Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rh(III)-catalyzed Switchable C–H Monoalkenylation and Dialkenylation of 2-(1*H*-Pyrazol-1-yl)Pyridine with Alkenes *via* Rollover Cyclometalation

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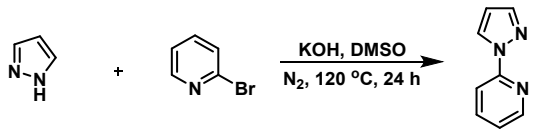
General information:

The ^{1}H NMR, ^{19}F NMR, ^{31}P NMR and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$ or DMSO-d_6. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) or DMSO-d_6 (δ = 2.50 and 39.50) as internal standards All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates. Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

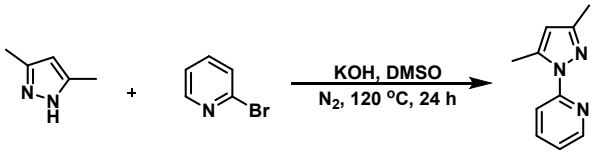
Preparation of Starting Materials:

General Procedure 1:



SI-1 SI-2 1

A 100ml two-necked flask was charged with the pyrazole (**SI-1**,0.05 mol), KOH (0.125 mol, 7.0 g), 2-bromopyridine (**SI-2**，0.05 mol), and dry DMSO (20.0 mL) under nitrogen atmosphere. The resulting mixture was stirred in an oil bath at 120 °C until the end of the reaction. The mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The organic phase was dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel (decreasing hexane/ethyl acetate ratio) and then get yellow soild product **1**.

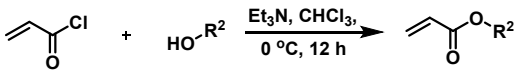


SI-1' SI-2 1'

A 100 ml two-necked flask was charged with the pyrazole (**SI-1'**, 0.05 mol), KOH

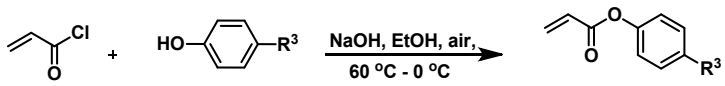
(0.125 mol, 7.0 g), 2-bromopyridine (**SI-2**, 0.05 mol), and dry DMSO (20.0 mL) under nitrogen atmosphere. The resulting mixture was stirred in an oil bath at 120 °C until the end of the reaction. The mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The organic phase was dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel (decreasing hexane/ethyl acetate ratio) and then get yellow oil product **1'**.

General Procedure 2:



SII-1 **SII-2** **2g, 2h, 2m**

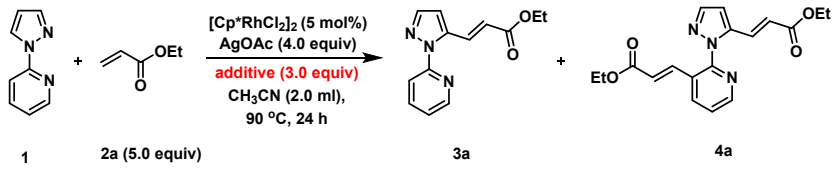
A mixture of Et_3N (3.0 equiv) and **SII-2** (1.0 equiv) in $CHCl_3$ (0.005 mol/15 mL) was stirred at 0 °C for 10 min. Then **SII-1** (1.1 equiv) was added drop wise to the reaction mixture. The reaction was stirred at 0 °C for 12 h until the starting material was disappeared. The mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash column chromatography to give **2g, 2h, 2m**.



SII-1 **SII-3** **2j-2l**

A mixture of NaOH (1.0 equiv) and **SII-3** (1.0 equiv) in EtOH (0.01 mol/20 mL) was stirred at 60 °C for 30 min. Then **SII-1** (1.1 equiv) was added drop wise to the reaction mixture at 0 °C for 1.5 h until the starting material was disappeared. The mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash column chromatography to give **2j-2l**.

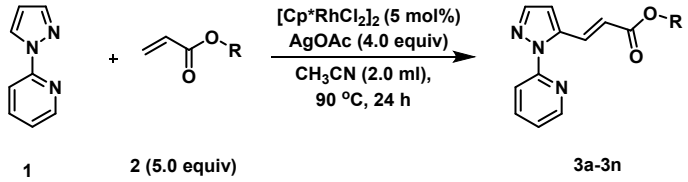
Optimization of Reaction Conditions:



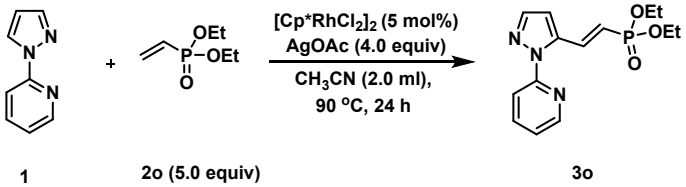
additive = HCOOH, 3a, 80%; 4a, 0%; additive = CF_3COOH, 3a, 64%; 4a, 0%
additive = Ph-COOH, 3a, 45%; 4a, 53%; additive = HOAc, 3a, 0%; 4a, 89%
additive = NaOAc, 3a, 39%; 4a, 0%; additive = KOAc, 3a, 20%; 4a, 0%
additive = $Cu(OAc)_2$, 3a, 0%; 4a, 0%

In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), **2a** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), additive (0.6 mmol, 3.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 °C for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the products **3a** and **4a**.

General Procedure for the Synthesis of 3 and 4:

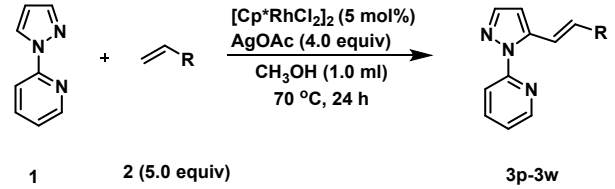


In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), **2** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 °C for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the products **3a-3n**.

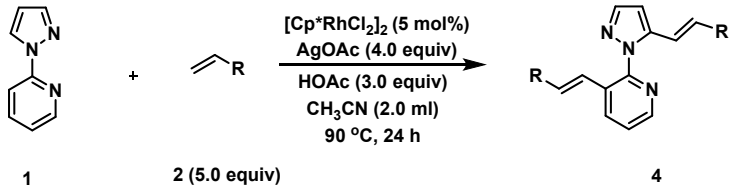


In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), **2o** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 °C for 24 h. When the reaction was finished, the

mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the product **3o**.

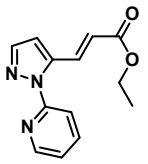


In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), **2** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeOH (1.0 mL).The reaction mixture was heated to 70 °C for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the products **3p-3w**.



In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), **2** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), HOAc (36.0 mg, 0.6 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 °C for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the products **4**.

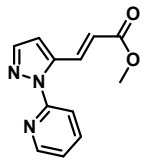
Characterization of Products:



ethyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3a**)

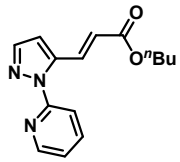
Yellow oil (43 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.8 Hz, 1H), 8.46 (d, *J* = 16.0 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.77 (d, *J*

= 1.6 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 152.8, 147.9, 140.9, 139.5, 138.7, 133.2, 122.1, 120.7, 116.8, 108.0, 60.6, 14.2. **ESI-MS**: Calcd for $C_{13}H_{13}N_3O_2$: [M+H$^+$] 244.1086, found 244.1091.



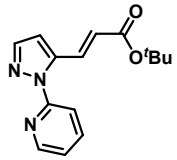
methyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3b**)

Gray solid (36 mg, 79%); **M.P.**: 88 - 90 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.4 Hz, 1H), 8.39 (d, *J* = 16.0 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.61 (s, 1H), 7.22 – 7.18 (m, 1H), 6.69 (s, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 152.8, 147.9, 140.9, 139.4, 138.8, 133.4, 122.1, 120.2, 116.8, 108.1, 51.8. **ESI-MS**: Calcd for $C_{12}H_{11}N_3O_2$: [M+H$^+$] 230.0893, found 230.0896.



butyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3c**)

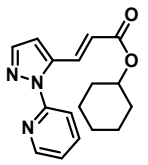
Yellow oil (34 mg, 63%); **M.P.**: 54 - 56 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.8 Hz, 1H), 8.47 (d, *J* = 16.0 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.69 (d, *J* = 1.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.77 (d, *J* = 1.6 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.49 – 1.39 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 152.8, 147.9, 140.9, 139.5, 138.7, 133.2, 122.1, 120.7, 116.8, 108.0, 64.5, 30.7, 19.1, 13.7. **ESI-MS**: Calcd for $C_{15}H_{17}N_3O_2$: [M+H$^+$] 272.1399, found 272.1410.



tert-butyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3d**)

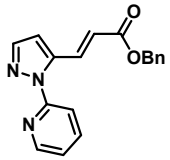
Yellow oil (39 mg, 72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.4 Hz, 1H), 8.32 (d, *J* = 16.0 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8,

152.8, 147.9, 140.9, 139.6, 138.7, 132.1, 122.6, 122.1, 116.9, 107.8, 80.7, 28.1. **ESI-MS**: Calcd for $C_{15}H_{17}N_3O_2$: [M+H$^+$] 272.1399, found 272.1405.



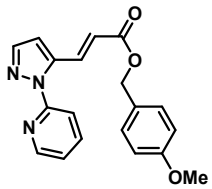
cyclohexyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3e**)

Gray solid (44 mg, 74%); **M.P.**: 109-111 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.4 Hz, 1H), 8.46 (d, *J* = 16.0 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.75 (d, *J* = 1.6 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.92 – 4.85 (m, 1H), 1.90 – 1.84 (m, 2H), 1.77 – 1.73 (m, 2H), 1.57 – 1.28 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 152.8, 147.8, 140.9, 139.5, 138.7, 132.9, 122.0, 121.2, 116.7, 107.9, 72.7, 31.5, 25.3, 23.6. **ESI-MS**: Calcd for $C_{17}H_{19}N_3O_2$: [M+H$^+$] 298.1555, found 298.1566.



benzyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3f**)

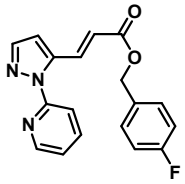
Yellow oil (48 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 16.0 Hz, 1H), 8.51 – 8.46 (m, 1H), 7.89 – 7.82 (m, 2H), 7.68 – 7.66 (m, 1H), 7.43 – 7.32 (m, 5H), 7.26 – 7.22 (m, 1H), 6.75 (d, *J* = 1.6 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.25 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 152.9, 147.9, 141.0, 139.5, 138.8, 136.0, 133.9, 128.6, 128.2, 128.2, 122.1, 120.3, 116.8, 108.2, 66.4. **ESI-MS**: Calcd for $C_{18}H_{15}N_3O_2$: [M+H$^+$] 306.1242, found 306.1249.



4-methoxybenzyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3g**)

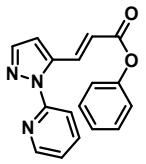
Yellow oil (59 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 – 8.48 (m, 2H), 7.89 – 7.82 (m, 2H), 7.67 (d, *J* = 1.2 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.18 (s, 2H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 159.6, 152.8, 147.9, 140.9, 139.5, 138.7, 133.7, 130.0,

128.0, 122.1, 120.4, 116.7, 113.9, 108.1, 66.2, 55.2. **ESI-MS**: Calcd for $C_{19}H_{17}N_3O_3$: [M+H$^+$] 336.1348, found 336.1350.



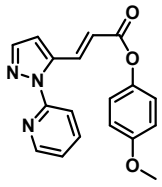
4-fluorobenzyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3h**)

Yellow oil (55 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.38 (m, 2H), 7.76 (dd, *J* = 16.4, 15.6 Hz, 2H), 7.57 (s, 1H), 7.29 (s, 2H), 7.15 (s, 1H), 6.95 (t, *J* = 8.4 Hz, 2H), 6.66 (s, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 5.11 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 163.7, 161.3, 152.7, 147.7, 140.9, 139.3, 133.9, 131.7 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 9.0 Hz), 122.0, 119.9, 116.6, 115.4 (d, *J* = 21.0 Hz), 108.1 (d, *J* = 3.0 Hz), 65.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.56. **ESI-MS**: Calcd for $C_{18}H_{14}FN_3O_2$: [M+H$^+$] 323.3274, found 323.3279.



phenyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3i**)

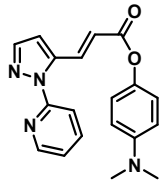
Yellow solid (41 mg, 70%); **M.P.**: 103-104 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 16.0 Hz, 1H), 8.42 (d, *J* = 4.0 Hz, 1H), 7.84 – 7.74 (m, 2H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.20 – 7.14 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 1.2 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 152.8, 150.8, 147.9, 141.1, 139.3, 138.8, 135.1, 129.4, 125.8, 122.2, 121.6, 119.7, 116.8, 108.5 (d, *J* = 2.0 Hz). **ESI-MS**: Calcd for $C_{17}H_{13}N_3O_2$: [M+H$^+$] 292.1086, found 292.1090.



4-methoxyphenyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3j**)

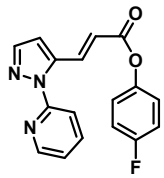
White solid (51 mg, 80%); **M.P.**: 103-105 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 16.0 Hz, 1H), 8.41 (d, *J* = 4.4 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.62 (s,1H), 7.18 – 7.14 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.74 (s, 1H), 6.49 (d, *J* = 16.0 Hz, 1H),

3.70 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 157.1, 152.7, 147.8, 144.1, 141.0, 139.2, 138.7, 134.8, 122.2, 122.1, 119.6, 116.7, 114.3, 108.4, 55.5. **ESI-MS**: Calcd for $C_{18}H_{15}N_3O_3$: [M+H$^+$] 322.1191, found 322.1196.



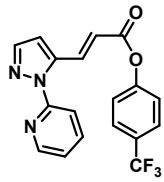
4-(dimethylamino)phenyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3k**)

Gray solid (48 mg, 72%); **M.P.**: 128-129 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 16.0 Hz, 1H), 8.49 (d, *J* = 4.4 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.69 (d, *J* = 1.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.01 (d, *J* = 9.2 Hz, 2H), 6.81 (d, *J* = 1.2 Hz, 1H), 6.71 (d, *J* = 9.2 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 2.92 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 152.8, 148.7, 148.0, 141.5, 141.0, 139.4, 138.8, 134.5, 122.2, 121.8, 120.1, 116.8, 113.1, 108.4, 40.9. **ESI-MS**: Calcd for $C_{19}H_{18}N_4O_2$: [M+H$^+$] 335.1508, found 335.1515.



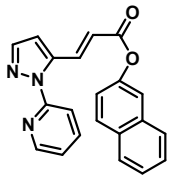
4-fluorophenyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3l**)

Pink solid (45 mg, 73%); **M.P.**: 92-94 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 16.4 Hz, 1H), 8.50 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.15 – 7.05 (m, 4H), 6.84 (d, *J* = 1.6 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 161.4, 159.0, 152.7, 147.8, 146.5, 146.5, 141.0, 139.1, 138.8, 135.4, 122.3 (d, *J* = 9.0 Hz), 122.2, 119.2, 116.7, 116.0 (d, *J* = 24.0 Hz), 108.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.92. **ESI-MS**: Calcd for $C_{17}H_{12}FN_3O_2$: [M+H$^+$] 310.0992, found 310.0996.



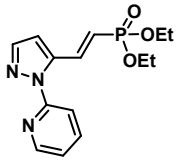
4-(trifluoromethyl)phenyl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3m**)

Yellow solid (40 mg, 56%); **M.P.**: 120-122 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 16.0 Hz, 1H), 8.52 (s, 1H), 7.95 – 7.85 (m, 2H), 7.73 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.26 (m, 3H), 6.86 (s, 1H), 6.59 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 153.2, 152.7, 147.9, 141.1, 139.0, 138.9, 135.9, 128.0 (q, *J* = 33.0 Hz), 126.8 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 270.0 Hz), 122.3, 122.1, 118.8, 116.7, 108.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.14. **ESI-MS**: Calcd for $C_{18}H_{12}F_3N_3O_2$: [M+H$^+$] 360.0960, found 360.0964.



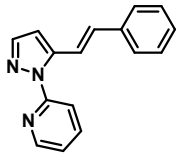
naphthalen-2-yl (E)-3-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)acrylate (**3n**)

White solid (64 mg, 94%); **M.P.**: 102-104 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 16.0 Hz, 1H), 8.53 (d, *J* = 4.4 Hz, 1H), 7.73 – 7.87 (m, 5H), 7.74 (d, *J* = 1.2 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.26 – 7.19 (m, 2H), 6.88 (d, *J* = 1.6 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 152.8, 148.3, 147.9, 141.1, 139.2, 138.8, 135.2, 133.7, 131.4, 129.4, 127.7, 127.6, 126.5, 125.7, 122.2, 121.1, 119.6, 118.5, 116.7, 108.6. **ESI-MS**: Calcd for $C_{21}H_{15}N_3O_2$: [M+H$^+$] 342.1242, found 342.1251.



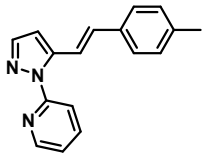
diethyl (E)-(2-(1-(pyridin-2-yl)-1H-pyrazol-5-yl)vinyl)phosphonate (**3o**)

Yellow oil (44 mg, 71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.4 Hz, 1H), 8.26 (dd, *J* = 17.6, 22.4 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.72 (d, *J* = 1.6 Hz, 1H), 6.20 (t, *J* = 18.0 Hz, 1H), 4.17 – 4.10 (m, 4H), 1.34 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.8, 147.8, 140.8, 140.2 (d, *J* = 30.0 Hz), 138.7, 137.0 (d, *J* = 9.0 Hz), 122.1,117.7, 116.6, 115.8, 107.9 (d, *J* = 6.0 Hz) , 62.0 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 4.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.07. **ESI-MS**: Calcd for $C_{14}H_{18}N_3O_3P$: [M+H$^+$] 308.1164, found 308.1164.



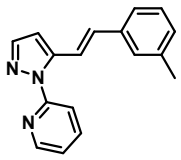
(E)-2-(5-styryl-1H-pyrazol-1-yl)pyridine (**3p**)

Yellow oil (40 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 – 8.43 (m, 1H), 7.87 (d, *J* = 16.4 Hz, 1H), 7.82 – 7.73 (m, 2H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.21 – 7.13 (m, 2H), 7.02 (d, *J* = 16.4 Hz, 1H), 6.62 (d, *J* = 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 147.8, 142.6, 141.0, 138.6, 136.9, 131.9, 128.7, 128.1, 126.8, 121.7, 118.0, 117.1, 105.5. **ESI-MS**: Calcd for $C_{16}H_{13}N_3$: [M+H$^+$] 248.1187, found 248.1191.



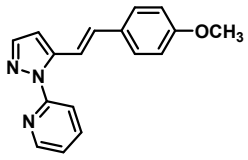
(E)-2-(5-(4-methylstyryl)-1H-pyrazol-1-yl)pyridine (**3q**)

Yellow oil (36 mg, 68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (dd, J = 4.8, 1.2 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.84 – 7.79 (m, 1H), 7.68 (d, J = 1.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 16.4 Hz, 1H), 6.70 (d, J = 1.6 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 147.6, 142.6, 140.8, 138.4, 137.9, 134.0, 131.7, 129.2, 126.6, 121.5, 116.9, 116.8, 105.1, 21.1. **ESI-MS:** Calcd for $C_{17}H_{15}N_3$: [M+H$^+$] 262.1344, found 262.1353.



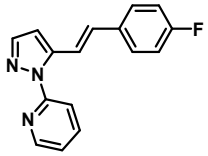
(E)-2-(5-(3-methylstyryl)-1H-pyrazol-1-yl)pyridine (**3r**)

Yellow oil (35 mg, 67%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.44 (m, 1H), 7.85 – 7.75 (m, 3H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.19 – 7.14 (m, 2H), 6.99 (d, *J* = 16.4 Hz, 2H), 6.61 (d, *J* = 1.6 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 147.8, 142.6, 140.9, 138.5, 138.2, 136.8, 132.0, 128.9, 128.5, 127.5, 123.9, 121.7, 117.6, 117.1, 105.4, 21.4. **ESI-MS**: Calcd for $C_{17}H_{15}N_3$: [M+H$^+$] 262.1344, found 262.1346.



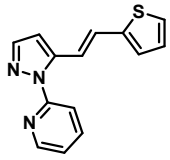
(E)-2-(5-(4-methoxystyryl)-1H-pyrazol-1-yl)pyridine (**3s**)

Yellow oil (34 mg, 61%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H), 7.92 – 7.81 (m, 3H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.08 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 2.0 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 153.5, 147.7, 142.9, 140.9, 138.5, 131.5, 129.7, 128.1, 121.6, 117.1, 115.7, 114.1, 105.0, 105.0, 55.3, 55.2. **ESI-MS**: Calcd for $C_{17}H_{15}N_3O$: [M+H$^+$] 278.1293, found 278.1295.



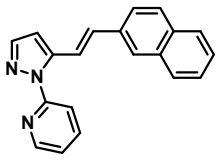
(E)-2-(5-(4-fluorostyryl)-1H-pyrazol-1-yl)pyridine (**3t**)

Yellow oil (32 mg, 61%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.39 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.00 – 6.94 (m, 3H), 6.61 (d, *J* = 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 153.4, 147.7, 142.3, 140.9, 138.6, 133.1 (d, *J* = 4.0 Hz), 130.6, 128.3 (d, *J* = 8.0 Hz), 121.7, 117.7 (d, *J* = 3.0 Hz), 117.1, 115.6 (d, *J* = 22.0 Hz), 105.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.35. **ESI-MS**: Calcd for $C_{16}H_{12}FN_3$: [M+H$^+$] 266.1093, found 266.1097.



(E)-2-(5-(2-(thiophen-2-yl)vinyl)-1H-pyrazol-1-yl)pyridine (**3u**)

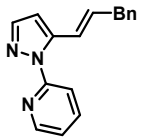
Yellow oil (23 mg, 46%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.0 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.61 – 7.56 (m, 1H), 7.48 (s, 1H), 7.05 – 6.97 (m, 3H), 6.90 (d, *J* = 3.2 Hz, 1H), 6.81 – 6.78 (m, 1H), 6.48 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 147.3, 142.0, 141.8, 140.6, 138.2, 127.4, 126.5, 124.8, 124.4, 121.3, 117.1, 116.5, 105.2. **ESI-MS**: Calcd for $C_{14}H_{11}N_3S$: [M+H$^+$] 254.0752, found 254.0756.



(E)-2-(5-(2-(naphthalen-2-yl)vinyl)-1H-pyrazol-1-yl)pyridine (**3v**)

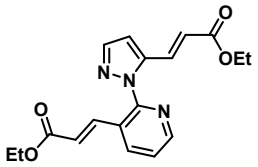
Yellow oil (33 mg, 55%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 16.0 Hz, 1H), 8.44 (d, *J* = 4.4 Hz, 1H), 7.86 – 7.72 (m, 5H), 7.65 (d, *J* = 1.2 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.44

– 7.37 (m, 2H), 7.25 – 7.17 (m, 2H), 6.79 (d, *J* = 1.6 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 163.7, 161.3, 152.7, 147.7, 140.9, 139.2, 138.7, 133.9, 131.7, 131.7, 130.1, 130.0, 122.0, 119.9, 116.6, 115.5, 115.2, 108.1, 108.1, 65.6. **ESI-MS**: Calcd for $C_{20}H_{15}N_3$: [M+H$^+$] 298.1344, found 298.1351.



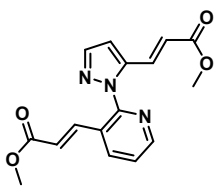
(E)-2-(5-(3-phenylprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridine (**3w**)

Yellow oil (24 mg, 45%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.0 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.53 (s, 1H), 7.25 – 7.06 (m, 7H), 6.41 – 6.24 (m, 2H), 6.18 (s, 1H), 4.01 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 147.4, 143.2, 140.6, 138.3, 137.3, 131.9, 128.4, 127.2, 126.4, 126.1, 121.3, 116.2, 108.1, 108.0, 31.7. **ESI-MS**: Calcd for $C_{17}H_{15}N_3$: [M+H$^+$] 262.1344, found 262.1345.



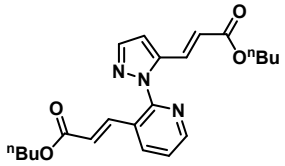
ethyl (E)-3-(2-(5-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4a**)

Yellow soild (61 mg, 89%); **M.P.**: 114-115 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 1.6, 4.8 Hz, 1H), 8.10 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 6.4 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 6.80 (d, *J* = 1.6 Hz, 1H), 6.38 (d, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 7.2 Hz, 1H), 4.23 – 4.16 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 165.7, 149.6, 149.5, 141.2, 140.0, 138.2, 136.8, 130.5, 127.0, 124.1, 122.1, 121.0, 107.0, 60.6, 14.1. **ESI-MS**: Calcd for $C_{18}H_{19}N_3O_4$: [M+H$^+$] 342.1454, found 342.1454.



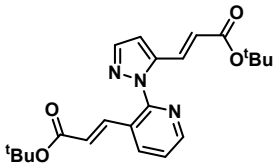
methyl (E)-3-(2-(5-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4b**)

Gray soild (46 mg, 73%); **M.P.**: 143-144 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 4.4, 1.2 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 5.6 Hz, 1H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.47 – 7.43 (m, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.39 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 7.1 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 166.2, 149.7, 149.6, 141.3, 139.9, 138.6, 136.9, 130.8, 126.9, 124.1, 121.6, 120.5, 107.2, 107.1, 51.8. **ESI-MS**: Calcd for $C_{16}H_{15}N_3O_4$: [M+H$^+$] 314.1141, found 314.1140.



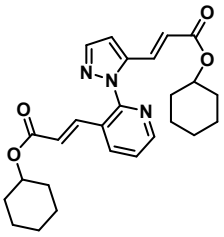
butyl (E)-3-(2-(5-((E)-3-butoxy-3-oxoprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4c**)

Colorless oil (65 mg, 82%); **M.P.**: 118-120 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.52 (d, *J* = 9.2 Hz, 1H), 7.44 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.80 (d, *J* = 1.6 Hz, 1H), 6.39 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.16 – 4.12 (m, 4H), 1.66 – 1.58 (m, 4H), 1.42 – 1.32 (m, 4H), 0.94 – 0.89 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 165.8,149.6, 149.5, 141.2, 140.0, 138.2, 136.7, 130.5, 126.9, 124.1, 122.0, 120.9, 106.9, 64.5, 30.5, 19.0, 13.5. **ESI-MS**: Calcd for $C_{22}H_{27}N_3O_4$: [M+H$^+$] 398.2080, found 398.2080.



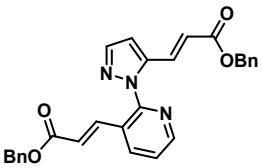
tert-butyl (E)-3-(2-(5-((E)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4d**)

Yellow soild (69 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.71 (d, *J* = 1.2 Hz, 1H), 7.46 – 7.37 (m, 3H), 6.76 (d, *J* = 2.0 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 6.28 (d, *J* = 10.0 Hz, 1H), 1.45 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 165.0, 149.6, 149.4, 141.1, 140.1, 137.1, 136.5, 129.5, 127.2, 124.1, 124.0, 122.8, 106.6, 80.8, 27.9. **ESI-MS**: Calcd for $C_{22}H_{27}N_3O_4$: [M+H$^+$] 398.2080, found 398.2074.



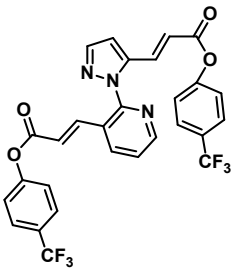
cyclohexyl(E)-3-(2-(5-((E)-3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4e**)

Yellow oil (78 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.11 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.44 (dd, *J* = 8.0, 4.2 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 6.39 (d, *J* = 9.2 Hz, 1H), 6.35 (d, *J* = 9.2 Hz, 1H), 4.87 – 4.78 (m, 2H), 1.86 – 1.81 (m, 4H), 1.71 – 1.68 (m, 4H), 1.51 – 1.34 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 165.2, 149.6, 149.5, 141.2, 140.1, 138.0, 136.7, 130.3, 127.1, 124.1, 122.7, 121.6, 106.9, 72.9, 31.5, 25.2, 23.5. **ESI-MS**: Calcd for $C_{26}H_{31}N_3O_4$: [M+H$^+$] 450.2393, found 450.2398.



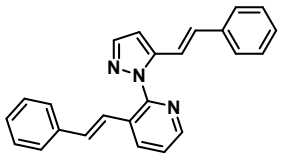
benzyl (E)-3-(2-(5-((E)-3-(benzyloxy)-3-oxoprop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4f**)

Yellow oil (63 mg, 68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.43 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.38 – 7.32 (m, 10H), 6.82 (d, *J* = 1.6 Hz, 1H), 6.46 (d, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 6.8 Hz, 1H), 5.21 (d, *J* = 2.4 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.6, 149.6, 141.3, 139.9, 138.9, 136.8, 135.7, 135.6, 131.2, 128.4, 128.2, 128.1, 128.0, 126.8, 124.1, 121.6, 120.5, 107.2, 66.4. **ESI-MS**: Calcd for $C_{28}H_{23}N_3O_4$: [M+H$^+$] 466.1767, found 466.1763.



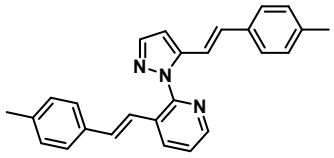
4-(trifluoromethyl)phenyl (E)-3-(2-(5-((E)-3-oxo-3-(4-(trifluoromethyl)phenoxy)prop-1-en-1-yl)-1H-pyrazol-1-yl)pyridin-3-yl)acrylate (**4m**)

Yellow soild (42 mg, 37%); **M.P.**: 152-154 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.83 (d, *J* = 4.7 Hz, 1H), 7.80 (d, *J* = 4.8 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.62 – 7.58 (m, 4H), 7.45 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.22 – 7.18 (m, 4H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.56 (d, *J* = 6.8 Hz, 1H), 6.52 (d, *J* = 6.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 163.8, 153.1, 150.1, 149.9, 141.7, 141.4, 139.8, 137.3, 133.4, 128.4 (d, *J* = 2.0 Hz), 128.1 (d, *J* = 3.0 Hz), 126.8 (q, *J* = 4.0 Hz), 126.4, 124.2, 123.8 (q, *J* = 270.0 Hz), 122.0, 120.0 (d, *J* = 104.0 Hz), 108.1 (d, *J* = 5.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.23. **ESI-MS**: Calcd for $C_{28}H_{17}F_6N_3O_4$: [M+H$^+$] 574.1201, found 574.1199.



3-((E)-styryl)-2-(5-((E)-styryl)-1H-pyrazol-1-yl)pyridine (**4p**)

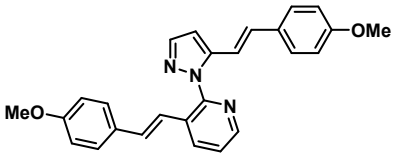
Yellow oil (49 mg, 70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.35 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.30 – 7.12 (m, 10H), 7.00 (d, *J* = 5.6 Hz, 1H), 6.96 (d, *J* = 5.6 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.2, 147.4, 142.6, 140.7, 136.4, 136.3, 135.2, 132.6, 132.1, 130.3, 128.6, 128.5, 128.3, 128.1, 126.8, 126.5, 124.2, 122.1, 115.3, 103.6. **ESI-MS**: Calcd for $C_{24}H_{19}N_3$: [M+H$^+$] 350.1657, found 350.1657.



3-((E)-4-methylstyryl)-2-(5-((E)-4-methylstyryl)-1H-pyrazol-1-yl)pyridine (**4q**)

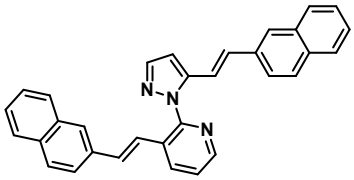
Yellow soild (50 mg, 66%); **M.P.**: 129-131ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.15 (dd, *J* = 13.2, 8.0 Hz, 4H), 7.02 – 6.95 (m, 5H), 6.92 (d, *J* = 6.4 Hz, 1H), 6.74 (d, *J* = 6.4 Hz, 1H), 6.70 (d, *J* = 6.4 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 2.22 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 147.2, 142.8, 140.7, 138.3, 138.1, 135.0,

133.8, 133.7, 132.6, 132.2, 130.6, 129.3, 129.2, 126.7, 126.5, 124.2, 121.0, 114.4, 103.3, 21.2. **ESI-MS**: Calcd for $C_{26}H_{23}N_3$: [M+H$^+$] 378.1970, found 378.1970.



