Electronic supporting information

Direct arylation reaction catalyzed by a PEPPSI-type palladium complex with an amido-functionalized triazole-based mesoionic carbene ligand

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Table S1. Crystallographic data

	4a	**4a'**	**5**
empirical formula	$C_{22}H_{21}I_2N_5OPd$	$C_{40}H_{38}IN_9O_2Pd$	$C_{23}H_{21}Cl_2N_5O_2Pd$
formula weight	731.61	910.09	576.75
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	19.6520(7)	9.9641(7)	12.9633(9)
b, Å	13.9047(4)	20.8540(16)	7.2635(5)
c, Å	9.4467(3)	18.8602(14)	24.2734(17)
α, deg	90	90	90
β, deg	97.452(2)	104.447(5)	93.041(5)
γ, deg	90	90	90
V, Å^3	2559.56(14)	3795.1(5)	2282.3(3)
T, K	150(2)	150(2)	150(2)
Z	4	4	4
F(000)	1396	1824	1160
no. of unique data	5574	8293	4978
no. of params refined	306	483	299
R_1[a] [$I > 2\sigma I$]	0.0585	0.0776	0.0446
wR_2[b] (all data)	0.1715	0.2191	0.1128

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$

Chart S1. Frontier orbital energies (eV) of free carbenes Tm and Tn1 at M062X/6-31G* level of theory.

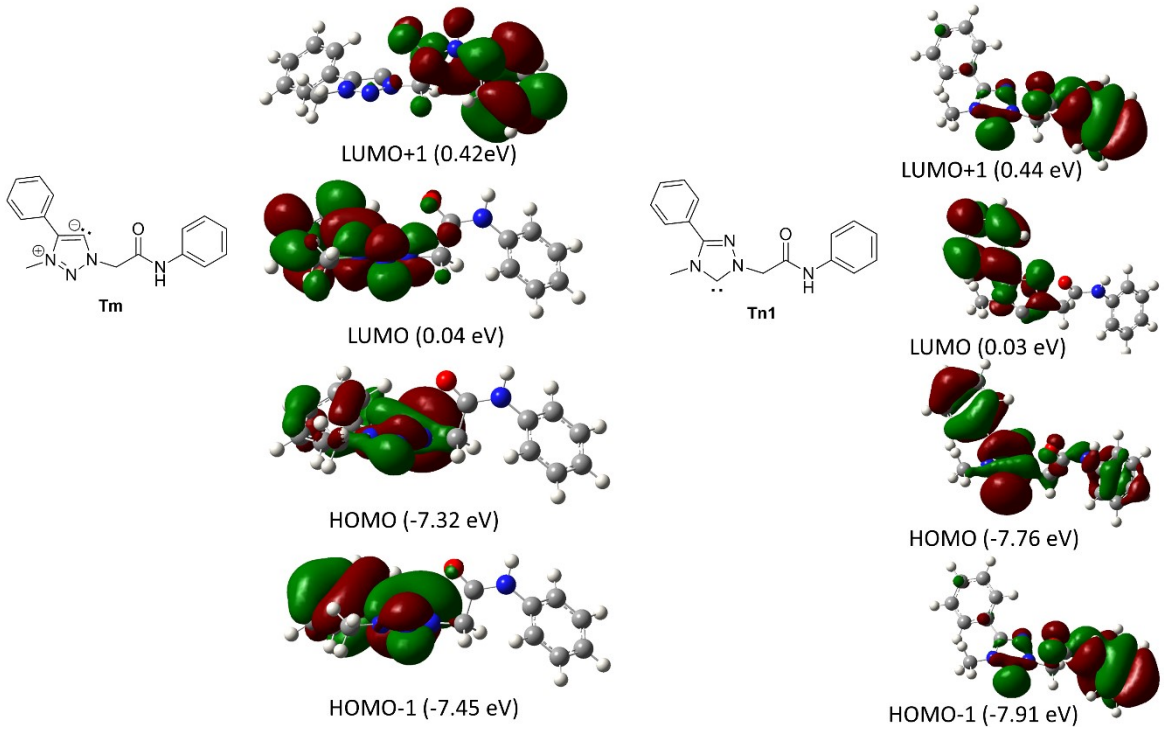


Chart S2. Frontier orbital energies (eV) of free carbenes Tn2 and Nn at M062X/6-31G* level of theory.

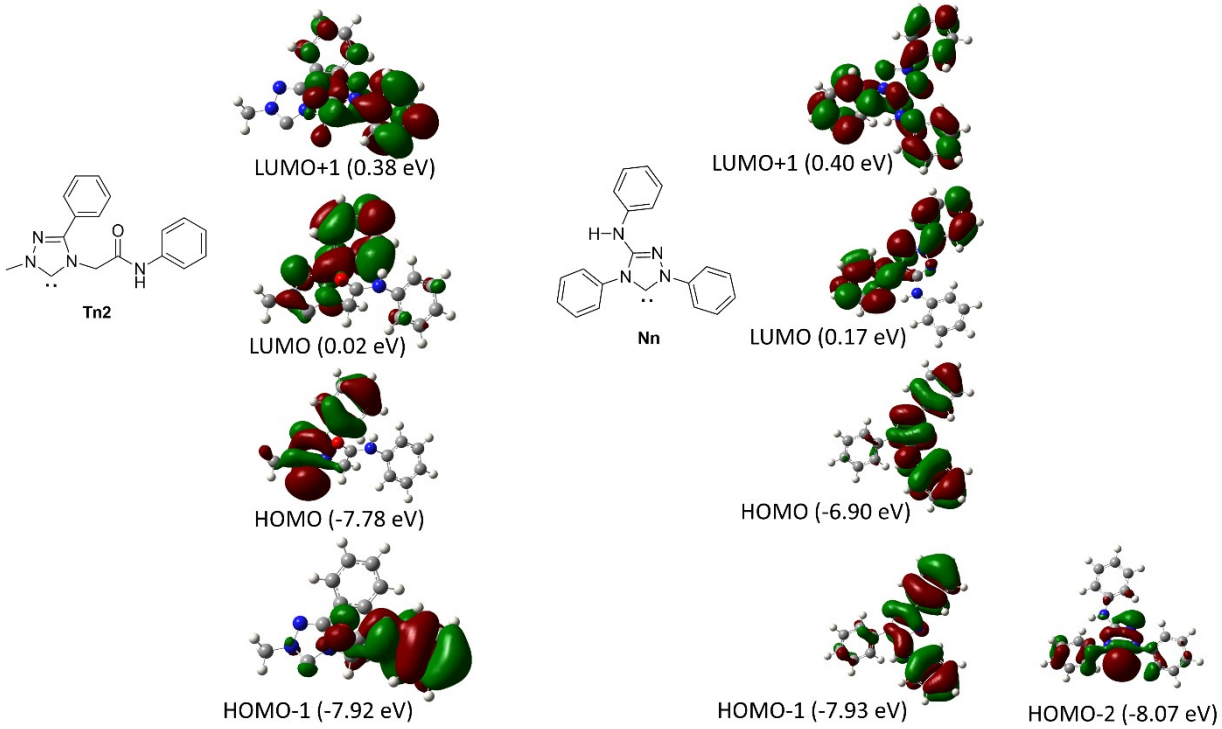


Chart S3. Frontier orbital energies (eV) of free carbenes Im and In1 at M062X/6-31G* level of theory.

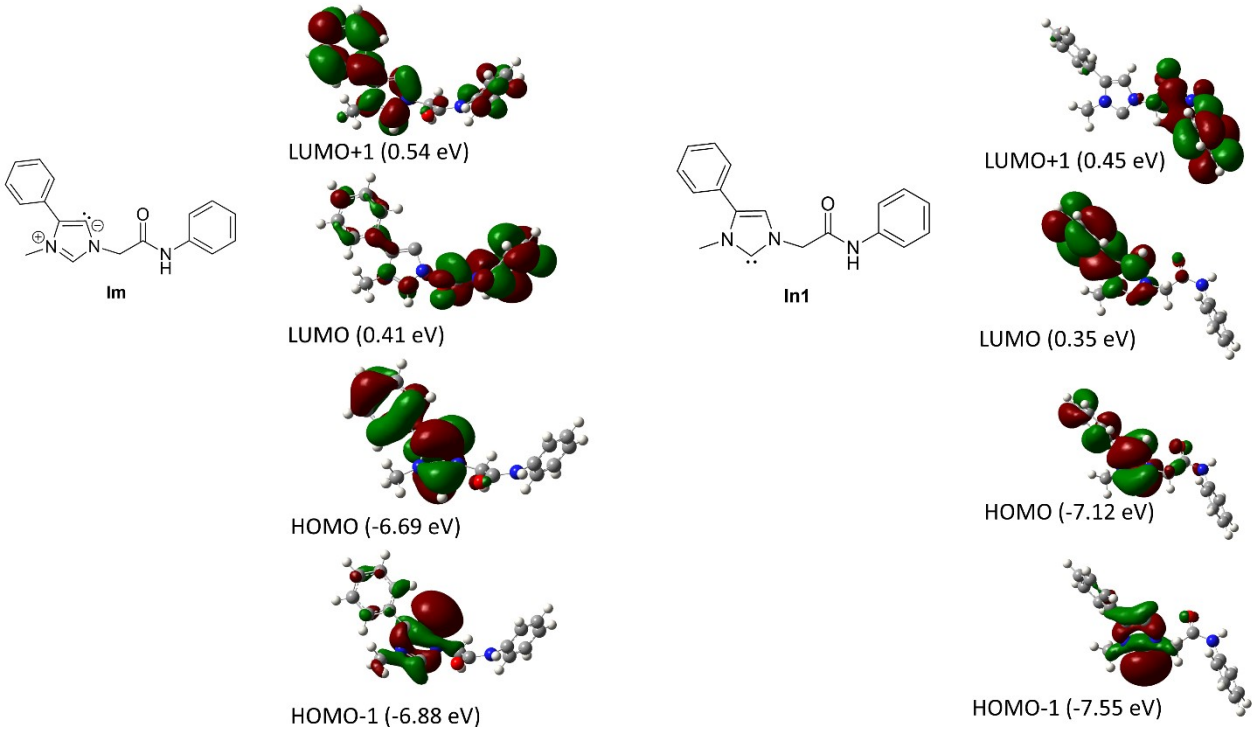
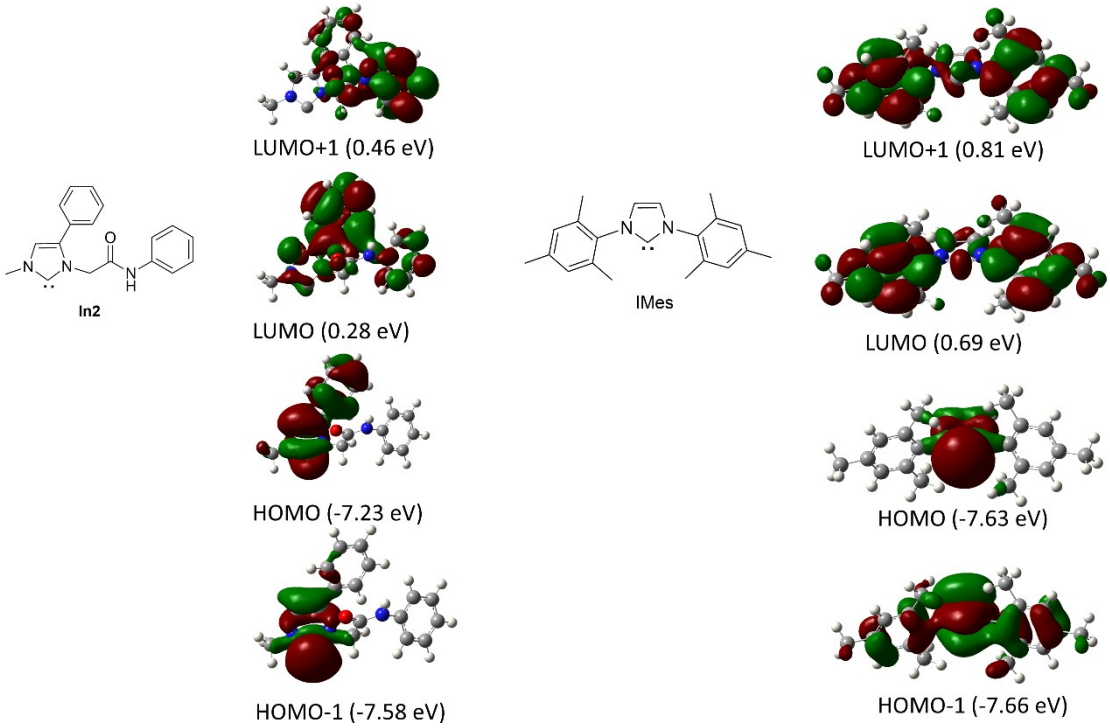


Chart S4. Frontier orbital energies (eV) of free carbenes In2 and IMes at M062X/6-31G* level of theory.



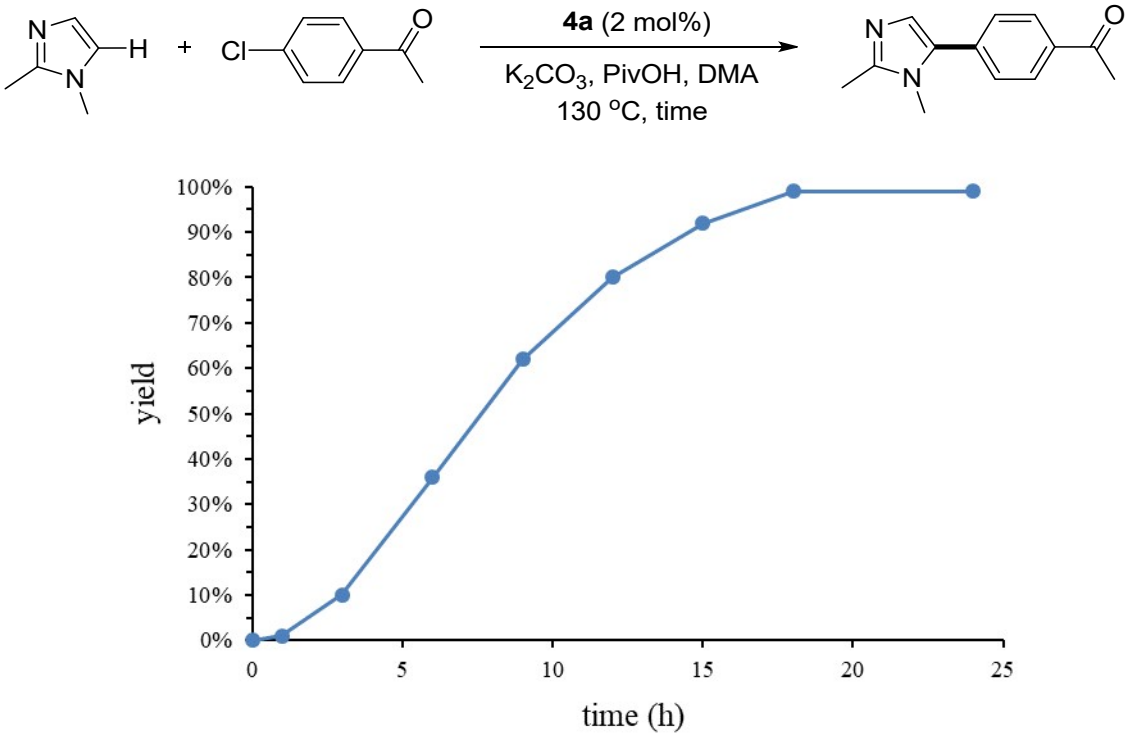


Figure S1. A time-yield curve of the reaction between 4-chloroacetophenone and 1,2-dimethylimidazole catalyzed by complex **4a**. Reaction conditions: 1,2-dimethylimidazole (2 mmol), 4-chloroacetophenone (1 mmol), K_2CO_3 (2 mmol), PivOH (0.3 mmol), DMA (5 mL), **4a** (2 mol%), 130 ºC. GC yield using benzophenone as an internal standard.

