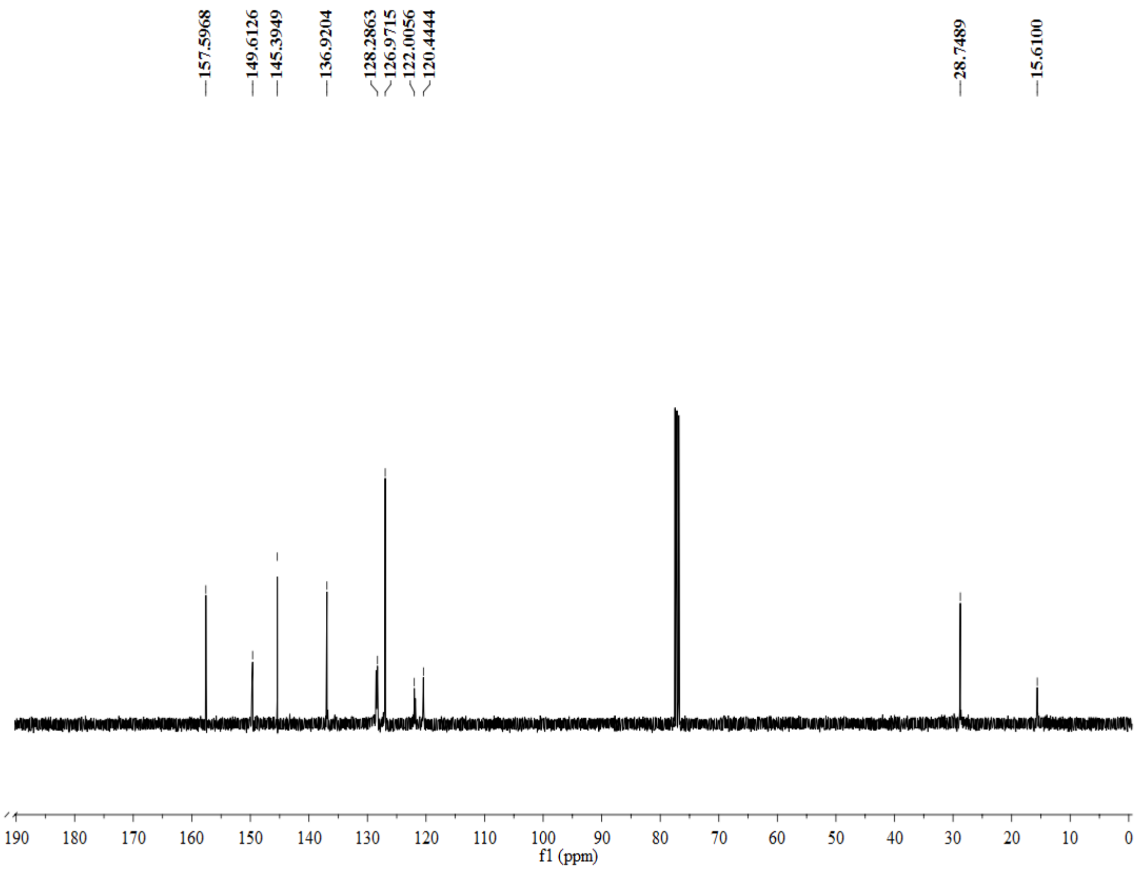


Figure S53. ^{13}C-NMR spectrum of 3ar in $CDCl_3$.

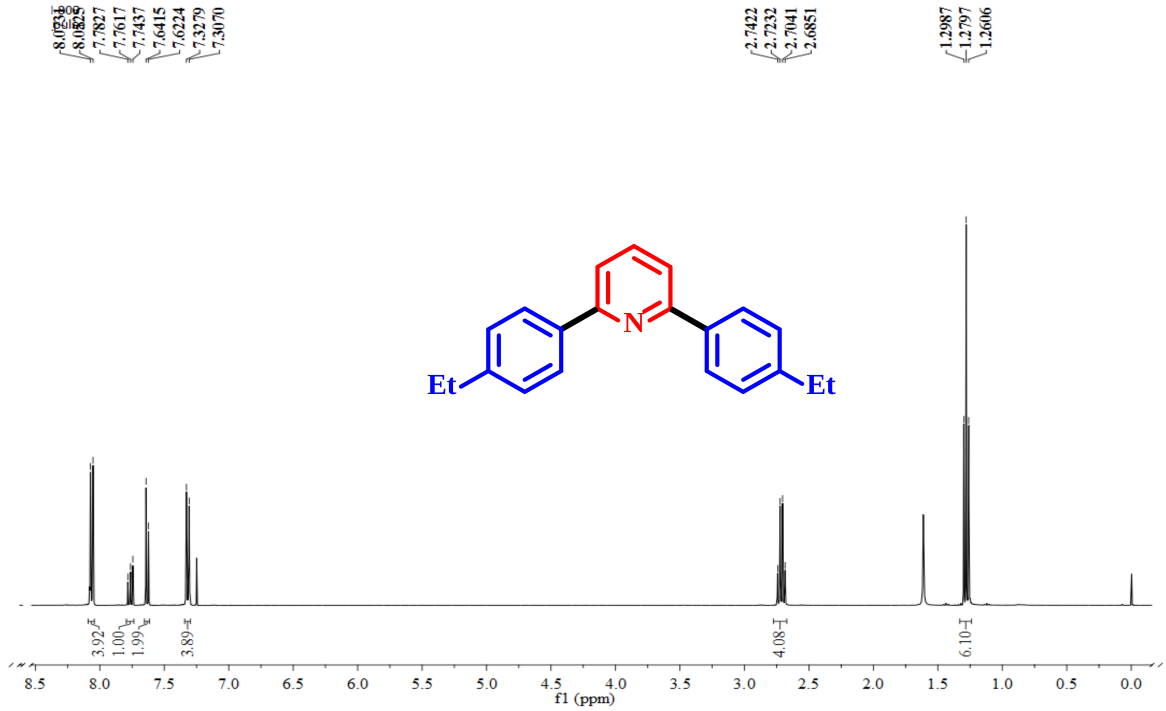


Figure S54. ^{1}H-NMR spectrum of 3as in $CDCl_3$.

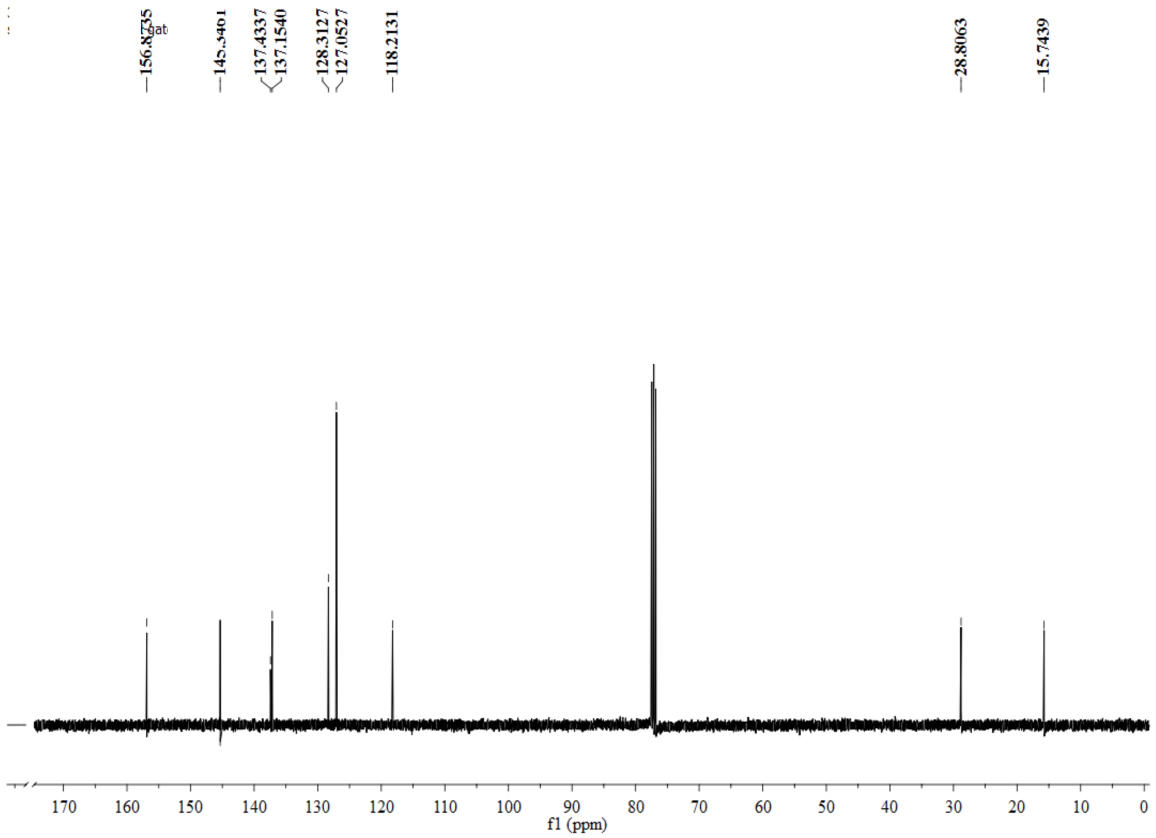


Figure S55. ^{13}C-NMR spectrum of 3as in $CDCl_3$.

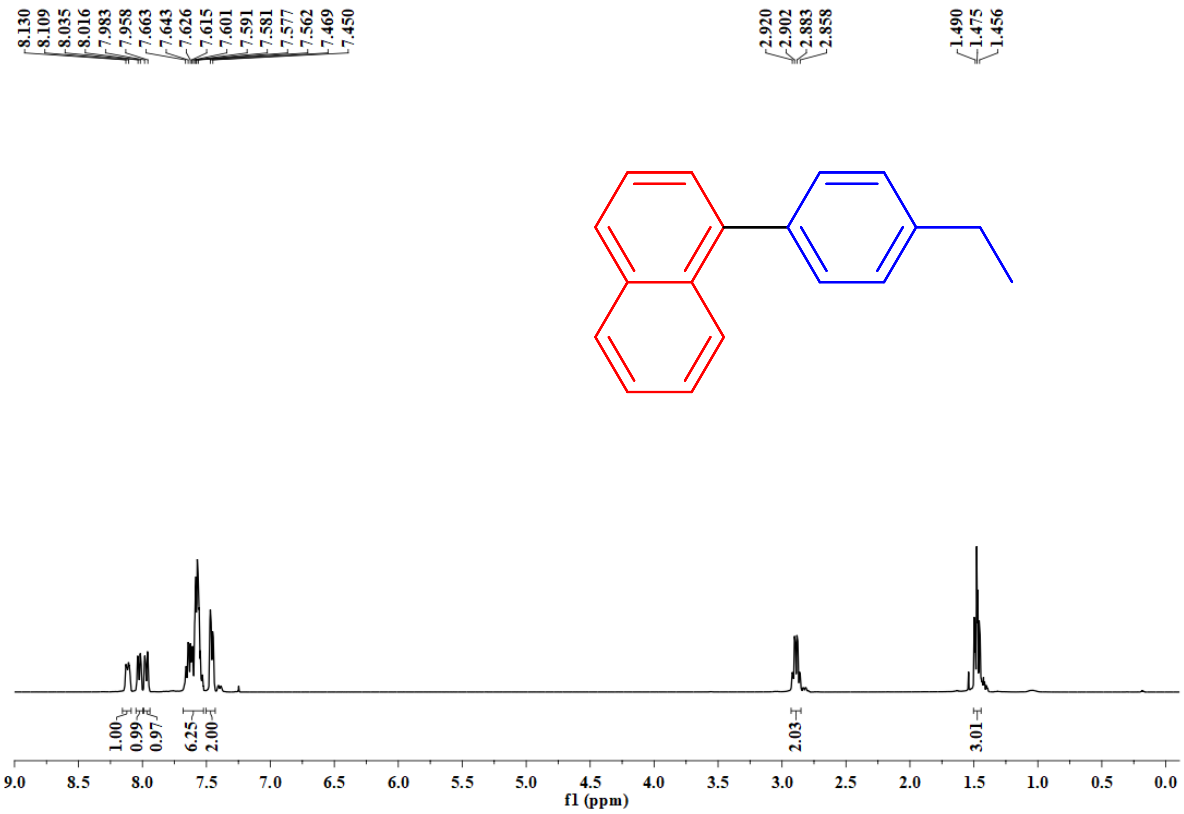


Figure S56. ^{1}H-NMR spectrum of 3at in $CDCl_3$.

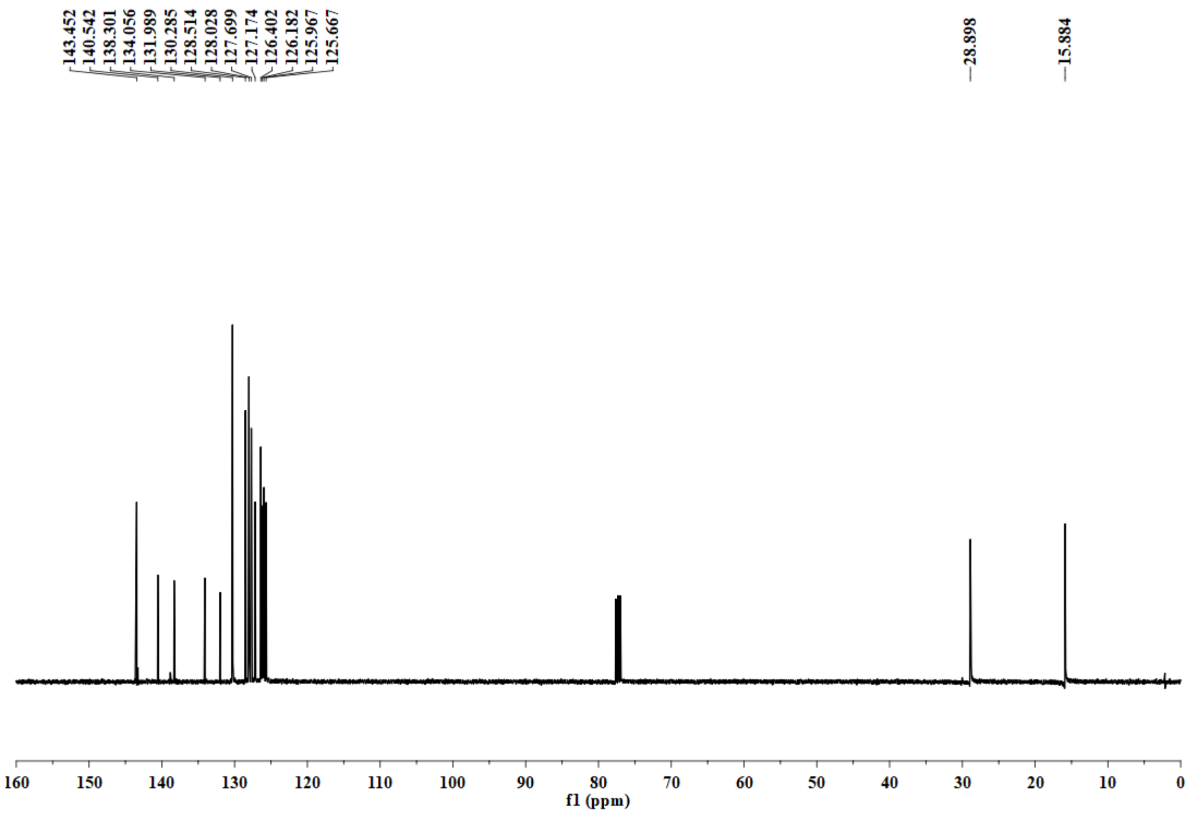


Figure S57. ^{13}C-NMR spectrum of 3at in $CDCl_3$.

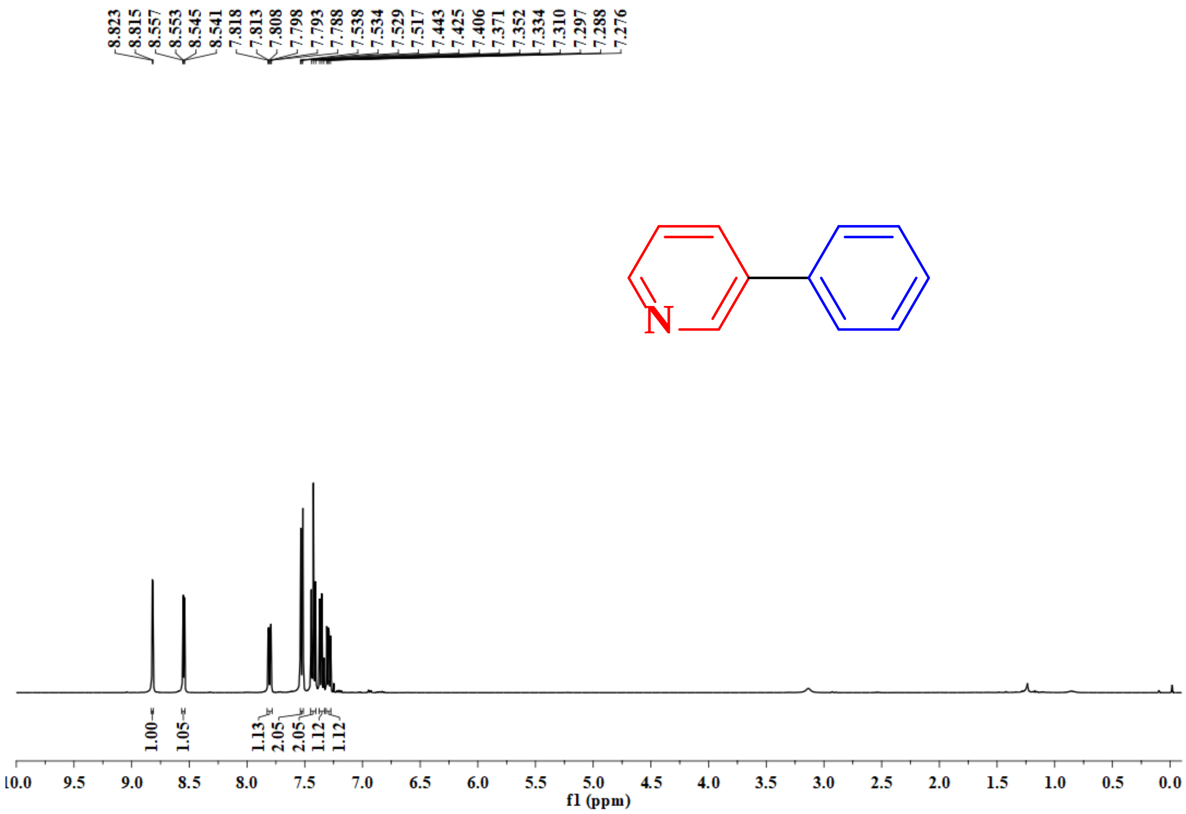


Figure S58. ^{1}H-NMR spectrum of 3au in $CDCl_3$.

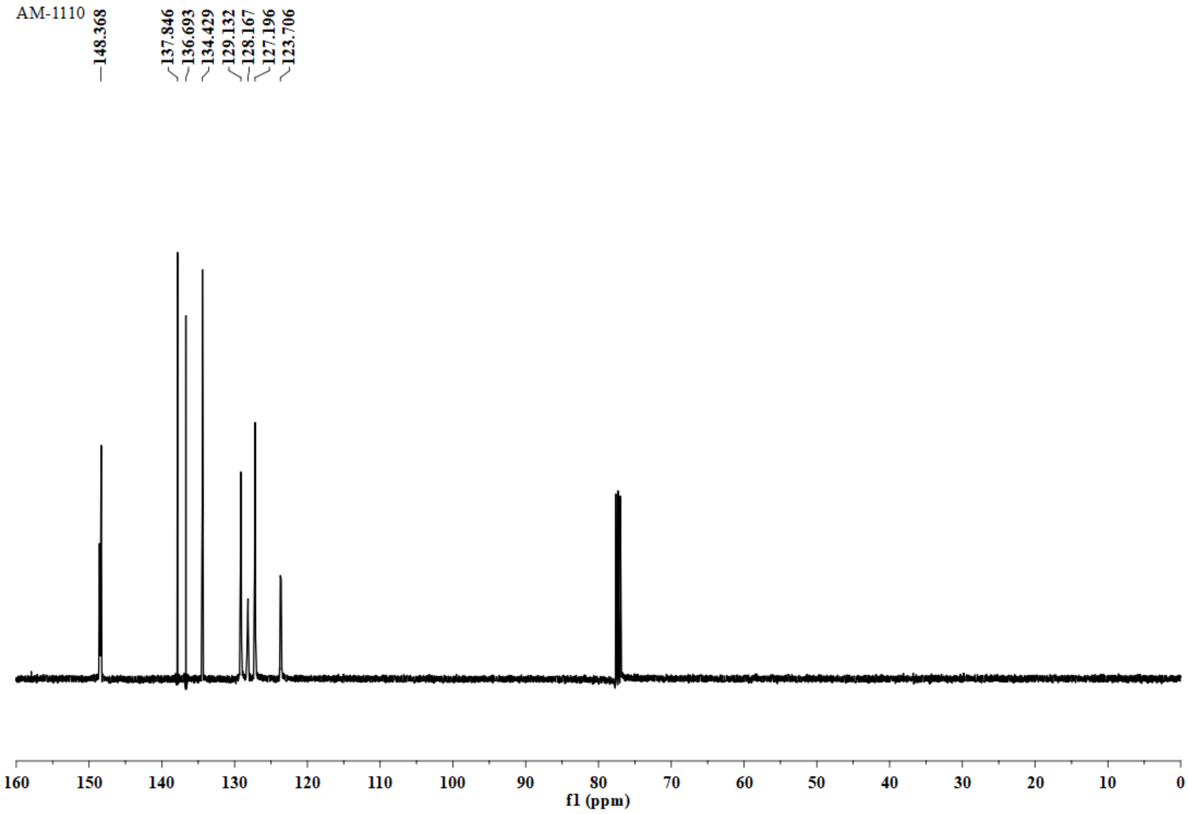


Figure S59. ^{13}C-NMR spectrum of 3au in $CDCl_3$.

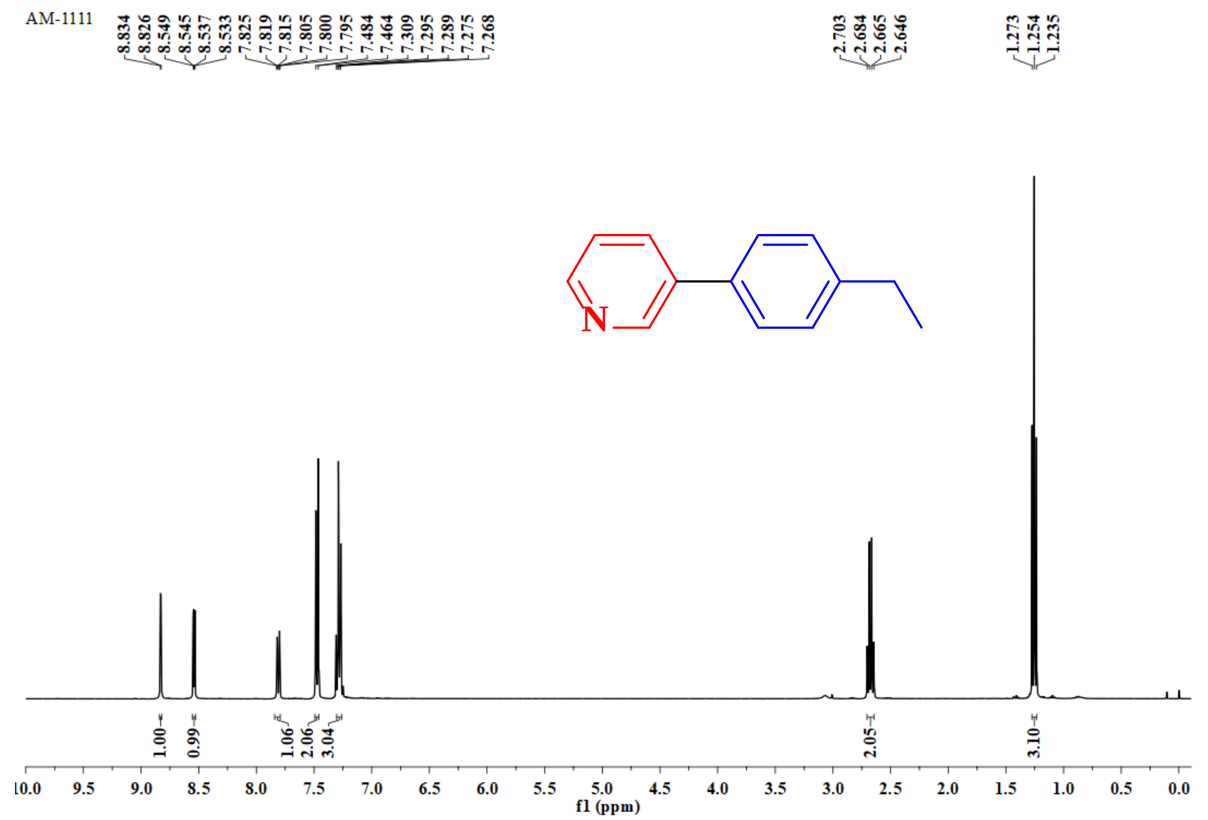


Figure S60. ^{1}H-NMR spectrum of 3av in $CDCl_3$.

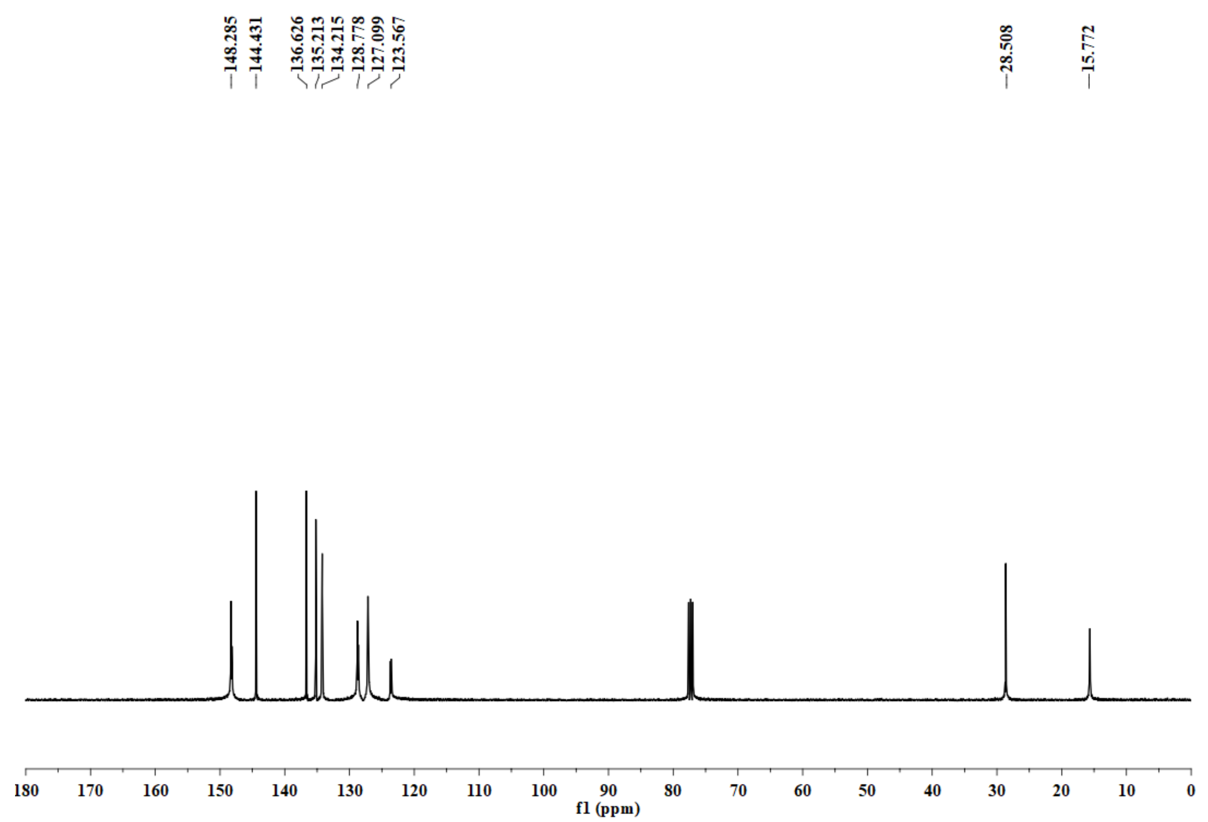


Figure S61. ^{13}C-NMR spectrum of 3av in $CDCl_3$.

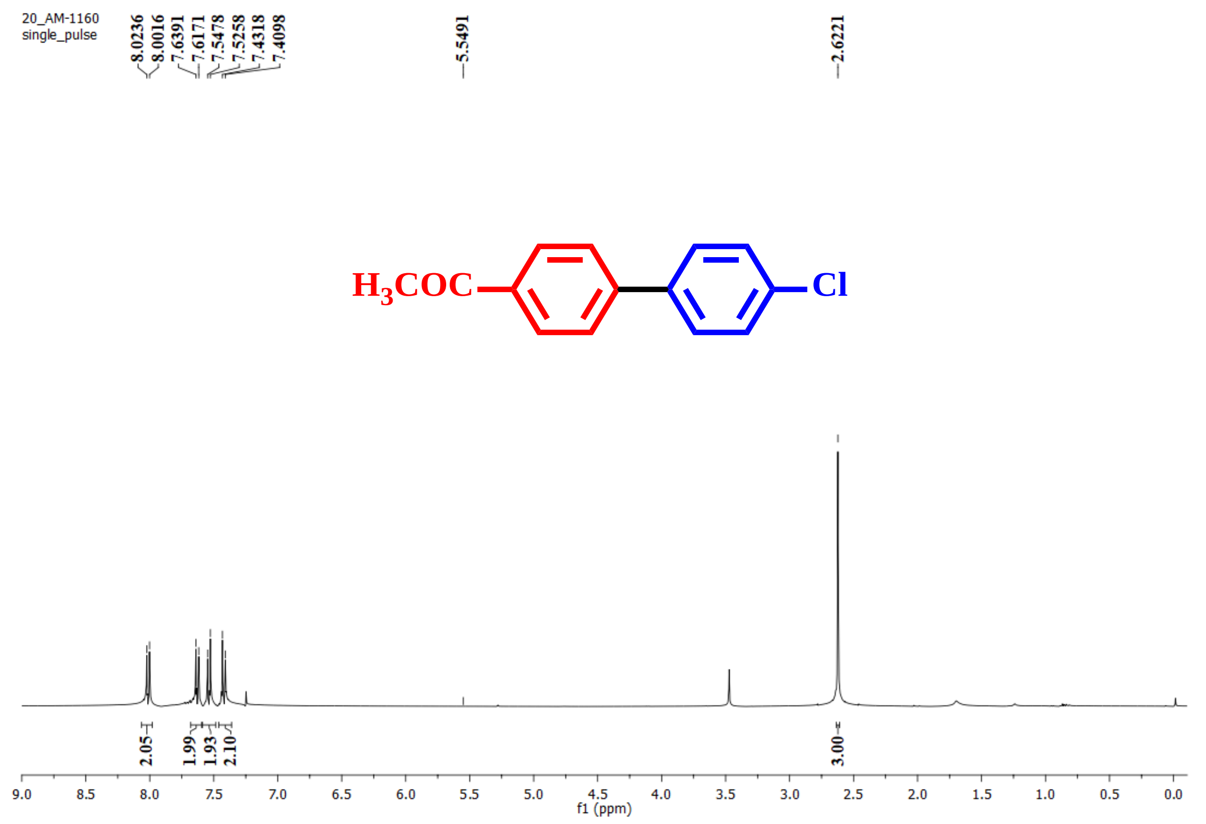


Figure S62. ^{1}H-NMR spectrum of 3ba in $CDCl_3$.

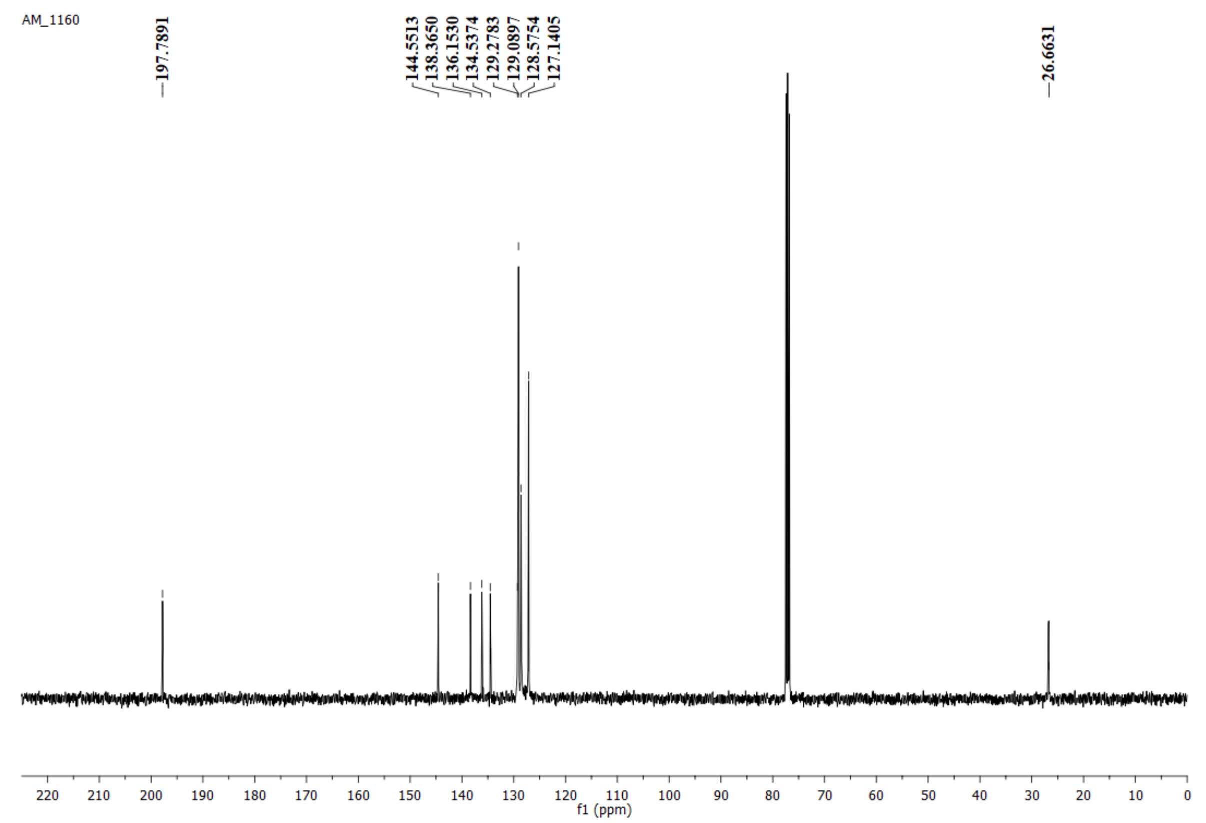


Figure S63. ^{13}C-NMR spectrum of 3ba in $CDCl_3$.

