Unsymmetrical Pincer N‑Heterocyclic Carbene–Nitrogen–Phosphine Chelated Palladium(II) Complexes: Synthesis, Structure, and Reactivity in Direct Csp^2–H Arylation of Benzoxazoles

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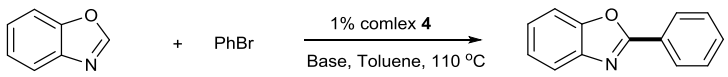
Table S1. Effect of base to the arylation of benzoxazole [a]



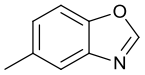
Entry	Base	Conv.(%)
1	--	0
2	N,N,N',N'-tetramethylethylenediamine	0
3	N,N-dimethyl-4-aminopyridine	0
4	$^{i}Pr_2NEt$	0
5	NEt_3	0
6	NaOMe	3
7	KOMe	2
8	Na_2CO_3	1
9	K_2CO_3	2
10	Cs_2CO_3	8
11	K_3PO_4	9
12	$LiOH \cdot H_2O$	2
13	NaOH	60(28)
14	KOH	20
15	$LiO^{t}Bu$	59(26)
16	$NaO^{t}Bu$	83(40)
17	$KO^{t}Bu$	59

[a] Reaction Condition: PhBr (1.2 mmol), benzoxazole (1 mmol), complex **4** (0.01 mmol),

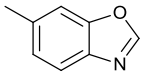
base (1 mmol), toluene (4 ml) and reaction time 24 h. All conversions were determined by GC and yields in parenthesis based on dodecane (100 μL) as internal standard.

Synthesis procedure of substituted benzoxale substrates.

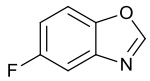
4-methy-2-animophenol (10 mmol, 1.23 g) was added into 2-neck round bottom flask, then, tirethyl orthoformate (25 ml) was injected under argon. Mixture was stirred and heated to reflux 4 h. After the reaction ended, all volatile was evaporated in *ca*. 80 ^{o}C. Residual was purified by column chromatography to provide corresponding product 5-methylbenzoxazole (440 mg, 33% yield).



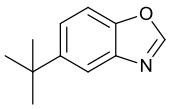
^{1}H NMR($CDCl_3$, 400MHz) δ 8.06 (s, 1H), 7.58 (s, 1H), 7.45 (d, 1H, *J* = 8.4 Hz), 7.20 (d, 1H, *J* = 8.4 Hz), 2.48 (s, 3H). ^{13}C NMR($CDCl_3$, 400MHz) δ 152.6, 148.2, 140.2, 134.5, 126.8, 120.4, 110.3, 21.4.



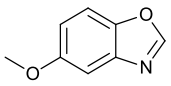
^{1}H NMR($CDCl_3$, 400MHz) δ 8.03 (s, 1H), 7.66 (d, 1H, *J* = 8.0 Hz), 7.39 (s, 1H), 7.19 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR($CDCl_3$, 400MHz) δ 152.0, 150.3, 137.8, 136.1, 125.9, 119.9, 111.1, 21.7.



^{1}H NMR($CDCl_3$, 400MHz) δ 8.13 (s, 1H), 7.4-7.6 (m, 2H), 7.1-7.2 (m, 1H). ^{13}C NMR($CDCl_3$, 400MHz) δ 160.1 (d, *J* = 239.3 Hz), 154.1, 146.3, 140.9 (d, *J* = 13.2 Hz), 113.5 (d, *J* = 26.3), 111.3 (d, *J* = 9.9 Hz), 107.0 (d, *J* = 25.5 Hz).



^{1}H NMR($CDCl_3$, 400MHz) δ 8.07 (s, 1H), 7.81 (d, 1H, *J* = 1.6 Hz), 7.4-7.6 (m, 2H), 1.39 (s, 9H). ^{13}C NMR($CDCl_3$, 400MHz) δ 152.6, 148.2, 148.0, 140.0, 123.4, 117.0, 110.1, 34.9, 31.8.



^{1}H NMR($CDCl_3$, 400MHz) δ 8.07 (s, 1H), 7.46 (d, 1H, *J* = 8.8 Hz), 7.27 (m, 1H), 6.99 (m, 1H), 3.86 (s, 3H). ^{13}C NMR($CDCl_3$, 400MHz) δ 157.4, 153.3, 144.6, 140.9, 114.5, 111.1, 103.1, 56.0.

Crystal data for complex 4

CCDC No. of Complex **4** • **2DMF** is **1561781.**

Table S2. Crystallographic data for complex **4**.

Empirical formula	$C_{31}H_{38}Cl_2N_5O_2PPd$
Formula weight	720.93
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.0500(3)
b/Å	9.27913(15)
c/Å	21.2208(4)
α/°	90
β/°	90.8903(15)
γ/°	90
Volume/Å^3	3356.93(10)
Z	4
ρ_{calc}g/cm^3	1.426
μ/mm^{-1}	6.654
F(000)	1480.0
Crystal size/mm^3	1.0 × 0.4 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.34 to 145.52
Index ranges	-20 ≤ h ≤ 21, -11 ≤ k ≤ 7, -26 ≤ l ≤ 20
Reflections collected	21676
Independent reflections	5989 [R_{int} = 0.0557, R_{sigma} = 0.0451]
Data/restraints/parameters	5989/0/384
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.1266
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.1322
Largest diff. peak/hole / e Å^{-3}	1.12/-0.77

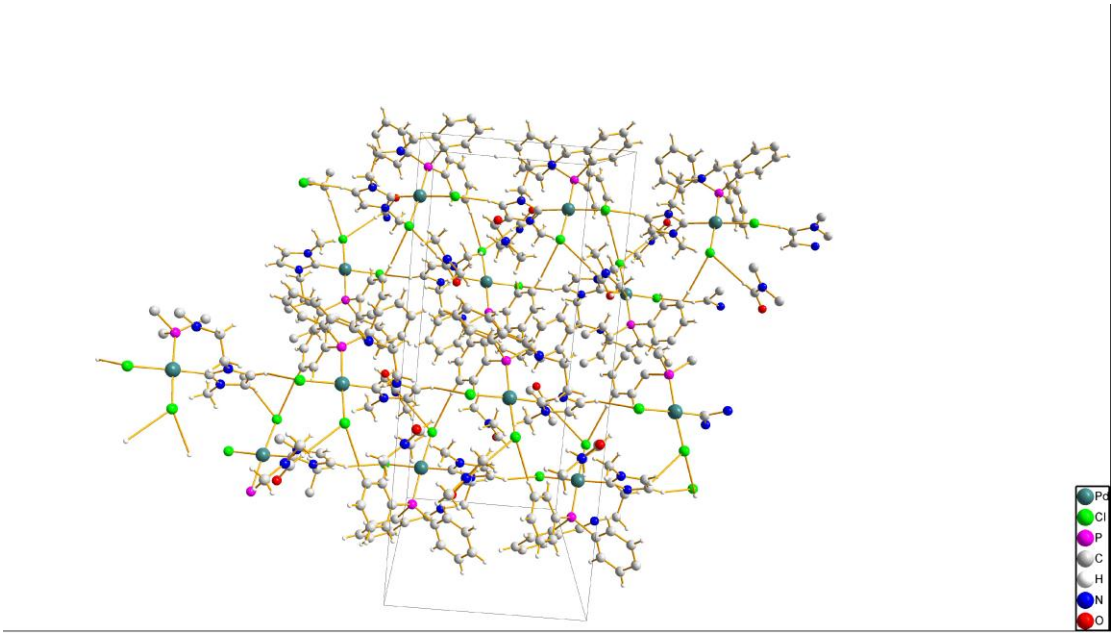


Figure S1. Packing diagram of complex **4**.

HR-MS result of reaction mixture (8 h)

Chemical Formula: $C_{42}H_{44}N_4O_3PPd^+$
Exact Mass: 789.2180
Molecular Weight: 790.2170
m/z: 789.2186 (100.0%), 791.2190 (97.5%), 788.2202 (81.7%), 790.2219 (45.4%), 792.2224 (44.0%), 793.2203 (42.9%)

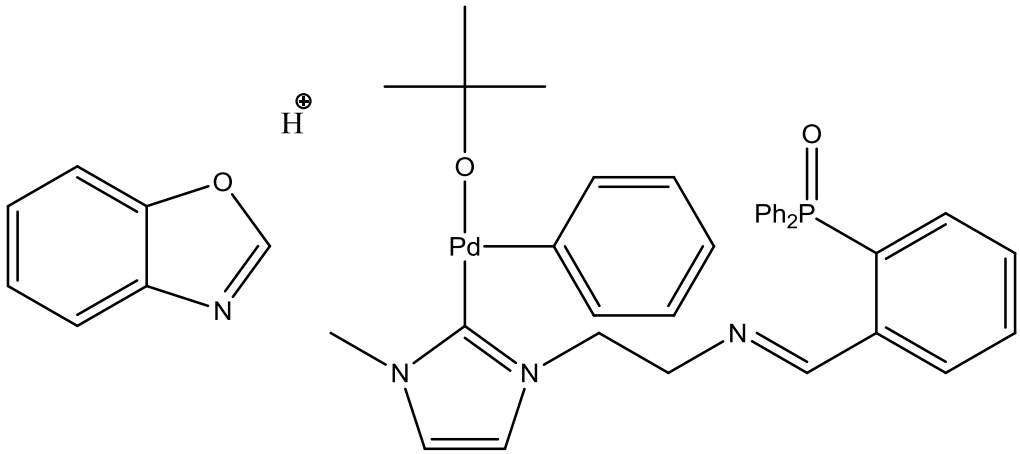


Figure S2. The palladium species captured by HR-MS.

EDX analysis of palladium species

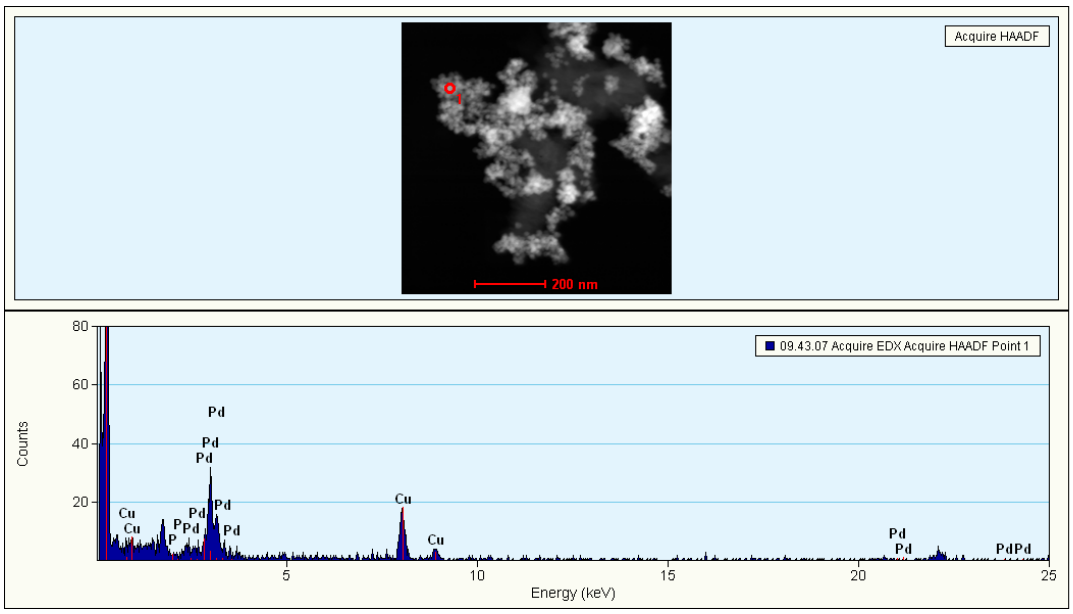


Figure S3. HAADF-STEM image of palladium species after 14 h.

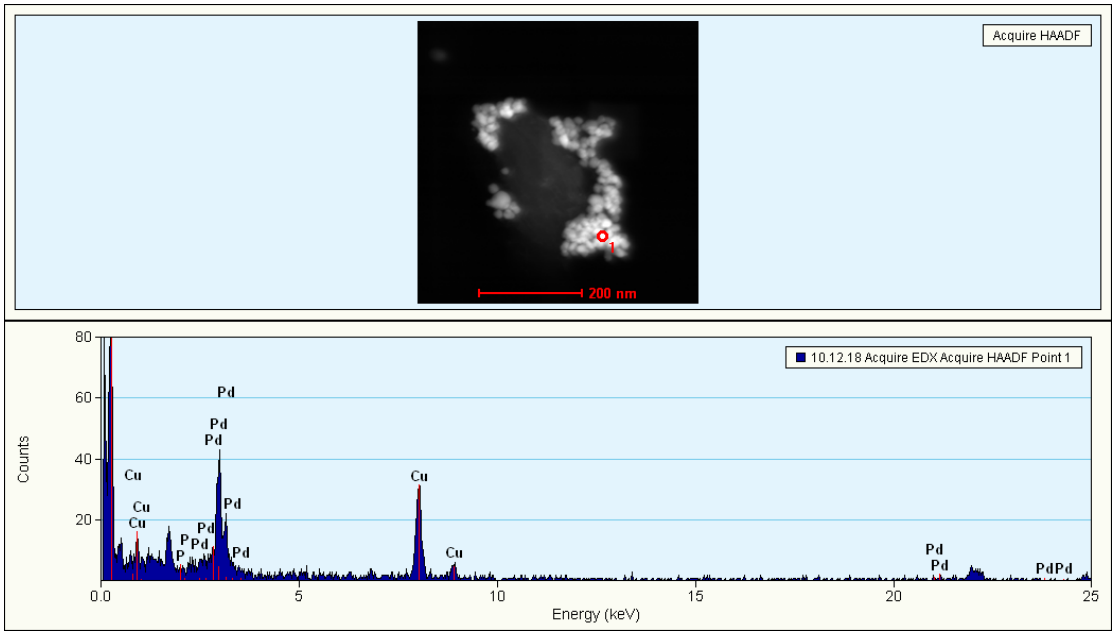


Figure S4. HAADF-STEM image of palladium species after 24 h.

NMR spectra of the ligands, complexes and 2-substituted benzoxazoles

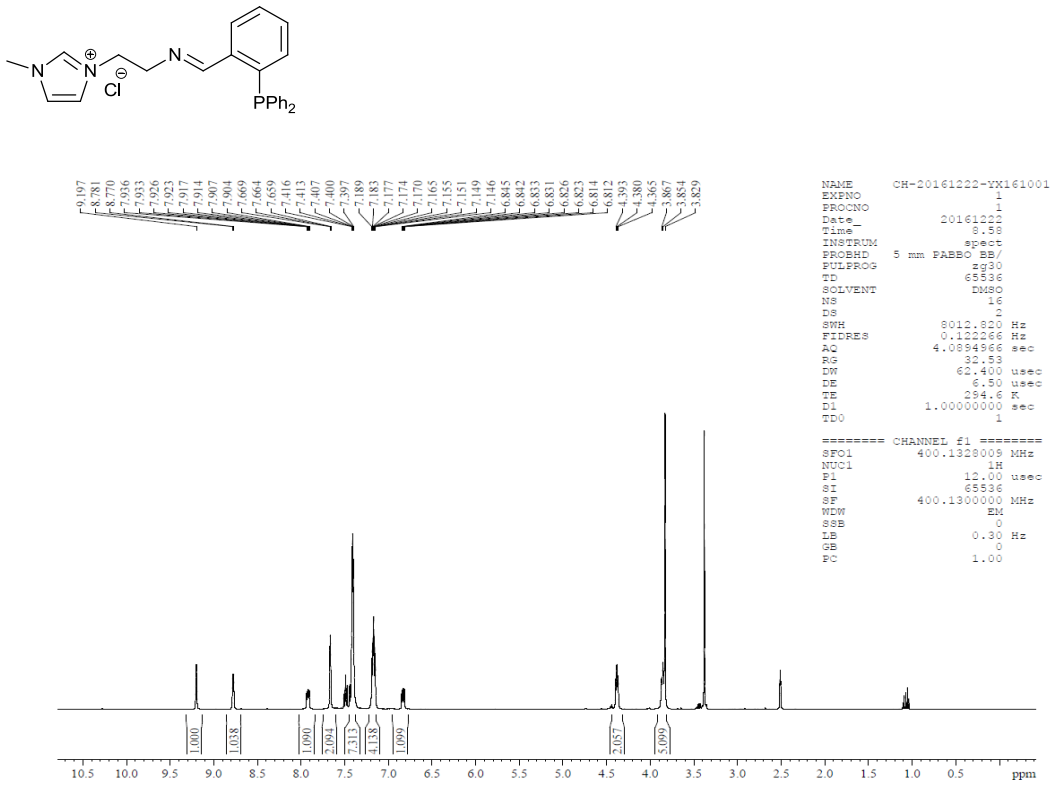


Figure S5. ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6) of 3-{2-{[2-(diphenylphosphino)benzyliene]amino}-ethyl}-1-methyl-1*H*-imidazole-3-ium chloride (**2**).

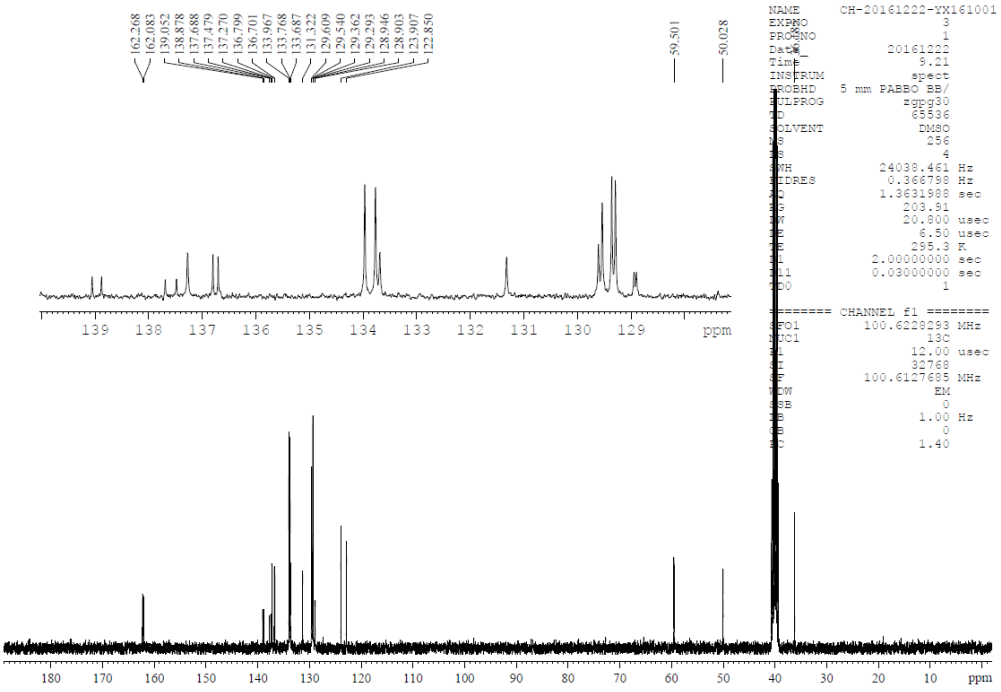


Figure S6. ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of 3-{2-{[2-(diphenylphosphino)benzyliene]amino}-ethyl}-1-methyl-1*H*-imidazole-3-ium chloride (**2**).

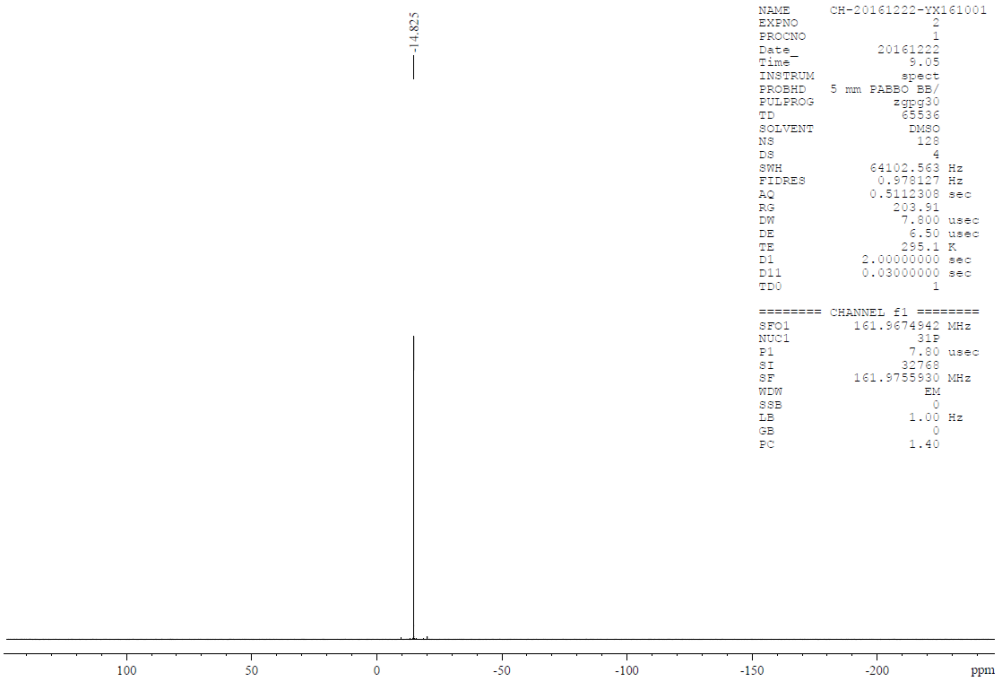


Figure S7. ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6) of 3-{2-{[2-(diphenylphosphino)benzyliene]amino}-ethyl}-1-methyl-1*H*-imidazole-3-ium chloride (**2**).