3-((E)-4-methoxystyryl)-2-(5-((E)-4-methoxystyryl)-1H-pyrazol-1-yl)pyridine (**4s**)

White soild (58 mg, 71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.23 – 7.16 (m, 4H), 6.94 (d, *J* = 6.0 Hz, 1H), 6.90 (d, *J* = 5.6 Hz, 1H), 6.75 – 6.70 (m, 4H), 6.64 (d, *J* = 5.2 Hz, 1H), 6.61 – 6.59 (m, 2H), 3.68 (s, 3H), 3.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 159.6, 149.0, 147.0, 143.0, 140.7, 134.8, 132.2, 131.7, 130.7, 129.3, 129.2, 128.1, 127.8, 124.2, 119.8, 114.0, 113.2, 103.0, 55.2. **ESI-MS**: Calcd for $C_{26}H_{23}N_3O_2$: [M+H$^+$] 410.1868, found 410.1872.

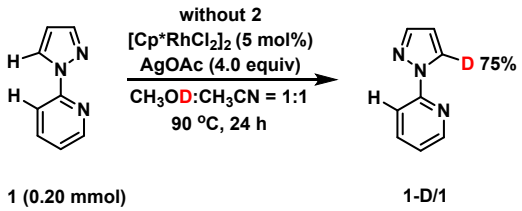


3-((E)-2-(naphthalen-2-yl)vinyl)-2-(5-((E)-2-(naphthalen-2-yl)vinyl)-1H-pyrazol-1-yl)pyridine (**4v**)

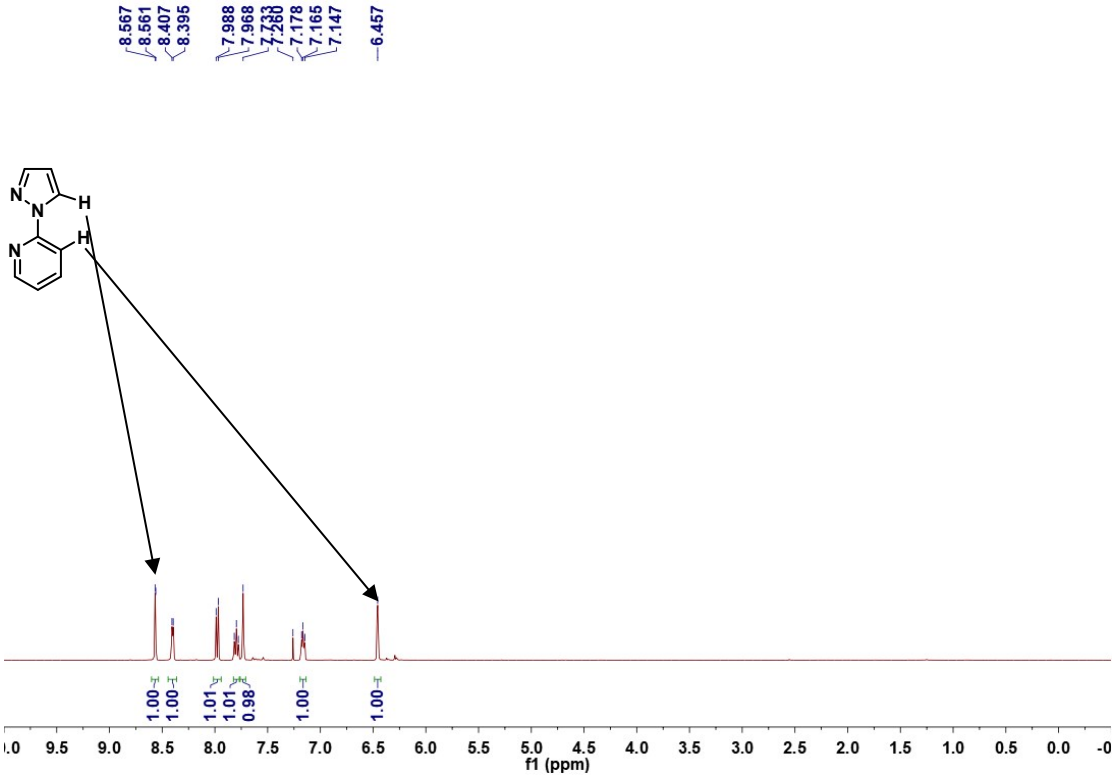
White soild (45 mg, 45%); **M.P.**: 86-87 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.69 (d, *J* = 1.6 Hz, 1H) 7.67 – 7.58 (m, 8H), 7.44 – 7.36 (m, 3H), 7.34 – 7.29 (m, 4H) 7.18 (d, *J* = 5.2 Hz, 1H), 7.14 (d, *J* = 5.6 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.93 (d, *J* = 9.2 Hz, 1H), 6.73 (d, *J* = 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 147.6, 142.9, 140.9, 135.3, 134.1, 134.0, 133.4, 133.4, 133.3, 133.2, 132.8, 132.3, 130.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.4, 126.3, 126.2, 124.3, 123.4, 123.2, 122.5, 115.7, 103.8, 103.7. **ESI-MS**: Calcd for $C_{32}H_{23}N_3$: [M+H$^+$] 450.1970, found 450.1970.

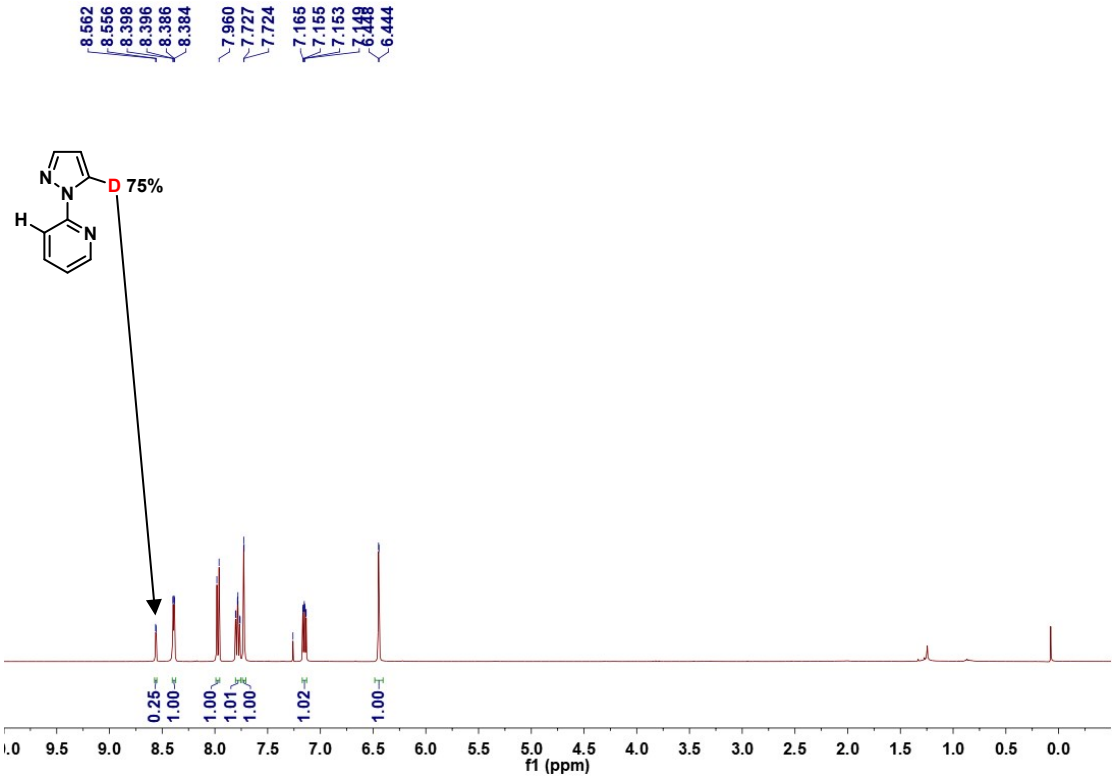
Control Experiments

a) C-H activation reversibility:



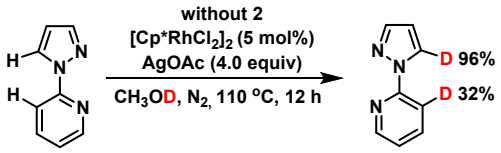
In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), AgOAc (133.5 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous CH_3OD:MeCN = 1:1 (2.0 mL). The reaction mixture was heated to 90 °C for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the product **1-D**.



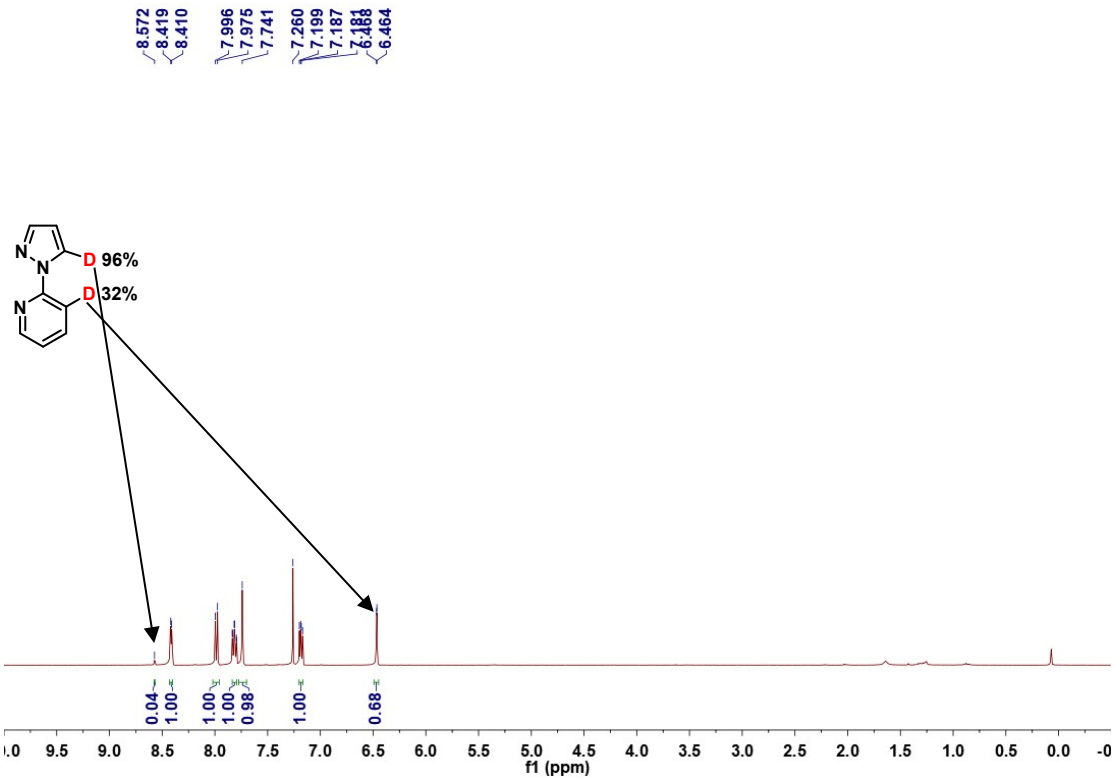


b) KIE by parallel experiments:

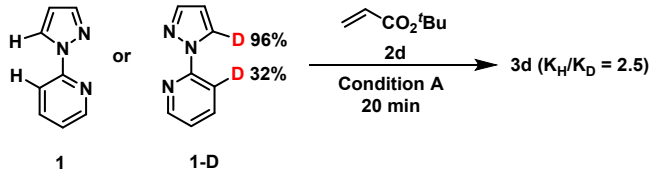
Preparation of Starting Material:



In a 50 mL sealed tube, the mixture of **1** (0.20 mmol), AgOAc (133.5 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous CH_3OD (2.0 mL). The reaction mixture was heated to 110 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the product **1-D**.



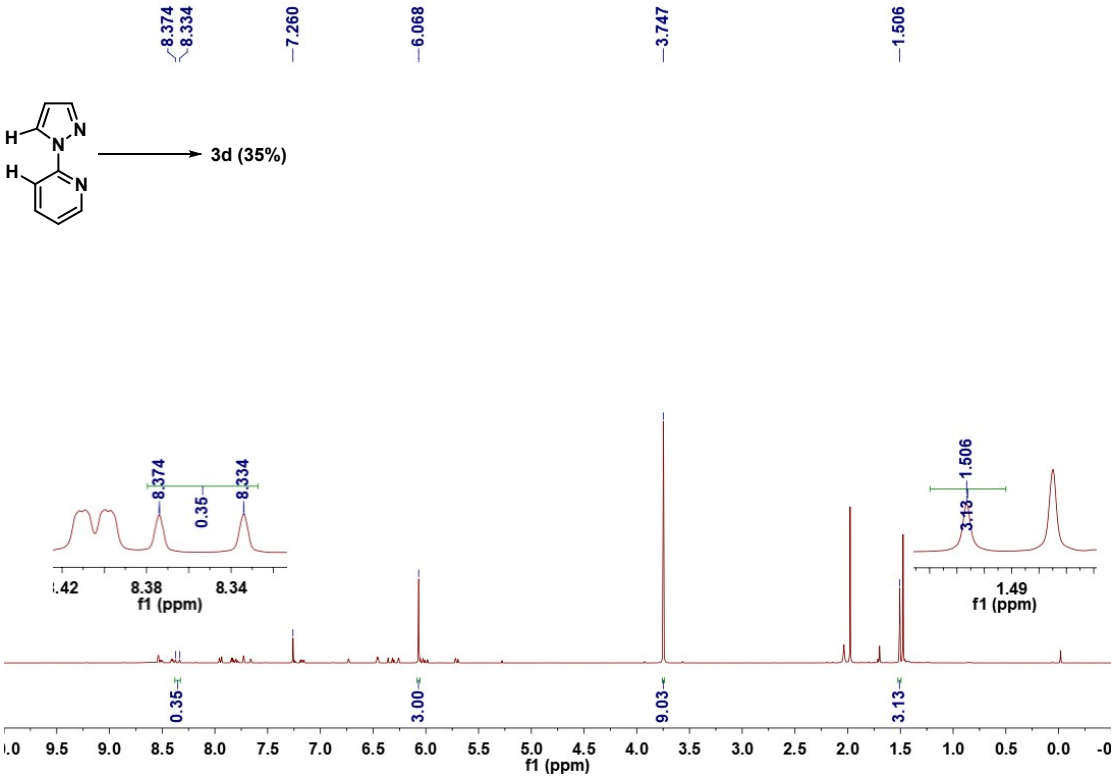
Parallel experiments:

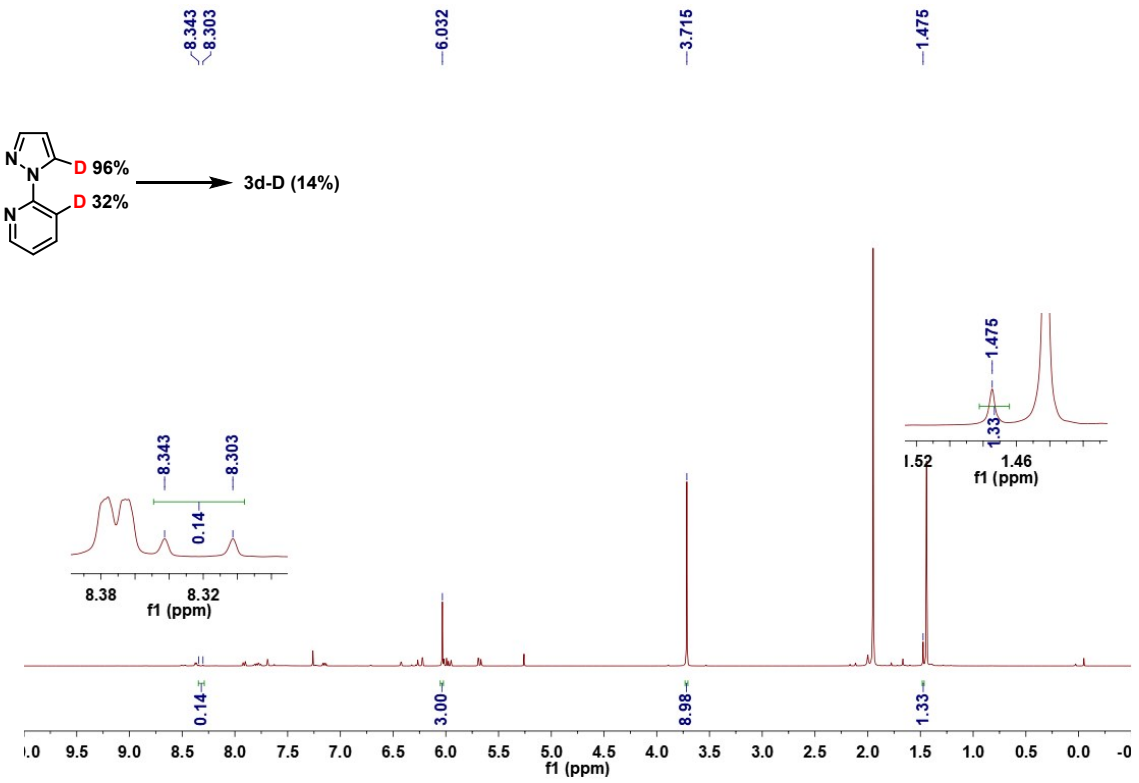


In a 50 mL sealed tube, the mixture of **1** or **1-D** (0.20 mmol), **2d** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous CH_3CN (2.0 mL). The reaction mixture was heated to 90 °C for 20 min. The solvent was removed in vacuum and ^1H NMR was taken using 0.20 mmol 1,3,5-trimethoxybenzene as the internal standard.

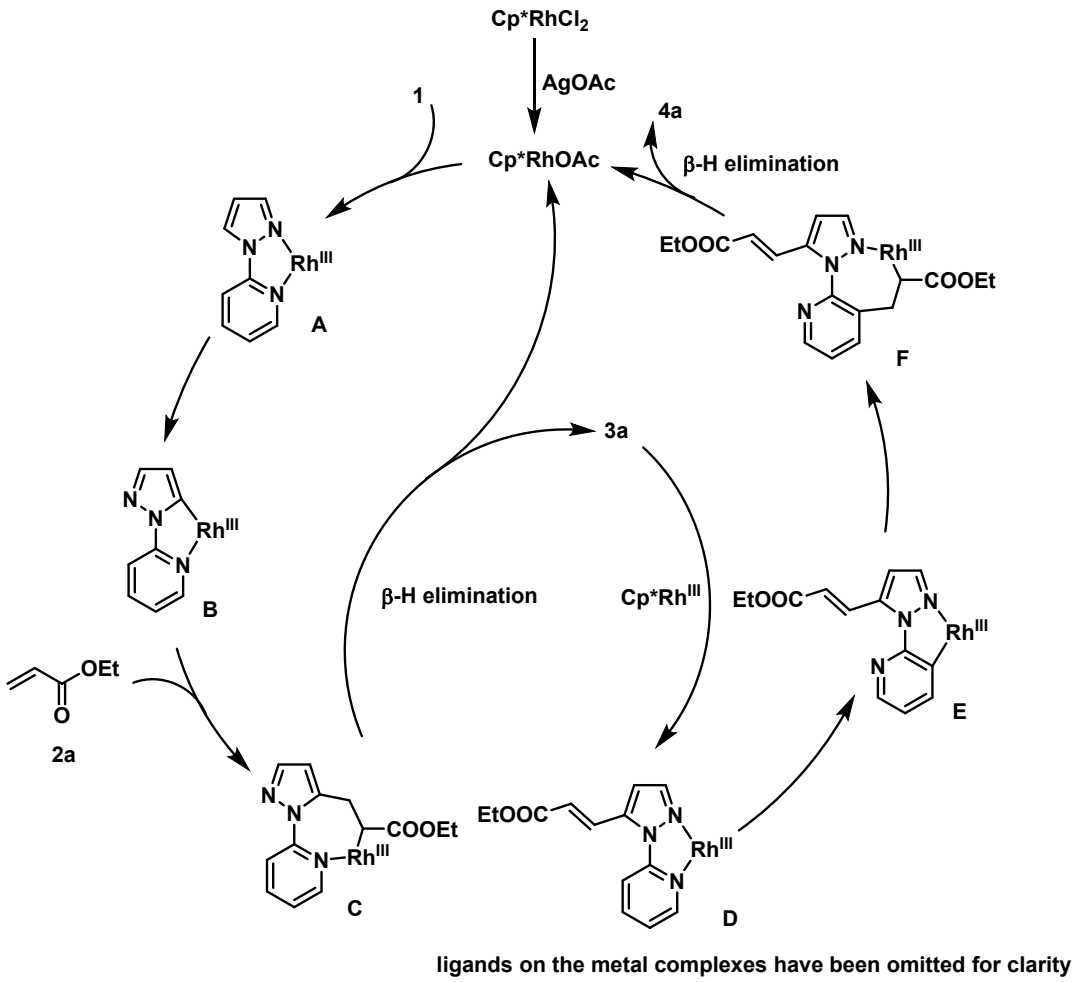
The reaction of **1-D** (28 mg, 0.2 mmol, 1.0 equiv) with **2d** (128 mg, 1.0 mmol, 5.0 equiv) provided the product **3d-D** in 14% yield. The ratio of **3d**: **3d-D** was 2.5.

The KIE of 3d


8.374
8.334
7.260
6.068
3.747
1.506
3d (35%)
8.374
8.334
0.35
8.38
8.34
f1 (ppm)
1.506
3.13
1.49
f1 (ppm)
0.35
3.00
9.03
3.13
f1 (ppm)

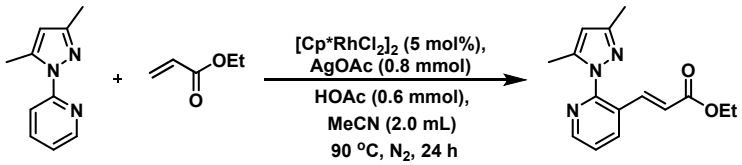

8.343
8.303
6.032
3.715
1.475
D 96%
D 32%
3d-D (14%)
0.14
3.00
8.98
1.33
f1 (ppm)

Proposed Mechanism:



ligands on the metal complexes have been omitted for clarity

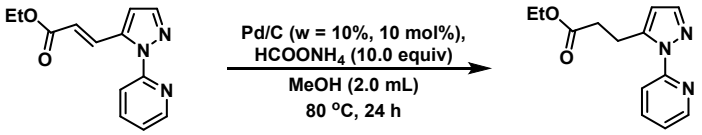
Synthetic Transformations:



In a 50 mL sealed tube, the mixture of **1'** (0.20 mmol), **2a** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), HOAc (36.0 mg, 0.6 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 °C for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the product **5** (30 mg, 56%)

as a yellow oil.

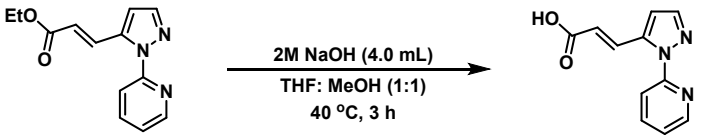
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 6.35 (d, *J* = 16.4 Hz, 1H), 6.02 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 150.7, 150.2, 149.5, 141.4, 139.2, 136.3, 126.6, 123.4, 121.4, 107.4, 107.4, 60.6, 14.2, 13.5, 12.0. **ESI-MS**: Calcd for $C_{15}H_{17}N_3O_2$: [M+H$^+$] 272.1399, found 272.1396.



3a 6

To an oven-dried 50 mL sealed tube was added substrate **3a** (48.7 mg, 0.2 mmol, 1.0 equiv), HCO_2NH_4 (126.0 mg, 2.0 mmol, 10.0 equiv), Pd/C (w = 10%, 21 mg, 0.02 mmol, 10 mol%) in MeOH (2.0 mL). The mixture was stirred at 80 °C for 24 h followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by silica gel chromatography to give **6** (49 mg, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.58 (d, *J* = 1.2 Hz, 1H), 7.27 – 7.16 (m, 1H), 6.23 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.48 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 153.4, 147.5, 143.5, 141.5, 138.3, 121.2, 116.0, 107.8, 60.4, 33.6, 23.4, 14.2. **ESI-MS**: Calcd for $C_{13}H_{15}N_3O_2$: [M+H$^+$] 246.1242, found 246.1247.

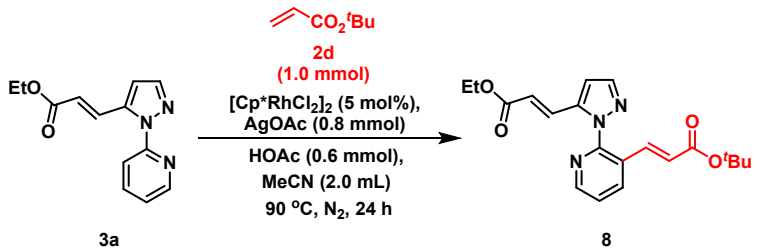


3a 7

To an 50 mL sealed tube was added substrate **3a** (48.7 mg, 0.2 mmol, 1.0 equiv), 2M NaOH aqueous (4.0 ml) in THF:MeOH = 1:1 (2.0 mL) and the reaction mixtures were stirred at 40 °C for 3 h. The progress of the reactions was monitored by thin-layer chromatography (TLC) analysis. The resulting mixture was added dilute hydrochloric acid to PH = 7 and then extracted with ethyl acetate (3 × 10.0 mL). The organic phases (dried with Na_2SO_4) were then evaporated under reduced pressure and the residues

chromatographed on silica gel column in order to obtain the products white solid **7** (43 mg, 99%).

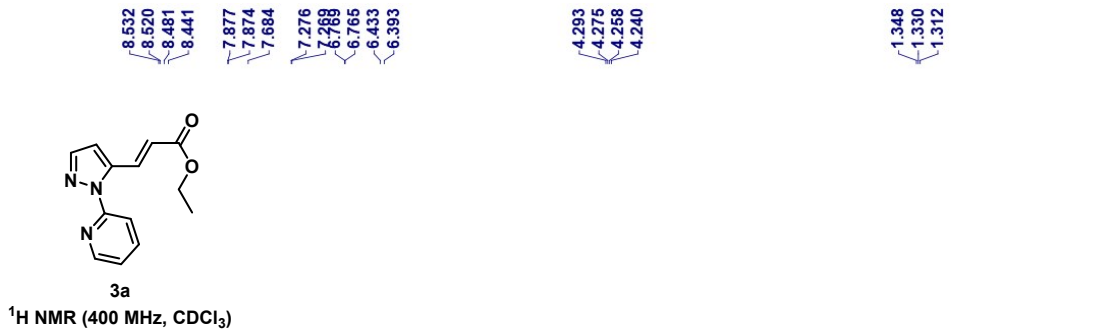
M.P.: 187-189 ºC. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 8.56 (dd, J = 4.8, 1.2 Hz, 1H), 8.32 (d, J = 16.0 Hz, 1H), 8.05 – 8.00 (m, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 1.6 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.14 (d, J = 1.6 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.4, 152.4, 148.0, 141.3, 139.6, 139.1, 132.3, 122.8, 121.8, 117.0, 108.7. **ESI-MS**: Calcd for $C_{11}H_9N_3O_2$: [M+H$^+$] 216.0773, found 216.0779.



In a 50 mL sealed tube, the mixture of **3a** (0.20 mmol), **2d** (1.0 mmol), AgOAc (133.5 mg, 0.8 mmol), HOAc (36.0 mg, 0.6 mmol), [Cp*RhCl$_2$]$_2$ (6.2 mg, 0.01 mmol), were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 ºC for 24 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the products **8** (52 mg, 71%) as a yellow oil.

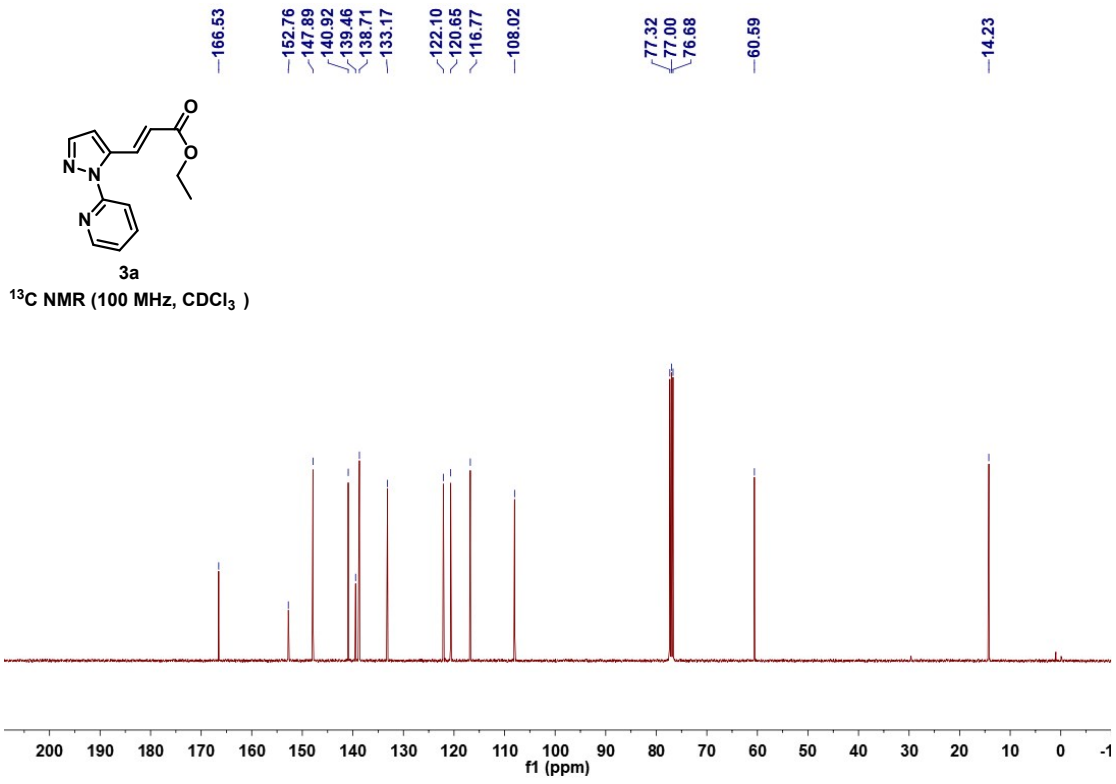
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 3.6 Hz, 1H), 8.13 (dd, J = 8.0, 1.6 Hz, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.54 (d, J = 15.6 Hz, 1H), 7.44 – 7.42 (m, 2H), 6.81 (d, J = 1.6 Hz, 1H), 6.37 (d, J = 5.6 Hz, 1H), 6.33 (d, J = 5.6 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.48 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 165.1, 149.7, 149.5, 141.3, 140.1, 137.2, 136.6, 130.7, 127.4, 124.2, 124.1, 124.1, 107.1, 81.0, 60.7, 28.1, 14.2. **ESI-MS**: Calcd for $C_{20}H_{23}N_3O_4$: [M+H$^+$] 370.1767, found 370.1762.

