Supporting Information

Biomass-derived activated carbon supported copper catalyst: An efficient heterogeneous magnetic catalyst for the base-free Chan-Lam coupling and oxidations

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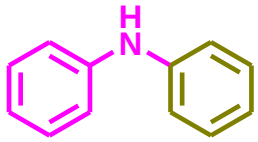
S1. Spectral details of compounds 3a-3j

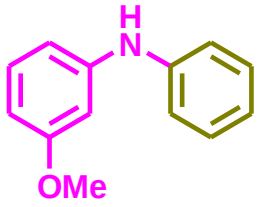


Diphenylamine (3a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J*= 8 Hz, 4H, Ar-H), 7.49 (t, *J*= 8 Hz, 4H, Ar-H), 7.39 (t, *J* = 8 Hz, 2H, Ar-H) and 5.75 (bs, 1H, NH, exchangeable with D_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.21, 130.92, 129.35, 117.61.

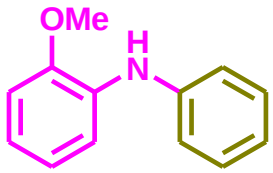
***N*-(4-Methoxyphenyl)benzenamine (3b)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.12 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.97 – 6.87 (m, 5H, Ar-H), 5.56 (bs, 1H, NH, exchangeable withD_2O), 3.85 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.29, 145.21, 135.93, 129.42, 122.23, 119.59, 115.48, 114.71, 55.48.



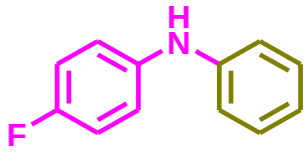
***N*-(3-Methoxyphenyl)benzenamine (3c)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.11 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.89-6.95 (m, 3H, Ar-H), 6.79 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.63 (s, 1H, Ar-H), 5.74 (bs, 1H, NH, exchangeable with D_2O), 3.76 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ160.16, 145.52, 143.56, 130.49, 129.41, 121.19, 118.76, 110.32, 107.04, 103.46, 55.26.



***N*-(2-Methoxyphenyl)benzenamine (3d)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.29 (m, 3H, Ar-H), 7.18 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.97 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.91-6.87 (m, 3H, Ar-H), 5.18 (bs, 1H, NH, exchangeable with D_2O), 3.92 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ148.28, 143.65, 139.11, 129.72, 129.03, 128.15, 122.28, 117.61, 117.35, 112.83, 56.79.



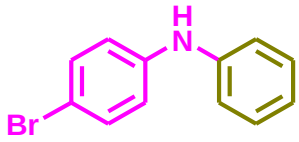
***N*-(4-Fluorophenyl)benzenamine (3e)**

1H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.9 Hz, 2H, Ar-H), 7.08 (dd, *J* = 8.9, 4.8 Hz, 2H, Ar-H),7.03-6.98 (m, 4H, Ar-H), 6.93 (t, *J* = 7.3 Hz, 1H, Ar-H), 5.61 (bs, 1H, NH, exchangeable with D_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.03 (d, *J* = 240.2 Hz), 143.91, 138.90 (d, *J* = 2.5 Hz), 129.41, 120.59, 120.52, 116.76, 115.94 (d, *J* = 22.5 Hz).

***N*-(4-Chlorophenyl)benzenamine (3f)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.23 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.07 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.96-7.03 (m, 3H, Ar-H), 5.70 (bs, 1H, NH, exchangeable with

D_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.64, 141.87, 129.47, 129.28, 124.20, 121.51, 118.83, 118.09.

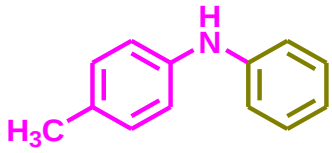


***N*-(4-Bromophenyl)benzenamine (3g)**

^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (t, *J*= 8 Hz, 2H, Ar-H), 7.375 (d, *J*= 12 Hz, 2H, Ar-H), 7.16 (t, *J*= 8 Hz, 1H, Ar-H), 7.08 (d, *J*= 8 Hz, 2H, Ar-H),6.96 (d,*J*= 8 Hz, 2H, Ar-H),5.74 (bs, 1H, NH, exchangeable with D_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ140.79, 138.17, 130.28,128.70,127.13, 122.05, 116.62,113.11.

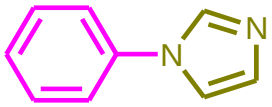
***N*-(2-Fluorophenyl)benzenamine (3h)**

^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.6 Hz, 3H), 7.38 (t, *J* = 3.6 Hz, 3H), 7.15 (dd, *J* = 8.6, 2.5 Hz, 3H), 5.38 (bs, 1H, NH, exchangeable with D_2O) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.45 (d, J = 234 Hz), 142.27, 133.28 (d, J = 70 Hz), 129.92, 125.93, 122.92, 122.21 (J = 68 Hz), 121.04 (d, J = 32 Hz), 119.22, 114.71 (d, J = 105 Hz).



***N*-(4-Methylphenyl) benzenamine (3i)**

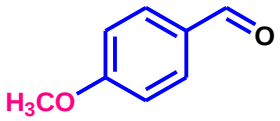
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, 4H, J=8 Hz, Ar-H), 7.47 (t, 3H, J=8 Hz, Ar-H), 7.33 (t, 2H, J=8 Hz, Ar-H), 2.51 (s, 3H, CH_3), 5.84 (bs, 1H, NH, exchangeable with D_2O) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.31, 138.57, 130.91, 129.25, 124.21, 119.23, 117.88, 114.55, 22.92.



1-Phenyl-1*H*-imidazole (3j)

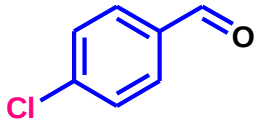
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H, H_{im}), 7.58-7.54 (m, 2H, Ar-H), 7.51 (d, *J* = 7.2 Hz, 1H, H_{im}), 7.48 -7.44 (m, 2H, 1H_{im}, 1Ar-H), 7.41 (d, *J* = 12.5 Hz, 2H, Ar-H);^{13}C NMR (101 MHz, $CDCl_3$) δ 136.90, 136.04, 130.26, 129.06, 128.32, 122.07, 119.65.

S2. Spectral details of compounds 5a-5j



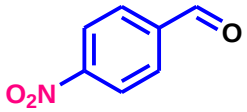
4-Methoxybenzaldehyde (5a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H, CHO), 7.66 (d, *J*= 8.7 Hz, 2H, ArH), 6.83 (d, *J*= 8.6 Hz, 2H, ArH), 3.69 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.71, 164.50, 131.93, 129.62, 114.20, 55.23.



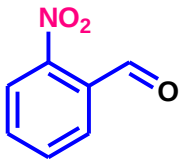
4-Chlorobenzaldehyde (5b)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (s, 1H, CHO), 7.84 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.53 (d, *J* = 8.3 Hz, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.05, 140.96, 134.58, 130.60, 129.31.



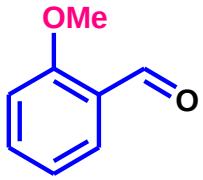
4-Nitrobenzaldehyde (5c)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 1H, CHO), 8.43 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.11 (d, *J* = 8.5 Hz, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.63, 151.87, 140.03, 130.63, 124.35.



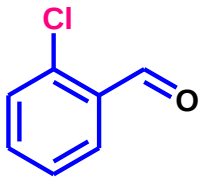
2-Nitrobenzaldehyde (5d)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.42 (s, 1H, CHO), 8.13 (d, J = 8 Hz, 1H, Ar-H), 7.96 (d, J = 8 Hz, 1H, Ar-H), 7.76-7.84 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.24, 149.48, 133.92, 133.56, 131.22, 129.27, 124.32.



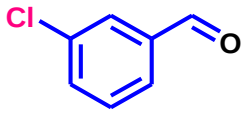
2-Methoxybenzaldehyde (5e)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.50 (s, 1H, Ar-H), 7.86 (d, J = 7.7 Hz, 1H, Ar-H), 7.58 (t, J = 7.9 Hz, 1H, Ar-H), 7.01-7.08 (m, 2H, Ar-H), 3.96 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.90, 161.81, 135.91, 128.55, 124.49, 120.69, 111.68, 55.74.



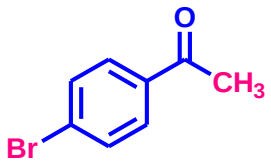
2-Chlorobenzaldehyde (5f)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (s, 1H, CHO), 7.79 (d, J = 7.6, 1H, Ar-H), 7.44-7.27 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.69, 137.78, 135.15, 132.28, 130.53, 129.26, 127.25.



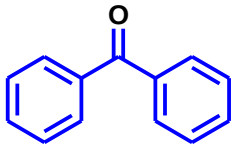
3-Chlorobenzaldehyde (5g)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H, CHO), 7.77 (s, 1H, Ar-H), 7.71 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.53 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.42 (t, *J* = 7.8 Hz, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.81, 137.96, 135.33, 134.30, 130.36, 129.12,127.98.



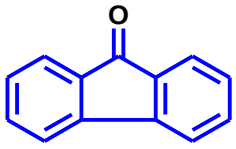
4-Bromoacetophenone (5h)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.63 (d, *J* = 8.3 Hz, 2H, Ar-H), 2.61 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.08, 135.73, 131.75, 129.87, 128.48, 26.46.



Benzophenone (5i)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.62 (t, *J* = 7.4 Hz, 2H, Ar-H), 7.51 (t, *J* = 7.6 Hz, 4H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.01, 137.61, 132.44, 129.99, 128.41.



Fluorenone (5j)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.55-7.49 (m, 4H), 7.32 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.45, 144.52, 134.54, 133.94, 129.26, 124.36,

120.33.

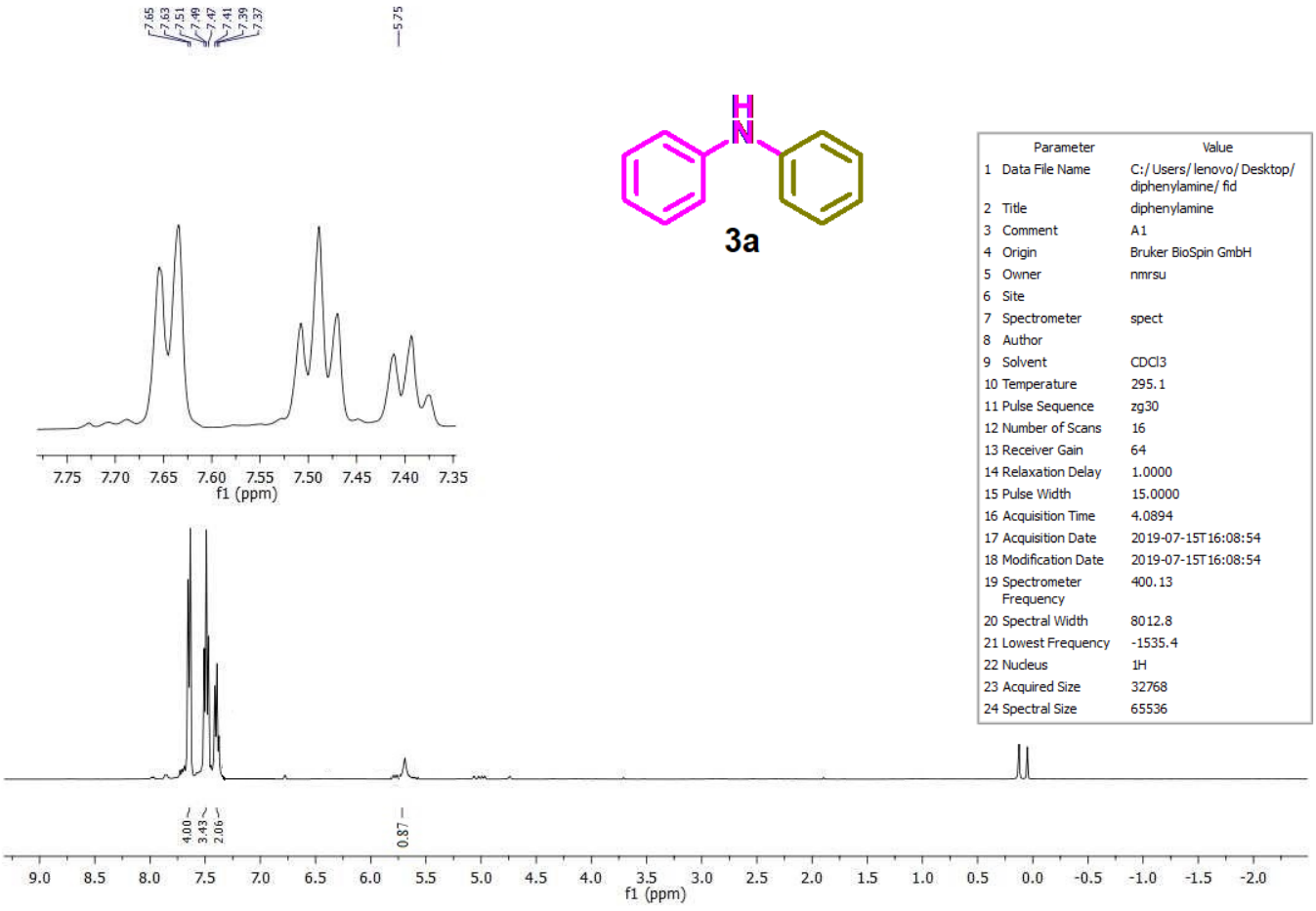


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Figure S1. [1]H NMR spectra of diphenylamine.

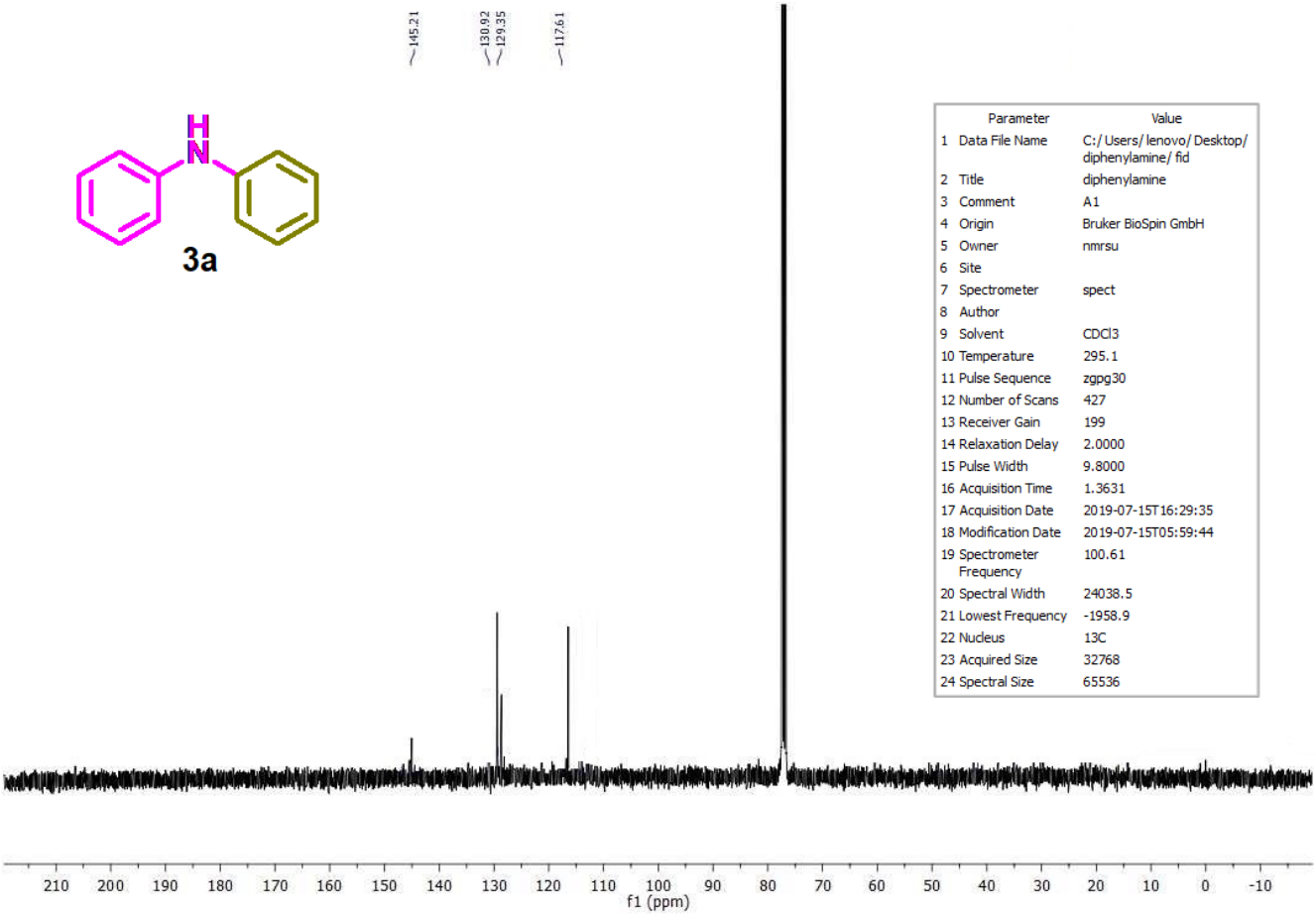


Figure S2. [13]C NMR spectra of diphenylamine.

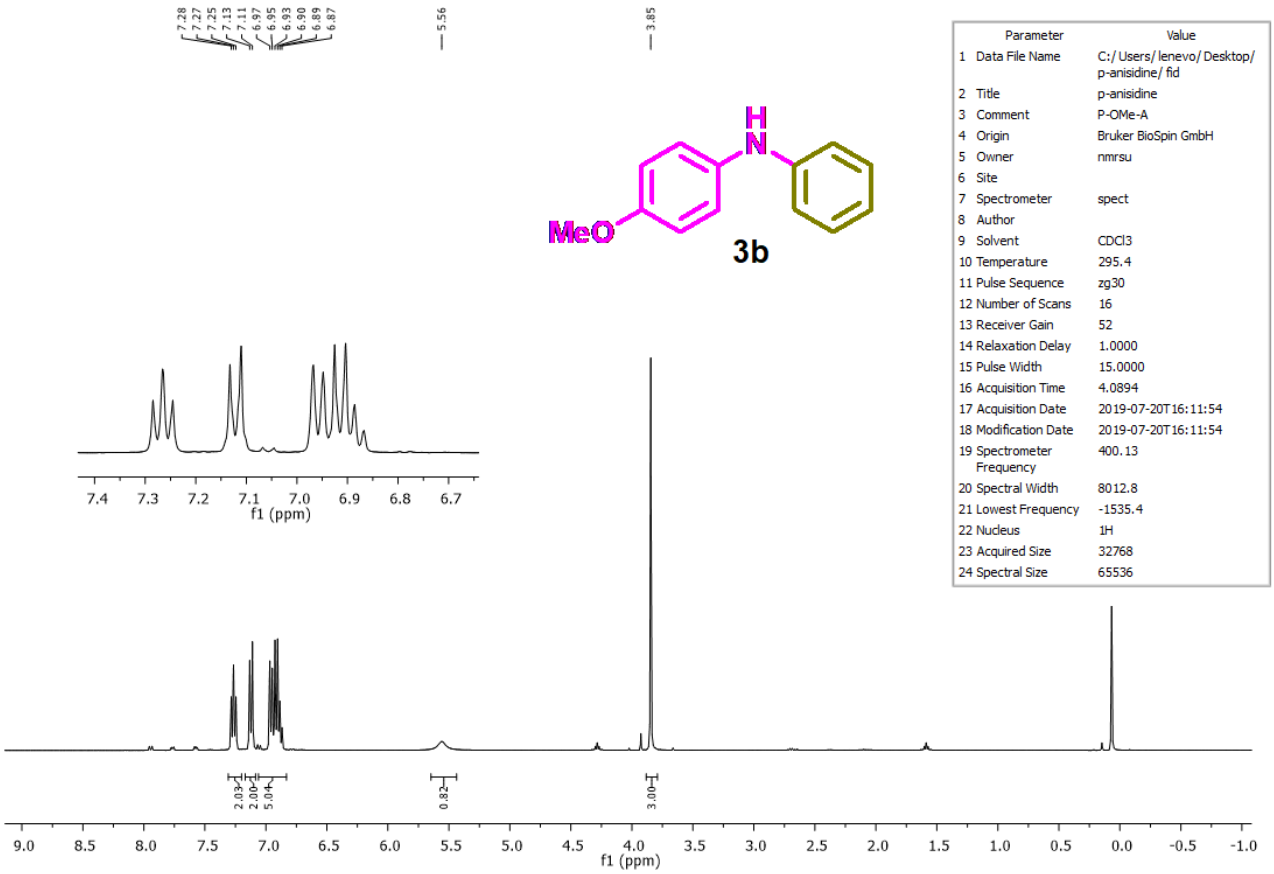


Figure S3. ^{1}H NMR spectra of *N*-(4-Methoxyphenyl)benzenamine.