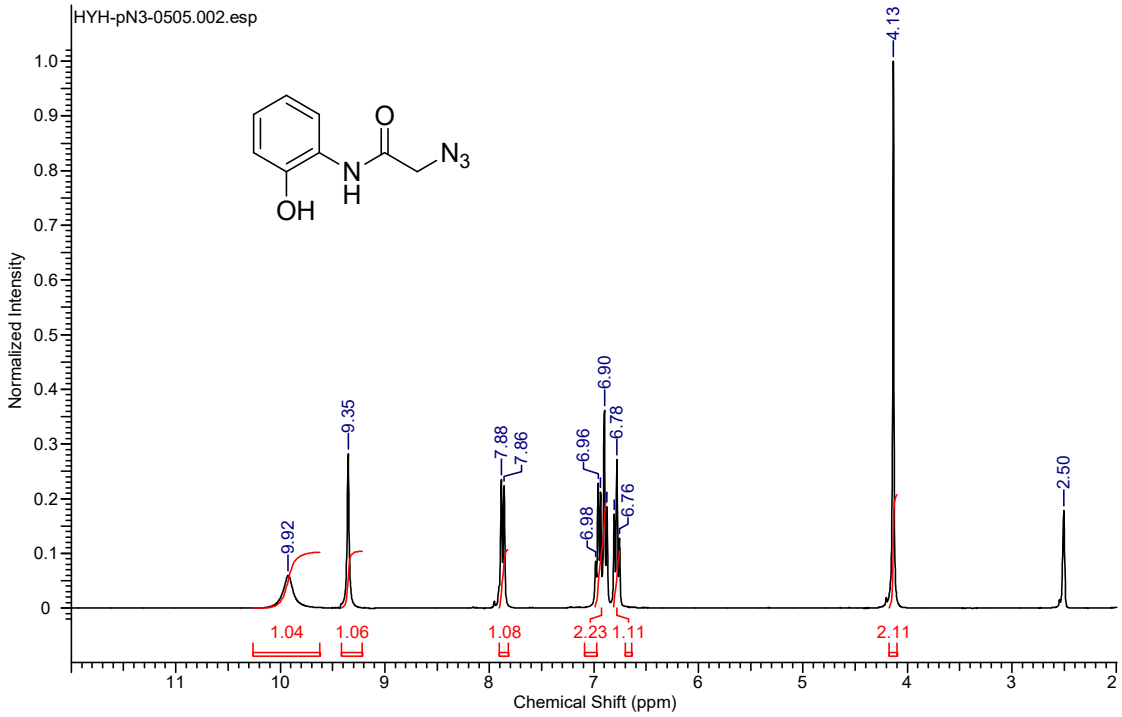


Figure S2. ^{1}H NMR spectrum of 2-azido-*N*-(2-hydroxyphenyl)acetamide

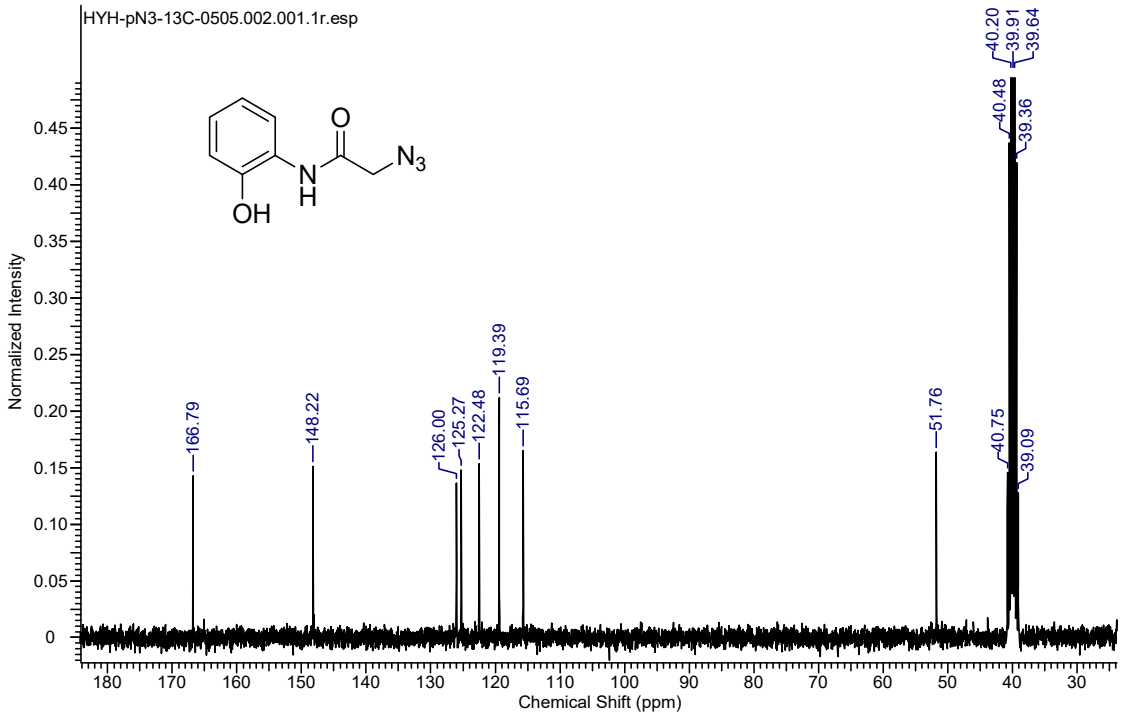


Figure S3. ^{13}C{^{1}H} NMR spectrum of 2-azido-*N*-(2-hydroxyphenyl)acetamide

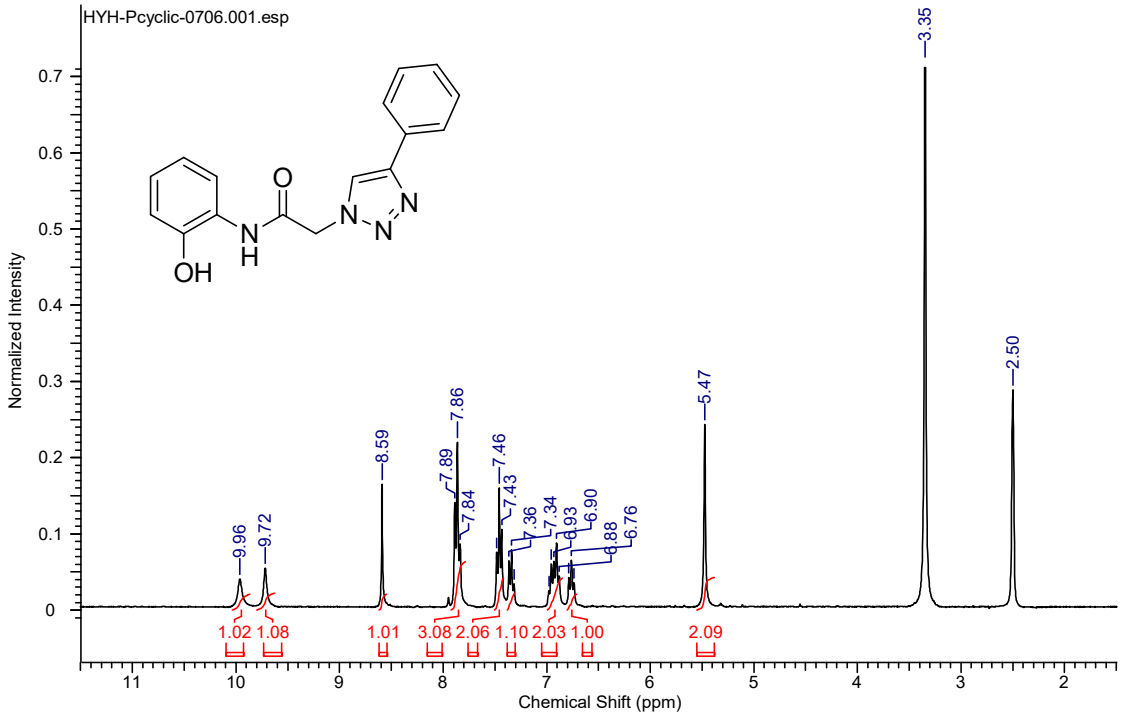


Figure S4. ^{1}H NMR spectrum of **7b**

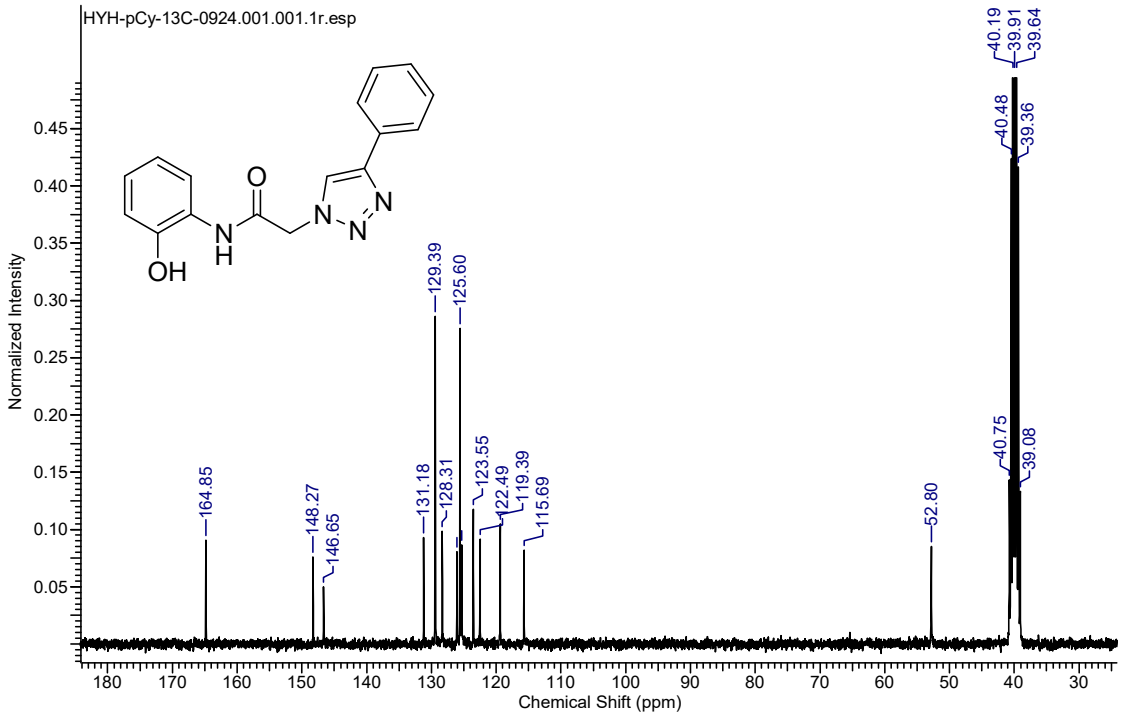


Figure S5. ^{13}C{^{1}H} NMR spectrum of **7b**

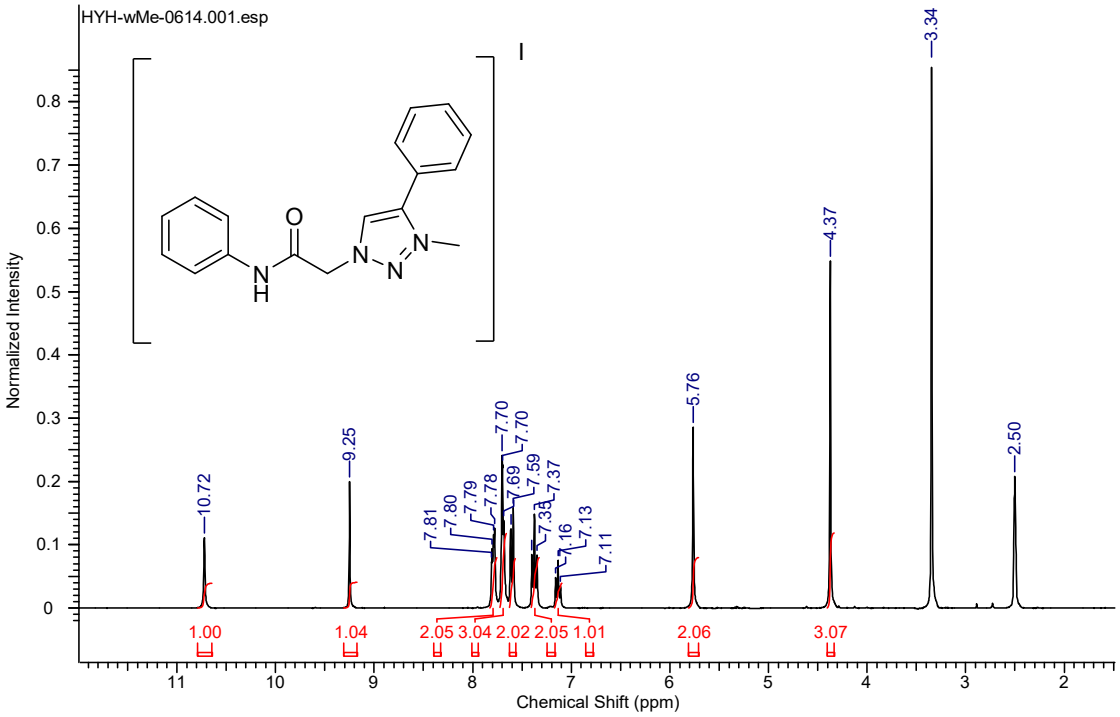


Figure S6. ^{1}H NMR spectrum of **8a**

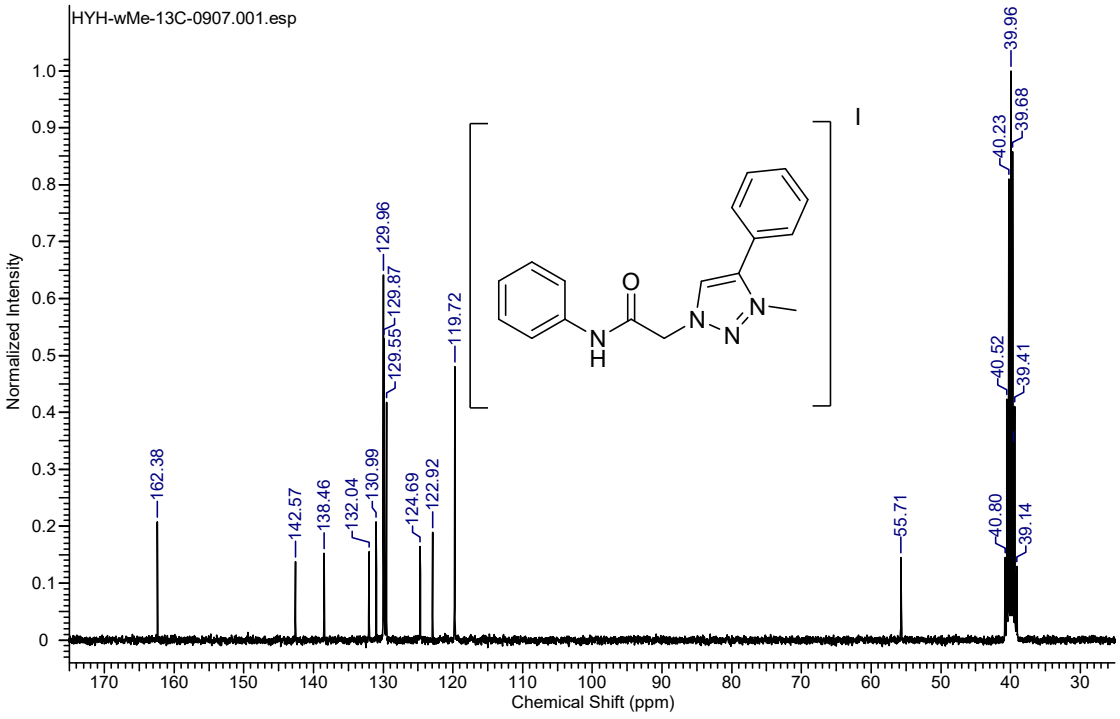


Figure S7. ^{13}C{^{1}H} NMR spectrum of **8a**