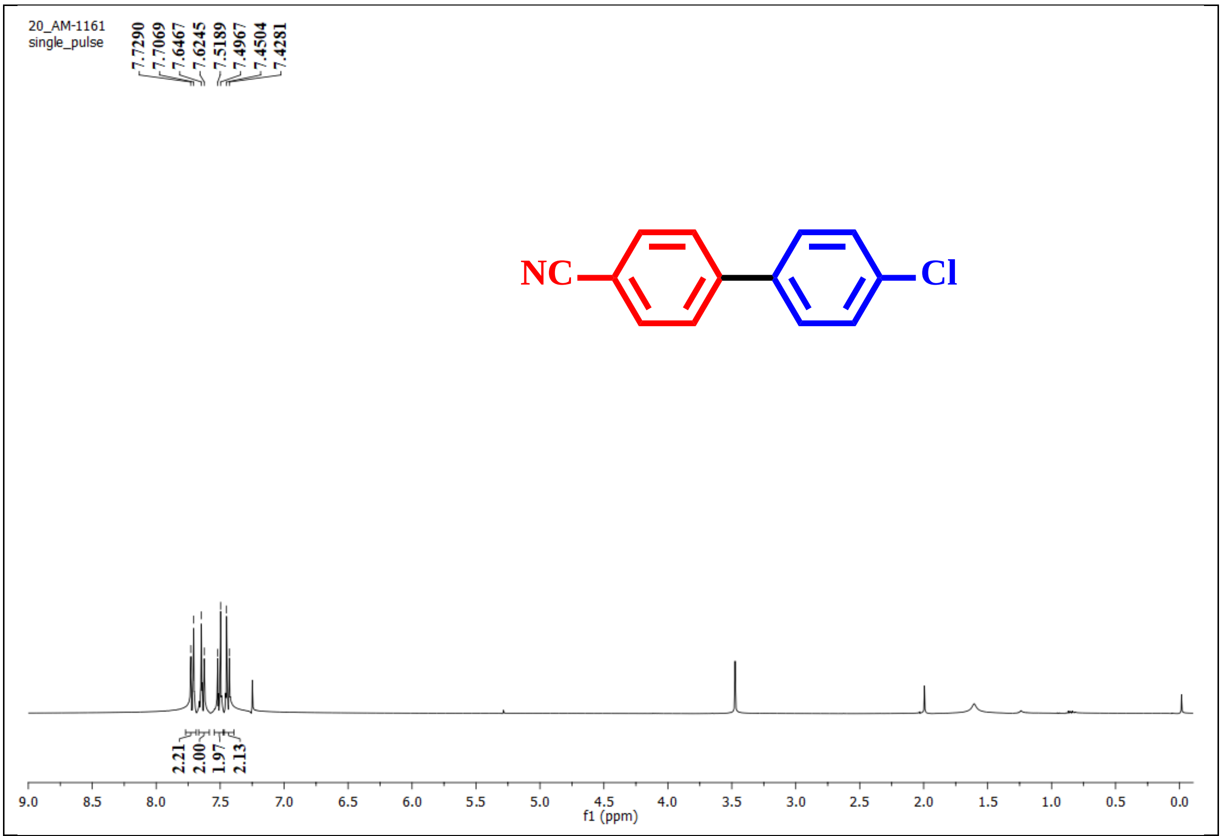


Figure S64. ^{1}H-NMR spectrum of 3bb in $CDCl_3$.

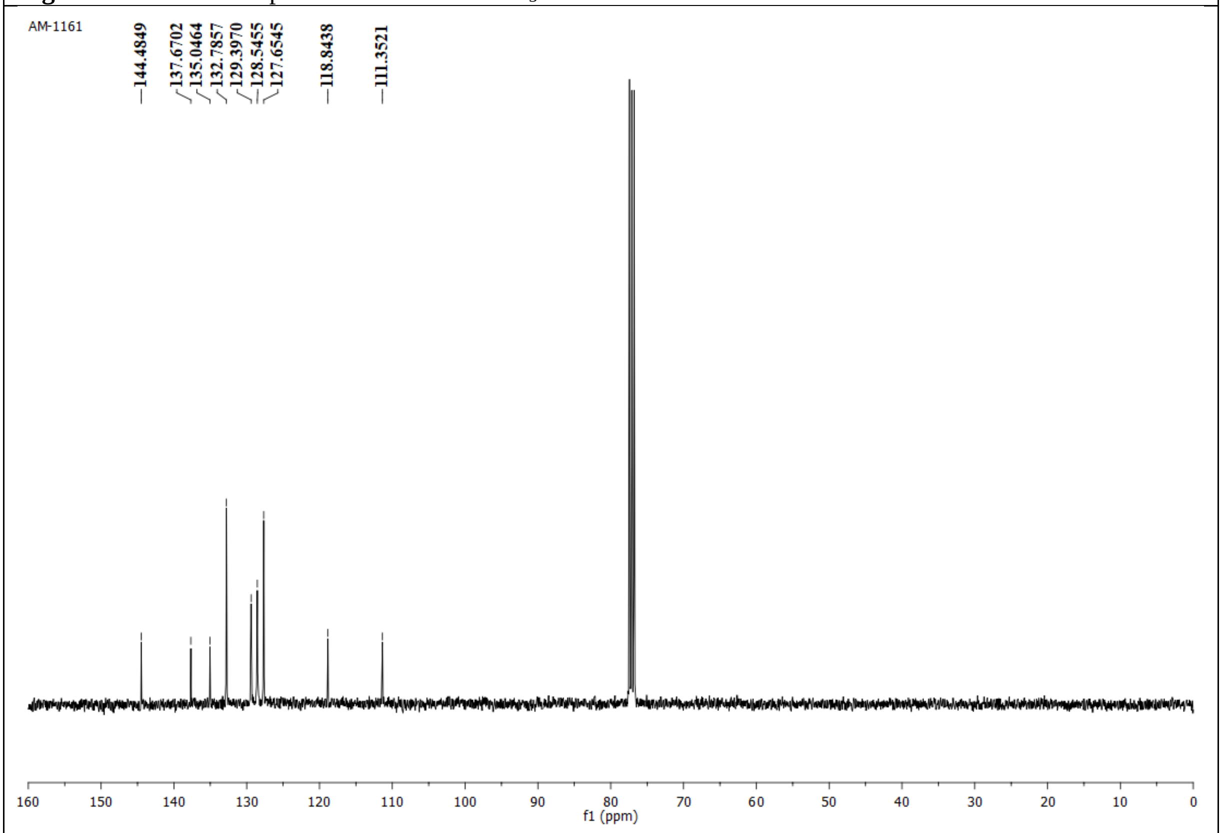


Figure S65. ^{13}C-NMR spectrum of 3bb in $CDCl_3$.

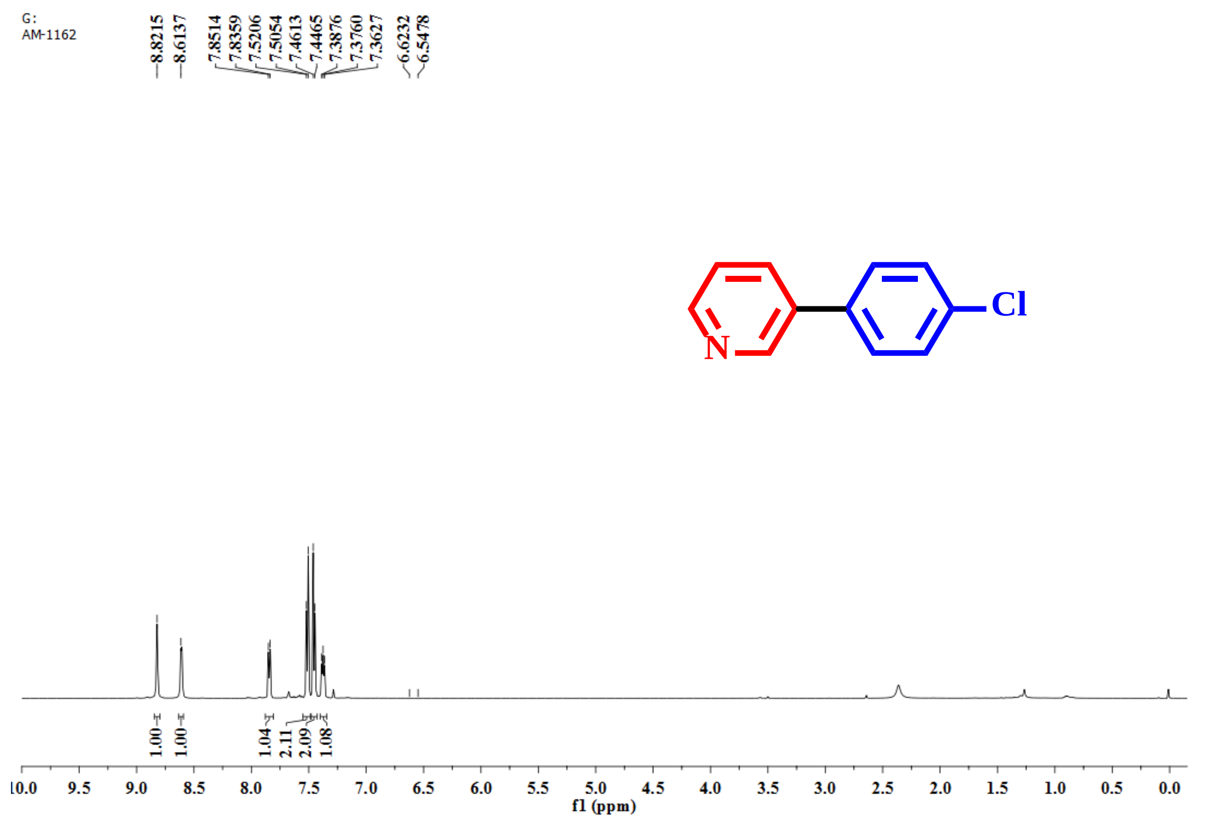


Figure S64. ^{1}H-NMR spectrum of 3bc in $CDCl_3$.

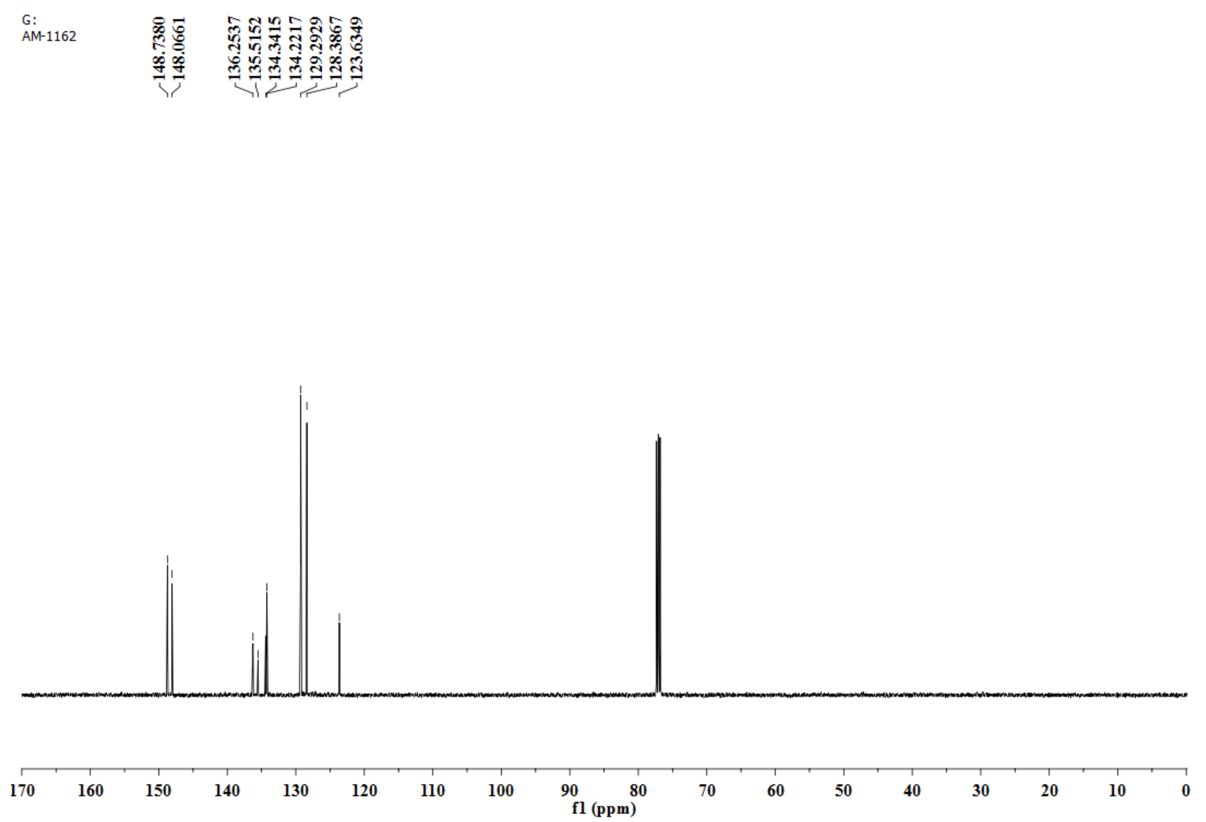


Figure S67. ^{13}C-NMR spectrum of 3bc in $CDCl_3$.

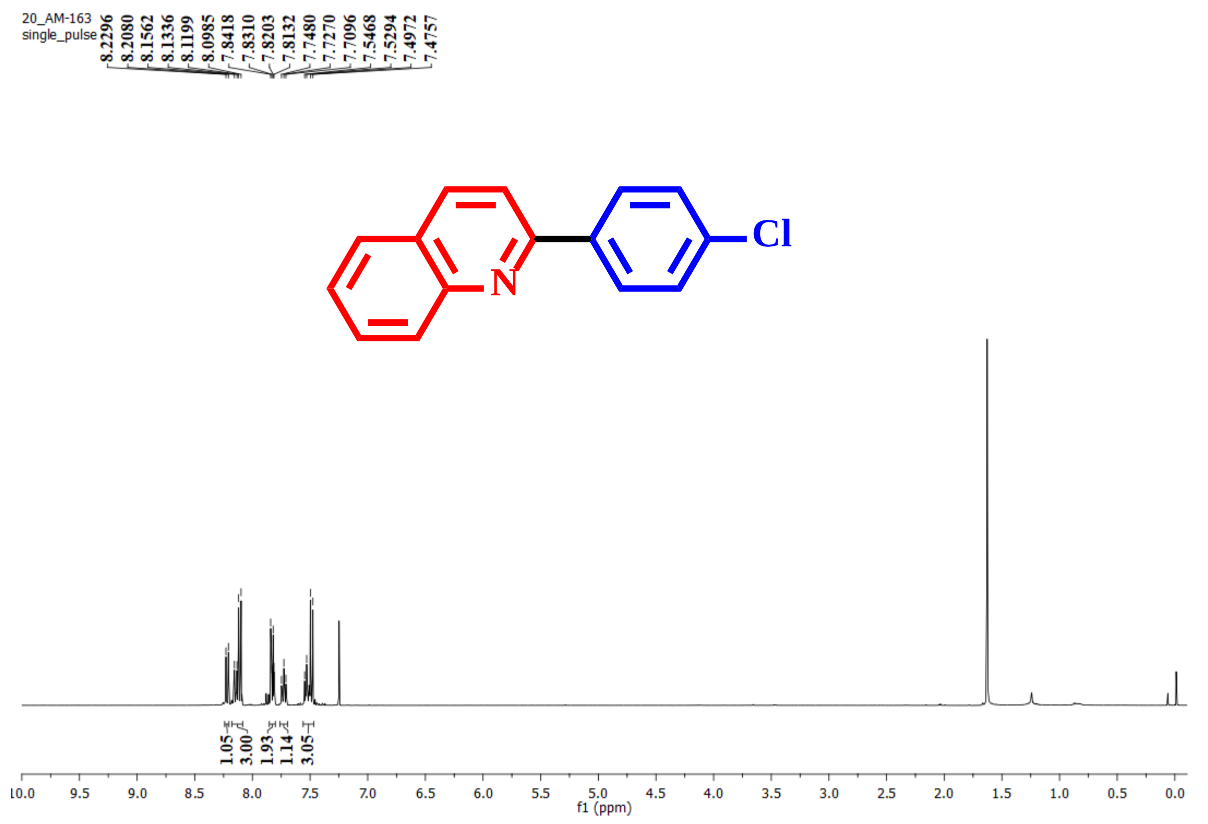


Figure S68. ^{1}H-NMR spectrum of 3bd in $CDCl_3$.

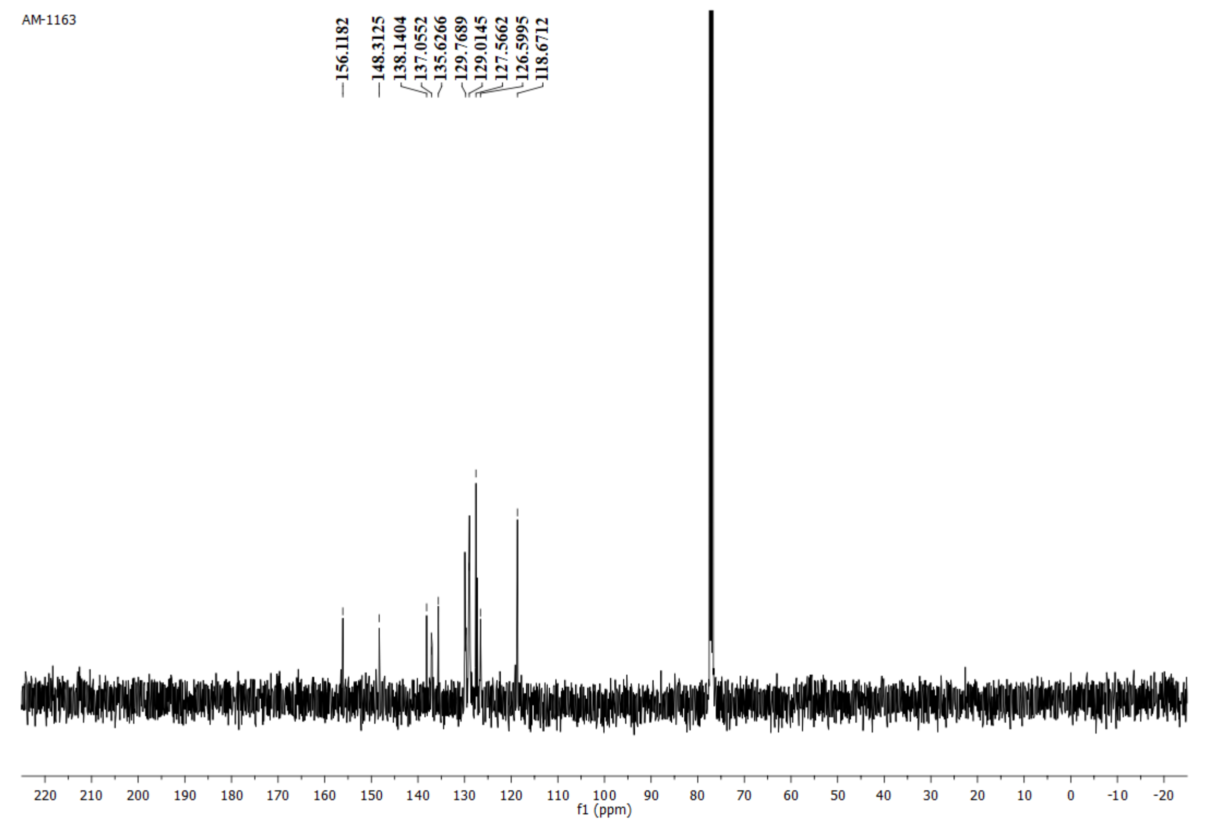


Figure S69. ^{13}C-NMR spectrum of 3bd in $CDCl_3$.

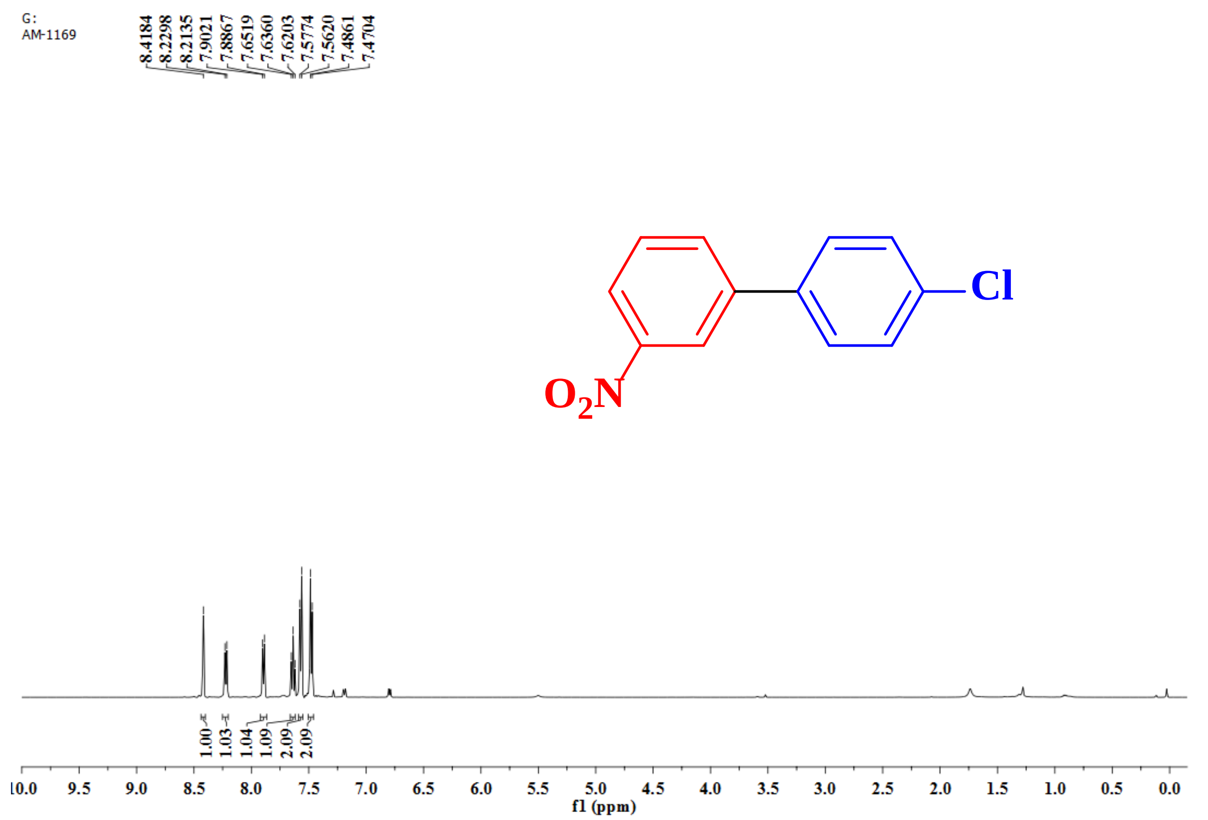


Figure S70. [1]H-NMR spectrum of 3be in $CDCl_3$.

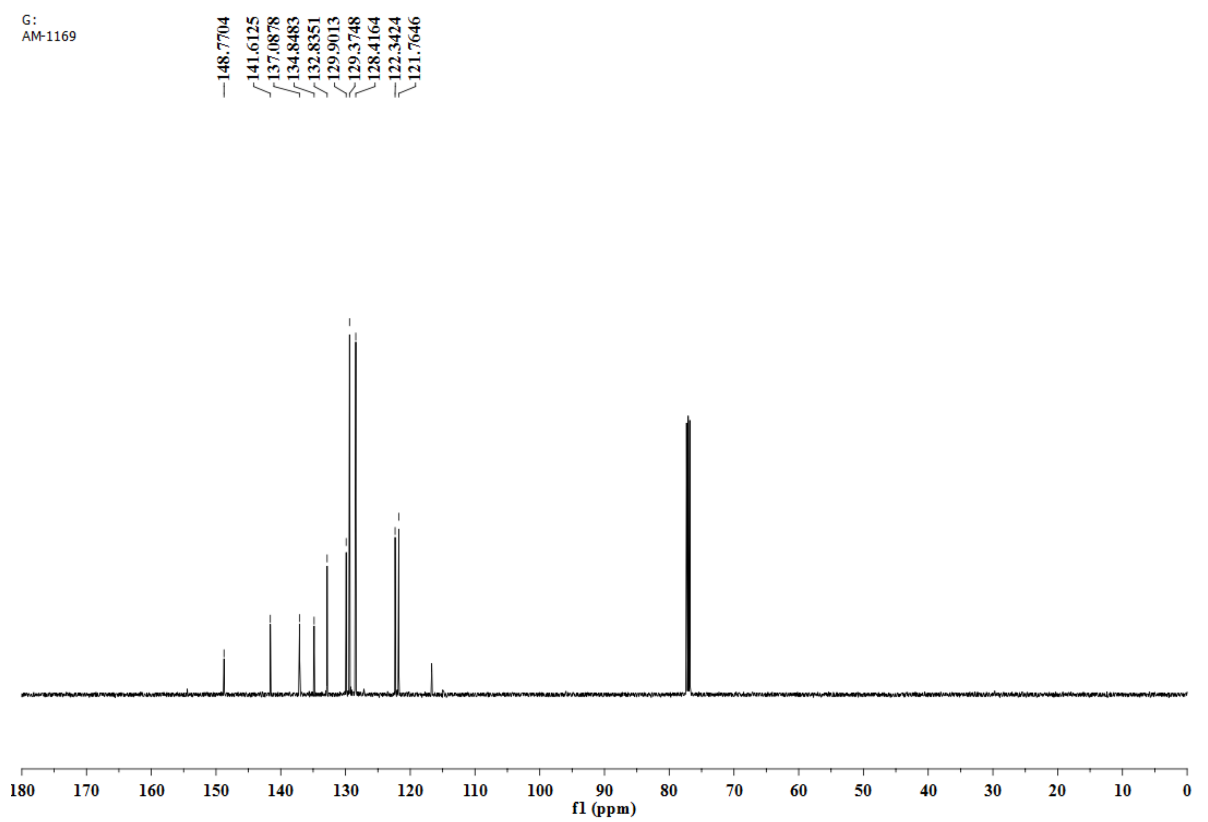


Figure S71. [13]C-NMR spectrum of 3be in $CDCl_3$.

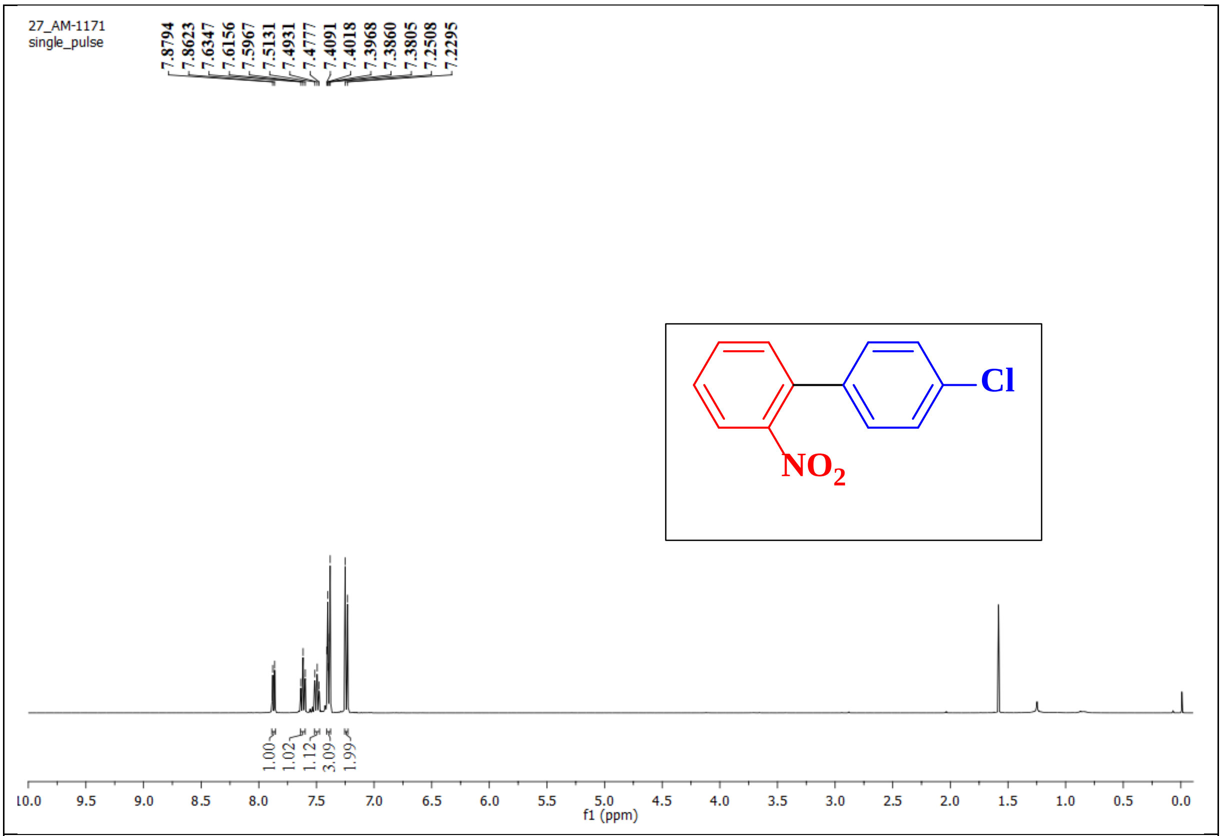


Figure S72. ^{1}H-NMR spectrum of 3bf in $CDCl_3$.

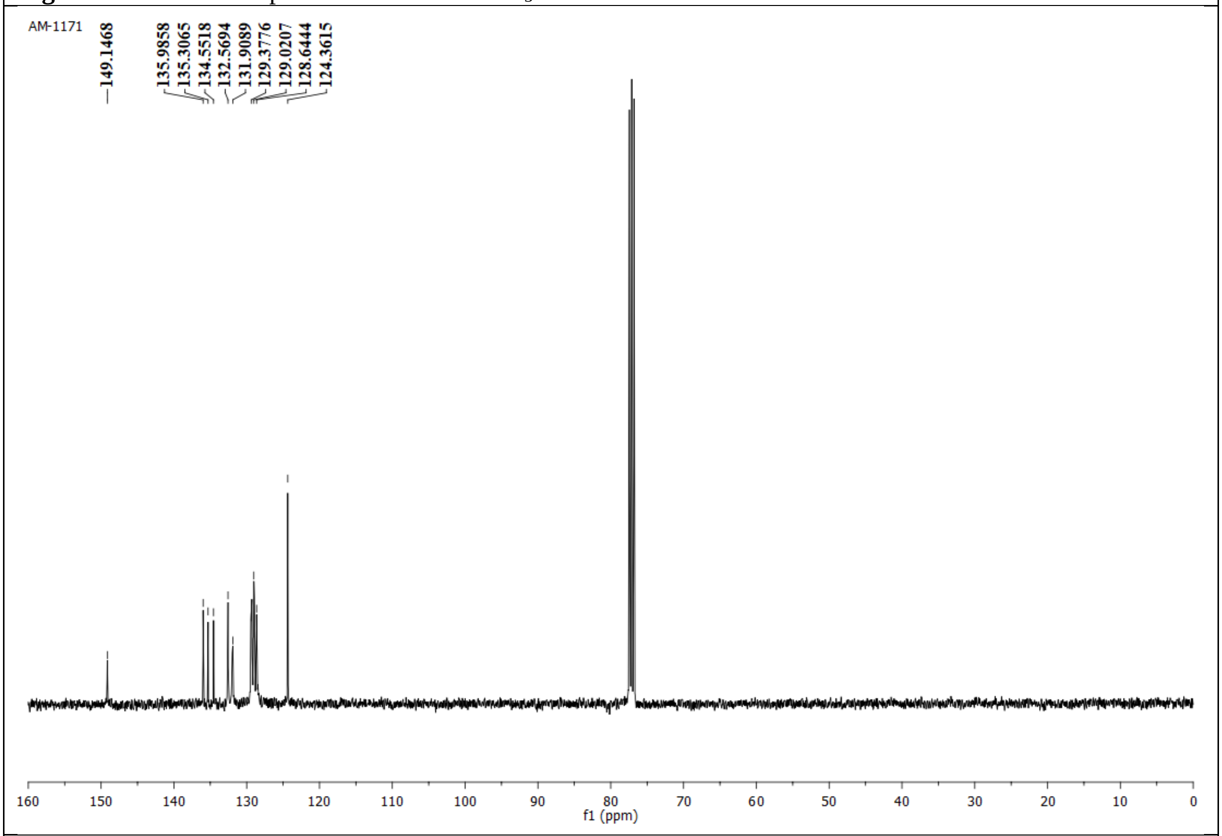


Figure S73. ^{13}C-NMR spectrum of 3bf in $CDCl_3$.

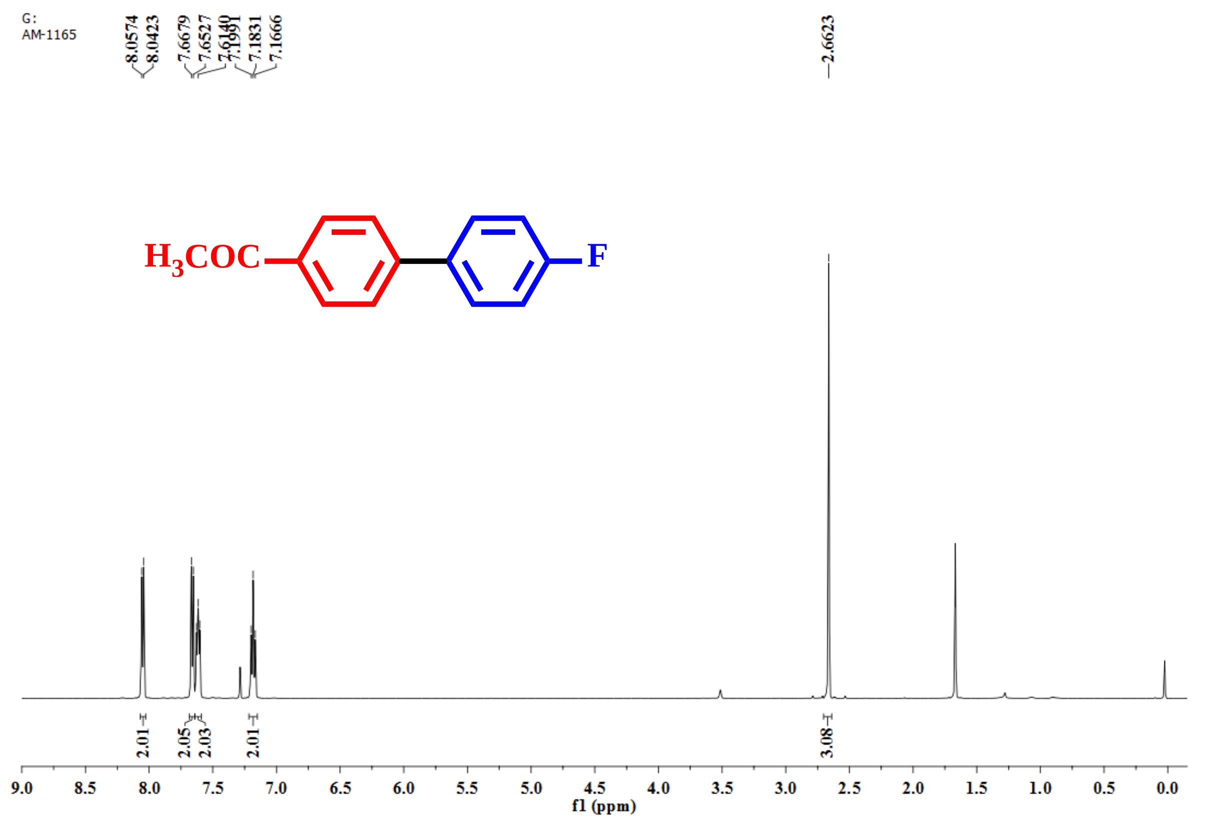


Figure S74. ^{1}H-NMR spectrum of 3ca in $CDCl_3$.