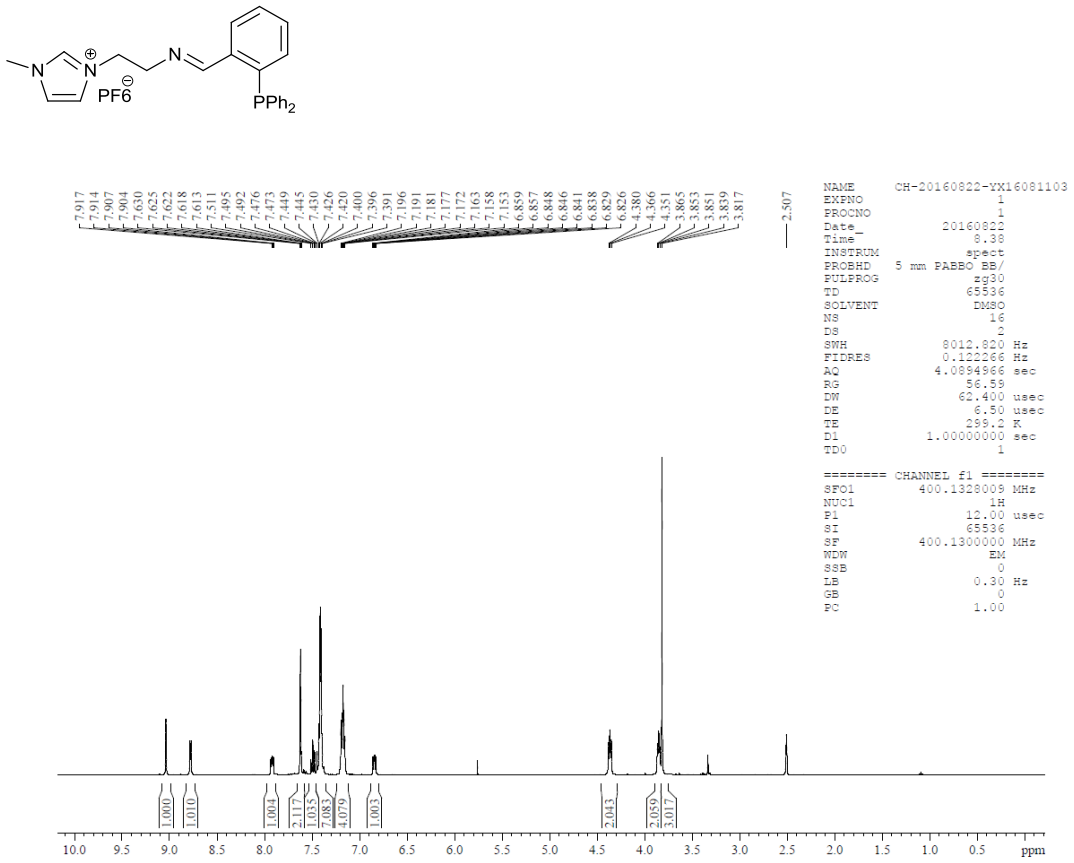


Figure S8. ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6) of 3-{2-{[2-(diphenylphosphino)benzylidene]amino}-ethyl}-1-methyl-1*H*-im-idazol-3-ium hexafluorophosphate (**3**).

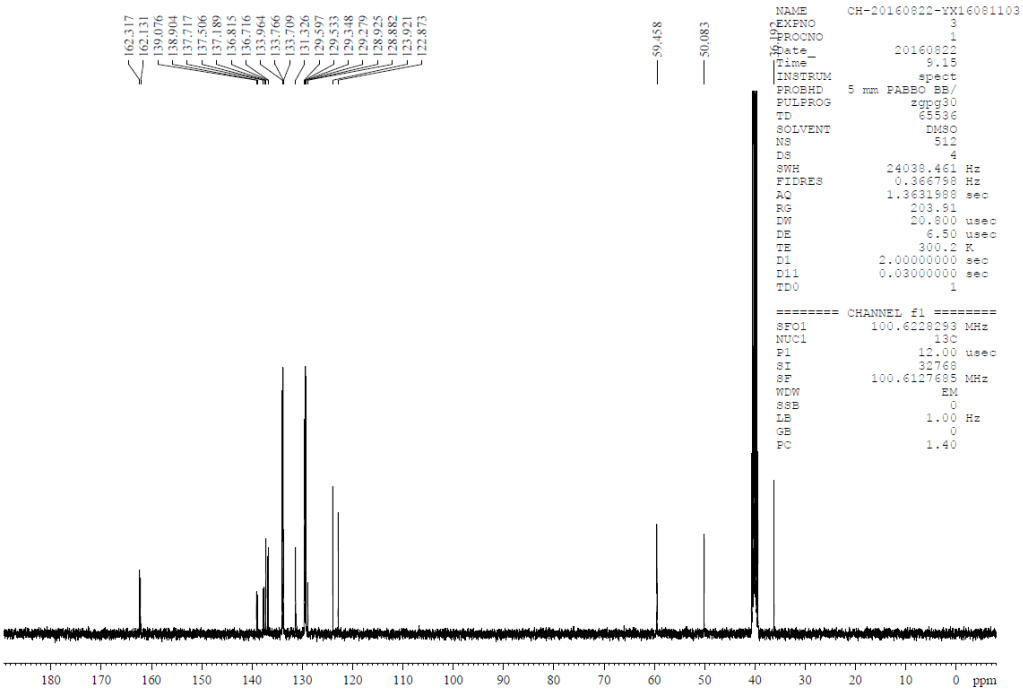


Figure S9. ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of 3-{2-{[2-(diphenylphosphino)benzylidene]amino}-ethyl}-1-methyl-1*H*-im-idazol-3-ium hexafluorophosphate (**3**).

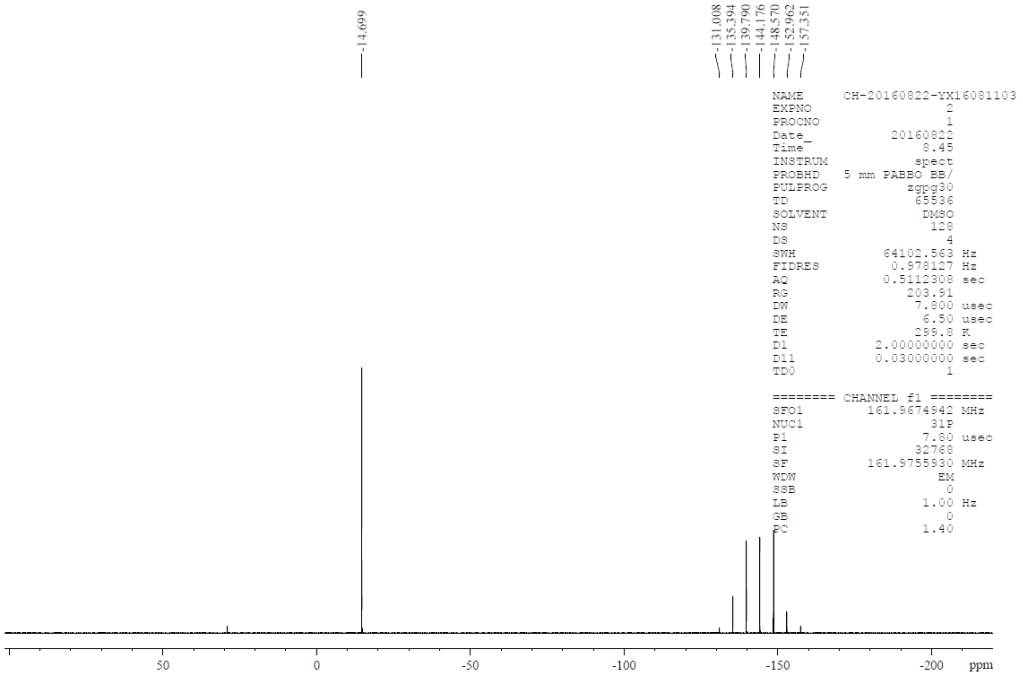
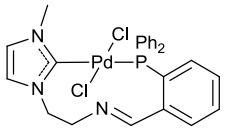


Figure S10. ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6) of 3-{2-{[2-(diphenylphosphino)benzylidene]amino}-ethyl}-1-methyl-1*H*-im-idazol-3-ium hexafluorophosphate (**3**).



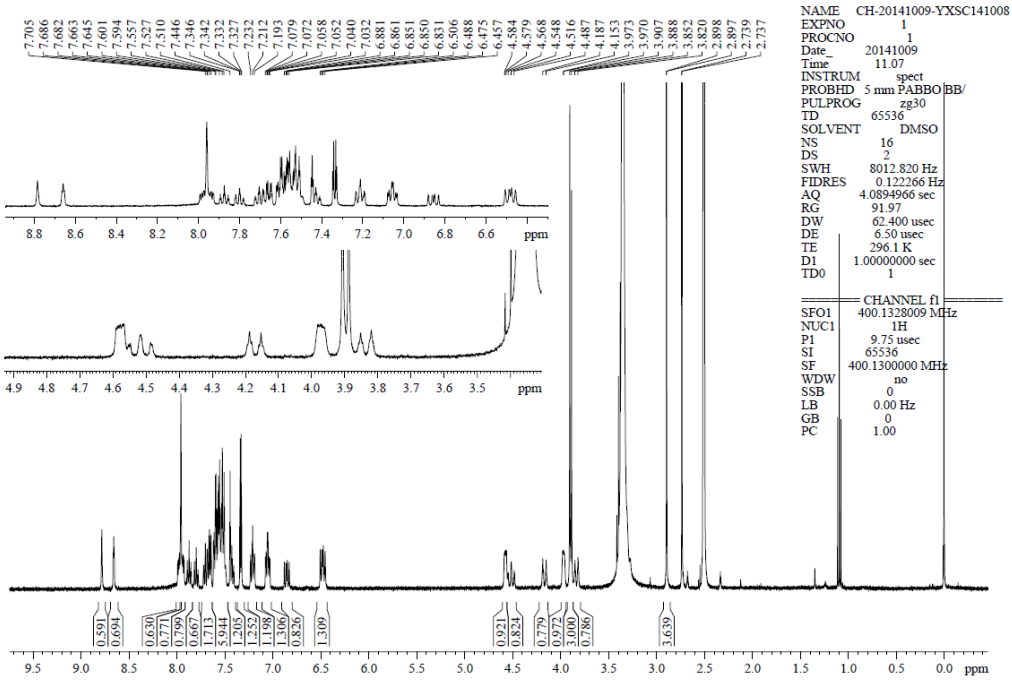


Figure S11. ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6) of complex **4** before adding 10 equiv of LiCl.

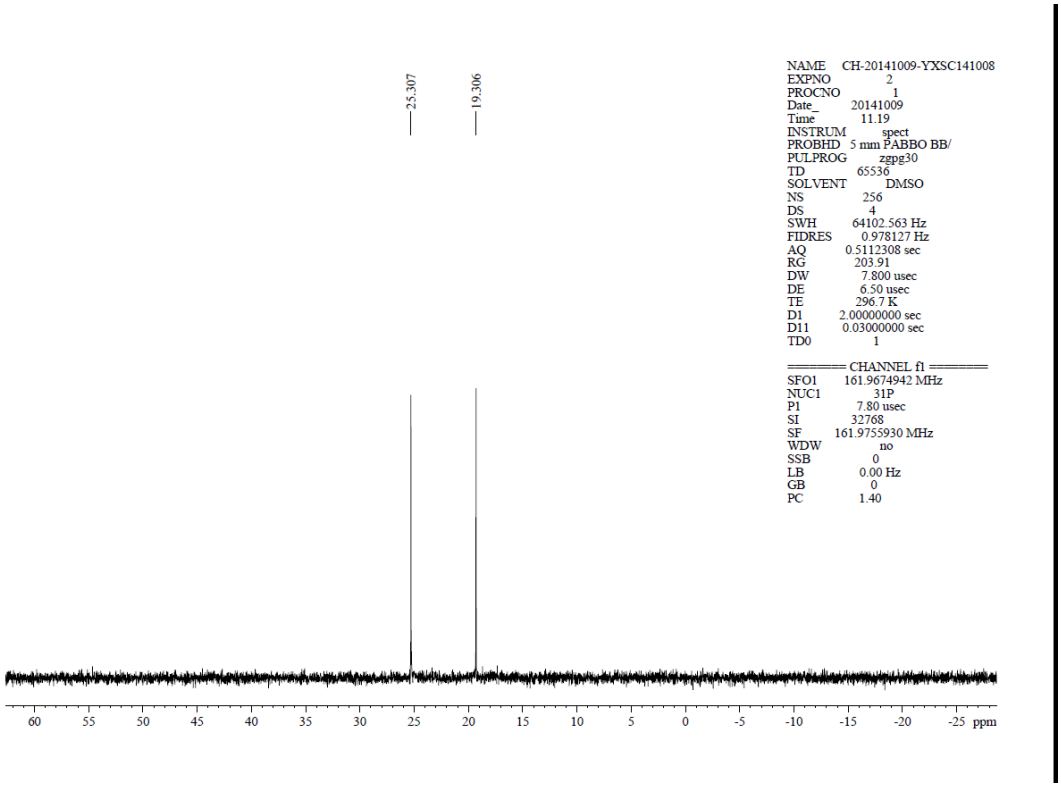


Figure S12. ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6) of complex **4** before adding 10 equiv of LiCl.

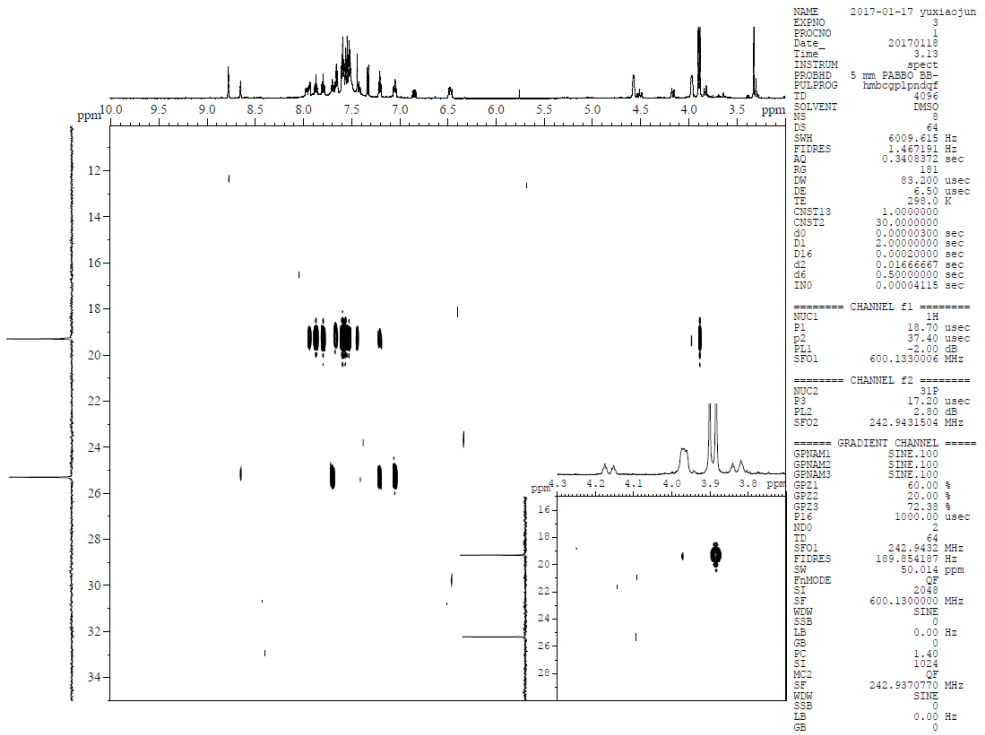


Figure S13. ^{1}H-^{31}P HMBC of complex **4** before adding 10 equiv of LiCl.

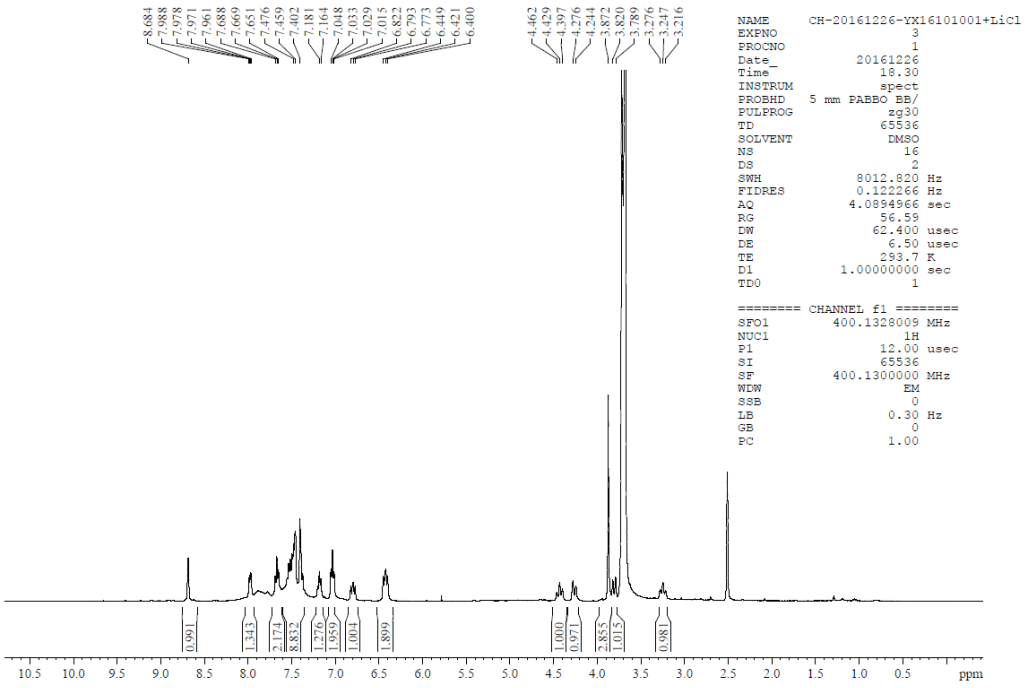


Figure S14. ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6) of complex **4** after adding 10 equiv of LiCl.

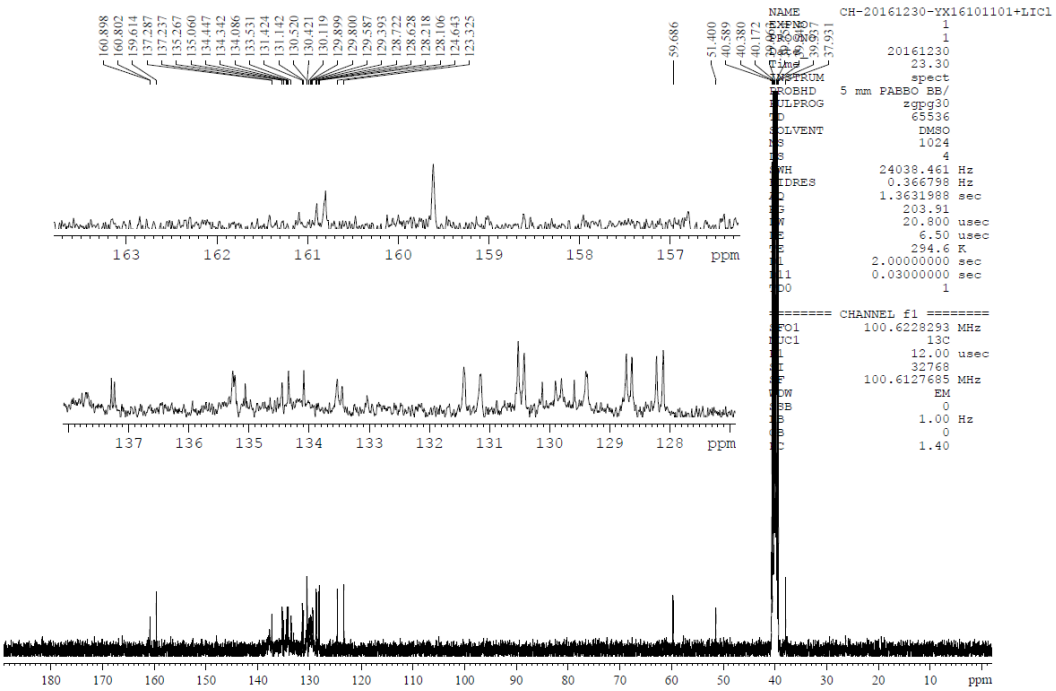


Figure S15. ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of complex **4** after adding 10 equiv of LiCl.

