Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Radical 1,2-Addition of Bromoarenes to Alkynes via Dual Photoredox and Nickel Catalysis

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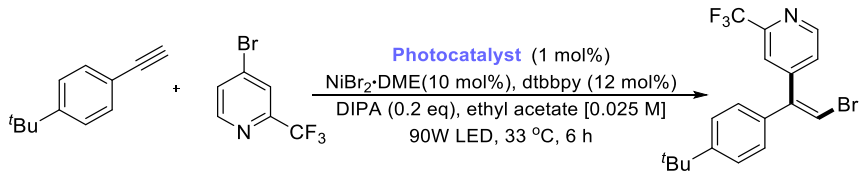
1. General Information.

Commercial reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates.^{1}H, ^{19}F NMR, and ^{13}C NMR spectra were recorded on Bruker 400 (400, 376, and 100 MHz) and Bruker 600 (600, 564, and 150 MHz), and are internally referenced to residual solvent signals (for $CDCl_3$, δ 7.26 and 77.0 ppm). Data for ^{1}H NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. All alkynes were used from commercial suppliers or prepared using standard literature procedures or the preparation procedures descried in this supporting information.

2. Optimization of the Reaction Conditions

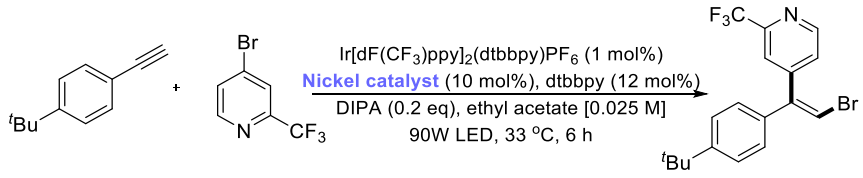
Table S1. Photocatalyst effect.



1, 0.1 mmol **2,** 1.5 eq **3**

Entry	Photocatalyst	GC yield
1	$Ir[dF(CF_3)ppy]_2(bpy)PF_6$	36%
2	$Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$	96%
3	$Ir[dF(CF_3)ppy]_2(phen)PF_6$	46%
4	$Ir[dF(CF_3)ppy]_2F\text{-}piv$	50%
5	$Ir(ppy)_3$	0%
6	$Ir(ppy)_2(dtbpy)PF_6$	0%
7	$Ru(bpy)_3(PF_6)_2$	0%
8	$Ru(phen)_3Cl_2 \cdot 6H_2O$	0%
9	[9-Mes-Acr][ClO_4]	0%

Table S2. Nickel catalyst effect.

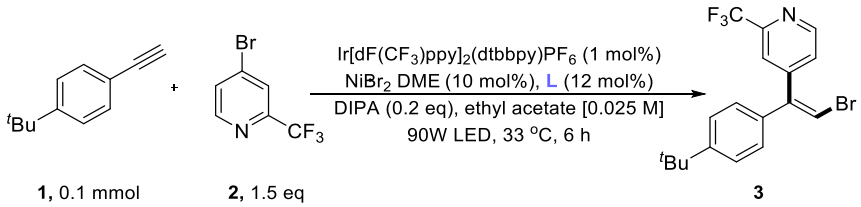


1, 0.1 mmol **2,** 1.5 eq **3**

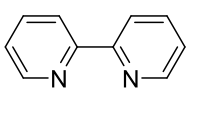
Entry	Nickel catalyst	GC yield
1	$NiBr_2 \cdot DME$	96%
2	$NiBr_2 \cdot bpy$	81%
3	$NiBr_2 \cdot dtbbpy$	52%

4	$NiBr_2 \cdot (PPh_3)_2$	93%
5	$NiBr_2$	45%
6	$NiCl_2 \cdot DME$	86%
7	$NiCl_2(PPh)_3$	85%
8	$NiCl_2 \cdot Py_4$	87%
9	$Ni(COD)_2$	72%

Table S3. Ligand effect.



1, 0.1 mmol **2,** 1.5 eq **3**



L1
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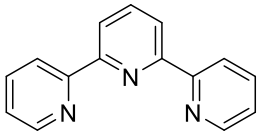
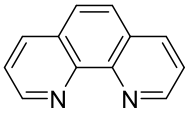


L2
2%



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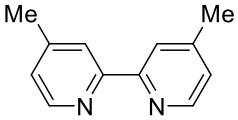

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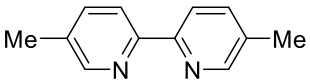

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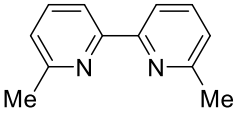

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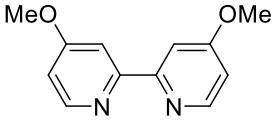

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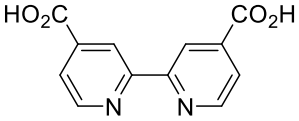

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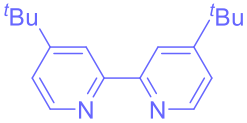
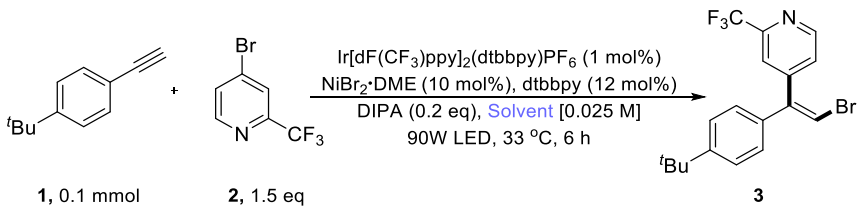


L9
96%

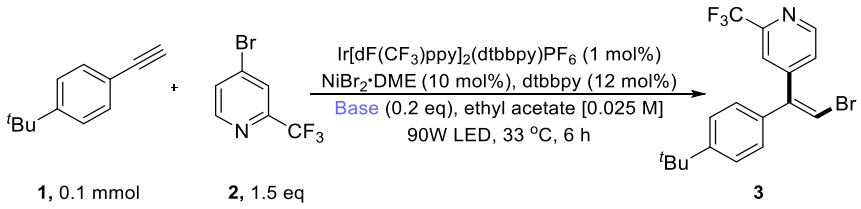
Table S4. Solvent effect.



1, 0.1 mmol **2,** 1.5 eq **3**

Entry	Solvents	GC yield
1	DMSO	0%
2	DMA	37%
3	1,4-dioxane	16%
4	toluene	0%
5	acetone	23%
6	DME	0%
7	THF	56%
8	ethyl acetate	96%

Table S5. Base effect.



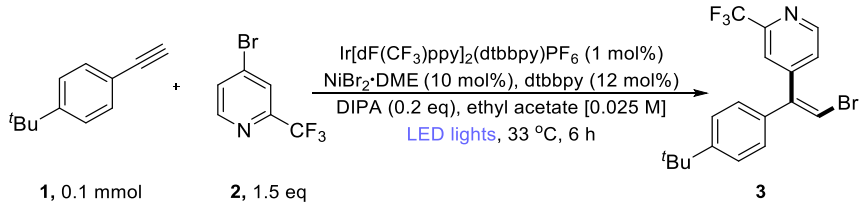
1, 0.1 mmol **2,** 1.5 eq **3**

Entry	Base	GC yield
1	KH_2PO_4	44%
2	K_3PO_4	40%
3	K_2HPO_4	78%
4	Na_2HPO_4	62%

5	Et_3N	79%
6	DIPEA[a]	83%
7	DIPA[b]	96%
8	DBU[c]	84%
9	DCHA[d]	86%

[a] N-ethyl-N-isopropylpropan-2-amine; [b] diisopropylamine; [c] 1,8-diazabicyclo[5.4.0]undec-7-ene; [d] dicyclohexylamine.

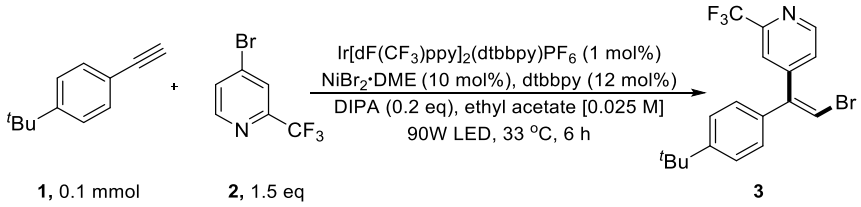
Table S6. LED light effect



1, 0.1 mmol **2,** 1.5 eq **3**

Entry	LED lights	GC yield
1	3W blue band	0%
2	5W blue LED	9%
3	15W blue LED	14%
4	40W blue LED	63%
5	90W blue LED	96%

Table S7. Control experiment.



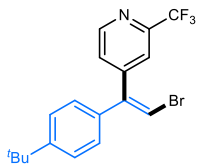
1, 0.1 mmol **2,** 1.5 eq **3**

Entry	Control reaction	GC yield
1	w/o photocatalyst	0%
2	w/o nickel catalyst	0%
3	w/o ligand	0%
4	w/o light	0%
5	w/o base	79%

3. General Procedure for Photoredox/Nickel-Catalyzed 1,2-Addition of Alkynes

To a flame-dried 12 mL reaction vial was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.6 mg , 0.024 mmol, 0.12 equiv.), the vial was introduced into a nitrogen-filled glove box and charged with $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.). The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, ethyl acetate (8 mL), 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.) and 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.) was added by syringe. Once added, the reaction mixture was then irradiated with a 90 W blue LED lamp (at approximately 3.5 cm away from the light source) with cooling from a fan for 6 hours. After evaporation in vacuo, purification by column chromatography on silica gel to afford the product. The Z/E isomers of products **3, 4,** and **35** were determined by NOSEY and/or X-ray, and the stereo-configuration of the other alkenes was assigned by analogy of ^{1}H NMR chemical shift.

4. Characterizations of Products



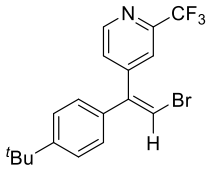
4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine [3]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (31.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (70.5 mg, 92%, Z/E = 49:51). (the Z and E isomers were determined by NOESY).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.0 Hz, 0.49H) , 8.64 (d, *J* = 5.1 Hz, 0.51H), 7.64(s, 0.48H) ,7.54 (s, 0.51H), 7.45 (m, 1.5H), 7.38 – 7.32 (m, 1H), 7.27 (d, *J* = 1.4 Hz, 0.5H), 7.23 – 7.18 (m, 1H), 7.10 – 7.06 (m, 1H),7.06 (s, 0.5H), 6.91 (s , 0.47H), 1.36 (s, 4.59H), 1.32 (s, 4.41H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.91 (s, 1.43F), -67.95 (s, 1.58F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.29 (151.94), 150.30 (150.27), 149.86 (149.01), 148.77 (148.43, q, *J* = 34.7 Hz), 143.78 (143.50), 135.58 (133.57), 129.11 (127.05), 125.84 (125.62), 127.27 (124.71),122.81 (120.09, q, *J* = 274.3 Hz) 121.34 (118.54, q, *J* = 2.8Hz), 110.54 (107.11), 34.77 (34.69), 31.24 (31.13).

HRMS (ESI) Calcd for $C_{14}H_{17}BrF_3N^+$ (M+H): 384.0569, found: 384.0570.

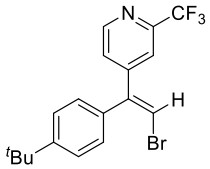


(Z)-4-(2-bromo-1-(4-(tert-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (3-Z):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 5.0 Hz, 1H), 7.64 (s, 1H), 7.45 (d, J = 5.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.91 (s, 1H), 1.32 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.93 (s, 3F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.29, 150.26, 149.00, 148.56 (q, J = 34.7 Hz), 143.50, 135.58, 127.26, 127.05, 125.84, 121.45 (q, J = 247.5 Hz), 121.29 (q, J = 2.7 Hz), 107.11, 34.69, 31.14.

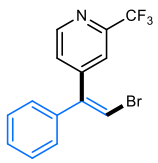


(E)-4-(2-bromo-1-(4-(tert-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (3-E):

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 5.1 Hz, 1H), 7.54 (s, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 6.6 Hz, 1H), 7.20 (d, J = 8.3 Hz, 2H), 7.06 (s, 1H), 1.36 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.97 (s, 3F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.94, 150.30, 148.61 (q, J = 34.3 Hz), 149.84, 143.78, 133.57, 129.11, 125.61, 124.69, 121.41 (q, J = 274.3 Hz), 118.48 (q, J = 2.7 Hz), 110.53, 34.77, 31.24.



4-(2-Bromo-1-phenylvinyl)-2-(trifluoromethyl)pyridine [4]: According to the general procedure, ethynylbenzene (20.4 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL,

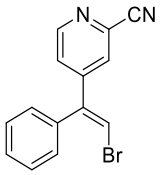
0.04 mmol, 0.2 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (60.8 mg, 93%, Z/E = 42:58). (the E isomer was determined by NOESY).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.0 Hz, 0.41H), 8.64 (d, *J* = 5.1 Hz, 0.57H), 7.64 (s, 0.41H), 7.52 (s, 0.57H), 7.45 (m, 2H), 7.35 (m, 1H), 7.30 – 7.23 (m, 2H), 7.16 (m, 1H), 7.14 (s, 0.57H), 6.94 (s, 0.41H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.95 (s, 1.26F), -68.01 (s, 1.74F).

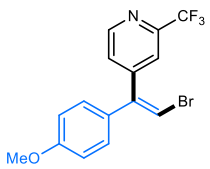
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.35 (150.30), 149.36 (148.82), 148.55 (148.79, q, *J* = 34.4 Hz), 143.90 (143.69), 136.76 (138.57), 129.39 (128.91), 128.99 (128.99)，128.80 (127.44), 124.39 (127.19), 122.79 (120.06, q, *J* = 274.4 Hz), 121.27 (118.32, q, *J* = 2.8 Hz), 111.19 (107.95).

HRMS (ESI) Calcd for $C_{14}H_{10}BrF_3N^+$ (M+H): 327.9943, found: 327.9944.



(E)-4-(2-bromo-1-phenylvinyl)picolinonitrile (4-E):

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, J = 5.1 Hz, 1H), 7.52 (s, 1H), 7.50 – 7.42 (m, 3H), 7.27 (s, 3H), 7.14 (s, 1H).



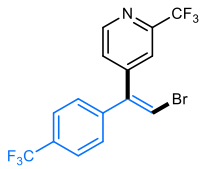
4-(2-Bromo-1-(4-methoxyphenyl)vinyl)-2-(trifluoromethyl)pyridine [5]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.4 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (62.8 mg, 88%, Z/E = 40:60).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.0 Hz, 0.39H), 8.64 (d, *J* = 5.1 Hz, 0.59H), 7.63 (s, 0.39H), 7.51 (s, 0.59H), 7.45 (m, 0.38H), 7.28 (m, 0.61H), 7.21 (d, *J* = 8.8 Hz, 1.20H), 7.08 (d, *J* = 8.8 Hz, 0.81H), 7.03 (s, 0.59H), 6.97 (d, *J* = 8.8 Hz, 1.20H), 6.85 (d, *J* = 8.8 Hz, 0.85H), 6.83 (s, 0.37H), 3.86 (s, 1.77H), 3.81 (s, 1.17H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.94 (s, 1.16F), -67.98 (s, 1.80F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.84 (160.17), 150.27 (150.23), 149.93 (149.11), 148.82 (148.72, q, *J* = 34.5 Hz), 143.49 (143.17), 130.86 (128.70), 128.82 (131.11), 124.56 (127.22), 122.75 (122.80, q, *J* = 274.5 Hz), 118.57 (121.30, q, *J* = 2.8 Hz), 114.09 (11.25), 110.31 (105.98), 55.25 (55.31).

HRMS (ESI) Calcd for $C_{15}H_{12}BrF_3N^+$ (M+H): 358.0049, found: 358.0051.



4-(2-Bromo-1-(4-(trifluoromethyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine [6]: According to the general procedure, 1-ethynyl-4-(trifluoromethyl)benzene (34.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

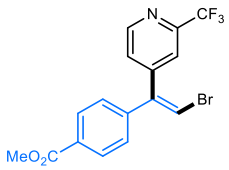
(2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (69.4 mg, 88%, Z/E = 47:53).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.0 Hz, 0.44H), 8.67 (d, *J* = 5.1 Hz, 0.49H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 4.2 Hz, 1H), 7.60 (s, 0.47H), 7.51 (d, *J* = 1.1 Hz, 0.50H), 7.45 (m, 0.44H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.24 (m, 0.49H), 7.22 (s, 0.52H), 7.06 (s, 0.44H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.80 (s, 1.59F), -62.80 (s, 1.40F),-68.01 (s, 1.25F) ,-68.01 (s, 1.48F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.59 (150.56), 149.00 (148.91, q, *J* = 34.5 Hz), 148.52 (148.02), 142.78 (142.58), 141.90 (140.41), 131.02 (130.04, q, *J* = 33.4 Hz), 129.95 (127.77), 124.26 (127.06), 125.94 (125.90), 121.16 (121.11, q, *J* =274.4 Hz), 121.57 (121.52, q, *J* =273.4 Hz), 121.13 (118.14, q, *J* = 2.8 Hz), 112.46 (110.29).

HRMS (ESI) Calcd for $C_{15}H_9BrF_6N^+$ (M+H): 395.9817, found: 395.9821.



Methyl 4-(2-bromo-1-(2-(trifluoromethyl)pyridin-4-yl)vinyl)benzoate [7]: According to the general procedure, methyl 4-ethynylbenzoate (32.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and

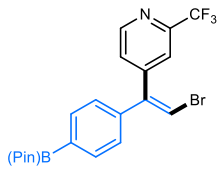
the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (61.4 mg, 80%, Z/E = 34:66).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 0.33H), 8.66 (d, *J* = 5.1 Hz, 0.64H), 8.15 – 8.11 (m, 1H), 8.02 – 7.98 (m, 0.64H), 7.62 (s, 0.33H), 7.49 (d, *J* = 1.0 Hz, 0.65H), 7.44 (dd, *J* = 4.9, 1.2 Hz, 0.33H), 7.39 – 7.33 (m, 1.34H), 7.25 – 7.21 (m, 1.32H), 7.20 (s, 0.63H), 7.07 (s, 0.31H), 3.95 (s, 1.89H), 3.92 (s, 0.93H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -68.00 (s, 0.97F), -68.06 (s, 1.96F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.35 (166.28), 150.50 (150.48), 149.02 (148.92, q, *J* = 34.8 Hz), 148.62 (148.17), 143.13 (142.89), 141.30 (142.61), 130.57 (130.50), 130.09 (130.15), 129.55 (127.36), 124.22 (127.10), 122.19 (122.25, q, *J* = 273 Hz) ,118.19 (121.17, q, *J* = 2.7 Hz), 112.12 (110.12), 52.31.

HRMS (ESI) Calcd for $C_{16}H_{12}BrF_3NO_2^+$ (M+H): 385.9998, found: 385.9997.



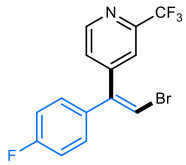
4-(2-Bromo-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)vinyl)-2-(trifluoromethyl)pyridine [8]: According to the general procedure, 4-Ethynylbenzeneboronic acid pinacol ester (49.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (65.2 mg, 72%, Z/E = 38:62).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 0.37H), 8.65 (d, *J* = 5.1 Hz, 0.61H), 7.93 (d, *J* = 8.1 Hz, 1.27H), 7.80 (d, *J* = 8.2 Hz, 0.75H), 7.65 (s, 0.38H), 7.53 (d, *J* = 0.8 Hz, 0.61H), 7.49 – 7.45 (m, 0.37H), 7.32 – 7.28 (m, 1.40H), 7.27 (m, 0.62H), 7.18 (d, *J* = 6.6 Hz, 1.35H), 7.01 (s, 0.37H), 1.39 (s, 7.37H), 1.36 (s, 4.61H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.97 (s, 1.08F), -68.02 (s,1.85F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.35 (150.29), 149.15 (148.62), 148.64 (148.71, q, *J* = 34.5 Hz), 143.89 (143.67),139.48 (141.07), 135.14 (135.26), 128.67, 126.73, 124.34 (127.21), 122.26 (122.31, q, *J* = 274.5 Hz), 118.28 (121.28, q, *J* = 2.7 Hz), 111.33 (108.71), 84.04, 24.86 (24.81).

HRMS (ESI) Calcd for $C_{20}H_{21}BBrF_3NO_2^+$ (M+H): 454.0795, found: 454.0777.



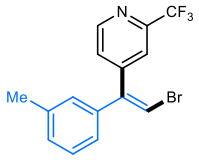
4-(2-Bromo-1-(4-fluorophenyl)vinyl)-2-(trifluoromethyl)pyridine [9]: According to the general procedure, 1-ethynyl-4-fluorobenzene (24.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (66.0 mg, 96%, Z/E = 45:55).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.5 Hz, 0.44H), 8.62 (d, *J* = 4.8 Hz, 0.55H),7.60 (s, 0.44H), 7.48 (s, 0.55H), 7.43 (d, *J* = 4.8 Hz, 0.45H), 7.21 – 7.13 (m, 1.56H), 7.12 – 7.02 (m, 2.55H), 7.00 – 6.89 (m, 1H), 6.81 (s, 0.44H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.97 (s, 1.33H), -68.03 (s, 1.77H), -111.62 (m, 0.45H), -111.79 (m, 0.35H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.24 (163.96, d, *J* = 250.0 Hz), 150.41 (150.37), 149.19(148.58) , 148.96 (148.61, q, *J* = 34.9 Hz), 142.95 (142.64), 134.77 (132.63, d, *J* = 3.5 Hz), 131.43 (129.29, d, *J* = 8.3 Hz), 127.08 (124.32), 125.46 (125.41, q, *J* = 274.4 Hz), 122.71 (118.29, q, *J* = 2.7 Hz), 116.06 (116.05, d, *J* = 21.5 Hz), 111.51 (107.84).

HRMS (ESI) Calcd for $C_{14}H_9BrF_4N^+$ (M+H): 345.9849, found: 345.9851.



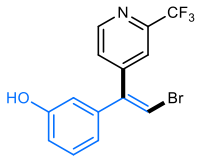
4-(2-Bromo-1-(m-tolyl)vinyl)-2-(trifluoromethyl)pyridine [10]: According to the general procedure, 1-ethynyl-3-methylbenzene (23.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (58.0 mg, 85%, Z/E = 41:59).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.9 Hz, 0.40H), 8.64 (d, *J* = 5.1 Hz, 0.57H), 7.64 (s, 0.39H), 7.53 (s, 0.57H), 7.46 – 7.43 (m, 0.41H), 7.35 (m, 0.59H), 7.27 – 7.23 (m, 1.16H), 7.24 – 7.22 (m, 0.81H), 7.11 (s, 0.58H), 7.08 – 7.04 (m, 1.13H), 6.98 – 6.93 (m, 0.84H), 6.91 (s, 0.41H), 2.39 (s, 1.69H) , 2.39 (s, 1.21H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.95 (1.21F), -68.00 (1.69F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.33 (150.26), 149.47 (148.93), 148.79 (148.67, q, *J* = 34.5 Hz), 144.05 (143.79), 138.58 (138.70), 136.70, 129.83 (129.76), 129.63 (128.76), 128.66 (128.09), 126.45 (127.20), 124.65 (124.43), 122.30 (122.35, q, *J* = 274.5 Hz), 118.30 (121.27, q, *J* = 2.8 Hz), 110.97 (107.71), 21.41 (21.34).

HRMS (ESI) Calcd for $C_{15}H_{12}BrF_3N^+$ (M+H): 342.0100, found: 342.0101.



3-(2-Bromo-1-(2-(trifluoromethyl)pyridin-4-yl)vinyl)phenol [11]: According to the general procedure, 3-ethynylphenol (23.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (49.2 mg, 72%, Z/E = 32:68).

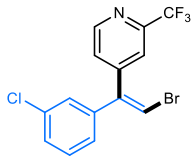
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 0.31H), 8.60 (d, *J* = 5.1 Hz, 0.66H), 7.66 – 7.51 (m, 1H), 7.47 – 7.44 (m, 0.31H), 7.35 – 7.27 (m, 1.39H), 7.22 (t, *J* = 7.9 Hz, 0.36H), 7.12 (s, 0.66H), 6.95 (s, 0.29H), 6.92 (m, 0.70H), 6.89 – 6.84 (m, 0.36H), 6.82 (dd, *J* = 7.6, 1.2 Hz, 0.68H), 6.80 – 6.75 (m, 0.34H), 6.75 – 6.71 (m, 0.68H), 6.54 – 6.51 (m, 0.59H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.72 (s, 0.96F), -67.81 (s, 2.00F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.27 (156.53), 150.08 (149.63), 149.86 (149.42), 148.60 (148.40), 143.43 (143.16), 138.02 (139.71), 130.15(130.19), 124.58 (127.51),

121.52 (119.29), 122.64 (122.56, q, J = 274.5 Hz), 118.50 (121.57, q, J = 2.8 Hz), 116.34 (116.26), 116.10 (114.51), 111.49 (108.25).

HRMS (ESI) Calcd for $C_{14}H_{10}BrF_3NO^+$ (M+H): 343.9892, found: 343.9894.



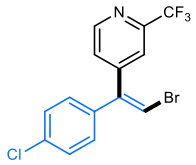
4-(2-Bromo-1-(3-chlorophenyl)vinyl)-2-(trifluoromethyl)pyridine [12]: According to the general procedure, 1-chloro-3-ethynylbenzene (27.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (61.9 mg, 86%, Z/E = 44:56).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 5.0 Hz, 0.42H), 8.58 (d, J = 5.1 Hz, 0.54H), 7.59 – 7.41 (m, 1H), 7.39 – 7.31 (m, 1.46H), 7.31 – 7.25 (m, 0.60H), 7.24 – 7.15 (m, 1.75H), 7.12 – 7.02 (m, 1.63H), 6.96 – 6.92 (m, 0.51H), 6.90 (s, 0.43H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.96 (s, 1.29F), -68.01 (s, 1.66F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.51 (150.47), 149.06 (148.95, q, J = 34.6 Hz), 148.67 (148.12), 142.69 (142.49), 138.44 (140.22), 134.77 (134.97), 130.19 (130.14), 129.44 (127.62), 129.11 (129.08), 127.45 (127.05), 125.64 (124.27), 122.67 (122.71, q, J = 274.5 Hz), 118.16 (121.14, q, J = 2.8 Hz), 112.15 (109.40).

HRMS (ESI) Calcd for $C_{14}H_9BrClF_3N^+$ (M+H): 361.9554, found: 361.9555.



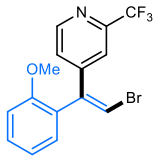
4-(2-Bromo-1-(4-chlorophenyl)vinyl)-2-(trifluoromethyl)pyridine [13]: According to the general procedure, 1-chloro-4-ethynylbenzene (27.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (64.1 mg, 89%, Z/E = 39:61).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 0.38H), 8.66 (d, *J* = 5.1 Hz, 0.59H), 7.62 (s, 0.37H), 7.50 (s, 0.62H), 7.45 (m, 1.35H), 7.32 (d, *J* = 8.5 Hz, 0.75H), 7.25 – 7.21 (m, 1.97H), 7.14 (s, 0.58H), 7.09 (d, *J* = 8.5 Hz, 0.81H), 6.94 (s, 0.37H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.98 (s, 1.15 F), -68.03(s, 1.79 F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (150.43), 148.97 (148.35), 148.88 (148.77, q, *J* = 34.6 Hz), 142.86 (142.61), 135.09 (137.01), 135.00 (135.16), 129.17 (130.86), 128.68, 124.43(127.10), 121.31 (120.36, q, *J* = 274.5 Hz), 121.16 (118.29, q, *J* = 2.8 Hz), 111.73 (108.56).

HRMS (ESI) Calcd for $C_{14}H_9BrClF_3N^+$ (M+H): 361.9554, found: 361.9555.



4-(2-Bromo-1-(2-methoxyphenyl)vinyl)-2-(trifluoromethyl)pyridine [14]: According to the general procedure, 1-ethynyl-2-methoxybenzene (26.4 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.),

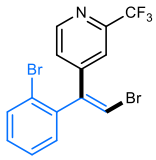
diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), NiBr$_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (64.3 mg, 90%, Z/E = 47:53).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.0 Hz, 0.46H), 8.61 (d, *J* = 5.1 Hz, 0.52H), 7.67 (s, 0.44H), 7.52 (d, *J* = 0.9 Hz, 0.52H), 7.44 (m, 1H), 7.36 (m, 0.48H), 7.26 – 7.18 (m, 2H), 7.07 (m, 0.54H), 6.98 (m, 1H), 6.86 (m, 0.46H), 6.81 (s, 0.44H), 3.68 (s, 1.63H), 3.58 (s, 1.44H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.90 (s, 1.37F), -67.98 (s, 1.53F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.46 (156.59), 150.23 (149.74), 148.84 (149.32), 148.70 (148.51, q, *J* = 34.5 Hz), 141.46 (141.19), 130.96 (130.78), 130.56 (130.62), 126.31 (128.16), 123.43 (125.59), 122.84 (122.93, q, *J* = 274.5 Hz), 120.86 (120.84), 117.43 (120.51, q, *J* =2.8 Hz), 111.53 (112.68), 111.42 (109.43), 55.48 (55.22).

HRMS (ESI) Calcd for $C_{15}H_{12}BrF_3NO^+$ (M+H): 358.0049, found: 358.0050.



4-(2-Bromo-1-(2-bromophenyl)vinyl)-2-(trifluoromethyl)pyridine [15]: According to the general procedure, 1-bromo-2-ethynylbenzene (36.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), NiBr$_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was

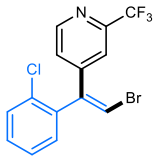
isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (76.3 mg, 94%, Z/E = 43:57).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.2 Hz, 0.42H), 8.56 (d, *J* = 5.2 Hz, 0.55H) 7.64-7.60 (m,0.92H), 7.50 (m, 0.44H), 7.44-7.23 (m, 2.39H), 7.25 – 7.13 (m, 2.41H), 6.71 (s, 0.42H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.95 (s, 1.32F), -68.00 (s, 1.62F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.62 (150.06), 149.07 (148.45, q, *J* = 34.5 Hz), 147.09 (147.13), 143.37 (142.47), 139.94 (137.85), 133.58 (133.67), 131.14 (131.65), 130.53 (130.62), 128.03 (127.86), 126.66, 123.49 (122.94), 120.12(117.81, q, *J* = 274.5 Hz), 117.32 (120.70, q, *J* = 2.9 Hz), 114.29 (111.81).

HRMS (ESI) Calcd for $C_{14}H_9Br_2F_3N^+$ (M+H): 407.9028, found: 407.9030.



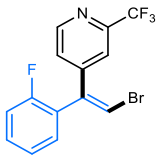
4-(2-Bromo-1-(2-chlorophenyl)vinyl)-2-(trifluoromethyl)pyridine [16]: According to the general procedure, 1-chloro-2-ethynylbenzene (27.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (60.5 mg, 84%, Z/E = 45:55).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.9 Hz, 0.42H), 8.57 (d, *J* = 4.9 Hz, 0.51H), 7.62 (d, *J* = 0.5 Hz, 0.43H), 7.46 – 7.40 (m, 1.44H), 7.33 (m, 1.68H), 7.28 – 7.24 (m, 1.69H), 7.22 – 7.17 (m, 0.69H), 7.15 (m, 0.52H), 6.73 (s, 0.43H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.96 (s, 1.46F), -68.02 (s, 1.55F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.57 (150.04), 149.03 (148.68, q, *J* = 34.5 Hz), 147.26 (147.35), 141.90 (141.16), 135.75 (137.93), 133.12 (133.09), 131.08 (131.48), 130.22 (130.47), 130.39 , 129.26 (129.17), 127.36 (127.24), , 122.73 (122.79, q, *J* = 274.5 Hz), 117.22 (120.50, q, *J* = 2.8 Hz), 114.25 (111.63).

HRMS (ESI) Calcd for $C_{14}H_9BrClF_3N^+$ (M+H): 361.9554, found: 361.9526.



4-(2-Bromo-1-(2-fluorophenyl)vinyl)-2-(trifluoromethyl)pyridine [17]: According to the general procedure, 1-fluoro-2-ethynylbenzene (24.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (55.7 mg, 81%, Z/E = 46:54).

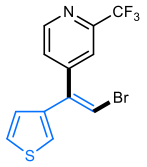
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.0 Hz, 0.45 H), 8.57 (d, *J* = 5.1 Hz, 0.53 H), 7.58 (s, 0.45 H), 7.45 (s, 0.51 H), 7.42 – 7.34 (m, 1H), 7.33 – 7.25 (m, 0.61H), 7.23 (s, 0.49H), 7.19 (m, 1.61 H), 7.14 – 7.05 (m, 1.49 H), 7.02 – 6.95 (m, 0.57 H), 6.88 (s, 0.49 H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.97 (s, 1.43 F), -68.05 (s, 1.50 F), -112.54 – -112.63 (m, 0.41 F), -112.64 – -112.72 (m, 0.45 F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.81 (160.58, d, *J* = 248.7 Hz), 150.52 (150.21), 149.03 (148.66, q, *J* = 35.0 Hz), 148.00 (148.27), 138.84 (138.13), 131.29 (130.70, d,

J = 2.9 Hz), 131.21 (130.98, d, *J* = 8.5 Hz), 130.70 (130.67), 126.50, 122.72 (122.79, q, *J* = 272.8 Hz), 124.56 (124.60), 117.45 (120.57, q, *J* = 2.8 Hz), 116.45 (116.52, d, *J* = 21.8 Hz), 114.25 (111.46).

HRMS (ESI) Calcd for $C_{14}H_9BrF_4N^+$ (M+H): 345.9849, found: 345.9851.



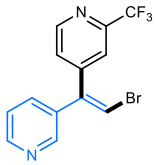
4-(2-Bromo-1-(thiophen-3-yl)vinyl)-2-(trifluoromethyl)pyridine [18]: According to the general procedure, 3-ethynylthiophene (21.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (63.7 mg, 96%, Z/E = 51:49).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 0.48H), 8.67 (d, *J* = 5.1 Hz, 0.46H), 7.65 (s, 0.49H), 7.55 (d, *J* = 0.9 Hz, 0.47H), 7.46 (m, 1H), 7.41 (m, 0.46H), 7.34 (m, 1H), 7.09 (m, 1H), 6.99 (s, 0.47H), 6.95 (s, 0.45H), 6.89 (m, 0.47H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.93 (s, 1.55F), -67.97 (s, 1.38F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.38 (150.33), 149.88 (148.66), 148.86 (148.89, q, *J* = 34.5 Hz), 139.30 (138.93), 138.61 (136.34), 128.10 (127.05), 126.84 (126.89), 125.10 (125.91), 123.94 (124.67), 122.76 (122.72, q, *J* = 274.5 Hz), 118.73 (121.01, q, *J* = 2.8 Hz), 107.12 (110.20).

HRMS (ESI) Calcd for $C_{12}H_8BrF_3NS^+$ (M+H): 333.9507, found: 333.9509.



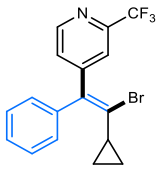
4-(2-Bromo-1-(pyridin-3-yl)vinyl)-2-(trifluoromethyl)pyridine [19]: According to the general procedure, 3-ethynylpyridine (20.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (56.2 mg, 86%, Z/E = 43:57).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.9 Hz, 0.46H), 8.73 – 8.69 (m, 1.25H), 8.64 – 8.63 (m, 0.48H), 8.59 (d, *J* = 1.7 Hz, 0.62H), 8.53 (d, *J* = 2.0 Hz, 0.47H), 7.67 – 7.62 (m, 1H), 7.53 (s, 0.63H), 7.49 – 7.42 (m, 1.63H), 7.31 (s, 0.51H), 7.28 (s, 1H), 7.06 (s, 0.46H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -68.02 (s, 1.26F), -68.06 (s,1.67F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.62 (150.59), 150.16 (148.02), 149.95 (149.99), 148.44 (147.69), 149.15 (149.04, q, *J* = 34.5 Hz), 140.79 (140.66), 137.05 (134.65), 132.89 (134.56), 124.21 (126.97), 123.63, 122.15 (122.20, q, *J* = 274.5 Hz), 118.17 (121.04, q, *J* = 2.8 Hz), 113.21 (109.86).

HRMS (ESI) Calcd for $C_{13}H_9BrF_3N_2^+$ (M+H): 328.9896, found: 328.9897.



4-(2-Bromo-2-cyclopropyl-1-phenylvinyl)-2-(trifluoromethyl)pyridine [20]: According to the general procedure, (cyclopropylethynyl)benzene (33.6 mg, 0.20 mmol,

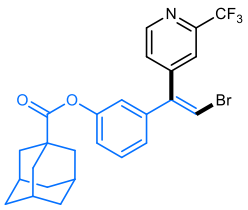
1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (24.3 mg, 32%, Z/E = 40:60).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.0 Hz, 0.40H), 8.67 (d, *J* = 5.0 Hz, 0.59H), 7.76 (s, 0.47H), 7.62 (s, 0.62H), 7.56 (d, *J* = 6.4 Hz, 1.0H), 7.42 – 7.28 (m, 3.0H), 7.23 – 7.16 (m, 2.0H), 1.80 -1.73 (m, 1H), 0.99 – 0.92 (m, 2H), 0.82 – 0.77 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.98 (s, 1.78F), -68.01(s, 1.23F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.81, 150.10, 148.42 (q, *J* = 34.5 Hz), 141.91, 137.77, 134.14, 129.42, 128.52, 127.94, 127.03, 121.43 (q, *J* = 274.3 Hz), 121.12 (q, *J* = 2.7 Hz), 18.07 (17.50), 9.25 (10.01).

HRMS (ESI) Calcd for $C_{17}H_{14}BrF_3N^+$ (M+H): 368.0256, found: 368.0285.



3-(2-Bromo-1-(2-(trifluoromethyl)pyridin-4-yl)vinyl)phenyl (*3R,5R,7R*)-adamantane-1-carboxylate [21]: According to the general procedure, 3-ethynylphenyl (*3R,5R,7R*)-adamantane-1-carboxylate (56.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was

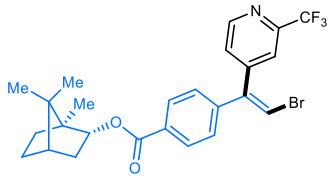
isolated by flash chromatography (PE: ethyl acetate= 20:1) as a white solid (82.6 mg, 82%, Z/E = 43:57).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.0 Hz, 0.43H), 8.64 (d, *J* = 5.1 Hz, 0.57H), 7.65 (s, 0.47H), 7.56 (d, *J* = 1.0 Hz, 0.56H), 7.49 – 7.41 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 0.50H), 7.25 (dd, *J* = 5.2, 1.6 Hz, 0.60H), 7.15 (s, 0.60H), 7.14 – 7.04 (m, 1.48H), 7.00 – 6.91 (m, 1.52H), 6.89 (t, *J* = 1.9 Hz, 0.46H), 2.10 – 2.02 (m, 9H), 1.76 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.94 (s, 1.38F), -67.97 (s, 1.62F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.85 (175.95), 151.32 (151.40), 150.48 (150.40), 148.92 (148.80, q, *J* = 34.5 Hz), 148.87 (148.31), 143.03 (142.80), 137.85 (139.82), 129.78, 126.52 (124.71), 124.47 (127.16), 122.70 (122.13), 120.97 (120.01, q, *J* = 274.5 Hz), 120.62 (122.31), 118.11 (121.24, q, *J* = 2.8 Hz), 111.81 (109.01), 41.01, 38.66, 36.35 (36.33), 27.81 (27.79).

HRMS (ESI) Calcd for $C_{25}H_{24}BrF_3NO_2^+$ (M+H): 506.0937, found: 506.0938.



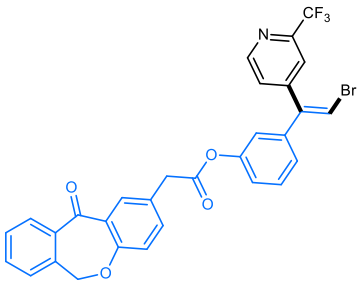
(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(2-bromo-1-(2-(trifluoromethyl)pyridin-4-yl)vinyl)benzoate [22]: According to the general procedure, (*1S,2R,4S*)-1,7,7-trimethylbicyclo[*2.2.1*]heptan-2-yl 4-ethynylbenzoate (56.4 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a white solid (91.5 mg, 90%, Z/E =38:62).

^{1}H NMR (400 MHz, $CDCl_3$)δ 8.81 (d, *J* = 5.0 Hz, 0.38H), 8.66 (d, *J* = 5.1 Hz, 0.62H), 8.17 (d, *J* = 8.5 Hz, 1.24H), 8.03 (d, *J* = 8.5 Hz, 0.76H), 7.62 (s, 0.38H), 7.51 (s, 0.62H), 7.37 (d, *J* = 8.3 Hz, 1.24H), 7.25 – 7.22 (m, 1.14H), 7.21 (s, 0.62H), 7.06 (s, 0.38H), 5.17 – 5.08 (m, 1H), 2.55 – 2.44 (m, 1H), 2.18 – 2.02 (m, 1H), 1.81 – 1.77 (m, 1H), 1.77 – 1.69 (m, 1H), 1.48 – 1.22 (m, 2H), 1.18 – 1.06 (m, 1H), 0.97 (s, 1.86H), 0.96 (s, 1.14H), 0.92 (d, *J* = 3.9 Hz, 3.72H), 0.90 (d, *J* = 3.6 Hz, 2.28H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.99 (s, 1.14F), -68.03 (s, 1.86F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.11 (166.00), 150.50 (150.46), 148.65 (148.23), 149.03 (148.69, q, *J* = 34.8 Hz), 143.16 (142.94), 141.13 (142.47), 131.25 (131.20), 130.03 (130.07), 129.53 (127.36), 124.25 (127.12), 121.28 (121.33, q, *J* = 274.7 Hz), 118.18 (121.15, q, *J* = 2.8 Hz), 112.12 (109.96), 80.90 (89.89), 49.08 (49.07), 47.88 (47.86), 44.92 (44.89), 36.87 (36.85), 28.05 (28.03), 27.36 (27.32), 19.68 (19.67), 18.88 (18.86), 13.61 (13.58).

HRMS (ESI) Calcd for $C_{25}H_{26}BrF_3NO_2^+$ (M+H): 508.1094, found: 508.1095.



3-(2-Bromo-1-(2-(trifluoromethyl)pyridin-4-yl)vinyl)phenyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate [23]: According to the general procedure, 3-ethynylphenyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (76.8 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 µL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 µL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL,

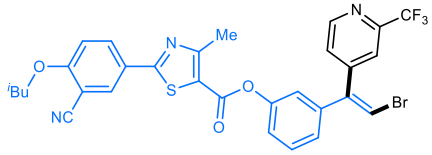
0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 5:1) as a white solid (86.6 mg, 73%, Z/E = 47:53).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.0 Hz, 0.47H), 8.64 (d, *J* = 5.0 Hz, 0.53H), 8.21 (s, 1H), 7.90 (m, 1H), 7.64 (s, 0.48H), 7.56 (m, 1.55H), 7.39 (m, 3H), 7.39 – 7.30 (m, 1.56H), 7.25 – 7.16 (m, 1H), 7.14 (s, 0.53H), 7.14 – 7.08 (m, 1H), 7.07 (s, 0.51H), 7.06 (d, *J* = 2.6 Hz, 1H), 7.00 – 6.92 (m, 1.5H),5.20 (s, 0.90H), 5.19 (s, 1.08H), 3.89 (s, 1.09H), 3.87 (s, 0.91H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.91 (s, 1.42F), -67.96 (s, 1.55F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.74, 169.65 (169.56), 160.54, 150.94 (150.85), 150.46 (150.42), 148.80 (148.26), 142.93 (148.82, q, *J* = 34.5 H), 142.86, 142.65, 139.86, 140.31, 136.24, 137.95, 135.45 (136.20), 127.83, 127.82, 127.14, 126.80, 126.90, 126.89, 125.22, 124.99, 122.64, 124.43, 121.98 (122.13), 122.68 (122.73, q, *J* = 274.5 Hz), 118.13 (121.22, q, *J* =2.8 Hz), 111.92 (109.19), 73.67, 40.17 (40.12).

HRMS (ESI) Calcd for $C_{30}H_{20}BrF_3NO_4^+$ (M+H): 594.0522, found: 594.0524.



3-(2-Bromo-1-(2-(trifluoromethyl)pyridin-4-yl)vinyl)phenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate [24]: According to the general procedure,3-ethynylphenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (33.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 µL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 µL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash

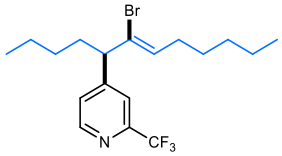
chromatography (PE: ethyl acetate= 20:1) as a white solid (116.6 mg, 89%, Z/E = 58:42).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 5.0 Hz, 0.58H), 8.67 (d, *J* = 5.1 Hz, 0.42H), 8.20 (m, 1H), 8.14 – 8.09 (m, 1H), 7.67 (s, 0.58H), 7.57 (s, 0.43H), 7.54 – 7.45 (m, 1H), 7.41 (m, 0.62H), 7.35 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.17 (m, 0.79H), 7.09 – 7.03 (m, 1.61H), 7.02 (s, 1H), 3.92 (s, 1H), 3.90 (s, 1H), 2.82 (s, 1.22H), 2.80 (s, 1.67H), 2.21 (m, 1H), 1.10 (s, 3H), 1.08 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.94 (s, 1.74F), -67.98 (s, 1.24F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.40 (168.33), 163.46 (163.33), 162.73 (162.71), 160.15 (160.16), 150.52 (150.47), 148.84 (148.24), 148.90 (149.02, q, *J* = 34.6 Hz), 142.65 (142.84), 140.05(138.14), 132.65 (132.21), 130.04 (130.02), 127.16 (127.24), 125.68 (125.71), 125.24, 124.45, 122.45 (122.40, q, *J* = 274.5Hz), 122.79 (122.19), 121.23 (118.19, q, *J* =2.8 Hz), 120.73 (122.30), 120.03 (120.21), 115.26, 112.68, 112.00, 109.33, 103.07, 75.73, 28.11, 19.00, 17.70.

HRMS (ESI) Calcd for $C_{30}H_{24}BrF_3N_3O_3S^+$ (M+H): 642.0668, found: 642.0670.



4-(5-Bromododec-6-en-6-yl)-2-(trifluoromethyl)pyridine [25]: According to the general procedure, dodec-6-yne (33.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), K_2HPO_4 (6.8 mg, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash

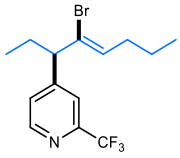
chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (39.1 mg, 50%, Z/E = 29:71).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.0 Hz, 1H), 7.57 (s, 1H), 7.40 (d, *J* = 5.0 Hz, 1H), 5.99 (t, *J* = 6.9 Hz, 1H), 3.60 (dd, *J* = 8.2, 6.9 Hz, 1H), 2.29 – 2.15 (m, 2H), 2.06 – 1.94 (m, 1H), 1.80 – 1.68 (m, 1H), 1.52 – 1.26 (m, 10H), 0.94 – 0.85 (m, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.88 (s, 0.86F), -67.88 (s, 2.13F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.41, 149.91, 148.07 (q, *J* = 34.5 Hz), 131.60 (130.65), 128.75, 125.77, 121.59 (q, *J* = 273.0 Hz), 119.88 (q, *J* = 2.6 Hz) 54.67, 32.24 (32.00), 31.45 (31.05), 30.91 (31.15), 30.47, 29.33 (29.69), 26.79 (28.01), 22.43 (22.25), 13.96 (13.99), 13.86 (13.91).

HRMS (ESI) Calcd for $C_{18}H_{26}BrF_3N^+$ (M+H): 392.1195, found: 392.1197.



4-(3-Bromooct-4-en-4-yl)-2-(trifluoromethyl)pyridine [26]: According to the general procedure, oct-4-yne (22.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), K_2HPO_4 (6.8 mg, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (25.5 mg, 38%, Z/E = 57:43).

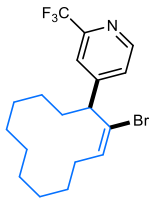
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (t, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.40 (d, *J* = 4.9 Hz, 1H), 6.00 (dd, *J* = 11.8, 6.8 Hz, 1H), 3.65 – 3.58 (m, 0.53H), 3.55 – 3.47 (m, 0.37H),

2.30 – 2.15 (m, 2H), 2.12 – 1.94 (m, 1H), 1.77 (m, 1H), 1.55 – 1.42 (m, 1H), 1.35 – 1.14 (m, 1H), 1.06 – 0.85 (m, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.88 (s, 1.74F), -67.90 (s, 1.26F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.33 (153.23), 149.92, 148.25 (q, *J* = 34.3 Hz), 132.90 (131.62), 128.64 (128.22), 121.60 (q, *J* = 272.3 Hz), 119.90, 117.52, 54.34 (56.48), 34.47 (33.18), 24.71 (25.44), 21.66 (20.35), 13.79 (13.68), 12.83 (11.84).

HRMS (ESI) Calcd for $C_{14}H_{18}BrF_3N^+$ (M+H): 336.0569, found: 336.0570.



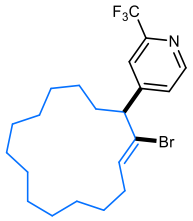
4-(2-Bromocyclododec-2-en-1-yl)-2-(trifluoromethyl)pyridine [27]: According to the general procedure, cyclododecyne (32.8 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), K_2HPO_4 (6.8 mg, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (24.9 mg, 32%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.1 Hz, 1H), 7.61 (s, 1H), 7.44 (d, *J* = 4.9 Hz, 1H), 6.29 (m, 1H), 3.77 (m, 1H), 2.43 – 2.41 (m, 1H), 2.18 – 1.99 (m, 2H), 1.85 – 1.70 (m, 2H), 1.70 – 1.50 (m, 4H), 1.36 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.84 (s, 3.0F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.22, 149.80, 148.13 (q, *J* = 34.5 Hz), 134.62, 127.76, 125.76, 121.68 (q, *J* = 272.6 Hz), 119.80 (q, *J* = 2.5 Hz), 117.61, 52.54, 31.18, 29.19, 28.04, 26.22, 25.20, 25.16, 23.82, 23.51, 23.22.

HRMS (ESI) Calcd for $C_{18}H_{24}BrF_3N^+$ (M+H): 390.1039, found: 390.1040.



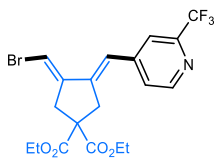
4-(2-Bromocyclopentadec-2-en-1-yl)-2-(trifluoromethyl)pyridine [28]: According to the general procedure, cyclopentadecyne (41.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), K_2HPO_4 (6.8 mg, 0.04 mmol, 0.2 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (27.6mg, 32%).

^{1}H NMR (400 MHz,) δ 8.64 (d, *J* = 5.1 Hz, 1H), 7.58 (s, 1H), 7.35 (d, *J* = 5.0 Hz, 1H), 6.02 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.65 (dd, *J* = 11.8, 3.3 Hz, 1H), 2.45-2.36 (m, 1H), 2.25 – 2.01 (m, 3H), 1.72 – 1.10 (m, 20H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.84 (s, 3.0F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.70, 149.86, 148.17 (q, *J* = 34.5 Hz), 132.97, 128.81, 125.53, 121.64 (q, *J* = 273.7 Hz), 119.69 (q, *J* = 2.6 Hz), 53.95, 31.88, 30.30, 27.15, 27.05, 26.98, 26.94, 26.85, 26.54, 26.48, 25.51.

HRMS (ESI) Calcd for $C_{21}H_{30}BrF_3N^+$ (M+H): 432.1508, found: 432.1509.



Dimethyl -3-(bromomethylene)-4-((2-(trifluoromethyl)pyridin-4-yl)methylene)cyclopentane-1,1-dicarboxylate [29]: According to the general procedure, diethyl 2,2-di(prop-2-yn-1-yl)malonate (47.2 mg, 0.20 mmol, 1.0 equiv.),

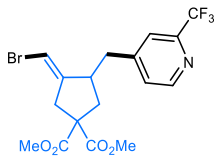
4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 5:1) as a pale-yellow oil (45.0 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.63 (m, 1H), 7.63 – 7.53 (m, 1H), 7.44 (dd, *J* = 10.0, 5.0 Hz, 1H), 6.85 – 5.83 (m, 2H), 4.31 – 4.05 (m, 4H), 3.75 – 3.08 (m, 3H), 1.54 (d, *J* = 6.7 Hz, 1H), 1.32 – 1.13 (m, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.03 (s, 1.27F), -68.06 (s, 0.63F), -68.14 (s, 0.12F), -68.15 (s, 0.98F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.55 (170.43, 169.92, 169.30), 152.67, 150.50 (150.33, 150.27, 150.11), 148.95 (q, *J* = 34.5 Hz), 146.99 (145.72, 144.88, 143.94), 140.24 (143.07, 140.85), 127.23 (125.64, 125.18, 123.37), 122.80 (121.41, 120.37, 119.97, 117.47), 122.84 (q, *J* = 274.5 Hz), 117.46 (119.95, 121.39, 119.80, q, *J* = 2.8 Hz), 107.89 (103.27), 70.36 (62.16,62.12, 62.04), 61.61 (57.66, 56.31), 40.50 (43.71, 41.70, 40.20), 21.94 (21.03), 14.02 (14.07, 13.94).

HRMS (ESI) Calcd for $C_{19}H_{20}BrF_3NO_4^+$ (M+H): 462.0522, found: 462.0523.



Dimethyl 3-(bromomethylene)-4-((2-(trifluoromethyl)pyridin-4-yl)methyl)cyclopentane-1,1-dicarboxylate [30]: According to the general procedure, dimethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (42.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine

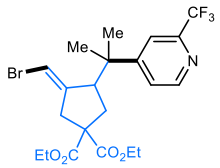
(5.6 μL, 0.04 mmol, 0.2 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 9:1) as a pale-yellow oil (68.3 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 7.52 (d, *J* = 19.7 Hz, 1H), 7.32 (d, *J* = 4.2 Hz, 1H), 6.16 (s, 0.30H), 5.96 (s, 0.66H), 3.81 – 3.68 (m, 6H), 3.18 – 3.13 (m, 1H), 3.07 – 2.92 (m, 1H), 2.75 – 2.40 (m, 2H), 1.92 (dd, *J* = 13.0, 10.2 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.91 (m, 3.0F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.49 (171.39), 150.31, 150.21,148.60 (q, *J* = 34.5 Hz), 147.41, 126.71, 120.81 (q, *J* = 2.6 Hz), 120.29(q, *J* = 274.5 Hz), 100.29, 57.57, 53.11, 53.08, 43.78, 41.02, 40.18, 39.03.

HRMS (ESI) Calcd for $C_{17}H_{18}BrF_3NO_4^+$ (M+H): 436.0366, found: 436.0367.



Diethyl 3-(bromomethylene)-4-(2-(2-(trifluoromethyl)pyridin-4-yl)propan-2-yl)cyclopentane-1,1-dicarboxylate [31]: According to the general procedure, diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (42.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was

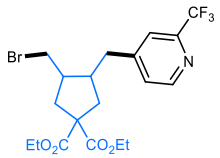
isolated by flash chromatography (PE: ethyl acetate= 5:1) as a pale-yellow oil (30.4 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 – 8.58 (m, 1H), 7.64 – 7.45 (m, 1H), 7.40 – 7.27 (m, 1H), 5.96 (s, 0.31H), 5.45 (s, 0.49H), 4.28 – 4.10 (m, 4H), 3.68 – 3.29 (m, 2H), 3.06 – 2.65 (m, 2H), 2.16 – 2.05 (m, 1H), 1.82 – 1.52 (m, 6H), 1.29 – 1.22 (m, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -67.90 (m, 3.0F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.27, 151.21, 149.90, 149.60 (q, J = 34.5 Hz), 135.43, 126.78, 121.64 (q, J = 2.74.5 Hz), 120.87 (q, J = 2.7 Hz), 117.62, 61.17, 57.58, 45.72, 31.00, 26.00, 17.87, 16.00, 14.05.

HRMS (ESI) Calcd for $C_{21}H_{26}BrF_3NO_4^+$ (M+H): 492.0992, found: 492.0994.



diethyl 3-(bromomethyl)-4-((2-(trifluoromethyl)pyridin-4-yl)methyl)cyclopentane-1,1-dicarboxylate [32]： According to the general procedure, diethyl 2,2-diallylmalonate (48.0 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (40.0 μL, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 5:1) as a pale-yellow oil (81.9 mg, 88%, cis/trans = 85:15). (Cis/trans isomer determined by NOESY).

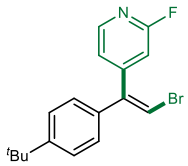
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 4.9 Hz, 1H), 7.53 (s, 0.85H), 7.49 (s, 0.15H), 7.38 (d, J = 4.2 Hz, 0.85H), 7.32 (d, J = 4.8 Hz, 0.15H), 4.24 – 4.12 (m, 4H), 3.58 –

3.31 (m, 2H), 2.89 (dd, *J* = 12.6, 3.4 Hz, 1H), 2.57 (m, 3H), 2.48 – 2.37 (m, 1H), 2.14 (m, 3H), 1.26 – 1.19 (m, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.95 (s, 2.47F), -67.97 (s, 0.52F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.40, 171.98, 151.61 (151.22), 149.97 (150.06), 148.35 (149.03, q, *J* = 34.5 Hz), 127.05 (126.66), 124.26(124.22, q, *J* = 272.5 Hz), 121.05 (120.73, q, *J* = 2.7 Hz), 61.85, 61.75 (61.69), 58.61 (57.98), 45.16 (46.35), 42.56 (43.71), 37.87 (39.49), 37.05 (39.31), 33.33 (38.89), 32.43 (35.56), 13.95, 13.92.

HRMS (ESI) Calcd for $C_{19}H_{24}BrF_3NO_4^+$ (M+H): 466.0835, found: 466.0837.



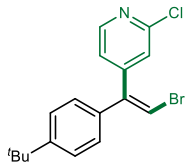
4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-fluoropyridine [33]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 4-bromo-2-fluoropyridine (54.9 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (54.2 mg, 82%, Z/E =38:62).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.4 Hz, 0.37H), 8.14 (d, *J* = 5.4 Hz, 0.62H) 7.44 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.11 (m, 0.39H), 7.10 (d, *J* = 8.5 Hz, 0.77H), 7.03 (m, 0.41H), 7.03 (s, 0.62H), 6.90 (s, 0.35H), 6.86 (s, 0.36H), 6.73 (s, 0.60H), 1.36 (s, 5.52H) , 1.31 (s, 3.46H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.32 (s, 0.36F), -67.73 (s, 0.59F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.93 (164.71, d, *J* = 238.5 Hz), 153.48 (152.64, d, *J* = 8.2 Hz), 151.77 (152.13), 147.65 (147.79, d, *J* = 15.4 Hz), 143.83 (143.60), 133.84 (135.71), 129.08 (126.98), 125.50 (125.73), 119.74 (122.28, d, *J* = 4.1 Hz), 110.05 (106.60), 107.84 (110.45, d, *J* = 37.8 Hz), 34.75 (34.67), 31.26 (31.15).

HRMS (ESI) Calcd for $C_{17}H_{18}FN^+$ (M+H): 334.0601, found: 334.0600.

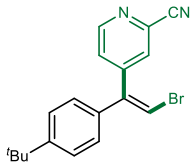


4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-chloropyridine [34]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 4-bromo-2-chloropyridine (57.6 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (65.1 mg, 93%, Z/E = 51:49).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.0 Hz, 0.49H), 8.30 (d, *J* = 5.2 Hz, 0.47H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 3.6, 1.2 Hz, 0.59H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 5.2, 1.5 Hz, 0.51H), 6.99 (s, 0.45H), 6.85 (s, 0.47H), 1.36 (s, 4.24H), 1.31 (s, 4.67H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.17 (151.97), 151.81 (151.75), 151.13 (150.29), 149.80 (149.68), 143.64 (143.40), 135.66 (133.71), 129.09 (127.01), 125.75 (125.52), 124.91 (123.29), 122.42 (120.82), 110.08 (106.76), 34.66 (34.75), 31.25 (31.14).

HRMS (ESI) Calcd for $C_{17}H_{18}BrClN^+$ (M+H): 350.0306, found: 350.0310.

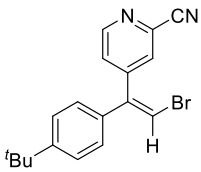


4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)picolinonitrile [35]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 4-bromopicolinonitrile (54.9 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 8:1) as a pale-yellow oil (58.3 mg, 86%, Z/E = 51:49). (the Z and E isomers were determined by NOESY, and the E isomer was also confirmed by crystallographic data).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.0 Hz, 0.46H), 8.63 (d, *J* = 5.2 Hz, 0.45H), 7.64 (m, 0.51H), 7.50 (m, 0.52H), 7.48 (m, 0.47H), 7.48 – 7.45 (m, 1H), 7.38 – 7.33 (m, 1.48H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 0.48H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.90 (s, 0.50H), 1.37 (s, 4.17H), 1.32 (s, 4.43H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.47 (152.12), 151.27, 149.31 (148.63), 143.06 (142.77), 135.35 (134.26), 133.20 (134.19), 129.29 (127.76), 129.03 (127.12), 126.73 (124.67), 125.90 (125.75), 117.05, 111.25 (107.52), 34.69 (34.78), 31.12 (31.22).

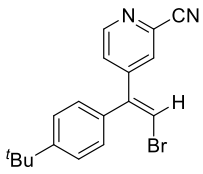
HRMS (ESI) Calcd for $C_{18}H_{18}BrN_2^+$ (M+H): 341.0648, found: 341.0650.



(Z)-4-(2-bromo-1-(4-(tert-butyl)phenyl)vinyl)picolinonitrile (Z-35):

^{1}H NMR (600 MHz, CDCl3) δ 8.76 (d, J = 5.0 Hz, 1H), 7.64 (s, 1H), 7.51 (d, J = 5.0 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.91 (s, 1H), 1.32 (s, 9H).

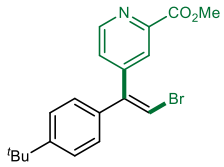
^{13}C NMR (150 MHz, CDCl3) δ 152.35, 151.19, 148.54, 142.68, 135.25, 134.08, 129.19, 127.70, 127.05, 125.83, 116.98, 107.47, 34.60, 31.04.



(*E*)-4-(2-bromo-1-(4-(tert-butyl)phenyl)vinyl)picolinonitrile (*E*-35):

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, J = 5.2 Hz, 1H), 7.48 (s, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.36 (dd, J = 5.1, 1.4 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.09 (s, 1H), 1.36 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.99, 151.20, 149.19, 142.94, 134.13, 133.14, 128.97, 126.66, 125.66, 124.64, 117.00, 111.26, 34.69, 31.16.



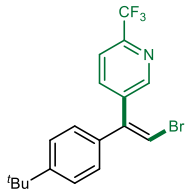
Methyl -4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)picolinate [36]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), methyl 4-bromopicolinate (64.8 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (64.2 mg, 86%, Z/E = 47:53).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 0.47H), 8.65 (d, *J* = 5.1 Hz, 0.53H), 8.05 – 8.03 (m, 1H), 7.46 – 7.41 (m, 1.58H), 7.36 – 7.30 (m, 1H), 7.24 (m, 0.52H), 7.21

– 7.18 (m, 1H), 7.10 – 7.06 (m, 1H), 7.05 (s, 0.50H), 6.88 (s, 0.44H), 4.01 (s, 1.48H), 4.01 (s, 1.63H), 1.36 (s, 4.80H) , 1.31 (s, 4.35H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.60 (165.57), 152.11 (151.76), 150.07 (150.04), 149.49 (148.64), 148.24, 143.99 (143.78), 133.82 (135.78), 129.13 (127.06), 125.97 (127.78), 125.53 (125.75), 123.16 (125.30), 110.03 (106.74), 53.01 (52.99), 34.75 (34.66), 31.25 (31.15).

HRMS (ESI) Calcd for $C_{19}H_{21}BrNO_2^+$ (M+H): 374.0750, found: 374.0751.



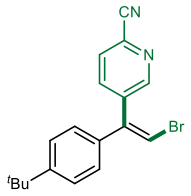
5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine [37]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromo-2-(trifluoromethyl)pyridine (67.5 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (72.8 mg, 95%, Z/E =40:60).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 1.8 Hz, 0.38H), 8.63 (d, *J* = 1.8 Hz, 0.57H), 7.82 (m, 0.42H), 7.73 (d, *J* = 8.1 Hz, 0.42H), 7.64 (dd, *J* = 8.1, 2.0 Hz, 0.64H), 7.60 (d, *J* = 8.2 Hz, 0.65H), 7.44 (d, *J* = 8.5 Hz, 1.23H), 7.35 (d, *J* = 8.5 Hz, 0.84H), 7.23 (d, *J* = 8.5 Hz, 1.26H), 7.10 (d, *J* = 8.6 Hz, 0.86H), 6.92 (s, 0.38H), 6.91 (s, 0.57H), 1.36 (s, 5.34H), 1.31 (s, 3.71H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.85 (s, 1.16F), -67.86 (s, 1.85F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.83 (152.17), 148.51 (150.82), 147.36 (147.34, q, *J* = 34.5 Hz), 142.68 (142.46), 138.56 (139.56), 136.18 (138.10), 134.16, 129.16 (127.11), 125.52 (125.78), 120.09 (122.36, q, *J* = 2.8Hz), 122.36 (122.39, q, *J* = 274.5Hz), 108.28 (107.27), 34.74 (34.66), 31.23 (31.14).

HRMS (ESI) Calcd for $C_{18}H_{18}BrF_3N^+$ (M+H): 384.0569, found: 384.0570.

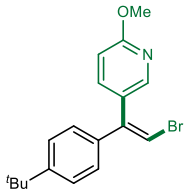


5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)picolinonitrile [38]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromopicolinonitrile (54.9 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (56.3 mg, 83%, Z/E =60:40).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 0.60H), 8.62 (s, 0.40H), 7.81 – 7.74 (m, 1H), 7.66 – 7.59 (m, 1H), 7.44 (d, *J* = 8.4 Hz, 0.80H), 7.35 (d, *J* = 8.4 Hz, 1.21H), 7.20 (d, *J* = 8.4 Hz, 0.80H), 7.08 (d, *J* = 8.4 Hz, 1.20H), 6.96 (s, 0.40H), 6.92 (s, 0.60H), 1.35 (s, 3.60H), 1.31 (s, 5.40H)**.**

^{13}C NMR (100 MHz, $CDCl_3$) δ, 151.96, 149.54 (152.32), 142.18 (142.46), 138.62 (139.79), 138.13 (135.54), 135.85 (133.72), 132.71 (132.57), 127.98 (128.05), 127.12 (129.09), 125.84 (125.61), 117.12, 107.67 (109.51), 34.65 (34.73), 31.10 (31.20).

HRMS (ESI) Calcd for $C_{18}H_{18}BrN_2^+$ (M+H): 341.0648, found: 341.0650.

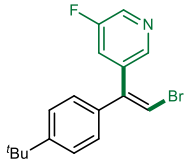


5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-methoxypyridine [39]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromo-2-methoxypyridine (56.4 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 8:1) as a pale-yellow oil (45.7 mg, 66%, Z/E = 45:55).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.0 Hz, 0.45H), 8.04 (d, *J* = 2.3 Hz, 0.54H), 7.51 (m, 0.58H), 7.42 – 7.39 (m, 1H),7.39-7.37 (m, 0.65H), 7.35 – 7.31 (m, 1H), 7.24 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.77 (m, 0.53H), 6.75 (s, 0.49H), 6.66 (m, 1H), 3.98 (s, 1.37H), 3.93 (s, 1.65H), 1.35 (s, 4.99H), 1.31 (s, 4.17H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.84 (163.57), 151.58 (151.19), 145.62 (147.97), 143.45 (143.38), 137.84 (140.02), 135.23 (137.43), 130.41 (127.99), 129.26 (127.32), 125.21 (125.51), 110.56 (110.37), 103.68 (105.15), 53.57 (55.55), 34.71 (31.64), 31.32 (31.23).

HRMS (ESI) Calcd for $C_{18}H_{21}BrNO^+$ (M+H): 346.0801, found: 346.0801.



3-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-5-fluoropyridine [40]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.),

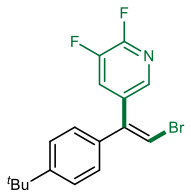
3-bromo-5-fluoropyridine (52.8 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (59.6 mg, 89%, Z/E = 48:52).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.38 (m, 0.51H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.20 – 7.15 (m, 0.56H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.87 (s, 0.48H), 6.86 (s, 0.52H), 1.35 (s, 4.77H), 1.35 (s, 4.36H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -126.61 (d, *J* = 8.8 Hz, 0,48F), -126.83 (d, *J* = 9.3 Hz, 0.52F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.15 (164.92, d, *J* = 239.0 Hz), 152.03 (151.68), 146.17 (146.46, d, *J* = 6.3Hz), 142.53 (142.24), 137.45 (137.27, d, *J* = 5.3 Hz), 136.35 (134.29), 129.13 (125.46), 127.10 (125.70, d, *J* = 27.6 Hz), 121.70 (124.02,d, *J* = 18.7 Hz), 107.52 (106.95), 34.73 (34.65), 31.25 (31.16).

HRMS (ESI) Calcd for $C_{17}H_{18}BrFN_2^+$ (M+H): 334.0601, found: 334.0605.



5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2,3-difluoropyridine [41]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromo-2,3-difluoropyridine (58.2 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL,

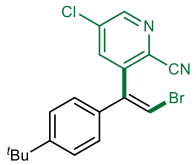
0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (69.0 mg, 97%, Z/E =42:58).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 0.42H), 7.91 (s, 0.58H), 7.53 (m, 0.50H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.29 (m, 0.66H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.86 (s, 0.43H), 6.81 (s, 0.59H), 1.36 (s, 5.37H) , 1.36 (s, 3.81H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -86.88 – -87.40 (m, 0.41F), -87.40 – -88.04 (m, 0.55F), -139.51 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.49 (150.02, dd, *J* = 240.5, 14.8 Hz), 151.91 (152.24), 144.99 (dd, *J* = 262.1, 28.7 Hz), 139.87 (142.61, dd, *J* = 12.9, 5.6 Hz), 141.66 (141.50), 134.16 (136.24), 129.09 (125.55), 125.80 (127.11), 128.00 (127.96, d, *J* = 15.5 Hz), 125.55 (125.80), 107.23 (107.71), 34.76 (34.68), 31.24 (31.16).

HRMS (ESI) Calcd for $C_{17}H_{17}BrF_2N^+$ (M+H): 352.0507, found: 352.0506.

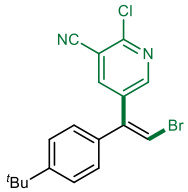


3-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-5-chloropicolinonitrile [42]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 3-bromo-5-chloropicolinonitrile (54.9 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (57.8 mg, 77%, Z/E = 37:63).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.59 (m, 0.37H), 8.59 – 8.48 (m, 0.63H), 7.72 (dd, *J* = 39.4, 2.1 Hz, 0.36H), 7.56 (dd, *J* = 43.0, 2.3 Hz, 0.66H), 7.36 – 7.31 (m, 1H), 7.29 – 7.26 (m, 1H),7.18 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.01 (q, *J* = 2.2 Hz, 0.53H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.81 – 6.80 (m, 0.37H), 1.25(s, 3.37H), 1.23(s, 5.66H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.62 (152.39), 151.51 (151.30), 149.38 (149.16), 141.18 (142.74140.64), 140.34 (139.52), 138.37 (137.99), 137.81 (137.21), 135.61 (134.23), 133.24 (131.59), 126.04 (126.54), 125.58 (129.14), 120.65 (115.29), 110.22 (111.68), 34.71 (34.79), 31.10 (31.17).

HRMS (ESI) Calcd for $C_{18}H_{17}BrClN_2^+$ (M+H): 375.0258, found: 375.0234.

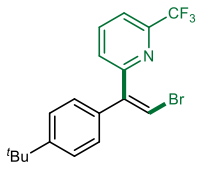


5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-chloronicotinonitrile [43]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromo-2-chloronicotinonitrile (65.1 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (54.9 mg, 73%, Z/E = 45:55).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.4 Hz, 0.45H), 8.58 (d, *J* = 2.4 Hz, 0.55H), 8.12 (d, *J* = 2.4 Hz, 0.46H), 7.94 (d, *J* = 2.4 Hz, 0.55H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.92 (m, 1H), 1.36 (s, 4.07H), 1.32 (s, 4.93H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.63 (153.95), 152.63 (152.30), 151.52 (151.29), 150.76 (151.73), 143.46 (144.32), 141.13 (140.69), 135.53 (134.26), 127.15 (129.01), 126.01 (125.82), 118.60, 114.36 (113.33), 110.53 (112.06), 108.08 (109.06), 34.71 (34.79), 31.11 (31.20).

HRMS (ESI) Calcd for $C_{18}H_{17}BrClN_2^+$ (M+H): 375.0258, found: 375.0234.



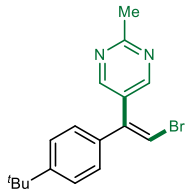
2-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-6-(trifluoromethyl)pyridine [44]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 2-bromo-6-(trifluoromethyl)pyridine (67.5 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (74.6 mg, 97%, Z/E = 30:70).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (t, *J* = 7.8 Hz, 0.33H), 7.88 (s, 0.70H), 7.69 (dt, *J* = 8.7, 4.2 Hz, 1H), 7.57 – 7.55 (m, 0.71H), 7.55 – 7.54 (m, 0.30H), 7.48 (d, *J* = 8.4 Hz, 1.43H), 7.33 (d, *J* = 8.6 Hz, 0.66H), 7.23 (d, *J* = 8.4 Hz, 1.48H), 7.17 (d, *J* = 8.6 Hz, 0.66H), 7.04 (d, *J* = 8.0 Hz, 0.72H), 6.93 (s, 0.30H), 1.38 (s, 6.19H), 1.30 (s, 2.96H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.82 (s,0.89F), -68.10 (s, 2.11F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.04 (158.38), 151.35 (151.68), 147.78 (q, *J* = 34.8 Hz), 143.67 (145.53), 138.05 (137.68), 133.93 (135.61), 129.14 (126.86), 125.65 (125.58), 124.59 (127.79), 121.39 (121.35, q, *J* = 277.4 Hz), 118.79 (119.29, q, *J* = 2.6 Hz), 114.74 (107.65), 34.75 (34.64), 31.35 (31.20).

HRMS (ESI) Calcd for $C_{18}H_{18}BrF_3N^+$ (M+H): 384.0569, found: 384.0574.

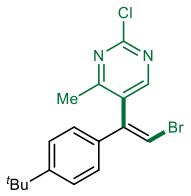


5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-methylpyrimidine [45]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromo-2-methylpyrimidine (52.0 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (49.0 mg, 74%, Z/E =48:52).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.47 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.87 (s, 0.48H), 6.79 (s, 0.52H), 2.79 (s, 1.44H), 2.71 (s, 1.58H), 1.34 (s, 4.62H) , 1.34 (s, 4.40H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.44 (167.40), 155.26 (157.52), 152.13 (151.78), 140.60 (140.75), 133.87 (136.14), 131.70 (129.94), 129.10 (127.09), 125.47 (125.77), 106.63 (107.21), 34.72 (34.65), 31.22 (31.14), 25.73 (25.93).

HRMS (ESI) Calcd for $C_{17}H_{20}BrN_2^+$ (M+H): 331.0804, found: 331.0804.



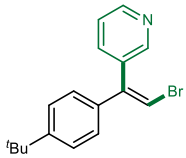
5-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-chloro-4-methylpyrimidine [46]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 5-bromo-2-chloro-4-methylpyrimidine (62.1 mg, 0.3 mmol, 1.5

equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (63.6 mg, 87%, Z/E =59:41).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 0.59H), 8.22 (s, 0.41H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.15 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.91 (s, 0.41H), 6.44 (s, 0.58H), 2.23 (s, 1.18H), 2.08 (s, 1.83H), 1.20 (s, 5.43H), 1.18 (s, 3.63H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.20 (169.05), 159.41 (160.24), 158.18, 152.18 (152.46), 139.57 (140.18), 133.55 (134.39), 133.22 (131.10), 128.71 (126.06), 125.42 (125.99), 107.98 (108.98), 34.75 (34.69), 31.16 (31.11), 22.96 (22.22).

HRMS (ESI) Calcd for $C_{17}H_{19}BrClN_2^+$ (M+H): 365.0415, found: 365.0419.

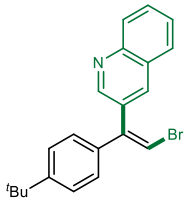


3-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)pyridine [47]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 3-bromopyridine (47.4 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (53.7 mg, 85%, Z/E =51:49). (^{1}H NMR spectra were recorded on Bruker 400 and ^{13}C NMR spectra were recorded on Bruker 600).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 – 8.43 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 0.48H), 7.48 (d, *J* = 7.5 Hz, 0.48H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.23 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 0.48H), 6.78 (s, 0.46H) 1.35 (s, 4.39H), 1.31 (s, 4.60H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.74 (151.38), 150.57 (150.50), 148.93 (149.03), 148.41 (148.46), 143.97 (143.47), 137.18 (136.84), 135.03 (134.80), 127.13 (129.22), 125.57 (123.09),123.09, 106.18, 34.69 (34.61), 31.17 (31.26).

HRMS (ESI) Calcd for $C_{17}H_{19}BrN^+$ (M+H): 316.0695, found: 315.0697.

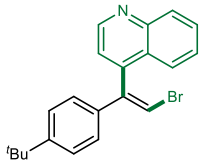


3-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)quinoline [48]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (62.4 mg, 0.20 mmol, 1.0 equiv.), 3-bromoquinoline (62.4 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (52.7 mg, 73%, Z/E = 41:59).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 0.41H), 7.76 (s, 0.59H), 7.65 (s, 0.52H), 7.54 (s, 0.33H), 7.46 – 7.40 (m, 1H), 7.37 – 7.31 (m, 1H), 7.26 – 7.22 (m, 1.65H), 7.18 – 7.13 (m, 1.50H), 6.85 (d, *J* = 1.8 Hz, 0.60H), 6.65 (d, *J* = 1.9 Hz, 0.42H), 3.88 (s, 2.19H), 3.87 (s, 1.19H), 1.36 (s, 5.45H), 1.32 (s, 3.63H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.80, 151.33 (151.37), 146.27 (147.32), 143.53, 137.19 (136.75), 136.98 (132.35), 129.85, 129.74 (129.46), 129.25, 129.06, 127.60 (127.98), 127.53, 127.27 (125.62), 126.89 (126.88), 117.09, 106.47, 34.62, 31.16.

HRMS (ESI) Calcd for $C_{21}H_{21}BrN^+$ (M+H): 366.0852, found: 366.0852.

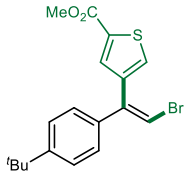


4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)quinoline [49]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), 4-bromoquinoline (62.4 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (46.7 mg, 64%, Z/E = 66:34).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 – 8.97 (m, 0.66H), 8.93 – 8.89 (m, 0.34H), 8.18 (dd, *J* = 8.4, 2.7 Hz, 0.67H), 8.12 (dd, *J* = 8.4, 2.5 Hz, 0.35H), 7.88 (dd, *J* = 8.4, 1.9 Hz, 0.34H), 7.79 (dd, *J* = 8.3, 2.0 Hz, 0.66H), 7.76 – 7.65 (m, 1H), 7.55 – 7.33 (m, 1H), 7.33 – 7.28 (m, 3H), 7.16 – 7.16 (m, 1H), 7.14 – 7.13 (m, 0.63H), 6.65 (d, *J* = 3.2 Hz, 0.34H), 1.28 -1.31 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.87 (151.61), 150.26 (150.01), 148.65 (148.70), 146.00 (147.68), 143.06 (142.44), 135.61 (134.66), 129.97 (129.82), 129.62 (129.45), 128.64, 127.03 (126.91), 126.06, 125.76, 125.22 (125.48), 121.65, 107.53 (107.30), 34.62 (34.69), 31.13 (31.18).

HRMS (ESI) Calcd for $C_{21}H_{21}BrN^+$ (M+H): 366.0852, found: 366.0855.

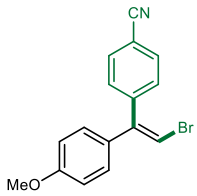


Methyl -4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)thiophene-2-carboxylate [50]: According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (36.0 μL, 0.20 mmol, 1.0 equiv.), methyl 4-bromothiophene-2-carboxylate (66.3 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (84.5 mg, 94%, Z/E = 41:59).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 0.40H), 7.76 (s, 0.58H), 7.65 (s, 0.51H), 7.54 (s, 0.32H), 7.43 – 7.41 (m, 1H), 7.34 – 7.32 (m, 1H),7.25 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.18 – 7.12 (m, 1H), 6.85 (s, 0.60H), 6.65 (s, 0.41H), 3.88 – 3.87 (m, 3H), 1.36(s, 4.91H), 1.32 (s, 4.35H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.39 (162.51), 151.23 (151.65), 142.45 (140.86), 140.72 (139.60), 135.07(137.34), 134.95 (133.80), 132.76 (132.91), 131.78 (129.52), 128.83 (127.36), 125.28 (125.49), 105.63 (105.09), 52.27 (52.22), 34.68 (34.62), 31.29 (31.21).

HRMS (ESI) Calcd for $C_{18}H_{20}BrO_2S^+$ (M+H): 379.0362, found: 379.0338.



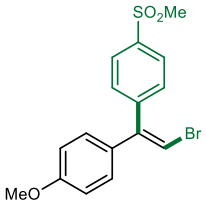
4-(2-Bromo-1-(4-methoxyphenyl)vinyl)benzonitrile [51]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 4-

bromobenzonitrile (108.5 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (62.4 mg, 96%, Z/E = 45:55).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.82 (s, 0.41H), 6.75 (s, 0.51H), 3.85 (s, 1.30H) , 3.85 (s, 1.68H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.90 (159.56), 145.37 (145.03), 144.84 (144.08), 132.06 (132.18), 132.08 (129.95), 130.50 (130.93), 128.71 (128.24), 118.64 (118.58), 114.02 (113.82), 111.68 (111.57), 104.80 (107.71), 55.29 (55.22).

HRMS (ESI) Calcd for $C_{16}H_{13}BrNO^+$ (M+H): 314.0175, found: 314.0183.



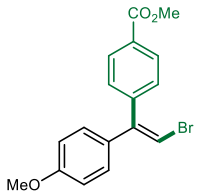
1-(2-Bromo-1-(4-(methylsulfonyl)phenyl)vinyl)-4-methoxybenzene [52]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-4-(methylsulfonyl)benzene (146.4 mg, 0.6mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and

the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (58.7 mg, 80%, Z/E =45:55).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.87 – 6.75 (m, 2H), 3.85 (s, 1.33H), 3.85 (s, 1.66H), 3.12 (s, 1.67H) , 3.05 (s, 1.31H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.98 (159.65), 146.51 (145.13), 148.86 (145.01), 139.84 (139.80), 132.23 (130.13), 130.80 (131.02), 128.80 (128.59), 127.42 (127.57), 114.10 (113.89), 104.93 (107.81), 55.37 (55.31), 44.49.

HRMS (ESI) Calcd for $C_{16}H_{16}BrO_3S^+$ (M+H): 366.9998, found: 366.9998.

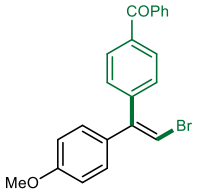


Methyl -4-(2-bromo-1-(4-methoxyphenyl)vinyl)benzoate [53]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), methyl 4-bromobenzoate (134.4 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (46.9 mg, 68%, Z/E =52:48).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1.02H), 7.96 (d, *J* = 8.6 Hz, 0.87H), 7.38 (d, *J* = 8.4 Hz, 1.01H), 7.28 (d, *J* = 8.6 Hz, 0.90H), 7.24 (d, *J* = 8.8 Hz, 0.86H), 7.11 (d, *J* = 8.9 Hz, 1.03H), 6.94 (d, *J* = 8.8 Hz, 0.85H), 6.83 (s, 0.54H), 6.81 (s, 0.89H), 6.73 (s, 0.49H), 3.94 (s, 1.53H), 3.91 (s, 1.29H), 3.85 (s, 1.27H), 3.80 (s, 1.54H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83 (166.73), 159.81 (159.46), 145.6 (145.68), 144.11 (145.48), 132.67 (130.62), 129.81 (131.05), 129.59 (129.71), 128.78 (127.72), 113.96 (113.73), 106.61 (104.22), 55.34 (55.27), 52.19.

HRMS (ESI) Calcd for $C_{17}H_{16}BrO_3^+$ (M+H): 347.0277, found: 347.0279.

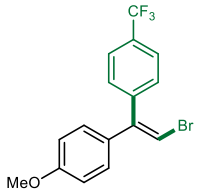


(4-(2-Bromo-1-(4-methoxyphenyl)vinyl)phenyl)(phenyl)methanone [54]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), (4-bromophenyl)(phenyl)methanone (156.6 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (56.1 mg, 72%, Z/E = 43:57).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2.17H), 7.82 – 7.77 (m, 0.86H), 7.76 – 7.72 (m, 0.82H), 7.59 (m, 1H), 7.49 (m, 2H), 7.45 – 7.40 (m, 1.09H), 7.35 – 7.31 (m, 0.84H), 7.28 (d, *J* = 2.0 Hz, 0.97H), 7.14 (d, *J* = 8.8 Hz, 1.10H), 6.95 (d, *J* = 8.8 Hz, 0.83H), 6.85 (d, *J* = 2.7 Hz, 0.97H), 6.79 (d, *J* = 32.6 Hz, 1.08H), 3.85 (s, 1.20H), 3.81 (s, 1.58H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.30 (196.10), 159.83 (159.49), 145.59 (145.71), 143.65 (145.00), 137.54 (134.50), 136.90 (134.96), 132.74 (130.62), 132.50 (132.51), 130.27 (131.07), 130.07 (130.10), 129.74 (130.00), 128.35 (128.86), 127.62, 113.99 (113.77), 104.30 (106.69), 55.36 (55.29).

HRMS (ESI) Calcd for $C_{22}H_{18}BrO_2^+$ (M+H): 393.0485, found: 393.0487.



1-(2-Bromo-1-(4-(trifluoromethyl)phenyl)vinyl)-4-methoxybenzene [55]:

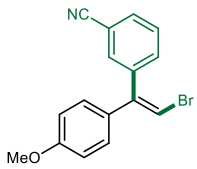
According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-4-(trifluoromethyl)benzene (135.0 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (pure PE) as a pale-yellow oil (57.8 mg, 81%, Z/E = 55:45).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.79 (s, 0.51H), 6.75 (s, 0.42H), 3.86 (s, 1.65H), 3.81 (s, 1.35H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56 (s, 1.35F), -62.60(s, 1.65F).

^{13}C NMR (100 MHz, $CDCl_3$) δ159.50 (159.83), 145.32 (145.21), 144.60 (143.01), 130.46 (132.54), 130.01(129.98, q, *J* = 34.6 Hz), 128.75 (129.78), 128.04 (128.75), 125.37 (125.26, q, *J* = 3.7 Hz),124.20 (124.75, q, *J* = 271.8 Hz), 113.74 (113.97), 106.50 (104.38), 55.23 (55.30).

HRMS (ESI) Calcd for $C_{16}H_{13}BrF_3O^+$ (M+H): 357.0096, found: 357.0096.

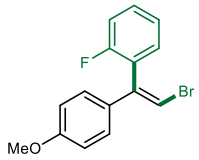


3-(2-Bromo-1-(4-methoxyphenyl)vinyl)benzonitrile [56]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 3-bromobenzonitrile (108.5 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (50.5 mg, 80%, Z/E = 55:45).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 0.42H), 7.62 – 7.51 (m, 2H), 7.48 (m, 1H), 7.41 (m, 1H), 7.22 (d, *J* = 8.7 Hz, 0.57H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.78 (s, 0.51H), 6.75 (s, 0.41H), 3.85 (s, 1.65H),3.81 (d, *J* = 1.29H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.91 (159.58), 144.50 (144.33), 142.28 (140.54), 134.18 (133.27), 131.80 (131.46), 131.22 (131.37), 130.91 (128.71), 129.24(129.12), 129.92 (132.11), 118.38 (118.48), 113.86 (114.05), 112.67 (112.53), 106.76 (104.82), 55.23 (55.29).

HRMS (ESI) Calcd for $C_{16}H_{13}BrNO^+$ (M+H): 314.0175, found: 314.0183.



1-(2-Bromo-1-(4-methoxyphenyl)vinyl)-2-fluorobenzene [57]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-2-fluorobenzene (104.4 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4

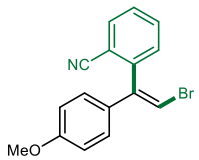
mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (pure PE) as a pale-yellow oil (62.2 mg, 99%, Z/E = 48:52).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 0.54H), 7.24 – 7.19 (m, 1.13H), 7.19 – 7.14 (m, 0.69H), 7.13 – 7.10 (m, 0.67H), 7.10 – 7.04 (m, 2H), 7.03 – 6.91 (m, 1.08H), 6.85 – 6.79 (m, 1H), 6.74 (s, 1H), 6.74 – 6.69 (m, 1H), 6.62 (s, 0.44H), 3.73 (s, 1.41H), 3.73 (s, 1.56H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.45 (m, 0.51F), -113.78 (m, 0.48F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.63 (161.04, d, *J* = 248.9 Hz), 159.65 (159.19), 141.02 (140.33), 131.87 (130.92), 131.41 (131.14, d, *J* = 3.5 Hz), 129.96 (129.66, d, *J* = 8.0 Hz), 128.86 (126.99, d, *J* = 13.2 Hz), 127.87 (130.45), 124.07 (124.02, d, *J* = 3.6 Hz), 116.14 (116.04, d, *J* = 20.9 Hz), 113.93 (113.46), 107.47 (106.08), 55.15 (55.25).

HRMS (ESI) Calcd for $C_{15}H_{13}BrFO^+$ (M+H): 307.0128, found: 307.0130.

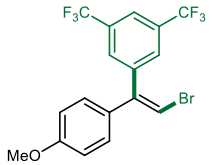


2-(2-Bromo-1-(4-methoxyphenyl)vinyl)benzonitrile [58]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 2-bromobenzonitrile (108.5 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (54.4 mg, 87%, Z/E =49:51).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.8, 0.9 Hz, 0.50H), 7.66 (m, 1H), 7.52 (m, 1H), 7.45 – 7.35 (m, 1H), 7.36 – 7.28 (m, 1.54H), 7.18 – 7.05 (m, 1H), 6.91 (m, 1.54H), 6.87 – 6.81 (m, 1H), 6.71 (s, 0.48H), 3.82 (s, 1.47H) , 3.79 (s, 1.52H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.57 (159.87), 145.09 (142.87), 143.41, 133.15 (133.58), 132.76 (132.55), 131.03 (128.12), 131.00 (129.81), 130.39 (130.27), 128.31, 117.55 (117.31), 113.54 (114.09), 111.95 (112.87), 108.13 (106.77), 55.25 (55.17).

HRMS (ESI) Calcd for $C_{16}H_{13}BrNO^+$ (M+H): 314.0175, found: 314.0183.



1-(2-Bromo-1-(4-methoxyphenyl)vinyl)-3,5-bis(trifluoromethyl)benzene [59]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-3,5-bis(trifluoromethyl)benzene (175.8 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 50:1) as a pale-yellow oil (70.0 mg, 83%, Z/E = 40:60).

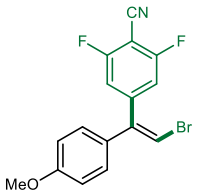
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 0.36H), 7.82 (s, 0.56H), 7.66 (s, 0.74H) , 7.66 (s, 1.13H), 7.29 – 7.22 (m, 1.27H), 7.10 (d, *J* = 8.8 Hz, 1H), 7.01 – 6.93 (m, 1H), 6.87 (s, 0.35H), 6.85 (s, 1H), 6.81 (s, 0.36H), 3.86 (s, 1.72H), 3.82 (s, 1.16H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84 (s, 2.32F), -62.89 (s, 3.54F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.15 (159.82), 143.31 (144.17), 141.36 (143.93), 131.76 (131.495, q, *J* = 33.4 Hz), 130.99 (128.78), 130.05 (127.69), 129.50, 127.69

(130.08), 123.11 (123.23, q, J = 271.1 Hz), 121.87, 114.04 (114.26), 107.95 (105.63), 55.33 (55.26).

HRMS (ESI) Calcd for $C_{17}H_{12}BrF_6O^+$ (M+H): 424.9970, found: 424.9969.



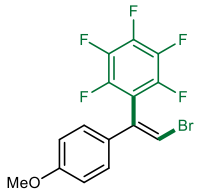
4-(2-Bromo-1-(4-methoxyphenyl)vinyl)-2,6-difluorobenzonitrile [60]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2,6-difluorobenzonitrile (129.8 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (66.5 mg, 96%, Z/E = 45:55).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.8 Hz, 1H), 7.11 – 7.05 (m, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 3.5 Hz, 1H), 6.96 (s, 0.44H), 6.91 (d, J = 8.6 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.78 (s, 0.54H), 3.86 (s, 1.34H), 3.82 (s, 1.65H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.44 (s, 0.38F), -103.46 (s, 0.50F), -103.54 (s, 0.49), -103.56 (s, 0.60F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.96 (162.47, dd, J = 262.3, 4.8 Hz), 160.23 (159.90), 147.65 (148.74, t, J = 9.0 Hz), 143.30 (143.64 ,t, J = 9.0 Hz), 128.73 (130.94), 128.69 (130.82), 114.26 (114.13), 113.66 (111.08, dd, J = 20.2, 3.6 Hz), 109.06 (d, J = 2.1 Hz), 106.06 (110.50), 91.67 (91.34, t, J = 19.3 Hz), 55.33 (55.26).

HRMS (ESI) Calcd for $C_{16}H_{11}BrF_2NO^+$ (M+H): 349.9987, found: 350.0307.



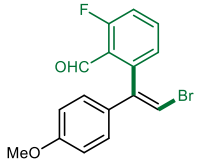
1-(2-Bromo-1-(4-methoxyphenyl)vinyl)-2,3,4,5,6-pentafluorobenzene [61]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-2,3,4,5,6-pentafluorobenzene (148.2 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (71.3 mg, 94%, Z/E = 36:64).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 0.74H), 7.16 (d, *J* = 8.8 Hz, 1.24H), 7.02 (s, 0.59H), 6.91 (d, *J* = 8.9 Hz, 0.77H), 6.86 (d, *J* = 8.9 Hz, 1.28H), 6.66 (s, 0.35H), 3.83 (s, 1.11H) , 3.83 (s, 1.82H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.41 (m, 1.00F), -140.64 (m, 0.60F), -153.65 (s, 0.51F), -153.94 (s, 0.32F), -161.47 (m, 1.56F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.25 (159.75), 143.76 (144.27, d, *J* = 247.6 Hz), 139.54 (139.35, d, *J* = 254.4 Hz), 136.71 (136.42, dt, *J* = 27.0, 12.9 Hz), 133.29 (130.97), 129.67 (128.87), 127.46 (129.97), 115.80 (115.84, t, *J* = 17.2 Hz), 114.35 (113.79), 110.21 (111.10), 55.34 (55.26).

HRMS (ESI) Calcd for $C_{15}H_9BrF_5O^+$ (M+H): 378.9751, found: 378.9751.



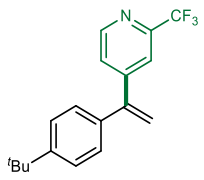
2-(2-Bromo-1-(4-methoxyphenyl)vinyl)-6-fluorobenzaldehyde [62]: According to the general procedure, 1-ethynyl-4-methoxybenzene (26.2 mg, 0.20 mmol, 1.0 equiv.), 2-bromo-6-fluorobenzaldehyde (121.8 mg, 0.6 mmol, 3.0 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (65.4 mg, 98%, Z/E =46:54).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 0.43H), 10.32 (s, 0.50H), 7.93 (m, 0.44H), 7.83 (m, 0.52H), 7.52 (m, 0.46H), 7.46 (m, 0.54H), 7.35 (d, *J* = 7.6 Hz, 0.38H), 7.31 (d, *J* = 8.8 Hz, 1.16H), 7.23 (t, *J* = 7.7 Hz, 0.55H), 7.16 (d, *J* = 8.9 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 6.89 (s, 0.44H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.75 (s, 0.50H), 3.83 (s, 1.59H) , 3.80 (s, 1.37H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.04 (m, 0.46F), -123.75 (m, 0.54F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.13 (187.06), 161.86 (161.54, d, *J* = 250.0 Hz), 159.51 (159.96), 139.28 (139.92), 137.87 (137.12, d, *J* = 4.7 Hz), 130.29 (131.29), 130.25 (128.35, d, *J* = 12.0 Hz), 113.72 (114.18), 108.53 (108.49), 107.02, 55.35 (55.27).

HRMS (ESI) Calcd for $C_{16}H_{13}BrFO_2^+$ (M+H): 335.0077, found: 335.0077.



4-(1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine [63]:

According to a literature procedure[1]. A mixture of 4-(2-bromo-1-(4-(*tert*-butyl)-phenyl)-vinyl)-2-(trifluoromethyl)-pyridine (77.6 mg, 0.2 mmol) in anhydrous THF (6

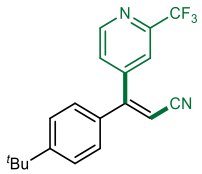
mL) was degassed by bubbling argon for few minutes. Then, $PdCl_2(PPh_3)_2$ (7.1 mg, 0.01 mmol, 5.0 mol%), TMEDA (108 mg, 0.72 mmol, 3.64 equiv.) and finally $NaBH_4$ (21.2 mg, 0.56 mmol, 2.8 equiv.) were introduced in sequence. The mixture was stirred at room temperature or heated at 65 °C under argon for 20 hours. The residue was taken up in brine and extracted with ethyl acetate. The extract was washed with water, brine and then dried over anhydrous Na_2SO_4. Evaporation of the solvent left the crude product which was purified by column chromatography over silica gel (PE: ethyl acetate= 20:1) to provide 4-(1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine as a pale yellow oil (54.8 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.68 (d, *J* = 0.7 Hz, 1H), 7.44 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.24 – 7.20 (m, 2H), 5.69 (s, 1H), 5.62 (s, 1H), 1.36 (s, 9H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.90 (s, 3F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.80, 150.96, 150.06, 148.44 (d, *J* = 34.3 Hz), 146.83, 135.95, 127.66, 125.57, 121.59 (q, *J* = 274.3 Hz), 119.49 (d, *J* = 2.8 Hz), 118.86, 117.68, 34.64, 31.24.

HRMS (ESI) Calcd for $C_{18}H_{19}F_3N^+$ (M+H): 306.1464, found: 306.1465.



3-(4-(*tert*-butyl)phenyl)-3-(2-(trifluoromethyl)pyridin-4-yl)acrylonitrile [64]:

According to a literature procedure[2l]. Mixture of 4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (77.6 mg, 0.2 mmol), $K_4Fe(CN)_6 \cdot 3H_2O$ (84.5 mg, 0.2 mmol), anhydrous KF (13.9 mg, 0.24 mmol) and CuI (1.9 mg, 0.01 mol) in DMF (1 mL)was heated with stirring at 120 °C under argon for 15 hours. The reaction mixture was filtered to separate the solid catalyst. The filtrate

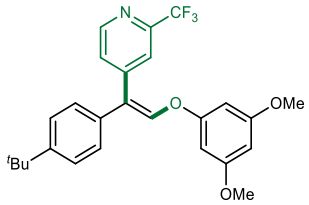
was extracted with Et_2O. The extract was washed with water, brine and then dried over anhydrous Na_2SO_4. Evaporation of the solvent left the crude product which was purified by column chromatography over silica gel (PE: ethyl acetate= 20:1) to provide 3-(4-(*tert*-butyl)phenyl)-3-(2-(trifluoromethyl)pyridin-4-yl)acrylonitrile as a pale yellow oil (73.0 mg, 90%, Z/E = 47:53).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.0 Hz, 0.47H), 8.64 (d, *J* = 5.1 Hz, 0.53H), 7.65 (s, 0.47H), 7.55 (d, *J* = 1.0 Hz, 0.53H), 7.48 – 7.43 (m, 1.52H), 7.38 – 7.34 (m, 1H), 7.28 – 7.27 (m, 0.47H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.06 (s, 0.53H), 6.91 (s, 0.47H), 1.37 (s, 4.76H), 1.32 (s, 4.24H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.90 (s, 1.41F), -67.94 (s, 1.59F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.93 (152.29), 150.29 (150.25), 149.83 (149.00), 148.61 (148.54, q, *J* = 34.3 Hz), 143.78 (143.50), 135.58 (133.57), 129.11 (127.04), 125.60 (125.83), 124.68 (127.25), 121.47 (121.51, q, *J* = 274.3 Hz), 118.53 (121.34, d, *J* = 2.8 Hz), 110.59 , 107.15, 34.75 (34.66), 31.22 (31.12).

