Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper-Catalyzed Direct C-H Fluoroalkenylation of Heteroarenes

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Supporting information

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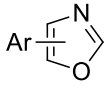
1. General information

Commercially available reagents were used without further purification. Reactions were carried out under a nitrogen atmosphere using oven or flame-dried glassware. Anhydrous solvents were purchased from Sigma-Aldrich. THF (Na/benzophenone), CH_2Cl_2 (CaH_2) and toluene (CaH_2) were dried and distillated prior to use. *t*-BuOLi was sublimated before use. All reactions were monitored by thin-layer chromatography with Merck silica gel 60 F254 pre-coated aluminium plates (0.25 mm). Flash chromatography was carried out using Silicaflash P60 silica gel (40-60 μm). Melting points (mp) were determined on a Fisher Scientific hot stage melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using a Bruker Avance-300 spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C) and 282 MHz (^{19}F), respectively. The chemical shifts (δ) were calibrated on residual proton and carbon resonance of $CDCl_3$ (^{1}H, 7.26 ppm and ^{13}C, 77.2 ppm). In the ^{13}C NMR spectra, signals corresponding to CH, CH_2, or CH_3 groups were assigned from DEPT-135. The multiplicity signals were indicated with the common abbreviations s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and the combinations thereof. IR spectra were recorded on Perkin Elmer Spectrum 100 FT IR spectrometer. Low resolution mass spectra (MS) were performed with Jeol JMS-AX500 spectrometer in chemical ionisation (CI) or electrospray ionisation (ESI). High resolution mass spectra (HRMS) were recorded on a LC Waters Acquity coupled to a Waters LCT Premier XE instrument.

Preparation of some reactants:

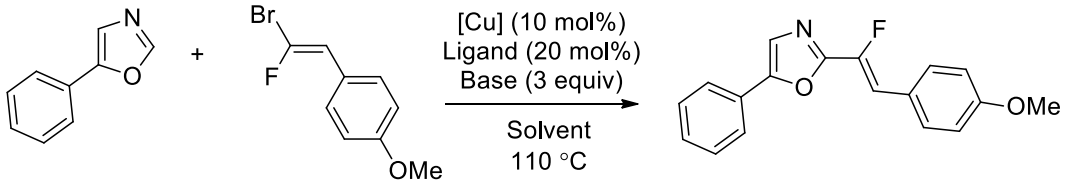
- *Gem*-bromofluoroalkenes were synthetized according to X. Lei, G. Dutheuil, X. Pannecoucke and J. -C. Quirion, *Org. Lett.*, 2004, **6**, 2101; from the appropriate aldehyde and tribromofluoromethane.
- Phenyloxazoles **2a** – **2d** were synthetized according to A. M. van Leusen, B. E. Hoogenboom and H. Siderius, *Tetrahedron Lett.*, 1972, **13**, 3114; from tosylmethylisocyanide and appropriate aldehyde.



Ar = 5-phenyl; **2a**
Ar = 5-(4-methoxyphenyl); **2b**
Ar = 5-(4-trifluoromethylphenyl); **2c**
Ar = 5-naphtyl; **2d**
Ar = 4-phenyl; **2e**

2. Optimization of the reaction conditions

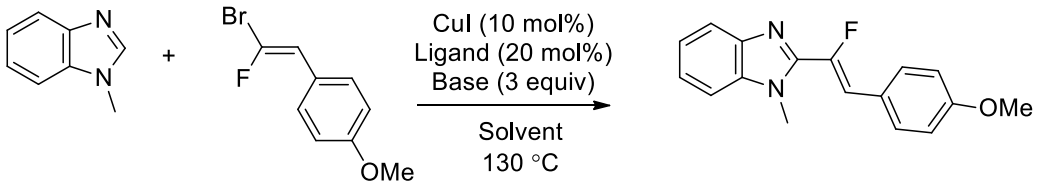
a. Optimization of the copper-catalyzed fluoroalkenylation on 5-phenyl-1,3-oxazole



Entry[a]	[Cu]	Ligand	Base	Solvent	Yield [%][b]
1	CuI	Phen	*t*-BuOLi	1,4-Dioxane	51
2	CuI	Phen	*t*-BuOLi	Toluene	29
3	CuI	Phen	*t*-BuOLi	DMF	1
4	CuI	PPh_3	*t*-BuOLi	1,4-Dioxane	83
5	***CuI***	***dppe***	***t-BuOLi***	***1,4-Dioxane***	***96***
6	CuI	-	*t*-BuOLi	1,4-Dioxane	65
7	CuI	L_1[c]	*t*-BuOLi	1,4-Dioxane	51
8	CuI	PCy_3HBF_4	*t*-BuOLi	1,4-Dioxane	51
9	CuI	L_2[d]	*t*-BuOLi	1,4-Dioxane	81
10	CuI (5 mol%)	dppe	*t*-BuOLi	1,4-Dioxane	85
11	CuI	dppe	*t*-BuOLi (2 equiv)	1,4-Dioxane	80
12	CuI	dppe	K_2CO_3	1,4-Dioxane	0
13	-	dppe	*t*-BuOLi	1,4-Dioxane	0
14	$Cu(OTf)_2$	dppe	*t*-BuOLi	1,4-Dioxane	65
15	$CuCl_2$	dppe	*t*-BuOLi	1,4-Dioxane	73
16	$Cu(OAc)_2$	dppe	*t*-BuOLi	1,4-Dioxane	49
17	CuBr	-	*t*-BuOLi	1,4-Dioxane	63
18	CuBr	dppe	*t*-BuOLi	1,4-Dioxane	66
19[e]	CuI	dppe	*t*-BuOLi	1,4-Dioxane	19
20[f]	CuI	dppe	*t*-BuOLi	1,4-Dioxane	42
21[g]	CuI	dppe	*t*-BuOLi	1,4-Dioxane	28
22[h]	CuI	dppe	*t*-BuOLi	1,4-Dioxane	0

[a]Reaction conditions: [Cu] (10 mol%), ligand (20 mol%), base (3 equiv), solvent (0.25 M), 110 °C, 12 h. [b]Yield based on isolated product after flash chromatography. [c]L_1 = 3,4,7,8-$(Me)_4$-1,10-Phen. [d]L_2 = *Trans-N,N'*-dimethylcyclohexa-1,2-diamine. [e]Under air atmosphere. [f]With 50 mg of 4 Å molecular sieve. [g]With 5 mol% of water. [h]With 10 mol% of water.

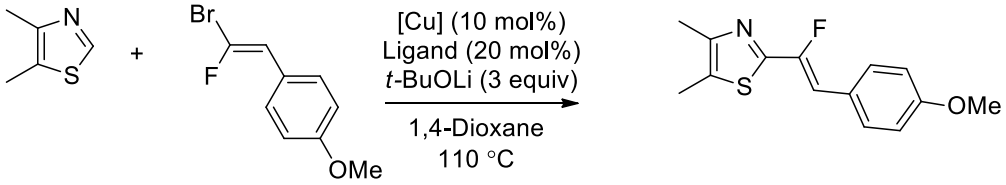
b. Optimization of the copper-catalyzed fluoroalkenylation on 1-methyl-1*H*-benzo[d]imidazole



Entry[a]	Ligand	Base	Solvent	Yield [%][b]
1	Phen	*t*-BuOLi	1,4-Dioxane	0[d]
2	Phen	*t*-BuOLi	1,4-Dioxane	43
3	Phen	*t*-BuOLi	DMF	0
4	dppe	*t*-BuOLi	1,4-Dioxane	Traces
5	***L₂*** [c]	***t-BuOLi***	***1,4-Dioxane***	***54***
6	L_2 [c]	Cs_2CO_3	1,4-Dioxane	0
7	L_2 [c]	K_2CO_3	1,4-Dioxane	39
8	L_2 [c]	*t*-BuOK	1,4-Dioxane	0

[a]Reaction conditions: CuI (10 mol%), ligand (20 mol%), base (3 equiv), solvent (0.25 M), 130 °C, 12 h. [b]Yield based on isolated product after flash chromatography. [c]L_2 = *Trans-N,N'*-dimethylcyclohexa-1,2-diamine. [d]Performed at 110 °C.

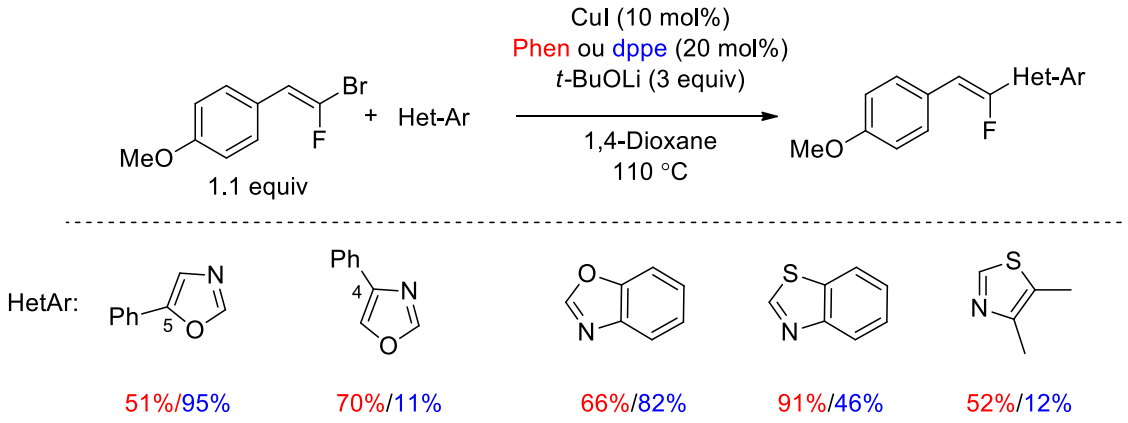
c. Optimization of the copper-catalyzed fluoroalkenylation on 4,5-dimethylthiazole



Entry[a]	[Cu]	Ligand	Yield [%][b]
1	CuCl	Phen	30
2	CuBr	Phen	29
3	CuI	Phen	52
4	***CuI (20 mol%)***	***Phen (40 mol%)***	***71***
5	CuI	dppe	12

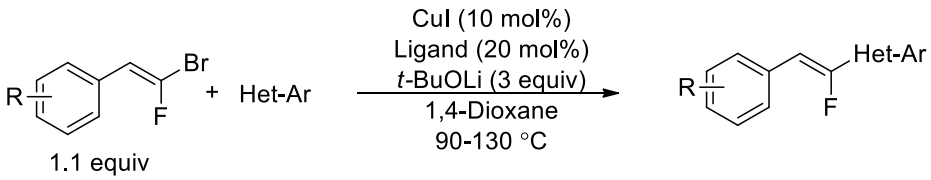
[a]Reaction conditions: [Cu] (10 mol%), ligand (20 mol%), base (3 equiv), 1,4-dioxane (0.25 M), 130 °C, 12 h. [b]Yield based on isolated product after flash chromatography.

d. Comparison between dppe and Phen ligands for the coupling of different heteroaryles



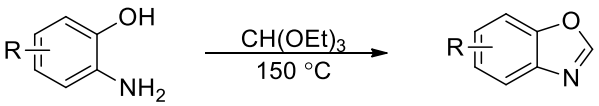
3. General procedures

a. General procedure for cross-coupling reaction



In a dry vial, was added *gem*-bromofluoroalkene (1.1 equiv), heteroaryle (1 equiv), CuI (10 mol%), ligand (20 mol%) and *t*-BuOLi (3 equiv). The vial was flushed under argon, then filled with dry 1,4-dioxane (4 mL/mmol). The reaction mixture was heated for the night at 110 °C. The mixture was poured into aqueous NH_4Cl solution (25 mL), then was extracted with CH_2Cl_2 (25 mL) three time, then dried over $MgSO_4$, filtered and concentrated. The crude was purified over silica gel column to afford the pure product.

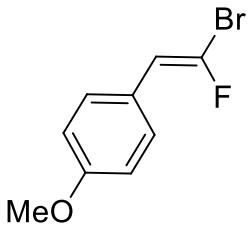
b. Synthesis of benzoxazoles



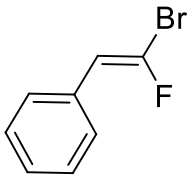
To triethylorthoformate (1.5 ml/mmol) was added 2-aminophenol (1 equiv). The mixture was heated for the night at 150 °C. After distillation to remove EtOH and $CH(OEt)_3$, the crude was then purified over silica gel column to afford the pure benzoxazole.

4. Experimental data

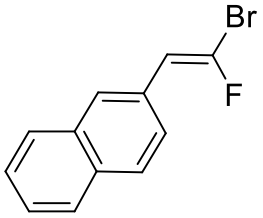
a. *Gem*-bromofluoroalkenes – Compounds **1A - 1H**



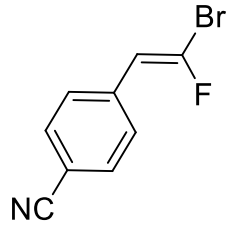
(*E*)-1-(2-Bromo-2-fluorovinyl)-4-methoxybenzene (1A): mixture of *E*/*Z* (1/1) 1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (9.6 mmol, 2.2 g), LiHMDS (5.7 mmol, 5.7 mL), THF (50 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1A** in 45% yield (1.0 g) as a yellow solid. Exhibited spectral data were identical to previous report: X. Lei, G. Dutheuil, X. Pannecoucke and J. -C. Quirion, *Org. Lett.*, 2004, **6**, 2101.



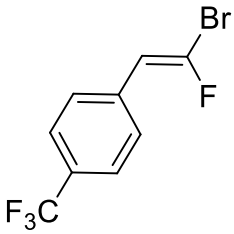
(*E*)-1-(2-Bromo-2-fluorovinyl)benzene (1B): mixture of *E*/*Z* (1/1) 1-(2-bromo-2-fluorovinyl)-benzene (4.8 mmol, 1.0 g), LiHMDS (2.9 mmol, 3.2 mL), THF (25 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1B** in 49% yield (0.5 g) as a colorless oil. IR: 3061, 1646, 1495, 1448, 1041, 914, 846, 831, 806 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.23 (m, 5H), 5.98 (d, *J* = 32.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -67.8 (d, *J* = 32.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.0 (d, *J* = 329.3 Hz, Cq), 132.6 (d, *J* = 4.5 Hz, Cq), 128.8 (s, 2xCH), 128.2 (d, *J* = 7.5 Hz, 2xCH), 128.0 (d, *J* = 2.3 Hz, CH), 113.2 (d, *J* = 6.0 Hz, CH). MS (CI-TOF): *m/z* 200 [M+H^+]. HRMS (CI-TOF): calcd for C_8H_7BrF *m/z* 200.9715 [M+H^+], found: 200.9712.



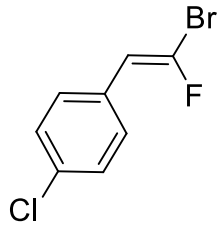
(*E*)-2-(2-Bromo-2-fluorovinyl)naphthalene (1C): mixture of *E*/*Z* (1/1) 2-(2-bromo-2-fluorovinyl)naphthalene (10.4 mmol, 2.6 g), LiHMDS (6.3 mmol, 7.0 mL), THF (50 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1C** in 45% yield (1.2 g) as a colorless solid. Exhibited spectral data were identical to previous report: X. Lei, G. Dutheuil, X. Pannecoucke and J. -C. Quirion, *Org. Lett.*, 2004, **6**, 2101.



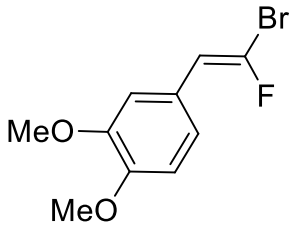
(*E*)-4-(2-Bromo-2-fluorovinyl)benzonitrile (1D): mixture of *E*/*Z* (3/2) 4-(2-bromo-2-fluorovinyl)benzonitrile (7.4 mmol, 1.7 g), LiHMDS (4.4 mmol, 4.4 mL), THF (40 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1D** in 55% yield (0.9 g) as a colorless solid.
Exhibited spectral data were identical to previous report: X. Lei, G. Dutheuil, X. Pannecoucke and J. -C. Quirion, *Org. Lett.*, 2004, **6**, 2101.



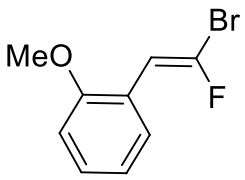
(*E*)-1-(2-Bromo-2-fluorovinyl)-4-trifluoromethylbenzene (1E): mixture of *E*/*Z* (1/1) 1-(2-bromo-2-fluorovinyl)-4-trifluoromethylbenzene (4.8 mmol, 1.3 g), LiHMDS (2.9 mmol, 2.9 mL), THF (25 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1E** in 29% yield (0.4 g) as a colorless liquid. Exhibited spectral data were identical to previous report: X. Lei, G. Dutheuil, X. Pannecoucke and J. -C. Quirion, *Org. Lett.*, 2004, **6**, 2101.



(*E*)-1-(2-Bromo-2-fluorovinyl)-4-chlorobenzene (1F): mixture of *E*/*Z* (1/1) 1-(2-bromo-2-fluorovinyl)-4-chlorobenzene (2.12 mmol, 0.50 g), LiHMDS (1.28 mmol, 1.28 mL), THF (10 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1F** in 50% yield (250 mg) as a colorless liquid, which sometimes crystallized at room temperature. IR: 3081, 2937, 2838, 1647, 1598, 1580, 1487, 1461, 1436, 1280, 1247, 1111, 1026, 818 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (m, 4H), 5.94 (d, *J* = 33.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -67.1 (d, *J* = 32.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.4 (d, *J* = 329.3 Hz, Cq), 133.6 (d, *J* = 3.8 Hz, Cq), 131.0 (d, *J* = 4.5 Hz, Cq), 129.3 (d, *J* = 8.3 Hz, 2xCH), 128.9 (s, 2xCH), 112.1 (d, *J* = 6.0 Hz, CH). MS (CI-TOF): *m/z* 234 [M+H^+]. HRMS (CI-TOF): calcd for C_8H_6BrClF *m/z* 234.9325 [M+H^+], found: 234.9337.

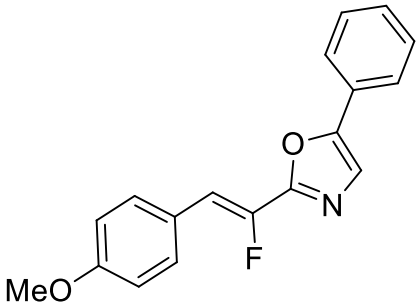


(*E*)-4-(2-Bromo-2-fluorovinyl)-1,2-dimethoxybenzene (1G): mixture of *E*/*Z* (1/1) 4-(2-bromo-2-fluorovinyl)-1,2-dimethoxybenzene (3.8 mmol, 1.0 g), LiHMDS (2.3 mmol, 2.3 mL), THF (25 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1G** in 50% yield (0.5 g) as a yellow liquid. Exhibited spectral data were identical to previous report: X. Lei, G. Dutheuil, X. Pannecoucke and J. -C. Quirion, *Org. Lett.*, 2004, **6**, 2101.

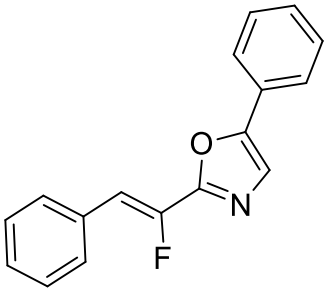


(*E*)-1-(2-Bromo-2-fluorovinyl)-2-methoxybenzene (1H): mixture of *E*/*Z* (55/45) 1-(2-bromo-2-fluorovinyl)-2-methoxybenzene (5.40 mmol, 1.24 g), LiHMDS (3.20 mmol, 3.2 mL), THF (25 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE) affording compound **1H** in 52% yield (645 mg) as a yellow oil. IR: 3081, 2837, 1646, 1598, 1580, 1487, 1461, 1436, 1247, 1111, 1026, 818 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.43 (d, *J* = 33.0 Hz, 1H), 3.84 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -69.1 (d, *J* = 33.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8 (d, *J* = 1.2 Hz, Cq), 133.5 (d, *J* = 330.2 Hz, Cq), 129.3 (d, *J* = 14.1 Hz, CH), 129.2 (s, CH), 121.4 (d, *J* = 4.9 Hz, Cq), 120.8 (s, CH), 110.7 (d, *J* = 0.6 Hz, CH), 107.0 (d, *J* = 4.6 Hz, CH), 55.6 (s, CH_3). MS (CI-TOF): *m/z* 230 [$M+H^+$]. HRMS (ESI-TOF): calcd for C_9H_9BrFO *m/z* 230.9821 [$M+H^+$], found: 230.9821.

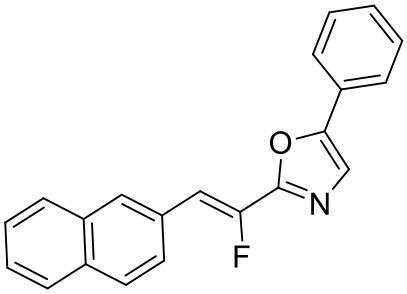
b. Variation of *gem*-bromofluoroalkene - Compounds **3Aa - 3Ha**



(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-5-phenyloxazole (3Aa): (*E*)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Aa** in 96% yield (56 mg) as a colorless solid. Exhibited spectral data were identical to previous report: C. Schneider, D. Masi, S. Couve-Bonnaire, X. Pannecoucke and C. Hoarau, *Angew. Chem. Int. Ed.*, 2013, **52**, 3246.

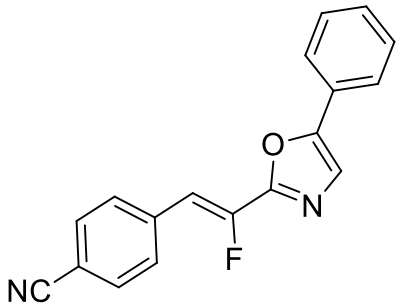


(*Z*)-2-(1-Fluoro-2-phenylvinyl)-5-phenyloxazole (3Ba): (*E*)-(2-bromo-2-fluorovinyl)-benzene (0.22 mmol, 44 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Ba** in 89% yield (47 mg) as a colorless solid. mp 89-91 °C (CH_2Cl_2/PE). IR: 3050, 1531, 1487, 1444, 1354, 1137, 1025, 957, 943, 820 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (m, 4H), 7.49-7.32 (m, 7H), 6.79 (d, *J* = 37.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -126.5 (d, *J* = 37.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2 (d, *J* = 37.5 Hz, Cq), 152.2 (s, Cq), 146.1 (d, *J* = 255.1 Hz, Cq), 132.1 (d, *J* = 3.9 Hz, Cq), 129.7 (d, *J* = 7.8 Hz, 2xCH), 129.10 (s, 2xCH), 129.06 (s, CH), 128.9 (s, 2xCH), 128.8 (s, CH), 127.4 (s, Cq), 124.5 (s, 2xCH), 123.8 (d, *J* = 1.3 Hz, CH), 111.5 (d, *J* = 5.0 Hz. CH). MS (ESI-TOF): *m/z* 266 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{17}H_{13}FNO$ *m/z* 266.0981 [M+H^+], found: 266.0968.

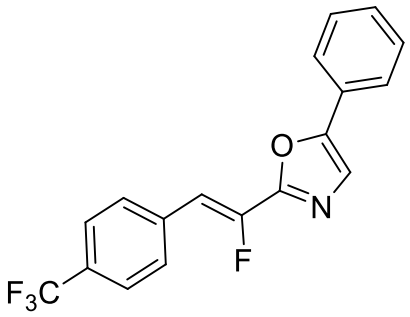


(*Z*)-2-(1-Fluoro-2-(naphth-2-yl)vinyl)-5-phenyloxazole (3Ca): (*E*)-2-(2-bromo-2-fluorovinyl)naphthalene (0.22 mmol, 55 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 3/7) affording compound **3Ca** in 94% yield (59 mg) as a yellow solid. mp 149-151 °C (CH_2Cl_2/PE). IR: 3057, 1660, 1593, 1531, 1485, 1449, 1344, 1320, 1062, 963, 949, 905, 875, 821 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.90-7.80 (m, 4H), 7.72 (d, *J* = 6.4 Hz, 2H), 7.52-7.45 (m, 5H), 7.40 (d, *J* = 6.4 Hz, 1H), 6.96 (d, *J*

= 37.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -126.5 (d, *J* = 37.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2 (s, Cq), 146.2 (d, *J* = 253.5 Hz, Cq), 133.4 (s, Cq), 133.2 (d, *J* = 1.5 Hz, Cq), 129.7 (s, Cq), 129.7 (d, *J* = 7.5, CH), 129.6 (s, Cq), 129.1 (s, 2xCH), 129.1 (s, CH), 128.5 (d, *J* = 2.3 Hz, CH), 127.8 (s, CH), 127.4 (s, Cq), 126.9 (s, CH), 126.8 (s, CH), 126.7 (s, CH), 126.6 (s, CH), 124.5 (s, 2xCH), 123.9 (s, CH), 111.7 (d, *J* = 4.5 Hz, CH). MS (ESI-TOF): *m/z* 316 [M+H$^+$]. HRMS (ESI-TOF): calcd for $C_{21}H_{15}FNO$ *m/z* 316.1138 [M+H$^+$], found: 316.1136.

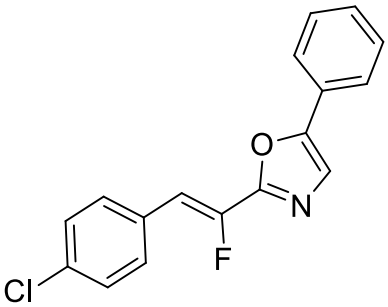


(*Z*)-4-(2-Fluoro-2-(5-phenyloxazol-2-yl)vinyl)benzonitrile (3Da): (*E*)-4-(2-bromo-2-fluorovinyl)benzonitrile (0.22 mmol, 50 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Da** in 45% yield (26 mg) as a yellow solid. Exhibited spectral data were identical to previous report: C. Schneider, D. Masi, S. Couve-Bonnaire, X. Pannecoucke and C. Hoarau, *Angew. Chem. Int. Ed.*, 2013, **52**, 3246.

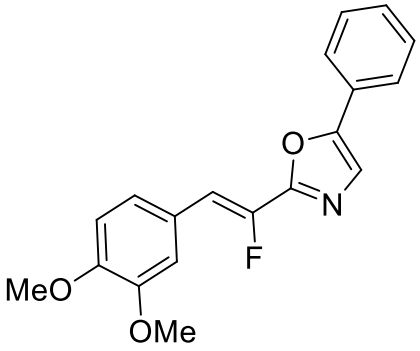


(*Z*)-2-(1-Fluoro-2-(4-trifluoromethylphenyl)vinyl)-5-phenyloxazole (3Ea): (*E*)-1-(2-bromo-2-fluorovinyl)-4-trifluoromethylbenzene (0.22 mmol, 59 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Ea** in 62% yield (40 mg) as a yellow solid. mp 89-91 °C (CH_2Cl_2/PE). IR: 1615, 1486, 1406, 1322,

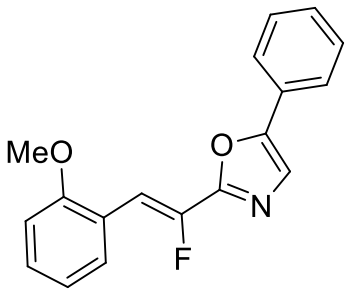
1167, 1115, 1066, 971, 958, 876, 828 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.51-7.33 (m, 4H), 6.81 (d, *J* = 36.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.8 (s, 3F), -123.6 (d, *J* = 36.6 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6 (d, *J* = 36.2 Hz, Cq), 152.7 (s, Cq), 147.3 (d, *J* = 258.1 Hz, Cq), 135.5 (d, *J* = 2.6 Hz, Cq), 130.4 (qd, *J* = 32.7, 2.8 Hz, Cq), 129.8 (d, *J* = 8.1 Hz, 2xCH), 129.4 (s, CH), 129.2 (s, 2xCH), 127,2 (s, Cq), 125.4 (q, *J* = 276.9 Hz, Cq), 125.9 (q, *J* = 3.7 Hz, 2xCH), 124.5 (s, 2xCH), 124.0 (d, *J* = 1.4 Hz, CH), 110.0 (d, *J* = 4.8 Hz, CH). MS (ESI-TOF): *m/z* 334 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{18}H_{12}F_4NO$ *m/z* 334.0855 [M+H^+], found: 334.0851.