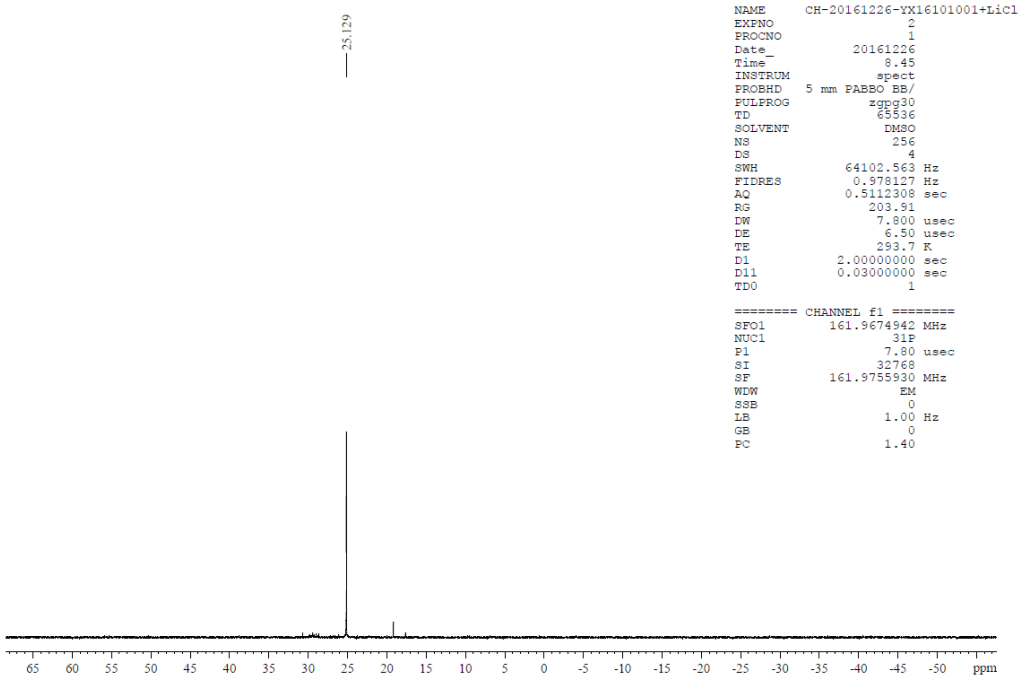


Figure S16. ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6) of complex **4** after adding 10 equiv of LiCl.

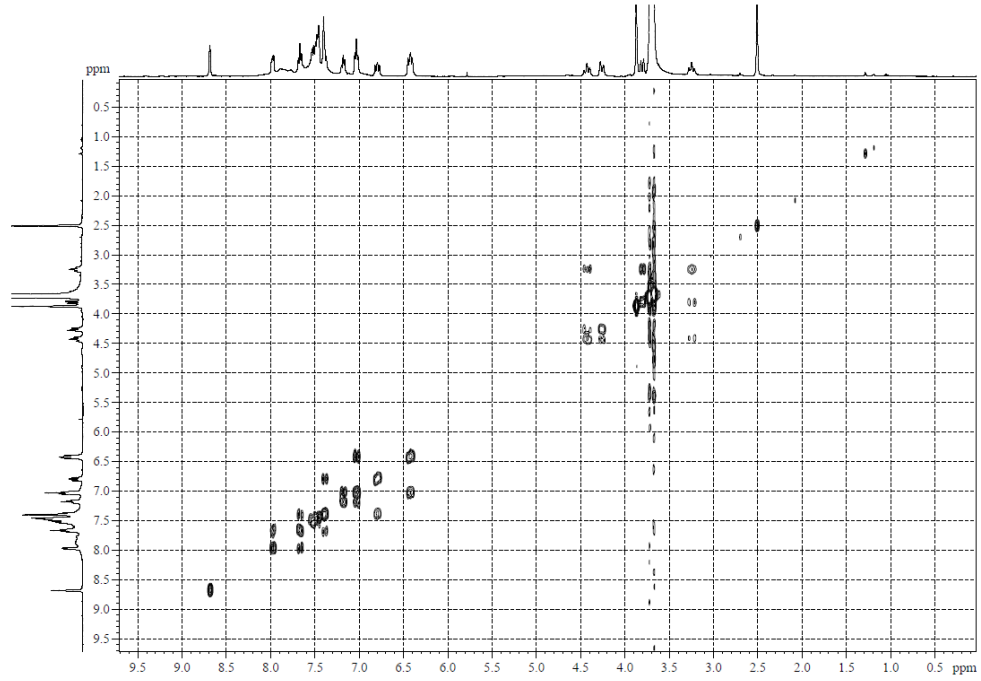


Figure S17. ^{1}H-^{1}H COSY of complex **4** after adding 10 equiv of LiCl.

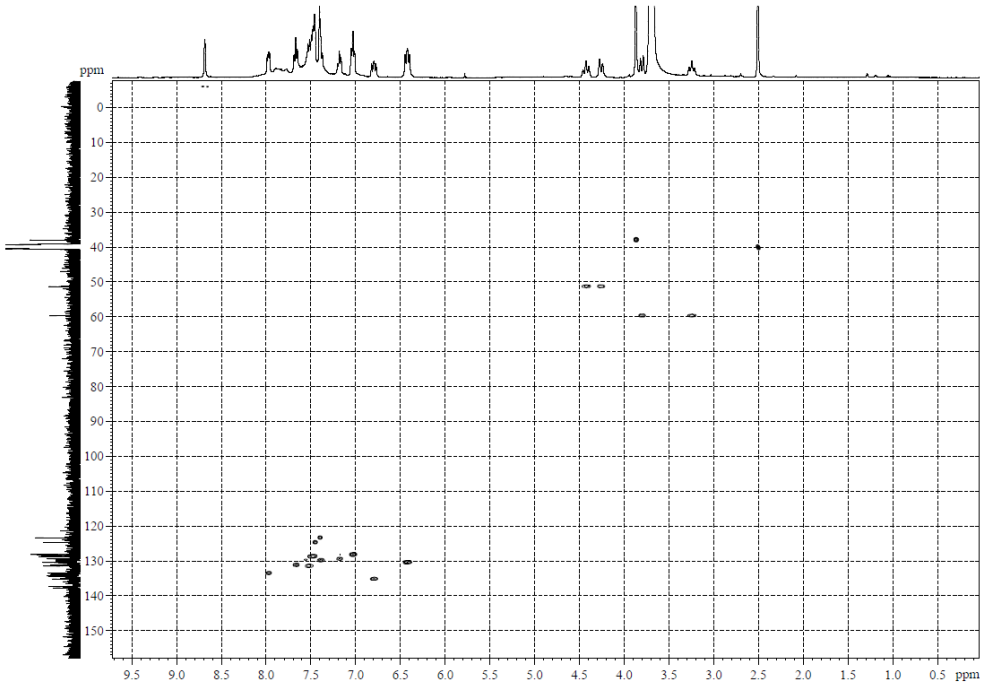


Figure S18. HSQC spectrum of complex **4** after adding 10 equiv of LiCl.

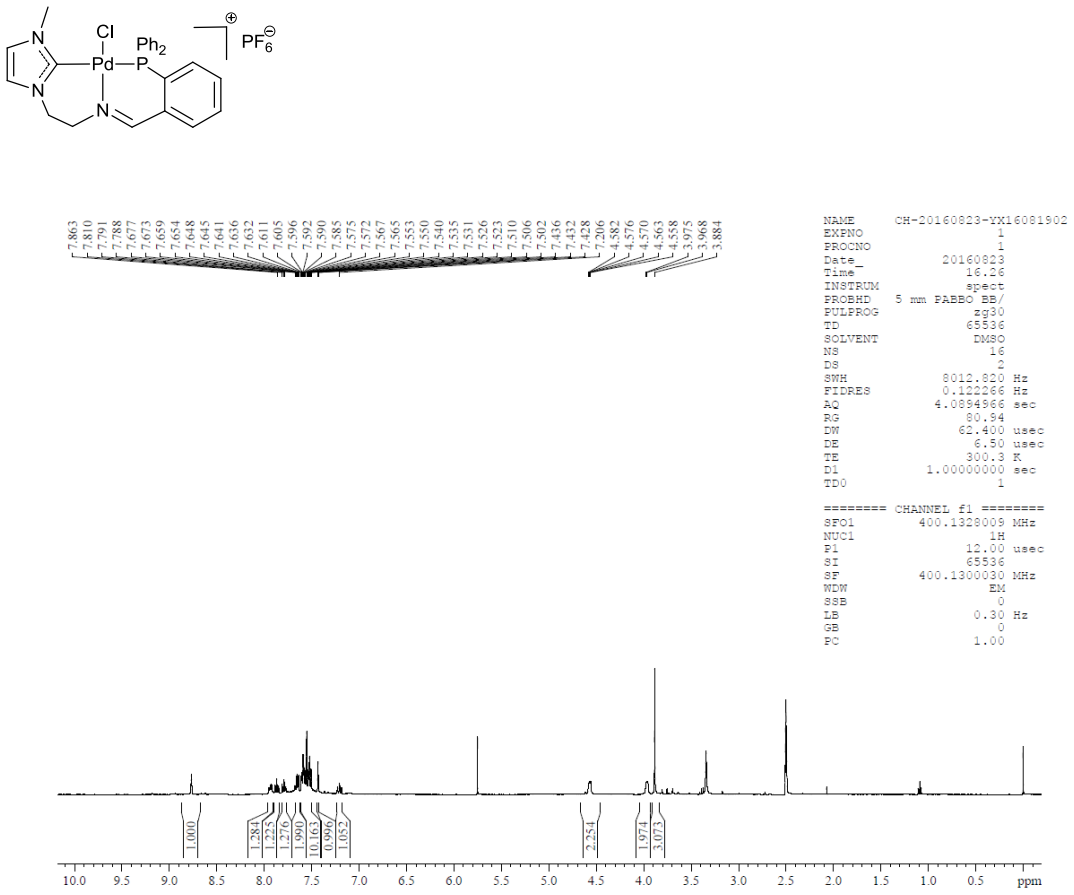


Figure S19. ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6) of complex **5·PF$_6$**.

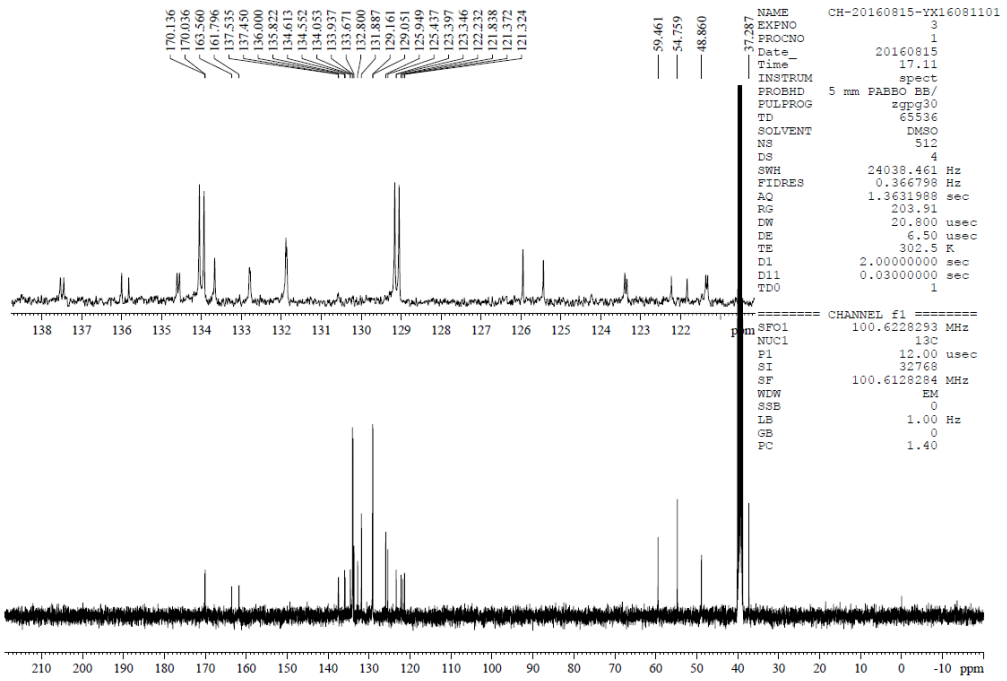


Figure S20. ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of complex **5·PF$_6$**.

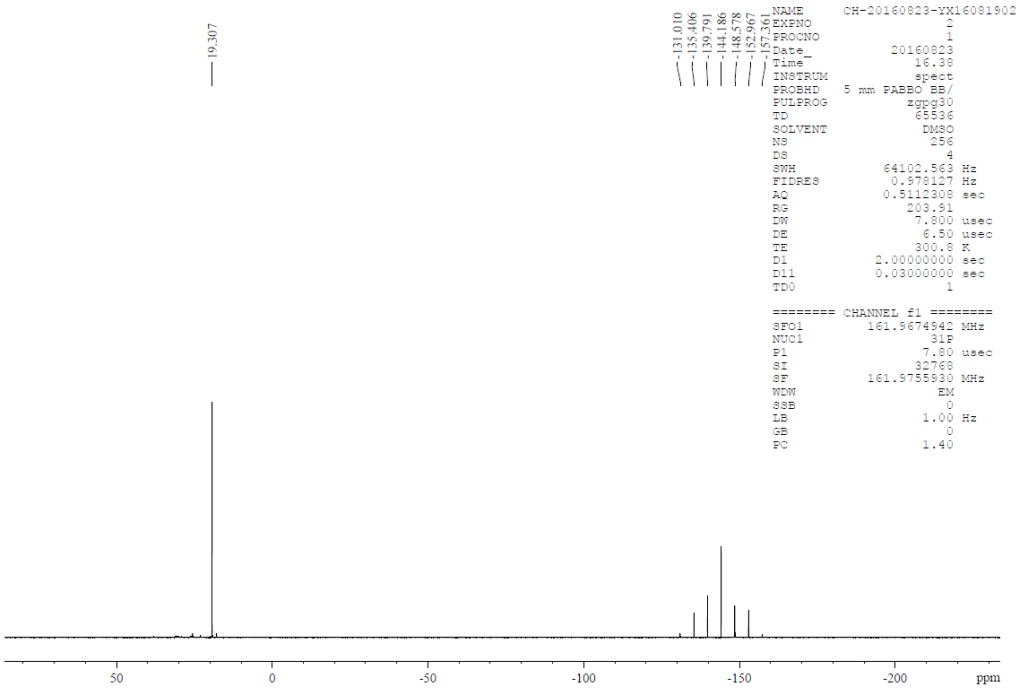


Figure S21. ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6) of complex **5·PF$_6$**.

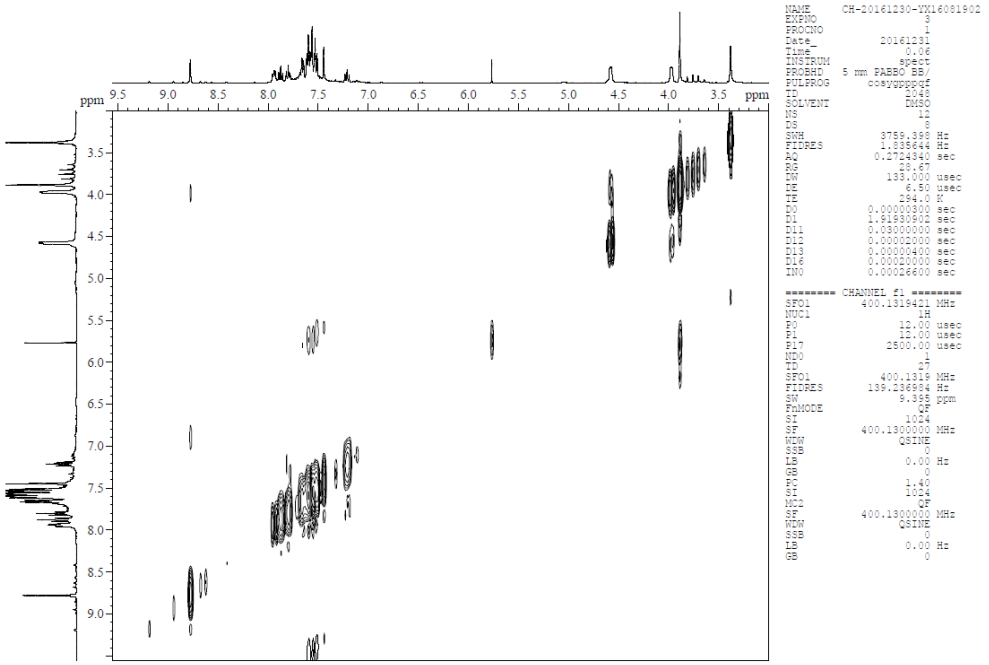


Figure S22. ^{1}H-^{1}H COSY of complex **5·PF$_6$**.

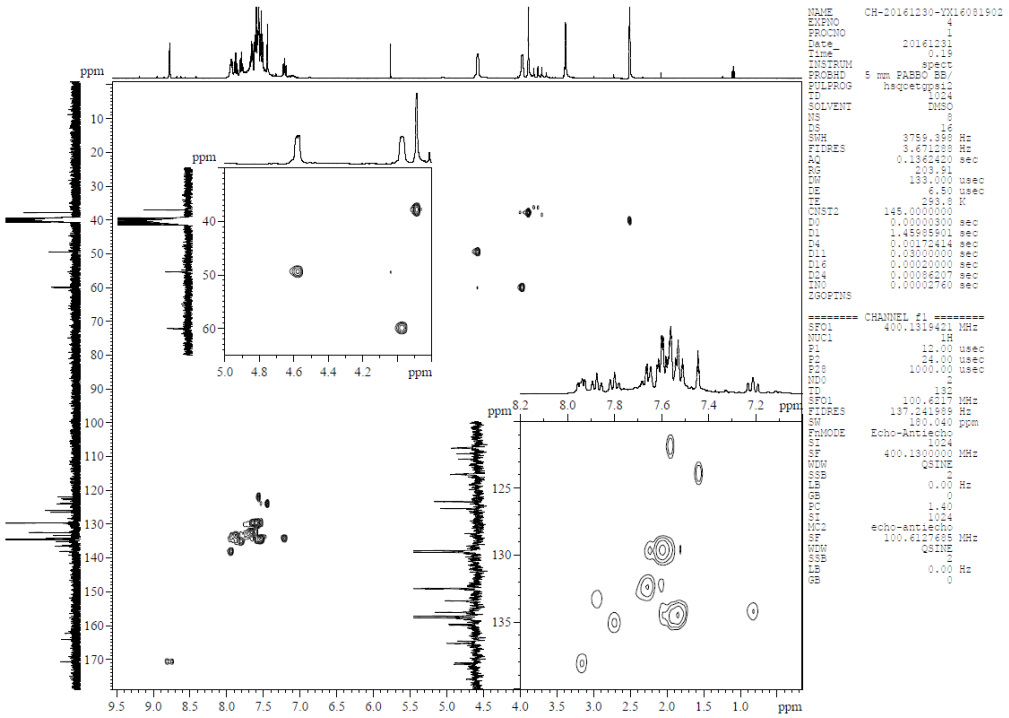
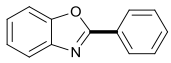


Figure S23. HSQC spectrum of complex **5·PF$_6$**.



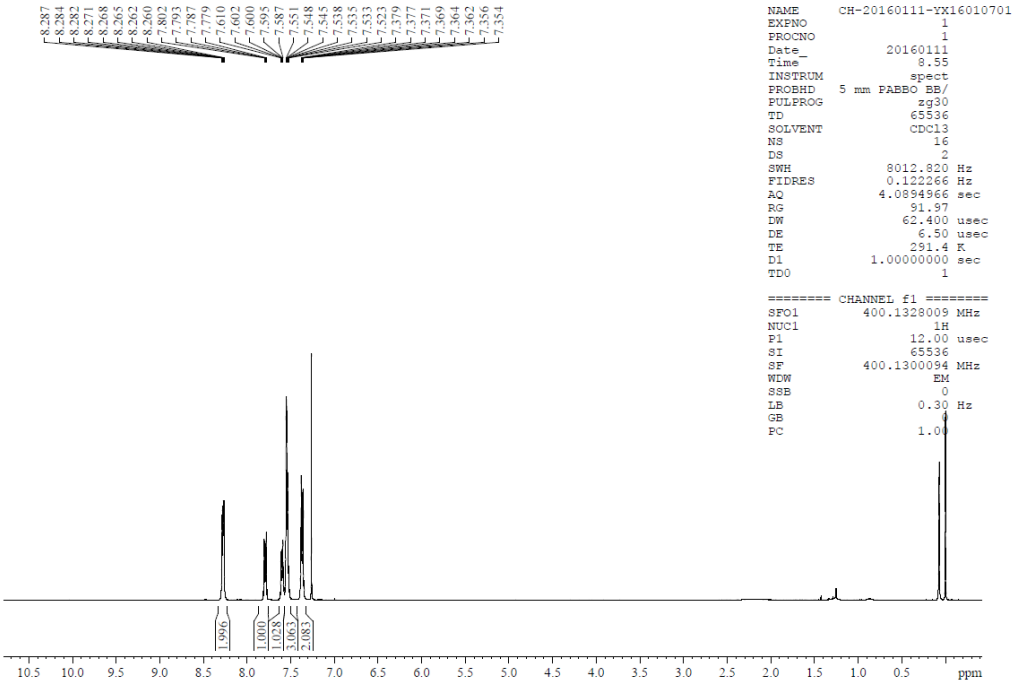


Figure S24. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-phenylbenzoxazole (**6a**).