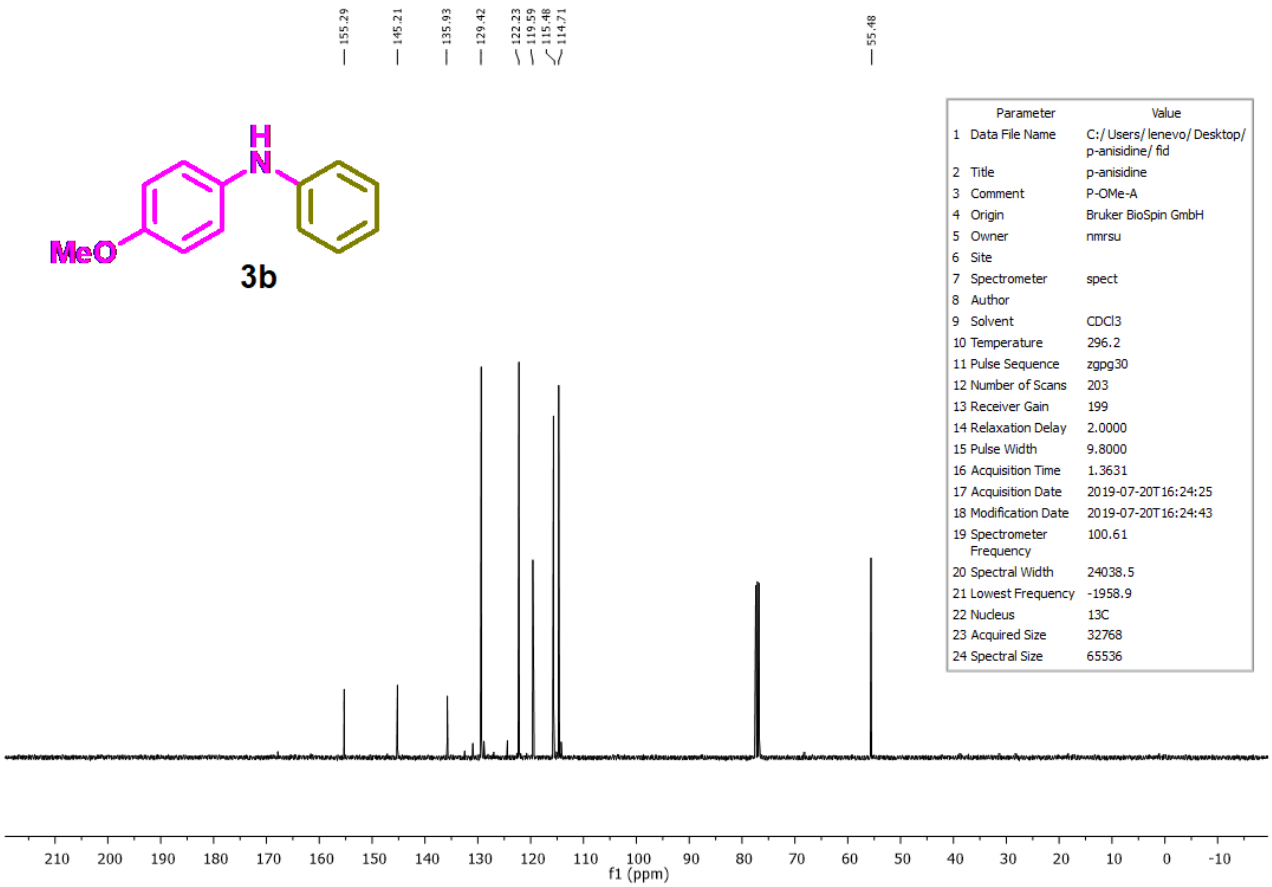


Figure S4. ^{13}C NMR spectra of *N*-(4-Methoxyphenyl)benzenamine.

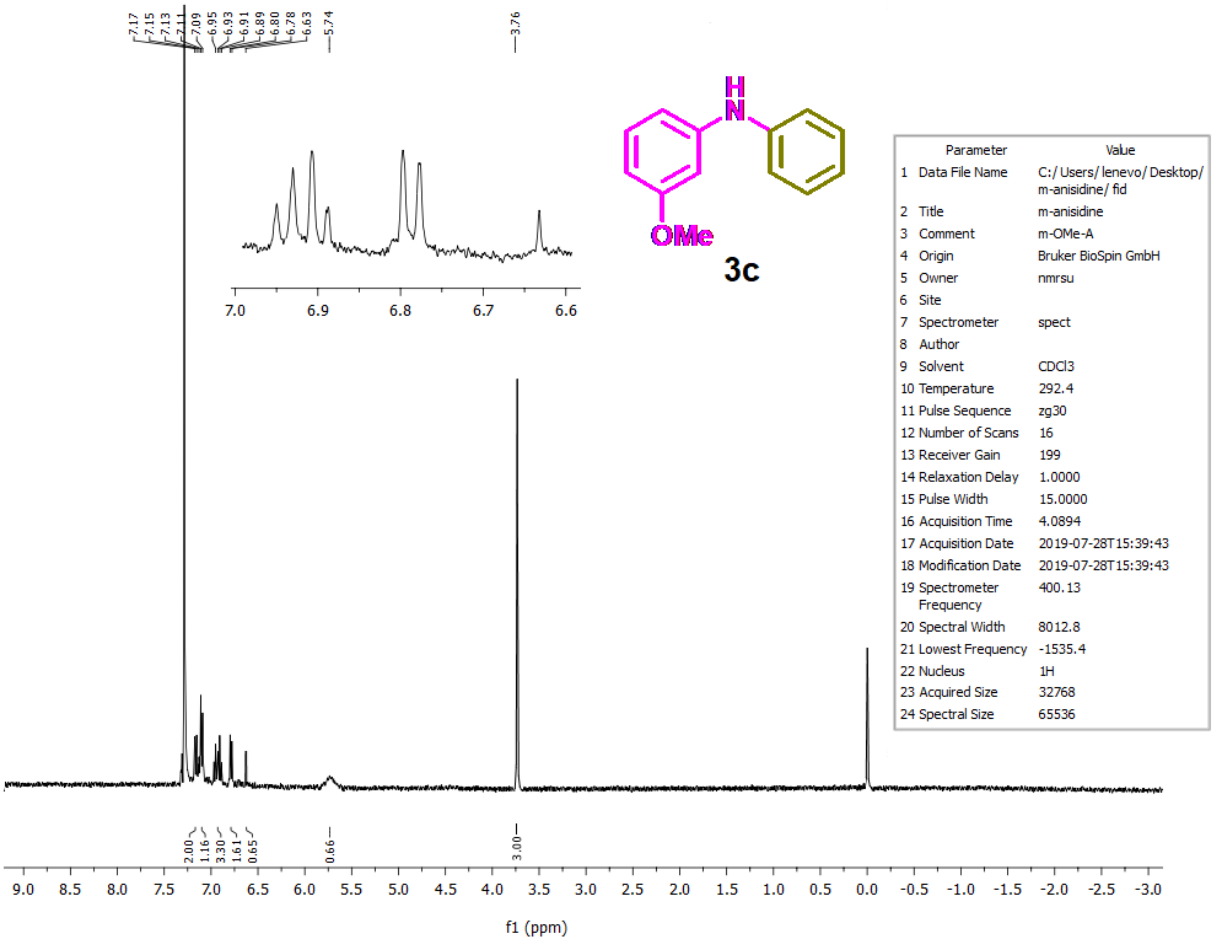


Figure S5. ^{1}H NMR spectra of *N*-(3-Methoxyphenyl)benzenamine.

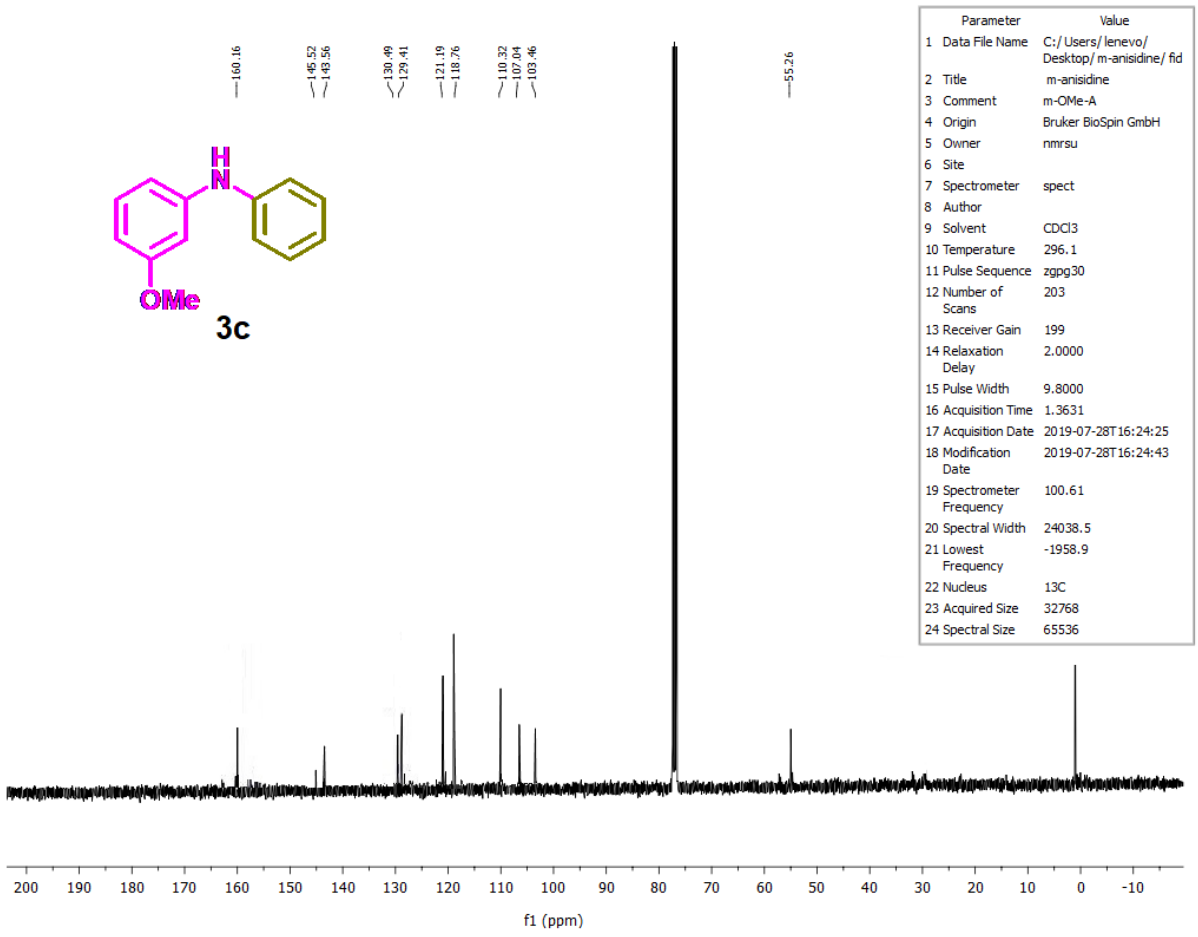


Figure S6. ^{13}C NMR spectra of *N*-(3-Methoxyphenyl)benzenamine.

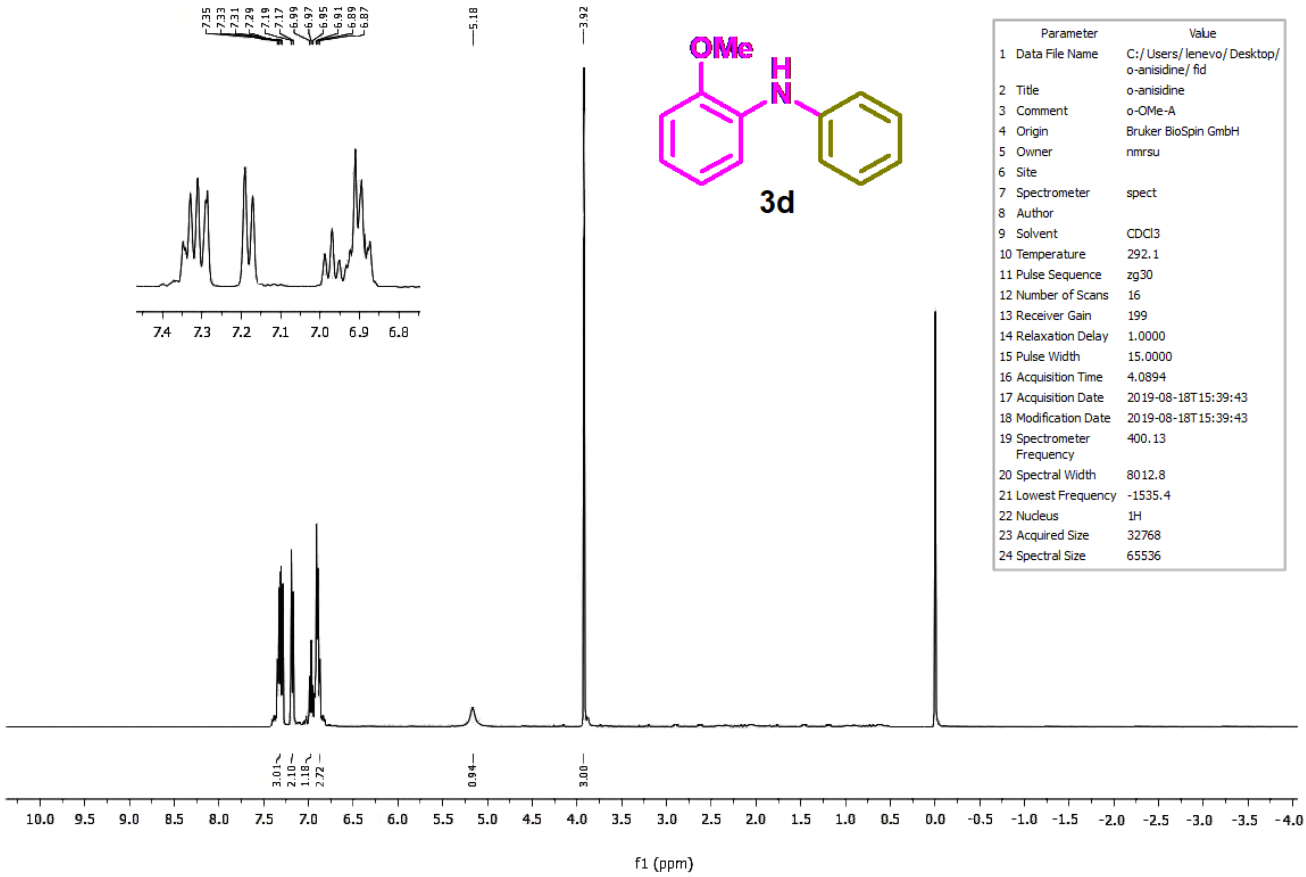


Figure S7. ^{1}H NMR spectra of *N*-(2-Methoxyphenyl)benzenamine.

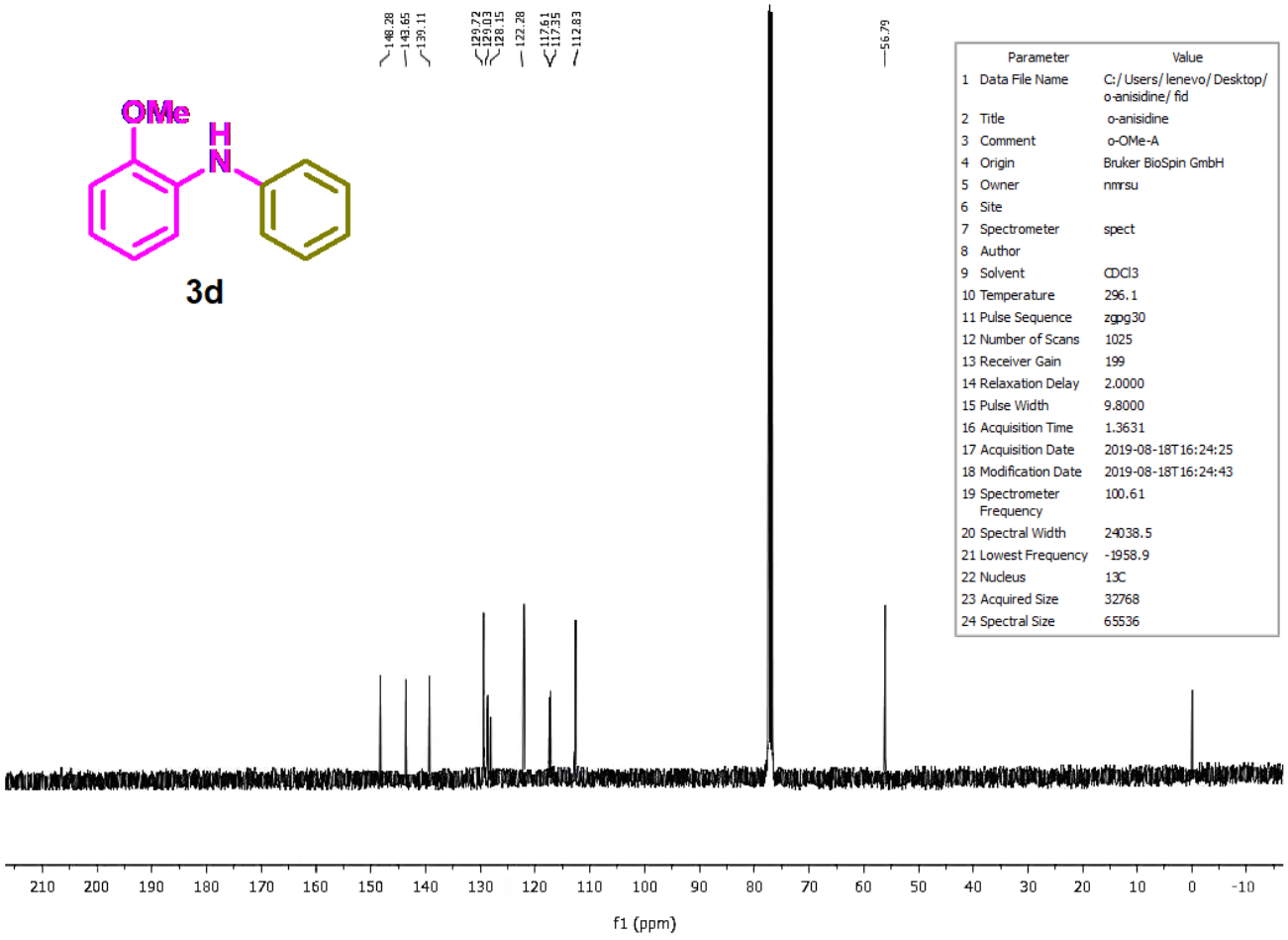


Figure S8. ^{13}C NMR spectra of *N*-(2-Methoxyphenyl)benzenamine.

