Electronic Supplementary Information (ESI) for:

A highly efficient and recyclable CuI@UiO-67-bpy catalyst for direct sp^2 C–H arylation of azoles†

Tingting Li,[a] Nan Li,[a] Dabin Shi[a]*

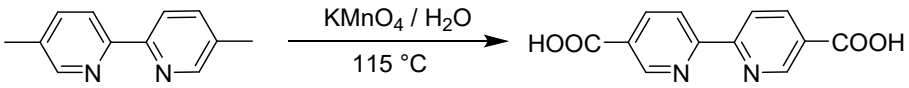
[a] *Key Laboratory of Biocatalysis & Chiral Drug Synthesis of Guizhou Province, School of Pharmacy, Zunyi Medical University, Zunyi 563000, P. R. China.*

Contents

---

* Corresponding author: Prof. Dabin shi
E-mail: sdb007.student@sina.com

1. Synthesis of H_2bpy



A mixture of 5,5'-dimethyl-2,2'-bipyridine (1 eq, 4 g, 21.7 mmol) and potassium permanganate (35 eq, 24g, 751.8 mmol) in 250 mL of H_2O was heated for 2 h (115 ºC), cooled at rt and filtrated trough celite. The filtrate was cooled to 4 ºC and acidified with HCl until precipitation of a white solid, which was filtrated, washed with water, and lyophilized to afford the desired product in a 90% yield (4.7 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.20 (s, 2H), 8.57 (d, J = 7.8 Hz, 2H), 8.45 (d, J = 8.1 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): 166.1, 157.4, 150.4, 138.6, 127.2, 121.2.

2. IR spectra of MOF I and MOF II

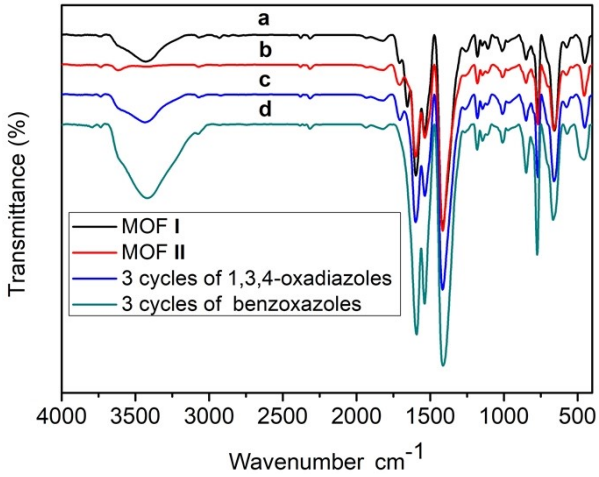


Fig. S1 IR spectra, (a) MOF **I** as-synthesized pristine sample, (b) MOF **II** as-synthesized pristine sample, (c) MOF **II** after 3 runs catalysis recycle for C5 arylation of 1,3,4-oxadiazoles, (d) MOF **II** after 3 runs catalysis recycle for C2 arylation of benzoxazoles.

3. XPS survey of MOF I and MOF II

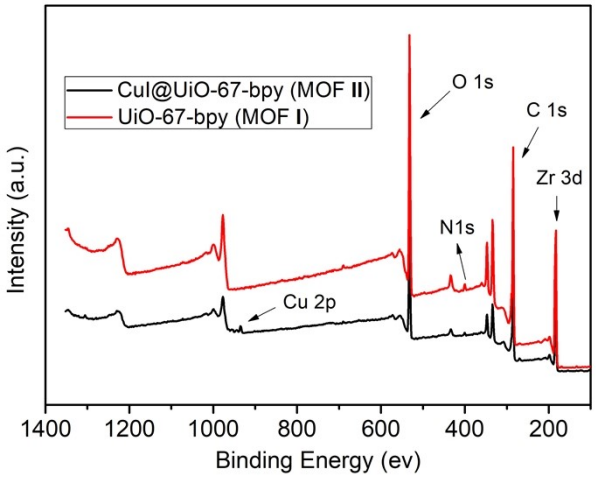


Fig. S2 Complete analysis of MOF **I** and MOF **II** through XPS survey.

4. XPS spectra of N 1s region of MOF I and MOF II

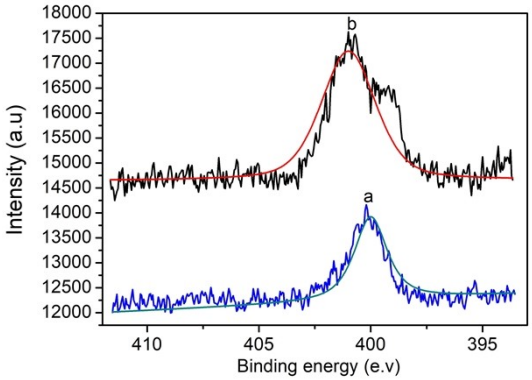


Fig. S3 XPS spectra of the N 1s region for (a) MOF **I** and (b) MOF **II**.

5. TGA curves of MOF I and MOF II

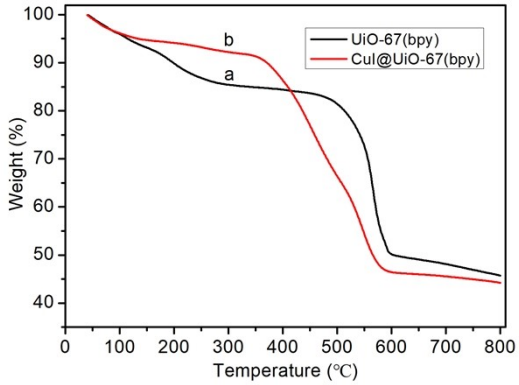
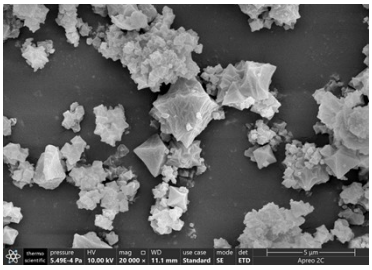


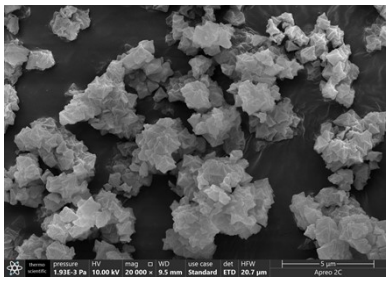
Fig. S4 TGA curves of **I** MOF (a) and MOF **II** (b) recorded under argon atmosphere between 35 and 800 ℃ with a heating rate of 10 ℃ min^{-1}.

6. SEM image of reused MOF II

(a)



(b)



(c)

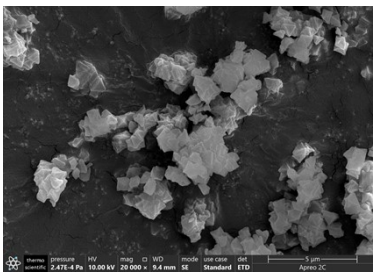
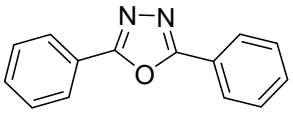


Fig. S5 (a) SEM images of MOF **II** before catalysis, (b) SEM images of MOF **II** after 3 runs catalysis recycle for C5 arylation of 1,3,4-oxadiazoles, (c) SEM images of MOF **II** after 3 runs catalysis recycle for C2 arylation of benzoxazoles.

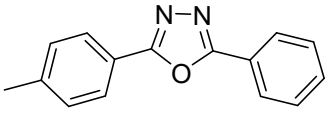
7. Characterization of compound 3

diphenyl-1,3,4-oxadiazole (3a)



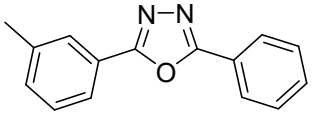
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.11 (m, 4H), 7.59–7.49 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 131.7, 129.1, 126.9, 123.9.

2-phenyl-5-(*p*-tolyl)-1,3,4-oxadiazole (3b)



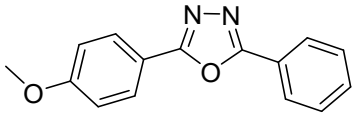
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.10 (m, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.31 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.5, 164.1, 142.1, 131.4, 129.6, 128.8, 126.6, 123.7, 120.8, 109.8, 21.5.

2-phenyl-5-(m-tolyl)-1,3,4-oxadiazole (3c)



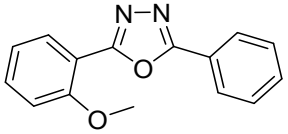
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.09 (m, 2H), 8.00 – 7.87 (m, 2H), 7.58 – 7.48 (m, 3H), 7.41 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.7, 164.5, 138.9, 132.5, 131.7, 129.0, 128.9, 127.4, 126.9, 124.0, 123.9, 123.7, 21.3.

2-(4-methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (3d)



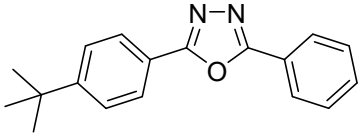
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.09 (m, 2H), 8.08 (d, J = 8.9 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.02 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 163.9, 162.2, 131.4, 128.8, 128.6, 126.6, 123.7, 116.0, 114.3, 55.3.

2-(2-methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (3e)



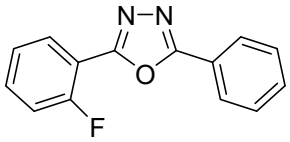
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.08 (m, 2H), 8.00 (dd, J = 7.8, 1.8 Hz, 1H), 7.57 – 7.44 (m, 4H), 7.12 – 7.02 (m, 2H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 163.3, 157.9, 133.2, 131.6, 130.4, 129.0, 126.9, 124.1, 120.7, 112.9, 112.0, 56.1.

2-(4-(*tert*-butyl) phenyl)-5-phenyl-1,3,4-oxadiazole (3f)



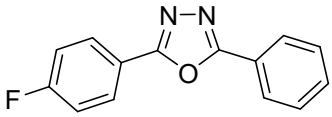
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.10 (m, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.57 – 7.48 (m, 5H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 164.3, 155.4, 131.6, 129.1, 126.9, 126.8, 126.1, 123.9, 121.0, 35.1, 31.1.

2-(2-fluorophenyl)-5-phenyl-1,3,4-oxadiazole (3g)



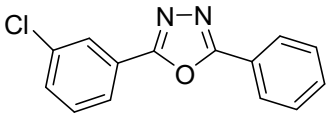
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.11 (m, 3H), 7.59 – 7.48 (m, 4H), 7.30 (t, J = 8.0 Hz, 1H), 7.27 – 7.21 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.90, 161.41 (d, J = 4.9 Hz), 159.96 (d, J = 258.3 Hz), 133.50 (d, J = 8.5 Hz), 131.8, 129.7, 129.1, 127.0, 124.7 (d, J = 3.8 Hz), 123.7, 117.0 (d, J = 20.9 Hz), 112.4 (d, J = 11.8 Hz).

2-(4-fluorophenyl)-5-phenyl-1,3,4-oxadiazole (3h)



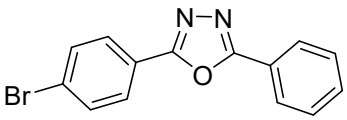
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.07 (m, 4H), 7.57 – 7.47 (m, 3H), 7.20 (t, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.74 (d, J = 253.0 Hz), 164.6, 163.7, 131.8, 129.2 (d, J = 8.9 Hz), 129.1, 126.9, 123.7, 120.2 (d, J = 3.4 Hz), 116.4 (d, J = 22.2 Hz).

2-(3-chlorophenyl)-5-phenyl-1,3,4-oxadiazole (3i)



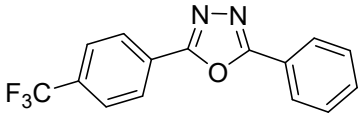
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.08 (m, 3H), 8.01 (d, J = 7.5 Hz, 1H), 7.59 – 7.42 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.8, 163.4, 135.2, 131.9, 131.7, 130.4, 129.1, 126.9, 126.8, 125.5, 125.0, 123.6.

2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (3j)



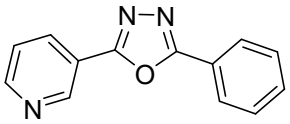
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.9, 1.7 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.58 – 7.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.7, 163.8, 132.4, 131.9, 129.1, 128.3, 126.9, 126.4, 123.6, 122.8.

2-(4-(trifluoromethyl) phenyl)-5-phenyl-1,3,4-oxadiazole (3k)



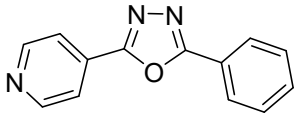
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.64 – 7.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1, 163.4, 133.3 (d, J = 33.1 Hz), 132.1, 129.2, 127.2, 127.1, 126.1 (q, J = 3.7 Hz), 124.9, 123.5, 122.2.

2-phenyl-5-(pyridin-3-yl)-1,3,4-oxadiazole (3l)



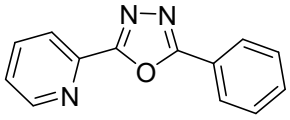
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.77 (d, J = 4.0 Hz, 1H), 8.42 (dd, J = 8.0, 1.7 Hz, 1H), 8.12 (dt, J = 8.1, 1.9 Hz, 2H), 7.61 – 7.44 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 162.4, 152.1, 147.7, 134.2, 132.1, 129.1, 127.0, 123.9, 123.4, 120.4.

2-phenyl-5-(pyridin-4-yl)-1,3,4-oxadiazole (3m)



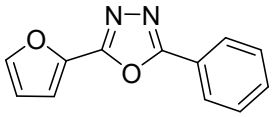
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.83 (s, 2H), 8.08 (d, J = 32.3 Hz, 4H), 7.62 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 165.2, 162.9, 151.1, 132.9, 131.1, 129.9, 127.4, 123.4, 120.8.

2-phenyl-5-(pyridin-2-yl)-1,3,4-oxadiazole (3n)



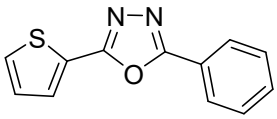
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, J = 4.4 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 8.20 (dd, J = 7.9, 1.5 Hz, 2H), 7.90 (t, J = 8.2 Hz, 1H), 7.59 – 7.39 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6, 163.7, 150.2, 143.5, 137.4, 132.0, 129.0, 127.3, 125.8, 123.5, 123.3.

2-(furan-2-yl)-5-phenyl-1,3,4-oxadiazole (3o)



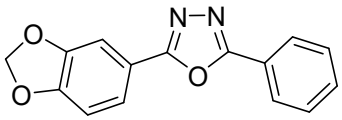
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.1 Hz, 2H), 7.64 (s, 1H), 7.56 – 7.42 (m, 3H), 7.20 (d, J = 3.5 Hz, 1H), 6.60 – 6.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.9, 157.4, 145.7, 139.4, 131.8, 129.1, 126.9, 123.4, 114.1, 112.2.

2-phenyl-5-(thiophen-2-yl)-1,3,4-oxadiazole (3p)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.03 (m, 2H), 7.81 (dt, J = 3.7, 1.2 Hz, 1H), 7.57 – 7.44 (m, 4H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 160.8, 131.7, 130.2, 129.8, 129.1, 128.2, 126.9, 125.2, 123.6.

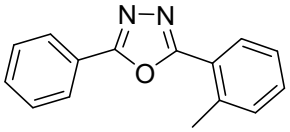
2-(1,3-benzodioxol-5-yl)-5-phenyl-1,3,4-oxadiazole (3q)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.1 Hz, 1H), 7.57 (s, 1H), 7.55 – 7.44

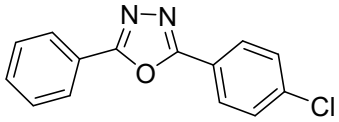
(m, 3H), 6.93 (d, J = 8.1 Hz, 1H), 6.06 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 164.2, 150.6, 148.3, 131.6, 129.0, 126.8, 123.9, 122.0, 117.7, 108.9, 107.0, 101.8.

2-phenyl-5-(o-tolyl)-1,3,4-oxadiazole (3r)



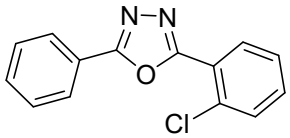
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.08 (m, 2H), 8.02 (d, J = 8.1 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.45 – 7.37 (m, 1H), 7.37 – 7.30 (m, 2H), 2.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.8, 164.1, 138.4, 131.8, 131.7, 131.2, 129.1, 128.9, 126.9, 126.2, 123.9, 122.9, 22.2.

2-(4-chlorophenyl)-5-phenyl-1,3,4-oxadiazole (3s)



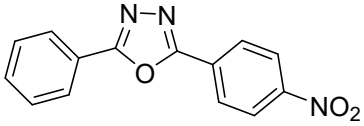
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 7.4 Hz, 2H), 7.57 – 7.43 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.7, 163.7, 137.9, 131.9, 129.4, 129.1, 128.1, 126.9, 123.6, 122.3.

2-(2-chlorophenyl)-5-phenyl-1,3,4-oxadiazole (3t)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 7.6, 2.0 Hz, 2H), 8.09 (dd, J = 7.6, 1.9 Hz, 1H), 7.58 – 7.38 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1, 163.0, 133.0, 132.4, 131.9, 131.3, 131.2, 129.1, 127.1, 127.0, 123.7, 123.2.

2-(4-nitrophenyl)-5-phenyl-1,3,4-oxadiazole (3u)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, J = 9.0 Hz, 2H), 8.32 (d, J = 9.0 Hz, 2H), 8.15 (dd, J = 8.1, 1.5 Hz, 2H), 7.64 – 7.51 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5, 162.8, 149.5, 132.3, 129.4, 129.2, 127.8, 127.1, 124.4, 123.3.