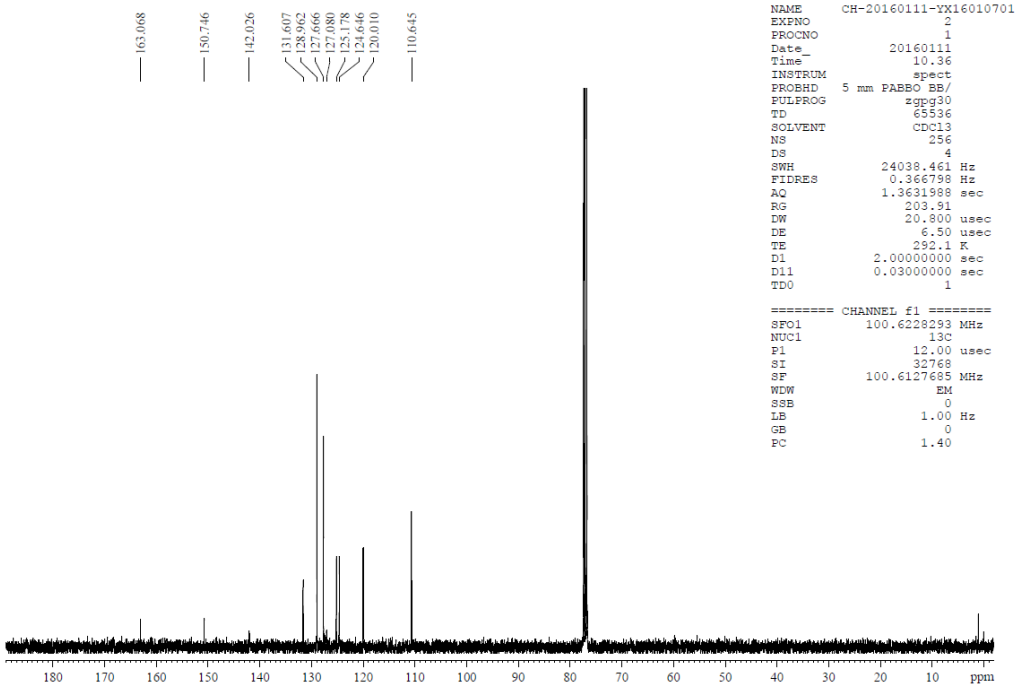
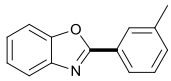


Figure S25. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-phenylbenzoxazole (**6a**).



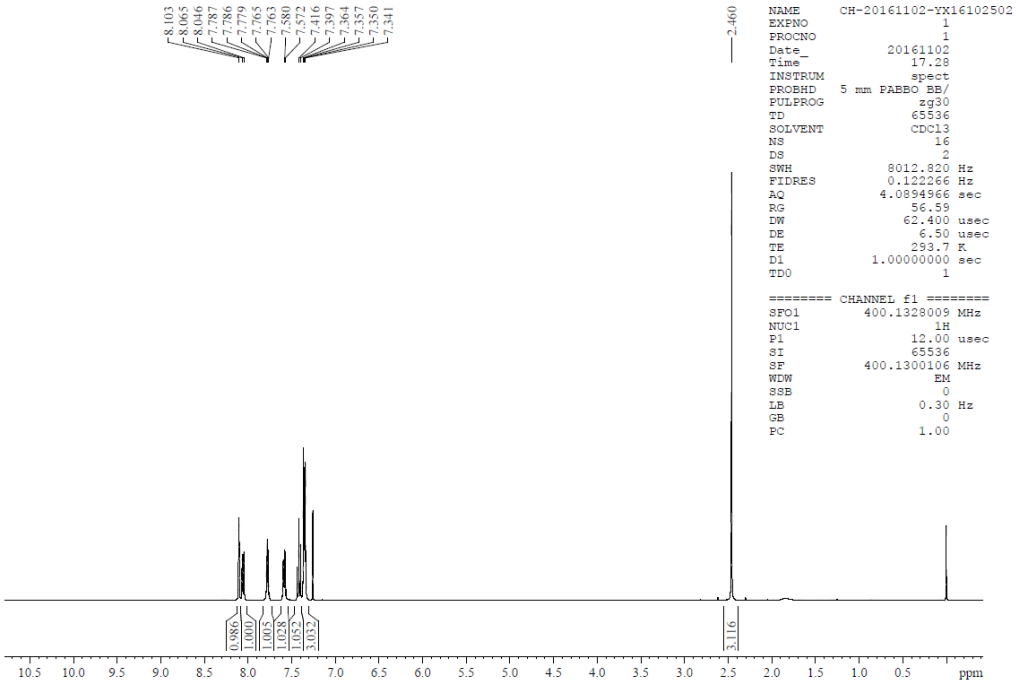


Figure S26. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(m-tolyl)benzoxazole (**6b**).

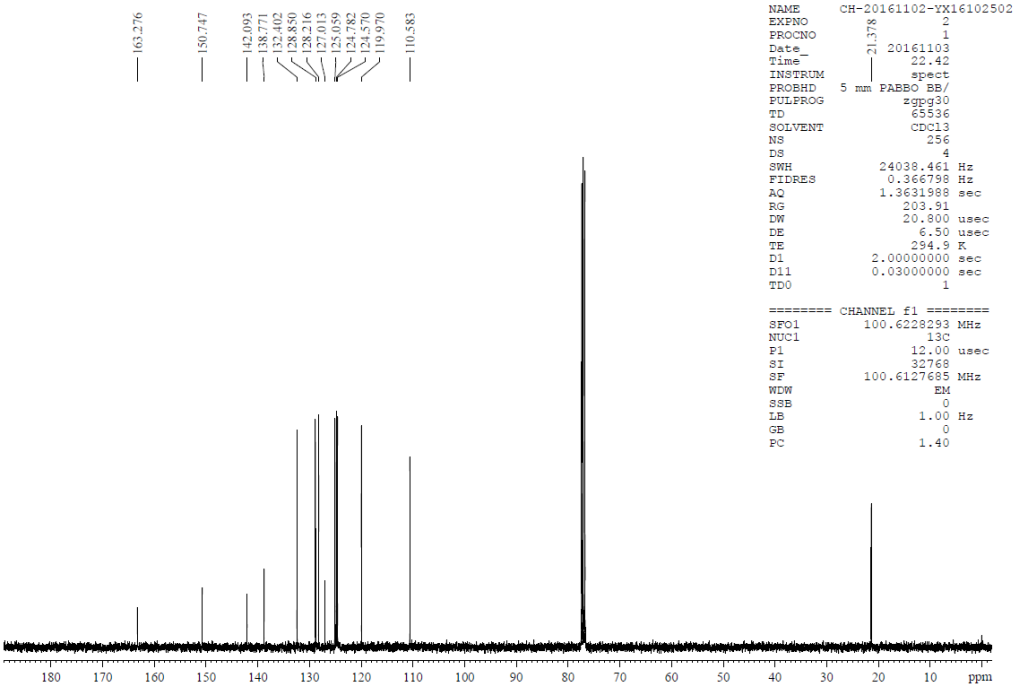
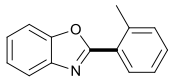


Figure S27. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(m-tolyl)benzoxazole (**6b**).



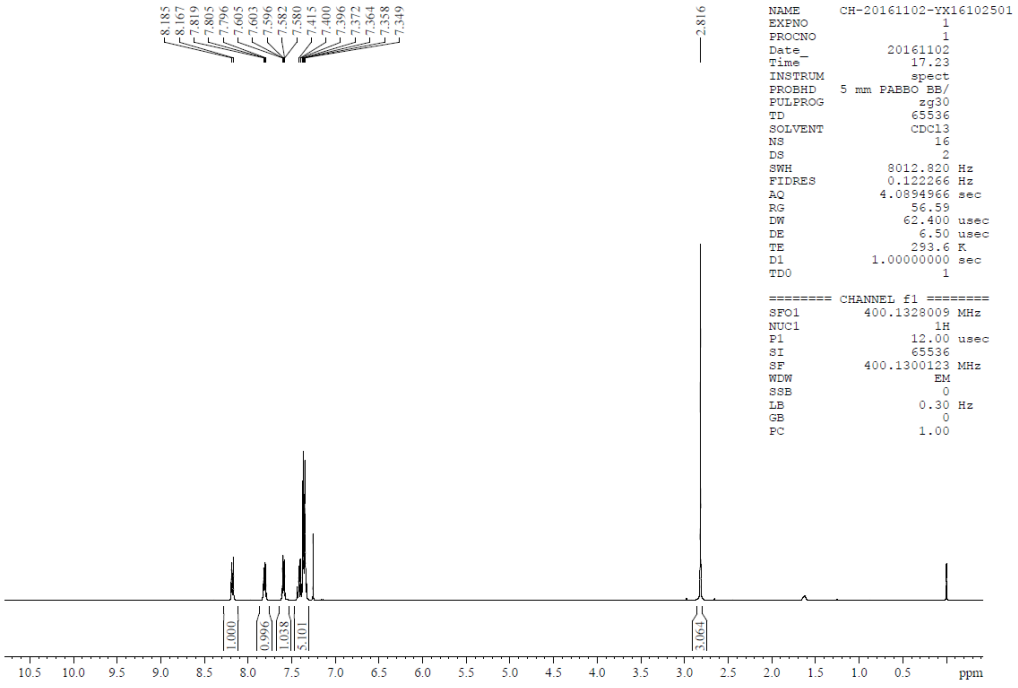


Figure S28. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(o-tolyl)benzoxazole (**6c**).

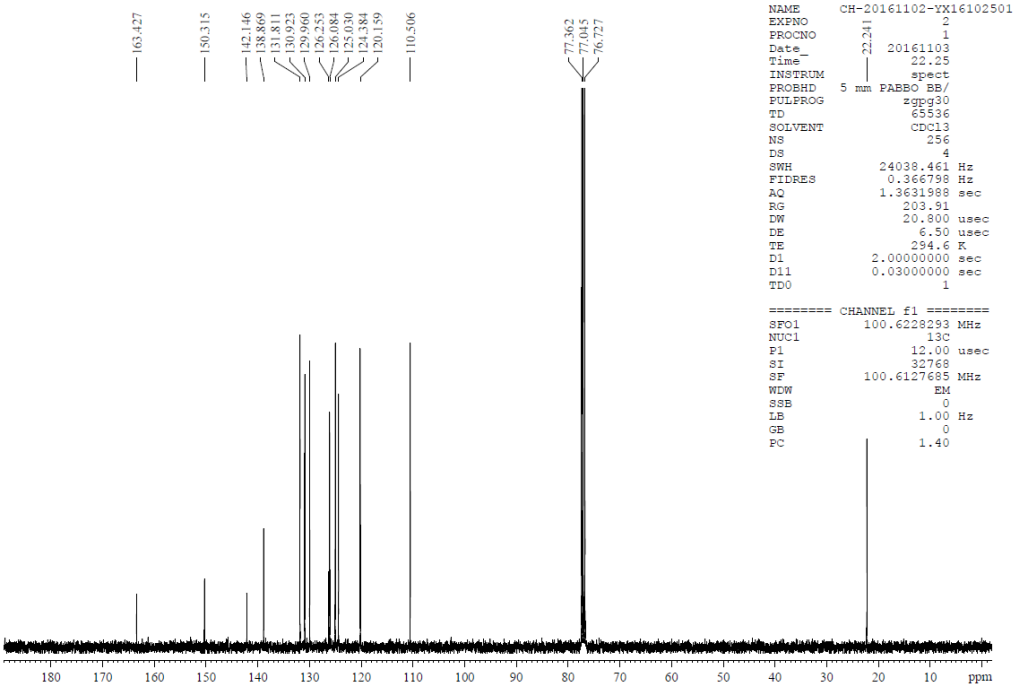
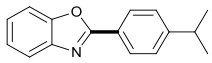


Figure S29. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(o-tolyl)benzoxazole (**6c**).



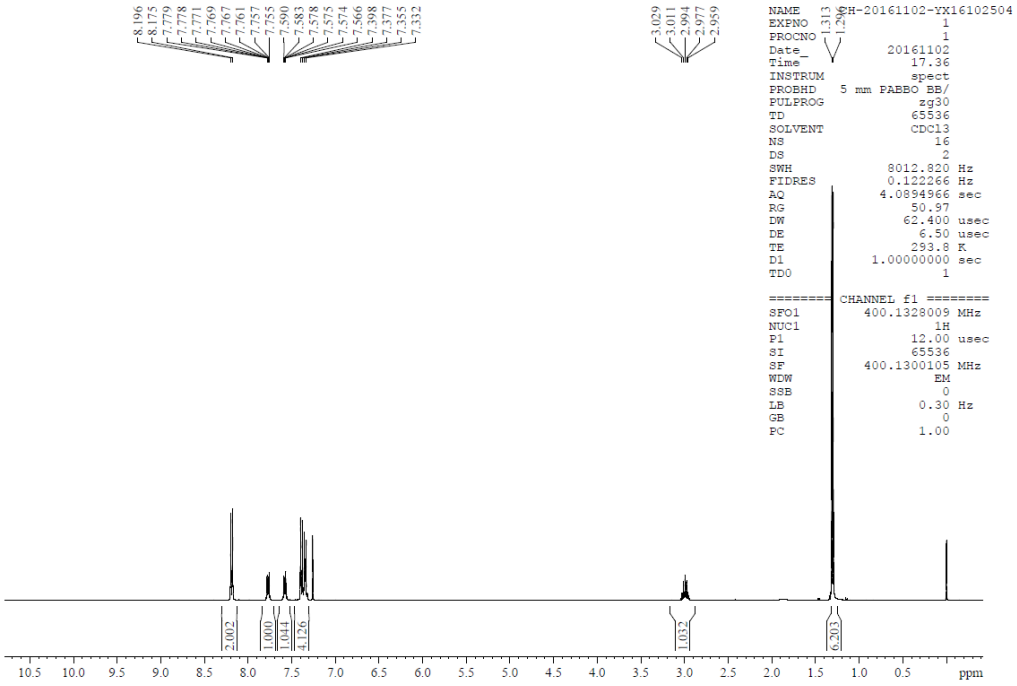


Figure S30. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(4-isopropylphenyl)benzoxazole (**6d**).

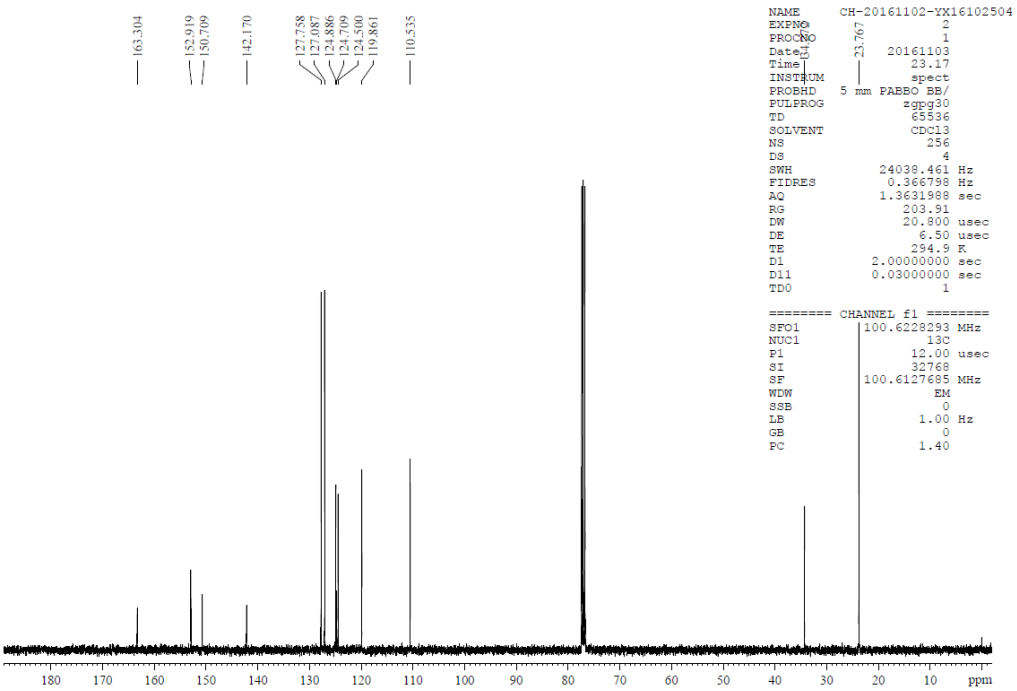
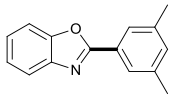


Figure S31. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(4-isopropylphenyl)benzoxazole (**6d**).



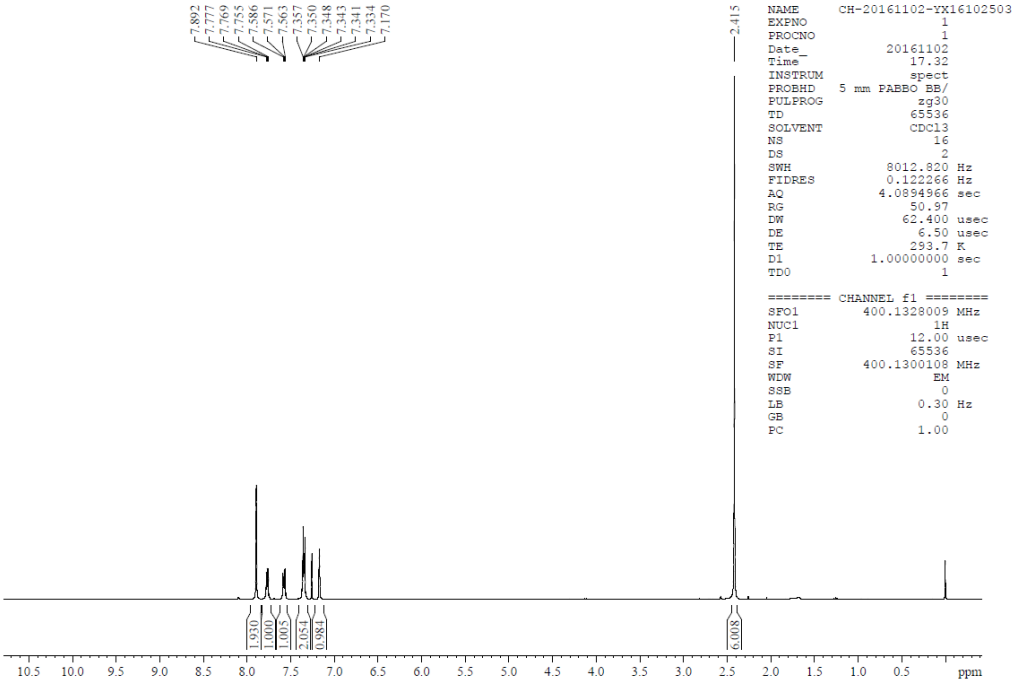


Figure S32. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(3,5-dimethylphenyl)benzoxazole (**6e**).

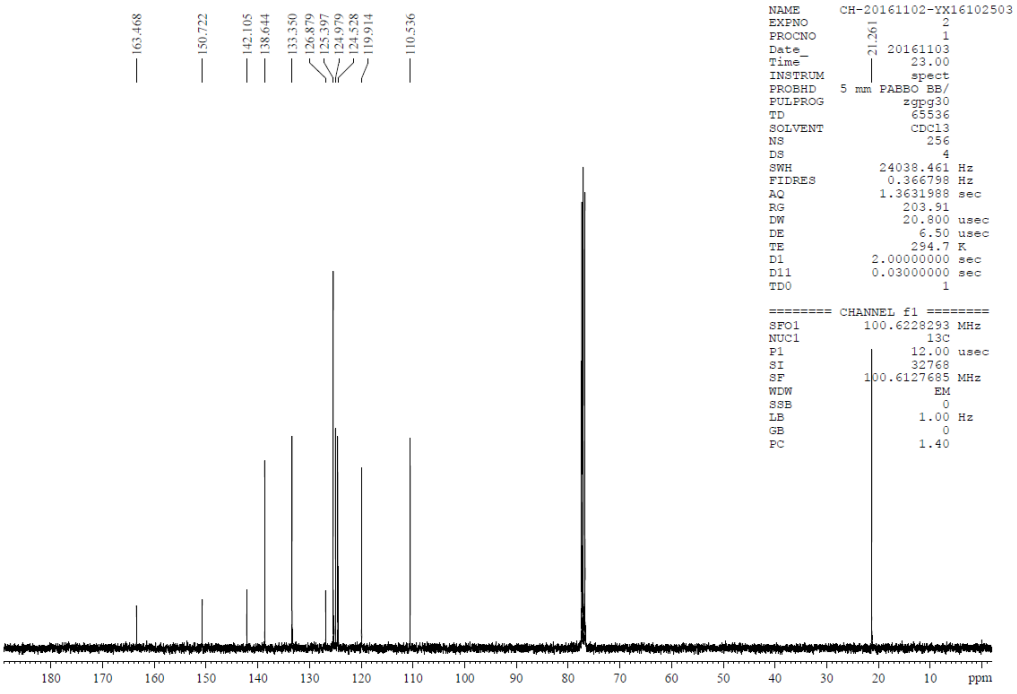


Figure S33. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(3,5-dimethylphenyl)benzoxazole (**6e**).