NMR Spectra



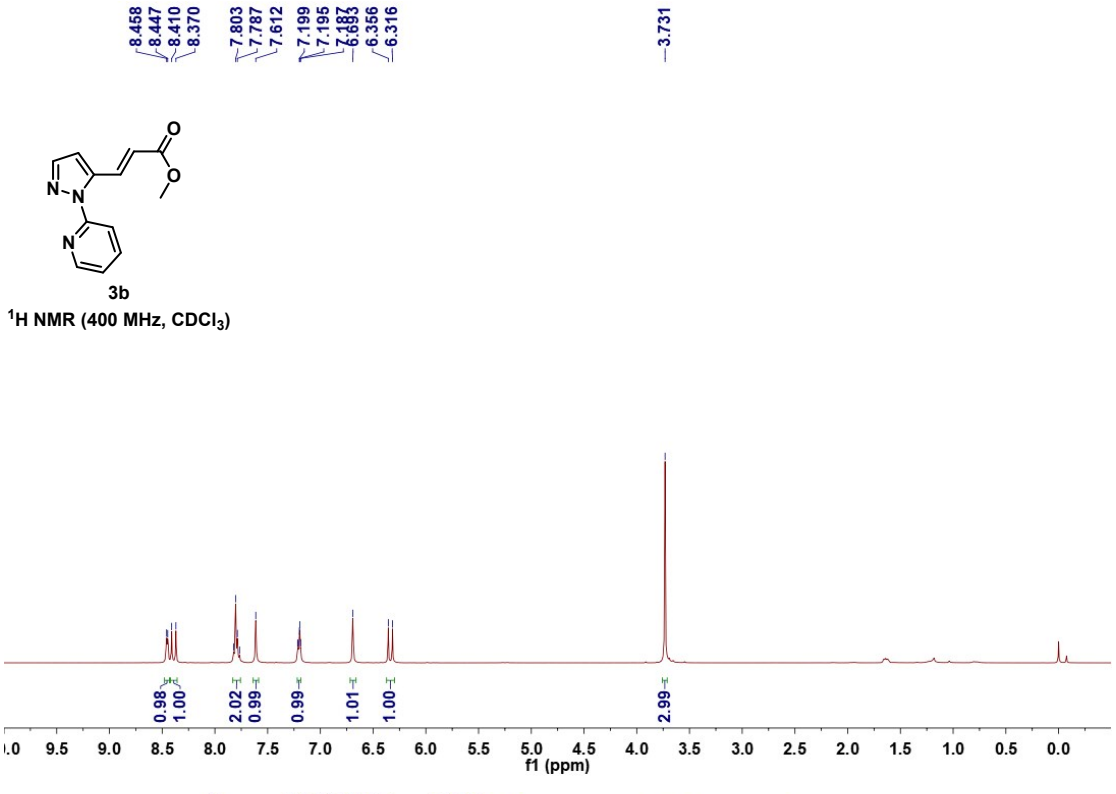
3a

^{1}H NMR (400 MHz, $CDCl_3$)



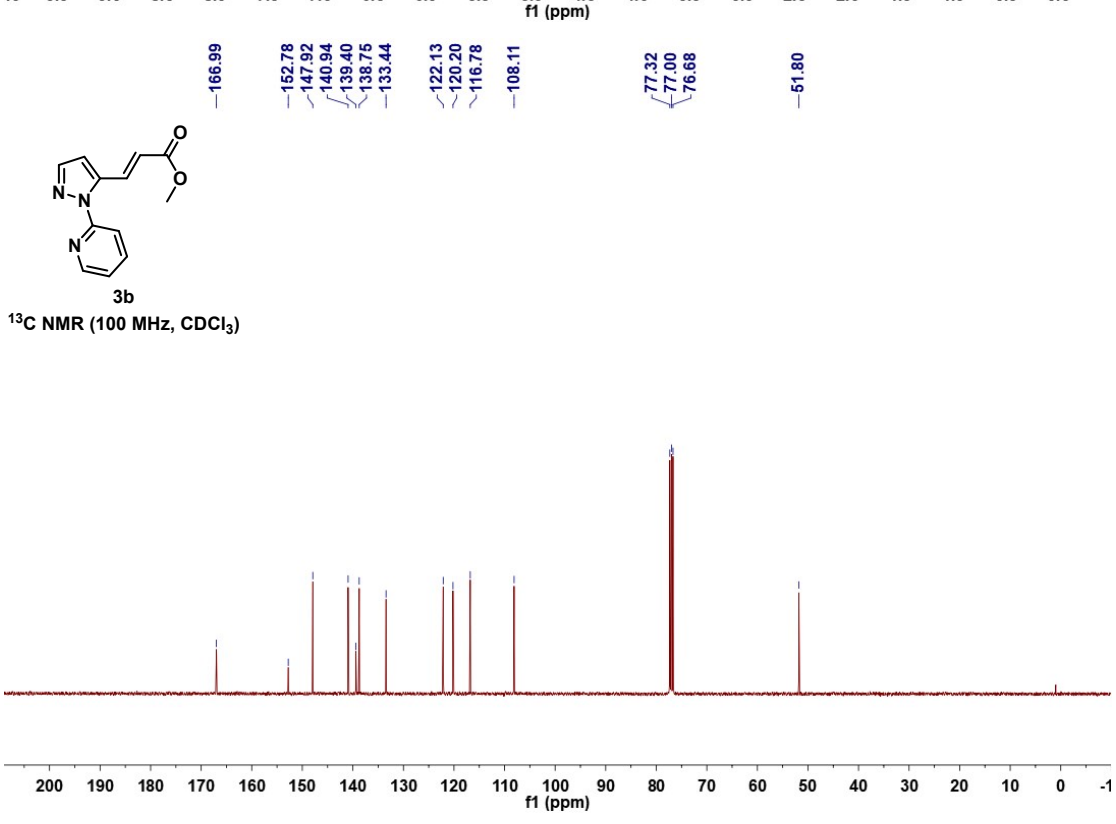
3a

^{13}C NMR (100 MHz, $CDCl_3$)



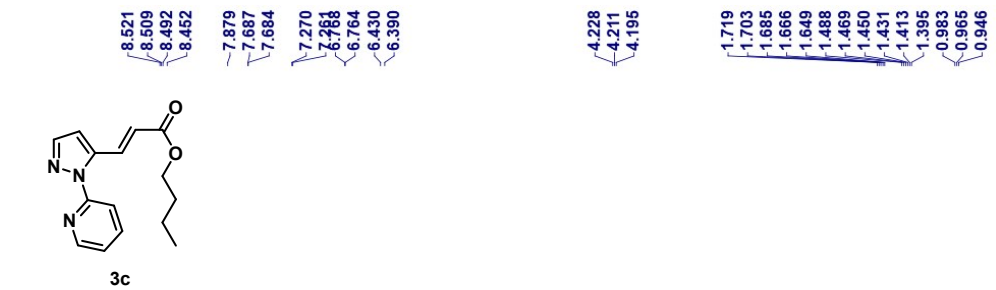
3b

^{1}H NMR (400 MHz, $CDCl_3$)



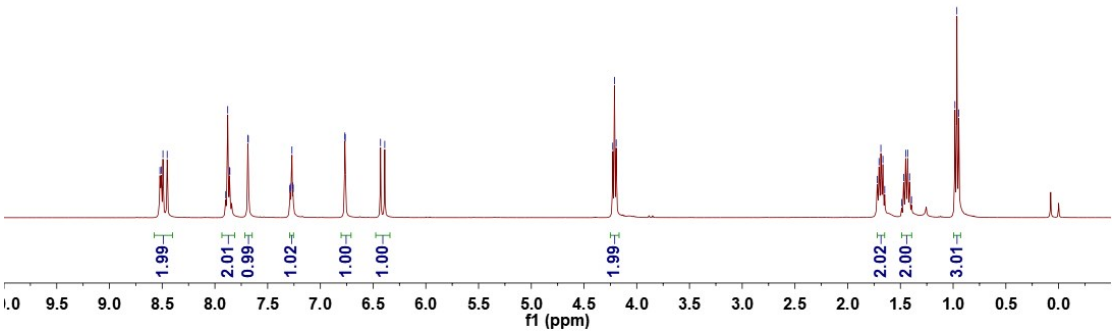
3b

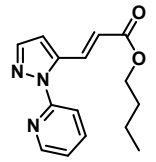
^{13}C NMR (100 MHz, $CDCl_3$)



3c

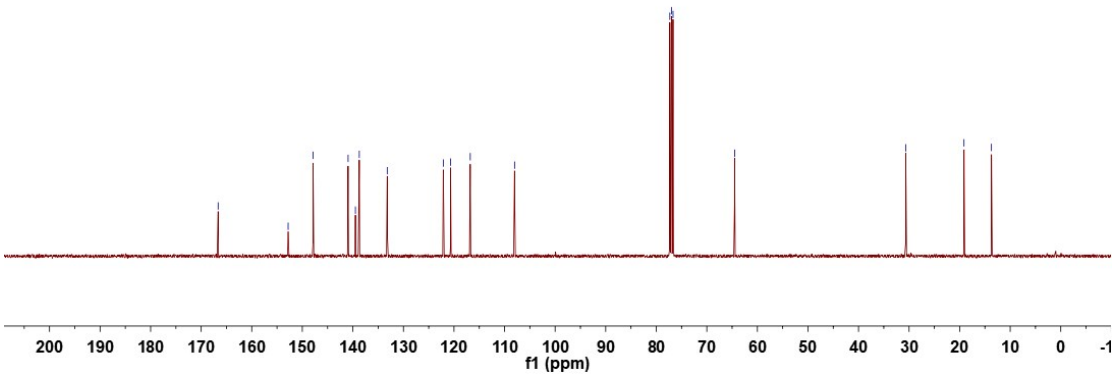
^{1}H NMR (400 MHz, $CDCl_3$)

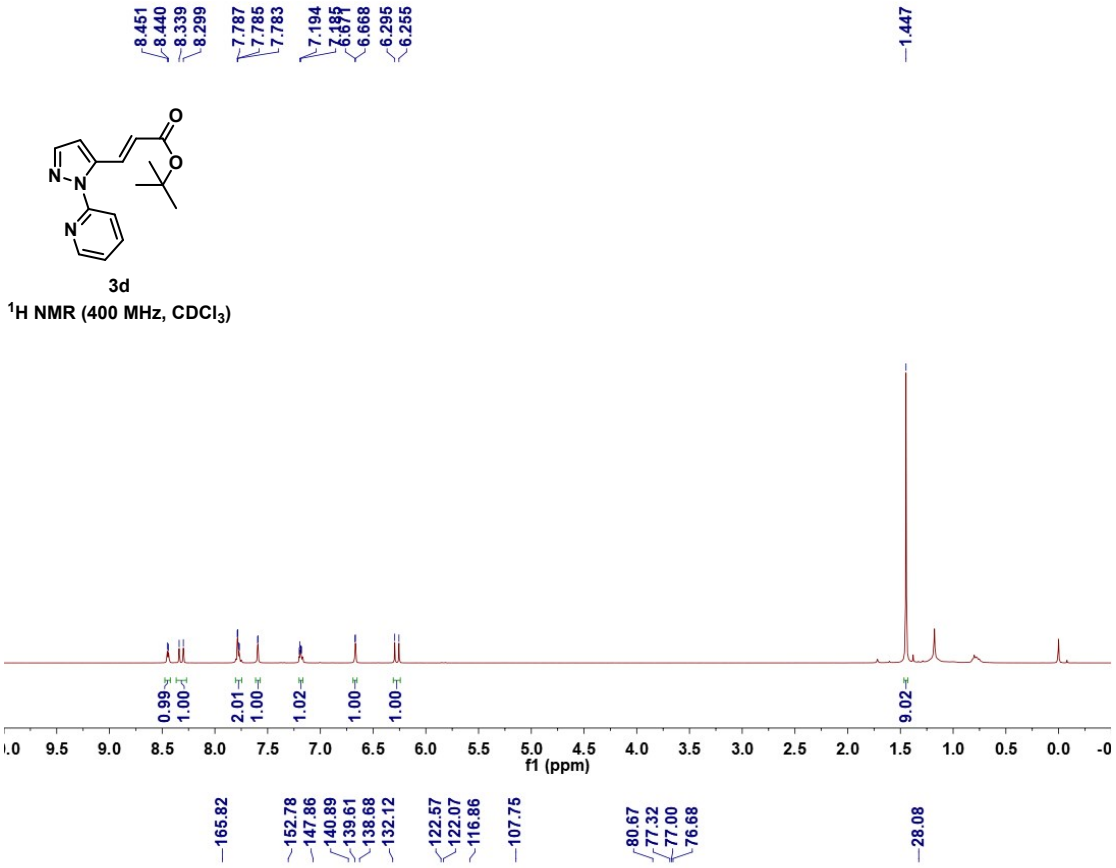




3c

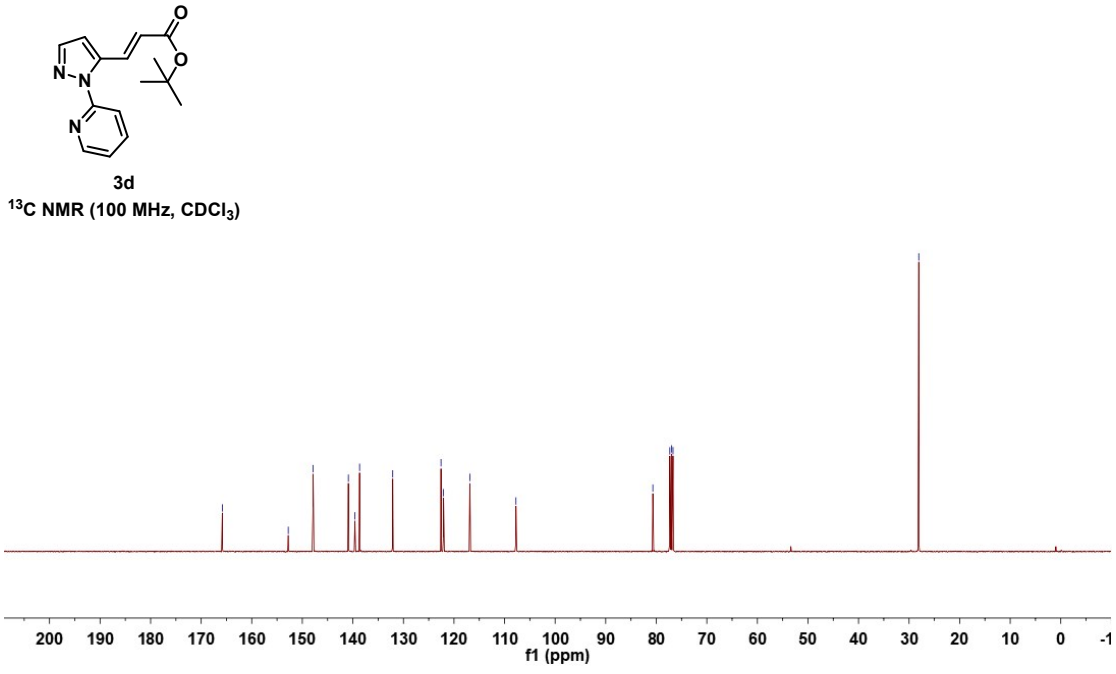
^{13}C NMR (100 MHz, $CDCl_3$)





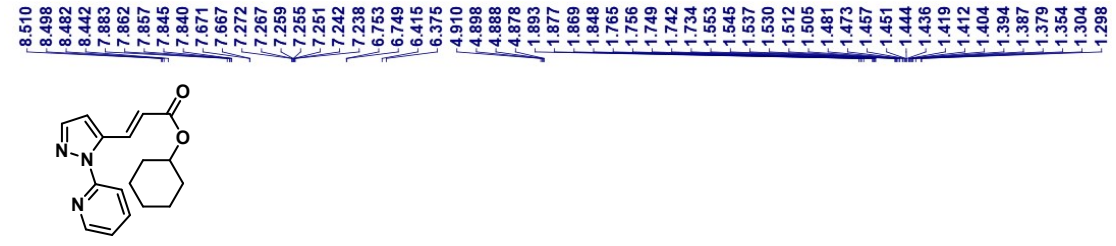
3d

^{1}H NMR (400 MHz, $CDCl_3$)



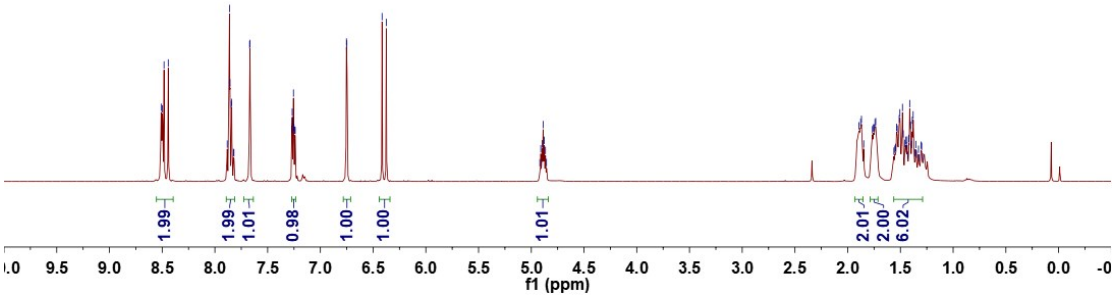
3d

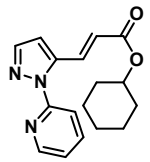
^{13}C NMR (100 MHz, $CDCl_3$)



3e

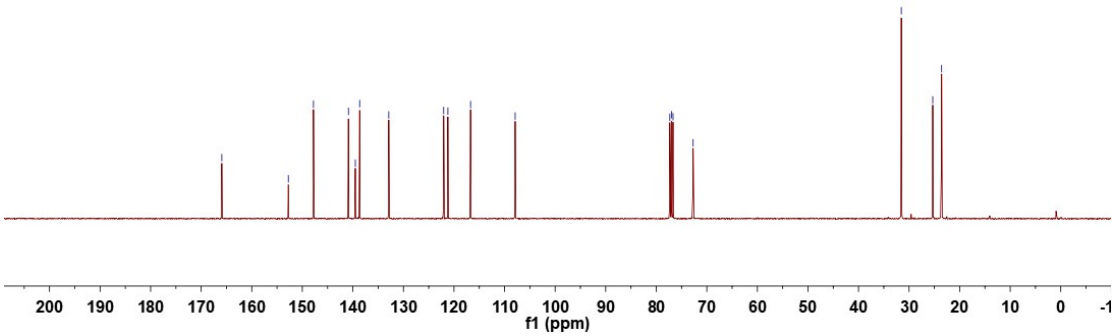
^{1}H NMR (400 MHz, $CDCl_3$)

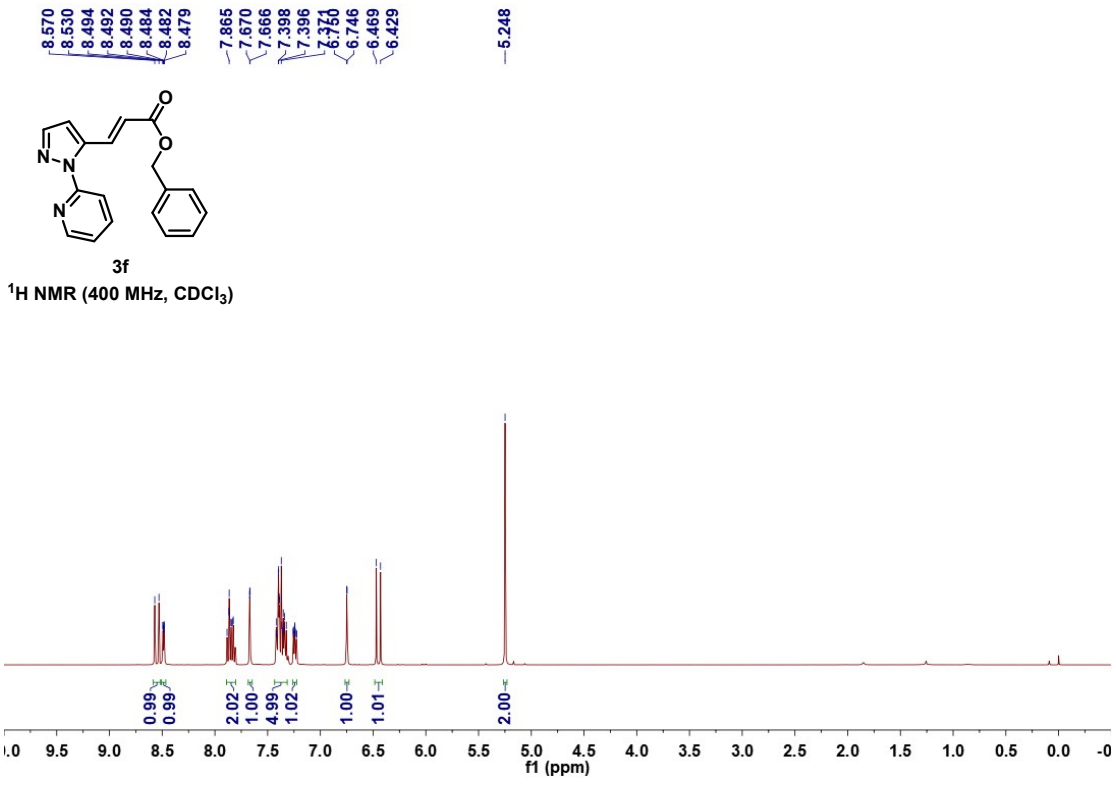




3e

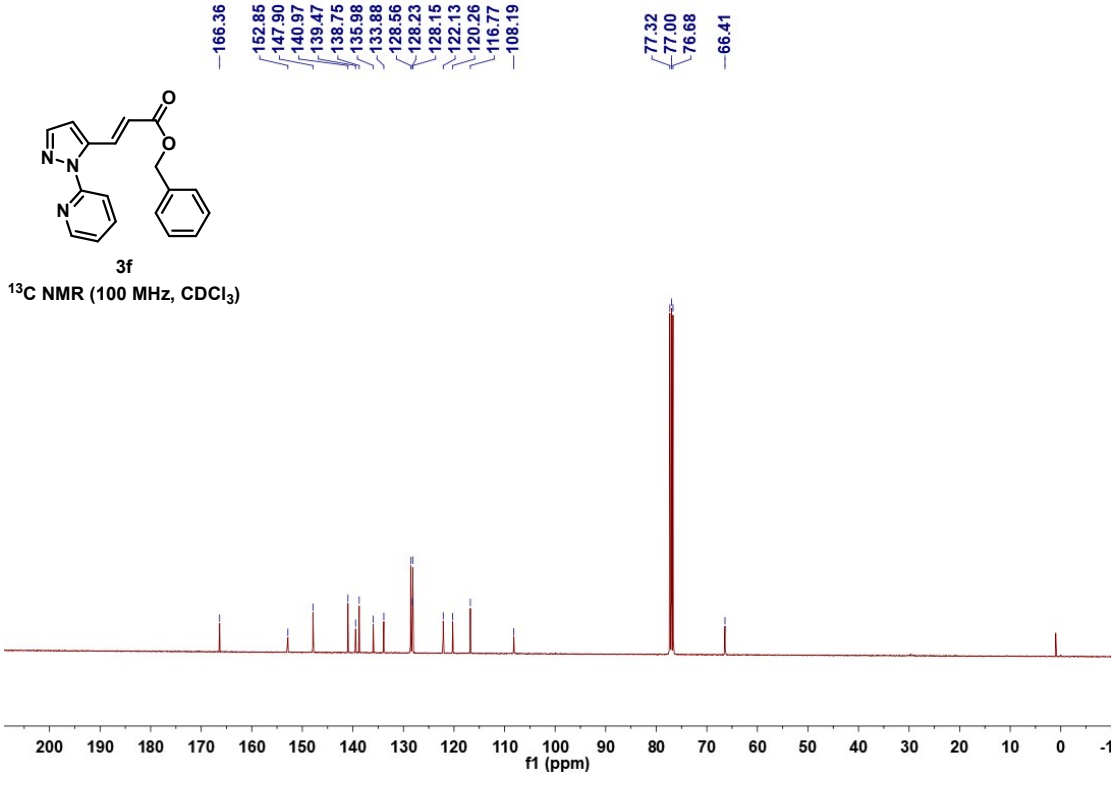
^{13}C NMR (100 MHz, $CDCl_3$)





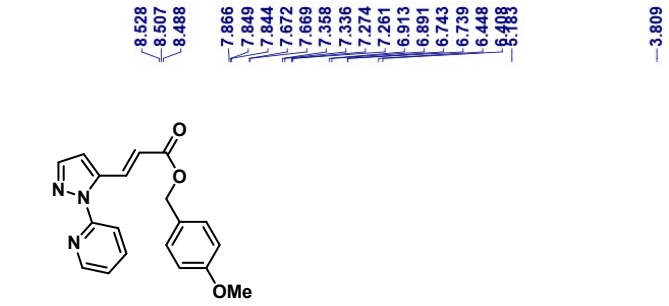
3f

^{1}H NMR (400 MHz, $CDCl_3$)



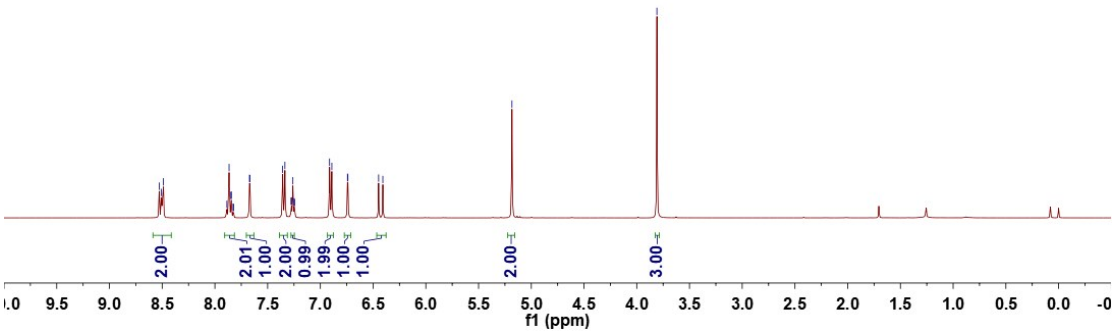
3f

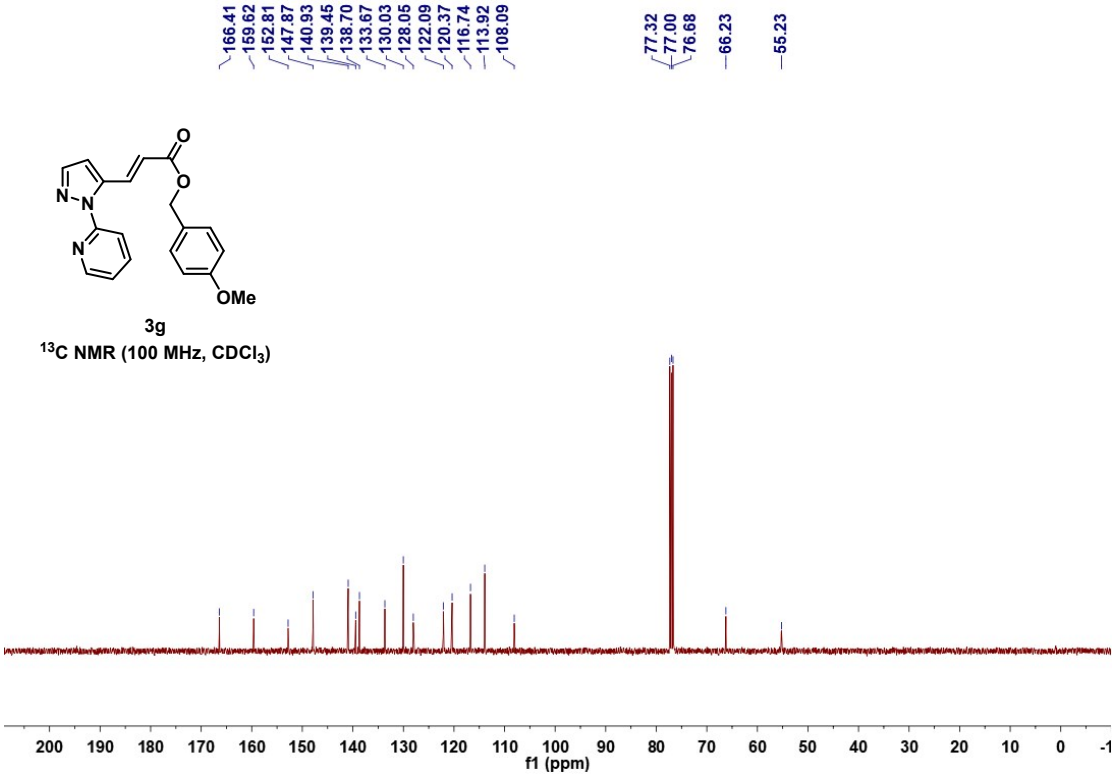
^{13}C NMR (100 MHz, $CDCl_3$)



3g

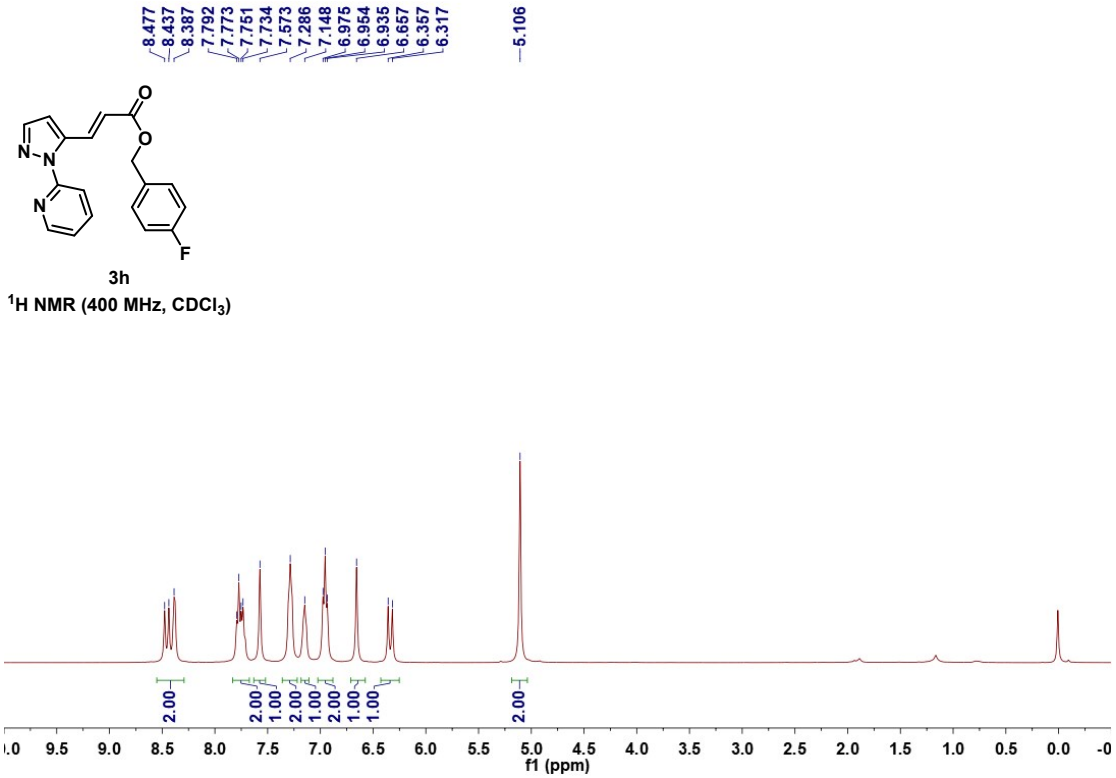
^{1}H NMR (400 MHz, $CDCl_3$)





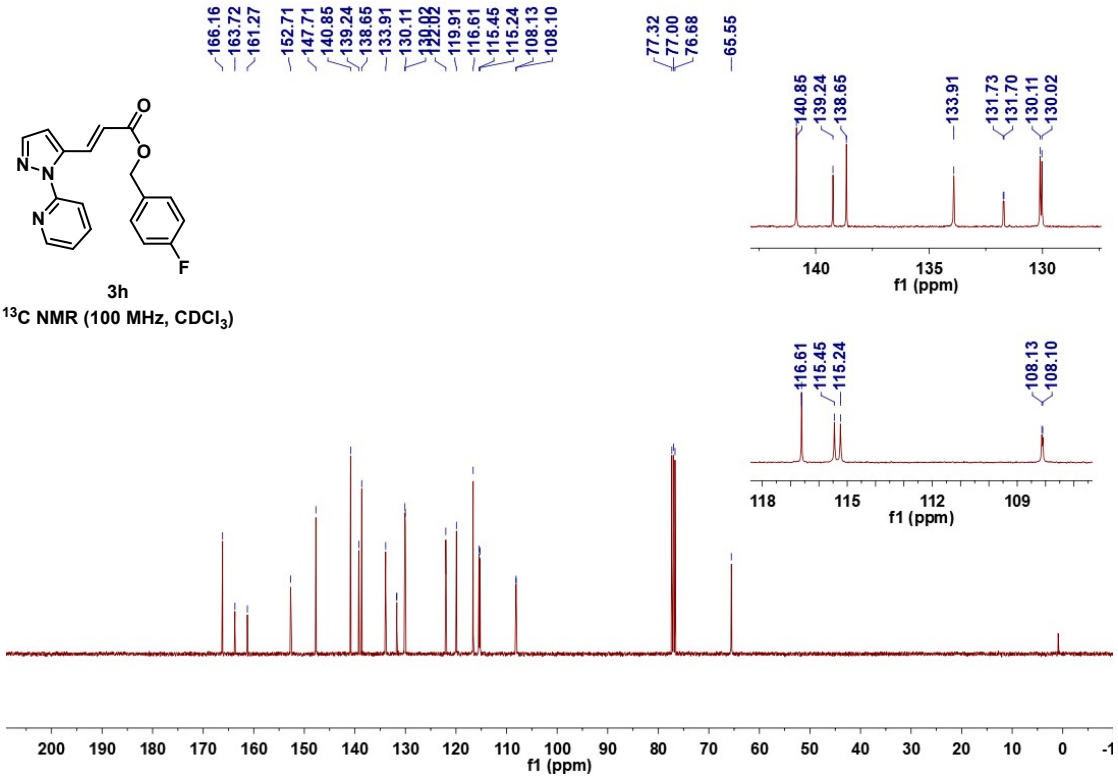
3g

^{13}C NMR (100 MHz, $CDCl_3$)