HRMS (ESI) Calcd for $C_{19}H_{18}F_3N_2^+$ (M+H): 331.1417, found: 331.1418.



4-(1-(4-(*tert*-butyl)phenyl)-2-(3,5-dimethoxyphenoxy)vinyl)-2-(trifluoromethyl)pyridine [65]:

According to a literature procedure[3]. In a 10 mL round bottom flask a mixture of 4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (77.6 mg, 0.2 mmol), 3,5-dimethoxyphenol (30.8 mg, 0.2 mmol), Cs_2CO_3 (130.4 mg, 2 mmol), $Ni(acac)_2$ (2.6 mg, 0.01 mmol), CuI (1.9 mg, 0.01 mmol) and NMP (0.6 mL) was heated at 100 °C under argon for 8 hours. The reaction mixture was then allowed to cool and was extracted with ethyl acetate. The extract was washed with water and brine. Then the organic phase was dried over anhydrous Na_2SO_4 and evaporated to leave the crude

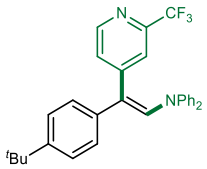
product, which was purified by column chromatography over silica gel (PE: ethyl acetate= 20:1) to provide the pure 4-(1-(4-(*tert*-butyl)phenyl)-2-(3,5-dimethoxyphenoxy)vinyl)-2-(trifluoromethyl)pyridine as a pale yellow oil (66.3 mg, 73%, Z/E = 43:57).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.1 Hz, 0.43H), 8.65 (d, *J* = 5.1 Hz, 0.57H), 7.81 (s, 0.44H), 7.62 (d, *J* = 1.0 Hz, 0.56H), 7.56 (dd, *J* = 5.1, 1.2 Hz, 0.44H), 7.48 – 7.41 (m, 2H), 7.38 (dd, *J* = 5.1, 1.4 Hz, 0.58H), 7.33 – 7.30 (m, 1H), 7.23 – 7.19 (m, 1H), 7.12 (s, 0.57H), 7.06 (s, 0.43H), 6.32 – 6.28 (m, 3H), 3.79 (s, 2.59H), 3.79 (s, 3.41H), 1.38 (s, 9H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.90 (s, 1.30F), -67.91 (s, 1.70F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.70 (161.75), 158.78 (158.53), 151.07 (151.21), 150.06 (149.92), 149.72 (146.76), 148.22 (148.67, q, *J* = 34.2 Hz), 142.82 (142.89), 131.44 (134.16), 129.44 (128.33), 125.53 (125.83), 125.03 (126.89), 122.75 (121.85), 121.47 (121.51, q, *J* = 274.3 Hz) ,118.88 (121.01, q, *J* = 2.7 Hz), 96.09 (96.12), 95.87 (95.51), 55.54, 34.70 (34.65), 31.30 (31.31).

HRMS (ESI) Calcd for $C_{26}H_{27}F_3NO_3^+$ (M+H): 458.1938, found: 458.1940.



N-(2-(4-(*tert*-butyl)phenyl)-2-(2-(trifluoromethyl)pyridin-4-yl)vinyl)-N-phenylaniline [66]:

According to a literature procedure[4]. CuI (1.9 mg, 0.01 mmol), diphenylamine (18.6 mg, 0.11 mmol) and ^{t}BuONa (19.2 mg, 0.2 mmol) were added to pre-dried a screw capped test tube with a Teflon-lined septum. The tube was then evacuated and backfilled with N_2 and this procedure was repeated three times. Toluene (1 mL) was added by syringe at room temperature, stirred for 30 seconds, then 4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (38.3 mg, 0.1 mmol) was added.

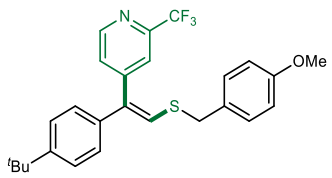
The tube was then sealed with a Teflon valve and the reaction mixture was stirred at 140 °C for 18 hours. The mixture was cooled to room temperature. Water (5 mL) and ethyl acetate (5 mL) were added and stirred for 30 min. The aqueous layer was washed with ethyl acetate for three times. The organic phase was combined. The solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel (PE: ethyl acetate= 20:1) to provide the pure N-(2-(4-(*tert*-butyl)phenyl)-2-(2-(trifluoromethyl)pyridin-4-yl)vinyl)-N-phenylaniline as a pale yellow oil (36.0 mg, 76%, Z/E = 27:73).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 0.27H), 8.71 (d, *J* = 5.0 Hz, 0.73H), 7.77 (s, 0.72H), 7.65 (s, 0.27H), 7.56 – 7.54 (m, 0.73H), 7.53 – 7.50 (m, 1.47H), 7.47 – 7.44 (m, 0.27H), 7.44 – 7.42 (m, 1.52H), 7.30 – 7.27 (m, 3H), 7.11 – 7.06 (m, 6H), 6.95 – 6.91 (m, 3H), 1.35 (s, 6.65H), 1.33 (s, 2.35H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.93 (s, 0.67F), -67.97 (s, 2.33F).

^{13}C NMR (150 MHz, CDCl3) δ 153.26 (152.30), 149.96 (150.26), 149.89 (148.20, q, *J* = 34.2 Hz), 143.09 (143.51), 133.55, 131.79, 129.31, 127.94, 127.26, 127.05, 125.84, 125.63, 122.84 (q, *J* = 274.5 Hz), 122.35 (q, *J* = 2.9 Hz), 120.96, 118.38, 117.77, 107.11, 97.76, 96.39, 85.12, 34.96 (34.69), 31.09 (31.14).

HRMS (ESI) Calcd for $C_{30}H_{28}F_3N_2^+$ (M+H): 473.2199, found: 473.2199.



4-(1-(4-(*tert*-butyl)phenyl)-2-((4-methoxybenzyl)thio)vinyl)-2-(trifluoromethyl)pyridine [67]:

According to a literature procedure[5]. An argon flushed schlenk was charged with KOH (0.3 mmol) and Cu_2O (0.0075 mmol). Then distilled dioxane (1.0 mL) was added, followed by -(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (68.9 mg, 0.18 mmol) and then (4-methoxyphenyl)methanethiol (23.1mg, 0.15 mmol).

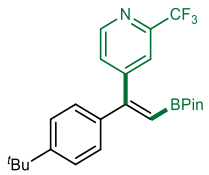
The schlenk was sealed and heated at 110 °C in a sand bath. After stirring at this temperature for 24 hours, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate. The resulting solution was filtered through a pad of celite then washed with ethyl acetate and concentrated in vacuo to give the crude material which was then purified by column chromatography to afford the desired product.4-(1-(4-(*tert*-butyl)phenyl)-2-((4-methoxybenzyl)thio)vinyl)-2-(trifluoromethyl)pyridine (64.5 mg, 71%, Z/E = 55:45) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 0.55H), 8.54 (d, *J* = 5.2 Hz, 0.45H), 7.59 (s, 0.55H), 7.44 – 7.38 (m, 2H), 7.34 – 7.30 (m, 1H), 7.30 – 7.26 (m, 0.94H), 7.26-7.25 (m, 0.87H), 7.17-7.15 (m, 1.43H), 7.03 – 6.97 (m, 1H), 6.94 (s, 0.45H), 6.92 – 6.86 (m, 2H), 6.73 (s, 0.55H), 4.00 (s, 0.90H), 3.96 (s, 1.10H), 3.81 (s, 3H), 1.35 (s, 4.07H), 1.32 (s, 4.94H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.90 (s, 1.35F), -67.91 (s, 1.65F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.02 (159.09), 150.87 (151.29), 150.09 (149.97), 149.30 (150.34), 148.35 (148.23, q, *J* = 34.3 Hz), 137.12 (134.34), 135.40 (133.98), 131.58 (128.97), 129.99 (130.12), 128.12(128.73), (), 126.72 (129.03), 125.56 (125.67), 127.17 (123.62), 121.57(121.64, q, *J* = 274.4Hz), 121.23 (117.52, q, *J* = 2.8 Hz), 114.19 (114.20), 55.27 (55.26), 38.42 (38.26), 34.54 (34.68), 31.20 (31.25).

HRMS (ESI) Calcd for $C_{26}H_{27}F_3NOS^+$ (M+H): 458.1760, found: 458.1762.



4-(1-(4-(*tert*-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2-(trifluoromethyl)pyridine [68]:

According to a literature procedure[6]. To an oven-dried flask was added 4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (57.5 mg, 0.15 mmol),,

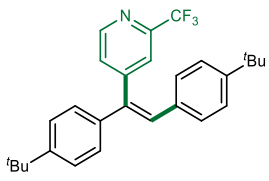
bis(pinacolato)diboron (41.9mg, 0.165 mmol), and AcOK (44.1 mg, 0.45 mmol.). The flask was sealed, 1,4-dioxane (1 mL) was added and the reaction mixture was degassed with argon for 15 min. To the reaction mixture was added $Pd(dppf)Cl_2$•DCM (5.5 mg, 0.0075 mmol.) and the flask was resealed and purged with argon. The reaction mixture was stirred at 90°C for 16 hours. After the reaction was complete (observed by TLC), the reaction was cooled to rt and the solvent was removed in vacuo. Et_2O was added and the crude residue was filtered through a layer of Celite eluting the product with Et_2O. The filtrate was washed with H_2O, brine, dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified by column chromatography (SiO2, specified combination of solvents) (PE: ethyl acetate= 20:1) to provide 4-(1-(4-(*tert*-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2-(trifluoromethyl)pyridine as a pale yellow oil (49.7 mg, 77%, Z/E = 48:52).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.9 Hz, 0.48H), 8.63 (d, *J* = 5.1 Hz, 0.52H), 7.64 (s, 1H), 7.41 – 7.30 (m, 3H), 7.16 (dd, *J* = 10.4, 8.5 Hz, 2H), 6.18 (d, *J* = 1.4 Hz, 1H), 1.31 (s, 5.19H), 1.26 (s, 4.29H), 1.15 (s, 6.12H), 1.13 (s, 5.70H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.82 (s, 1.44F), -67.92 (s, 1.56F)..

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.13, 151.95 (151.85), 151.69, 150.06 (150.11), 148.37 (q, *J* = 34.1 Hz), 136.46, 127.71, 125.62 (124.96), 125.03 (129.24), 122.71 (122.78, q, *J* =274.3Hz), 118.85 (119.56, q, *J* = 2.7 Hz), 117.76, 83.73, 34.68, 31.33 (31.29), 24.63.

HRMS (ESI) Calcd for $C_{24}H_{30}BF_3NO_2^+$ (M+H): 432.2316, found: 432.2318.



4-(1,2-bis(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine [69]:

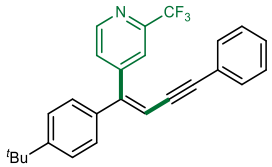
According to a literature procedure[1]. General procedure for the Suzuki-Miyaura cross-couplings of 4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (77.6 mg, 0.2 mmol), (4-(*tert*-butyl)phenyl)boronic acid (46.3 mg, 0.26 mmol), cesium carbonate (195.6 mg, 0.6 mmol), 1,4-dioxane (1.5 mL) and H_2O (0.5 mL) was degassed by bubbling argon for few minutes and then $Pd_2(dba)_3$(4.6 mg, 0.026 mmol), tri(2-furyl)phosphine (TFP) (6.9 mg, 0.15 mmol) were added. The mixture was heated at 65 °C for the proper time under argon. After cooling, the mixture was taken up in ethyl acetate and washed two times with brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure. Evaporation of the solvent left the crude product which was purified by column chromatography over silica gel (PE: ethyl acetate= 20:1) to provide 4-(1,2-bis(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine as a white solid (80.7 mg, 92%, Z/E = 49:51).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.9 Hz, 0.49H), 8.61 (d, *J* = 5.1 Hz, 0.51H), 7.66 (s, 0.50H), 7.55 (s, 0.50H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.41 – 7.36 (m, 1.54H), 7.32 (dd, *J* = 5.1, 1.5 Hz, 0.51H), 7.23 – 7.16 (m, 3H), 7.14 (d, *J* = 5.8 Hz, 1H), 7.12 (s, 0.49H), 7.10 (s, 0.50H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 1.40 (s, 4.46H), 1.35 (s, 4.66H), 1.28 (s, 4.48H) , 1.28 (s, 4.51H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -67.87(s, 1.53F), -67.98 (s, 1.47F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.73 (151.36), 151.41 (151.39), 151.01 (151.00), 149.95 (150.30), 148.60 (148.26, q, *J* =34.4Hz), 138.37 (135.09), 137.80 (137.88), 133.03 (132.17), 130.43 (128.33), 129.73 (129.55), 129.13 (127.12), 125.55 (126.15), 125.14 (125.31), 124.35, 121.71 (121.51, q, *J* =274.6 Hz), 118.04 (122.43, q, *J* =2.8 Hz), 34.71 (34.62), 34.61 (34.58), 31.35 (31.24), 31.13.

HRMS (ESI) Calcd for $C_{28}H_{31}F_3N^+$ (M+H): 438.2403, found: 438.2405.



4-(1-(4-(*tert*-butyl)phenyl)-4-phenylbut-1-en-3-yn-1-yl)-2-(trifluoromethyl)pyridin [70]:

According to a literature procedure[7]. To a solution of 4-(2-bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2 (trifluoromethyl)pyridine (77.6 mg, 0.2 mmol), $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol, 3 mol%), and copper(I) iodide (0.8 mg, 0.004 mmol, 2 mol %) in of Et_2NH (0.5 mL), cooled in an ice-bath, was added (20.4 mg, 0.2 mmol). Then the temperature was raised to room temperature and solid $Et_2NH{\cdot}HCl$ formed gradually. After stirring for 12 hours, the reaction mixture was diluted with hexane and filtered through celite, and the filter cake was washed with hexane. 2 M hydrochloric acid was added to the resulting hexane solution in an ice-bath to remove diethylamine from the organic layer. The organic layer was washed with aqueous ammonium chloride and water. Evaporation of the solvent left the crude product which was purified by column chromatography over silica gel (PE: ethyl acetate= 20:1) to provide 4-(1-(4-(*tert*-butyl)phenyl)-4-phenylbut-1-en-3-yn-1-yl)-2-(trifluoromethyl)pyridine as a white solid (89.0 mg, 85%, Z/E = 47:53).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.0 Hz, 0.47H), 8.68 (d, *J* = 5.1 Hz, 0.53H), 8.00 (s, 0.47H), 7.67 (s, 0.53H), 7.61 – 7.58 (m, 0.53H), 7.50 – 7.43 (m, 2H), 7.43 – 7.39 (m, 1.65H), 7.34 – 7.28 (m, 5H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.42 (s, 0.47H), 6.39 (s, 0.53H), 1.40 (s, 4.77H), 1.36 (s, 4.24H).

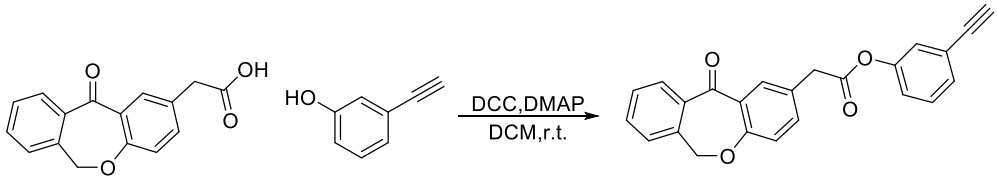
^{19}F NMR (564 MHz, $CDCl_3$) δ -67.73(s, 1.41F), -67.88(s, 1.59F).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.17 (152.48), 150.65 (148.98), 150.15 (149.88),148.51(148.20, q, *J*=34.5Hz), 148.40 (148.11), 136.06 (133.92), 131.56 (131.41), 129.55 (128.39), 128.69 (128.66), 128.32 (127.38), 127.36 (124.95), 125.19 (125.74), 122.94 (122.61), 121.65 (121.52, q, *J*=274.4Hz), 118.83(121.53, q, *J*=2.8Hz), 111.23 (109.76), 96.98 (96.10), 88.20 (87.46), 34.78 (34.70), 31.25 (31.17).

HRMS (ESI) Calcd for $C_{26}H_{23}F_3N^+$ (M+H): 406.1777, found: 406.1778.

5. General Procedures for the Synthesis of Alkynes

Alkynes was prepared according to a literature procedure.[8]

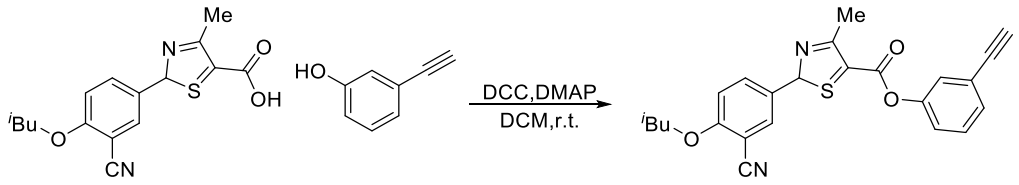


3-Ethynylphenyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate [S1]:

To a solution of 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid (294.8 mg, 1.1 mmol) and 3-ethynylphenol (118 mg, 1.0 mmol), N,N'-dicyclohexylcarbodiimide (223 mg, 1.1 mmol) ,4-dimethylaminopyridine (12.2 mg, 0.1 mmol) in DCM (4.0 mL). The reaction mixture was stirred at room temperature for 10 hours. The reaction was filter by diatomite then filtrate diluted with ethyl acetate. The organic layer was washed with water and brine. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude material was purified by flash chromatography to afford the product (292.6 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.3 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.56 (td, *J* = 7.5, 1.3 Hz, 1H), 7.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.1 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.34 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.11 – 7.06 (m, 2H), 5.21 (s, 2H), 3.88 (s, 2H), 3.08 (s, 1H).

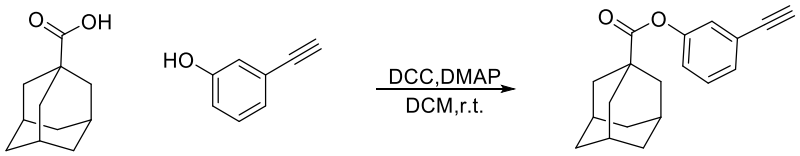
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.79, 169.56, 160.65, 150.33, 140.37, 136.21, 135.47, 132.82, 132.59, 129.69, 129.48, 129.30 (d, *J* = 6.7 Hz), 127.82, 126.95, 125.23, 125.07, 123.41, 122.25, 121.29, 82.47, 78.08, 73.62, 40.20.



3-Ethynylphenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate [S2]: To a solution of 2-(3-cyano-4-isobutoxyphenyl)-4-methyl-2H-1λ^3-thiazole-5-carboxylic acid (347.6 mg, 1.1 mmol) and 3-ethynylphenol (118 mg, 1.0 mmol), N,N'-dicyclohexylcarbodiimide (223 mg, 1.1 mmol) ,4-dimethylaminopyridine (12.2 mg, 0.1 mmol) in DCM (4.0 mL). The reaction mixture was stirred at room temperature for 10 hours. The reaction was filter by diatomite then filtrate diluted with ethyl acetate. The organic layer was washed with water and brine. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude material was purified by flash chromatography to afford the product (329.7 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.1 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.39 (dt, *J* = 15.6, 7.7 Hz, 2H), 7.35 (s, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.12 (s, 1H), 2.82 (s, 3H), 2.21 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.30, 163.28, 162.68, 160.07, 149.91, 132.66, 132.21, 129.96, 129.45, 125.74, 125.23, 123.61, 122.36, 120.23, 115.28, 112.66, 103.07, 82.39, 78.27, 75.72, 28.13, 19.02, 17.70.

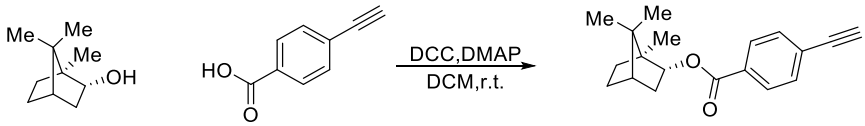


3-Ethynylphenyl (3*R*,5*R*,7*R*)-adamantane-1-carboxylate [S3]: To a solution of (3*R*,5*R*,7*R*)-adamantane-1-carboxylic acid (198.0 mg, 1.1 mmol) and 3-ethynylphenol (118 mg, 1.0 mmol), N,N'-dicyclohexylcarbodiimide (223 mg, 1.1 mmol) ,4-dimethylaminopyridine (12.2 mg, 0.1 mmol) in DCM (4.0 mL). The reaction mixture was stirred at room temperature for 10 hours. The reaction was filter by diatomite then filtrate diluted with ethyl acetate. The organic layer was washed with

water and brine. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude material was purified by flash chromatography to afford the product (238.4 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.18 (d, *J* = 1.6 Hz, 1H), 7.05 (dt, *J* = 7.3, 2.1 Hz, 1H), 3.08 (s, 1H), 2.09 (s, 3H), 2.04 (d, *J* = 2.8 Hz, 6H), 1.77 (d, *J* = 2.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.90, 150.87, 129.34, 129.26, 125.30, 123.35, 122.47, 82.68, 77.88, 41.06, 38.74, 36.44, 27.90.



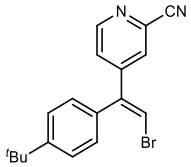
(1*S*, 2*S*, 4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-ethynylbenzoate [S4]:

To a solution of 4-ethynylbenzoic acid (169.7 mg, 1.1 mmol) and (1*S*, 2*S*, 4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (118 mg, 1.0 mmol), N,N'-dicyclohexylcarbodiimide (223 mg, 1.1 mmol) ,4-dimethylaminopyridine (12.2 mg, 0.1 mmol) in DCM (4.0 mL). The reaction mixture was stirred at room temperature for 10 hours. The reaction was filter by diatomite then filtrate diluted with ethyl acetate. The organic layer was washed with water and brine. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude material was purified by flash chromatography to afford the product (165.8 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 5.13 – 2.41 (m, 1H), 3.23 (s, 1H), 2.54 – 2.41 (m, 1H), 2.17 – 2.05 (m, 1H), 1.87 – 1.77 (m, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.44 – 1.41 (m, 1H), 1.35 – 1.28 (m, 1H), 1.11 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.97 (s, 3H), 0.91 (d, *J* = 3.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.14, 132.05, 130.89, 129.37, 126.55, 82.88, 80.87, 79.89, 49.11, 47.90, 44.97, 36.88, 28.07, 27.39, 19.71, 18.90, 13.61.

6. Crystallographic Data for Compound 35



(CCDC 2043179)

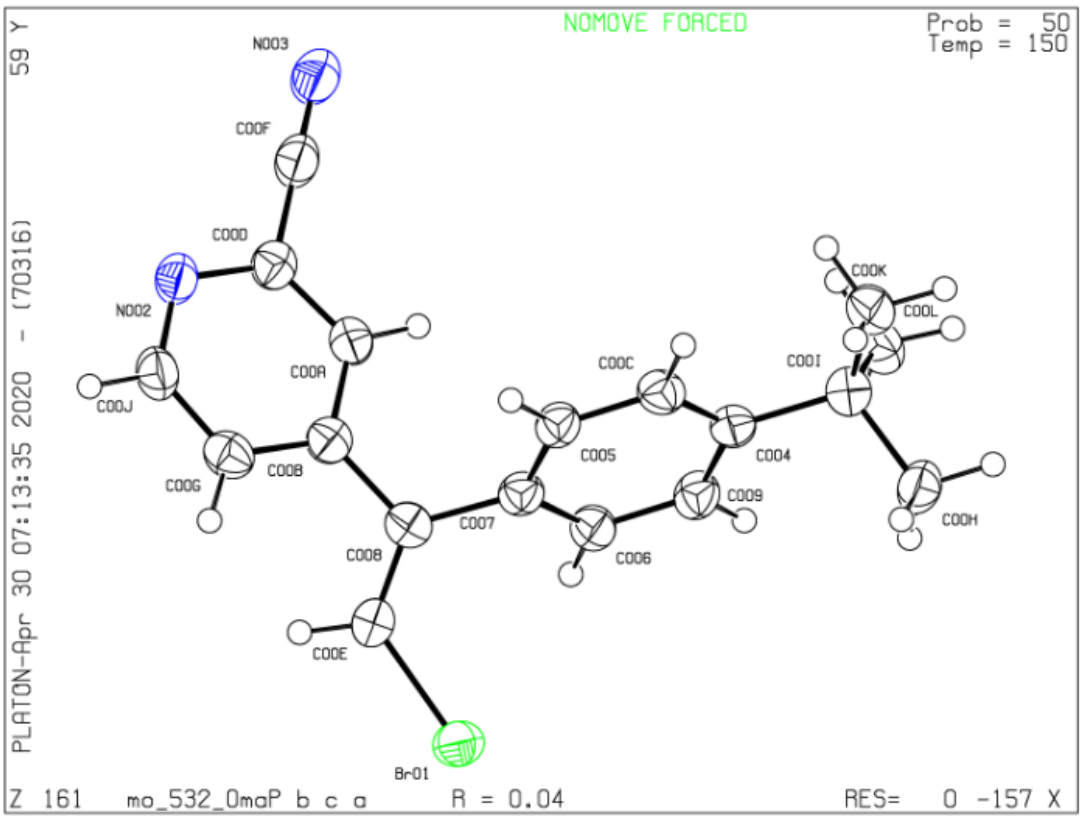


Table S8 Crystal data and structure refinement for compound 28

Identification code	mo_532_0ma
Empirical formulla	$C_{18}H_{17}BrN_2$
Formula weight	341.24
Temperature/K	150.2
Crystal system	Triclinic
Space group	P1

a/Å, b/Å, c/Å	12.3914(12), 11.5252(9), 22.193(2)
α/°, β/°, γ/°	90, 90, 90
Volume/Å^3	3169.4(5)
Z	8
ρ_{calc}mg/mm^3	1.430
m/mm^{-1}	2.589
F(000)	1392
Crystal size/mm^3	0.2 × 0.15 × 0.1
Theta range for data collection	2.464 to 26.395°
Index ranges	-15 ≤ h ≤ 15, -14 ≤ k ≤ 13, -27 ≤ l ≤ 27
Reflections collected	37056
Independent reflections	3224[R(int) = 0.0945]
Data/restraints/parameters	3224/0/193
Goodness-of-fit on F^2	1.032
Final R indexes [I>2σ (I)]	R_1 = 0.0434, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0759, wR_2 = 0.1135
Largest diff. peak/hole / e Å^{-3}	0.721/-0.300

Table S9 Atomic Coordinates (Å×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_532_0ma. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(equiv.)
Br01	4062.6(3)	2033.9(3)	5774.1(2)	43.05(15)
N002	4775(3)	7066(3)	7447.7(14)	39.4(7)
N003	2851(3)	9061(3)	7138.3(17)	57.2(10)
C004	2325(3)	5561(3)	4533.3(17)	34.9(9)
C005	3826(3)	5705(3)	5224.5(17)	34.6(9)
C006	2482(3)	4263(3)	5392.1(17)	35.6(9)
C007	3444(3)	4787(3)	5573.9(17)	34.2(8)
C008	4030(3)	4425(3)	6130.7(17)	33.7(8)
C009	1940(3)	4641(3)	4880.2(18)	38(9)
C00A	3662(3)	6328(3)	6635.7(17)	35.9(8)
C00B	4301(3)	5337(3)	6576(17)	34.7(9)
C00C	3280(3)	6082(3)	4716.7(17)	36.5(9)
C00D	3938(3)	7146(3)	7064.6(17)	36.6(8)
C00E	4291(3)	3337(3)	6274.6(18)	37.3(9)
C00F	3313(4)	8200(4)	7113(19)	44(10)
C00G	5180(3)	5252(3)	6965.4(18)	39.9(9)
C00H	1674(4)	4974(4)	3502.6(18)	44.3(10)
C00I	1691(3)	5956(3)	3971.1(18)	41(9)
C00J	5375(3)	6118(3)	7382.6(19)	43.6(10)
C00K	2197(4)	7035(4)	3681(2)	52.5(11)
C00L	518(4)	6233(4)	4142(2)	55.3(12)

Table S10 Anisotropic Displacement Parameters (Å2×103) for mo_532_0ma. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+...+2hka×b×U12]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	43(2)	36.5(2)	49.6(2)	-5.75(19)	-3.9(2)	2.39(18)
N002	42(18)	42(17)	34.2(17)	-0.4(15)	-6.4(14)	-5.7(16)
N003	58(2)	58(2)	55(2)	-16(2)	-18(2)	9(2)
C004	38(2)	32.8(19)	34(2)	-3(16)	0.3(17)	4.8(17)
C005	33(2)	35.3(19)	36(2)	-2.7(16)	-1.8(16)	-2.2(15)
C006	38(2)	35(2)	35(2)	1.3(16)	-0.6(18)	-1(17)
C007	32(2)	34.1(19)	37(2)	-4(16)	0.1(16)	1.9(16)
C008	29.4(18)	36.1(19)	36(2)	1.7(16)	4.2(17)	1.7(16)
C009	33(2)	40(2)	41(2)	-3.5(18)	-3.8(18)	-3.3(16)
C00A	36(2)	38(2)	34(2)	3.3(17)	-2.9(17)	0(16)
C00B	36(2)	35.4(19)	33(2)	2.2(16)	2.6(16)	-2.7(16)
C00C	42(2)	32.3(19)	36(2)	3.7(17)	2.8(17)	-1.7(17)
C00D	39(2)	39(2)	32(19)	1.7(16)	2.6(17)	-4.3(17)
C00E	38(2)	40(2)	33(2)	-2.9(16)	-3.3(17)	-1.8(16)
C00F	47(2)	49(3)	37(2)	-5.1(19)	-7.6(19)	-3(2)
C00G	34(2)	39(2)	47(2)	3.6(18)	-0.3(18)	3.1(17)
C00H	54(3)	46(2)	33(2)	-2(18)	-5.7(19)	-7(2)
C00I	44(2)	41(2)	38(2)	-0.1(18)	-4.5(19)	1.7(18)
C00J	43(2)	47(2)	41(2)	4.3(19)	-13.1(19)	-1(2)
C00K	72(3)	38(2)	47(2)	8(2)	-15(2)	-4(2)
C00L	49(3)	62(3)	55(3)	6(2)	-5(2)	17(2)

Table S11 Bond Lengths for mo_532_0ma.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	C00E	1.889(4)	C007	C008	1.493(5)
N002	C00D	1.344(5)	C008	C00B	1.481(5)
N002	C00J	1.330(5)	C008	C00E	1.334(5)
N003	C00F	1.147(5)	C00A	C00B	1.396(5)
C004	C009	1.395(5)	C00A	C00D	1.382(5)
C004	C00C	1.388(5)	C00B	C00G	1.393(5)
C004	C00I	1.542(5)	C00D	C00F	1.445(6)
C005	C007	1.395(5)	C00G	C00J	1.382(6)
C005	C00C	1.385(5)	C00H	C00I	1.537(6)
C006	C007	1.396(5)	C00I	C00K	1.535(6)
C006	C009	1.390(5)	C00I	C00L	1.536(6)

Table S12 Bond Angles for mo_532_0ma.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N002	C00D	C00A	125.5(4)	C00C	C004	C00I	122.9(3)
N002	C00D	C00F	115.1(3)	C00C	C005	C007	121.6(4)
N002	C00J	C00G	124.6(4)	C00D	C00A	C00B	118.9(4)
N003	C00F	C00D	177.0(5)	C00E	C008	C007	125.4(3)
C005	C007	C006	117.2(3)	C00E	C008	C00B	116.9(3)
C005	C007	C008	120.4(3)	C00G	C00B	C008	122.8(3)
C005	C00C	C004	121.3(4)	C00G	C00B	C00A	116.2(4)
C006	C007	C008	122.3(3)	C00H	C00I	C004	109.7(3)

C006	C009	C004	121.7(4)	C00J	N002	C00D	114.7(3)
C008	C00E	Br01	124.8(3)	C00J	C00G	C00B	120.1(4)
C009	C004	C00I	119.8(3)	C00K	C00I	C004	111.8(3)
C009	C006	C007	120.9(4)	C00K	C00I	C00H	108.5(3)
C00A	C00B	C008	121.0(3)	C00K	C00I	C00L	108.8(4)
C00A	C00D	C00F	119.5(4)	C00L	C00I	C004	110.1(3)
C00B	C008	C007	117.7(3)	C00L	C00I	C00H	107.9(4)
C00C	C004	C009	117.3(4)				

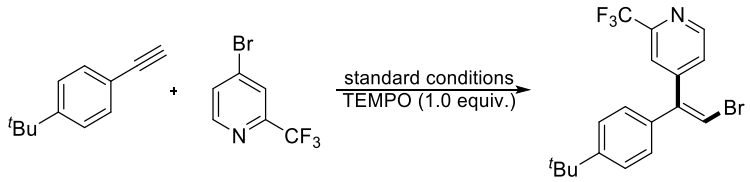
Table S13 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for mo_532_0ma.

Atom	*x*	*y*	*z*	U(equiv.)
H005	4478.01	6080.73	5337.62	41
H006	2193.6	3639.35	5621.35	43
H009	1291.77	4262.85	4763.56	46
H00A	3048.01	6438.01	6385.99	43
H00C	3564.11	6710.19	4489.38	44
H00E	4614.76	3207.5	6656.78	45
H00G	5645.63	4598.87	6944.16	48
H00B	2416.25	4766.57	3394.05	67
H00D	1287.24	5234.86	3142.13	67
H00F	1308.86	4295.16	3672.89	67
H00J	5979.73	6028.38	7641.32	52
H00H	2208.78	7671.3	3973.63	79
H00I	1769.23	7266.07	3329.05	79
H00K	2936.36	6857.86	3553.5	79

H00L	193.35	5557.58	4339.53	83
H00M	107.63	6421.16	3776.88	83
H00N	503.29	6897.22	4417.25	83

7. Mechanistic Studies

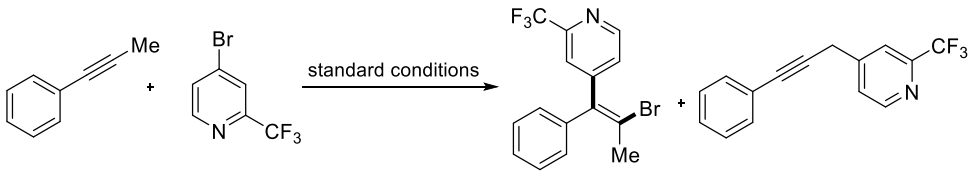
7.1 Radical inhibition experiment



1, 0.1 mmol **2,** 1.5 eq **3**

According to the general procedure, 1-(*tert*-butyl)-4-ethynylbenzene (18.0 μL, 0.10 mmol, 1.0 equiv.), 4-bromo-2-trifluoromethylpyridine (20.0 uL, 0.15 mmol, 1.5 equiv.), diisopropylamine (2.8 μL, 0.02 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 1.0 mol%), $NiBr_2$•DME (3.1 mg, 0.02 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy ,0.012 mmol, 0.12 equiv.) and TEMPO (15.6 mg, 0.1 mmol, 1.0 equiv.) in ethyl acetate(4 mL, 0.025M) were used. After 6 hours, the result mixture was analysis by GCMS. The TEMPO completely shut down the reaction.

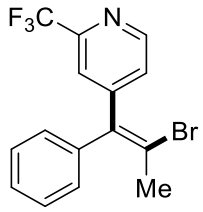
7.2 Observation of HAT byproduct



71, 0.2 mmol **2,** 1.5 eq **72** 15% **73** 10%

According to the general procedure, prop-1-yn-1-ylbenzene (22.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-(trifluoromethyl)pyridine (67.5 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours, the result mixture was concentrated in vacuo and the product 4-(2-Bromo-1-phenylprop-1-en-1-yl)-2-(trifluoromethyl)pyridine was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (10.3

mg, 15%, Z/E = 45:55). And the byproduct 4-(3-phenylprop-2-yn-1-yl)-2-(trifluoromethyl)pyridine was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (5.2 mg, 10%).



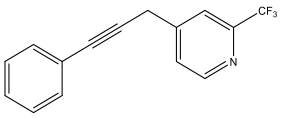
4-(2-Bromo-1-phenylprop-1-en-1-yl)-2-(trifluoromethyl)pyridine [72]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.7 Hz, 1H), 7.60 (s, 0.50H), 7.50 (s, 0.47H), 7.43 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 7.19 – 7.13 (m, 1H), 2.47 (s, 1.46H), 2.46 (s, 1.53H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.96 (s, 1.54F), -67.97 (s, 1.46F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.28, 150.00 (150.19), 148.53 (148.19, q, *J* = 33.5 Hz), 138.55 (141.17), 138.43 (138.49), 129.09 (128.52), 128.81 (129.15), 128.19 (128.08), 126.85 (126.57), 124.07 (124.81), 121.47 (121.34, q, *J* = 274.3 Hz) , 120.61(121.01, q, *J* = 2.7 Hz), 120.59, 27.33 (27.45).

HRMS (ESI) Calcd for $C_{15}H_{12}BrF_3N^+$ (M+H): 342.0100, found: 342.0101.



4-(3-Phenylprop-2-yn-1-yl)-2-(trifluoromethyl)pyridine [73]: According to the general procedure, prop-1-yn-1-ylbenzene (22.6 mg, 0.20 mmol, 1.0 equiv.), 4-bromo-2-(trifluoromethyl)pyridine (67.5 mg, 0.3 mmol, 1.5 equiv.), diisopropylamine (5.6 μL, 0.04 mmol, 0.2 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 1.0 mol%), $NiBr_2$•DME (6.2 mg, 0.02 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.4 mg ,0.024 mmol, 0.12 equiv.) in ethyl acetate (8 mL, 0.025M) were used. After 6 hours,

the result mixture was concentrated in vacuo and the product was isolated by flash chromatography (PE: ethyl acetate= 20:1) as a pale-yellow oil (5.2 mg, 10%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 1H), 7.76 (s, 1H), 7.59 (d, *J* = 4.9 Hz, 1H), 7.47 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.36 – 7.30 (m, 3H), 3.93 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.97(s, 3F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.13, 148.51 (q, *J* = 34.5 Hz), 148.03, 131.67, 128.44, 128.39, 125.86, 124.05 (q, *J* = 243.3 Hz), 122.69, 120.07 (q, *J* = 2.8 Hz), 84.50, 83.88, 25.46.

HRMS (ESI) Calcd for $C_{15}H_{11}F_3N^+$ (M+H): 262.0838, found: 262.0839.

7.3 Stern-Volmer Fluorescent quenching experiments

Stern-Volmer quenching experiments were carried by Edinburgh Fluorescence Spectrometer FS5, using a 0.01 mM solution of photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ and variable concentrations (0.05, 0.10, 0.15, 0.20, 0.25 mM) of, 1-(*tert*-butyl)-4-ethynylbenzene, diisopropylamine and Ni(II) complex **74** in solvent ethyl acetate. The samples were prepared in 4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box. The intensity of the emission peak at 496 nm (λ_{ex} = 378nm) expressed as the ratio I_0/I, where I_0 is the emission intensity of photocatalyst at 496 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Stern-Volmer plots for each component are given in the Supplementary Figures below.

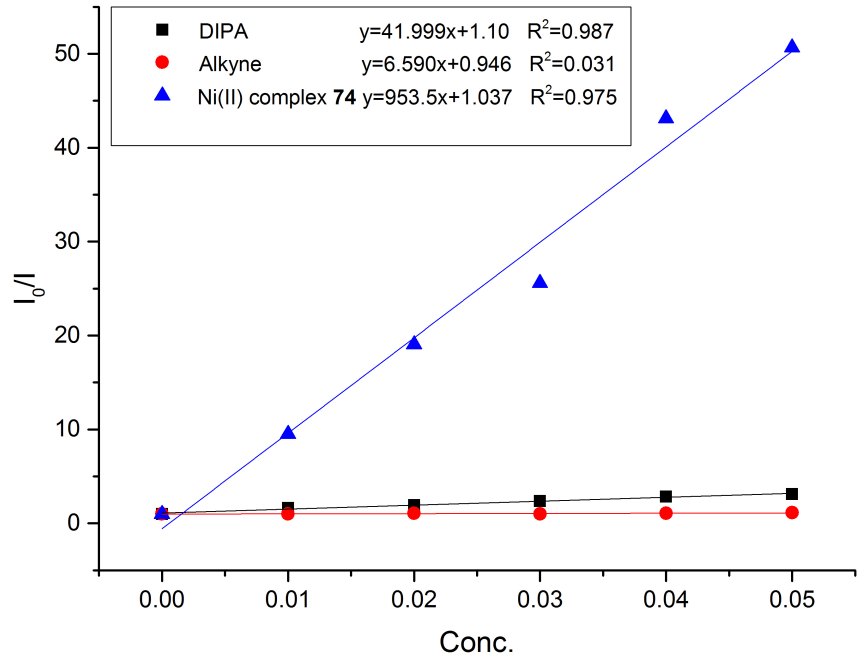
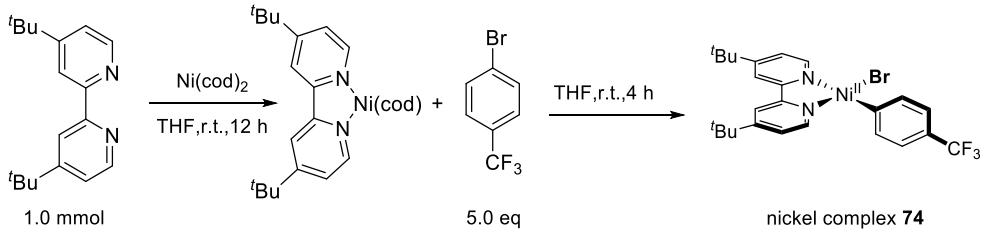


Figure S1 Stern-Volmer Fluorescent quenching studies.

7.4 Stoichiometric experiments with Ni(II) complex

(*a*) Preparation of Ni(II) complex 74



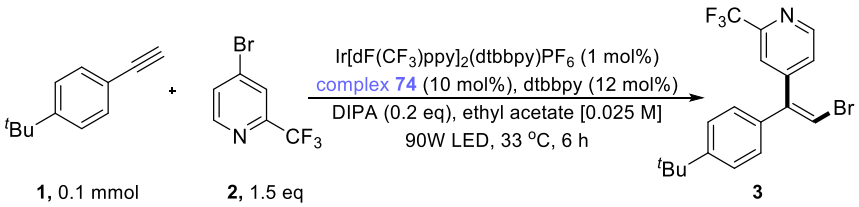
According to a literature procedure[9]. In a nitrogen filled glove box, a 50 mL round bottom flask containing a stirring bar was charged with $Ni(COD)_2$ (138 mg, 0.5 mmol, 1.0 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (134 mg, 0.5 mmol, 1.0 equiv.) and dry THF (5 mL) giving a dark purple mixture which was stirred for 12 hours at 25 ºC. 1-bromo-4-(trifluoromethyl)benzene (0.7 mL, 2.5 mmol, 5.0 equiv.) was added and stirred for additional 4 hours. Dry pentane (30 mL) was added to the deep red colored

mixture and filtered. The resulting precipitate was washed with pentane and dried to afford Ni(II) complex **74** as a brown solid (365 mg, 66% yield). The product was used without further purification. The complex was stored in a nitrogen filled glove box at -35 ºC.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.14 (s, 1H), 7.76-7.68 (m, 4H), 7.42 (br, 1H), 7.09 (br, 4H), 1.34 (s, 18H).

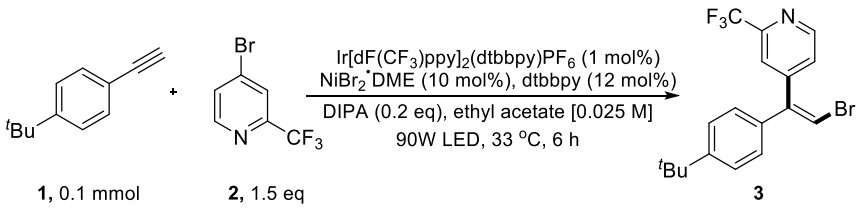
^{19}F NMR (376 MHz, CD_2Cl_2) δ-61.91.

(*b*) Ni(II) complex 74 as the nickel catalyst



According to the general procedure. To a flame-dried 8 mL reaction vial was charged with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1.1 mg, 0.001 mmol, 1.0 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (3.3 mg, 0.12 mmol, 12 mol%), the vial was introduced into a nitrogen-filled glove box and charged with Ni(II) complex **74** (0.6 mg, 0.01 mmol, 10 mol%.). The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, ethyl acetate (4 mL)， diisopropylamine (2.8 μL, 0.02 mmol, 0.2 equiv.), 1-(*tert*-butyl)-4-ethynylbenzene (18.0 μL, 0.10 mmol, 1.0 equiv.) and 4-bromo-2-trifluoromethylpyridine (20.0 μL, 0.15 mmol, 1.5 equiv.) was added by syringe. Once added, the reaction mixture was then irradiated with a 90 W blue LED lamp (at approximately 3.5 cm away from the light source) with cooling from a fan for 6 hours. The reaction mixtures were analyzed by ^{1}H NMR with an internal standard and GC-MS.

7.5 Light ON/OFF experiments over time



According to the general procedure. To a flame-dried 8 mL reaction vial was charged with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1.1 mg, 0.001 mmol, 1.0 mol%)，4,4'-di-*tert*-butyl-2,2'-bipyridine (3.3 mg , 0.012 mmol, 0.12 equiv.) and , the vial was introduced into a nitrogen-filled glove box and charged with $NiBr_2$•DME (3.1mg, 0.01 mmol, 0.1 equiv.). The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, ethyl acetate (4 mL), diisopropylamine (2.8 μL, 0.02 mmol, 0.2 equiv.), 1-(*tert*-butyl)-4-ethynylbenzene (18.0 μL, 0.10 mmol, 1.0 equiv.) and 4-bromo-2-trifluoromethylpyridine (20.0 μL, 0.15 mmol, 1.5 equiv.) was added by syringe. Once added, the reaction mixture was then irradiated with a 90 W blue LED lamp (at approximately 3.5 cm away from the light source) with cooling from a fan. The reaction mixtures were analyzed by GC with an internal standard. (Note: From the same reaction vial take 10 μL reaction mixture for analysis in every response time).

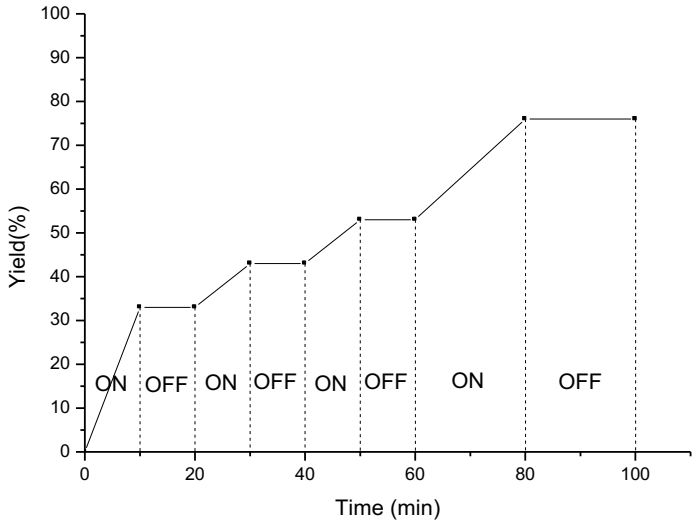


Figure S2 Light/dark experiments

7.6 Determination of quantum yield

We utilized protocol reported by Shunsuke and co-workers to determine the photon flux of blue LED[10]. All solutions were stored in the black vial and stored in the dark when not in use. Measurements were performed with the lights off to protect the samples from ambient light as much as possible.

a) Preparation of stock solutions

A 0.15 M solution of ferrioxalate was obtained by dissolving potassium ferrioxalate trihydrate($[K_3Fe^{III}(C_2O_4)_3]\bullet 3H_2O$; 1.11 g, 2.26 mmol) in 0.05 M H_2SO_4 (prepared by fresh deionized water) (15 mL total volume).

A buffered phenanthroline solution was obtained by dissolving 1,10-phenanthroline (10.0mg) and sodium acetate (2.25g) in 0.5M H_2SO_4 (prepared by fresh deionized water) (10 mL total volume) **[10]**.

b) Determination of background Fe^{2+} concentration

2 mL of the ferrioxalate solution was added to a 8 mL vial. Next, 0.35 mL of the phenanthroline solution was added and the mixture was stored in the dark for 1 hour. Then the solution was transferred to a cuvette and a UV–vis spectrum was measured using UV–vis absorption spectrometer (lambda 950). The absorbance value at 510 nm was recorded. This process was repeated twice. Average value: 0.551565.

c) Determination of photon flux

2 mL of the ferrioxalate solution was added to a 8 mL vial. The vial was immediately irradiated with blue LED (λ_{max}= 469 nm) for 10 seconds and removed from the blue LED. Then, 0.35 mL of the phenanthroline solution was added to the ferrioxalate solution, and the resulting mixture was stored in the dark for 1 hour. Then the solution was transferred to a cuvette and the UV–vis spectrum was measured. The absorbance value at 510 nm was recorded. This process was repeated twice. Average value: 1.744978.

d) Calculations

The amount of Fe^{2+}formed was calculated according to the following equation:

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

where V is the volume of the sample analyzed (3.5 mL), ΔA is the difference in average absorbances (between irradiated and unirradiated ferrioxalate solutions) at 510 nm, *l* is the path length, and ε is the molar absorptivity at 510 nm[11].

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{(0.00235\ L)(1.193413)}{(3\ cm)(11100\ {}^{L}/_{mol \cdot cm})} = 8.42198 \cdot 10^{-8}\ mol$$

The fraction of light absorbed by the ferrioxalate actinometer was calculated by the following equation:

$$f = 1 - 10^{-A}$$

where A is the absorbance at 468 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline (**Figure S3**).

$$f = 1 - 10^{-A} = 1\text{-}10^{-0.494388} = 0.67966$$

The photon flux was calculated using the following equation:

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer at 468 nm[11], t is the time and f is the fraction of light absorbed by the ferrioxalate actinometer solution.

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{8.42198 \cdot 10^{-8} mol}{(0.92) \cdot (10s) \cdot (0.67966)}$$

$$= 1.3469 \cdot 10^{-8}\ {einsterin}/{s}$$

e) Determination of fraction of light absorbed at 468 nm for the ferrioxalate solution

The absorbance at 468 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline was measured to be 0.494388.

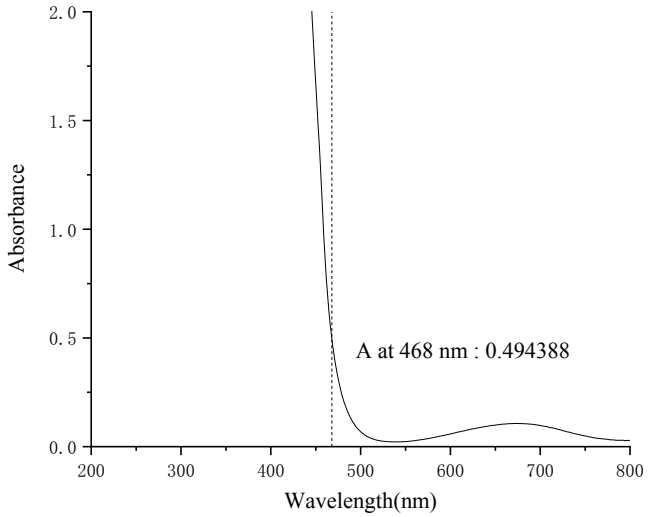


Figure S3 UV-vis absorbance spectra of ferrioxalate solution

f) Absorbance of photocatalyst Ir[df(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$

The absorbance of Ir[df(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ in ethyl acetate was measured at the reaction concentration of 300 μM or a dilute concentration of 25 μM (Figure xx). The absorbance at 468 nm for a 300 μM is 0.735811.

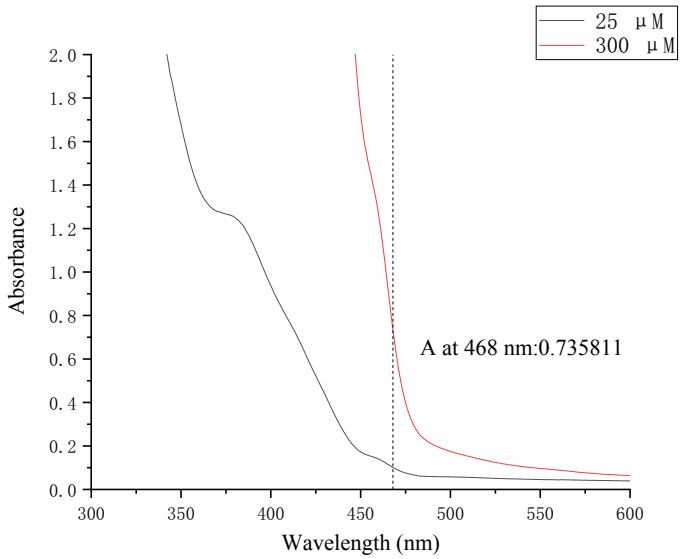
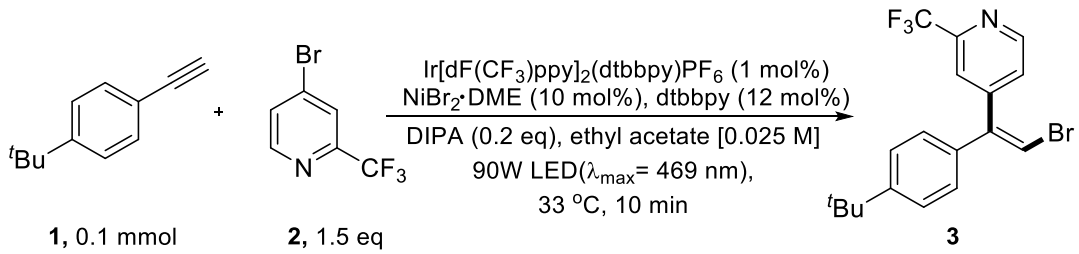


Figure S4 UV-vis absorbance spectra of Ir[df(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ black line: 25 μM in ethyl acetate, red line: 300 μM in ethyl acetate.

g) Determination of quantum yield



According to the general procedure. To a flame-dried 8 mL reaction vial was charged with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1.1 mg, 0.001 mmol, 1.0 mol%)，4,4'-di-*tert*-butyl-2,2'-bipyridine (3.3 mg , 0.012 mmol, 0.12 equiv.) , and the vial was introduced into a nitrogen-filled glove box and charged with $NiBr_2$•DME (3.1mg, 0.01 mmol, 0.1 equiv.). The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, ethyl acetate (4 mL), diisopropylamine (2.8 μL, 0.02 mmol, 0.2 equiv.), 1-(*tert*-butyl)-4-ethynylbenzene (18.0 μL, 0.10 mmol, 1.0 equiv.) and 4-bromo-2-trifluoromethylpyridine (20.0 μL, 0.15 mmol, 1.5 equiv.) was added by syringe. Once added, the reaction mixture was then irradiated with one 90 W blue LED lamp (λ_{max}= 469 nm) for 600 seconds. After irradiation, the reaction mixtures were analyzed by GC with an internal standard. Provide the desired product (4.7 % GC yield).

The quantum yield (Φ) was calculated using the following equation:

$$\Phi = \frac{mol\ \text{product}}{\text{photon flux} \cdot \text{t} \cdot f}$$

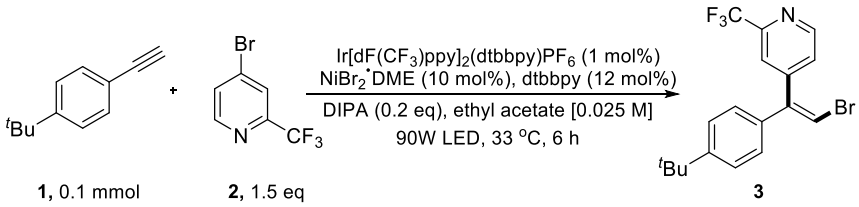
Where t is the reaction time and f is the fraction of light absorbed by photocatalyst that was calculated using the following equation:

$$\text{f} = 1-10^{-A} = 1\text{-}10^{-0.73581} = 0.816$$

Where A is the absorbance at 468nm of the photocatalyst solution (300 μM in ethyl acetate) (**Figure S4**).

$$\Phi = \frac{mol\ \text{product}}{\text{photon flux} \cdot \text{t} \cdot f} = \frac{0.0000047\ mol}{\left(1.3469 \cdot 10^{-8}\ einsterin/_{S}\right) \cdot (600s) \cdot (0.816)} = 0.68$$

7.7 Time-course studies



1, 0.1 mmol **2,** 1.5 eq **3**

According to the general procedure. To a flame-dried 8 mL reaction vial was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (1.1 mg, 0.001 mmol, 1.0 mol%)，4,4'-di-*tert*-butyl-2,2'-bipyridine (3.3 mg , 0.012 mmol, 0.12 equiv.) and the vial was introduced into a nitrogen-filled glove box and charged with NiBr$_2$•DME (3.1mg, 0.01 mmol, 0.1 equiv.). The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, ethyl acetate (4 mL), diisopropylamine (2.8 μL, 0.02 mmol, 0.2 equiv.), 1-(*tert*-butyl)-4-ethynylbenzene (18.0 μL, 0.10 mmol, 1.0 equiv.) and 4-bromo-2-trifluoromethylpyridine (20.0 μL, 0.15 mmol, 1.5 equiv.) was added by syringe. Once added, the reaction mixture was then irradiated with a 90 W blue LED lamp (at approximately 3.5 cm away from the light source) with cooling from a fan. The reaction mixtures were analyzed by GC with an internal standard.

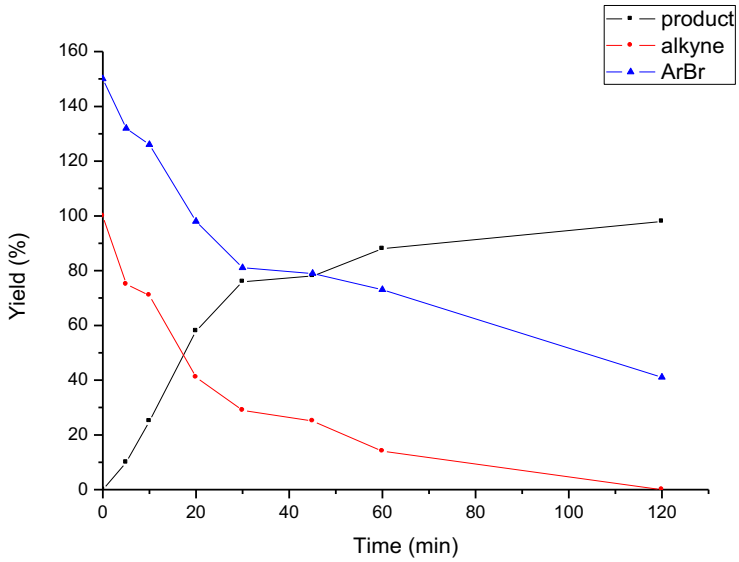
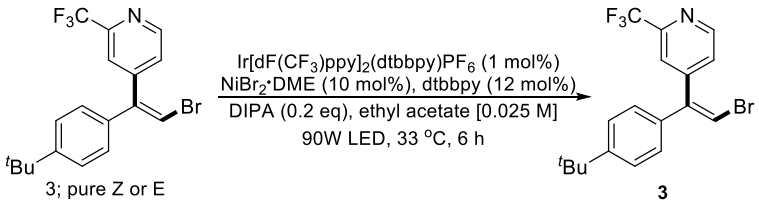


Figure S5 Time course studies

7.8 Isomerization of product



To a flame-dried 8 mL reaction vial was charged with 4,4'-di-*tert*-butyl-2,2'-bipyridine (3.3 mg , 0.012 mmol, 0.12 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 1.0 mol%) and 4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (pure Z or pure E 38.4 mg , 0.1 mmol, 1.0 equiv.), the vial was introduced into a nitrogen-filled glove box and charged with $NiBr_2$•DME (3.1mg, 0.02 mmol, 0.1 equiv.). The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, ethyl acetate (4 mL), diisopropylamine (2.8 μL, 0.02 mmol, 0.2 equiv.) was added by syringe. Once added, the reaction mixture was then irradiated with a 90 W blue LED lamp (at approximately 3.5 cm away from the light source) with cooling from a fan. The reaction mixtures were analyzed by GC with an internal standard.

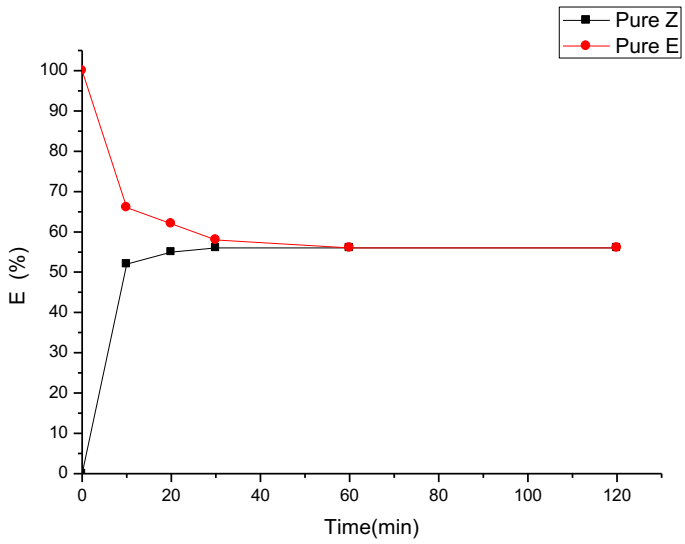
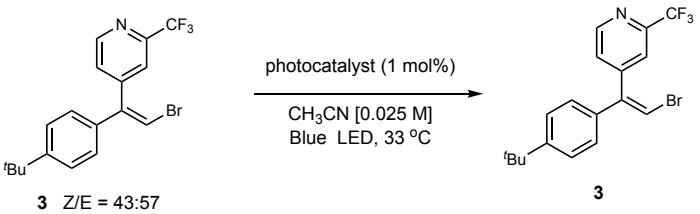


Figure S6 Isomerization of product

7.9. Isomerization studies of products with different photocatalysts

To a flame-dried 8 mL reaction vial was charged with 4-(2-Bromo-1-(4-(*tert*-butyl)phenyl)vinyl)-2-(trifluoromethyl)pyridine (19.4 mg , 0.05 mmol) and photocatalysts (1 mol%), the vial was introduced into a nitrogen-filled glove box and charged with N_2. The tube was sealed with a Teflon-lined screw cap and taken out from the glovebox, Acetonitrile (2 mL) was added by syringe. Once added, the reaction mixture was then irradiated with a 90 W blue LED lamp (at approximately 3.5 cm away from the light source) with cooling from a fan. The reaction mixtures were analyzed by GC with an internal standard.

Table S14. Photoisomerization studies of compound 3.

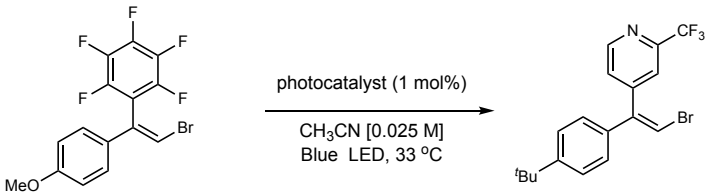


3 Z/E = 43:57 **3**

Entry	Photocatalyst	Z/E
1	Benzophenone	48:52
2	4,4'-Dibromobenzophenone	50:50
3	Thioxanthen-9-one	54:46
4	Xanthone	49:51
5	9-Fluorenone	46:54
6	Naphthalene	48:52
7	Anthracene	51:49
8	Pyrene	53:47
9	Riboflavin	42:58
10	Fluorescein	47:53

11	Methylene Blue trihydrate	46:54
12	Acid Red 94	41:59
13	Rhodamine 6G	41:59
14	4CzIPn	49:51
15	Eosin Y	49:51
16	Ponceau 3R	47:53
17	$Ir(ppy)_3$	60:40
18	No photocatalyst	46:54

Table S15. Photoisomerization studies of compound 59.



59 Z/E = 36:64

59

Entry	Photocatalyst	Z/E
1	Benzophenone	83:17
2	Naphthalene	80:20
3	Anthracene	57:43
4	Pyrene	50:50
5	Riboflavin	58:42
6	Acid Red 94	36:64
7	Rhodamine 6G	40:60
8	4CzIPn	18:82
9	Eosin Y	86:14
10	Ponceau 3R	39:61

11	$Ir(ppy)_3$	13:87
12	No photocatalyst	84:16

8. References

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[10] A. Kaga, X. Wu, J. Y. J. Lim, H. Hayashi, Y. Lu, E. K. L. Yeow, S. Chiba, *Beilstein J. Org. Chem.* **2018**, *14*, 3047-3058.

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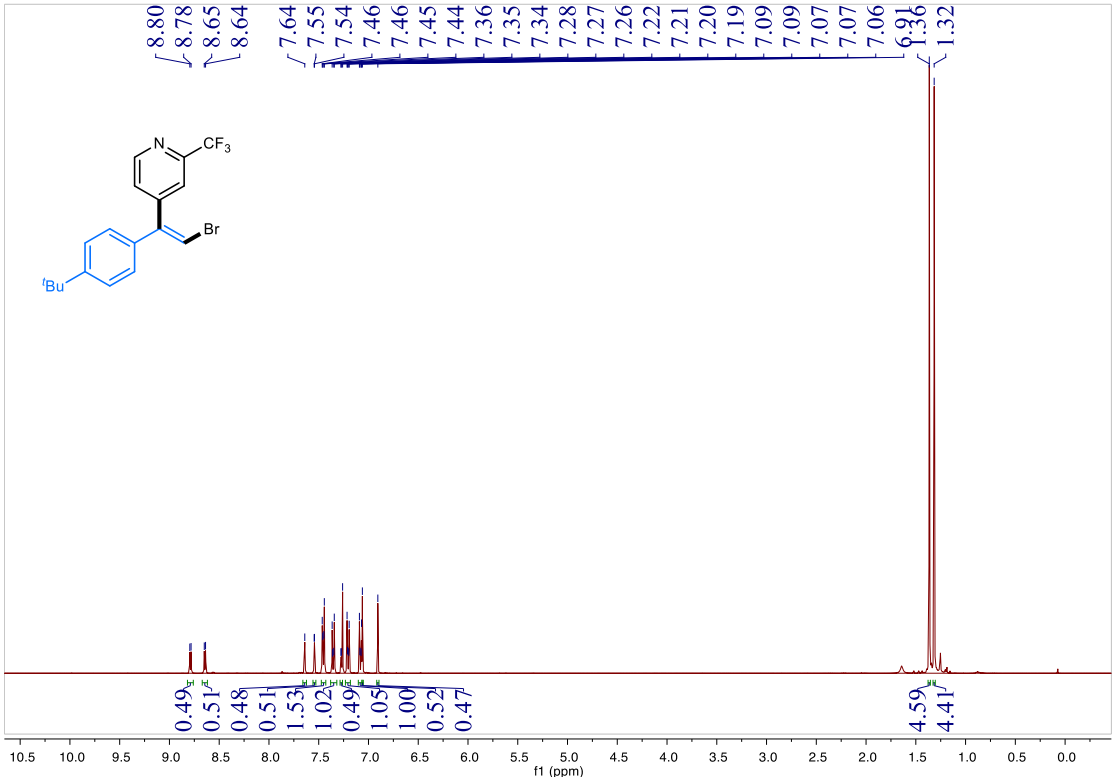
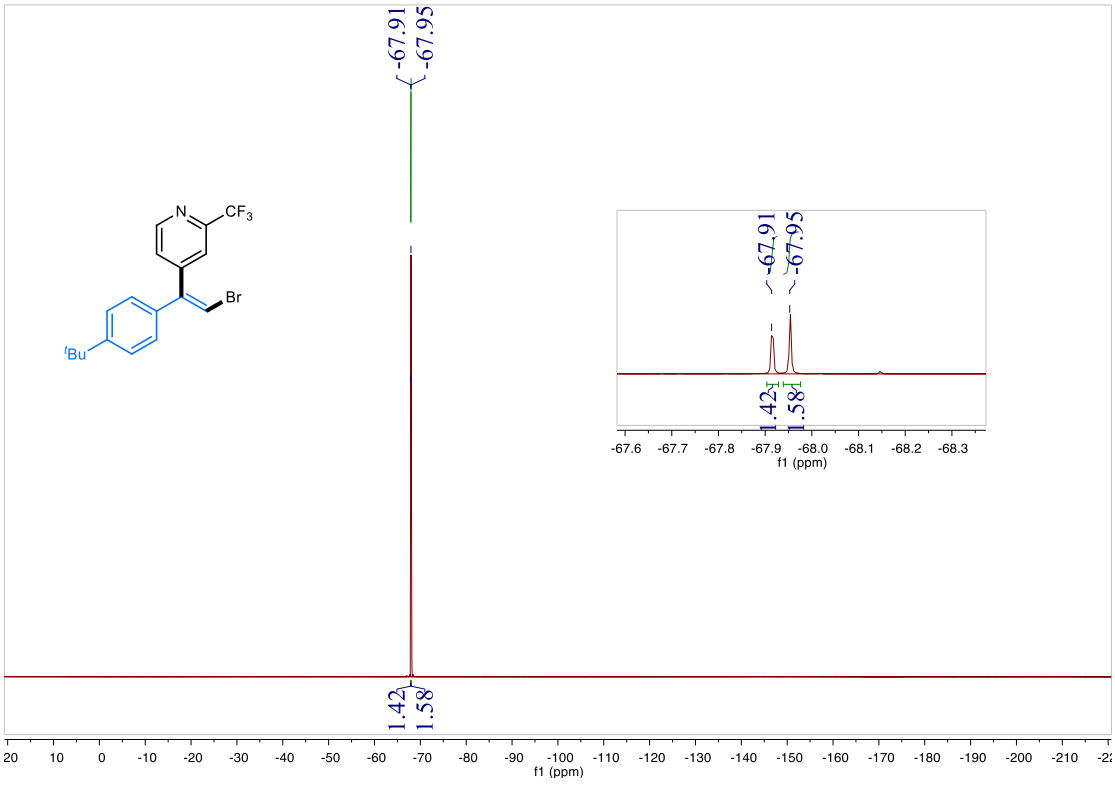
9. NMR Spectra

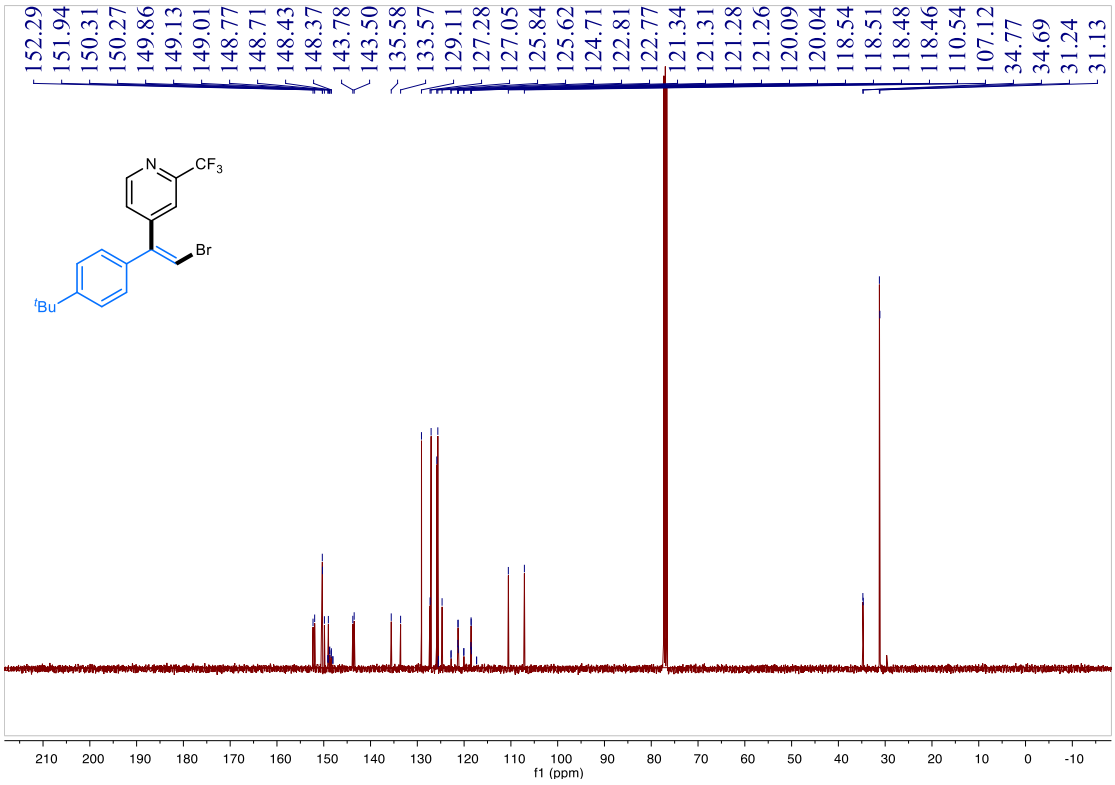
3; ^{1}H NMR (600 MHz, $CDCl_3$)



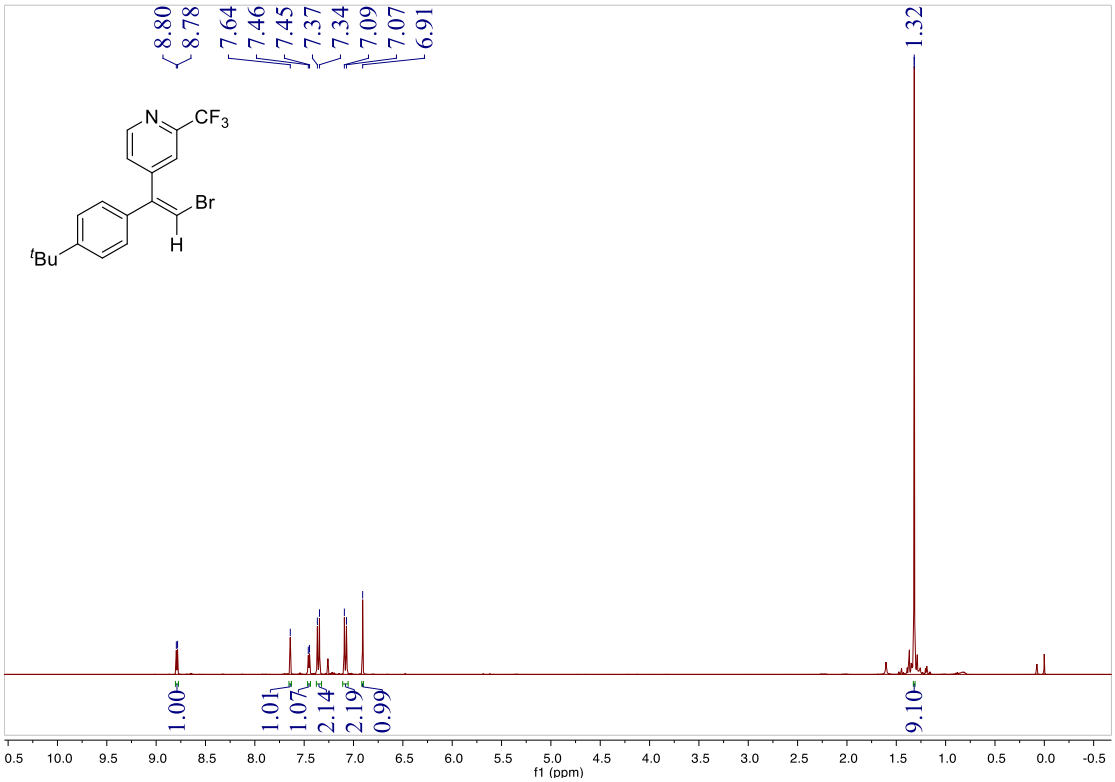
3; ^{19}F NMR (376 MHz, $CDCl_3$)



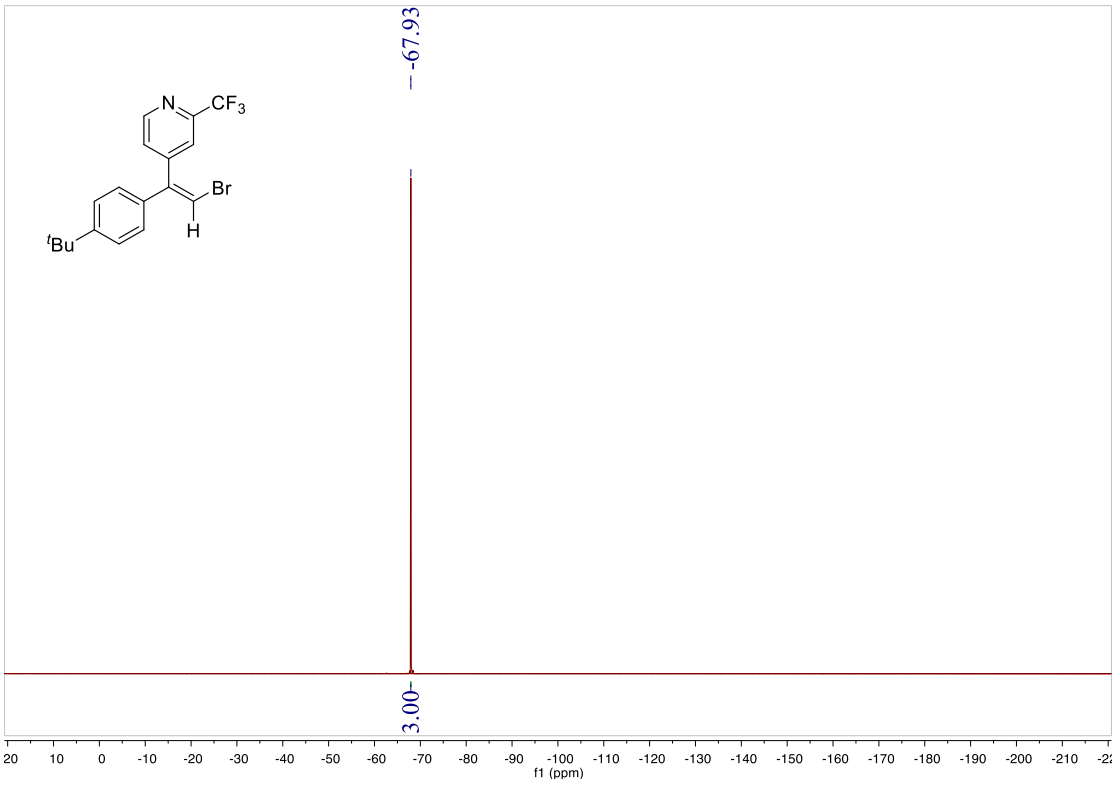
3; ^{13}C NMR (100 MHz, $CDCl_3$)



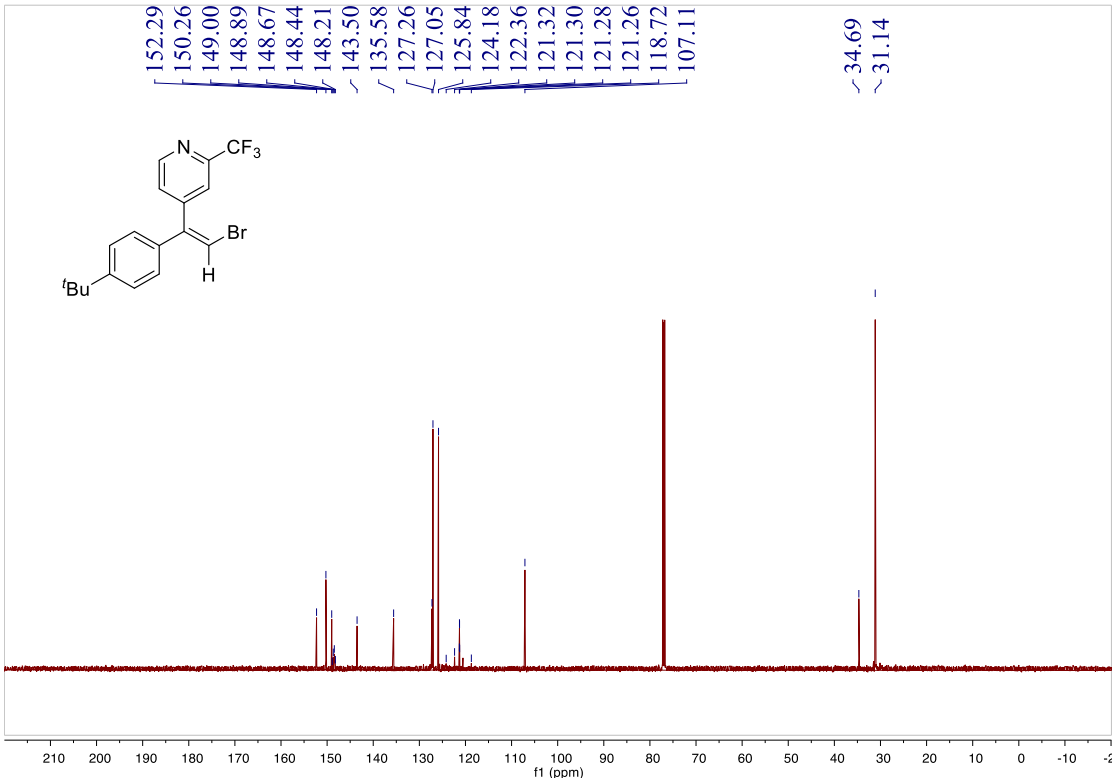
Z-3; ^{1}H NMR (400 MHz, $CDCl_3$)



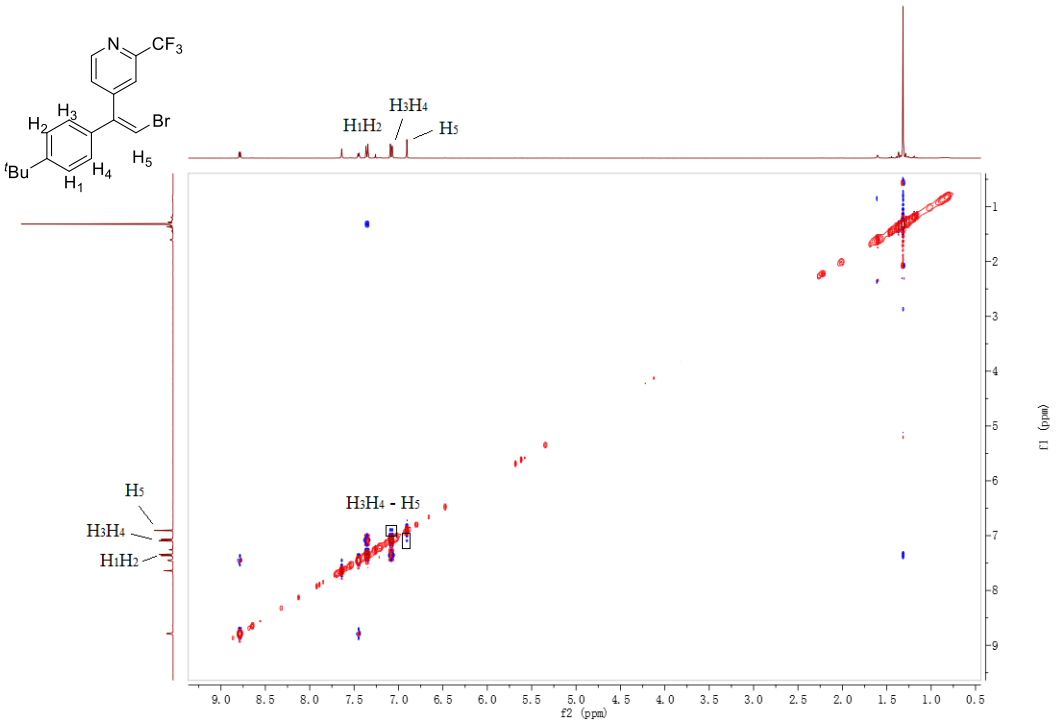
Z-3; ^{19}F NMR (377 MHz, $CDCl_3$)

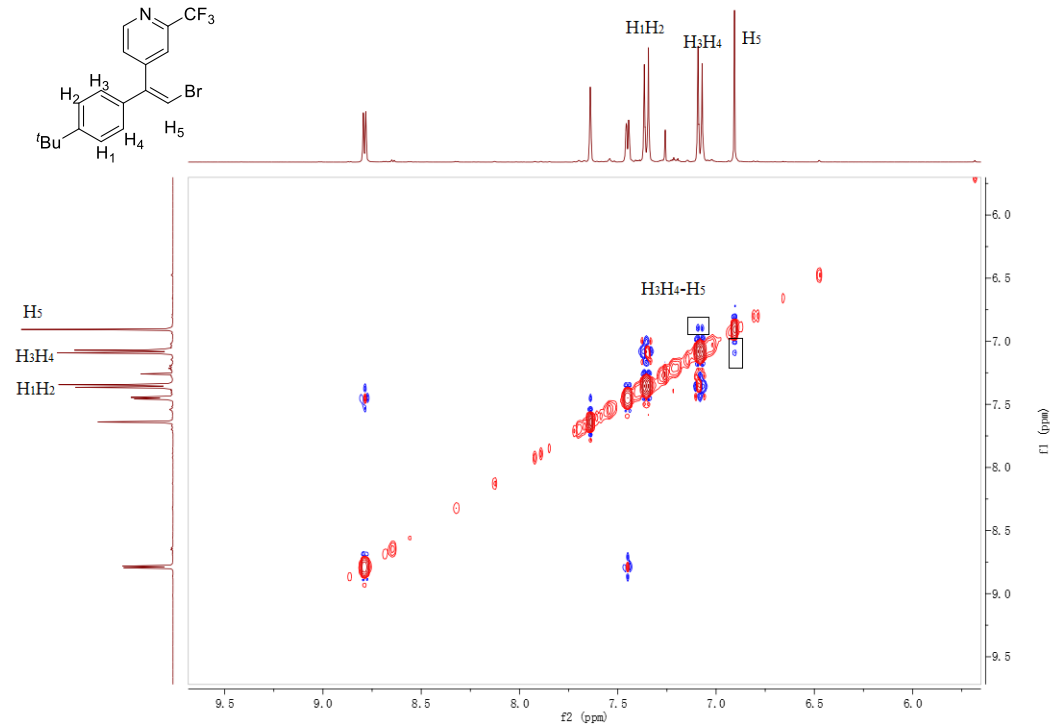


Z-3; ^{13}C NMR (150 MHz, $CDCl_3$)

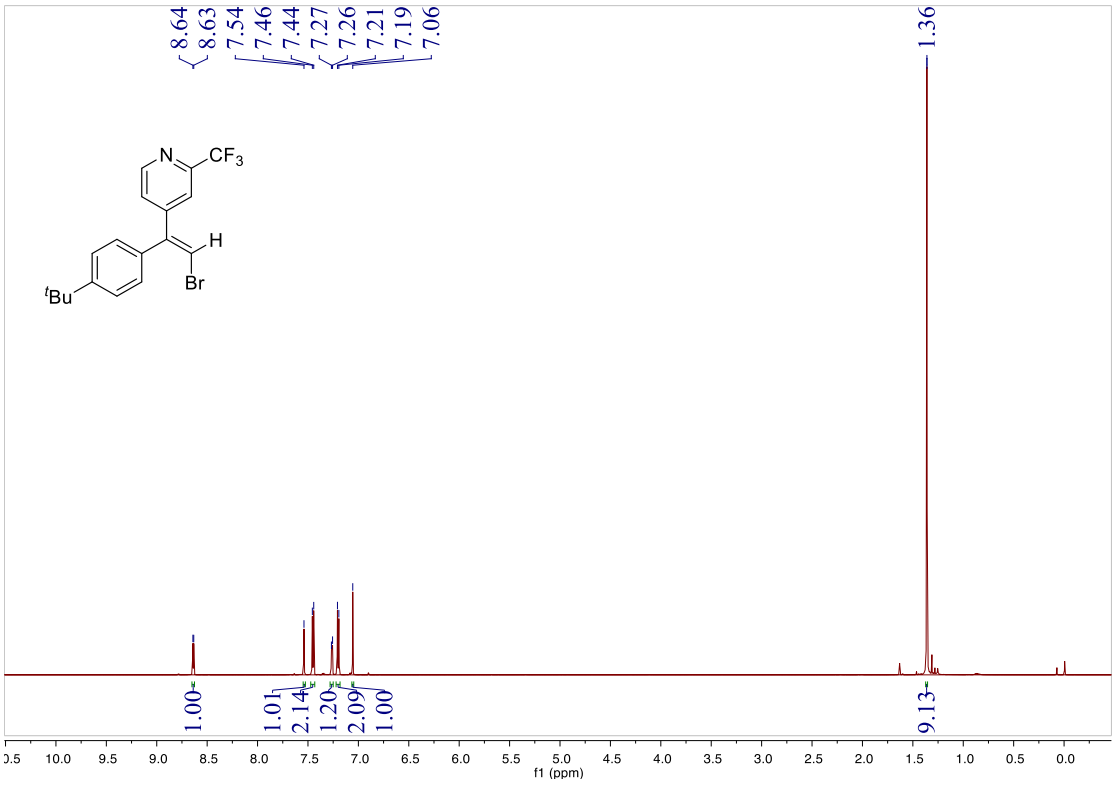


Z-3; NOESY

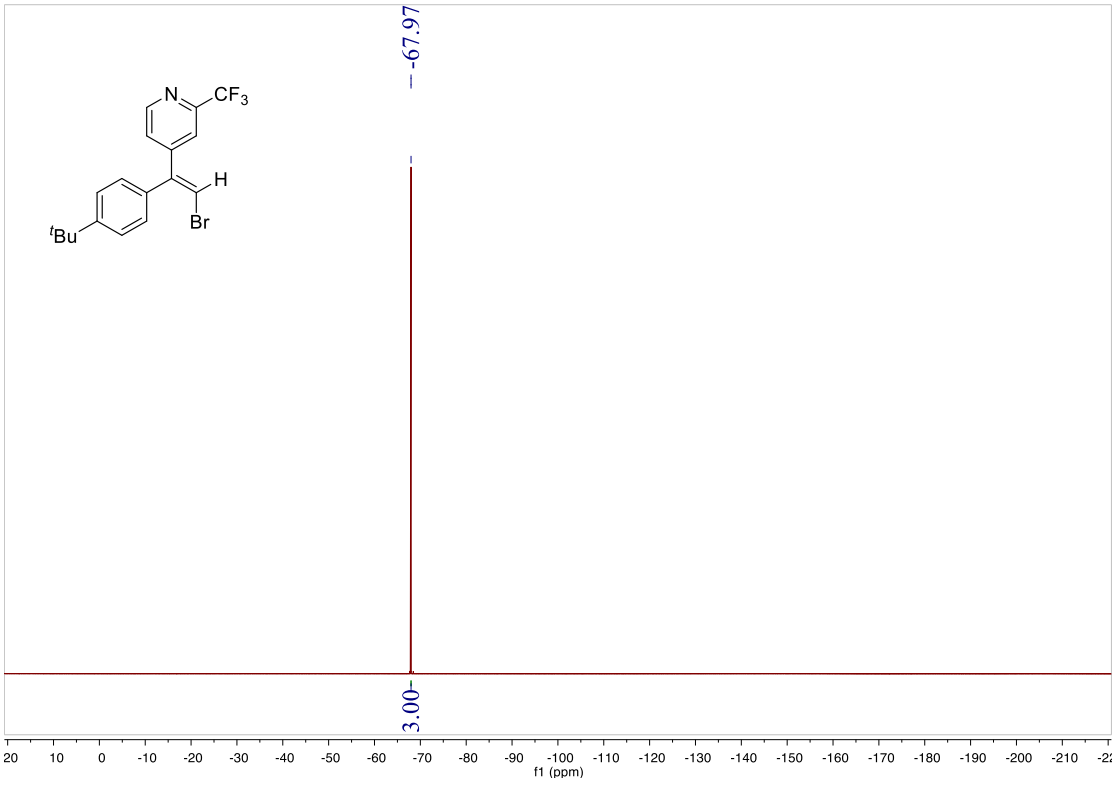

N
CF3
Br
H2
H3
H4
H5
H1
tBu
H3H4
H1H2
H5
H3H4 - H5
f2 (ppm)
f1 (ppm)


N
CF3
Br
H2
H3
H4
H5
H1
tBu
H1H2
H3H4
H5
H3H4-H5
f2 (ppm)
f1 (ppm)

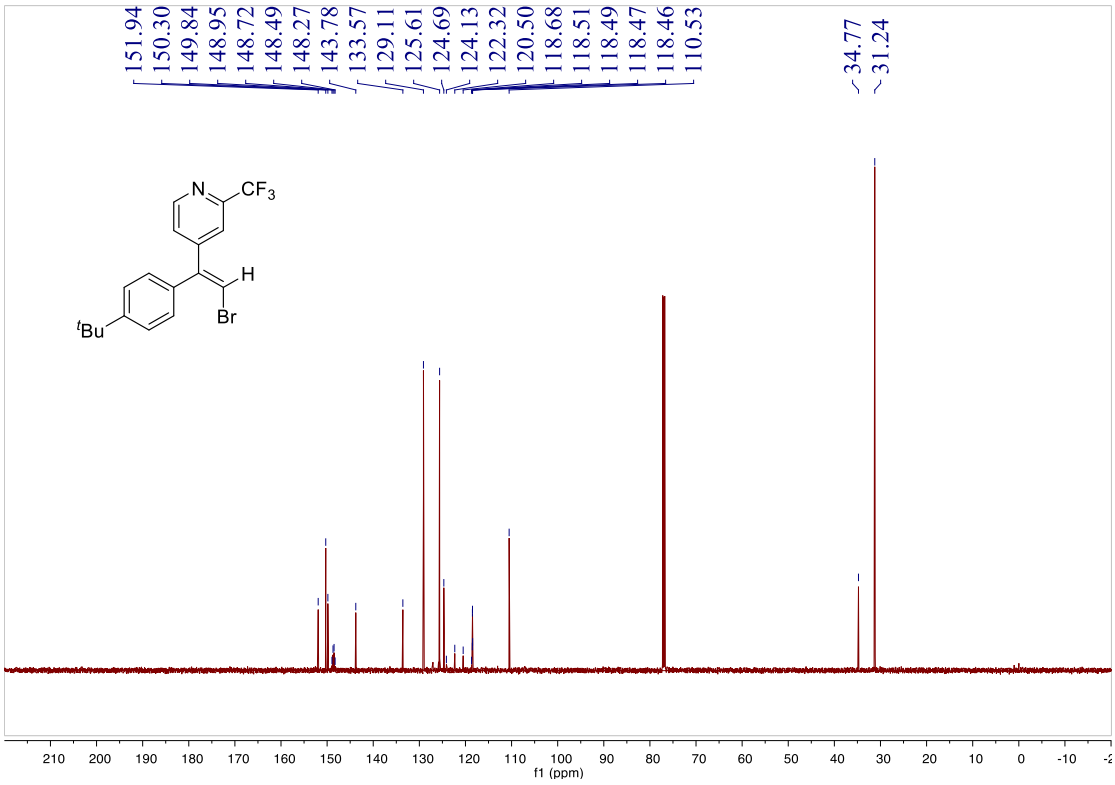
E-3; ^{1}H NMR (600 MHz, $CDCl_3$)



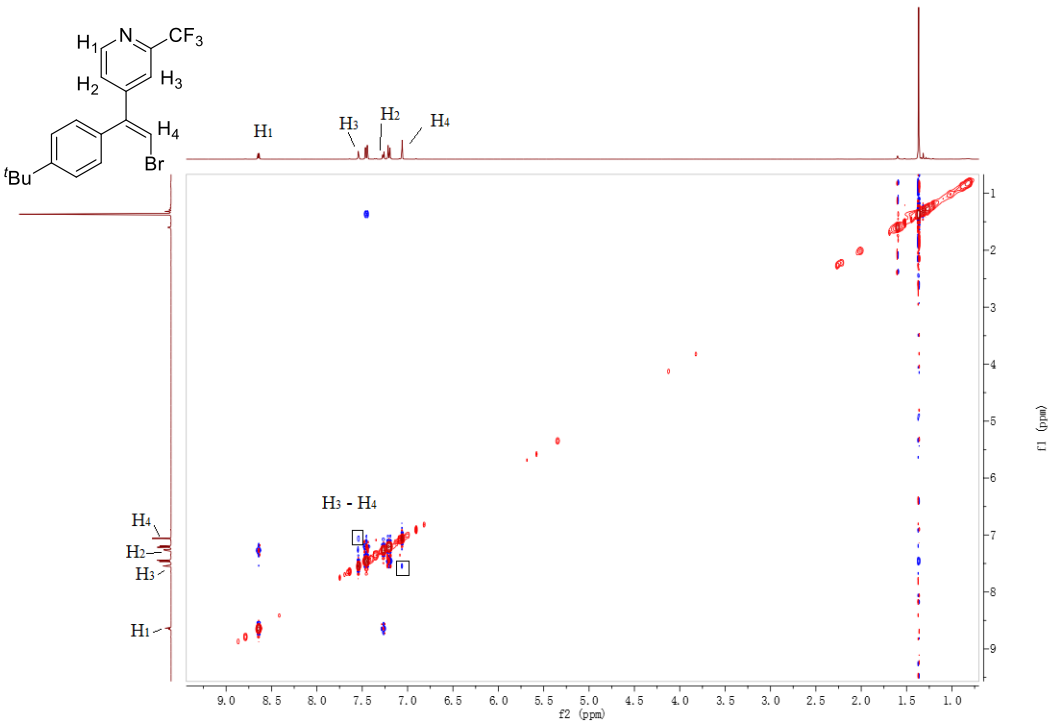
E-3; ^{19}F NMR (377 MHz, $CDCl_3$)

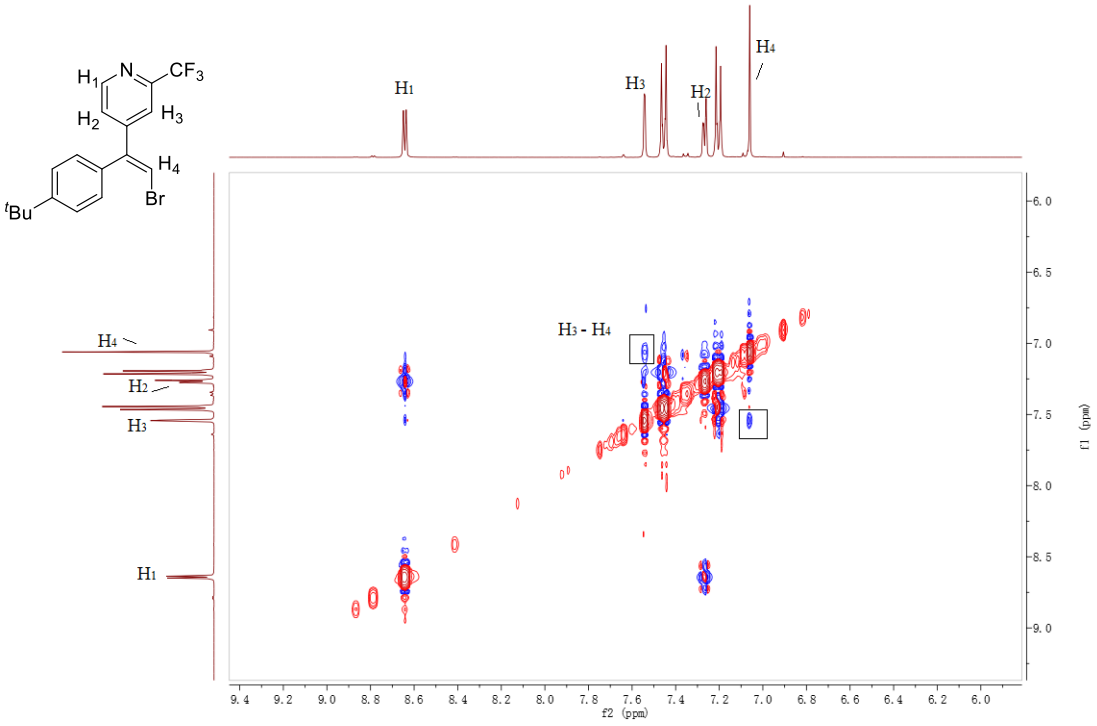


E-3; ^{13}C NMR (150 MHz, $CDCl_3$)

