Supporting Information

Rhodium(III)-Catalyzed Imidoyl C–H Activation for Annulations to Azolopyrimidines

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1. General Information

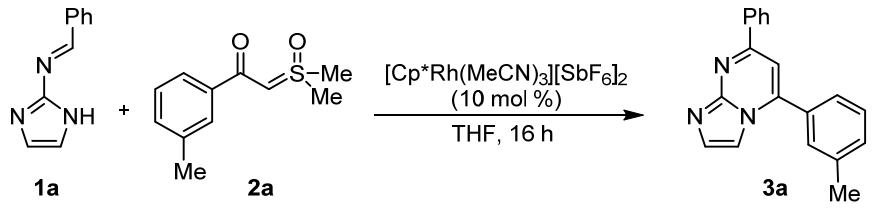
Flasks were fitted with rubber septa. Reactions were conducted under air unless noted. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230−400 mesh). Commercial reagents were used as received with the following exceptions: dichloromethane, 1,4-dioxane, and tetrahydrofuran were dried by passing through columns of activated alumina. Triethylamine was distilled from CaH_2 at 760 Torr. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent. Data are represented as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet), coupling constants in Hertz (Hz), integration). The mass spectral data were obtained on an Agilent 6550A quadrupole time-of-flight LC/MS spectrometer (ESI-TOF).

2. Optimization Data

Optimization of reaction between (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine (1a) and 2-(dimethyl(oxo)-λ⁶-sulfanylidene)-1-(m-tolyl)ethan-1-one (2a):

Optimization of the reaction was performed with iminyl azole **1a** and sulfoxonium ylide **2a** (Table S1). Beginning at 80 °C in THF, low but measurable yield of heterocycle **3a** was obtained (entry 1). The inclusion of 2.0 equiv PivOH was next found to be beneficial (entry 2). In three separate experiments, we observed yield improvements with the additional inclusion of NaOAc (entry 3), the additional inclusion of 3Å molecular sieves (entry 4), and an increase in temperature to 100 °C (entry 5). Taken together, these three changes in conditions improved the yield to 75% (entry 6). Although the exclusion of PivOH (entry 7) was not detrimental for the parent reaction, we found its inclusion to significantly help for many other ylides and imines. AcOH was inferior to PivOH as an acid additive (entry 8). Based on precedent by the Li group in C–H functionalization with sulfoxonium ylides followed by cyclodehydration, we attempted to use $Zn(OTf)_2$ as a Lewis acid additive with no success (entry 11).[1] We confirmed that the process was indeed Rh(III)-catalyzed by excluding catalyst altogether (entry 10), and the catalyst system $[Cp^*RhCl_2]_2/AgSbF_6$ also facilitated the reaction in a good yield (entry 11, next page). Wishing to run the reaction in a solvent at or below its boiling temperature, we switched to 1,4-dioxane (entries 12 and 13), with no appreciable change in yield. The conditions in entry 13 were taken as standard for the substrate scope experiments.

Table S1. Reaction of Azolo Imine **1a** with Sulfoxonium Ylide **2a**.[a]



Entry	Temperature	Variation from Initial Conditions	Yield **3a** (%)[b]
1	80 °C	None	10
2	80 °C	PivOH (2.0 equiv)	28
3	80 °C	PivOH (2.0 equiv) + NaOAc (1.0 equiv)	50
4	80 °C	PivOH (2.0 equiv) + 3Å molecular sieves	35
5	100 °C	PivOH (2.0 equiv)	44
6	100 °C	PivOH (2.0 equiv) + NaOAc (1.0 equiv) + 3Å molecular sieves	75
7	100 °C	NaOAc (1.0 equiv) + 3Å molecular sieves	69
8	100 °C	AcOH (2.0 equiv) + NaOAc (1.0 equiv) + 3Å molecular sieves	62
9	100 °C	$Zn(OTf)_2$ (50 mol%) + 3Å molecular sieves	<5

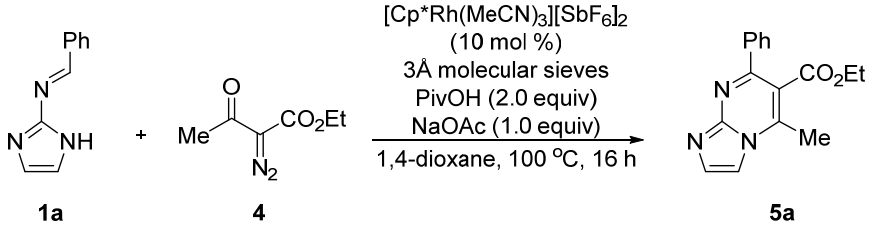
10	100 °C	As entry 6, excluded $[Cp^*Rh(MeCN)_3][SbF_6]_2$	<5
11	100 °C	As entry 6 with $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%) as catalyst system	71
12	100 °C	As entry 6 with $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%) as catalyst system in 1,4-dioxane	66
13	100 °C	As entry 6 in 1,4-dioxane	76 (80)[c]

[a]Conditions: **1a** (0.10 mmol), **2a** (1.5 equiv), 0.1 M, 16 h. [b]Yield determined by ^{1}H-NMR relative to 1,3,5-trimethoxybenzene as external standard. [c]0.30 mmol **1a**, isolated yield after chromatography on silica.

Optimization of reaction between (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine (1a) and ethyl 2-diazo-3-oxobutanoate (4):

Optimization of the reaction was performed with iminyl azole **1a** and diazoketone **4** (Table S2). The reaction conditions employed for the coupling between imines **1** and sulfoxonium ylides **2** were employed as a starting point (entry 1). The exclusion of PivOH (entry 2) or NaOAc (entry 3) both resulted in diminished yields. A slight decrease in yield was also observed when the reaction was performed at 80 °C (entry 4). The catalyst system $[Cp^*RhCl_2]_2/AgSbF_6$, in which $AgSbF_6$ acts as a halide abstractor, also facilitated the reaction in a good yield (entry 5). In the absence of a rhodium catalyst, no product formation was observed (entry 6).

Table S2. Reaction of Azolo Imine **1a** with diazoketone **4**.[a]



1a **4** **5a**

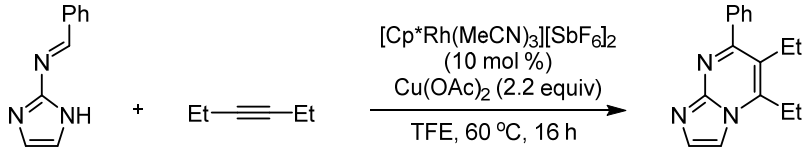
Entry	Variation from Optimized Conditions	Yield **5a** (%)[b]
1	None	66 (79)[c]
2	Excluded PivOH	52
3	Excluded NaOAc	43
4	Reaction performed at 80 °C	61
5	$[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%) as catalyst system	62
6	Excluded $[Cp^*Rh(MeCN)_3][SbF_6]_2$	<5

[a]Conditions: **1a** (0.10 mmol), **4** (1.5 equiv), 0.1 M, 16 h. [b]Yield determined by ^{1}H-NMR relative to 1,3,5-trimethoxybenzene as external standard. [c]0.30 mmol **1a**, isolated yield after chromatography on silica.

Optimization of reaction between (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine (1a) and 3-hexyne (6a):

Optimization of the reaction was performed with iminyl azole **1a** and 3-hexyne **6a** (Table S3). A solvent screen revealed that THF (entry 2) and 1,4-dioxane (entry 3) gave low yields in the coupling with alkynes, despite being efficient solvents in the couplings with sulfoxonium ylides and diazoketones. Other solvents that are commonly employed in rhodium(III)-catalyzed C–H functionalization were then tested. 1,2-DCE (entry 5) and MeOH (entry 6) gave improved yields, with TFE giving the highest yield (entry 1). Using $[Cp^*RhCl_2]_2/AgSbF_6$ as the catalyst system resulted in similar yields (7). No product formation was observed, when the rhodium catalyst (entry 8) or the copper(II) oxidant (entry 9) were excluded.

Table S3. Reaction of Azolo Imine **1a** with 3-hexyne **6a**.[a]



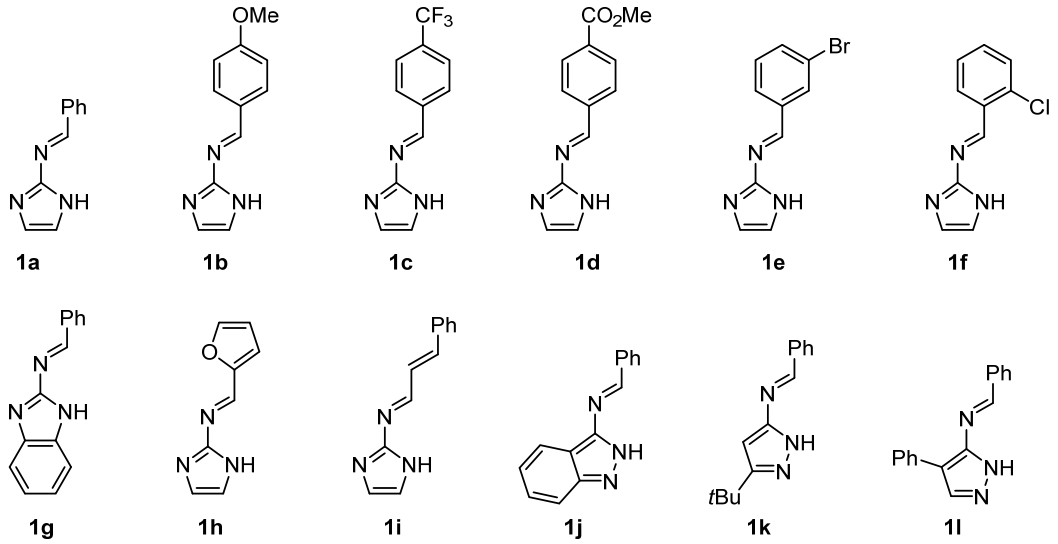
1a **6a** **7a**

Entry	Variation from Optimized Conditions	Yield **7a** (%)[b]
1	None	65 (66)[c]
2	THF as solvent	31
3	1,4-dioxane as solvent	21
4	PhMe as solvent	36
5	1,2-DCE as solvent	58
6	MeOH as solvent	62
7	$[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%) as catalyst system	67
8	Excluded $[Cp^*Rh(MeCN)_3][SbF_6]_2$	<5
9	Excluded $Cu(OAc)_2$	<5

[a]Conditions: **1a** (0.10 mmol), **6a** (1.5 equiv), 0.1 M, 16 h. [b]Yield determined by ^{1}H-NMR relative to 1,3,5-trimethoxybenzene as external standard. [c]0.30 mmol **1a**, isolated yield after chromatography on silica.

3. Synthesis and Characterization of Azolo Imines 1

Iminyl azoles **1a–c** were formed according to literature procedures.[2] Imines **1d–f,h–j,l** were synthesized in analogous fashion by coupling of the appropriate amine and aldehyde. Imine **1g** was synthesized according to a literature procedure.[3] Synthesis of imine **1k** is described below. Spectral data for imines **1a–c**,**g** matched those reported in the literature.



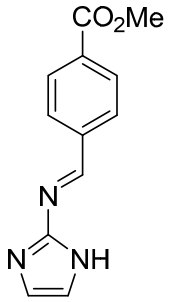
General Procedure A: Synthesis of azolo imines 1

To a solution of aldehyde (1.0 equiv) in dichloromethane (1 M) were added sequentially aminoazole sulfate (1.0 equiv), titanium(IV) ethoxide (1.6 equiv), and triethylamine (2 equiv). The reaction mixture was stirred at ambient temperature for 18 h. The reaction mixture was quenched with H_2O (2 x volume of dichloromethane). The resulting solid was filtered and washed with dichloromethane. The filtrate was transferred to a separatory funnel, and the layers were separated. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then the crude material was filtered through a plug of silica with 50% EtOAc/hexanes. Subsequently, the imine was recrystallized in EtOAc/hexanes (yields for imines were not optimized).

General Procedure B: Synthesis of azolo imines 1

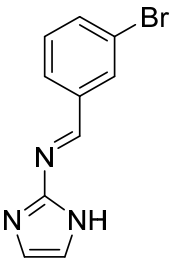
To a solution of aldehyde (1.5 equiv) in tetrahydrofuran (1 M) were added sequentially amine (1.0 equiv) and titanium(IV) ethoxide (1.6 equiv). The reaction mixture was stirred at ambient temperature for 18 h. *N*,*N*,*N'*,*N'*-Tetrakis(2-hydroxyethyl)ethylenediamine was then added to the solution (equal volume to tetrahydrofuran) and the mixture was stirred at 55 °C for 15 min. The mixture was cooled to room temperature and transferred to a separatory funnel where it was quenched with NH_4OH and brine and extracted with EtOAc. The organic phases were combined, dried with $MgSO_4$ and concentrated *in vacuo*. The product was purified by silica gel column chromatography (yields for imines were not optimized).

Methyl (*E*)-4-(((1*H*-imidazol-2-yl)imino)methyl)benzoate (1d)



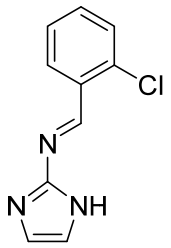
Synthesized according to General Procedure A**:** Methyl 4-formylbenzoate (2.6 mL, 20 mmol, 1.0 equiv), 2-aminoimidazole sulfate (2.64 g, 20.0 mmol, 1.0 equiv), triethylamine (5.6 mL, 40 mmol, 2.0 equiv), titanium(IV) ethoxide (6.7 mL, 32 mmol, 1.6 equiv), and dichloromethane (20 mL). Recrystallization (EtOAc/hexanes) afforded **1d** (353 mg, 8%) as a yellow solid. FTIR (neat) 1723, 1281, 1110, 737, 729, 718, 436 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 12.45 (s, 1H), 9.21 (s, 1H), 8.09–8.07 (m, 4H), 7.21 (s, 1H), 6.97 (s, 1H), 3.89 (s, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 165.8, 157.8, 150.2, 139.8, 131.7, 129.7, 128.8, 128.1, 117.6, 52.4. HRMS (ESI/$[M+H]^+$): calcd for $C_{12}H_{12}N_3O_2^+$: 230.0924; Found 230.0924.

(*E*)-1-(3-Bromophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine (1e)



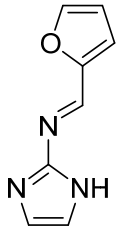
Synthesized according to General Procedure A**:** *m*-Bromobenzaldehyde (3.3 mL, 29 mmol, 1.0 equiv), 2-aminoimidazole sulfate (3.88 g, 28.6 mmol, 1.0 equiv), triethylamine (8.0 mL, 57 mmol, 2.0 equiv), titanium(IV) isopropoxide (13.6 mL, 57.4 mmol, 1.6 equiv), and dichloromethane (30 mL). Recrystallization (EtOAc/hexanes) afforded **1e** (2.88 g, 39%) as a grey solid. FTIR (neat) 1614, 1560, 1451, 1427, 1344, 1265, 1204, 1106, 1068, 996, 889, 784, 739, 678 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 11.59 (bs, 1H), 9.19 (s, 1H), 8.13 (d, J = 1.9 Hz, 1H), 7.91 (dt, J = 7.8; 1.2 Hz, 1H), 7.68 (ddd, J = 7.9; 1.9; 1.2 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.11 (bs, 2H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 158.1, 151.1, 139.0, 134.6, 131.3, 131.2, 128.5, 123.0. Note: two carbons were not observed due the slow exchange of the N-H proton, which causes these signals of the imidazole carbons to be broadened.[4] HRMS (ESI/$[M+H]^+$): calcd for $C_{10}H_9BrN_3^+$: 249.9974 and 251.9954; Found 249.9975 and 251.9956.

(*E*)-1-(2-Chlorophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine (1f)



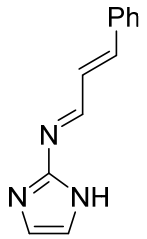
Synthesized according to General Procedure A**:** 2-Chlorobenzaldehyde (1.1 mL, 10 mmol, 1.0 equiv), 2-aminoimidazole sulfate (1.32 g, 10.0 mmol, 1.0 equiv), triethylamine (2.8 mL, 20 mmol, 2.0 equiv), titanium(IV) ethoxide (3.4 mL, 16 mmol, 1.6 equiv), and dichloromethane (10 mL). Recrystallization (EtOAc/hexanes) afforded **1f** (527 mg, 26%) as a yellow solid. FTIR (neat) 1607, 1452, 1107, 754, 742, 730, 687 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 12.48 (s, 1H), 9.49 (s, 1H), 8.15 (dd, *J* = 7.8; 1.8 Hz, 1H), 7.60 (dd, *J* = 7.8; 1.2 Hz, 1H), 7.56 (dt, *J* = 7.2; 1.8 Hz, 1H), 7.49 (tt, *J* = 7.2; 1.2 Hz, 1H), 7.21 (s, 1H), 6.96 (s, 1H). ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 154.5, 150.3, 135.3, 133.1, 132.4, 130.3, 128.0, 127.8, 127.7, 117.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{10}H_9ClN_3^+$: 206.0480; Found 206.0484.

(*E*)-1-(Furan-2-yl)-*N*-(1*H*-imidazol-2-yl)methanimine (1h)



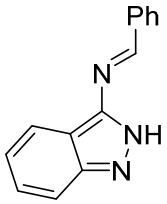
Synthesized according to General Procedure A**:** Furfural (2.4 mL, 29 mmol, 1.0 equiv), 2-aminoimidazole sulfate (3.88 g, 28.6 mmol, 1.0 equiv), triethylamine (8.0 mL, 57 mmol, 2.0 equiv), titanium(IV) isopropoxide (13.6 mL, 57.4 mmol, 1.6 equiv), and dichloromethane (30 mL). Recrystallization (EtOAc/hexanes) afforded **1h** (940 mg, 20%) as a brown solid. FTIR (neat) 1608, 1561, 1481, 1451, 1367, 1266, 1104, 1020, 934, 883, 749, 722 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 12.32 (bs, 1H), 8.91 (s, 1H), 7.96–7.94 (m, 1H), 7.23 (d, *J* = 3.5 Hz, 1H), 7.12 (bs, 1H), 6.91 (bs, 1H), 6.72 (dd, *J* = 3.5, 1.7 Hz, 1H). ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 151.7, 150.7, 146.9, 146.4, 127.6 (br), 118.4, 116.9 (br), 112.8. HRMS (ESI/$[M+H]^+$): calcd for $C_8H_8N_3O^+$: 162.0662; Found 162.0665.

(1*E*,2*E*)-*N*-(1*H*-Imidazol-2-yl)-3-phenylprop-2-en-1-imine (1i)



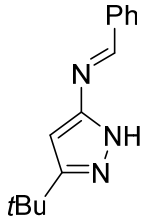
Synthesized according to General Procedure A**:** Cinnamaldehyde (2.5 mL, 20 mmol, 1.0 equiv), 2-aminoimidazole sulfate (2.64 g, 20.0 mmol, 1.0 equiv), triethylamine (5.6 mL, 40 mmol, 2.0 equiv), titanium(IV) ethoxide (6.7 mL, 32 mmol, 1.6 equiv), and dichloromethane (20 mL). Recrystallization (EtOAc/hexanes) afforded **1i** (581 mg, 17%) as a yellow solid. FTIR (neat) 1587, 1112, 986, 750, 721 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 12.20 (bs, 1H), 8.91 (d, *J* = 9.3 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.48–7.34 (m, 4H), 7.13 (bs, 1H), 7.12 (dd, *J* = 15.9; 9.3 Hz, 1H), 6.91 (bs, 1H). ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 160.5, 151.0 (br), 144.9, 135.5, 129.7, 128.9, 128.0, 127.7, 116.9 (br). HRMS (ESI/$[M+H]^+$): calcd for $C_{12}H_{12}N_3^+$: 198.1026; Found 198.1026.

(*E*)-*N*-(2*H*-Indazol-3-yl)-1-phenylmethanimine (1j)



Synthesized according to General Procedure B**:** Benzaldehyde (2.3 mL, 23 mmol, 1.5 equiv), 2*H*-indazol-3-amine (2.00 g, 15.0 mmol, 1.0 equiv), titanium(IV) ethoxide (7.1 mL, 24 mmol, 1.6 equiv), and tetrahydrofuran (15 mL). Purification by silica gel column chromatography (10%, then 20%, then 30% EtOAc/hexanes) afforded **1j** (1.71 g, 51%) as a yellow solid. In a solution of $(CD_3)_2SO$, this compound existed as a 3:1 ratio of its two tautomers. For characterization, *denotes minor isomer, + denotes overlap of signals of both isomers, whereas no sign denotes signal of major isomer. FTIR (neat) 1050, 1023, 1001, 823, 759, 499 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 13.01 (s, 1H), 11.63 (s, 1H)*, 9.24 (s, 1H), 9.16 (s, 1H)*, 8.09–8.04 (m, 2H), 8.04–8.00 (m, 2H)*, 7.98–7.93 (m, 2H)$^+$, 7.85 (d, *J* = 9.4 Hz, 1H)*, 7.72 (d, *J* = 9.4 Hz, 1H)*, 7.59–7.16 (m, 9)$^+$, 6.95 (ddd, *J* = 7.9; 6.2; 1.4 Hz, 1H)*. ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 160.3, 160.0, 150.6, 149.6, 147.4, 141.5, 141.0, 139.4, 136.2, 136.1, 131.60, 131.55, 128.9, 128.68, 128.66, 128.4, 126.8, 126.6, 121.2, 120.9, 120.7, 120.3, 120.0, 117.8, 117.7, 117.1, 113.4, 111.2, 110.6, 109.3. HRMS (ESI/$[M+H]^+$): calcd for $C_{14}H_{12}N_3^+$: 222.1026; Found 222.1026.

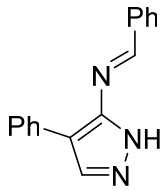
(*E*)-*N*-(3-(*tert*-Butyl)-1*H*-pyrazol-5-yl)-1-phenylmethanimine (1k)



3-*tert*-Butyl-1*H*-pyrazol-5-amine (1.67 g, 12.0 mmol, 1.2 equiv) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv) were dissolved in dichloromethane (20 mL) containing 3Å molecular sieves (approximately 10 g) in a flame-dried 100-mL flask. The mixture was stirred at ambient temperature for 18 h. The suspension was filtered through filter paper and then through basic alumina eluting with dichloromethane. Then it was concentrated *in vacuo*. Following concentration under high vacuum, the compound was obtained in a 94:6 ratio by weight with dichloromethane that could not be further removed, in 74% yield. The material was applied in this form in subsequent reactions. FTIR (neat) 1622, 1578, 1463, 1366, 1312, 1286, 1236, 1168, 1011,

1001, 757, 707, 691 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 12.47 (s, 1H), 8.84 (s, 1H), 7.90 (dd, *J* = 6.7; 3.0 Hz, 2H), 7.56–7.40 (m, 3H), 6.22 (s, 1H), 1.29 (s, 9H). ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 158.9, 158.1, 153.6, 136.4, 131.1, 128.8, 128.3, 91.8, 30.7, 30.0. HRMS (ESI/$[M+H]^+$): calcd for $C_{14}H_{18}N_3^+$: 228.1495; Found 228.1495.

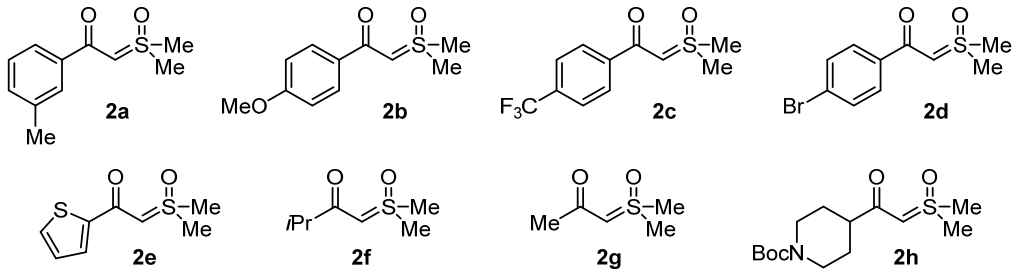
(*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine (1l)



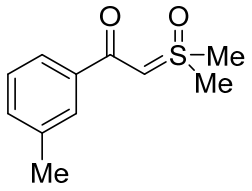
Synthesized according to General Procedure B**:** Benzaldehyde (1.5 mL, 15 mmol, 1.5 equiv), 4-phenyl-1*H*-pyrazol-5-amine (1.59 g, 10.0 mmol, 1.0 equiv), titanium(IV) ethoxide (4.8 mL, 16 mmol, 1.6 equiv), and tetrahydrofuran (15 mL). Purification by silica gel column chromatography (10%, then 20%, then 30% EtOAc/hexanes) afforded **1l** (1.38 g, 56%) as a white solid. FTIR (neat) 1989, 1265, 764, 731, 697 cm^{-1}. ^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 12.87 (s, 1H), 9.06 (s, 1H), 8.19 (d, *J* = 1.6 Hz, 1H), 7.99 (dd, *J* = 6.7; 2.9 Hz, 2H), 7.92–7.81 (m, 2H), 7.64–7.48 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H). ^{13}C-NMR (100 MHz, $(CD_3)_2SO$) δ 159.1, 154.3, 136.2, 132.9, 131.4, 128.9, 128.6, 128.4, 128.1, 126.8, 125.7, 114.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{16}H_{14}N_3^+$: 248.1182; Found 248.1183.

4. Synthesis and Characterization of Sulfoxonium Ylides 2

The syntheses of all sulfoxonium ylides other than **2a** have been previously reported. Ylides **2b** and **2c** were formed according to Wu *et al*.[5] Ylides **2d**–**f** were formed according to Phelps *et al*.[6] Ylide **2a** was synthesized in analogous fashion, as detailed below. Ylides **2g** and **2h** were formed according to Barday *et al*.[7] Spectral data for ylides **2b**–**h** matched those reported in the literature.



2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-(m-tolyl)ethan-1-one (2a)



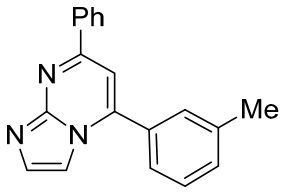
Trimethylsulfoxonium iodide (9.90 g, 45.0 mmol, 3.0 equiv) was dissolved in anhydrous THF (150 mL) in a flame-dried 250-mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. To this reaction mixture was added solid sodium *tert*-butoxide (4.54 g, 47.3 mmol, 3.15 equiv), and the suspension was heated to reflux for 2 h. The flask was cooled to room temperature, and *m*-toluoyl chloride (1.98 mL, 2.32 g, 15.0 mmol, 1.0 equiv) was added dropwise by syringe. The reaction mixture was stirred at room temperature for 18 h, then the reaction was quenched with H_2O (250 mL). The aqueous layer was extracted with EtOAc (3 x 150 mL), then the pooled organic extracts were washed with brine (150 mL). The organic layer was dried over $NaSO_4$, filtered, and concentrated *in vacuo*. The resulting solid was added to a 50-mL round-bottom flask, suspended in 16 mL EtOAc, and heated to 50 °C for 1 h, resulting in full dissolution of solids. The mixture was then cooled to room temperature with constant stirring, resulting in precipitation of pure ylide **2a**, which was filtered through a Buchner funnel under vacuum and washed with cold EtOAc. Drying *in vacuo* afforded **2a** (1.49 g, 47%) as a white solid. FTIR (neat) 1531, 1420, 1390, 1174, 1076, 1037, 867, 736, 438 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.57 (d, J = 7.3 Hz, 1H), 7.28–7.22 (m, 2H), 4.96 (s, 1H), 3.49 (s, 6H), 2.37 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 182.6, 138.9, 137.9, 131.6, 128.2, 127.3, 123.8, 68.3, 42.6, 21.5. HRMS (ESI/[M+H]$^+$): calcd for $C_{11}H_{15}O_2S^+$: 211.0787; Found 211.0788.

5. Synthesis and Characterization of Heterocycles 3

General Procedure C: Rh(III)-catalyzed coupling of imines with sulfoxonium ylides

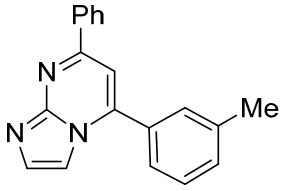
To a flame-dried microwave tube in a glove box was added the imine (**1**, 1.0 equiv), the sulfoxonium ylide (**2**, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.1 equiv), pivalic acid (2.0–4.0 equiv), sodium acetate (1.0 equiv), 3Å molecular sieves and 1,4-dioxane or tetrahydrofuran (0.1 M). The tube was capped, and the reaction mixture was stirred at the indicated temperature for 16 h. The reaction mixture was cooled to ambient temperature and filtered through a plug of Celite with dichloromethane. The solvent was removed *in vacuo* and the crude reaction mixture was subjected to silica gel column chromatography to yield the product.

7-Phenyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidine (3a)



Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (95 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3a** (69 mg, 80%) as a yellow foam. FTIR (neat) 1614, 1599, 1581, 1528, 1505, 1483, 1388, 1352, 1294, 1272, 1248, 1151, 1138, 907, 792, 779, 764, 727, 701, 650 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.1 Hz, 2H), 7.81 (s, 1H), 7.65 (s, 1H), 7.55–7.47 (m, 6H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.33 (s, 1H), 2.49 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 157.0, 150.1, 146.5, 139.6, 137.3, 135.8, 132.7, 131.9, 130.5, 129.5, 129.0, 128.6, 127.5, 125.1, 109.2, 105.8, 21.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{19}H_{16}N_3^+$: 286.1339; Found 286.1340.

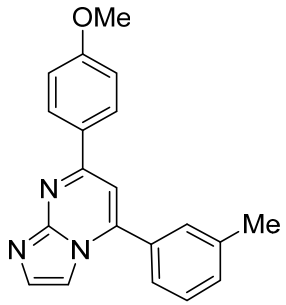
7-Phenyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidine (3a) – 1 mmol Benchtop Preparation



To a flame-dried 10-20 mL microwave tube was added (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (171 mg, 1.00 mmol, 1.00 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (315 mg, 1.50 mmol, 1.50 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (83.3 mg, 0.100 mmol, 0.100 equiv), pivalic acid (204 mg, 2.00 mmol, 2.00 equiv), sodium acetate (82.0 mg, 1.00 mmol, 1.00 equiv), 3Å molecular sieves (approximately 250 mg), and 1,4-dioxane (10.0 mL). The tube was capped with a teflon-lined septum, and the reaction mixture was flushed under nitrogen for ten minutes. The nitrogen line was removed, and the reaction mixture was stirred at 100 °C for 16 h. The reaction mixture was cooled to ambient temperature and filtered through a plug of Celite with dichloromethane. The solvent was removed *in vacuo* and the crude reaction

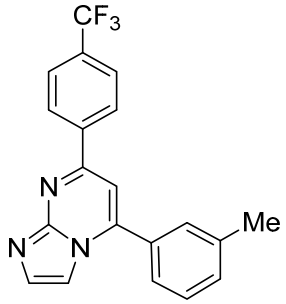
mixture was subjected to silica gel column chromatography (40% acetone/hexanes) to afford **3a** (235 mg, 82%) as a yellow foam. Spectroscopic data agreed with that reported above.

7-(4-Methoxyphenyl)-5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidine (3b)



Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-(4-methoxyphenyl)methanimine **1b** (60 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (95 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3b** (70 mg, 74%) as a yellow foam. FTIR (neat) 1599, 1579, 1531, 1509, 1484, 1274, 1239, 1173, 1151, 1137, 1028, 906, 832, 789, 724, 700, 644, 571, 523 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.76 (s, 1H), 7.60 (s, 1H), 7.55–7.47 (m, 3H), 7.42 (d, J = 7.1 Hz, 1H), 7.27 (s, 1H), 7.02 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 2.49 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 161.8, 156.6, 150.3, 146.3, 139.6, 135.4, 132.8, 131.8, 129.9, 129.4, 129.0, 128.6, 125.1, 114.3, 109.0, 105.3, 55.6, 21.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{18}N_3O^+$: 316.1444; Found 316.1444.

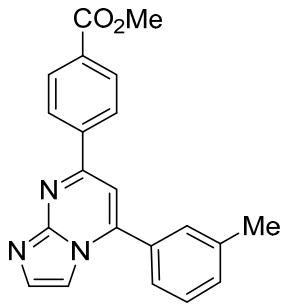
5-(*m*-Tolyl)-7-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyrimidine (3c)



Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-(4-(trifluoromethyl)phenyl)methanimine **1c** (72 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (95 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3c** (86 mg, 81%) as a yellow solid. FTIR (neat) 1618, 1532, 1324, 1274, 1165, 1124, 1075, 1065, 704 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.1 Hz, 2H), 7.86 (s, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.69 (s, 1H), 7.57–7.49 (m, 3H),

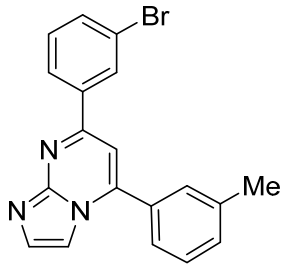
7.44 (d, J = 7.2 Hz, 1H), 7.34 (s, 1H), 2.50 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 155.1, 149.8, 146.9, 140.6, 139.8, 136.4, 132.4, 132.1, 132.0 (q, J = 33.4 Hz), 129.5, 128.6, 127.7, 125.9 (q, J = 3.6 Hz), 125.1, 124.1 (q, J = 272.2 Hz), 109.5, 105.6, 21.6. ^{19}F-NMR (376 MHz, $CDCl_3$) δ –62.8. HRMS (ESI/[M+H]$^+$): calcd for $C_{20}H_{15}F_3N_3^+$: 354.1213; Found 354.1214.

Methyl 4-(5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidin-7-yl)benzoate (3d)



Synthesized according to General Procedure C: Methyl (*E*)-4-(((1*H*-imidazol-2-yl)imino)methyl)benzoate **1d** (69 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (95 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3d** (76 mg, 74%) as an orange solid. FTIR (neat) 1720, 1612, 1530, 1484, 1435, 1273, 1149, 1140, 1108, 779, 728, 704 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.3 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.85 (s, 1H), 7.68 (s, 1H), 7.55–7.49 (m, 3H), 7.43 (d, J = 7.4 Hz, 1H), 7.36 (s, 1H), 3.95 (s, 3H), 2.49 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.8, 155.5, 150.0, 146.7, 141.4, 139.7, 136.5, 132.5, 132.1, 131.7, 130.2, 129.5, 128.6, 127.4, 125.1, 109.5, 105.8, 52.4, 21.6. HRMS (ESI/[M+H]$^+$): calcd for $C_{21}H_{18}N_3O_2^+$: 344.1394; Found 344.1394.

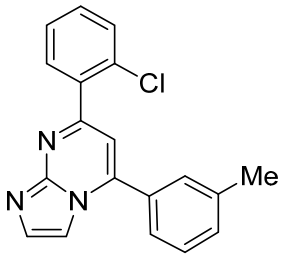
7-(3-Bromophenyl)-5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidine (3e)



Synthesized according to General Procedure C: (*E*)-1-(3-Bromophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine **1e** (75 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (95 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3e** (85 mg, 78%) as a yellow solid. FTIR (neat) 1597, 1525, 1504, 1474, 1281, 1267, 1150, 1139, 1072, 907, 847, 770, 725, 702, 690, 674, 644, 609 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.82 (s, 1H), 7.66 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.55–

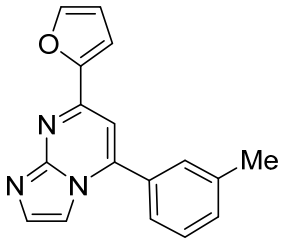
7.48 (m, 3H), 7.43 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.27 (s, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 155.2, 149.9, 146.7, 139.7, 139.3, 136.3, 133.3, 132.5, 132.0, 130.48, 130.46, 129.5, 128.6, 126.0, 125.1, 123.3, 109.4, 105.5, 21.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{19}H_{15Br}N_3^+$: 364.0444 and 366.0423; Found 364.0444 and 366.0425.

7-(2-Chlorophenyl)-5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidine (3f)



Synthesized according to General Procedure C: (*E*)-1-(2-Chlorophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine **1f** (75 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (62 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and tetrahydrofuran (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3f** (49 mg, 51%) as an orange foam. FTIR (neat) 1613, 1524, 1503, 1475, 1274, 1150, 1139, 1093, 1048, 906, 793, 759, 728, 703, 644, 609 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88–7.85 (m, 2H), 7.72 (d, J = 1.6 Hz, 1H), 7.56–7.53 (m, 2H), 7.51–7.47 (m, 2H), 7.44–7.37 (m, 3H), 7.31 (s, 1H), 2.48 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.0, 149.9, 145.3, 139.6, 137.7, 136.0, 132.5, 132.3, 132.1, 132.0, 130.7, 130.4, 129.5, 128.6, 127.4, 125.2, 110.0, 109.3, 21.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{19}H_{15}ClN_3^+$: 320.0949; Found 320.0949.

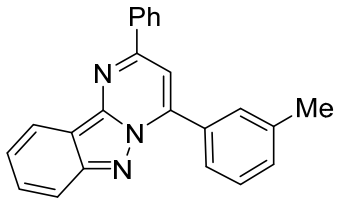
7-(Furan-2-yl)-5-(*m*-tolyl)imidazo[1,2-*a*]pyrimidine (3g)



Synthesized according to General Procedure C: (*E*)-1-(Furan-2-yl)-*N*-(1*H*-imidazol-2-yl)methanimine **1h** (48 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (62 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3g** (41 mg, 50%) as a brown oil. FTIR (neat) 1615, 1593, 1522, 1477, 1279, 1223, 1151, 1139, 1093, 1015, 908, 884, 790, 727, 700, 635 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 1.5 Hz, 1H), 7.62 (d, J = 1.5 Hz, 1H), 7.59 (d, J = 0.9 Hz, 1H), 7.54–7.46 (m, 3H), 7.43–7.38 (m, 2H), 7.30 (s, 1H), 6.60 (dd, J = 3.5; 1.7 Hz, 1H), 2.48 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ

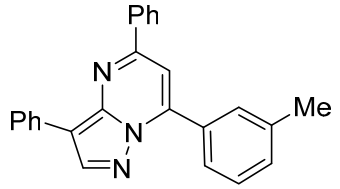
152.5, 149.8, 148.8, 146.5, 144.7, 139.6, 135.9, 132.5, 131.9, 129.4, 128.6, 125.1, 113.0, 111.9, 109.4, 104.4, 21.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{17}H_{14}N_3O^+$: 276.1131; Found 276.1133.

2-Phenyl-4-(*m*-tolyl)pyrimido[1,2-*b*]indazole (3h)



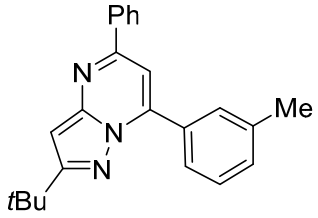
Synthesized according to General Procedure C: (*E*)-*N*-(2*H*-Indazol-3-yl)-1-phenylmethanimine **1j** (66 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (62 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (20% acetone/hexanes) afforded **3h** (81 mg, 81%) as a yellow solid. FTIR (neat) 1634, 1581, 1540, 1484, 1461, 1358, 1187, 1161, 1136, 1119, 907, 857, 767, 752, 728, 689, 642, 633, 616, 579, 478, 440 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.2 Hz, 1H), 8.29 (d, *J* = 7.1 Hz, 2H), 8.01–7.99 (m, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.73 (s, 1H), 7.62 (ddd, *J* = 8.3; 6.6; 1.1 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.50–7.55 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.33–7.30 (m, 1H), 2.53 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 152.7, 151.7, 145.7, 145.1, 138.8, 137.5, 132.0, 131.9, 130.3, 130.0, 129.9, 129.2, 128.9, 127.3, 126.8, 121.4, 120.8, 116.8, 114.0, 108.8, 21.8. HRMS (ESI/$[M+H]^+$): calcd for $C_{23}H_{18}N_3^+$: 336.1495; Found 336.1495.

3,5-Diphenyl-7-(*m*-tolyl)pyrazolo[1,5-*a*]pyrimidine (3i)



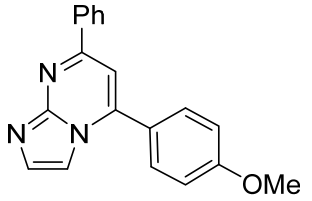
Synthesized according to General Procedure C: (*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine **1l** (74 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (62 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (20% acetone/hexanes) afforded **3i** (96 mg, 88%) as a yellow solid. FTIR (neat) 1606, 1583, 1561, 1521, 1489, 1369, 1247, 1189, 907, 880, 847, 788, 764, 728, 691, 663, 648, 602 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.26–8.23 (m, 4H), 7.88–7.85 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.54–7.49 (m, 4H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.38 (s, 1H), 7.33–7.92 (m, 1H), 2.51 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 156.0, 147.3, 146.0, 143.0, 138.7, 137.5, 132.6, 131.9, 131.5, 130.5, 129.8, 129.0, 128.84, 128.77, 127.5, 126.5, 126.4, 126.2, 110.7, 105.3, 21.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{25}H_{20}N_3^+$: 362.1652; Found 362.1653.

2-(*tert*-Butyl)-5-phenyl-7-(*m*-tolyl)pyrazolo[1,5-*a*]pyrimidine (3j)



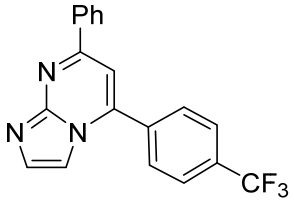
Synthesized according to General Procedure C: (*E*)-*N*-(3-(*tert*-Butyl)-1*H*-pyrazol-5-yl)-1-phenylmethanimine **1k** (73 mg, 94% mass purity, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (62 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (123 mg, 1.20 mmol, 4.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 120 °C. Purification by silica gel column chromatography (20% acetone/hexanes) afforded **3j** (59 mg, 57%) as a yellow oil. FTIR (neat) 1599, 1583, 1551, 1510, 1485, 1459, 1363, 1240, 1151, 770, 734, 692, 627 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.3; 1.5 Hz, 2H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.50–7.44 (m, 2H), 7.39–7.37 (m, 1H), 7.30 (s, 1H), 6.64 (s, 1H), 2.49 (s, 3H), 1.44 (s, 9H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 168.1, 155.6, 150.6, 146.3, 138.2, 138.1, 131.8, 131.7, 130.2, 130.1, 129.0, 128.4, 127.3, 126.8, 104.2, 93.2, 33.2, 30.6, 21.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{23}H_{24}N_3^+$: 342.1965; Found 342.1963.

5-(4-Methoxyphenyl)-7-phenylimidazo[1,2-*a*]pyrimidine (3k)



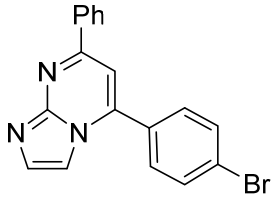
Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-methoxyphenyl)ethan-1-one **2b** (102 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3k** (70 mg, 78%) as a yellow solid. FTIR (neat) 1607, 1533, 1510, 1501, 1491, 1464, 1440, 1296, 1254, 1180, 1161, 1141, 1027, 908, 834, 779, 766, 730, 689, 646, 637, 576 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.8; 1.9 Hz, 2H), 7.78 (s, 1H), 7.70–7.64 (m, 3H), 7.51–7.45 (m, 3H), 7.27 (s, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.7, 156.9, 150.2, 146.2, 137.4, 135.8, 130.4, 129.6, 128.9, 127.4, 124.9, 114.9, 109.0, 105.4, 55.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{19}H_{16}N_3O^+$: 302.1288; Found 302.1288.

7-Phenyl-5-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyrimidine (3l)



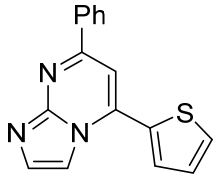
Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one **2c** (119 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3l** (42 mg, 41%) as a yellow solid. FTIR (neat) 1610, 1533, 1324, 1271, 1169, 1128, 1065, 1019, 845, 766, 689 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23–8.19 (m, 2H), 7.93–7.87 (m, 4H), 7.83 (d, *J* = 1.5 Hz, 1H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.53–7.49 (m, 3H), 7.35 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 156.9, 150.0, 144.6, 137.0, 136.4, 136.2, 133.2 (d, *J* = 33.0 Hz), 130.8, 129.1, 128.7, 127.5, 126.7 (q, *J* = 3.7 Hz), 123.6 (d, *J* = 272.5 Hz), 108.9, 106.2. ^{19}F-NMR (376 MHz, $CDCl_3$) δ –63.0. HRMS (ESI/$[M+H]^+$): calcd for $C_{19}H_{13}F_3N_3^+$: 340.1056; Found 340.1056.

5-(4-Bromophenyl)-7-phenylimidazo[1,2-*a*]pyrimidine (3m)



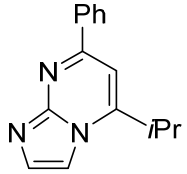
Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 1-(4-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2d** (124 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and tetrahydrofuran (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3m** (76 mg, 73%) as a yellow solid. FTIR (neat) 1612, 1588, 1527, 1482, 1382, 1352, 1272, 1156, 1141, 1069, 1011, 906, 827, 778, 765, 726, 696, 643 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.8; 1.8 Hz, 2H), 7.80 (s, 1H), 7.70–7.74 (m, 2H), 7.63–7.60 (m, 2H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.51–7.46 (m, 3H), 7.29 (s, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 156.9, 150.0, 145.0, 137.0, 136.1, 132.9, 131.5, 130.6, 129.6, 129.0, 127.4, 125.6, 108.9, 105.8. HRMS (ESI/$[M+H]^+$): calcd for $C_{18}H_{13}BrN_3^+$: 350.0287 and 352.0267; Found 350.0287 and 352.0267.

7-Phenyl-5-(thiophen-2-yl)imidazo[1,2-a]pyrimidine (3n)



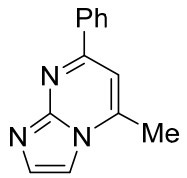
Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(thiophen-2-yl)ethan-1-one **2e** (91 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3n** (64 mg, 76%) as a yellow solid. FTIR (neat) 1603, 1581, 1531, 1491, 1469, 1428, 1396, 1377, 1359, 1291, 1271, 1243, 1147, 909, 856, 776, 763, 696, 656 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8; 1.9 Hz, 2H), 7.98 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.76 (dd, *J* = 3.7; 1.2 Hz, 1H), 7.65 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.53–7.46 (m, 4H), 7.30 (dd, *J* = 5.1; 3.7 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 156.6, 150.3, 139.7, 137.1, 136.3, 133.6, 130.6, 129.35, 129.34, 129.0, 128.5, 127.5, 109.5, 105.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{16}H_{12}N_3S^+$: 278.0746; Found 278.0748.

5-Isopropyl-7-phenylimidazo[1,2-*a*]pyrimidine (3o)



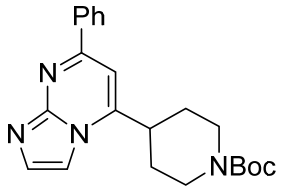
Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 1-(dimethyl(oxo)-λ^6-sulfanylidene)-3-methylbutan-2-one **2f** (73 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3o** (49 mg, 69%) as a colorless oil. FTIR (neat) 1614, 1528, 1508, 1495, 1465, 1406, 1347, 1271, 1248, 1145, 911, 782, 766, 729, 689 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.0; 1.7 Hz, 2H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.53 (d, *J* = 1.5 Hz, 1H), 7.52–7.44 (m, 3H), 7.20 (s, 1H), 3.30 (hept, *J* = 6.9 Hz, 1H), 1.48 (d, *J* = 6.9 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 157.1, 153.1, 149.9, 137.6, 135.8, 130.4, 128.9, 127.5, 107.7, 101.4, 30.5, 19.9. HRMS (ESI/$[M+H]^+$): calcd for $C_{15}H_{16}N_3^+$: 238.1339; Found 238.1342.

5-Methyl-7-phenylimidazo[1,2-*a*]pyrimidine (3p)



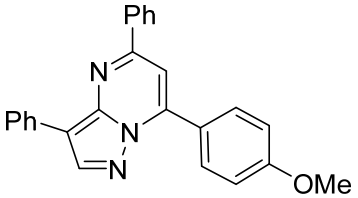
Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 1-(dimethyl(oxo)-λ^6-sulfanylidene)propan-2-one **2g** (60 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3p** (32 mg, 51%) as a yellow solid. FTIR (neat) 1620, 1530, 1506, 1496, 1467, 1450, 1370, 1349, 1289, 1273, 1146, 908, 781, 762, 725, 693, 650 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.18–8.15 (m, 2H), 7.83 (d, *J* = 1.4 Hz, 1H), 7.50–7.45 (m, 3H), 7.43 (d, *J* = 1.4 Hz, 1H), 7.18 (s, 1H), 2.68 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 156.6, 149.7, 143.5, 137.3, 136.0, 130.4, 128.9, 127.4, 107.7, 105.5, 18.8. HRMS (ESI/$[M+H]^+$): calcd for $C_{13}H_{12}N_3^+$: 210.1026; Found 210.1029.

tert-Butyl 4-(7-phenylimidazo[1,2-*a*]pyrimidin-5-yl)piperidine-1-carboxylate (3q)



Synthesized according to General Procedure C: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), *tert*-butyl 4-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)piperidine-1-carboxylate **2h** (137 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and tetrahydrofuran (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **3q** (84 mg, 74%) as a yellow solid. FTIR (neat) 1683, 1616, 1528, 1451, 1424, 1366, 1273, 1235, 1166, 1131, 1118, 912, 766, 731, 696 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.16 (dt, *J* = 7.8; 1.5 Hz, 2H), 7.84 (s, 1H), 7.54 (s, 1H), 7.51–7.46 (m, 3H), 7.16 (d, *J* = 2.3 Hz, 1H), 4.38 (br s, 2H), 3.08 (tt, *J* = 12.0; 3.4 Hz, 1H), 2.94 (s, 2H), 2.16 (apparent d, *J* = 12.6 Hz, 2H), 1.82–1.72 (m, 2H), 1.49 (s, 9H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 157.0, 154.7, 150.0, 149.9, 137.4, 136.2, 130.5, 129.0, 127.5, 107.4, 102.0, 80.2, 43.9 (br), 38.9, 29.4, 28.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{22}H_{27}N_4O_2^+$: 379.2129; Found 379.2129.

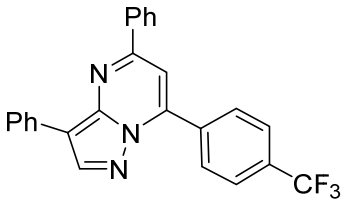
7-(4-Methoxyphenyl)-3,5-diphenylpyrazolo[1,5-*a*]pyrimidine (3r)



Synthesized according to General Procedure C: (*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine **1l** (74 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-methoxyphenyl)ethan-1-one **2b** (102 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (20%

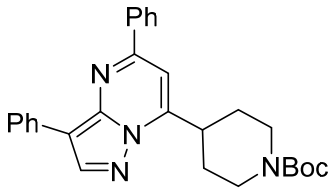
acetone/hexanes) afforded **3r** (97 mg, 85%) as a yellow solid. FTIR (neat) 1606, 1561, 1507, 1494, 1377, 1296, 1258, 1231, 1179, 1028, 907, 828, 765, 729, 709, 692, 668 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.26–8.22 (m, 4H), 8.10 (d, *J* = 8.8 Hz, 2H), 7.58–7.54 (m, 2H), 7.53–7.48 (m, 3H), 7.38 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 161.9, 156.0, 146.9, 146.2, 143.0, 137.7, 132.7, 131.1, 130.5, 129.1, 128.9, 127.5, 126.5, 126.2, 123.8, 114.3, 110.6, 104.6, 55.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{25}H_{20}N_3O^+$: 378.1601; Found 378.1605.

3,5-Diphenyl-7-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (3s)



Synthesized according to General Procedure C: (*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine **1l** (74 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one **2c** (119 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (20% acetone/hexanes) afforded **3s** (109 mg, 87%) as an orange solid. FTIR (neat) 1608, 1565, 1497, 1376, 1323, 1169, 1126, 1067, 1018, 925, 909, 852, 834, 766, 732, 692, 677 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.25–8.18 (m, 6H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.59–7.53 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 (s, 1H), 7.40–7.29 (m, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 156.0, 146.0, 145.5, 143.3, 137.2, 135.0, 133.0, 132.7, 132.2, 130.8, 129.9, 129.2, 128.9, 127.5, 126.6, 126.5, 125.9 (q, *J* = 3.7 Hz), 111.3, 105.6. ^{19}F-NMR (376 MHz, $CDCl_3$) δ –63.0. HRMS (ESI/$[M+H]^+$): calcd for $C_{25}H_{17}F_3N_3^+$: 416.1369; Found 416.1368.

***tert*-Butyl 4-(3,5-diphenylpyrazolo[1,5-*a*]pyrimidin-7-yl)piperidine-1-carboxylate (3t)**



Synthesized according to General Procedure C: (*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine **1l** (74 mg, 0.30 mmol, 1.0 equiv), *tert*-butyl 4-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)piperidine-1-carboxylate **3h** (137 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (20% acetone/hexanes) afforded **3t** (102 mg, 75%) as a yellow solid. FTIR (neat) 1687, 1613, 1566, 1523, 1449, 1425, 1388, 1366, 1295, 1276, 1235, 1167, 1125, 946, 767, 732, 693 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.20–8.17 (m, 4H), 7.56–7.47 (m, 5H), 7.28 (tt, *J* = 7.3; 1.3 Hz, 1H), 7.14 (s, 1H), 4.37 (br s, 2H), 3.80 (tt, *J* = 12.2; 3.4 Hz, 1H),

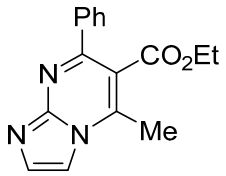
3.00 (br s, 2H), 2.28–2.23 (m, 2H), 1.78 (br s, 2H), 1.51 (s, 9H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 156.1, 154.8, 152.3, 145.2, 142.5, 137.6, 132.5, 130.5, 129.1, 128.9, 127.5, 126.4, 126.2, 110.9, 101.6, 79.9, 44.0 (br), 36.8, 29.5, 28.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{28}H_{31}N_4O_2^+$: 455.2442; Found 455.2442.

6. Synthesis and Characterization of Heterocycles 5

General Procedure D: Rh(III)-catalyzed coupling of imines with diazoketones

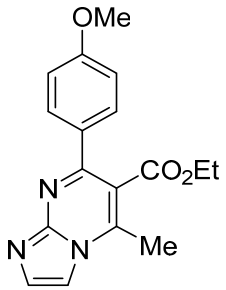
To a flame-dried microwave tube in a glove box was added the imine (**1**, 1.0 equiv), the diazoketone (**4**, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.1 equiv), pivalic acid (2.0-4.0 equiv), sodium acetate (1.0 equiv), 3Å molecular sieves and 1,4-dioxane (0.1 M). The tube was capped, and the reaction mixture was stirred at the indicated temperature for 16 h. The reaction mixture was cooled to ambient temperature and the solvent was removed *in vacuo*. The crude reaction mixture was subjected to silica gel column chromatography to yield the product.

Ethyl 5-methyl-7-phenylimidazo[1,2-*a*]pyrimidine-6-carboxylate (5a)



Synthesized according to General Procedure D: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **5a** (67 mg, 79%) as a brown oil. FTIR (neat) 1716, 1607, 1503, 1292, 1202, 1144, 1056 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 7.93 (d, J = 1.5 Hz, 1H), 7.85 (d, J = 1.5 Hz, 1H), 7.69–7.64 (m, 2H), 7.53–7.47 (m, 3H), 4.16 (q, J = 7.1 Hz, 2H), 2.85 (s, 3H), 1.00 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 167.6, 156.9, 148.4, 145.6, 140.3, 137.3, 130.1, 129.2, 128.9, 115.7, 110.6, 62.5, 16.6, 13.8. HRMS (ESI/$[M+H]^+$): calcd for $C_{16}H_{16}N_3O_2^+$: 282.1237; Found 282.1237.

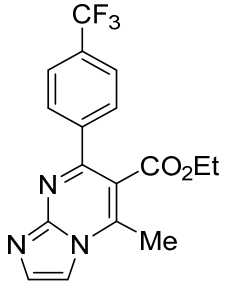
Ethyl 7-(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyrimidine-6-carboxylate (5b)



Synthesized according to General Procedure D: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-(4-methoxyphenyl)methanimine **1b** (60 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **5b** (68 mg, 73%) as a yellow oil. FTIR (neat) 1717, 1600, 1502, 1289, 1248, 1175 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 7.88 (s, 1H), 7.81 (s, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 2.82 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (150 MHz,

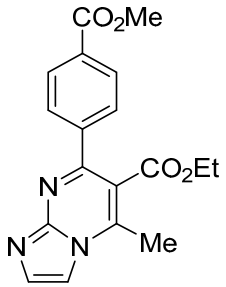
$(CD_3)_2CO$) δ 167.8, 161.8, 156.3, 148.6, 145.2, 137.1, 132.4, 130.5, 115.6, 114.6, 110.3, 62.6, 55.8, 16.5, 14.0. HRMS (ESI/$[M+H]^+$): calcd for $C_{17}H_{18}N_3O_3^+$: 312.1343; Found 312.1345.

Ethyl 5-methyl-7-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyrimidine-6-carboxylate (5c)



Synthesized according to General Procedure D: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-(4-(trifluoromethyl)phenyl)methanimine **1c** (72 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **5c** (92 mg, 88%) as a white solid. FTIR (neat) 1713, 1604, 1503, 1324, 1105 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 7.99 (s, 1H), 7.89 (m, 5H), 4.18 (q, J = 7.1 Hz, 2H), 2.89 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 167.2, 155.4, 148.2, 146.4, 144.20 (q, J = 1.8 Hz), 137.7, 131.3 (q, J = 32.2 Hz), 129.7, 126.2 (q, J = 3.8 Hz), 125.2 (q, J = 272.1 Hz), 115.4, 111.0, 62.7, 16.7, 13.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ –63.1. HRMS (ESI/$[M+H]^+$): calcd for $C_{17}H_{15}F_3N_3O_2^+$: 350.1111; Found 350.1112.

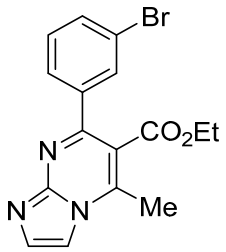
Ethyl 7-(4-(methoxycarbonyl)phenyl)-5-methylimidazo[1,2-*a*]pyrimidine-6-carboxylate (5d)



Synthesized according to General Procedure D: Methyl (*E*)-4-(((1*H*-imidazol-2-yl)imino)methyl)benzoate **1d** (69 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (25%, then 40% acetone/hexanes) afforded **5d** (77 mg, 75%) as a yellow solid. FTIR (neat) 1717, 1279, 1196, 751 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 8.15–8.12 (m, 2H), 7.97 (d, J = 1.5 Hz, 1H), 7.89 (d, J = 1.5 Hz, 1H), 7.80–7.77 (m, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 2.88 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 167.3, 166.8, 155.7, 148.2, 146.2, 144.6, 137.7, 131.6, 120.2, 129.2, 115.4,

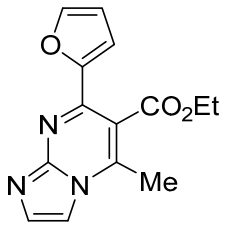
110.9, 62.7, 52.5, 16.7, 13.9. HRMS (ESI/[M+H]$^+$): calcd for $C_{18}H_{18}N_3O_4^+$: 340.1292; Found 340.1292.

Ethyl 7-(3-bromophenyl)-5-methylimidazo[1,2-*a*]pyrimidine-6-carboxylate (5e)



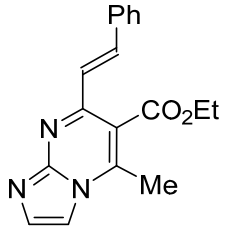
Synthesized according to General Procedure D: (*E*)-1-(3-Bromophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine **1e** (75 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (25%, then 40% acetone/hexanes) afforded **5e** (78 mg, 72%) as brown solid. FTIR (neat) 1721, 1504, 1292, 1148, 685 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.82 (t, *J* = 1.9 Hz, 1H), 7.60–7.50 (m, 3H), 7.28 (t, *J* = 7.9 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.76 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 166.7, 155.2, 147.5, 144.2, 140.7, 137.2, 132.5, 131.3, 130.0, 126.9, 122.5, 115.2, 109.0, 62.4, 16.6, 13.7. HRMS (ESI/[M+H]$^+$): calcd for $C_{16}H_{15}BrN_3O_2^+$: 360.0342 and 362.0322; Found 360.0343 and 362.0323.

Ethyl 7-(furan-2-yl)-5-methylimidazo[1,2-*a*]pyrimidine-6-carboxylate (5f)



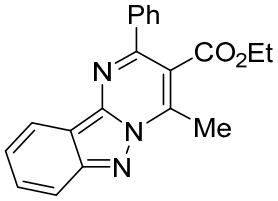
Synthesized according to General Procedure D: (*E*)-1-(Furan-2-yl)-*N*-(1*H*-imidazol-2-yl)methanimine **1h** (48 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (30%, then 50% acetone/hexanes) afforded **5f** (63 mg, 77%) as a white solid. FTIR (neat) 1729, 1293, 1180, 739, 720 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 7.89 (d, *J* = 1.5 Hz, 1H), 7.83 (d, *J* = 1.5 Hz, 1H), 7.80 (dd, *J* = 1.8; 0.9 Hz, 1H), 7.26 (dd, *J* = 3.5; 0.8 Hz, 1H), 6.69 (dd, *J* = 3.5; 1.8 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.77 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 167.0, 152.8, 148.2, 145.9, 145.0, 144.7, 137.6, 113.6, 113.3, 113.0, 110.8, 62.8, 16.4, 14.4. HRMS (ESI/[M+H]$^+$): calcd for $C_{14}H_{14}N_3O_3^+$: 272.1030; Found 272.1030.

Ethyl (*E*)-5-methyl-7-styrylimidazo[1,2-*a*]pyrimidine-6-carboxylate (5g)



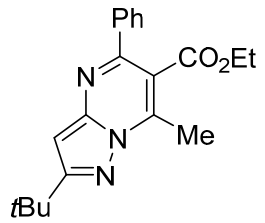
Synthesized according to General Procedure D: (1*E*,2*E*)-*N*-(1*H*-Imidazol-2-yl)-3-phenylprop-2-en-1-imine **1i** (59 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (30%, then 40% acetone/hexanes) afforded **5g** (46 mg, 50%) as a yellow solid. FTIR (neat) 1719, 1600, 1195, 1147, 1060, 687 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 8.03 (d, *J* = 15.4 Hz, 1H), 7.94–7.88 (m, 2H), 7.71–7.67 (m, 2H), 7.45–7.40 (m, 2H), 7.39–7.32 (m, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.81 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 166.9, 152.8, 148.0, 145.5, 138.1, 136.9, 136.1, 130.2, 129.8, 128.6, 123.8, 116.4, 110.9, 63.1, 16.9, 14.5. HRMS (ESI/$[M+H]^+$): calcd for $C_{18}H_{18}N_3O_2^+$: 308.1394; Found 308.1394.

Ethyl 4-methyl-2-phenylpyrimido[1,2-*b*]indazole-3-carboxylate (5h)



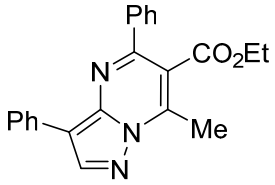
Synthesized according to General Procedure D: (*E*)-*N*-(2*H*-Indazol-3-yl)-1-phenylmethanimine **1j** (66 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 100 °C. Purification by silica gel column chromatography (5%, then 10%, then 30% ethyl acetate/hexanes) afforded **5h** (61 mg, 61%) as a yellow crystalline solid. FTIR (neat) 1718, 1634, 1267, 1181, 755 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 8.28–8.21 (m, 1H), 7.87–7.80 (m, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.69–7.61 (m, 1H), 7.60–7.49 (m, 3H), 7.35–7.26 (m, 1H), 4.26 (q, *J* = 7.5 Hz, 2H), 3.03 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 167.1, 152.7, 152.6, 145.4, 143.1, 139.8, 130.9, 130.2, 129.3, 129.2, 121.8, 121.7, 118.7, 117.4, 114.7, 62.9, 15.8, 13.9. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{18}N_3O_2^+$: 332.1394; Found 332.1393.

Ethyl 2-(*tert*-butyl)-7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidine-6-carboxylate (5i)



Synthesized according to General Procedure D: (*E*)-*N*-(3-(*tert*-Butyl)-1*H*-pyrazol-5-yl)-1-phenylmethanimine **1k** (73 mg, 94% mass purity, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (123 mg, 1.20 mmol, 4.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 120 °C. Purification by silica gel column chromatography (2.5%, then 5% ethyl acetate/hexanes) afforded **5i** (43 mg, 43%) as a yellow oil. FTIR (neat) 2962, 1720, 1606, 1290, 1192, 1157, 1053, 781, 696 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.61–7.55 (m, 2H), 7.46–7.39 (m, 3H), 6.59 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.92 (s, 3H), 1.43 (s, 9H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 169.5, 167.2, 155.8, 148.0, 146.5, 139.7, 129.2, 128.5, 128.0, 113.4, 94.2, 61.9, 33.3, 30.5, 15.1, 13.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{24}N_3O_2^+$: 338.1863; Found 338.1863.

Ethyl 7-methyl-3,5-diphenylpyrazolo[1,5-*a*]pyrimidine-6-carboxylate (5j)



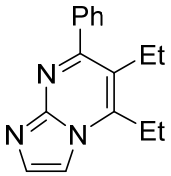
Synthesized according to General Procedure D: (*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine **1l** (74 mg, 0.30 mmol, 1.0 equiv), ethyl diazoacetoacetate **4** (62 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), pivalic acid (123 mg, 1.20 mmol, 4.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The reaction mixture was stirred at 120 °C. Purification by silica gel column chromatography (10%, then 20% ethyl acetate/hexanes) afforded **5j** (101 mg, 94%) as a yellow solid. FTIR (neat) 1712, 1601, 1180, 1049, 766, 694 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.16–8.07 (m, 2H), 7.76–7.68 (m, 2H), 7.51–7.47 (m, 3H), 7.47–7.42 (m, 2H), 7.27 (tt, J = 7.3; 1.3 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.97 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 167.0, 156.1, 146.6, 144.1, 143.7, 139.4, 131.9, 129.6, 128.9, 128.6, 128.3, 126.6, 126.5, 114.6, 111.7, 62.2, 15.1, 13.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{22}H_{20}N_3O_2^+$: 358.1550; Found 358.1550.