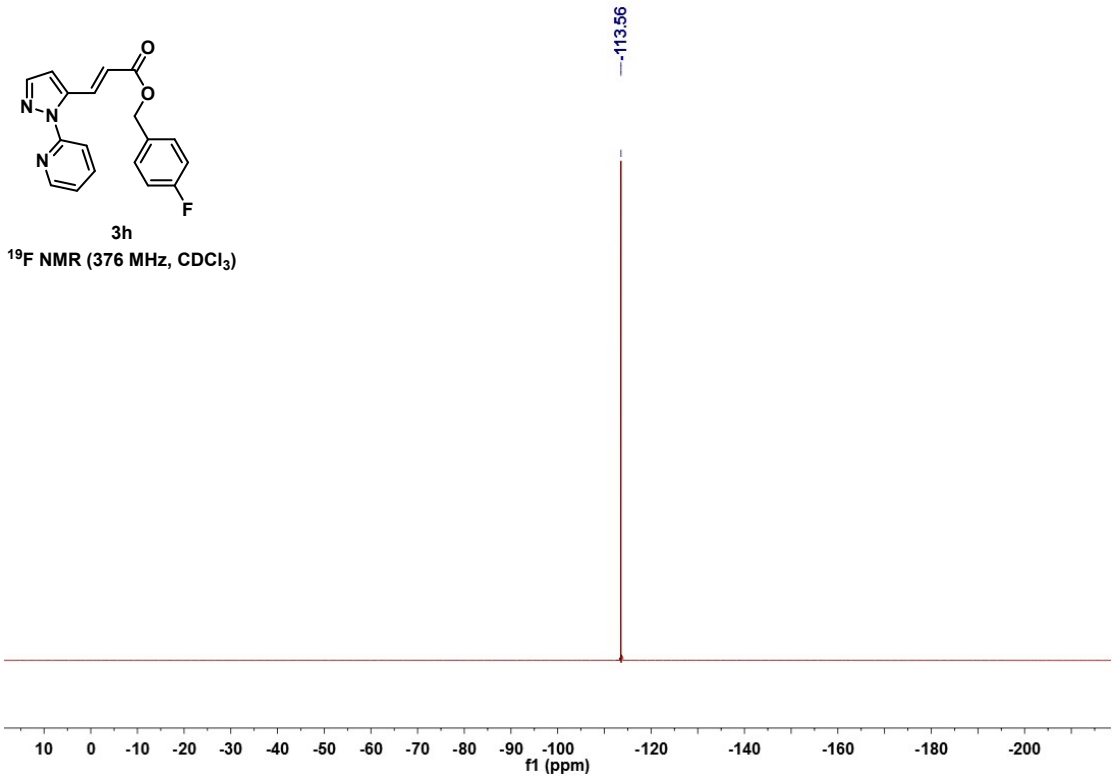
3h

^{1}H NMR (400 MHz, $CDCl_3$)



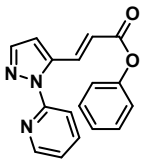
3h

^{13}C NMR (100 MHz, $CDCl_3$)



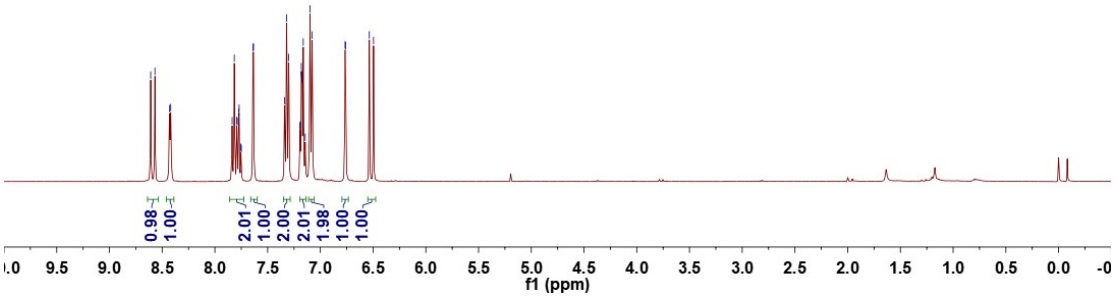
3h

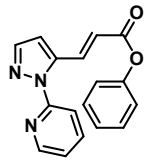
^{19}F NMR (376 MHz, $CDCl_3$)



3i

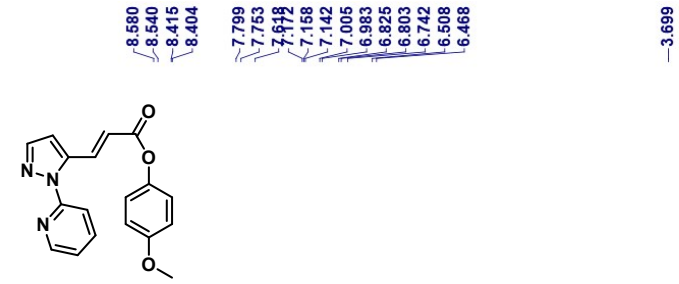
^{1}H NMR (400 MHz, $CDCl_3$)





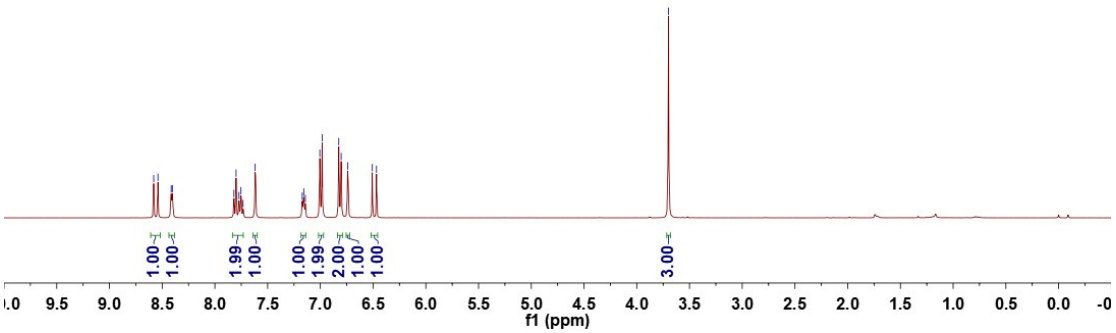
3i

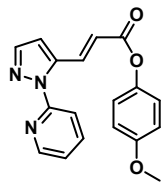
^{13}C NMR (100 MHz, $CDCl_3$)



3j

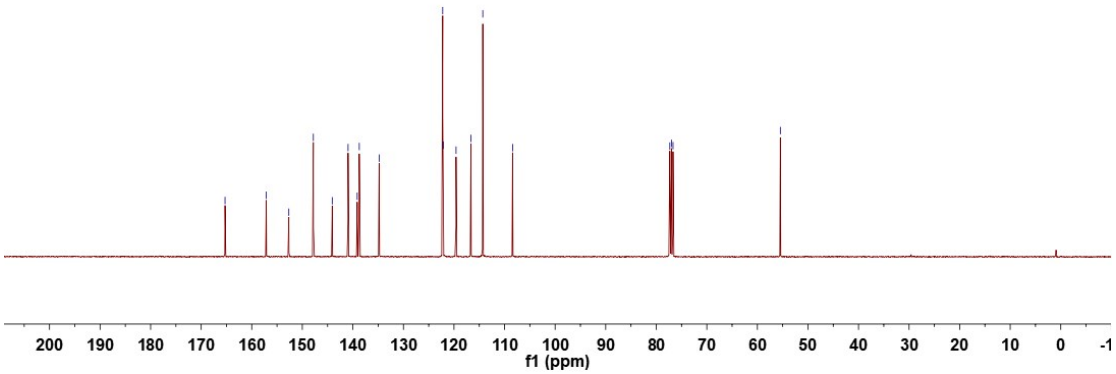
^{1}H NMR (400 MHz, $CDCl_3$)

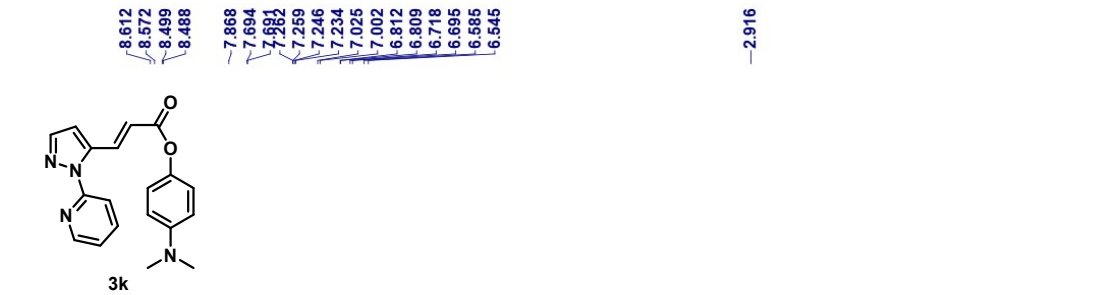




3j

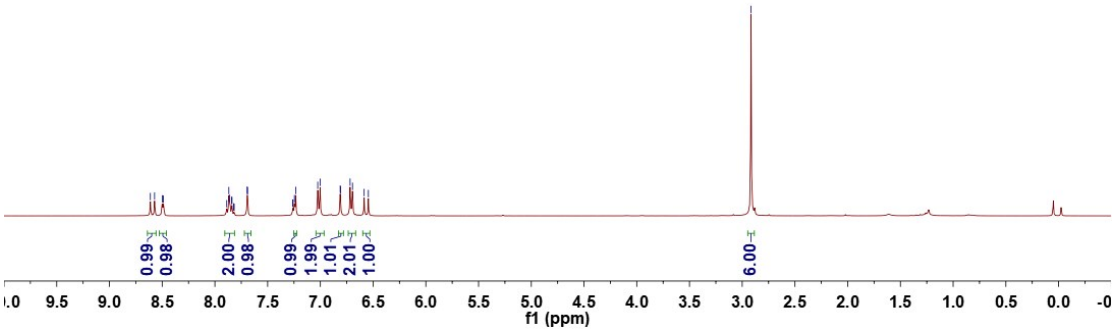
^{13}C NMR (100 MHz, $CDCl_3$)

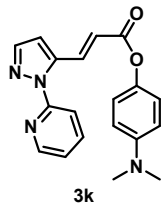




3k

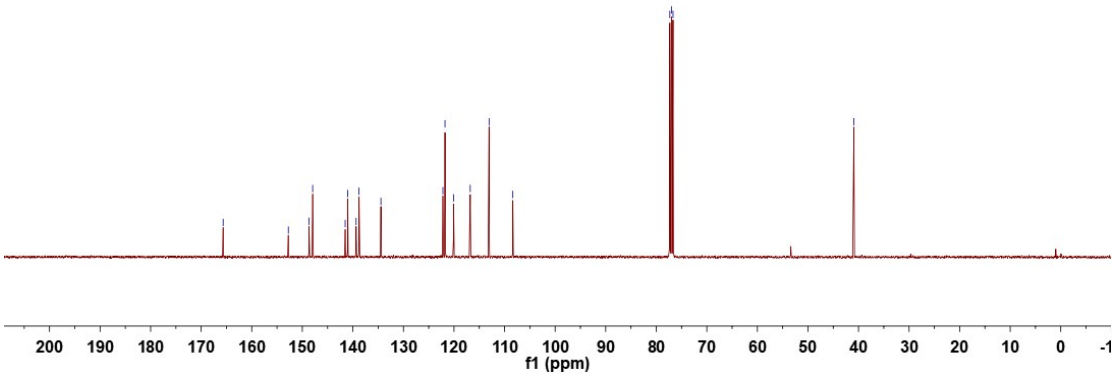
^{1}H NMR (400 MHz, $CDCl_3$)

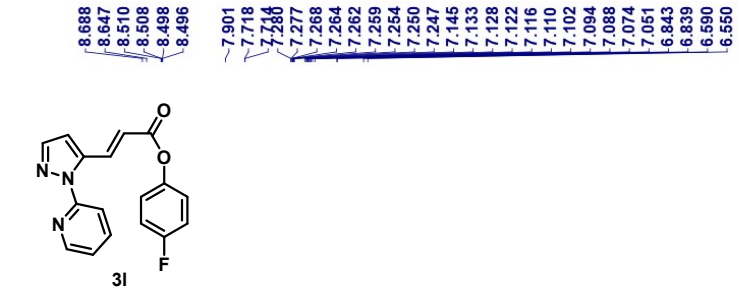




3k

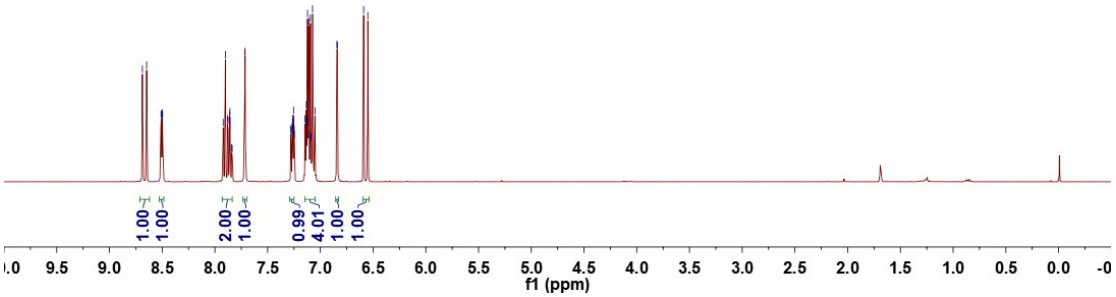
^{13}C NMR (100 MHz, $CDCl_3$)

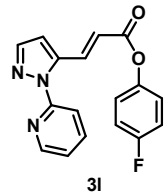




3l

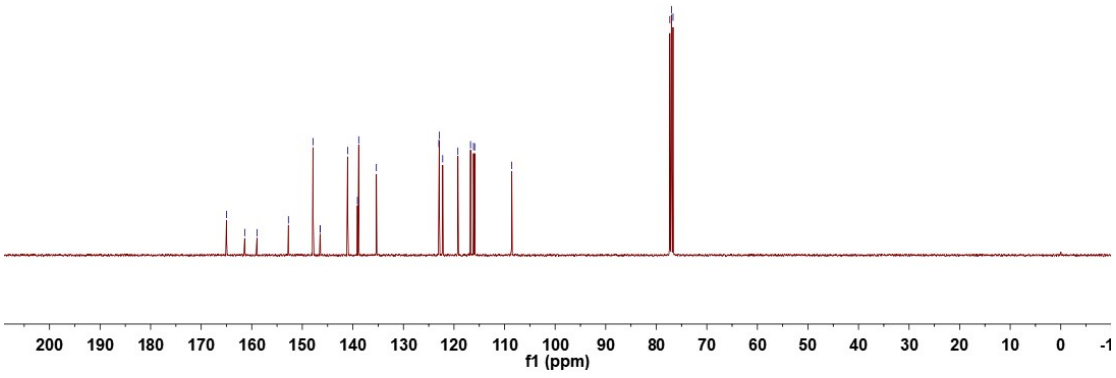
^{1}H NMR (400 MHz, $CDCl_3$)

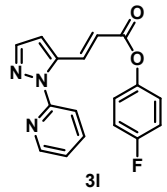




3l

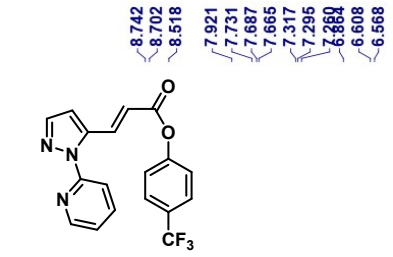
^{13}C NMR (100 MHz, $CDCl_3$)





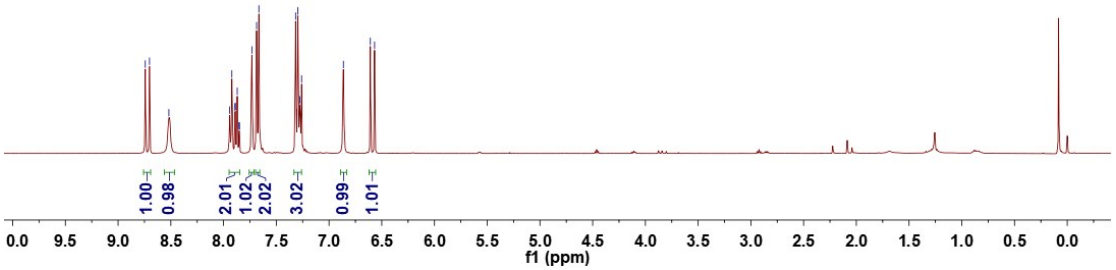
3l

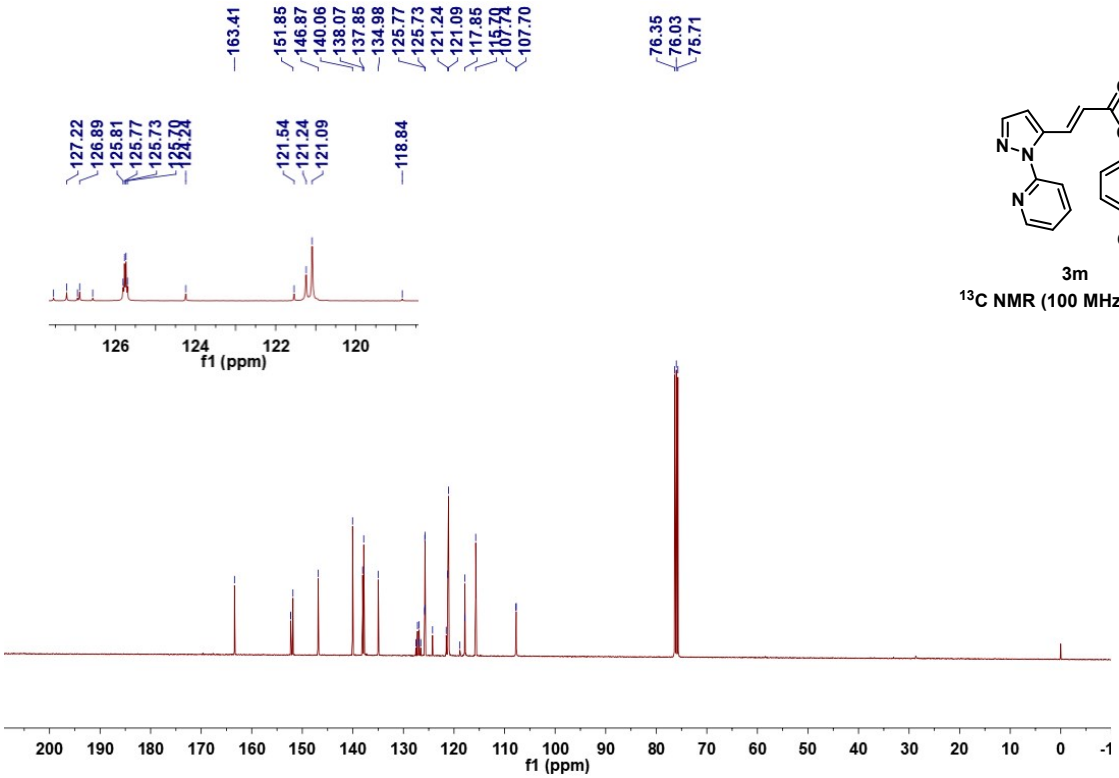
^{19}F NMR (376 MHz, $CDCl_3$)



3m

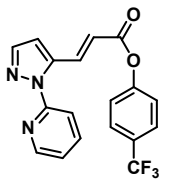
^{1}H NMR (400 MHz, $CDCl_3$)





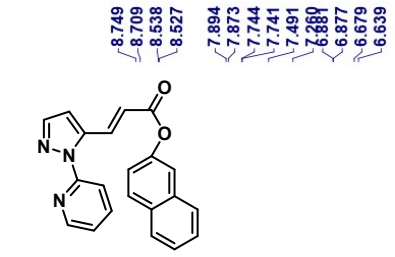
3m

^{13}C NMR (100 MHz, $CDCl_3$)



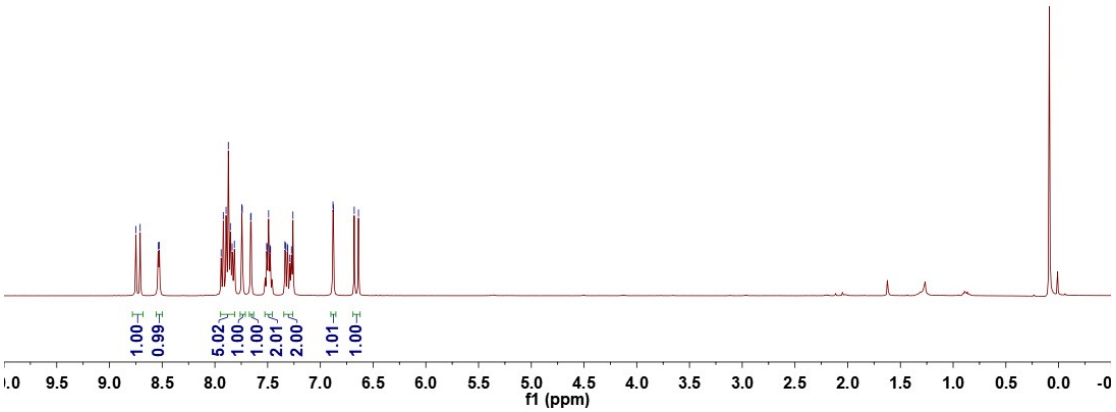
3m

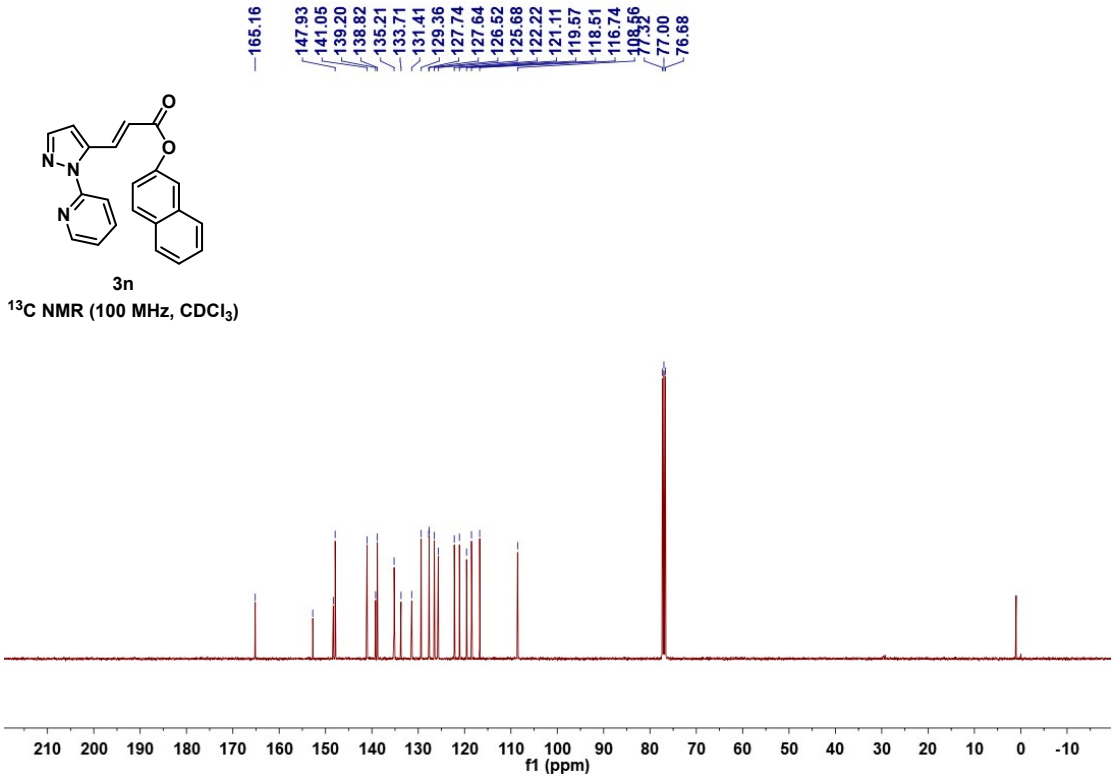
^{19}F NMR (376 MHz, $CDCl_3$)



3n

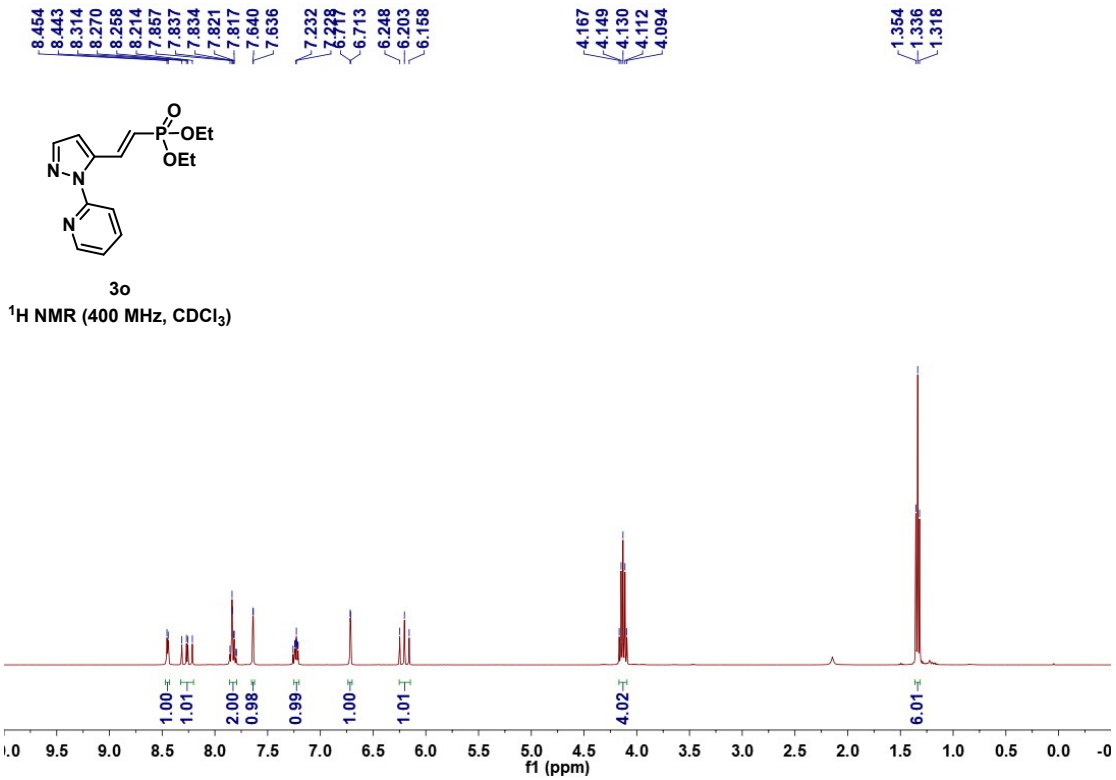
^{1}H NMR (400 MHz, $CDCl_3$)





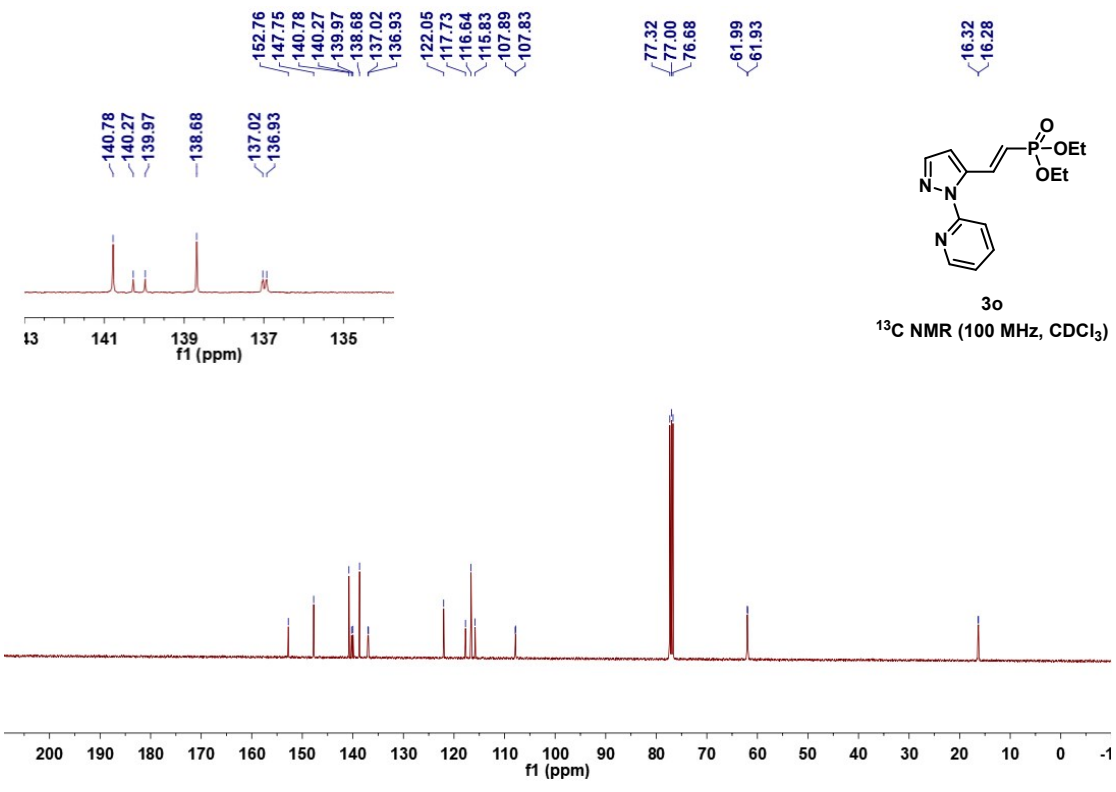
3n

^{13}C NMR (100 MHz, $CDCl_3$)



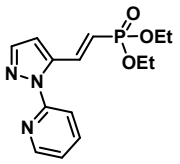
3o

^{1}H NMR (400 MHz, $CDCl_3$)



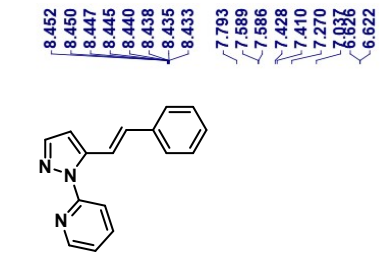
3o

^{13}C NMR (100 MHz, $CDCl_3$)



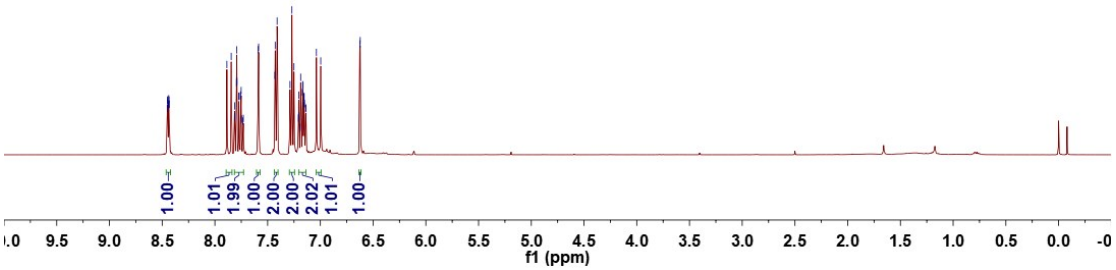
3o

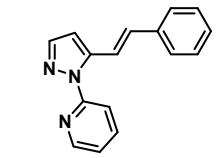
^{31}P NMR (162 MHz, $CDCl_3$)



3p

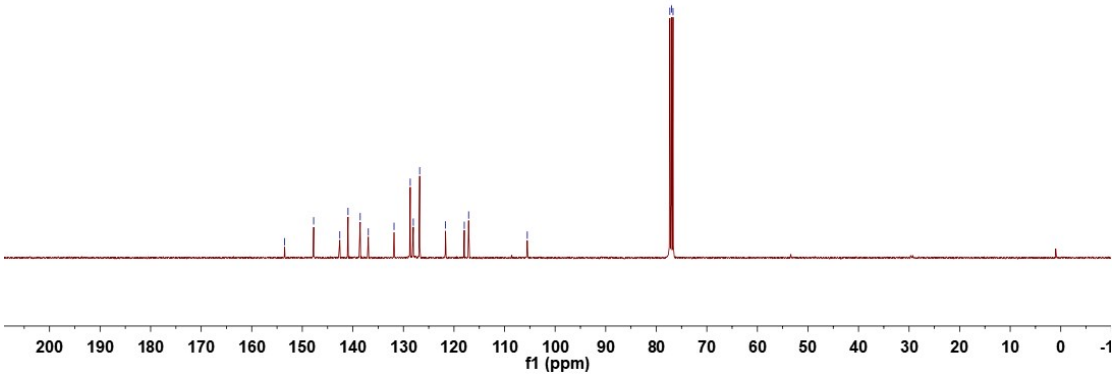
^{1}H NMR (400 MHz, $CDCl_3$)

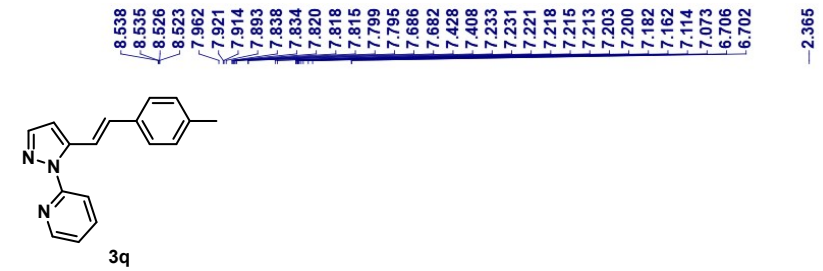




3p

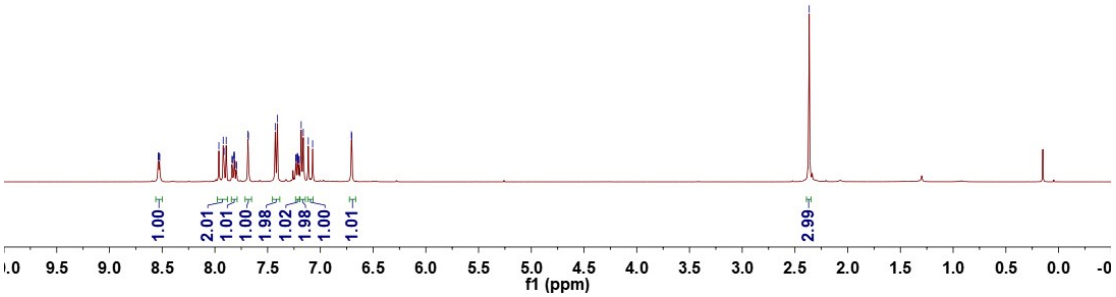
^{13}C NMR (100 MHz, $CDCl_3$)