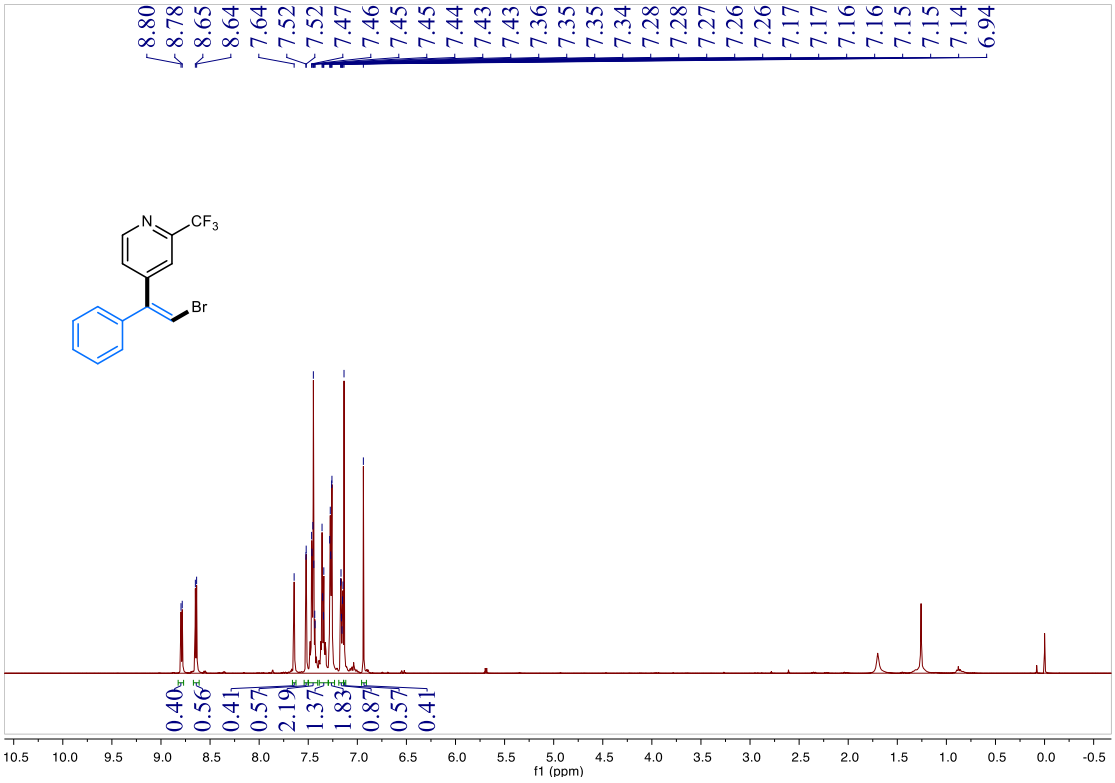


E-3; NOESY

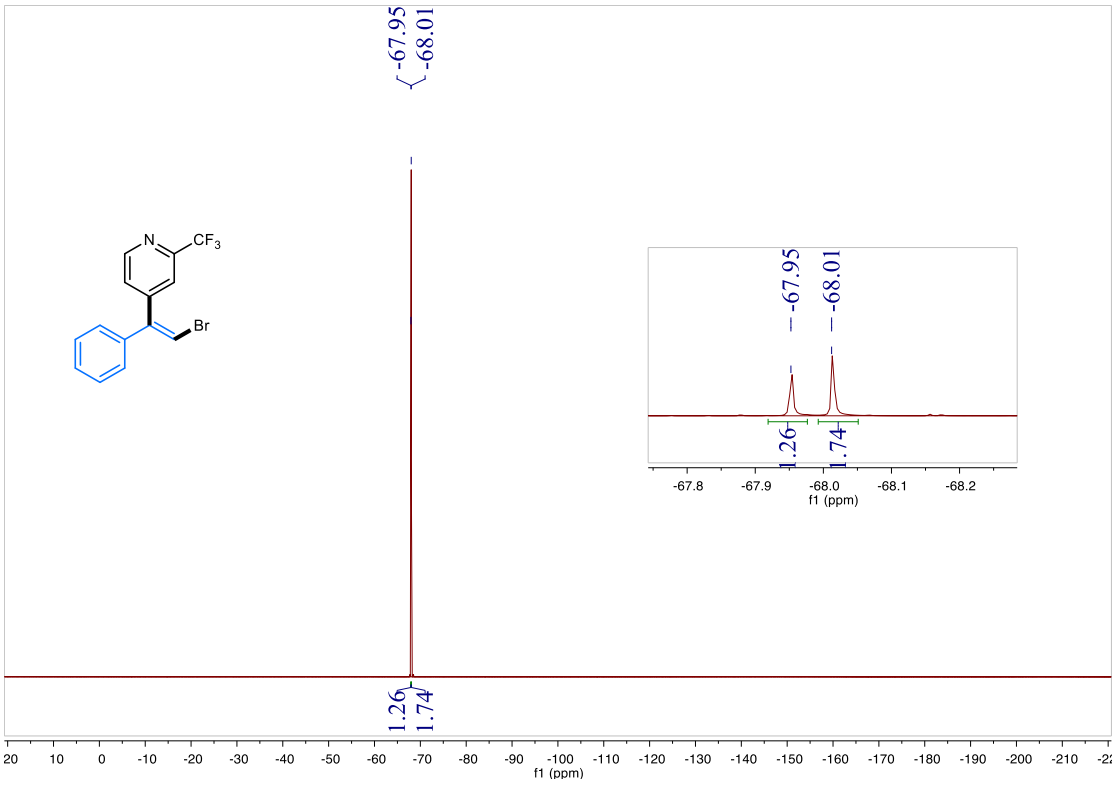




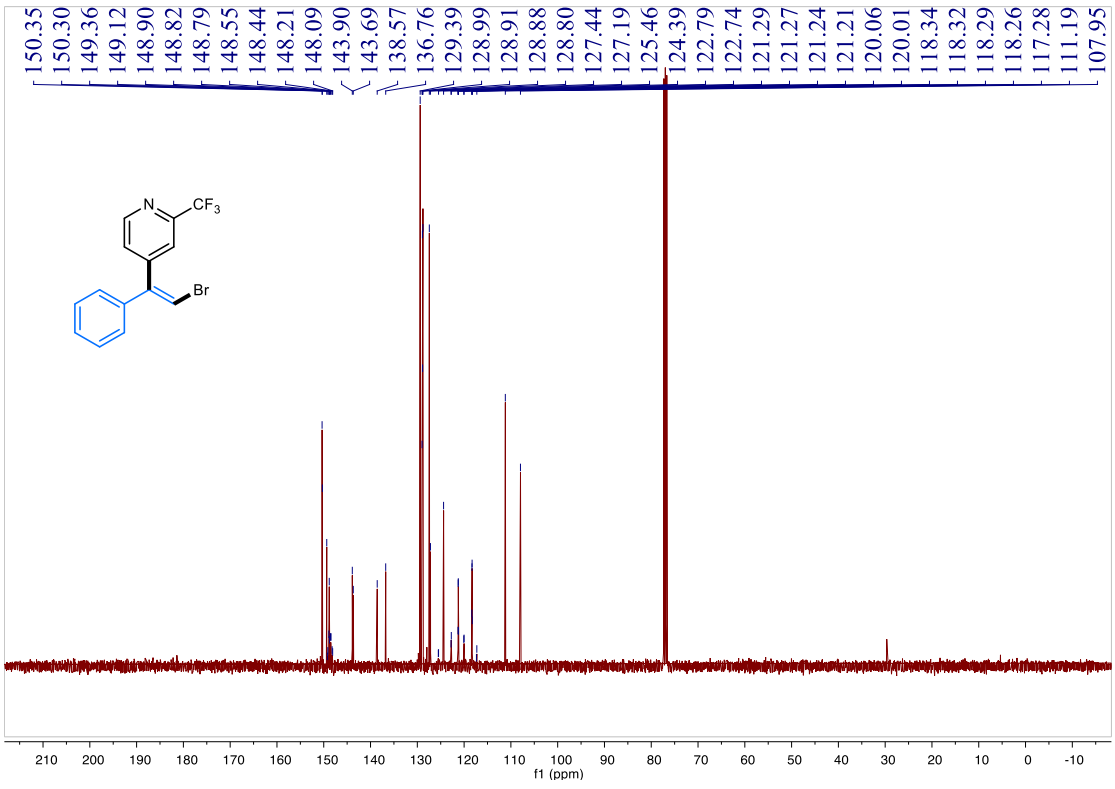
4; ^{1}H NMR (400 MHz, $CDCl_3$)



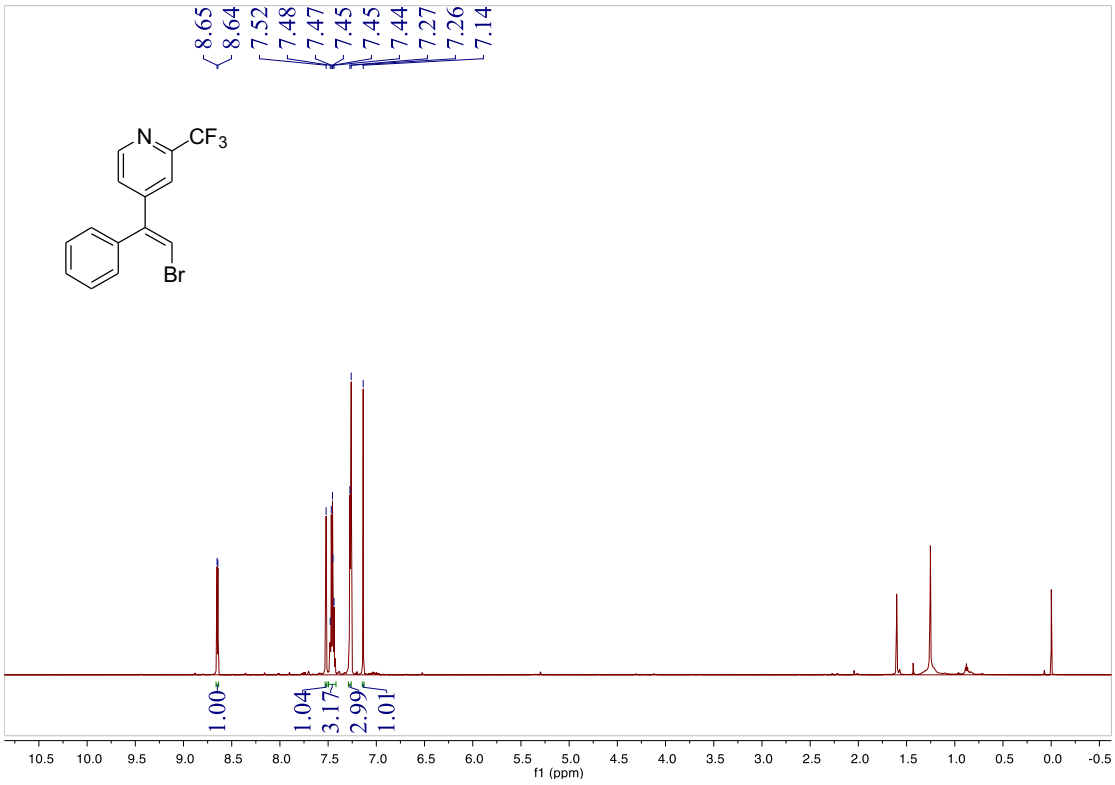
4; ^{19}F NMR (376 MHz, $CDCl_3$)



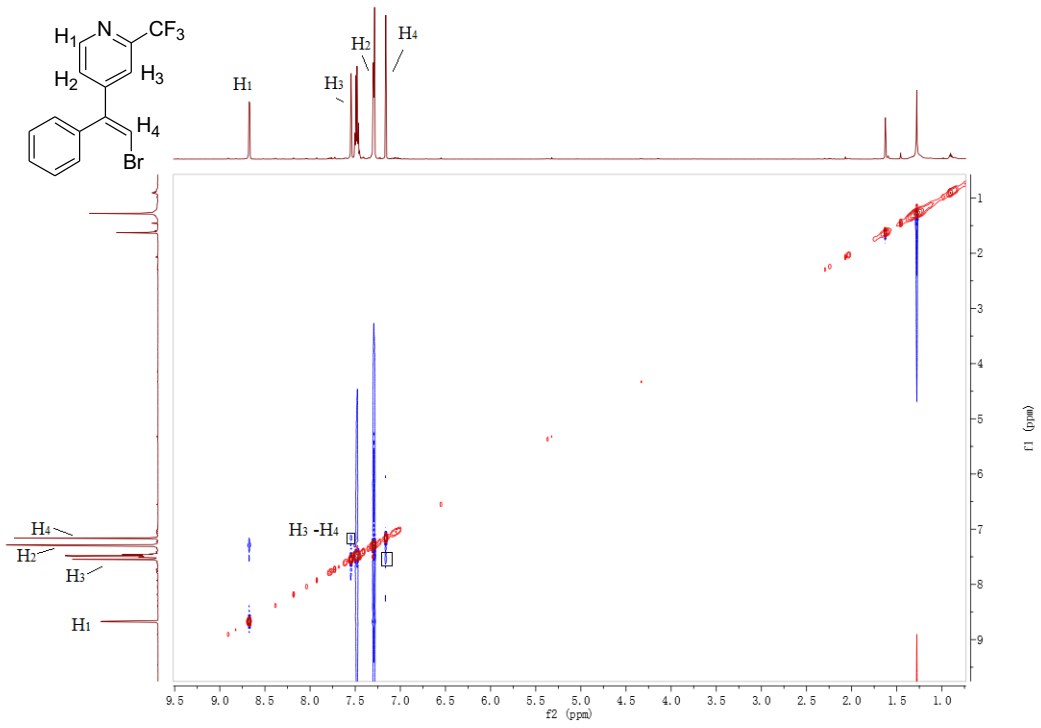
4; ^{13}C NMR (100 MHz, $CDCl_3$)

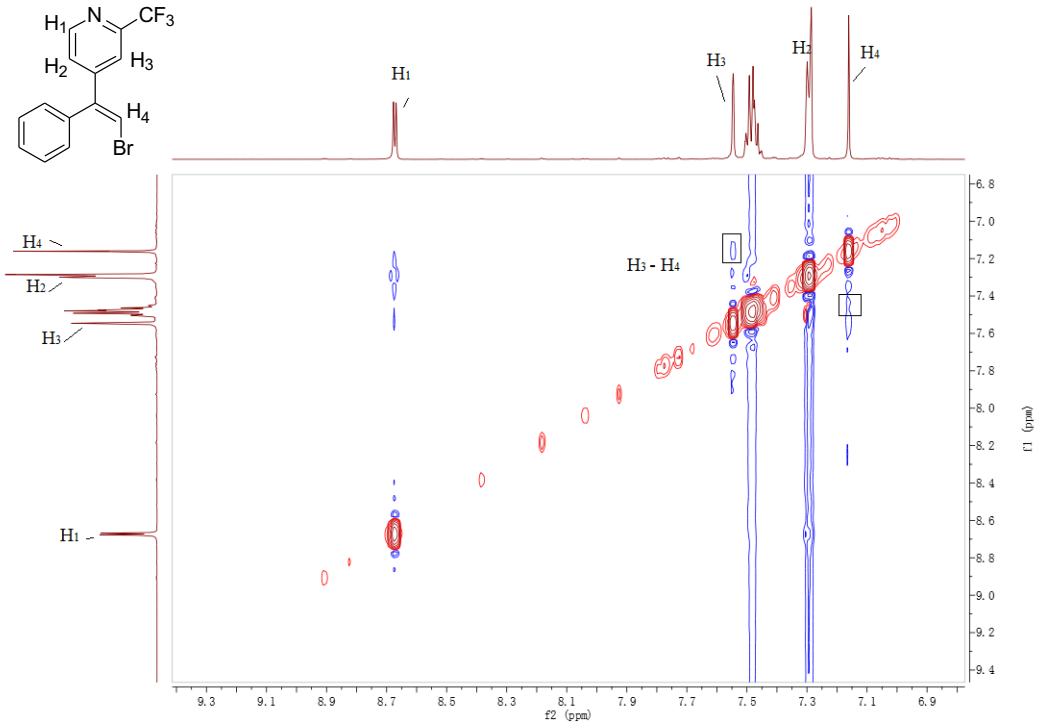


E-4; ^{1}H NMR (600 MHz, $CDCl_3$)

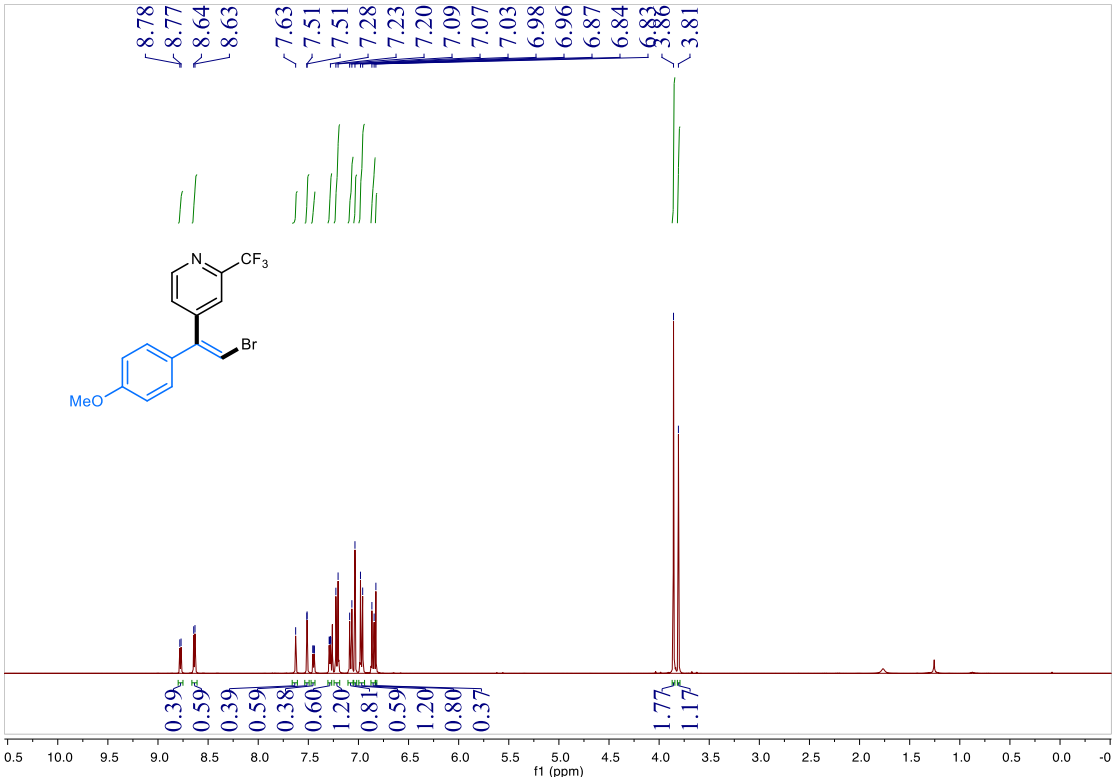


E-4; NOESY

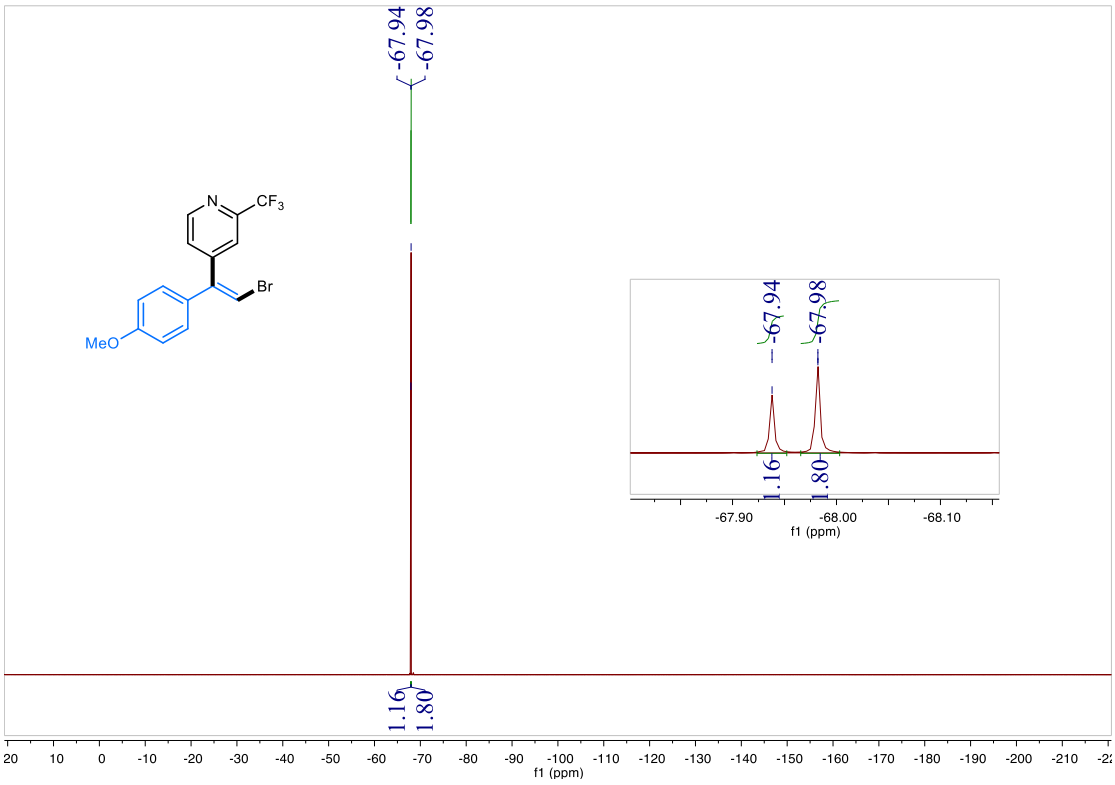




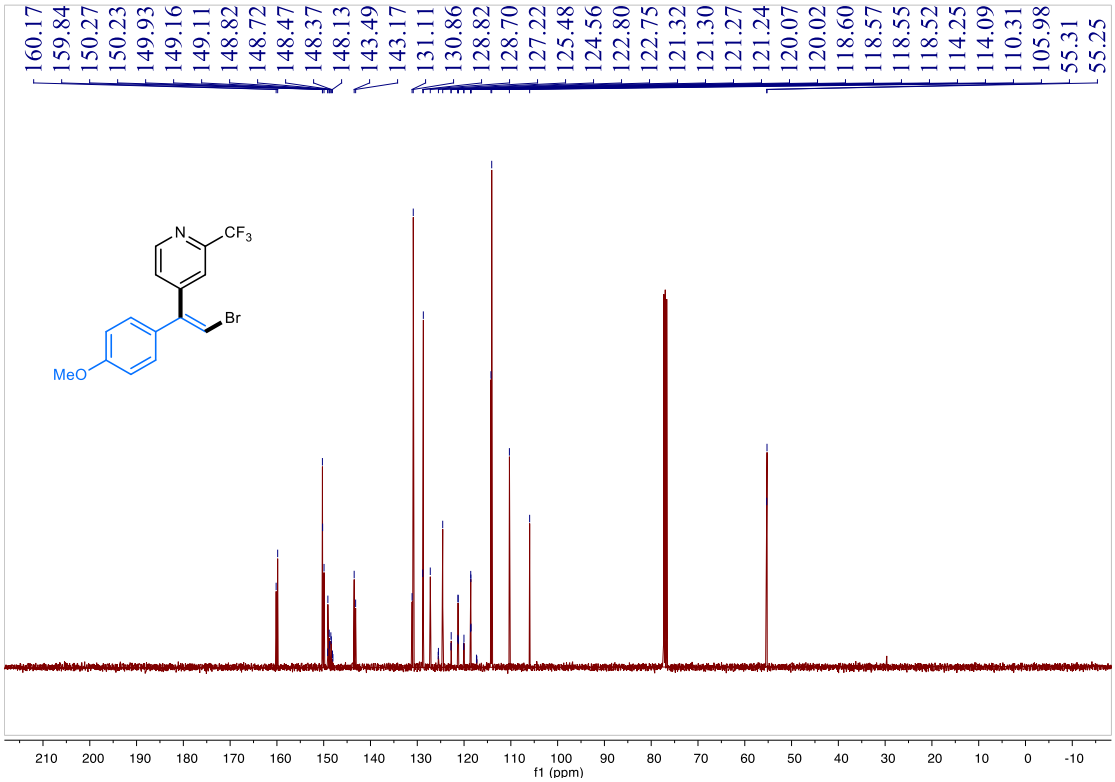
5; ^{1}H NMR (400 MHz, $CDCl_3$)



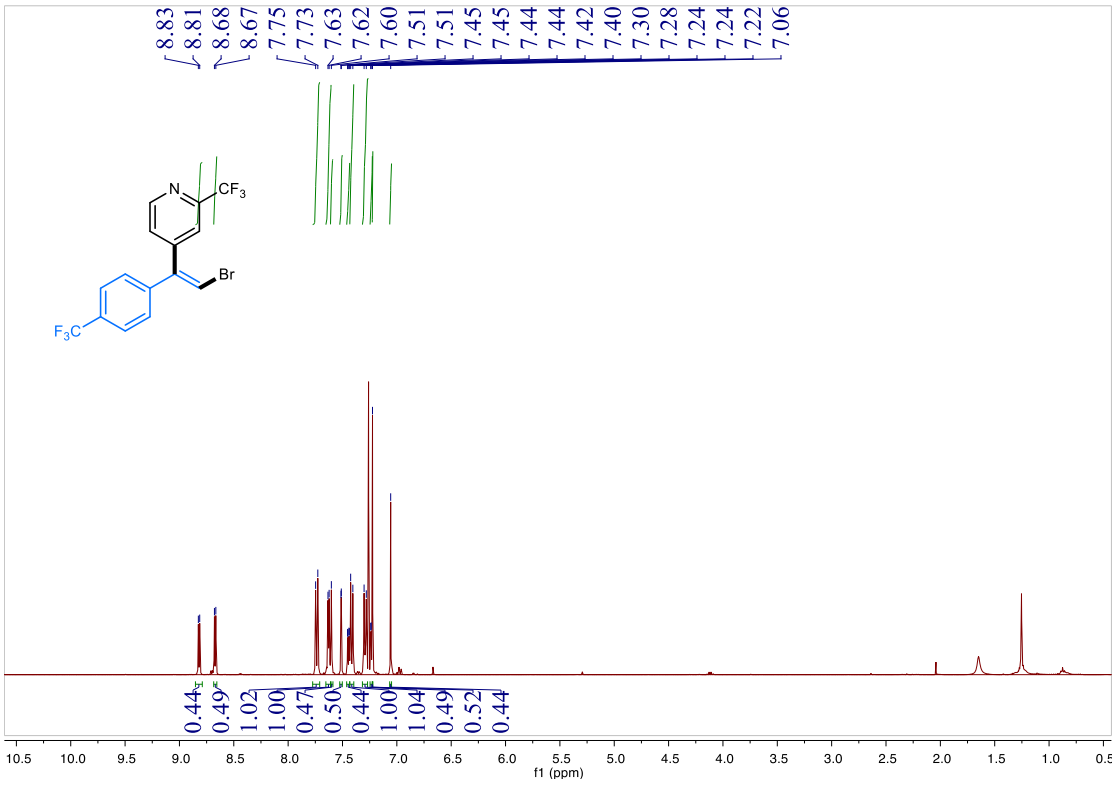
5; ^{19}F NMR (376 MHz, $CDCl_3$)



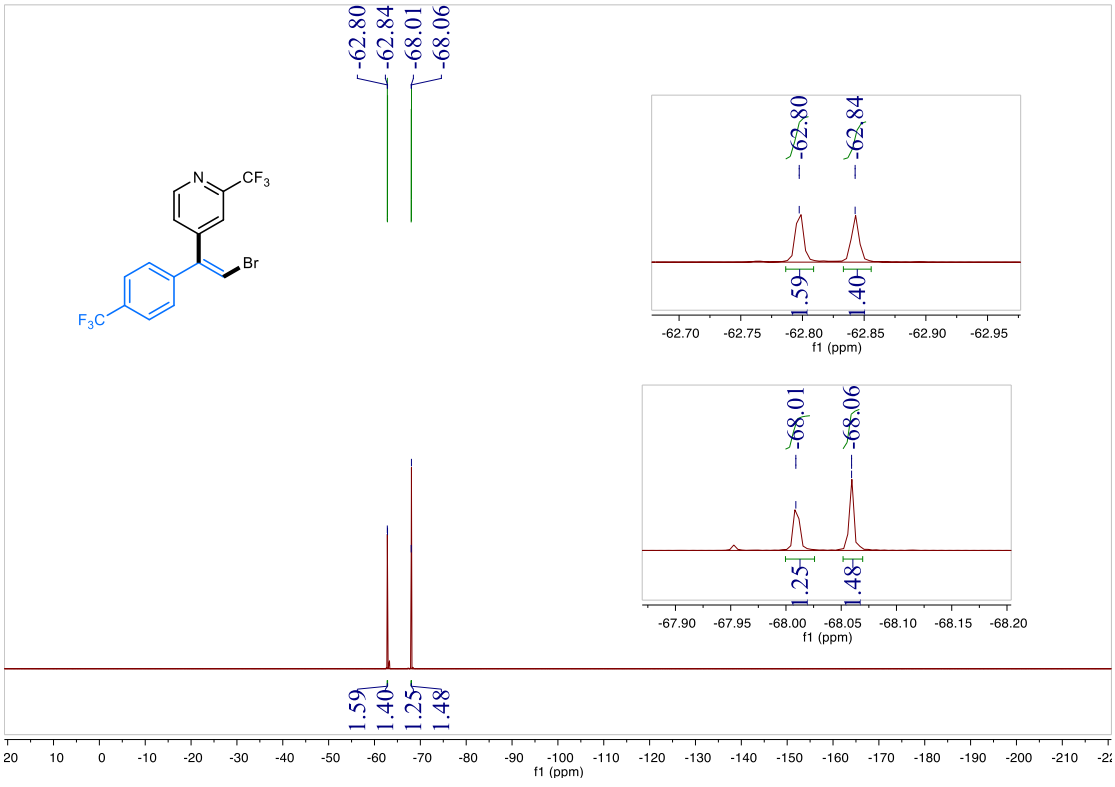
5; ^{13}C NMR (100 MHz, $CDCl_3$)



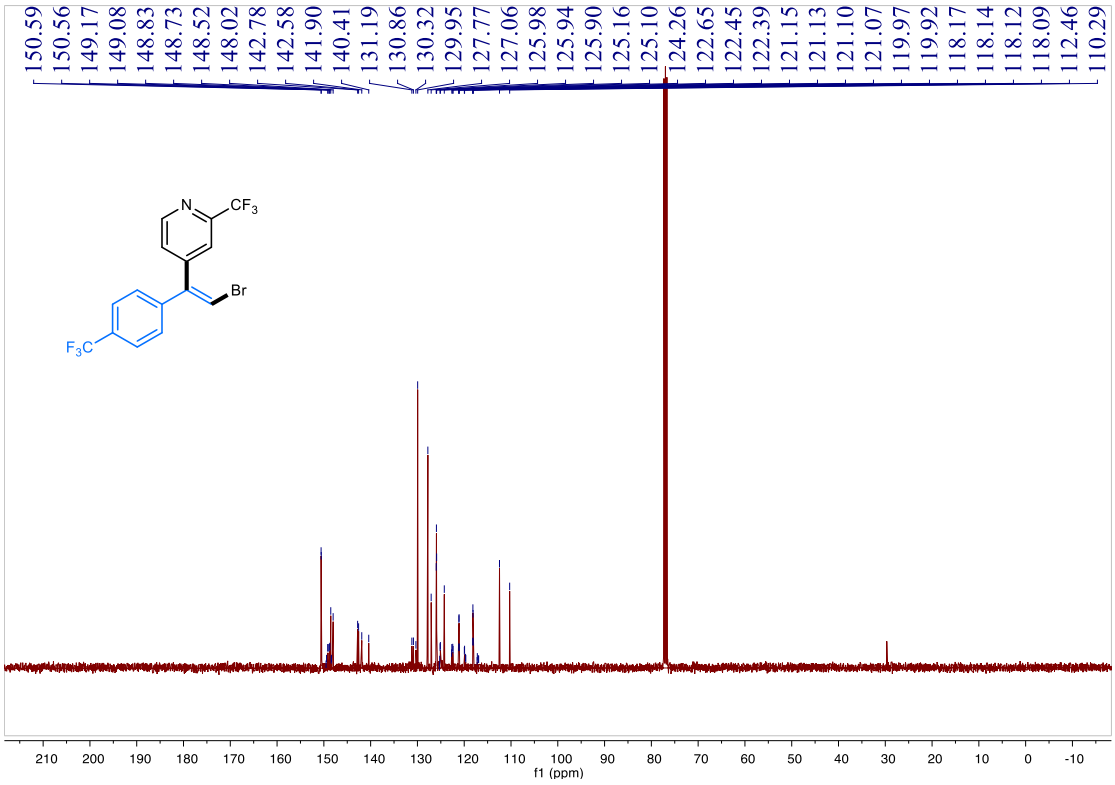
6; ^{1}H NMR (400 MHz, $CDCl_3$)



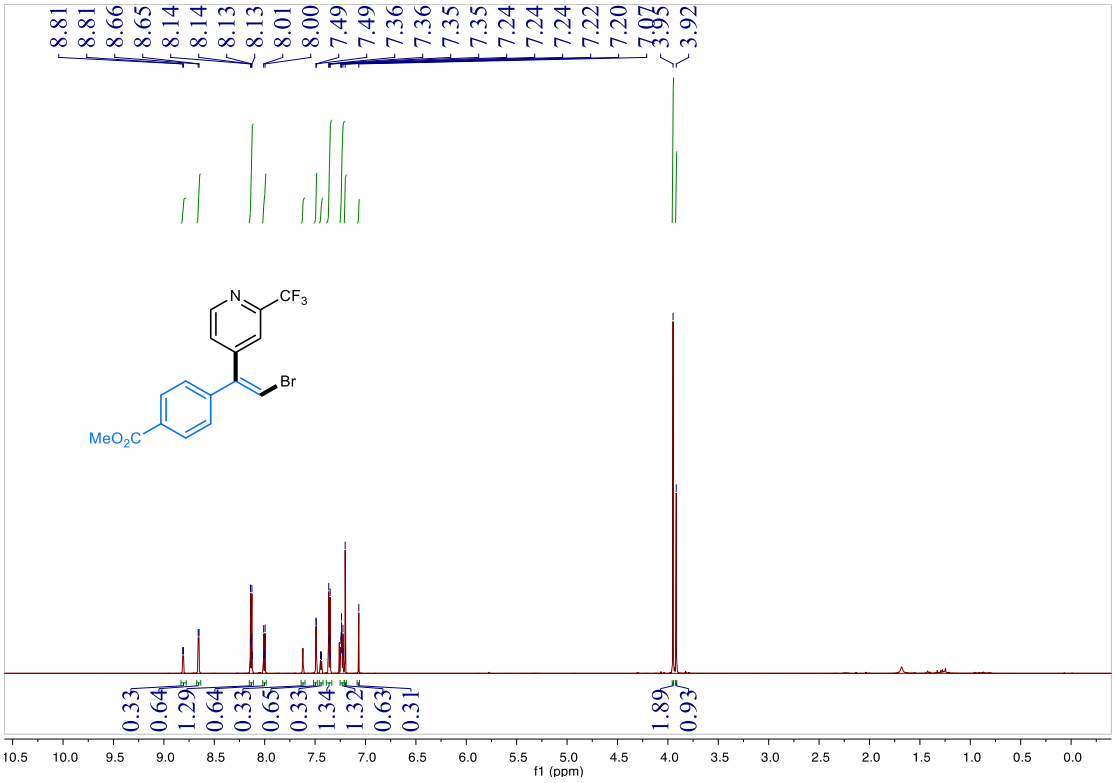
6; ^{19}F NMR (376 MHz, $CDCl_3$)



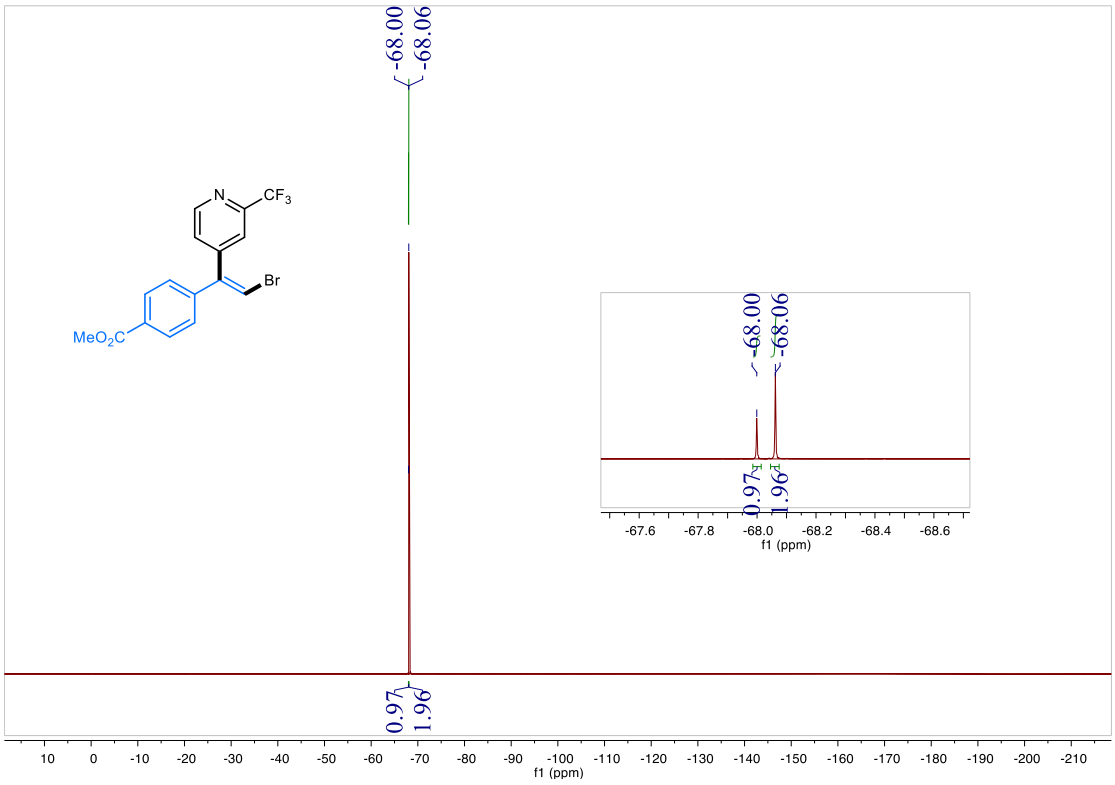
6; ^{13}C NMR (100 MHz, $CDCl_3$)



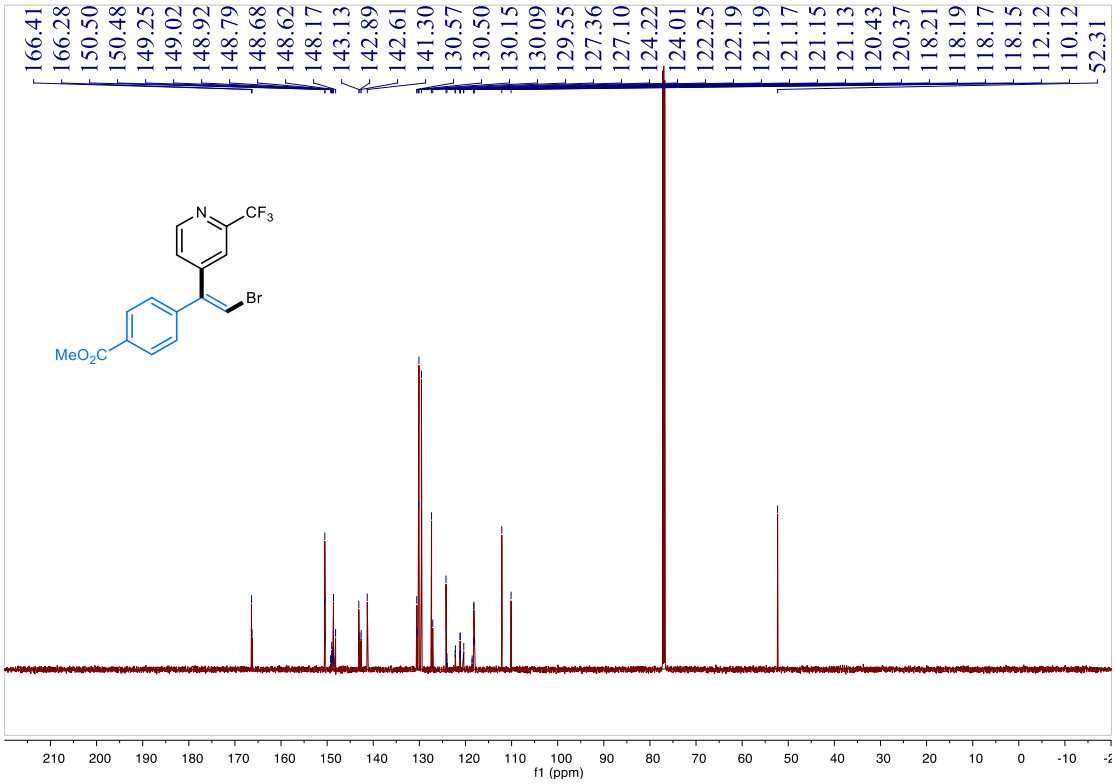
7; ^{1}H NMR (600 MHz, $CDCl_3$)



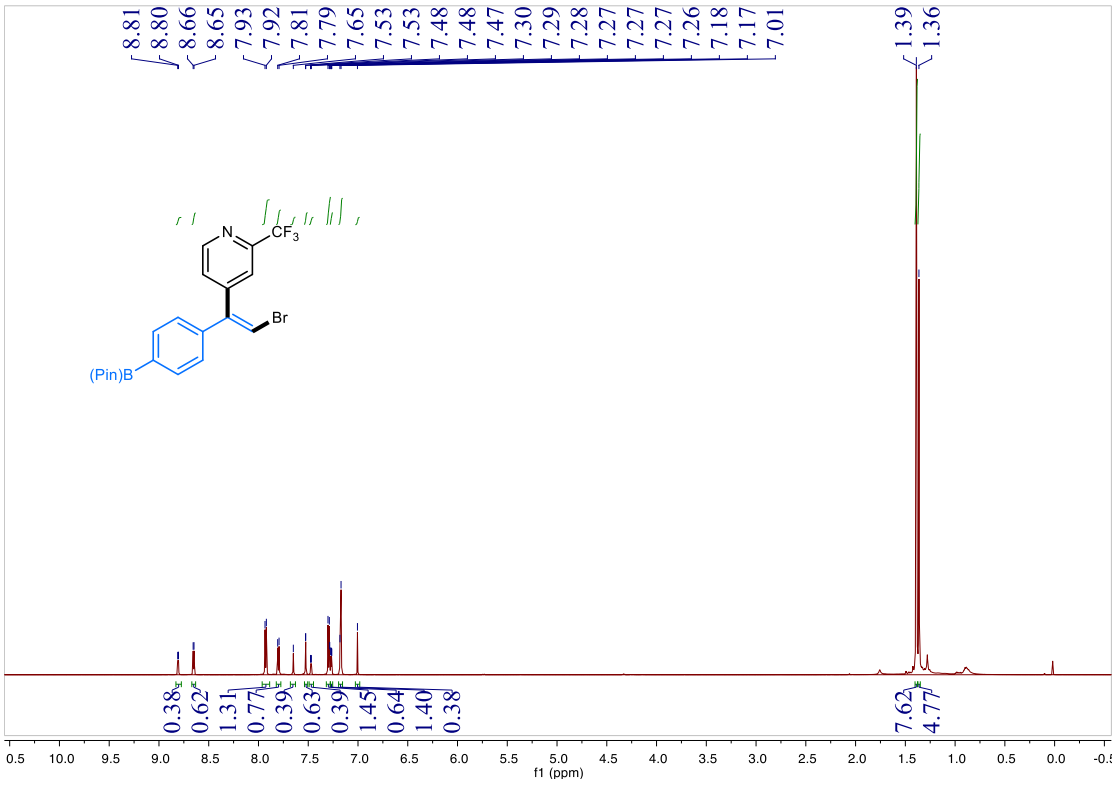
7; ^{19}F NMR (564 MHz, $CDCl_3$)



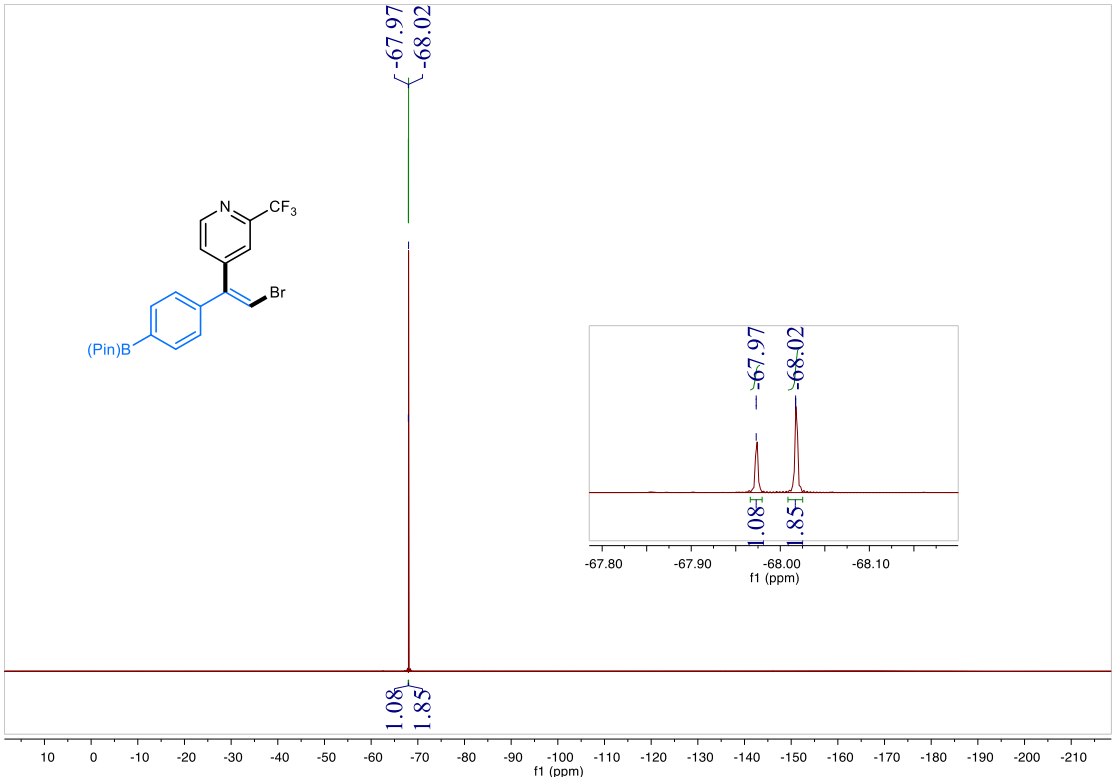
7; ^{13}C NMR (150 MHz, $CDCl_3$)



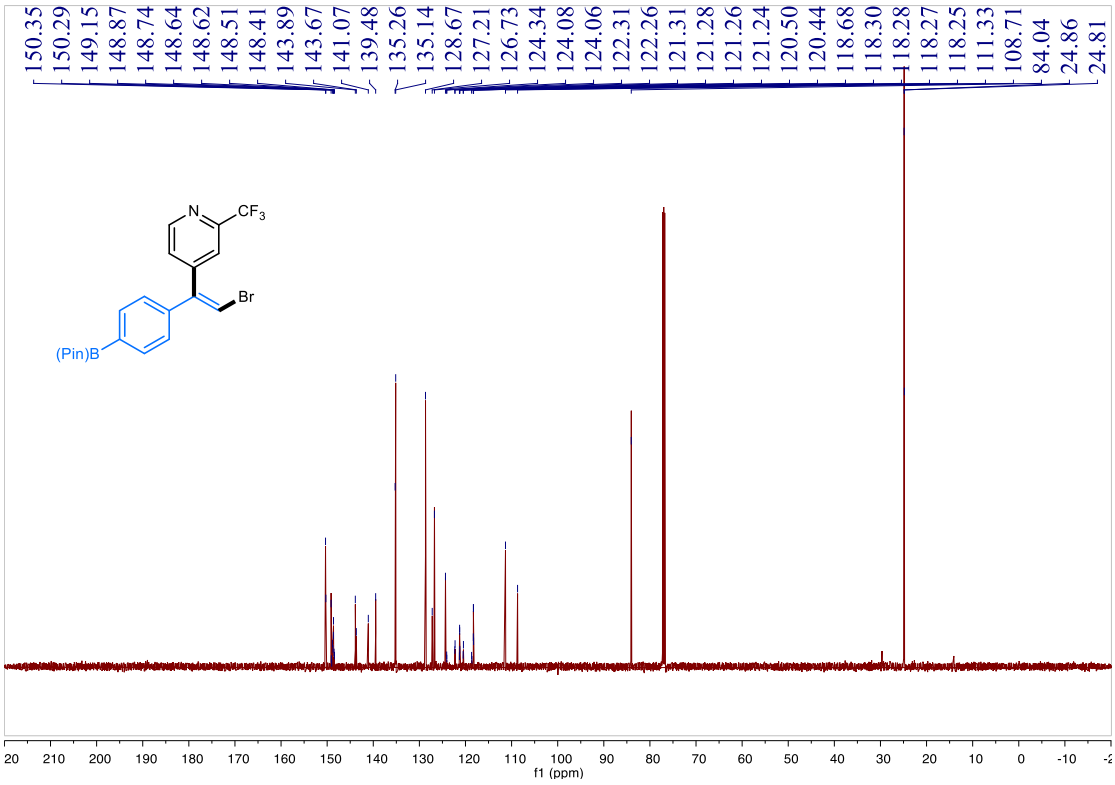
8; ^{1}H NMR (600 MHz, $CDCl_3$)



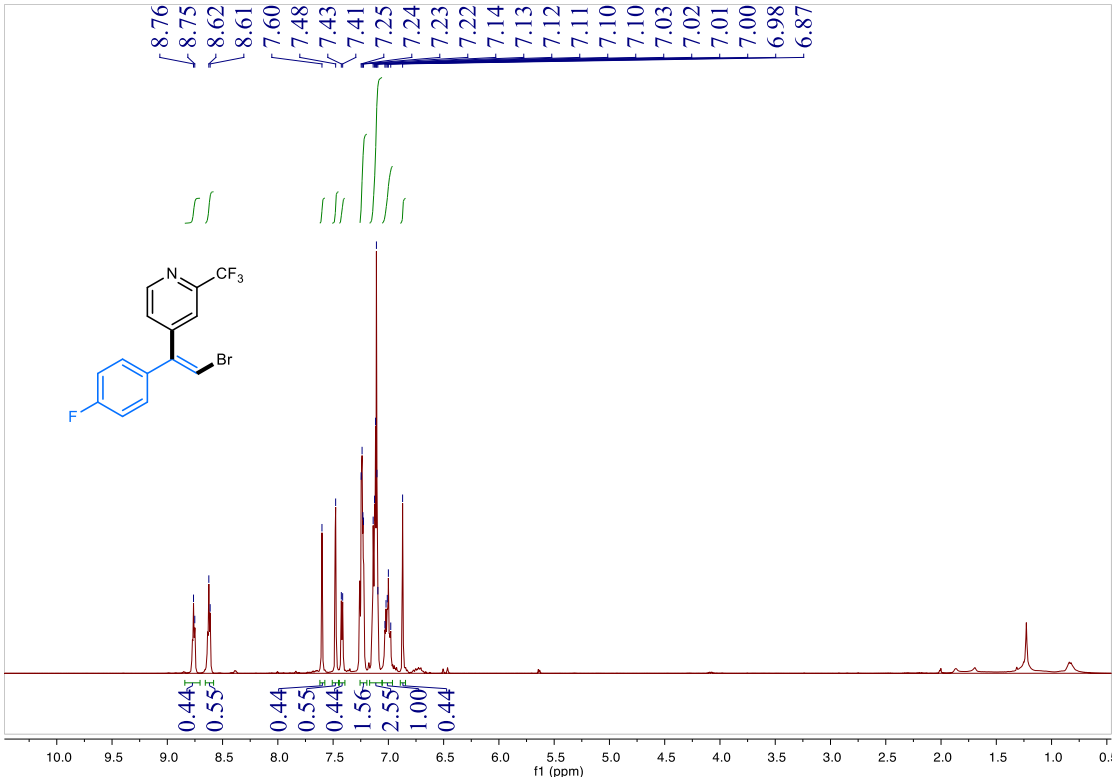
8; ^{19}F NMR (564 MHz, $CDCl_3$)



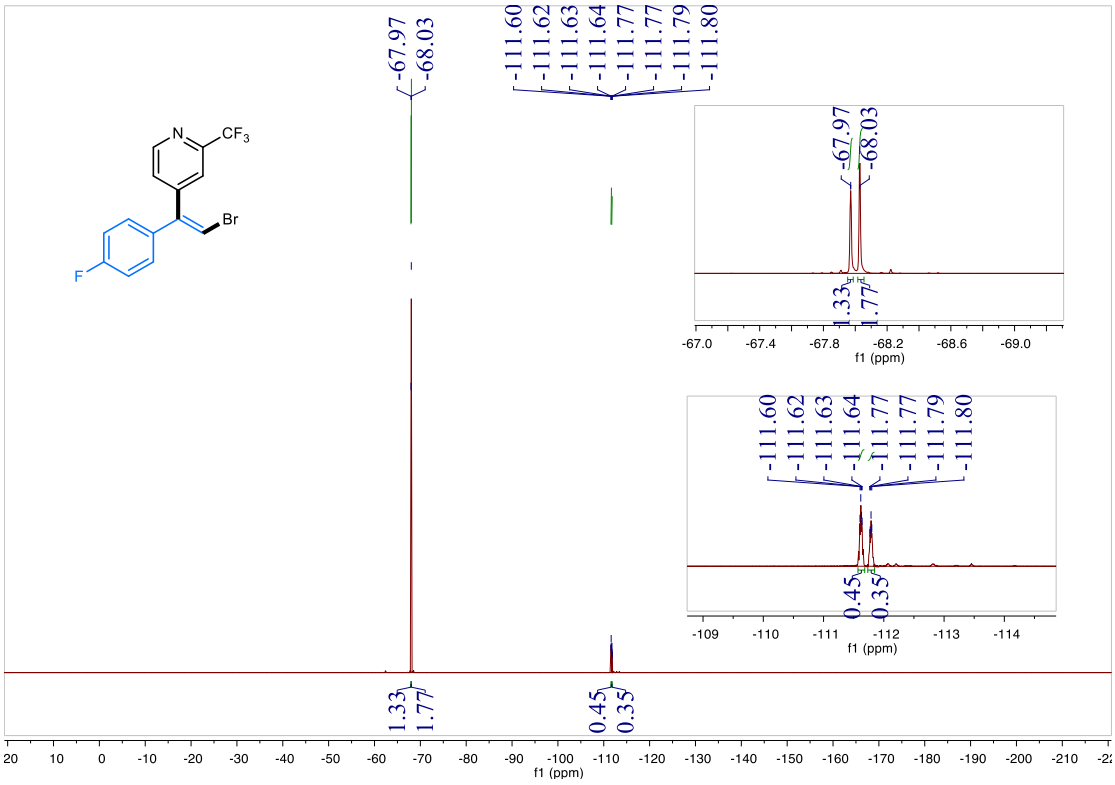
8; ^{13}C NMR (150 MHz, $CDCl_3$)



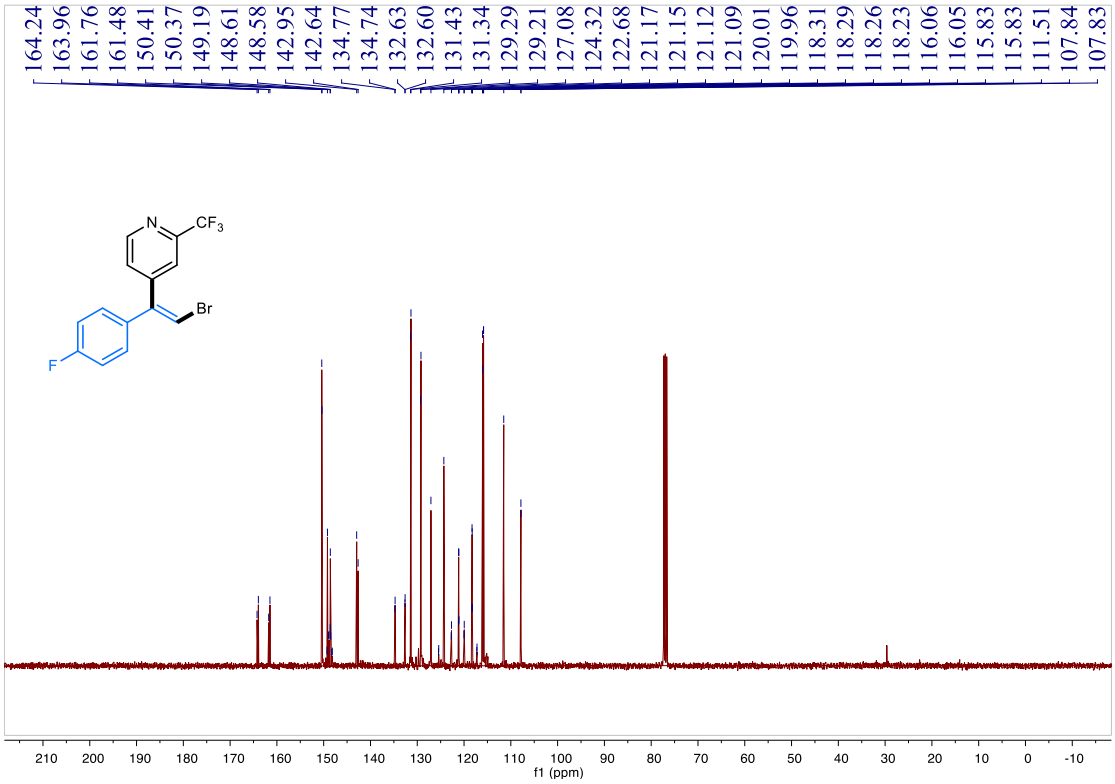
9; ^{1}H NMR (400 MHz, $CDCl_3$)



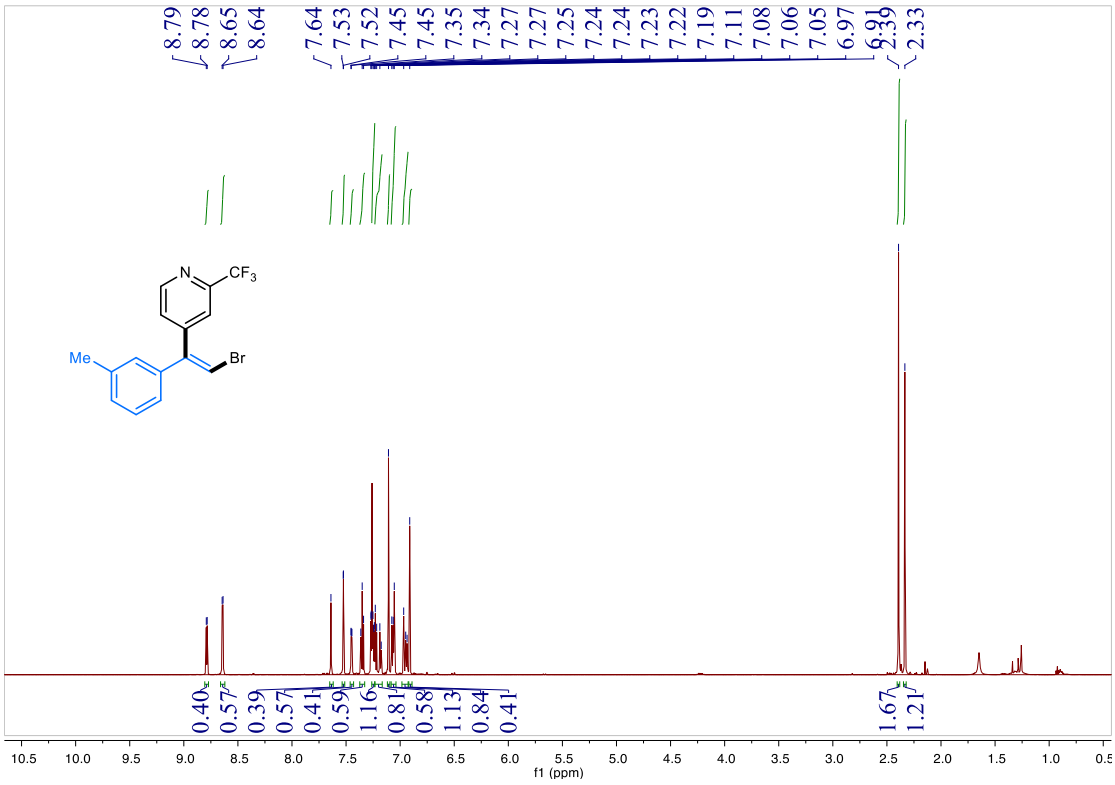
9; ^{19}F NMR (376 MHz, $CDCl_3$)



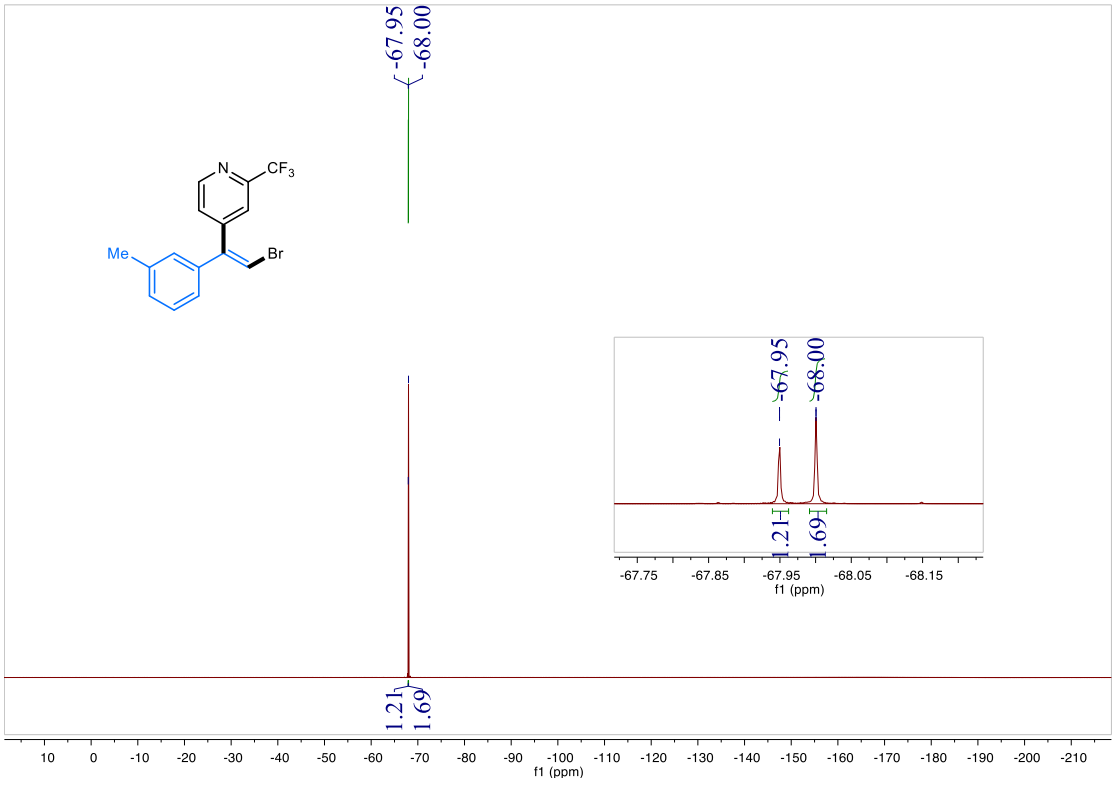
9; ^{13}C NMR (100 MHz, $CDCl_3$)



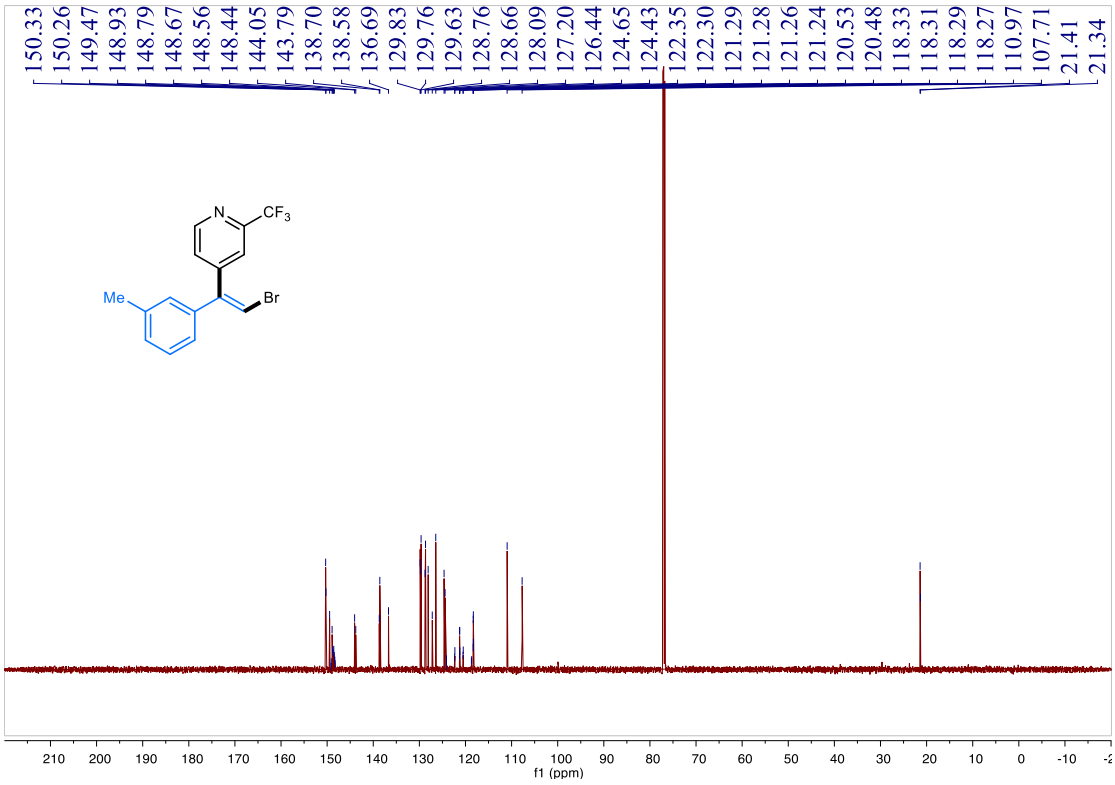
10; ^{1}H NMR (600 MHz, $CDCl_3$)



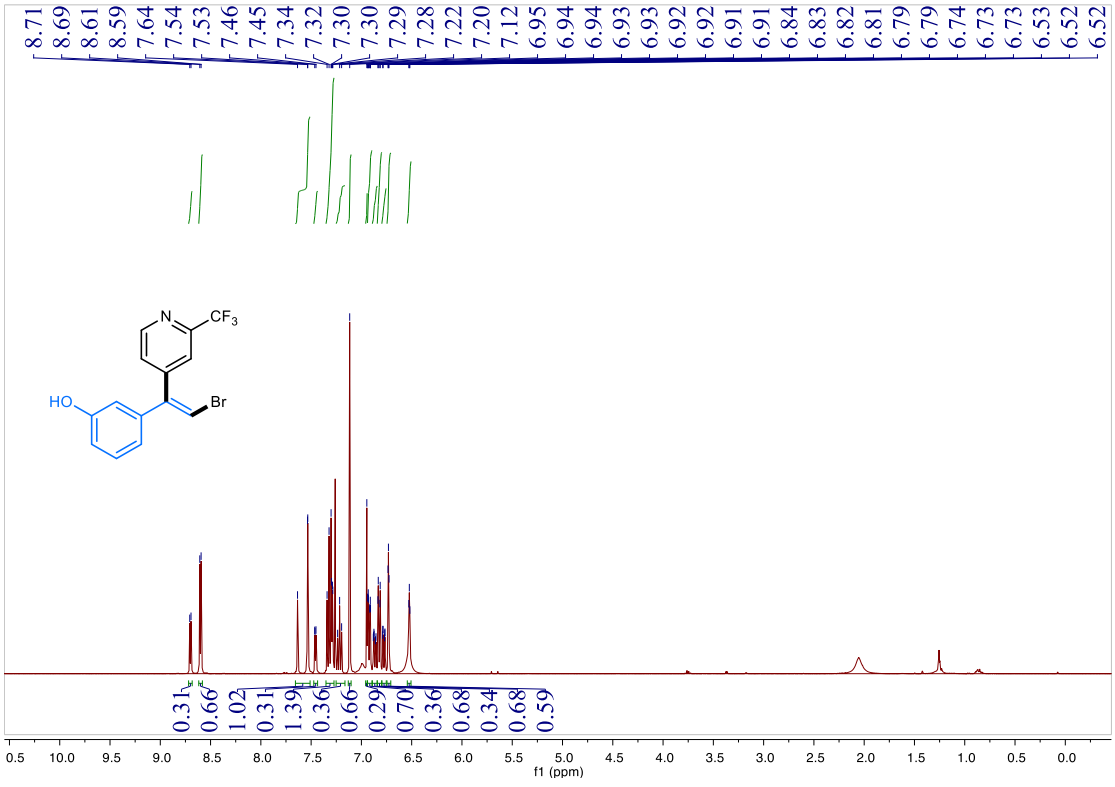
10; ^{19}F NMR (564 MHz, $CDCl_3$)



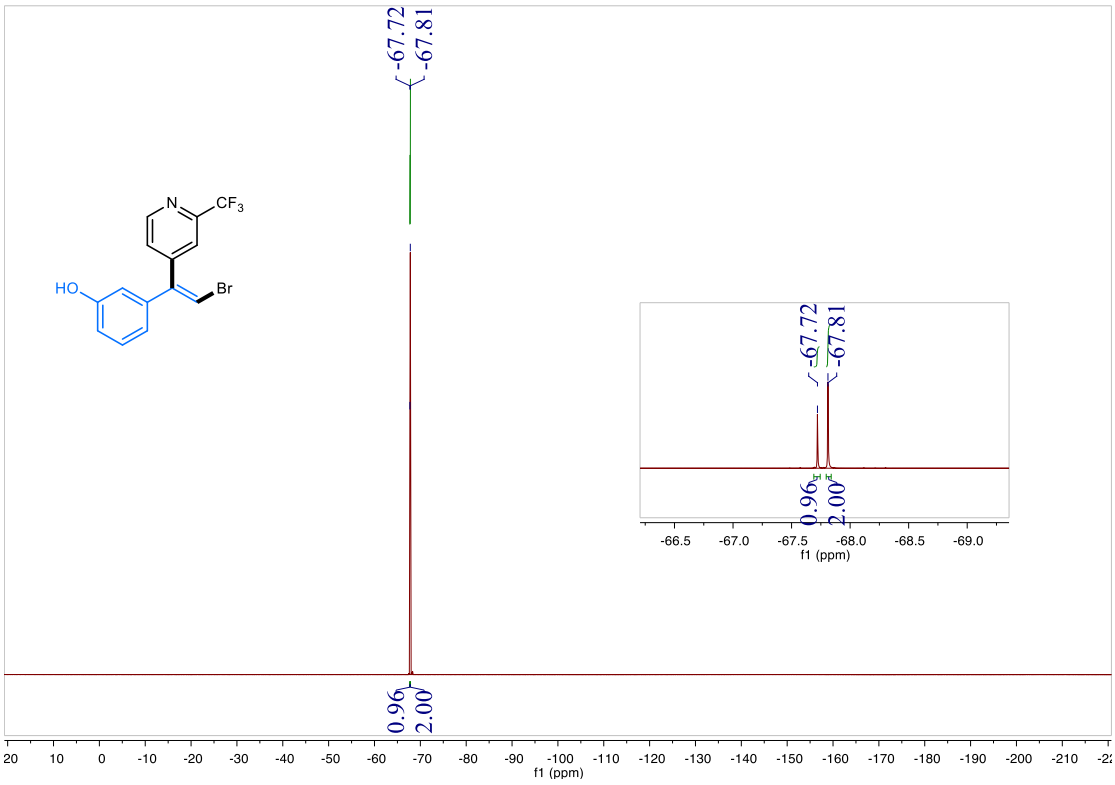
10; ^{13}C NMR (150 MHz, $CDCl_3$)



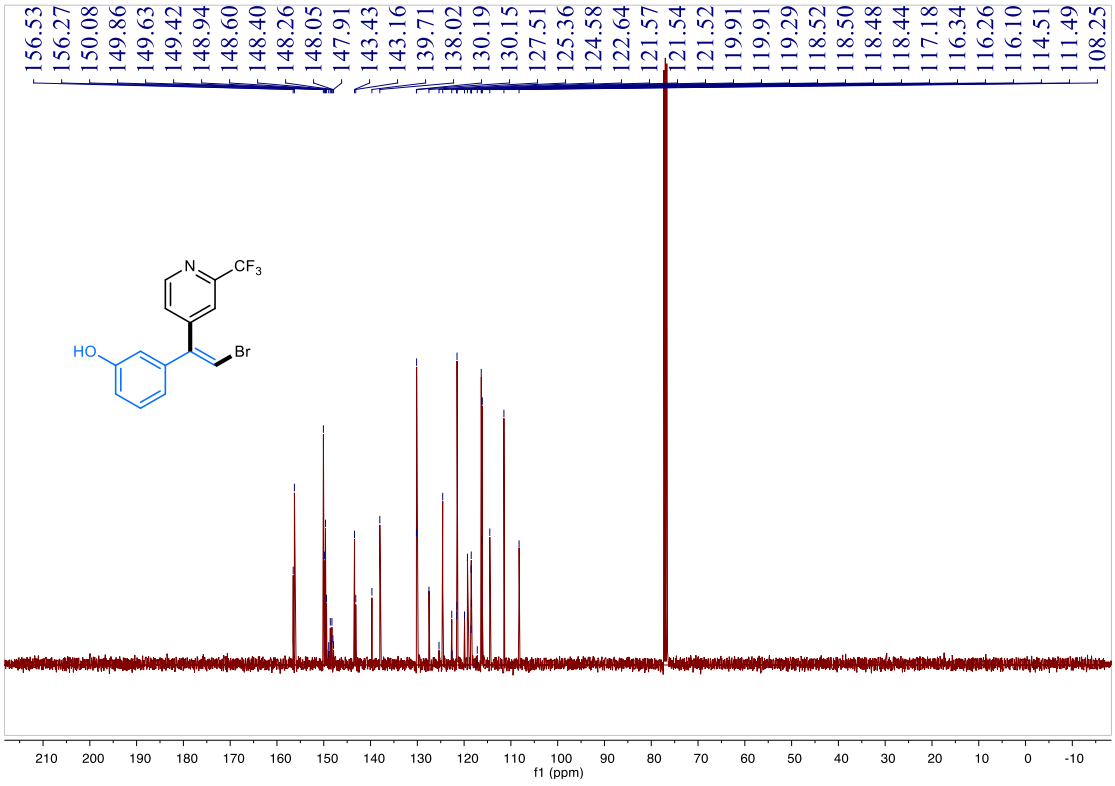
11; ^{1}H NMR (400 MHz, $CDCl_3$)



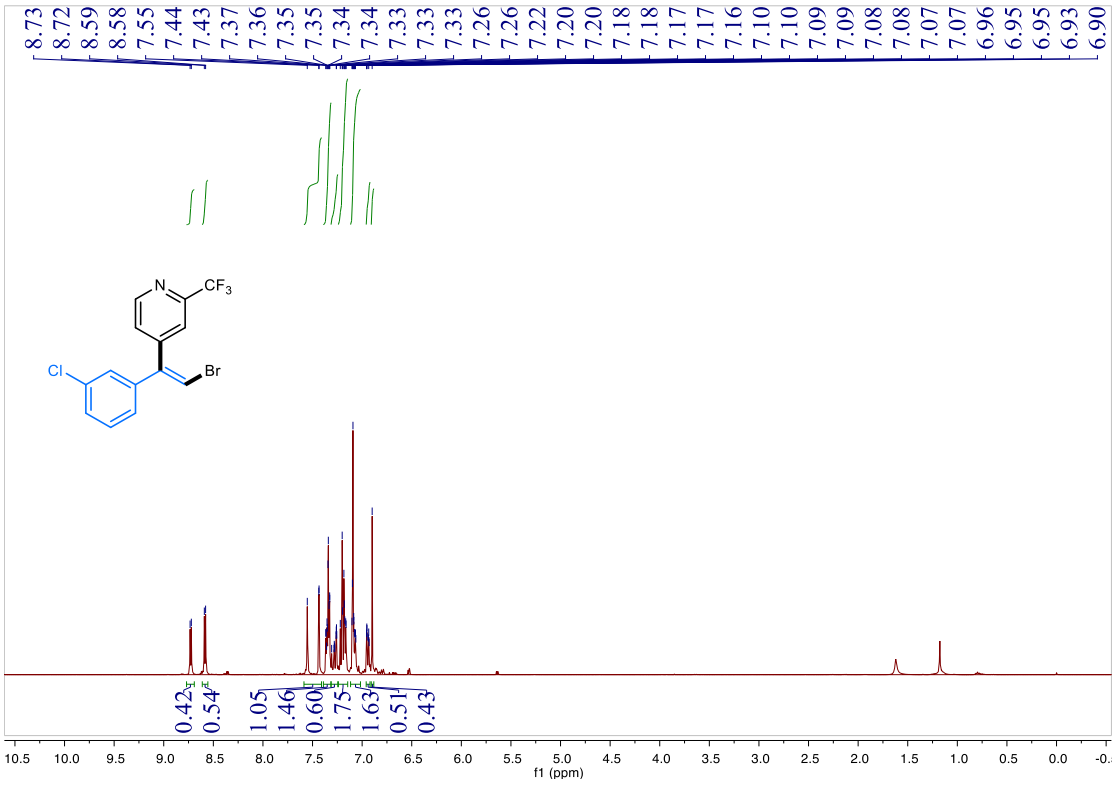
11; ^{19}F NMR (376 MHz, $CDCl_3$)



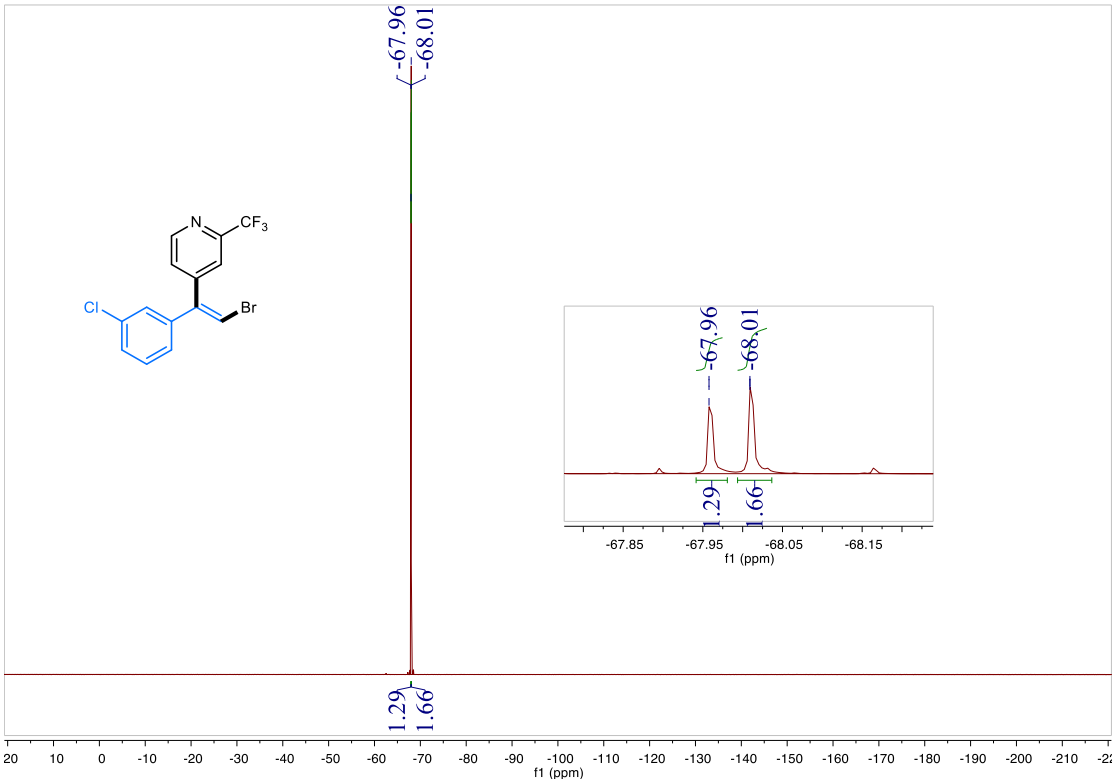
11; ^{13}C NMR (100 MHz, $CDCl_3$)



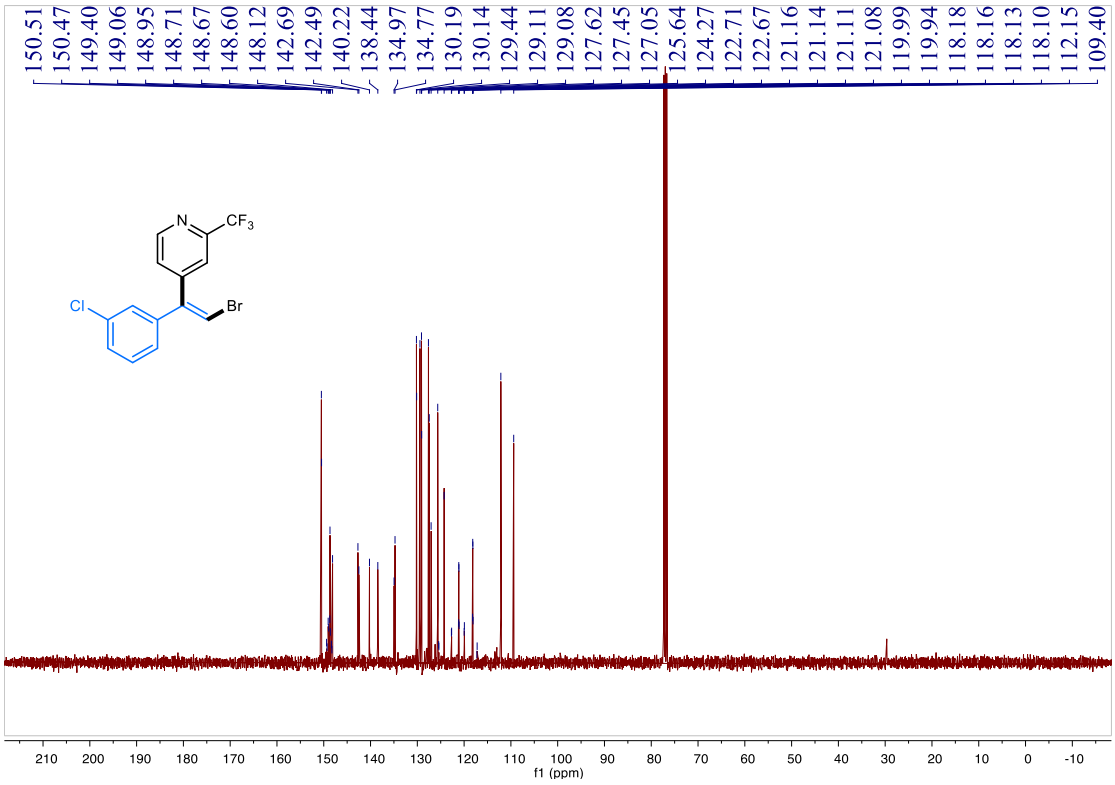
12; ^{1}H NMR (400 MHz, $CDCl_3$)



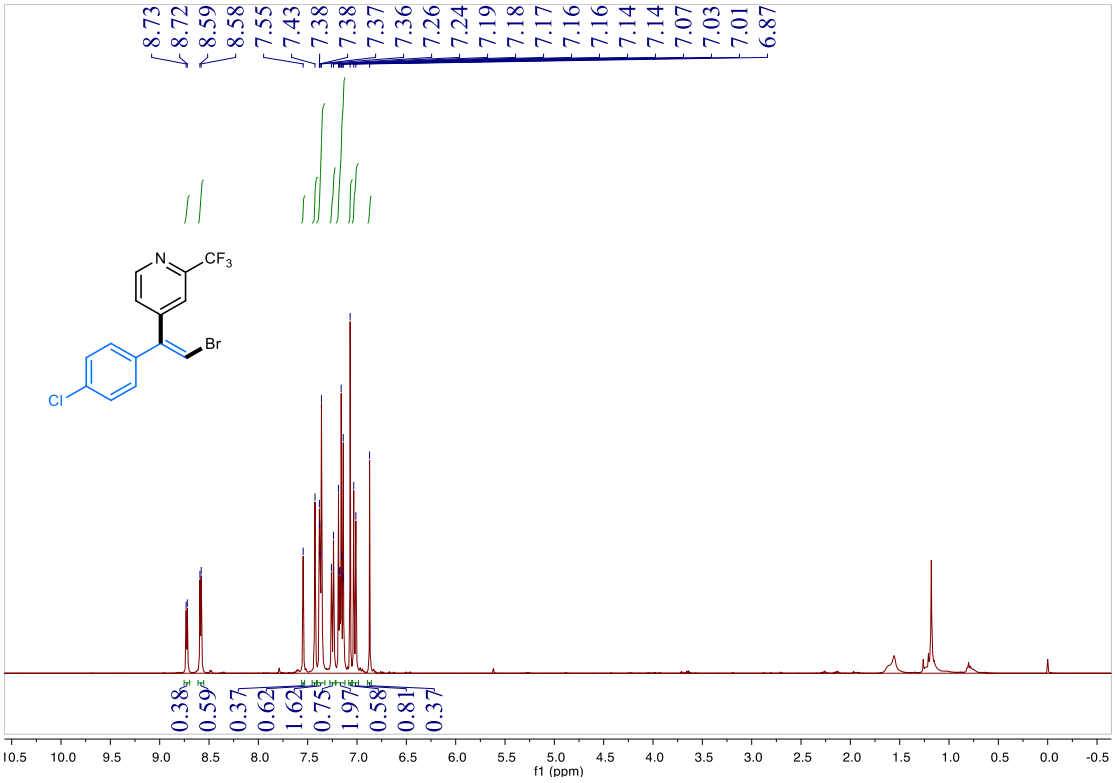
12; ^{19}F NMR (376 MHz, $CDCl_3$)



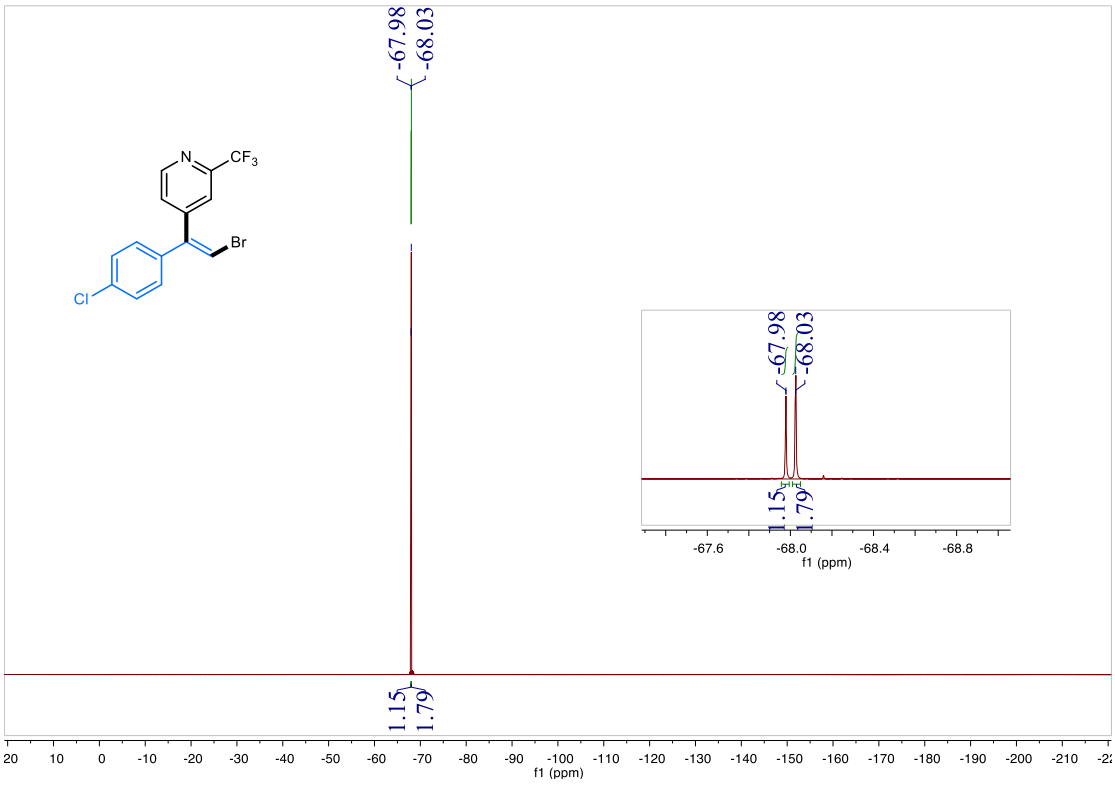
12; ^{13}C NMR (101 MHz, $CDCl_3$)



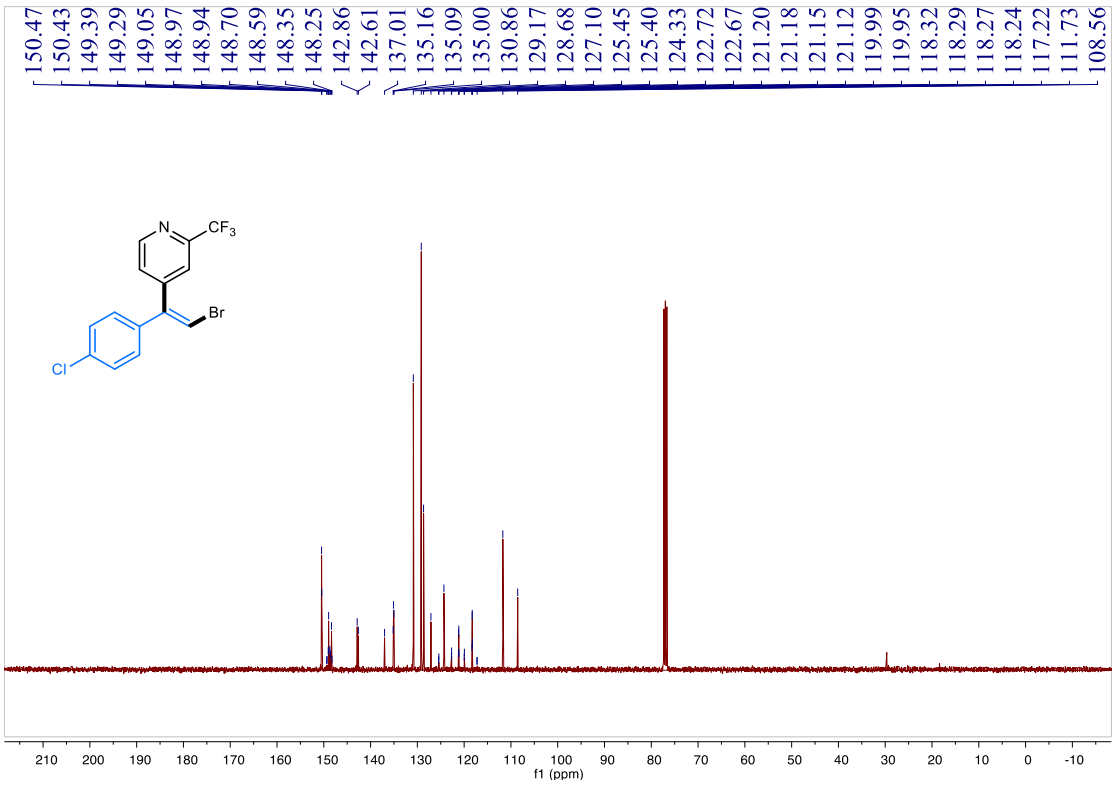
13; ^{1}H NMR (400 MHz, $CDCl_3$)



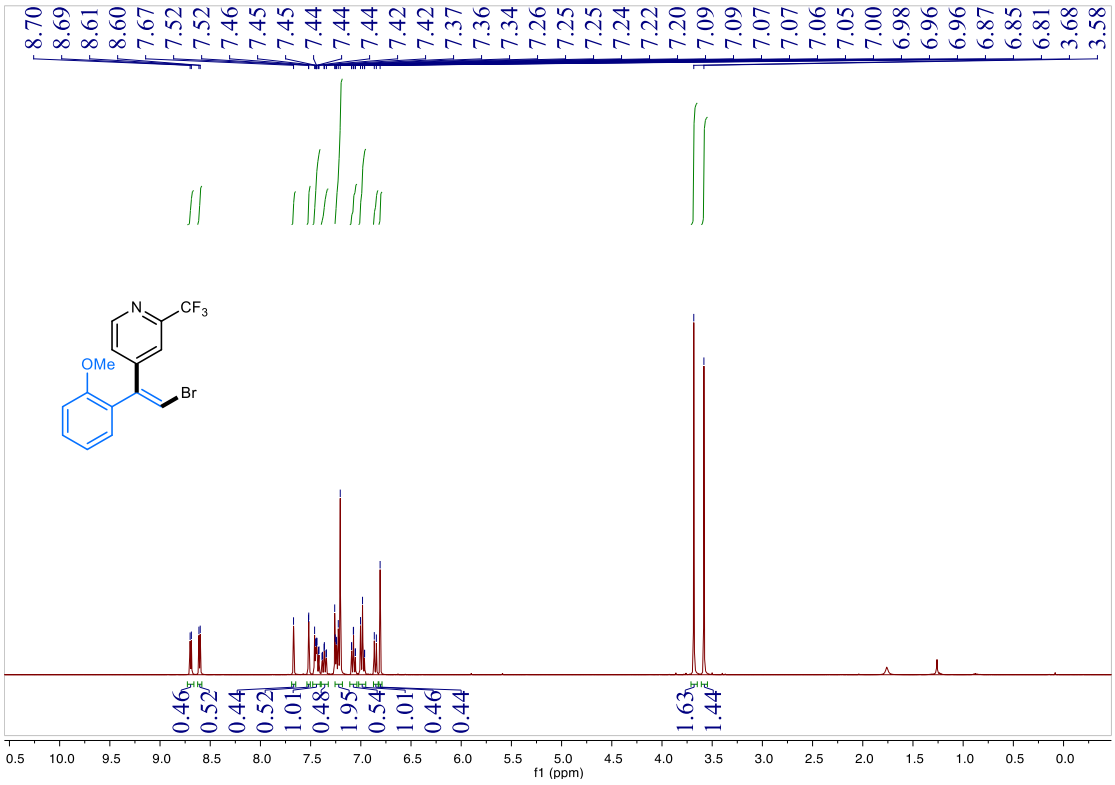
13; ^{19}F NMR (376 MHz, $CDCl_3$)



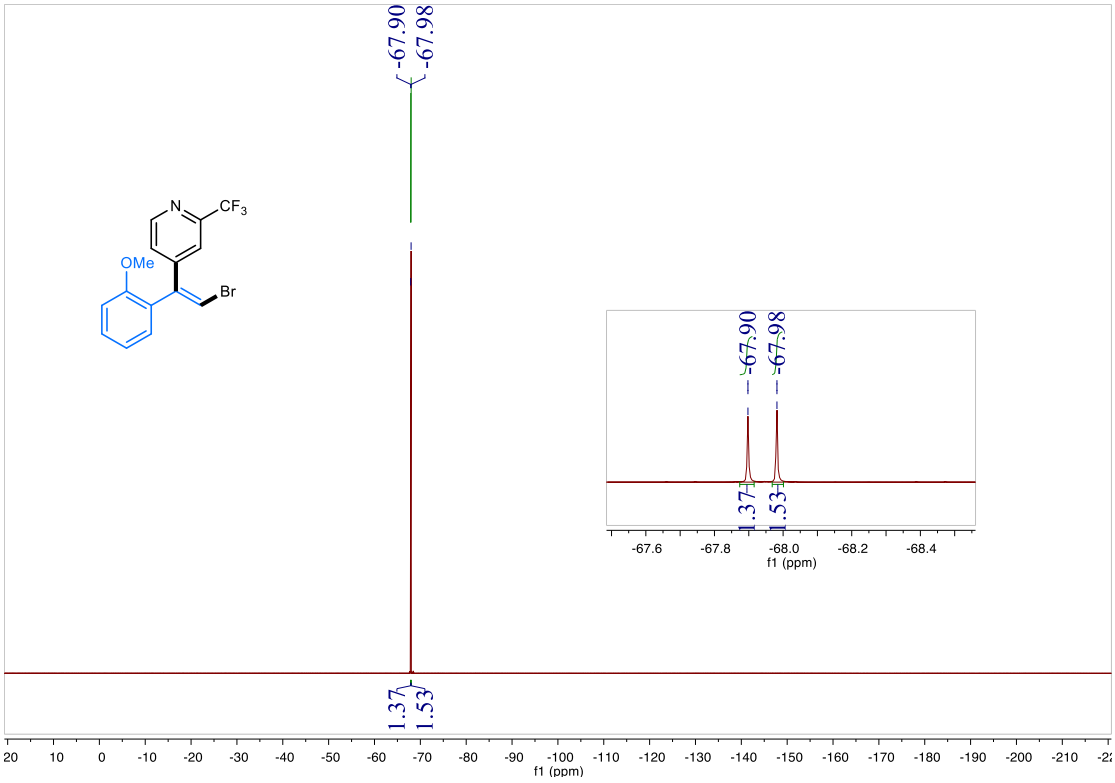
13; ^{13}C NMR (100 MHz, $CDCl_3$)