(*Z*)-2-(1-Fluoro-2-(4-chlorophenyl)vinyl)-5-phenyloxazole (3Fa): (*E*)-1-(2-bromo-2-fluorovinyl)-4-chlorobenzene (0.22 mmol, 52 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Fa** in 71% yield (42 mg) as a colorless solid. mp 139-141 °C (CH_2Cl_2/PE). IR: 3066, 1653, 1486, 1408, 1351, 1335, 1138, 1082, 1012, 957, 941, 874, 810 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.47-7.41 (m, 3H), 7.40-7.34 (m, 3H), 6.73 (d, *J* = 37.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -125.9 (d, *J* = 36.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9 (d, *J* = 33.8 Hz, Cq), 152.3 (s, Cq), 146.4 (d, *J* = 254.3 Hz, Cq), 134.6 (d, *J* = 3.8 Hz, Cq), 130.9 (d, *J* = 8.0 Hz, 2xCH), 130.7 (d, *J* = 3.8 Hz, Cq), 129.2 (s, 3xCH), 129.1 (s, 2xCH), 127.3 (s, Cq), 124.6 (d, *J* = 7.1 Hz, 2xCH), 123.9 (d, *J* = 1.4 Hz, CH), 110.3 (d, *J* = 5.0 Hz, CH). MS (ESI-TOF): *m/z* 302 [M+H^+], 300 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{17}H_{12}{}^{35}ClFNO$ *m/z* 300.0591 [M+H^+], found: 300.0596.



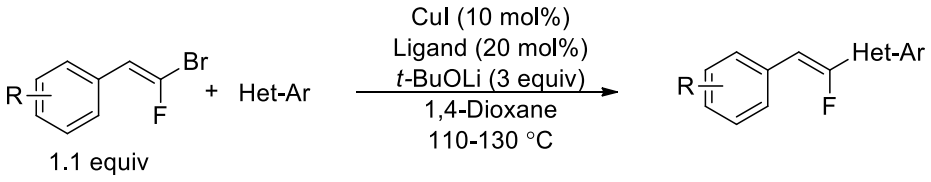
(*Z*)-2-(1-Fluoro-2-(3,4-dimethoxyphenyl)vinyl)-5-phenyloxazole (3Ga): (*E*)-1-(2-bromo-2-fluorovinyl)-3,4-dimethoxybenzene (0.22 mmol, 57 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Ga** in 68% yield (44 mg) as a yellow solid. mp 120-122 °C (CH_2Cl_2/PE). IR: 3113, 2833, 1585, 1530, 1514, 1413, 1338, 1263, 1144, 1072, 1018, 869, 848, 803 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.71-7.67 (m, 2H), 7.48-7.42 (m, 3H), 7.38-7.36 (m, 1H), 7.30 (s, 1H), 7.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 37.7 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -129.6 (d, *J* = 37.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9 (s, Cq), 149.8 (s, Cq), 149.7 (s, Cq), 149.0 (s, Cq), 145.0 (d, *J* = 252.1 Hz, Cq), 129.1 (s, 2xCH), 129.0 (s, CH), 127.5 (s, Cq), 125.0 (d, *J* = 4.0 Hz, Cq), 124.5 (s, 2xCH), 123.7 (s, CH), 123.4 (d, *J* = 7.2 Hz, CH), 112.2 (d, *J* = 9.2 Hz, CH), 111.5 (d, *J* = 5.0 Hz, CH), 111.2 (s, CH), 56.0 (s, CH_3), 55.9 (s, CH_3). MS (ESI-TOF): *m/z* 326 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{19}H_{17}FNO_3$ *m/z* 326.1192 [M+H^+], found: 326.1187.



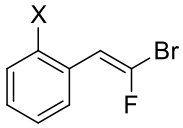
(*Z*)-2-(1-Fluoro-2-(2-methoxyphenyl)vinyl)-5-phenyloxazole (3Ha): (*E*)-1-(2-bromo-2-fluorovinyl)-2-methoxybenzene (0.22 mmol, 51 mg), 5-phenyloxazole (0.20 mmol, 29 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 3/7) affording compound **3Ha** in 58% yield (34 mg)

as a colorless solid. mp 135-137 °C (CH_2Cl_2/PE). IR: 3098, 2924, 1570, 1532, 1485, 1463, 1435, 1350, 1284, 1242, 1111, 1024, 957, 944, 851, 844, 821 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.73 (m, 1H), 7.71 (s, 1H), 7.51-7.29 (m, 5H), 7.28 (d, *J* = 39.0 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -128.1 (d, *J* = 39.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0 (s, Cq), 156.9 (s, Cq), 152.0 (s, Cq), 146.1 (d, *J* = 254.1 Hz, Cq), 130.6 (d, *J* = 13.7 Hz, CH), 130.2 (d, *J* = 2.0 Hz, CH), 129.1 (s, 2xCH), 129.0 (s, CH), 127.5 (s, Cq), 124.5 (s, 2xCH), 123.8 (s, CH), 121.0 (s, Cq), 120.9 (s, CH), 110.7 (s, CH), 105.3 (d, *J* = 3.4 Hz, CH), 55.7 (s, CH_3). MS (ESI-TOF): *m/z* 296 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{18}H_{15}FNO_2$ *m/z* 296.1087 [M+H^+], found: 296.1077.

c. Reluctant substrates



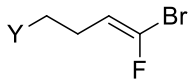
Ortho EWG on *gem*-bromofluoroalkene



X = F, Cl, CN

Results: degradation of starting material in basic conditions

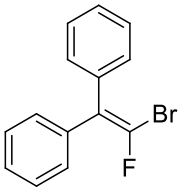
Alkyl *gem*-bromofluoroalkene



Y = Ph, OTBDPS

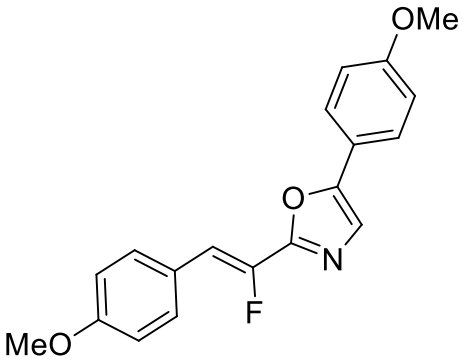
Results: no reaction at 110 °C; traces at 130 °C

Tetrasubstitued *gem*-bromofluoroalkene

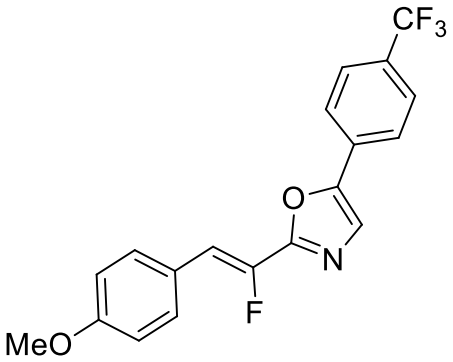


Results: traces of final product

d. Variation of phenyloxazole – Compounds **3Ab - 3Ce**

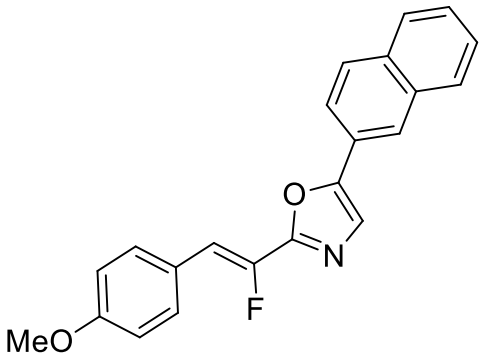


(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-5-(4-methoxyphenyl)oxazole (3Ab): (*E*)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 5-(4-methoxyphenyl)oxazole (0.20 mmol, 35 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 2/8) affording compound **3Ab** in 74% yield (48 mg) as a colorless solid. mp 93-95 °C (EtOAc/PE). IR: 2926, 2842, 1604, 1535, 1497, 1300, 1250, 1174, 1021, 953, 879, 822 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.7, 1.3 Hz, 4H), 7.31 (s, 1H), 6.96 (m, 4H), 6.70 (d, *J* = 37.9 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -129.7 (d, *J* = 37.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.2 (s, Cq), 159.9 (d, *J* = 3.0 Hz, Cq), 152.0 (s, Cq), 145.0 (d, *J* = 250.5 Hz, Cq), 131.2 (d, *J* = 7.5 Hz, 2xCH), 126.0 (s, 2xCH), 124.9 (s, Cq), 124.9 (s, Cq), 122.1 (s, CH), 120.3 (s, Cq), 114.5 (s, 2xCH), 114.4 (s, 2xCH), 110.8 (d, *J* = 5.3 Hz, CH), 55.4 (s, CH_3), 55.3 (s, CH_3). MS (ESI-TOF): *m/z* 326 [$M+H^+$]. HRMS (ESI-TOF): calcd $C_{19}H_{17}FNO_3$ *m/z* 326.1192 [$M+H^+$], found: 326.1187.



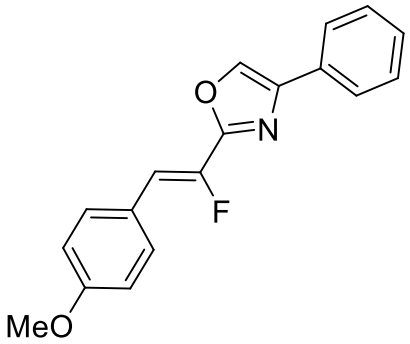
(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-5-(4-trifluoromethylphenyl)oxazole (3Ac): (*E*)-1-(2-bromo-2-fluorovinyl)-2-methoxybenzene (0.22 mmol, 51 mg), 5-(4-trifluoromethyl-

phenyl)oxazole (0.20 mmol, 43 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 4/6) affording compound **3Ac** in 83% yield (60 mg) as a yellow solid. mp 145-147 °C (CH_2Cl_2/PE). IR: 1700, 1613, 1546, 1413, 1322, 1249, 1165, 1111, 1095, 1069, 954, 871, 842, 824 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.50 (s, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 37.7 Hz, 1H), 3.76 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.7 (s, 3F), -130.1 (d, *J* = 37.7 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.3 (d, *J* = 3.3 Hz, Cq), 156.4 (d, *J* = 37.4 Hz, Cq), 150.4 (s, Cq), 144.7 (d, *J* = 252.2 Hz, Cq), 131.5 (d, *J* = 8.0 Hz, 2xCH), 130.8 (s, Cq), 130.4 (s, Cq), 126.2 (q, *J* = 3.8 Hz, 2xCH), 125.5 (d, *J* = 1.5 Hz, CH), 124.6 (d, *J* = 4.0 Hz, Cq), 124.5 (s, 2xCH), 124.0 (q, *J* = 272.0 Hz, Cq), 114.5 (s, 2xCH), 112.2 (d, *J* = 5.2 Hz, CH), 55.5 (s, CH_3). MS (ESI-TOF): *m/z* 364 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{19}H_{14}F_4NO_2$ *m/z* 364.0961 [M+H^+], found: 364.0967.

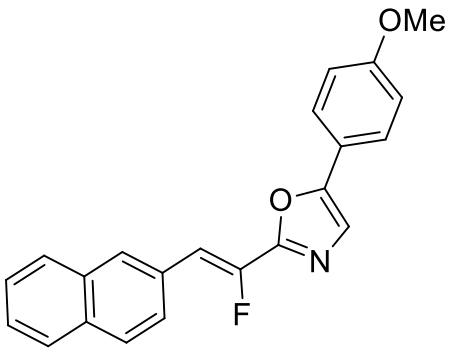


(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-5-(naphth-2-yl)oxazole (3Ad): (*E*)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 5-(naphthal-2-yl)oxazole (0.20 mmol, 39 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 1/9) affording compound **3Ad** in 80% yield (60 mg) as a yellow solid. mp 135-137 °C (CH_2Cl_2/PE). IR: 3133, 1605, 1529, 1504, 1254, 1182, 1114, 1073, 1024, 948, 886, 863, 836, 811 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.90 (m, 2H), 7.85 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.60-7.46 (m, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 37.8 Hz, 1H), 3.86 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -129.8 (d, *J* = 37.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1(d, *J* = 2.9 Hz, Cq), 156.0 (d, *J* = 37.4 Hz, Cq), 152.0 (s, Cq), 145.0 (d, *J* = 249.8 Hz, Cq), 133.5 (s, Cq),

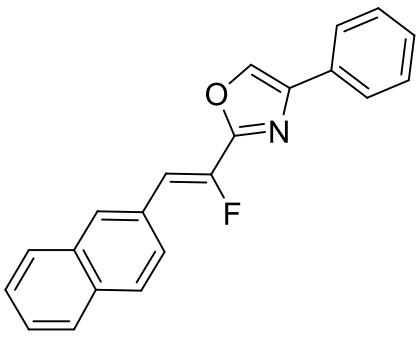
133.4 (s, Cq), 131.3 (d, *J* = 8.3 Hz, 2xCH), 129.0 (s, CH), 128.4 (s, CH), 128.0 (s, CH), 127.0 (s, CH), 126.9 (s, CH), 124.9 (s, Cq), 124.8 (s, Cq), 124.3 (s, CH), 123.5 (s, CH), 122.2 (s, CH), 114.5 (s, 2xCH), 111.4 (d, *J* = 5.3 Hz, CH), 55.4 (s, CH_3). MS (ESI-TOF): *m/z* 346 [$M+H^+$]. HRMS (ESI-TOF): calcd for $C_{22}H_{17}FNO_2$ *m/z* 346.1243 [$M+H^+$], found: 346.1238.



(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-4-phenyloxazole (3Ae): *(E)*-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 4-phenyloxazole (0.20 mmol, 26 μL), CuI (0.02 mmol, 4 mg), Phen (0.04 mmol, 7 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **3Ae** in 70% yield (41 mg) as a yellow solid. mp 138-140 °C (CH_2Cl_2/PE). IR: 1606, 1545, 1508, 1485, 1453, 1296, 1255, 1179, 1117, 1077, 1032, 940, 866, 811 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 1.5 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.54-7.29 (m, 3H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 38.0 Hz, 1H), 3.84 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -129.5 (dd, *J* = 38.0, 1.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1 (d, *J* = 3.3 Hz, Cq), 156.4 (d, *J* = 37.3 Hz, Cq), 145.0 (d, *J* = 252.4 Hz, Cq), 142.5 (s, Cq), 133.9 (s, CH), 131.4 (d, *J* = 7.9 Hz, 2xCH), 130.6 (s, Cq), 128.9 (s, 2xCH), 128.6 (s, CH), 125.9 (s, 2xCH), 124.8 (d, *J* = 4.0 Hz, Cq), 114.4 (s, 2xCH), 111.7 (d, *J* = 5.2 Hz, CH), 55.4 (s, CH_3). MS (ESI-TOF): *m/z* 296 [$M+H^+$]. HRMS (ESI-TOF): calcd for $C_{18}H_{15}FNO_2$ *m/z* 296.1088 [$M+H^+$], found: 296.1087.

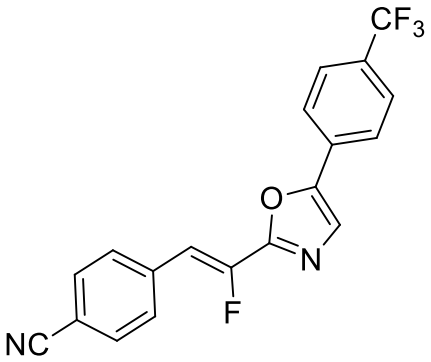


(*Z*)-2-(1-Fluoro-2-(naphth-2-yl)vinyl)-5-(4-methoxyphenyl)oxazole (3Cb): (*E*)-2-(2-bromo-2-fluorovinyl)naphthalene (0.22 mmol, 55 mg), 5-(4-methoxyphenyl)oxazole (0.20 mmol, 35 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 2/8) affording compound **3Cb** in 70% yield (48 mg) as a colorless solid. mp 151-153 °C (EtOAc/PE). IR: 2937, 1616, 1497, 1461, 1425, 1309, 1255, 1177, 1070, 1019, 935, 907, 867, 817 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.91-7.77 (m, 4H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.50 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.35 (s, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 37.9 Hz, 1H), 3.86 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -126.4 (d, *J* = 37.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4 (s, Cq), 152.3 (s, Cq), 146.4 (d, *J* = 253.5 Hz, Cq), 133.5 (s, Cq), 133.2 (d, *J* = 2.1 Hz, Cq), 129.8 (s, Cq), 129.8 (s, Cq), 128.5 (s, CH), 128.5 (s, CH), 127.8 (s, CH), 126.9 (s, CH), 126.8 (s, CH), 126.7 (s, CH), 126.6 (s, CH), 126.1 (s, 2xCH), 122.4 (s, CH), 120.3 (s, Cq), 114.6 (s, 2xCH), 111.2 (d, *J* = 5.3 Hz, CH), 55.5 (s CH_3). MS (ESI-TOF): *m/z* 346 [$M+H^+$]. HRMS (ESI-TOF): calcd for $C_{22}H_{17}FNO_2$ *m/z* 346.1243 [$M+H^+$], found: 346.1256.

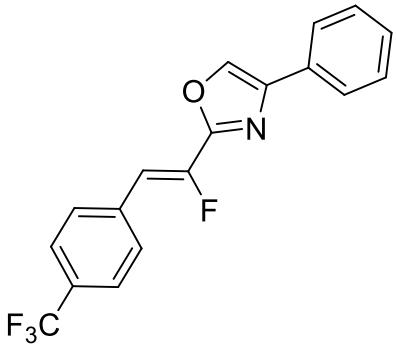


(*Z*)-2-(1-Fluoro-2-(naphth-2-yl)vinyl)-4-phenyloxazole (3Ce): (*E*)-2-(2-bromo-2-fluorovinyl)naphthalene (0.22 mmol, 55 mg), 4-phenyloxazole (0.20 mmol, 26 μL), CuI (0.02 mmol, 4 mg), Phen (0.04 mmol, 7 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel

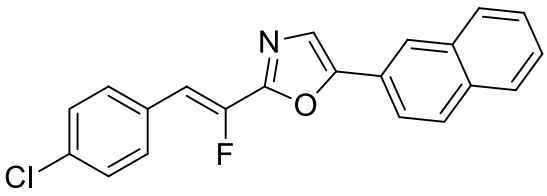
column chromatography (PE/CH_2Cl_2, 8/2) affording compound **3Ce** in 99% yield (62 mg) as a yellow solid. mp 181-183 °C (CH_2Cl_2/PE). IR: 3055, 1538, 1449, 1272, 1118, 1080, 941, 907, 870, 836, 819 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.99 (d, *J* = 1.7 Hz, 1H), 7.92-7.78 (m, 6H), 7.56-7.33 (m, 5H), 6.99 (d, *J* = 37.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -126.2 (dd, *J* = 37.5, 1.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2 (d, *J* = 37.5 Hz, Cq), 146.3 (d, *J* = 254.3 Hz, Cq), 142.7 (s, Cq), 134.2 (s, CH), 133.5 (s, Cq), 133.3 (d, *J* = 1.5 Hz, Cq), 130.5 (s, Cq), 129.8 (d, *J* = 8.3 Hz, CH), 129.6 (d, *J* = 3.8 Hz, Cq), 129.0 (s, 2xCH), 128.7 (s, CH), 128.6 (s, CH), 128.6 (s, CH), 127.8 (s, CH), 127.0 (s, CH), 126.8 (d, *J* = 8.3 Hz, CH), 126.7 (s, CH), 125.9 (s, 2xCH), 112.1 (d, *J* = 5.3 Hz, CH). MS (ESI-TOF): *m/z* 316 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{21}H_{15}FNO$ *m/z* 316.1138 [M+H^+], found: 316.1149.



(*Z*)-4-(2-Fluoro-2-(5-(4-trifluoromethylphenyl)oxazol-2-yl)vinyl)benzonitrile (3Dc): (*E*)-4-(2-bromo-2-fluorovinyl)benzonitrile (0.22 mmol, 50 mg), 5-(4-trifluoromethyl-phenyl)oxazole (0.20 mmol, 43 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 3/7) affording compound **3Dc** in 75% yield (57 mg) as a colorless solid. mp 182-184 °C (CH_2Cl_2/PE). IR: 2926, 2226, 1620, 1603, 1533, 1413, 1322, 1164, 1111, 1069, 942, 843, 827 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83-7.67 (m, 9H), 6.84 (d, *J* = 36.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.8 (s, 3F), -122.1 (d, *J* = 36.0 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1 (d, *J* = 36.8 Hz, Cq), 151.3 (s, Cq), 147.5 (d, *J* = 258.8 Hz, Cq), 136.3 (d, *J* = 3.8 Hz, Cq), 132.6 (s, 2xCH), 131.0 (q, *J* = 32.3 Hz, Cq), 130.3 (s, Cq), 130.1 (d, *J* = 8.3 Hz, 2xCH), 126.3 (q, *J* = 3.8 Hz, 2xCH), 125.8 (s, CH), 124.8 (s, 2xCH), 123.9 (q, *J* = 270.8 Hz, Cq), 118.6 (s, Cq), 112.2 (d, *J* = 3.0 Hz, Cq), 110.3 (d, *J* = 4.5 Hz, CH). MS (ESI-TOF): *m/z* 359 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{19}H_{11}F_4N_2O$ *m/z* 359.0808 [M+H^+], found: 359.0807.



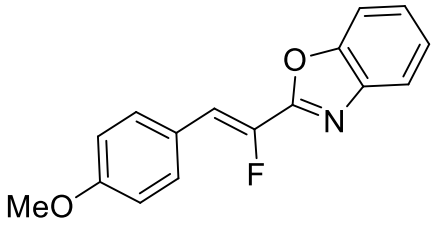
(*Z*)-2-(1-Fluoro-2-(4-trifluoromethylphenyl)vinyl)-4-phenyloxazole (3Ee): *(E)*-1-(2-bromo-2-fluorovinyl)-4-trifluoromethylbenzene (0.22 mmol, 59 mg), 4-phenyloxazole (0.20 mmol, 26 μL), CuI (0.02 mmol, 4 mg), Phen (0.04 mmol, 7 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 4/6) affording compound **3Ee** in 61% yield (40 mg) as a yellow solid. mp 165-167 °C (CH_2Cl_2/PE). IR: 3106, 1613, 1549, 1415, 1322, 1167, 1106, 1066, 1017, 939, 871, 844, 803 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 1.4 Hz, 1H), 7.86-7.77 (m, 4H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.50-7.40 (m, 3H), 6.88 (d, *J* = 36.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.8 (s, 3F), -123.4 (d, *J* = 36.6 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3 (d, *J* = 37.1 Hz, Cq), 147.3 (d, *J* = 258.6 Hz, Cq), 146.6 (s, Cq), 142.9 (d, *J* = 1.6 Hz, Cq), 142.4 (s, Cq), 130.8 (qd, *J* = 32.5, 3.1 Hz, Cq), 129.8 (d, *J* = 7.5 Hz, 2xCH), 129.0 (s, 2xCH), 128.8 (s, CH), 125.8 (s, 2xCH), 125.7 (s, CH), 125.6 (q, *J* = 3.8 Hz, 2xCH), 123.8 (q, *J* = 273.1 Hz, Cq), 110.4 (d, *J* = 4.5 Hz, CH). MS (ESI-TOF): *m/z* 334 [$M+H^+$]. HRMS (ESI-TOF): calcd for $C_{18}H_{12}F_4NO$ *m/z* 334.0855 [$M+H^+$], found: 334.1099.



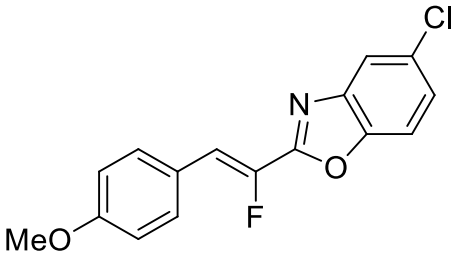
(*Z*)-2-(2-(4-Chlorophenyl)-1-fluorovinyl)-5-(naphth-2-yl)oxazole (3Fd): (*E*)-1-(2-bromo-2-fluorovinyl)-4-chlorobenzene (0.22 mmol, 52 mg), 5-(naphth-2-yl)oxazole (0.20 mmol, 39 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 2/8) affording compound **3Fd** in 59% yield (42 mg) as a yellow solid. mp 149-151 °C (CH_2Cl_2/PE). IR: 3055, 1660, 1489, 1333, 1090, 1066, 955, 866, 833, 810 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.87 (m, 3H), 7.72

(d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.53 (m, 3H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 37.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -125.9 (d, *J* = 37.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3 (d, *J* = 254.8 Hz, Cq), 136.3 (s, Cq), 134.7 (d, *J* = 3.0 Hz, Cq), 133.4 (s, CH), 133.4 (d, *J* = 4.2 Hz, Cq), 130.9 (d, *J* = 7.7 Hz, CH), 130.6 (s, Cq), 130.5 (s, Cq) 129.2 (s, 2xCH), 129.1 (s, CH), 129.0 (s, CH), 128.4 (s, CH), 128.0 (s, CH), 127.0 (d, *J* = 6.7 Hz, 2xCH), 124.6 (s, Cq), 123.6 (s, CH), 122.0 (s, CH), 119.3 (s, Cq), 110.4 (d, *J* = 4.1 Hz, CH). MS (ESI-TOF): *m/z* 350 [M+H$^+$]. HRMS (ESI-TOF): calcd for $C_{21}H_{14}{}^{35}ClFNO$ *m/z* 350.0748 [M+H$^+$], found: 350.0736.

e. Variation of heteroaryle - Compounds **4Aa - 7G**

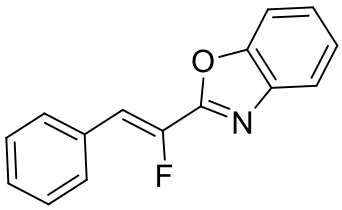


(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)benzo[d]oxazole (4Aa): (*E*)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), benzo[d]oxazole (0.20 mmol, 24 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **4Aa** in 82% yield (44 mg) as a yellow solid. Exhibited spectral data were identical to previous report: C. Schneider, D. Masi, S. Couve-Bonnaire, X. Pannecoucke and C. Hoarau, *Angew. Chem. Int. Ed.*, 2013, **52**, 3246.