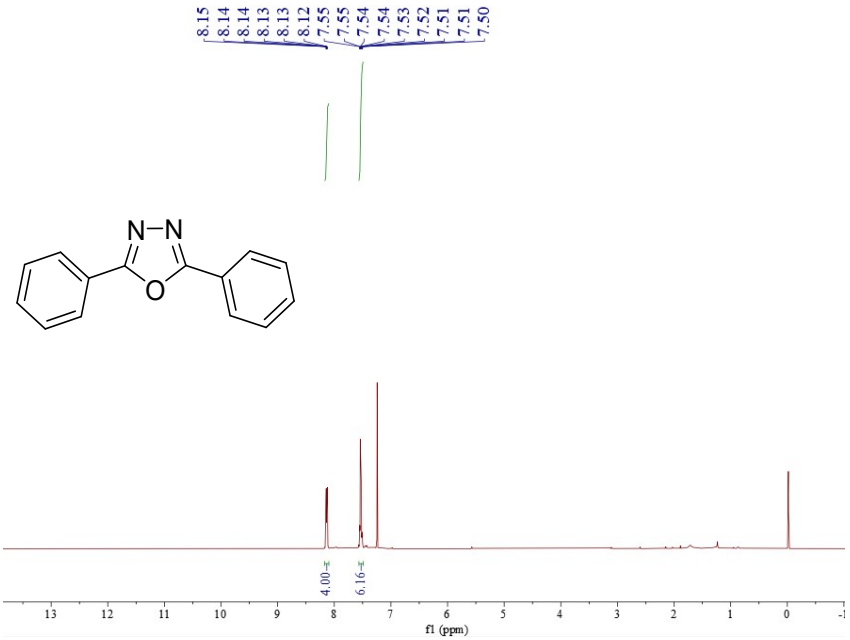


Fig. S6 ^{1}H NMR of **3a**

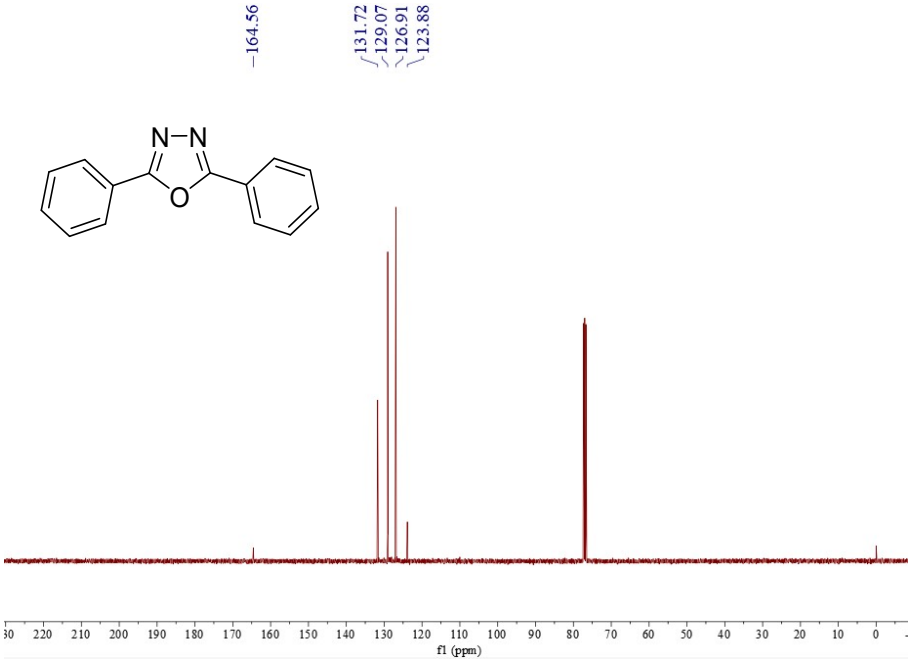


Fig. S7 ^{13}C NMR of **3a**

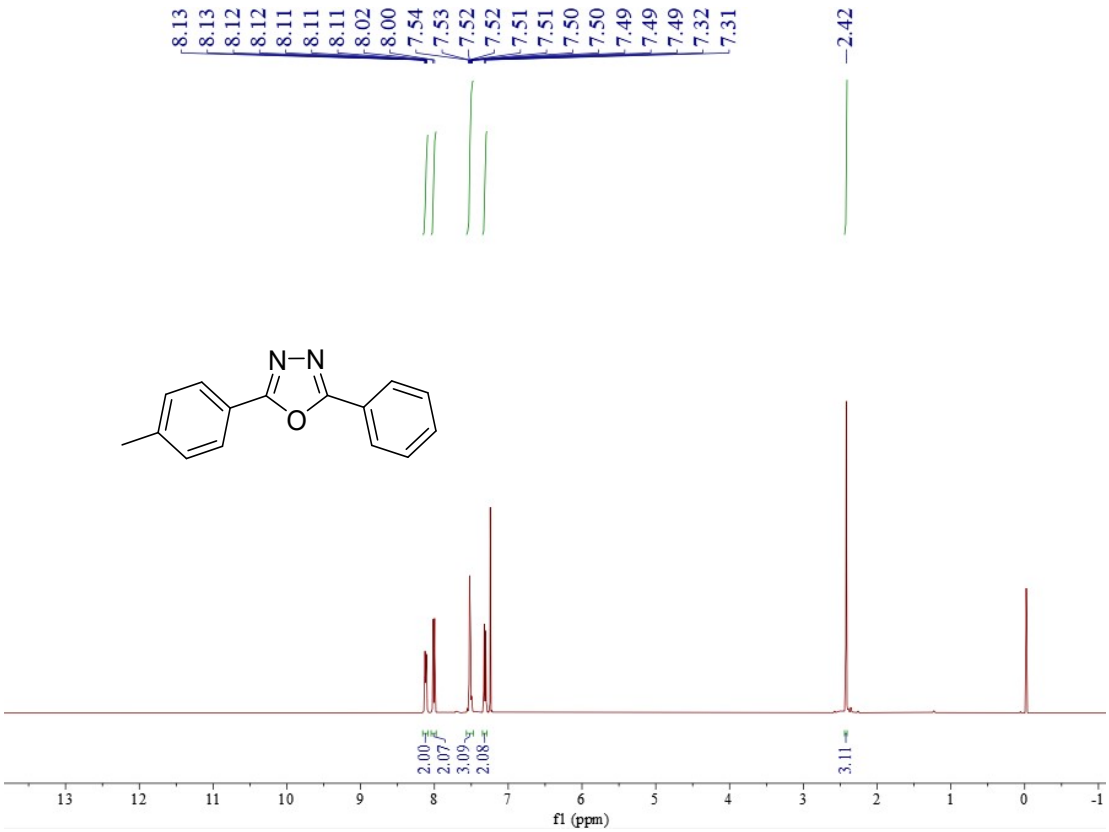


Fig. S8 ^{1}H NMR of **3b**

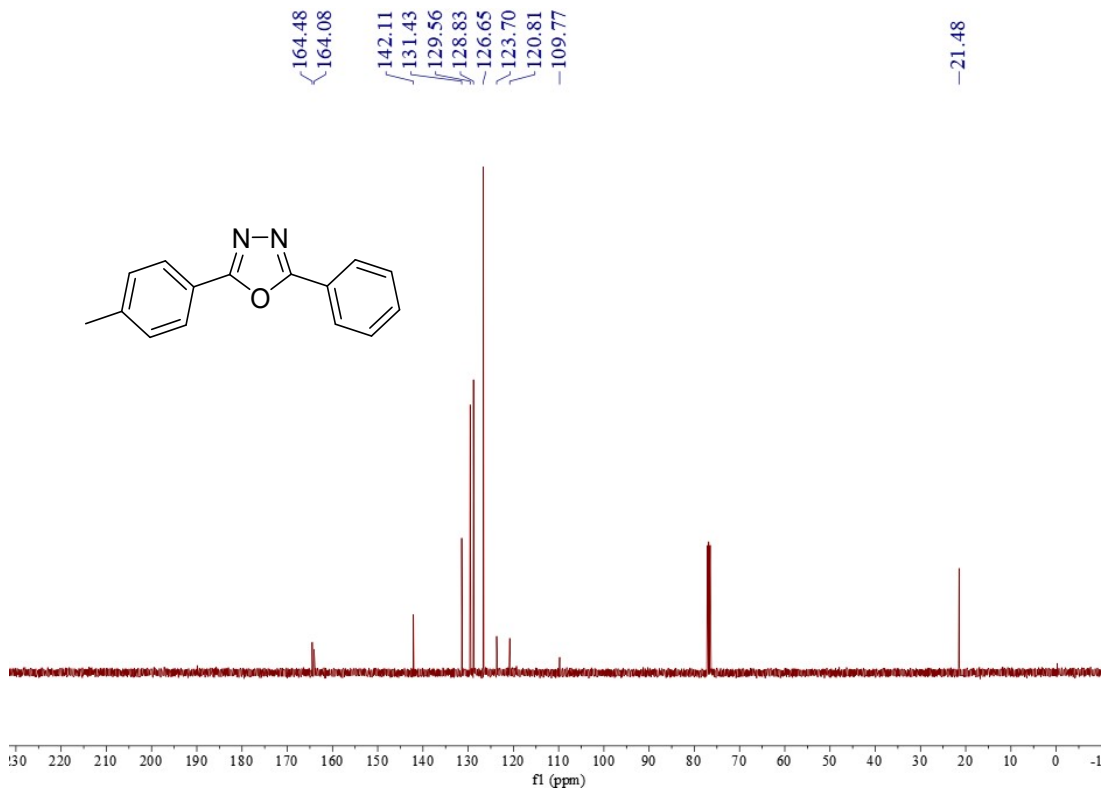


Fig. S9 ^{13}C NMR of **3b**

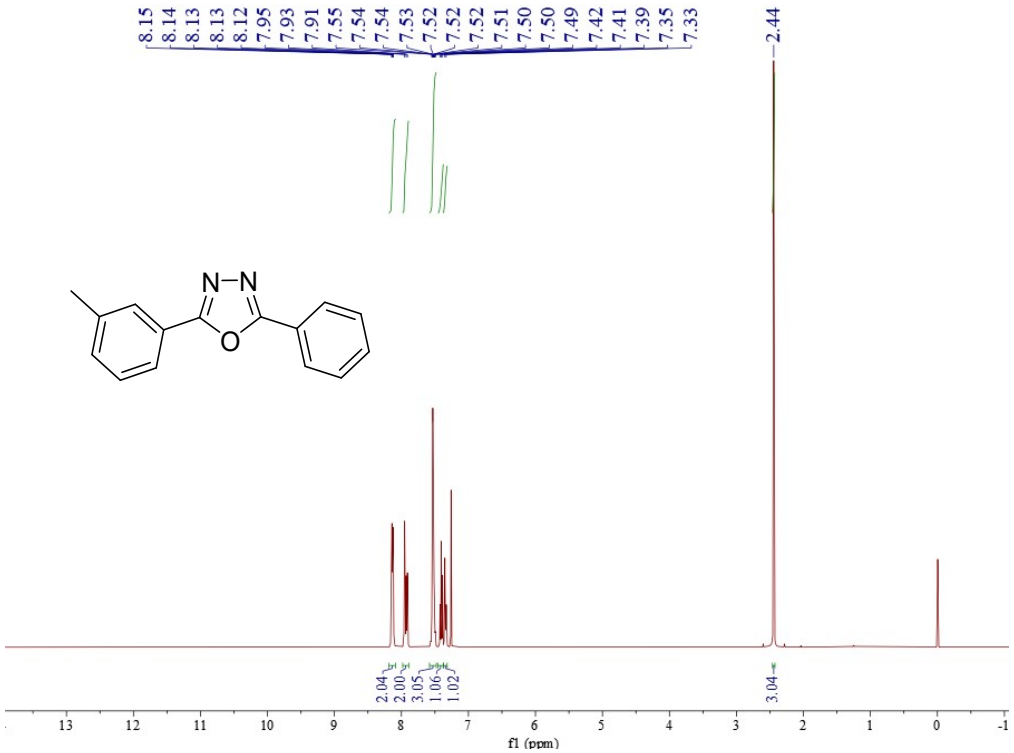


Fig. S10 ^{1}H NMR of **3c**

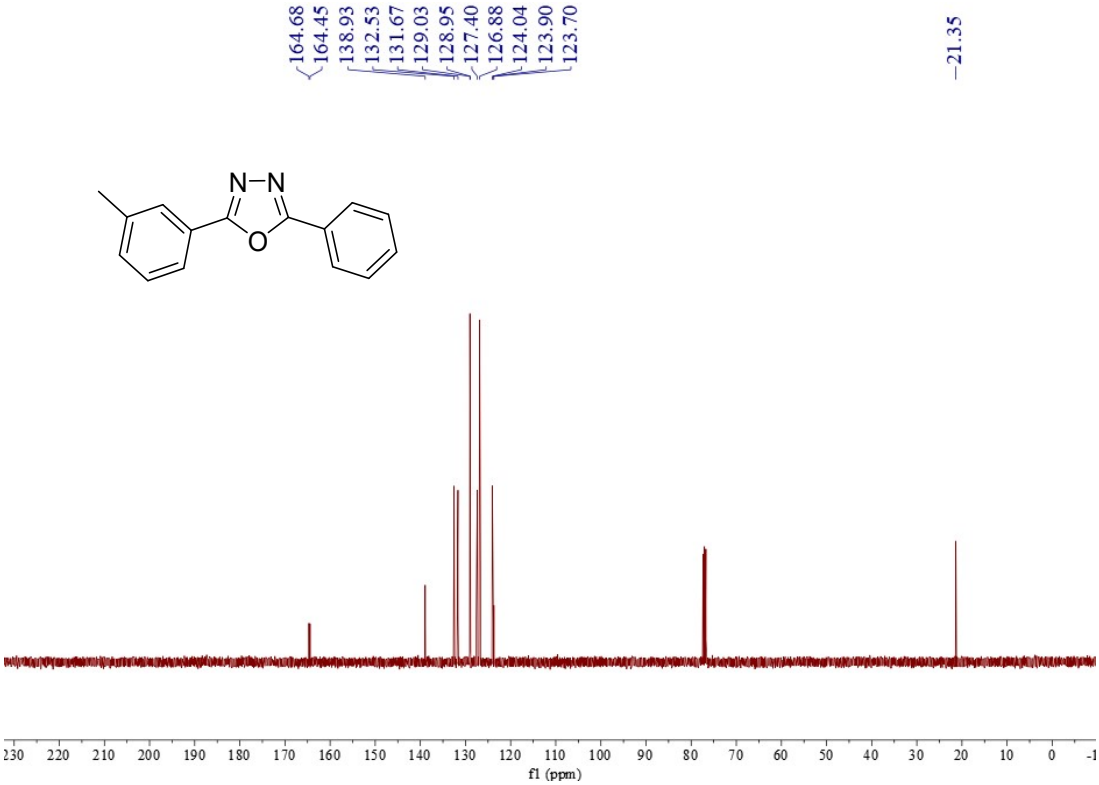


Fig. S11 ^{13}C NMR of **3c**

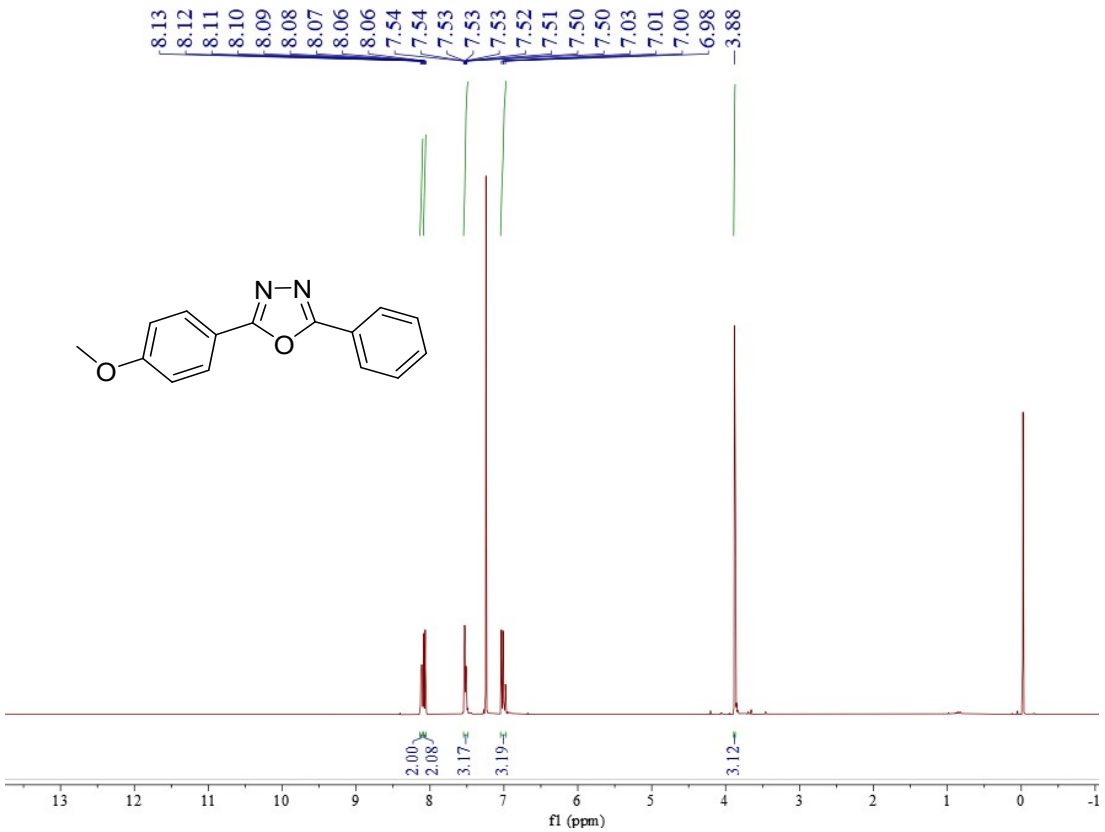


Fig. S12 ^{1}H NMR of **3d**

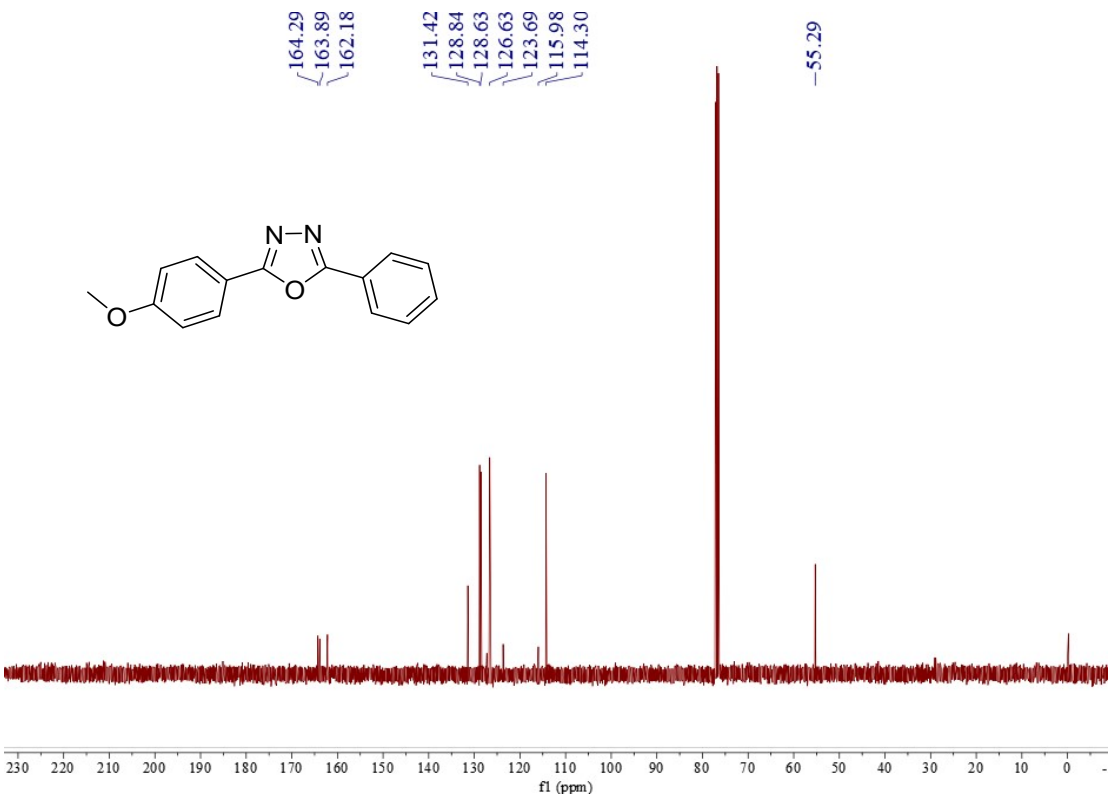


Fig. S13 ^{13}C NMR of **3d**

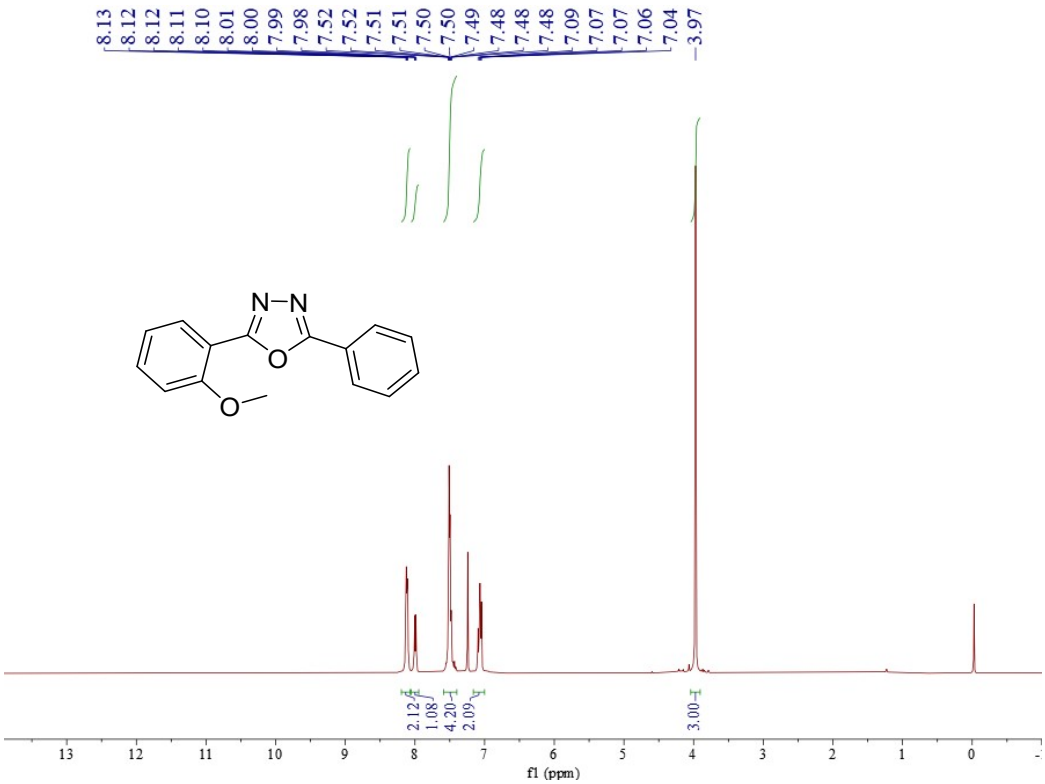


Fig. S14 ^{1}H NMR of **3e**

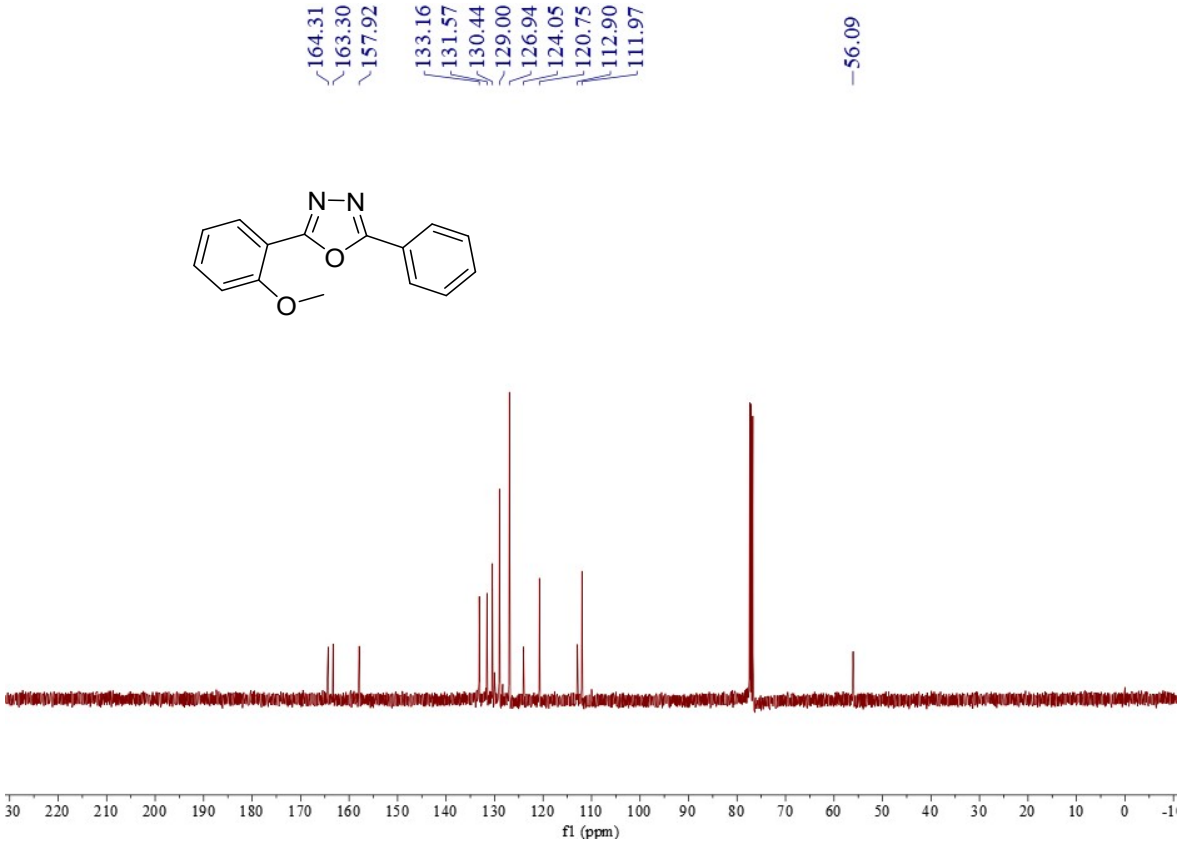


Fig. S15 ^{13}C NMR of **3e**

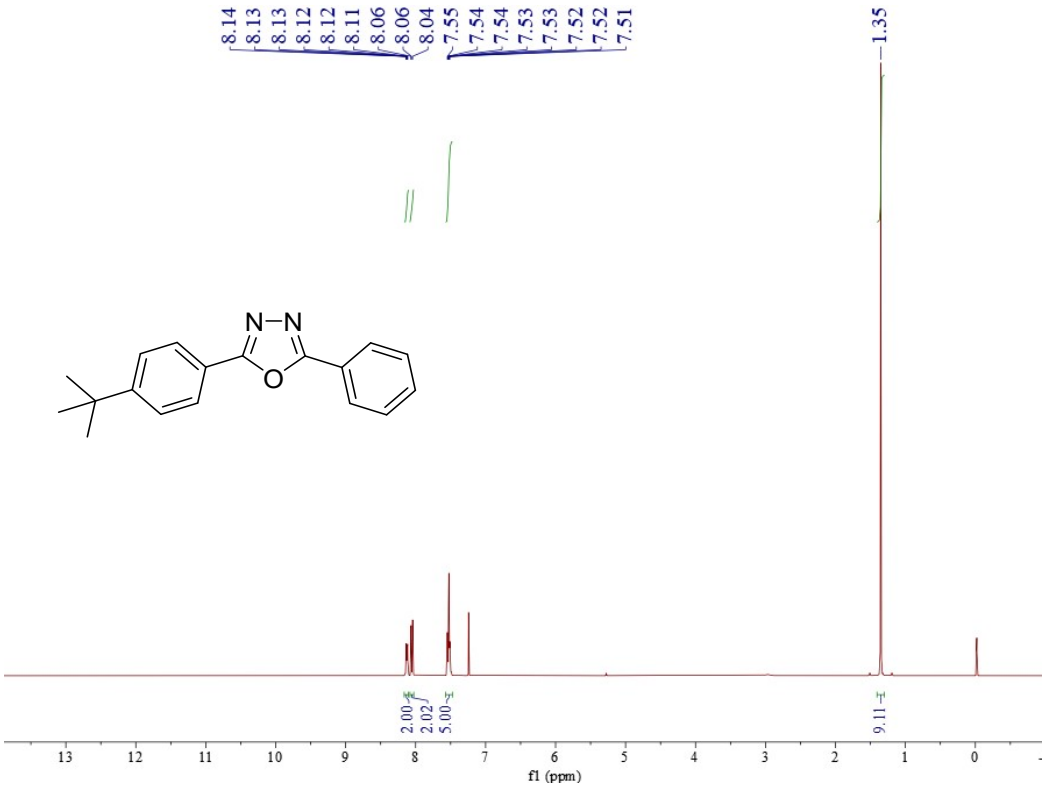


Fig. S16 ^{1}H NMR of **3f**

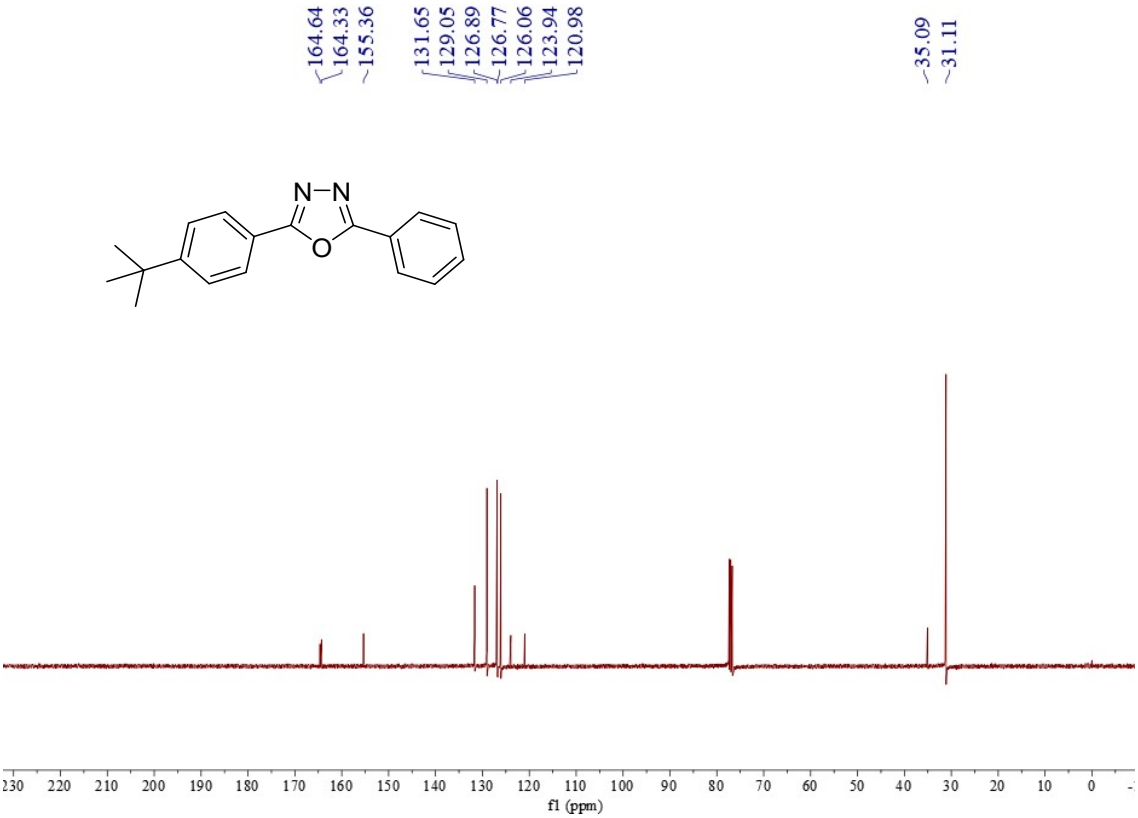


Fig. S17 ^{13}C NMR of **3f**

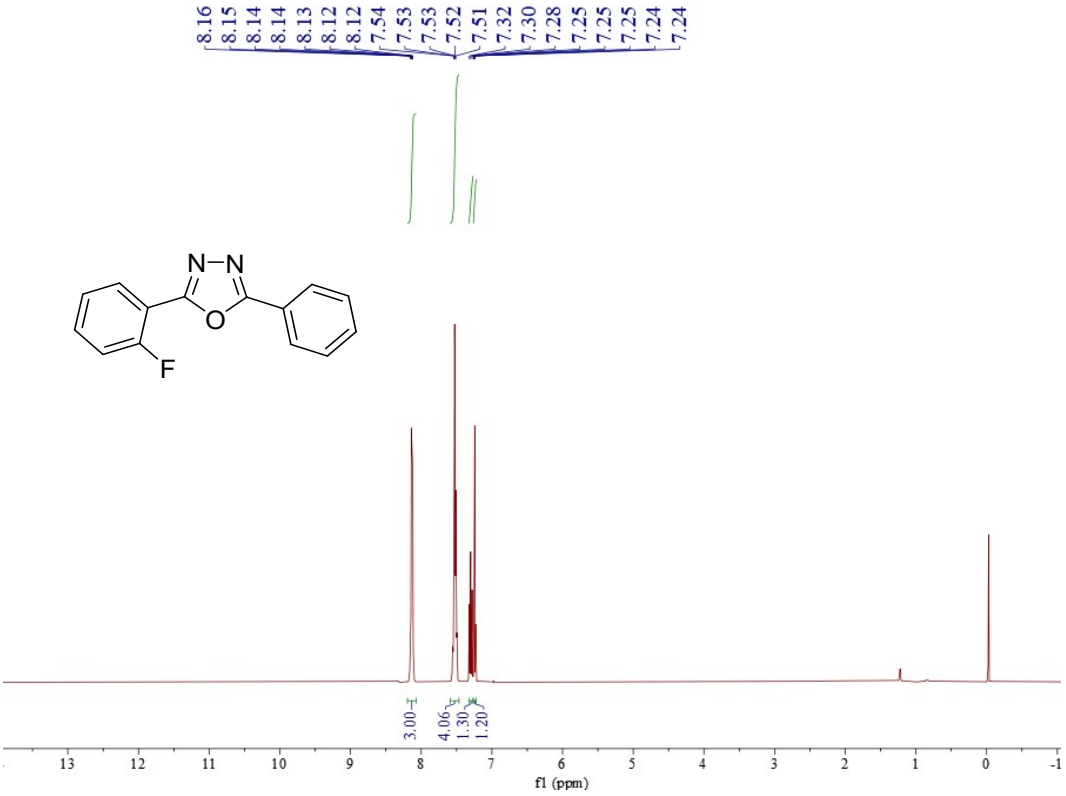


Fig. S18 ^{1}H NMR of **3g**

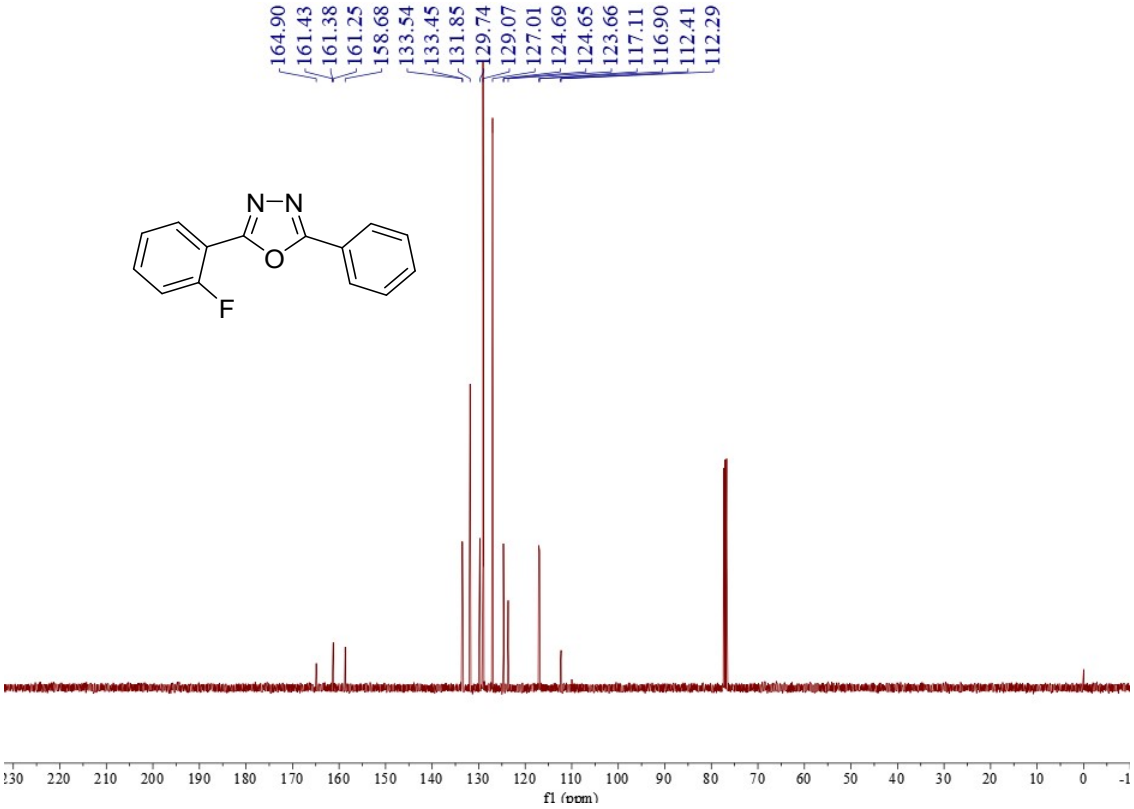


Fig. S19 ^{13}C NMR of **3g**

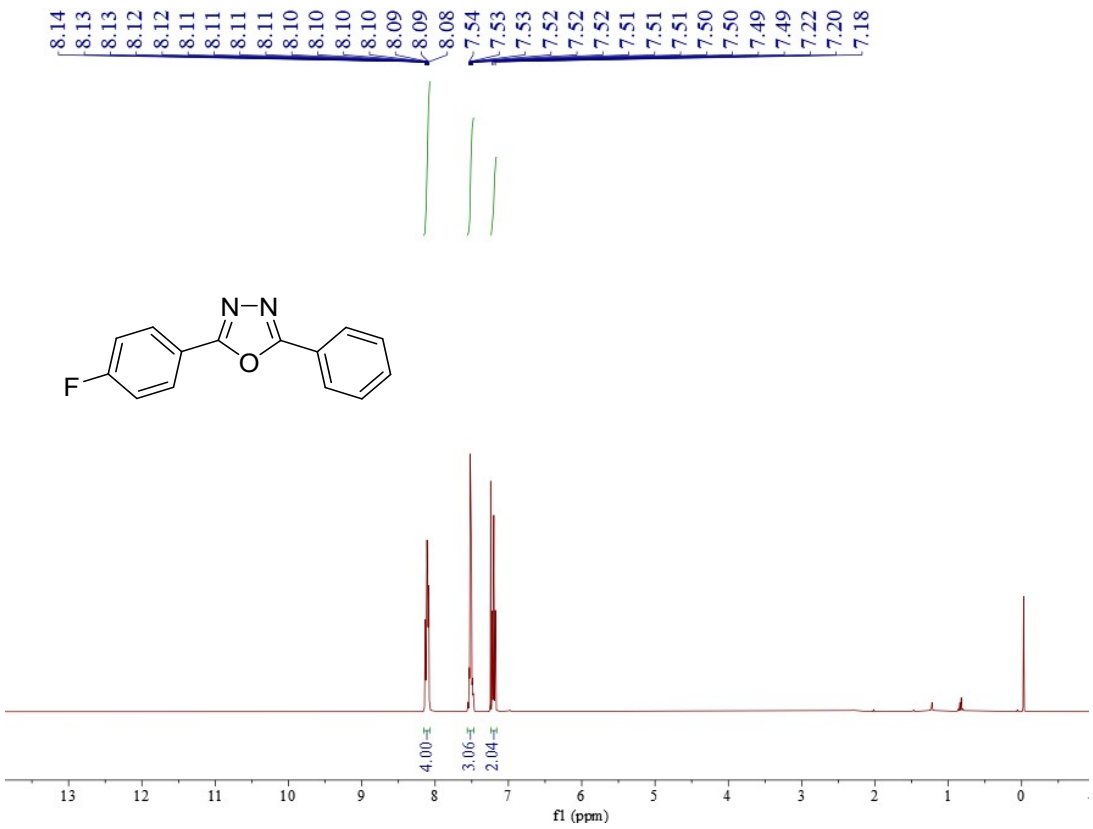


Fig. S20 ^{1}H NMR of **3h**

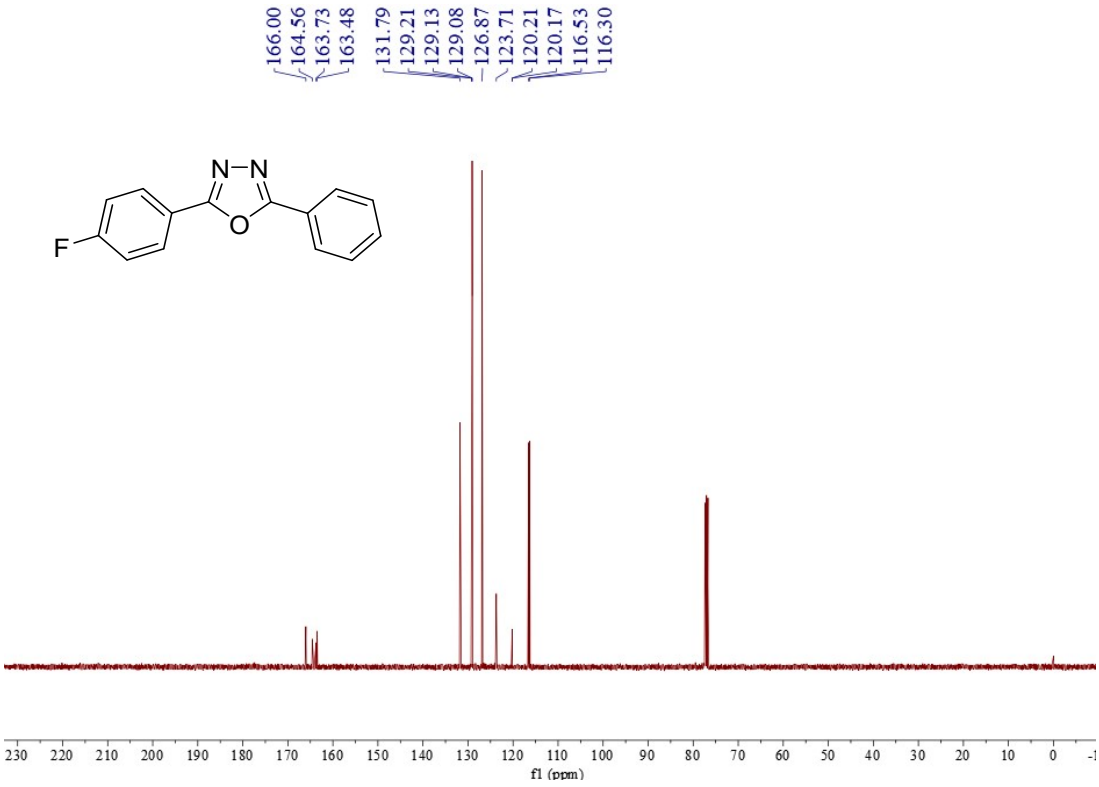


Fig. S21 ^{13}C NMR of **3h**

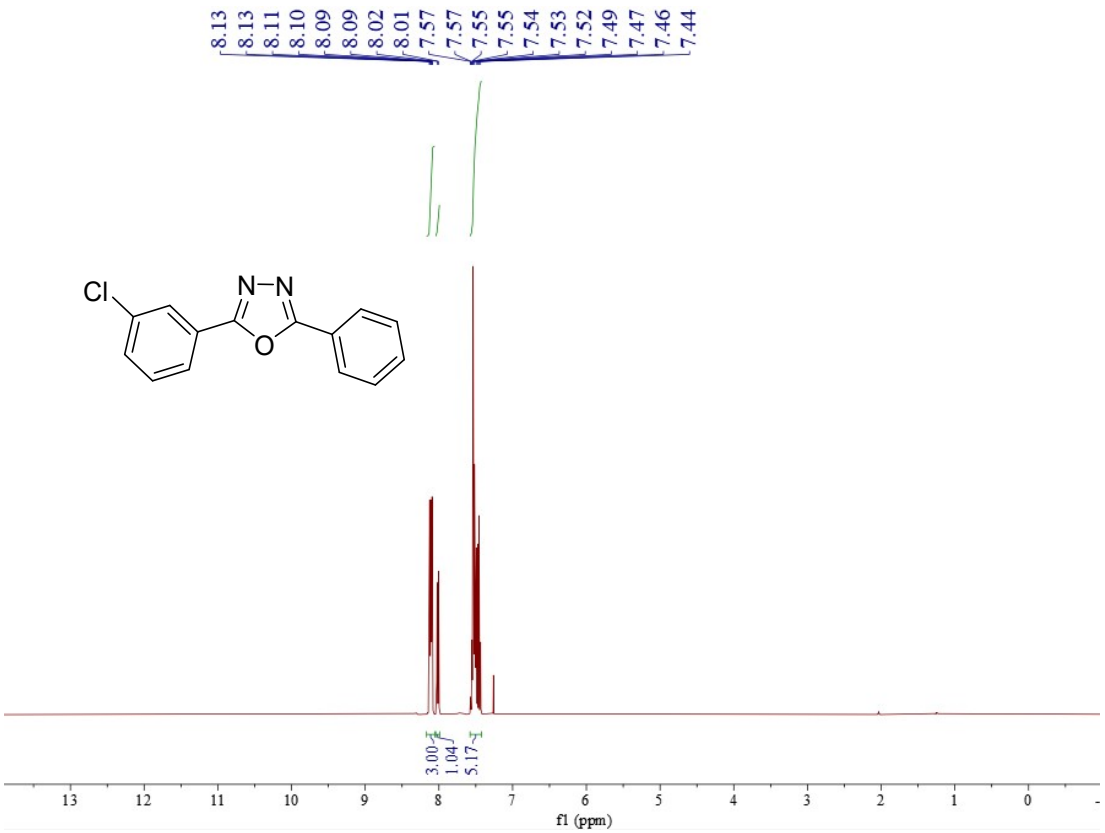


Fig. S22 ^{1}H NMR of **3i**

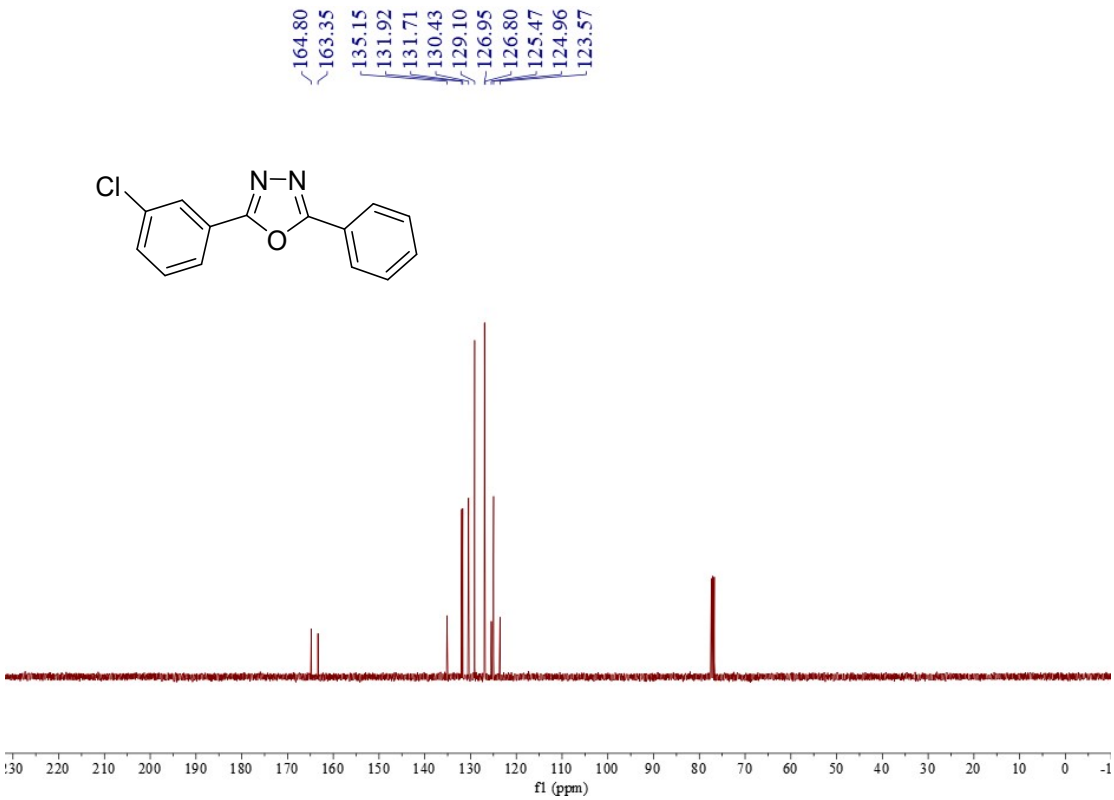


Fig. S23 ^{13}C NMR of **3i**

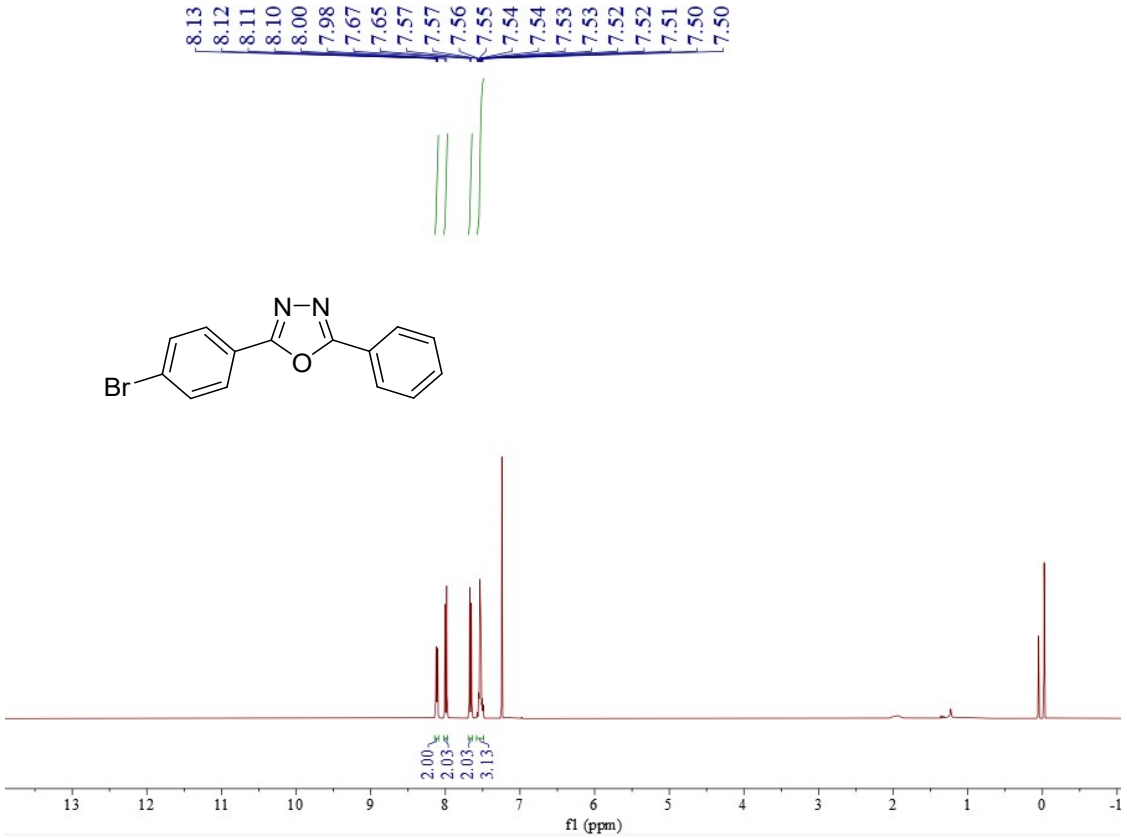


Fig. S24 ^{1}H NMR of **3j**

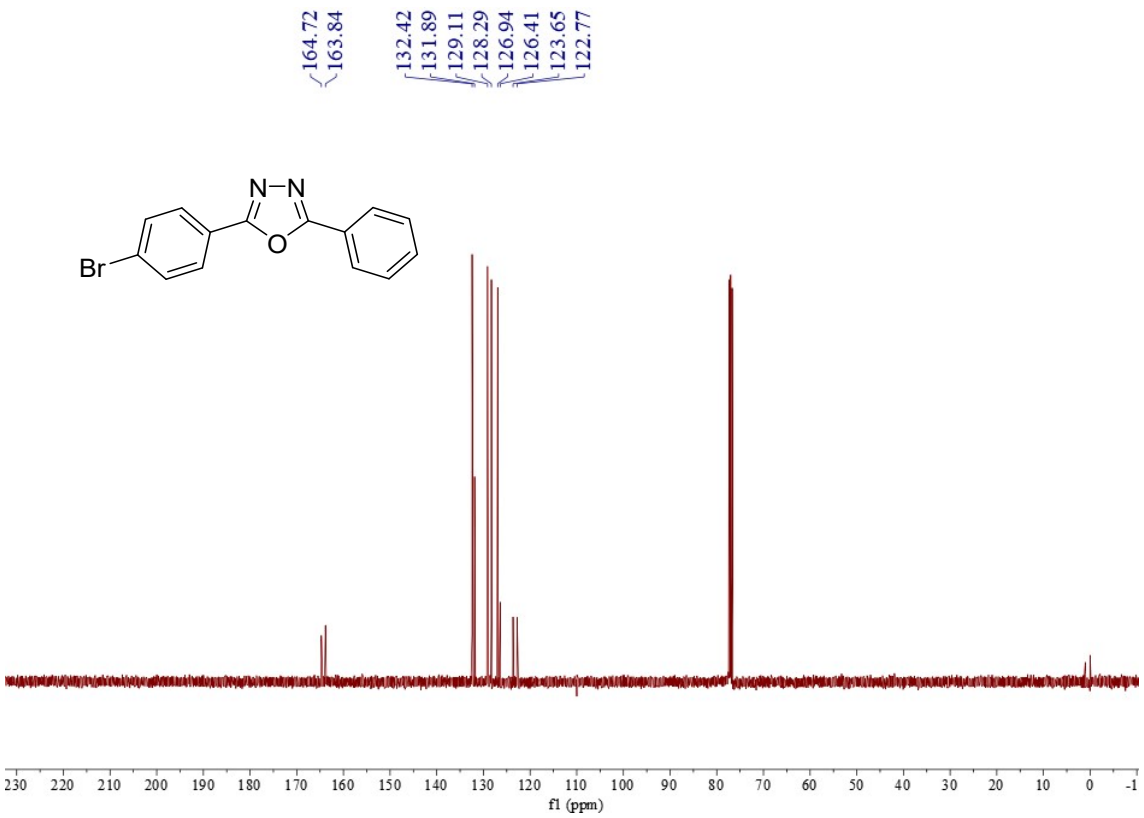


Fig. S25 ^{13}C NMR of **3j**

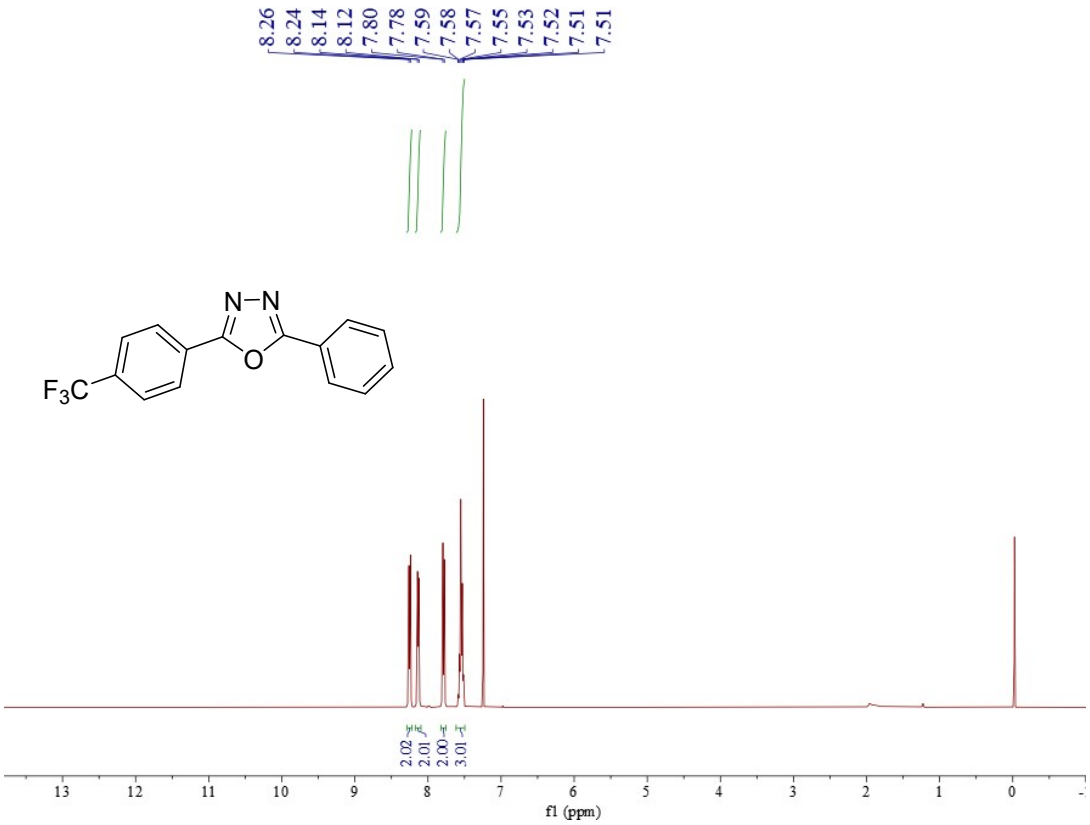


Fig. S26 ^{1}H NMR of **3k**

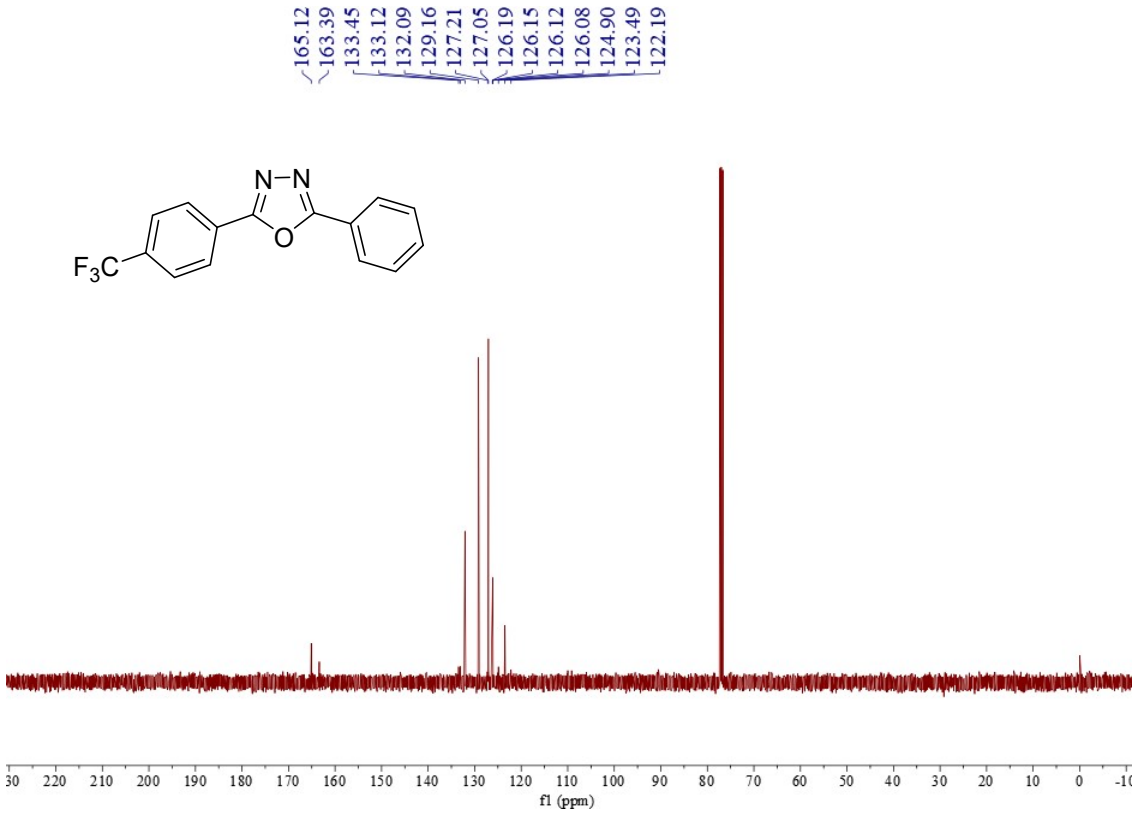


Fig. S27 ^{13}C NMR of **3k**

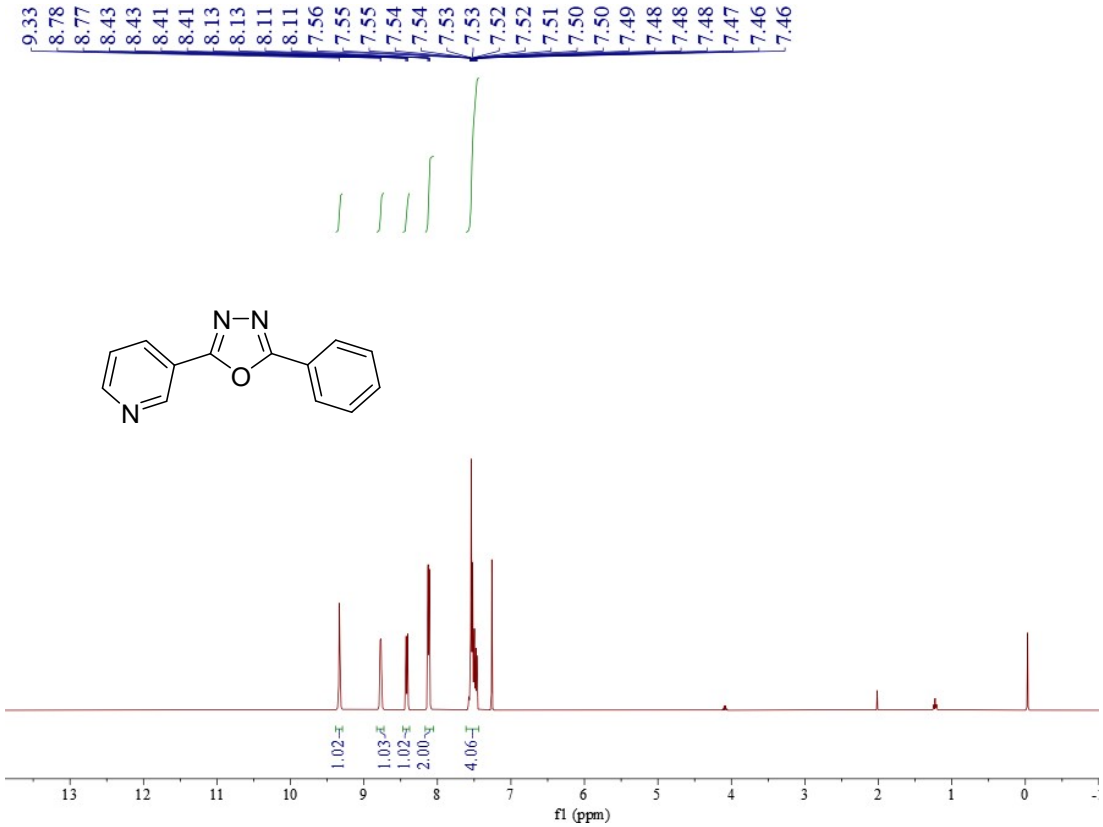


Fig. S28 ^{1}H NMR of **3l**

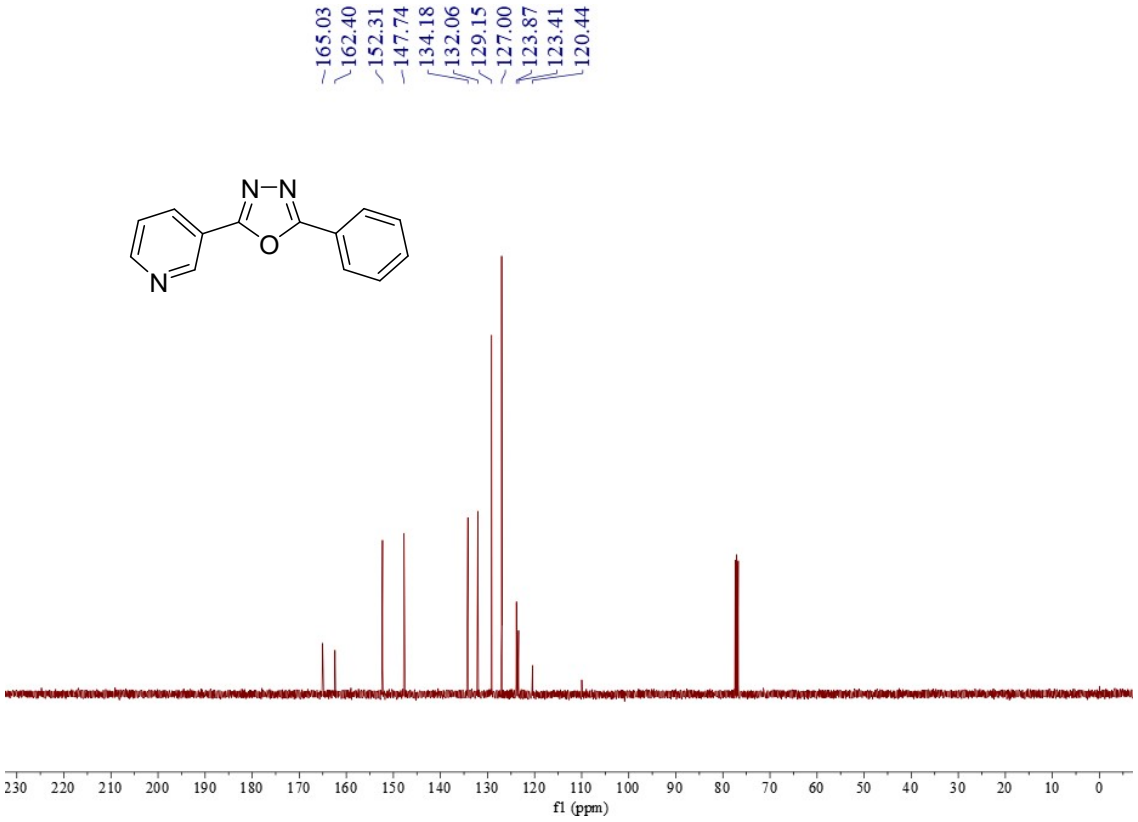


Fig. S29 ^{13}C NMR of **3l**

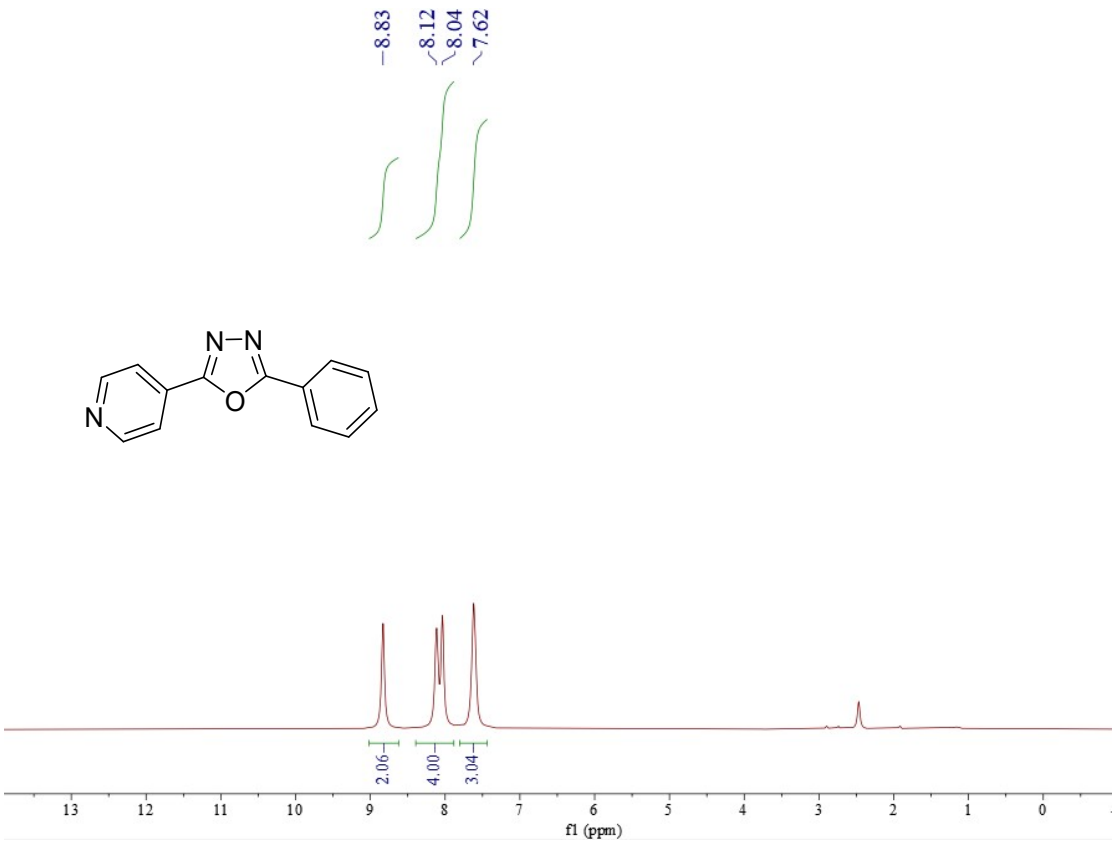


Fig. S30 ^{1}H NMR of **3m**

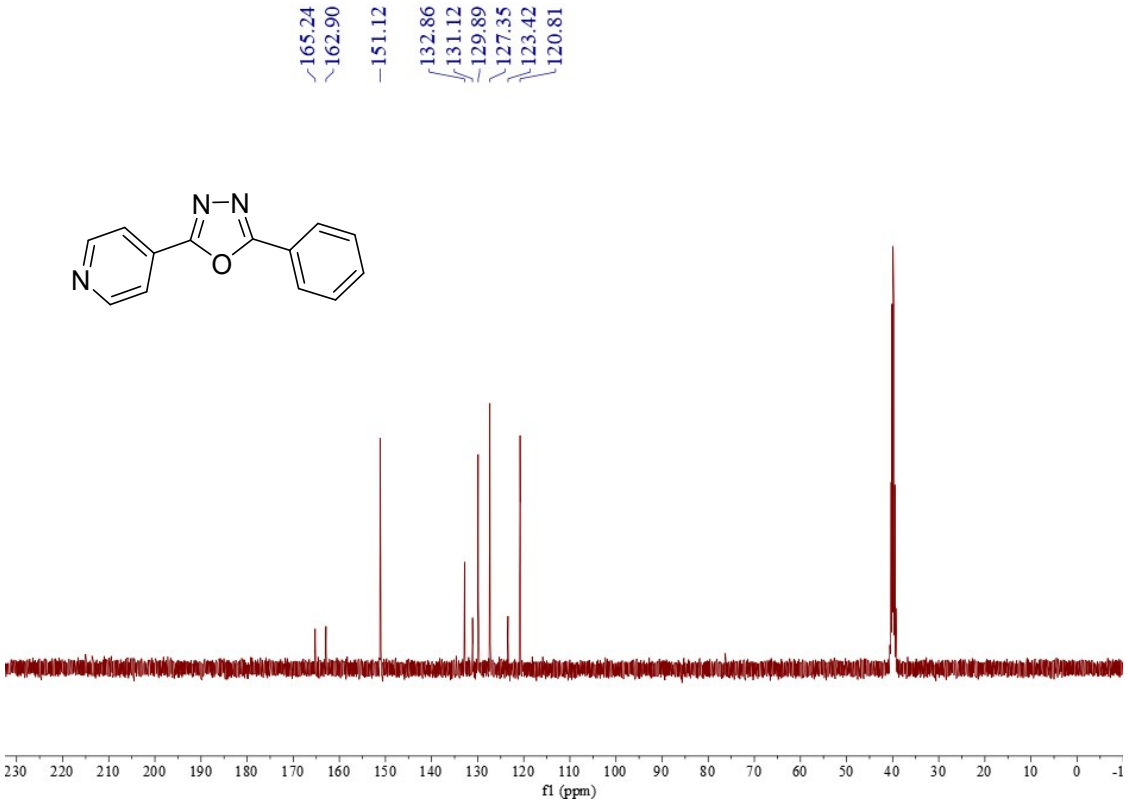


Fig. S31 ^{13}C NMR of **3m**

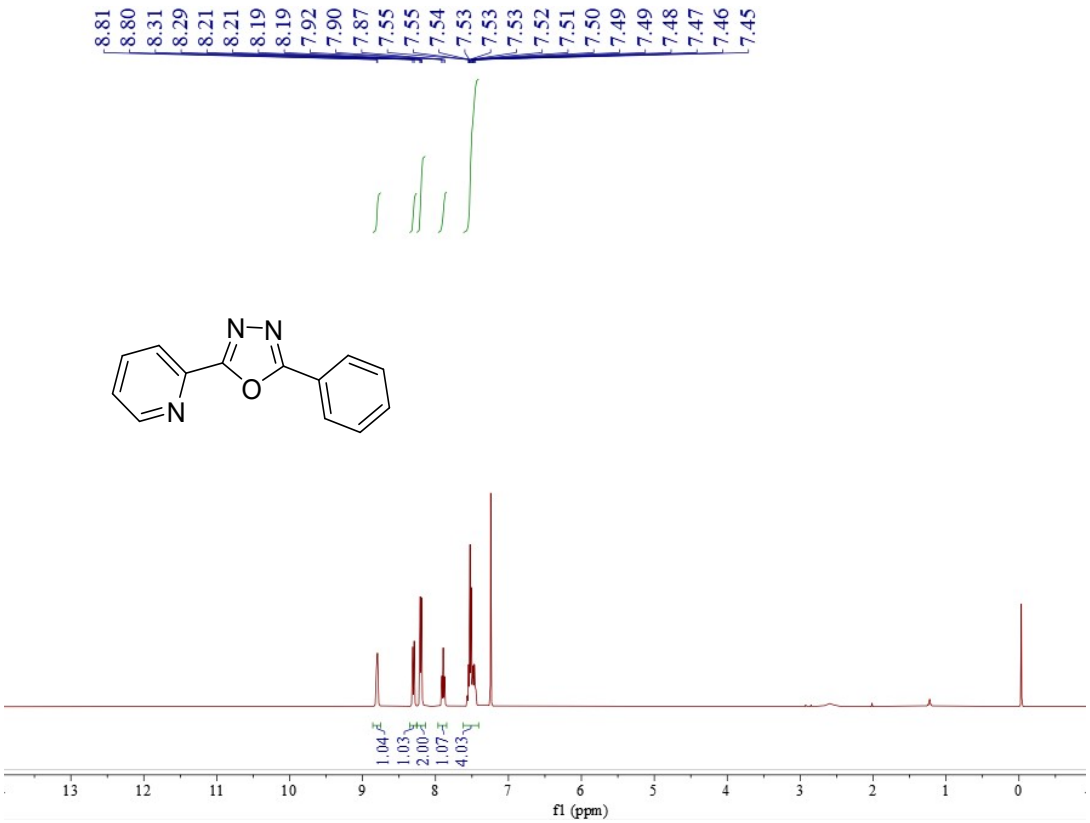


Fig. S32 ^{1}H NMR of **3n**

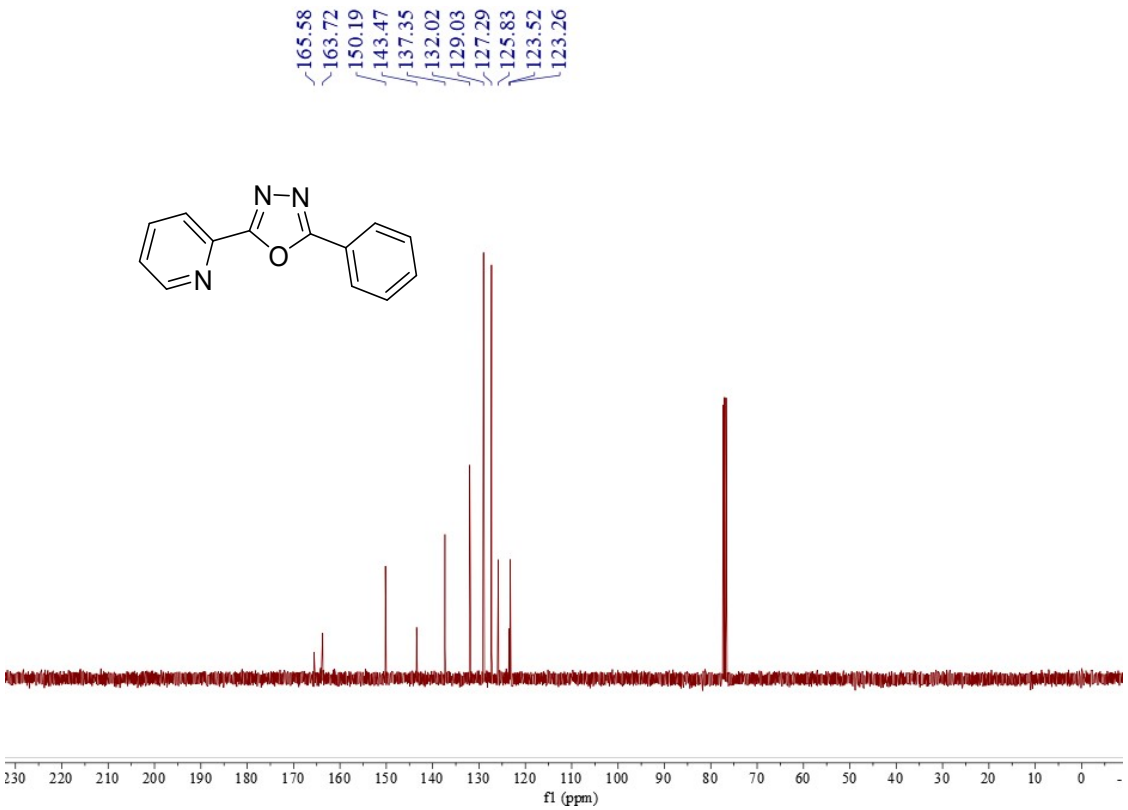


Fig. S33 ^{13}C NMR of **3n**

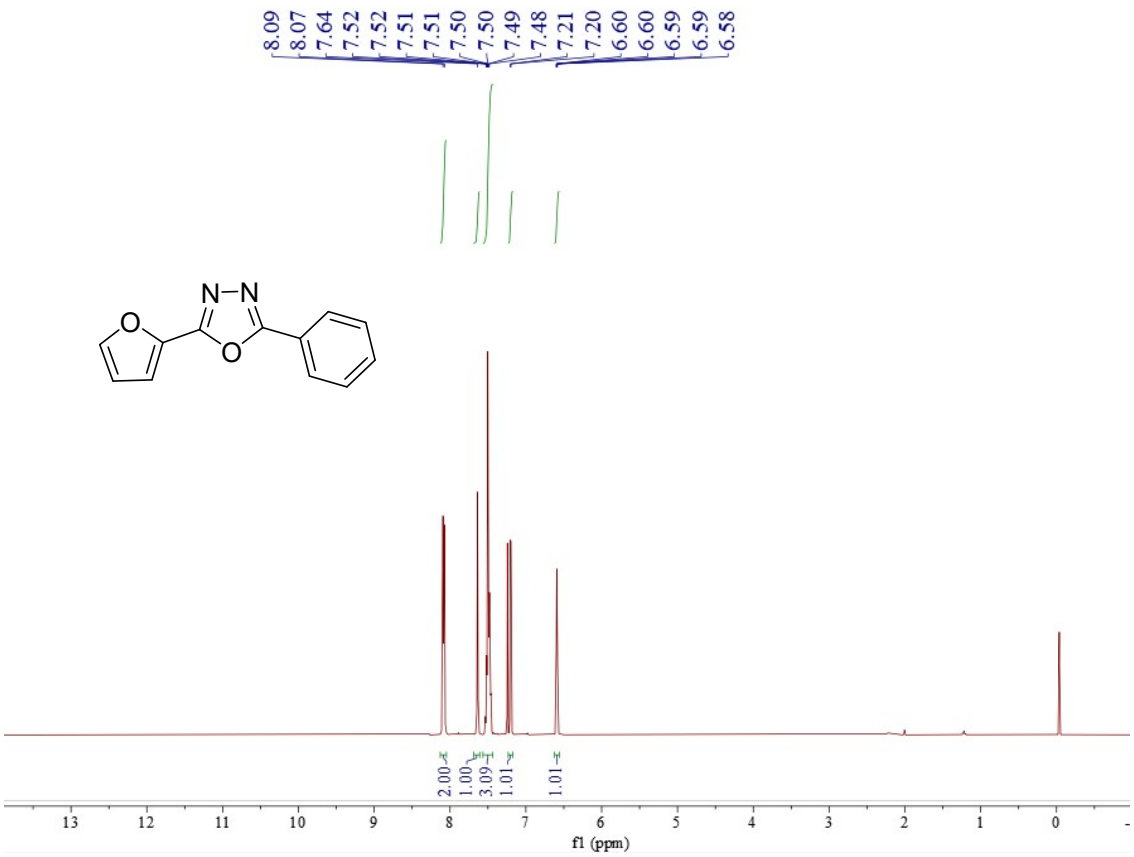


Fig. S34 ^{1}H NMR of **3o**

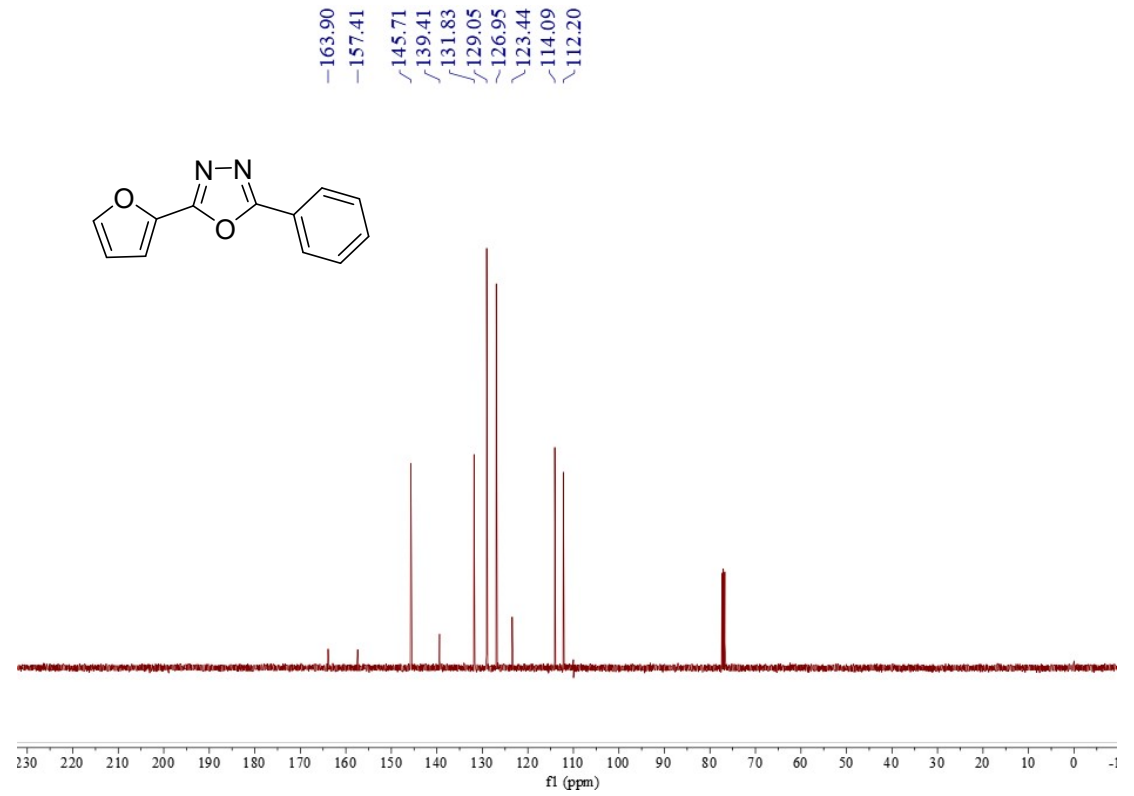


Fig. S35 ^{13}C NMR of **3o**

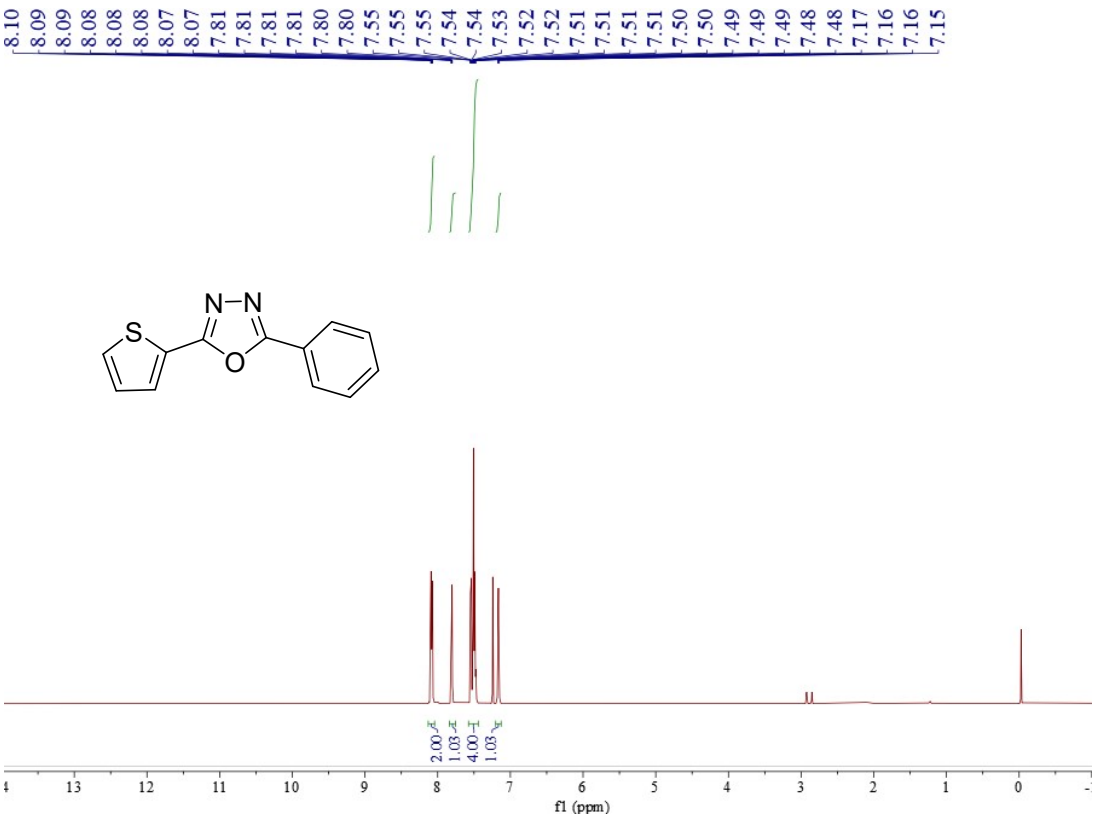


Fig. S36 ^{1}H NMR of **3p**

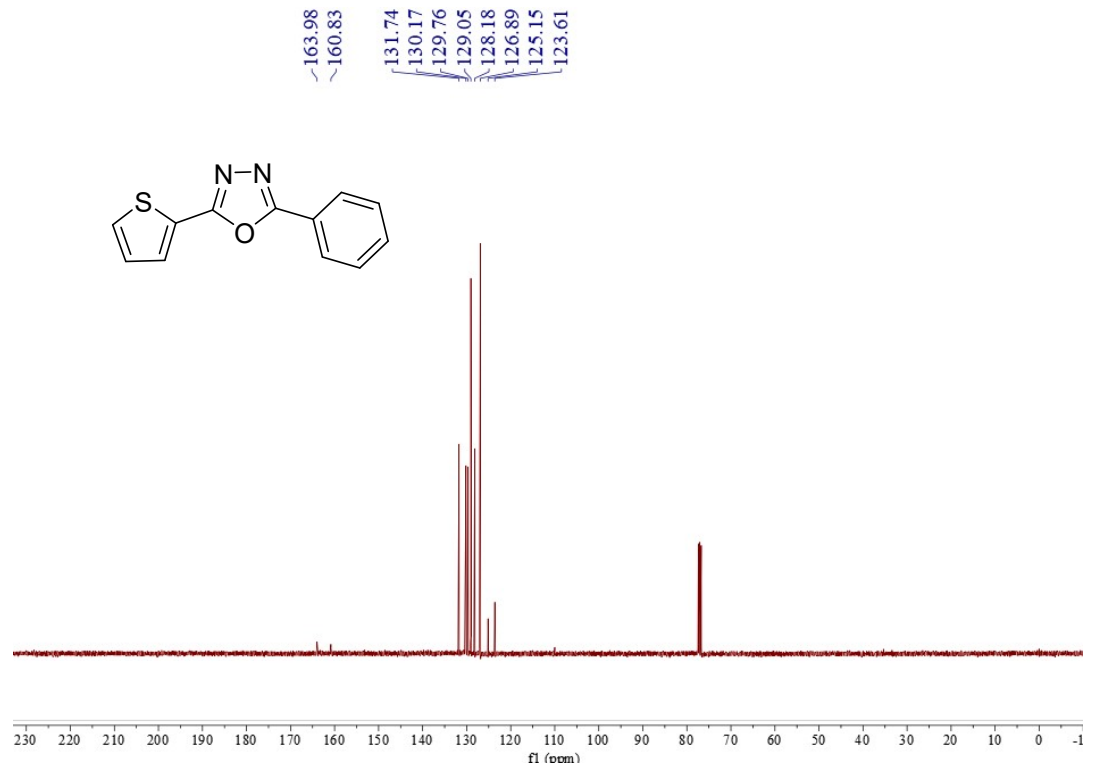


Fig. S37 ^{13}C NMR of **3p**

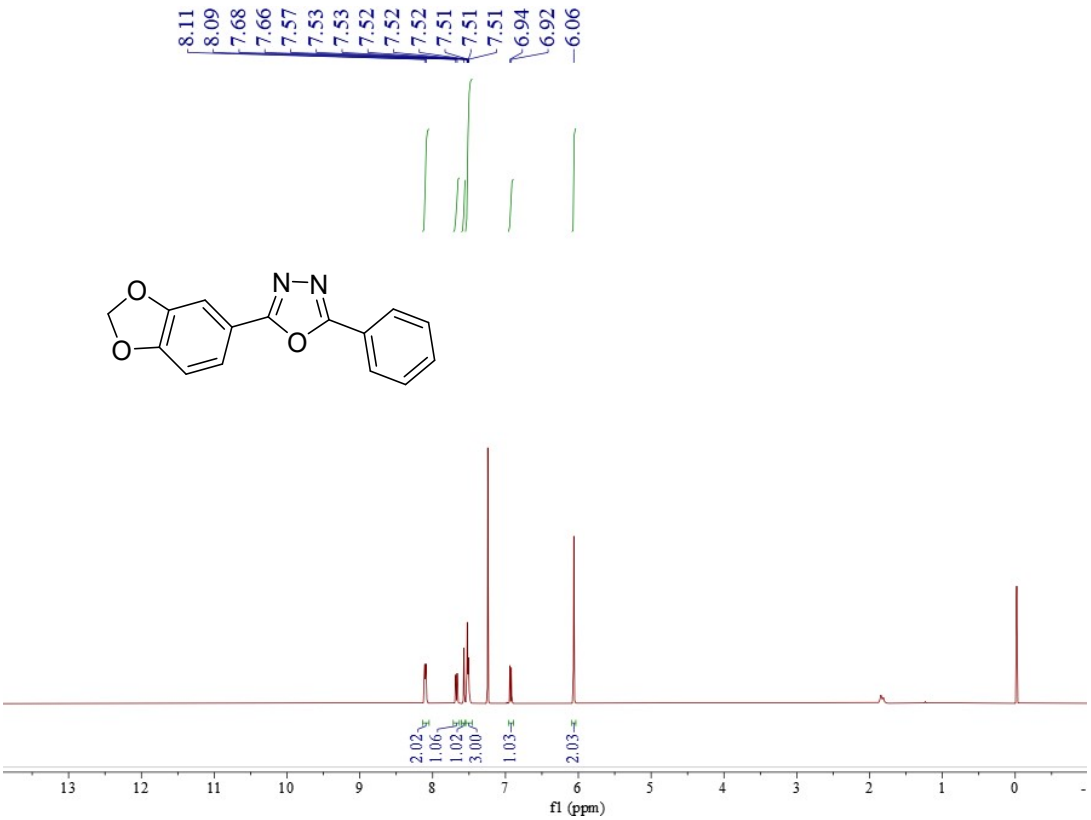


Fig. S38 ^{1}H NMR of **3q**

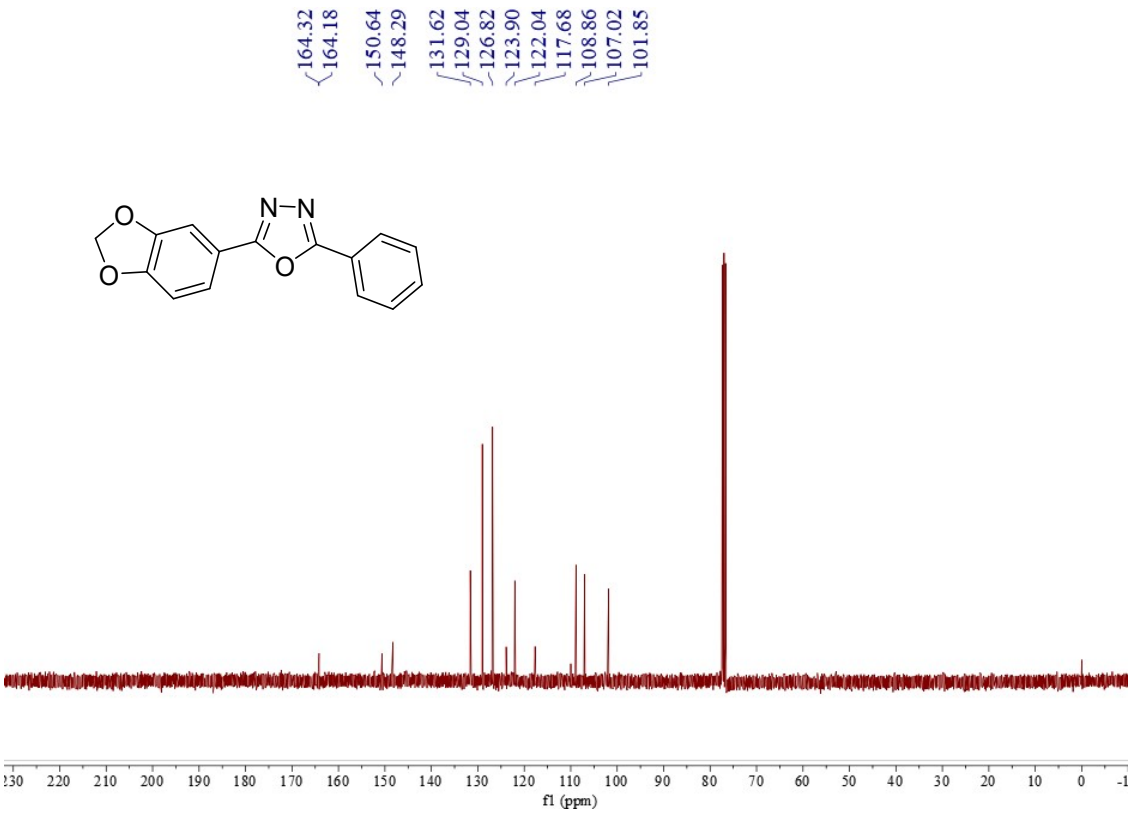


Fig. S39 ^{13}C NMR of **3q**

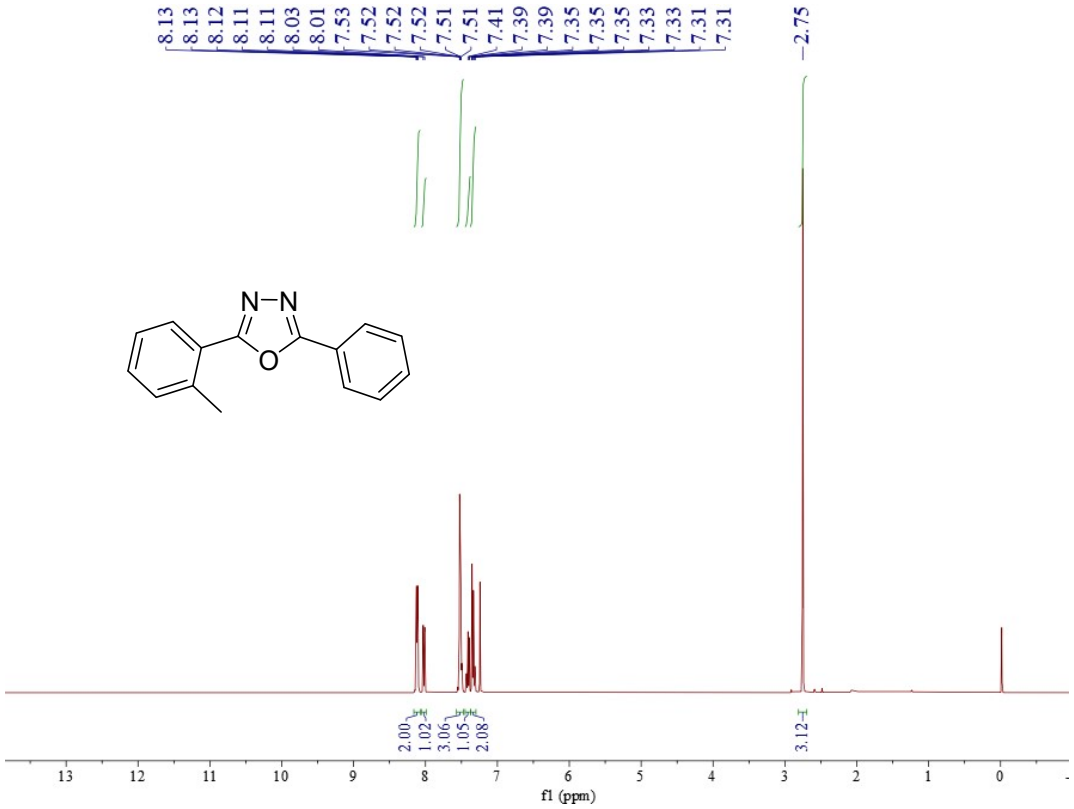


Fig. S40 ^{1}H NMR of **3r**