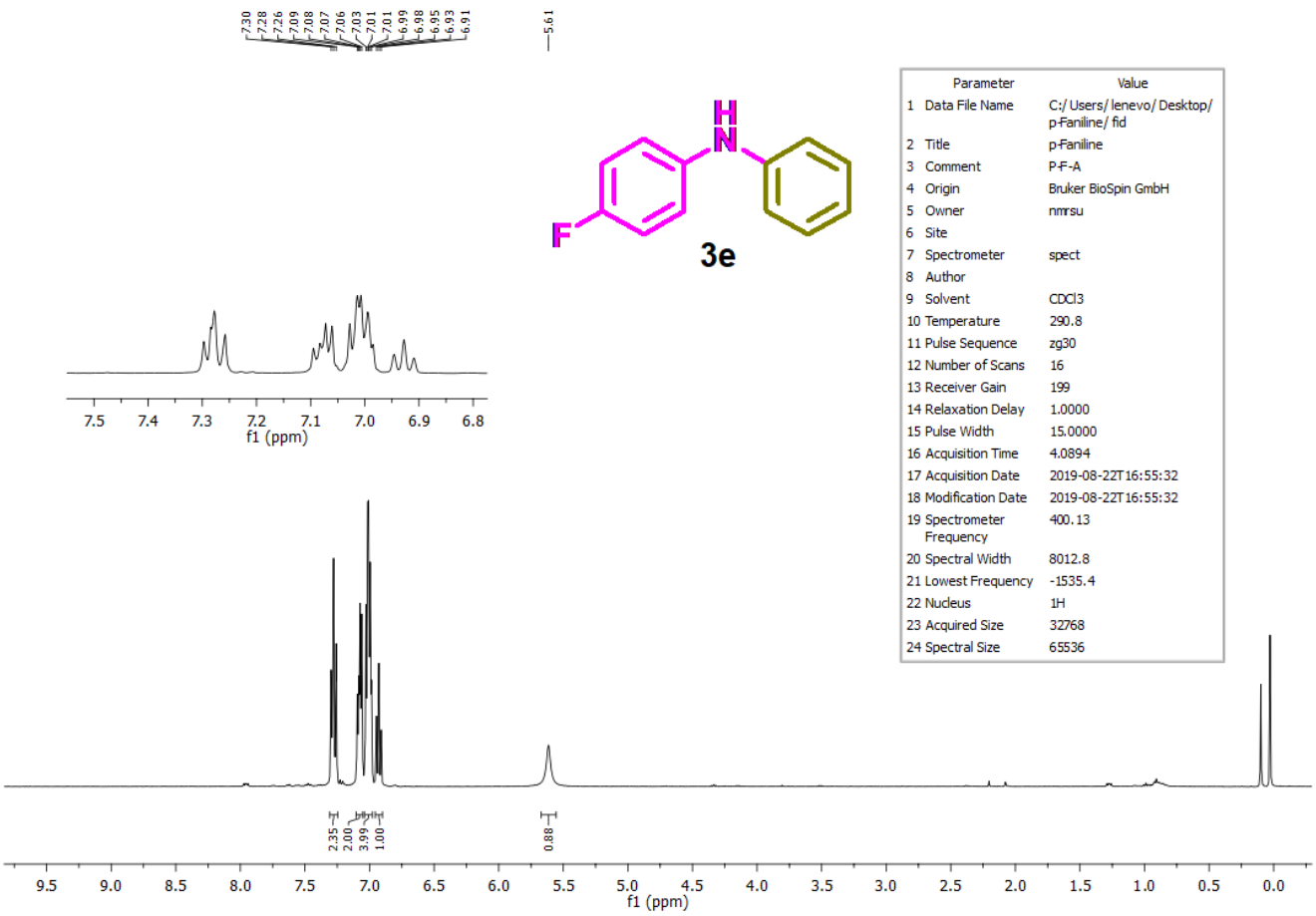


Figure S9. ^{1}H NMR spectra of *N*-(4-Fluorophenyl)benzenamine.

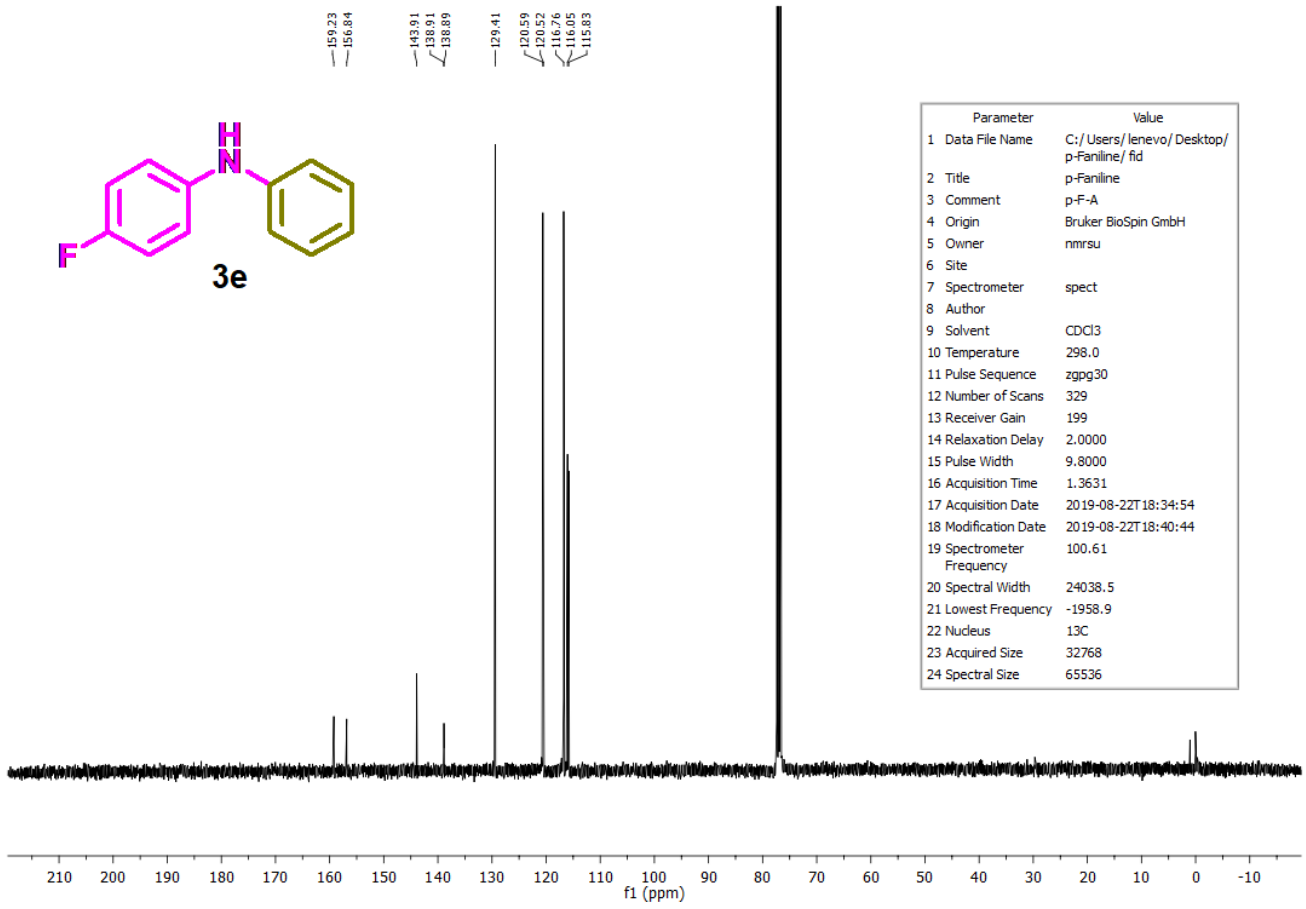


Figure S10. ^{13}C NMR spectra of *N*-(4-Fluorophenyl)benzenamine.

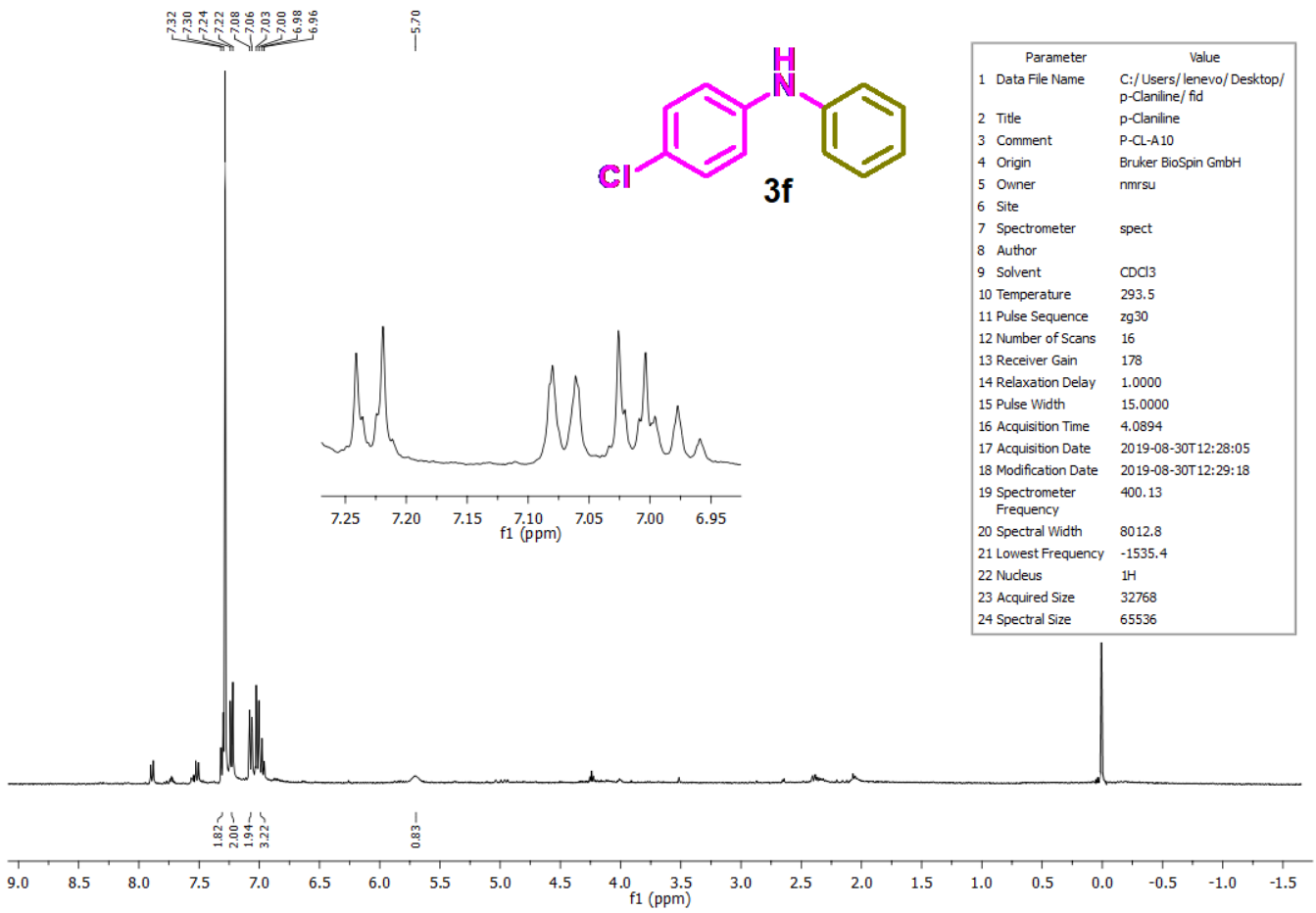


Figure S11. ^{1}H NMR spectra of *N*-(4-Chlorophenyl)benzenamine.

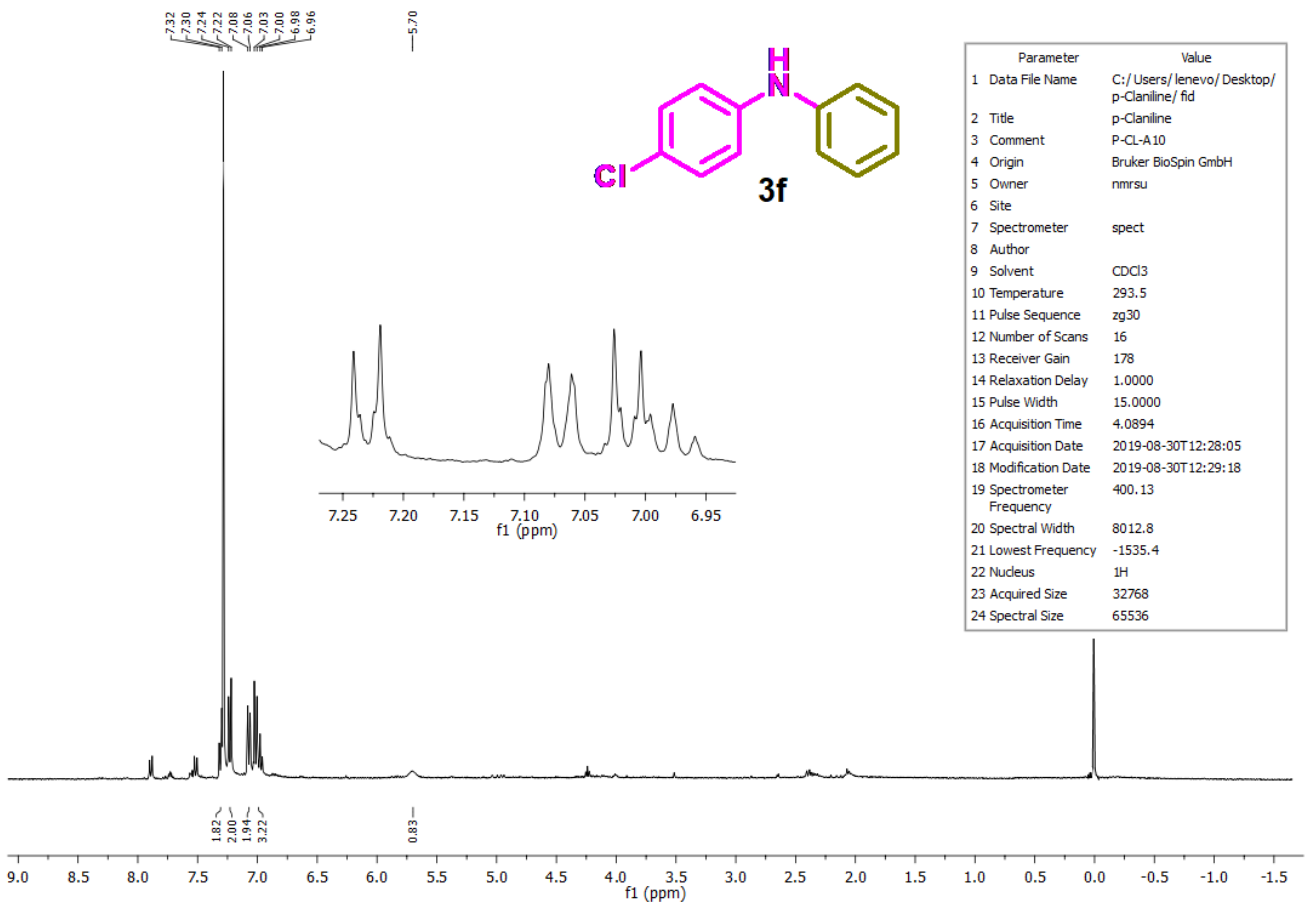


Figure S12. ^{13}C NMR spectra of *N*-(4-Chlorophenyl)benzenamine.

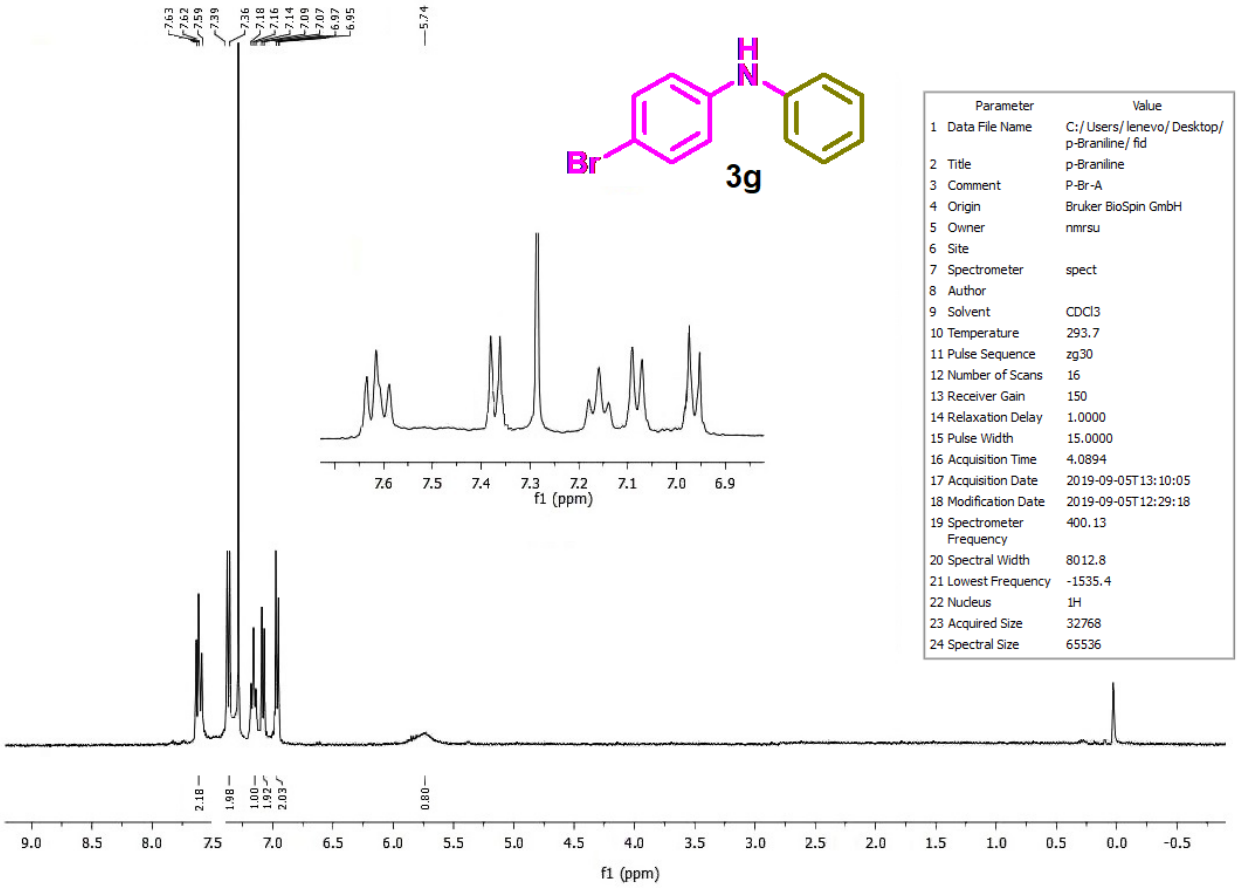


Figure S13. ^{1}H NMR spectra of *N*-(4-Bromophenyl)benzenamine.