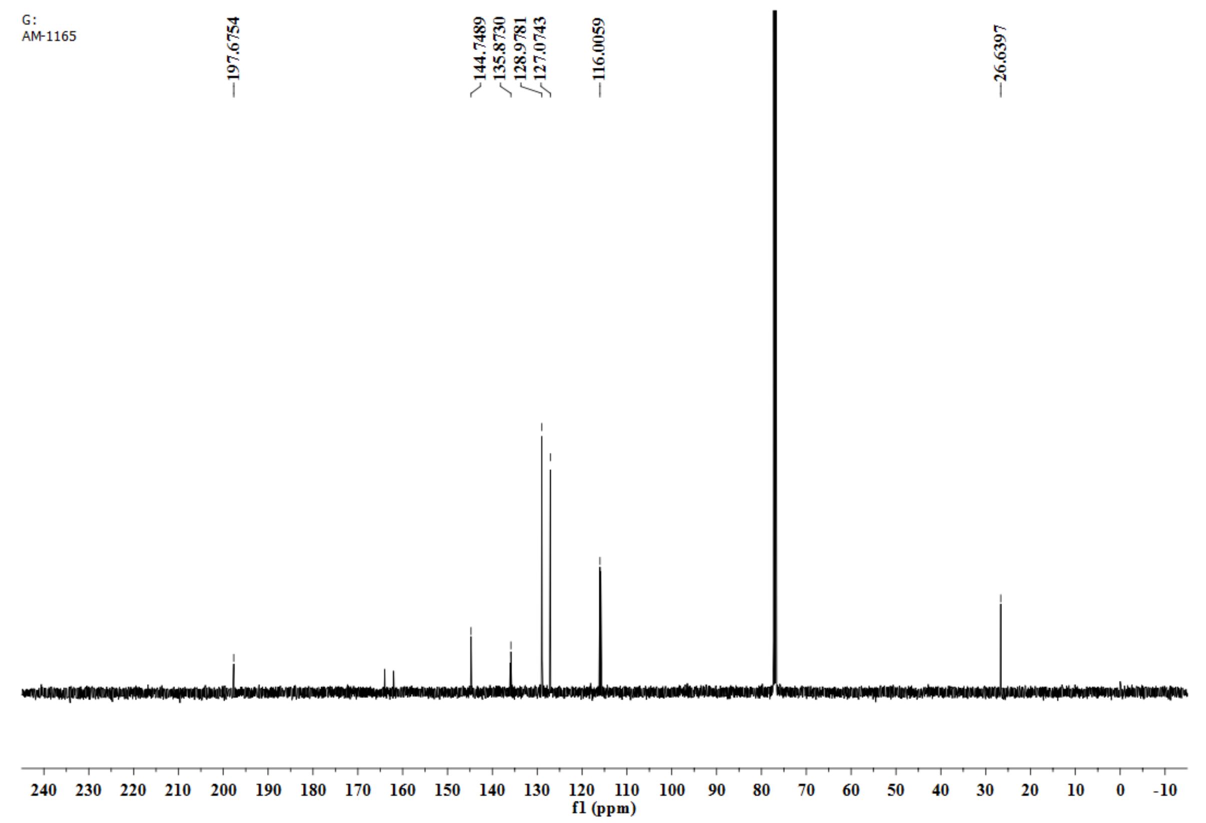


Figure S75. ^{13}C-NMR spectrum of 3ca in $CDCl_3$.

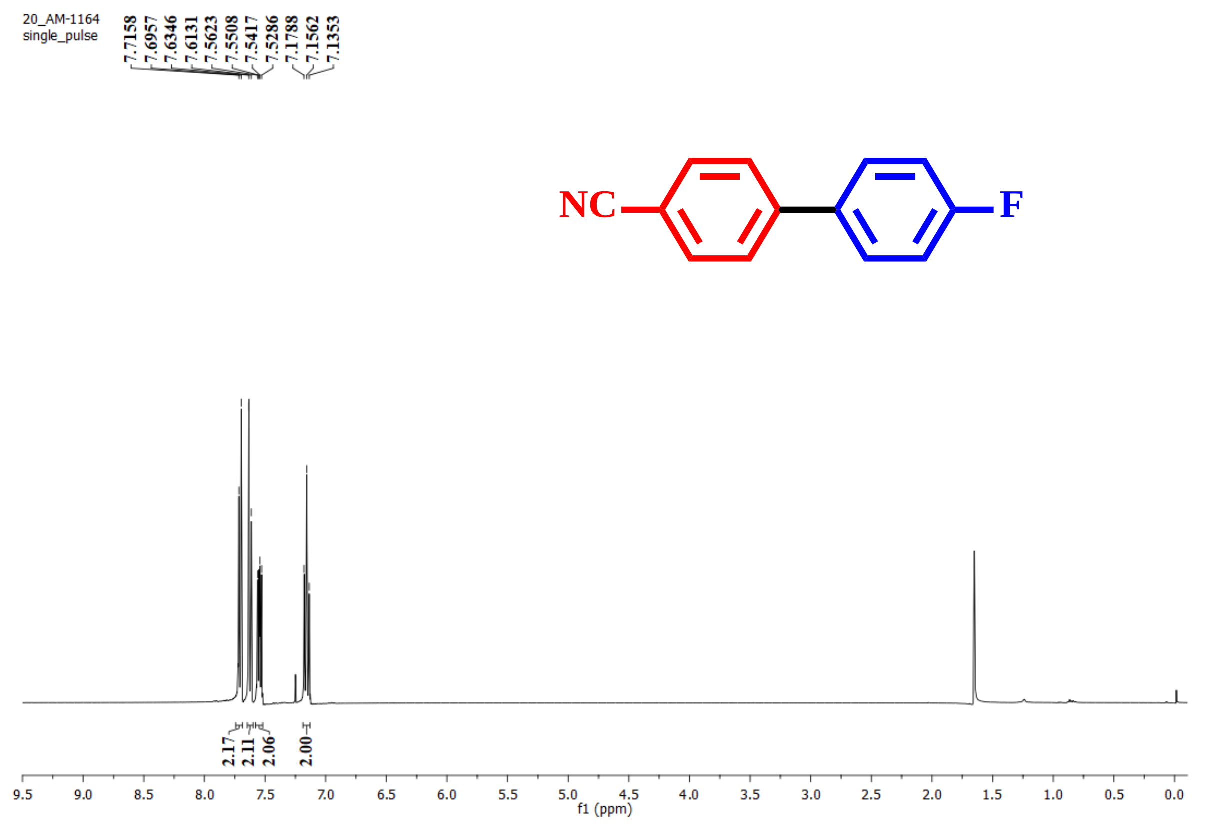


Figure S76. ^{1}H-NMR spectrum of 3cb in $CDCl_3$.

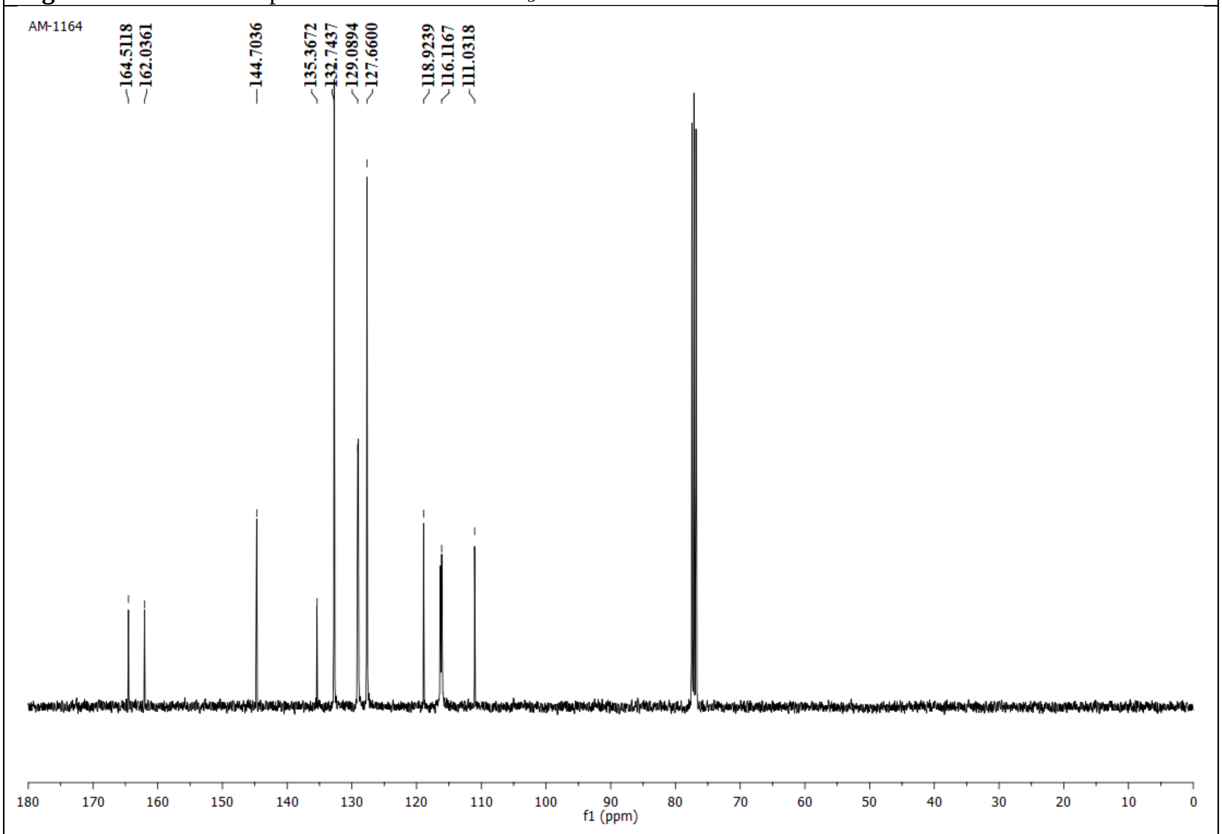


Figure S77. ^{13}C-NMR spectrum of 3cb in $CDCl_3$.

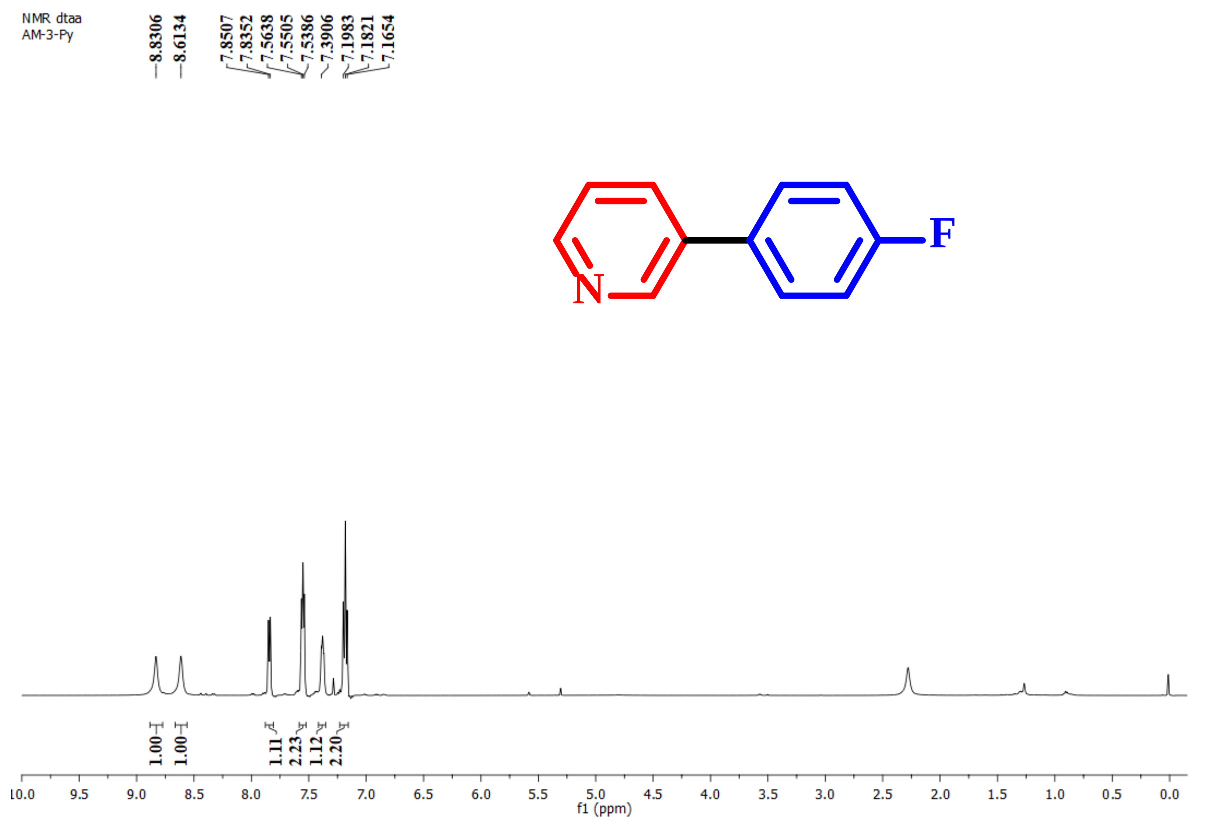


Figure S78. ^{1}H-NMR spectrum of 3cc in $CDCl_3$.

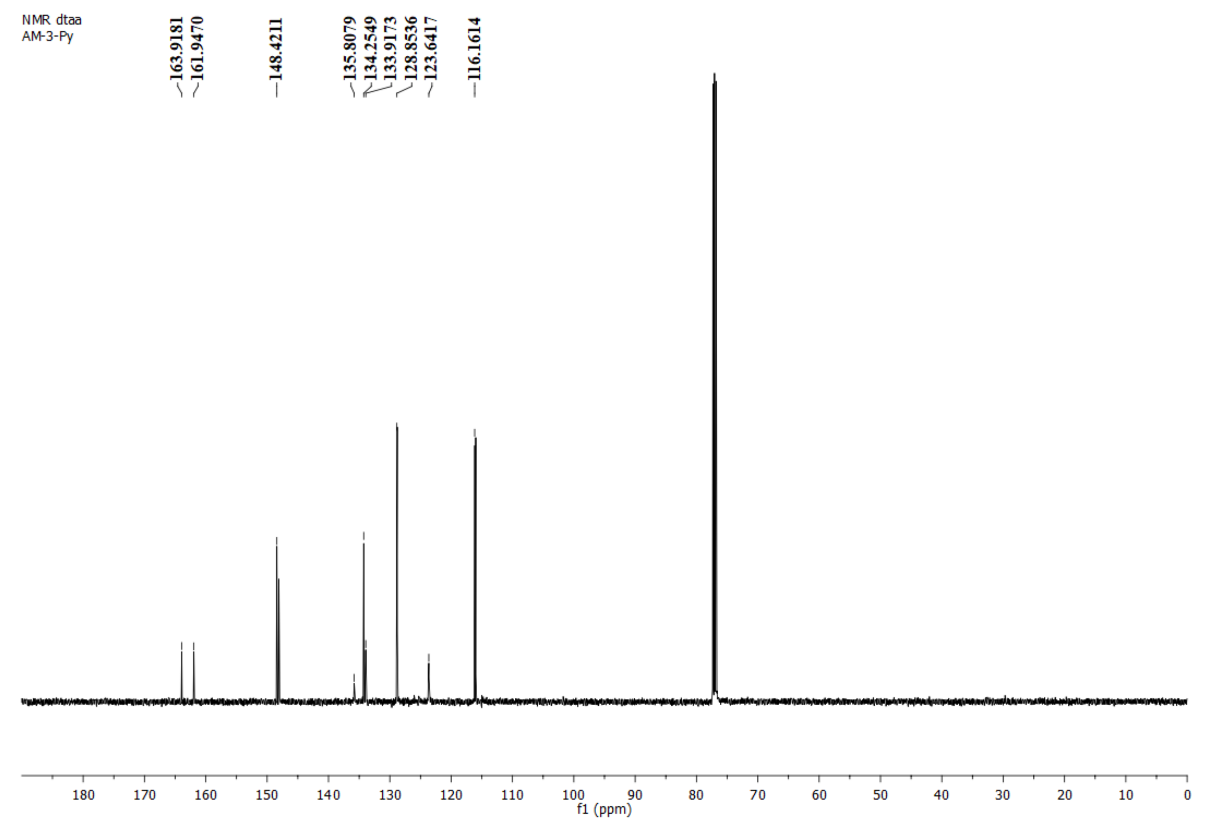


Figure S79. ^{13}C-NMR spectrum of 3cc in $CDCl_3$.

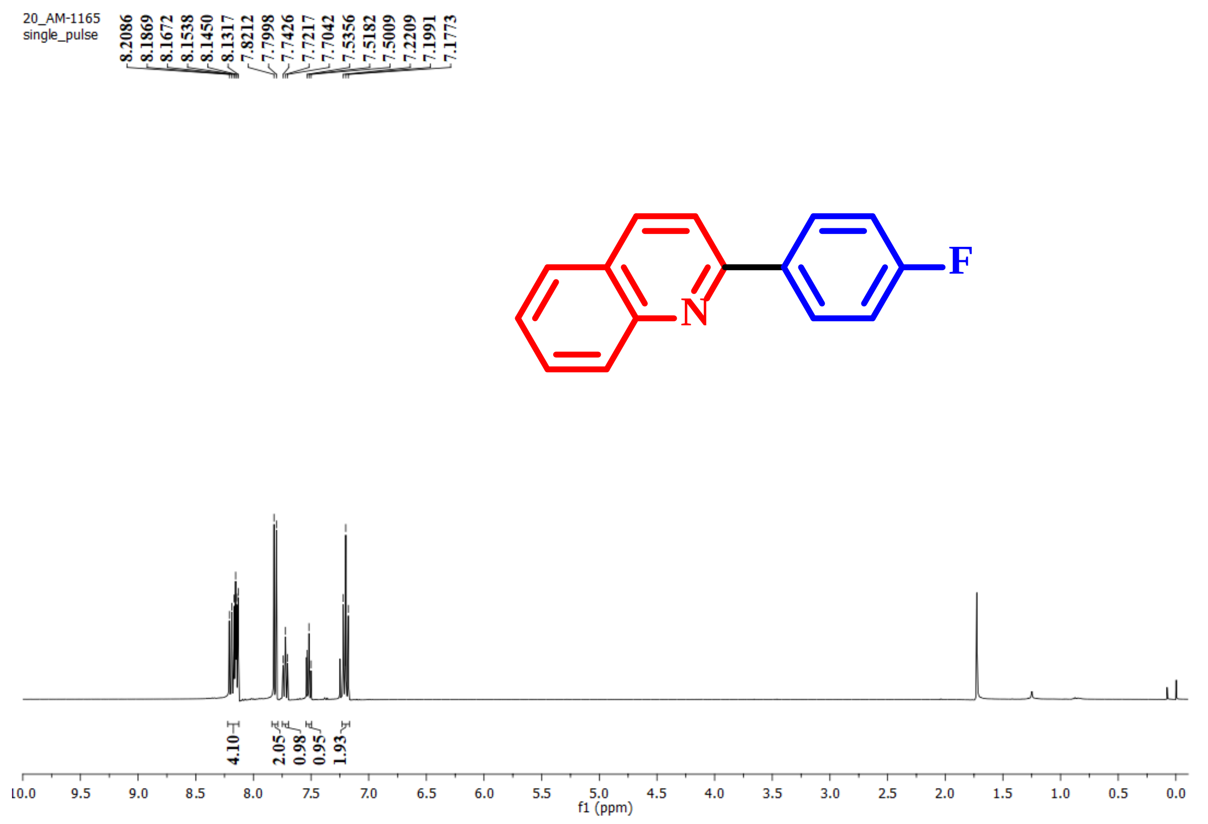


Figure S80. ^{1}H-NMR spectrum of 3cd in $CDCl_3$.

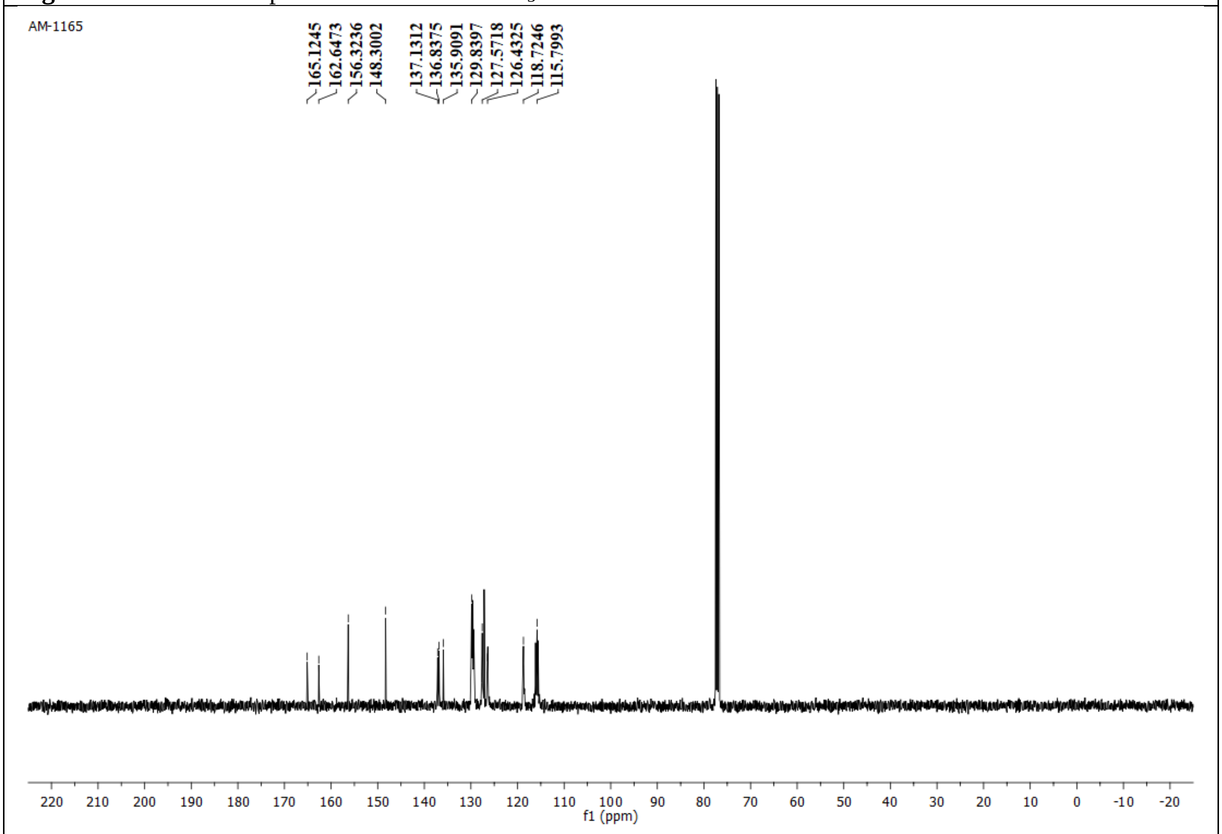


Figure S81. ^{13}C-NMR spectrum of 3cd in $CDCl_3$.

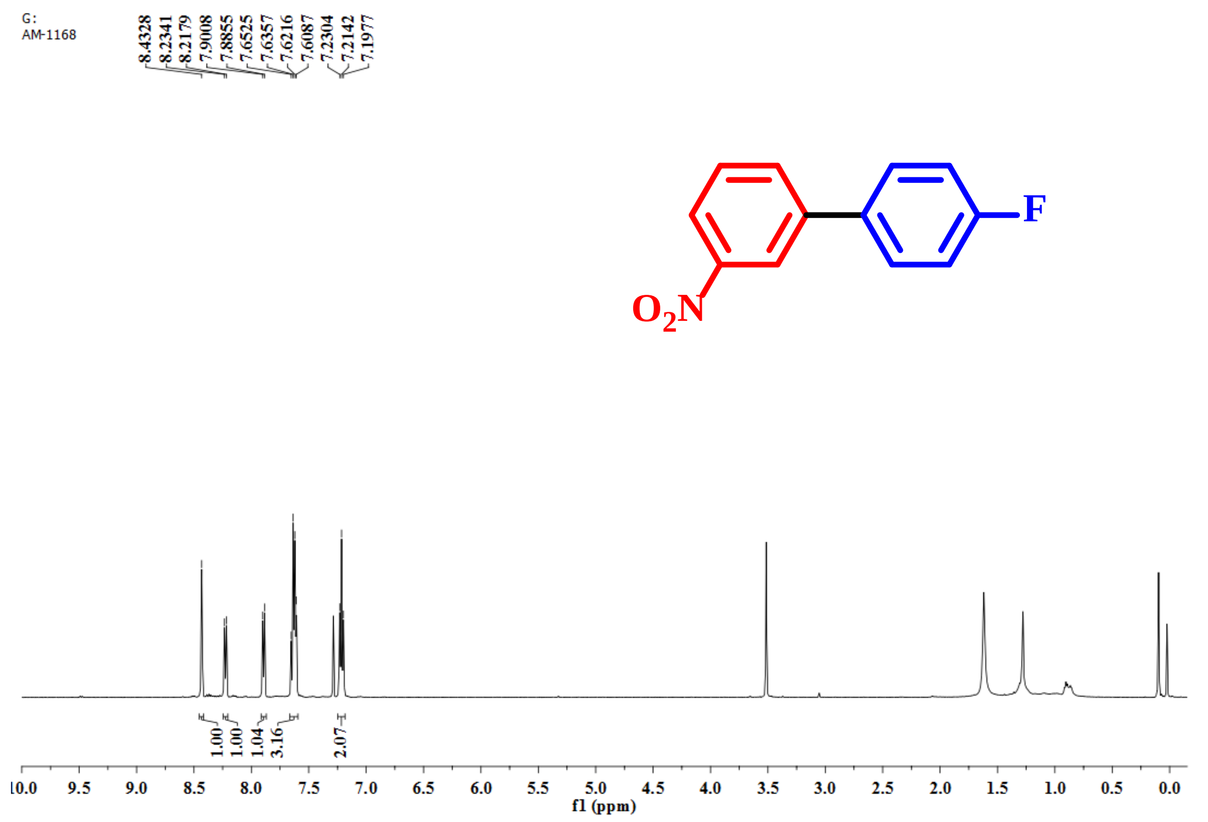


Figure S82. ^{1}H-NMR spectrum of 3ce in $CDCl_3$.

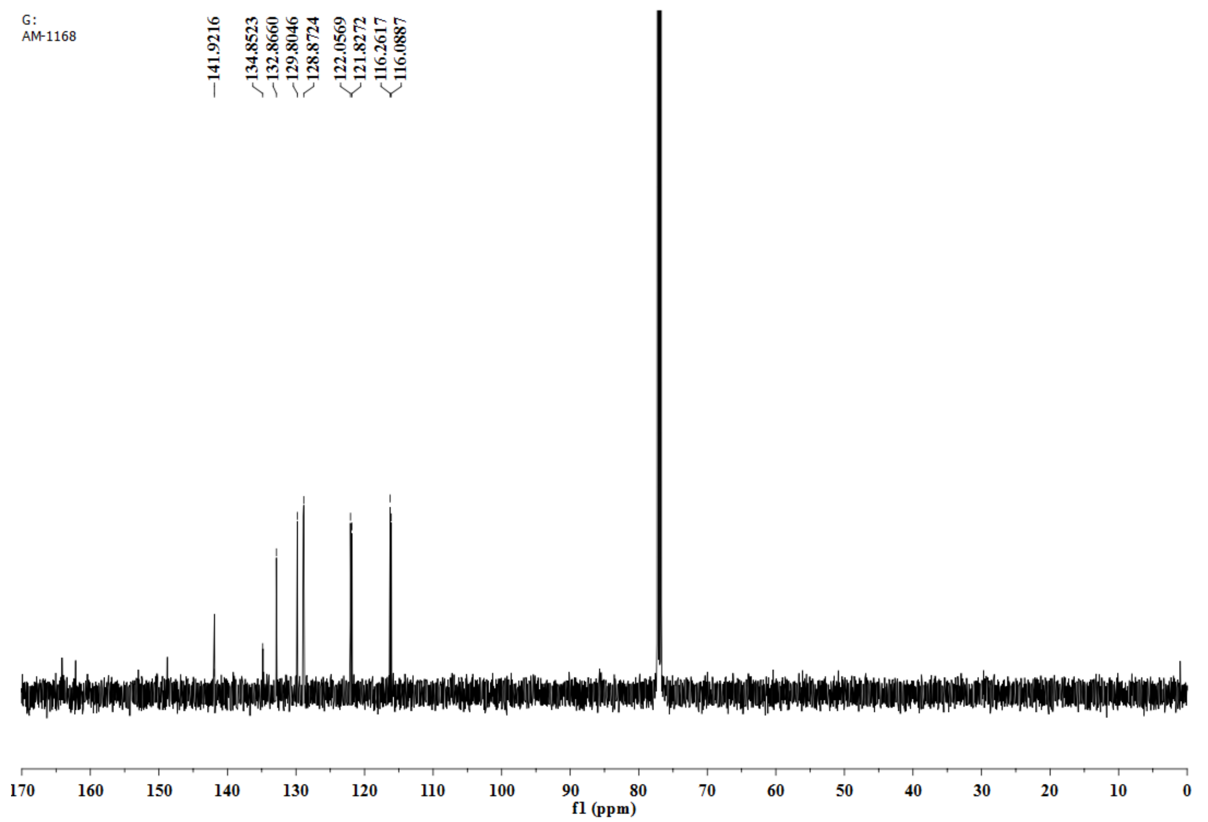


Figure S83. ^{13}C-NMR spectrum of 3ce in $CDCl_3$.

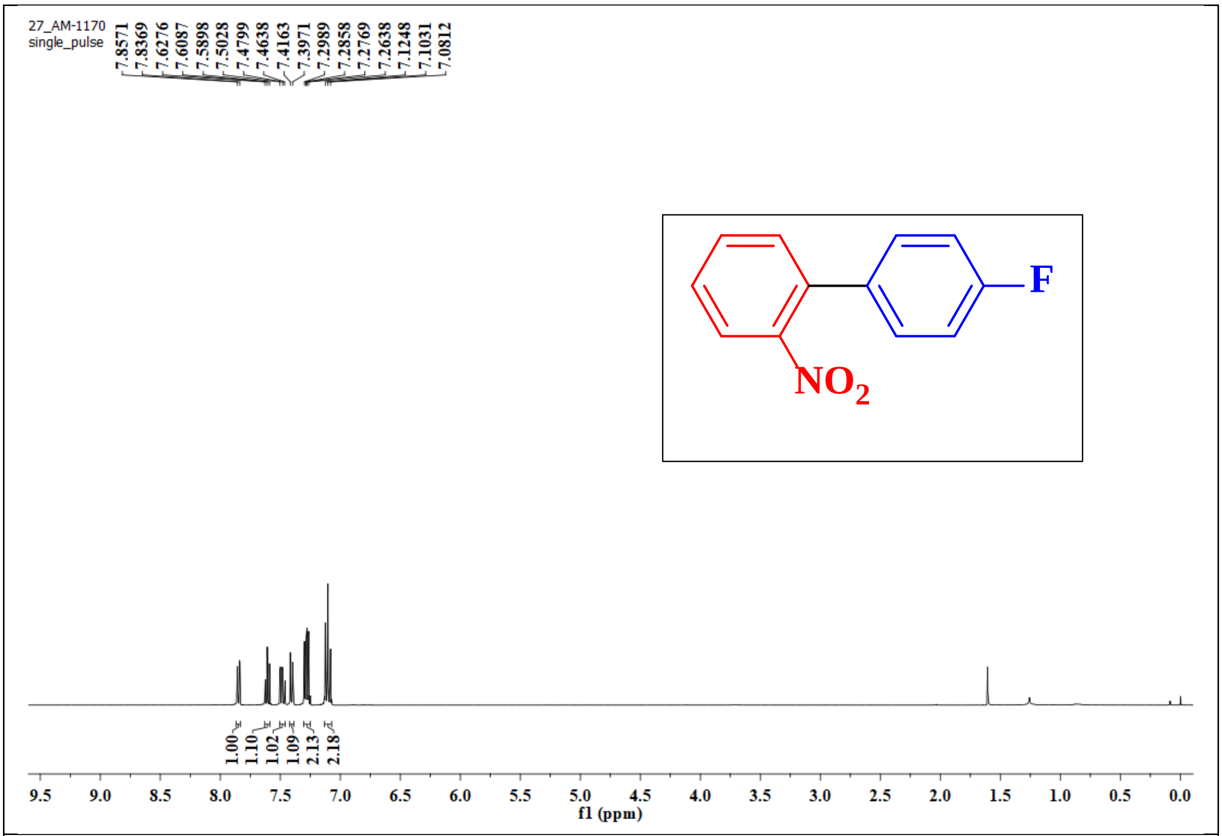


Figure S84. ^{1}H-NMR spectrum of 3cf in $CDCl_3$.