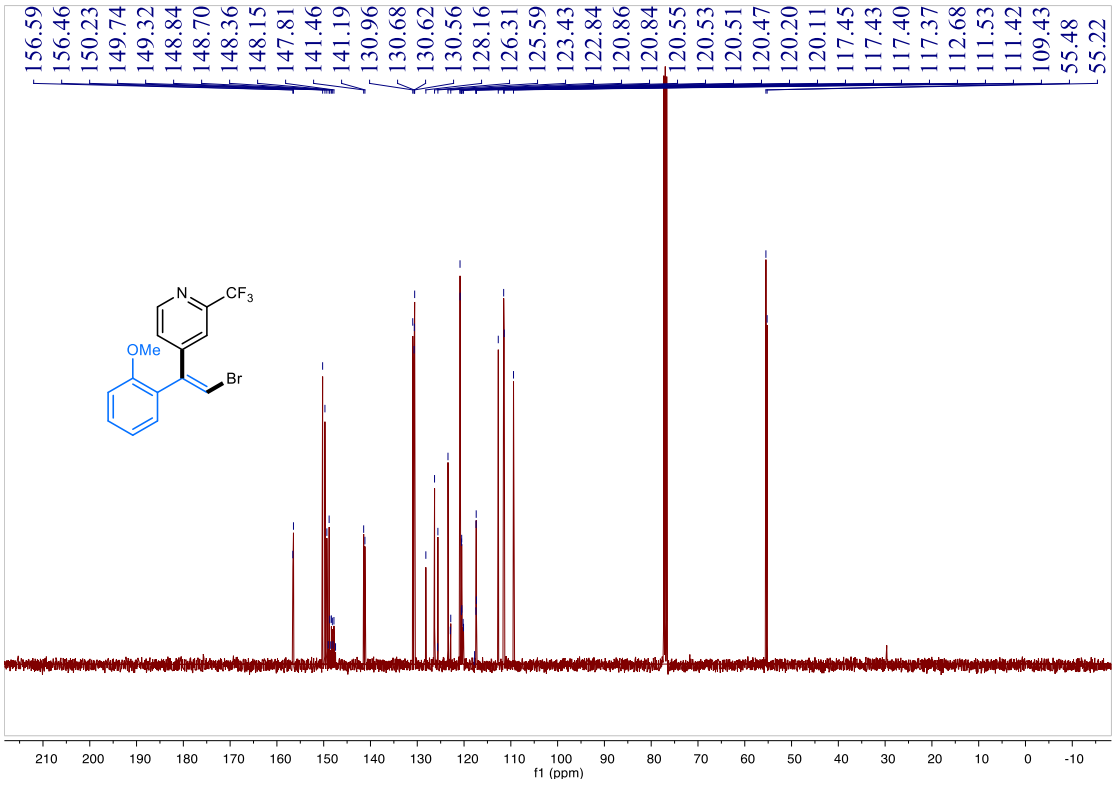
14; ^{1}H NMR (400 MHz, $CDCl_3$)



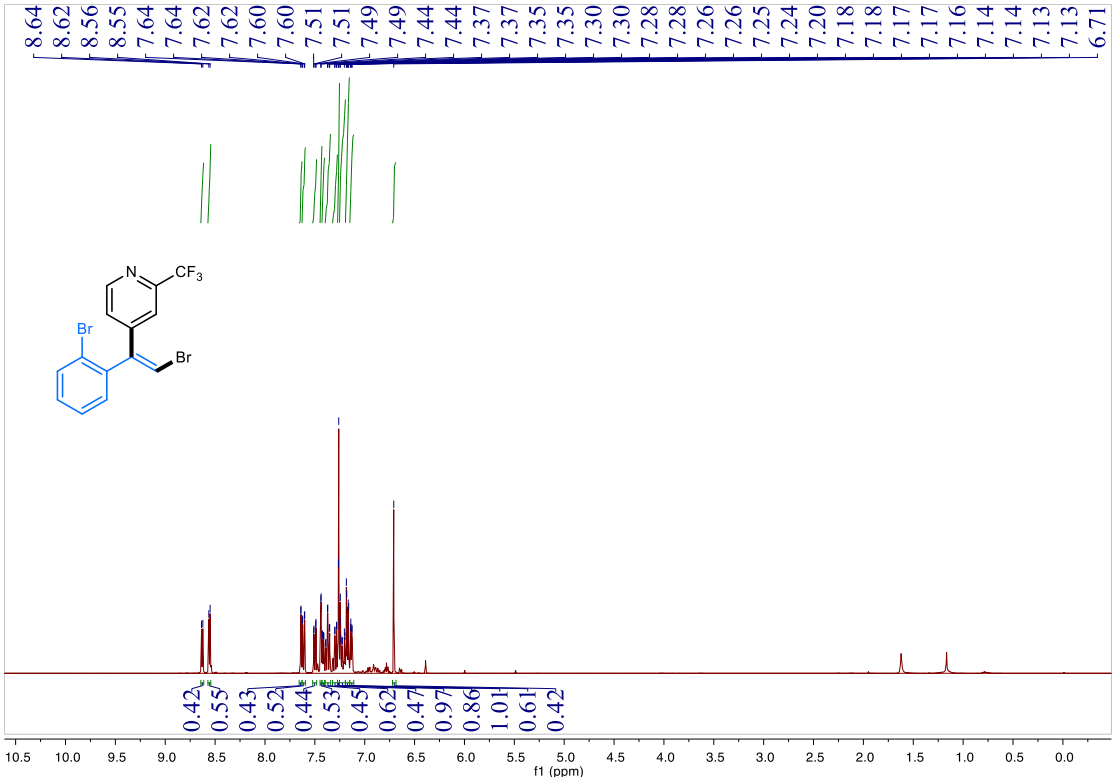
14; ^{19}F NMR (376 MHz, $CDCl_3$)



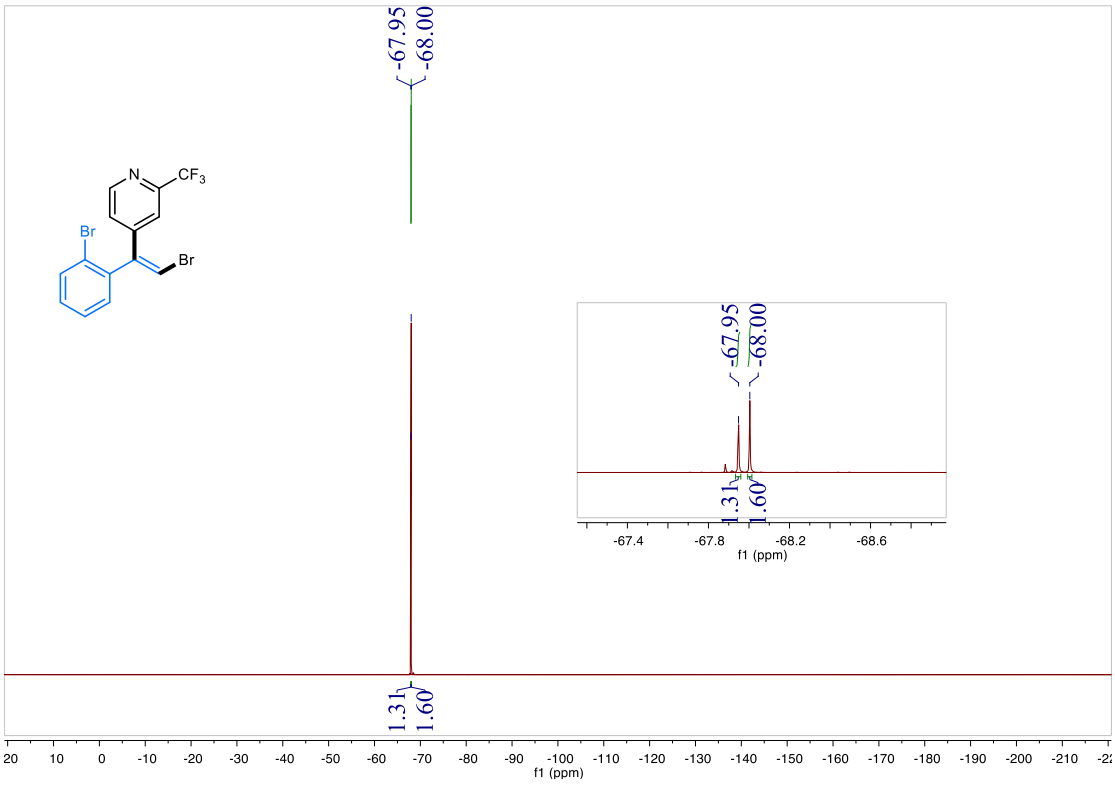
14; ^{13}C NMR (100 MHz, $CDCl_3$)



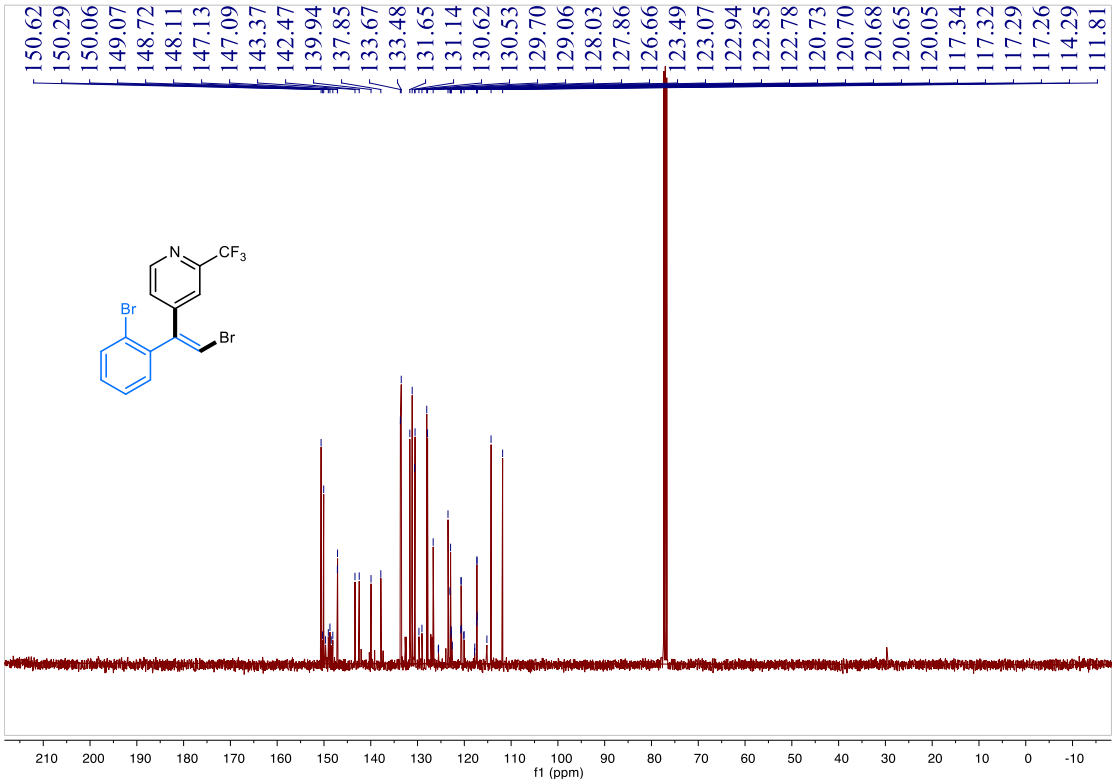
15; ^{1}H NMR (400 MHz, $CDCl_3$)



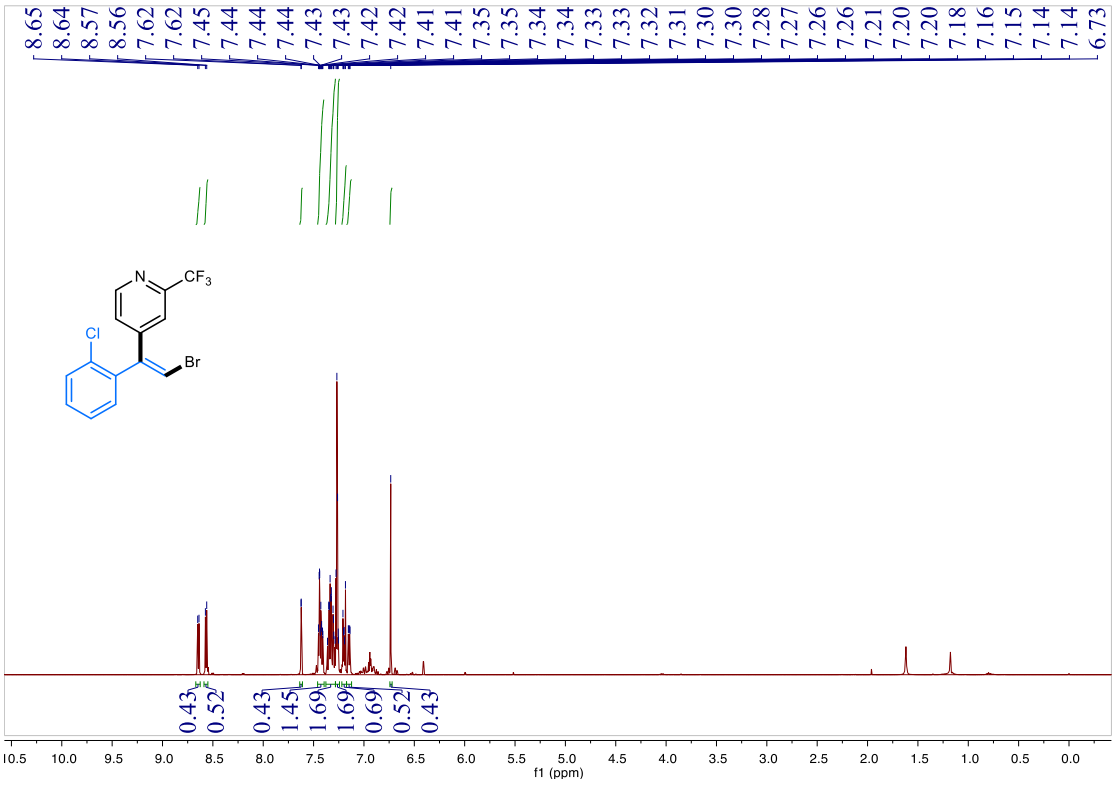
15; ^{19}F NMR (376 MHz, $CDCl_3$)



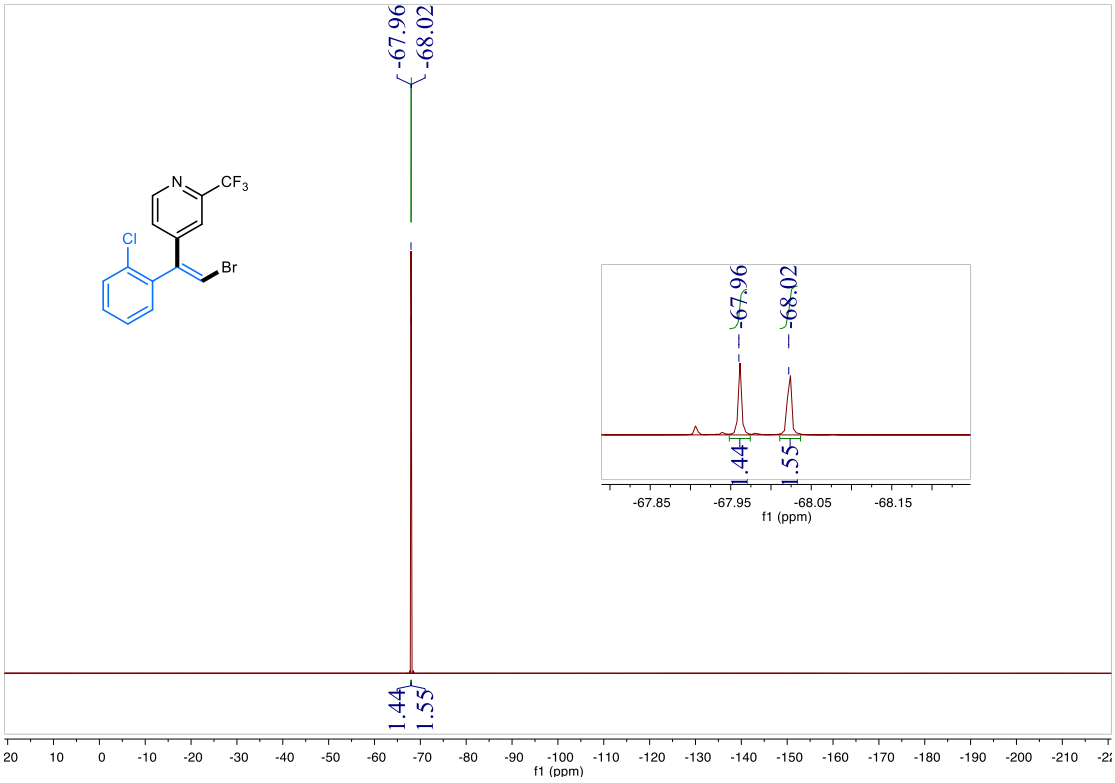
15; ^{13}C NMR (100 MHz, $CDCl_3$)



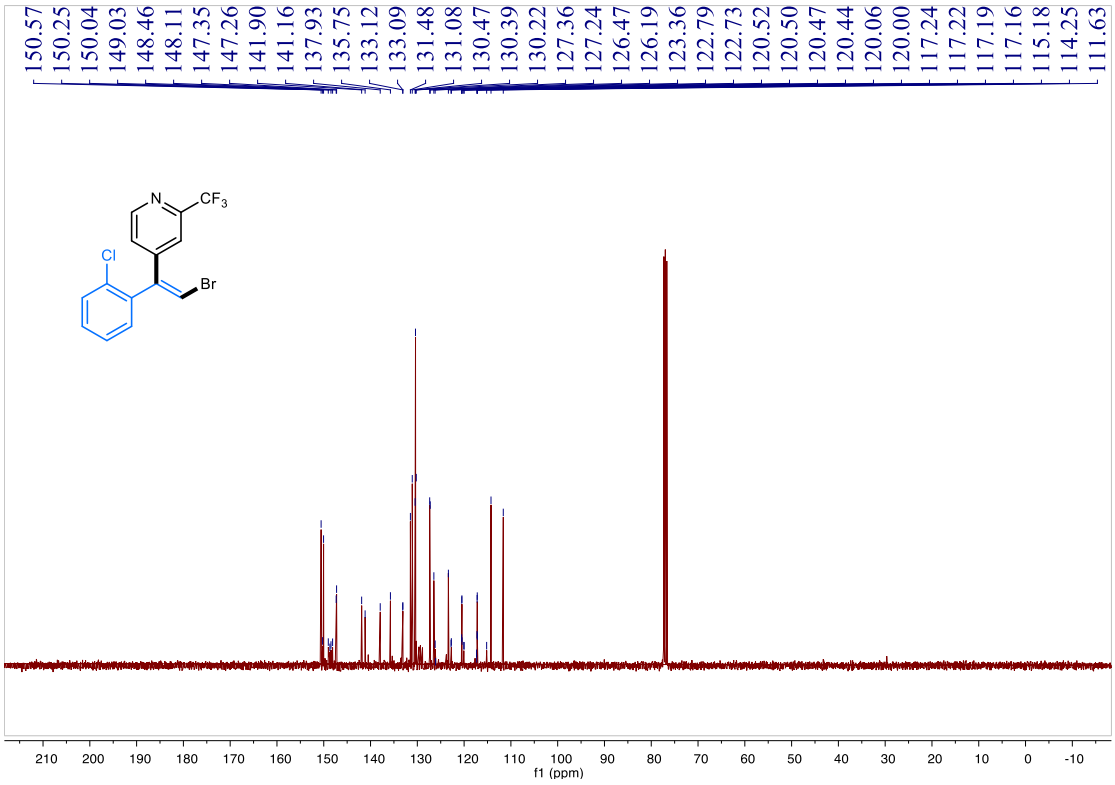
16; ^{1}H NMR (400 MHz, $CDCl_3$)



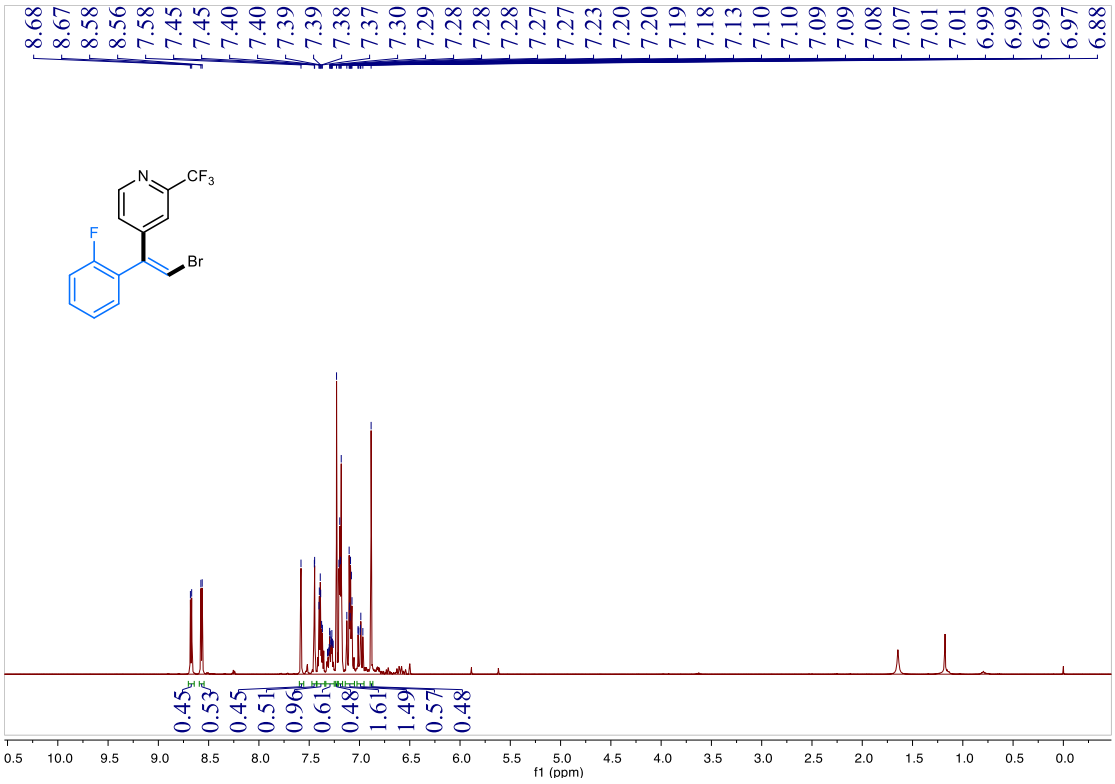
16; ^{19}F NMR (376 MHz, $CDCl_3$)



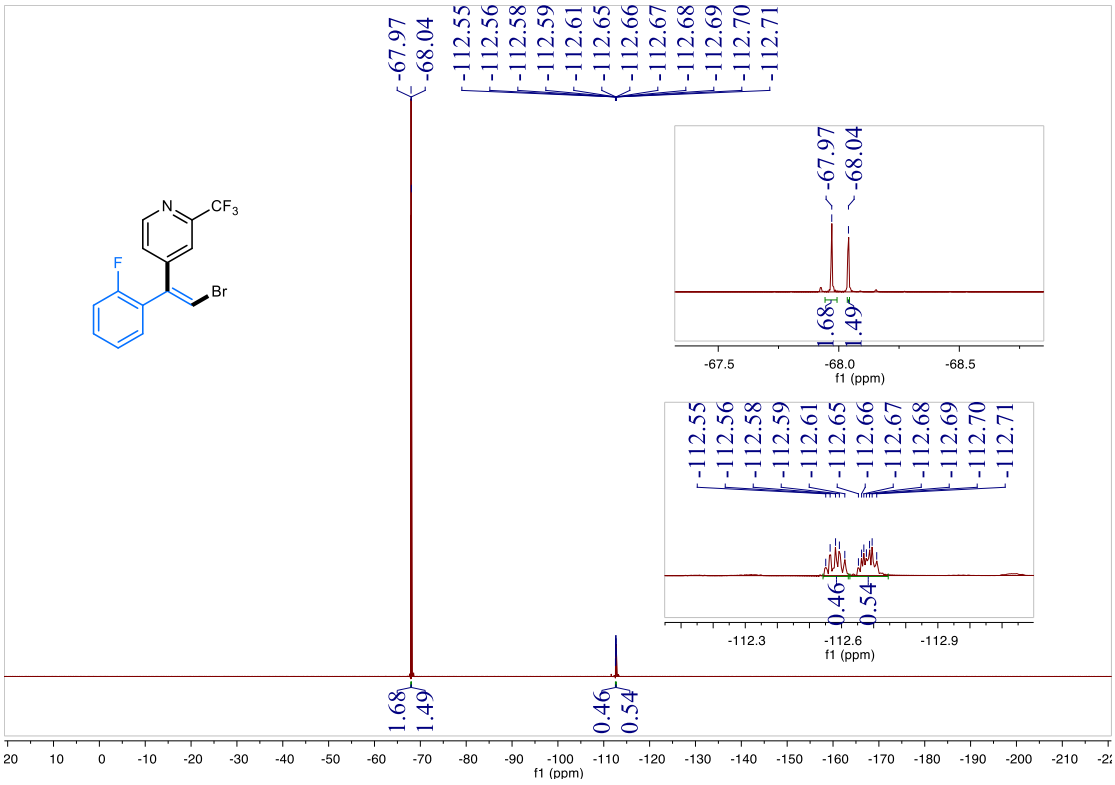
16; ^{13}C NMR (100 MHz, $CDCl_3$)



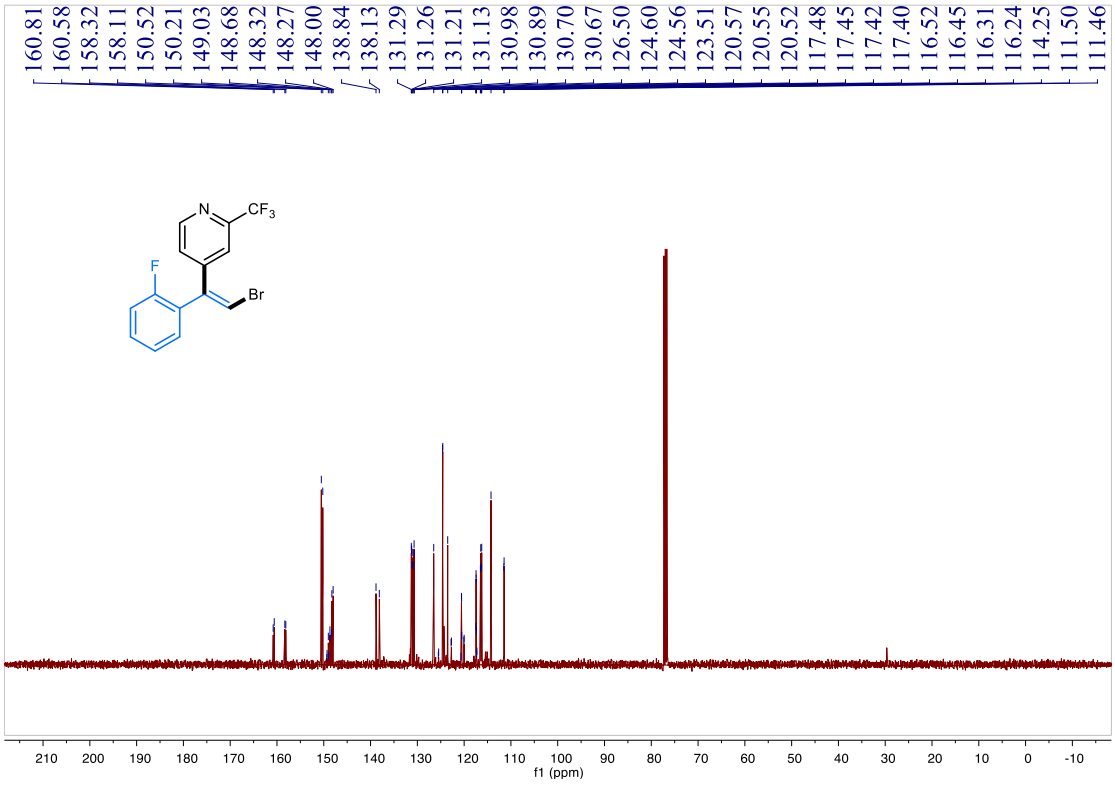
17; ^{1}H NMR (400 MHz, $CDCl_3$)



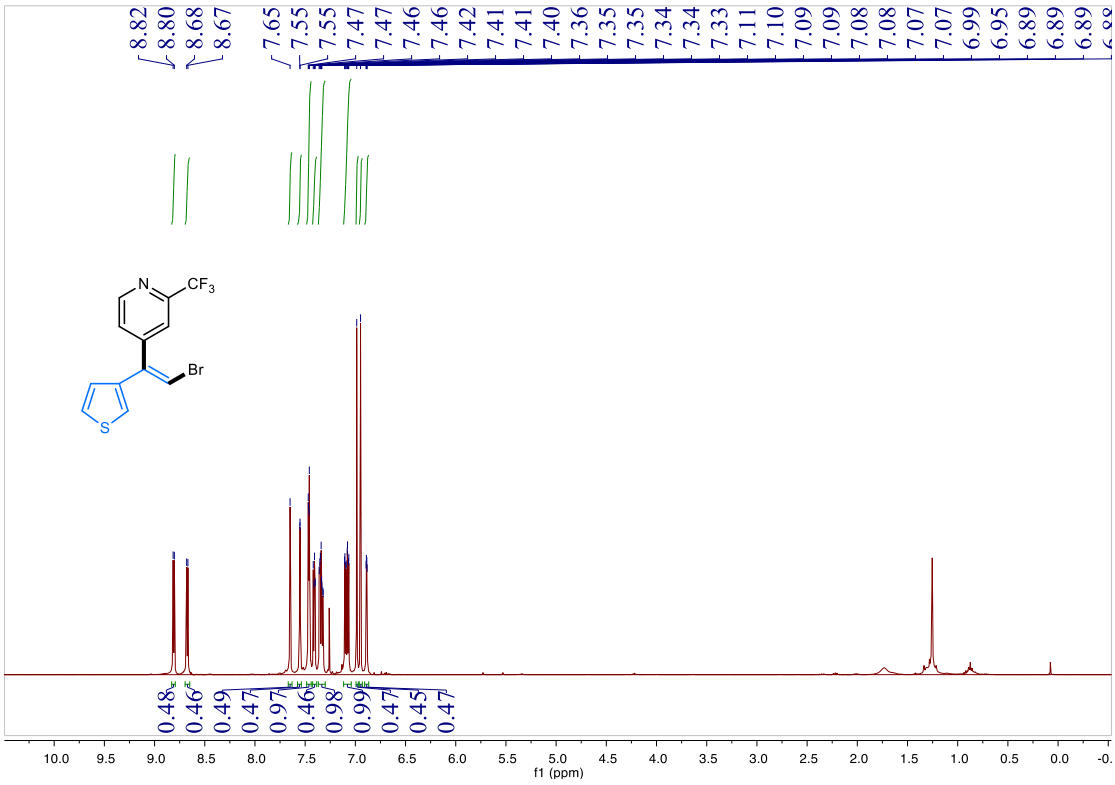
17; ^{19}F NMR (376 MHz, $CDCl_3$)



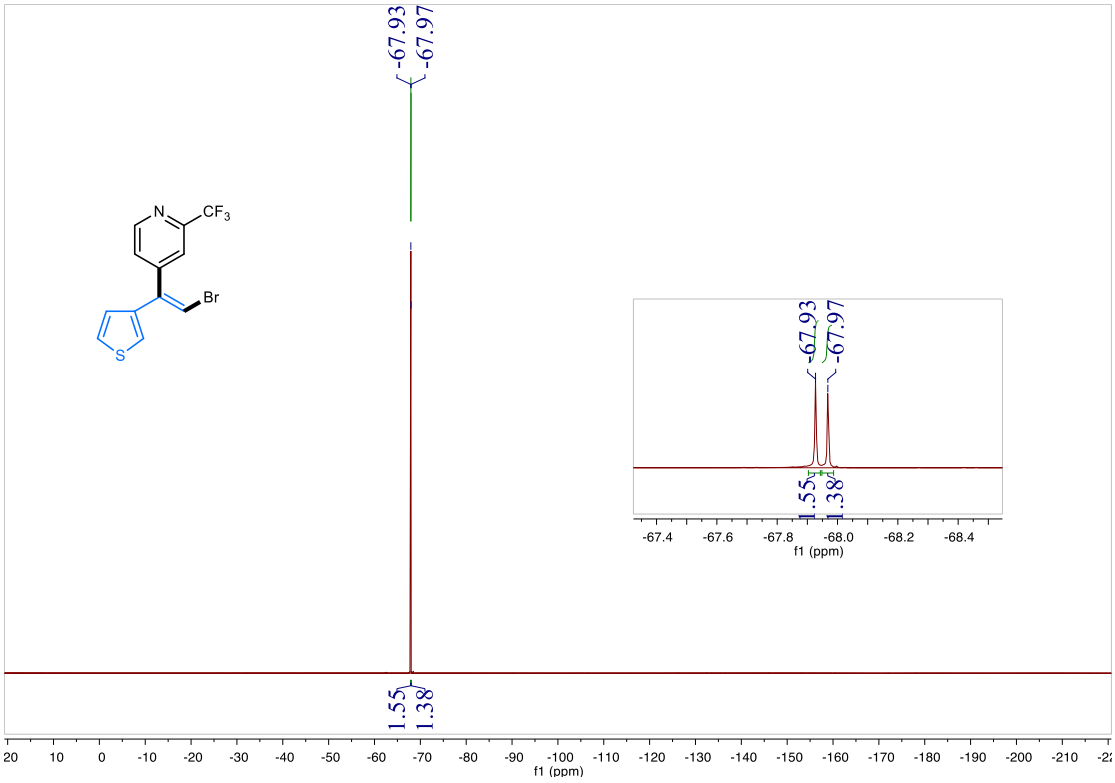
17; ^{13}C NMR (100 MHz, $CDCl_3$)



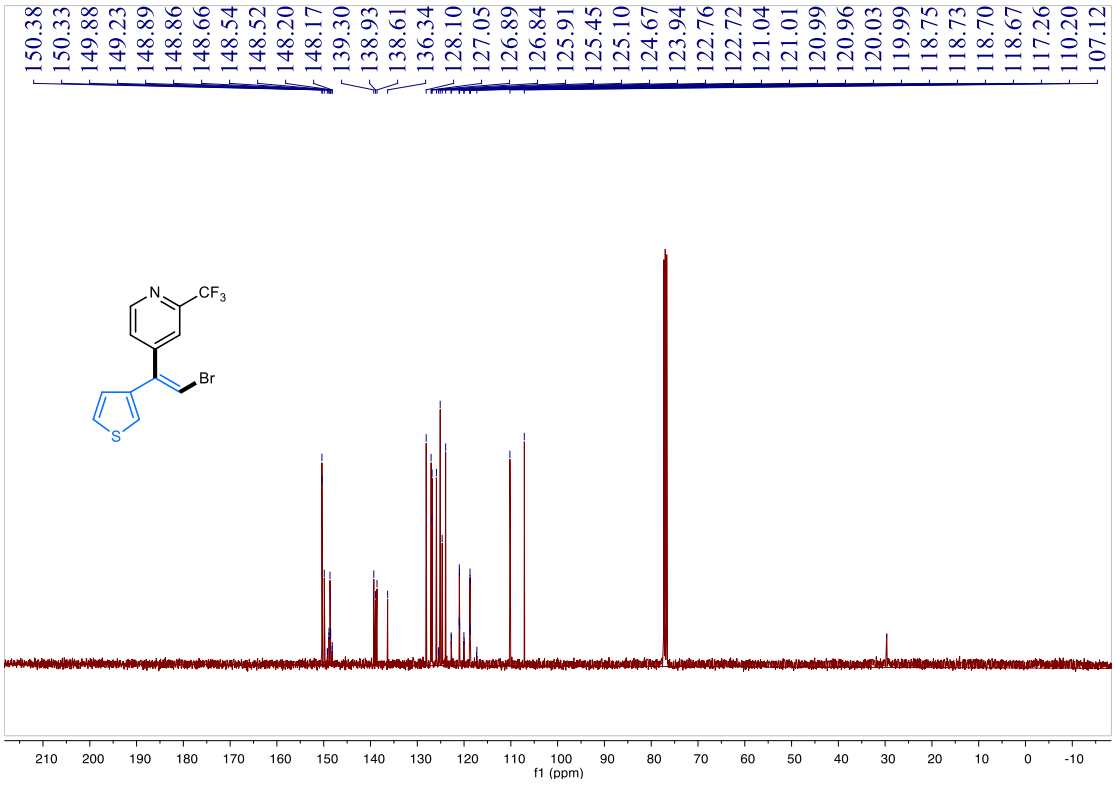
18; ^{1}H NMR (400 MHz, $CDCl_3$)



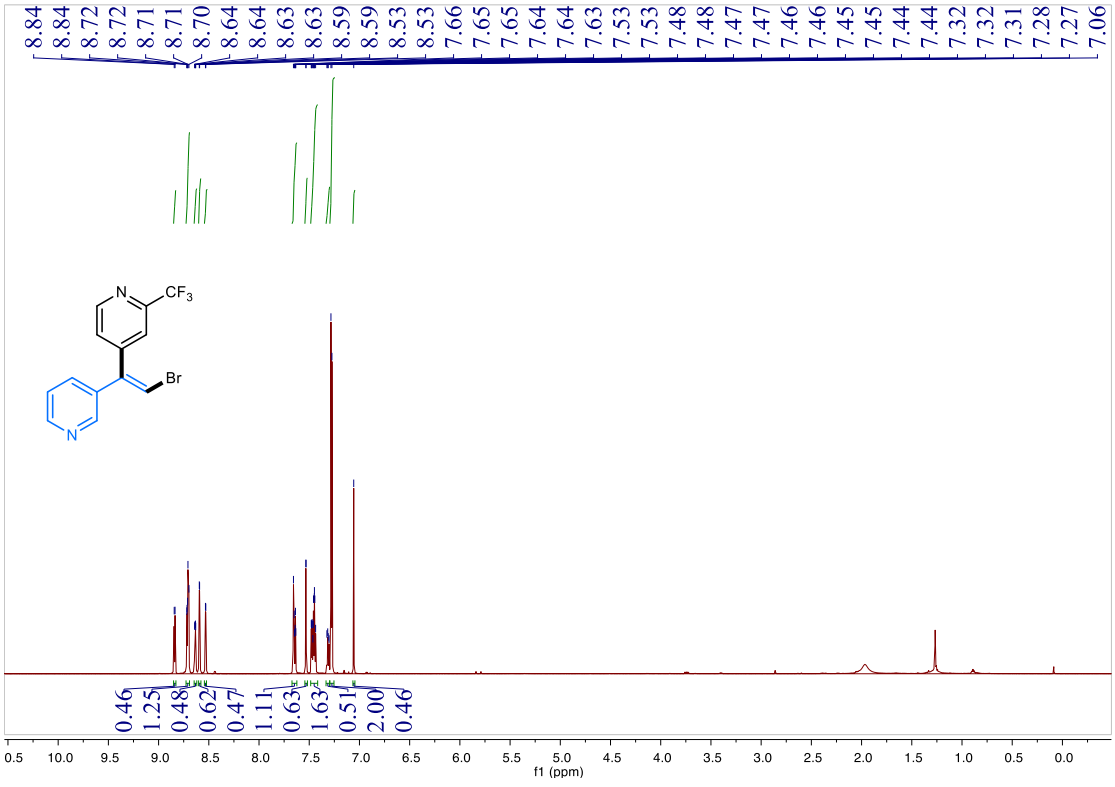
18; ^{19}F NMR (376 MHz, $CDCl_3$)



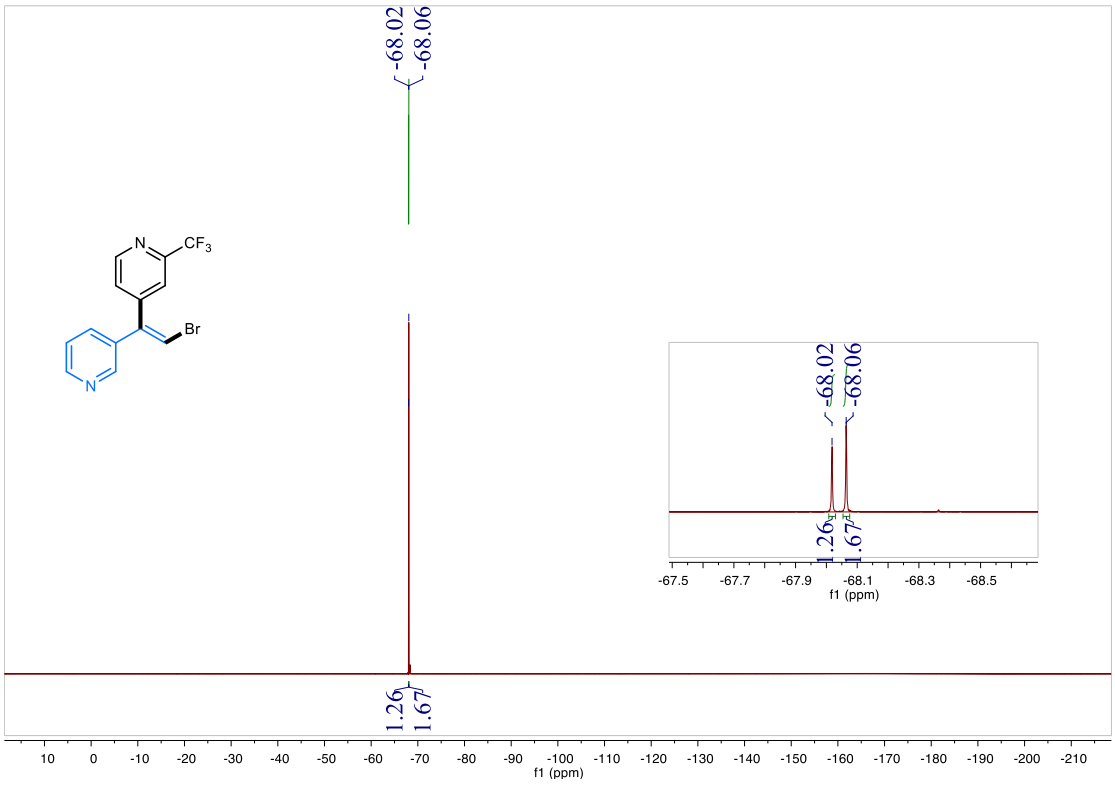
18; ^{13}C NMR (100 MHz, $CDCl_3$)



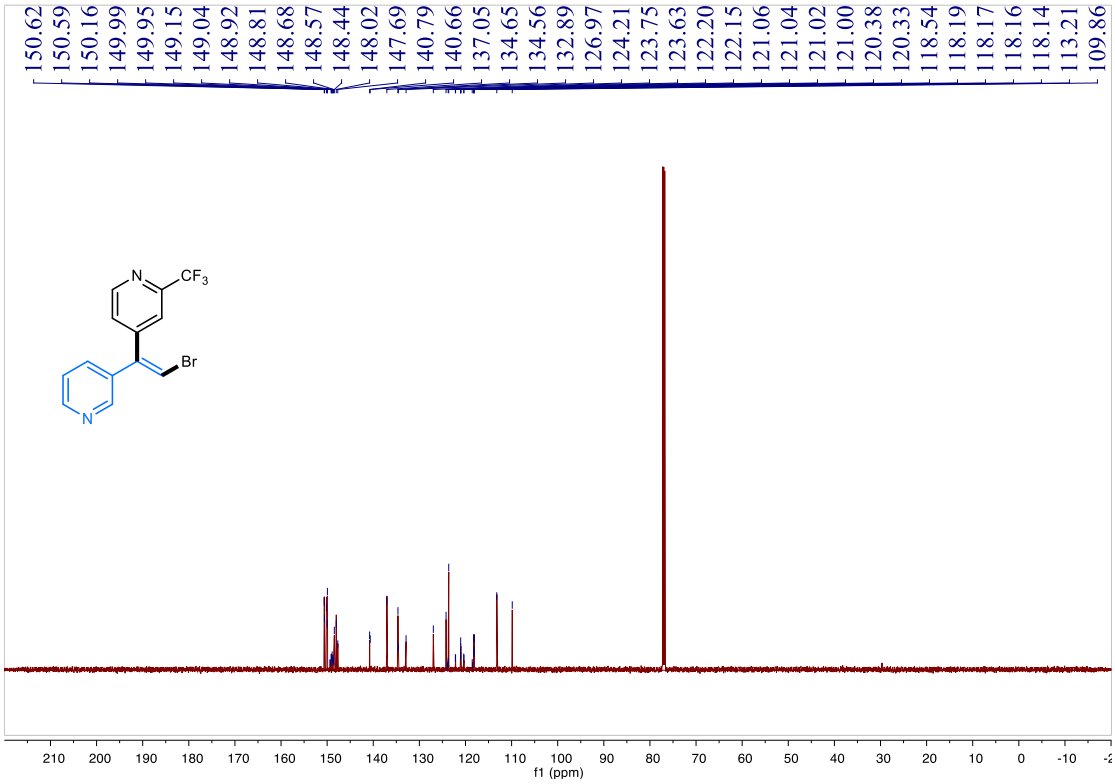
19; ^{1}H NMR (600 MHz, $CDCl_3$)



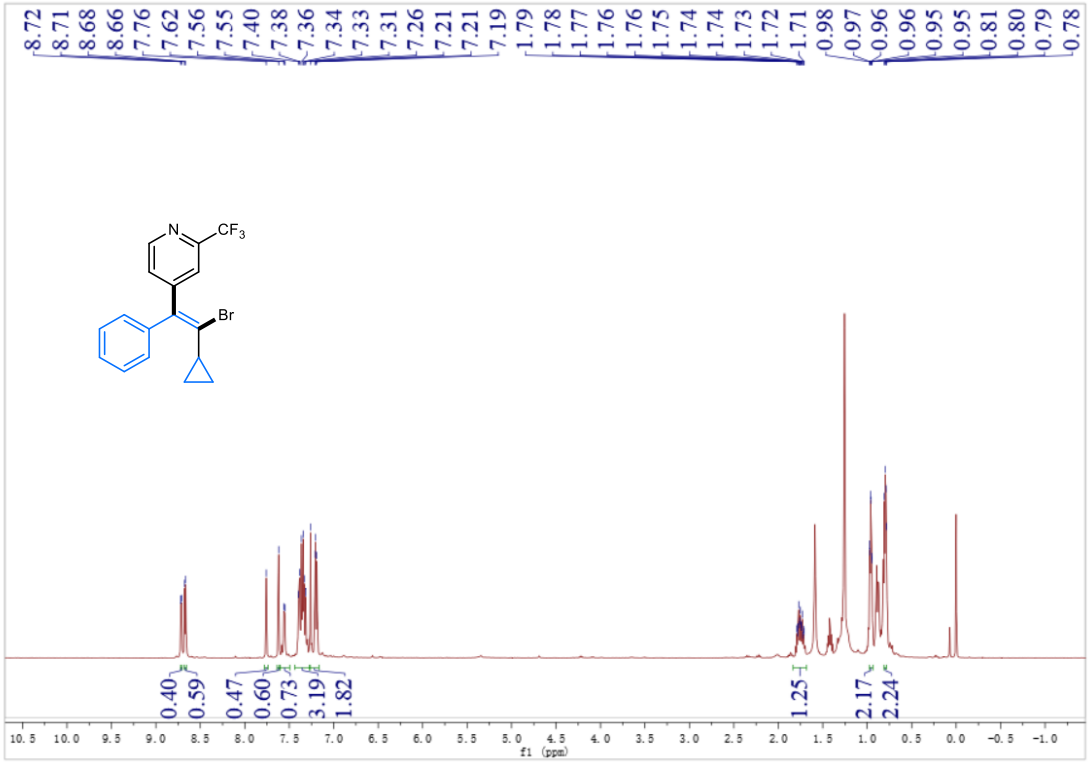
19; ^{19}F NMR (575 MHz, $CDCl_3$)



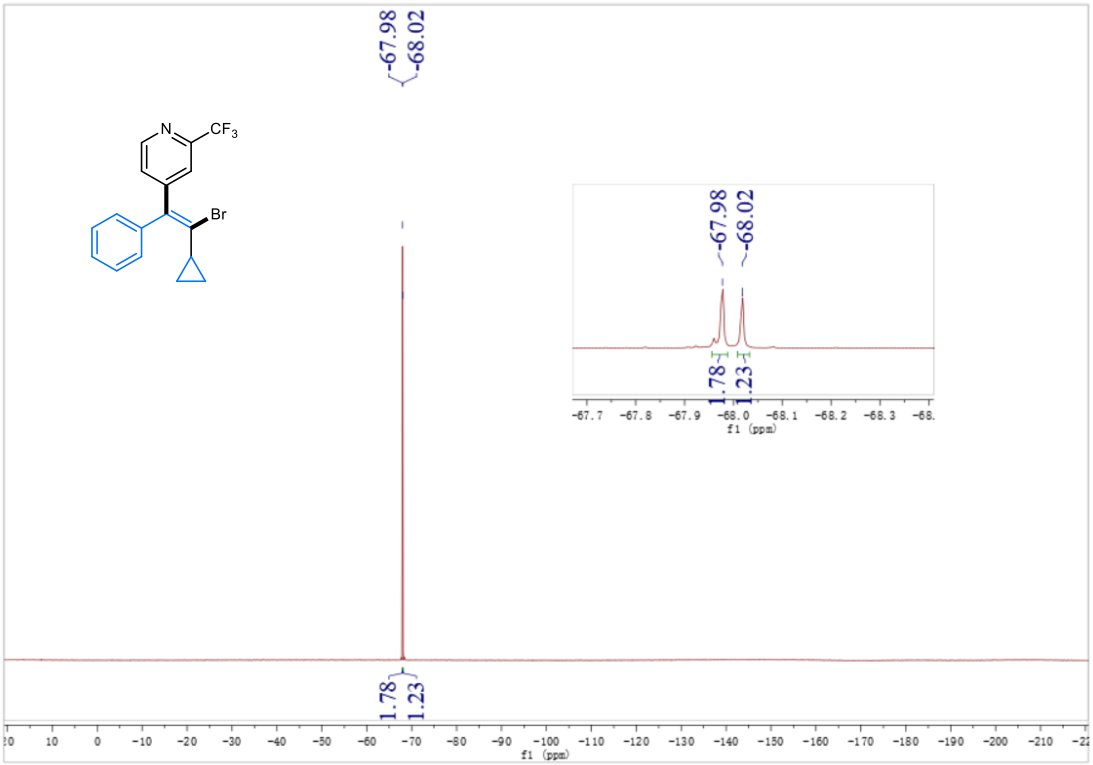
19; ^{13}C NMR (150 MHz, $CDCl_3$)



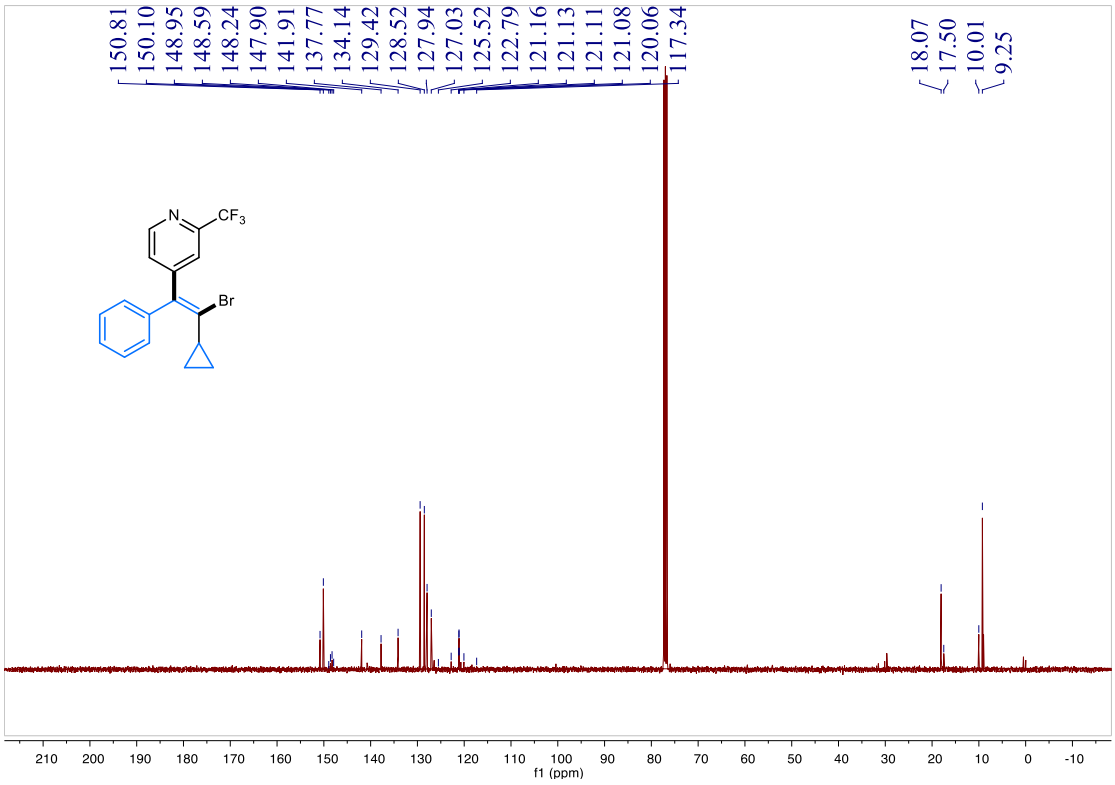
20; ^{1}H NMR (400 MHz, $CDCl_3$)



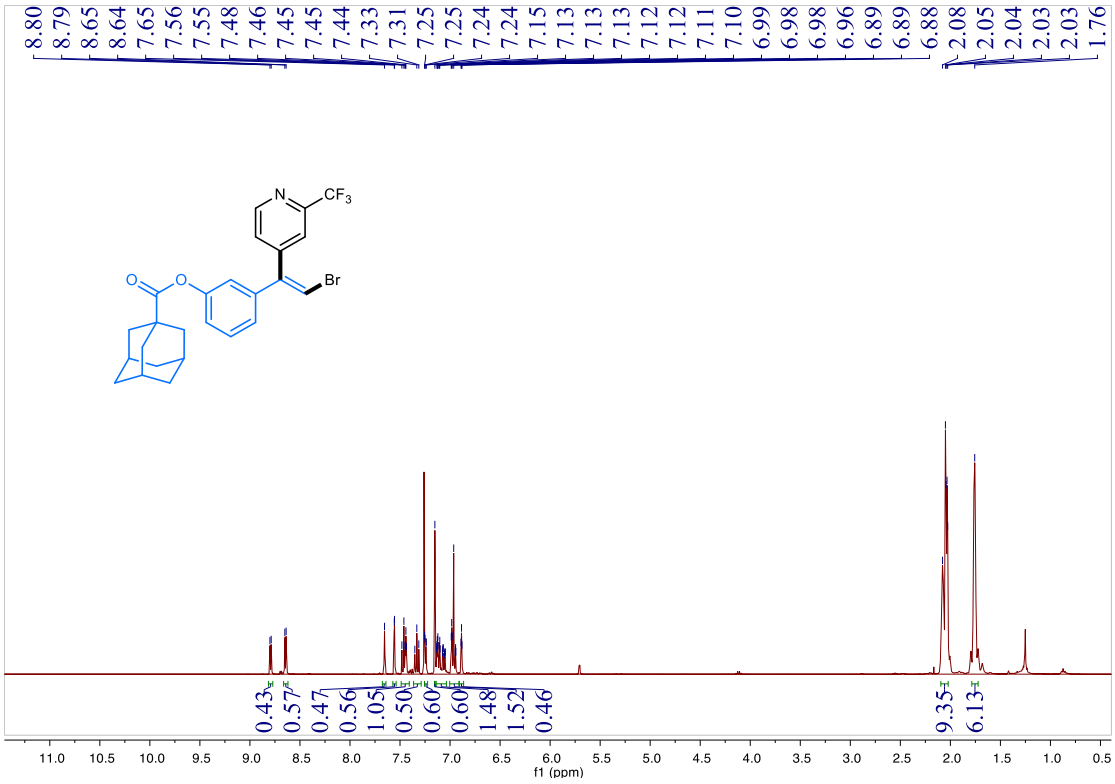
20; ^{19}F NMR (376 MHz, $CDCl_3$)



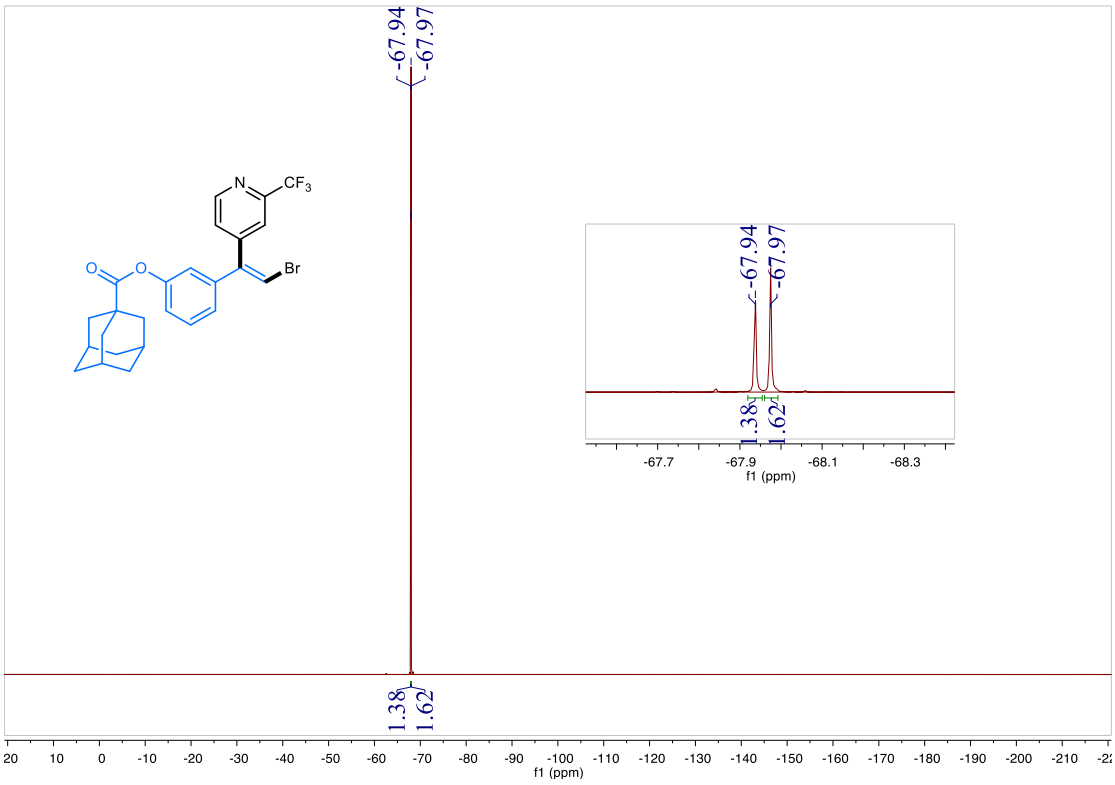
20; ^{13}C NMR (100 MHz, $CDCl_3$)



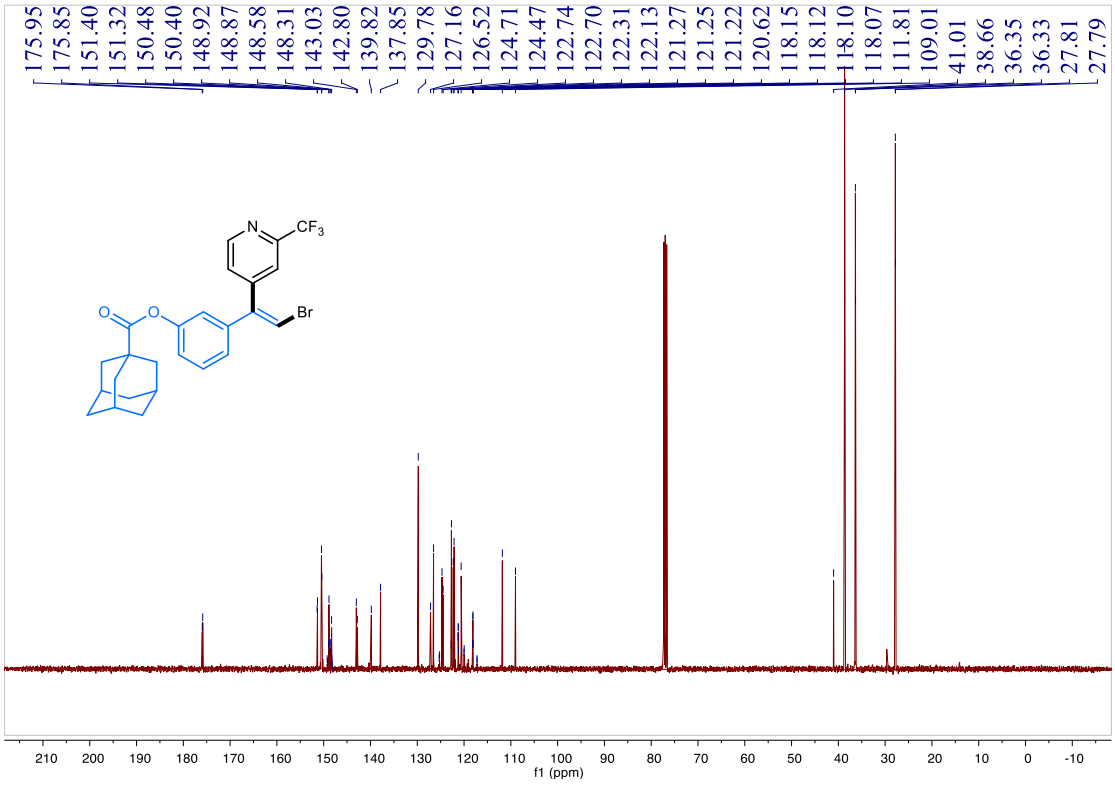
21; ^{1}H NMR (400 MHz, $CDCl_3$)



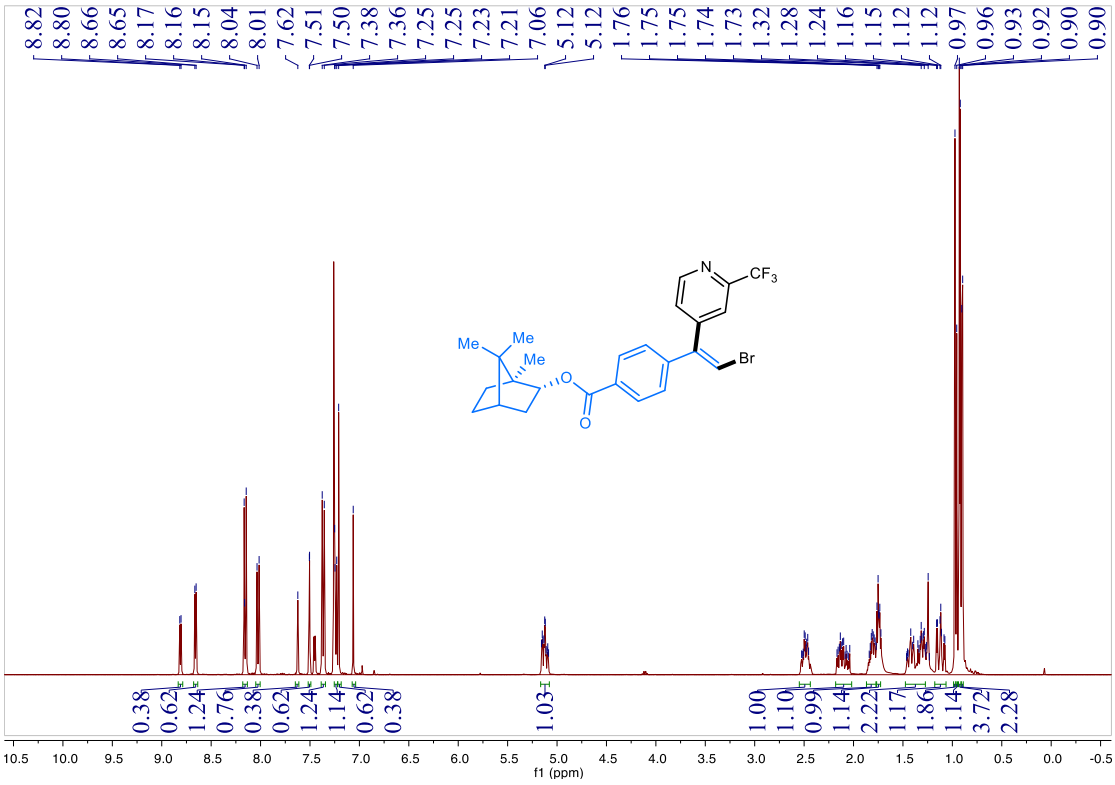
21; ^{19}F NMR (376 MHz, $CDCl_3$)



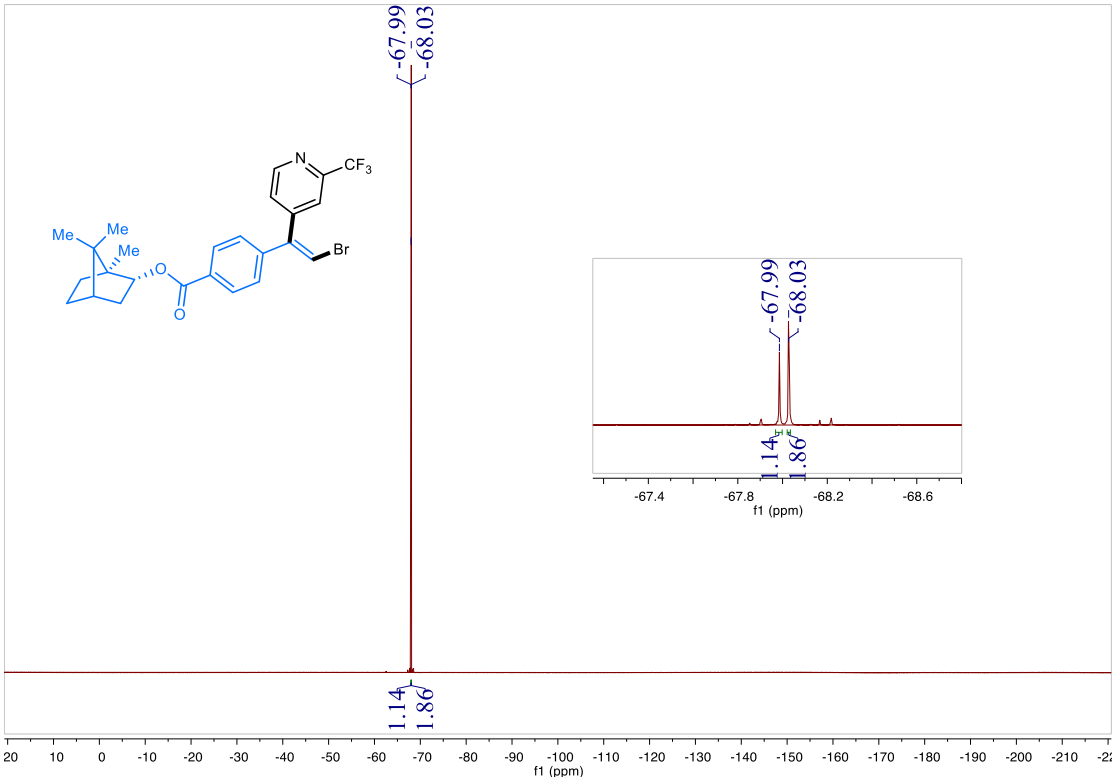
21; ^{13}C NMR (100 MHz, $CDCl_3$)



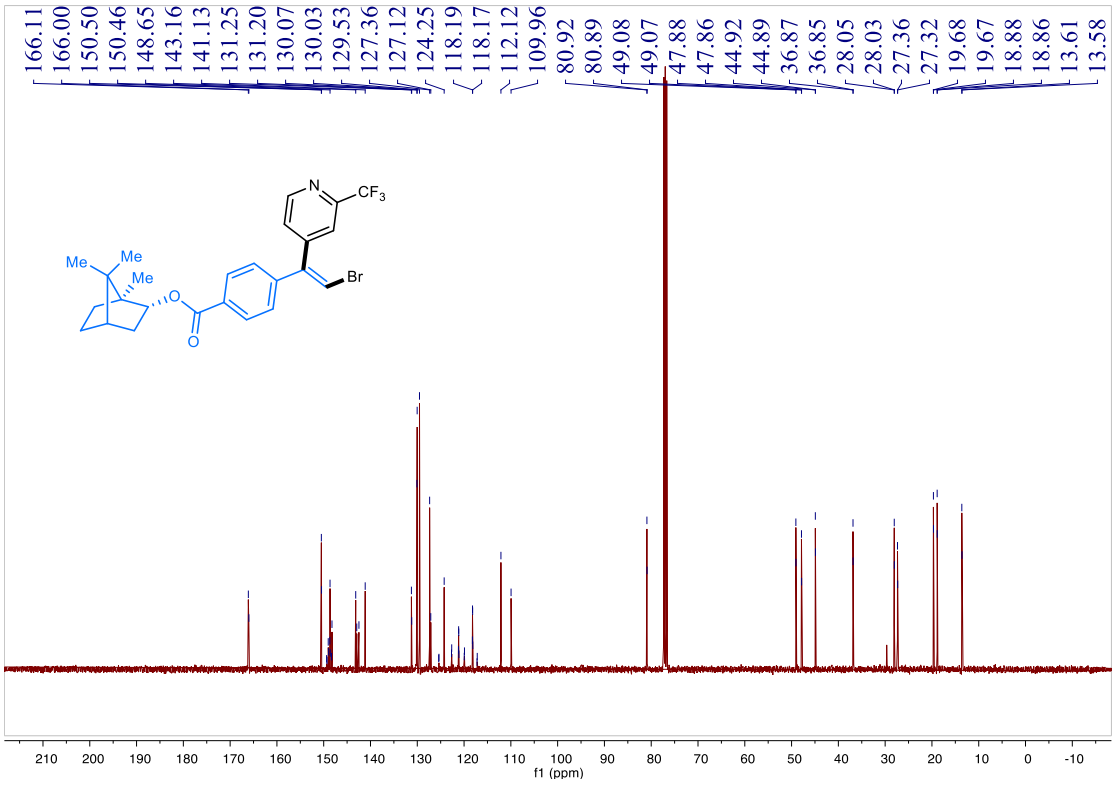
22; ^{1}H NMR (400 MHz, $CDCl_3$)



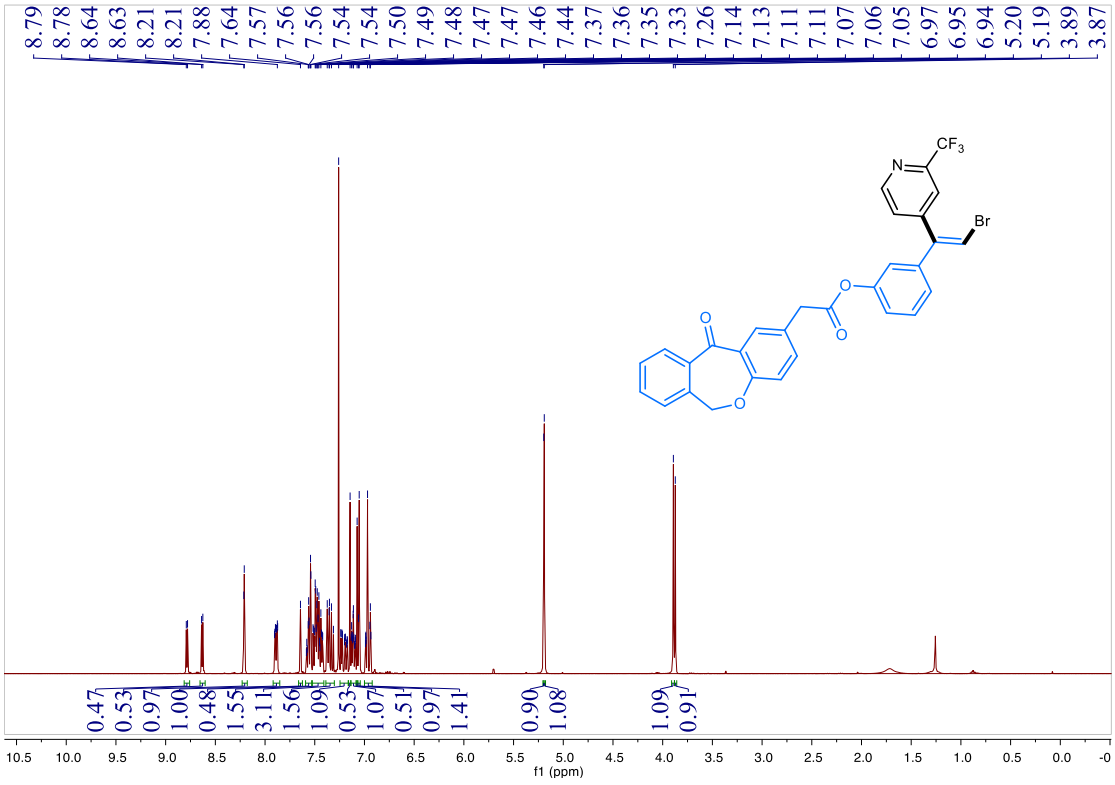
22; ^{19}F NMR (376 MHz, $CDCl_3$)



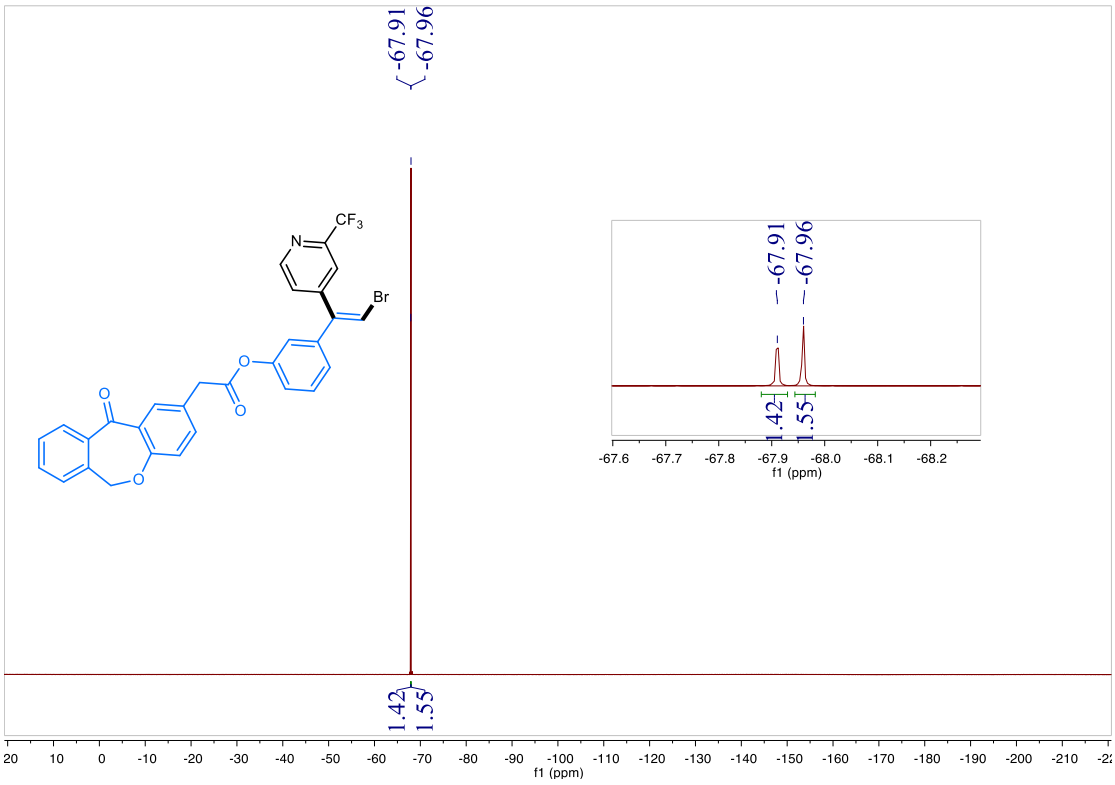
22; ^{13}C NMR (100 MHz, $CDCl_3$)



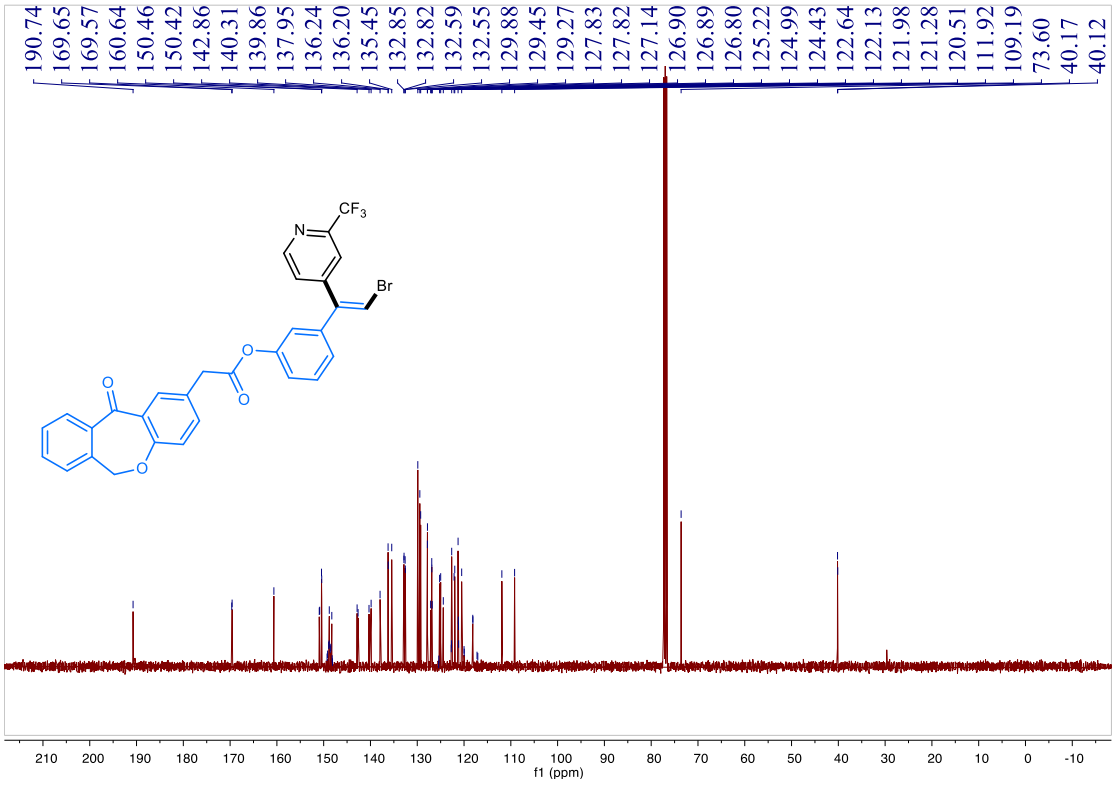
23; ^{1}H NMR (400 MHz, $CDCl_3$)



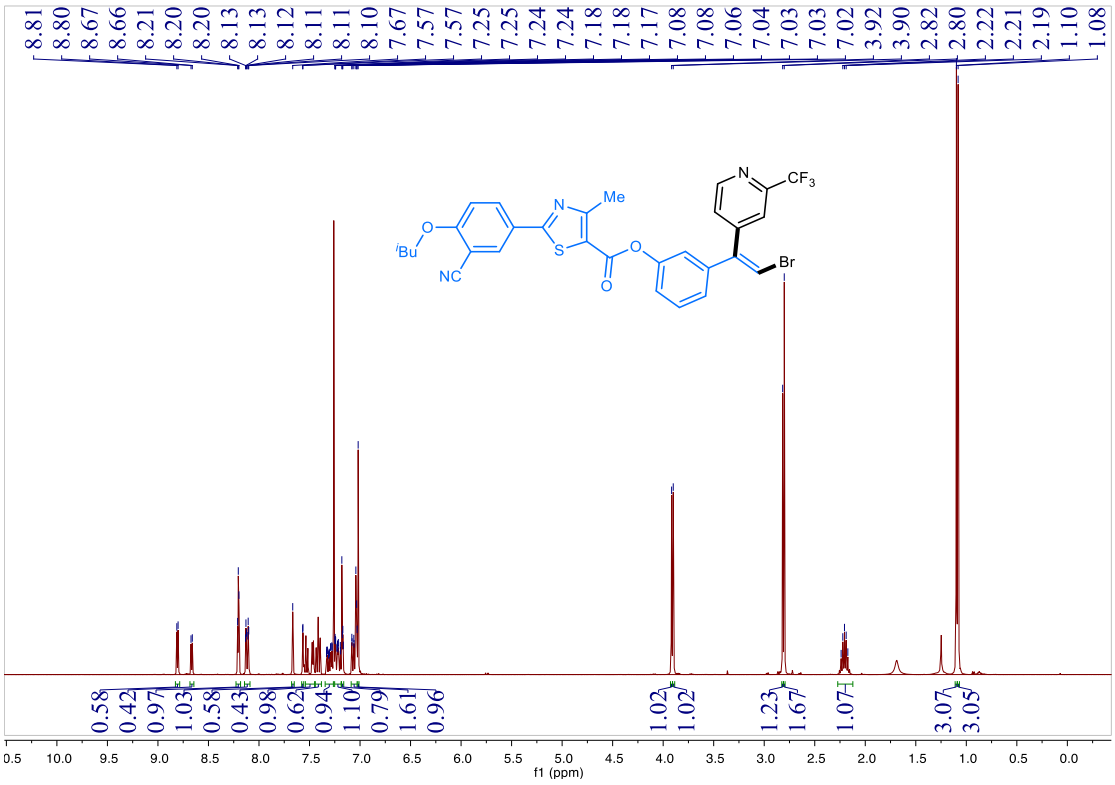
23; ^{19}F NMR (376 MHz, $CDCl_3$)



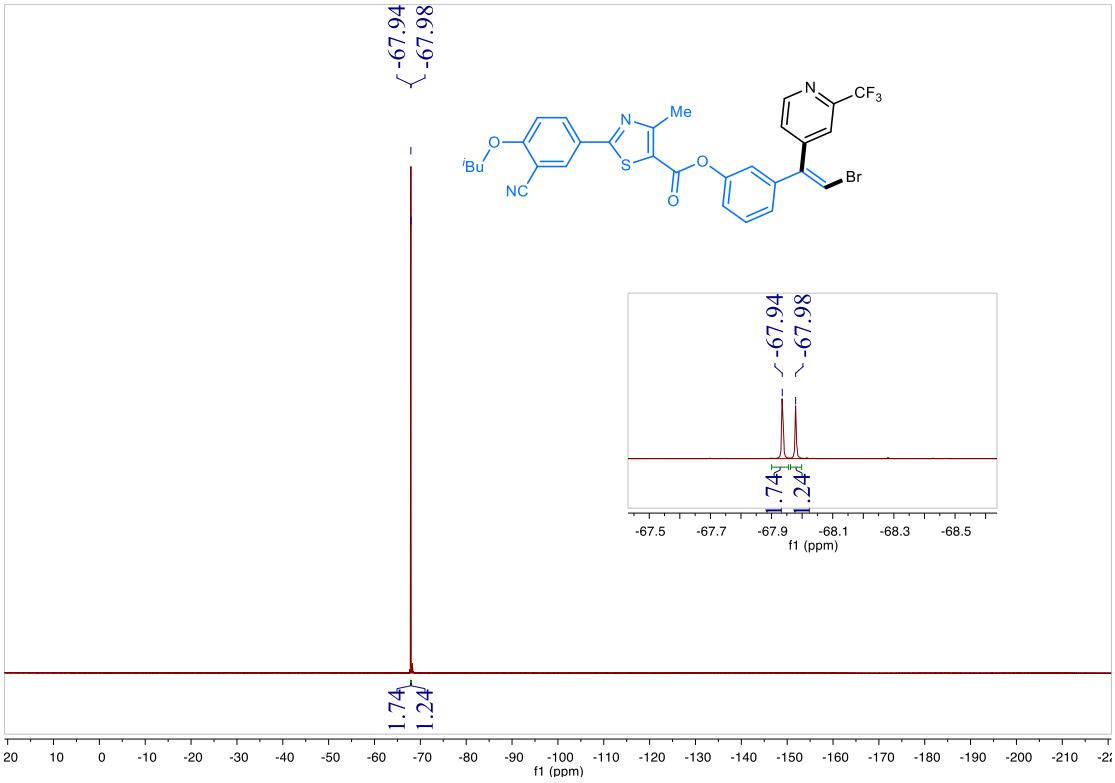
23; ^{13}C NMR (100 MHz, $CDCl_3$)



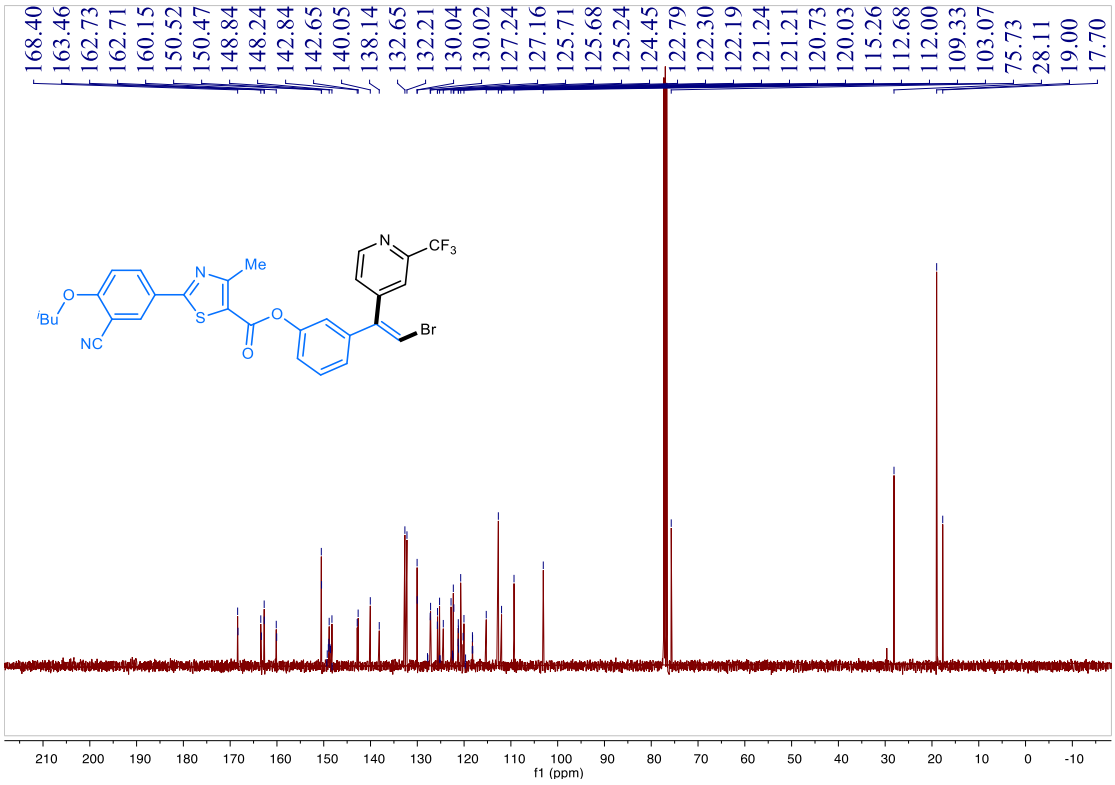
24; ^{1}H NMR (400 MHz, $CDCl_3$)



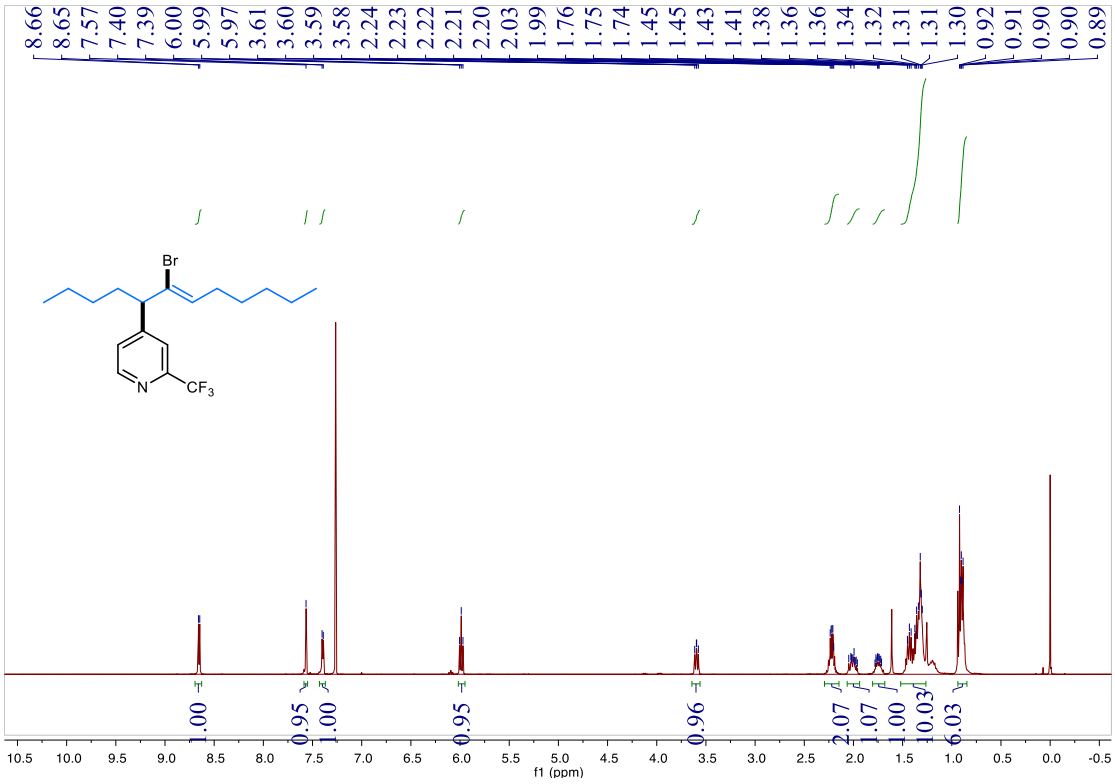
24; ^{19}F NMR (376 MHz, $CDCl_3$)



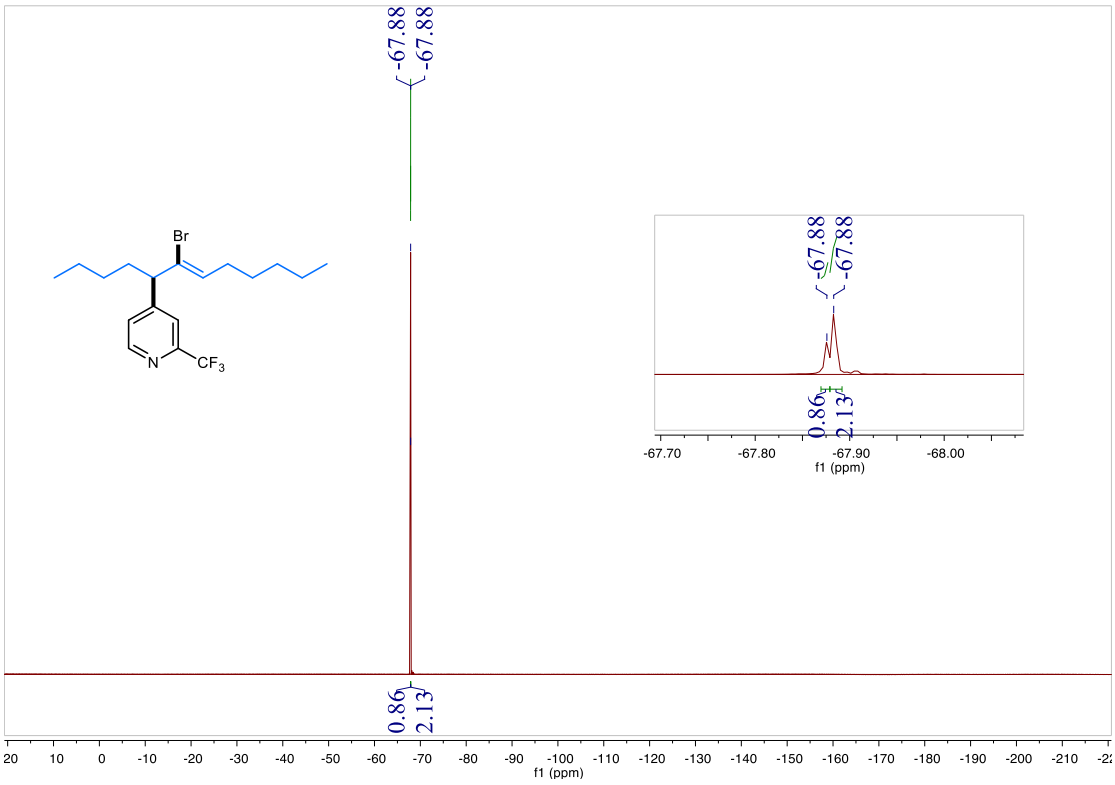
24; ^{13}C NMR (100 MHz, $CDCl_3$)



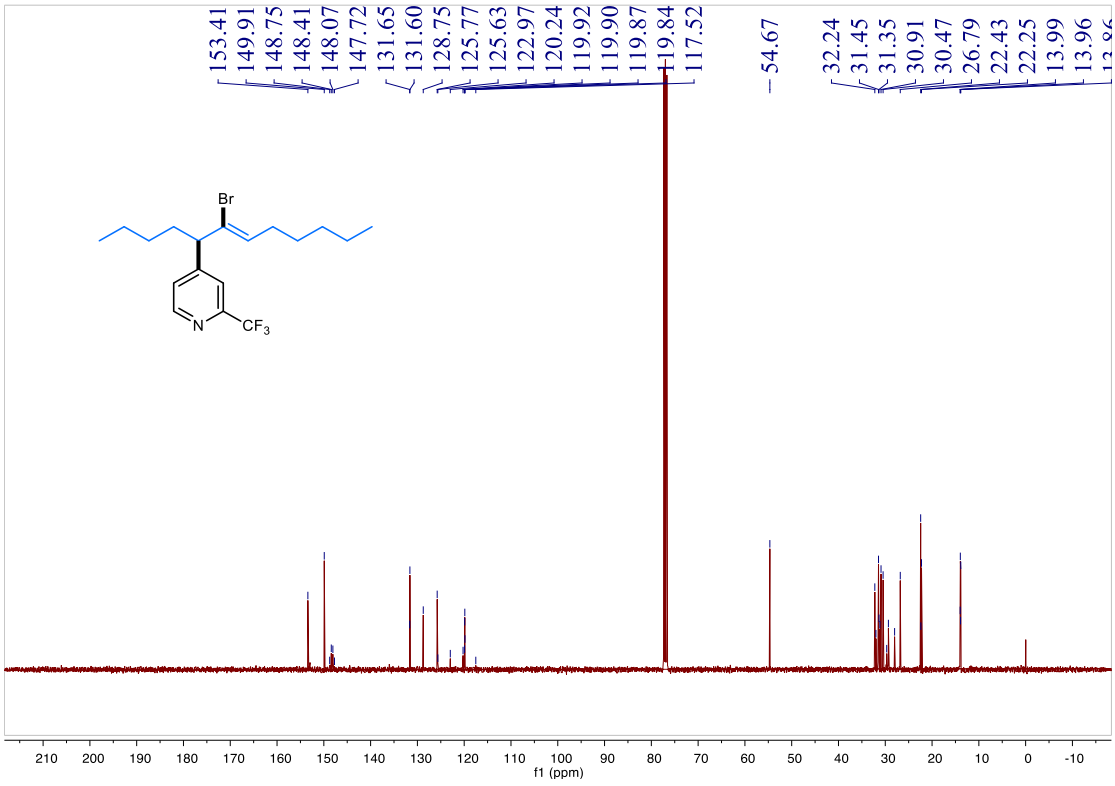
25; ^{1}H NMR (400 MHz, $CDCl_3$)



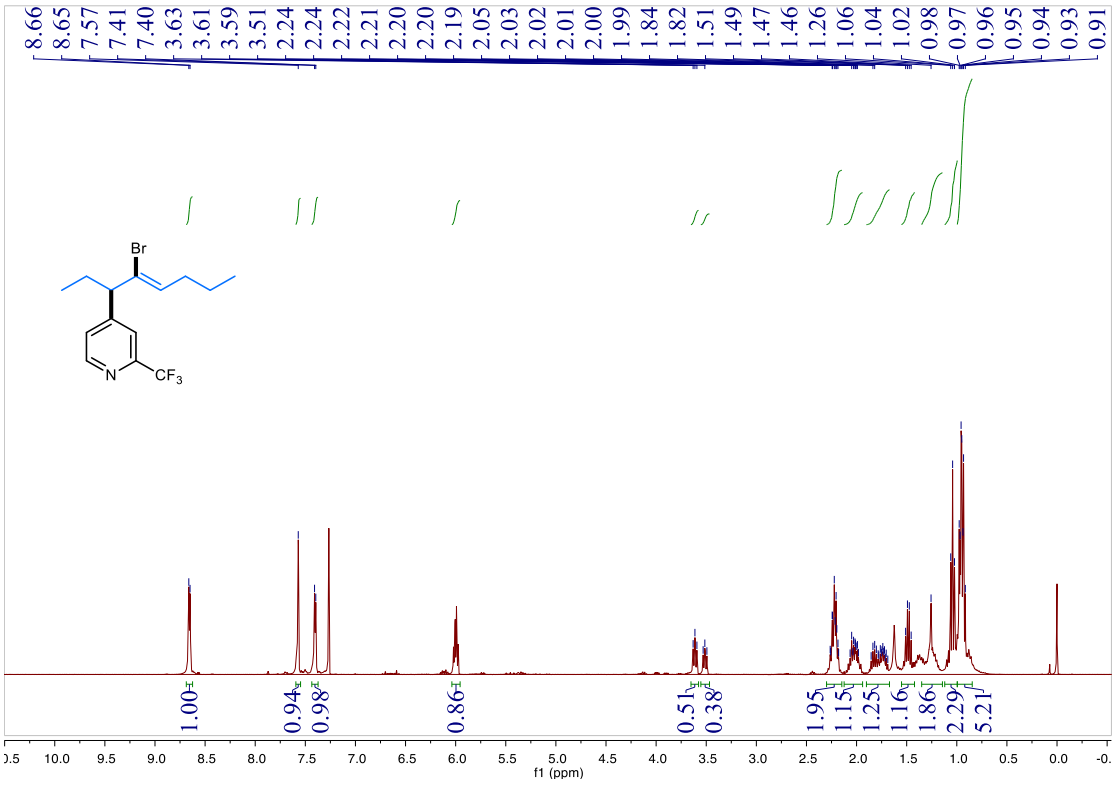
25; ^{19}F NMR (376 MHz, $CDCl_3$)



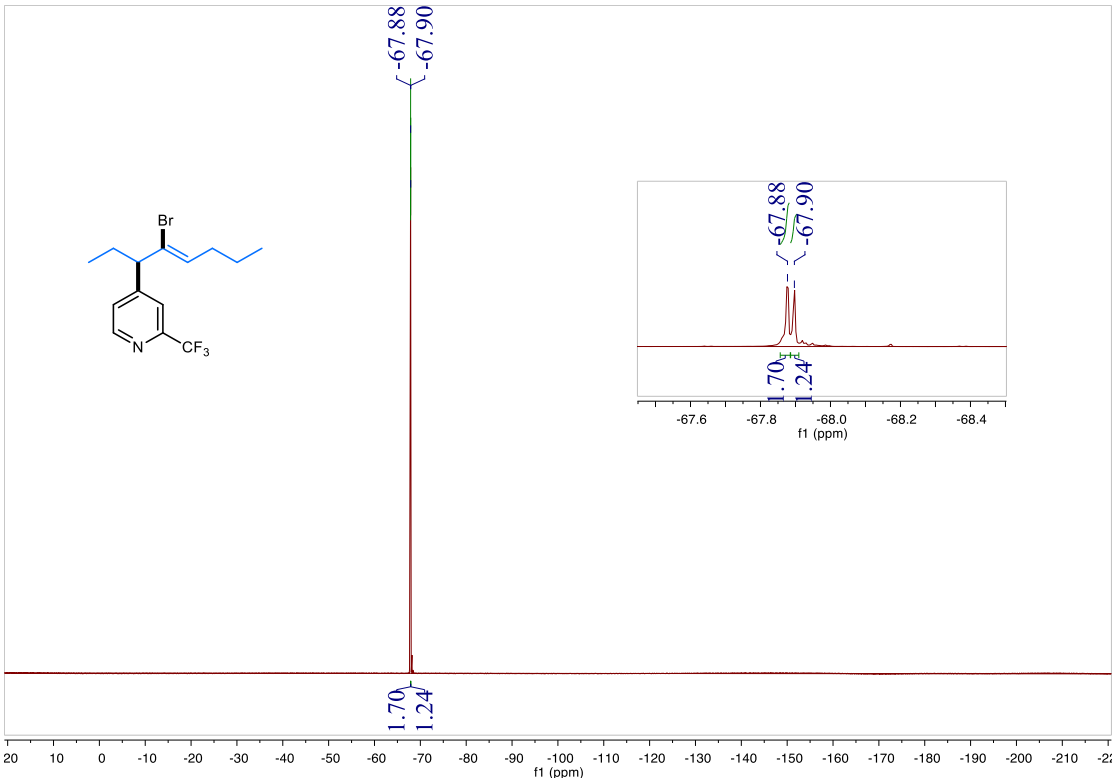
25; ^{13}C NMR (100 MHz, $CDCl_3$)