7. Synthesis and Characterization of Heterocycles 7

General Procedure E: Rh(III)-catalyzed coupling of imines with alkynes

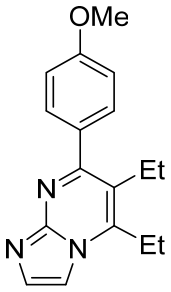
To a flame-dried microwave tube in a glove box was added the imine (**1**, 1.0 equiv), the alkyne (**6**, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.1 equiv), $Cu(OAc)_2•H_2O$ (2.2 equiv), and trifluoroethanol (0.1 M). The tube was capped and the reaction mixture was stirred at the indicated temperature for the indicated amount of time. The reaction mixture was cooled to rt and concentrated. The crude reside was diluted with 28% aq. NH_3 (10 mL) and brine (10 mL) and extracted with CH_2Cl_2 (4 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography.

5,6-Diethyl-7-phenylimidazo[1,2-*a*]pyrimidine (7a)



Synthesized according to General Procedure E: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (50% acetone/hexanes) afforded **7a** (48 mg, 65%) as a white crystalline solid. FTIR (neat) 3105, 2973, 1606, 1505, 1282, 702 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.64–7.38 (m, 6H), 3.09 (q, *J* = 7.6 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.40 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 161.2, 148.2, 146.0, 139.8, 135.9, 128.6, 128.5, 128.3, 119.8, 107.7, 22.7, 21.3, 15.7, 10.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{16}H_{18}N_3^+$: 252.1495; Found 252.1498.

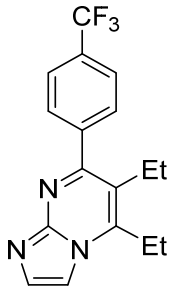
5,6-Diethyl-7-(4-methoxyphenyl)imidazo[1,2-*a*]pyrimidine (7b)



Synthesized according to General Procedure E: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-(4-methoxyphenyl)methanimine **1b** (60 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (50%, then 60% acetone/hexanes) afforded **7b** (58 mg, 69%) as a white solid. FTIR (neat) 3125, 2973, 1599, 1244, 1023, 640 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 7.84 (d, *J* = 1.5 Hz, 1H), 7.71 (d, *J* = 1.5 Hz, 1H), 7.53–7.49 (m, 2H), 7.09–7.02 (m, 2H), 3.88 (s, 3H), 3.21 (q, *J* = 7.6 Hz, 2H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.39 (t, *J* = 7.6

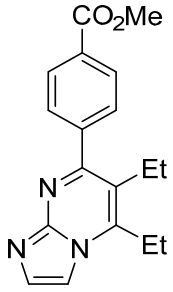
Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 161.1, 160.8, 148.7, 147.1, 135.9, 133.6, 130.8, 120.2, 114.2, 108.9, 55.6, 22.9, 21.7, 15.8, 11.0. HRMS (ESI/$[M+H]^+$): calcd for $C_{17}H_{20}N_3O^+$: 282.1601; Found 282.1602.

5,6-Diethyl-7-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyrimidine (7c)



Synthesized according to General Procedure E: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-(4-(trifluoromethyl)phenyl)methanimine **1c** (72 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (40%, then 50% acetone/hexanes) afforded **7c** (67 mg, 70%) as a white solid. FTIR (neat) 2938, 1495, 1323, 1120, 1106, 1068, 856 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$) δ 7.94 (bs, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.81 (bs, 1H), 7.80 (d, J = 8.0 Hz, 2H), 3.26 (q, J = 7.6 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.41 (t, J = 7.6 Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$) δ 159.8, 147.8, 145.2, 136.4, 130.6 (q, J = 32.9 Hz), 130.2, 125.9 (q, J = 3.6 Hz), 125.3, (q, J = 271.3 Hz), 119.9, 109.5, 23.0, 21.6, 15.7, 10.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ –63.0. HRMS (ESI/$[M+H]^+$): calcd for $C_{17}H_{17}F_3N_3^+$: 320.1369; Found 320.1369.

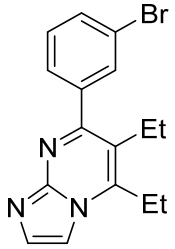
Methyl 4-(5,6-diethylimidazo[1,2-*a*]pyrimidin-7-yl)benzoate (7d)



Synthesized according to General Procedure E: Methyl (*E*)-4-(((1*H*-Imidazol-2-yl)imino)methyl)benzoate **1d** (69 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **7d** (77 mg, 83%) as a white solid. FTIR (neat) 1722, 1279, 1103, 763 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 2H), 7.86 (s, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.53 (s, 1H), 3.95 (s, 3H), 3.09 (q, J = 7.6 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 1.41 (t, J = 7.6 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 166.9, 160.0, 147.8, 146.2, 144.1, 136.2, 130.3, 129.6, 128.8, 119.6,

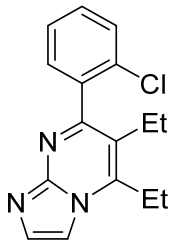
107.8, 52.4, 22.7, 21.2, 15.7, 10.7. HRMS (ESI/[M+H]$^+$): calcd for $C_{18}H_{20}N_3O_2^+$: 310.1550; Found 310.15490.

7-(3-Bromophenyl)-5,6-diethylimidazo[1,2-*a*]pyrimidine (7e)



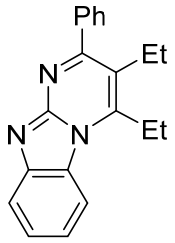
Synthesized according to General Procedure E: (*E*)-1-(3-Bromophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine **1e** (75 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (25 mg, 0.03 mmol, 0.10 equiv), Cu(OAc)$_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (30%, then 50% acetone/hexanes) afforded **7e** (68 mg, 68%) as a white solid. FTIR (neat) 3123, 1596, 1499, 1283, 1252, 1145, 1053, 763 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.68 (t, *J* = 2.0 Hz, 1H), 7.58 (ddd, *J* = 7.9; 2.0; 1.1 Hz, 1H), 7.52 (s, 1H), 7.45 (dt, *J* = 7.9; 1.1 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 3.09 (q, *J* = 7.6 Hz, 2H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.41 (t, *J* = 7.6 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 159.4, 147.8, 146.3, 141.7, 136.2, 131.8, 129.9, 127.3, 122.4, 119.6, 107.8, 22.7, 21.3, 15.8, 10.7. HRMS (ESI/[M+H]$^+$): calcd for $C_{16}H_{17}BrN_3^+$: 330.0600 and 332.0580; Found 330.0599 and 332.0581.

7-(2-Chlorophenyl)-5,6-diethylimidazo[1,2-*a*]pyrimidine (7f)



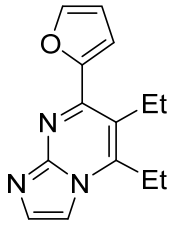
Synthesized according to General Procedure E: (*E*)-1-(2-Chlorophenyl)-*N*-(1*H*-imidazol-2-yl)methanimine **1f** (75 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (25 mg, 0.03 mmol, 0.10 equiv), Cu(OAc)$_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (25%, then 50% acetone/hexanes) afforded **7f** (41 mg, 47%) as a white solid. FTIR (neat) 2970, 2934, 1604, 1501, 1282, 1148, 727, 700 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.55 (d, *J* = 1.4 Hz, 1H), 7.49–7.45 (m, 1H), 7.42–7.35 (m, 3H), 3.09 (q, *J* = 7.6 Hz, 2H), 2.64 (dq, *J* = 14.9; 7.6 Hz, 1H), 2.49 (dq, *J* = 14.9; 7.6 Hz, 1H), 1.43 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 159.1, 147.9, 145.8, 138.4, 135.9, 132.6, 130.5, 130.0, 129.6, 126.9, 120.6, 107.9, 22.7, 21.3, 15.8, 10.7. HRMS (ESI/[M+H]$^+$): calcd for $C_{16}H_{17}ClN_3^+$: 286.1106; Found 286.1108.

3,4-Diethyl-2-phenylbenzo[4,5]imidazo[1,2-*a*]pyrimidine (7g)



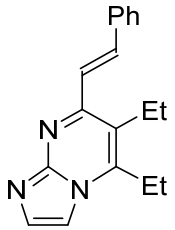
Synthesized according to General Procedure E: (*E*)-N-(1*H*-Benzo[*d*]imidazol-2-yl)-1-phenylmethanimine **1g** (66 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (10, then 20, then 30% Et_2O/CH_2Cl_2) afforded **7g** (84 mg, 93%) as a yellow crystalline solid. FTIR (neat) 2964, 2932, 1590, 1490, 1307, 723, 702 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.58–7.54 (m, 2H), 7.51 (ddd, *J* = 8.4; 7.1; 1.1 Hz, 1H), 7.48–7.39 (m, 3H), 7.32 (ddd, *J* = 8.4; 7.1; 1.1 Hz, 1H), 3.42 (q, *J* = 7.6 Hz, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.51 (t, *J* = 7.6 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 166.2, 150.7, 150.6, 145.6, 139.6, 128.9, 128.4, 128.2, 127.1, 125.6, 121.4, 120.5, 118.6, 115.0, 22.5, 21.0, 15.8, 11.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{20}N_3^+$: 302.1652; Found 302.1653.

5,6-Diethyl-7-(furan-2-yl)imidazo[1,2-*a*]pyrimidine (7h)



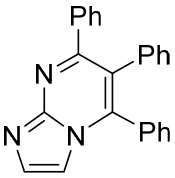
Synthesized according to General Procedure E: (*E*)-1-(Furan-2-yl)-*N*-(1*H*-imidazol-2-yl)methanimine **1h** (48 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (30%, then 50% acetone/hexanes) afforded **7h** (51 mg, 71%) as a yellow oil. FTIR (neat) 2975, 2931, 1599, 1512, 1454, 1153, 1011, 744 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.4 Hz, 1H), 7.61 (dd, *J* = 1.8; 0.9 Hz, 1H), 7.47 (d, *J* = 1.4 Hz, 1H), 7.32 (dd, *J* = 3.5; 0.9 Hz, 1H), 6.58 (dd, *J* = 3.5; 1.8 Hz, 1H), 3.08 (q, *J* = 7.5 Hz, 2H), 3.04 (q, *J* = 7.5, 2H), 1.38 (t, *J* = 7.5 Hz, 3H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 153.6, 148.7, 148.3, 146.2, 144.1, 136.3, 118.7, 114.0, 112.2, 107.8, 22.4, 21.0, 15.8, 10.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{14}H_{16}N_3O^+$: 242.1288; Found 242.1290.

(*E*)-5,6-Diethyl-7-styrylimidazo[1,2-*a*]pyrimidine (7i)



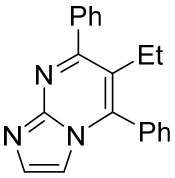
Synthesized according to General Procedure E: (1*E*,2*E*)-*N*-(1*H*-Imidazol-2-yl)-3-phenylprop-2-en-1-imine **1i** (59 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 μL, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (25%, then 40% acetone/hexanes) afforded **7i** (62 mg, 75%) as a yellow oil. FTIR (neat) 2968, 1592, 1514, 1449, 718, 691 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 15.4 Hz, 1H), 7.80 (s, 1H), 7.64–7.61 (m, 2H), 7.45 (s, 1H), 7.42–7.37 (m, 2H), 7.36–7.31 (m, 2H), 3.04 (q, *J* = 7.7 Hz, 2H), 2.86 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.7 Hz, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 154.6, 148.5, 144.9, 137.9, 136.7, 135.8, 129.0, 128.9, 127.8, 122.2, 119.4, 107.7, 22.5, 20.5, 15.7, 10.9. HRMS (ESI/$[M+H]^+$): calcd for $C_{18}H_{20}N_3^+$: 278.1652; Found 278.1652.

5,6,7-Triphenylimidazo[1,2-*a*]pyrimidine (7j)



Synthesized according to General Procedure E: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), diphenylacetylene **6b** (80 mg, 0.45 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (25 mg, 0.03 mmol, 0.10 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (40% acetone/hexanes) afforded **7j** (79 mg, 75%) as a white crystalline solid. FTIR (neat) 1476, 1262, 1145, 763, 694 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.76 (bs, 1H), 7.41–7.31 (m, 5H), 7.27–7.19 (m, 4H), 7.18–7.14 (m, 2H), 7.09–7.01 (m, 3H), 6.91–6.87 (m, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 159.2, 148.6, 144.1, 138.9, 135.8, 135.3, 131.7, 131.6, 130.0, 129.9, 129.2, 129.0, 128.6, 128.0, 127.7, 127.3, 121.4, 109.7. HRMS (ESI/$[M+H]^+$): calcd for $C_{24}H_{18}N_3^+$: 348.1495; Found 348.1495.

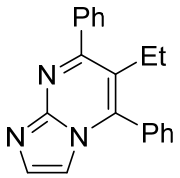
6-Ethyl-5,7-diphenylimidazo[1,2-*a*]pyrimidine (7k)



Synthesized according to General Procedure E: (*E*)-*N*-(1*H*-Imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 1-phenyl-1-butyne **6c** (64 μL, 0.45 mmol, 1.5 equiv),

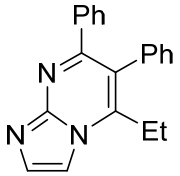
[Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (25 mg, 0.03 mmol, 0.10 equiv), Cu(OAc)$_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The reaction mixture was stirred at 60 °C for 16 h. Purification by silica gel column chromatography (25%, then 40% acetone/hexanes) afforded **7k** (70 mg, 78%) as mixture of regioisomers in a 2.8:1 ratio. The mixture appeared as a yellow oil. The two isomers would partially overlap; however, it was found that by preparative TLC (50% acetone/hexanes), it was possible to obtain each isomer for analysis. The structures were assigned by ^{1}H-NMR NOESY experiments.

6-Ethyl-5,7-diphenylimidazo[1,2-*a*]pyrimidine (7ka)



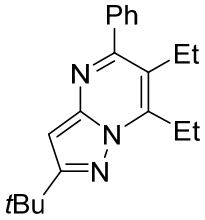
Major isomer, R_f (50% acetone/hexanes) = 0.53. FTIR (neat) 2921, 1482, 1259, 696 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.67–7.57 (m, 5H), 7.52–7.39 (m, 5H), 6.96 (s, 1H), 2.57 (q, J = 7.5 Hz, 2H), 0.76 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 161.5, 148.1, 143.7, 139.6, 135.3, 131.8, 130.4, 129.8, 128.8, 128.67, 128.65, 128.4, 121.1, 109.5, 21.8, 15.1. HRMS (ESI/[M+H]$^+$): calcd for $C_{20}H_{18}N_3^+$: 300.1495; Found 300.1495.

5-Ethyl-6,7-diphenylimidazo[1,2-*a*]pyrimidine (7kb)



Minor isomer, R_f (50% acetone/hexanes) = 0.40. FTIR (neat) 2919, 1486, 1267, 695 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.56 (s, 1H), 7.39–7.30 (m, 5H), 7.24–7.09 (m, 5H), 2.88 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 159.0, 148.6, 146.6, 139.0, 136.3, 135.9, 131.0, 130.0, 128.7, 128.5, 128.0, 127.7, 121.1, 108.1, 23.7, 10.8. HRMS (ESI/[M+H]$^+$): calcd for $C_{20}H_{18}N_3^+$: 300.1495; Found 300.1495.

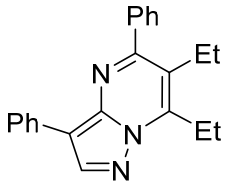
2-(*tert*-Butyl)-6,7-diethyl-5-phenylpyrazolo[1,5-*a*]pyrimidine (7l)



Synthesized according to General Procedure E: (*E*)-*N*-(3-(*tert*-Butyl)-1*H*-pyrazol-5-yl)-1-phenylmethanimine **1k** (73 mg, 94% purity by mass, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), [Cp*RhCl$_2$]$_2$ (9 mg, 0.015 mmol, 0.05 equiv), AgOAc (110 mg, 0.66 mmol, 2.2 equiv), pivalic acid (123 mg, 1.20 mmol, 4.0 equiv), and tetrahydrofuran (3 mL). The reaction mixture was stirred at 100 °C for 16 h. Purification by silica gel column chromatography (2.5%,

then 5% ethyl acetate/hexanes) afforded **7l** (42 mg, 46%) as a yellow oil. FTIR (neat) 2960, 1602, 1501, 1358, 798, 701 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.48–7.39 (m, 5H), 6.46 (s, 1H), 3.29 (q, *J* = 7.5 Hz, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 3H), 1.43 (s, 9H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 167.2, 159.5, 148.4, 147.3, 140.4, 128.42, 128.39, 128.35, 118.2, 92.1, 33.0, 30.7, 21.3, 21.2, 15.9, 11.3. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{26}N_3^+$: 308.2121; Found 308.2122.

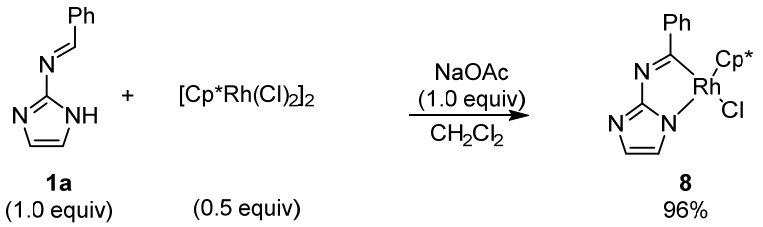
6,7-Diethyl-3,5-diphenylpyrazolo[1,5-*a*]pyrimidine (7m)



Synthesized according to General Procedure E: (*E*)-1-Phenyl-*N*-(4-phenyl-1*H*-pyrazol-5-yl)methanimine **1l** (74 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (9 mg, 0.015 mmol, 0.05 equiv), AgOAc (110 mg, 0.66 mmol, 2.2 equiv), pivalic acid (123 mg, 1.20 mmol, 4.0 equiv), and tetrahydrofuran (3 mL). The reaction mixture was stirred at 100 °C for 16 h. Purification by silica gel column chromatography (5% ethyl acetate/hexanes) afforded **7m** (81 mg, 83%) as a yellow solid. FTIR (neat) 2978, 1602, 1496, 1300, 763, 693 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.10 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.61–7.55 (m, 2H), 7.54–7.44 (m, 3H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.21 (tt, *J* = 7.3; 1.3 Hz, 1H), 3.35 (q, *J* = 7.5 Hz, 2H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.48 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 160.2, 148.6, 143.4, 141.9, 140.3, 132.7, 128.8, 128.7, 128.3, 126.2, 125.9, 119.7, 110.2, 21.4, 21.3, 15.7, 11.6. HRMS (ESI/$[M+H]^+$): calcd for $C_{22}H_{22}N_3^+$: 328.1808; Found 328.1807.

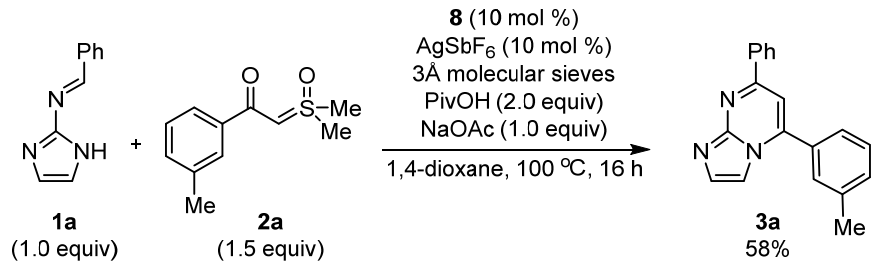
8. Experiments with Rhodacycle 8

Generation of Rh(III) imine complex



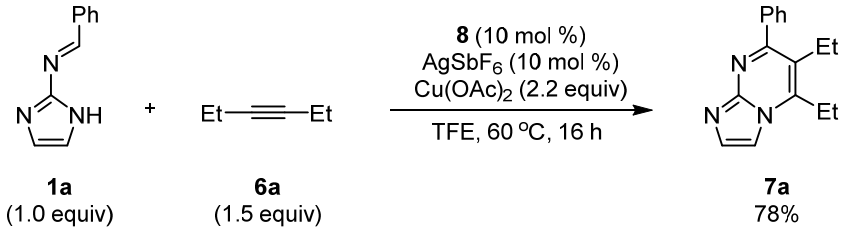
To a flame-dried microwave tube in a glove box was added (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine (34 mg, 0.20 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (62 mg, 0.10 mmol, 0.5 equiv), NaOAc (16 mg, 0.20 mmol, 1.0 equiv) and dichloromethane (5 mL). The tube was capped, and the reaction mixture was stirred at 40 °C for 18 h. The reaction mixture was cooled to ambient temperature, and the mixture was filtered through a pad of dry celite into a 20 mL vial inside the glovebox. The solvent was slowly removed to yield the desired complex (85 mg, 96%) as a brown solid. FTIR (neat) 1707, 1563, 1450, 1022, 699 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.81–7.78 (m, 2H), 7.46–7.39 (m, 3H), 6.93 (d, *J* = 1.7 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 1.47 (s, 15H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 159.1 (d, *J* = 1.9 Hz), 146.6, 129.53, 129.52 (d, *J* = 113.3 Hz) 127.8, 127.2, 123.3, 115.5, 97.1 (d, *J* = 6.2 Hz), 9.1. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{24}ClN_3Rh^+$: 444.0708; Found 444.0707.

Reaction of imine 1a and sulfoxonium ylide 2a



To a flame-dried microwave tube in a glove box was added (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (95 mg, 0.45 mmol, 1.5 equiv), rhodacycle **8a** (13 mg. 0.03 mmol, 0.1 equiv), $AgSbF_6$ (10 mg, 0.03 mmol, 0.1 equiv), pivalic acid (61 mg, 0.60 mmol, 2.0 equiv), sodium acetate (25 mg, 0.30 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (3 mL). The tube was capped, and the reaction mixture was stirred at 100 °C for 16 h. The reaction mixture was cooled to ambient temperature and filtered through a plug of Celite with dichloromethane. The solvent was removed *in vacuo* and the crude reaction mixture was subjected to silica gel column chromatography (40% acetone/hexanes) to afford **3a** (50 mg, 58%) as a yellow foam. Spectroscopic data agreed with that reported above.

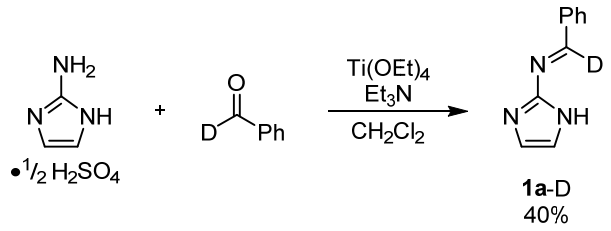
Reaction of imine 1a and alkyne 6a



To a flame-dried microwave tube in a glove box was added (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine **1a** (51 mg, 0.30 mmol, 1.0 equiv), 3-hexyne **6a** (51 µL, 0.45 mmol, 1.5 equiv), rhodacycle **8a** (13 mg. 0.03 mmol, 0.1 equiv), $AgSbF_6$ (10 mg, 0.03 mmol, 0.1 equiv), $Cu(OAc)_2$ (120 mg, 0.66 mmol, 2.2 equiv), and trifluoroethanol (3 mL). The tube was capped and the reaction mixture was stirred at 60 °C for 16 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The crude reside was diluted with 28% aq. NH_3 (10 mL) and brine (10 mL) and extracted with CH_2Cl_2 (4 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography (50% acetone/hexanes) to afford **7a** (59 mg, 78%) as a white crystalline solid. Spectroscopic data agreed with that reported above.

9. Studies with Deuterated 1a-D

Synthesis of Azolo imine 1a-D

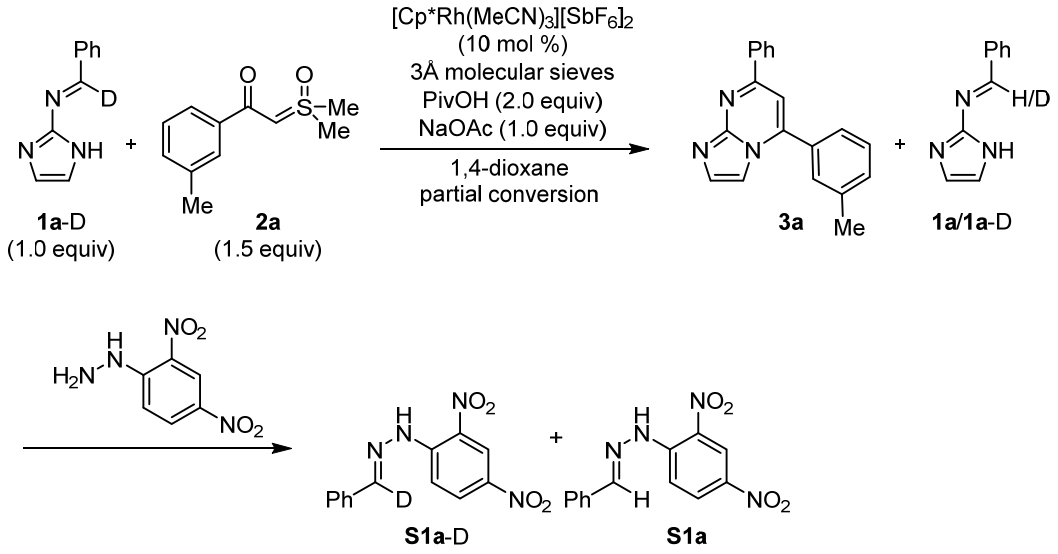


To a solution of deuterobenzaldehyde (278 mg, 2.60 mmol, 1.0 equiv) in dichloromethane (8 mL) were added sequentially 2-aminoimidazole sulfate (344 mg, 2.60 mmol, 1.0 equiv), titanium(IV) ethoxide (0.87 mL, 4.2 mmol, 1.6 equiv), and triethylamine (0.73 mL, 5.2 mmol, 2 equiv). The reaction mixture was stirred at ambient temperature for 18 h. The reaction was quenched with H_2O (2 x volume of dichloromethane). The resulting solid was filtered and washed with dichloromethane. The filtrate was transferred to a separatory funnel, and the layers were separated. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then the crude material was filtered through a plug of silica with 50% EtOAc/hexanes. Subsequently, the imine was recrystallized in EtOAc/hexanes to afford (*E*)-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine-d **1a**-D (179 mg, 40%) as an off-white solid. FTIR (neat) 1593, 1575, 1542, 1450, 1231, 1107, 995, 738, 688, 581 cm^{-1}. ^{1}H-NMR (600 MHz, $(CD_3)_2SO$) δ 12.31 (br s, 1H), 7.95 (d, J = 7.3 Hz, 2H), 7.57–7.50 (m, 3H), 7.15 (s, 1H), 6.91 (s, 1H). ^{13}C-NMR (150 MHz, $(CD_3)_2SO$) δ 158.9 (t, J = 25.0 Hz), 150.6, 135.6, 131.7, 129.0, 128.6, 127.6, 116.9. HRMS (ESI/$[M+H]^+$): calcd for $C_{10}H_9DN_3^+$: 173.0932; Found 173.0927.

Determination of Deuterium/Protium Exchange

Exchange experiments were performed using an indirect mass spectrometric assay. Reactions were run to partial conversion, then treated with (2,4-dinitrophenyl)hydrazine until all remaining imine **1a**/**1a**-D had converted to protio- or deutero-(*Z*)-1-benzylidene-2-(2,4-dinitrophenyl)hydrazine **S1a**/**S1a**-D (Scheme S1). The ratio of isomers **S1a**/**S1a**-D was determined on the crude reaction mixture by LC/MS.

Scheme S1. Experimental Design for Exchange Studies



Reaction Procedure

To a flame-dried microwave tube in a glove box was added (*E*)-1-deutero-*N*-(1*H*-imidazol-2-yl)-1-phenylmethanimine **1a**-D (34 mg, 0.20 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (63 mg, 0.30 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (17 mg, 0.02 mmol, 0.10 equiv), pivalic acid (41 mg, 0.40 mmol, 2.0 equiv), sodium acetate (16 mg, 0.20 mmol, 1.0 equiv), 3Å molecular sieves (approximately 70 mg), and 1,4-dioxane (2 mL). The tube was capped, and the reaction mixture was stirred at 100 °C for 30 min (Figure S1) or 60 min (Figure S2). The reaction mixture was cooled to ambient temperature and filtered through a plug of Celite with exactly 2 mL 1,4-dioxane. The resultant solution was split in half. From the first half, the solvent was removed *in vacuo* and the crude reaction mixture was subjected to ^{1}H NMR analysis (with 1,3,5-trimethoxybenzene as an external standard) to determine conversion. The second half of the solution was treated with (2,4-dinitrophenyl)hydrazine (30% H_2O, 71 mg, 0.25 mmol, 2.5 equiv relative to starting imine), and stirred at reflux (80 °C) until TLC indicated consumption of all **1a**-D (150 minutes). The crude material was then loaded onto LC/MS and assessed for protium/deuterium exchange.

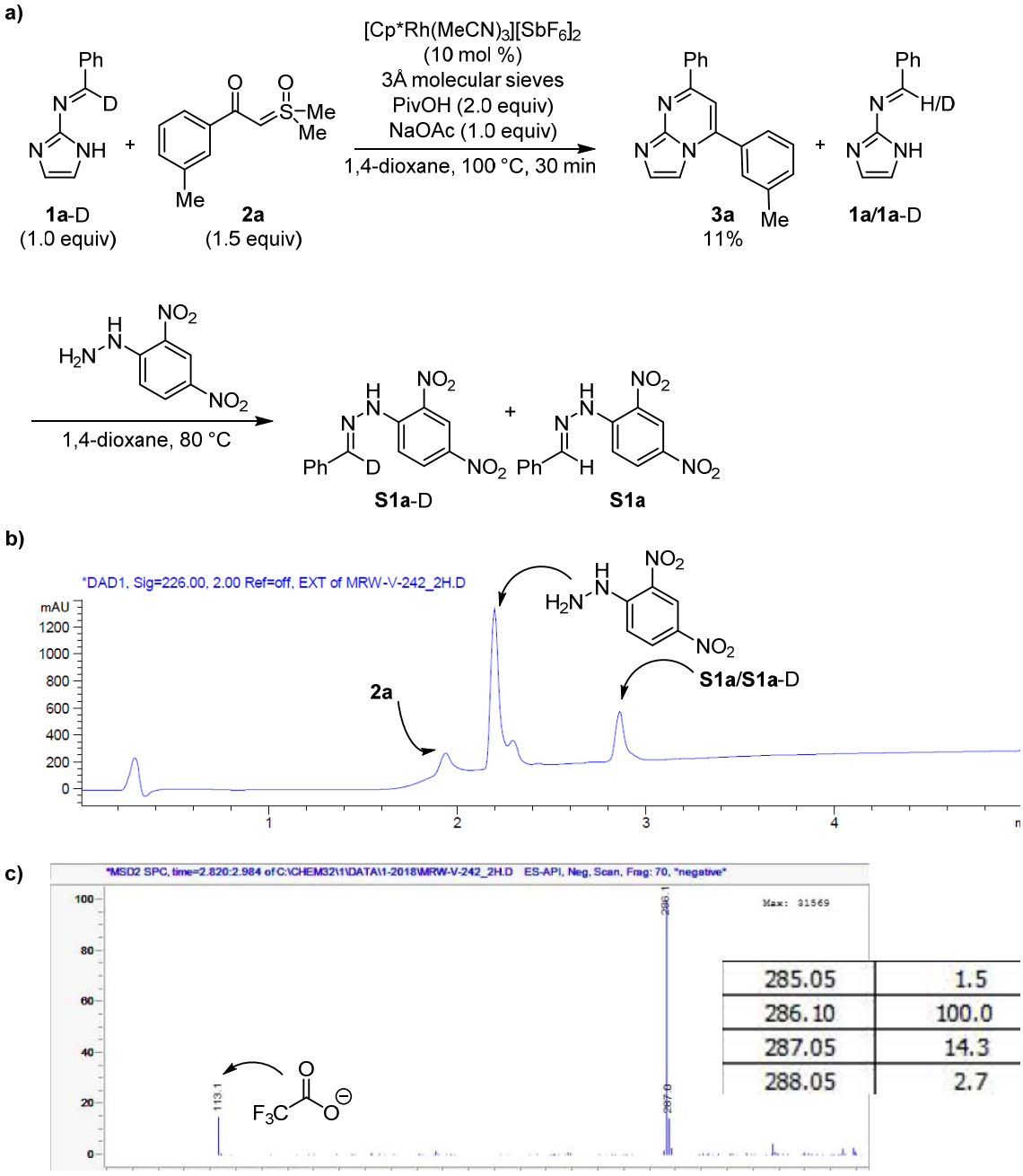


Figure S1. Reaction at 11% conversion. (a) Reaction set-up. (b) LC trace of crude reaction material at 226 nm. (c) Negative channel mass spectrum of **S1a**/**S1a**-D peak at 2.90 min with ion intensities.

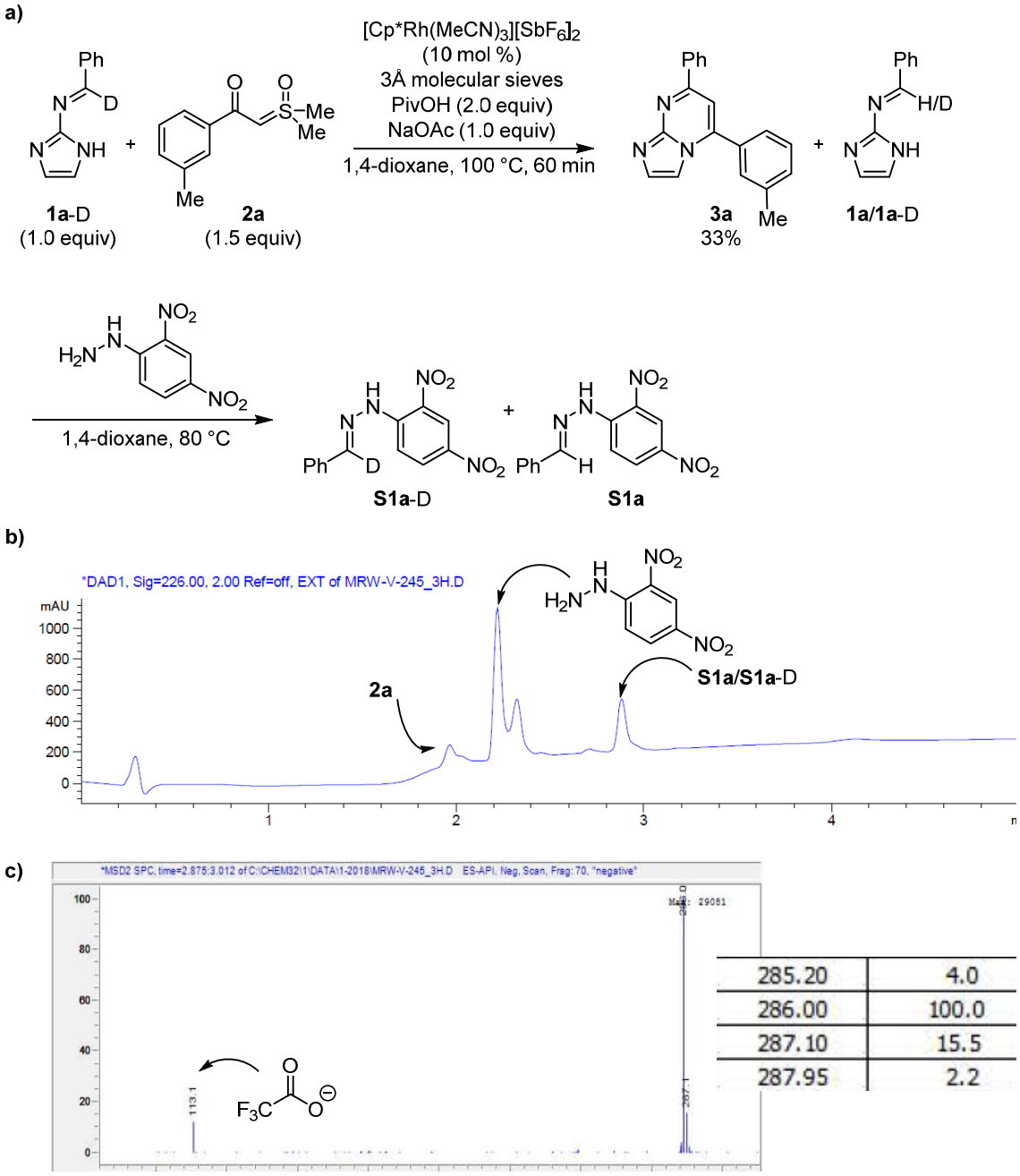


Figure S2. Reaction at 33% conversion. (a) Reaction set-up. (b) LC trace of crude reaction material at 226 nm. (c) Negative channel mass spectrum of **S1a**/**S1a**-D peak at 2.90 min with ion intensities.

Control Experiment

As a control, deuteroimine **1a**-D (17 mg, 0.10 mmol, 1.0 equiv), (2,4-dinitrophenyl)hydrazine (30% H_2O, 70 mg, 0.25 mmol, 2.5 equiv), PivOH (20 mg, 0.20 mmol, 2.0 equiv), and NaOAc (8.0 mg, 0.10 mmol, 1.0 equiv) were dissolved in 1,4-dioxane (2.0 mL) and the reaction was stirred at reflux (80 °C) until TLC indicated consumption of all **1a**-D (150 minutes). The crude material was then loaded onto LC/MS and assessed for the presence of trace protioimine **1a** (Figure S3). This revealed less than 0.3% protioimine **1a** in the deuterated sample.

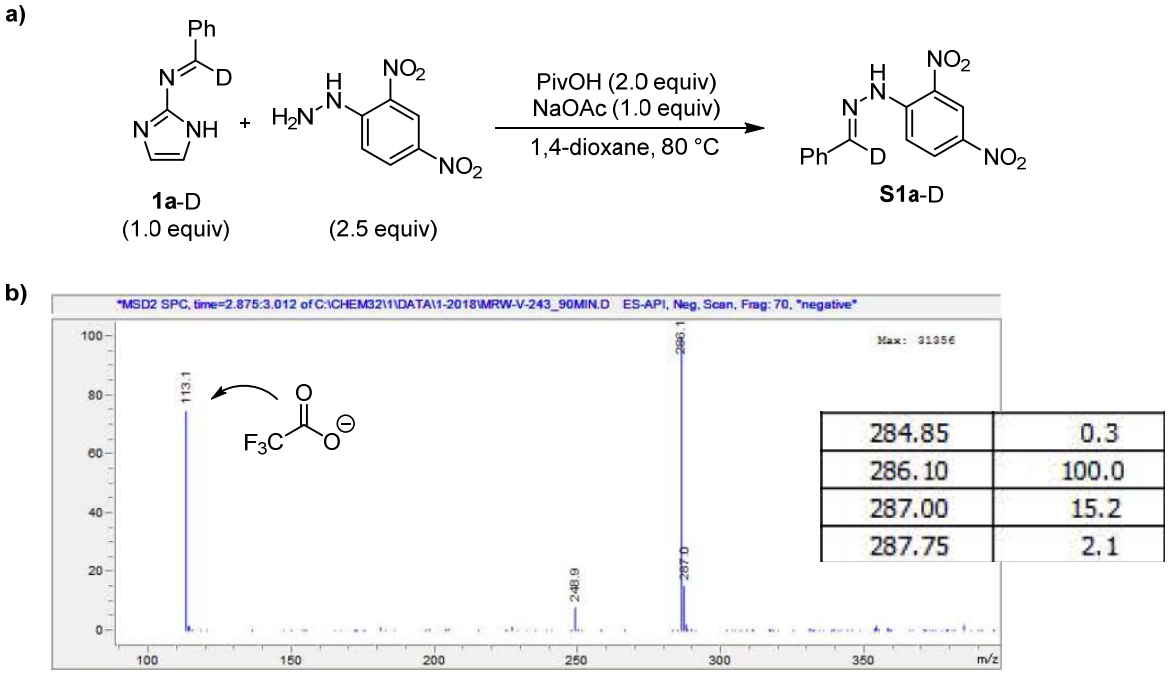
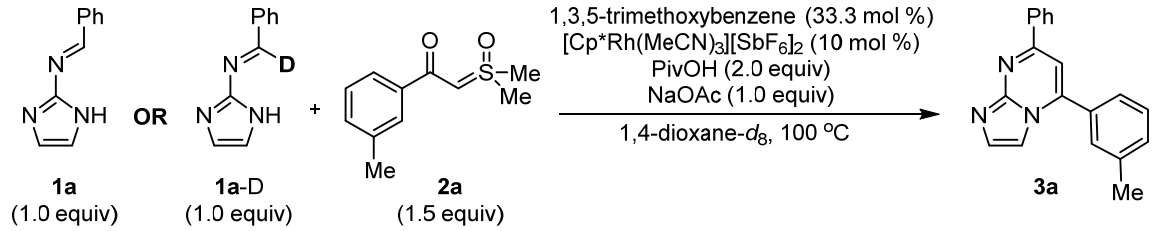


Figure S3. Reaction of **1a**-D with (2,4-dinitrophenyl)hydrazine. (a) Reaction scheme. (b) Negative channel mass spectrum of **S1a**-D peak at 2.90 min with ion intensities.

Initial Rate Measurements for Kinetic Isotope Effect Studies



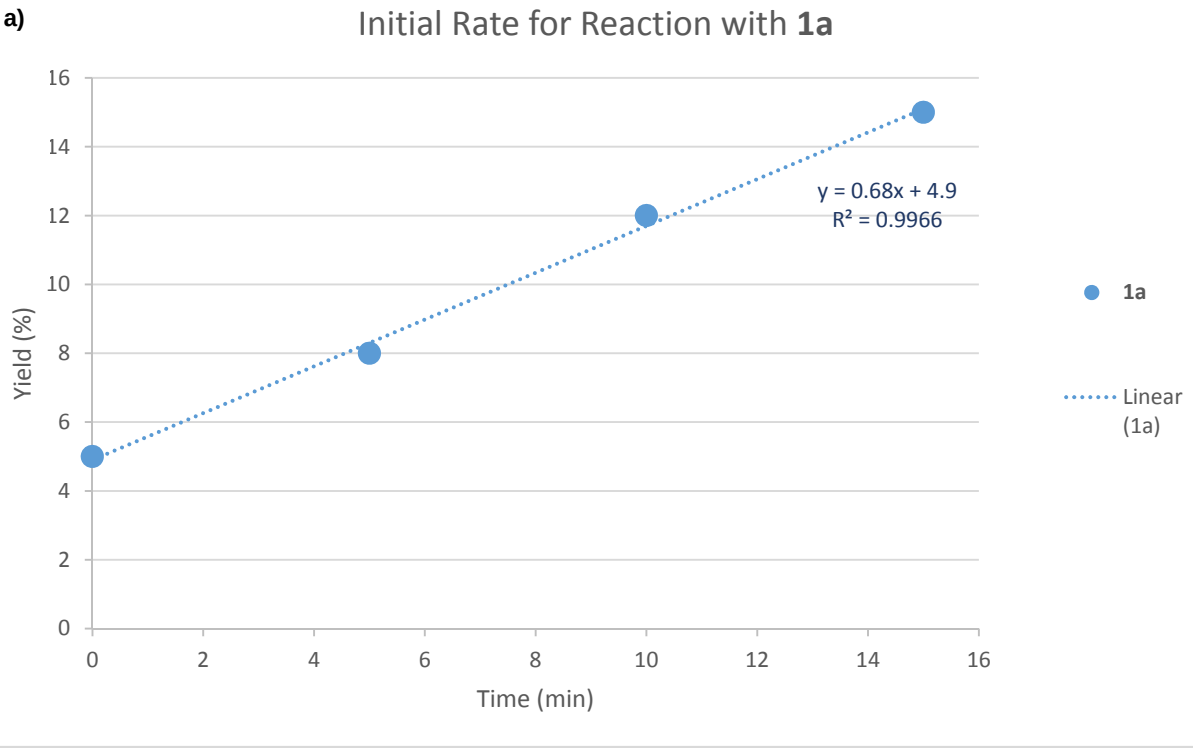
To an oven-dried J. Young NMR tube in a glove box was added imine (**1a**: 17.1 mg, 0.100 mmol, 1.0 equiv; or **1a**-D: 17.2 mg, 0.100 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(*m*-tolyl)ethan-1-one **2a** (31.5 mg, 0.150 mmol, 1.5 equiv), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 0.010 mmol, 0.10 equiv), pivalic acid (20.4 mg, 0.200 mmol, 2.0 equiv), sodium acetate (8.2 mg, 0.100 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol, 0.33 equiv), and 1,4-dioxane-d_8 (1 mL). The tube was sealed, removed from the glove box, and inserted into a 500 MHz NMR instrument that had been previously equilibrated to 100 °C. Once the magnet had been shimmed, measurements for imine disappearance, ylide disappearance, and product formation were recorded every 5 min, based on internal standard 1,3,5-trimethoxybenzene (Table S4). Each experiment was run twice. Measurements for imine consumption were not possible for **1a**-D as the diagnostic ^{1}H NMR signal for **1a** had been deuterated.

Table S4. Kinetics for Reactions of Imines **1a** and **1a**-D.

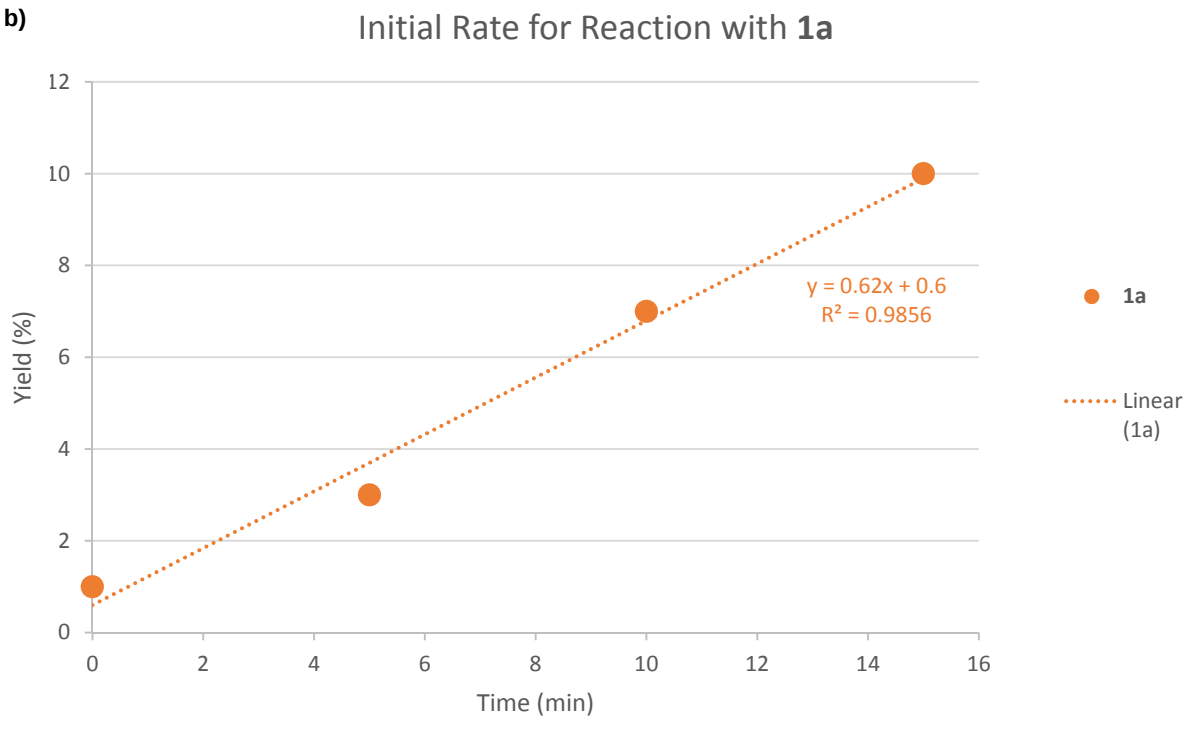
1a - Run 1				**1a** - Run 2			
Time (min)	yield (%)	**1a** (%)	**2a** (%)	Time (min)	yield (%)	**1a** (%)	**2a** (%)
0	1	82	93	0	5	95	80
5	3	83	86	5	8	92	76
10	7	78	82	10	12	87	73
15	10	76	78	15	15	79	70
20	12	74	75	20	18	80	72
1a-D - Run 1				**1a**-D - Run 2			
Time (min)	yield (%)	**1a**-D (%)	**2a** (%)	Time (min)	yield (%)	**1a**-D (%)	**2a** (%)
0	2	ND	95	0	1	ND	88
5	5	ND	91	5	3	ND	82
10	7	ND	89	10	5	ND	79
15	9	ND	86	15	7	ND	80
20	11	ND	84	20	8	ND	77

Initial rate data for each experiment was graphed and the averaged slopes of the linear fits were used to calculate a kinetic isotope effect of $k_H/k_D = 1.5 \pm 0.09$ (Figure S4).

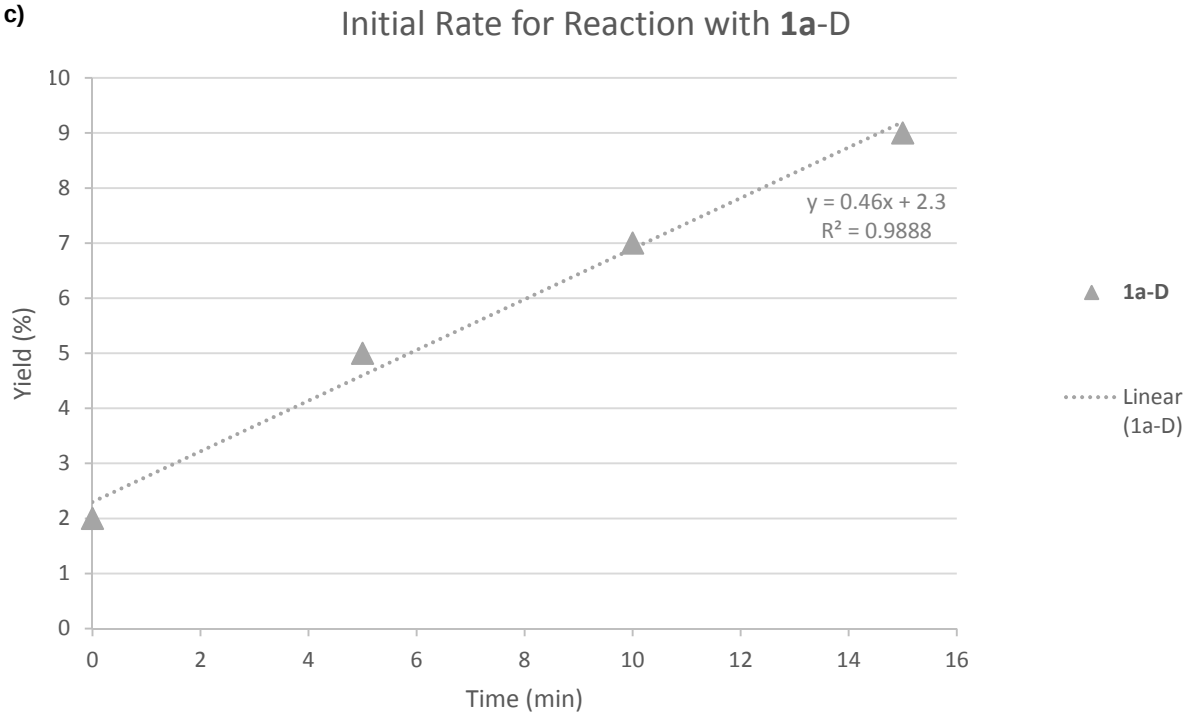
a)


Initial Rate for Reaction with 1a
Yield (%)
Time (min)
y = 0.68x + 4.9
R² = 0.9966
1a
Linear (1a)

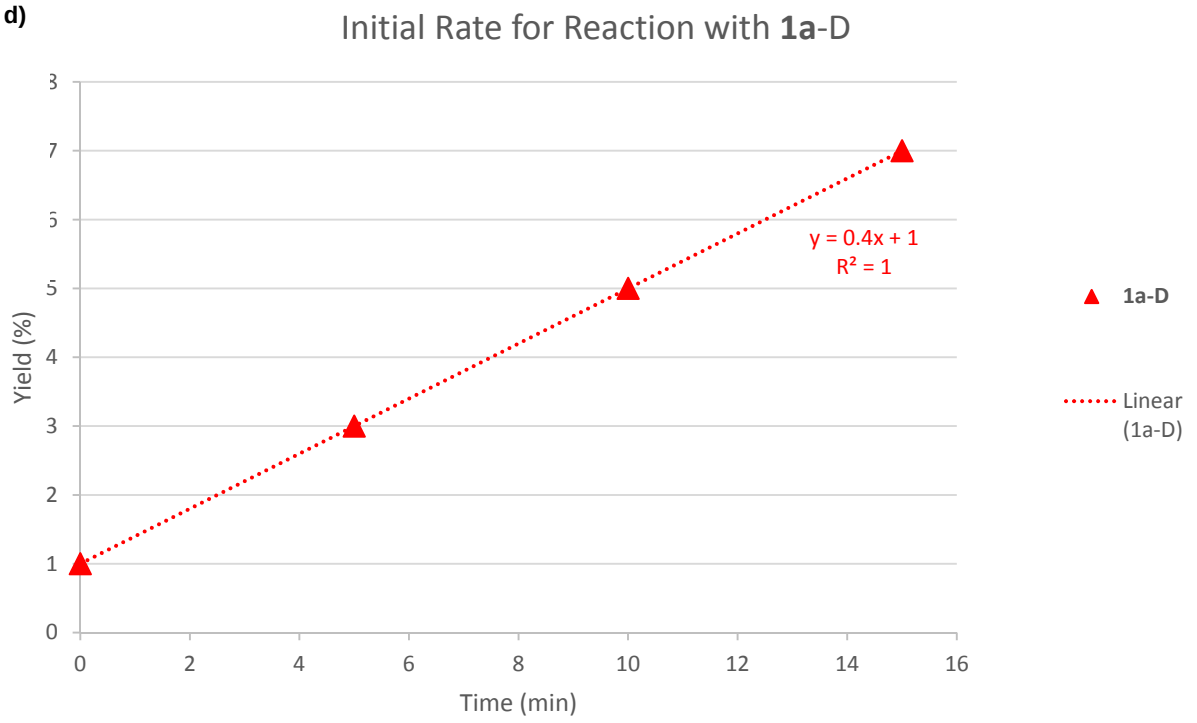
b)


Initial Rate for Reaction with 1a
Yield (%)
Time (min)
y = 0.62x + 0.6
R² = 0.9856
1a
Linear (1a)

c)



d)



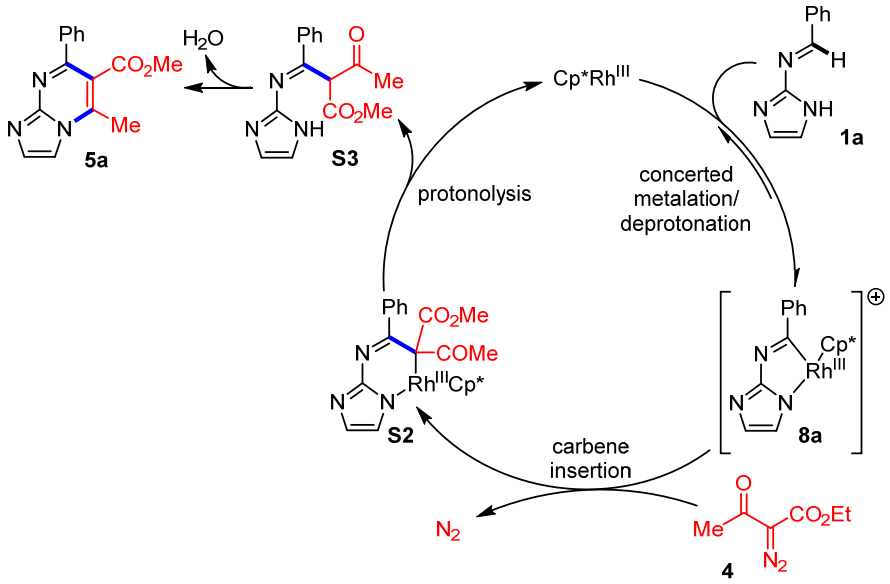
e)

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{0.65 \pm 0.021}{0.43 \pm 0.021} = 1.5 \pm 0.09$$

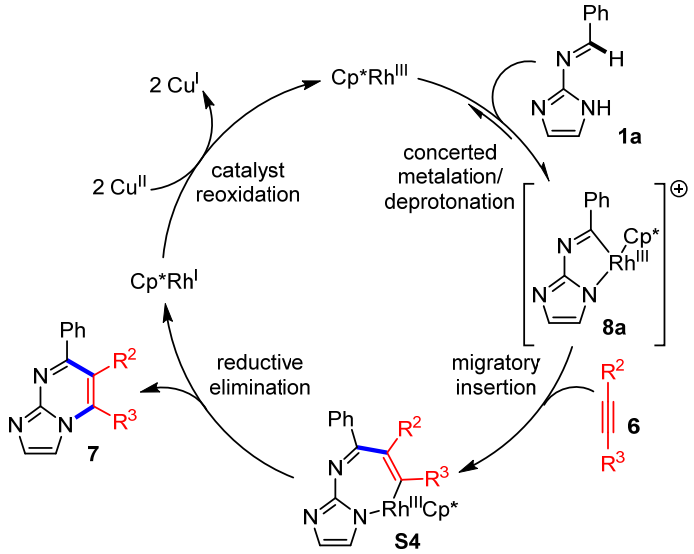
I e S4. Initial Rates for Reaction of a) and b) **1a** and c) and d) **1a**-D. e) Calculation of KIE.