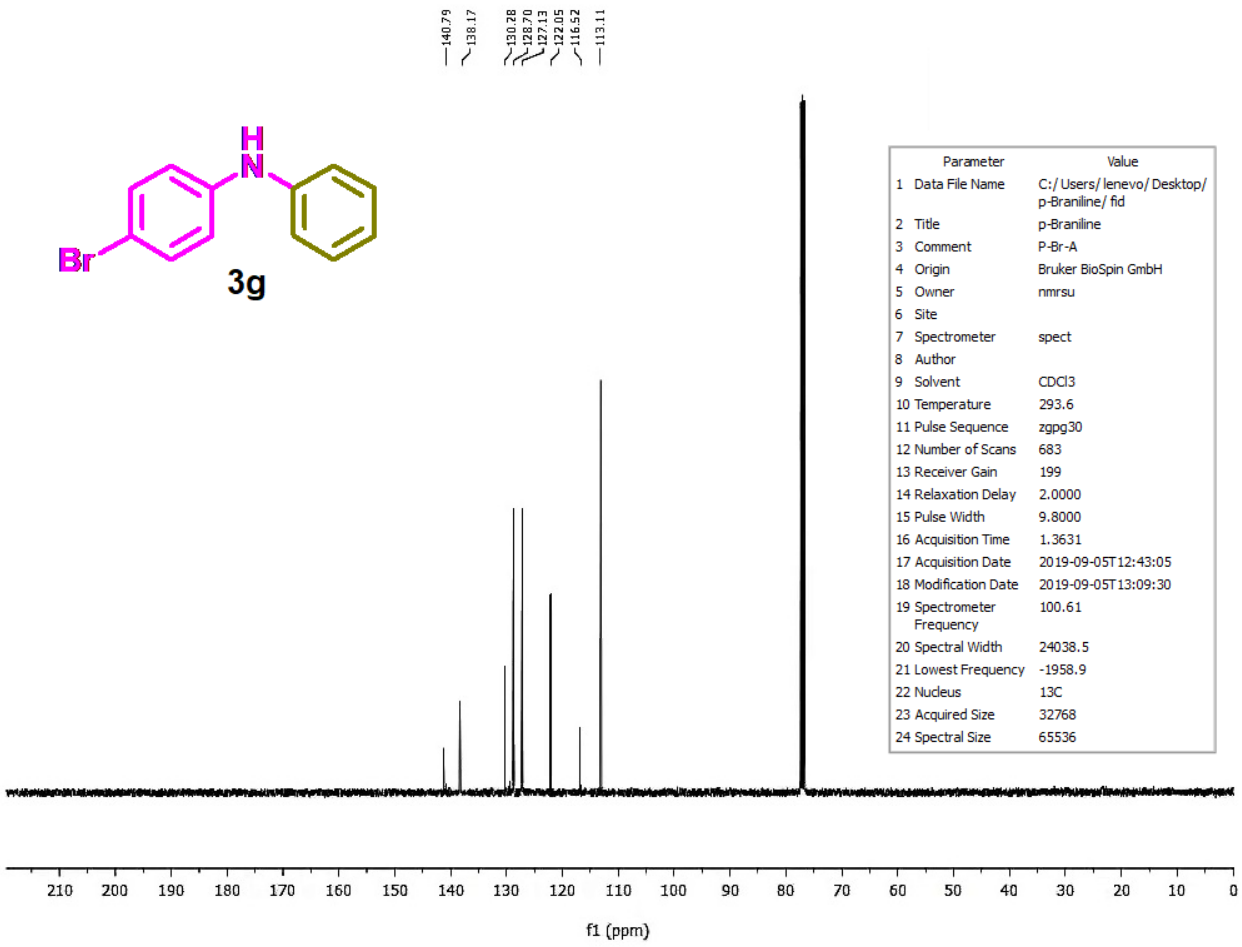


Figure S14. ^{13}C NMR spectra of *N*-(4-Bromophenyl)benzenamine.

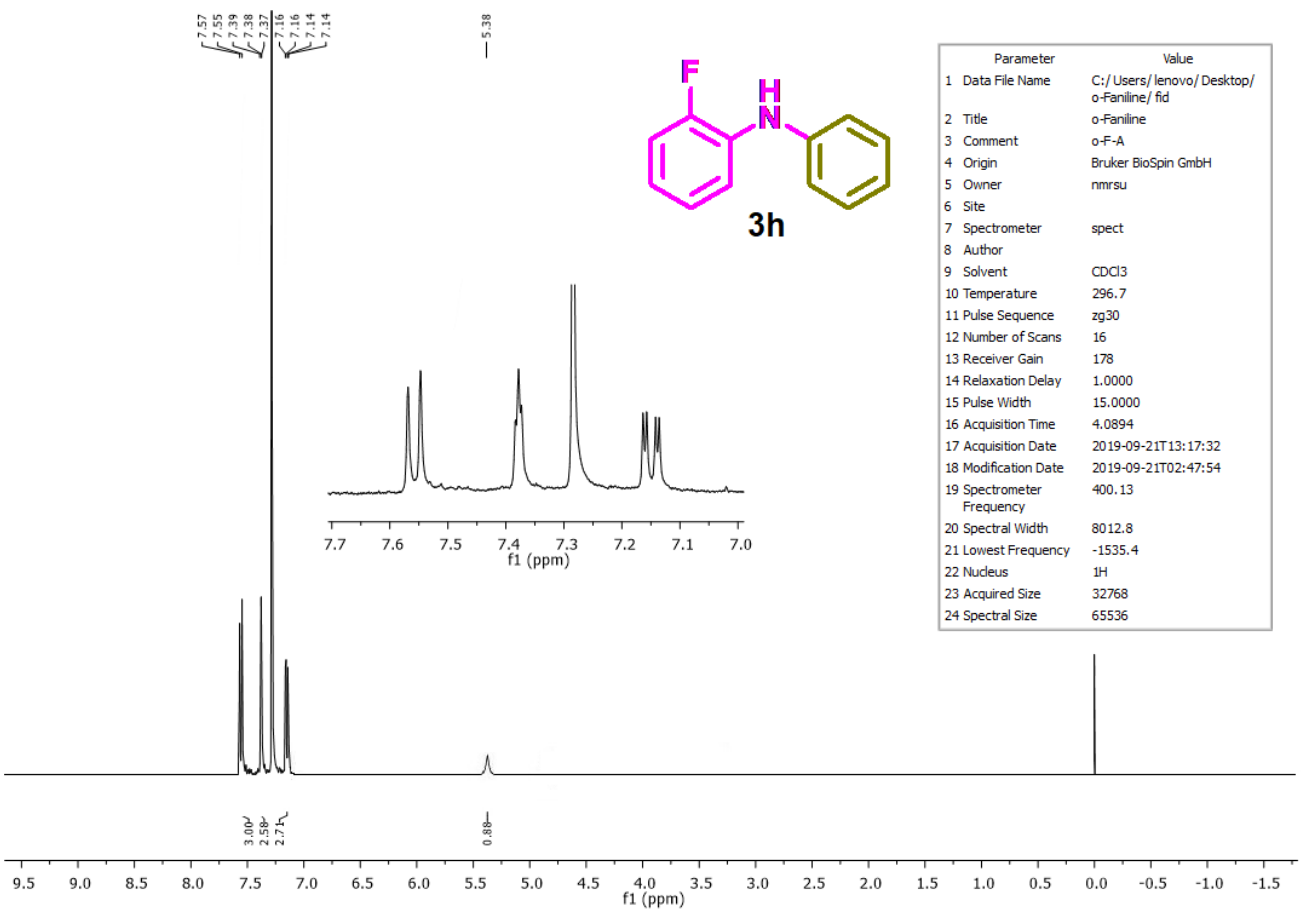


Figure S15. ^{1}H NMR spectra of *N*-(2-Fluorophenyl)benzenamine.

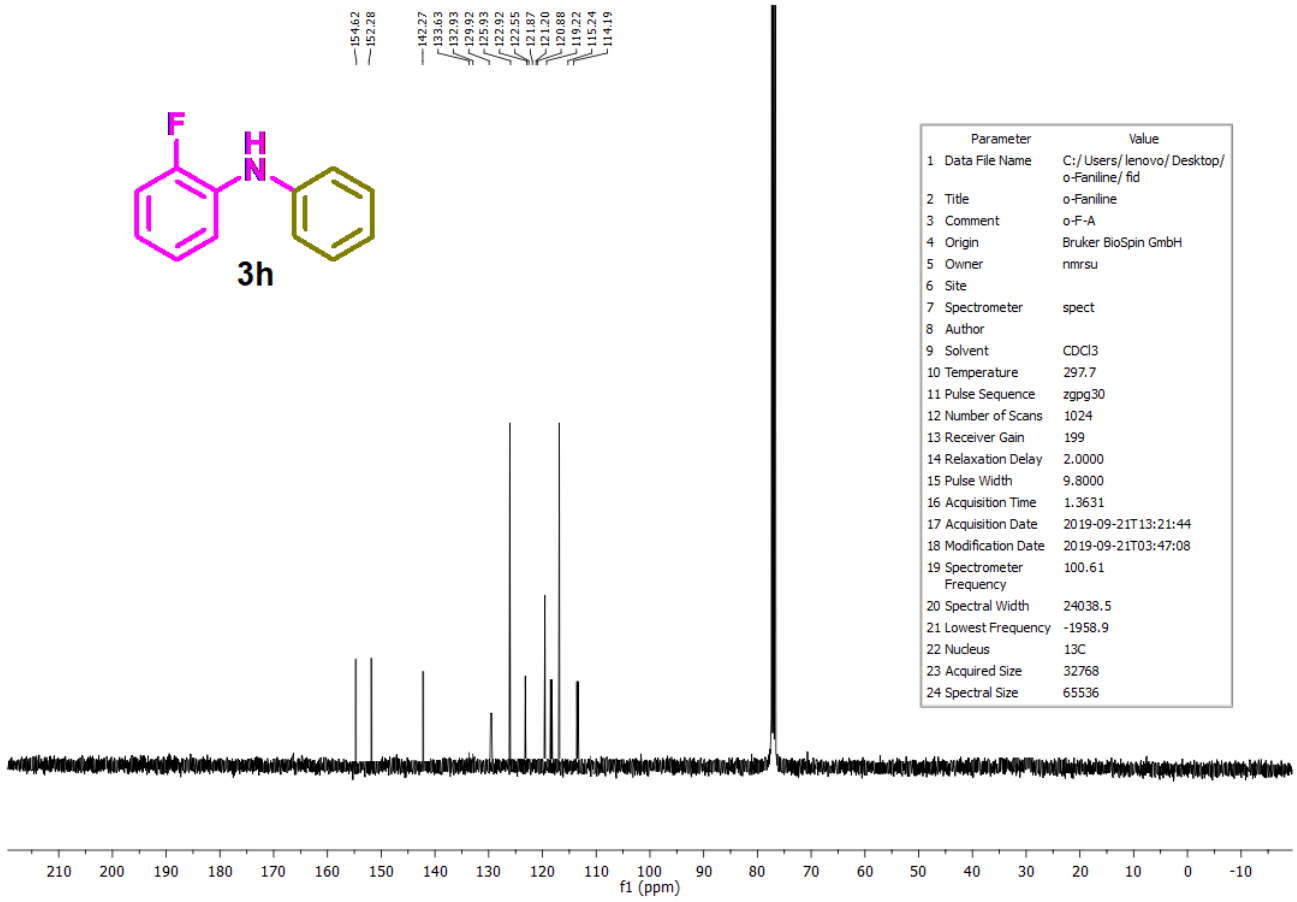


Figure S16. ^{13}C NMR spectra of *N*-(2-Fluorophenyl)benzenamine.

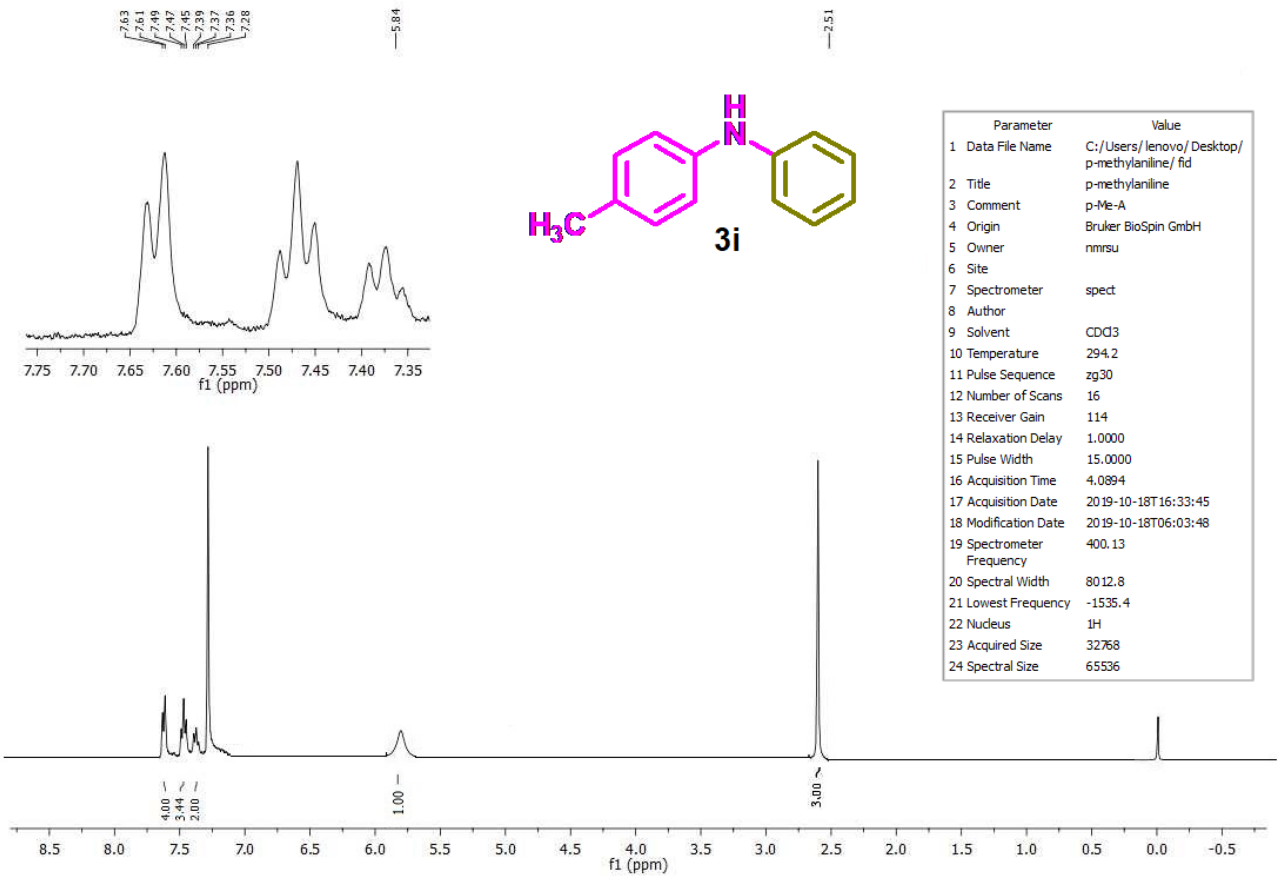


Figure S17. ^{1}H NMR spectra of *N*-(4-Methylphenyl) benzenamine.

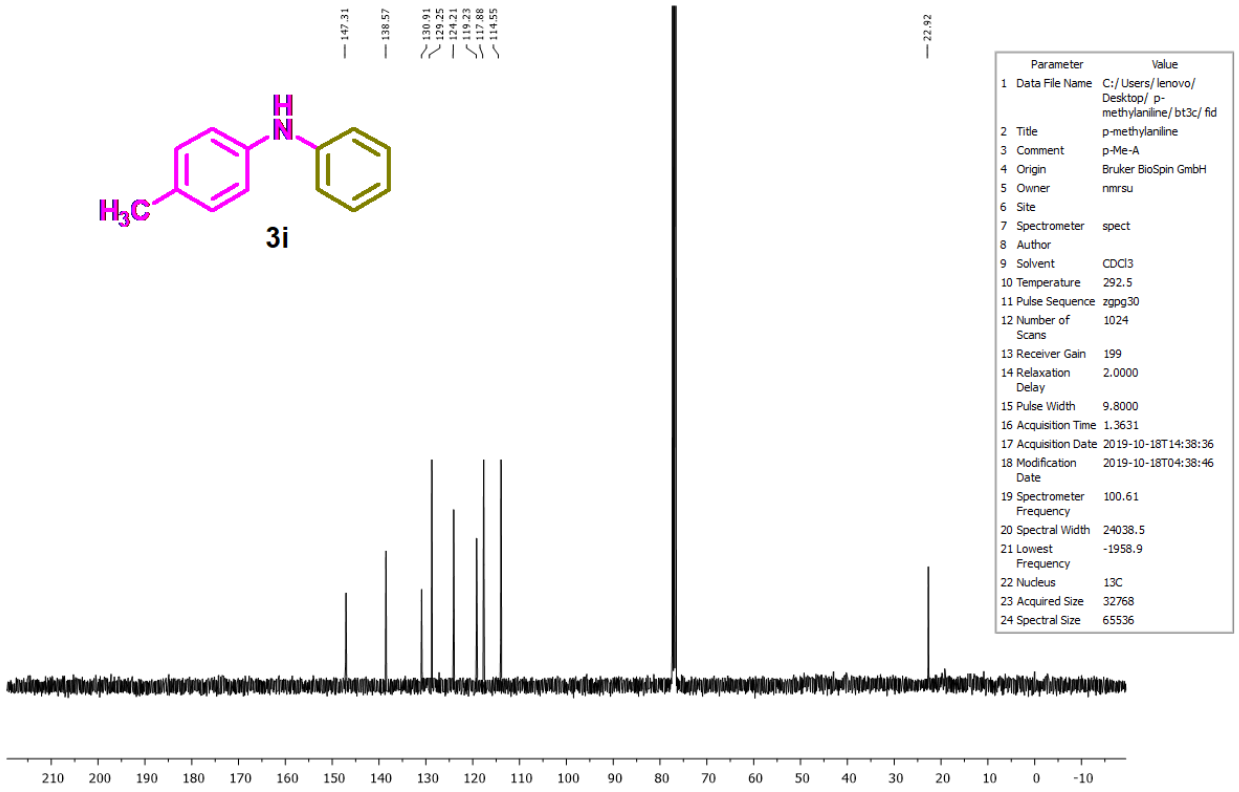


Figure S18. ^{13}C NMR spectra of *N*-(4-Methylphenyl) benzenamine.

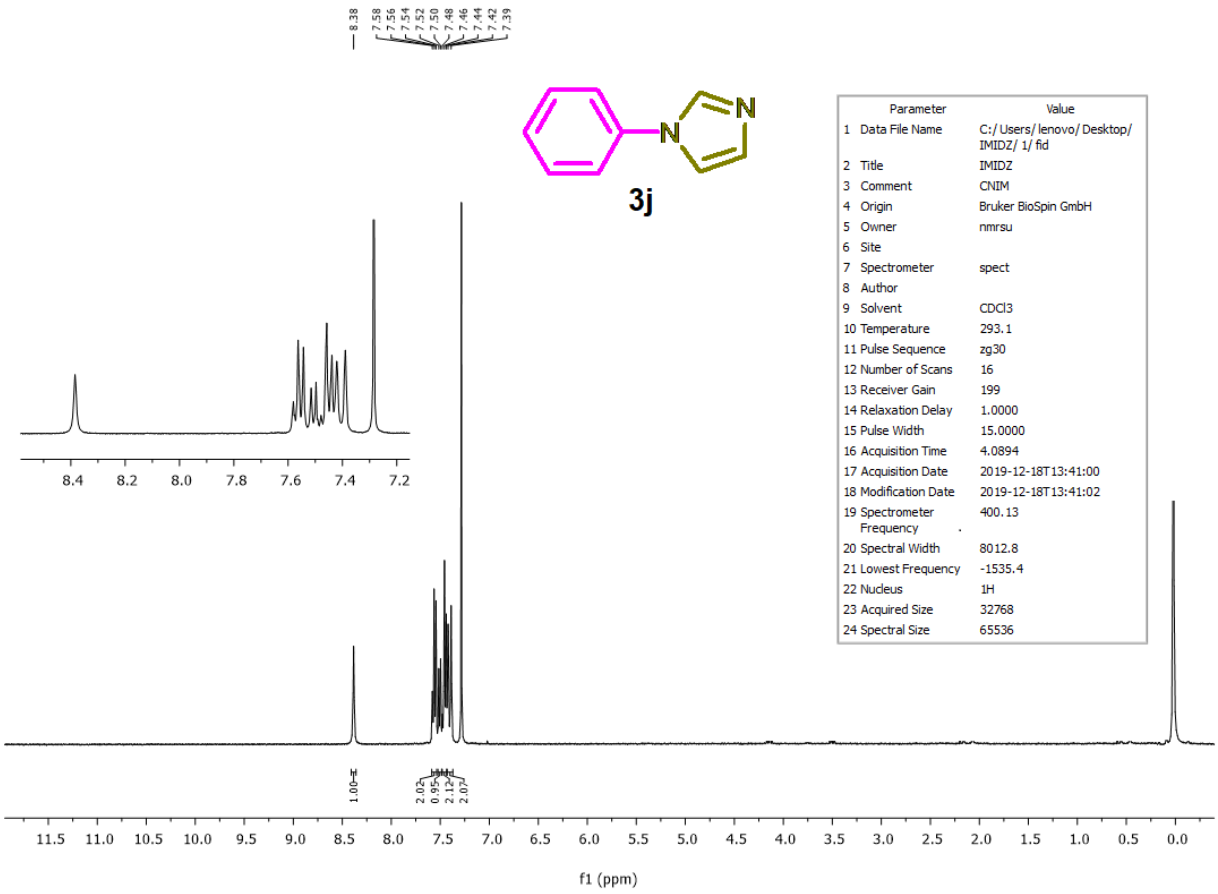


Figure S19. ^{1}H NMR spectra of 1-Phenyl-1*H*-imidazole.