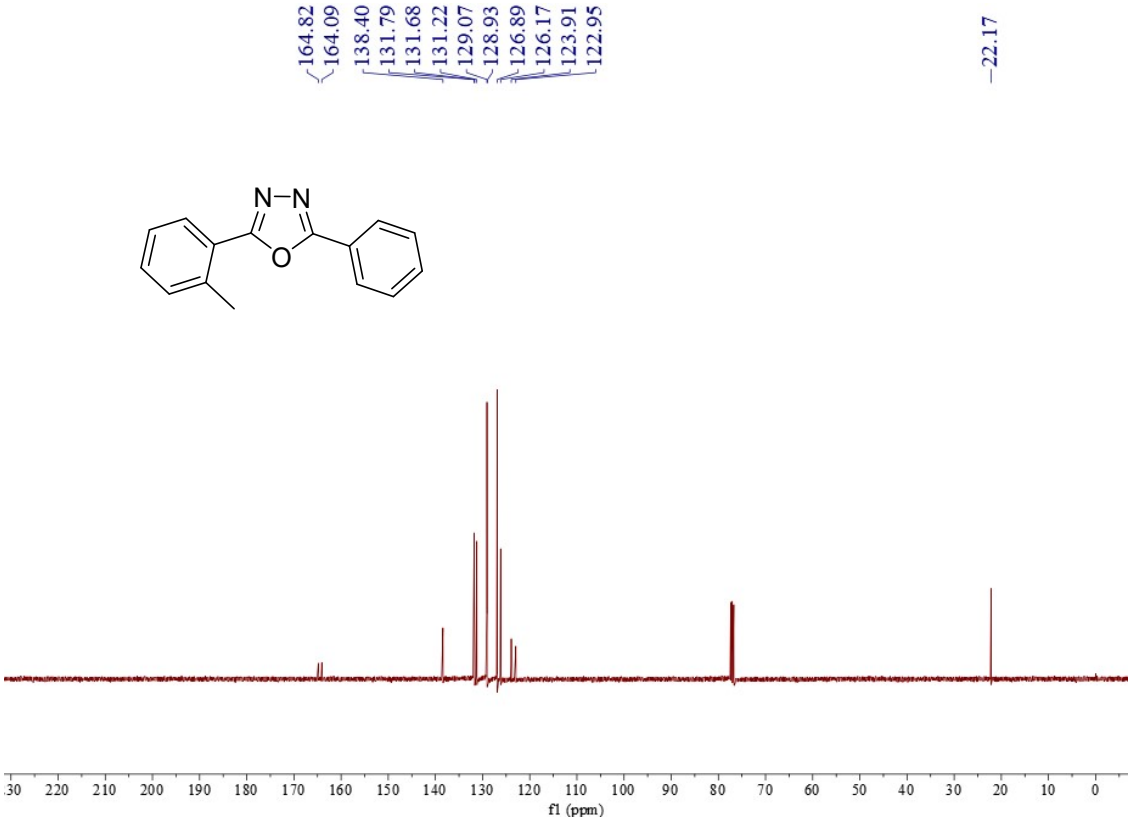


Fig. S41 ^{13}C NMR of **3r**

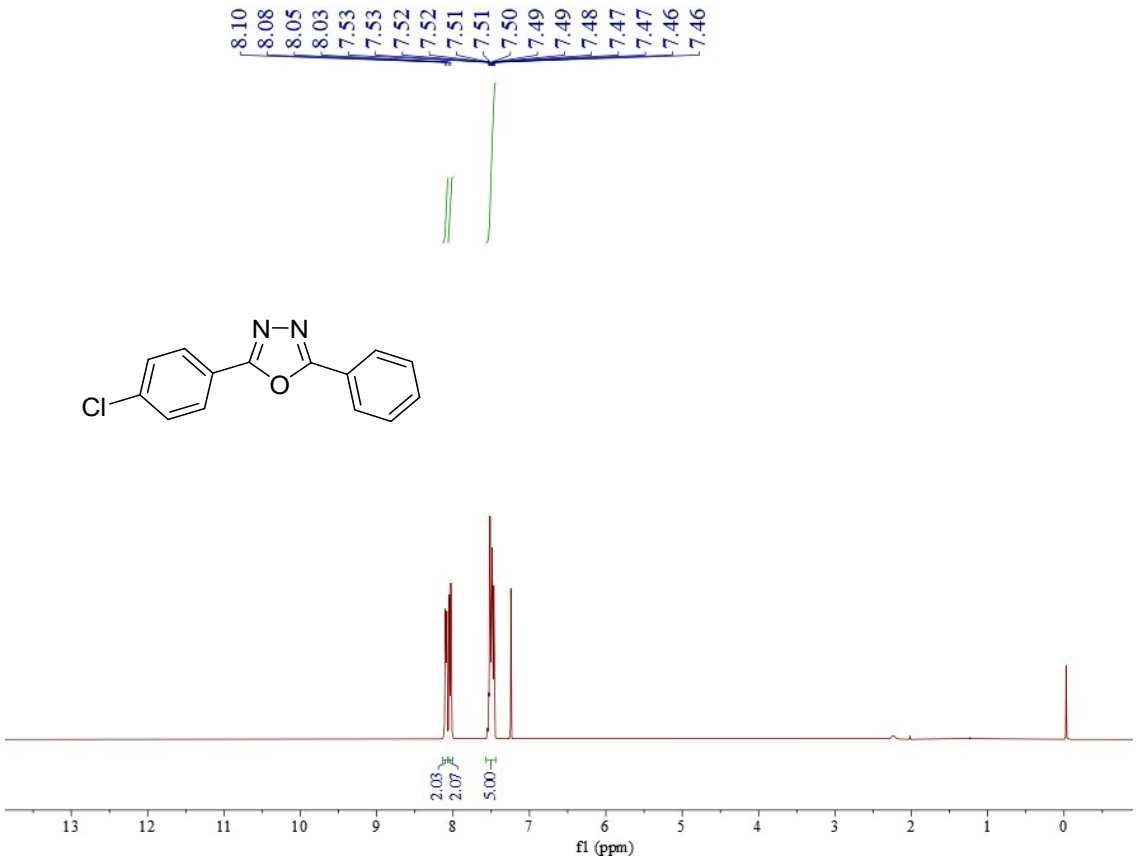


Fig. S42 ^{1}H NMR of **3s**

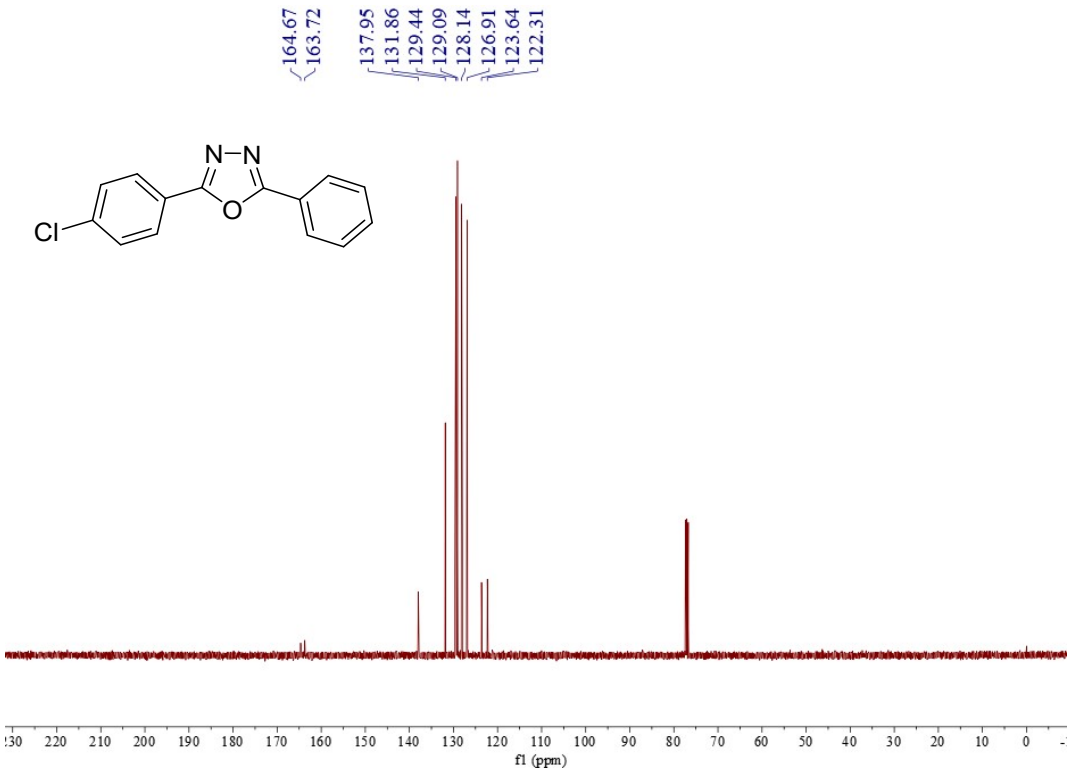


Fig. S43 ^{13}C NMR of **3s**

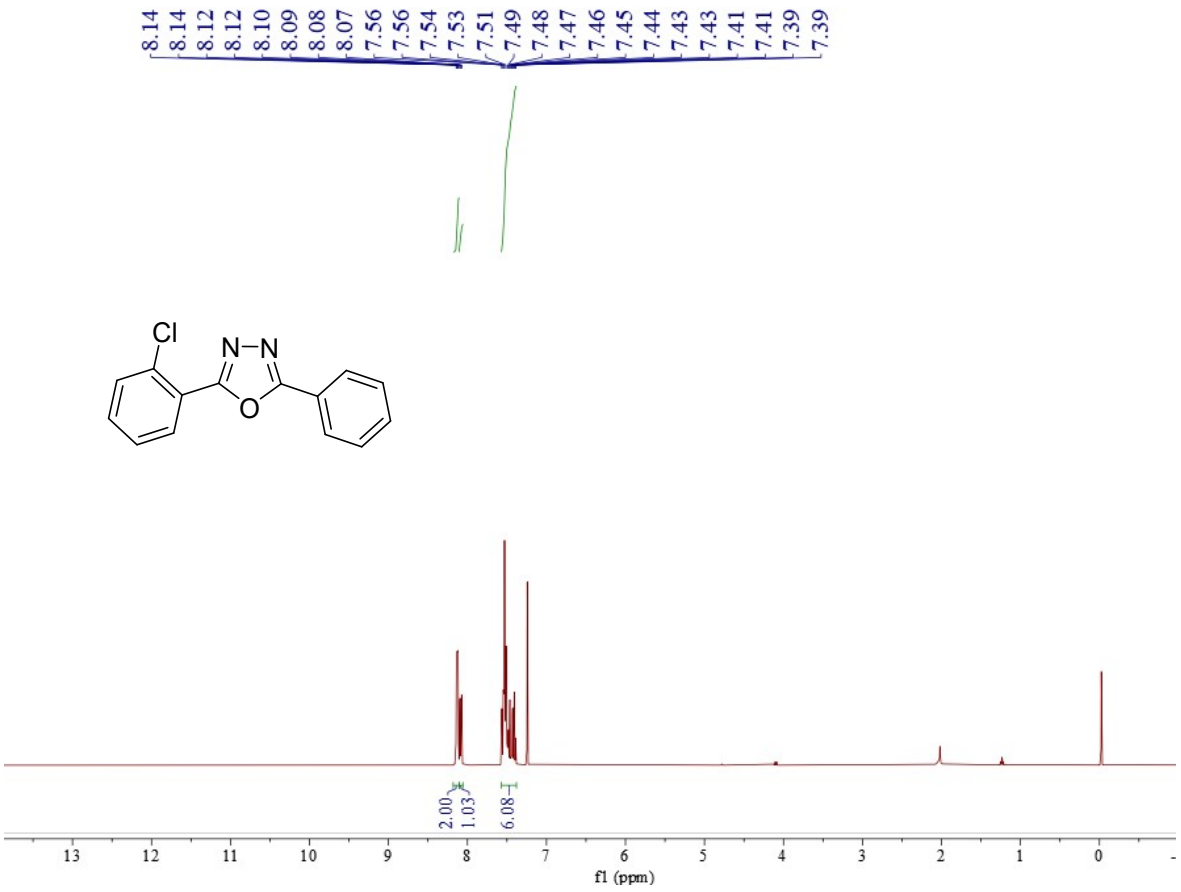


Fig. S44 ^{1}H NMR of **3t**

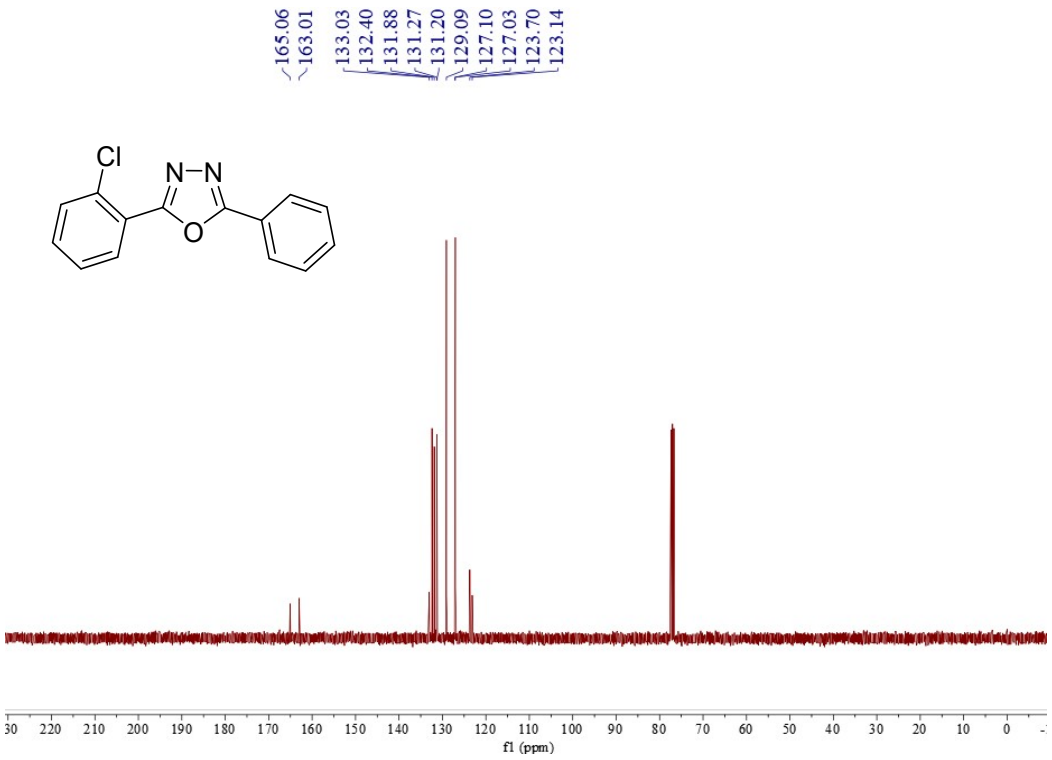


Fig. S45 ^{13}C NMR of **3t**

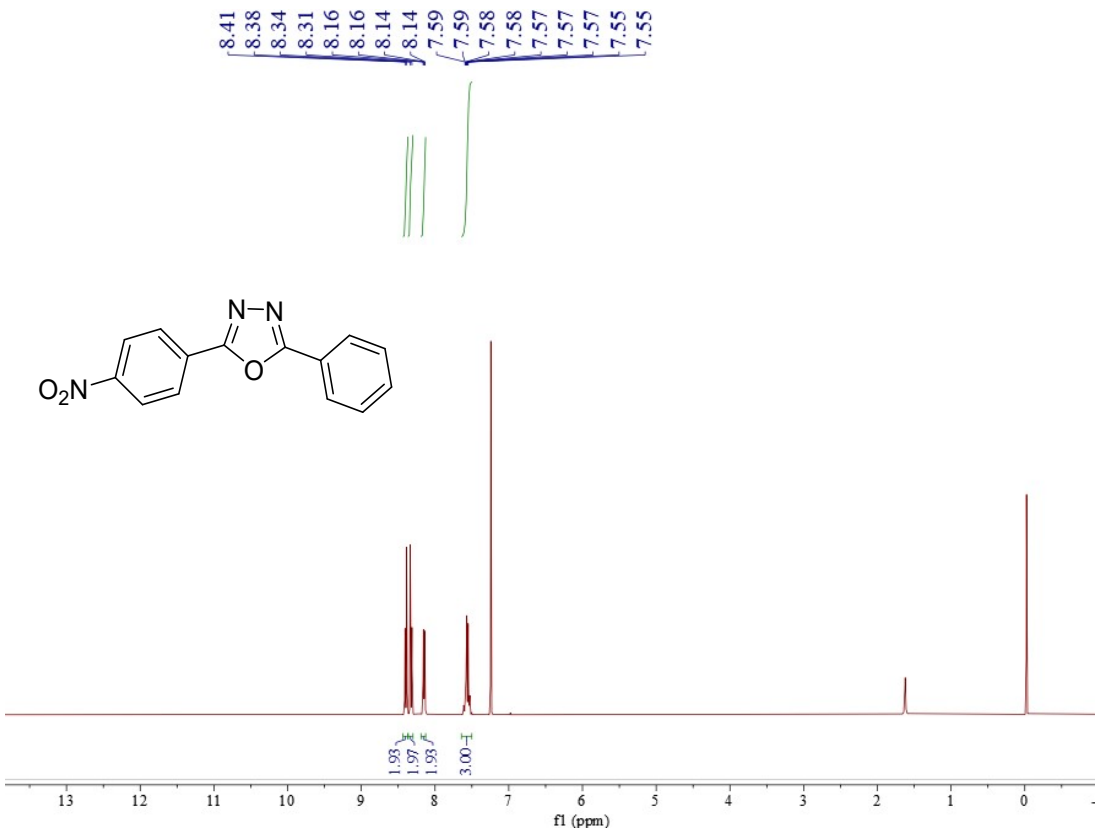


Fig. S46 ^{1}H NMR of **3u**

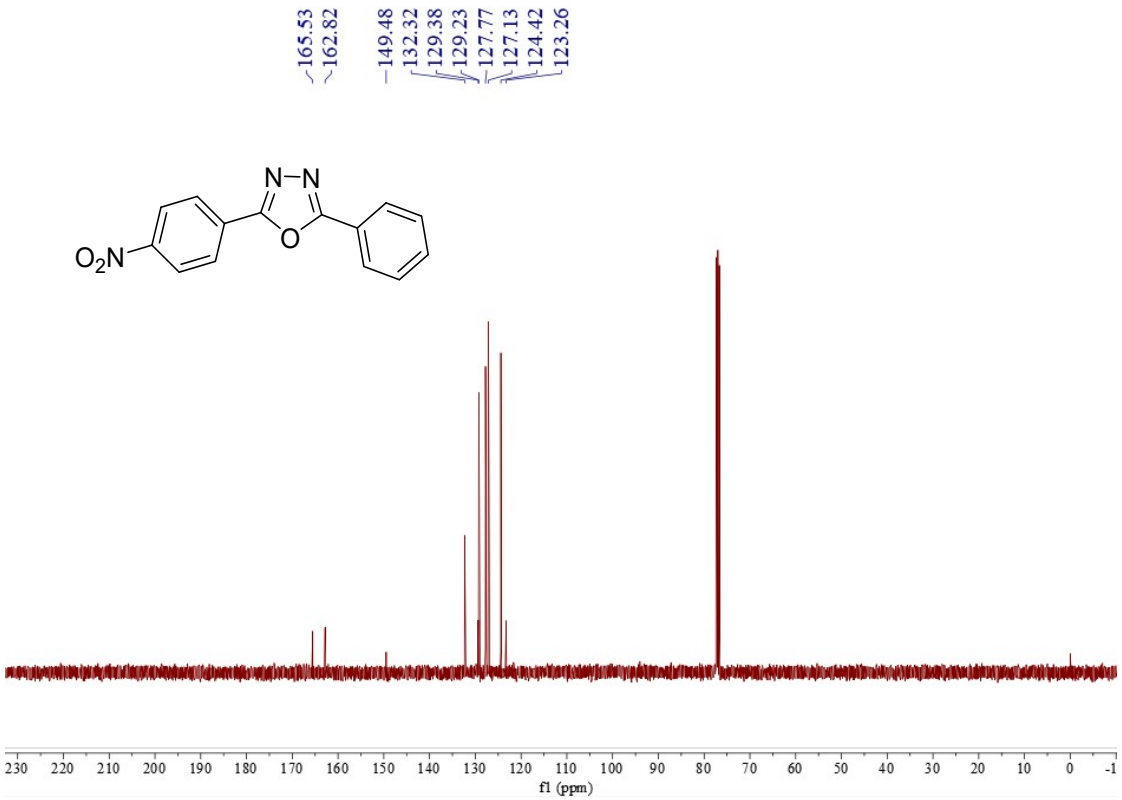
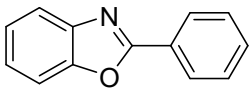


Fig. S47 ^{13}C NMR of **3u**

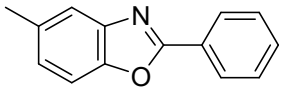
8. Characterization of compound 7

2-phenyl-benzoxazole (7a)



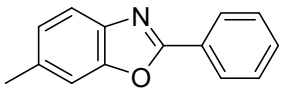
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.25 (m, 2H), 7.83 –7.76 (m, 1H), 7.59 – 7.54 (m, 1H), 7.57 – 7.52 (m, 3H), 7.38 – 7.34 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.0, 150.6, 141.6, 131.7, 129.0, 127.7, 126.8, 125.3, 124.7, 119.9, 110.6.

2-phenyl-5-methylbenzoxazole (7b)



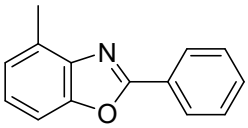
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.23 (m, 2H), 7.61 – 7.50 (m, 4H), 7.47 (d, J = 8.3 Hz, 1H), 7.21 – 7.14 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 149.1, 141.8, 134.6, 131.6, 128.9, 127.6, 127.0, 126.3, 119.8, 110.0, 21.5.

6-methyl-2-phenylbenzoxazole (7c)



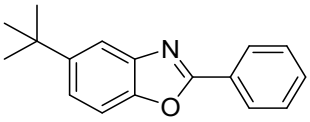
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 – 8.20 (m, 2H), 7.69 (d , J = 7.7 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.40 (s, 1H), 7.18 (d, J = 7.7 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 150.6, 139.3, 135.4, 131.1, 128.6, 127.1, 126.8, 125.5, 118.9, 110.5, 21.4.

4-methyl-2-phenylbenzo[*d*]oxazole (7d)



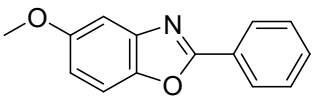
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 – 8.26 (m, 2H), 7.55 – 7.51 (m, 3H), 7.43 – 7.39(m, 1H), 7.19 – 7.25(m, 1H), 7.19 – 7.12 (m, 1H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 150.5, 141.5, 131.0, 130.7, 128.7, 127.6, 127.2, 124.7, 124.6, 107.5, 16.5.

5-(*tert*-butyl)-2-phenylbenzo[*d*]oxazole (7e)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.23 (m, 2H), 7.81(s, 1H), 7.55 – 7.48 (m, 4H), 7.42 (dd, J = 8.6, 1.6 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.2, 148.1, 141.9, 131.4, 128.9, 127.5, 127.3, 122.9, 116.5, 109.7, 34.9, 31.7.

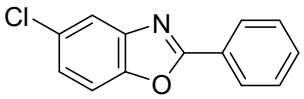
5-methoxy-2-phenylbenzo[*d*]oxazole (7f)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.21 (m, 2H), 7.56 – 7.50 (m, 3H), 7.47 (d, J = 8.9 Hz, 1H), 7.27 (d,

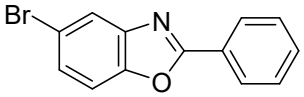