10. Catalytic Cycles

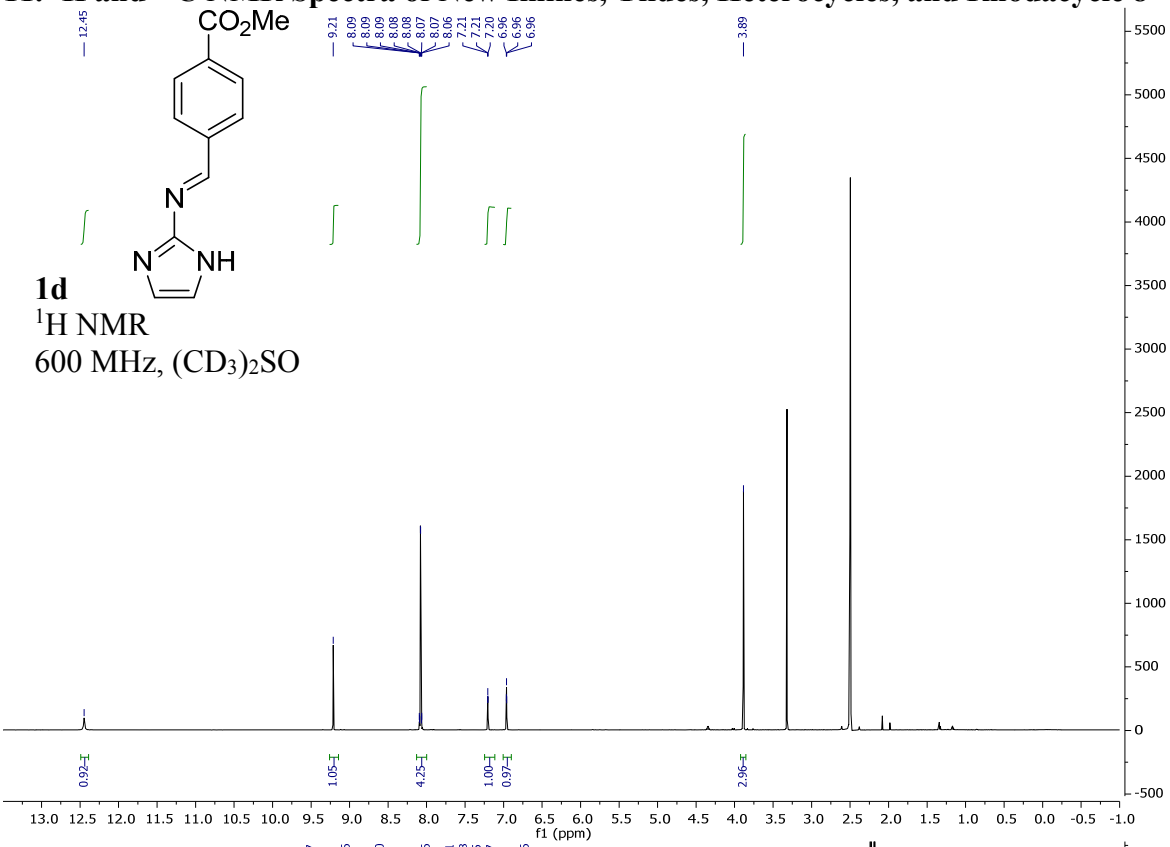
Scheme S2. Proposed Mechanism of Rhodium(III)-Catalyzed C–H Functionalizations of Iminyl Azoles with Diazoketone **4**



Scheme S3. Proposed Mechanism of Rhodium(III)-Catalyzed C–H Functionalizations of Iminyl Azoles with Alkynes **6**



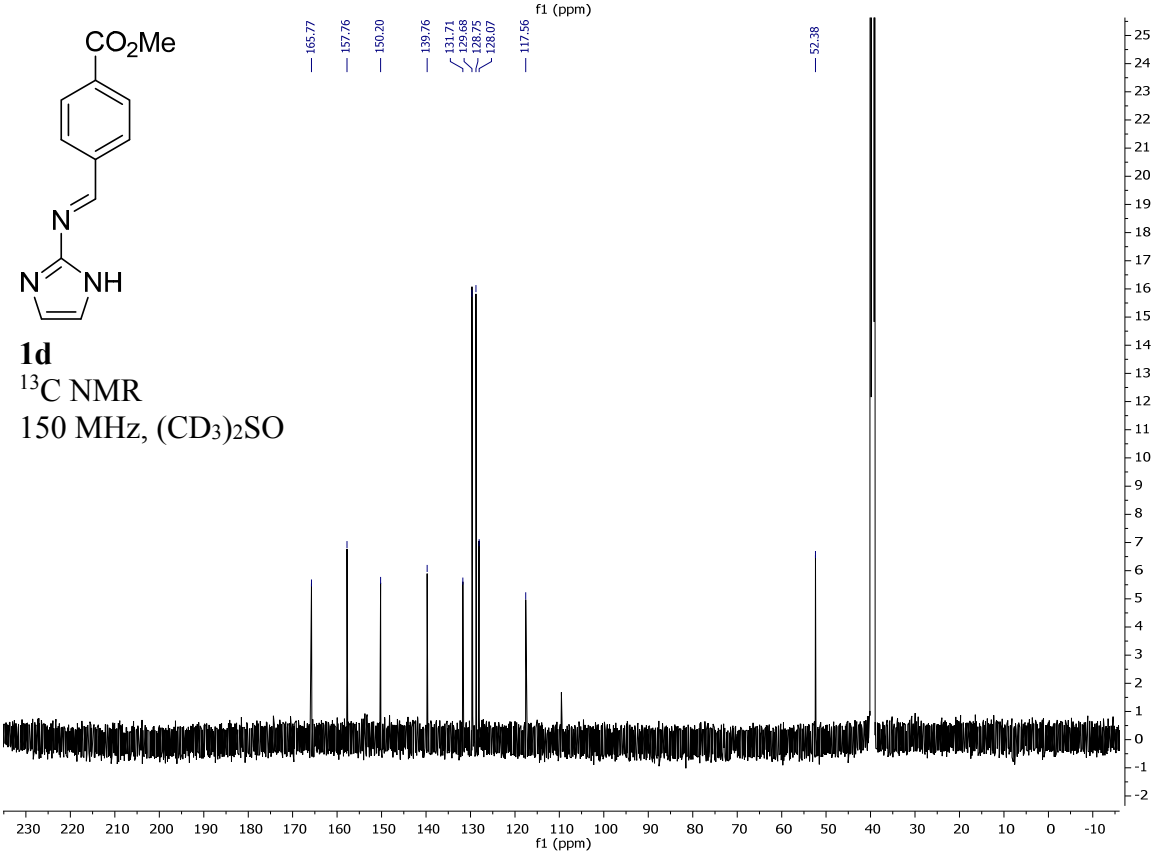
11. ^{1}H and ^{13}C NMR Spectra of New Imines, Ylides, Heterocycles, and Rhodacycle 8



1d

^{1}H NMR

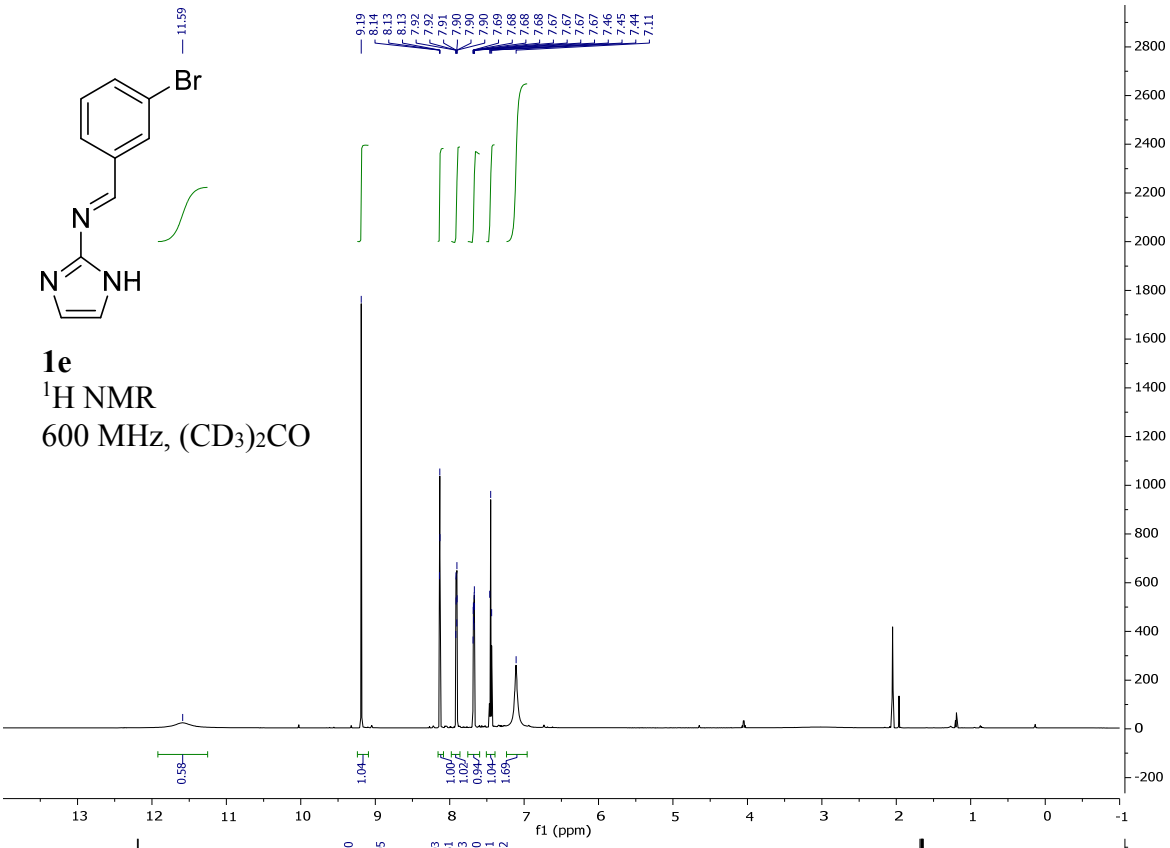
600 MHz, $(CD_3)_2SO$



1d

^{13}C NMR

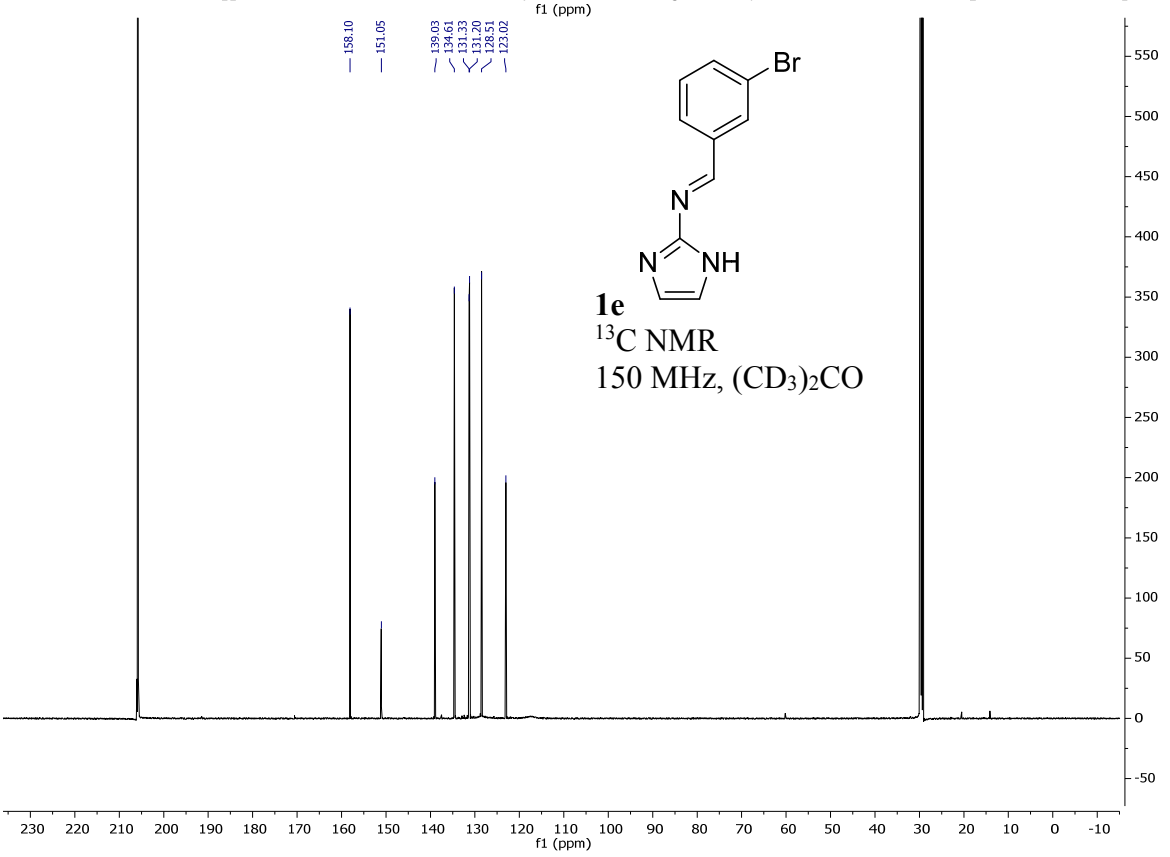
150 MHz, $(CD_3)_2SO$



1e

^{1}H NMR

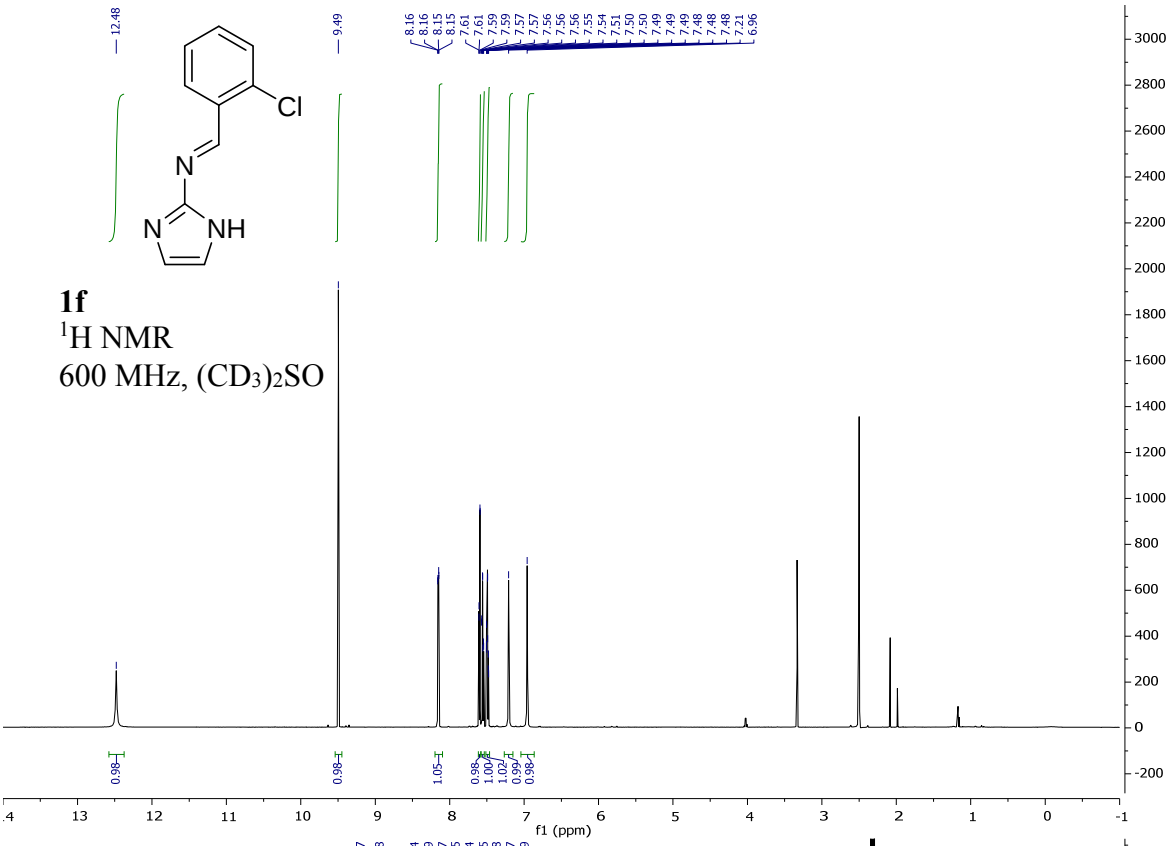
600 MHz, $(CD_3)_2CO$



1e

^{13}C NMR

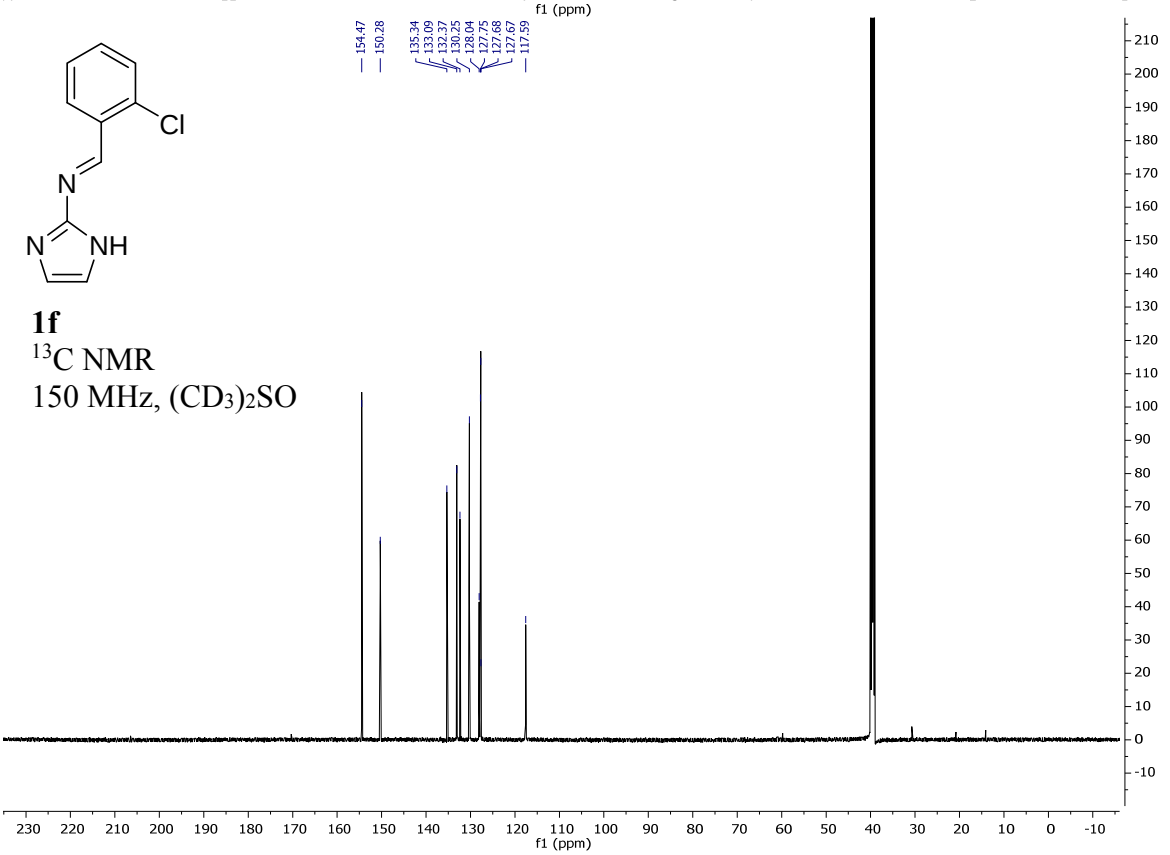
150 MHz, $(CD_3)_2CO$



1f

^{1}H NMR

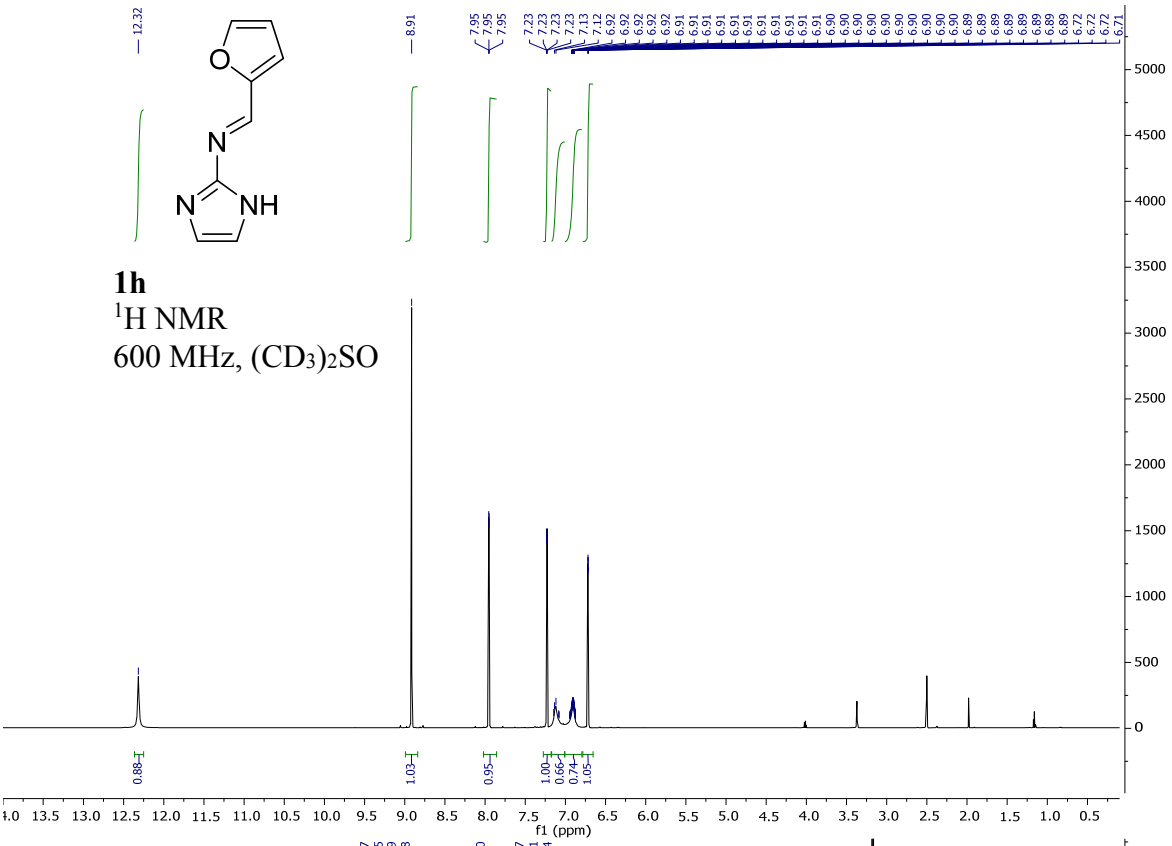
600 MHz, $(CD_3)_2SO$



1f

^{13}C NMR

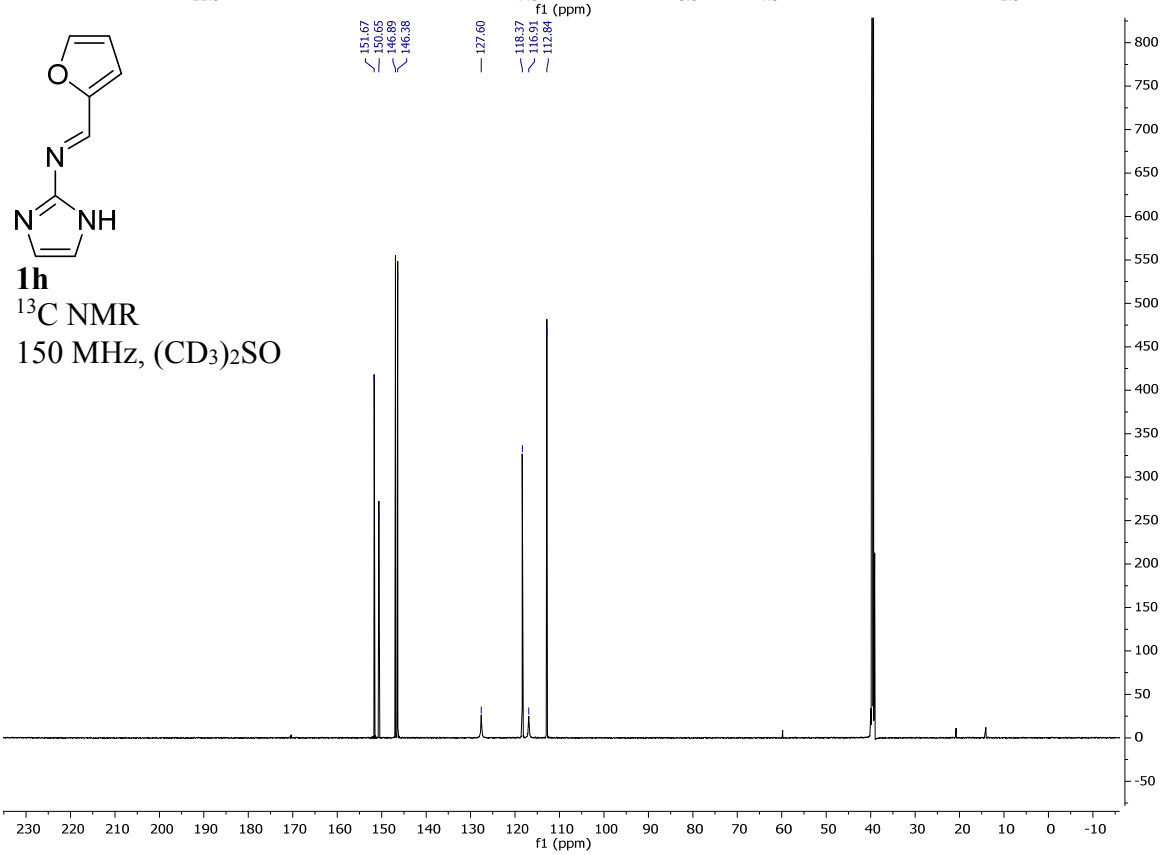
150 MHz, $(CD_3)_2SO$



1h

^{1}H NMR

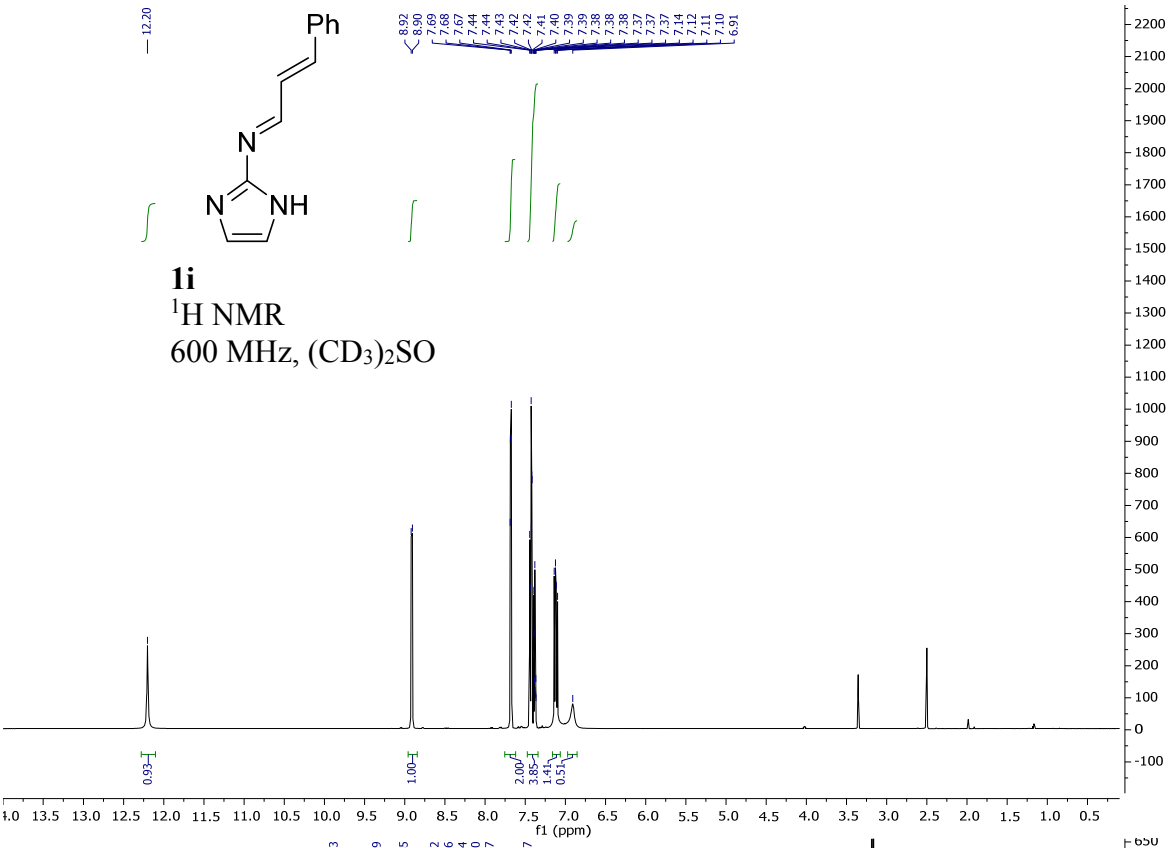
600 MHz, $(CD_3)_2SO$



1h

^{13}C NMR

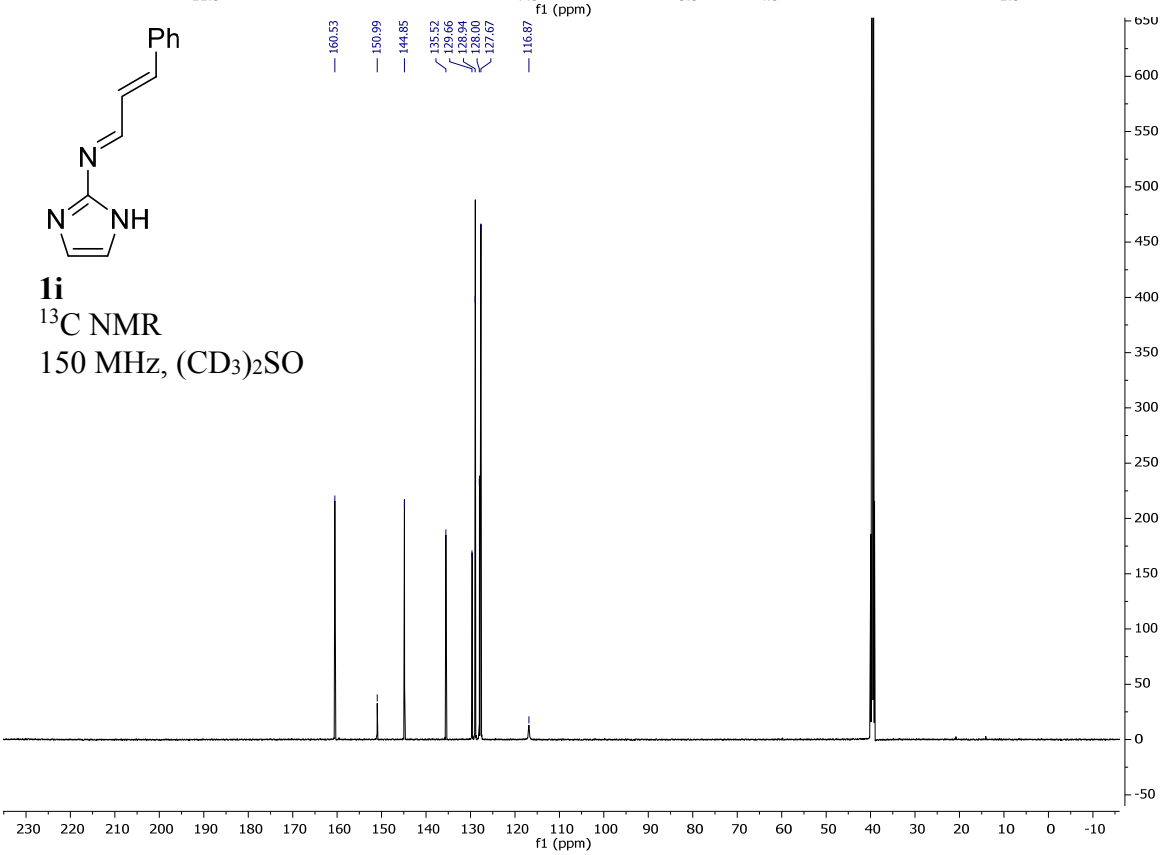
150 MHz, $(CD_3)_2SO$



1i

^{1}H NMR

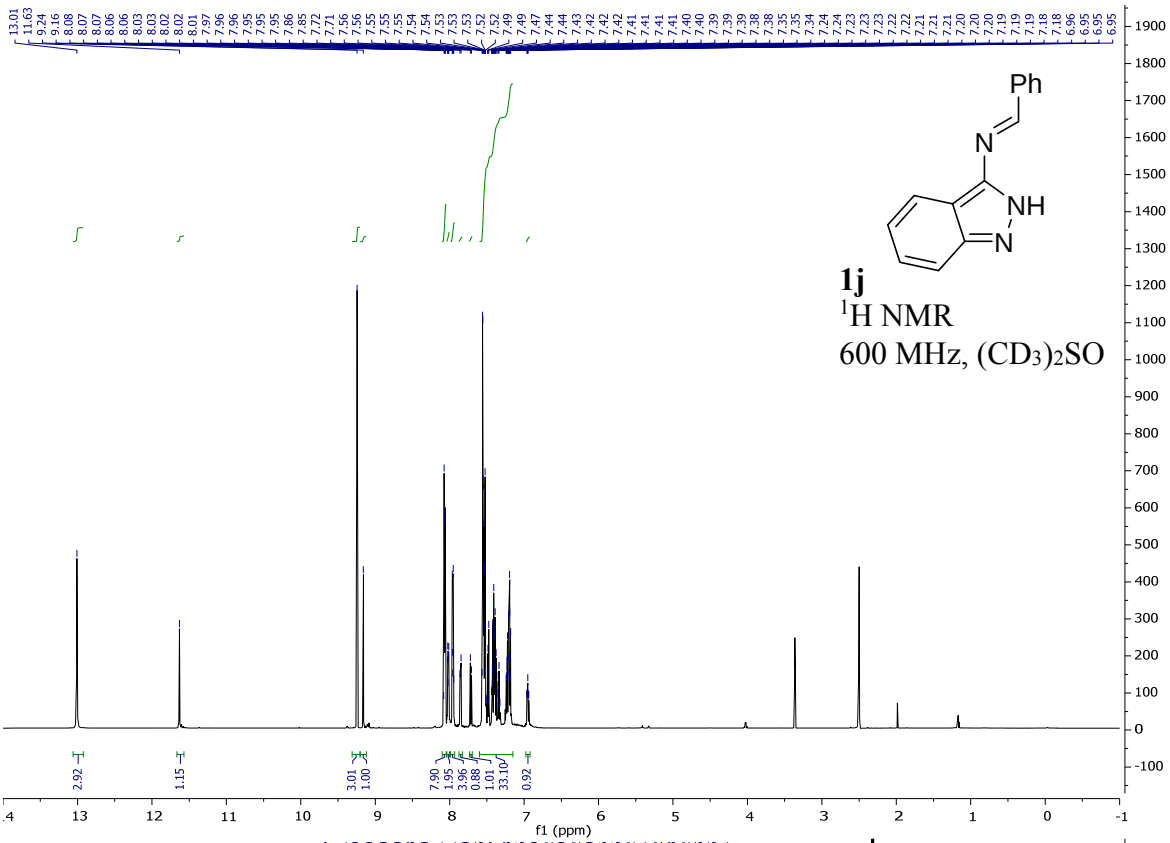
600 MHz, $(CD_3)_2SO$

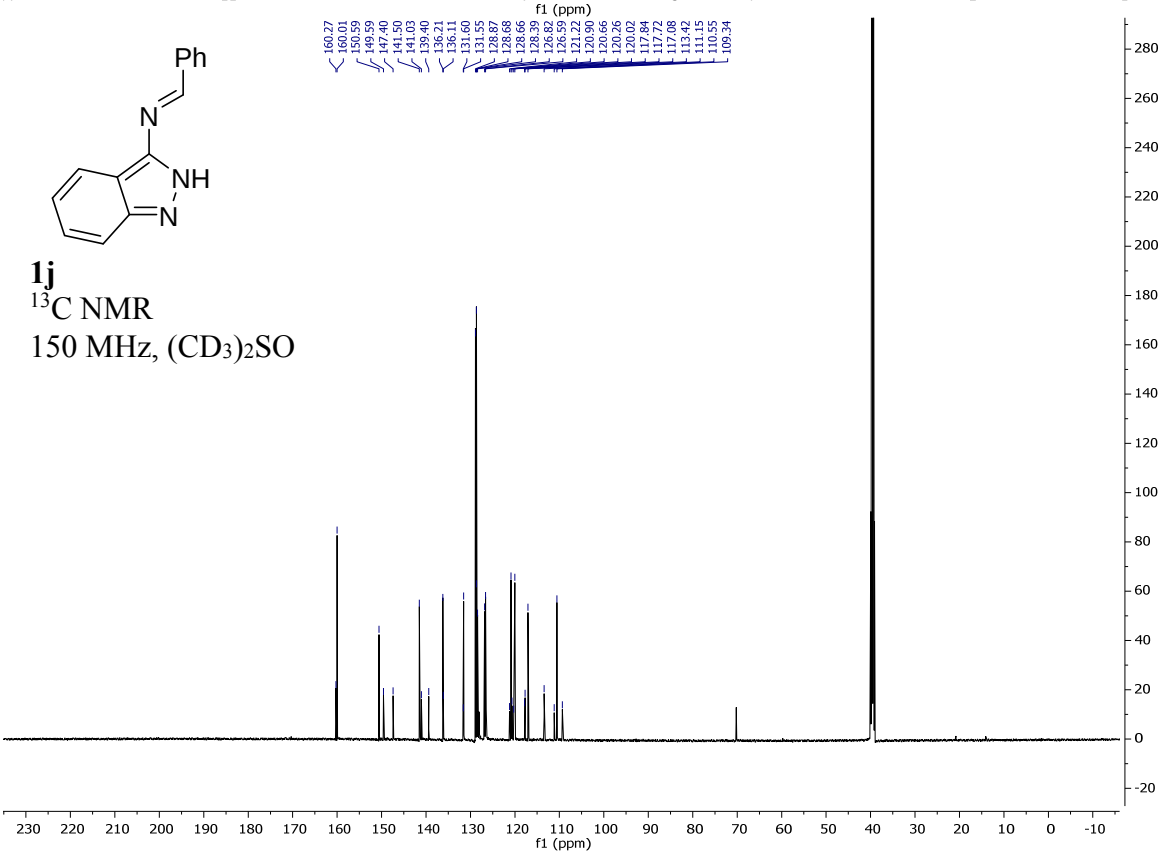


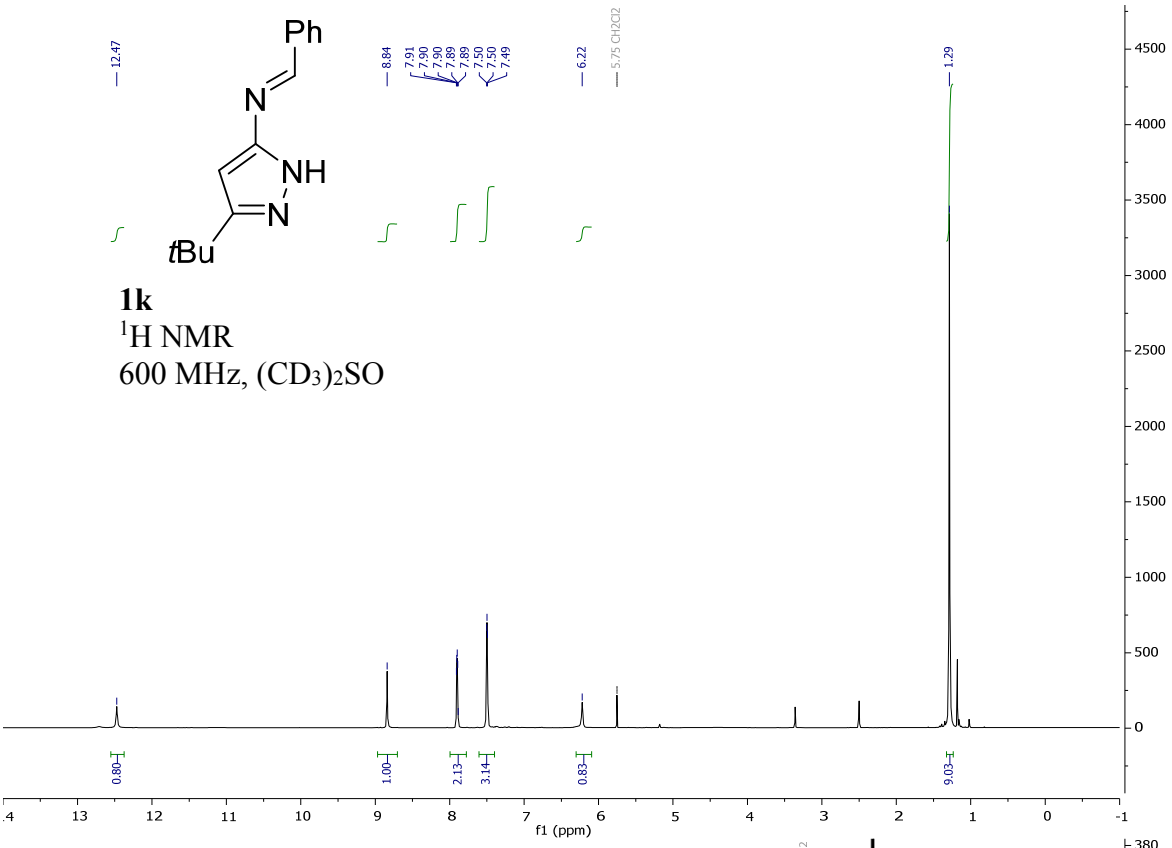
1i

^{13}C NMR

150 MHz, $(CD_3)_2SO$


Ph
N
NH
N
1j
1H NMR
600 MHz, (CD3)2SO
f1 (ppm)

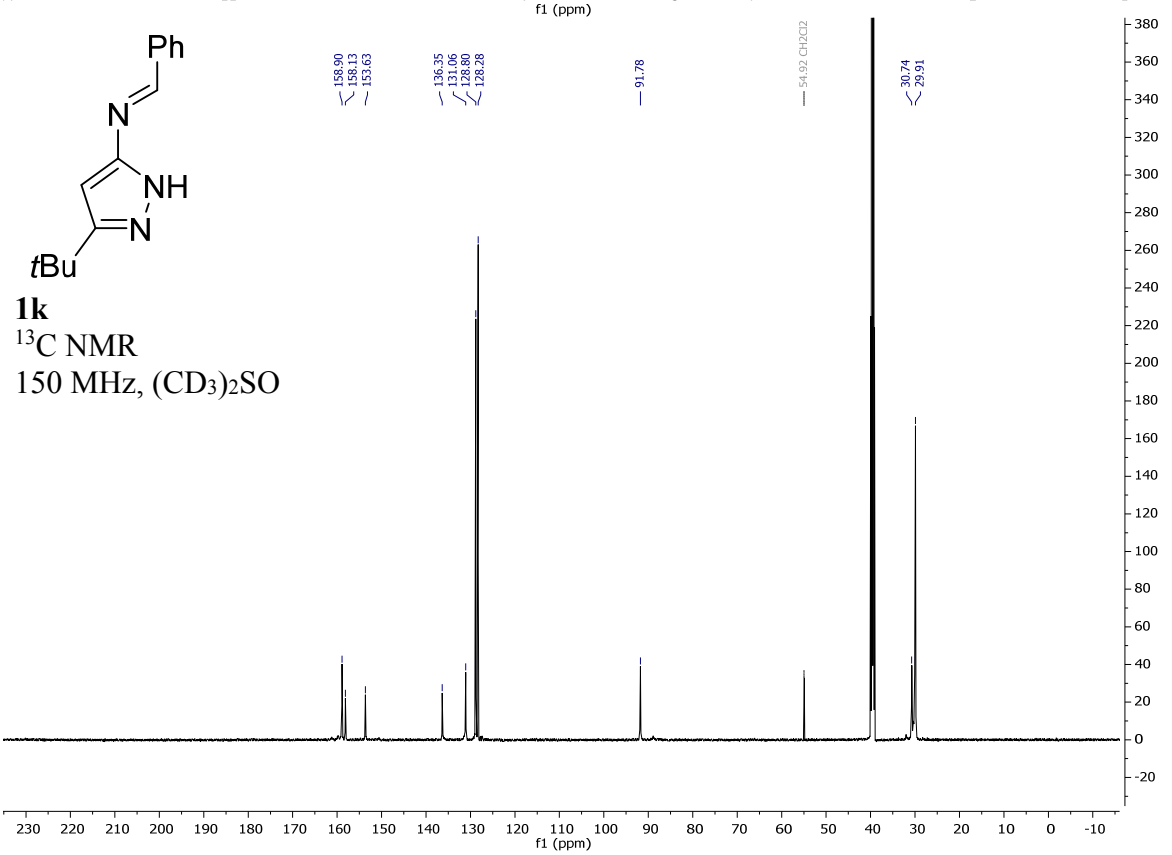

Ph
N
NH
N
1j
13C NMR
150 MHz, (CD3)2SO
f1 (ppm)



1k

^{1}H NMR

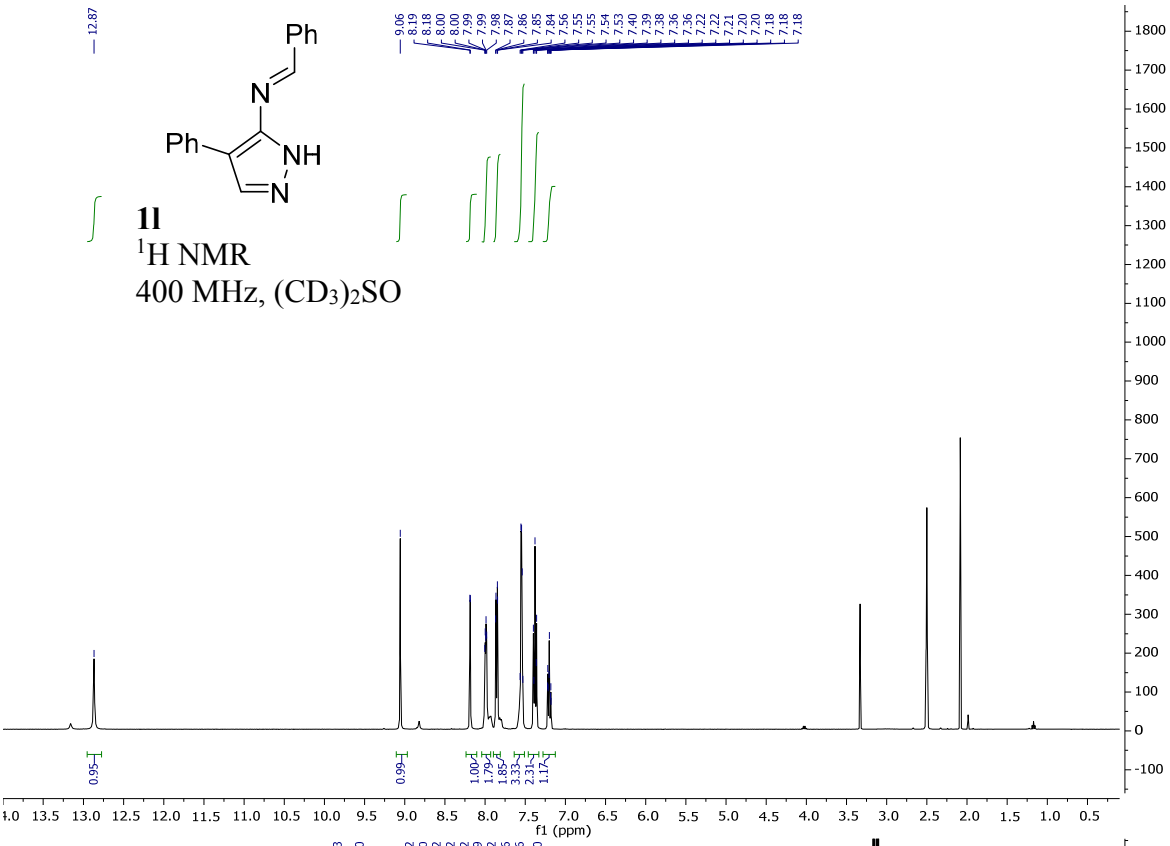
600 MHz, $(CD_3)_2SO$



1k

^{13}C NMR

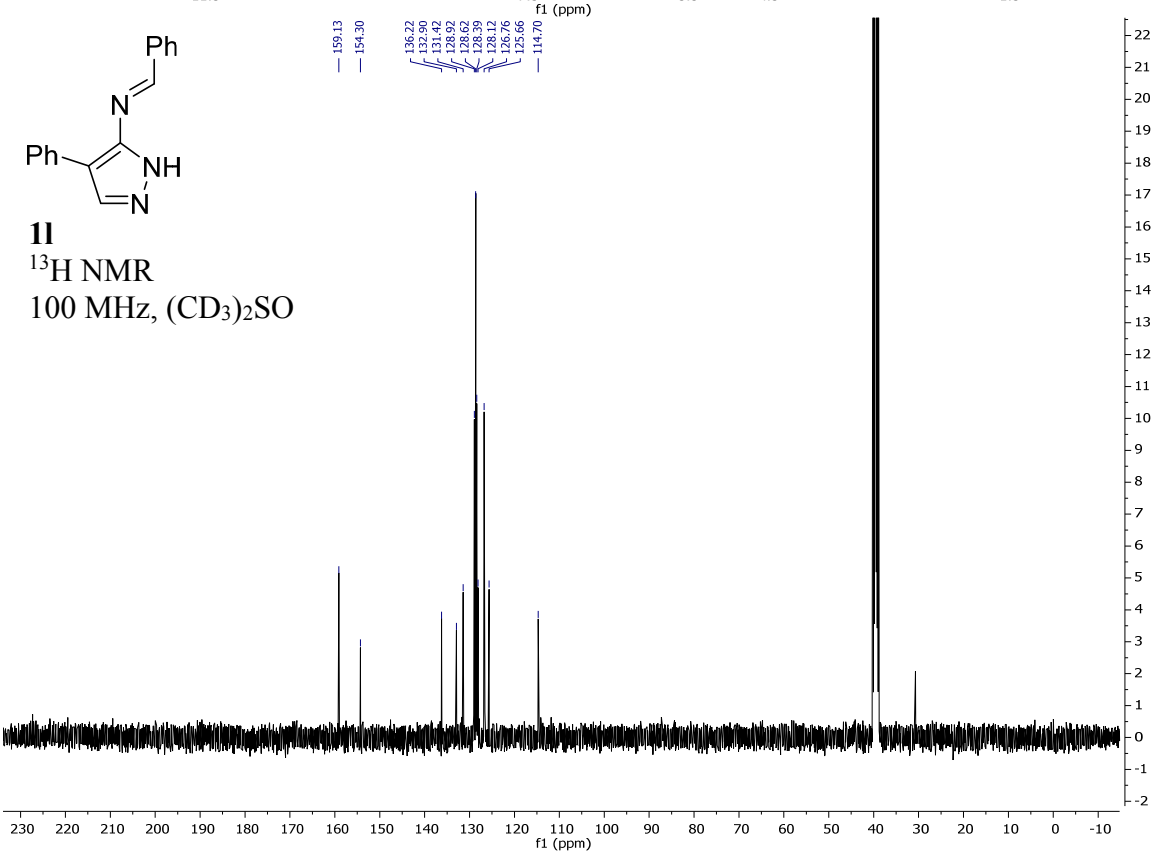
150 MHz, $(CD_3)_2SO$



1l

^{1}H NMR

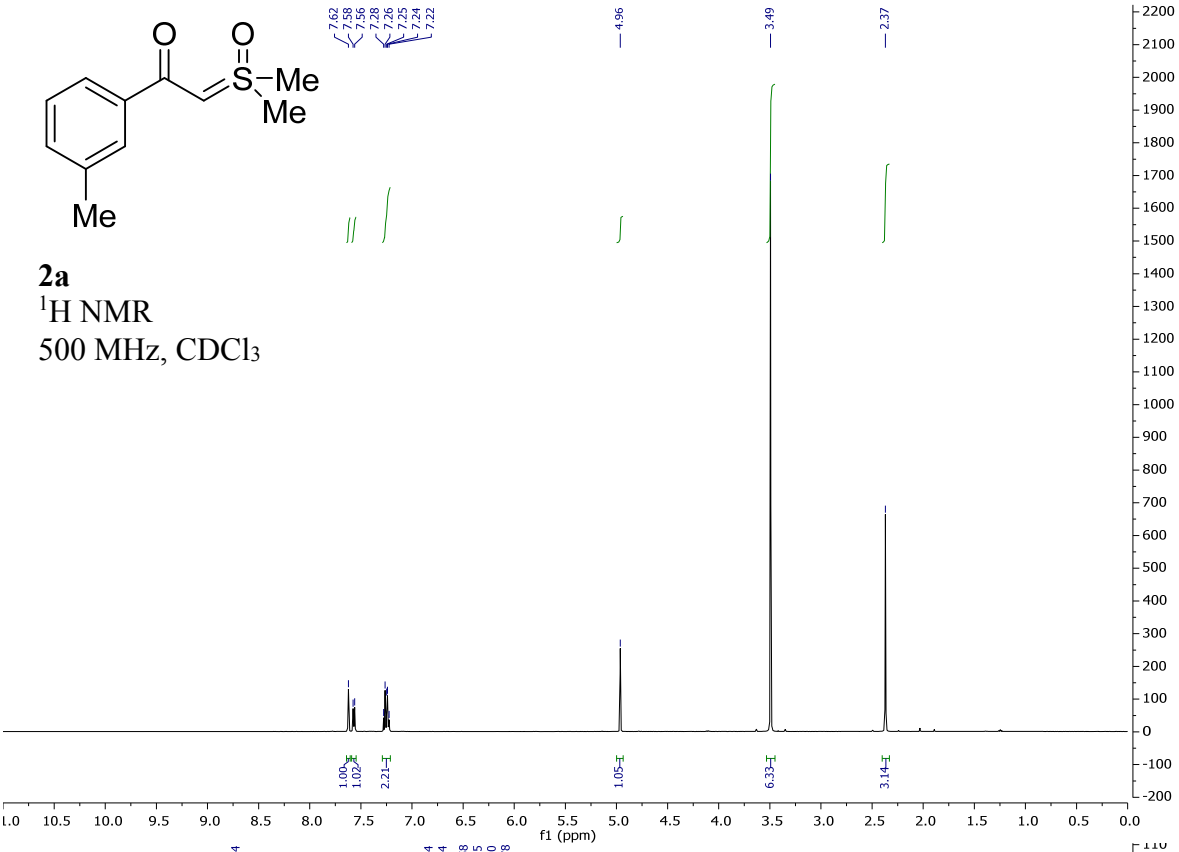
400 MHz, $(CD_3)_2SO$



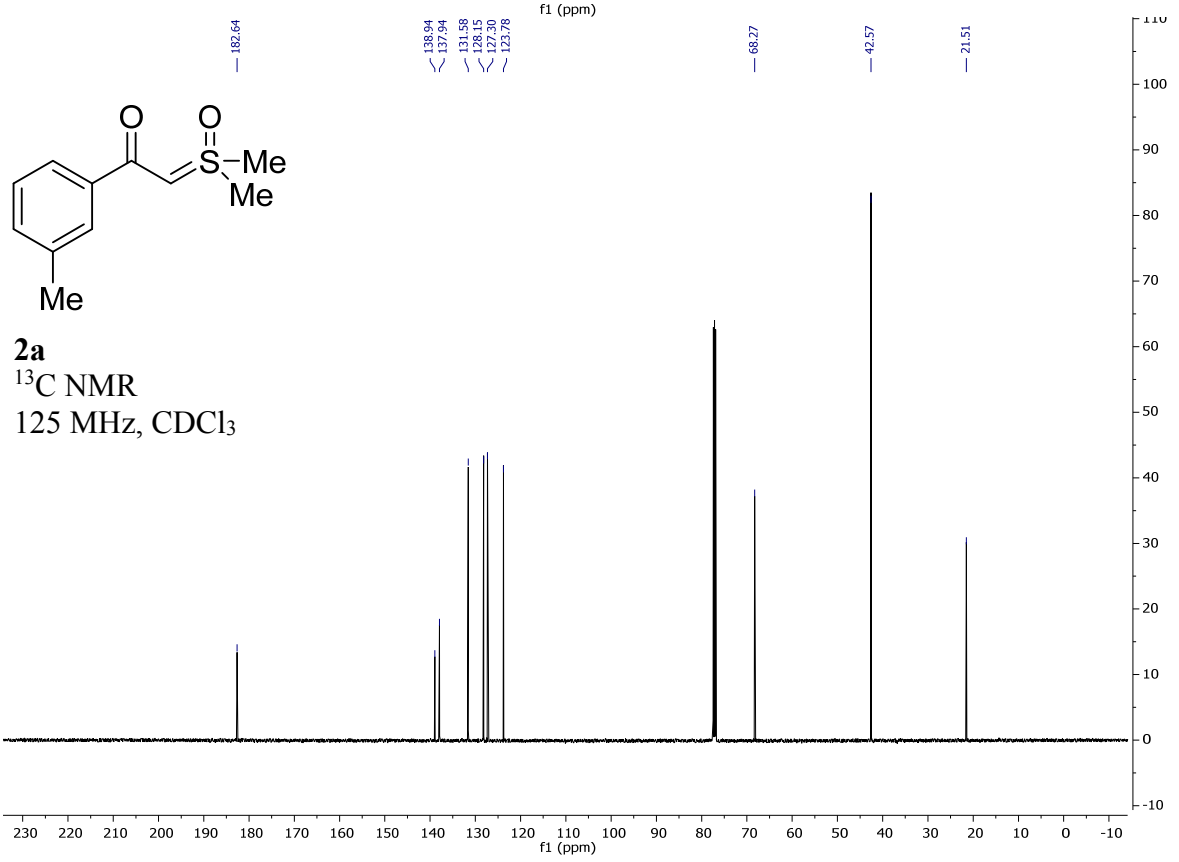
1l

^{13}H NMR

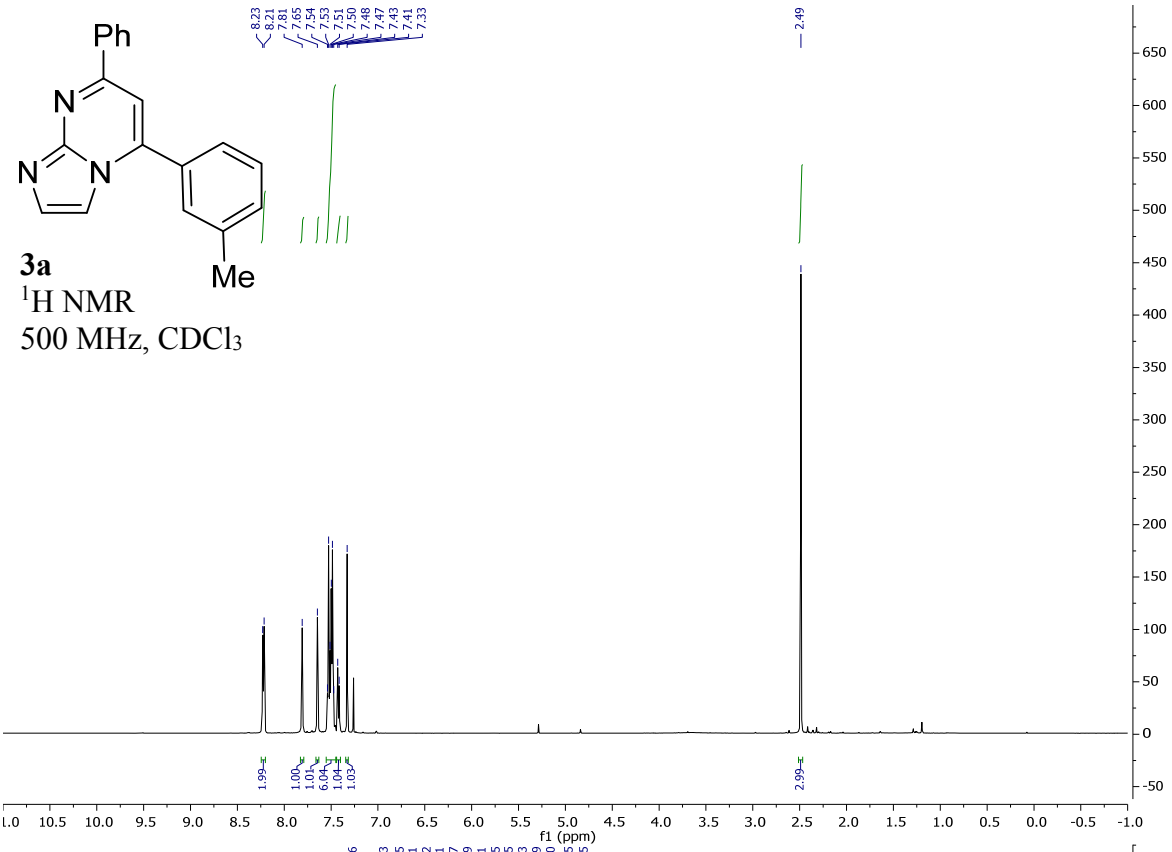
100 MHz, $(CD_3)_2SO$

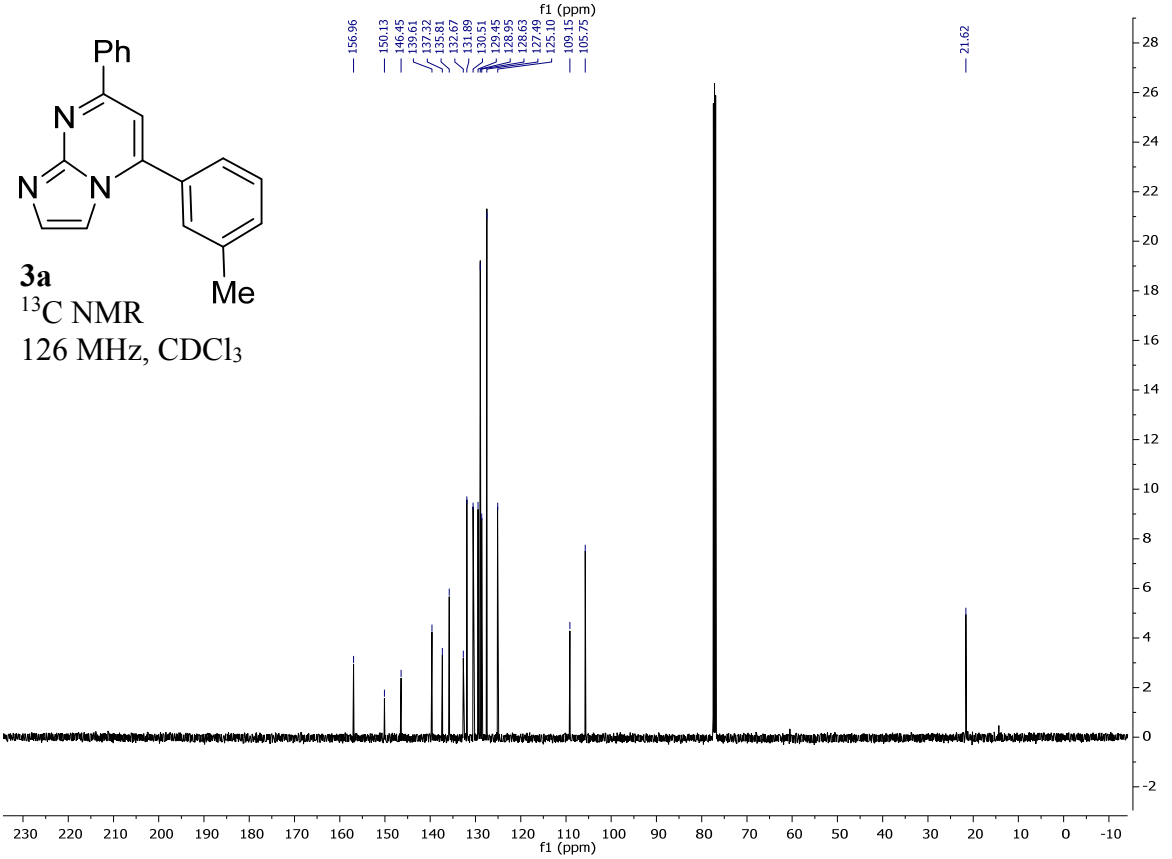


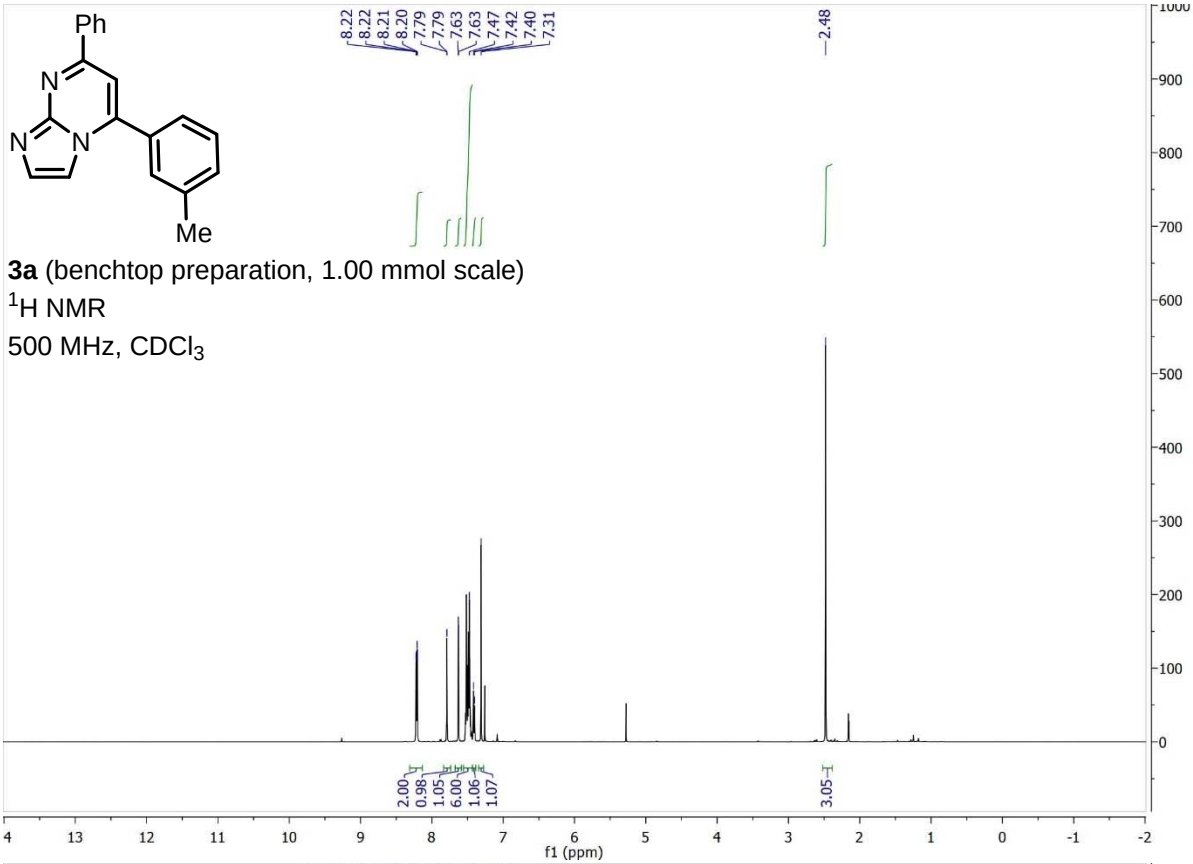
2a
^{1}H NMR
500 MHz, $CDCl_3$



2a
^{13}C NMR
125 MHz, $CDCl_3$


Ph
N
N
N
Me
3a
1H NMR
500 MHz, CDCl3
8.23
8.21
7.81
7.65
7.54
7.53
7.51
7.50
7.48
7.47
7.43
7.41
7.33
2.49
1.99
1.00
1.01
6.04
1.04
1.03
2.99
f1 (ppm)

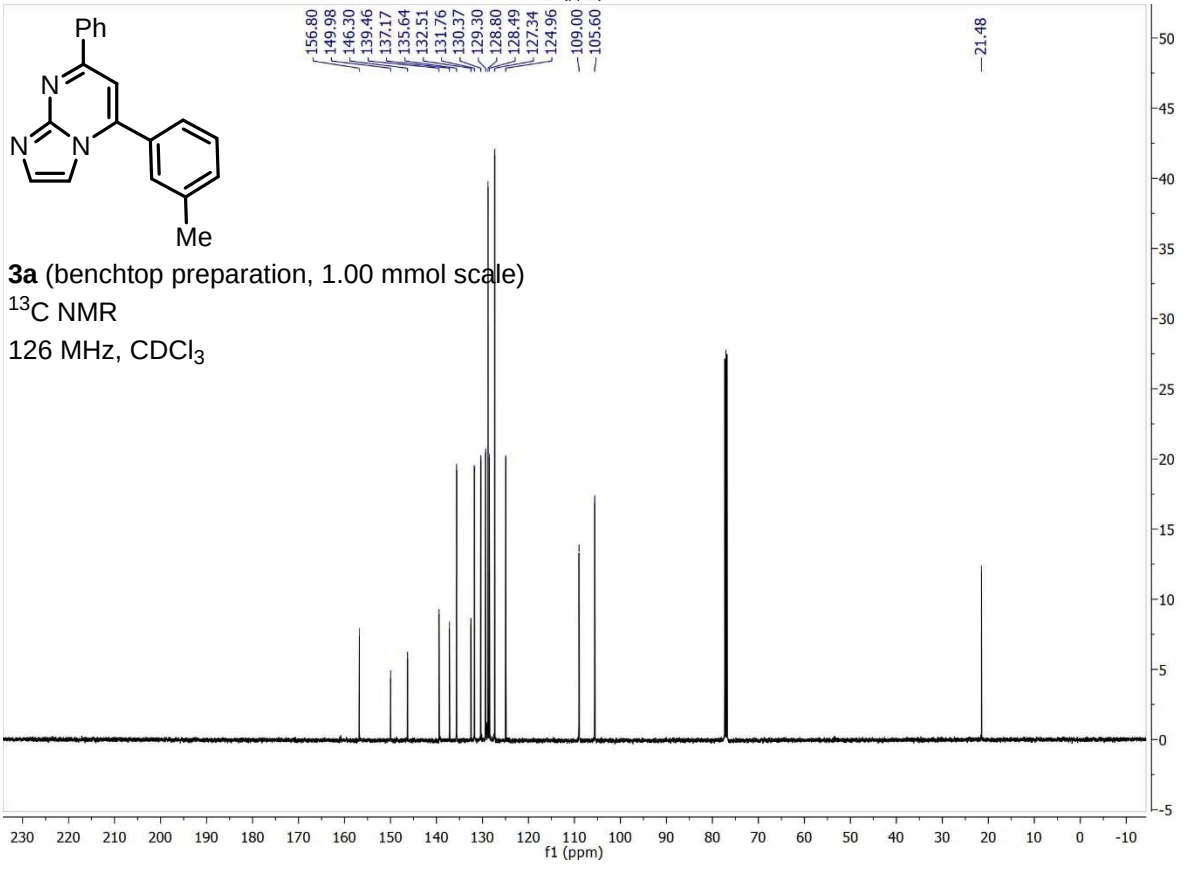

Ph
N
N
N
Me
3a
13C NMR
126 MHz, CDCl3
156.96
150.13
146.45
139.61
137.32
135.81
132.67
131.89
130.51
129.45
128.95
128.63
127.49
125.10
109.15
105.75
21.62
f1 (ppm)



3a (benchtop preparation, 1.00 mmol scale)