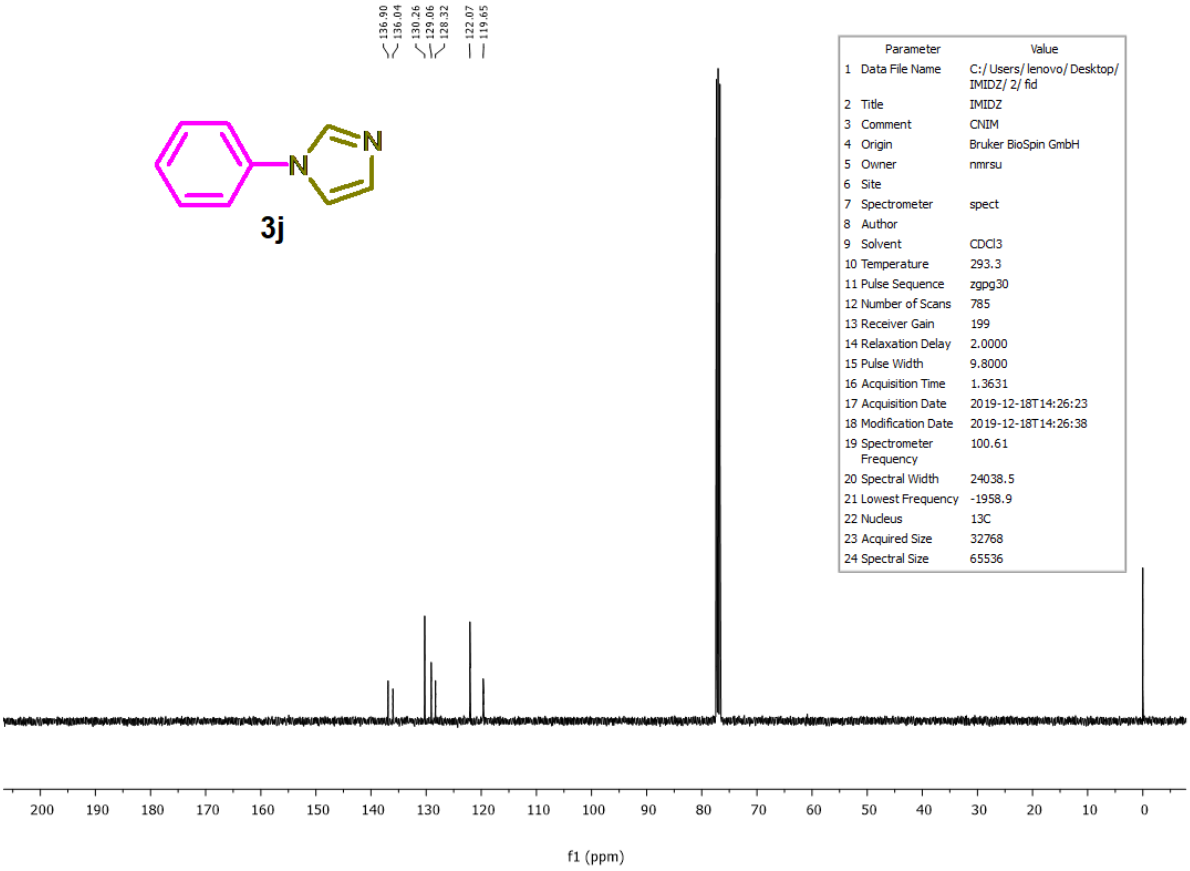


Figure S20. ^{13}C NMR spectra of 1-Phenyl-1*H*-imidazole.

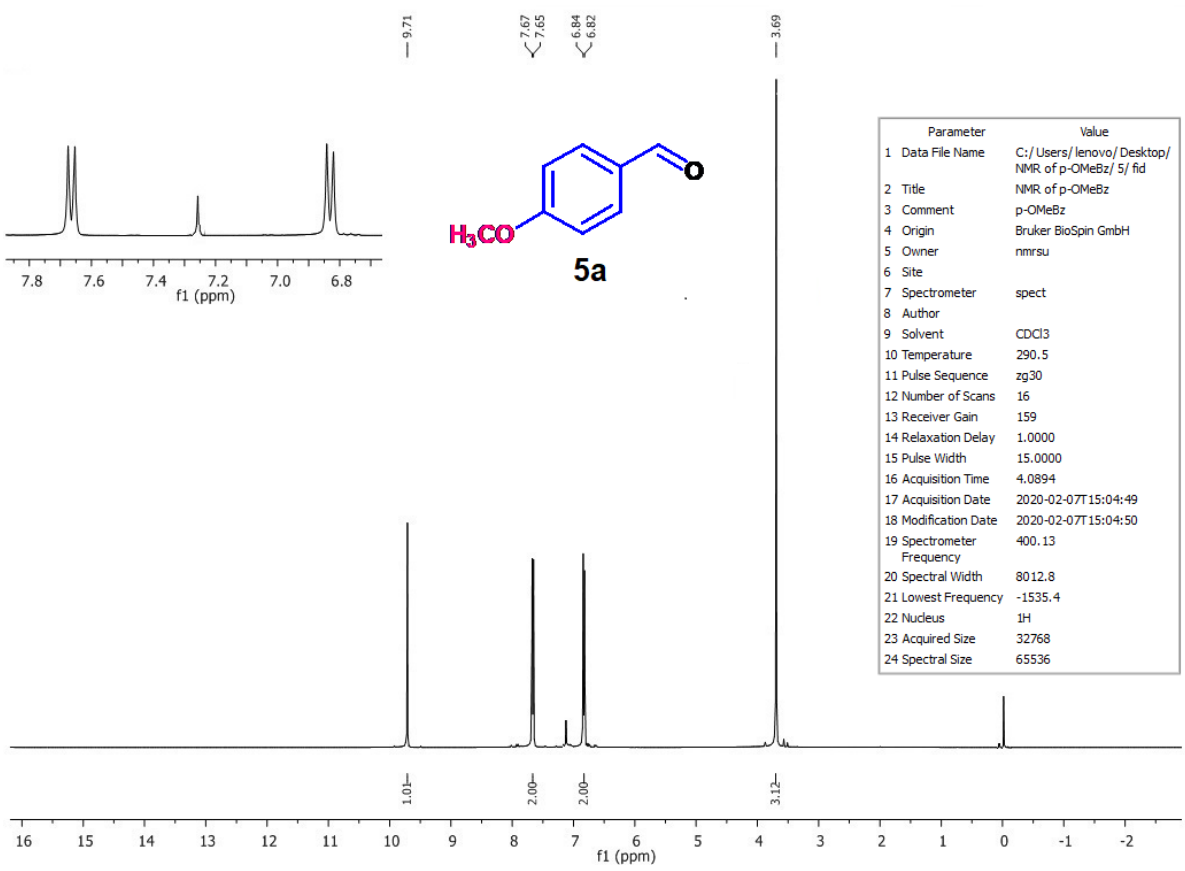


Figure S21. ^{1}H NMR spectra of 4-Methoxybenzaldehyde.

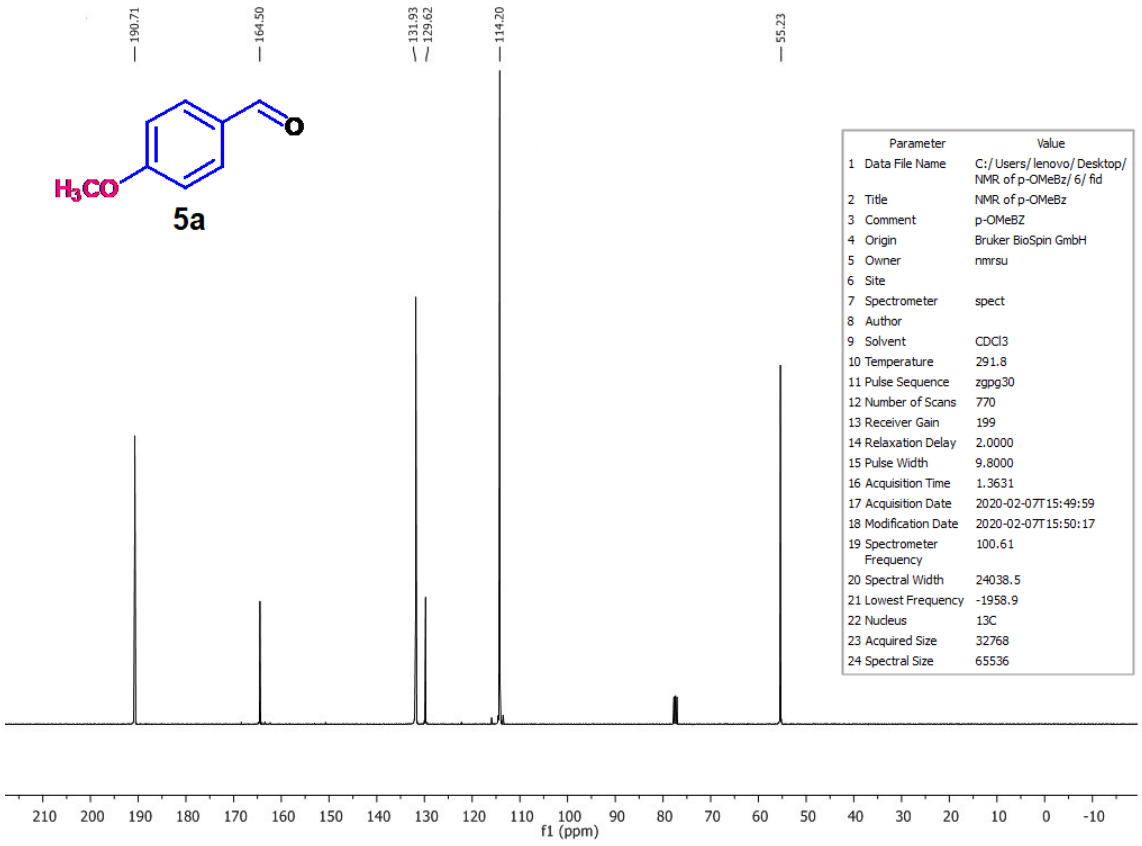


Figure S22. ^{13}C NMR spectra of 4-Methoxybenzaldehyde.

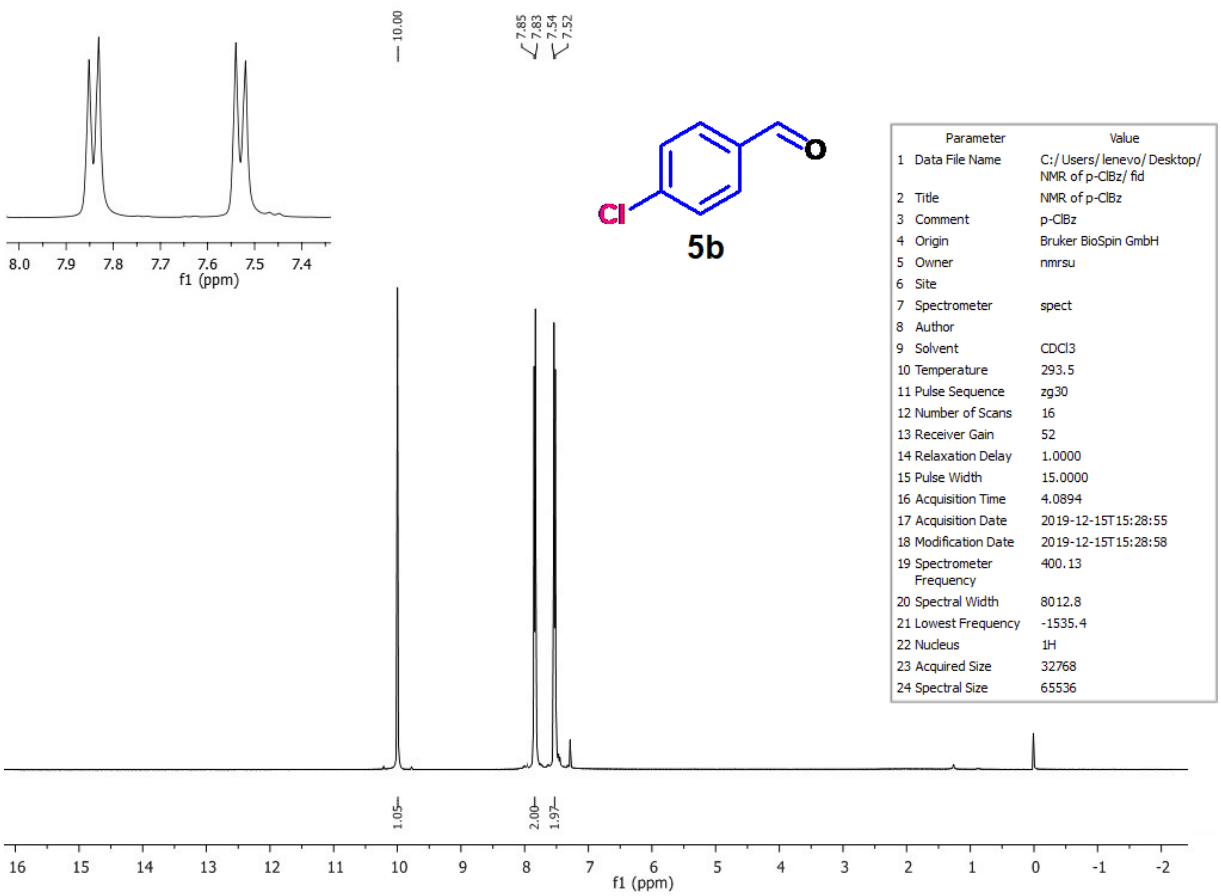


Figure S23. ^{1}H NMR spectra of 4-Chlorobenzaldehyde.

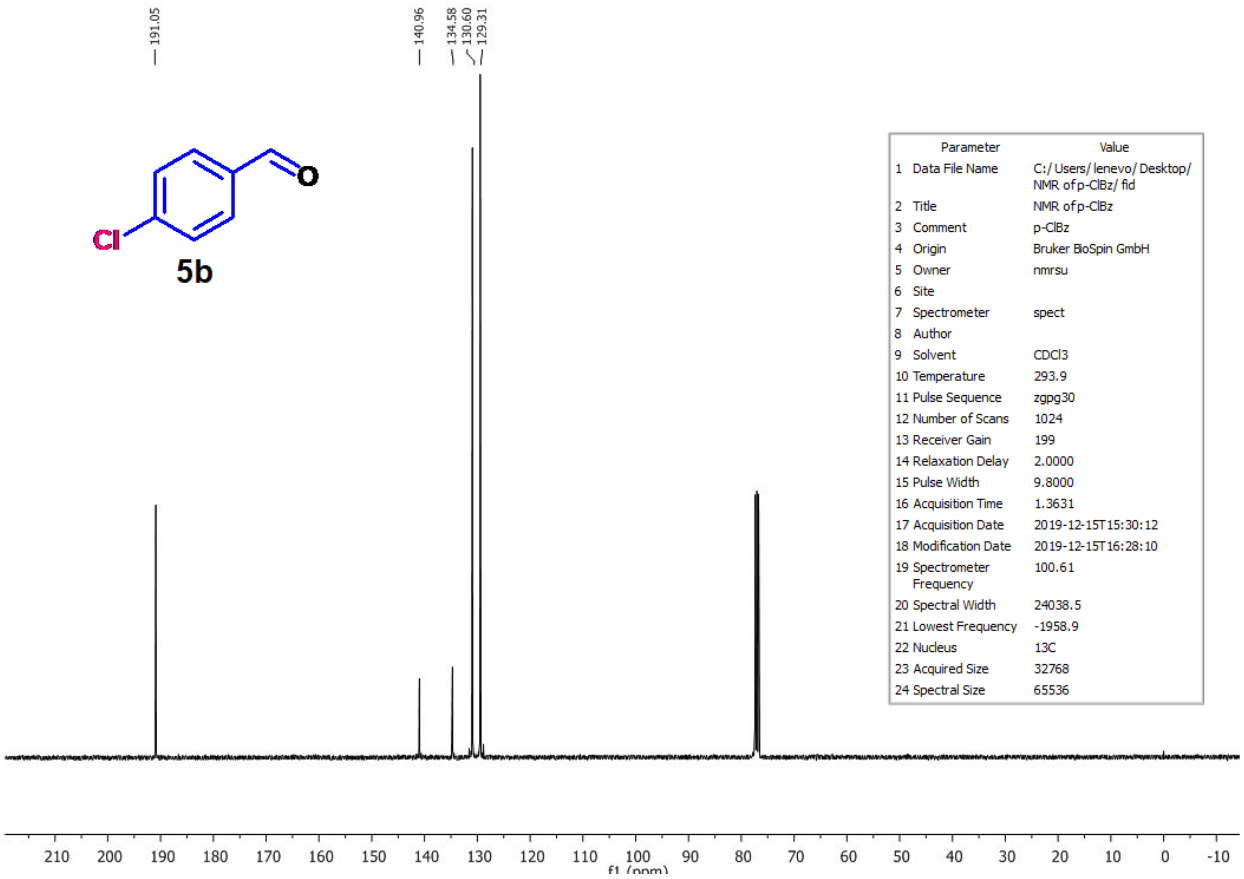


Figure S24. ^{13}C NMR spectra of 4-Chlorobenzaldehyde.

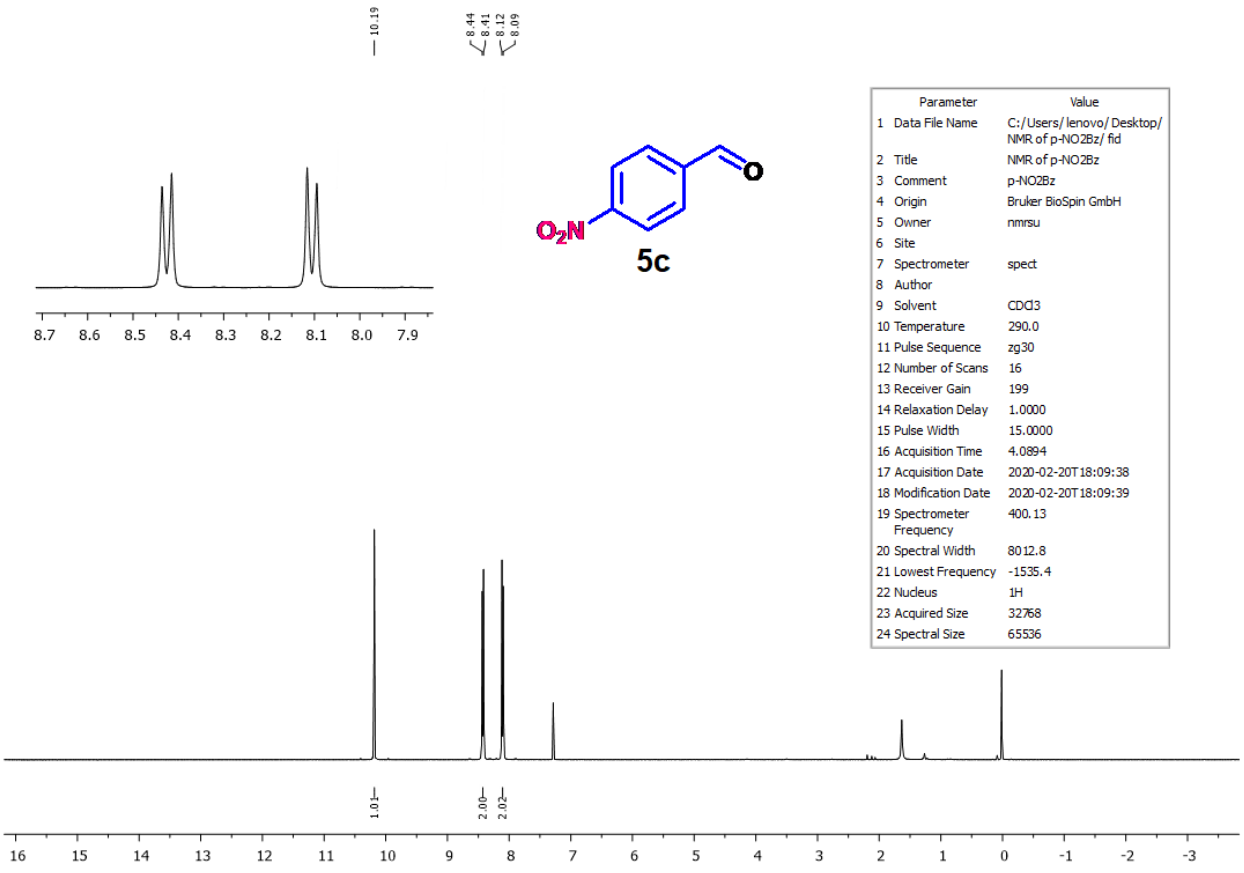


Figure S25. ^{1}H NMR spectra of 4-Nitrobenzaldehyde.