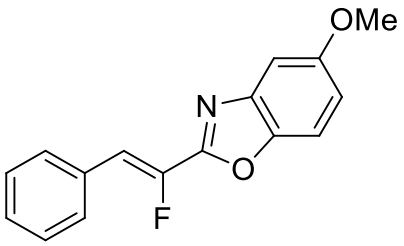


(*Z*)-5-Chloro-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)benzo[d]oxazole (4Ab): *(E)*-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 5-chlorobenzo[d]oxazole (0.20 mmol, 31 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48

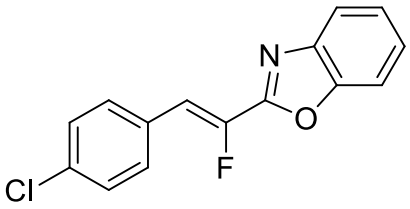
mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 8/2) affording compound **4Ab** in 70% yield (42 mg) as a colorless solid. mp 159-161 °C (CH_2Cl_2/PE). IR: 3093, 2959, 2216, 1660, 1605, 1542, 1449, 1259, 1179, 1071, 1021, 937, 841, 821, 803 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 1.4 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.33 (dd, *J* = 8.6, 1.4 Hz, 1H), 6.95 (d, *J* = 37.3 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -130.3 (d, *J* = 37.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.7 (d, *J* = 3.3 Hz, Cq), 158.7 (d, *J* = 36.5 Hz, Cq), 149.2 (s Cq), 144.2 (d, *J* = 252.3 Hz, Cq), 142.9 (s, Cq), 131.9 (d, *J* = 8.1 Hz, 2xCH), 130.7 (s, Cq), 126.1 (s, CH), 124.3 (d, *J* = 4.1 Hz, Cq), 120.4 (s, CH), 115.3 (d, *J* = 4.6 Hz, CH), 114.6 (s, 2xCH), 111.4 (s, CH), 55.5 (s, CH_3). MS (ESI-TOF): *m/z* 304 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{16}H_{12}{}^{35}ClFNO_2$ *m/z* 304.0541 [M+H^+], found: 304.0539.



(*Z*)-2-(1-Fluoro-2-phenylvinyl)benzo[d]oxazole (4Ba): (*E*)-(2-bromo-2-fluorovinyl)benzene (0.22 mmol, 44 mg), benzo[d]oxazole (0.20 mmol, 24 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **4Ba** in 53% yield (25 mg) as a colorless solid. mp 93-95 °C (CH_2Cl_2/PE). IR: 2920, 2223, 1548, 1449, 1341, 1234, 1110, 1066, 935, 838 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.81-7.77 (m, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.61-7.55 (m, 1H), 7.49-7.33 (m, 5H), 7.02 (d, *J* = 37.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -126.4 (d, *J* = 37.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.9 (d, *J* = 36.6 Hz, Cq), 150.6 (s, Cq), 145.8 (d, *J* = 255.5 Hz, Cq), 141.5 (s, Cq), 131.6 (d, *J* = 4.1 Hz, Cq), 130.0 (d, *J* = 7.9 Hz, 2xCH), 129.4 (d, *J* = 2.7 Hz, CH), 128.9 (s, 2xCH), 126.1 (s, CH), 125.1 (s, CH), 120.6 (s, CH), 114.5 (d, *J* = 4.6 Hz, CH), 110.7 (s, CH). MS (ESI-TOF): *m/z* 240 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{15}H_{11}FNO$ *m/z* 240.0825 [M+H^+], found: 240.0823.

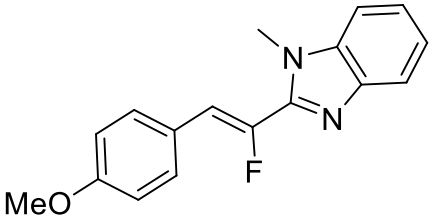


(*Z*)-2-(1-Fluoro-2-phenylvinyl)-5-methoxybenzo[d]oxazole (4Bc): *(E)*-1-(2-bromo-2-fluorovinyl)benzene (0.22 mmol, 45 mg), 5-methoxybenzo[d]oxazole (0.20 mmol, 30 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5 to 3/7) affording compound **4Bc** in 99% yield (55 mg) as a colorless solid. mp 109-111 °C (CH_2Cl_2/PE). IR: 2919, 2220, 1607, 1545, 1484, 1435, 1339, 1273, 1113, 1073, 833, 812 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.51-7.37 (m, 4H), 7.27 (m, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 7.00 (d, *J* = 37.1 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -126.5 (d, *J* = 37.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9 (s, Cq), 157.7 (d, *J* = 36.6 Hz, Cq), 146.0 (d, *J* = 255.4 Hz, Cq), 145.4 (s, Cq), 142.5 (s, Cq), 131.8 (d, *J* = 4.3 Hz, Cq), 130.1 (d, *J* = 7.9 Hz, 2xCH), 129.4 (d, *J* = 2.3 Hz, CH), 129.0 (s, 2xCH), 115.0 (s, CH), 114.3 (d, *J* = 4.6 Hz, CH), 111.0 (s, CH), 103.2 (s, CH), 56.1 (s, CH_3). MS (ESI-TOF): *m/z* 270 [$M+H^+$]. HRMS (ESI-TOF): calcd for $C_{16}H_{13}FNO_2$ *m/z* 270.0930 [$M+H^+$], found: 270.0930.

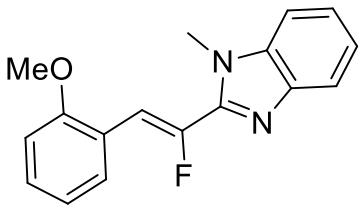


(*Z*)-2-(2-(4-chlorophenyl)-1-fluorovinyl)benzo[d]oxazole (4Fa): (*E*)-1-(2-bromo-2-fluorovinyl)-4-chlorobenzene (0.22 mmol, 52 mg), benzo[d]oxazole (0.20 mmol, 24 mg), CuI (0.02 mmol, 4 mg), dppe (0.04 mmol, 16 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **4Fa** in 74% yield (40 mg) as a yellow solid. mp 143-145 °C (CH_2Cl_2/PE). IR: 3060, 2219, 1659, 1544, 1450, 1335, 1242, 1098, 1064, 937, 866, 839, 809 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85-7.75 (m, 1H), 7.69-7.55 (m, 3H), 7.48-7.37 (m, 4H), 6.98 (d, *J* = 36.7 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$):

δ -125.7 (d, *J* = 36.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7 (s, Cq), 146.2 (d, *J* = 255.0 Hz, Cq), 141.6 (s, Cq), 135.4 (s, Cq), 133.8 (s, Cq), 131.2 (d, *J* = 8.3 Hz, 2xCH), 130.2 (s, Cq), 129.3 (s, 2xCH), 126.3 (s, CH), 125.3 (s, CH), 120.8 (s, CH), 113.4 (d, *J* = 4.5 Hz, CH), 110.9 (s, CH). MS (ESI-TOF): *m/z* 274 [M+H$^+$]. HRMS (ESI-TOF): calcd for $C_{15}H_{10}{}^{35}ClFNO$ *m/z* 274.0435 [M+H$^+$], found: 274.0439.

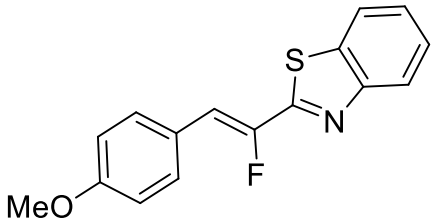


(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1-methyl-1H-benzo[d]imidazole (5A): *(E)*-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 1-methyl-1H-benzo[d]imidazole (0.20 mmol, 26 mg), CuI (0.02 mmol, 4 mg), *trans-N,N′*-dimethyl-1,2-cyclohexanediamine (0.04 mmol, 7 μL), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **5A** in 54% yield (31 mg) as an orange solid. mp 125-127 °C (CH_2Cl_2/PE). IR: 3045, 2931, 1605, 1512, 1393, 1297, 1253, 1177, 1027, 870, 825 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79-7.74 (m, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.40-7.29 (m, 3H), 6.97 (d, *J* = 39.9 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.97 (d, *J* = 3.4 Hz, 3H), 3.84 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ - 122.6 (dq, *J* = 39.9, 3.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8 (d, *J* = 3.3 Hz, Cq), 148.7 (d, *J* = 252.6 Hz, Cq), 146.3 (d, *J* = 32.4 Hz, Cq), 142.8 (d, *J* = 2.3 Hz, Cq), 136.7 (s, Cq), 131.2 (d, *J* = 8.0 Hz, 2xCH), 125.3 (d, *J* = 3.6 Hz, Cq), 123.5 (s, CH), 123.0 (s, CH), 119.9 (s, CH), 114.3 (s, 2xCH), 112.9 (d, *J* = 6.5 Hz, CH), 109.6 (s, CH), 55.4 (s, OCH_3), 31.9 (d, *J* = 10.8 Hz, NCH_3). MS (ESI-TOF): *m/z* 283 [M+H$^+$]. HRMS (ESI-TOF): calcd for $C_{17}H_{16}FN_2O$ *m/z* 283.1247 [M+H$^+$], found: 283.1241.

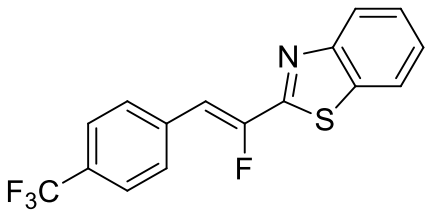


(*Z*)-2-(1-Fluoro-2-(2-methoxyphenyl)vinyl)-1-methyl-1H-benzo[d]imidazole (5H): (*E*)-1-(2-bromo-2-fluorovinyl)-2-methoxybenzene (0.22 mmol, 51 mg), 1-methyl-1H-benzo[d]imidazole (0.20 mmol, 26 mg), CuI (0.02 mmol, 4 mg), *trans-N,N′*-dimethyl-1,2-

cyclohexanediamine (0.04 mmol, 7 μL), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **5H** in 55% yield (31 mg) as a brown solid. mp 101-103 °C (CH_2Cl_2/PE). IR: 3036, 2933, 1597, 1462, 1387, 1245, 1053, 1025, 856 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 5.7 Hz, 1H), 7.38 (d, *J* = 40.6 Hz, 1H), 7.30-7.16 (m, 4H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.93 (d, *J* = 2.3 Hz, 3H), 3.83 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -119.9 (d, *J* = 40.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.2 (s, Cq), 149.7 (d, *J* = 254.8 Hz, Cq), 142.9 (s, Cq), 142.9 (s, Cq), 130.3 (d, *J* = 13.4 Hz, CH), 129.9 (d, *J* = 1.8 Hz, CH), 123.6 (s, CH), 123.0 (s, CH), 121.43 (s, Cq), 121.38 (s, Cq), 120.7 (s, CH), 120.2 (s, CH), 110.7 (s, CH), 109.7 (s, CH), 107.3 (d, *J* = 4.8 Hz, CH), 55.6 (s, OCH_3), 31.9 (d, *J* = 9.6 Hz, NCH_3). MS (ESI-TOF): *m/z* 283 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{17}H_{16}FN_2O$ *m/z* 283.1247 [M+H^+], found: 283.1252.

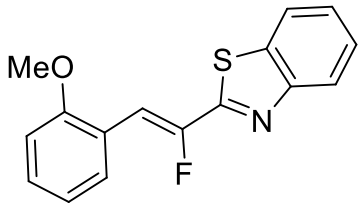


(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)benzo[d]thiazole (6A): (*E*)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), benzo[d]thiazole (0.20 mmol, 22 μL), CuI (0.02 mmol, 4 mg), phenanthroline (0.04 mmol, 7 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **6A** in 91% yield (52 mg) as a yellow solid. Exhibited spectral data were identical to previous report: C. Schneider, D. Masi, S. Couve-Bonnaire, X. Pannecoucke and C. Hoarau, *Angew. Chem. Int. Ed.*, 2013, **52**, 3246.



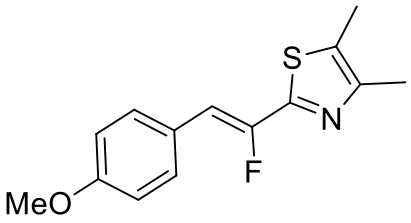
(*Z*)-2-(1-Fluoro-2-(4-trifluoromethylphenyl)vinyl)benzo[d]thiazole (6E): (*E*)-1-(2-bromo-2-fluorovinyl)-4-trifluoromethylbenzene (0.22 mmol, 59 mg), benzo[d]thiazole (0.20 mmol, 22

μL), CuI (0.02 mmol, 4 mg), phenanthroline (0.04 mmol, 7 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **6E** in 41% yield (26 mg) as a yellow solid. mp 123-125 °C (CH_2Cl_2/PE). IR: 3063, 1699, 1614, 1413, 1321, 1253, 1169, 1106, 1066, 997, 865, 831 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.56 (m, 1H), 7.45 (m, 1H), 7.12 (d, *J* = 37.8 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.8 (s, 3F), -111.6 (d, *J* = 37.8 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4 (d, *J* = 39.0 Hz, Cq), 153.7 (d, *J* = 2.2 Hz, Cq), 152.9 (d, *J* = 256.0 Hz, Cq), 135.9-135.4 (m, Cq), 135.2 (s, Cq), 130.4 (qd, *J* = 32.7, 2.8 Hz, Cq), 130.1 (d, *J* = 8.1 Hz, 2xCH), 127.1 (s, CH), 126.1 (s, CH), 125.9 (q, *J* = 3.6 Hz, 2xCH), 124.0 (q, *J* = 270.8 Hz, Cq), 123.7 (s, CH), 122.0 (s, CH), 109.1 (d, *J* = 6.0 Hz, CH). MS (ESI-TOF): *m/z* 324 [$M+H^+$]. HRMS (ESI-TOF): calcd for $C_{16}H_{10}F_4NS$ *m/z* 324.0470 [$M+H^+$], found: 324.0467.

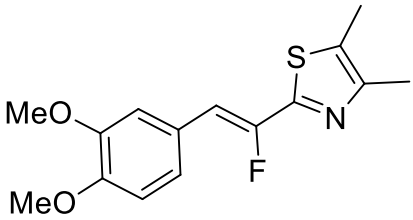


(*Z*)-2-(1-Fluoro-2-(2-methoxyphenyl)vinyl)benzo[d]thiazole (6H): *(E)*-1-(2-bromo-2-fluorovinyl)-2-methoxybenzene (0.22 mmol, 51 mg), benzo[d]thiazole (0.20 mmol, 22 μL), CuI (0.02 mmol, 4 mg), phenanthroline (0.04 mmol, 7 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **6H** in 54% yield (31 mg) as a yellow solid. mp 99-101 °C (CH_2Cl_2/PE). IR: 2922, 1727, 1597, 1576, 1481, 1456, 1291, 1244, 1231, 1183, 1053, 1027, 935, 877 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.50 (dd, *J* = 39.0, 1.8 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 3.87 (d, *J* = 2.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.6 (d, *J* = 39.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4 (d, *J* = 37.5 Hz, Cq), 157.3 (d, *J* = 15.0 Hz, Cq), 153.7 (d, *J* = 15.0 Hz, Cq), 151.5 (d, *J* = 251.5 Hz, Cq), 134.8 (s, Cq), 130.6 (d, *J* = 15.0 Hz, CH), 130.2 (d, *J* = 4.5 Hz, CH), 126.6 (s, CH), 125.5 (s, CH), 123.4 (s, CH), 121.7 (s, CH), 120.9 (d, *J* = 4.5 Hz, Cq), 120.8 (s, CH), 110.7 (s, CH), 105.0 (d, *J* = 4.5 Hz,

CH), 55.7 (s, CH_3). MS (ESI-TOF): *m/z* 286 [M+H$^+$]. HRMS (ESI-TOF): calcd for $C_{16}H_{13}FNOS$ *m/z* 286.0702 [M+H$^+$], found: 286.0697.



(*Z*)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-4,5-dimethylthiazole (7A): *(E)*-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.22 mmol, 51 mg), 4,5-dimethylthiazole (0.20 mmol, 21 μL), CuI (0.04 mmol, 8 mg), phenanthroline (0.08 mmol, 14 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **7A** in 72% yield (37 mg) as a yellow solid. Exhibited spectral data were identical to previous report: K. Rousée, C. Schneider, S. Couve-Bonnaire, X. Pannecoucke, V. Levacher and C. Hoarau, *Chem. Eur. J.*, 2014, **10**, 15000.

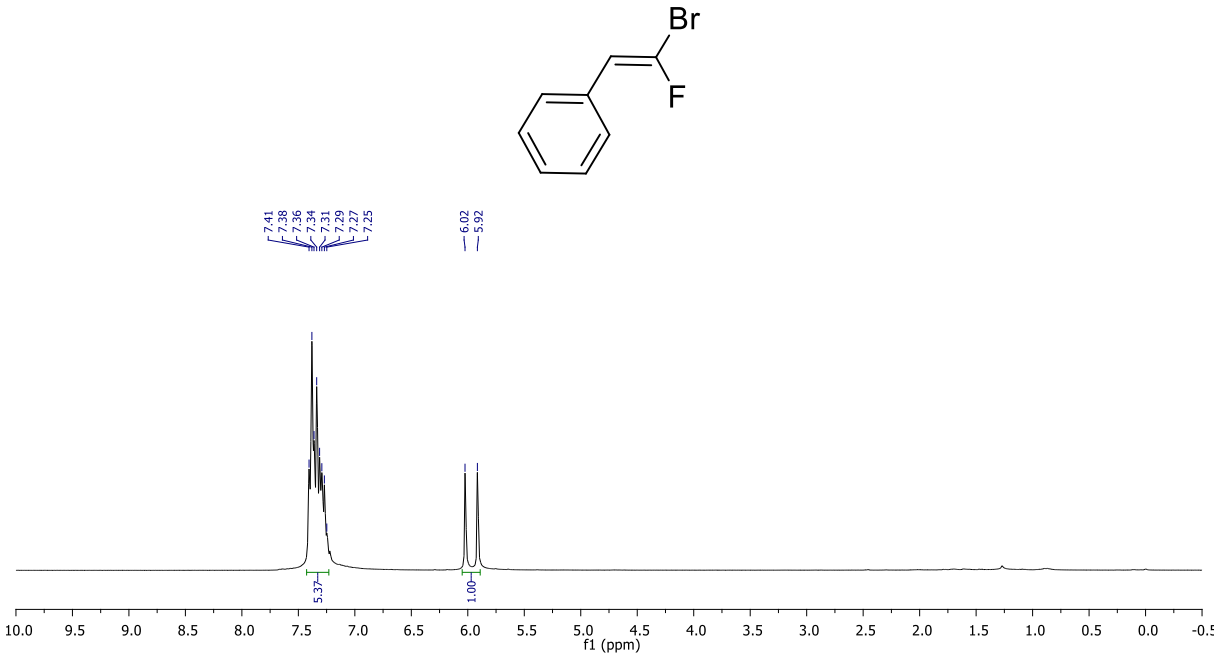


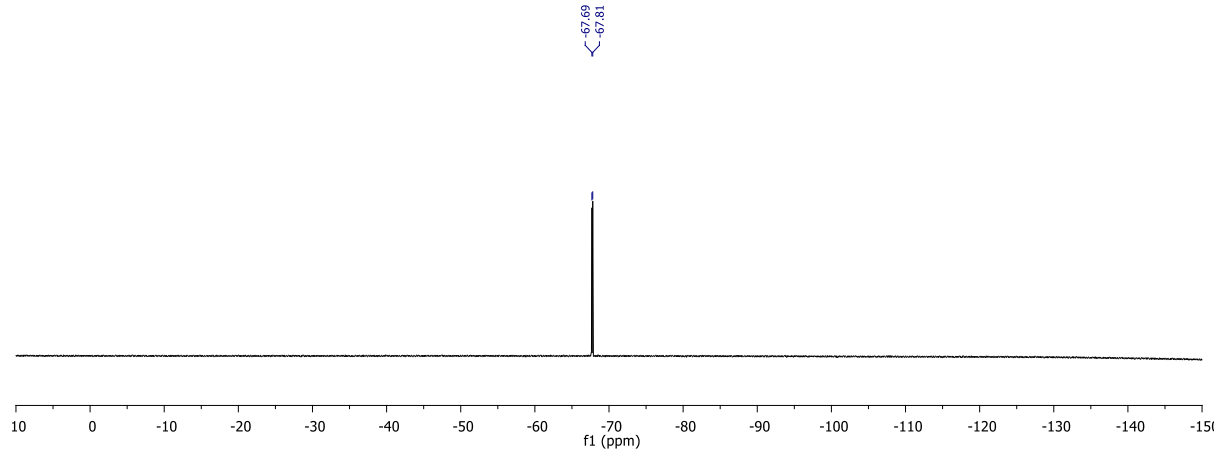
(*Z*)-2-(1-Fluoro-2-(3,4-dimethoxyphenyl)vinyl)-4,5-dimethylthiazole (7G): *(E)*-1-(2-bromo-2-fluorovinyl)-3,4-dimethoxybenzene (0.22 mmol, 57 mg), 4,5-dimethylthiazole (0.20 mmol, 21 μL), CuI (0.04 mmol, 8 mg), phenanthroline (0.08 mmol, 14 mg), *t*-BuOLi (0.60 mmol, 48 mg), 1,4-dioxane (0.8 mL) were reacted according to general procedure. The crude product was purified by silica gel column chromatography (PE/CH_2Cl_2, 5/5) affording compound **7G** in 86% yield (42 mg) as a yellow solid. mp 106-108 °C (CH_2Cl_2/PE). IR: 2917, 1512, 1439, 1268, 1242, 1156, 1143, 1024, 848, 803 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (s, 1H), 7.17 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 39.6 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -117.0 (d, *J* = 39.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4 (d, *J* = 39.3 Hz, Cq), 150.9 (d, *J* = 248.6 Hz,

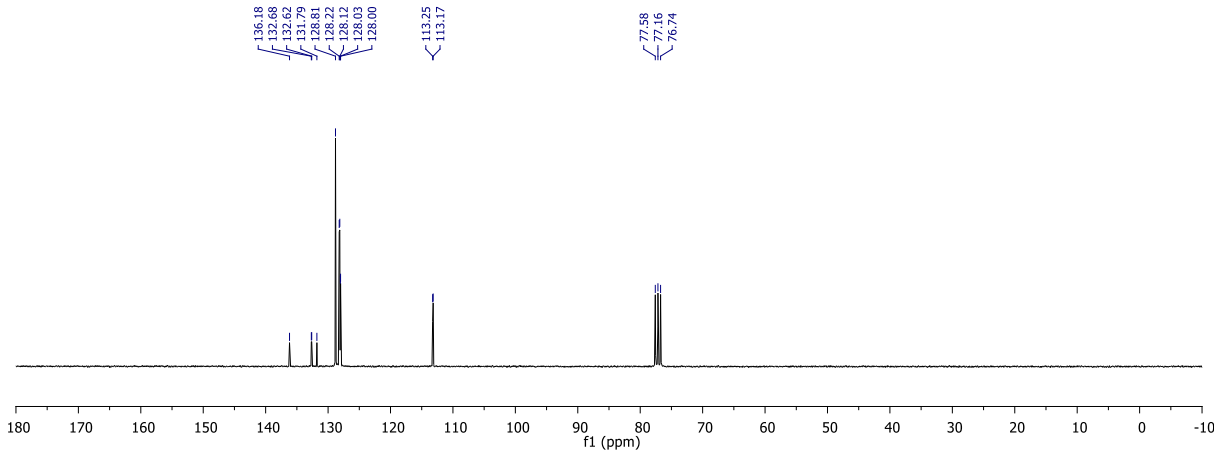
Cq), 150.0 (d, *J* = 2.2 Hz, Cq), 149.2 (d, *J* = 3.2 Hz, Cq), 148.9 (s, Cq), 127.6 (s, Cq), 125.7 (d, *J* = 3.7 Hz, Cq), 123.0 (d, *J* = 7.0 Hz, CH), 112.1 (d, *J* = 9.2 Hz, CH), 111.2 (s, CH), 106.6 (d, *J* = 6.8 Hz, CH), 56.0 (s, CH_3), 55.9 (s, CH_3), 15.0 (s, CH_3), 11.6 (s, CH_3). MS (ESI-TOF): *m/z* 294 [M+H^+]. HRMS (ESI-TOF): calcd for $C_{15}H_{17}FNO_2S$ *m/z* 294.0964 [M+H^+], found: 294.0962.