^{1}H NMR

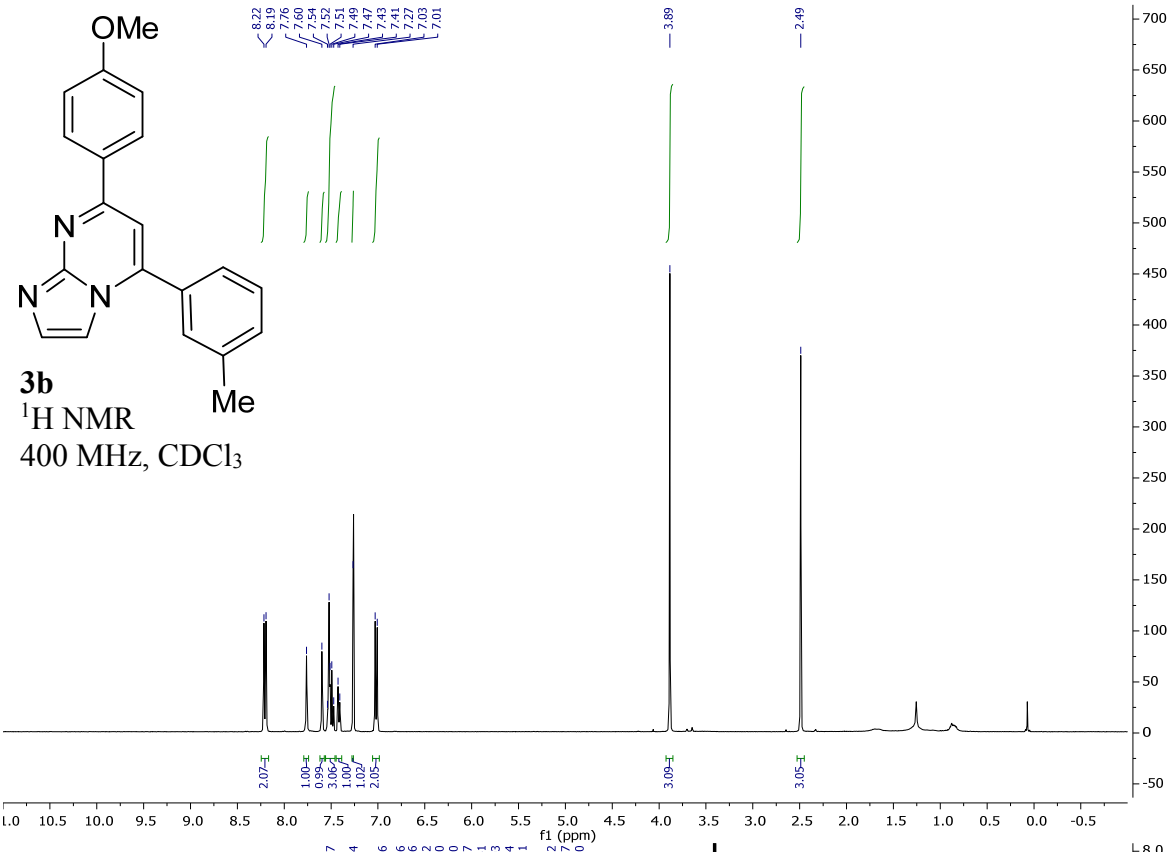
500 MHz, $CDCl_3$

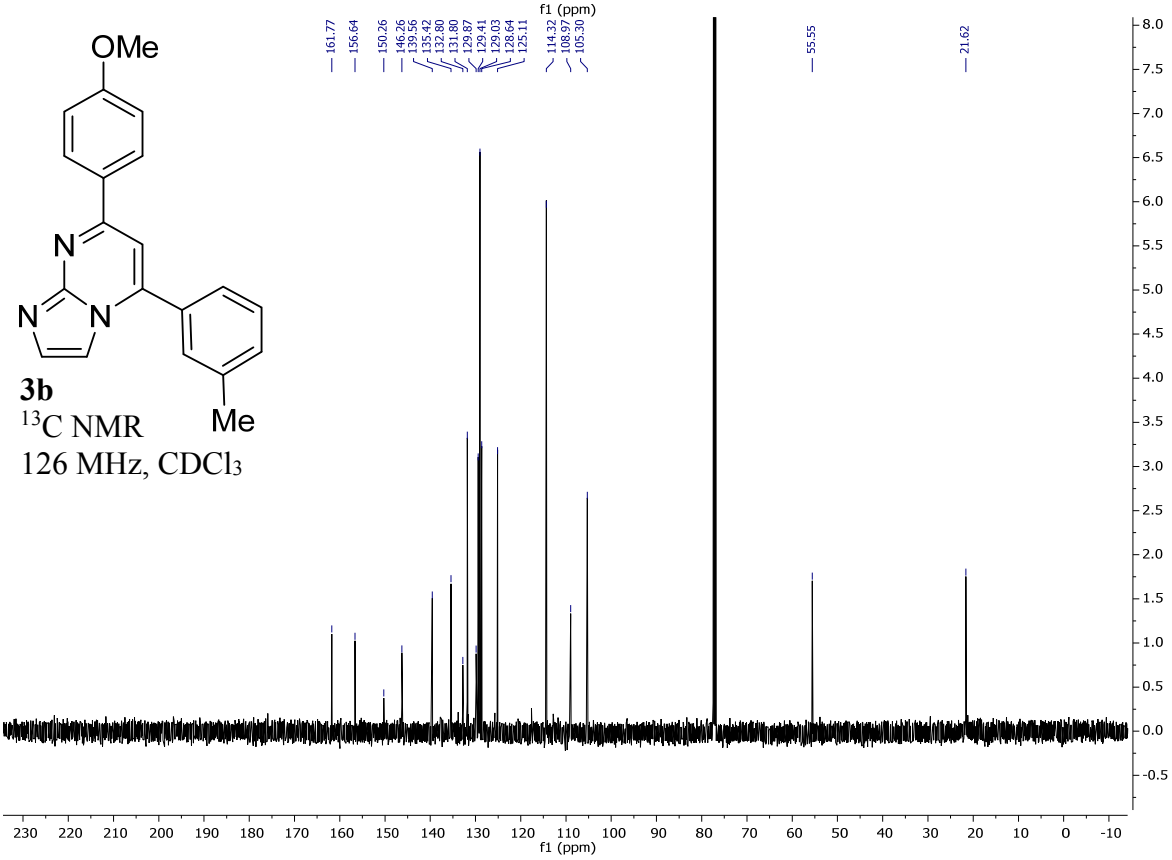


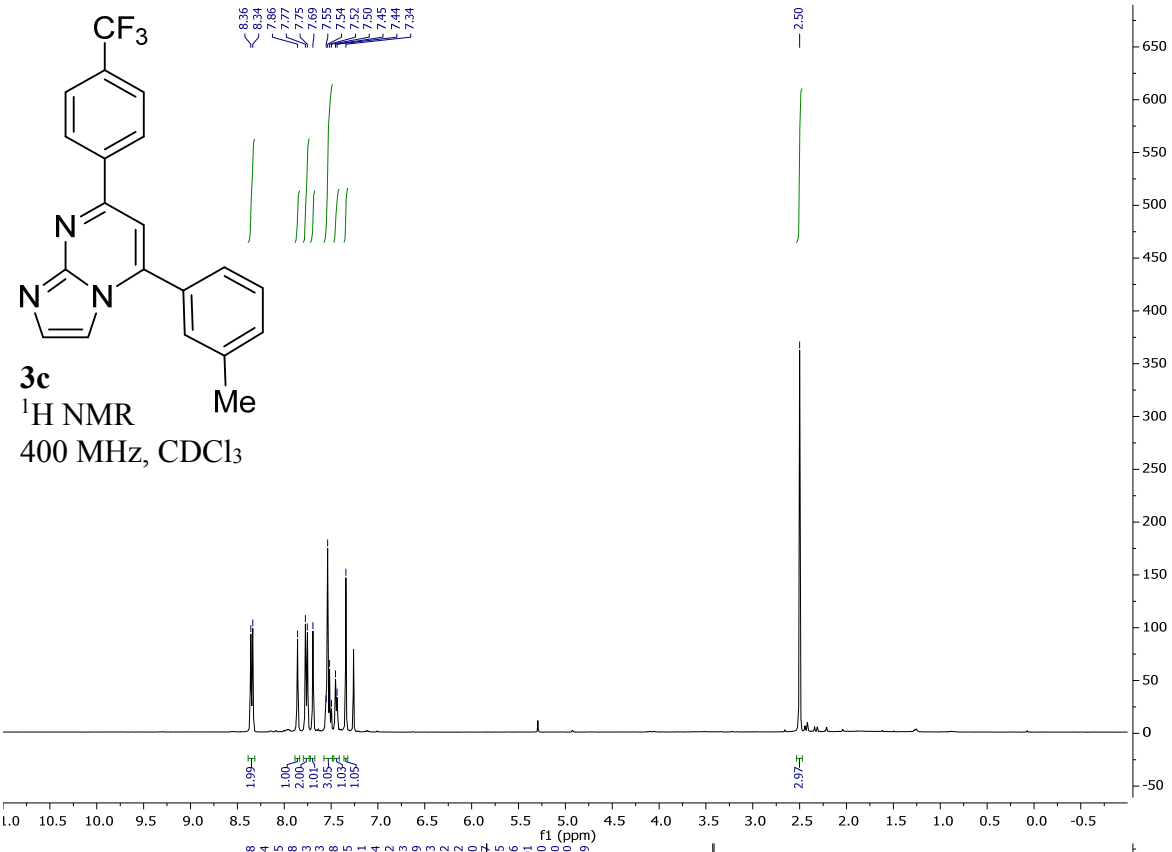
3a (benchtop preparation, 1.00 mmol scale)

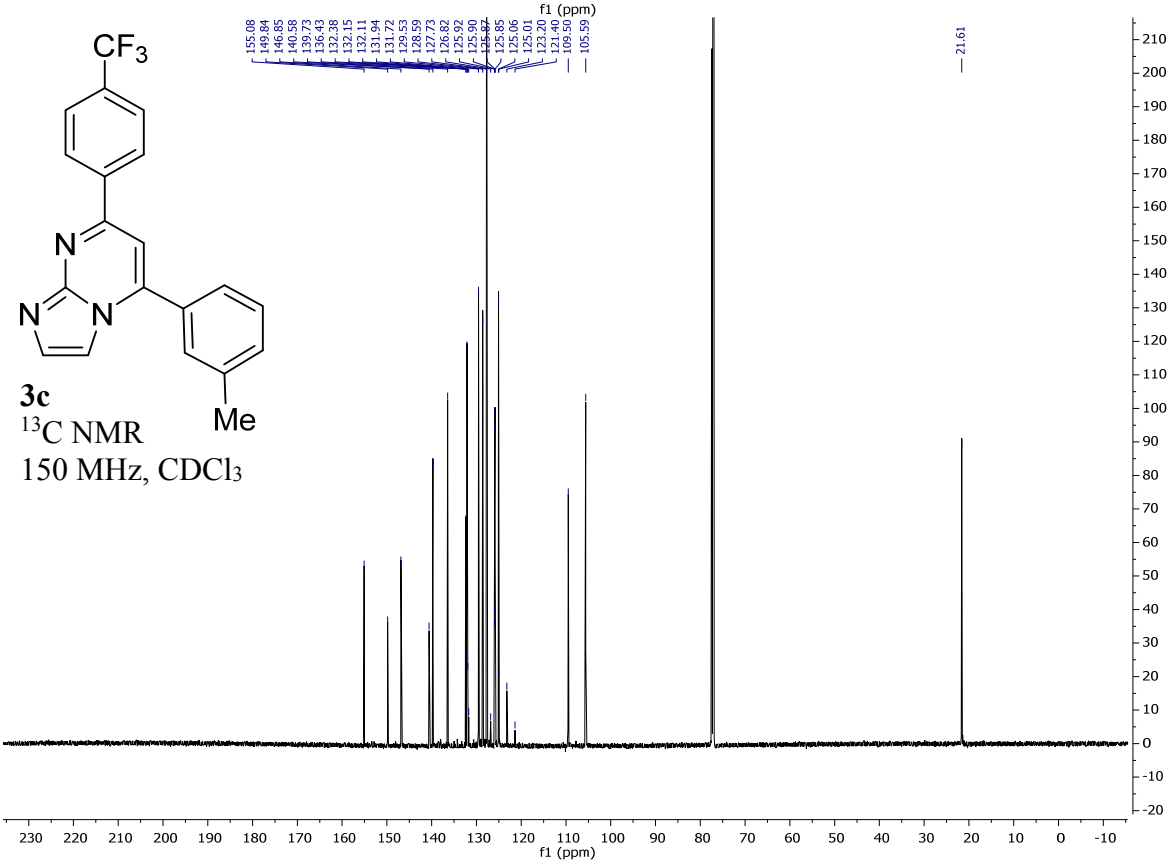
^{13}C NMR

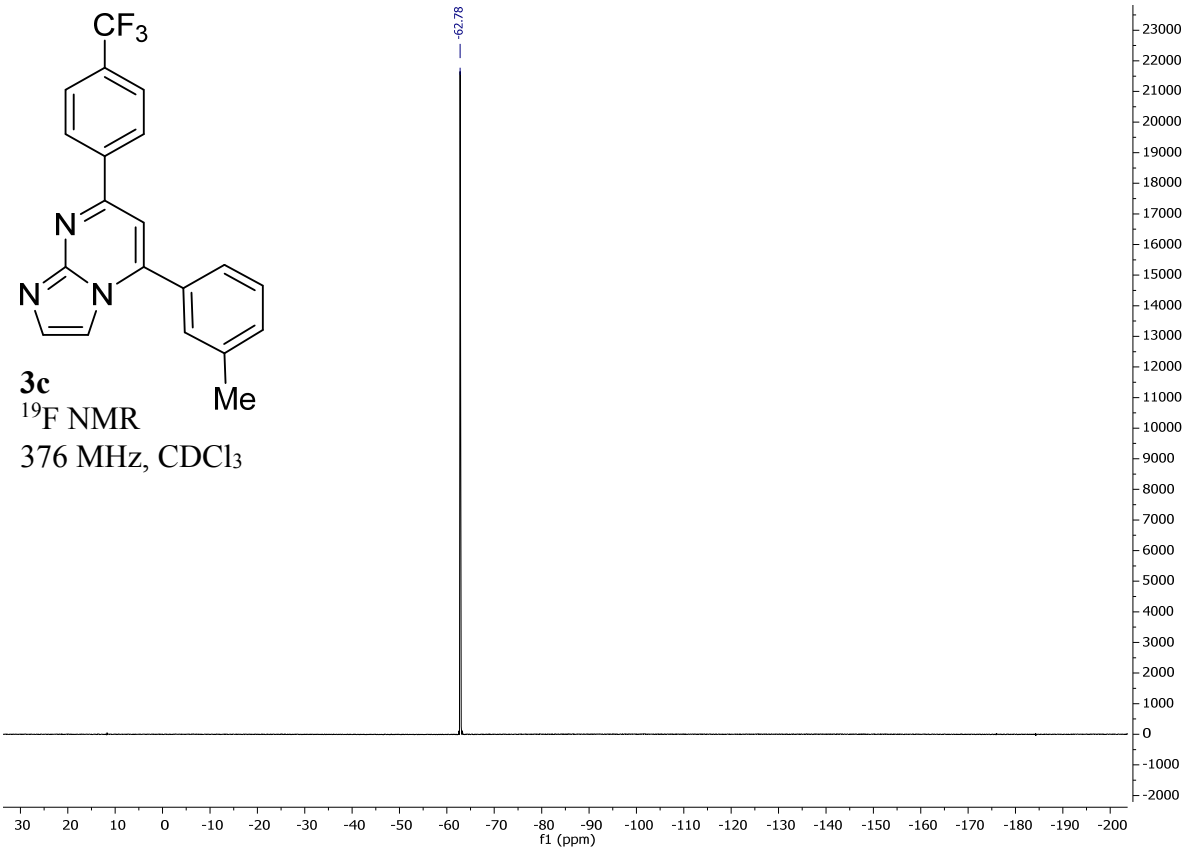
126 MHz, $CDCl_3$


OMe
N
N
N
Me
3b
1H NMR
400 MHz, CDCl3
8.22
8.19
7.76
7.60
7.54
7.52
7.51
7.49
7.47
7.43
7.41
7.27
7.03
7.01
3.89
2.49
2.07
1.00
0.99
3.06
1.00
1.02
2.05
3.09
3.05
f1 (ppm)


OMe
N
N
N
Me
3b
13C NMR
126 MHz, CDCl3
161.77
156.64
150.26
146.26
139.55
135.42
132.80
131.80
129.87
129.41
129.03
128.64
125.11
114.32
108.97
105.30
55.55
21.62
f1 (ppm)


CF3
N
N
N
Me
3c
1H NMR
400 MHz, CDCl3
8.36
8.34
7.86
7.77
7.75
7.69
7.55
7.54
7.52
7.50
7.45
7.44
7.34
2.50
1.99
1.00
2.00
1.01
3.05
1.03
1.05
2.97
f1 (ppm)

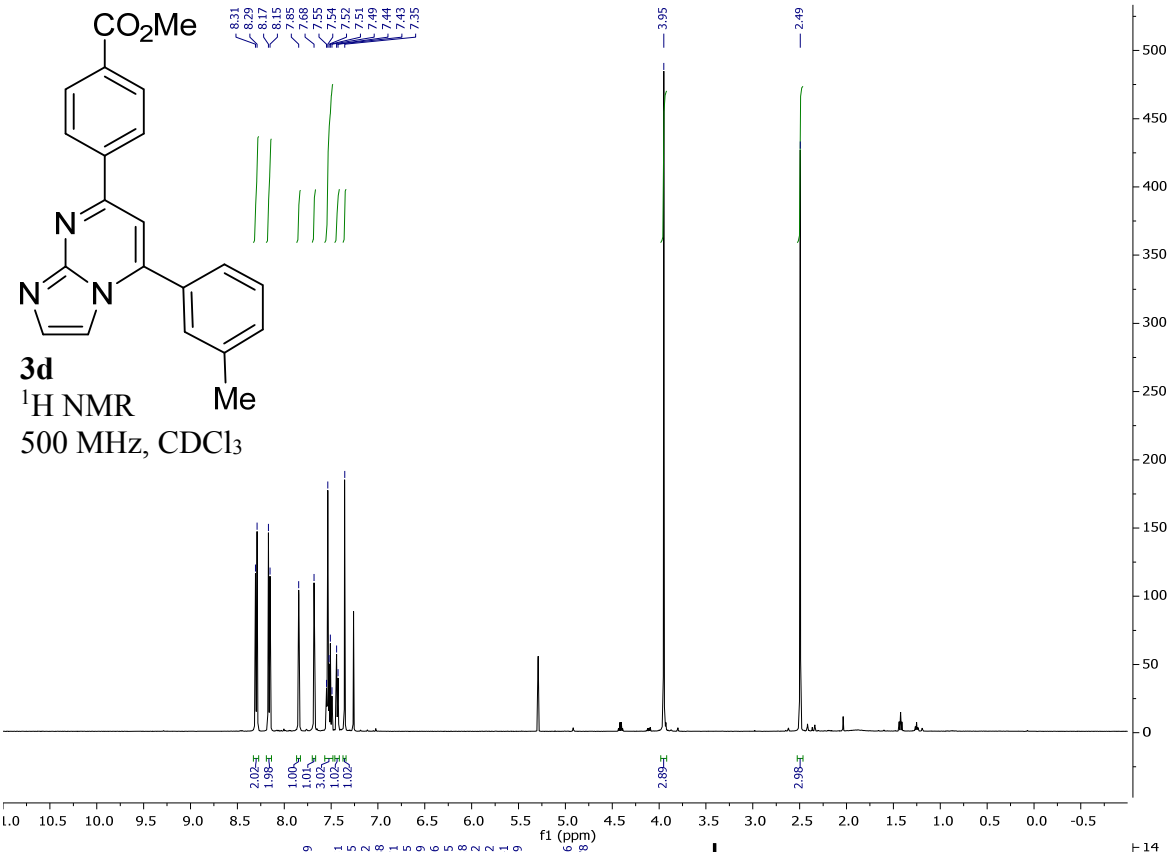

CF3
N
N
N
Me
3c
13C NMR
150 MHz, CDCl3
155.08
149.84
146.85
140.58
139.73
136.43
132.38
132.15
132.11
131.94
131.72
129.53
128.59
127.73
126.82
125.92
125.90
125.87
125.85
125.06
125.01
123.20
121.40
109.50
105.59
21.61
f1 (ppm)

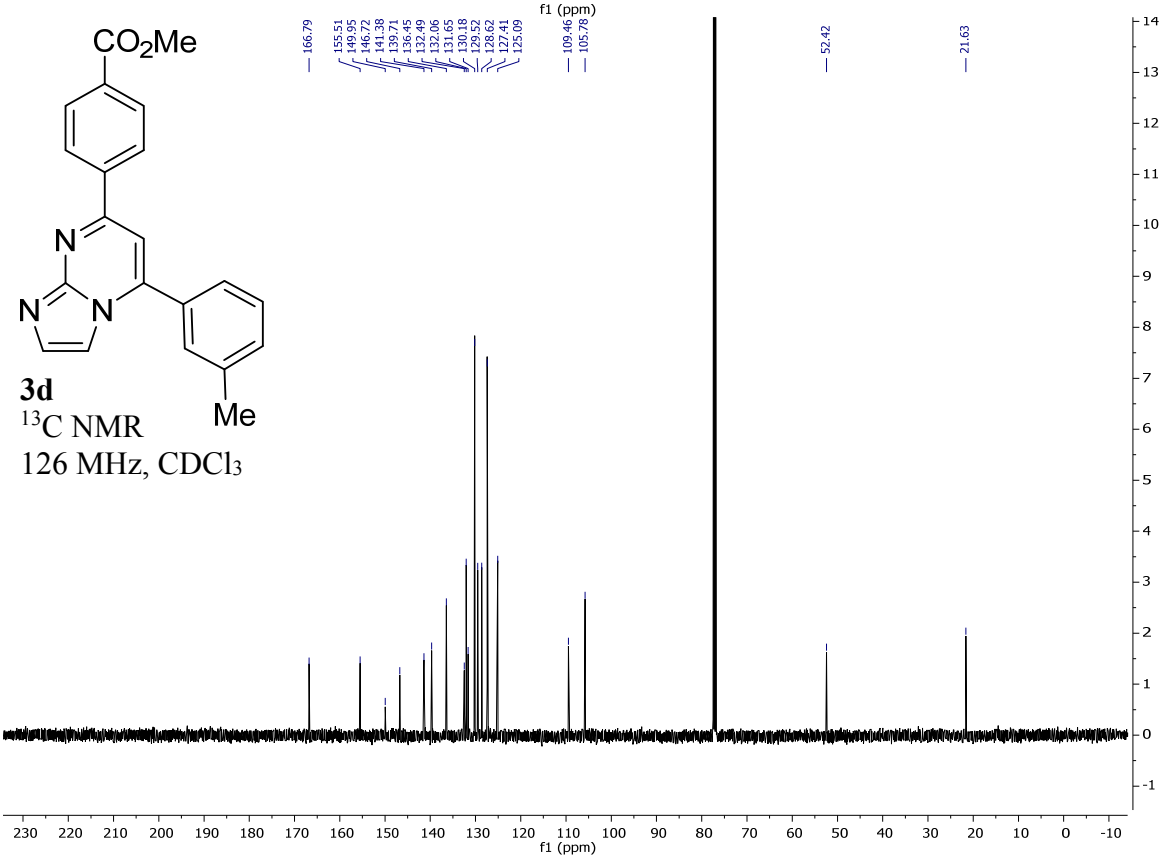


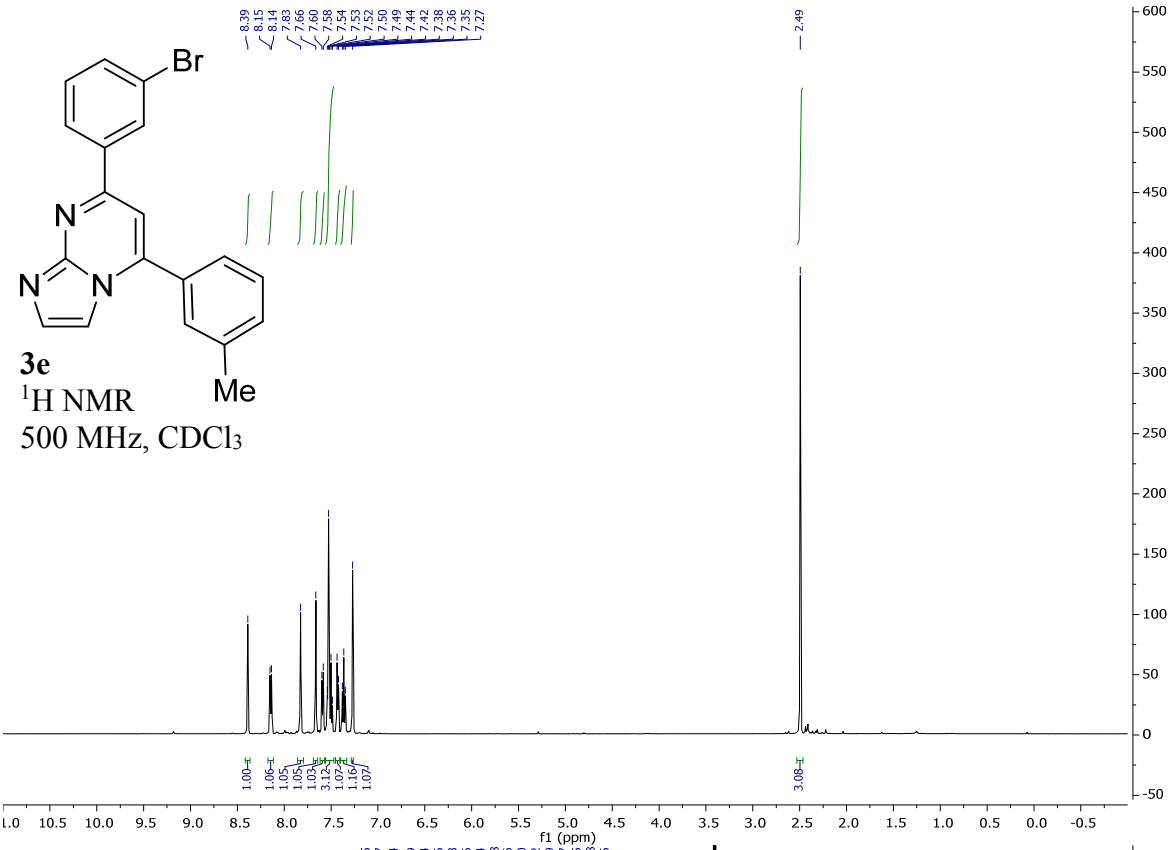
3c

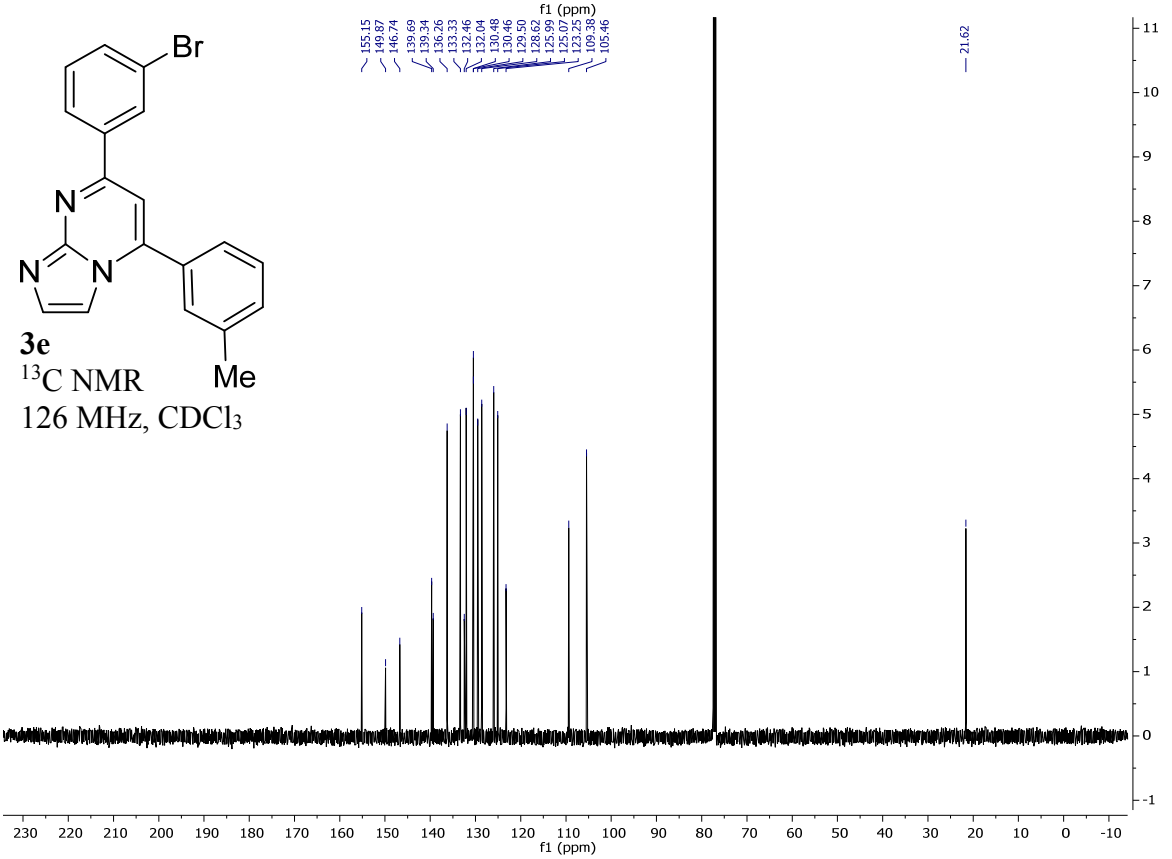
^{19}F NMR

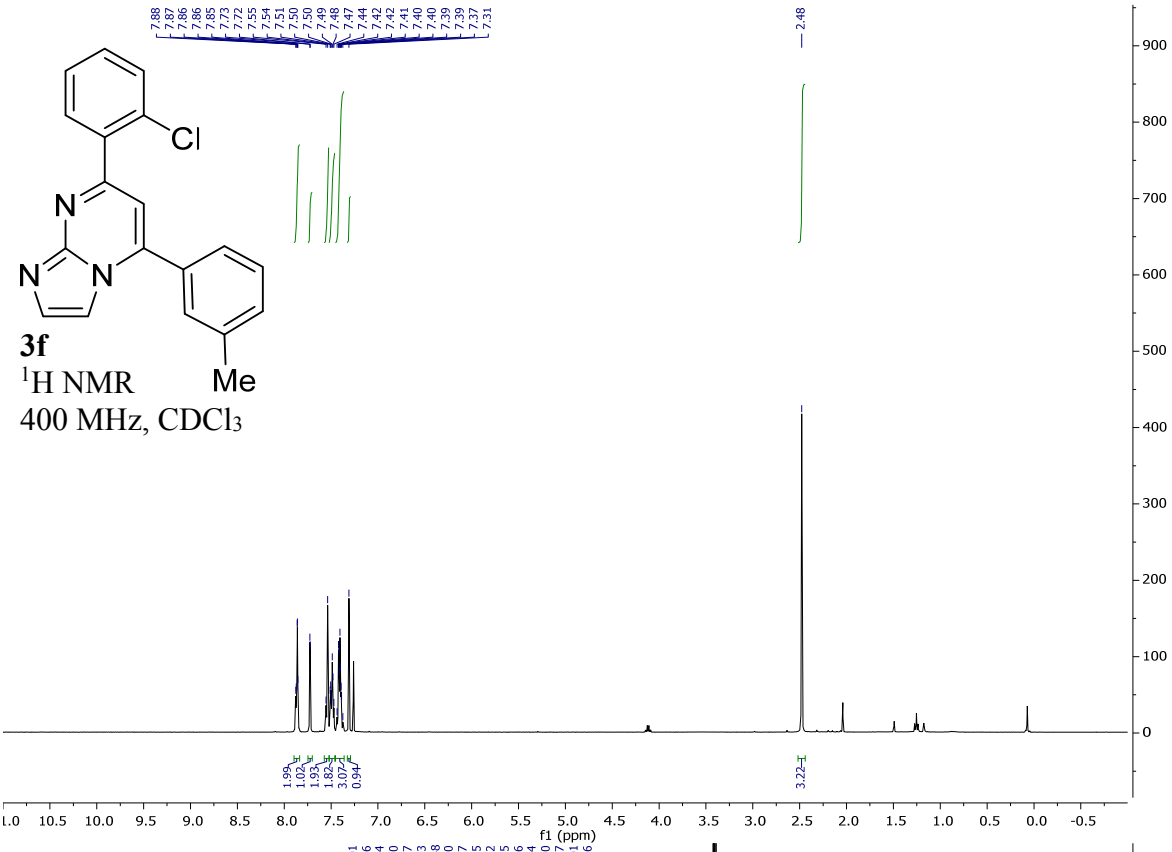
376 MHz, $CDCl_3$

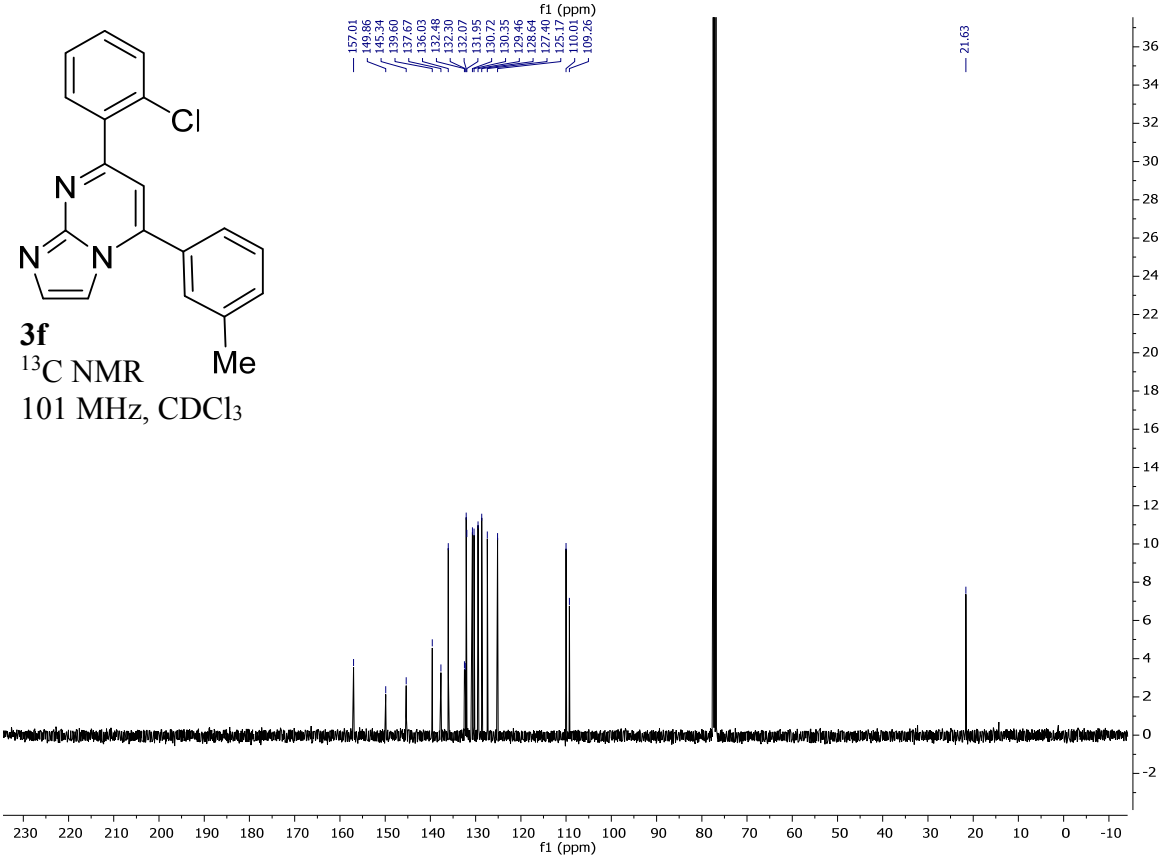

CO2Me
N
N
N
Me
3d
1H NMR
500 MHz, CDCl3
8.31
8.29
8.17
8.15
7.85
7.68
7.55
7.54
7.52
7.51
7.49
7.44
7.43
7.35
3.95
2.49
2.02
1.98
1.00
1.01
3.02
1.02
1.02
2.89
2.98
f1 (ppm)

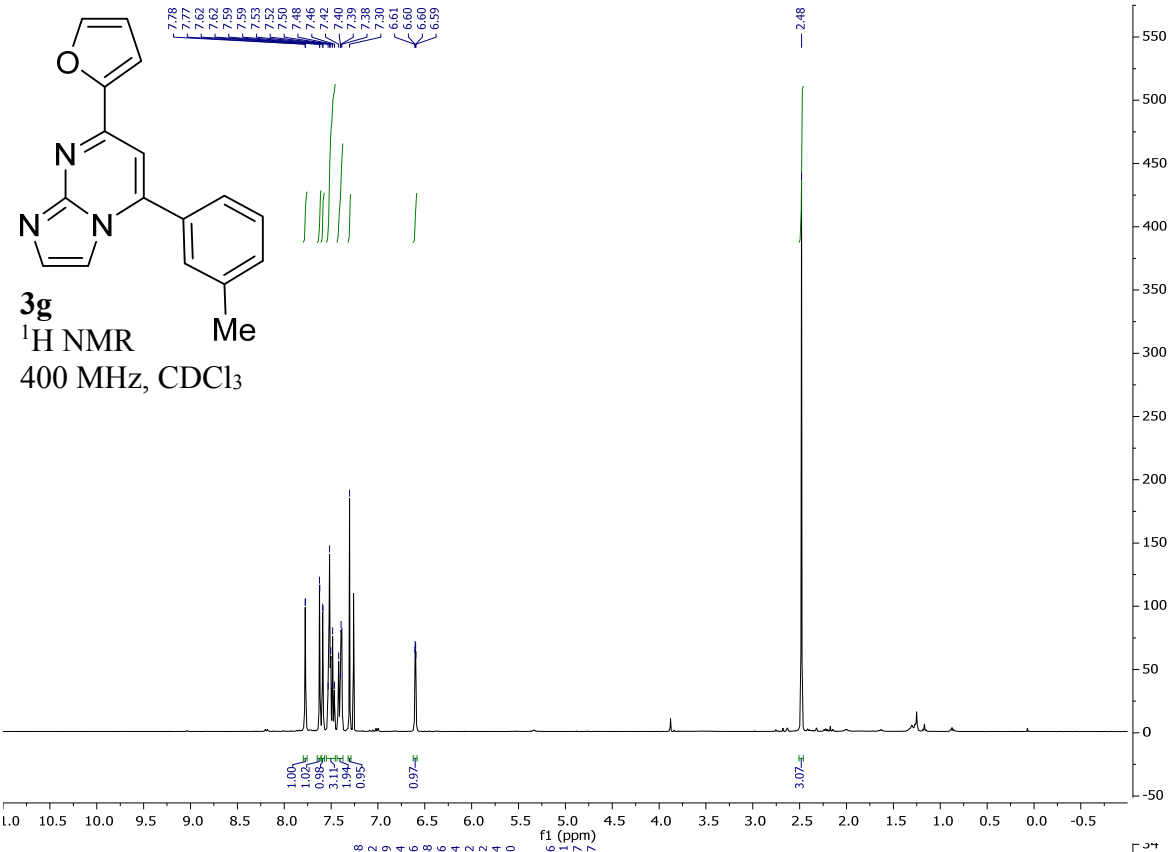

CO2Me
N
N
N
Me
3d
13C NMR
126 MHz, CDCl3
166.79
155.51
149.95
146.72
141.38
139.71
136.45
132.49
132.06
131.65
130.18
129.52
128.62
127.41
125.09
109.46
105.78
52.42
21.63
f1 (ppm)

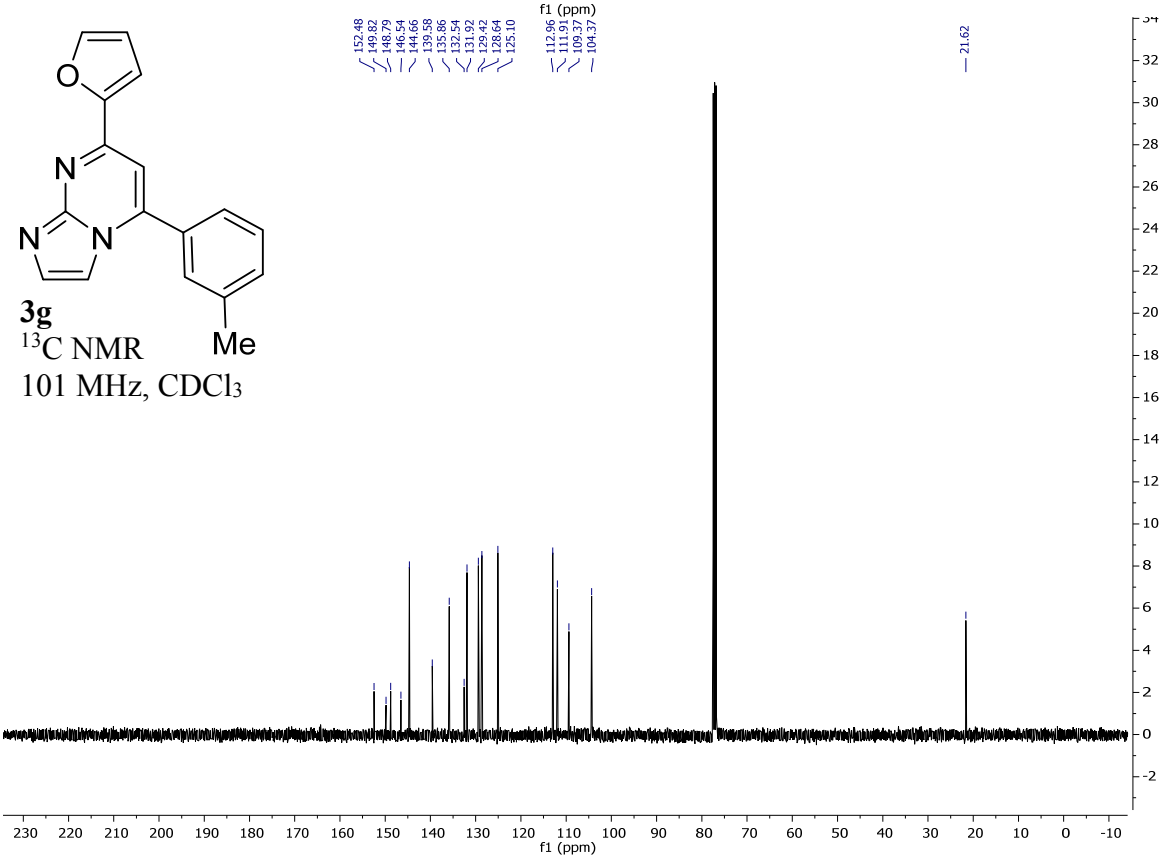

Br
N
N
N
Me
3e
1H NMR
500 MHz, CDCl3
8.39
8.15
8.14
7.83
7.66
7.60
7.58
7.54
7.53
7.52
7.50
7.49
7.44
7.42
7.38
7.36
7.35
7.27
2.49
1.00
1.06
1.05
1.05
1.03
3.12
1.07
1.16
1.07
3.08
f1 (ppm)

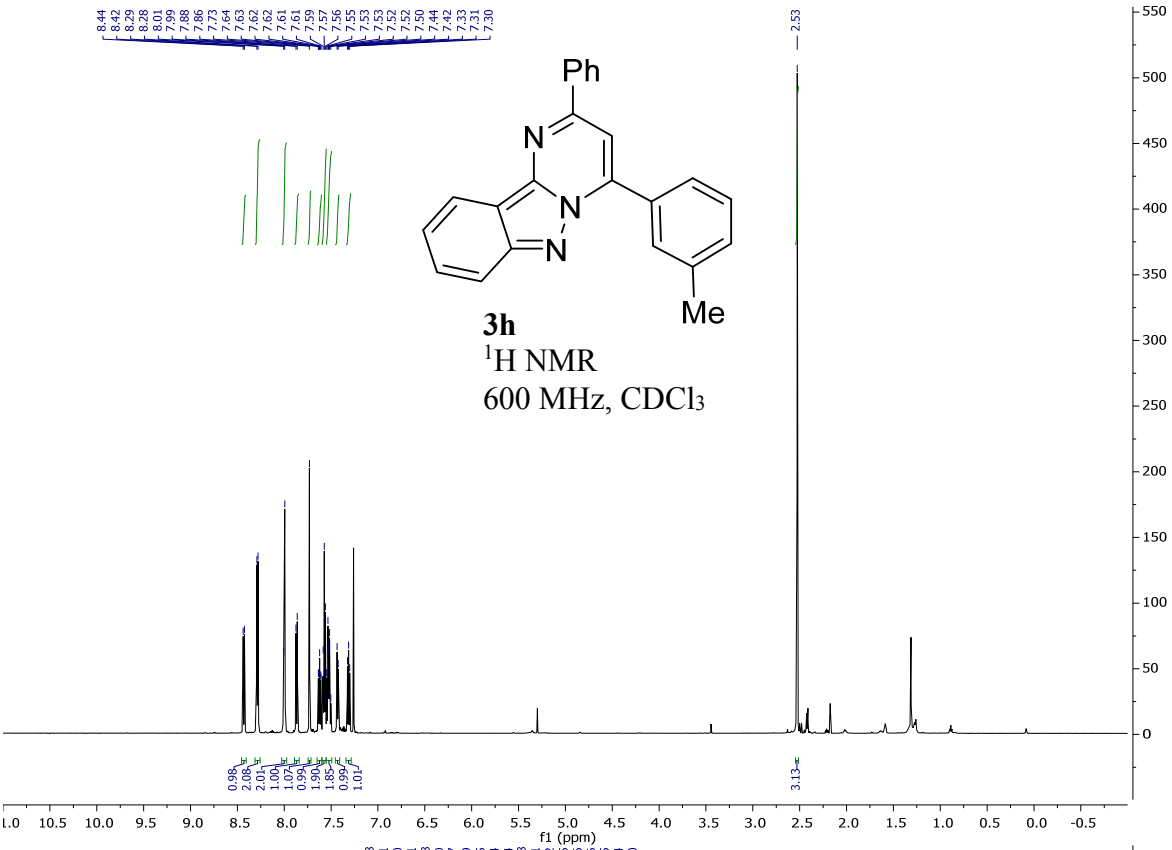

Br
N
N
N
Me
3e
13C NMR
126 MHz, CDCl3
155.15
149.87
146.74
139.69
139.34
136.26
133.33
132.46
132.04
130.48
130.46
129.50
128.62
125.99
125.07
123.25
109.38
105.46
21.62
f1 (ppm)

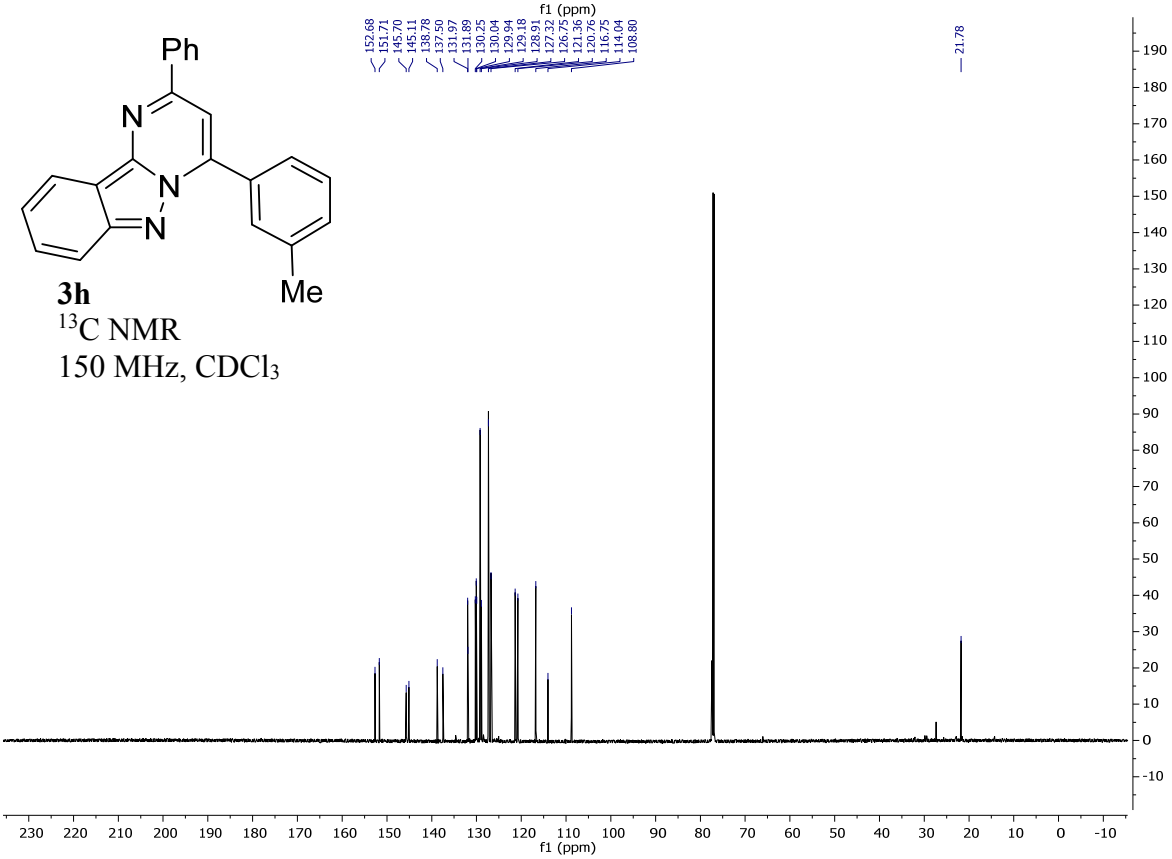

Cl
N
N
N
Me
3f
1H NMR
400 MHz, CDCl3
f1 (ppm)

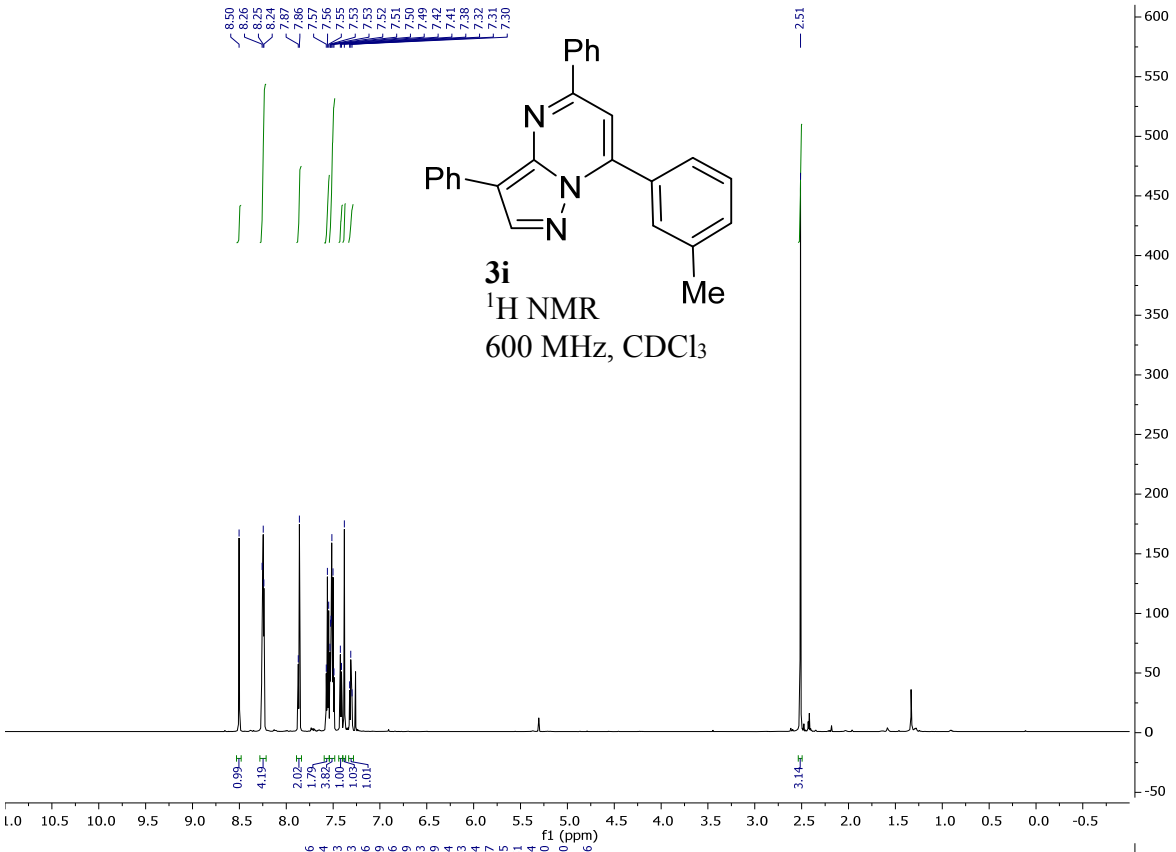

Cl
N
N
N
Me
3f
13C NMR
101 MHz, CDCl3
f1 (ppm)

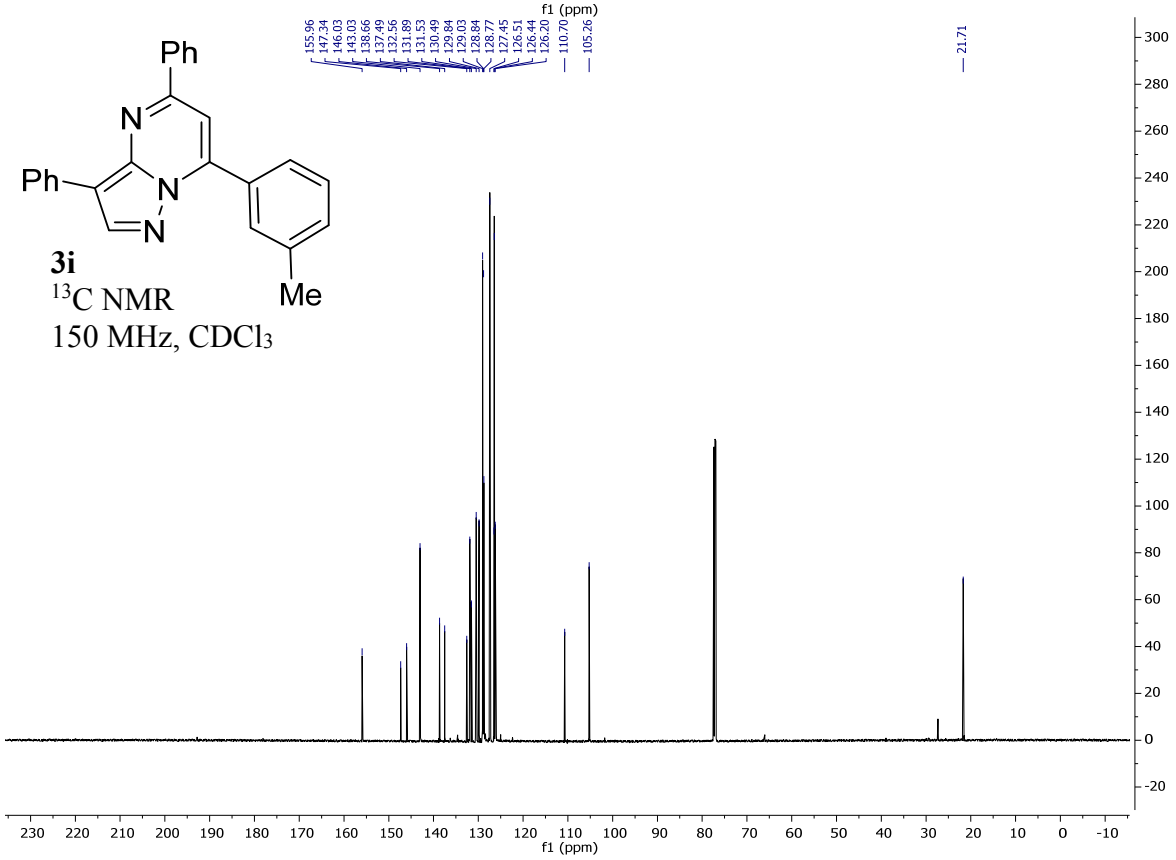

7.78
7.77
7.62
7.62
7.59
7.59
7.59
7.53
7.52
7.50
7.48
7.46
7.42
7.40
7.39
7.38
7.30
6.61
6.60
6.60
6.59
2.48
O
N
N
N
Me
3g
1H NMR
400 MHz, CDCl3
1.00
1.02
0.98
3.11
1.94
0.95
0.97
3.07
f1 (ppm)

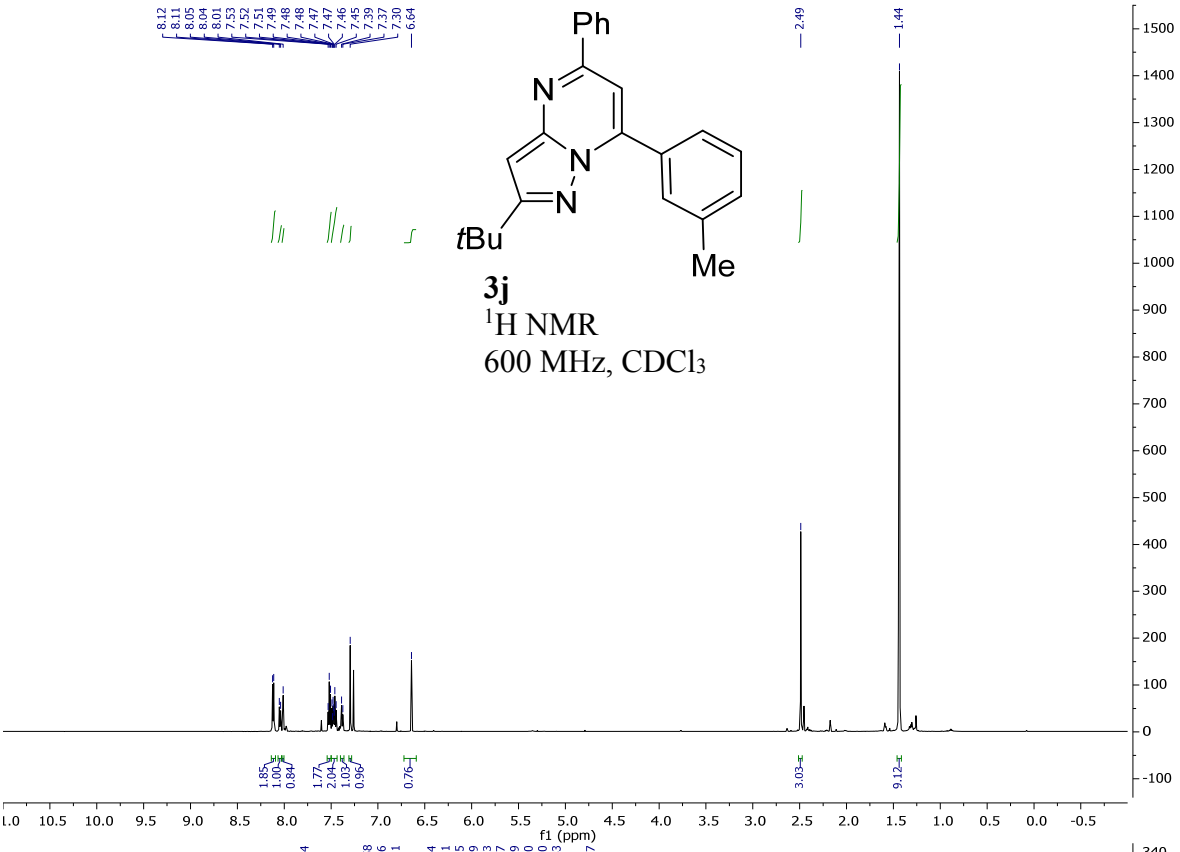

152.48
149.82
148.79
146.54
144.66
139.58
135.86
132.54
131.92
130.42
128.64
125.10
112.96
111.91
109.37
104.37
21.62
O
N
N
N
Me
3g
13C NMR
101 MHz, CDCl3
f1 (ppm)

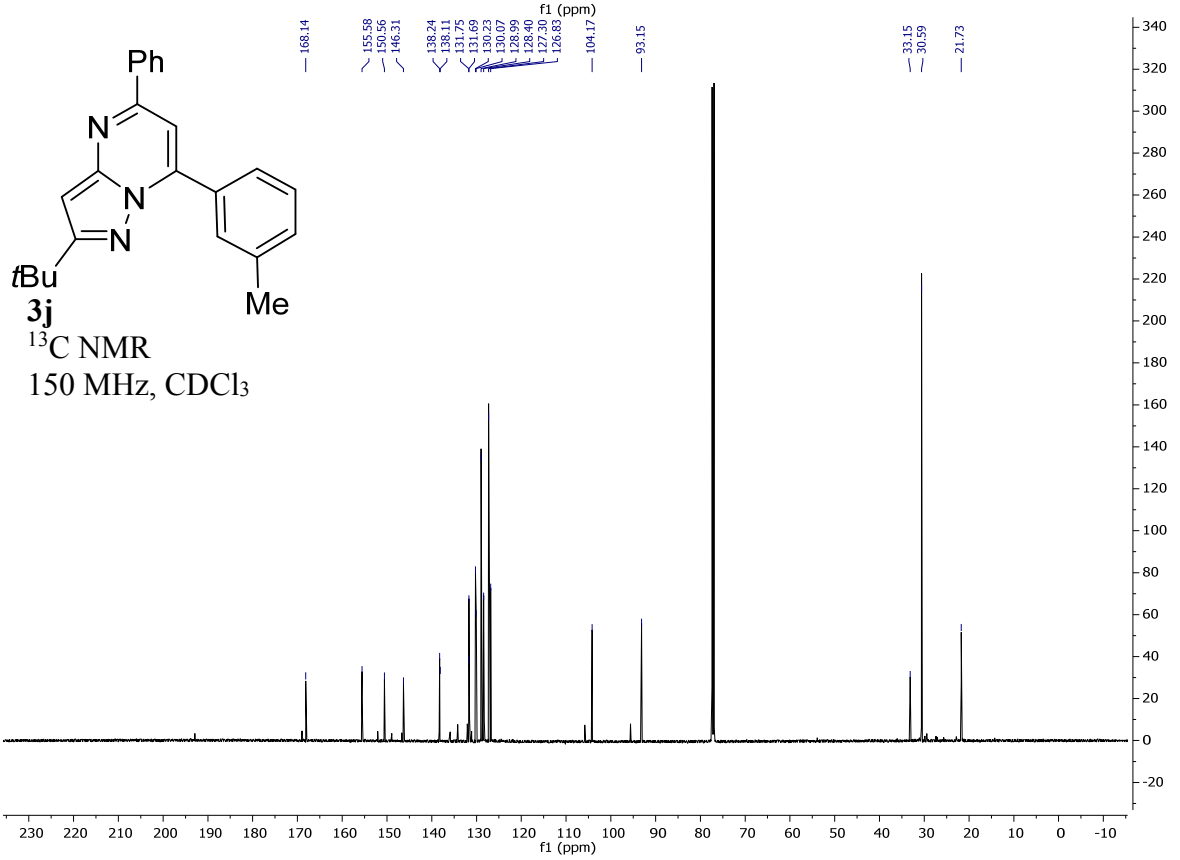

Ph
N
N
N
Me
3h
1H NMR
600 MHz, CDCl3
f1 (ppm)

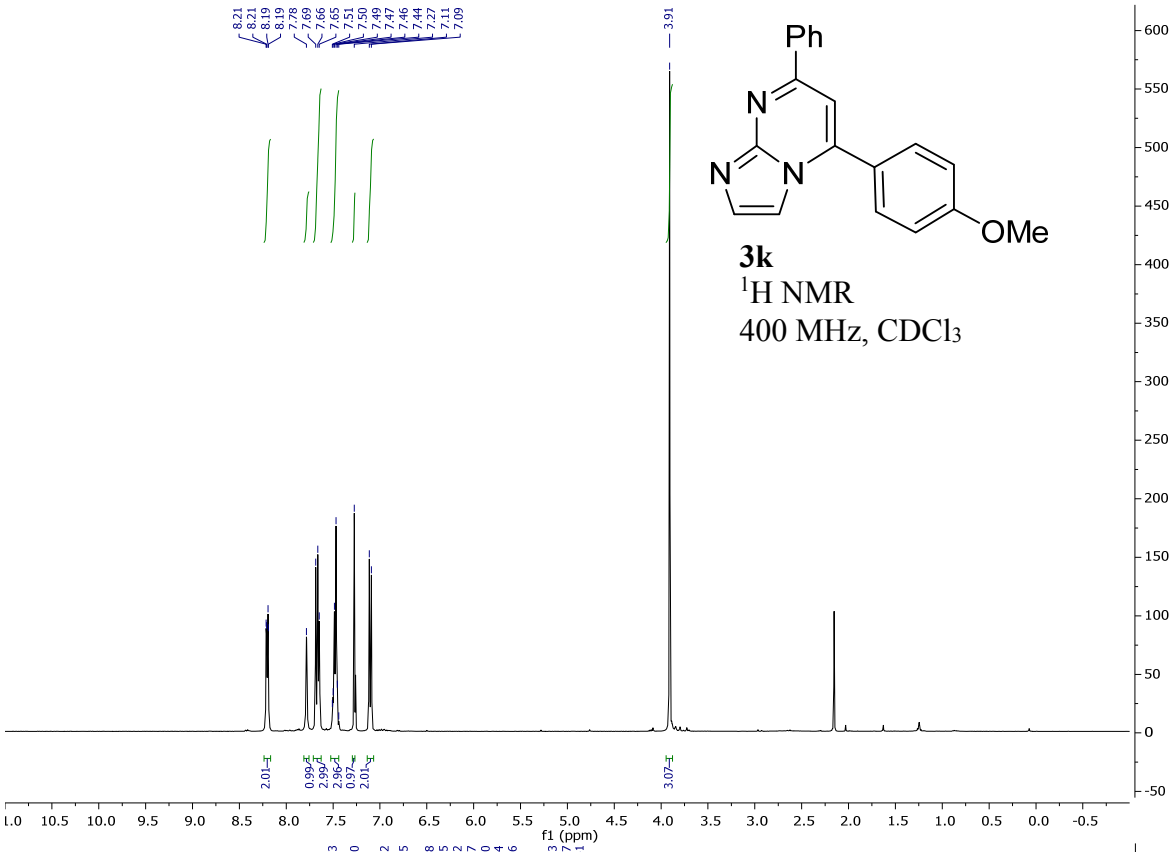

Ph
N
N
N
Me
3h
13C NMR
150 MHz, CDCl3
f1 (ppm)


Ph
N
Ph
N
N
Me
3i
1H NMR
600 MHz, CDCl3


Ph
N
Ph
N
N
Me
3i
13C NMR
150 MHz, CDCl3


Ph
N
N
N
tBu
Me
3j
1H NMR
600 MHz, CDCl3
f1 (ppm)

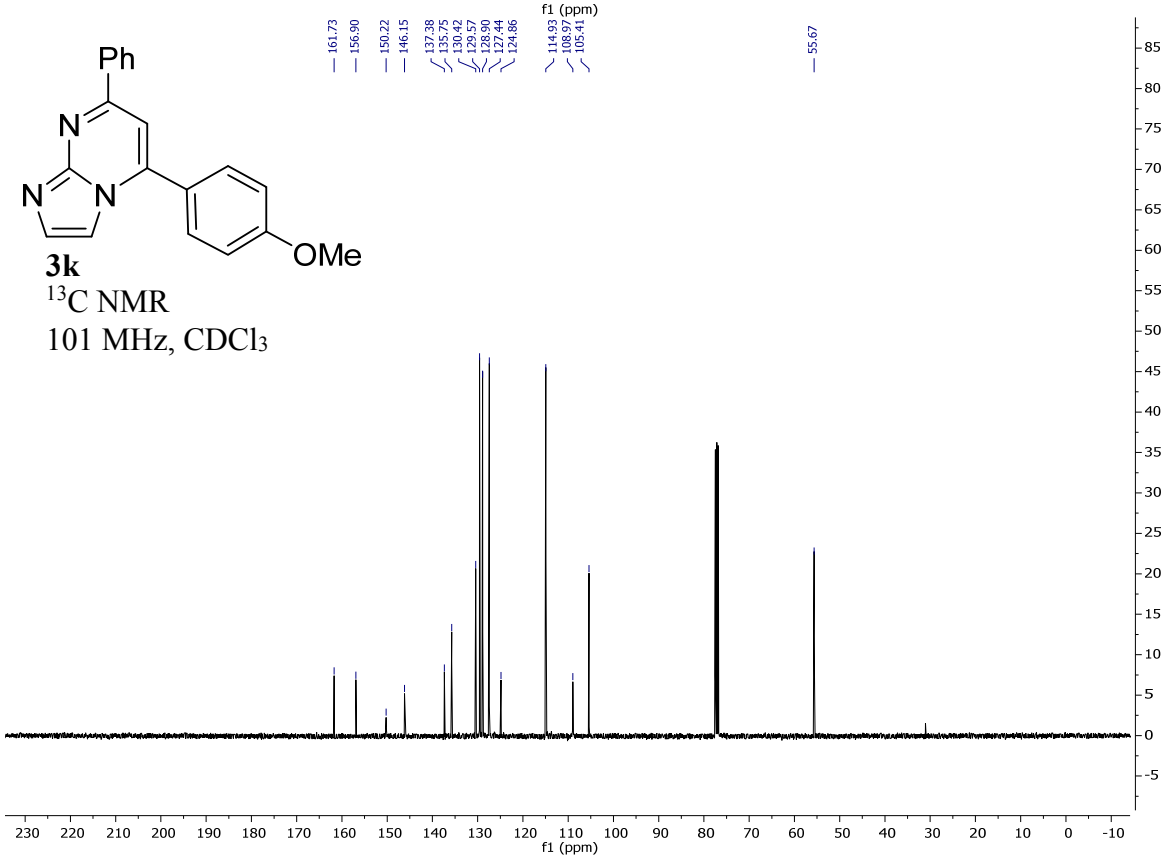

Ph
N
N
N
tBu
Me
3j
13C NMR
150 MHz, CDCl3
f1 (ppm)