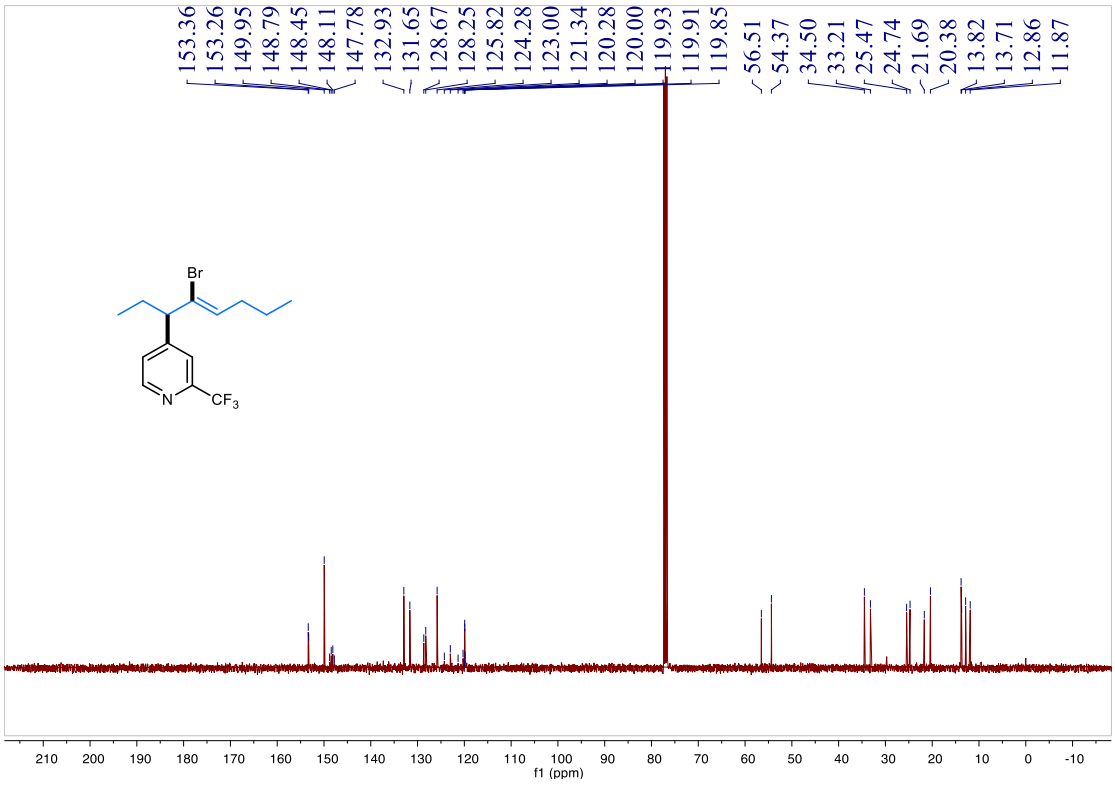
26; ^{1}H NMR (400 MHz, $CDCl_3$)



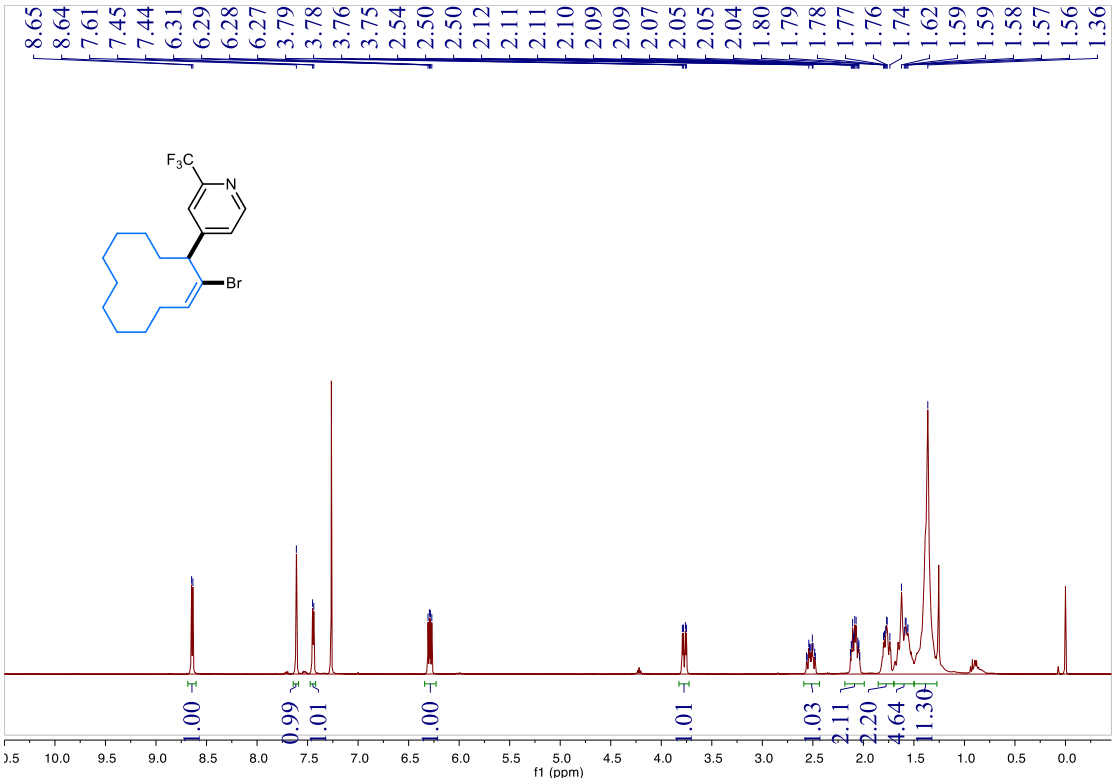
26; ^{19}F NMR (376 MHz, $CDCl_3$)



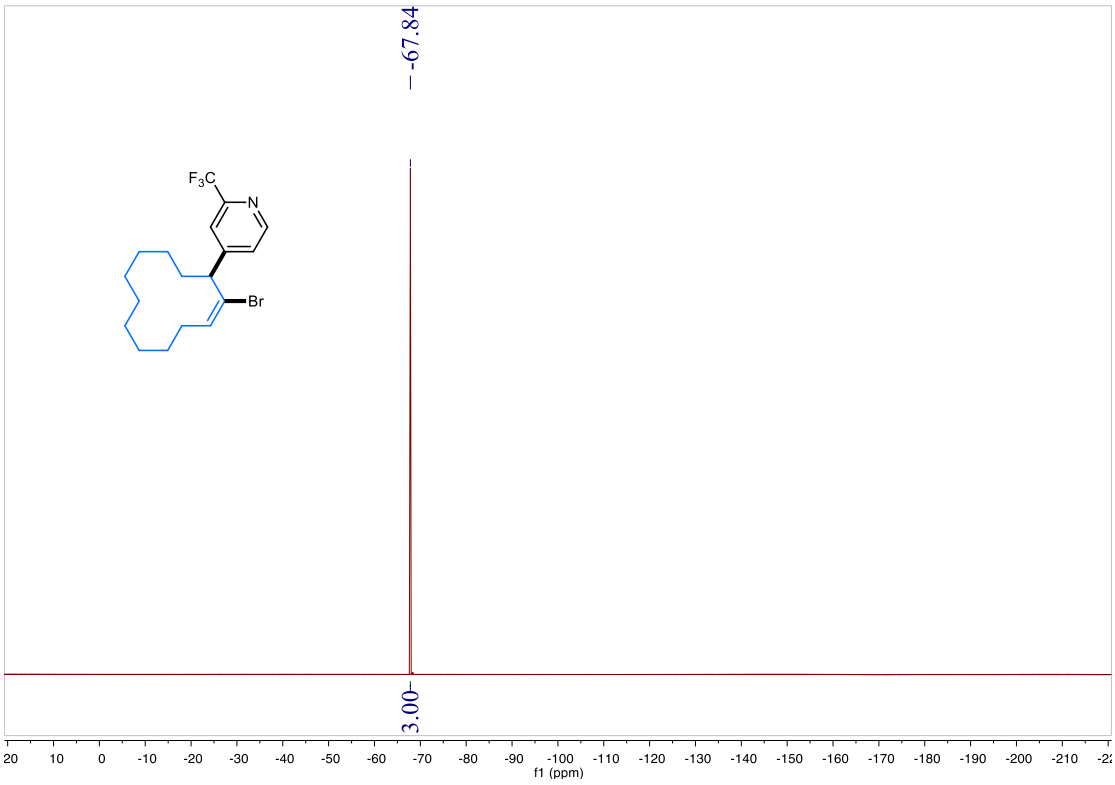
26; ^{13}C NMR (100 MHz, $CDCl_3$)



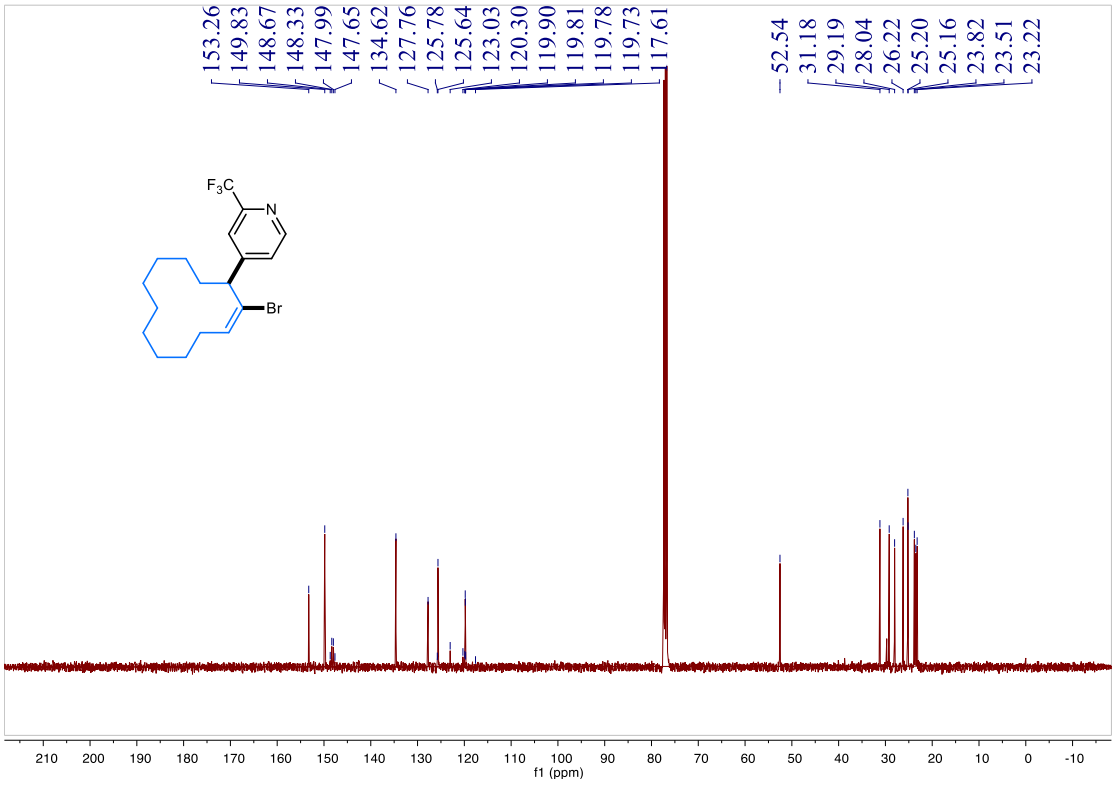
27; ^{1}H NMR (400 MHz, $CDCl_3$)



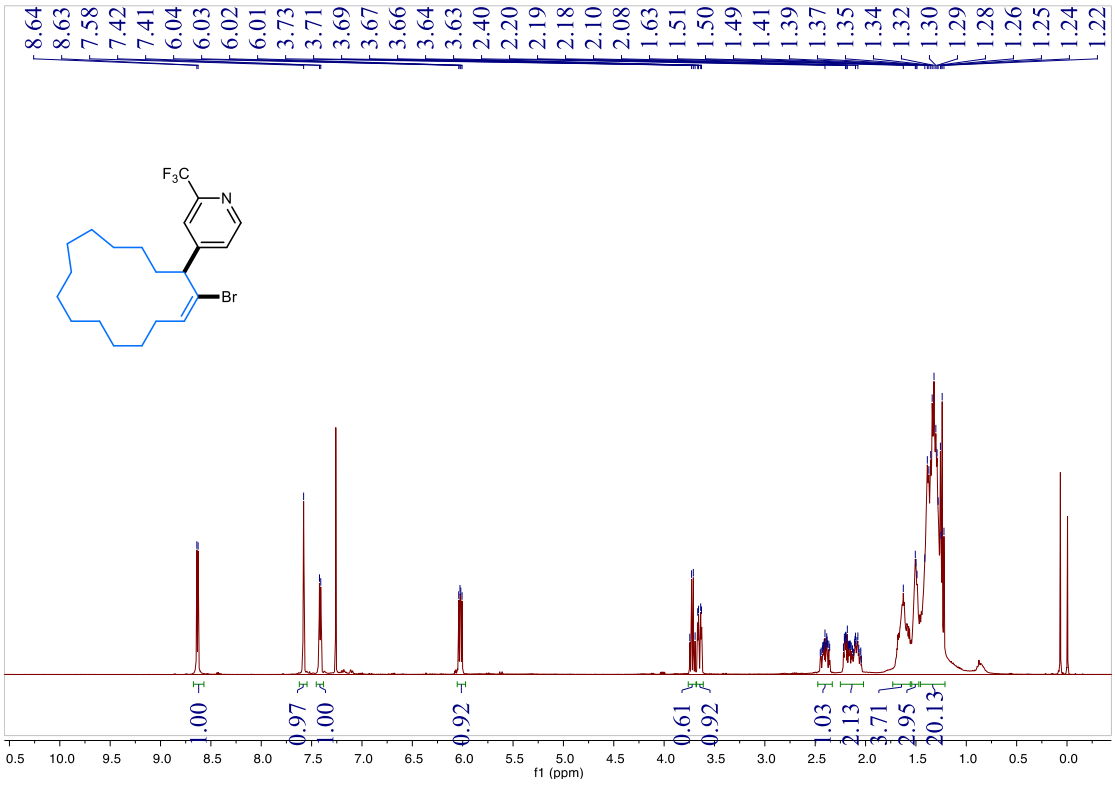
27; ^{19}F NMR (376 MHz, $CDCl_3$)



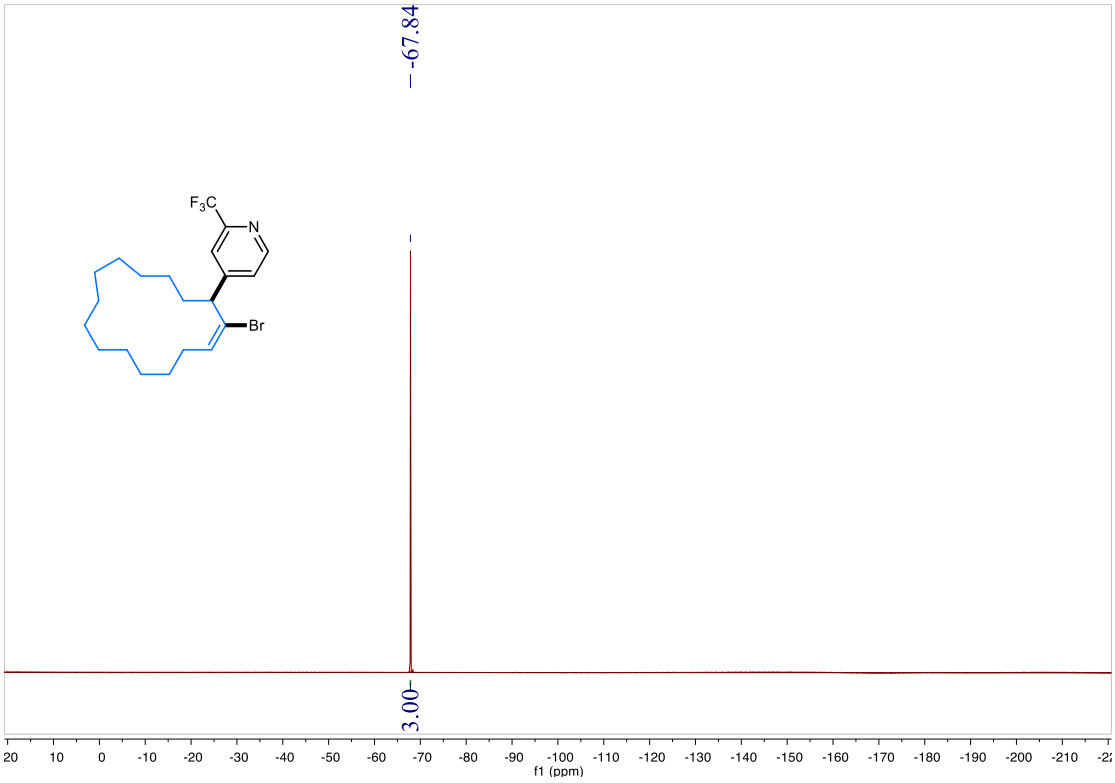
27; ^{13}C NMR (100 MHz, $CDCl_3$)



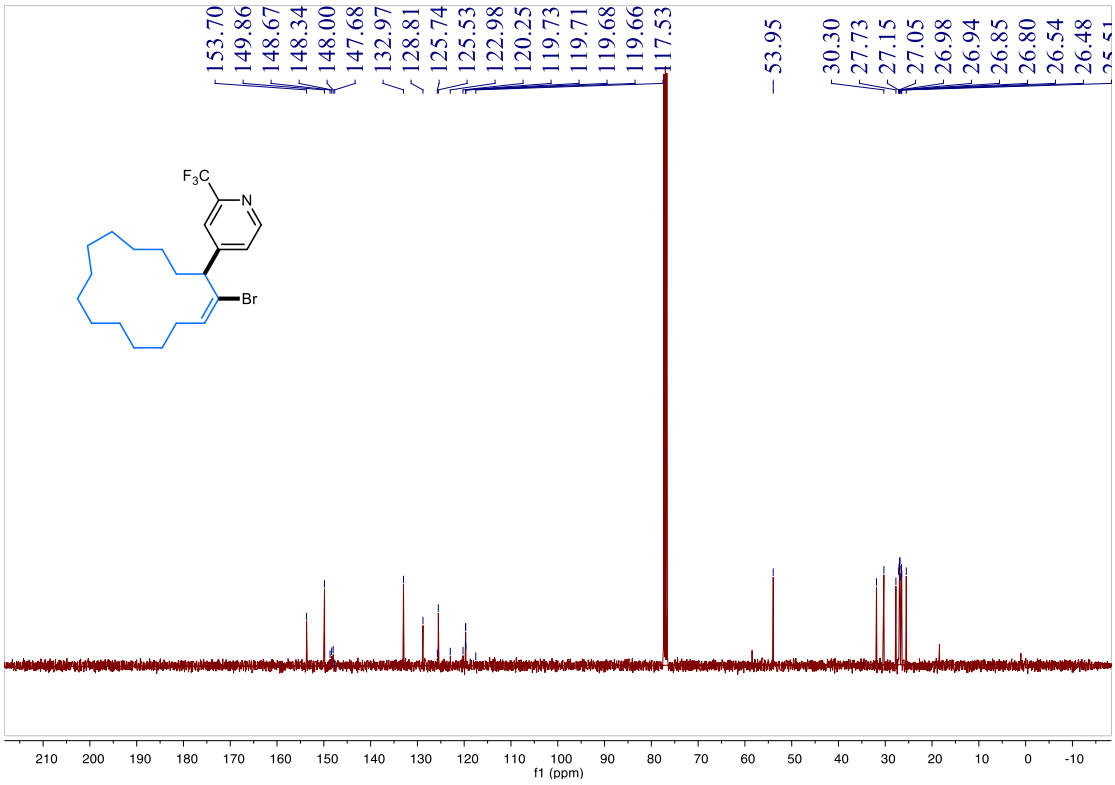
28; ^{1}H NMR (400 MHz, $CDCl_3$)



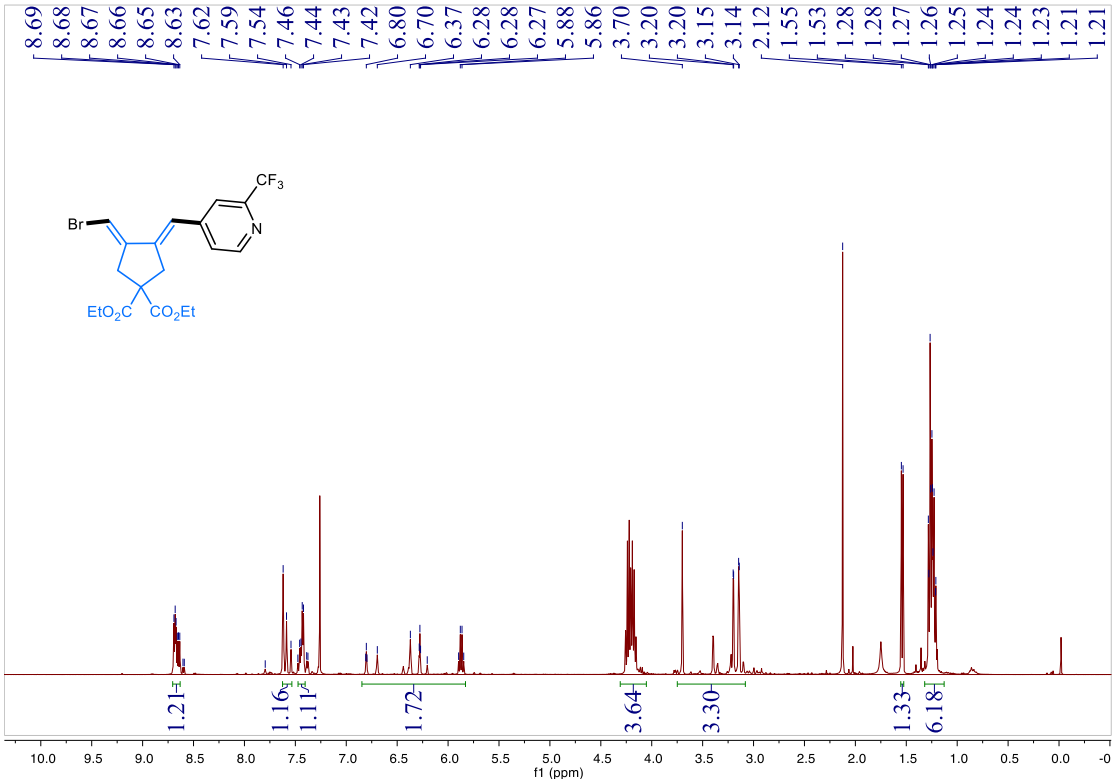
28; ^{19}F NMR (376 MHz, $CDCl_3$)



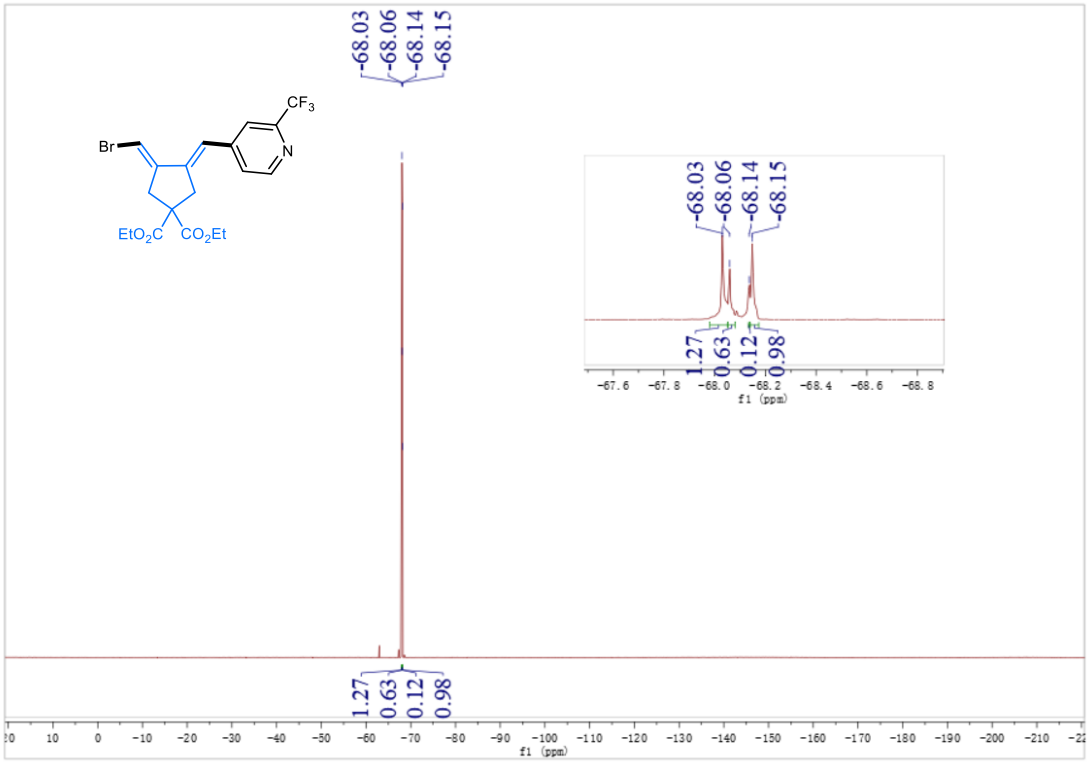
28; ^{13}C NMR (100 MHz, $CDCl_3$)



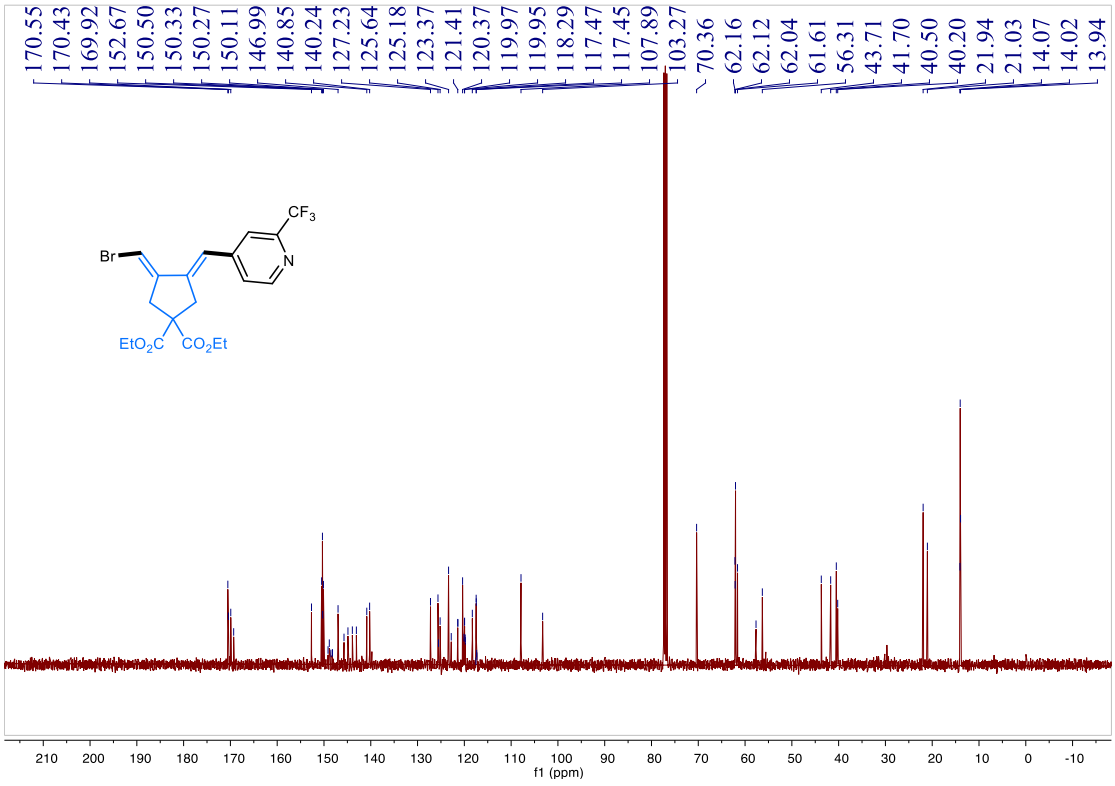
29; ^{1}H NMR (400 MHz, $CDCl_3$)



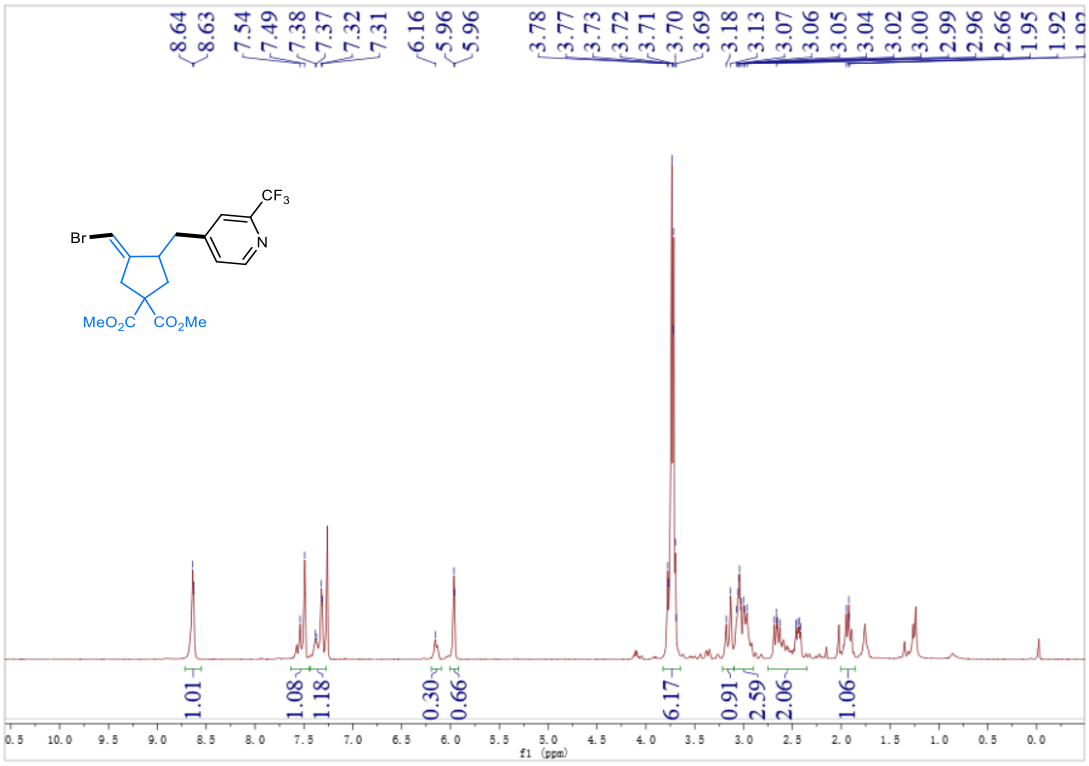
29; ^{19}F NMR (376 MHz, $CDCl_3$)



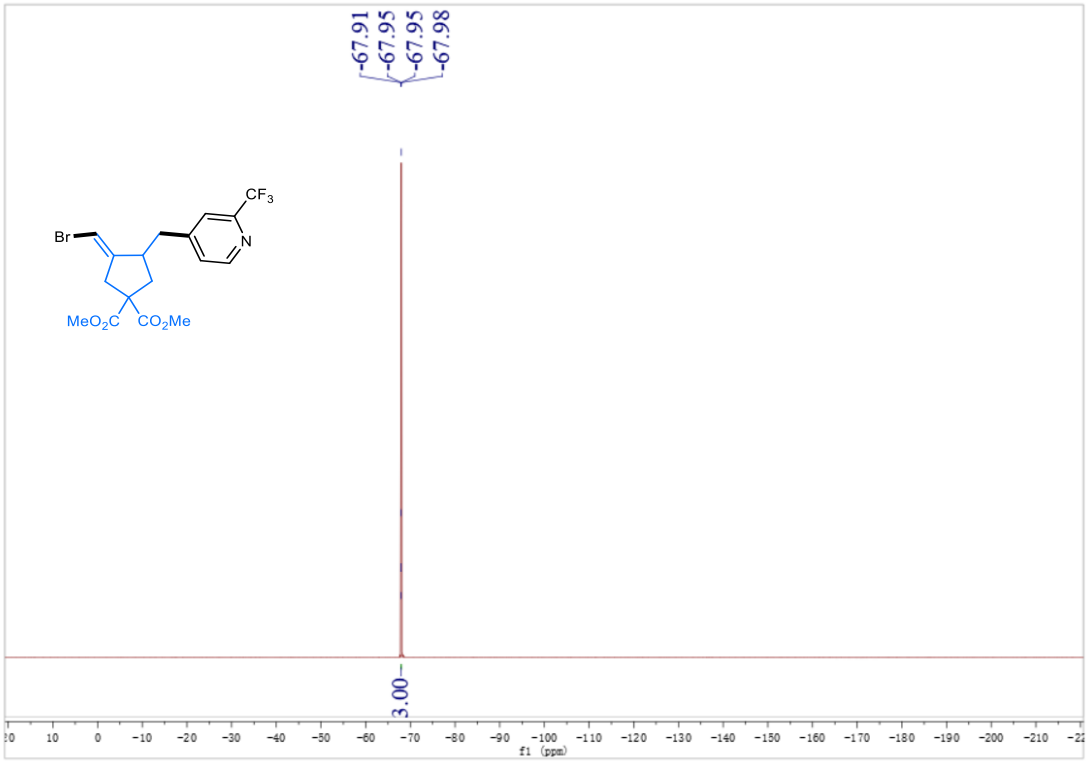
29; ^{13}C NMR (100 MHz, $CDCl_3$)



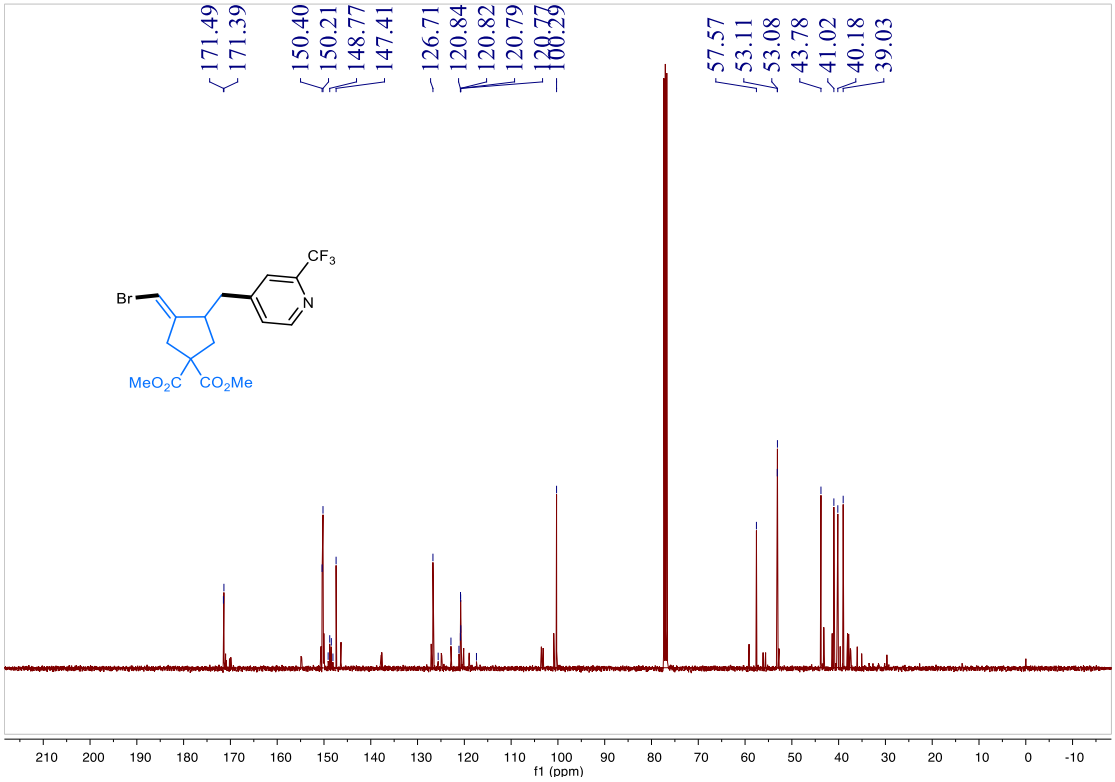
30; ^{1}H NMR (400 MHz, $CDCl_3$)



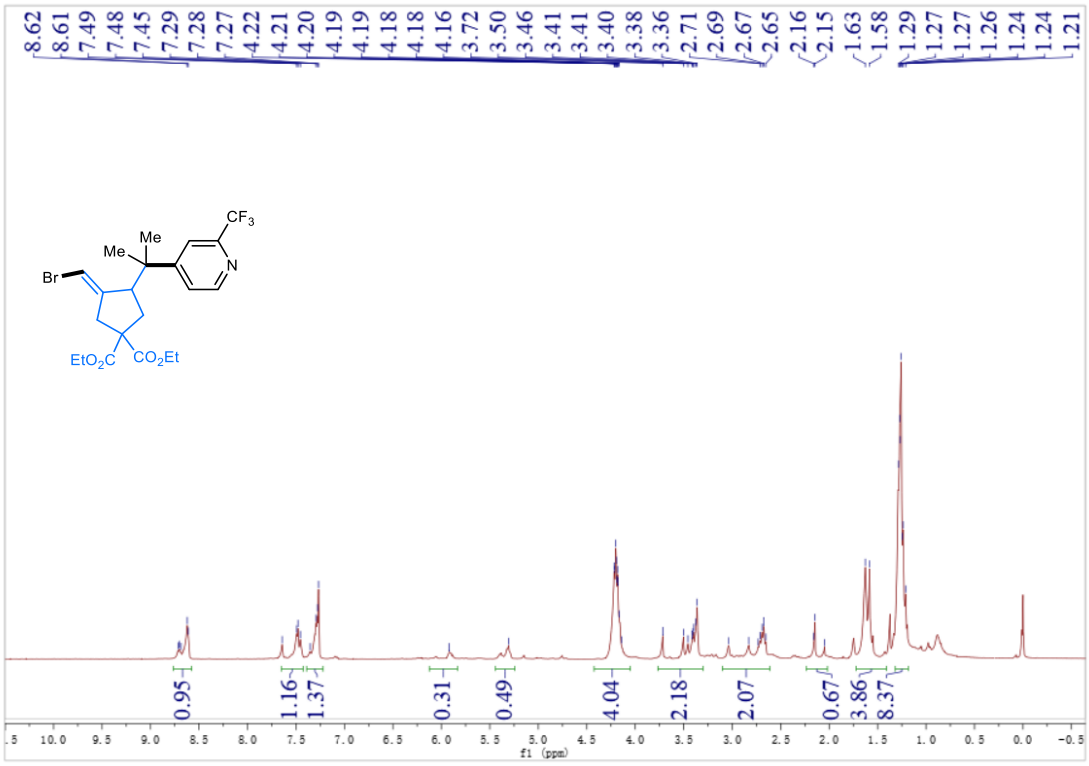
30; ^{19}F NMR (376 MHz, $CDCl_3$)



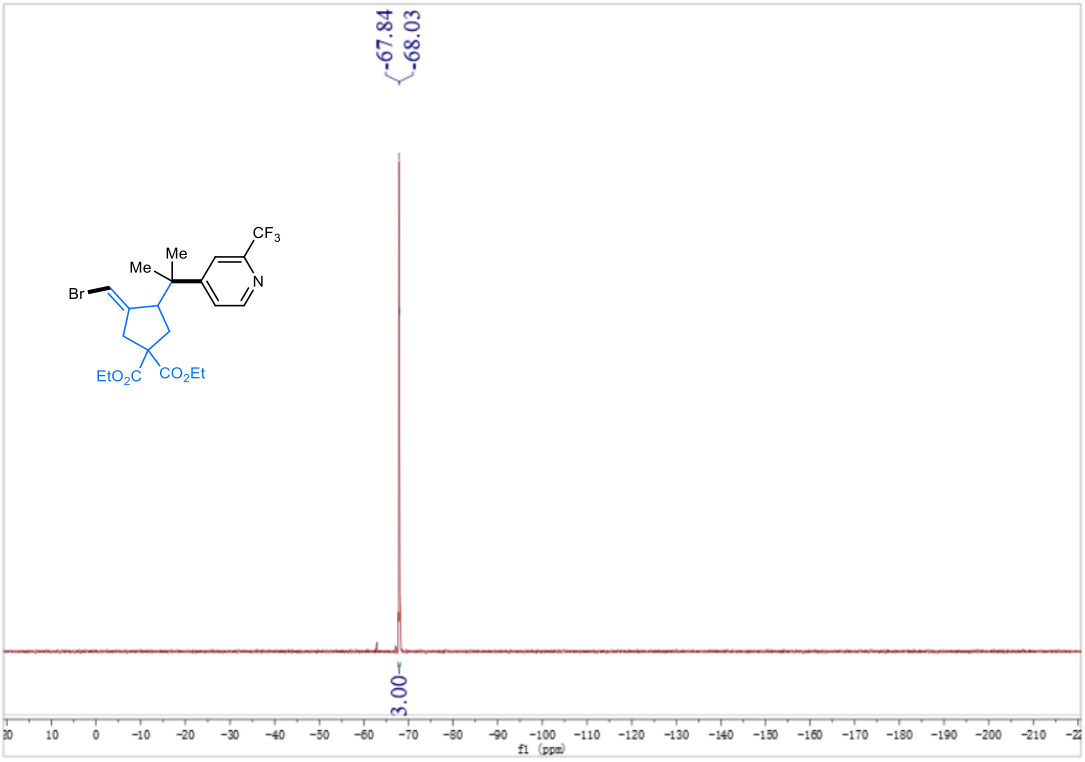
30; ^{13}C NMR (100 MHz, $CDCl_3$)



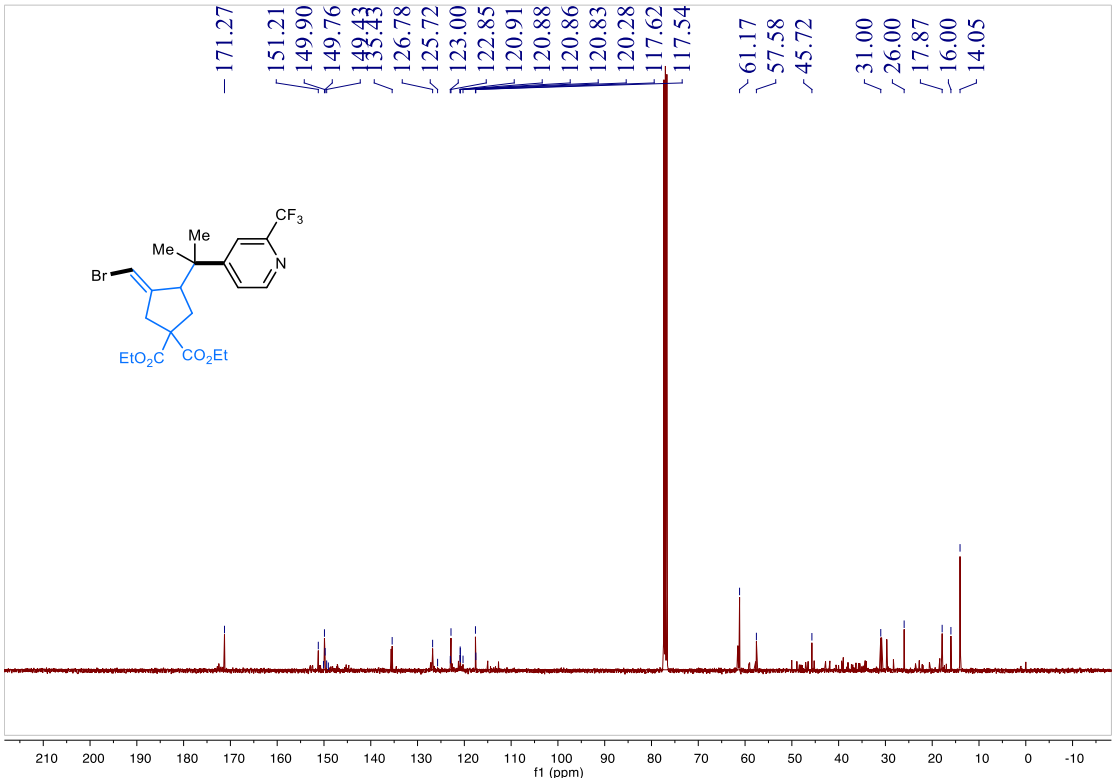
31; ^{1}H NMR (400 MHz, $CDCl_3$)



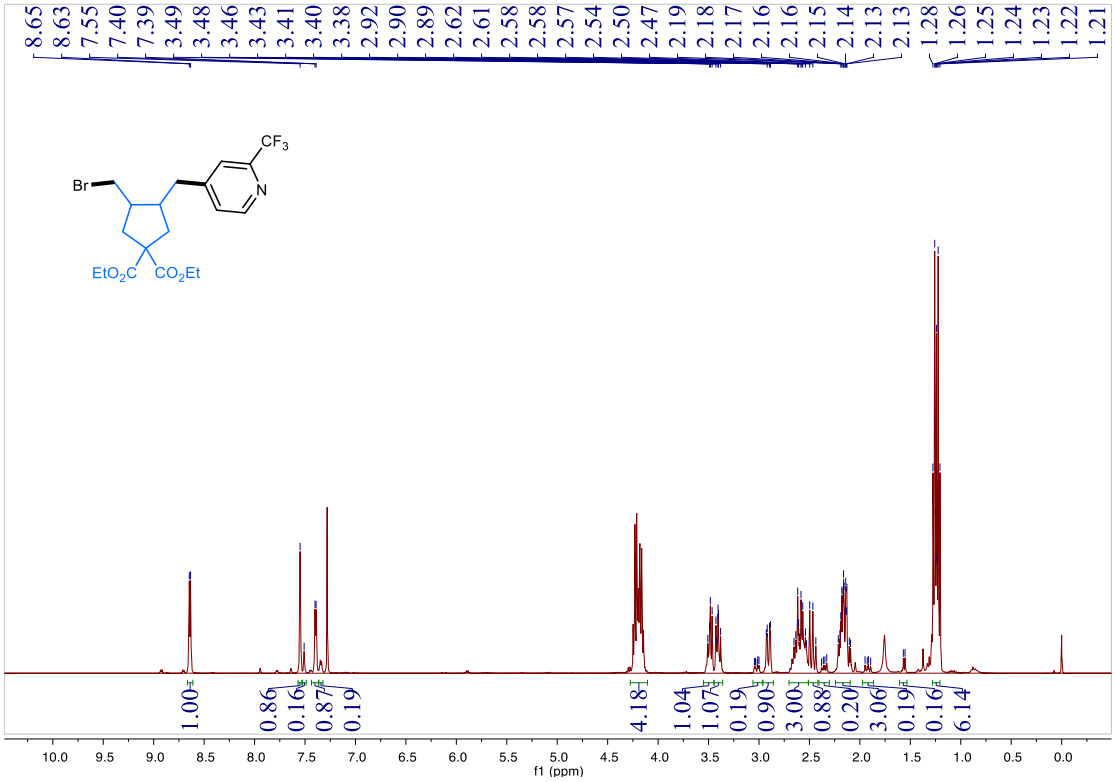
31; ^{19}F NMR (376 MHz, $CDCl_3$)



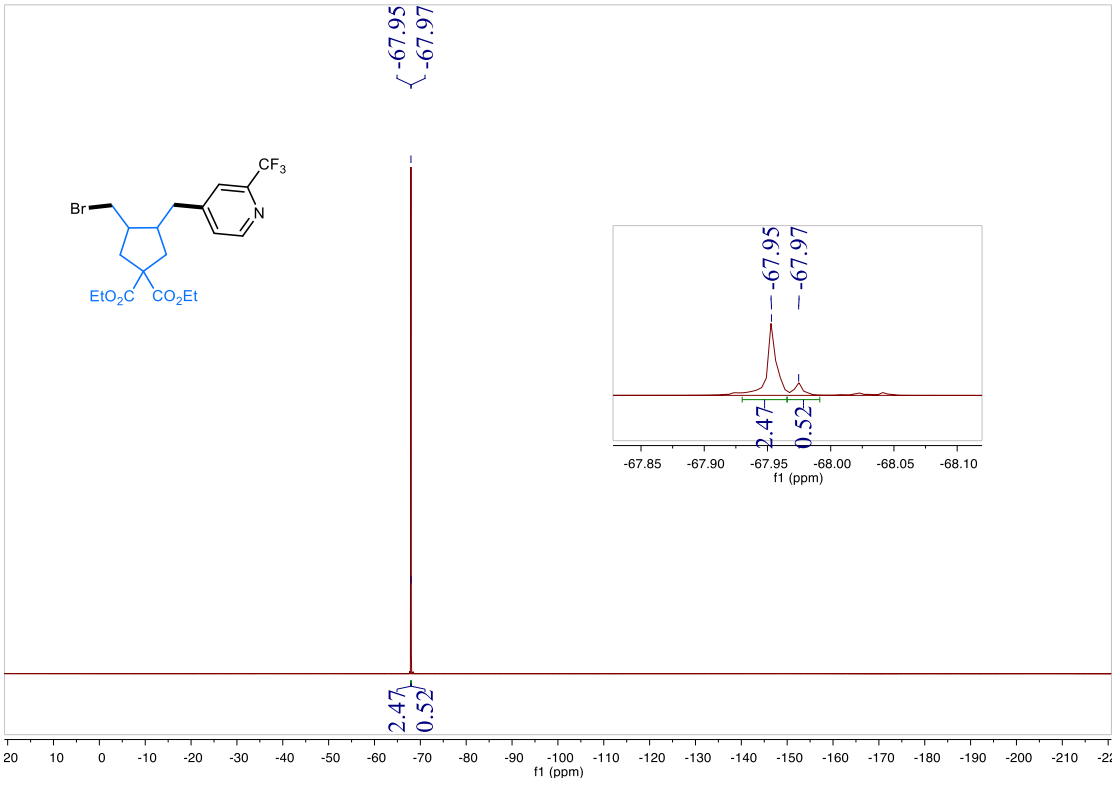
31; ^{13}C NMR (100 MHz, $CDCl_3$)



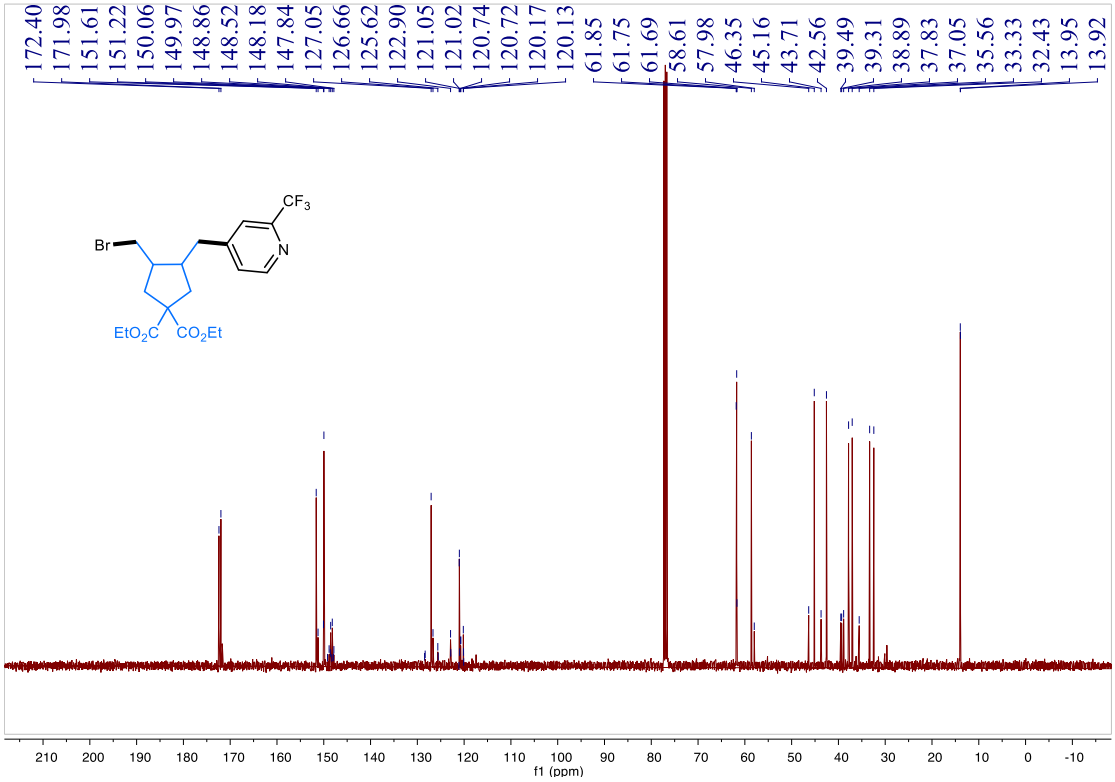
32; ^{1}H NMR (400 MHz, $CDCl_3$)



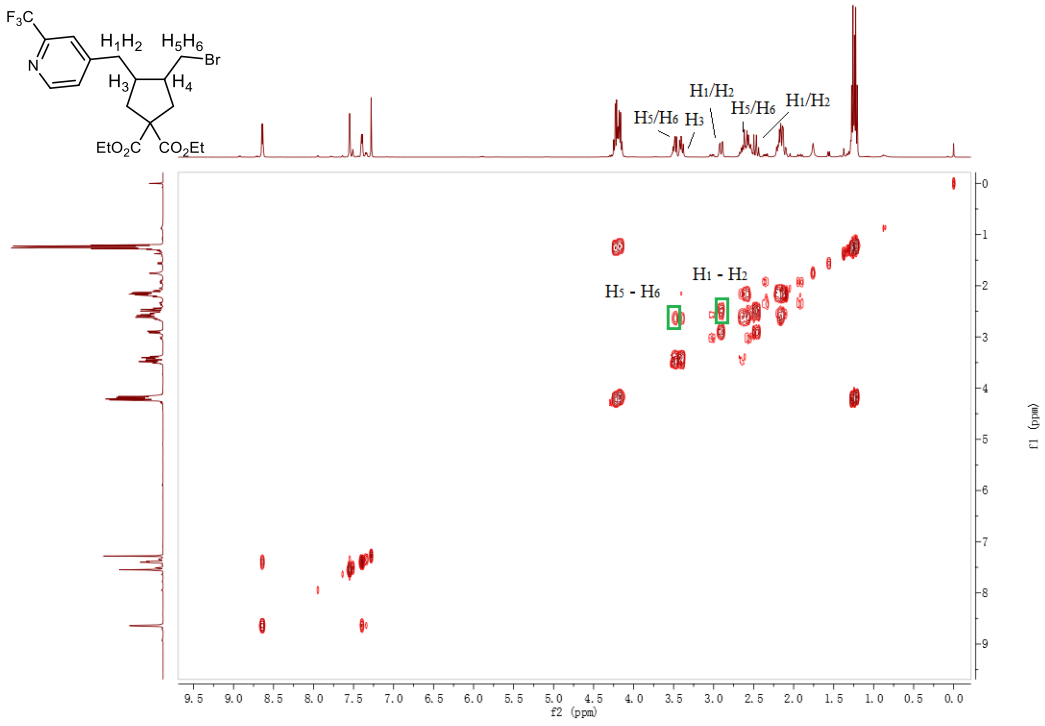
32; ^{19}F NMR (376 MHz, $CDCl_3$)

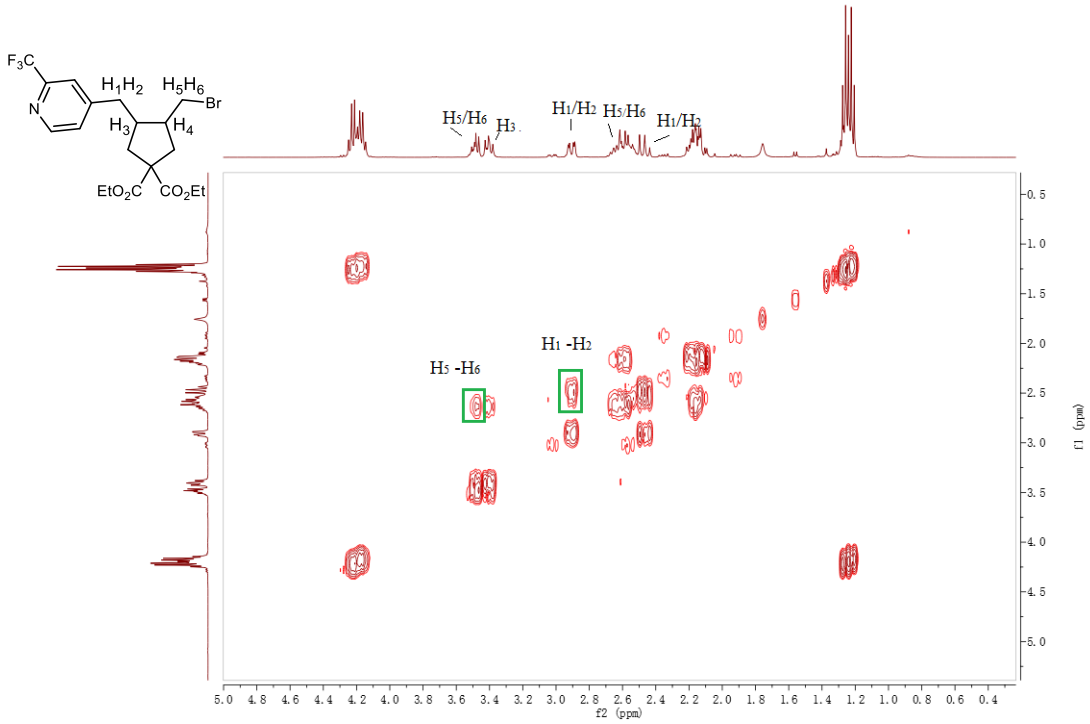


32; ^{13}C NMR (100 MHz, $CDCl_3$)



32; COSY

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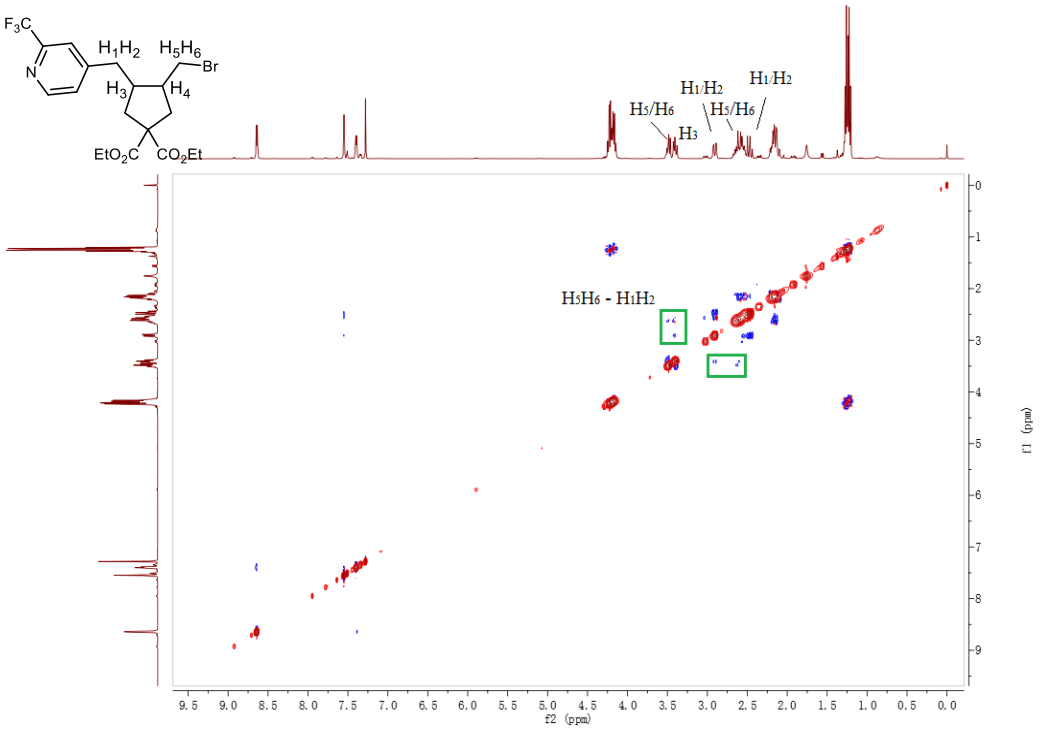
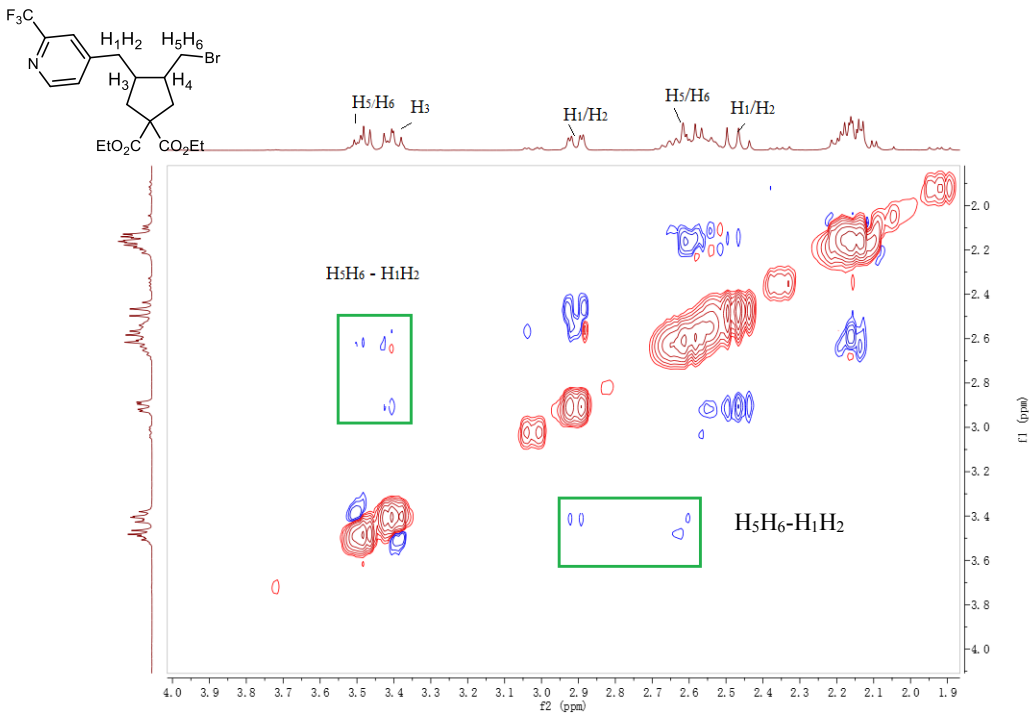
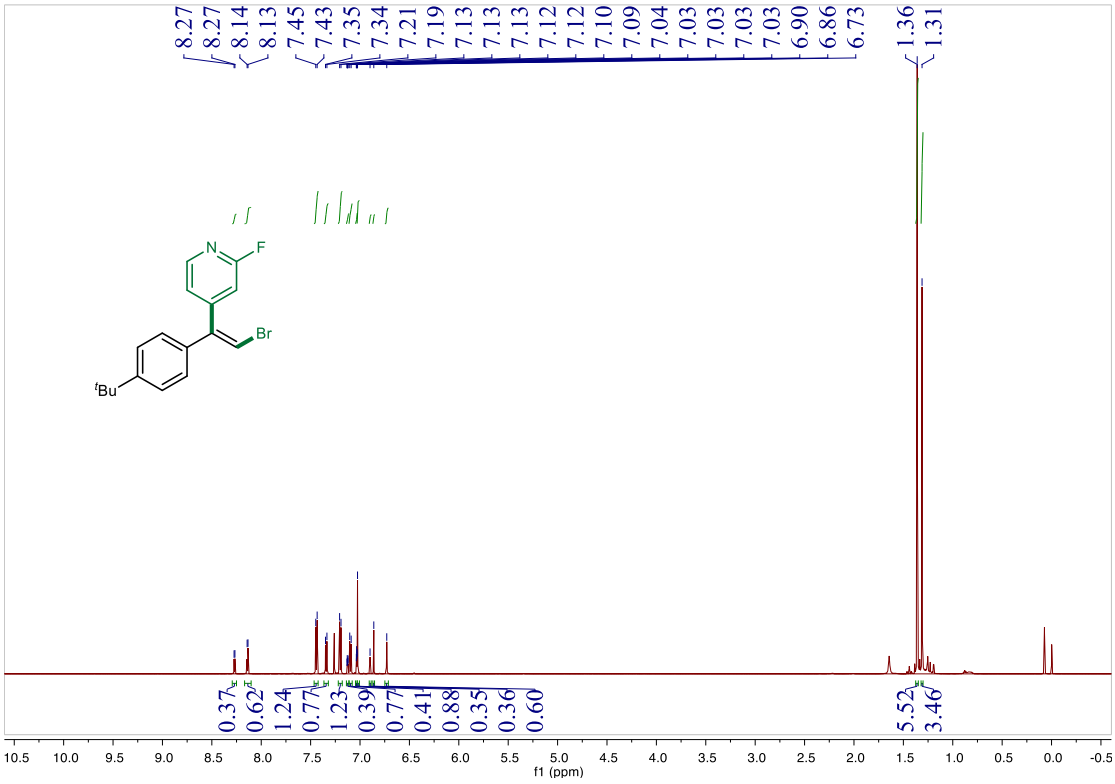
H5H6
Br
H3
H4
EtO2C
CO2Et
H5/H6
H3
H1/H2
H5/H6
H1/H2
H5 -H6
H1 -H2
f2 (ppm)
f1 (ppm)

32; NOESY

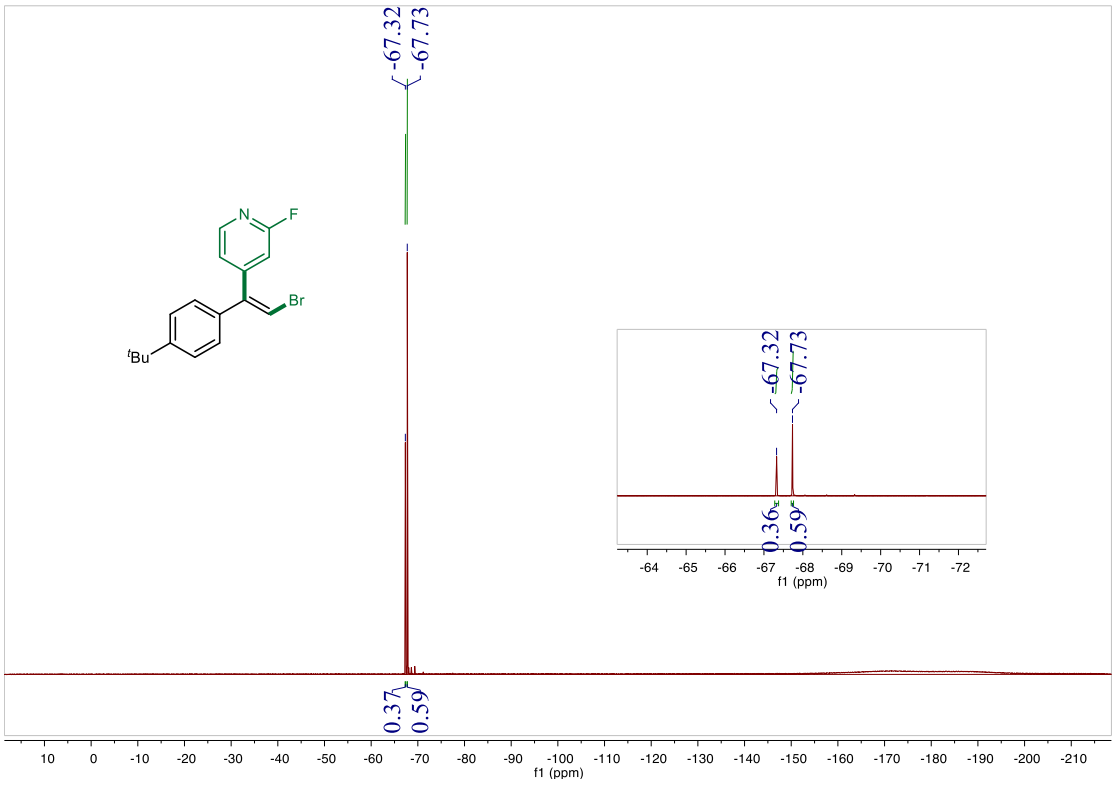

F3C
H1H2
H5H6
Br
H3
H4
EtO2C
CO2Et
H1/H2
H1/H2
H5/H6
H5/H6
H3
H5H6 - H1H2
f2 (ppm)
f1 (ppm)



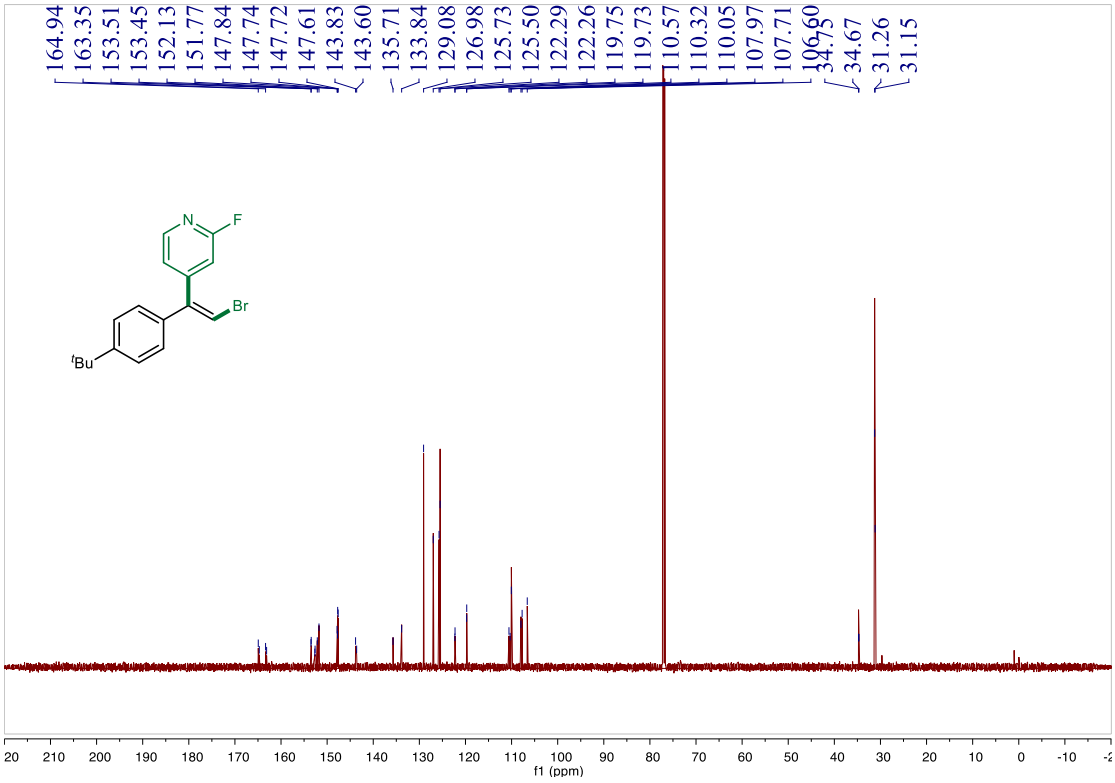
33; ^{1}H NMR (600 MHz, $CDCl_3$)



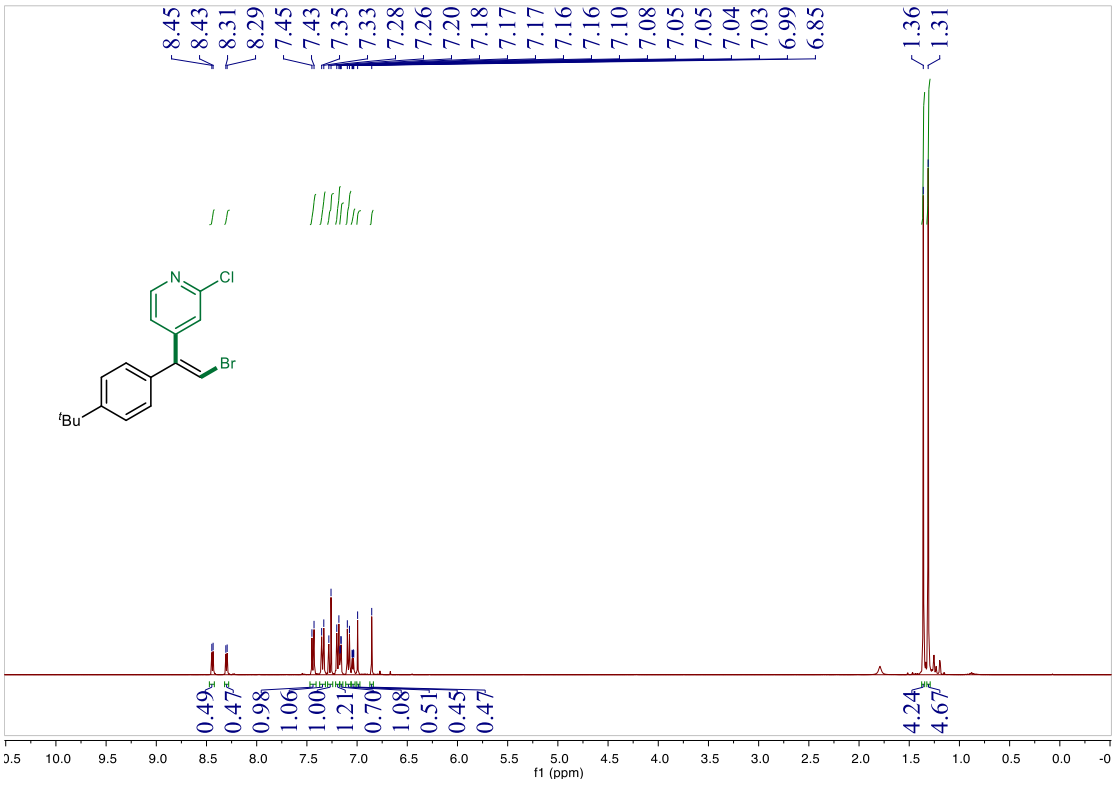
33; ^{19}F NMR (564 MHz, $CDCl_3$)



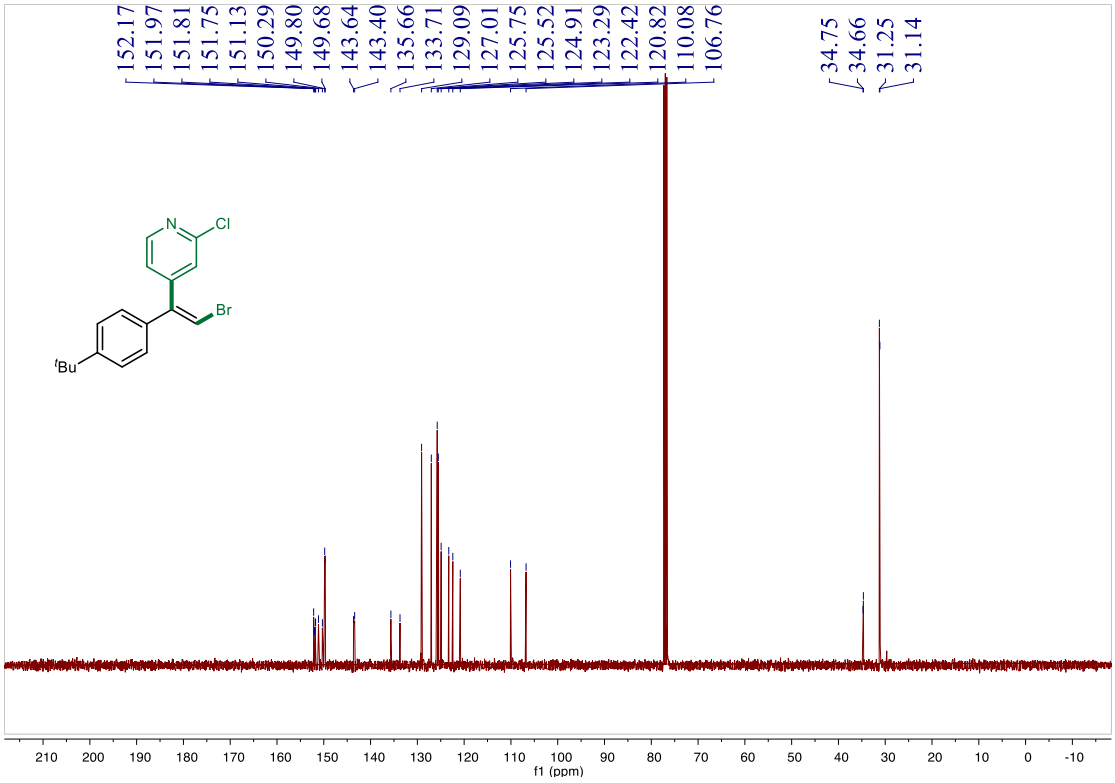
33; ^{13}C NMR (150 MHz, $CDCl_3$)



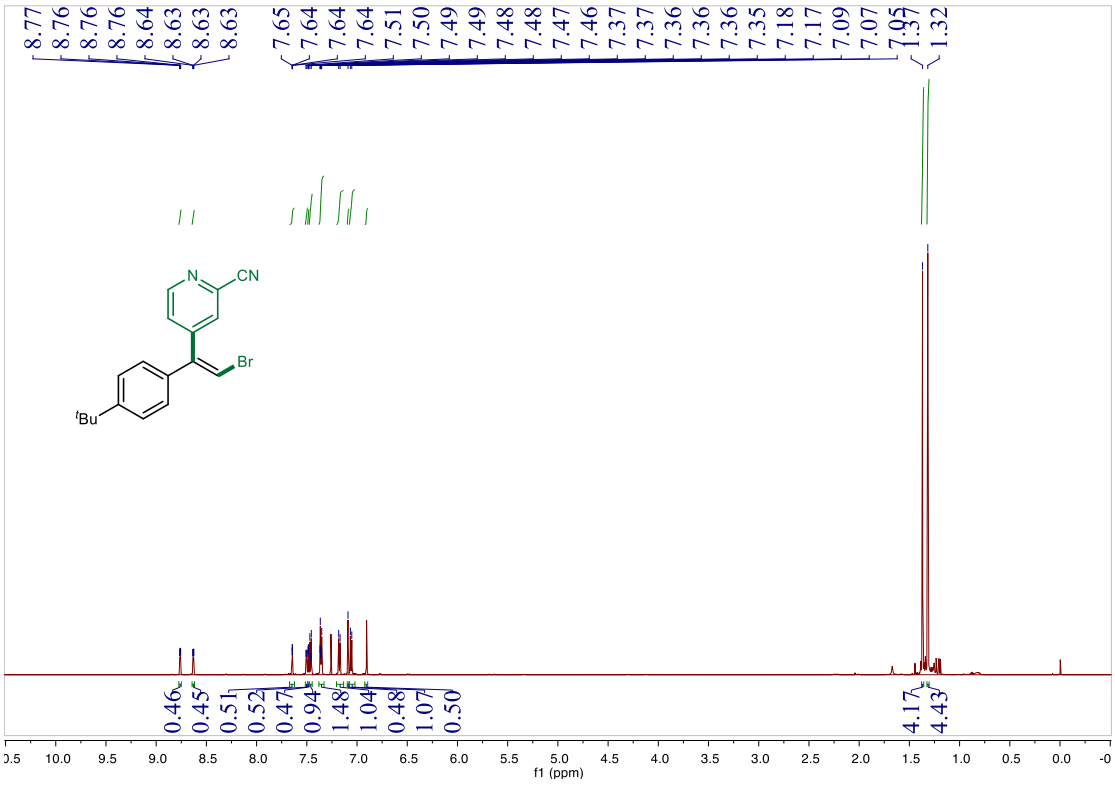
34; ^{1}H NMR (400 MHz, $CDCl_3$)



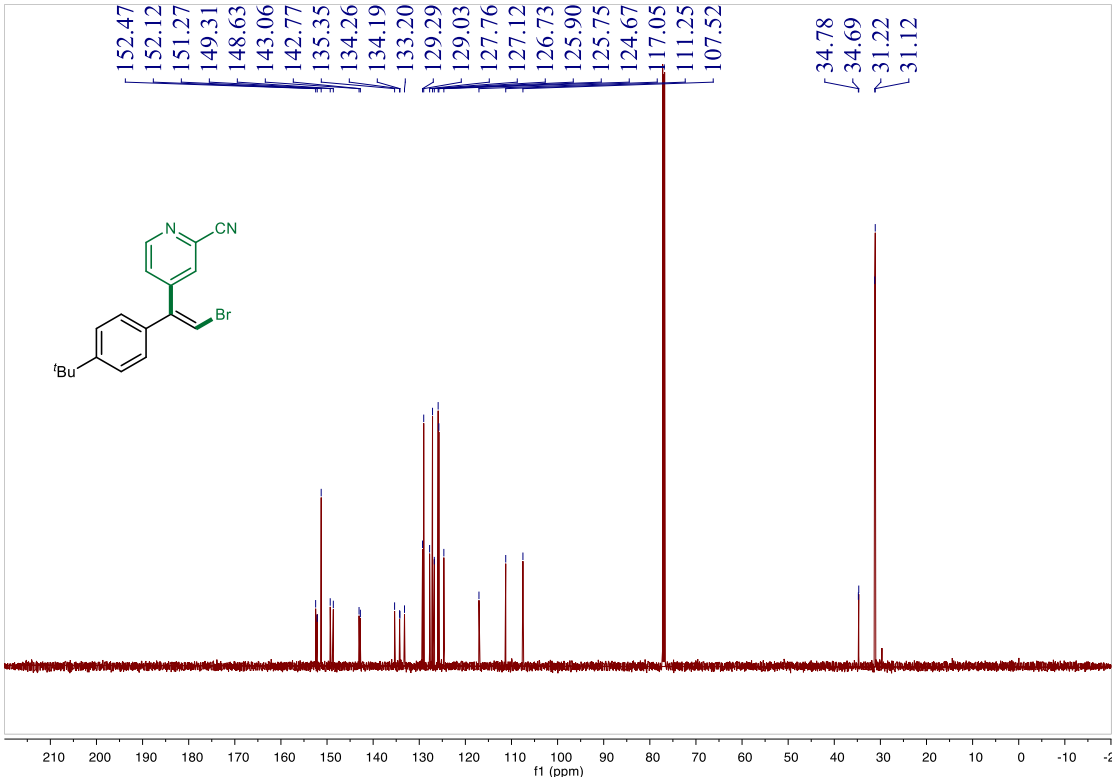
34; ^{13}C NMR (100 MHz, $CDCl_3$)



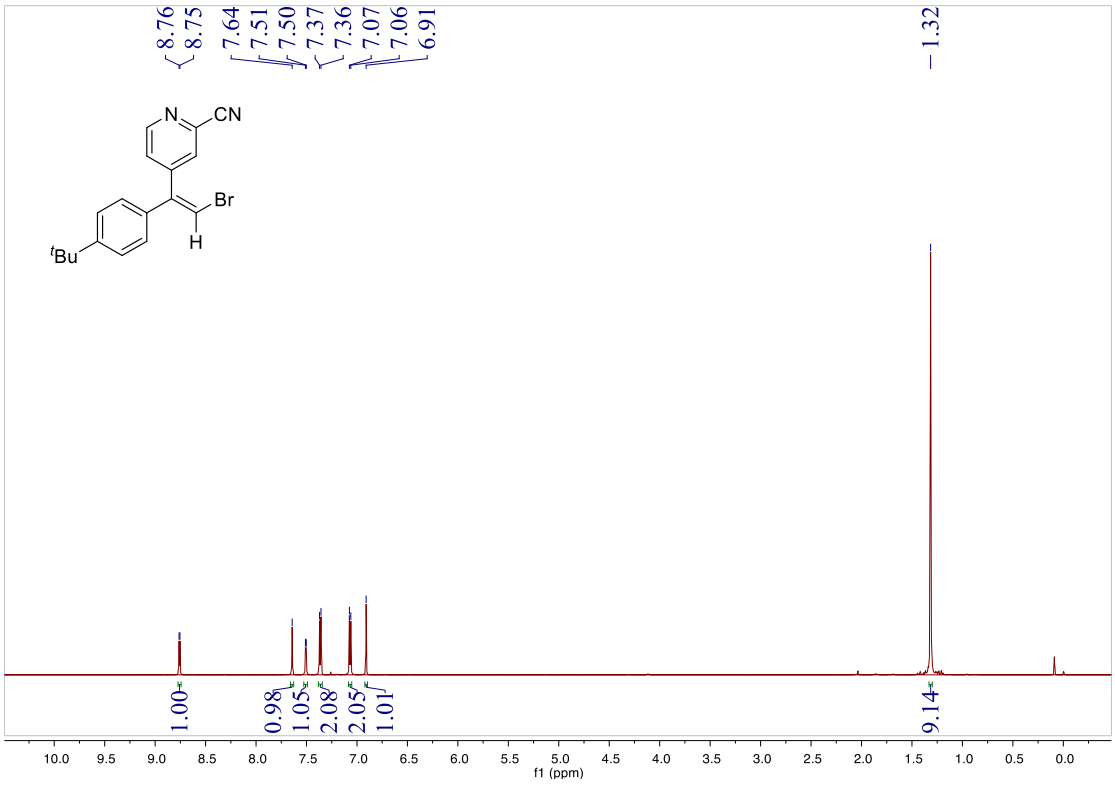
35; ^{1}H NMR (600 MHz, $CDCl_3$)



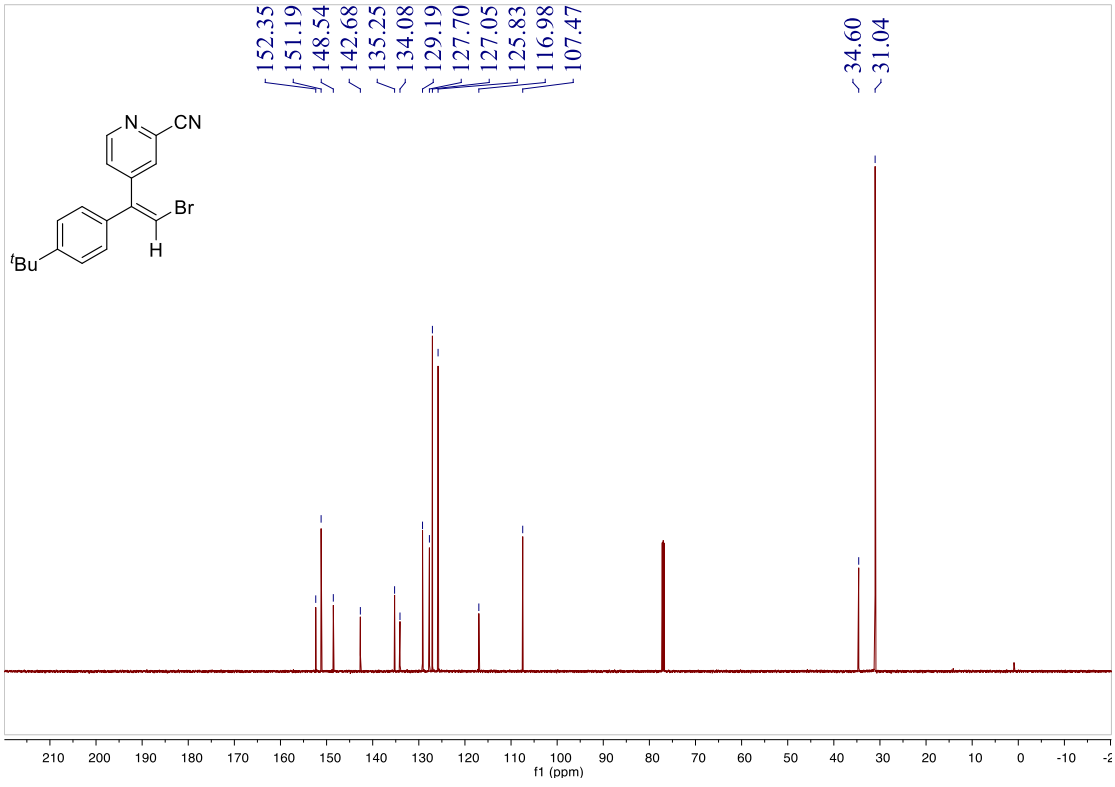
35; ^{13}C NMR (150 MHz, $CDCl_3$)



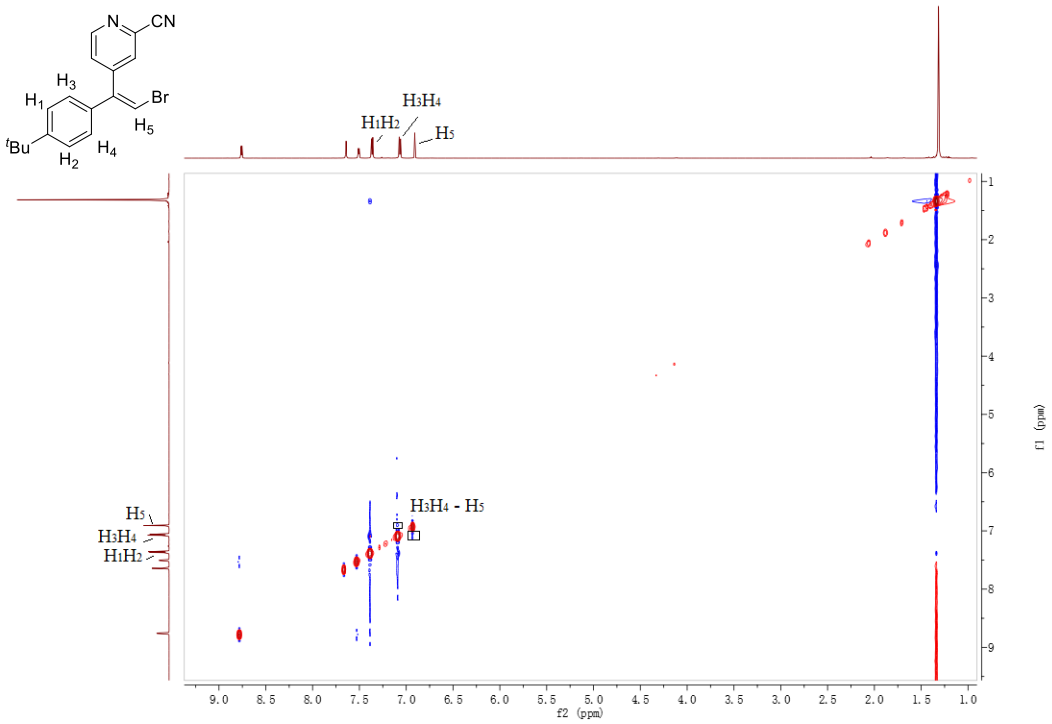
Z-35; ^{1}H NMR (600 MHz, $CDCl_3$)

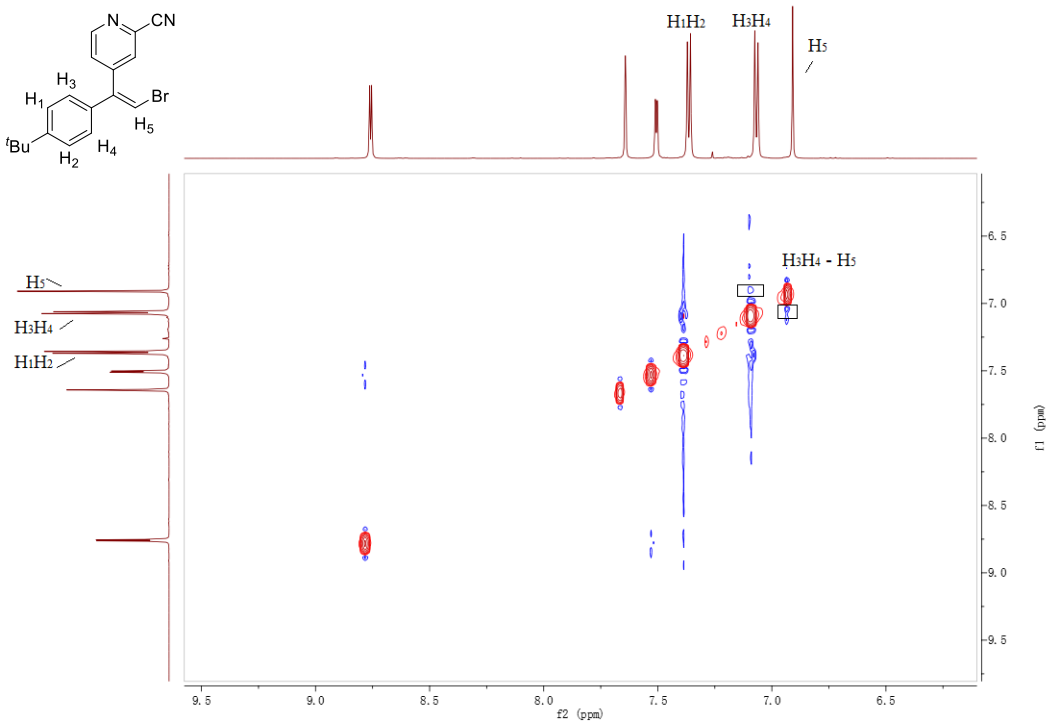


Z-35; ^{13}C NMR (150 MHz, $CDCl_3$)

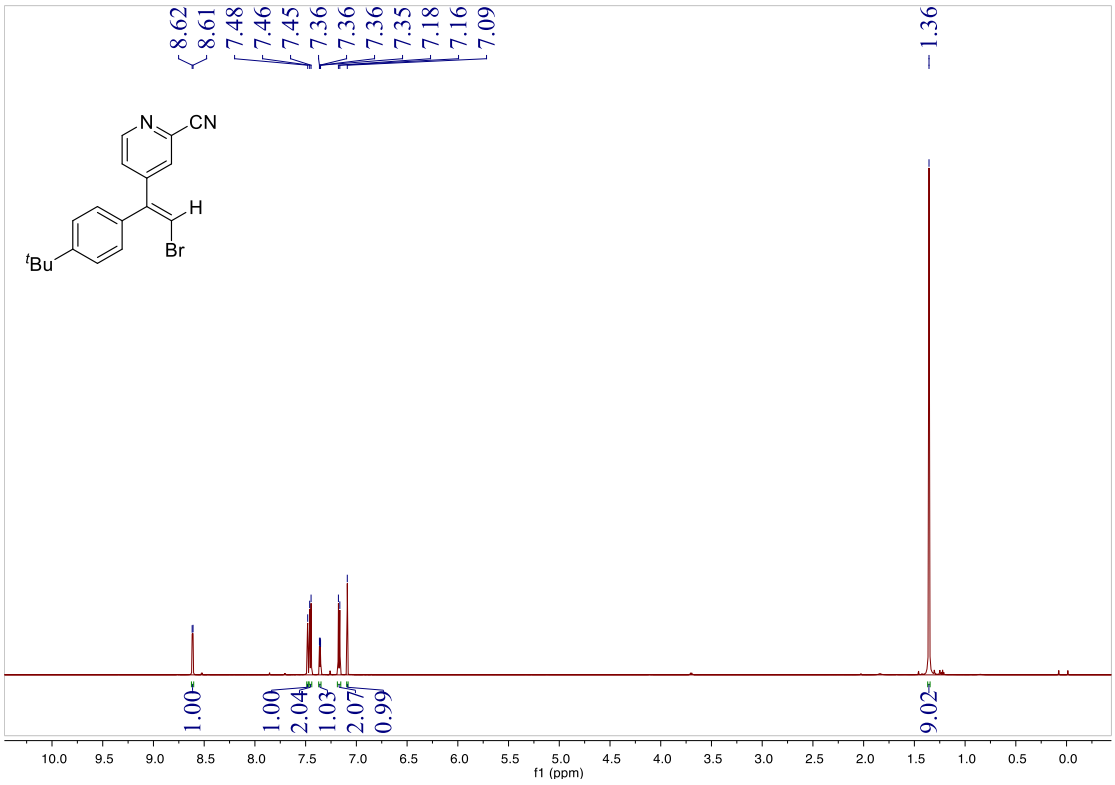


Z-35; NOESY

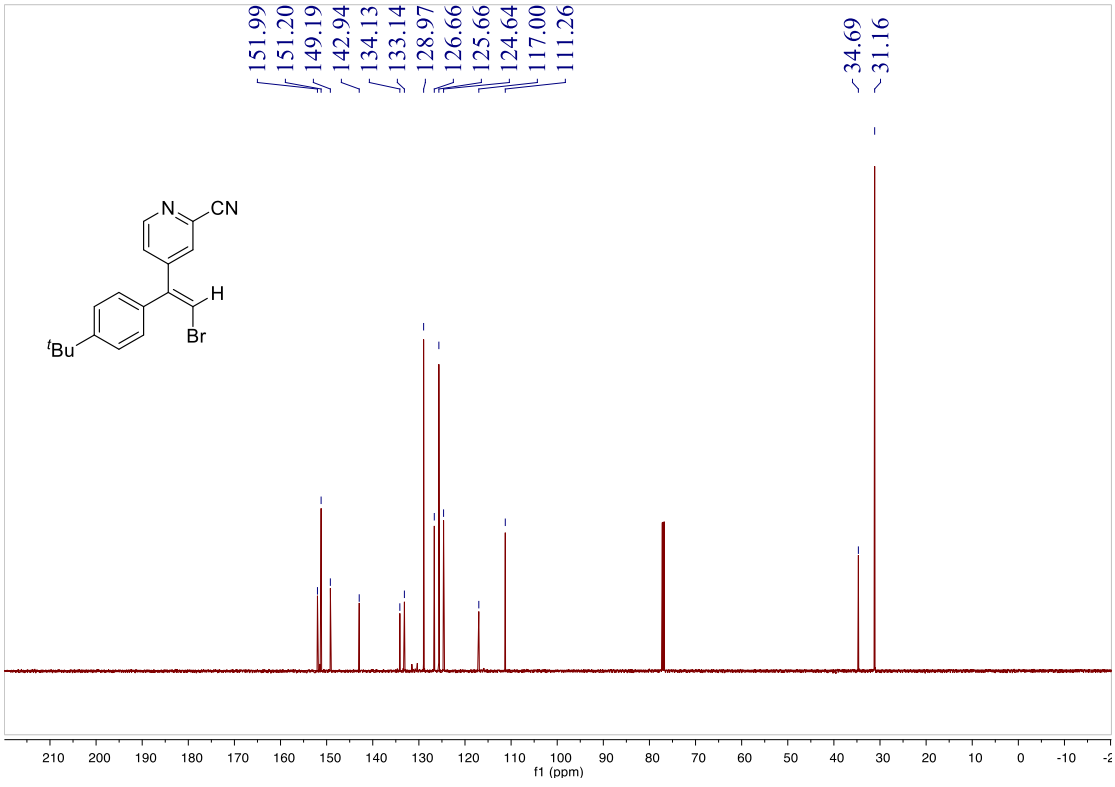

N
CN
H3
H1
Br
H5
tBu
H4
H2
H3H4
H1H2
H5
H3H4 - H5
H5
H3H4
H1H2
f2 (ppm)
f1 (ppm)


N
CN
H3
H1
Br
H5
tBu
H4
H2
H1H2
H3H4
H5
H3H4 - H5
H5
H3H4
H1H2
f2 (ppm)
f1 (ppm)