J = 2.5 Hz, 1H), 6.98 – 6.94 (m, 1H), 3.88 (s, 3H); ^{13}CNMR (101 MHz, $CDCl_3$): δ 164.1, 157.7, 145.6, 142.8, 131.9, 129.2, 127.8, 127.3, 114.2, 111.1, 102.9, 56.2.

phenyl-5-chlorobenzoxazole (7g)



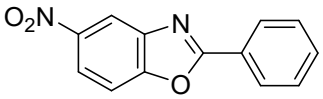
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.21 (m, 2H), 7.75 (dd, *J* = 2.1 Hz, 1H), 7.63 – 7.47 (m, 4H), 7.36 – 7.27 (dd, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.4, 149.3, 143.2, 131.9, 130.1, 129.0, 128.7, 127.7, 126.6, 125.4, 119.9, 110.3.

4-bromo-2-phenylbenzo[*d*]oxazole (7h)



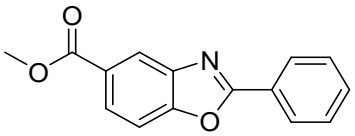
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.89 (t, *J* = 1.2 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.45 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.4, 150.0, 143.9, 132.3, 129.3, 128.4, 128.0, 126.8, 123.2, 117.6, 112.1.

5-nitro-2-phenylbenzo[*d*]oxazole (7i)



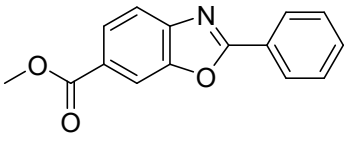
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 2.3 Hz, 1H), 8.32 (dd, 1H), 8.26 (d, *J* = 6.9 Hz, 2H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.59 – 7.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 154.3, 145.4, 142.5, 132.6, 129.1, 128.0, 125.9, 121.1, 116.3, 110.7.

2-phenylbenzo[*d*]oxazole-5-carboxylates (7j)



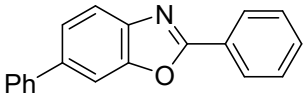
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 1.2 Hz, 1H), 8.26 (dd, *J* = 7.9, 1.7 Hz, 2H), 8.11 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.50 (m, 3H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 164.3, 153.6, 142.1, 132.0, 129.0, 127.8, 127.1, 126.5, 121.9, 110.4, 52.4.

methyl 2-phenylbenzoxazole-6-carboxylate (7k)



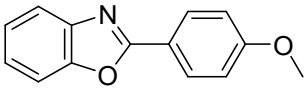
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 – 8.25 (m, 3H), 8.10 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.80 (dd, *J* = 8.4 Hz, 1H), 7.61 – 7.50 (m, 3H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.2, 129.0, 127.9, 126.5 (d, *J* = 31.1 Hz), 119.5, 112.3, 52.4.

2,6-diphenylbenzoxazole (7l)



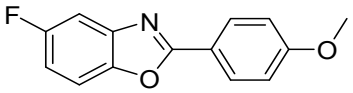
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 – 8.26 (m, 2H), 7.99 (m, 1H), 7.70 – 7.62 (m, 3H), 7.62 – 7.57 (m, 1H), 7.57 – 7.52 (m, 3H), 7.53 – 7.44 (m, 2H), 7.43 – 7.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.7, 151.6, 142.7, 141.0, 138.5, 131.7, 128.9 (d, J = 23.4 Hz), 127.6, 127.5, 127.3, 127.1, 124.8, 118.4, 110.6.

2-(4-methoxyphenyl) benzoxazole (7m)



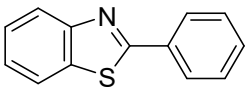