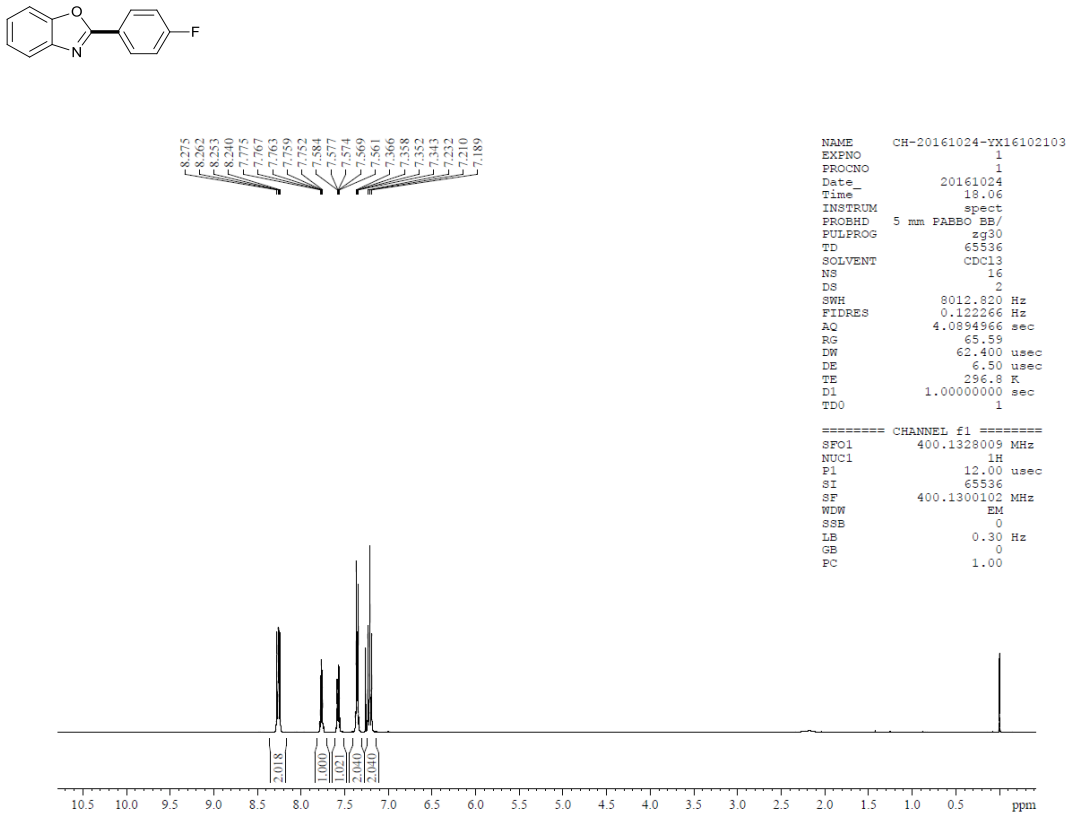


Figure S34. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(4-fluorophenyl)benzoxazole (**6f**).

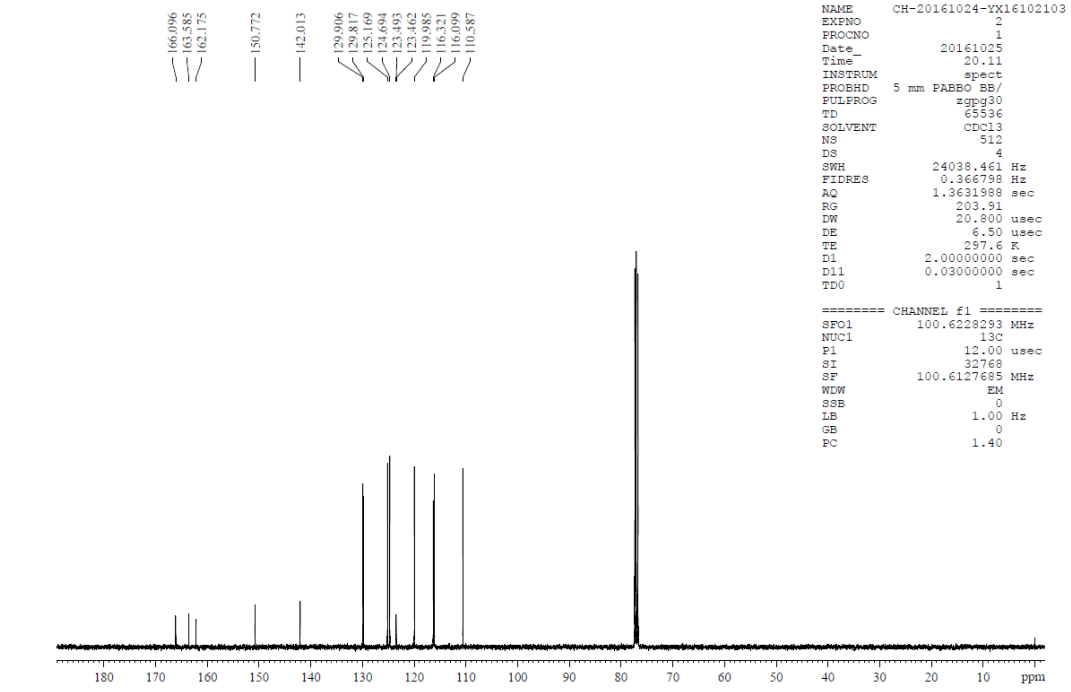
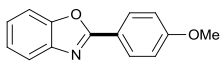


Figure S35. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(4-fluorophenyl)benzoxazole (**6f**).



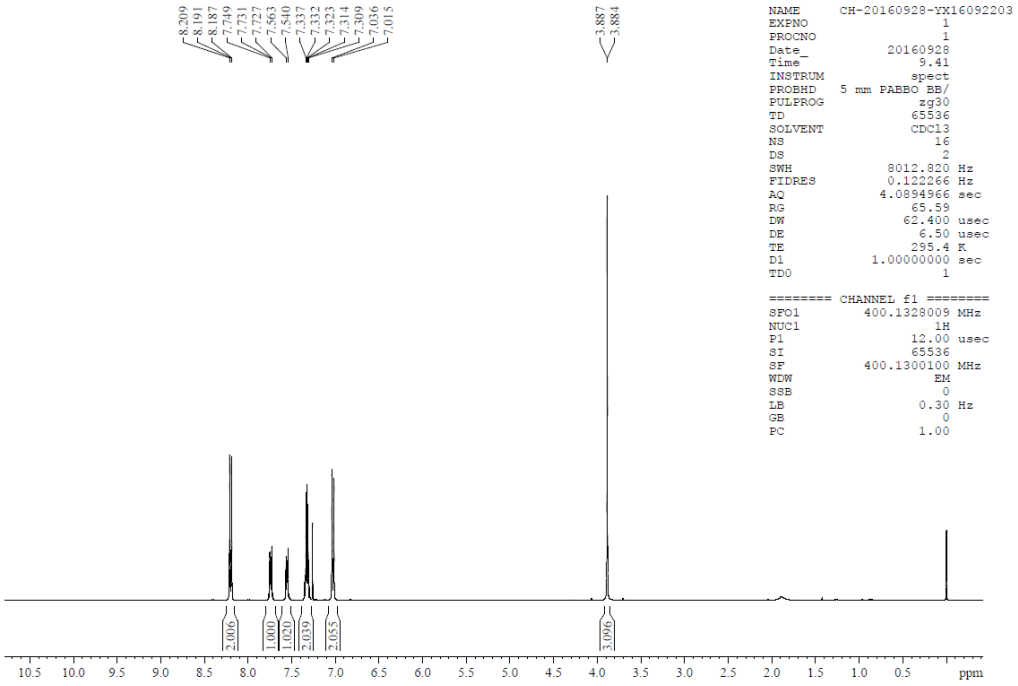


Figure S36. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(4-methoxyphenyl)benzoxazole (**6g**).

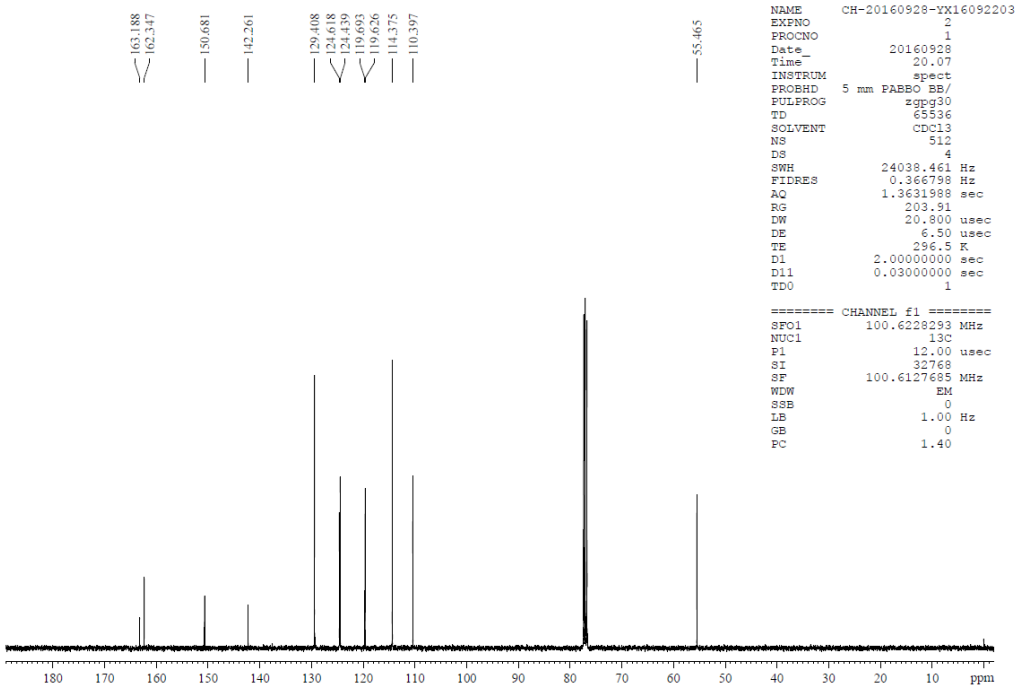


Figure S37. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(4-methoxyphenyl)benzoxazole (**6g**).

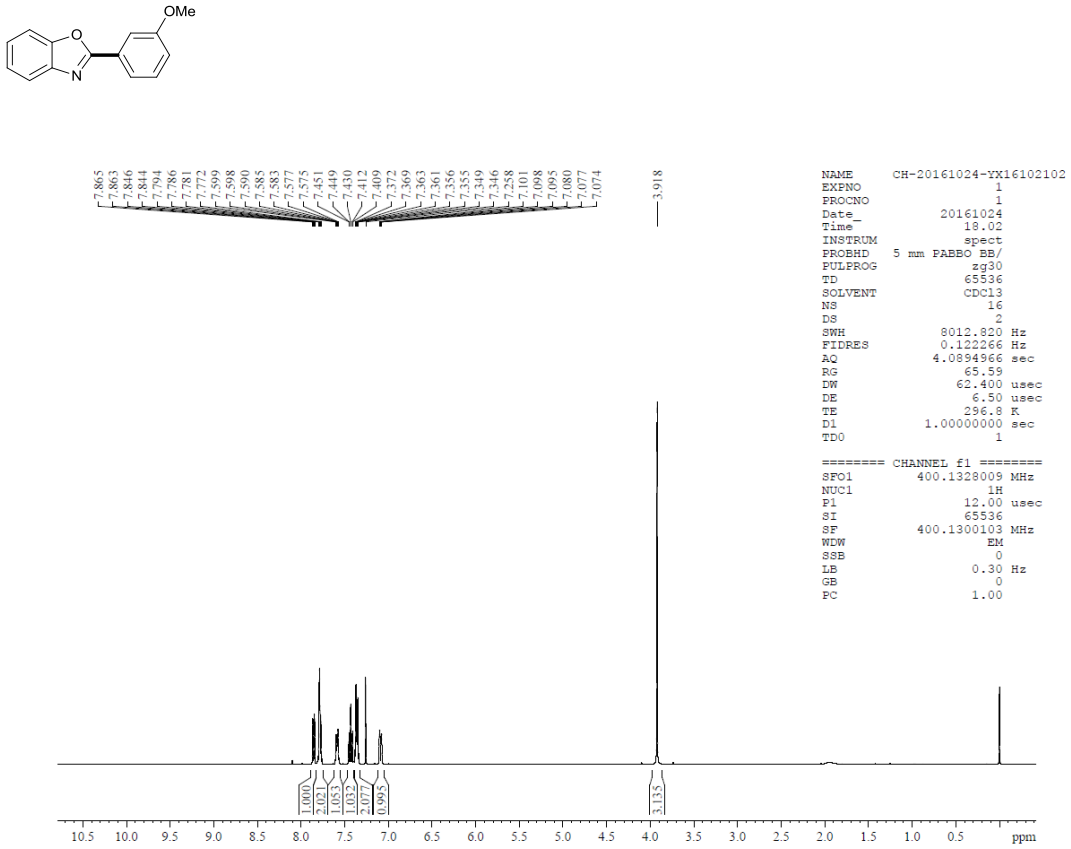


Figure S38. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(3-methoxyphenyl)benzoxazole (**6h**).

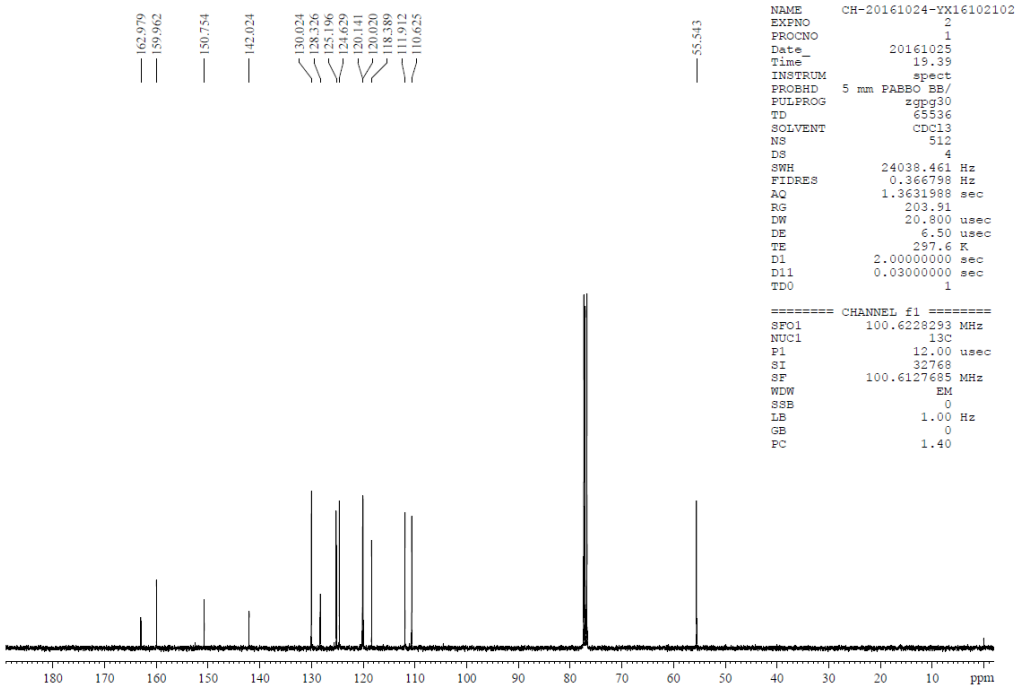


Figure S39. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(3-methoxyphenyl)benzoxazole (**6h**).

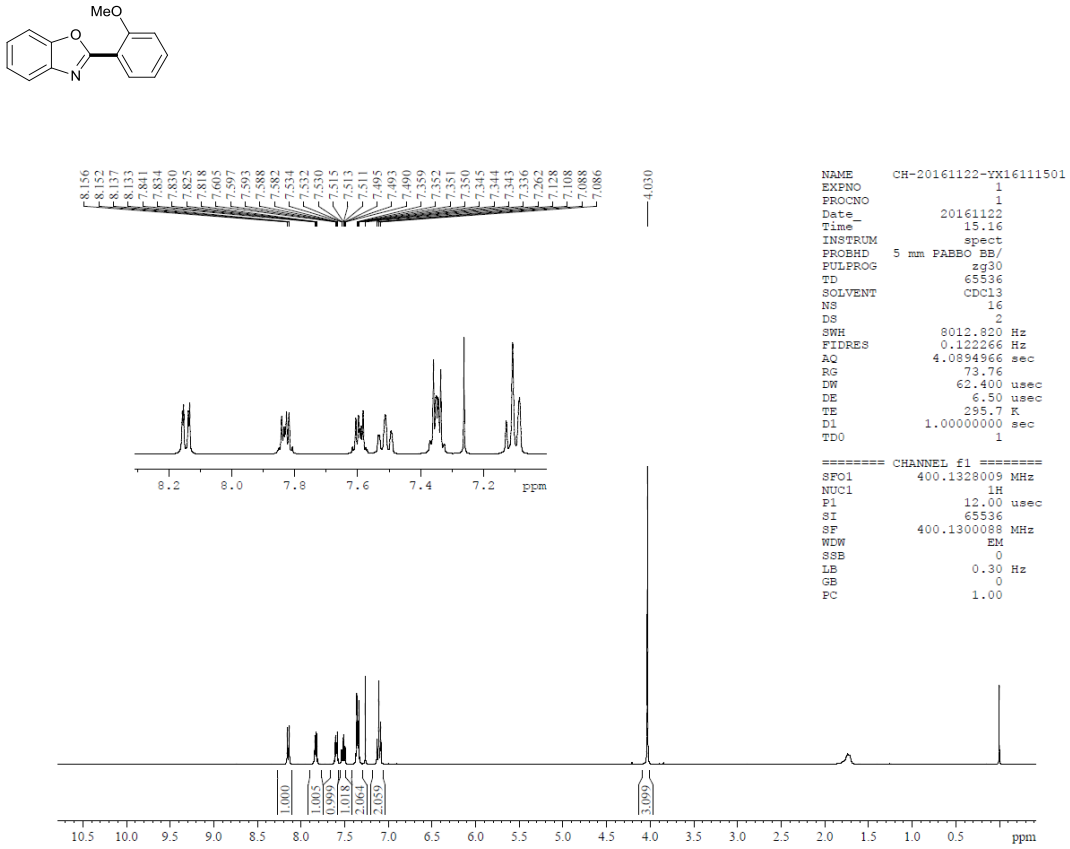


Figure S40. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(2-methoxyphenyl)benzoxazole (**6i**).

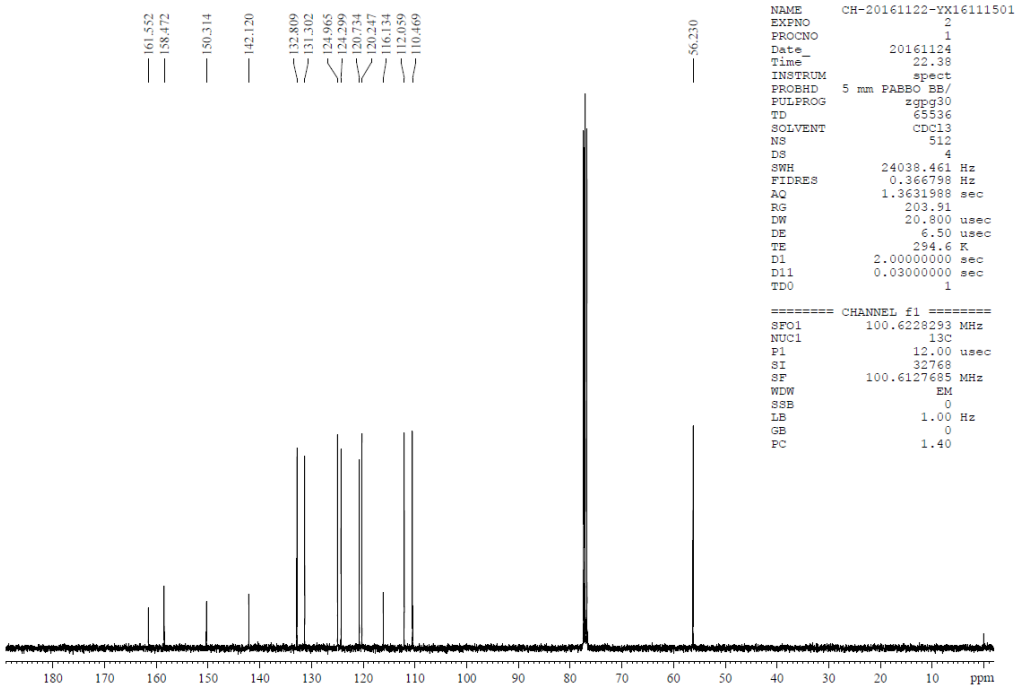


Figure S41. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(2-methoxyphenyl)benzoxazole (**6i**).