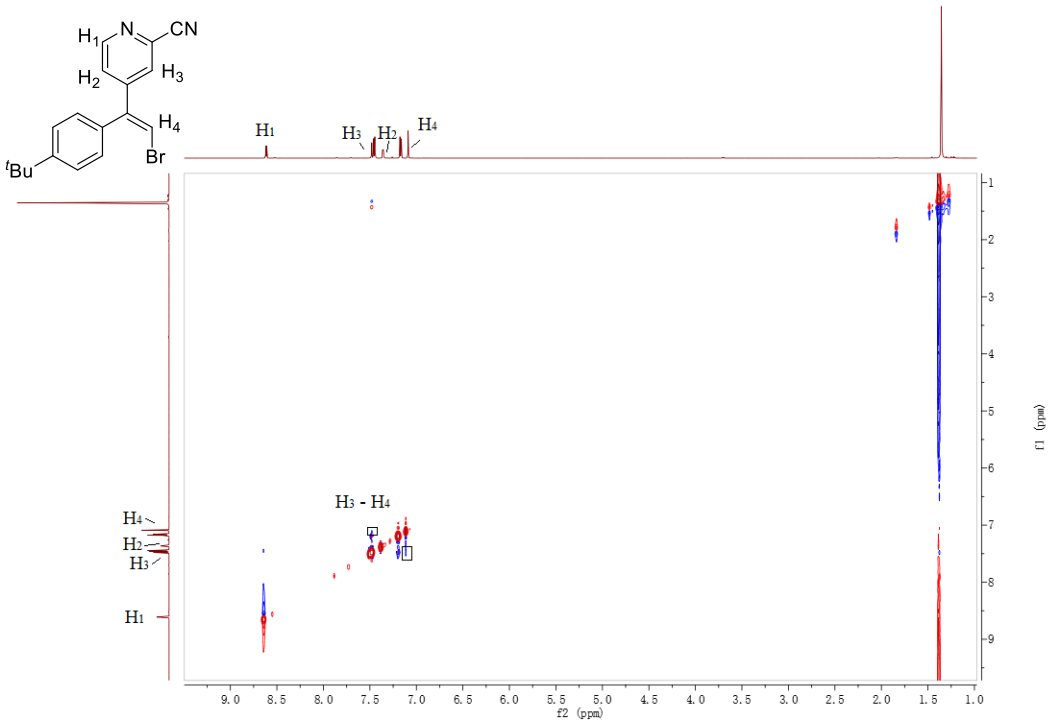
E-35; ^{1}H NMR (600 MHz, $CDCl_3$)

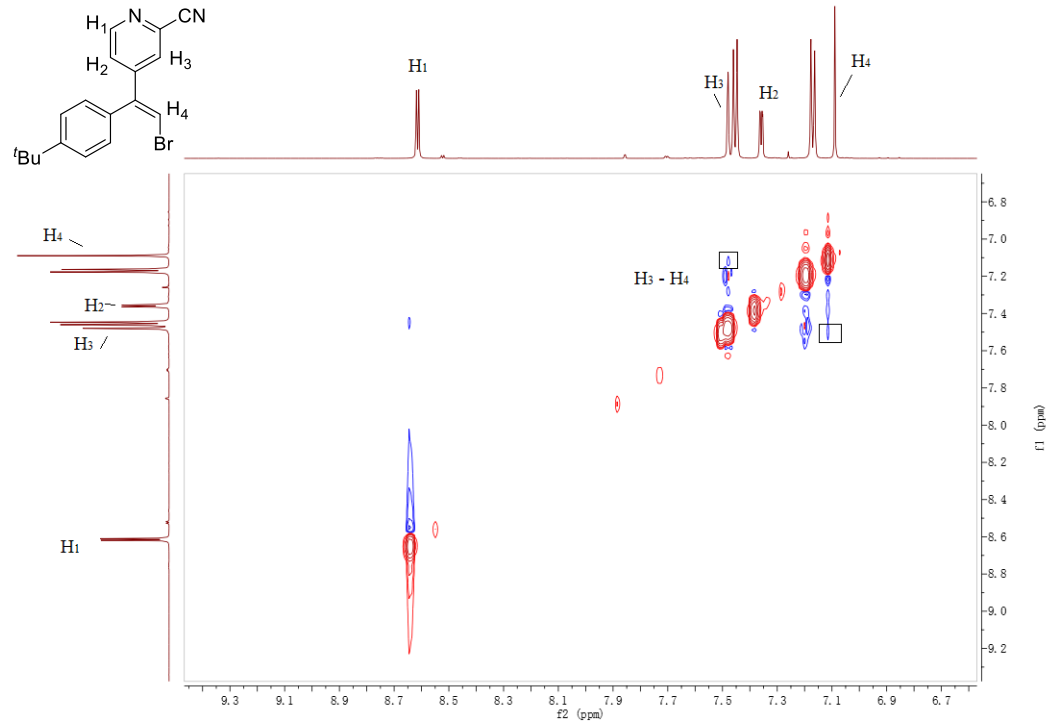


E-35; ^{13}C NMR (150 MHz, $CDCl_3$)

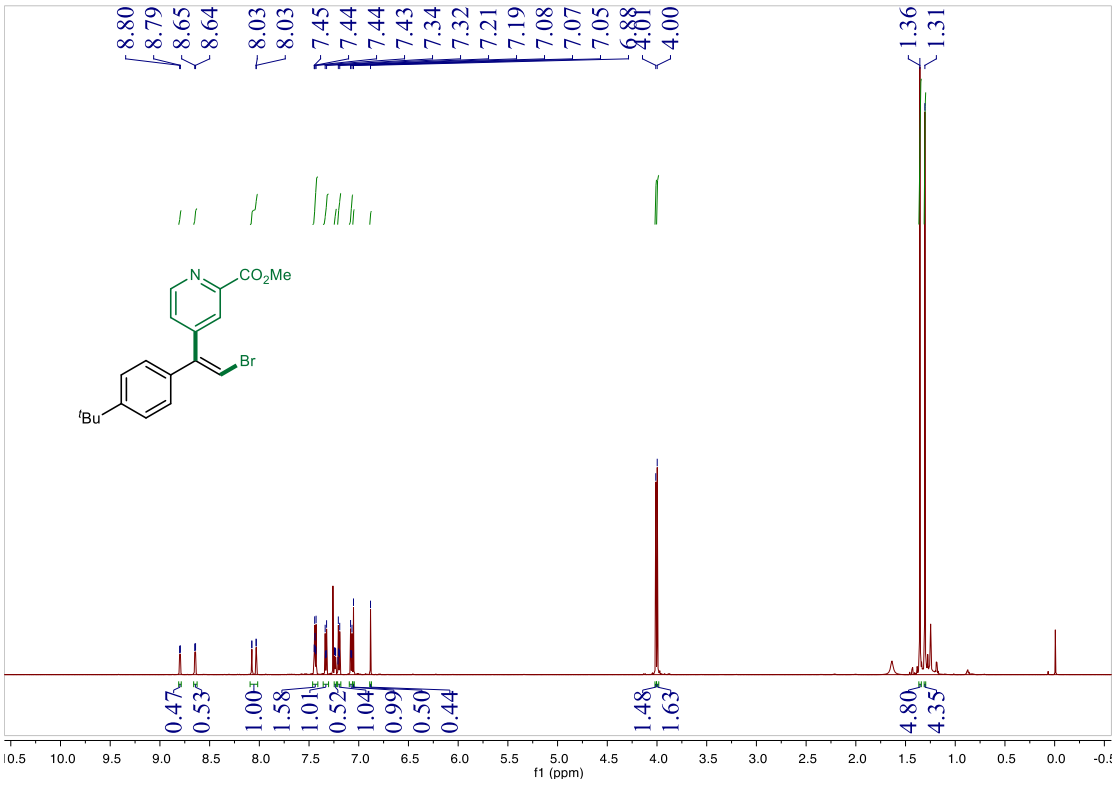


E-35; NOESY

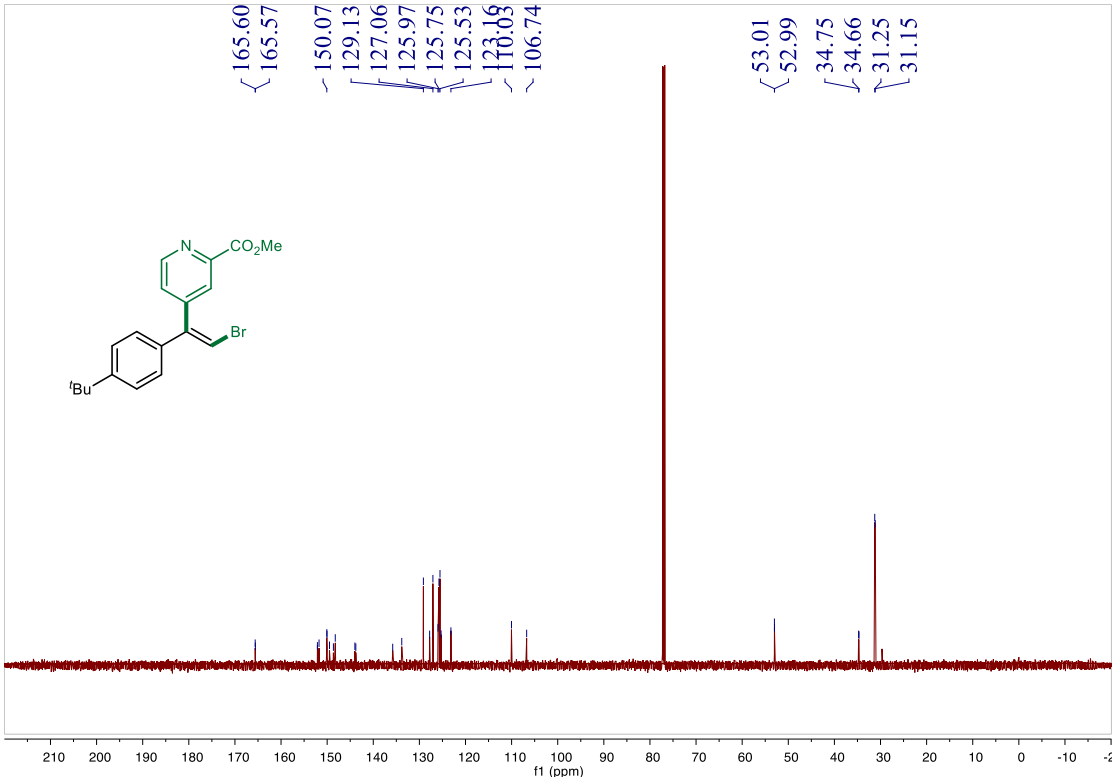

H1
N
CN
H2
H3
H4
tBu
Br
H1
H3
H2
H4
H3 - H4
H4
H2
H3
H1
f2 (ppm)
f1 (ppm)


H1
N
CN
H2
H3
H4
tBu
Br
H1
H3
H2
H4
H3 - H4
H4
H2
H3
H1
f2 (ppm)
f1 (ppm)

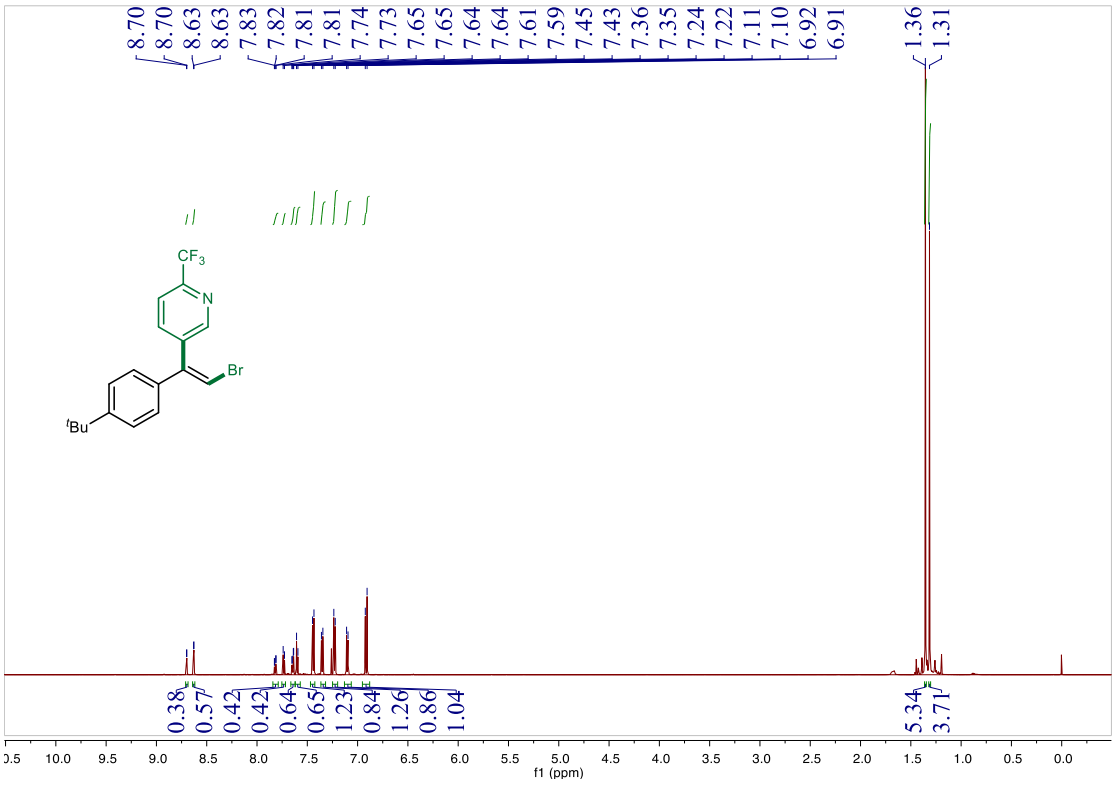
36; ^{1}H NMR (400 MHz, $CDCl_3$)



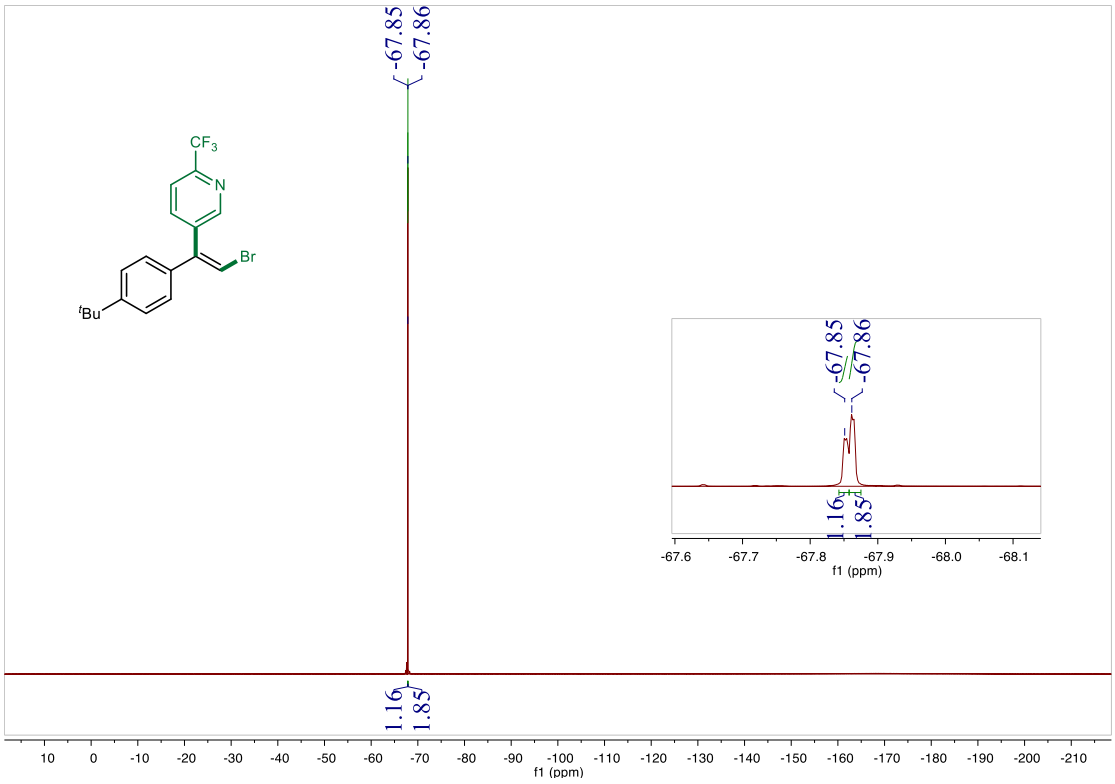
36; ^{13}C NMR (100 MHz, $CDCl_3$)



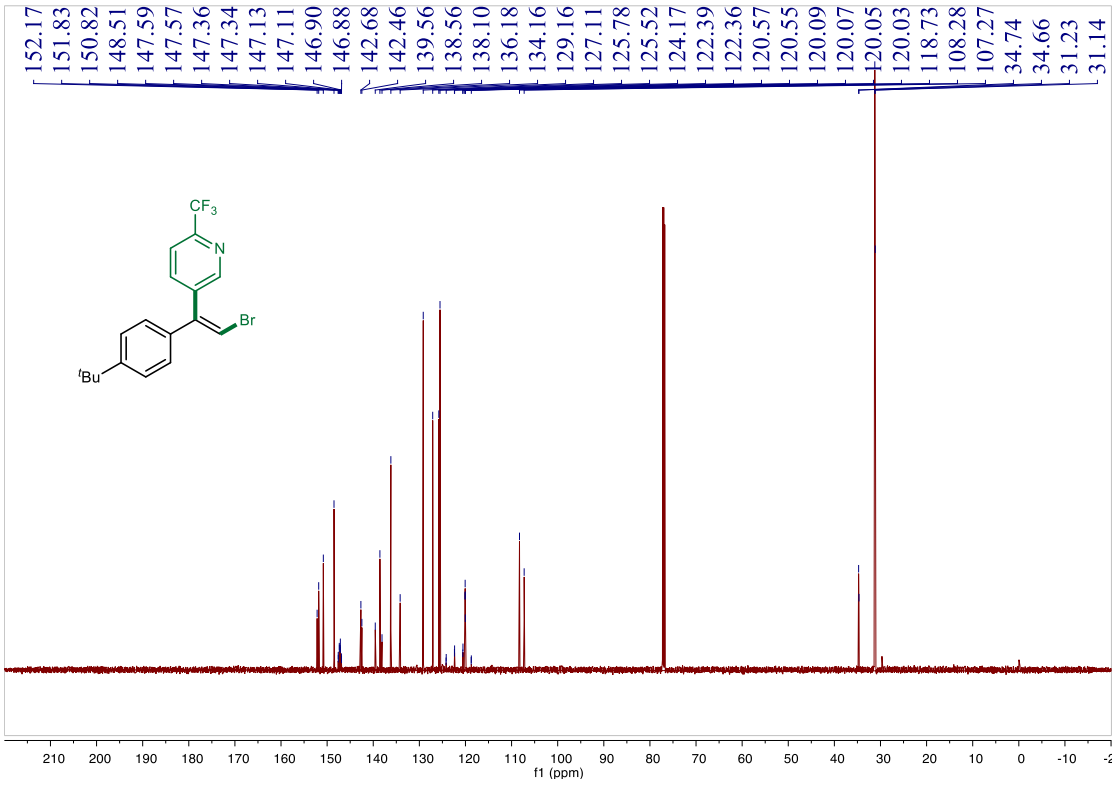
37; ^{1}H NMR (600 MHz, $CDCl_3$)



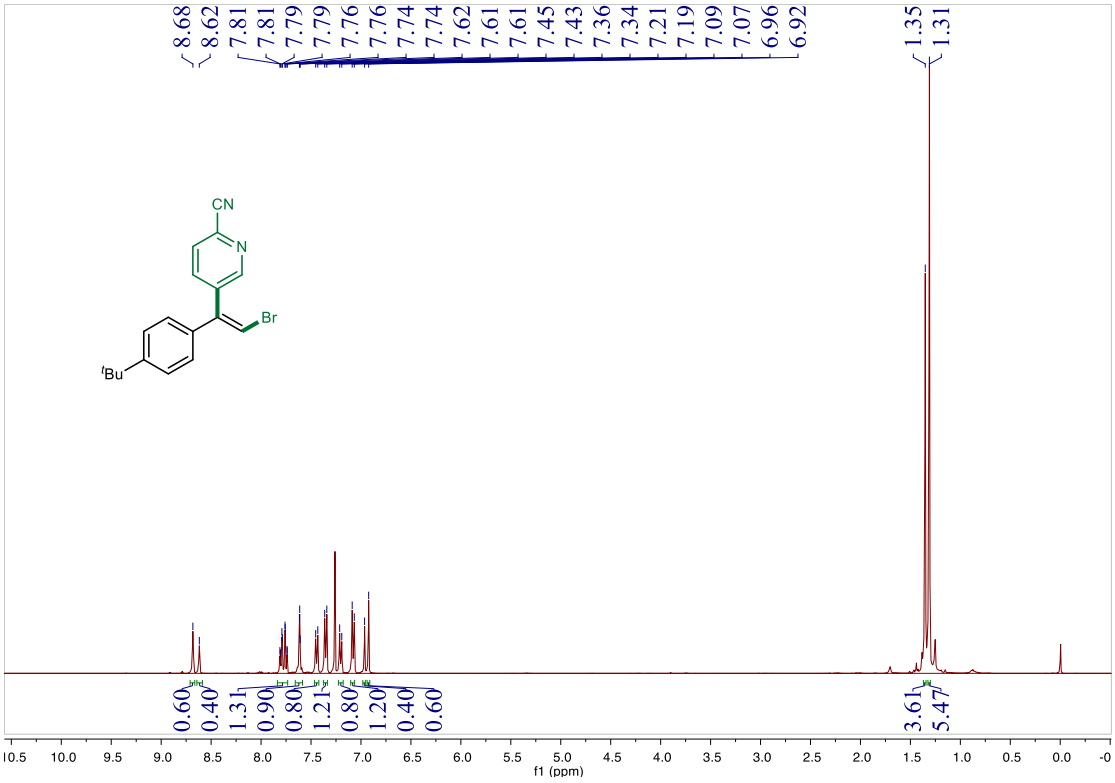
37; ^{19}F NMR (564 MHz, $CDCl_3$)



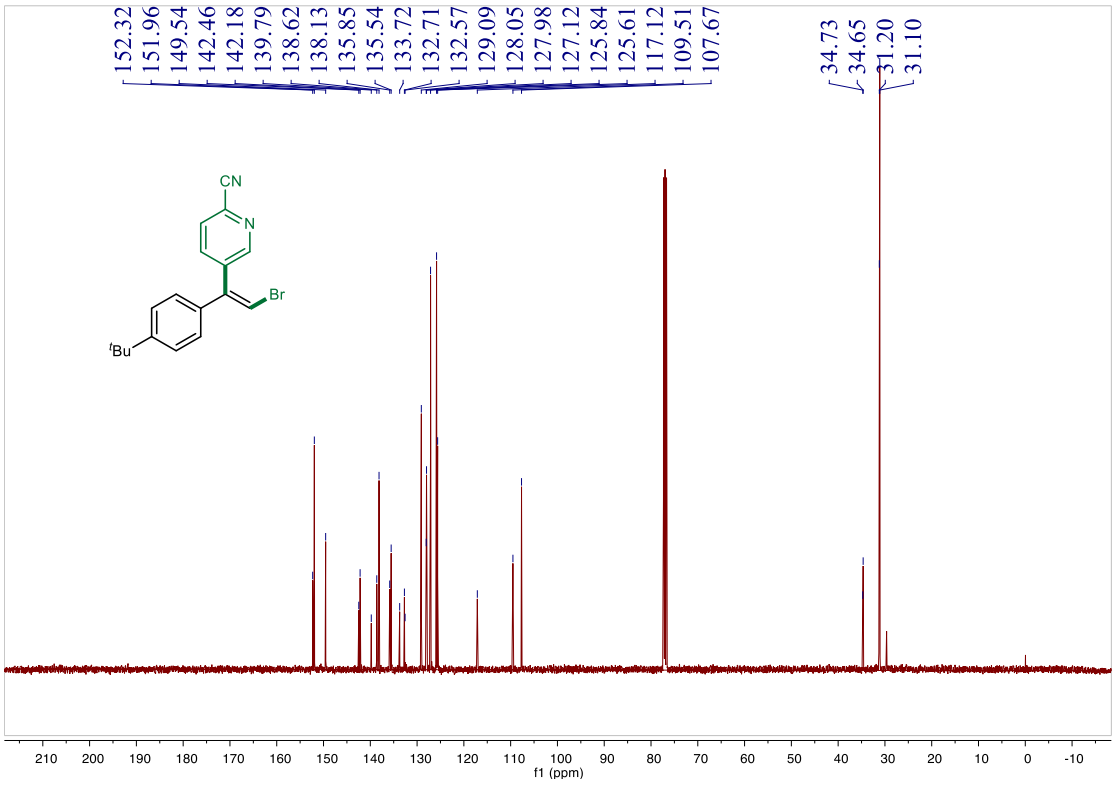
37; ^{13}C NMR (150 MHz, $CDCl_3$)



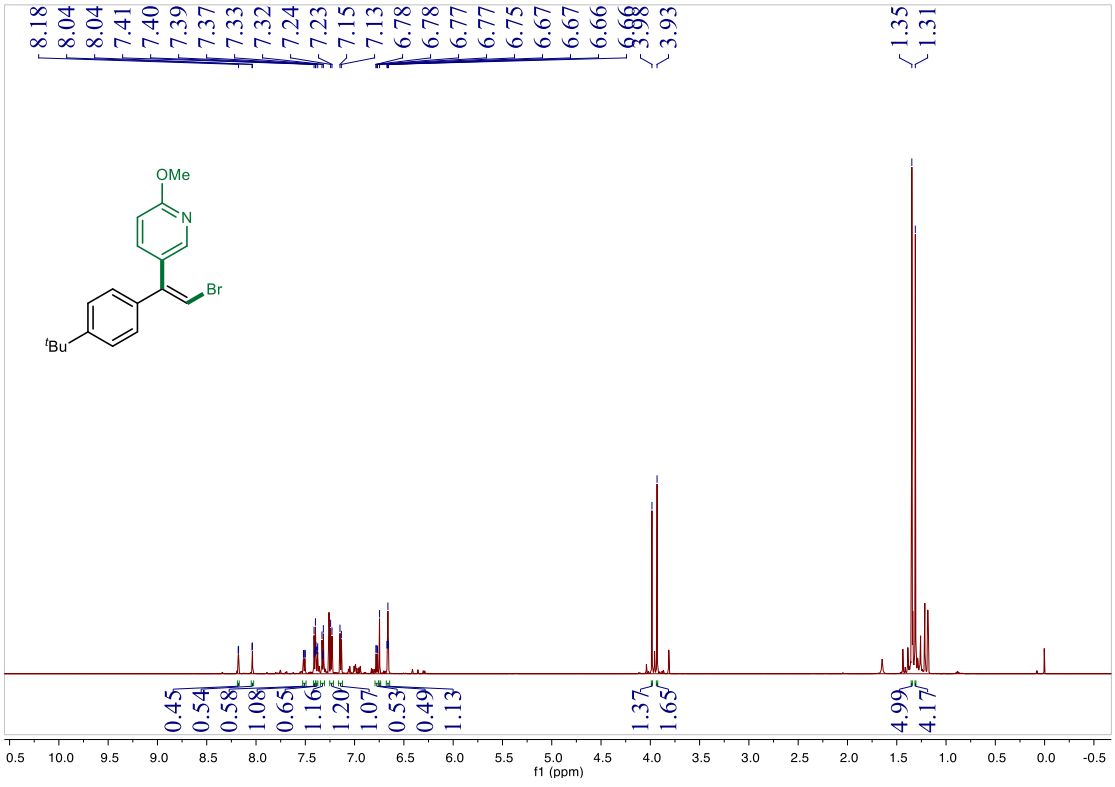
38; ^{1}H NMR (400 MHz, $CDCl_3$)



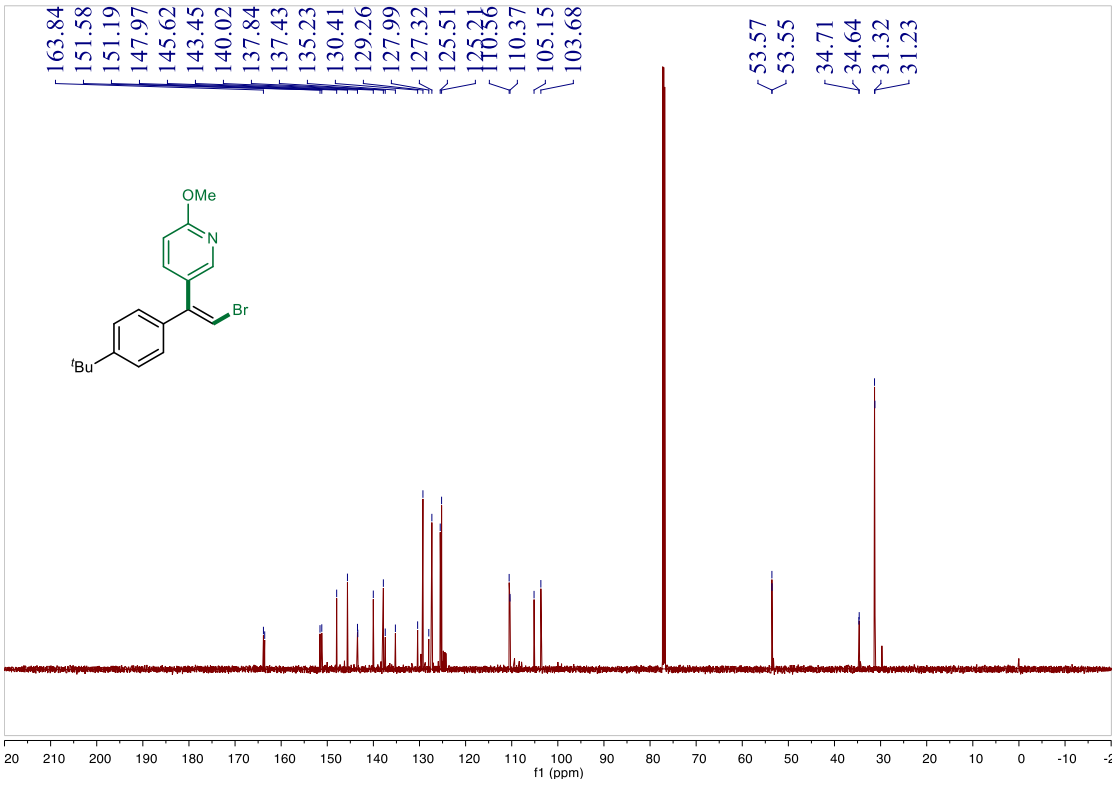
38; ^{13}C NMR (100 MHz, $CDCl_3$)



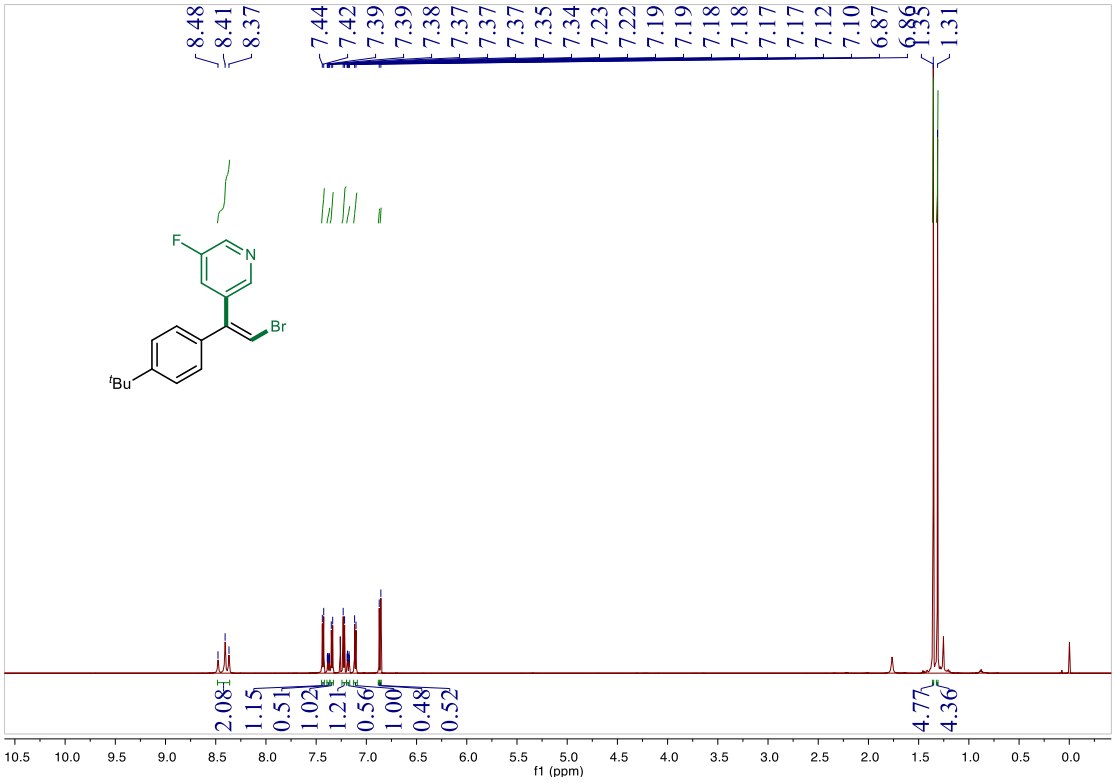
39; ^{1}H NMR (600 MHz, $CDCl_3$)



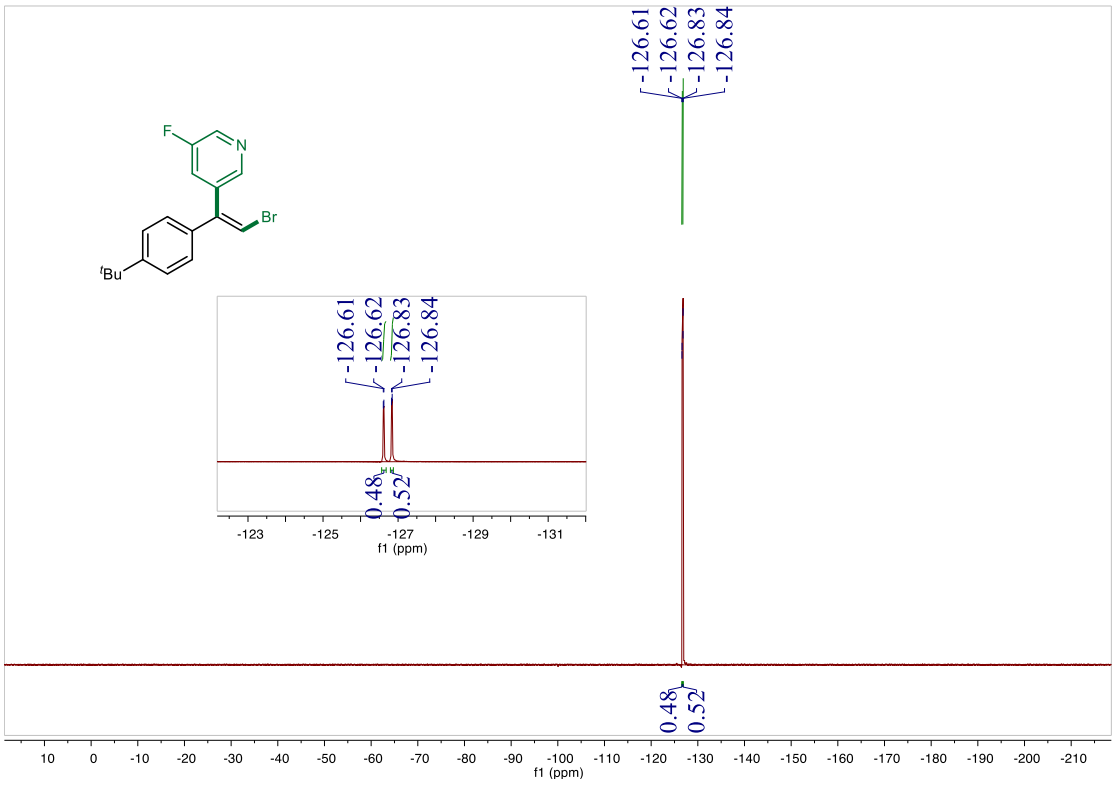
39; ^{13}C NMR (150 MHz, $CDCl_3$)



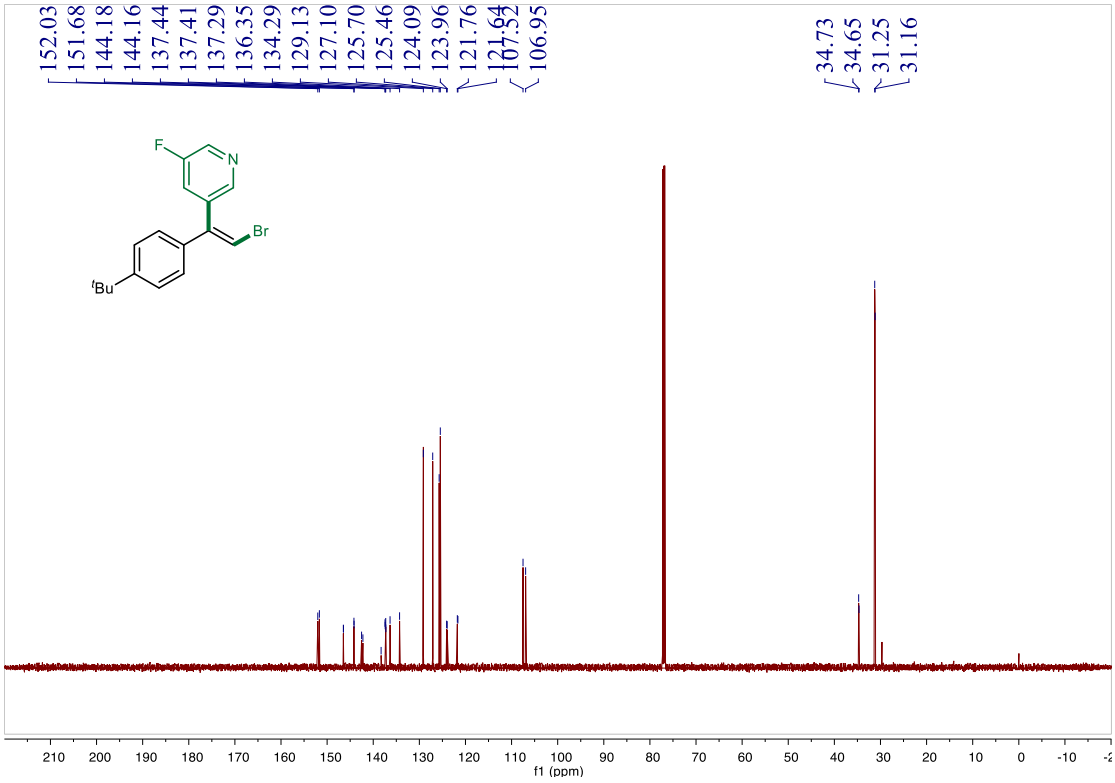
40; ^{1}H NMR (600 MHz, $CDCl_3$)



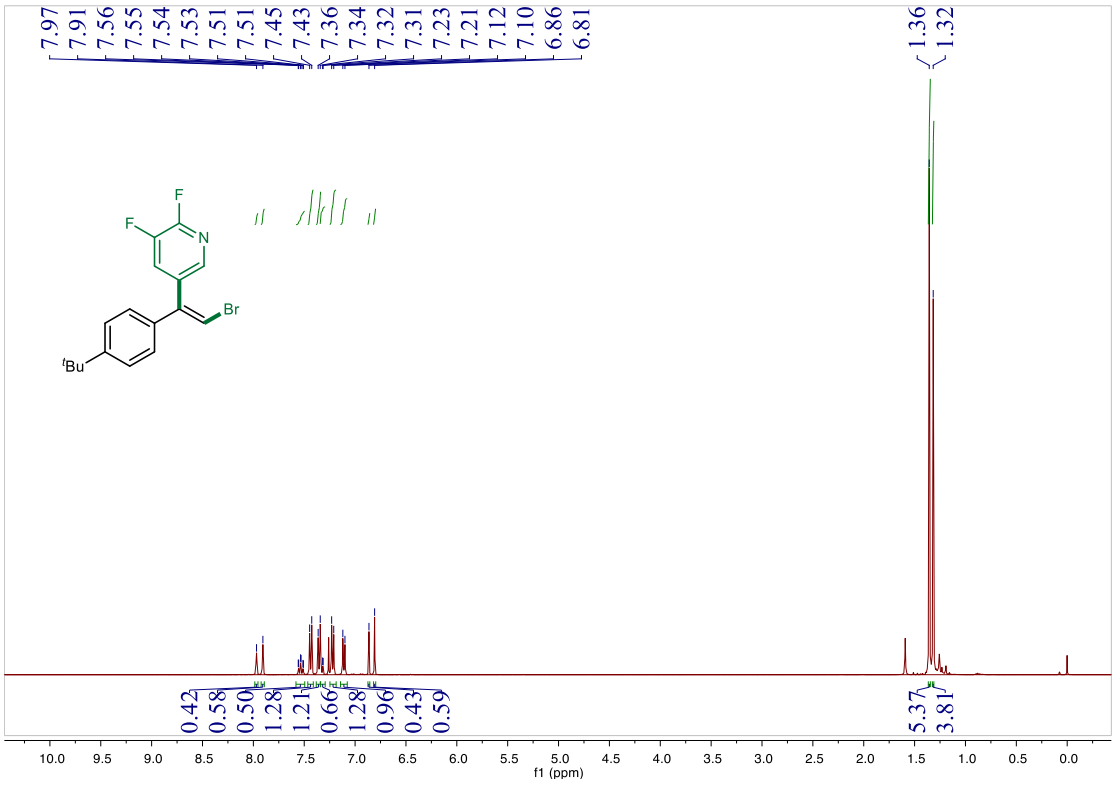
40; ^{19}F NMR (564 MHz, $CDCl_3$)



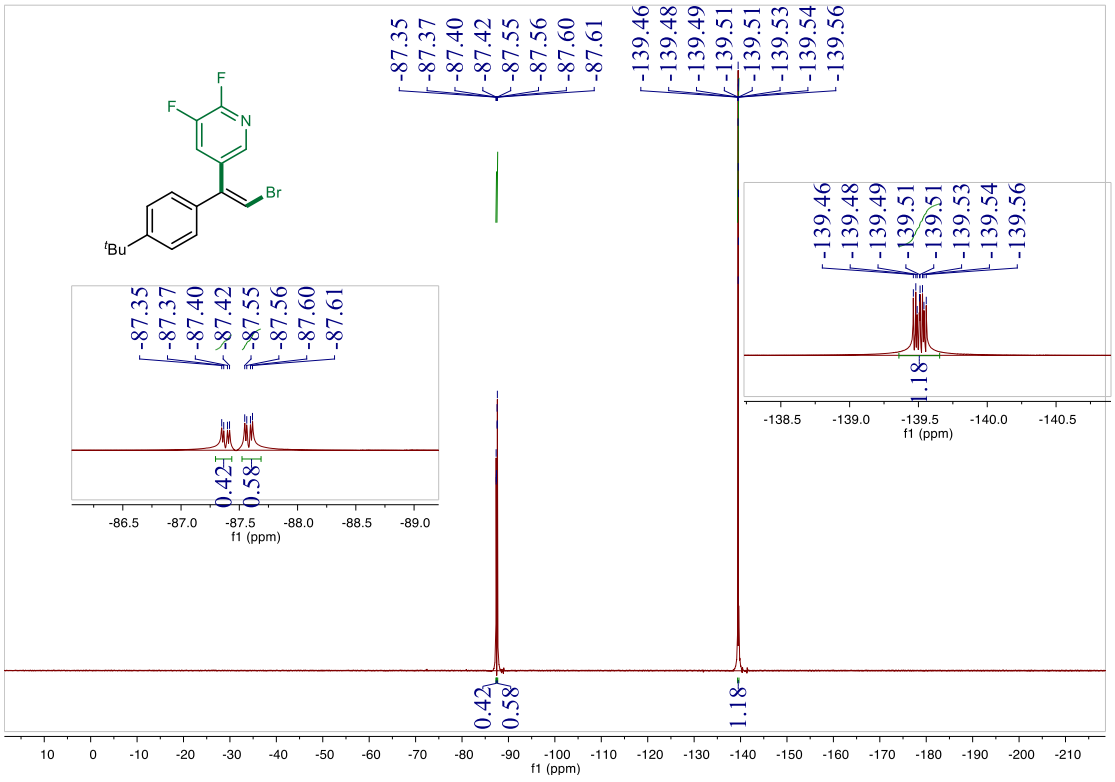
40; ^{13}C NMR (150 MHz, $CDCl_3$)



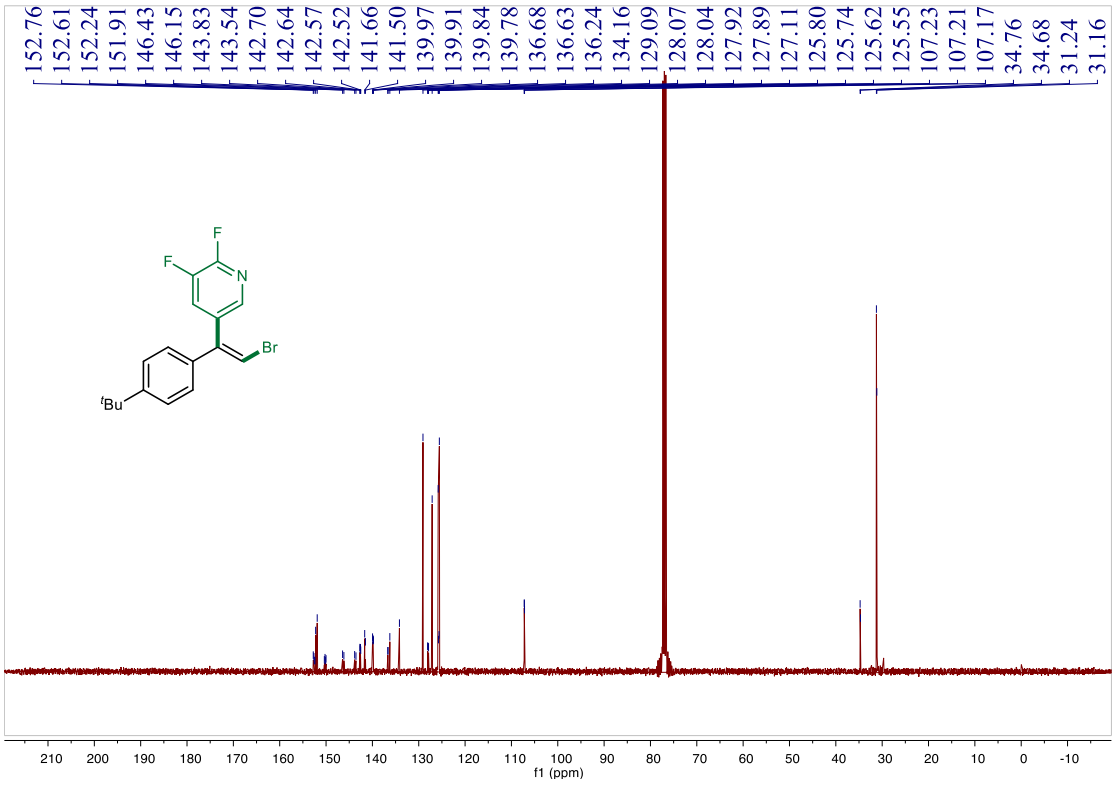
41; ^{1}H NMR (400 MHz, $CDCl_3$)



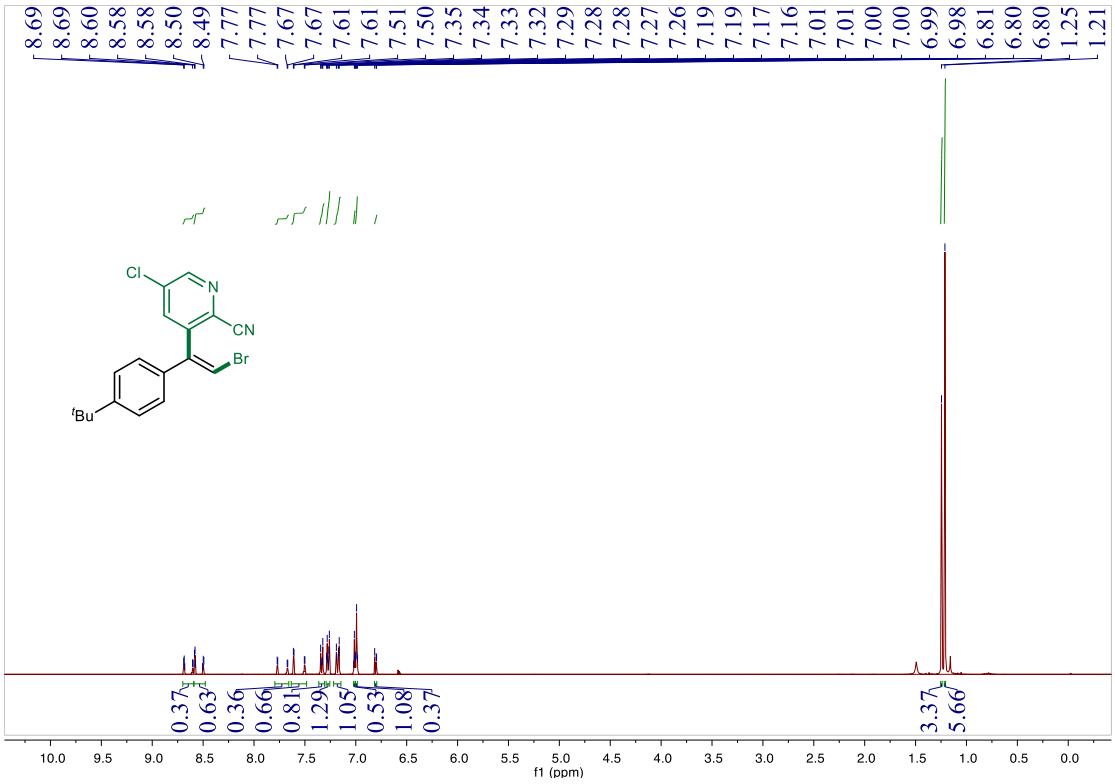
41; ^{19}F NMR (376 MHz, $CDCl_3$)



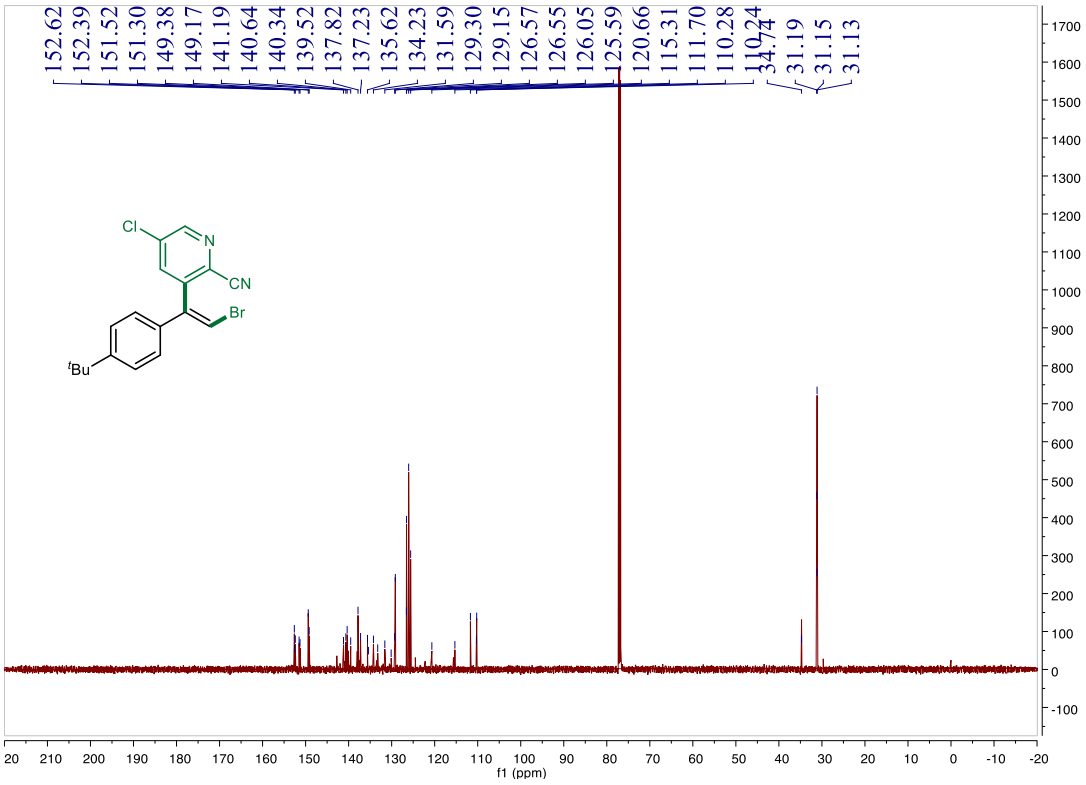
41; ^{13}C NMR (100 MHz, $CDCl_3$)



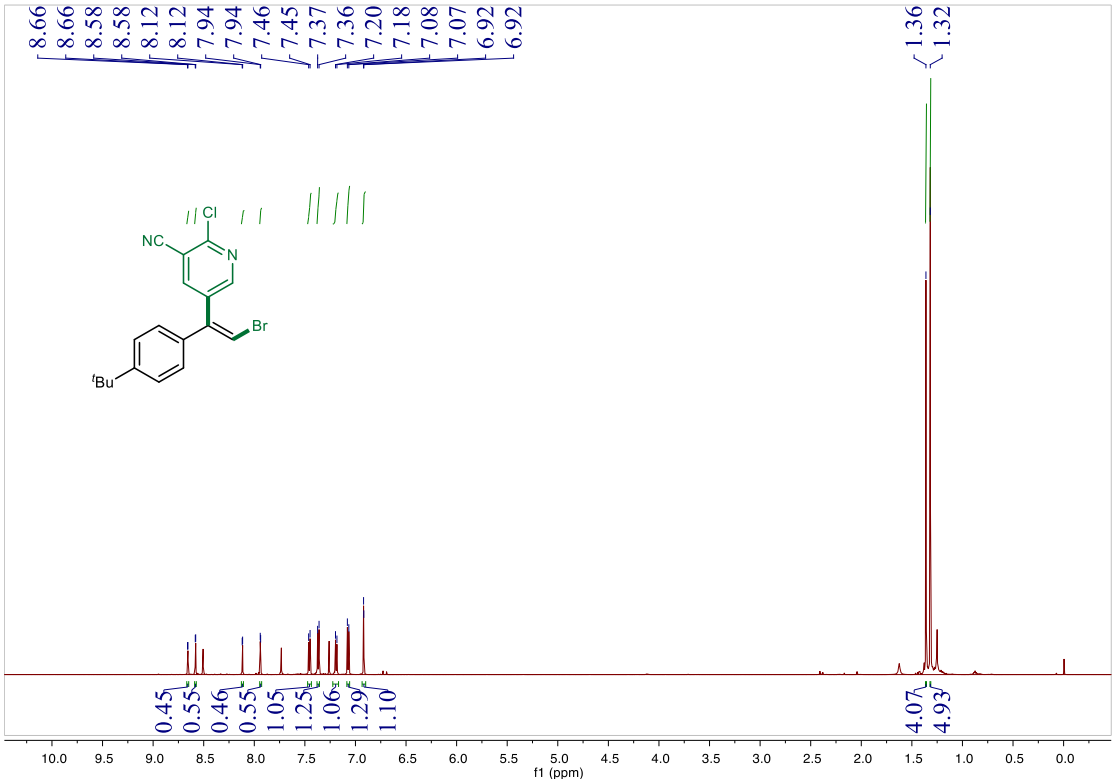
42; ^{1}H NMR (400 MHz, $CDCl_3$)



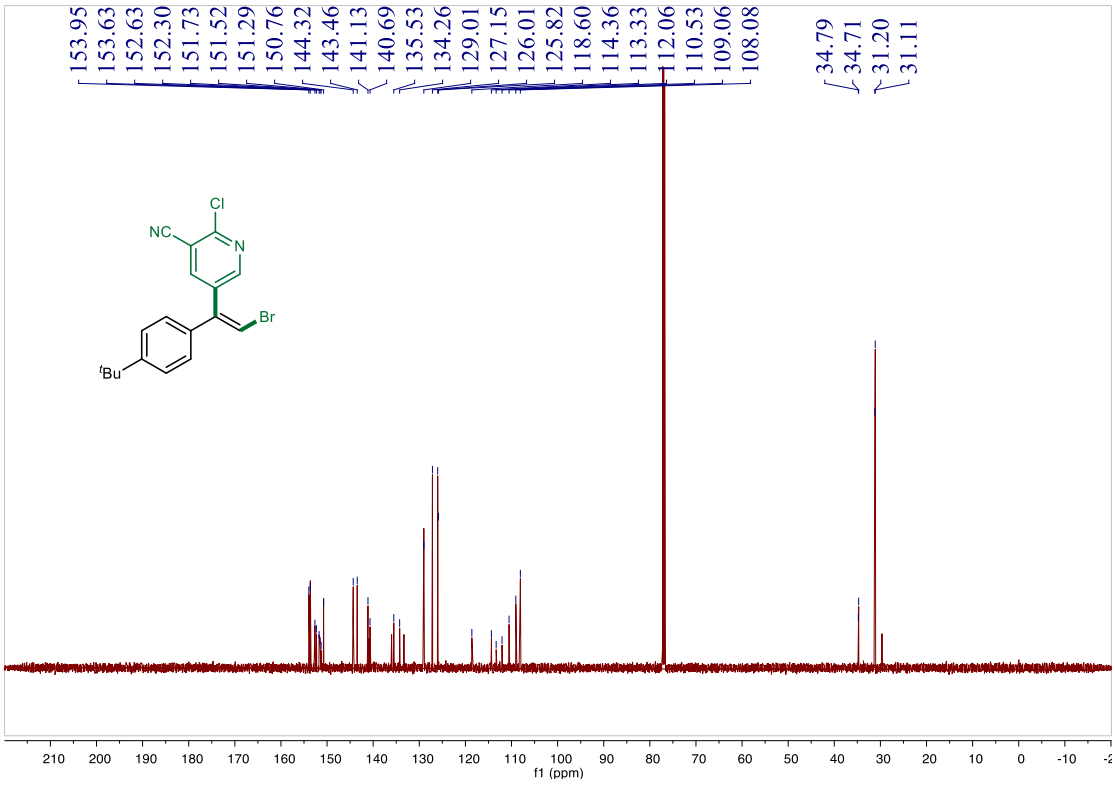
42; ^{13}C NMR (100 MHz, $CDCl_3$)



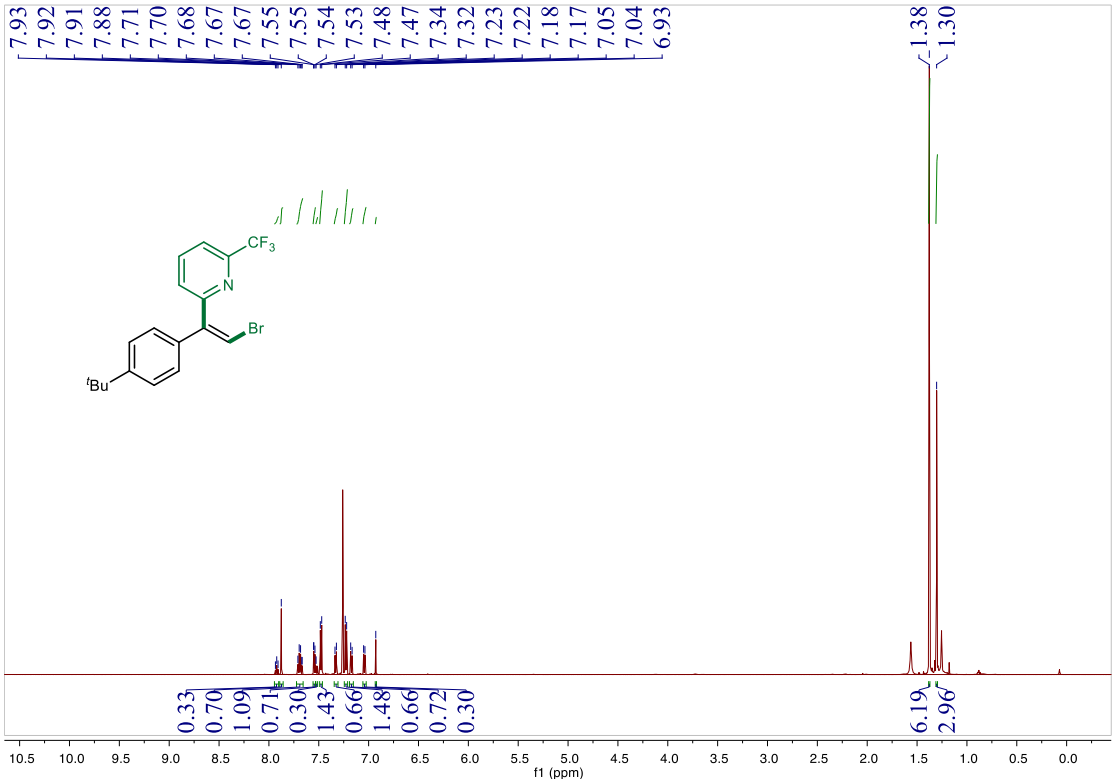
43; ^{1}H NMR (400 MHz, $CDCl_3$)



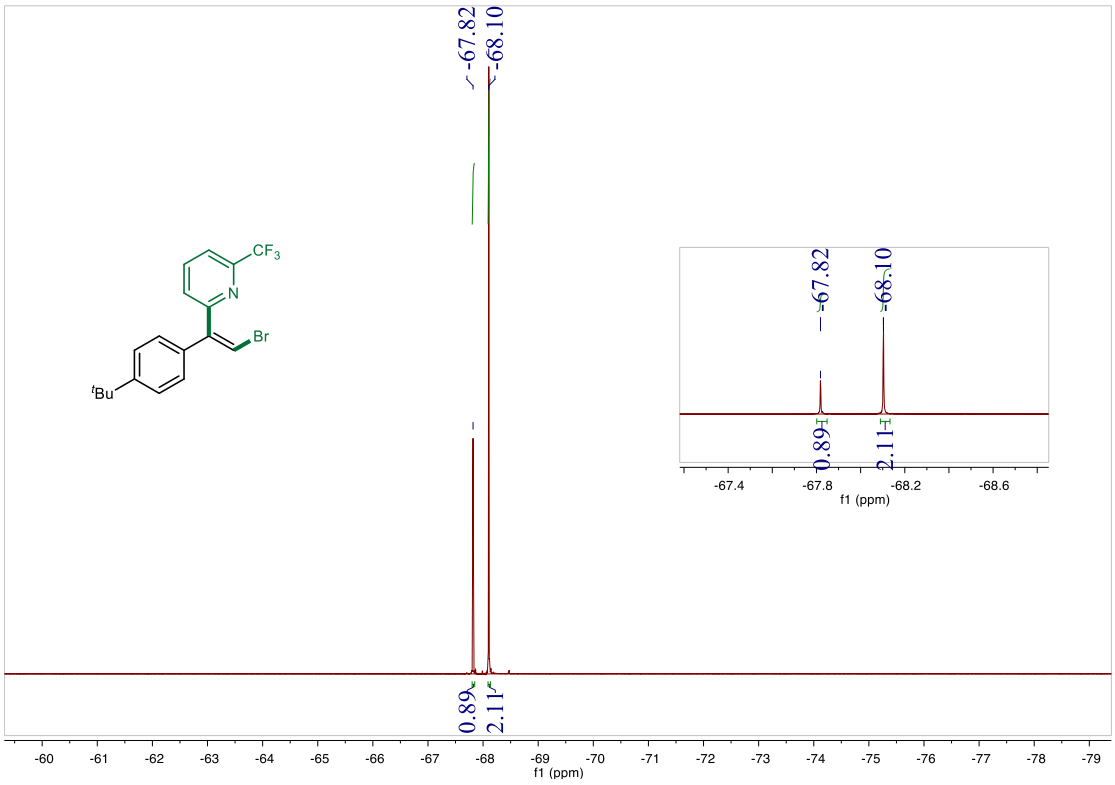
43; ^{13}C NMR (100 MHz, $CDCl_3$)



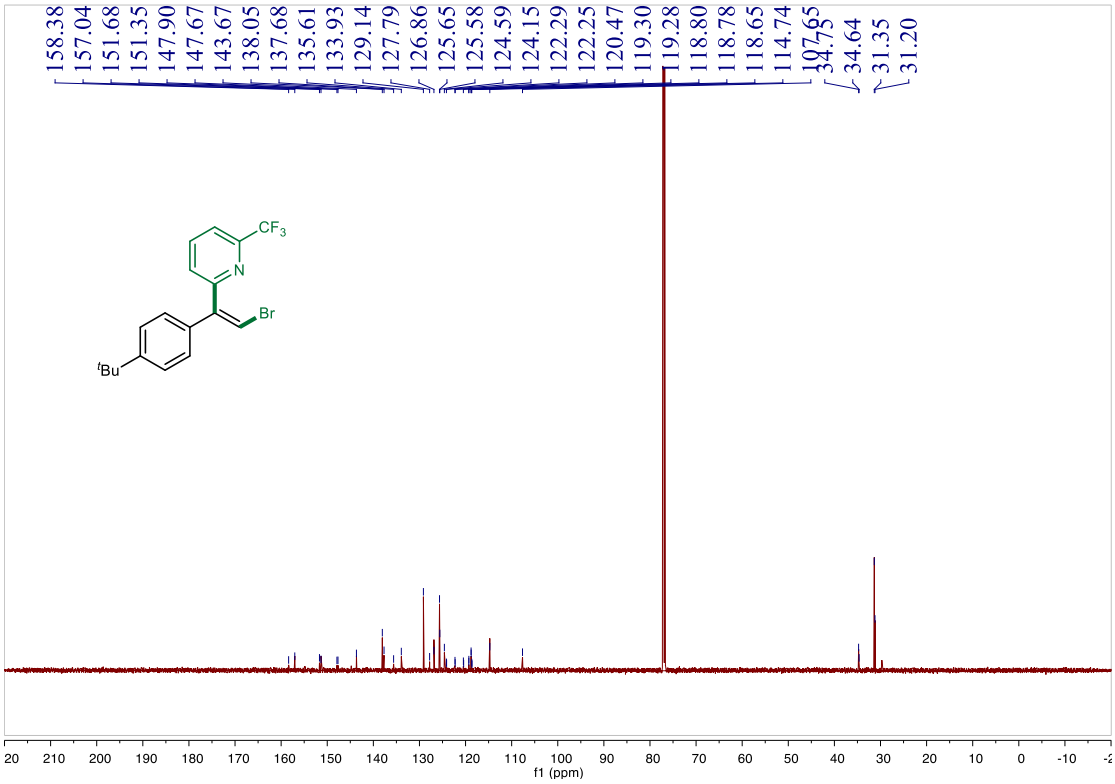
44; ^{1}H NMR (600 MHz, $CDCl_3$)



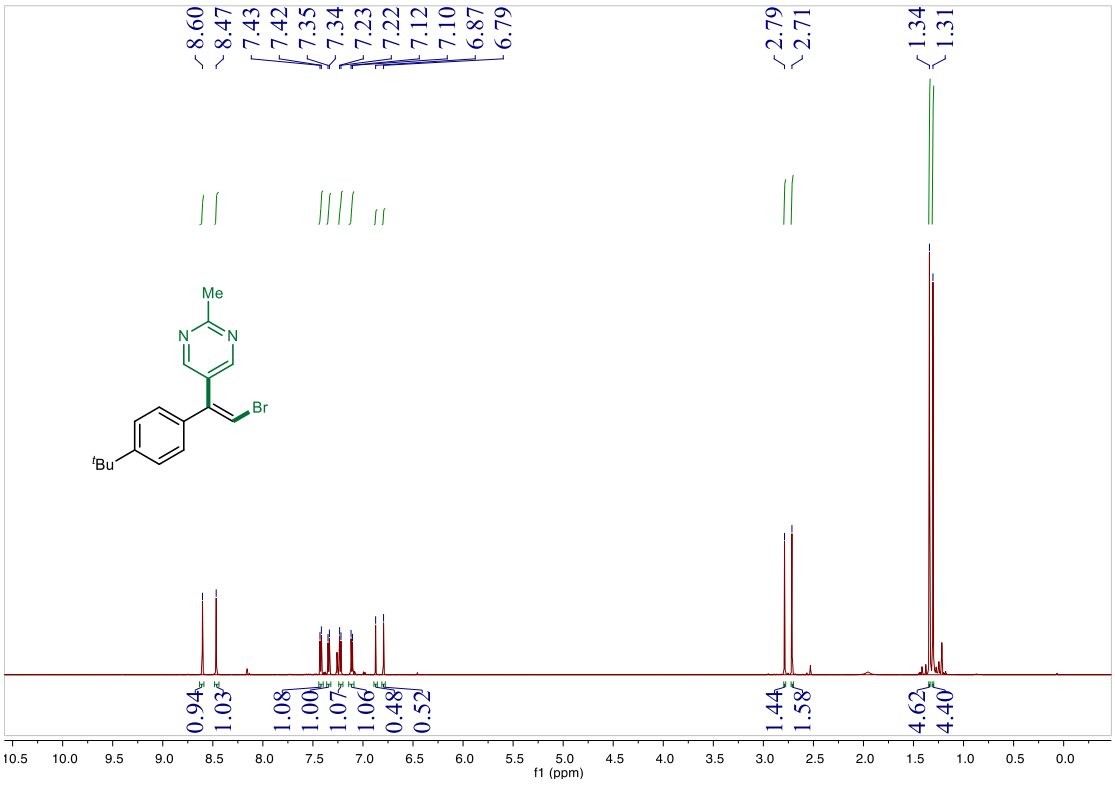
44; ^{19}F NMR (564 MHz, $CDCl_3$)



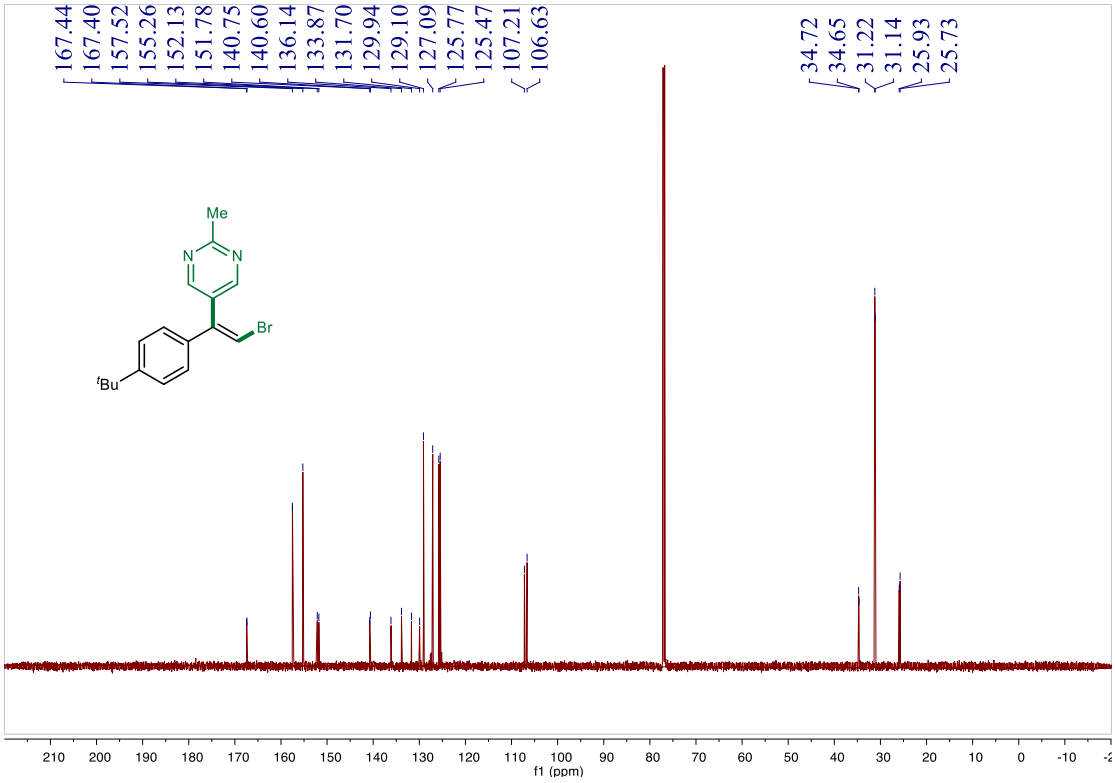
44; ^{13}C NMR (150 MHz, $CDCl_3$)



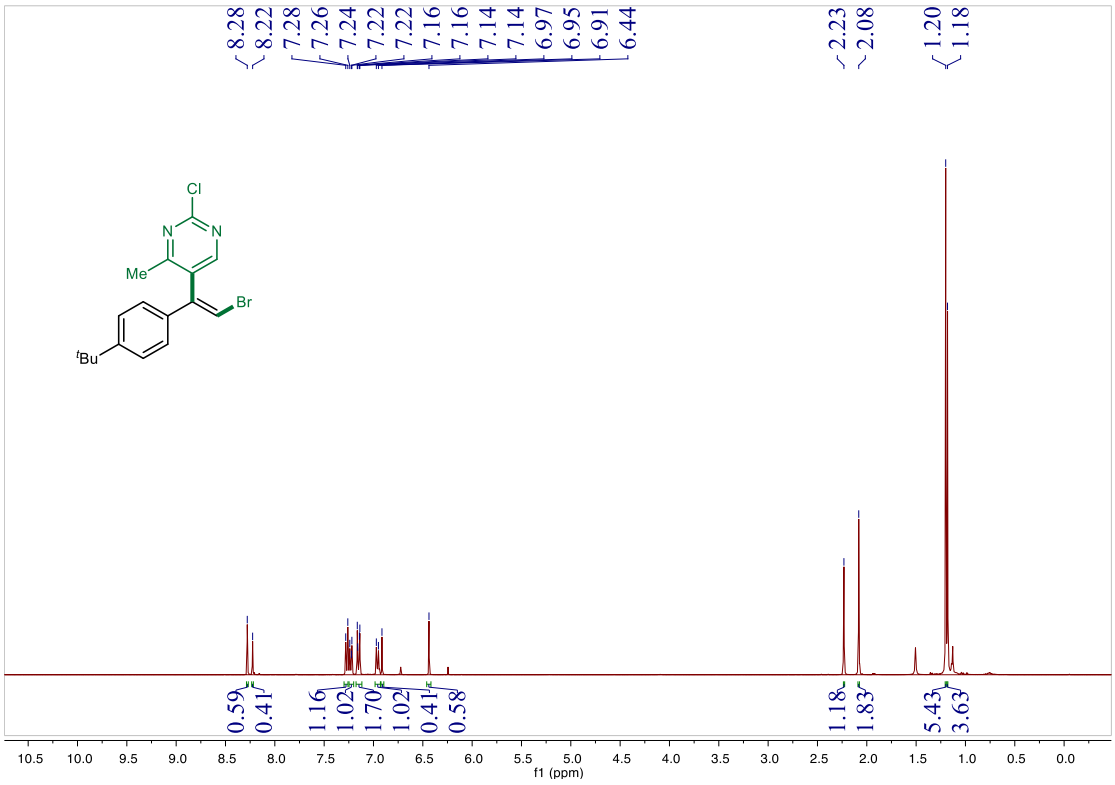
45; ^{1}H NMR (600 MHz, $CDCl_3$)



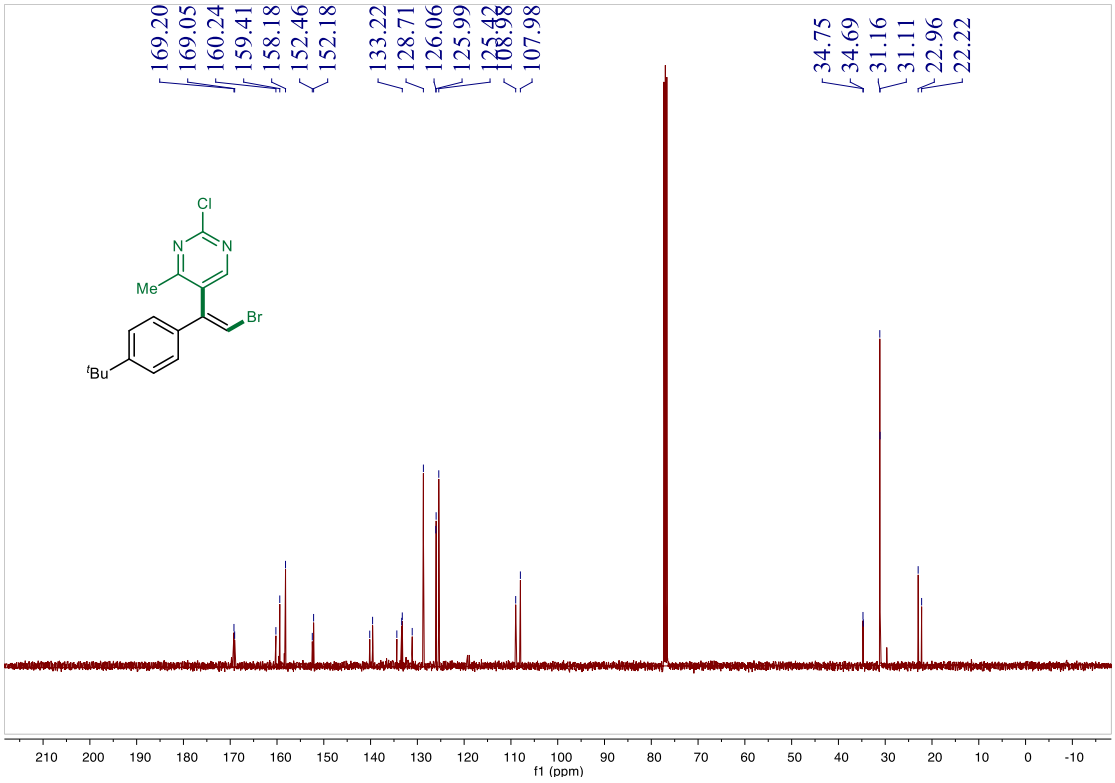
45; ^{13}C NMR (150 MHz, $CDCl_3$)



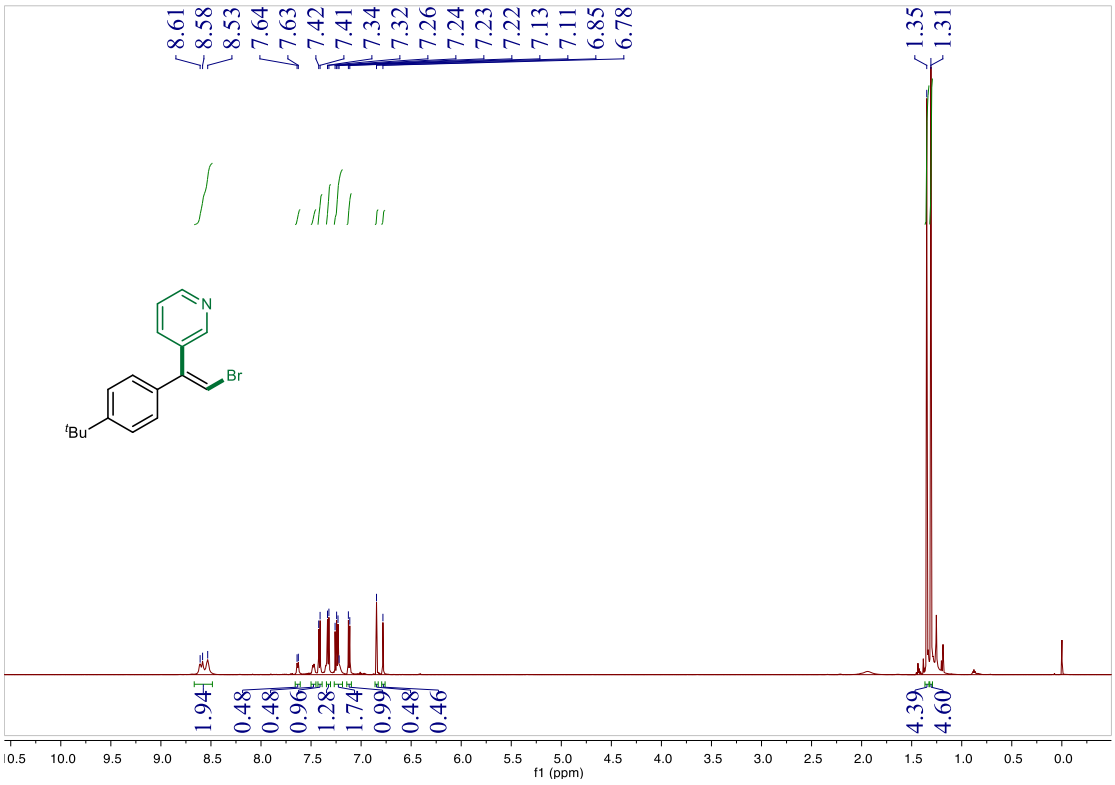
46; ^{1}H NMR (400 MHz, $CDCl_3$)



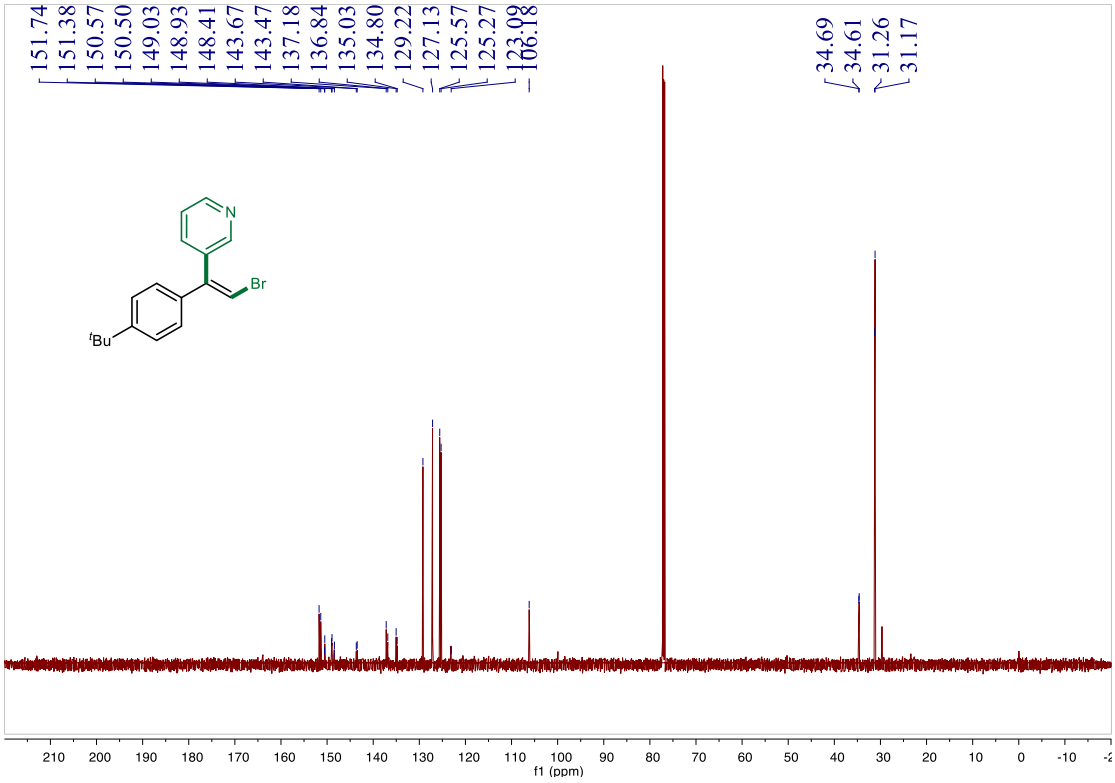
46; ^{13}C NMR (100 MHz, $CDCl_3$)



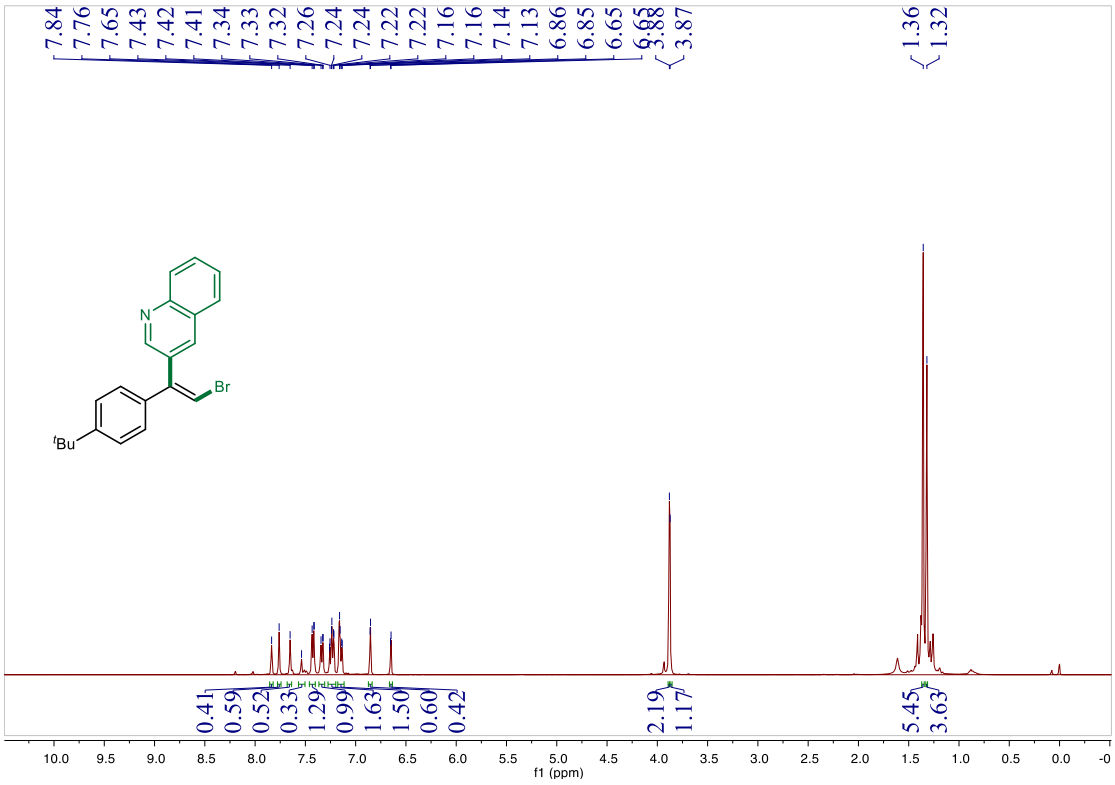
47; ^{1}H NMR (600 MHz, $CDCl_3$)



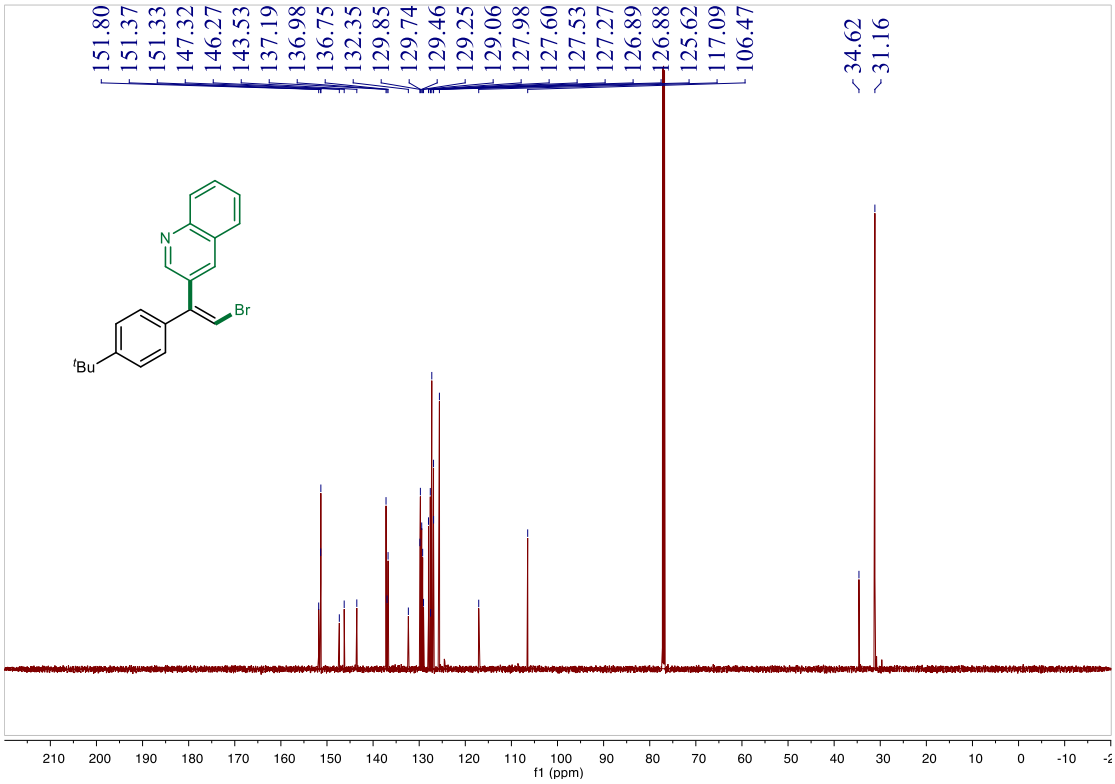
47; ^{13}C NMR (150 MHz, $CDCl_3$)



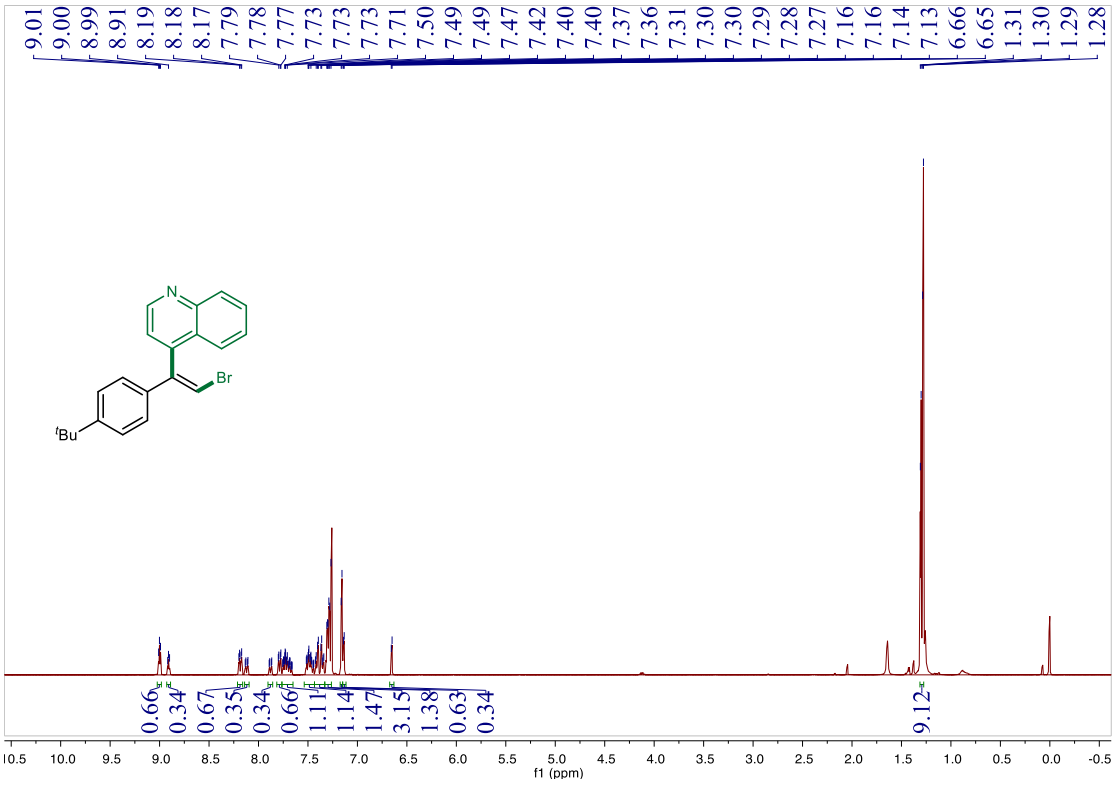
48; ^{1}H NMR (600 MHz, $CDCl_3$)



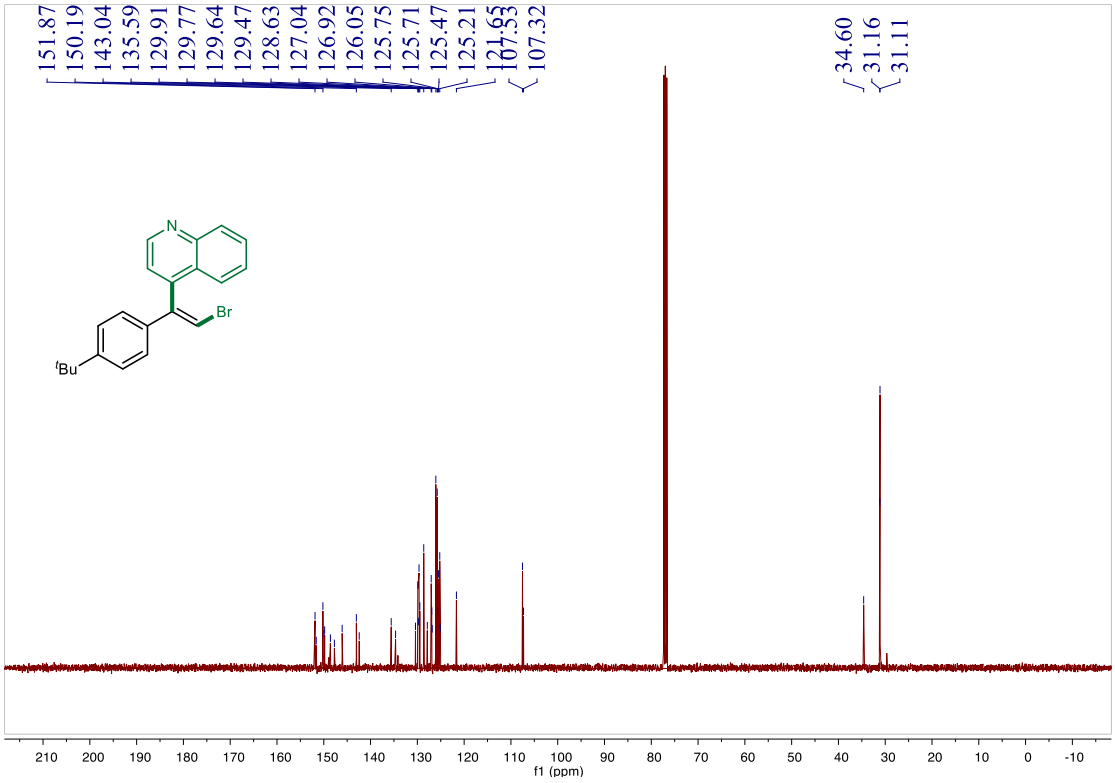
48; ^{13}C NMR (100 MHz, $CDCl_3$)



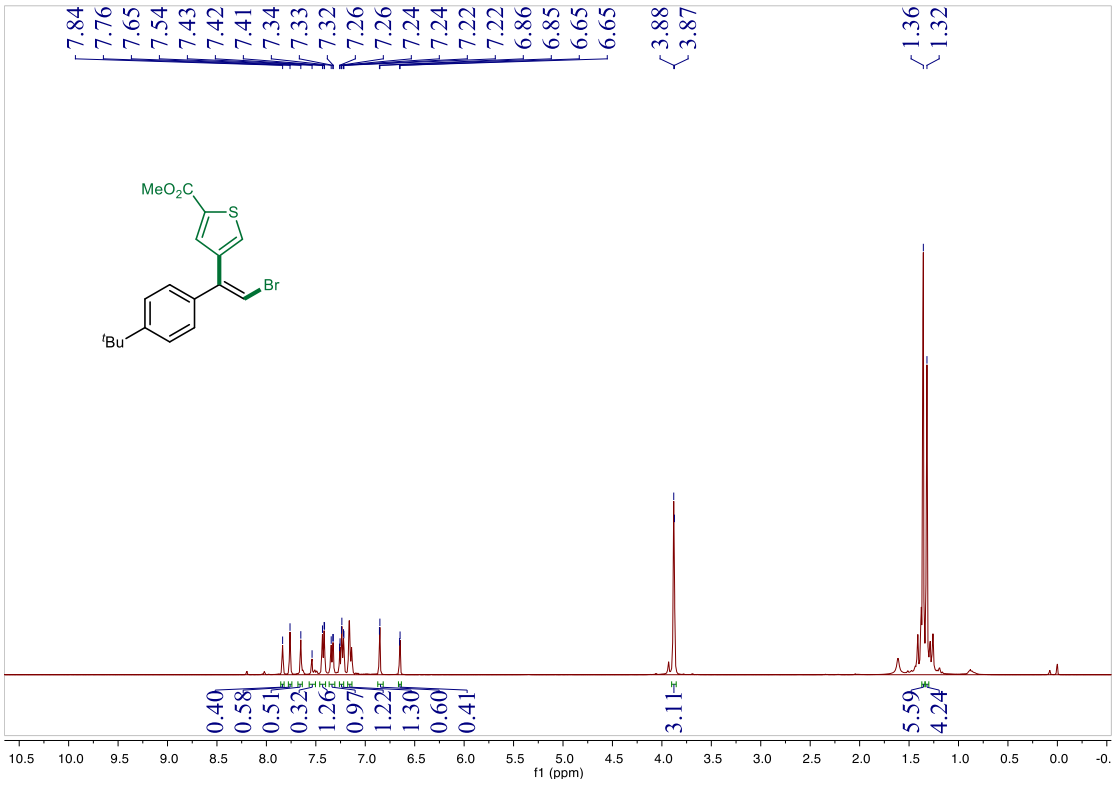
49; ^{1}H NMR (400 MHz, $CDCl_3$)



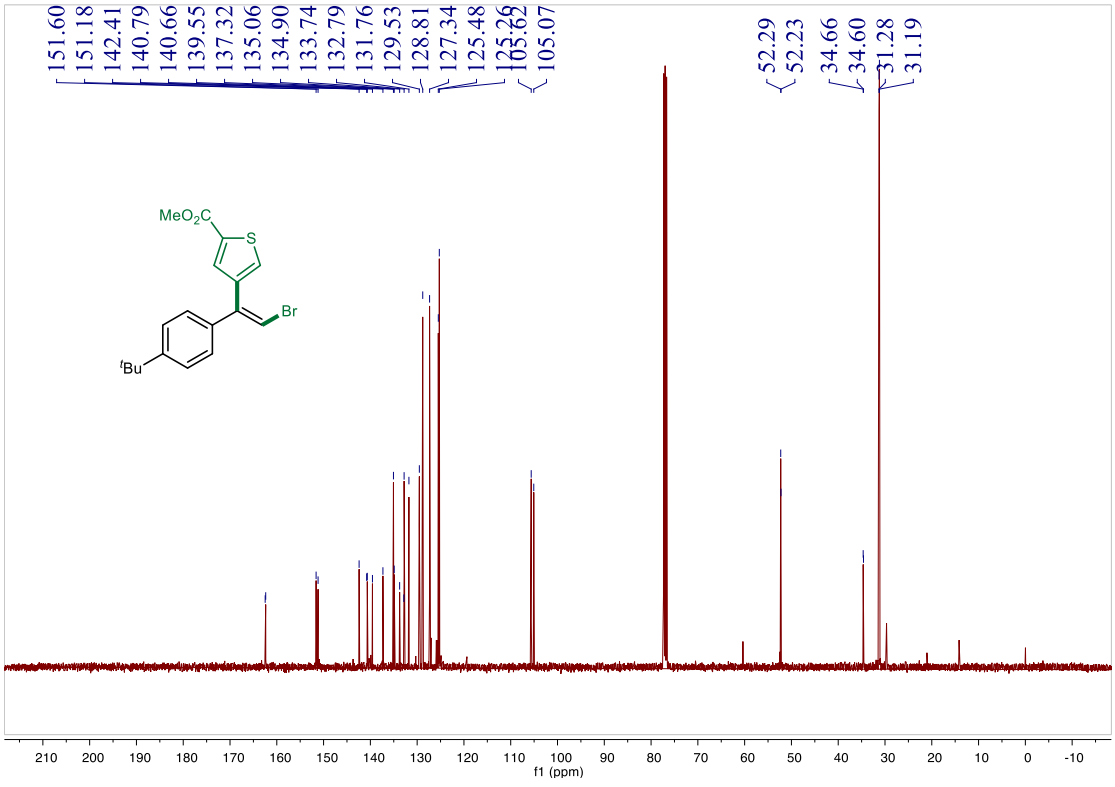
49; ^{13}C NMR (100 MHz, $CDCl_3$)