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, 2H), 7.88 – 7.73 (m, 1H), 7.67 – 7.54 (m, 1H), 7.41 – 7.34 (m, 2H), 7.06 (d, J = 5.5 Hz, 2H), 3.91(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 150.7, 142.2, 129.7, 125.0, 124.9, 119.7, 119.2, 114.5, 110.6, 55.5.

5-fluoro-2-(4-methoxyphenyl) benzo[*d*]oxazole (7n)



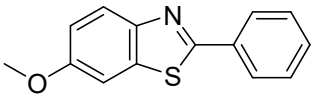
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.6 Hz, 2H), 7.52 – 7.38 (m, 2H), 7.09 – 7.00 (m, 3H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 164.7, 162.8, 147.1, 129.7, 118.9, 115.3, 112.6, 111.9, 106.5, 106.2, 56.0.

2-phenylbenzothiazole (7o)



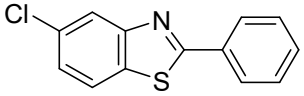
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.15 (m, 3H), 7.93 (d, J = 8.0 Hz, 1H), 7.59 – 7.51 (m, 4H), 7.44 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 154.1, 135, 133.1, 131.0, 128.7, 127.2, 126.0, 124.9, 122.9, 121.3.

6-methoxy-2-phenylbenzothiazole (7p)



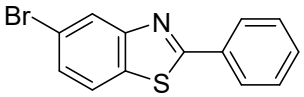
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 2H), 8.00 (d, J = 9.0 Hz, 1H), 7.49 (s, 3H), 7.36 (s, J = 2.6 Hz, 1H), 7.11 (d, J = 9.0, 2.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 158.1, 148.6, 137.6, 134.6, 131.1, 129.3, 127.6, 123.8, 116.1, 104.4, 56.1.

4-chloro-2-phenylbenzoxazole (7q)



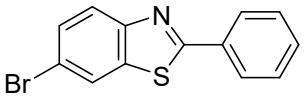
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 4.8 Hz, 2H), 7.76 (d, J = 1.8 Hz, 1H), 7.57 (d, J = 4.8 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.33 (dd, J = 6.5Hz, 1.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 150.3, 143.1, 132.0, 130.0, 129.0, 127.7, 126.6, 125.4, 119.9, 111.3.

5-bromo-2-phenylbenzo[*d*]thiazole (7r)



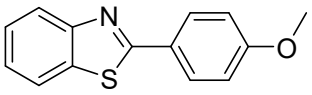
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 1.4 Hz, 1H), 8.11 – 8.08 (m, 2H), 7.77 (d, J = 6.4 Hz, 1H), 7.54 – 7.49 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 155.8, 133.8, 132.0, 131.9, 129.4, 128.8, 128.0, 126.2, 123.0, 120.4.

6-bromo-2-phenylbenzo[*d*]thiazole (7s)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.07 (m), 8.05 (d, J = 1.4 Hz, 1H), 7.95 (d, J = 6.5 Hz, 1H), 7.60 (dd, J = 6.5, 1.4 Hz), 7.54 – 7.47 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 152.6, 136.1, 132.8, 131.4, 130.0, 129.2, 127.7, 124.5, 124.2, 118.9.

2-(4-methoxyphenyl) benzo[*d*]thiazole (7t)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.03 (m, J = 7.6 Hz, 3H), 7.88 (t, J = 6.3 Hz, 1H), 7.48 (d, J = 6.3 Hz, 1H), 7.37 (d, J = 5.7 Hz, 1H), 7.01 (d, J = 6.6 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 162.0, 158.7, 137.0, 129.2, 126.3, 124.9, 122.6, 121.5, 114.4, 55.5.