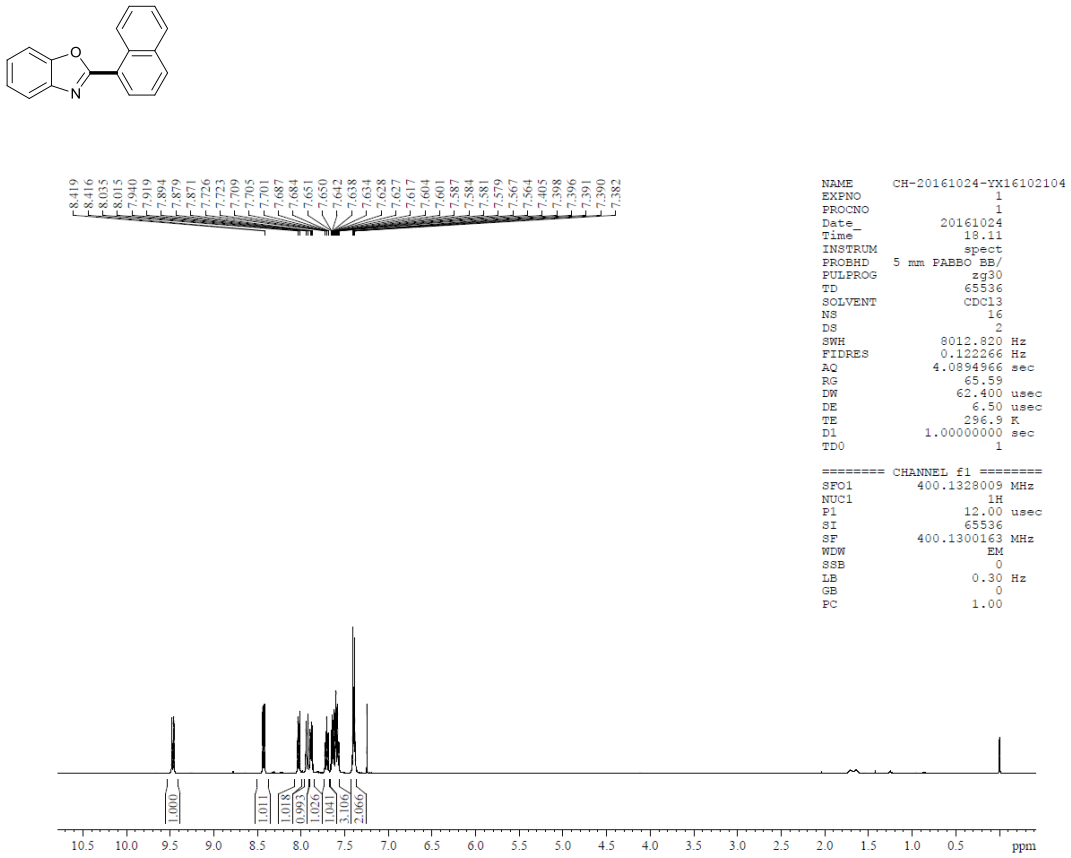


Figure S42. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(naphthalen-1-yl)benzoxazole (**6j**).

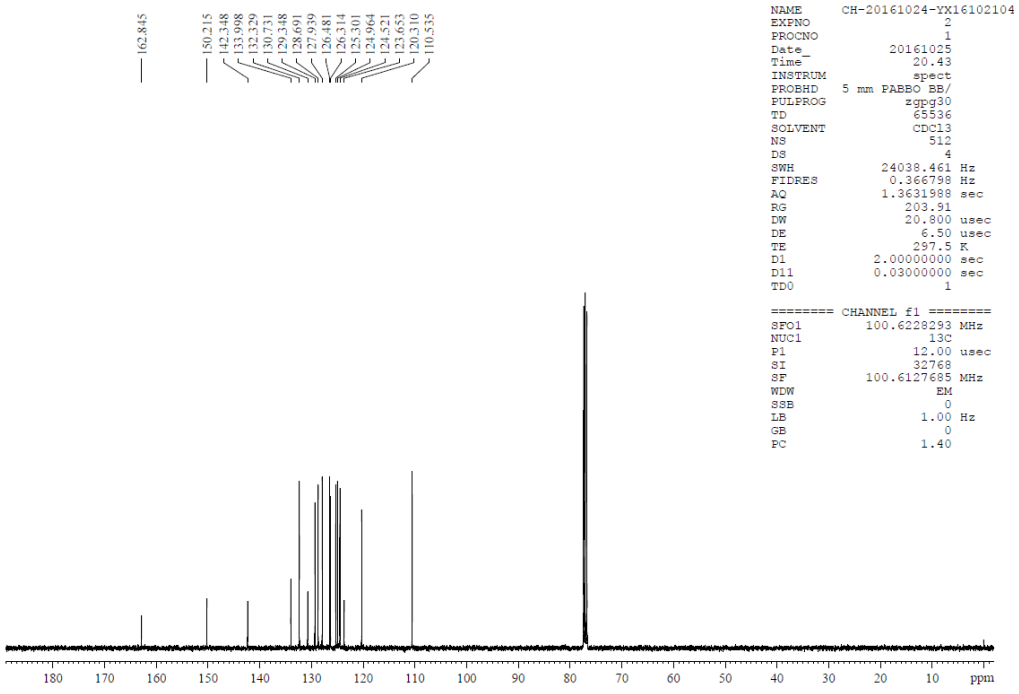


Figure S43. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(naphthalen-1-yl)benzoxazole (**6j**).

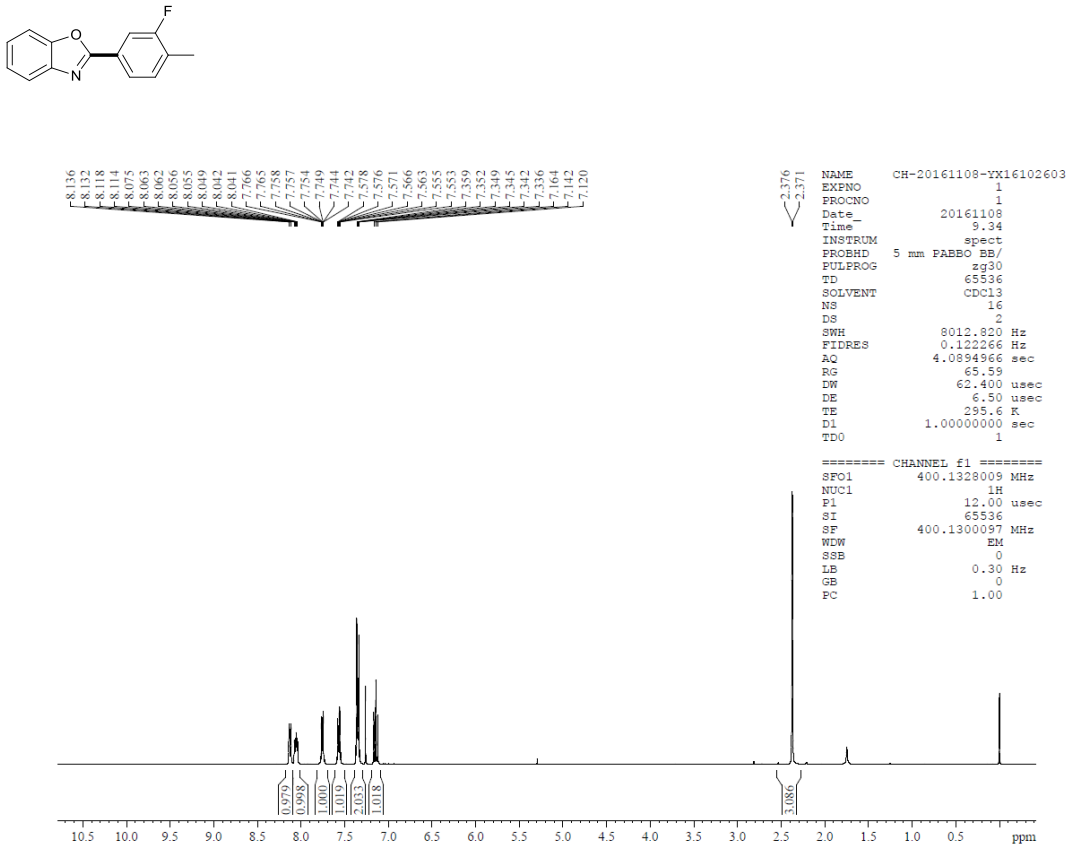


Figure S44. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(3-fluoro-4-methylphenyl)benzoxazole (**6k**).

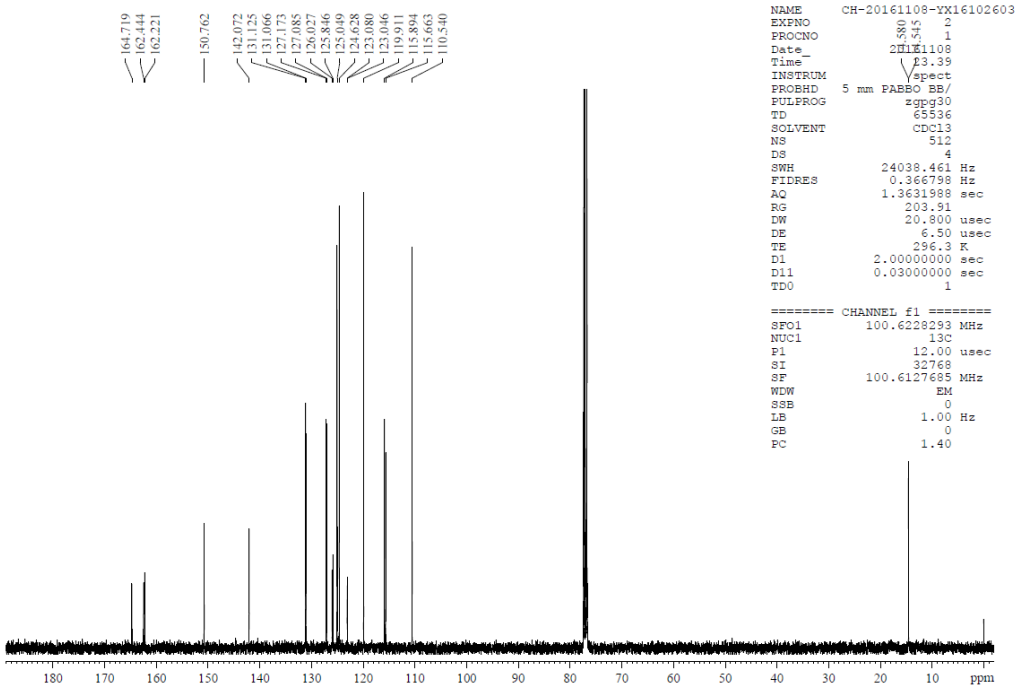
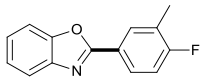


Figure S45. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(3-fluoro-4-methylphenyl)benzoxazole (**6k**).



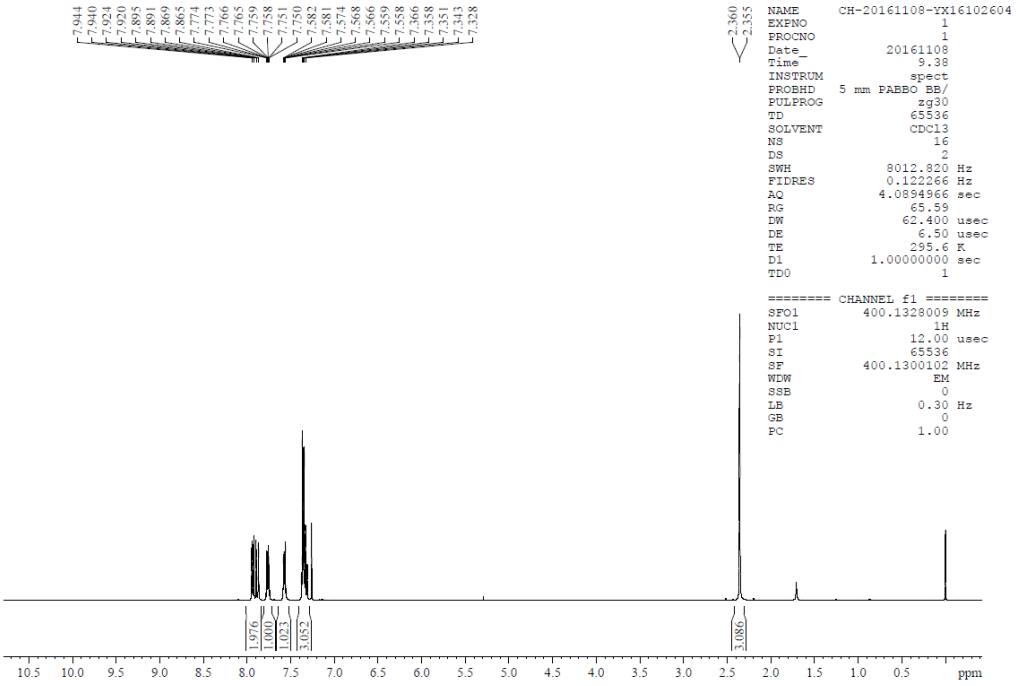


Figure S46. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(4-fluoro-3-methylphenyl)benzoxazole (**6l**).

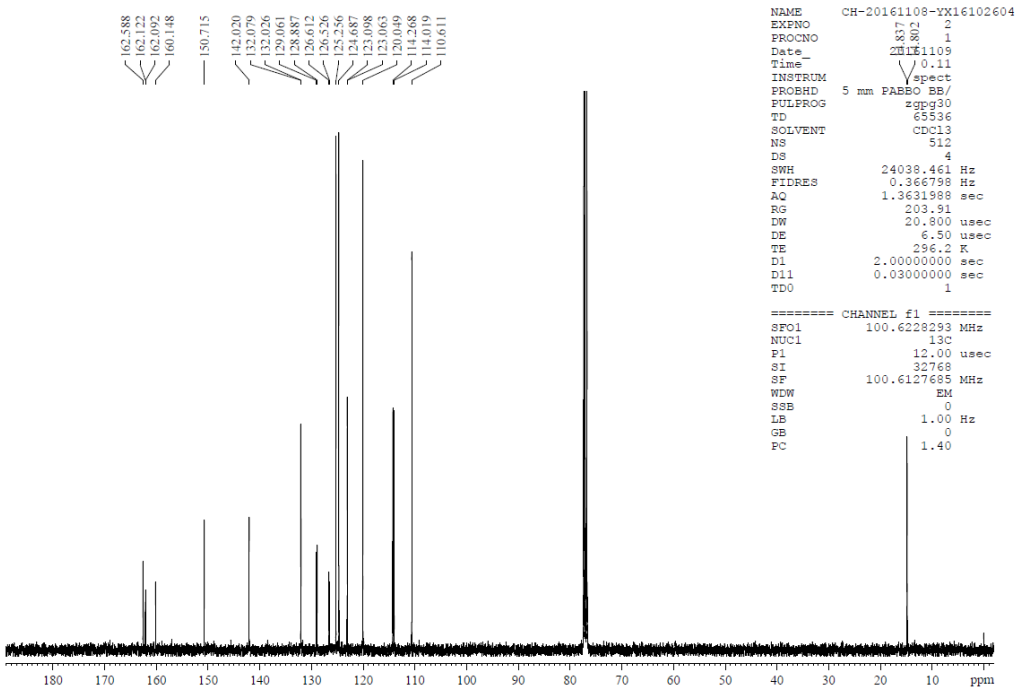
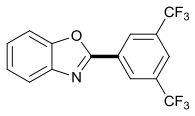


Figure S47. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(4-fluoro-3-methylphenyl)benzoxazole (**6l**).



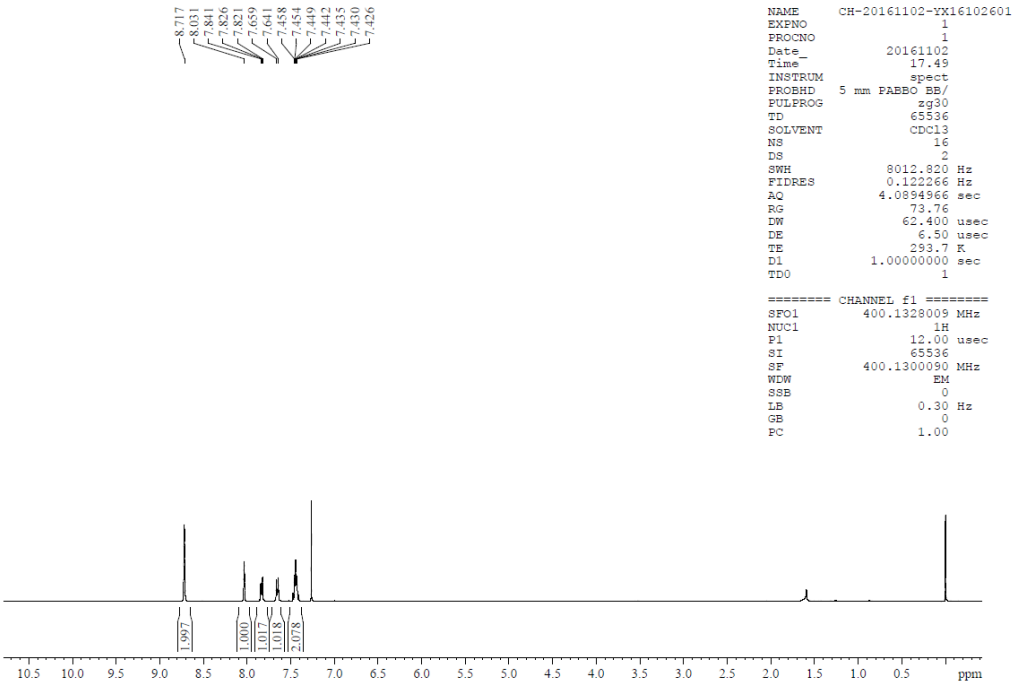


Figure S48. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(3,5-bis(trifluoromethyl)phenyl)benzoxazole (**6m**).

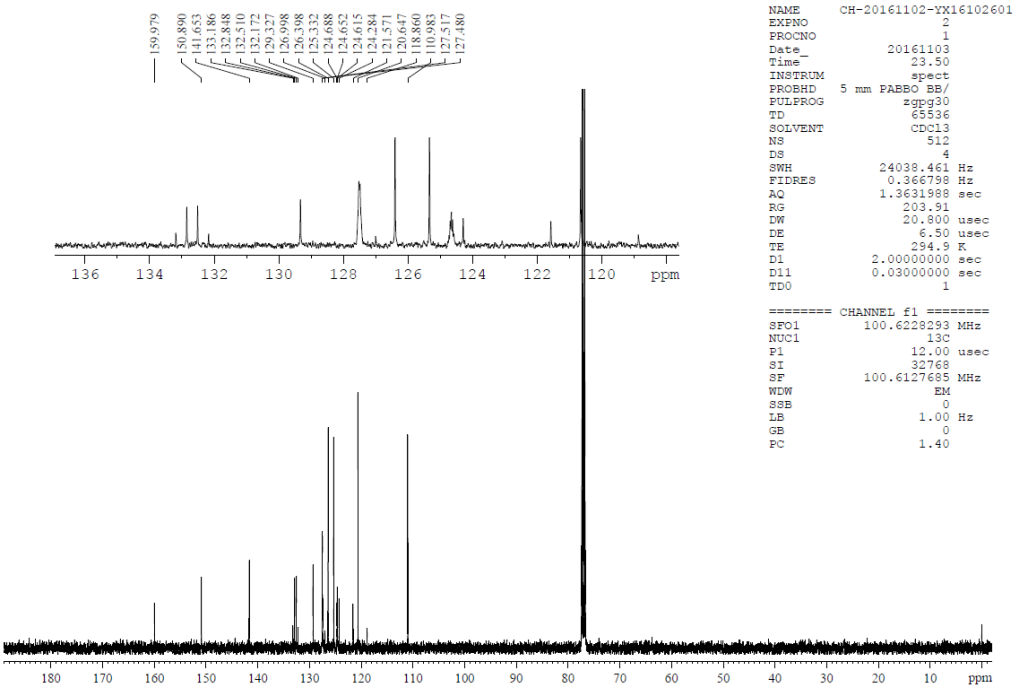


Figure S49. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(3,5-bis(trifluoromethyl)phenyl)benzoxazole (**6m**).