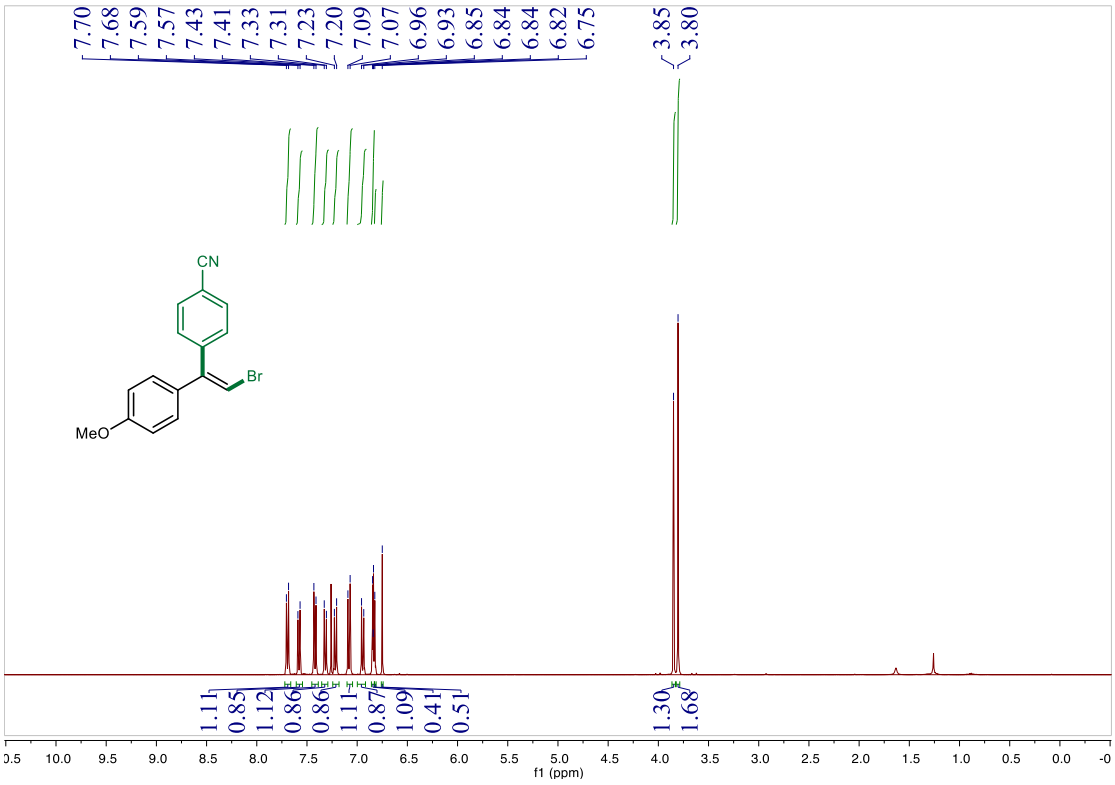
50; ^{1}H NMR (400 MHz, $CDCl_3$)



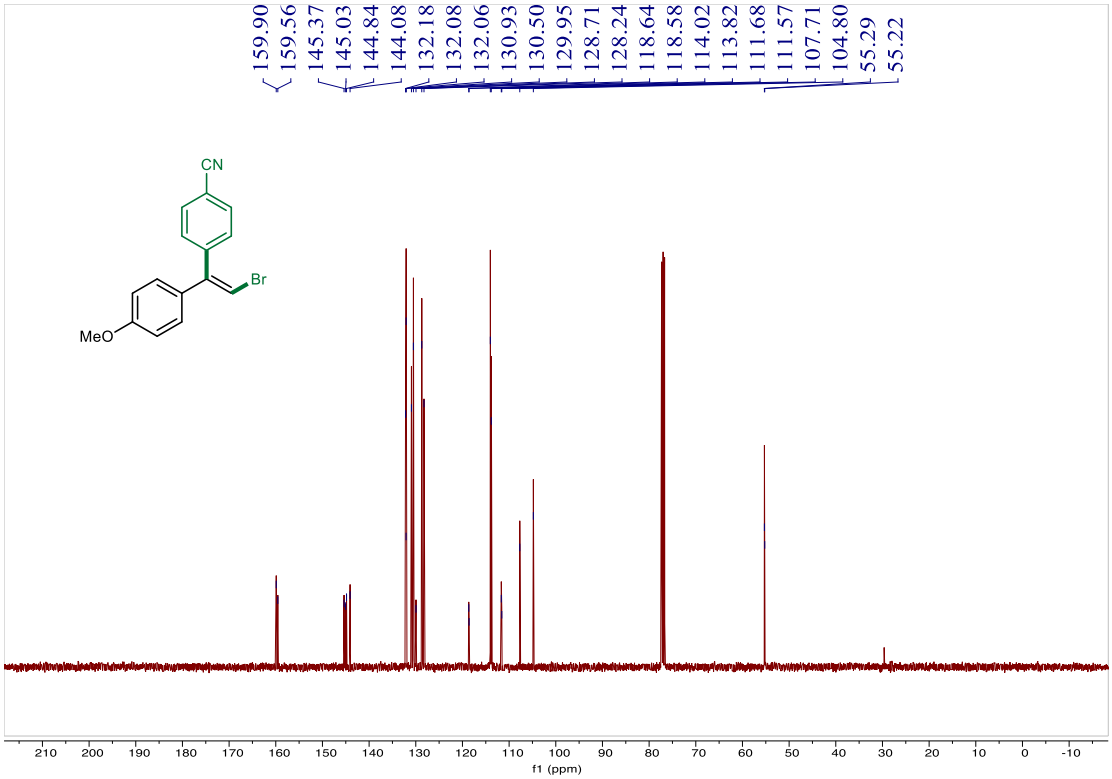
50; ^{13}C NMR (100 MHz, $CDCl_3$)



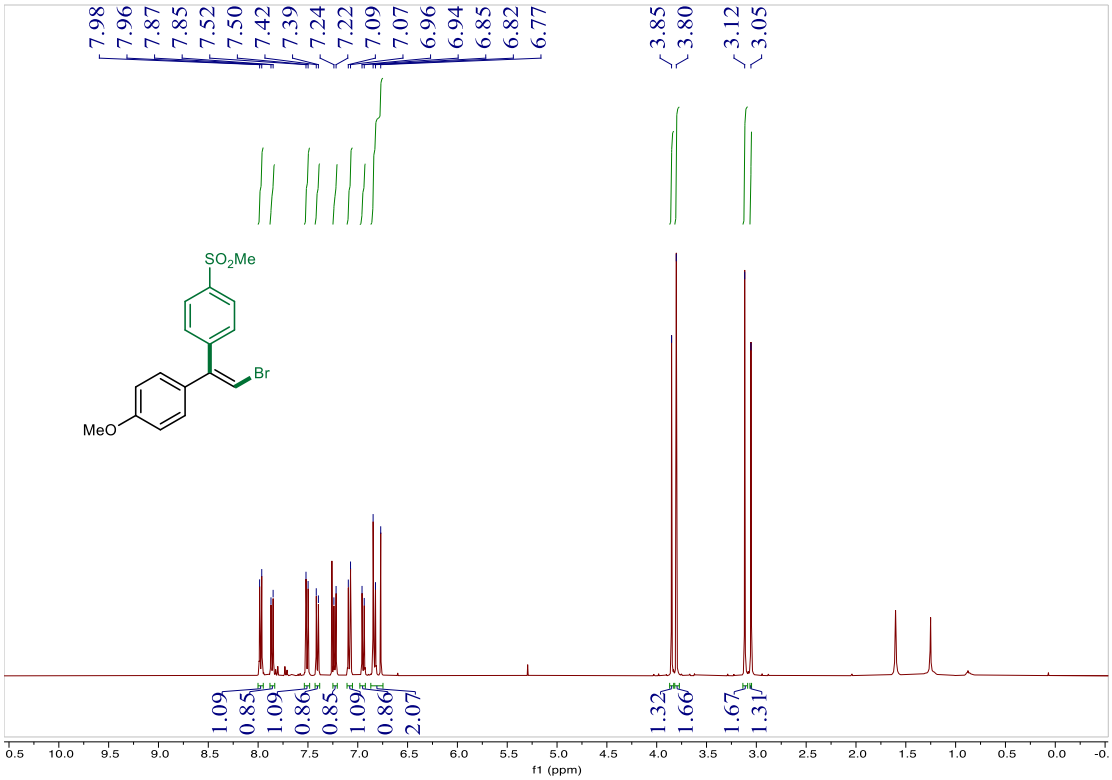
51; ^{1}H NMR (400 MHz, $CDCl_3$)



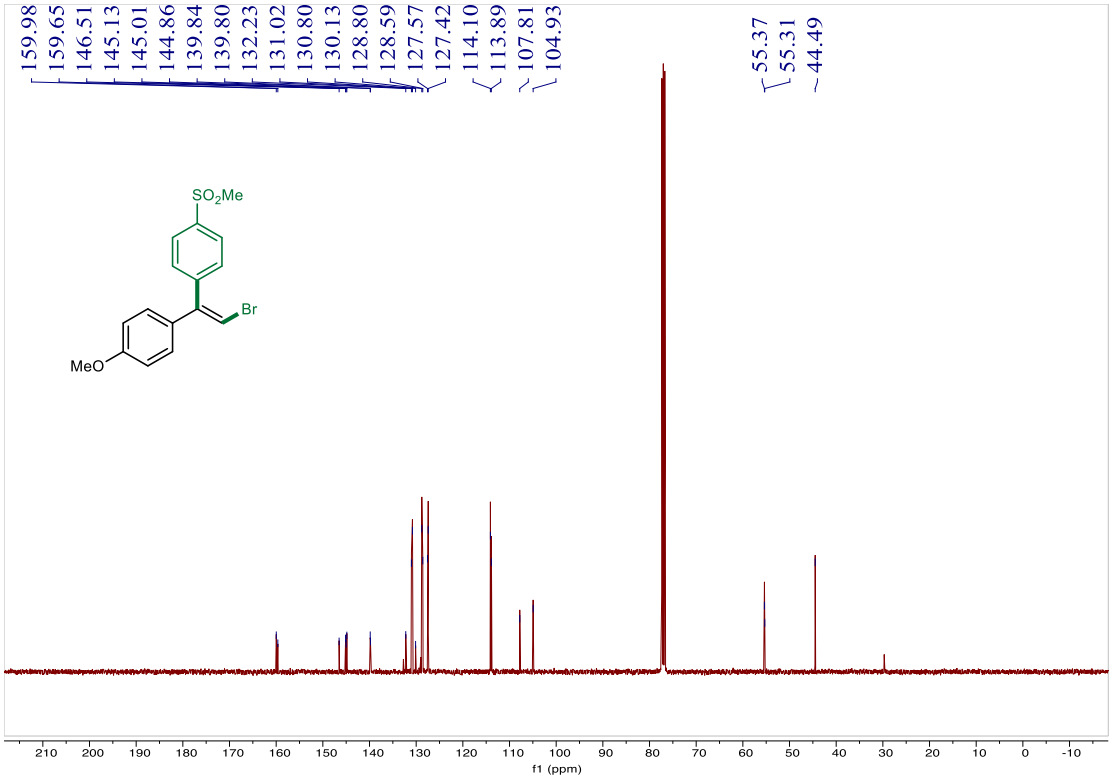
51; ^{13}C NMR (100 MHz, $CDCl_3$)



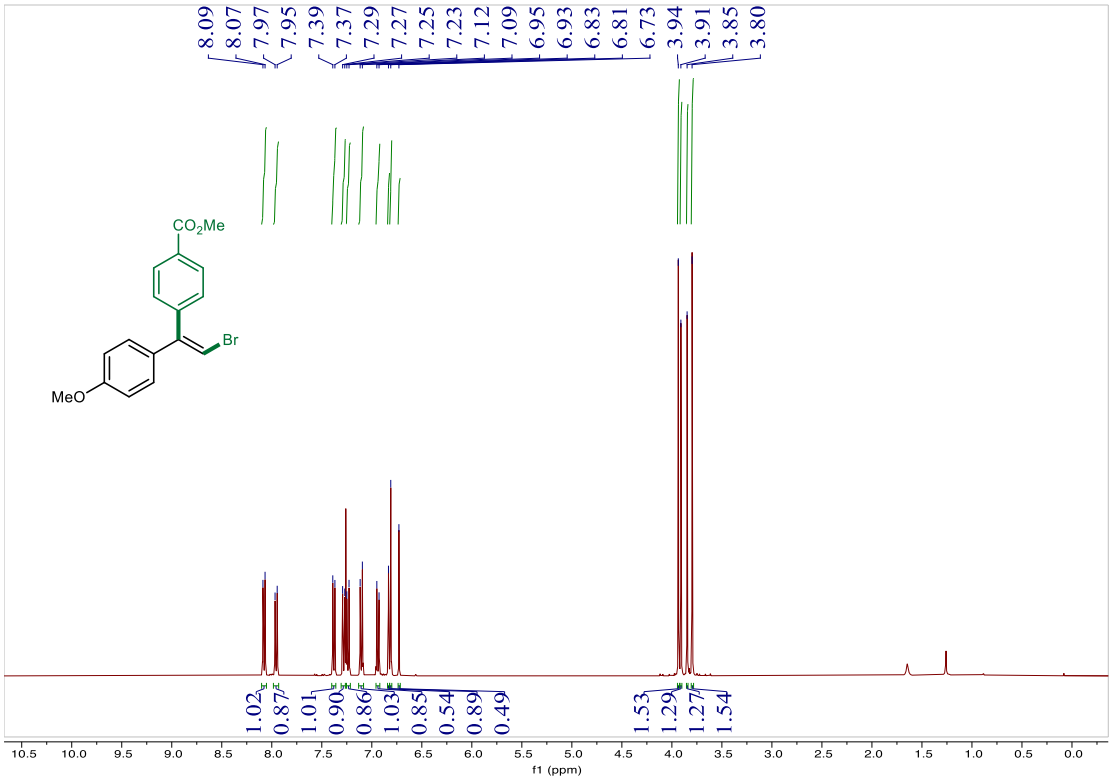
52; ^{1}H NMR (400 MHz, $CDCl_3$)



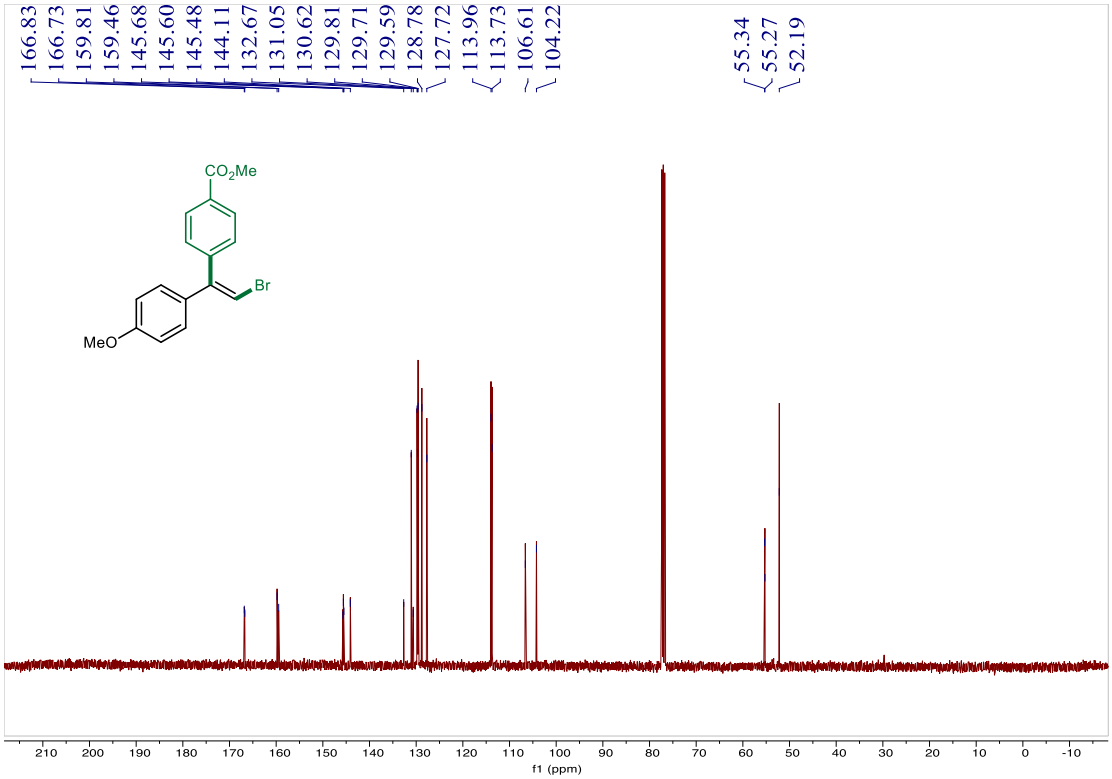
52; ^{13}C NMR (100 MHz, $CDCl_3$)



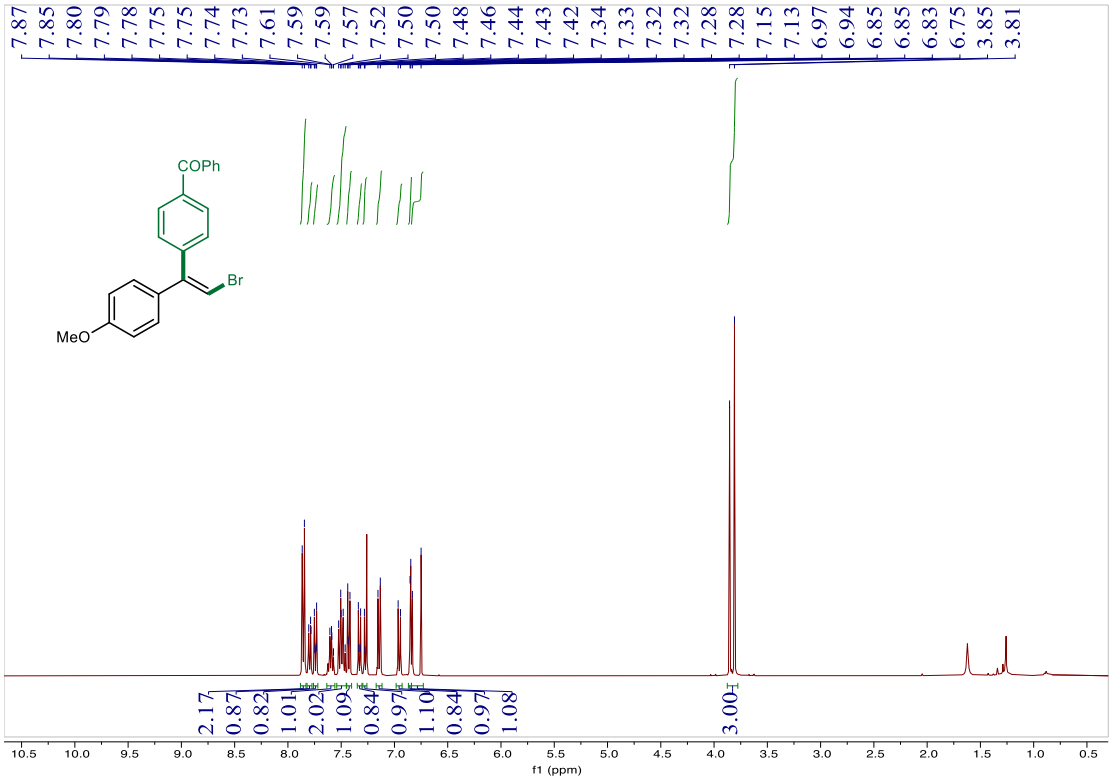
53; ^{1}H NMR (400 MHz, $CDCl_3$)



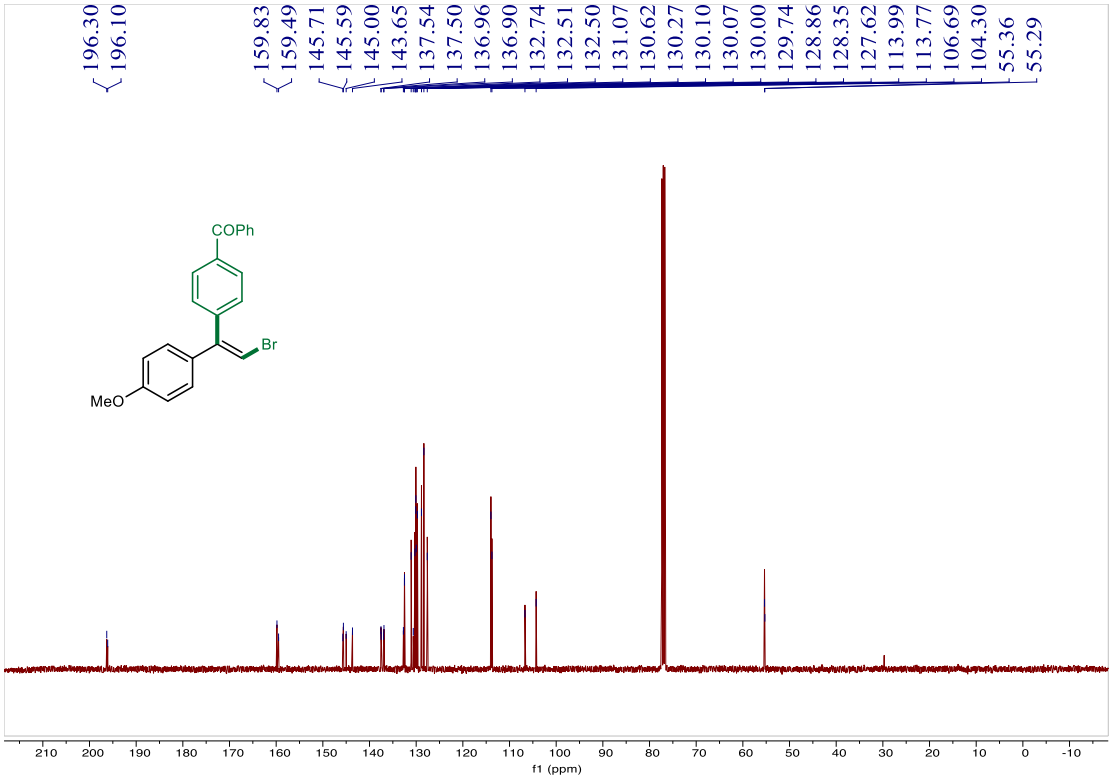
53; ^{13}C NMR (100 MHz, $CDCl_3$)



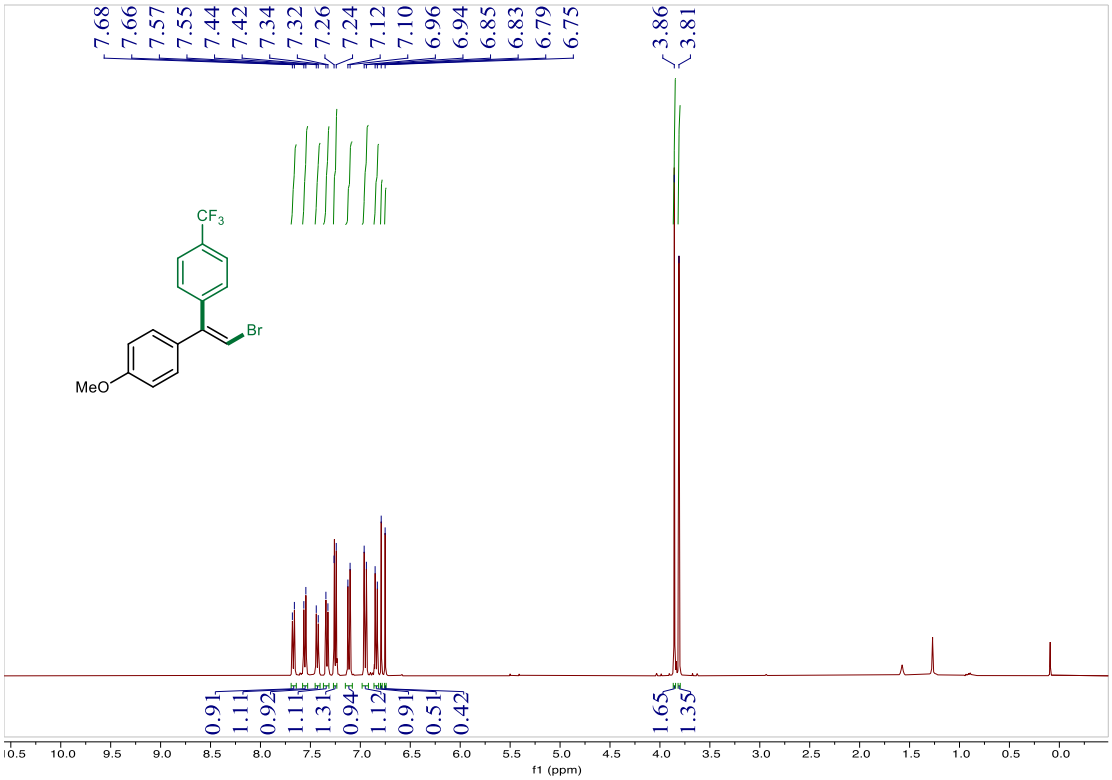
54; ^{1}H NMR (400 MHz, $CDCl_3$)



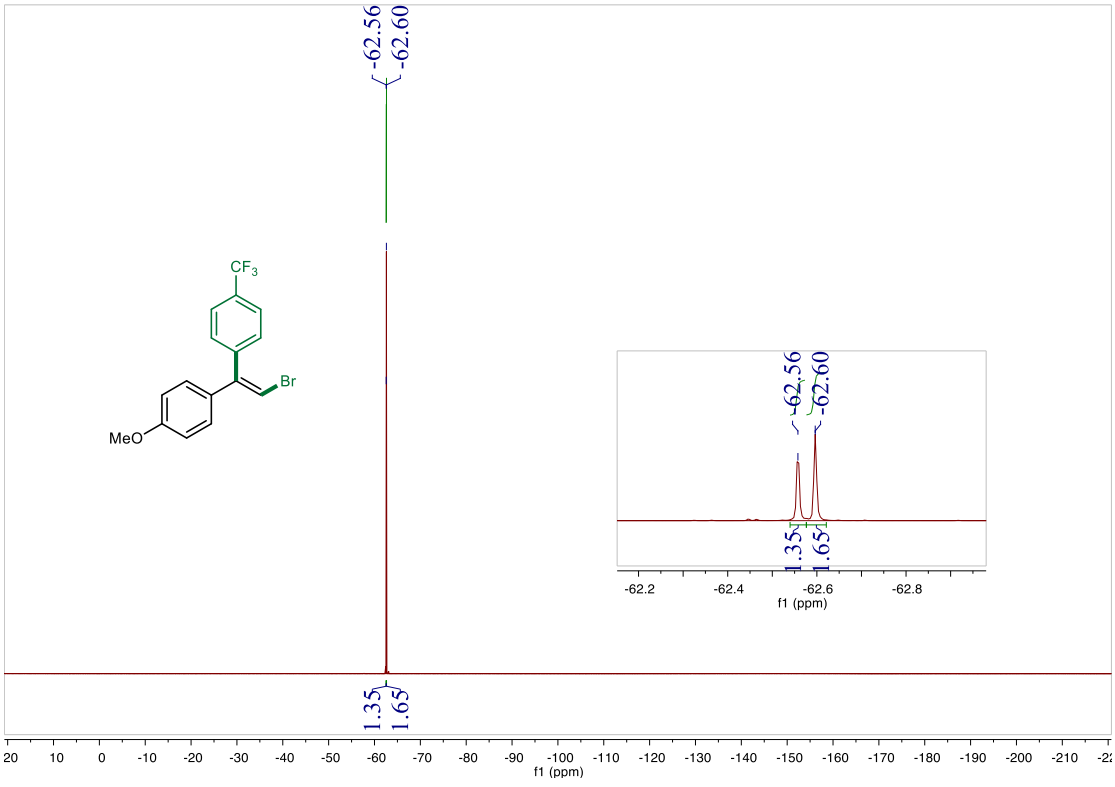
54; ^{13}C NMR (100 MHz, $CDCl_3$)



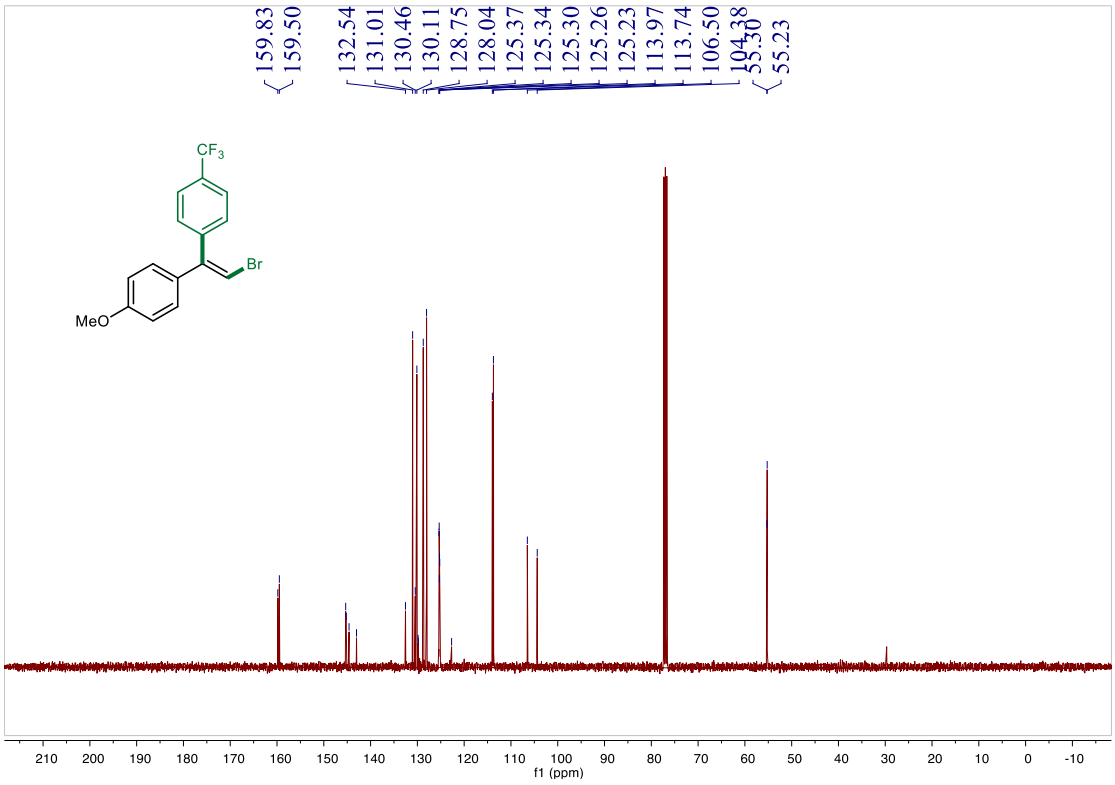
55; ^{1}H NMR (400 MHz, $CDCl_3$)



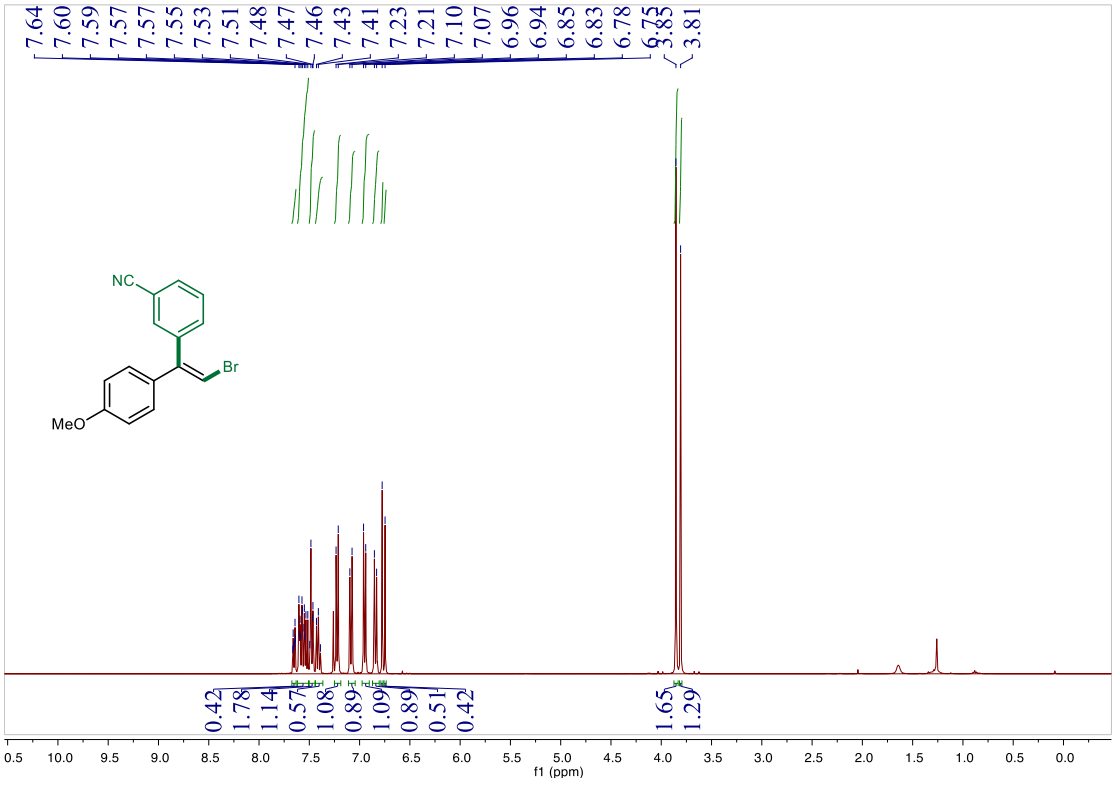
55; ^{19}F NMR (376 MHz, $CDCl_3$)



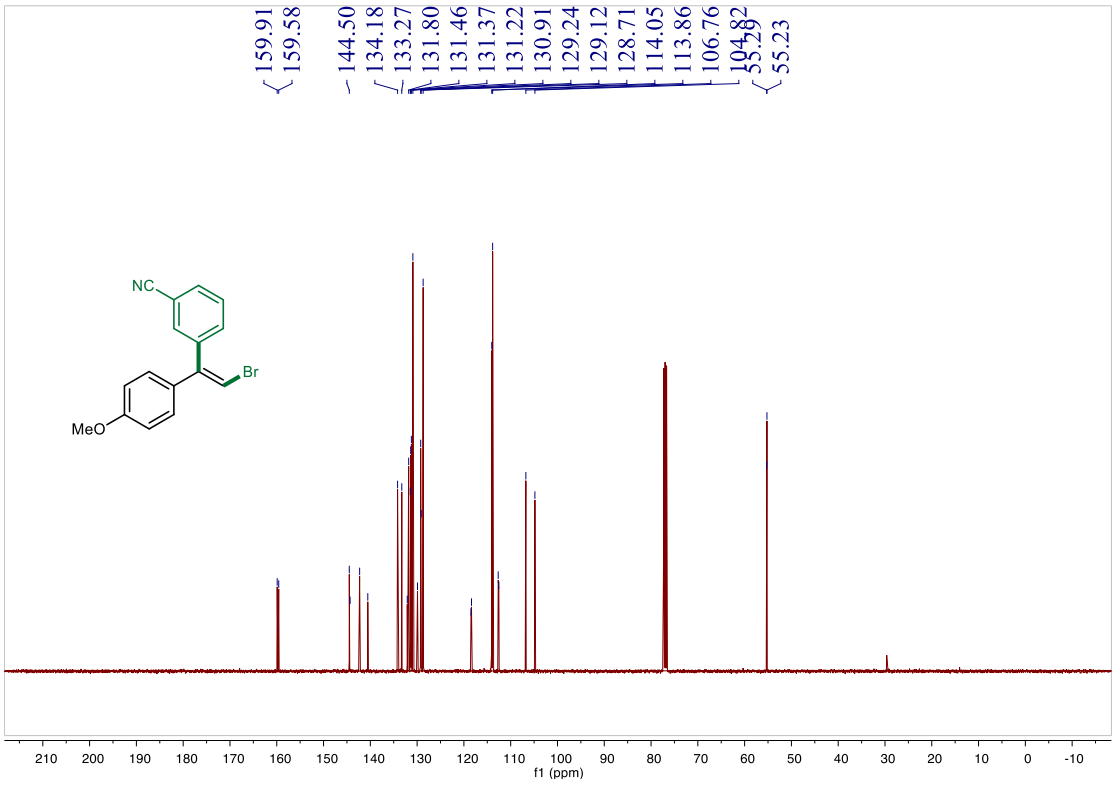
55; ^{13}C NMR (100 MHz, $CDCl_3$)



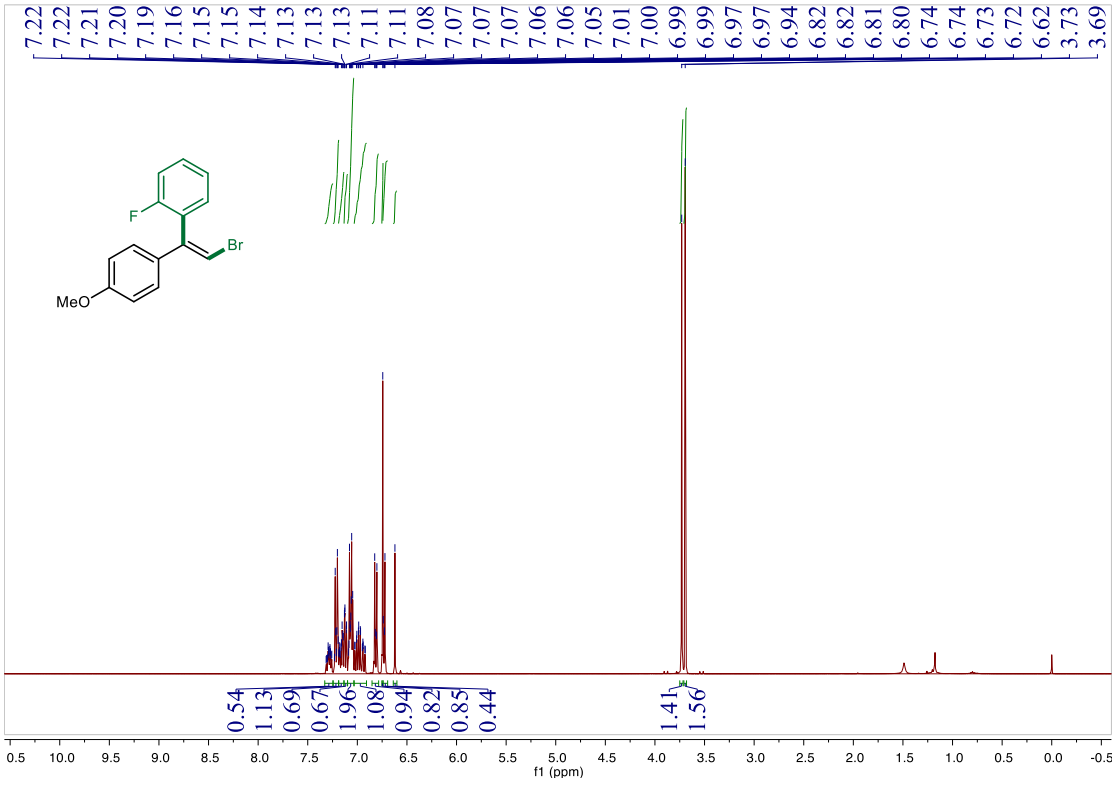
56; ^{1}H NMR (400 MHz, $CDCl_3$)



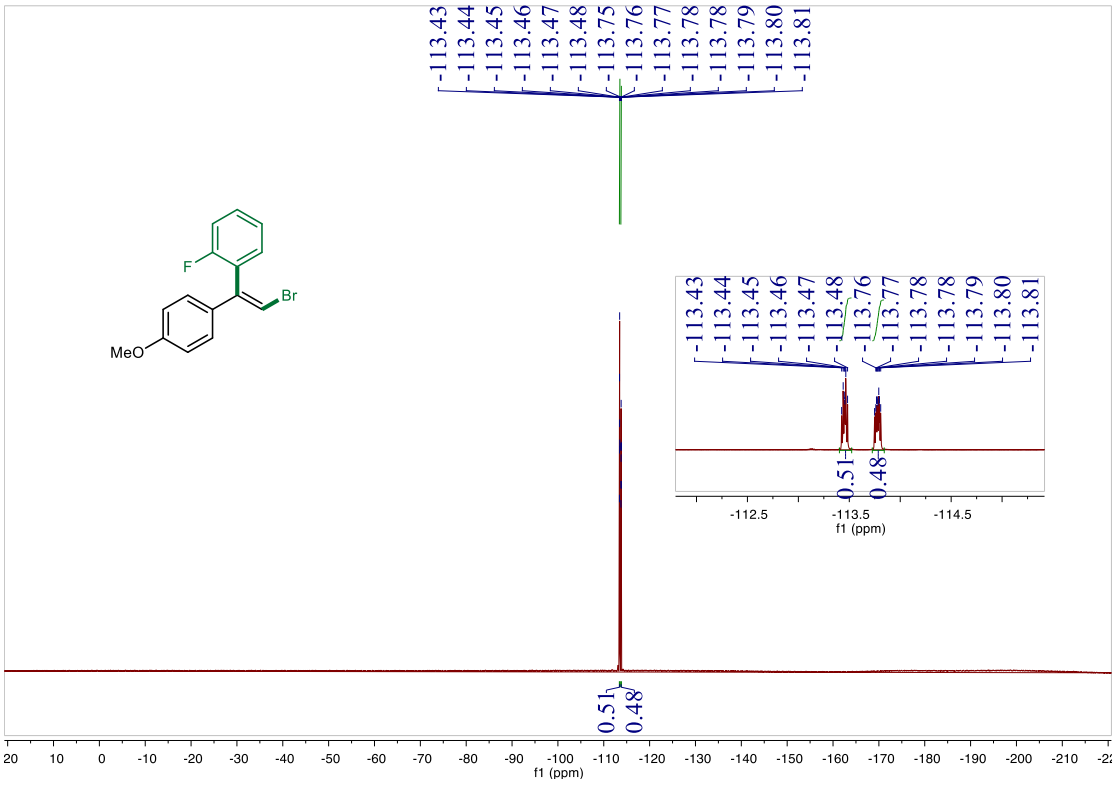
56; ^{13}C NMR (100 MHz, $CDCl_3$)



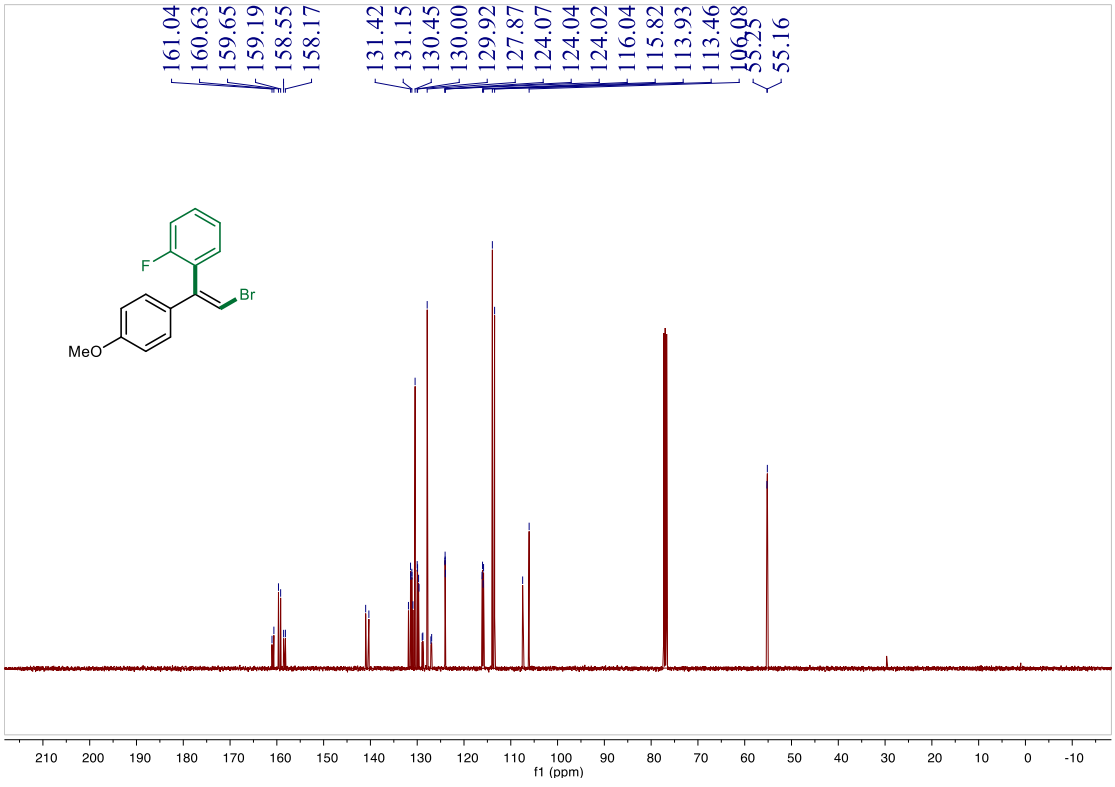
57; ^{1}H NMR (400 MHz, $CDCl_3$)



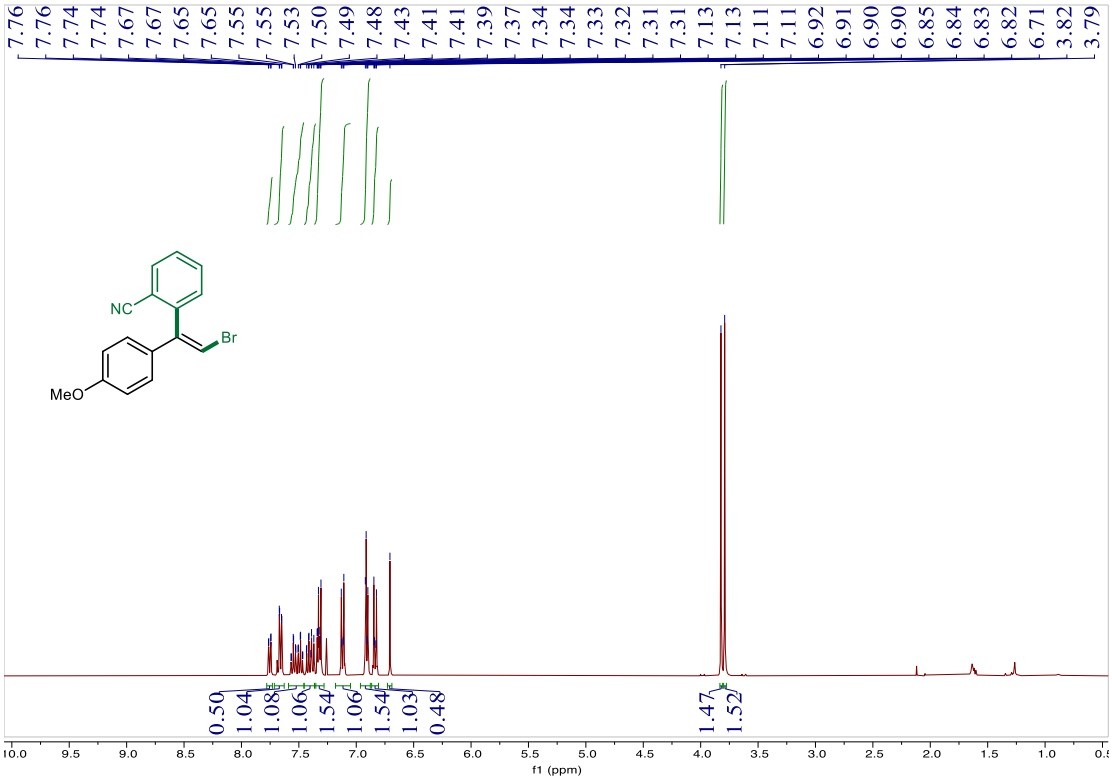
57; ^{19}F NMR (376 MHz, $CDCl_3$)



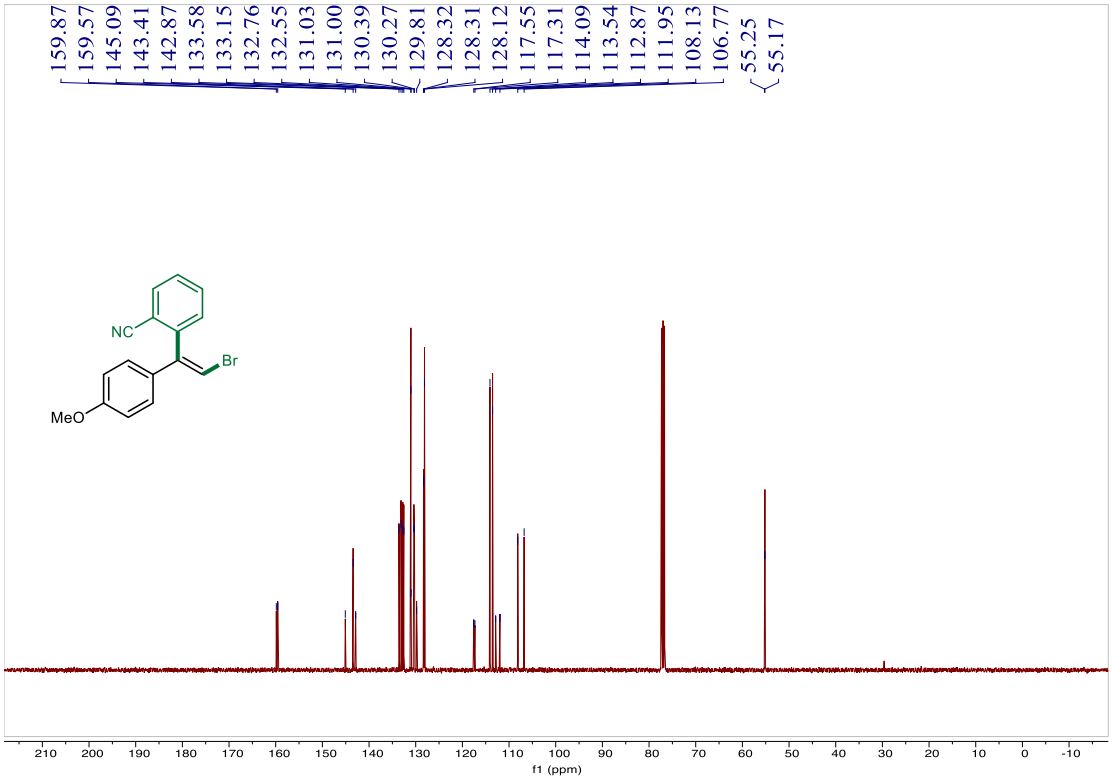
57; ^{13}C NMR (100 MHz, $CDCl_3$)



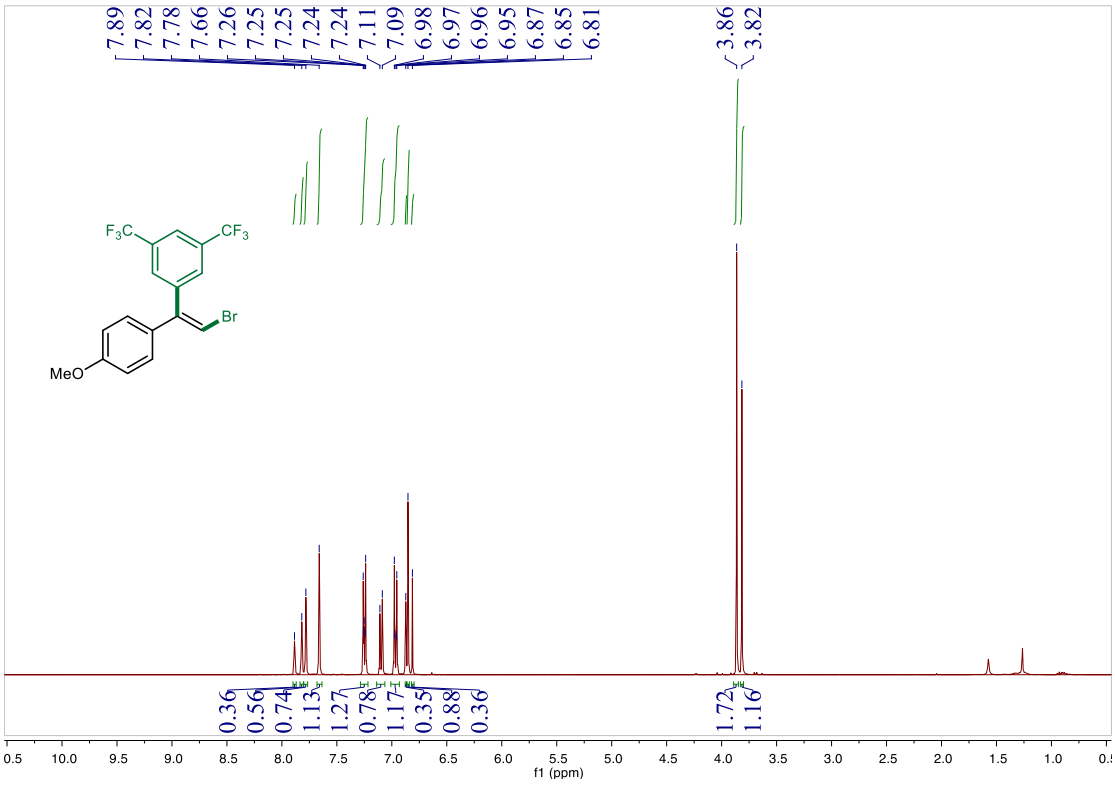
58; ^{1}H NMR (400 MHz, $CDCl_3$)



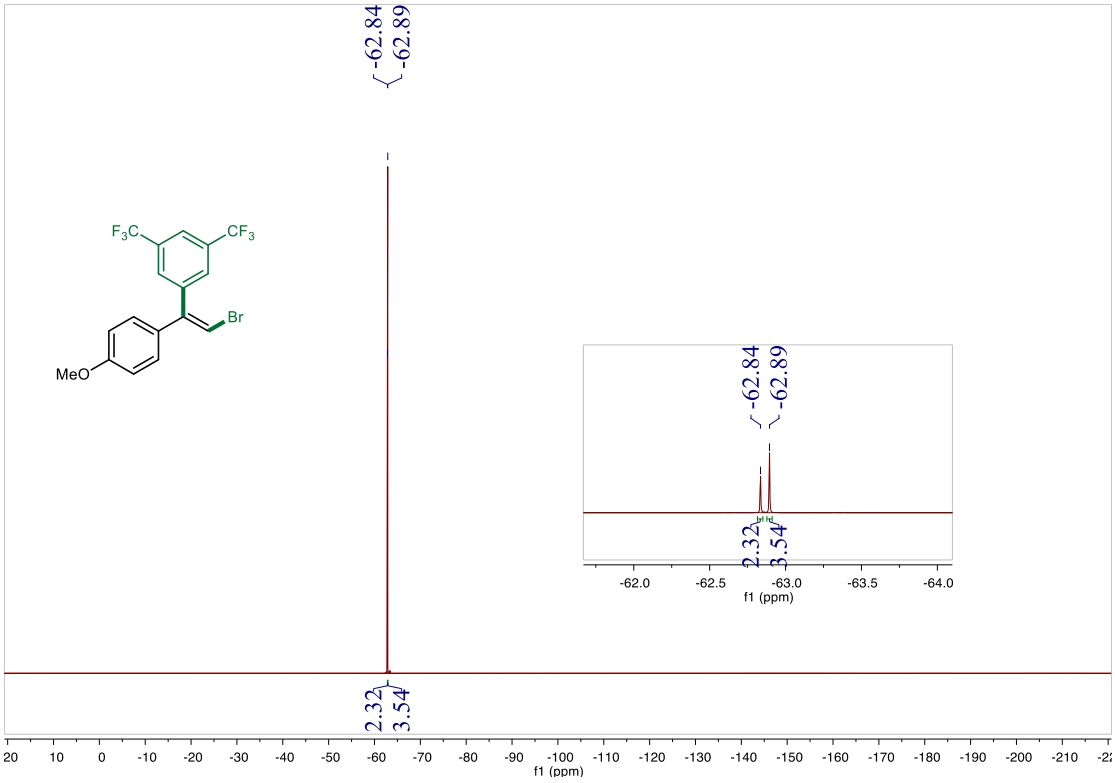
58; ^{13}C NMR (100 MHz, $CDCl_3$)



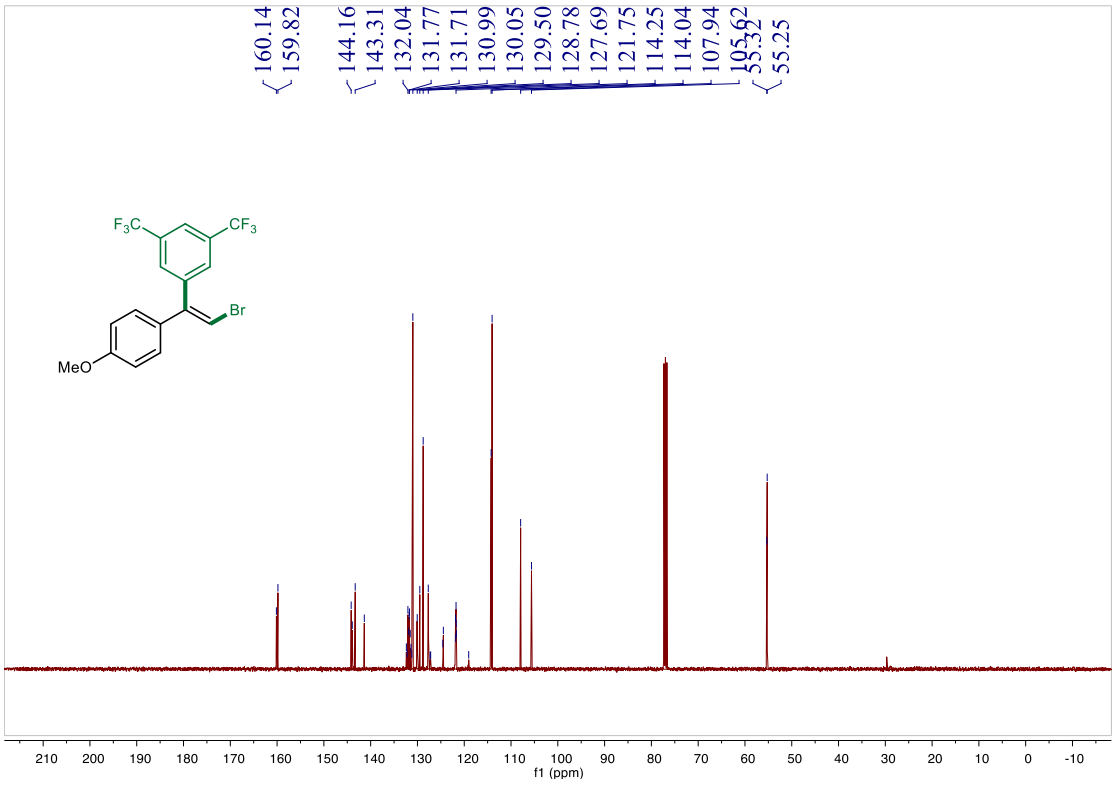
59; ^{1}H NMR (400 MHz, $CDCl_3$)



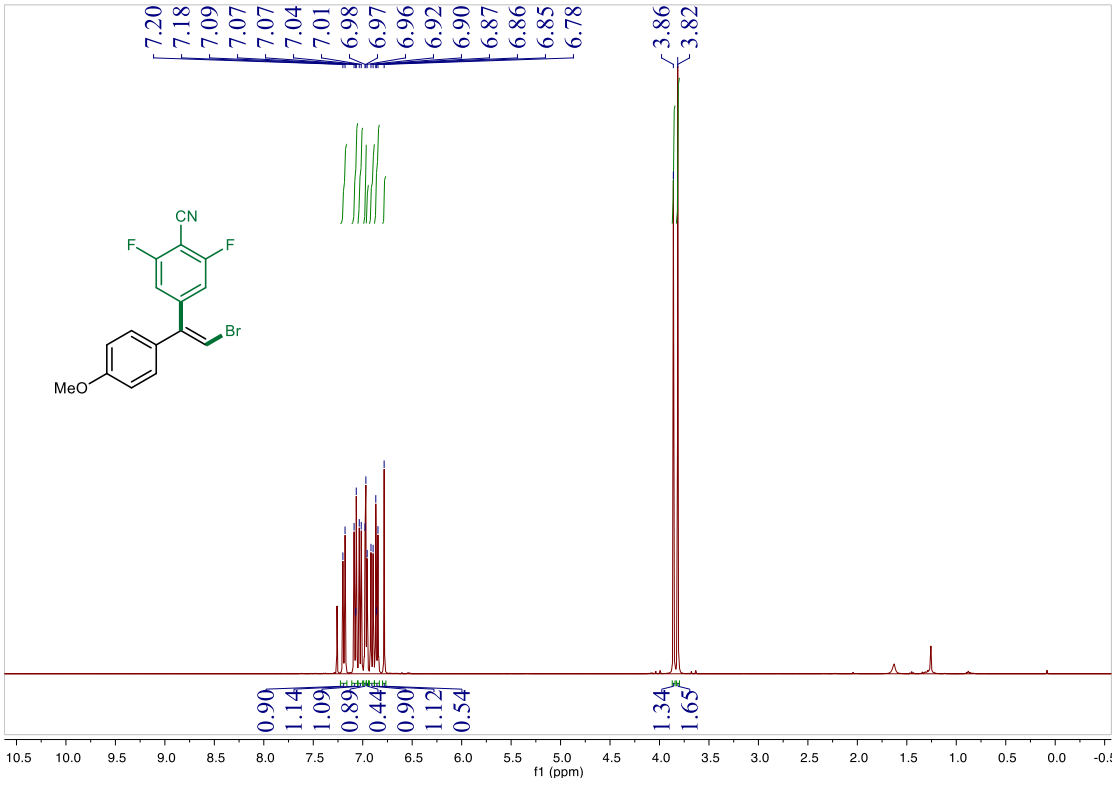
59; ^{19}F NMR (376 MHz, $CDCl_3$)



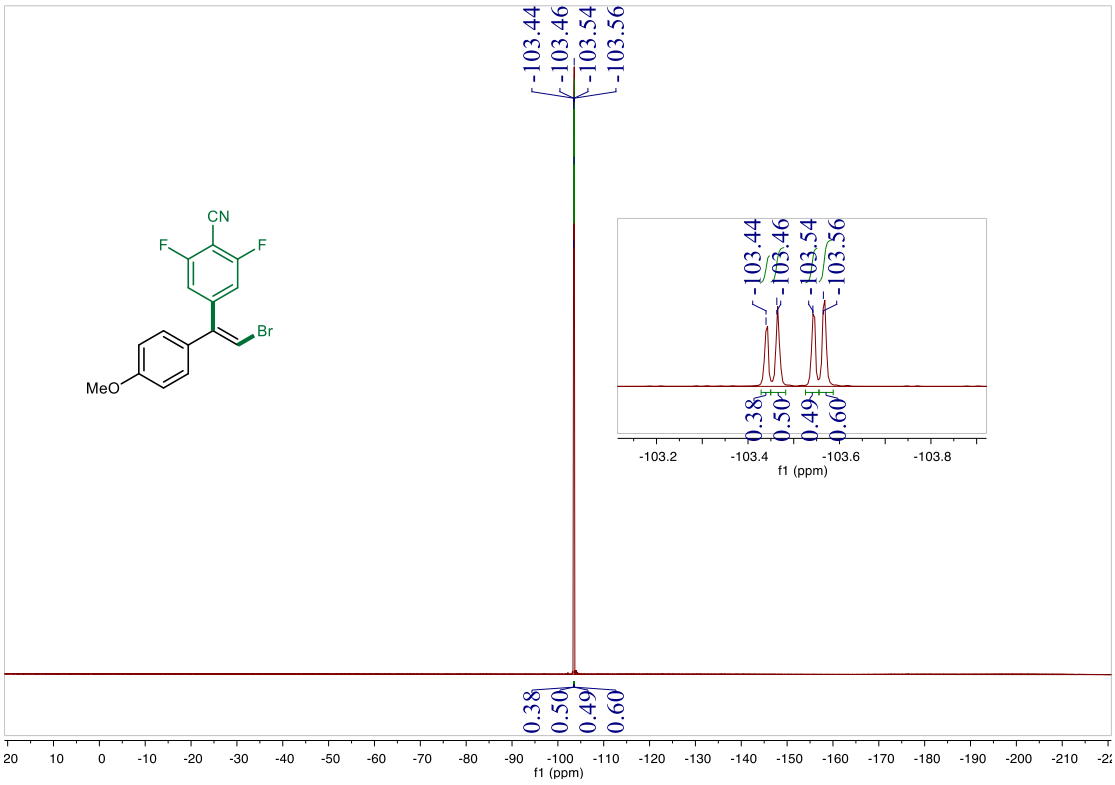
59; ^{13}C NMR (100 MHz, $CDCl_3$)



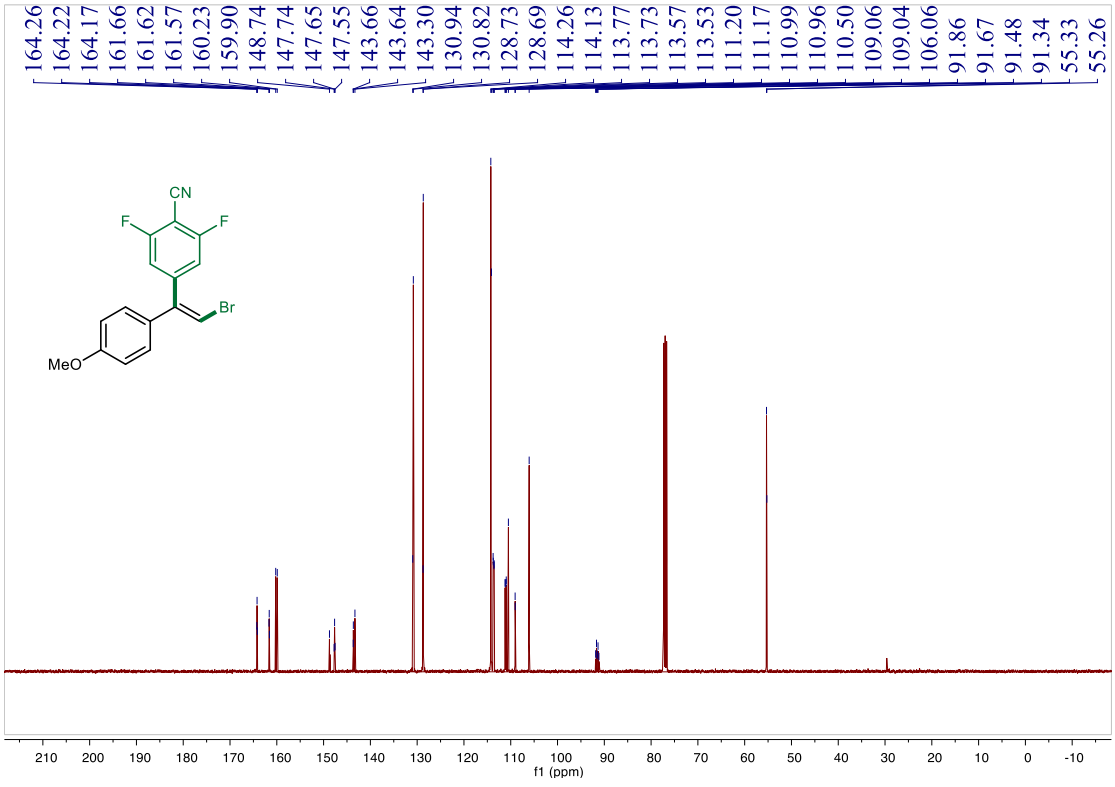
60; ^{1}H NMR (400 MHz, $CDCl_3$)



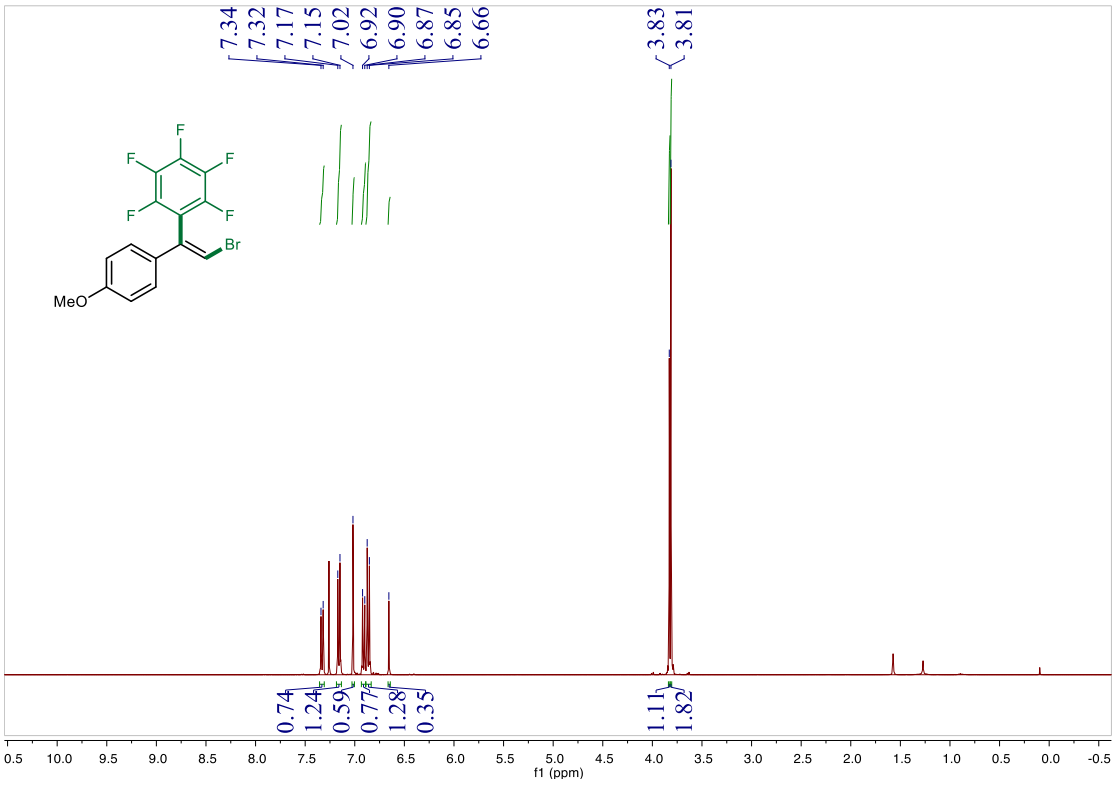
60; ^{19}F NMR (376 MHz, $CDCl_3$)



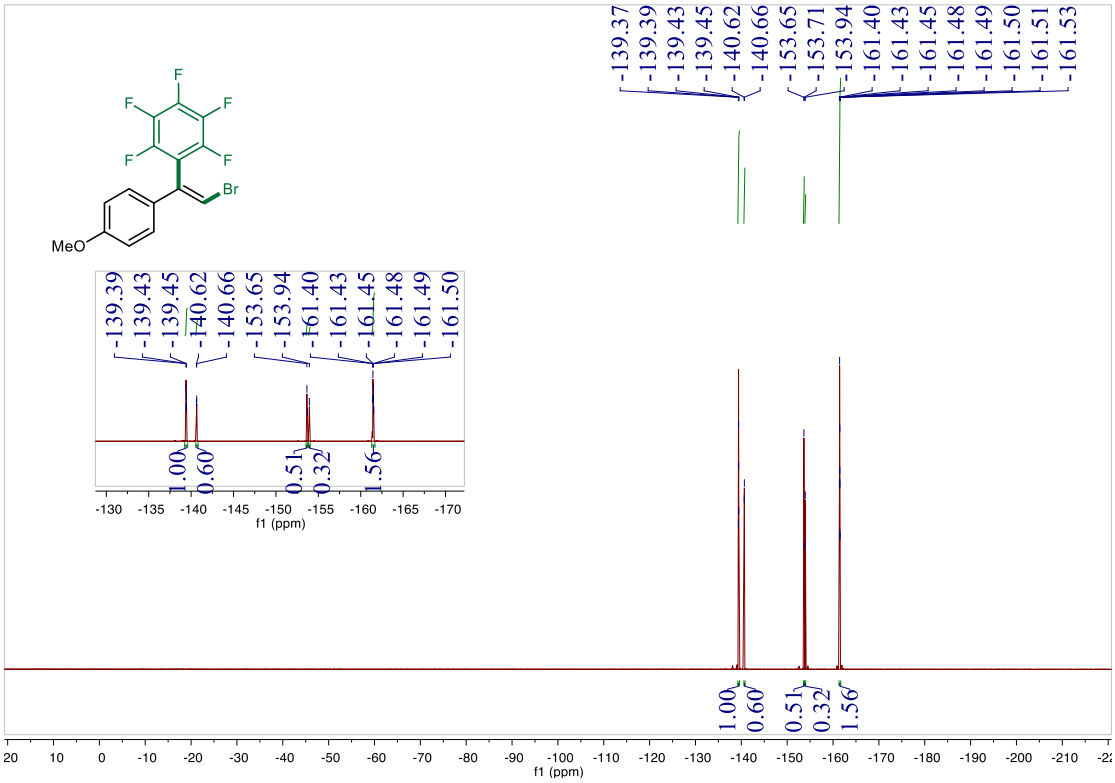
60; ^{13}C NMR (100 MHz, $CDCl_3$)



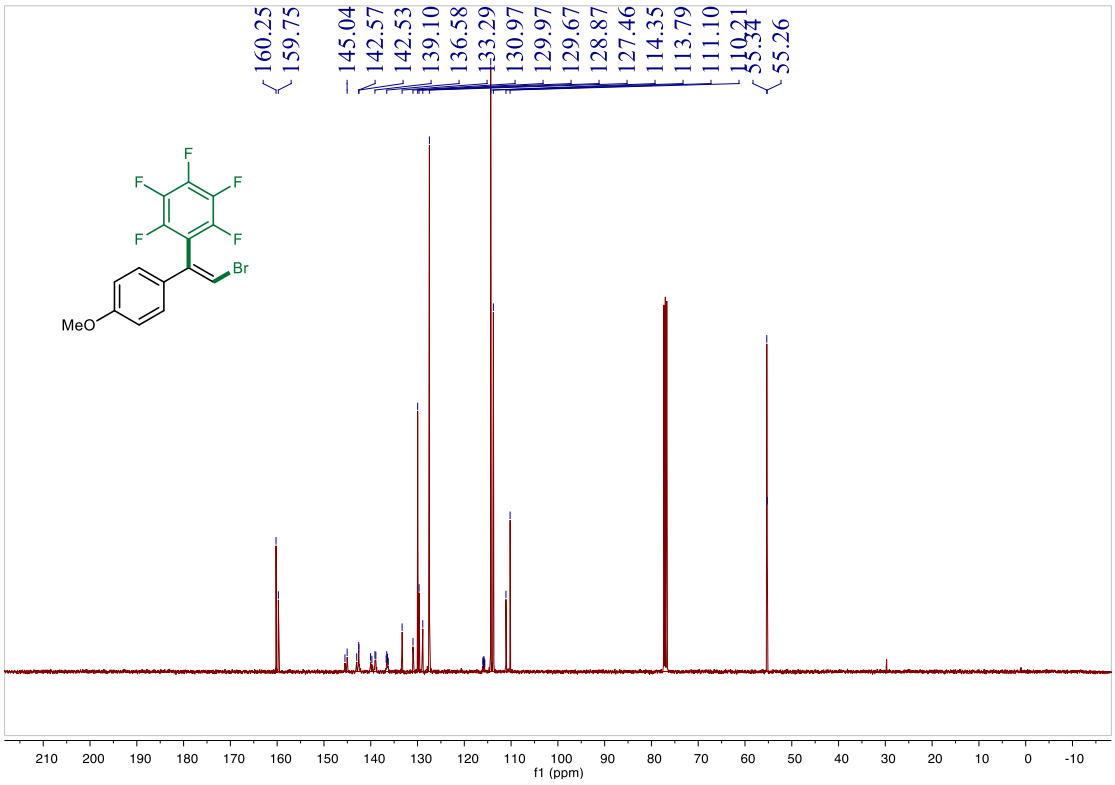
61; ^{1}H NMR (400 MHz, $CDCl_3$)



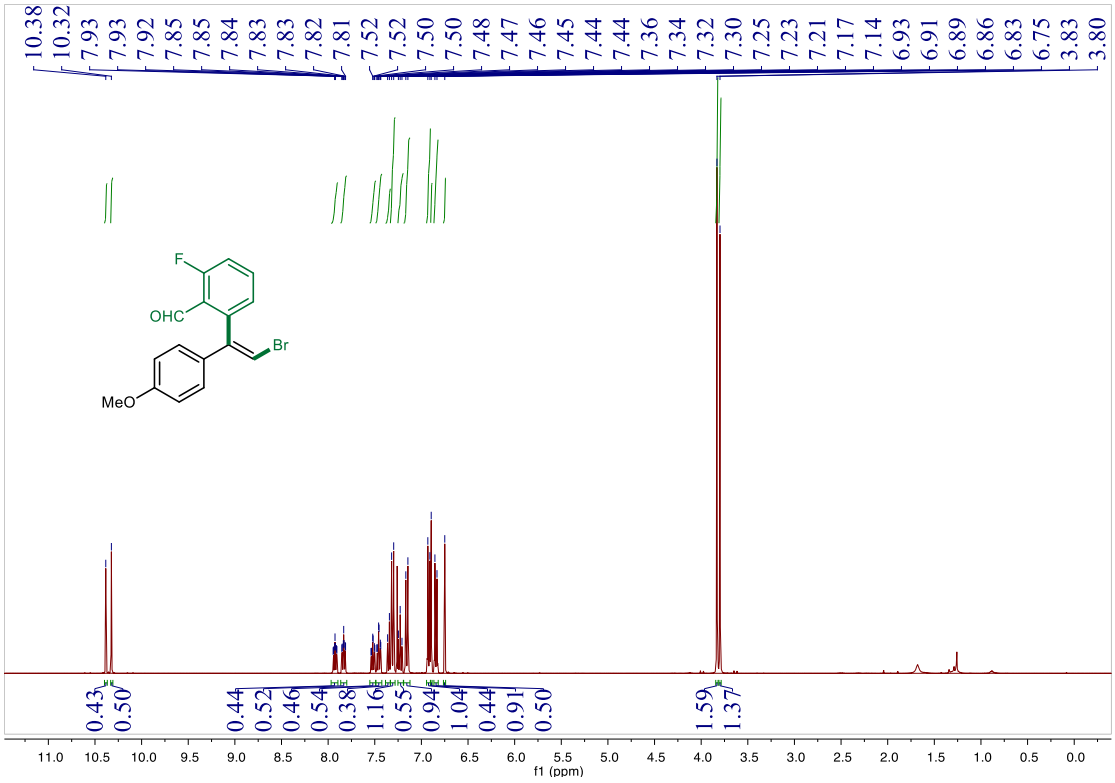
61; ^{19}F NMR (376 MHz, $CDCl_3$)



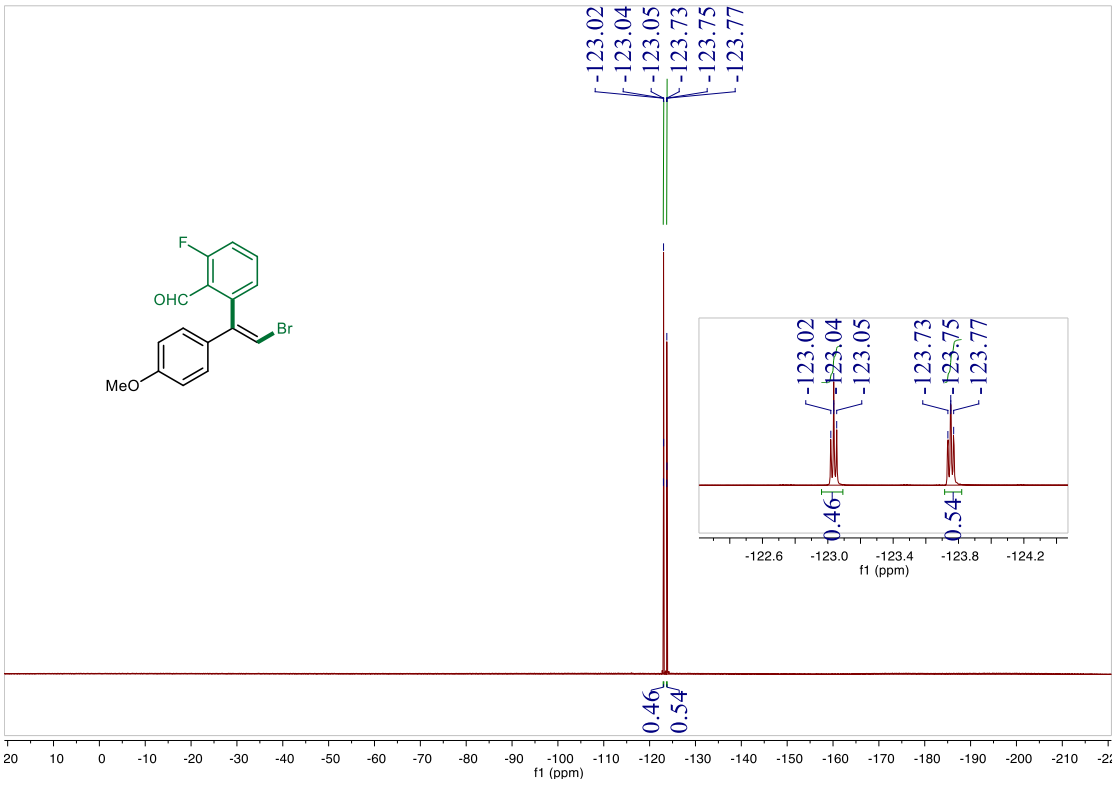
61; ^{13}C NMR (100 MHz, $CDCl_3$)



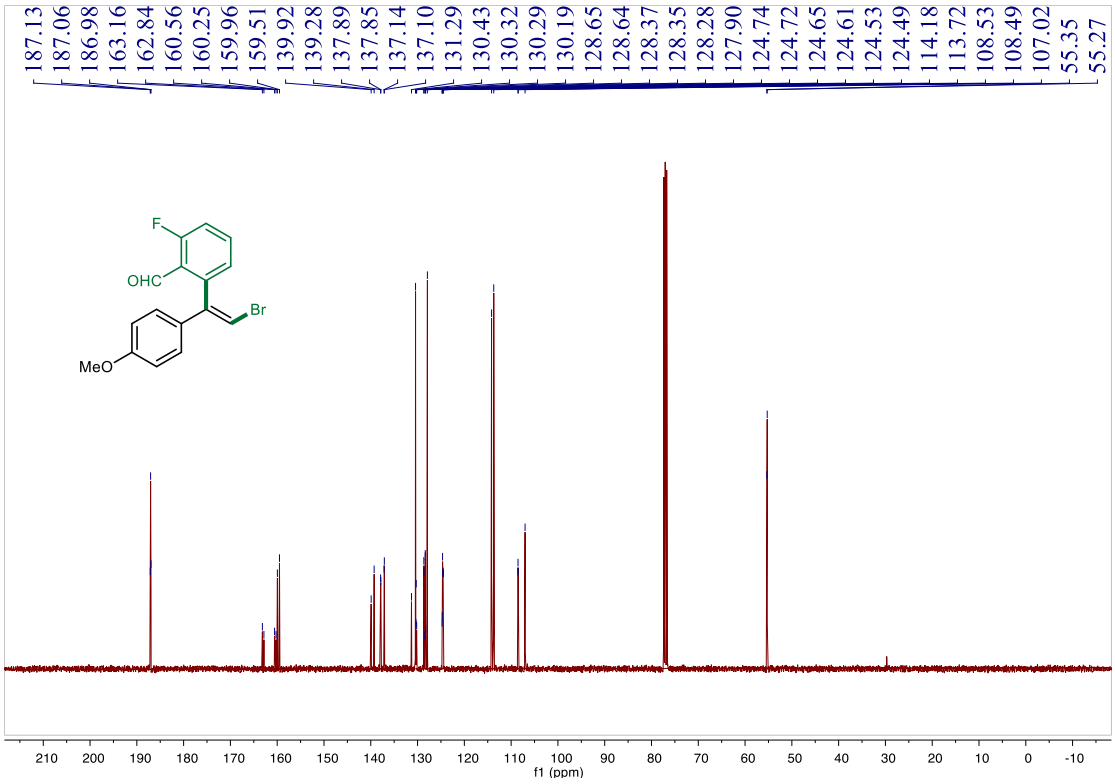
62; ^{1}H NMR (400 MHz, $CDCl_3$)



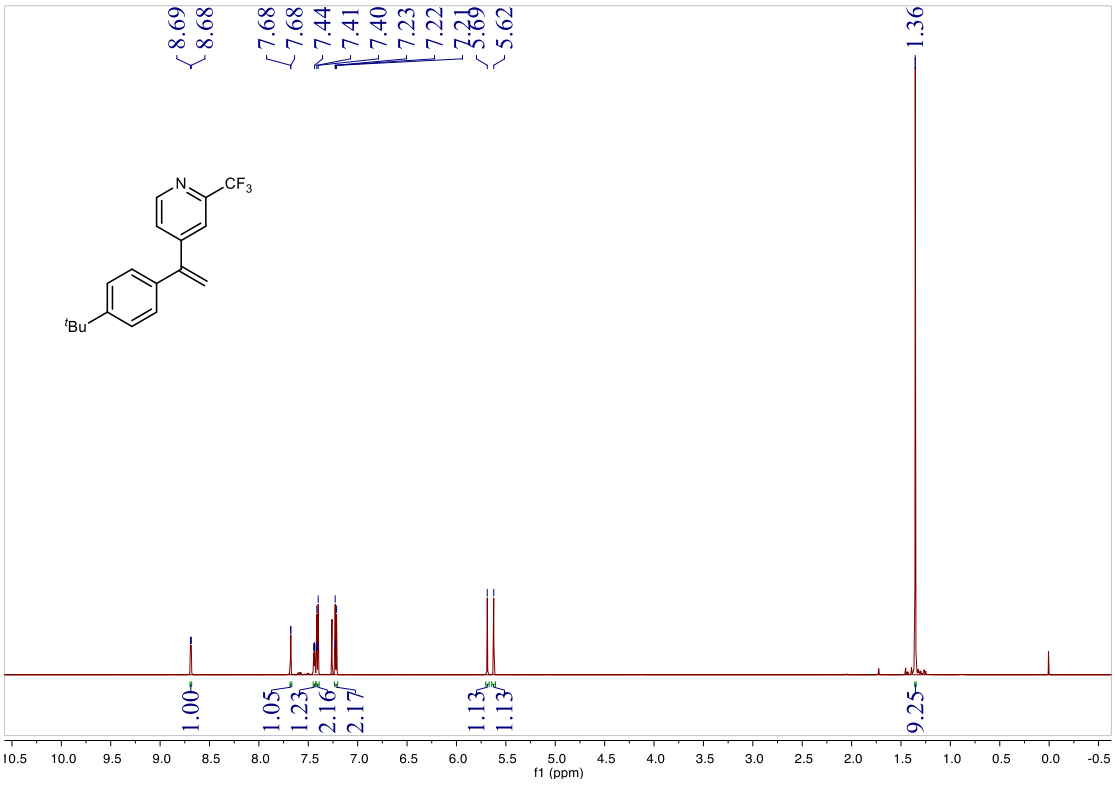
62; ^{19}F NMR (376 MHz, $CDCl_3$)



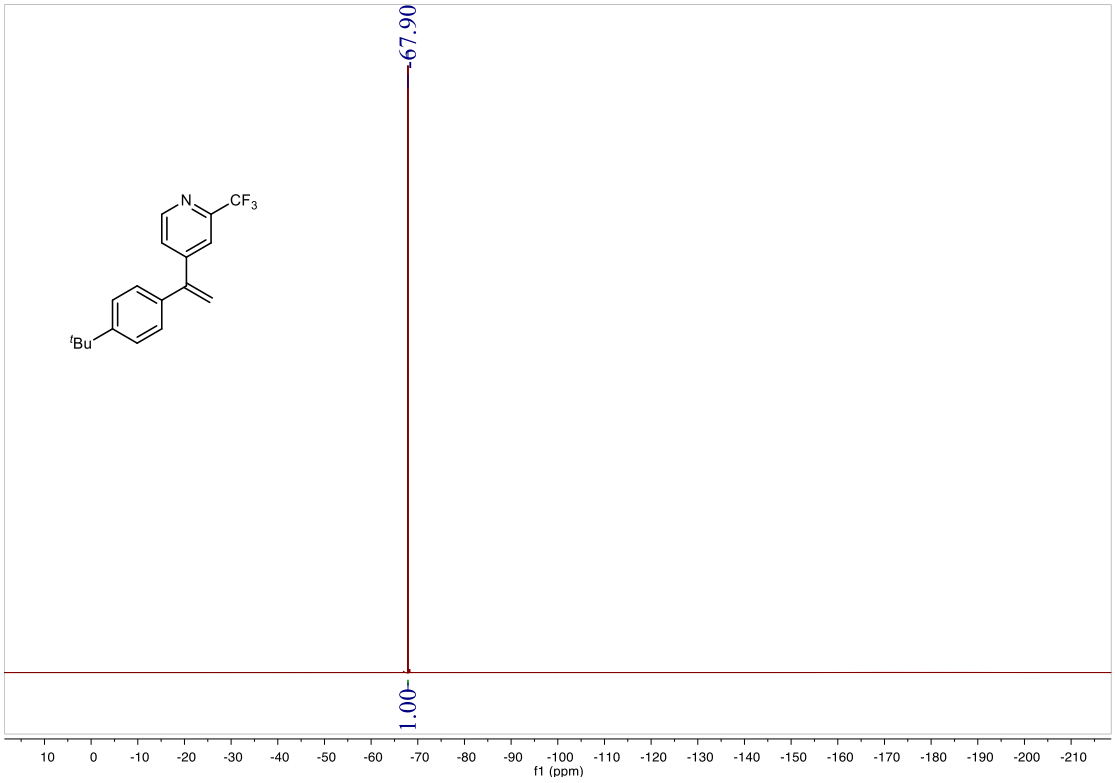
62; ^{13}C NMR (100 MHz, $CDCl_3$)



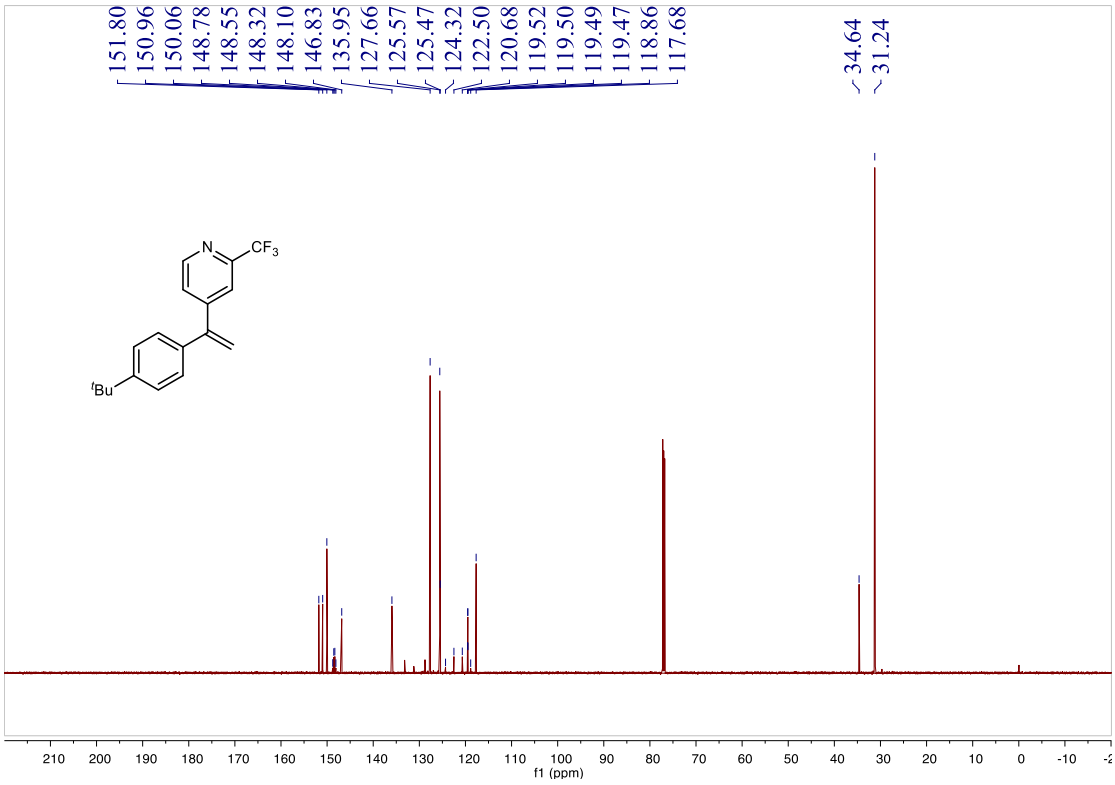
63; ^{1}H NMR (600 MHz, $CDCl_3$)



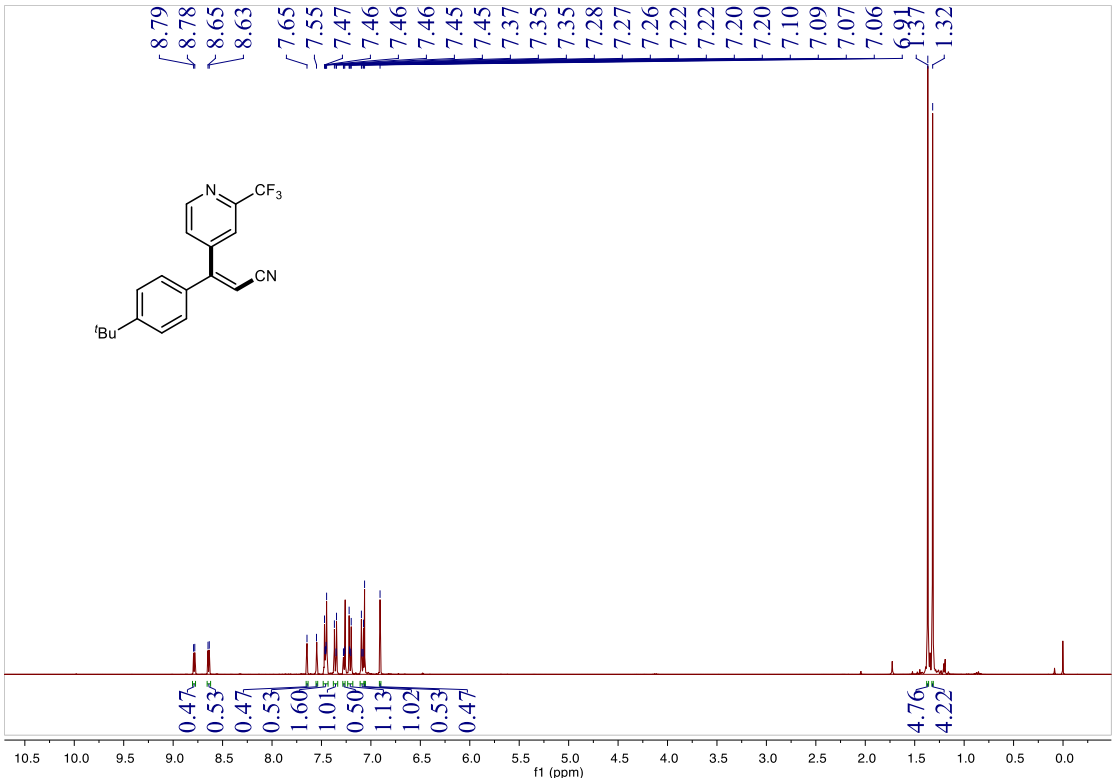
63; ^{19}F NMR (564 MHz, $CDCl_3$)



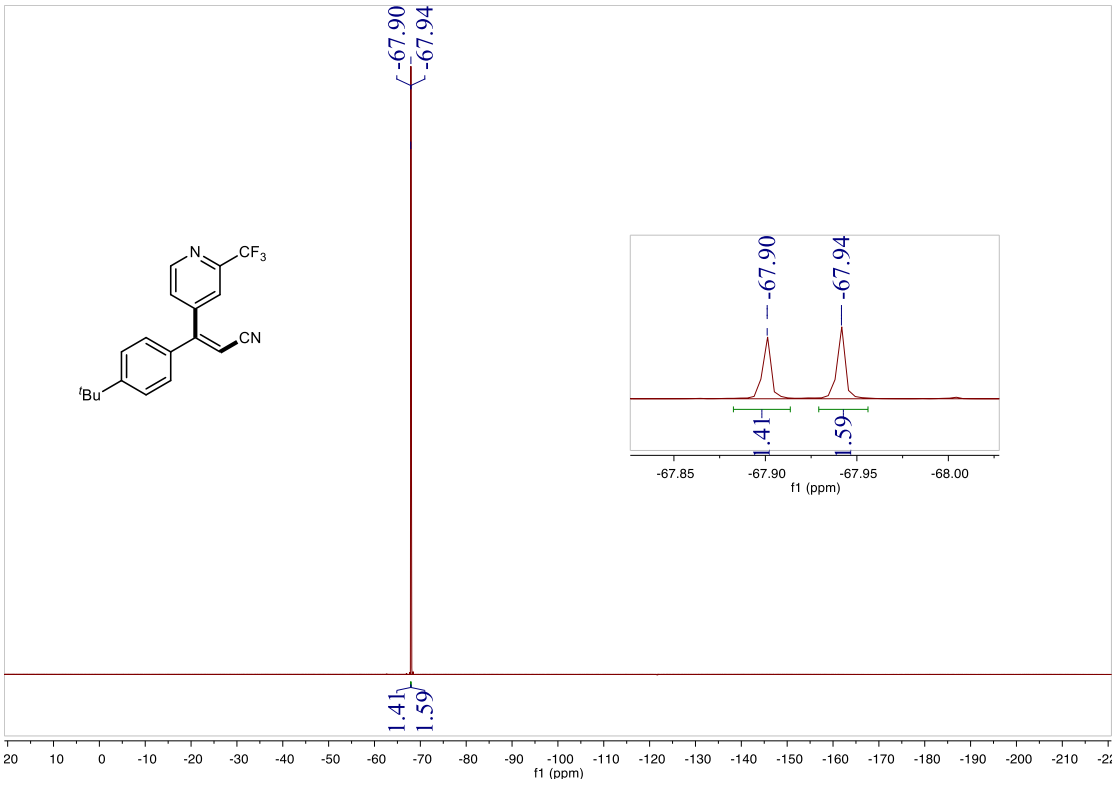
63; ^{13}C NMR (150 MHz, $CDCl_3$)



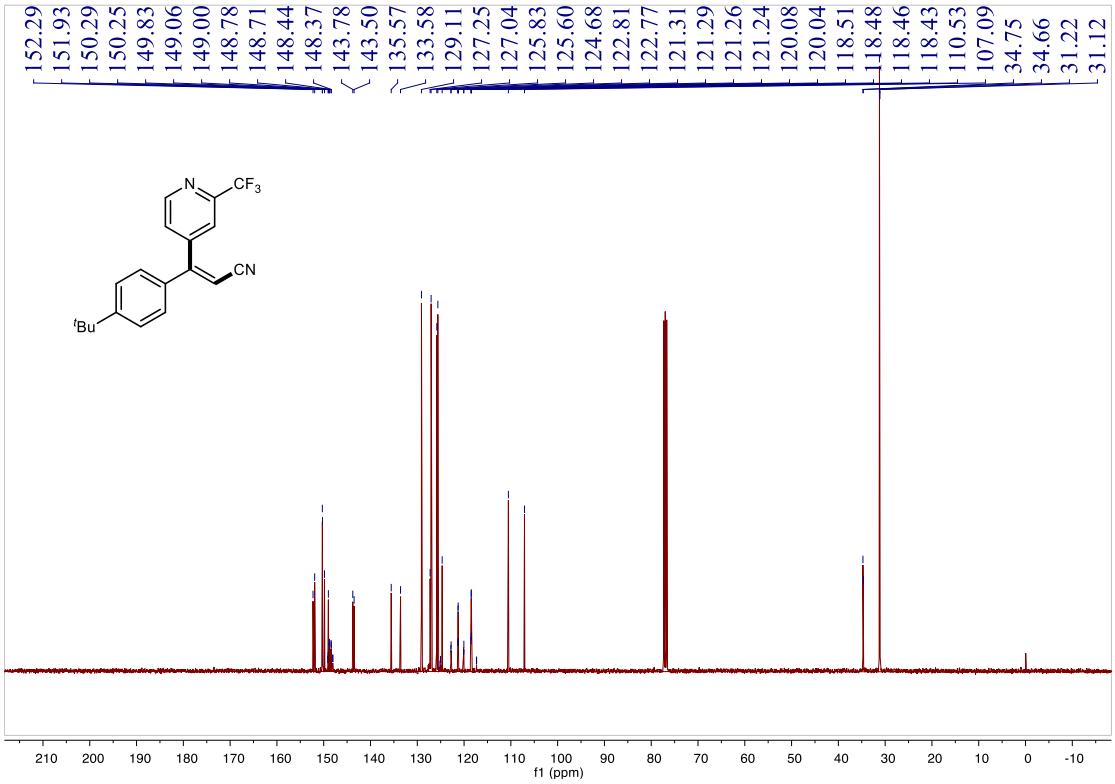
64; ^{1}H NMR (400 MHz, $CDCl_3$)