3k

^{1}H NMR

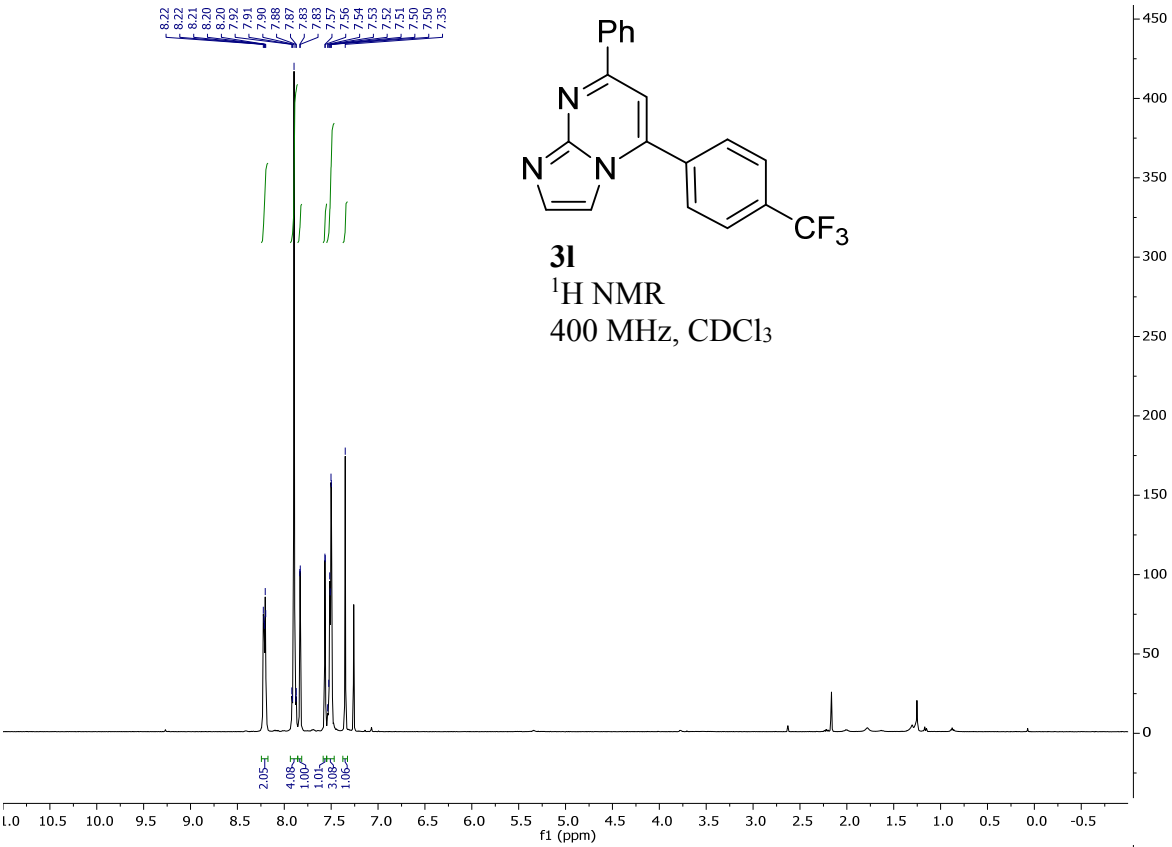
400 MHz, $CDCl_3$



3k

^{13}C NMR

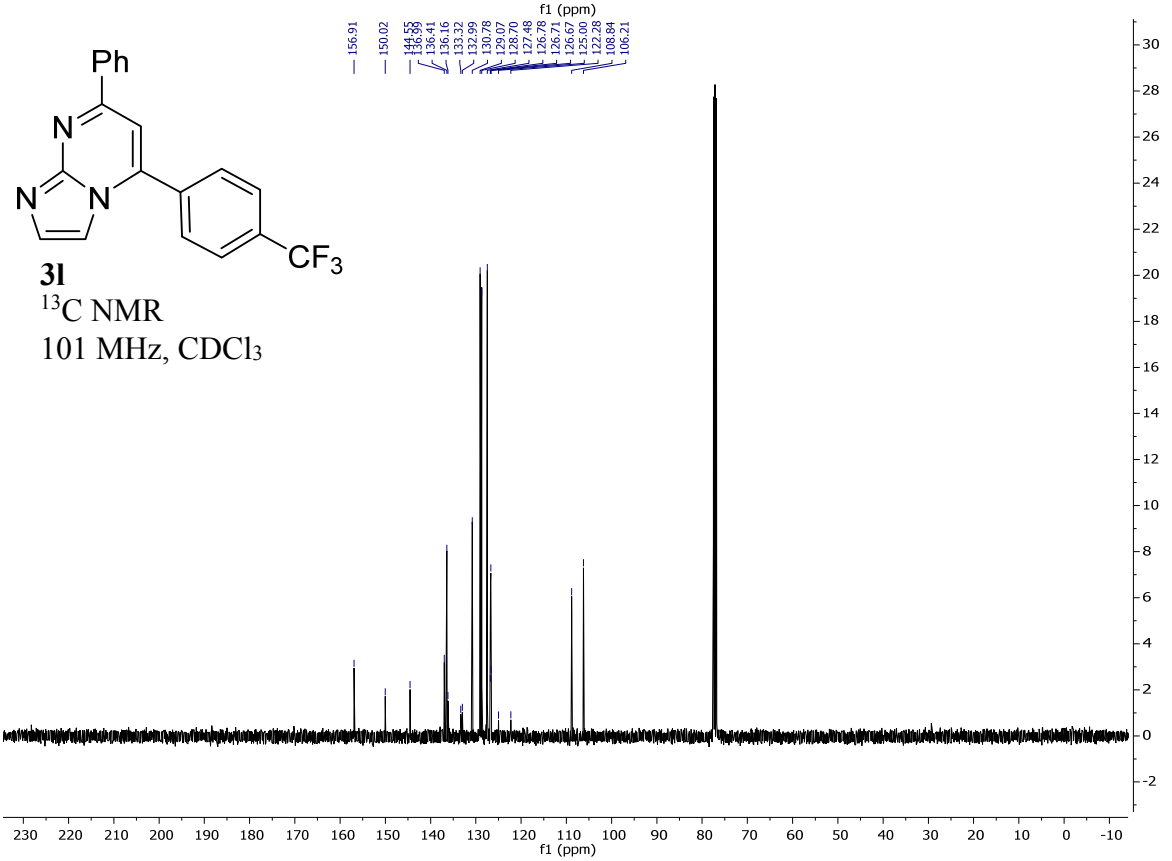
101 MHz, $CDCl_3$



3l

^{1}H NMR

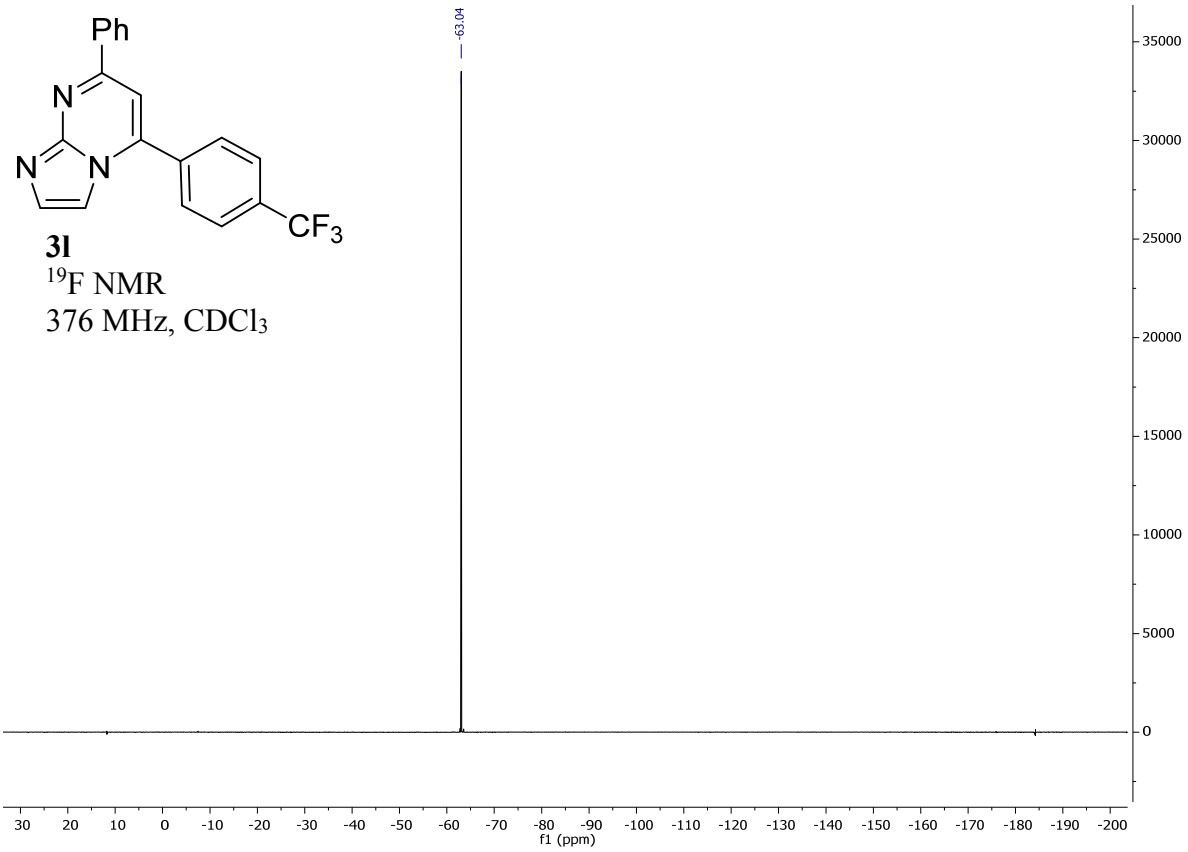
400 MHz, $CDCl_3$



3l

^{13}C NMR

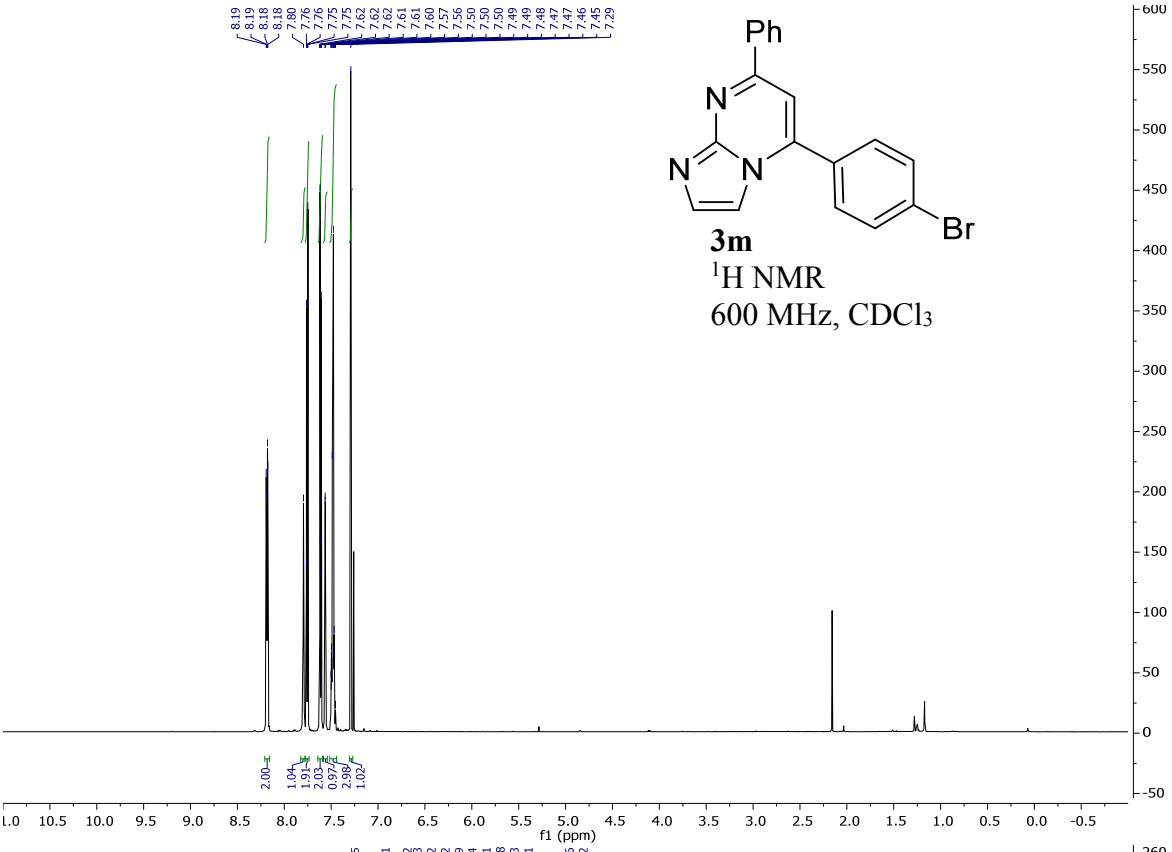
101 MHz, $CDCl_3$

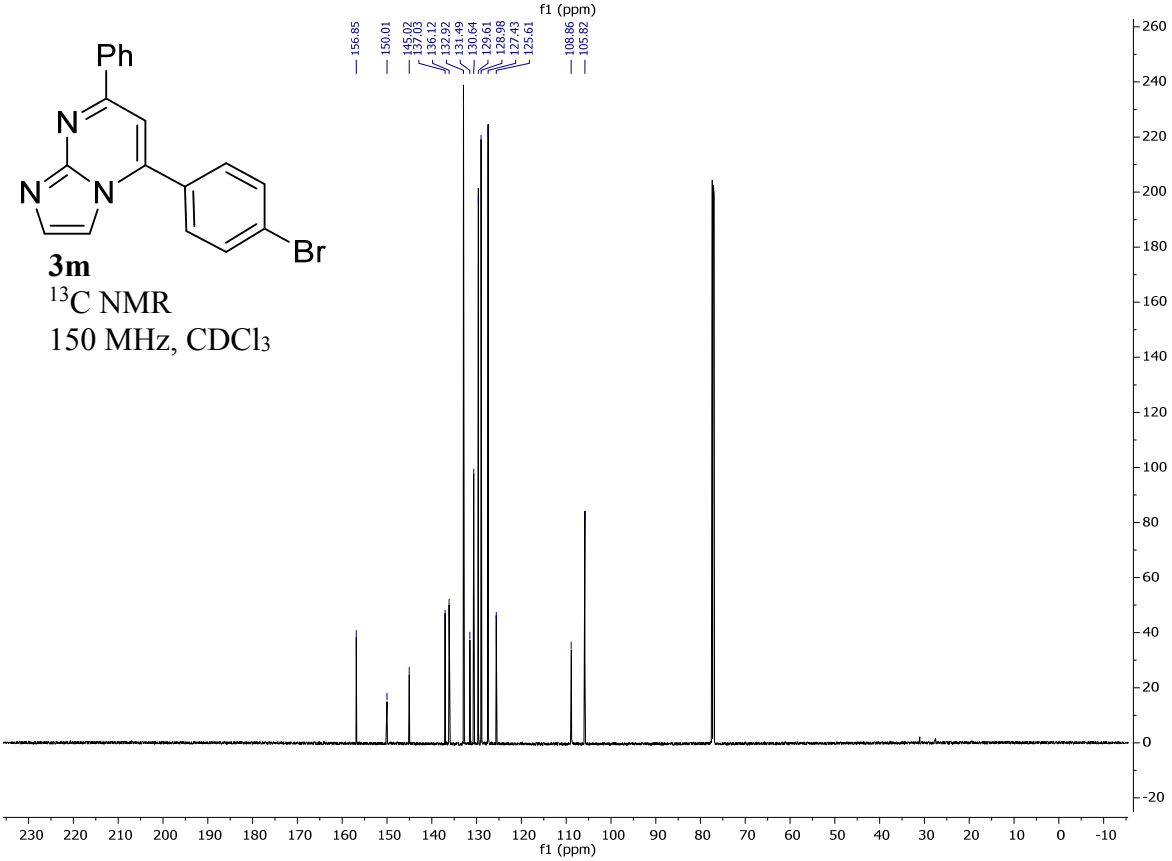


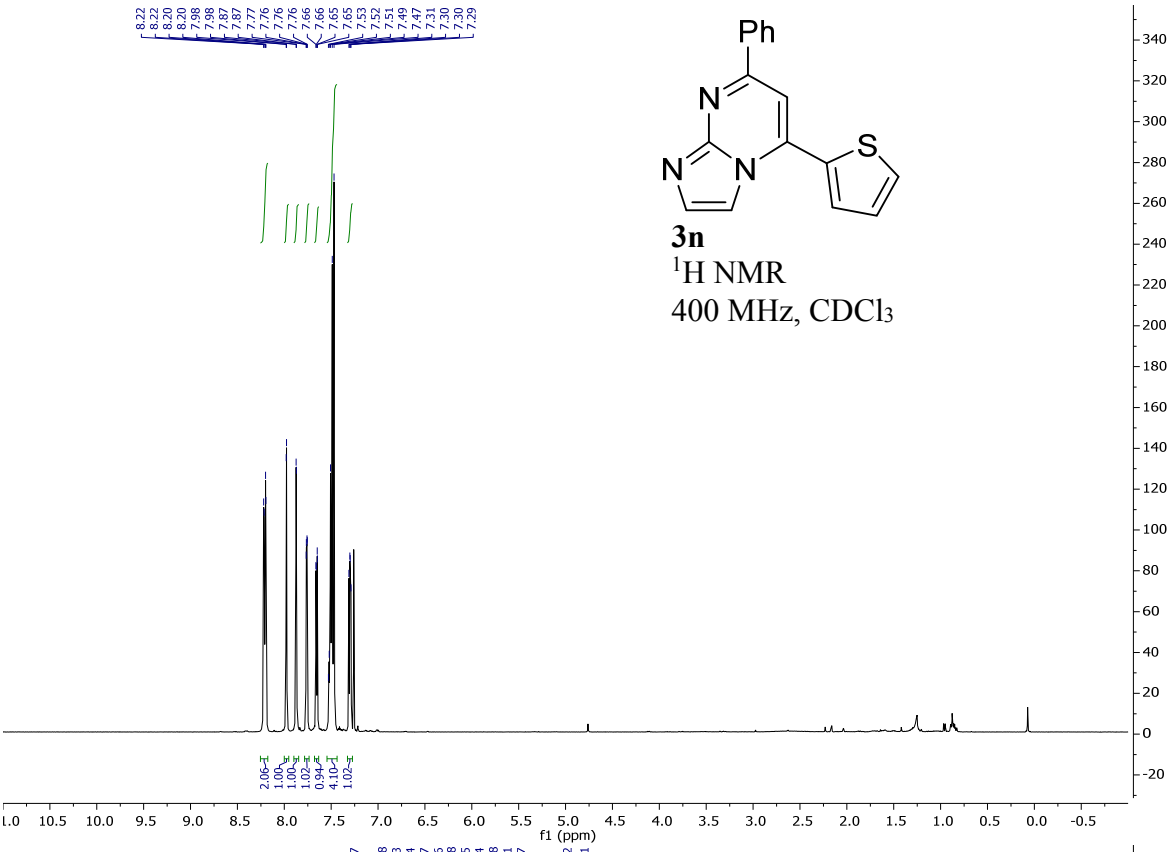
3l

^{19}F NMR

376 MHz, $CDCl_3$


Ph
N
N
N
Br
3m
1H NMR
600 MHz, CDCl3
f1 (ppm)

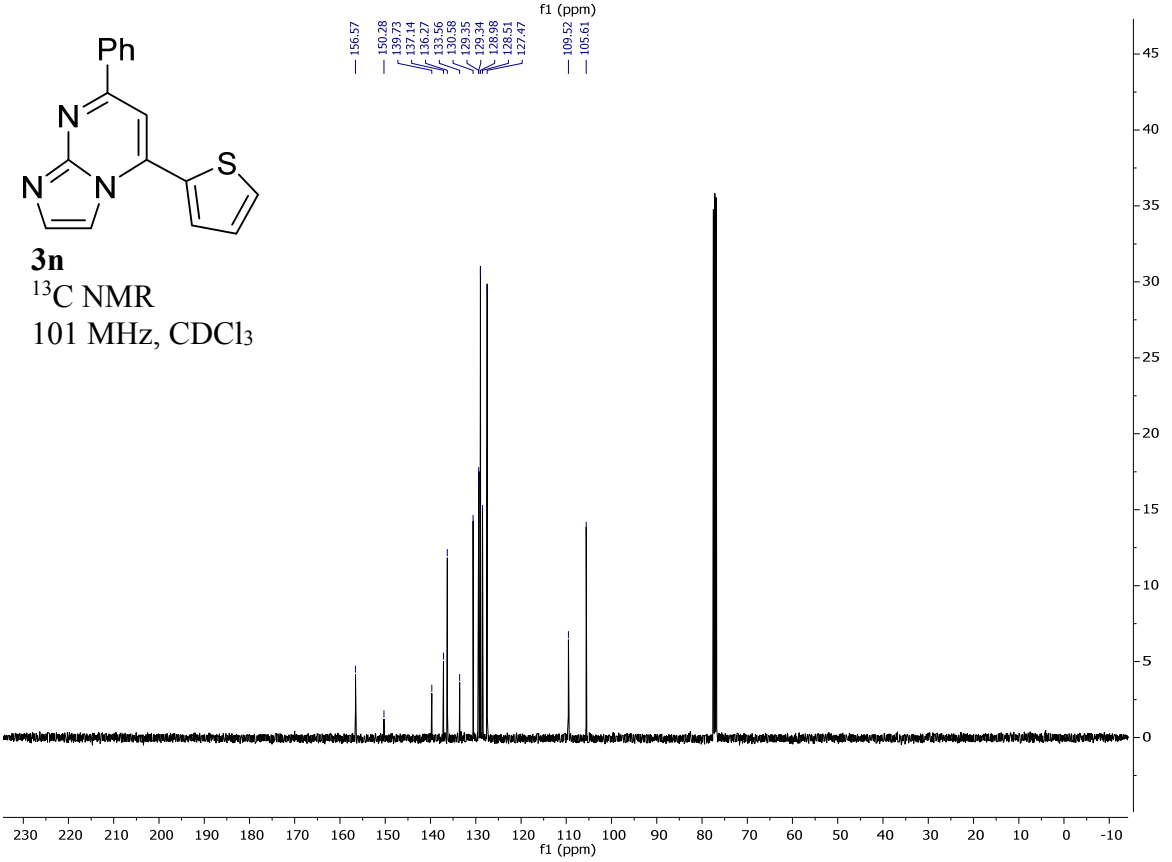

Ph
N
N
N
Br
3m
13C NMR
150 MHz, CDCl3
f1 (ppm)



3n

^{1}H NMR

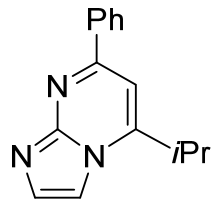
400 MHz, $CDCl_3$



3n

^{13}C NMR

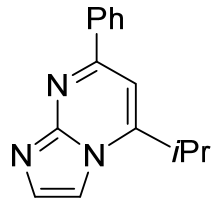
101 MHz, $CDCl_3$



3o

^{1}H NMR

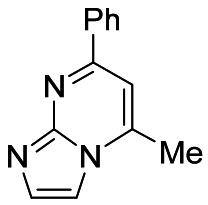
400 MHz, $CDCl_3$



3o

^{13}H NMR

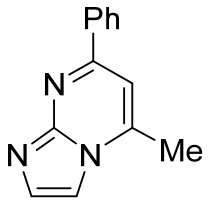
126 MHz, $CDCl_3$



3p

^{1}H NMR

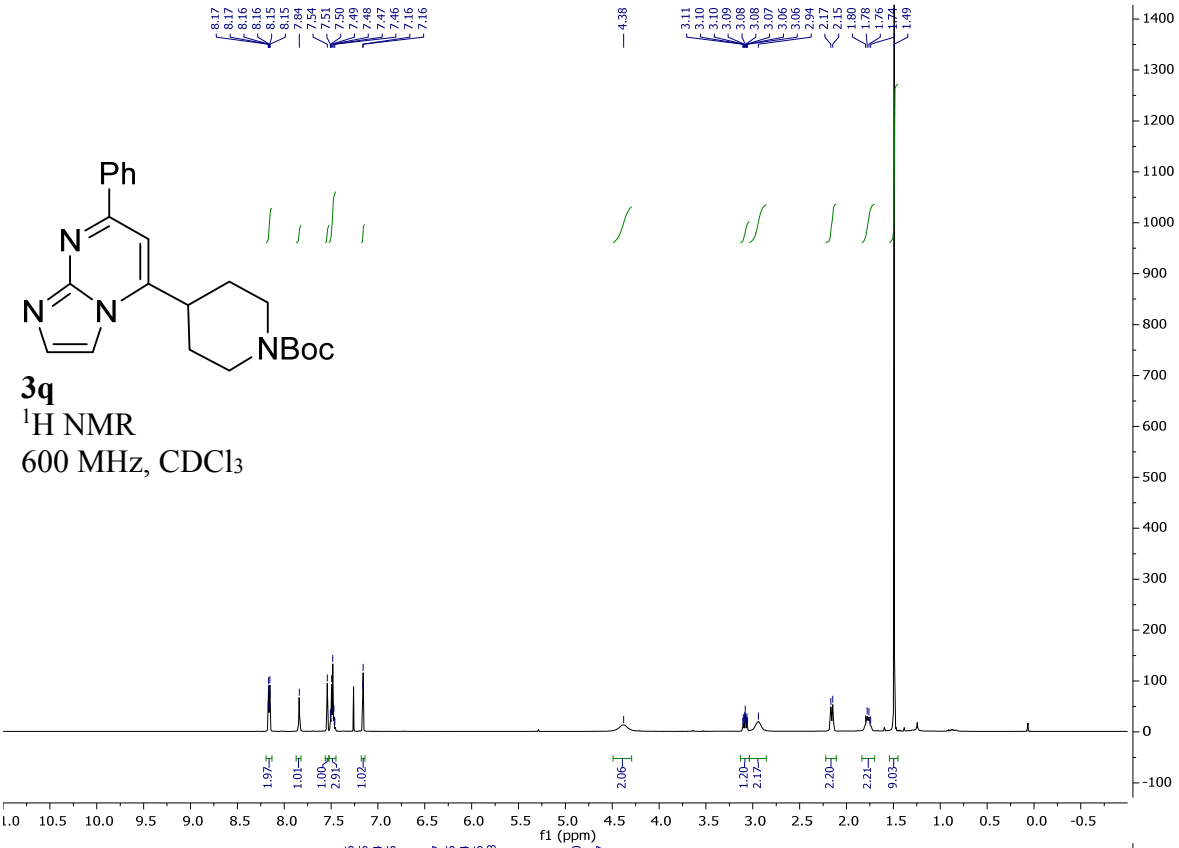
600 MHz, $CDCl_3$



3p

^{13}C NMR

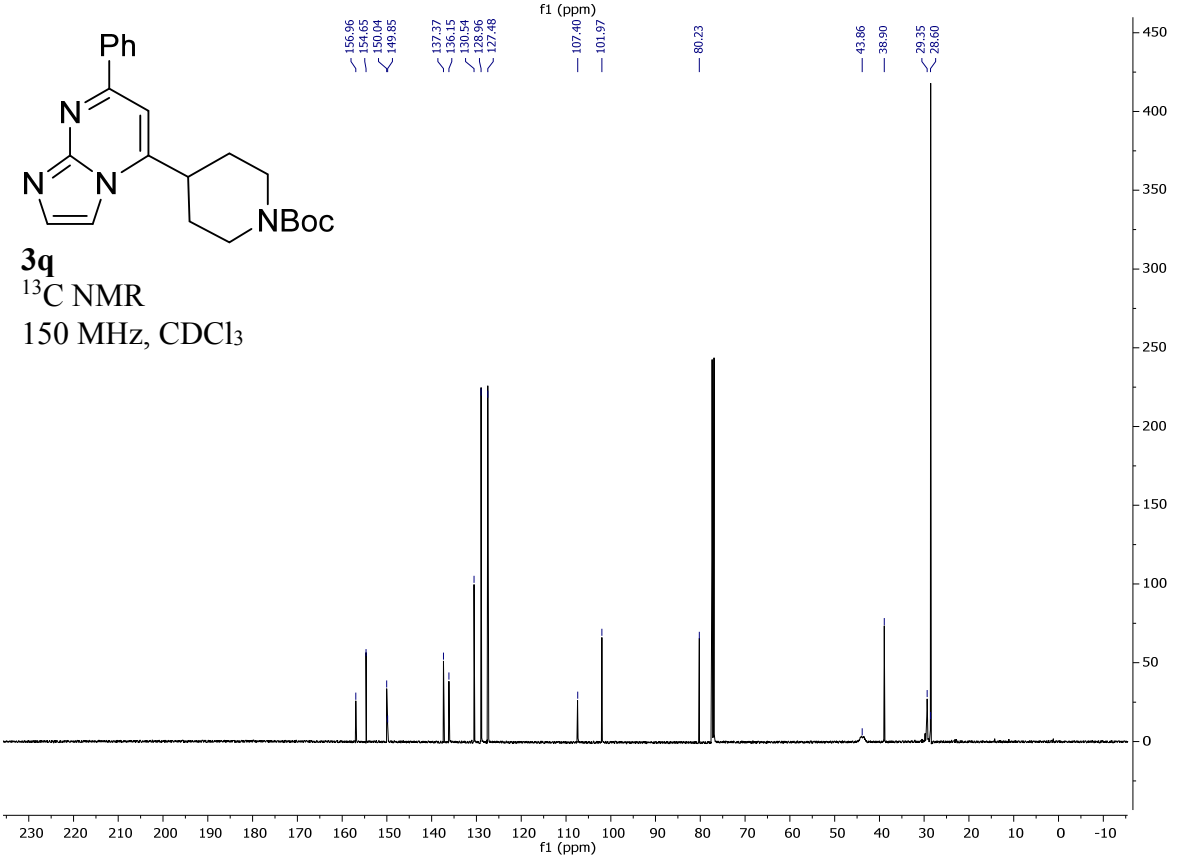
150 MHz, $CDCl_3$



3q

^{1}H NMR

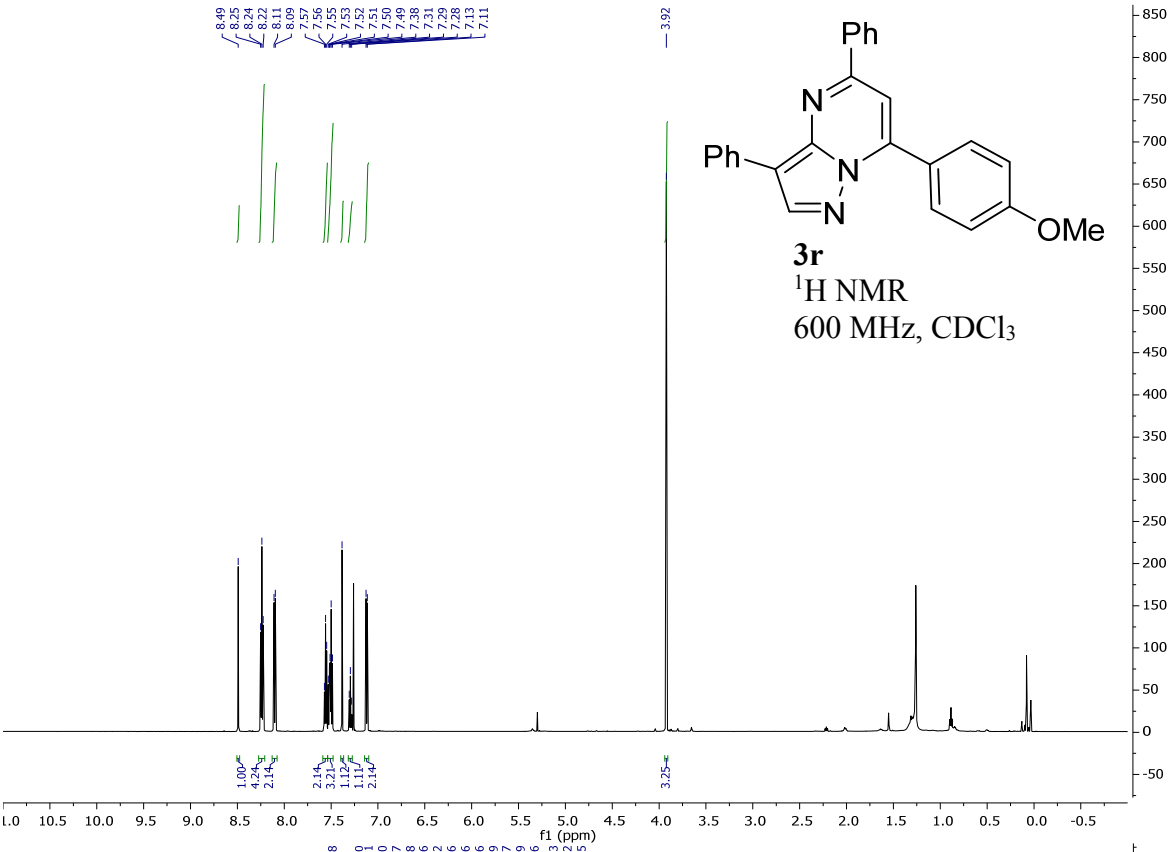
600 MHz, $CDCl_3$



3q

^{13}C NMR

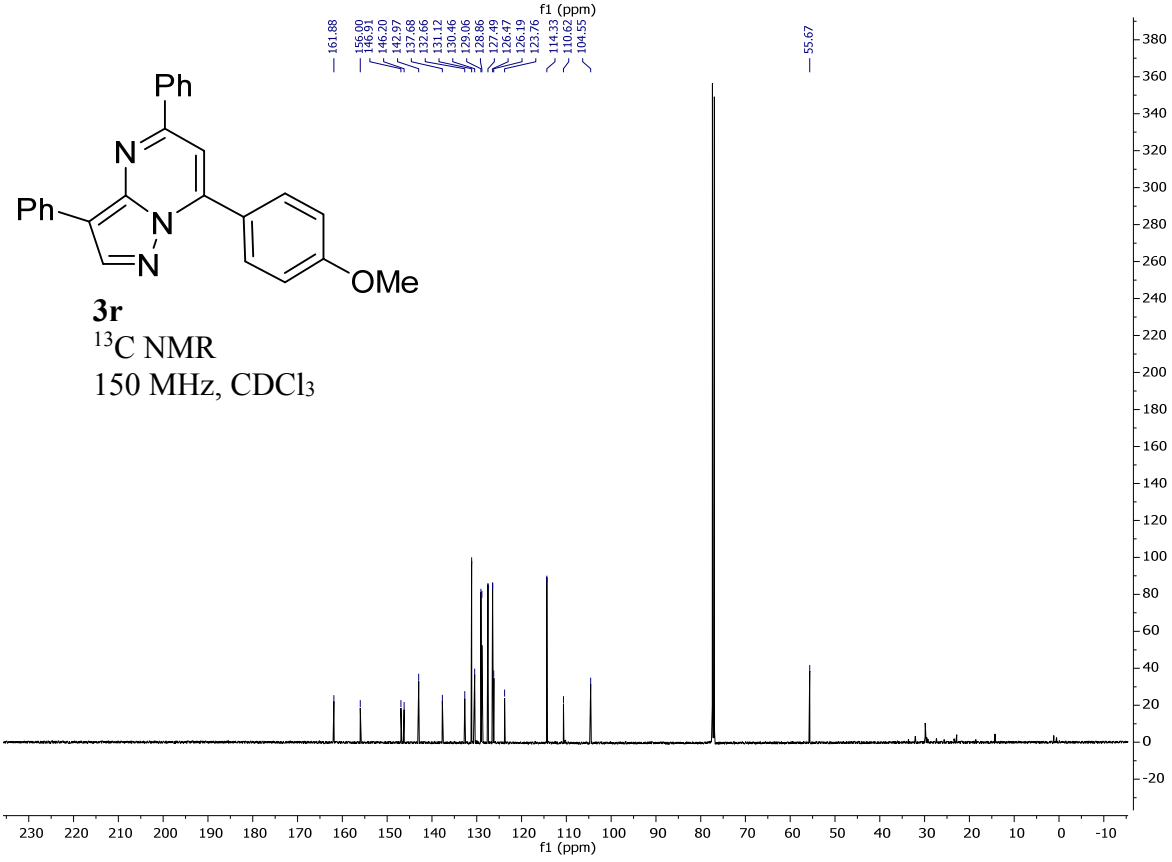
150 MHz, $CDCl_3$



3r

^{1}H NMR

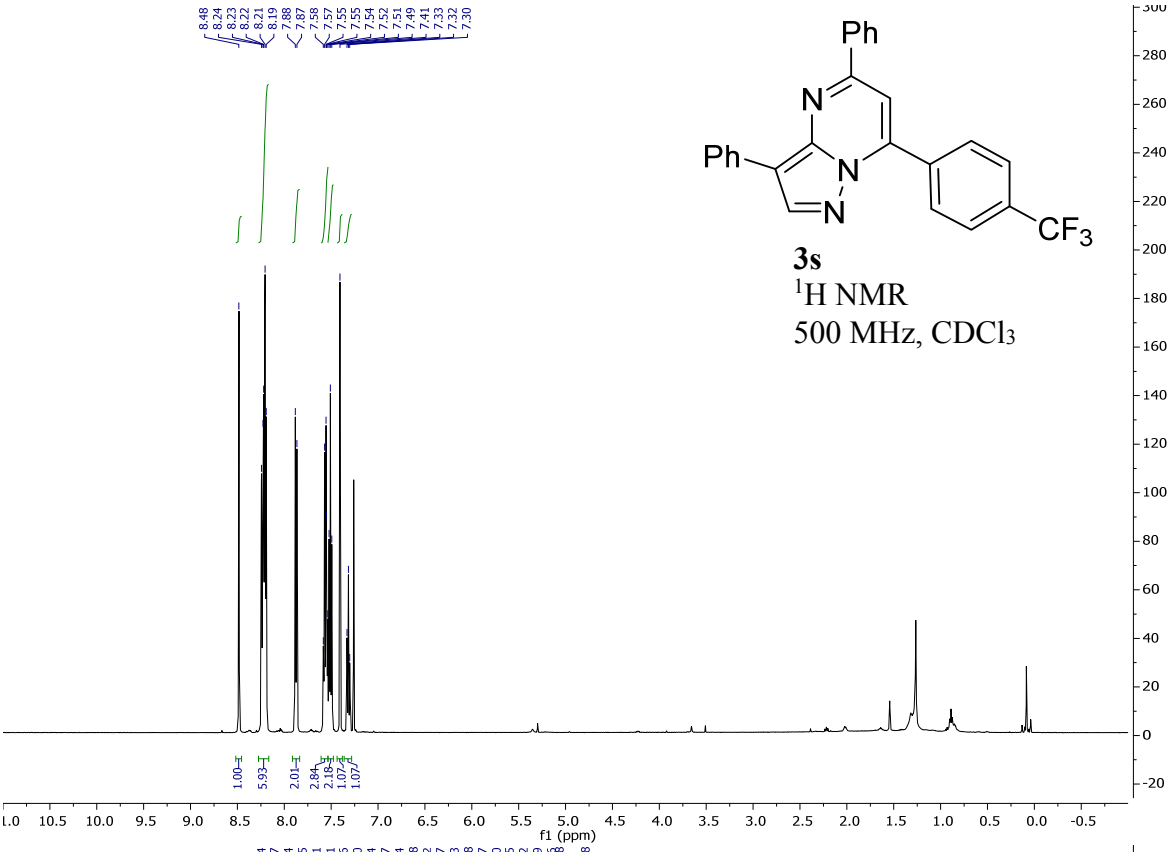
600 MHz, $CDCl_3$



3r

^{13}C NMR

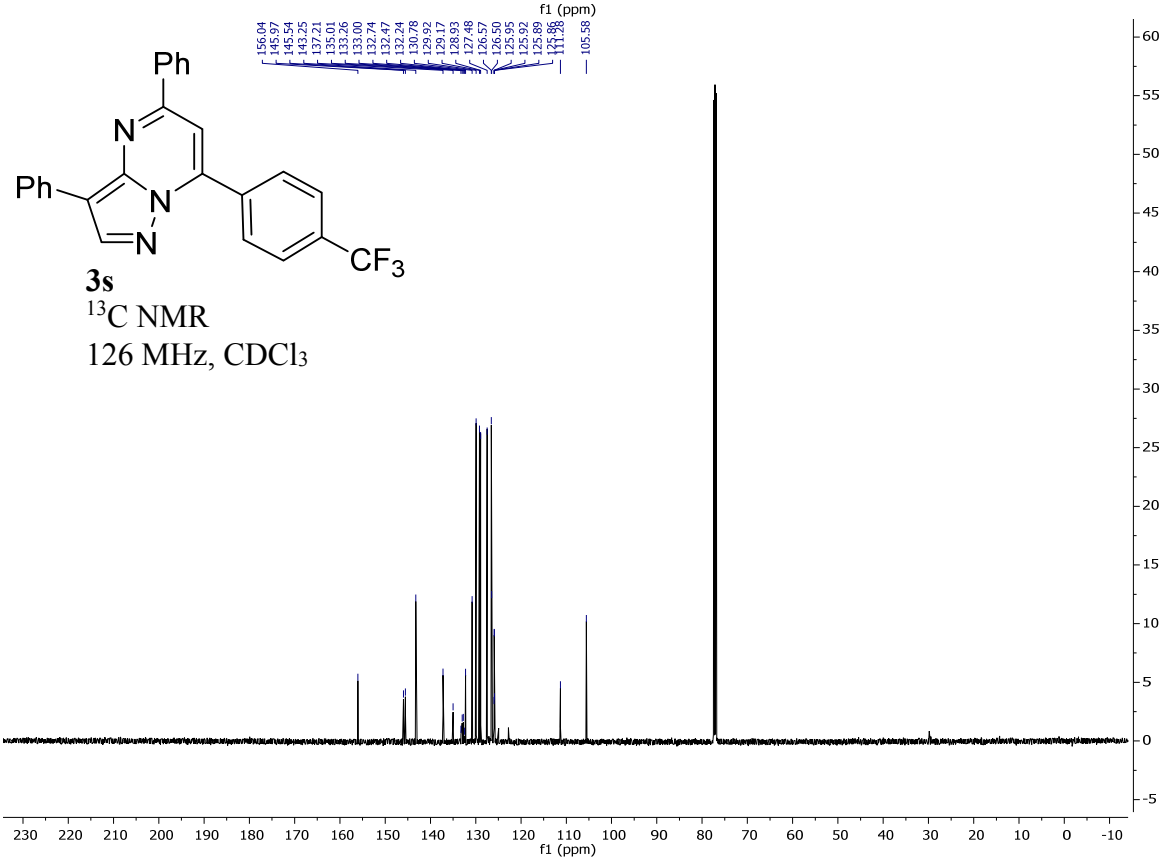
150 MHz, $CDCl_3$



3s

^{1}H NMR

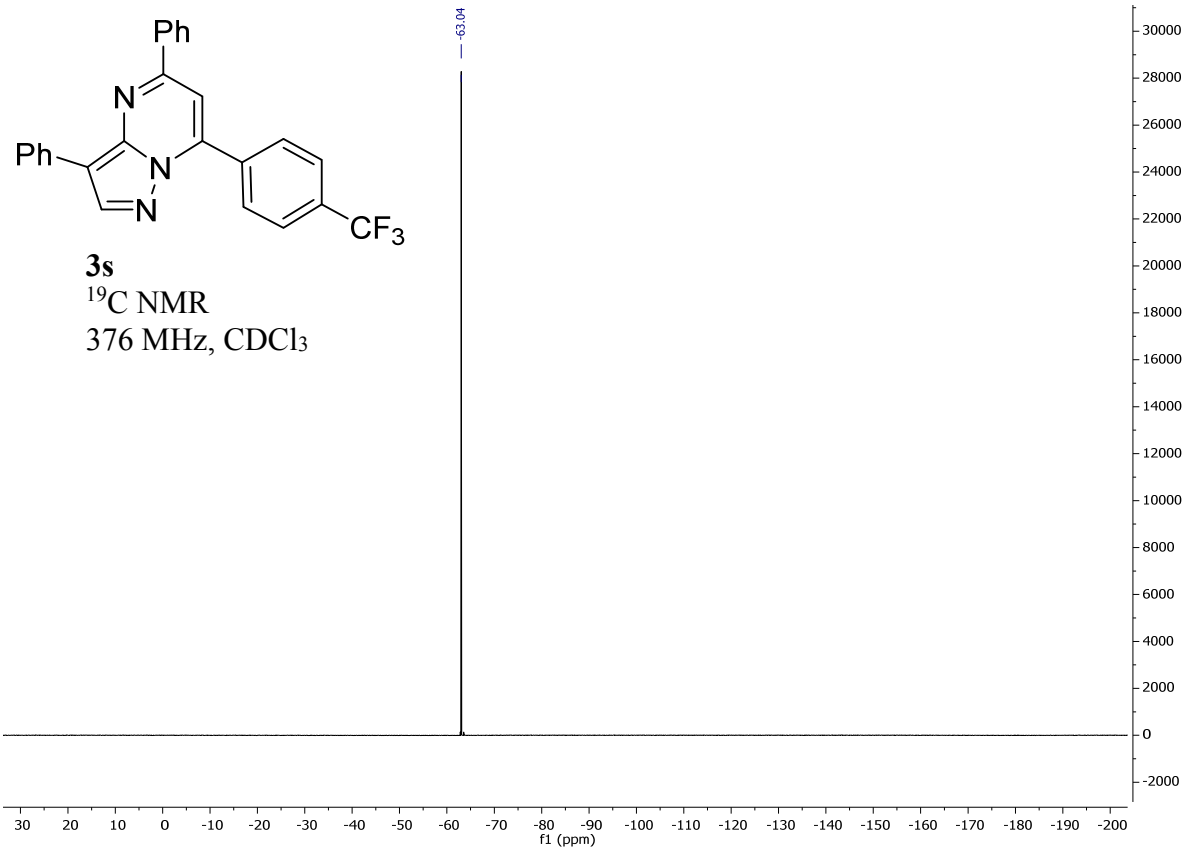
500 MHz, $CDCl_3$



3s

^{13}C NMR

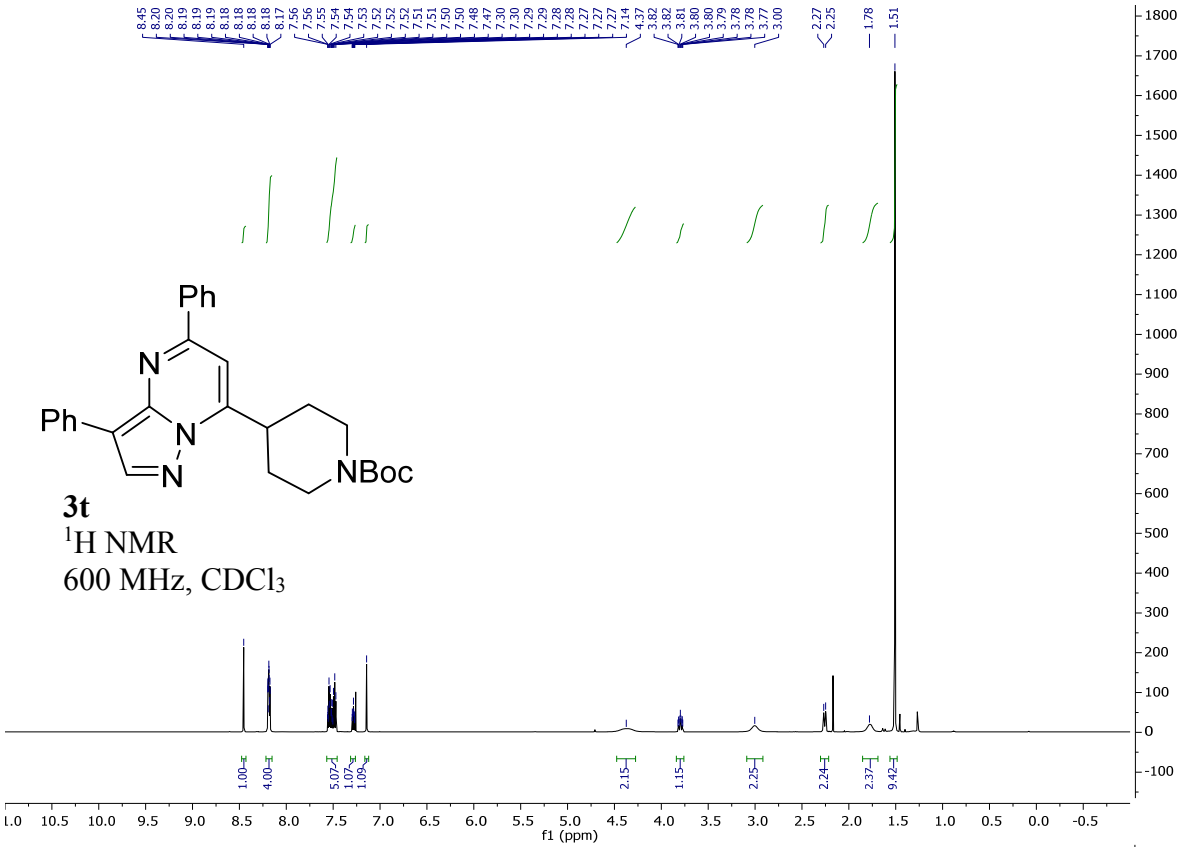
126 MHz, $CDCl_3$



3s

^{19}C NMR

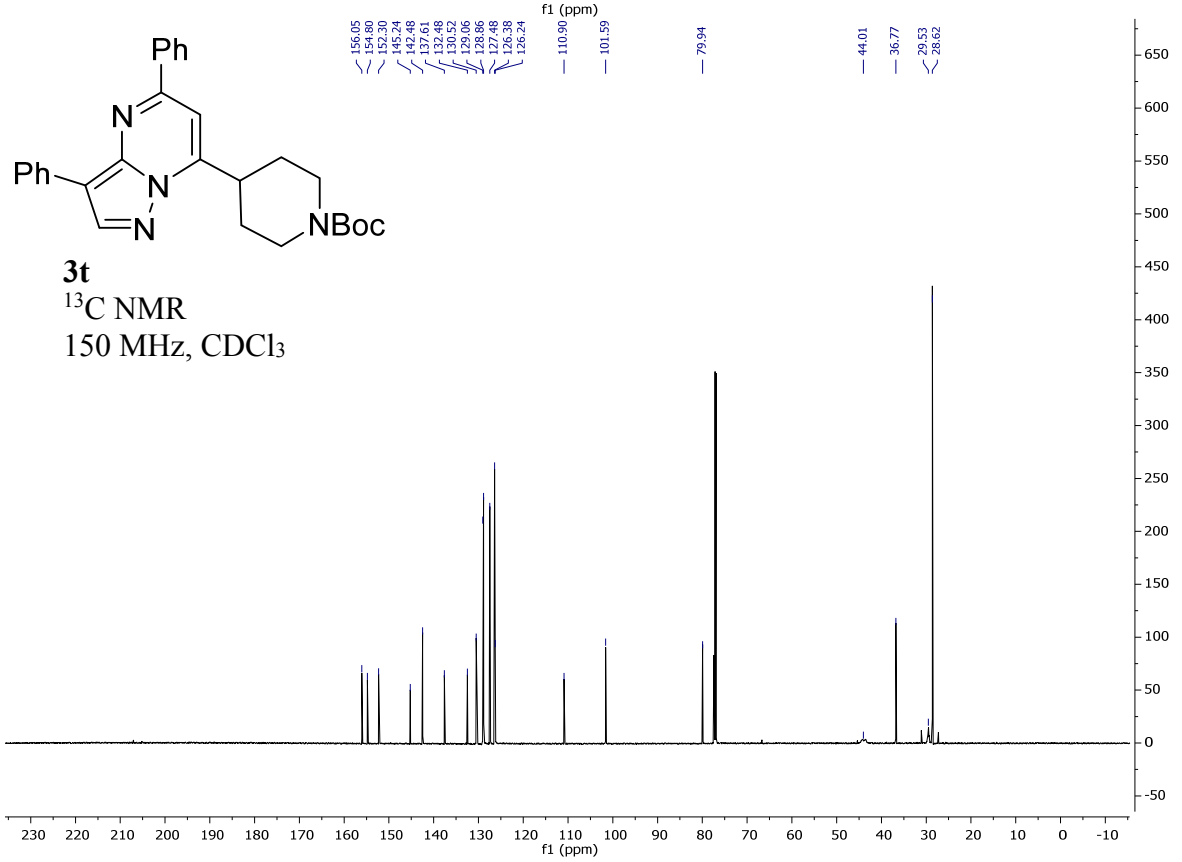
376 MHz, $CDCl_3$



3t

^{1}H NMR

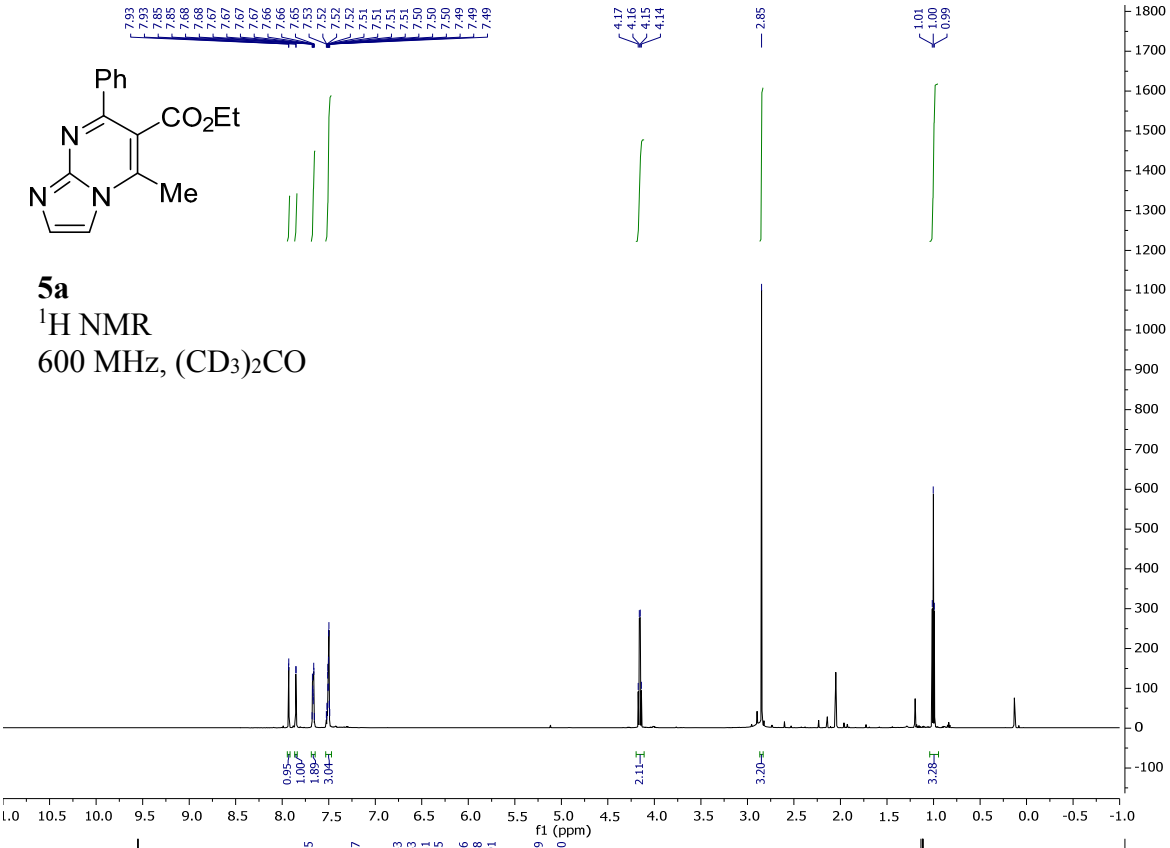
600 MHz, $CDCl_3$

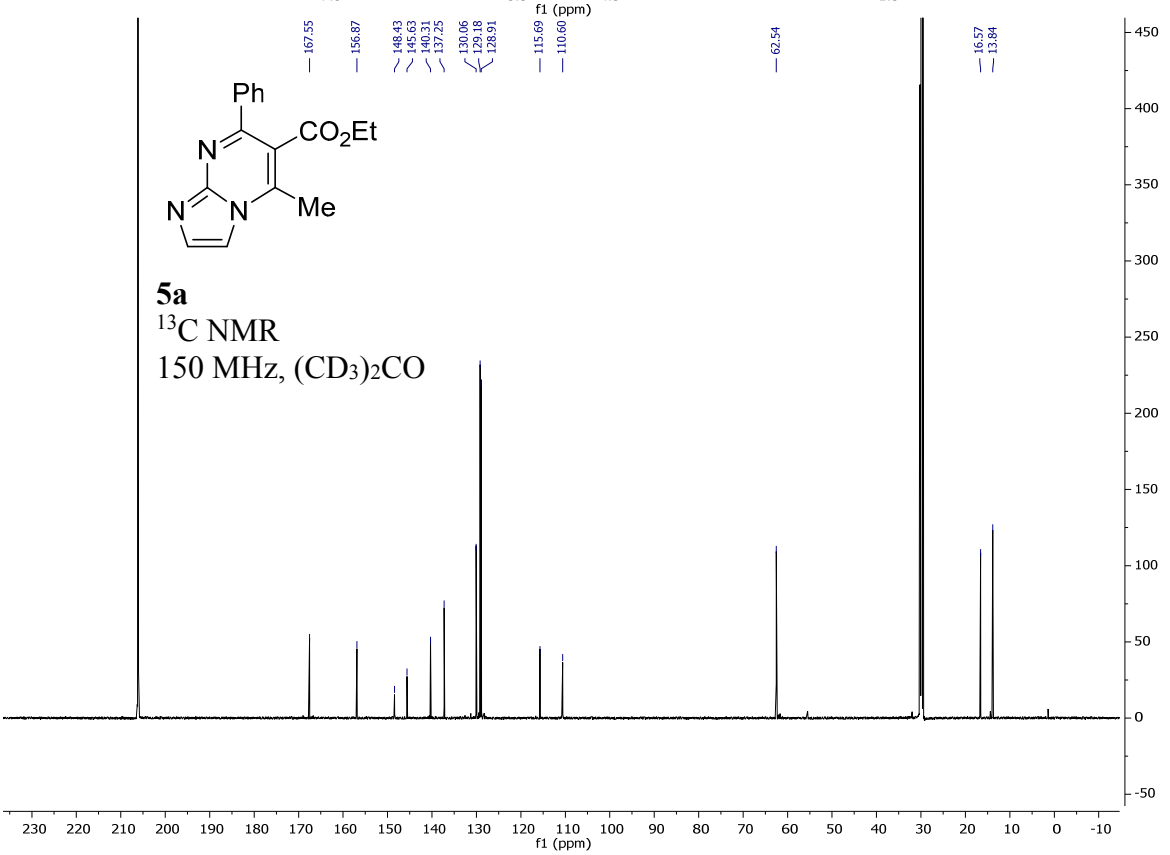


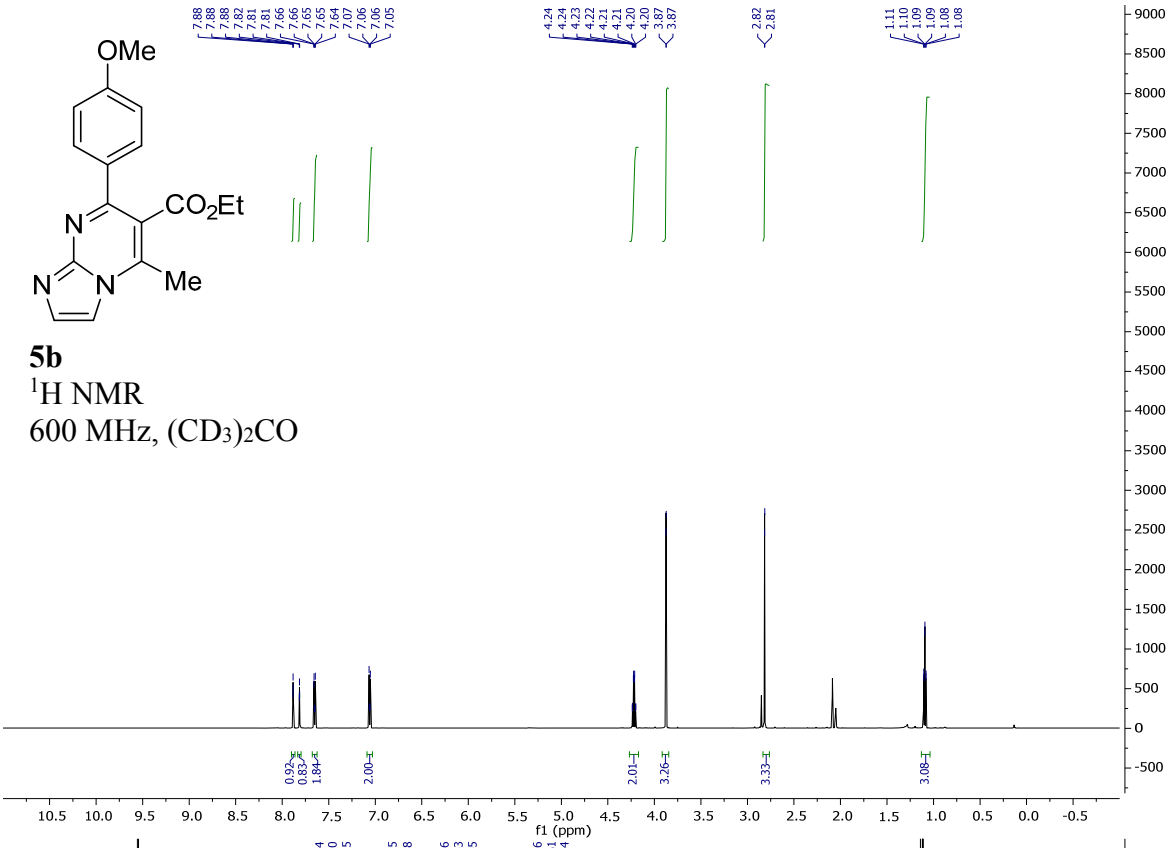
3t

^{13}C NMR

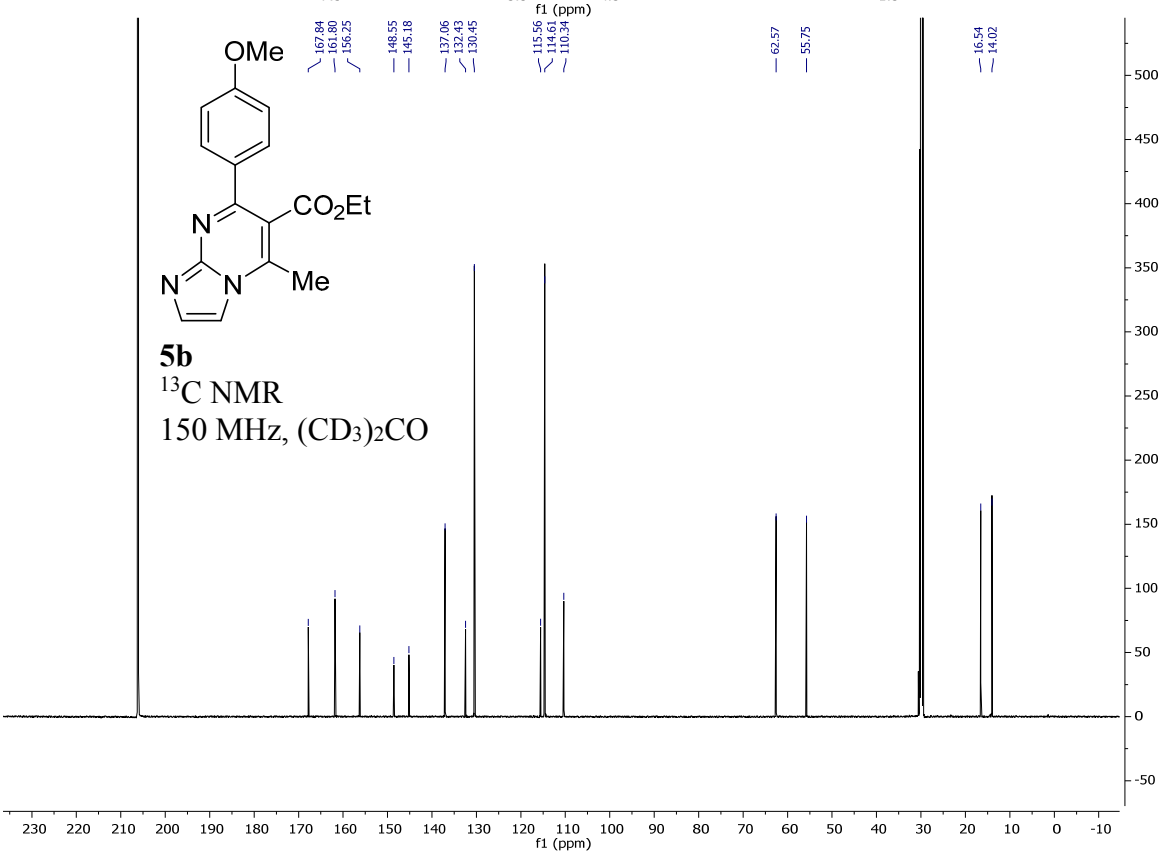
150 MHz, $CDCl_3$


Ph
CO2Et
N
N
N
Me
5a
1H NMR
600 MHz, (CD3)2CO
f1 (ppm)