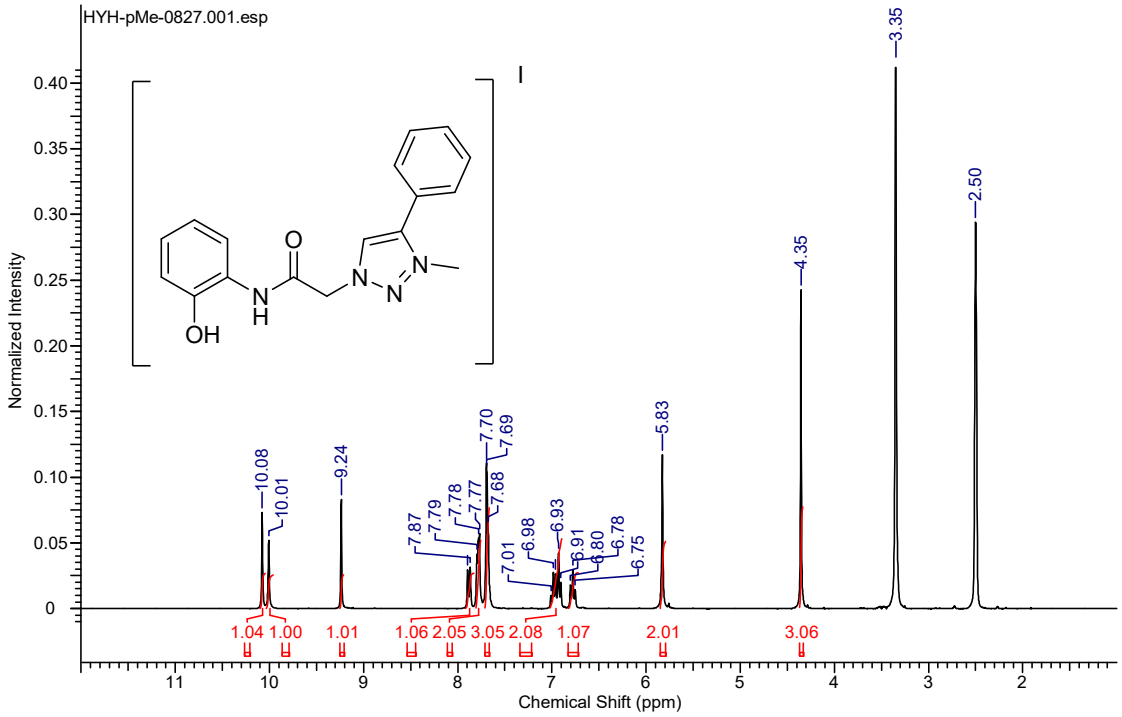


Figure S8. ^{1}H NMR spectrum of **8b**

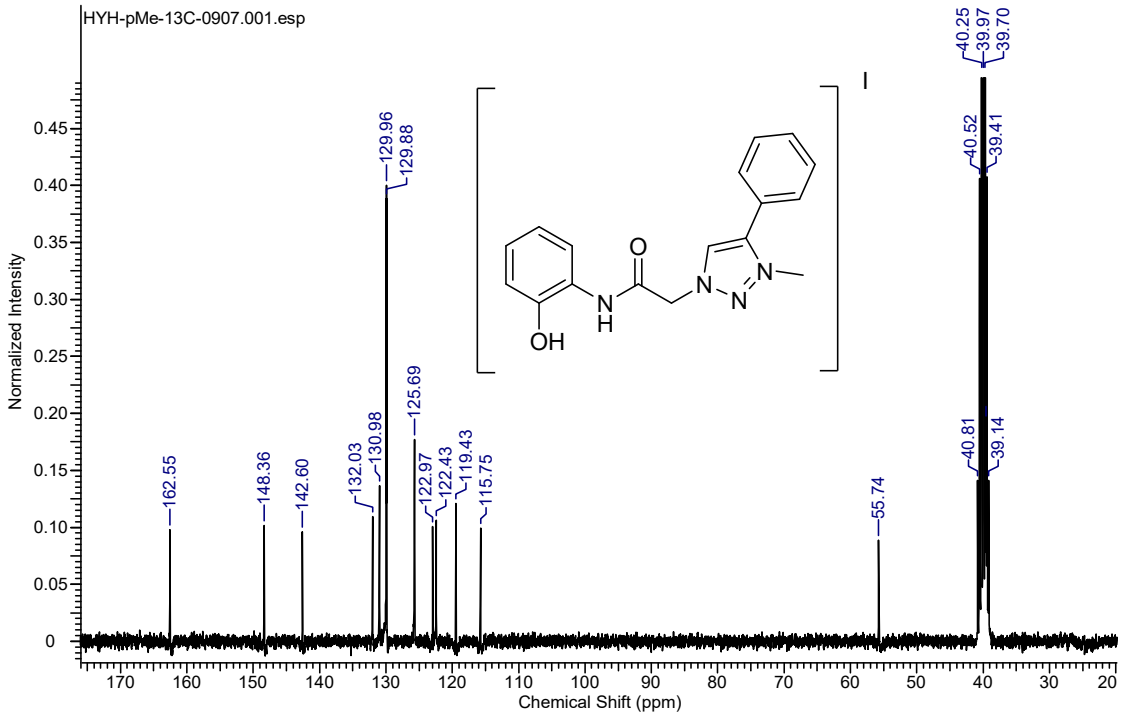


Figure S9. ^{13}C{^{1}H} NMR spectrum of **8b**

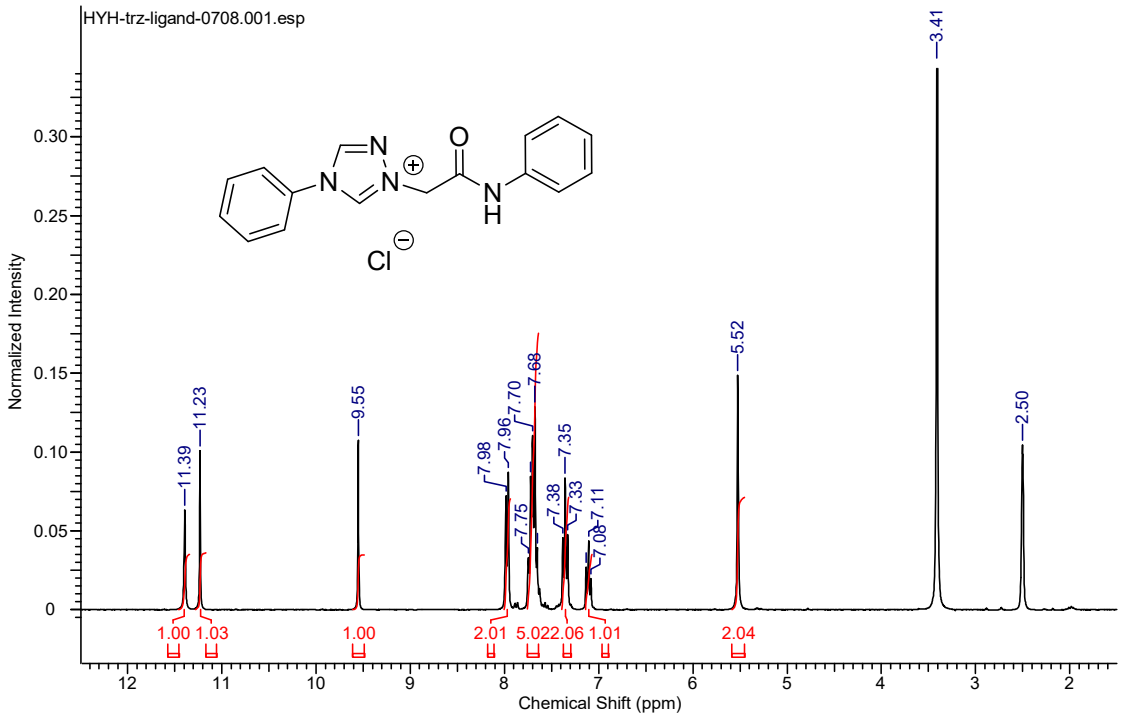


Figure S10. ^{1}H NMR spectrum of **9**

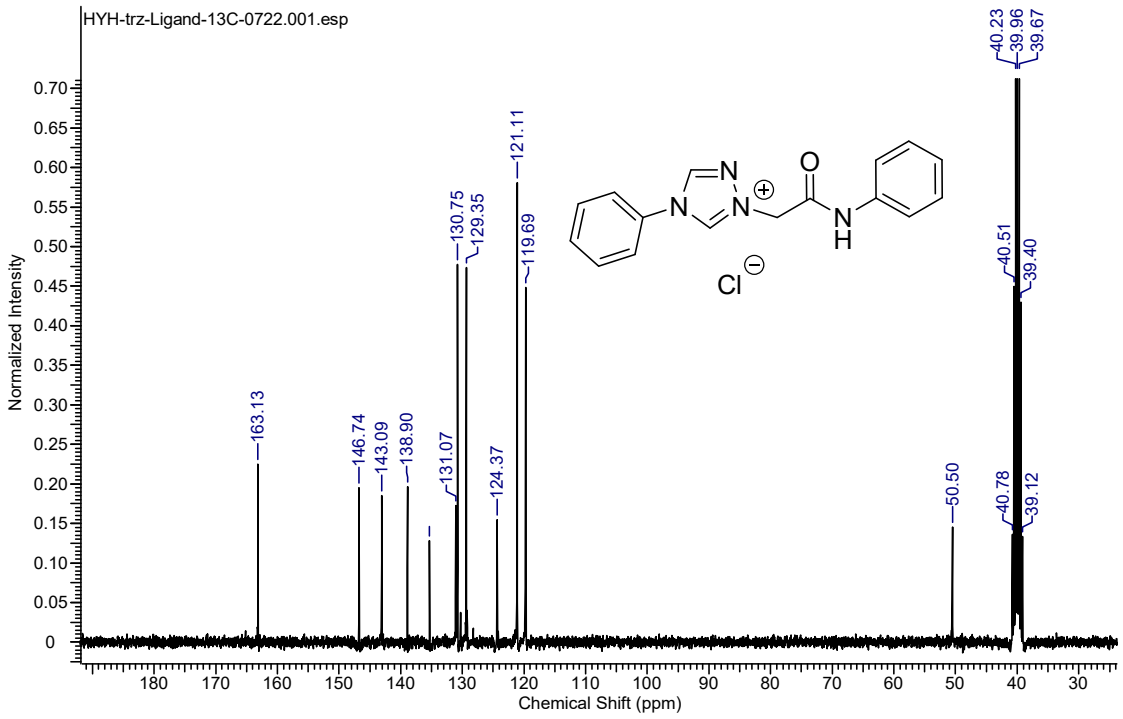


Figure S11. ^{13}C{^{1}H} NMR spectrum of **9**

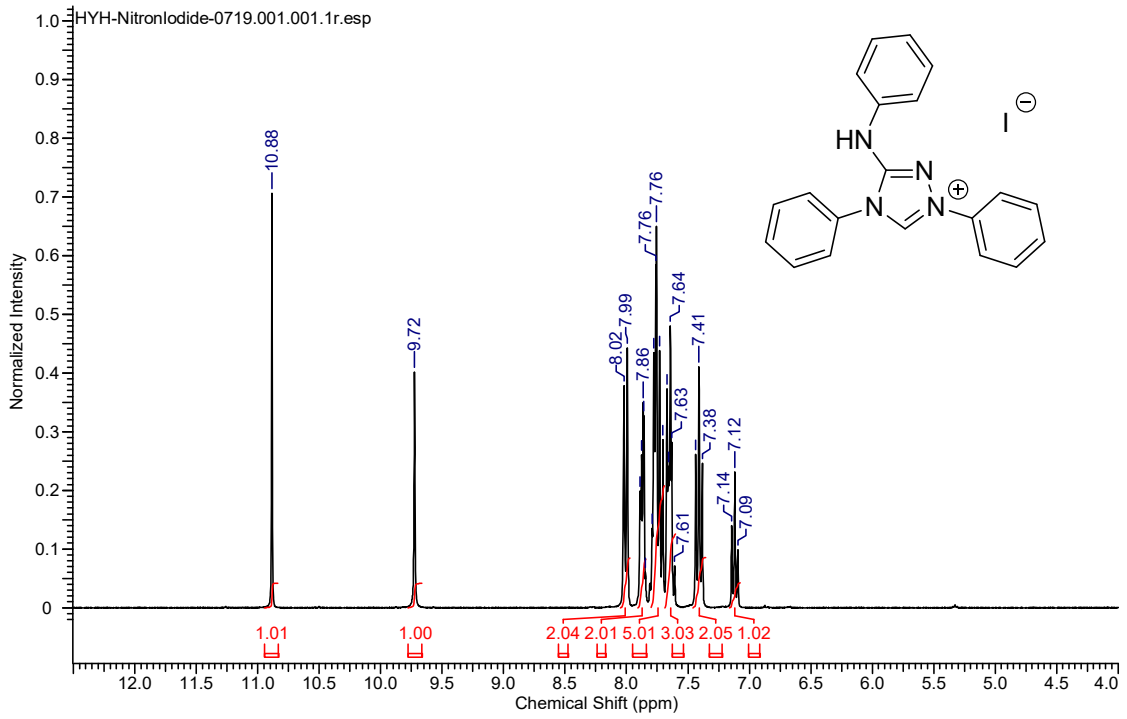


Figure S12. ^{1}H NMR spectrum of 3-Anilino-1,4-diphenyl-4*H*-1,2,4-triazol-1-ium iodide

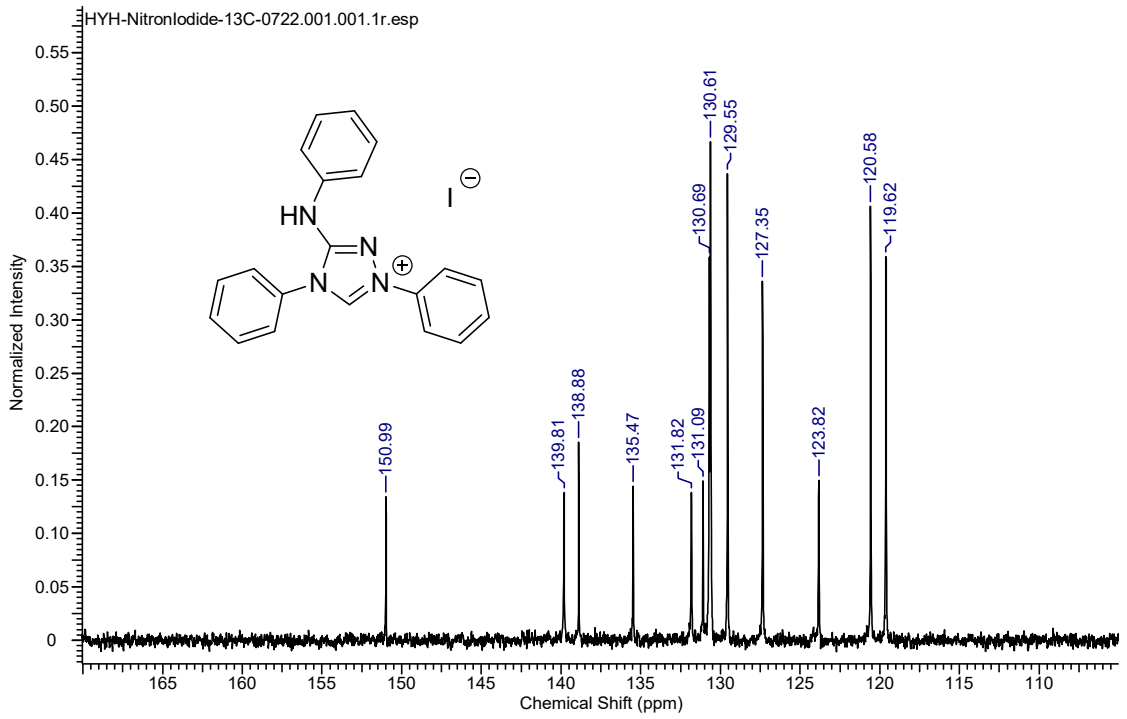


Figure S13. ^{13}C{^{1}H} NMR spectrum of 3-Anilino-1,4-diphenyl-4*H*-1,2,4-triazol-1-ium iodide