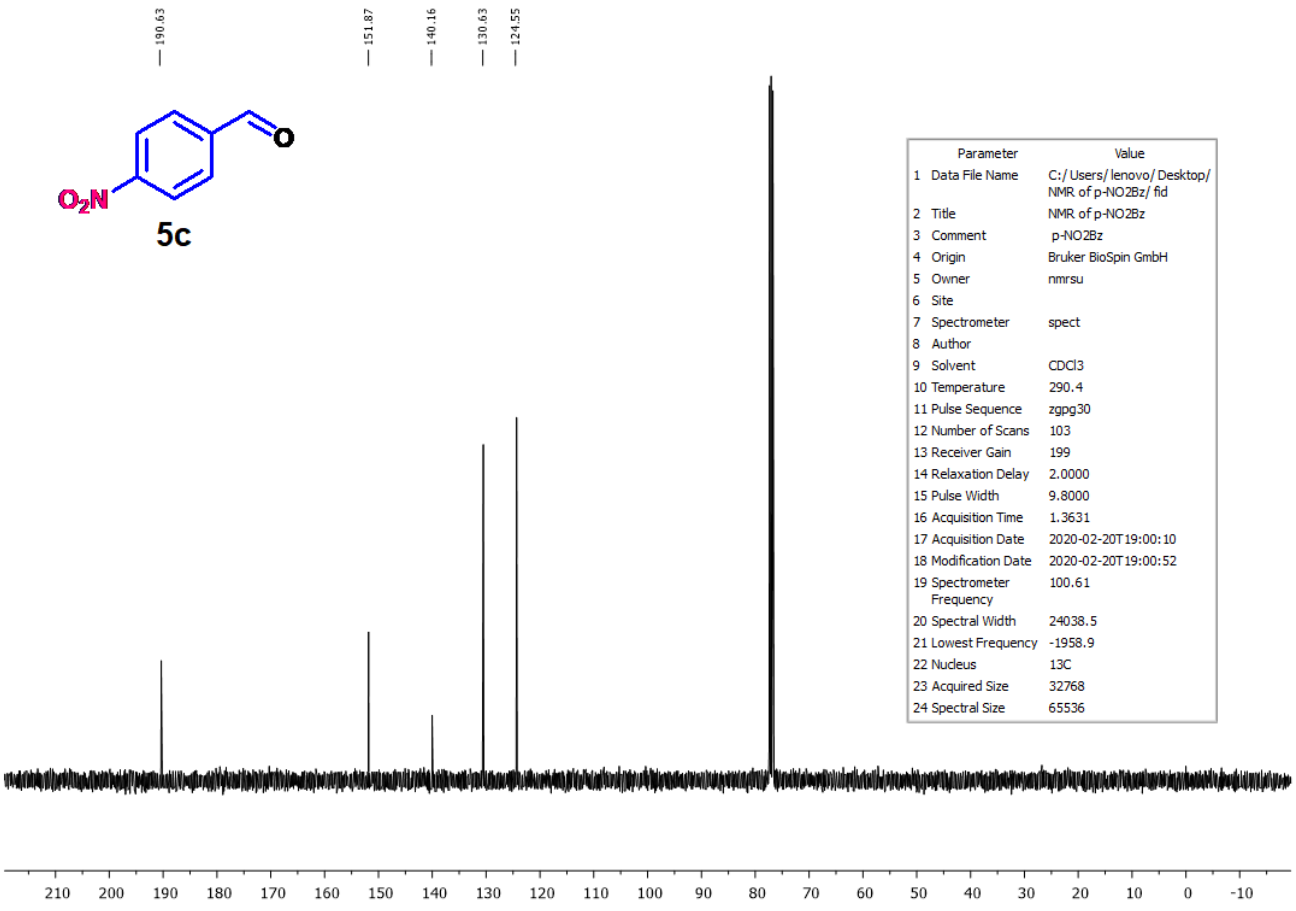


Figure S26. ^{13}C NMR spectra of 4-Nitrobenzaldehyde.

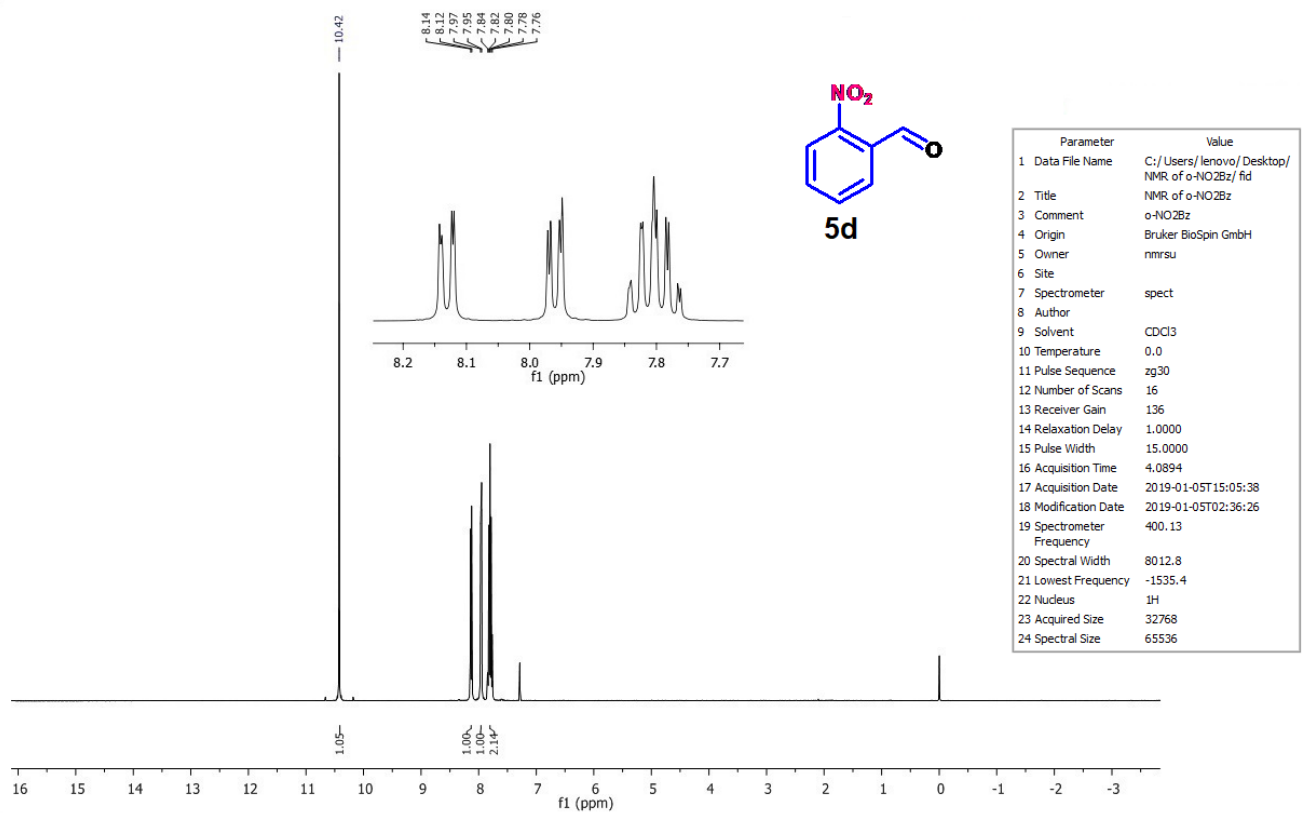


Figure S27. ^{1}H NMR spectra of 2-Nitrobenzaldehyde.

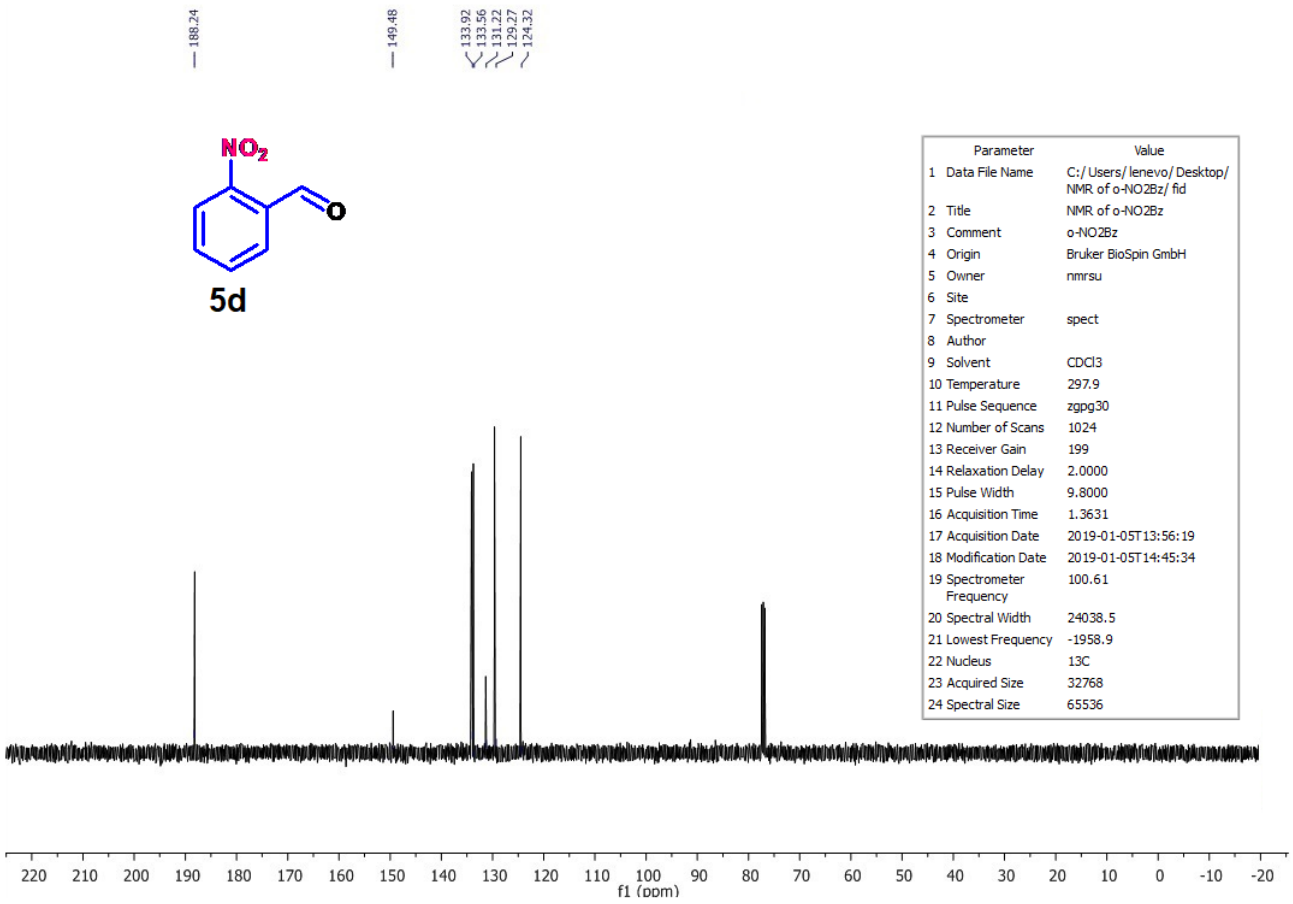
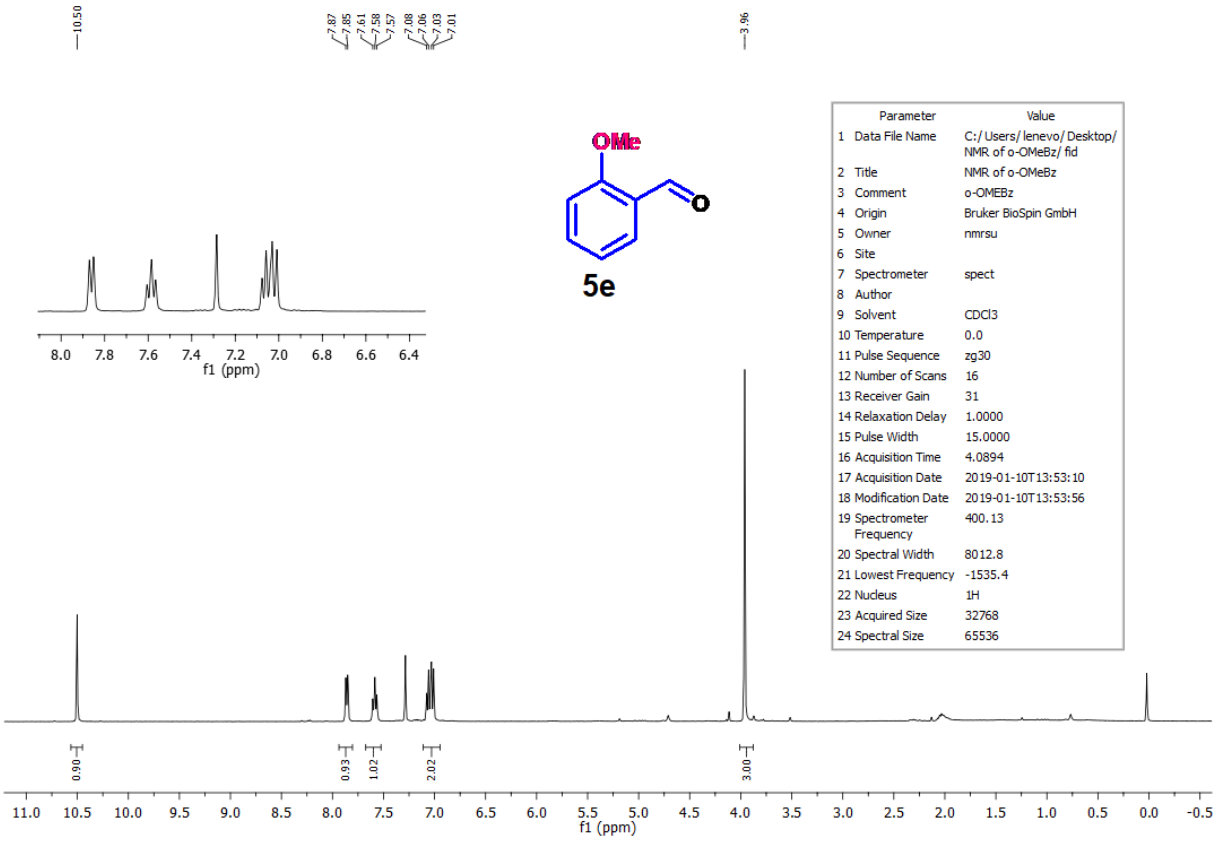


Figure S28. ^{13}C NMR spectra of 2-Nitrobenzaldehyde.



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3	Comment	o-OMEBz
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6	Site	
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8	Author	
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Figure S29. ^{1}H NMR spectra of 2-Methoxybenzaldehyde.

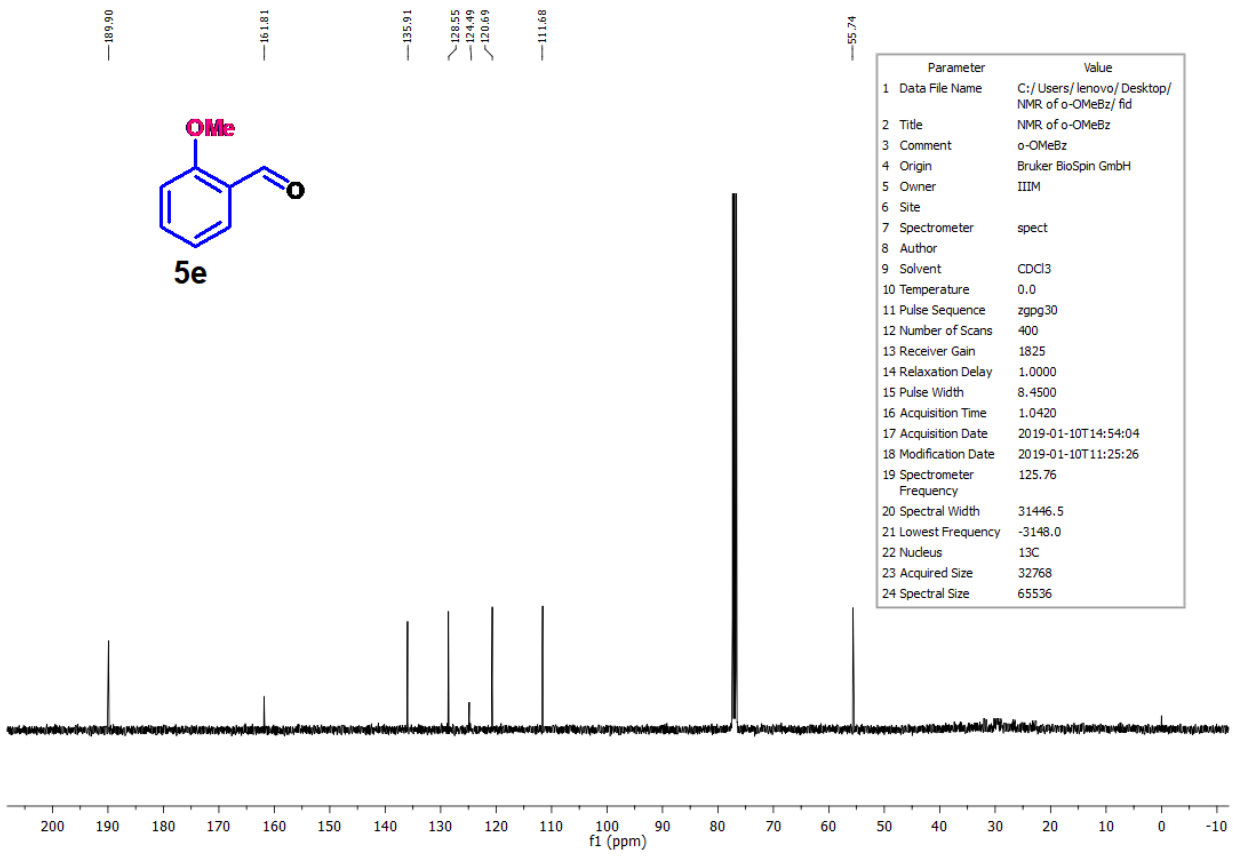

Figure S30. ^{13}C NMR spectra of 2-Methoxybenzaldehyde.