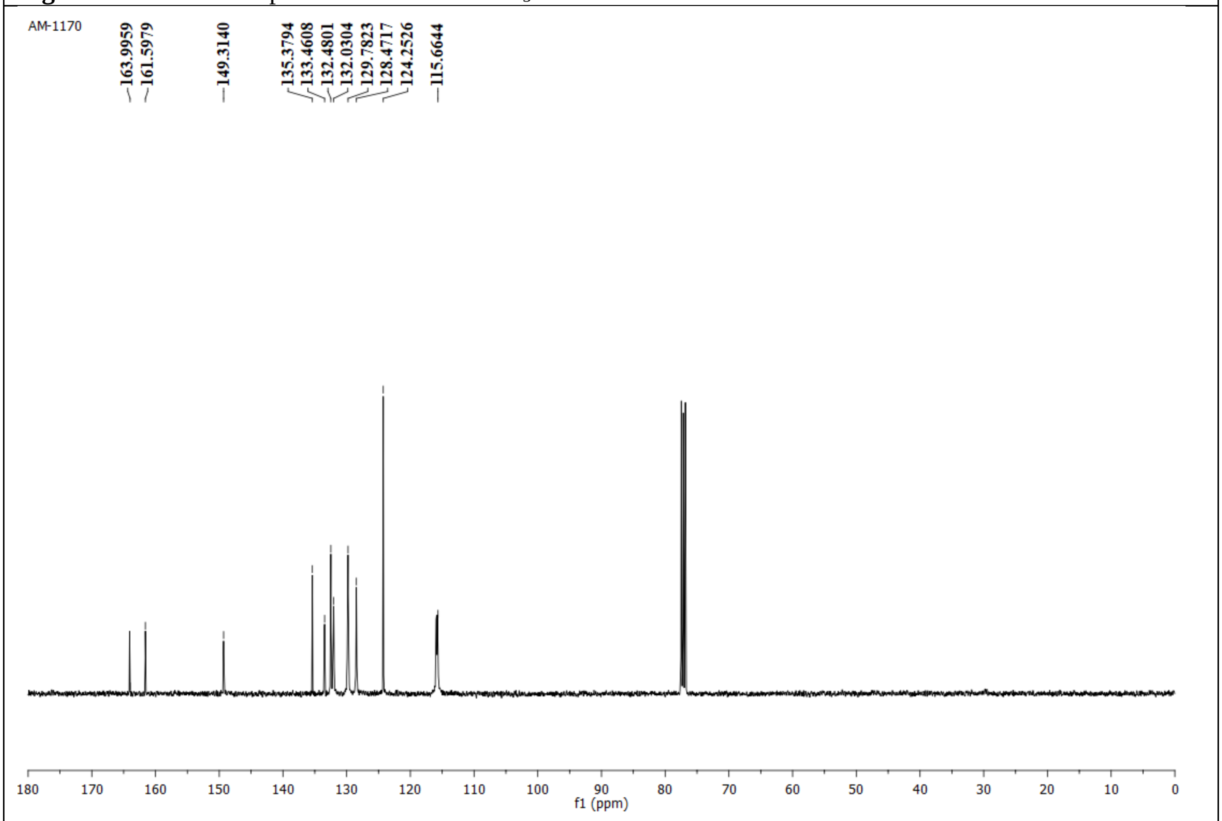


Figure S85. ^{13}C-NMR spectrum of 3cfin $CDCl_3$.

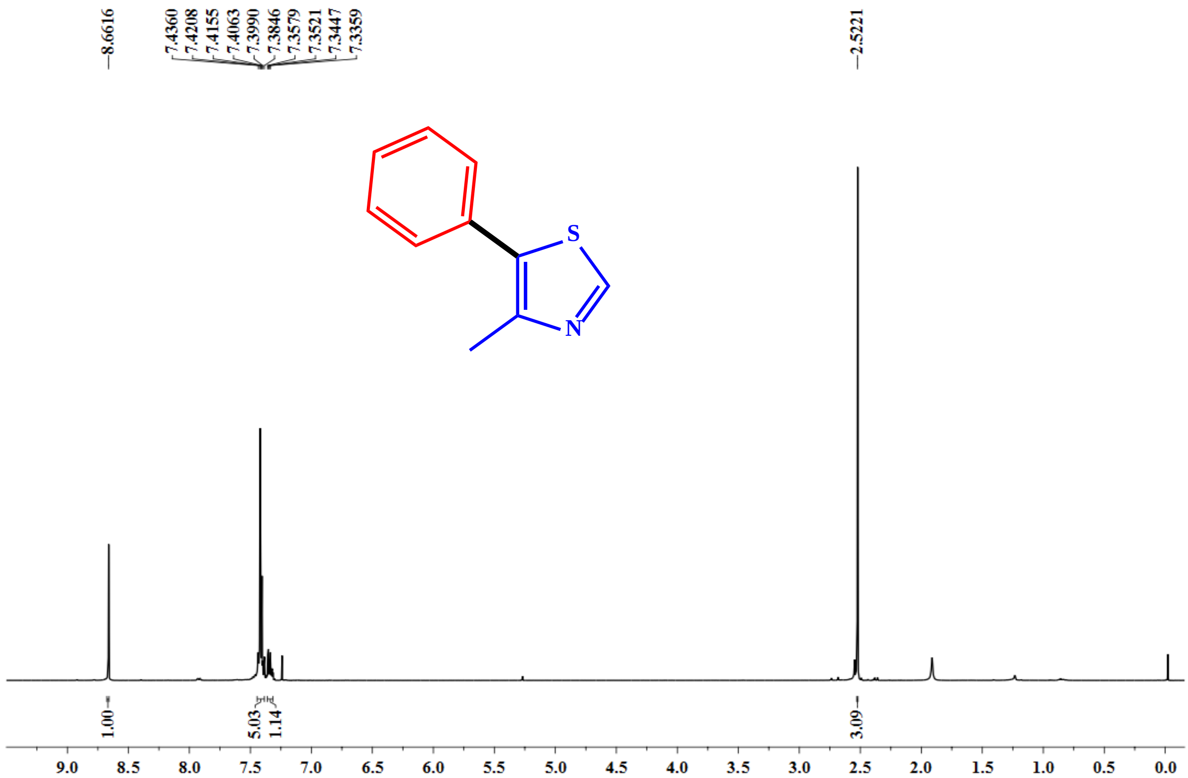


Figure S86. ^{1}H-NMR spectrum of 6a in $CDCl_3$.

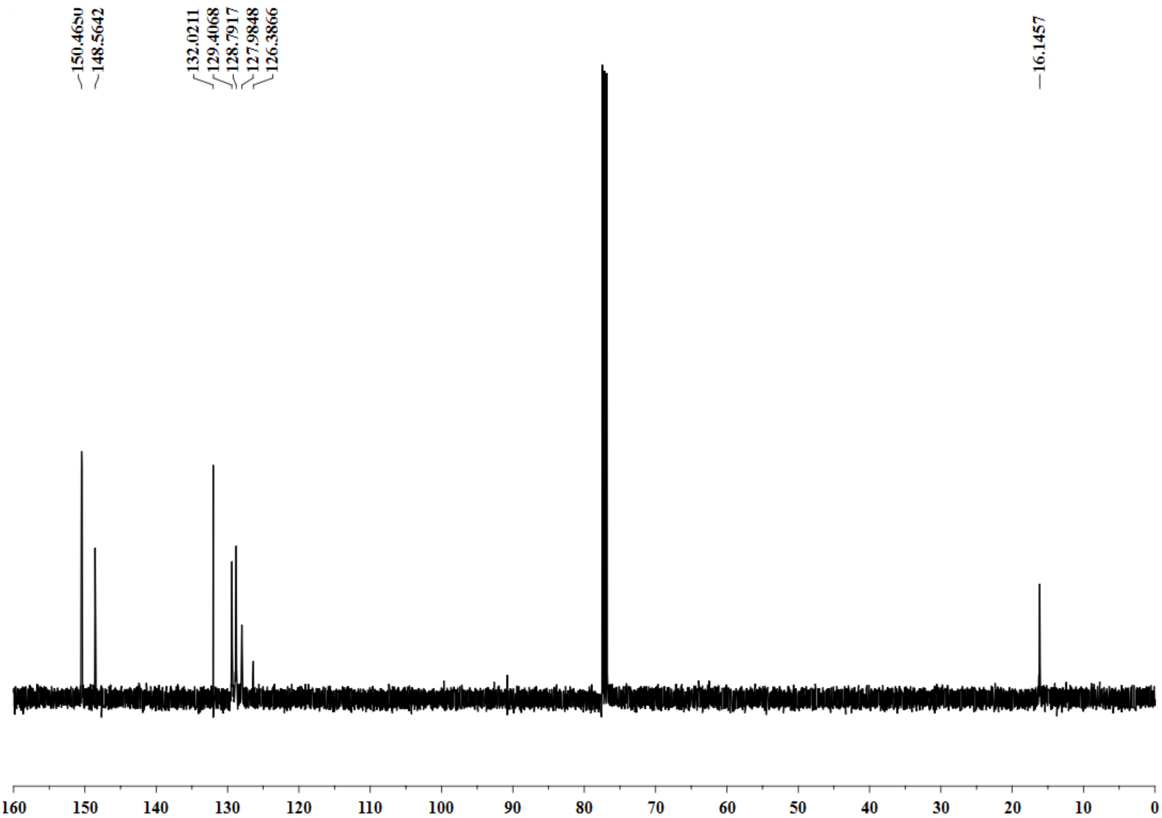


Figure S87. ^{13}C-NMR spectrum of 6a in $CDCl_3$.

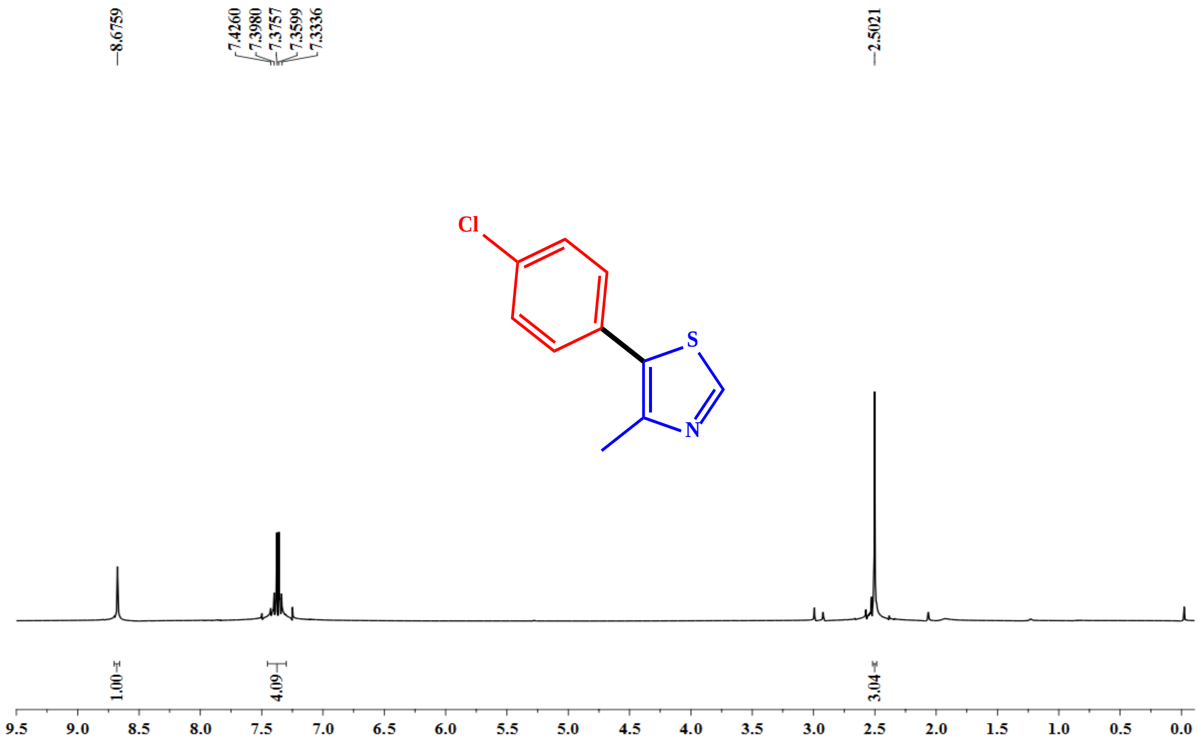


Figure S88. ^{1}H-NMR spectrum of 6b in $CDCl_3$.

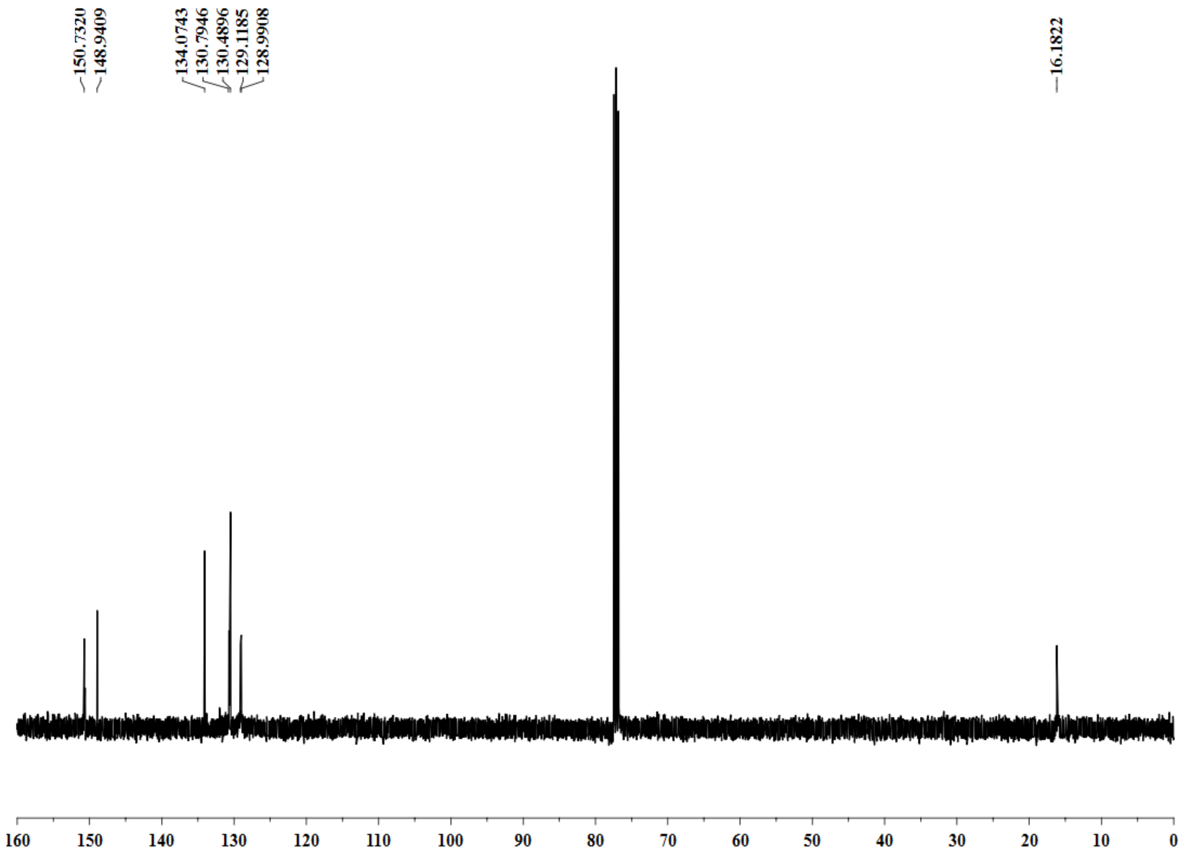


Figure S89. ^{14}C-NMR spectrum of 6b in $CDCl_3$.

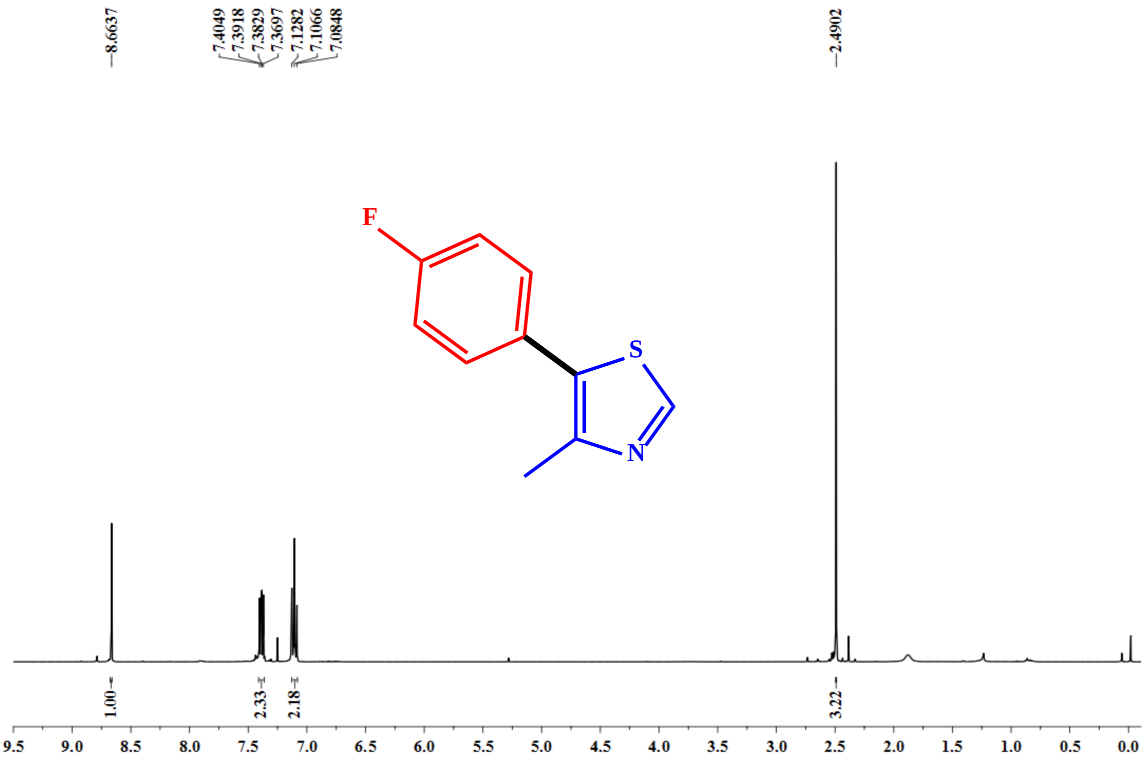


Figure S90. ^{1}H-NMR spectrum of 6c in $CDCl_3$.

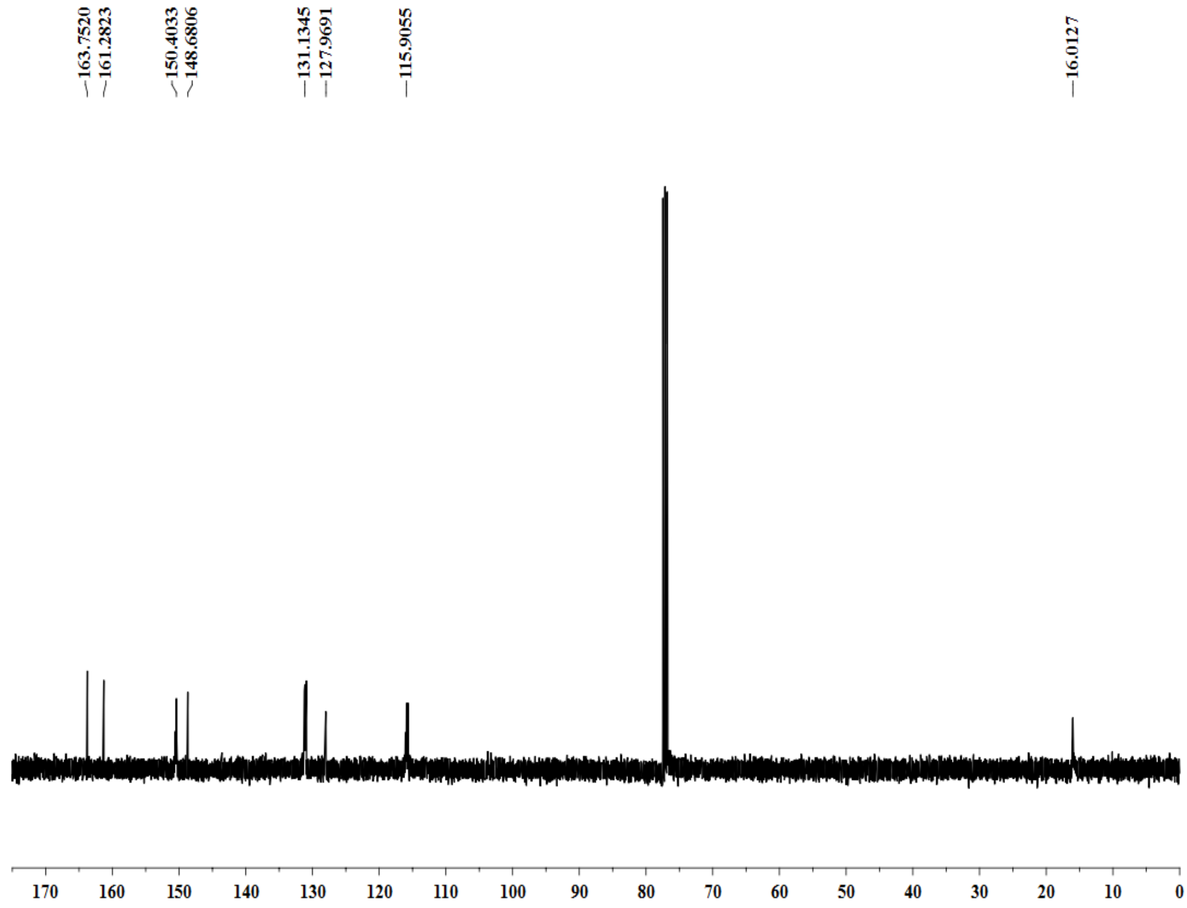


Figure S91. ^{13}C-NMR spectrum of 6c in $CDCl_3$.

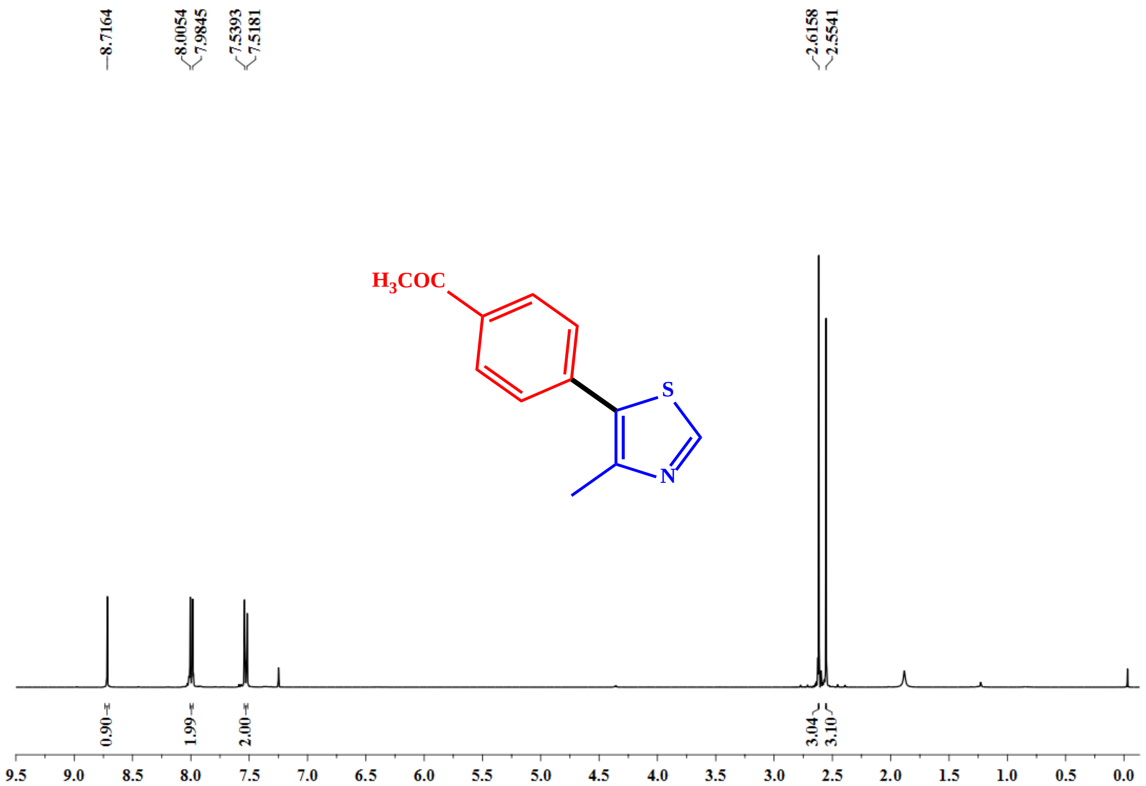


Figure S92. ^{1}H-NMR spectrum of 6d in $CDCl_3$.

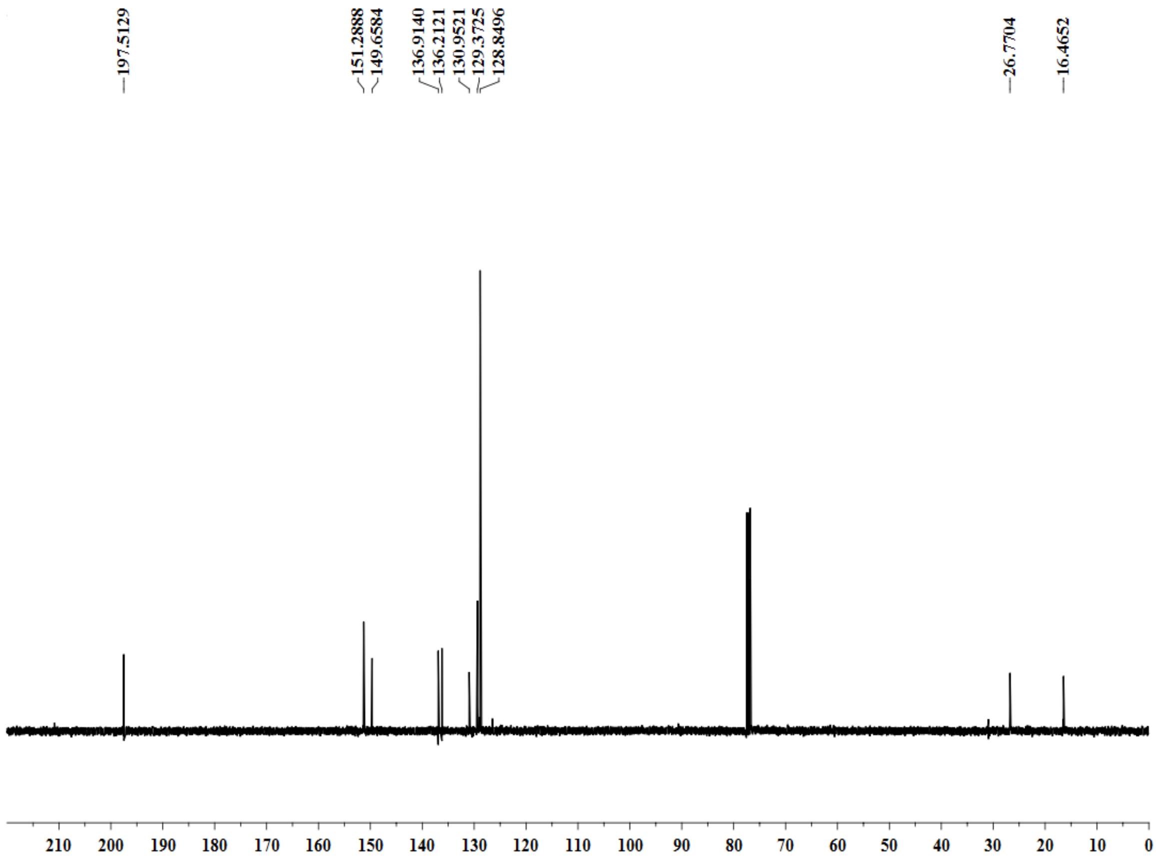


Figure S93. ^{13}C-NMR spectrum of 6d in $CDCl_3$.

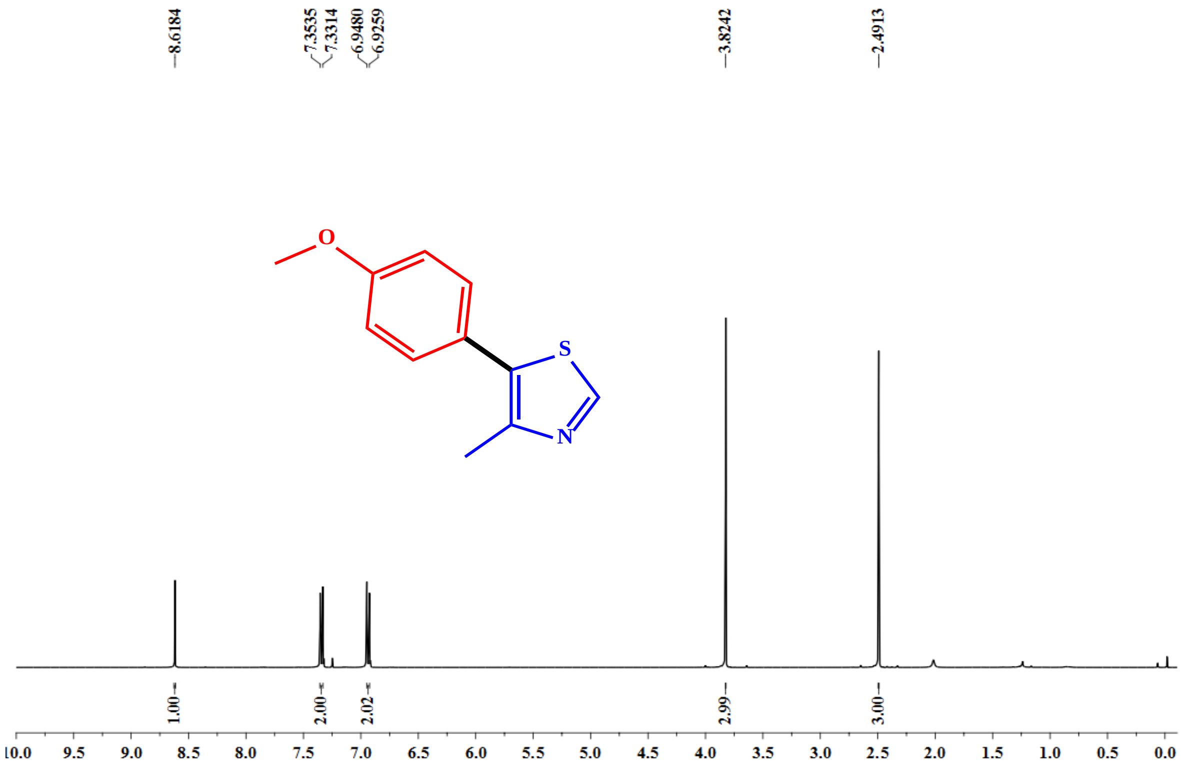


Figure S94. ^{1}H-NMR spectrum of 6e in $CDCl_3$.

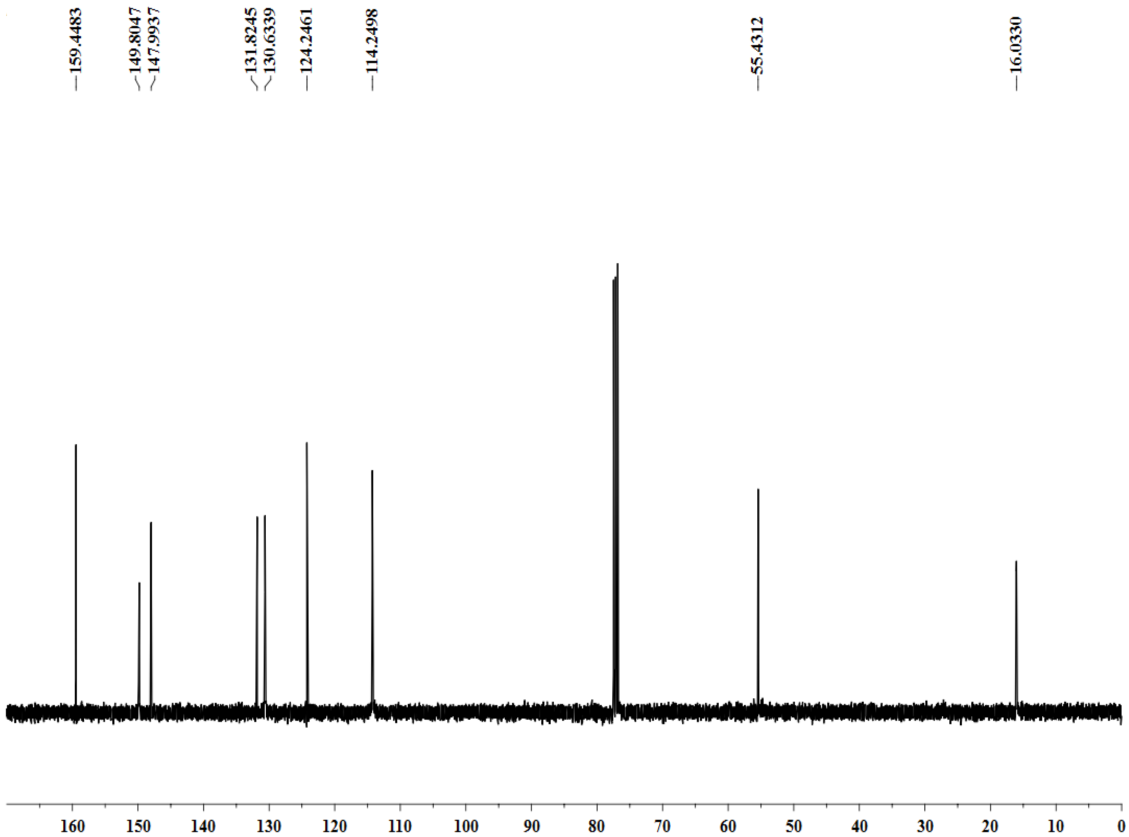


Figure S95. ^{13}C-NMR spectrum of 6e in $CDCl_3$.

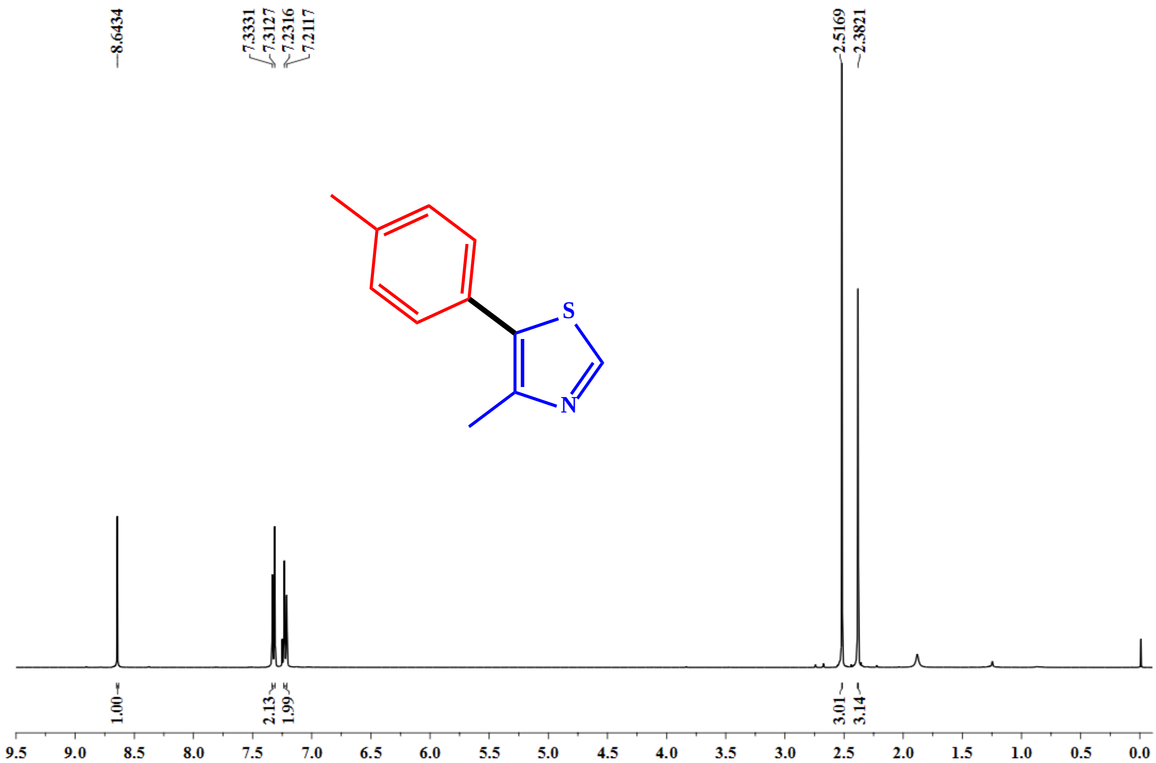


Figure S96. ^{1}H-NMR spectrum of 6f in $CDCl_3$.