5. ^{1}H, ^{13}C and ^{19}F NMR spectra

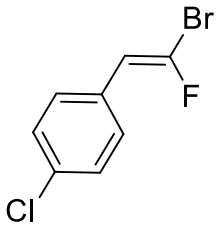
Gem-bromofluoroalkene **1B**

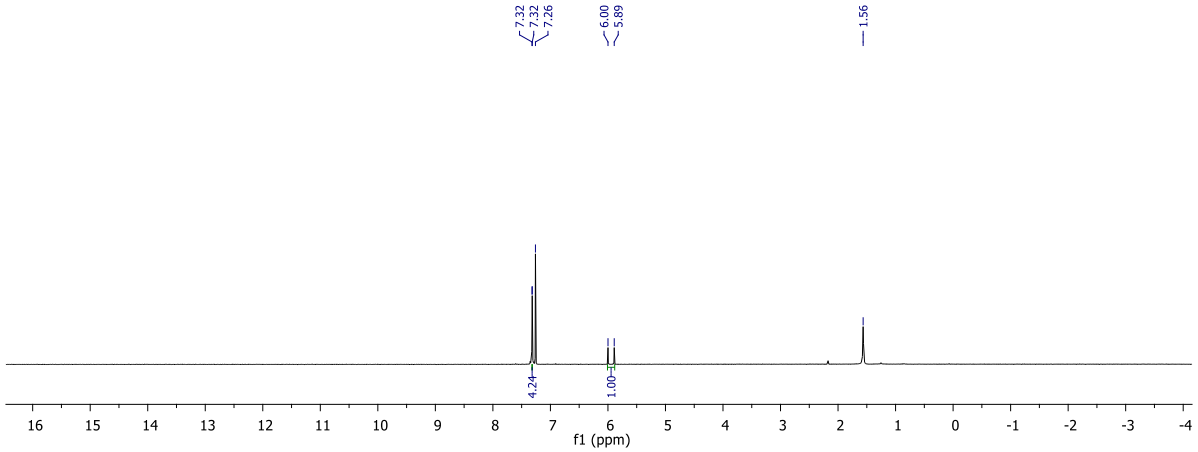


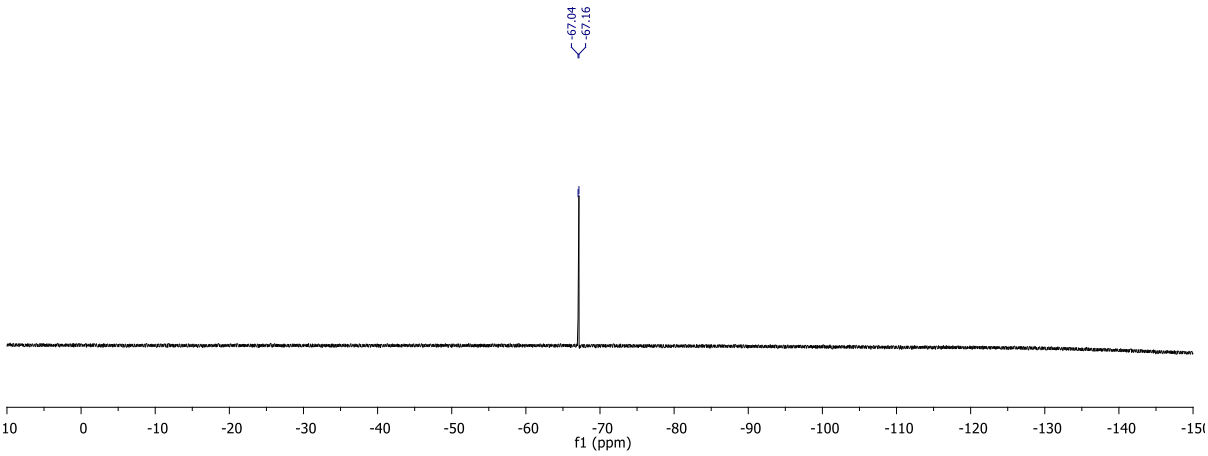


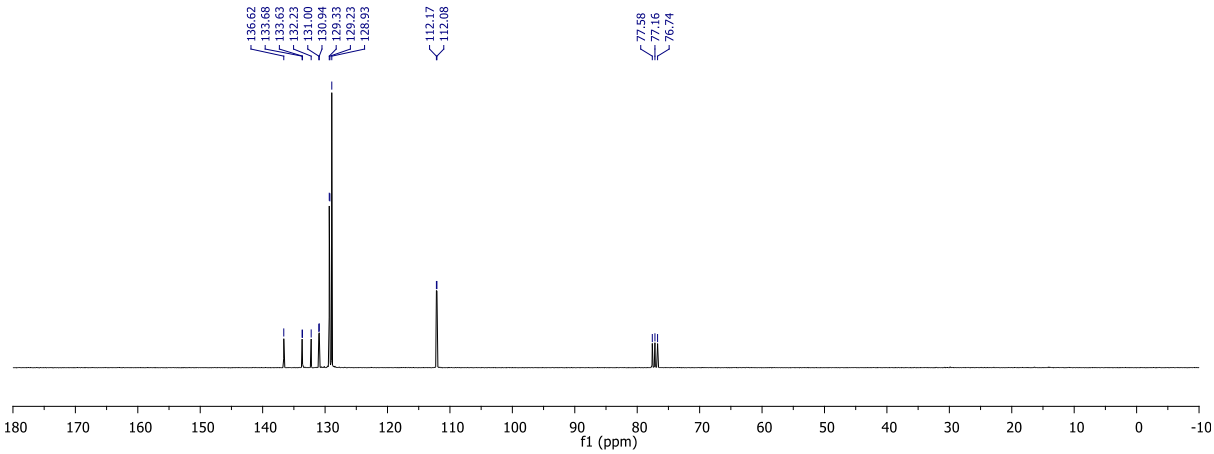


Gem-bromofluoroalkene **1F**

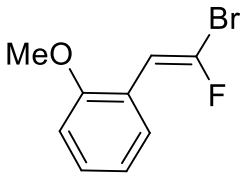


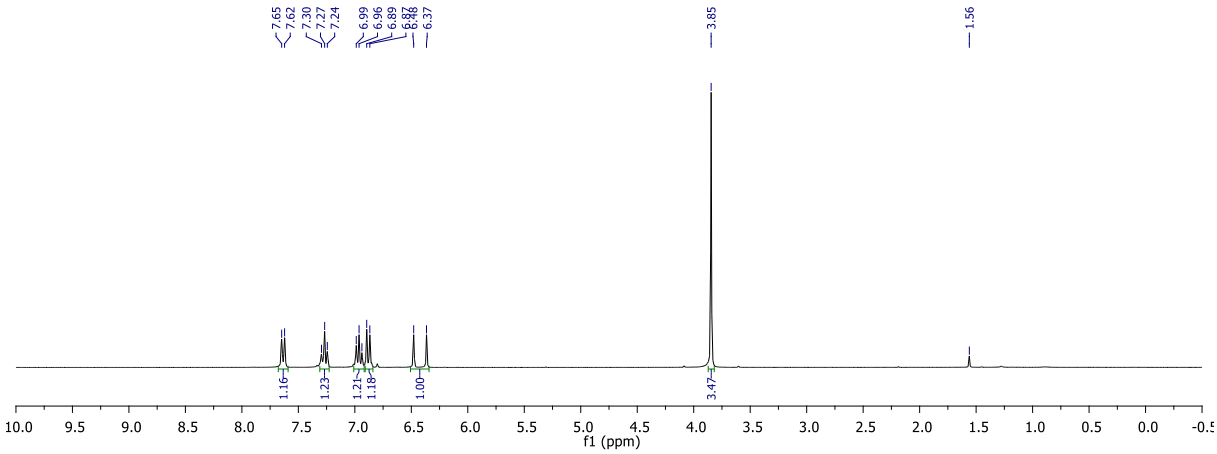


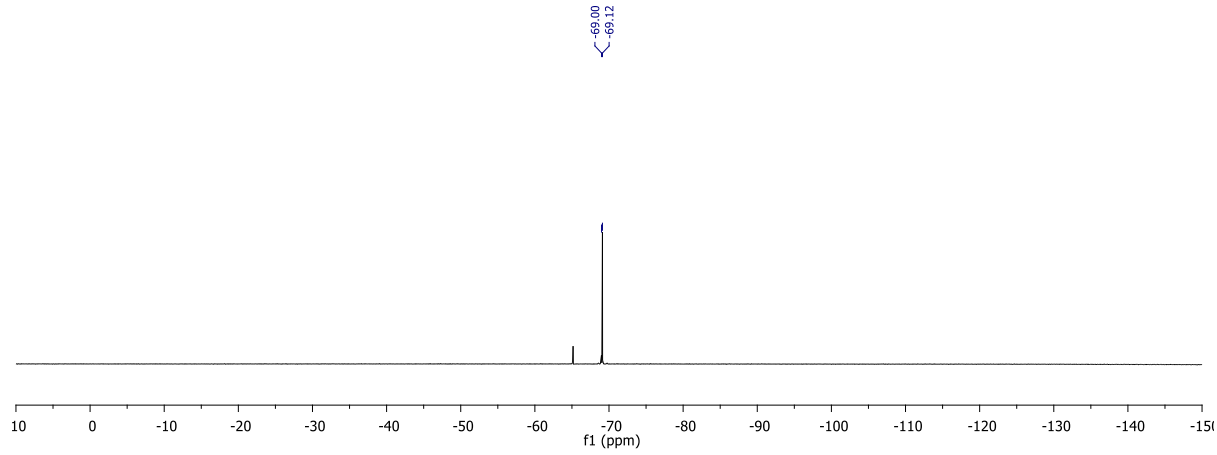


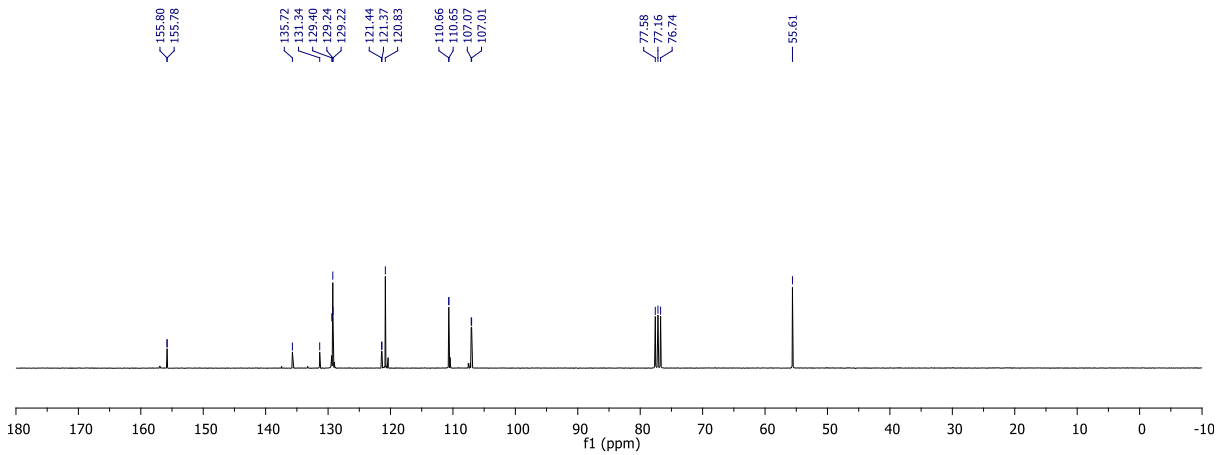


Gem-bromofluoroalkene **1H**

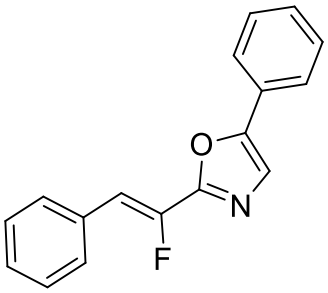


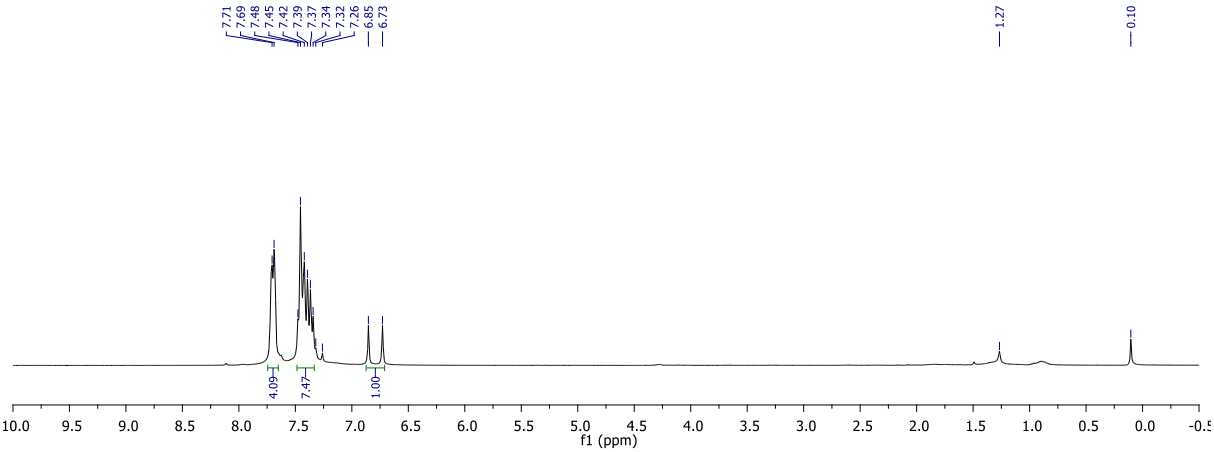


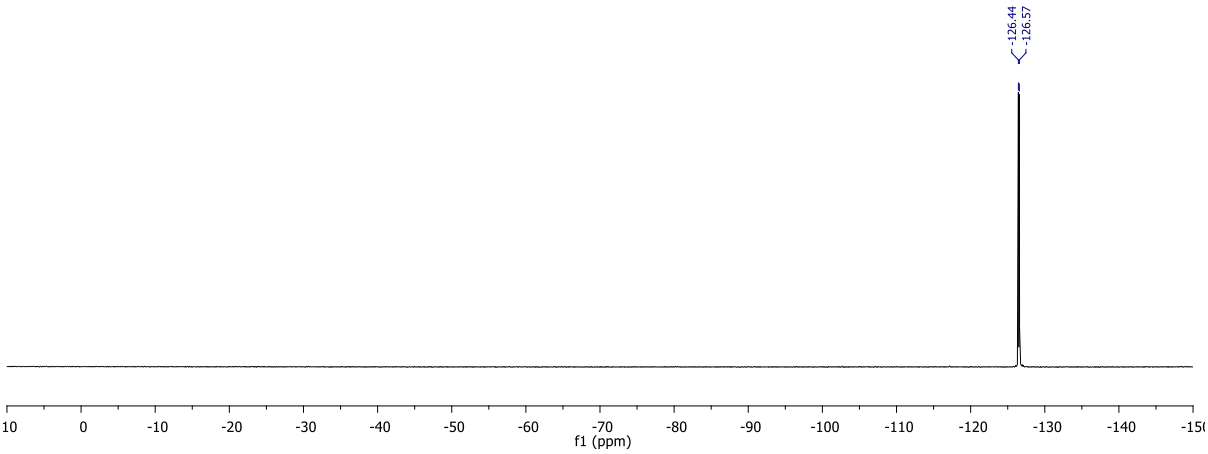


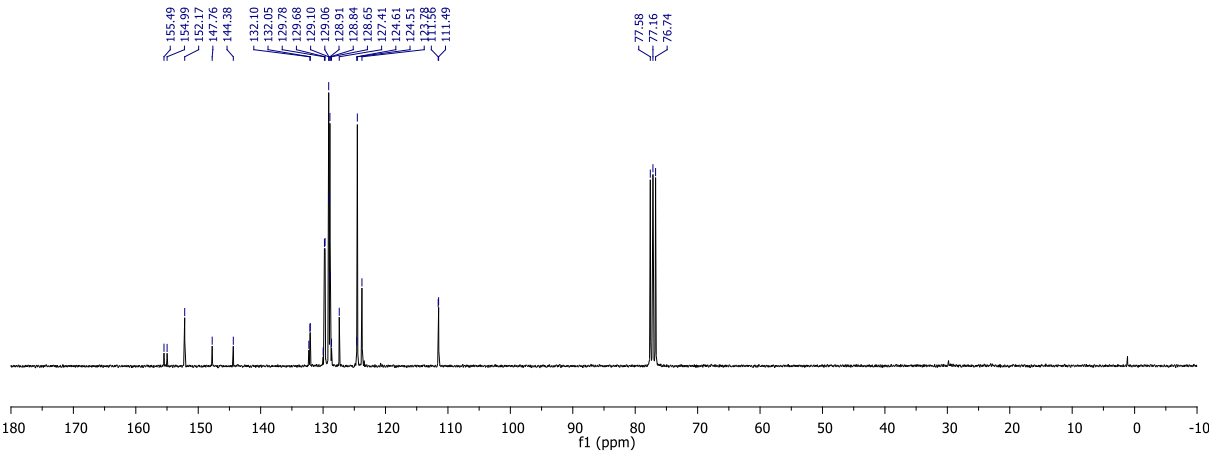


Heteroaryle **3Ba**

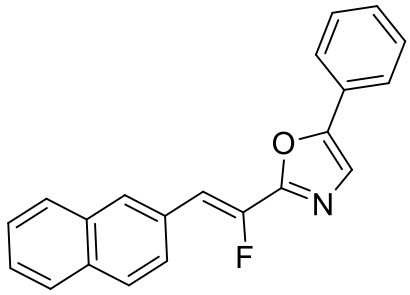


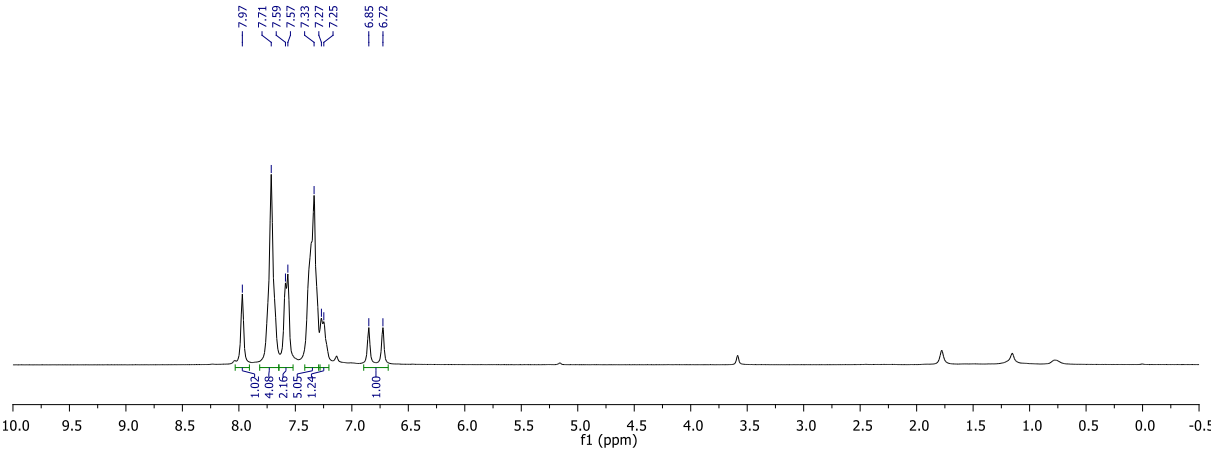


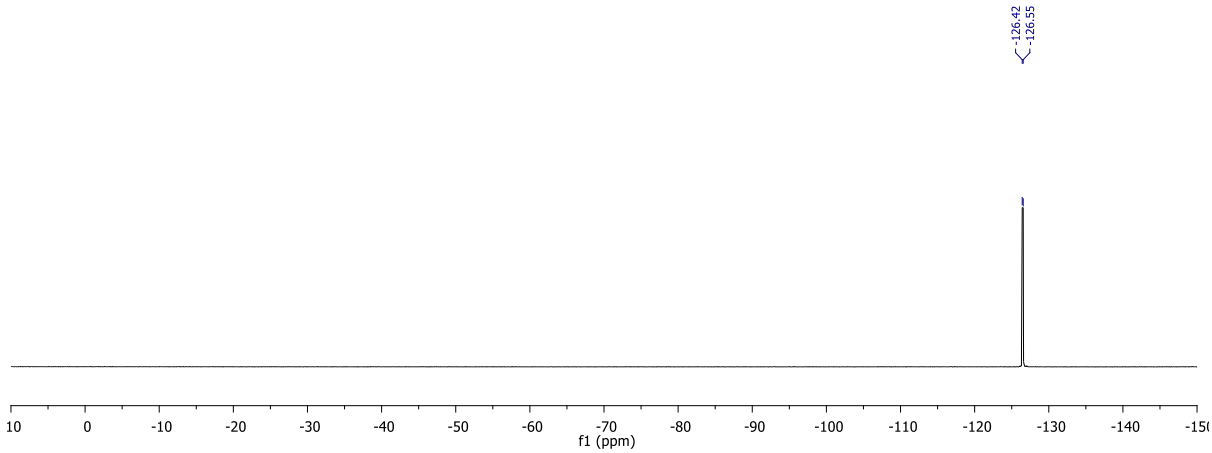


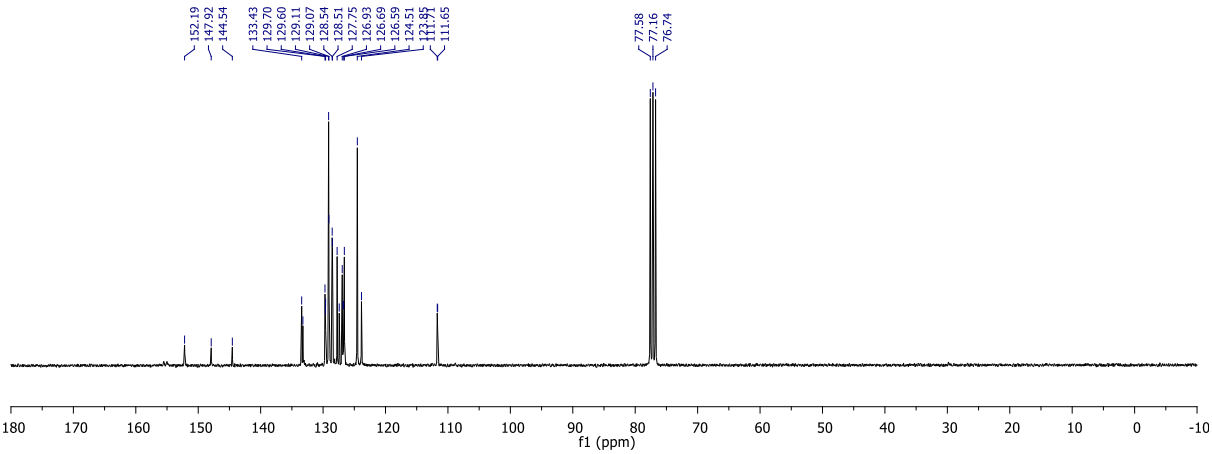


Heteroaryle **3Ca**

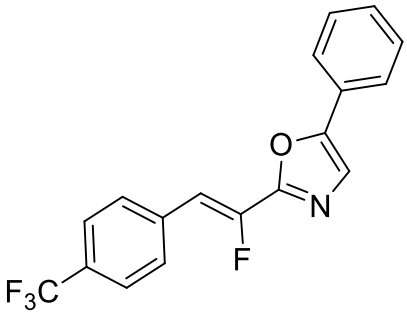


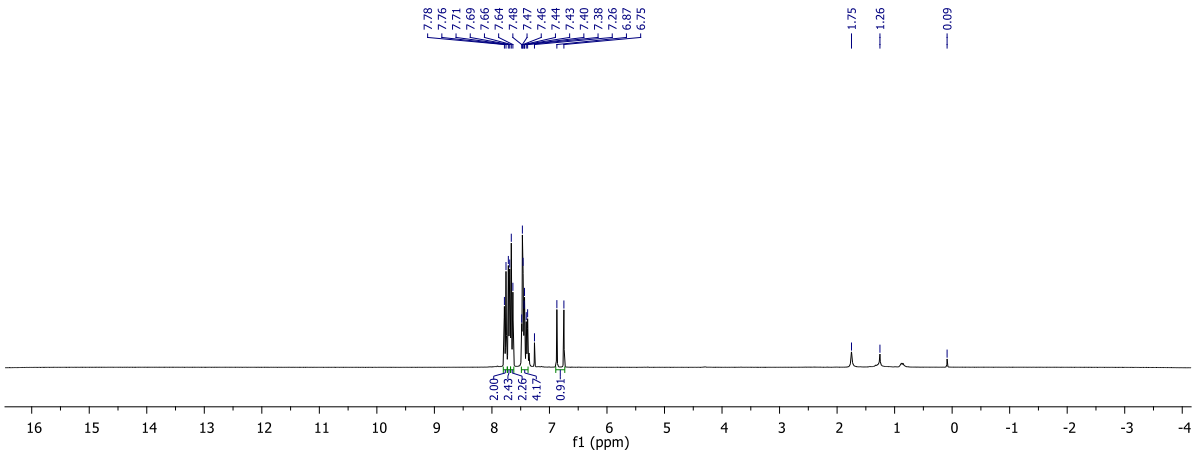


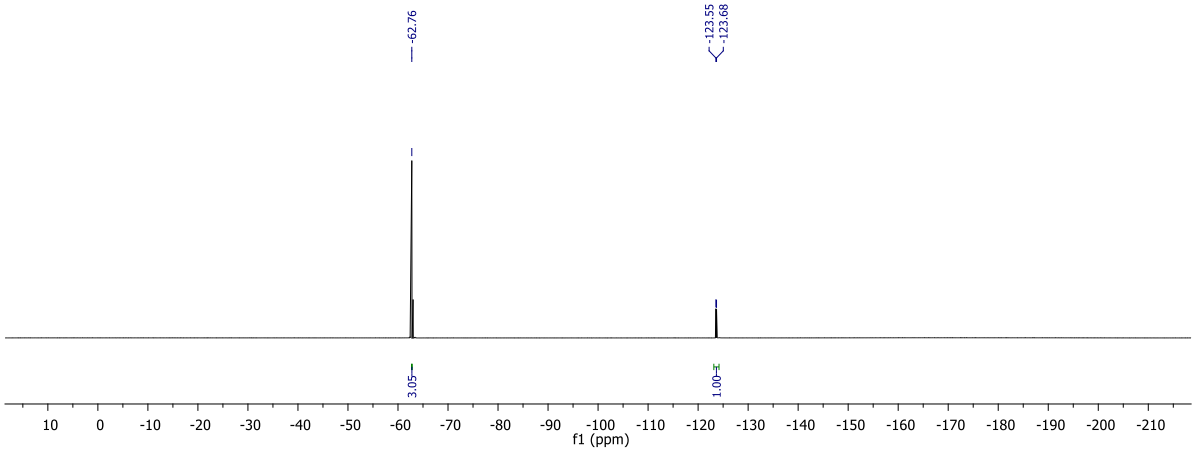


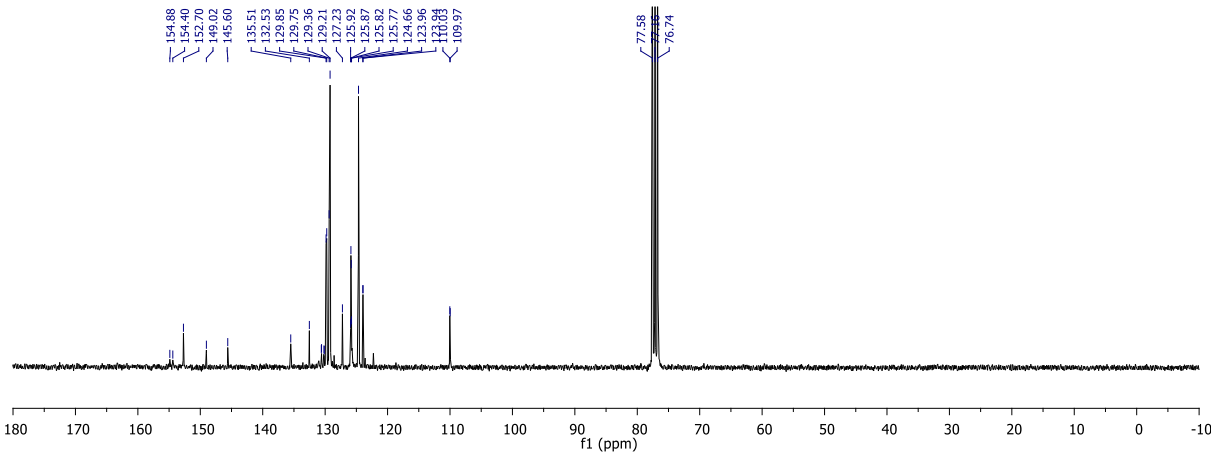


Heteroaryle **3Ea**