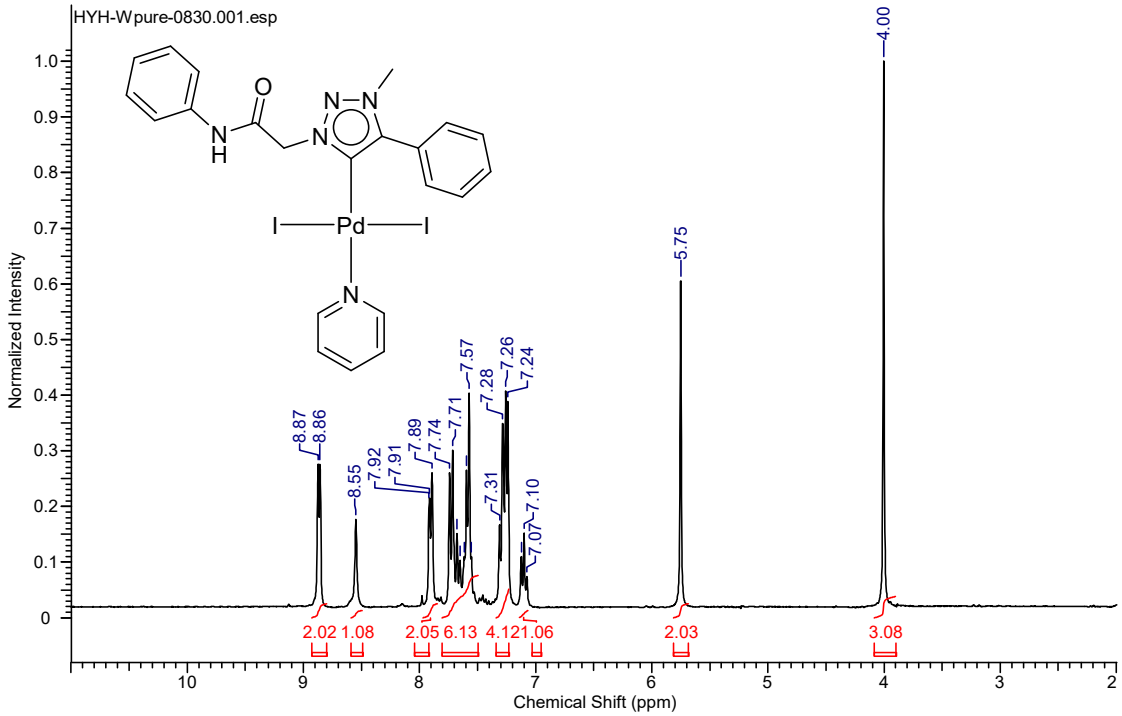


Figure S14. ^{1}H NMR spectrum of **4a**

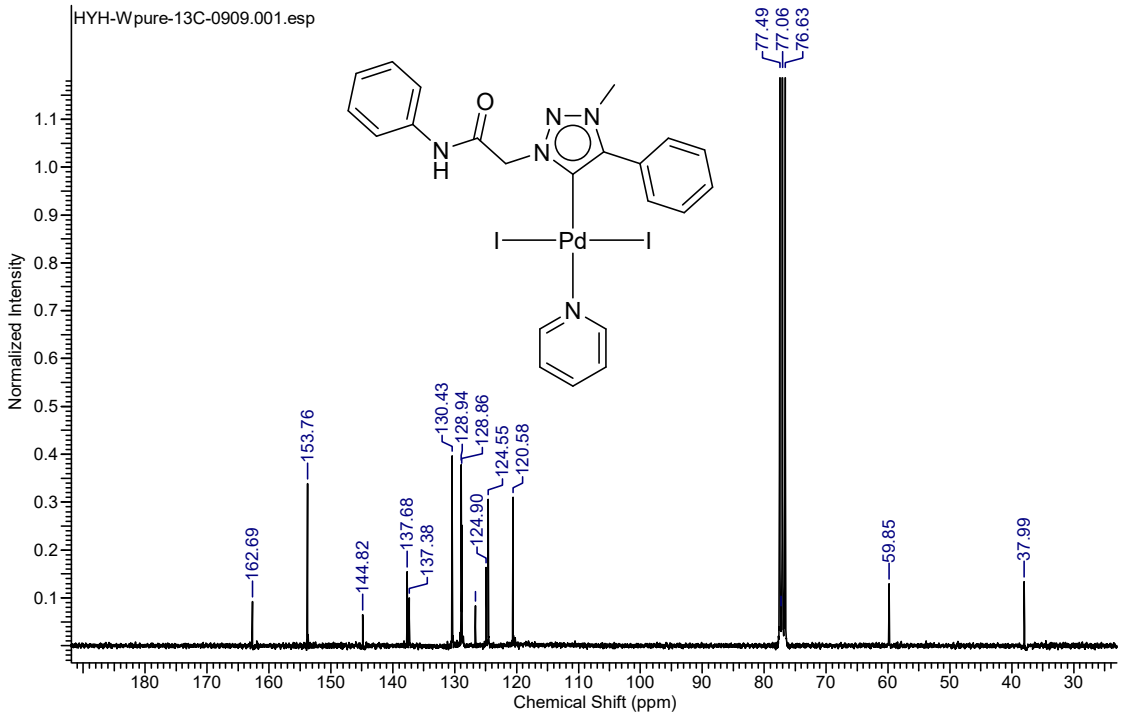


Figure S15. ^{13}C{^{1}H}NMR spectrum of **4a**

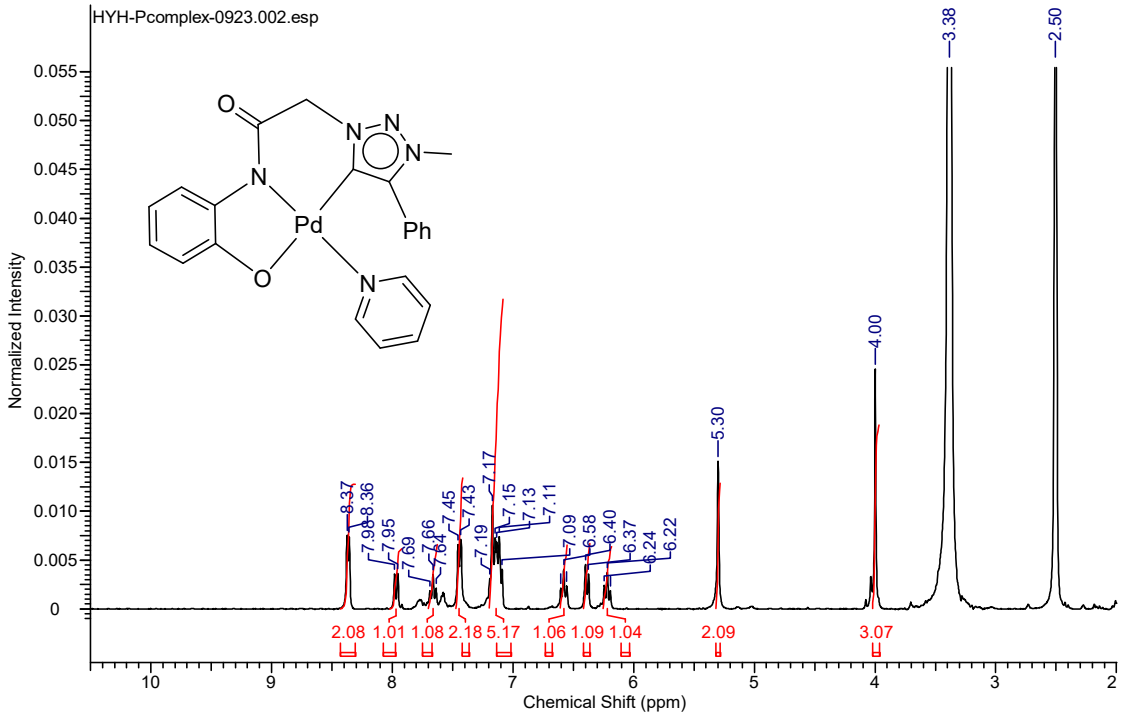


Figure S16. ^{1}H NMR spectrum of **4b**

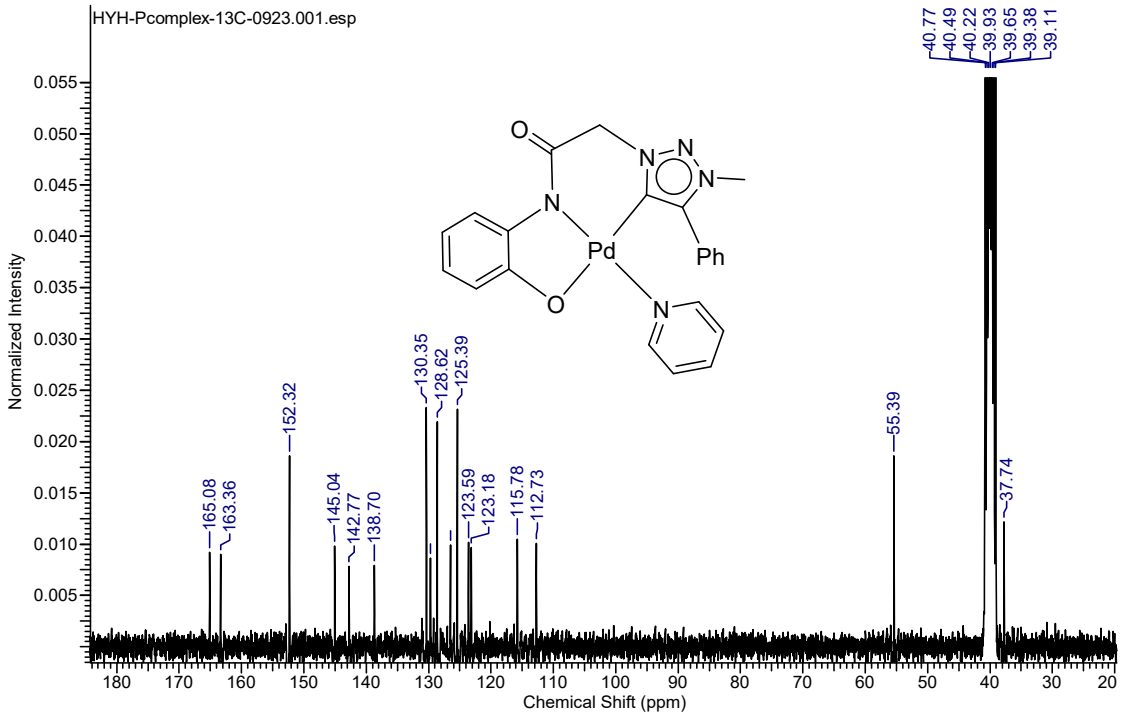


Figure S17. ^{13}C{^{1}H} NMR spectrum of **4b**

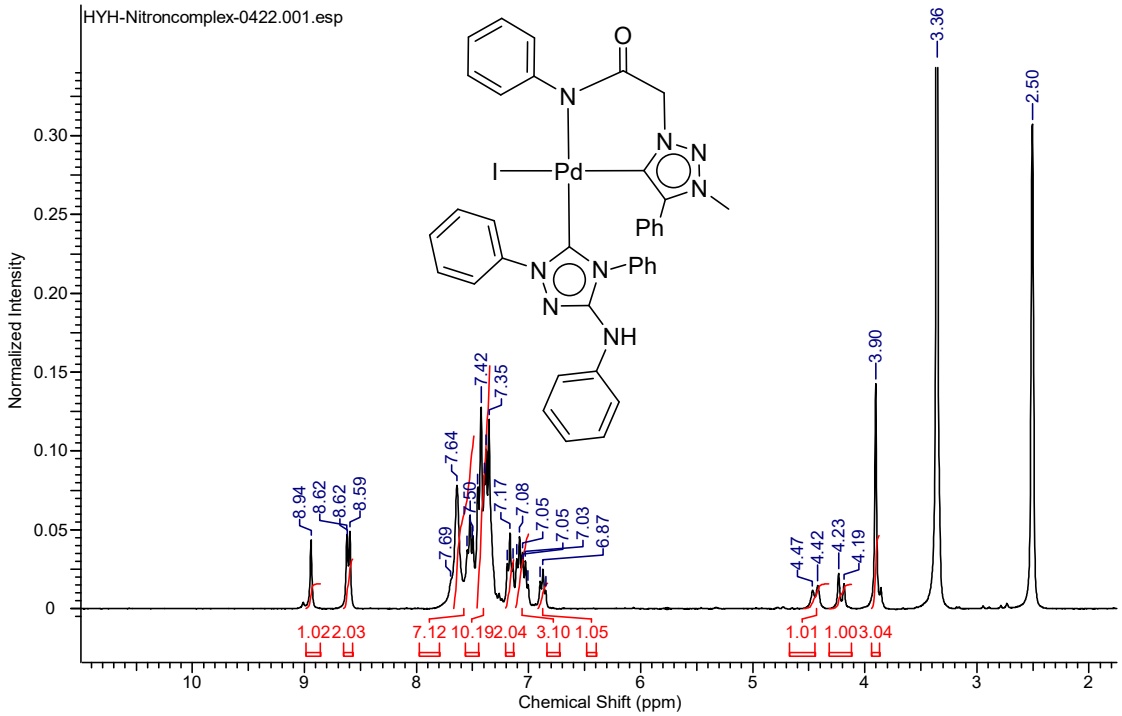


Figure S18. ^{1}H NMR spectrum of **4a'**

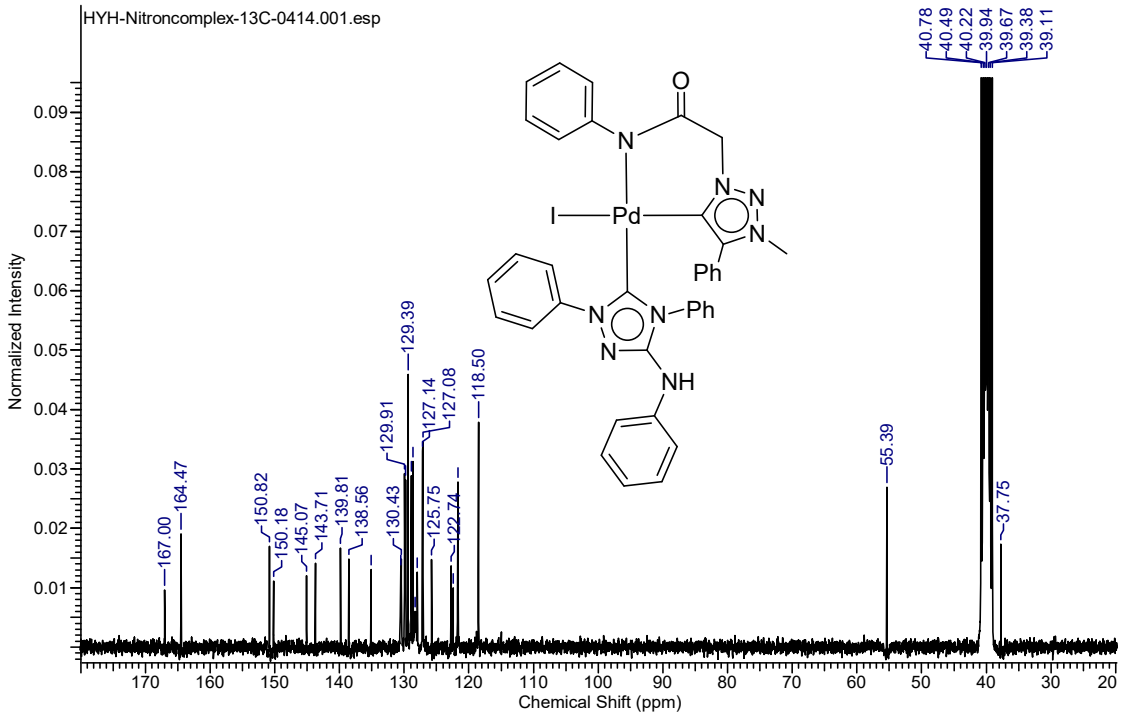


Figure S19. ^{13}C{^{1}H} NMR spectrum of **4a'**

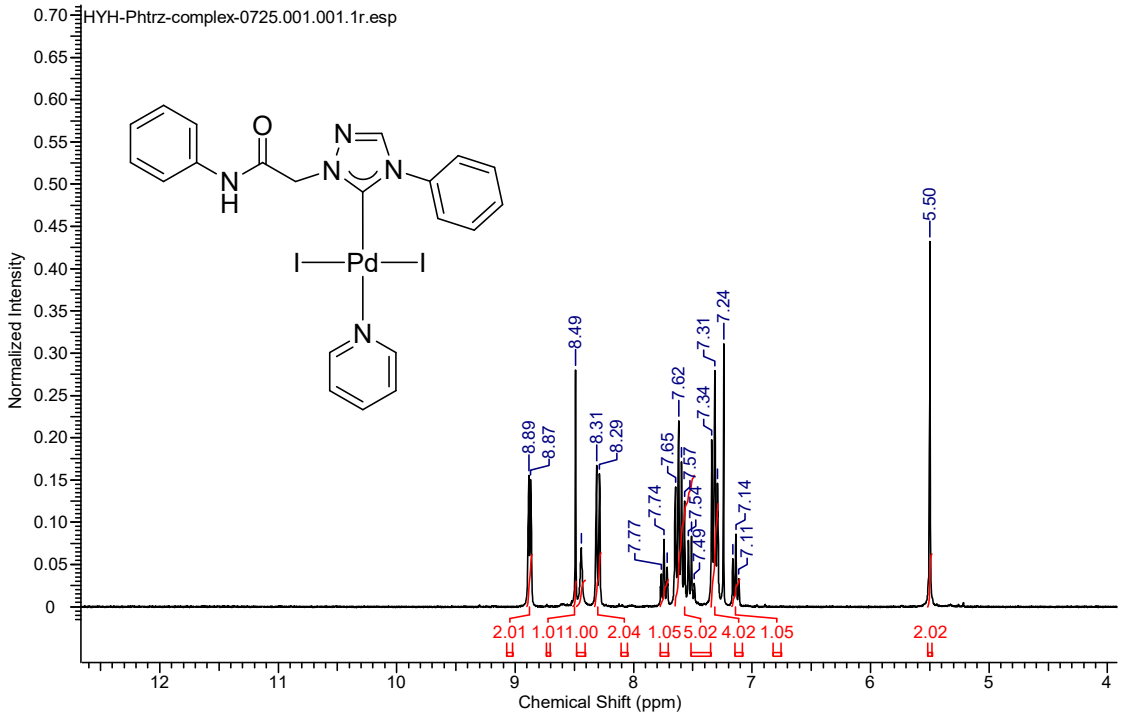


Figure S20. ^{1}H NMR spectrum of **5**

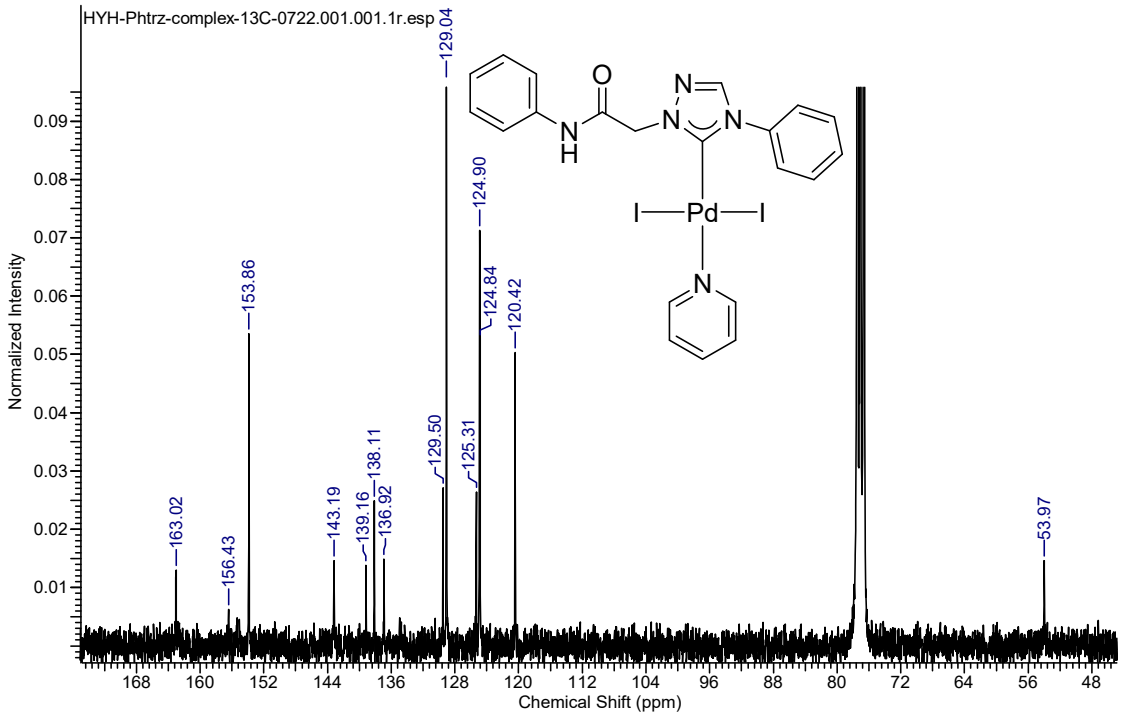


Figure S21. ^{13}C{^{1}H} NMR spectrum of **5**

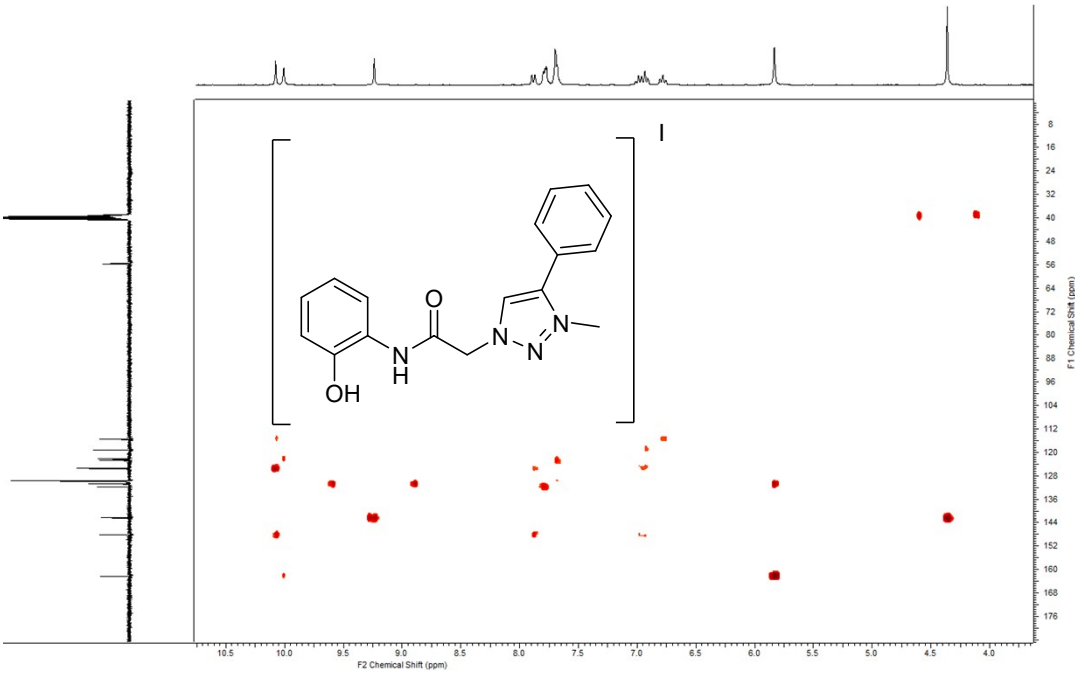


Figure S22. HMBC spectrum of **8b**

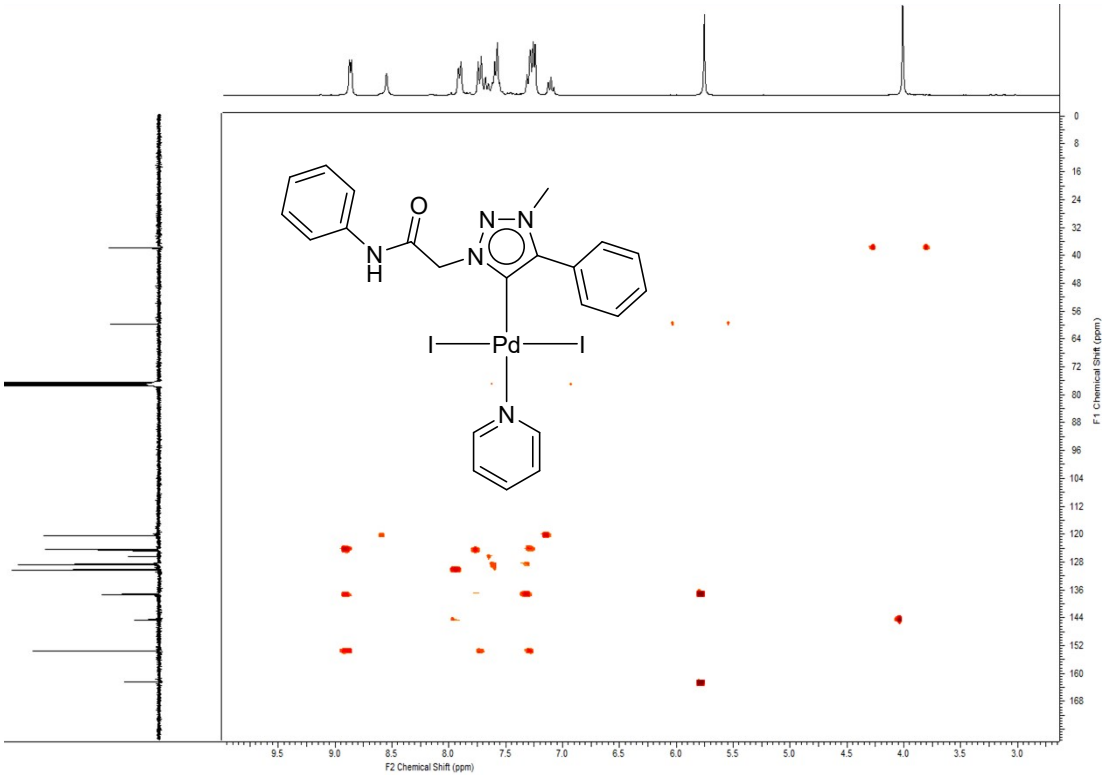


Figure S23. HMBC spectrum of **4a**

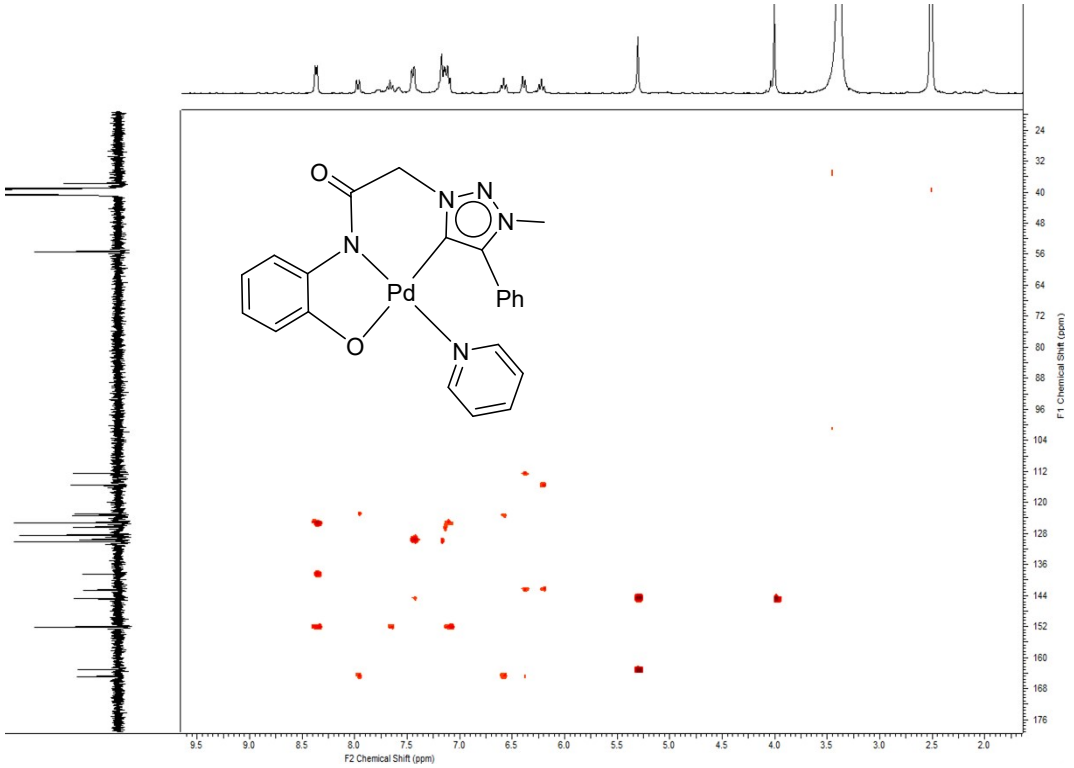


Figure S24. HMBC spectrum of **4b**

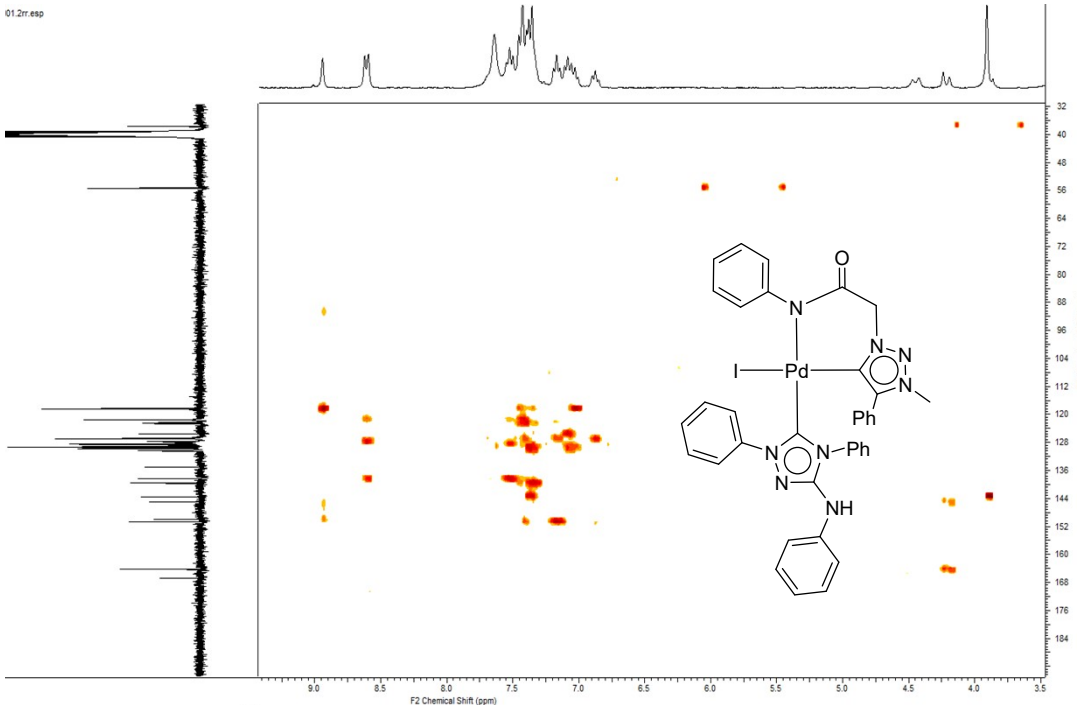


Figure S25. HMBC spectrum of **4a'**

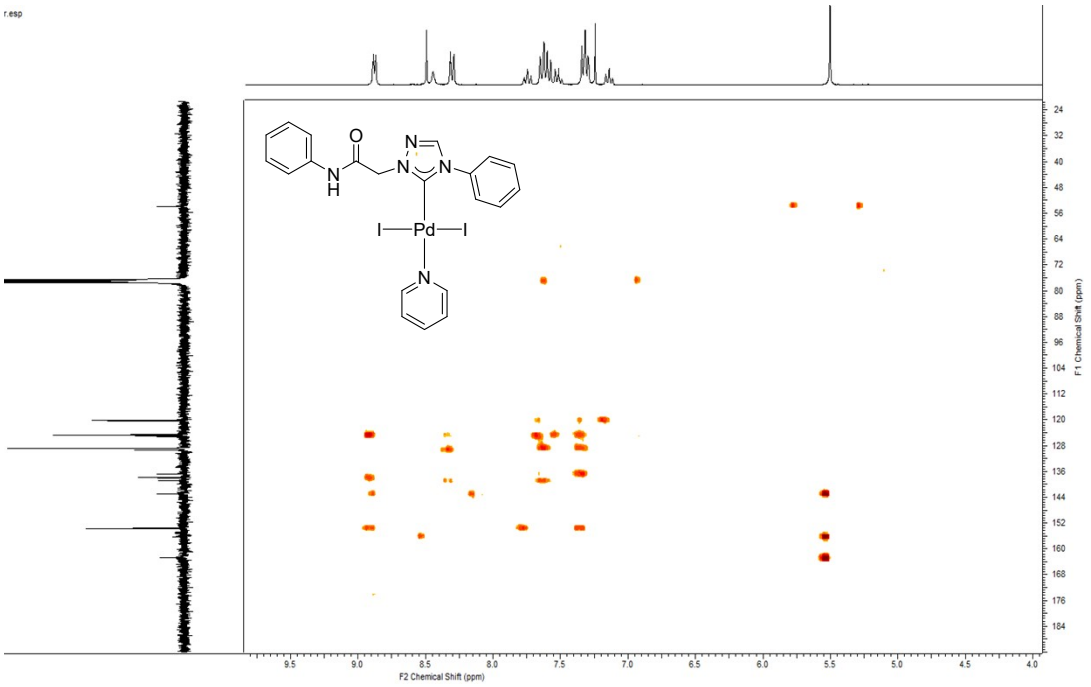


Figure S26. HMBC spectrum of **5**

^{1}H NMR data of catalytic products:

1-(4-(1,2-Dimethyl-1*H*-imidazol-5-yl)phenyl)ethanone (10).[1] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 3.56 (s, 3H, CH_3), 7.05 (s, 1H, imi *H*), 7.45 (d, 2H, *J* = 9.0 Hz, Ar *H*), 8.00 (d, 2H, *J* = 9.0 Hz, Ar *H*).

4-(1,2-Dimethyl-1*H*-imidazol-5-yl)benzonitrile (11).[2] Creamy white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 7.03 (s, 1H, imi *H*), 7.44 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.68 (d, 2H, *J* = 9.0 Hz, Ar *H*).

1,2-Dimethyl-5-(4-nitrophenyl)-1*H*-imidazole (12).[2] Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 3.59 (s, 3H, CH_3), 7.09 (s, 1H, imi *H*), 7.50 (d, 2H, *J* = 9.0 Hz, Ar *H*), 8.23 (d, 2H, *J* = 6.0 Hz, Ar *H*).

1,2-Dimethyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (13).[2] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H, CH_3), 3.53 (s, 3H, CH_3), 7.02 (s, 1H, imi *H*), 7.44 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.66 (d, 2H, *J* = 6.0 Hz, Ar *H*).