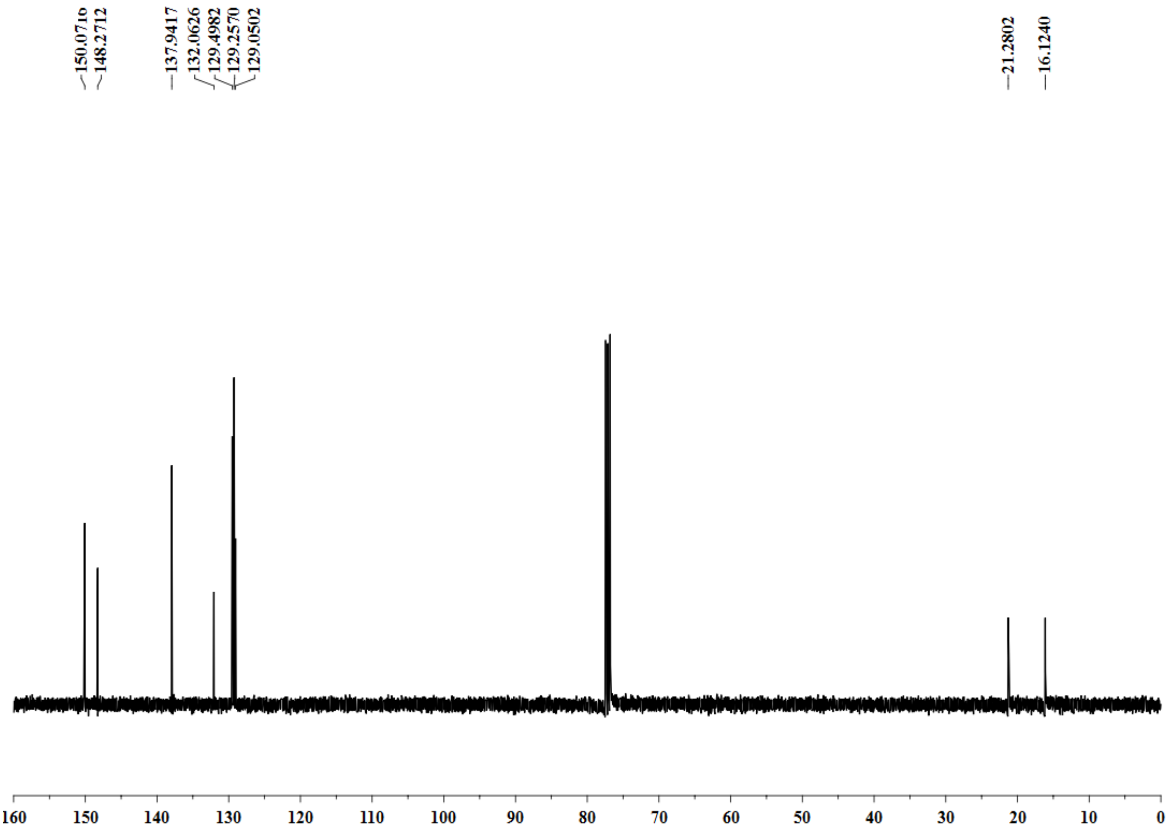


Figure S97. ^{13}C-NMR spectrum of 6f in $CDCl_3$.

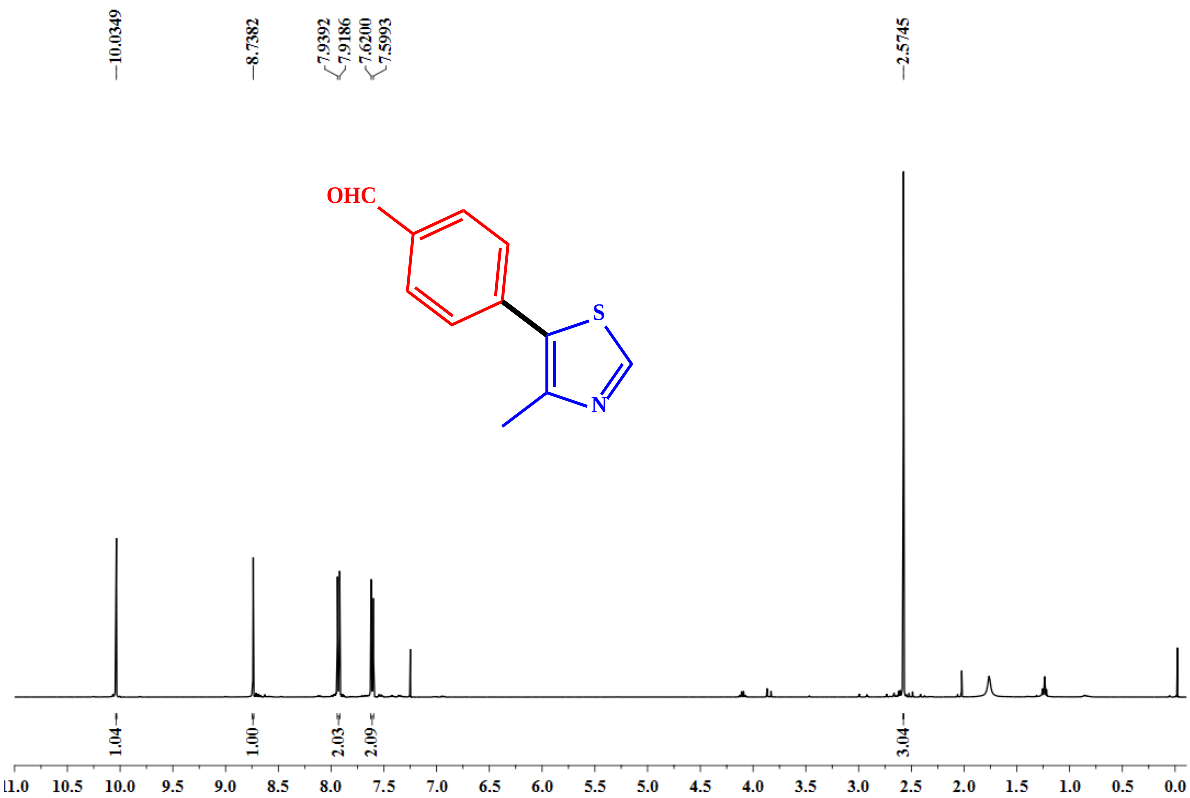


Figure S98. ^{1}H-NMR spectrum of 6g in $CDCl_3$.

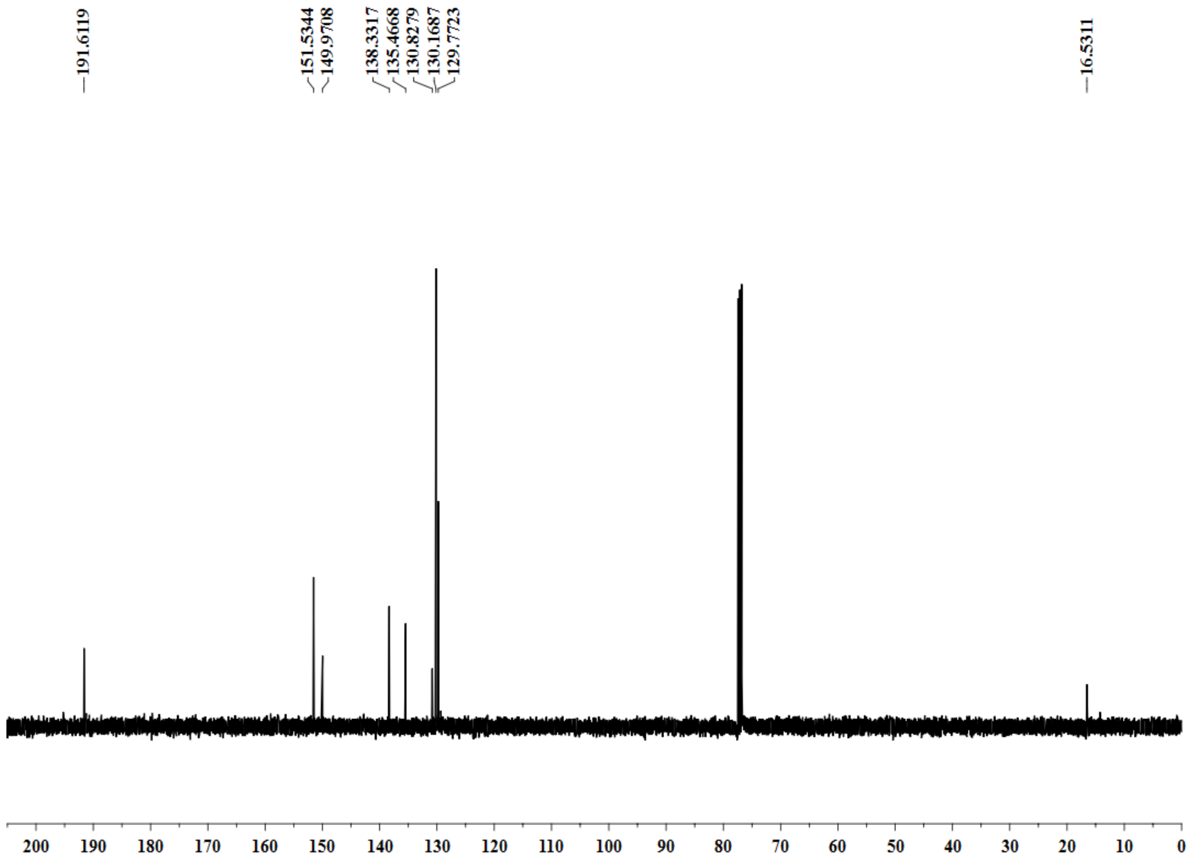


Figure 99. ^{13}C-NMR spectrum of 6g in $CDCl_3$.

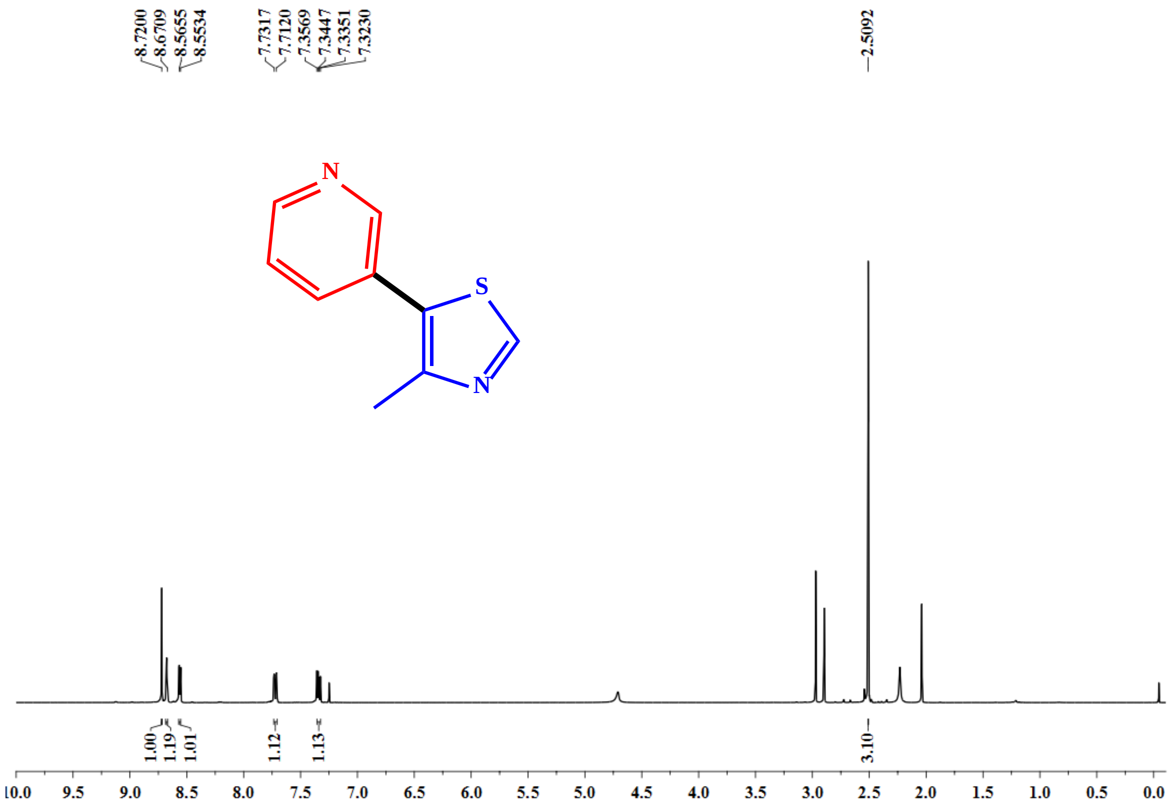


Figure S100. ^{1}H-NMR spectrum of 6h in $CDCl_3$.

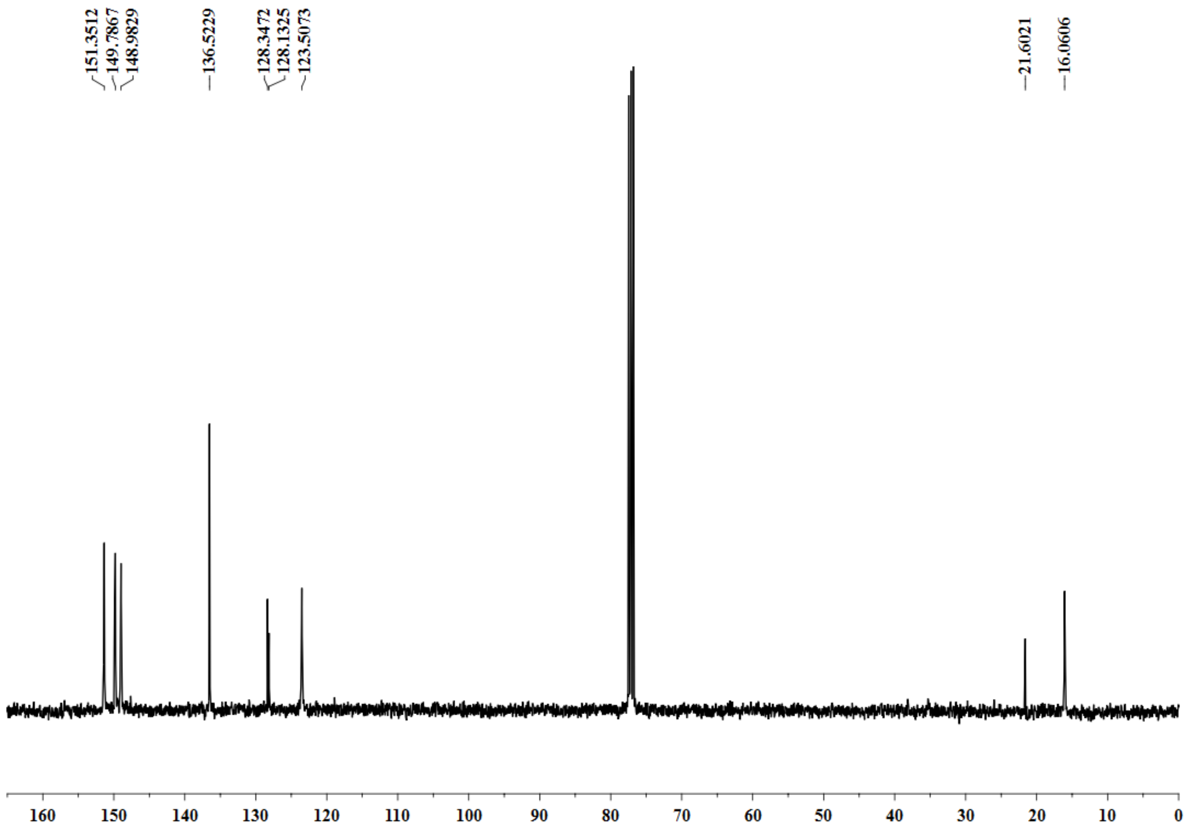


Figure S101. ^{13}C-NMR spectrum of 6h in $CDCl_3$.

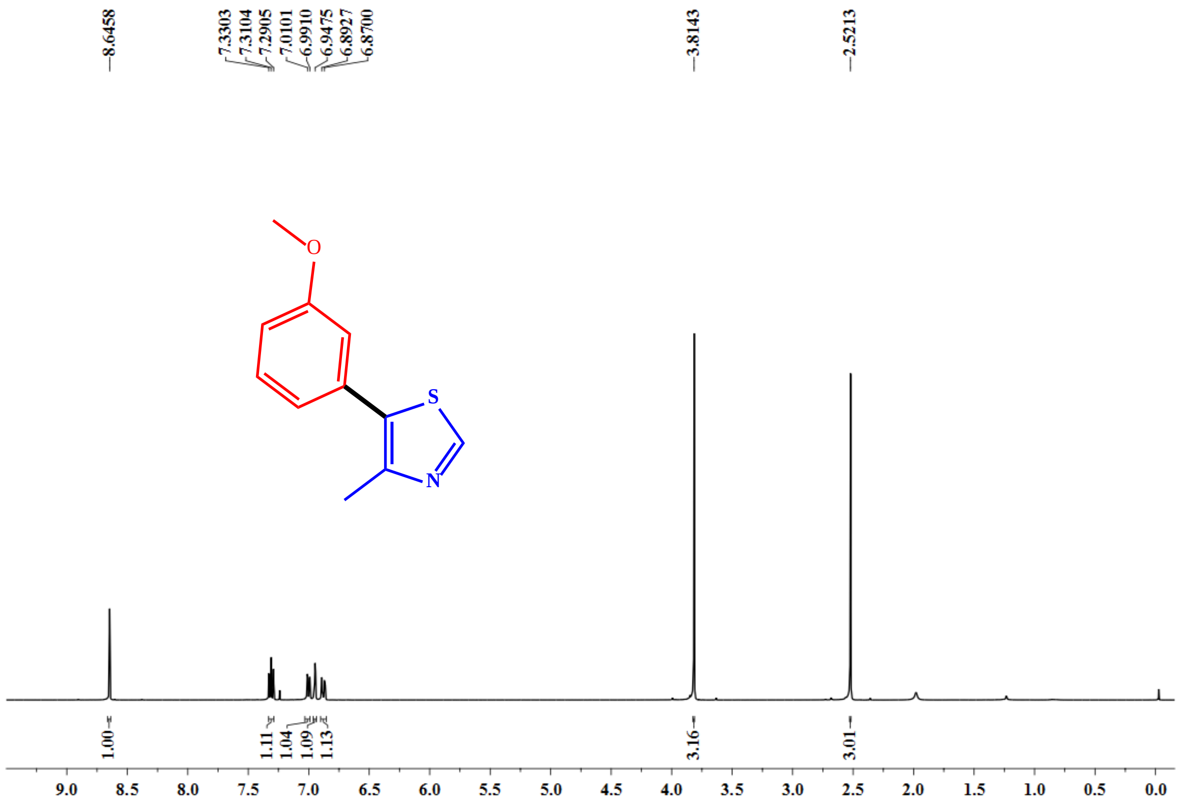


Figure S102. ^{1}H-NMR spectrum of 6i in $CDCl_3$.

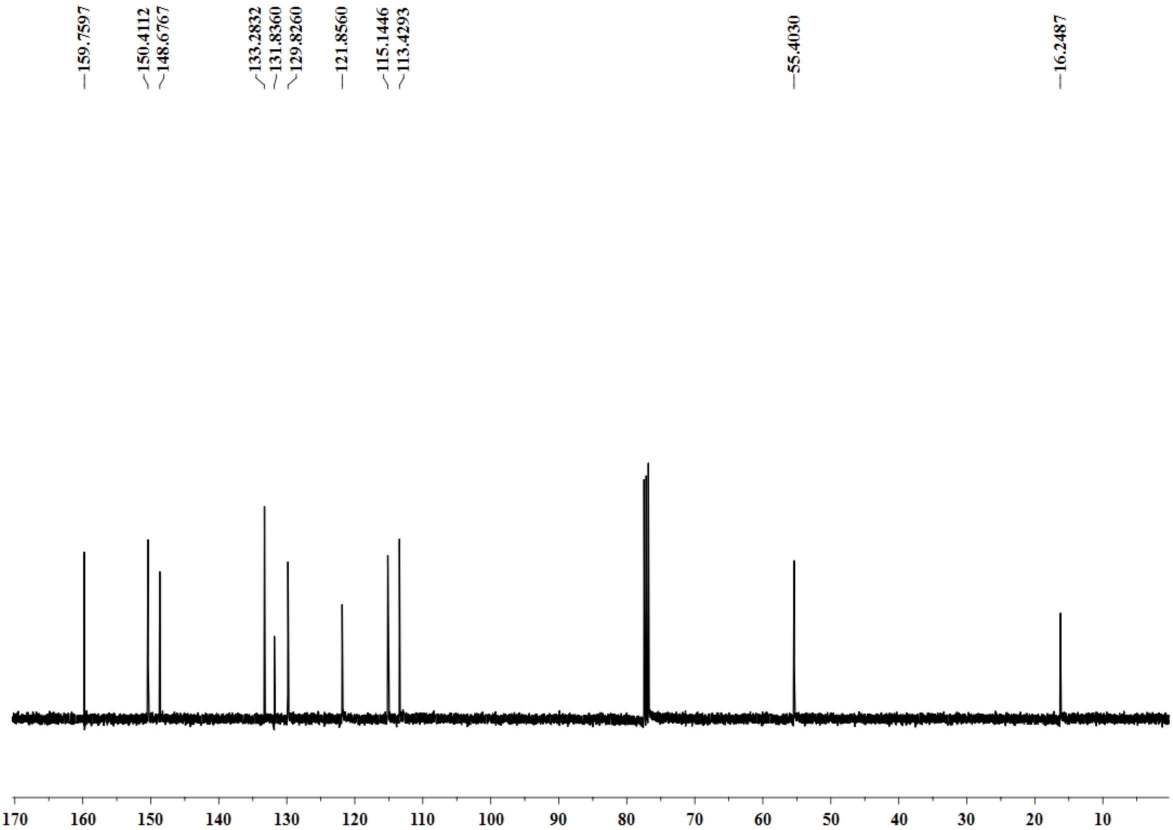


Figure S103. ^{13}C-NMR spectrum of 6i in $CDCl_3$.

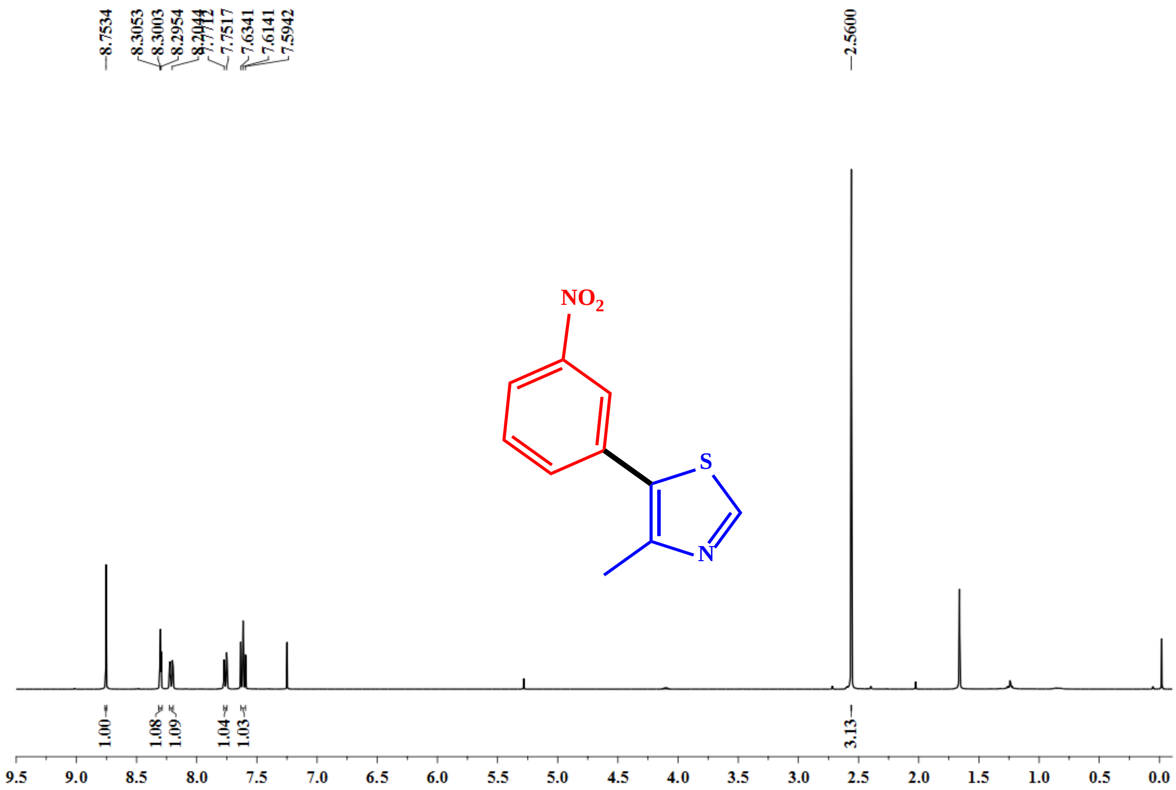


Figure S104. ^{1}H-NMR spectrum of 6j in $CDCl_3$.

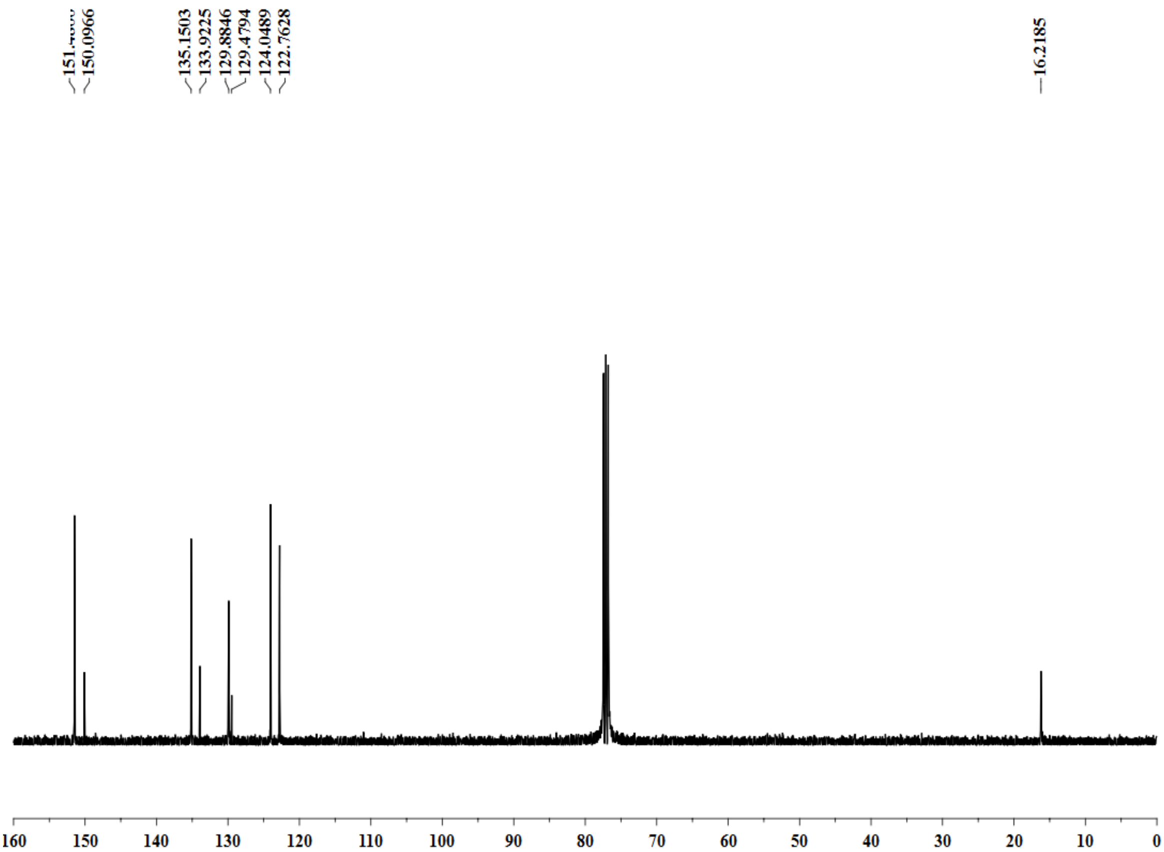


Figure S105. ^{13}C-NMR spectrum of 6j in $CDCl_3$.

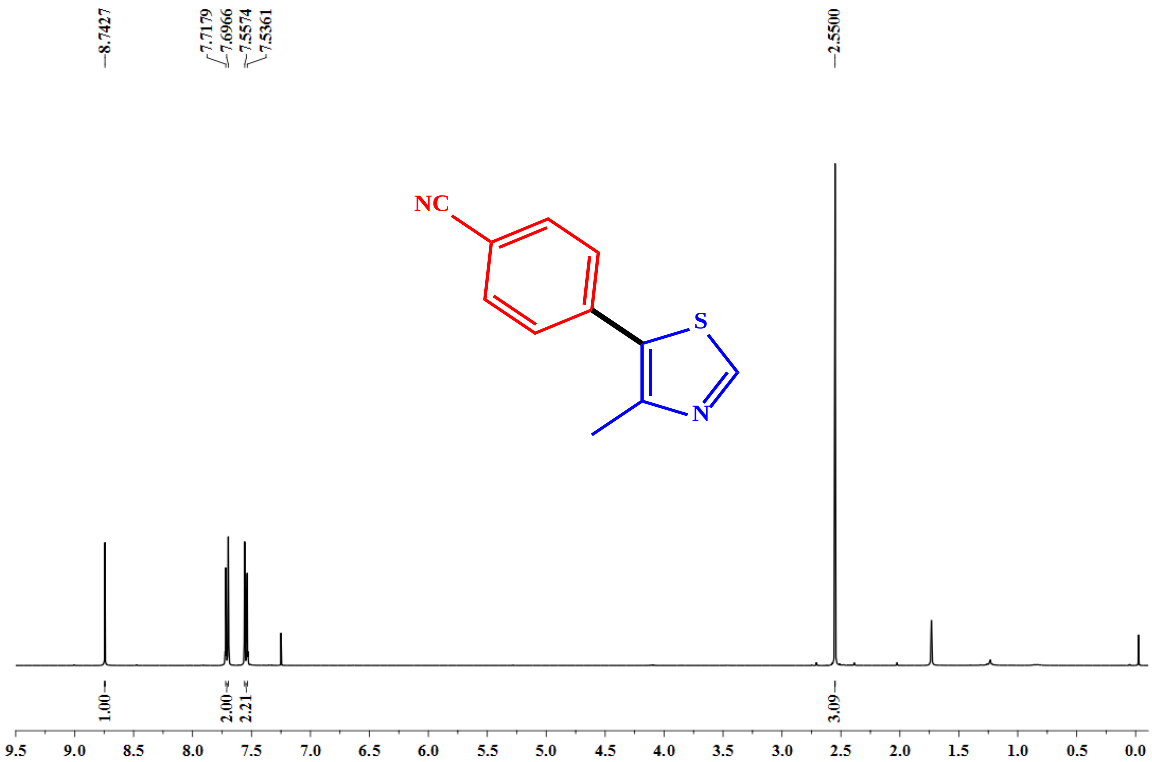


Figure S106. ^{1}H-NMR spectrum of 6k in $CDCl_3$.

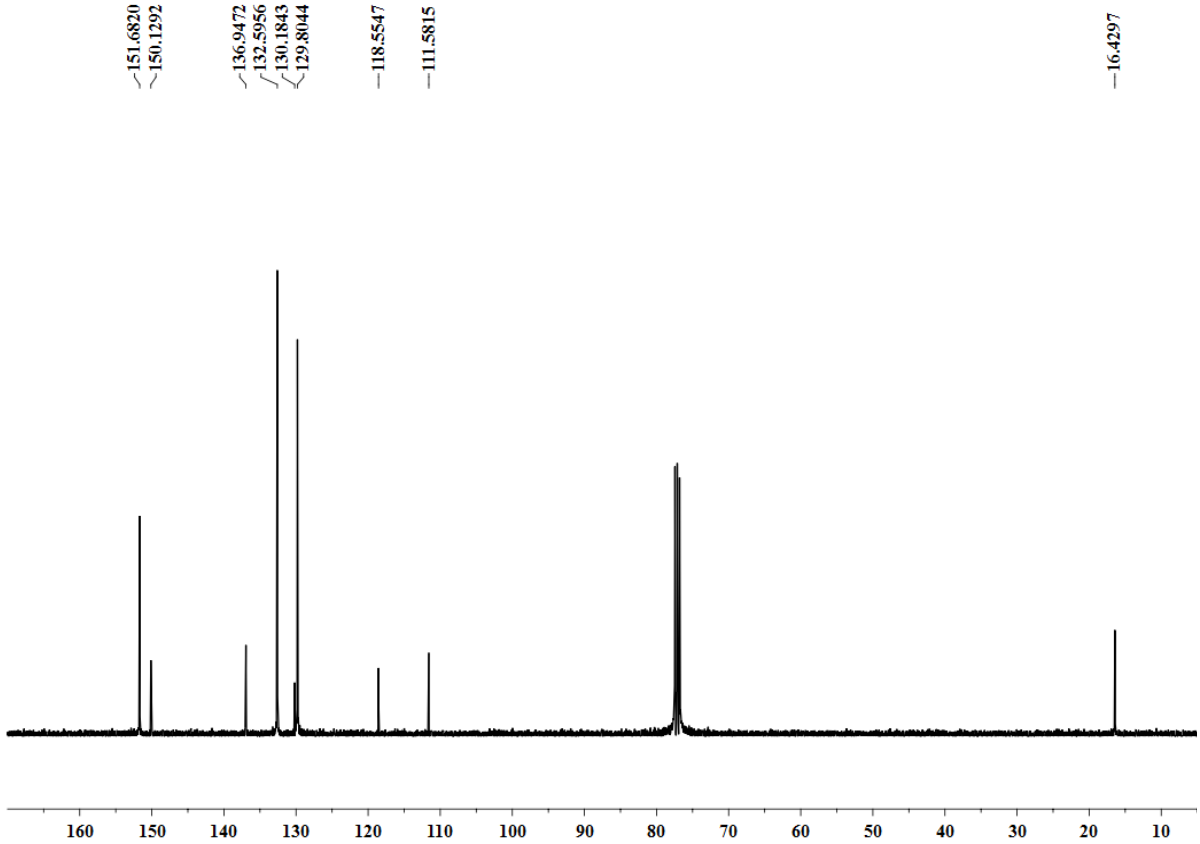


Figure S107. ^{13}C-NMR spectrum of 6k in $CDCl_3$.