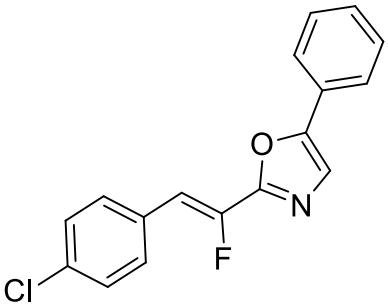


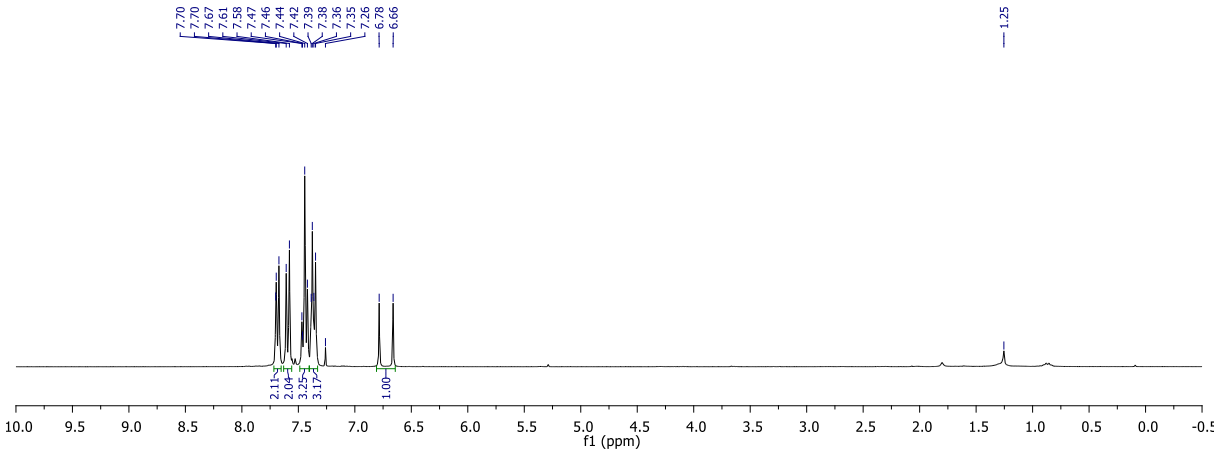


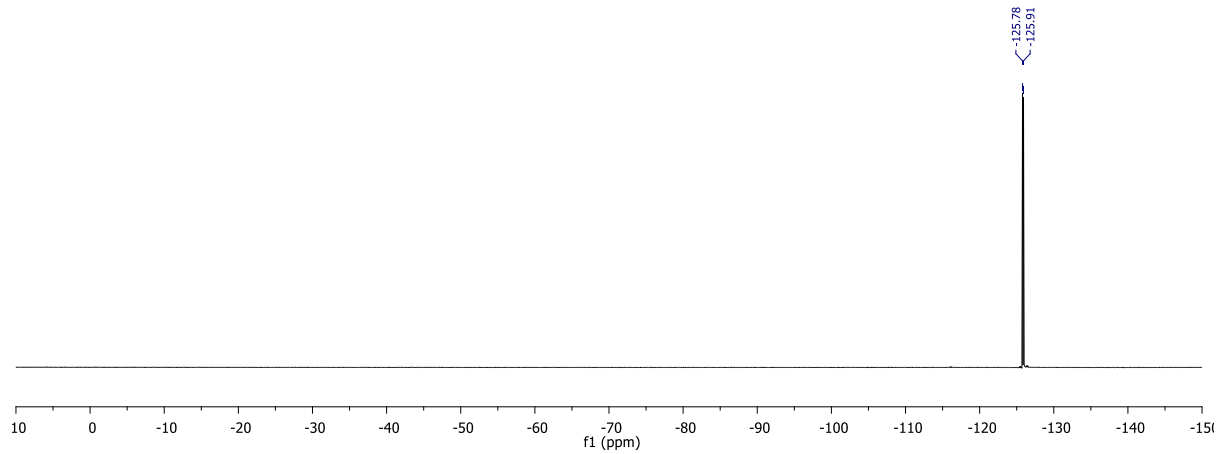


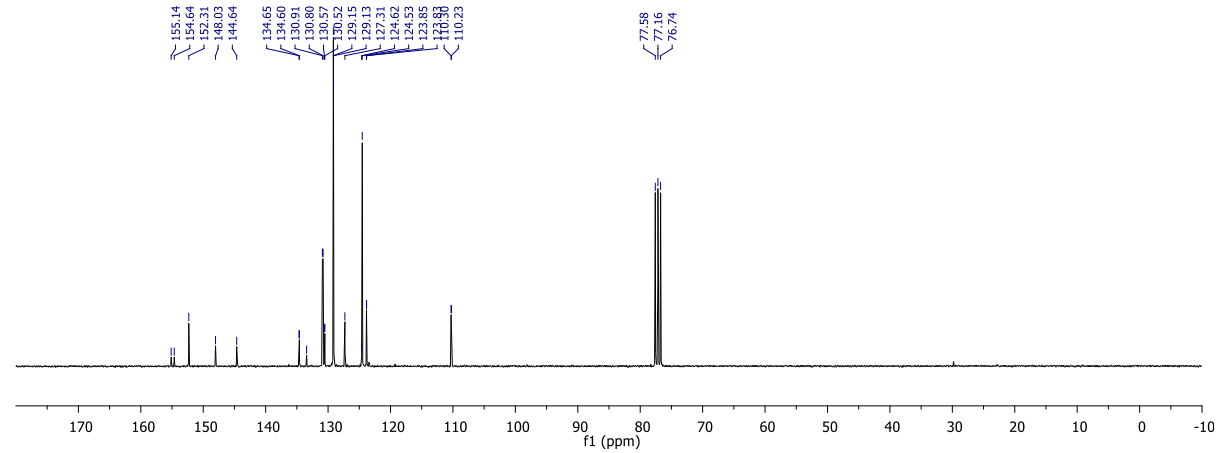


Heteroaryle **3Fa**









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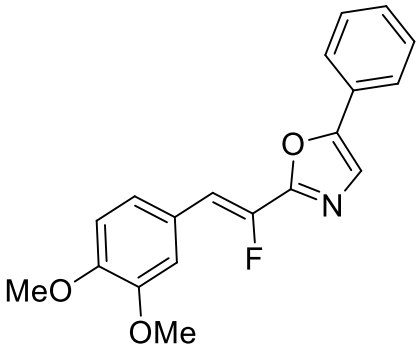
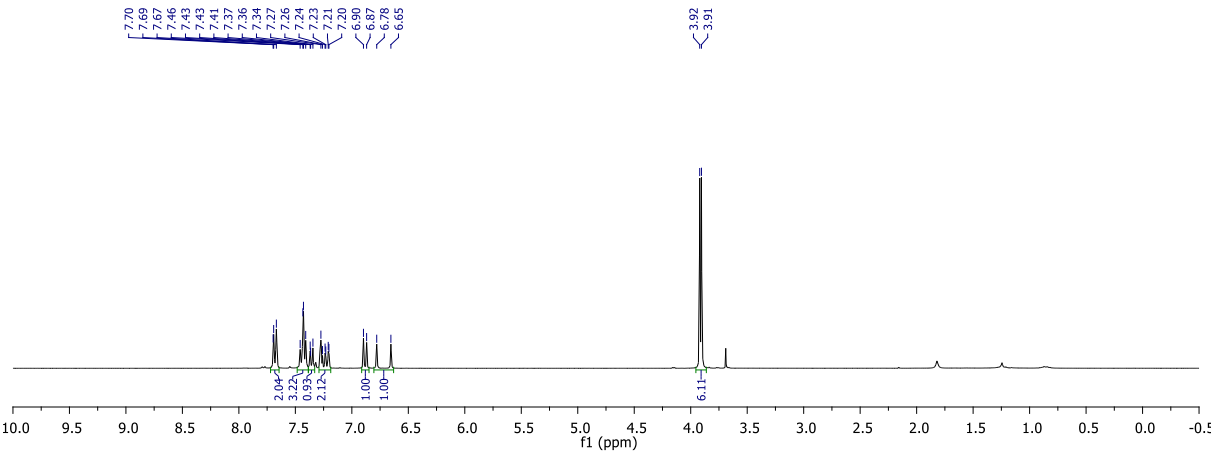
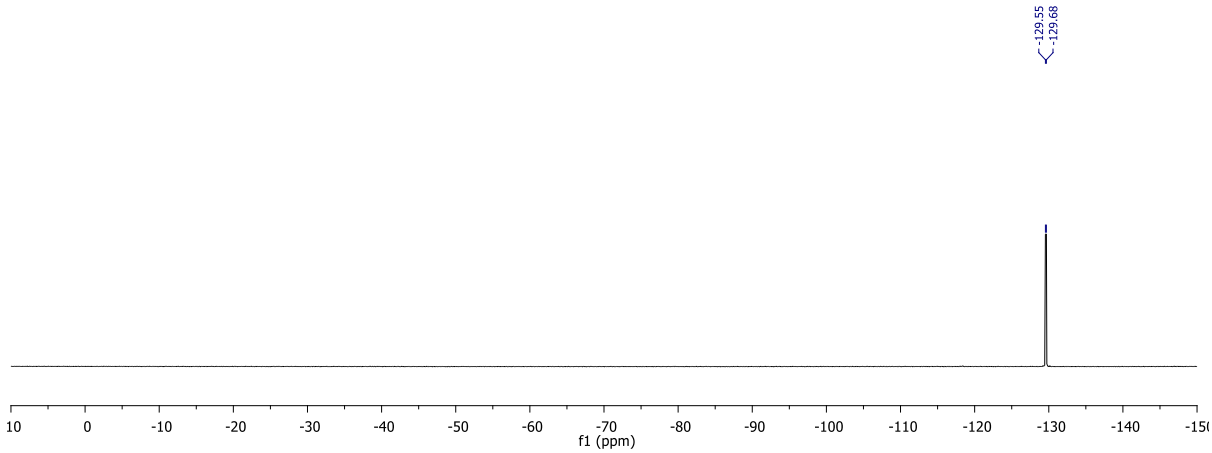
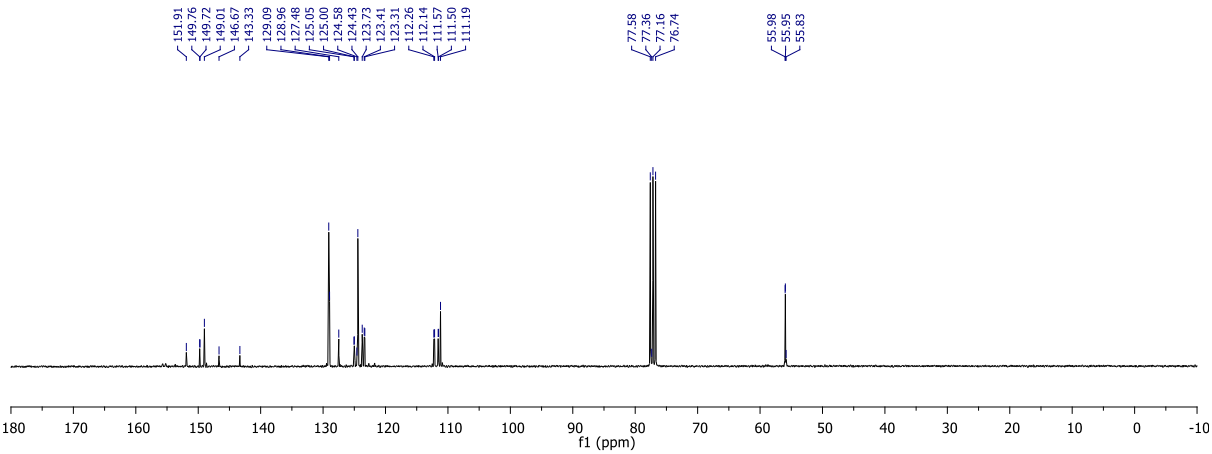
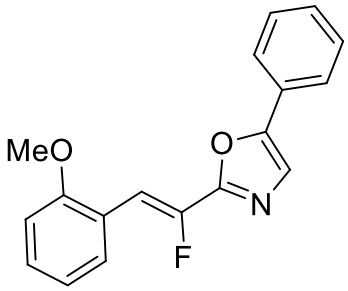


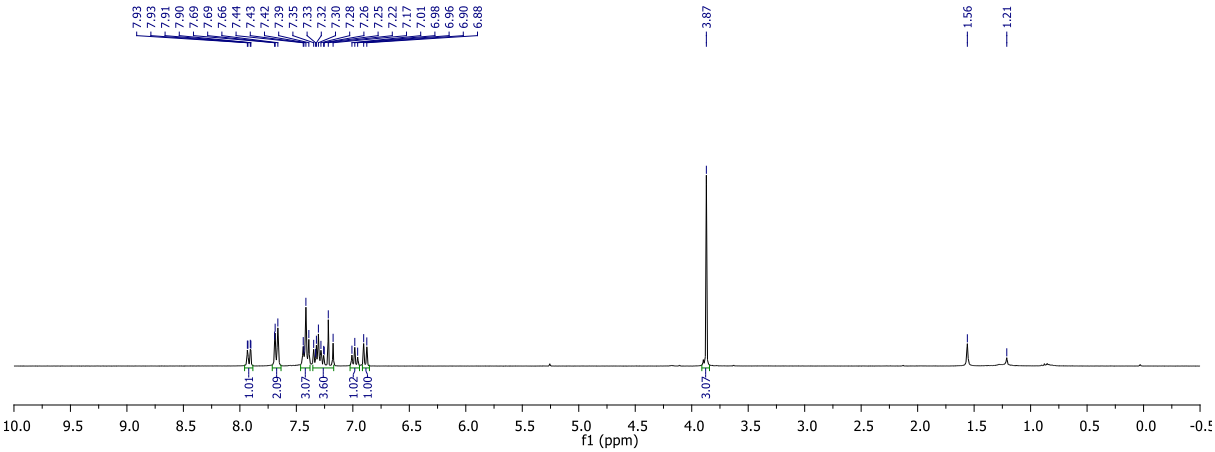


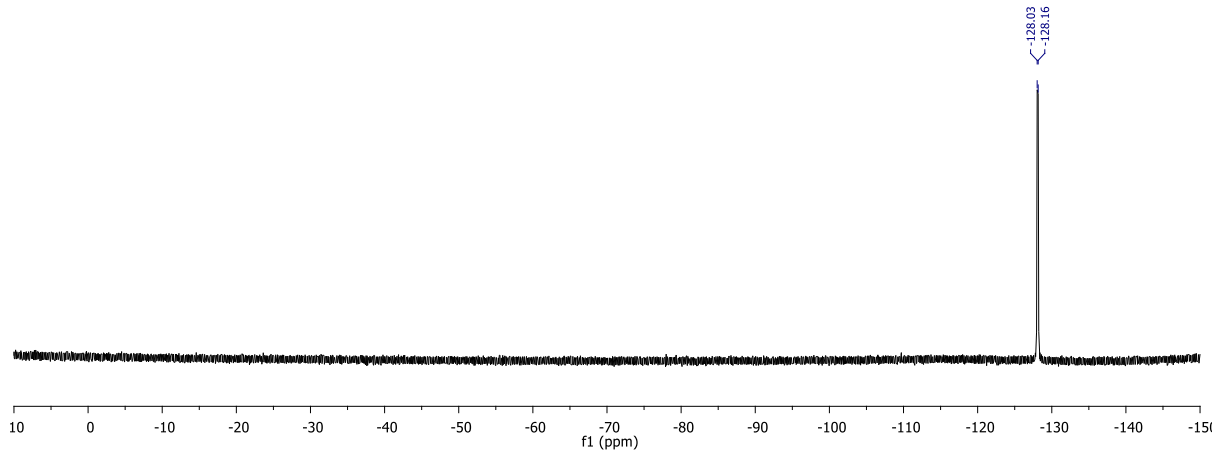


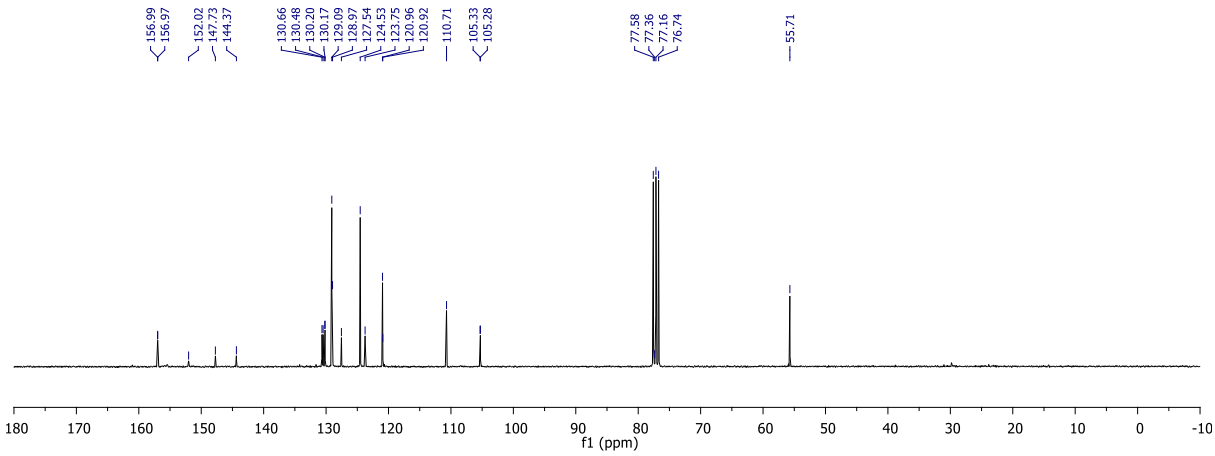


Heteroaryle **3Ha**

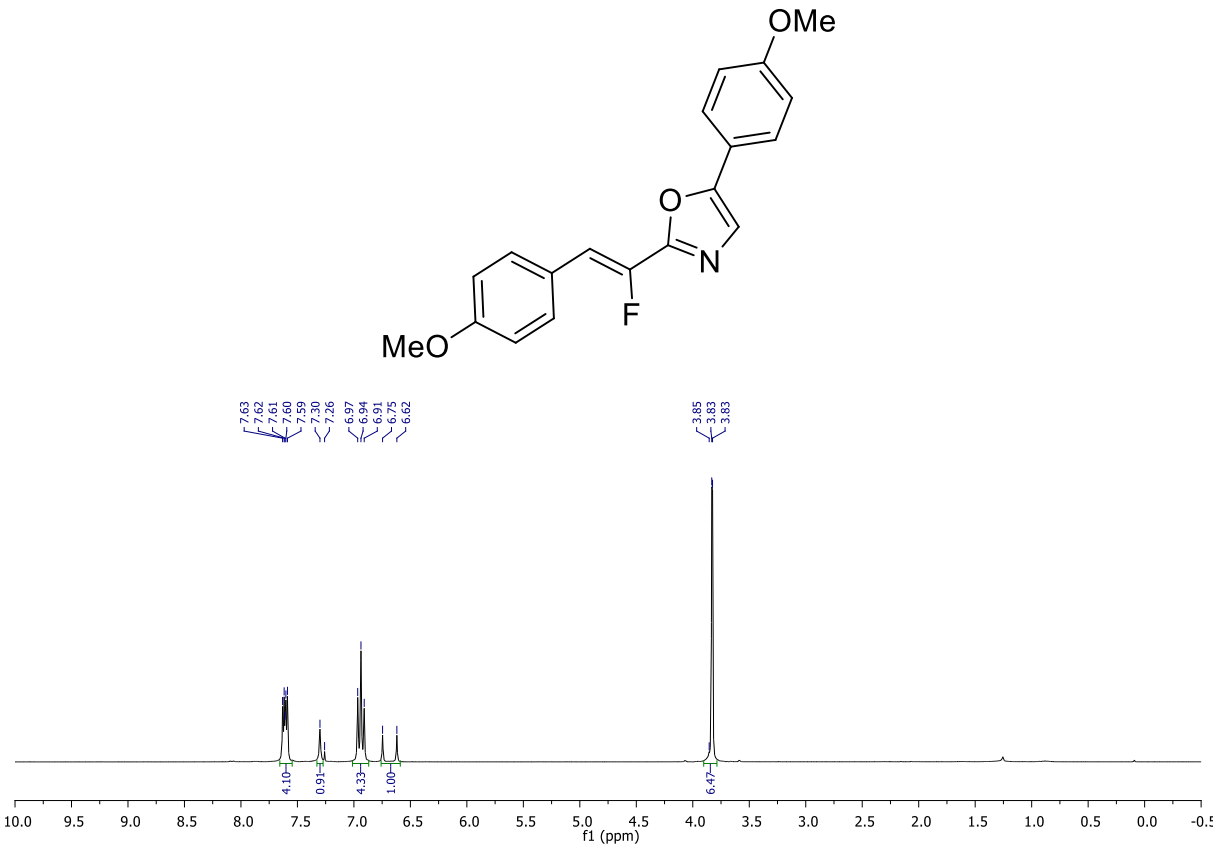


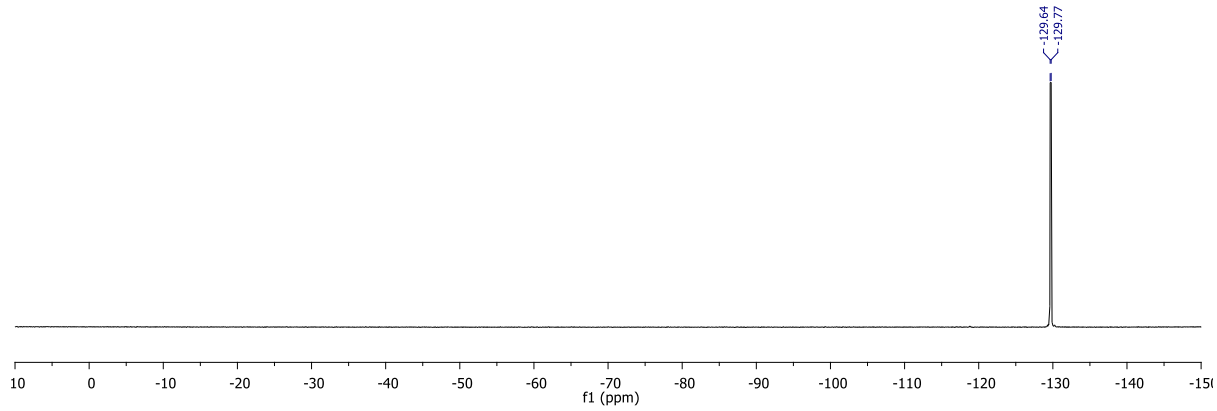


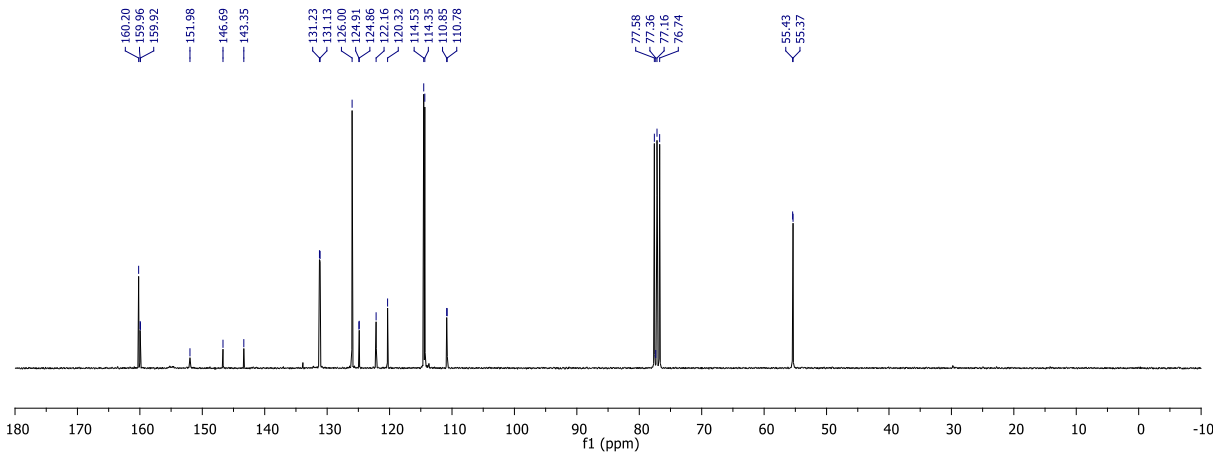




Heteroaryle **3Ab**







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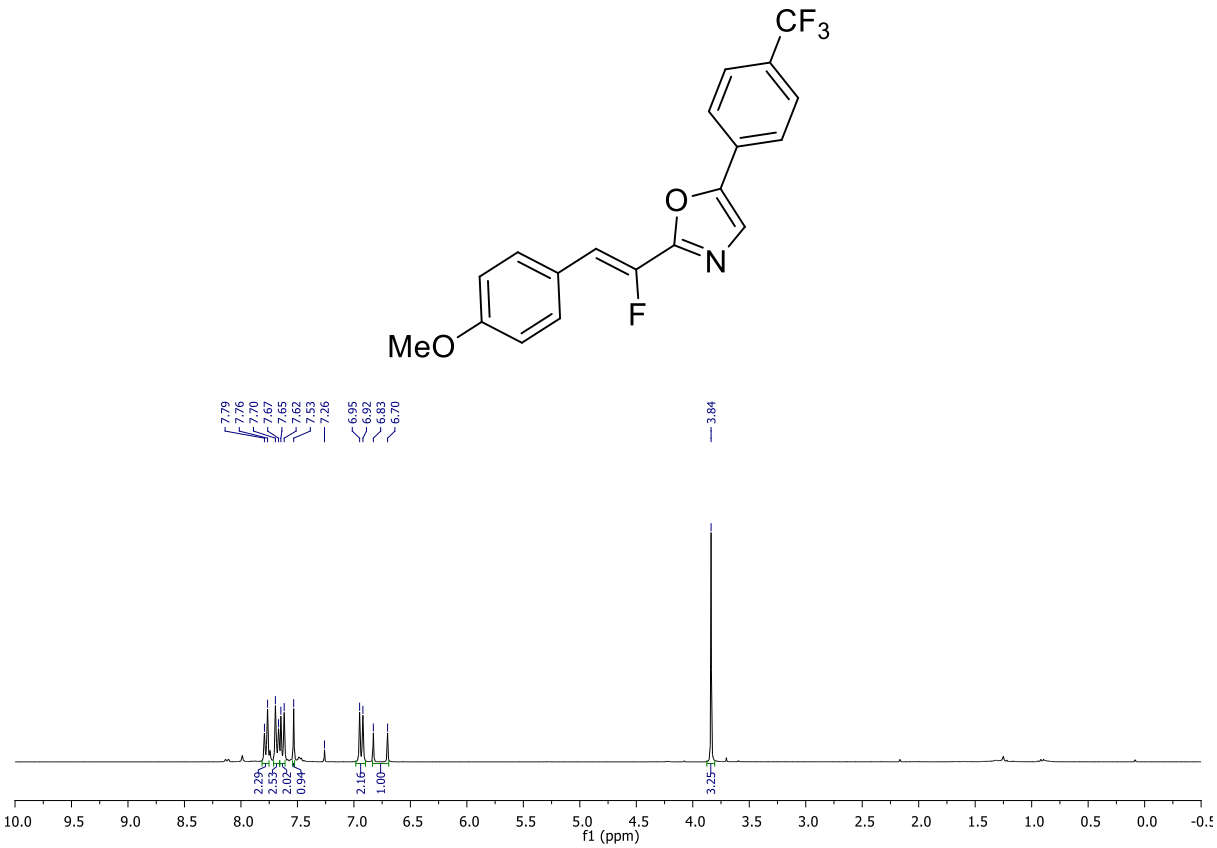

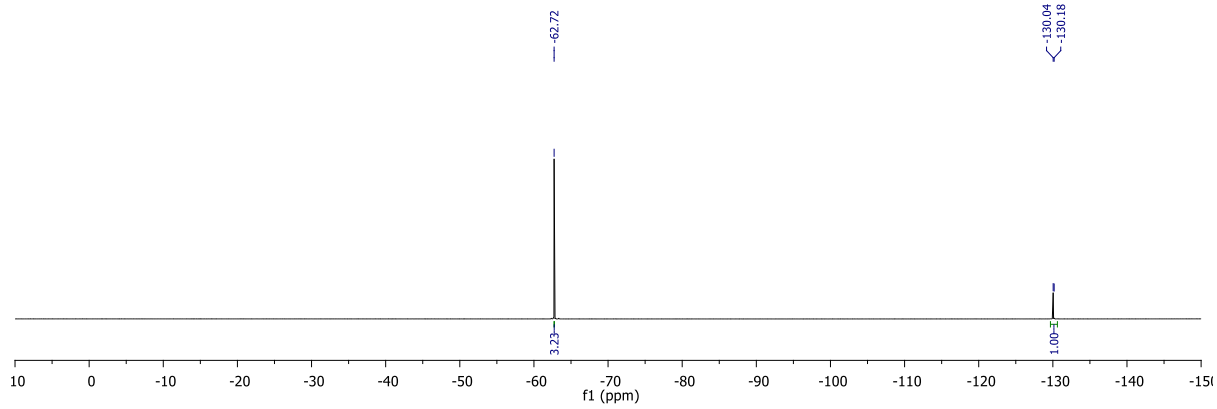

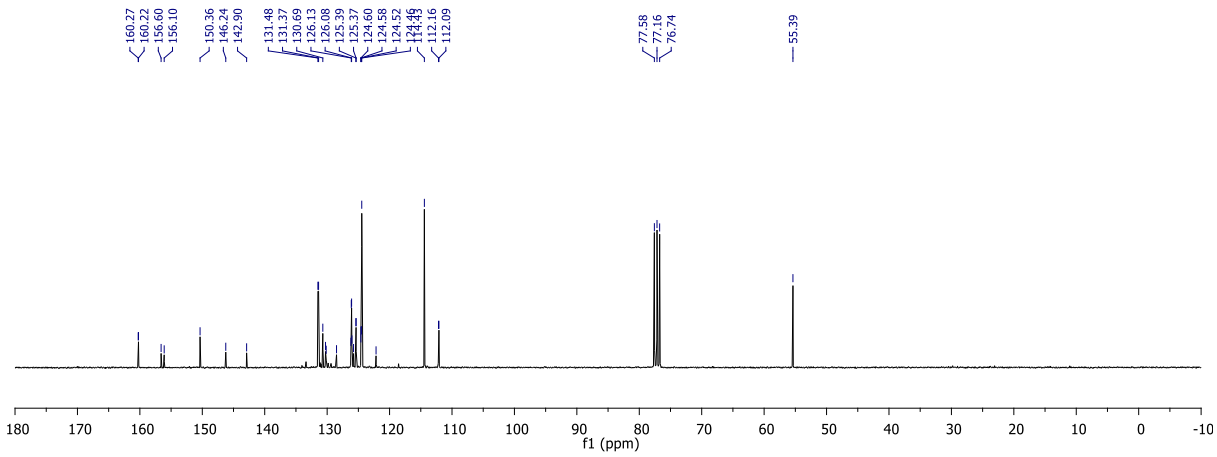

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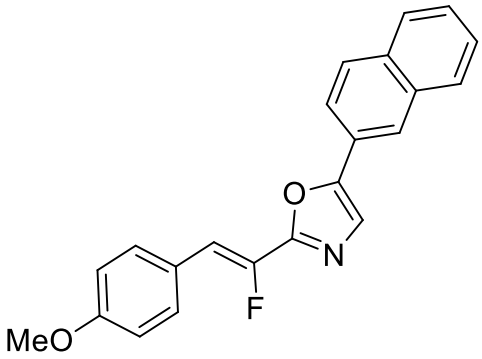