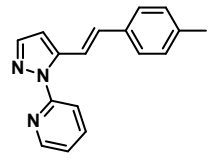




3q

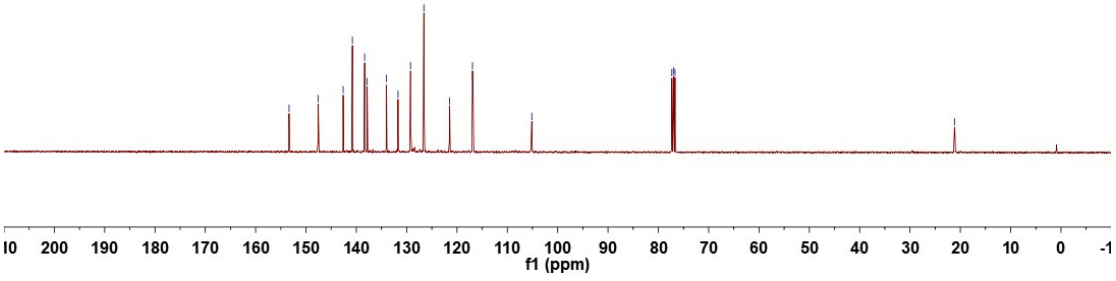
^{1}H NMR (400 MHz, $CDCl_3$)

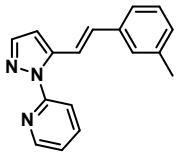




3q

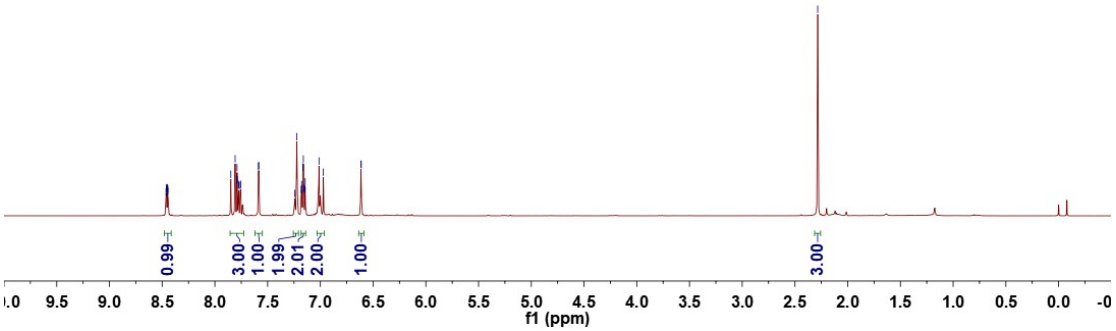
^{13}C NMR (100 MHz, $CDCl_3$)

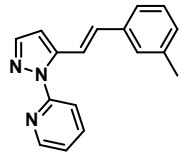




3r

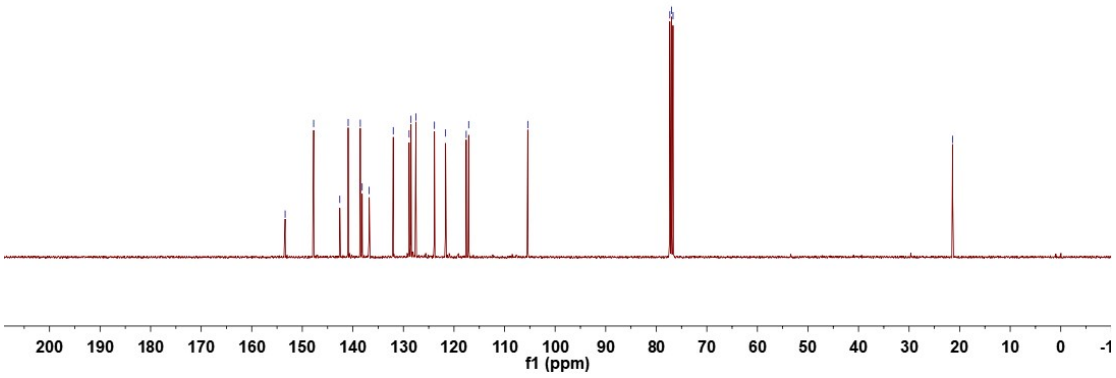
^{1}H NMR (400 MHz, $CDCl_3$)

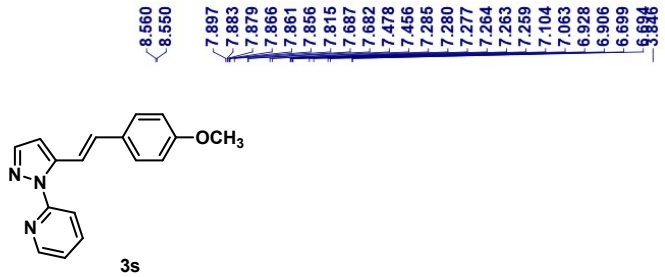




3r

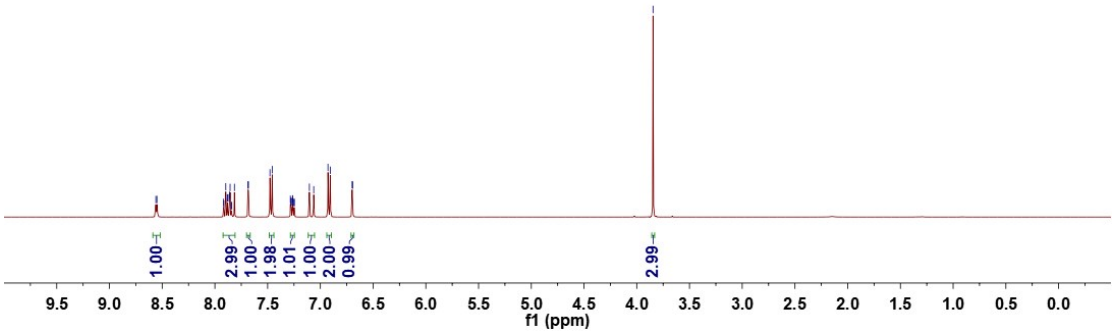
^{13}C NMR (100 MHz, $CDCl_3$)

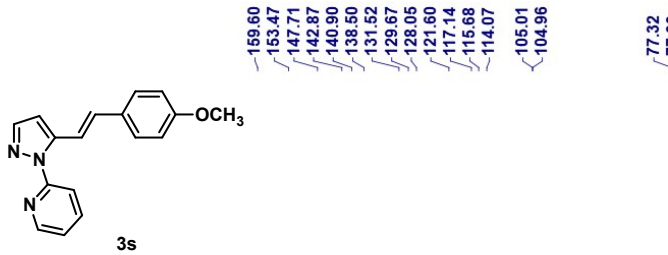




3s

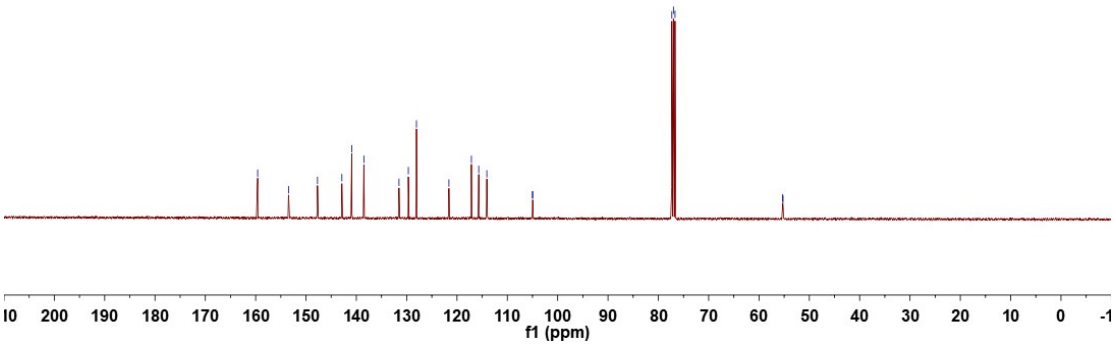
^{1}H NMR (400 MHz, $CDCl_3$)

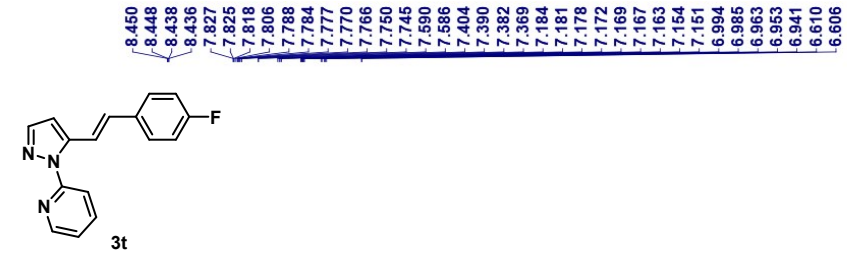




3s

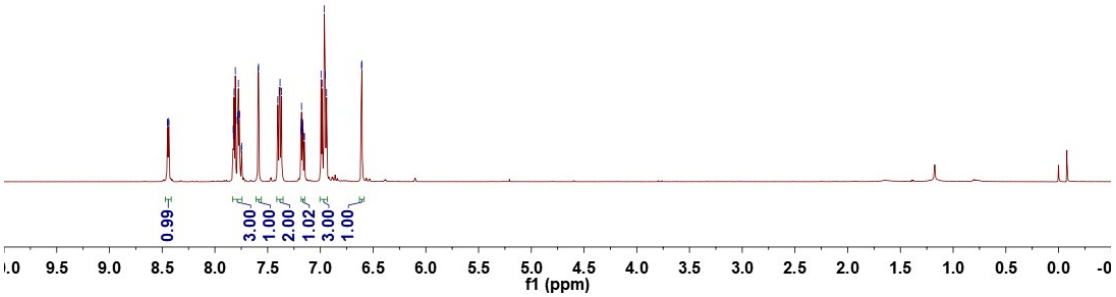
^{13}C NMR (100 MHz, $CDCl_3$)

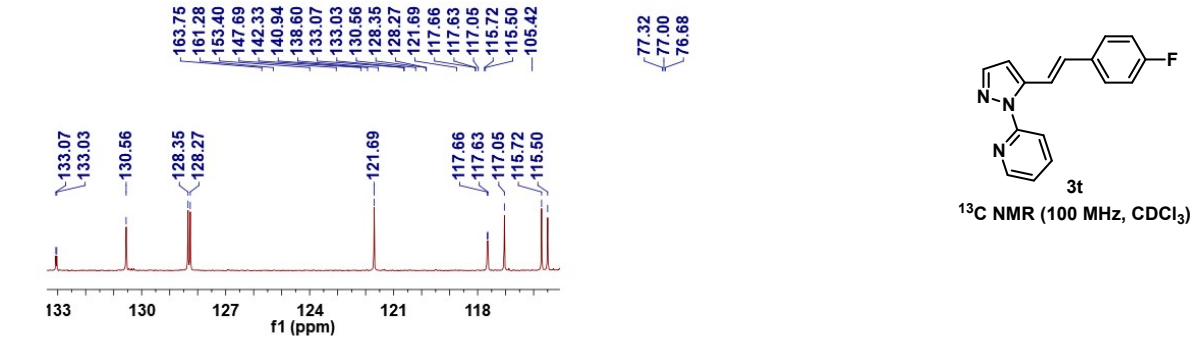




3t

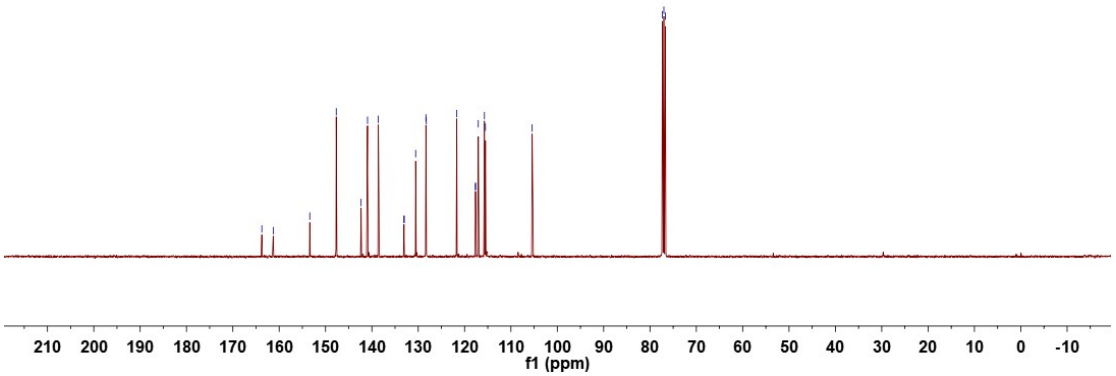
^{1}H NMR (400 MHz, $CDCl_3$)

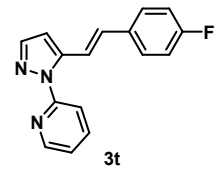




3t

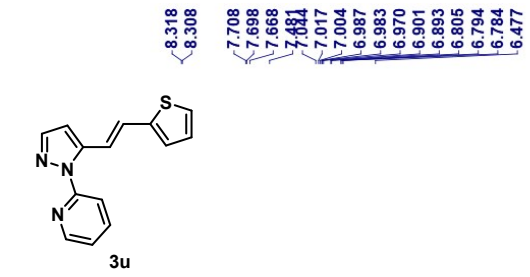
^{13}C NMR (100 MHz, $CDCl_3$)





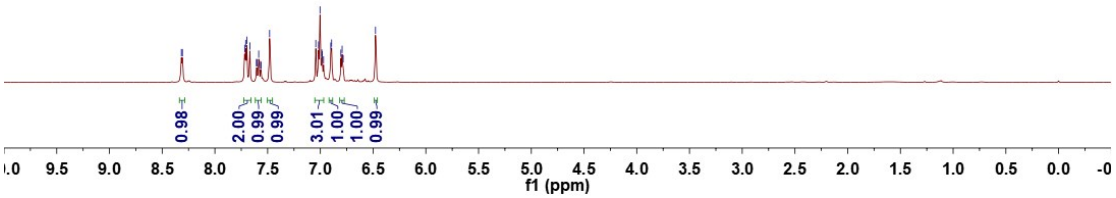
3t

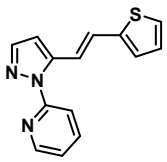
^{19}F NMR (376 MHz, $CDCl_3$)



3u

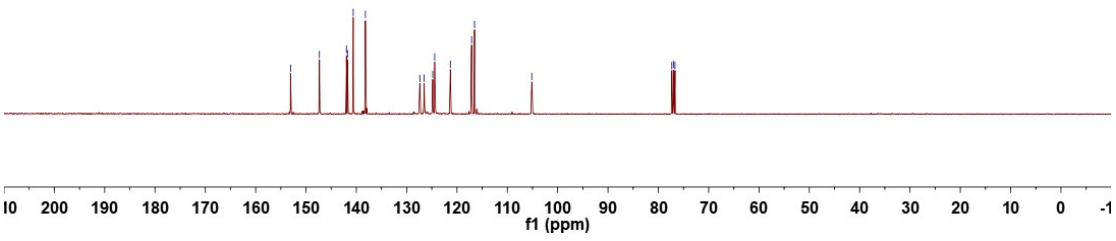
^{1}H NMR (400 MHz, $CDCl_3$)

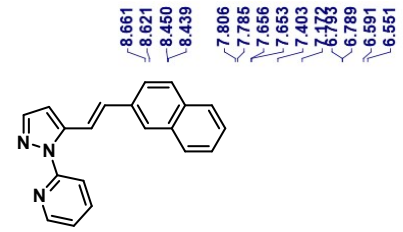




3u

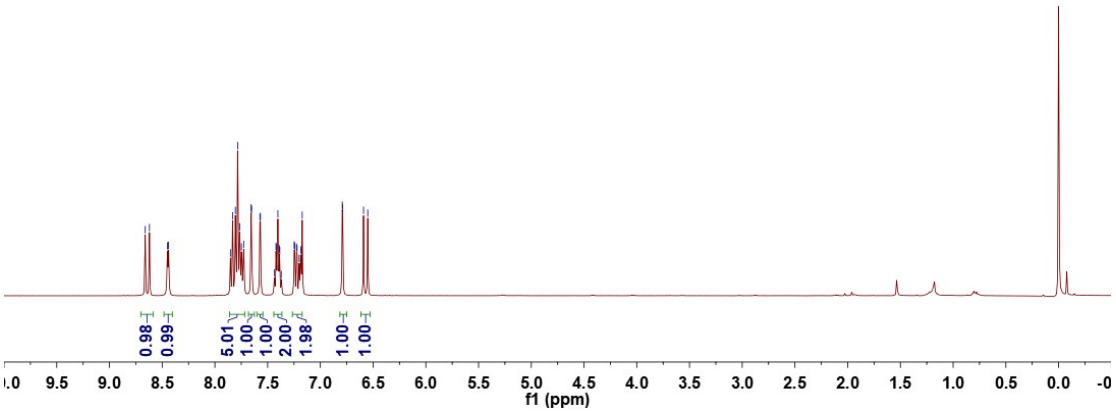
^{13}C NMR (100 MHz, $CDCl_3$)

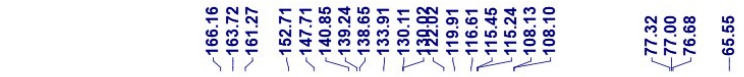


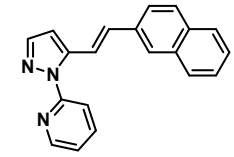


3v

^{1}H NMR (400 MHz, $CDCl_3$)

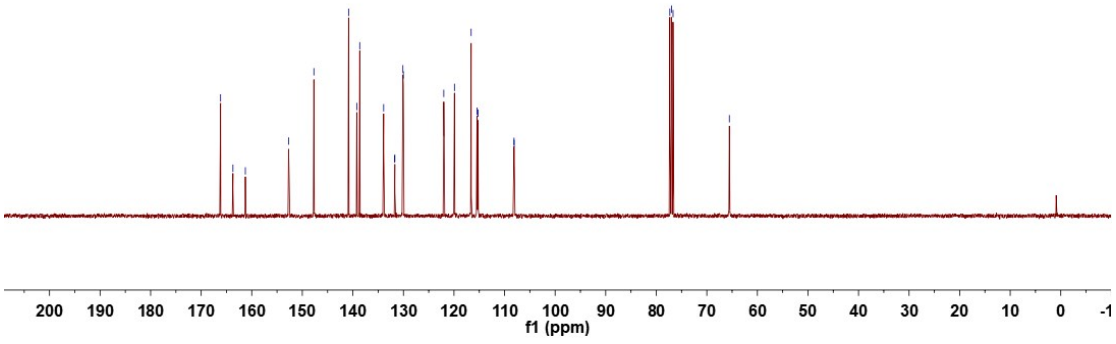


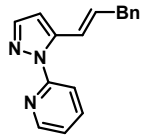




3v

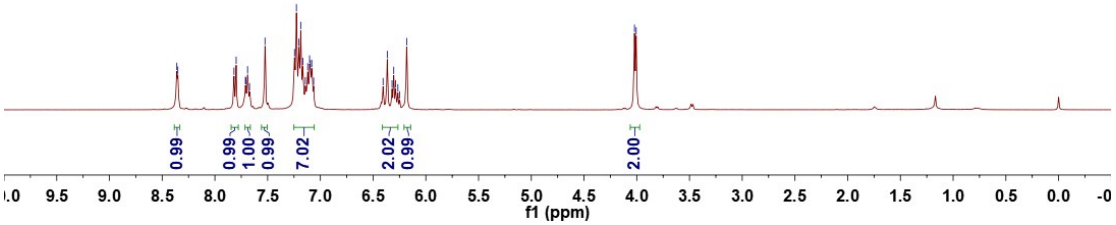
^{13}C NMR (100 MHz, $CDCl_3$)

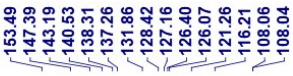


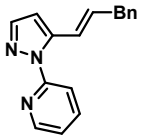


3w

^{1}H NMR (400 MHz, $CDCl_3$)

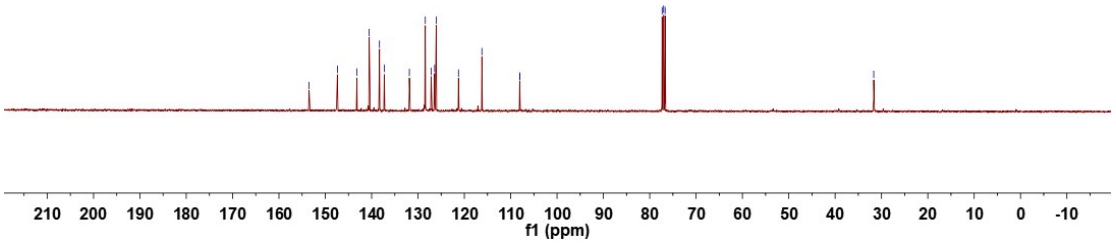


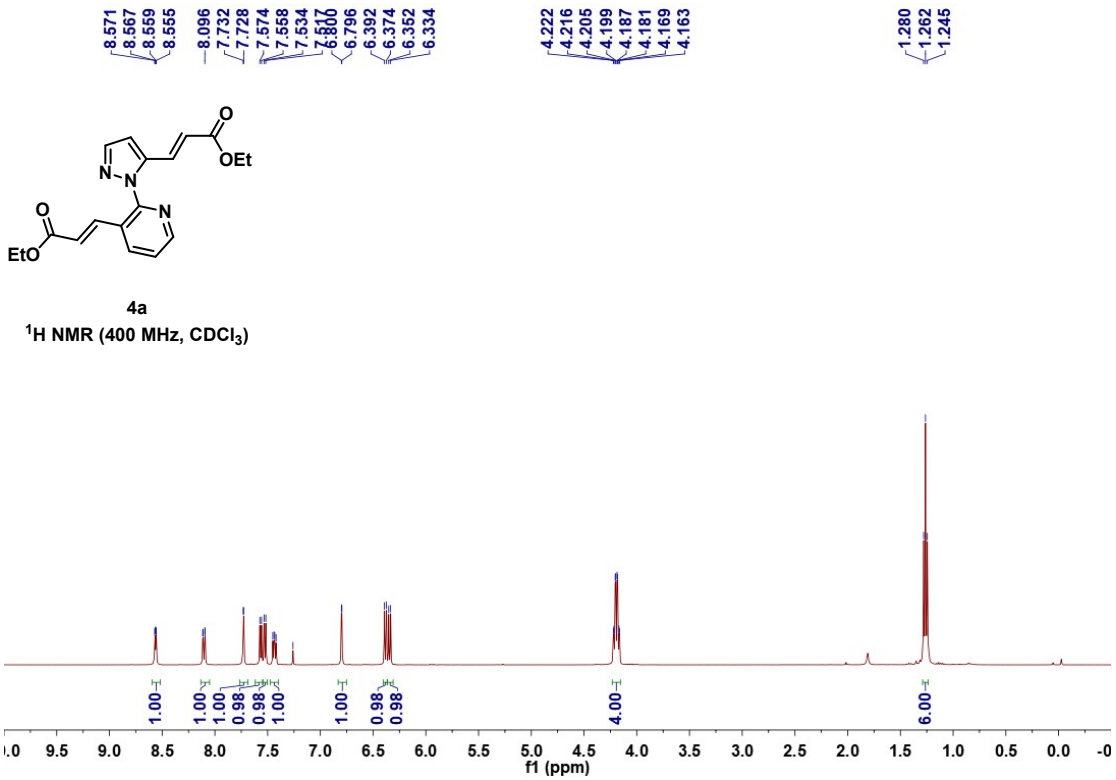




3w

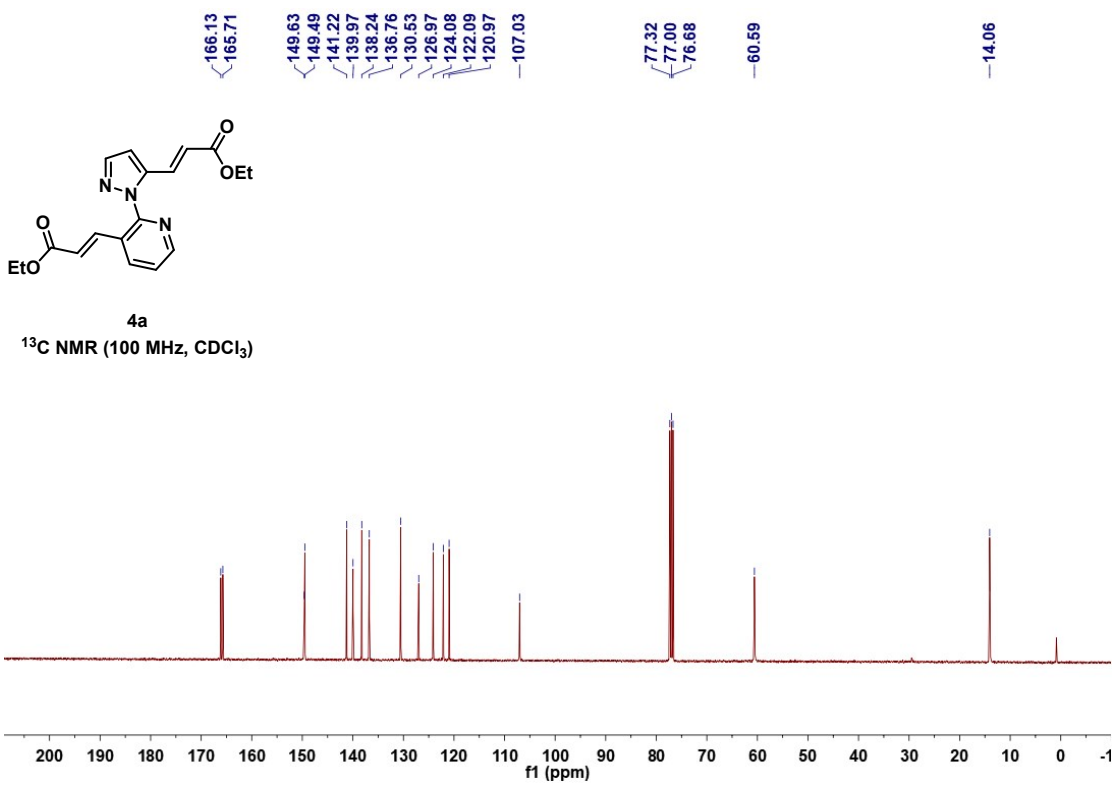
^{13}C NMR (100 MHz, $CDCl_3$)





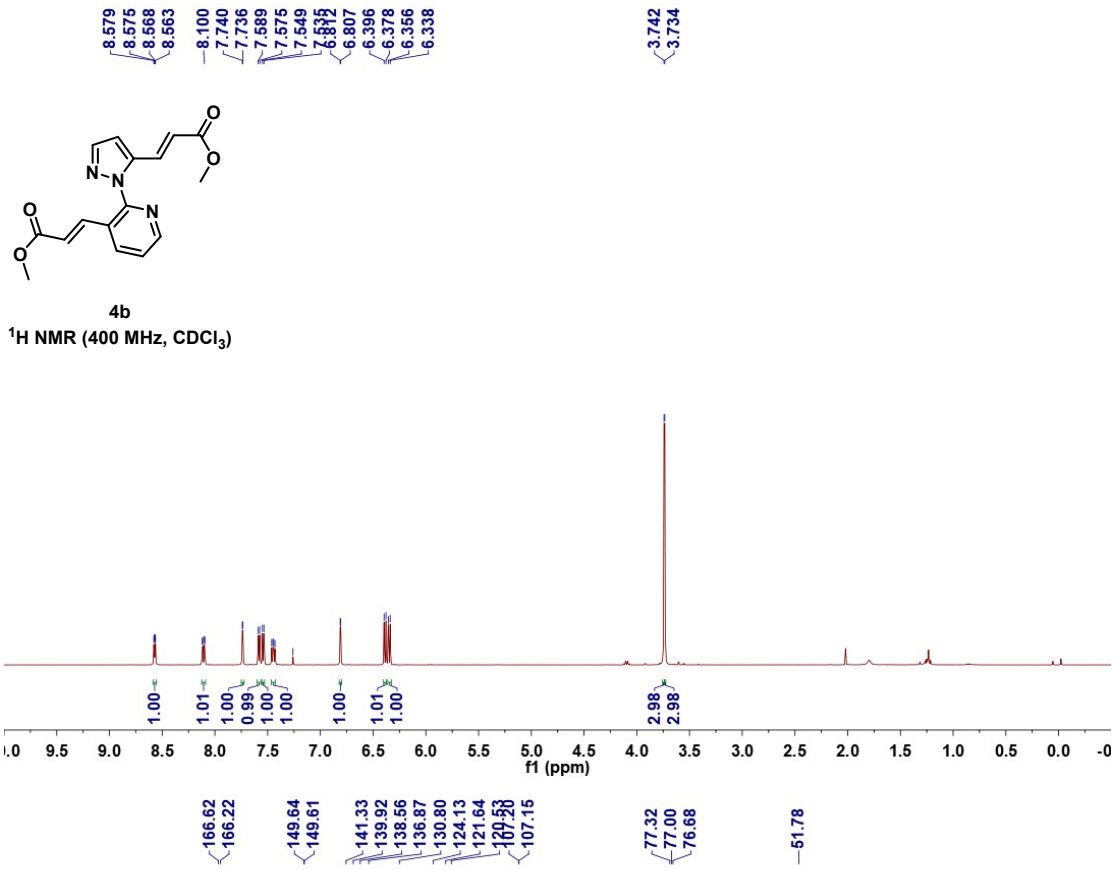
4a

^{1}H NMR (400 MHz, $CDCl_3$)



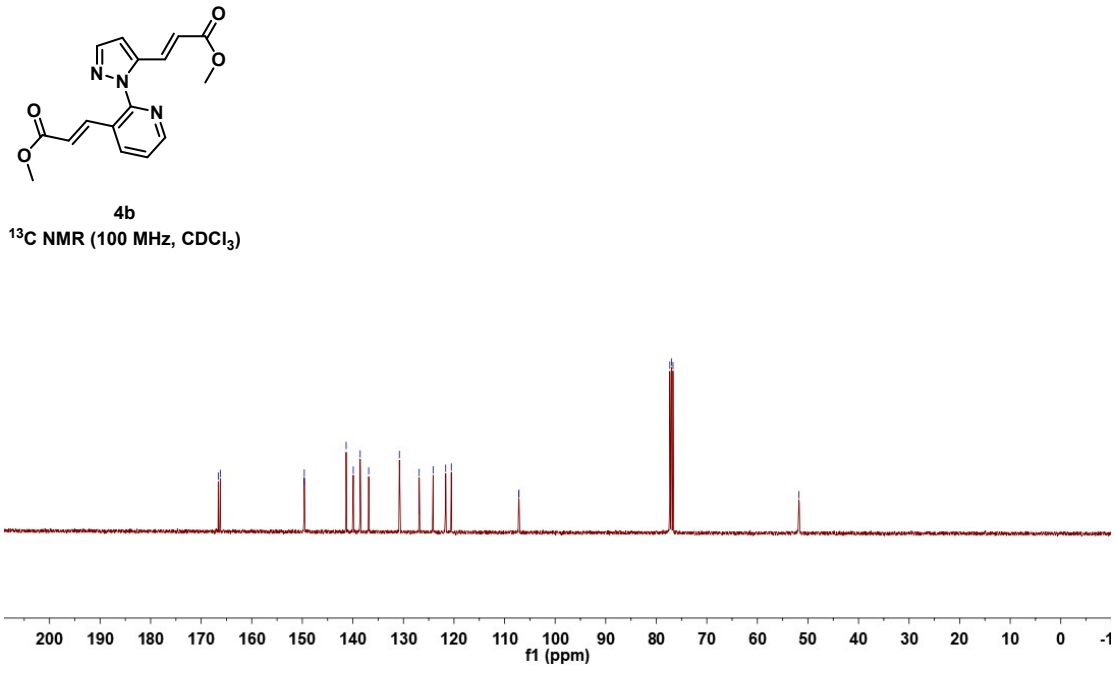
4a

^{13}C NMR (100 MHz, $CDCl_3$)



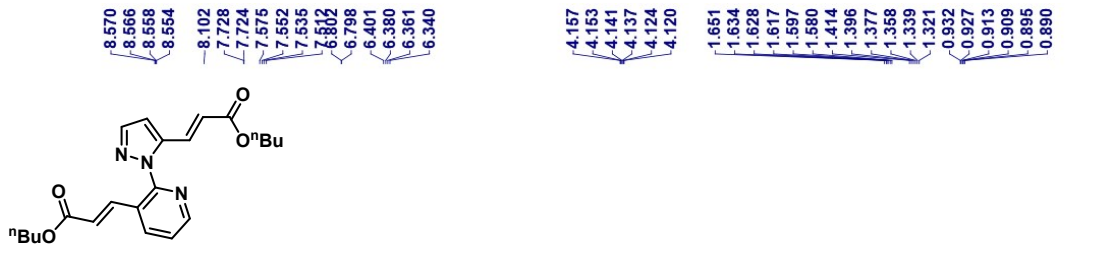
4b

^{1}H NMR (400 MHz, $CDCl_3$)