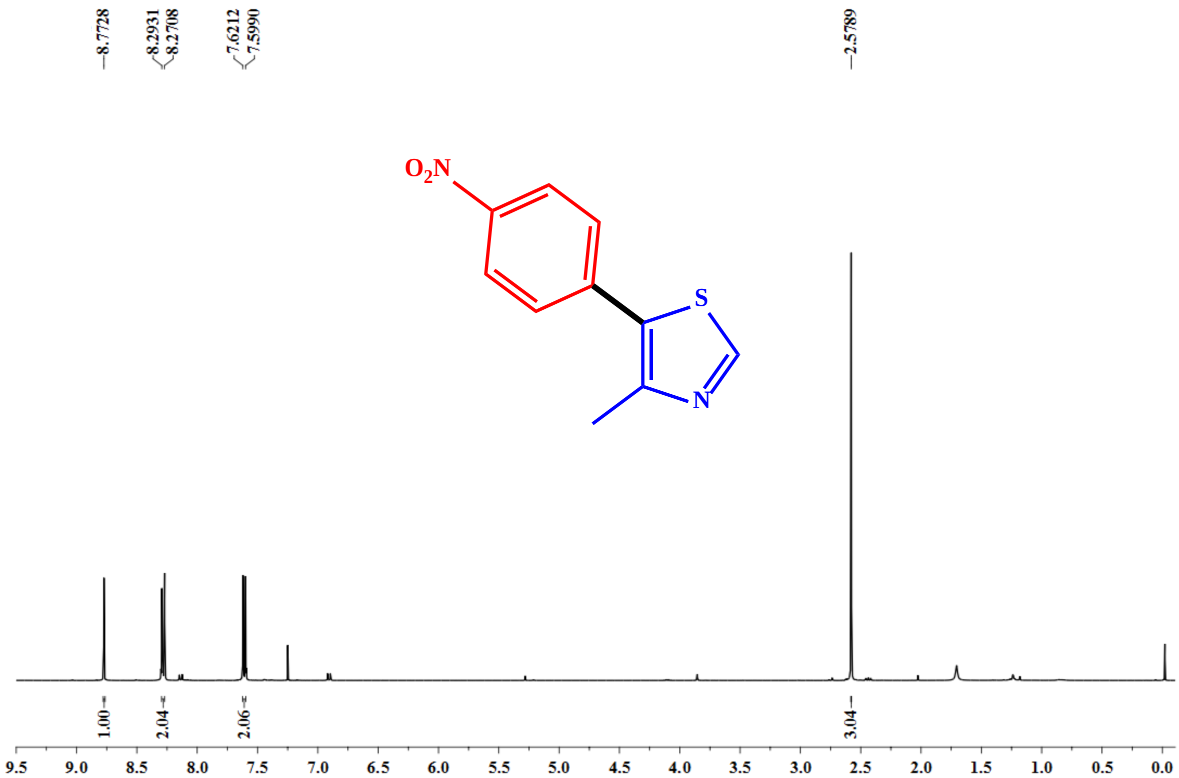


Figure S108. ^{1}H-NMR spectrum of 6l in $CDCl_3$.

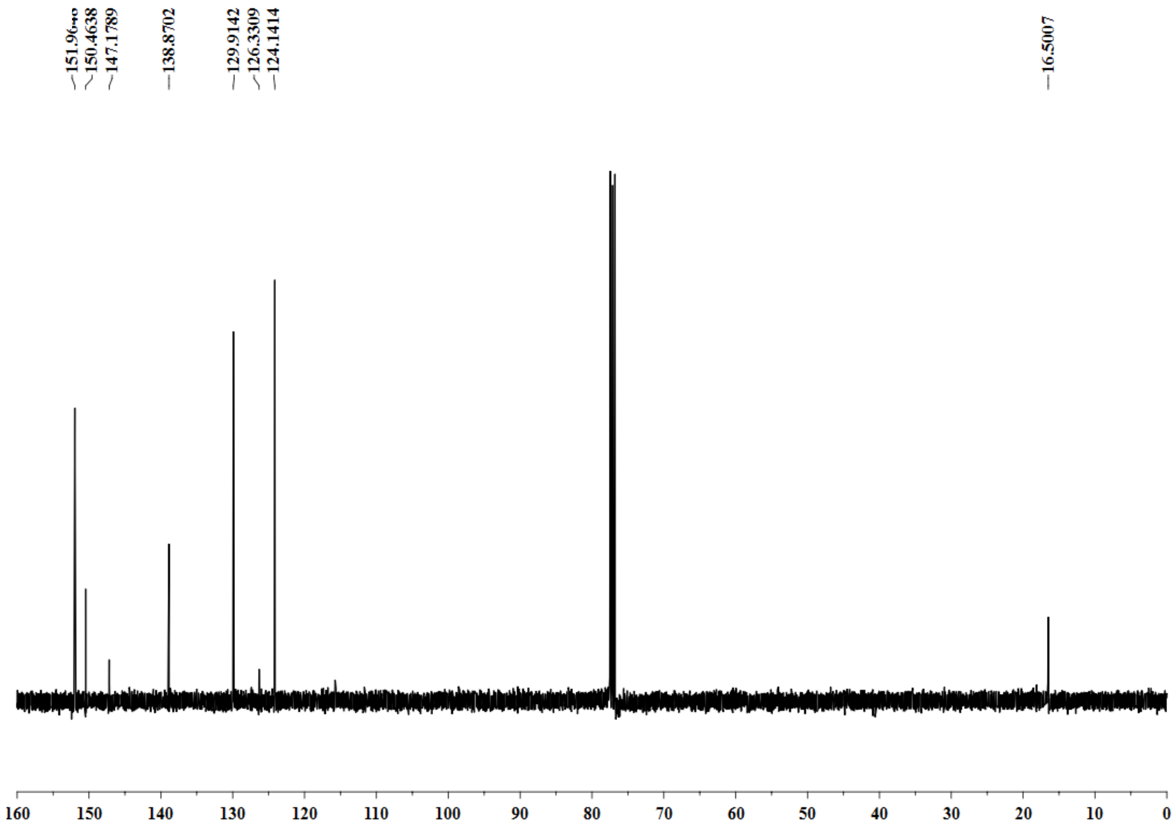


Figure S109. ^{13}C-NMR spectrum of 6l in $CDCl_3$.

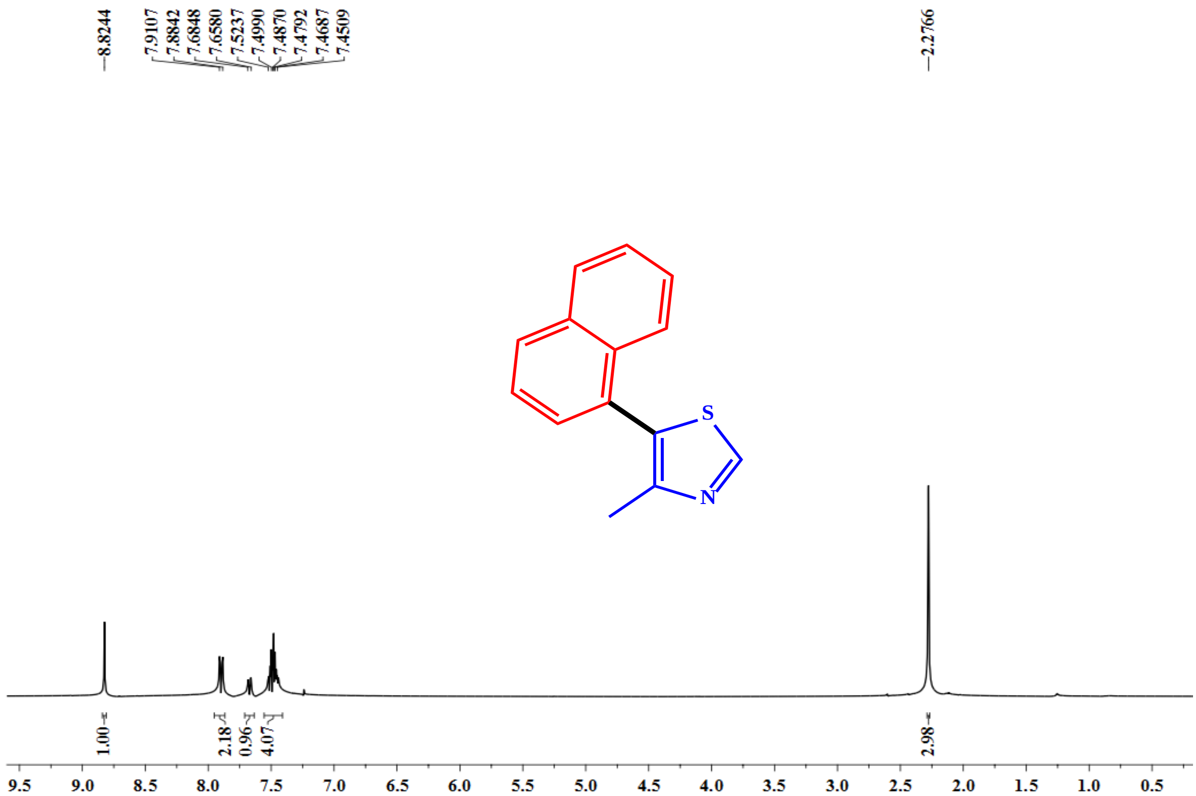


Figure S110. ^{1}H-NMR spectrum of 6m in $CDCl_3$.

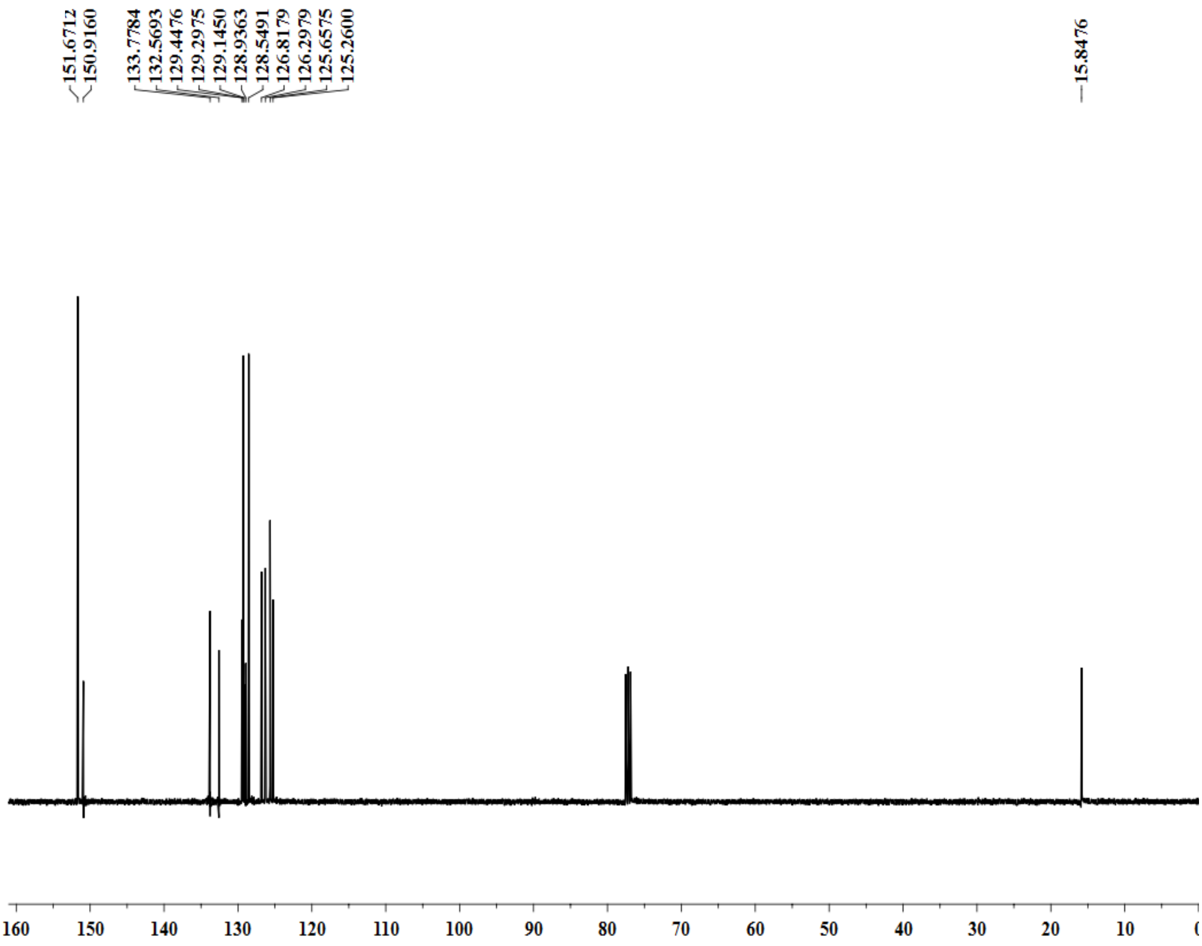


Figure S111. ^{13}C-NMR spectrum of 6m in $CDCl_3$.

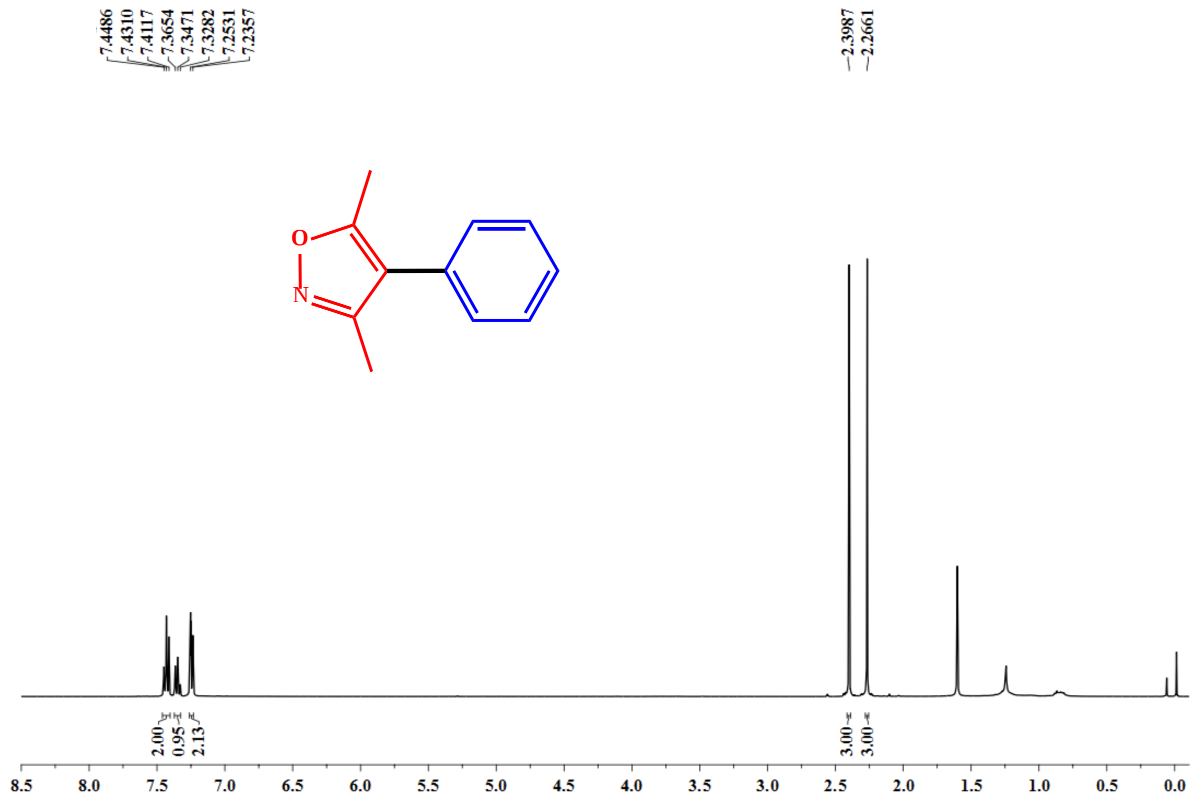


Figure S112. ^{1}H-NMR spectrum of 8a in $CDCl_3$.

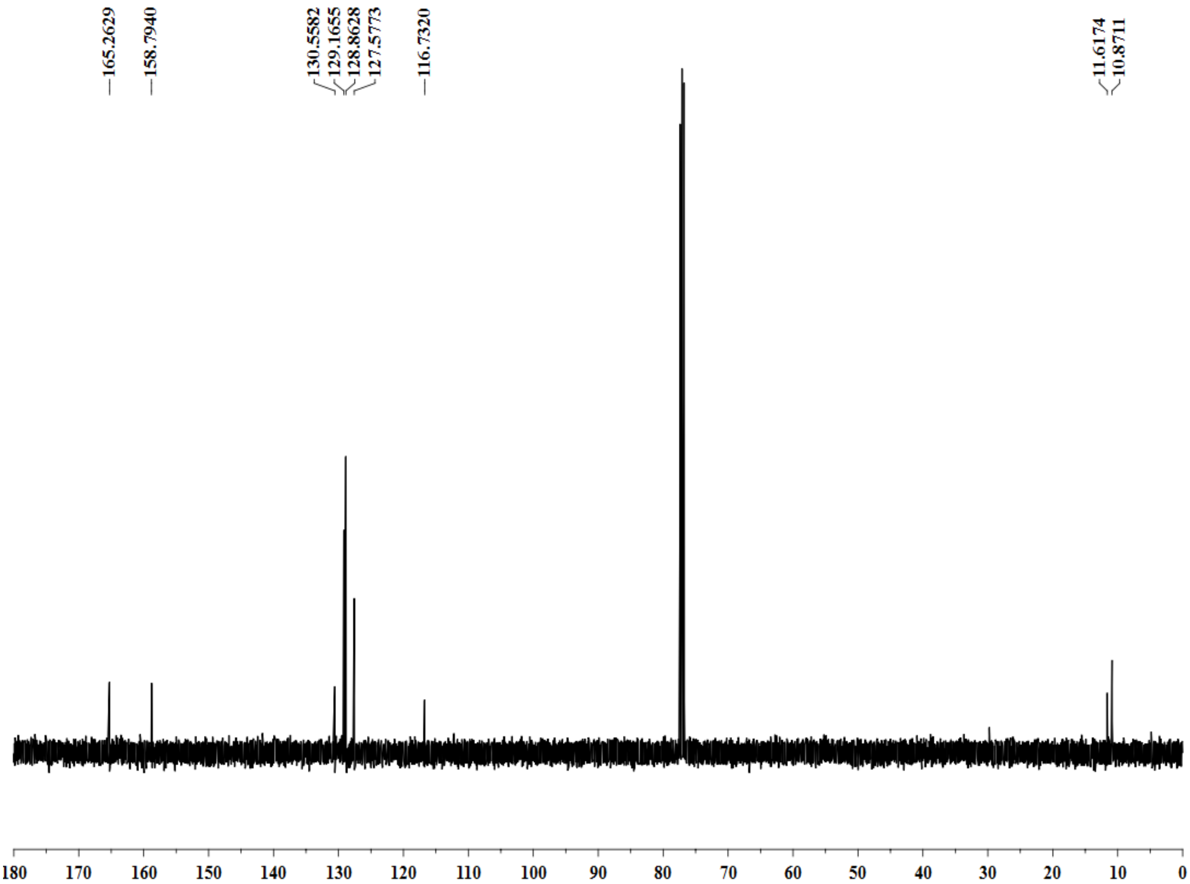


Figure S113. ^{13}C-NMR spectrum of 8a in $CDCl_3$.

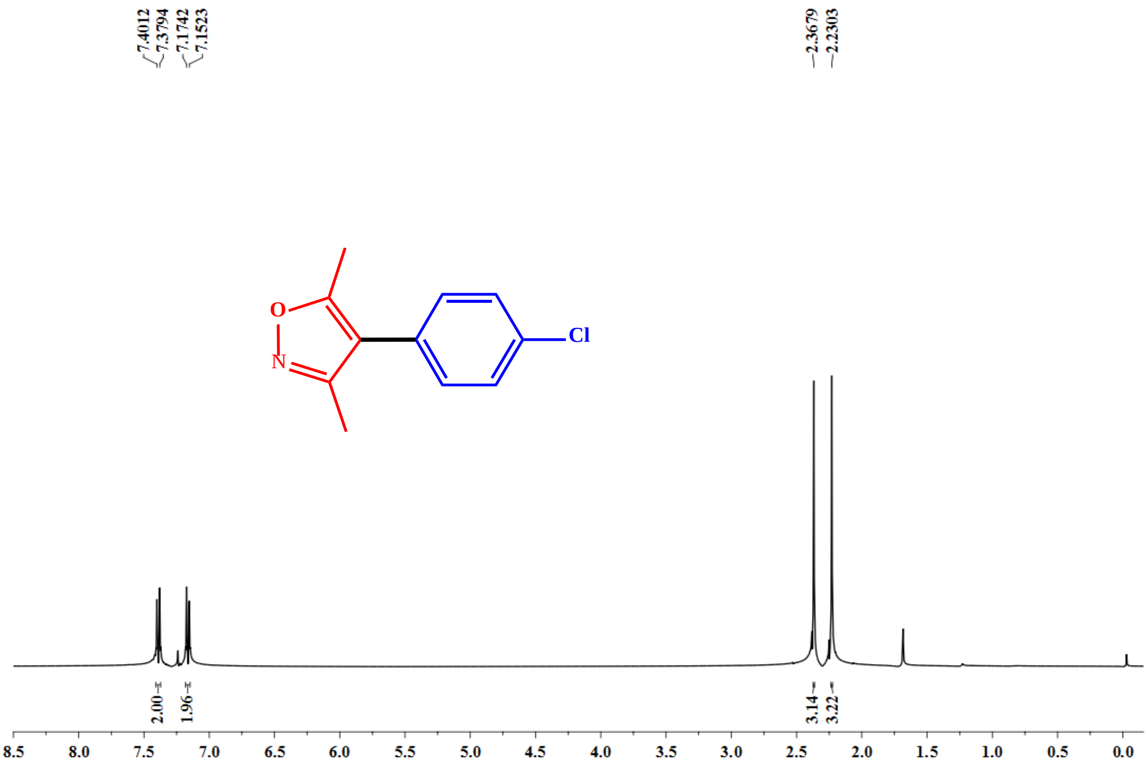


Figure S114. ^{1}H-NMR spectrum of 8b in $CDCl_3$.

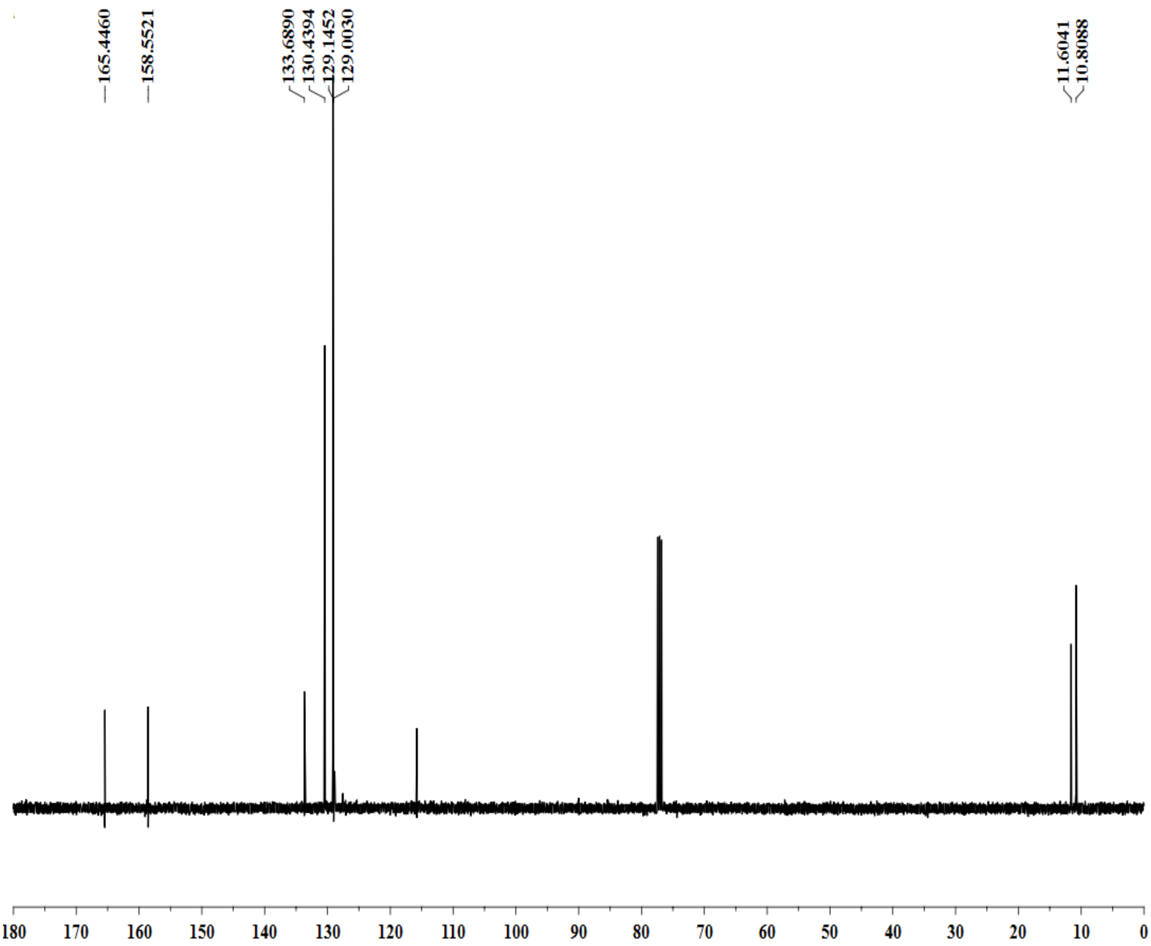


Figure S115. ^{13}C-NMR spectrum of 8b in $CDCl_3$.

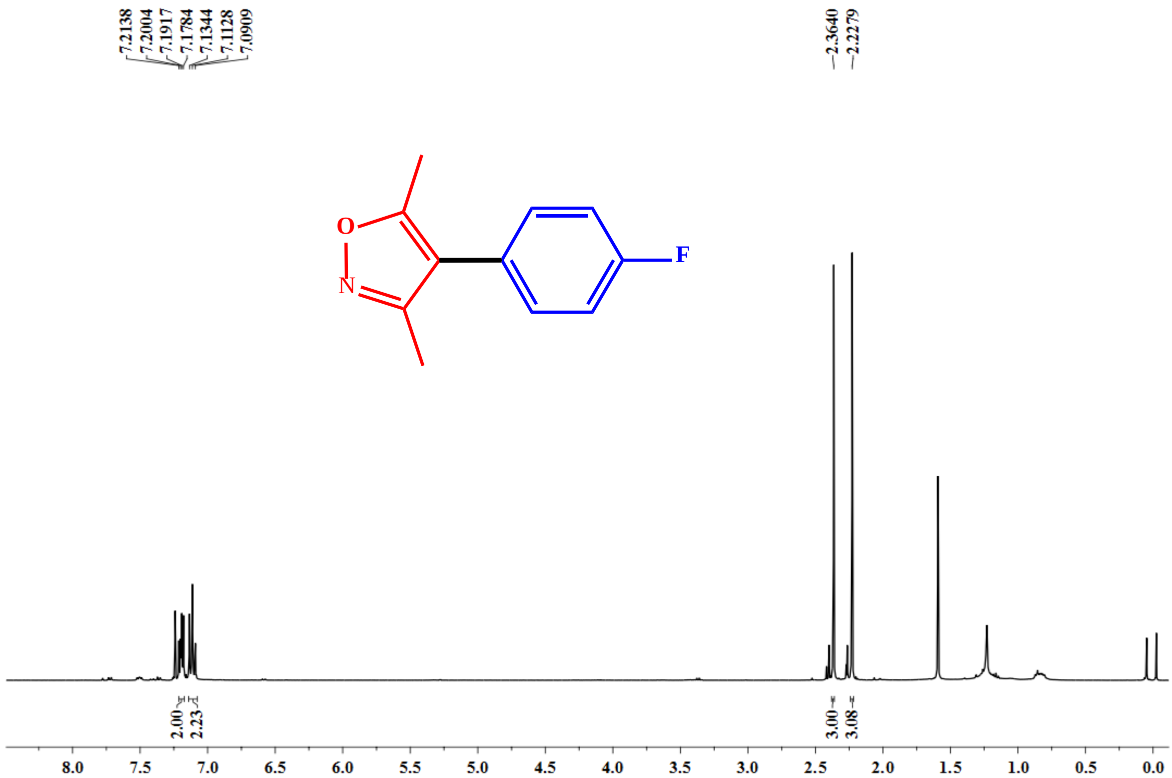


Figure S116. ^{1}H-NMR spectrum of 8c in $CDCl_3$.

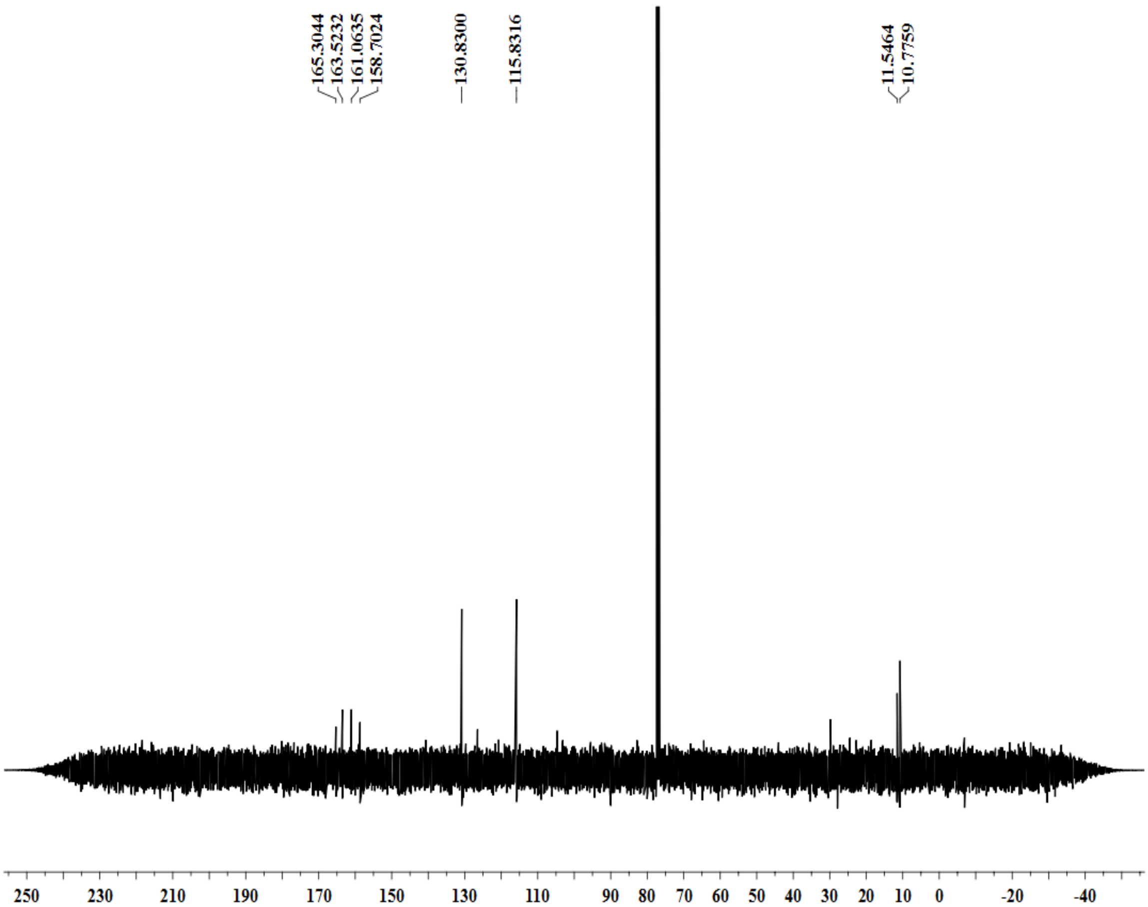


Figure S117. ^{13}C-NMR spectrum of 8c in $CDCl_3$.

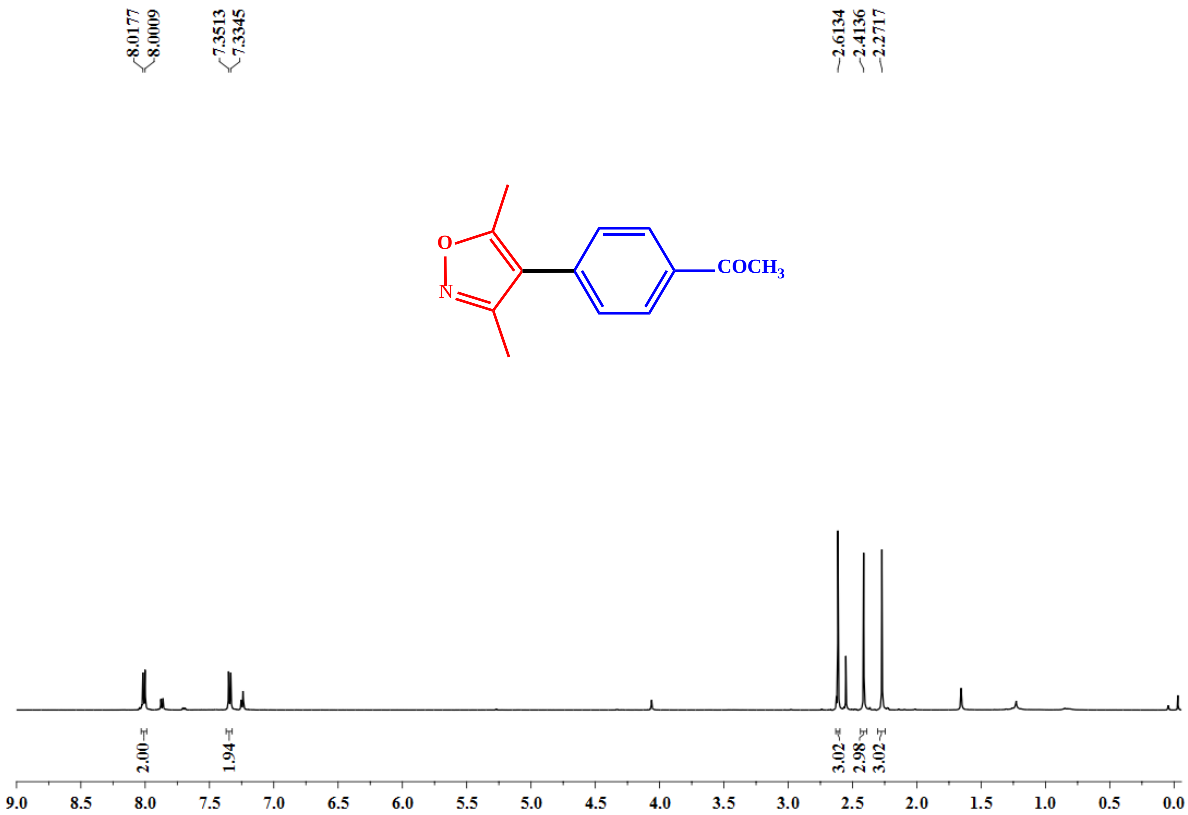


Figure S118. ^{1}H-NMR spectrum of 8d in $CDCl_3$.