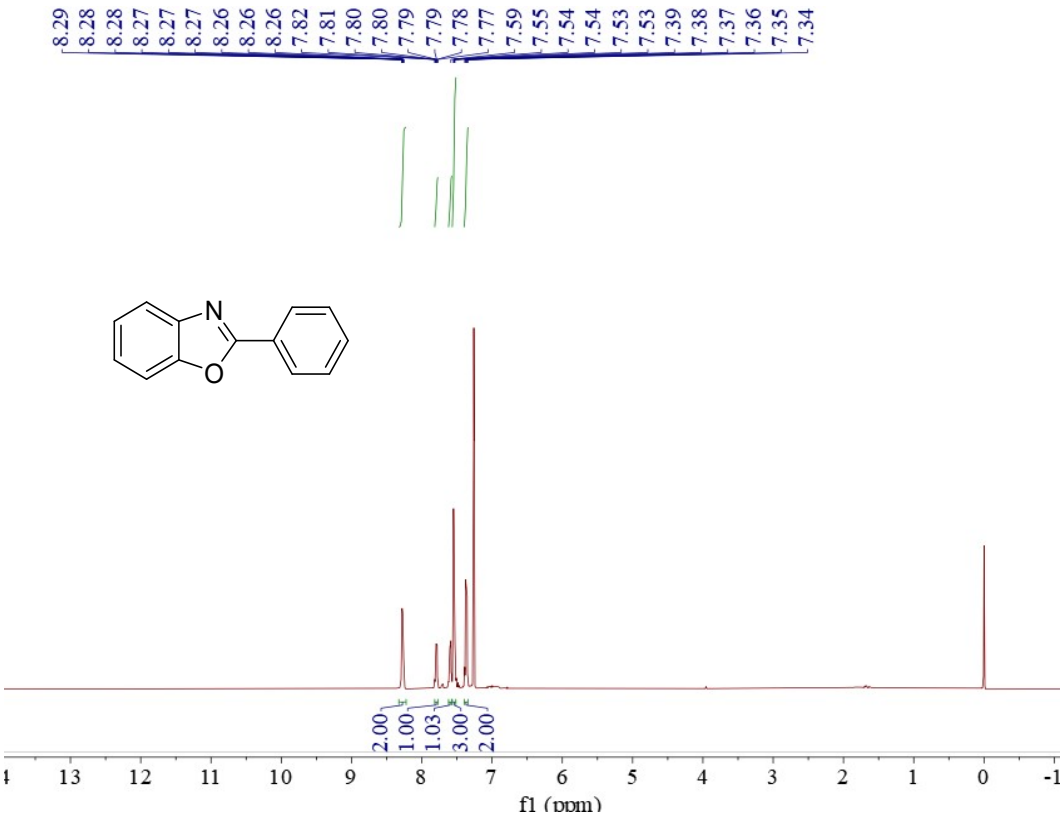


Fig. S48 ^{1}H NMR of **7a**

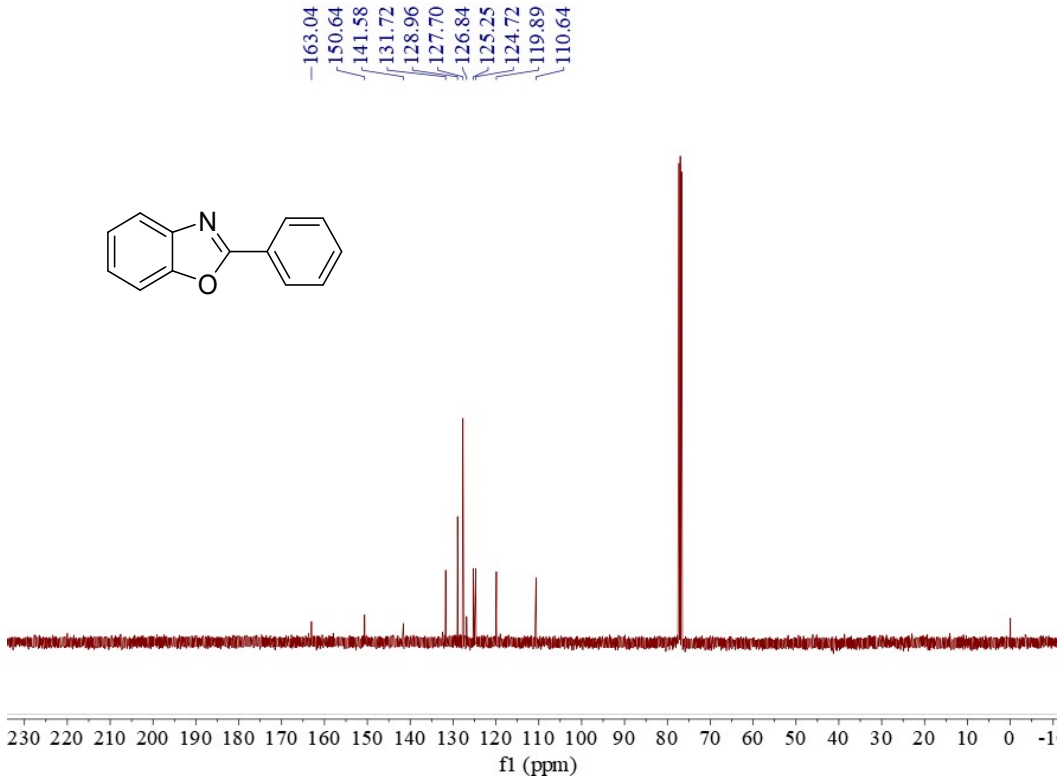


Fig. S49 ^{13}C NMR of **7a**

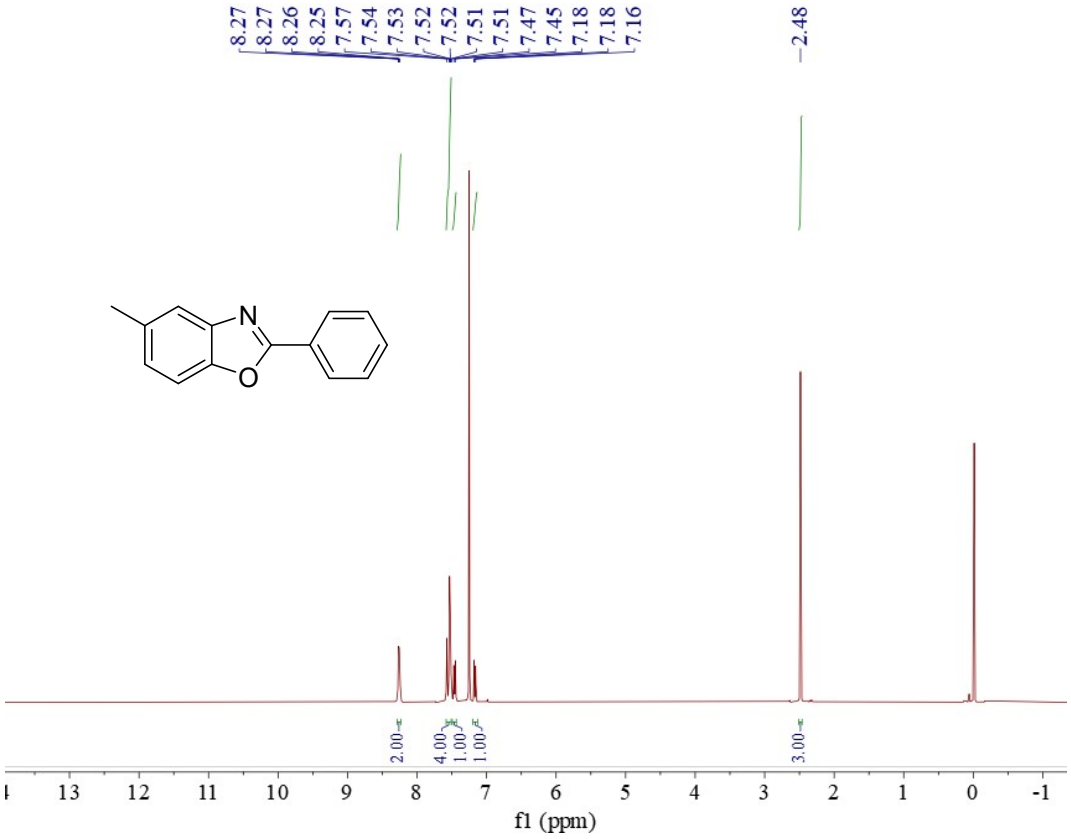


Fig. S50 ^{1}H NMR of **7b**

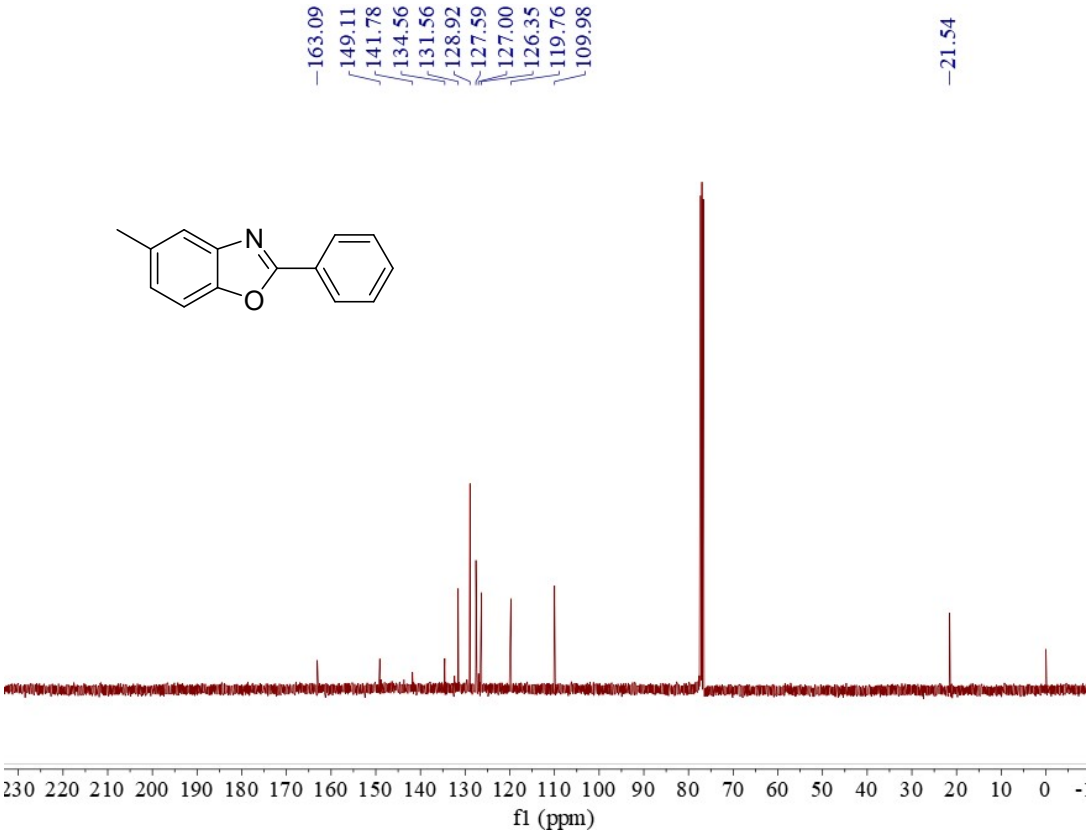


Fig. S51 ^{13}C NMR of **7b**

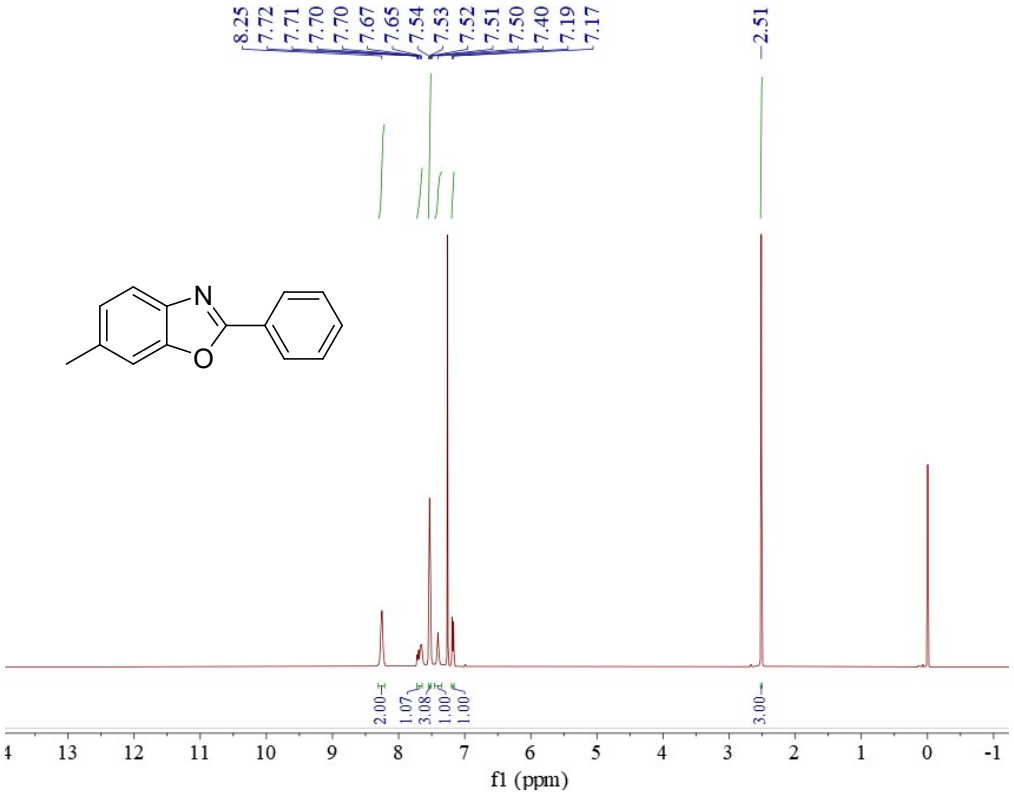


Fig. S52 ^{1}H NMR of **7c**

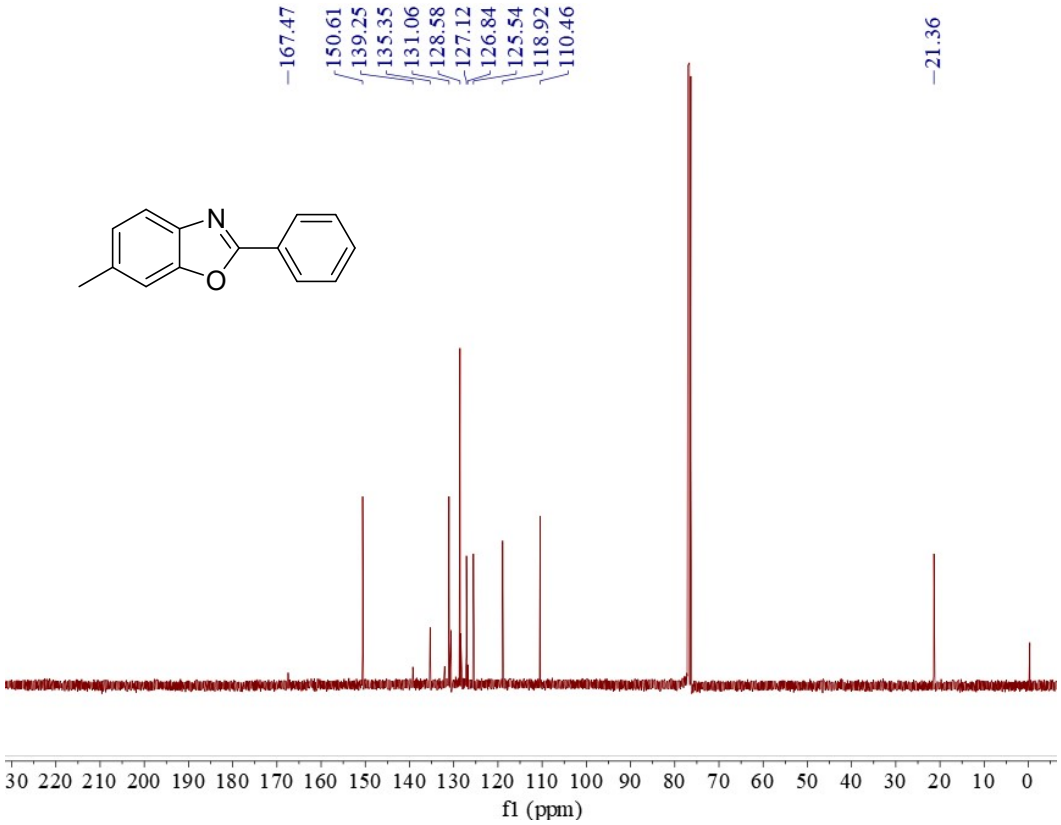


Fig. S53 ^{13}C NMR of **7c**

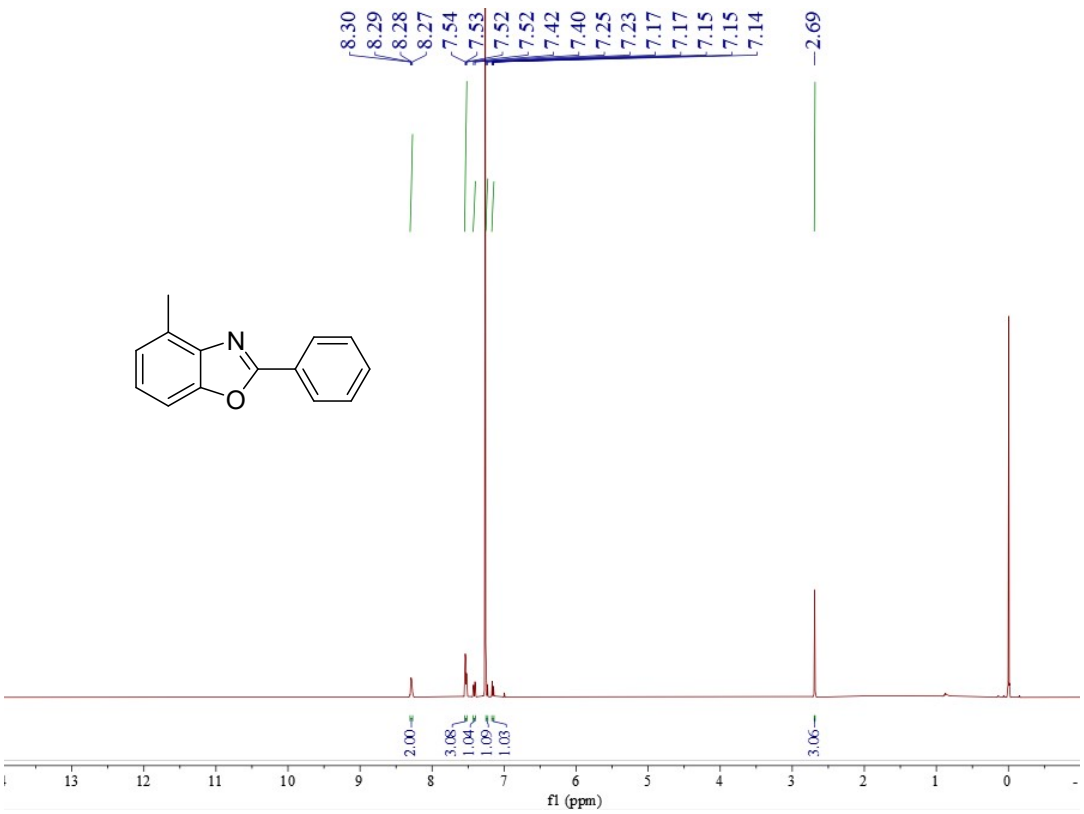


Fig. S54 ^{1}H NMR of **7d**

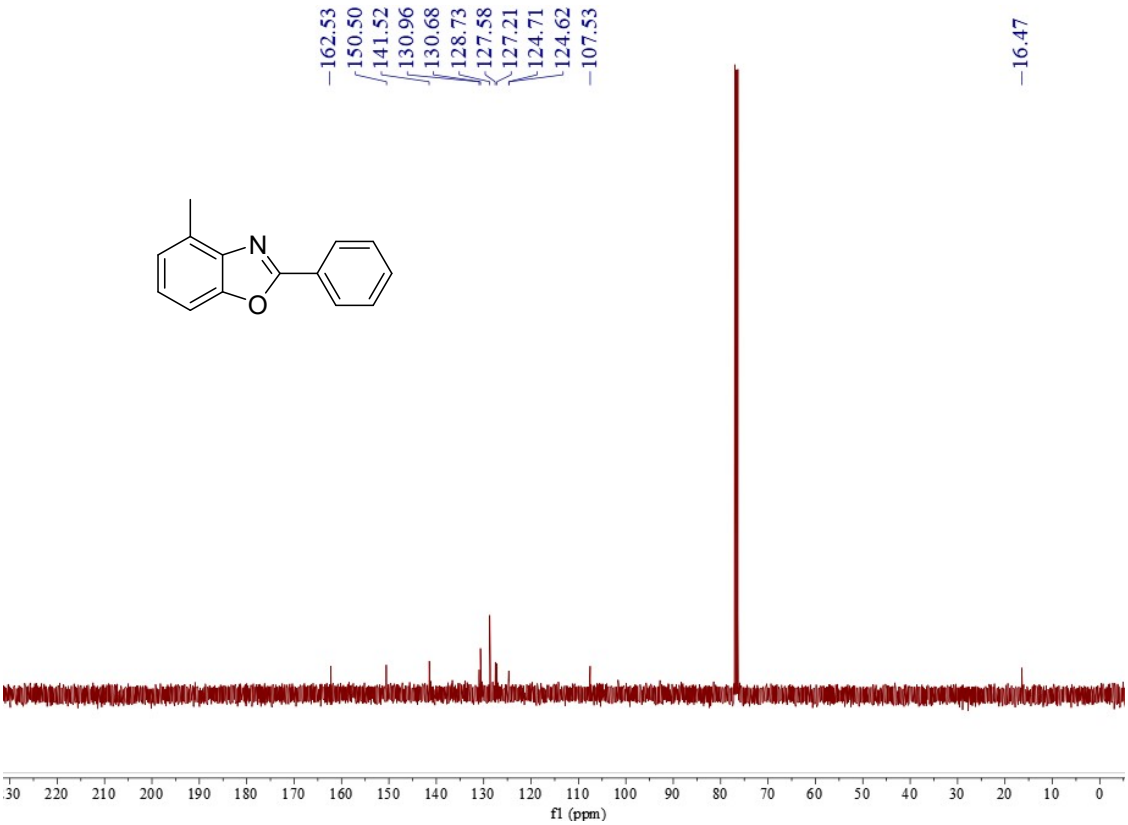


Fig. S55 ^{13}C NMR of **7d**

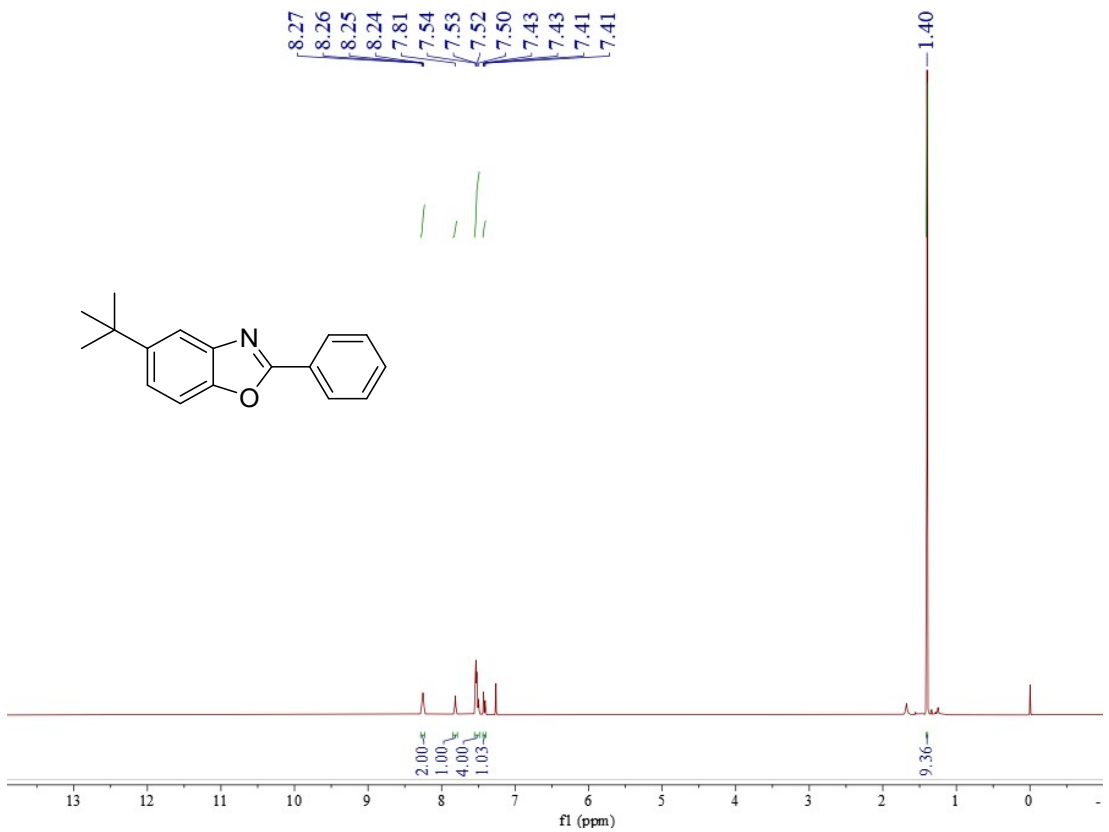


Fig. S56 ^{1}H NMR of **7e**

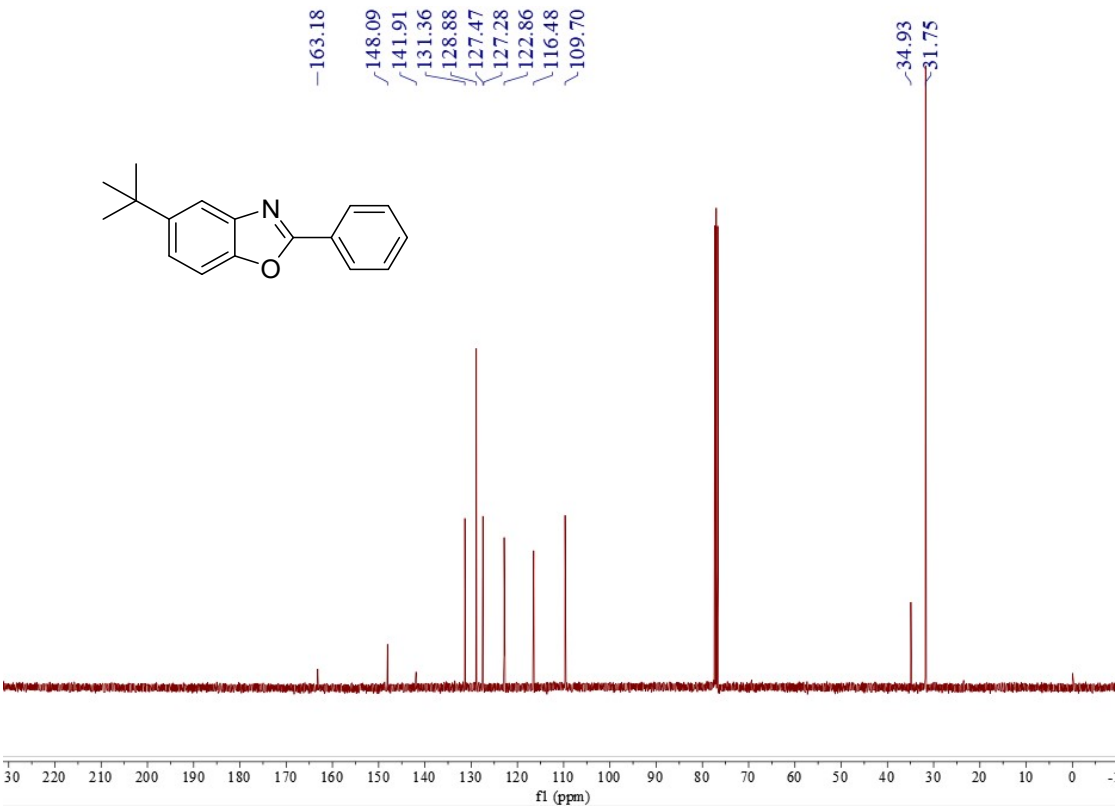


Fig. S57 ^{13}C NMR of **7e**

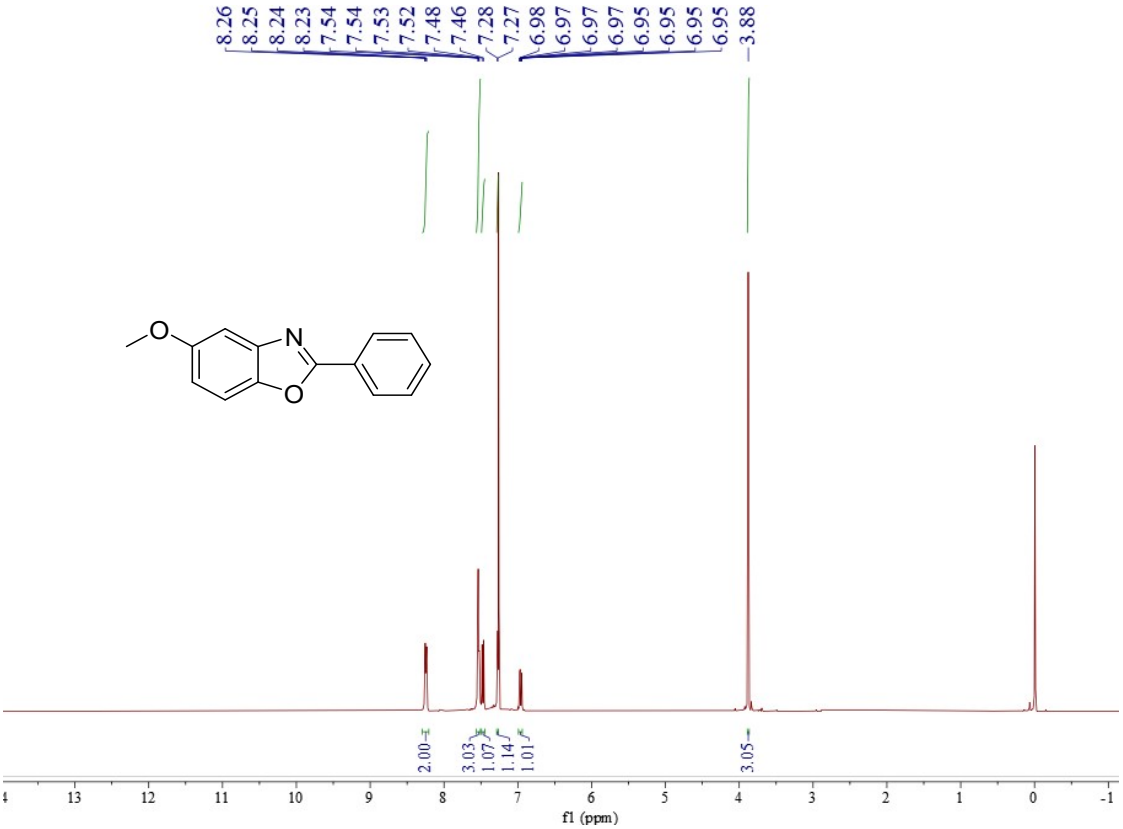


Fig. S58 ^{1}H NMR of **7f**

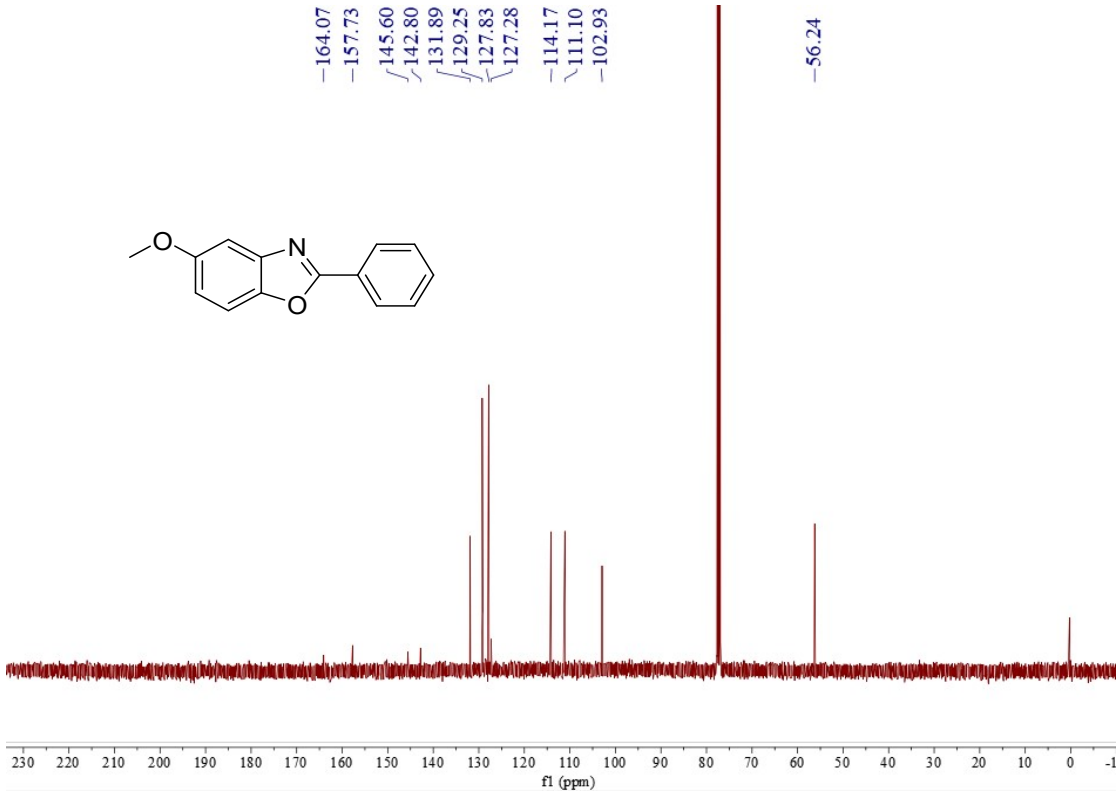


Fig. S59 ^{13}C NMR of **7f**

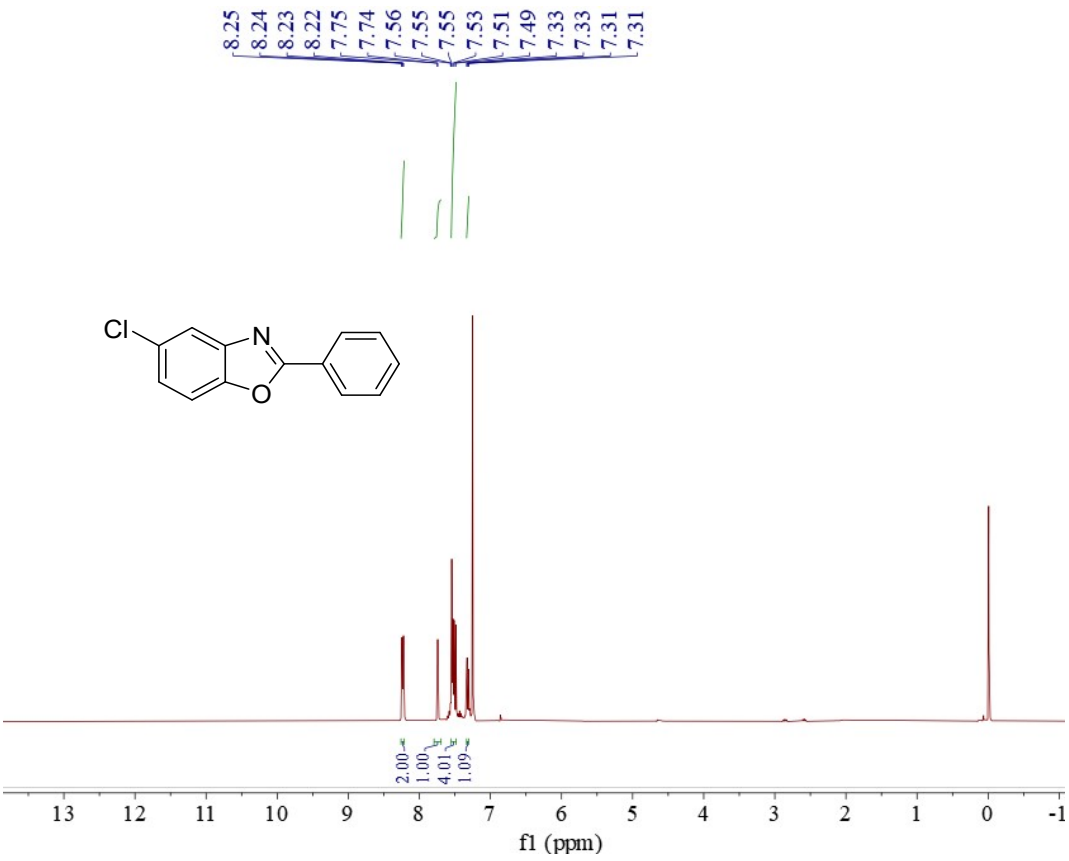


Fig. S60 ^{1}H NMR of **7g**

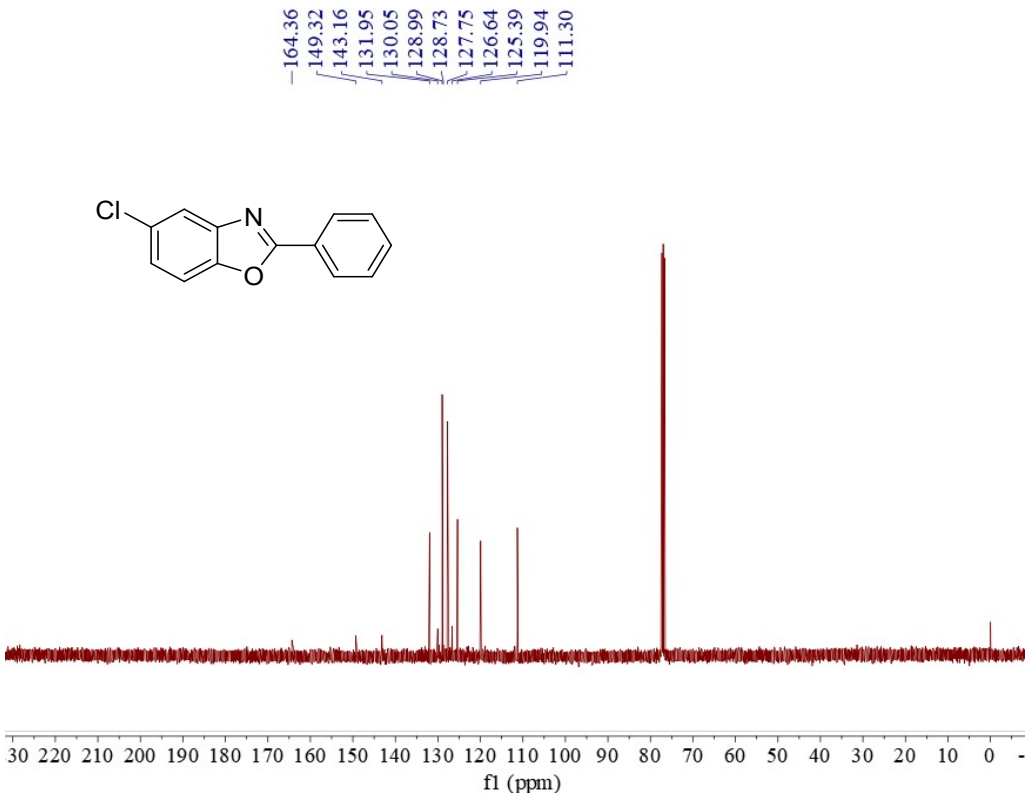


Fig. S61 ^{13}C NMR of **7g**