5-(4-Methoxyphenyl)-1,2-dimethyl-1*H*-imidazole (14).[3] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 3.45 (s, 3H, CH_3), 3.81 (s, 3H, CH_3) 6.86 (s, 1H, imi *H*), 6.93 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.24 (d, 2H, *J* = 6.0 Hz, Ar *H*).

1-(4-(1-Methyl-1*H*-imidazol-5-yl)phenyl)ethanone (15).[4] Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 7.13 (s, 1H, imi *H*), 7.42–7.49 (m, 3H, imi *H*, Ar *H*), 7.95 (d, 2H, *J* = 9.0 Hz, Ar *H*).

1-Methyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (16).[5] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (s, 3H, CH_3), 7.15 (s, 1H, imi *H*), 7.49 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.56 (s, 1H, imi *H*), 7.67 (d, 2H, *J* = 6.0 Hz, Ar *H*).

4-(1-Methyl-1*H*-imidazol-5-yl)benzonitrile (17).[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (s, 3H, CH_3), 7.16 (s, 1H, imi *H*), 7.47 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.52 (s, 1H, imi *H*), 7.67 (d, 2H, *J* = 6.0 Hz, Ar *H*).

1-Methyl-5-(4-(nitrophenyl)-1*H*-imidazole (18).[6] Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ

3.74 (s, 3H, CH_3), 7.25 (s, 1H, imi *H*), 7.55–7.58 (m, 3H, imi *H*, Ar *H*), 8.29 (d, 2H, *J* = 9.0 Hz, Ar *H*).

1-(4-(Imidazo[1,2-*a*]pyridin-3-yl)phenyl)ethanone (19).[7] Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 3H, CH_3), 6.86 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.24 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.65–7.78 (m, 4H, Ar *H*, imi *H*), 8.09 (d, 2H, *J* = 9.0 Hz, Ar *H*), 8.39 (d, 1H, *J* = 6.0 Hz, Ar *H*).

4-(Imidazo[1,2-*a*]pyridin-3-yl)benzonitrile (21).[7] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (t, 1H, *J* = 9.0 Hz, A *H*), 7.26 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.66–7.79 (m, 6H, imi *H*, Ar *H*), 8.35 (d, 1H, *J* = 6.0 Hz, Ar *H*).

3-(4-Nitrophenyl)imidazo[1,2-*a*]pyridine (22).[7] Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.27 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.68–7.74 (m, 3H, Ar *H*), 7.82 (s, 1H, imi *H*), 8.32–8.40 (m, 3H, Ar *H*).