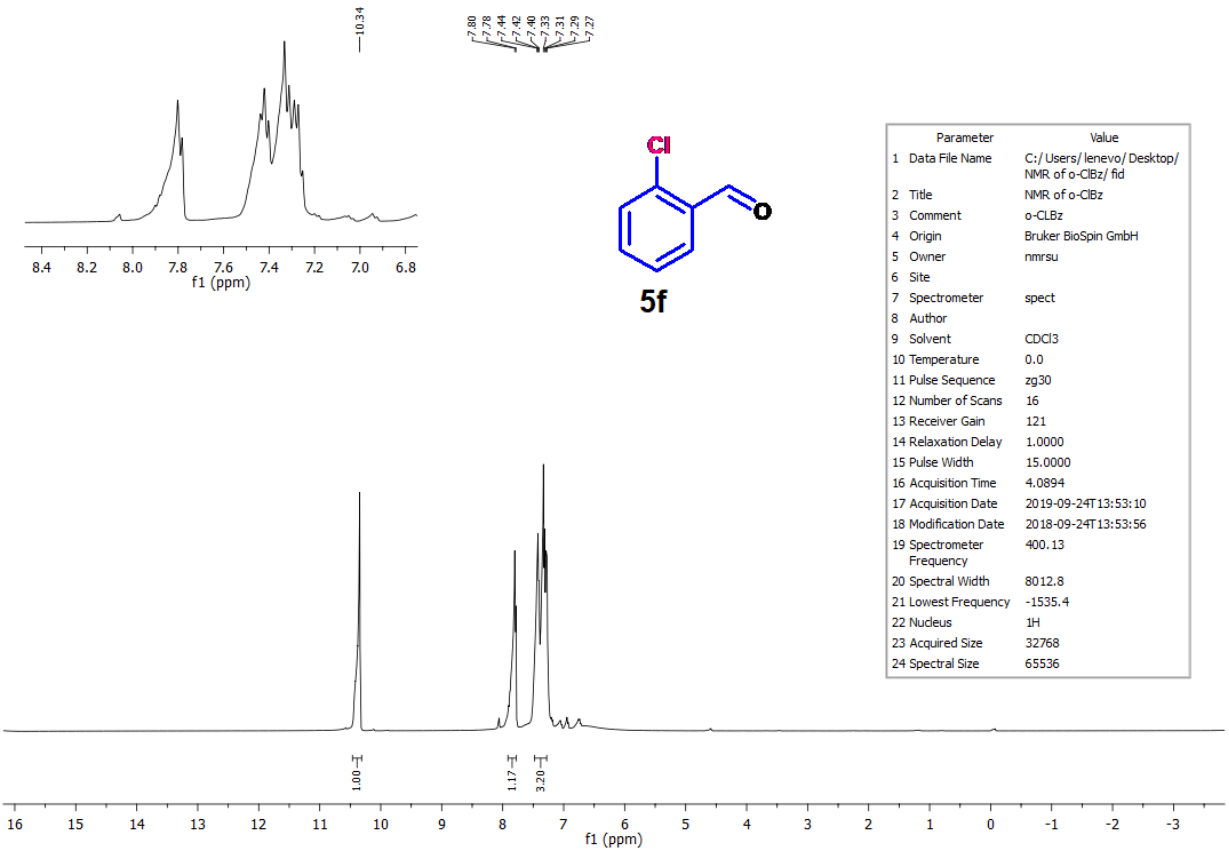

Figure S31. ^{1}H NMR spectra of 2-Chlorobenzaldehyde.

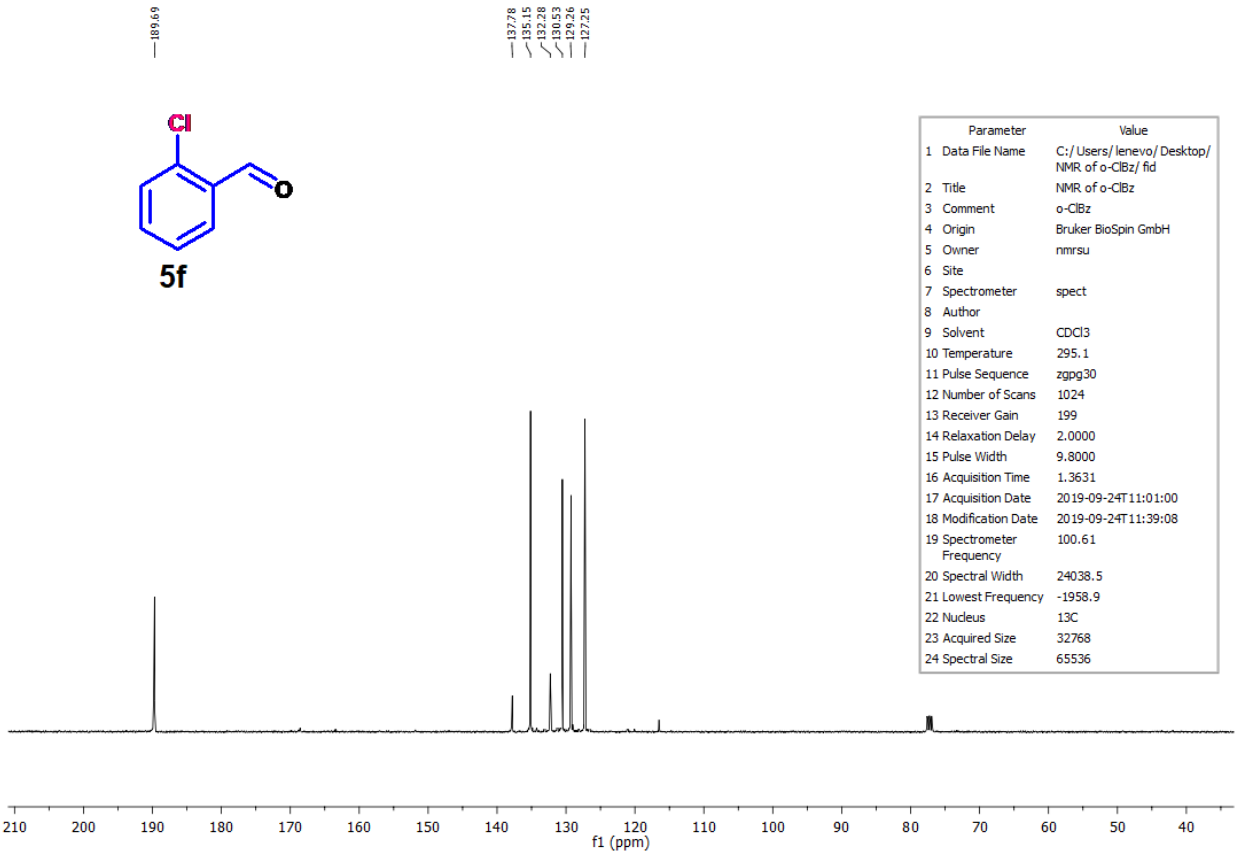

Figure S32. ^{13}C NMR spectra of 2-Chlorobenzaldehyde.

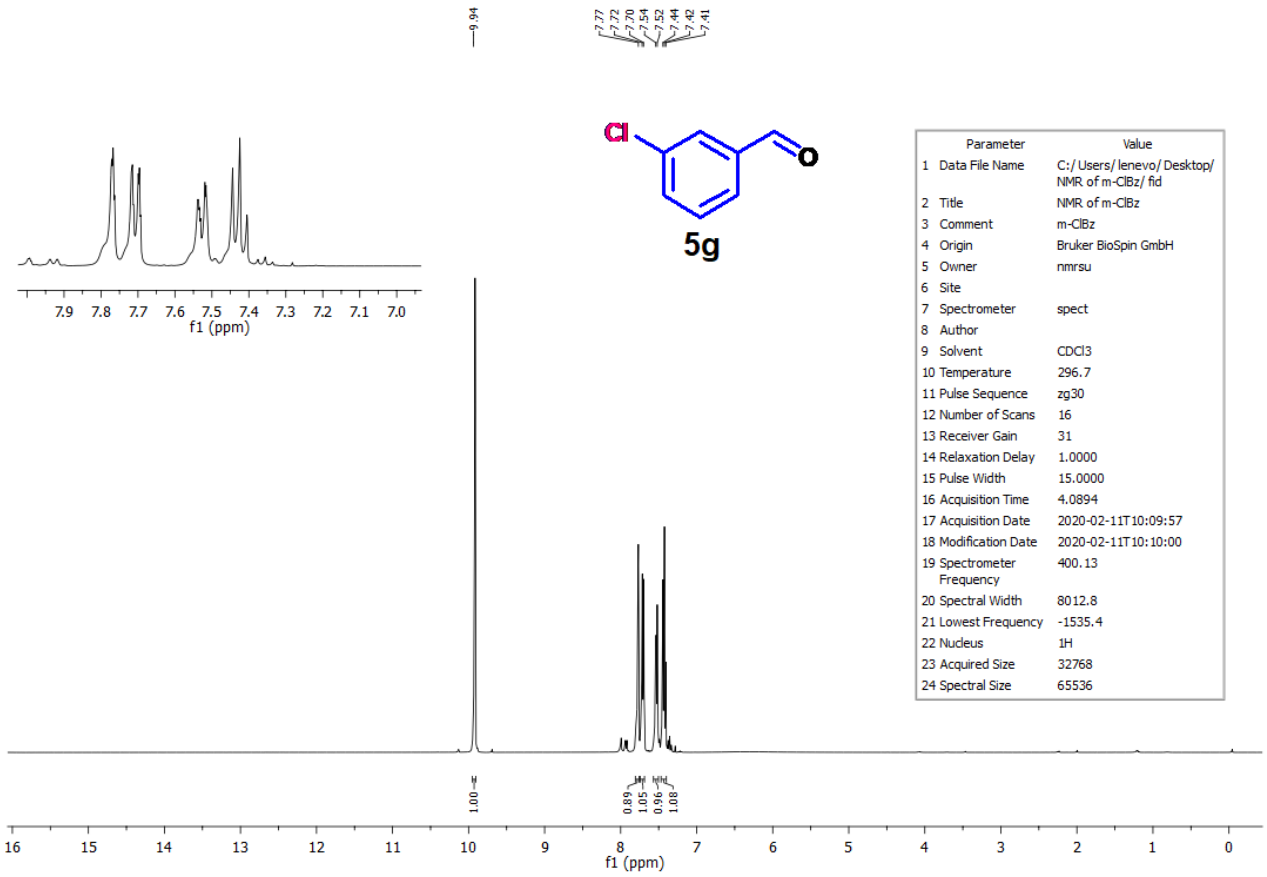

Figure S33. ^{1}H NMR spectra of 3-Chlorobenzaldehyde.

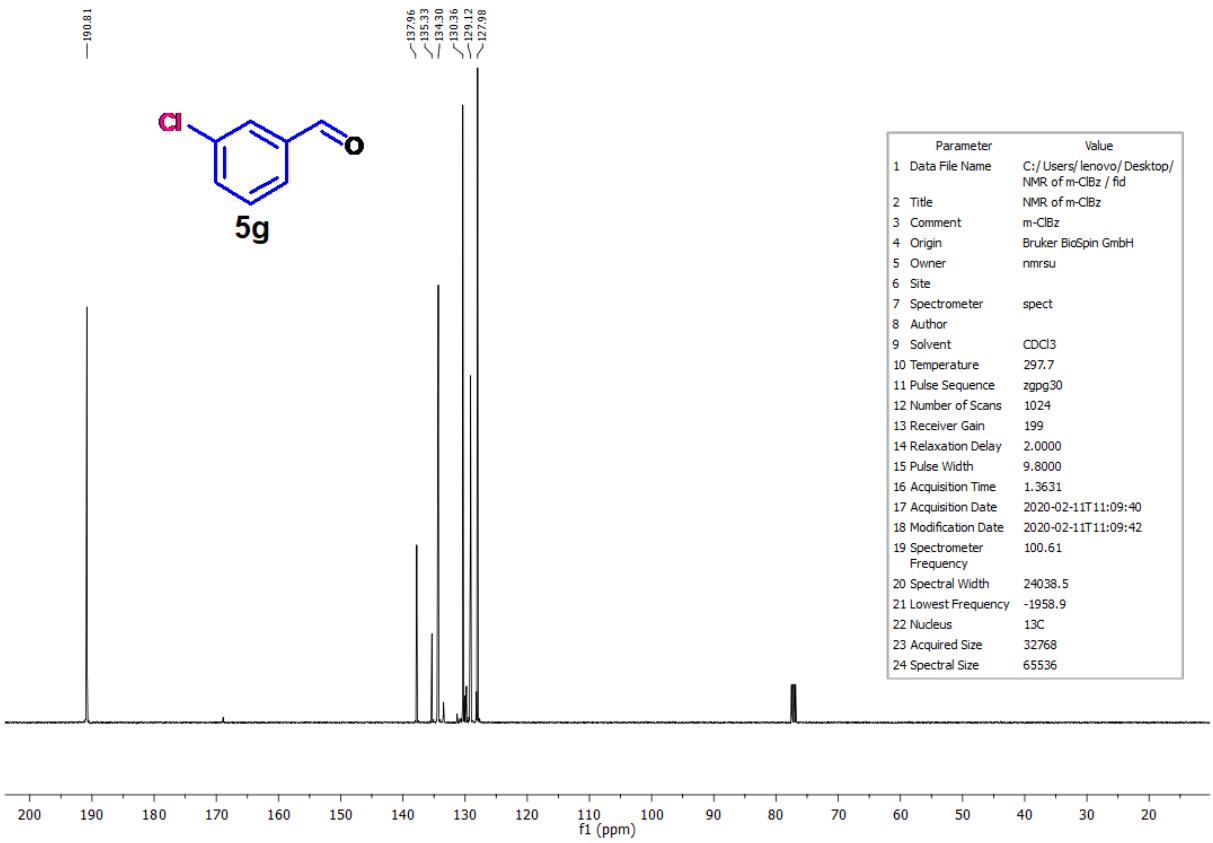

Figure S34. ^{13}C NMR spectra of 3-Chlorobenzaldehyde.

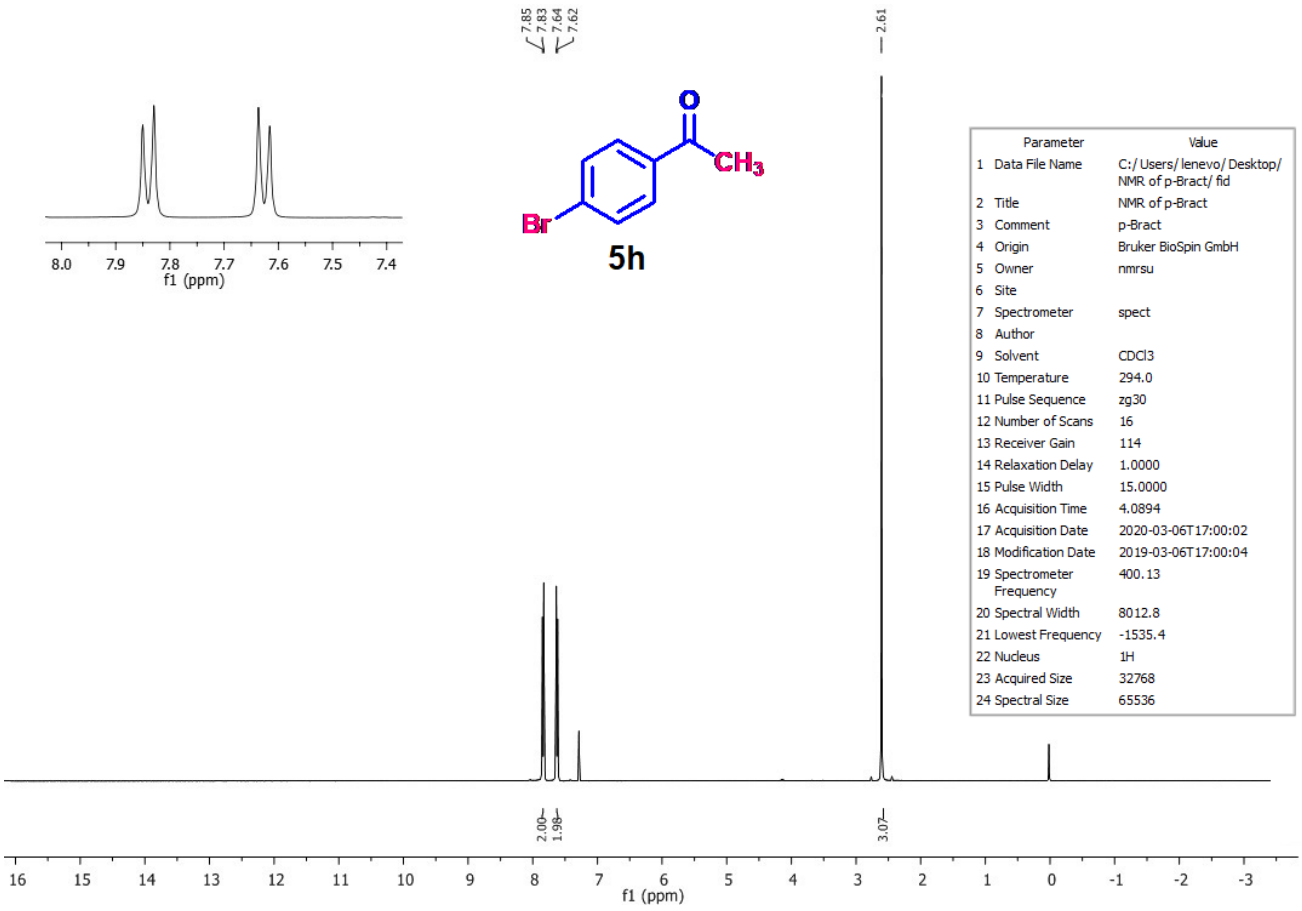

Figure S35. ^{1}H NMR spectra of 4-Bromoacetophenone.

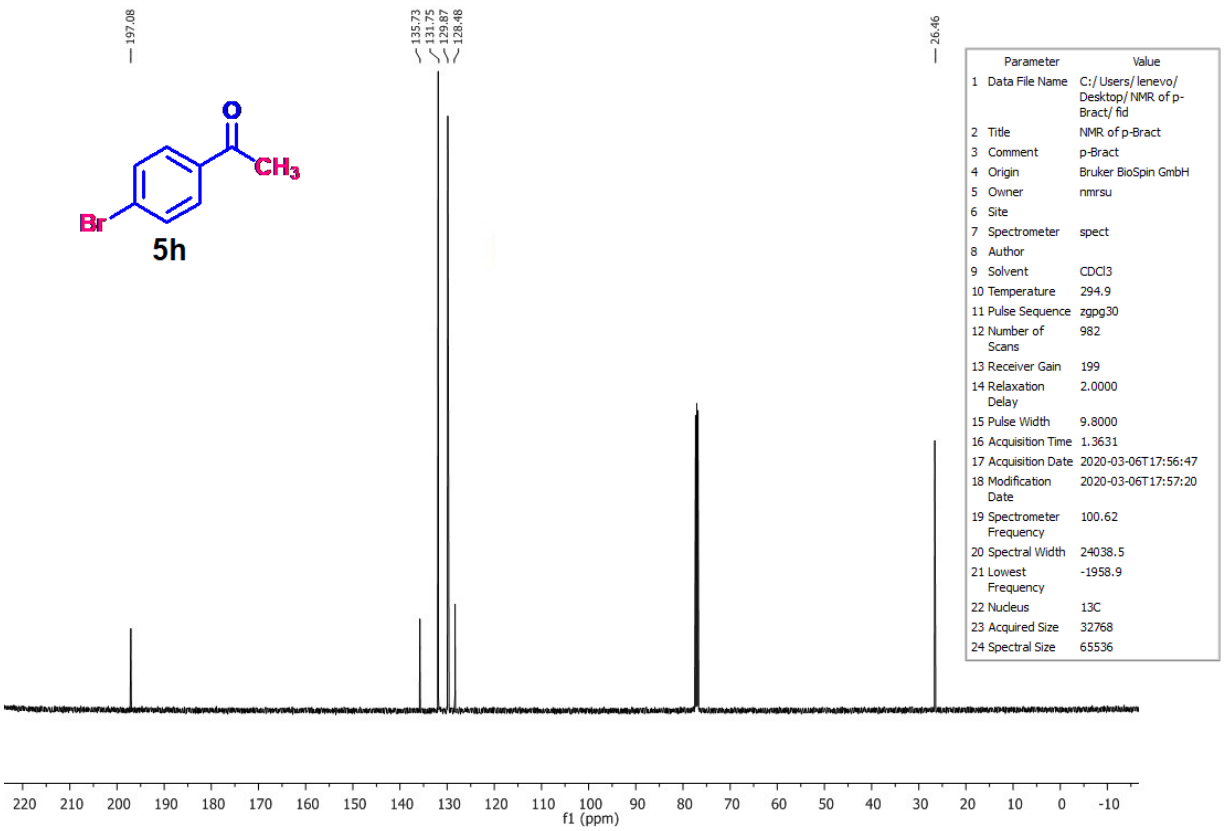

Figure S36. ^{13}C NMR spectra of 4-Bromoacetophenone.