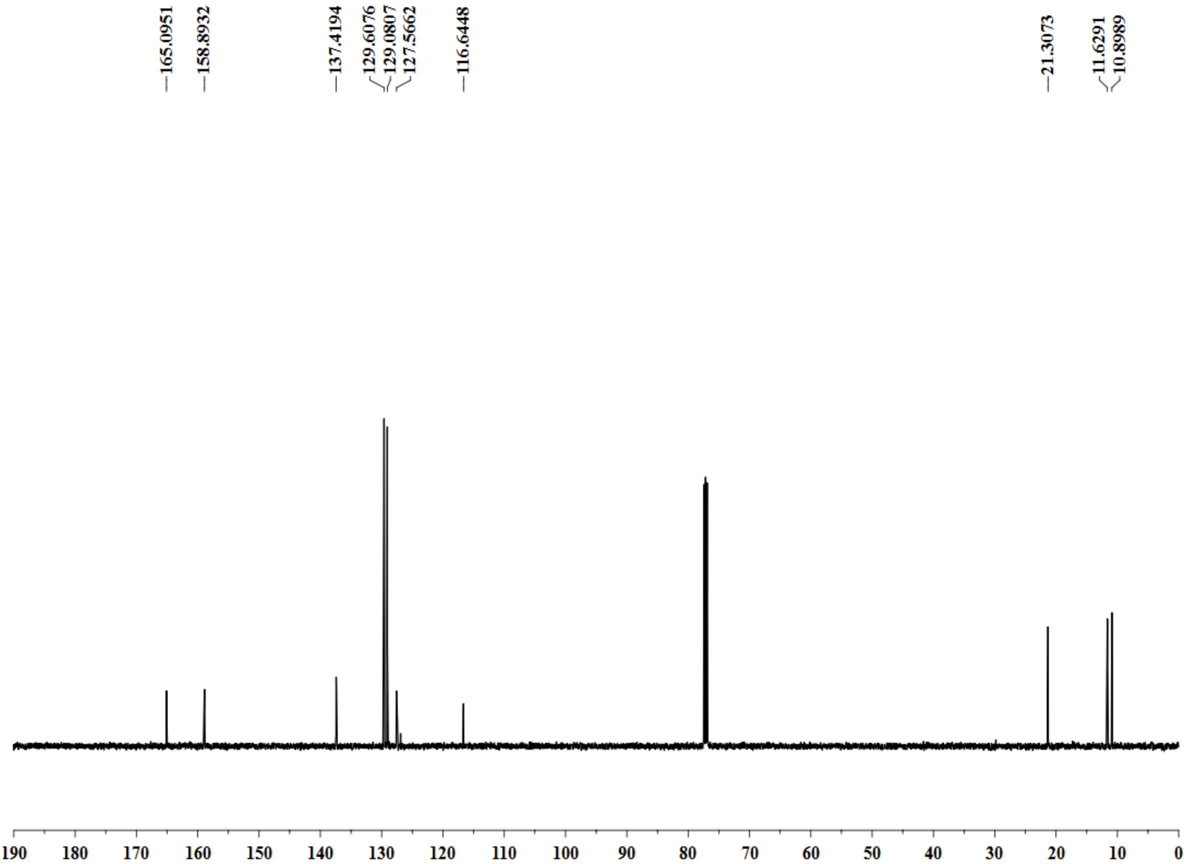


Figure S119. ^{13}C-NMR spectrum of 8d in $CDCl_3$.

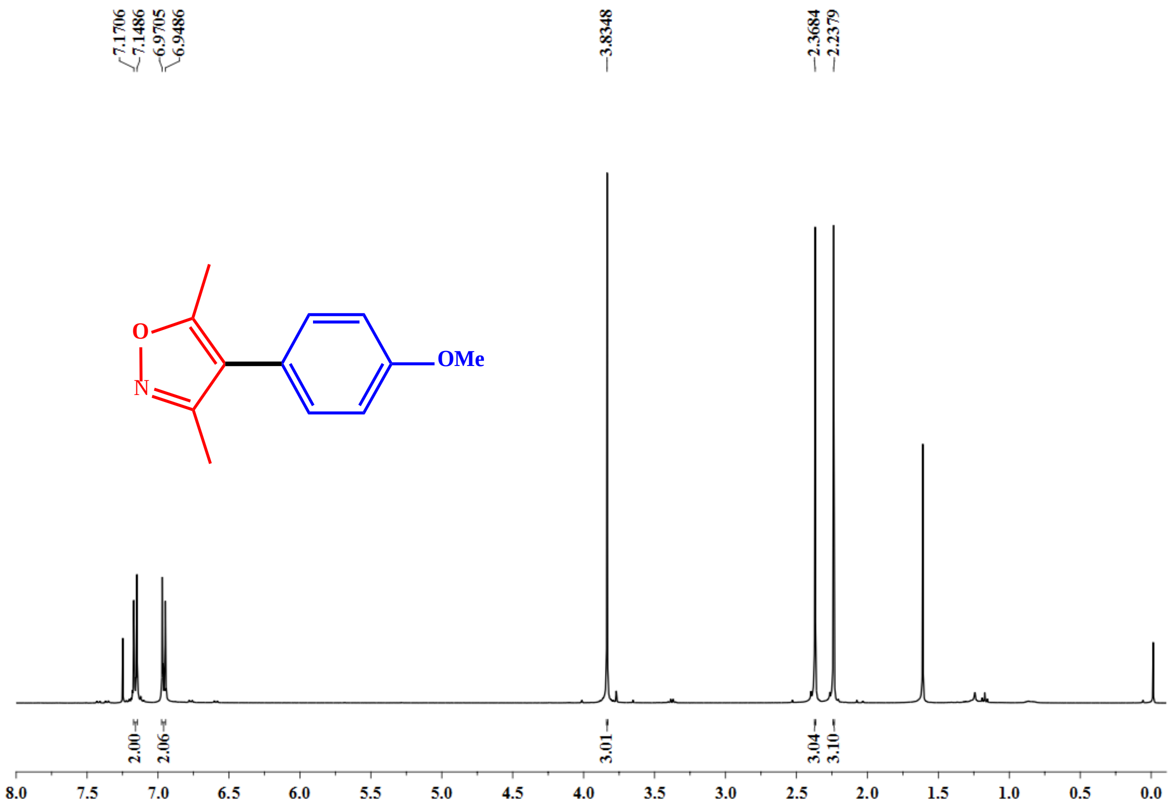


Figure S120. ^{13}C-NMR spectrum of 8e in $CDCl_3$.

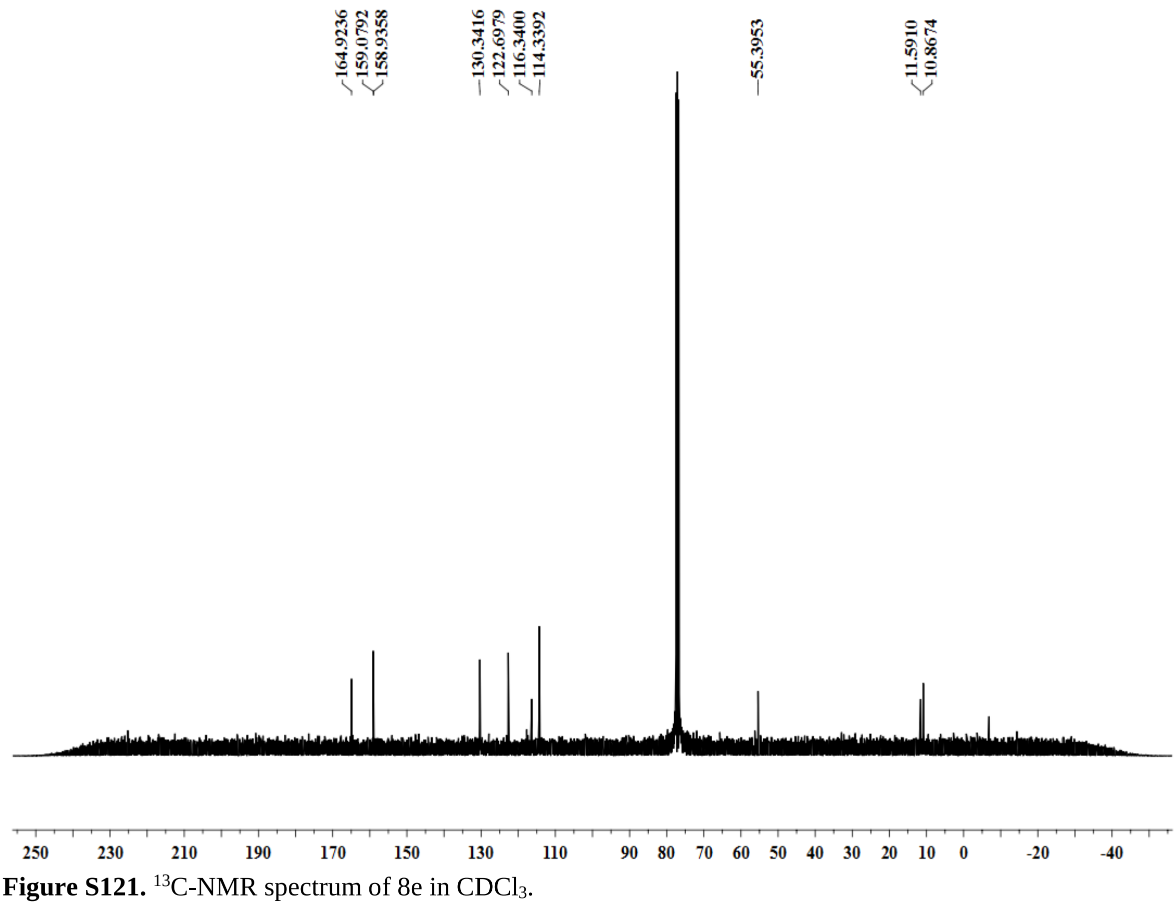


Figure S121. ^{13}C-NMR spectrum of 8e in $CDCl_3$.

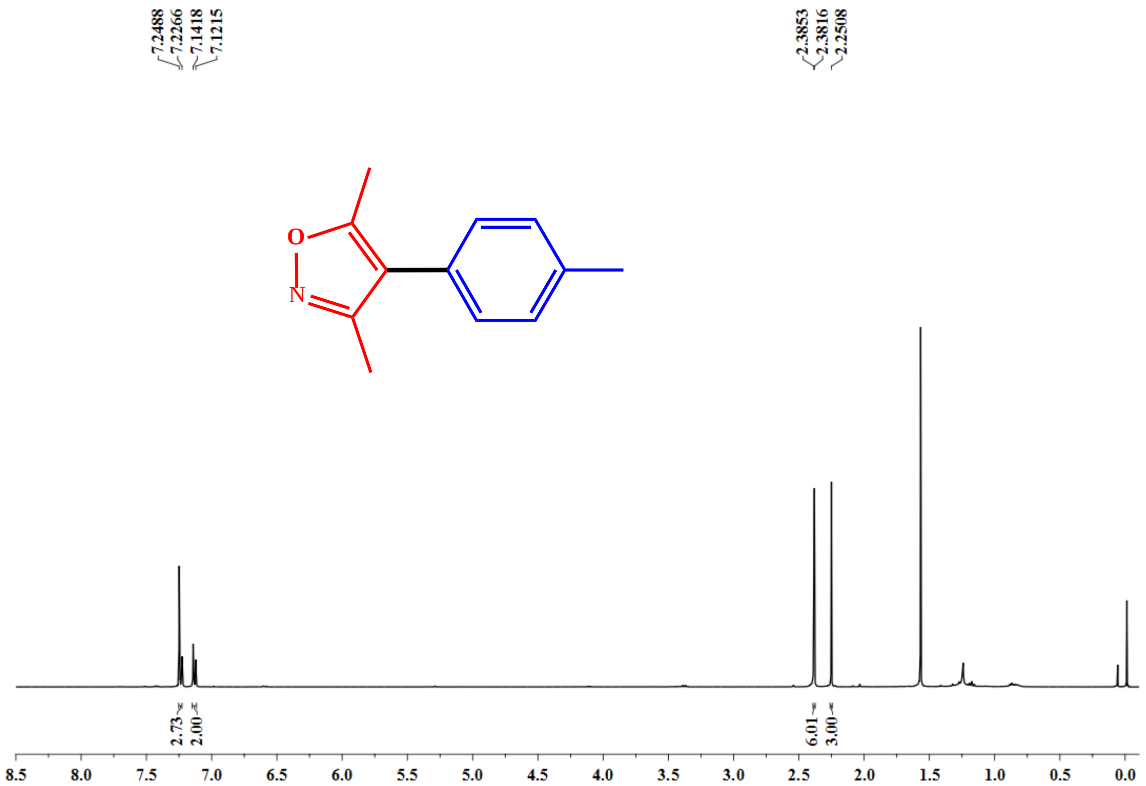


Figure S122. ^{1}H-NMR spectrum of 8f in $CDCl_3$.

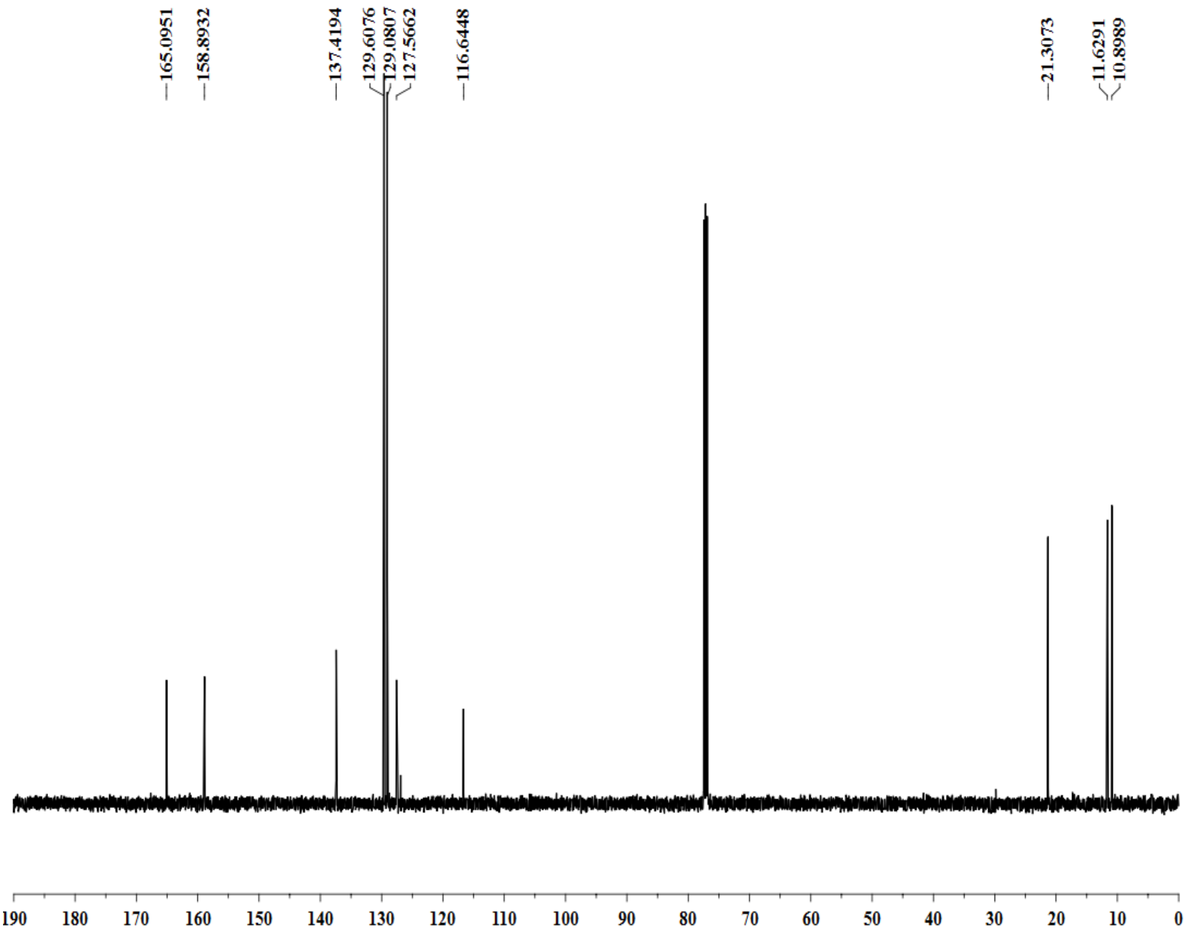


Figure S123. ^{13}C-NMR spectrum of 8f in $CDCl_3$.

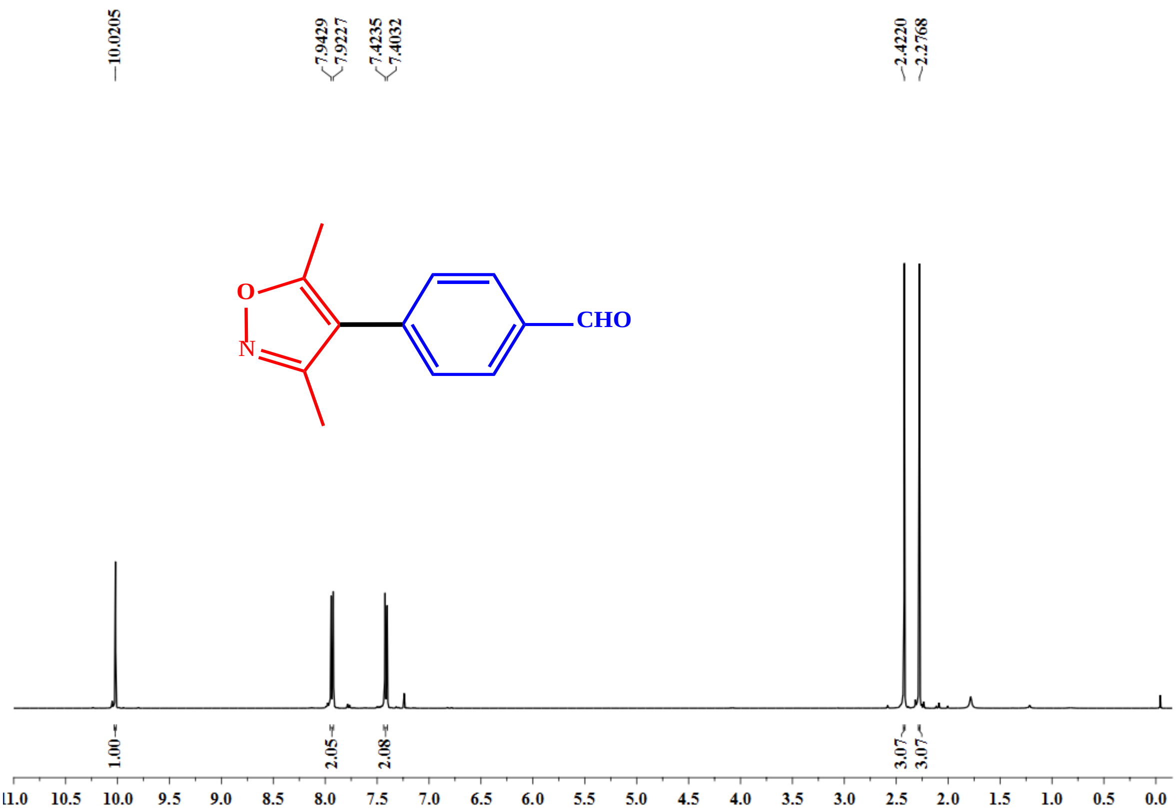


Figure S124. ^{1}H-NMR spectrum of 8g in $CDCl_3$.

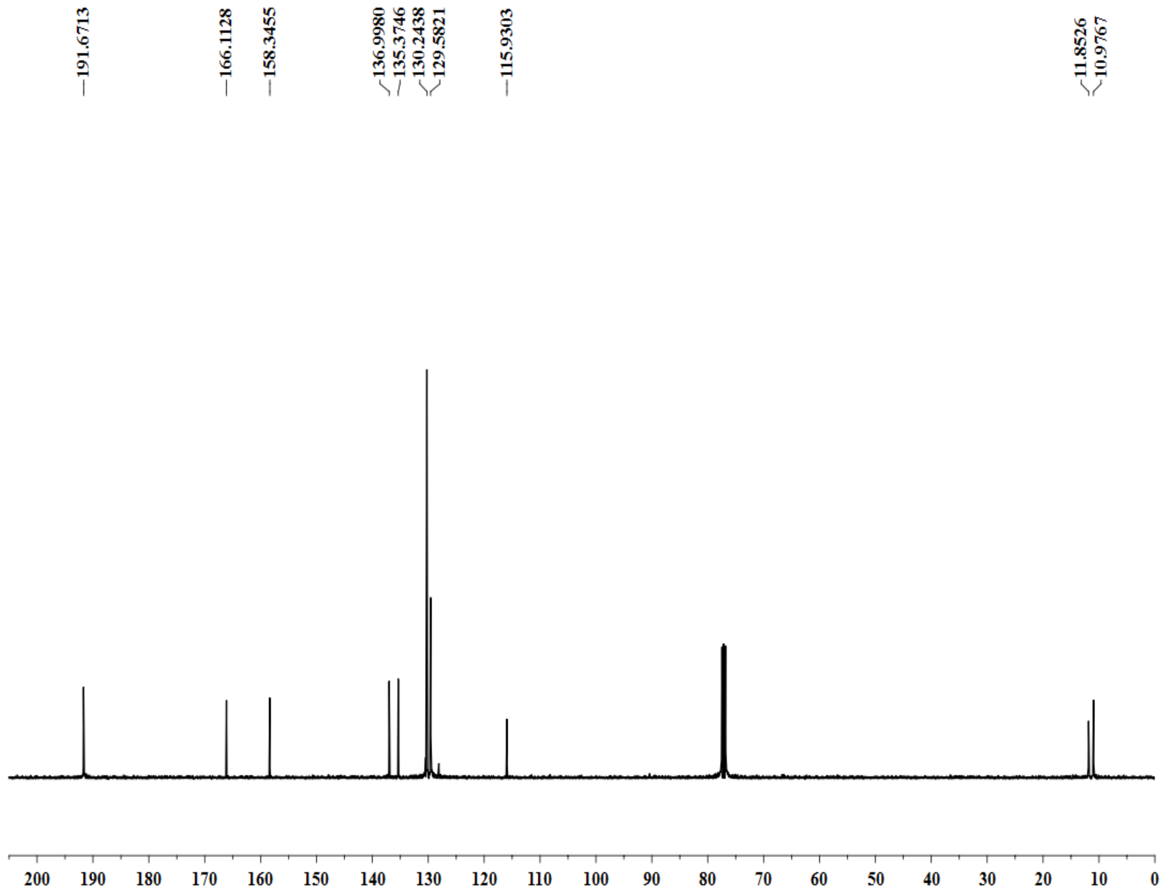


Figure S125. ^{13}C-NMR spectrum of 8g in $CDCl_3$.

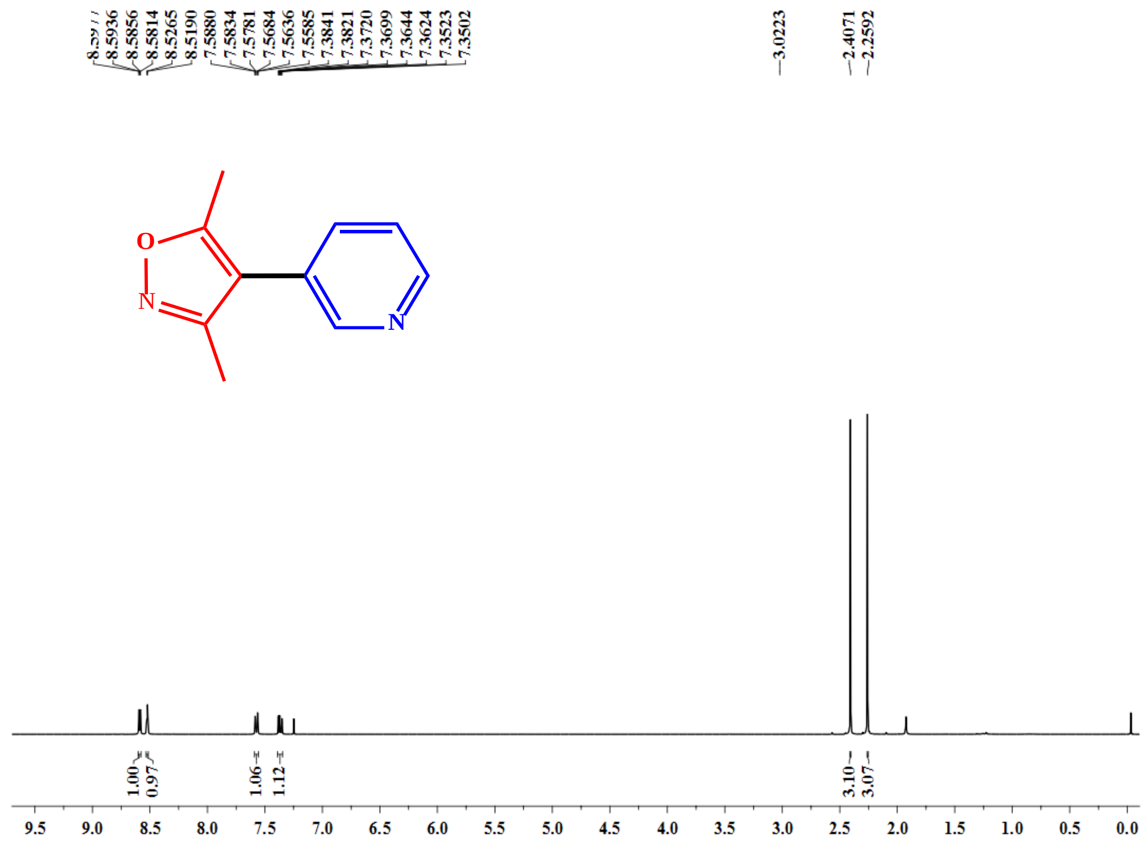


Figure S126. ^{1}H-NMR spectrum of 8h in $CDCl_3$.

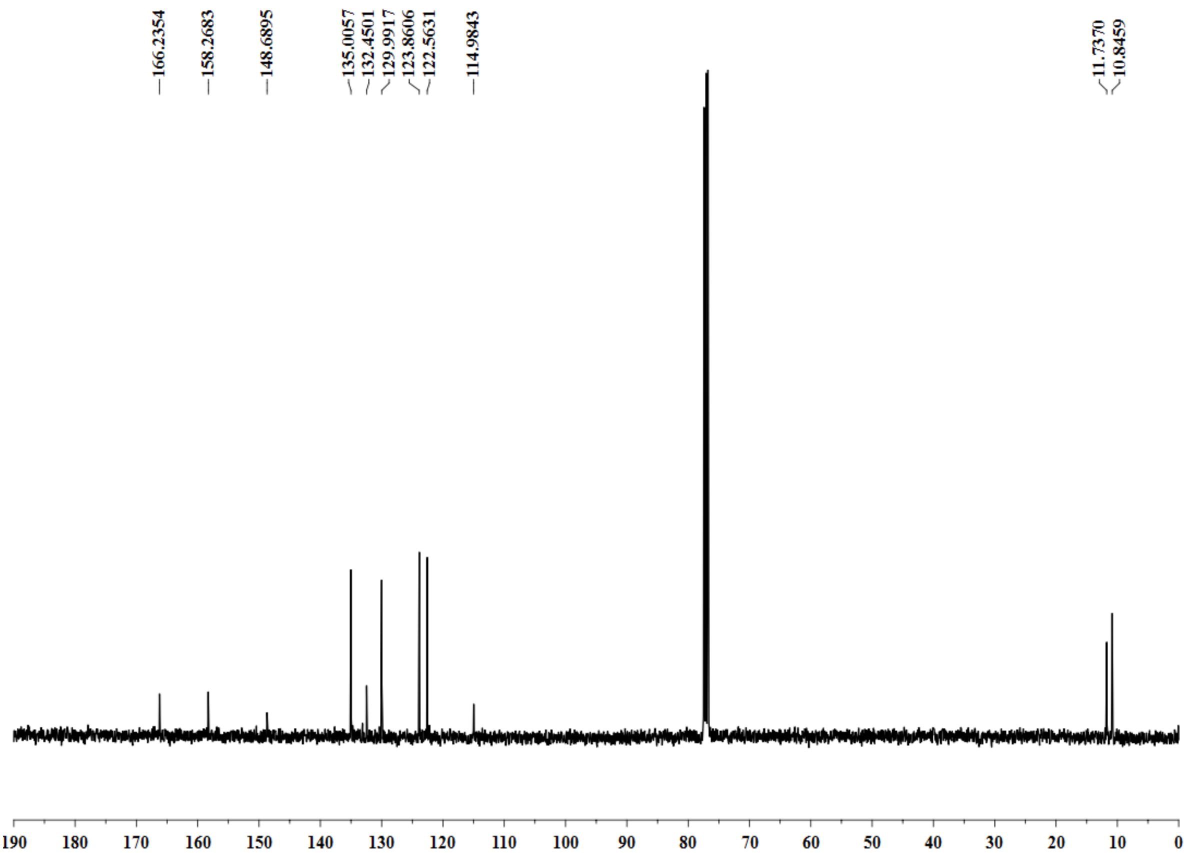


Figure S127. ^{13}C-NMR spectrum of 8h in $CDCl_3$.

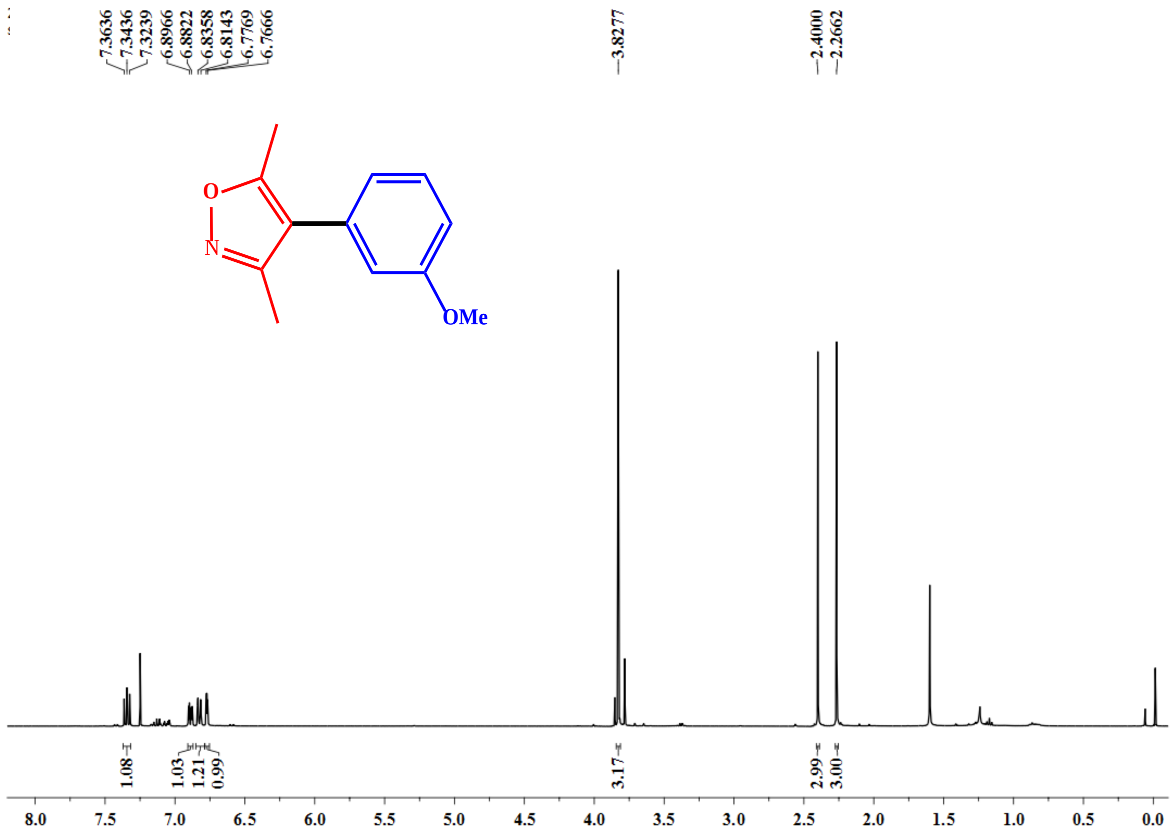


Figure S128. ^{1}H-NMR spectrum of 8i in $CDCl_3$.

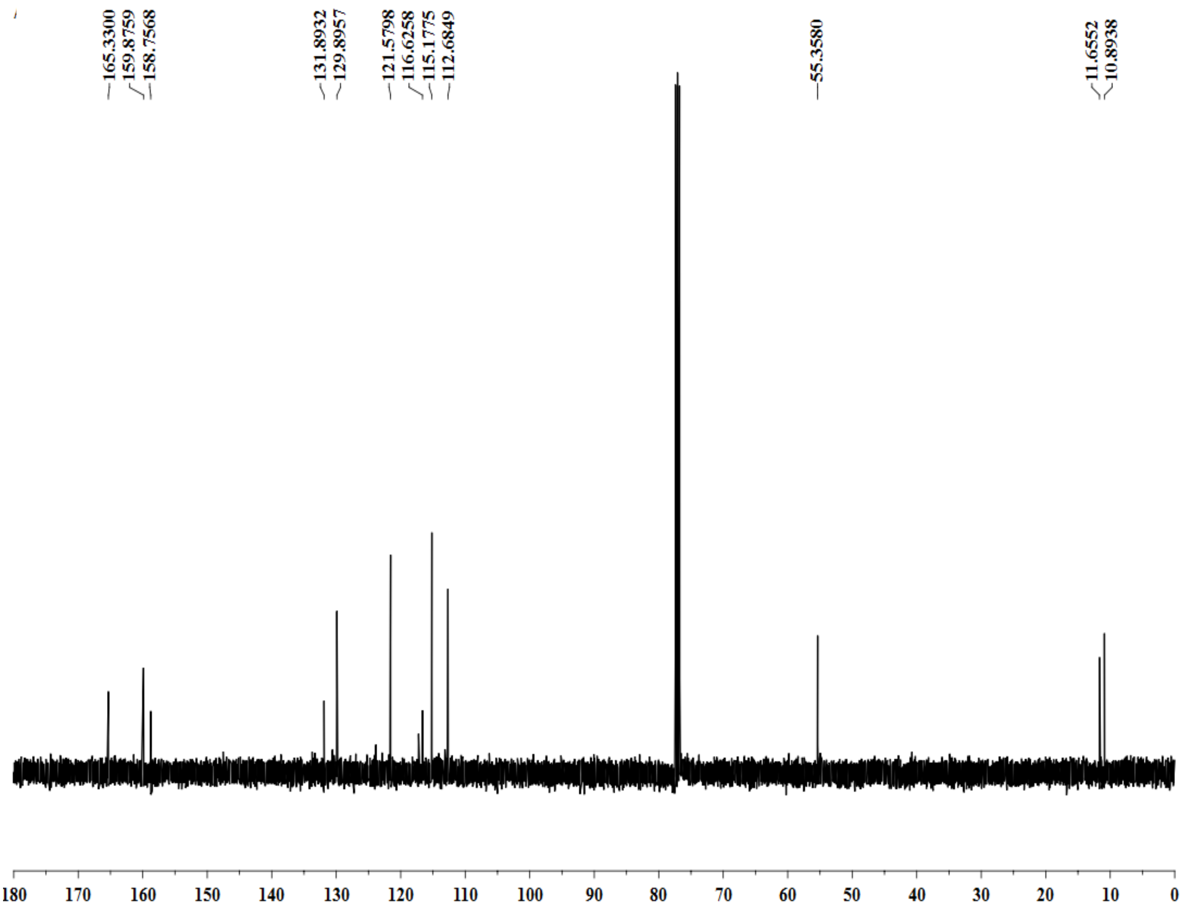


Figure S129. ^{13}C-NMR spectrum of 8i in $CDCl_3$.