3-(4-(Trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (23).[7] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.24 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.67–7.77 (m, 6H, imi *H*, Ar *H*), 8.34 (d, 1H, *J* = 6.0 Hz, Ar *H*).

Methyl 4-(imidazo[1,2-*a*]pyridin-3-yl)benzoate (24).[7] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H, CH_3), 6.85 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.22 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.62–7.69 (m, 3H, Ar *H*), 7.76 (s, 1H, imi *H*), 8.16 (d, 2H, *J* = 9.0 Hz, Ar *H*), 8.38 (d, 1H, *J* = 9.0 Hz, Ar *H*).

3-(4-Methoxyphenyl)imidazo[1,2-*a*]pyridine (25).[7] Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H, CH_3), 6.76 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.03 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.15 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.44 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.61–7.65 (m, 2H, Ar *H*, imi *H*), 8.23 (d, 1H, *J* = 6.0 Hz, Ar *H*).

3-(3-Methoxyphenyl)imidazo[1,2-*a*]pyridine (26).[8] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H, CH_3), 6.79 (t, 1H, *J* = 6.0 Hz, Ar *H*), 6.94 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.06–7.20 (m, 3H, Ar *H*) 7.41 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.63–7.68 (m, 2H, Ar *H*, imi *H*), 8.35 (d, 1H, *J* = 9.0 Hz, Ar *H*).

3-(3,4,5-Trimethoxyphenyl)imidazo[1,2-*a*]pyridine (27). Brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 9H, CH_3), 6.67 (s, 2H, Ar *H*), 6.76 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.14 (t, 1H, *J* = 6.0

Hz, Ar *H*), 7.58–7.61 (m, 2H, Ar *H*, imi *H*), 8.26 (d, 1H, J = 9.0 Hz, Ar *H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 56.27 (*C*H_3), 60.95 (*C*H_3), 105.5, 112.7, 118.1, 123.4, 124.4, 124.6 (quaternary *C*), 125.7 (quaternary *C*), 131.9, 138.1 (quaternary *C*), 145.8 (quaternary *C*), 153.8 (quaternary *C*). HRMS (ESI) *m*/*z* calcd for $C_{16}H_{16}N_2O_3$ $[M]^+$ 284.1161, found 284.1166.

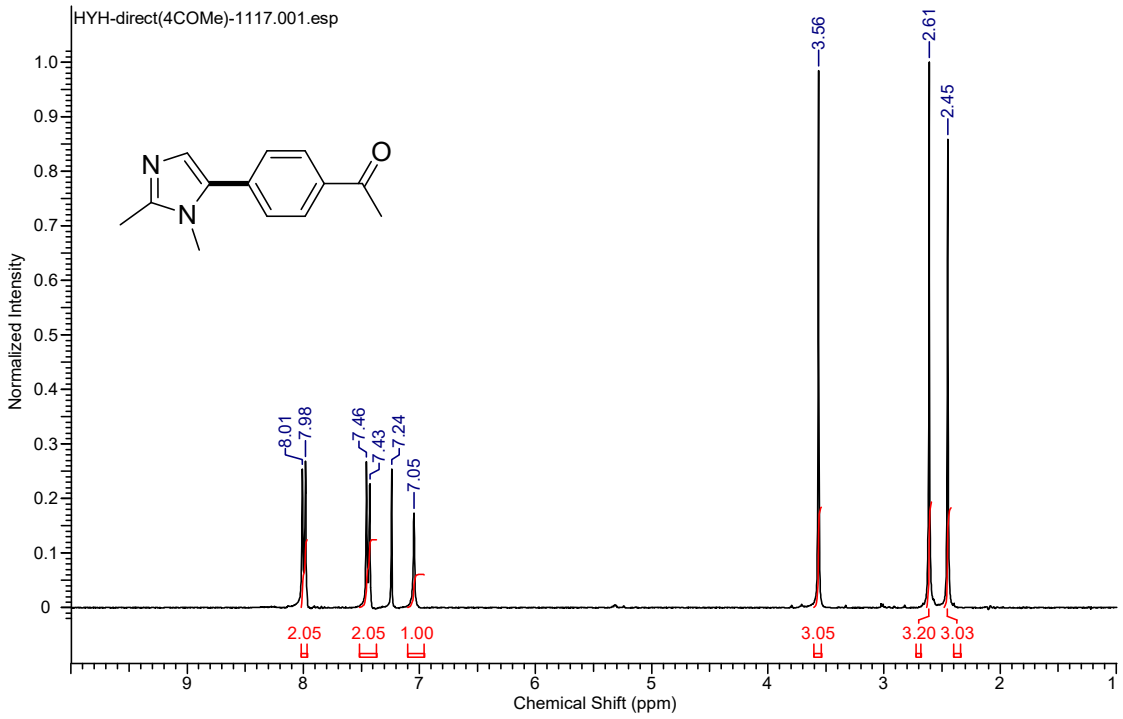


Figure S27. ^{1}H NMR spectrum of 1-(4-(1,2-dimethyl-1*H*-imidazol-5-yl)phenyl)ethanone **(10)**

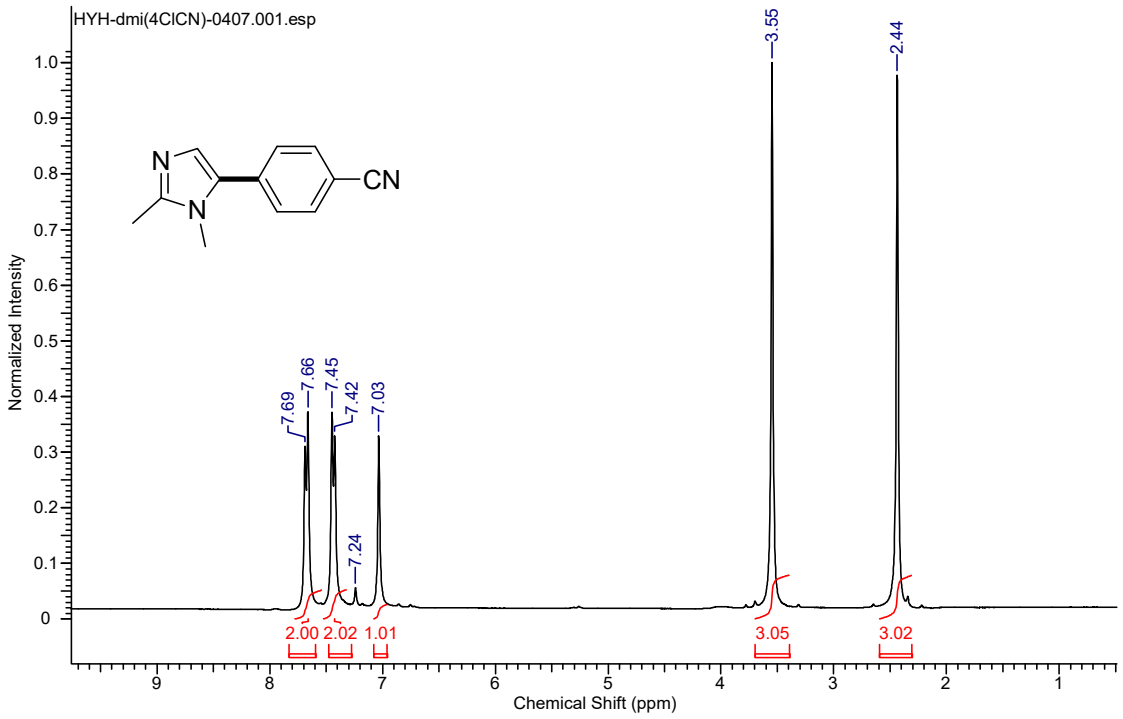


Figure S28. ^{1}H NMR spectrum of 4-(1,2-dimethyl-1*H*-imidazol-5-yl)benzonitrile **(11)**

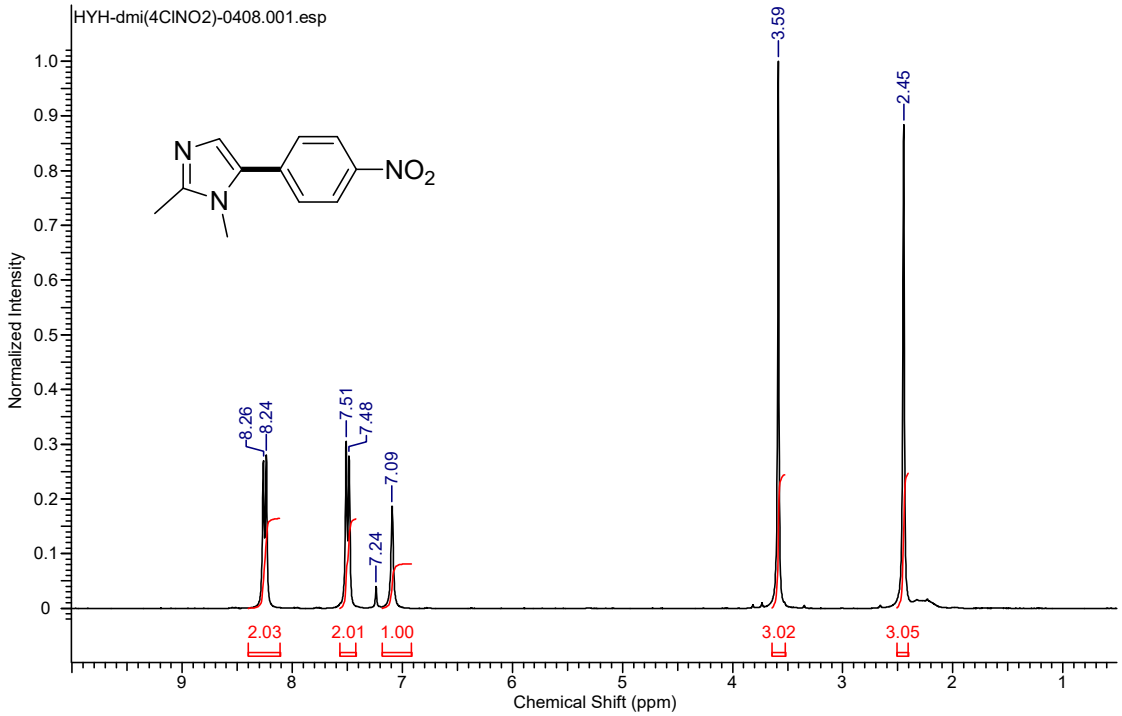


Figure S29. ^{1}H NMR spectrum of 1,2-dimethyl-5-(4-nitrophenyl)-1*H*-imidazole **(12)**

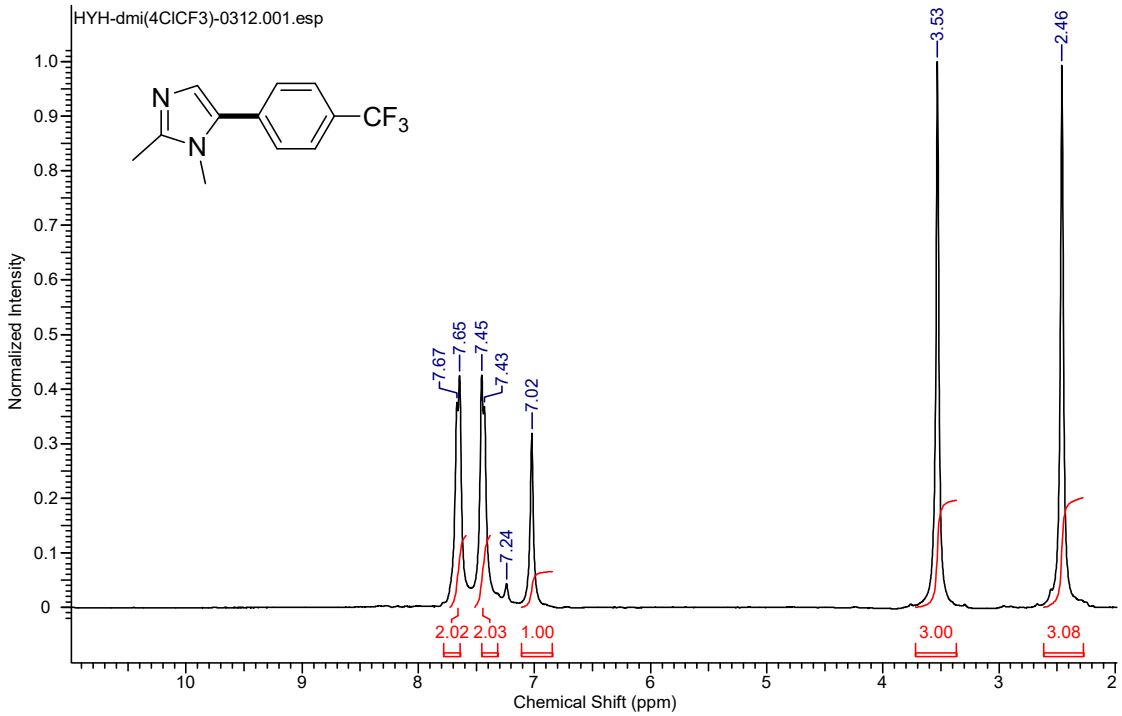


Figure S30. ^{1}H NMR spectrum of 1,2-dimethyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazole **(13)**

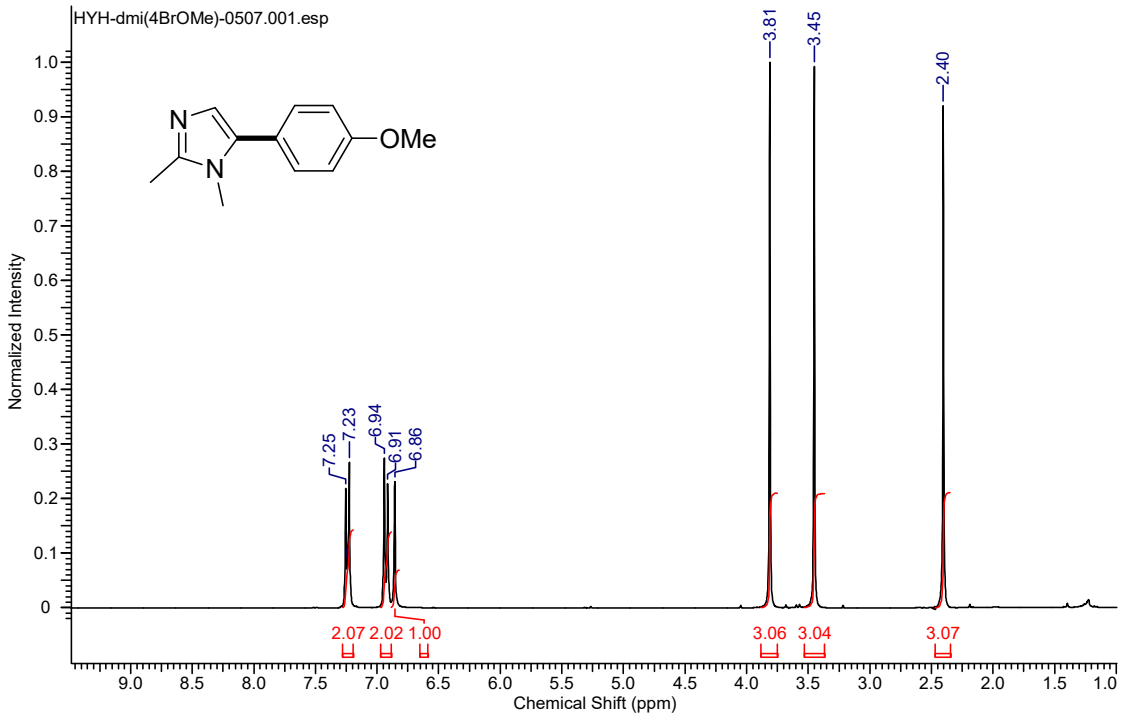


Figure S31. ^{1}H NMR spectrum of 5-(4-methoxyphenyl)-1,2-dimethyl-1*H*-imidazole **(14)**