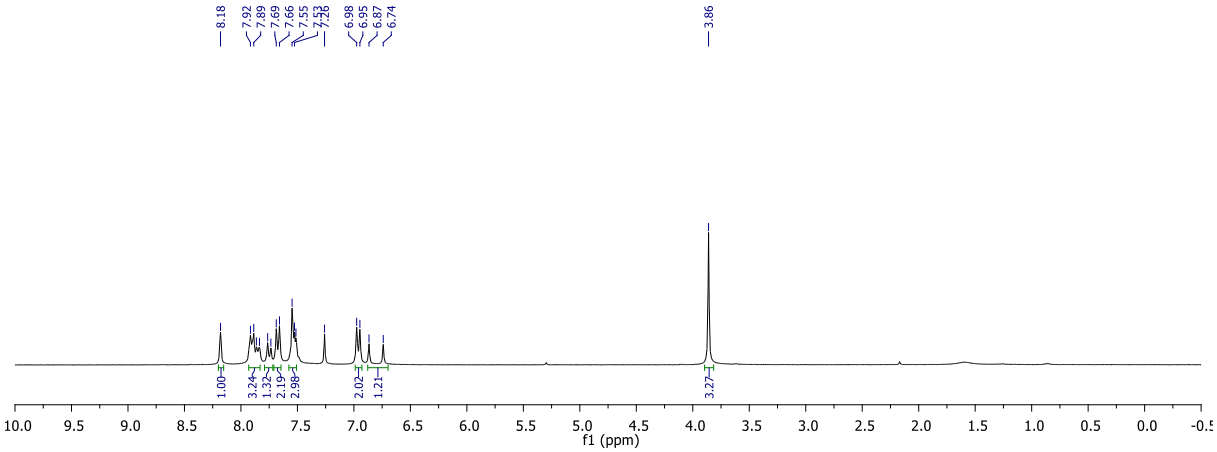

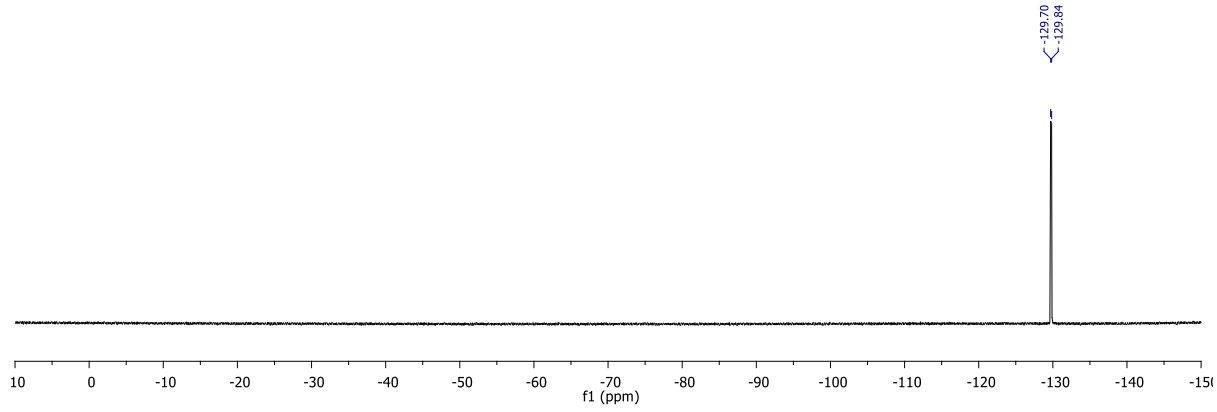

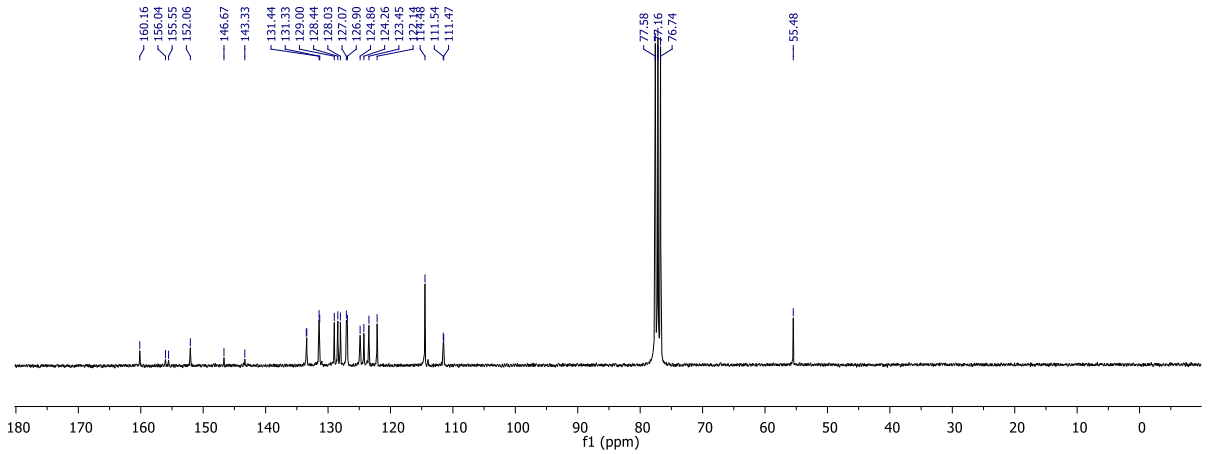

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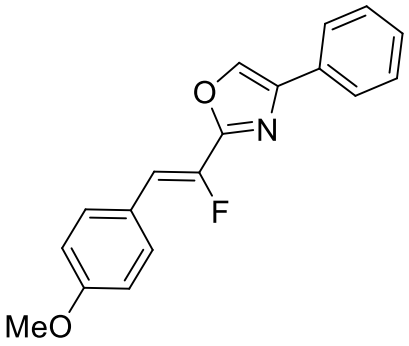

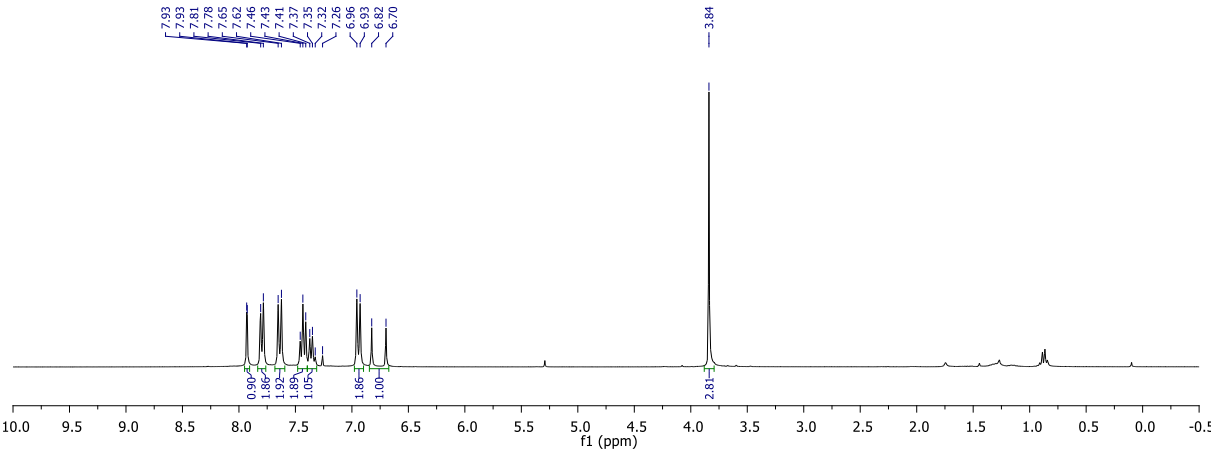

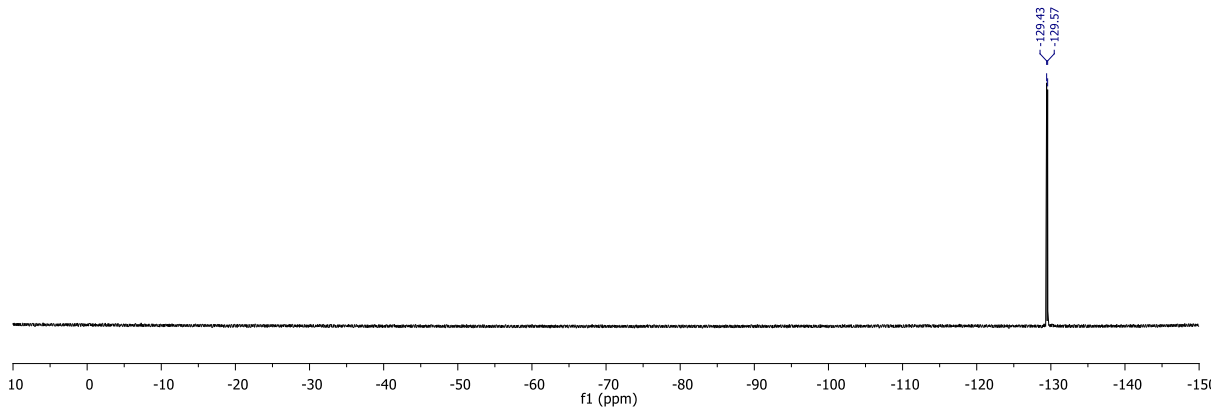

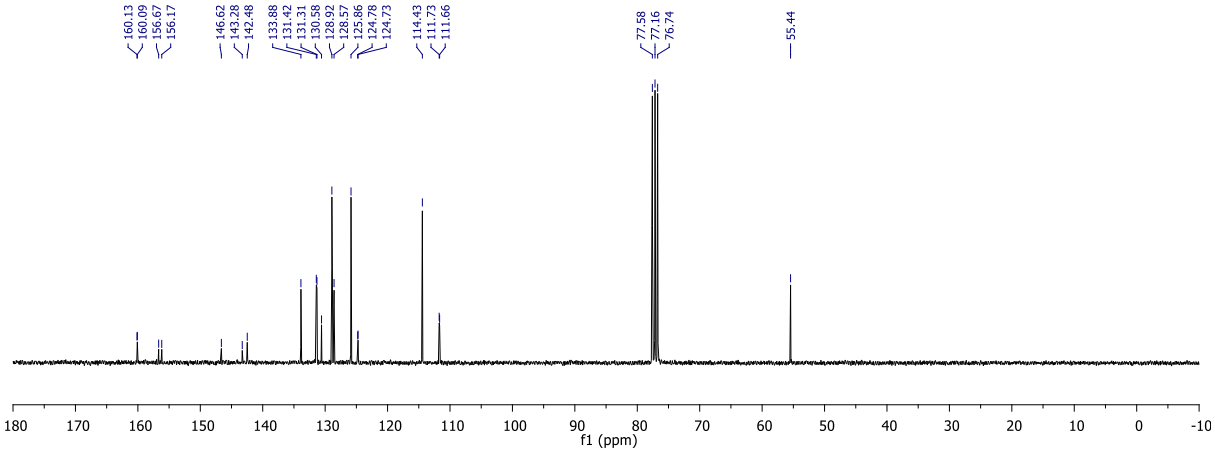

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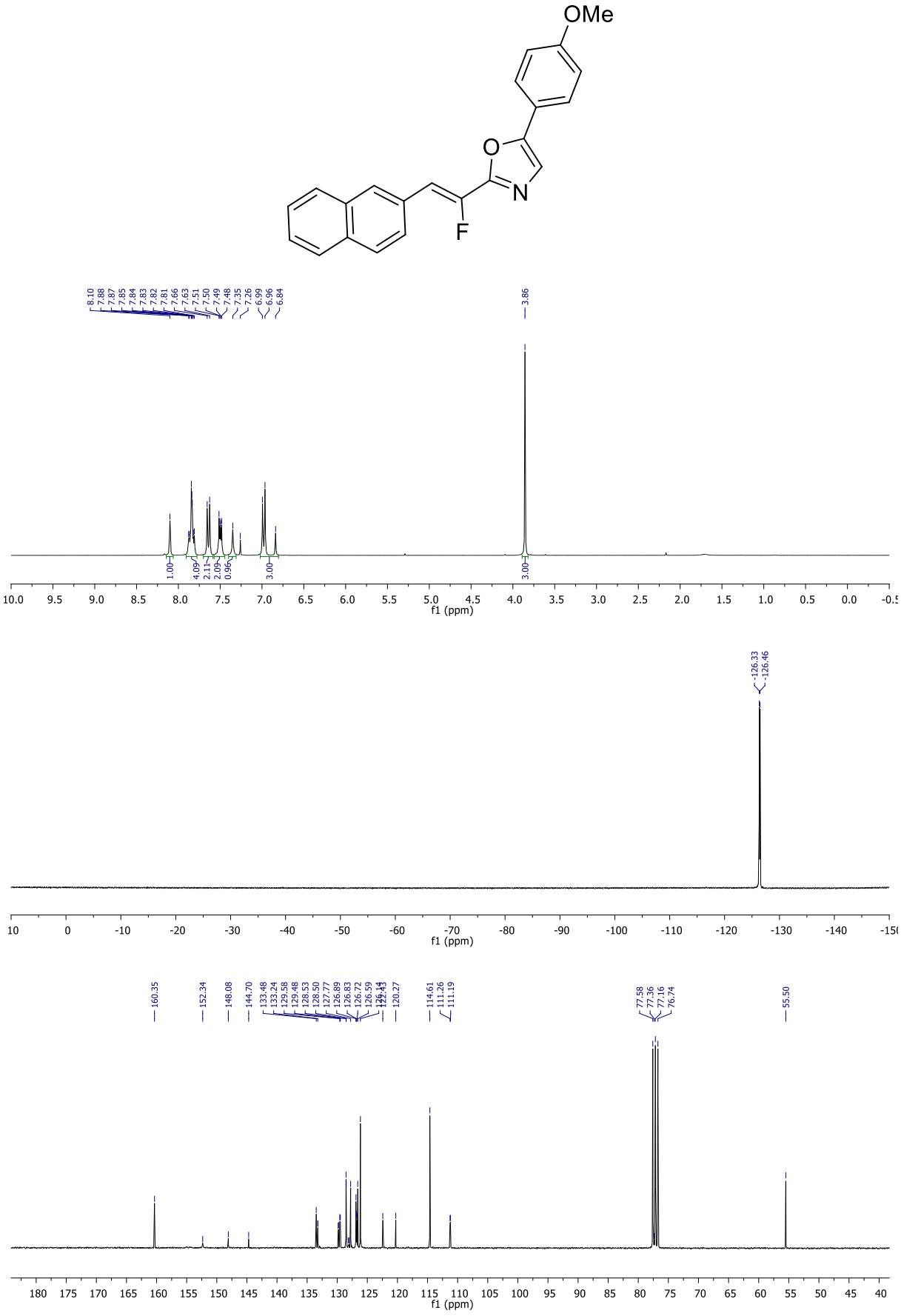
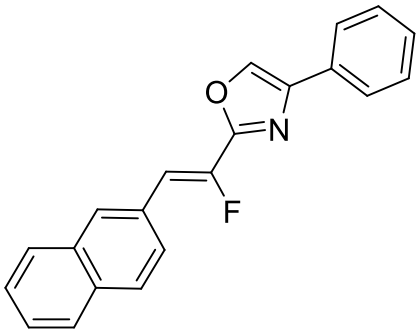
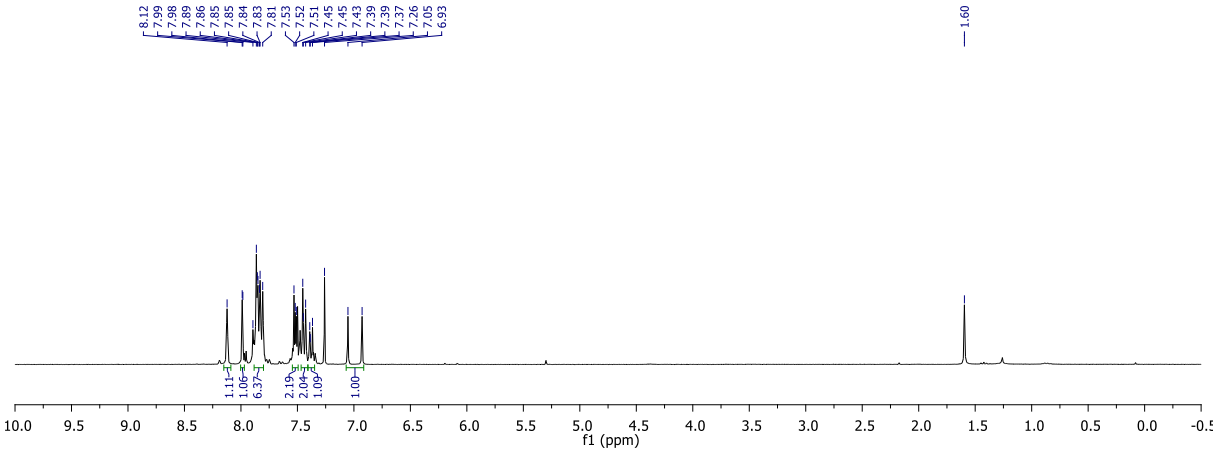
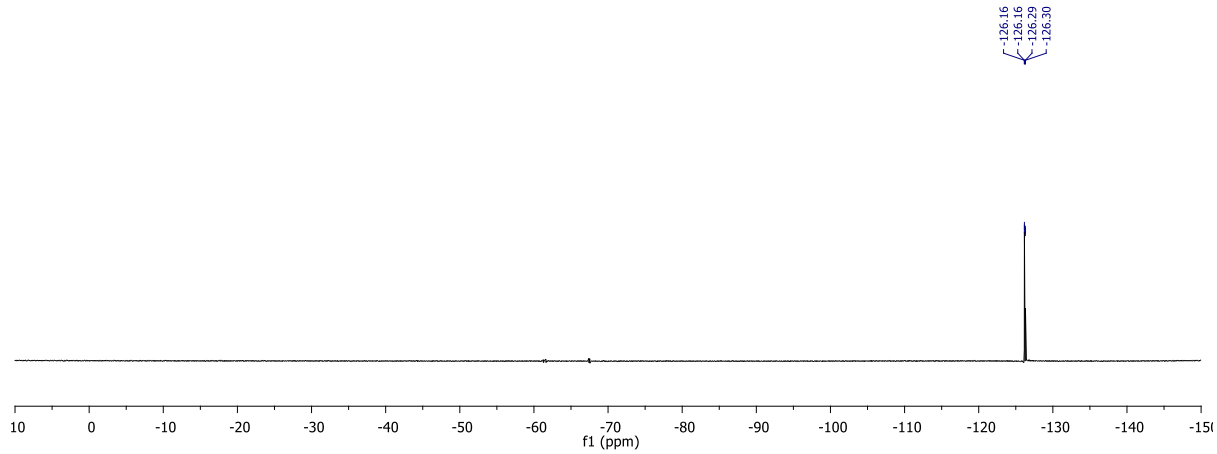
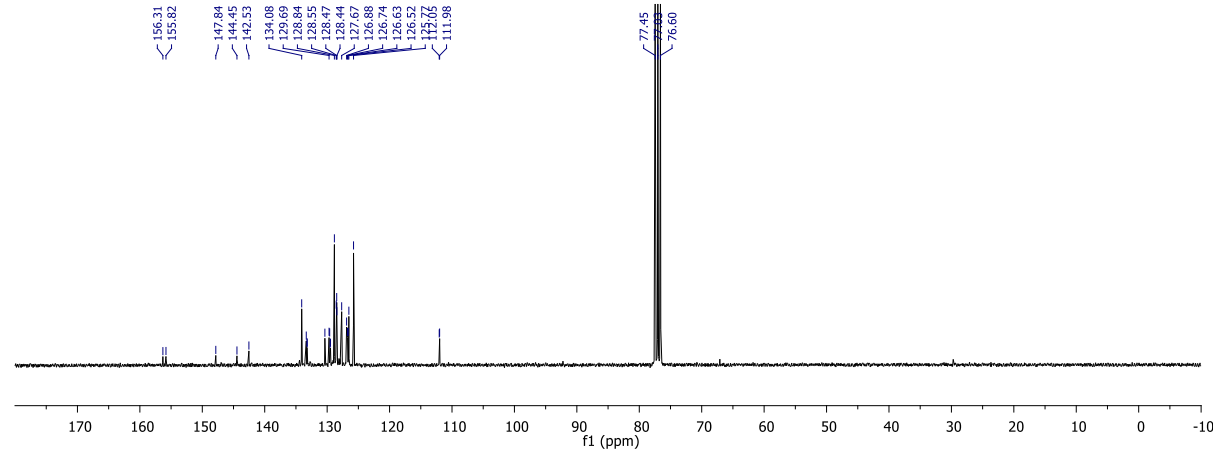