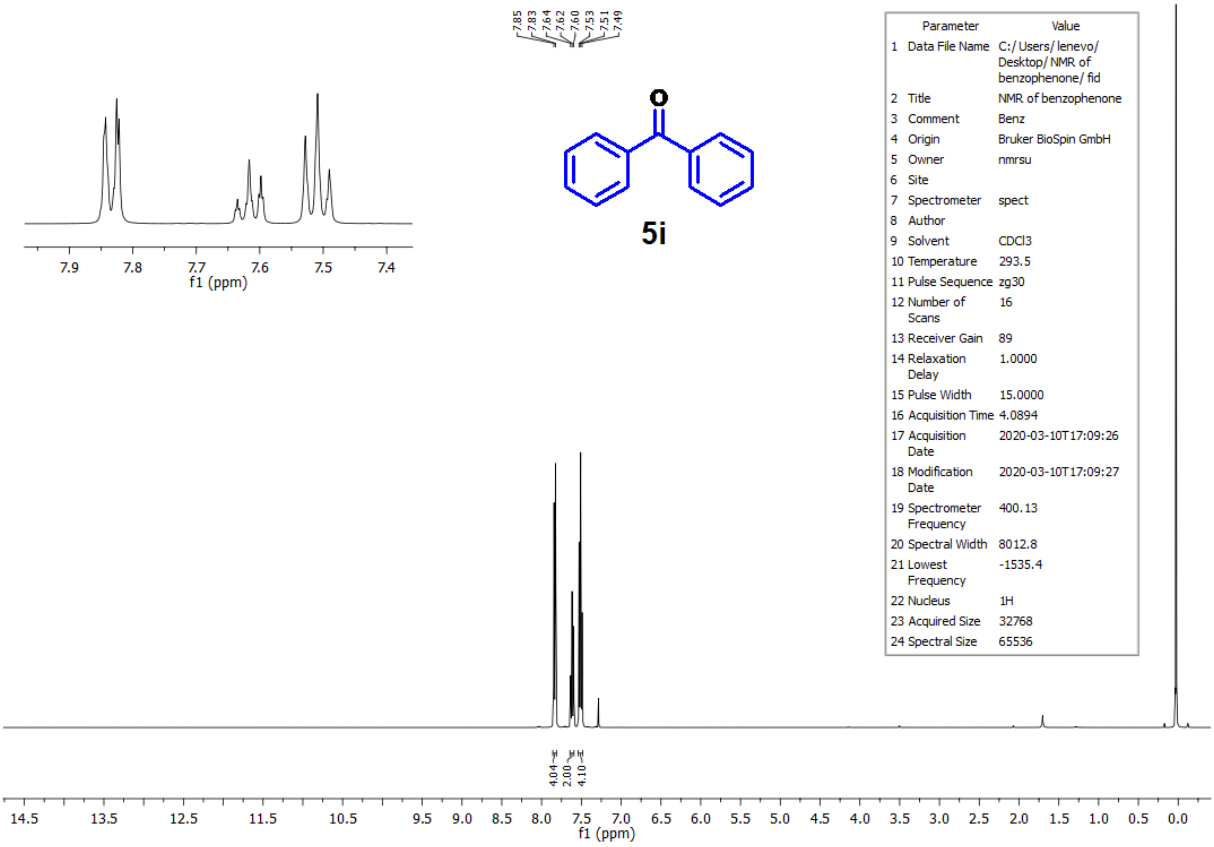

Figure S37. ^{1}H NMR spectra of benzophenone.

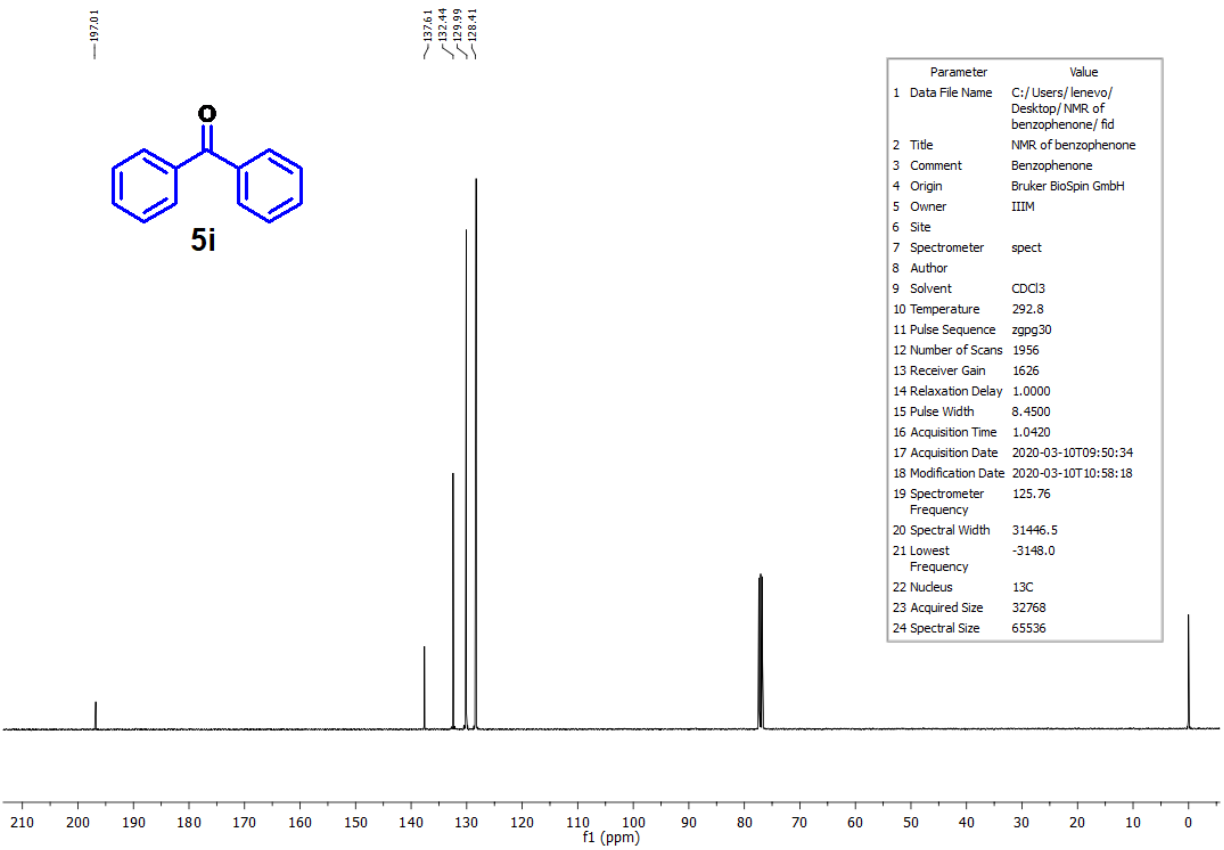

Figure S38. ^{13}C NMR spectra of benzophenone.

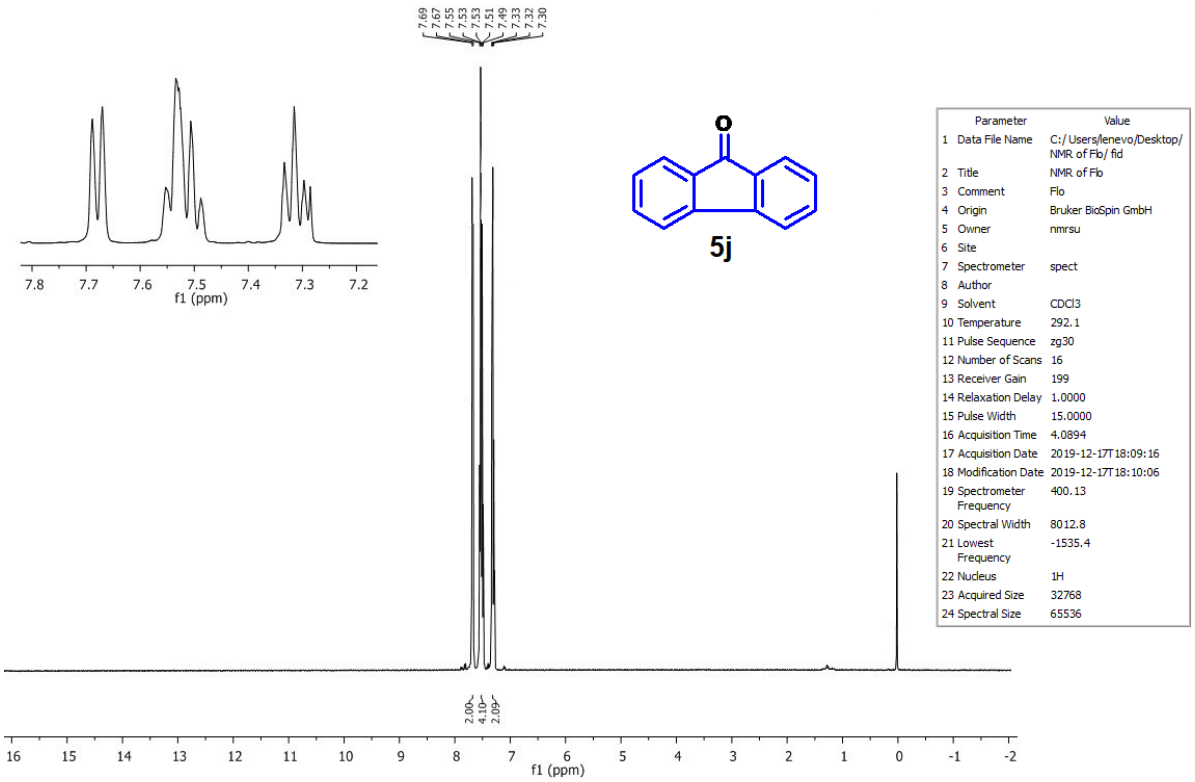

Figure S39. ^{1}H NMR spectra of fluorenone.

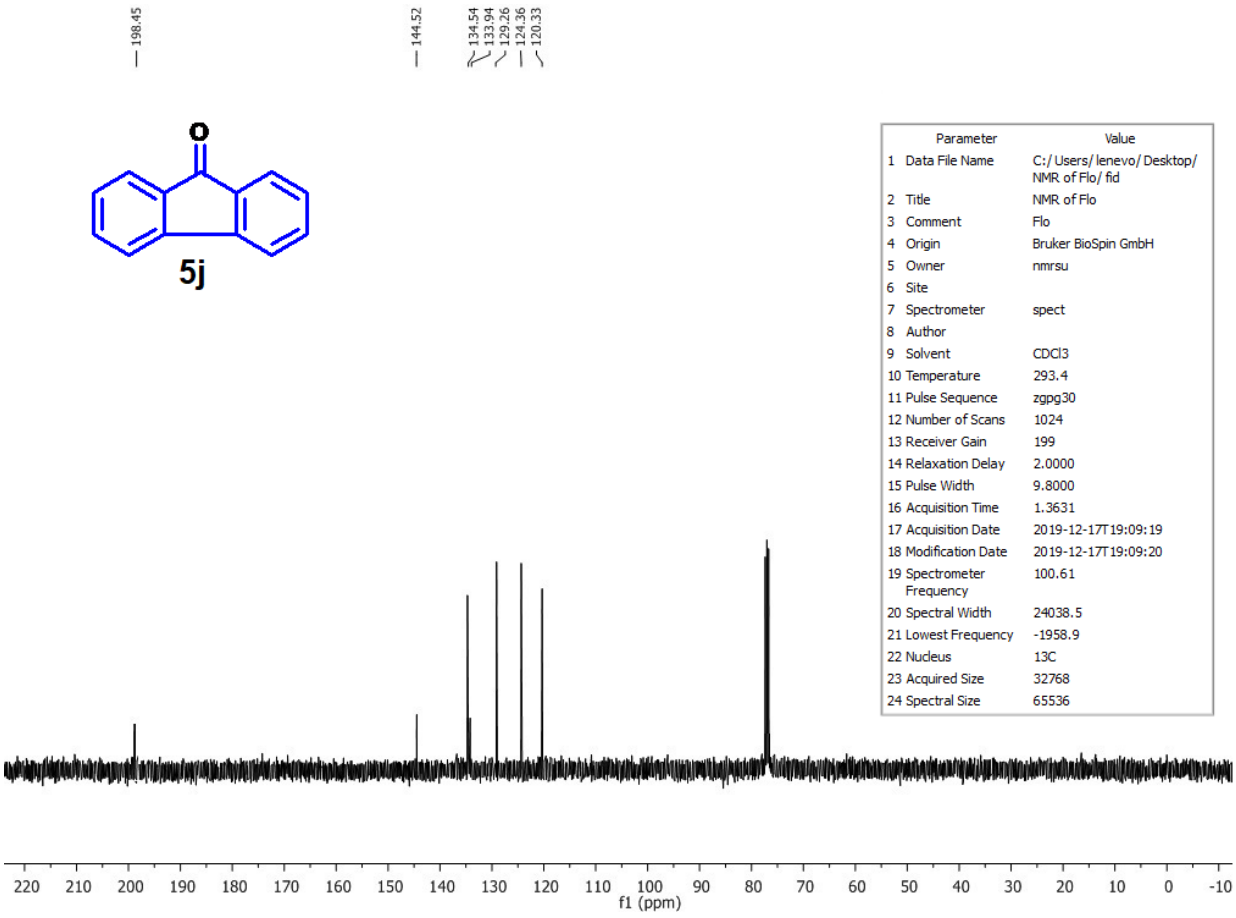

Figure S40. ^{13}C NMR spectra of fluorenone.

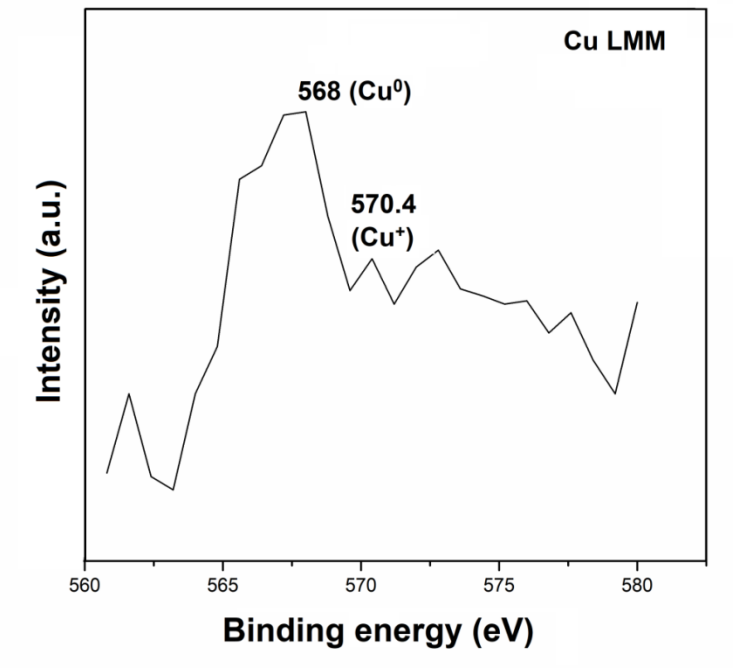

Figure S41. Cu LMM Auger spectrum of Cu@KF-C/$CoFe_2O_4$.

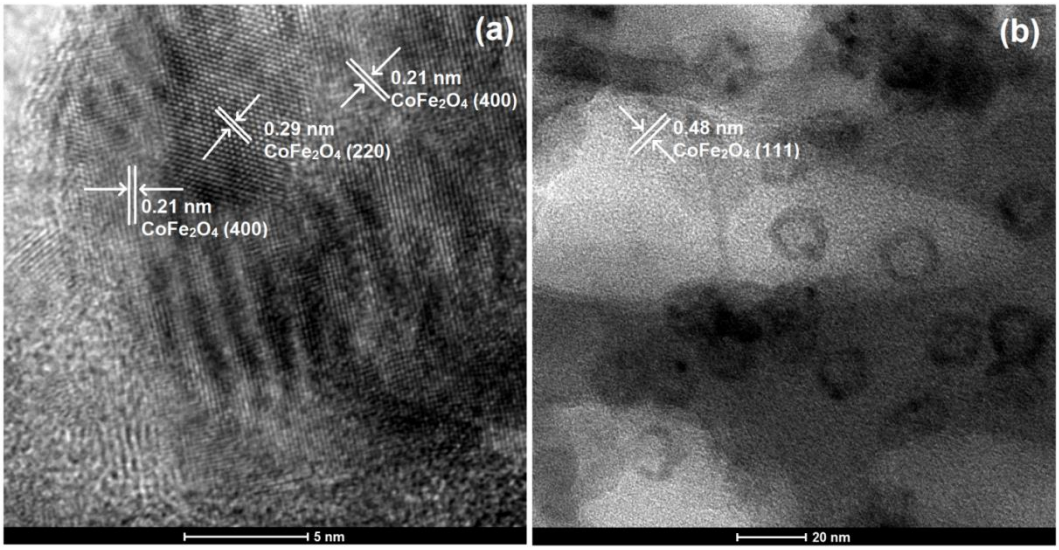

Figure S42. HR-TEM micrographs shows d-spacing of cobalt ferrite (a,b).

Table S1. Atomic percentage table of various elements present in all of the four catalysts using XPS analysis.

Elements	Analysis-content (At %)			
	Catalyst			
	Cu@KF C/$CoFe_2O_4$	Cu@KF-C/$NiFe_2O_4$	Cu@KF-C/$ZnFe_2O_4$	Cu@KF-C/$CuFe_2O_4$
C	56.31	52.22	55.67	49.60
O	23.18	32.20	32.28	36.76
K	1.67	1.45	1.40	1.35
F	1.80	1.70	1.62	1.58
Fe	7.67	7.97	5.98	6.99
Co	6.44	-	-	-
Ni	-	2.80	-	-
Zn	-	-	1.65	-
Cu	2.93	1.66	1.40	3.72

Table S2. Compared atomic percentage for Cu@KFC/$CoFe_2O_4$ using XPS and SEM-EDX analysis.

Elements	Bulk atomic percentage determined by SEM-EDX analysis	Surface atomic percentage determined by XPS analysis
C	49.07	56.31
O	38.81	23.18
K	1.31	1.67
F	1.68	1.80
Fe	4.37	7.67
Co	2.43	6.44
Cu	2.33	2.93

Table S3. Comparison of the catalytic activity of Cu@KF-C/$CoFe_2O_4$ with some reported catalytic systems for the Chan-Lam coupling of 4-methoxyaniline with phenyl boronic acid.

S. No.	Catalyst	Catalyst amount	Reaction conditions	Time (h)	Yield (%)	TOF (h^{-1})	Reference
1	MPI-Cu (1:1)	0.1 mmol	CH_2Cl_2, O_2, r.t.	24	65	0.27	44
2	Polymer supported Cu (II)	0.026 mmol	K_2CO_3, DMSO, 140°C	12	86	2.75	18
3	$CoFe_2O_4$@SiO_2-NH_2-Furfural-Cu$(OAc)_2$	0.078 mmol	Et_3N, CH_3OH, r.t.	5	80	2.05	45
4	Cu@PI-COF	20 mg	MeOH:H_2O, r.t.	8	92	3.7	46
5	Cu@KF-C/$CoFe_2O_4$	0.022 mmol	EtOH, 90°C	2	85	19.32	This work

Table S4. Comparison of the catalytic activity of Cu@KF-C/$CoFe_2O_4$with some reported catalytic systems for oxidation of 4-chlorobenzylalcohol.

S. No.	Catalyst	Catalyst amount	Reaction conditions	Time (h)	Yield (%)	TOF (h^{-1})	Reference
1	[Cu_2(μ-$O_2CC_6H_5$)$_4$(4-Etpy)$_2$]	0.5 mol %	TBHP, MeOH, 65°C	5	78	31.2	47
2	[Cu_2(μ-$O_2CC_6H_5$)$_4$(4-DMAP)$_2$]	0.5 mol%	TBHP, MeOH, 65°C	5	75	30	47
3	STA-12(Co)	2 mol%	TBHP, EtOAc, 60°C	3	58	9.6	48
4	CAPS-CuO	60 mg	O_2,Toluene, 100°C	24	75	0.34	49
5	Cu@KF-C/$CoFe_2O_4$	2.22 mol%	TBHP, EtOH, 80°C	2.5	80	14.54	This work