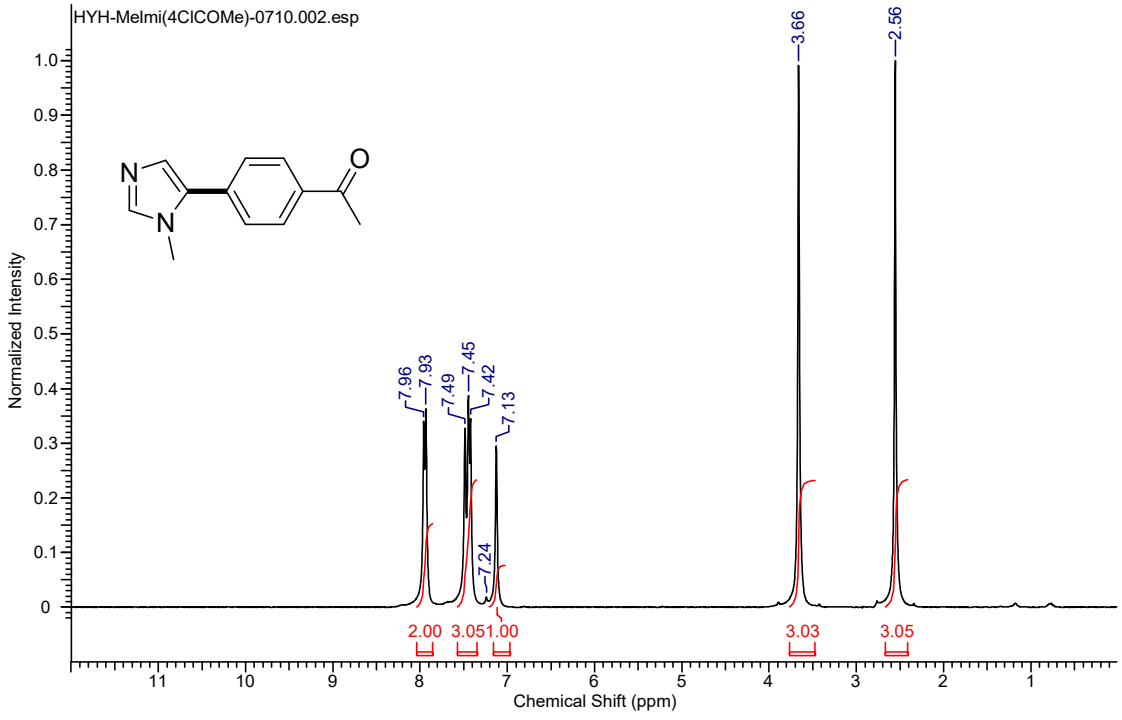


Figure S32. ^{1}H NMR spectrum of 1-(4-(1-Methyl-1*H*-imidazol-5-yl)phenyl)ethanone **(15)**

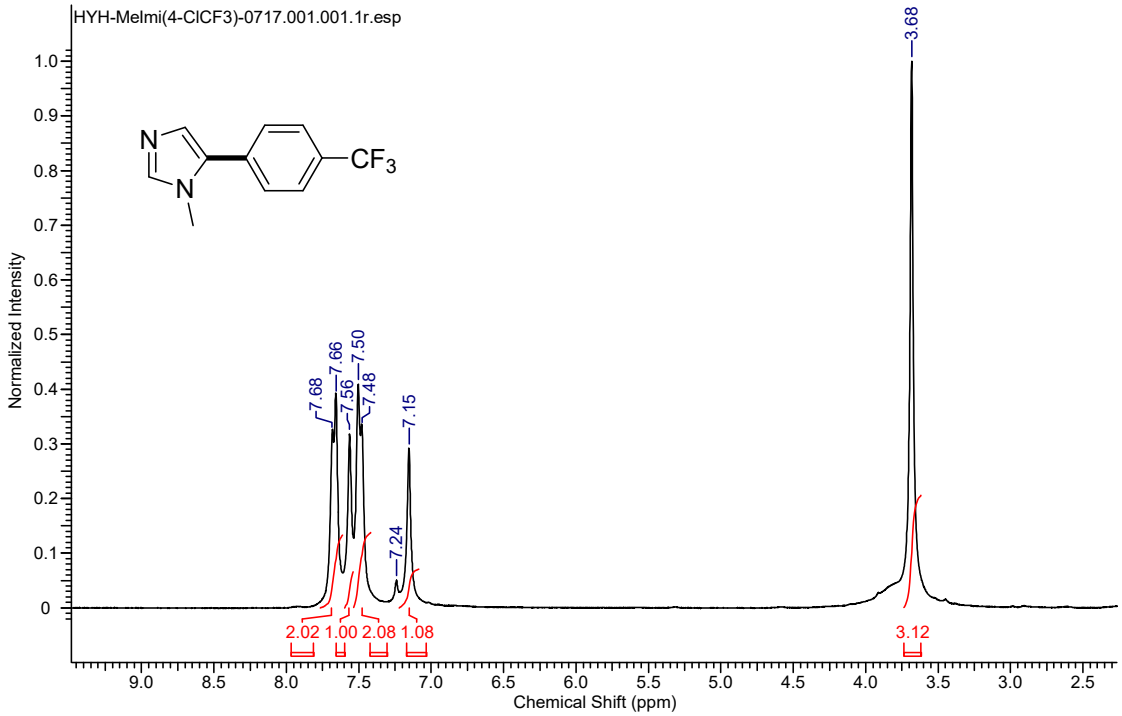


Figure S33. ^{1}H NMR spectrum of 1-methyl-5-(4-(trifluoromethyl)phenyl)-1*H*-imidazole **(16)**

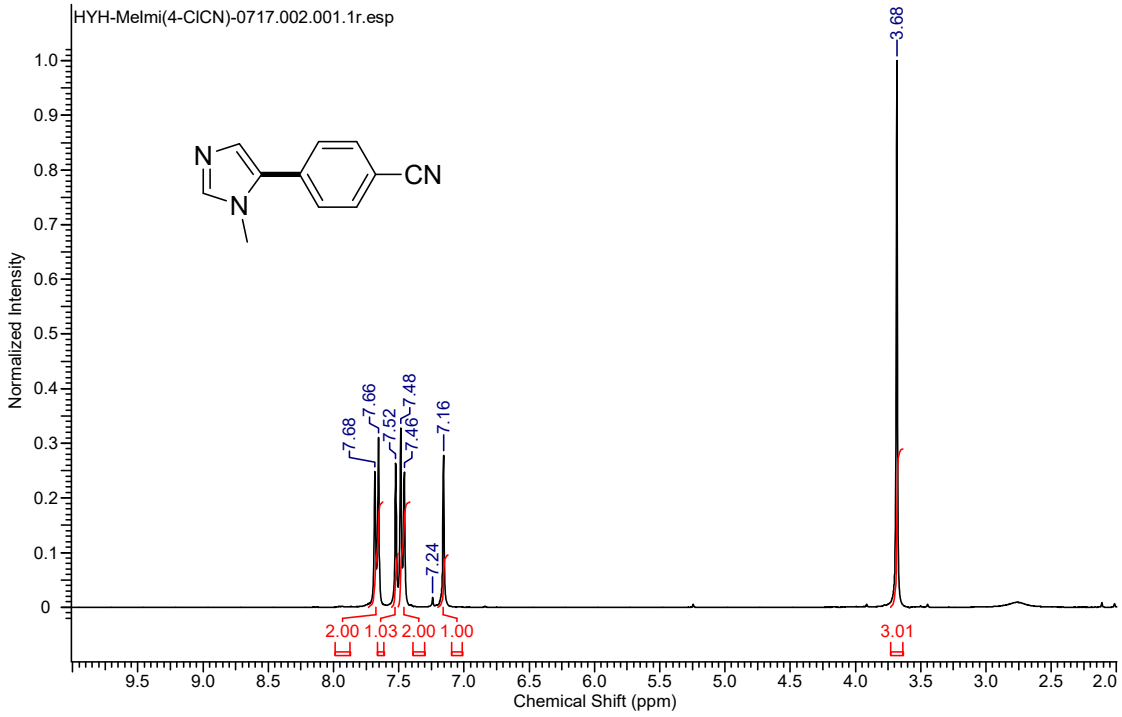


Figure S34. ^{1}H NMR spectrum of 4-(1-methyl-1*H*-imidazol-5-yl)benzonitrile **(17)**

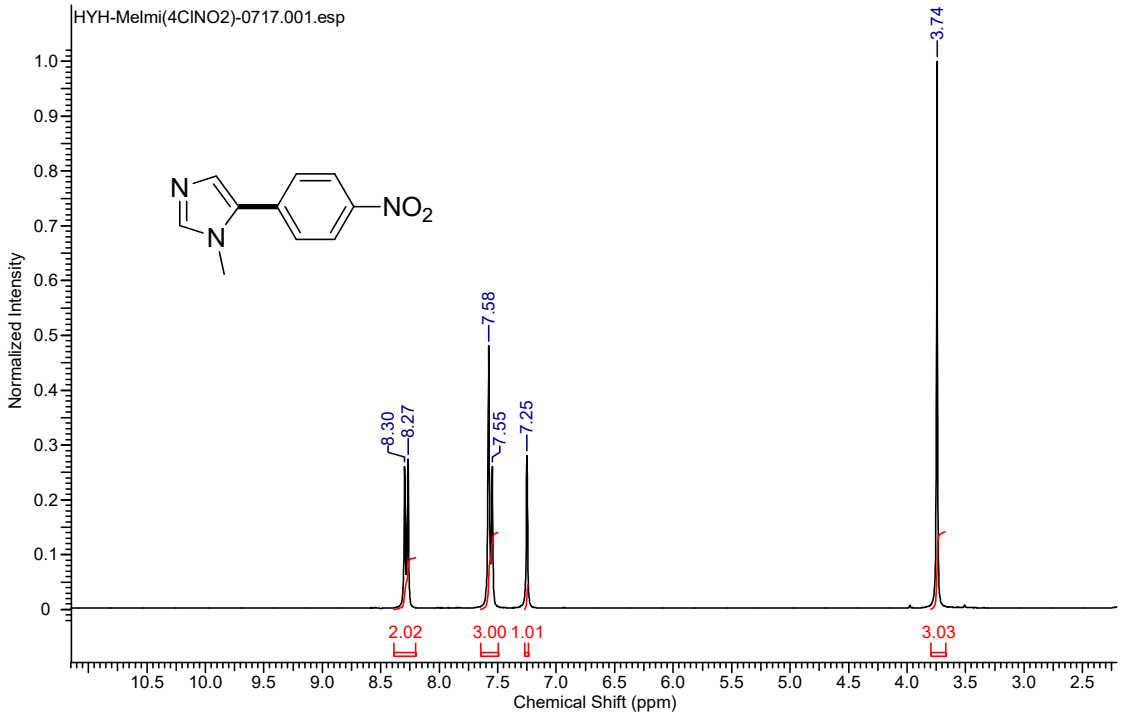


Figure S35. ^{1}H NMR spectrum of 1-methyl-5-(4-(nitrophenyl)-1*H*-imidazole **(18)**

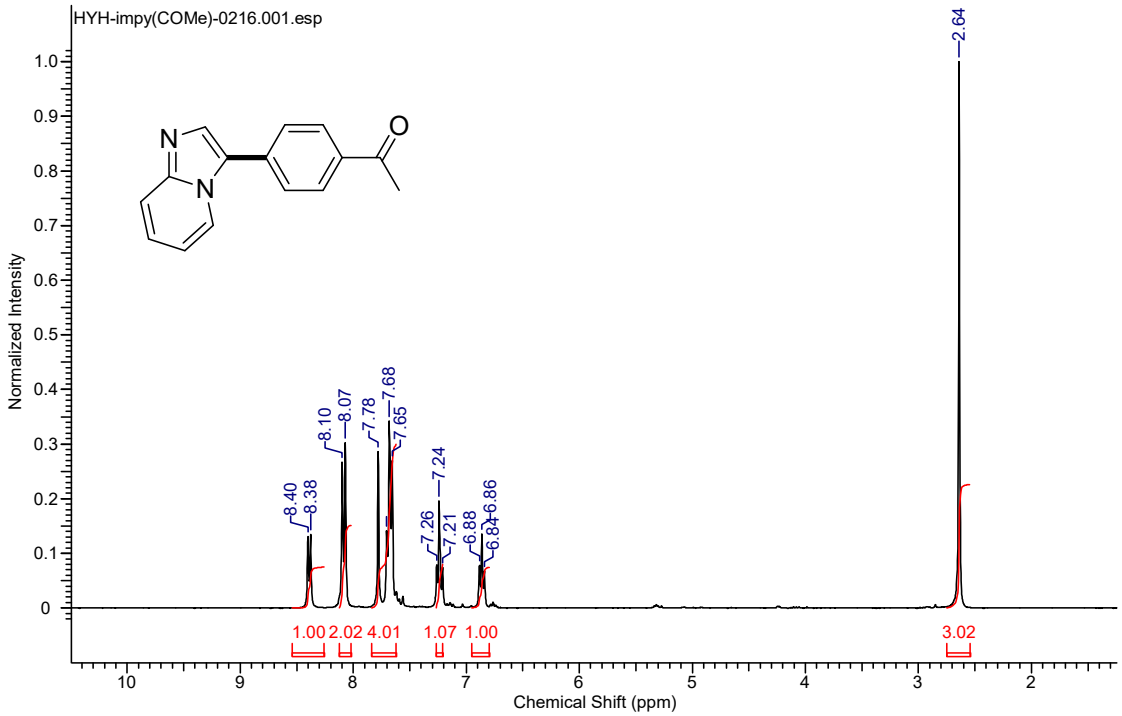


Figure S36. ^{1}H NMR spectrum of 1-(4-(imidazo[1,2-*a*]pyridin-3-yl)phenyl)ethanone **(19)**

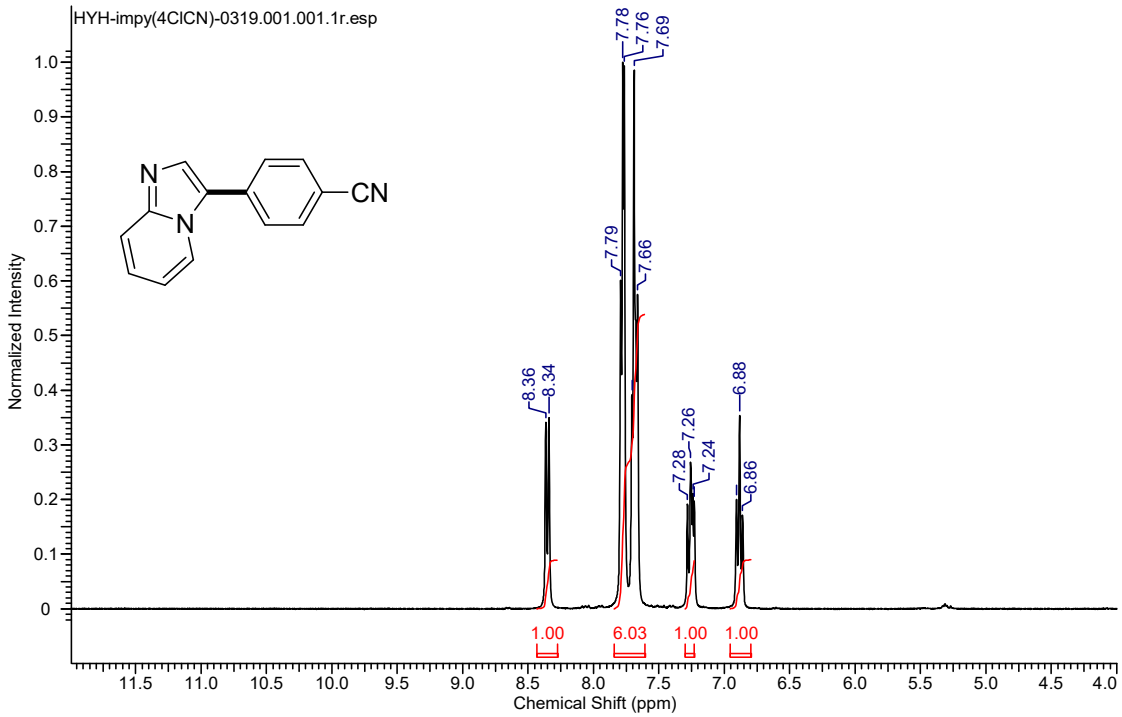


Figure S37. ^{1}H NMR spectrum of 4-(imidazo[1,2-*a*]pyridin-3-yl)benzonitrile **(21)**

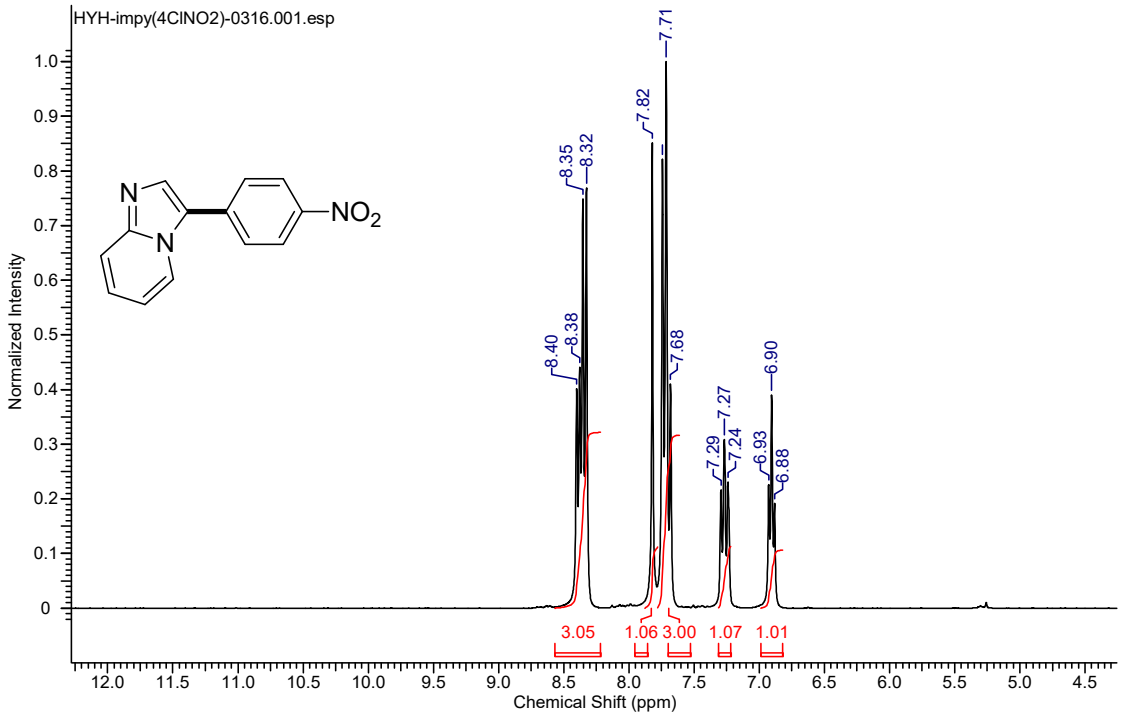


Figure S38. ^{1}H NMR spectrum of 3-(4-nitrophenyl)imidazo[1,2-*a*]pyridine **(22)**