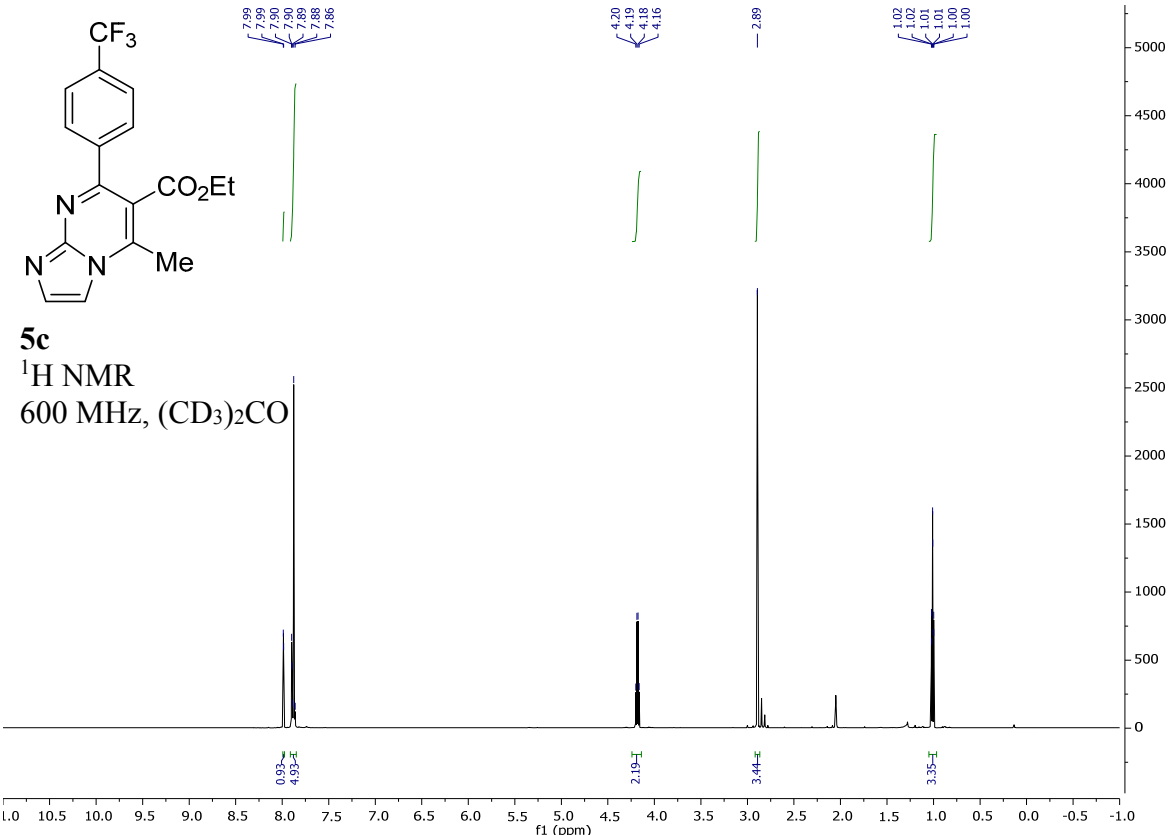

Ph
CO2Et
N
N
N
Me
5a
13C NMR
150 MHz, (CD3)2CO
f1 (ppm)



5b
^{1}H NMR
600 MHz, $(CD_3)_2CO$



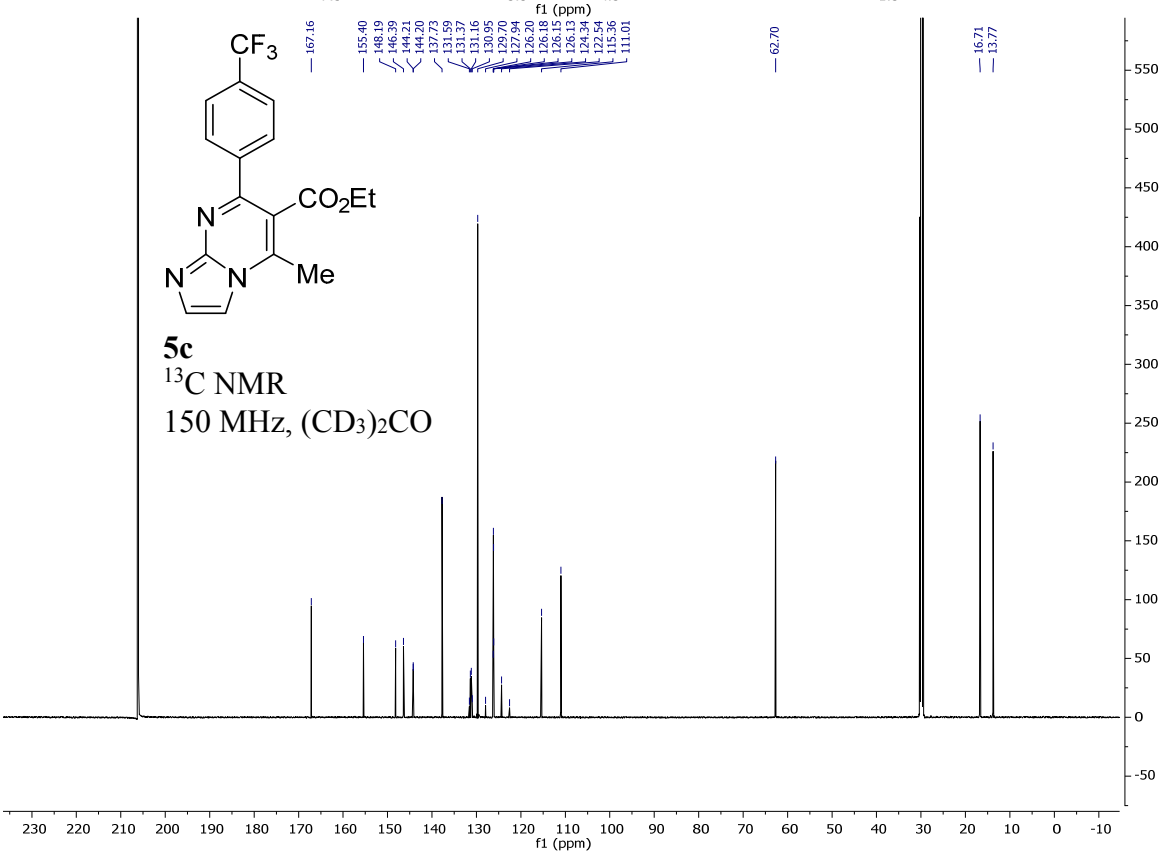
5b
^{13}C NMR
150 MHz, $(CD_3)_2CO$



5c

^{1}H NMR

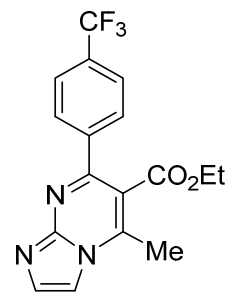
600 MHz, $(CD_3)_2CO$



5c

^{13}C NMR

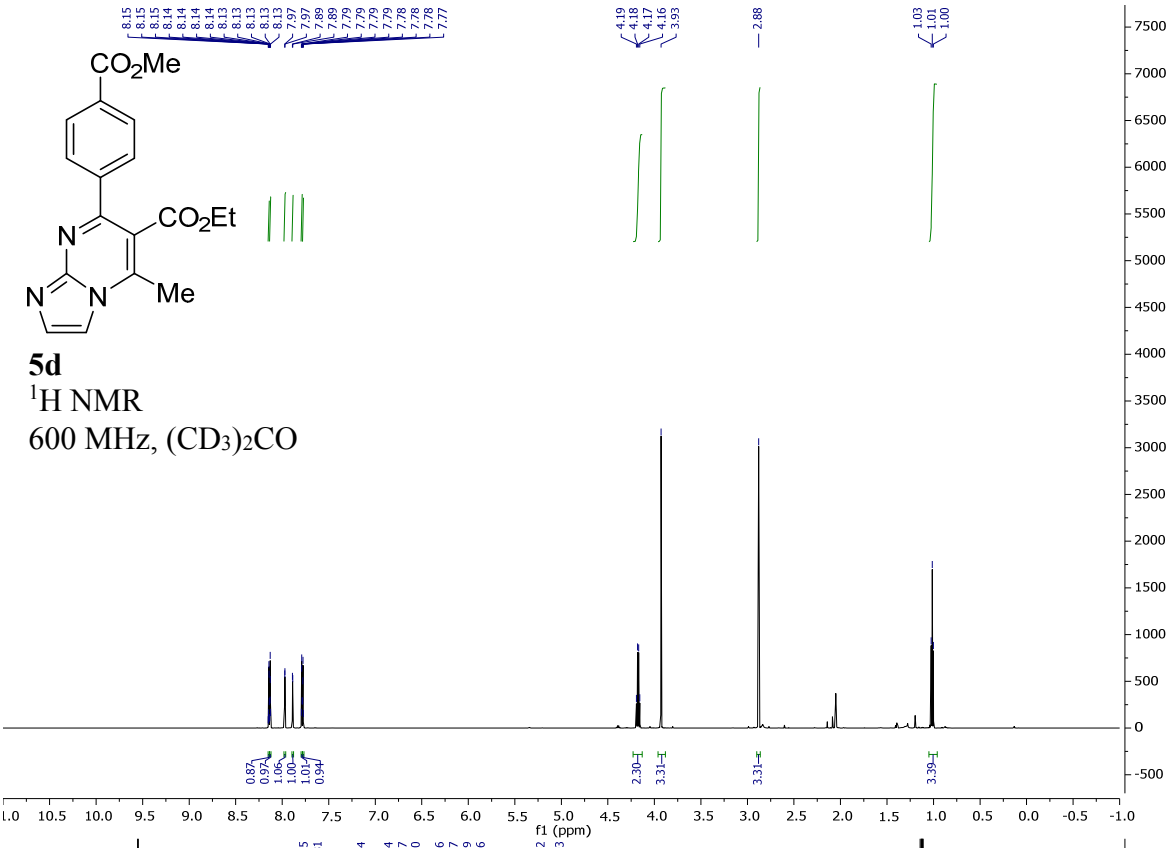
150 MHz, $(CD_3)_2CO$

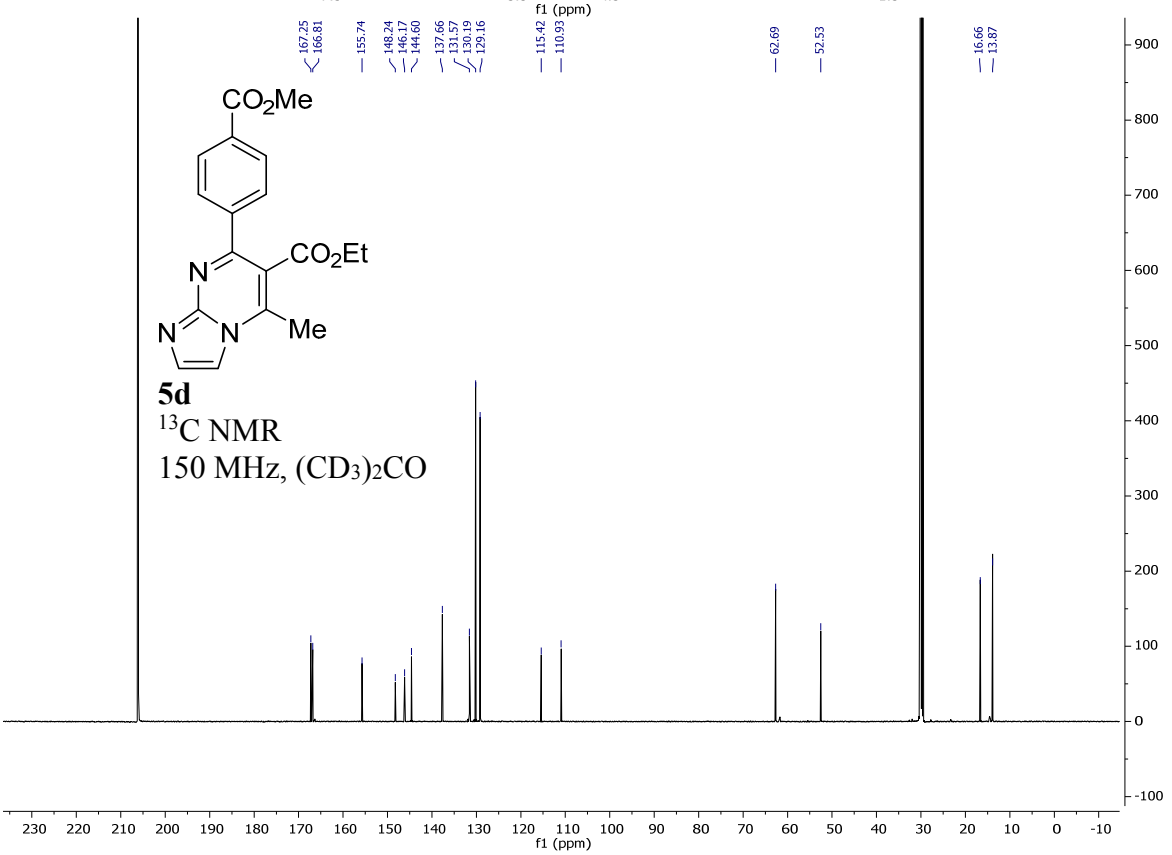


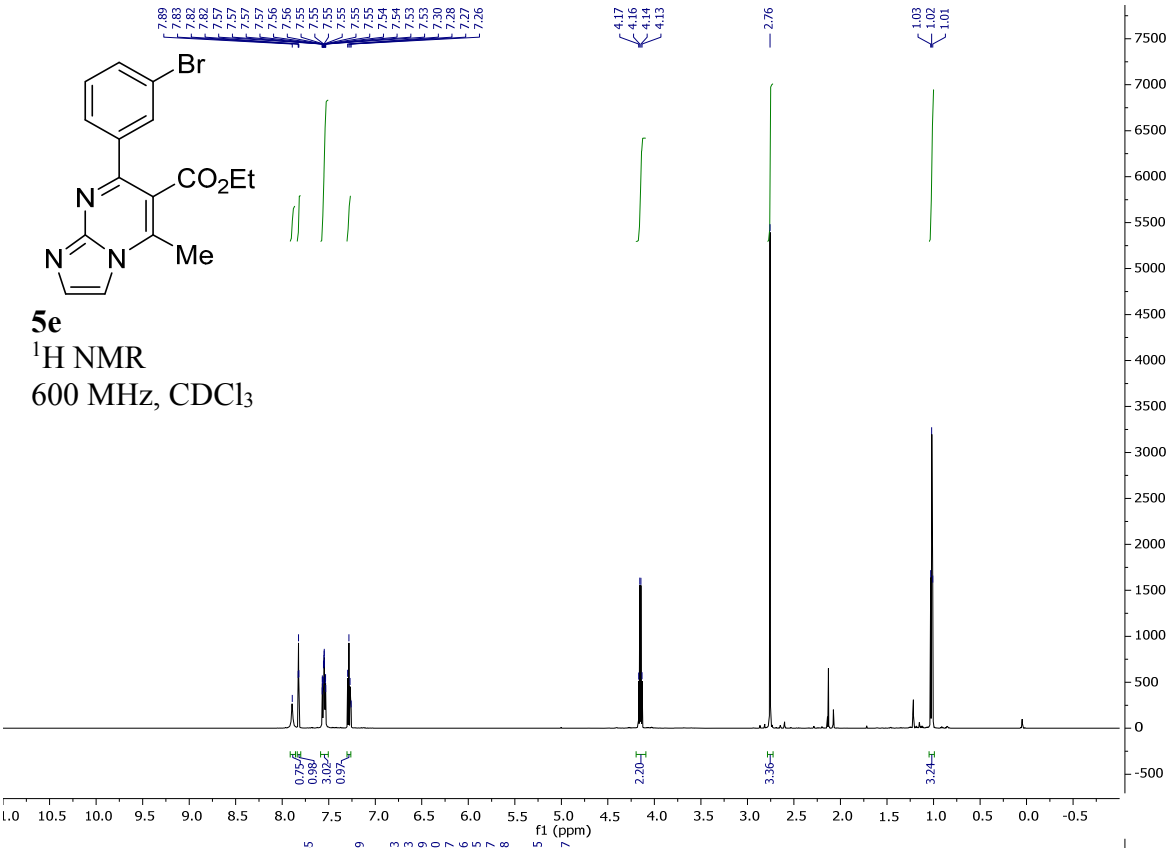
5c

^{19}F NMR

376 MHz, $(CD_3)_2CO$


CO2Me
CO2Et
N
N
N
Me
5d
1H NMR
600 MHz, (CD3)2CO
f1 (ppm)

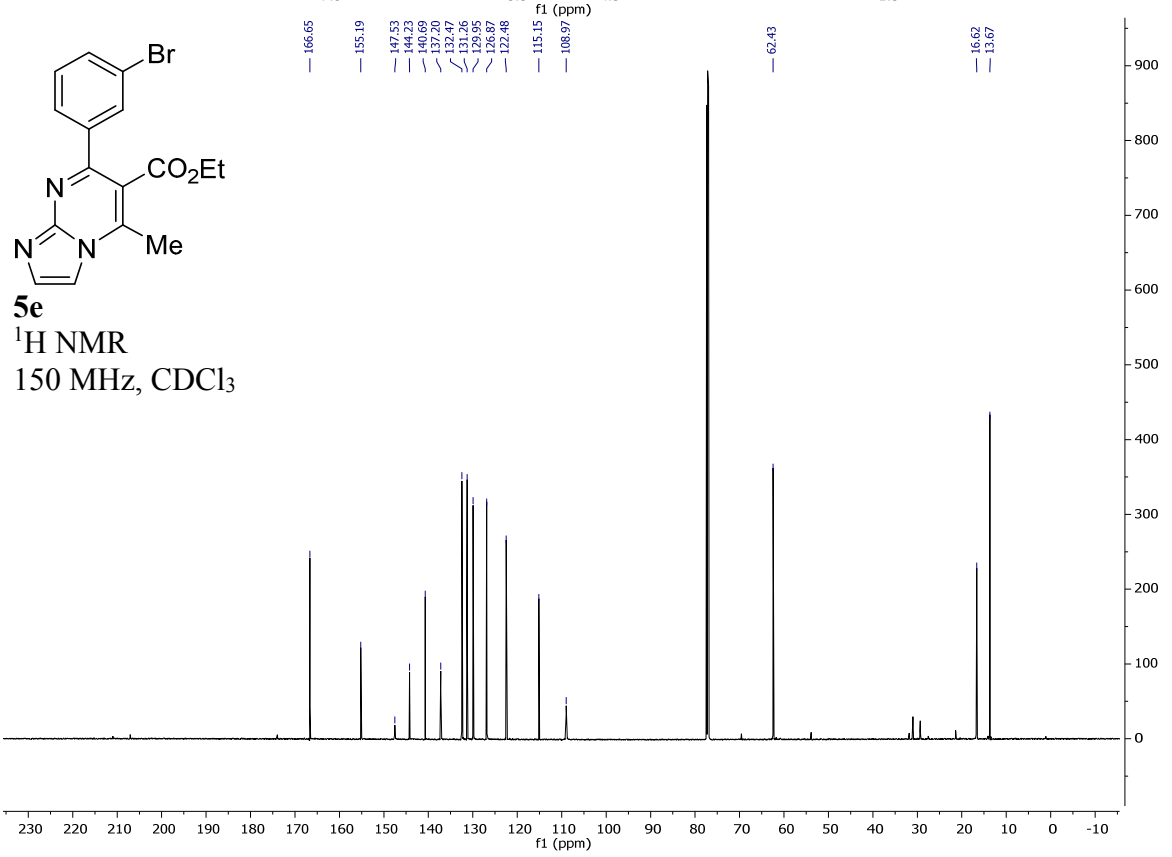

CO2Me
CO2Et
N
N
N
Me
5d
13C NMR
150 MHz, (CD3)2CO
f1 (ppm)