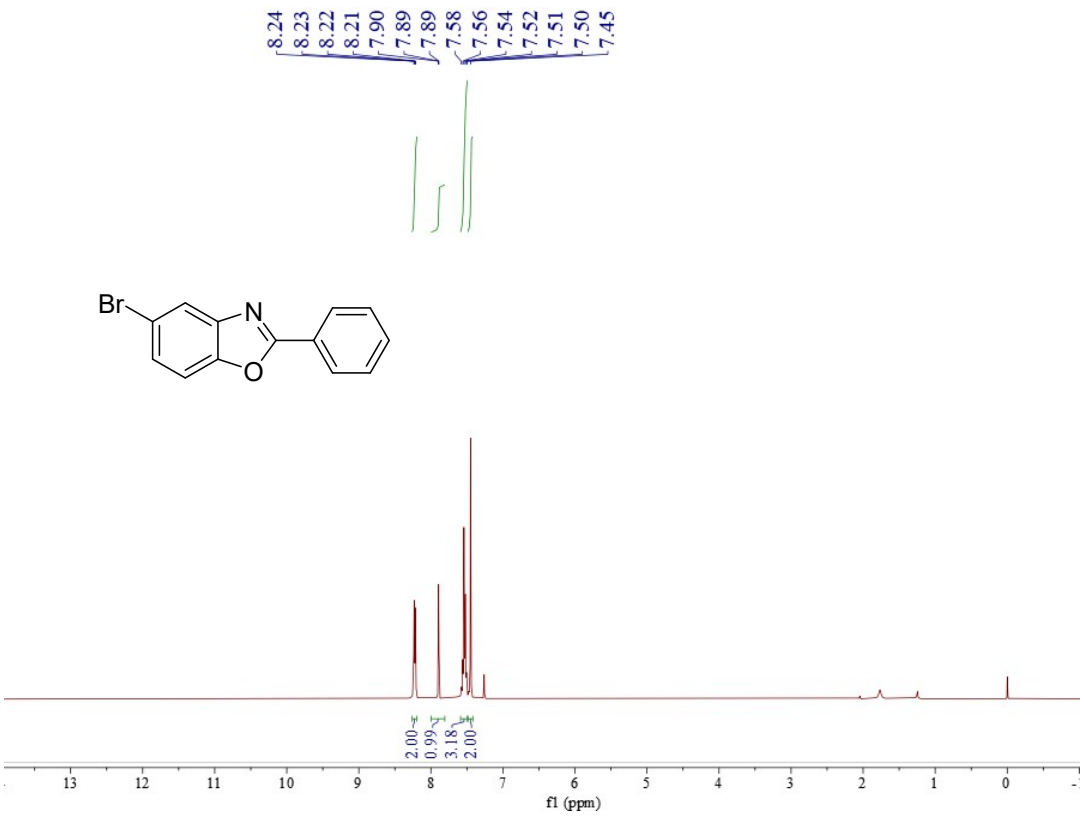


Fig. S62 ^{1}H NMR of **7h**

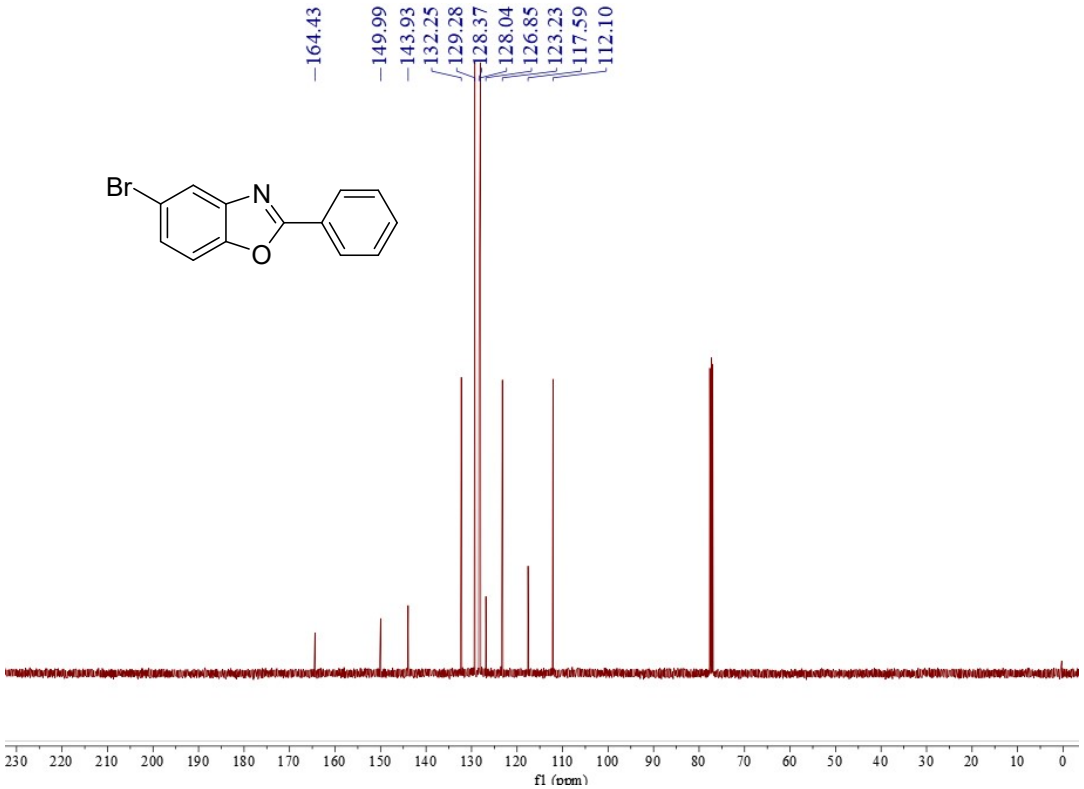


Fig. S63 ^{13}C NMR of **7h**

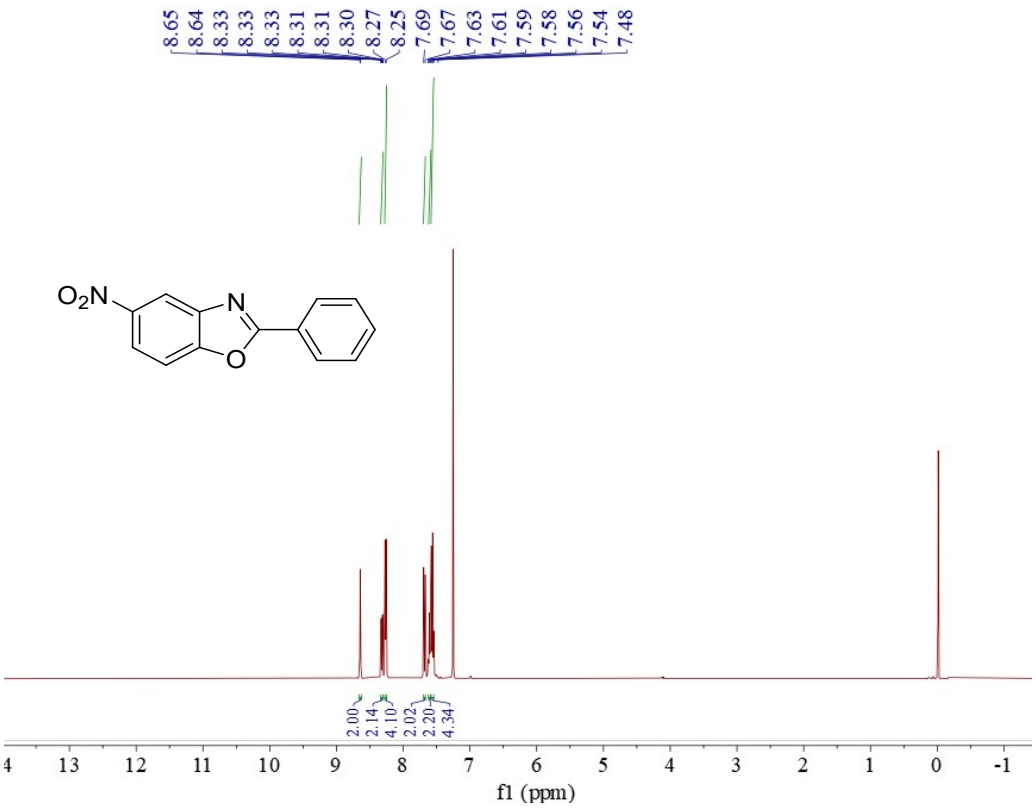


Fig. S64 ^{1}H NMR of **7i**

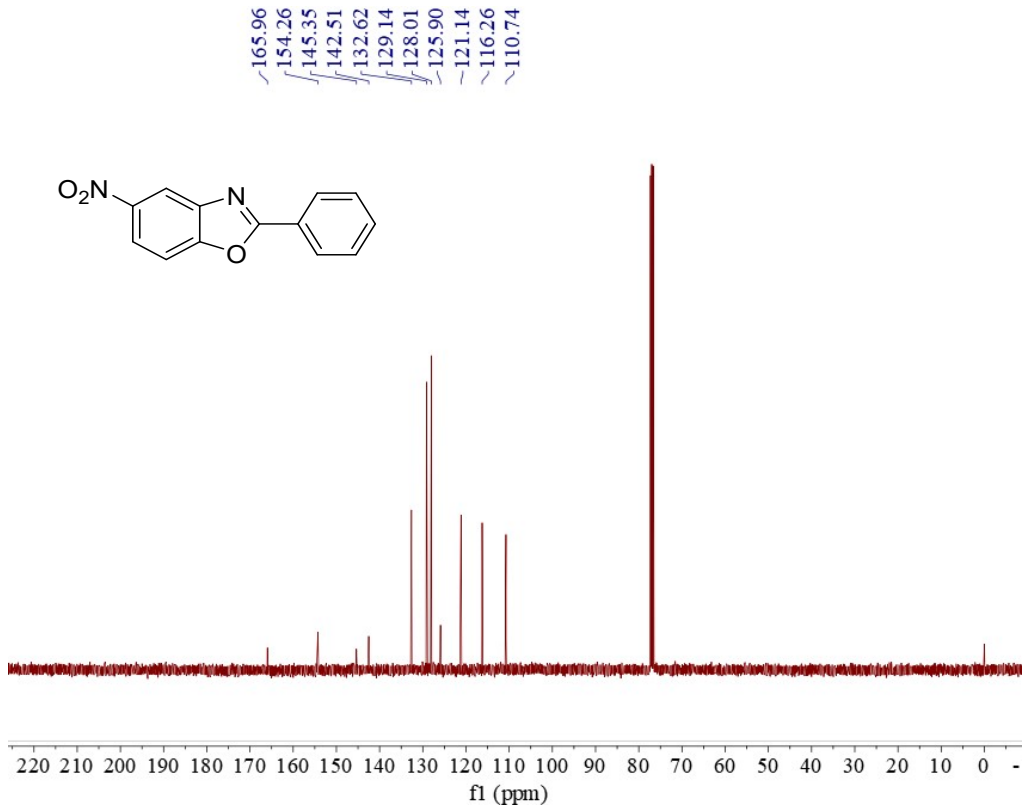


Fig. S65 ^{13}C NMR of **7i**

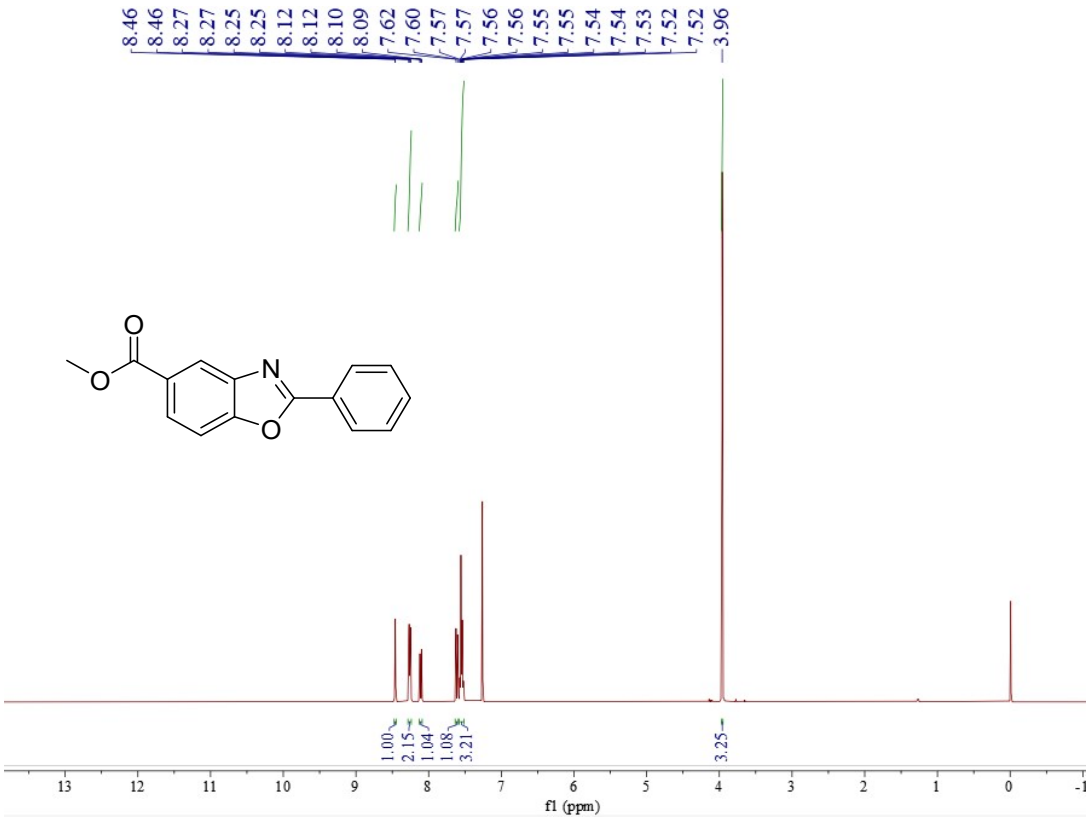


Fig. S66 ^{1}H NMR of **7j**

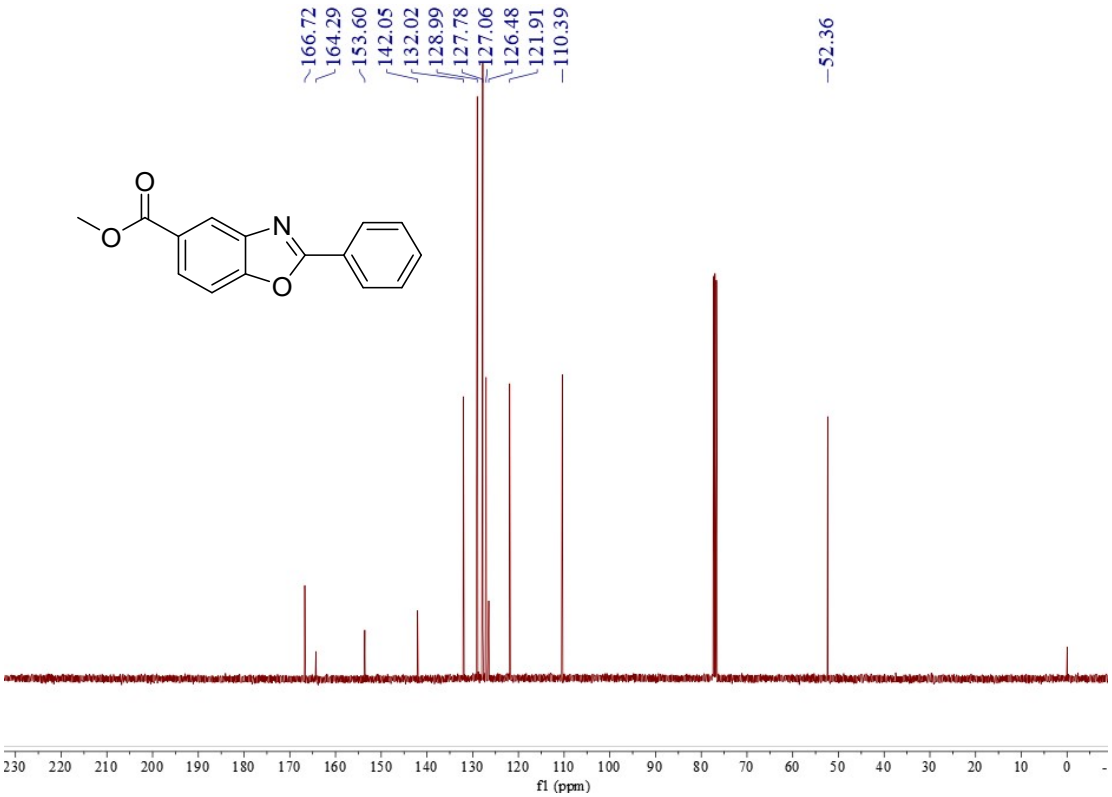


Fig. S67 ^{13}C NMR of **7j**

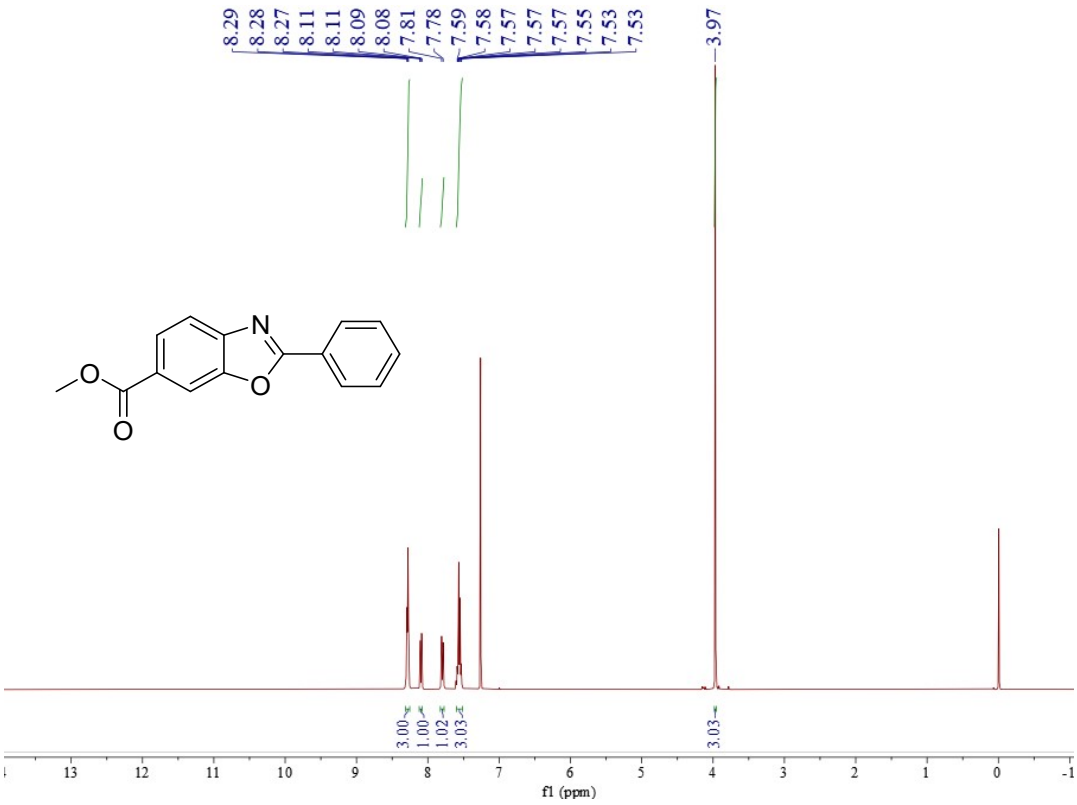


Fig. S68 ^{1}H NMR of **7k**

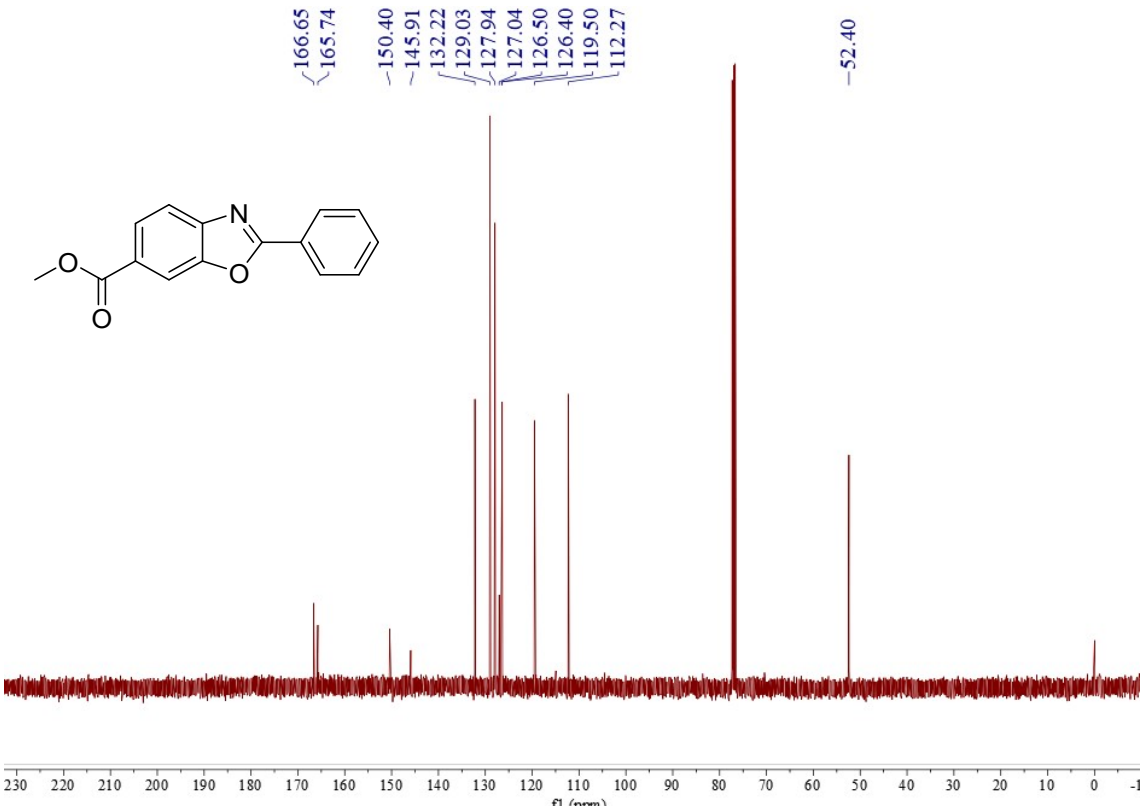


Fig. S69 ^{13}C NMR of **7k**

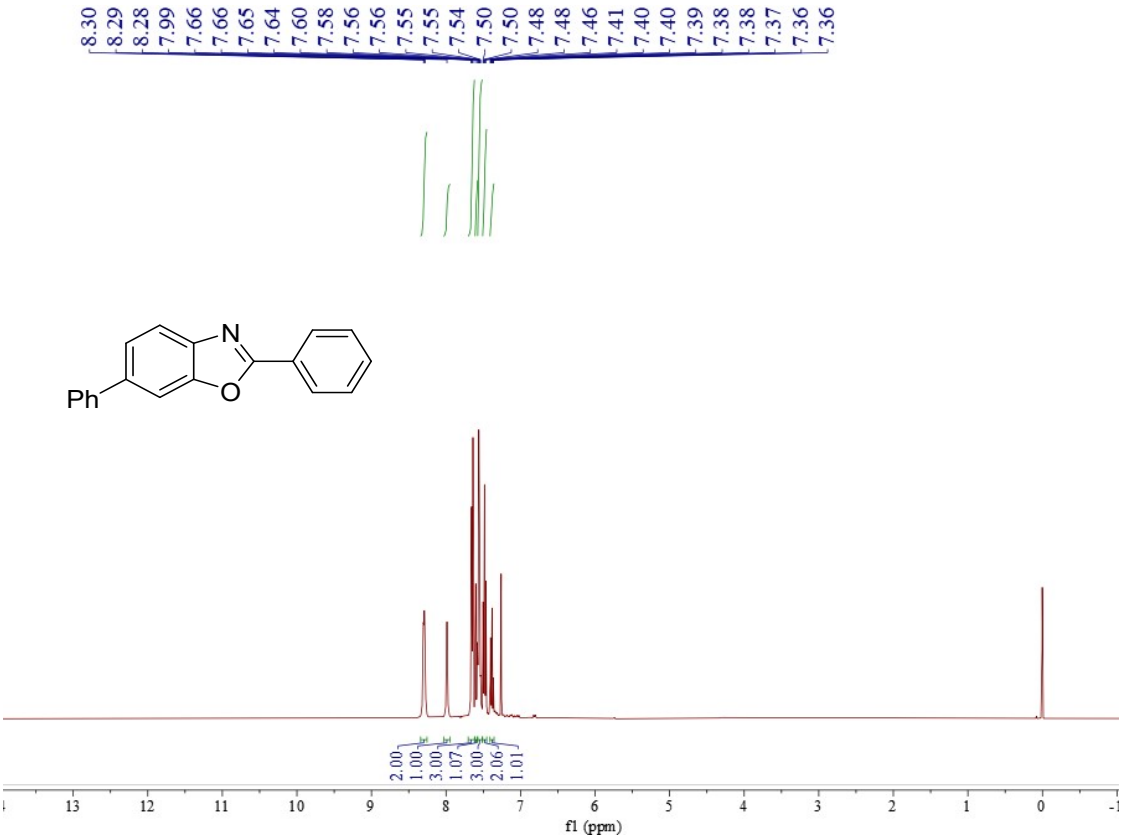


Fig. S70 ^{1}H NMR of **7l**

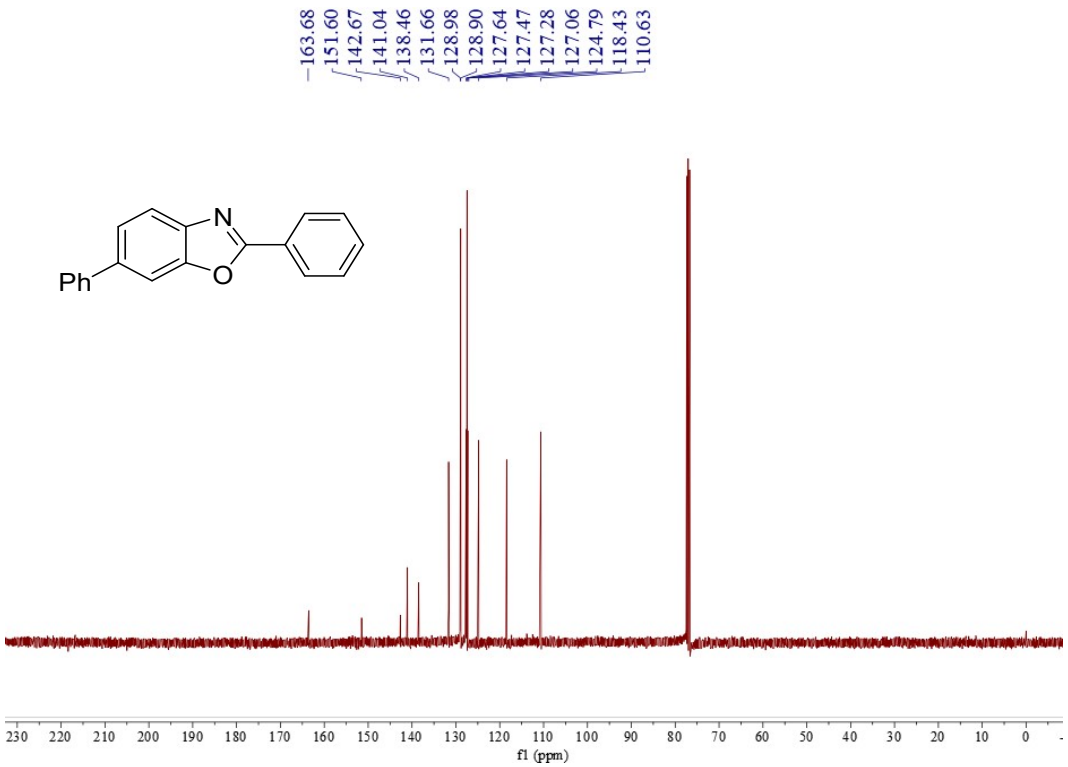


Fig. S71 ^{13}C NMR of **7l**

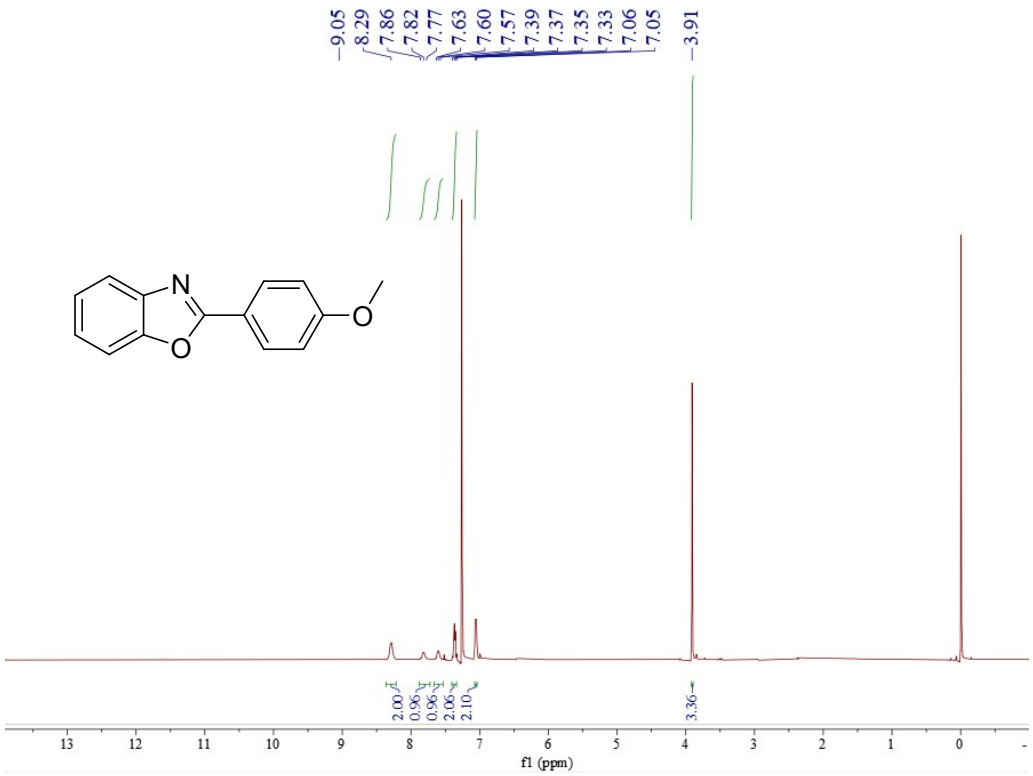


Fig. S72 ^{1}H NMR of **7m**

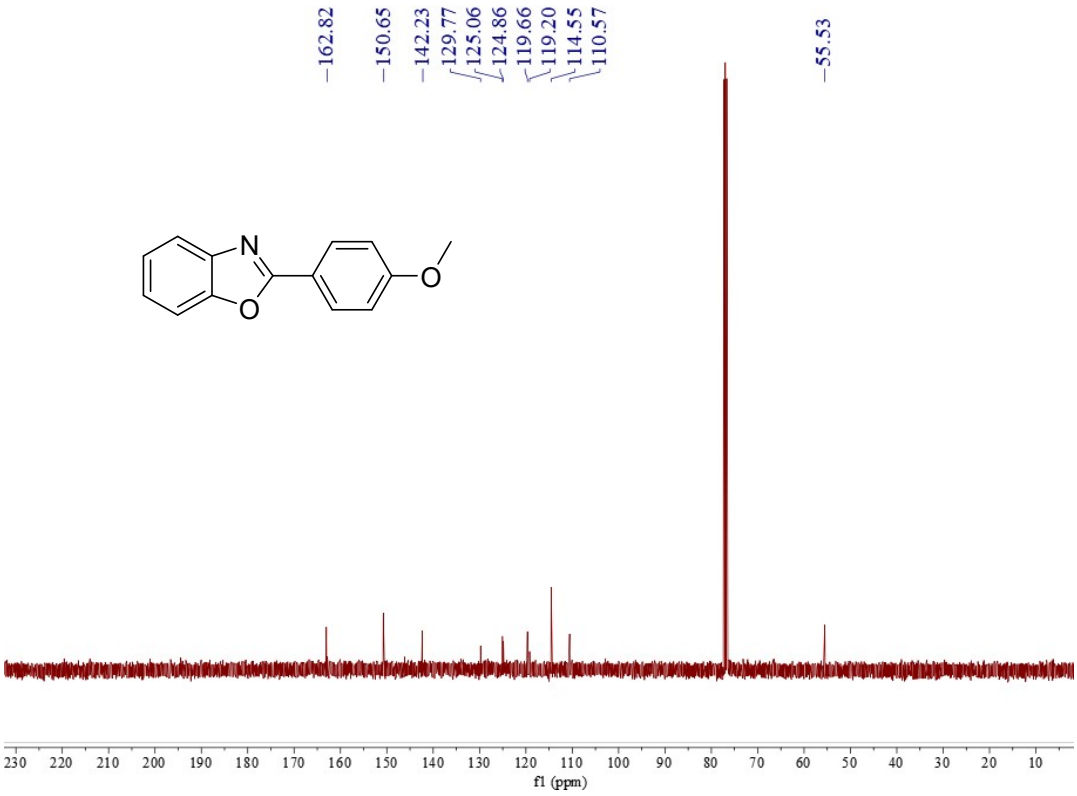


Fig. S73 ^{13}C NMR of **7m**

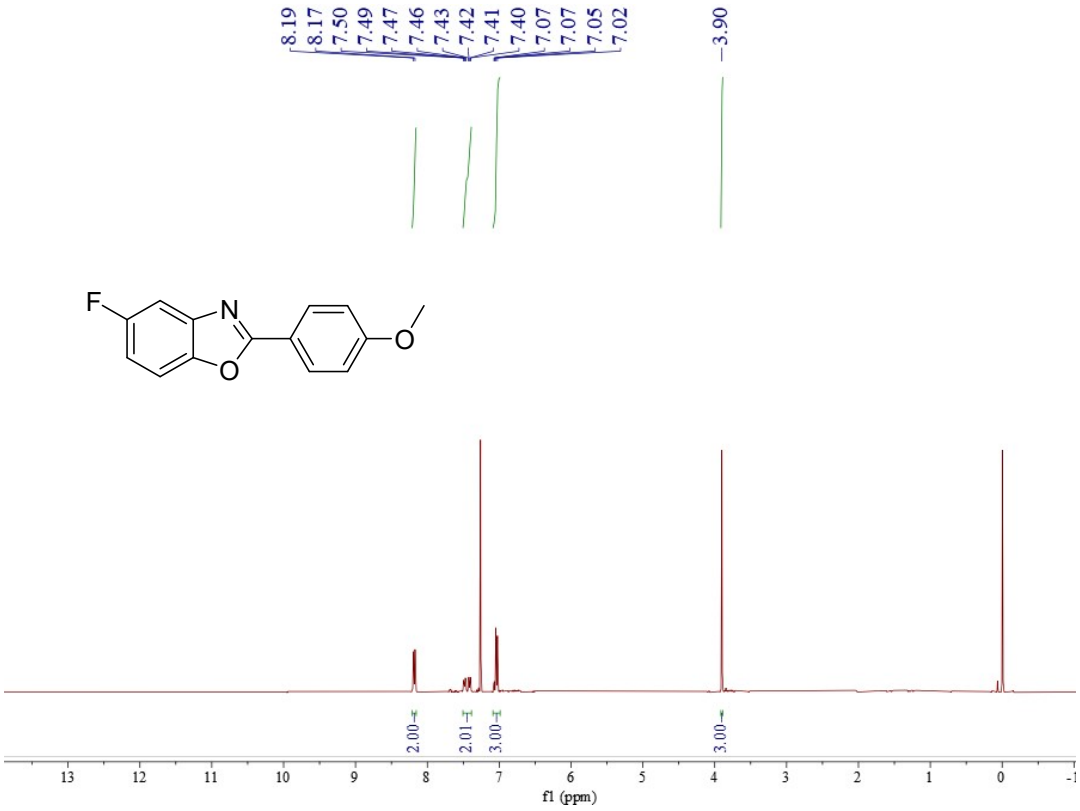


Fig. S74 ^{1}H NMR of **7n**

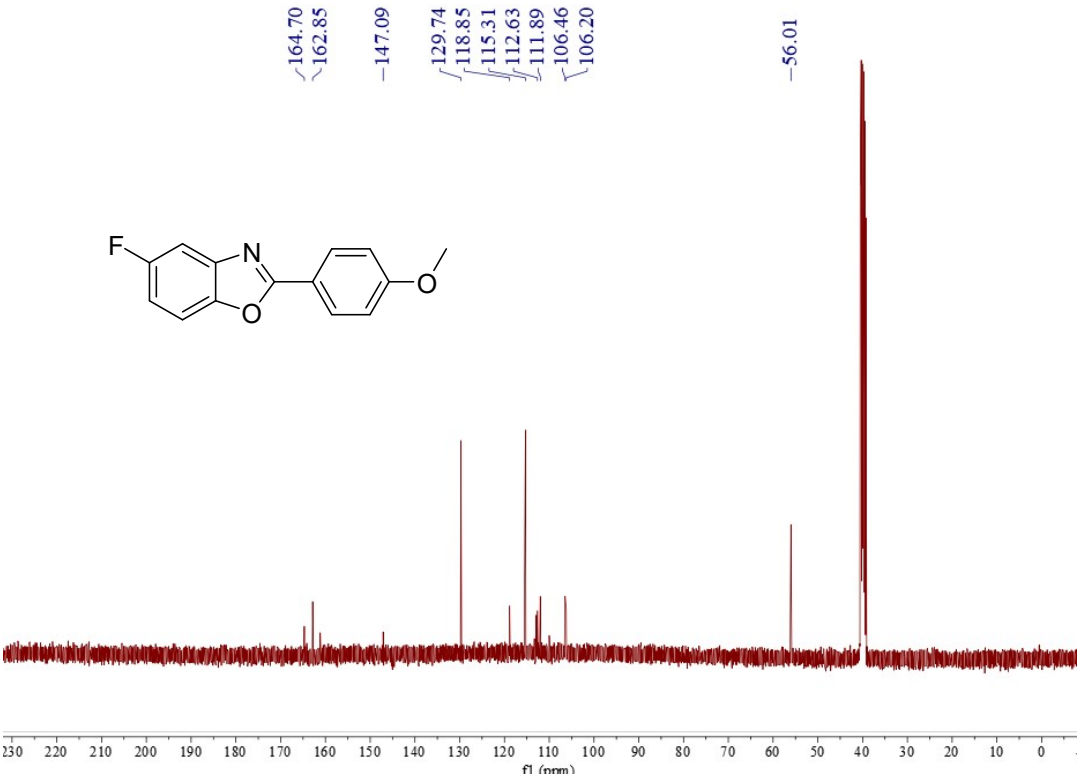


Fig. S75 ^{13}C NMR of **7n**

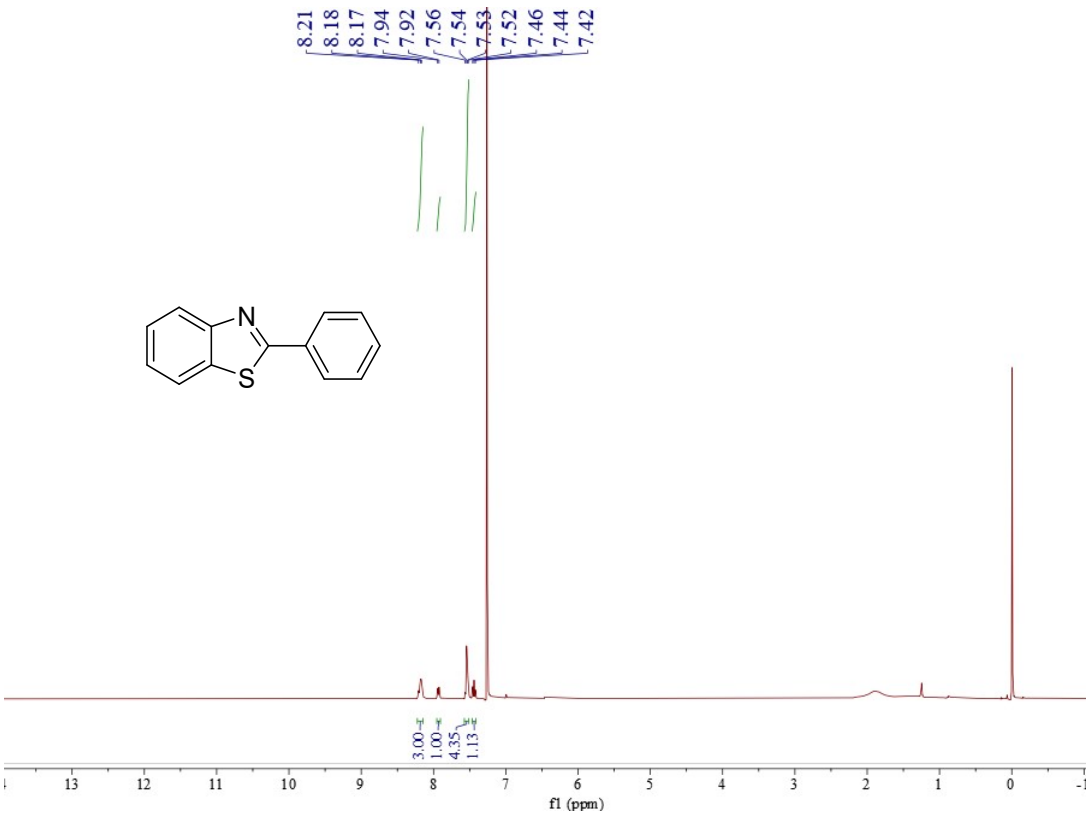