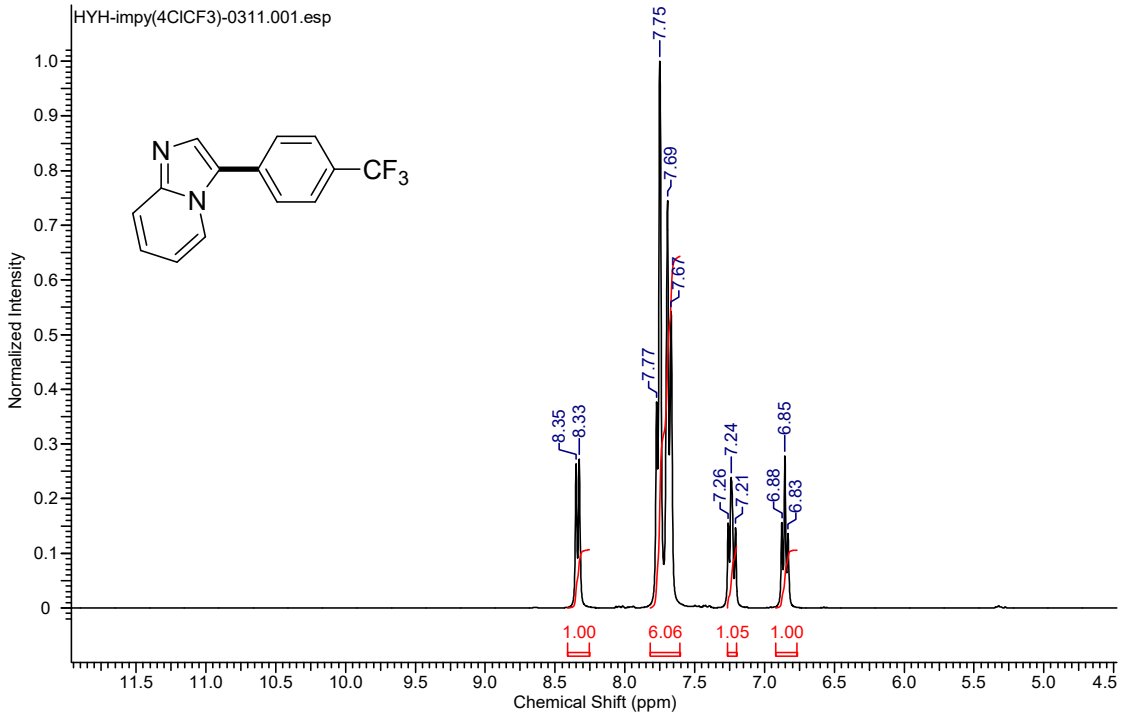


Figure S39. ^{1}H NMR spectrum of 3-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine **(23)**

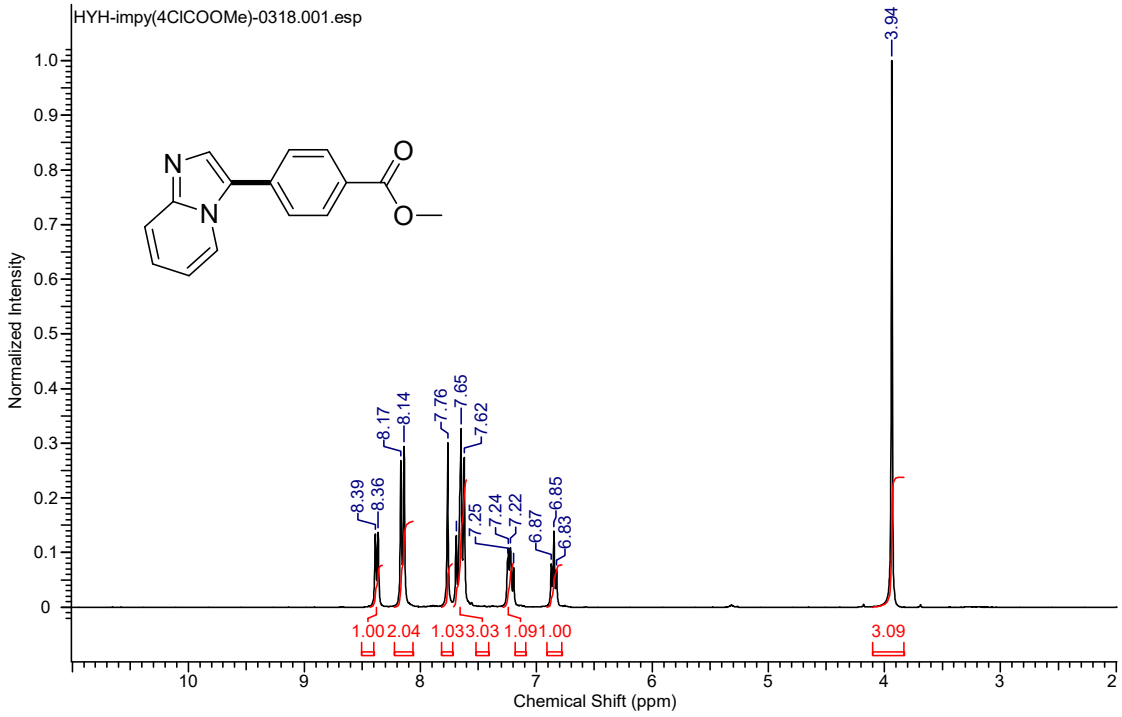


Figure S40. ^{1}H NMR spectrum of methyl 4-(imidazo[1,2-*a*]pyridin-3-yl)benzoate **(24)**

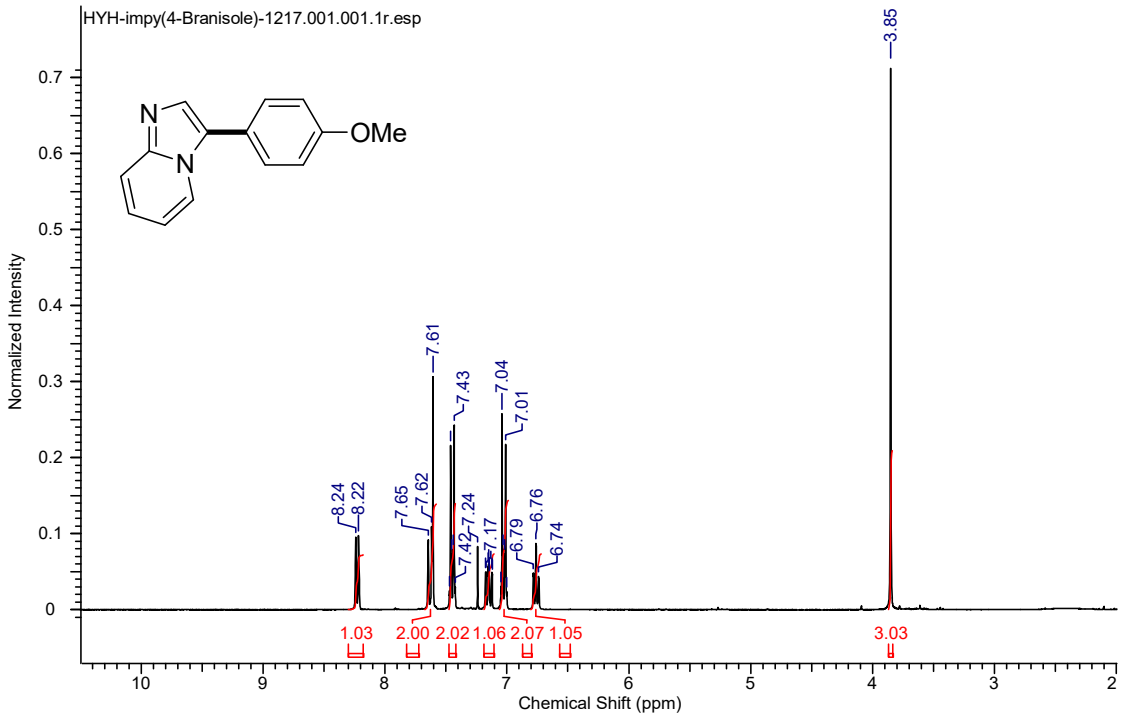


Figure S41. ^{1}H NMR spectrum of 3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine **(25)**

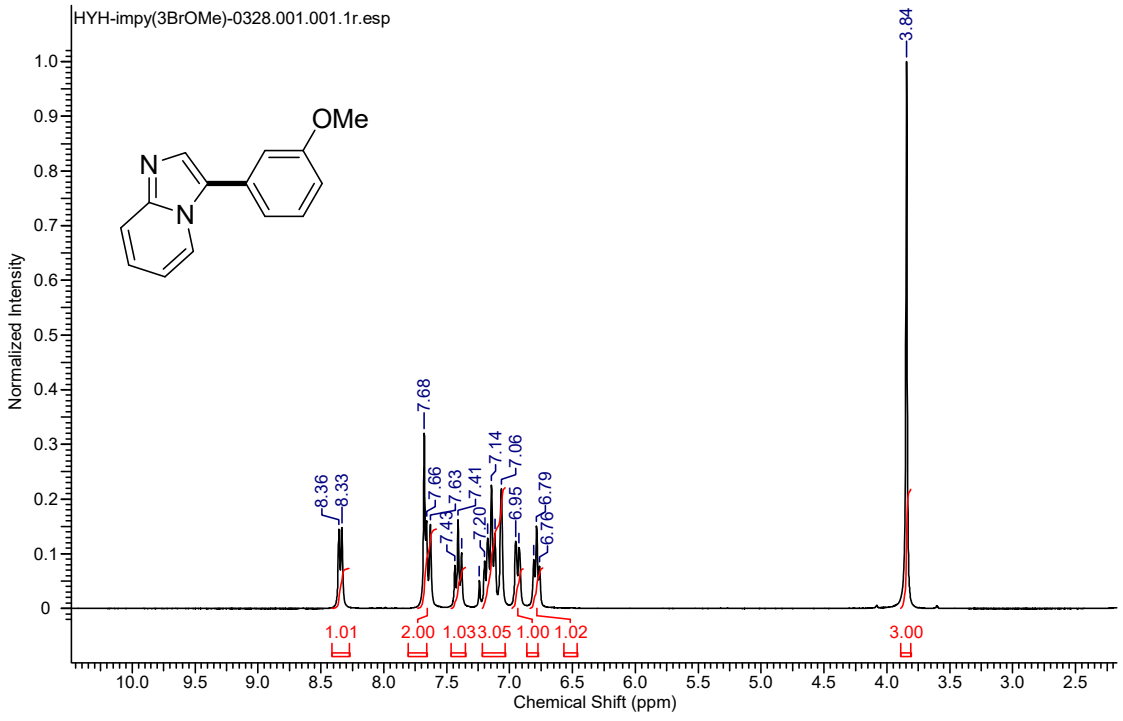


Figure S42. ^{1}H NMR spectrum of 3-(3-methoxyphenyl)imidazo[1,2-*a*]pyridine **(26)**

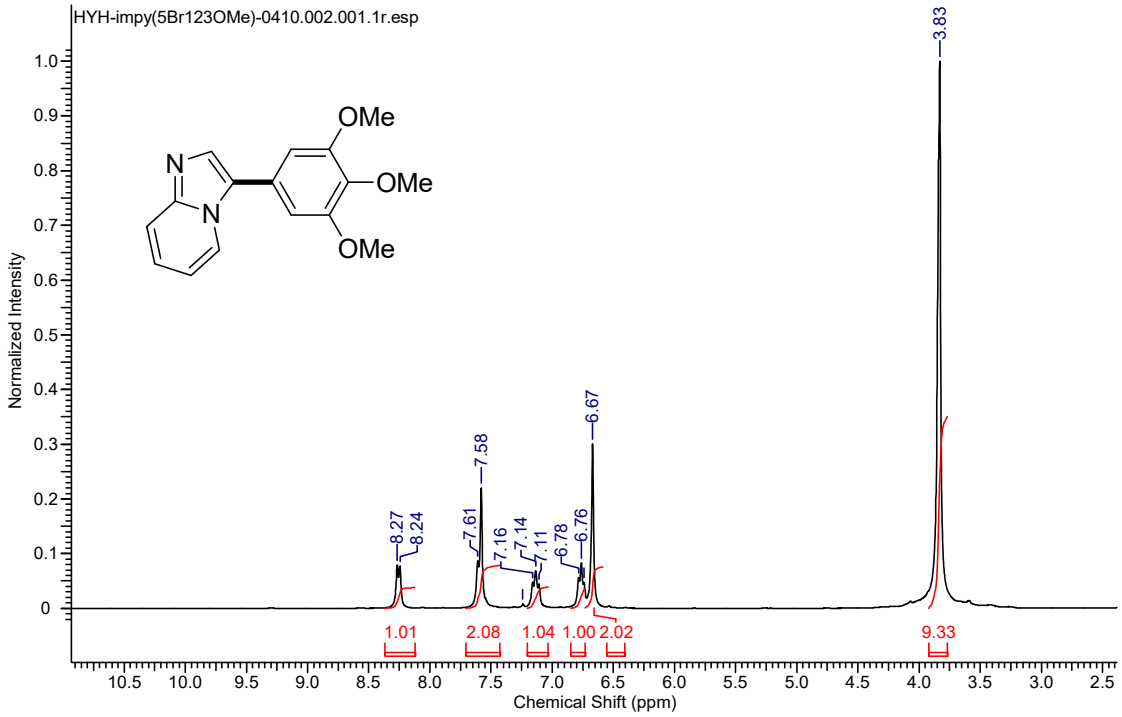


Figure S43. ^{1}H NMR spectrum of 3-(3,4,5-trimethoxyphenyl)imidazo[1,2-*a*]pyridine **(27)**

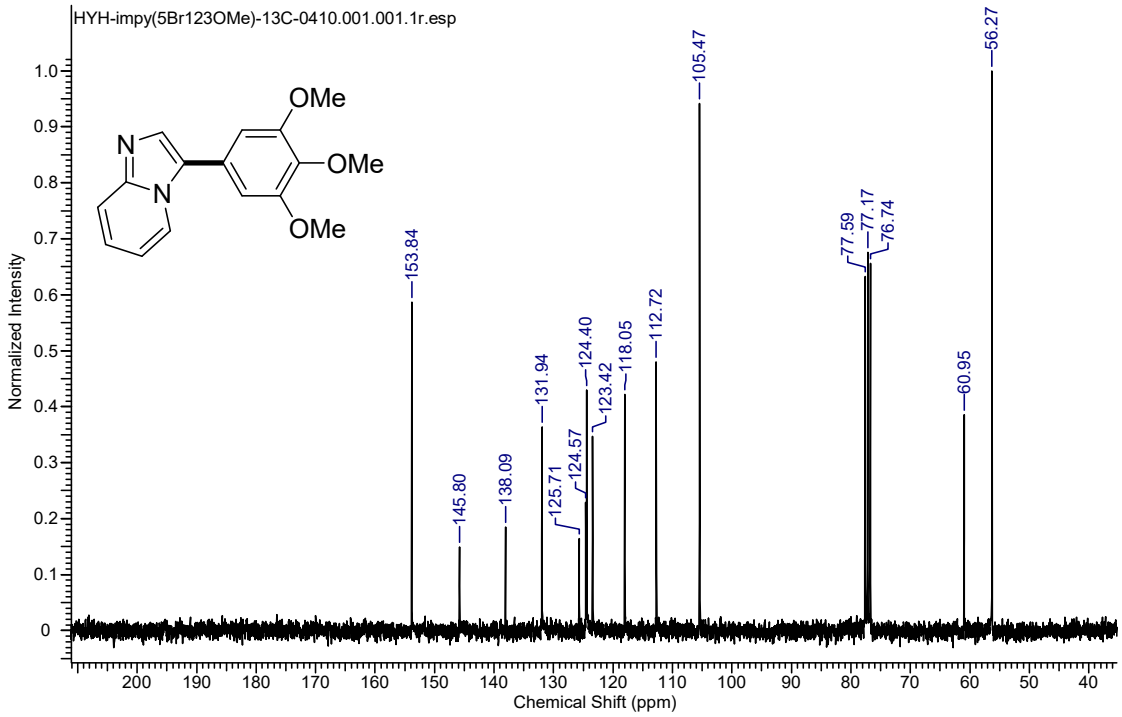


Figure S44. ^{1}H NMR spectrum of 3-(3,4,5-trimethoxyphenyl)imidazo[1,2-*a*]pyridine **(27)**

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