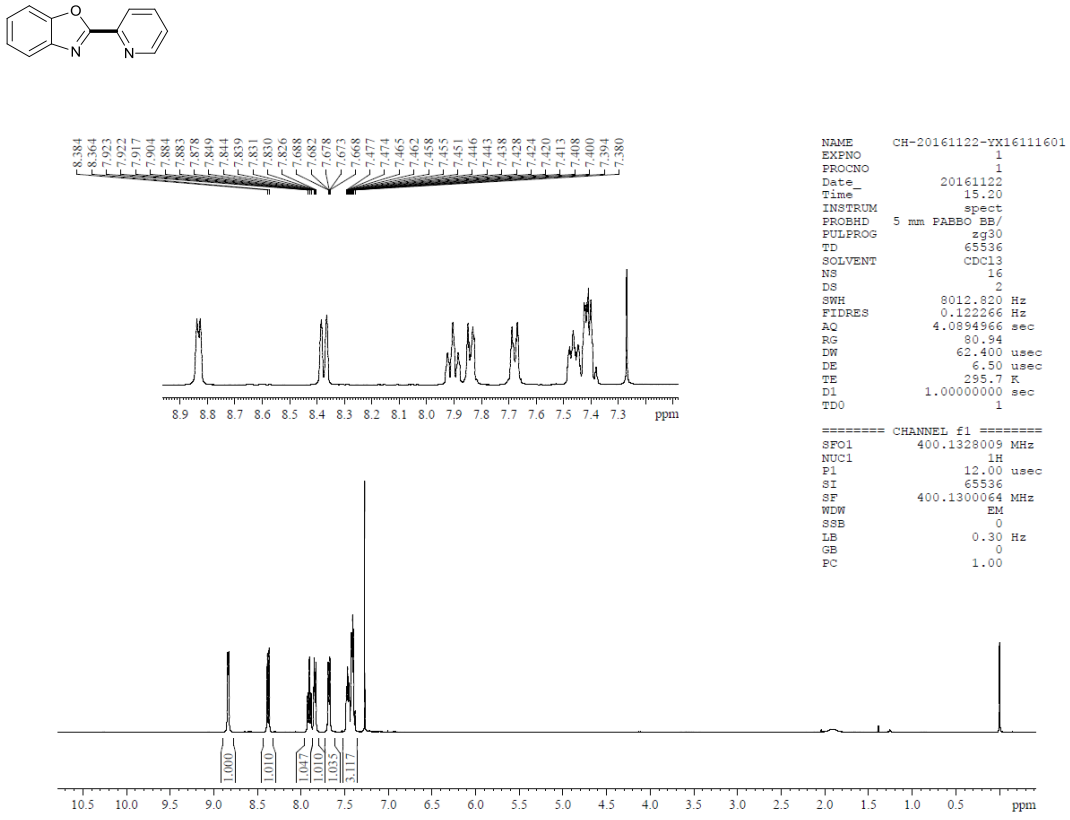


Figure S50. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(pyridin-2-yl)benzoxazole (**6n**).

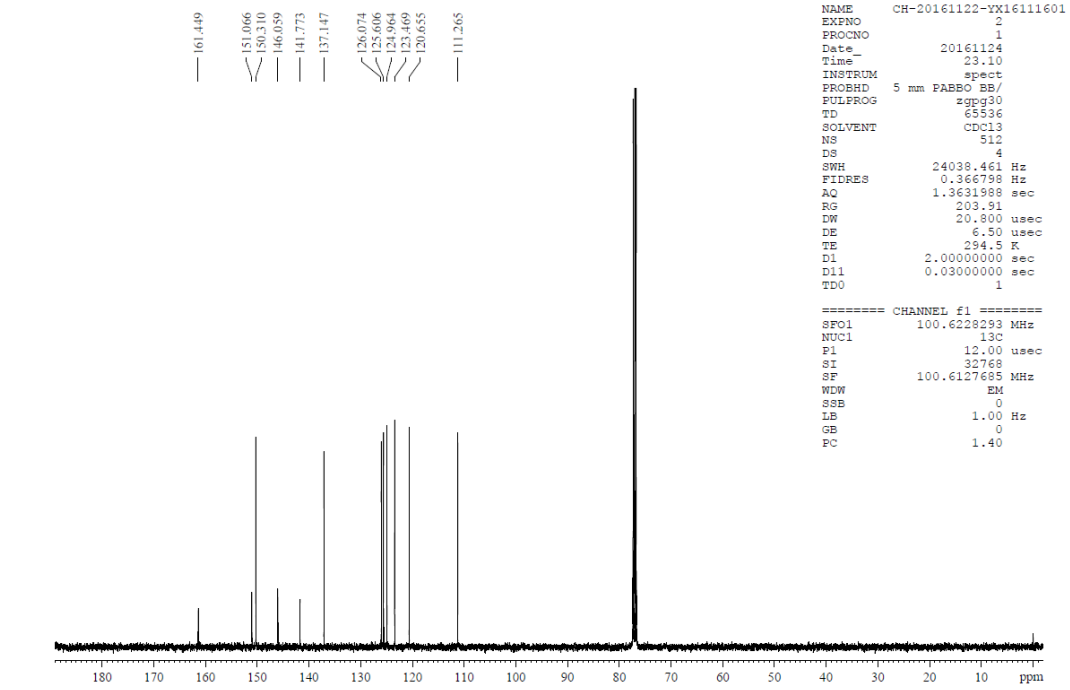
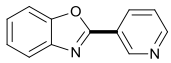


Figure S51. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(pyridin-2-yl)benzoxazole

(**6n**).



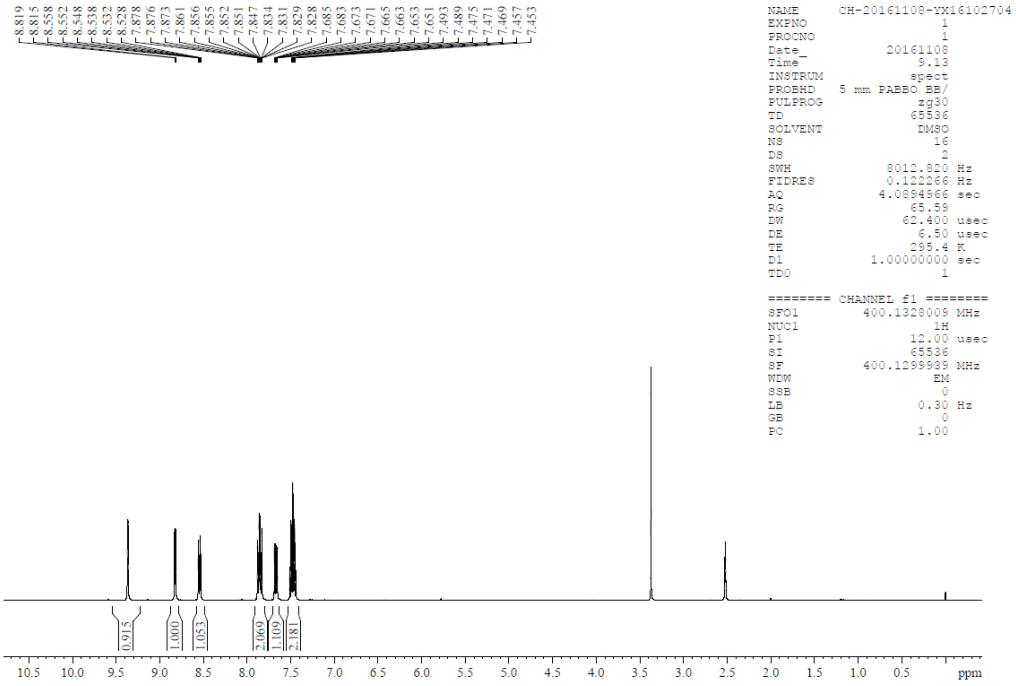


Figure S52. ^{1}H NMR spectrum (400.1 MHz, DMSO-d_6) of 2-(pyridin-3-yl)benzoxazole (**6o**).

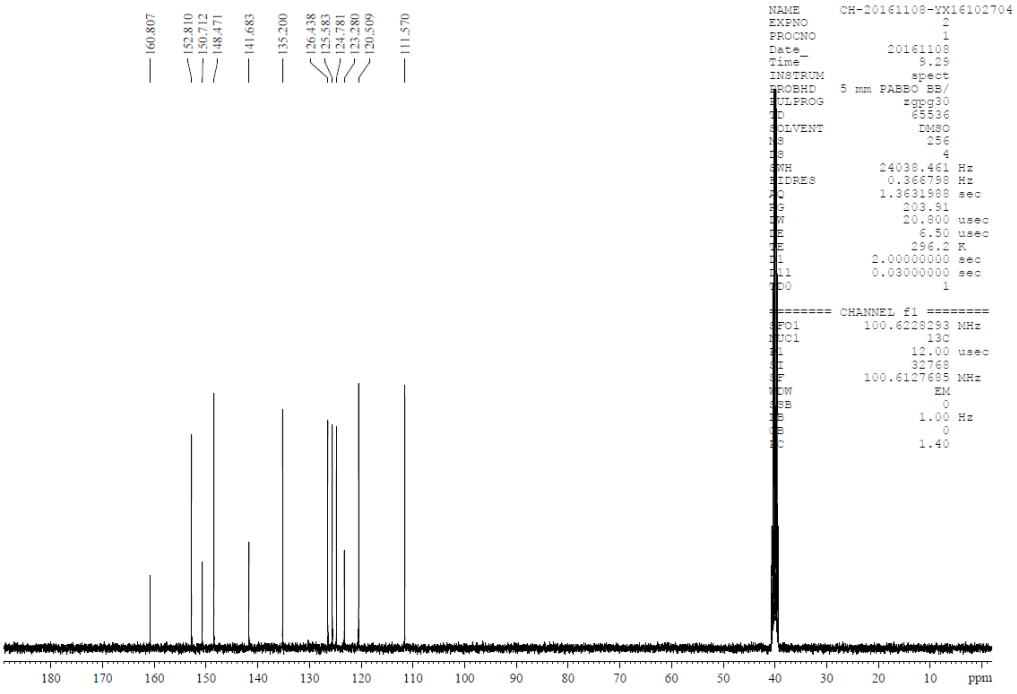
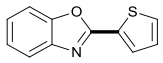


Figure S53. ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of 2-(pyridin-3-yl)benzoxazole (**6o**).



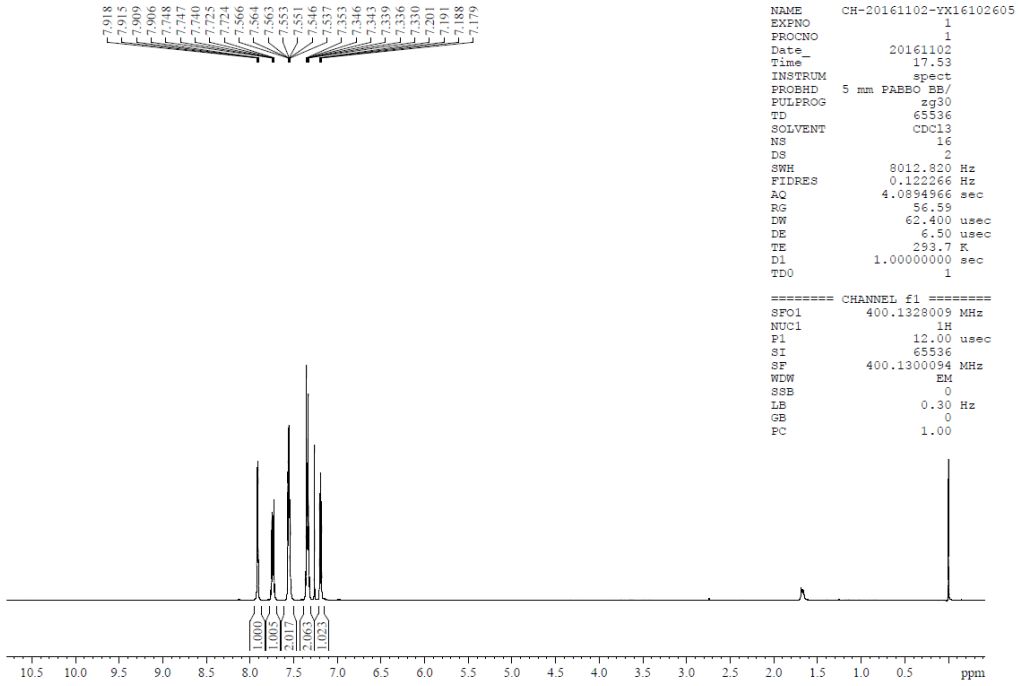


Figure S54. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(thiophen-2-yl)benzoxazole (**6p**).

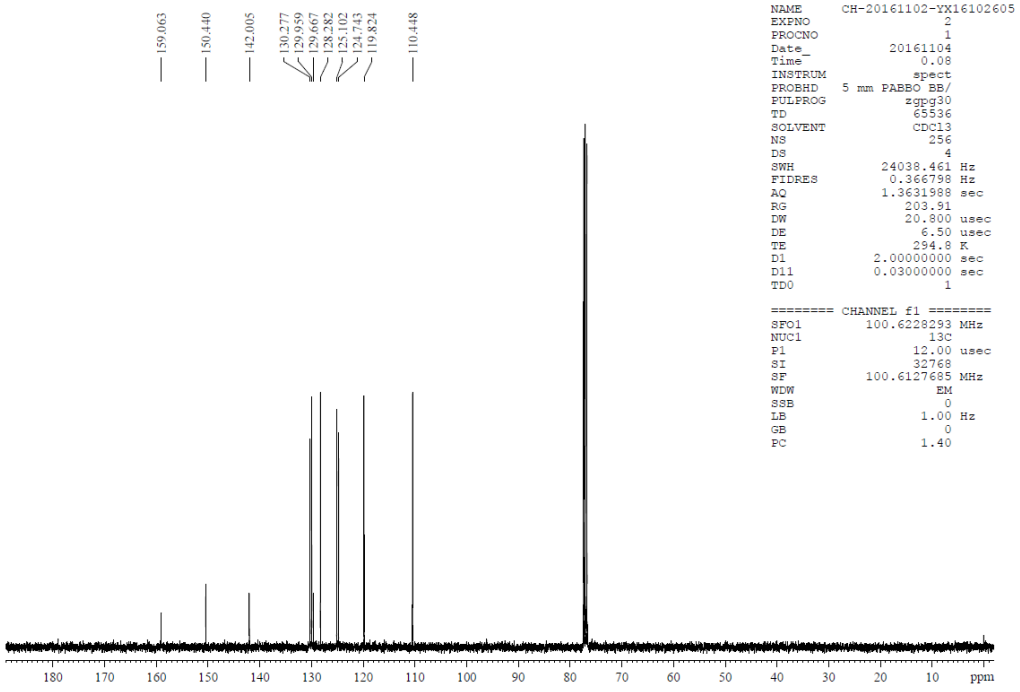
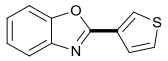


Figure S55. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(thiophen-2-yl)benzoxazole (**6p**).



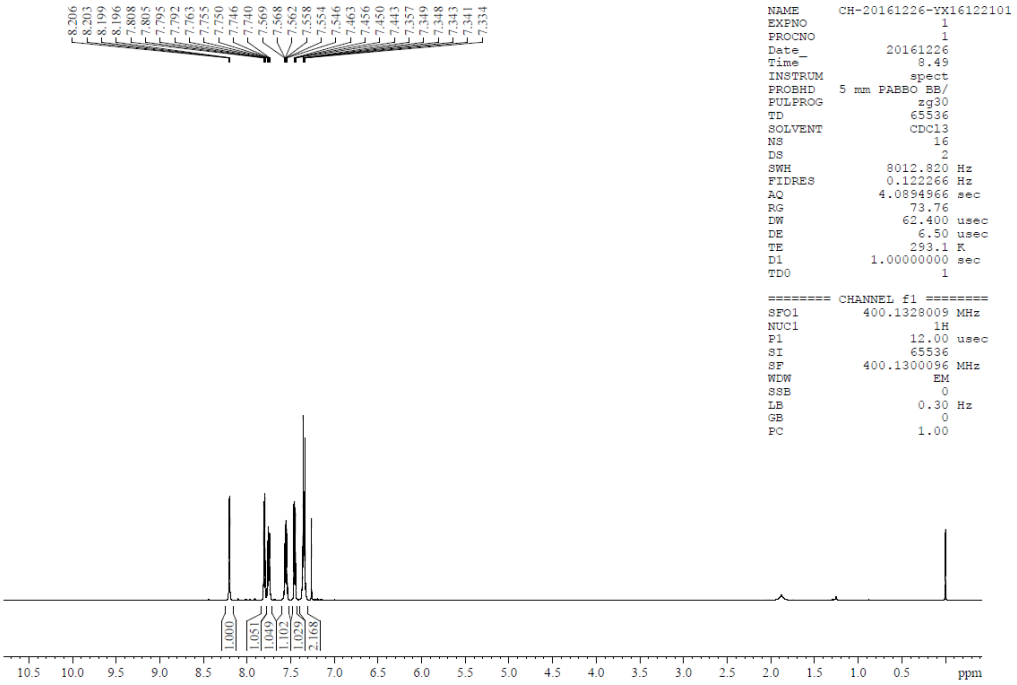


Figure S56. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 2-(thiophen-3-yl)benzoxazole (**6q**).

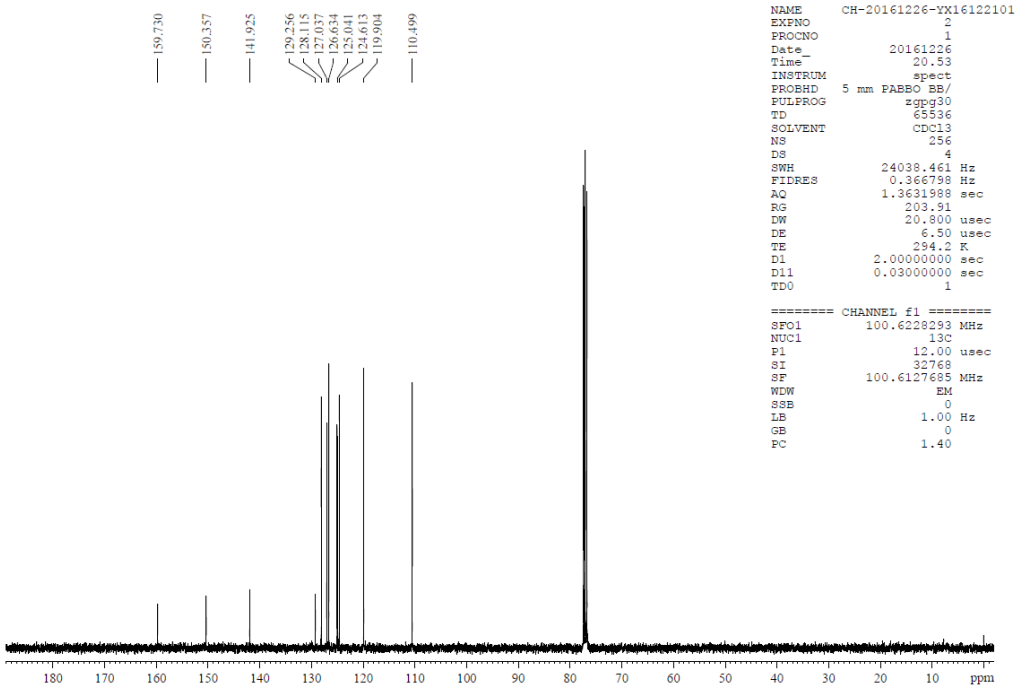
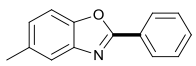


Figure S57. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-(thiophen-3-yl)benzoxazole (**6q**).



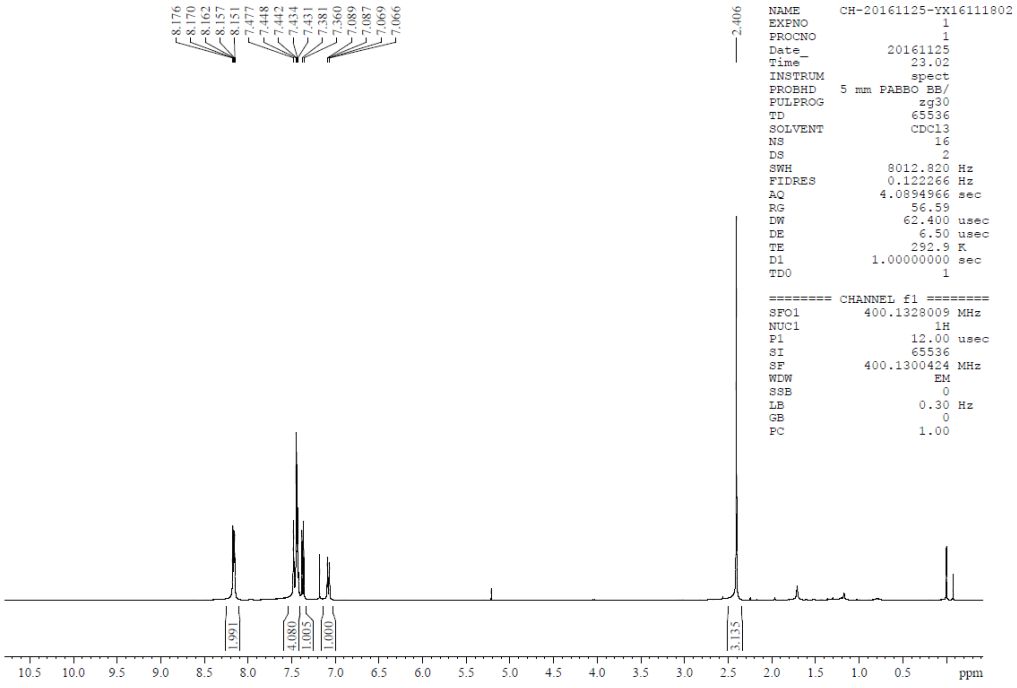


Figure S58. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 5-methyl-2-phenylbenzoxazole (**6r**).