5e

^{1}H NMR

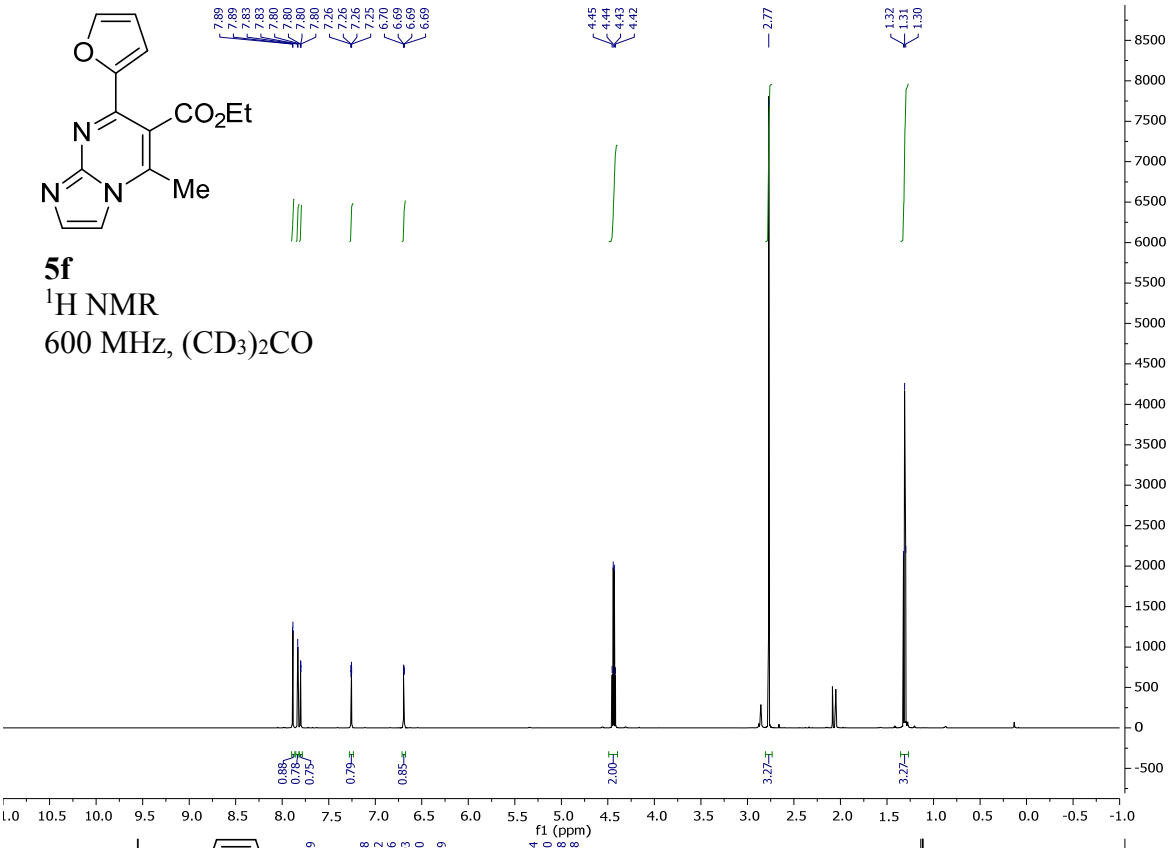
600 MHz, $CDCl_3$



5e

^{1}H NMR

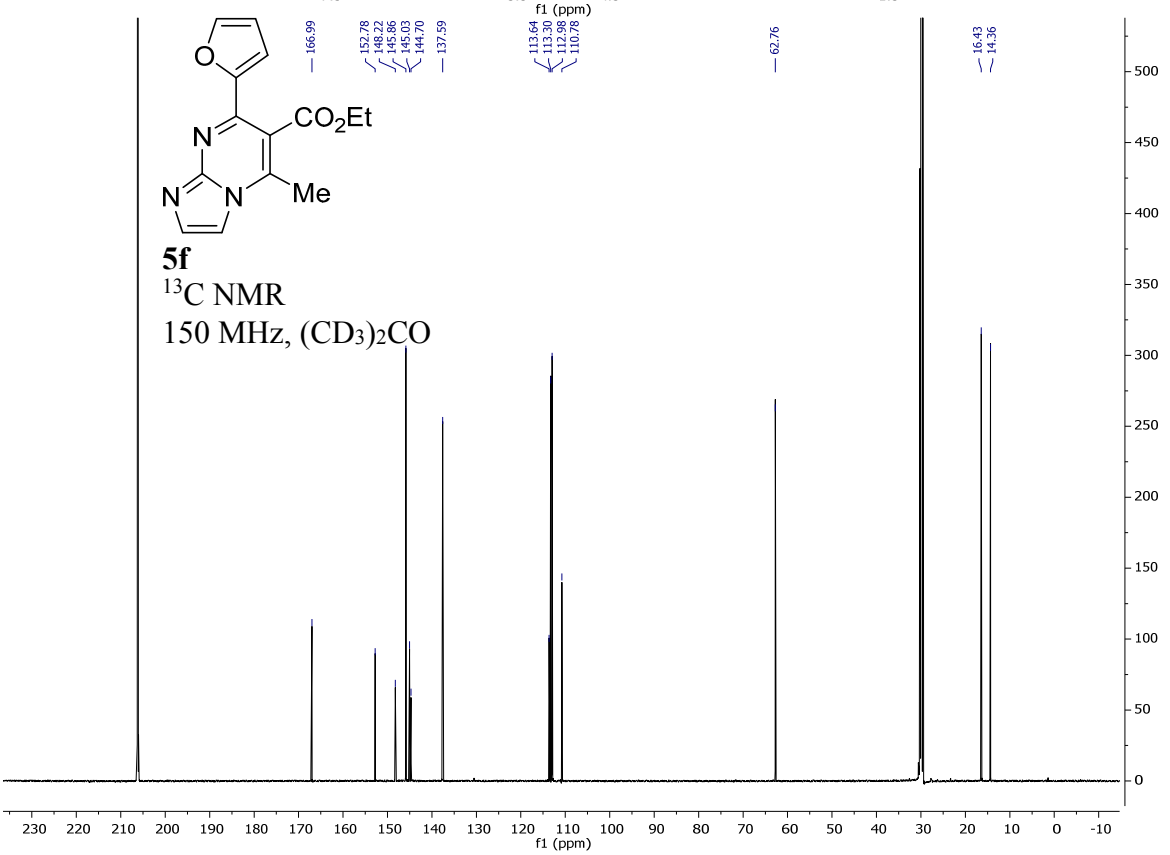
150 MHz, $CDCl_3$



5f

^{1}H NMR

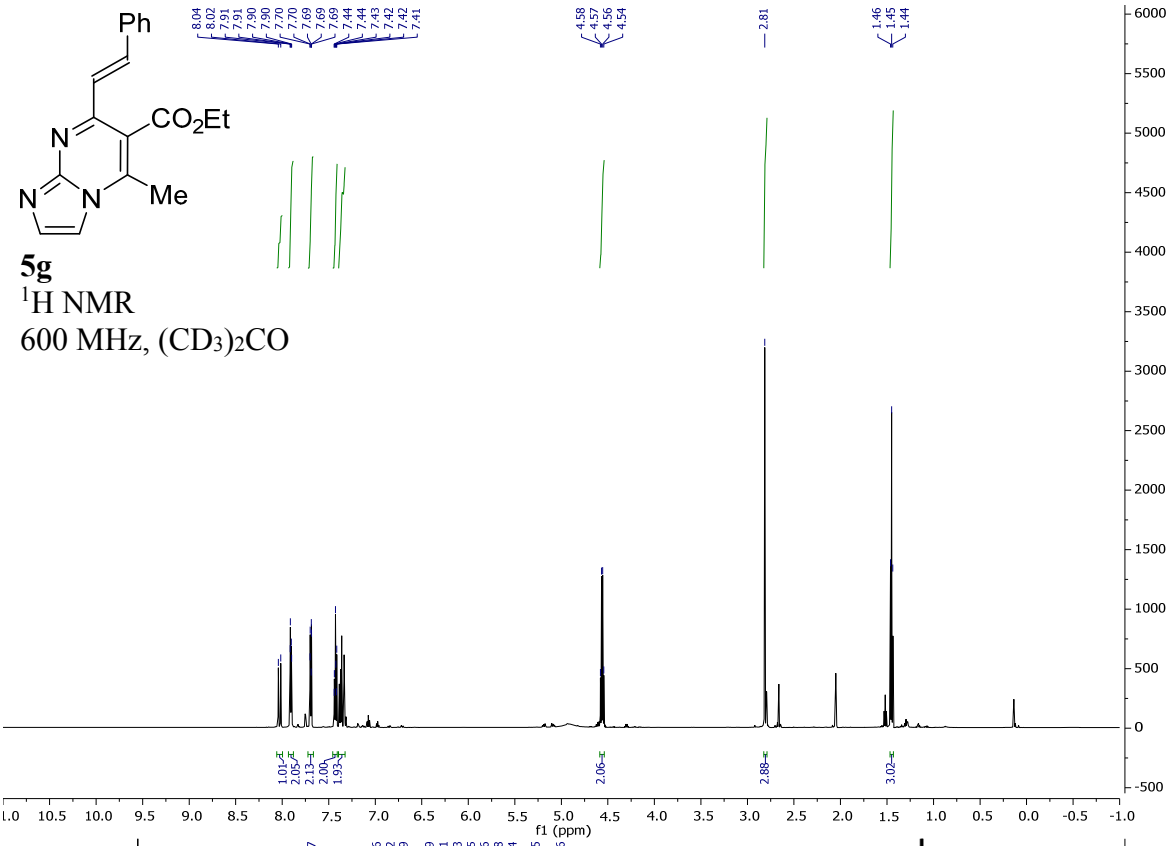
600 MHz, $(CD_3)_2CO$



5f

^{13}C NMR

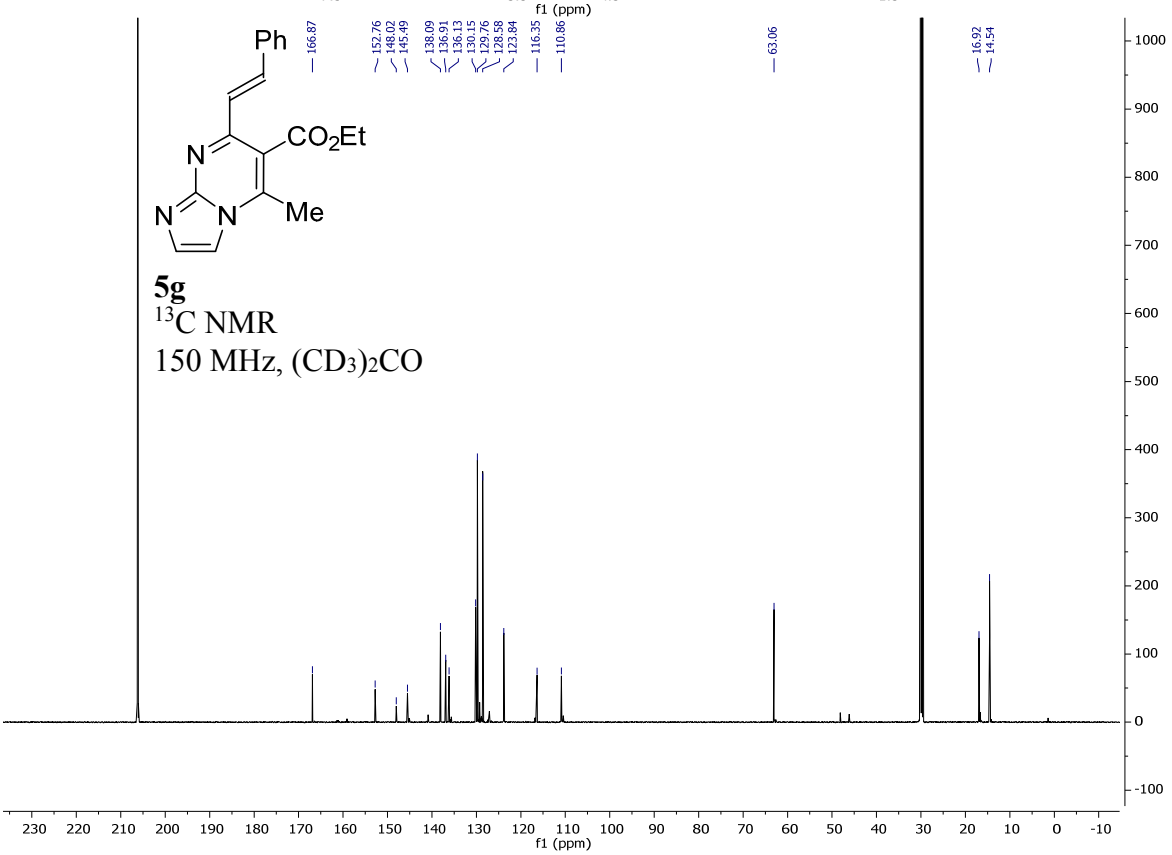
150 MHz, $(CD_3)_2CO$



5g

^{1}H NMR

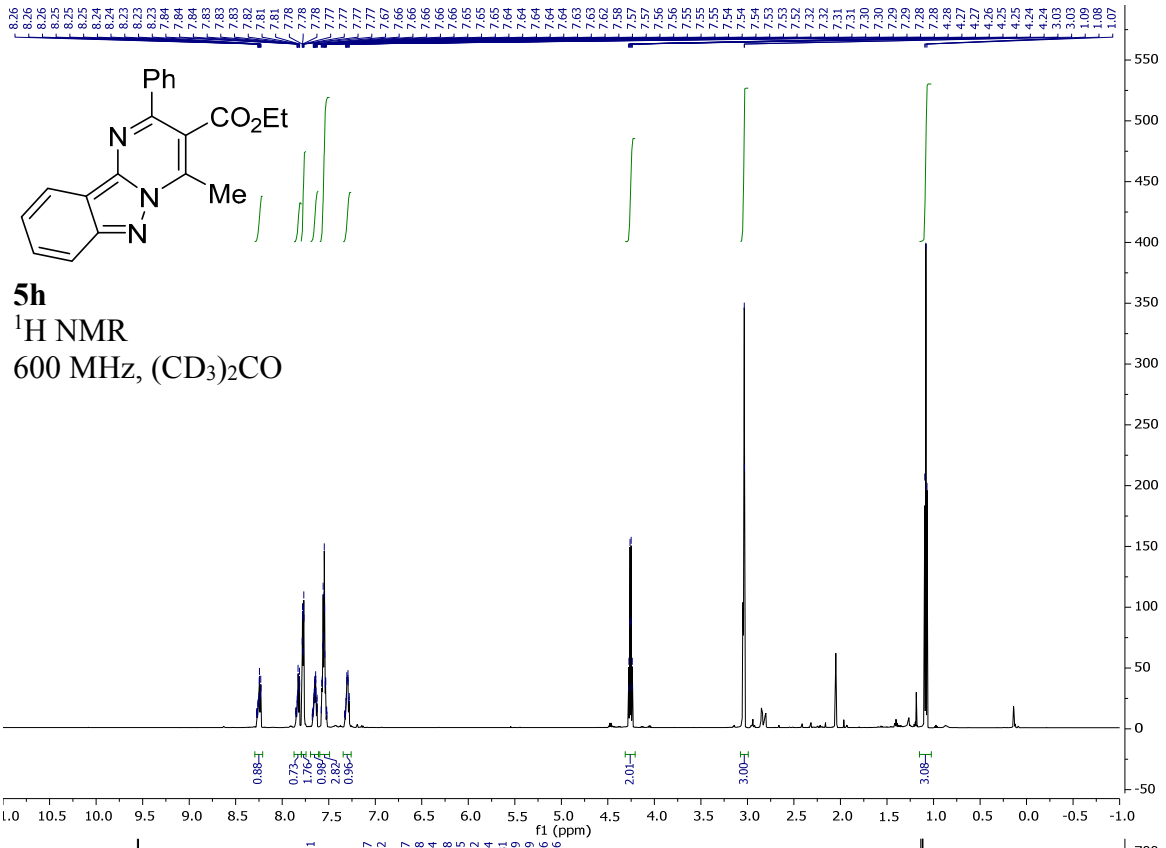
600 MHz, $(CD_3)_2CO$



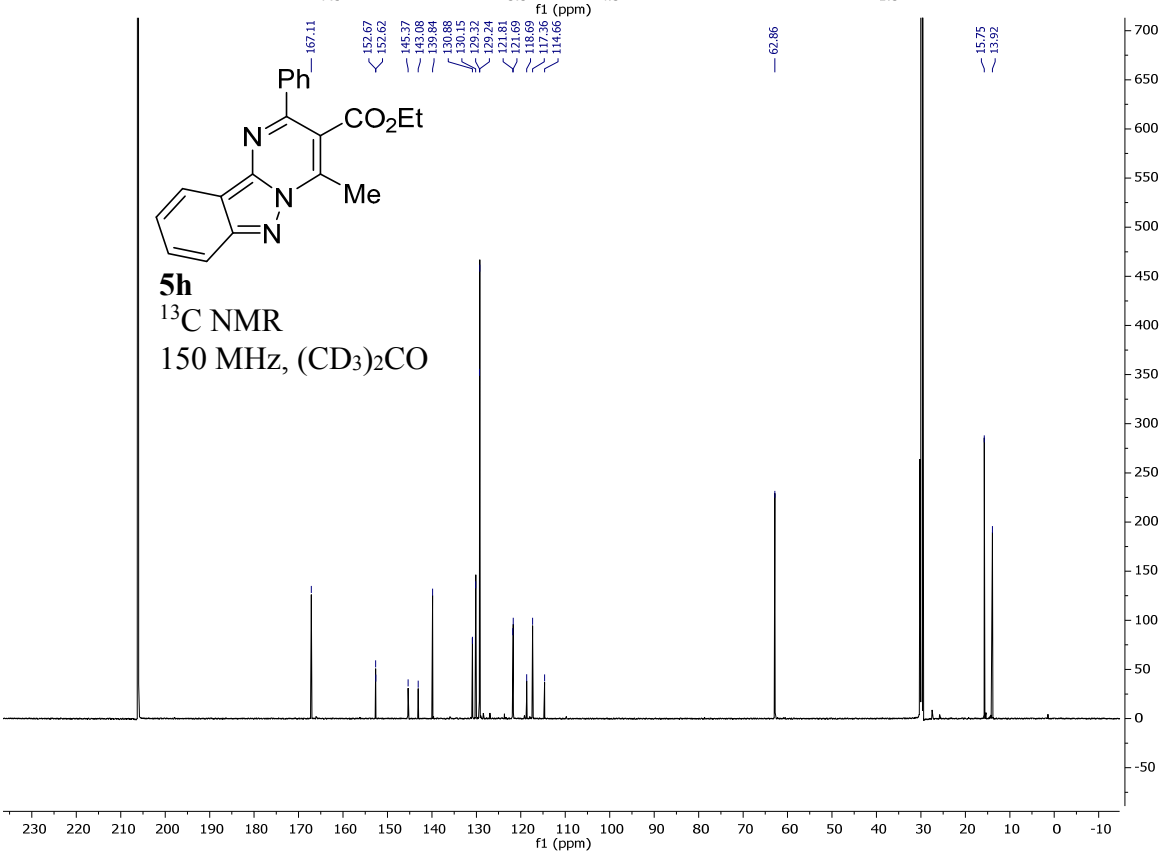
5g

^{13}C NMR

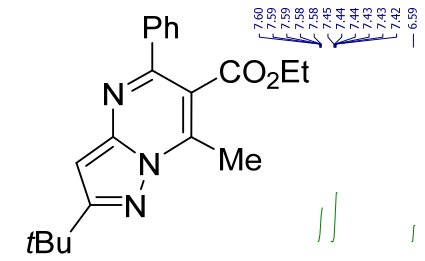
150 MHz, $(CD_3)_2CO$



5h
^{1}H NMR
600 MHz, $(CD_3)_2CO$



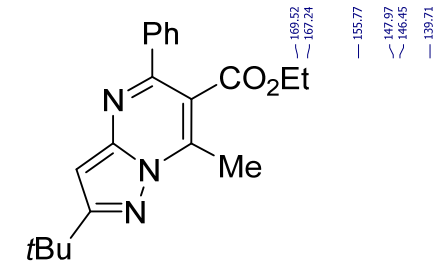
5h
^{13}C NMR
150 MHz, $(CD_3)_2CO$



5i

^{1}H NMR

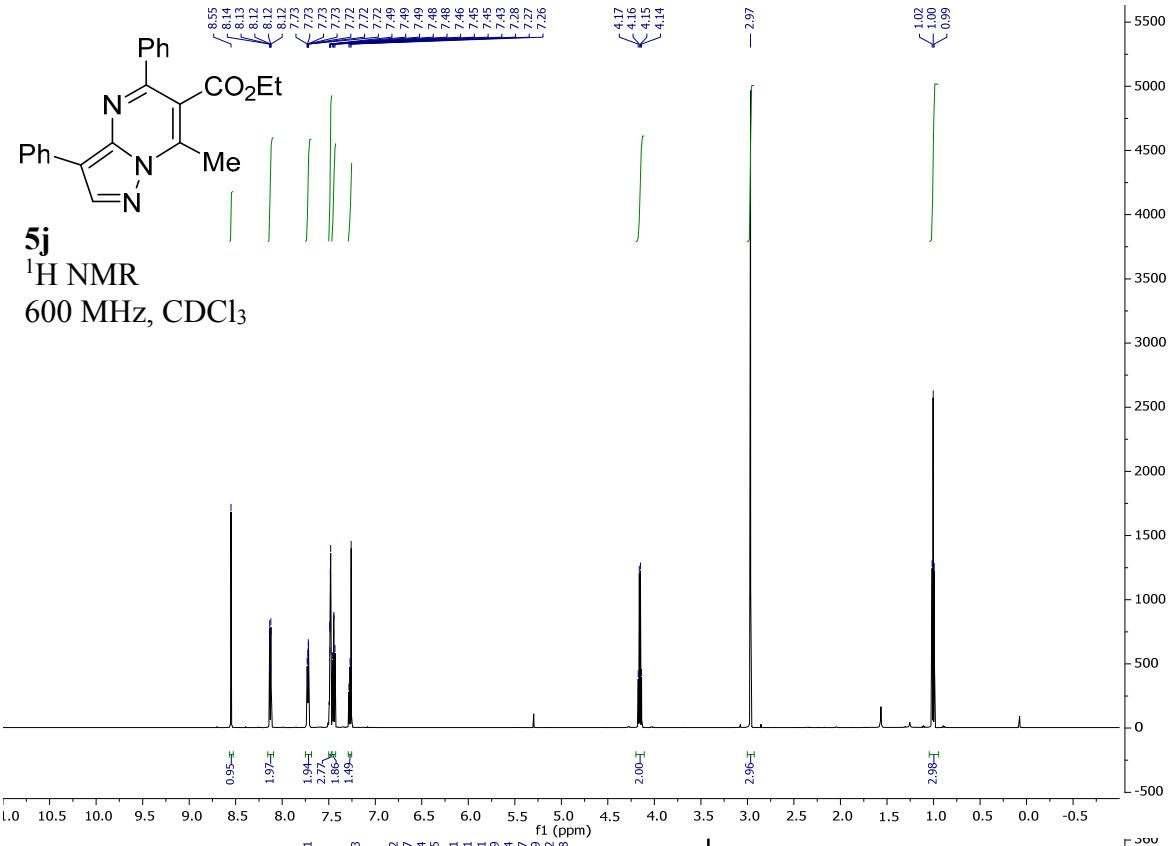
600 MHz, $CDCl_3$



5i

^{13}C NMR

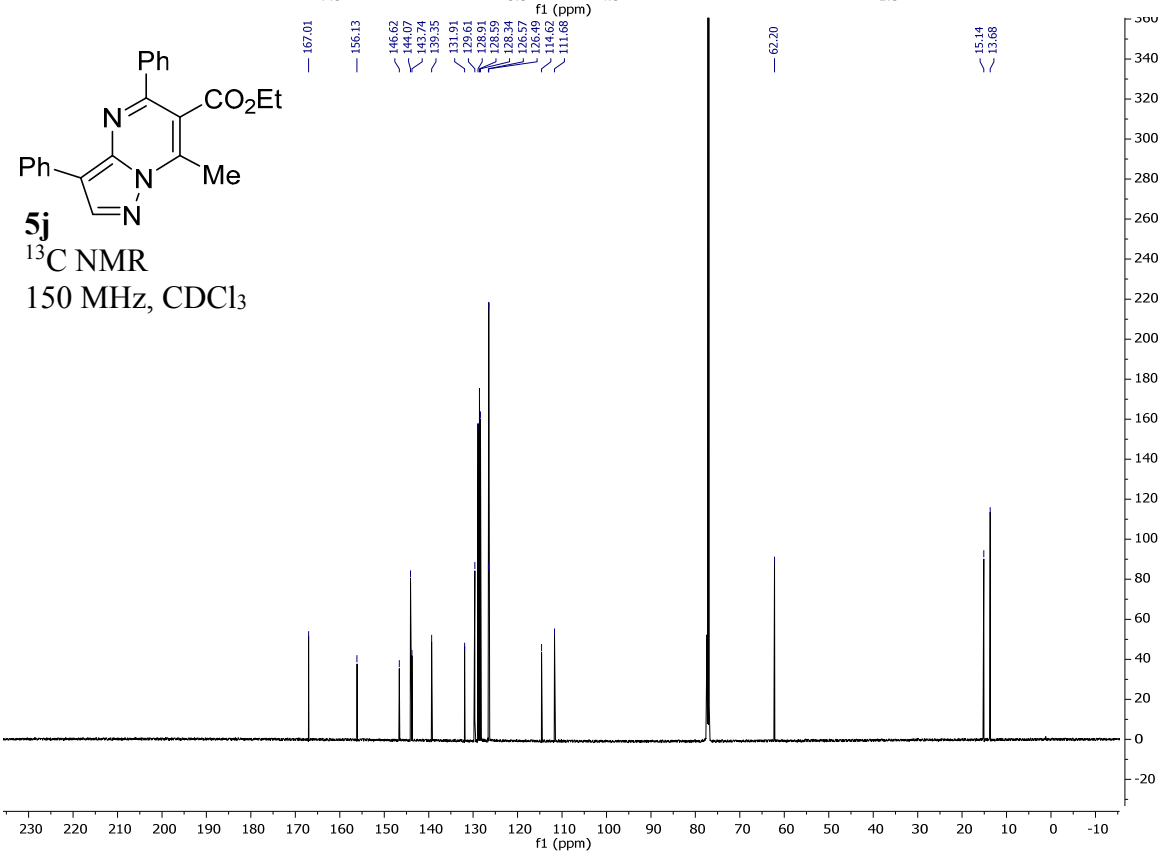
150 MHz, $CDCl_3$



5j

^{1}H NMR

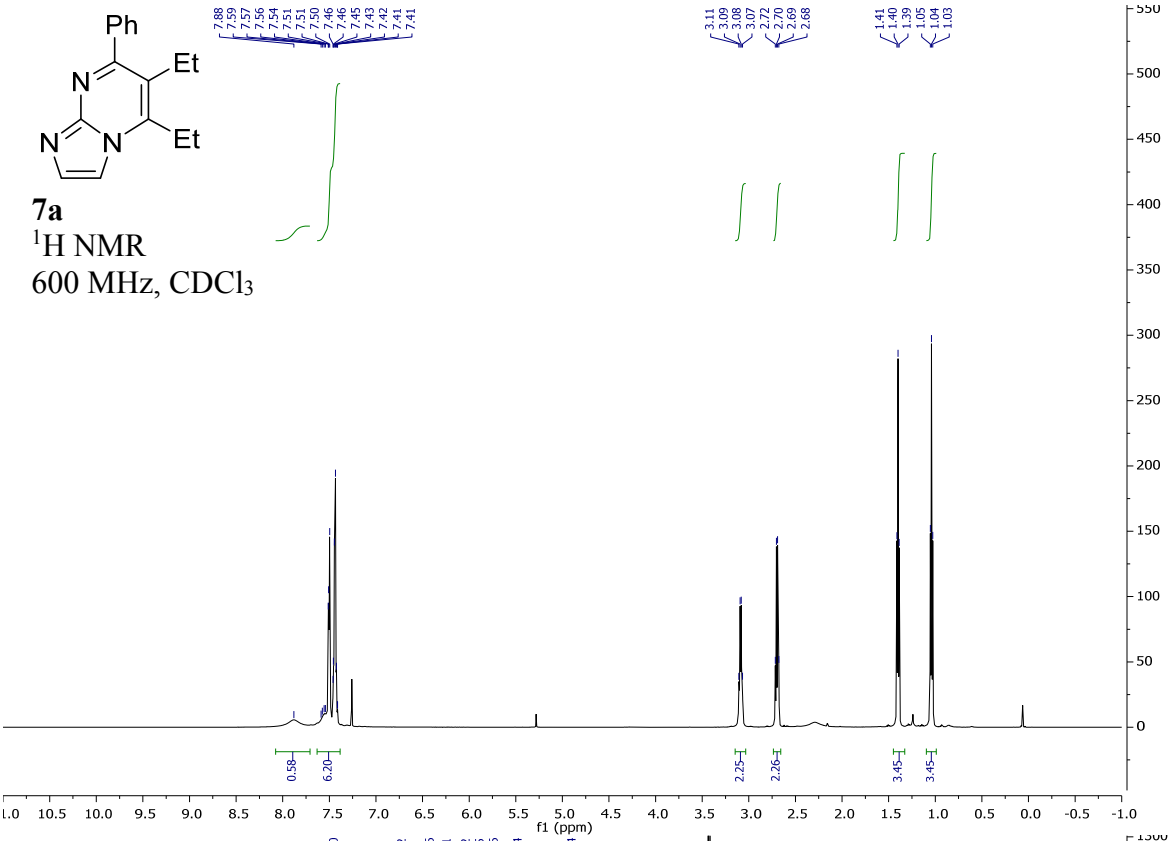
600 MHz, $CDCl_3$



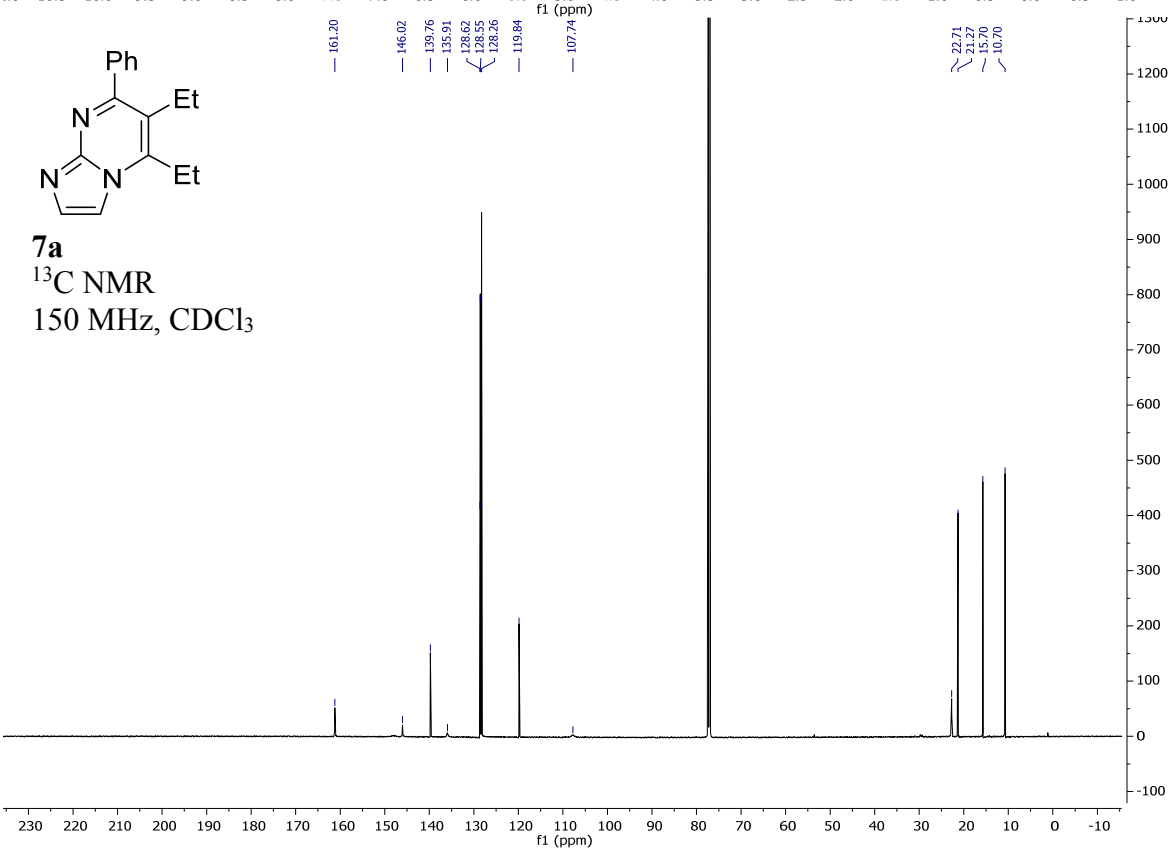
5j

^{13}C NMR

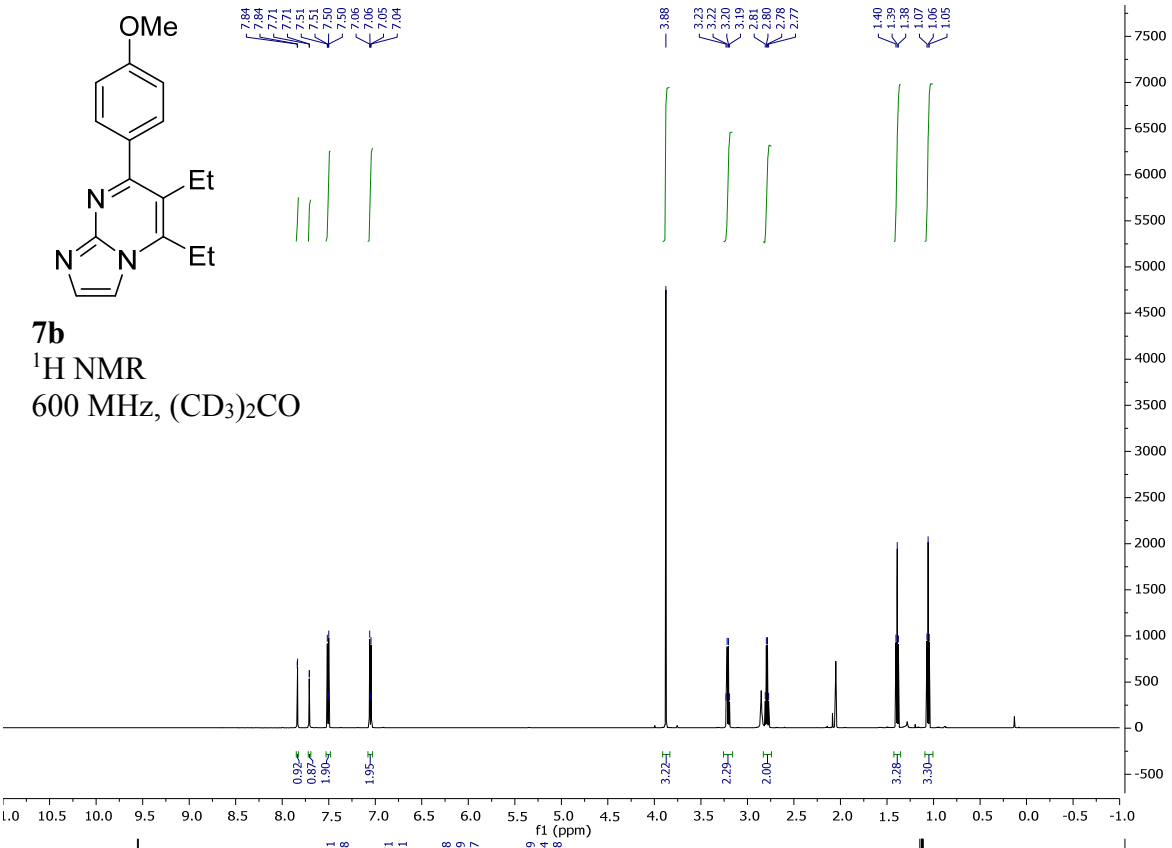
150 MHz, $CDCl_3$



7a
^{1}H NMR
600 MHz, $CDCl_3$



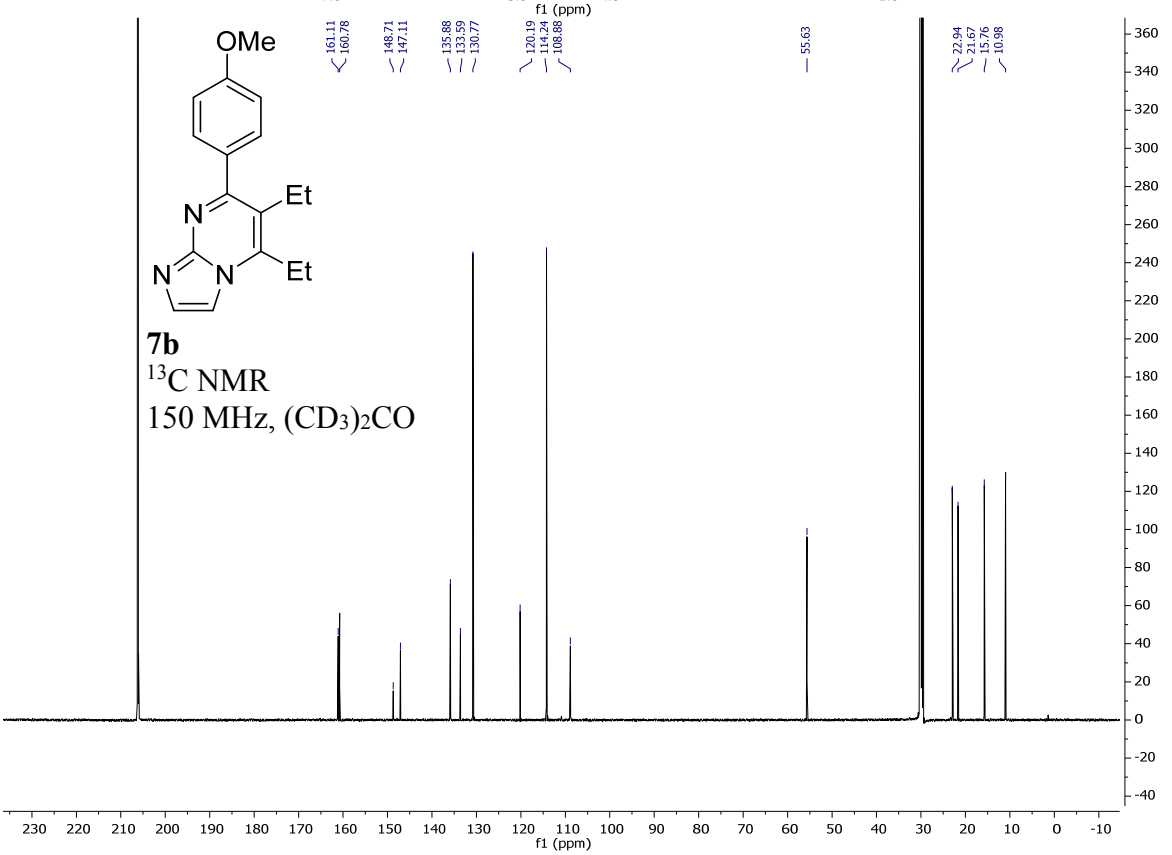
7a
^{13}C NMR
150 MHz, $CDCl_3$



7b

^{1}H NMR

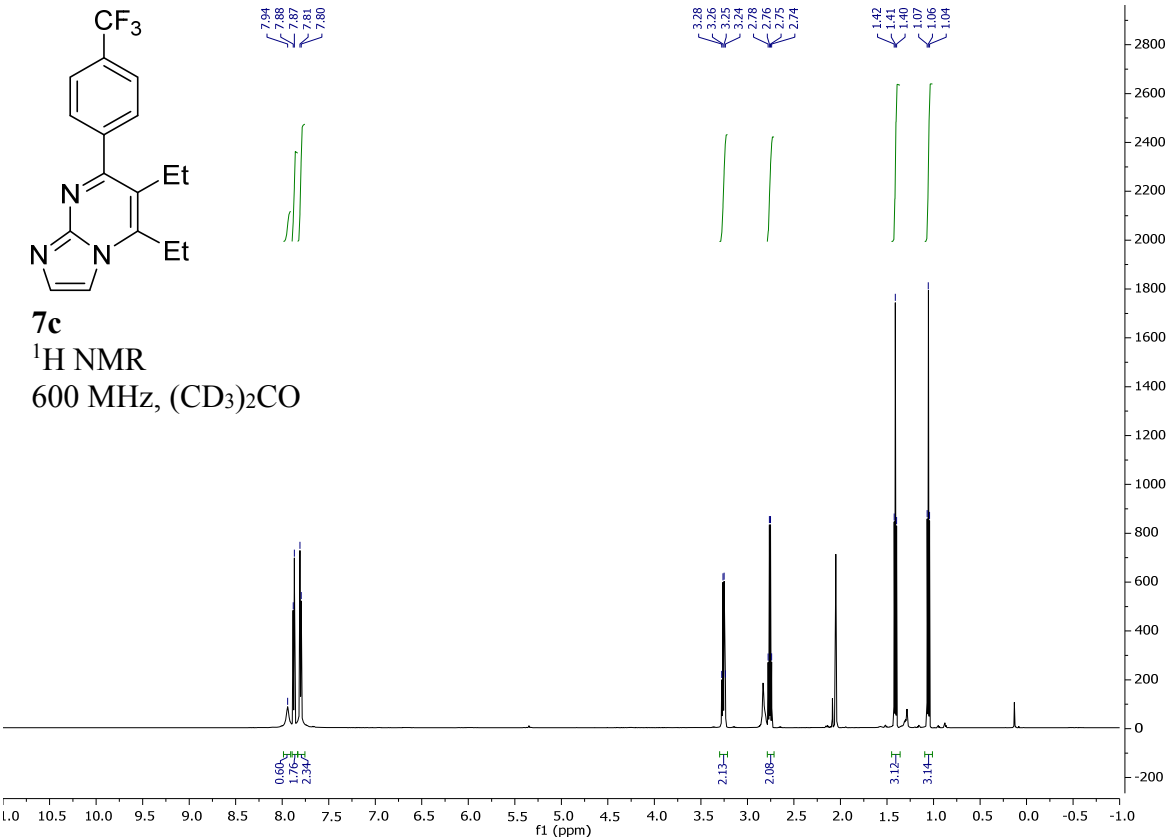
600 MHz, $(CD_3)_2CO$



7b

^{13}C NMR

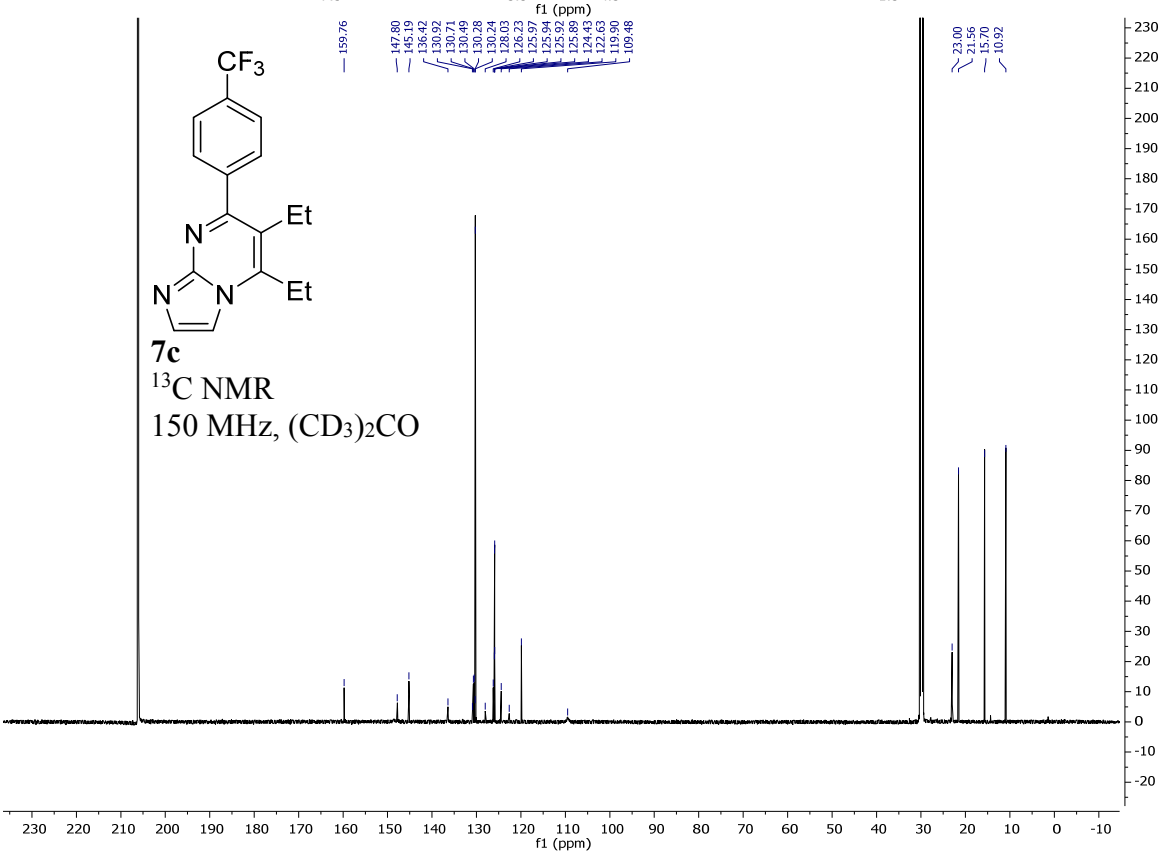
150 MHz, $(CD_3)_2CO$



7c

^{1}H NMR

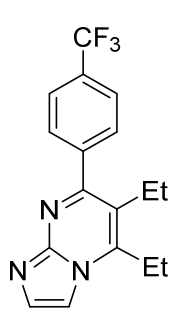
600 MHz, $(CD_3)_2CO$



7c

^{13}C NMR

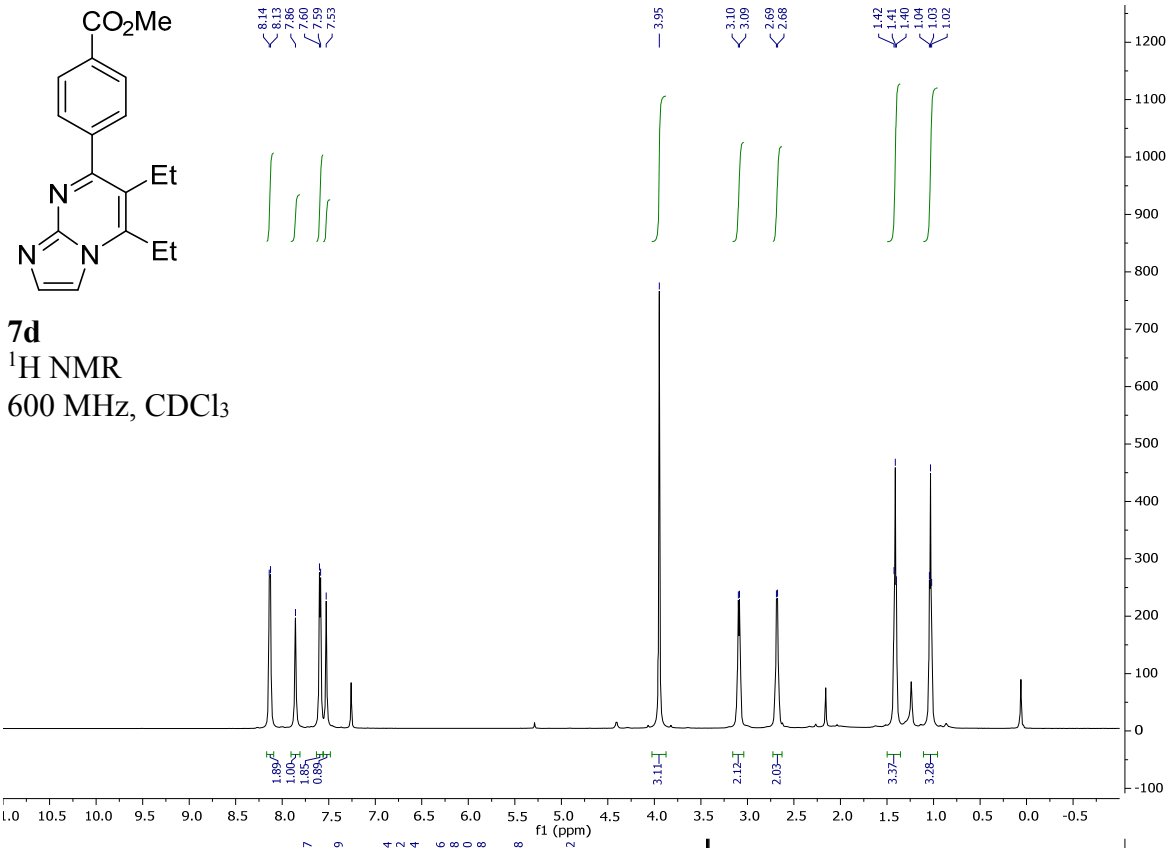
150 MHz, $(CD_3)_2CO$



7c

^{19}F NMR

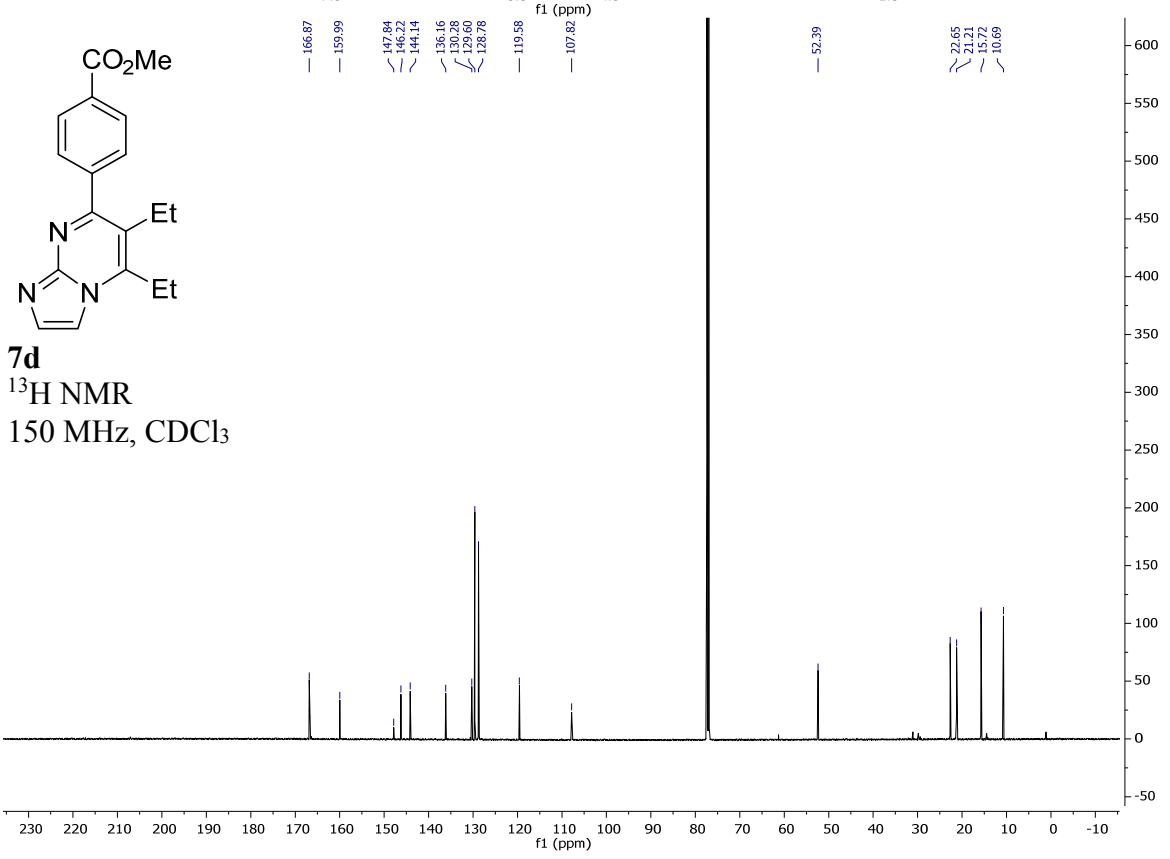
376 MHz, $(CD_3)_2CO$



7d

^{1}H NMR

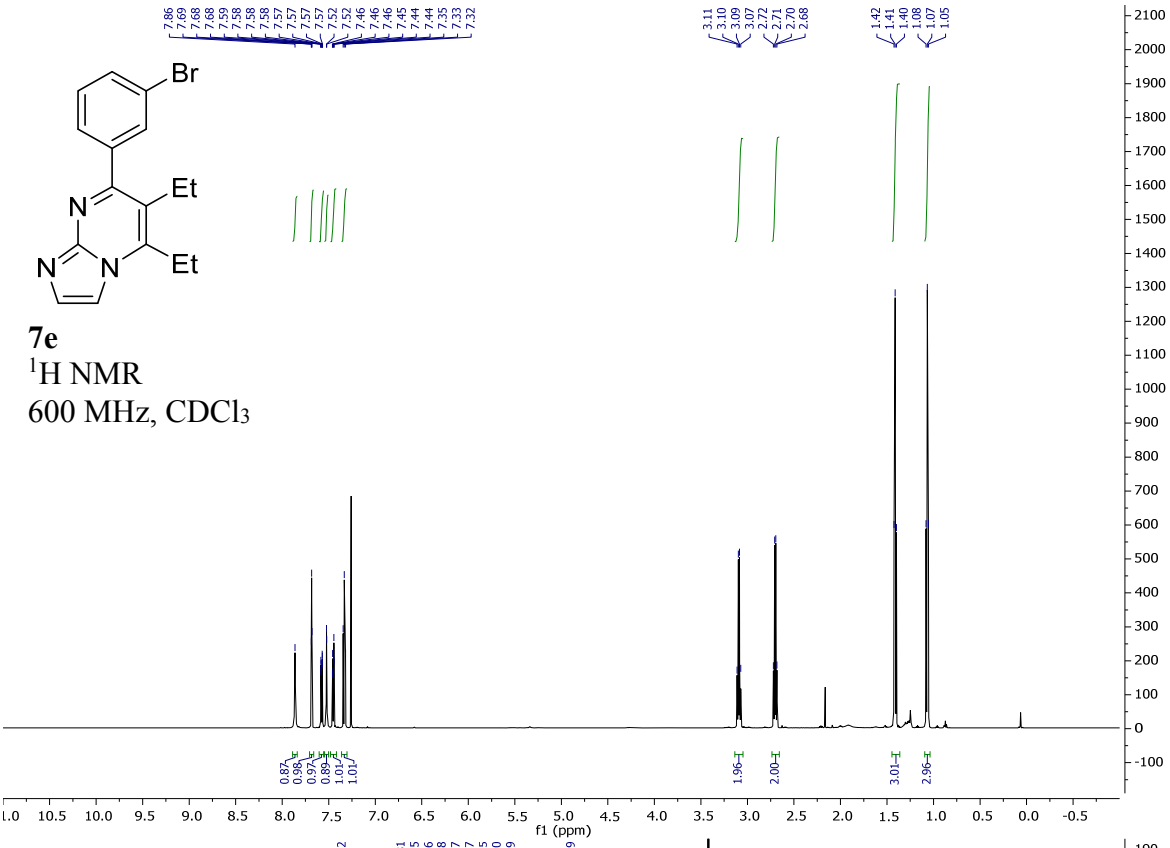
600 MHz, $CDCl_3$



7d

^{13}H NMR

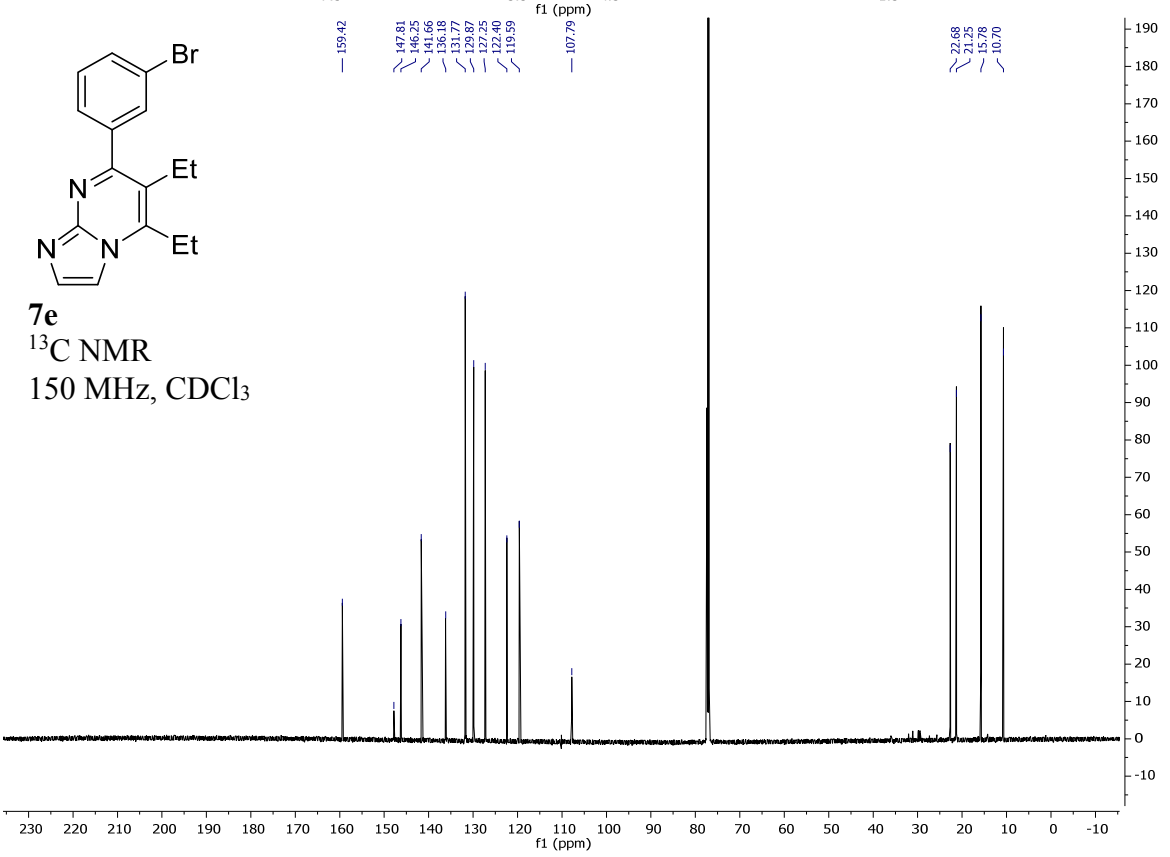
150 MHz, $CDCl_3$



7e

^{1}H NMR

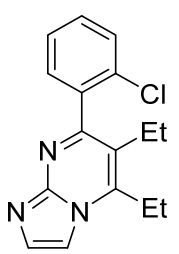
600 MHz, $CDCl_3$



7e

^{13}C NMR

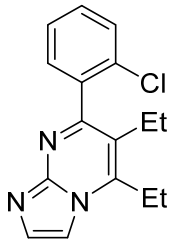
150 MHz, $CDCl_3$



7f

^{1}H NMR

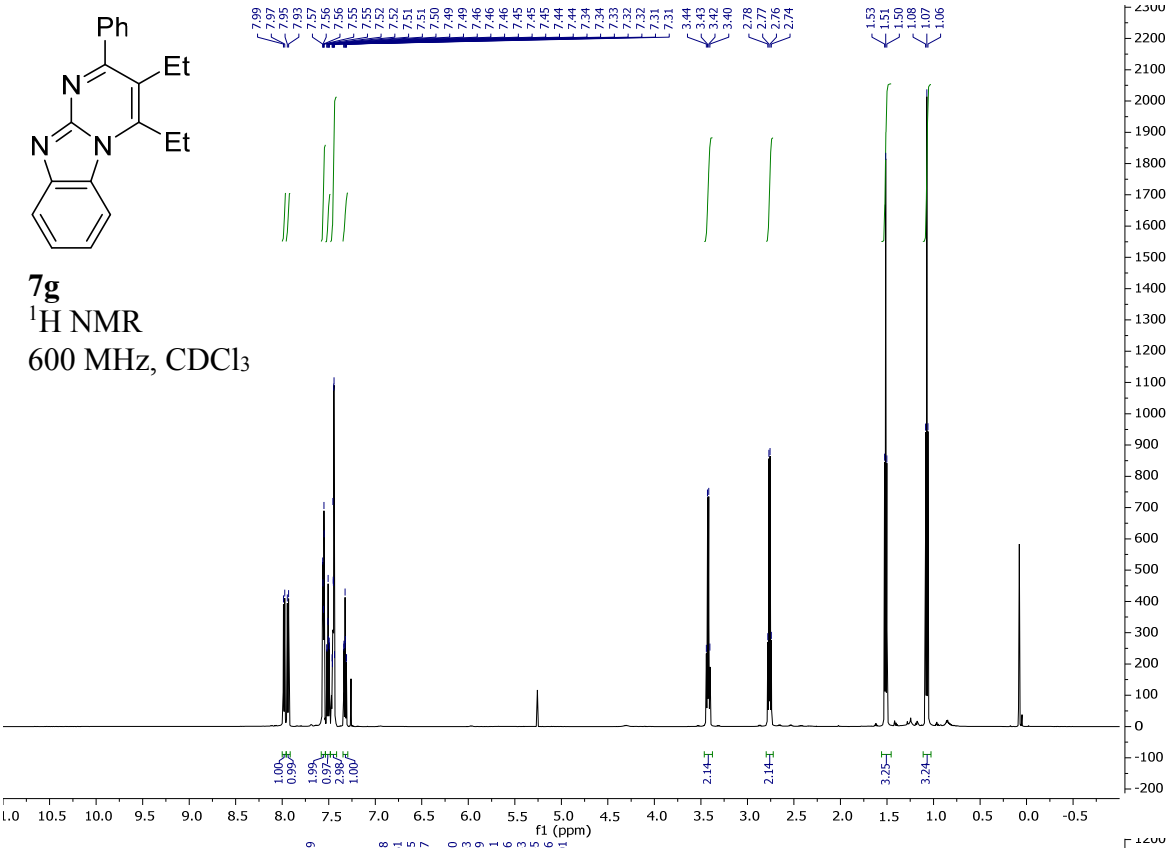
600 MHz, $CDCl_3$



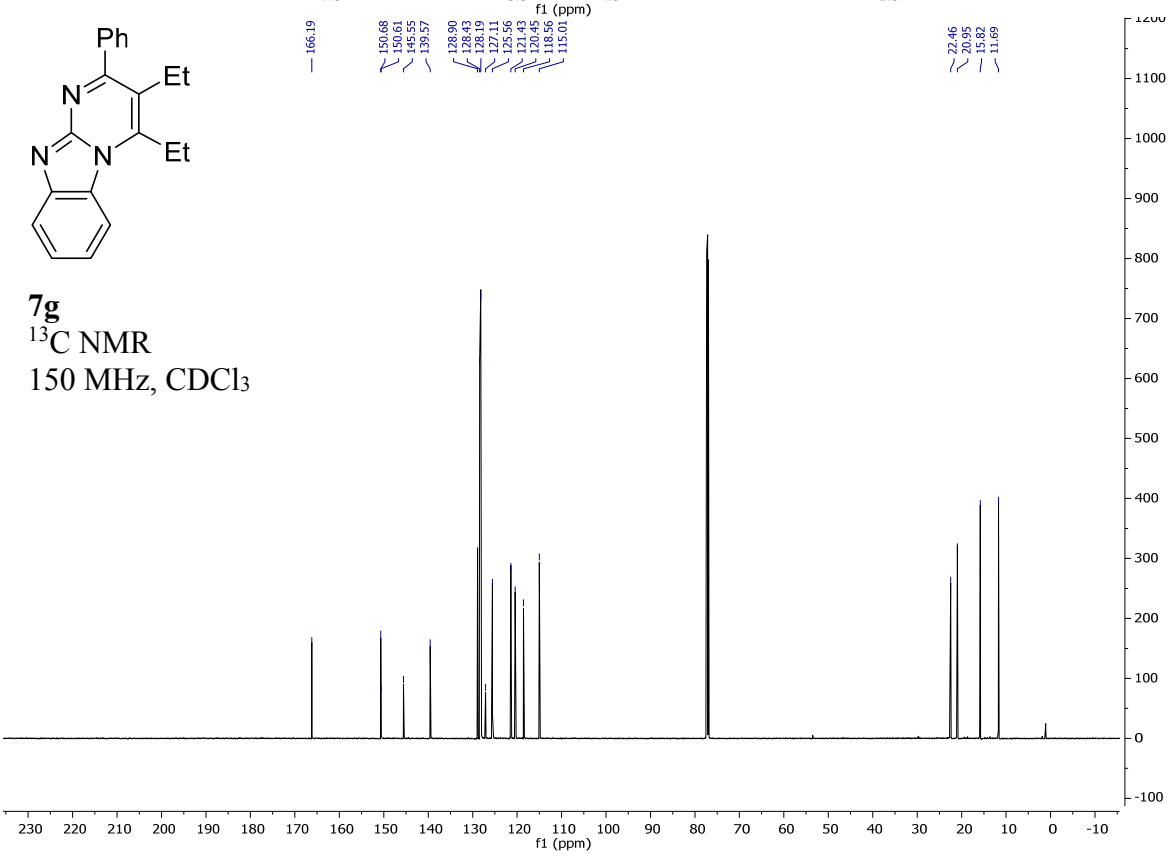
7f

^{13}C NMR

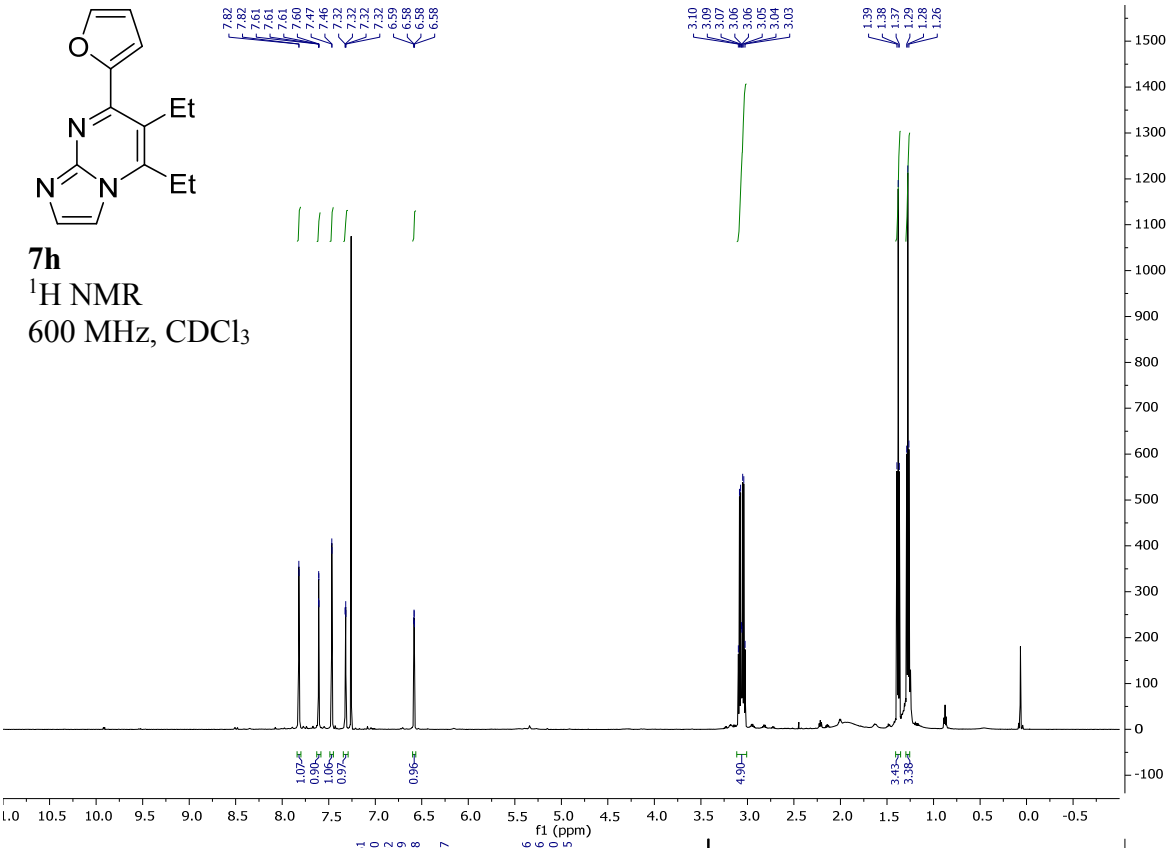
150 MHz, $CDCl_3$



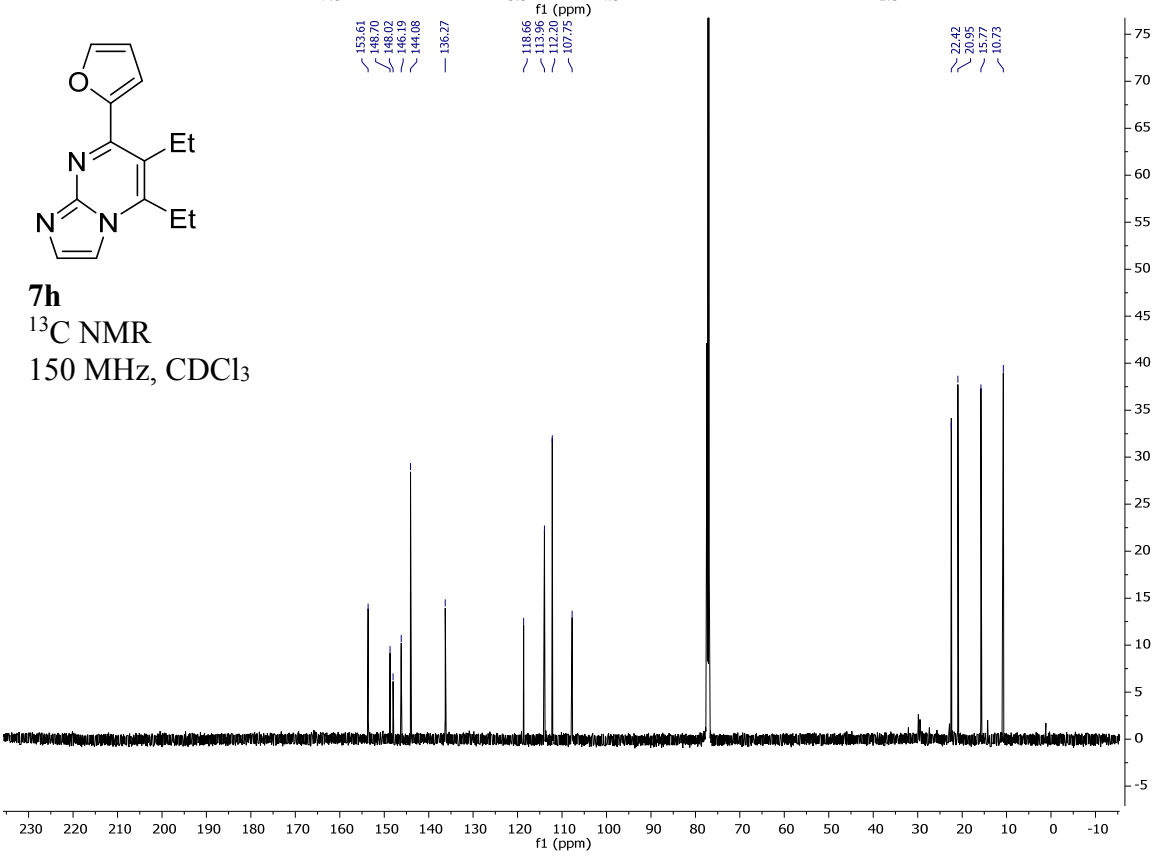
7g
^{1}H NMR
600 MHz, $CDCl_3$



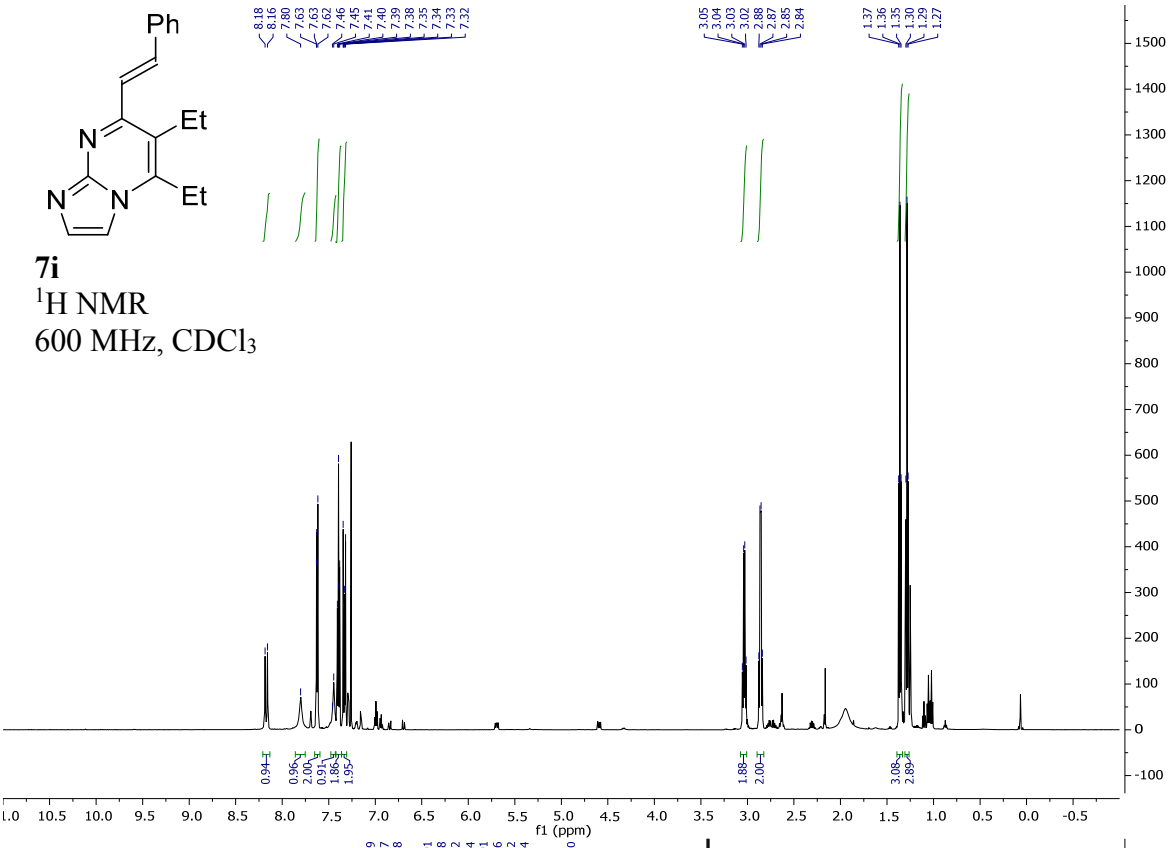
7g
^{13}C NMR
150 MHz, $CDCl_3$



7h
^{1}H NMR
600 MHz, $CDCl_3$



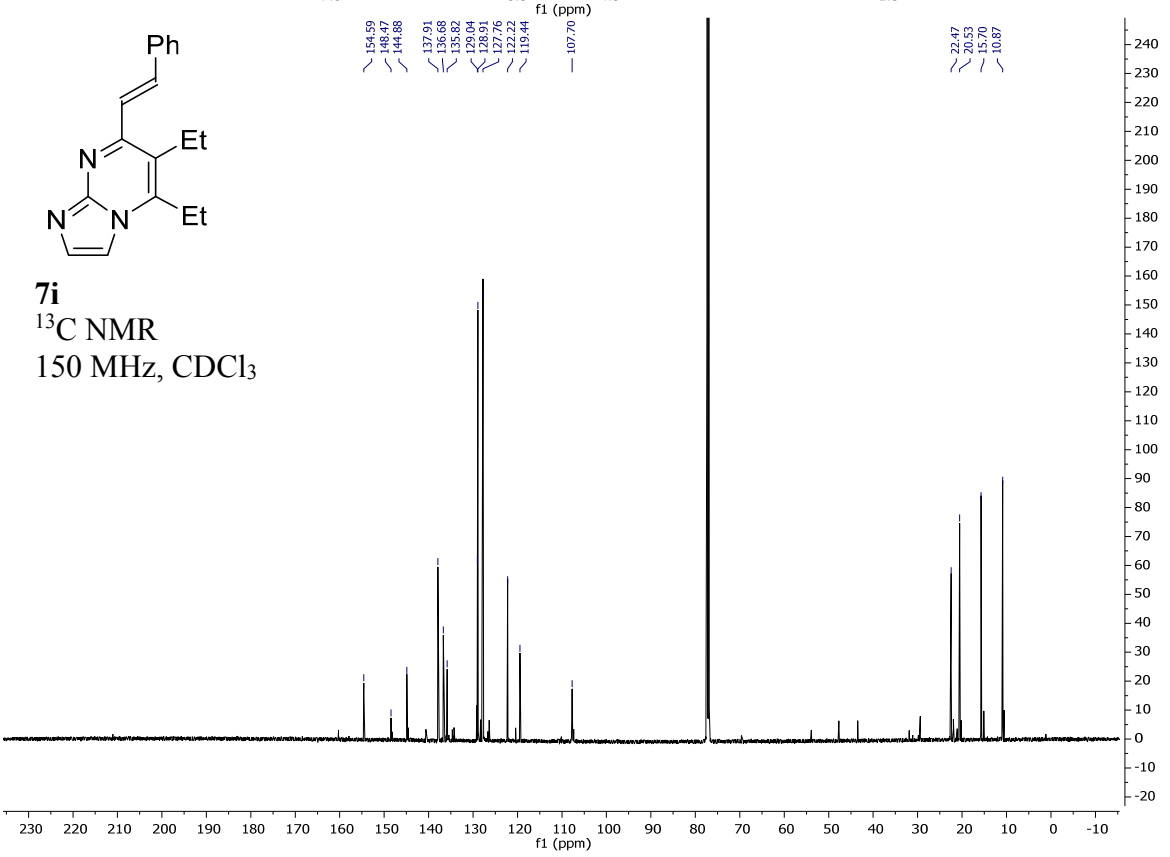
7h
^{13}C NMR
150 MHz, $CDCl_3$



7i

^{1}H NMR

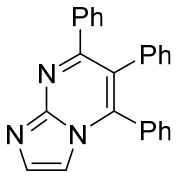
600 MHz, $CDCl_3$



7i

^{13}C NMR

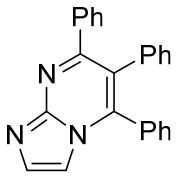
150 MHz, $CDCl_3$



7j

^{1}H NMR

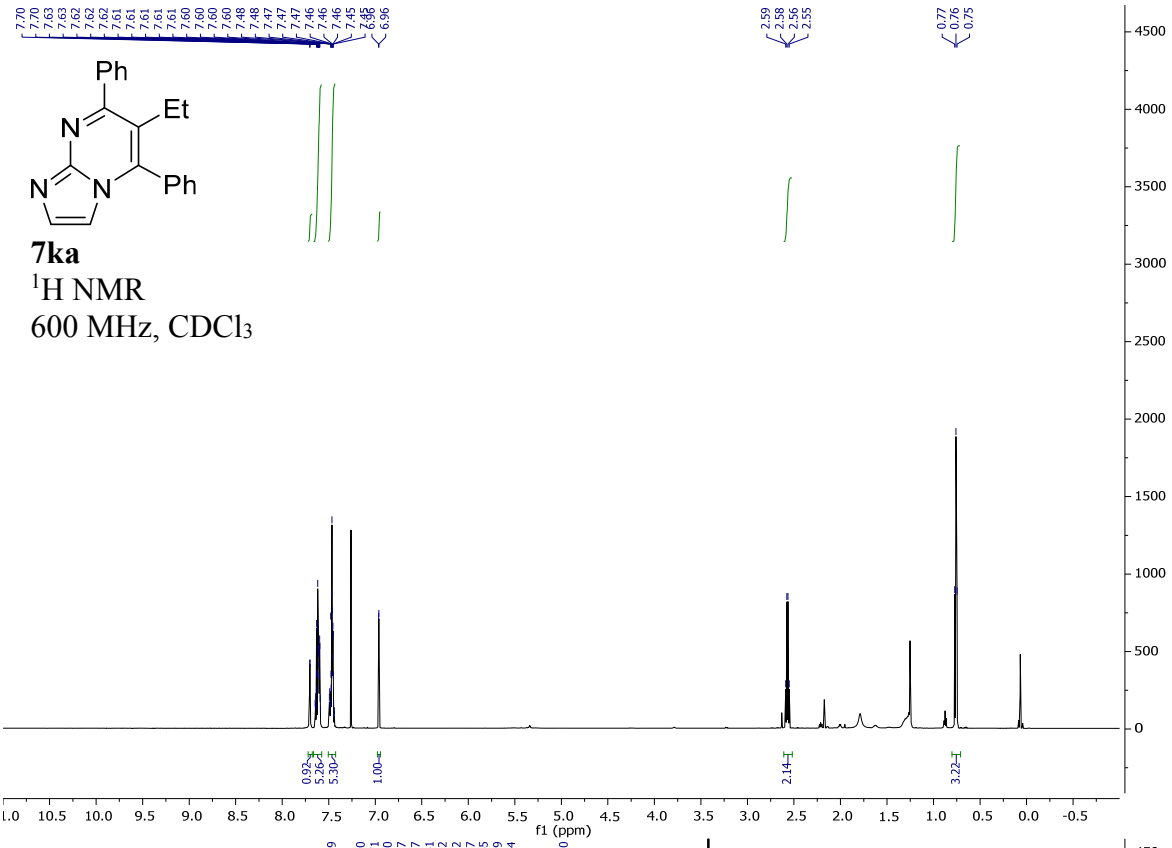
600 MHz, $CDCl_3$



7j

^{13}C NMR

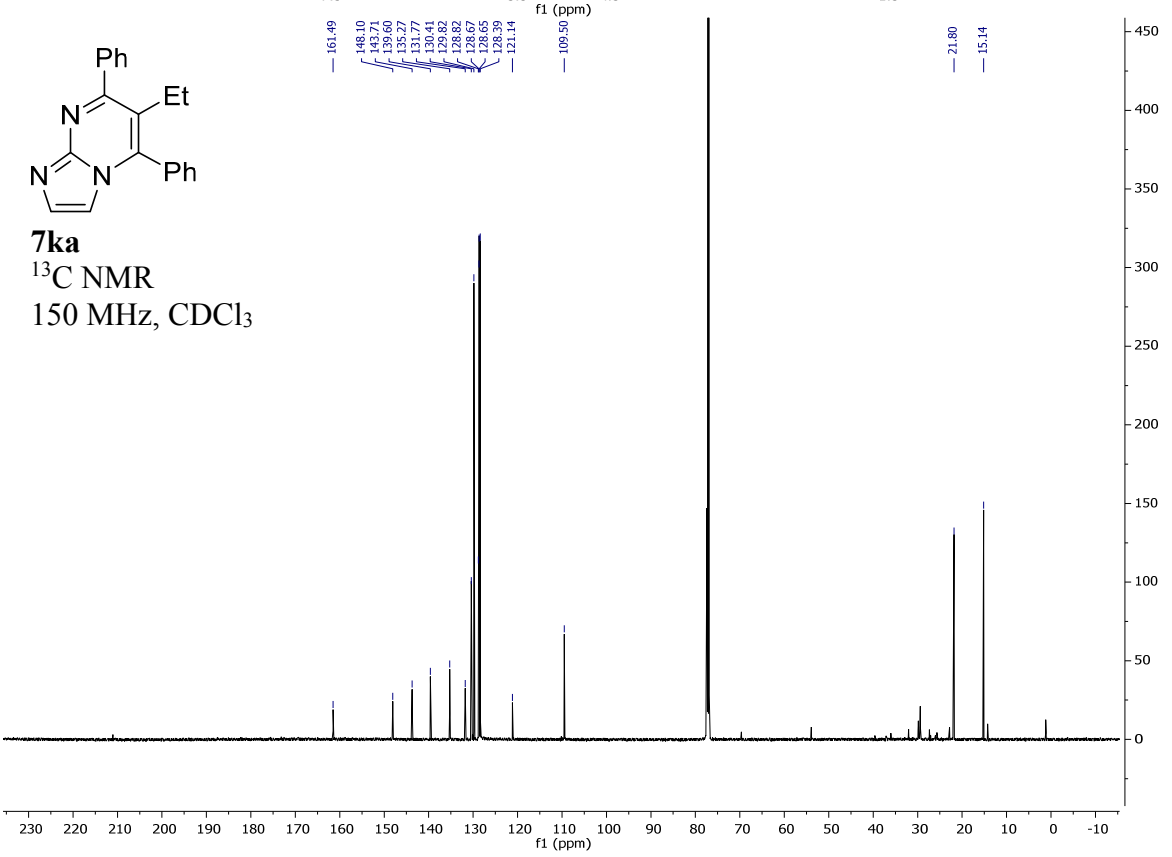
150 MHz, $CDCl_3$



7ka

^{1}H NMR

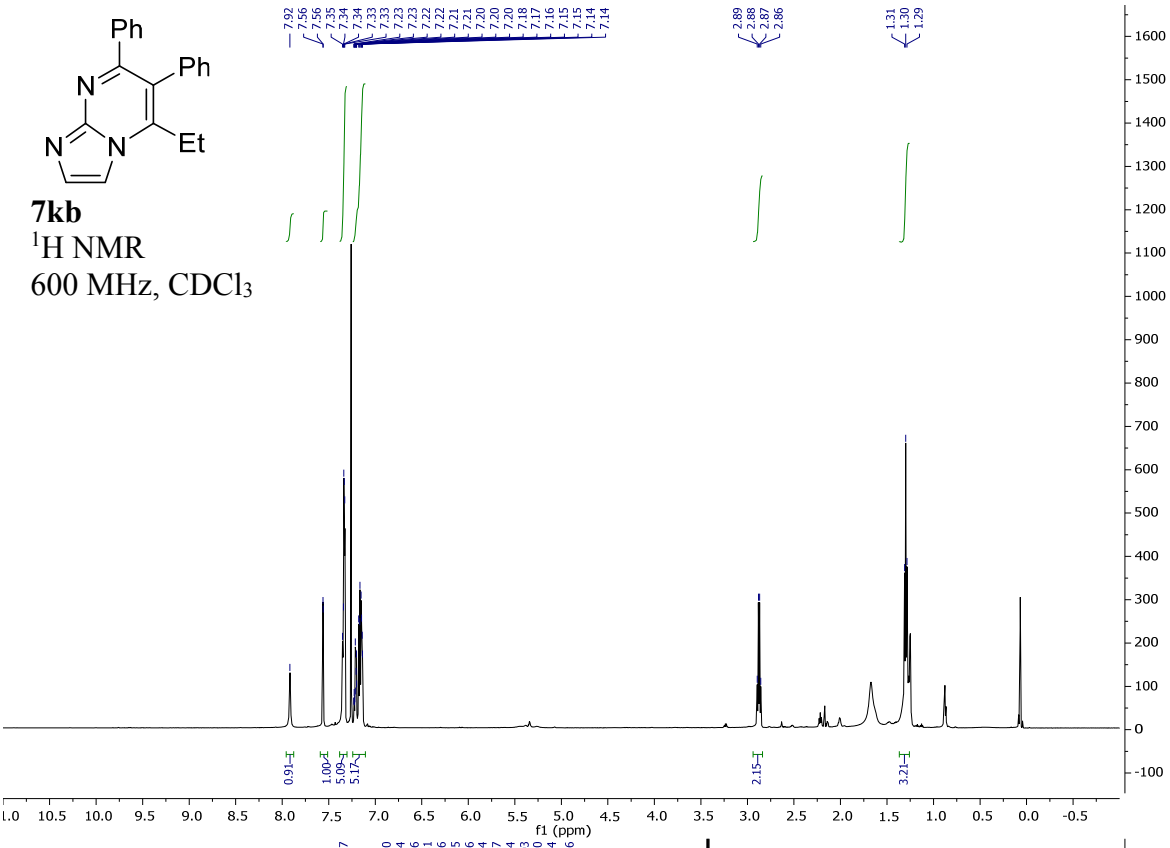
600 MHz, $CDCl_3$



7ka

^{13}C NMR

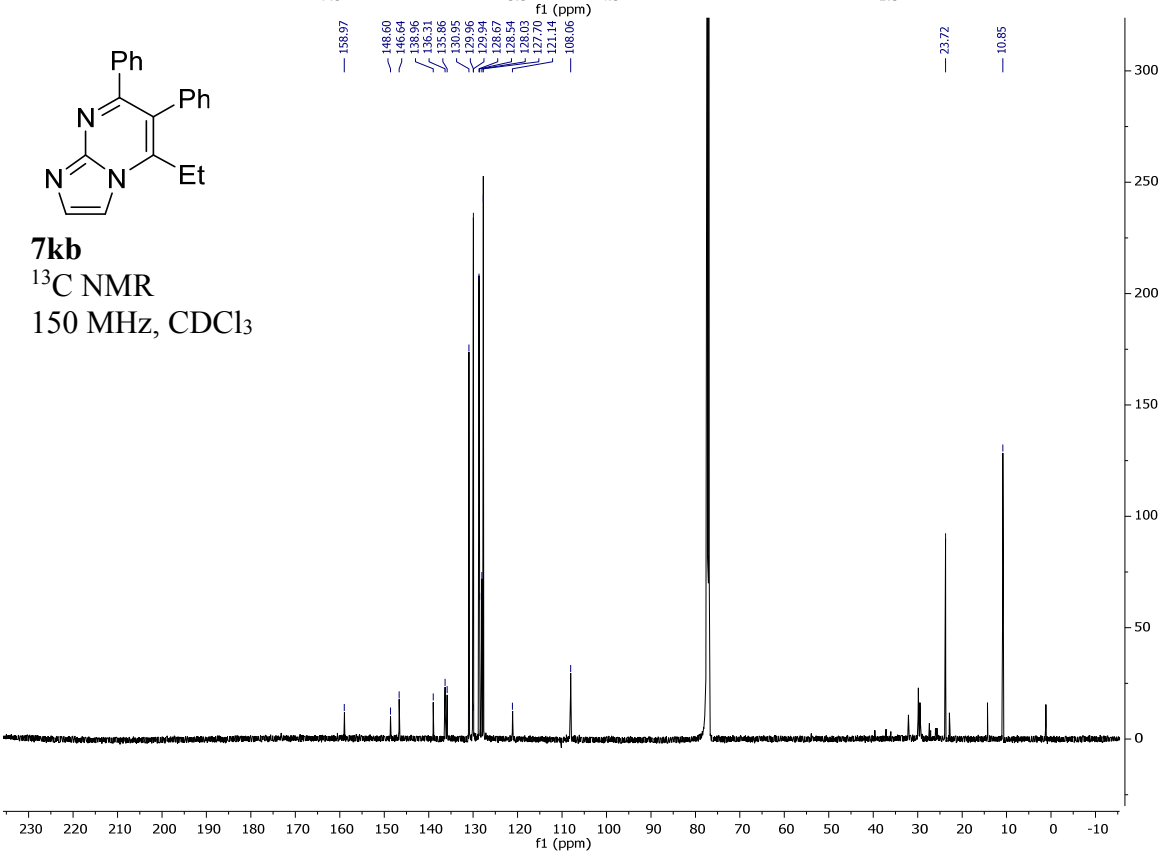
150 MHz, $CDCl_3$



7kb

^{1}H NMR

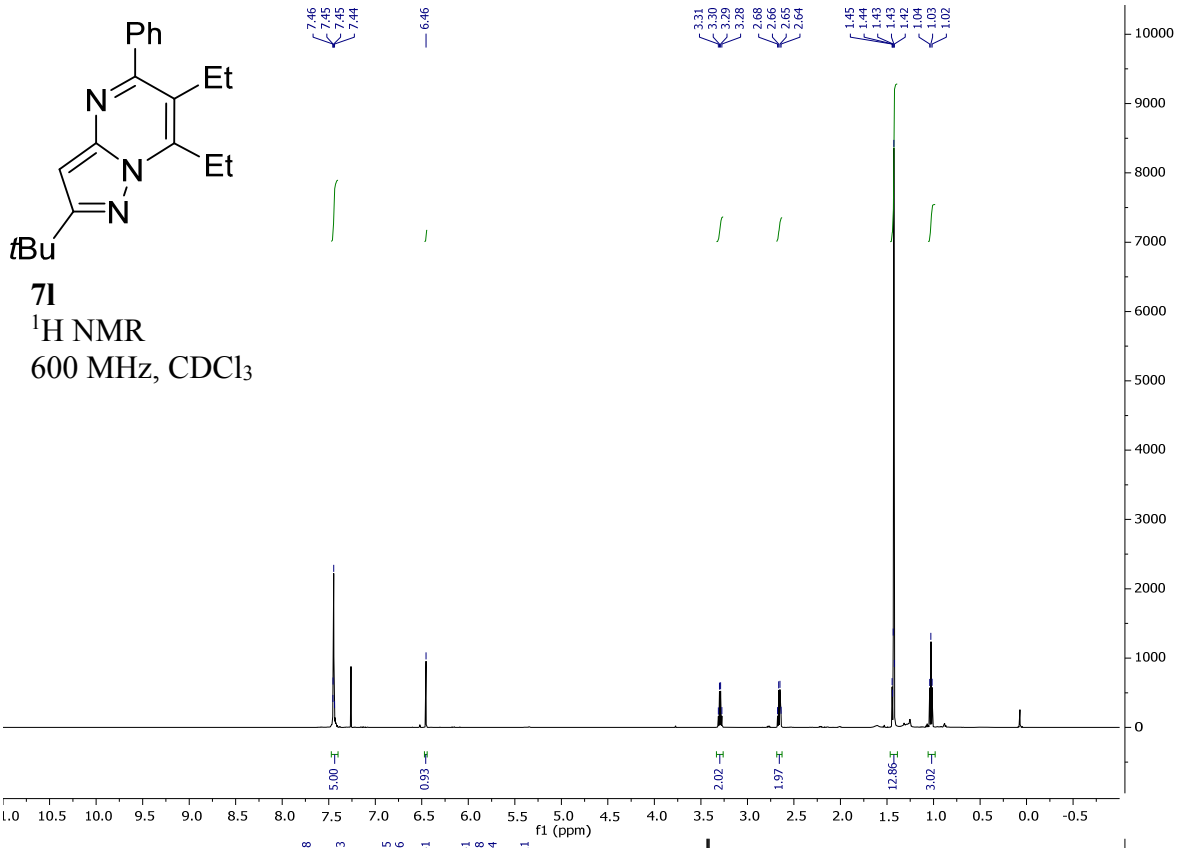
600 MHz, $CDCl_3$



7kb

^{13}C NMR

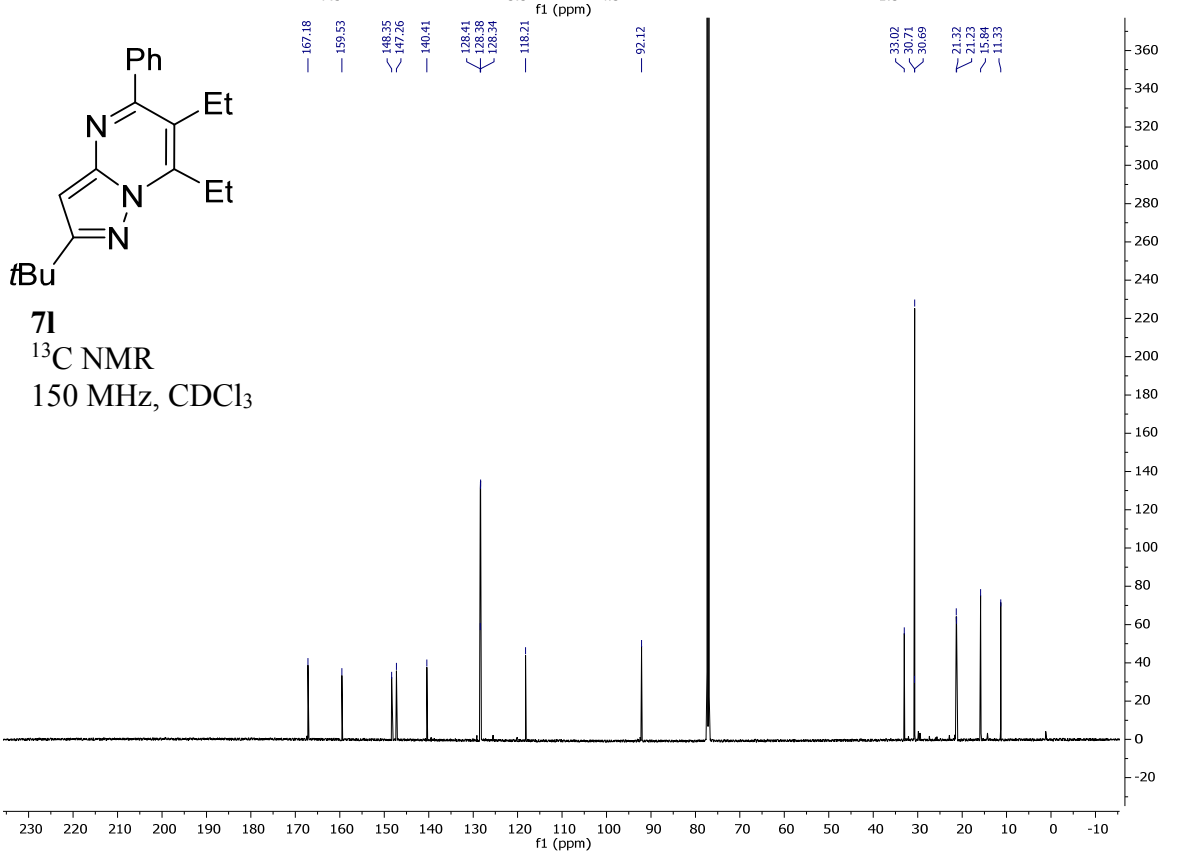
150 MHz, $CDCl_3$



7l

^{1}H NMR

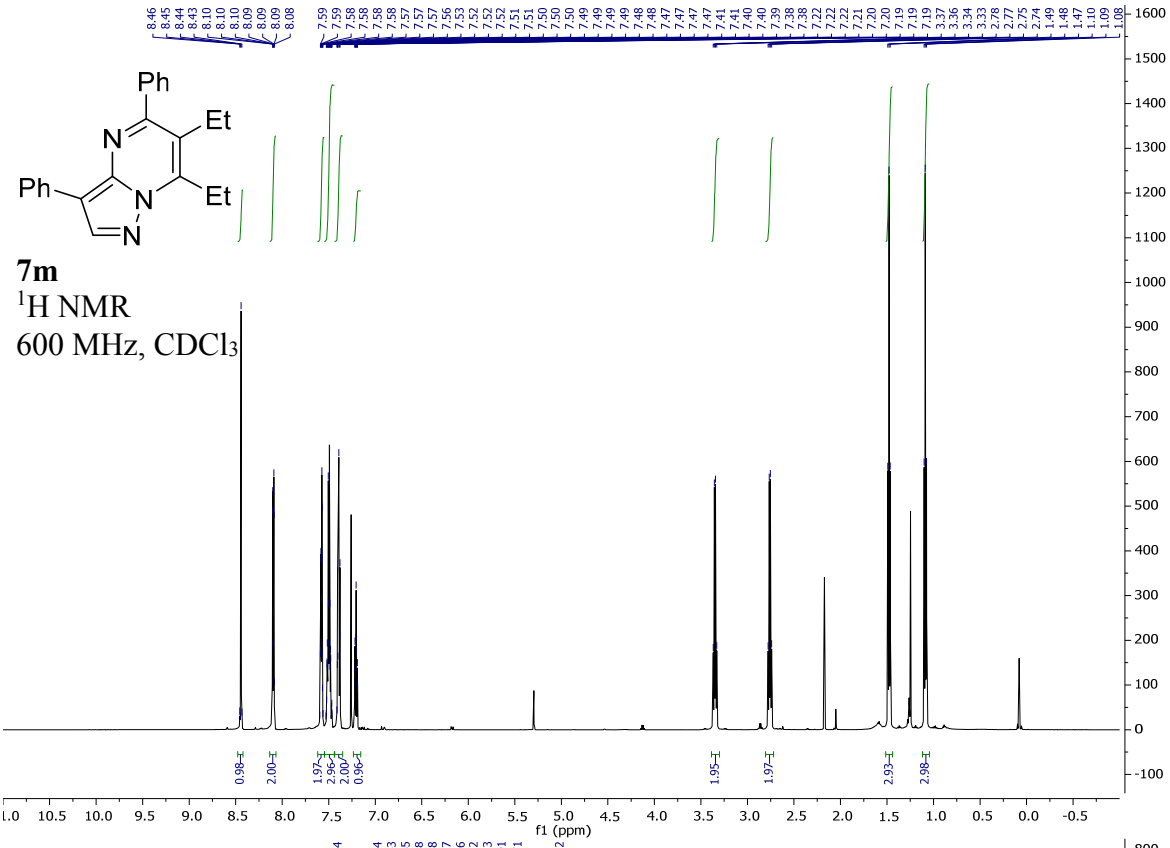
600 MHz, $CDCl_3$



7l

^{13}C NMR

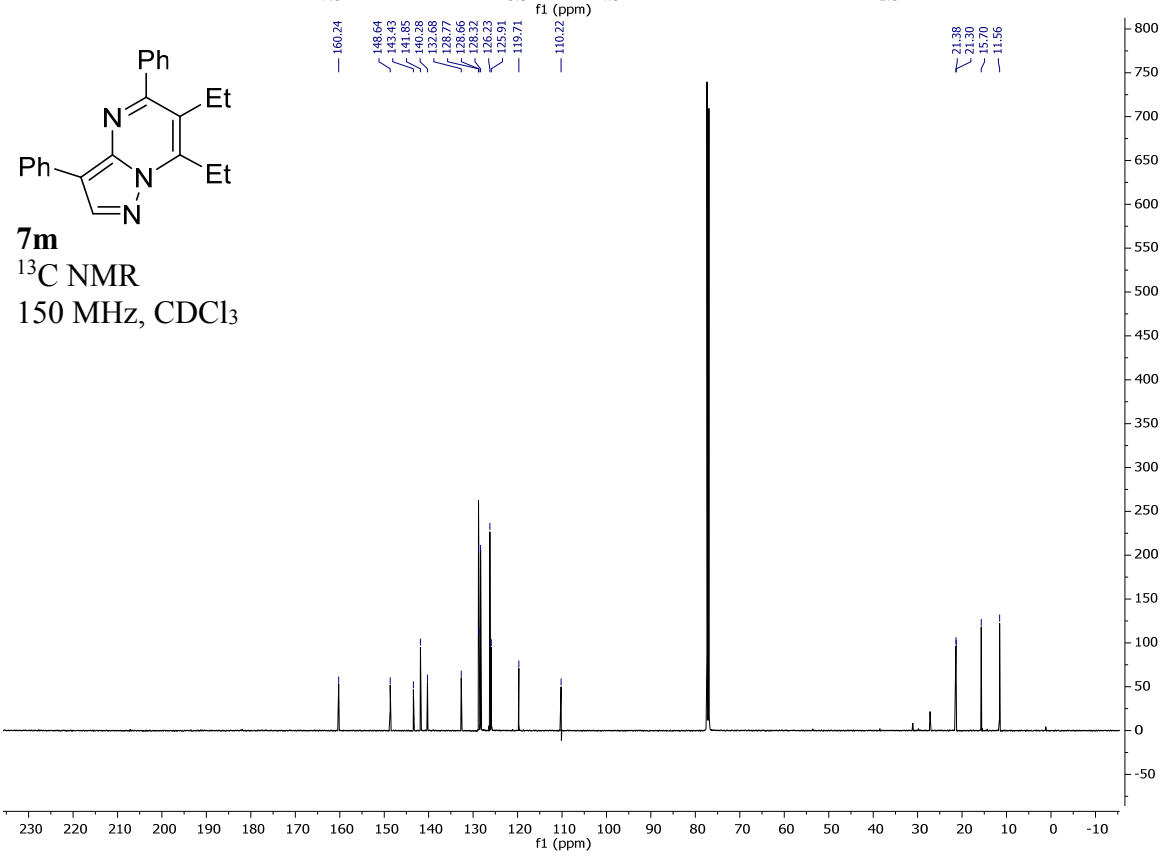
150 MHz, $CDCl_3$



7m

^{1}H NMR

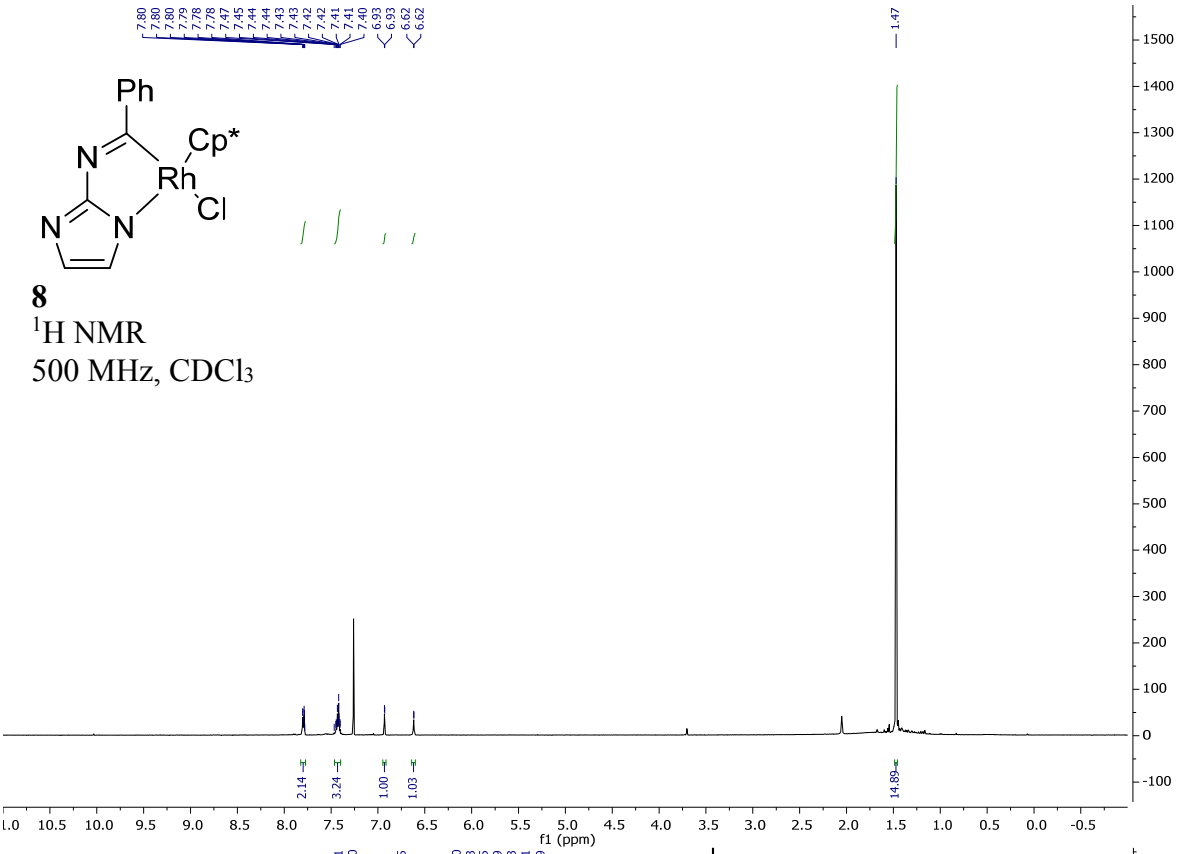
600 MHz, $CDCl_3$



7m

^{13}C NMR

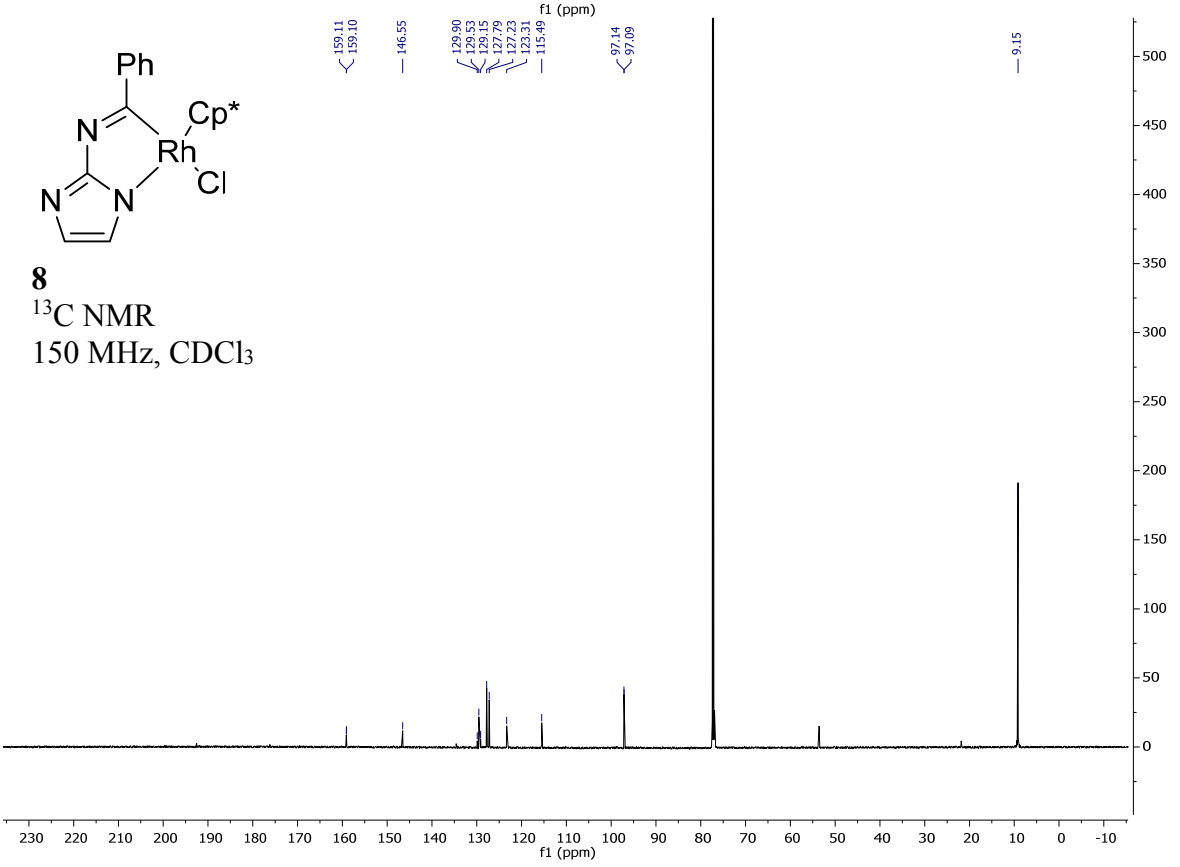
150 MHz, $CDCl_3$



8

^{1}H NMR

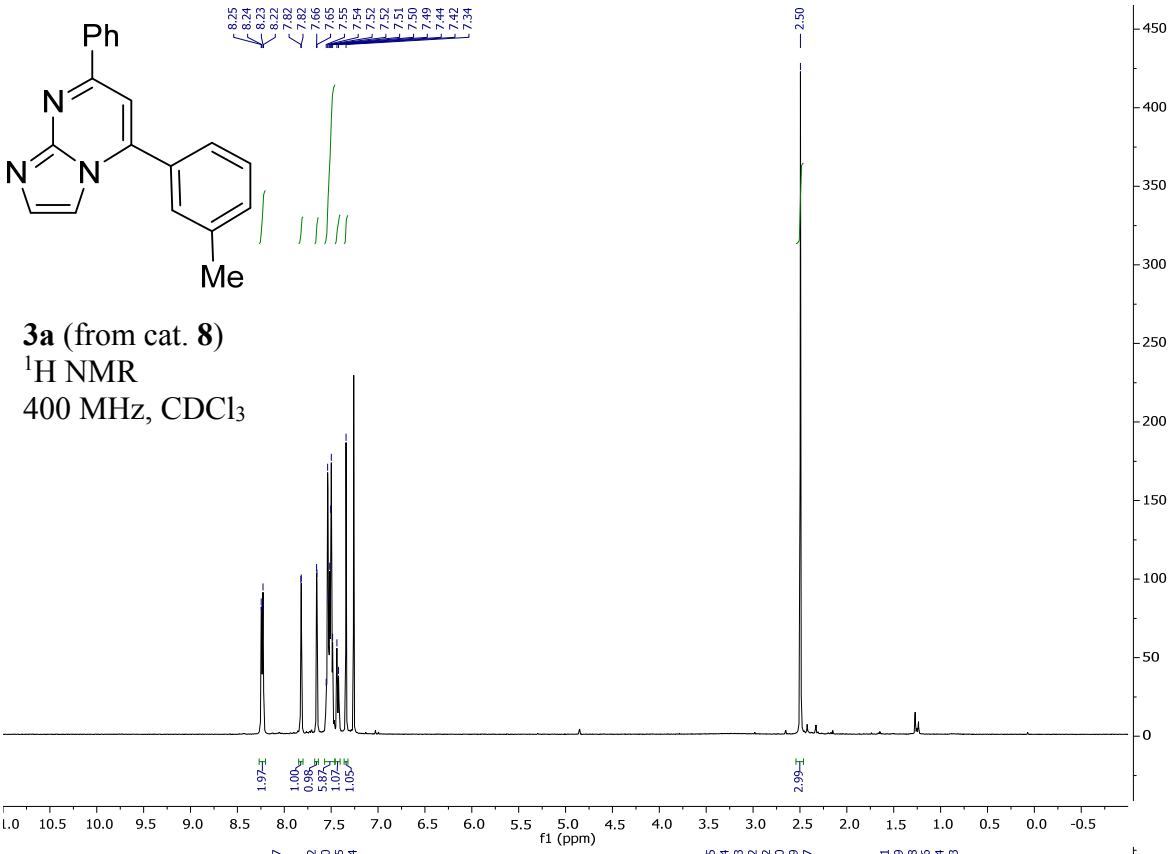
500 MHz, $CDCl_3$



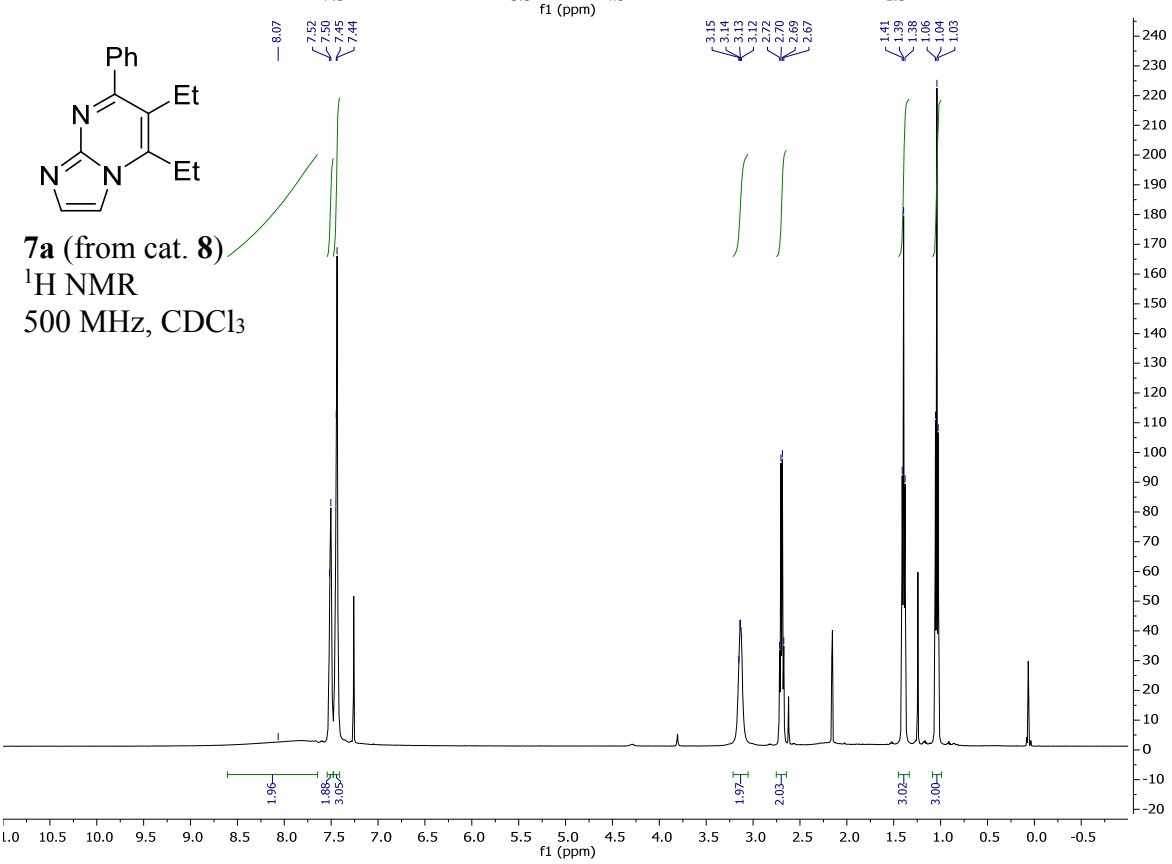
8

^{13}C NMR

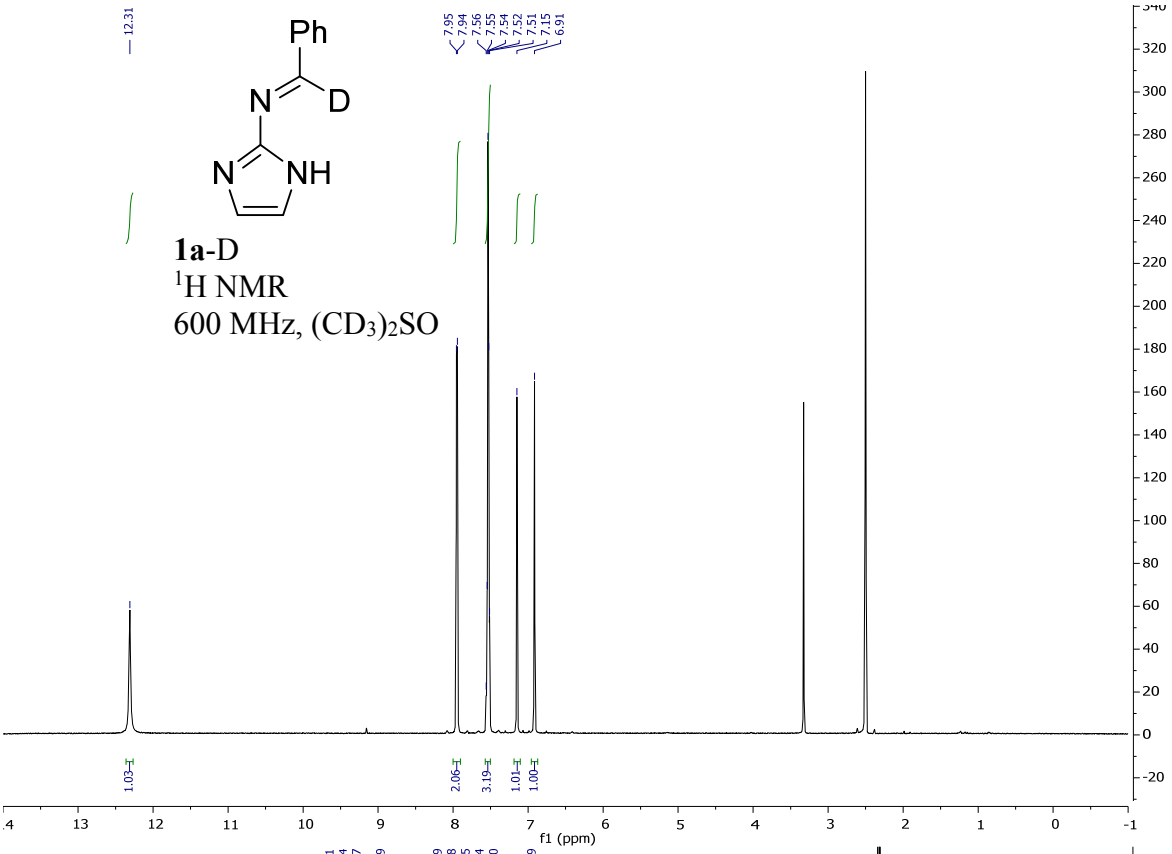
150 MHz, $CDCl_3$



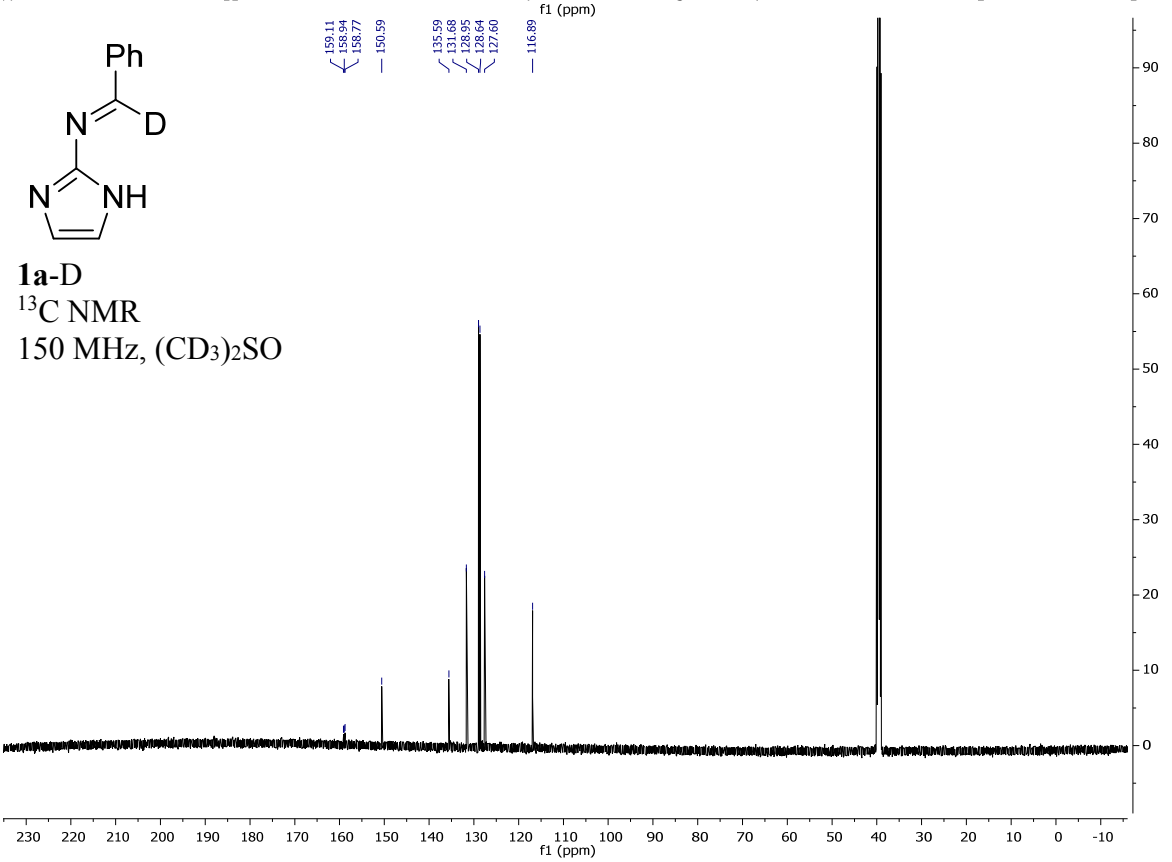
3a (from cat. **8**)
^{1}H NMR
400 MHz, $CDCl_3$



7a (from cat. **8**)
^{1}H NMR
500 MHz, $CDCl_3$



1a-D
^{1}H NMR
600 MHz, $(CD_3)_2SO$



1a-D
^{13}C NMR
150 MHz, $(CD_3)_2SO$

12. X-Ray Crystallography Information

Product 3c

Crystal growth

Single crystals of **3c** were achieved by dissolving **3c** (~15 mg) in acetone (0.5 mL) and slow evaporation of the solvent over the course of three days.

Data Collection

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 007C-17038. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound 007C-17038 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1585369 (007C-17038) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

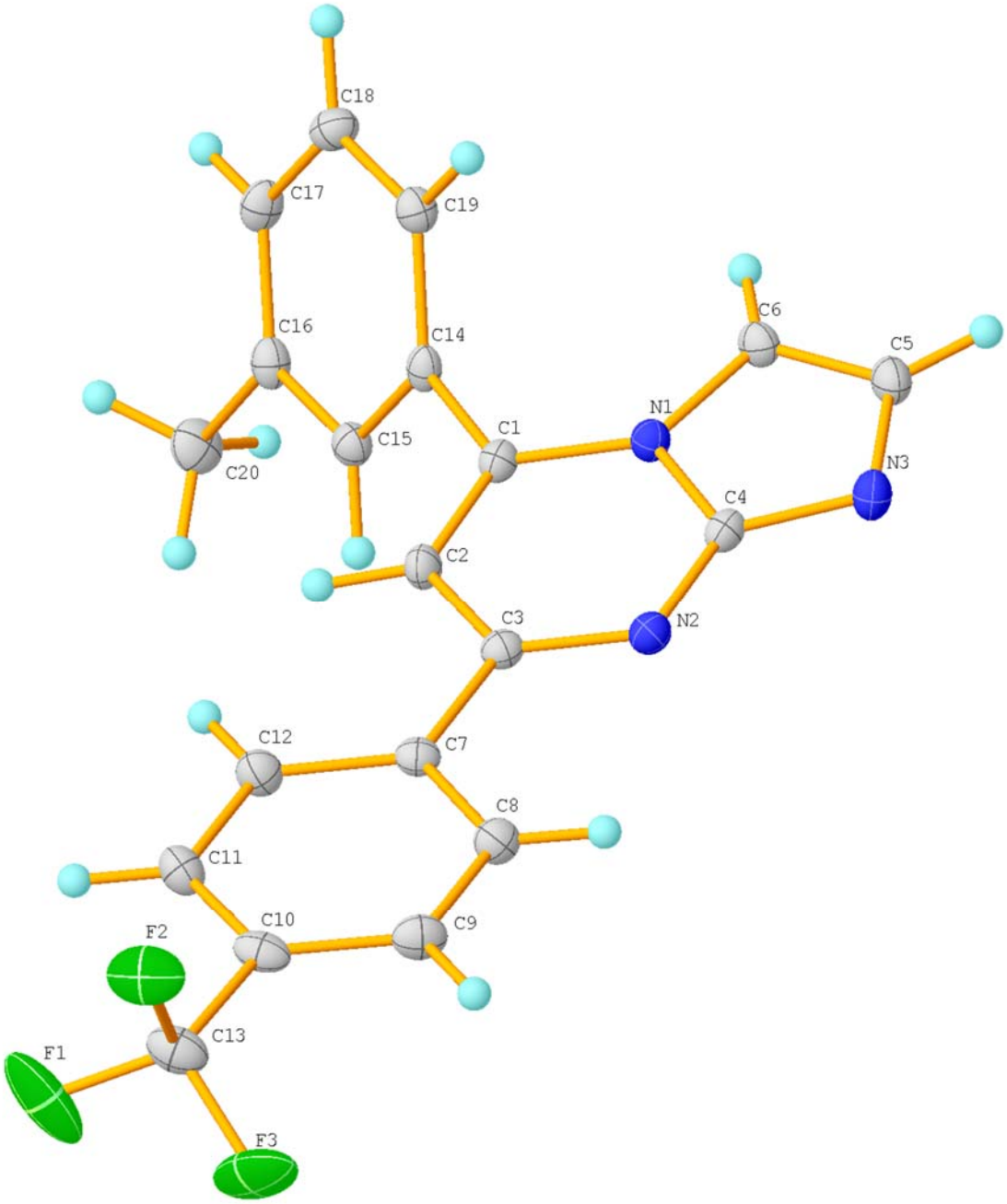


Figure S5. The complete numbering scheme of 007c-17038 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S5. Crystal data and structure refinement for 007c-17038

Identification code	007c-17038
Empirical formula	C20 H14 F3 N3
Formula weight	353.34
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	a = 7.3317(3) Å	α= 95.002(3)°.
	b = 10.9257(3) Å	β= 104.723(3)°.
	c = 11.0990(5) Å	γ = 108.954(3)°.
Volume	799.13(5) $Å^3$	
Z	2	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	0.113 mm^{-1}	
F(000)	364	
Crystal size	0.100 x 0.050 x 0.050 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	3.010 to 27.479°.	
Index ranges	-9<=h<=9, -14<=k<=14, -13<=l<=14	
Reflections collected	15659	
Independent reflections	3667 [R(int) = 0.0238]	
Observed reflections (I > 2sigma(I))	3188	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.90130	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3667 / 0 / 236	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.1017	
R indices (all data)	R1 = 0.0439, wR2 = 0.1053	
Largest diff. peak and hole	0.341 and -0.295 e.$Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007c-17038. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	176(1)	3976(1)	7961(1)	50(1)
F(2)	2636(1)	5310(1)	9490(1)	33(1)
F(3)	2782(2)	3483(1)	8754(1)	42(1)
N(1)	8049(1)	8720(1)	3576(1)	14(1)
N(2)	8029(2)	7396(1)	5207(1)	15(1)
N(3)	10945(2)	8447(1)	4554(1)	18(1)
C(1)	6023(2)	8498(1)	3326(1)	14(1)
C(2)	5032(2)	7740(1)	4041(1)	15(1)
C(3)	6096(2)	7219(1)	5003(1)	14(1)
C(4)	9008(2)	8133(1)	4490(1)	14(1)
C(5)	11225(2)	9246(1)	3680(1)	18(1)
C(6)	9496(2)	9433(1)	3064(1)	16(1)
C(7)	5047(2)	6471(1)	5844(1)	14(1)
C(8)	6086(2)	5932(1)	6760(1)	18(1)
C(9)	5155(2)	5266(1)	7578(1)	19(1)
C(10)	3166(2)	5126(1)	7485(1)	18(1)
C(11)	2107(2)	5649(1)	6577(1)	20(1)
C(12)	3047(2)	6316(1)	5763(1)	18(1)
C(13)	2189(2)	4470(1)	8409(1)	23(1)
C(14)	5034(2)	9086(1)	2320(1)	14(1)
C(15)	3381(2)	8252(1)	1321(1)	16(1)
C(16)	2302(2)	8762(1)	401(1)	17(1)
C(17)	2902(2)	10124(1)	517(1)	18(1)

C(18)	4552(2)	10964(1)	1507(1)	18(1)
C(19)	5639(2)	10452(1)	2410(1)	16(1)
C(20)	554(2)	7848(1)	-692(1)	23(1)

Table S7. Bond lengths [Å] and angles [°] for 007c-17038.

F(1)-C(13)	1.3344(16)
F(2)-C(13)	1.3426(15)
F(3)-C(13)	1.3374(16)
N(1)-C(1)	1.3738(15)
N(1)-C(6)	1.3787(15)
N(1)-C(4)	1.4063(14)
N(2)-C(3)	1.3226(15)
N(2)-C(4)	1.3494(15)
N(3)-C(4)	1.3304(15)
N(3)-C(5)	1.3708(15)
C(1)-C(2)	1.3643(16)
C(1)-C(14)	1.4841(15)
C(2)-C(3)	1.4297(15)
C(2)-H(2)	0.9500
C(3)-C(7)	1.4897(15)
C(5)-C(6)	1.3660(16)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(12)	1.3985(17)
C(7)-C(8)	1.4017(16)
C(8)-C(9)	1.3879(17)
C(8)-H(8)	0.9500
C(9)-C(10)	1.3916(18)
C(9)-H(9)	0.9500
C(10)-C(11)	1.3913(17)
C(10)-C(13)	1.4984(16)
C(11)-C(12)	1.3885(17)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(14)-C(15)	1.3974(15)
C(14)-C(19)	1.3977(16)
C(15)-C(16)	1.3972(16)
C(15)-H(15)	0.9500
C(16)-C(17)	1.3928(17)
C(16)-C(20)	1.5095(16)
C(17)-C(18)	1.3934(17)
C(17)-H(17)	0.9500
C(18)-C(19)	1.3902(16)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(1)-N(1)-C(6)	132.52(10)
C(1)-N(1)-C(4)	120.66(10)
C(6)-N(1)-C(4)	106.80(9)
C(3)-N(2)-C(4)	117.35(10)
C(4)-N(3)-C(5)	104.81(10)

C(2)-C(1)-N(1)	116.92(10)
C(2)-C(1)-C(14)	123.56(10)
N(1)-C(1)-C(14)	119.52(10)
C(1)-C(2)-C(3)	120.28(10)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
N(2)-C(3)-C(2)	122.42(10)
N(2)-C(3)-C(7)	117.33(10)
C(2)-C(3)-C(7)	120.24(10)
N(3)-C(4)-N(2)	127.01(10)
N(3)-C(4)-N(1)	110.72(10)
N(2)-C(4)-N(1)	122.24(10)
C(6)-C(5)-N(3)	112.60(10)
C(6)-C(5)-H(5)	123.7
N(3)-C(5)-H(5)	123.7
C(5)-C(6)-N(1)	105.06(10)
C(5)-C(6)-H(6)	127.5
N(1)-C(6)-H(6)	127.5
C(12)-C(7)-C(8)	118.67(11)
C(12)-C(7)-C(3)	121.47(10)
C(8)-C(7)-C(3)	119.83(11)
C(9)-C(8)-C(7)	120.70(11)
C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(10)	119.77(11)
C(8)-C(9)-H(9)	120.1
C(10)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	120.33(11)
C(11)-C(10)-C(13)	119.65(12)
C(9)-C(10)-C(13)	119.95(11)
C(12)-C(11)-C(10)	119.68(11)
C(12)-C(11)-H(11)	120.2
C(10)-C(11)-H(11)	120.2
C(11)-C(12)-C(7)	120.85(11)
C(11)-C(12)-H(12)	119.6
C(7)-C(12)-H(12)	119.6
F(1)-C(13)-F(3)	106.98(11)
F(1)-C(13)-F(2)	105.87(11)
F(3)-C(13)-F(2)	105.66(10)
F(1)-C(13)-C(10)	112.84(11)
F(3)-C(13)-C(10)	112.96(11)
F(2)-C(13)-C(10)	111.99(10)
C(15)-C(14)-C(19)	120.18(10)
C(15)-C(14)-C(1)	118.64(10)
C(19)-C(14)-C(1)	121.03(10)
C(16)-C(15)-C(14)	120.91(11)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(17)-C(16)-C(15)	118.20(10)
C(17)-C(16)-C(20)	121.42(10)
C(15)-C(16)-C(20)	120.38(11)
C(16)-C(17)-C(18)	121.27(10)
C(16)-C(17)-H(17)	119.4
C(18)-C(17)-H(17)	119.4
C(19)-C(18)-C(17)	120.30(11)
C(19)-C(18)-H(18)	119.8

C(17)-C(18)-H(18)	119.8
C(18)-C(19)-C(14)	119.12(11)
C(18)-C(19)-H(19)	120.4
C(14)-C(19)-H(19)	120.4
C(16)-C(20)-H(20A)	109.5
C(16)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(16)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 007c-17038. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	27(1)	72(1)	31(1)	21(1)	9(1)	-10(1)
F(2)	52(1)	29(1)	19(1)	4(1)	17(1)	11(1)
F(3)	71(1)	27(1)	47(1)	23(1)	38(1)	22(1)
N(1)	14(1)	15(1)	14(1)	3(1)	5(1)	6(1)
N(2)	16(1)	15(1)	14(1)	3(1)	4(1)	7(1)
N(3)	15(1)	22(1)	19(1)	4(1)	6(1)	9(1)
C(1)	14(1)	16(1)	14(1)	2(1)	4(1)	6(1)
C(2)	12(1)	17(1)	16(1)	4(1)	4(1)	6(1)
C(3)	15(1)	13(1)	14(1)	2(1)	4(1)	5(1)
C(4)	15(1)	16(1)	14(1)	2(1)	3(1)	8(1)
C(5)	16(1)	19(1)	21(1)	3(1)	8(1)	6(1)
C(6)	16(1)	18(1)	17(1)	4(1)	9(1)	6(1)
C(7)	16(1)	12(1)	13(1)	1(1)	4(1)	4(1)
C(8)	18(1)	18(1)	16(1)	4(1)	4(1)	7(1)
C(9)	24(1)	18(1)	15(1)	5(1)	4(1)	7(1)
C(10)	24(1)	14(1)	14(1)	1(1)	6(1)	1(1)
C(11)	16(1)	21(1)	20(1)	4(1)	7(1)	4(1)
C(12)	18(1)	19(1)	17(1)	5(1)	5(1)	6(1)
C(13)	27(1)	20(1)	18(1)	4(1)	8(1)	3(1)
C(14)	13(1)	20(1)	14(1)	6(1)	7(1)	8(1)
C(15)	15(1)	17(1)	17(1)	4(1)	7(1)	6(1)
C(16)	14(1)	23(1)	15(1)	4(1)	5(1)	8(1)
C(17)	19(1)	24(1)	15(1)	8(1)	6(1)	12(1)
C(18)	22(1)	16(1)	19(1)	6(1)	8(1)	9(1)
C(19)	15(1)	18(1)	15(1)	4(1)	5(1)	6(1)
C(20)	19(1)	26(1)	20(1)	4(1)	1(1)	7(1)

Table S9. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for 007c-17038.

	x	y	z	U(eq)
H(2)	3628	7556	3898	18
H(5)	12482	9629	3519	22
H(6)	9327	9944	2423	20
H(8)	7442	6023	6823	21

H(9)	5873	4907	8199	23
H(11)	748	5549	6514	23
H(12)	2322	6673	5143	22
H(15)	2986	7325	1266	19
H(17)	2171	10489	-91	22
H(18)	4937	11891	1566	22
H(19)	6778	11022	3078	20
H(20A)	1021	7742	-1434	34
H(20B)	-510	8222	-896	34
H(20C)	17	6989	-458	34

Table S10. Torsion angles [°] for 007c-17038.

C(6)-N(1)-C(1)-C(2)	-179.11(11)
C(4)-N(1)-C(1)-C(2)	2.84(16)
C(6)-N(1)-C(1)-C(14)	0.45(18)
C(4)-N(1)-C(1)-C(14)	-177.60(9)
N(1)-C(1)-C(2)-C(3)	0.29(16)
C(14)-C(1)-C(2)-C(3)	-179.25(10)
C(4)-N(2)-C(3)-C(2)	2.05(16)
C(4)-N(2)-C(3)-C(7)	-176.58(9)
C(1)-C(2)-C(3)-N(2)	-2.89(17)
C(1)-C(2)-C(3)-C(7)	175.70(10)
C(5)-N(3)-C(4)-N(2)	-177.49(11)
C(5)-N(3)-C(4)-N(1)	0.47(13)
C(3)-N(2)-C(4)-N(3)	178.96(11)
C(3)-N(2)-C(4)-N(1)	1.20(16)
C(1)-N(1)-C(4)-N(3)	178.14(10)
C(6)-N(1)-C(4)-N(3)	-0.37(13)
C(1)-N(1)-C(4)-N(2)	-3.78(16)
C(6)-N(1)-C(4)-N(2)	177.71(10)
C(4)-N(3)-C(5)-C(6)	-0.42(13)
N(3)-C(5)-C(6)-N(1)	0.20(13)
C(1)-N(1)-C(6)-C(5)	-178.16(11)
C(4)-N(1)-C(6)-C(5)	0.09(12)
N(2)-C(3)-C(7)-C(12)	175.25(10)
C(2)-C(3)-C(7)-C(12)	-3.41(16)
N(2)-C(3)-C(7)-C(8)	-3.19(15)
C(2)-C(3)-C(7)-C(8)	178.15(10)
C(12)-C(7)-C(8)-C(9)	-0.48(17)
C(3)-C(7)-C(8)-C(9)	178.01(10)
C(7)-C(8)-C(9)-C(10)	0.27(18)
C(8)-C(9)-C(10)-C(11)	0.08(18)
C(8)-C(9)-C(10)-C(13)	-176.84(11)
C(9)-C(10)-C(11)-C(12)	-0.22(18)
C(13)-C(10)-C(11)-C(12)	176.71(11)
C(10)-C(11)-C(12)-C(7)	0.01(18)
C(8)-C(7)-C(12)-C(11)	0.33(17)
C(3)-C(7)-C(12)-C(11)	-178.12(10)
C(11)-C(10)-C(13)-F(1)	26.20(17)
C(9)-C(10)-C(13)-F(1)	-156.86(12)
C(11)-C(10)-C(13)-F(3)	147.69(12)
C(9)-C(10)-C(13)-F(3)	-35.37(16)
C(11)-C(10)-C(13)-F(2)	-93.15(14)
C(9)-C(10)-C(13)-F(2)	83.79(14)

C(2)-C(1)-C(14)-C(15)	-57.84(15)
N(1)-C(1)-C(14)-C(15)	122.63(12)
C(2)-C(1)-C(14)-C(19)	117.65(13)
N(1)-C(1)-C(14)-C(19)	-61.88(15)
C(19)-C(14)-C(15)-C(16)	-0.35(17)
C(1)-C(14)-C(15)-C(16)	175.18(10)
C(14)-C(15)-C(16)-C(17)	-0.81(17)
C(14)-C(15)-C(16)-C(20)	178.37(11)
C(15)-C(16)-C(17)-C(18)	1.07(17)
C(20)-C(16)-C(17)-C(18)	-178.10(11)
C(16)-C(17)-C(18)-C(19)	-0.17(18)
C(17)-C(18)-C(19)-C(14)	-1.00(17)
C(15)-C(14)-C(19)-C(18)	1.26(17)
C(1)-C(14)-C(19)-C(18)	-174.16(10)

Symmetry transformations used to generate equivalent atoms:

Product 7a

Crystal growth

Single crystals of **7a** were achieved by dissolving **7a** (~15 mg) in acetone (0.5 mL) and slow evaporation of the solvent over the course of three days.

Data Collection

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007-16124. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound 007-16124 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1585370 (007-16124) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

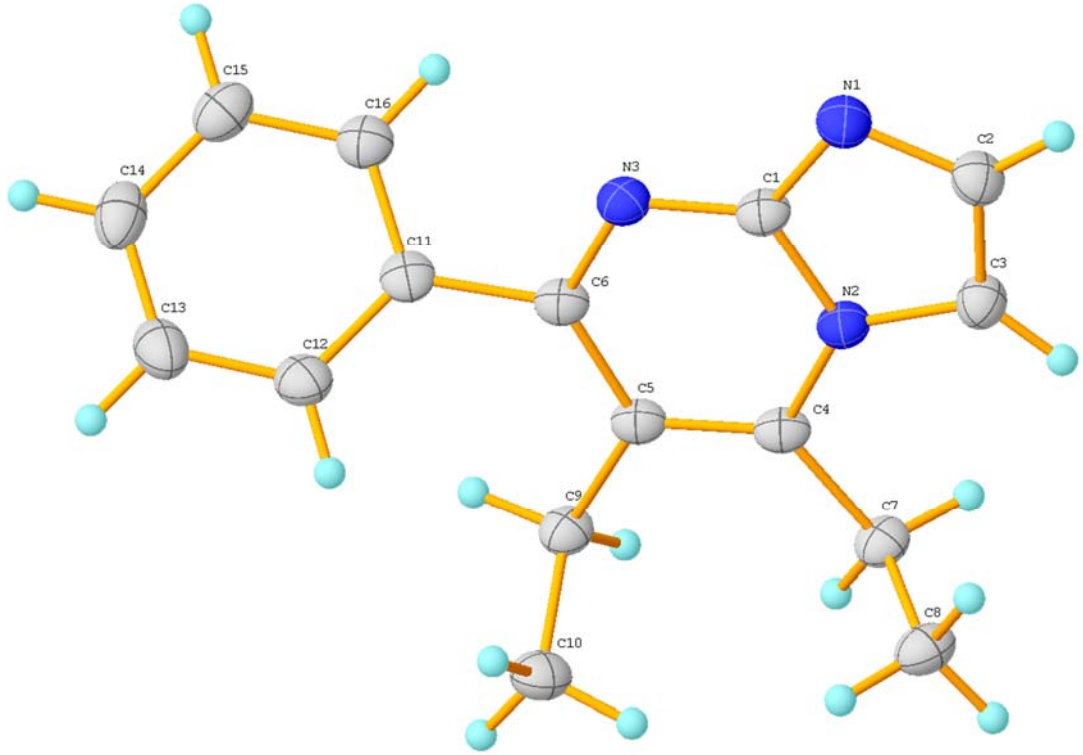


Figure S6. The complete numbering scheme 007-16124 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S11. Crystal data and structure refinement for 007-16124.

Identification code	007-16124	
Empirical formula	C32 H34 N6	
Formula weight	502.65	
Temperature	93(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.205(2) Å	α= 90°.
	b = 6.7028(5) Å	β= 101.591(3)°.
	c = 13.6630(10) Å	γ = 90°.
Volume	2620.1(3) $Å^3$	
Z	4	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.601 mm^{-1}	
F(000)	1072	
Crystal size	0.200 x 0.020 x 0.020 mm^3	
Theta range for data collection	6.187 to 67.766°.	
Index ranges	-34<=h<=34, -8<=k<=8, -16<=l<=16	
Reflections collected	44198	
Independent reflections	2364 [R(int) = 0.0678]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.777	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2364 / 0 / 174	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0867	
R indices (all data)	R1 = 0.0366, wR2 = 0.0896	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.199 and -0.144 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007-16124. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	7108(1)	6440(2)	5738(1)	27(1)
N(2)	6915(1)	6847(1)	7240(1)	23(1)
N(3)	6515(1)	4335(1)	6152(1)	24(1)
C(1)	6833(1)	5800(2)	6338(1)	24(1)
C(2)	7370(1)	7923(2)	6265(1)	28(1)
C(3)	7263(1)	8210(2)	7184(1)	27(1)
C(4)	6677(1)	6395(2)	7990(1)	23(1)
C(5)	6345(1)	4915(2)	7803(1)	22(1)
C(6)	6274(1)	3908(2)	6852(1)	23(1)
C(7)	6816(1)	7580(2)	8935(1)	26(1)
C(8)	6620(1)	9708(2)	8833(1)	31(1)
C(9)	6084(1)	4304(2)	8609(1)	25(1)
C(10)	5700(1)	5751(2)	8765(1)	32(1)
C(11)	5943(1)	2211(2)	6581(1)	25(1)
C(12)	5476(1)	2281(2)	6674(1)	31(1)
C(13)	5184(1)	661(2)	6394(1)	37(1)
C(14)	5353(1)	-1053(2)	6026(1)	36(1)
C(15)	5814(1)	-1128(2)	5915(1)	32(1)

C(16)	6106(1)	492(2)	6185(1)	27(1)

Table S13. Bond lengths [Å] and angles [°] for 007-16124.

N(1)-C(1)	1.3290(14)
N(1)-C(2)	1.3681(15)
N(2)-C(3)	1.3801(15)
N(2)-C(4)	1.3820(14)
N(2)-C(1)	1.3959(14)
N(3)-C(6)	1.3275(14)
N(3)-C(1)	1.3395(15)
C(2)-C(3)	1.3689(16)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-C(5)	1.3743(16)
C(4)-C(7)	1.5008(15)
C(5)-C(6)	1.4412(15)
C(5)-C(9)	1.5170(14)
C(6)-C(11)	1.4901(16)
C(7)-C(8)	1.5321(17)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.5310(16)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.3963(16)
C(11)-C(16)	1.3967(16)
C(12)-C(13)	1.3860(18)
C(12)-H(12)	0.9500
C(13)-C(14)	1.384(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.3848(18)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3849(17)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(1)-N(1)-C(2)	104.73(9)
C(3)-N(2)-C(4)	132.15(10)
C(3)-N(2)-C(1)	106.40(9)
C(4)-N(2)-C(1)	121.41(10)
C(6)-N(3)-C(1)	117.92(9)
N(1)-C(1)-N(3)	126.90(10)
N(1)-C(1)-N(2)	111.37(10)
N(3)-C(1)-N(2)	121.73(10)
N(1)-C(2)-C(3)	112.18(10)
N(1)-C(2)-H(2)	123.9
C(3)-C(2)-H(2)	123.9
C(2)-C(3)-N(2)	105.32(10)
C(2)-C(3)-H(3)	127.3

N(2)-C(3)-H(3)	127.3
C(5)-C(4)-N(2)	117.43(10)