Heteroaryle **3Ce**

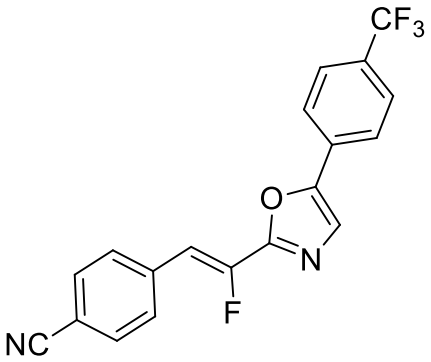


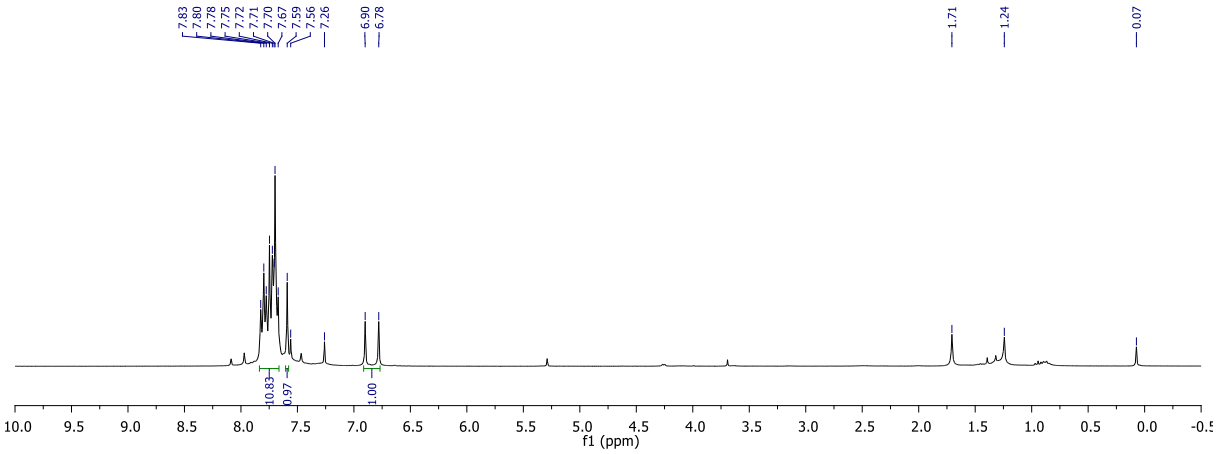


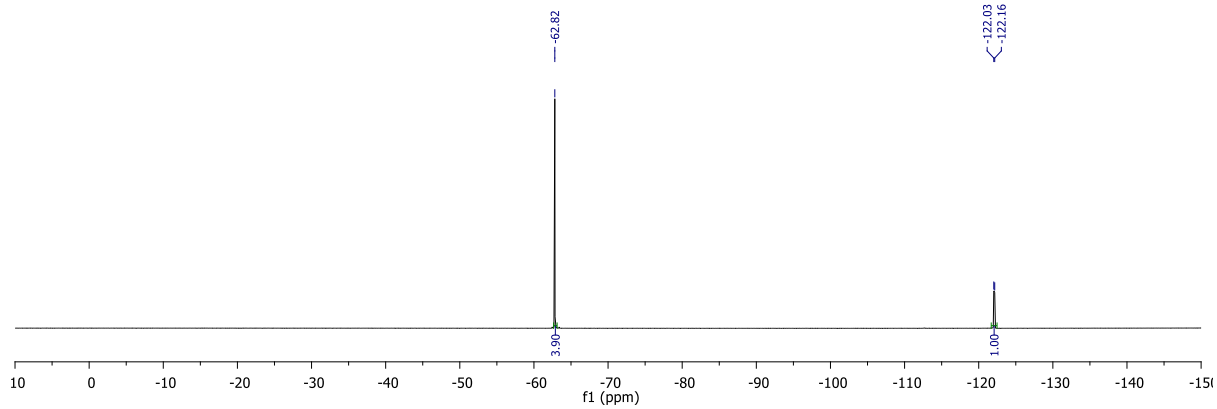


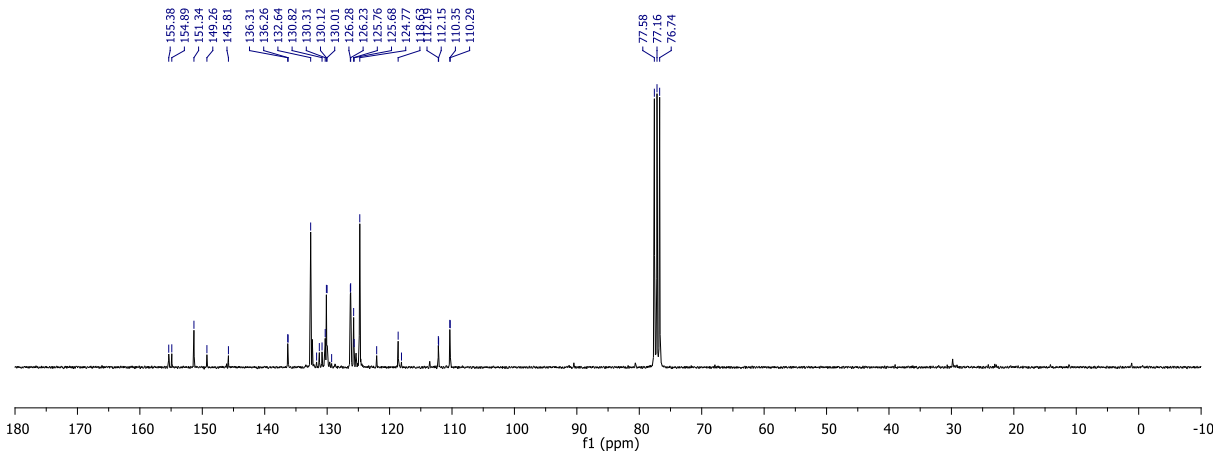


Heteroaryle **3Dc**

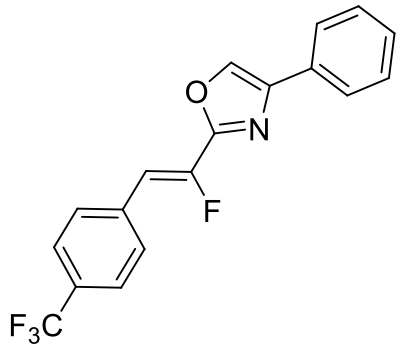


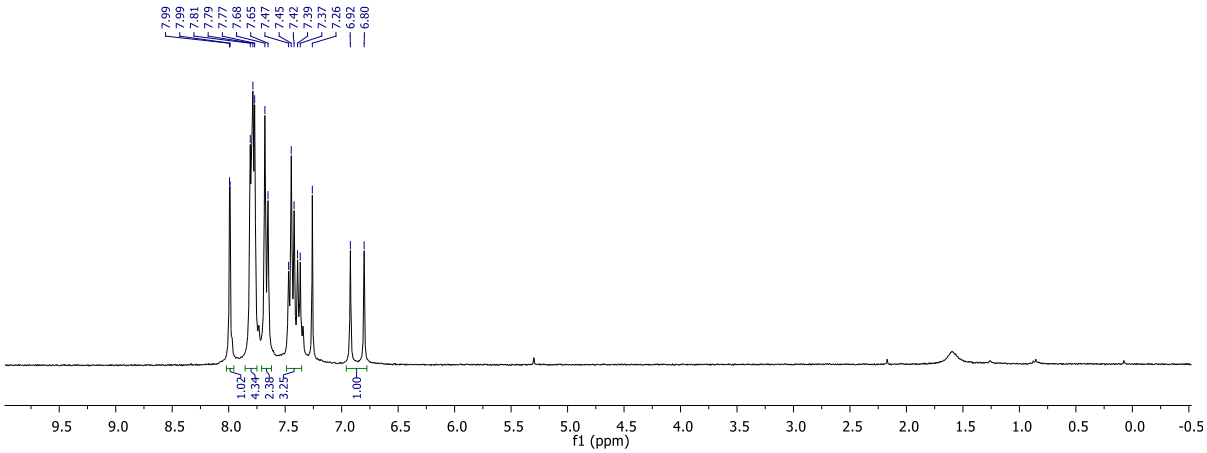


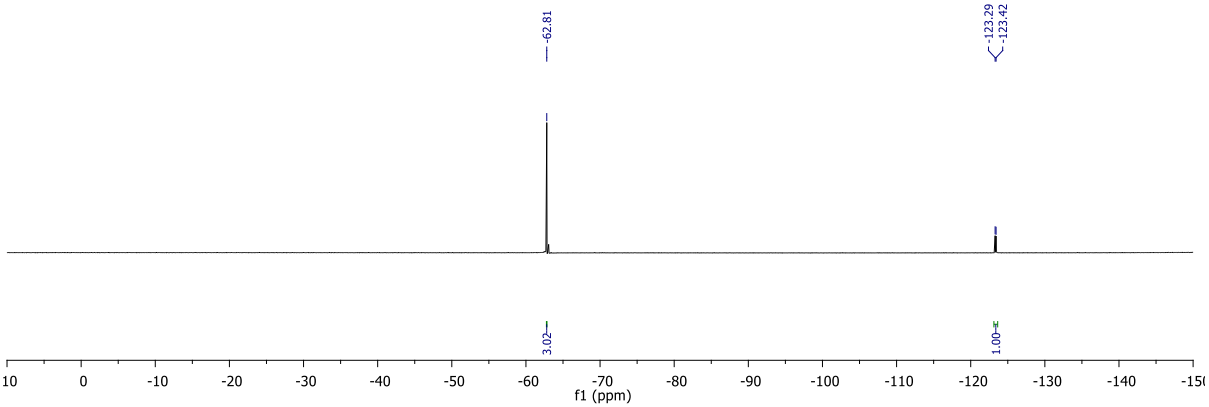


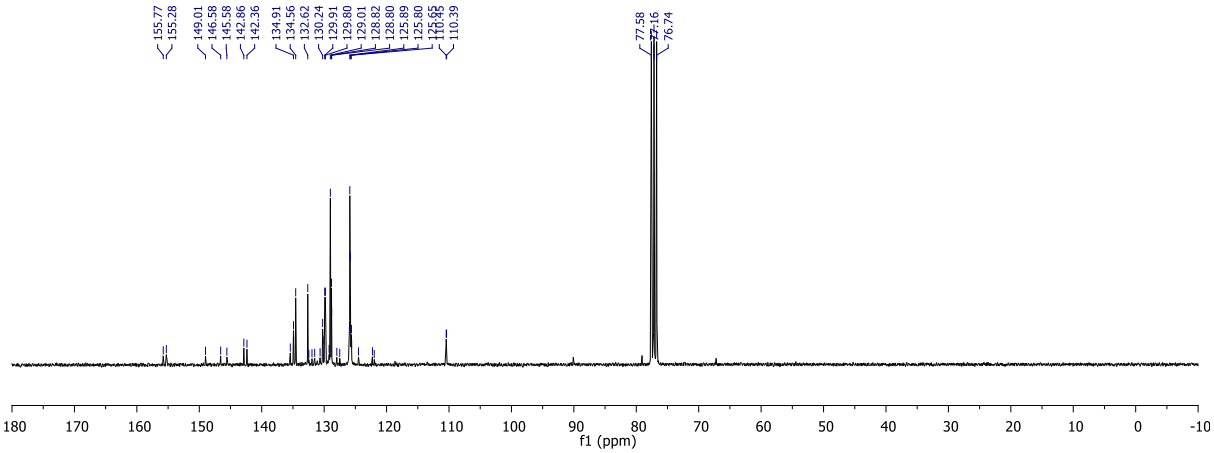


Heteroaryle **3Ee**

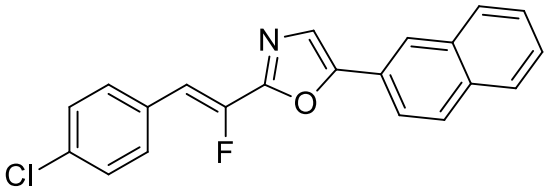


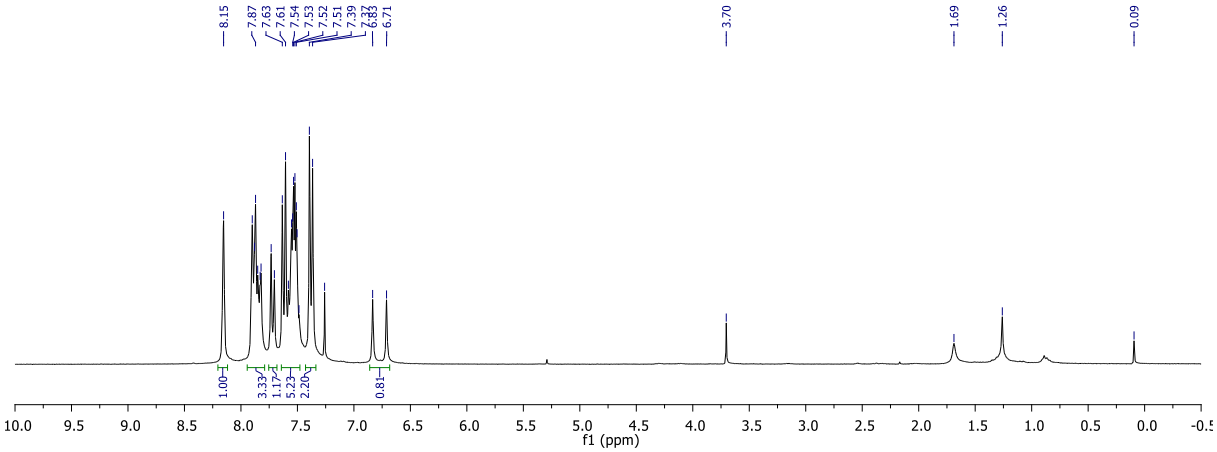


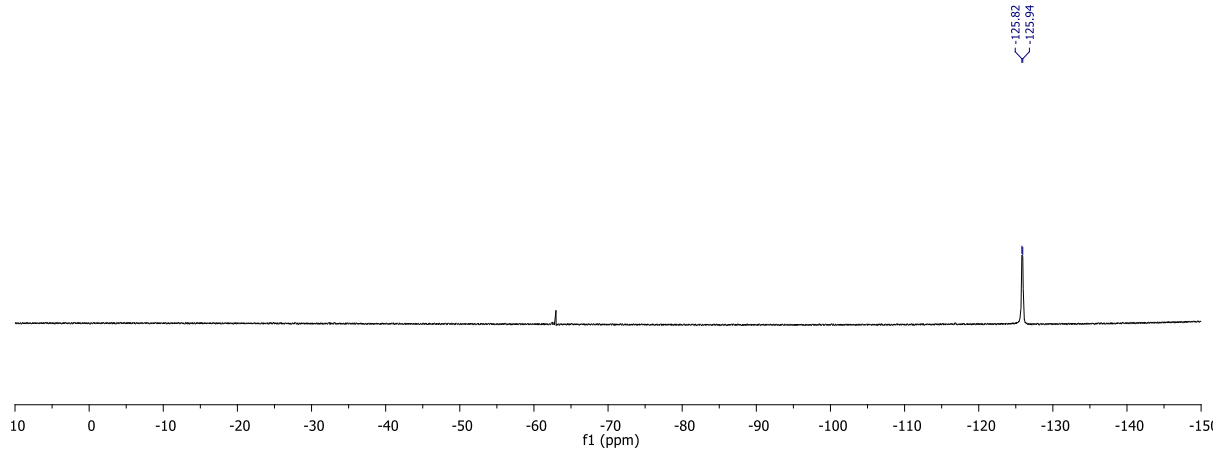


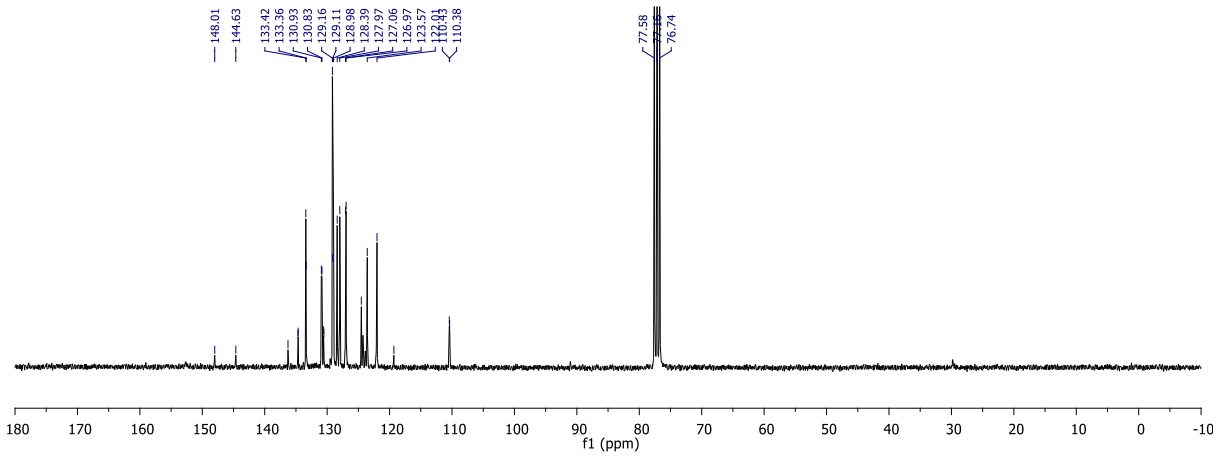


Heteroaryle **3Fd**

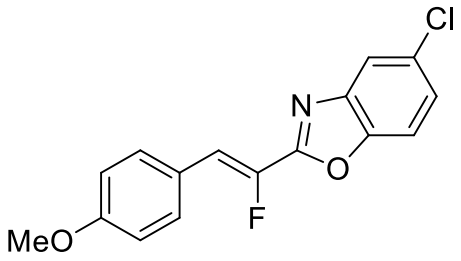


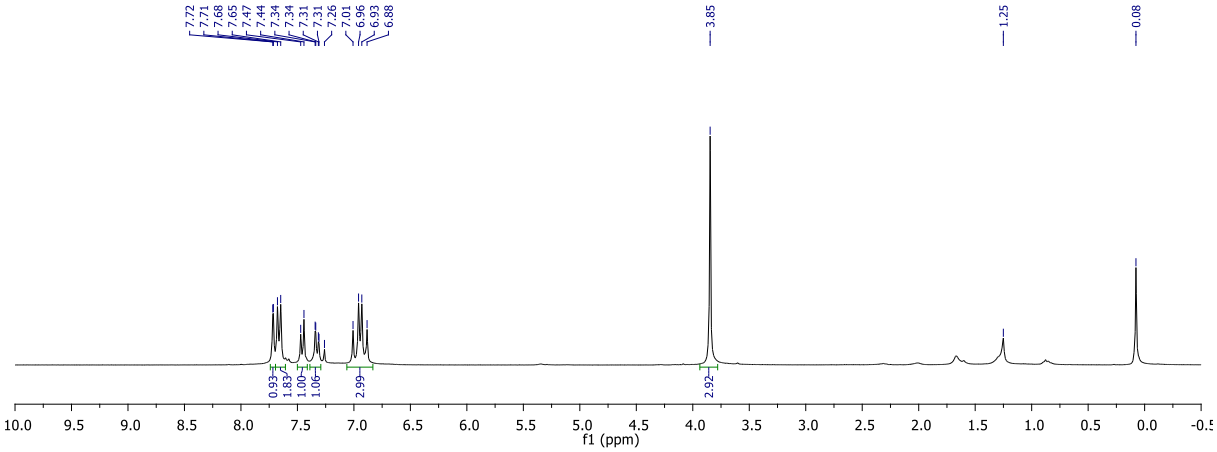


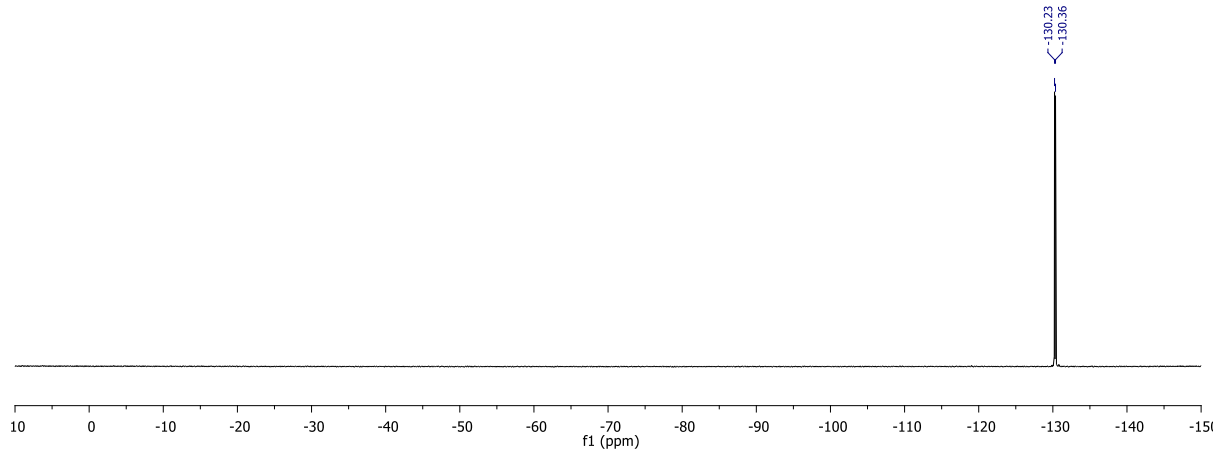


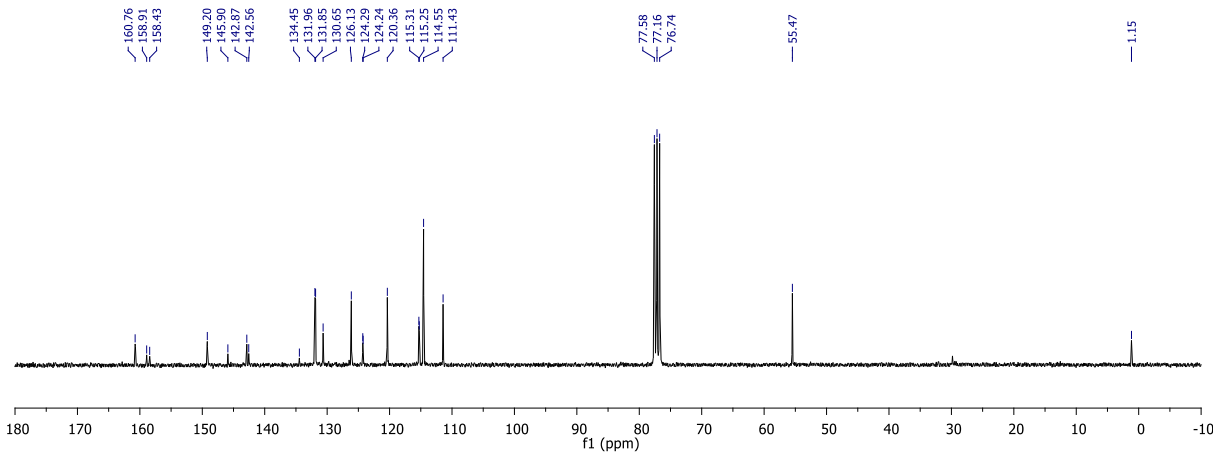


Heteroaryle **4Ab**









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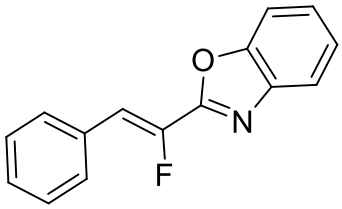

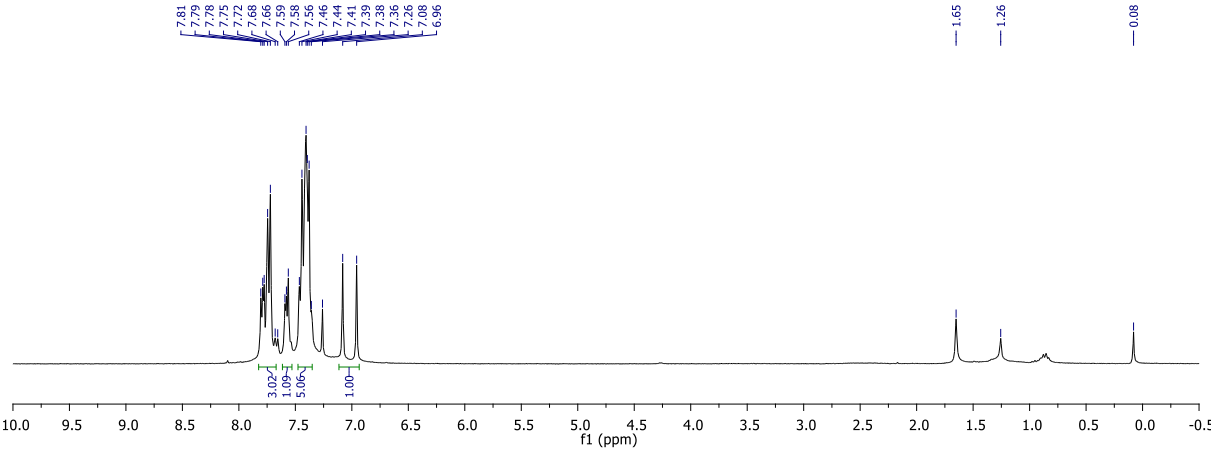

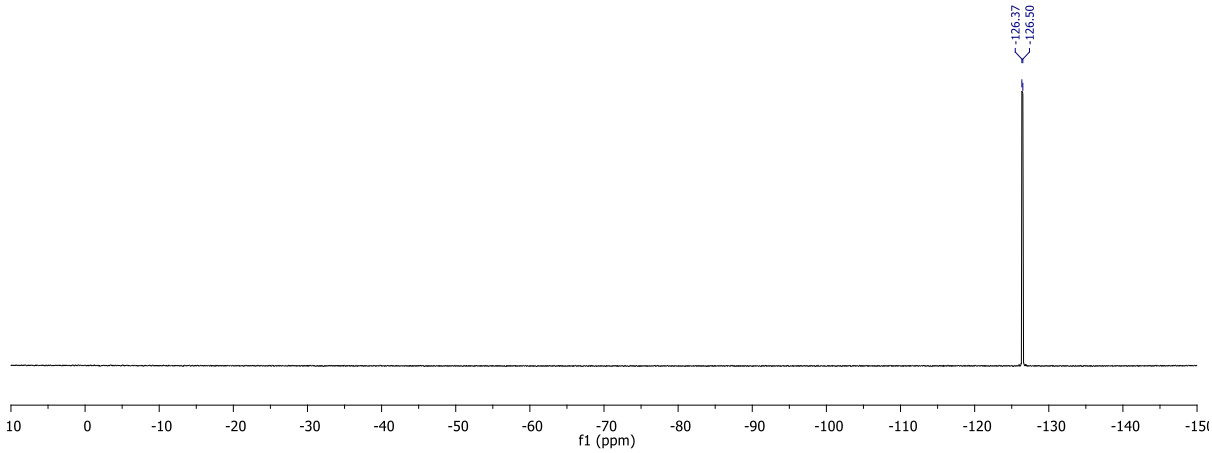

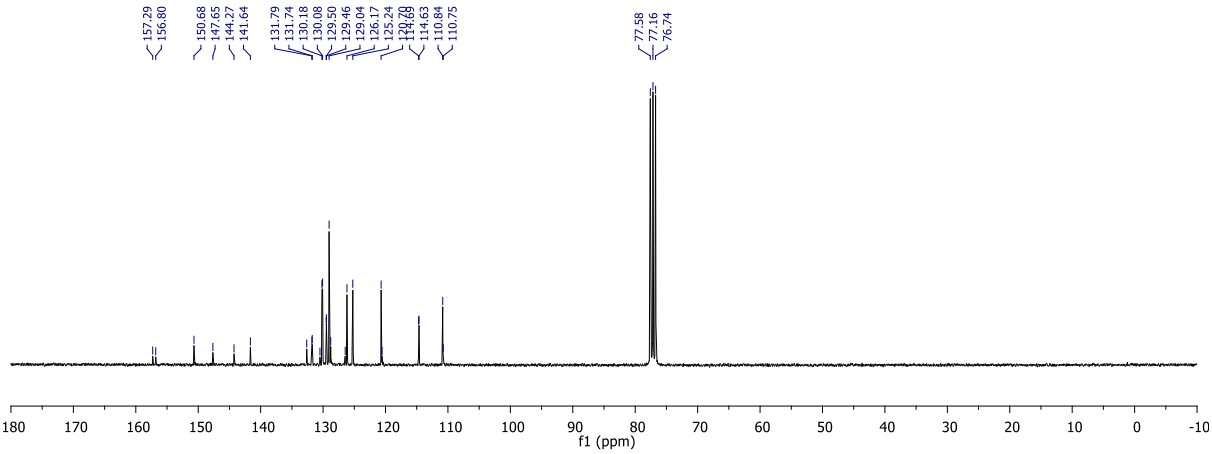

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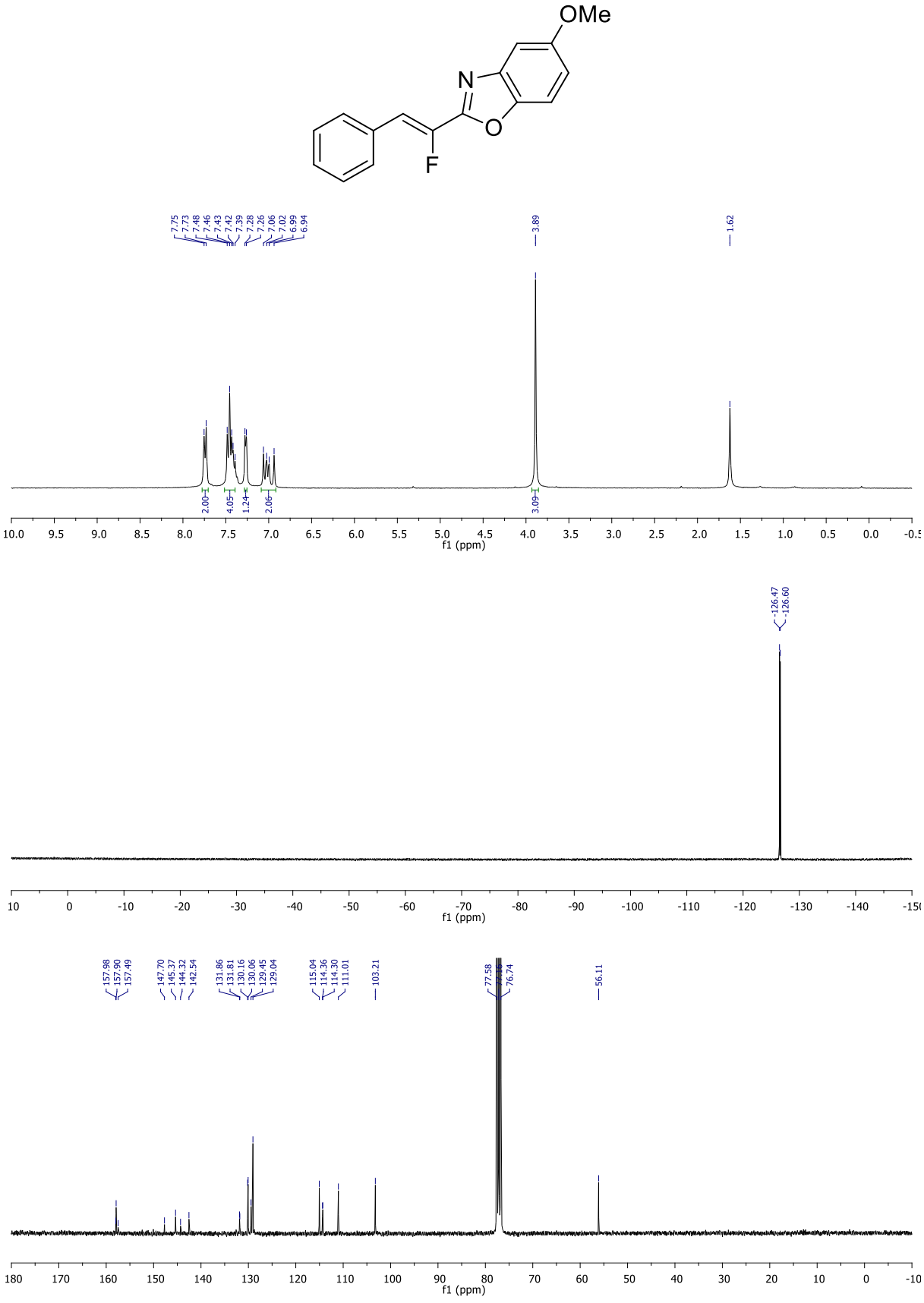