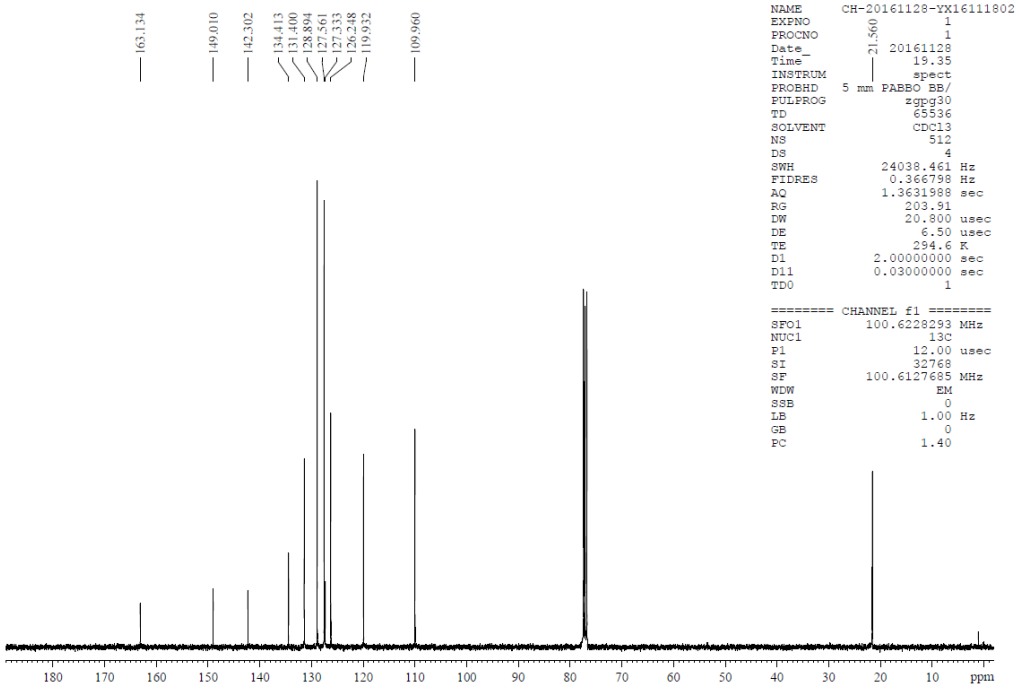
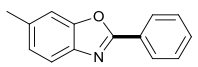


Figure S59. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 5-methyl-2-phenylbenzoxazole (**6r**).



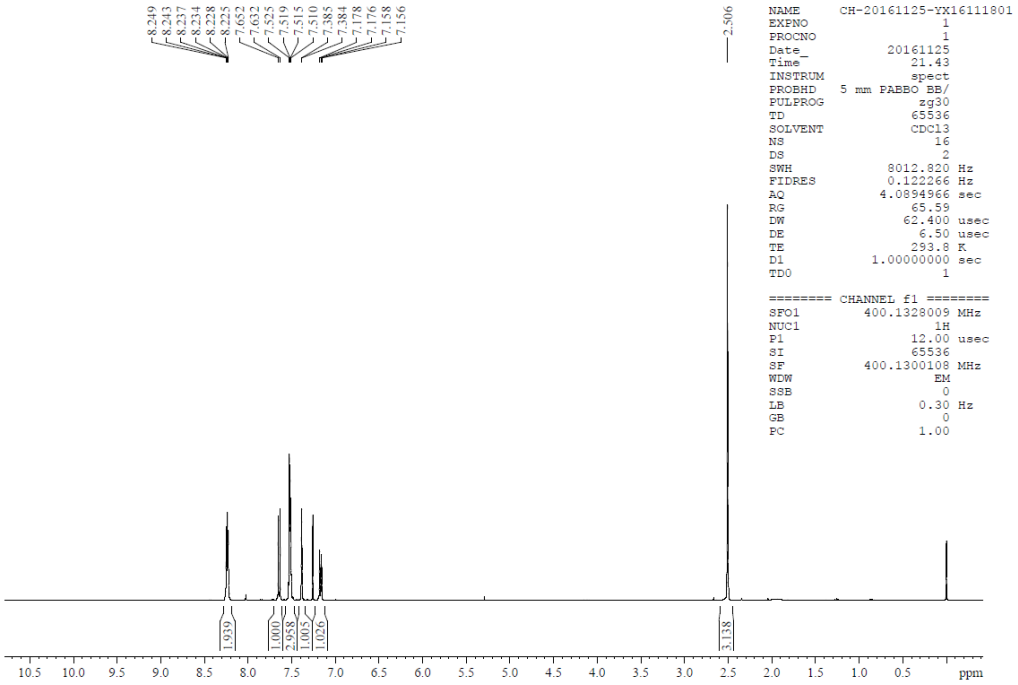


Figure S60. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 6-methyl-2-phenylbenzoxazole (**6s**).

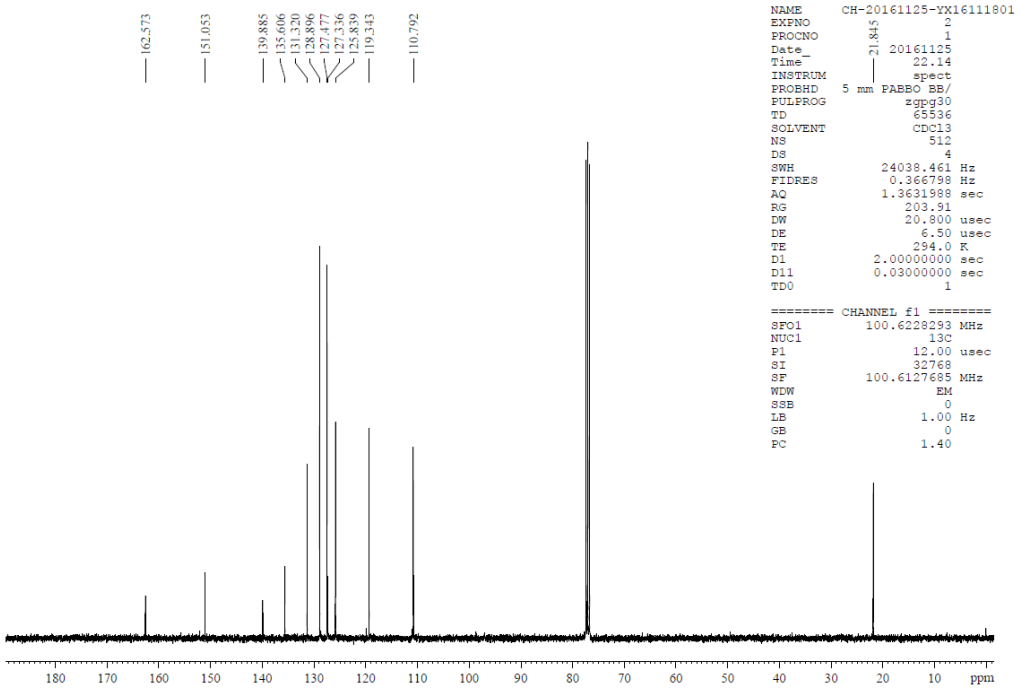
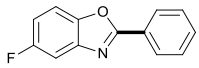


Figure S61. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 6-methyl-2-phenylbenzoxazole (**6s**).



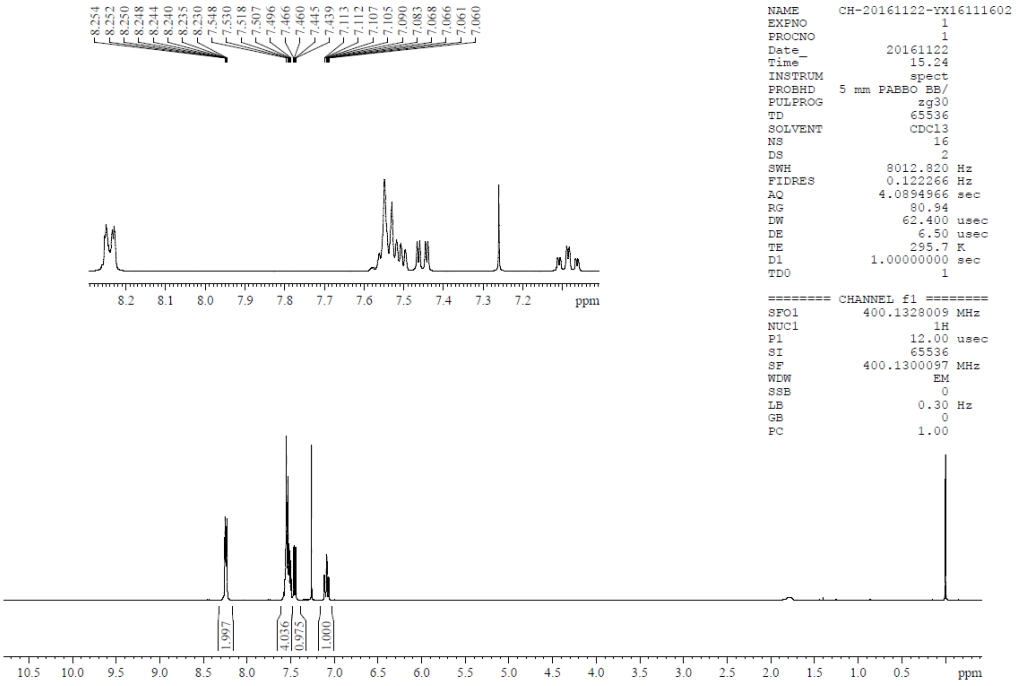


Figure S62. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 5-fluoro-2-phenylbenzoxazole (**6t**).

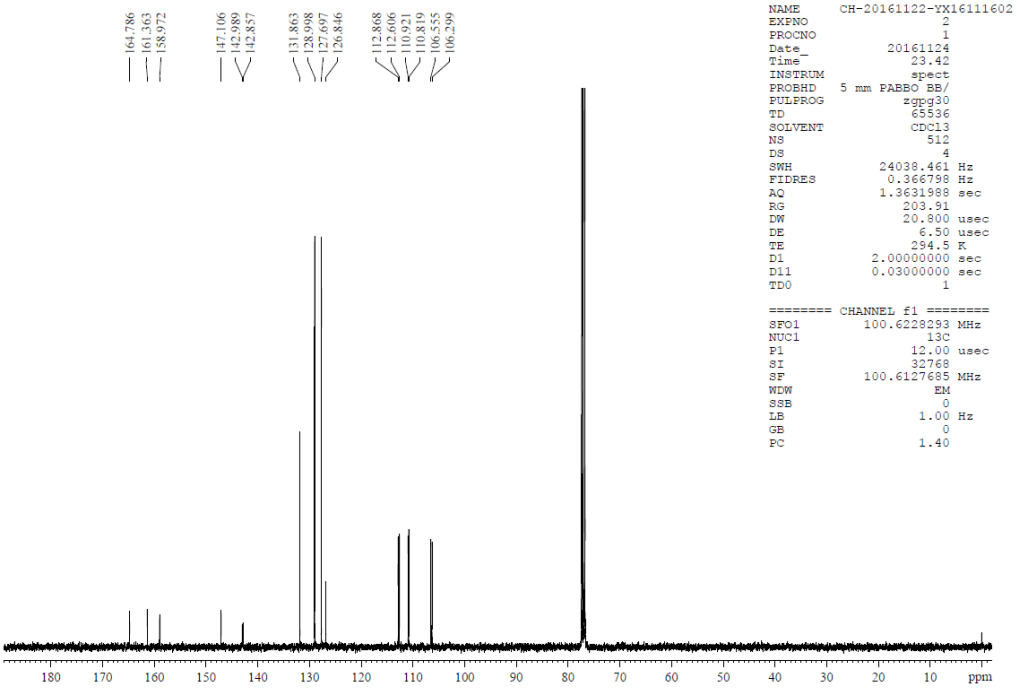
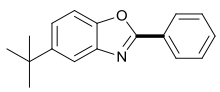


Figure S63. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 5-fluoro-2-phenylbenzoxazole (**6t**).



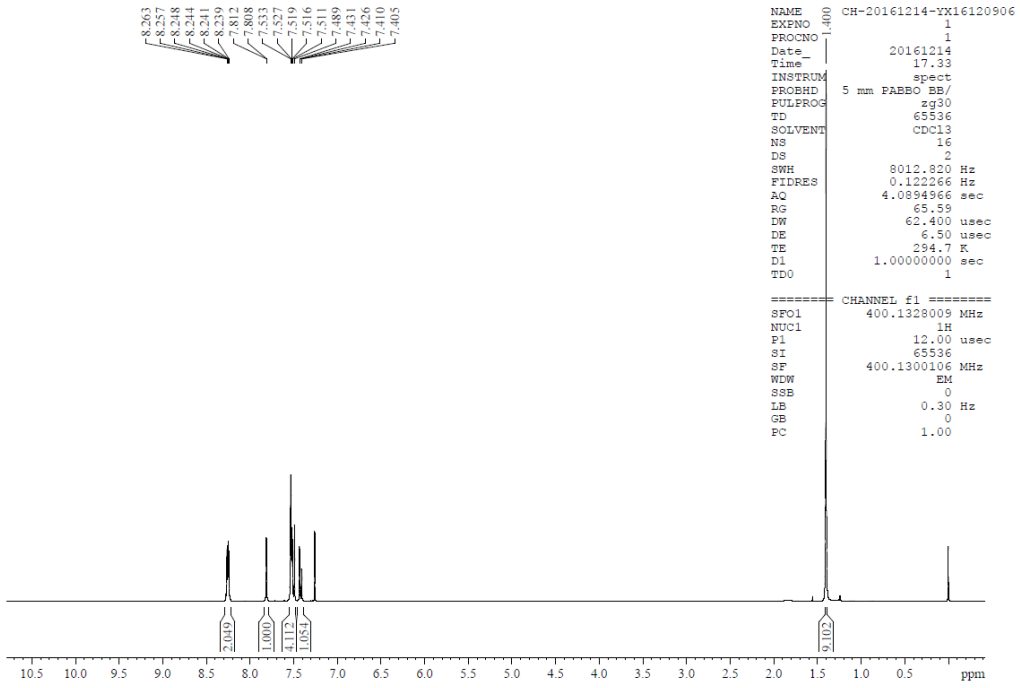


Figure S64. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 5-(tert-butyl)-2-phenylbenzoxazole (**6u**).

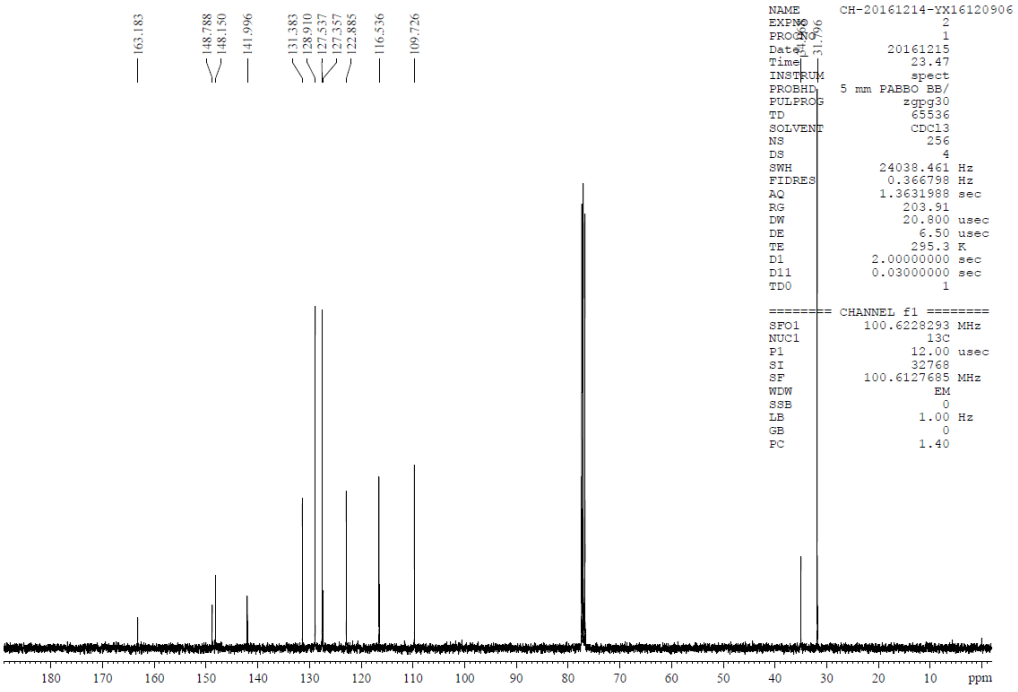
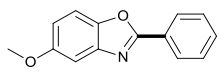


Figure S65. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 5-(tert-butyl)-2-phenylbenzoxazole (**6u**).



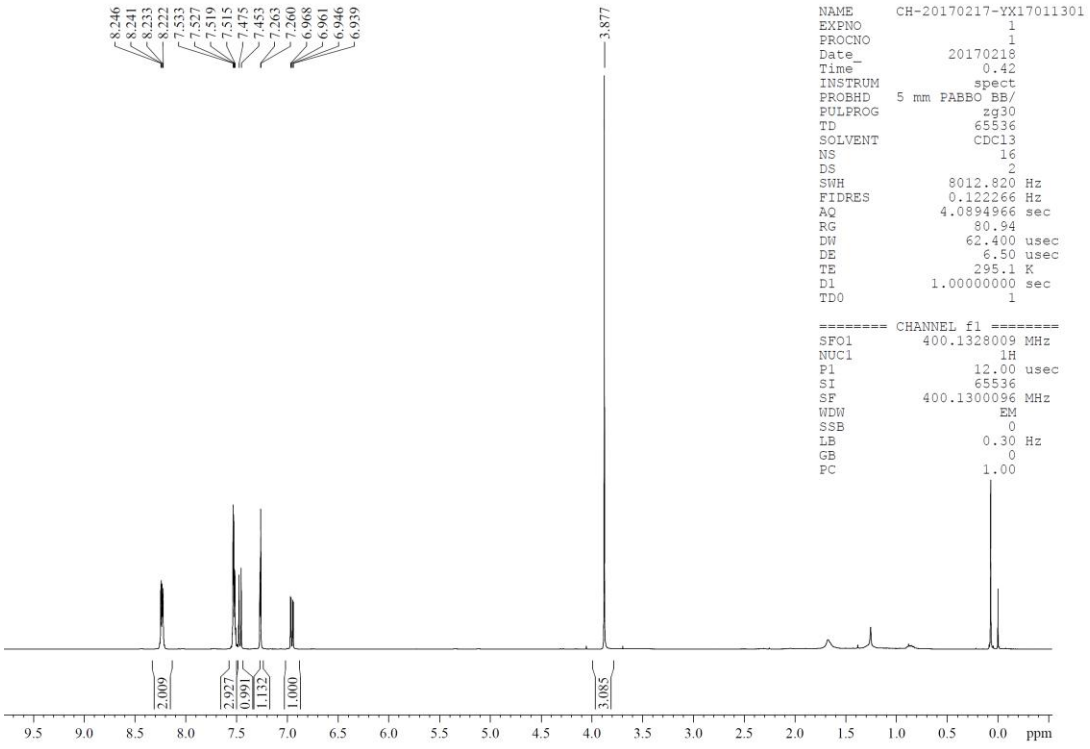


Figure S66. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of 5-methoxy-2-phenylbenzoxazole.

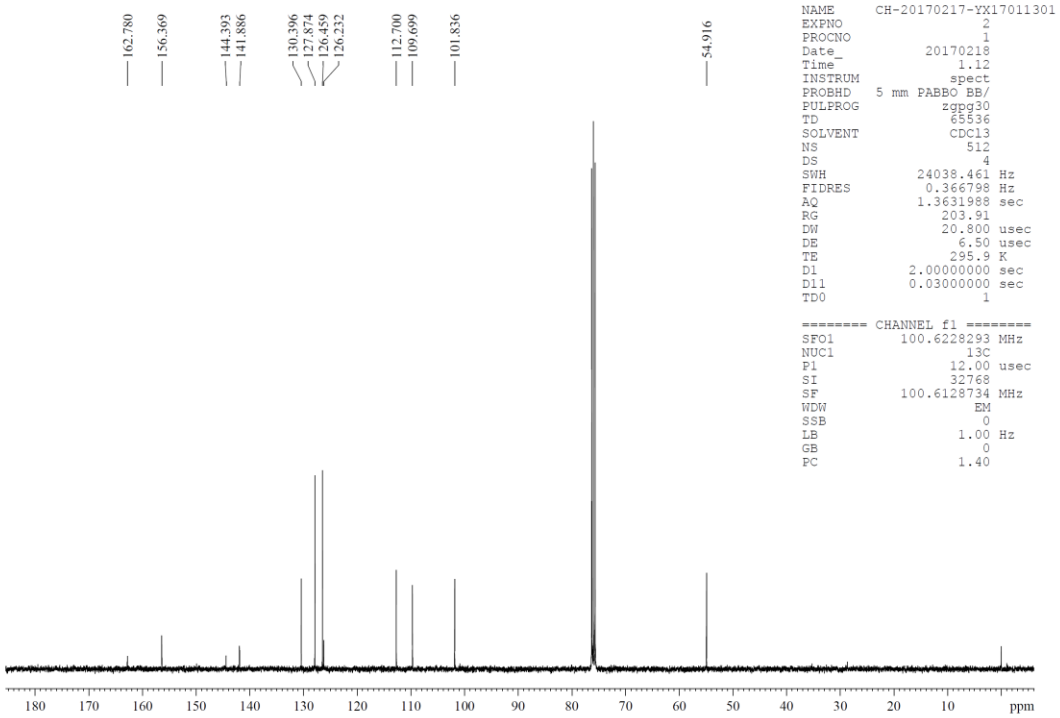


Figure S67. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 5-methoxy-2-phenylbenzoxazole.