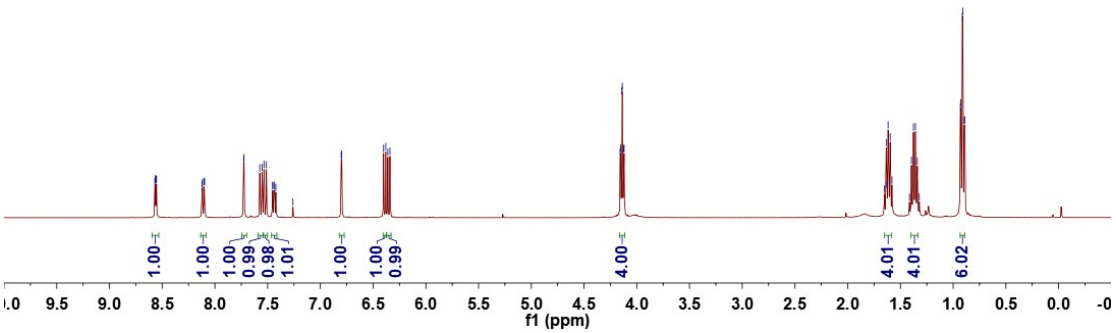
4b

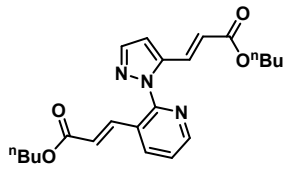
^{13}C NMR (100 MHz, $CDCl_3$)



4c

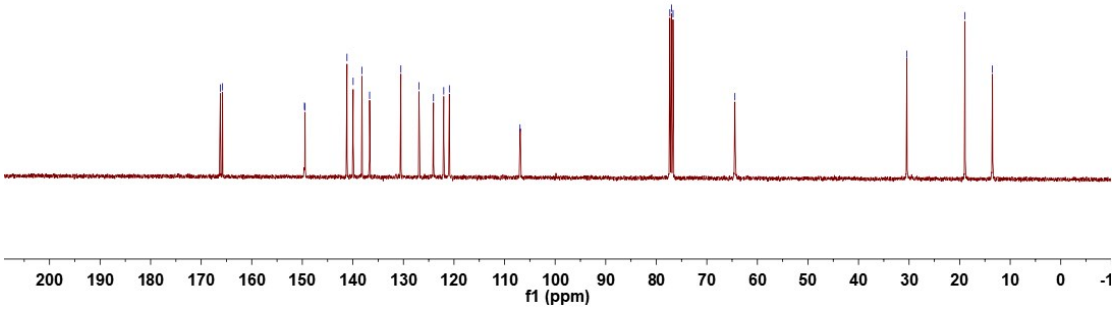
^{1}H NMR (400 MHz, $CDCl_3$)

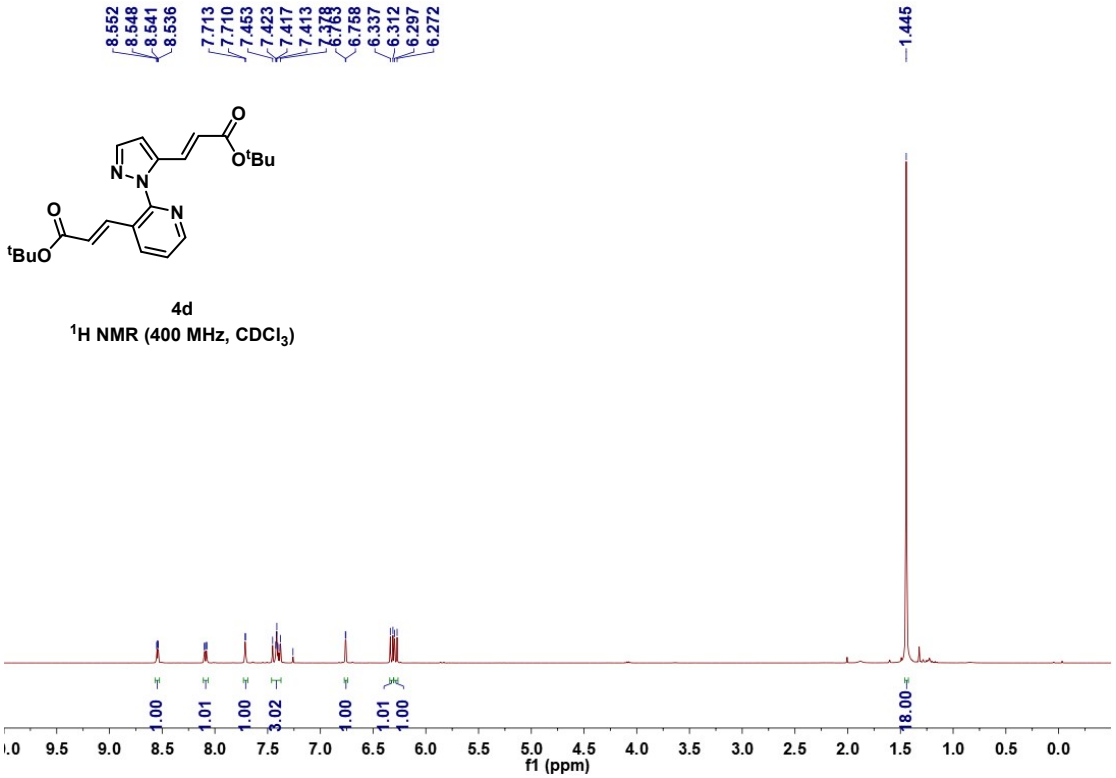




4c

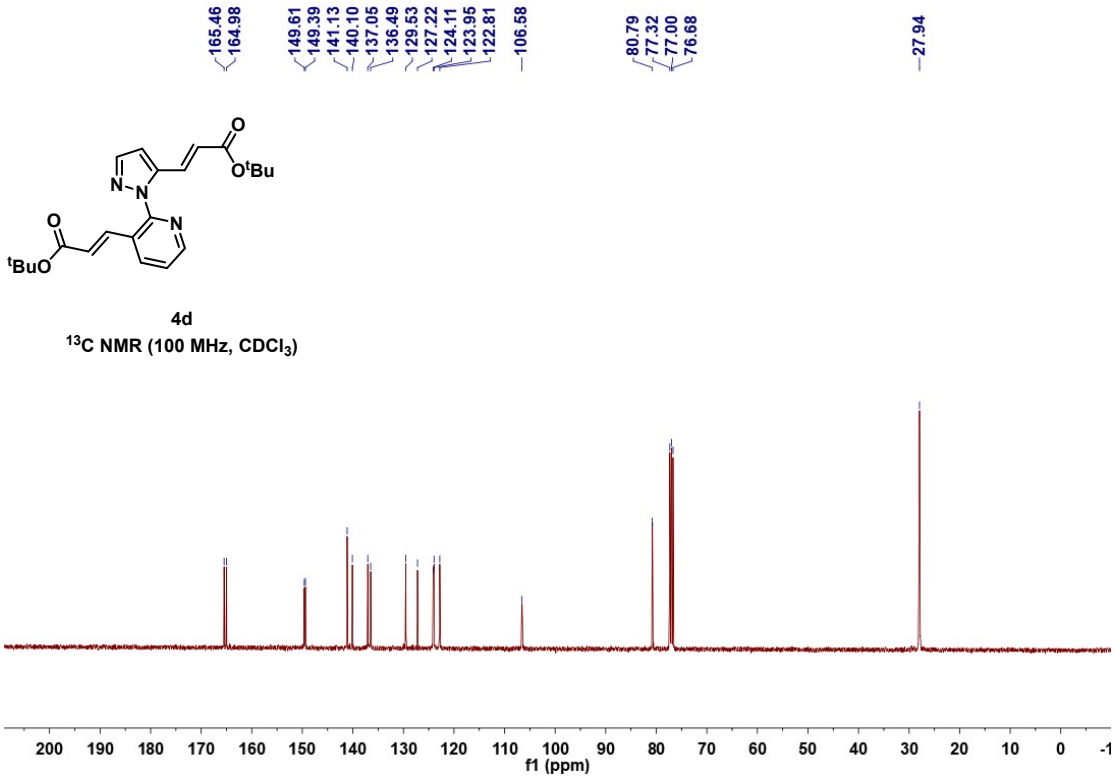
^{13}C NMR (100 MHz, $CDCl_3$)





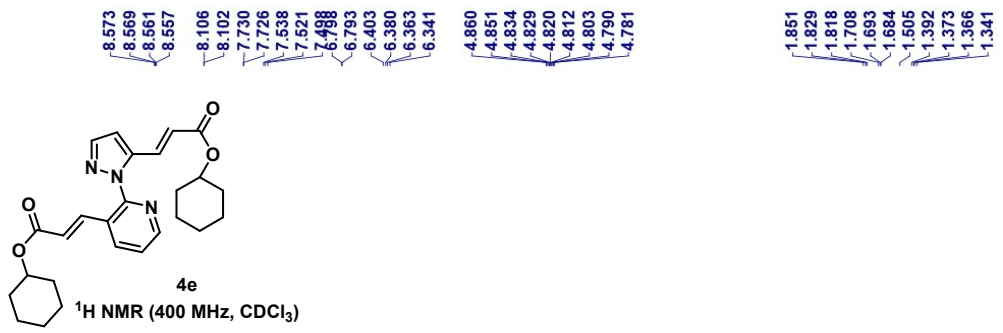
4d

^{1}H NMR (400 MHz, $CDCl_3$)



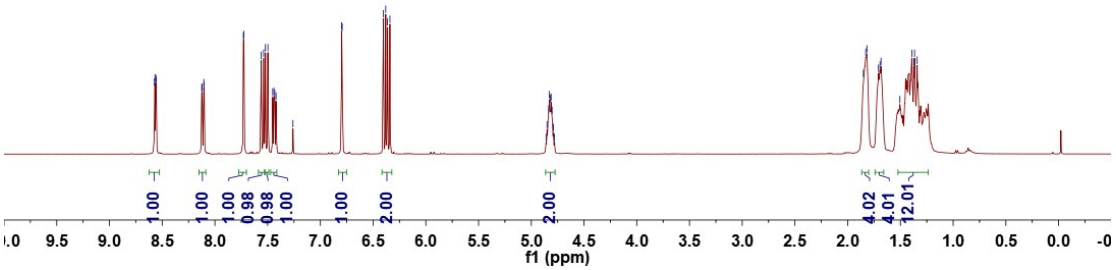
4d

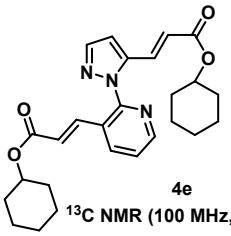
^{13}C NMR (100 MHz, $CDCl_3$)



4e

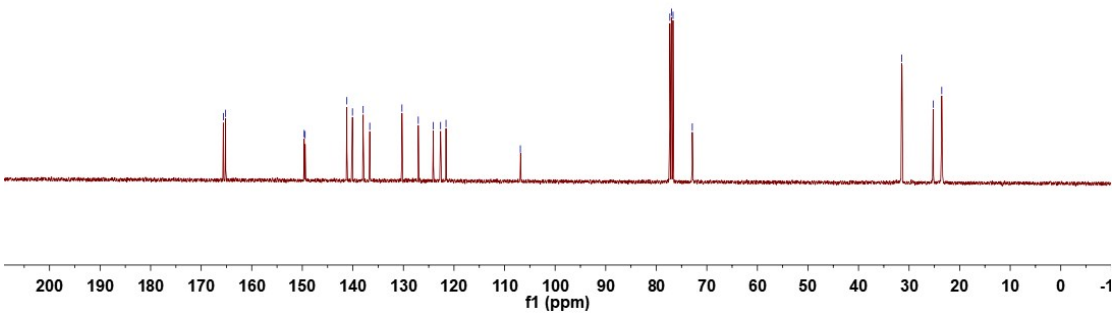
^{1}H NMR (400 MHz, $CDCl_3$)

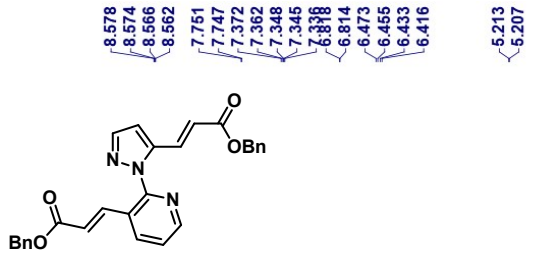




4e

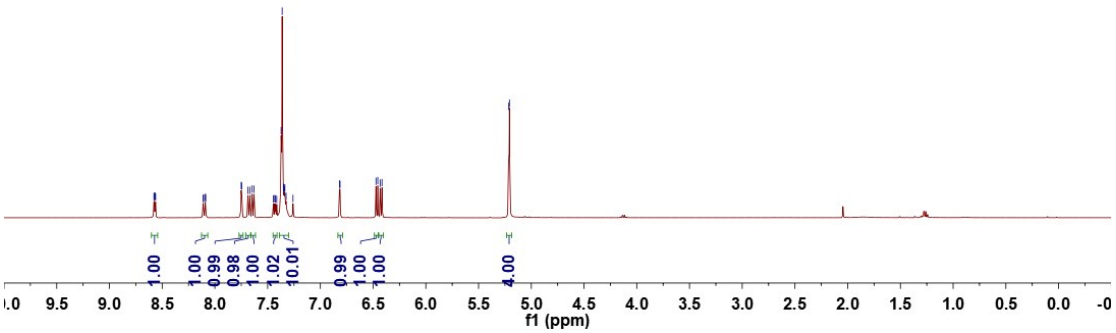
^{13}C NMR (100 MHz, $CDCl_3$)

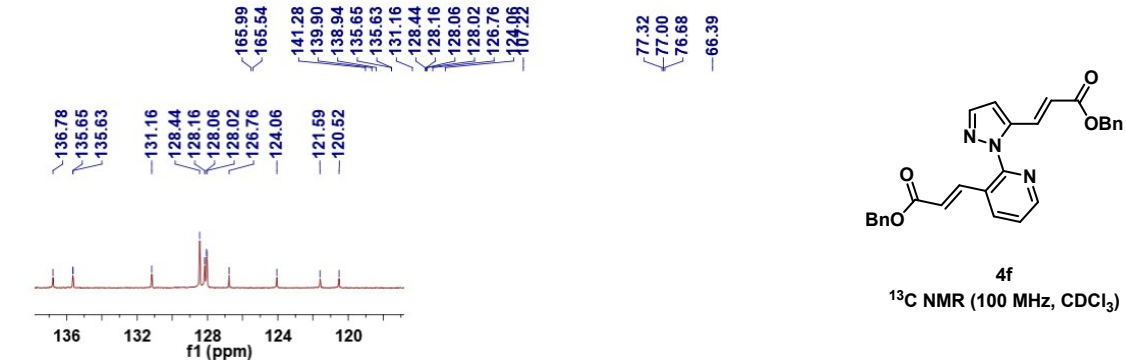




4f

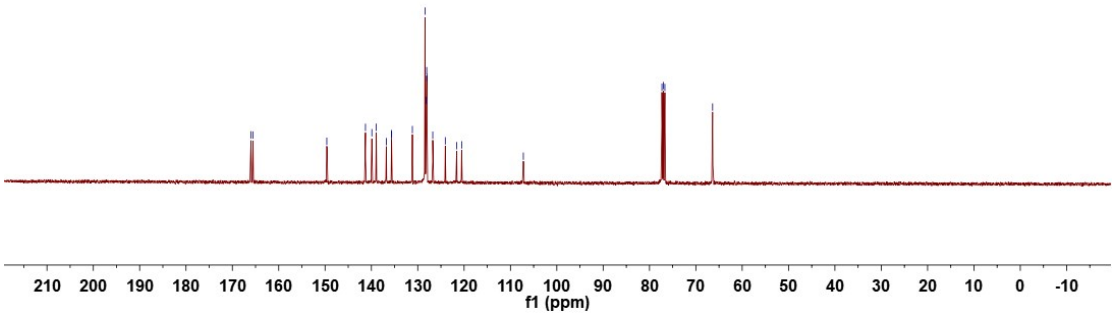
^{1}H NMR (400 MHz, $CDCl_3$)

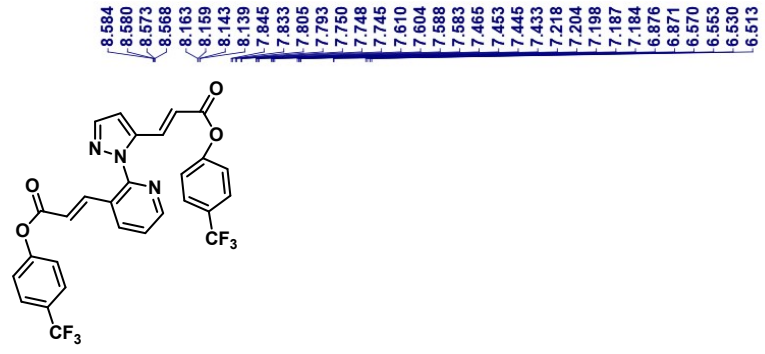




4f

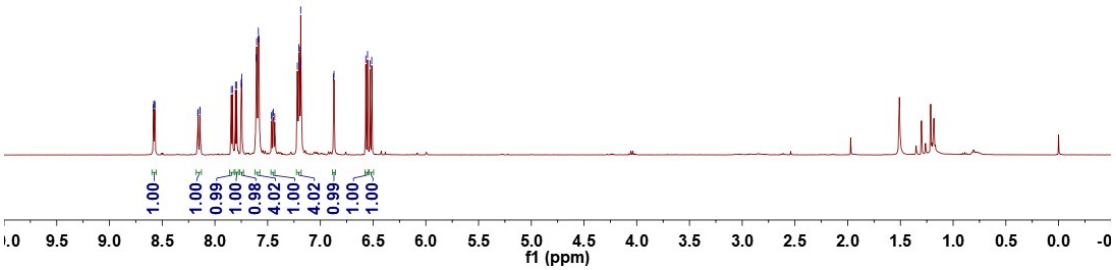
^{13}C NMR (100 MHz, $CDCl_3$)

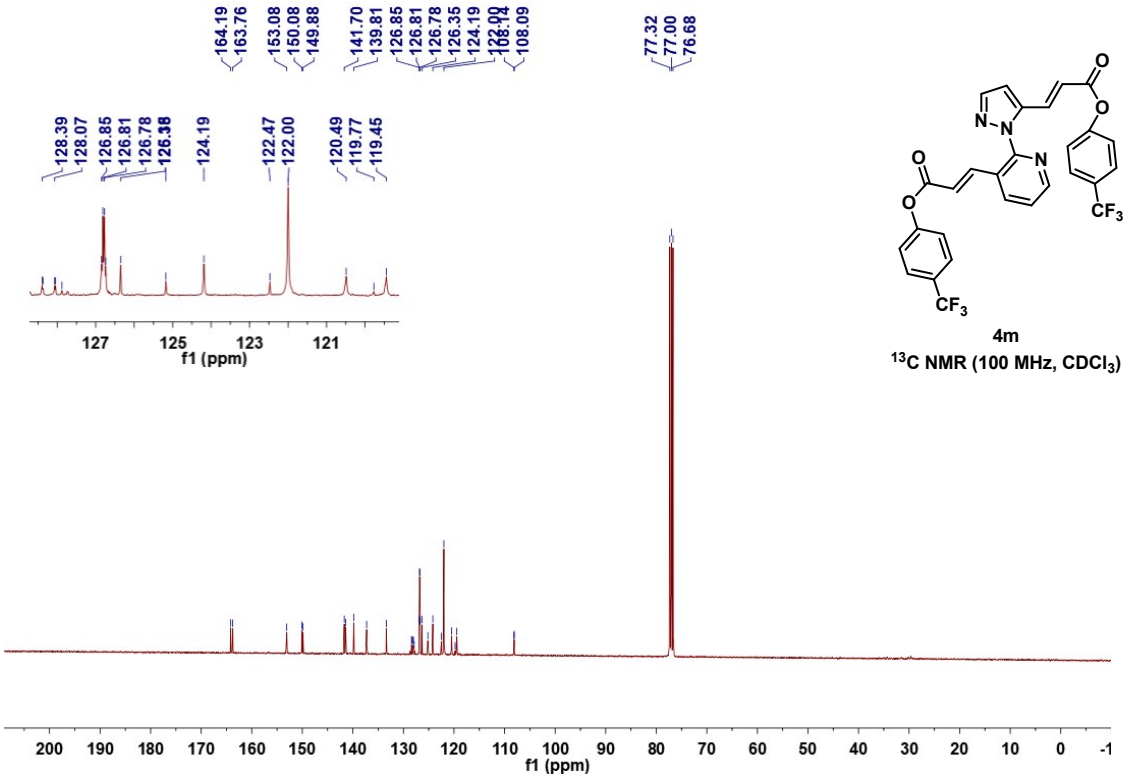




4m

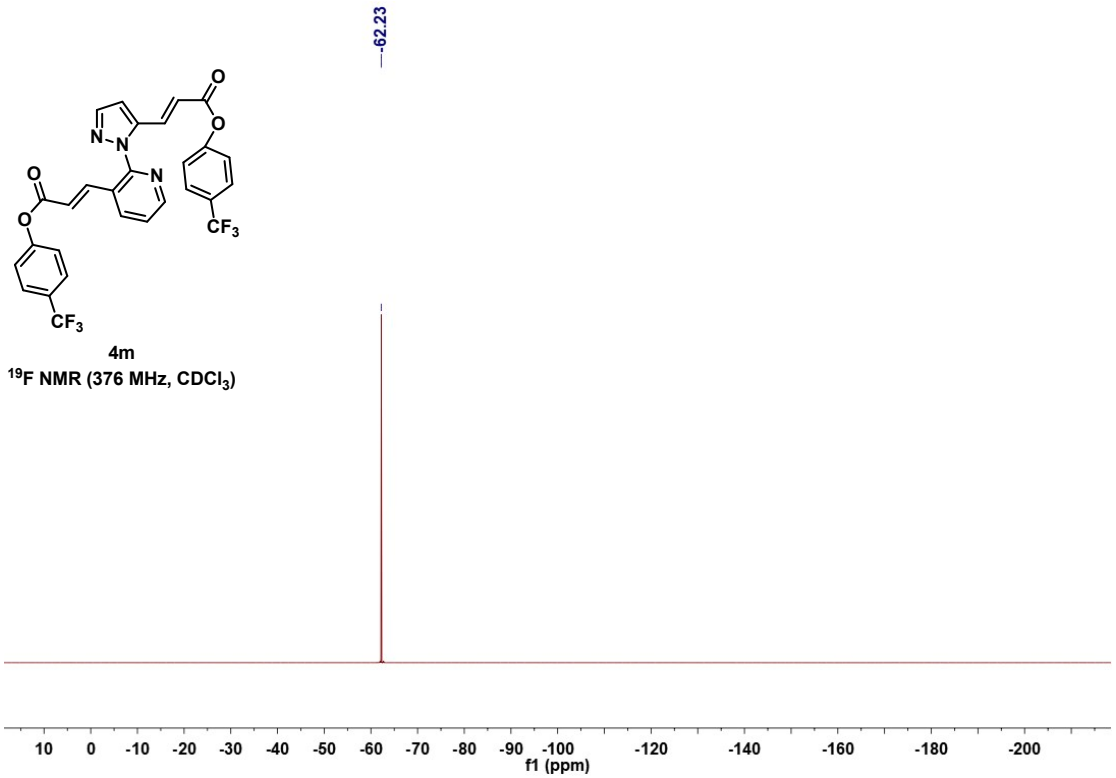
^{1}H NMR (400 MHz, $CDCl_3$)





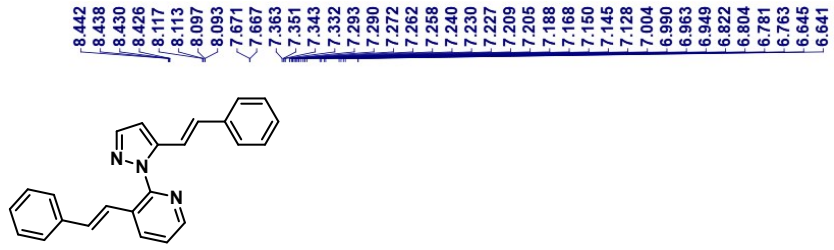
4m

^{13}C NMR (100 MHz, $CDCl_3$)



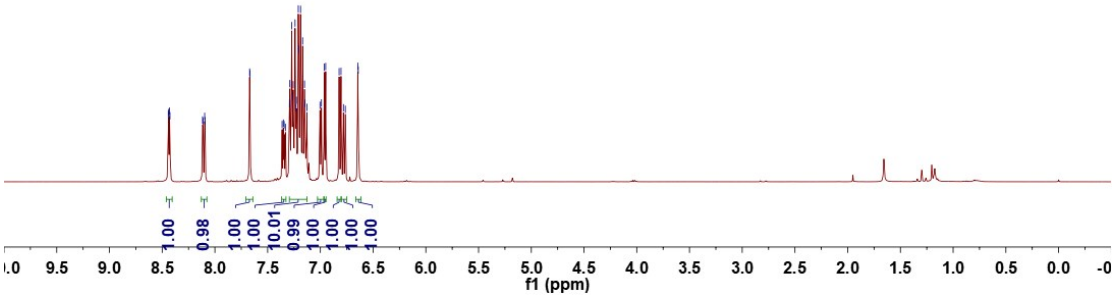
4m

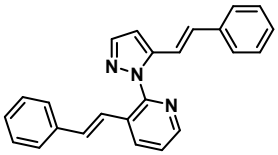
^{19}F NMR (376 MHz, $CDCl_3$)



4p

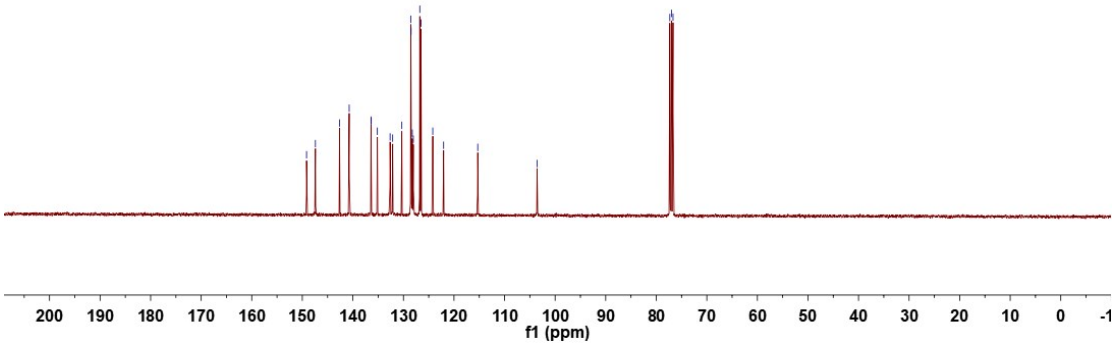
^{1}H NMR (400 MHz, $CDCl_3$)

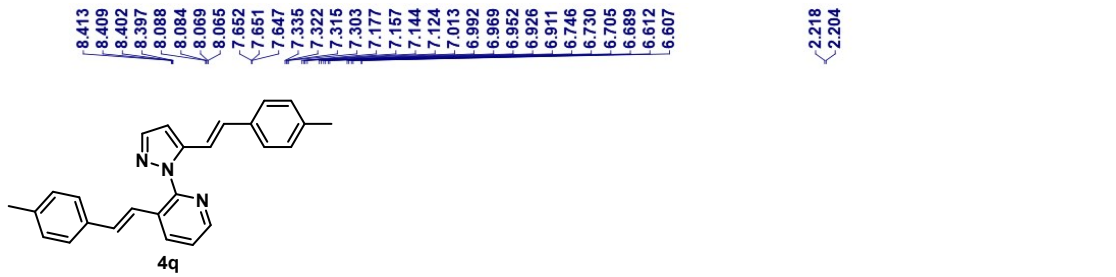




4p

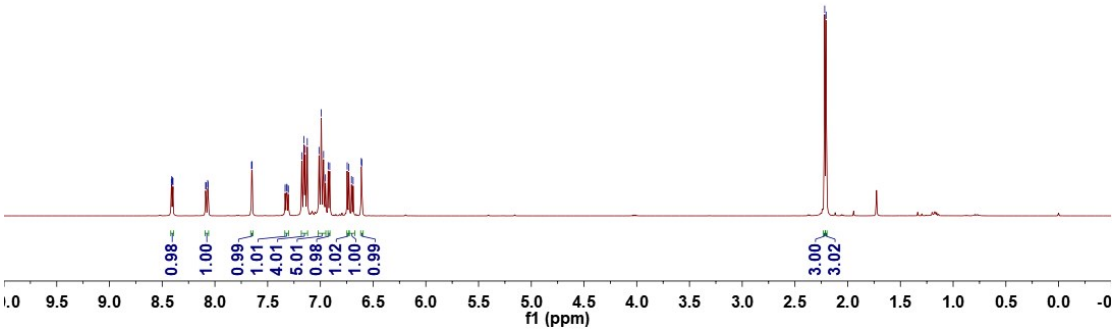
^{13}C NMR (100 MHz, $CDCl_3$)

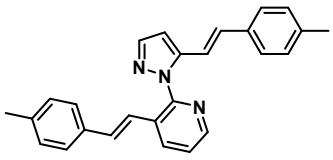




4q

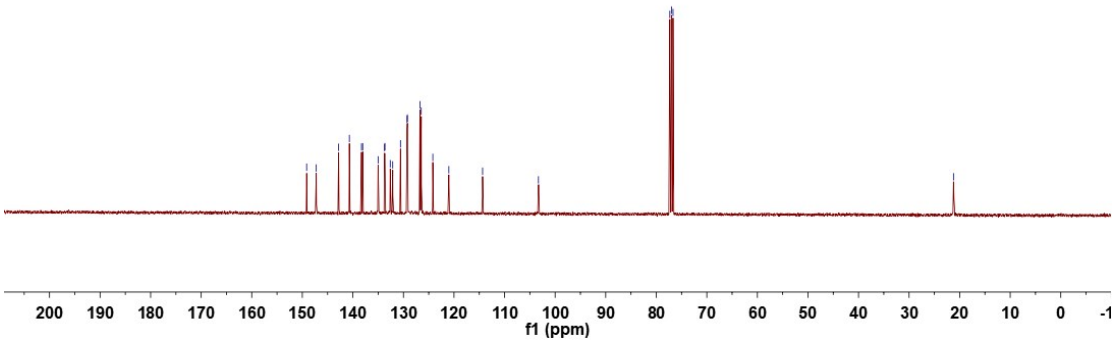
^{1}H NMR (400 MHz, $CDCl_3$)

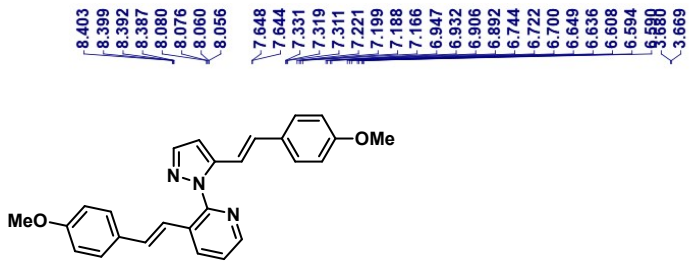




4q

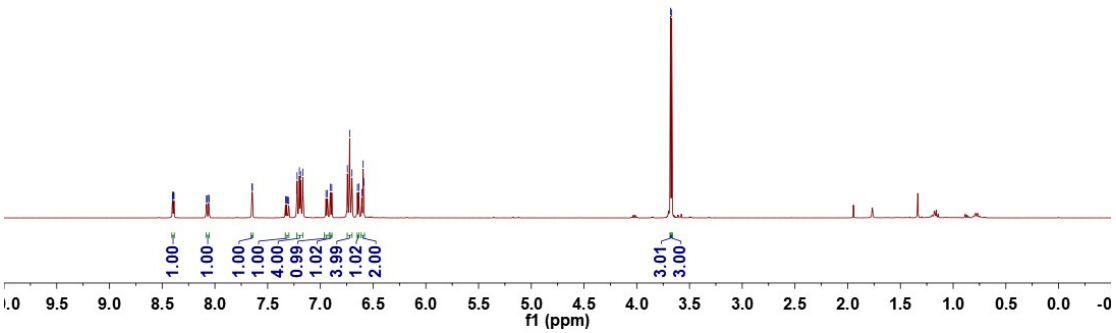
^{13}C NMR (100 MHz, $CDCl_3$)