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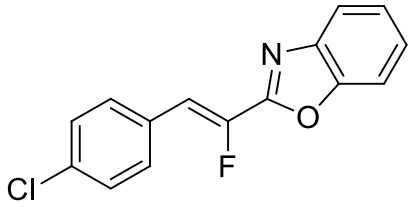
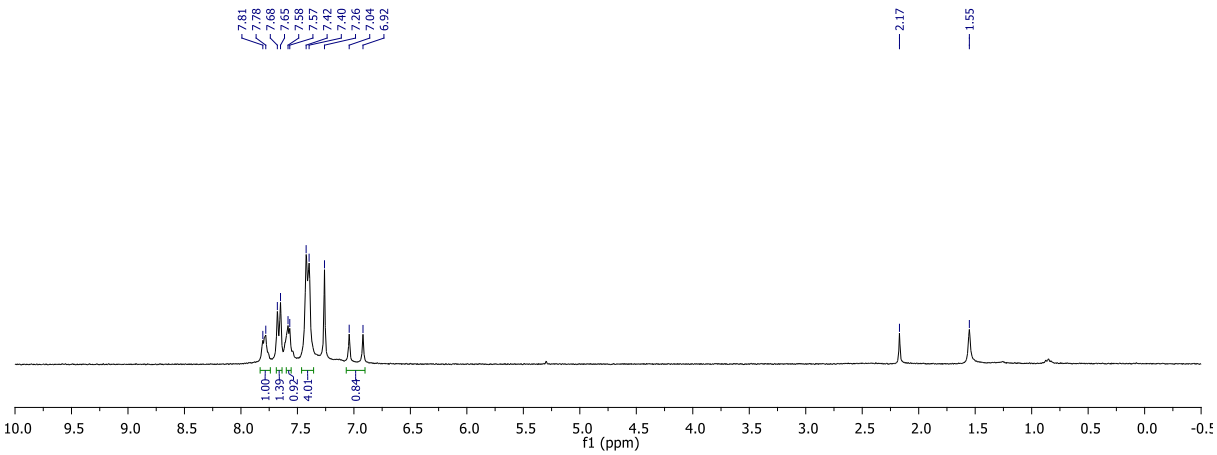
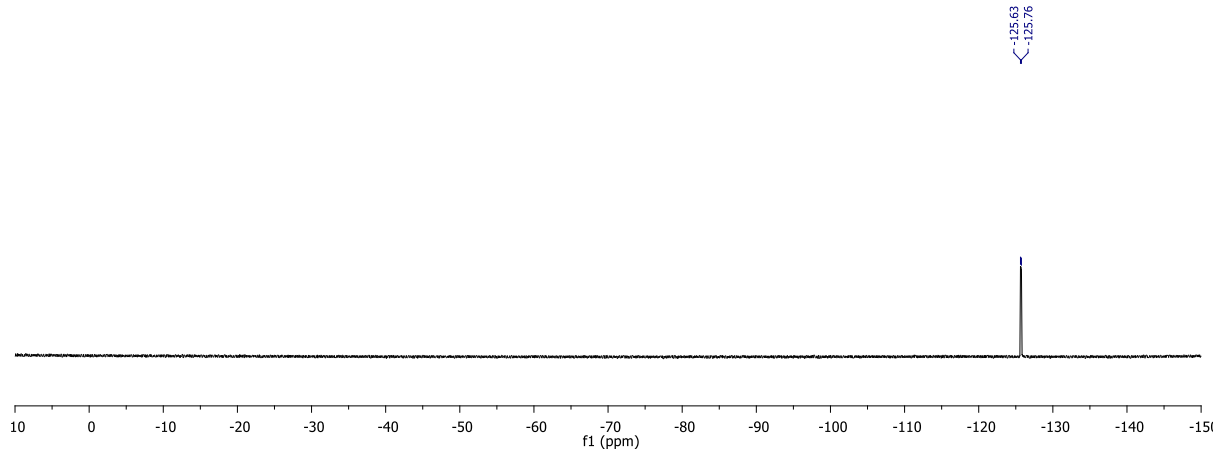
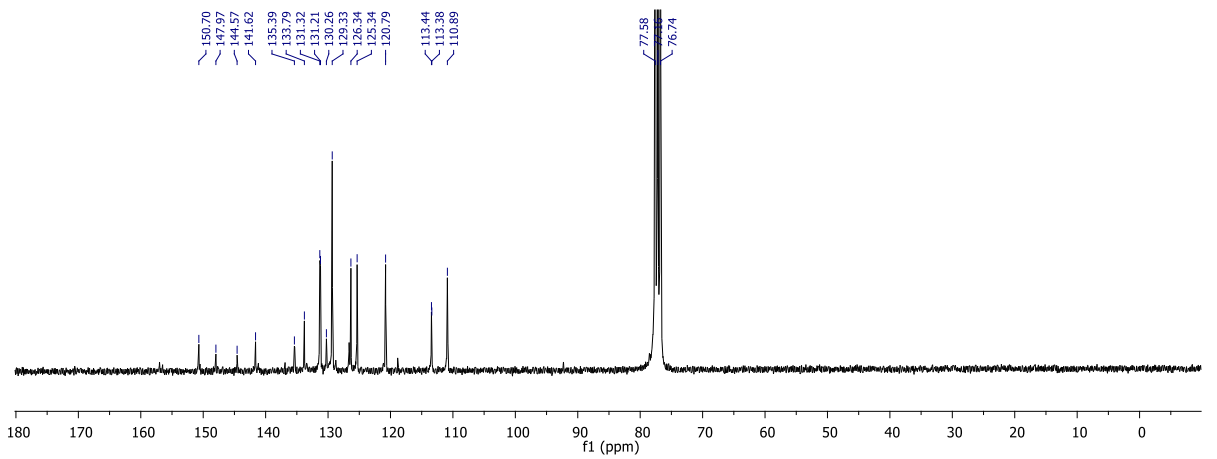
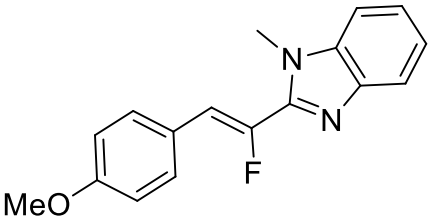


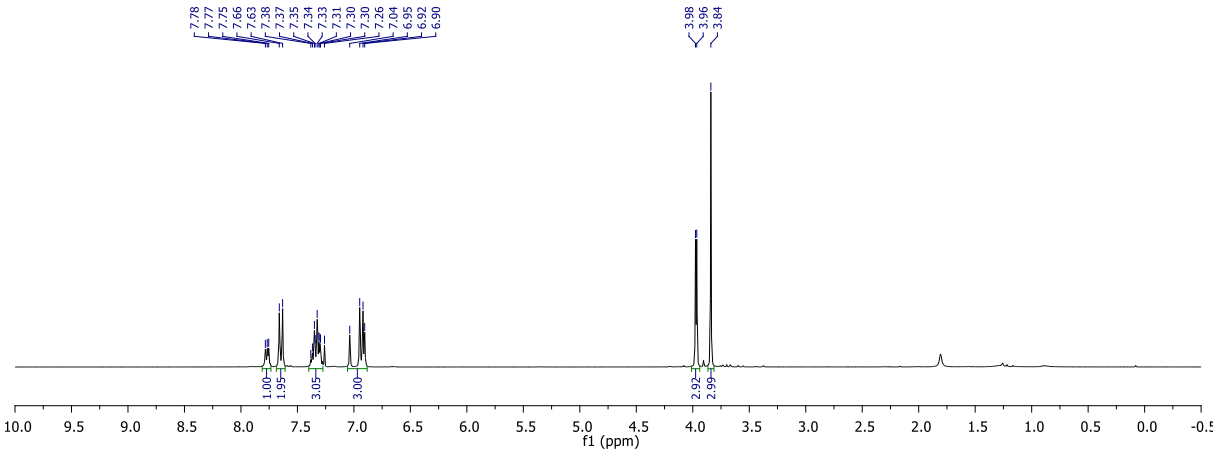


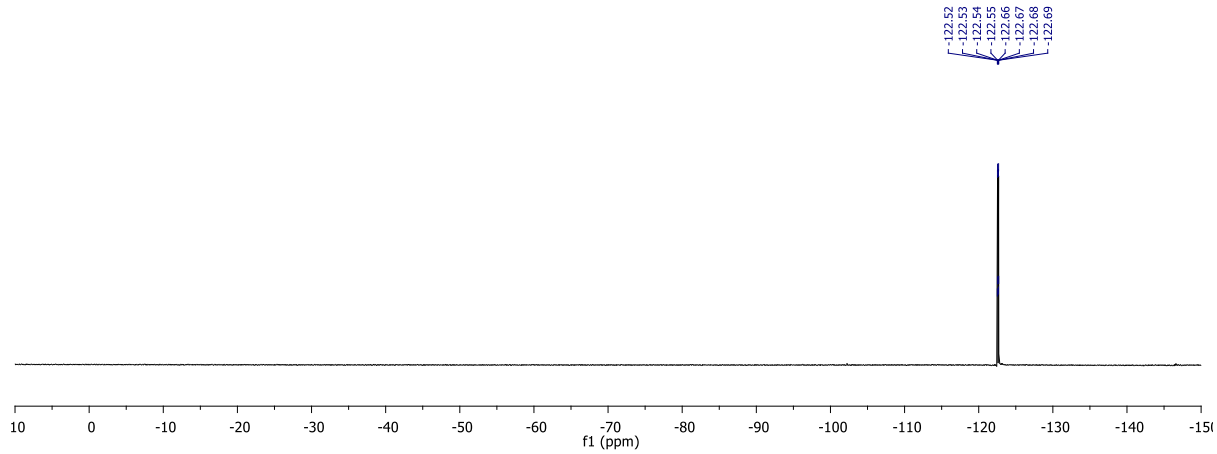


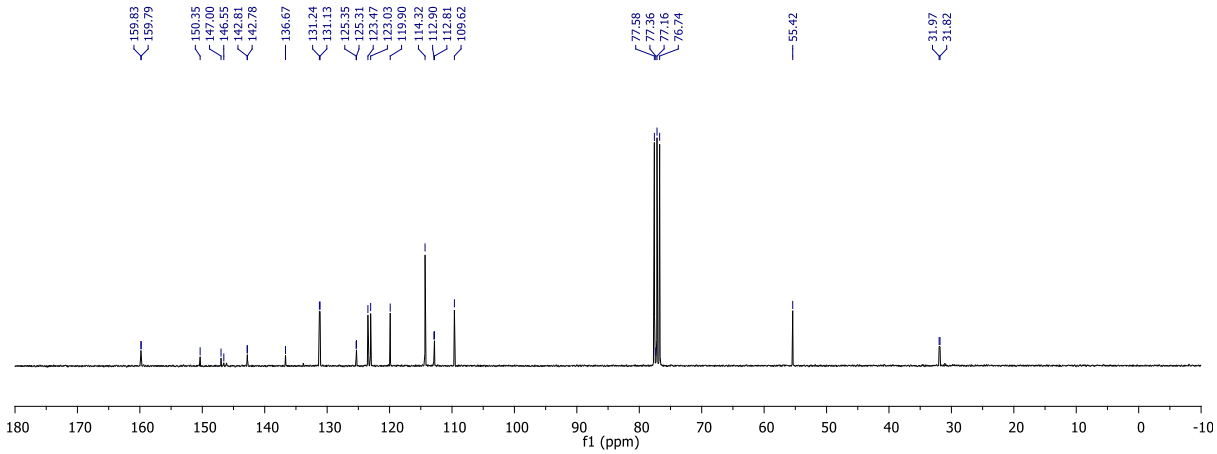


Heteroaryle **5A**

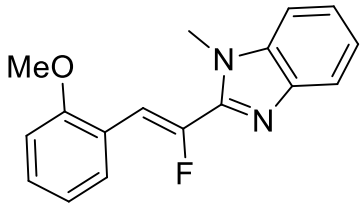


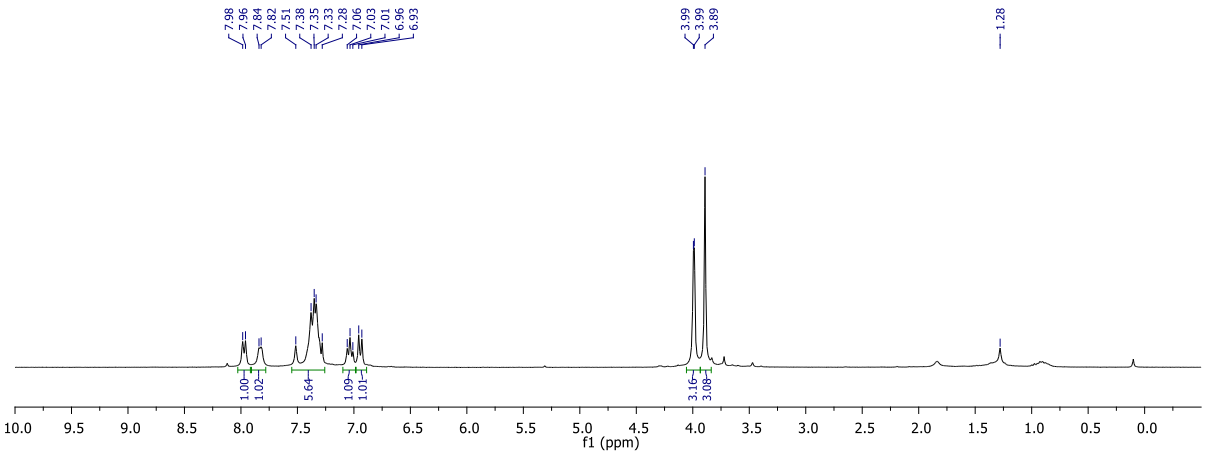


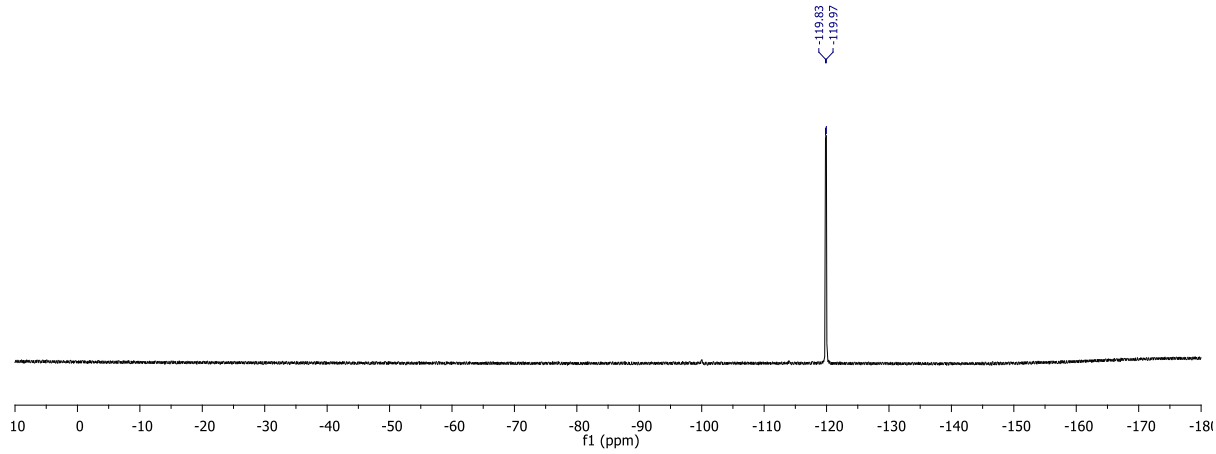


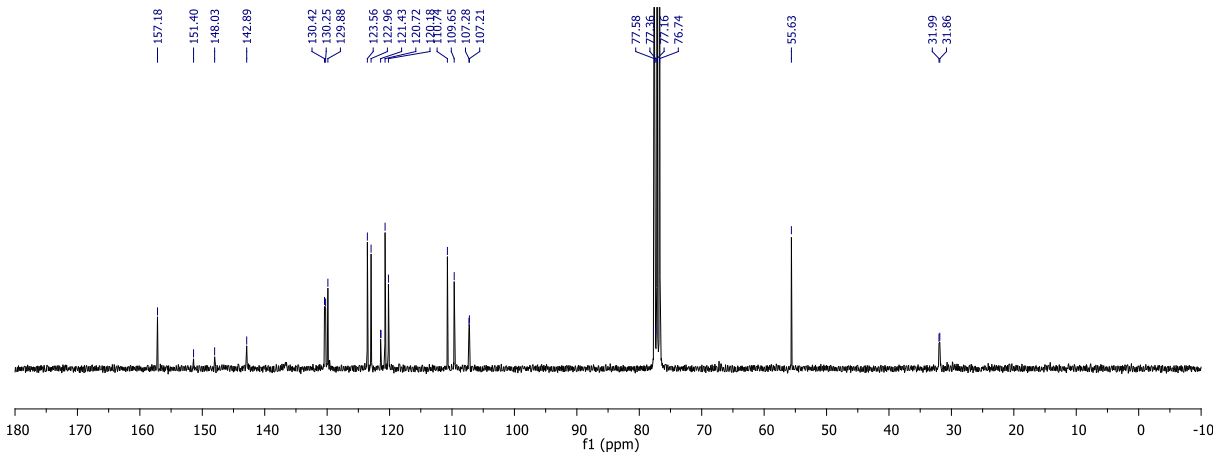


Heteroaryle **5H**

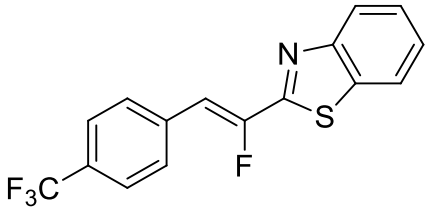


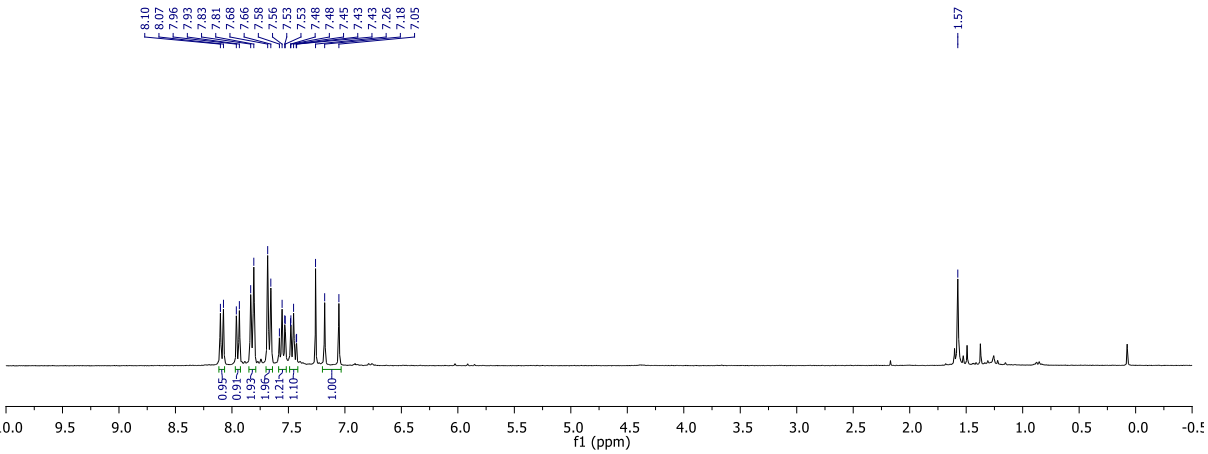


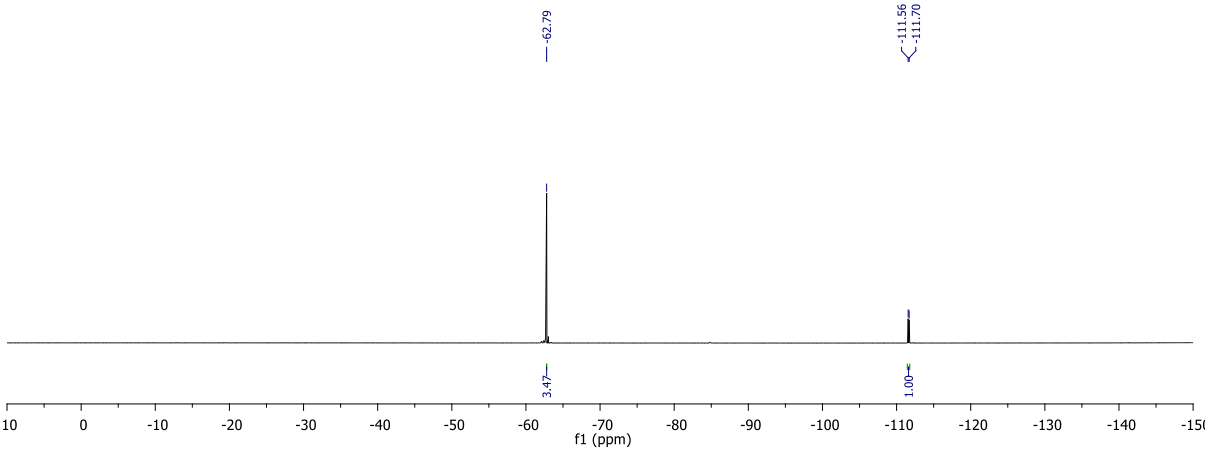


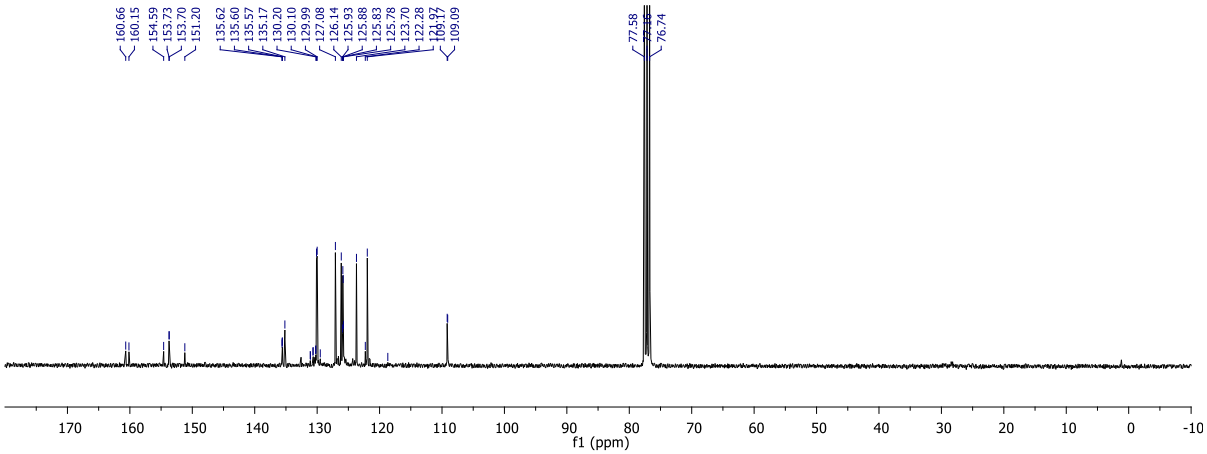


Heteroaryle **6E**

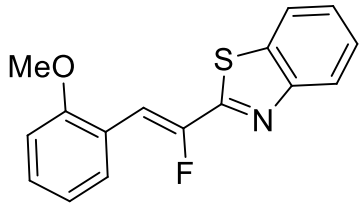


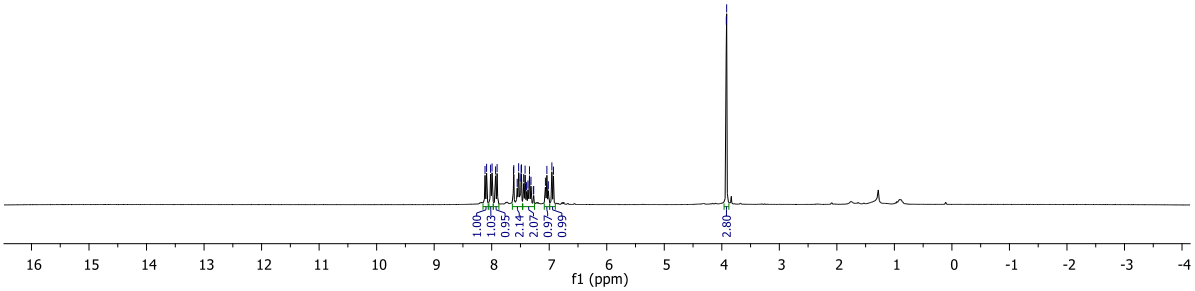


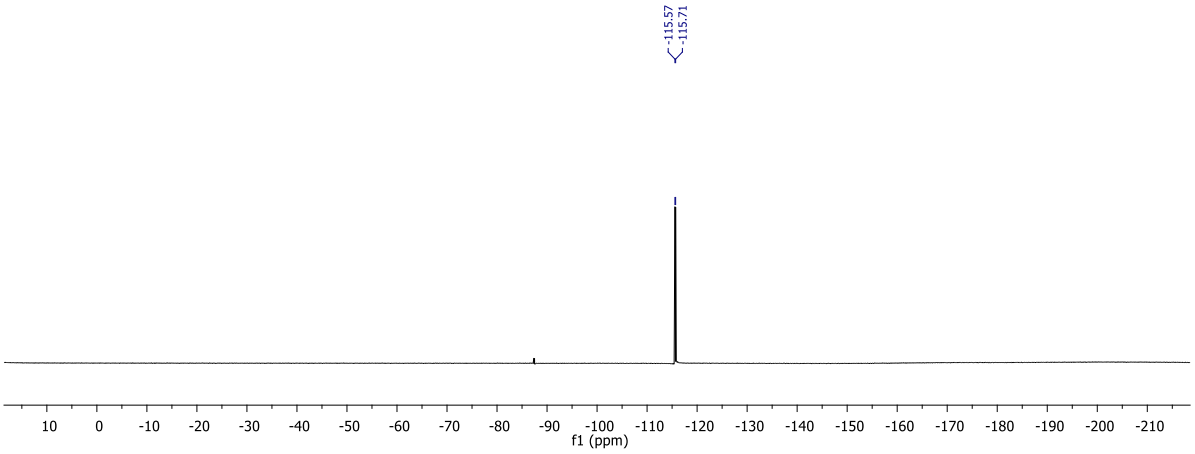


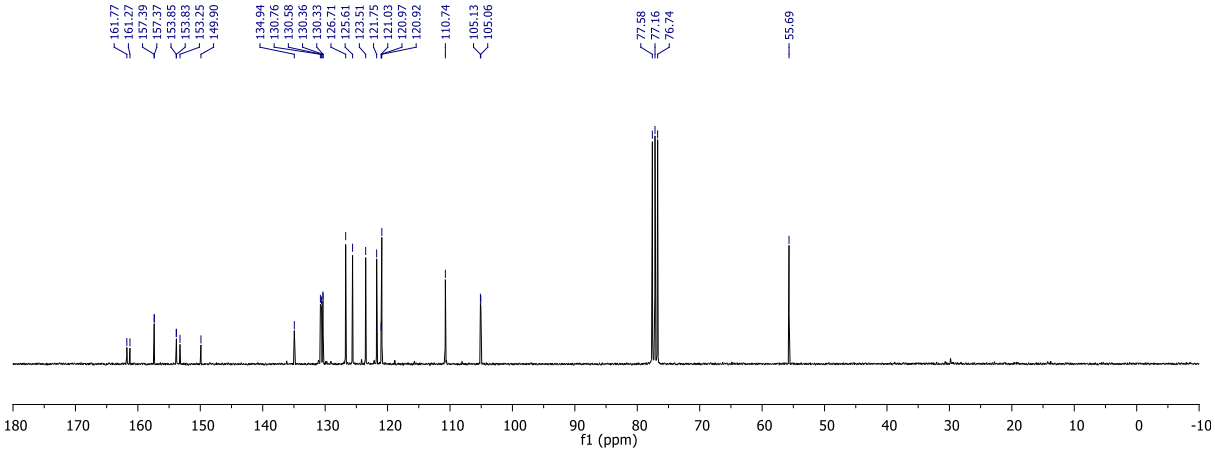


Heteroaryle **6H**









Heteroaryle **7G**