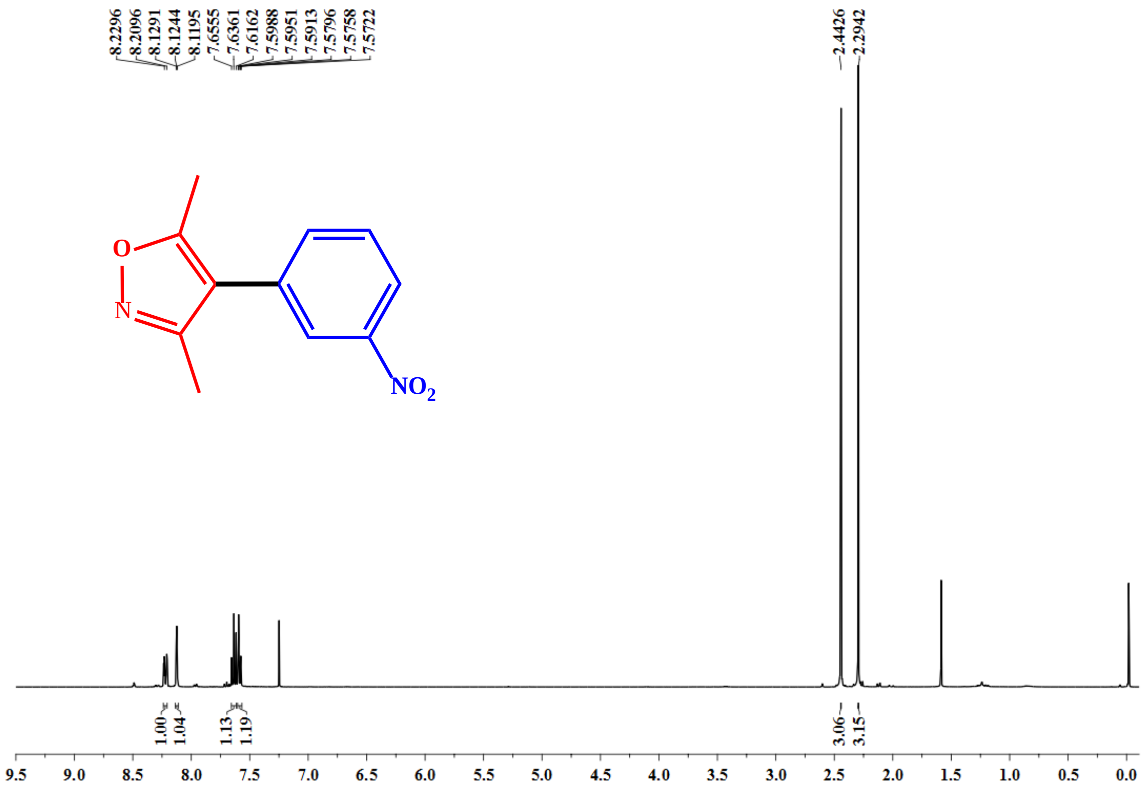


Figure S130. ^{1}H-NMR spectrum of 8j in $CDCl_3$.

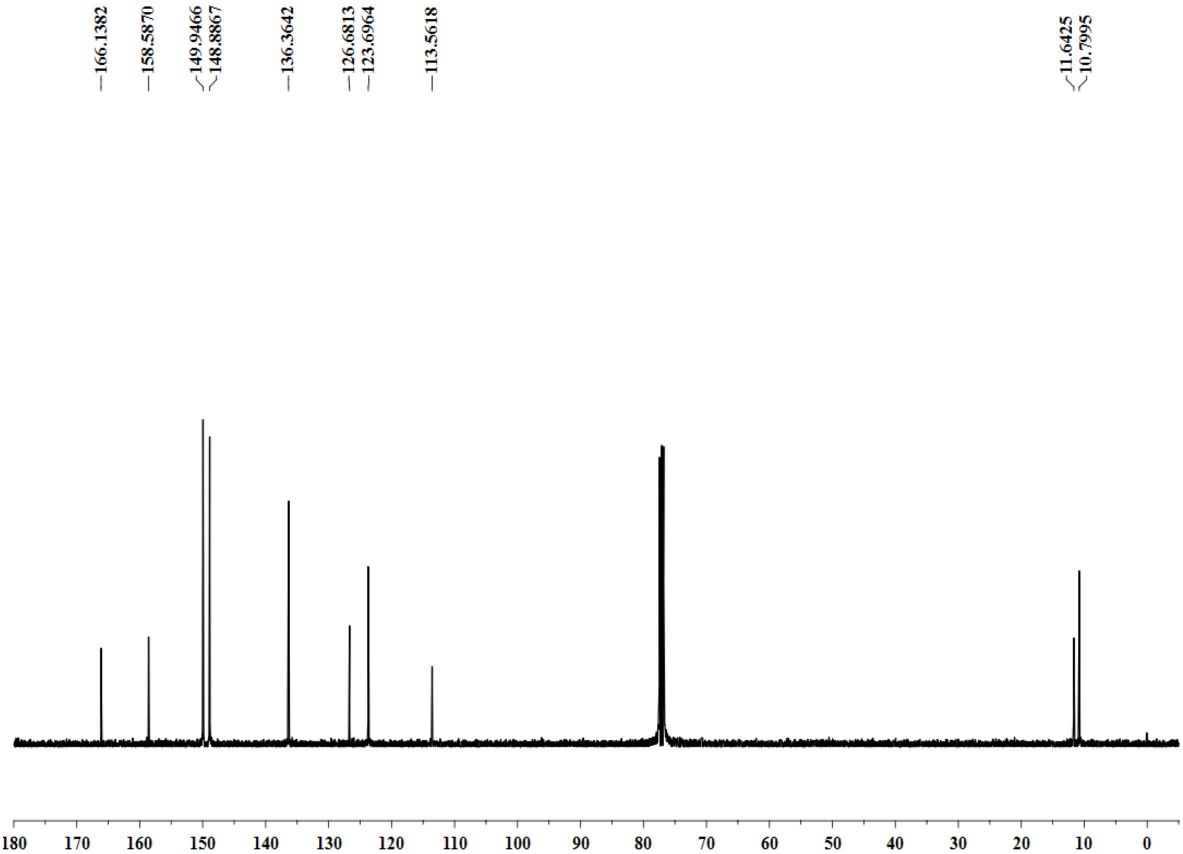


Figure S131. ^{13}C-NMR spectrum of 8j in $CDCl_3$.

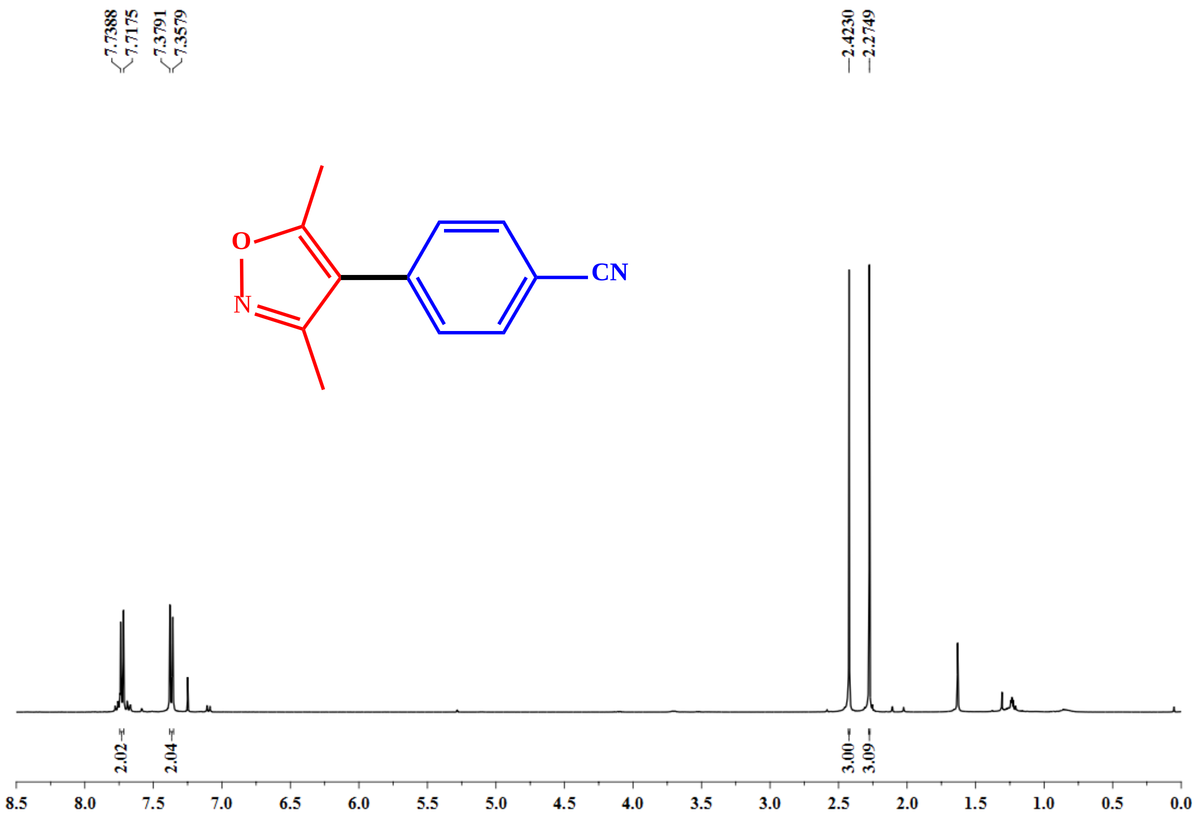


Figure S132. ^{1}H-NMR spectrum of 8k in $CDCl_3$.

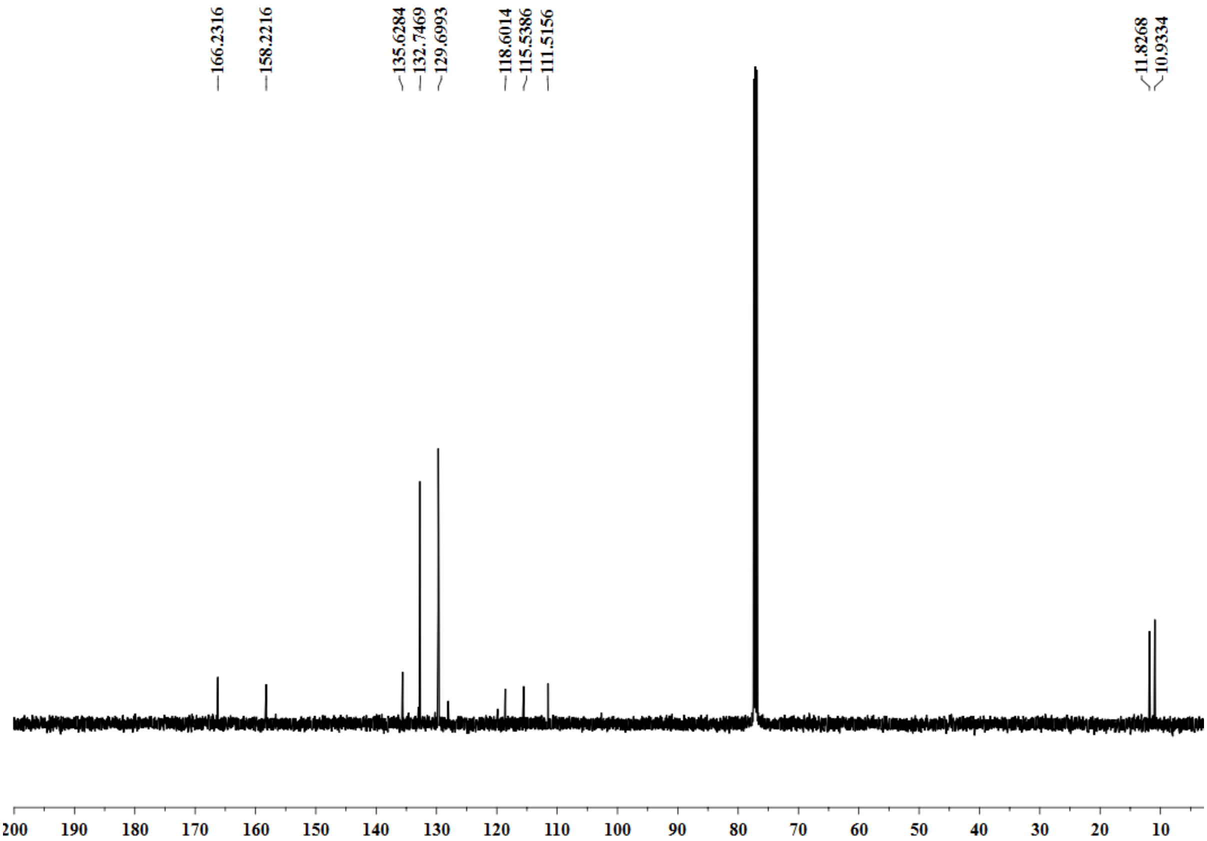


Figure S133. ^{13}C-NMR spectrum of 8k in $CDCl_3$.

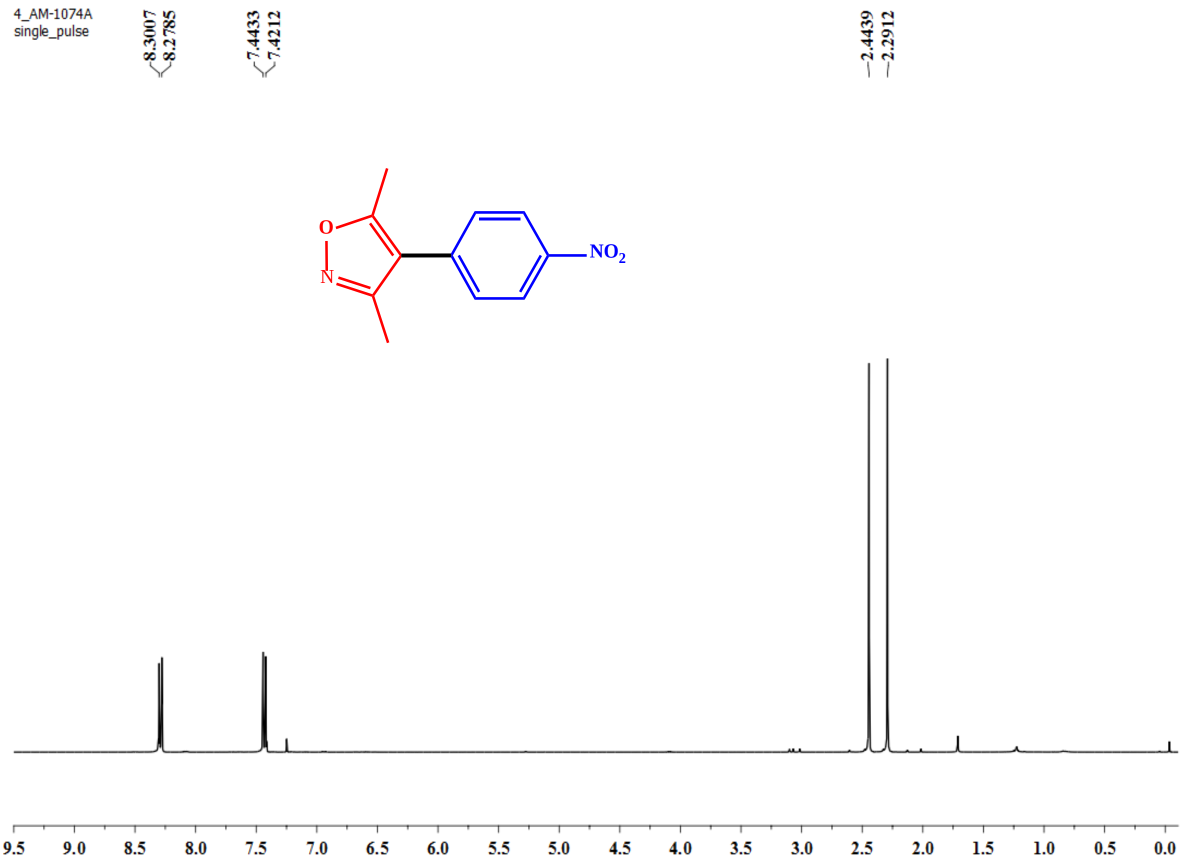


Figure S134. ^{1}H-NMR spectrum of 8l in $CDCl_3$.

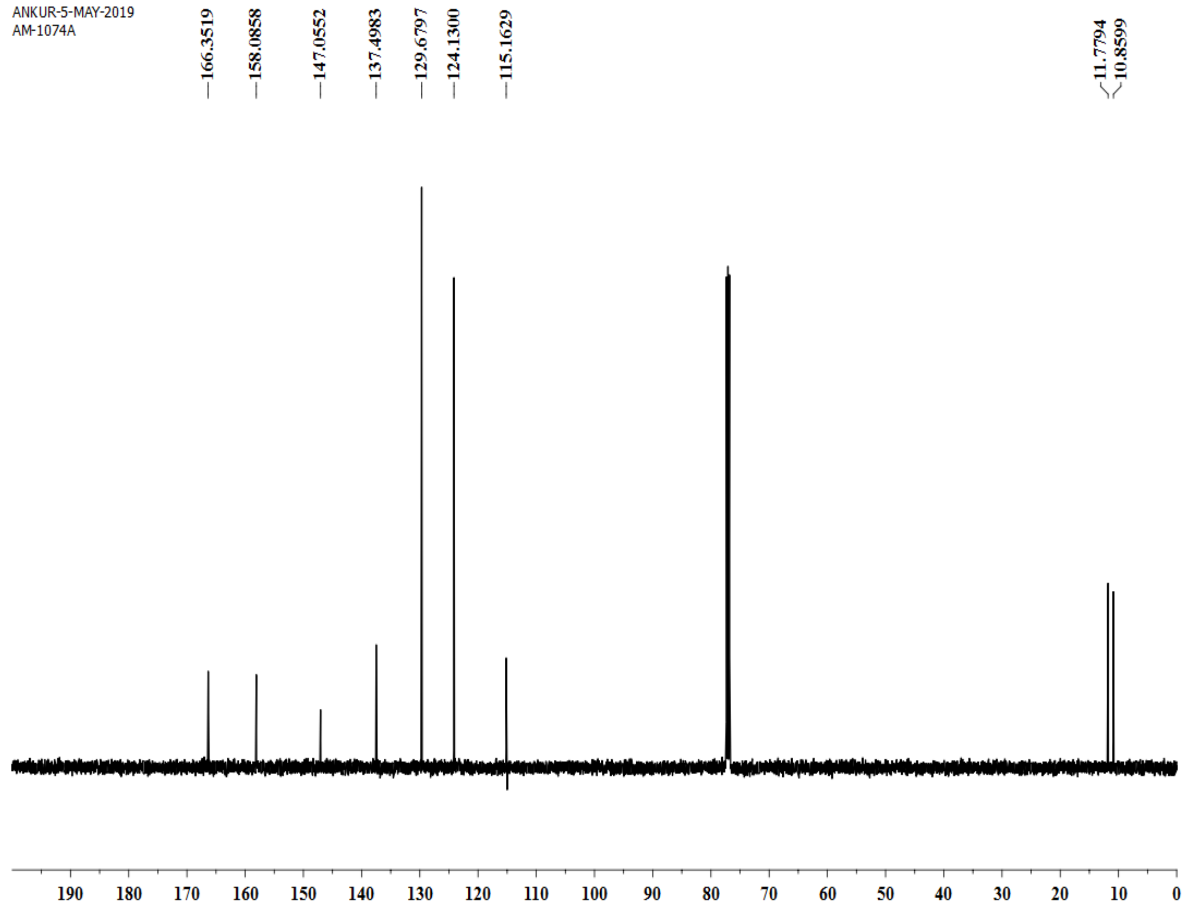


Figure S135. ^{13}C-NMR spectrum of 8l in $CDCl_3$.

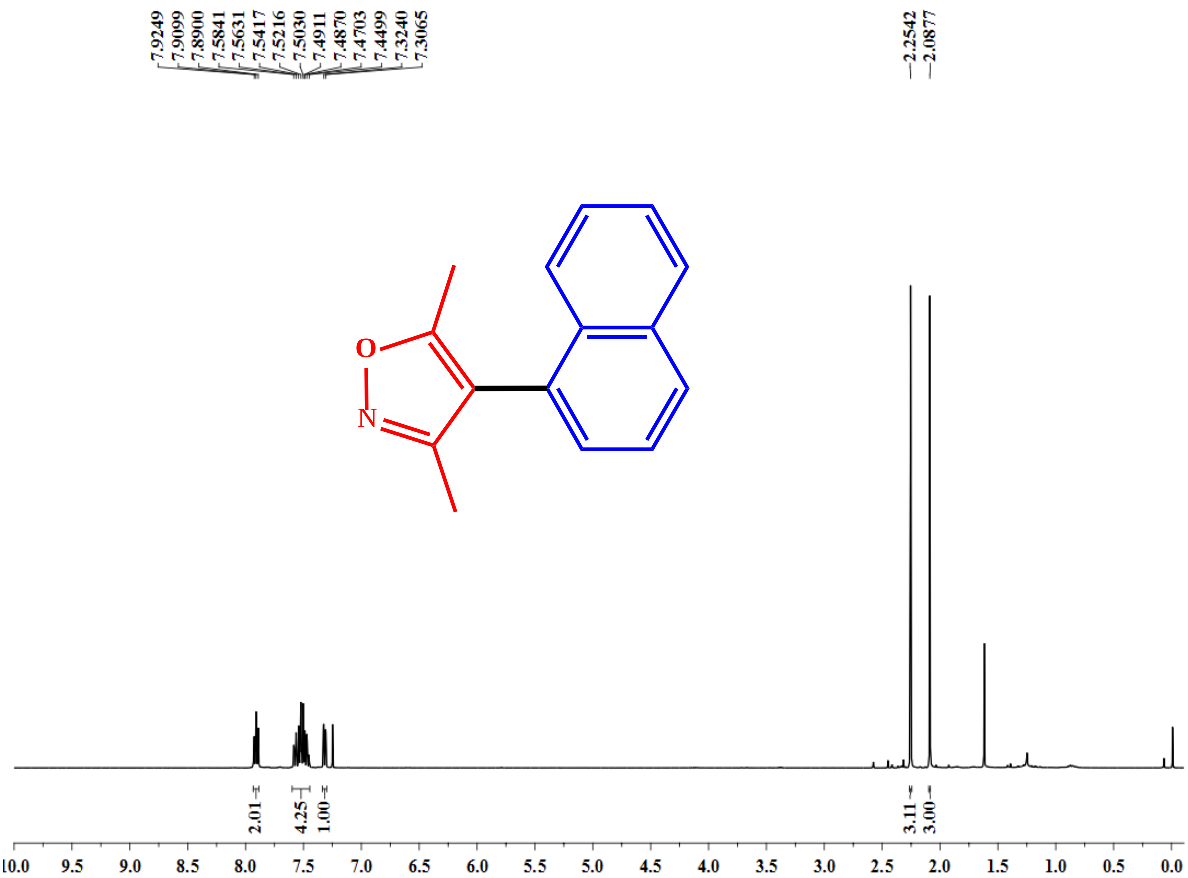


Figure S136. ^{1}H-NMR spectrum of 8m in $CDCl_3$.

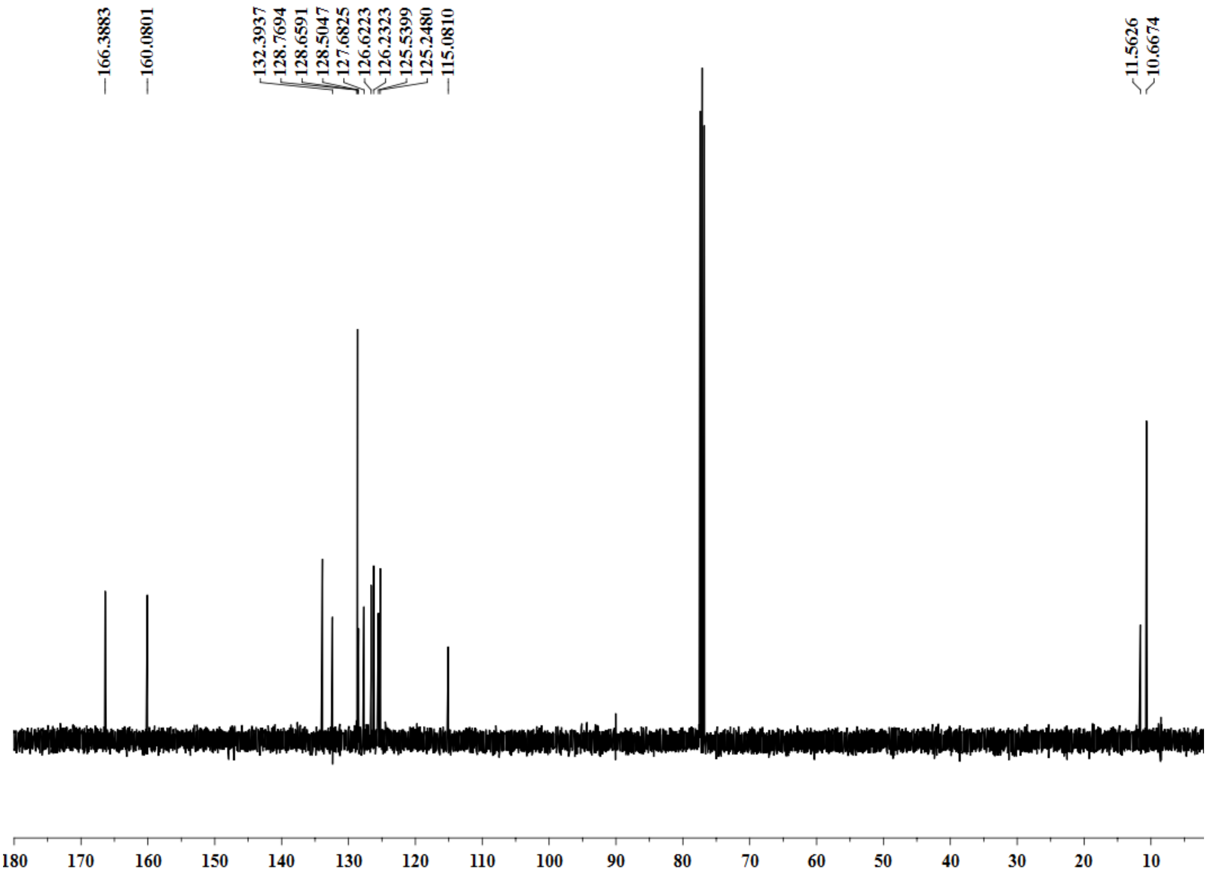


Figure S137. ^{13}C-NMR spectrum of 8m in $CDCl_3$.

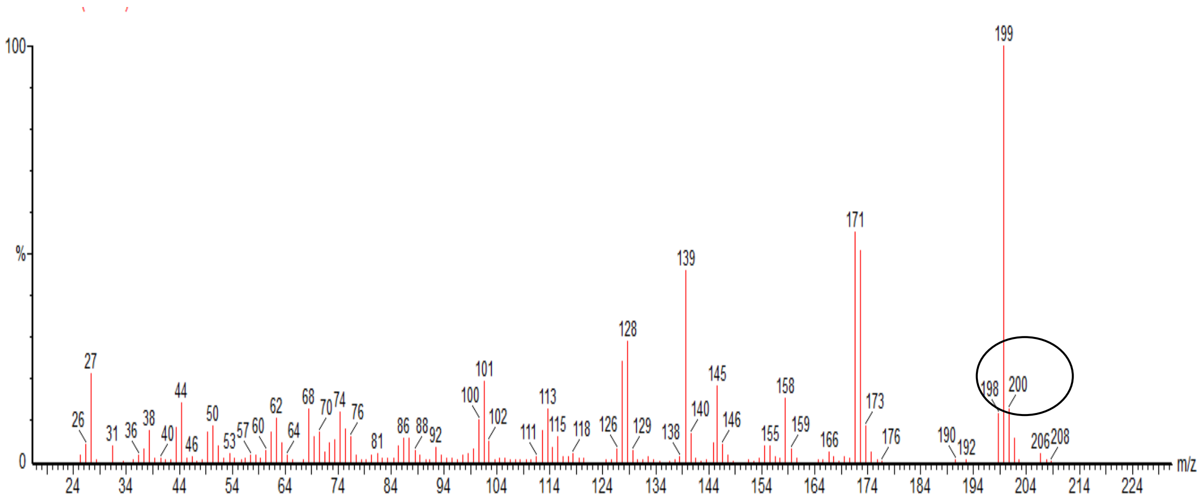


Figure S138. GC-MS mass spectrum of 6k.

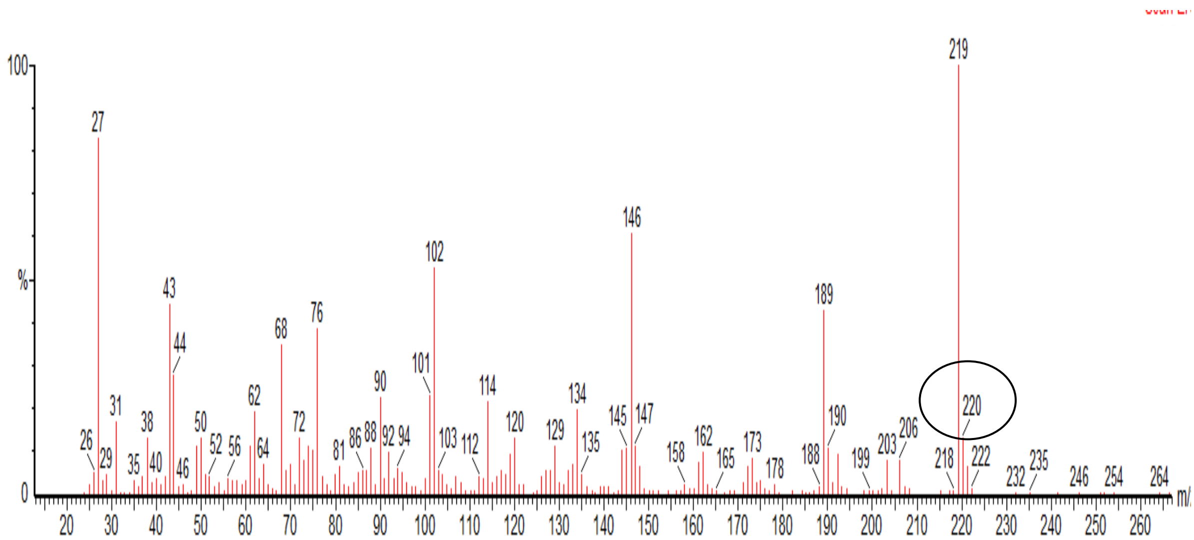


Figure S139. GC-MS mass spectrum of 6l.

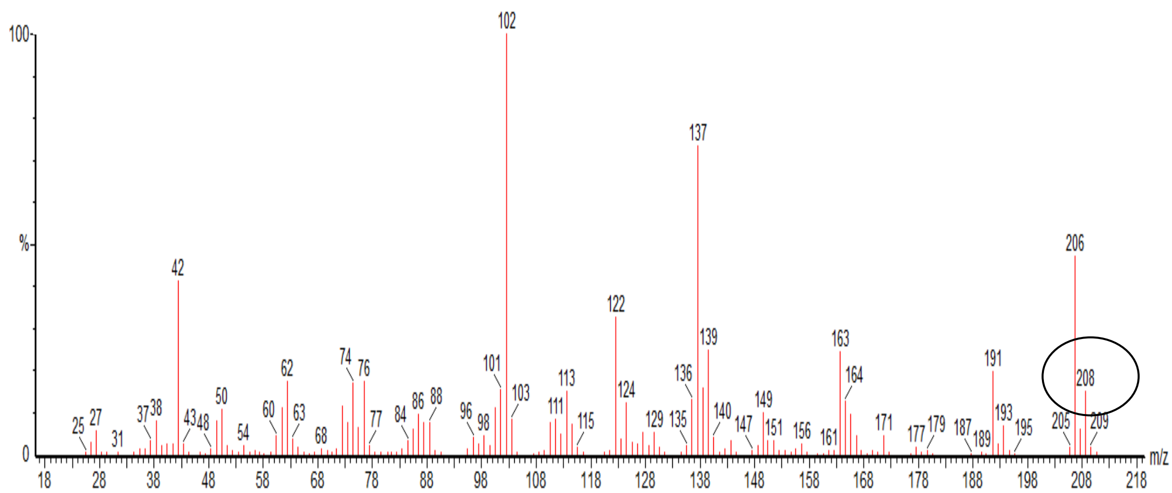


Figure S140. GC-MS mass spectrum of 8b.

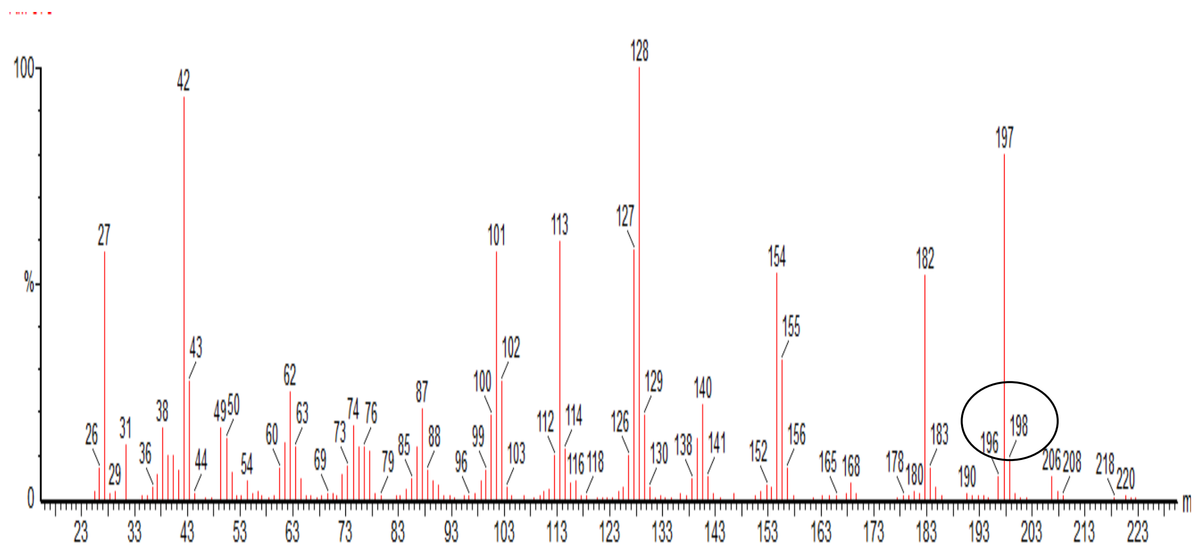


Figure S141. GC-MS mass spectrum of 8k.

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