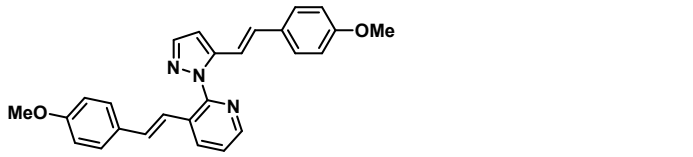




4s

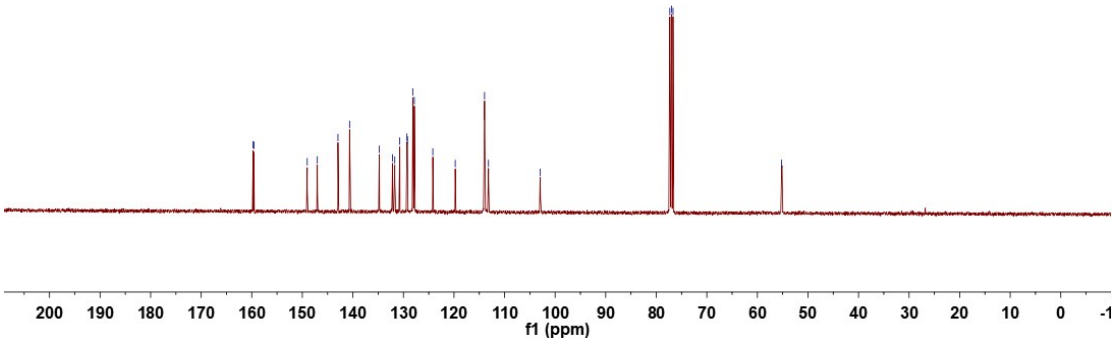
^{1}H NMR (400 MHz, $CDCl_3$)

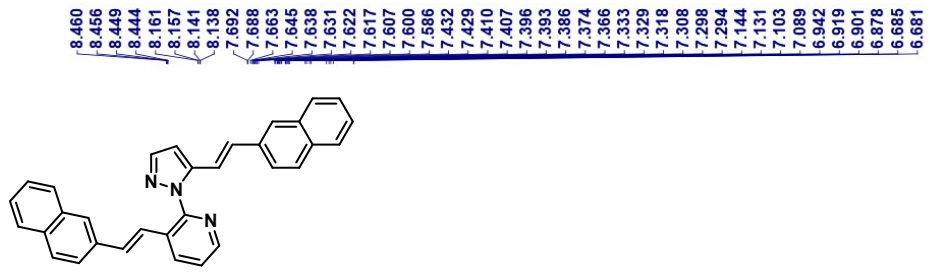




4s

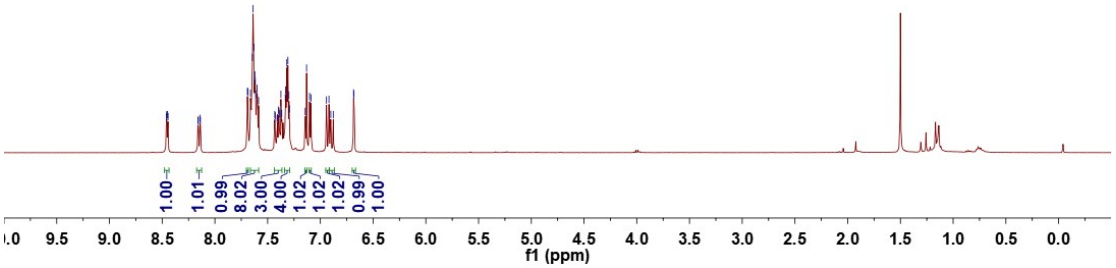
^{13}C NMR (100 MHz, $CDCl_3$)

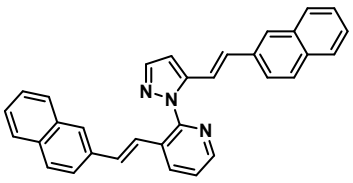




4v

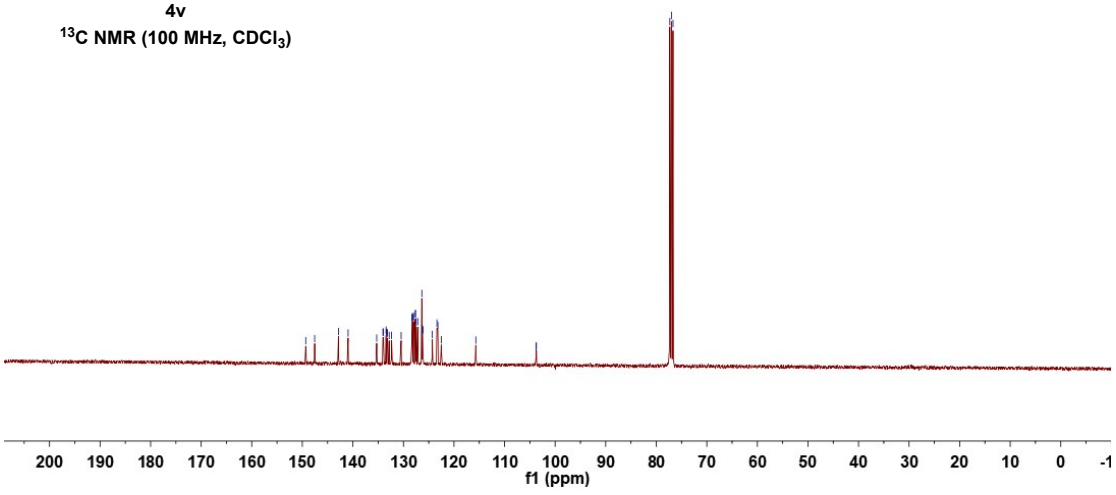
^{1}H NMR (400 MHz, $CDCl_3$)

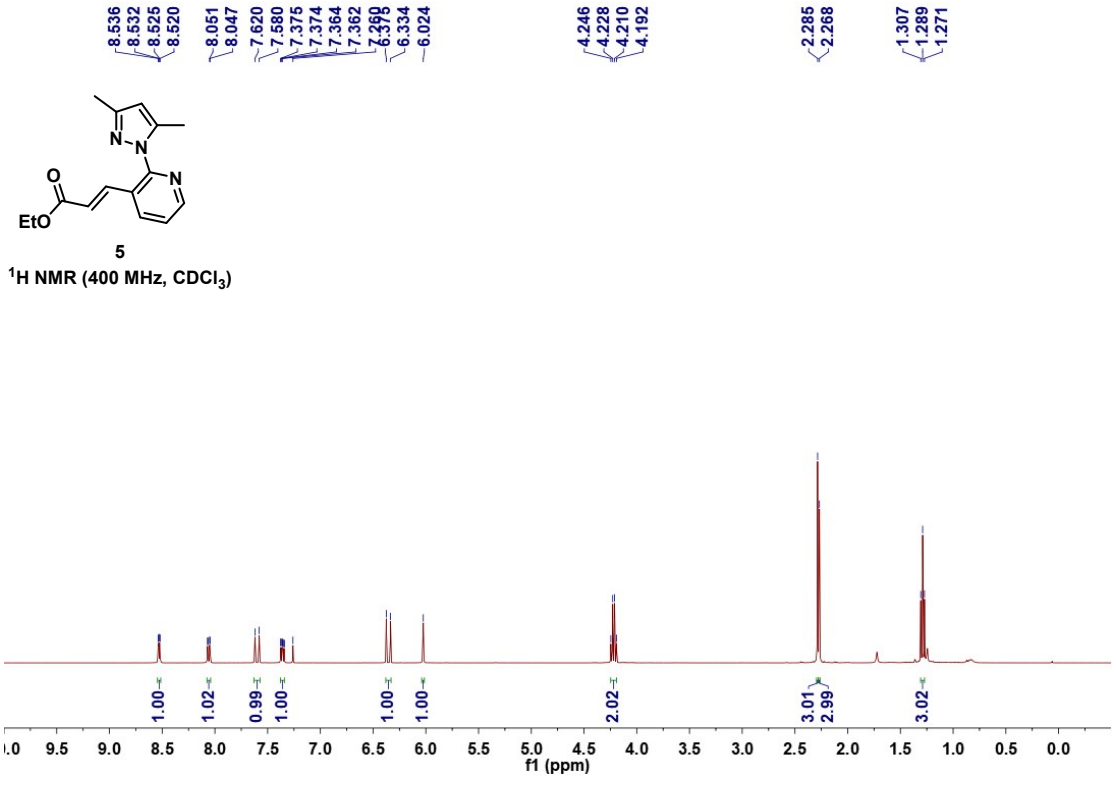




4v

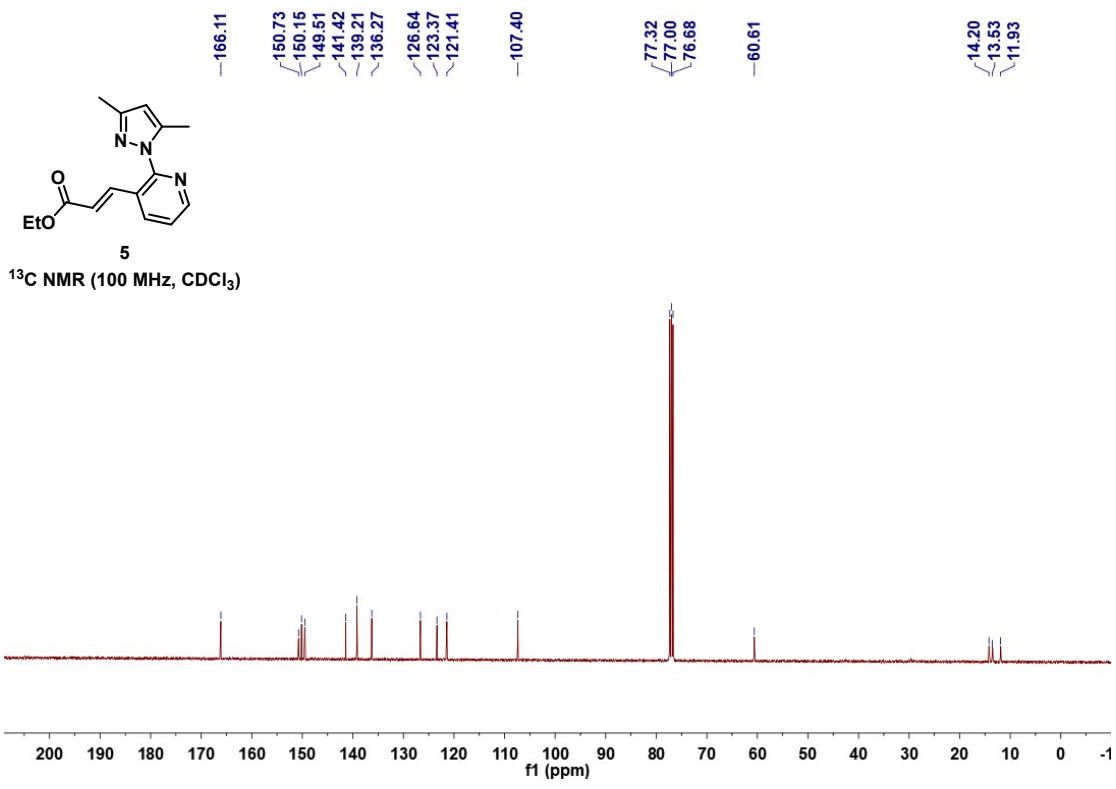
^{13}C NMR (100 MHz, $CDCl_3$)





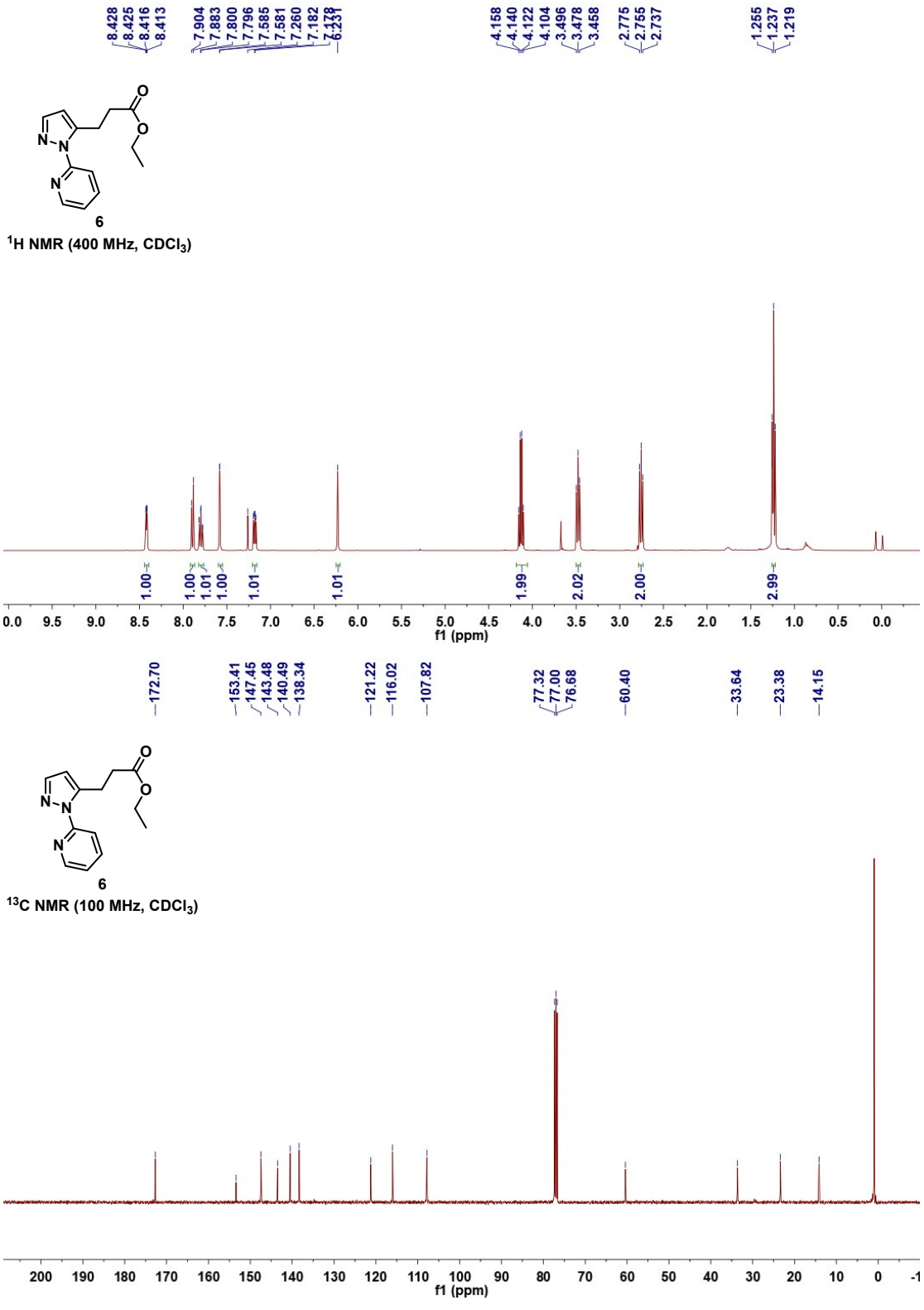
5

^{1}H NMR (400 MHz, $CDCl_3$)



5

^{13}C NMR (100 MHz, $CDCl_3$)

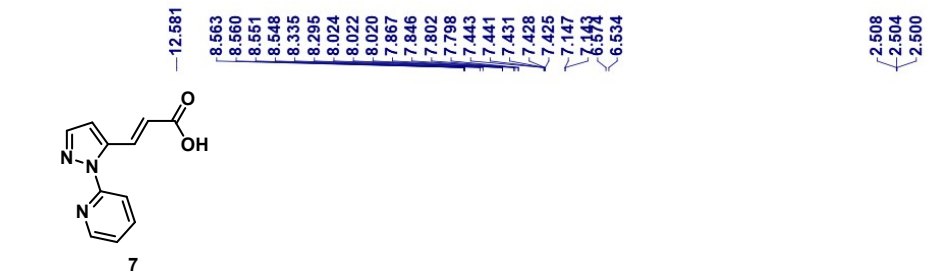


6

^{1}H NMR (400 MHz, $CDCl_3$)

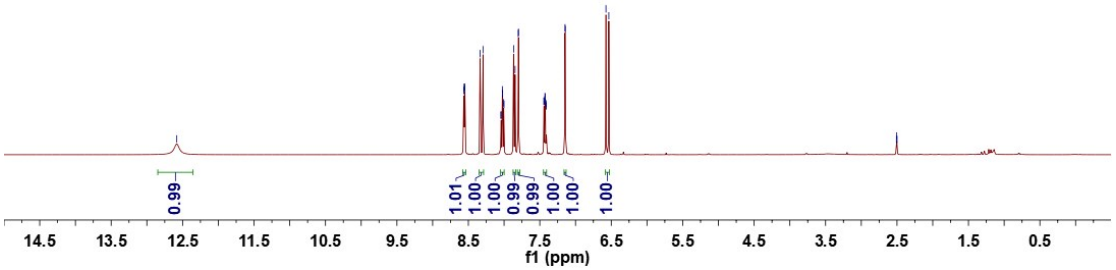
6

^{13}C NMR (100 MHz, $CDCl_3$)



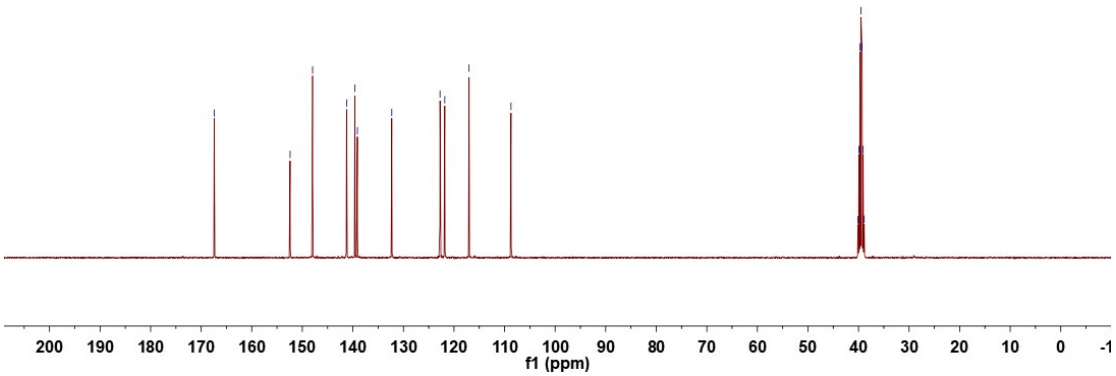
7

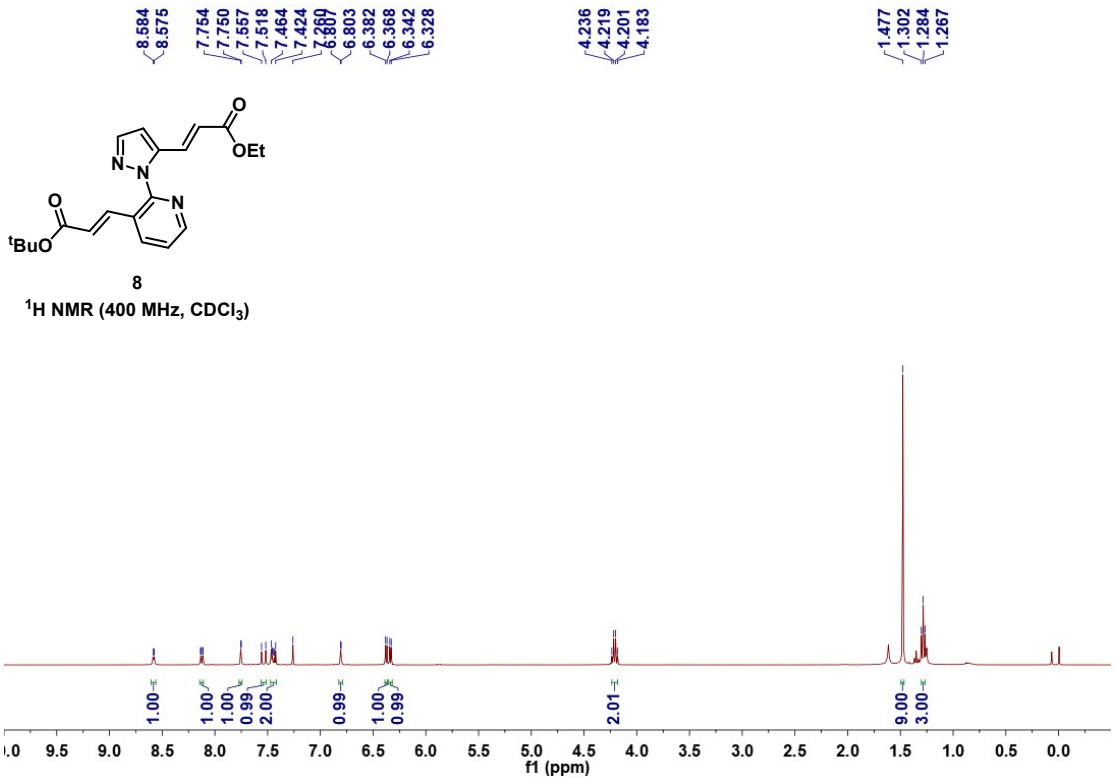
^{1}H NMR (400 MHz, DMSO-d_6)



7

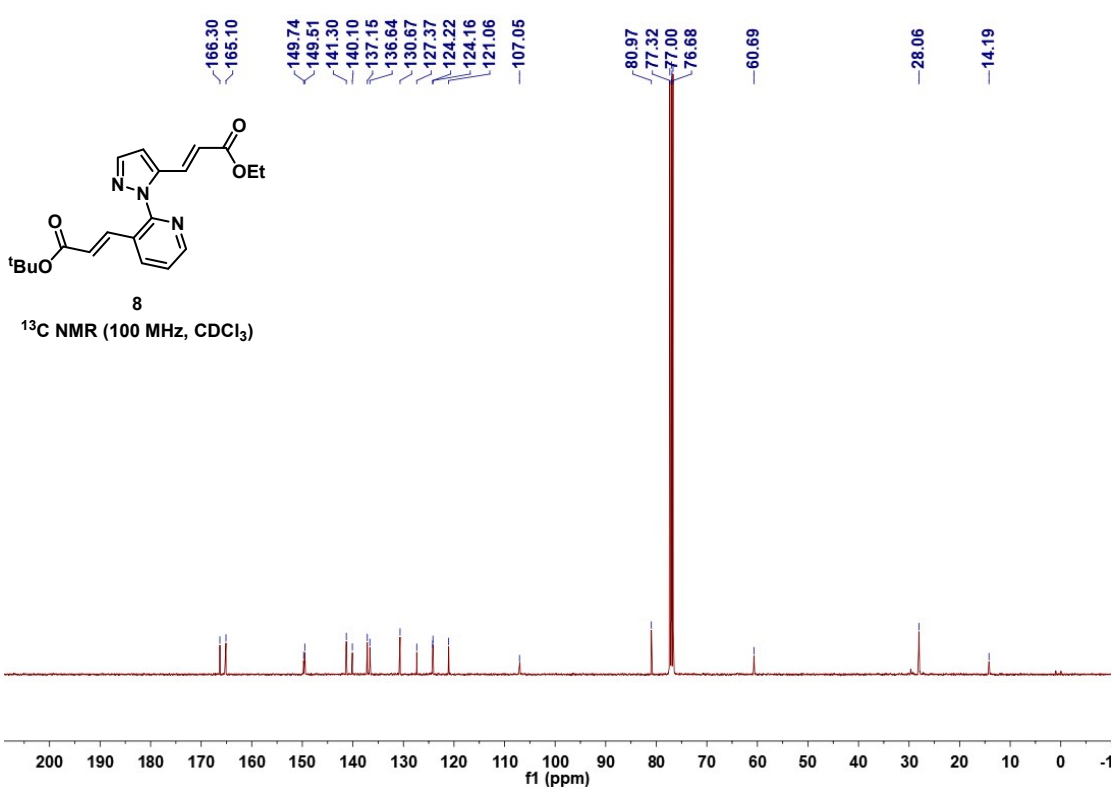
^{13}C NMR (100 MHz, DMSO-d_6)





8

^{1}H NMR (400 MHz, $CDCl_3$)



8

^{13}C NMR (100 MHz, $CDCl_3$)

Crystallography:

Single crystals of complexes **3i** (CCDC reference number 2036012) and **4a** (CCDC reference number 2039563) suitable for X-ray diffraction were obtained by crystallization from petroleum ether/CH_2Cl_2 (2:1). Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo Kα radiation (ω−2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for these complexes. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Tables 1-14.

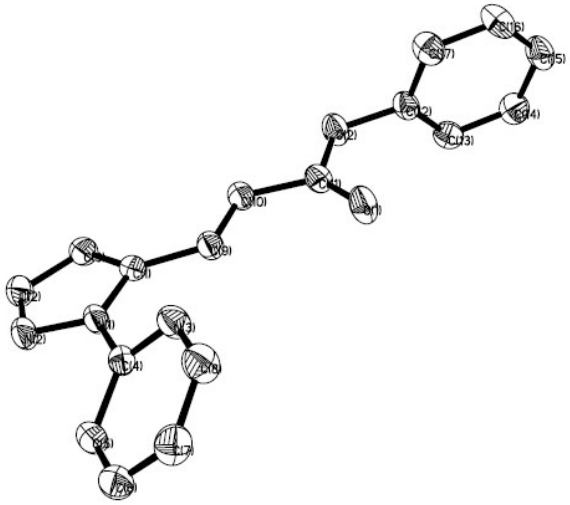


Figure 1. ORTEP drawing for the product **3i**.

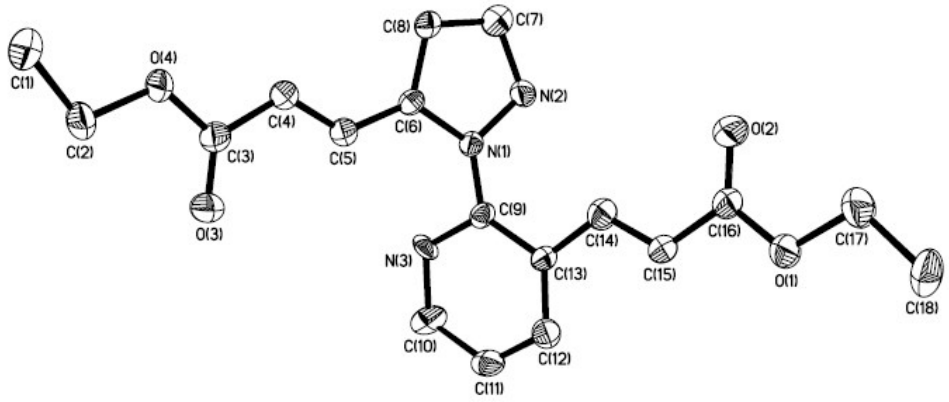


Figure 2. ORTEP drawing for the product **4a**.

X-Ray Crystallographic Data of 3i and 4a:

X-Ray crystallographic data of **3i**:

Table 1. Crystal data and structure refinement for N200907A.

Identification code	n200907a
Empirical formula	$C_{17}H_{13}N_3O_2$
Formula weight	291.30
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.3313(8) A alpha = 108.233(2) deg.
	b = 9.8531(9) A beta = 107.923(2) deg.
	c = 10.1569(9) A gamma = 93.672(2) deg.
Volume	741.52(12) A^3
Z, Calculated density	2, 1.305 Mg/m^3
Absorption coefficient	0.088 mm^-1
F(000)	304
Crystal size	0.220 x 0.210 x 0.180 mm
Theta range for data collection	2.211 to 26.499 deg.
Limiting indices	-10<=h<=6, -10<=k<=12, -10<=l<=12
Reflections collected / unique	4877 / 3072 [R(int) = 0.0128]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3072 / 0 / 199
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1050
R indices (all data)	R1 = 0.0524, wR2 = 0.1122
Extinction coefficient	n/a
Largest diff. peak and hole	0.155 and -0.176 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for N200907A. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	5028(1)	3387(1)	2185(1)	45(1)
N(2)	5372(2)	4243(1)	1445(1)	55(1)
N(3)	4976(2)	1004(1)	2154(1)	54(1)
O(1)	2451(2)	2022(1)	5737(1)	64(1)
O(2)	585(1)	3552(1)	5902(1)	58(1)
C(1)	3909(2)	3896(1)	2887(1)	42(1)
C(2)	4461(2)	5278(2)	1688(2)	55(1)
C(3)	3535(2)	5119(2)	2574(2)	50(1)
C(4)	5845(2)	2154(1)	2116(1)	43(1)
C(5)	7457(2)	2220(2)	1997(2)	57(1)
C(6)	8185(2)	1000(2)	1875(2)	64(1)
C(7)	7306(2)	-222(2)	1897(2)	64(1)
C(8)	5735(2)	-162(2)	2054(2)	63(1)
C(9)	3388(2)	3257(1)	3836(1)	44(1)
C(10)	2222(2)	3676(2)	4440(2)	49(1)
C(11)	1815(2)	2970(1)	5404(2)	45(1)
C(12)	5(2)	2914(1)	6776(2)	46(1)
C(13)	651(2)	3572(2)	8279(2)	52(1)
C(14)	-9(2)	2996(2)	9123(2)	59(1)
C(15)	-1279(2)	1789(2)	8461(2)	62(1)
C(16)	-1897(2)	1140(2)	6952(2)	66(1)
C(17)	-1250(2)	1703(2)	6098(2)	60(1)

Table 3. Bond lengths [A] and angles [deg] for N200907A.

N(1)-N(2)	1.3619(14)
N(1)-C(1)	1.3694(16)
N(1)-C(4)	1.4235(16)
N(2)-C(2)	1.3171(19)
N(3)-C(4)	1.3224(17)
N(3)-C(8)	1.3376(19)
O(1)-C(11)	1.1912(16)
O(2)-C(11)	1.3594(16)
O(2)-C(12)	1.4108(15)
C(1)-C(3)	1.3711(18)
C(1)-C(9)	1.4539(17)
C(2)-C(3)	1.388(2)
C(2)-H(2)	0.9300
C(3)-H(3)	0.9300
C(4)-C(5)	1.3842(19)
C(5)-C(6)	1.370(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.378(2)
C(6)-H(6)	0.9300
C(7)-C(8)	1.369(2)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
C(9)-C(10)	1.3240(18)
C(9)-H(9)	0.9300
C(10)-C(11)	1.4685(18)
C(10)-H(10)	0.9300
C(12)-C(13)	1.367(2)
C(12)-C(17)	1.370(2)
C(13)-C(14)	1.384(2)
C(13)-H(13)	0.9300
C(14)-C(15)	1.373(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.372(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.378(2)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
N(2)-N(1)-C(1)	111.68(10)
N(2)-N(1)-C(4)	117.49(10)
C(1)-N(1)-C(4)	130.82(10)
C(2)-N(2)-N(1)	104.74(11)
C(4)-N(3)-C(8)	116.16(12)

C(11)-O(2)-C(12)	116.48(10)
N(1)-C(1)-C(3)	105.65(11)
N(1)-C(1)-C(9)	124.03(11)
C(3)-C(1)-C(9)	130.19(12)
N(2)-C(2)-C(3)	111.98(12)
N(2)-C(2)-H(2)	124.0
C(3)-C(2)-H(2)	124.0
C(1)-C(3)-C(2)	105.94(12)
C(1)-C(3)-H(3)	127.0
C(2)-C(3)-H(3)	127.0
N(3)-C(4)-C(5)	124.51(13)
N(3)-C(4)-N(1)	116.52(11)
C(5)-C(4)-N(1)	118.97(12)
C(6)-C(5)-C(4)	117.75(14)
C(6)-C(5)-H(5)	121.1
C(4)-C(5)-H(5)	121.1
C(5)-C(6)-C(7)	119.17(14)
C(5)-C(6)-H(6)	120.4
C(7)-C(6)-H(6)	120.4
C(8)-C(7)-C(6)	118.40(14)
C(8)-C(7)-H(7)	120.8
C(6)-C(7)-H(7)	120.8
N(3)-C(8)-C(7)	123.97(14)
N(3)-C(8)-H(8)	118.0
C(7)-C(8)-H(8)	118.0
C(10)-C(9)-C(1)	124.56(12)
C(10)-C(9)-H(9)	117.7
C(1)-C(9)-H(9)	117.7
C(9)-C(10)-C(11)	120.02(12)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
O(1)-C(11)-O(2)	122.79(12)
O(1)-C(11)-C(10)	126.47(12)
O(2)-C(11)-C(10)	110.73(11)
C(13)-C(12)-C(17)	121.83(13)
C(13)-C(12)-O(2)	118.80(13)
C(17)-C(12)-O(2)	119.28(13)
C(12)-C(13)-C(14)	118.44(14)
C(12)-C(13)-H(13)	120.8
C(14)-C(13)-H(13)	120.8
C(15)-C(14)-C(13)	120.50(14)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	120.04(14)

C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(15)-C(16)-C(17)	120.05(15)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(12)-C(17)-C(16)	119.14(14)
C(12)-C(17)-H(17)	120.4
C(16)-C(17)-H(17)	120.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for N200907A. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	46(1)	49(1)	52(1)	28(1)	24(1)	10(1)
N(2)	58(1)	62(1)	65(1)	40(1)	31(1)	13(1)
N(3)	53(1)	50(1)	70(1)	27(1)	29(1)	12(1)
O(1)	81(1)	61(1)	82(1)	40(1)	54(1)	31(1)
O(2)	63(1)	65(1)	73(1)	39(1)	43(1)	26(1)
C(1)	36(1)	46(1)	46(1)	19(1)	14(1)	6(1)
C(2)	57(1)	57(1)	66(1)	38(1)	23(1)	12(1)
C(3)	47(1)	52(1)	59(1)	27(1)	20(1)	13(1)
C(4)	45(1)	50(1)	41(1)	21(1)	18(1)	11(1)
C(5)	52(1)	68(1)	68(1)	36(1)	31(1)	15(1)
C(6)	59(1)	86(1)	71(1)	40(1)	36(1)	31(1)
C(7)	76(1)	64(1)	66(1)	28(1)	34(1)	33(1)
C(8)	70(1)	51(1)	81(1)	29(1)	35(1)	15(1)
C(9)	46(1)	45(1)	48(1)	20(1)	19(1)	7(1)
C(10)	47(1)	54(1)	55(1)	27(1)	22(1)	12(1)
C(11)	47(1)	44(1)	50(1)	16(1)	24(1)	9(1)
C(12)	49(1)	50(1)	54(1)	22(1)	31(1)	18(1)
C(13)	49(1)	50(1)	57(1)	14(1)	22(1)	10(1)
C(14)	64(1)	70(1)	48(1)	18(1)	27(1)	17(1)
C(15)	70(1)	70(1)	68(1)	31(1)	45(1)	17(1)
C(16)	70(1)	58(1)	70(1)	12(1)	38(1)	-5(1)
C(17)	67(1)	62(1)	48(1)	8(1)	28(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for N200907A.

	x	y	z	U(eq)
H(2)	4440	6026	1311	66
H(3)	2810	5720	2889	61
H(5)	8026	3065	2000	68
H(6)	9259	995	1779	77
H(7)	7768	-1066	1807	77
H(8)	5161	-981	2094	76
H(9)	3912	2501	4032	53
H(10)	1660	4418	4255	58
H(13)	1514	4387	8723	62
H(14)	409	3430	10147	71
H(15)	-1719	1411	9036	75
H(16)	-2753	321	6505	79
H(17)	-1661	1265	5075	72

Table 6. Torsion angles [deg] for N200907A.