Fig. S76 ^{1}H NMR of **7o**

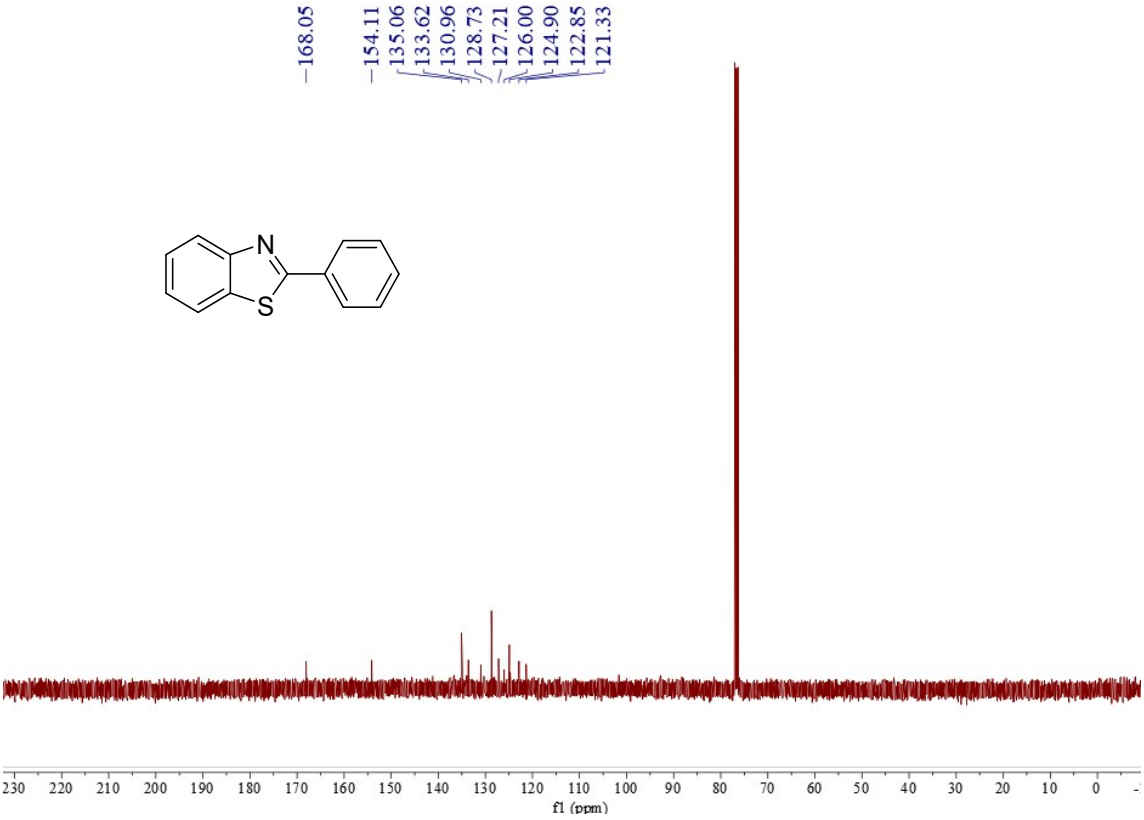


Fig. S77 ^{13}C NMR of **7o**

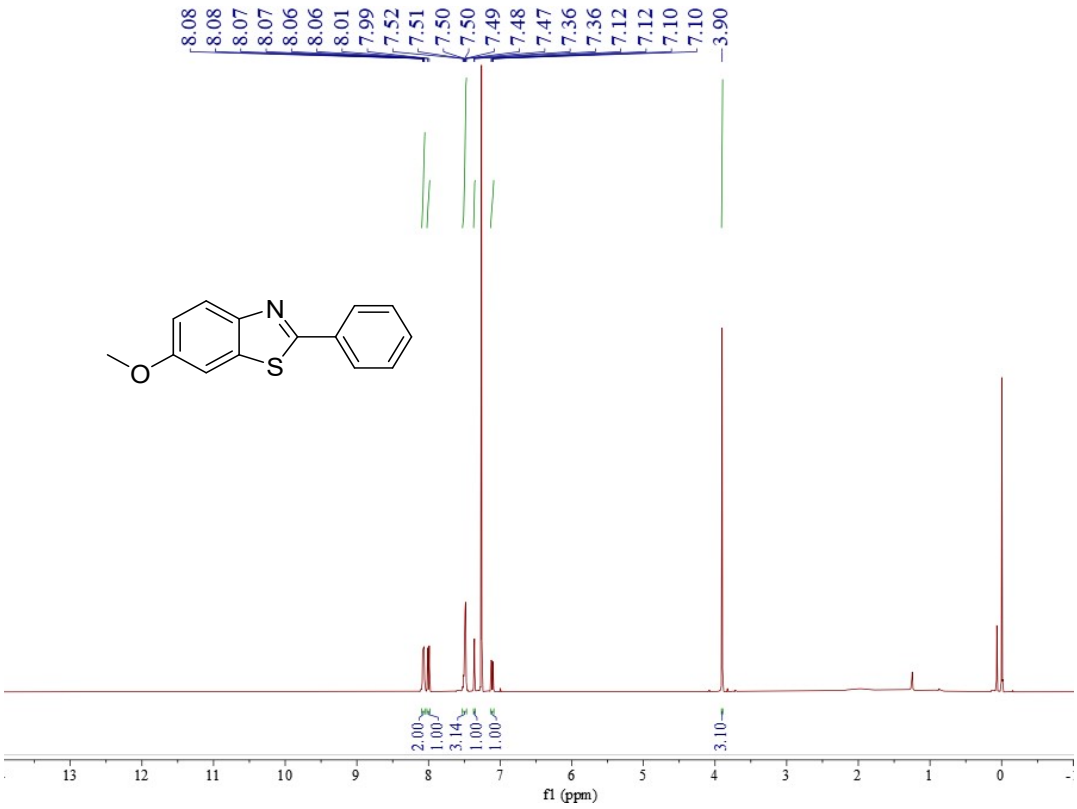


Fig. S78 ^{1}H NMR of **7p**

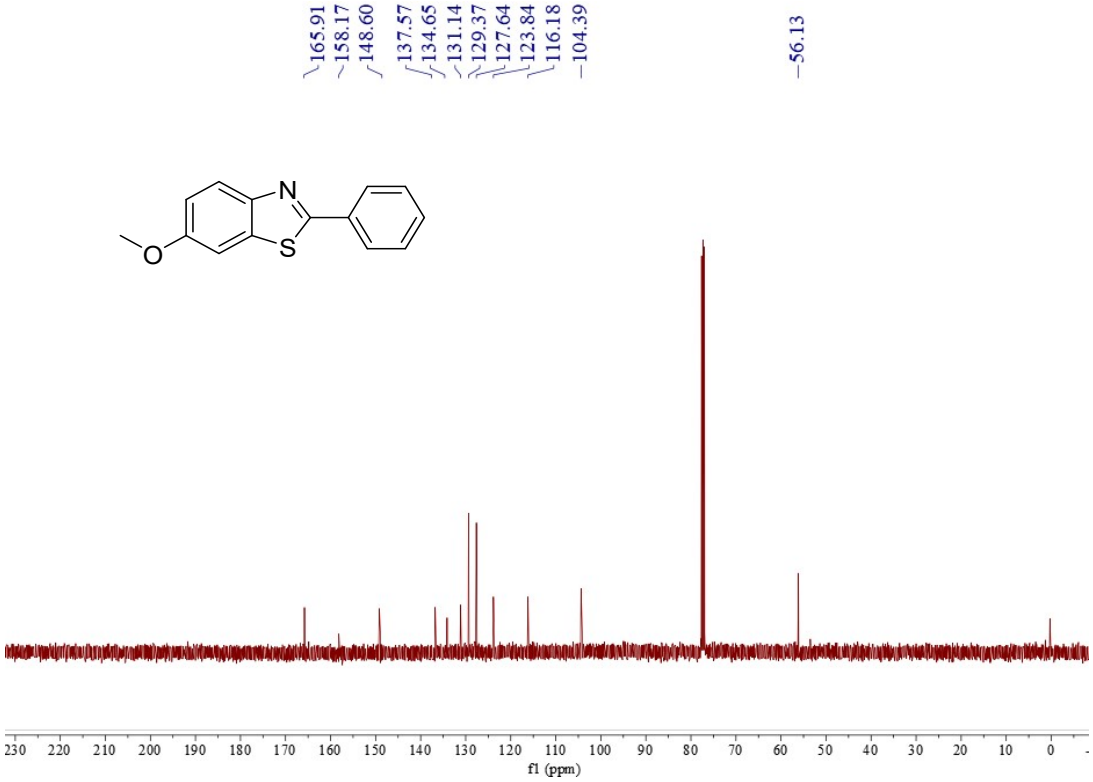


Fig. S79 ^{13}C NMR of **7p**

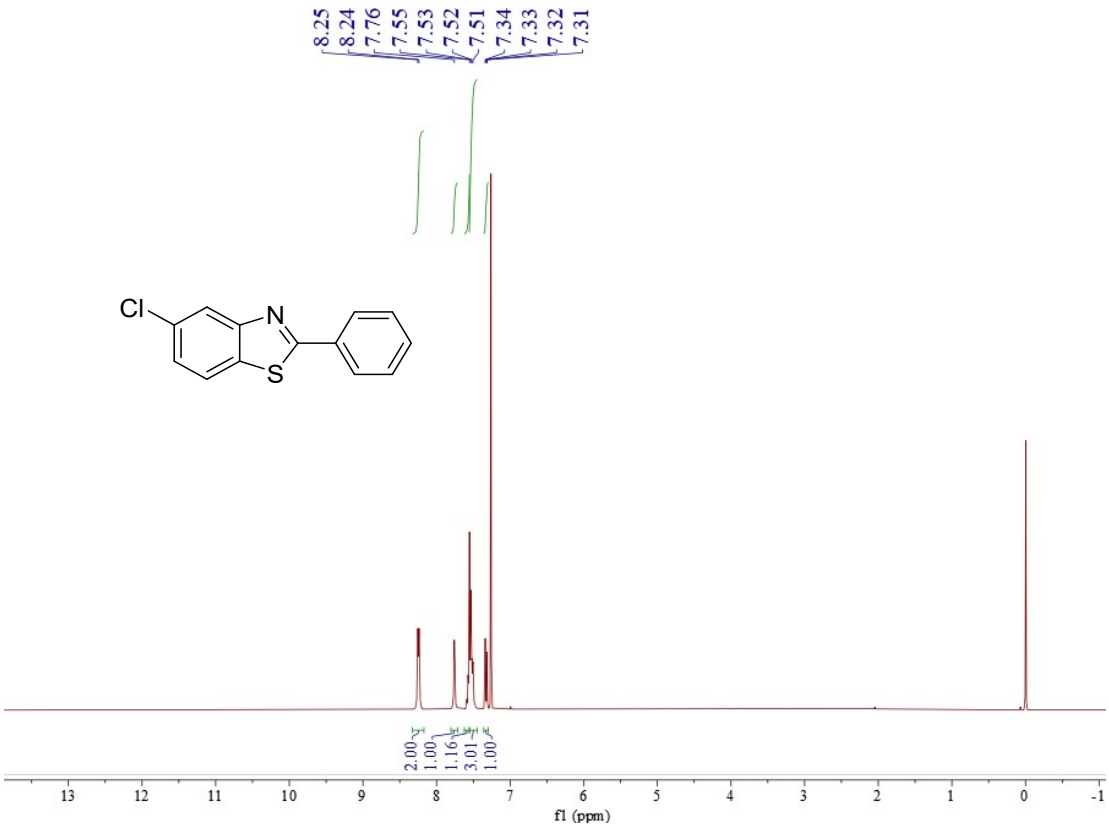


Fig. S80 ^{1}H NMR of **7q**

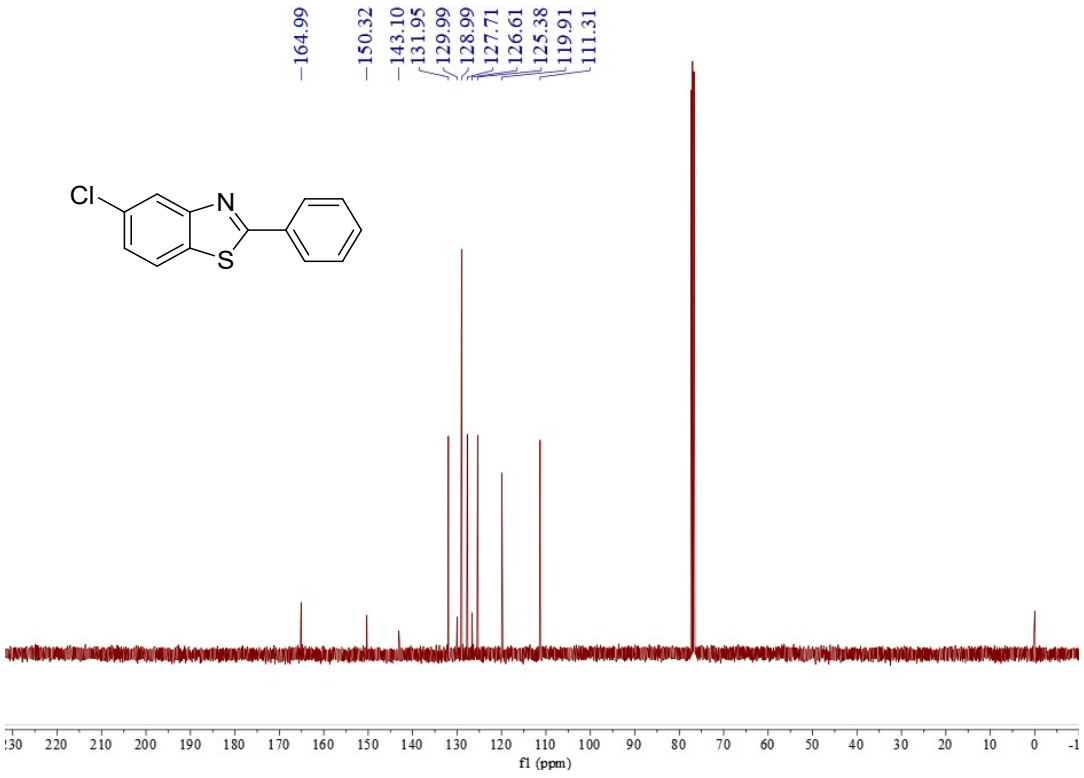


Fig. S81 ^{13}C NMR of **7q**

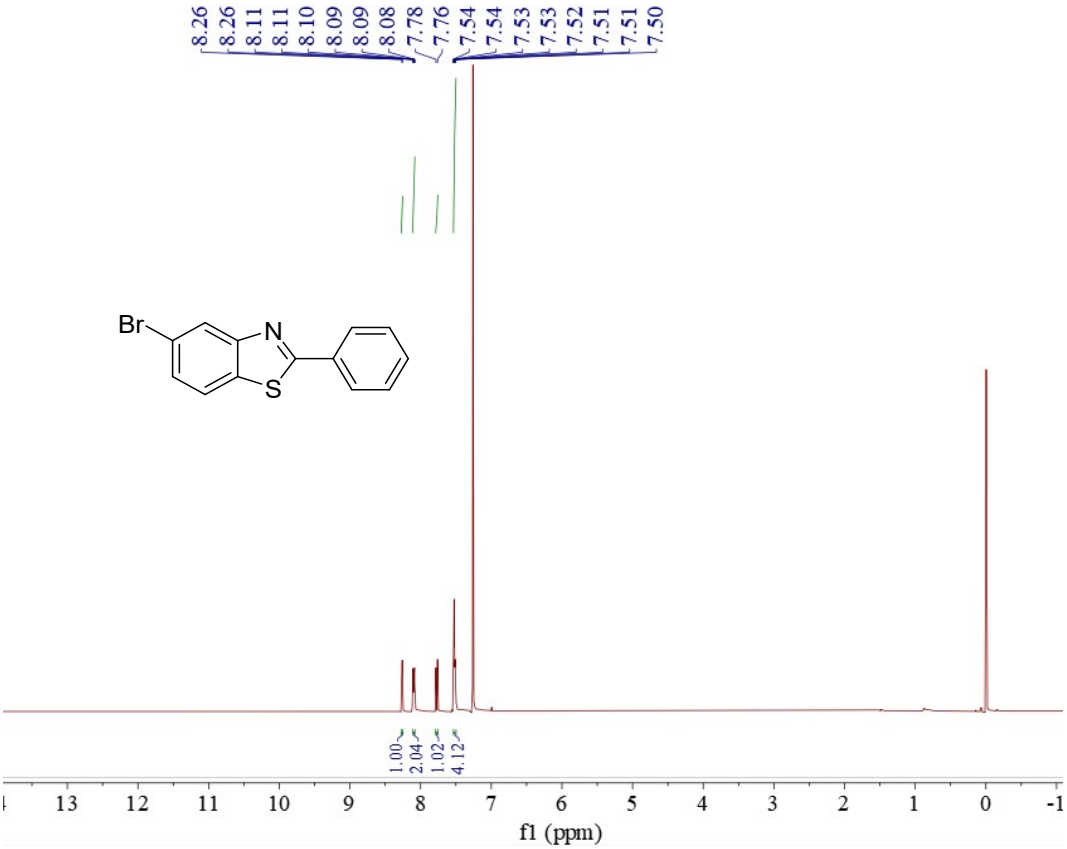


Fig. S82 ^{1}H NMR of **7r**

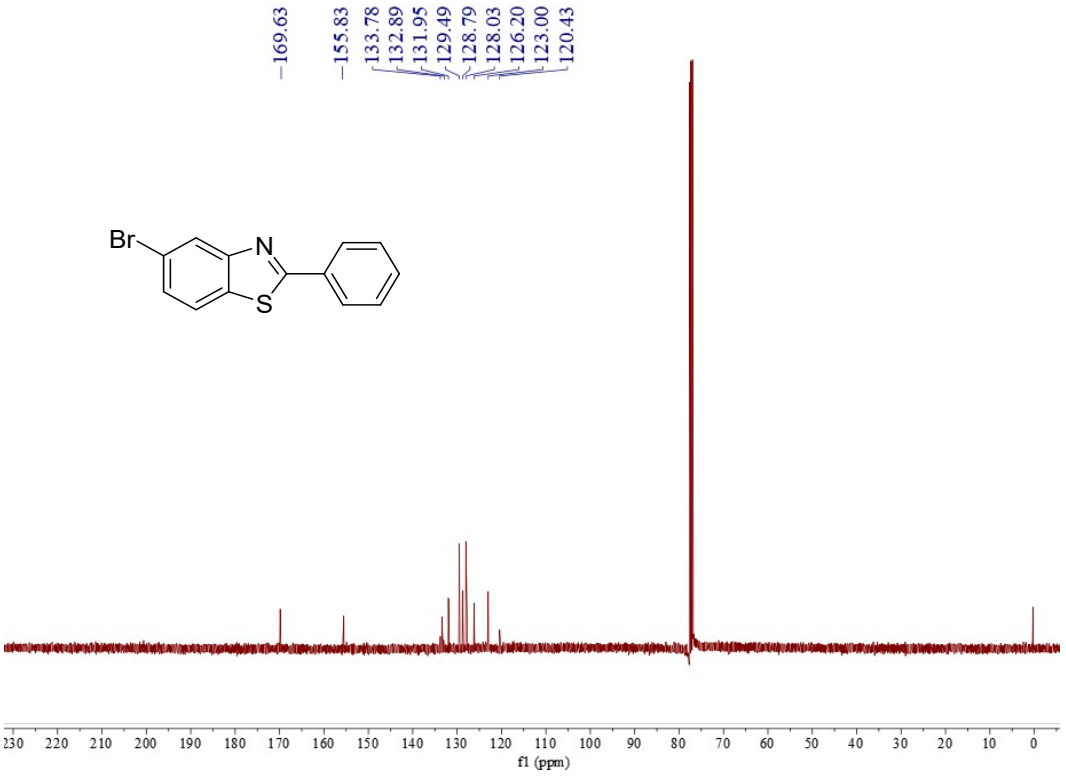


Fig. S83 ^{13}C NMR of **7r**

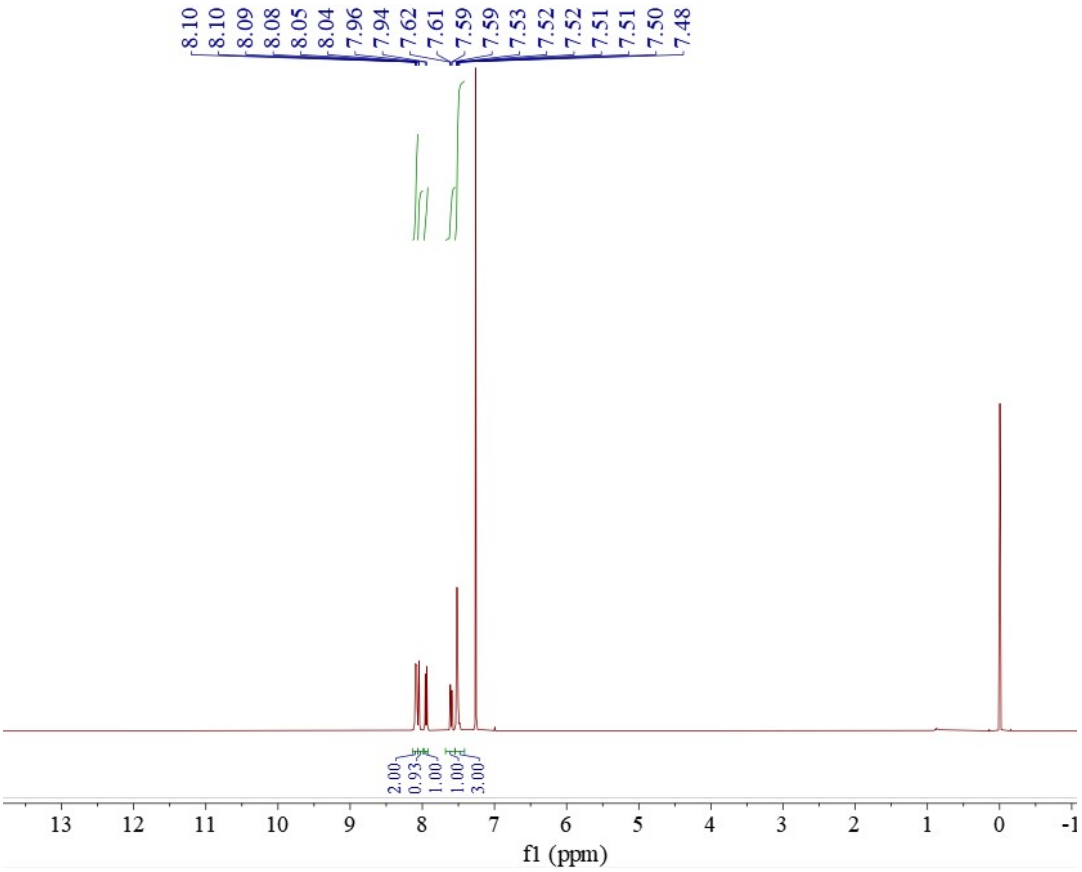


Fig. S84 ^{1}H NMR of **7s**

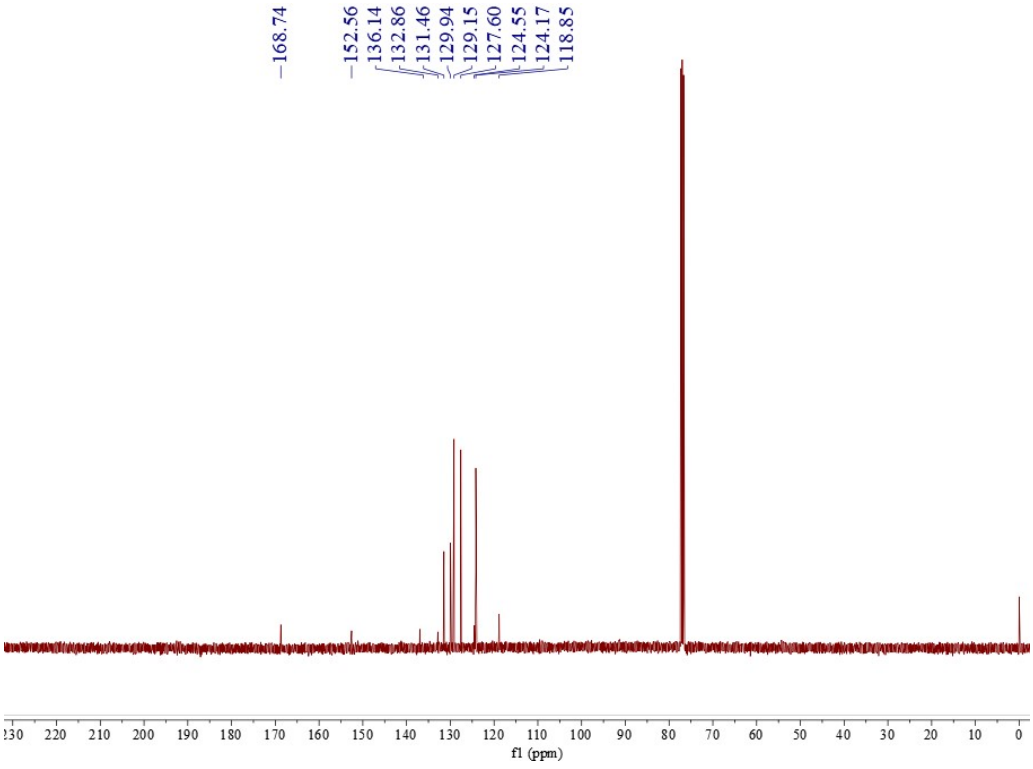


Fig. S85 ^{13}C NMR of **7s**

Fig. S86 ^{1}H NMR of **7t**

Fig. S87 ^{13}C NMR of **7t**

[1] J. Gómez-González , Y. Pérez, G. Sciortino, L. Roldan-Martín, J. Martínez-Costas, J.-D. Maréchal, I. Alfonso, M. V. López, M. E. Vázquez, Dynamic stereoselection of peptide helicates and their selective labeling of DNA replication foci in cells, Angew. Chem. Int. Ed. 60(2020) 8859–8866.