C(5)-C(4)-C(7)	126.91(10)
N(2)-C(4)-C(7)	115.66(10)
C(4)-C(5)-C(6)	118.33(10)
C(4)-C(5)-C(9)	119.88(10)
C(6)-C(5)-C(9)	121.71(10)
N(3)-C(6)-C(5)	123.15(10)
N(3)-C(6)-C(11)	113.37(9)
C(5)-C(6)-C(11)	123.39(10)
C(4)-C(7)-C(8)	112.53(9)
C(4)-C(7)-H(7A)	109.1
C(8)-C(7)-H(7A)	109.1
C(4)-C(7)-H(7B)	109.1
C(8)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(5)-C(9)-C(10)	114.83(9)
C(5)-C(9)-H(9A)	108.6
C(10)-C(9)-H(9A)	108.6
C(5)-C(9)-H(9B)	108.6
C(10)-C(9)-H(9B)	108.6
H(9A)-C(9)-H(9B)	107.5
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	118.55(11)
C(12)-C(11)-C(6)	123.25(11)
C(16)-C(11)-C(6)	118.16(10)
C(13)-C(12)-C(11)	120.44(12)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	120.44(11)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	119.63(12)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
C(14)-C(15)-C(16)	120.23(12)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	120.68(11)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 007-16124. The anisotropic

displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	31(1)	32(1)	21(1)	1(1)	8(1)	-2(1)
N(2)	26(1)	26(1)	17(1)	0(1)	4(1)	1(1)
N(3)	28(1)	28(1)	17(1)	0(1)	5(1)	0(1)
C(1)	27(1)	27(1)	16(1)	1(1)	4(1)	2(1)
C(2)	29(1)	30(1)	25(1)	2(1)	7(1)	-3(1)
C(3)	28(1)	28(1)	24(1)	-1(1)	4(1)	-3(1)
C(4)	27(1)	25(1)	17(1)	2(1)	5(1)	5(1)
C(5)	26(1)	25(1)	17(1)	2(1)	4(1)	5(1)
C(6)	25(1)	25(1)	18(1)	2(1)	4(1)	4(1)
C(7)	32(1)	29(1)	17(1)	-1(1)	4(1)	-1(1)
C(8)	42(1)	29(1)	24(1)	-3(1)	9(1)	0(1)
C(9)	31(1)	27(1)	18(1)	1(1)	6(1)	-1(1)
C(10)	35(1)	35(1)	27(1)	-2(1)	13(1)	2(1)
C(11)	29(1)	30(1)	15(1)	2(1)	4(1)	0(1)
C(12)	31(1)	40(1)	22(1)	-4(1)	7(1)	0(1)
C(13)	31(1)	53(1)	28(1)	-6(1)	8(1)	-9(1)
C(14)	42(1)	40(1)	25(1)	-1(1)	4(1)	-15(1)
C(15)	42(1)	29(1)	25(1)	-1(1)	3(1)	-1(1)
C(16)	30(1)	31(1)	20(1)	2(1)	4(1)	1(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 007-16124.

	x	y	z	U(eq)
H(2)	7600	8666	6020	33
H(3)	7399	9149	7679	32
H(7A)	7161	7642	9120	31
H(7B)	6702	6891	9481	31
H(8A)	6727	10390	8285	47
H(8B)	6730	10436	9458	47
H(8C)	6277	9657	8690	47
H(9A)	6312	4167	9248	30
H(9B)	5942	2976	8437	30
H(10A)	5493	6029	8121	47
H(10B)	5841	6998	9053	47
H(10C)	5518	5151	9220	47
H(12)	5357	3447	6931	37
H(13)	4866	728	6456	44
H(14)	5154	-2172	5849	43
H(15)	5929	-2294	5653	39
H(16)	6421	433	6100	33

Table S16. Torsion angles [°] for 007-16124.

C(2)-N(1)-C(1)-N(3)	-179.31(11)
C(2)-N(1)-C(1)-N(2)	-0.02(12)
C(6)-N(3)-C(1)-N(1)	179.77(11)
C(6)-N(3)-C(1)-N(2)	0.55(16)

C(3)-N(2)-C(1)-N(1)	-0.08(12)
C(4)-N(2)-C(1)-N(1)	-178.20(10)
C(3)-N(2)-C(1)-N(3)	179.26(10)
C(4)-N(2)-C(1)-N(3)	1.14(16)
C(1)-N(1)-C(2)-C(3)	0.11(13)
N(1)-C(2)-C(3)-N(2)	-0.16(13)
C(4)-N(2)-C(3)-C(2)	177.97(11)
C(1)-N(2)-C(3)-C(2)	0.14(12)
C(3)-N(2)-C(4)-C(5)	-179.59(11)
C(1)-N(2)-C(4)-C(5)	-2.02(15)
C(3)-N(2)-C(4)-C(7)	-0.14(17)
C(1)-N(2)-C(4)-C(7)	177.43(9)
N(2)-C(4)-C(5)-C(6)	1.29(15)
C(7)-C(4)-C(5)-C(6)	-178.10(10)
N(2)-C(4)-C(5)-C(9)	177.98(9)
C(7)-C(4)-C(5)-C(9)	-1.40(17)
C(1)-N(3)-C(6)-C(5)	-1.28(16)
C(1)-N(3)-C(6)-C(11)	-177.97(9)
C(4)-C(5)-C(6)-N(3)	0.36(16)
C(9)-C(5)-C(6)-N(3)	-176.27(10)
C(4)-C(5)-C(6)-C(11)	176.71(10)
C(9)-C(5)-C(6)-C(11)	0.08(16)
C(5)-C(4)-C(7)-C(8)	-104.76(13)
N(2)-C(4)-C(7)-C(8)	75.85(12)
C(4)-C(5)-C(9)-C(10)	76.58(13)
C(6)-C(5)-C(9)-C(10)	-106.85(12)
N(3)-C(6)-C(11)-C(12)	-131.62(11)
C(5)-C(6)-C(11)-C(12)	51.71(16)
N(3)-C(6)-C(11)-C(16)	46.28(14)
C(5)-C(6)-C(11)-C(16)	-130.40(11)
C(16)-C(11)-C(12)-C(13)	1.11(17)
C(6)-C(11)-C(12)-C(13)	179.00(11)
C(11)-C(12)-C(13)-C(14)	0.47(19)
C(12)-C(13)-C(14)-C(15)	-1.51(19)
C(13)-C(14)-C(15)-C(16)	0.94(18)
C(14)-C(15)-C(16)-C(11)	0.66(17)
C(12)-C(11)-C(16)-C(15)	-1.68(16)
C(6)-C(11)-C(16)-C(15)	-179.67(10)

Symmetry transformations used to generate equivalent atoms:

Rhodacycle 8

Crystal growth
Single crystals of **8** were achieved by recrystallization in tetrahydrofuran.

Data Collection
Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007b-17101. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The THF molecule is disordered across crystallographic glide plane. The special position constraints were suppressed and the THF model extends past the asymmetric unit with all atoms at half occupancy. The full numbering scheme of compound 007b-17101 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1585355 (007b-17101) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

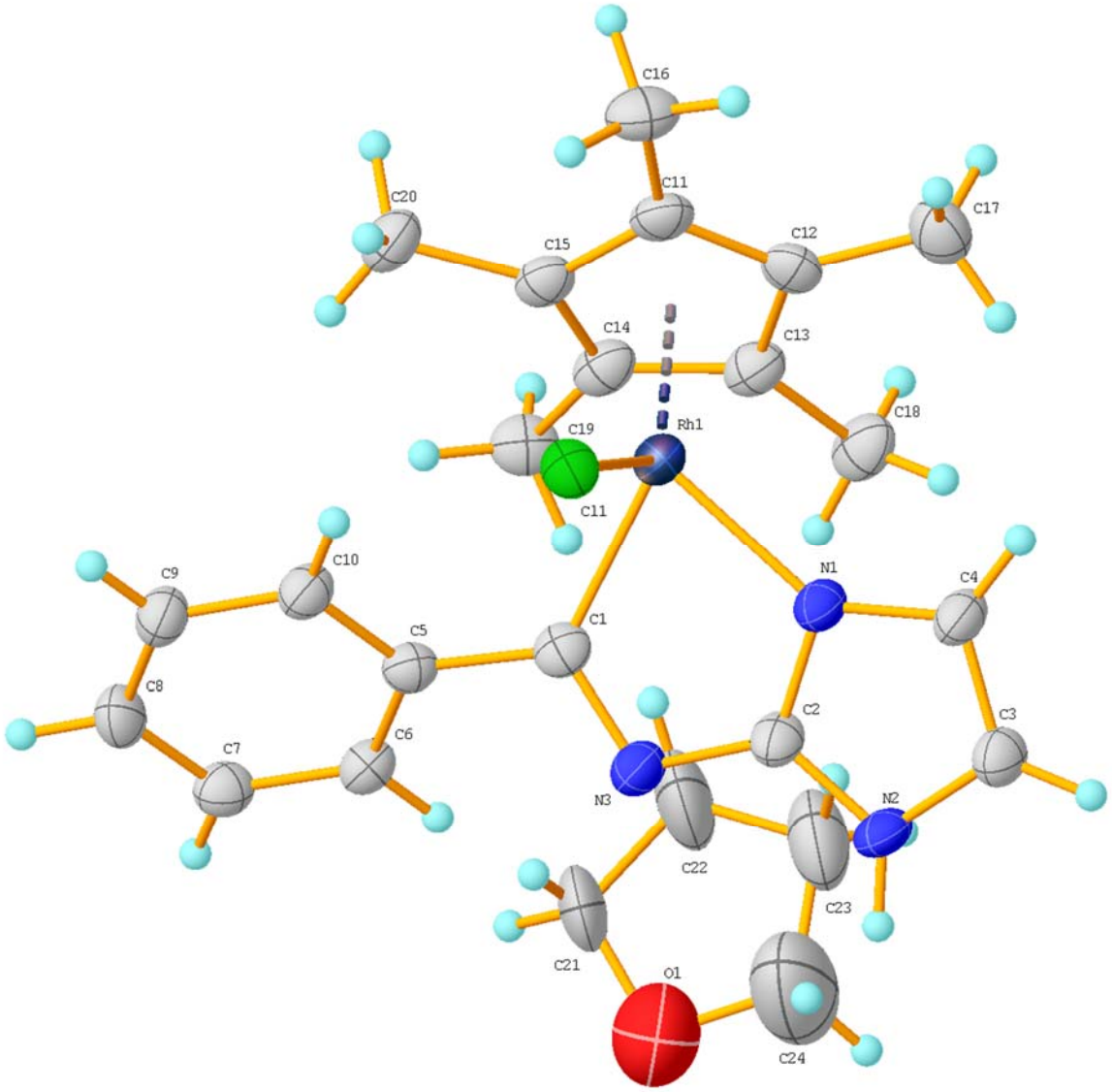


Figure S7. The complete numbering scheme of 007b-17101 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S17. Crystal data and structure refinement for 007b-17101.

Identification code	007b-17101	
Empirical formula	C22 H27 Cl N3 O0.50 Rh	
Formula weight	479.82	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.4841(9) Å	α= 90°.
	b = 9.3563(2) Å	β= 91.787(3)°.
	c = 14.9795(5) Å	γ = 90°.
Volume	4130.3(2) Å^3	
Z	8	
Density (calculated)	1.543 Mg/m^3	

Absorption coefficient	7.981 mm^{-1}
F(000)	1968
Crystal size	0.100 x 0.050 x 0.010 mm^3
Crystal color and habit	Red Plate
Diffractometer	Rigaku Saturn 944+ CCD
Theta range for data collection	2.999 to 67.115°.
Index ranges	-35<=h<=35, -11<=k<=11, -17<=l<=17
Reflections collected	8567
Independent reflections	8567 [R(int) = 0.0951]
Observed reflections (I > 2sigma(I))	7343
Completeness to theta = 67.115°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.54567
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	8567 / 34 / 277
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1572
R indices (all data)	R1 = 0.0672, wR2 = 0.1636
Largest diff. peak and hole	3.775 and -1.248 e.$Å^{-3}$

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007b-17101. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	6338(1)	7018(1)	6060(1)	27(1)
Cl(1)	6544(1)	7745(2)	4594(1)	32(1)
N(1)	5669(2)	7639(5)	5820(4)	28(1)
N(2)	4985(2)	6906(5)	5411(4)	33(1)
N(3)	5616(2)	5237(5)	5319(4)	31(1)
C(1)	6054(2)	5248(6)	5499(4)	28(1)
C(2)	5421(2)	6542(6)	5516(4)	30(1)
C(3)	4950(2)	8313(7)	5659(5)	33(1)
C(4)	5371(2)	8754(7)	5908(5)	32(1)
C(5)	6305(2)	3955(6)	5265(4)	27(1)
C(6)	6126(2)	2598(7)	5438(4)	30(1)
C(7)	6350(2)	1385(7)	5167(4)	32(1)
C(8)	6750(2)	1503(7)	4705(5)	35(2)
C(9)	6933(2)	2847(7)	4542(5)	33(1)
C(10)	6714(2)	4061(7)	4831(4)	31(1)
C(11)	6925(2)	8117(7)	6794(4)	33(2)
C(12)	6529(2)	8399(7)	7263(4)	32(1)
C(13)	6332(2)	7029(7)	7479(4)	33(1)
C(14)	6628(2)	5921(7)	7221(4)	33(1)
C(15)	6982(2)	6580(7)	6742(4)	30(1)
C(16)	7242(2)	9180(8)	6398(5)	42(2)
C(17)	6335(3)	9831(8)	7481(5)	43(2)
C(18)	5905(3)	6850(8)	8003(5)	41(2)
C(19)	6574(2)	4364(7)	7420(5)	37(2)
C(20)	7391(2)	5868(8)	6381(5)	38(2)
C(21)	5284(7)	1580(20)	7151(17)	77(6)
O(1)	4836(7)	1620(30)	6853(17)	121(7)
C(22)	5339(11)	2500(30)	7940(20)	96(12)
C(23)	4991(8)	3620(20)	7774(13)	75(6)
C(24)	4683(15)	2980(40)	7110(30)	150(20)

Table S19. Bond lengths [Å] and angles [°] for 007b-17101.

Rh(1)-C(1)	2.027(6)
Rh(1)-N(1)	2.077(5)
Rh(1)-C(13)	2.126(7)
Rh(1)-C(15)	2.168(6)
Rh(1)-C(14)	2.172(6)
Rh(1)-C(11)	2.268(6)
Rh(1)-C(12)	2.274(6)
Rh(1)-Cl(1)	2.3945(16)
N(1)-C(2)	1.331(8)
N(1)-C(4)	1.373(8)
N(2)-C(2)	1.335(8)
N(2)-C(3)	1.373(8)
N(2)-H(2)	0.8800
N(3)-C(1)	1.310(8)
N(3)-C(2)	1.385(8)
C(1)-C(5)	1.467(9)
C(3)-C(4)	1.352(9)
C(3)-H(3)	0.9500
C(4)-H(4)	0.9500
C(5)-C(10)	1.391(9)
C(5)-C(6)	1.402(9)
C(6)-C(7)	1.380(9)
C(6)-H(6)	0.9500
C(7)-C(8)	1.391(10)
C(7)-H(7)	0.9500
C(8)-C(9)	1.393(10)
C(8)-H(8)	0.9500
C(9)-C(10)	1.383(9)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-C(12)	1.406(10)
C(11)-C(15)	1.450(9)
C(11)-C(16)	1.500(10)
C(12)-C(13)	1.449(10)
C(12)-C(17)	1.497(10)
C(13)-C(14)	1.416(10)
C(13)-C(18)	1.513(10)
C(14)-C(15)	1.427(9)
C(14)-C(19)	1.496(9)
C(15)-C(20)	1.493(9)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-O(1)	1.38(2)
C(21)-C(22)	1.47(2)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
O(1)-C(24)	1.40(3)
C(22)-C(23)	1.48(2)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.45(2)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900

C(1)-Rh(1)-N(1)	77.2(2)
C(1)-Rh(1)-C(13)	113.7(2)
N(1)-Rh(1)-C(13)	97.7(2)
C(1)-Rh(1)-C(15)	112.7(3)
N(1)-Rh(1)-C(15)	161.4(2)
C(13)-Rh(1)-C(15)	64.2(3)
C(1)-Rh(1)-C(14)	95.3(2)
N(1)-Rh(1)-C(14)	128.2(2)
C(13)-Rh(1)-C(14)	38.5(3)
C(15)-Rh(1)-C(14)	38.4(2)
C(1)-Rh(1)-C(11)	150.6(3)
N(1)-Rh(1)-C(11)	131.6(2)
C(13)-Rh(1)-C(11)	62.8(3)
C(15)-Rh(1)-C(11)	38.1(2)
C(14)-Rh(1)-C(11)	63.3(2)
C(1)-Rh(1)-C(12)	151.9(2)
N(1)-Rh(1)-C(12)	100.9(2)
C(13)-Rh(1)-C(12)	38.3(3)
C(15)-Rh(1)-C(12)	62.7(2)
C(14)-Rh(1)-C(12)	63.4(3)
C(11)-Rh(1)-C(12)	36.1(3)
C(1)-Rh(1)-Cl(1)	88.01(17)
N(1)-Rh(1)-Cl(1)	91.65(16)
C(13)-Rh(1)-Cl(1)	157.75(19)
C(15)-Rh(1)-Cl(1)	104.04(18)
C(14)-Rh(1)-Cl(1)	139.83(18)
C(11)-Rh(1)-Cl(1)	96.00(18)
C(12)-Rh(1)-Cl(1)	120.10(18)
C(2)-N(1)-C(4)	105.8(5)
C(2)-N(1)-Rh(1)	110.6(4)
C(4)-N(1)-Rh(1)	143.4(4)
C(2)-N(2)-C(3)	107.1(5)
C(2)-N(2)-H(2)	126.4
C(3)-N(2)-H(2)	126.4
C(1)-N(3)-C(2)	111.2(5)
N(3)-C(1)-C(5)	116.5(5)
N(3)-C(1)-Rh(1)	118.9(4)
C(5)-C(1)-Rh(1)	124.6(4)
N(1)-C(2)-N(2)	111.1(5)

N(1)-C(2)-N(3)	121.7(6)
N(2)-C(2)-N(3)	127.1(6)
C(4)-C(3)-N(2)	106.8(6)
C(4)-C(3)-H(3)	126.6
N(2)-C(3)-H(3)	126.6
C(3)-C(4)-N(1)	109.1(6)
C(3)-C(4)-H(4)	125.5
N(1)-C(4)-H(4)	125.5
C(10)-C(5)-C(6)	119.2(6)
C(10)-C(5)-C(1)	120.3(5)
C(6)-C(5)-C(1)	120.5(6)
C(7)-C(6)-C(5)	120.3(6)
C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(6)-C(7)-C(8)	120.1(6)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	119.9(6)
C(7)-C(8)-H(8)	120.0
C(9)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	119.9(6)
C(10)-C(9)-H(9)	120.0
C(8)-C(9)-H(9)	120.0
C(9)-C(10)-C(5)	120.5(6)
C(9)-C(10)-H(10)	119.7
C(5)-C(10)-H(10)	119.7
C(12)-C(11)-C(15)	108.2(6)
C(12)-C(11)-C(16)	127.6(6)
C(15)-C(11)-C(16)	124.1(6)
C(12)-C(11)-Rh(1)	72.2(4)
C(15)-C(11)-Rh(1)	67.2(3)
C(16)-C(11)-Rh(1)	125.7(5)
C(11)-C(12)-C(13)	106.9(6)
C(11)-C(12)-C(17)	127.4(7)
C(13)-C(12)-C(17)	125.7(6)
C(11)-C(12)-Rh(1)	71.7(4)
C(13)-C(12)-Rh(1)	65.3(4)
C(17)-C(12)-Rh(1)	126.5(5)
C(14)-C(13)-C(12)	109.4(6)
C(14)-C(13)-C(18)	126.1(6)
C(12)-C(13)-C(18)	124.1(6)
C(14)-C(13)-Rh(1)	72.5(4)
C(12)-C(13)-Rh(1)	76.4(4)
C(18)-C(13)-Rh(1)	123.5(5)
C(13)-C(14)-C(15)	106.7(6)
C(13)-C(14)-C(19)	126.1(6)
C(15)-C(14)-C(19)	127.2(6)
C(13)-C(14)-Rh(1)	69.0(4)
C(15)-C(14)-Rh(1)	70.7(4)
C(19)-C(14)-Rh(1)	125.4(5)
C(14)-C(15)-C(11)	108.3(6)
C(14)-C(15)-C(20)	127.0(6)
C(11)-C(15)-C(20)	124.0(6)
C(14)-C(15)-Rh(1)	70.9(4)
C(11)-C(15)-Rh(1)	74.7(4)
C(20)-C(15)-Rh(1)	128.2(5)

C(11)-C(16)-H(16A)	109.5
C(11)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(11)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(1)-C(21)-C(22)	109.0(18)
O(1)-C(21)-H(21A)	109.9
C(22)-C(21)-H(21A)	109.9
O(1)-C(21)-H(21B)	109.9
C(22)-C(21)-H(21B)	109.9
H(21A)-C(21)-H(21B)	108.3
C(21)-O(1)-C(24)	104(2)
C(21)-C(22)-C(23)	102.7(19)
C(21)-C(22)-H(22A)	111.2
C(23)-C(22)-H(22A)	111.2
C(21)-C(22)-H(22B)	111.2
C(23)-C(22)-H(22B)	111.2
H(22A)-C(22)-H(22B)	109.1
C(24)-C(23)-C(22)	103.8(19)
C(24)-C(23)-H(23A)	111.0
C(22)-C(23)-H(23A)	111.0
C(24)-C(23)-H(23B)	111.0
C(22)-C(23)-H(23B)	111.0
H(23A)-C(23)-H(23B)	109.0
O(1)-C(24)-C(23)	111(2)
O(1)-C(24)-H(24A)	109.4
C(23)-C(24)-H(24A)	109.4
O(1)-C(24)-H(24B)	109.4
C(23)-C(24)-H(24B)	109.4
H(24A)-C(24)-H(24B)	108.0

Symmetry transformations used to generate equivalent atoms:

Table S20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 007b-17101. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	22(1)	30(1)	30(1)	-1(1)	2(1)	0(1)
Cl(1)	34(1)	30(1)	32(1)	1(1)	5(1)	-2(1)
N(1)	22(3)	25(2)	38(3)	1(2)	3(2)	-1(2)
N(2)	19(3)	32(3)	48(3)	-1(2)	1(2)	-4(2)
N(3)	24(3)	30(3)	40(3)	0(2)	1(2)	1(2)
C(1)	27(3)	31(3)	27(3)	3(2)	3(2)	-2(3)
C(2)	25(3)	24(3)	41(4)	2(3)	5(3)	-2(2)
C(3)	29(4)	27(3)	43(4)	1(3)	1(3)	3(3)
C(4)	22(3)	30(3)	46(4)	1(3)	3(3)	2(3)
C(5)	25(3)	29(3)	28(3)	0(2)	-2(2)	-1(2)
C(6)	24(3)	33(3)	32(3)	2(3)	1(3)	1(3)
C(7)	30(3)	30(3)	37(3)	2(3)	-1(3)	-2(3)
C(8)	35(4)	29(3)	41(4)	-4(3)	-1(3)	8(3)
C(9)	27(3)	34(3)	38(4)	-1(3)	4(3)	4(3)
C(10)	25(3)	29(3)	39(4)	2(3)	1(3)	1(3)
C(11)	25(3)	44(4)	31(3)	-4(3)	-7(3)	-3(3)
C(12)	33(4)	39(3)	25(3)	-8(3)	-5(3)	-2(3)
C(13)	26(3)	44(4)	30(3)	0(3)	1(3)	-2(3)
C(14)	26(3)	44(4)	28(3)	3(3)	-1(3)	0(3)
C(15)	25(3)	39(3)	27(3)	0(3)	-4(3)	0(3)
C(16)	34(4)	43(4)	48(4)	2(3)	-4(3)	-11(3)
C(17)	48(5)	44(4)	37(4)	-10(3)	-4(3)	6(3)
C(18)	32(4)	59(5)	31(4)	-2(3)	6(3)	3(3)
C(19)	39(4)	37(4)	35(4)	6(3)	-1(3)	-4(3)
C(20)	26(3)	50(4)	38(4)	0(3)	3(3)	5(3)
C(21)	64(10)	61(10)	107(15)	-49(11)	6(9)	21(8)
O(1)	84(11)	117(13)	163(18)	-47(12)	10(10)	12(9)
C(22)	95(16)	78(15)	113(17)	-53(15)	-2(15)	35(16)
C(23)	84(13)	54(8)	88(16)	-17(8)	24(13)	18(10)
C(24)	120(20)	130(20)	180(30)	-70(20)	-40(20)	54(17)

Table S21. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^{\ 3}$) for 007b-17101.

	x	y	z	U(eq)
H(2)	4762	6348	5219	40
H(3)	4680	8870	5656	40
H(4)	5449	9687	6111	39
H(6)	5850	2513	5744	35
H(7)	6230	468	5295	39
H(8)	6899	669	4502	42
H(9)	7208	2930	4231	39
H(10)	6844	4975	4733	37
H(16A)	7307	8895	5785	62
H(16B)	7525	9211	6757	62
H(16C)	7101	10128	6392	62

H(17A)	6457	10554	7081	65
H(17B)	6416	10077	8101	65
H(17C)	6004	9798	7403	65
H(18A)	5680	7562	7804	61
H(18B)	5977	6984	8640	61
H(18C)	5782	5889	7903	61
H(19A)	6254	4097	7349	56
H(19B)	6681	4171	8034	56
H(19C)	6754	3803	7006	56
H(20A)	7328	4850	6289	57
H(20B)	7648	5979	6806	57
H(20C)	7465	6309	5810	57
H(21A)	5483	1919	6675	93
H(21B)	5371	588	7307	93
H(22A)	5647	2919	7983	115
H(22B)	5281	1966	8495	115
H(23A)	4832	3850	8327	90
H(23B)	5129	4500	7539	90
H(24A)	4378	2886	7365	175
H(24B)	4657	3606	6583	175

Table S22. Torsion angles [°] for 007b-17101.

C(2)-N(3)-C(1)-C(5)	-176.2(5)
C(2)-N(3)-C(1)-Rh(1)	3.3(7)
C(4)-N(1)-C(2)-N(2)	-0.2(8)
Rh(1)-N(1)-C(2)-N(2)	176.3(4)
C(4)-N(1)-C(2)-N(3)	177.7(6)
Rh(1)-N(1)-C(2)-N(3)	-5.8(8)
C(3)-N(2)-C(2)-N(1)	0.1(8)
C(3)-N(2)-C(2)-N(3)	-177.7(6)
C(1)-N(3)-C(2)-N(1)	2.0(9)
C(1)-N(3)-C(2)-N(2)	179.6(6)
C(2)-N(2)-C(3)-C(4)	0.0(8)
N(2)-C(3)-C(4)-N(1)	-0.1(8)
C(2)-N(1)-C(4)-C(3)	0.2(8)
Rh(1)-N(1)-C(4)-C(3)	-174.2(6)
N(3)-C(1)-C(5)-C(10)	134.6(6)
Rh(1)-C(1)-C(5)-C(10)	-44.9(8)
N(3)-C(1)-C(5)-C(6)	-42.4(8)
Rh(1)-C(1)-C(5)-C(6)	138.1(5)
C(10)-C(5)-C(6)-C(7)	-1.1(9)
C(1)-C(5)-C(6)-C(7)	175.9(6)
C(5)-C(6)-C(7)-C(8)	-1.1(10)
C(6)-C(7)-C(8)-C(9)	2.0(10)
C(7)-C(8)-C(9)-C(10)	-0.6(10)
C(8)-C(9)-C(10)-C(5)	-1.7(10)
C(6)-C(5)-C(10)-C(9)	2.6(10)
C(1)-C(5)-C(10)-C(9)	-174.5(6)
C(15)-C(11)-C(12)-C(13)	-1.8(7)
C(16)-C(11)-C(12)-C(13)	177.8(6)
Rh(1)-C(11)-C(12)-C(13)	56.0(4)
C(15)-C(11)-C(12)-C(17)	179.9(6)
C(16)-C(11)-C(12)-C(17)	-0.5(11)
Rh(1)-C(11)-C(12)-C(17)	-122.4(7)

C(15)-C(11)-C(12)-Rh(1)	-57.7(4)
C(16)-C(11)-C(12)-Rh(1)	121.8(7)
C(11)-C(12)-C(13)-C(14)	5.6(7)
C(17)-C(12)-C(13)-C(14)	-176.0(6)
Rh(1)-C(12)-C(13)-C(14)	65.6(5)
C(11)-C(12)-C(13)-C(18)	178.6(6)
C(17)-C(12)-C(13)-C(18)	-3.0(11)
Rh(1)-C(12)-C(13)-C(18)	-121.4(7)
C(11)-C(12)-C(13)-Rh(1)	-60.0(5)
C(17)-C(12)-C(13)-Rh(1)	118.4(6)
C(12)-C(13)-C(14)-C(15)	-7.2(7)
C(18)-C(13)-C(14)-C(15)	-180.0(6)
Rh(1)-C(13)-C(14)-C(15)	61.0(4)
C(12)-C(13)-C(14)-C(19)	172.7(6)
C(18)-C(13)-C(14)-C(19)	-0.1(11)
Rh(1)-C(13)-C(14)-C(19)	-119.2(7)
C(12)-C(13)-C(14)-Rh(1)	-68.2(5)
C(18)-C(13)-C(14)-Rh(1)	119.1(7)
C(13)-C(14)-C(15)-C(11)	6.0(7)
C(19)-C(14)-C(15)-C(11)	-173.8(6)
Rh(1)-C(14)-C(15)-C(11)	65.9(4)
C(13)-C(14)-C(15)-C(20)	176.1(6)
C(19)-C(14)-C(15)-C(20)	-3.8(11)
Rh(1)-C(14)-C(15)-C(20)	-124.0(6)
C(13)-C(14)-C(15)-Rh(1)	-59.9(4)
C(19)-C(14)-C(15)-Rh(1)	120.2(7)
C(12)-C(11)-C(15)-C(14)	-2.6(7)
C(16)-C(11)-C(15)-C(14)	177.8(6)
Rh(1)-C(11)-C(15)-C(14)	-63.5(4)
C(12)-C(11)-C(15)-C(20)	-173.1(6)
C(16)-C(11)-C(15)-C(20)	7.3(10)
Rh(1)-C(11)-C(15)-C(20)	126.1(6)
C(12)-C(11)-C(15)-Rh(1)	60.8(5)
C(16)-C(11)-C(15)-Rh(1)	-118.7(6)
C(22)-C(21)-O(1)-C(24)	29(4)
O(1)-C(21)-C(22)-C(23)	-30(4)
C(21)-C(22)-C(23)-C(24)	19(5)
C(21)-O(1)-C(24)-C(23)	-16(5)
C(22)-C(23)-C(24)-O(1)	-3(6)

Symmetry transformations used to generate equivalent atoms:

Table S23. Hydrogen bonds for 007b-17101 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...N(3)#1	0.88	2.01	2.871(7)	165.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

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