C(1)-N(1)-N(2)-C(2)	-0.19(16)
C(4)-N(1)-N(2)-C(2)	179.80(12)
N(2)-N(1)-C(1)-C(3)	0.08(15)
C(4)-N(1)-C(1)-C(3)	-179.91(13)
N(2)-N(1)-C(1)-C(9)	-176.08(12)
C(4)-N(1)-C(1)-C(9)	3.9(2)
N(1)-N(2)-C(2)-C(3)	0.23(17)
N(1)-C(1)-C(3)-C(2)	0.06(15)
C(9)-C(1)-C(3)-C(2)	175.89(13)
N(2)-C(2)-C(3)-C(1)	-0.19(18)
C(8)-N(3)-C(4)-C(5)	-0.6(2)
C(8)-N(3)-C(4)-N(1)	178.48(13)
N(2)-N(1)-C(4)-N(3)	-147.65(12)
C(1)-N(1)-C(4)-N(3)	32.3(2)
N(2)-N(1)-C(4)-C(5)	31.51(18)
C(1)-N(1)-C(4)-C(5)	-148.50(14)
N(3)-C(4)-C(5)-C(6)	1.6(2)
N(1)-C(4)-C(5)-C(6)	-177.50(13)
C(4)-C(5)-C(6)-C(7)	-0.9(2)
C(5)-C(6)-C(7)-C(8)	-0.6(2)
C(4)-N(3)-C(8)-C(7)	-1.0(2)
C(6)-C(7)-C(8)-N(3)	1.7(3)
N(1)-C(1)-C(9)-C(10)	-175.21(13)
C(3)-C(1)-C(9)-C(10)	9.6(2)
C(1)-C(9)-C(10)-C(11)	-178.95(12)
C(12)-O(2)-C(11)-O(1)	-3.8(2)
C(12)-O(2)-C(11)-C(10)	176.57(12)
C(9)-C(10)-C(11)-O(1)	0.7(2)
C(9)-C(10)-C(11)-O(2)	-179.70(12)
C(11)-O(2)-C(12)-C(13)	99.37(15)
C(11)-O(2)-C(12)-C(17)	-84.12(16)
C(17)-C(12)-C(13)-C(14)	-0.8(2)
O(2)-C(12)-C(13)-C(14)	175.59(12)
C(12)-C(13)-C(14)-C(15)	0.3(2)
C(13)-C(14)-C(15)-C(16)	0.3(2)
C(14)-C(15)-C(16)-C(17)	-0.3(3)
C(13)-C(12)-C(17)-C(16)	0.8(2)
O(2)-C(12)-C(17)-C(16)	-175.56(13)
C(15)-C(16)-C(17)-C(12)	-0.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for N200907A [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-Ray crystallographic data of **4a**:

Table 8 Crystal data and structure refinement for a201019a_sq.

Identification code	a201019a_sq
Empirical formula	$C_{18}H_{19}N_3O_4$
Formula weight	340.84
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.9764(3)
b/Å	13.0721(4)
c/Å	14.7472(5)
α/°	76.686(3)
β/°	81.794(3)
γ/°	89.401(3)
Volume/Å^3	1851.86(11)
Z	4
ρ_{calc}g/cm^3	1.222
μ/mm^{-1}	0.727
F(000)	718.0
Crystal size/mm^3	0.2 × 0.17 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.224 to 134.136
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 14, -17 ≤ l ≤ 12
Reflections collected	12492
Independent reflections	6603 [R_{int} = 0.0512, R_{sigma} = 0.0690]
Data/restraints/parameters	6603/52/464
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.1402, wR_2 = 0.3068
Final R indexes [all data]	R_1 = 0.1613, wR_2 = 0.3175
Largest diff. peak/hole / e Å^{-3}	0.51/-0.45

Table 9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for a201019a_sq. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	8963(5)	7711(4)	3612(4)	70.9(16)
O2	6957(5)	7502(5)	3176(5)	79.1(18)
O3	6623(5)	758(4)	3112(4)	66.7(15)
O4	4416(5)	424(3)	3540(4)	63.7(14)
C1	3371(9)	-1157(7)	4481(8)	85(3)
C2	4697(8)	-650(5)	4025(6)	65(2)
C3	5481(7)	1037(5)	3104(5)	50.2(16)
C4	5059(7)	2082(5)	2629(5)	51.8(16)
C5	5934(6)	2831(5)	2194(5)	49.1(16)
C14	8160(7)	5986(5)	2225(5)	52.7(16)
C15	8829(7)	6539(5)	2655(6)	55.2(18)
C16	8128(7)	7283(5)	3180(6)	56.6(18)
C17	8350(9)	8498(7)	4094(8)	81(3)
C18	9475(10)	9016(6)	4399(6)	74(2)
N1	6701(9)	4683(12)	1320(13)	34.5(17)
N2	6028(10)	5618(9)	955(10)	44.7(14)
C7	4611(9)	5403(7)	1163(7)	50(3)
C8	4408(10)	4334(7)	1656(7)	37(3)
C6	5699(13)	3890(8)	1753(11)	37(2)
C9	7984(9)	4619(14)	1418(13)	36.7(19)
N3	8482(9)	3870(11)	932(11)	45(6)
C10	9872(10)	3759(8)	722(7)	62(4)
C11	10763(8)	4398(8)	1000(7)	58(4)
C12	10265(13)	5147(9)	1486(11)	49(4)
C13	8876(14)	5257(12)	1696(13)	42(2)
N1A	7824(10)	4583(14)	1302(14)	36.7(19)
N2A	8672(12)	3843(12)	946(12)	49(7)
C7A	9998(11)	3981(9)	1150(8)	62(4)
C8A	9969(14)	4806(11)	1631(12)	49(4)
C6A	8626(17)	5178(13)	1725(15)	42(2)
C9A	6465(11)	4653(13)	1406(15)	34.5(17)
N3A	6162(10)	5670(12)	965(12)	44.7(14)
C10A	4861(11)	5899(7)	757(8)	50(3)
C11A	3863(9)	5111(8)	988(7)	54(4)
C12A	4167(12)	4093(7)	1429(8)	37(3)
C13A	5467(15)	3864(9)	1638(13)	37(2)

O5	-468(5)	12837(4)	3548(4)	56.8(12)
O6	1719(5)	12635(4)	3073(4)	71.3(16)
O7	2101(4)	5777(4)	3077(4)	58.8(13)
O8	4119(5)	5399(3)	3544(4)	59.1(13)
C19	-1344(10)	13949(7)	4525(8)	89(3)
C20	-85(8)	13631(6)	4008(6)	59.5(18)
C21	552(7)	12408(5)	3099(5)	50.2(16)
C22	74(6)	11621(5)	2642(5)	48.1(15)
C23	940(7)	11058(5)	2204(5)	48.3(15)
C32	3183(6)	7841(4)	2206(4)	46.3(15)
C33	3878(7)	7072(5)	2629(5)	51.8(16)
C34	3252(7)	6023(5)	3101(5)	46.2(15)
C35	3610(8)	4322(5)	4019(6)	60.7(19)
C36	4785(10)	3756(6)	4414(7)	78(2)
N4	1668(8)	9660(12)	1321(11)	36.2(19)
C24	669(13)	10234(9)	1768(10)	40(2)
C25	-624(10)	9833(7)	1706(8)	47(3)
C26	-424(8)	9011(8)	1220(7)	53(3)
N5	993(9)	8904(11)	983(9)	48.9(15)
C27	2954(8)	9655(9)	1454(10)	33(2)
C28	3850(12)	8849(6)	1690(9)	39(2)
C29	5239(11)	9048(5)	1468(8)	47(3)
C30	5730(7)	10052(7)	1009(6)	53(3)
C31	4834(9)	10858(5)	773(8)	54(4)
N6	3445(8)	10660(8)	995(9)	44.2(16)
N4A	2817(10)	9729(11)	1270(11)	33(2)
C24A	3608(15)	8922(7)	1739(11)	39(2)
C26A	4935(13)	9340(7)	1675(9)	47(3)
C25A	4965(10)	10406(7)	1166(9)	53(4)
N5A	3655(11)	10646(8)	916(11)	44.2(16)
C27A	1438(12)	9611(15)	1458(14)	36.2(19)
C31A	447(17)	10295(12)	1700(12)	40(2)
C30A	-848(14)	10222(8)	1473(10)	47(3)
C29A	-1152(9)	9466(9)	1003(8)	64(5)
C28A	-162(12)	8782(10)	761(9)	53(3)
N6A	1134(10)	8854(13)	988(12)	48.9(15)

Table 10 Anisotropic Displacement Parameters ($Å^2×10^3$) for a201019a_sq. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	66(3)	68(3)	103(4)	-51(3)	-40(3)	17(3)
O2	53(3)	86(4)	121(5)	-57(4)	-33(3)	11(3)
O3	42(3)	55(3)	94(4)	-4(3)	-3(3)	4(2)
O4	49(3)	35(2)	93(4)	4(2)	6(3)	-3.5(19)
C1	71(5)	54(5)	118(8)	1(5)	-7(5)	-12(4)
C2	66(5)	37(3)	81(6)	1(3)	0(4)	2(3)
C3	43(4)	49(4)	57(4)	-13(3)	3(3)	-1(3)
C4	41(3)	41(3)	69(5)	-8(3)	0(3)	0(3)
C5	39(3)	41(3)	65(4)	-13(3)	1(3)	-1(3)
C14	54(4)	52(4)	58(4)	-19(3)	-17(3)	0(3)
C15	43(4)	49(4)	82(5)	-24(4)	-22(3)	3(3)
C16	52(4)	50(4)	77(5)	-22(4)	-27(4)	4(3)
C17	82(6)	76(6)	107(7)	-55(5)	-33(5)	19(5)
C18	107(7)	54(4)	71(5)	-18(4)	-39(5)	-8(4)
N1	33(3)	35(2)	35(3)	-12(2)	2(3)	-3(2)
N2	45(3)	40(3)	55(3)	-18(2)	-17(3)	6(2)
C7	53(6)	65(9)	36(8)	-25(5)	5(5)	-6(6)
C8	40(5)	46(6)	33(6)	-19(4)	-12(4)	-1(4)
C6	36(5)	40(3)	39(5)	-13(3)	-12(3)	-2(3)
C9	38(3)	38(2)	37(3)	-8(2)	-14(2)	-3(2)
N3	34(7)	31(11)	63(15)	-9(9)	14(7)	11(6)
C10	56(6)	67(7)	52(10)	27(6)	-36(6)	-11(5)
C11	35(7)	53(8)	69(9)	14(7)	1(6)	-5(6)
C12	55(7)	46(10)	50(6)	-13(8)	-18(6)	4(7)
C13	34(6)	38(4)	55(4)	-9(3)	-13(4)	-2(4)
N1A	38(3)	38(2)	37(3)	-8(2)	-14(2)	-3(2)
N2A	39(9)	45(14)	63(17)	-7(11)	-17(9)	1(8)
C7A	56(6)	67(7)	52(10)	27(6)	-36(6)	-11(5)
C8A	55(7)	46(10)	50(6)	-13(8)	-18(6)	4(7)
C6A	34(6)	38(4)	55(4)	-9(3)	-13(4)	-2(4)
C9A	33(3)	35(2)	35(3)	-12(2)	2(3)	-3(2)
N3A	45(3)	40(3)	55(3)	-18(2)	-17(3)	6(2)
C10A	53(6)	65(9)	36(8)	-25(5)	5(5)	-6(6)
C11A	41(7)	81(11)	48(8)	-28(8)	-13(6)	-5(7)
C12A	40(5)	46(6)	33(6)	-19(4)	-12(4)	-1(4)
C13A	36(5)	40(3)	39(5)	-13(3)	-12(3)	-2(3)
O5	49(3)	52(3)	74(3)	-32(2)	4(2)	-1(2)

O6	48(3)	75(4)	100(5)	-46(3)	-1(3)	2(2)
O7	40(3)	57(3)	75(3)	-4(2)	-13(2)	0(2)
O8	55(3)	36(2)	86(4)	-1(2)	-29(3)	2(2)
C19	88(6)	80(6)	105(8)	-56(6)	24(5)	-4(5)
C20	61(4)	52(4)	66(5)	-22(4)	2(4)	-6(3)
C21	45(4)	41(3)	61(4)	-12(3)	7(3)	5(3)
C22	40(3)	42(3)	66(4)	-21(3)	-6(3)	7(3)
C23	50(4)	47(3)	48(4)	-16(3)	2(3)	1(3)
C32	46(3)	45(3)	51(4)	-11(3)	-16(3)	1(3)
C33	46(4)	42(3)	68(5)	-9(3)	-14(3)	5(3)
C34	50(4)	43(3)	48(4)	-11(3)	-13(3)	5(3)
C35	67(5)	46(4)	64(5)	-1(3)	-9(4)	1(3)
C36	96(6)	49(4)	87(6)	-6(4)	-28(5)	21(4)
N4	34(3)	34(2)	37(4)	-7(2)	5(3)	1(2)
C24	30(5)	40(3)	50(4)	-11(3)	-3(3)	2(3)
C25	44(6)	42(8)	51(7)	-10(7)	1(5)	0(5)
C26	41(6)	54(6)	54(9)	2(6)	3(6)	5(5)
N5	45(3)	39(3)	67(4)	-13(3)	-20(3)	-1(2)
C27	37(3)	33(2)	33(4)	-8(2)	-14(2)	6(2)
C28	32(5)	38(3)	50(4)	-12(3)	-9(3)	6(3)
C29	41(6)	41(6)	60(7)	-11(5)	-13(5)	2(5)
C30	37(6)	79(9)	44(7)	-20(6)	3(5)	9(6)
C31	47(8)	68(10)	55(10)	-23(7)	-20(7)	20(7)
N6	33(4)	39(3)	61(4)	-20(3)	7(3)	-1(2)
N4A	37(3)	33(2)	33(4)	-8(2)	-14(2)	6(2)
C24A	32(5)	38(3)	50(4)	-12(3)	-9(3)	6(3)
C26A	41(6)	41(6)	60(7)	-11(5)	-13(5)	2(5)
C25A	62(11)	61(11)	49(11)	-25(8)	-29(9)	24(9)
N5A	33(4)	39(3)	61(4)	-20(3)	7(3)	-1(2)
C27A	34(3)	34(2)	37(4)	-7(2)	5(3)	1(2)
C31A	30(5)	40(3)	50(4)	-11(3)	-3(3)	2(3)
C30A	44(6)	42(8)	51(7)	-10(7)	1(5)	0(5)
C29A	41(8)	79(12)	64(11)	0(9)	-11(8)	1(8)
C28A	41(6)	54(6)	54(9)	2(6)	3(6)	5(5)
N6A	45(3)	39(3)	67(4)	-13(3)	-20(3)	-1(2)

Table 11 Bond Lengths for a201019a_sq.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C16	1.318(8)	O5	C20	1.445(8)
O1	C17	1.462(9)	O5	C21	1.325(7)
O2	C16	1.200(8)	O6	C21	1.197(8)
O3	C3	1.194(8)	O7	C34	1.203(8)
O4	C2	1.465(8)	O8	C34	1.319(8)
O4	C3	1.331(8)	O8	C35	1.479(8)
C1	C2	1.484(11)	C19	C20	1.481(10)
C3	C4	1.471(9)	C21	C22	1.471(9)
C4	C5	1.305(9)	C22	C23	1.324(9)
C5	C6	1.419(11)	C23	C24	1.421(11)
C5	C13A	1.516(12)	C23	C31A	1.498(12)
C14	C15	1.310(9)	C32	C33	1.304(9)
C14	C13	1.482(8)	C32	C28	1.474(7)
C14	C6A	1.457(8)	C32	C24A	1.461(8)
C15	C16	1.488(10)	C33	C34	1.487(9)
C17	C18	1.490(11)	C35	C36	1.497(11)
N1	N2	1.4200	N4	C24	1.4200
N1	C6	1.4200	N4	N5	1.4200
N1	C9	1.309(13)	N4	C27	1.324(12)
N2	C7	1.4200	C24	C25	1.4200
C7	C8	1.4200	C25	C26	1.4200
C8	C6	1.4200	C26	N5	1.4200
C9	N3	1.3900	C27	C28	1.3900
C9	C13	1.3900	C27	N6	1.3900
N3	C10	1.3900	C28	C29	1.3900
C10	C11	1.3900	C29	C30	1.3900
C11	C12	1.3900	C30	C31	1.3900
C12	C13	1.3900	C31	N6	1.3900
N1A	N2A	1.4200	N4A	C24A	1.4200
N1A	C6A	1.4200	N4A	N5A	1.4200
N1A	C9A	1.347(14)	N4A	C27A	1.367(15)
N2A	C7A	1.4200	C24A	C26A	1.4200
C7A	C8A	1.4200	C26A	C25A	1.4200
C8A	C6A	1.4200	C25A	N5A	1.4200
C9A	N3A	1.3900	C27A	C31A	1.3900
C9A	C13A	1.3900	C27A	N6A	1.3900
N3A	C10A	1.3900	C31A	C30A	1.3900
C10A	C11A	1.3900	C30A	C29A	1.3900

C11A	C12A	1.3900	C29A	C28A	1.3900
C12A	C13A	1.3900	C28A	N6A	1.3900

Table 12 Bond Angles for a201019a_sq.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	O1	C17	114.4(6)	C21	O5	C20	115.2(5)
C3	O4	C2	116.8(5)	C34	O8	C35	115.9(5)
O4	C2	C1	106.7(6)	O5	C20	C19	106.9(6)
O3	C3	O4	123.2(6)	O5	C21	C22	111.7(6)
O3	C3	C4	125.6(6)	O6	C21	O5	123.9(6)
O4	C3	C4	111.3(6)	O6	C21	C22	124.4(6)
C5	C4	C3	122.0(6)	C23	C22	C21	121.0(6)
C4	C5	C6	129.1(8)	C22	C23	C24	128.8(8)
C4	C5	C13A	120.6(8)	C22	C23	C31A	120.7(9)
C15	C14	C13	120.6(8)	C33	C32	C28	120.8(7)
C15	C14	C6A	130.1(9)	C33	C32	C24A	129.7(8)
C14	C15	C16	121.3(6)	C32	C33	C34	122.1(6)
O1	C16	C15	111.8(6)	O7	C34	O8	124.5(6)
O2	C16	O1	124.1(7)	O7	C34	C33	124.0(6)
O2	C16	C15	124.0(6)	O8	C34	C33	111.4(5)
O1	C17	C18	106.8(7)	O8	C35	C36	105.9(6)
N2	N1	C6	108.0	N5	N4	C24	108.0
C9	N1	N2	125.7(13)	C27	N4	C24	122.8(12)
C9	N1	C6	124.9(13)	C27	N4	N5	126.6(12)
C7	N2	N1	108.0	N4	C24	C23	125.1(9)
N2	C7	C8	108.0	C25	C24	C23	126.9(9)
C6	C8	C7	108.0	C25	C24	N4	108.0
N1	C6	C5	126.5(9)	C24	C25	C26	108.0
C8	C6	C5	125.5(9)	N5	C26	C25	108.0
C8	C6	N1	108.0	N4	N5	C26	108.0
N1	C9	N3	104.7(13)	N4	C27	C28	132.7(11)
N1	C9	C13	133.5(12)	N4	C27	N6	104.4(10)
N3	C9	C13	120.0	C28	C27	N6	120.0
C10	N3	C9	120.0	C27	C28	C32	113.8(8)
N3	C10	C11	120.0	C29	C28	C32	126.1(8)
C12	C11	C10	120.0	C29	C28	C27	120.0
C11	C12	C13	120.0	C28	C29	C30	120.0
C9	C13	C14	112.2(10)	C29	C30	C31	120.0
C12	C13	C14	127.8(10)	C30	C31	N6	120.0

C12	C13	C9	120.0	C31	N6	C27	120.0
N2A	N1A	C6A	108.0	C24A	N4A	N5A	108.0
C9A	N1A	N2A	129.9(14)	C27A	N4A	C24A	118.1(13)
C9A	N1A	C6A	121.2(14)	C27A	N4A	N5A	130.8(13)
N1A	N2A	C7A	108.0	N4A	C24A	C32	127.7(10)
C8A	C7A	N2A	108.0	N4A	C24A	C26A	108.0
C7A	C8A	C6A	108.0	C26A	C24A	C32	124.3(10)
N1A	C6A	C14	126.9(12)	C24A	C26A	C25A	108.0
N1A	C6A	C8A	108.0	N5A	C25A	C26A	108.0
C8A	C6A	C14	125.0(12)	C25A	N5A	N4A	108.0
N1A	C9A	N3A	107.6(14)	N4A	C27A	C31A	130.9(14)
N1A	C9A	C13A	130.0(13)	N4A	C27A	N6A	104.6(14)
N3A	C9A	C13A	120.0	C31A	C27A	N6A	120.0
C10A	N3A	C9A	120.0	C27A	C31A	C23	113.2(11)
N3A	C10A	C11A	120.0	C27A	C31A	C30A	120.0
C10A	C11A	C12A	120.0	C30A	C31A	C23	126.8(11)
C13A	C12A	C11A	120.0	C29A	C30A	C31A	120.0
C9A	C13A	C5	113.0(9)	C28A	C29A	C30A	120.0
C12A	C13A	C5	126.8(9)	N6A	C28A	C29A	120.0
C12A	C13A	C9A	120.0	C28A	N6A	C27A	120.0

Table 13 Torsion Angles for a201019a_sq.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C3	C4	C5	-3.1(12)	O5	C21	C22	C23	-176.0(6)
O4	C3	C4	C5	176.6(7)	O6	C21	C22	C23	3.9(12)
C2	O4	C3	O3	-1.6(11)	C20	O5	C21	O6	0.9(11)
C2	O4	C3	C4	178.7(7)	C20	O5	C21	C22	-179.2(6)
C3	O4	C2	C1	177.9(7)	C21	O5	C20	C19	-175.7(7)
C3	C4	C5	C6	-175.9(10)	C21	C22	C23	C24	176.5(9)
C3	C4	C5	C13A	174.5(10)	C21	C22	C23	C31A	-177.1(10)
C4	C5	C6	N1	177.4(9)	C22	C23	C24	N4	-179.1(8)
C4	C5	C6	C8	-3.7(18)	C22	C23	C24	C25	0.3(16)
C4	C5	C13A	C9A	166.0(8)	C22	C23	C31A	C27A	-166.8(8)
C4	C5	C13A	C12A	-8.2(18)	C22	C23	C31A	C30A	13.1(17)
C14	C15	C16	O1	176.0(7)	C23	C24	C25	C26	-179.6(13)
C14	C15	C16	O2	-7.2(13)	C23	C31A	C30A	C29A	-179.9(15)
C15	C14	C13	C9	170.2(8)	C32	C33	C34	O7	5.4(11)
C15	C14	C13	C12	-8.2(18)	C32	C33	C34	O8	-175.0(7)
C15	C14	C6A	N1A	177.6(11)	C32	C28	C29	C30	-177.4(13)

C15	C14	C6A	C8A	2(2)	C32	C24A	C26A	C25A	179.5(16)
C16	O1	C17	C18	-170.8(7)	C33	C32	C28	C27	-166.9(7)
C17	O1	C16	O2	-0.3(12)	C33	C32	C28	C29	10.6(14)
C17	O1	C16	C15	176.5(7)	C33	C32	C24A	N4A	178.7(10)
N1	N2	C7	C8	0.0	C33	C32	C24A	C26A	-0.7(18)
N1	C9	N3	C10	166.6(16)	C34	O8	C35	C36	176.8(7)
N1	C9	C13	C14	19.5(18)	C35	O8	C34	O7	1.2(10)
N1	C9	C13	C12	-162(2)	C35	O8	C34	C33	-178.4(6)
N2	N1	C6	C5	179.1(13)	N4	C24	C25	C26	0.0
N2	N1	C6	C8	0.0	N4	C27	C28	C32	-24.9(15)
N2	N1	C9	N3	-125.0(12)	N4	C27	C28	C29	157.3(16)
N2	N1	C9	C13	39(2)	N4	C27	N6	C31	-163.0(13)
N2	C7	C8	C6	0.0	C24	N4	N5	C26	0.0
C7	C8	C6	C5	-179.1(13)	C24	N4	C27	C28	129.4(12)
C7	C8	C6	N1	0.0	C24	N4	C27	N6	-70.7(12)
C6	N1	N2	C7	0.0	C24	C25	C26	N5	0.0
C6	N1	C9	N3	70.3(15)	C25	C26	N5	N4	0.0
C6	N1	C9	C13	-125.8(14)	N5	N4	C24	C23	179.6(13)
C9	N1	N2	C7	-166.8(19)	N5	N4	C24	C25	0.0
C9	N1	C6	C5	-14.0(17)	N5	N4	C27	C28	-30(2)
C9	N1	C6	C8	166.9(19)	N5	N4	C27	N6	129.6(10)
C9	N3	C10	C11	0.0	C27	N4	C24	C23	16.6(15)
N3	C9	C13	C14	-178.6(15)	C27	N4	C24	C25	-163.0(15)
N3	C9	C13	C12	0.0	C27	N4	N5	C26	162.1(15)
N3	C10	C11	C12	0.0	C27	C28	C29	C30	0.0
C10	C11	C12	C13	0.0	C28	C32	C33	C34	-175.9(8)
C11	C12	C13	C14	178.3(18)	C28	C27	N6	C31	0.0
C11	C12	C13	C9	0.0	C28	C29	C30	C31	0.0
C13	C14	C15	C16	179.3(11)	C29	C30	C31	N6	0.0
C13	C9	N3	C10	0.0	C30	C31	N6	C27	0.0
N1A	N2A	C7A	C8A	0.0	N6	C27	C28	C32	177.7(11)
N1A	C9A	N3A	C10A	164.1(18)	N6	C27	C28	C29	0.0
N1A	C9A	C13A	C5	25.4(16)	N4A	C24A	C26A	C25A	0.0
N1A	C9A	C13A	C12A	-160(2)	N4A	C27A	C31A	C23	-27.8(16)
N2A	N1A	C6A	C14	-176(2)	N4A	C27A	C31A	C30A	152(2)
N2A	N1A	C6A	C8A	0.0	N4A	C27A	N6A	C28A	-158.7(15)
N2A	N1A	C9A	N3A	-127.4(15)	C24A	C32	C33	C34	177.6(11)
N2A	N1A	C9A	C13A	35(3)	C24A	N4A	N5A	C25A	0.0
N2A	C7A	C8A	C6A	0.0	C24A	N4A	C27A	C31A	130.3(13)
C7A	C8A	C6A	C14	177(2)	C24A	N4A	C27A	N6A	-74.3(13)

C7A	C8A	C6A	N1A	0.0	C24A	C26A	C25A	N5A	0.0
C6A	C14	C15	C16	-175.9(13)	C26A	C25A	N5A	N4A	0.0
C6A	N1A	N2A	C7A	0.0	N5A	N4A	C24A	C32	-179.4(17)
C6A	N1A	C9A	N3A	65.1(16)	N5A	N4A	C24A	C26A	0.0
C6A	N1A	C9A	C13A	-133.0(14)	N5A	N4A	C27A	C31A	-27(2)
C9A	N1A	N2A	C7A	-169(2)	N5A	N4A	C27A	N6A	128.4(13)
C9A	N1A	C6A	C14	-6(2)	C27A	N4A	C24A	C32	18.4(18)
C9A	N1A	C6A	C8A	170.0(19)	C27A	N4A	C24A	C26A	-162.2(16)
C9A	N3A	C10A	C11A	0.0	C27A	N4A	N5A	C25A	159.1(19)
N3A	C9A	C13A	C5	-174.6(13)	C27A	C31A	C30A	C29A	0.0
N3A	C9A	C13A	C12A	0.0	C31A	C27A	N6A	C28A	0.0
N3A	C10A	C11A	C12A	0.0	C31A	C30A	C29A	C28A	0.0
C10A	C11A	C12A	C13A	0.0	C30A	C29A	C28A	N6A	0.0
C11A	C12A	C13A	C5	173.8(15)	C29A	C28A	N6A	C27A	0.0
C11A	C12A	C13A	C9A	0.0	N6A	C27A	C31A	C23	179.9(13)
C13A	C9A	N3A	C10A	0.0	N6A	C27A	C31A	C30A	0.0

Table 14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for a201019a_sq.

Atom	*x*	*y*	*z*	U(eq)
H1A	2773.36	-1106.33	4017.2	128
H1B	2981.82	-809.66	4959.61	128
H1C	3498.99	-1884.34	4760.49	128
H2A	5283.5	-638.46	4493.92	78
H2B	5139.62	-1031.96	3578.99	78
H4	4139.05	2211.53	2639.1	62
H5A	6838.86	2645.78	2169.56	59
H5B	6852.09	2730.84	2225.56	59
H14	7227.09	6051.59	2250.83	63
H14A	7243.88	6131.91	2239.56	63
H15	9760.81	6465.6	2632.87	66
H17A	7703.64	8165.13	4635.63	97
H17B	7880.74	9010.98	3672.09	97
H18A	10220.61	9167.63	3895.51	111
H18B	9763.52	8555.89	4939.42	111
H18C	9164.81	9659.18	4557.84	111
H7	3935.38	5877.7	1004.3	60
H8	3575.4	3986.87	1877.19	45
H10	10204.97	3258.2	396.62	75

H11	11693.16	4324.03	859.59	70
H12	10862.05	5574.07	1671.88	59
H7A	10752.15	3598.22	994.85	75
H8A	10702.01	5059.05	1847.58	59
H10A	4658.29	6579.79	461.8	60
H11A	2993.02	5263.71	848.84	65
H12A	3499.02	3565.63	1584.23	45
H19A	-2017.78	14106.23	4112.1	134
H19B	-1158.99	14560.95	4746.31	134
H19C	-1670.3	13385.12	5051.74	134
H20A	344.65	14230.69	3545.5	71
H20B	546.31	13348.93	4440.42	71
H22	-851.63	11516.66	2660.74	58
H23	1851.21	11224.44	2176.9	58
H23A	1864.36	11137.25	2208.16	58
H32	2253.64	7751.19	2229.68	56
H32A	2279.76	7675.35	2200.53	56
H33	4795.82	7183.84	2635.2	62
H35A	3290.14	3974.18	3572.79	73
H35B	2869.6	4341.28	4517.8	73
H36A	5515.95	3759.38	3913.18	117
H36B	4515.35	3043.24	4720.65	117
H36C	5078.26	4102.48	4861.38	117
H25	-1455.75	10068.06	1941.28	56
H26	-1101.25	8613.02	1082.05	64
H29	5838.36	8508.22	1626.55	56
H30	6659.43	10184.67	860.84	64
H31	5163.08	11530.04	465.75	65
H26A	5658.62	8979.67	1922.21	56
H25A	5710.12	10865.44	1022.46	64
H30A	-1510.77	10679.8	1635.16	56
H29A	-2018.93	9417.19	851.01	77
H28A	-365.26	8275.6	446.39	64