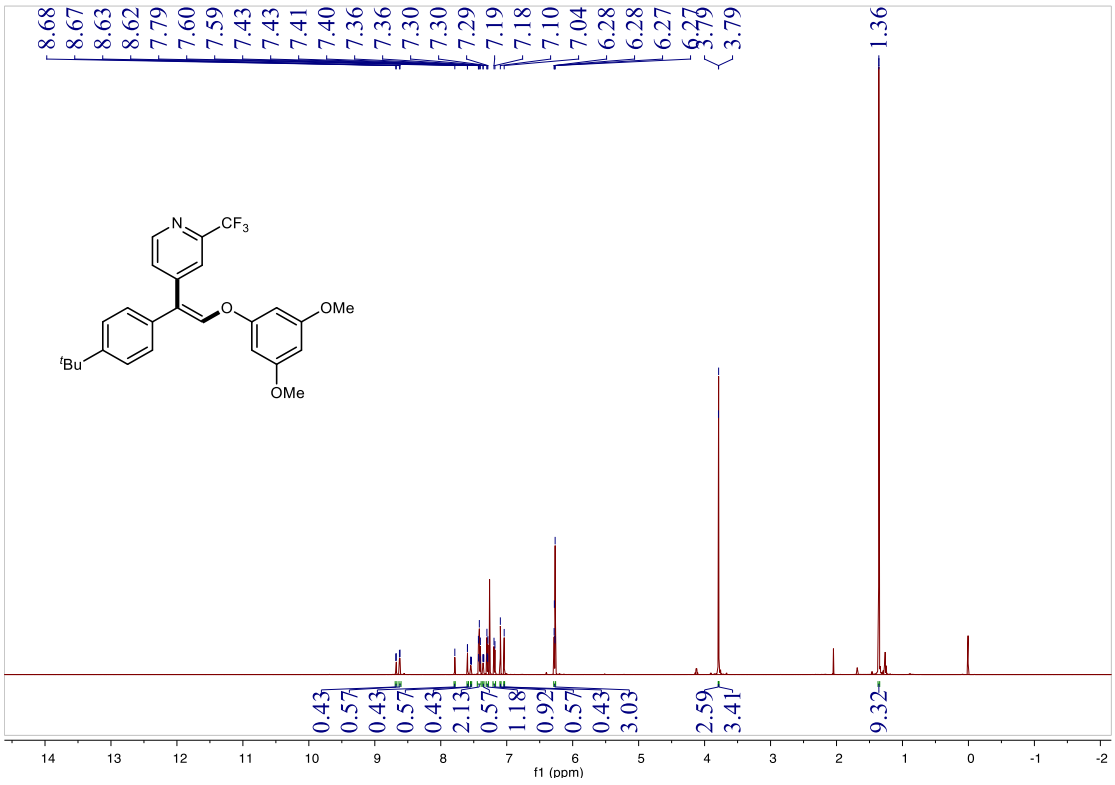
64; ^{19}F NMR (376 MHz, $CDCl_3$)



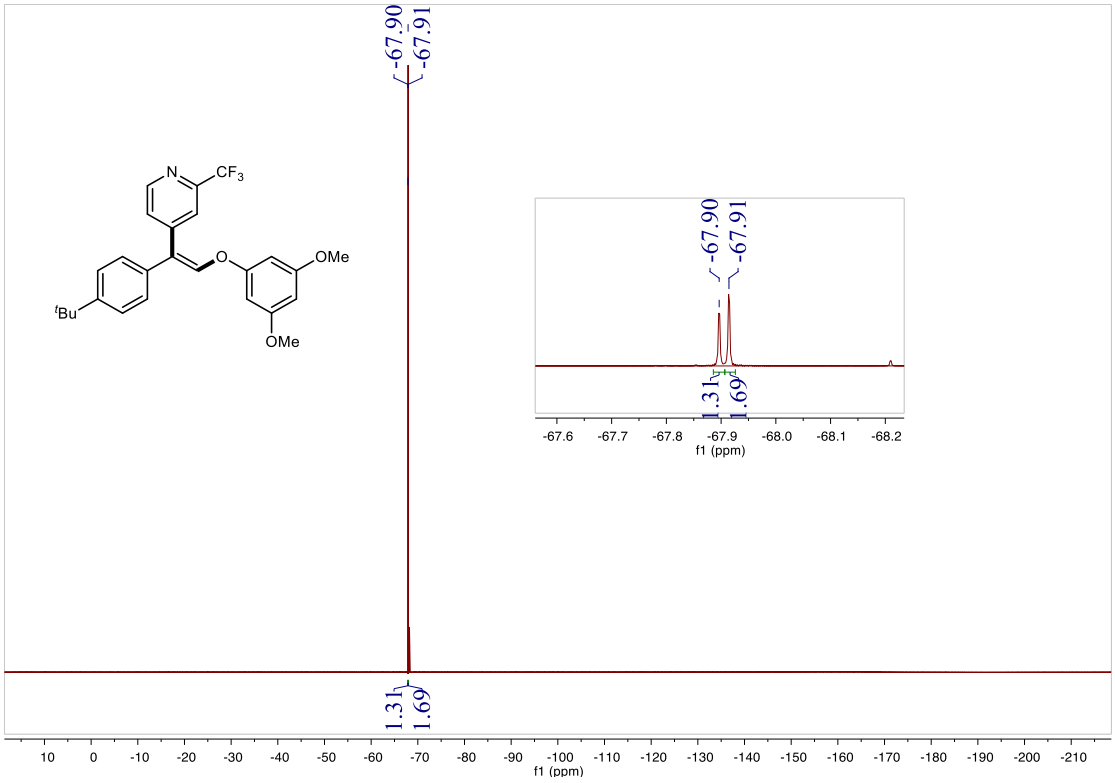
64; ^{13}C NMR (100 MHz, $CDCl_3$)



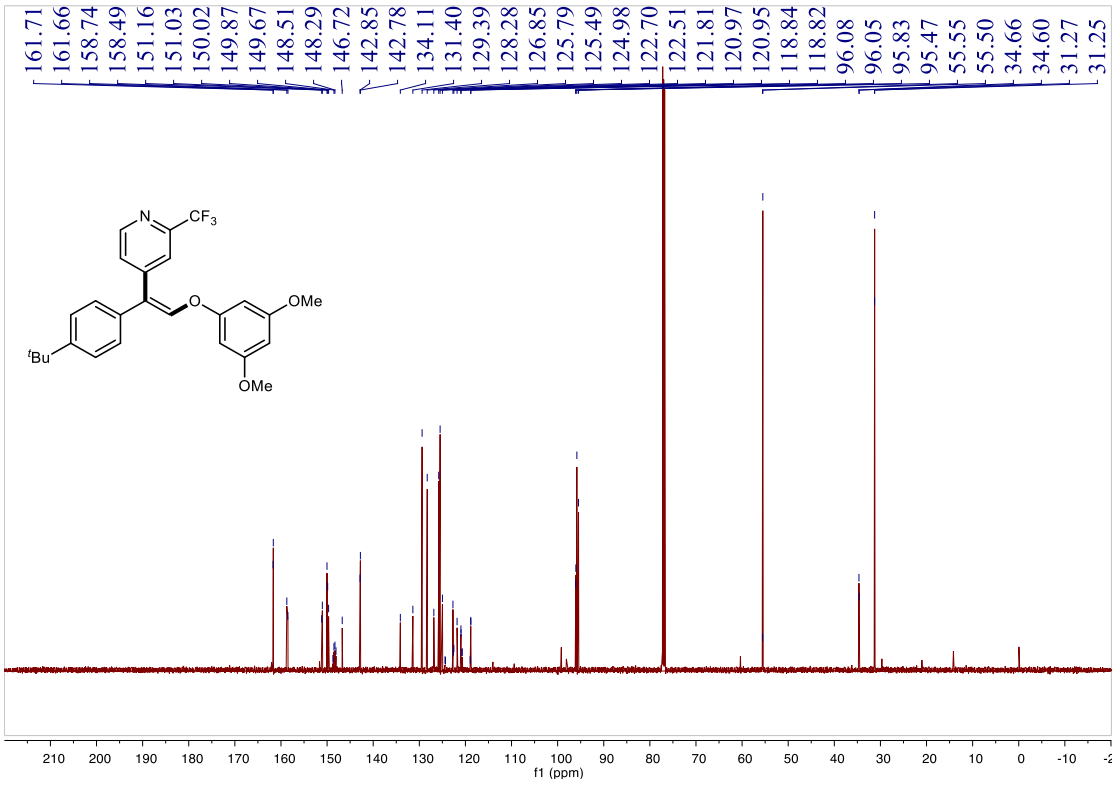
65; ^{1}H NMR (600 MHz, $CDCl_3$)



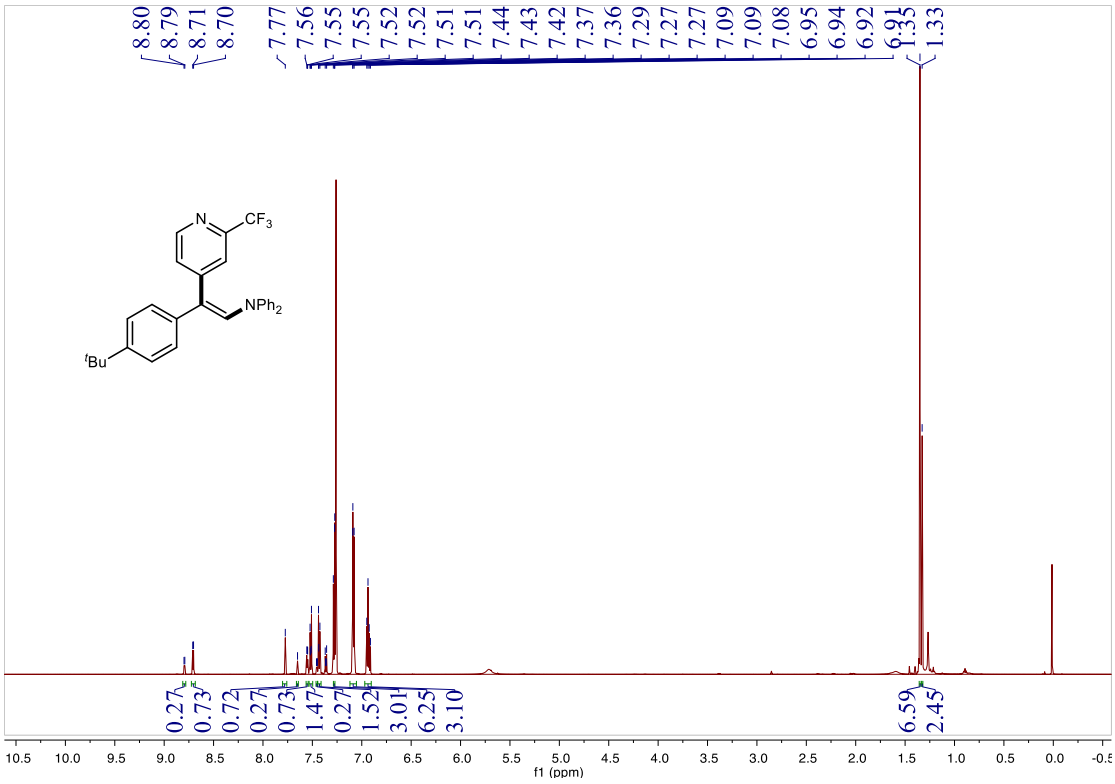
65; ^{19}F NMR (564 MHz, $CDCl_3$)



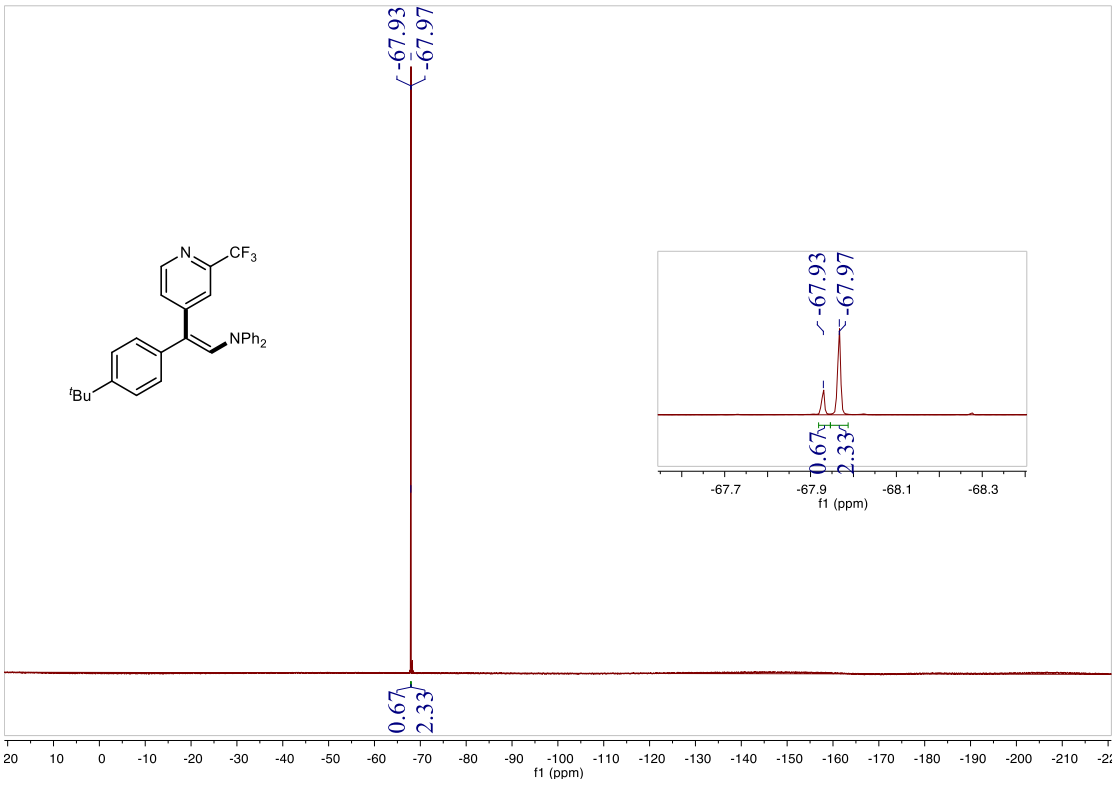
65; ^{13}C NMR (150 MHz, $CDCl_3$)



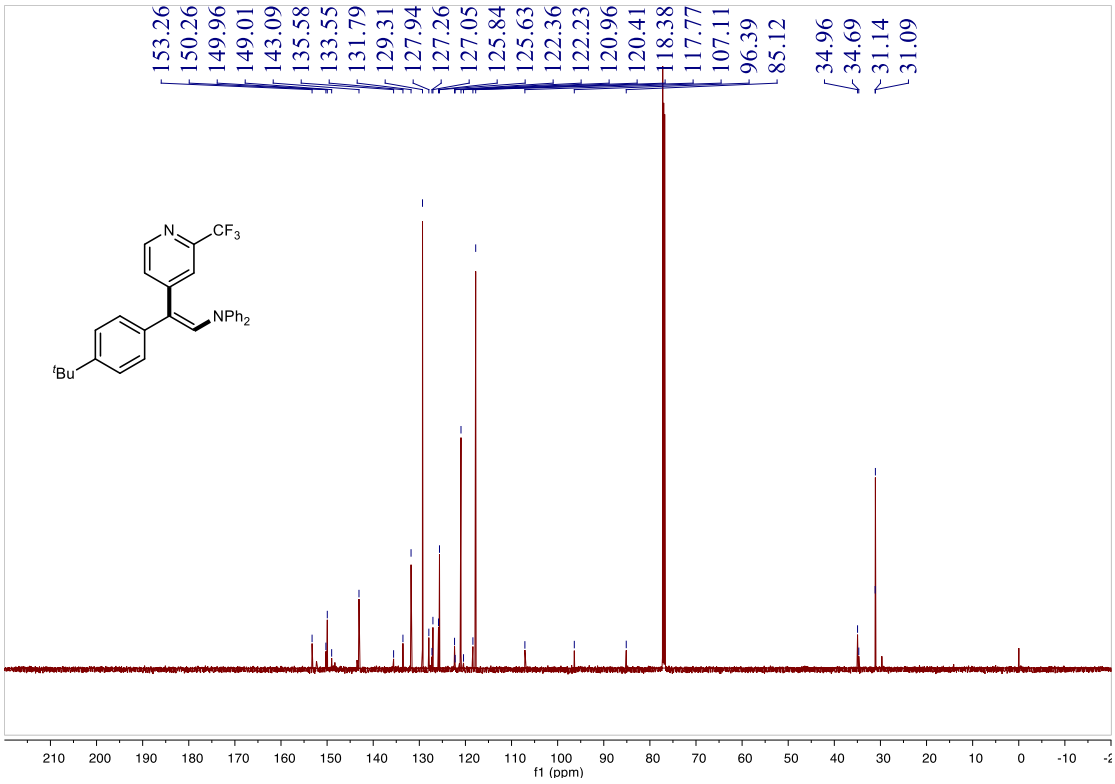
66; ^{1}H NMR (600 MHz, $CDCl_3$)



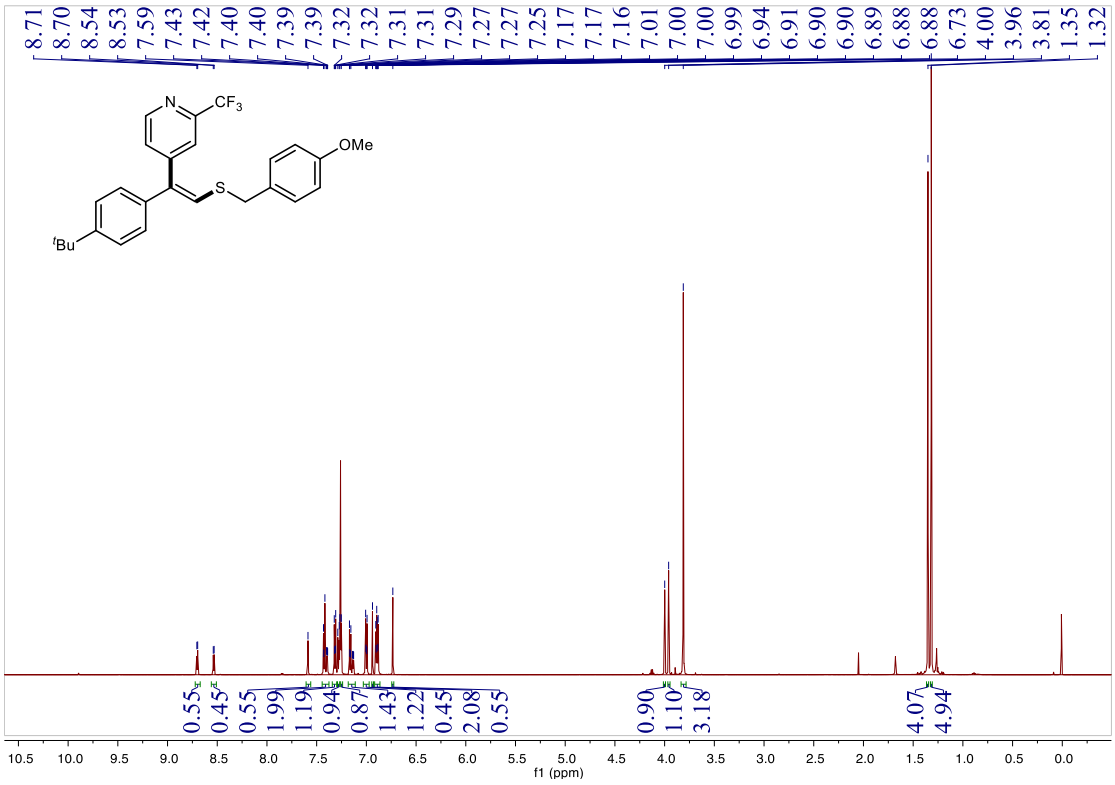
66; ^{19}F NMR (564 MHz, $CDCl_3$)



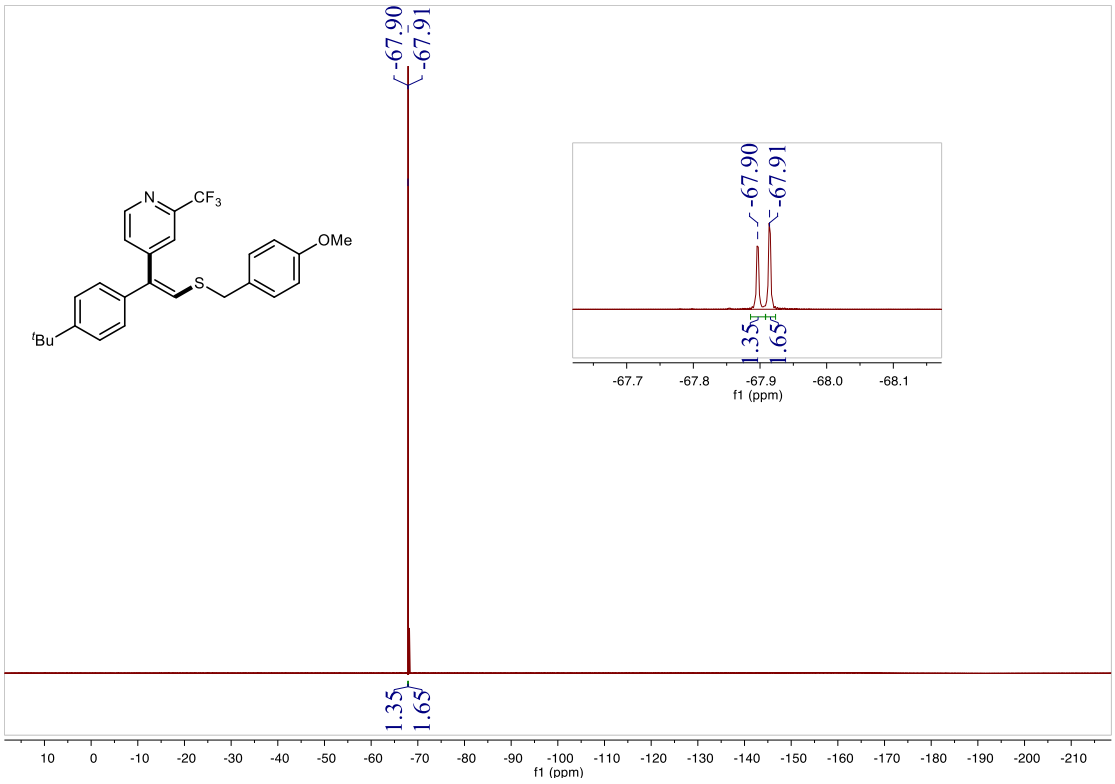
66; ^{13}C NMR (150 MHz, $CDCl_3$)



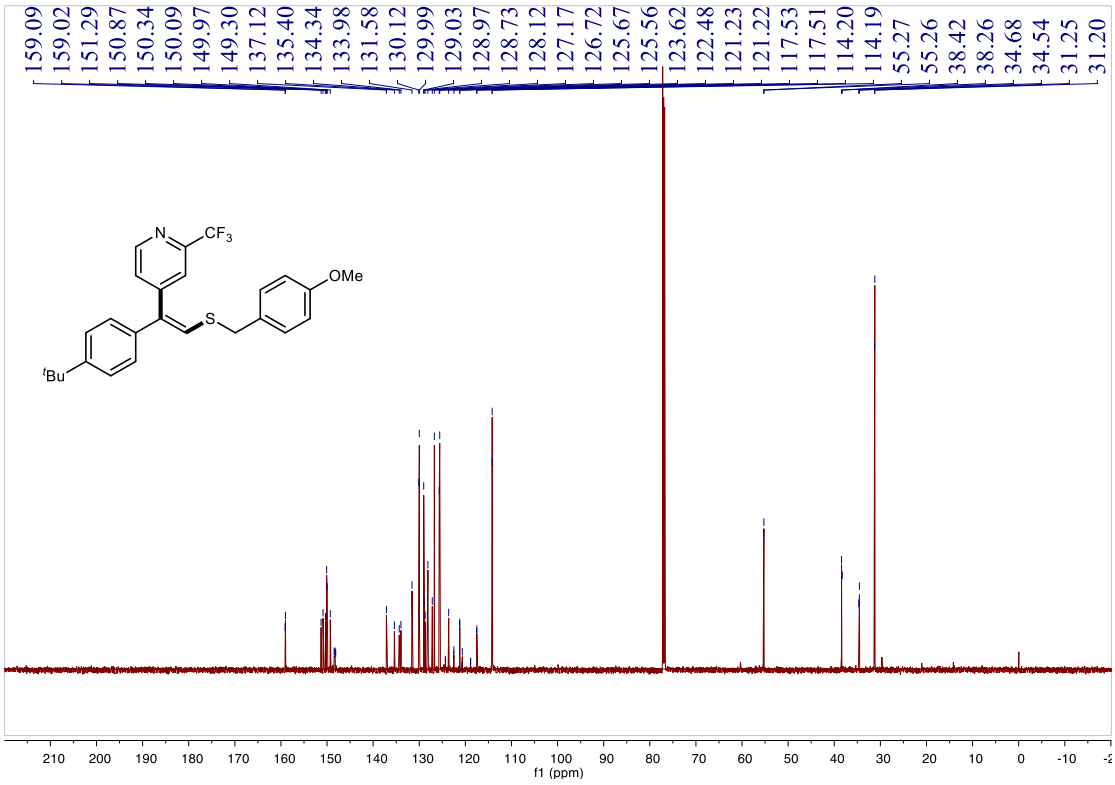
67; ^{1}H NMR (600 MHz, $CDCl_3$)



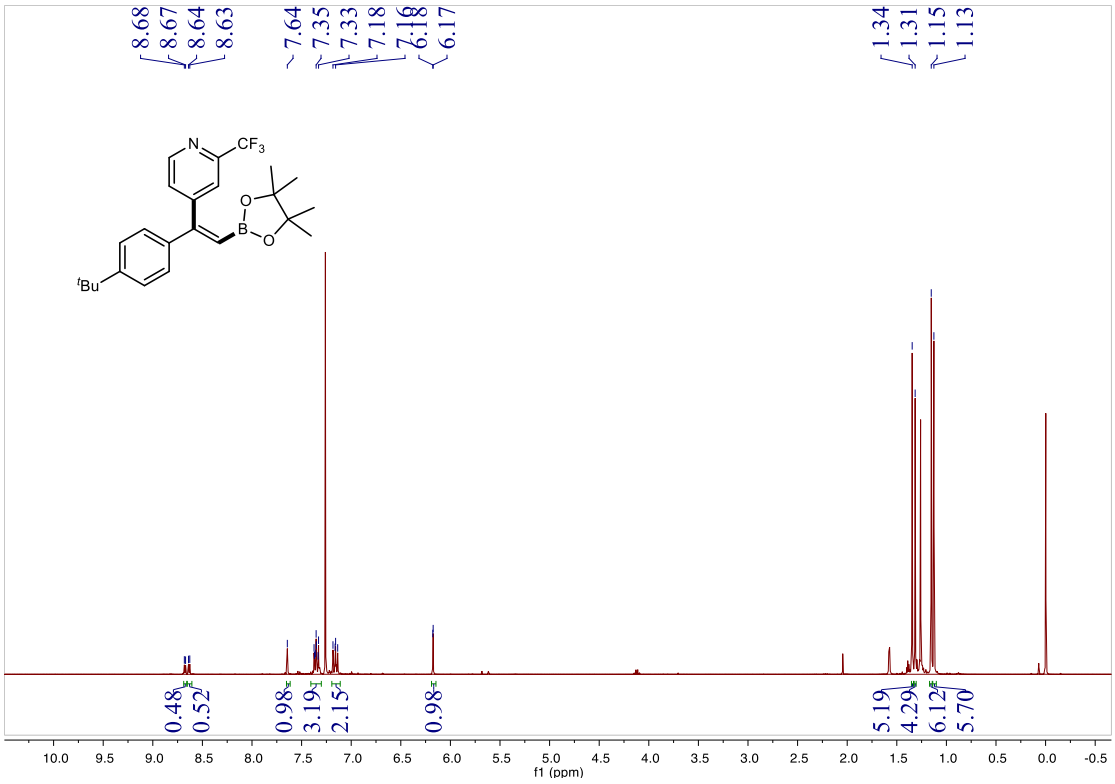
67; ^{19}F NMR (564 MHz, $CDCl_3$)



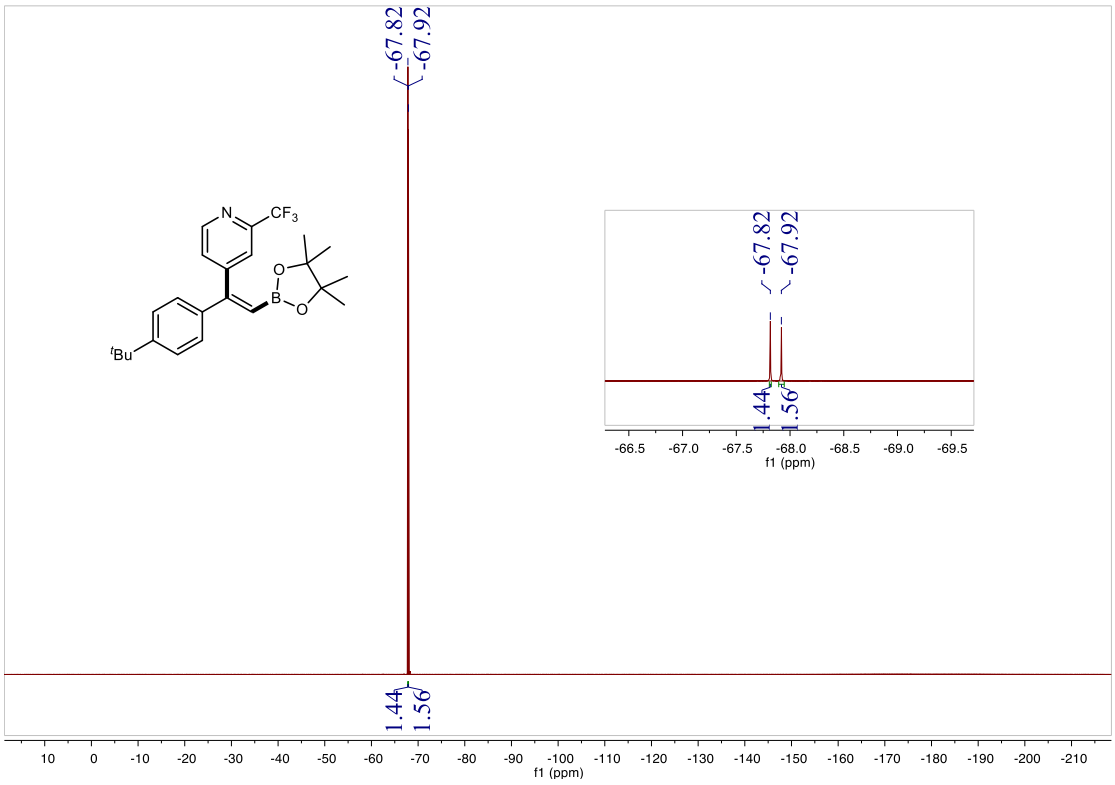
67; ^{13}C NMR (150 MHz, $CDCl_3$)



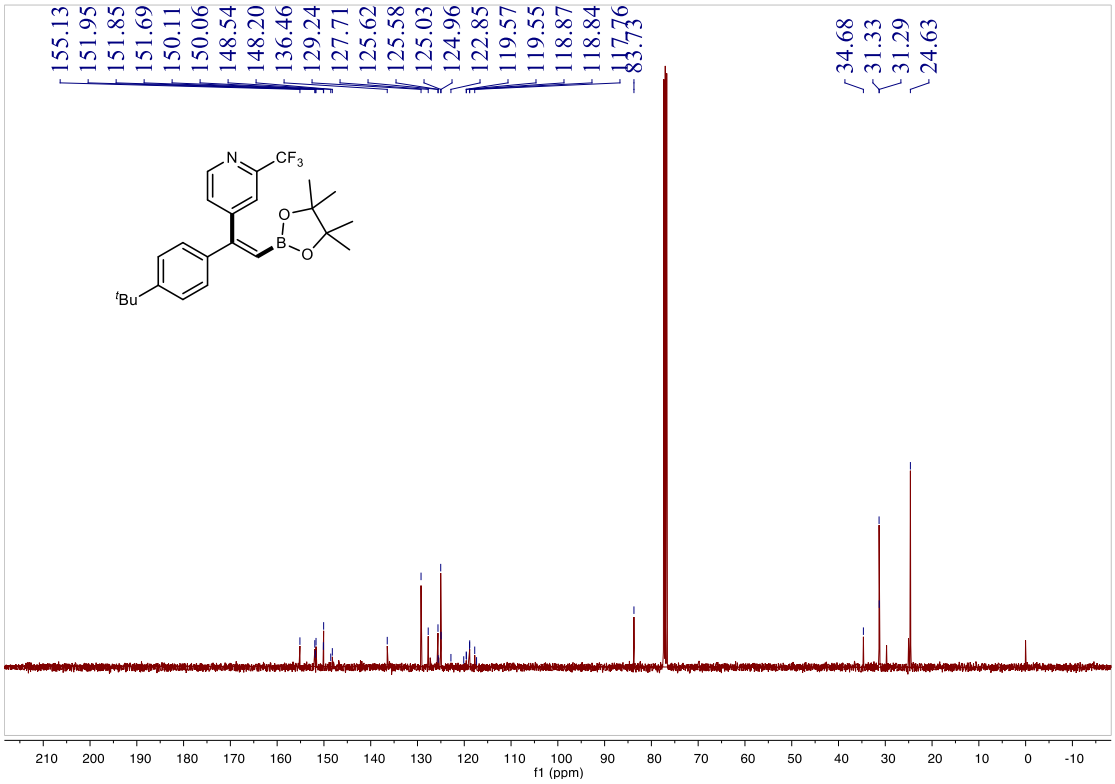
68; ^{1}H NMR (400 MHz, $CDCl_3$)



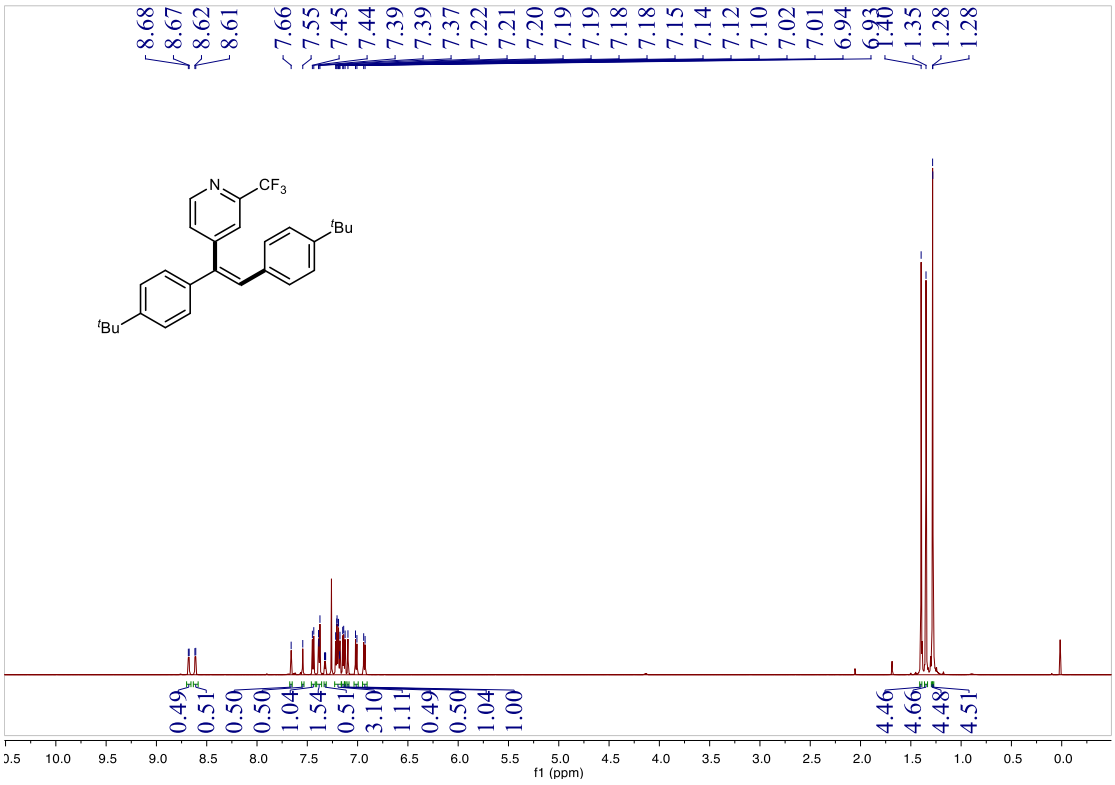
68; ^{19}F NMR (376 MHz, $CDCl_3$)



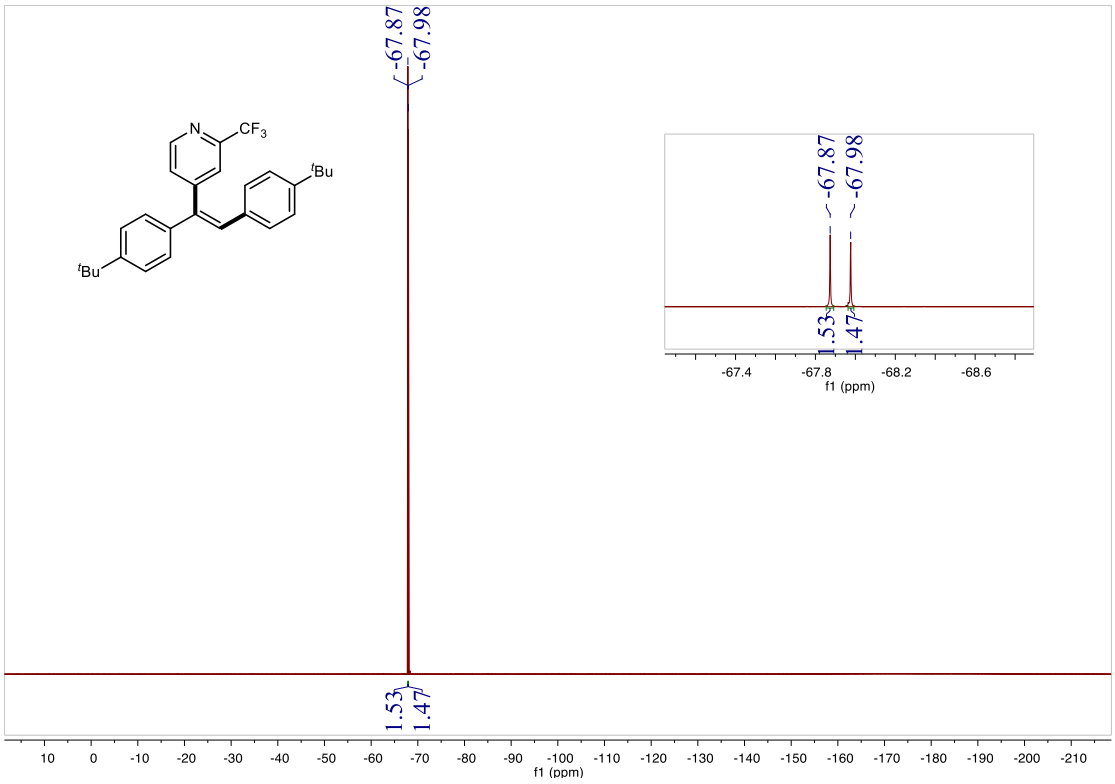
68; ^{13}C NMR (100 MHz, $CDCl_3$)



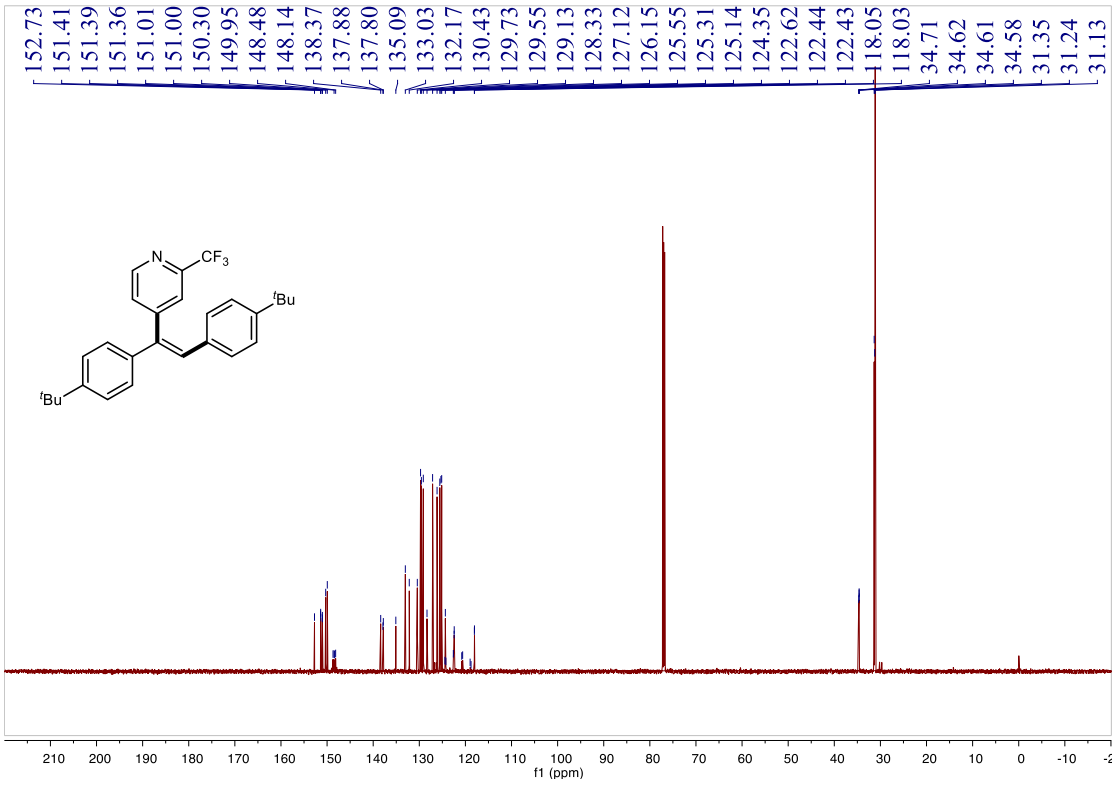
69; ^{1}H NMR (600 MHz, $CDCl_3$)



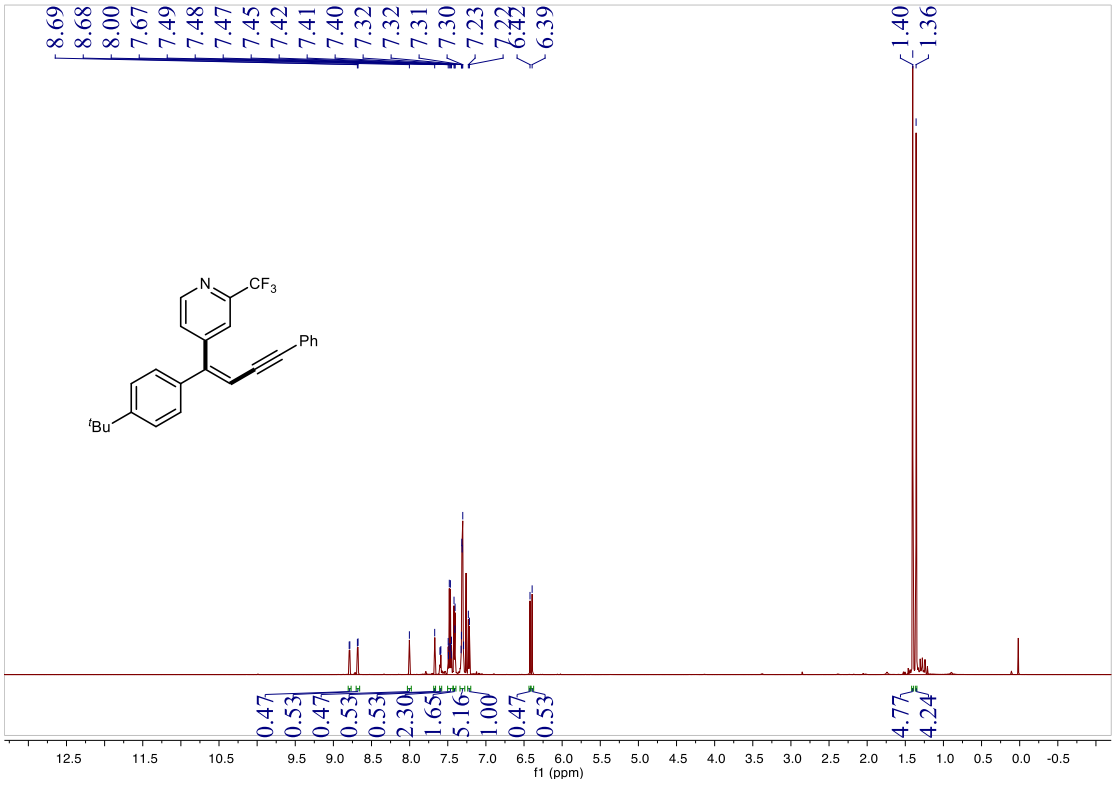
69; ^{19}F NMR (564 MHz, $CDCl_3$)



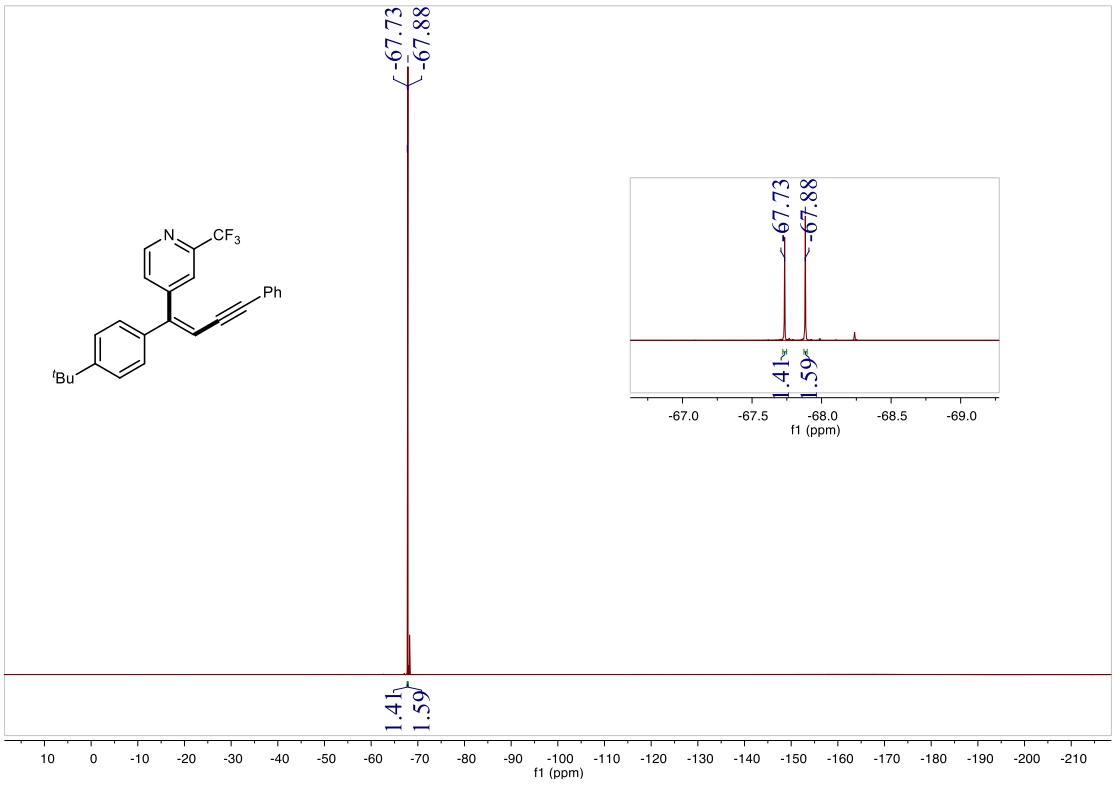
69; ^{13}C NMR (150 MHz, $CDCl_3$)



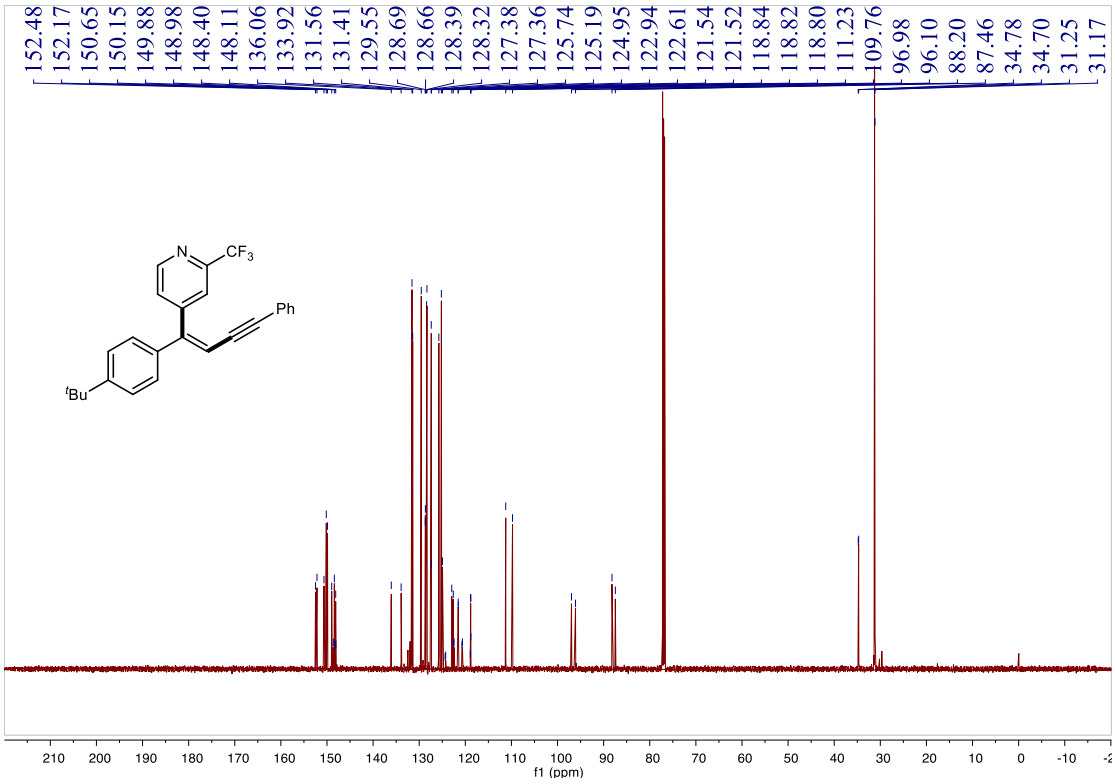
70; ^{1}H NMR (600 MHz, $CDCl_3$)



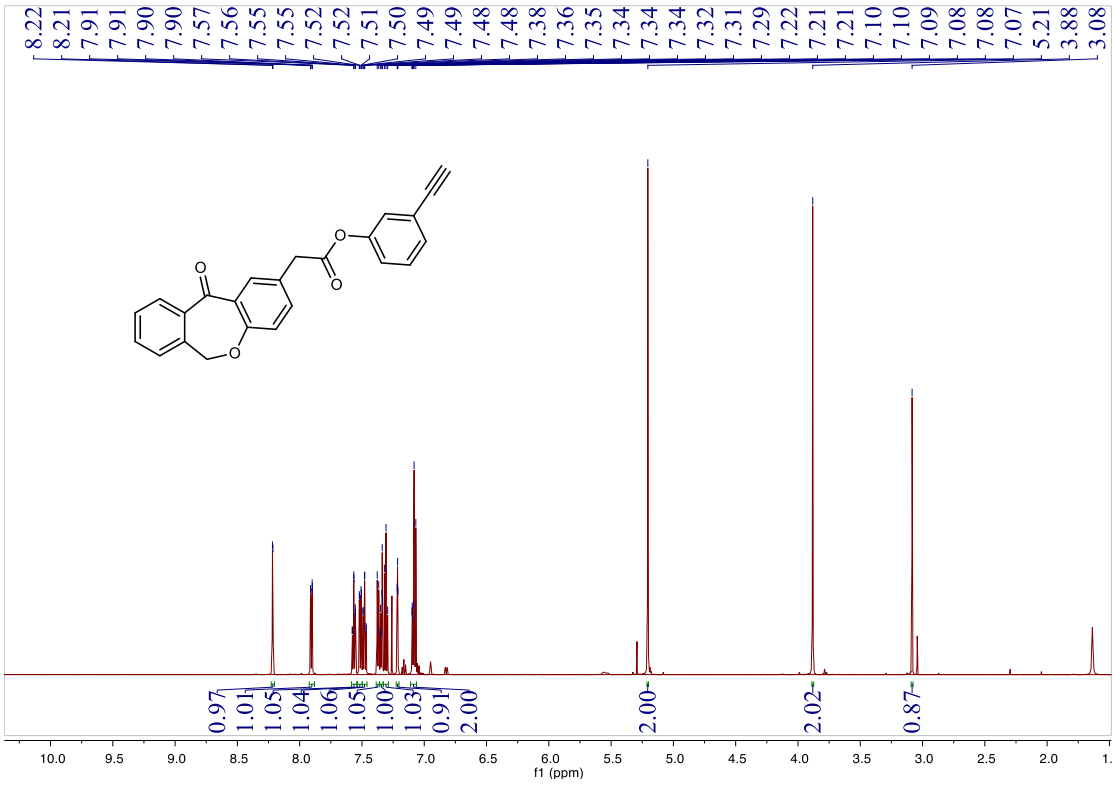
70; ^{19}F NMR (564 MHz, $CDCl_3$)



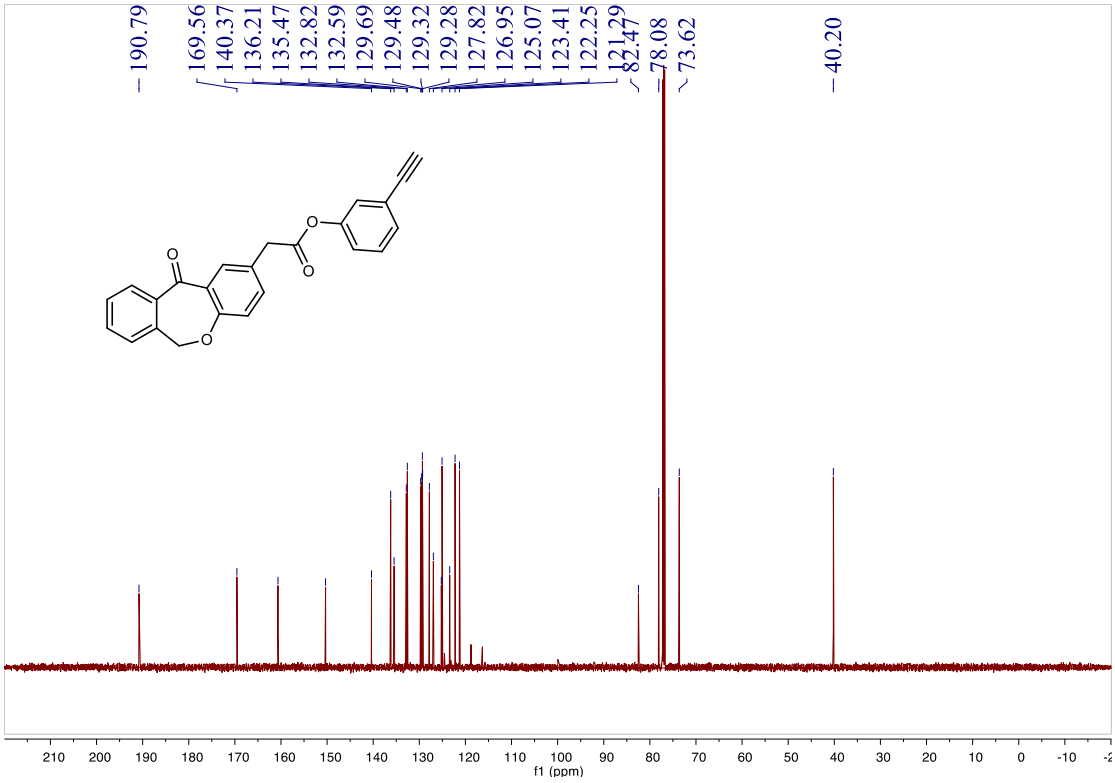
70; ^{13}C NMR (150 MHz, $CDCl_3$)



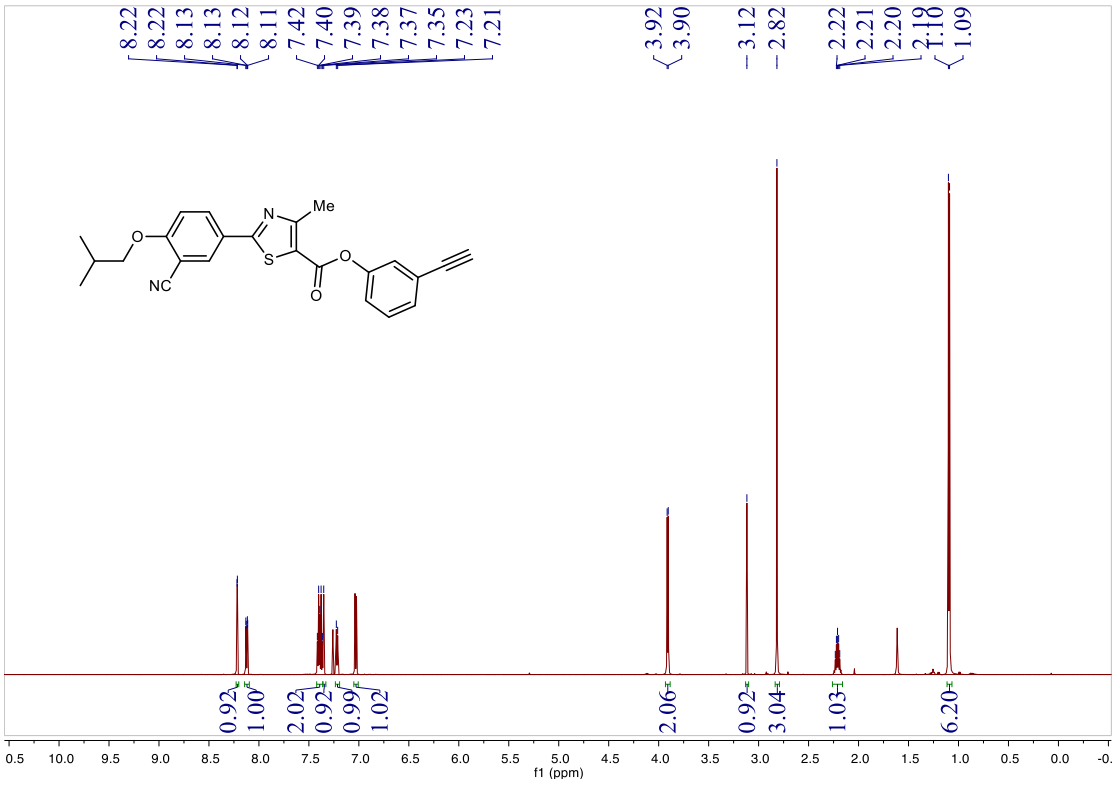
S1; ^{1}H NMR (600 MHz, $CDCl_3$)



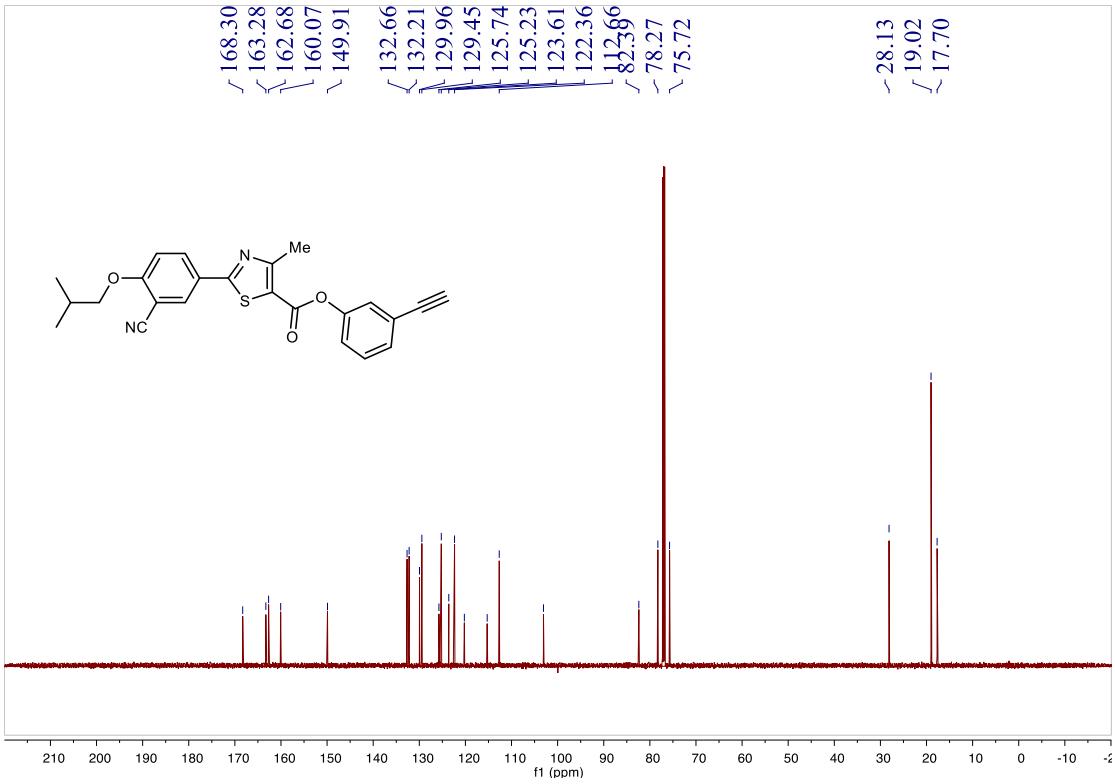
S1; ^{13}C NMR (150 MHz, $CDCl_3$)



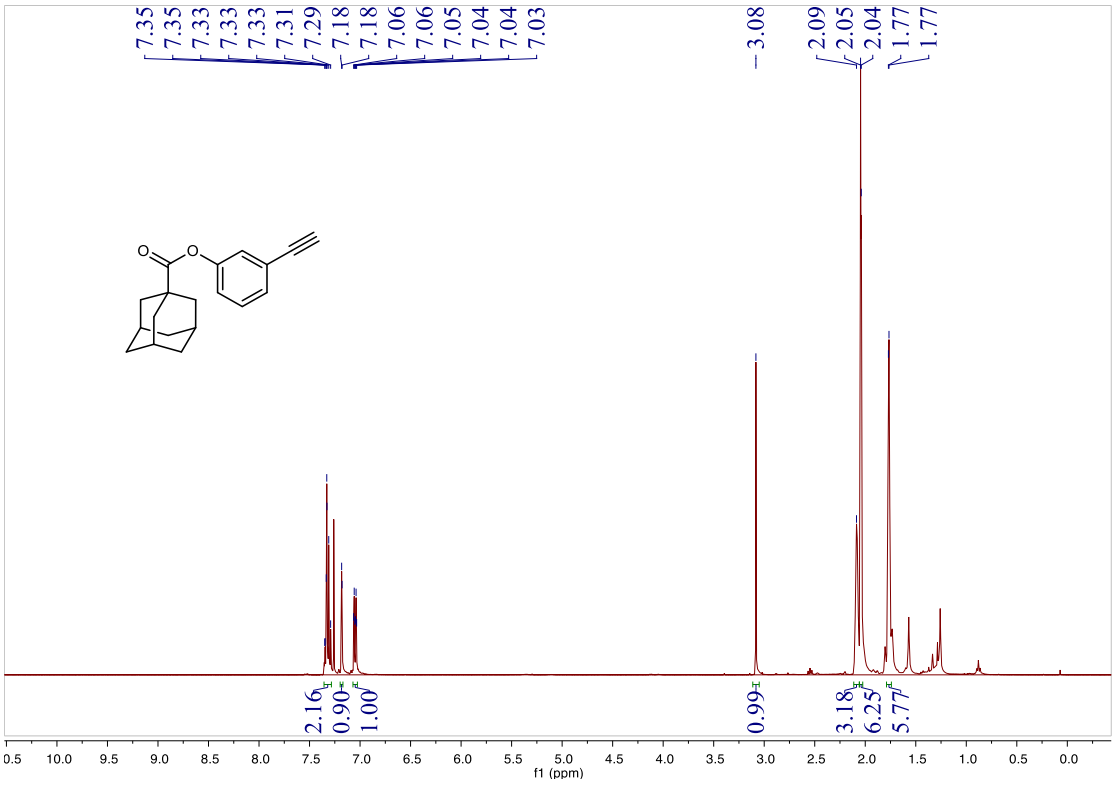
S2;^{1}H NMR (600 MHz, $CDCl_3$)



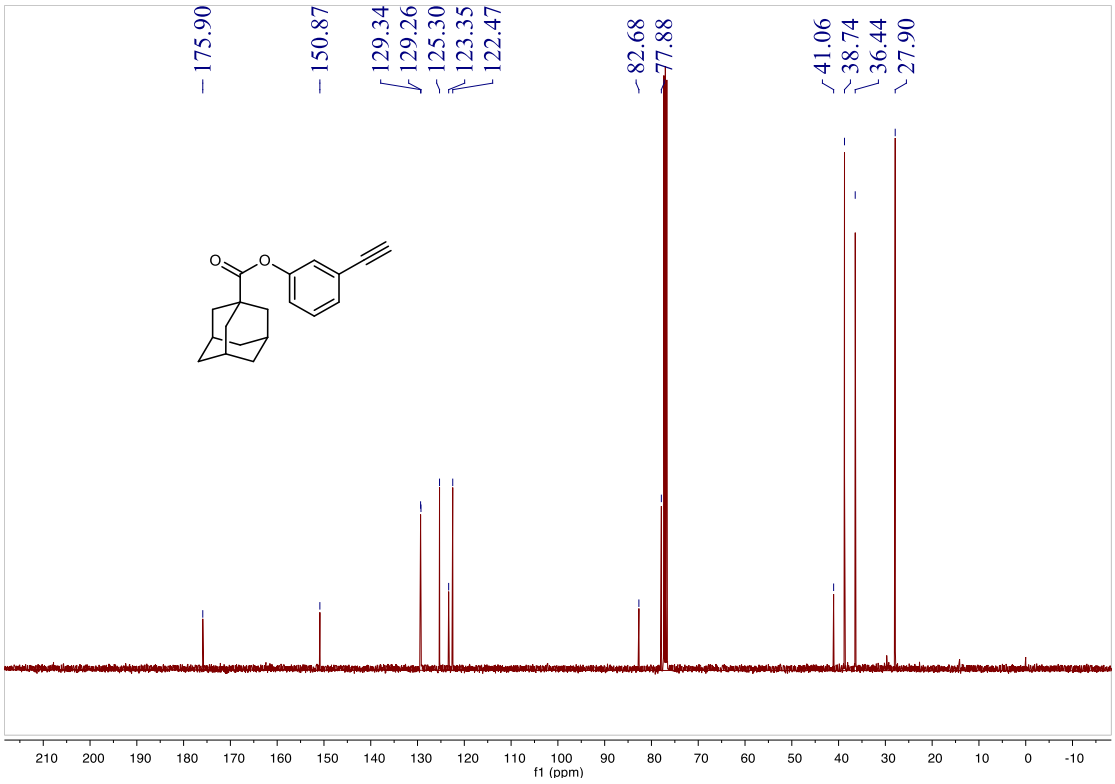
S2; ^{13}C NMR (150 MHz, $CDCl_3$)



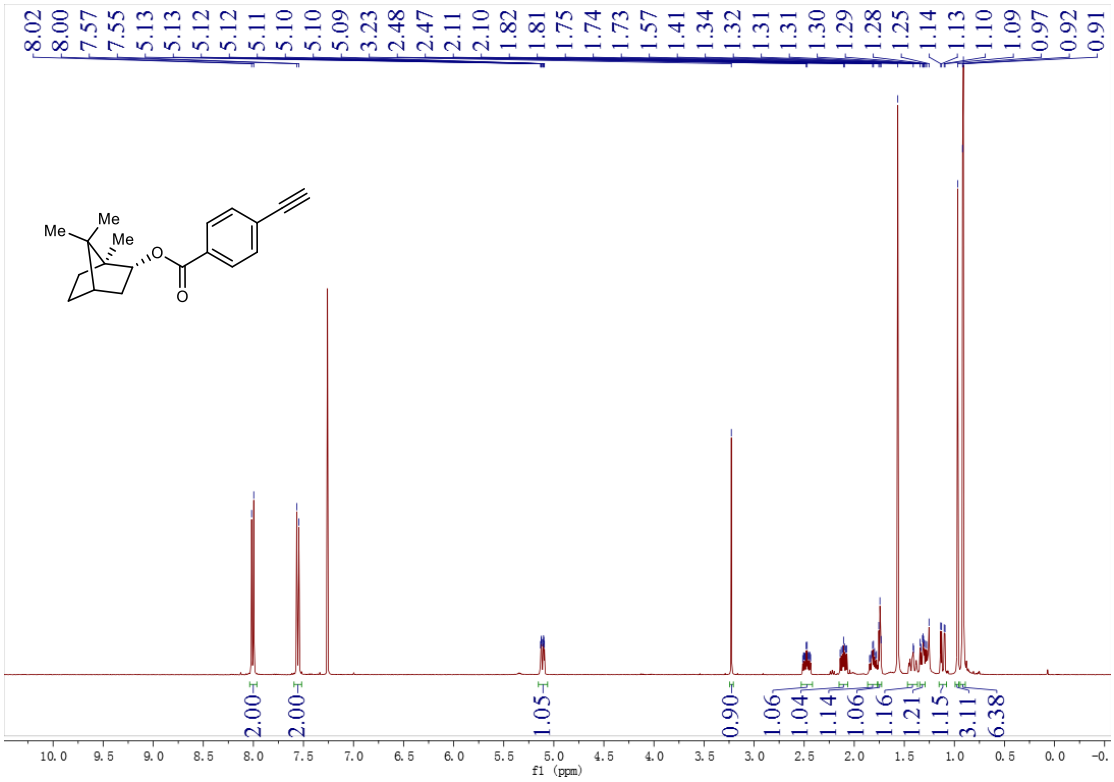
S3; ^{1}H NMR (400 MHz, $CDCl_3$)



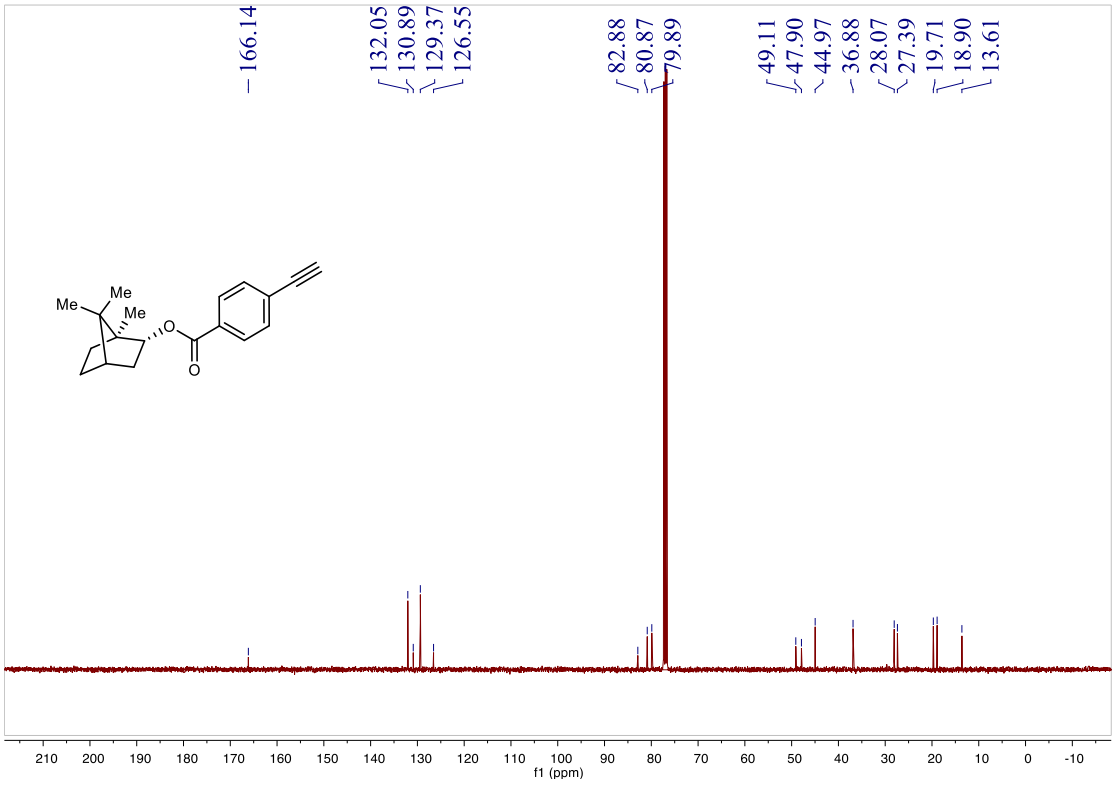
S3; ^{13}C NMR (100 MHz, $CDCl_3$)



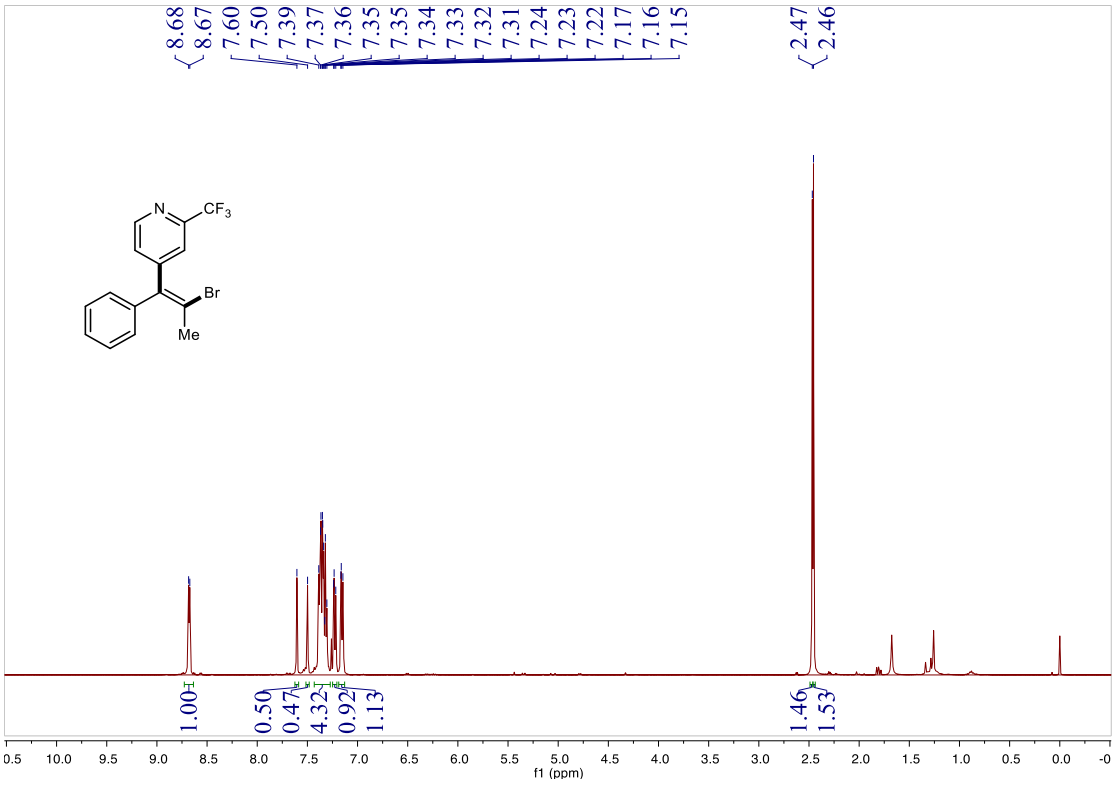
S4; ^{1}H NMR (400 MHz, $CDCl_3$)



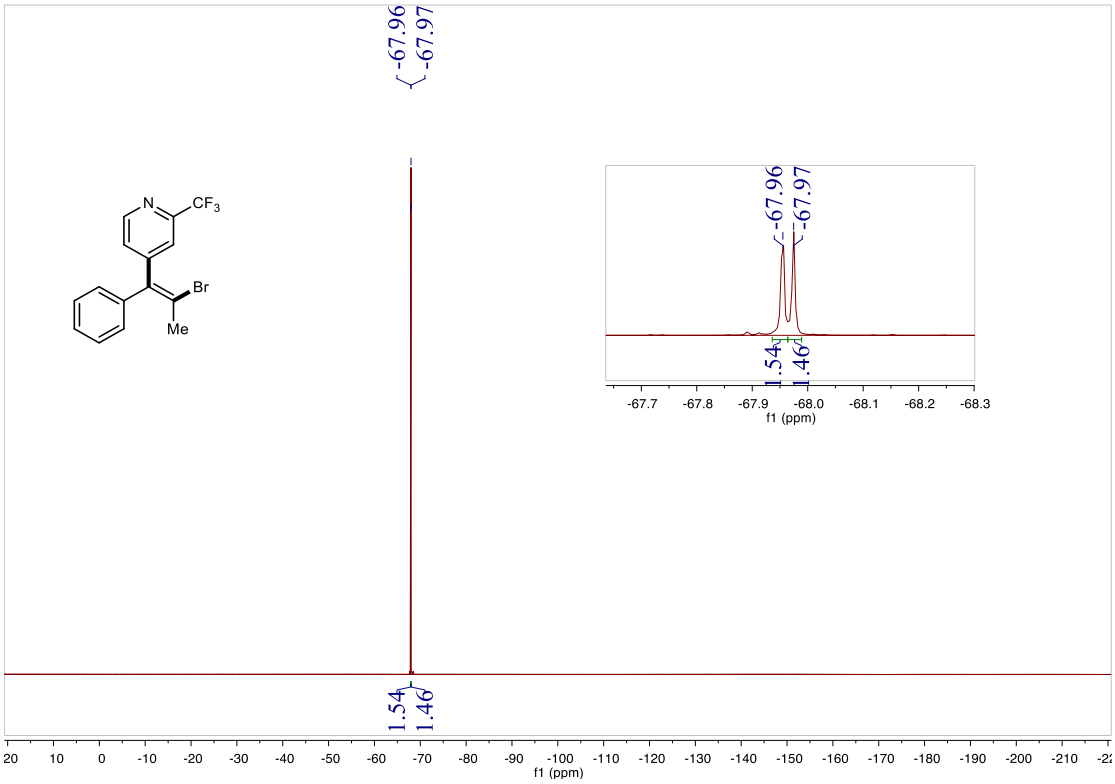
S4; ^{13}C NMR (100 MHz, $CDCl_3$)



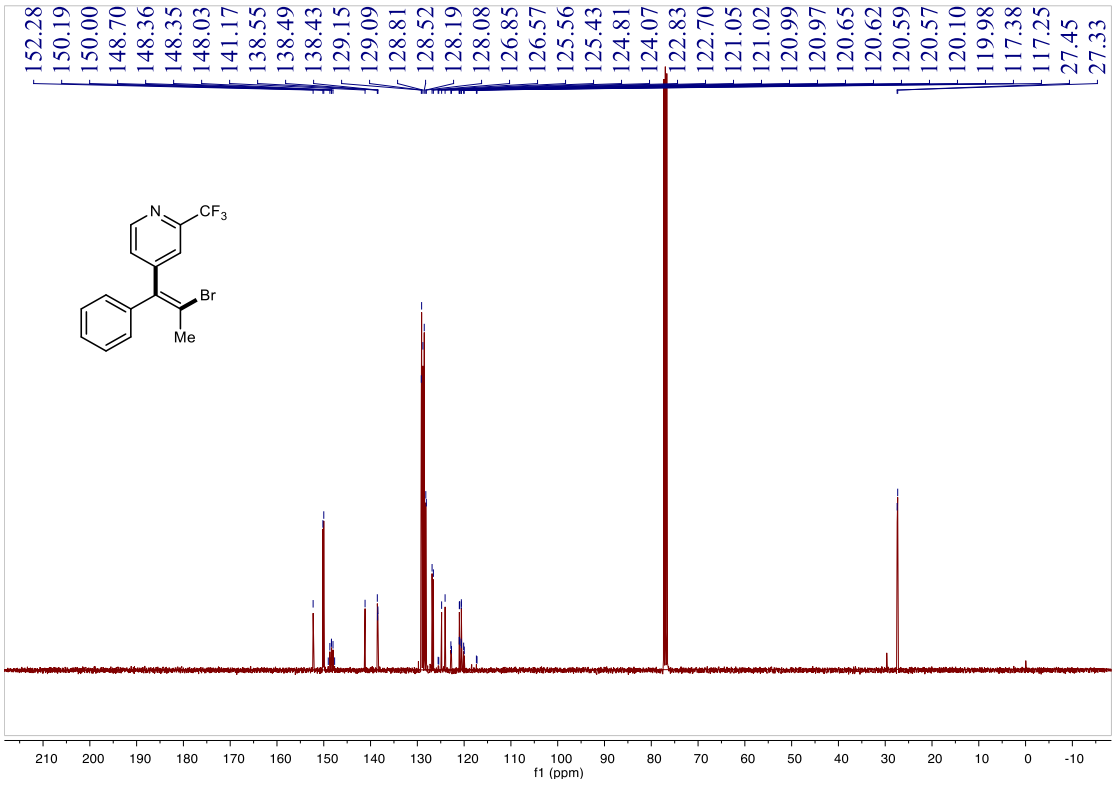
72; ^{1}H NMR (400 MHz, $CDCl_3$)



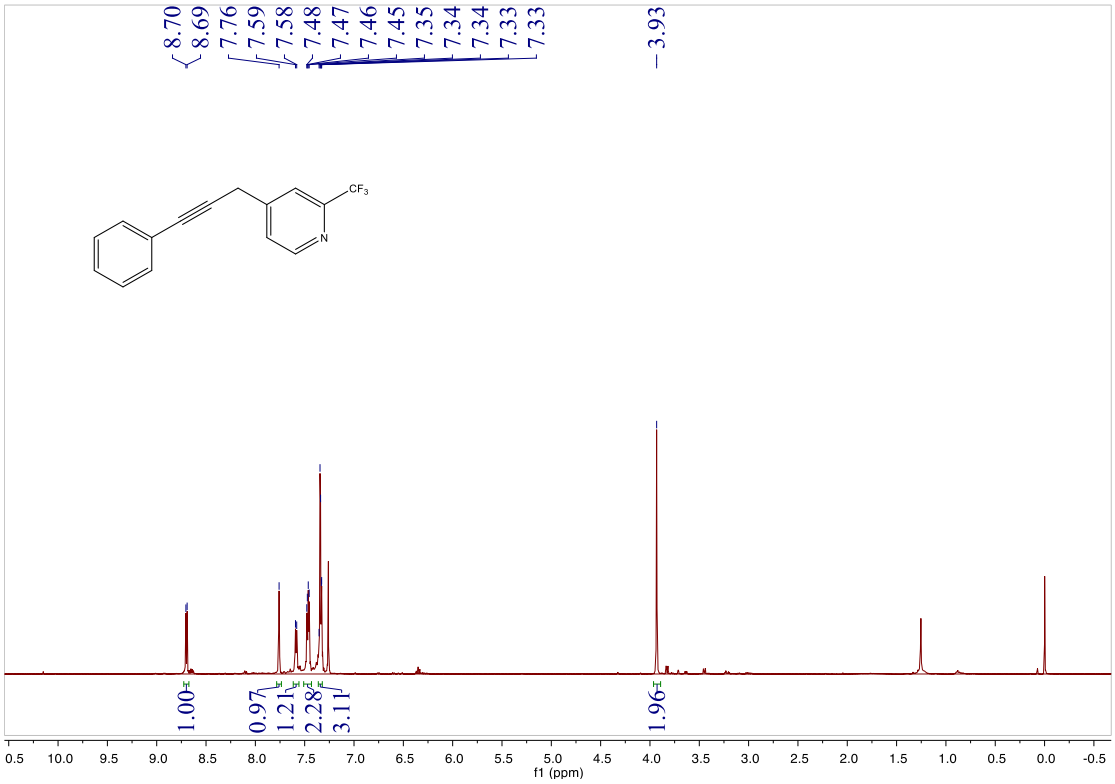
72; ^{19}F NMR (376 MHz, $CDCl_3$)



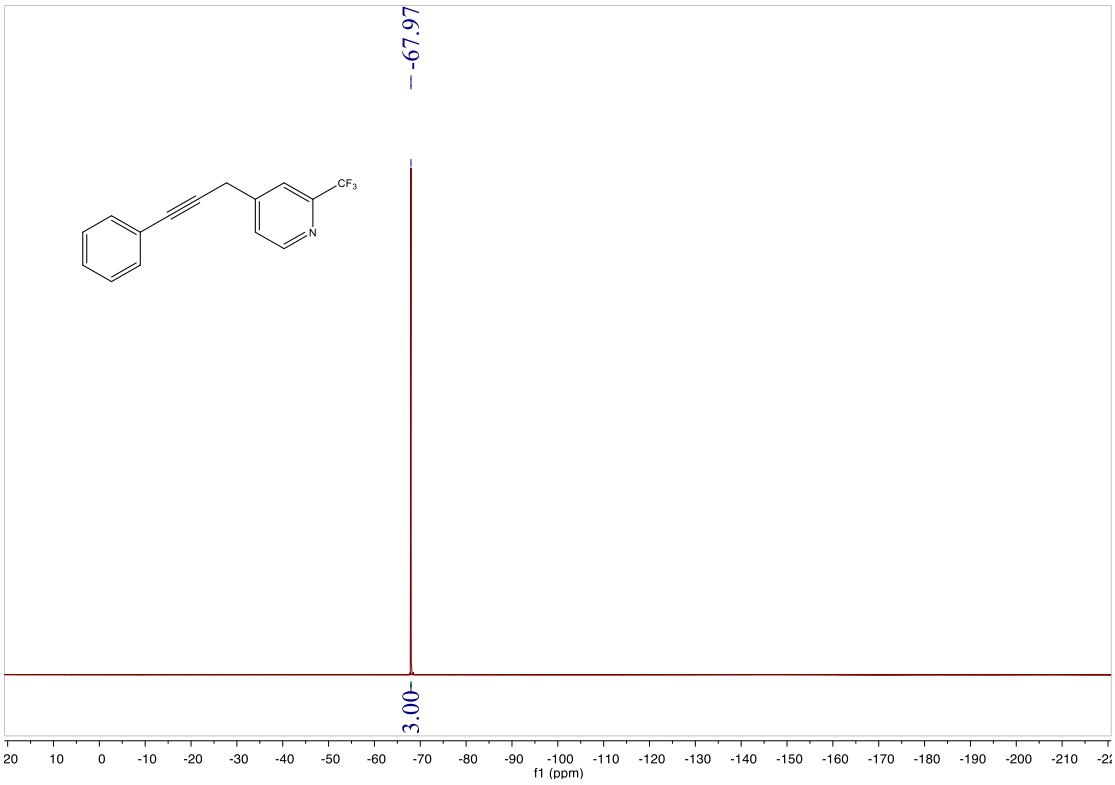
72; ^{13}C NMR (100 MHz, $CDCl_3$)



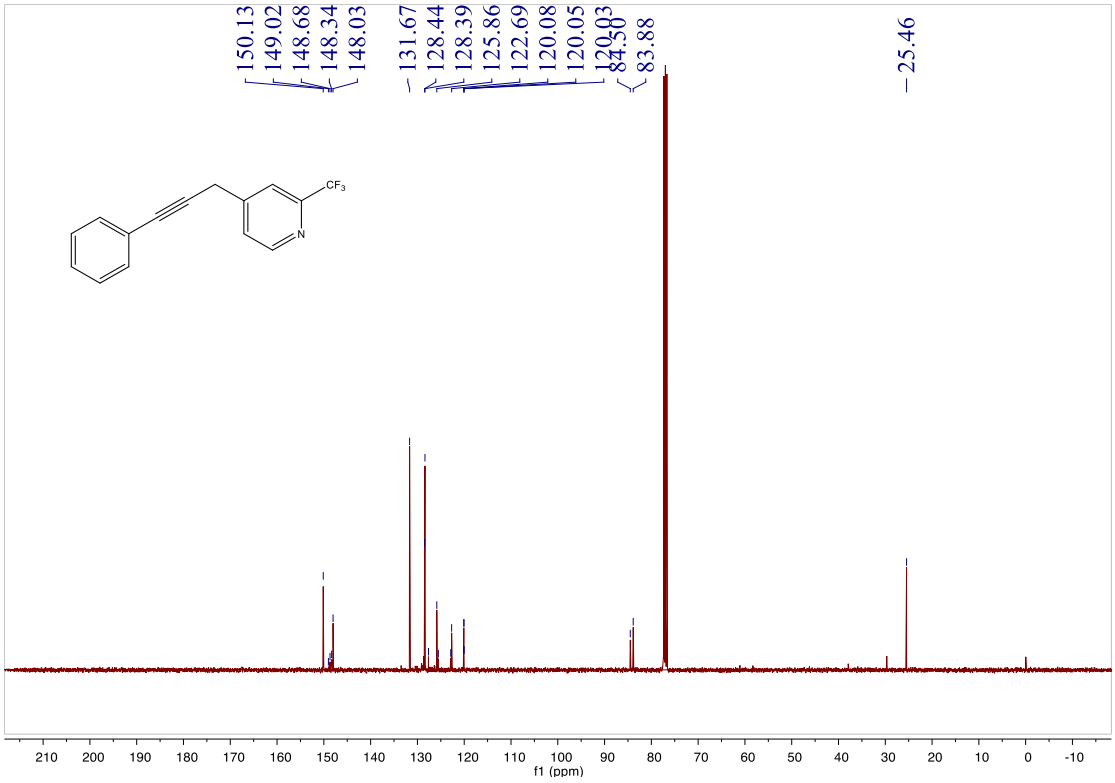
73; ^{1}H NMR (400 MHz, $CDCl_3$)



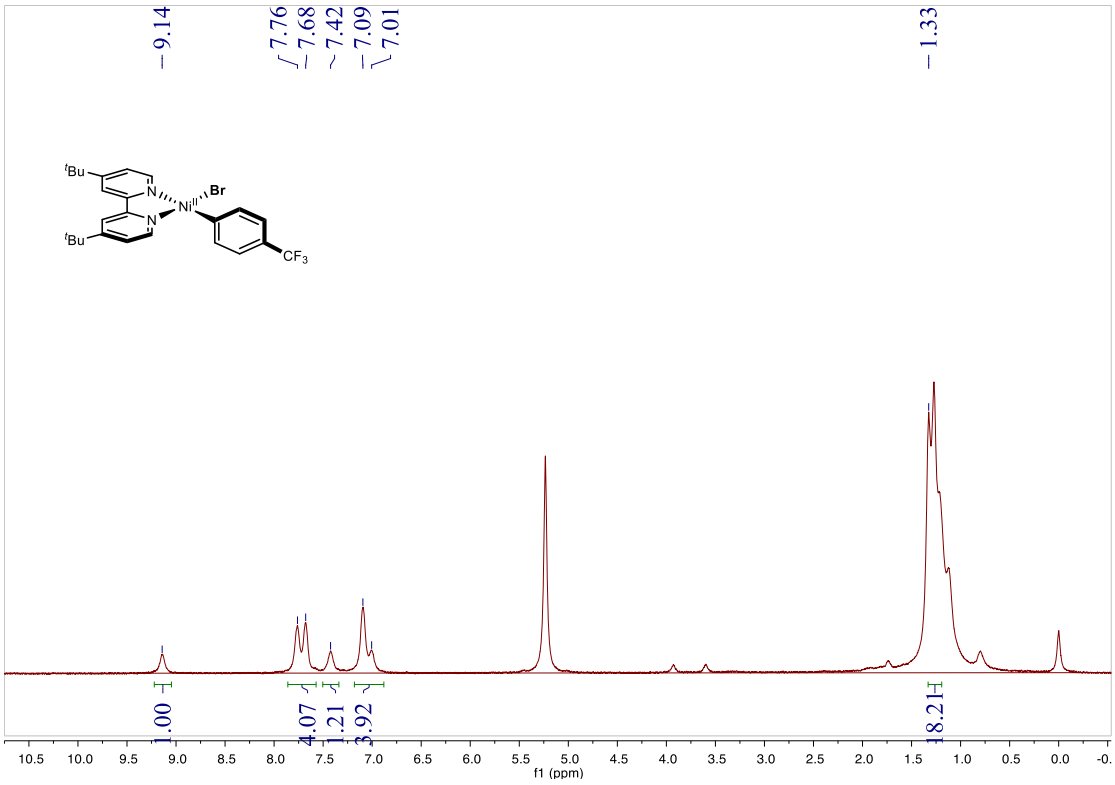
73; ^{19}F NMR (376 MHz, $CDCl_3$)



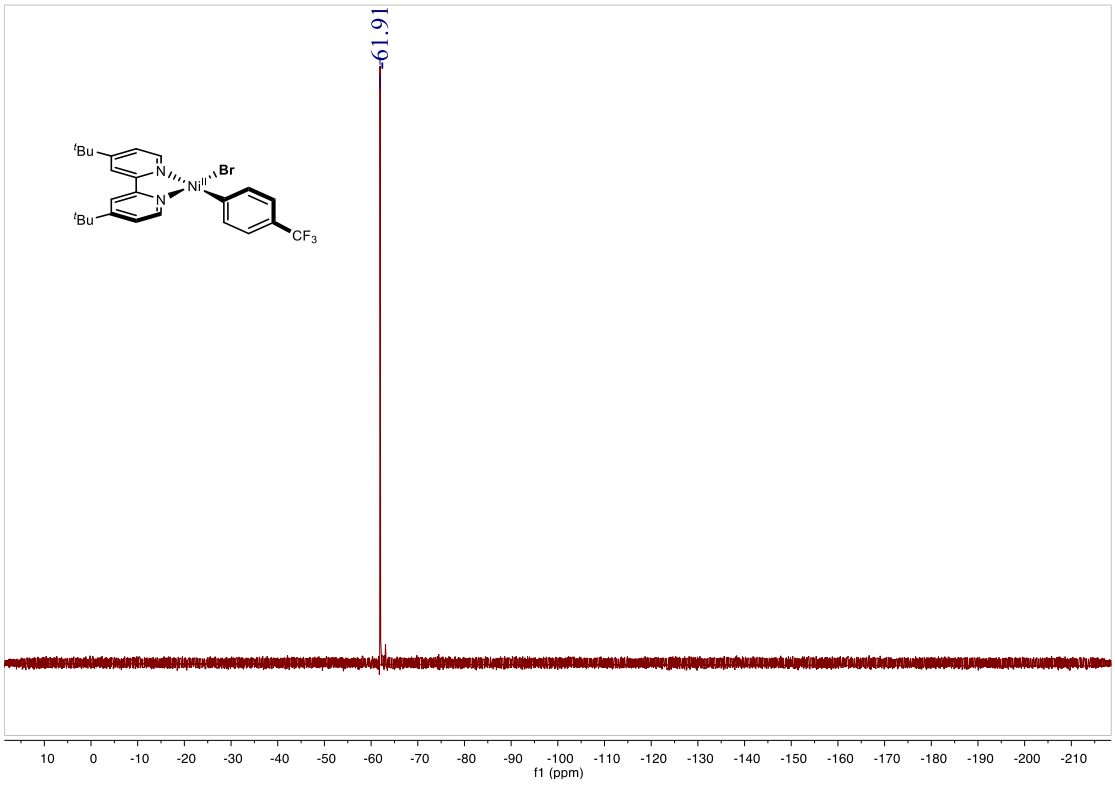
73; ^{13}C NMR (100 MHz, $CDCl_3$)



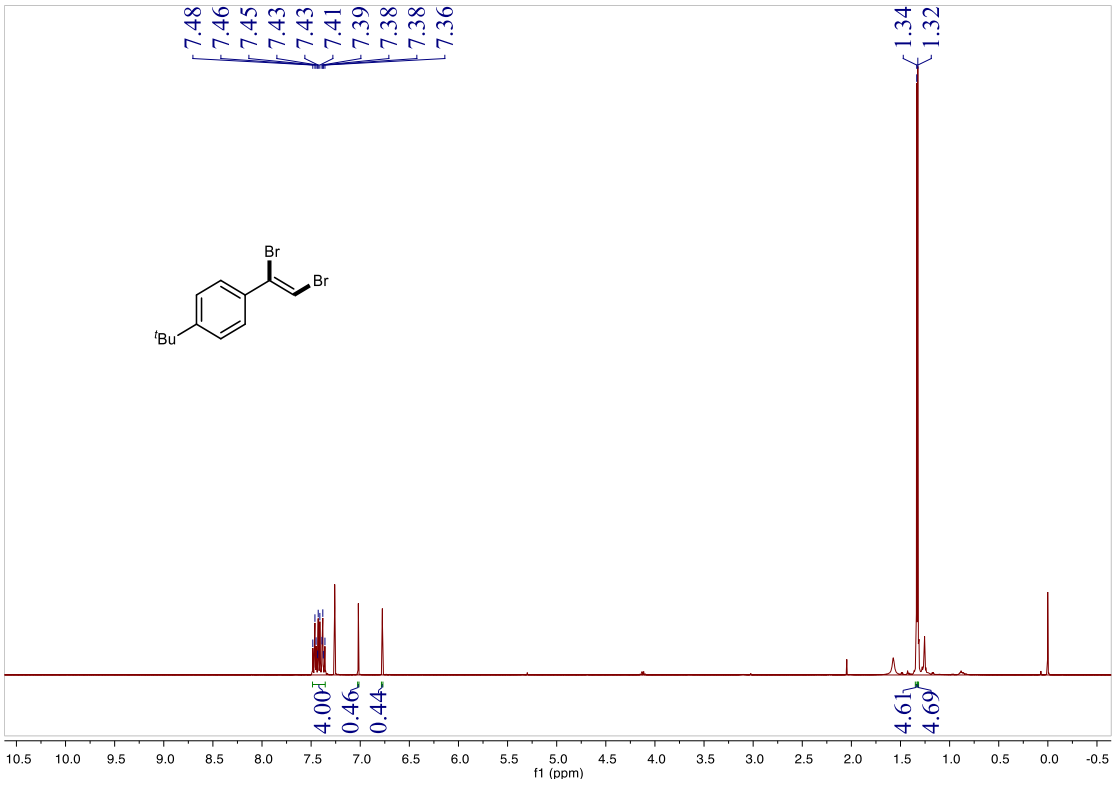
74; ^{1}H NMR (400 MHz, CD_2Cl_2)



74; ^{19}F NMR (376 MHz, CD_2Cl_2)



76; ^{1}H NMR (400 MHz, $CDCl_3$)



76; ^{13}C NMR (100 MHz, $CDCl_3$)